Supplementary Information (SI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2025

Brønsted Basic TMMM-Hydrotrope Combined Catalytic System for Synthesis of Diverse Dihydropyranochromenes in Water at Ambient Temperature

Archana Rajmane^{a*}, Aishwarya Jadhav^a, Nita Patil^b, Arjun Kumbhar^{a*}

^aDepartment of Chemistry, Vivekanand College, Kolhapur (Empowered Autonomous), Maharashtra, 416003, India

^bNational Chemical Laboratory, CSIR, Pune, Maharashtra, 411008, India

Email: archanarajmane1396@rediffmail.com

- 1. General Remarks
- 2. General procedure for the synthesis of Tris(bromomethyl)mesitylene (TBMM)
- 3. General procedure for the synthesis of Tris(morpholinomethyl)mesitylene (TMMM)
- 4. General procedure for the synthesis of Dihydropyrano[3,2-*b*]pyrans
- 5. General procedure for the synthesis of Dihydropyrano[3,2-c]chromenes
- 6. General procedure for the synthesis of 2-Amino-4H-benzo[b]pyrans
- 7. General procedure for the synthesis of 2-Aminobenzochromene
- 8. Spectral Data of Tris(morpholinomethyl)mesitylene (TMMM)
- 9. Spectral Data of Chromenes Derivatives

10. Spectra of Synthesized Compounds

1. General Remarks: All reactions were carried out in a round-bottom flask at RT. Chemical reagents and anhydrous solvents were purchased from commercial suppliers (TCI and Sigma-Aldrich chemical companies) and used as purchased. Thin layer chromatography (TLC) was performed using silica gel pre-coated aluminium plates, visualized with UV light at 254 nm or under iodine. ¹H NMR and ¹³C NMR were recorded with Bruker (400, and 600 Mz) spectrometers using CDCl₃ and DMSO solvents Chemical shifts for ¹H NMR are referred to as internal TMS (0 ppm), and chemical shifts for ¹³C NMR are referenced to the carbon resonance of the solvent (CDCl₃: δ 77.0 ppm). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. General procedure for the synthesis of Tris(bromomethyl)mesitylene (TBMM): In a

round bottom flask, a solution of mesitylene (0.10 mol), paraformaldehyde (0.33 mol), and 31 % HBr in acetic acid (70 mL) was stirred in acetic acid (20 mL) at 90°C for 12 h. After completion of the reaction as analyzed by TLC, the reaction mixture was added to ice-cold water. The obtained white precipitate was filtered, washed with cold water (3×100 mL), and dried in a

vacuum to afford TBMM with 97% yield.

3. General procedure for the synthesis of Tris(morpholinomethyl)mesitylene (TMMM): A round bottom flask containing a solution of TBMM (1 mmol), K_2CO_3 (4 mmol), and morpholine (3.2 mmol) in MeCN (5 mL) was stirred at RT for 48 h. After completion of the reaction as analyzed by TLC, the reaction mixture was added to ice-cold water. The obtained white precipitate was filtered, washed with water (3×50 mL), and dried in a vacuum with to yield the TMMM with 94% yield.

4. General procedure for the synthesis of Dihydropyrano[3,2-*b*]pyrans: In a round-bottom flask containing 40% aqueous NaPTS solution (5 mL), was added TMMM (5 mol%), substituted aromatic aldehyde (1 mmol), malononitrile (1 mmol) and Kojic acid (1 mmol). The resulting reaction mixture was stirred at RT. After completion of the reaction as analyzed by TLC, the solid precipitate was filtered, washed with water (3 x 5 mL), and dried in an oven. The crude product was recrystallized by hot ethanol.

5. General procedure for the synthesis of Dihydropyrano[3,2-*c*]chromenes: In a roundbottom flask containing 40% aqueous NaPTS solution (5 mL), was added TMMM (5 mol%), substituted aromatic aldehyde (1 mmol), malononitrile (1 mmol) and 4-hydroxycoumarin (1 mmol). The resulting reaction mixture was stirred at RT. After completion of the reaction as analyzed by TLC, the solid precipitate was filtered, washed with water (3 x 5 mL), and dried in an oven. The crude product was recrystallized by hot ethanol.

6. General procedure for the synthesis of 2-Amino-4*H*-benzo[*b*]pyrans: In a round-bottom flask containing 40% aqueous NaPTS solution (5 mL), was added TMMM (5 mol%), substituted aromatic aldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol). The resulting reaction mixture was stirred at RT. After completion of the reaction as analyzed by TLC, the solid precipitate was filtered, washed with water (3 x 5 mL), and dried in an oven. The crude product was recrystallized by hot ethanol.

7. General procedure for the 2-Aminobenzochromene: In a round-bottom flask containing 40% aqueous NaPTS solution (5 mL), TMMM (5 mol%), substituted aromatic aldehyde (1 mmol), malononitrile (1 mmol) and Lawsone (1 mmol) was added. The resulting reaction mixture was stirred at 80°C. After completion of the reaction as analyzed by TLC, the solid precipitate was filtered, washed with water (3 x 5 mL), and dried in an oven. The crude product was recrystallized by hot ethanol.

8. Spectral Data of Tris(morpholinomethyl)mesitylene (TMMM): ¹H NMR (CDCl₃, 600 MHz): δ(ppm) 2.43 (s, 9H), 2.46 (t, 12H), 3.55 (s, 6H), 3.63 (t, 12H); ¹³C NMR (CDCl₃, 151 MHz): δ (ppm) 16.52, 53.31, 56.87, 67.42, 132.26, 137.98.

9. Spectral data of Dihydropyrano chromenes:

- Compound 4a:¹H NMR (DMSO-d₆, 400 MHz): δ(ppm) 4.06-4.14 (m, 2H), 5.08 (s, 1H), 5.60 (s, 1H), 6.29 (s, 1H), 7.33 (s, 2H), 7.66 (t, 1H), 7.77 (d, *J*= 7.8 Hz, 1H), 8.12-8.16 (m, 2H); ¹³C NMR (DMSO-d6, 100 MHz): δ(ppm) 55.1, 59.6, 112.7, 119.7,123.0,123.7,131.5,134.8, 137.4,143.3,148.5,160.0,169.2,169.8.
- Compound 4b:¹H NMR (DMSO-d6, 600 MHz):δ(ppm) 4.14-4.29 (m, 2H), 4.88 (s, 1H), 5.69 (t, 1H), 6.36 (s, 1H), 729 (s, 2H), 7.35 (d, *J*= 8.3, 2H), 7.48 (d, *J*= 8.3, 2H); ¹³C NMR (DMSO-d6, 101 MHz): δ (ppm) 55.9, 59.7, 111.7, 119.9, 129.5, 130.1, 132.6, 133.1, 137.0, 140.3, 149.0, 159.8, 160.5, 168.8, 170.1.
- Compound 4e:¹H NMR (DMSO-d6, 400 MHz):δ(ppm) 3.75 (s, 3H), 4.10-4.25 (m, 2H),
 4.73 (s, 1H), 5.68 (t, 1H), 6.33 (s, 1H), 6.94 (d, *J*= 7.8 Hz, 2H), 7.18-7.22 (m, 4H);¹³C NMR (DMSO-d6, 100 MHz):δ(ppm) 55.3, 56.6, 59.7, 77.2, 112.0, 114.7, 116.6, 119.8,
 129.3, 133.2, 133.8, 136.7, 159.54, 159.3, 159.4, 168.4, 170.0.
- 4. Compound 4g:¹H NMR (DMSO-d6, 500 MHz):δ(ppm) 4.12-4.23 (m, 2H), 4.85 (s, 1H), 6.34 (s, 1H), 7.26-7.29 (m, 4H), 7.59 (d, *J*= 8.4 Hz, 2H), 7.87 (s, 1H); ¹³C NMR (DMSO-d6, 125 MHz):δ(ppm) 55.6, 59.8, 82.4, 111.9, 118.9, 121.7, 130.4, 132.5, 132.9, 136.7, 140.5, 148.7. 160.0, 160.7, 168.7, 170.0.
- Compound 4h:¹H NMR (DMSO-d6, 400 MHz):δ(ppm) 3.76 (s, , 3H), 4.20 (m, 2H), 4.67 (s, 1H), 5.68 (t, *J*= 6.1, 1H), 6.33 (s, 1H), 6.66 (d, *J*= 9.8, 1H), 6.77-6.83 (m, 3H), 7.16 (s, 2H), 9.06 (s, 1H); ¹³C NMR (DMSO-d6, 101 MHz):δ(ppm) 55.65, 56.01, 60.03, 111.78, 120.30, 116.22, 120.26, 120.63, 131.94, 136.32, 146.97, 148.38, 149.88, 159.68, 168.54, 169.94.
- 6. Compound 6a: ¹H NMR (DMSO-d6, 600 MHz):δ (ppm): 4.66 (s, 1H), 7.45-7.53 (m, 4H), 7.58 (d, J= 8.7, 2H), 7.72 (t, J= 7.8, 1H), 7.90 (d, J= 7.4, 1H), 8.16 (d, J= 8.7, 2H);
 ¹³C NMR (d6-DMSO, 151 MHz):δ (ppm) 56.99, 103.47, 113.85, 117.18, 119.40, 124.80, 125.50, 129.55, 130.10, 133.71, 147.05, 151.10, 152.62, 154.03, 159.25, 159.80.
- 7. Compound 6b:¹H NMR (DMSO-d6, 400 MHz):δ(ppm) 4.49 (s, 1H), 7.31 (d, J= 8.5, 2H), 7.37 (d, J= 8.4, 2H), 7.44-7.52 (m, 4H), 7.72 (t, J= 8.4, 1H), 7.90 (d, J= 6.9, 1H);
 ¹³C NMR (d6-DMSO, 101 MHz):δ (ppm): 36.95, 57.87, 103.97, 113.59, 117.07, 119.54, 123.17, 125.26, 128.89, 130.11, 132.40, 133.50, 142.92, 152.67, 154.19, 158.52, 159.89.

- 8. Compound 6d:¹H NMR (DMSO-d6, 400 MHz):δ (ppm) 4.51 (s, 1H), 7.29 (d, J= 5.1 Hz, 2H), 7.44-7.52 (m, 6H), 7.72 (t, J= 8.4 Hz, 1H), 7.90 (d, J= 7.0 Hz, 1H); ¹³C NMR (d6-DMSO, 101 MHz):δ (ppm) 37.36, 57.82, 103.68, 117.18, 119.66, 125.27, 127.49, 130.63, 130.75, 131.18, 133.68, 146.57, 152.94, 154.36, 158.53, 159.96.
- 9. Compound 6e: ¹H NMR (DMSO-d6 400 MHz):δ (ppm) 3.72 (s,3H), 4.40 (s, 1H), 6.87 (d, J= 8.0 Hz, 2H), 7.18 (d, J= 8.0 Hz, 2H), 7.36 (s, 2H), 7.43-7.50 (m, 2H), 7.69 (t, J= 7.3 Hz, 1H), 7.90 (d, J= 7.5 Hz, 1H); ¹³C NMR (d6-DMSO, 101 MHz):δ(ppm) 36.78, 55.51, 58.70, 105.00, 113.47, 114.49, 117.00, 119.63, 122.91, 125.24, 129.32, 133.30, 135.94, 152.73, 153.73, 158.38, 158.68, 159.98.
- 10. Compound 6h: ¹H NMR (DMSO-d6, 600 MHz):δ (ppm) 2.91 (s, 6H), 4.37 (s, 1H), 6.71 (d, J= 8.6 Hz, 2H), 7.10 (d, J= 8.7 Hz, 2H), 7.36 (s, 2H), 7.50-7.55 (m, 2H), 7.75 (t, J= 8.5 Hz, 1H), 7.95 (d, J= 8.0 Hz, 1H); ¹³C NMR (d6-DMSO, 100 MHz):δ (ppm) 54.85, 58.51, 103.89, 112.03, 112.76, 115.34, 118.99, 122.03, 123.79, 127.50, 130.50, 131.92, 149.29, 151.54, 152.54, 157.39, 159.27
- 11. Compound 6i:¹H NMR (DMSO-d6, 600 MHz):δ(ppm) 3.68 (s, 3H), 4.31 (s, 1H), 6.57 (d, *J*= 8.0 Hz, 1H), 6.66 (d, *J*= 8.0 Hz, 1H), 6.77 (s, 1H), 7. 27 (s, 2H), 7.38-7.43 (m, 2H), 7.64 (t, *J*= 7.7 Hz, 1H), 7.84 (d, *J*= 7.8 Hz, 1H), 8.87 (s, 1H); ¹³C NMR (d6-DMSO, 100 MHz):δ (ppm) 37.00, 55.57, 58.89, 104.98, 112.37, 113.12, 116.05, 117.16, 119.73, 120.09, 123.47, 124.89, 133.02, 134.85, 145.93, 147.85, 152.60, 153.67, 158.45, 160.36
- Compound 6j:¹H NMR (DMSO-d6, 600 MHz):δ(ppm) 4.58 (s, 1H), 7.45-7.50 (m, 6H),
 7.71 (t, *J*= 7.9 Hz, 1H), 7.77 (d, *J*= 8.3 Hz, 2H), 7.89 (d, *J*= 9.0 Hz, 1H); ¹³C NMR (d6-DMSO, 151 MHz):δ(ppm) 37.42, 57.62, 103.39, 110.24, 113.21, 117.03, 118.55, 119.40,
 122.40, 124.73, 129.18, 132.78, 133.64, 149.32, 152.33, 154.12, 158.33, 160.06
- 13. Compound 6k:¹H NMR (DMSO-d6, 400 MHz):δ(ppm) 1.11 (s, 3H), 4.01 (q, 2H), 4.83 (s, 1H), 7.45-7.56 (m, 4H), 7.72 (t, *J*= 7.5 Hz, 1H), 7.97-8.01 (m, 3H), 8.13 (d, *J*= 8.4 Hz, 3H); ¹³C NMR (d6-DMSO, 100 MHz):δ (ppm) 14.50, 36.24, 59.86, 76.15, 105.84, 113.49, 117.06, 123.24, 123.47, 124.74, 125.40, 129.92, 132.11, 133.43, 146.44, 152.71, 154.02, 158.97, 160.31, 167.71
- 14. Compound 8a:¹H NMR (CDCl₃, 200 MHz):δ (ppm) 0.99 (s, 3H), 1.06 (s, 3H), 2.17 (s, 2H), 2.40 (s, 2H), 4.35 (s, 1H), 4.53 (s, 2H), 7.18-7.28 (m, 5H) ¹³C NMR (50 MHz, CDCl₃):δ(ppm) 26.85, 28.40, 31.74, 35.10, 40.28, 50.38, 126.70, 127.71, 128.26, 142.31, 157.30, 161.23, 195.36
- 15. Compound 8b:¹H NMR (DMSO-d6, 400 MHz):δ(ppm) 0.96 (s, 3H), 1.05 (s, 3H), 2.15 (dd, J= 35.3, 16.3 Hz, 2H), 2.17 (s, 2H), 4.40 (s, 1H), 6.07 (s, 2H), 7.36 (d, J= 8.4 Hz, 2H)

2H), 8.07 (d, *J*= 8.4 Hz, 2H); ¹³C NMR (d6-DMSO, 101 MHz):δ(ppm): 27.96, 29.55, 32.70, 37.04, 51.62, 59.98, 113.12, 119.96, 124.65, 129.63, 147.34, 151.98, 159.13, 163.16, 196.45

- 16. Compound 8d: ¹H NMR (CDCl₃, 400 MHz):δ(ppm) 1.03 (s, 3H), 1.11 (s, 3H), 2.17 (dd, J= 35.3, 16.3 Hz, 2H), 2.28 (s, 3H), 2.95 (s, 2H), 4.28 (s, 1H), 5.88 (s, 2H), 7.05-7.10 (m, 4H); ¹³C NMR (101 MHz, CDCl₃):δ(ppm) 20.58, 26.61, 28.08, 31.42, 34.51, 49.86, 59.89, 112.93, 119.25, 126.54, 128.25, 135.61, 140.47, 158.05, 161.35, 194.96
- 17. Compound 8g: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 0.89 (s, 3H), 0.97 (s, 3H), 2.17 (dd, J= 52.2, 16.1 Hz, 2H), 2.43 (d, 4H), 3.25 (s, 1H), 4.00 (s, 1H), 7.02 (s, 2H), 7.10 (d, 1H), 7.18-7.24 (m, 2H), 7.32 (d, J= 7.9, Hz, 1H); ¹³C NMR (d6-DMSO, 101 MHz):δ(ppm) 27.26, 28.72, 32.61, 35.72, 50.58, 58.04, 112.44, 119.89, 122.13, 126.84, 129.99, 130.63, 131.21, 148.20, 159.33, 163.50, 196.10
- 18. Compound 8j: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 0.90 (s, 3H), 0.97 (s, 3H), 2.16 (dd, *J*= 59.3, 16.1 Hz, 2H), 2.37-2.48 (m, 3H), 3.64 (s, 3H), 4.01 (s, 1H), 6.45 (d, dd, *J*= 9.6 Hz, 1H), 6.58-6.61 (m, 2H), 6.83 (s, 2H), 8.71 (s,1H); ¹³C NMR (d6-DMSO, 101 MHz) δ (ppm): 27.23, 29.15, 32.22, 35.73, 50.51, 55.96, 59.30, 112.03, 113.64, 115.90, 119.65, 120.49, 136.37, 136.58, 145.72, 147.78, 158.89, 162.63, 196.30
- 19. Compound 8k: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 0.90 (s, 3H), 1.05-1.10 (m, 6H), 2.26 (dd, J= 59.3, 16.1 Hz, 2H), 2.47-2.61 (m, 3H), 3.33 (s, 1H), 3.94 (q, 2H), 4.62 (s, 1H), 7.42 (d, J= 8.5, 2H), 7.70 (s, 2H), 8.10 (d, J= 8.5, 2H); ¹³C NMR (d6-DMSO, 101 MHz):δ(ppm) 14.40, 26.66, 29.13, 32.61, 34.52, 50.38, 59.52, 76.87, 114.71, 129.76, 129.58, 146.50, 154.56, 163.50, 168.05, 196.36
- 20. Compound 8I: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 0.89 (s, 3H), 1.04 (s, 3H), 1.08 (t, 3H), 2.24 (dd, J= 59.3, 16.1 Hz, 1H), 2.44-2.58 (m, 3H), 3.33 (s, 1H), 3.94 (q, 2H), 4.49 (s, 1H), 7.15 (d, J= 8.4 Hz, 2H), 7.25 (d, J= 8.5 Hz, 2H), 7.59 (s, 2H); ¹³C NMR (d6-DMSO, 101 MHz):δ (ppm) 14.67, 27.07, 29.07, 32.33, 33.68, 59.39, 77.65, 115.69, 128.13, 130.21, 130.98, 145.71, 159.96, 162.88, 168.26, 196.15
- 21. Compound 10a: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 4.87 (s, 1H), 7.49 (s, 2H), 7.67 (d, J= 8.7 Hz, 2H), 7.82-7.95 (m, 3H), 8.10 (d, J= 7.7 Hz, 1H), 8.19 (d, J= 8.7 Hz, 2H), ; ¹³C NMR (d6-DMSO, 100 MHz):δ(ppm) 36.70, 57.37, 119.50, 121.08, 124.37, 126.34, 126.80, 129.67, 131.34, 131.60, 134.69, 135.09, 147.14, 149.99, 151.54, 159.02, 177.71, 182.44
- **22.** Compound 10c: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 4.65 (s, 1H), 7.28 (t, *J*= 7.8 Hz, 1H), 7.35-7.38 (m, 2H), 7.43 (d, *J*= 7.8 Hz, 1H), 7.55 (t, *J*= 1.7 Hz, 3H), 8.83-8.90

(m, 3H), 8.06 (dd, *J*= 6.1, 2.6 Hz, 1H); ¹³C NMR (d6-DMSO, 100 MHz):δ(ppm) 36.73, 57.60, 119.63, 121.38, 122.47, 126.28, 126.52, 127.48, 130.49, 130.86, 131.17, 131.24, 131.48, 134.61, 134.94, 147.09, 149.93, 158.79, 177.33, 183.24

23. Compound 10k: ¹H NMR (d6-DMSO, 400 MHz):δ(ppm) 1.13 (t, 3H), 4.01 (q, 2H), 5.01 (s, 1H), 7.56 (d, J= 8.6 Hz, 2H), 7.84-7.89 (m, 3H), 7.97-8.05 (m, 1H), 8.12 (d, J= 8.6 Hz, 2H) ; ¹³C NMR (d6-DMSO, 100 MHz):δ(ppm) 14.50, 35.56, 59.69, 76.16, 115.44, 123.71, 124.73, 126.31, 130.19, 131.45, 132.13, 134.99, 137.75, 146.67, 149.48, 152.97, 159.46, 167.94, 177.66, 188.33

10. NMR spectra of synthesized compounds



Fig. 2: ¹³C NMR spectrum of TMMM



Fig. 4: ¹³C NMR spectrum of compound 4a







Fig. 8: ¹³C NMR spectrum of compound 4e



Fig. 10: ¹³C NMR spectrum of compound 4g



Fig. 12: ¹³C NMR spectrum of compound 4h



Fig. 14: ¹³C NMR spectrum of compound 6a



Fig. 16: ¹³C NMR spectrum of compound 6b



Fig. 18: ¹³C NMR spectrum of compound 6d

Fig. 20: ¹³C NMR spectrum of compound 6e

Fig. 22: ¹³C NMR spectrum of compound 6h

Fig. 24: ¹³C NMR spectrum of compound 6i

6]

Fig. 28: ¹H NMR spectrum of compound 6k

-4.55

-2.40

~1.06

8a

7.28 7.24 7.19 7.18

Fig. 30: ¹³C NMR spectrum of compound 8a

Fig. 32: ¹H NMR spectrum of compound 8b

8d

Fig. 34: ¹³C NMR spectrum of compound 8d

Fig. 36: ¹H NMR spectrum of compound 8g

Fig. 38: ¹³C NMR spectrum of compound 8j

Fig. 40: ¹³C NMR spectrum of compound 8k

Fig. 42: ¹³C NMR spectrum of compound 81

Fig. 44: ¹³C NMR spectrum of compound 10a

Fig. 46: ¹H NMR spectrum of compound 10c

Fig. 48: ¹³C NMR spectrum of compound 10k