Electronic Supplementary Information

An ionic Fe-based metal-organic-framework with 4′-pyridyl-2,2′;6′,2′′-terpyridine for catalytic hydroboration of alkynes

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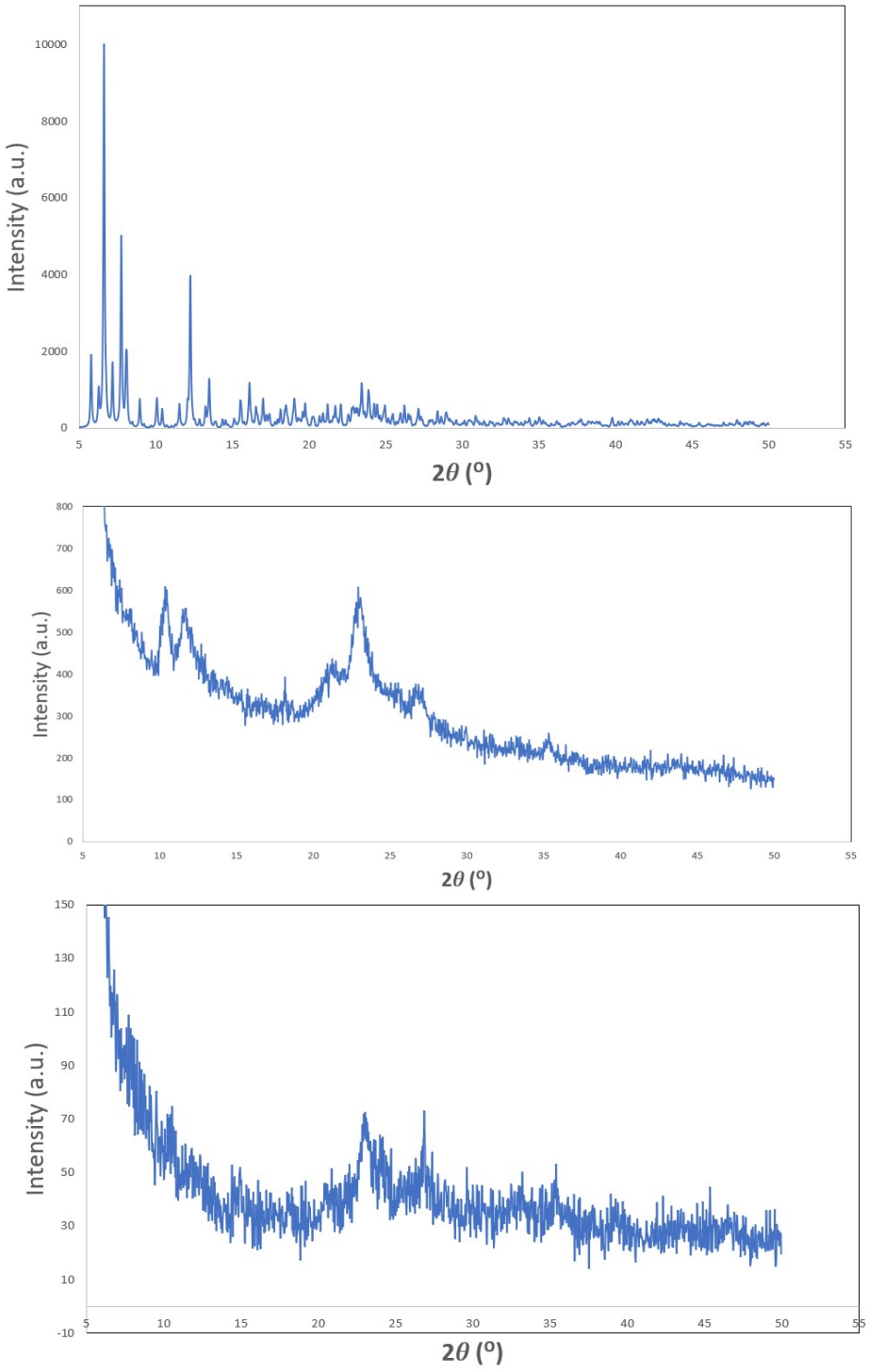
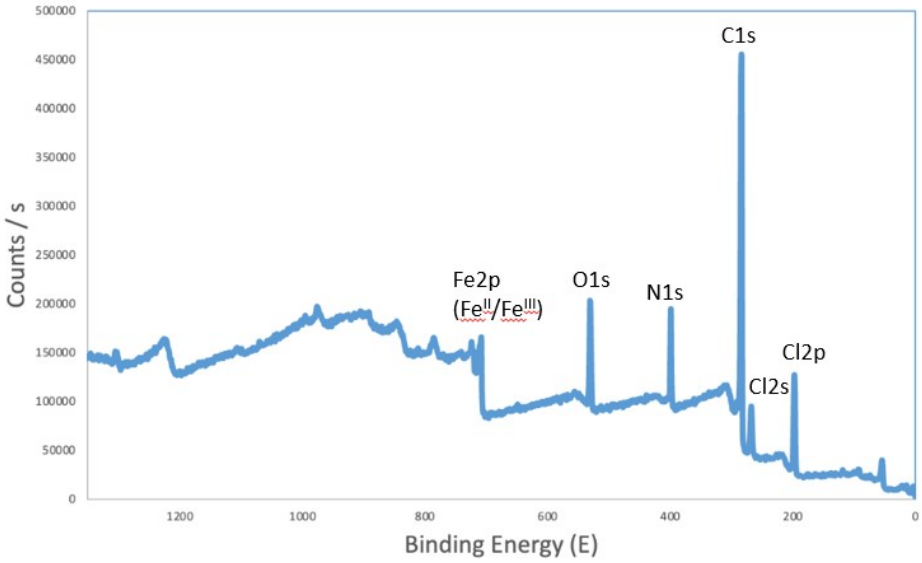


Figure S1. The measured PXRD pattern of sample **1** after being dried in the air (green line) and the calculated PXRD pattern of **1** from the single-crystal X-ray diffraction data (violet line).

Before catalysis



After catalysis

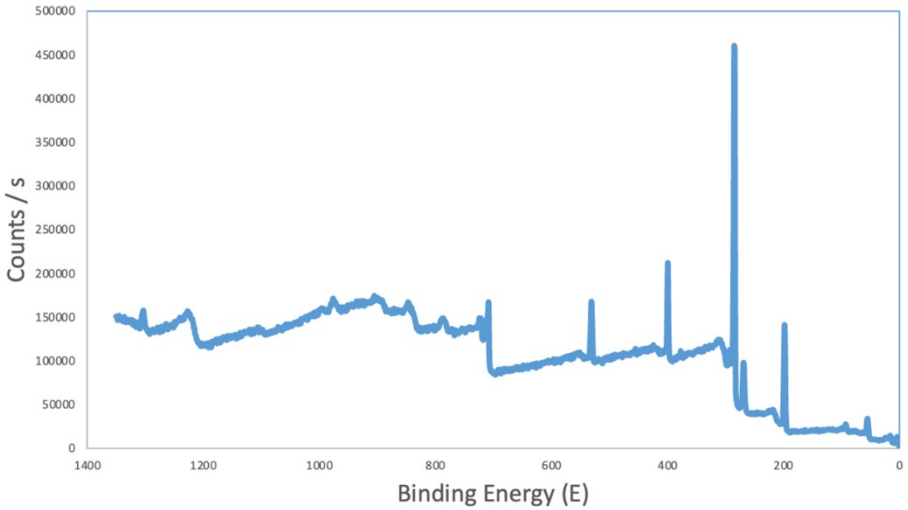


Figure S2. The XPS surveys of sample **1** before and after being used in catalysis.

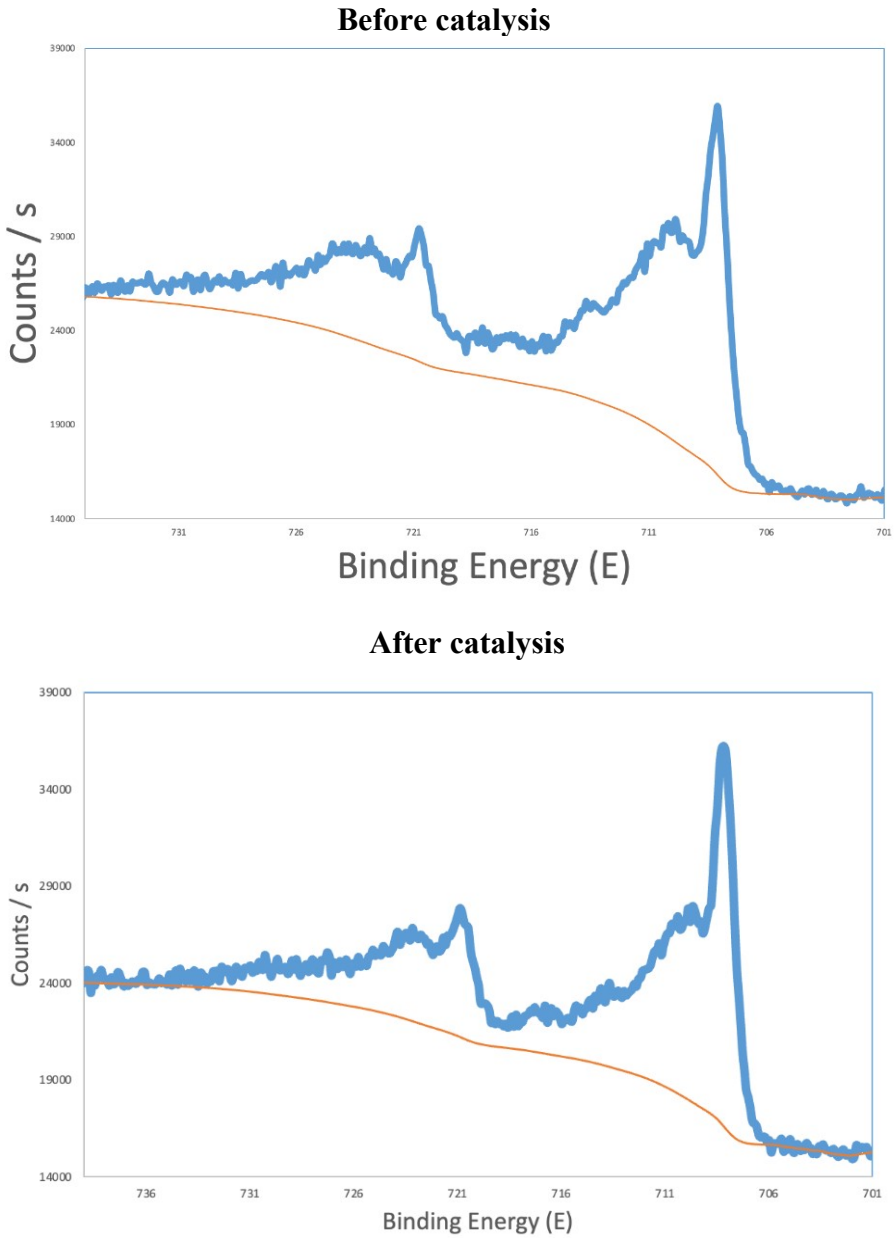


Figure S3. The XPS profiles of Fe2p in **1** before and after being used in catalysis. The presence of both Fe^{2+} and Fe^{3+} is in good agreement with known mixed-valent iron compounds in the literature.[1]

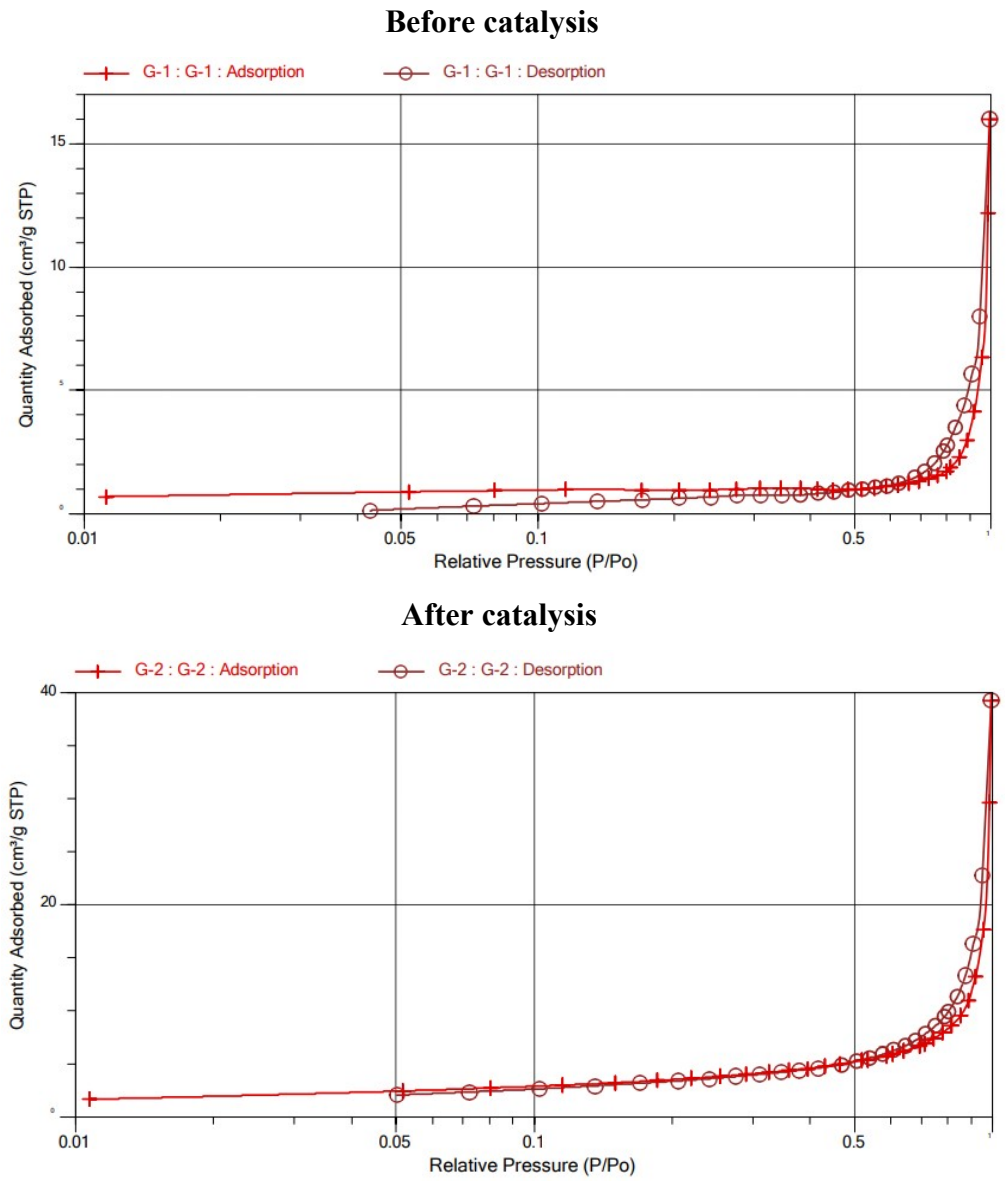


Figure S4. The N_2 absorption/desorption isotherms of **1** before and after being used in catalysis.

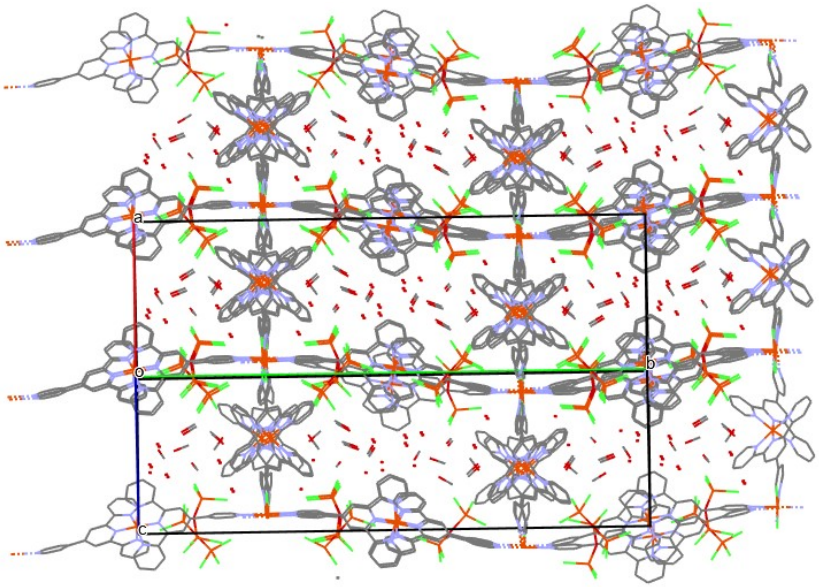


Fig. S5. The 3-D packing structure in **1** driven by π···π stacking showing large pores that are partially occupied by the counterions $Cl_3FeOFeCl_3$ and co-crystallised solvent molecules.

Table S1. Crystal, intensity collection, and refinement data.

	1	**2**
lattice	Monoclinic	Triclinic
formula	$C_{86}H_{92}Cl_{14}Fe_7N_{16}O_{14}$	$C_{43}H_{31.5}Cl_{9.5}Fe_4N_8O_{1.5}$
formula weight	2461.00	1244.44
space group	$P2_1/n$	$P\text{-}1$
a/Å	15.759(2)	11.4061(12)
b/Å	44.011(6)	14.7072(15)
c/Å	17.302(3)	16.0129(17)
α/°	90	101.764(2)
β/°	108.840(8)	110.162(2)
γ/°	90	92.028(2)
V/Å^3	11357(3)	2452.3(4)
Z	4	2
temperature (K)	130(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.) g cm^{-3}	1.439	1.685
μ (Mo Kα), mm^{-1}	1.259	1.723
θ max, deg.	25.027	30.247
no. of data collected	201893	69494
no. of data	20069	14450
no. of parameters	1245	619
R_1 [$I > 2\sigma(I)$]	0.1335	0.0706
wR_2 [$I > 2\sigma(I)$]	0.3060	0.1662
R_1 [all data]	0.1533	0.1451
wR_2 [all data]	0.3157	0.2045
GOF	1.152	1.026
R_{int}	0.1261	0.1221

Spectroscopic data for selective products

3a:[2] Colorless oil. Yield: 161 mg (70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 18.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.20 (d, *J* = 18.5 Hz, 1H), 1.34 (s, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 137.7, 129.0, 128.7, 127.2, 83.5, 25.0 ppm. GC-MS (m/z): 230 (calc. 230).

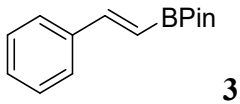
3c:[2] Yellowish oil. Yield: 164 mg (66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 18.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.20 (d, *J* = 18.5 Hz, 1H), 1.34 (s, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3 (d, *J* = 248.7 Hz), 148.3, 133.9, 128.8 (d, *J* = 8.2 Hz), 115.7 (d, *J* = 21.6 Hz), 83.5, 24.9 ppm. GC-MS (m/z): 248 (calc. 248).

3h:[2] Colorless oil. Yield: 155 mg (80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.07 (dd, *J* = 17.8, 9.3 Hz, 1H), 5.48 (d, *J* = 17.8 Hz, 1H), 1.51 (dq, *J* = 8.7, 4.1 Hz, 1H), 1.29 – 1.17 (m, 12H), 0.79 (dd, *J* = 8.1, 2.4 Hz, 2H), 0.58 – 0.45 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 83.1, 24.9, 17.1, 8.0 ppm. GC-MS (m/z): 194 (calc. 194).

3k:[2] Colorless oil. Yield: 160 mg (77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.63 (dtd, *J* = 18.3, 9.4, 8.1, 5.1 Hz, 1H), 5.82 (dddd, *J* = 17.0, 10.2, 6.1, 3.0 Hz, 1H), 5.48 – 5.42 (m, 1H), 5.05 – 4.99 (m, 1H), 4.99 – 4.94 (m, 1H), 2.25 (dd, *J* = 10.0, 4.4 Hz, 2H), 2.17 (dd, *J* = 8.7, 5.1 Hz, 2H), 1.28 – 1.24 (m, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 138.0, 114.8, 83.0, 35.1, 32.3, 29.7, 24.8 ppm. GC-MS (m/z): 208 (calc. 208).

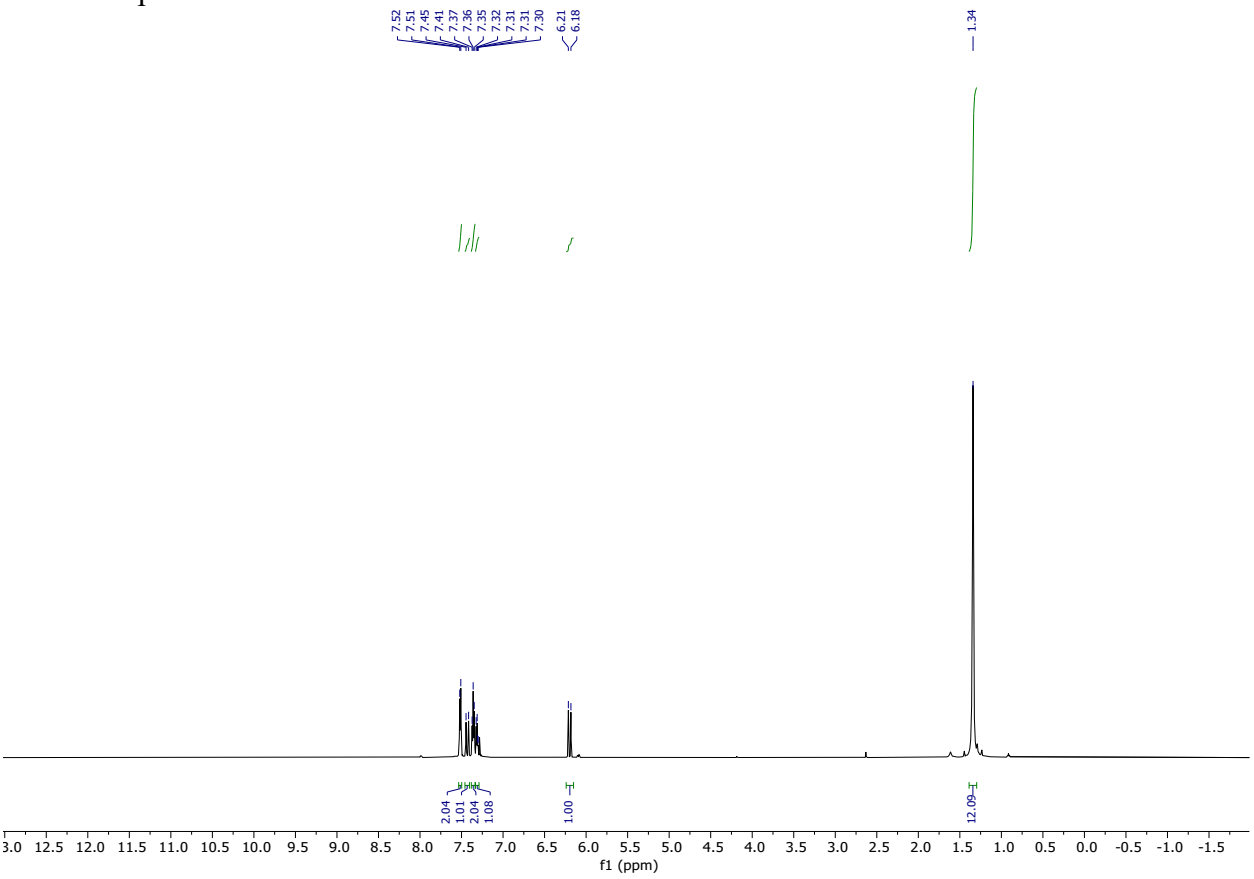
3l:[2] Colorless oil. Yield: 159 mg (71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.64 (dt, *J* = 18.1, 4.7 Hz, 1H), 5.90 (dq, *J* = 16.2, 5.3 Hz, 1H), 5.71 (dt, *J* = 18.2, 1.9 Hz, 1H), 5.37 – 5.22 (m, 1H), 5.22 – 5.06 (m, 1H), 4.06 (dd, *J* = 4.7, 1.8 Hz, 2H), 3.99 (d, *J* = 5.8 Hz, 2H), 1.26 (s, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 134.7, 116.9, 83.3, 71.7, 71.3, 24.8 ppm. GC-MS (m/z): 224 (calc. 224).

Copies of ^{1}H and ^{13}C NMR spectra for isolated products.

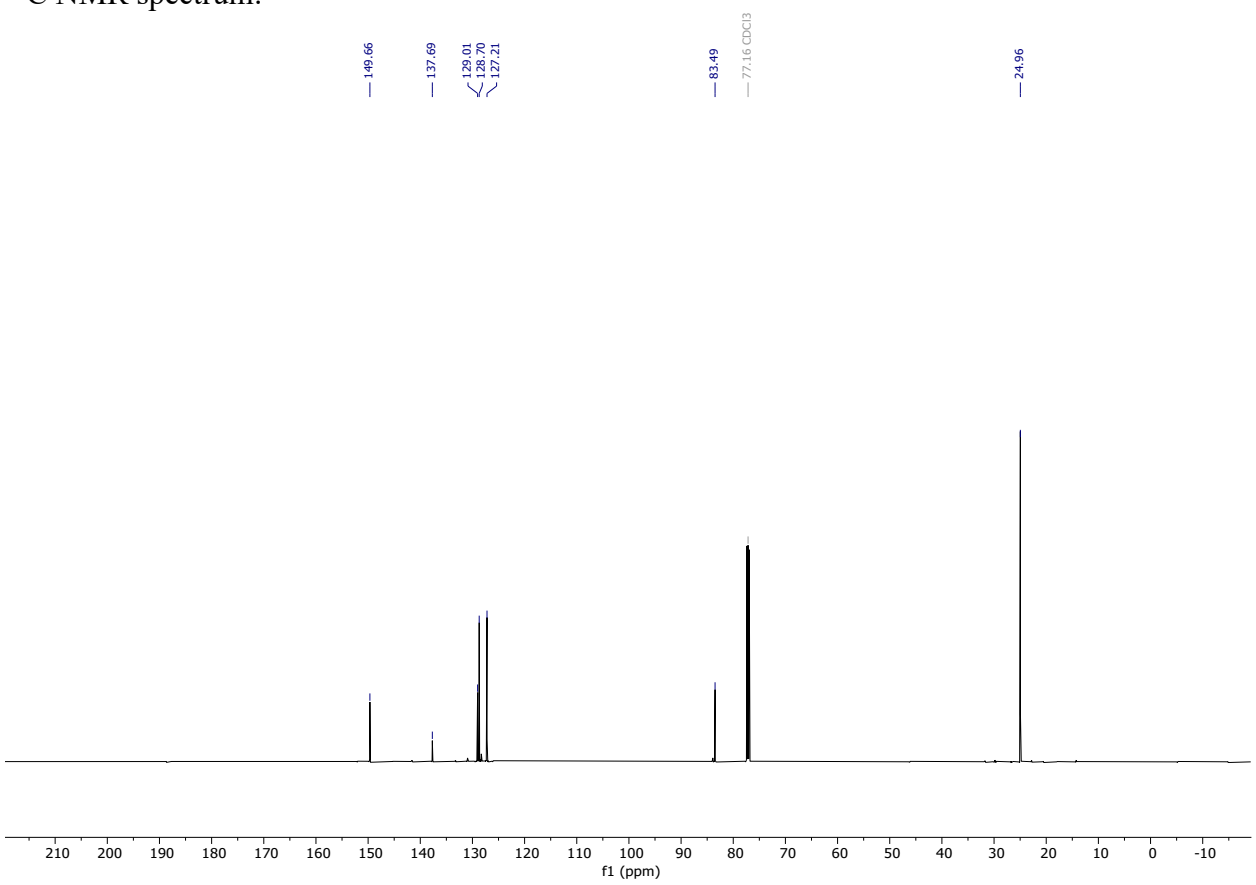


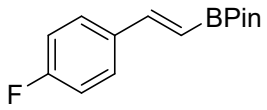
3a

^{1}H NMR spectrum:



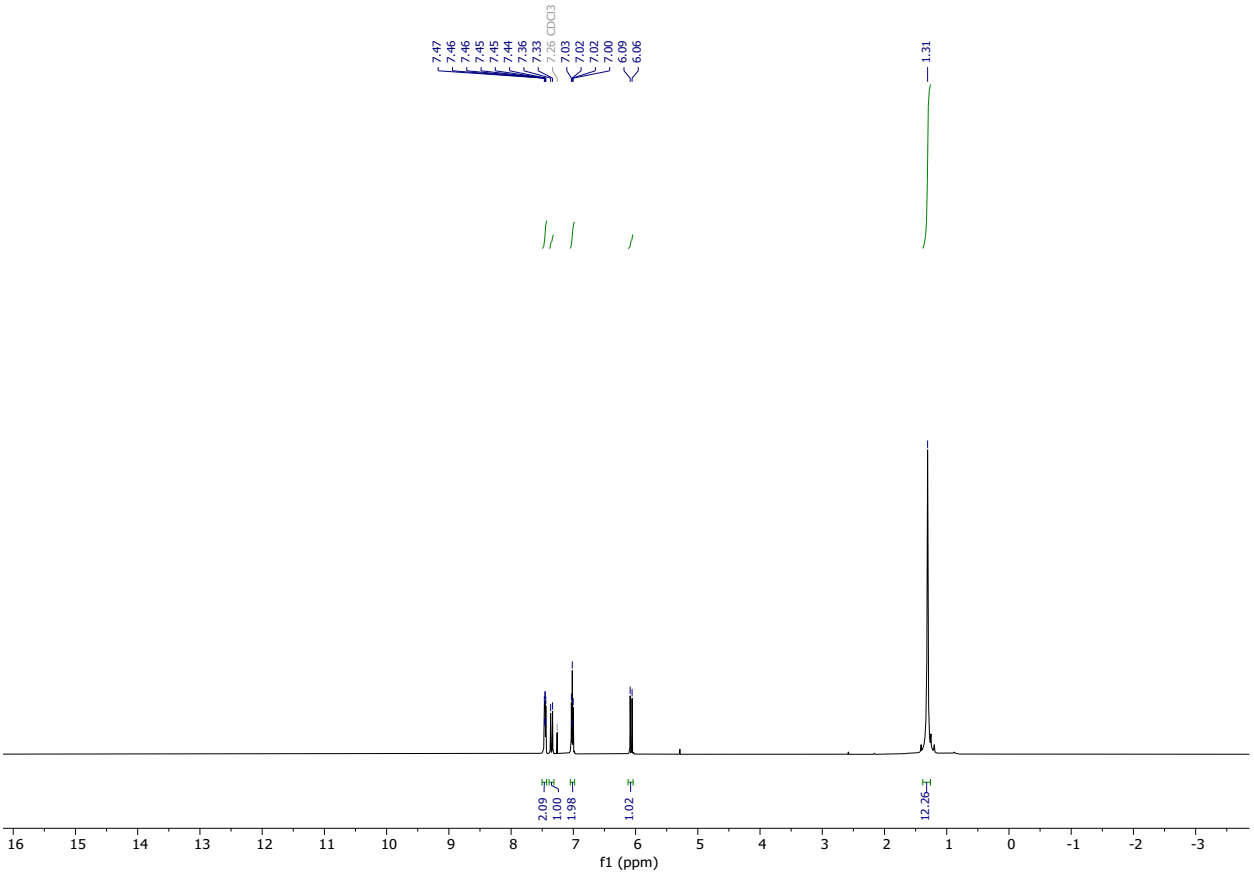
^{13}C NMR spectrum:



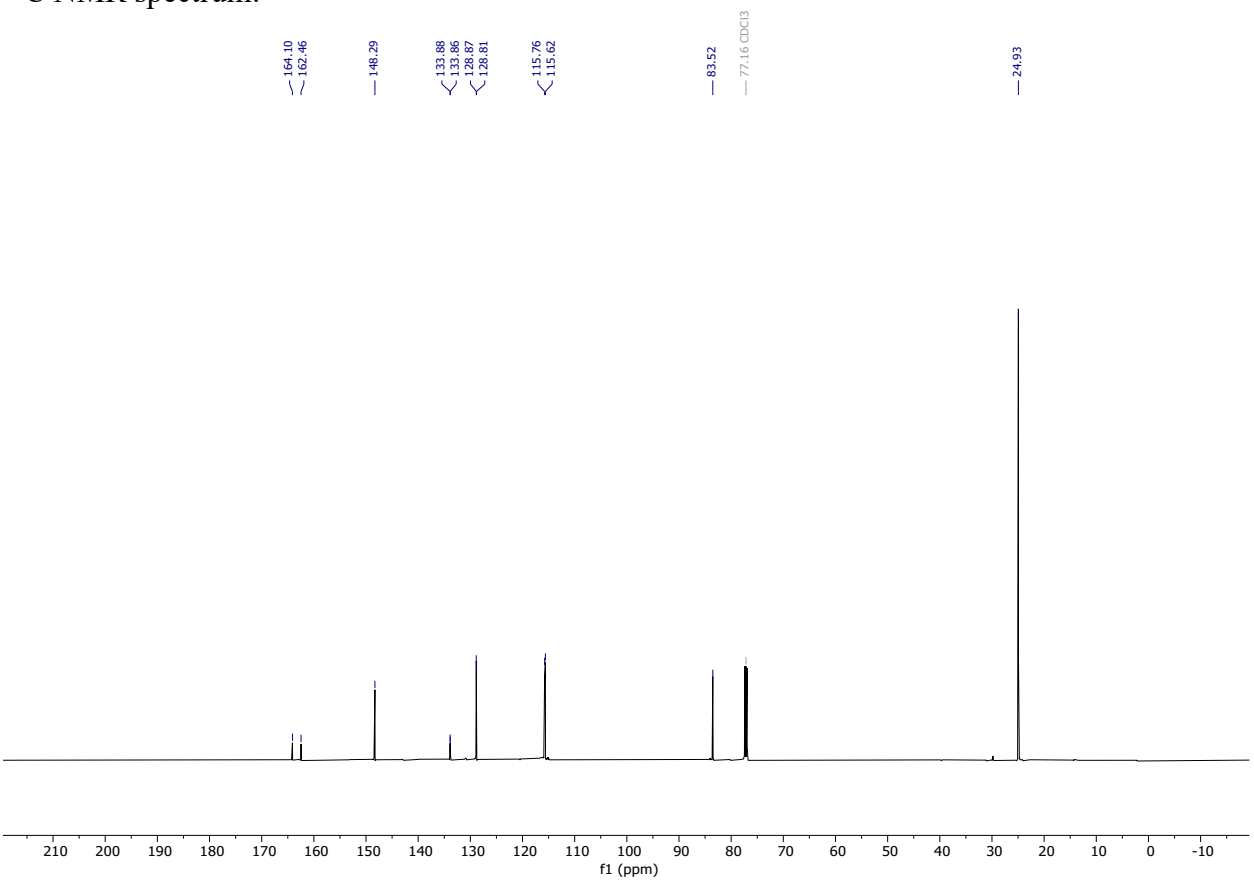


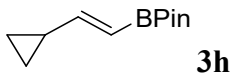
3c

^{1}H NMR spectrum:



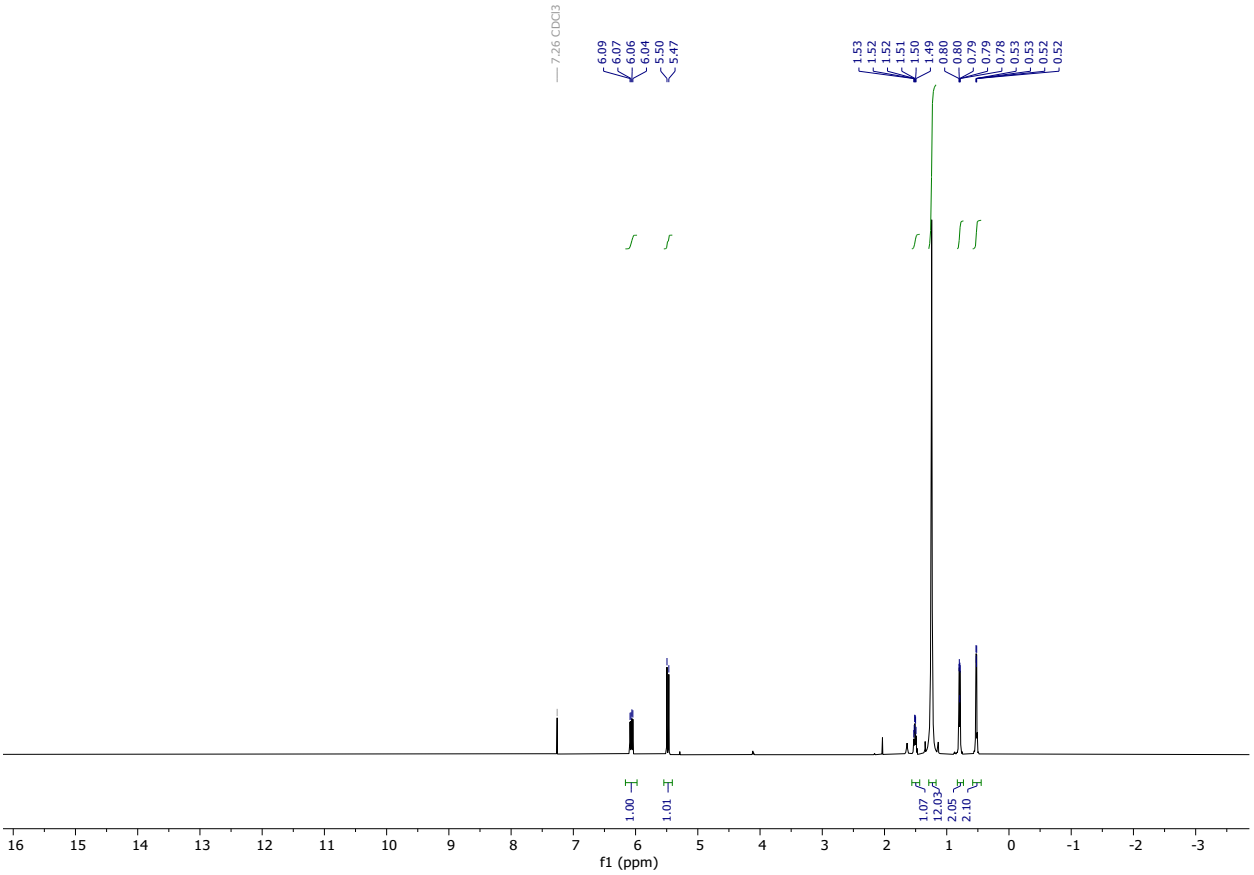
^{13}C NMR spectrum:



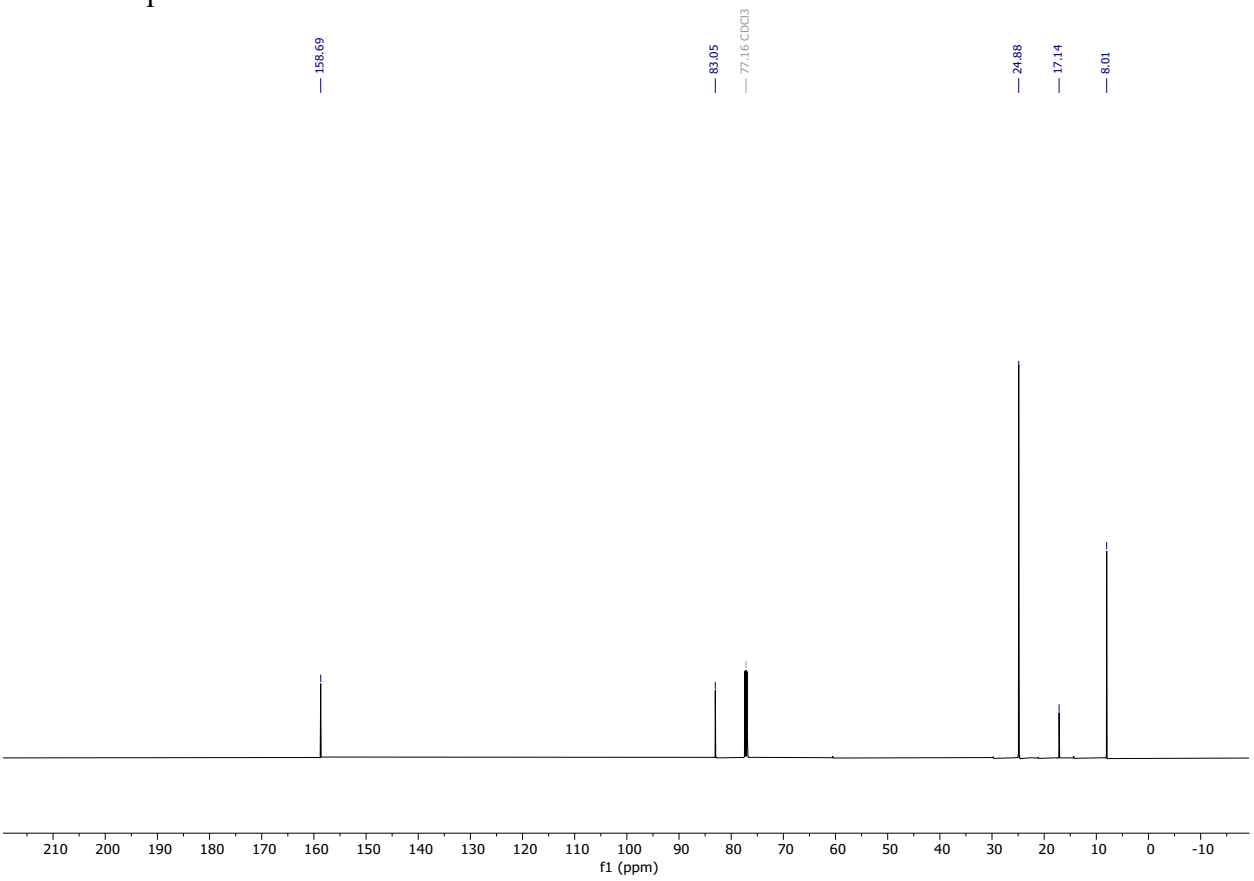


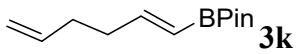
3h

^{1}H NMR spectrum:



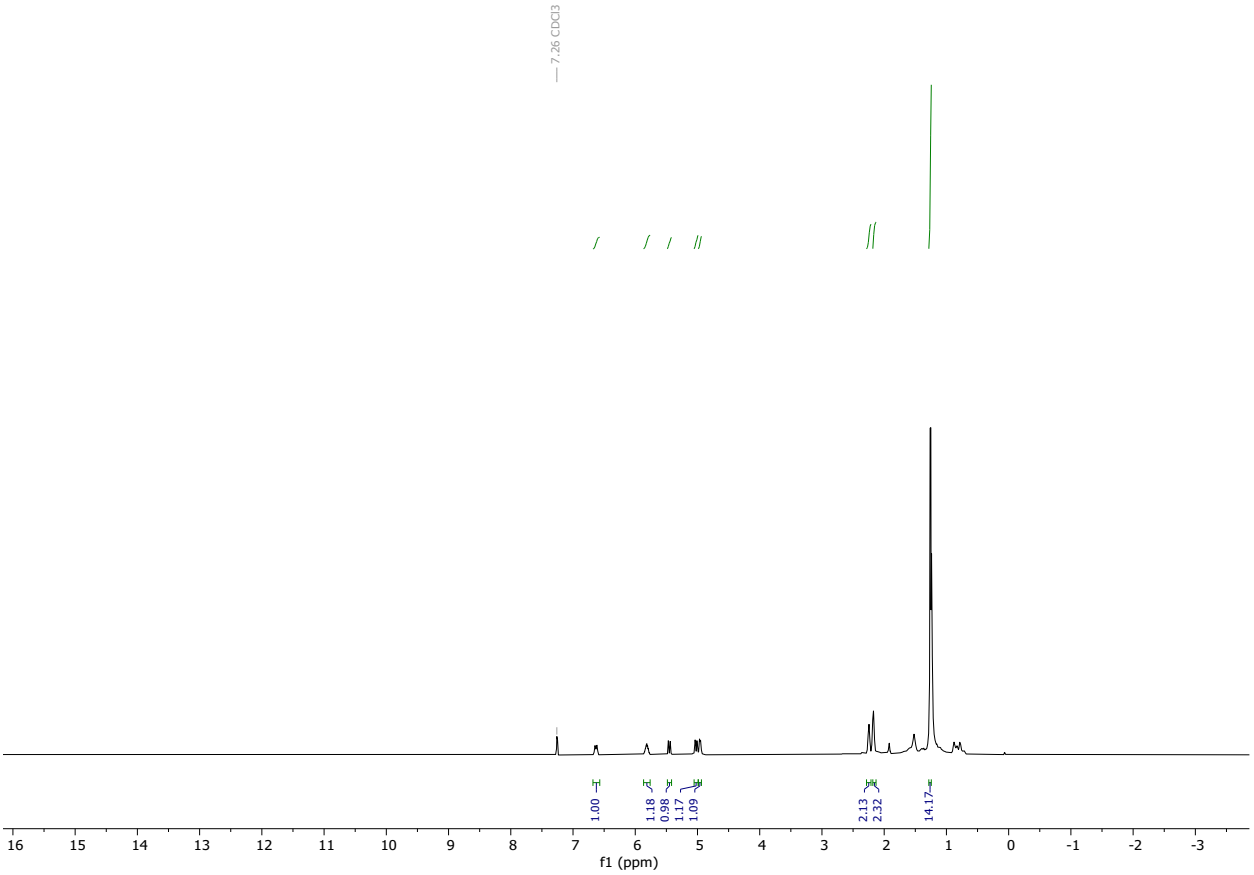
^{13}C NMR spectrum:



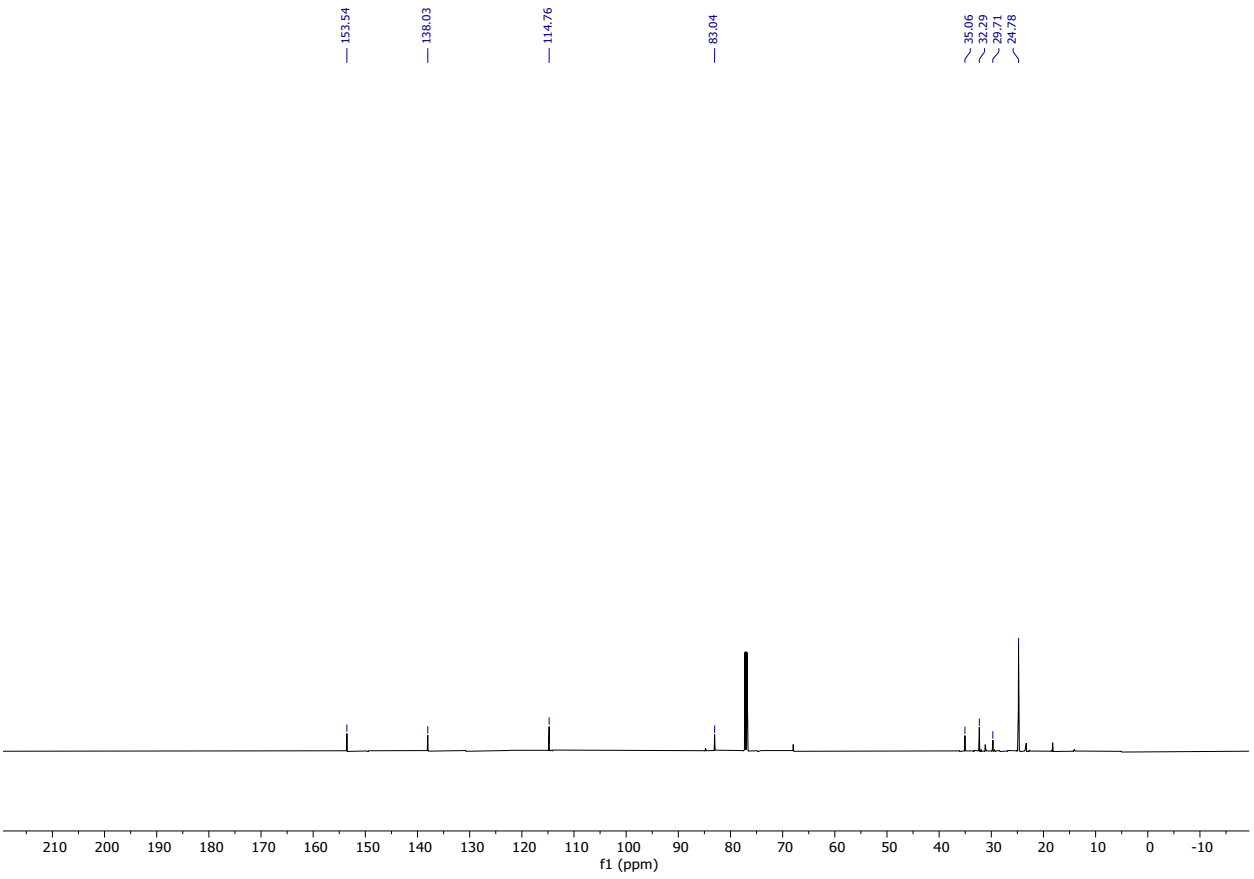


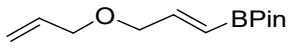
3k

^{1}H NMR spectrum:



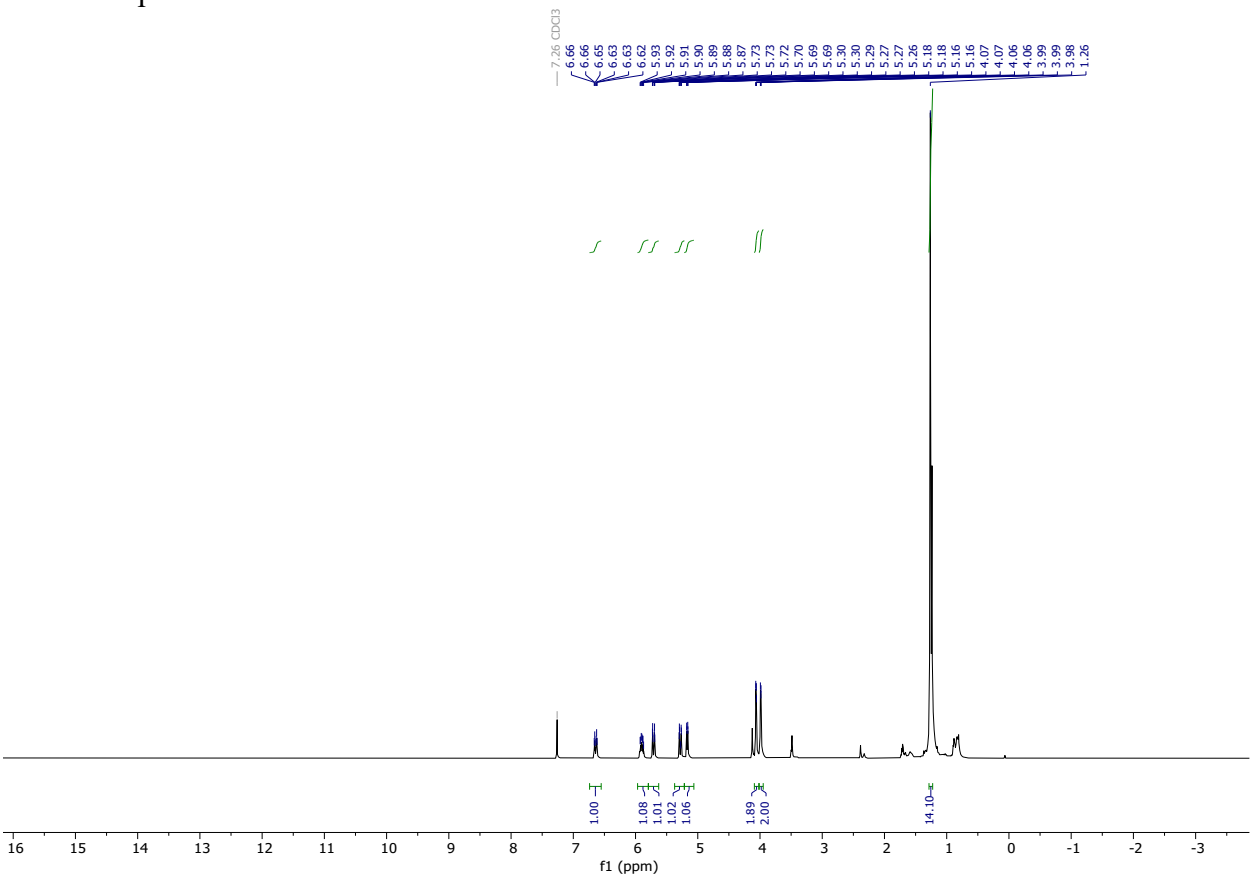
^{13}C NMR spectrum:



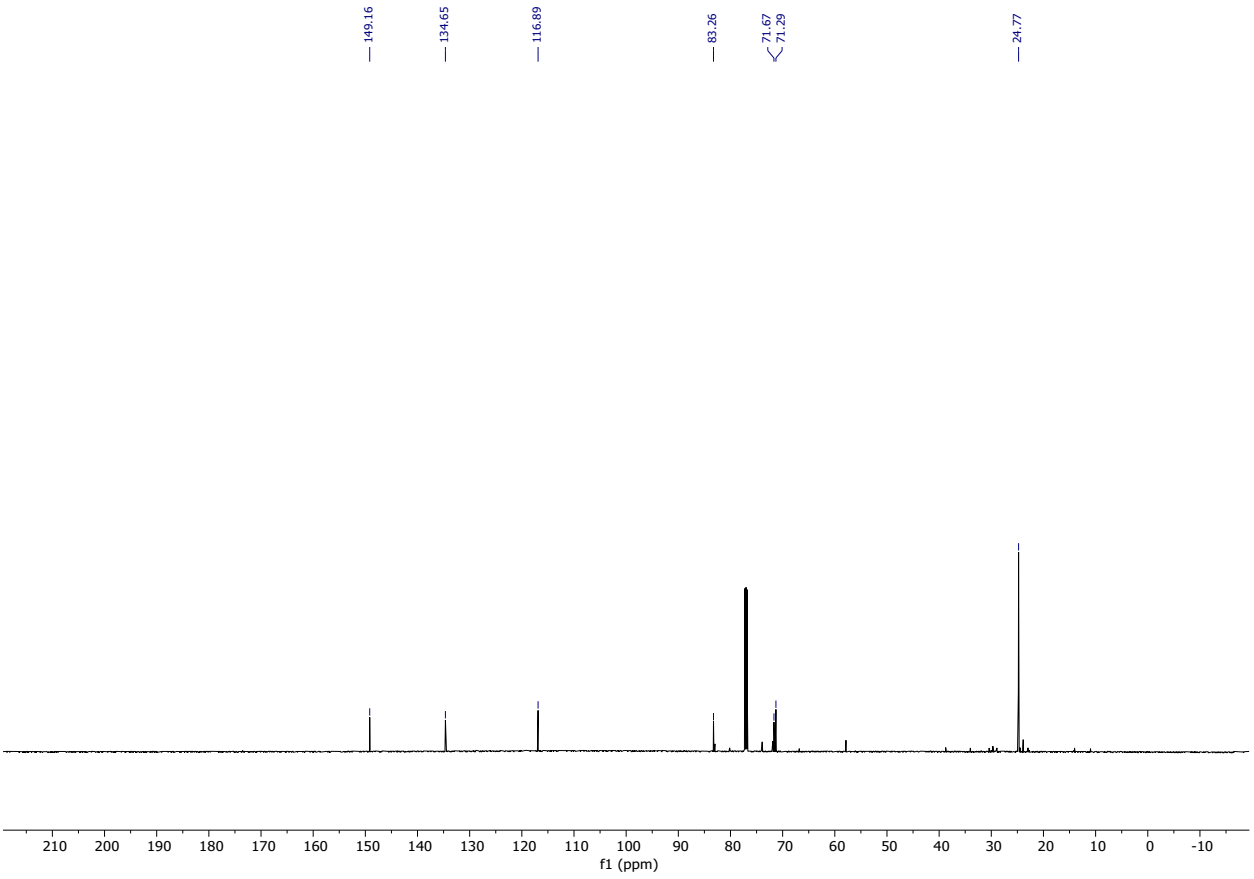


3l

^{1}H NMR spectrum:



^{13}C NMR spectrum:



References:

1. M. Mullet, V. Khare and C. Ruby, *Surf. Interface Anal*. 2008, **40**, 323–328.
2. G. Zhang, H. Zeng; S. Zheng, M.C. Neary and P.A. Dub, *ACS Catal.* 2022, **12**, 5425-5429.