

## Supporting Information

### **Acetyl Acetone Covalent Triazine Framework: An Efficient Carbon Capture and Storage Material and a Highly Stable Heterogeneous Catalyst**

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**Synthesis of linker 4,4'-malonyldibenzonitrile (acac-CN):**

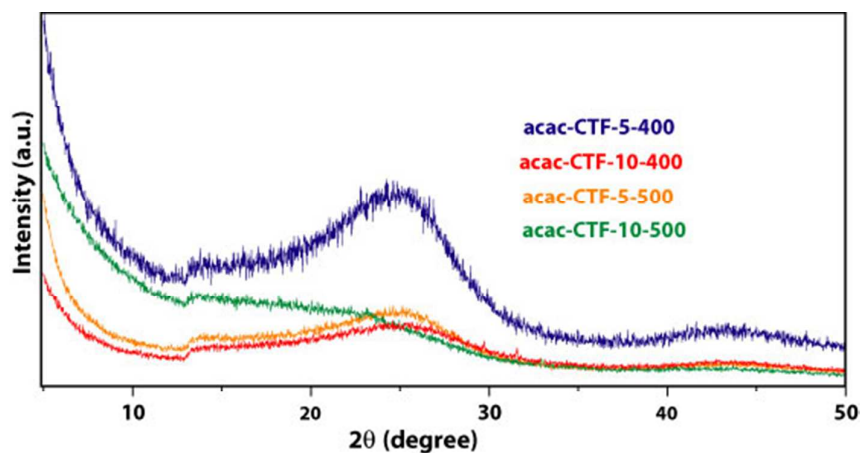
A 1.66 g (41.51 mmol) of NaH (60% in mineral oil) was dispersed in 50 mL of anhydrous tetrahydrofuran (THF) under argon atmosphere and stirred for 30 minutes. The heterogeneous mixture was transferred to ice bath and to that solid 4-acetylbenzonitrile (2.0 g, 13.7 mmol) was added. Once the mixture become slightly yellow in color, a solution of methyl 4-cyanobenzoate (2.42 g, 15.03 mmol) in anhydrous THF (10 mL) was then added dropwise over a period of 30 min under Ar. The whole mixture was stirred for 1 h in ice bath followed by 1 h in room temperature. The mixture was refluxed for 24 h under Ar and then quenched with ice. The pH of the reaction mixture was adjusted to neutral by the slow addition of 1 N of HCl and linker was recovered by filtration and washed with distilled H<sub>2</sub>O. The sticky yellow solids were washed with hot EtOH several times to afford pure linker as a pale-yellow solid. Yield: 85%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.11 (d, *J*=8.7, 4 H), 7.844 (d, *J*=8.4, 4 H), 6.878 (s, 1 H); IR (KBr, cm<sup>-1</sup>): 3460, 3100, 3060, 3050, 2230, 1700, 1610, 1570, 1510, 1430, 1320, 1290, 1180, 1120, 1020, 935, 862, 769, 744, 692.

**Table S1. Synthetic conditions and abbreviations used for acac-CTFs.<sup>a</sup>**

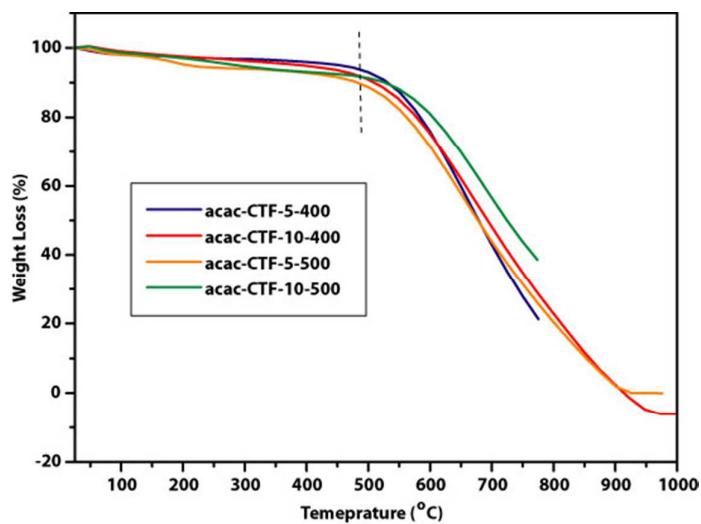
Sl. No	acac Linker : ZnCl <sub>2</sub>	Temperature (°C)	Yield (%)	abbreviations
1	1:5	400	55	acac-CTF-5-400
2	1:10	400	54	acac-CTF-10-400
3	1:5	500	45	acac-CTF-5-500
4	1:10	500	40	acac-CTF-10-500

<sup>a</sup>48 h**Table S2. Elemental Analysis of all the obtained acac-CTFs and V@acac-CTF-10-400.**

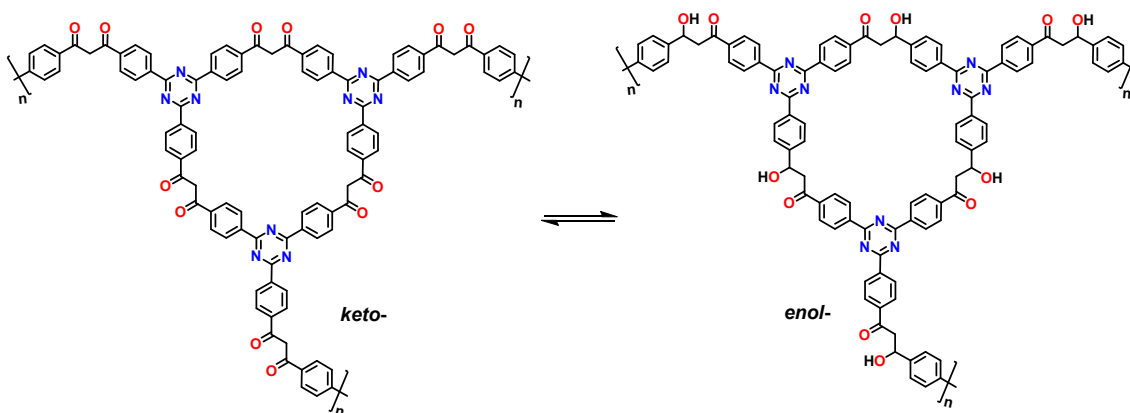
	acac-CTFs					V@acac-CTF	
Element	Calculated (%)	Found (%)				Calculated (%)	Found (%)
		5-400	10-400	5-500	10-500		10-400
C	74.44	83.256	80.231	82.501	83.619	59.87	65.670
H	3.68	2.923	2.678	1.449	1.125	4.11	2.756
N	10.21	5.442	3.908	<b>5.070</b>	4.227	6.35	3.028
O	11.67	3.225	4.929	<b>5.021</b>	4.395	18.13	16.273
C/N	7.290	15.298	20.529	16.272	19.550	9.428	21.687
C/O	6.378	25.518	16.227	16.431	19.550	3.302	4.035



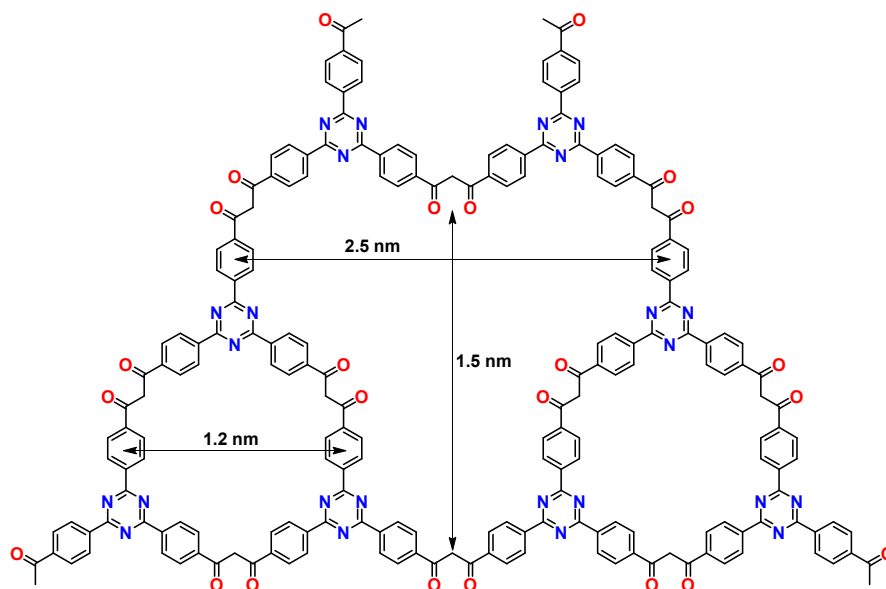
**Figure S1.** Powder X-ray diffraction (PXRD) spectra of acac-CTFs.



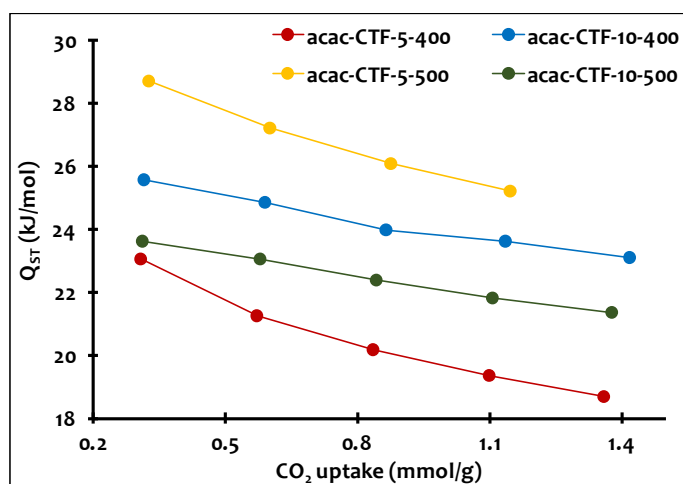
**Figure S2.** Thermogravimetric analysis spectra of acac-CTFs.



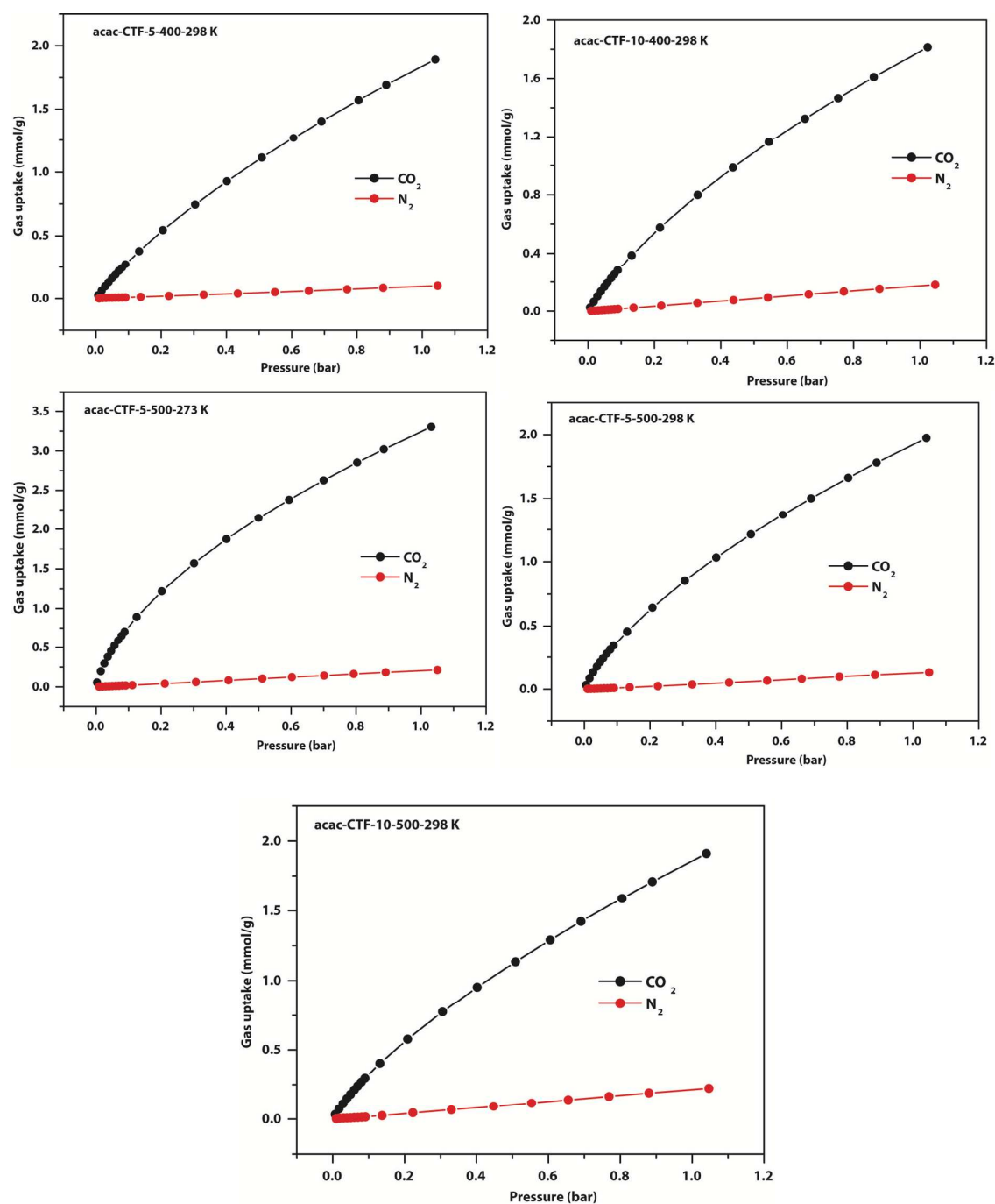
**Scheme S1.** Possible keto-enol tautomer formation during the CTF synthesis.



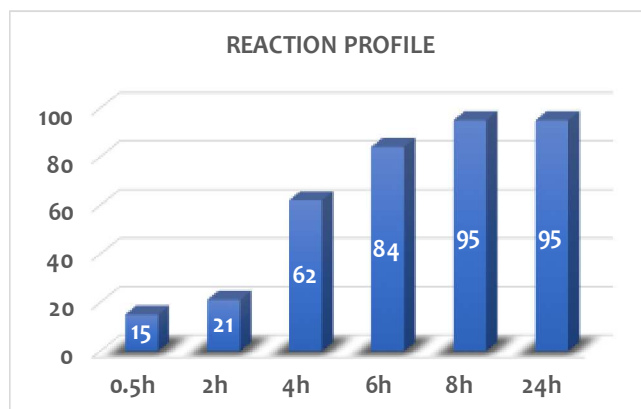
**Scheme S2.** Schematic representation of supermicropores (1.2 nm) and mesopores (2.5 nm) present in acac-CTF material.



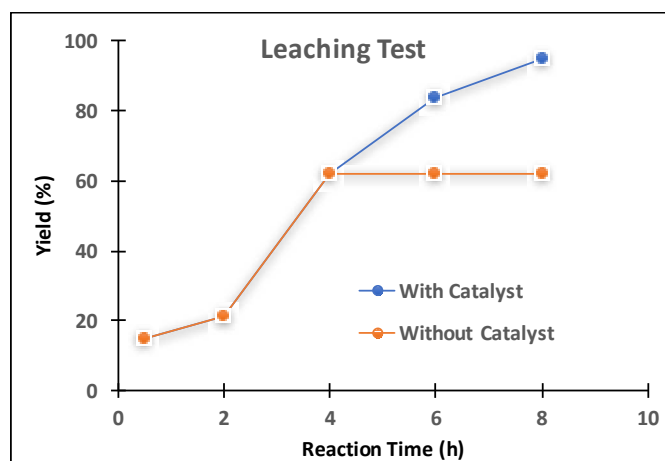
**Figure S3.** Isosteric heat ( $Q_{st}$ ) of CO<sub>2</sub> adsorption for all acac-CTFs.



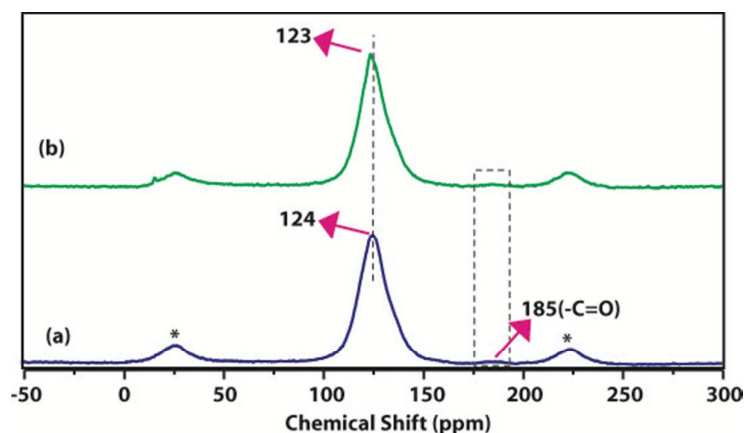
**Figure S4.** CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms of acac-CTFs measured at 298 K and 1 bar.



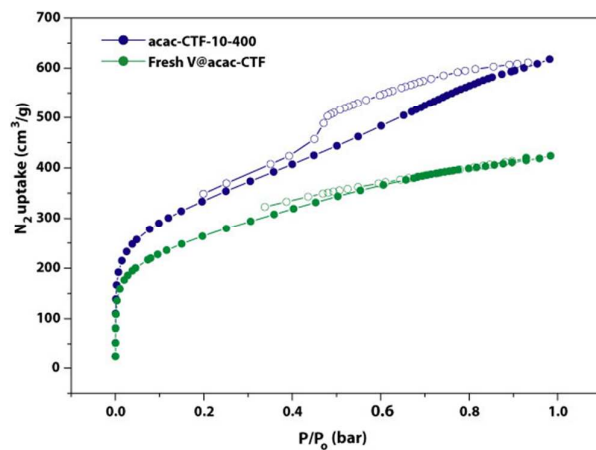
**Figure S5.** Time dependent yield of the modified Mannich reactions using V@acac-CTF catalyst (Yields are calculated using Mesitylene as internal standard).



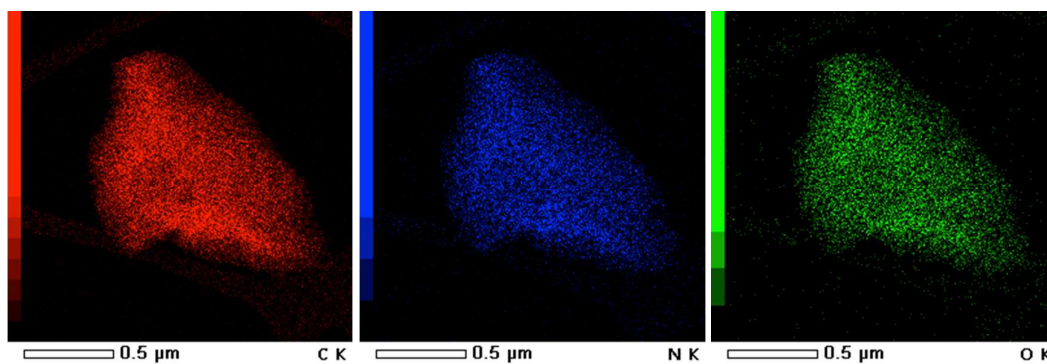
**Figure S6.** Reaction profile with or without the catalyst (after separating the catalyst from the reaction mixture via hot-filtration technique).



**Figure S7.**  $^{13}\text{C}$  CP-MAS ssNMR spectral comparison between pristine acac-CTF (a) and fresh V@acac-CTF catalyst (b).

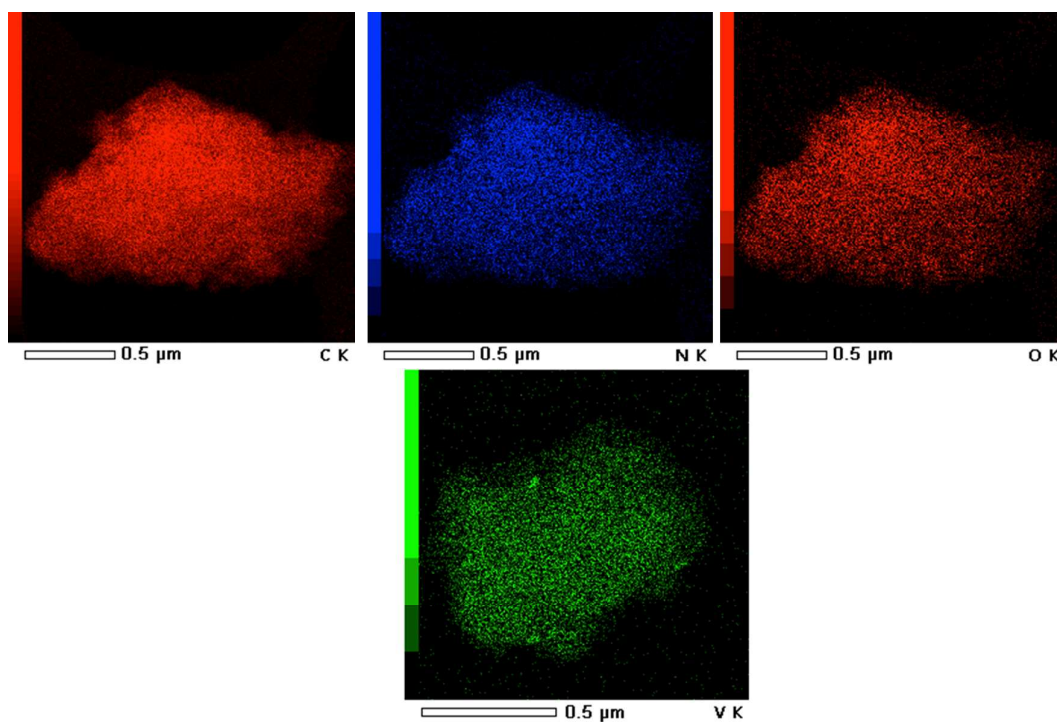


**Figure S8.** Nitrogen adsorption/desorption isotherms of acac-CTF, fresh V@acac-CTF and recovered V@acac-CTF measured at 77 K, filled and empty symbols represent adsorption and desorption, respectively.

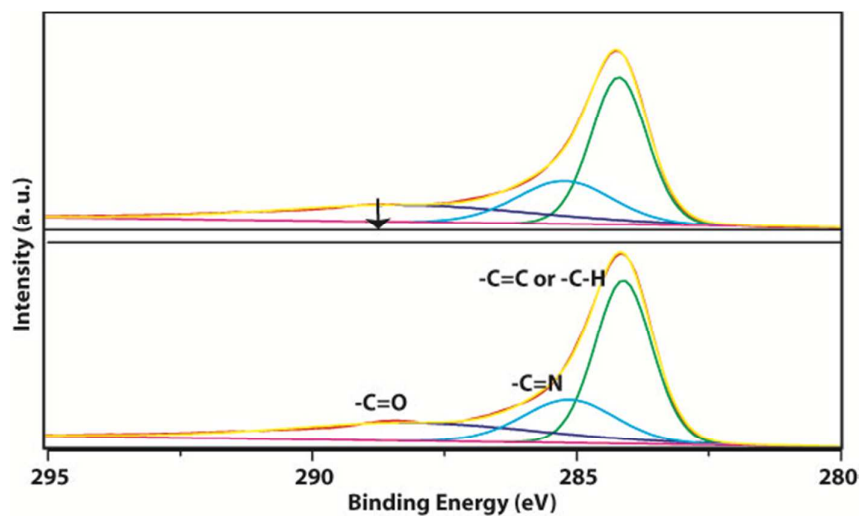


**Figure S9.** Bright-field scanning transmission electron microscopy of acac-CTF showing uniform distribution of C, N, O elements on the pristine acac-CTF.

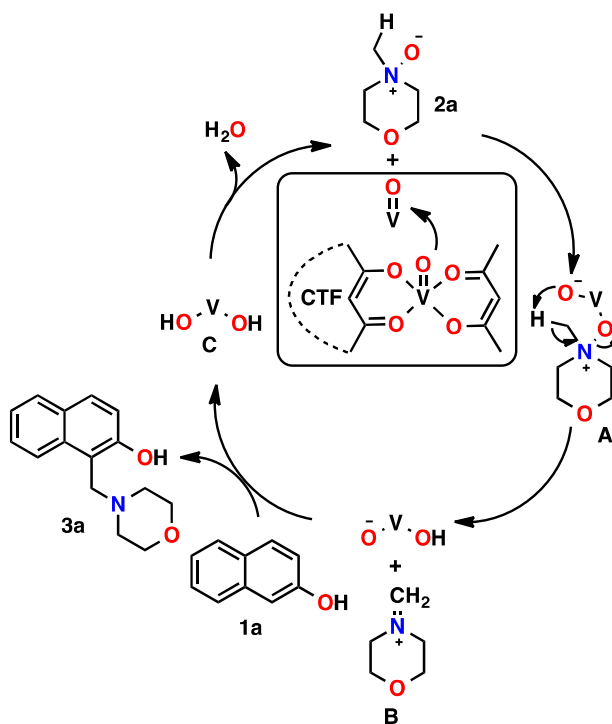




**Figure S10.** Bright-field scanning transmission electron microscopy of V@acac-CTF showing uniform distribution of C, N, O and V elements.



**Figure S11.** Deconvoluted XPS spectra of C 1s for (a) fresh V@acac-CTF catalyst (b) recovered V@acac-CTF catalyst after the five-catalytic cycle (c).

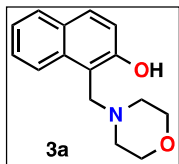


**Scheme S3.** Proposed mechanism of modified Mannich reaction.

#### General procedure for the modified Mannich reaction.

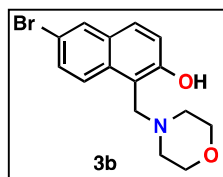
40 mg of V@acac-CTF, 2-naphthol (396 mg, 2.75 mmol) and NMO (322 mg, 22.75 mmol) were transferred to a schlenk flask and evacuated for 30 mins followed by Ar filling. To that 10 mL of dichloromethane (anhydrous) and mesitylene (0.382 mL, 2.75 mmol) were added and the mixture could stir at 40°C for 8 h. After the completion of reaction, the heterogeneous mixture could cool to room temperature. It gave a clear solution with black catalysts and the latter was filtered out. The solution was evaporated to dryness to afford pure Mannich base (**3a**) in quantitative yield. **3b-3i** were obtained by following same procedure. In some cases, where complete conversion was not obtained, the pure products were separated by column chromatography (hexane/ethylacetate (1:1) mixture).

#### 1-(morpholinomethyl)naphthalen-2-ol (**3a**):



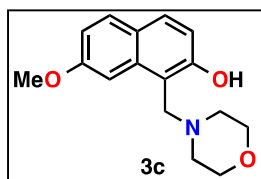
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.50-7.45 (m, 1H), 7.34-7.28 (m, 1H), 7.14 (d, *J* = 9.0 Hz, 1H), 4.16 (s, 2H), 3.8 (br, 4H), 2.68 (br, 4H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 156.1, 132.7, 129.4, 128.9, 128.6, 126.4, 122.5, 120.9, 119.0, 110.3, 66.9, 56.7, 53.1.

#### 6-bromo-1-(morpholinomethyl)naphthalen-2-ol (**3b**):



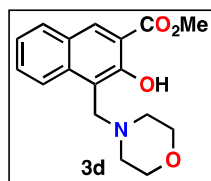
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* = 2.4 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.60 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 1H), 4.17 (s, 2H), 3.88 (br, 4H), 2.72 (br, 4H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 156.2, 132.4, 129.8, 129.19, 129.14, 126.2, 123.9, 123.66, 123.6, 111.6, 64.8, 53.3, 52.5.

**7-methoxy-1-(morpholinomethyl)naphthalen-2-ol (3c):**



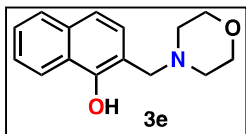
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (d,  $J$  = 8.6 Hz, 1H), 7.73 (d,  $J$  = 4.5 Hz, 1H), 7.69 (s, 1H), 7.19 (d,  $J$  = 2.7 Hz, 1H), 7.06 (d,  $J$  = 2.4 Hz, 1H), 4.17 (s, 2H), 4.01 (s, 3H), 3.90 (br, 4H), 2.76 (br, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.3, 156.7, 133.9, 130.4, 129.1, 123.9, 116.5, 114.2, 109.3, 100.7, 66.8, 56.9, 55.2, 53.1.

**Methyl 3-hydroxy-4-(morpholinomethyl)-2-naphthoate (3d):**



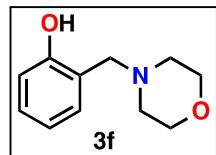
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.53 (s, 1H), 7.84 (d,  $J$  = 7.8 Hz, 1H), 7.73 (d,  $J$  = 8.4 Hz, 1H), 7.56-7.51 (m, 1H), 7.38-7.33 (m, 1H), 4.06 (s, 5H), 3.81-3.72 (m, 4H), 2.57-2.51 (m, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.0, 156.4, 131.2, 131.0, 130.7, 128.8, 127.9, 123.5, 122.8, 116.8, 114.9, 68.5, 53.2, 53.0, 51.0.

**2-(morpholinomethyl)naphthalen-1-ol (3e):**



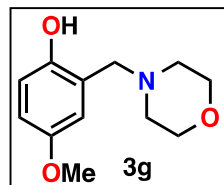
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30-8.26 (m, 1H), 7.76-7.74 (m, 1H), 7.49-7.43 (m, 2H), 7.30 (d,  $J$  = 8.2 Hz, 1H), 7.04 (d,  $J$  = 8.2 Hz, 1H), 4.02 (s, 2H), 3.80-3.76 (m, 4H), 2.56 (br, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 133.6, 127.2, 126.4, 125.7, 125.6, 124.5, 122.1, 118.2, 112.7, 66.4, 59.2, 54.5.

**2-(morpholinomethyl)phenol (3f):**



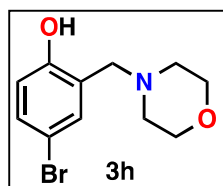
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18 (d,  $J$  = 8.2, 1H), 6.97 (t,  $J$  = 8.2 Hz, 1H), 6.82-6.79 (m, 1H), 6.76 (d,  $J$  = 7.6 Hz, 1H), 3.72 (s, 2H), 3.56 (br, 4H), 2.56 (br, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.2, 129.4, 128.6, 121.9, 120.1, 115.8, 66.8, 58.9, 54.9.

**4-methoxy-2-(morpholinomethyl)phenol (3g):**



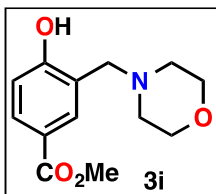
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.89 (d,  $J$  = 8.6 Hz, 1H), 6.84 (d,  $J$  = 7.4 Hz, 1H), 6.74 (d,  $J$  = 8.2 Hz, 1H), 3.74 (s, 2H), 3.54 (br, 4H), 2.48 (br, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 156.2, 124.2, 116.5, 114.6, 114.2, 66.4, 59.8, 54.2.

**4-bromo-2-(morpholinomethyl)phenol (3h)**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (s, 1H), 7.24 (d,  $J$  = 7.6 Hz, 1H), 6.72 (d,  $J$  = 8.4 Hz, 1H), 3.70 (s, 2H), 3.56 (br, 4H), 2.42 (br, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 132.4, 126.2, 122.8, 120.7, 112.2, 68.2, 57.8, 55.6.

**Methyl 4-hydroxy-3-(morpholinomethyl)benzoate (3i)**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (d,  $J$  = 8.2 Hz, 1H), 7.72 (d,  $J$  = 6.8 Hz, 1H), 7.42 (d,  $J$  = 8.2 Hz, 1H), 3.90 (s, 3H), 3.74 (s, 2H), 3.62 (br, 4H), 2.52 (br, 4H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.0, 162.6, 130.2, 128.4, 122.2, 122.2, 115.5, 66.4, 60.2, 55.6, 50.2.