Electronic supplementary information (ESI)

Metal-Organic Frameworks Incorporating Azobenzene-based Ligands as Heterogenous Lewis-Acid Catalyst for Cyanosilylation of Imines †

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Table S1. Selected bond lengths (Å) and angles (°) for **1** and **2.**

1			
Zn1-O1	1.9309(18)	Zn1-O3#1	1.9410(17)
Zn1-O5	2.049(2)	Zn1-N2	2.024(2)
O1-Zn1-O3#1	120.66(8)	O1-Zn1-O5	103.98(8)
O3#1-Zn1-O5	101.82(8)	O1-Zn1-N2	128.77(9)
O3#1-Zn1-N2	101.31(8)	N2-Zn1-O5	93.75(8)
2			
Cd1-O1	2.288(2)	Cd1-O2	2.596(2)
Cd1-O3	2.269(2)	Cd1-O4#1	2.387(2)
Cd1-O5	2.272(2)	Cd1-N1	2.303(2)
O1-Cd1-O2	85.78(9)	O1-Cd1-O4#1	171.54(8)
O3-Cd1-O1	97.86(9)	O3-Cd1-O2	53.04(7)
O3-Cd1-O4#1	90.50(8)	O3-Cd1-O5#2	88.88(8)
O4#1-Cd1-O2	100.34(7)	O5#2-Cd1-N1	132.04(8)
O5#2-Cd1-O1	82.80(9)	O5#2-Cd1-O2	138.13(7)
O5#2-Cd1-O4#1	96.20(8)	O1-Cd1-N1	84.98(9)
O3-Cd1-N1	138.80(9)	N1-Cd1-O2	86.49(8)
N1-Cd1-O4#1	89.55(7)		

Symmetry codes: #1 x-1, y-1, z; for **1**. #1 -x, -y+1, -z+1; #2 x+1, y+1, z for **2**.

Table S2. Hydrogen bonding data of **1** and **2**.

1				
D–H···A	d(*D*–H) (Å)	d(H···A) (Å)	d(*D*···A) (Å)	*D*–H···A (°)
O5-H5A···O2	0.84	1.87	2.704(3)	173
O5-H5B···O6	0.70	1.95	2.653(3)	178
O6-H6A···O7	0.87	2.22	2.830(5)	127
O6-H6B···O7	0.87	1.95	2.767(4)	156
O7-H7A···O(4)	0.87	1.86	2.701(3)	164
O7-H7B···N(3)	0.87	2.19	3.022(4)	161
2				
D–H···A	d(*D*–H) (Å)	d(H···A) (Å)	d(*D*···A) (Å)	*D*–H···A (°)
O1-H1A···O2	1.04	1.72	2.742(3)	170
C9-H9···O2	0.95	2.43	3.181(3)	136
C9-H9···O1	0.95	2.59	3.462(4)	152
C13-H13···O4	0.95	2.44	3.198(4)	136

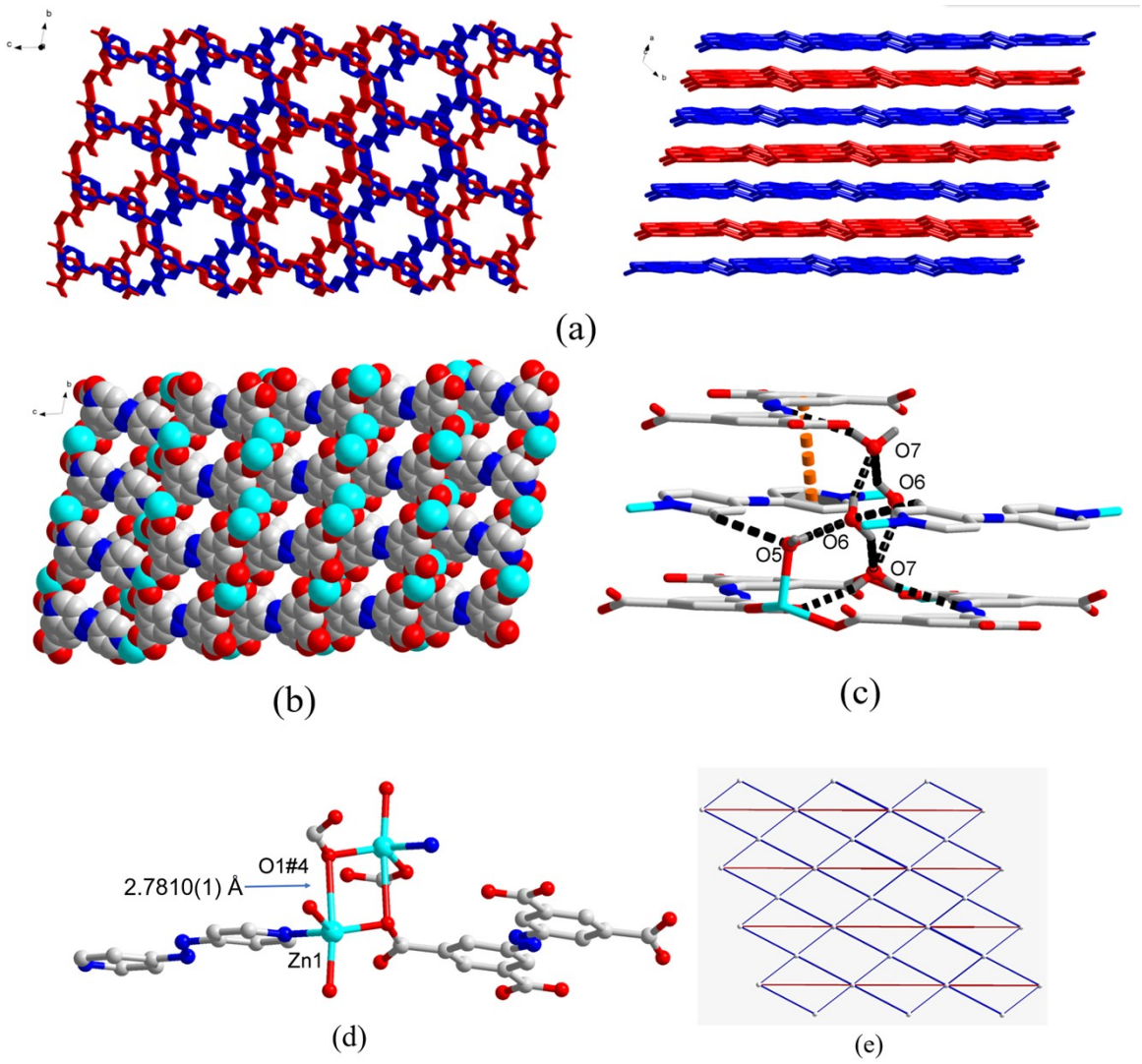


Fig. S1. (a) The 3D supramolecular framework formed by the stacking of the 2D coordination networks. (b) Space filling mode representation of the structure of **1** along the a-axis. (c) The hydrogen bonds and π…π interactions among the adjacent coordination networks and free water molecules in the pore. (d) The binuclear Zn(II) node bridged by the weak Zn-O interactions. Symmetry code: #4 -x, -y, 1-z. (e) Topological representation of the 3D framework of complex **1**.

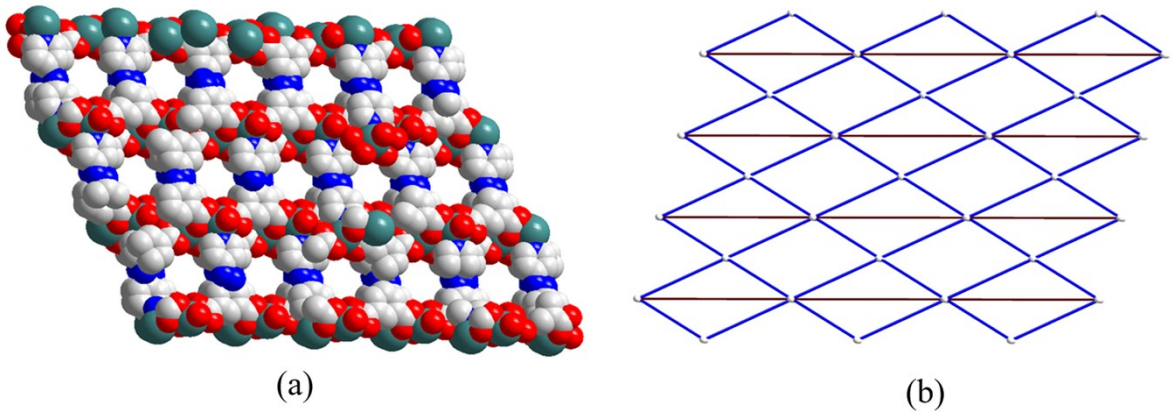


Fig. S2. (a) Space filling mode representation of the structure of **2** along a-axis. (b) Topological representation of the 3D framework of complex **2**.

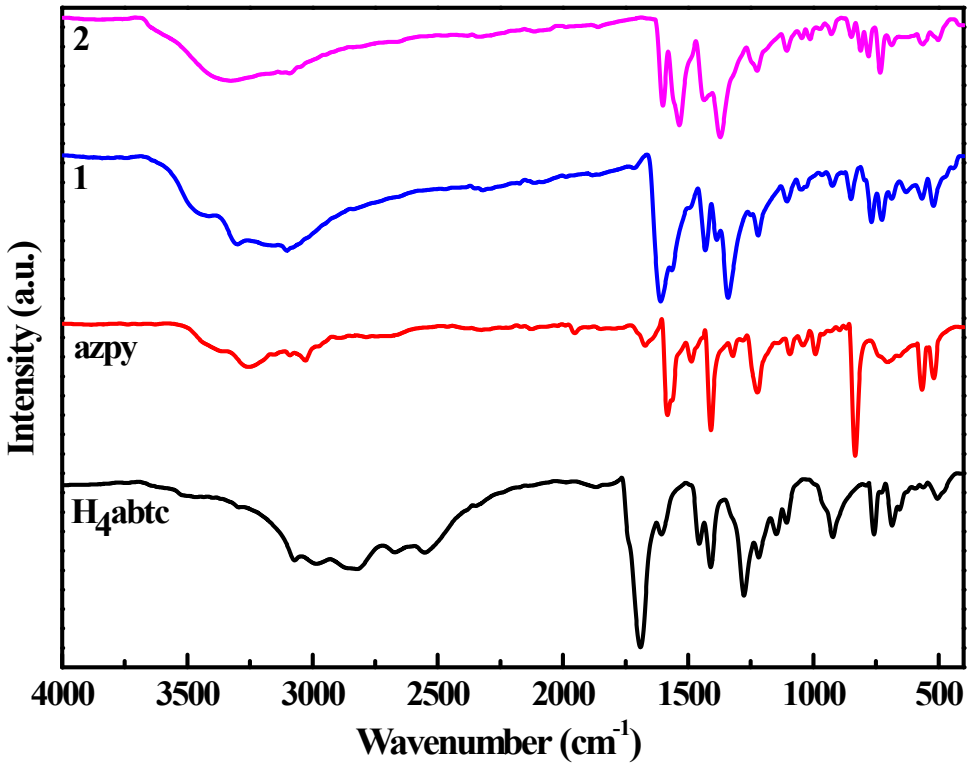
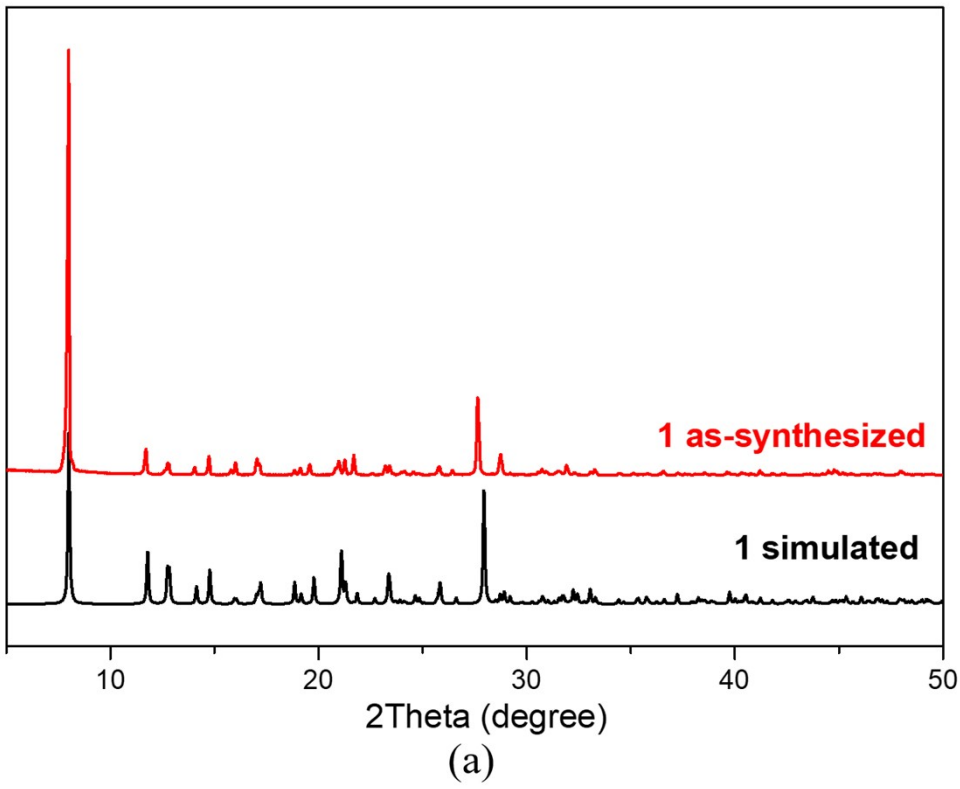


Fig. S3. FTIR spectra of H_4abtc, azpy, and complexes **1** and **2**.



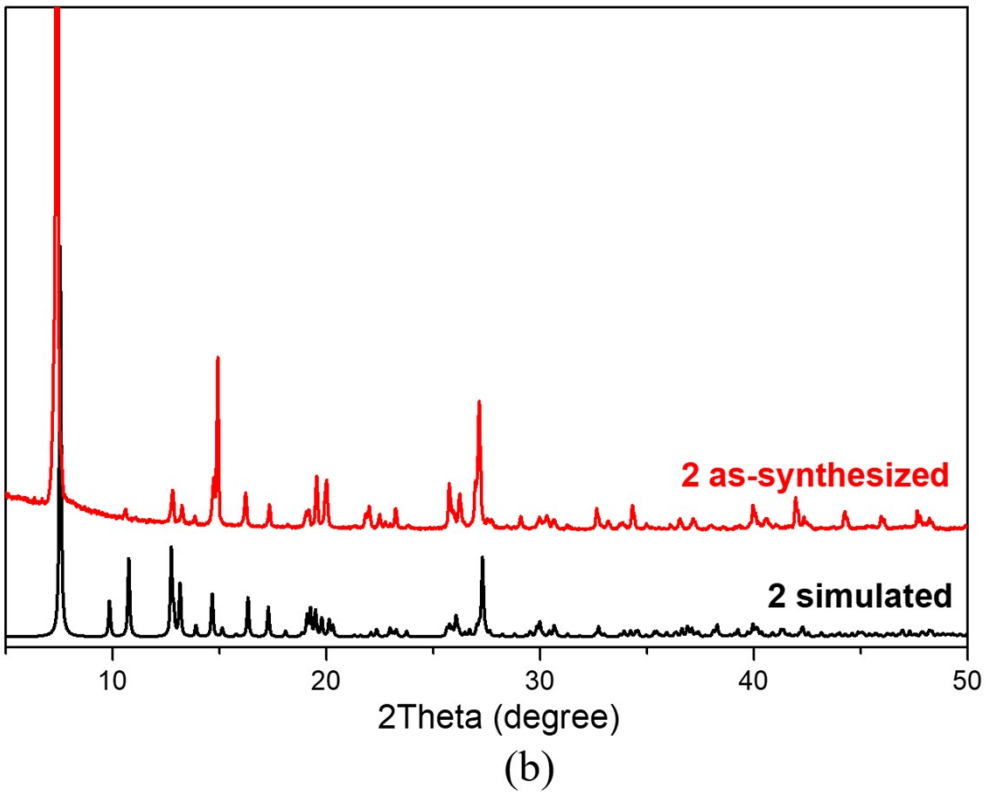
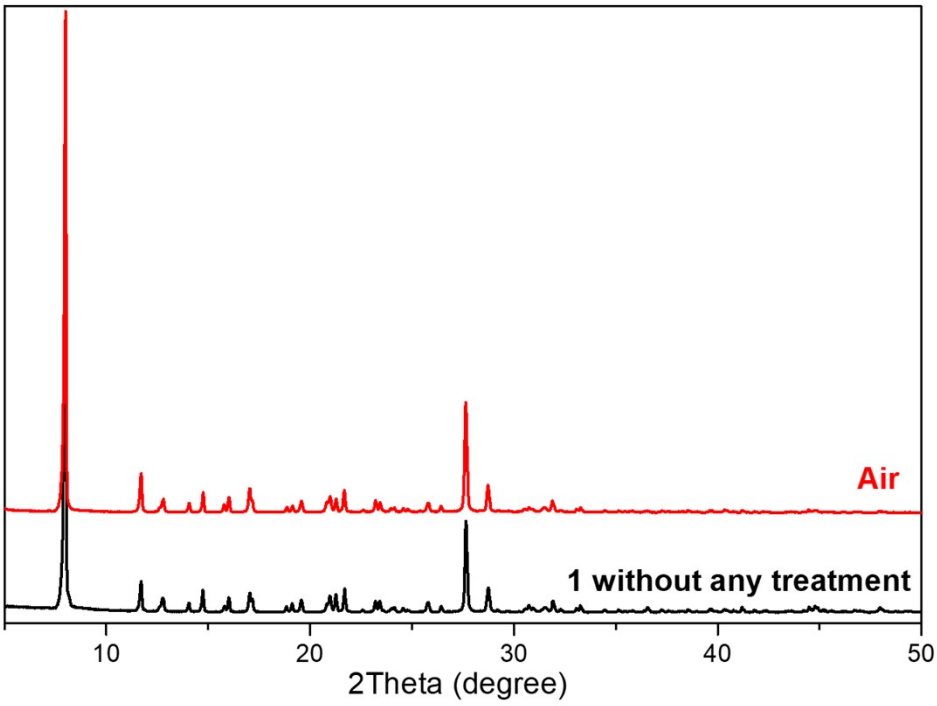
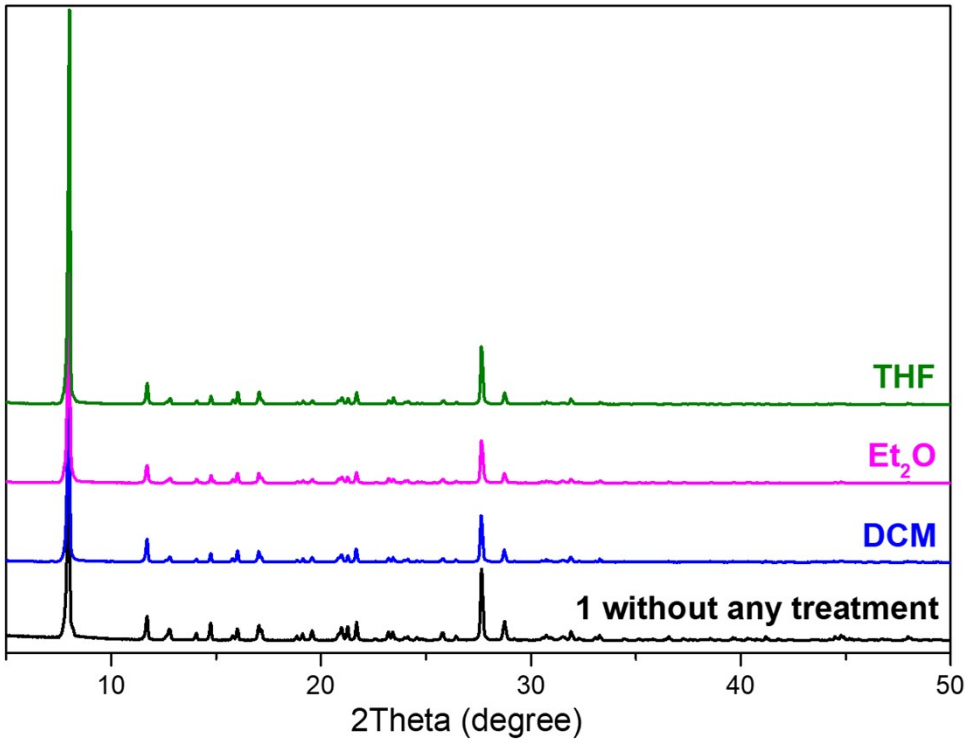


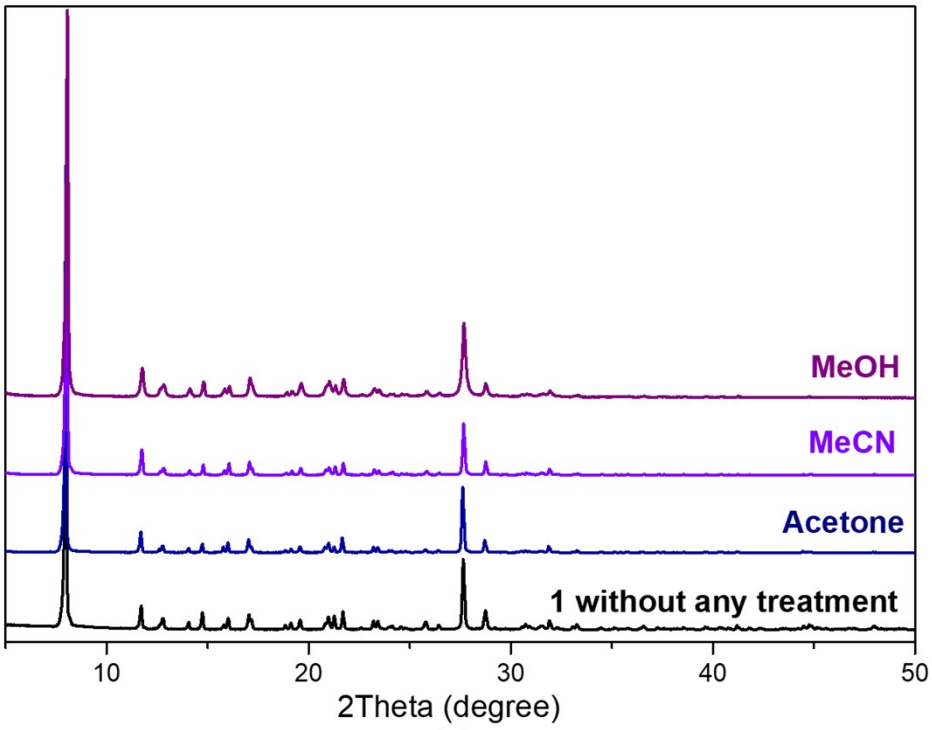
Fig. S4. PXRD patterns of **1** (a) and **2** (b).


Air
1 without any treatment
10
20
30
40
50
2Theta (degree)

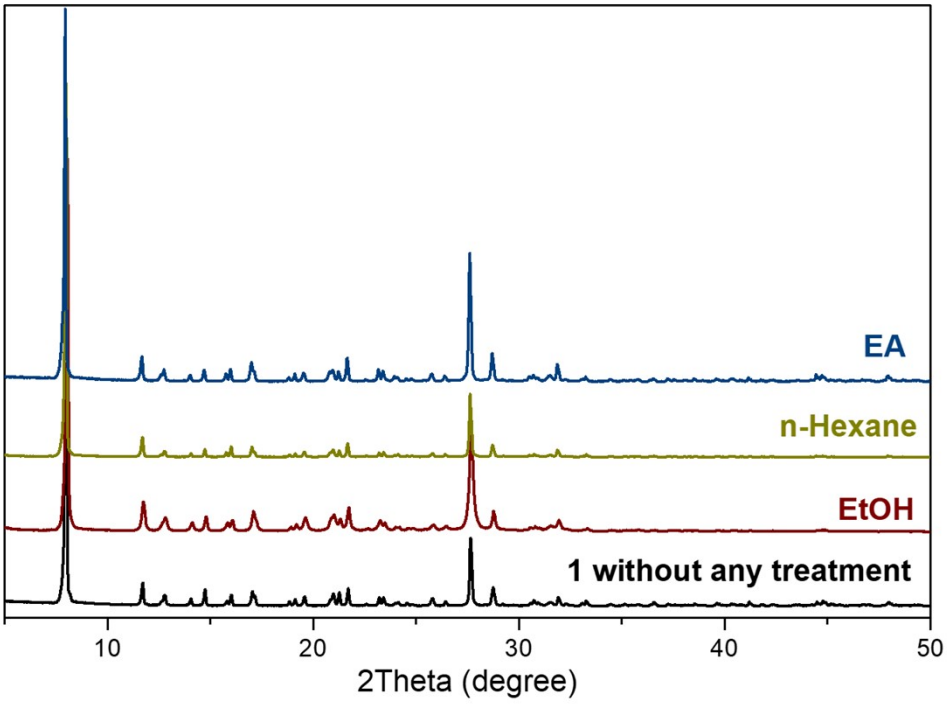
(a)


THF
Et2O
DCM
1 without any treatment
10
20
30
40
50
2Theta (degree)

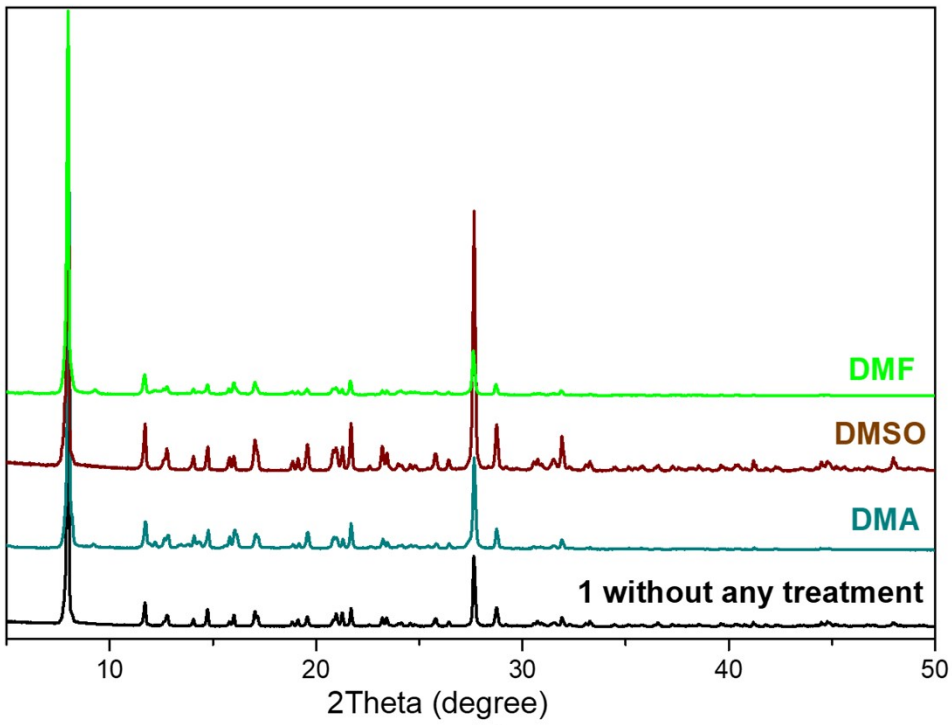
(b)


MeOH
MeCN
Acetone
1 without any treatment
10
20
30
40
50
2Theta (degree)

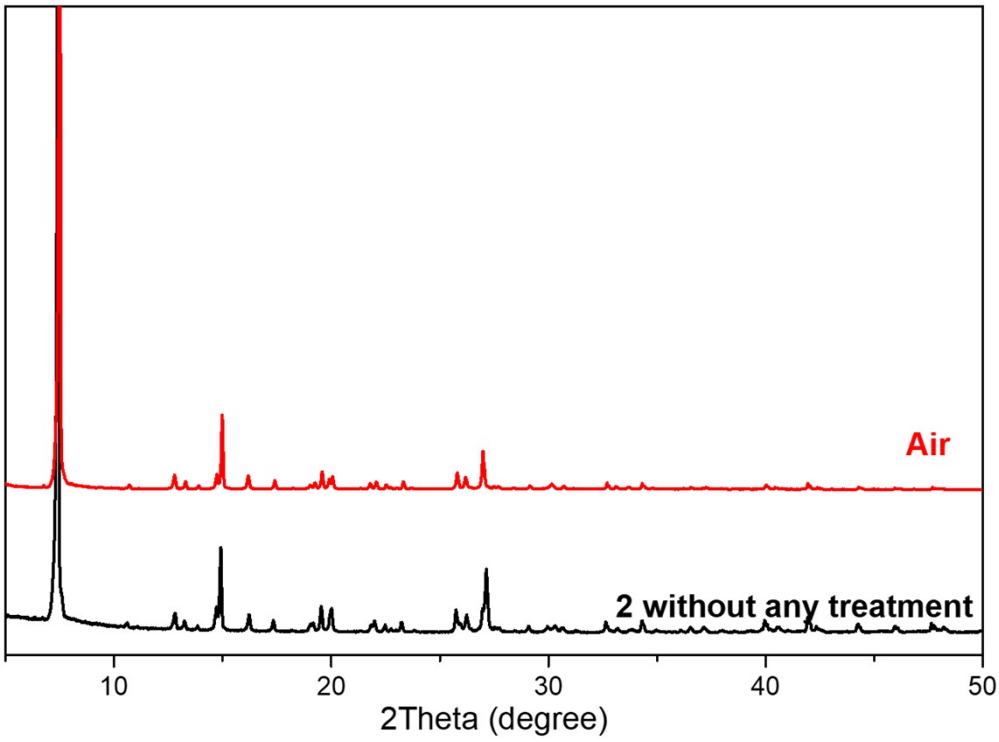
(c)


EA
n-Hexane
EtOH
1 without any treatment
10
20
30
40
50
2Theta (degree)

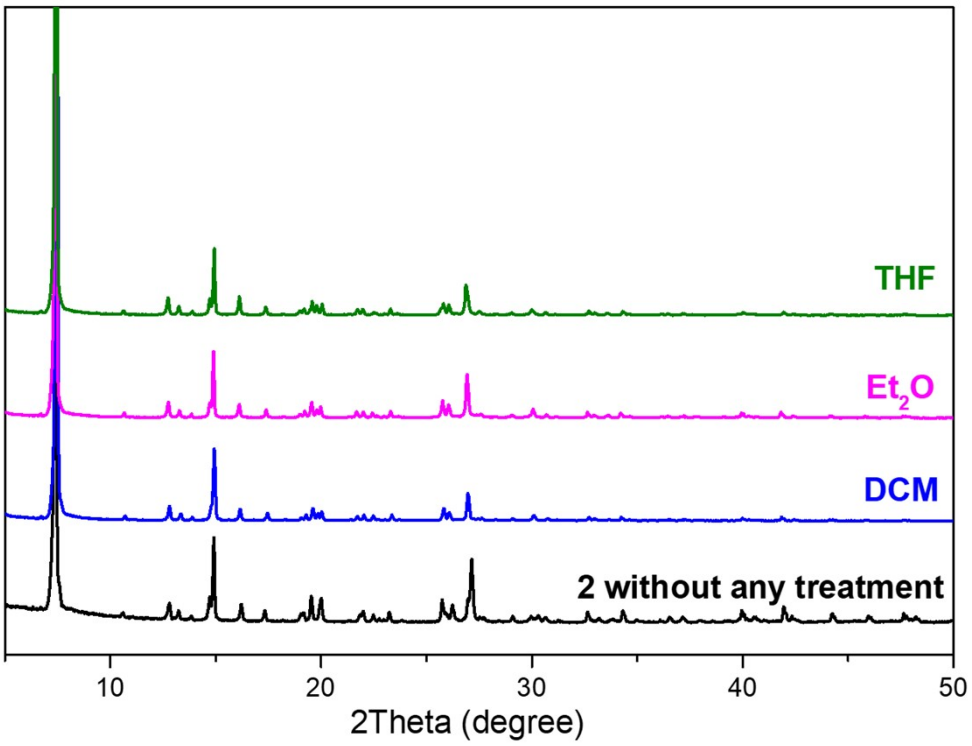
(d)


DMF
DMSO
DMA
1 without any treatment
10
20
30
40
50
2Theta (degree)

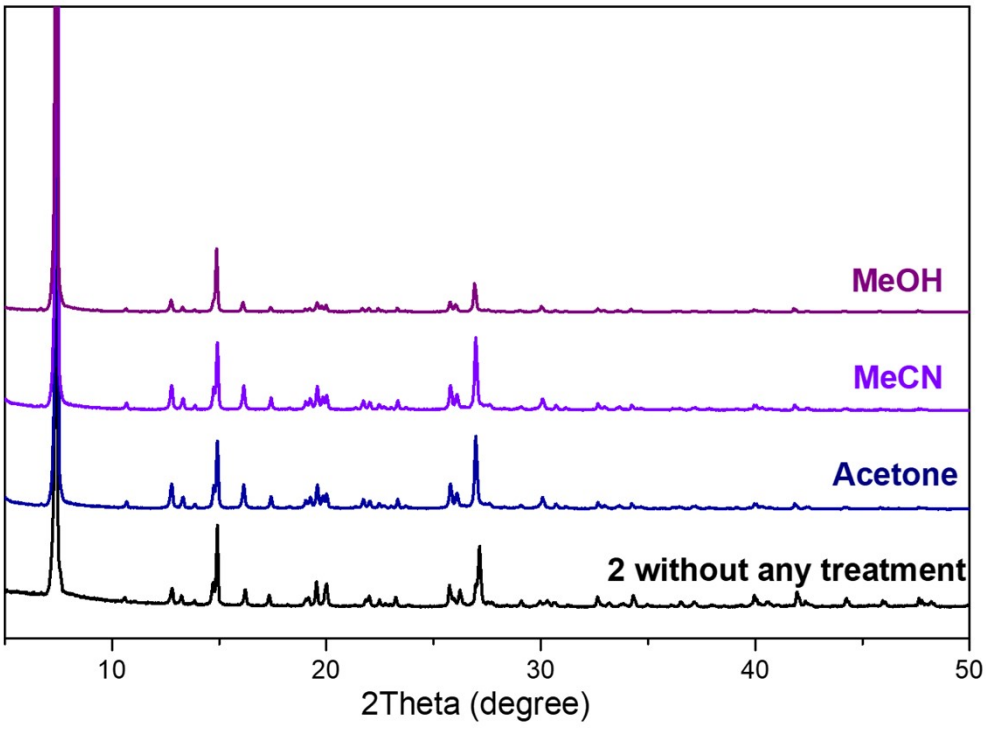
(e)


Air
2 without any treatment
10
20
30
40
50
2Theta (degree)

(f)


THF
Et2O
DCM
2 without any treatment
10
20
30
40
50
2Theta (degree)

(g)


MeOH
MeCN
Acetone
2 without any treatment
10
20
30
40
50
2Theta (degree)

(h)

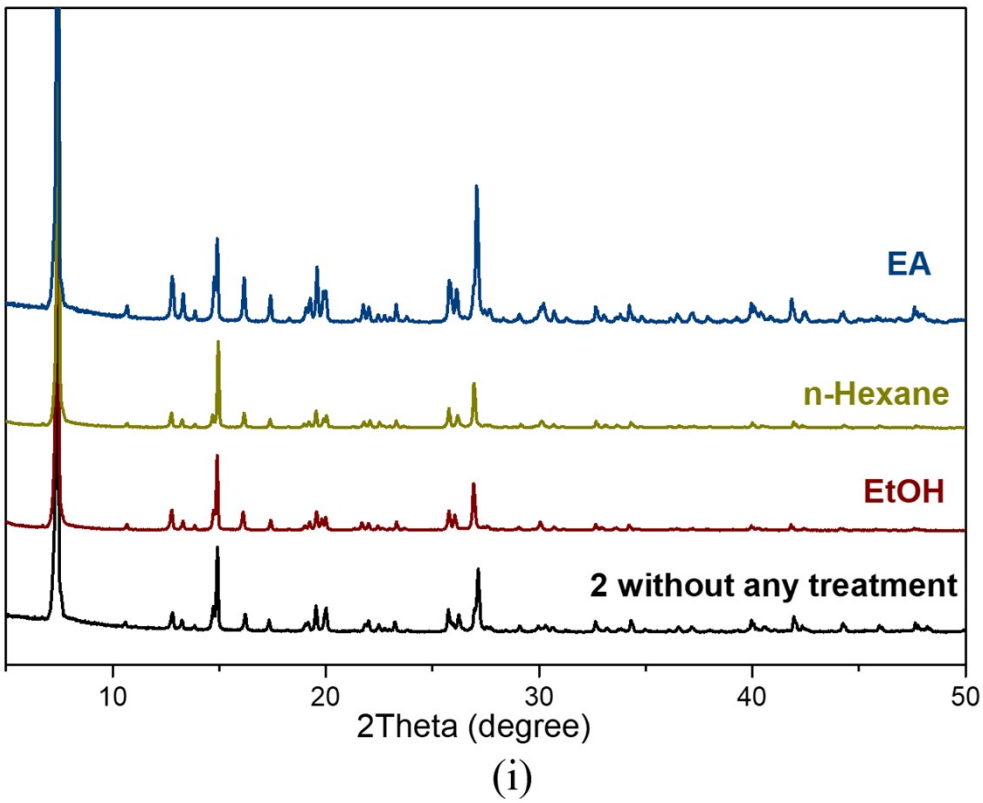
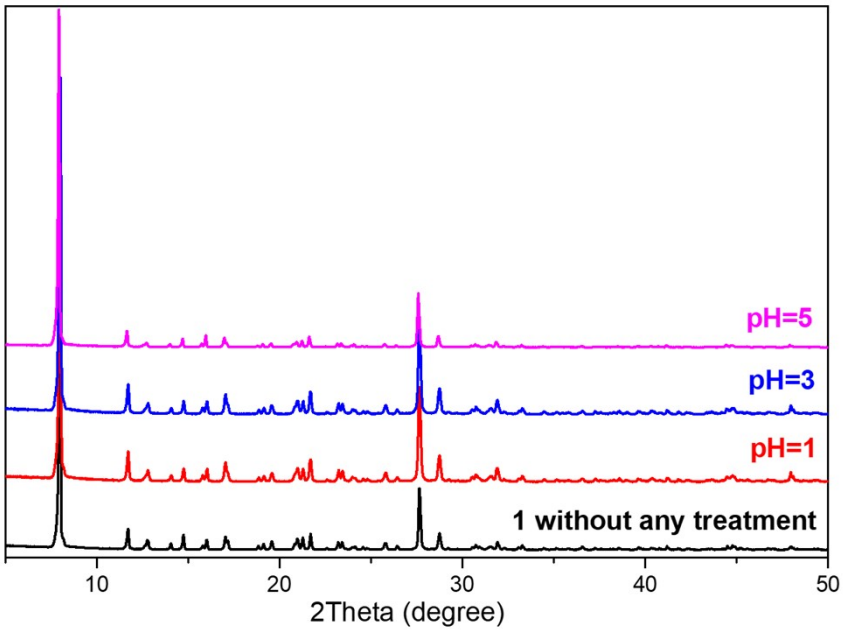
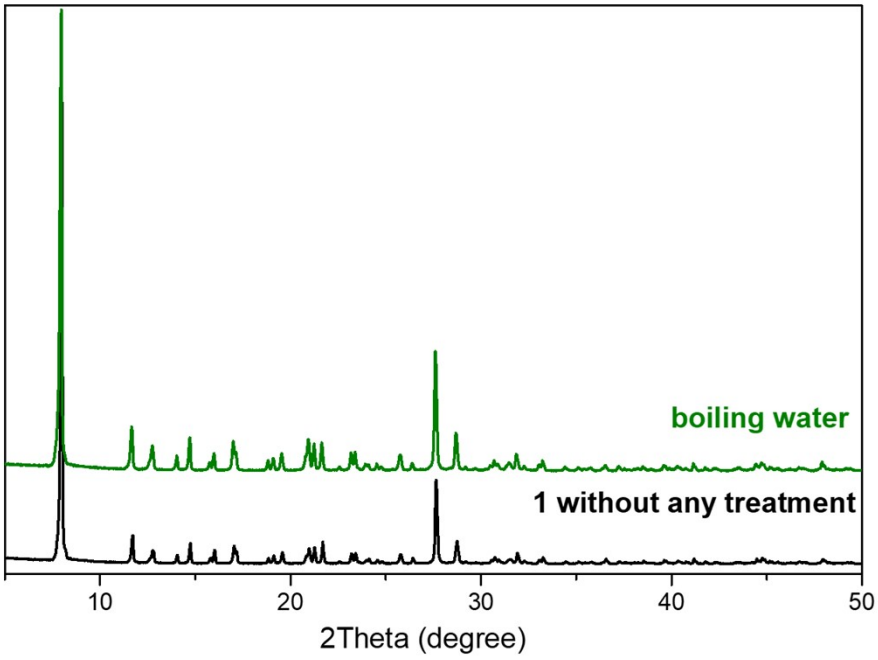


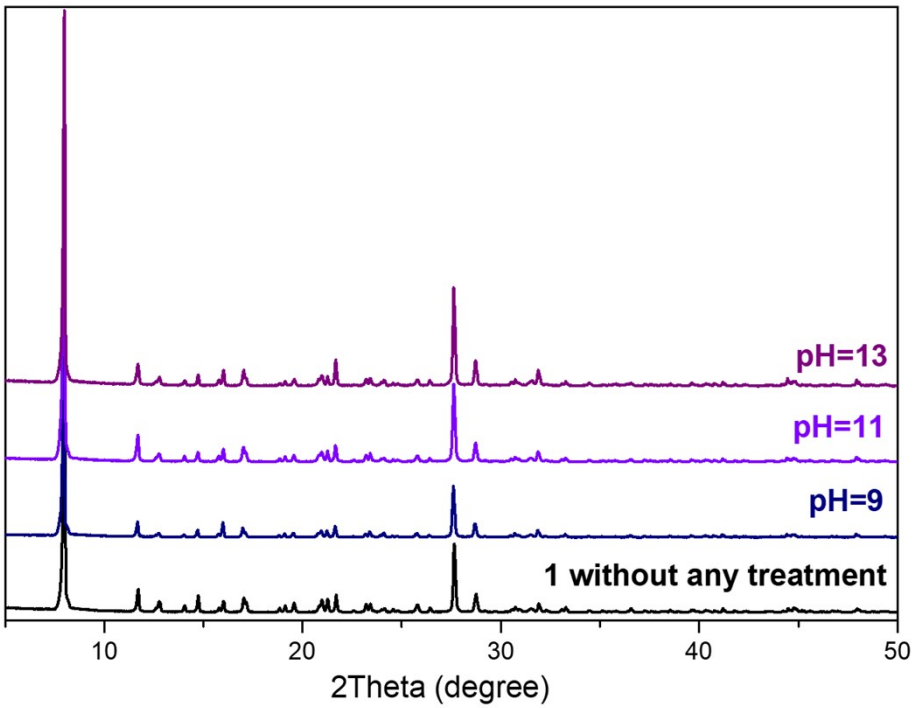
Fig. S5. PXRD patterns of complexes **1** (a-e) and **2** (f-j) after exposing to air for one month and immersing in different organic solvent.


pH=5
pH=3
pH=1
1 without any treatment
10
20
30
40
50
2Theta (degree)

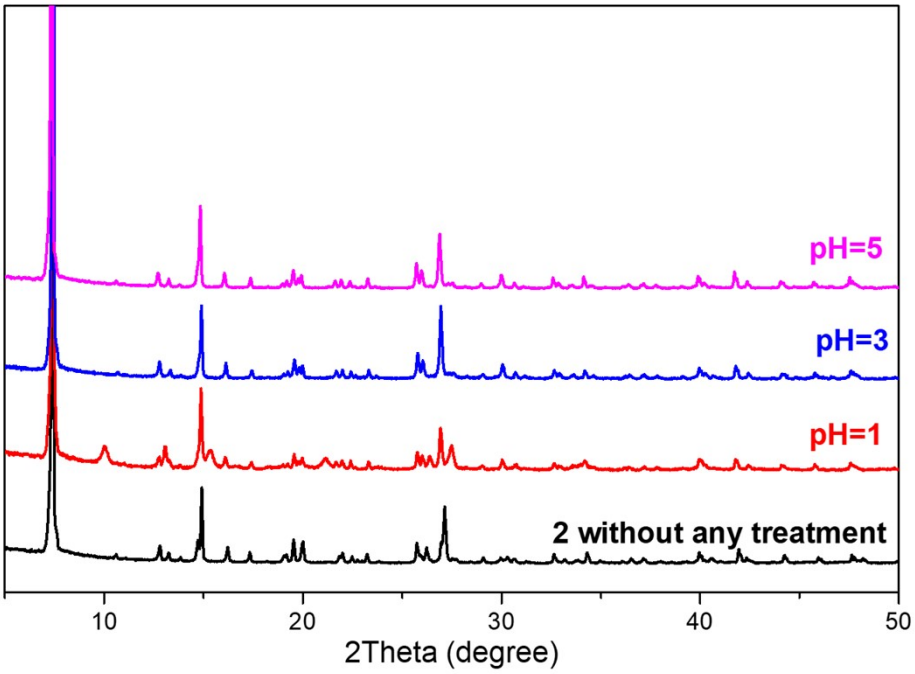
(a)


boiling water
1 without any treatment
10
20
30
40
50
2Theta (degree)

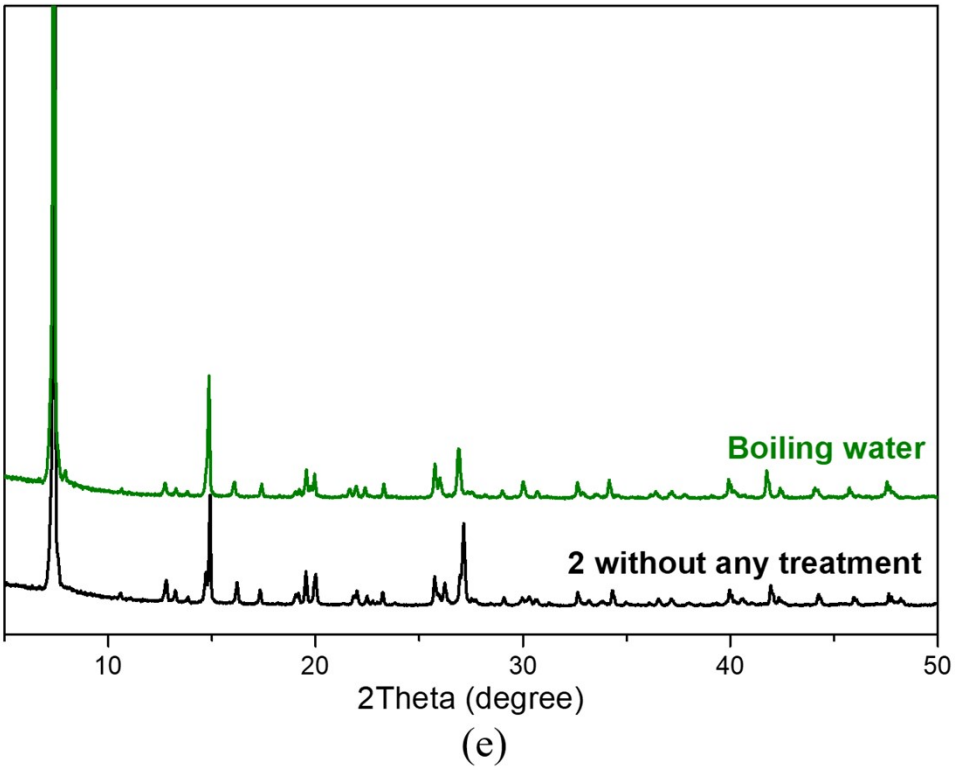
(b)


pH=13
pH=11
pH=9
1 without any treatment
10
20
30
40
50
2Theta (degree)

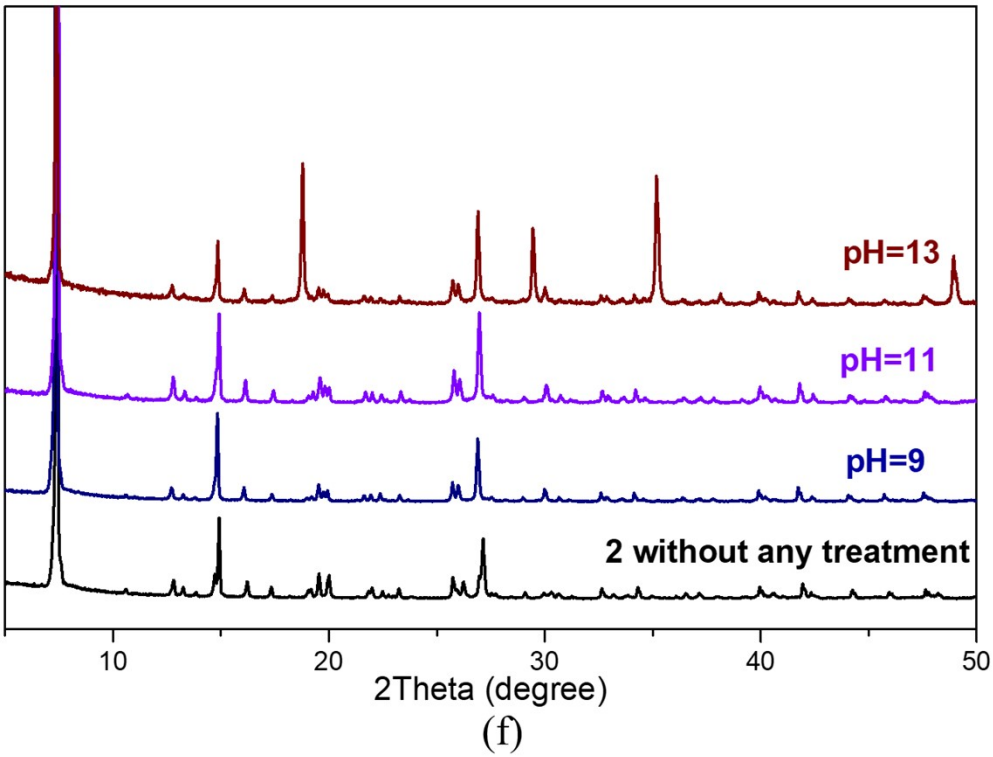
(c)


pH=5
pH=3
pH=1
2 without any treatment
10
20
30
40
50
2Theta (degree)

(d)

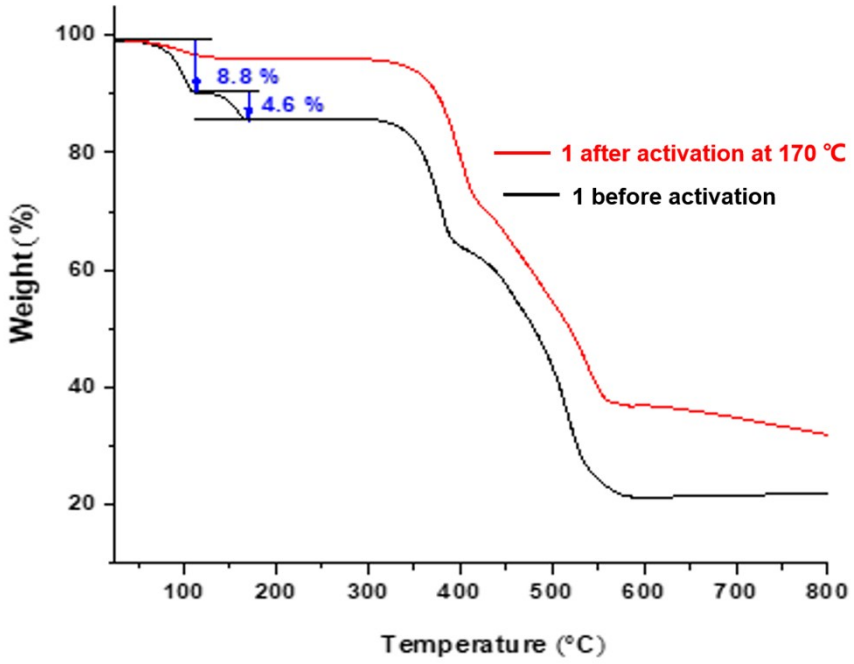


(e)

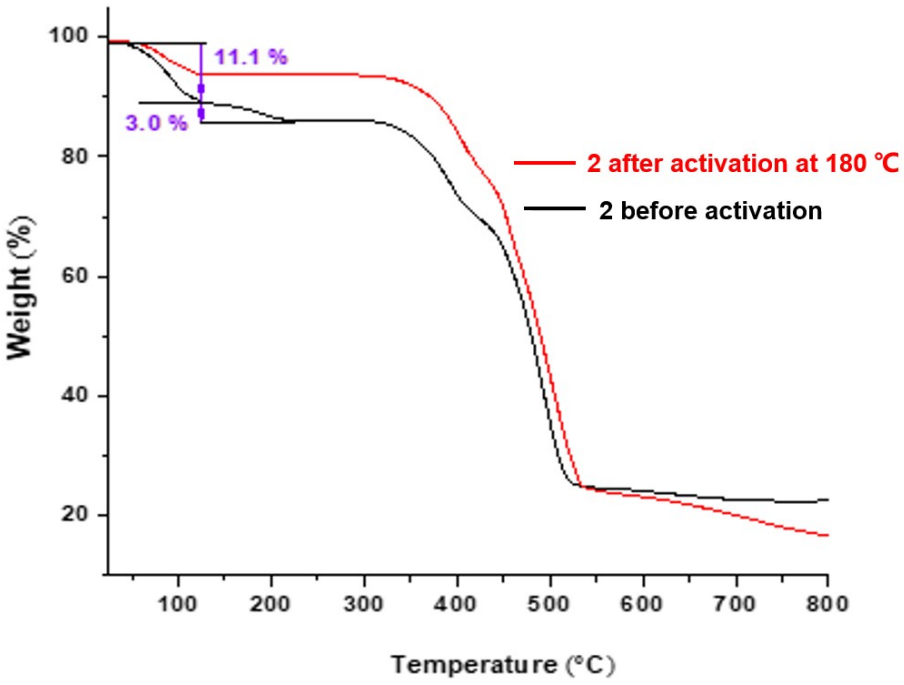


(f)

Fig. S6. PXRD patterns of complexes **1** (a-c) and **2** (d-f) after soaking in aqueous solution with varying pH and boiling water.

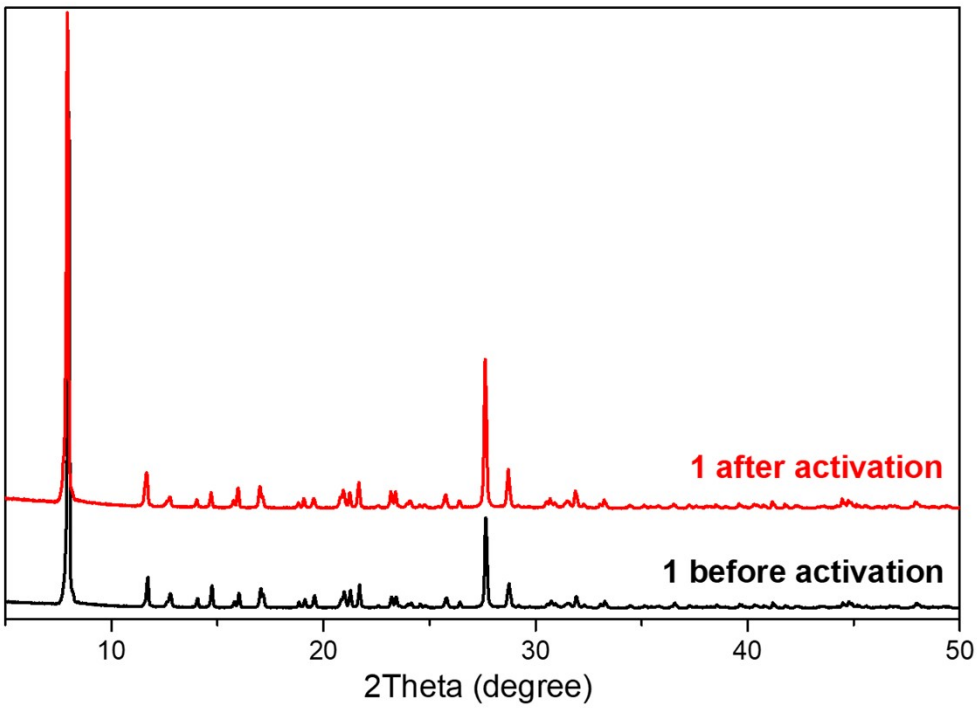


(a)

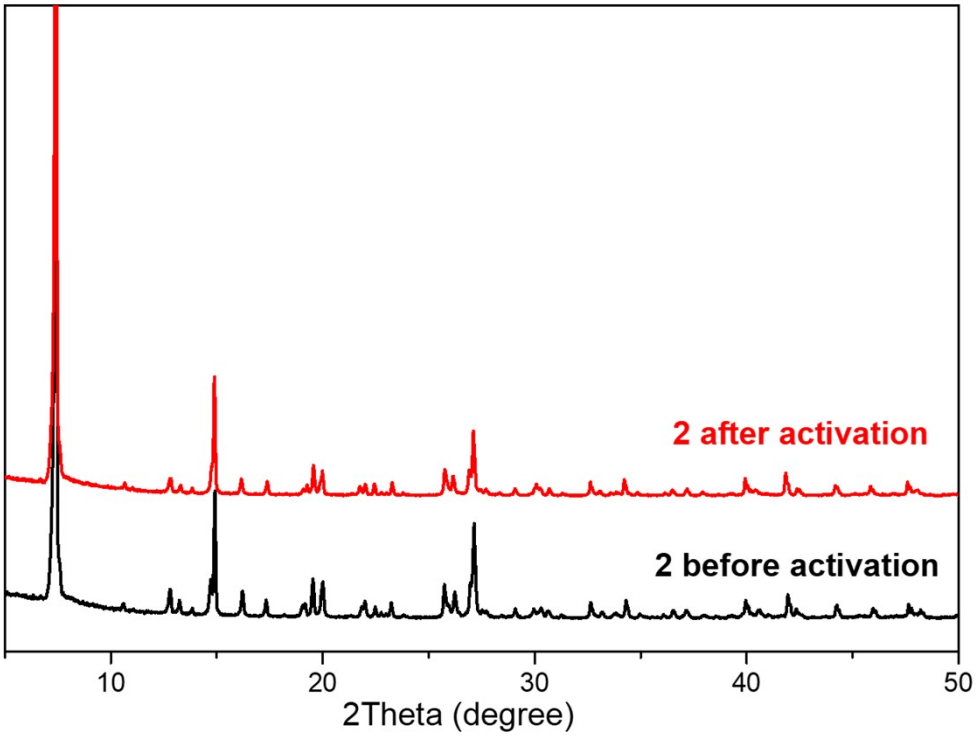


(b)

Fig. S7. TG curves of complexes **1** (a) and **2** (b) before and after activation.



(a)



(b)

Fig. S8. PXRD patterns of complexes **1** (a) and **2** (b) before and after activation.

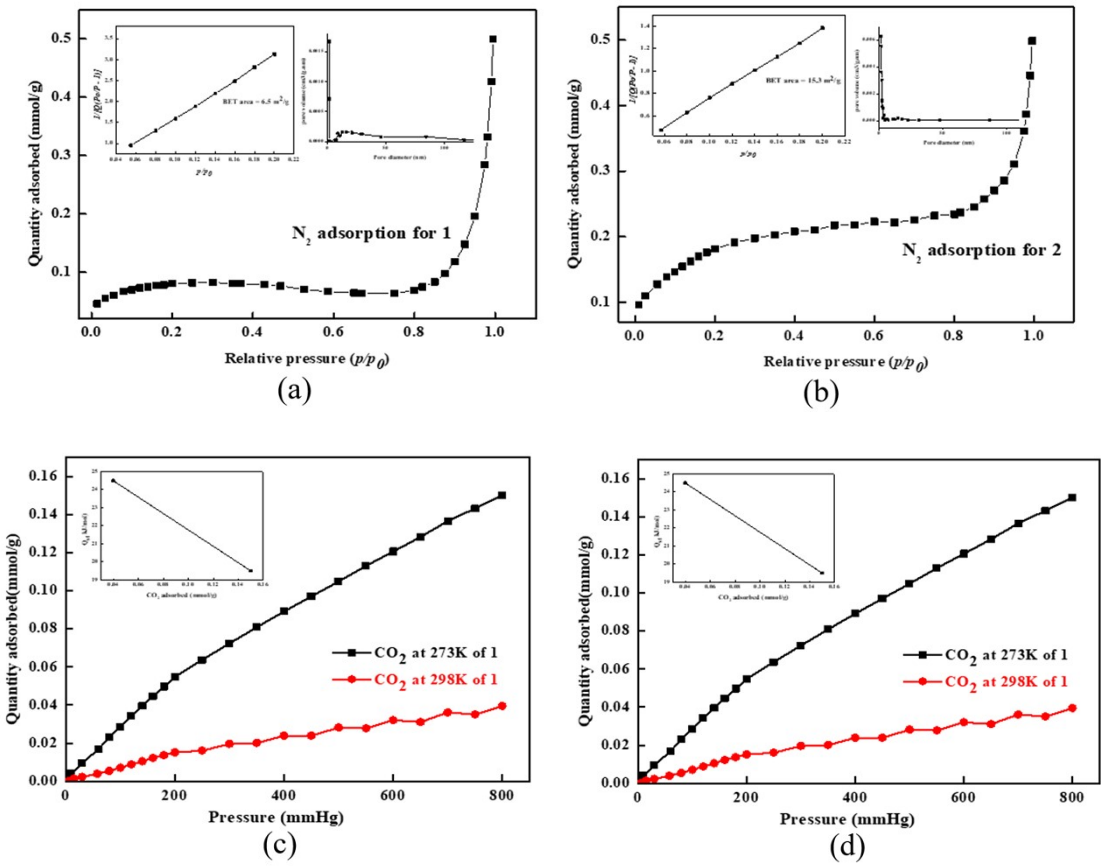
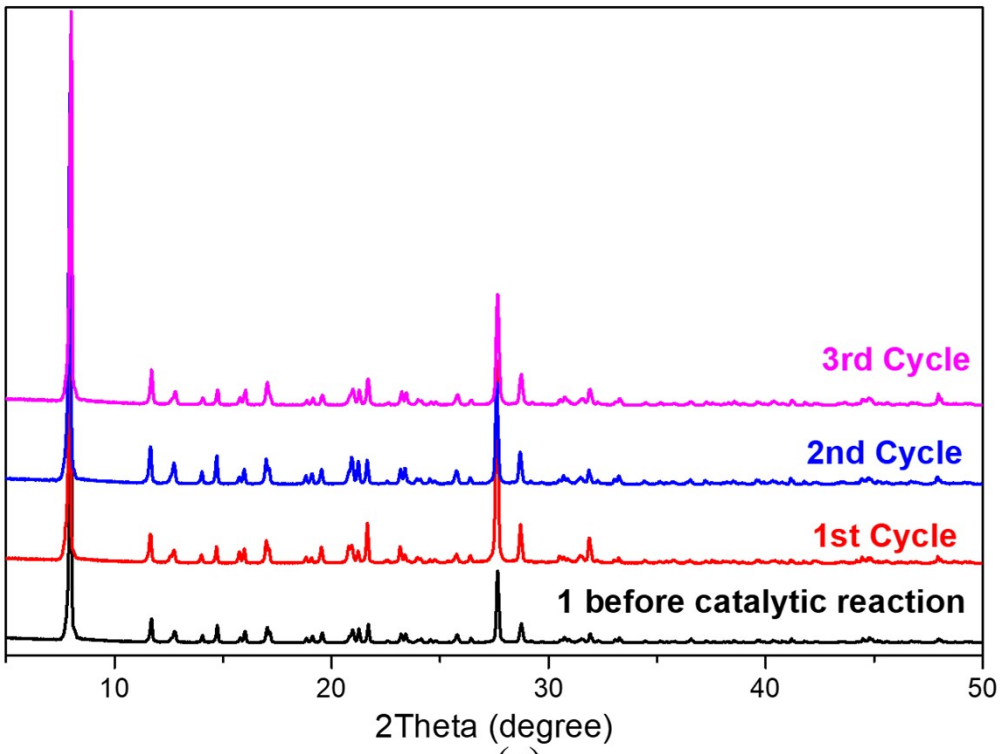
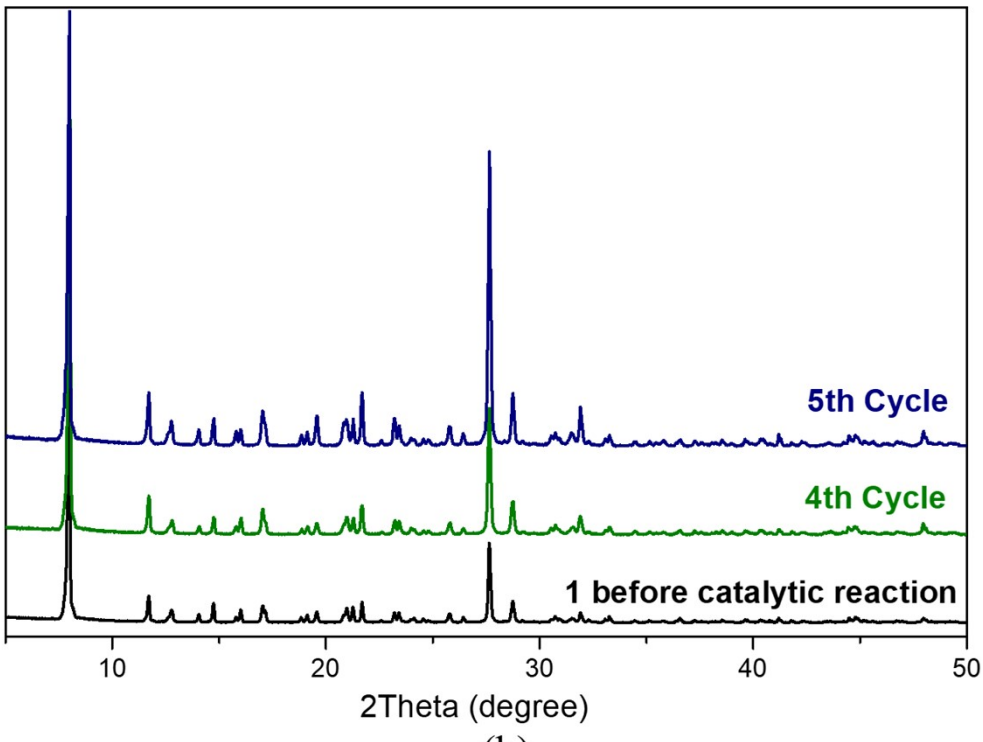


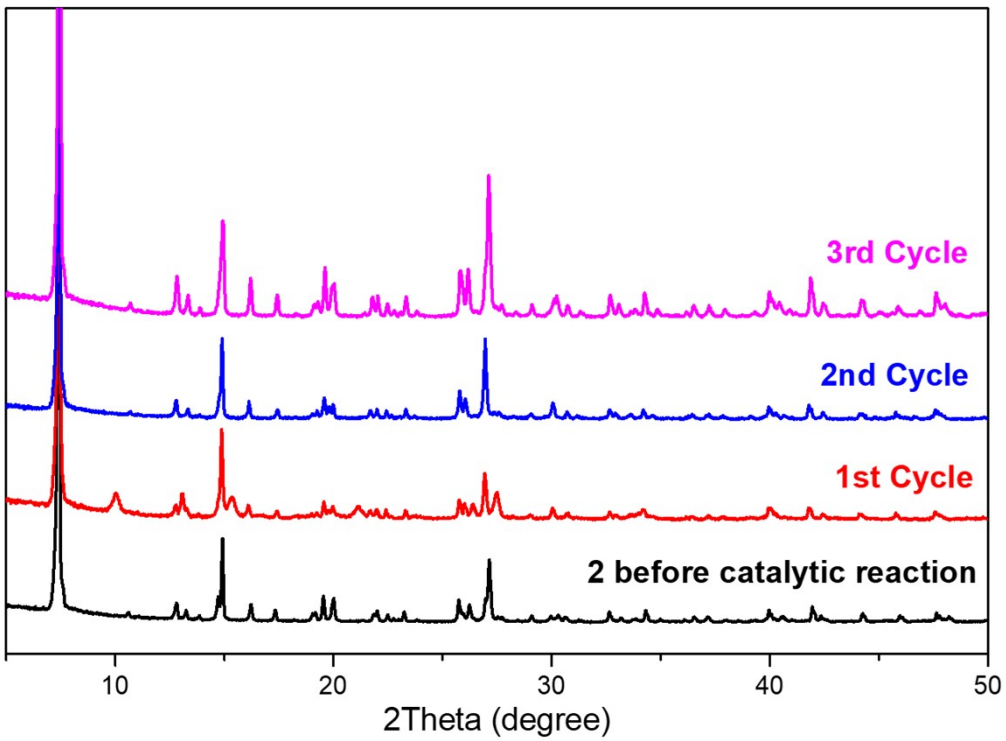
Fig. S9. N_2 adsorption isotherms, BET surface area and BJH PVD at 77 K for framework: (a) **1**; (b) **2** and CO_2 adsorption isotherms and Isosteric heat of adsorption for framework: (c) **1**; (d) **2** at 273 K and 298 K.


3rd Cycle
2nd Cycle
1st Cycle
1 before catalytic reaction
10
20
30
40
50
2Theta (degree)

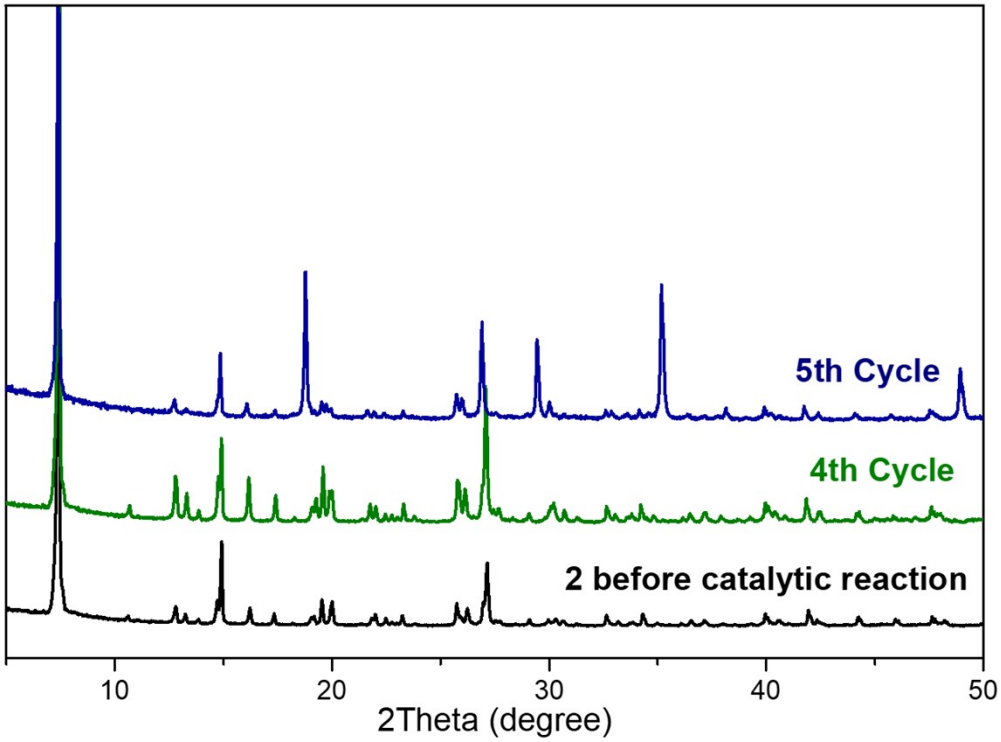
(a)


5th Cycle
4th Cycle
1 before catalytic reaction
10
20
30
40
50
2Theta (degree)

(b)



(c)



(d)

Fig. S10. PXRD patterns of complexes **1** (a,b) and **2** (c,d) after catalysis reactions.

NMR and HRMS (ESI) data description.

1. 3,3',5,5'-Azobenzene tetracarboxylic acid (H_4abtc): Orange colored solid, yield, 4.30 g, 91%. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.58 (s, 4H), 8.67 (d, J = 7.3 Hz, 6H).
^{13}C NMR δ: 166.31, 166.08, 152.17, 133.27, 132.96, 132.54, 128.99, 127.42, 125.17, 40.54, 40.34, 40.18, 40.12, 39.92, 39.71, 39.50, 39.29. (**Fig. S11a)**
HRMS (ESI) m/z calcd for $C_{16}H_9N_2O_8$ (M-H^+) 357.0359, found 357.0361.

2. 4,4′-azobipyridine (azpy): Orange colored solid, yield, 2.15 g, 86%. ^{1}H NMR (400 MHz, DMSO- d_6) δ = 8.95 - 8.84 (d, 4H), 7.86 - 7.78 (d, 4H).
^{13}C NMR δ: 156.70, 156.66, 153.19, 152.37, 152.22, 151.88, 150.30, 116.59, 116.49, 111.94, 40.61, 40.40, 40.20, 39.99, 39.78, 39.57, 39.36. (**Fig. S11b)**
HRMS (ESI) m/z calcd for $C_{10}H_9N_4$ (M+H^+) 185.0827, found 185.0819.

3. 2-phenyl-2-(phenylamino) acetonitrile: Yellowish colored solid, yield, 84.3 mg, 93% for **1** and 86.97 mg, 96% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (dd, J = 6.6, 2.8 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.23 (t, J = 7.8 Hz, 2H), 6.87 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 7.9 Hz, 2H), 5.37 (d, J = 8.3 Hz, 1H), 4.07 (d, J = 8.3 Hz, 1H).
^{13}C NMR δ: 144.78, 134.00, 129.64, 129.57, 129.39, 127.34, 120.27, 118.37, 114.24, 77.52, 77.20, 76.89, 50.19. **(Fig. S12)**
HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2$ (M+H^+) 209.1079, found 209.1071; calcd for $C_{13}H_{12}N$ (M-CN^-) 182.0964, found 182.0962.

4. 4-phenyl-2-(phenylamino) but-3-enenitrile: Malate colored crystalline solid, yield, 93 mg, 89% for **1** and 95 mg, 91% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 - 7.42 (m, 2H), 7.42 - 7.23 (m, 5H), 7.05 (dd, J = 15.9, 1.7 Hz, 1H), 6.91 (tt, J = 7.4, 1.1 Hz, 1H), 6.82 – 6.74 (m, 2H), 6.28 (dd, J = 15.9, 5.2 Hz, 1H), 5.06 (ddd, J = 9.3, 5.1, 1.7 Hz, 1H), 3.91 (d, J = 9.3 Hz, 1H).
^{13}C NMR δ: 144.47, 135.15, 134.94, 129.64, 128.98, 128.88, 126.98, 121.00, 120.44, 117.71, 114.43, 77.37, 77.05, 76.73, 47.80. **(Fig. S13)**
HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2$ (M+H^+) 235.1235, found 235.1223; calcd for $C_{15}H_{14}N$ (M-CN^-) 208.1121, found 208.1119.

5. 4-phenyl-2-(pyridin-3-ylamino) but-3-enenitrile: Malate colored crystalline solid, yield, 91 mg, 87% for **1** and 96 mg, 90% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 - 8.12 (m, 2H), 7.46 – 7.28 (m, 5H), 7.20 (ddd, *J* = 8.3, 4.7, 0.7 Hz, 1H), 7.13 - 7.01 (m, 2H), 6.26 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.06 (ddd, *J* = 9.0, 5.2, 1.7 Hz, 1H), 4.36 (d, *J* = 9.0 Hz, 1H).

^{13}C NMR δ: 141.50, 140.79, 137.37, 135.69, 134.70, 129.15, 128.92, 127.00, 123.97, 120.41, 120.27, 117.15, 77.38, 77.06, 76.74, 47.35. **(Fig. S14)**

HRMS (ESI) m/z calcd for $C_{15}H_{14}N_3$ ($M+H^+$) 236.1188, found 236.1176.

6. 2-(naphthalen-2-ylamino)-4-phenylbut-3-enenitrile: Yellow colored solid, yield, 112 mg, 86% for **1** and 87%, 113 mg for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (ddd, *J* = 9.4, 7.5, 1.6 Hz, 3H), 7.46 - 7.28 (m, 7H), 7.14 - 7.04 (m, 2H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.32 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.18 (ddd, *J* = 9.3, 5.2, 1.7 Hz, 1H), 4.07 (d, *J* = 9.2 Hz, 1H).

^{13}C NMR δ: 142.07, 135.36, 134.91, 134.61, 129.63, 129.03, 128.90, 128.77, 127.72, 127.59, 127.01, 126.79, 126.58, 123.52, 120.77, 117.85, 117.63, 107.46, 77.37, 77.05, 76.73, 47.68. **(Fig. S15)**

HRMS (ESI) m/z calcd for $C_{20}H_{17}N_2$ ($M+H^+$) 285.1392, found 285.1385; calcd for $C_{19}H_{16}N$ ($M-CN^-$) 258.1277, found 258.1271.

7. 2-(4-methoxyphenyl)-2-(naphthalen-2-ylamino) acetonitrile: Light yellow colored solid, yield, 109 mg, 83% for **1** and 87%, 114 mg for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 - 7.67 (m, 3H), 7.57 - 7.49 (m, 2H), 7.42 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.29 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.97 - 6.89 (m, 2H), 5.47 (s, 1H), 4.15 (s, 1H), 3.83 (s, 3H).

^{13}C NMR δ: 160.53, 142.37, 134.64, 129.54, 128.73, 128.67, 127.70, 126.76, 126.57, 125.84, 123.41, 118.37, 117.76, 114.72, 107.05, 77.37, 77.05, 76.73, 55.47, 49.64. **(Fig. S16)**

HRMS (ESI) m/z calcd for $C_{19}H_{17}N_2O$ ($M+H^+$) 289.1341, found 289.1337; calcd for $C_{18}H_{16}N$ ($M-CN^-$), 262.1226 found 262.1219.

8. 2-(2-fluoroyphenyl)-2-(naphthalen-2-ylamino) acetonitrile: Light yellow colored solid, yield, 105 mg, 84% for **1** and 86%, 108 mg for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 - 7.64 (m, 4H), 7.50 - 7.39 (m, 2H), 7.33 - 7.15 (m, 3H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.74 (s, 1H), 4.23 (s, 1H).

^{13}C NMR δ: 161.41, 158.92, 142.03, 134.56, 131.86, 131.78, 129.61, 129.03, 129.00, 128.82, 127.71, 126.79, 126.61, 125.16, 125.12, 123.58, 121.63, 121.49, 117.79, 117.54, 116.53, 116.32, 107.48, 77.36, 77.05, 76.73, 44.70, 44.65. **(Fig. S17)**

HRMS (ESI) m/z calcd for $C_{18}H_{14}FN_2$ ($M+H^+$) 277.1137, found 277.1141; calcd for $C_{17}H_{13}FN$ ($M-CN^-$) 250.1021, found 262.1019.

9. (2-fluoroyphenyl)amino-4-phenylbut-3-enenitrile: Light malate colored crystalline product, yield, 85%, 95mg for 1 and 98mg, 87% for 2. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 - 7.42 (m, 2H), 7.41 - 7.29 (m, 3H), 7.20 - 6.97 (m, 3H), 6.94 - 6.80 (m, 2H), 6.30 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.09 (ddd, *J* = 9.2, 5.2, 1.7 Hz, 1H), 4.20 (dd, *J* = 9.5, 2.9 Hz, 1H).

^{13}C NMR δ: 153.32, 150.93, 135.58, 134.80, 132.96, 132.84, 129.08, 128.89, 127.02, 124.87, 124.84, 120.51, 120.22, 120.15, 117.35, 115.35, 115.17, 114.06, 114.03, 77.36, 77.04, 76.72, 47.48. **(Fig. S18)**

HRMS (ESI) m/z calcd for $C_{16}H_{14}FN_2$ ($M+H^+$) 253.1141, found 253.1137, calcd for $C_{15}H_{13}FN$ ($M-CN^-$) 226.1016, found 226.1020.

10. 2-(4-methoxyphenyl)-2-(phenylamino) acetonitrile: Whitish yellow colored crystalline product, yield, 88 mg, 83% for **1** and 90 mg,85% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 - 7.39 (m, 2H), 7.24 - 7.15 (m, 2H), 6.93 - 6.85 (m, 2H), 6.82 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.73 - 6.65 (m, 2H), 5.28 (d, *J* = 7.9 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR δ: 159.41, 143.72, 128.53, 127.60, 124.93, 119.16, 117.40, 113.62, 113.08, 76.32, 76.01, 75.69, 54.41, 48.65. **(Fig. S19)**

HRMS (ESI) m/z calcd for $C_{15}H_{15}N_2O$ ($M+H^+$) 239.1184, found 239.1179; calcd for $C_{14}H_{14}N$ ($M-CN^-$) 212.1070, found 212.1069.

11. 2-(4-methoxyphenyl)-2-(pyridine-3-ylamino) acetonitrile: Whitish yellow colored crystalline product, yield, 87 mg, 82% for **1** and 89 mg, 84% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 - 8.01 (m, 2H), 7.55 - 7.46 (m, 2H), 7.20 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.08 (ddd, *J* = 8.3, 3.0, 1.4 Hz, 1H), 7.02 - 6.94 (m, 2H), 5.37 (d, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR δ: 160.65, 141.45, 140.87, 137.24, 128.64, 125.15, 123.91, 120.15, 117.78, 114.81, 77.34, 77.03, 76.71, 55.47, 49.28. **(Fig. S20)**

HRMS (ESI) m/z calcd for $C_{14}H_{14}N$ ($M-CN^-$) 213.1022, found 213.1020.

12. 2-((2-fluorophenyl)amino)-2-(4-methoxyphenyl) acetonitrile: Whitish yellow colored crystalline product, yield, 93 mg, 81% for **1** and 95 mg, 83% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 - 7.48 (m, 2H), 7.13 - 7.00 (m, 2H), 7.00 - 6.95 (m, 2H), 6.91 (td, *J* = 8.3, 1.6 Hz, 1H), 6.83 (dddd, *J* = 8.1, 7.5, 5.0, 1.6 Hz, 1H), 5.39 (d, *J* = 8.1 Hz, 1H), 4.25 (dd, *J* = 8.1, 3.1 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR δ: 160.58, 153.17, 150.78, 133.26, 133.14, 128.66, 125.45, 124.84, 124.80, 119.97, 119.90, 118.08, 115.23, 115.05, 114.74, 113.82, 113.79, 77.35, 77.23, 77.03, 76.71, 55.45, 49.37. **(Fig. S21)**

HRMS (ESI) m/z calcd for $C_{15}H_{14}FN_2O$ ($M+H^+$) 257.1090, found 257.1077; calcd for $C_{14}H_{13}FNO$ ($M-CN^-$) 230.0976, found 230.0970.

13. 2-(2-fluorophenyl)-2-(pyridine-4-ylamino) acetonitrile: Whitish yellow colored crystalline product, yield, 84 mg, 83% for **1** and 86 mg, 85% for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 2.8 Hz, 1H), 8.13 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.64 (td, *J* = 7.6, 1.8 Hz, 1H), 7.55 - 7.33 (m, 1H), 7.28 - 7.10 (m, 4H), 5.63 (d, *J* = 8.4 Hz, 1H), 4.63 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR δ: 161.31, 158.82, 141.50, 140.80, 137.26, 132.05, 131.97, 128.98, 128.96, 125.20, 125.16, 124.00, 121.04, 120.91, 120.38, 117.05, 116.54, 116.33, 77.37, 77.05, 76.74, 44.30, 44.26. **(Fig. S22)**

HRMS (ESI) m/z calcd for $C_{13}H_{11}FN_3$ ($M+H^+$) 228.0937, found 228.0925.

14. 2-(2-fluorophenyl)-2-((2-fluorophenyl) amino) acetonitrile: Whitish yellow colored crystalline product, yield, 85%, 93 mg for **1** and 88%, 96 mg for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67-7.62 (td, J = 7.6, 1.8 Hz, 1H), 7.44 (dddd, *J* = 8.2, 7.2, 5.3, 1.8 Hz, 1H), 7.25 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (ddd, *J* = 9.7, 8.3, 1.2 Hz, 1H), 7.09 (tt, *J* = 7.7, 1.1 Hz, 1H), 7.04 (ddd, *J* = 11.4, 8.1, 1.4 Hz, 1H), 6.94 (td, *J* = 8.3, 1.6 Hz, 1H), 6.91 - 6.77 (m, 1H), 5.64 (d, *J* = 8.6 Hz, 1H), 4.34 (d, *J* = 5.9 Hz, 1H).

^{13}C NMR δ: 161.35, 158.87, 153.29, 150.90, 132.93, 132.81, 131.97, 131.89, 129.00, 128.97, 125.18, 125.14, 124.89, 124.86, 121.33, 121.19, 120.37, 120.30, 117.31, 116.52, 116.31, 115.35, 115.16, 114.07, 114.04, 77.40, 77.08, 76.76, 44.37. **(Fig. S23)**

HRMS (ESI) m/z calcd for $C_{14}H_{11}F_2N_2$ ($M+H^+$) 245.0890, found 245.076; calcd for $C_{13}H_{10}F_2N$ ($M-CN^-$) 218.0776, found 218.0769.

^{1}H and ^{13}C NMR spectra for H_4abtc, azpy linkers, and Cyanosilylation reaction products.

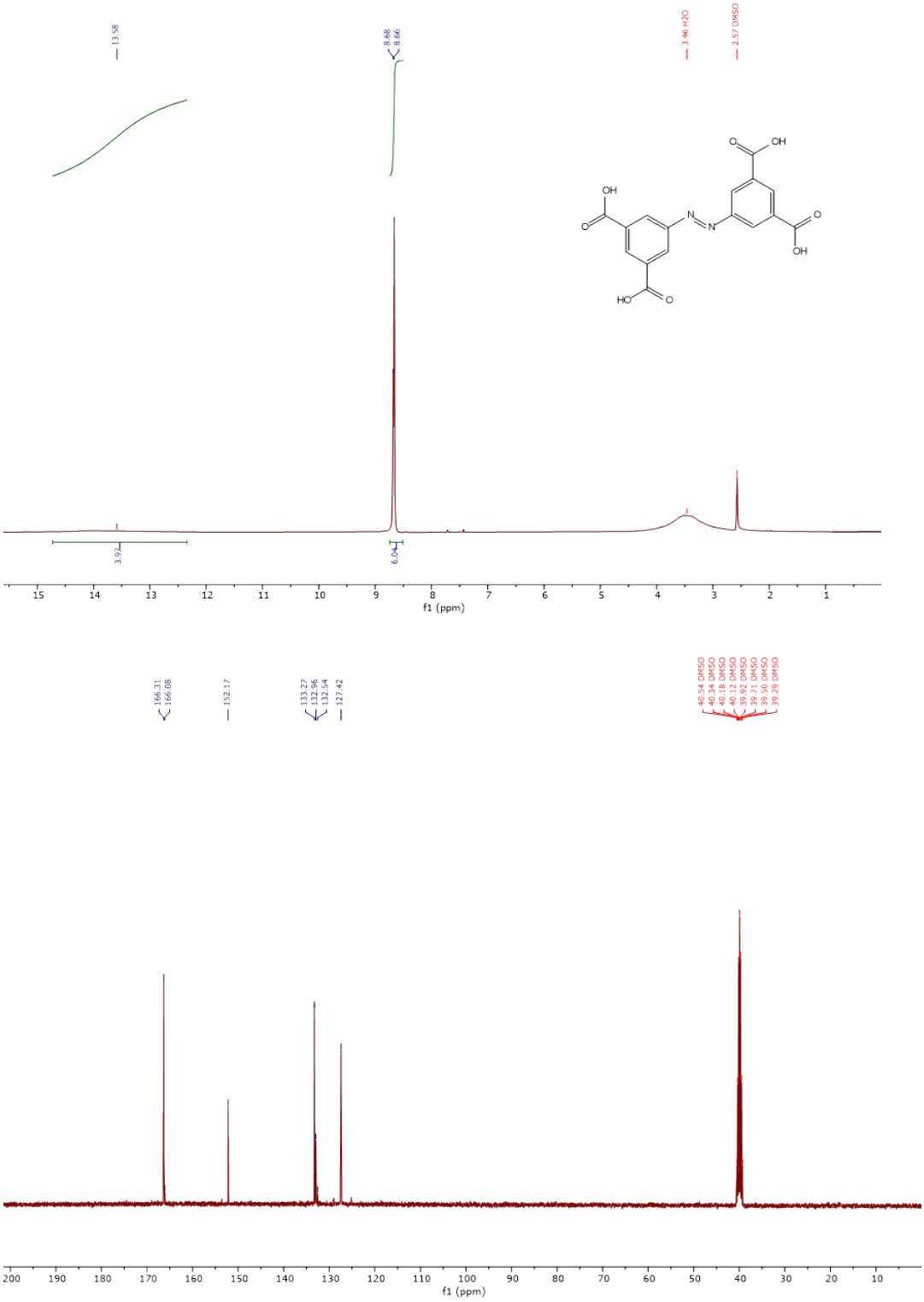


Fig. S11a. ^{1}H and ^{13}C NMR of H_4abtc.

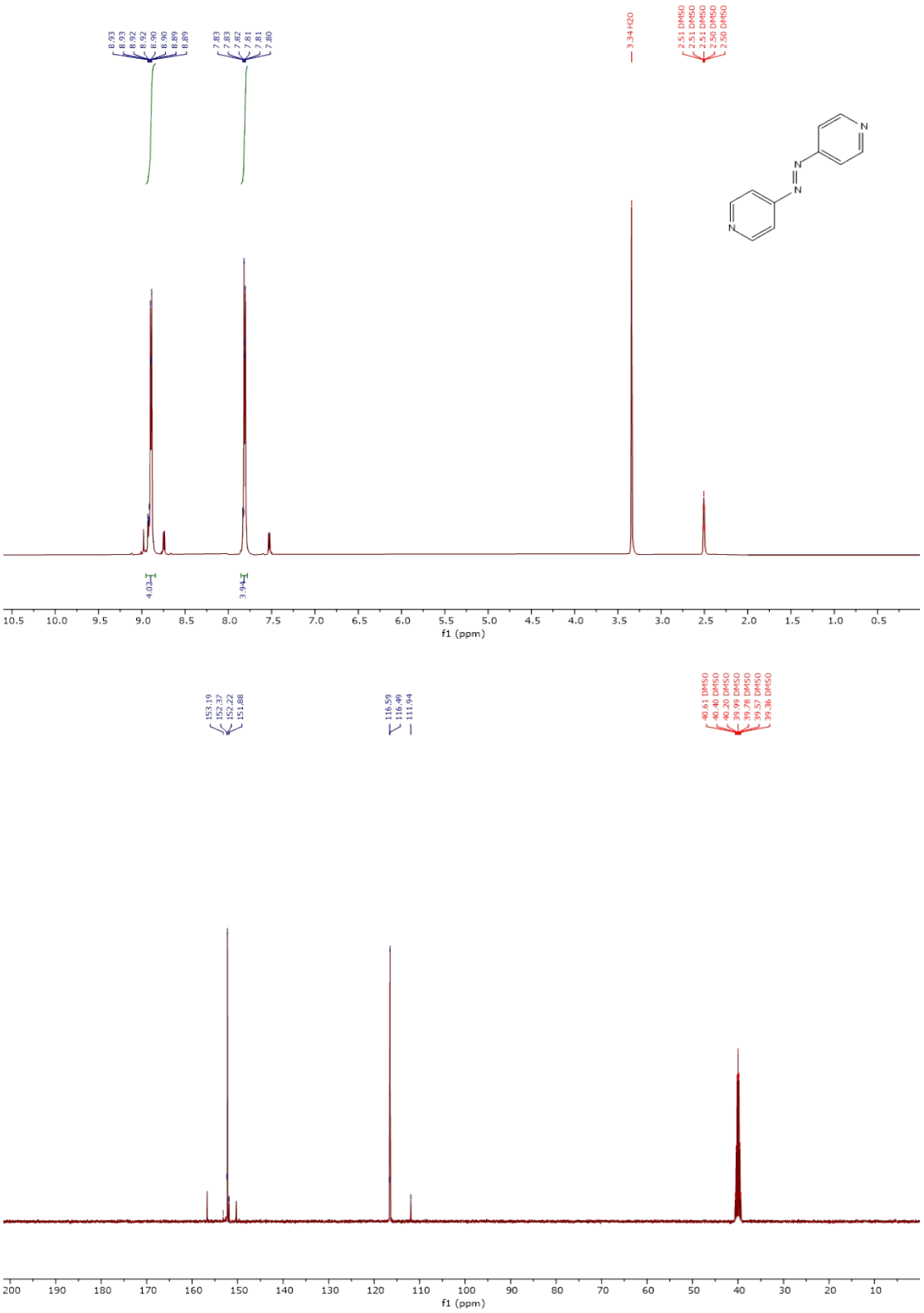


Fig. S11b. ^{1}H and ^{13}C NMR of azpy.

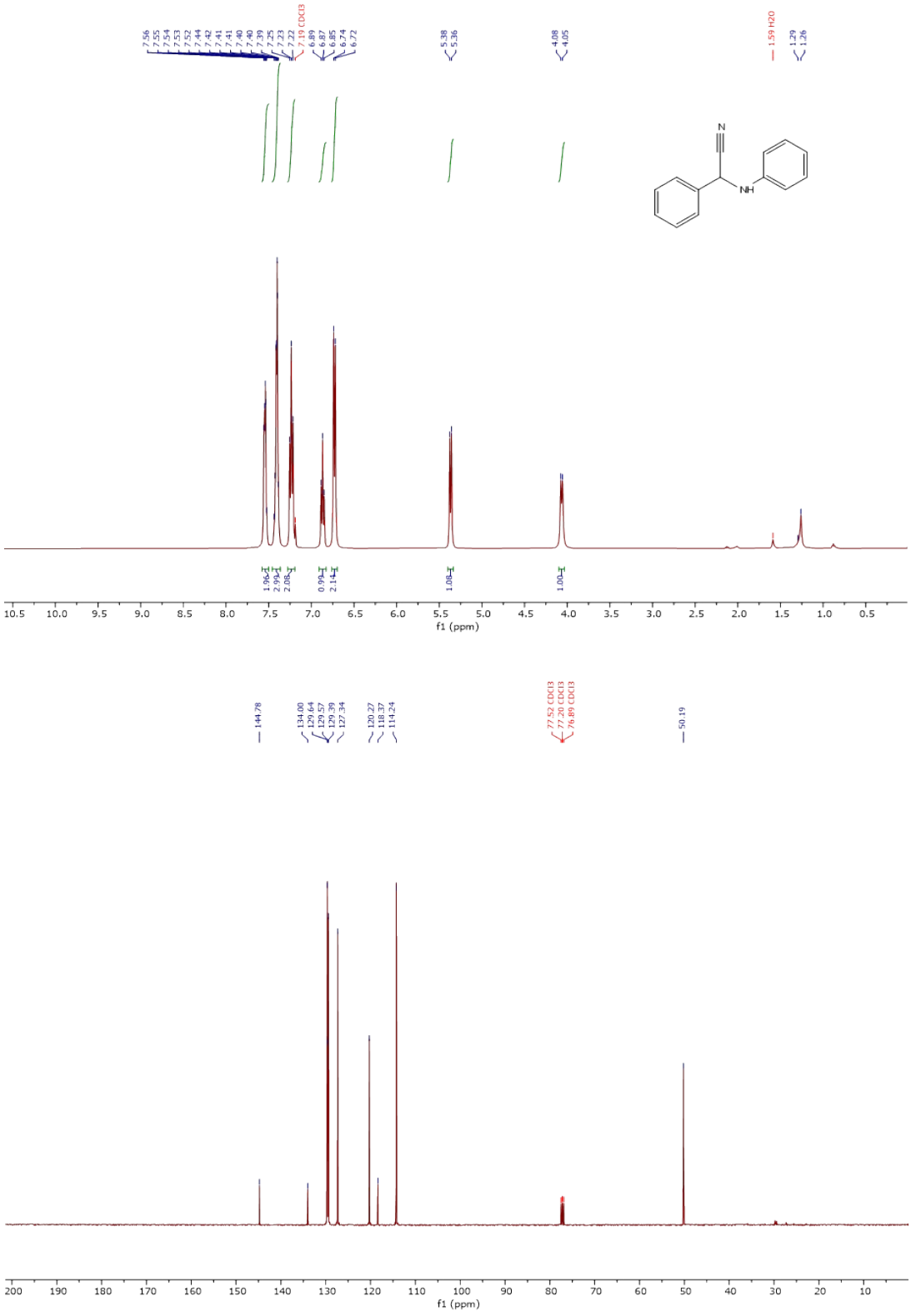


Fig. S12. ^{1}H and ^{13}C NMR of 2-phenyl-2-(phenylamino)acetonitrile.

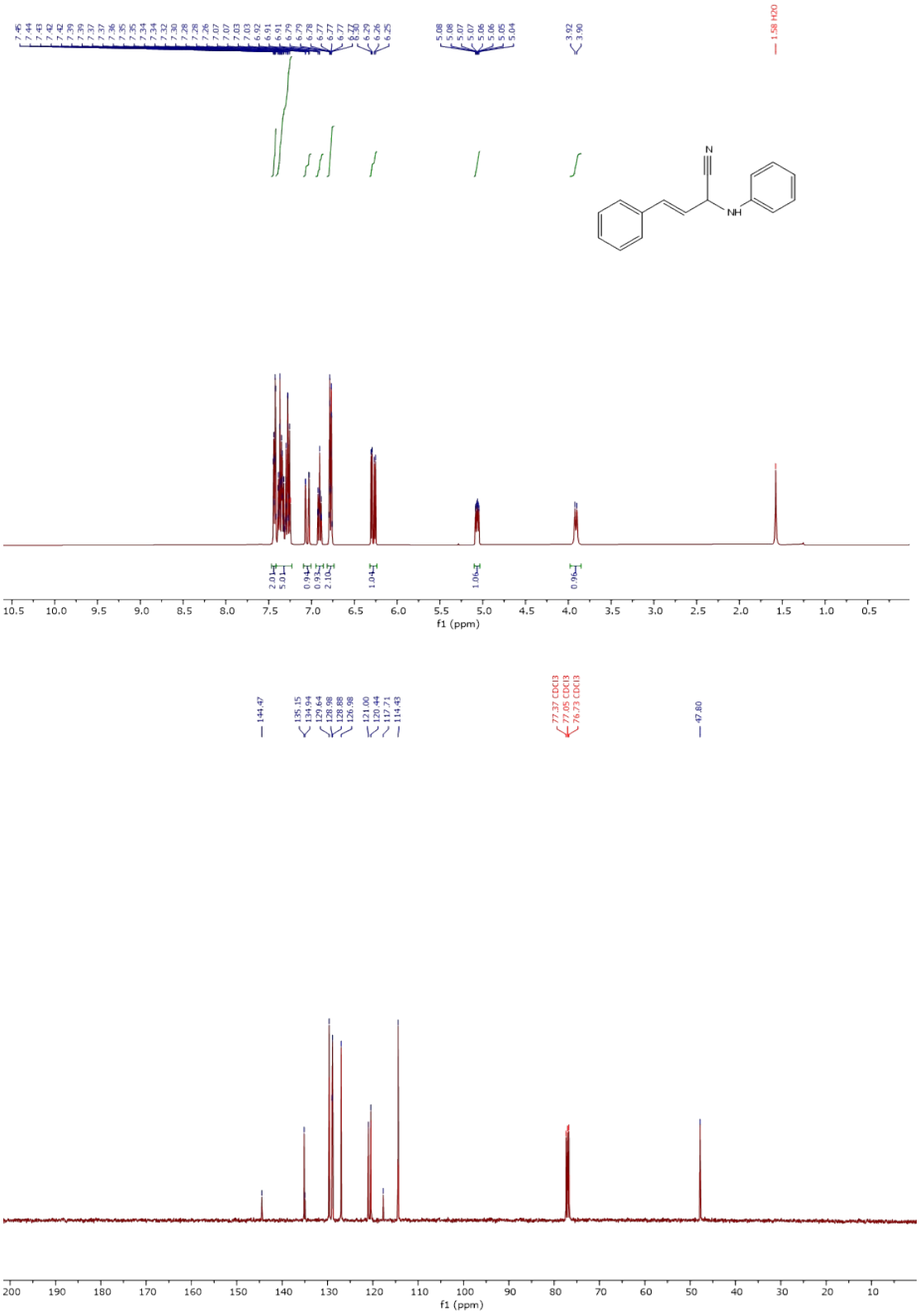


Fig. S13. ^{1}H and ^{13}C NMR of 4-phenyl-2-(phenylamino) but-3-enenitrile.

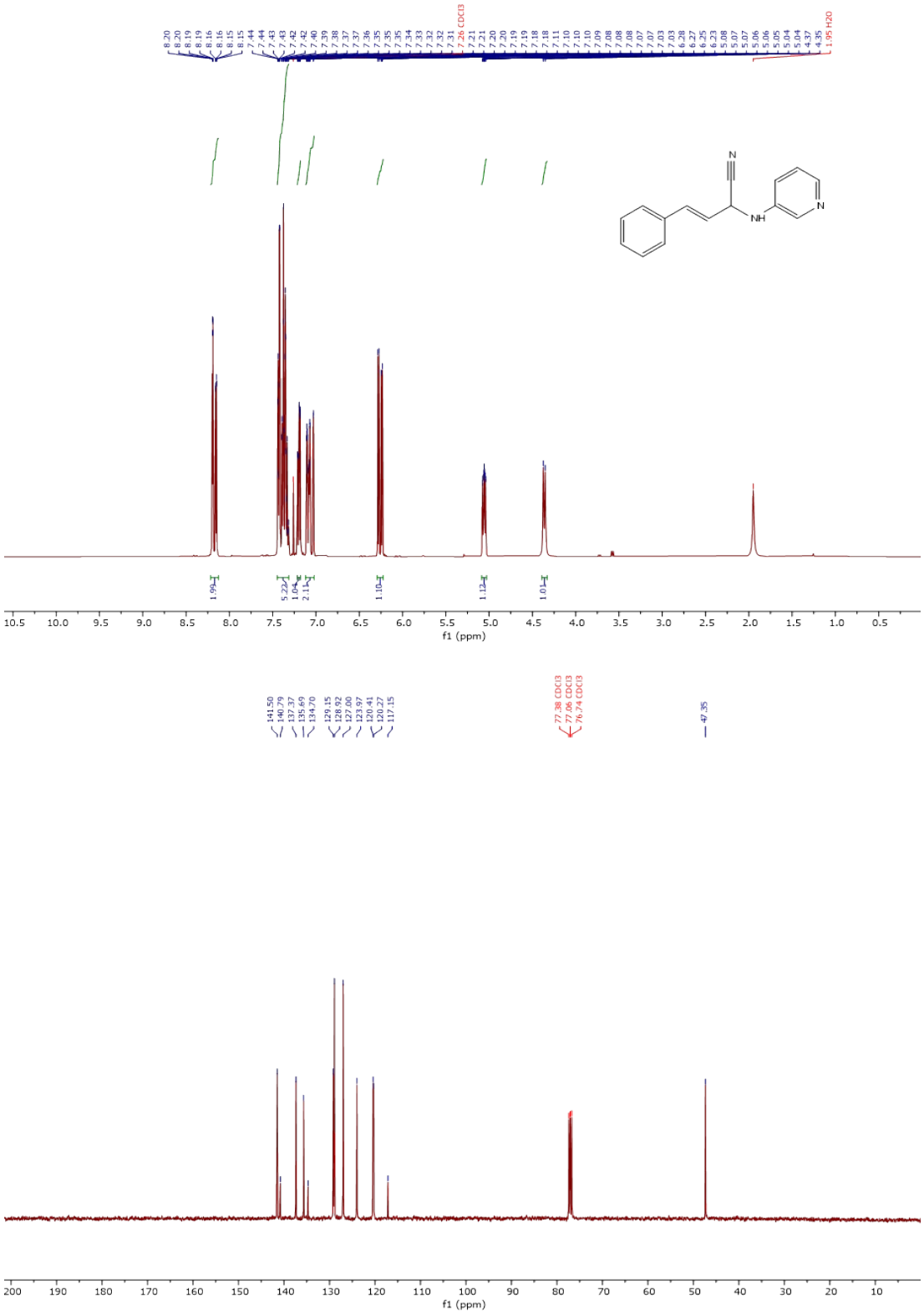


Fig. S14. ^{1}H and ^{13}C NMR of 4-phenyl-2-(pyridin-3-ylamino) but-3-enenitrile.

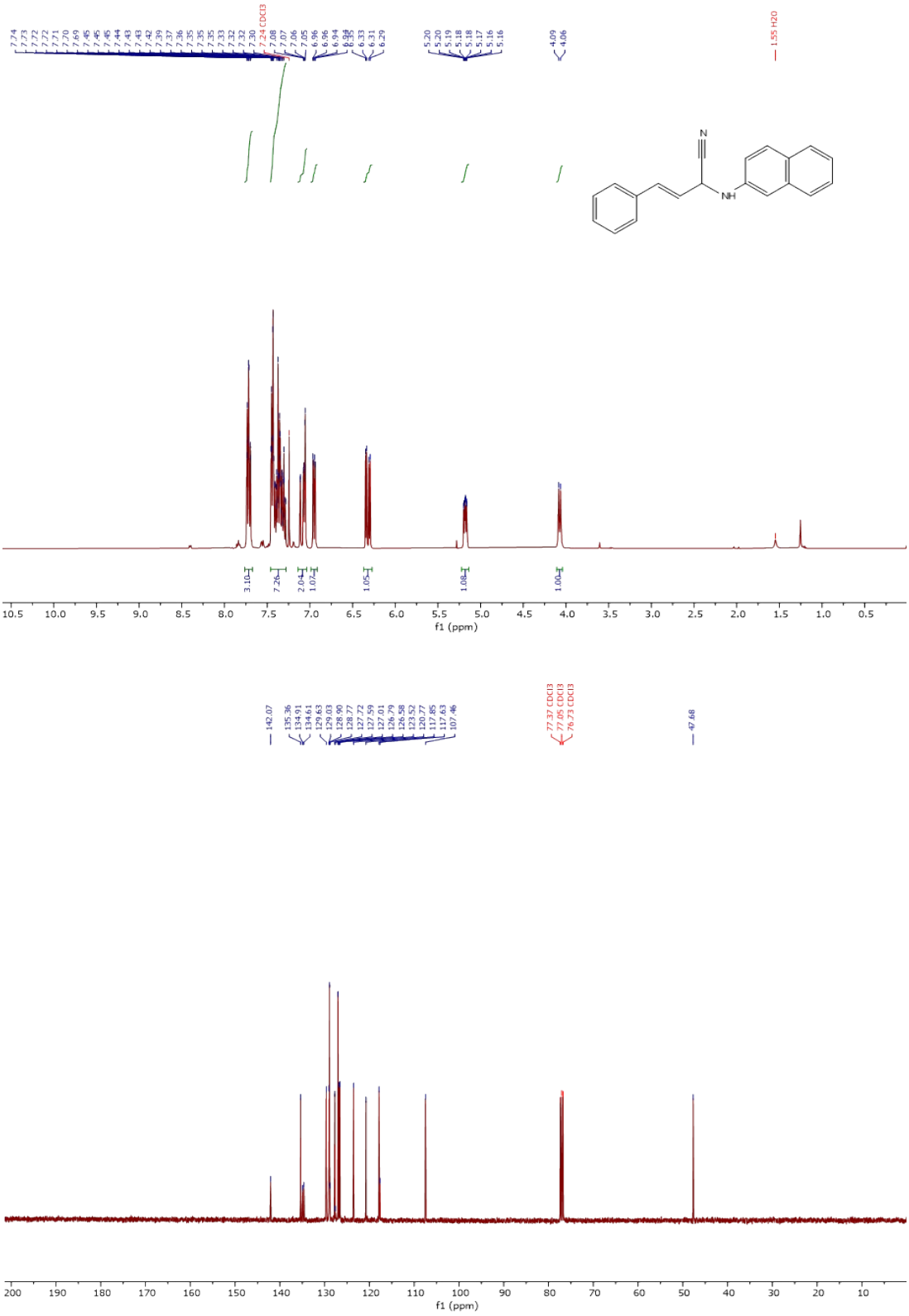


Fig. S15. ^{1}H and ^{13}C NMR of 2-(naphthalen-2-ylamino)-4-phenylbut-3-enenitrile.

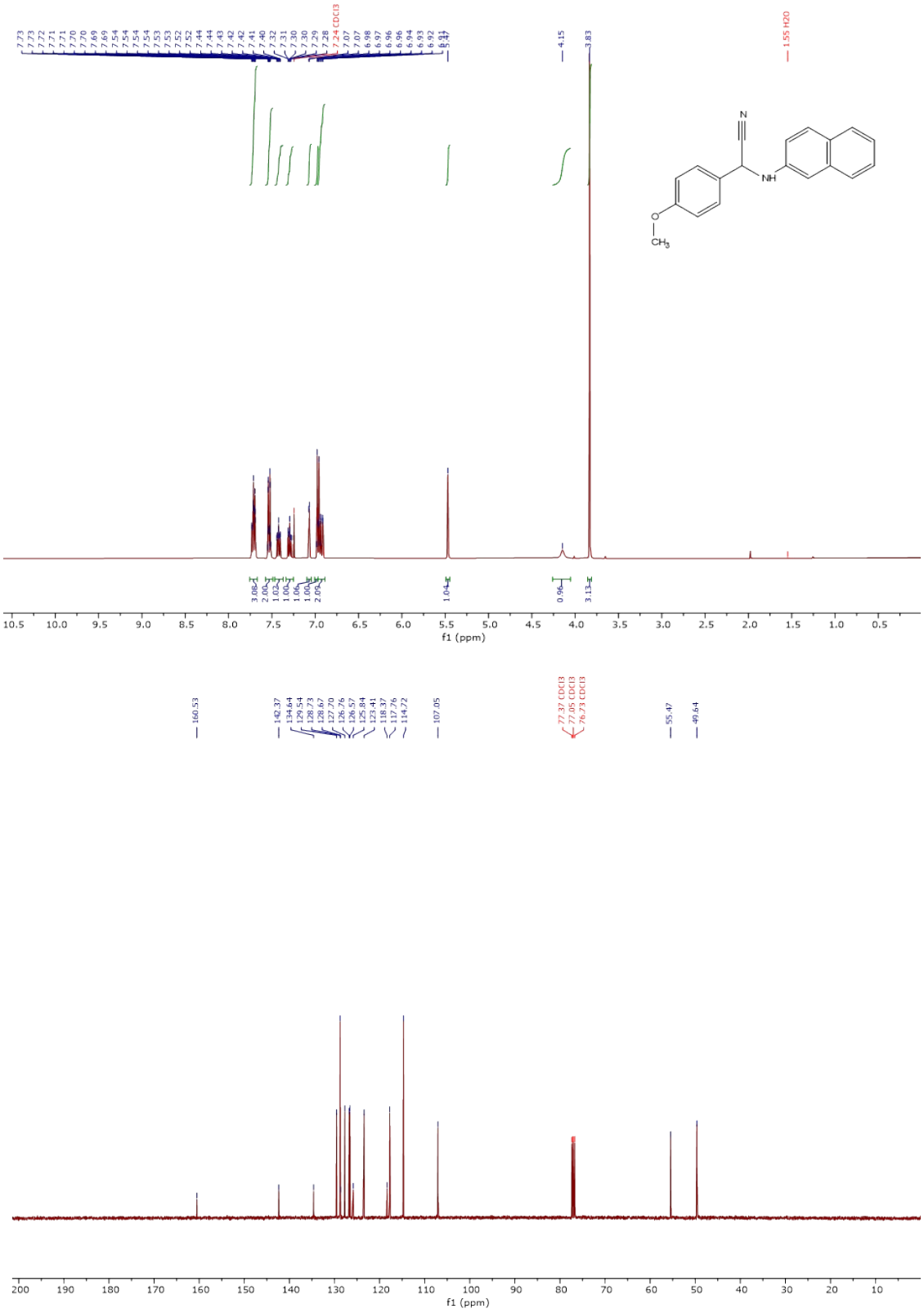


Fig. S16. ^{1}H and ^{13}C NMR of 2-(4-methoxyphenyl)-2-(naphthalen-2-ylamino) acetonitrile.

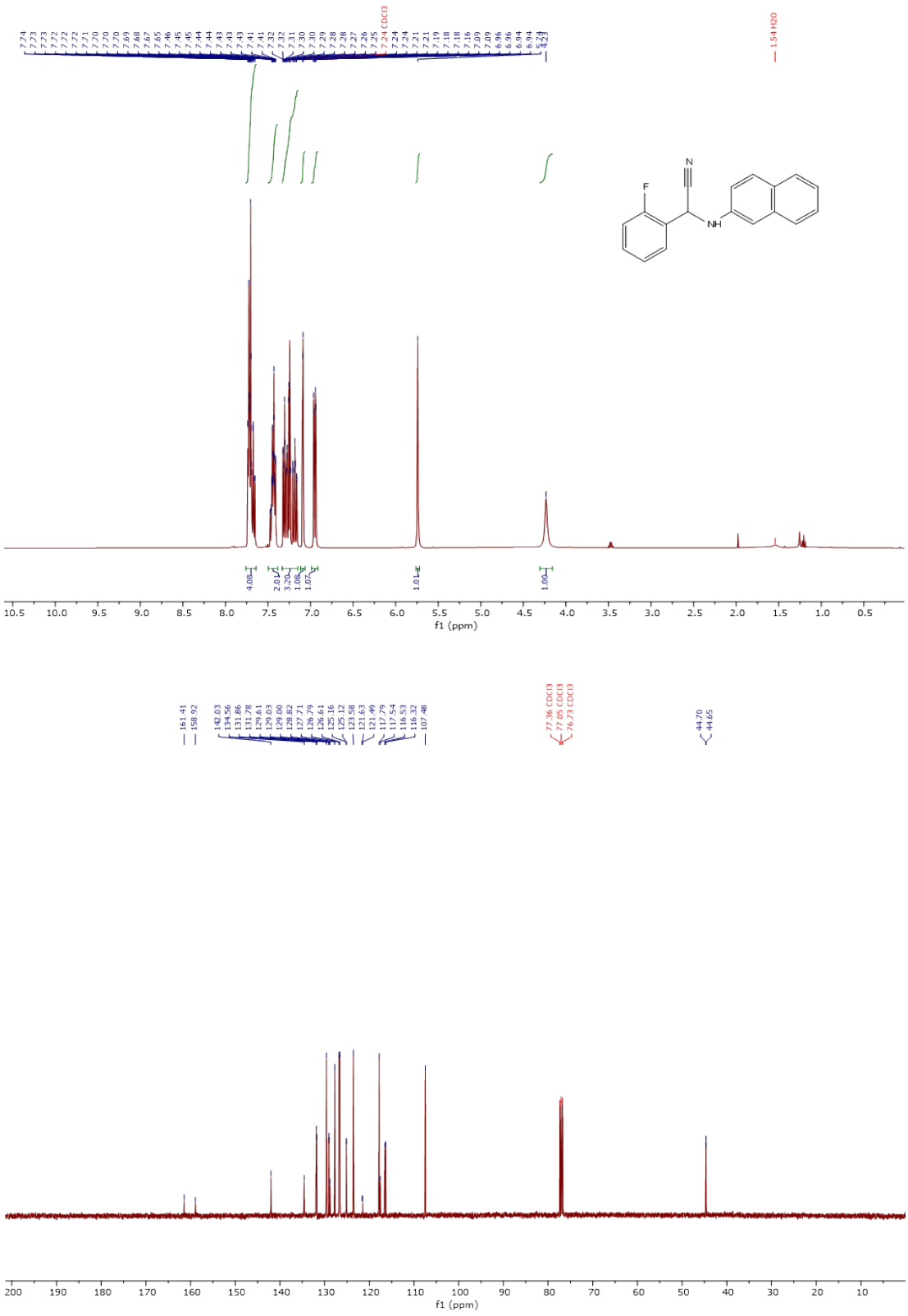


Fig. S17. ^{1}H and ^{13}C NMR of 2-(2-fluoroyphenyl)-2-(naphthalen-2-ylamino) acetonitrile.

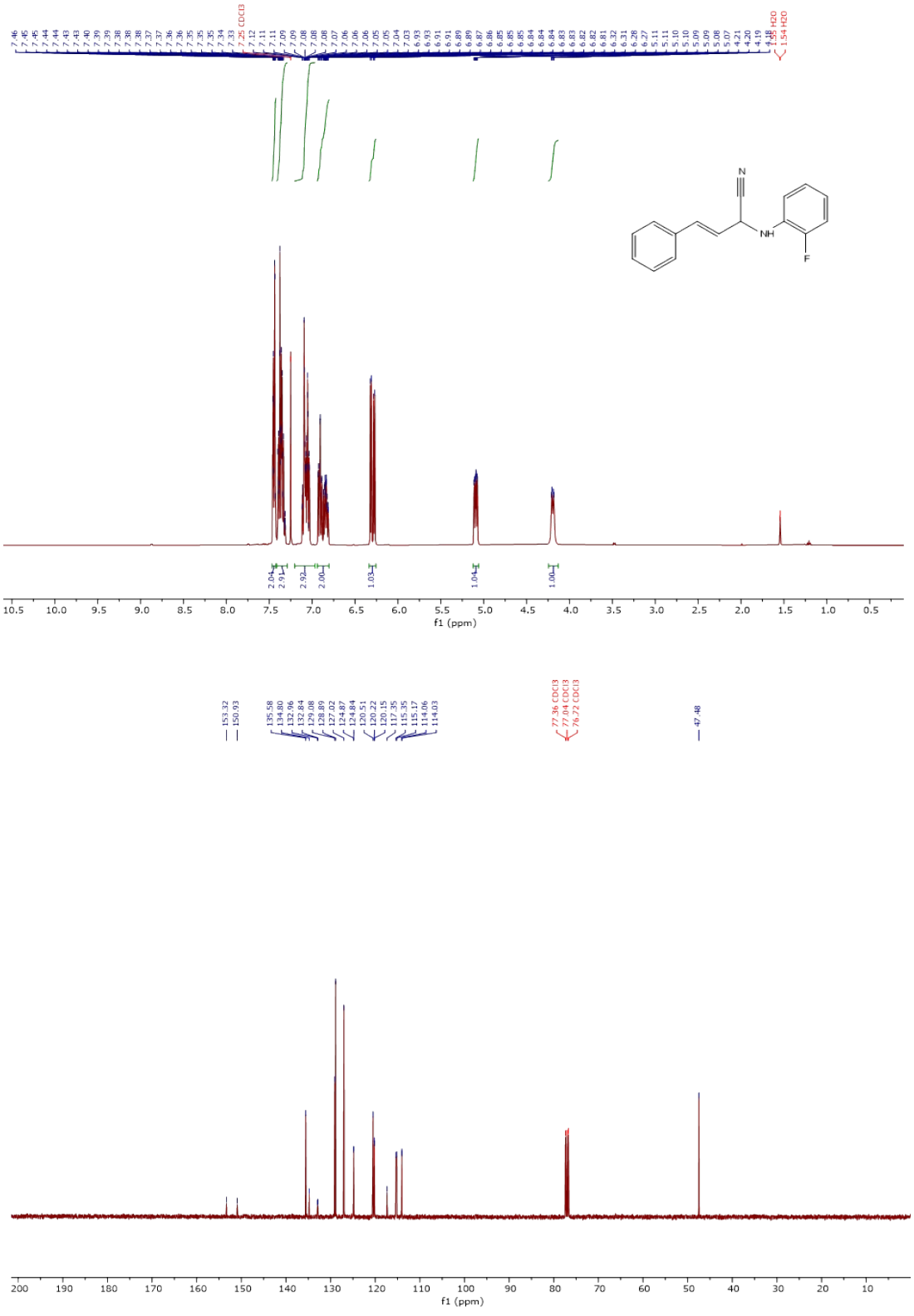


Fig. S18. ^{1}H and ^{13}C NMR of (2-fluoroyphenyl)amino-4-phenylbut-3-enenitrile.

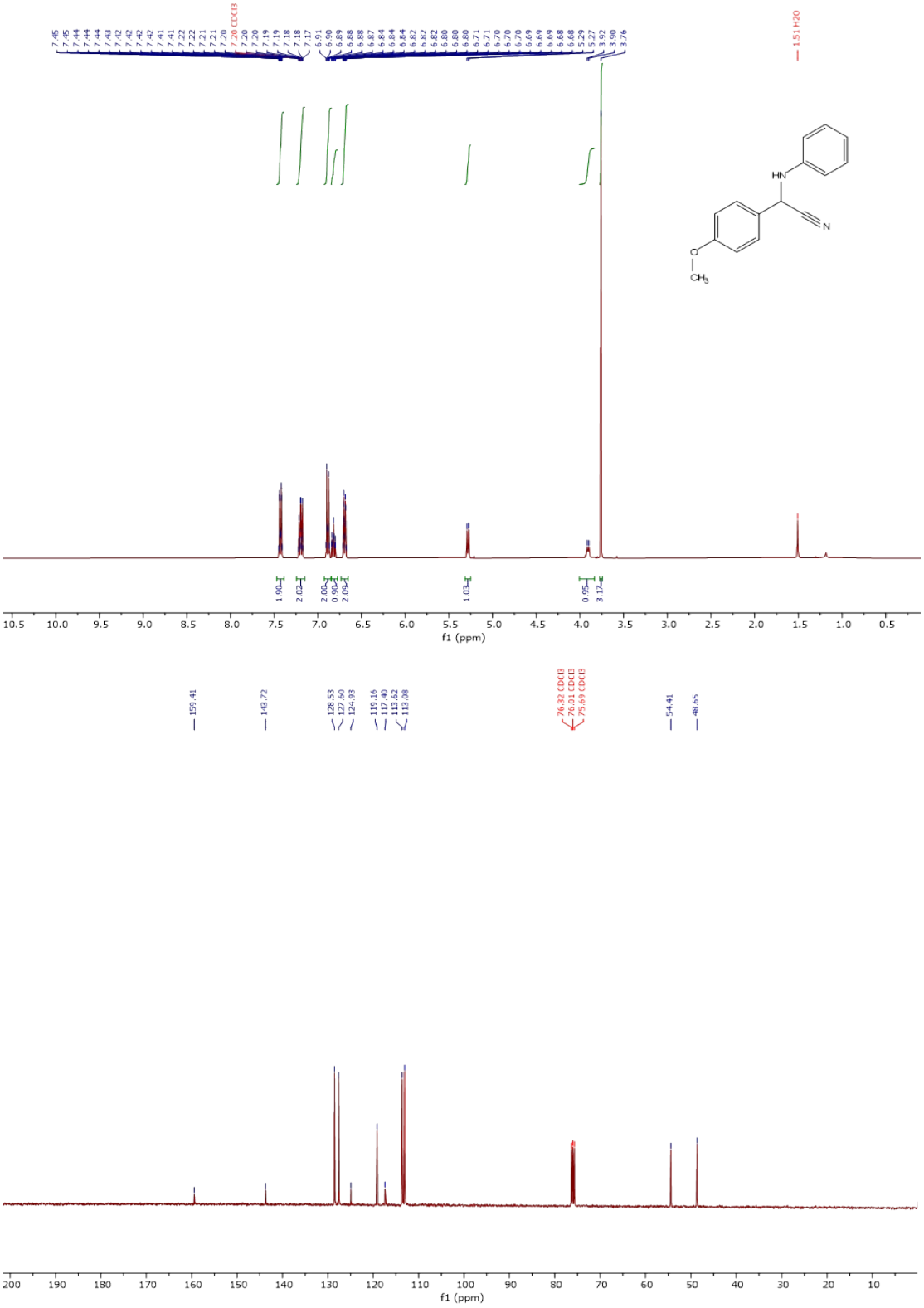


Fig. S19. ^{1}H and ^{13}C NMR of 2-(4-methoxyphenyl)-2-(phenylamino) acetonitrile.

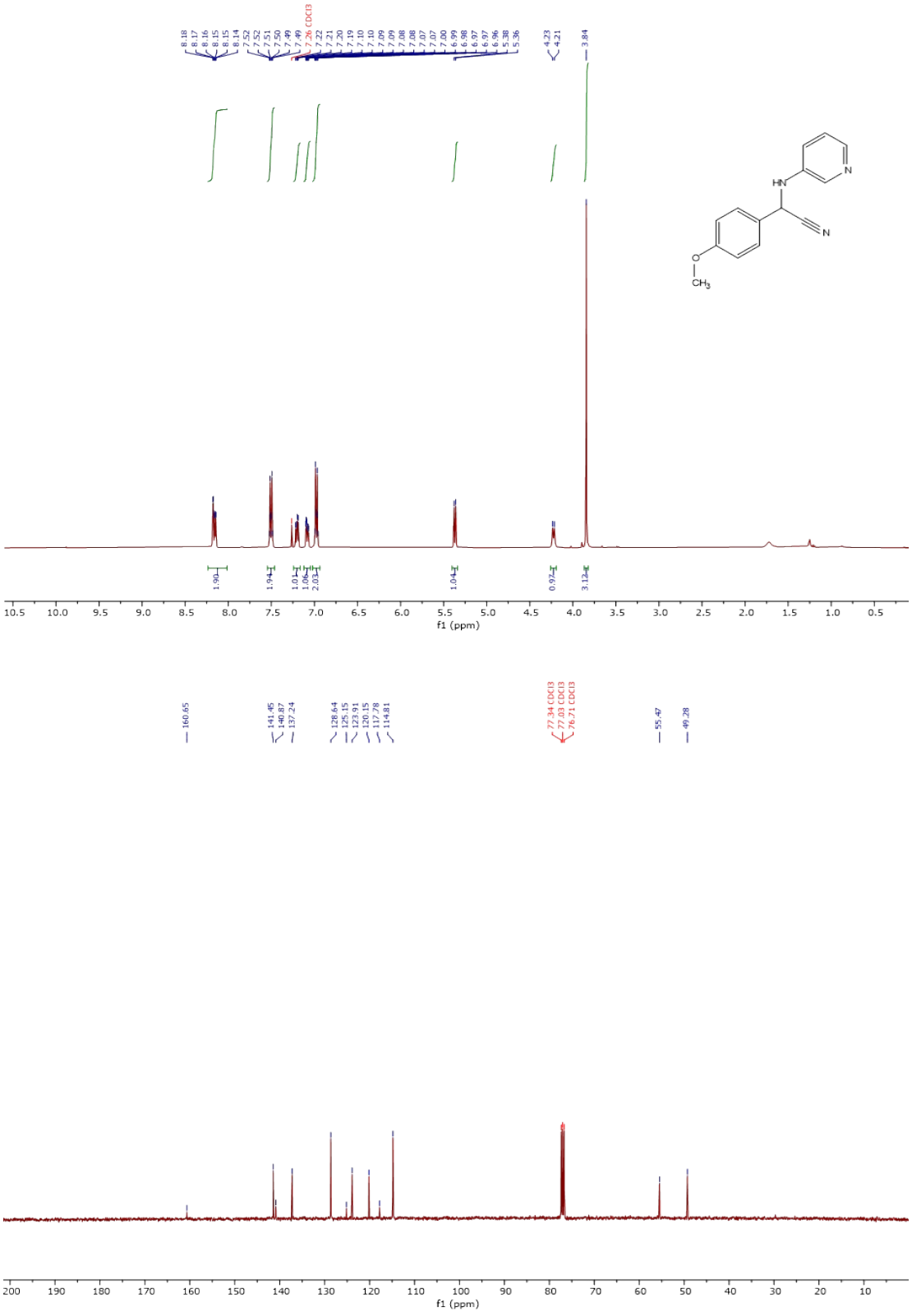


Fig. S20. ^{1}H and ^{13}C NMR of 2-(4-methoxyphenyl)-2-(pyridine-3-ylamino) acetonitrile.

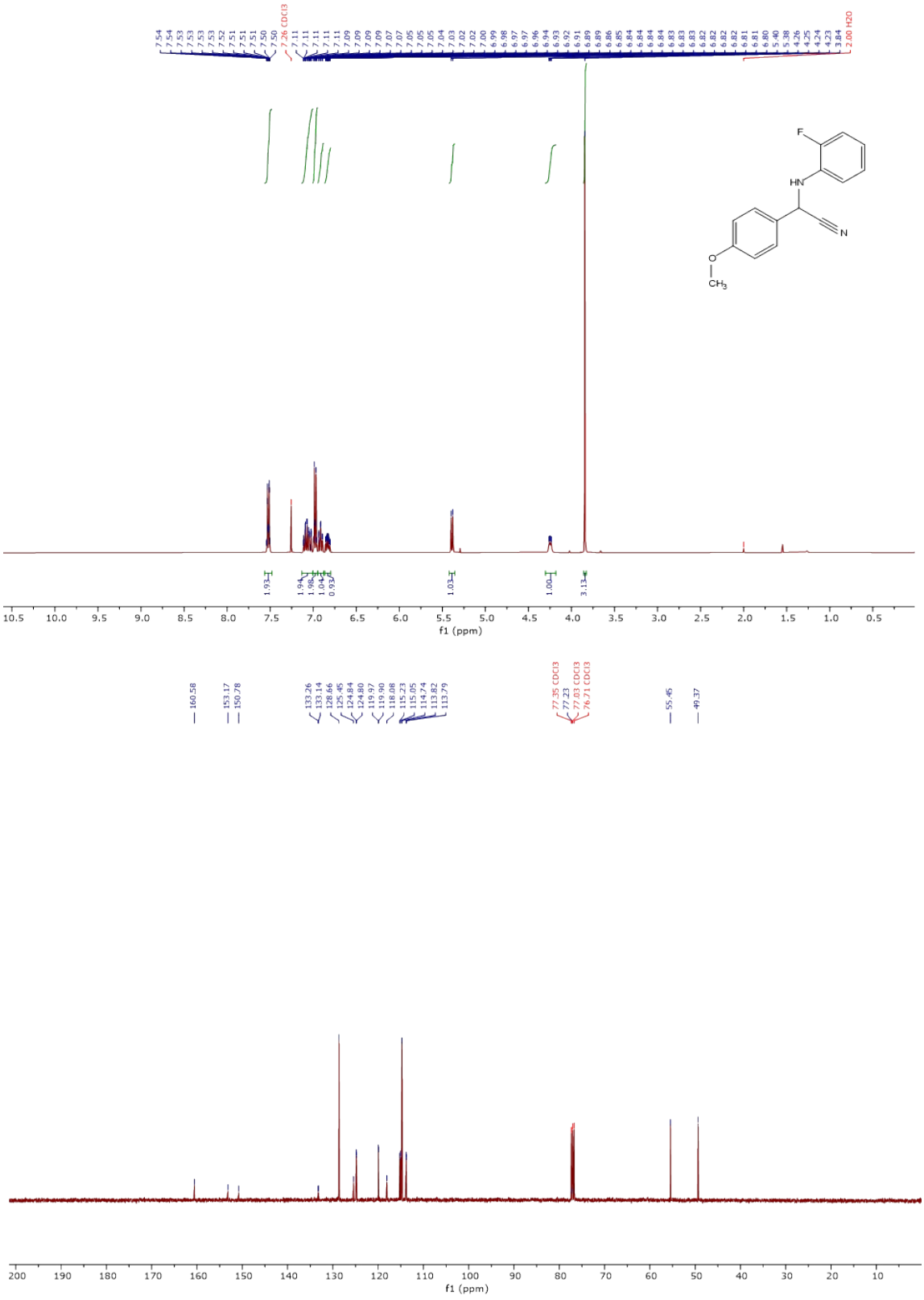


Fig. S21. ^{1}H and ^{13}C NMR of 2-((2-fluorophenyl)amino)-2-(4-methoxyphenyl) acetonitrile.

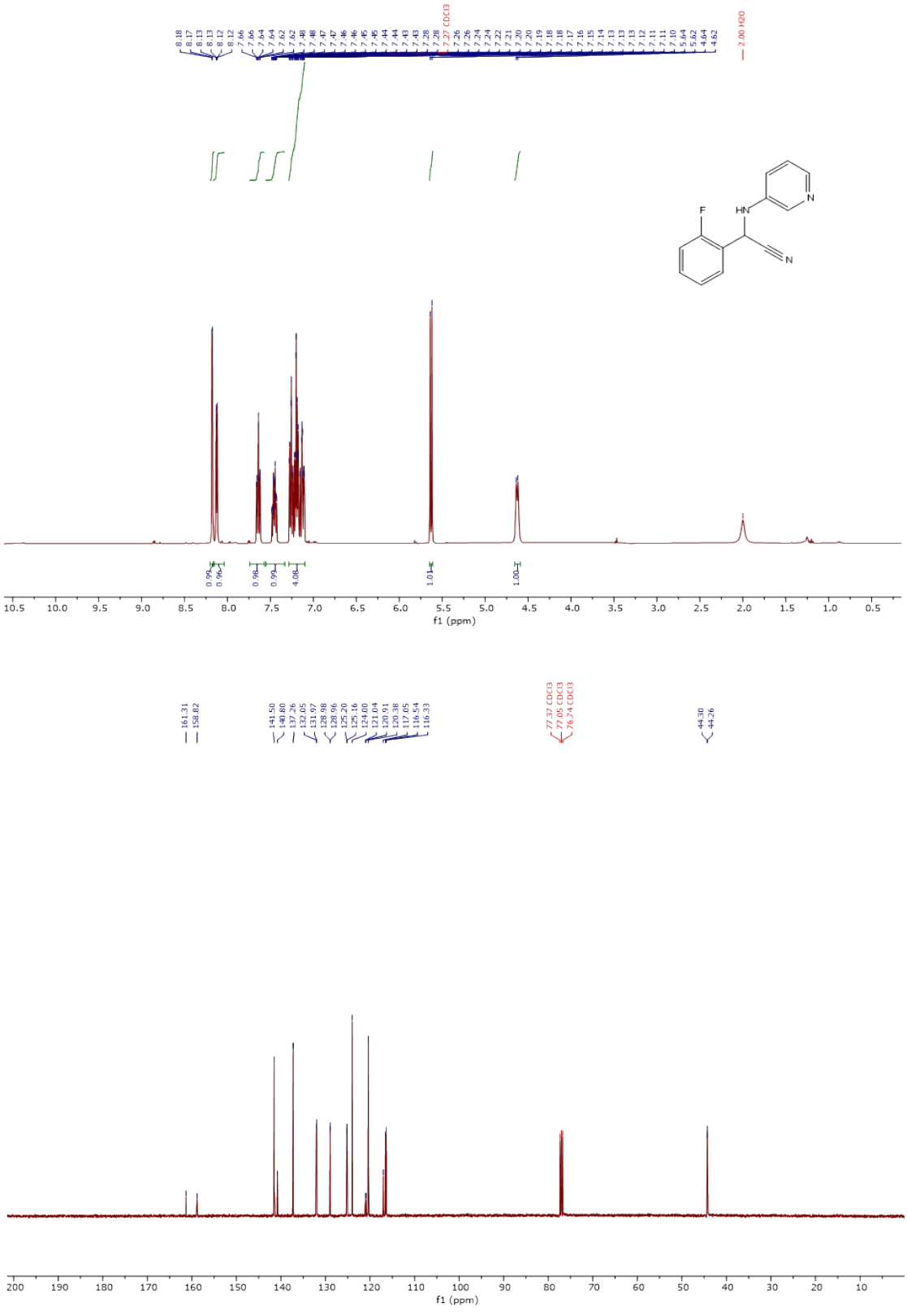


Fig. S22. ^{1}H and ^{13}C NMR of 2-(2-fluorophenyl)-2-(pyridine-4-ylamino) acetonitrile.

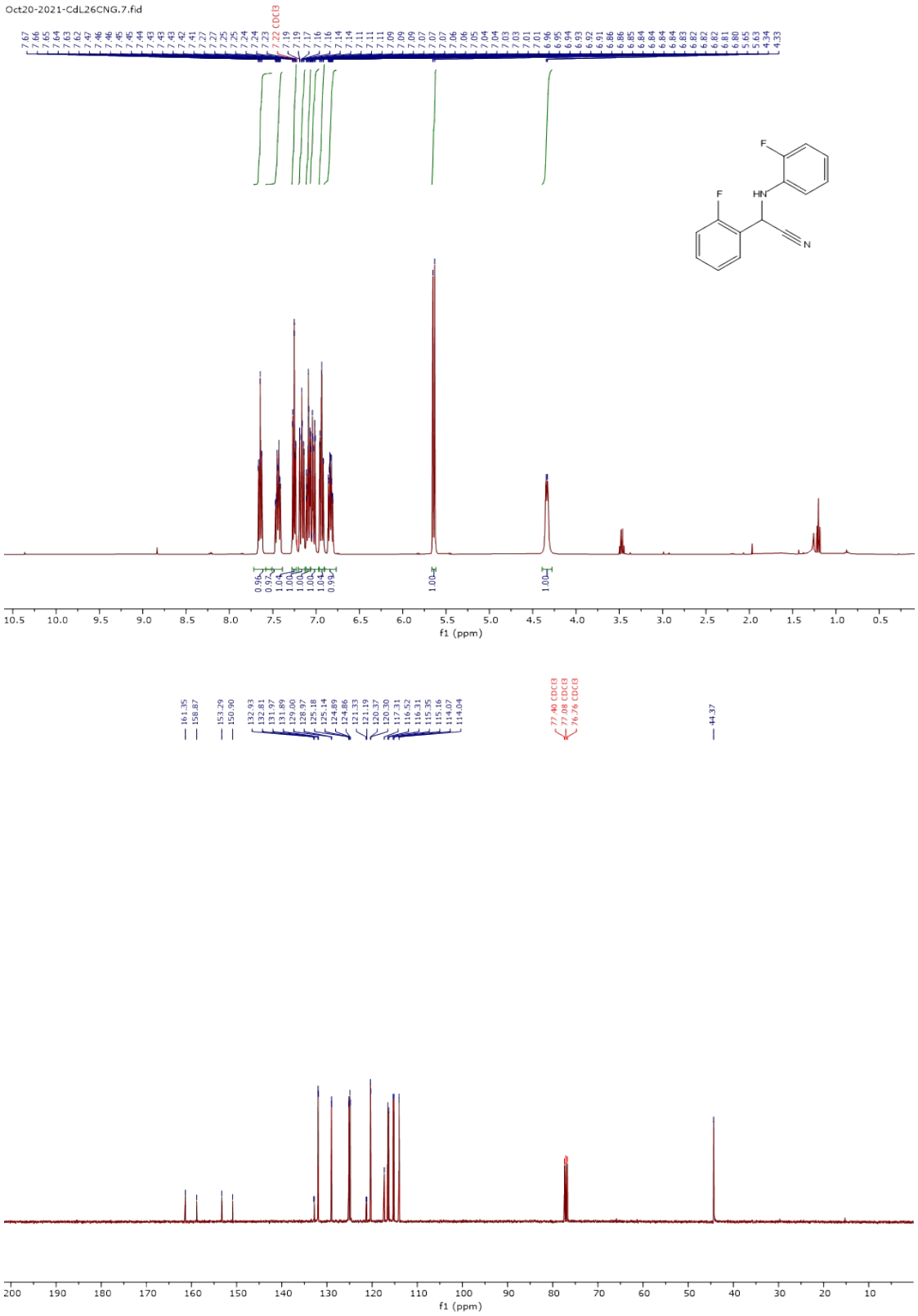
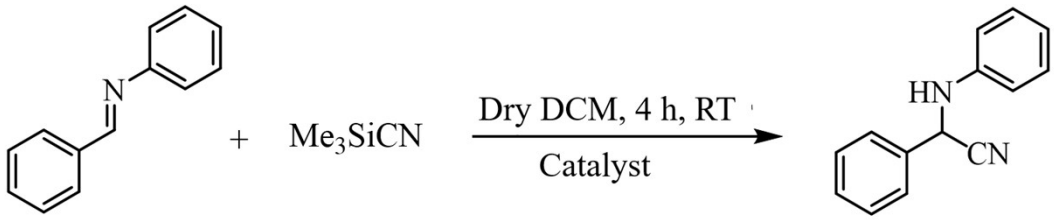


Fig. S23. ^{1}H and ^{13}C NMR of 2-(2-fluorophenyl)-2-((2- fluorophenyl) amino) acetonitrile.

Table S3. Comparison of **1** and **2** as catalysts with some other reported catalysts for the imines



Entry No.	Catalysts	Conditions and Yield (%)	References
1	**1**	4hrs, RT and 93	This work
	2	4hrs, RT and 95	
2	(i) $[Cu(L)(H_2O)]\cdot 2H_2O$	4hrs, RT and 81	S1
	(ii) [Zn(L)]	4hrs, RT and 80	
	(iii) $[Ag(HL)(CH_3CN)]$	4hrs, RT and 72	
	(i) $[Cu(L)(H_2O)]\cdot 2H_2O$	5hrs, RT and 97	
	(ii) [Zn(L)]	5hrs, RT and 98	
	(iii) [Ag(HL)(CH3CN)]	5hrs, RT and 92	
3	(i) $[Cd(L)(H_2O)]\cdot H_2O$	4hrs, RT and 81	S2
	(ii) [Cd(L)	4hrs, RT and 70	
4	(i) $[Cu_2(\mu_3\text{-}OH)(H_2O)\{NIPA\}\text{-}(CN_4H)]\cdot(H_2O)$	6hrs, RT and 95	S3
	(ii) $[Cu_2(\mu_3\text{-}OH)(H_2O)\{NIPA\}\text{-}(CN_5\text{-}H_2)]\cdot(H_2O)$	6hrs, RT and 53	
5	$\{[In_3(NIPA)_3(HNIPA)(OH)_2]\cdot 4H_2O\}_n$	24hrs, RT and 96	S4

cyanosilylation reaction.

H_2L = 5-(3,5-dimethyl-1H-pyrazol-1-yl) 1,3-benzenedicarboxylic acid; H_2NIPA = 5-nitroisophthalic acid; CN_4H = tetrazole; $CN_5\text{-}H_2$ = aminotetrazole.

Reference

S1. N. Kumar, T. Rom, V. Singh and A. K. Paul, *Cryst. Growth. Des.*, 2020, **20**, 5277-5288.

S2. N. Kumar and A. K. Paul, *Inorg. Chem.*, 2020, **59**, 1284-1294.

S3. D. Sarma, K. V. Ramanujachary, N. Stock and S. Natarajan, *Cryst. Growth. Des.*, 2011, **11**, 1357-1369.

S4. J. Chai, P. Zhang, J. Xu, H. Qi, J. Sun, S. Jing, X. Chen, Y. Fan and L. Wang, *Inorg. Chim. Acta*., 2018, **479**, 165-171.