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A new synthesis of pyrroles by the condensation of cyclopropenes and nitriles mediated by gallium(III) and indium(III) salts

Shuki Araki,* Takashi Tanaka, Shinya Toumatsu and Tsunehisa Hirashita
Omohi College, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan. E-mail: araki@ach.nitech.ac.jp; Fax: +81-52-735-5206

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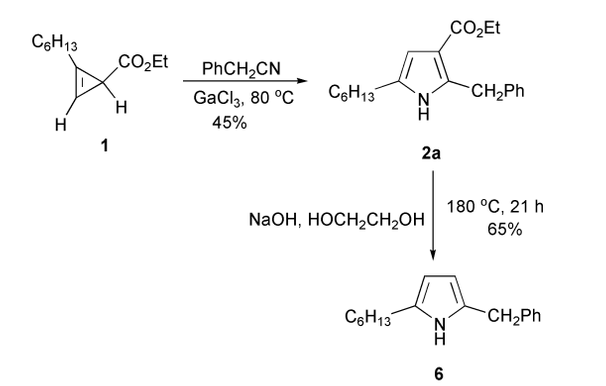
Gallium(III) and indium(III) halides were found to mediate the condensation of cyclopropenes and nitriles to give pyrrole derivatives in moderate yields. When excess nitrile was present, diazepine was also formed.

Introduction

Halometallation reactions of carbon–carbon multiple bonds are useful transformations of alkenes and alkynes to polyfunctional organic molecules. As a part of our study on carbometallation reactions with organogallium and organoindium reagents,[1] we intended to develop new halogallation and haloindation reactions of cyclopropenes with gallium and indium halides. When the reaction of cyclopropene **1** with $GaCl_3$ was first attempted in acetonitrile, no chlorogallation occurred; but a small amount of a pyrrole derivative was isolated from the reaction mixture. The pyrrole was found to be formed from the condensation of cyclopropene **1** and the solvent acetonitrile. This unexpected result prompted us to investigate systematically the reaction of cyclopropene with nitrile mediated by $GaCl_3$.

Results and discussion

By using phenylacetonitrile as a nitrile counterpart, cyclopropene **1** was treated with $GaCl_3$ at 80 °C for 2 h. The reaction was quenched with water and chromatographic purification gave pyrrole **2a** in 45% yield. Although four isomers **2a**,**3**–**5** could be anticipated depending on the addition mode of the nitrile to the two C–C single bonds of **1** (Scheme 1), only a single isomer was formed from this reaction. The chemical shift (6.26 ppm) of the pyrrole ring proton of **2a** indicates that this is a β-proton, because the chemical shifts of the parent pyrrole ring protons are 6.68 ppm for the α- and 6.22 for the β-protons.[2] Therefore, the possibility for **5** can be ruled out. The structure of **2a** was finally deduced after hydrolysis and decarboxylation. When **2a** was heated at 180 °C in alkaline ethylene glycol, the decarboxylation product **6** was obtained in 65% yield, whose two ring protons resonate at 5.79 and 5.85 ppm with *J* 3.0 Hz. This fact indicates that pyrrole **6** has two β-protons, and hence the structure of **2a** is confirmed to be 2-benzyl-3-ethoxycarbonyl-5-hexylpyrrole.



Scheme 1

Although the yield is not very high, the selective formation of **2a** prompted us to investigate the scope of this pyrrole synthesis in detail. Benzonitrile was chosen as a nitrile component and the condensation with **1** was examined under various reaction conditions. The results are summarized in Table 1. The $GaCl_3$-mediated reaction under the same conditions as phenylacetonitrile (without solvent, 80 °C, 2 h) gave 53% yield of the expected pyrrole **2b**. Again, no isomeric pyrroles were formed. The reaction at room temperature lowered the yield (22%). When this reaction was carried out by the slow addition of **1** to a mixture of $GaCl_3$ and a two-fold excess of benzonitrile, diazepine **7** was also obtained in 10% yield, together with **2b** (36%). Next, activity of various Lewis acids was examined (Table 1, entries 4–8). Of the three gallium(III) halides tested, $GaCl_3$ gives the best yield. Indium(III) halides were less effective than gallium(III) halides. When GaI_3 and InI_3 were used, ethyl 4-oxodecanoate (**8**) was a by-product, probably owing to moisture in these metal iodides. Other Lewis acids, such as $TiCl_4$, $AlCl_3$ and BF_3 etherate, did not give the pyrrole at all.

The reaction of **1** with benzonitrile was also carried out in various solvents (Table 2). Compared with the neat condition, the reactions in solvents gave lower yields of **2b**, of which the highest yield was attained in dichloromethane. Chloroform gave much lower yield. In aromatic solvents, the yields were only modest. In protic and polar solvents such as 2-propanol and DMF, no reaction proceeded, probably owing to the strong coordination of the solvent to the Lewis acid.

Next, different nitriles were subjected to the condensation with cyclopropene in the presence of $GaCl_3$ or $InCl_3$ (Table 3). Acetonitrile, 3-phenylbutanenitrile, 2-cyanothiophene, and 2-trifluoromethylbenzonitrile all gave the corresponding pyrroles **2c**–**f** in modest yields (entries 1–4). With 2,3-dimethylcyclopropene-1-carboxylate, the 2,3,4,5-tetrasubstituted pyrrole **2g** was obtained (entry 5). The cyclopropene bearing a hydroxymethyl group at the C3 carbon gave amide **9** upon treatment with acetonitrile (entry 6).

Reaction mechanism

The most probable reaction course of the present pyrrole synthesis is illustrated in Scheme 2. The Lewis acid coordinates to the double bond of the cyclopropene, where the positive charge develops on the substituted carbon. Nucleophilic attack of the nitrile to this carbon followed by a ring expansion to the five-membered ring furnishes the pyrrole precursor; when an excess nitrile is present, two molecules of the nitrile successively react

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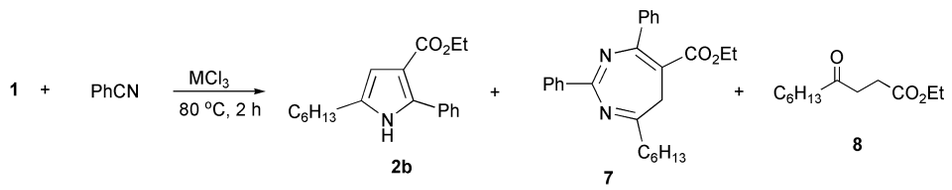
Table 1 Reaction of **1** and benzonitrile without solvent[a]



Entry	MCl_3	Yield (%)		
		2b	**7**	**8**
1	$GaCl_3$	53	0	0
2[b]	$GaCl_3$	22	0	0
3[c]	$GaCl_3$	36	10	0
4	$GaBr_3$	35	0	0
5	GaI_3	27	0	39
6	$InCl_3$	17	0	0
7	$InBr_3$	30	0	0
8	InI_3	10	0	19

[a] Unless otherwise noted, reactions were carried out at 80 °C for 2 h without solvent. [b] At room temperature for 6 h. [c] A two-fold excess of PhCN was used.

Table 2 Reaction of **1** and benzonitrile in various solvents[a]

Entry	Solvent	*t*	Yield (%)	
			2b	**8**
1	None	2 h	53	0
2	Dichloromethane	2 h	45	0
3	Chloroform	2 h	7	9
4	Hexane	4 h	33	0
5	Benzene	5 h	17	0
6[b]	Toluene	4 h	4	9
7[b]	2-Propanol	24 h	No reaction	
8[b]	DMF	24 h	No reaction	

[a] Unless otherwise noted, reactions were carried out at the refluxing temperature. [b] At 80 °C.

to give the seven-membered intermediate. The formation of keto ester **8** is considered to be initiated by the addition of hydrogen halide, formed by the hydrolysis of the catalysts, and amide **9** is deemed to be obtained *via* the $InCl_3$-mediated cyclopropene ring opening followed by the coupling with the nitrile (Scheme 3).

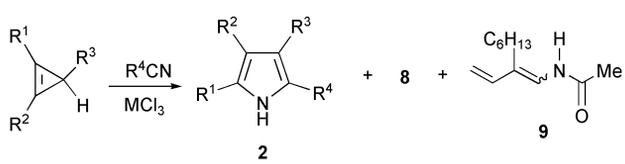
In summary, a new synthesis of pyrroles *via* the condensation of cyclopropenes and nitriles has been found. Pyrrole derivatives are important compounds from synthetic and biological standpoints, and numerous synthetic methods have hitherto been developed for this heterocycle.[3] However, the synthesis of pyrroles from cyclopropene derivatives is quite limited. Few examples include reaction of trithiocyclopropenium salts[4] and cyclopropenethiones[5] with amines, treatment of cyclopropenones with imines,[6] reaction of triafulvenes with isonitriles[7] and photolysis of 3-acylcyclopropene imines.[8] The reaction developed in the present work gives isomerically pure pyrroles. Although the yields are not very high, the selective formation of a single isomer of pyrrole makes the present methodology attractive.

Experimental

General

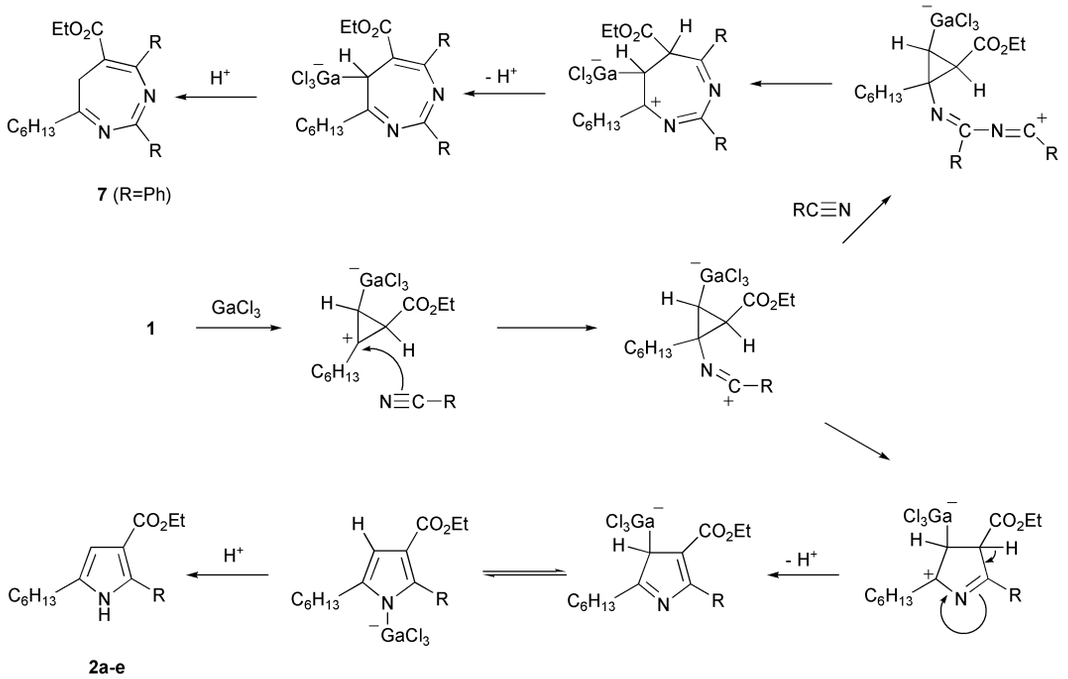
Melting points were determined with a hot-stage apparatus and are uncorrected. Infrared spectra were taken for potassium bromide discs with a JASCO A-102 instrument. ^1H and ^{13}C

Table 3 Pyrrole synthesis from various cyclopropenes and nitriles[a]

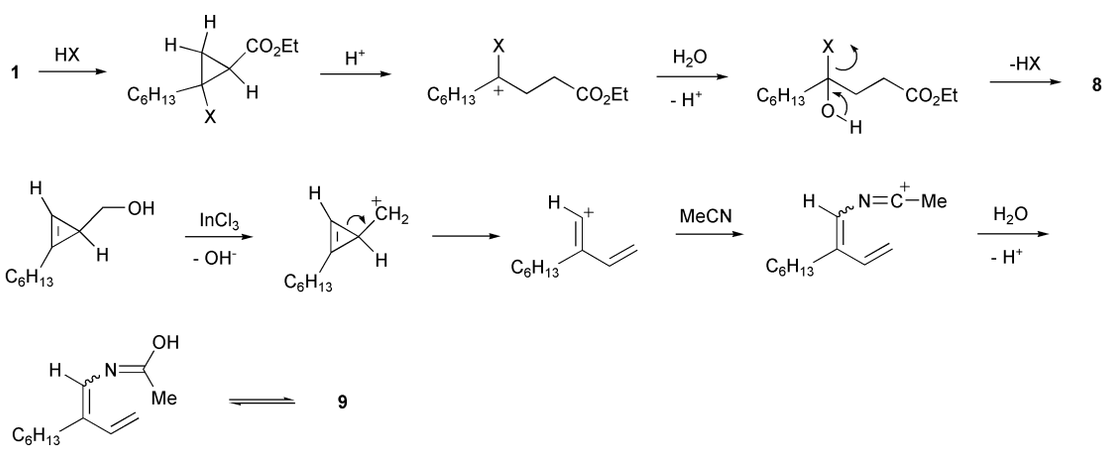


Entry	R^1	R^2	R^3	R^4	MCl_3	Product and yield (%)	
1	C_6H_{13}	H	CO_2Et	Me	$GaCl_3$	**2c** 17	**8** 26
2	C_6H_{13}	H	CO_2Et	$Ph(CH_2)_3$	$GaCl_3$	**2d** 51	
3	C_6H_{13}	H	CO_2Et		$GaCl_3$	**2e** 28	
4	C_6H_{13}	H	CO_2Et		$GaCl_3$	**2f** 23	
5[b]	Me	Me	CO_2Et	$PhCH_2$	$GaCl_3$	**2g** 24	
6[c]	C_6H_{13}	H	CH_2OH	Me	$InCl_3$	**2h** 0	**9** 13

[a] Unless otherwise noted, reactions were carried out at 80 °C for 2–3 h without solvent. [b] At 80 °C for 24 h. [c] At room temperature for 2 h with a large excess of MeCN.



Scheme 2



Scheme 3

NMR spectra were run in $CDCl_3$ with a Varian Gemini 200 spectrometer (200 MHz and 50 MHz, respectively) and referenced using either the residual non-deuterated solvent or tetramethylsilane. *J*-Values are given in Hz. Mass spectra were measured with a Hitachi M-2000S spectrometer (EI, 70 eV). Elemental analyses were performed with a Perkin Elmer 2400 II CHNS/O instrument. The cyclopropenes used in this work were prepared according to literature methods.[1,9]

2-Benzyl-3-ethoxycarbonyl-5-hexylpyrrole (2a). A mixture of $GaCl_3$ (0.25 g, 1.4 mmol), phenylacetonitrile (0.17 g, 1.4 mmol) and cyclopropene **1** (0.28 g, 1.4 mmol) was heated without solvent at 80 °C for 2 h. After being cooled to room temperature, the reaction was quenched by hydrochloric acid (1 M, 5 ml) and the product was extracted with diethyl ether. The extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (ethyl acetate–hexane gradient) to yield **2a** (0.20 g, 45%); colourless oil; (Found: C, 76.68; H, 8.79; N, 4.27. Calc. for $C_{20}H_{27}NO_2$ (313.4): C, 76.64; H, 8.68; N, 4.47%); ν_{max}/cm^{-1} 3320, 3200, 3085, 3045, 2945, 2870, 1662, 1598, 1520, 1496, 1452, 1370, 1340, 1322, 1220, 1080, 1030, 780, 720 and 698; δ_H 0.86 (3H, t, *J* = 6.8, Me), 1.25 (6H, m, CH_2), 1.33 (3H, t, *J* = 7.1, Me), 1.43–1.61 (2H, m, CH_2), 2.43 (2H, t, *J* = 7.5, CH_2), 4.27 (2H, q, *J* = 7.1, OCH_2), 4.33 (2H, s, CH_2), 6.27 (1H, d, *J* = 3.0, CH), 7.21–7.36 (5H, m, Ph) and 7.61 (1H, br s, NH); δ_C 14.0, 14.5, 22.5, 27.3, 28.8, 29.1, 31.5, 33.2, 59.3, 106.6, 117.7, 126.6, 128.7, 128.9, 131.5, 136.0, 138.5 and 165.6; *m*/*z* 313 (M^+, 51%), 284 (100), 268 (10), 242 (40), 213 (9), 196 (8) and 168 (11).

Decarboxylation of 2a. Synthesis of 2-benzyl-5-hexylpyrrole (6). A mixture of **2a** (0.11 g, 0.36 mmol) and sodium hydroxide (29 mg, 0.72 mmol) in ethylene glycol (2 ml) was heated at 180 °C for 21 h. After being cooled to room temperature, the mixture was diluted with water and the product was extracted with dichloromethane. The extracts were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product (76 mg), which was purified by column chromatography on silica gel (AcOEt:hexane = 1 : 20) to give **6** (56 mg, 65%). Colourless oil (Found: C, 84.28; H, 9.95; N, 5.69. Calc. for $C_{17}H_{23}N$ (174.2): C, 84.59; H, 9.61; N, 5.84%); ν_{max}/cm^{-1} 3435, 3370, 3040, 2945, 2855, 1584, 1496, 1450, 1412, 1168, 1070, 1030, 762, 720 and 702; δ_H 0.87 (3H, t, *J* = 6.6, Me), 1.27 (6H, m, CH_2), 1.49–1.60 (2H, m, CH_2), 2.50 (2H, t, *J* = 7.5, CH_2), 3.93 (2H, s, CH_2), 5.79 (1H, t, *J* = 3.0, CH), 5.85 (1H, t, *J* = 3.0, CH), 7.17–7.35 (5H, m, Ph) and 7.48 (1H, br s, NH); δ_C 14.1, 22.6, 27.8, 29.0, 30.0, 31.6, 34.1, 104.6, 106.4, 126.2, 128.5, 128.6, 128.8, 132.3 and 139.9; *m*/*z* 241 (M^+, 35%) and 179 (100).

Synthesis of pyrroles by the $GaCl_3$-(or $InCl_3$)-mediated reaction of cyclopropene and nitrile. The following reactions represent the general procedures.

Table 1, entry 3. Cyclopropene **1** (0.17 g, 0.88 mmol) was added slowly over a period of 2 h to a mixture of benzonitrile (0.18 g, 1.8 mmol) and $GaCl_3$ (0.15 g, 0.88 mmol) at 80 °C, and the mixture was stirred for 1 h. Hydrochloric acid (1 M, 5 ml) was added and the product was extracted with diethyl ether. The extracts were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product (0.29 g), which was purified by column chromatography on silica gel (AcOEt : hexane = 20 : 1) to give **2b** (94 mg, 36%) and **7** (35 mg, 10%).

3-Ethoxycarbonyl-5-hexyl-2-phenylpyrrole (2b). Colourless oil (Found: C, 76.36; H, 8.83; N, 4.55. Calc. for $C_{19}H_{25}NO_2$ (299.4): C, 76.21; H, 8.42; N, 4.68%); ν_{max}/cm^{-1} 3310, 2940, 2870, 1668, 1590, 1524, 1482, 1450, 1432, 1368, 1320, 1270, 1228, 1158, 1108, 1036, 1022, 984, 910, 816, 784, 762 and 696; δ_H 0.90 (3H, t, J = 6.4, Me), 1.25 (3H, t, J = 7.1, Me), 1.21–1.43 (6H, m, CH_2), 1.53–1.74 (2H, m, CH_2), 2.59 (2H, t, J = 7.6, CH_2), 4.20 (2H, q, J = 7.1, OCH_2), 6.42 (1H, d, J = 3.0, CH), 7.32–7.44 (3H, m, Ph), 7.56–7.61 (2H, m, Ph) and 8.08 (1H, br s, NH); δ_C 14.0, 14.2, 22.5, 27.3, 28.9, 29.2, 31.6, 59.5, 108.4, 111.7, 127.7, 127.9, 128.8, 132.3, 133.0, 135.8 and 165.3; *m*/*z* 299 (M^+, 70%), 254 (12), 228 (100), 200 (21), 182 (7), 156 (9), 155 (4) and 114 (3).

5-Ethoxycarbonyl-7-hexyl-2,4-diphenyl-6*H*-[1,3]diazepine (7). Colourless crystals; mp 63.0–64.1 °C (from hexane) (Found: C, 74.04; H, 7.08; N, 6.45. Calc. for $C_{26}H_{30}O_2N_2{\cdot}H_2O$ (420.6): C, 74.26; H, 7.19; N, 6.66%); ν_{max}/cm^{-1} 2960, 2930, 2850, 1728, 1546, 1492, 1450, 1412, 1396, 1324, 1236, 1210, 1180, 1160, 1090, 1012, 950, 906, 824, 780, 754 and 700; δ_H 0.91 (3H, t, J = 6.0, Me), 1.25 (3H, t, J = 7.2, Me), 1.22–1.62 (6H, m, CH_2), 1.89 (2H, quin, J = 7.5, CH_2), 2.81 (2H, t, J = 7.5, CH_2), 3.72 (2H, s, CH_2), 4.18 (2H, q, J = 7.2, CH_2), 7.20–7.64 (8H, m, Ph) and 8.49–8.54 (2H, m, Ph); δ_C 14.06, 14.13, 22.6, 27.8, 29.3, 31.7, 34.7, 34.9, 61.2, 121.1, 128.27, 128.32, 128.4, 128.8, 129.0, 130.3, 137.9, 138.9, 162.4, 166.5, 170.5 and 170.9; *m*/*z* 402 (M^+, 17%), 401 (10), 374 (6), 373 (8), 359 (9), 345 (16), 333 (25), 332 (100), 331 (36), 329 (11), 317 (20), 304 (8), 303 (33), 271 (6), 260 (11), 259 (39), 258 (16), 114 (16), 104 (11) and 69 (13).

Table 1, entry 5. A mixture of GaI_3 (0.25 g, 0.57 mmol), benzonitrile (59 mg, 0.57 mmol) and cyclopropene **1** (0.11 g, 0.82 mmol) was heated at 80 °C for 2 h. After being cooled to room temperature, the reaction was quenched by hydrochloric acid (1 M, 5 ml) and the product was extracted with diethyl ether. The extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (ethyl acetate–hexane gradient) to yield **2b** (47 mg, 27%) and **8** (47 mg, 39%); **ethyl 4-oxodecanoate (8):**[10] δ_H 0.88 (3H, t, J = 6.6 Hz, 3H, Me), 1.25 (3H, t, J = 7.1 Hz, Me), 1.28 (6H, m, CH_2), 2.45 (2H, t, J = 7.4 Hz, 2H, CH_2), 2.53–2.60 (2H, m, CH_2), 2.69–2.75 (2H, m, CH_2) and 4.13 (2H, q, J = 7.1 Hz, CH_2).

Other pyrroles **2c**–**g** were similarly prepared and characterized.

3-Ethoxycarbonyl-5-hexyl-2-methylpyrrole (2c). Colourless crystals; mp 55–58 °C (from hexane) (Found: C, 70.77; H, 9.99; N, 5.89. Calc. for $C_{14}H_{23}NO_2$ (237.4): C: 70.85, H: 9.77 N: 5.90%); ν_{max}/cm^{-1} 3340, 2955, 2940, 2855, 1668, 1600, 1526, 1448, 1400, 1372, 1340, 1320, 1224, 1096, 1020, 990, 808, 780 and 718; δ_H 0.88 (3H, t, J = 6.6, Me), 1.29 (6H, m, CH_2), 1.33 (3H, t, J = 7.1, Me), 1.56 (2H, m, CH_2), 2.49 (2H, t, J = 7.4, CH_2), 2.49 (3H, s, Me), 4.25 (2H, q, J = 7.1, OCH_2), 6.22 (1H, d, J = 2.9, CH) and 7.81 (1H, br.s, NH); δ_C 13.2, 14.0, 14.5, 22.5, 27.3, 28.9, 29.3, 31.6, 59.2, 106.5, 111.4, 130.8, 134.0 and 165.8; *m*/*z* 238 (12%), 237 (M^+, 68), 209 (4), 208 (24), 194 (3), 193 (4), 192 (27), 180 (4), 167 (28), 166 (100), 164 (8), 152 (4), 150 (4), 139 (3), 138 (38), 134 (4), 121 (4), 93 (14) and 107 (4).

3-Ethoxycarbonyl-5-hexyl-2-(3-phenylpropyl)pyrrole (2d). Colourless oil (Found: C, 77.02; H, 9.70; N, 3.97. Calc. for $C_{22}H_{31}NO_2$ (341.5): C, 77.38; H, 9.15; N, 4.10%); δ_H 0.88 (3H, t, J = 6.5, Me), 1.18–1.40 (9H, m, CH_2 and Me), 1.50–1.64 (2H, m, CH_2), 1.96 (2H, quin, J = 7.7, CH_2), 2.48 (2H, t, J = 7.7, CH_2), 2.66 (2H, t, J = 7.7, CH_2), 2.94 (2H, t, J = 7.7, CH_2), 4.23 (2H, q, J = 7.1, CH_2), 6.22 (1H, d, J = 2.8, CH), 7.12–7.36 (5H, m, Ph) and 7.81 (1H, br.s, NH); δ_C 13.9, 14.4, 22.4, 27.0, 27.2, 28.8, 29.1, 31.2, 31.5, 35.5, 59.1, 106.5, 110.8, 125.6, 128.2, 128.3, 131.0, 138.2, 141.9 and 165.8; ν_{max}/cm^{-1} 3320, 2940, 2860, 1664, 1592, 1524, 1496, 1456, 1368, 1340, 1296, 1220, 1170, 1150, 1090, 1022, 906, 810, 780, 742 and 698; *m*/*z* 341 (M^+, 100%), 312 (15), 296 (15), 271 (15), 270 (70), 268 (5), 250 (24), 238 (7), 237 (37), 236 (81), 208 (23), 204 (8), 198 (5), 196 (5), 192 (10), 178 (6), 167 (7), 166 (18), 165 (7), 164 (37), 150 (16), 138 (6), 137 (6), 134 (5), 120 (6), 117 (11), 106 (13), 105 (17), 104 (6), 94 (6), 93 (13), 91 (33), 79 (7), 77% (7) and 65 (5).

3-Ethoxycarbonyl-5-hexyl-2-(2-thienyl)pyrrole (2e). Colourless oil (Found: C, 67.34; H, 7.88; N, 4.01. Calc. for $C_{17}H_{23}NO_2S$ (305.4): C, 66.85; H, 7.59; N, 4.59%); δ_H 0.90 (3H, t, J = 6.6, Me), 1.32 (3H, t, J = 7.1, Me) 1.21–1.43 (6H, m, CH_2), 1.55–1.72 (2H, m, CH_2), 2.58 (2H, t, J = 7.5, CH_2), 4.27 (2H, q, J = 7.1, OCH_2), 6.40 (1H, d, J = 3.2, CH), 7.07 (1H, dd, J = 5.1, 3.7 Hz, CH), 7.30 (1H, dd, J = 5.1, 1.3, CH), 7.50 (1H, dd, J = 3.7, 1.3, CH) and 8.11 (1H, br s, NH); δ_C 14.0, 14.4, 22.5, 27.3, 28.9, 29.1, 31.6, 59.7, 108.8, 112.4, 125.4, 126.7, 127.1, 128.8, 133.1, 133.5 and 164.9; ν_{max}/cm^{-1} 3320, 2940, 2870, 1670, 1598, 1536, 1484, 1444, 1364, 1348, 1300, 1250, 1220, 1150, 1102, 1076, 1046, 1020, 946, 932, 850, 826, 780 and 698; *m*/*z* 305 (M^+, 13%), 304 (64), 259 (10), 235 (7), 234 (15), 233 (100), 205 (39), 188 (13), 187 (8), 162 (15), 161 (8), 160 (10), 121 (6), 120 (6), 110 (11), 109 (8) and 94 (18).

3-Ethoxycarbonyl-5-hexyl-2-(2-trifluoromethylphenyl)pyrrole (2f). Colourless crystals; mp 57.2–58.9 °C (from hexane); HRMS (70 eV) Found 367.1783. Calc. for $C_{20}H_{24}F_3NO_2$ 367.1759; δ_H 0.89 (3H, t, J = 6.6, Me), 1.07 (3H, t, J = 7.2, Me), 1.31 (6H, m, CH_2), 1.54–1.69 (2H, m, CH_2), 2.59 (2H, t, J = 7.5, CH_2), 4.07 (2H, q, J = 7.2, OCH_2), 6.42 (1H, d, J = 3.2, CH), 7.44–7.62 (3H, m, Ph), 7.71–7.78 (1H, m, Ph) and 8.08 (1H, br s, NH); δ_C 13.9, 14.0, 22.5, 27.2, 28.7, 29.1, 31.5, 59.2, 107.2, 114.2, 123.9 (q, J = 271, CF_3), 125.7 (q, J = 5.2), 128.4, 129.3 (q, J = 29.8), 130.9, 131.5, 131.6, 132.9, 133.5 and 164.7; ν_{max}/cm^{-1} 3280, 2920, 2860, 1678, 1608, 1590, 1572, 1530, 1480, 1458, 1378, 1318, 1250, 1224, 1180, 1164, 1136, 1110, 1062, 1036, 990, 958, 818, 784 and 766;*m*/*z* 367 (M^+, 78%), 338 (6), 322 (14), 297 (24), 296 (100), 294 (7), 276 (13), 268 (9), 249 (5), 248 (31), 228 (26), 224 (24), 223 (6), 204 (15), 184 (5), 183 (6) and 154 (10).

2-Benzyl-3-ethoxycarbonyl-4,5-dimethylpyrrole (2g). mp 124.5–125.0 °C (from AcOEt–hexane); Found: C, 74.32; H, 7.29; N, 5.39. Calc. for $C_{16}H_{19}NO_2$ (257.3): C, 74.68; H, 7.44; N, 5.44); ν_{max}/cm^{-1} 3300, 2945, 1658, 1616, 1496, 1464, 1428, 1390, 1378, 1370, 1342, 1260, 1172, 1144, 1088, 1034, 788, 758 and 710; δ_H 1.33 (t, J = 7.1, 3H, Me), 2.05 (s, 3H, Me), 2.17 (s, 3H, Me), 4.28 (q, J = 7.1, 2H, OCH_2), 4.30 (s, 2H, CH_2), 7.20–7.37 (m, 5H, Ph) and 7.42 (br s, 1H, NH); δ_C 10.6, 10.9, 14.5, 33.8, 59.1, 116.3, 122.8, 126.6, 127.8, 128.8, 129.0, 135.6, 138.6 and 166.3; *m*/*z* 257 (M^+, 43%), 228 (100), 211 (19), 196 (4), 182 (15) and 168 (14).

Table 3, entry 6; *N*-(2-Hexylbuta-1,3-dienyl)acetamide (9). A mixture of 1-hexyl-3-(hydroxymethyl)cyclopropene (0.15 g, 1.0 mmol) and $InCl_3$ (0.27 g, 1.2 mmol) in acetonitrile (5 ml) was stirred at room temperature for 2 h. Hydrochloric acid (1 M, 5 ml) was added and the product was extracted with

diethyl ether. The extracts were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product (0.13 g), which was purified by column chromatography on silica gel (AcOEt : hexane = 1 : 6 to 1 : 3) to give **9** (25 mg, 13%). Colourless crystals; mp <30 °C; ν_{max}/cm^{-1} 3330, 3240, 2935, 2855, 1670, 1640, 1518, 1366, 1304, 1268, 1164, 992 and 888; δ_H 0.88 (3H, t, J = 6.8, Me), 1.28 (6H, m, CH_2), 1.43 (2H, m, CH_2), 2.09 (3H, s, Me), 2.07–2.20 (2H, m, CH_2), 5.17 (1H, dd, J = 11.0, 1.4, CH), 5.26 (1H, dd, J = 17.3, 1.4, CH), 6.44 (1H, dd, J = 17.3, 11.0, CH), 6.69 (1H, d, J = 10.7, CH) and 7.23 (1H, br s, NH); δ_C 14.0, 22.6, 23.2, 28.6, 29.2, 31.1, 31.6, 114.0, 119.8, 120.3, 130.3 and 167.3; *m*/*z* 196 (6%), 195 (M^+, 41), 180 (3), 166 (6), 153 (9), 152 (20), 139 (4), 138 (25), 136 (13), 124 (19), 110 (10) and 96 (10). This compound is very labile and satisfactory elemental analysis data were not obtained.

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