J. Chem. Sci. Vol. 127, No. 5, May 2015, pp. 821–831. © Indian Academy of Sciences.
DOI 10.1007/s12039-015-0837-7

(±)Methanodibenzodiazocine tethered [C-H]$^{\delta+}$ functional site: Study towards benzoin condensation and Baylis-Hillman reactions

ARRURI SATHYANARAYANA and GANESAN PRABUSANKAR*
Department of Chemistry, Indian Institute of Technology Hyderabad, ODF Estate, Yeddumailaram, Telengana, India 502 205
e-mail: prabu@iith.ac.in

MS received 18 June 2014; revised 25 November 2014; accepted 3 December 2014

Abstract. New heterocyclic ring systems consisting of (±) methanodibenzodiazocine and imidazolium/ benzimidazolium salts were synthesized in very good yield. Subsequently, these halide salts were subjected to the anion exchange reaction with KPF_6 to yield the corresponding azolium salts in excellent yield. The possible applications of these newly prepared salts were investigated in homogeneous catalysis. Remarkable changes in the catalytic activity were observed by varying the bulkiness of N-substituent at imidazole. Catalytic activity of these newly prepared salts was tested for the benzoin condensation reaction. Exclusive formation of benzoin products were observed in good yield. Similarly, the dimerization of cyclohexen-1-one to Baylis-Hillman type product, 2-(3-oxocyclohexyl)-2-cyclohexen-1-one was studied.

Keywords. Tröger's base; Imidazolium salt; N-Heterocyclic carbenes; C-H bond activation.

1. Introduction

The cationic imidazolium systems with rigid or unusual molecular platforms are uncommon and such molecular assemblies have been employed as organocatalyst or model systems to simulate the biological processes that take place in the living organism. Namely, the supramolecular system based on a tetrathiafulvalene calix[4]pyrrole and a dicationicbisimidazoliumquinone to understand the artificial ion mediated electron transfer process;[1] highly selective water soluble anthraceneimidazolium receptors for sensing CT-DNA[2] and DNA.[3] Besides, the (±)-2,8-dimethylene-6H,12H-5,11-methanodibenzo[*b*, *f*][1,5]diazocine, known as Tröger's base (TB) linked with imidazolium salts, TB[CH_2-Im-CH_2-Mes]$^{2+}2X^-$, where Im = imidazolium; Mes = 2,4,6-trimethylbenzene; X = Br (**3a**), PF_6 (**3b**) and BF_4 (**3c**) were used as organocatalysts for synthesis of 2-hydroxy-1,2-diferrocenyl-ethan-1-one and 1,2-diferrocenylethanedione from ferrocenealdehyde.[4a] This synthetic methodology is proved to be the most efficient synthetic protocol to derive 1,2-diferrocenylethanedione using organocatalysts.

Although the importance of the century old TB skeleton has been a subject of focus in last several decades, the examples based on Tröger's base tethered heterocyclic ring systems are still rare.[4,5] Thus, in this paper we report a series of Tröger's base attached imidazolium and benzimidazolium salts, TB[CH_2-Im-CH_2-Ar]$_2^+2X^-$, where Ar = C_6F_5, X = Br (**4a**), PF_6 (**4b**); Ar = 1-Naphthyl, X = Cl (**5a**), PF_6 (**5b**) and TB[CH_2-BIm-CH_2-Ar]$_2^+2X^-$, where BIm = Benzimidazolium; Ar = Mes, X = Br (**6a**), PF_6 (**6b**); Ar = C_6F_5, X = Br (**7a**), PF_6 (**7b**); Ar = 1-Naphthyl, X = Cl (**8a**), PF_6 (**8b**). Molecules **4a**–**8a** and **4b**–**8b** were fully characterized. The possible applications of these newly prepared salts were demonstrated in the carbon-carbon bond formation reactions.

2. Experimental

2.1 *General remarks*

All manipulations were carried out under nitrogen using Schlenk vacuum line techniques and argon glove box. The solvents were purchased from commercial sources and purified according to standard procedures.[6] **1**, **2** and **3** were synthesized by previously reported methods.[4a] Starting materials were purchased from commercial sources and used without further purification. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV−Vis spectra were measured on a T90+ UV-Visible spectrophotometer. NMR spectra were recorded on Bruker Ultrashield-400 MHz spectrometers at 25°C unless otherwise stated. Chemical shifts are given relative to Me_4Si and were referenced to the solvent resonances as

*For correspondence

internal standards. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF. The crystal structure of **2** was measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 150 K. The structure of **2** was solved by direct methods using the SIR-97 program[7] and refined with a full matrix least-squares method on F2 using the SHELXL-97 program.[8,9]

2.2 *Synthesis of TB-[CH_2-BIm]$_2$ (**2**)*

2 was synthesized by modifying the previously reported procedure. Cooled (−15°C) trifluoroacetic acid (40 mL) was added to 4-(methyl benzimidazole) aniline (2.000 g, 8.957 mmol) at −15°C then paraformaldehyde (0.430 g, 14.332 mmol) was added to the reaction mixture at same temperature and stirred for 40 h at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice (120 g), then 30% aq. ammonia solution (40 mL) was added to the reaction mixture (until pH = 9–10) then extracted with dichloromethane (3 × 30 mL) and the organic extract was washed with brine solution, dried over an anhydrous Na_2SO_4, organic solvent was evaporated under reduced pressure to result crude gummy compound. Crude compound was purified by column chromatography (100–200 silica gel) and the desired product **2** was eluted by 10% MeOH:DCM mixture. Yellow solid yield: 80% (based on 4-(methyl benzimidazole) aniline). M.p. 219–222°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (s, 2H, BIm NC*H*N), 7.81–7.79 (m, 2H, Ar*H*), 7.28–7.20 (m, 6H, Ar*H*), 7.06–7.04 (d, $J_{H,H}$ = 8 Hz, 2H, Ar*H*), 7.00–6.97 (dd, $J_{H,H}$ = 10, 8.4 Hz, 2H, Ar*H*), 6.67 (s, 2H, Ar*H*), 5.16 (s, 4H, BIm CH_2Ar), 4.59–4.55 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.21 (s, 2H, NCH_2N), 4.05–4.01 (d, $J_{H,H}$ = 16.8 Hz, 2H, *endo*CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.90 (Ar*C*), 143.75 (Ar*C*), 142.98 (Ar*C*), 133.74 (Ar*C*), 131.11 (Ar*C*), 128.21 (Ar*C*), 126.25 (Ar*C*), 125.57 (Ar*C*), 125.51 (Ar*C*), 122.96 (Ar*C*), 122.16 (Ar*C*), 120.29 (Ar*C*), 109.81 (Ar*C*), 66.53 (N*C*H_2N), 58.40 (N*C*H_2Ar), 48.14 (BIm-*C*H_2-Ar) ppm. FT-IR (neat): 3051 (w), 2924 (m), 2853 (w), 1613 (w), 1494 (s), 1450 (m), 1356 (m), 1325 (m), 1288 (m), 1262 (m) 1204 (m), 1110 (m), 742 (s) cm^{-1}. HRMS: *m/z* [M + H]$^+$ calcd for $C_{31}H_{26}N_6$: 483.2297; found: 483.2258.

2.3 *General procedure for the synthesis of the azolium halides, **4a–8a***

An oven dried Schlenk tube was charged with **1** or **2** (1 eq.), aryl methyl halide (2.2 eq.) and dry acetone, then the reaction mixture was stirred at 60°C for 4–48 h under nitrogen atmosphere. After completion of reaction, the expected product was formed as an insoluble solid, which was filtered then washed with acetone (2 × 5 mL) and diethyl ether (3 × 5 mL). Finally the free flowing solid was dried for 2–3 h under high vacuum.

2.4 *General Procedure for the synthesis of the azolium PF_6^- salts, **4b–8b***

Imidazolium or benzimidazolium halide (1 eq.), was dissolved in hot water and KPF_6 (2.5 eq.) was dissolved in normal water separately then both were mixed under stirring to produce a white precipitate immediately. The resulted white precipitate was filtered to get crude compound, which was washed with methanol, dissolved in acetone, dried over sodium sulphate, filtered and solvent was evaporated under reduced pressure to give an analytically pure compound.

2.5 *Synthesis of TB-[CH_2-Im-$CH_2-C_5F_5$]$_2^+$2Br$^-$ (**4a**)*

Reaction mixture was stirred at 60°C for 4 h. White solid. Yield: 80% (based on **1**). M.p. >250°C (decom.). ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.48 (s, 2H, Im NC*H*N), 7.84 (s, 2H, Im*H*), 7.78 (s, 2H, Im*H*), 7.24–7.22 (d, $J_{H,H}$ = 7.6 Hz, 2H, Ar*H*), 7.17–7.15 (d, $J_{H,H}$ = 8 Hz, 2H, Ar*H*), 7.05 (s, 2H, Ar*H*), 5.63 (s, 4H, C_5F_5-CH_2-Im), 5.29 (s, 4H, Im-CH_2-Ar), 4.64–4.60 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.19 (s, 2H, NCH_2N), 4.11–4.07 (d, $J_{H,H}$ = 17.2 Hz, 2H, *endo*CH_2) ppm. ^{13}C NMR is not clear due to ^{13}C &^{19}F coupling. FT-IR (neat): 3051 (w), 2945 (w), 1561 (w), 1526 (m), 1507 (s), 1429 (w), 1351 (w), 1161(m), 1126 (m), 1035 (m), 1014 (m), 967 (m) cm^{-1}. Anal. Calcd for $C_{37}H_{26}Br_2F_{10}N_6$: C, 49.14; H, 2.90; N, 9.29. found: C, 49.2; H, 3.0; N, 9.3.

2.6 *Synthesis of TB-[CH_2-Im-$CH_2-C_5F_5$]$_2^+$2PF$_6^-$ (**4b**)*

White solid. Yield: 92% (based on **4b**). M.p. 206 – 208°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.35 (s, 2H, Im NC*H*N), 7.78–7.74 (d, 4H, Im*H*), 7.19–7.16 (m, 4H, Ar*H*), 7.02 (s, 2H, Ar*H*), 5.61 (s, 4H, Ar-CH_2-Im), 5.24 (s, 4H, Im-CH_2-Ar), 4.65–4.60 (d, $J_{H,H}$ = 17.2 Hz, 2H, *exo*CH_2), 4.20 (s, 2H, NCH_2N), 4.12–4.07 (d, $J_{H,H}$ = 17.2 Hz, 2H, *endo*CH_2) ppm. ^{13}C NMR is not clear due to ^{13}C &^{19}F coupling. ^{31}P NMR (DMSO-d_6, 161 MHz) δ − 126.29 to −152.64 (septet) ppm. FT-IR (neat): 3163 (w), 1659 (w), 1562 (w), 1511 (m), 1159 (m), 1128 (m), 1039 (w), 831 (s) cm^{-1}.Anal. Calcd for

$C_{37}H_{26}F_{22}N_6P_2$: C, 42.96; H, 2.53; N, 8.12. found: C, 43.0; H, 2.4; N, 7.9.

2.7 *Synthesis of TB-[CH_2-Im-CH_2-(1-Naphthyl)]$_2^+$ 2Cl^- (**5a**)*

Reaction mixture was stirred at 60°C for 48 h. Pale brown solid. Yield: 60% (based on **1**). M.p. 215–217°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.57 (s, 2H, Im NC*H*N), 8.13-8.11 (m, 2H, Ar*H*), 8.02–8.00 (d, $J_{H,H}$ = 6 Hz, 4H, Ar*H*), 7.80 (s, 4H, Ar*H*), 7.62–7.53 (m, 8H, Ar*H*), 7.21–7.19 (d, $J_{H,H}$ = 8 Hz, 2H, Ar*H*), 7.14–7.12 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 6.97 (s, 2H, Ar*H*), 5.94 (s, 4H, Im-CH_2-Nap), 5.27 (s, 4H, Im-CH_2-Ar), 4.59–4.55 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.17 (s, 2H, NCH_2N), 4.05-4.01 (d, $J_{H,H}$ = 16.8 Hz, 2H, *endo*CH_2) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ 148.45(Ar*C*), 136.42 (ImN*C*N), 133.48 (Ar*C*), 130.43 (Ar*C*), 130.01 (Ar*C*), 129.81 (Ar*C*), 128.98 (Ar*C*), 128.47 (Ar*C*), 128.14 (Ar*C*), 128.08 (Ar*C*), 127.26 (Ar*C*), 127.20 (Ar*C*), 126.88 (Ar*C*), 126.50 (Ar*C*), 125.72 (Ar*C*), 125.35 (Ar*C*), 123.11 (Ar*C*), 122.93 (Ar*C*), 122.69 (Ar*C*), 65.86 (N*C*H_2N), 57.95 (N*C*H_2-Ar), 51.56 (Im-*C*H_2-Ar), 50.02 (Im-*C*H_2-Nap) ppm. FT-IR (neat): 2922 (w), 1554 (m), 1510 (w), 1492 (w), 1141 (w), 825 (s) cm^{-1}. Anal. Calcd for $C_{45}H_{40}Cl_2N_6$: C, 73.46; H, 5.48; N, 11.42. found: C, 73.6; H, 5.4; N, 11.3.

2.8 *Synthesis of TB-[CH_2-Im-CH_2-(1-Naphthyl)]$_2^+$ 2PF_6^- (**5b**)*

Brownish white solid. Yield: 68% (based on **5a**). M.p. 156–158°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.30 (s, 2H, Im NC*H*N), 8.08–8.02 (m, 6H, Ar*H*), 7.77–7.75 (d, $J_{H,H}$ = 9.6 Hz, 4H, Ar*H*), 7.64–7.53 (m, 8H, Ar*H*), 7.20–7.13 (m, 4H, Ar*H*), 6.93 (s, 2H, Ar*H*), 5.90 (s, 4H, Im-CH_2-Ar), 5.23 (s, 4H, Im-CH_2-Nap), 4.62–4.57 (d, $J_{H,H}$ = 17.2 Hz, 2H, *exo*CH_2), 4.19 (s, 2H, NCH_2N), 4.07–4.03 (d, $J_{H,H}$ = 16.8 Hz, 2H, *endo*CH_2) ppm.^{13}C NMR (DMSO-d_6, 100 MHz) δ 148.45 (ArC), 136.32(Im N*C*N), 136.19 (Ar*C*), 133.43 (Ar*C*), 130.36 (Ar*C*), 129.80 (Ar*C*), 128.92 (Ar*C*), 128.43 (Ar*C*), 127.94 (Ar*C*), 127.16 (Ar*C*), 127.02 (Ar*C*), 126.72 (Ar*C*), 126.43 (Ar*C*), 125.63 (Ar*C*), 125.33 (Ar*C*), 123.12 (Ar*C*), 123.07 (Ar*C*), 122.69 (Ar*C*), 122.61(Ar*C*), 65.81 (N*C*H_2N), 57.87 (N*C*H_2Ar), 51.62 (Im-*C*H_2-Ar), 50.03(Im-*C*H_2-Nap) ppm. ^{31}P NMR (DMSO-d_6, 161 MHz) δ − 130.99 to −157.34 (septet) ppm. FT-IR (neat): 3154 (w), 2922 (w), 1554 (m), 1510 (w), 1492 (m), 1453 (w), 1207 (m), 1141 (m), 825 (s) cm^{-1}. Anal. Calcd for $C_{45}H_{40}F_{12}N_6P_2$: C, 56.61; H, 4.22; N, 8.80. Found: C, 56.5; H, 4.4; N, 8.7.

2.9 *Synthesis of TB-[CH_2-BIm-CH_2-Mes]$_2^+$2Br^- (**6a**)*

Reaction mixture was stirred at 60°C for 6 h. White solid. Yield: 91% (based on **2**). M.p. >360°C (decom.). ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.50 (s, 2H, BIm NC*H*N), 8.07–7.94 (m, 4H, Ar*H*), 7.68–7.63 (m, 4H, Ar*H*), 7.36–7.02 (m, 10H, Ar*H*), 5.67 (s, 4H, Mes-CH_2-Ar), 5.57 (s, 4H, BIm-CH_2-Ar), 4.58–4.54 (d, $J_{H,H}$ = 14.4 Hz, 2H, *exo*CH_2), 4.14 (s, 2H, NCH_2N), 4.04–4.00 (d, $J_{H,H}$ = 14.8 Hz 2H, *endo*CH_2), 2.29 (s, 6H, Mes-*para*CH_3), 2.23 (s, 12H, Mes-*ortho*CH_3) ppm.^{13}C NMR(DMSO-d_6, 100 MHz) δ 148.19 (Ar*C*), 141.33 (N*C*HN), 138.73 (Ar*C*), 138.30 (Ar*C*), 131.64 (Ar*C*), 130.93 (Ar*C*), 129.53 (Ar*C*), 129.33 (Ar*C*), 128.32 (Ar*C*), 126.82 (Ar*C*), 126.73 (Ar*C*), 126.54 (Ar*C*), 125.84 (Ar*C*), 125.18 (Ar*C*), 114.00 (Ar*C*), 113.91 (Ar*C*), 65.77 (N*C*H_2N), 57.87 (N*C*H_2Ar), 49.31 (BIm-*C*H_2-Ar), 45.29 (BIm-*C*H_2-Mes), 20.67 (Mes-*para*CH_3), 19.34 (Mes-*ortho*CH_3) ppm. FT-IR (neat): 3123 (w), 2951 (m), 2920 (m), 2855 (w), 1612 (m), 1560 (s), 1493 (s), 1430 (m), 1190 (m) cm^{-1}. Anal. Calcd for $C_{51}H_{52}Br_2N_6$: C, 67.40; H, 5.77; N, 9.5. found: C, 67.3; H, 5.9; N, 9.3.

2.10 *Synthesis of TB-[CH_2-BIm-CH_2-Mes]$_2^+$ 2PF_6^- (**6b**)*

Yellowish white solid. Yield: 89% (based on **6a**). M.p. 182–184°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.38 (s, 2H, BIm NC*H*N), 8.08–8.06 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 7.93–7.90 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 7.72–7.68 (t, $J_{H,H}$ = 7.6, 8.0 Hz, 2H, Ar*H*), 7.65–7.61 (t, $J_{H,H}$ = 8.0, 7.6 Hz, 2H, Ar*H*), 7.21–7.19 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 7.14–7.12 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*), 7.04 (s, 4H, MesAr*H*), 7.01 (s, 2H, BIm*H*), 5.64 (s, 4H, BIm-CH_2-Ar), 5.53 (s, 4H, BIm-CH_2-Mes), 4.59–4.55 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.15 (s, 2H, NCH_2N), 4.04–4.00 (d, $J_{H,H}$ = 17.2 Hz, 2H, *endo*CH_2), 2.31 (s, 6H, Mes-*para*CH_3), 2.23 (s, 12H, Mes-*ortho*CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ 148.26 (Ar*C*), 141.21 (Ar*C*), 138.76 (Ar*C*), 138.28 (BIm NC*N*), 131.64 (Ar*C*), 130.94 (Ar*C*), 129.50 (Ar*C*), 129.22 (Ar*C*), 128.30 (Ar*C*), 126.78 (Ar*C*), 126.73 (Ar*C*), 126.68 (Ar*C*), 126.45 (Ar*C*), 125.67 (Ar*C*), 125.17 (Ar*C*), 113.89 (Ar*C*), 113.79 (Ar*C*), 65.72 (N*C*H_2N), 57.83 (N*C*H_2Ar), 49.29 (BIm-*C*H_2-Ar), 45.09 (BIm-*C*H_2-Mes), 20.60 (Mes-*para*CH_3), 19.20 (Mes-*ortho*CH_3) ppm. ^{31}P NMR (DMSO-d_6, 161 MHz) δ − 130.98 to −157.33 (septet) ppm. FT-IR

(neat): 2915 (w), 1612 (w), 1562 (m), 1492 (w), 1428 (w), 1377 (w), 1185 (w), 828 (s), 742 (m) cm^{-1}. Anal. Calcd for $C_{51}H_{52}F_{12}N_6P_2$: C, 58.96; H, 5.04; N, 8.09. Found: C, 58.8; H, 5.2; N, 8.1.

2.11 *Synthesis of TB-[CH_2-BIm-CH_2 − C_5F_5]$_2^+$ 2Br^- (**7a**)*

Reaction mixture was stirred at 60°C for 48 h. Brownish white solid. Yield: 72% (based on **2**). M.p. >360°C(decom.). ^{1}H NMR(DMSO-d_6, 400 MHz) δ 11.11 (s, 2H, BIm NC*H*N), 7.72–7.61 (m, 4H, Ar*H*), 7.55–7.45 (m, 4H, Ar*H*), 7.37–7.13 (m, 4H, Ar*H*), 6.98–6.95 (m, 2H, Ar*H*), 6.00 (s, 4H, BIm-CH_2-Ar), 5.67–5.61 (m, 4H, BIm-CH_2-PFP), 4.54–4.49 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.08 (s, 2H, NCH_2N), 4.06–4.04 (d, $J_{H,H}$ = 16.8 Hz, 2H, *endo*CH_2) ppm. FT-IR (neat): 3117 (w), 2947 (w), 1657 (w), 1611 (w), 1560 (w), 1504 (s), 1425 (m), 1347 (m), 1206 (m), 1122 (m), 1032 (m), 963 (m), 748 (m) cm^{-1}. Anal. Calcd for $C_{45}H_{30}Br_2F_{10}N_6$: C, 53.80; H, 3.01; N, 8.37. Found: C, 53.8; H, 3.0; N, 8.4.

2.12 *Synthesis of TB-[CH_2-BIm-CH_2 − C_5F_5]$_2^+$ 2PF_6^- (**7b**)*

Brownish white solid. Yield: 83% (based on **7a**). M.p. 185–187°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.96 (s, 2H, BIm NC*H*N), 8.00–7.95 (t, $J_{H,H}$ = 8.4, 8.4 Hz, 4H, Ar*H*), 7.74–7.70 (t, $J_{H,H}$ = 7.6, 8.0 Hz, 2H, Ar*H*), 7.66–7.62 (t, $J_{H,H}$ = 8.0, 7.6 Hz, 2H, Ar*H*), 7.30–7.28 (m, 2H, Ar*H*), 7.16–7.14 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 7.10 (s, 2H, Ar*H*), 5.95 (s, 4H, BIm-CH_2-Ar), 5.60 (s, 4H, BIm-CH_2-PFP), 4.61–4.57 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.17 (s, 2H, NCH_2N), 4.08–4.04 (d, $J_{H,H}$ = 16.8 Hz, 2H, *endo*CH_2) ppm. ^{31}P NMR (DMSO-d_6, 161 MHz) δ − 131.04 to −157.39 (septet) ppm. FT-IR (neat): 2923 (w), 2854 (w), 1612 (m), 1565 (s), 1510 (w), 1450 (w), 1299 (m), 1124 (m), 1028 (s), 831 (s) cm^{-1}. Anal. Calcd for $C_{45}H_{30}F_{22}N_6P_2$: C, 47.63; H, 2.66; N, 7.41. found:C, 47.5; H, 2.8; N, 7.4.

2.13 *Synthesis of TB-[CH_2-BIm-CH_2-(1-Naphthyl)]$_2^+$ 2Cl^- (**8a**)*

Reaction mixture was stirred at 60°C for 48 h.brownish white solid. Yield: 61% (based on **2**). M.p. 222–224°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 10.06 (s, 2H, BIm NC*H*N), 8.13–8.11 (d, $J_{H,H}$ = 7.6 Hz, 2H, Ar*H*), 8.05–7.99 (m, 8H, Ar*H*), 7.65–7.59 (m, 8H, Ar*H*), 7.56–7.50 (m, 4H, Ar*H*), 7.29–7.27 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*), 7.15–7.13 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 7.03 (s, 2H, Ar*H*), 6.28 (s, 4H, BIm-CH_2-Ar), 5.60 (s, 4H, BIm-CH_2-Nap), 4.58–4.54 (d, $J_{H,H}$ = 17.2 Hz, 2H, *exo*CH_2), 4.17 (s, 2H, NCH_2N), 4.03–3.99 (d, $J_{H,H}$ = 16.8,Hz, 2H, *endo*CH_2) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ 148.08 (Ar*C*), 142.77 (Ar*C*), 133.44 (BIm N*C*N), 131.33 (Ar*C*), 130.86 (Ar*C*), 130.34 (Ar*C*), 129.58 (Ar*C*), 129.26 (Ar*C*), 129.01 (Ar*C*), 128.93 (Ar*C*), 128.85 (Ar*C*), 128.31 (Ar*C*), 127.37 (Ar*C*), 127.14 (Ar*C*), 127.04 (Ar*C*), 126.80 (Ar*C*), 126.66 (Ar*C*), 126.42 (Ar*C*), 125.53 (Ar*C*), 125.18 (Ar*C*), 122.92 (Ar*C*), 114.13 (Ar*C*), 114.02 (Ar*C*), 65.69 (N*C*H_2N), 57.81 (N*C*H_2Ar), 49.28 (BIm-*C*H_2-Ar), 48.23 (BIm-*C*H_2-Nap) ppm. FT-IR (neat): 3052 (w), 2925 (m), 2853 (w), 1656 (w), 1613 (m), 1559 (s), 1493 (s), 1439 (m), 1370 (m), 1205 (m), 1188 (s), 1016 (m), 789 (s), 744 (s) cm^{-1}. Anal. Calcd for $C_{53}H_{44}Cl_2N_6$: C, 76.16; H, 5.31; N, 10.05. found: C, 76.3; H, 5.1; N, 10.1.

2.14 *Synthesis of TB-[CH_2-BIm-CH_2-(1-Naphthyl)]$_2^+$ 2PF_6^- (**8b**)*

White solid. Yield: 80% (based on **8a**). M.p. 202–204°C. ^{1}H NMR(DMSO-d_6, 400 MHz) δ 9.82 (s, 2H, BIm NC*H*N), 8.09–7.98 (m, 10H, Ar*H*), 7.67–7.59 (m, 8H, Ar*H*), 7.57–7.49 (m, 4H, Ar*H*), 7.26–7.24 (d, $J_{H,H}$ = 8.0 Hz, 2H, Ar*H*), 7.15–7.13 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar*H*), 6.99 (s, 2H, Ar*H*), 6.26 (s, 4H, BIm-CH_2-Ar), 5.57 (s, 4H, BIm-CH_2-Nap), 4.58–4.54 (d, $J_{H,H}$ = 16.8 Hz, 2H, *exo*CH_2), 4.16 (s, 2H, NCH_2N), 4.03–3.99 (d, $J_{H,H}$ = 16.8 Hz, 2H, *endo*CH_2) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz) δ 148.38 (Ar*C*), 142.52 (Ar*C*), 133.45 (BIm N*C*HN), 131.40 (Ar*C*), 130.89 (Ar*C*), 130.35 (Ar*C*), 129.65 (Ar*C*), 129.01 (Ar*C*), 128.95 (Ar*C*), 128.85 (Ar*C*), 128.40 (Ar*C*), 127.47 (Ar*C*), 127.40 (Ar*C*), 127.13 (Ar*C*), 126.98 (Ar*C*), 126.86 (Ar*C*), 126.55 (Ar*C*), 126.44 (Ar*C*), 125.54 (Ar*C*), 125.23 (Ar*C*), 122.80 (Ar*C*), 114.08 (Ar*C*), 113.94 (Ar*C*), 65.74 (N*C*H_2N), 57.83 (N*C*H_2-Ar), 49.35 (BIm-*C*H_2-Ar), 48.20 (BIm-*C*H_2-Nap) ppm. ^{31}P NMR (DMSO-d_6, 161 MHz) δ −130.98 to −157.33 (septet) ppm. FT-IR (neat): 3146 (w), 2917 (w), 2851 (w), 1613 (w), 1563 (m), 1493 (m), 1443 (w), 1188 (w), 1012 (w), 831 (s), 744 (m) cm^{-1}. Anal. Calcd for $C_{53}H_{44}F_{12}N_6P_2$: C, 60.34; H, 4.20; N, 7.97. found: C, 60.3; H, 4.1; N, 8.1.

2.15 *General procedure for catalytic benzoin condensation*

An oven-dried Schlenk tube was charged with magnetic stirrer bar and catalyst (2.5 mol%), and then dried under vacuum for 5–15 min. After that, solvent (3 mL)

and distilled benzaldehyde (0.943 mmole) were added under nitrogen atmosphere at room temperature, and then evacuated for a few seconds and refilled with nitrogen. After that, KO^{t}Bu (5 mol%) was added to the reaction mixture under nitrogen condition at room temperature. The reaction progress was monitored by TLC. After 20 h, the reaction mixture was diluted with water (10 mL) and ethyl acetate (10 mL). The organic phase was separated, washed with brine solution (7 mL), dried over an anhydrous sodium sulphate, the reaction mass was concentrated under reduced pressure to get crude compound. The crude compound was purified by column chromatography (silica gel 100–200 mesh) the desired compound was eluted in 10% EtOAc: pet-ether, the product analysis were matched with reported values.[10]

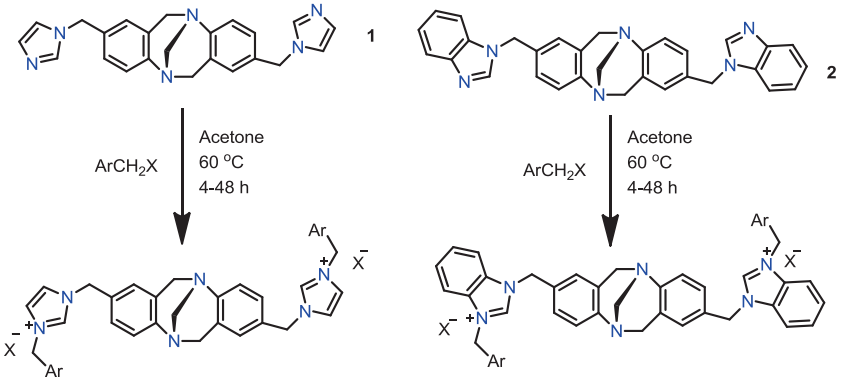
2.16 *General procedure for catalysts **3a**, **3b** and **3c** mediated Baylis-Hillman reaction*

An oven dried Schlenk tube was charged with magnetic stirrer bar and catalyst **3a** or **3b** or **3c** (2.5–7.5 mol%), then dried under vacuum for 5–15 min. After that, solvent (3 mL) and cyclohexenone (1.041 mmol) was added under nitrogen atmosphere at room temperature then evacuated for few seconds and refilled with nitrogen, after that KO^{t}Bu (5–15 mol%) was added to the reaction mixture under nitrogen condition at room temperature. The reaction progress was monitored by TLC. After 4 h, the reaction mixture was diluted with water (10 mL) and ethyl acetate (10 mL). The organic phase was separated, washed with brine solution (7 mL), dried over an anhydrous sodium sulphate, the reaction mass was concentrated under reduced pressure to get crude compound. The crude compound was purified by column chromatography (silica gel 100–200 mesh) the desired compound was eluted by 8% EtOAc: pet-ether, the product analyses were matched with reported values.[11,22]

3. Results and Discussion

3.1 *Synthesis and characterization*

The derivatives of TB supported imidazolium and benzimidazolium salts, **4–8** were synthesized by following the synthetic procedure optimized for **1** and **3** in very good yield (scheme 1).[4a] The yield of the product ranges from 60 to 92%. Notably, **4–8** were isolated without any quaternary ammonium salts at bridgehead nitrogen atoms.[12] Compounds **2** and **4–8** were fully characterized. The ^{1}H NMR chemical shift value of **3a–8a** for imidazolium NC*H*N, proton fall in the range from δ 9.17 to 11.11 ppm, while the ^{1}H NMR chemical shift value of **3b–8b** for NC*H*N, proton appears between δ 9.03 to 9.96 ppm. The *endo* and *exo* NCH_2Ar proton chemical shift values of **3a–8a** and **3b–8b** are almost comparable. Except **3b** and **8b**, the NCH_2N protons chemical shift values of **4b–7b** are slightly higher than that of corresponding halogen ion derivatives, **4a–7a**. Furthermore the molecular skeleton of **3a** and **6a** were confirmed by DEPT, HSQC and HMBC correlations, and the similar molecular skeleton also expected for other derivatives, **3b–8b**, **3c**, **4a**, **5a**, **7a**, and **8a** (see supporting information). Figure 1 presents



Scheme 1. Synthesis of **4–8**.

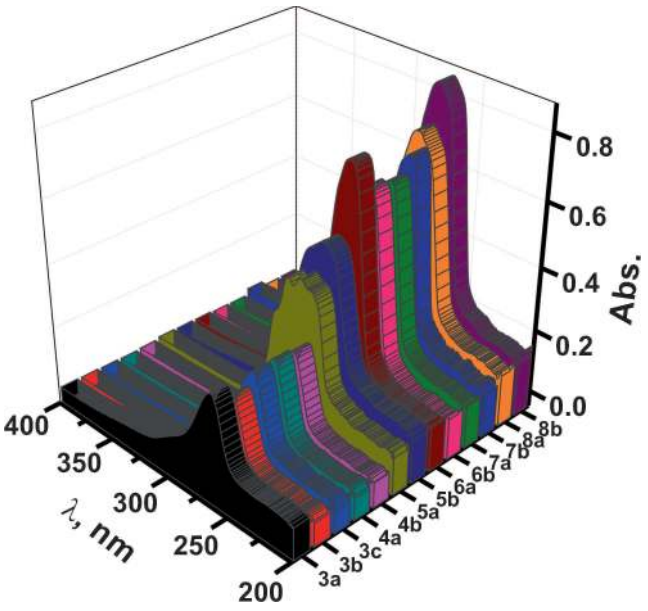


Figure 1. UV-vis absorption spectra of **3**–**8** in DMSO (2.64×10^{-5} M).

the optical spectra of the azolium salts in DMSO. The UV−vis spectra of **5**–**8** demonstrate significant diversity compared to **3**–**4**. The absorption spectra of **3**–**4** are nearly identical. The absorption spectrum of **8b** is much stronger than **3**–**7** and **8a**. Notably, the UV-vis absorption spectra of **5**–**8** shows bathochromic shifts compared to **3**–**4**.

The structure of **2** was further confirmed by single crystal X-ray diffraction technique (figure 2).[13] Compound **2** crystallized in the orthorhombic space group, *P22121*. Selected bond lengths and bond angles are listed in the caption of figure 2. Molecule **2** represents a rare structurally characterized TB linked azole skeleton.[4b] As shown in figure 2, the "V" shaped TB skeleton is linked with benzimidazole through methylene group to result the "Mexican hat" shape structure to the molecule. The C(10)−N(2)− C(10) angle is 99.32(1)°, which is almost comparable with 2,8-dimethyl-5,11-methano-5, 6,11,12-tetrahydro-dibenzo-[*b*, *f*][1,5]diazocine (92.8–97.4°).[14] The N(3) −C(10)−C(4) angle is 111.5(4)°. The N(2)−C(1)− N(2) angle is 110.5(5)°. N(9)−C(3) bond distance is 1.289(7) Å. N(2)−C(1) bond distance is 1.429(6) Å. As shown in the packing diagram, molecule is packed in a layer form through O−H· · · N type of hydrogen bonding between lattice water molecule and bezimidazole nitrogen (figure 3). The donor-acceptor bond distance of O−H· · ·N is 2.913 Å.

3.2 *Application of **3**–**8** incarbon-carbon bond formation reactions*

In general, the organocatalyst-mediated benzoin condensation reactions were carried-out in THF using KO^{t}Bu to obtain the best output or to avoid the solubility issues.[4a] Unlike the conventional route, the present

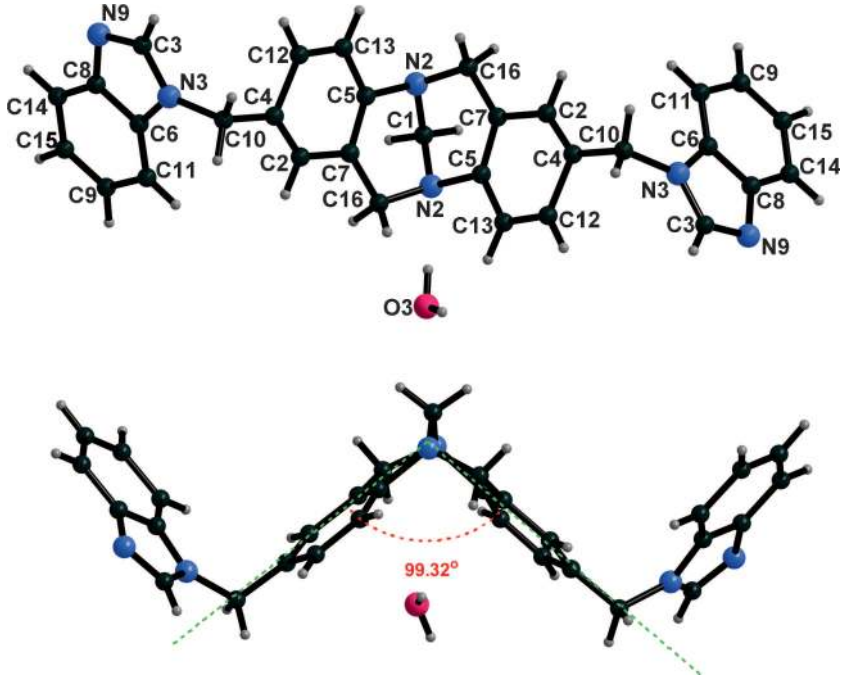


Figure 2. The solid state structure of **2**. Selected bond distances (Å) and angles (°): C(1)−N(2), 1.429(6); N(2)−C(16), 1.383(8); N(2)−C(5), 1.539(8); N(3)−C(3), 1.335(7); N(3)−C(6), 1.389(6); N(3)−C(10), 1.494(6); C(8)−N(9), 1.413(9); N(9)−C(3), 1.289(7); N(2)−C(1)−N(2)#1, 110.5(5); C(4)−C(10)−N(3), 111.5(4).

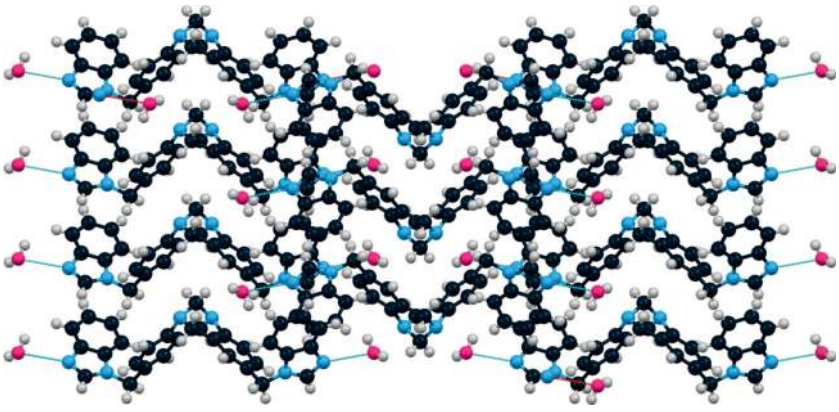
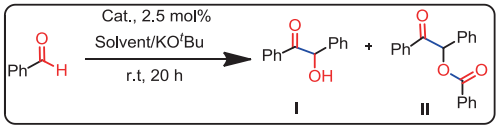


Figure 3. The molecular packing of **2** through O—H· · ·N hydrogen bonding.

Table 1. Benzoin Condensation reactions mediated by catalysts **3a-3c**.

Entry	Cat[a,b].	Solvent	Starting material conversion (%)	I Yield (%)[c]	II Yield (%)[c]
1	**3a**	Toluene	99	91	8
2	**3a**	Fluorobenzene	99	94	5
3	**3a**	1,4-Dioxane	99	95	4
4	**3b**	Toluene	97	89	8
5	**3b**	Fluorobenzene	96	92	5
6	**3b**	1,4-Dioxane	94	94	5
7	**3c**	Toluene	98	79	18
8	**3c**	Fluorobenzene	98	89	10
9	**3c**	1,4-Dioxane	99	90	9

[a]2.5% of catalyst loading,
[b]Base-KO^{t}Bu,
[c]Isolated yields are 4–5% less than calculated.



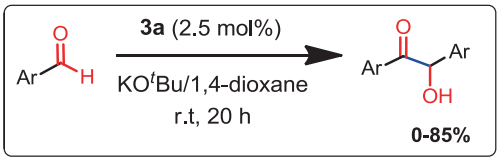
Scheme 2. Catalysts **3a**, **3c** and **3a**–**8a** mediated Benzoin Condensation reaction.

Table 2. Benzoin Condensation reaction mediated by catalysts **3a**–**8a**.

Entry	Cat.	Starting material conversion (%)	I Yield (%)[a]	II Yield (%)[a]
1	**3a**	99	95	4
2	**4a**	91	76	8
3	**5a**	96	72	24
4	**6a**	87	79	6
5	**7a**	89	81	8
6	**8a**	80	73	4

[a]Isolated yields are 4–5% less than calculated. Isolated yields after column chromatography.

studies were accomplished using catalysts, **3a**, **3b**, and **3c** in toluene, fluorobenzene and 1,4-dioxane (table 1, scheme 2). Moreover, toluene, fluorobenzene



Scheme 3. Benzoin Condensation reaction mediated by catalyst **3a** with different aryl aldehydes.

or 1,4-dioxane reaction medium can also reduce the moisture absorbance in comparison with THF medium. Catalysts **3a**, **3b** and **3c** gave desired benzoin product (**I**) as a major yield (from 79 to 94% yield) along with Cannizzaro product (**II**)[15] as a side product (from 5 to 18% yield) with the loading of 2.5 mol% catalyst. When the catalyst loading was 1 mol%, the starting material was consumed over a period of 4 days. Further increment in the catalyst loading (5 mol%) did not improve the catalyst performance. Notably, the catalyst **3a** in 1,4-dioxane gave **I** in excellent yield (95%). The efficiency of starting material conversion for catalysts **3a**, **3b** and **3c** were nearly comparable (94 to 99%, table 1). However, catalyst **3a** in 1,4-dioxane is very selective towards benzoin condensation reaction.

Table 3. Benzoin Condensation reaction with catalyst **3a** (2.5 mol%), KO^{t}Bu (7 mol%) as a base, in 1,4-dioxane solvent at r.t., for 20 h.

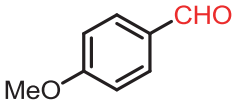
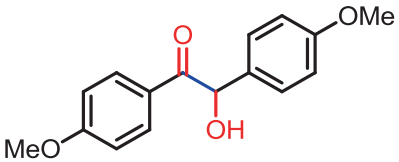
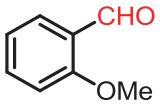
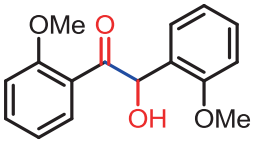
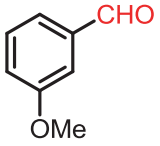
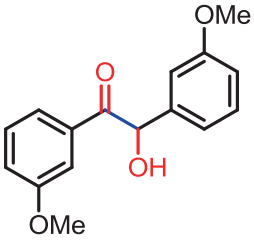
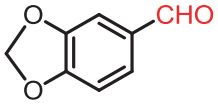
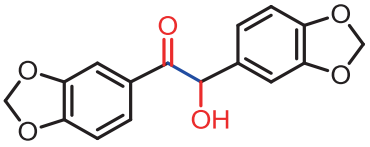
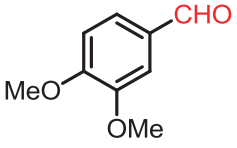
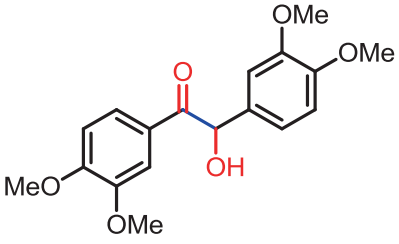
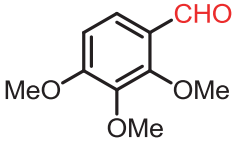
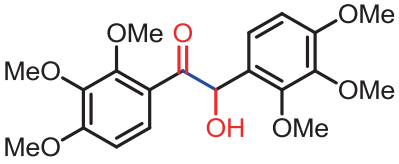
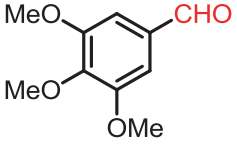
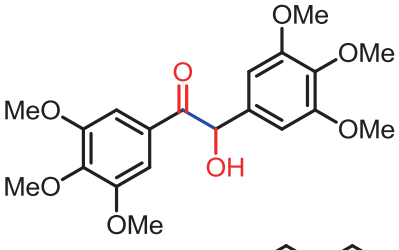
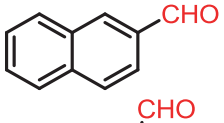
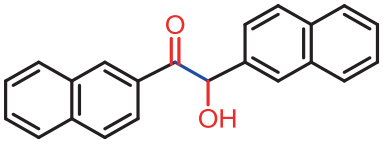
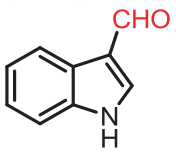
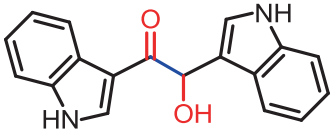
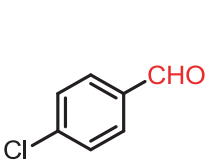
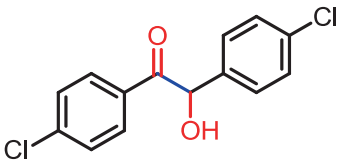
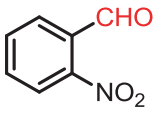
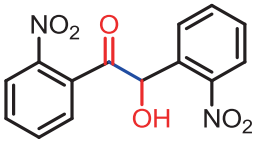
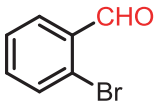
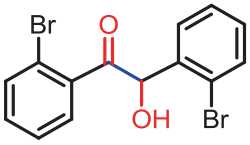
Entry	Starting material	Product	Yield (%)[a]
1			72
2			69
3			83
4			68
5			66
6			68
7			78
8			82
9			0

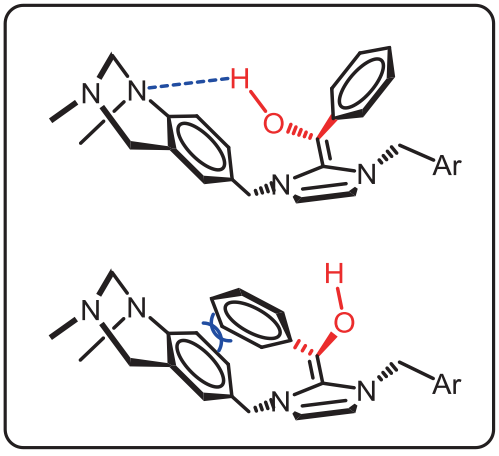
Table 3. *Continued.*

Entry	Starting material	Product	Yield (%)[a]
10			85
11			0
12			64

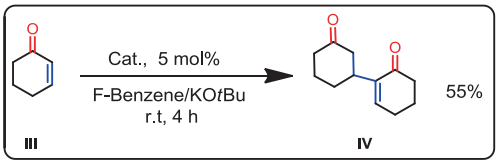
[a]Isolated yields after column chromatography.

Therefore, catalysts **4a**, **5a**, **6a**, **7a** and **8a** were tested for the benzoin condensation reaction in 1,4-dioxane (table 2). Among **3a**–**8a**, **3a** produced only **I** in excellent yield (with starting material conversion of 94%, yield of **I** is 94%), while **5a** gave both **I** (72%) as well as **II** (24%). Therefore **3a** turned out to be the better catalyst for benzoin condensation. Yield of the benzoin product and the loading of catalyst are almost comparable with literature.[16]

Subsequently, we have extended the benzoin condensation on substituted aryl aldehydes using **3a** as a catalyst (scheme 3, table 3). For example, the 3-methoxy benzaldehyde (83%, entry 1, table 3) gave better yield than 2-methoxy benzaldehyde (69%, entry 2, table 3) and 4-methoxy benzaldehyde (72%, entry 3, table 3). Similarly, the 3,4-di substituted benzaldehydes were converted in better yield (68%, entry 4 and 66%, entry 5, table 3). Notably, 3,4,5-trimethoxy benzaldehyde (78%, entry 7, table 3) afforded better yield than 2,3,4-trimethoxy benzaldehyde (68%, entry 6, table 3), which can be explained by more steric hindrance around aldehyde in 2,3,4-trimethoxy benzaldehyde than 3,4,5-trimethoxy benzaldehyde. Moreover, the products of entry 6 and 7 are considered to be the useful building blocks in many biologically important molecules.[17] In general, these are derived from benzoin condensation reaction using toxic KCN as catalyst.[18] Electron rich aldehydes like 2-naphthaldehyde (entry 8, table 3) produced 82% yield, while the indole 3-carboxaldehyde (entry 9, table 3) and 2-nitro benzaldehyde (entry 11, table 3) gave 0% yield. The zero conversion in entry 9 and 11 can be attribute to the deactivate nature of NH or NO_2 groups towards the reactive carbene site. Moreover, N-Boc protected indole-3-carboxaldehyde



Scheme 4. Top: the proposed Breslow intermediate through hydrogen bonding at enol form with TB nitrogen; Bottom: unfavourable Breslow intermediate.



Scheme 5. Baylis-Hillman reaction mediated by catalysts **3a**, **3b** and **3c**.

was not activated by catalyst **3a**. 2-bromobenzaldehyde gave poor yield (64%, entry 12, table 3) compared to 4-chlororbenzaldehyde (85%, entry 10, table 3).

Although the NHC plays major role in benzoin condensation reactions, the role of TB can't be excluded. For example, Wu *et al.* reported the TB mediated asymmetric Mannich reaction via the TB stabilized enol hydroxyl group by O−H···N hydrogen bonding.[19] The

Table 4. Baylis-Hillman reaction.

S. No.	Cat.	Loading mol%	Base loading mol%	Solvent	Yield	Time
1	**3a**	5 mol%	9 mol%	Fluorobenzene	55%	4 h
2	**3a**	2.5 mol%	5 mol%	Fluorobenzene	52%	24 h
3	**3a**	7.5 mol%	15 mol%	Fluorobenzene	55%	4 h
4	**3a**	5 mol%	9 mol%	Toluene	0%	4 h
5	**3a**	5 mol%	9 mol%	1,4-Dioxane	0%	4 h
6	**3a**	5 mol%	Without base	Fluorobenzene	0%	24 h
7	**3b**	5 mol%	9 mol%	Fluorobenzene	50%	4 h
8	**3c**	5 mol%	9 mol%	Fluorobenzene	48%	4 h
9	Without cat.	0	10 mol%	Fluorobenzene	15%	24 h

similar mechanistic pathway was also proposed for the formationof 1,2-diferrocenylethanedione from ferrocene aldehyde by **3a**, **3b** and **3c**.[4a] Thus, the catalysts **3a, 3b, 3c** and **4a**–**8a** mediated benzoin condensation should also proceed through Breslow intermediate, where the hydrogen bonding should exist between enol form and TB nitrogen (scheme 4), thus Breslow intermediate is the driving force to enhance the reaction towards the product.

Since **3a** has shown the best activity in comparison with other catalysts in benzoin condensation reaction, the catalytic activity of former under mild condition for the activation of α, β-unsaturated cyclic ketone (**III**) was tested (scheme 5). The catalytic conversion was carried out in the presence of KO^{t}Bu (5–15 mol%) using selected solvents such as fluorobenzene, 1,4-dioxane and toluene (table 4). Surprisingly, as observed for the benzoin condensation, fluorobenzene showed the best conversion rate with 5 mol% catalyst and 9 mol% KO^{t}Bu within 4 h to produce the Baylis-Hillman product, 2-(3-oxocyclohexyl)-2-cyclohexen-1-one (**IV**) (55%). Yield of **IV** decreased when the same conversion was carried out using **3b** (50%) or **3c** (48%). Similarly, the catalytic transformation by **3a** in toluene or in 1,4-dioxane did not yield any product. When the catalyst loading was decreased to 2.5 mol%, the reaction time increased to 24 h with 52% yield. Further increment in the catalyst loading (7.5 mol%) did not improve the yield. It is also important to note that the tertiary amines[11] or ionic liquids[20] can also act as catalyst for Baylis-Hillman reactions, hence we performed the **3a** mediated Baylis-Hillman reaction without base and the reaction did not work. Since the alkoxy bases can also activate **III** to produce trace amountof **IV**,[21] the reaction was carried out in the presence of KO^{t}Bu without catalyst, which resulted the formation of **IV** in 15% yield. The NHC mediated cyclohexenone dimerization is very rare.[20] Thus, we assume that both the Tröger's bases as well as imidazolium salts are responsible for the catalytic activity of **3a**, **3b** or **3c**. However, we cannot offer further evidence at present. The results are consistent with reported yield of **IV**.[22]

4. Conclusions

We synthesized and characterized Tröger's-base **4**–**8** in good yields. The new molecules **3a**–**8a** were used as organocatalysts in benzoin condensation reactions. Catalyst **3a** was very selective towards benzoin condensation reaction (exclusive formation of **I** with 94% yield) in 1,4-dioxane. Furthermore, **3a** showed better activity for condensation of α, β-unsaturated cyclic ketone (**III**) to Baylis-Hillman product, 2-(3-oxocyclohexyl)-2-cyclohexen-1-one (**IV**) in fluorobenzene. In the cases of benzoin condensation reactions, the catalyst loading was appreciably low.[10,23,24]

Supplementary Information

CCDC 931490 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. NMR spectra and characterization table are available at www.ias.ac.in/chemsci.

Acknowledgments

We thank CSIR (01(2529)/11/EMR-II) for the financial support. AS thank UGC for the fellowship. We thank, Dr. Natarajan Sampath, SCB, SASTRA University for solving single crystal X-ray structure of molecule **2**.

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13. X-ray crystal structure analysis of **2**: $C_{15.5}H_{15}N_3O$, $M = 259.30$, Orthorhombic, space group *P22121*, $a = 5.2286(4)$ Å, $b = 10.8928(11)$ Å, $c = 24.975(2)$ Å, $V = 1422.4(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.211$ mg/mm^3, $T = 150$ K, $F(000) = 548$, $\mu(Cu_{K\alpha}) = 0.626$ mm^{-1}, needle, 3259 reflections measured, 2130 unique ($R_{int} = 0.0307$), 181 parameters, $R_1 = 0.0854$ ($I > 2\sigma(I)$), $wR_2 = 0.2061$ ($I > 2\sigma(I)$), GOF = 1.009
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