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Synthesis of Fused Pyrido[a]imidazoles

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Abstract: A new method based on the reaction of 4-bromo-1,3-diphenyl-2buten-1-one with imidazoles and benzimidazoles was proposed to obtain imidazo[1,2-*a*]pyridinium and pyrido[2,1-*b*]benzimidazolium salts.

Keywords: Annelation; Benzimidazolium ylide; γ-Bromodypnone; Imidazo[1,2*a*]pyridine; Imidazolium ylide; Pyrido[2,1-*b*]benzimidazole

Application of heterocyclic ylides in the synthesis of fused systems with a bridgehead nitrogen atom is one of the most general strategies for constructing complex structures. The strongly polarized triad of atoms, $^{\delta-}$ C'-N⁺-C^{$\delta-$}, gives rise to an ambident reactivity of ylide species toward electrophiles. The reaction can involve both cyclic and acyclic anionic moieties of the ylide structure, the latter pathway being mostly inherent in 1,3-dipolar cycloadditions to activated unsaturated compounds.^[1] For instance, it underlies the indolizine nucleus formation that results from treating 1-(4-oxo-2,4-diphenyl-2-butenyl)pyridinium salts with bases.^[2] The dipnone residue has a twofold effect in this reaction: it acts both as an active methylene site facilitating pyridinium ylide formation and as a dipolarophile. The reported evidence suggests^[3,4] that conversions of this kind are also possible for 1-substituted imidazoles and benzimidazoles. 4-Bromo-1,3-diphenyl-2-buten-1-one (y-bromodipnone) (1), if reacted with heterocyclic bases, readily furnishes quaternary salts already at room temperature.^[2] Accordingly, we started from

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1-R-imidazoles and 1-R-benzimidazoles to obtain, under similar conditions, 3-alkyl-1-(4-oxo-2,4-diphenyl-2-butenyl)-3H-benzimidazol-1-ium bromides (**2a,b**) and 1-R-3-(4-oxo-2,4-diphenyl-2-butenyl)-1H-imidazol-3-ium bromides (**3a–c**) in high yields (74–92%, Scheme 1).

The salts prepared can be cyclized with bases of various strengths. We applied the reagents most commonly used in such syntheses, namely Et_3N , pyridine, morpholine, and K_2CO_3 . Heating salts **2a,b** and **3a–c** with excess Et_3N in acetone for 2 h (a short time compared to that necessary for the cyclization of the analogous pyridinium salts) resulted in two corresponding types of products. On the basis of elemental analysis, it was clear that both of them contained a halogen atom, whereas the supposed structures of their heterocyclic nuclei, pyrrolo[1,2-*a*]benzimidazole and pyrrolo[1,2-*a*]imidazole, were at variance with the measured IR and ¹H NMR spectra. The ¹H NMR spectrum recorded in DMSO-*d*₆ for the product of conversion of 3-methylbenzimidazolium bromide **2a** displayed a signal of the methylene group appearing as an AB spin system (²*J* = 16.0 Hz) at 5.81 ppm and a one-proton singlet at 6.45 ppm. A one-proton singlet observed at 7.67 ppm (in the absorption region of aromatic protons) proved sensitive to the water content



Scheme 1. Pyrido[a]imidazolium salts preparation.

in the solvent (DMSO- d_6/H_2O) and completely exchanged with D₂O. The products resulting from the conversion of compounds **2a,b** and **3a–c** in the presence of pyridine, morpholine, or K₂CO₃ all demonstrated the same feature in their ¹H NMR spectra: the one-proton singlet peaks in the downfield region (8.05–10.18 ppm), which exhibited no exchange with D₂O.

The previously discussed spectral data, along with the mass spectrometric results for the reaction products, suggest the formation of pyrido[2,1-b]benzimidazolium bromide from salts 2a,b and imidazo [1,2-a]pyridinium bromide from salts 3a-c. A highly plausible mechanism for this conversion implies that initially bases induce the formation of benzimidazolium and imidazolium ylides, with the negatively charged atom $C_{(2)}$ of the heterocycle. As the second stage, the ylides cyclize via the addition of the dipnone residue to the carbonyl group. Salt 2a reacts in this way in the presence of Et₃N to afford 9-hydroxy-10-methyl-7,9diphenyl-6H,9H,10H-pyrido[2,1-b]benzimidazol-5-ium bromide (4). The conversion of salts 2a,b and 3a-c in the presence of pyridine, morpholine, or K₂CO₃ involves dehydration, thus leading to aromatic products, 10-alkyl-7,9-diphenyl-10H-pyrido[2,1-b]benzimidazol-5-ium bromides (5a,b) and 1-R-6,8-diphenyl-1*H*-imidazo[1,2-a]pyridin-4-ium bromides (6a-c). The nature of the bases used exerts no significant effect on the yields of salts 5a,b and 6a-c; however, morpholine appears to be the most appropriate reagent (in addition to high yields, it affords the best product purity).

For unequivocal structural determination of the products obtained, the ¹³C NMR spectra of compounds 4, 5b, and 6a were measured, and two-dimensional (2D) homonuclear (COSY) and heteronuclear (HMBC and HMOC) correlation spectroscopy were employed. The ¹³C NMR spectra were edited by the DEPT technique. Moreover, the 2D NOESY experiments were performed to determine the spatial proximity of certain protons. As a result, the spectra of the three structures under study revealed the correlations of the pyridinic protons at positions 8 and 6 (5 and 7 for **6a**). Formation of the fused (benz)imidazopyridine nucleus is corroborated by the spatial proximity of the pyridinic proton 5-H (for 6a) or 8-H (for 5b) to the imidazolic proton 3-H or the benzimidazolic proton 4-H, respectively. Besides, the presence of a hydroxyl group in compound 4 is evidenced by the 2D NOESY spectral data: the negative NOE values are detected for the signals of water protons and the presumably hydroxylic proton (at 7.76 ppm), thus pointing to the exchange process. The data on heteronuclear correlations for compounds 4, 5b, and **6a** (see Table 1) permitted us to completely assign ¹H and ¹³C NMR signals and hence to draw a solid conclusion about the structures concerned. The signal assignments and the structurally significant HMBC correlations (indicated by arrows) are demonstrated in Fig. 1.

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Table 1. Heteronuclear correlations for compounds 4, 5b, and 6a

4				.,	5b			6a
¹ H NMR	HMQC	HMBC	¹ H NMR	HMQC	HMBC	¹ H NMR	HMQC	HMBC
8.32		132.53, 128.09	10.07	126.53	140.0, 139.5, 134.42, 129.57, 127.46	9.54		137.12, 134.78, 134.36, 129.84, 115.84
8.03	114.0	130.72, 127.45	9.01	115.6	133.39, 130.33	8.57		137.12, 129.25
7.80		130.72, 115.0, 114.0	8.46	139.5	140.0, 134.42, 126.53	8.29		137.12, 115.84, 38.10
7.54	129.73	129.6, 126.2, 69.51	8.15	113.4	127.46, 125.67	8.08		137.12, 134.78, 134.04, 126.62
7.49		149.28, 132.53, 129.73, 126.48, 115.0	8.07	128.15	129.96, 129.57, 128.15	7.87	127.80	129.84, 129.77, 127.79
7.45		149.28, 140.9, 129.73, 126.48	7.91	130.52	133.39,115.6	7.65	130.79	130.18, 127.58
7.39		149.28, 140.9, 135.56, 46.11	7.80	125.67	127.46, 113.4	7.59	130.18, 130.07	134.04, 130.79
6.45	125.84		7.75	130.33	130.48, 130.34, 127.06	7.54		134.78
5.81	46.11	149.28, 140.9, 130.73, 129.3, 125.84	7.66	129.45, 130.52	134.42, 130.33, 129.57	7.48		127.79
3.77	33.06	149.28,132.53	7.57	129.96	134.42, 129.96, 128.15	3.45	38.10	137.12, 129.25
			7.50	129.57	128.15			
			4.11	41.42	140.0, 133.39,			
			1.06	14.51	14.51 41.42			



Figure 1. Signal assignments (¹H NMR, δ ; ¹³C NMR, δ) and the structurally significant HMBC correlations for substrances **5b** (A), **4** (B), and **6a** (C).

EXPERIMENTAL

General

¹H and ¹³C NMR spectra were measured on a Varian-400 instrument at 400 and 100 MHz, respectively, using tetramethylsilane as the internal standard. Chemical shifts are reported in ppm. IR spectra were recorded in KBr disks on a Pye Unicam SP3-300 spectrometer. Mass spectra used Agilent 100 series (chemical ionization (CI), acetonytril, 0.05% formic acid). Melting points were determined on a Boetius apparatus and are uncorrected. 4-Bromo-1,3-diphenyl-2-buten-1-one was prepared by the known procedure.^[5]

3-Methyl-1-(4-oxo-2,4-diphenyl-2-butenyl)-3*H*-benzimidazol-1-ium Bromide (2a)

To a solution of γ -bromodypnone **1** (10.7 g, 35.5 mmol) in benzene (50 mL), 1-methyl-1*H*-benzimidazole (4.69 g, 35.5 mmol) was added.

The mixture was left alone at room temperature for 2 days, and the solid precipitated was filtered off, washed thoroughly with benzene and acetone, and crystallized from nitromethane to yield **2a** (14.15 g, 92%) as white crystals. Mp 182–184 °C. IR (KBr): ν 1670 (C=O), 1620 (C=N⁺), 1220, 770 cm⁻¹; ¹H NMR (DMSO-*d*₆): δ 10.17 (s, 1H, 2-H), 8.15 (d, 2H, ³*J* = 8.0 Hz, 2"-H, 6"-H), 8.09 (m, 1H, 7-H), 7.95 (m, 1H, 4-H), 7.80 (m, 2H, 2'-H, 6'-H), 7.70–7.55 (m, 6H, 5-H, 6-H, 3"-H–5"-H, = CHCO-), 7.36 (m, 3H, 3'-H–5'-H), 6.21 (s, 2H, CH₂), 4.10 (s, 3H, CH₃). Anal. calcd. for C₂₄H₂₁BrN₂O: C, 66.52; H, 4.88; Br 18.44; N, 6.46. Found: C, 66.48; H, 4.85; Br, 18.45; N, 6.48.

3-Ethyl-1-(4-oxo-2,4-diphenyl-2-butenyl)-3*H*-benzimidazol-1-ium Bromide (2b)

Compound **2b** was prepared by the procedure described for **2a**, using 5.19 g (35.5 mmol) of 1-ethyl-1*H*-benzimidazole. Yield 12.07 g (76%); mp: 180–182°C (CH₃NO₂); ¹H NMR (DMSO-*d*₆): δ 10.27 (s, 1H, 2-H), 8.14 (d, 2H, ³*J* = 8.0 Hz, 2"-H, 6"-H), 8.04 (m, 1H, 7-H), 7.98 (m, 1H, 4-H), 7.73 (m, 2H, 2'-H, 6'-H), 7.70–7.57 (m, 6H, 5-H, 6-H, 3"-H–5'-H, =CHCO-), 7.33 (m, 3H, 3'-H–5'-H), 6.25 (s, 2H, C⁽¹⁾H₂), 4.53 (q, 2H, ³*J* = 6.5 Hz, C⁽³⁾H₂), 1.45 (t, 3H, ³*J* = 6.5 Hz, CH₃). Anal. calcd. for C₂₅H₂₃BrN₂O: C, 67.12; H, 5.18; Br, 17.86; N, 6.26. Found: C, 67.09; H, 5.14; Br, 17.88; N, 6.25.

1-Methyl-3-(4-oxo-2,4-diphenyl-2-butenyl)-1*H*-imidazol-3-ium Bromide (3a)

Compound **3a** was prepared by the procedure described for **2a**, using 2.91 g (35.5 mmol) of 1-methyl-1*H*-imidazole. Yield 12.92 g (95%); mp: 219–220°C (CH₃NO₂); ¹H NMR (DMSO-*d*₆): δ 10.38 (s, 1H, 2-H), 8.13 (d, 2H, ³*J* = 8.0 Hz, 2"-H, 6"-H), 7.78 (m, 2H, 2"-H, 6'-H), 7.72–7.67 (m, 4H, 4-H, 5-H, =CHCO-, 4"-H), 7.57 (t, 2H, ³J = 7.5 Hz, 3"-H, 5"-H), 7.45 (m, 3H, 3'-H–5'-H), 5.83 (s, 2H, CH₂), 3.88 (s, 3H, CH₃). Anal. calcd. for C₂₀H₁₉BrN₂O: C, 62.67; H, 5.00; Br, 20.85; N, 7.31. Found: C, 62.62; H, 4.93; Br, 20.87; N, 7.35.

1-Ethyl-3-(4-oxo-2,4-diphenyl-2-butenyl)-1H-imidazol-3-ium Bromide (3b)

Compound **3b** was prepared by the procedure described for **2a**, using 3.41 g (35.5 mmol) of 1-ethyl-1*H*-imidazole. Yield 12.27 g (87%); mp: 200–202 °C (CH₃NO₂); IR (KBr): ν 1670 (C=O), 1630 (C=N⁺), 1470,

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1230, 1160, 790, 710 cm⁻¹; ¹H NMR (DMSO-*d*₆): δ 9.56 (s, 1H, 2-H), 8.11 (d, 2H, ³*J* = 7.5 Hz, 2'-H, 6'-H), 7.78 (m, 3H, 4-H, 2'-H, 6'-H), 7.72 (s, 1H, 5-H), 7.67 (t, 1H, ³*J* = 7.5 Hz, 4'-H), 7.62 (s, 1H, =CHCO-), 7.56 (t, 2H, ³*J* = 7.5 Hz, 3'-H, 5'-H), 7.42 (m, 3H, 3'-H-5'-H), 5.87 (s, 2H, C⁽³⁾H₂), 4.22 (q, 2H, ³*J* = 7.0 Hz, C⁽¹⁾H₂), 1.39 (t, 3H, ³*J* = 7.0 Hz, CH₃). Anal. calcd. for C₂₁H₂₁BrN₂O: C, 63.48; H, 5.33; Br, 20.11; N, 7.05. Found: C, 63.42; H, 5.30; Br, 20.13; N, 7.09.

3-(4-Oxo-2,4-diphenyl-2-butenyl)-1-(2-pyridinyl)-1*H*-imidazol-3-ium Bromide (3c)

Compound **3c** was prepared by the procedure described for **2a**, using 5.15 g (35.5 mmol) of 2 (1*H*-imidazol-1-yl)pyridine. Yield 11.72 g (74%); mp: 222–224 °C (CH₃NO₂); ¹H NMR (DMSO-*d*₆): δ 10.46 (s, 1H, 2-H), 8.60 [d, 1H, ³*J* = 4.8 Hz, 6-H(Py)], 8.56 (s, 1H, 5-H), 8.15 [m, 4H, 4-H(Py), 5-H(Py), 2'-H, 6'-H], 8.00 (s, 1H, 4-H), 7.86 (d, 2H, ³*J* = 7.0 Hz, Hz, 2'-H, 6'-H), 7.69 (m, 2H, 4'-H, =CHCO-), 7.59 [m, 3H, 3-H(Py), 3'-H, 5'-H], 7.44 (m, 3H, 3'-H–5'-H), 6.04 (s, 2H, CH₂). Anal. calcd. for C₂₄H₂₀BrN₃O: C, 64.58; H, 4.52; Br, 17.90; N, 9.41. Found: C, 64.53; H, 4.48; Br, 17.91; N, 9.45.

9-Hydroxy-10-methyl-7,9-diphenyl-6*H*,9*H*,10*H*-pyrido[2,1*b*]benzimidazol-5-ium Bromide (4)

The mixture of 3-methyl-benzimidazolium bromide 2a (4.33 g. 10.0 mmol) and Et₃N (15 mL) in acetone (50 mL) was heated under reflux for 2 h, and the solid precipitated after cooling to room temperature was filtered off, washed thoroughly with acetone, and crystallized from acetonitrile to yield 4 (3.55 g, 82%) as white crystals. Mp 287–289°C. IR (KBr): ν 3400 (OH), 1550, 1450, 1060, 760 cm⁻¹; ¹H NMR (DMSO- d_6): δ 8.32 (d, 1H, ${}^{3}J = 8.0$ Hz, 4-H), 8.03 (d, 1H, ${}^{3}J = 8.0$ Hz, 1-H), 7.80-7.74 (m, 5H, 2-H, 3-H, 2'-H, 6'-H, OH), 7.54 (d, 2H, ${}^{3}J = 7.5$ Hz, 2'-H, 6'-H), 7.49–7.39 (m, 6H, 3'-H–5'-H, 3'-H–5'-H), 6.45 (s, 1H, 8-H), 5.81 (dd, 2H, ${}^{2}J = 16.0$ Hz, CH₂), 3.77 (s, 3H, CH₃). ${}^{13}C$ NMR (DMSO- d_6): δ149.28 (C-9a), 140.9 (C-1'), 135.56 (C-1'), 132.53 (C-10a), 130.72 (C-4a), 129.88, 129.73 (2C), 129.6 (2C), 129.4, 129.3 (C-7), 128.09 (C-2), 127.45 (C-3), 126.48 (2C), 126.2 (2C), 125.84 (C-8), 115.0 (C-4), 114.0 (C-1), 69.51 (C-9), 46.11 (C-6), 33.06 (CH₃). MS: m/z 337.2 ([M-Br-OH]⁺, 100%), 338.2 (40%), 353.0 ([M-Br]⁺, 60%). Anal. calcd. for C₂₄H₂₁BrN₂O: C, 66.52; H, 4.88; Br, 18.44; N, 6.46; Found: C, 66.46; H, 4.86; Br, 18.47; N, 6.47.

10-Methyl-7,9-diphenyl-10*H*-pyrido[2,1-*b*]benzimidazol-5-ium Bromide (5a)

of 3-methyl-benzimidazolium bromide The mixture **2a** (4.33 g. 10.0 mmol) and morpholine (15 mL) in acetone (50 mL) was heated under reflux for 2h, and the solid precipitated after cooling to room temperature was filtered off, washed thoroughly with acetone, and crystallized from acetonitrile to yield 5a (3.28 g, 79%) as white crystals. Mp 292-294 °C. IR (KBr): v1620 (C=N⁺), 1530, 1490, 770, 700 cm⁻¹; ¹H NMR (DMSO- d_6): δ 10.13 (s, 1H, 6-H), 9.05 (d, 1H, ${}^{3}J = 8.0$ Hz, 4-H), 8.41 (s, 1H, 8-H), 8.13 (d, 1H, ${}^{3}J = 8.0$ Hz, 1-H), 8.04 (d, 2H, ${}^{3}J = 8.0$ Hz, 2'-H, 6'-H), 7.91 (t, 1H, ${}^{3}J = 8.0$ Hz, 2-H), 7.79 (t, 1H, ${}^{3}J = 8.0$ Hz, 3-H), 7.73 (m, 2H, 2'-H, 6'-H), 7.64 (m, 3H, 3'-H-5'-H), 7.58 (t, 2H, ${}^{3}J = 8.0 \text{ Hz}, 3'-\text{H}, 5'-\text{H}), 7.51 \text{ (t, 1H, } {}^{3}J = 8.0 \text{ Hz}, 4'-\text{H}), 3.65 \text{ (s, 3H, }$ CH₃). MS: m/z 337.2 ([M-Br]⁺, 100%), 339.2 (40%). Anal. calcd. for C₂₄H₁₉BrN₂: C, 69.41; H, 4.61; Br, 19.24; N, 6.72. Found: C, 69.37; H, 4.56; Br, 19.26; N, 6.75.

10-Ethyl-7,9-diphenyl-10H-pyrido[2,1-b]benzimidazol-5-ium Bromide (5b)

Compound 5b was prepared by the procedure described for 4, using 4.47 g (10.0 mmol) of 3-ethyl-benzimidazolium bromide 2b. Yield, 3.09 g (72%); mp: 310–311 °C (CH₃CN); IR (KBr): ν 1620 (C=N⁺), 1500, 1480, 780, 700 cm⁻¹; ¹H NMR (DMSO- d_6): δ 10.07 (s, 1H, 6-H), 9.01 (d, 1H, ${}^{3}J = 8.0$ Hz, 4-H), 8.46 (s, 1H, 8-H), 8.15 (d, 1H, ${}^{3}J = 8.0$ Hz, 1-H), 8.07 (d, 2H, ${}^{3}J = 8.0$ Hz, 2'-H, 6'-H), 7.91 (t, 1H, ${}^{3}J = 8.0$ Hz, 2-H), 7.80 (t, 1H, ${}^{3}J = 8.0$ Hz, 3-H), 7.75 (m, 2H, 2'-H, 6'-H), 7.66 (m, 3H, 3'-H-5'-H), 7.57 (t, 2H, ${}^{3}J = 8.0$ Hz, 3'-H, 5'-H), 7.50 (t, 1H, ${}^{3}J = 8.0$ Hz, 4'-H), 4.11 (q, 2H, ${}^{3}J = 6.8$ Hz, CH₂), 1.06 (t, 3H, ${}^{3}J = 6.8$ Hz, CH₃). ${}^{13}C$ NMR (DMSO- d_6): $\delta 140.0$ (C-9a), 139.5 (C-8), 134.42 (C-1⁷, C-1⁷), 133.39 (C-10a), 130.52 (C-4'), 130.48 (C-2), 130.33 (C-2', C-6'), 129.96 (C-3', C-5'), 129.83 (C-4'), 129.57 (C-7), 129.45 (C-3', C-5'), 128.15 (C-2', C-6'), 127.46 (C-4a), 127.06 (C-9), 126.53 (C-6), 125.67 (C-3), 115.6 (C-4), 113.4 (C-1), 41.42 (CH₂), 14.51 (CH₃). MS: m/z 351.2 ([M-Br]⁺, 100%), 321.0 (20%). Anal. calcd. for $C_{25}H_{21}BrN_2$: C, 69.94; H, 4.93; Br, 18.61; N, 6.52. Found: C, 69.89; H, 4.90; Br, 18.60; N, 6.54.

1-Methyl-6,8-diphenyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium Bromide (6a)

Compound **6a** was prepared by the procedure described for **2a**, using 3.83 g (10.0 mmol) of 1-methyl-imidazolium bromide **3a**. Yield, 3.25 g (89%); mp: 352-354 °C (*i*-PrOH); IR (KBr): ν 1610 (C=N⁺), 1500,

760, 700 cm⁻¹; ¹H NMR (DMSO- d_6): δ 9.54 (s, 1H, 5-H), 8.57 (s, 1H, 3-H), 8.29 (s, 1H, 2-H), 8.08 (s, 1H, 7-H), 7.87 (d, 2H, ${}^{3}J = 7.5$ Hz, 2'-H, 6'-H), 7.65 (m, 2H, 2'-H, 6'-H), 7.59 (m, 3H, 3'-H–5'-H), 7.54 (t, 2H, ${}^{3}J = 7.5$ Hz, 3'-H, 5'-H), 7.48 (t, 1H, ${}^{3}J = 7.5$ Hz, 4'-H), 3.45 (s, 3H, CH₃). ¹³C NMR (DMSO- d_6): δ 137.12 (C-4a), 134.78 (C-1'), 134.36 (C-7), 134.04 (C-1'), 130.79 (C-2', C-6'), 130.18 (C-4'), 130.07 (C-3', C-5'), 129.84 (C-6), 129.77 (C-4'), 129.25 (C-2), 129.1 (C-3', C-5'), 127.79 (C-2', C-6'), 127.58 (C-8), 126.62 (C-5), 115.84 (C-3), 38.10 (CH₃). MS: m/z 285.2 ([M-Br]⁺, 100%), 286.2 (30%). Anal. calcd. for C₂₀H₁₇BrN₂: C, 65.76; H, 4.69; Br, 21.88; N, 7.67. Found: C, 65.72; H, 4.64; Br, 21.90; N, 7.69.

1-Ethyl-6,8-diphenyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium Bromide (6b)

Compound **6b** was prepared by the procedure described for **2a**, using 3.97 g (10.0 mmol) of 1-ethyl-imidazolium bromide **3b**. Yield, 3.3 g (87%); mp: 262–264 °C (*i*-PrOH); ¹H NMR (DMSO-*d*₆): δ 9.73 (s, 1H, 5-H), 8.75 (s, 1H, 3-H), 8.47 (s, 1H, 2-H), 8.05 (s, 1H, 7-H), 7.85 (d, 2H, ³*J* = 7.5 Hz, 2'-H, 6'-H), 7.65 (m, 2H, 2'-H, 6'-H), 7.60 (m, 3H, 3'-H-5'-H), 7.50 (t, 2H, ³*J* = 7.5 Hz, 3'-H, 5'-H), 7.48 (t, 1H, ³*J* = 7.5 Hz, 4'-H), 3.97 (q, 2H, ³*J* = 6.0 Hz, CH₂), 1.11 (t, 3H, ³*J* = 6.0 Hz, CH₃). MS: m/z 299.3 ([M-Br]⁺, 100%), 300.3 (30%). Anal. calcd. for C₂₁H₁₉BrN₂: C, 66.50; H, 5.05; Br, 21.07; N, 7.39. Found: C, 66.45; H, 5.00; Br, 21.10; N, 7.41.

6,8-Diphenyl-1-(2-pyridinyl)-1H-imidazo[1,2-a]pyridin-4-ium Bromide (6c)

Compound **6c** was prepared by the procedure described for **2b**, using 4.46 g (10.0 mmol) of 1-(2-pyridinyl)-imidazolium bromide **3c**. Yield 2.78 g (65%); mp: 295–296 °C (acetone); ¹H NMR (DMSO-*d*₆): δ 9.83 (s, 1H, 5-H), 8.91 (s, 1H, 3-H), 8.58 (s, 1H, 2-H), 8.29 (s, 1H, 7-H), 8.13 [d, 1H, ³*J* = 3.5 Hz, 6-H (Py)], 7.82 (d, 2H, ³*J* = 7.5 Hz, 2'-H, 6'-H), 7.67 [m, 1H, 4-H (Py)], 7.57 (m, 2H, 2'-H, 6'-H), 7.51 [m, 1H, 5-H (Py)], 7.41 [d, 1H, ³*J* = 8.0 Hz, 3-H (Py)], 7.30 (t, 1H, ³*J* = 7.5 Hz, 4'-H), 7.20–7.12 (m, 5H, 3'-H–5'-H, 3'-H, 5'-H). Anal. calcd. for C₂₄H₁₈BrN₃: C, 67.30; H, 4.24; Br, 18.66; N, 9.81. Found: C, 67.28; H, 4.20; Br, 18.66; N, 9.82.

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