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

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- 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. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded with Bruker (400, and 600 Mz) spectrometers using CDCl<sub>3</sub> and DMSO solvents Chemical shifts for <sup>1</sup>H NMR are referred to as internal TMS (0 ppm), and chemical shifts for <sup>13</sup>C NMR are referenced to the carbon resonance of the solvent (CDCl<sub>3</sub>:  $\delta$  77.0 ppm). Data are reported as follows: chemical shift ( $\delta$  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): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ(ppm) 2.43 (s, 9H), 2.46 (t, 12H), 3.55 (s, 6H), 3.63 (t, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 151 MHz): δ (ppm) 16.52, 53.31, 56.87, 67.42, 132.26, 137.98.

## 9. Spectral data of Dihydropyrano chromenes:

- Compound 4a:<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 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); <sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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:<sup>1</sup>H 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);<sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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);
  <sup>13</sup>C 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:<sup>1</sup>H 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);
  <sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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); <sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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:<sup>1</sup>H 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); <sup>13</sup>C 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:<sup>1</sup>H NMR (CDCl<sub>3</sub>, 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) <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):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:<sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):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: <sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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), ; <sup>13</sup>C 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: <sup>1</sup>H 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); <sup>13</sup>C 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: <sup>1</sup>H 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) ; <sup>13</sup>C 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: <sup>13</sup>C NMR spectrum of TMMM



Fig. 4: <sup>13</sup>C NMR spectrum of compound 4a







Fig. 8: <sup>13</sup>C NMR spectrum of compound 4e



Fig. 10: <sup>13</sup>C NMR spectrum of compound 4g



Fig. 12: <sup>13</sup>C NMR spectrum of compound 4h



Fig. 14: <sup>13</sup>C NMR spectrum of compound 6a



Fig. 16: <sup>13</sup>C NMR spectrum of compound 6b



Fig. 18: <sup>13</sup>C NMR spectrum of compound 6d



Fig. 20: <sup>13</sup>C NMR spectrum of compound 6e



Fig. 22: <sup>13</sup>C NMR spectrum of compound 6h



Fig. 24: <sup>13</sup>C NMR spectrum of compound 6i



6]





Fig. 28: <sup>1</sup>H NMR spectrum of compound 6k



-4.55

-2.40

~1.06

8a

7.28 7.24 7.19 7.18

Fig. 30: <sup>13</sup>C NMR spectrum of compound 8a



Fig. 32: <sup>1</sup>H NMR spectrum of compound 8b



8d

Fig. 34: <sup>13</sup>C NMR spectrum of compound 8d



Fig. 36: <sup>1</sup>H NMR spectrum of compound 8g



Fig. 38: <sup>13</sup>C NMR spectrum of compound 8j



Fig. 40: <sup>13</sup>C NMR spectrum of compound 8k



Fig. 42: <sup>13</sup>C NMR spectrum of compound 81



Fig. 44: <sup>13</sup>C NMR spectrum of compound 10a



Fig. 46: <sup>1</sup>H NMR spectrum of compound 10c



Fig. 48: <sup>13</sup>C NMR spectrum of compound 10k