

Supplementary Information

New Photocatalyst for Allylic aliphatic C-H Bond Activation and degradation of organic pollutants: Schiff's base Ti(IV) complexes

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Experimental

Spectral analysis of Ligands

3-(((2-mercapto-4,5-dimethylphenyl)imino)methyl)pyridine-2-thiol (MPPT)

The purify the material by recrystallized from methanol to get pure product (1.21 g) in 74% yield. Mp: 148 - 151 °C; ¹H-NMR (400 MHz, d₆-DMSO), δ (ppm): 9.13 (s, 1H, CH=N), 8.49 (s, 1H, CH=N), 8.24 – 7.21 (m, 7H, Ar-Hs), 5.89 (s, 1H, Pyridine-SH) and 3.16 (br, 1H, Ar-SH); ¹³C-NMR (100 MHz, CDCl₃) δ 181.82, 162.61, 153.39, 150.92, 144.56, 139.34, 138.12, 130.93, 128.76, 124.60, 121.07 and 117.19. HRMS (FAB+) cald. For C₁₂H₁₀N₂S₂: 246.3512 found: 246.36 (M⁺).

3-(((2-mercapto-4,5-dimethylphenyl)imino)methyl)pyridine-2-thiol (DMPMPT)

The crude material was triturated with 3:7 ratio of methanol and acetone to get pure product (1.25 g) in 79% yield. Mp: 176 - 178 °C; ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 8.87 (s, 1H, CH=N), 8.52 – 6.98 (m, 5H, Ar-Hs), 6.12 (s, 1H, Pyridine-SH), 3.46 (br, 1H, Ar-SH) and 2.54 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ 179.89, 163.31, 152.91, 150.41, 140.64, 136.83, 132.37, 129.66, 125.16, 123.02 and 22.21. HRMS (FAB+) cald. For C₁₄H₁₄N₂S₂: 274.4044 found: 274.41 (M⁺).

3-(((4,5-dichloro-2-mercaptophenyl)imino)methyl)pyridine-2-thiol (DCMPPT)

The crude product was triturated with 1:2 ratios of methanol and dichloromethane to get pure product (1.19 g) in 71% yield. Mp: 193 - 195 °C; ¹H-NMR (400 MHz, d₆-DMSO), δ (ppm): 13.06 (s, 1H, Pyridine-SH), 8.98 (s, 1H, CH=N), 8.61 – 7.27 (m, 5H, Ar-Hs) and 3.65 (br, 1H, Ar-SH); ¹³C-NMR (100 MHz, CDCl₃) δ 181.05, 161.89, 154.01, 152.65, 138.31, 134.08, 133.71, 128.44, 126.32, 124.24 and 121.96. HRMS (FAB+) cald. For C₁₄H₈Cl₂N₂S₂: 315.2413 found: 315.24 (M⁺).

3. Catalytic activity studies

General procedure for allylic oxidation, condensation, and cyclization

To a solution of Ti(IV) complex (1.25 μmol) and prop-1-en-1-ylbenzene (0.5 mmol) in 10 mL of 1:8 ratio of acetonitrile and water. After the reaction mixture stirred at ambient temperature for 1 h (reaction monitored through $^1\text{H-NMR}$) and added, 2-aminophenol (0.5 mmol) (monitored the reaction by TLC) solvent removed under reduced pressure. The residue was purified by recrystallization with ethanol to gave pure compound. All the products were characterized and shown supporting information.

Scheme 3

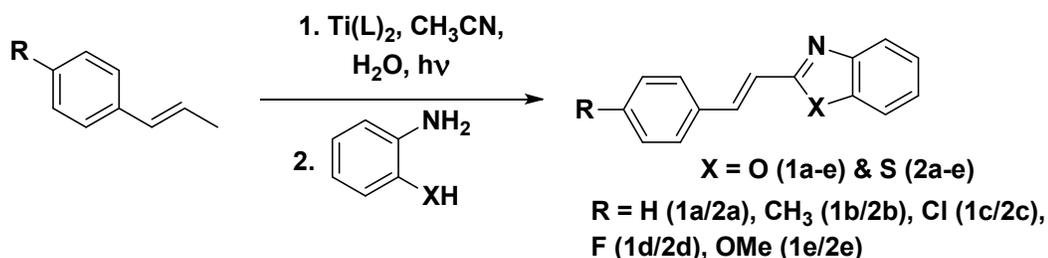
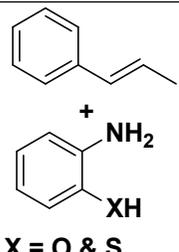
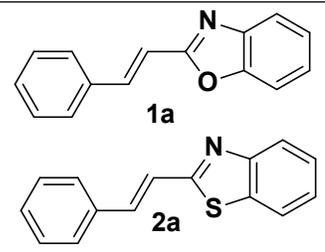
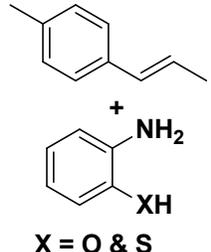
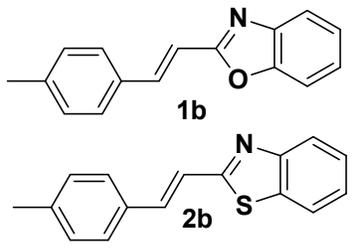
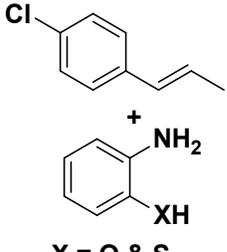
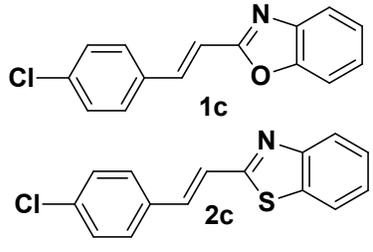
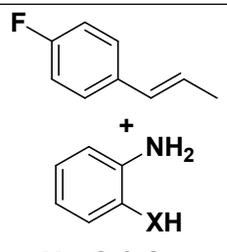
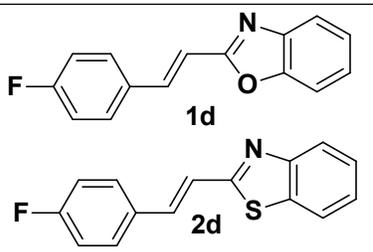
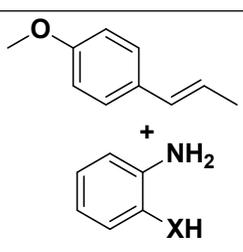
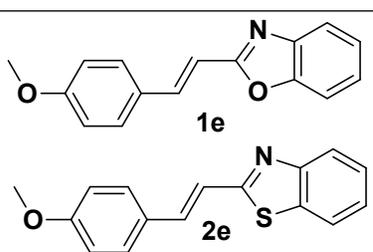


Table – S1: Photocatalytic oxidative cyclization in presence of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O

Substrate	Catalyst	Product	Yields (%)
 <p>X = O & S</p>	Ti(MPPT)O (C-1) Ti(DMPMPT)O (C-2) Ti(DCMPPT)O (C-3)	 <p>1a 2a</p>	88 (C-3) 63 (C-2) 79 (C-1) 89 (C-3) 71 (C-2) 83 (C-1)
 <p>X = O & S</p>	Ti(MPPT)O (C-1) Ti(DMPMPT)O (C-2) Ti(DCMPPT)O (C-3)	 <p>1b 2b</p>	85 (C-3) 61 (C-2) 68 (C-1) 83 (C-3) 69 (C-2) 71 (C-1)
 <p>X = O & S</p>	Ti(MPPT)O (C-1) Ti(DMPMPT)O (C-2) Ti(DCMPPT)O (C-3)	 <p>1c 2c</p>	90 (C-3) 79 (C-2) 88 (C-1) 92 (C-3) 73 (C-2) 87 (C-1)
 <p>X = O & S</p>	Ti(MPPT)O (C-1) Ti(DMPMPT)O (C-2) Ti(DCMPPT)O (C-3)	 <p>1d 2d</p>	92 (C-3) 79 (C-2) 84 (C-1) 91 (C-3) 69 (C-2) 83 (C-1)
 <p>X = O & S</p>	Ti(MPPT)O (C-1) Ti(DMPMPT)O (C-2) Ti(DCMPPT)O (C-3)	 <p>1e 2e</p>	84 (C-3) 59 (C-2) 62 (C-1) 88 (C-3) 56 (C-2) 64 (C-1)

Compound 1a: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 7.69 (m, 2H), 7.49 – 7.44 (m, 3H), 7.26 – 7.21 (m, 4H), 7.15 (d, 8Hz, 1H) and 7.09 (d, 7.6 Hz, 1H); HRMS (FAB+) cald. For $\text{C}_{15}\text{H}_{11}\text{NO}$: 221.254 found: 222.26 ($\text{M}^+ + 1$).

Compound 2a: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 8.23 (m, 1H), 7.89 – 7.83 (m, 2H), 7.48 (m, 4H), 7.25 (m, 2H) 7.04 (d, 8 Hz, 1H) and 6.82 (d, 7.8 Hz, 1H); HRMS (FAB+) cald. For $\text{C}_{15}\text{H}_{11}\text{NS}$: 237.3195 found: 238.32 ($\text{M}^+ + 1$).

Compound 1b: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 7.82 (m, 2H), 7.61 (m, 2H), 7.41 (m, 2H), 7.21 (m, 2H), 7.11 (d, 6.8 Hz, 1H), 6.92 (d, 7.1 Hz, 1H) and 2.48 (s, 3H); HRMS (FAB+) cald. For $\text{C}_{16}\text{H}_{13}\text{NO}$: 235.2805 found: 236.28 ($\text{M}^+ + 1$).

Compound 2b: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 8.19 (m, 1H), 7.93 (m, 1H), 7.56 – 7.49 (m, 4H), 7.28 (m, 2H), 7.11 (d, 5.8 Hz, 1H), 6.93 (d, 6.2 Hz, 1H) and 2.39 (s, 3H); HRMS (FAB+) cald. For $\text{C}_{16}\text{H}_{13}\text{NS}$: 251.3461 found: 252.35 ($\text{M}^+ + 1$).

Compound 1c: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 7.78 – 7.71 (m, 4H), 7.51 -7.46 (m, 4H), 7.16 (d, 11.2 Hz, 1H) and 7.06 (d, 10.8 Hz, 1H); HRMS (FAB+) cald. For $\text{C}_{15}\text{H}_{10}\text{ClNO}$: 255.699, found: 256.7 ($\text{M}^+ + 1$).

Compound 2c: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 8.17 (m, 1H), 8.06 (m, 1H), 7.63 (m, 2H), 7.58 – 7.51 (m, 4H), 7.12 (d, 8 Hz, 1H) and 7.07 (d, 7.4 Hz, 1H); HRMS (FAB+) cald. For $\text{C}_{15}\text{H}_{10}\text{ClNS}$: 271.7646, found: 272.77 ($\text{M}^+ + 1$).

Compound 1d: $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$), δ (ppm): 7.81 -7.78 (m, 4H), 7.46 (m, 2H), 7.29 (m, 2H), 7.08 (d, 10 Hz, 1H) and 6.99 (d, 9.4 Hz, 1H); HRMS (FAB+) cald. For $\text{C}_{15}\text{H}_{10}\text{FNO}$: 239.2444 found: 240.25 ($\text{M}^+ + 1$).

Compound 2d: ¹H-NMR (400 MHz, d₆-DMSO), δ (ppm): 8.12 (m, 1H), 7.88 (m, 1H), 7.76 (m, 2H), 7.52 (m, 2H), 7.21 (m, 2H), 7.09 (d, 8 Hz, 1H) and 6.95 (d, 7.6 Hz, 1H); HRMS (FAB+) cald. For C₁₅H₁₀FNS: 255.35 found: 256.35 (M⁺+1).

Compound 1e: ¹H-NMR (400 MHz, d₆-DMSO), δ (ppm): 7.86 (m, 2H), 7.59 (m, 2H), 7.43 (m, 2H), 7.08 (d, 8 Hz, 1H), 7.01 (d, 7.4 Hz, 1H) and 6.96 (m, 2H); HRMS (FAB+) cald. For C₁₆H₁₃NO₂: 251.0946, found: 252.095 (M⁺+1).

Compound 2e: ¹H-NMR (400 MHz, d₆-DMSO), δ (ppm): 8.21 (m, 1H), 7.96 (m, 1H), 7.64 – 7.58 (m, 4H), 7.06 (d, 11.8 Hz, 1H), 6.98 (d, 11.2 Hz, 1H), 6.92 (m, 2H) and 4.09 (s, 3H); HRMS (FAB+) cald. For C₁₆H₁₃NOS: 267.3455 found: 268.35 (M⁺+1).

Photocatalytic studies

The photocatalytic activity of all the complexes evaluated by degradation of Methylene blue (MB) and 4-dichlorophenol (2,4-DCP) using HEBER Visible Annular Type Photoreactor, model HVAR1234 (Haber Scientific, India) under visible light irradiation using 300 W tungsten lamp as a light source ($380\text{nm} \leq \lambda \leq 840\text{nm}$). In a general process, 100 mL of aqueous methylene blue solution (initial concentration, $C_0 = 5 \times 10^{-5} \text{ mol L}^{-1}$) was stirred with 0.05 g of catalyst individually in a cylindrical-shaped glass reactor at ambient temperature in air. The mixture was stirred in the dark for an hour at lower than the ambient temperature to form adsorption - desorption equilibrium. Then the solution was manifest to light with constant stirring. At fixed 20 min intervals, about 3 - 5 mL of solutions collected and centrifuged to remove the catalyst particles. The variation in the concentration of MB was obtained by recording the absorbance at 664 nm respectively using a UV-Vis spectrophotometer.

The fabrication of •OH radicals during photocatalysis under visible light irradiation followed by the measurement of fluorescence intensity as reported terephthalic acid (TA) probe.

The photo-generated $\bullet\text{OH}$ radicals attacked TA to form 2-hydroxyterephthalic acid (TAOH), which shows a characteristic fluorescence band centered at 425 nm. The increase in the fluorescence intensity is directly proportional to the concentration of photo-generated $\bullet\text{OH}$ radicals. The excitation wavelength fixed at 320 nm.