Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

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

L. Anders Hammarback,[1] Alan Robinson,[2] Jason M. Lynam[1]* and Ian J. S. Fairlamb[1]*

[1] Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK jason.lynam@york.ac.uk;

ian.fairlamb@york.ac.uk

[2] Syngenta Crop Protection AG, Münchwilen, Breitenloh 5, 433, Switzerland.

Contents

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 N_2 under sonication and stored in a solvent ampule under N_2. 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**[1] and Mn-hydroxyl clusters[2] 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 ^{1}H and ^{13}C respectively) or a Bruker 500 (500 and 125 MHz for ^{1}H and ^{13}C respectively). Chem-ical shifts are reported in parts per million and were referenced to the residual nondeuterated solvent of the deuterated solvent used ($CHCl_3$ TMH = 7.26 and TMC = 77.16 ($CDCl_3$), $CDHCl_2$ TMH = 5.31 and TMC = 54.0 (CD_2Cl_2), ^{1}H and ^{13}C respectively). Spectra was typically run at a temperature of 298 K (for $CDCl_3$) or 295 K (for $CD2Cl_2$). All ^{13}C NMR spectra were obtained with ^{1}H 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 ^{1}H 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. ^{1}H NMR chemical shifts are reported to two decimal places and ^{13}C 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 ReactIR ic_{10} 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*-Bu_2O (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 acryalte (**4b** or **4c**, 4.16 mmol, 1 eq.) was added, followed by Cy_2NH (0.17 mL, 0.83 mmol, 20 mol%). $MnBr(CO)_5$ (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 s pecific peaks in the metal carbonyl region (~2150-1800 cm^{-1}; peak resolution = ±4 cm^{-1}) were peak picked and moni-tored 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

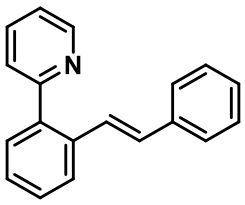
Adapted from literature procedure.[4] To a microwave vial equipped with a stirrer bar was added $MnBr(CO)_5$ (7 mg, 0.025 mmol, 10 mol%), Cy_2NH (10 µL, 0.05 mmol, 20 mol%), 2-phenylpyridine (70 µL, 0.50 mmol, 2 eq.) and alkyne/acrylate (0.25 mmol, 1 eq.). nBu_2O (0.6 mL) was then added and the solution 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 ^{1}H 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 flash equipped with stirrer bar was added dicyclohexylamine (0.43 mL, 2.50 mmol, 1 eq.) and Et_2O (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 Et_2O to afford the product.

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

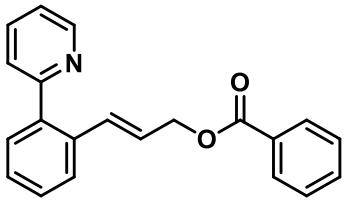


Synthesised using general procedure B from phenylacetylene **4a** (27 µL, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (petrol/Et_2O, 8:2, *v/v*) to afford a sticky oil (47 mg, 73%).

R_f 0.12 (petrol/Et_2O, 8:2, *v/v*); ^{1}H NMR (500 MHz, $CDCl_3$, 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); ^{13}C NMR (125 MHz, $CDCl_3$, 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, 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 $C_{19}H_{16}N$ 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

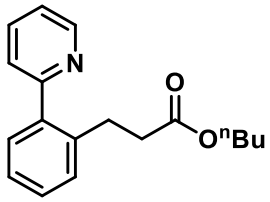


Synthesised using general procedure B from propargyl benzoate **4b** (36 µL, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (hexane/Et_2O, 6:4, *v/v*) to afford a sticky oil (33 mg, 42%).

R_f 0.12 (hexane/Et_2O, 6:4, *v/v*); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.70 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 8.05-8.00 (m, 2H), 7.71 (ddd, *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, $CDCl_3$, 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, 128.2, 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 $C_{21}H_{18}NO_2$ 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

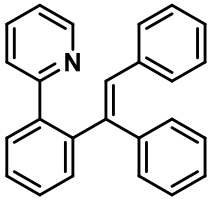


Synthesised using general procedure B from *n*-butyl acrylate **4b** (36 µL, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (petrol/EtOAc, 8.5:1.5, *v/v*) to afford a sticky oil (0.39 g, 55%).

R_f 0.19 (petrol/EtOAc, 8.5:1.5, *v/v*); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.67 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 7.75 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 7.40 (ddd, *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, $CDCl_3$, 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, 35.9, 30.8, 28.7, 19.2, 13.8; ESI-MS *m/z* (ion, %): 284 ([M+H]$^+$, 100); ESI-HRMS 284.1650 [M+H]$^+$ (calculated for $C_{18}H_{22}NO_2$ 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-(2-(1,2-Diphenylvinyl)phenyl)pyridine, 7



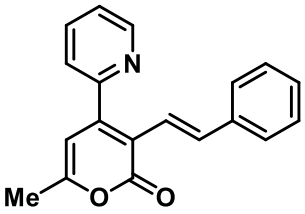
Synthesised using general procedure B from diphenylacetylene **6** (45 mg, 0.25 mmol, 1 eq.) and $EtCO_2H$ (4 µL, 0.05 mmol, 20 mol%). The crude material was purified by flash column chromatography (petrol/EtOAc, 8:2, *v/v*) to afford a white solid (17 mg, 20%).

R_f 0.09 (petrol/EtOAc, 8:2, *v/v*); ^{1}H NMR (500 MHz, $CDCl_3$, 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, $CDCl_3$, 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+H]$^+$, 100); ESI-HRMS 334.1587 [M+H]$^+$ (calculated for

$C_{18}H_{22}NO_2$ 334.1590); IR (solid-state, ATR, cm^{-1}): 3051, 3021, 1585, 1557, 1489, 1459, 1442, 1421, 1295, 1179, 1151, 1073, 1059, 1028, 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

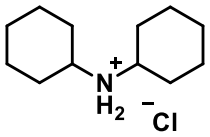


Synthesised using general procedure B from 4-(6'-methoxy-2'-pyridyl)-2-pyrone **7** (47 mg, 0.25 mmol, 1 eq.). The crude material was purified by flash column chromatography (petrol/toluene/EtOAc, 5.5:3:1.5, *v/v*) to afford a yellow solid (31 mg, 43%).

R_f 0.10 (petrol/toluene/EtOAc, 5.5:3:1.5, *v/v*); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.79 (ddd, *J* = 5.0, 1.5, 1.0 Hz, 1H), 7.91 (d, *J* = 16.0 Hz, 1H), 7.80 (td, 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); ^{13}C NMR (125 MHz, $CDCl_3$, 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 290.1176 $[M+H]^+$ (calculated for $C_{18}H_{22}NO_2$ 290.1176); IR (solid-state, ATR, cm^{-1}): 3052, 2922, 2854, 1703, 1630, 1583, 1514, 1488, 1465, 1430, 1384, 1345, 1327, 1304, 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

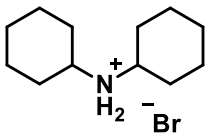


Synthesised using general procedure C with hydrochloric acid (37% in H_2O, 0.43 ml, 2.50 mmol, 1 eq.) to afford a white solid (0.54 g, quant.).

M_p 337–340 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 53.8, 29.3, 25.0, 24.9; ESI-MS *m/z* (ion, %): 182 ($[M]^+$, 100); ESI-HRMS *m/z*: 182.1907 $[M]^+$ (calc. for $C_{12}H_{24}N$ 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

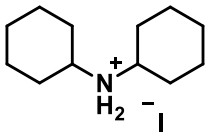


Synthesised using general procedure C with dicyclohexylamine (2.20 ml, 11.00 mmol, 1 eq.), hydrobromic acid (48% in H_2O, 1.24 ml, 11.00 mmol, 1 eq.) and Et_2O (20 ml) to afford a white solid (2.13 g, 74%).

M_p 325–327 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 54.3, 29.3, 24.9, 24.9; ESI-MS *m/z* (ion, %): 182 ($[M]^+$, 100); ESI-HRMS *m/z*: 182.1903 $[M]^+$ (calc. for $C_{12}H_{24}N$ 182.1903); IR (solid-state, ATR, cm^{-1}): 2929, 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

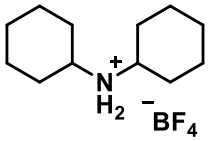


Synthesised using general procedure C with hydroiodic acid (57% in H_2O, 0.20 ml, 2.50 mmol, 1 eq.) to afford a white solid (0.59 g, 79%).

M_p 326–329 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (101 MHz, $CDCl_3$, 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 $C_{12}H_{24}N$ 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 H_2O, 1.24 ml, 11.00 mmol, 1 eq.) and Et_2O (20 ml) to afford a white solid (2.13 g, 74%).

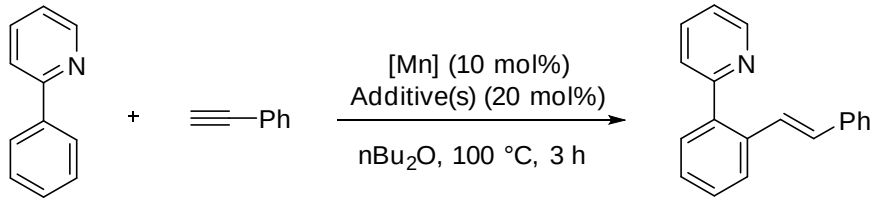
M_p 341–344 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.53 (m, 1H), 3.12 (tt, *J* = 11.5, 4.0 Hz, 2H), 2.06 (d, *J* = 12.5 Hz, 4H), 1.92–1.80 (m, 4H), 1.71–1.63 (m, 2H), 1.55–1.40 (m, 4H), 1.35–1.16 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 54.8, 29.2, 24.7, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$, δ): −2.1; ^{19}F NMR (376 MHz, $CDCl_3$, δ): −146.3, −146.3; ESI-MS *m/z* (ion, %): 182 ([M]$^+$, 100); ESI-HRMS *m/z*: 182.1901 [M]$^+$ (calc. for $C_{12}H_{24}N$ 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

3 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**.[a]



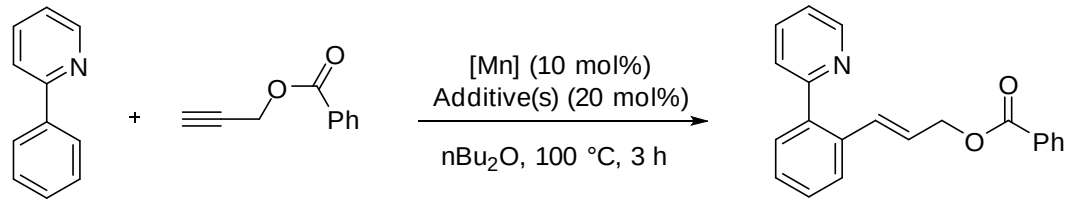
1, (2 eq.) **4a**, (1 eq.) **5a**

Entry	Pre-catalyst	Additive(s)	5a / %[b]
1	$MnBr(CO)_5$ (**2**)[c]	Cy_2NH[d]	76
2	$MnBr(CO)_5$ (**2**)[c]	Cy_2NH[d], $EtCO_2H$[e]	89
3	$Mn(ppy)(CO)_4$ (**3**)[f]	None	55
4	$Mn(ppy)(CO)_4$ (**3**)[f]	Cy_2NH[d]	58
5	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]Cl$[g]	49
6	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]Br$[h]	53
7	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]I$[i]	51
8	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]BF_4$[j]	57
9	$Mn(ppy)(CO)_4$ (**3**)[f]	$EtCO_2H$[e]	95

[a] 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*-Bu_2O (0.6 ml). [b] Crude conversion determined by ^1H NMR spectroscopy. [c] $MnBr(CO)_5$ (7 mg, 0.025 mmol, 10 mol%) added. [d] Cy_2NH (10 µl, 0.05 mmol, 20 mol%) added. [e] $EtCO_2H$ (4 µl, 0.05 mmol, 20 mol%) added, [f] $Mn(ppy)(CO)_4$ (8 mg, 0.025 mmol, 10 mol%) added. [g] $[Cy_2NH_2]Cl$ (11 mg, 0.05 mmol, 20 mol%) added. [h] $[Cy_2NH_2]Br$ (13 mg, 0.05 mmol, 20 mol%) added. [i] $[Cy_2NH_2]I$ (16 mg, 0.05 mmol, 20 mol%) added. [j] $[Cy_2NH_2]BF_4$ (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**.[a]



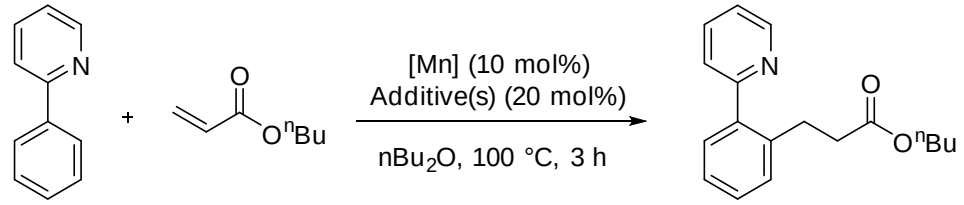
1, (2 eq.) **4b**, (1 eq.) **5b**

Entry	Pre-catalyst	Additive(s)	5b / %[b]
1	$MnBr(CO)_5$ (**2**)[c]	Cy_2NH[d]	54
2	$MnBr(CO)_5$ (**2**)[c]	Cy_2NH[d], $EtCO_2H$[e]	78
3	$Mn(ppy)(CO)_4$ (**3**)[f]	None	7
4	$Mn(ppy)(CO)_4$ (**3**)[f]	Cy_2NH[d]	8
5	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]Cl$[g]	68
6	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]Br$[h]	63
7	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]I$[i]	63
8	$Mn(ppy)(CO)_4$ (**3**)[f]	$[Cy_2NH_2]BF_4$[j]	67
9	$Mn(ppy)(CO)_4$ (**3**)[f]	$EtCO_2H$[e]	82
10	$Mn(ppy)(CO)_4$ (**3**)[f]	HCl[k]	5
11	$Mn(ppy)(CO)_4$ (**3**)[f]	HBr[l]	Trace
12	$Mn(ppy)(CO)_4$ (**3**)	HI[m]	Trace
13	$Mn(ppy)(CO)_4$ (**3**)	$HBF_4 \bullet OEt_2$[n]	62

[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*-Bu_2O (0.6 ml). [b] Crude conversion determined by ^1H NMR spectroscopy. [c] $MnBr(CO)_5$ (7 mg, 0.025 mmol, 10 mol%) added. [d] Cy_2NH (10 µl, 0.05 mmol, 20 mol%) added. [e] $EtCO_2H$ (4 µl, 0.05 mmol, 20 mol%) added, [f] $Mn(ppy)(CO)_4$ (8 mg, 0.025 mmol, 10 mol%) added. [g] $[Cy_2NH_2]Cl$ (11 mg, 0.05 mmol, 20 mol%) added. [h] $[Cy_2NH_2]Br$ (13 mg, 0.05 mmol, 20 mol%) added. [i] $[Cy_2NH_2]I$ (16 mg, 0.05 mmol, 20 mol%) added. [j] $[Cy_2NH_2]BF_4$ (14 mg, 0.05 mmol, 20 mol%) added. [k] HCl (37% in H_2O, 4 µl, 0.05 mmol, 20 mol%) added. [l] HBr (48% in H_2O, 6 µl, 0.05 mmol, 20 mol%) added. [m] HI (4 µl, 0.05 mmol, 20 mol%) added. [n] $HBF_4 \bullet OEt_2$ (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]



1, (2 eq.) **4c**, (1 eq.) **5c**

Entry	Pre-catalyst	Additive(s)	5b / %[b]
1	$MnBr(CO)_5$ (**2**)[c]	Cy_2NH[d]	79
2	$MnBr(CO)_5$ (**2**)[c]	Cy_2NH[d], $EtCO_2H$	17
3	$Mn(ppy)(CO)_4$ (**3**)	None	44
4	$Mn(ppy)(CO)_4$ (**3**)	Cy_2NH[d]	46
5	$Mn(ppy)(CO)_4$ (**3**)	$[Cy_2NH_2]Cl$	20
6	$Mn(ppy)(CO)_4$ (**3**)	$[Cy_2NH_2]Br$	27
7	$Mn(ppy)(CO)_4$ (**3**)	$[Cy_2NH_2]I$	19
8	$Mn(ppy)(CO)_4$ (**3**)	$[Cy_2NH_2]BF_4$	40
9	$Mn(ppy)(CO)_4$ (**3**)	$EtCO_2H$	26

[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_2O (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_2NH (10 µl, 0.05 mmol, 20 mol%) added. [e] $EtCO_2H$ (4 µl, 0.05 mmol, 20 mol%) added, [f] $Mn(ppy)(CO)_4$ (8 mg, 0.025 mmol, 10 mol%) added. [g] $[Cy_2NH_2]Cl$ (11 mg, 0.05 mmol, 20 mol%) added. [h] $[Cy_2NH_2]Br$ (13 mg, 0.05 mmol, 20 mol%) added. [i] $[Cy_2NH_2]I$ (16 mg, 0.05 mmol, 20 mol%) added. [j] $[Cy_2NH_2]BF_4$ (14 mg, 0.05 mmol, 20 mol%) added.

3.4 In situ IR spectroscopic monitoring of reaction with 4b catalysed by 3 (figure 2a)

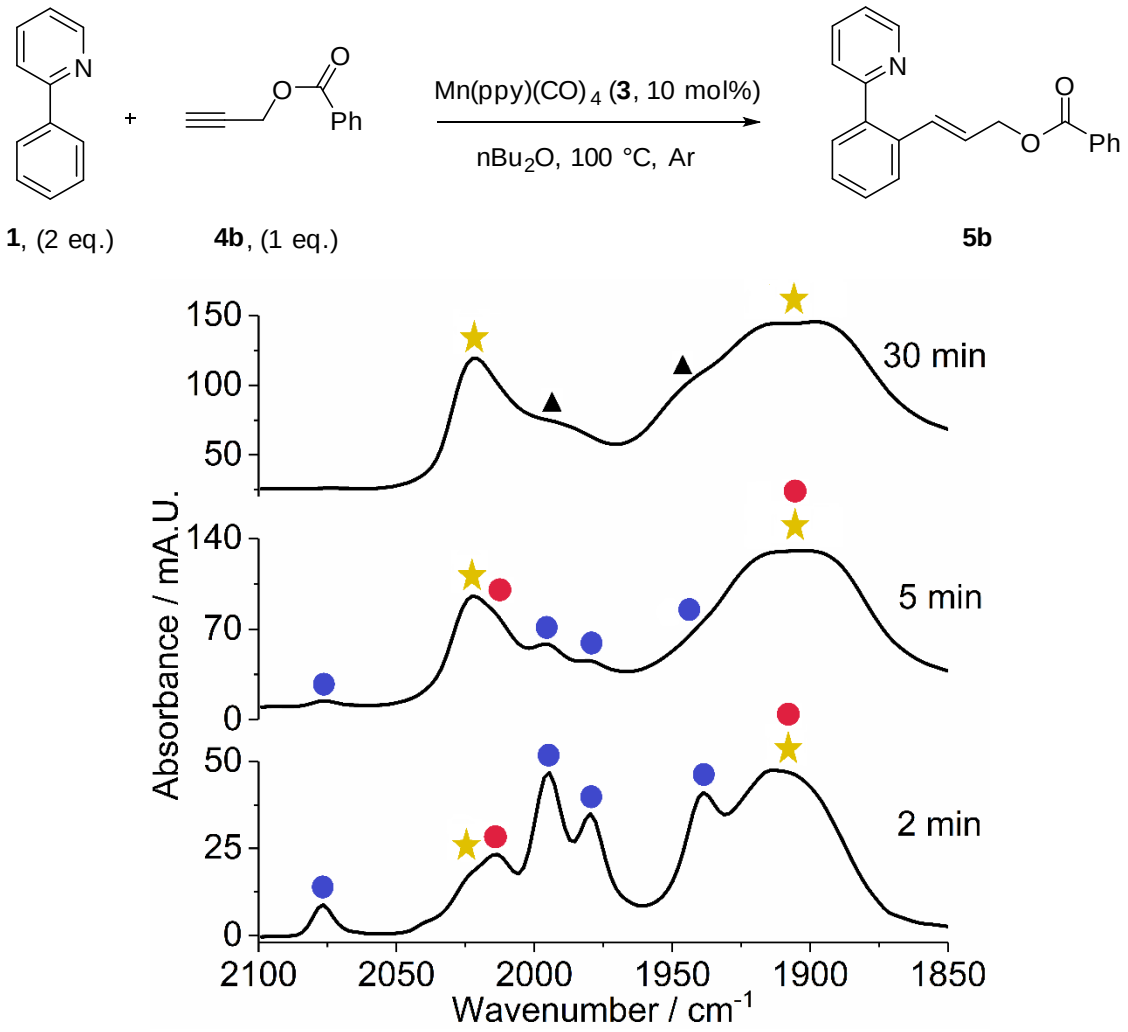


Figure S1. Reaction scheme and *in situ* IR spectra for the reaction of **4b** using $Mn(ppy)(CO)_4$ (**3**) as the precatalyst, showing the formation of new manganese carbonyl species over time from **3**. Reaction conditions (in order of addition): *n*-Bu_2O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 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%).

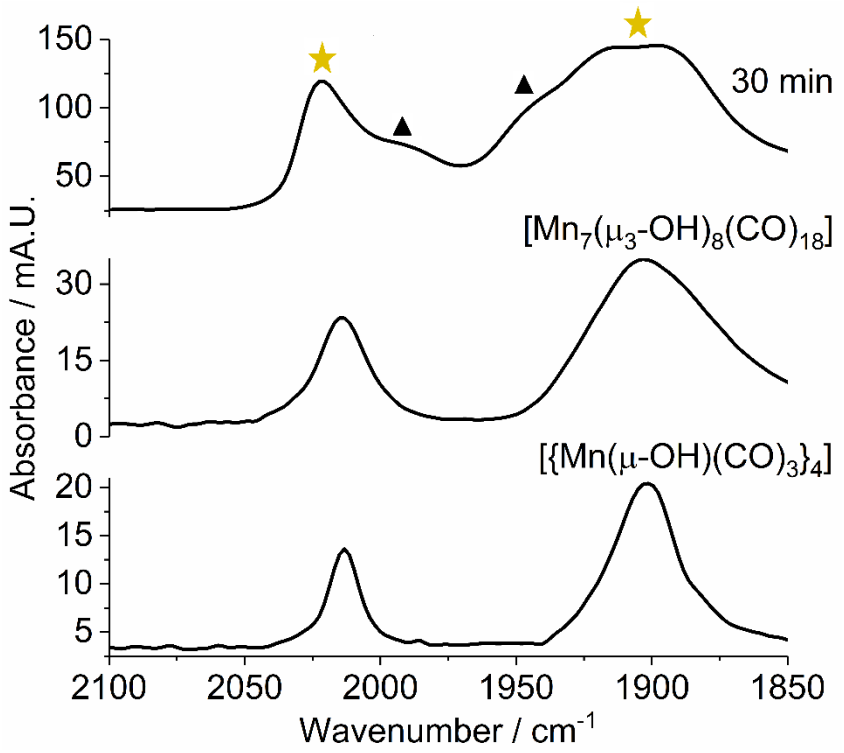
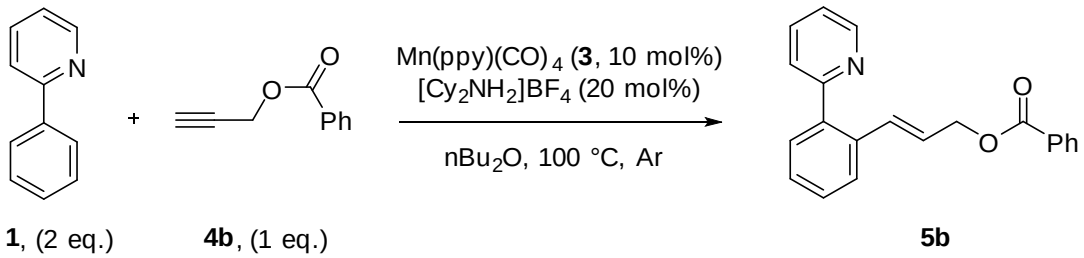


Figure S2. Comparison between the end spectrum of the reaction (30 min) with two Mn hydroxyl cluster compounds ([{Mn(μ–OH)(CO)$_3$}$_4$], and [Mn$_7$(μ$_3$–OH)$_8$(CO)$_{18}$]) heated at 100 °C in *n*-Bu$_2$O.

3.5 In situ IR spectroscopic monitoring of reaction with 4b and $[Cy_2NH_2]BF_4$ catalysed by 3 (figure 2b)



1, (2 eq.) **4b**, (1 eq.) **5b**

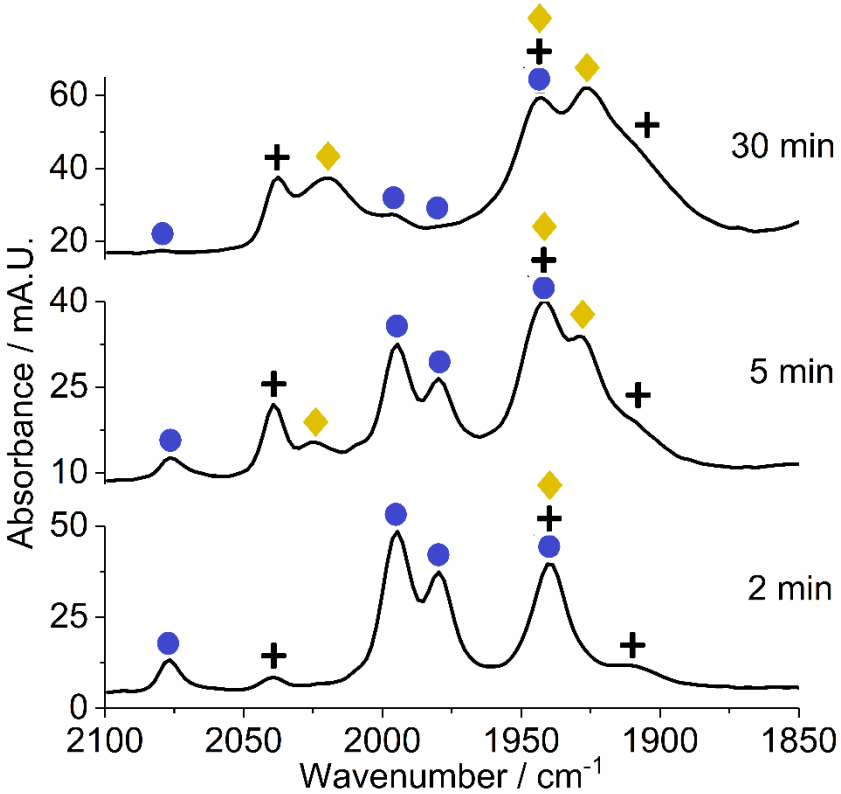


Figure S3. Reaction scheme and *in situ* IR spectra for the reaction of **4b** with $[Cy_2NH_2]BF_4$ added, using $Mn(ppy)(CO)_4$ (**3**) as the precatalyst, showing the formation of new manganese carbonyl species over time from **3**. Reaction conditions (in order of addition): *n*-Bu_2O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 mmol, 2 eq.), propargyl benzoate (0.60 ml, 4.16 mmol, 1 eq.), $[Cy_2NH_2]BF_4$ (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)

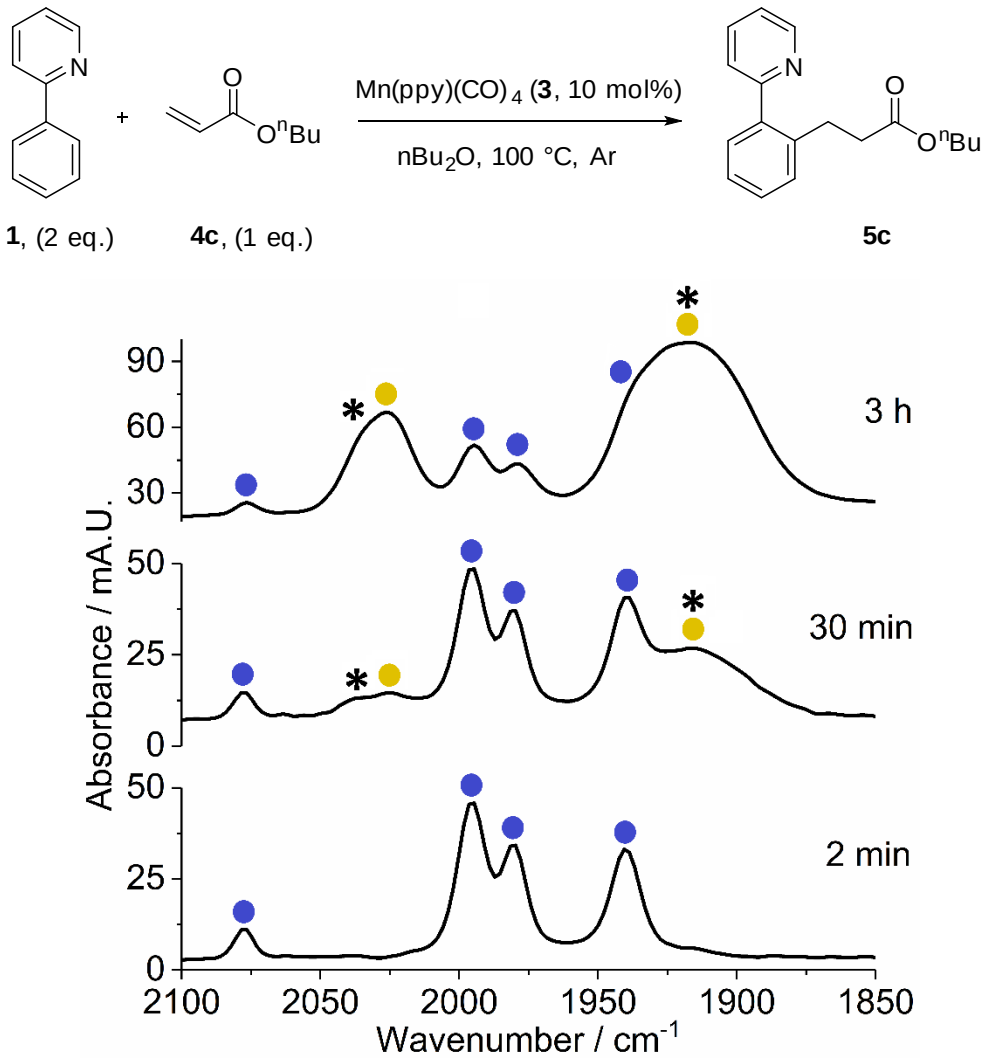


Figure S4. Reaction scheme and *in situ* IR spectra for the reaction of **4c** using $Mn(ppy)(CO)_4$ (**3**) as the precatalyst, showing the formation of new manganese carbonyl species over time from **3**. Reaction conditions (in order of addition): *n*-Bu_2O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 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%).

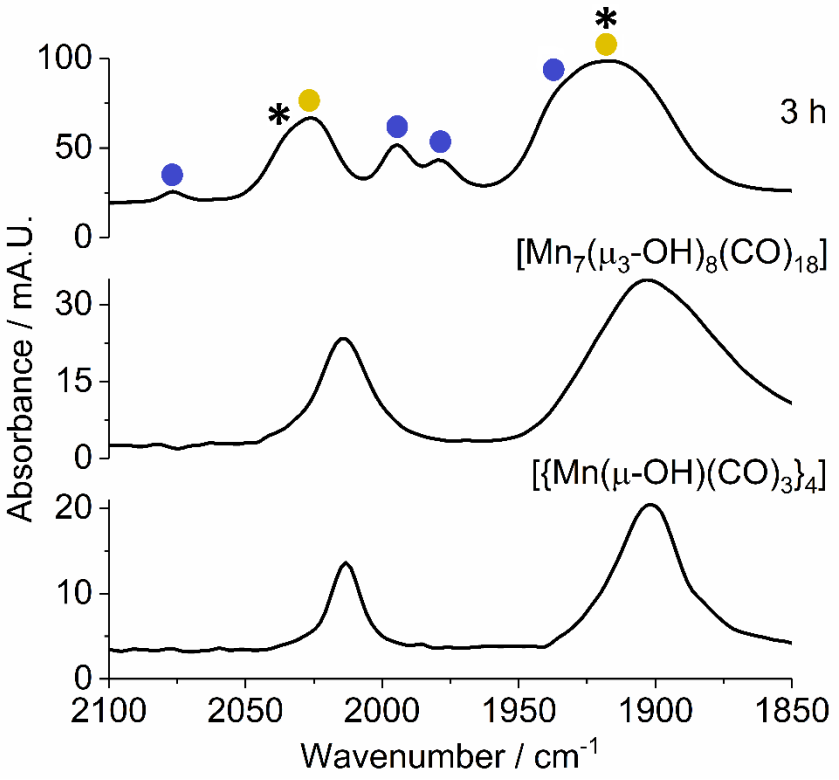


Figure S5. Comparison between the end spectrum of the reaction (3 h) with two Mn hydroxyl cluster compounds ([{Mn(μ–OH)(CO)$_3$}$_4$], and [Mn$_7$(μ$_3$–OH)$_8$(CO)$_{18}$]) heated at 100 °C in *n*-Bu$_2$O.

3.7 In situ IR spectroscopic monitoring of reaction with 4c and [Cy_2NH_2]Br catalysed by 3 (figure 2d)

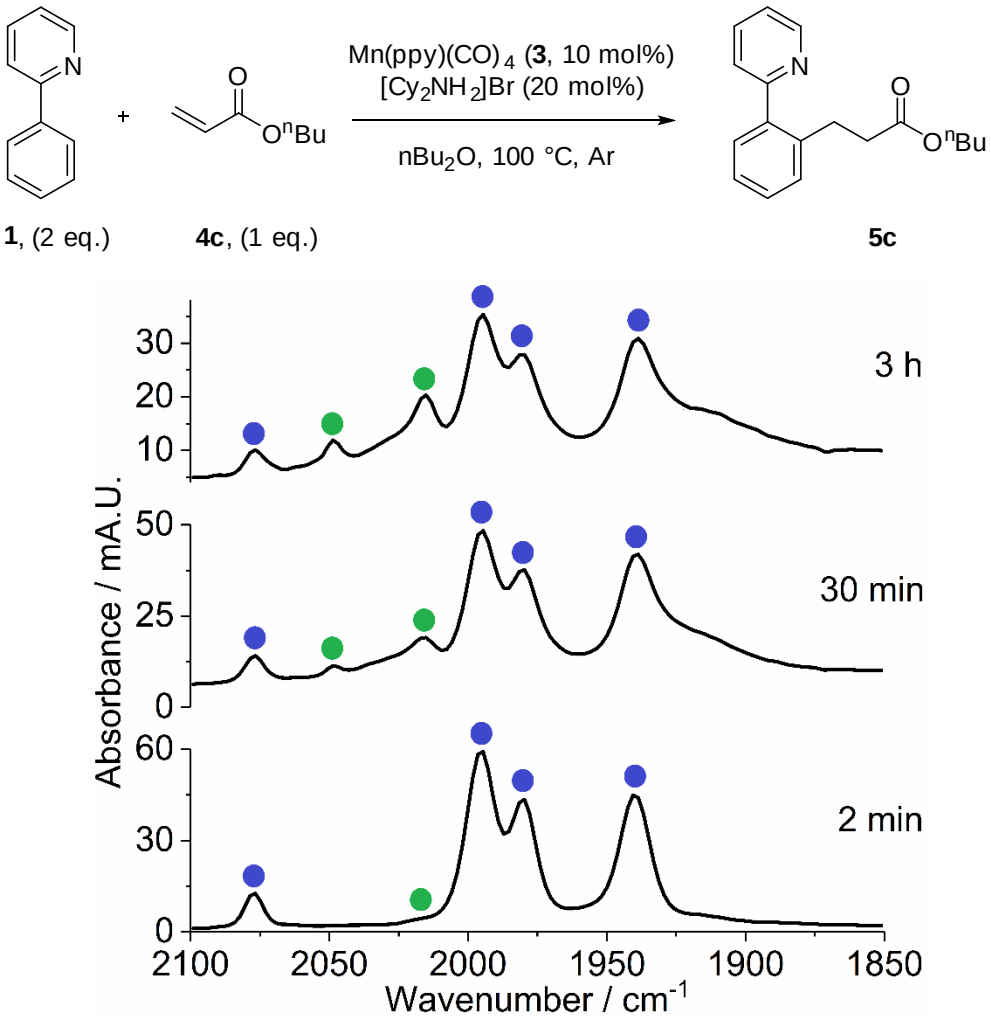


Figure S6. Reaction scheme and *in situ* IR spectra for the reaction of **4c** with [Cy_2NH_2]Br added, using $Mn(ppy)(CO)_4$ (**3**) as the precatalyst, showing the formation of new manganese carbonyl species over time from **3**. Reaction conditions (in order of addition): *n*-Bu_2O (10 ml), 2-phenylpyridine (1.19 ml, 8.32 mmol, 2 eq.), *n*-butyl acrylate (0.60 ml, 4.16 mmol, 1 eq.), [Cy_2NH_2]Br (0.218 g, 0.83 mmol, 20 mol%) and $Mn(ppy)(CO)_4$ (0.134 g, 0.42 mmol, 10 mol%).

4 NMR Spectra

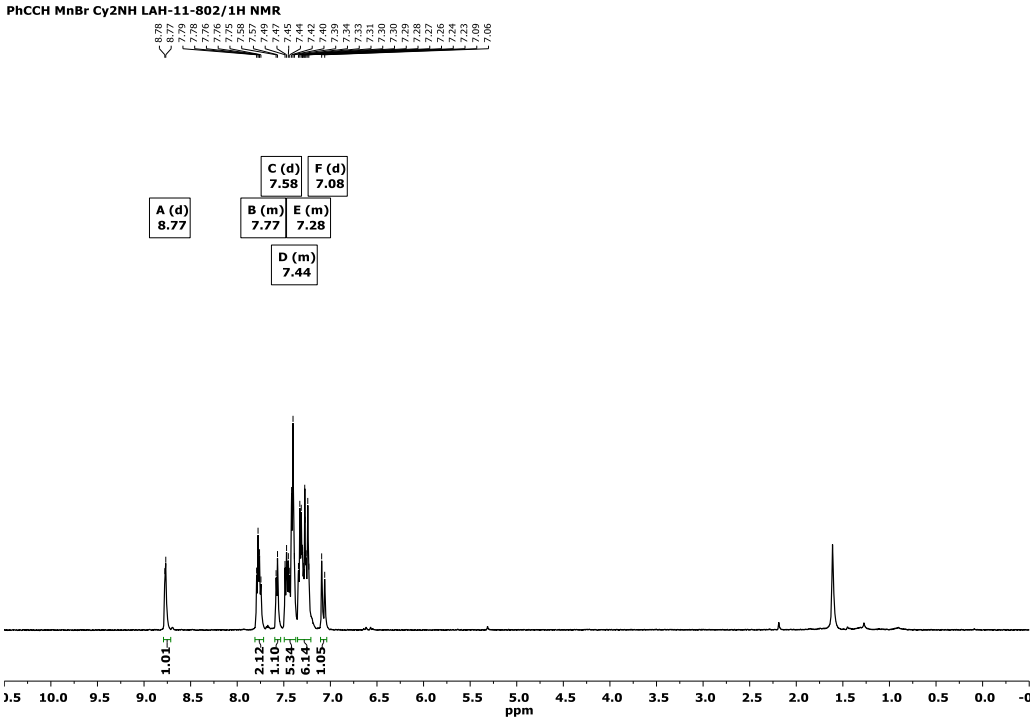


Figure S5. ^{1}H NMR spectrum of **5a** (500 MHz, $CDCl_3$)

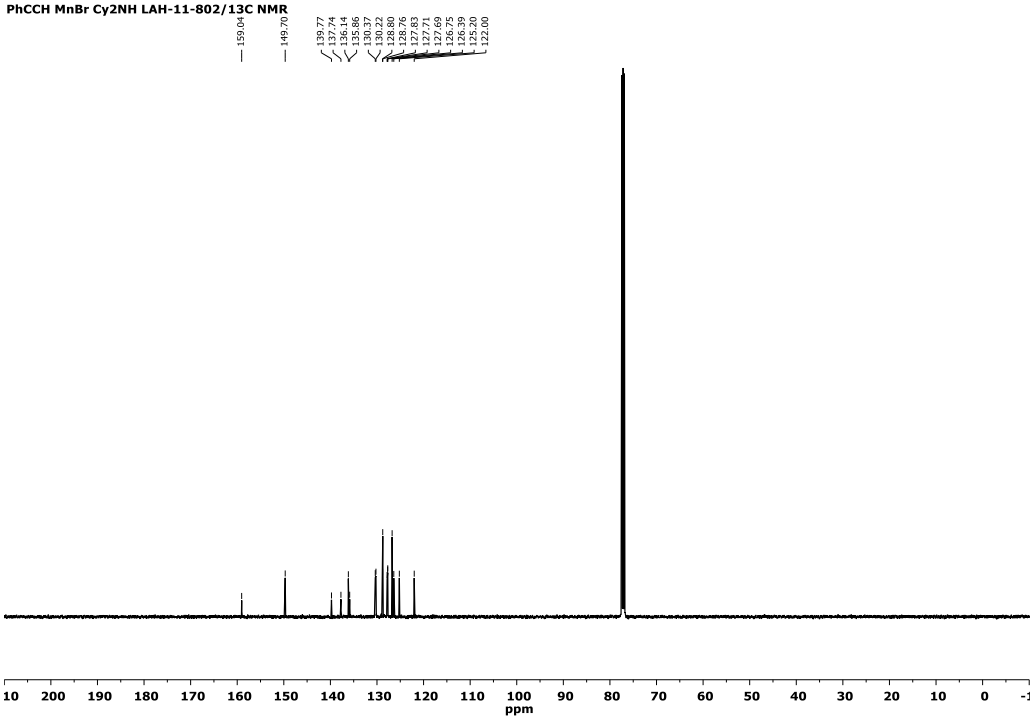


Figure S6. ^{13}C NMR spectrum of **5a** (126 MHz, $CDCl_3$)

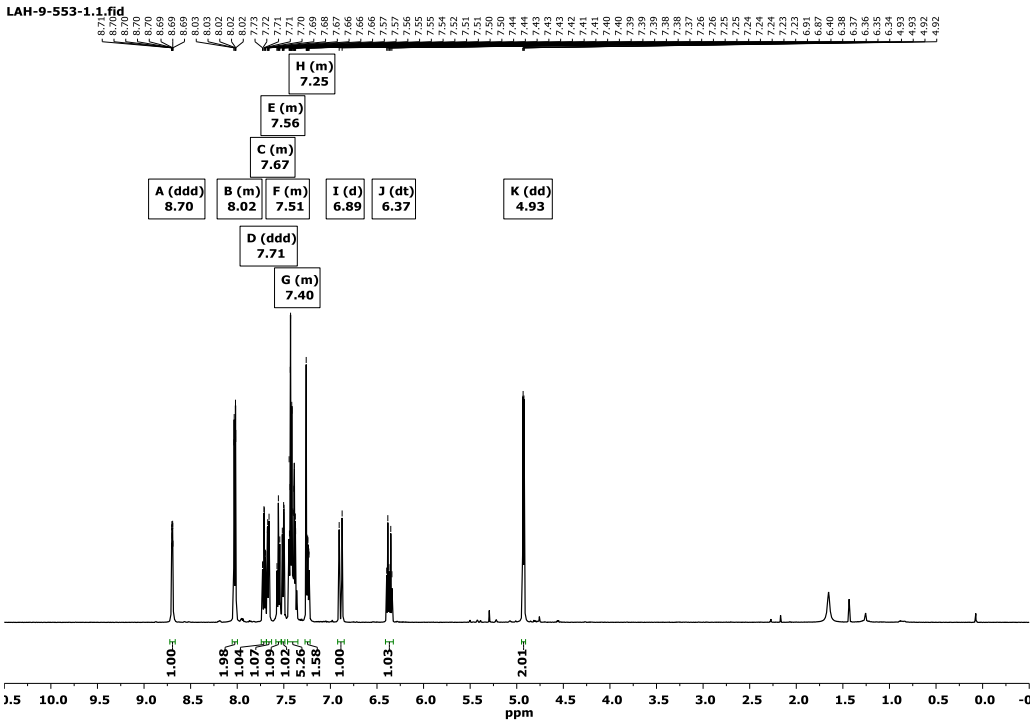


Figure S7. ^{1}H NMR spectrum of **5b** (500 MHz, $CDCl_3$)

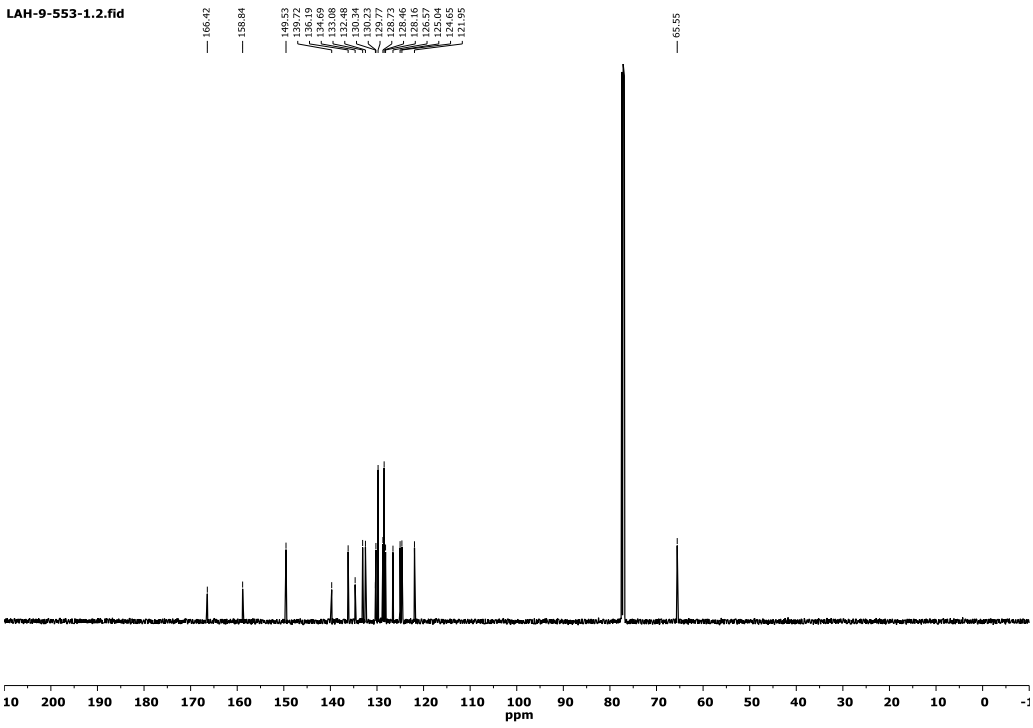


Figure S8. ^{13}C NMR spectrum of **5b** (126 MHz, $CDCl_3$)

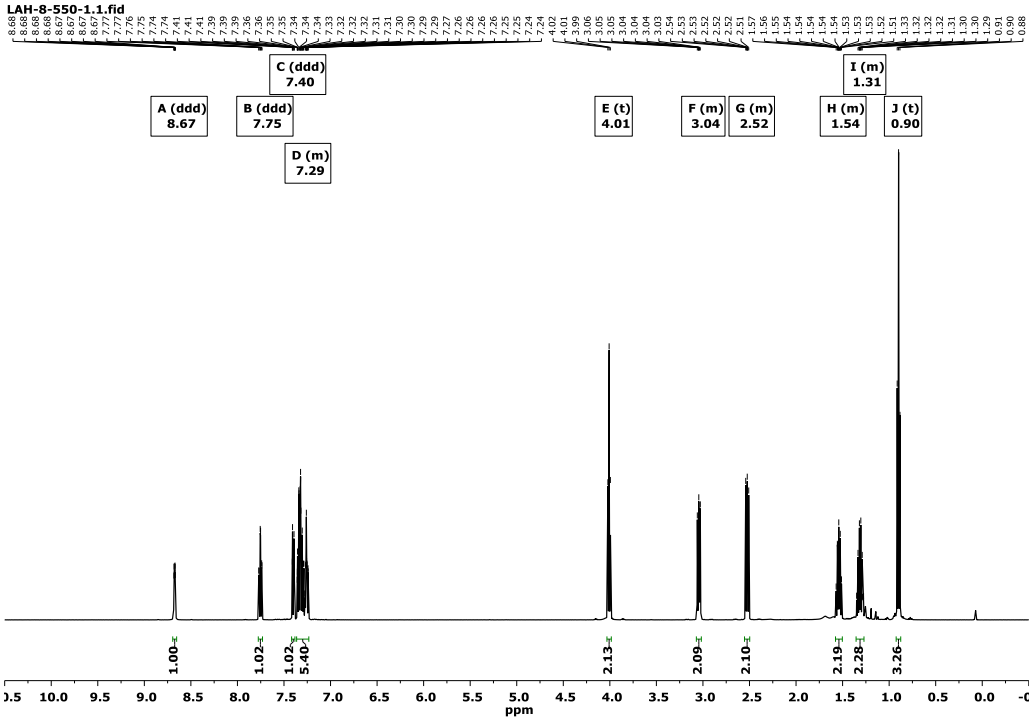


Figure S9. ^{1}H NMR spectrum of **5c** (500 MHz, $CDCl_3$)

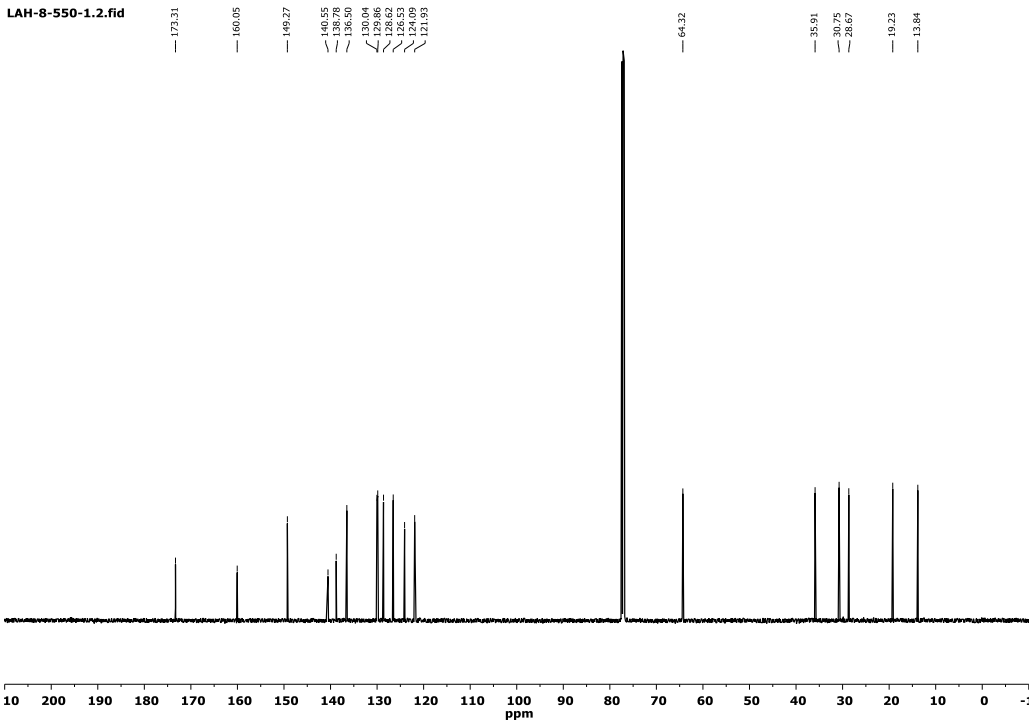


Figure S10. ^{13}C NMR spectrum of **5c** (126 MHz, $CDCl_3$)

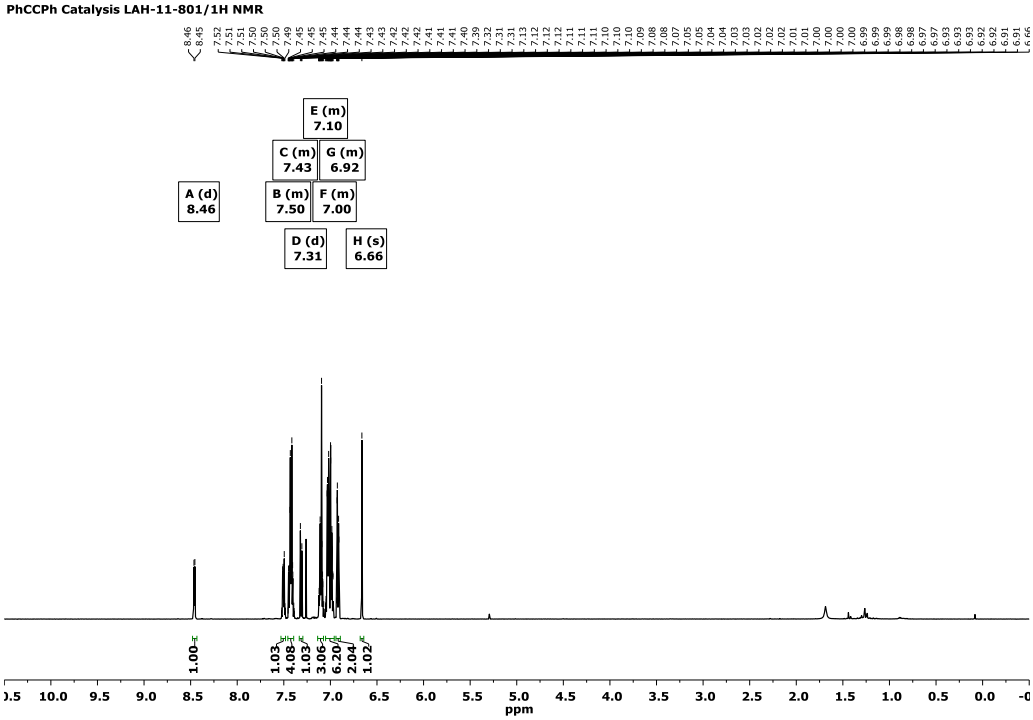


Figure S11. ^{1}H NMR spectrum of **7** (500 MHz, $CDCl_3$)

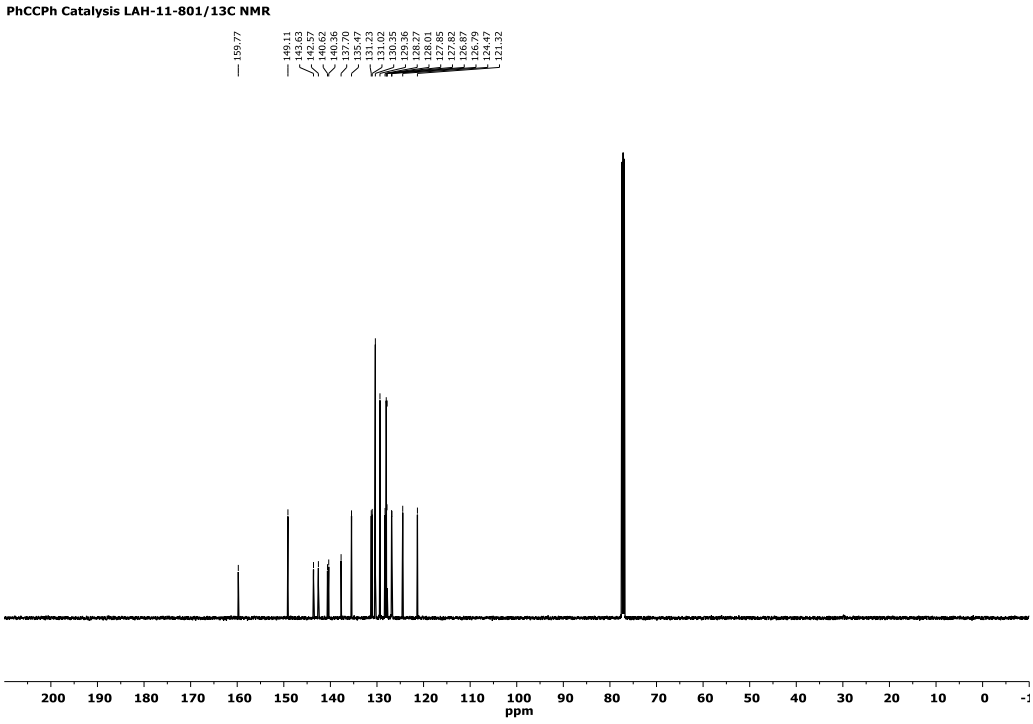


Figure S12. ^{13}C NMR spectrum of **7** (126 MHz, $CDCl_3$)

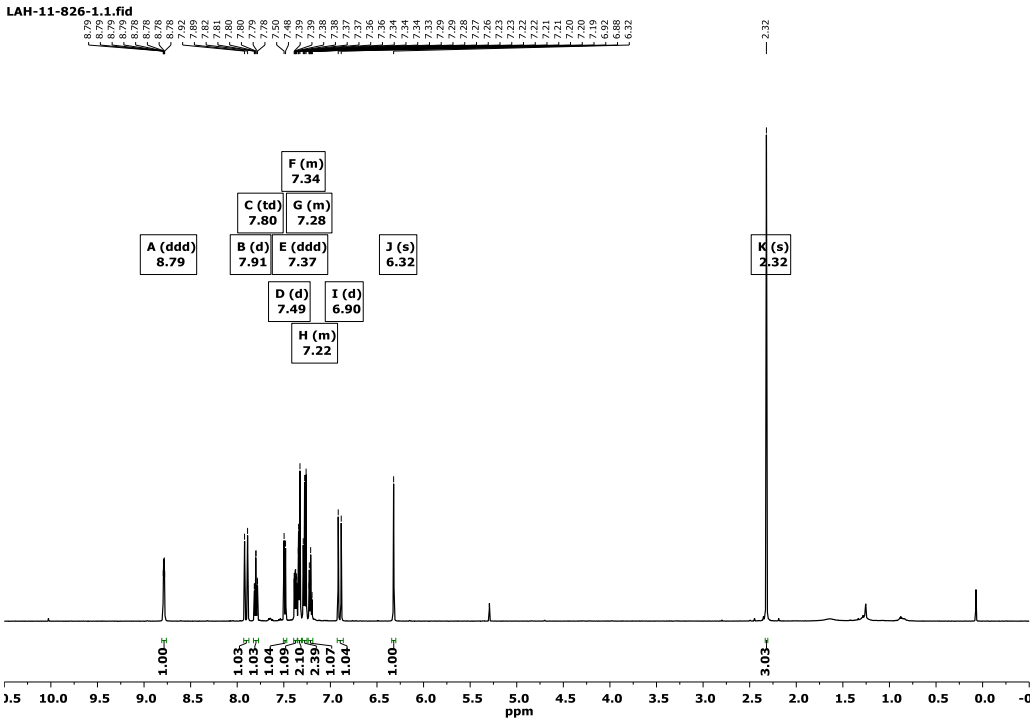


Figure S13. ^{1}H NMR spectrum of **9** (500 MHz, $CDCl_3$)

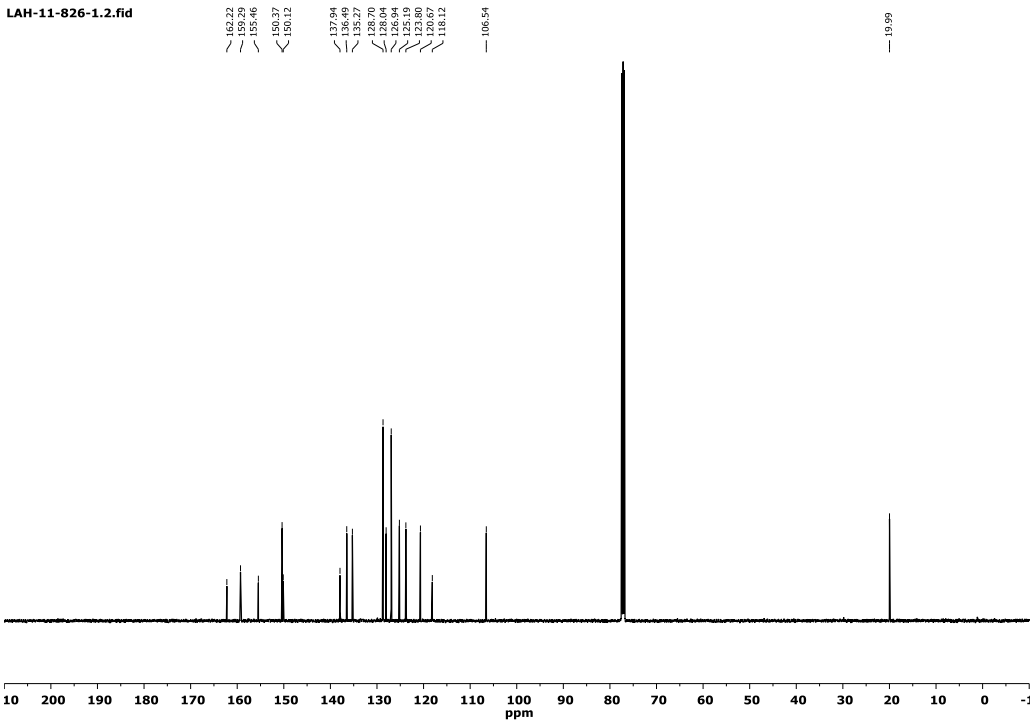


Figure S14. ^{13}C NMR spectrum of **9** (126 MHz, $CDCl_3$)

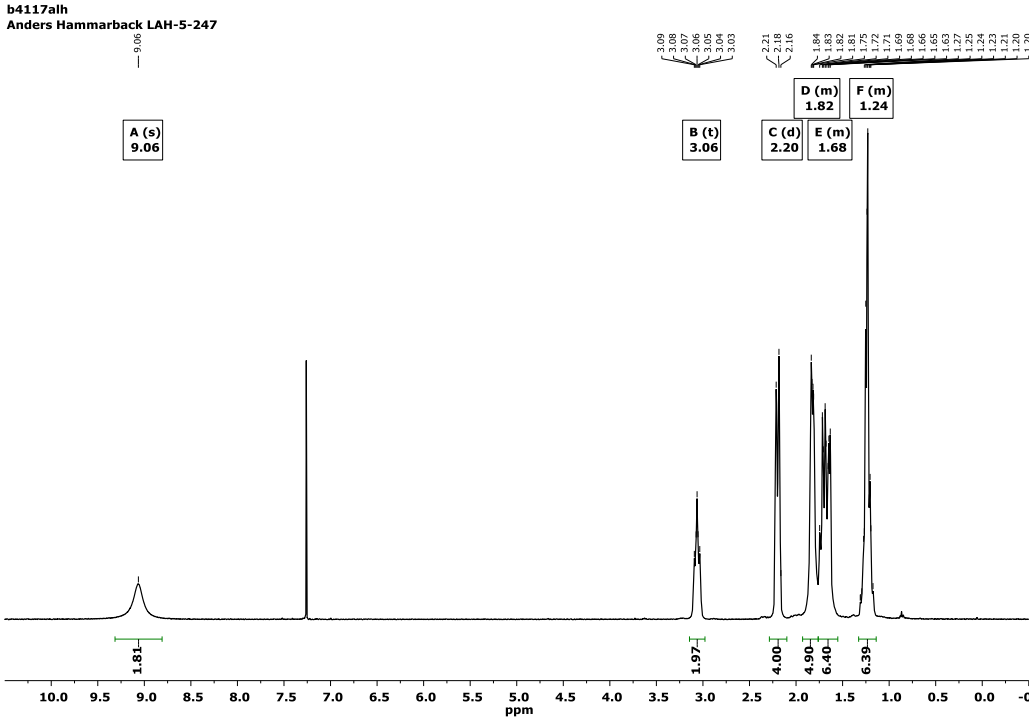


Figure S15. ^{1}H NMR spectrum of $[Cy_2NH_2]Cl$ (400 MHz, $CDCl_3$)

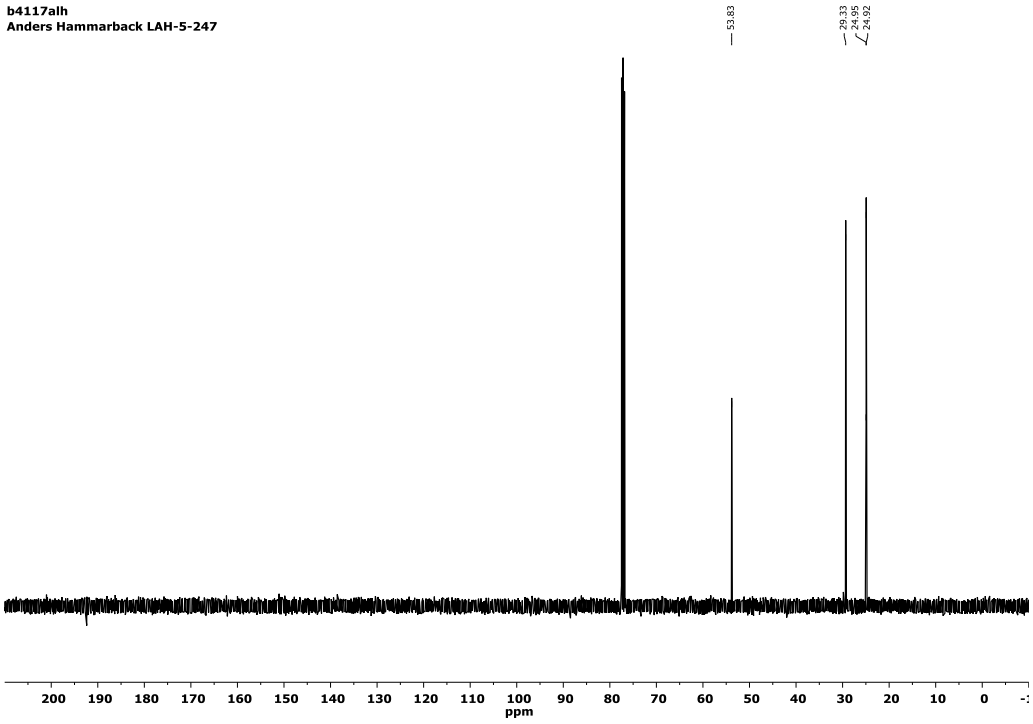


Figure S16. ^{13}C NMR spectrum of $[Cy_2NH_2]Cl$ (101 MHz, $CDCl_3$)

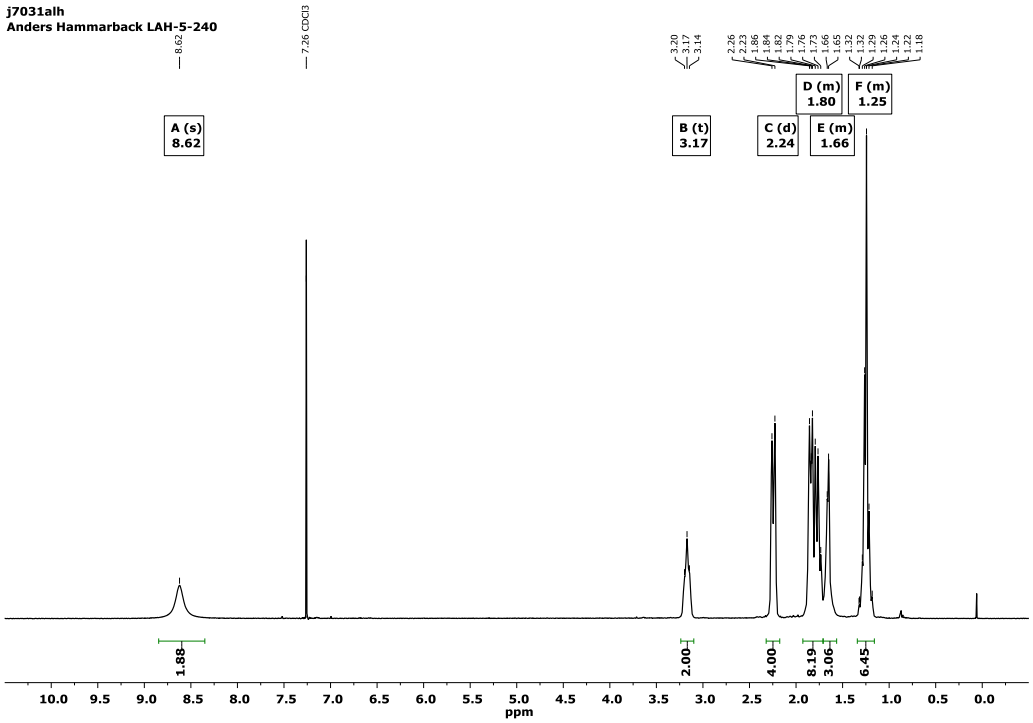


Figure S17. ^{1}H NMR spectrum of $[Cy_2NH_2]Br$ (400 MHz, $CDCl_3$)

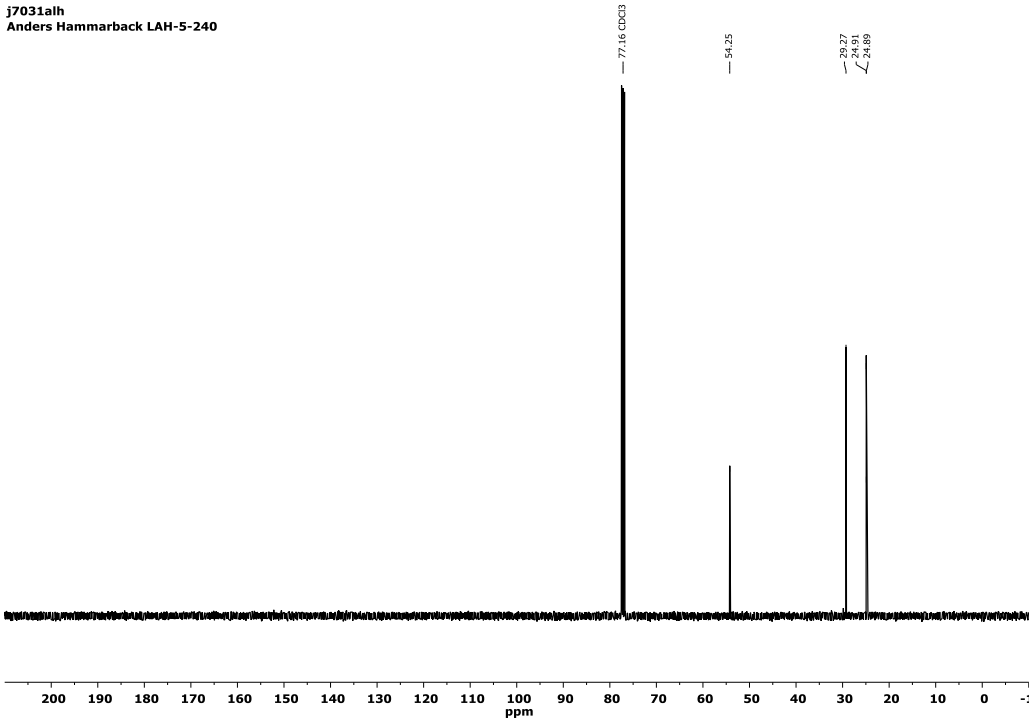


Figure S18. ^{13}C NMR spectrum of $[Cy_2NH_2]Br$ (101 MHz, $CDCl_3$)

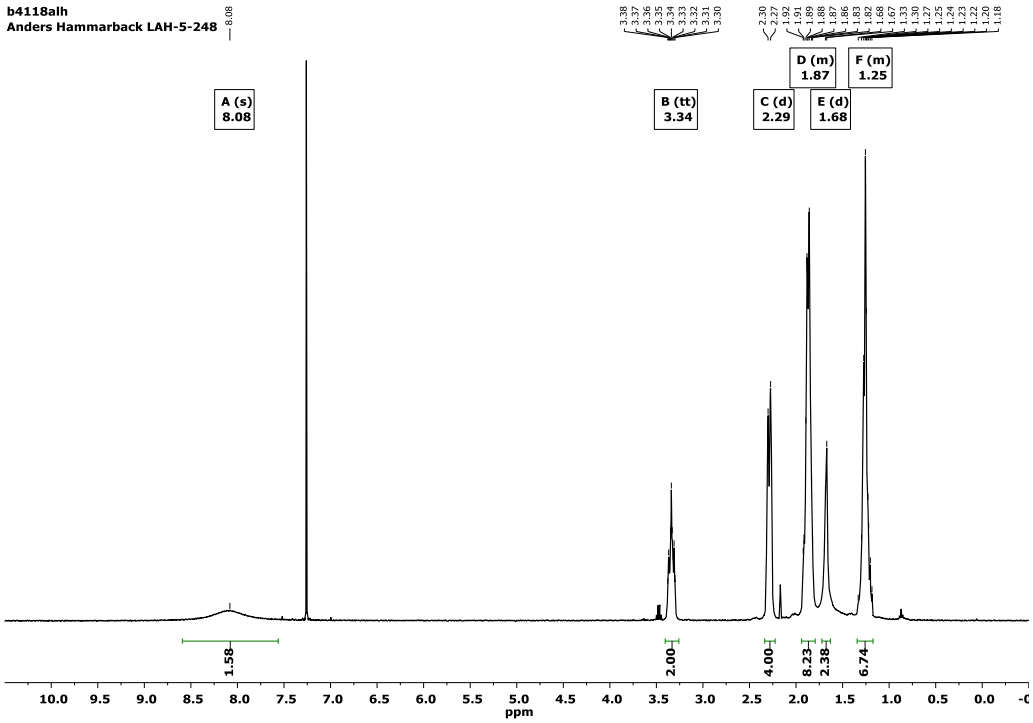


Figure S19. ^{1}H NMR spectrum of $[Cy_2NH_2]I$ (400 MHz, $CDCl_3$)

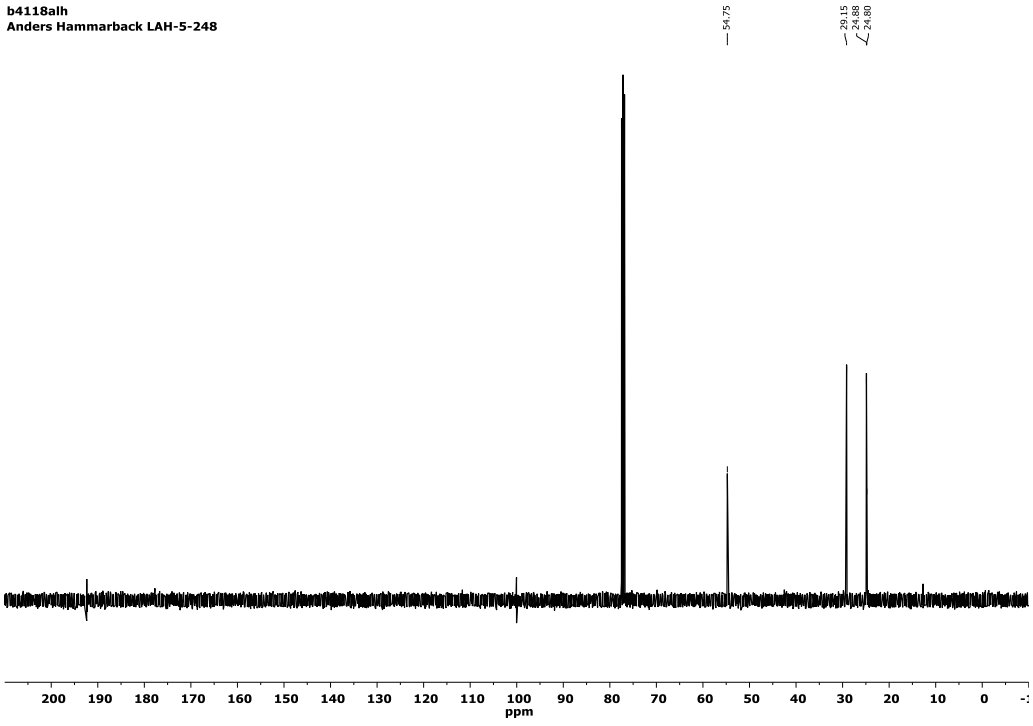


Figure S20. ^{13}C NMR spectrum of $[Cy_2NH_2]I$ (101 MHz, $CDCl_3$)

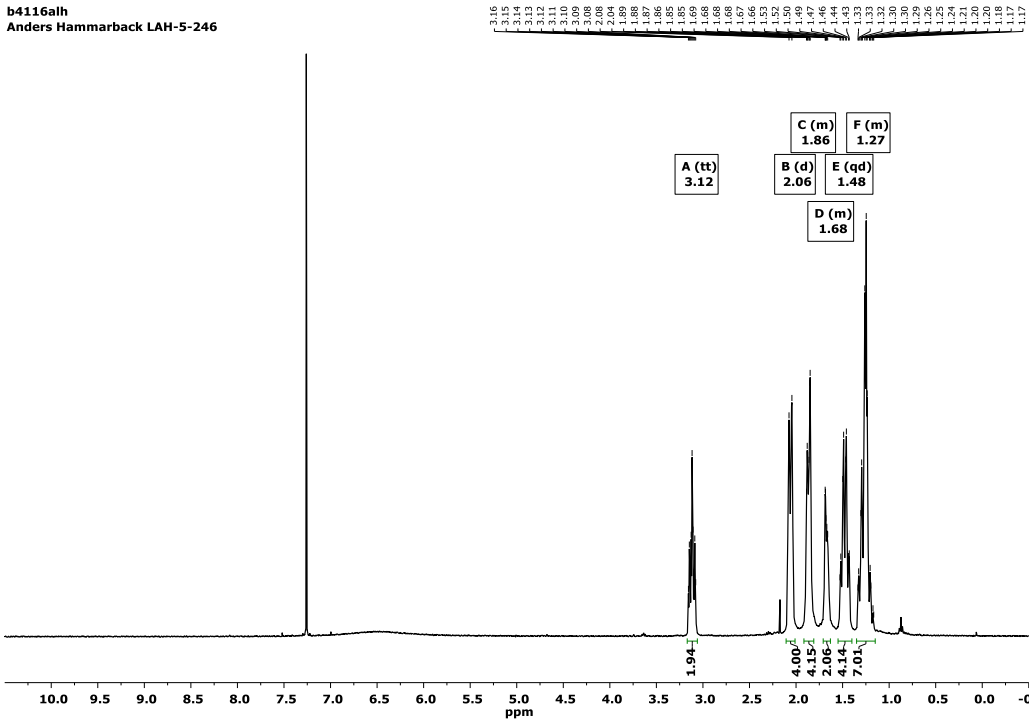


Figure S21. ^{1}H NMR spectrum of $[Cy_2NH_2]BF_4$ (400 MHz, $CDCl_3$)

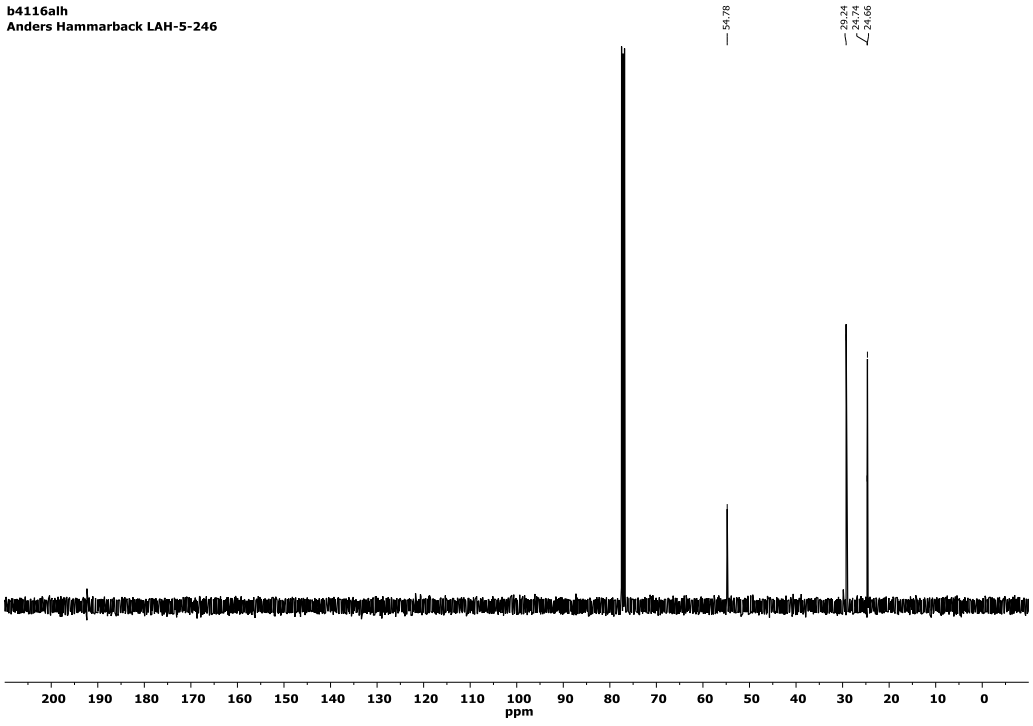


Figure S22. ^{13}C NMR spectrum of $[Cy_2NH_2]BF_4$ (101 MHz, $CDCl_3$)

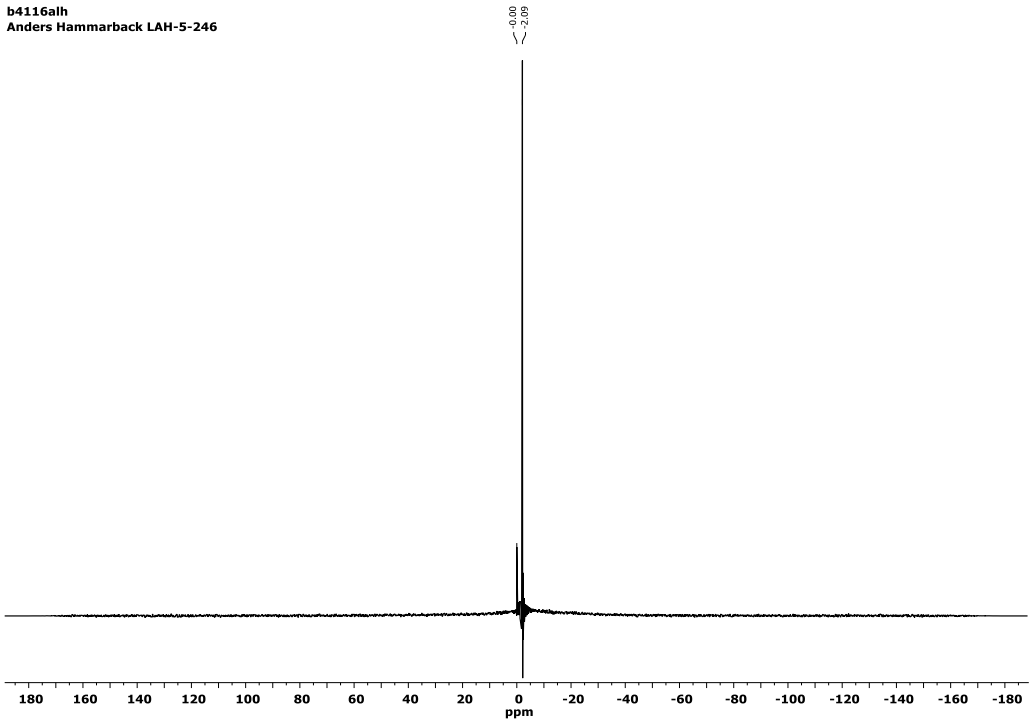


Figure S23. ^{11}B NMR spectrum of $[Cy_2NH_2]BF_4$ (128 MHz, $CDCl_3$)

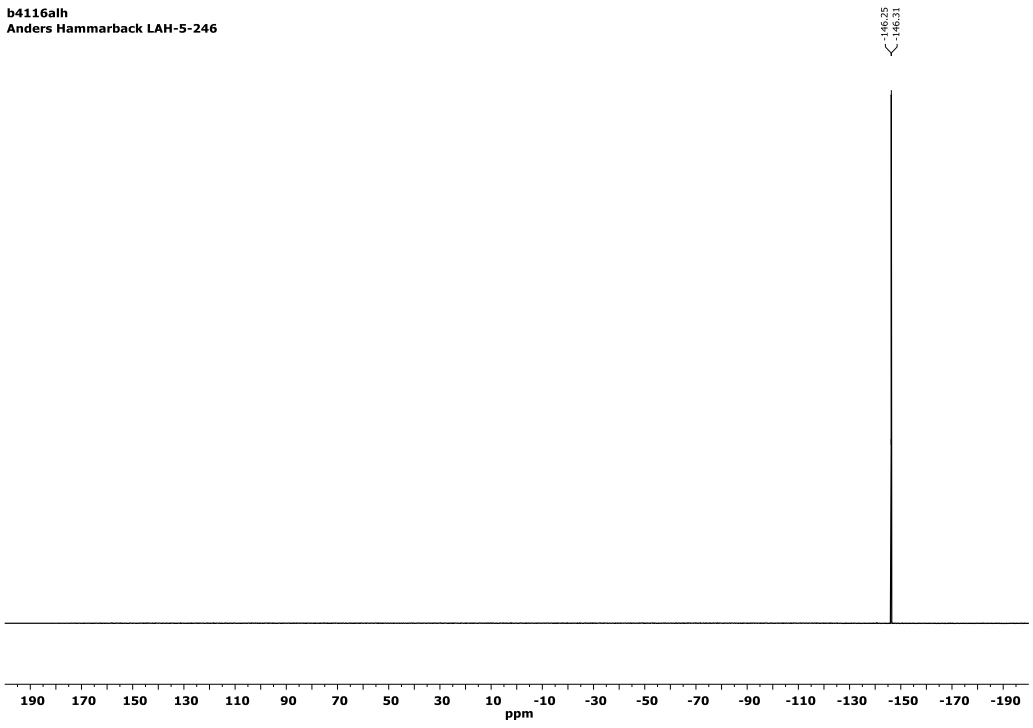


Figure S24. ^{19}F NMR spectrum of $[Cy_2NH_2]BF_4$ (376 MHz, $CDCl_3$)

5 References

1 N. P. Yahaya, K. M. Appleby, M. The, C. Wagner, E. Troschke, J. T. W. Bray, S. B. Duckett, L. A. Hammarback, J. S. Ward, J. Milani, N. E. Pridmore, A. C. Whitwood, J. M. Lynam and I. J. S. Fairlamb, *Angew. Chem. Int. Ed.*, 2016, **55**, 12455-12459.

2 M. D. Clerk and M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.*, 1991, 1607-1608.

3 W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923-2925.

4 B. Zhou, H. Chen and C. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 1264-1267.