Supporting Information for

Delineating the critical role of acid additives in Mn-catalysed C-H bond functionalisation processes


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1 General Information

1.1 Preparative and Laboratory Analysis

Reagents were purchased from Acros Organics, Alfa Aesar, Fluorochem, or Sigma-Aldrich and used as purchased unless otherwise stated. Dicyclohexylamine was degassed with N₂ under sonication and stored in a solvent ampule under N₂. Petroleum ether refers to the fraction of petroleum that is collected at 40–60 °C. Dry THF were obtained from a Pure Solv MD-7 solvent system and stored under nitrogen. THF was also degassed by bubbling nitrogen through the solvent under sonication. Reactions requiring anhydrous conditions were carried out using Schlenk techniques (high vacuum, liquid nitrogen trap on a standard in-house built dual line). Room temperature upper and lower limits are stated as 13–25 °C, but typically 21 °C was recorded. Compound 8' and Mn-hydroxyl clusters² were prepared by literature methods.

Think-layer chromatography (TLC) was carried out using Merck 5554 aluminum-backed silica plates (silica gel 60 F254), and spots were visualized using UV light (at 254 nm). Where necessary, plates were stained and heated with one of potassium permanganate, anisaldehyde or vanillin as appropriate. Retention factors (Rf) are reported in parentheses along with the solvent system used. Flash column chromatography was performed according to the method reported by Still et al.³ using Fluorochem silica gel 60 (particle size 40–63 µm) and a solvent system as stated in the text.

1.2 Instrument Details for Compound Characterisation Purposes

NMR spectra were obtained in the solvent indicated using a JEOL ECX400 or JEOL ECS400 spectrometer (400 and 101 MHz for ¹H and ¹³C respectively) or a Bruker 500 (500 and 125 MHz for ¹H and ¹³C respectively). Chemical shifts are reported in parts per million and were referenced to the residual nondeuterated solvent of the deuterated solvent used (CHCl₃ TMH = 7.26 and TMC = 77.16 (CDCl₃), CDHCl₂ TMH = 5.31 and TMC = 54.0 (CD₂Cl₂), ¹H and ¹³C respectively). Spectra was typically run at a temperature of 298 K (for CDCl₃) or 295 K (for CD₂Cl₂). All ¹³C NMR spectra were obtained with ¹H decoupling. NMR spectra were processed using Mes-tReNova software (version 11.0.3-18688, 2017). The spectra given below were typically saved as .emf files in Mes-tReNova and inserted into a Microsoft Word document. For the ¹H NMR spectra, the resolution varies from 0.15 to 0.5 Hz; the coupling constants have been quoted to ±0.5 Hz in all cases for consistency. ¹H NMR chemical shifts are reported to two decimal places and ¹³C NMR chemical shifts are reported to one decimal place.

Infrared spectra were obtained using a Unicam Research Series FTIR (KBr IR) or a Bruker APLHA-Platinum FTIR Spectrometer with a platinum–diamond ATR sampling module. Where indicated, reactions were monitored in situ using a Mettler Toledo ReactIR10 with a K6 conduit SiComp (silicon) probe and MCT detector.

MS spectra were measured using a Bruker Daltronics micrOTOF MS, Agilent series 1200LC with electrospray ionization (ESI and APCI) or on a Thermo LCQ using electrospray ionization, with <5 ppm error recorded for all HRMS samples. Mass spectral data are quoted as the m/z ratio along with the relative peak height in brackets (base peak = 100). Mass to charge ratios (m/z) are reported in Daltons. High-resolution mass spectra are reported with <5 ppm error.

Melting points were recorded using a Stuart digital SMP3 machine.
2 Synthetic Procedures and Compound Data

2.1 General Procedure A: Reaction monitoring using in situ IR spectroscopic analysis.
A 100 mL three necked round bottomed flask equipped with stirrer bar was attached to the ReactIR silicon tipped ATR-IR probe. A background spectrum was collected and n-Bu₂O (10 mL) added, before septa were attached to the side joints. Thereafter an internal thermocouple was attached through a septum and the solvent was deoxygenated with an argon balloon. After the temperature had reached a steady level a solvent background spectrum was recorded to be used as a reference.

The sample measurements thereafter started and 2-phenylpyridine (1, 1.19 mL, 8.32 mmol, 2 eq.) was added through a septum. After the corresponding IR peaks had stabilized, propargyl benzoate or n-butyl acrylate (4b or 4c, 4.16 mmol, 1 eq.) was added, followed by Cy₂NH (0.17 mL, 0.83 mmol, 20 mol%). MnBr(CO)₃ (114 mg, 0.42 mmol, 10 mol%) was added as the final reagent by rapid removal of the septum. IR spectra was recorded every 1 min and specific peaks in the metal carbonyl region (~2150-1800 cm⁻¹; peak resolution = ±4 cm⁻¹) were peak picked and monitored on individual experiment basis. The data was exported into a Microsoft Excel document where the relevant processing was performed. Graph plots were generated, and curve fitting performed, using OriginPro 2017 software (SR2, b9.4.2.380).

2.2 General Procedure B: Mn-catalysed C–H functionalisation reactions
Adapted from literature procedure. To a microwave vial equipped with a stirrer bar was added MnBr(CO)₃ (7 mg, 0.025 mmol, 10 mol%), Cy₂NH (10 µL, 0.05 mmol, 20 mol%), 2-phenylpyridine (70 µL, 0.50 mmol, 2 eq.) and alkyne/acrylate (0.25 mmol, 1 eq.). nBu₂O (0.6 mL) was then added and the solution was deoxygenated with argon balloon before heating at 100 °C for 3 hours.

After the completion of the reaction, an aliquot of the reaction mixture was taken. The aliquot was filtered through a Pasteur pipet (with cotton wool and Celite filter pad) into an NMR tube, after which a ¹H NMR spectrum was recorded of the sample to provide the product conversion.

2.3 General Procedure C: Synthesis of ammonium salts
To a 25 mL round bottomed flask equipped with stirrer bar was added dicyclohexylamine (0.43 mL, 2.50 mmol, 1 eq.) and Et₂O (5 mL). The relevant acid (2.50 mmol, 1 eq.) was thereafter added dropwise at room temperature and the reaction mixture was stirred for 30 minutes. After the reaction time the solid precipitate was collected by filtration and washed with Et₂O to afford the product.

2.4 (E)-2-(2-styrylphenyl)pyridine, 5a

Synthesised using general procedure B from phenylacetylene 4a (27 µL, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (petrol/Et₂O, 8:2, v/v) to afford a sticky oil (47 mg, 73%).

Rₜ 0.12 (petrol/Et₂O, 8:2, v/v); ¹H NMR (500 MHz, CDCl₃, δ): 8.77 (d, J = 5.0 Hz, 1H), 7.81-7.71 (m, 2H), 7.58 (d, J = 7.5, 1H), 7.50-7.36 (m, 5H), 7.36-7.21 (m, 6H), 7.08 (d, J = 16.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃, δ): 159.0, 149.7, 139.8, 137.7, 136.1, 135.9, 130.4, 130.2, 128.8, 128.8, 127.8, 127.7, 126.8, 126.4, 125.2, 122.0; ESI-MS m/z (ion, %): 258 [(M+H)⁺, 100]; ESI-HRMS 258.1280 [M+H]⁺ (calculated for C₁₉H₁₈N 258.1277); IR (solid-state, ATR, cm⁻¹): 3055, 3023, 1597, 1582, 1568, 1494, 1458, 1445, 1423, 1073, 1022, 988, 980, 795, 748, 728, 691, 644, 616, 533, 517.

Lab book reference number: LAH-11-802
2.5 (E)-3-((2-(pyridine-2-yl)phenyl)allyl benzoate, 5b

Synthesised using general procedure B from propargyl benzoate 4b (36 µL, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (hexane/EtOAc, 8:2, v/v) to afford a sticky oil (33 mg, 42%).

$R_f$ 0.12 (hexane/EtO, 6:4, v/v); $^1$H NMR (500 MHz, CDCl₃, δ): 8.70 (dd, $J = 5.0, 2.0, 1.0$ Hz, 1H), 8.05-8.00 (m, 2H), 7.71 (dd, $J = 7.5, 7.5, 2.0$ Hz, 1H), 7.69-7.65 (m, 1H), 7.58-7.53 (m, 1H), 7.52-7.49 (m, 1H), 7.45-7.35 (m, 5H), 7.27-7.22 (m, 1H), 6.89 (d, $J = 16.0$ Hz, 1H), 6.37 (dt, $J = 16.0, 6.0$ Hz, 1H), 4.93 (dd, $J = 6.0, 1.5$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl₃, δ): 166.4, 158.8, 149.5, 139.7, 136.2, 134.7, 133.1, 132.5, 130.3, 130.2, 129.8, 128.7, 128.5, 127.9, 127.8, 126.6, 125.0, 124.7, 122.0, 65.6; ESI-MS m/z (ion, %): 316 ([M⁺]+, 100); ESI-HRMS m/z: 316.1336 [M⁺] (calc. for C₂₁H₁₈NO₂ 316.1332); IR (solid-state, ATR, cm⁻¹): 1715, 1584, 1570, 1425, 1376, 1265, 1175, 1106, 1069, 1024, 963, 795, 749, 708.

Lab book reference number: LAH-8-553

2.6 n-butyl-3-((2-(pyridine-2-yl)phenyl)propanoate, 5c

Synthesised using general procedure B from n-butyl acrylate 4b (36 µL, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (petrol/EtOAc, 8:5:1.5, v/v) to afford a sticky oil (0.39 g, 55%).

$R_f$ 0.19 (petrol/EtOAc, 8:5:1.5, v/v); $^1$H NMR (500 MHz, CDCl₃, δ): 8.67 (dd, $J = 5.0, 2.0, 1.0$ Hz, 1H), 7.75 (dd, $J = 7.5, 7.5, 2.0$ Hz, 1H), 7.40 (dd, $J = 8.0, 1.0, 1.0$ Hz, 1H), 7.36-7.24 (m, 5H), 4.01 (t, $J = 6.5$ Hz, 2H), 3.07-3.02 (m, 2H), 2.55–2.50 (m, 2H), 1.57–1.51 (m, 2H), 1.35–1.27 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl₃, δ): 173.3, 160.1, 149.3, 140.6, 138.8, 136.5, 130.0, 129.9, 128.6, 126.5, 124.1, 121.9, 64.3, 35.1, 30.8, 28.7, 19.2, 13.8; ESI-MS m/z (ion, %): 284 ([M⁺]+, 100); ESI-HRMS 284.1650 [M⁺]+ (calculated for C₁₈H₂₃NO₂ 284.1645); IR (solid-state, ATR, cm⁻¹): 3350, 3056, 2957, 2930, 2872, 1729, 1650, 1586, 1518, 1470, 1426, 1387, 1306, 1230, 1176, 1113, 1025, 949, 814, 749, 696, 636, 502.

Lab book reference number: LAH-8-550

2.7 (E)-2-((1,2-Diphenylvinyl)phenyl)pyridine, 7

Synthesised using general procedure B from diphenylacetylene 6 (45 mg, 0.25 mmol, 1 eq.) and EtCO₂H (4 µL, 0.05 mmol, 20 mol%). The crude material was purified by flash column chromatography (petrol/EtOAc, 8:2, v/v) to afford a white solid (17 mg, 20%).

$R_f$ 0.09 (petrol/EtOAc, 8:2, v/v); $^1$H NMR (500 MHz, CDCl₃, δ): 8.46 (d, $J = 5.0$ Hz, 1H), 7.52-7.47 (m, 1H), 7.46-7.39 (m, 4H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.14-7.07 (m, 3H), 7.06-6.96 (m, 6H), 6.94-6.89 (m, 2H), 6.66 (s, 1H); $^{13}$C NMR (125 MHz, CDCl₃, δ): 159.8, 149.1, 143.6, 142.6, 140.6, 140.4, 137.7, 135.5, 131.2, 131.0, 130.4, 129.4, 128.3, 128.0, 127.9, 127.8, 126.9, 126.8, 124.5, 121.3; ESI-MS m/z (ion, %): 334 ([M⁺]+, 100); ESI-HRMS 334.1587 [M⁺]+ (calculated for
C₁₈H₂₂NO₂ 334.1590); IR (solid-state, ATR, cm⁻¹): 3051, 3021, 1585, 1489, 1459, 1442, 1421, 1295, 1179, 1151, 1073, 1059, 990, 946, 914, 878, 793, 782, 743, 715, 697, 615, 591, 546, 513, 497.

Lab book reference number: LAH-11-801

2.8  6-methyl-3-[(E)-2-phenylethenyl]-4-(pyridin-2-yl)-2H-pyran-2-one, 9

Synthesised using general procedure B from 4-(6'-methoxy-2'-pyridyl)-2-pyrone 7 (47 mg, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (petrol/toluene/EtOAc, 5.5:3:1.5, v/v) to afford a yellow solid (31 mg, 43%).

Rf 0.10 (petrol/toluene/EtOAc, 5.5:3:1.5, v/v); ¹H NMR (500 MHz, CDCl₃, δ): 8.79 (ddd, J = 5.0, 1.5, 1.0 Hz, 1H), 7.91 (d, J = 16.0 Hz, 1H), 7.80 (td, J = 7.5, 2.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.37 (ddd, J = 7.5, 5.0, 1.0 Hz, 1H), 7.35-7.32 (m, 2H), 7.31-7.25 (m, 2H), 7.24-7.19 (m, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.32 (s, 1H), 2.32 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, δ): 162.2, 159.3, 155.5, 150.4, 150.1, 137.9, 136.5, 135.3, 128.7, 128.0, 126.9, 125.2, 123.8, 120.7, 118.1, 106.5, 20.0; ESI-MS m/z (ion, %): 290 ([M+H]⁺, 68), 312 ([M+Na]⁺, 100); ESI-HRMS m/z: 290.1176 [M⁺] (calc. for C₁₈H₂₂NO₂ 290.1176); IR (solid-state, ATR, cm⁻¹): 3052, 2922, 2854, 1703, 1630, 1583, 1514, 1488, 1465, 1430, 1376, 1306, 1234, 1202, 1152, 1045, 1026, 988, 959, 882, 835, 797, 745, 673, 617, 580, 506.

Lab book reference number: LAH-8-550

2.9  Dicyclohexylammonium chloride

Synthesised using general procedure C with hydrochloric acid (37% in H₂O, 0.43 ml, 2.50 mmol, 1 eq.) to afford a white solid (0.54 g, quant.).

Mₚ 337–340 °C dec; ¹H NMR (400 MHz, CDCl₃, δ): 9.06 (s, 2H), 3.06 (t, J = 11.5 Hz, 2H), 2.20 (d, J = 12.0 Hz, 4H), 1.89–1.76 (m, 5H), 1.76–1.59 (m, 6H), 1.32–1.15 (m, 6H); ¹³C NMR (101 MHz, CDCl₃, δ): 53.8, 29.3, 25.0, 24.9; ESI-MS m/z (ion, %): 182 ([M⁺]⁺, 100); ESI-HRMS m/z: 182.1903 [M⁺] (calc. for C₁₂H₂₄N 182.1903); IR (solid-state, ATR, cm⁻¹): 2931, 2856, 2790, 2754, 2726, 2702, 2526, 2427, 2380, 1581, 1490, 1386, 1313, 1055, 1034, 965, 918, 894, 862.

Lab book reference number: LAH-5-247

2.10  Dicyclohexylammonium bromide

Synthesised using general procedure C with dicyclohexylamine (2.20 ml, 11.00 mmol, 1 eq.), hydrobromic acid (48% in H₂O, 1.24 ml, 11.00 mmol, 1 eq.) and Et₂O (20 ml) to afford a white solid (2.13 g, 74%).

Mₚ 325–327 °C dec; ¹H NMR (400 MHz, CDCl₃, δ): 8.62 (s, 2H), 3.17 (t, J = 10.5 Hz, 2H), 2.24 (d, J = 12.5 Hz, 4H), 1.90–1.71 (m, 8H), 1.70–1.59 (m, 3H), 1.33–1.16 (m, 6H); ¹³C NMR (101 MHz, CDCl₃, δ): 54.3, 29.3, 24.9, 24.9; ESI-MS m/z (ion, %): 182 ([M⁺]⁺, 100); ESI-HRMS m/z: 182.1907 [M⁺] (calc. for C₁₂H₂₄N 182.1903); IR (solid-state, ATR, cm⁻¹): 2931, 2854, 2801, 2757, 2520, 2421, 2358, 1460, 1347, 1312, 1050, 1034, 919, 895, 857.

Lab book reference number: LAH-5-240
2.11 Dicyclohexylammonium iodide

![Diagram of Dicyclohexylammonium Iodide]

Synthesised using general procedure C with hydroiodic acid (57% in H₂O, 0.20 ml, 2.50 mmol, 1 eq.) to afford a white solid (0.59 g, 79%).

Mₚ 326–329 °C dec; ¹H NMR (400 MHz, CDCl₃, δ): 8.08 (s, 2H), 3.34 (tt, J = 12.0, 4.0 Hz, 2H), 2.29 (d, J = 11.0 Hz, 4H), 1.94–1.80 (m, 8H), 1.68 (d, J = 6.0 Hz, 2H), 1.34–1.18 (m, 7H); ¹³C NMR (101 MHz, CDCl₃, δ): 54.8, 29.2, 24.9, 24.8; ESI-MS m/z (ion, %): 182 ([M⁺], 100); ESI-HRMS m/z: 182.1908 [M⁺] (calc. for C₁₂H₂₄N 182.1903); IR (solid-state, ATR, cm⁻¹): 2933, 2857, 2823, 2730, 2514, 2412, 1571, 1450, 1388, 1314, 1160, 1032, 968, 850.

Lab book reference number: LAH-5-248

2.12 Dicyclohexylammonium tetrafluoroborate

Synthesised using general procedure C with dicyclohexylamine (2.20 ml, 11.00 mmol, 1 eq.), tetrafluoroboric acid (48% in H₂O, 1.24 ml, 11.00 mmol, 1 eq.) and Et₂O (20 ml) to afford a white solid (2.13 g, 74%).

Mₚ 341–344 °C dec; ¹H NMR (400 MHz, CDCl₃, δ): 6.53 (m, 1H), 3.12 (tt, J = 11.5, 4.0 Hz, 2H), 2.06 (d, J = 12.5 Hz, 4H), 1.92–1.80 (m, 4H), 1.71–1.63 (m, 2H), 1.55–1.40 (m, 4H), 1.35–1.16 (m, 7H); ¹³C NMR (101 MHz, CDCl₃, δ): 54.8, 29.2, 24.7, 24.7; ¹¹B NMR (128 MHz, CDCl₃, δ): −2.1; ¹⁹F NMR (376 MHz, CDCl₃, δ): −146.3, −146.3; ESI-MS m/z (ion, %): 182 ([M⁺], 100); ESI-HRMS m/z: 182.1901 [M⁺] (calc. for C₁₂H₂₄N 182.1903); IR (solid-state, ATR, cm⁻¹): 3175, 3126, 2938, 2861, 1601, 1456, 1389, 1315, 1096, 1002, 850, 767.

Lab book reference number: LAH-5-246
Data Analysis and Individual Reaction Results

3.1 Effect of additives on reactions with phenylacetylene 4a

Table S1. Summary of the effects of additives on the reaction using phenylacetylene 4a.°

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<th>Pre-catalyst</th>
<th>Additive(s)</th>
<th>5a / %b</th>
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<tbody>
<tr>
<td>1</td>
<td>MnBr(CO)₅ (2)</td>
<td>Cy₂NH²</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>MnBr(CO)₅ (2)</td>
<td>Cy₂NH⁶, EtCO₂H⁶</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>None</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>Cy₂NH³</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>[Cy₂NH₃]Cl⁶</td>
<td>49</td>
</tr>
<tr>
<td>6</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>[Cy₂NH₃]Br⁶</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>[Cy₂NH₃]I⁶</td>
<td>51</td>
</tr>
<tr>
<td>8</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>[Cy₂NH₃]BF₄⁷</td>
<td>57</td>
</tr>
<tr>
<td>9</td>
<td>Mn(ppy)(CO)₄ (3)³</td>
<td>EtCO₂H⁸</td>
<td>95</td>
</tr>
</tbody>
</table>

° Standard reaction conditions: 2-phenylpyridine (70 µl, 0.5 mmol, 2 eq.), phenylacetylene (27 µl, 0.25 mmol, 1 eq.), additive(s) (0.05 mmol, 20 mol%), Mn-complex (0.025 mmol, 10 mol%) and N-Bu₂O (0.6 ml). b Crude conversion determined by H NMR spectroscopy. c MnBr(CO)₅ (7 mg, 0.025 mmol, 10 mol%) added. d Cy₂NH (10 µl, 0.05 mmol, 20 mol%) added. e EtCO₂H (4 µl, 0.05 mmol, 20 mol%) added, f Mn(ppy)(CO)₄ (8 mg, 0.025 mmol, 10 mol%) added. g [Cy₂NH₃]Cl (11 mg, 0.05 mmol, 20 mol%) added. h [Cy₂NH₃]Br (13 mg, 0.05 mmol, 20 mol%) added. i [Cy₂NH₃]I (16 mg, 0.05 mmol, 20 mol%) added. j [Cy₂NH₃]BF₄ (14 mg, 0.05 mmol, 20 mol%) added.
3.2 Effect of additives on reactions with propargyl benzoate 4b

Table S2. Summary of the effects of additives on the reaction using propargyl benzoate 4b.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pre-catalyst</th>
<th>Additive(s)</th>
<th>5b / %b</th>
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<tbody>
<tr>
<td>1</td>
<td>MnBr(CO)₅(2)c</td>
<td>Cy₂NH²</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>MnBr(CO)₅(2)c</td>
<td>Cy₂NH², EtCO₂H²</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>None</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>Cy₂NH²</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>[Cy₂NH₂]Cl²</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>[Cy₂NH₂]Br³</td>
<td>63</td>
</tr>
<tr>
<td>7</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>[Cy₂NH₂]I⁴</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>[Cy₂NH₂]BF₄j</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>EtCO₂H⁵</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>HCl⁶</td>
<td>5</td>
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<tr>
<td>11</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>HBr⁷</td>
<td>Trace</td>
</tr>
<tr>
<td>12</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>HI⁸</td>
<td>Trace</td>
</tr>
<tr>
<td>13</td>
<td>Mn(ppy)(CO)₄(3)l</td>
<td>HBF₄•OEt₂n</td>
<td>62</td>
</tr>
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</table>

a Standard reaction conditions: 2-phenylpyridine (70 µl, 0.5 mmol, 2 eq.), propargyl benzoate (36 µl, 0.25 mmol, 1 eq.), additive(s) (0.05 mmol, 20 mol%), Mn-complex (0.025 mmol, 10 mol%) and n-Bu₂O (0.6 ml). b Crude conversion determined by ¹H NMR spectroscopy. c MnBr(CO)₅(7 mg, 0.025 mmol, 10 mol%) added. d Cy₂NH(10 µl, 0.05 mmol, 20 mol%) added. e EtCO₂H (4 µl, 0.05 mmol, 20 mol%) added. f Mn(ppy)(CO)₄(8 mg, 0.025 mmol, 10 mol%) added. g [Cy₂NH₂]Cl (11 mg, 0.05 mmol, 20 mol%) added. h [Cy₂NH₂]Br (13 mg, 0.05 mmol, 20 mol%) added. i [Cy₂NH₂]I (16 mg, 0.05 mmol, 20 mol%) added. j [Cy₂NH₂]BF₄ (14 mg, 0.05 mmol, 20 mol%) added. k HCl (37% in H₂O, 4 µl, 0.05 mmol, 20 mol%) added. l HBr (48% in H₂O, 6 µl, 0.05 mmol, 20 mol%) added. m HI (4 µl, 0.05 mmol, 20 mol%) added. n HBF₄•OEt₂ (7 µl, 0.05 mmol, 20 mol%) added.
3.3 Effect of additives on reactions with \(n\)-butyl acrylate 4c

Table S3. Summary of the effects of additives on the reaction using \(n\)-butyl acrylate 4c.\(^a\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pre-catalyst</th>
<th>Additive(s)</th>
<th>5b / %(^b)</th>
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<tbody>
<tr>
<td>1</td>
<td>MnBr(CO)_5 (2)(^c)</td>
<td>Cy(_2)NH(^d)</td>
<td>79</td>
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<td>2</td>
<td>MnBr(CO)_5 (2)(^c)</td>
<td>Cy(_2)NH(^d), EtCO(_2)H</td>
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<tr>
<td>3</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>None</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>Cy(_2)NH(^d)</td>
<td>46</td>
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<td>5</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>[Cy(_2)NH(_2)]Cl</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>[Cy(_2)NH(_2)]Br</td>
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<tr>
<td>7</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>[Cy(_2)NH(_2)]I</td>
<td>19</td>
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<tr>
<td>8</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>[Cy(_2)NH(_2)]BF(_4)</td>
<td>40</td>
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<tr>
<td>9</td>
<td>Mn(ppy)(CO)_4 (3)</td>
<td>EtCO(_2)H</td>
<td>26</td>
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</tbody>
</table>

\(^a\) Standard reaction conditions: 2-phenylpyridine (70 µl, 0.5 mmol, 2 eq.), \(n\)-butyl acrylate (27 µl, 0.25 mmol, 1 eq.), additive(s) (0.05 mmol, 20 mol%), Mn-complex (0.025 mmol, 10 mol%) and \(n\)-Bu\(_2\)O (0.6 ml). \(^b\) Crude conversion determined by \(^1\)H NMR spectroscopy. \(^c\) MnBr(CO)\(_5\) (7 mg, 0.025 mmol, 10 mol%) added. \(^d\) Cy\(_2\)NH (10 µl, 0.05 mmol, 20 mol%) added. \(^e\) EtCO\(_2\)H (4 µl, 0.05 mmol, 20 mol%) added. \(^f\) Mn(ppy)(CO)_4 (8 mg, 0.025 mmol, 10 mol%) added. \(^g\) [Cy\(_2\)NH\(_2\)]Cl (11 mg, 0.05 mmol, 20 mol%) added. \(^h\) [Cy\(_2\)NH\(_2\)]Br (13 mg, 0.05 mmol, 20 mol%) added. \(^i\) [Cy\(_2\)NH\(_2\)]I (16 mg, 0.05 mmol, 20 mol%) added. \(^j\) [Cy\(_2\)NH\(_2\)]BF\(_4\) (14 mg, 0.05 mmol, 20 mol%) added.
3.4 In situ IR spectroscopic monitoring of reaction with 4b catalysed by 3 (figure 2a)

Figure S1. Reaction scheme and in situ IR spectra for the reaction of 4b using Mn(ppy)(CO)₄ (3) as the precatalyst, showing the formation of new manganese carbonyl species over time from 3. Reaction conditions (in order of addition): n-Bu₂O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 mmol, 2 eq.), propargyl benzoate (0.60 ml, 4.16 mmol, 1 eq.) and Mn(ppy)(CO)₄ (0.134 g, 0.42 mmol, 10 mol%).
Figure S2. Comparison between the end spectrum of the reaction (30 min) with two Mn hydroxyl cluster compounds ([Mn\(_7\)\(\mu_3\)-OH\(\delta\)(CO)\(_{18}\)] and [Mn\(_7\)\(\mu_3\)-OH\(\delta\)(CO)\(_{18}\)]) heated at 100 °C in n-Bu\(_2\)O.
3.5 In situ IR spectroscopic monitoring of reaction with 4b and [Cy₂NH₂]BF₄ catalysed by 3 (figure 2b)

![Reaction scheme and in situ IR spectra for the reaction of 4b with [Cy₂NH₂]BF₄ added, using Mn(ppy)(CO)₄ (3) as the precatalyst, showing the formation of new manganese carbonyl species over time from 3. Reaction conditions (in order of addition): n-Bu₂O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 mmol, 2 eq.), propargyl benzoate (0.60 ml, 4.16 mmol, 1 eq.), [Cy₂NH₂]BF₄ (0.224 g, 0.83 mmol, 20 mol%) and Mn(ppy)(CO)₄ (0.134 g, 0.42 mmol, 10 mol%).]
3.6  In situ IR spectroscopic monitoring of reaction with 4c catalysed by 3 (figure 2c)

Figure S4. Reaction scheme and in situ IR spectra for the reaction of 4c using Mn(ppy)(CO)$_4$ (3) as the precatalyst, showing the formation of new manganese carbonyl species over time from 3. Reaction conditions (in order of addition): $n$-Bu$_2$O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 mmol, 2 eq.), $n$-butyl acrylate (0.60 ml, 4.16 mmol, 1 eq.) and Mn(ppy)(CO)$_4$ (0.134 g, 0.42 mmol, 10 mol%).
Figure S55. Comparison between the end spectrum of the reaction (3 h) with two Mn hydroxyl cluster compounds ([Mn$_7$(μ$_3$-OH)$_8$(CO)$_{18}$] and [{Mn(μ-OH)(CO)$_3$)$_4$}] heated at 100 °C in n-Bu$_2$O.
3.7 In situ IR spectroscopic monitoring of reaction with 4c and [Cy$_2$NH$_2$]Br catalysed by 3 (figure 2d)

$$\begin{array}{c}
\text{N} \quad \text{Mn}(\text{ppy})(\text{CO})_4 \text{ (3, 10 mol\%)} \\
\text{[Cy$_2$NH$_2$]Br (20 mol\%)} \\
n\text{Bu}_2\text{O, 100 °C, Ar} \\
\end{array}$$

$1$, (2 eq.) $\rightarrow$ $4c$, (1 eq.) $\rightarrow$ $5c$

Figure S6. Reaction scheme and in situ IR spectra for the reaction of $4c$ with $[\text{Cy}_2\text{NH}_2]\text{Br}$ added, using $\text{Mn(ppy)(CO)}_4 \text{ (3)}$ as the precatalyst, showing the formation of new manganese carbonyl species over time from 3. Reaction conditions (in order of addition): $n\text{-Bu}_2\text{O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 mmol, 2 eq.), } n\text{-butyl acrylate (0.60 ml, 4.16 mmol, 1 eq.), } [\text{Cy}_2\text{NH}_2]\text{Br (0.218 g, 0.83 mmol, 20 mol\%)}$ and $\text{Mn(ppy)(CO)}_4 \text{ (0.134 g, 0.42 mmol, 10 mol\%).}$
NMR Spectra

Figure S5. $^1$H NMR spectrum of 5a (500 MHz, CDCl$_3$)

Figure S6. $^{13}$C NMR spectrum of 5a (126 MHz, CDCl$_3$)
Figure S7. $^1$H NMR spectrum of 5b (500 MHz, CDCl$_3$)

Figure S8. $^{13}$C NMR spectrum of 5b (126 MHz, CDCl$_3$)
Figure S9. $^1$H NMR spectrum of 5c (500 MHz, CDCl$_3$)

Figure S10. $^{13}$C NMR spectrum of 5c (126 MHz, CDCl$_3$)
Figure S11. $^1$H NMR spectrum of 7 (500 MHz, CDCl$_3$)

Figure S12. $^{13}$C NMR spectrum of 7 (126 MHz, CDCl$_3$)
Figure S13. $^1$H NMR spectrum of 9 (500 MHz, CDCl$_3$)

Figure S14. $^{13}$C NMR spectrum of 9 (126 MHz, CDCl$_3$)
Figure S15. $^1$H NMR spectrum of [Cy$_2$NH$_2$]Cl (400 MHz, CDCl$_3$)

Figure S16. $^{13}$C NMR spectrum of [Cy$_2$NH$_2$]Cl (101 MHz, CDCl$_3$)
**Figure S17.** $^1$H NMR spectrum of [Cy$_2$NH$_2$]Br (400 MHz, CDCl$_3$)

**Figure S18.** $^{13}$C NMR spectrum of [Cy$_2$NH$_2$]Br (101 MHz, CDCl$_3$)
Figure S19. $^1$H NMR spectrum of [Cy$_2$NH$_2$]I (400 MHz, CDCl$_3$)

Figure S20. $^{13}$C NMR spectrum of [Cy$_2$NH$_2$]I (101 MHz, CDCl$_3$)
Figure S21. $^1$H NMR spectrum of [Cy$_2$NH$_2$]BF$_4$ (400 MHz, CDCl$_3$)

Figure S22. $^{13}$C NMR spectrum of [Cy$_2$NH$_2$]BF$_4$ (101 MHz, CDCl$_3$)
Figure S23. $^{11}$B NMR spectrum of [Cy$_2$NH$_2$]BF$_4$ (128 MHz, CDCl$_3$)

Figure S24. $^{19}$F NMR spectrum of [Cy$_2$NH$_2$]BF$_4$ (376 MHz, CDCl$_3$)
5 References


