Pergamon

Tetrahedron 58 (2002) 10301–10307

TETRAHEDRON

Diastereoselective synthesis of *cis*-fused pyrano and furanobenzopyrans catalyzed by indium trichloride or triphenyl phosphonium perchlorate

Marimuthu Anniyappan, D. Muralidharan and Paramasivan T. Perumal*

Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

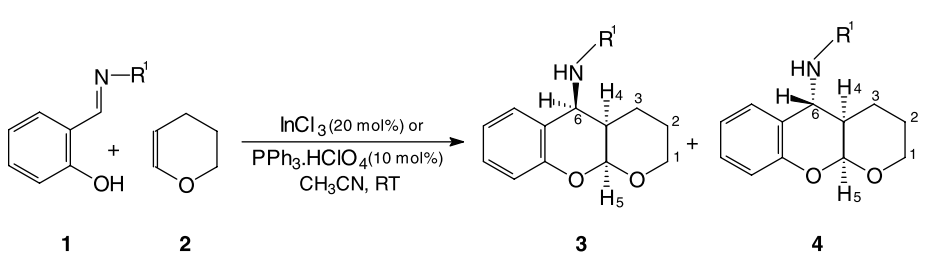
Received 28 August 2002; revised 4 October 2002; accepted 31 October 2002

Abstract—Indium trichloride ($InCl_3$) and triphenyl phosphonium perchlorate (TPP) are found to be effective catalysts for the cyclization of *o*-hydroxyaldimines with 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran at ambient temperature to afford novel pyrano and furanobenzopyran derivatives in excellent yields with high diastereoselectivity. One pot syntheses of pyrano and furanobenzopyrans from *o*-hydroxybenzaldehyde, aromatic amines and an enol ether under identical conditions is reported for the first time. Similarly, *o*-hydroxyaldimine reacted with ethyl vinyl ether to give 2-ethoxy-4-*N*-aryl aminobenzopyran in good yields. © 2002 Published by Elsevier Science Ltd.

1. Introduction

2*H*-1-Benzopyrans (chromenes) and 3,4-dihydro-2*H*-1-benzopyrans (chromans) are important classes of oxygenated heterocycles that have attracted much synthetic interest because of the biological activity of naturally occurring representatives.[1,2] Numerous 4-amino-benzopyrans and their derivatives have drawn considerable attention in the last decade as modulators of potassium channels influencing the activity of the heart and blood pressure.[3] Particularly, fused tetrahydropyrano benzopyran derivatives are frequently found in naturally occurring bioactive molecules. Recently, syntheses of angularly *trans*-fused pyrano benzopyrans by intramolecular 4+2 cycloaddition of *o*-quinonemethides using *p*-toluene-sulfonic acid as catalysts have been reported.[4] Yadav et al.[5] have reported the exclusive formation of the *cis* isomer of *cis*-fused pyrano and furano benzopyran using lithium tetrafluoroborate.

$InCl_3$ has been effectively employed as a catalyst for various transformations, including aldol condensations,[6] imino Diels–Alder reactions,[7] rearrangement of epoxides,[8] Prins-type cyclizations[9] and many other applications in organic synthesis.[10] $InCl_3$ has an edge over other catalysts like $Yb(OTf)_3$ or $Sc(OTf)_3$ as evidenced by the azidolysis of α,β-epoxyl derivatives in water at pH 4, where superior results can be attributed to its water tolerance.[11] Recently, we have reported the application of triphenylphosphonium perchlorate as an excellent catalyst for the imino Diels–Alder reactions[12] and electrophilic substitution reactions of indoles.[13] The TPP is inexpensive, easy to prepare and only 10 mol% is required for the cyclization reaction. In continuation of our interest in the application of $InCl_3$ and TPP, we herein describe a novel and efficient method for the synthesis of chromans using sub-stoichiometric amounts of $InCl_3$ (20 mol%) or TPP (10 mol%) under mild reaction conditions.



Scheme 1.

Keywords: indium trichloride; triphenyl phosphonium perchlorate; cyclization; pyrano and furanobenzopyrans.

* Corresponding author. Tel.: +91-44-4913289; fax: +91-44-4911589; e-mail: ptperumal@hotmail.com

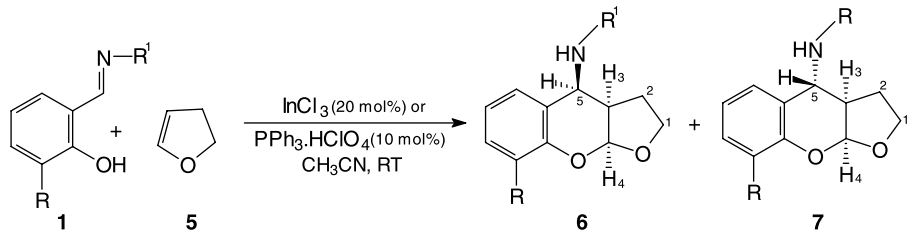
0040–4020/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4020(02)01412-6

Table 1. $InCl_3$ or TPP catalyzed formation of pyranobenzopyrans

Entry	Compound	R^1=	$InCl_3$		TPP		Ratio[a] (**3**/**4**)
			Time (h)	Yield (%)[b] (**3**+**4**)	Time (min)	Yield (%)[b] (**3**+**4**)	
1	**a**	C_6H_5	1	91	10	96	93:07
2	**b**	4-Me–C_6H_4	1.5	85	15	92	90:10
3	**c**	4-Br–C_6H_4	1.5	84	20	90	75:25
4	**d**	4-NO_2–C_6H_4	3	65	40	83	70:30

[a] Ratio of **3** and **4** was based on the ^1H NMR spectrum of product mixture.
[b] The product mixture were isolated by column chromatography.

Treatment of *o*-hydroxyaldimines (**1**) with 3,4-dihydro-2*H*-1-pyran (**2**) in the presence of $InCl_3$ or TPP in acetonitrile at ambient temperature afforded *cis*-fused pyrano chromanes as a mixture of **3** and **4** in 83–96% yields (Scheme 1 and Table 1). Similarly, various substituted salicylaldimines reacted well to give the corresponding *cis*-fused pyrano benzopyrans in good yields (Table 1). The reactions proceeded smoothly at ambient temperature in the presence of $InCl_3$ or TPP to give a non-separable mixture consisting of predominantly diastereoisomers **3** with a trace amount of **4**. However, in the case of substituted *N*-arylimines, the ratio of product **4** increased. The effect was pronounced with bulky substituents like Br and NO_2 (Table 1, entries 3, 4).



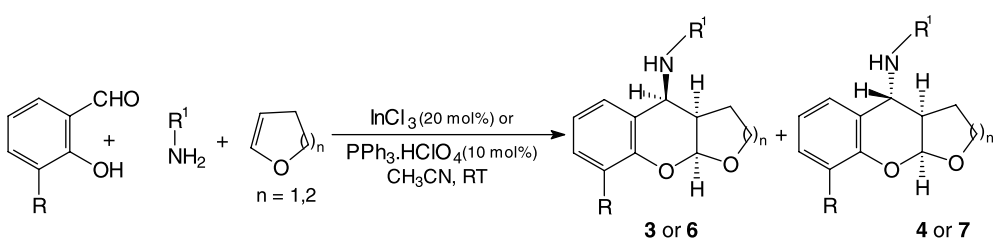
Scheme 2.

Table 2. $InCl_3$ or TPP catalyzed formation of furanobenzopyrans

Entry	R=	R^1=	$InCl_3$		TPP		Ratio[a] (**6**/**7**)
			Time (h)	Yield (%)[b] (**6**+**7**)	Time (min)	Yield (%)[b] (**6**+**7**)	
a	H	C_6H_5	0.5	93	10	98	85:15
b	H	4-Me–C_6H_4	1	89	30	95	80:20
c	H	4-Br–C_6H_4	1.5	87	30	92	78:22
d	OMe	C_6H_5	1.5	83	20	90	85:15

[a] Ratio of **6** and **7** was based on isolated yields.
[b] The products were isolated by column chromatography.

The ratio of **3** and **4** was determined from the ^1H NMR spectra of the products. The stereochemistry of product **3** was assigned based on the coupling constants and NOE studies. The six-membered tetrahydropyran ring is *cis*-fused, as indicated by the coupling constant J_{4-5}=2.5 Hz between H_5 (δ 5.47) and H_4 for **3b**. Also J_{4-6}=1.8 Hz (H_6, δ 4.88) for product **3b** and the presence of an NOE between H_6–H_5 and H_5–H_4, support that H_6 is *cis* to H_4. The product **4** differs from **3** having a different configuration at C_6. This is supported by the coupling constants, as well as the absence of an NOE between H_5–H_6 and H_5–H_4.

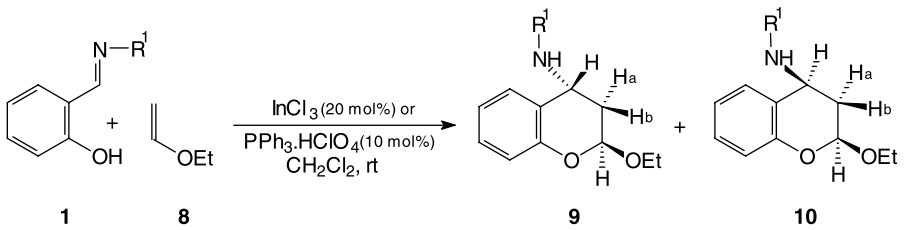


Scheme 3.

Table 3. $InCl_3$ or TPP-catalyzed one pot formation of pyrano and furanobenzopyran

Entry	R=	R^1=	*n*=	$InCl_3$		TPP		Ratio (**3**/**4**) or (**6**/**7**)
				Time (h)	Yield (%)	Time (min)	Yield (%)	
a	H	C_6H_5	1	2	87 (**6**+**7**)[a]	30	91 (**6**+**7**)[a]	83:17[b]
b	H	4-Me–C_6H_4	2	2.5	75 (**3**+**4**)[c]	30	92 (**3**+**4**)[c]	90:10[d]
c	H	4-Br–C_6H_4	1	3	72 (**6**+**7**)[a]	30	90 (**6**+**7**)[a]	77:23[b]
d	H	4-NO_2–C_6H_4	2	3	56 (**3**+**4**)[c]	40	83 (**3**+**4**)[c]	70:30[d]
e	OMe	C_6H_5	1	1.5	71 (**6**+**7**)[a]	30	93 (**6**+**7**)[a]	87:13[b]

[a] The products were isolated by column chromatography.
[b] Ratio of **6** and **7** was based on isolated yields.
[c] The product mixture were isolated by column chromatography.
[d] Ratio of **3** and **4** was based on the ^1H NMR spectrum of the product mixture.



Scheme 4.

Table 4. $InCl_3$ or TPP-catalyzed formation of 2-ethoxy-4-aryl aminobenzopyran

Entry	R^1	$InCl_3$		TPP		Ratio[a] (**9**/**10**)
		Time (h)	Yield (%)[b] (**9**+**10**)	Time (min)	Yield (%)[b] (**9**+**10**)	
a	C_6H_5	1.5	82	30	85	85:15
b	4-Me–C_6H_5	2.5	73	45	76	78:22
c	4-Br–C_6H_5	3	70	50	72	75:25

[a] Ratio of **9** and **10** was based on isolated yields.
[b] The products were isolated by column chromatography.

Extending the methodology further, treatment of *o*-hydroxyaldimines (**1**) with 2,3-dihydrofuran (**5**) in the presence of $InCl_3$ or TPP in acetonitrile at ambient temperature afforded the *cis*-fused furanochromanes as a mixture of diastereoisomers **6** and **7** in high yields (Scheme 2 and Table 2), in contrast to the earlier report that the *cis* isomer was exclusively obtained by using lithium tetrafluoroborate.[5] These diastereoisomers were isolated by column chromatography on silica gel (100–200 mesh) and the stereochemistry of the products was assigned by ^1H NMR spectroscopy based on chemical shift, coupling constant and NOE studies. The six-membered tetrahydropyran and five-membered tetrahydrofuran rings are *cis*-fused, as indicated by the coupling constant J_{3-4}=5.4 Hz between H_4 (δ 5.91) and H_3 for product **6b**. Also J_{3-5}=4.9 Hz (H_5, δ 4.98) for product **6b** and the presence of NOE between H_4–H_3 and H_4–H_5, support that H_5 is *cis* to H_3. The configuration at C_5 differs between **6** and **7** which is supported by the coupling constant of J_{3-4}=4.9 Hz between H_4 (δ 5.59) and H_3. Also J_{3-5}=2.0 Hz (H_5, δ 4.42) for product **7b**, as well as the absence of NOE between H_4–H_5 and H_4–H_3 so that H_5 is *trans* to H_3.

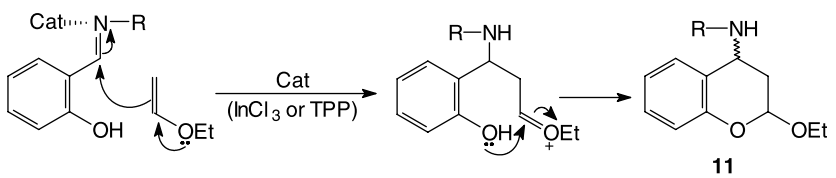
Considering the difficulties encountered with imines in general such as their instability at higher temperatures, the difficulty in purifying them by distillation and column chromatography as well as poor yields, studies were extended to examine the possibility of a one-pot synthesis. The reaction of *o*-hydroxybenzaldehyde, substituted aromatic amines and 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran in acetonitrile at ambient temperature catalyzed by $InCl_3$ or TPP in the presence of anhydrous Na_2SO_4 under mild conditions resulted in comparable yields (83–93%) of the pyrano and furanobenzopyran **3** and **4** or **6** and **7** (Scheme 3 and Table 3).

Furthermore, the reaction between *o*-hydroxyaldimines (**1**) and ethyl vinyl ether (**8**) in dichloromethane using 20 mol% $InCl_3$ or 10 mol% TPP at room temperature (Scheme 4 and Table 4) afforded the corresponding 2-ethoxy-4-*N*-aryl aminobenzo-pyran as a mixture of diastereoisomers **9** and **10** in high yields with high selectivity. These diastereoisomers were isolated by column chromatography on silica gel (100–200 mesh) and the stereochemistry of the products was assigned by ^1H NMR spectroscopy based on the chemical shift and coupling constant.[14]

The reactions probably proceed through activation of the imine by the catalyst followed by addition and subsequent cyclization of the enol ether resulting in the formation of the acetal **11** (Scheme 5).

It is observed that $InCl_3$ and TPP catalyze the reaction to proceed smoothly to yield products with high diastereoselectivity. However, the cyclization under these reaction conditions was hindered when the substituents R^1 group was benzyl, cyclohexyl, methyl and ethyl. The experimental procedure is very simple and the products are obtained in excellent yields with high diastereoselectivity. The choice of catalyst between $InCl_3$ and TPP or the solvent employed in the reaction did not have any significant influence on the ratio of the diastereomers of the products. Salient features of this method are that no side product is formed during the reaction and the products formed are stable, as the reaction conditions employed are mild. The reaction proceeds smoothly to completion within 10–40 min (TPP). It is of interest to note that the reactions of cyclic enol ether and ethyl vinyl ether with aldimines without a hydroxyl group at the *ortho* position gave the corresponding pyrano and furanoquinoline derivatives.[15]

In summary, this paper describes a novel method for the synthesis of linear *cis*-fused pyrano and furanobenzopyrans



Scheme 5.

from salicylaldimines and cyclic enol ethers using substoichiometric amounts of $InCl_3$ or TPP. We have shown that TPP effectively catalyzes the cyclization reaction in shorter reaction times in comparison with $InCl_3$. The catalyst is mild and cheap which has an advantage in that only 10 mol% is required for the reactions. In addition to its efficiency, operational simplicity and mild reaction conditions, this method provides high yields of products more so in the case of TPP with good diastereoselectivity in shorter duration, which makes it a very useful and attractive method for the synthesis of *cis*-fused pyrano and furanochromane derivatives.

2. Experimental

2.1. Material

We prepared the *o*-hydroxybenzaldimines from appropriate *o*-hydroxybenzaldehyde and aniline. The enol ether used was bought from Lancaster. Reagent grade acetonitrile and other solvents were used. The procedure does not require anhydrous solvent and inert atmosphere. All the products obtained were purified by column chromatography using silica gel (Merck, 100–200 mesh). Precautions to be taken to avoid heating of perchlorate salt to dryness considering its explosive nature.

2.2. General

IR measurements were done as KBr pellets for solids or as neat in the case of liquids using Perkin–Elmer Spectrum RXI FT-IR. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with JEOL 400 MHz (model GSX 400) high resolution NMR spectrometer. $CDCl_3$ was used as the solvent for the NMR spectral measurements and spectra were recorded in ppm with TMS as internal standard. The products were analyzed by GC–MS using a Perkin–Elmer Auto System XL Gas Chromatography with Turbo Mass spectrometer (EI, 70 eV), with helium as carrier gas at a flow rate of 1.0 mL/min, Perkin Elmer Elite series PE-5, capillary column (30 m×0.25 mm×1 μm), oven programmed between 100 and 260°C at the rate of 10°C/min. Melting points were determined in capillary tubes and are uncorrected. Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany).

2.3. Preparation of pyrano and furanobenzopyran

General procedure. A mixture of *o*-hydroxybenzaldimine (5 mmol), dihydropyran or dihydrofuran (6 mmol) and indium trichloride (20 mol%) or TPP (10 mol%) in 10 mL of acetonitrile was stirred at ambient temperature for the appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted by addition of water (20 mL) and extracted with ethyl acetate (2×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and the resulting product was purified by column chromatography on silica gel, eluted with ethyl acetate and petroleum ether mixture (10:90) to afford pure *cis*-fused pyrano and furanochromanes obtained as mixtures of **3** and **4** or pure **6** and **7**.

General procedure for one pot synthesis. To a mixture of *o*-hydroxybenzaldehyde (5 mmol), aniline (5 mmol), dihydropyran or dihydrofuran (6 mmol) and anhydrous Na_2SO_4 (1 g) in 20 mL of acetonitrile, indium trichloride (20 mol%) or TPP (10 mol%) was added. The resulting mixture was stirred at ambient temperature for the appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was worked up as described above.

2.3.1. *N*-Phenyl-*N*-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano-[2,3-*b*]chromen-5-ylamine (mixture of 3a and 4a, 1.35 g, 96%). Spectral data for **3a**: IR (KBr) 3347 (NH), 3053, 3029, 2936, 2865, 1602, 1515, 1485, 1311, 1133, 980, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.57–1.67 (m, 2H, H3), 1.87–1.96 (m, 2H, H2), 3.08–3.15 (m, 1H, H4), 3.82–3.95 (m, 3H, H1, including NH), 4.98 (d, 1H, H6, J=4.9 Hz), 5.89 (d, 1H, H5, J=5.4 Hz), 6.74, (d, 2H, J=7.8 Hz), 6.79 (t, 1H, J=7.6 Hz), 6.92–6.98 (m, 2H), 7.19–7.27 (m, 2H), 7.36 (d, 2H, J=7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) δ: 17.1, 24.2, 34.8, 50.9, 60.9, 96.4, 112.6, 113.2, 116.4, 118.1, 121.1, 126.7, 128.9, 129.5, 146.8, 153.1. EIMS: *m*/*z*: 281 (M^+). Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.68; H, 6.94; N, 4.76. For **4a**: ^1H NMR δ: 4.62 (d, 1H, H6, J=2.3 Hz), 5.65 (d, 1H, H5, J=5.4 Hz). ^{13}C NMR δ: 21.7, 24.3, 36.6, 53.3, 61.7, 94.6, 112.6, 117.0, 117.8, 118.0, 121.2, 121.8, 129.5, 130.4, 146.2, 153.0.

2.3.2. *N*-(4-Methylphenyl)-*N*-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromen-5-ylamine (mixture of 3b and 4b, 1.37 g, 92%). Spectral data for **3b**: IR (KBr) 3360 (NH), 3022, 2943, 2917, 2884, 1617, 1584, 1522, 1485, 1134, 972, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.18–1.62 (m, 4H, H2, H2′, H3, H3′), 2.18 (s, 3H, CH_3), 2.38–2.44 (m, 1H, H4), 3.62 (brs, NH, overlapped), 3.62–3.69 (m, 1H, H1), 3.89–3.96 (m, 1H, H1′), 4.88 (d, 1H, H6, J=1.8 Hz), 5.47 (d, 1H, H5, J=2.5 Hz), 6.45 (d, 1H, J=8.3 Hz), 6.55 (d, 2H, J=8.3 Hz), 6.81–6.94 (m, 1H), 6.95 (d, 2H, J=7.8 Hz), 7.11–7.17 (m, 1H), 7.36 (d, 1H, J=7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 17.0, 20.4, 24.1, 34.7, 51.1, 60.9, 96.3, 112.7, 113.3, 116.2, 120.7, 126.7, 127.0, 128.9, 130.0, 144.5, 153.0. EIMS: *m*/*z*: 295 (M^+). Anal. calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.41; H, 7.32; N, 4.53. For **4b**: ^1H NMR δ: 4.17 (d, 1H, H6, J=2.4 Hz), 5.37 (d, 1H, H5, J=2.5 Hz). ^{13}C NMR δ: 16.8, 21.7, 24.3, 36.6, 53.4, 61.7, 94.6, 116.9, 121.1, 121.2, 122.0, 127.2, 129.3, 129.9, 130.3, 144.1, 152.9.

2.3.3. *N*-(4-Bromophenyl)-*N*-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromen-5-ylamine (mixture of 3c and 4c, 1.62 g, 90%). Spectral data for **3c**: IR (KBr) 3398 (NH), 3037, 2940, 1590, 1494, 1310, 1135, 973, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.28–1.69 (m, 4H, H2, H3), 2.42–2.46 (m, 1H, H4), 3.71–3.85 (m, 1H, H1), 3.94–4.03 (m, 1H, H′1), 3.83 (brs, NH), 4.93 (d, 1H, H6, J=4.5 Hz), 5.52 (d, 1H, H5, J=2.3 Hz), 6.45 (d, 1H, J=8.7 Hz), 6.57 (d, 2H, J=8.7 Hz), 6.89 (t, 1H, J=6.3 Hz), 7.21–7.33 (m, 2H), 7.26 (d, 2H, J=6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) δ: 17.1, 19.7, 24.1, 34.7, 51.1, 60.93, 96.2, 109.5, 114.8, 116.5, 121.3, 126.6, 129.1, 132.2, 145.6, 152.3. EIMS: *m*/*z*: 360 (M^+). Anal. calcd for $C_{18}H_{18}BrNO_2$:

C, 60.01; H, 5.04; N, 3.89. Found: C, 60.18; H, 5.24; N, 3.72. For **4c**: ^{1}H NMR δ: 3.99 (brs, 1H, H6), 5.45 (brs, 1H, H5). ^{13}C NMR δ: 19.7, 21.8, 25.4, 30.7, 36.5, 53.2, 62.9, 94.5, 109.1, 114.2, 117.1, 121.3, 123.4, 129.6, 145.2, 152.1.

2.3.4. *N*-(4-Nitrophenyl)-*N*-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromen-5-ylamine (mixture of 3d and 4d, 1.35 g, 83%). Spectral data for **3d**: IR (KBr) 3339 (NH), 3062, 2968, 2930, 2900, 1603, 1538, 1489, 1334, 1269, 1113, 954, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.41–1.67 (m, 4H), 2.41–2.49 (m, 1H, H4), 3.71–3.79 (m, 1H, H1), 3.93–4.01 (m, 1H, H′1), 4.38 (brs. NH), 5.10 (d, 1H, H6, J=5.6 Hz), 5.55 (brs, 1H, H5), 6.54 (d, 1H, J=9.1 Hz), 6.66 (d, 1H, J=9.1 Hz), 6.90–7.25 (m, 4H), 8.11 (d, 2H, J=7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) δ: 17.4, 21.8, 24.1, 35.1, 51.1, 61.1, 96.0, 111.3, 111.6, 116.9, 117.4, 121.5, 126.4, 126.6, 129.7, 153.0. EIMS: *m*/*z*: 326 (M^+). Anal. calcd for $C_{18}H_{18}BrN_2O_4$: C, 60.25; H, 5.56; N, 3.58. Found: C, 60.05; H, 5.78; N, 3.72. For **4d**: ^{1}H NMR δ: 4.39 (d, 1H, H6, J=5.6 Hz), 5.39 (brs, 1H, H5). ^{13}C NMR δ: 17.2, 21.8, 36.9, 52.9, 62.0, 94.4, 95.9, 111.6, 111.9, 117.4, 120.1, 121.5, 126.7, 130.1, 130.2, 152.4.

2.3.5. *N*-Phenyl-*N*-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (6a, 1.11 g, 83%). The title compound was obtained as a colorless solid. Mp 110–112°C; IR (KBr) 3366 (NH), 3024, 2977, 2909, 1600, 1519, 1481, 1226, 1096, 1035, 938, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.49–1.68 (m, 1H, H2), 1.75–1.95 (m, 1H, H′2), 3.05–3.15 (m, 1H, H3), 3.77–3.95 (m, 3H, H1, including NH), 4.96 (brs, 1H, H5), 5.88 (brs, 1H, H4), 6.70–7.20 (m, 8H), 7.34 (d, 1H, J=6.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) δ: 23.9, 43.3, 48.8, 68.0, 102.4, 113.4, 117.2, 118.4, 121.9, 124.6, 126.2, 128.8, 129.6, 147.0, 152.9. EIMS: *m*/*z*: 267 (M^+). Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.62; H, 6.23; N, 5.36.

2.3.6. *N*-Phenyl-*N*-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (7a, 0.20 g, 15%). The title compound was obtained as a colorless solid. Mp 90–92°C; IR (KBr) 3363 (NH), 3022, 2942, 2856, 1601, 1504, 1454, 1224, 1041, 57, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23–1.70 (m, 1H, H2), 2.12–2.19 (m, 1H, H′2), 2.89–2.96 (m, 1H, H3), 3.90 (brs, NH overlapped), 3.91–3.98 (m, 1H, H1), 4.01–4.08 (m, 1H, H′1), 4.51 (brs, 1H, H5,), 5.66 (d, 1H, H4, J=4.7 Hz), 6.63 (d, 2H, J=8.0 Hz), 6.76 (t, 1H, J=7.3 Hz), 6.91–6.95 (m, 2H), 7.16–7.24 (m, 4H).). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) δ: 26.9, 43.3, 50,5, 67.8, 99.9, 113.0, 117.6, 118.1, 121.6, 121.7, 124.2, 129.5, 129.8, 146.3, 152.5. EIMS: *m*/*z*: 267 (M^+). Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.69; H, 6.15; N, 5.19.

2.3.7. *N*-(4-Methylphenyl)-*N*-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (6b, 1.07 g, 76%). the title compound was obtained as a colorless solid. Mp 80–82°C; IR (KBr) 3386 (NH), 2976, 2946, 2860, 1617, 1585, 1520, 1482, 1216, 1034, 979, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.61–1.66 (m, 1H, H2), 1.93–1.95 (m, 1H, H2′), 2.30 (s, 3H, CH_3), 3.11–3.16 (m, 1H, H3), 3.74 (brs, NH), 3.84–3.90 (m, 1H, H1), 3.93–3.97 (m, 1H, H1′), 4.98 (d, 1H, H5, J=4.9 Hz), 5.91 (d, 1H, H4, J=5.4 Hz), 6.70 (d, 2H, J=8.3 Hz), 6.70–6.75 (m, 2H), 7.07 (d, 2H, J=8.3 Hz), 7.22–7.28 (m, 1H), 7.41 (d, 1H, J=7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 20.7, 24.2, 43.5, 49.3, 68.3, 102.6, 113.9, 117.4, 122.1, 125.1, 126.5, 127.9, 129.0, 130.3, 144.9, 153.2. EIMS: *m*/*z*: 281 (M^+). Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.64; H, 6.53; N, 4.76.

2.3.8. *N*-(4-Methylphenyl)-*N*-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (7b, 0.27 g, 19%). The title compound was obtained as a colorless solid. Mp 108–110°C; IR (KBr) 3384 (NH), 3022, 2948, 1613, 1516, 1486, 1309, 1224, 1115, 1044, 955, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.55–1.65 (m, 1H, H2), 2.04–2.12 (m, 1H, H2′), 2.19 (s, 1H, CH_3), 2.82–2.88 (m, 1H, H3), 3.72 (brs, NH), 3.85–3.91 (m, 1H, H1), 3.96–4.01 (m, 1H, H1′), 4.42 (d, 1H, H5, J=2.0 Hz), 5.59 (d, 1H, H4, J=4.9 Hz), 6.50 (d, 2H, J=8.3 Hz), 6.84–6.88 (m, 2H), 6.96 (d, 2H, J=8.3 Hz), 7.14–7.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 20.3, 26.9, 43.2, 50.7, 67.7, 99.8, 113.2, 117.5, 121.6, 121.7, 127.3, 129.6, 129.7, 129.9, 144.0, 152.4; EIMS: *m*/*z*: 281 (M^+). Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.75; H, 6.46; N, 4.89.

2.3.9. *N*-(4-Bromophenyl)-*N*-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (6c, 1.24 g, 72%). The title compound was obtained as a colorless solid. Mp 107–109°C; IR (KBr) 3383 (NH), 3038, 2972, 2891, 1590, 1493, 1308, 1097, 982, 814, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.54–1.83 (m, 1H, H2), 1.90–1.94 (m, 1H, H′2), 3.08–3.14 (m, 1H, H3), 3.84–3.96 (m, 3H, H1, including NH), 4.93 (brs, 1H, H5), 5.90 (d, 1H, H4, J=5.4 Hz), 6.63 (d, 2H, J=8.8 Hz), 6.94–7.00 (m, 2H), 7.22–7.27 (m, 2H), 7.31 (d, 2H, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 24.2, 43.5, 49.2, 68.2, 102.5, 110.0, 115.2, 117.6, 122.2, 124.4, 126.3, 129.2, 132.5, 146.3, 153.2. EIMS: *m*/*z*: 346 (M^+). Anal. calcd for $C_{17}H_{16}BrNO_2$: C, 58.98; H, 4.66; N, 4.05. Found: C, 58.67; H, 4.43; N, 4.25.

2.3.10. *N*-(4-Bromophenyl)-*N*-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (7c, 0.35 g, 20%). The title compound was obtained as a colorless solid. Mp 124–126°C; IR (KBr) 3392 (NH), 3042, 2969, 2895, 1591, 1493, 1311, 1225, 1115, 1044, 955, 813, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.53–1.63 (m, 1H, H2), 2.06–2.08 (m, 1H, H′2), 2.74–2.84 (m, 1H, H3), 3.86–3.96 (m, 3H, H1, including NH), 4.39 (brs, 1H, H5), 5.57 (d, 1H, H4, J=4.9 Hz), 6.44 (d, 2H, J=8.8 Hz), 6.84–7.16 (m, 4H), 7.20 (d, 2H, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 27.2, 43.4, 50.8, 67.9, 100.1, 109.8, 114.8, 117.9, 121.6, 122.0, 129.9, 130.2, 132.4, 145.6, 152.7. EIMS: *m*/*z*: 346 (M^+). Anal. calcd for $C_{17}H_{16}BrNO_2$: C, 58.98; H, 4.66; N, 4.05. Found: C, 58.56; H, 4.57; N, 4.43.

2.3.11. *N*-(8-Methoxy-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-yl)-*N*-phenylamine (6d, 1.14 g, 76%). The title compound was obtained as a colorless solid. Mp 111–113°C; IR (KBr) 3387 (NH), 3049, 2943, 2893, 2837, 1600, 1480, 1273, 1047, 982, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48–1.58 (m, 1H, H2), 1.78–1.86 (m, 1H, H′2),

3.00–3.07 (m, 1H, H3), 3.78 (s, 3H, OCH_3), 3.70–3.86 (m, 3H, H1, including NH), 4.86 (brs, 1H, H5), 5.87 (d, 1H, H4, *J*=5.4 Hz), 6.63 (d, 2H, *J*=7.8 Hz), 6.68 (t, 1H, *J*=7.3 Hz), 6.75 (d, 1H, *J*=7.8 Hz), 6.82 (t, 1H, *J*=7.8 Hz), 6.88 (d, 1H, *J*=7.8 Hz), 7.12 (t, 2H, *J*=8.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 24.0, 43.4, 48.9, 56.0, 67.9, 102.7, 111.3, 113.3, 117.8, 118.2, 121.5, 126.1, 129.4, 141.8, 146.9, 148.5. EIMS: *m/z*: 297 (M^+). Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.98; H, 6.23; N, 4.95.

2.3.12. *N*-(8-Methoxy-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-yl)-*N*-phenylamine (7d, 0.20 g, 14%). The title compound was obtained as a colorless solid. Mp 119–121°C; IR (KBr) 3384 (NH), 3049, 2942, 2897, 2837, 1598, 1485, 1262, 1042, 952, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.57–1.67 (m, 1H, H2), 2.06–2.13 (m, 1H, H′2), 2.84–2.91 (m, 1H, H3), 3.80 (s, 3H, OCH_3), 3.82–3.90 (m, 2H, H1, including NH), 3.98–4.04 (m, 1H, H′1) 4.46 (d, 1H, H5, *J*=2.4 Hz), 5.67 (d, 1H, H4, *J*=4.9 Hz), 6.57 (d, 1H, *J*=7.8 Hz), 6.68 (t, 1H, *J*=7.3 Hz), 6.76–6.89 (m, 5H), 7.13 (t, 1H, *J*=7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 26.9, 43.3, 50.5, 55.9, 67.8, 100.3, 111.5, 112.9, 117.9, 121.2, 122.6, 128.4, 129.4, 141.8, 146.3, 148.6. EIMS: *m/z*: 297 (M^+). Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.76; H, 6.37; N, 4.81.

2.4. General procedure for preparation of 2-ethoxy-4-*N*-aryl amino benzopyran

To a mixture of *o*-hydroxy-benzaldimines (5 mmol) and indium trichloride (20 mol%) or TPP (10 mol%) in 10 mL of dichloromethane, ethyl vinyl ether (6 mmol) was added slowly at 0°C. The resulting reaction mixture was stirred at ambient temperature for an appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2×20 mL). The combined extracts were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100–200 mesh; ethyl acetate–hexane, 5:95) to afford pure *cis*-fused acetal **9** and **10**.

2.4.1. *N*-(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)-*N*-phenylamine (9a, 0.97 g, 72%). The title compound was obtained as a colorless liquid. IR (neat) 3390 (NH), 3048, 2973, 2926, 1600, 1498, 1453, 1308, 1110, 896, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, 3H, *J*=6.84 Hz), 2.13–2.19 (m, 1H), 2.34–2.38 (m, 1H), 3.51–3.59 (m, 1H), 3.84–3.91 (m, 1H), 4.57 (brs, NH), 4.67 (brs, 1H), 5.35 (t, 1H, *J*=2.9 Hz), 6.71–6.76 (m, 3H), 6.89 (d, 1H, *J*=8.3 Hz), 6.94 (t, 1H, *J*=8.0 Hz), 7.18–7.24 (m, 3H), 7.37 (d, 1H, *J*=7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 15.2, 31.5, 45.5, 64.2, 97.2, 114.2, 117.4, 117.9, 121.3, 124.1, 128.9, 129.3, 130.1, 147.4, 151.1. EIMS: *m/z*: 269 (M^+). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.63; H, 7.26; N, 5.03.

2.4.2. *N*-(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)-*N*-phenylamine (10a, 0.17 g, 13%). The title compound was obtained as a colorless liquid. IR (neat) 3395 (NH), 3050, 2974, 2926, 1601, 1494, 1295, 1106, 1018, 894, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (t, 3H, *J*=6.8 Hz), 1.97 (m, 1H), 2.36 (dt, 1H, *J*=6.7, 12.8 Hz), 3.65 (dq, 1H, *J*=6.8, 9.2 Hz), 3.78 (brs, NH), 3.94 (dq, 1H, *J*=6.8, 9.2 Hz), 4.91 (dd, 1H, *J*=5.4, 9.3 Hz), 5.28 (dd, 1H, *J*=2.4, 9.3 Hz), 6.70–6.76 (m, 3H), 6.87 (d, 1H, *J*=8.3 Hz), 6.92 (t, 1H, *J*=7.4 Hz), 7.18–.25 (m, 3H), 7.42 (d, 1H, *J*=7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 15.1, 33.4, 45.1, 64.2, 97.5, 113.0, 117.0, 117.7, 121.1, 124.9, 127.6, 128.8, 129.5, 147.2, 152.2. EIMS: *m/z*: 269 (M^+). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.92; H, 7.09; N, 5.32.

2.4.3. *N*-(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)-*N*-(4-methylphenyl)amine (9b, 0.84 g, 59%). The title compound was obtained as a colorless liquid. IR (neat) 3385 (NH), 3045, 2926, 1605, 1492, 1457, 1304, 1115, 896, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (t, 3H, *J*=6.5 Hz), 2.15–2.23 (m, 1H), 2.26 (s, 3H, CH_3), 2.37–2.41 (m, 1H), 3.53–3.58 (m, 1H), 3.81–3.89 (m, 1H), 4.32 (brs, NH), 4.69 (brs, 1H), 5.37 (t, 1H, *J*=2.8 Hz), 6.72 (d, 2H, *J*=8.4 Hz), 6.70–6.78 (m, 2H), 7.08 (d, 2H, *J*=8.5 Hz), 7.25–7.29 (m, 1H), 7.43 (d, 1H, *J*=7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 15.4, 20.2, 31.4, 45.3, 64.3, 97.3, 114.3, 117.5, 118.9, 121.5, 124.1, 128.9, 129.4, 130.1, 147.5, 151.2. EIMS: *m/z*: 283 (M^+). Anal. calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.52; H, 7.23; N, 4.73.

2.4.4. *N*-(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)-*N*-(4-methylphenyl)amine (10b, 0.24 g, 17%). The title compound was obtained as a colorless liquid. IR (neat) 3392 (NH), 3042, 2924, 1603, 1495, 1453, 1302, 1113, 895, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, 3H, *J*=6.7 Hz), 1.98 (m, 1H), 2.21 (s, 3H, CH_3), 2.35 (dt, 1H, *J*=6.5, 12.5 Hz), 3.64 (dq, 1H, *J*=6.6, 9.4 Hz), 3.79 (brs, NH), 3.95 (dq, 1H, *J*=6.7, 9.4 Hz), 4.92 (dd, 1H, *J*=5.6, 9.4 Hz), 5.26 (dd, 1H, *J*=2.4, 9.4 Hz), 6.62 (d, 2H, *J*=8.5 Hz), 6.72–6.79 (m, 2H), 7.09 (d, 2H, *J*=8.5 Hz), 7.24–7.27 (m, 1H), 7.45 (d, 1H, *J*=7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 15.7, 20.5, 31.8, 45.6, 64.1, 97.2, 114.6, 117.9, 118.4, 121.2, 124.4, 128.3, 129.7, 130.4, 147.6, 151.4. EIMS: *m/z*: 283 (M^+). Anal. calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.46; H, 7.58; N, 4.82.

2.4.5. *N*-(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)-*N*-(4-bromophenyl)amine (9c, 0.94 g, 54%). The title compound was obtained as a colorless solid. Mp 119–121°C. IR (KBr) 3394 (NH), 3026, 2972, 2927, 1589, 1491, 1454, 1304, 1109, 896, 813, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, 3H, *J*=6.5 Hz), 1.93 (m, 1H), 2.36–2.43 (m, 1H), 3.52–3.56 (m, 1H), 3.82–3.87 (m, 1H), 4.30 (brs, NH), 4.73 (brs, 1H), 5.58 (t, 1H, *J*=2.9 Hz), 6.64 (d, 2H, *J*=8.9 Hz), 6.93–7.01 (m, 2H), 7.21–7.29 (m, 2H), 7.32 (d, 2H, *J*=8.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 15.4, 32.5, 45.7, 64.5, 97.2, 114.4, 117.7, 117.9, 122.3, 124.5, 126.3, 129.4, 132.5, 146.4, 153.4. EIMS: *m/z*: 348 (M^+). Anal. calcd for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21; N, 4.02. Found: C, 58.24; H, 5.10; N, 4.24.

2.4.6. *N*-(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)-*N*-(4-bromophenyl)amine (10c, 0.31 g, 18%). The title compound was obtained as a colorless solid. Mp 109–111°C; IR (KBr) 3390 (NH), 3040, 2926, 1607, 1493, 1457, 1303,

1117, 896, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.24 (t, 3H, J=6.8 Hz), 1.92 (m, 1H), 2.34 (dt, 1H, J=6.8, 12.3 Hz), 3.63 (dq, 1H, J=6.8, 9.3 Hz), 3.76 (brs, NH), 3.92 (dq, 1H, J=6.8, 9.3 Hz), 4.91 (dd, 1H, J=5.5, 9.4 Hz), 5.29 (dd, 1H, J=2.5, 9.4 Hz), 6.45 (d, 2H, J=8.9 Hz), 6.85–7.19 (m, 4H), 7.21 (d, 2H, J=8.9 Hz), ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled) δ: 15.3, 33.6, 45.2, 64.3, 97.9, 113.6, 117.2, 117.4, 121.7, 122.3, 129.8, 130.4, 132.6. 145.7, 152.5. EIMS: m/z: 348 (M^+). Anal. calcd for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21; N, 4.02. Found: C, 58.81; H, 5.07; N, 4.14.

Acknowledgements

One of the authors (M. A.) thanks the Council of Scientific and Industrial Research, New Delhi, India for financial support.

References

1. (a) Schweizer, E. E.; Meeder-Nycz, O. In *Chromenes, Chromanes, Chromones*; Ellis, G. P., Ed.; Wiley-Interscience: New York, 1977; pp 11–139. (b) Bowers, W. S.; Ohta, T.; Cleere, J. S.; Marsella, P. A. *Science* **1976**, *193*, 542.
2. Hepworth, J. *Comprehensive Heterocyclic Chemistry*; Katrizky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 3, pp 737–883.
3. (a) Rovnyak, G. C.; Ahmed, S. Z.; Ding, C. Z.; Dzwonczyk, S.; Ferrara, F. N.; Humphreys, W. G.; Grover, G. J.; Santafianos, D.; Atwal, K. S.; Baird, A. J.; McLaughin, L. G.; Normandin, D. E.; Sleph, P. G.; Traeger, S. C. *J. Med. Chem.* **1997**, *40*, 24. (b) Evans, J. M.; Fake, C. S.; Hamilton, T. C.; Poyser, R. H.; Watts, E. A. *J. Med. Chem.* **1983**, *26*, 1582. (c) Buckle, D. R.; Arch, J. R. S.; Fenwick, A. E.; Hough-Frydrych, C. S. V.; Pinto, I. L.; Smith, D. G.; Taylor, S. G.; Tedder, J. M. *J. Med. Chem.* **1990**, *33*, 3028.
4. Miyazaki, H.; Honda, K.; Asami, M.; Inouse, S. *J. Org. Chem.* **1999**, *64*, 9507.
5. Yadav, J. S.; Subba Reddy, B. V.; Madhuri, Ch.; Sabitha, G.; Jagannath, B.; Kirankumar, S.; Kunwar, A. C. *Tetrahedron Lett.* **2001**, *42*, 6381–6384.
6. (a) Mukaiyama, T.; Ohno, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.* **1991**, 949. (b) Mukaiyama, T. *Org. React.* **1982**, *28*, 203. (c) Loh, T. P.; Pei, J.; Lin, M. *Chem. Commun.* **1996**, 2315. (d) Kobayashi, S.; Busujima, T.; Nagayama, S. *Tetrahedron Lett.* **1998**, *39*, 1579.
7. (a) Babu, G.; Perumal, P. T. *Tetrahedron Lett.* **1997**, *38*, 5025. (b) Babu, G.; Perumal, P. T. *Tetrahedron* **1998**, *54*, 1627. (c) Babu, G.; Nagarajan, R.; Perumal, P. T. *Synthesis* **2000**, 661. (d) Hadden, M.; Stevenson, P. J. *Tetrahedron Lett.* **1999**, *40*, 1215.
8. Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212.
9. Yang, J.; Viswanathan, G. S.; Li, C. J. *Tetrahedron Lett.* **1999**, *40*, 1627.
10. Ranu, B. C.; Hajra, A.; Jana, U. *J. Org. Chem.* **2000**, *65*, 6270.
11. Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.* **2001**, *66*, 3554.
12. Nagarajan, R.; Chitra, S.; Perumal, P. T. *Tetrahedon* **2001**, *57*, 3419.
13. Nagarajan, R.; Perumal, P. T. *Synth. Commun.* **2002**, *32*, 105.
14. Yadav, J. S.; Subba Reddy, B. V.; Aruna, M.; Venugopal, C.; Ramalingam, T.; Kiran Kumar, S.; Kunwar, A. C. *J. Chem. Soc., Perkin Trans. 1* **2002**, 165–171.
15. (a) Babu, G.; Perumal, P. T. *Tetrahedron Lett.* **1998**, *39*, 3225. (b) Sundararajan, G.; Prabagaran, N.; Varghese, B. *Org. Lett.* **2001**, *3*, 1973–1976.