Pergamon

Tetrahedron 55 (1999) 4793–4802

TETRAHEDRON

A novel synthesis of indolyl and benzo[*b*]thienyl imines and Diels-Alder reactions promoted by indium trichloride

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Received 23 November 1998; revised 19 January 1999; accepted 11 February 1999

Abstract

Anhydrous indium trichloride is found to catalyze the reaction of Schiff's bases derived from substituted anilines with 3-chloro-1*H*-indole-2-carboxaldehyde and 3-chlorobenzo[*b*]thiophene-2-carboxaldehyde which resulted in new route to indolyl and benzo[*b*]thienyl imines. These imines reacted with cyclopentadiene and 3,4-dihydro-2*H*-pyran to afford new quinoline derivatives in good yields.

Key words: catalysts; Diels-Alder reactions; imines; quinolines

Introdution

The Diels-Alder reaction of imines is a powerful synthetic method for the construction of nitrogen heterocycles[1,2]. We have recently reported an efficient synthesis of quinoline derivatives[3-5] by imino Diels-Alder reaction of Schiff's bases catalyzed by indium trichloride. In continuation of our research in imino Diels-Alder reactions, we examined the synthesis of β-carboline derivatives by imino Diels-Alder reaction of Schiff's bases catalyzed by indium trichloride. β-Carboline derivatives possess a wide range of biological activities. β-Carboline derivatives are most commonly synthesized by Pictet-Spengler reaction[6-8], although a few reports[9-11] are available for the construction of β-carboline derivatives by cycloaddition reactions.

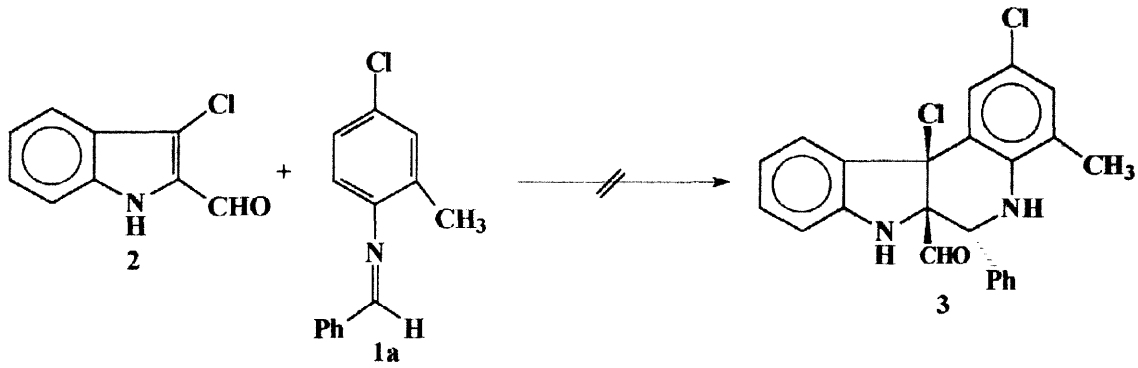
In this paper we describe the results obtained in an attempt to synthesize β-carboline derivatives by the reaction of Schiff's bases **1** with 3-chloro-1*H*-indole-2-carboxaldehyde **2** or with 3-chlorobenzo[*b*]thiophene-2-carboxaldehyde **5** and the synthesis of new quinoline derivatives by the imino Diels-Alder reaction of the newly formed imines with cyclopentadiene and 3,4-dihydro-2*H*-pyran catalyzed by indium trichloride.

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00151-9

Results and Discussion

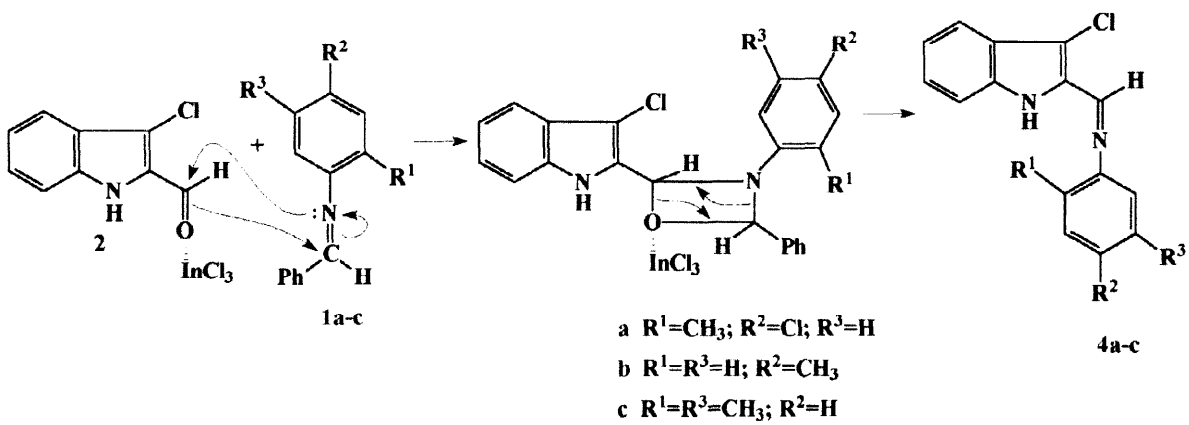
N-Benzylidene 4-chloro-2-methylaniline **1a** was treated with 3-chloro-1*H*-indole-2-carboxaldehyde **2** in the presence of 20 mol % indium trichloride and stirred at room temperature . After 2 h, new product was obtained in 75 % yield. We expected the formation of β-carboline derivative **3** (Scheme 1) , but examination of the spectral data revealed the formation of indolyl imine **4a** instead.

Scheme 1



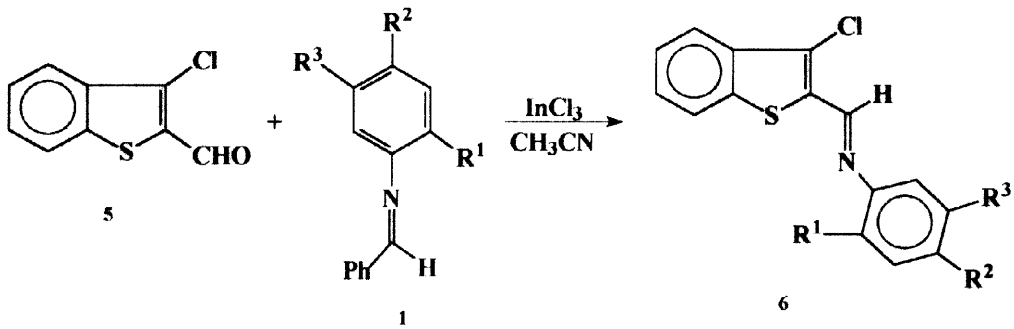
The structure of the product was confirmed by single crystal x-ray analysis [12]. The formation of an imines **4** by the reaction of an imines **1** with aldehydes was not reported in the literature. The above reaction is a simple and mild method for the preparation of indolyl imines; previously these were prepared by reacting aromatic amines with indole-3-carboxaldehyde which requires refluxing in toluene [13].The reaction may proceed through the coordination of indium trichloride with the carbonyl group of **2** and subsequent reaction with Schiff's bases **1** to form an oxazetidine intermediate which then forms the imines **4** as outlined in Scheme 2. Similar results were obtained with other Schiff's bases (Table 1).

Scheme 2



When we treated 3-chlorobenzo[*b*]thiophene-2-carboxaldehyde **5** in acetonitrile with *N*-benzylidene 4-chloro-2-methylaniline **1a** in the presence of indium trichloride, imine **6a** was obtained in 70 % yield (Scheme 3). Similar results were obtained with other Schiff's bases and the results are summarized in Table 1.

Scheme 3



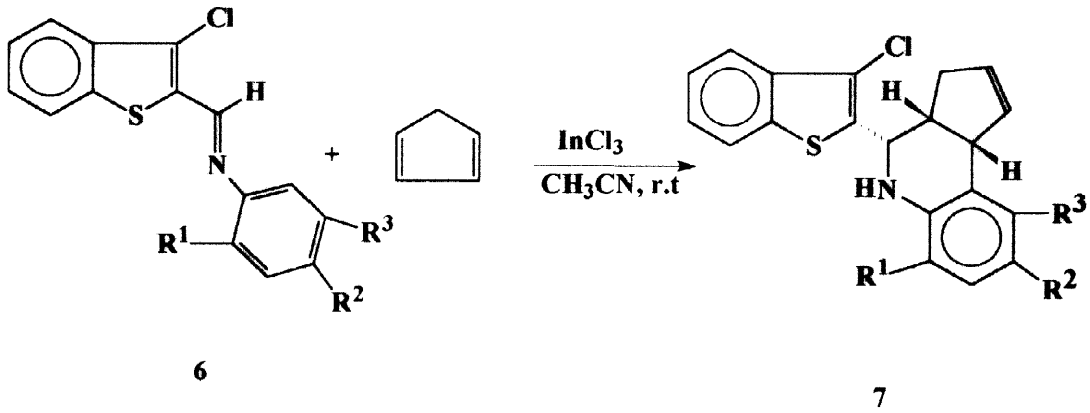
Next, we examined the reaction of the newly formed benzo[b]thienyl imine as a diene component for the imino Diels-Alder reaction with cyclopentadiene catalyzed by indium trichloride. Thus, imine **6b** in acetonitrile was treated with cyclopentadiene in the presence of

Table 1. Synthesis of indolyl and benzo[*b*]thienyl imines employing 20 mol % $InCl_3$.

Entry	Aldehyde	Schiff's base	Product	Substituents			Time(h)	Yield(%)
				R^1	R^2	R^3		
1	**2a**	**1a**	**4a**	CH_3	Cl	H	2	75
2	**2b**	**1b**	**4b**	H	CH_3	H	2	75
3	**2c**	**1c**	**4c**	CH_3	H	CH_3	2	75
4	**5a**	**1a**	**6a**	CH_3	Cl	H	1	70
5	**5b**	**1b**	**6b**	H	CH_3	H	1	80
6	**5c**	**1c**	**6c**	CH_3	H	CH_3	2	65
7	**5d**	**1d**	**6d**	H	Cl	H	1	75
8	**5e**	**1e**	**6e**	H	H	H	1	76

20 mol % indium trichloride and stirred at room temperature (Scheme 4). After 1 h the reaction afforded the anticipated quinoline derivative **7b** in 82 % yield. The results obtained with other imines are summarized in Table 2.

Scheme 4



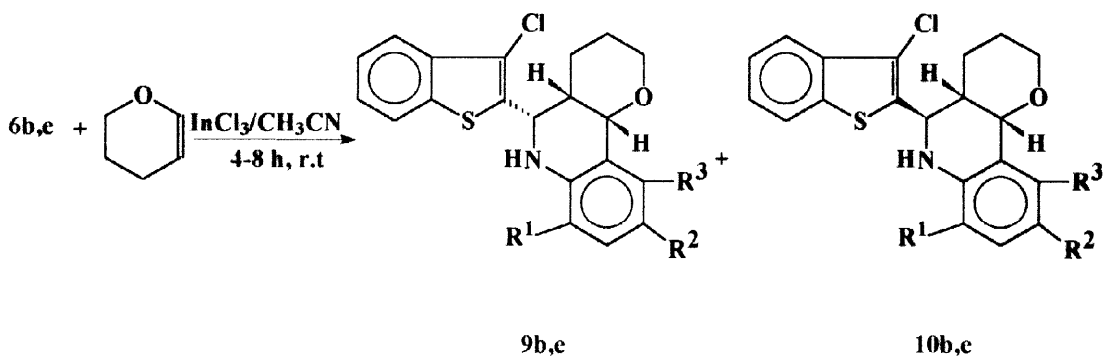
6 7

Table 2. Synthesis of Cyclopentaquinolines employing 20 mol % $InCl_3$.

Entry	Schiff's base	Product	Substituents			Yield(%)
	6	7	R^1	R^2	R^3	
1	a	a	CH_3	Cl	H	85
2	b	b	H	CH_3	H	82
3	d	d	H	Cl	H	92
4	e	e	H	H	H	81

When we treated imine **6b** with 3,4-dihydro-2*H*-pyran **8** in the presence of 20 mol % $InCl_3$, after 8 h pyranoquinolines **9b** and **10b** were obtained in a ratio of 68 : 32 in an overall yield of 57 %. In the case of imine **6e**, pyranoquinolines **9e** and **10e** were obtained in a ratio of 46 : 54 in an overall yield of 55% (Scheme 5).

Scheme 5



9b,e 10b,e

In conclusion, we have shown that indium trichloride catalyzes the synthesis of indolyl and benzo[*b*]thienyl imines and their Diels-Alder reaction with cyclopentadiene and 3,4-dihydro-2*H*-pyran to afford new quinoline derivatives.

Experimental

Mass spectra were recorded on Varian VG 70-70H mass spectrometer. Melting points were measured in capillary tubes and are uncorrected. Analytical thin layer chromatography was performed on precoated sheets of silica gel G of 0.25 mm thickness containing PF 254 indicator (Merck, Darmstadt). Column chromatography was performed with silica gel (60-120 mesh; SD Fine, Boisar). IR spectra were recorded as solids in KBr pellets on Nicolet Impact-400 spectrometer. NMR spectra were obtained on a Bruker spectrometer. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and the chemical shifts are given in δ relative to the internal standard TMS. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ and the chemical shift was given in δ relative to the solvent (77.0). Acetonitrile was distilled from calcium hydride and dried over 4 Å molecular sieves. The Schiff's bases were prepared according to the published procedure by the condensation of substited anilines with benzaldehyde [14]. 3-Chloro-1*H*-indole-2-carboxaldehyde and 3-chlorobenzo[*b*]thiophene-2-carboxaldehyde were prepared according to the procedure reported from our laboratory[15].

General procedure for the synthesis of 3-chloro-2-[*N*-(aryl)formimidoyl]indoles

To a stirred solution of Schiff's base **1a-c** (1 mmol) and 3-chloro-1*H*-indole-2-carboxaldehyde (1 mmol) in acetonitrile (7 ml) protected by guard tube was added indium trichloride (0.044 g, 20 mol %) and stirred at room temperature for 2 h. To the reaction mixture water (10 ml) was added and refrigerated for 30 min. The product obtained, was suction filtered and recrystallised from chloroform to afford pure formimidoyl indoles **4a-c.**

3-Chloro-2-[*N*-(4-chloro-2-methylphenyl)formimidoyl]indole(4a)

0.226 g (75%) of yellow solid ; Mp.155-156 °C; IR(KBr)3420, 2922, 1604, 1477, 1335, 745 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.52 (s, 1H), 7.68 (d, 1H, J = 7.8 Hz), 7.35-7.15 (m, 5H), 6.99 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 146.6, 135.1, 133.7, 130.9, 129.7, 126.2, 125.7, 125.4, 120.3, 118.7, 118.3, 112.1, 111.9, 111.2, 17.3; MS *m/z* 304, 302 (M^+); Anal. Calcd. for $C_{16}H_{12}Cl_2N_2$ C, 63.38; H, 3.99; N, 9.24. Found C, 63.70; H, 3.97; N, 9.29.

3-Chloro-2-[*N*-(4-methylphenyl)formimidoyl]indole (4b)

0.201 g (75%) of yellow solid; Mp.132-133 °C; IR(KBr) 3418, 2924, 1608, 1465 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (br s, 1H), 8.71 (s, 1H), 7.73-7.14 (m, 8H), 2.38 (s, 3H); ^{13}CNMR(75MHz, $CDCl_3$) δ 148.0, 146.6, 136.6, 135.8, 130.5, 129.9,128.3,126.0,121.0,120.7, 120.4, 119.1, 111.8, 21.0; MS *m/z* 268 (M^+), 270 (M+2); Anal. Calcd. for $C_{16}H_{13}ClN_2$ C, 71.51; H, 4.88; N, 10.42. Found C, 71.15; H, 4.86; N, 10.37.

3-Chloro-2-[*N*-(2,5-dimethylphenyl)formimidoyl]indole (4c)

0210 g (75%) of yellow solid ; Mp.152-53 °C; IR(KBr) 3415, 2928, 1612, 1470 cm^{-1}; ^1H (300 MHz, $CDCl_3$) δ 9.58 (br s, 1H), 8.58 (s, 1H), 7.70 (d, 1H, J = 7.6 Hz), 7.67-6.91 (m, 6H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 146.4, 135.9, 135.0, 129.9, 129.8, 128.6, 126.4, 125.4, 120.2, 118.6, 117.9, 112.2, 20.4, 16.9; MS *m/z* 284, 282 (M^+); Anal. Calcd. for $C_{17}H_{15}ClN_2$ C, 72.21; H, 5.35; N, 9.91. Found C, 72.57; H, 5.32; N, 9.96.

General procedure for the synthesis of 3-chloro-2-[*N*-(aryl)formimidoyl] benzo[*b*]thiphenes

To a stirred solution of Schiff's base **1a-e** (1 mmol) and 3-chlorobenzo[*b*]thiophene-2-carboxaldehyde **5** (0.197 g, 1 mmol) in acetonitrile (7 ml) protected by guard tube was added indium trichloride (0.044 g, 20 mol %) and stirred at room temperature for 1-2 h. Water (10 ml) was added and the mixture was refrigerated for 30 min. The product obtained was filtered and recrystallised from chloroform to afford pure formimidoyl benzo[*b*]thiophenes **6a-e.**

3-Chloro-2-[*N*-(4-chloro-2-methylphenyl)formimidoyl]benzo[*b*]thiophene (6a)

0.223 g (70%) of yellow solid; Mp.140-141 °C; IR(KBr) 3035, 2924, 1613, 1575, 1510, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.91-7.79 (m, 2H), 7.53-7.43 (m, 2H), 7.24 (m, 2H), 6.98 (d, 1H, J = 8.3 Hz), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ151.2, 149.3, 139.5, 137.2, 135.1, 134.8, 131.7, 130.3, 127.6, 126.6, 125.2, 122.9, 122.5, 119.3, 118.6, 18.4; MS *m/z* 321, 319(M^+); Anal.Calcd. for $C_{16}H_{11}Cl_2NS$ C, 60.00; H, 3.46; N, 4.37. Found C, 59.71; H, 3.48; N, 4.35.

3-Chloro-2-[*N*-(4-methylphenyl)formimidoyl]benzo[*b*]thiophene *(6b)*

0.228 g (80%) of yellow solid ; Mp.134-36 °C; IR(KBr) 3025, 2922, 2851, 1611, 1579, 1508, 1314, 754 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.89-7.79 (m, 2H), 7.46-7.18 (m, 6H), 2.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 148.2, 138.5, 136.9, 136.8, 135.7, 129.7, 127.4, 125.1, 122.9, 122.8, 122.3, 121.1, 21.0; MS *m/z* 287, 285(M^+); Anal.Calcd. for $C_{16}H_{12}ClNS$ C, 67.24; H, 4.23; N, 4.90. Found C, 66.91; H, 4.25; N, 4.88.

3-Chloro-2-[*N*-(2,5-dimethylphenyl)formimidoyl]benzo[*b*]thiophene (6c*)*

0.194 g (65%) of yellow solid ; Mp.111-113 °C; IR(KBr) 2960, 2928, 1728, 1609, 1498, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.89-7.81 (m, 2H), 7.46 (d, 2H, J = 4.0 Hz), 7.12-6.84 (m, 3H), 2.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 149.6, 138.7, 136.9, 136.2, 136.1, 130.2, 129.6, 127.3, 127.2, 125.1, 124.9, 122.8, 122.4, 118.1, 20.9, 17.3; MS *m/z* 301, 299 (M^+); Anal. Calcd. for $C_{17}H_{14}ClNS$ C, 68.10; H, 4.70; N, 4.67.Found C, 68.44; H, 4.68; N, 4.70.

3-Chloro-2-[*N*-(4-chlorophenyl)formimidoyl]benzo[*b*]thiophene (6d)

0.228 g (75%) of yellow solid ; Mp.129-130 °C; IR(KBr) 3048, 2925, 1665, 1612, 1584, 748cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.87-7.76 (m, 2H), 7.49-7.19 (m, 6H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 149.2, 138.7, 136.8, 135.2, 132.3, 129.8, 127.7, 126.0, 125.2, 122.9, 122.5; MS *m/z* 307, 305 (M^+); Anal. Calcd. for $C_{15}H_9Cl_2NS$ C, 58.84;H, 2.96; N, 4.57. Found C, 58.54; H, 2.95; N, 4.60.

3-Chloro-2-[*N*-(phenyl)formimidoyl]benzo[*b*]thiophene (6e)

0.205 g (76%) of yellow solid ;Mp.67-68 °C; IR(KBr) 3050, 2923, 1667, 1610, 1582, 1317, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.98-7.77 (m, 2H), 7.55-7.22 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 150.8, 138.6, 136.6, 136.8, 129.1, 127.5, 126.8, 125.7, 125.1, 123.6, 122.4, 120.2; MS *m/z* 271 (M^+); Anal. Calcd. for $C_{15}H_{10}ClNS$ C, 66.29; H, 3.71; N, 5.15. Found C, 65.96; H, 3.73; N, 5.13.

General procedure for the Diels-Alder reaction of 3-chloro-2-[*N*-(aryl)formimidoyl]benzo[*b*]thiophenes with cyclopentadiene

To a stirred solution of Schiff's base **6a-e** (1 mmol) and cyclopentadiene (0.132 g, 2 mmol) in acetonitrile (7 ml) protected by guard tube was added indium trichloride (0.044 g, 20 mol %) and stirred at room temperature for 1 h. To the reaction mixture aqueous sodium carbonate solution (5 ml) was added and extracted with chloroform (3 x 10 ml). The combined organic layer was washed with water (10 ml) and brine (10 ml), dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel and eluted with petroleum ether : ethyl acetate (95:5) to afford the quinolines **7a-e.**

8-Chloro-4-(3-chlorobenzo[b]thien-2-yl)-6-methyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (7a)

0.327 g (85%) of yellow solid ; Mp.154-155 °C; IR(KBr) 3340, 2925, 1508, 1249 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.49 (m, 2H), 6.94 (s, 1H), 6.89 (s, 1H), 5.84 (m, 1H), 5.71 (m, 1H), 5.23 (d, 1H, *J* = 2.7 Hz), 4.15 (d, 1H, *J* = 8.4 Hz), 3.83 (br s, 1H, NH), 3.26 (m, 1H), 2.85 (m, 1H), 2.13 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 139.1, 136.6, 136.5, 133.5, 130.6, 127.6, 127.3, 126.9, 126.3, 125.2, 124.9, 124.8, 123.5, 122.9, 117.3, 116.9, 52.8, 45.9, 42.6, 32.1, 17.0; MS *m/z* 387, 385 (M^+); Anal. Calcd. for $C_{21}H_{17}Cl_2NS$ C, 65.28; H, 4.43; N, 3.62 . Found C, 64.96; H, 4.41; N, 364.

4-(3-Chlorobenzo[*b*]thien-2-yl)-8-methyl-,3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (7b)

0.287 g (82%) of yellow solid; Mp.131-132 °C; IR(KBr) 3342, 2920, 1501, 1249 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (m, 2H), 7.49 (m, 2H), 6.96 (s, 1H), 6.90 (d, 1H, *J* = 8.0 Hz), 6.62 (d, 1H, *J* = 8.0 Hz), 5.95 (br s, 1H), 5.76 (br s, 1H), 5.25 (d, 1H, *J* = 3.0 Hz), 4.18 (d, 1H, *J* = 8.4 Hz), 3.82 (br s, 1H, NH), 3.32 (m, 1H), 2.94 (m, 1H), 2.32 (s, 3H), 2.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 139.5, 136.6, 136.5, 133.6, 130.2, 129.3, 129.0, 127.0, 125.8, 124.9, 124.7, 122.4, 121.1, 116.4, 116.2, 52.9, 45.7, 42.8, 32.0, 20.5; MS *m/z*

353, 351 (M^+); Anal. Calcd. for $C_{21}H_{18}ClNS$ C, 71.68; H, 5.16; N, 3.98; Found C,72.04; H, 5.13; N, 3.96.

8-Chloro-4-(3-chlorobenzo[*b*]thien-2-yl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (7d)

0.333 g (92%) of colourless solid ; Mp.109-110 °C; IR(KBr) 3336, 2927, 1488, 1254, 754 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (m, 2H), 7.52 (m, 2H), 7.05 (d, 1H, J = 1.7 Hz), 6.96 (dd, 1H, J = 8.0, 3.0 Hz), 6.56 (d, 1H, J = 8.5 Hz), 5.84 (m, 1H), 5.71 (m, 1H), 5.19 (d, 1H, J = 3.1 Hz), 4.10 (d, 1H, J = 8.3 Hz), 3.91 (br s, 1H, NH), 3.27 (m, 1H), 2.83 (m, 1H), 2.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 138.7, 136.6, 136.5, 133.0, 130.7, 129.2, 128.9, 127.6, 126.4, 125.5, 124.2, 122.5, 121.8, 117.3, 116.8, 52.8, 45.6, 42.6, 32.1; MS *m/z* 373,371 (M^+); Anal. Calcd. for $C_{20}H_{15}Cl_2NS$ C, 64.52; H, 4.06; N, 3.76. Found C, 64.84; H, 4.08; N, 3.74.

4-(3-Chlorobenzo[*b*]thien-2-yl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (7e)

0.273 g (81%) of colourless solid ; Mp. 96-97°C; IR(KBr) 3340, 2928, 1490, 1252, 750 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.82 (m, 2H), 7.08 (m, 2H), 6.85 (m, 1H), 6.67 (d, 1H, J = 7.9 Hz), 5.90 (br s, 1H), 5.71 (br s, 1H), 5.24 (d, 1H, J = 2.9 Hz), 4.27 (m, 1H), 3.83 (br s, 1H, NH), 3.30 (m, 1H), 2.89 (m, 1H), 2.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 139.3, 136.7, 136.5, 130.8, 130.3, 129.2, 126.3, 125.0, 124.8, 123.6, 122.5, 121.2, 119.9, 116.6, 116.2, 52.8, 45.7, 42.9, 32.2; MS *m/z* 339,337(M^+);Anal.Calcd.for$C_{20}H_{16}ClNS$ C, 71.10; H, 4.77; N, 4.15. Found C, 71.45; H, 4.75; N, 4.17.

General procedure for the Diels-Alder reaction of 3-chloro-2-[*N*-(aryl)formimidoyl]benzo[*b*]thiophenes with 3,4-dihydro-2*H*-pyran

To a stirred solution of Schiff's base **6b,e** (2.5 mmol) and 3,4-dihydro-2*H*-pyran (0.294 g, 3.75 mmol) in acetonitrile (10 ml) protected by guard tube was added indium trichloride (0.110 g, 20 mol %) and stirred at room temperature for 4-8 h. Aqueous sodium carbonate solution (10 ml) was added and the reaction mixture extracted with chloroform (3 x 10 ml). The combined organic layer was washed with water (10 ml) and brine (10 ml), dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel and eluted with petroleum ether : ethyl acetate (95:5) to afford the quinolines **9b,e** and **10b,e.**

(4aα,5β,10bα)-5-[3-chlorobenzo[b]thien-2-yl]-3,4,4a,5,6,10b-hexahydro-9-methyl-2*H*-pyrano[3,2-c]quinoline (9b)

0.359 g (39%) of colourless solid ; Mp.145-146 °C; IR(KBr) 3377, 2916, 2851, 1504, 1252 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 2H), 7.53-7.21 (m, 3H), 6.93 (d, 1H, J = 7.8 Hz), 6.57 (d, 1H, J = 8.0 Hz), 5.30 (d, 1H, J = 5.1 Hz), 5.16 (d, 1H, J = 1.3 Hz), 3.98 (br s, 1H, NH), 3.61-3.41 (m, 2H), 2.55 (m, 1H), 2.28 (s, 3H), 1.66-1.47 (m, 4H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 141.7, 138.6, 136.8, 136.5, 128.6, 127.4, 125.8, 125.0, 124.8, 122.4, 121.1, 120.5, 116.5, 115.1, 71.8, 60.6, 54.3, 36.4, 25.2, 20.6, 18.9; MS *m/z* 371,369(M^+); Anal. Calcd. for $C_{21}H_{20}ClNOS$ C, 68.19; H, 5.45; N, 3.79. Found C, 67.85; H, 5.42; N, 3.81.

(4aα,5α,10bα)-5-[3-chlorobenzo[*b*]thien-2-yl]-3,4,4a,5,6,10b-hexahydro-9-methyl-2*H*-pyrano[3,2-c]quinoline (10b)

0.166 g (18%) of colourless solid ; Mp.105-106 °C ; IR(KBr) 3404, 3360, 2924, 2851, 1505, 1256 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.57-7.38 (m, 2H), 7.24 (m, 1H), 7.10 (s, 1H), 6.94 (d, 1H, *J* = 8.1 Hz), 6.51 (d, 1H, *J* = 8.1 Hz), 5.41 (d, 1H, *J* = 10.8 Hz), 4.39 (d, 1H, *J* = 2.5 Hz), 4.14 (m, 2H), 3.71 (m, 1H), 2.34-2.18 (m, 4H), 1.71-1.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 137.1, 136.3, 131.0, 130.1, 129.6, 127.5, 125.4, 124.8, 123.1, 122.9, 121.7, 120.3, 114.6, 74.2, 68.7, 48.9, 40.0, 24.2, 22.4, 20.3; MS *m/z* 371, 369 (M^+); Anal.Calcd.for $C_{21}H_{20}ClNOS$ C, 68.19; H, 5.45; N, 3.79. Found C, 67.83; H, 5.43; N, 3.77.

(4aα,5β,10bα)-5-[3-chlorobenzo[b]thien-2-yl]-3,4,4a,5,6,10b-hexahydro--2*H*-pyrano[3,2-c] quinoline (9e*)*

0.224 g (25%) of colourless solid ; Mp.18145-182 °C; IR(KBr) 3376, 2918, 2850, 1506, 1252 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.46 (m, 3H), 7.24 (m, 1H), 6.87 (m, 1H), 6.62 (d, 1H, *J* = 7.9 Hz), 5.33 (d, 1H, *J* = 5.2 Hz), 5.21 (d, 1H, *J* = 2.2 Hz), 4.08 (br s, 1H, NH), 3.61-3.40 (m, 2H), 2.55 (m, 1H), 1.67-1.47 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 138.3, 136.8, 136.4, 128.0, 127.6, 125.1, 124.9, 122.4, 121.2, 120.6, 119.3, 116.7, 115.0, 717, 60.6, 54.3, 36.4, 25.2, 19.0 ; MS *m/z* 357, 355(M^+); Anal. Calcd. for $C_{20}H_{18}ClNOS$ C, 67.50; H, 5.09; N, 3.93. Found C, 6777; H, 5.11; N, 3.95.

(4aα,5α,10bα)-5-[3-chlorobenzo[*b*]thien-2-yl]-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-c] quinoline (10e)

0.263 g (30%) of colourless solid ; Mp.120-121 °C ; IR(KBr) 3372, 2916, 2845, 1504, 1252 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.48 (m, 2H), 7.39 (m, 1H), 7.14 (s, 1H), 6.78 (m, 1H), 6.57 (d, 1H, *J* = 7.9 Hz), 5.43 (d, 1H, *J* = 10.8 Hz), 4.43 (d, 1H, *J* = 2.4 Hz), 4.24 (br s, 1H), 4.14 (m, 1H), 3.75 (m, 1H), 2.20-1.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 140.2, 137.1, 136.3, 130.9, 129.4, 125.5, 124.8, 122.7, 121.8, 120.7, 119.1, 118.2, 114.5, 74.2, 68.7, 48.8, 39.8, 24.1, 22.3; MS *m/z* 357, 355 (M^+); Anal.Calcd.for $C_{20}H_{18}ClNOS$ C, 67.50; H, 5.09; N, 3.93. Found C, 67.18; H, 5.06; N, 3.92.

Acknowledgement: we thank the Council of Scientific and Industrial Research , New Delhi for financial support.

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