CSIRO PUBLISHING

Aust. J. Chem. **2013**, *66*, 241–251
http://dx.doi.org/10.1071/CH12359

Full Paper

$InCl_3$ Catalysed One-Pot Synthesis of Substituted Pyrroles and 2-Pyrones

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An efficient $InCl_3$ catalysed one-pot strategy has been developed for the synthesis of tetra-substituted pyrroles and tri-substituted 2-pyrones in very good yields. Tetra-substituted pyrroles were prepared from 1,4-enediones and β-dicarbonyls employing NH_4OAc as a nitrogen source, through a combination of Michael addition and Paal–Knorr methods. Tri-substituted 2-pyrones were synthesised from 1,4-ynediones and appropriate β-dicarbonyls using a sequential Michael addition and 6-*exo-trig* cyclisation.

Manuscript received: 31 July 2012.
Manuscript accepted: 24 October 2012.

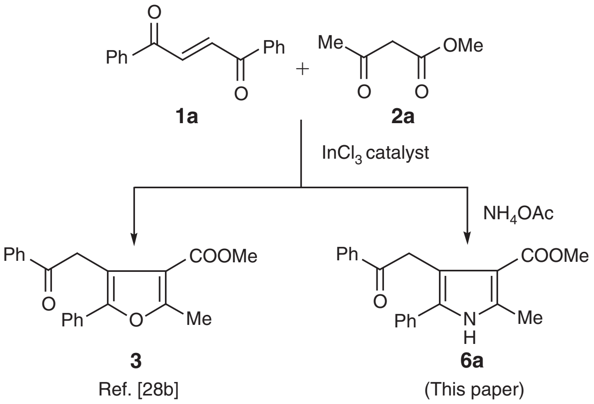
Introduction

The pyrrole[1] ring is one of the most common skeletal features found in heterocycles and natural products.[2] Generally pyrroles possess a broad spectrum of biological activities such as antimicrobial,[3a] telomerase inhibitory,[3b] antifungal,[3c] cardiotonic,[3d] pheromonal,[3e] and phytotoxic effects.[3f] The classical approaches for synthesising pyrroles are Knorr,[4] Hantzsch,[5] and Paal–Knorr[6] methods. Different catalytic methods based on $Ti(OPr\text{-}i)_4$,[7] $Cu(OTf)_2$,[8] $AgBF_4$,[9] $Bi(NO_3)_3$,[10] $PtCl_2$,[11] $Rh_2(oct)_4$ (oct = octanoate),[12] $Sc(OTf)_3$,[13] phosphomolybdic acid (PMA)/SiO_2,[14a] $Zn(OTf)_2$,[14b] $FeCl_3$[14c] and others[15] have also been reported to prepare various substituted pyrrole moieties. The main disadvantages of almost all these methods are the requirement of relatively expensive catalysts,[11–13] stoichiometric amounts of reagents,[10] an inert reaction atmosphere,[11,12] long and harsh reactions conditions[10] resulting in poor yield of the products,[10,12] and generation of toxic metal containing waste.[7,11,12] In addition, there are few reports in the literature of multi-component strategies for the synthesis of substituted pyrroles.[16] Due to the diverse medicinal properties of different pyrrole scaffolds, the syntheses of pyrroles is still unabated.

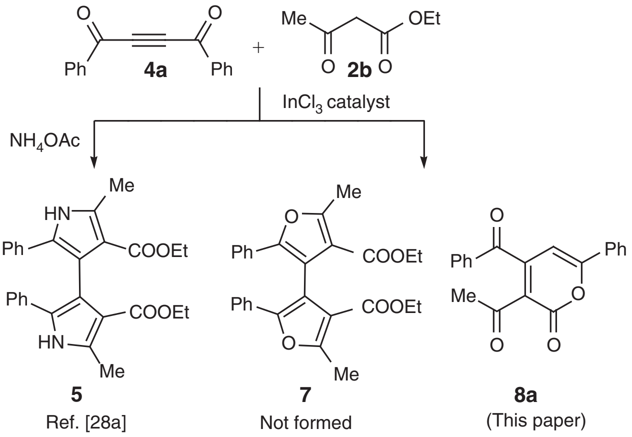
2-Pyrones[17] are another heterocyclic motif having various biological activities[18] and found in several natural products.[19] In addition to their biological activities, 2-pyrones have important applications in synthetic chemistry. 2-Pyrones have limited aromatic character, as a result they are valuable heterosubstituted dienes for the Diels–Alder [4 + 2] cycloaddition reaction.[20] The synthesis of 2-pyrones has been achieved by both non-metal-mediated[21] and transition metal-catalyzed procedures based on $[(Ph_3P)AuCl]$,[22a] $PdCl_2(PPh_3)_2$–Et_3N–CuI,[22b] $[Cp^*RhCl_2]_2$ (Cp^* = 1,2,3,4,5-pentamethylcyclopentadiene),[22c] and $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with N-heterocyclic carbenes (NHCs) as ligand.[22d] As with the pyrroles, most of the above methods need expensive catalysts,[22a,22c] stoichiometric reagents,[21b] inert reaction conditions,[21a] tedius and time consuming harsh conditions[22c] resulting in low yield of the products,[22c] and result in the undesired generation of toxic waste.[22d] To the best of our knowledge, there is no suitable literature precedence for the synthesis of 2-pyrone using simple Lewis acid catalysts. Consequently, the syntheses of 2-pyrone analogues continue to attract the attention of organic chemists.

Reactions catalysed by Lewis acids such as $AlCl_3$, $BF_3{\cdot}Et_2O$, $ZnCl_2$, $TiCl_4$, and $SnCl_2$ have brought about a radical change in the approach towards the synthesis of several important heterocycles. Indium belongs to the same group of the periodic table as boron and aluminium, still $InCl_3$ has become popular among synthetic organic chemists due to its capacity to ensure chemo- and regio-selectivity in various chemical transformations.[23,24] It is generally non-toxic in nature, recyclable, and immune to moisture.[25] In recent times, indium(III) chloride in particular has emerged as a potent Lewis acid catalyst for Diels–Alder,[26a] aldol,[26b] Friedel–Crafts,[26c] and various other organic transformations.[27]

In connection with one of our ongoing research projects for developing novel bioactive heterocyclic scaffolds,[28] we had earlier observed that the reaction of 1,2-dibenzoylethylene (**1a**) with methyl acetoacetate (**2a**) using $InCl_3$ as a catalyst afforded tetra-substituted furan **3**[28b] (Scheme 1), whereas the treatment of dibenzoylacetylene (**4a**) with ethyl acetoacetate (**2b**) and NH_4OAc yielded (±)-3,3′-bipyrrole **5**[28a] (Scheme 2). We soon realised that the introduction of NH_4OAc in the reaction between **1a** and **2a** led to the formation of a substituted pyrrole **6a** (Scheme 1). On the other hand, treating **4a** with **2b** in the absence of NH_4OAc resulted in the formation of substituted 2-pyrone **8a** instead of the expected 3,3′-bifuran **7** (Scheme 2). Accordingly, we set about optimising and examining the scope of these interesting transformations.



Scheme 1. Synthesis of furan **3** and pyrrole **6a**.



Scheme 2. Synthesis of (±)-3,3′-bipyrrole **5** and 2-pyrone **8a**.

Results and Discussion

Our initial efforts were focussed on reacting 1,2-dibenzoylethylene (**1a**, 1.0 equiv.) and methyl acetoacetate (**2a**, 1.0 equiv.) in the presence of ammonium acetate (1.1 equiv.) and 10 mol % of $InCl_3$ as a Lewis acid catalyst in acetonitrile at room temperature which afforded, to our delight, the pyrrole **6a** in reasonable yield (Table 1, entry 2). Conducting the same reaction in the absence of $InCl_3$ did not generate the pyrrole **6a**, instead **1a** and **2a** were fully recovered (Table 1, entry 1). In order to optimize the reaction conditions, various solvents and Lewis acid catalysts were screened (Table 1, entries 2–11). The study revealed that THF as solvent and 10 mol % of $InCl_3$ as a Lewis acid catalyst (Table 1, entry 5) gave the pyrrole **6a** in much improved yield (96 %). Increasing the catalyst loading to 20 mol % did not improve the product yield (Table 1, entry 6). It is pertinent to mention that the presence of water prevented pyrrole formation (Table 1, entry 7).

This optimized method was then exploited to prepare several substituted pyrroles **6b–s** (Table 2) from various substituted β-dicarbonyls **2a–e** and 1,4-enediones **1a–f**.[28a,29] When a mixture of **1a** and NH_4OAc was reacted with either ethyl benzoylacetate (**2d**) or benzoylacetone (**2e**) in the presence of 10 mol % of $InCl_3$, the desired pyrroles **6p** and **6q** were formed with low yields, which did not change even after prolonging the reaction at elevated temperatures (Table 2, entry 16, 17). The reaction of unsymmetrical 1,4-enedione **1f** with **2b** in the presence of NH_4OAc afforded the expected regioisomeric pyrroles **6r** and **6s** in approximately a 1.5 : 1 ratio in a total 61 % yield (Table 2, entry 18).

On the other hand, reaction of dibenzoylmethane (**2f**) with **1a** and NH_4OAc afforded, to our disappointment, 3-amino-1,3-diphenylprop-2-en-1-one (**9**)[30] as the only product instead of the expected pyrrole (Scheme 3), probably due to reduction of the nucleophilic character of **2f** by the presence of phenyl groups making it difficult to react with elctrophile **1a**.

The formation of pyrrole **6a** can be explained by the $InCl_3$-assisted Michael addition of **2a** to the Michael acceptor **1a** to form the Michael adduct **A**, which then undergoes further addition of ammonia followed by $InCl_3$-assisted cyclisation and dehydration (Scheme 4).

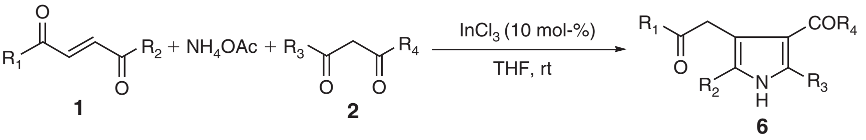
The reaction between dibenzoylacetylene (**4a**, 1.0 equiv.) and **2b** (1.0 equiv.) in the presence of $InCl_3$ (10 mol %) in THF, with the exclusion of NH_4OAc, afforded, to our surprise, tri-substituted 2-pyrone **8a** instead of the expected 3,3′-bifuran **7** at

Table 1. Optimization of reaction conditions for the synthesis of pyrrole 6a

Entry[A]	Catalyst	Solvent	Time [h][B]	Yield[C] [%]
1	None	CH_3CN	8	0
2	$InCl_3$ (10 mol-%)	CH_3CN	5	48
3	$InCl_3$ (10 mol-%)	MeOH	18	25
4	$InCl_3$ (10 mol-%)	*i*-PrOH	11	22
5	$InCl_3$ (10 mol-%)	THF	2	96
6	$InCl_3$ (20 mol-%)	THF	2	96
7	$InCl_3$ (10 mol-%)	THF/H_2O (7 : 3)	40	NR
8	$FeCl_3$ (10 mol-%)	THF	8	76
9	$ZnCl_2$ (10 mol-%)	THF	5.5	58
10	$AlCl_3$ (10 mol-%)	THF	10	55
11	Montmorillonite K10 (10 wt-%)	THF	18	51

[A] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), NH_4OAc (1.1 mmol), rt.
[B] Extension of the reaction time did not improve the product yield.
[C] Isolated yield. NR = no reaction.

Table 2. Synthesis of substituted pyrroles 6a–s



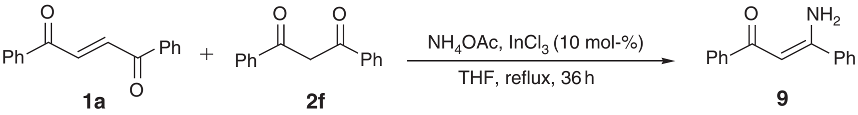
Entry[A]	1,4-Enedione	β-Dicarbonyl	Product	Time [h][B]	Yield[C] [%]
1	**1a**: $R_1 = R_2 = Ph$	**2a**: $R_3 = Me$; $R_4 = OMe$	**6a**	2	96[31]
2	**1a**	**2b**: $R_3 = Me$; $R_4 = OEt$	**6b**	2	93
3	**1a**	**2c**: $R_3 = R_4 = Me$	**6c**	2	94
4	**1b**: $R_1 = R_2 = 4\text{-Me-}C_6H_4$	**2a**	**6d**	2	94
5	**1b**	**2b**	**6e**	2.5	92
6	**1b**	**2c**	**6f**	2	94
7	**1c**: $R_1 = R_2 = 4\text{-Cl–}C_6H_4$	**2a**	**6g**	2.5	96
8	**1c**	**2b**	**6h**	3	91
9	**1c**	**2c**	**6i**	3	93
10	**1d**: $R_1 = R_2 = 4\text{-Br-}C_6H_4$	**2a**	**6j**	3.5	93
11	**1d**	**2b**	**6k**	3.5	94
12	**1d**	**2c**	**6l**	3	93
13	**1e**: $R_1 = R_2 = 3\text{-Cl–4-Me-}C_6H_3$	**2a**	**6m**	5	96
14	**1e**	**2b**	**6n**	5	92
15	**1e**	**2c**	**6o**	4.5	93
16	**1a**	**2d**: $R_3 = Ph$; $R_4 = OEt$	**6p**	24[D]	32
17	**1a**	**2e**: $R_3 = Me$; $R_4 = Ph$	**6q**	36[D]	41
18	**1f**: $R_1 = Ph$; $R_2 = Me$	**2b**	**6r**, **6s**	3	36, 25

[A] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), NH_4OAc (1.1 mmol).

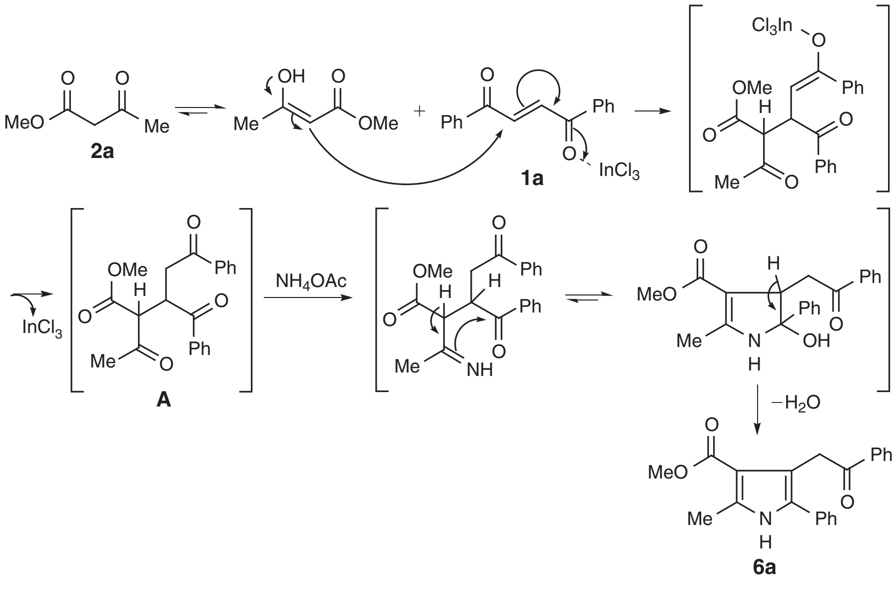
[B] Extension of the reaction time did not improve the product yield.

[C] Isolated yield.

[D] Reactions were performed at 65–70°C.



Scheme 3. Reaction of **1a** with **2f**.



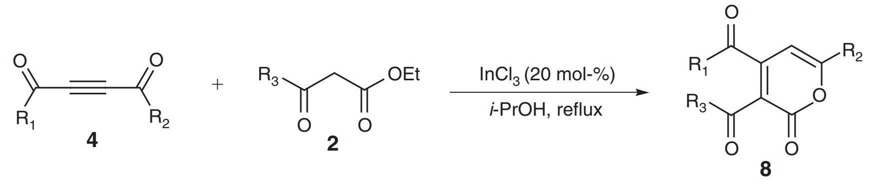
Scheme 4. Plausible mechanism for $InCl_3$ catalyzed formation of substituted pyrrole **6a**.

Table 3. Optimization of reaction conditions for the synthesis of 2-pyrone 8a

Entry[A]	Catalyst	Solvent	Time [h][B]	Yield[C] [%]
1	None	THF	10	0
2	$InCl_3$ (10 mol-%)	THF	10	39
3	$InCl_3$ (20 mol-%)	THF	10	47
4	$InCl_3$ (20 mol-%)	CH_3CN	12	23
5	$InCl_3$ (20 mol-%)	MeOH	7.5	79
6	$InCl_3$ (20 mol-%)	*i*-PrOH	6	85
7	$InCl_3$ (20 mol-%)	*i*-PrOH/H_2O (7 : 3)	8	84
8	$FeCl_3$ (20 mol-%)	*i*-PrOH	15	62
9	$ZnCl_2$ (20 mol-%)	*i*-PrOH	11	53
10	$AlCl_3$ (20 mol-%)	*i*-PrOH	24	40
11	Montmorillonite K10 (20 wt-%)	*i*-PrOH	24	35

[A] Reaction conditions: **4a** (1.0 mmol), **2b** (1.0 mmol), reflux.
[B] Extension of the reaction time did not improve the product yield.
[C] Isolated yield.

Table 4. Synthesis of substituted 2-pyrones 8a–f



Entry[A]	1,4-Ynedione	β-Dicarbonyl	Product	Time [h][B]	Yield[C] [%]
1	**4a**: $R_1 = R_2 = Ph$	**2b**: $R_3 = Me$	**8a**	6	85[32]
2	**4b**: $R_1 = R_2 = 4\text{-Me-}C_6H_4$	**2b**	**8b**	6	76[32]
3	**4c**: $R_1 = R_2 = 4\text{-Cl–}C_6H_4$	**2b**	**8c**	7	71
4	**4d**: $R_1 = R_2 = 4\text{-Br-}C_6H_4$	**2b**	**8d**	6.5	78
5	**4e**: $R_1 = R_2 = 3\text{-Cl–4-Me-}C_6H_3$	**2b**	**8e**	7	62
6	**4a**	**2d**: $R_3 = Ph$	**8f**	8	63

[A] Reaction conditions: **4** (1.0 mmol), **2** (1.0 mmol).
[B] Extension of the reaction time did not improve the product yield.
[C] Isolated yield.

elevated temperature (Table 3, entry 2). Conducting the same reaction in the absence of $InCl_3$ did not generate any product, instead **4a** and **2b** were fully recovered (Table 3, entry 1). Increasing the $InCl_3$ loading (20 mol %) improved the product yield only marginally (Table 3, entry 3). The best yield of **8a** was achieved (Table 3, entry 6) by employing *i*-PrOH and 20 mol % of $InCl_3$ among the various combinations of solvent and Lewis acid catalyst used in this reaction. It is important to mention that the presence of water had very little effect on the formation of **8a** (Table 3, entry 7).

With the above optimized reaction condition in hand, we turned our attention to prepare various other tri-substituted 2-pyrones **8b**–**f** by reacting different 1,4-ynediones **4a**–**e**[28a] with either **2b** or **2d**. The results are summarised in Table 4. Similarly, reaction between **4a** and **2d** afforded the 2-pyrone **8f** in reasonable yield (Table 4, entry 6).

Reaction of **4a**, which acts as a Michael acceptor with the Michael donor **2b** results in Michael adduct **B**, which follows the more preferred 6-*exo-trig* over 5-*exo-trig* cyclisation with elimination of EtOH to form 2-pyrone **8a** as the only product instead of 3,3′-bifuran **7** (Scheme 5).

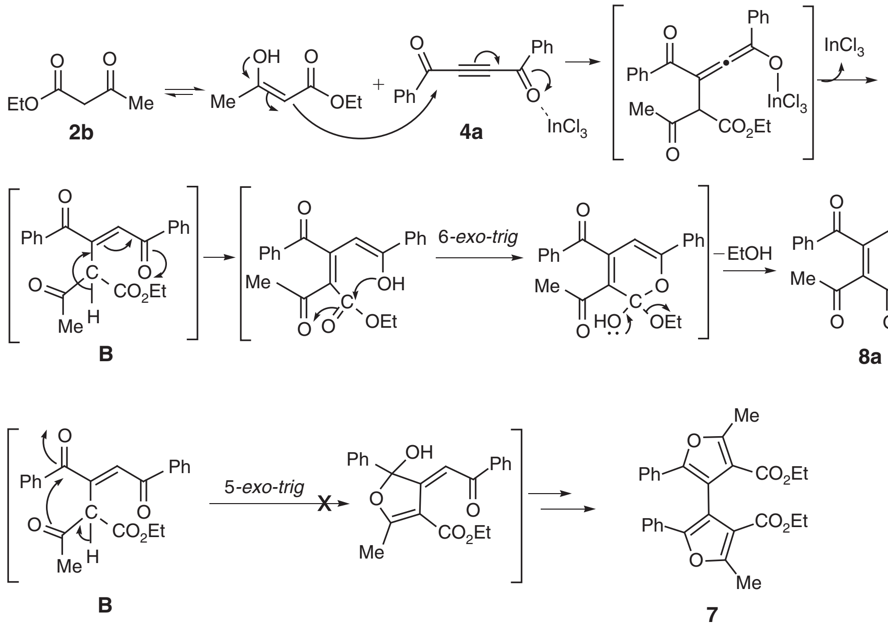
The structures of both tetra-substituted pyrroles **6a**–**s** and tri-substituted 2-pyrones **8a**–**f** have been deduced mainly by NMR spectroscopy, mass spectrometry (MS), and elemental analysis. Moreover the structures of **6a** (Fig. 1), **6d**, **6i**, **6l**, and **8a** (Fig. 2) have been confirmed by single crystal X-ray analysis (see Supplementary Material).

Conclusion

In conclusion, we have developed simple indium trichloride catalysed one-pot synthetic methodologies for the synthesis of tetra-substituted pyrroles and tri-substituted 2-pyrones in excellent yields under mild reaction conditions. Further studies involving screening of these compounds for specific biological activities are in progress and the results will be reported in due course.

Experimental

Melting points were determined in open glass capillaries and are uncorrected. NMR spectra were obtained using a Bruker DRX 600 (or Bruker AMX 300) NMR spectrometer with TMS (tetramethylsilane) as the internal standard. IR spectra were



Scheme 5. Plausible mechanism for InCl$_3$ catalysed formation of substituted 2-pyrone **8a**.

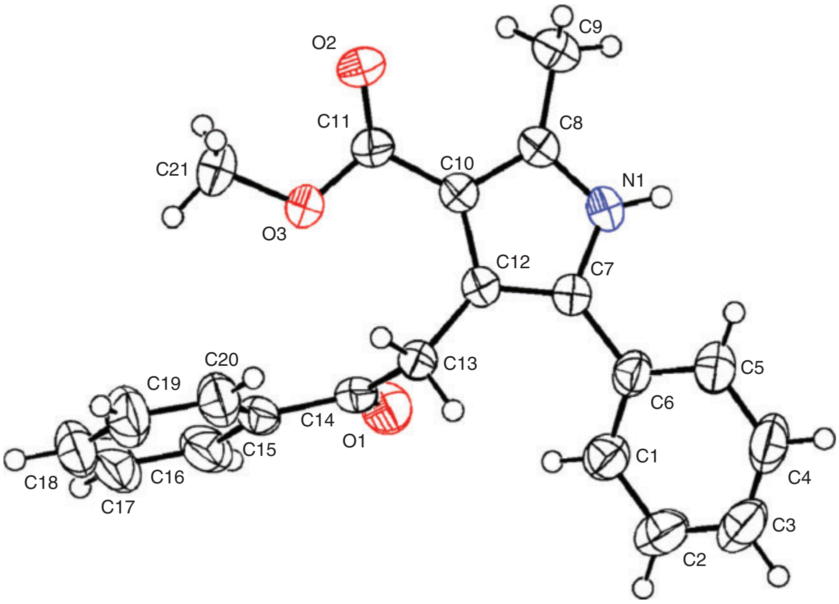


Fig. 1. *ORTEP* diagram of compound **6a**.

recorded on KBr discs and wavelengths are given in cm^{-1}. All chemical shift and coupling constant (J) values are reported in ppm and Hz respectively. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F$_{254}$ plates. Column chromatography was done over silica gel 60–120 mesh. All final compounds were characterised by ^{1}H, ^{13}C, and 2D NMR and MS analyses. Electron impact (EI) MS spectra were recorded on a GCMS-Shimadzu-QP5050A and electrospray ionization (ESI) MS spectra on a Waters Micromass Q-TOF MicroTM spectrometer. Elemental analyses were performed on a Perkin–Elmer CHN/O analyzer model 2400, series II. All reactions were carried out under an argon atmosphere. THF was dried by distillation over Na/benzophenone under a nitrogen atmosphere and all the other solvents were dried by using standard procedures. Anhydrous InCl$_3$ and all other reagents were used as received from commercial sources, with the exception of NH$_4$OAc, which was vacuum dried overnight before use.

General Procedure for the Synthesis of Tetra-Substituted Pyrroles *6a–s*

Anhydrous InCl$_3$ (22 mg, 10 mol %) and NH$_4$OAc (85 mg, 1.1 mmol) were added to a mixture of a 1,4-endione **1a**–**f** (1 mmol) and a β-dicarbonyl compound **2a**–**e** (1 mmol) in dry THF (15 mL). The reaction mixture was then stirred at an appropriate temperature for the indicated time (Table 2, entries 1–18). After complete disappearance of the starting material (monitored by TLC using methanol/chloroform, 1 : 9), the solvent was evaporated in a rotary evaporator. The reaction mixture was diluted with water (10 mL) and extracted with CHCl$_3$ (3 × 25 mL). The

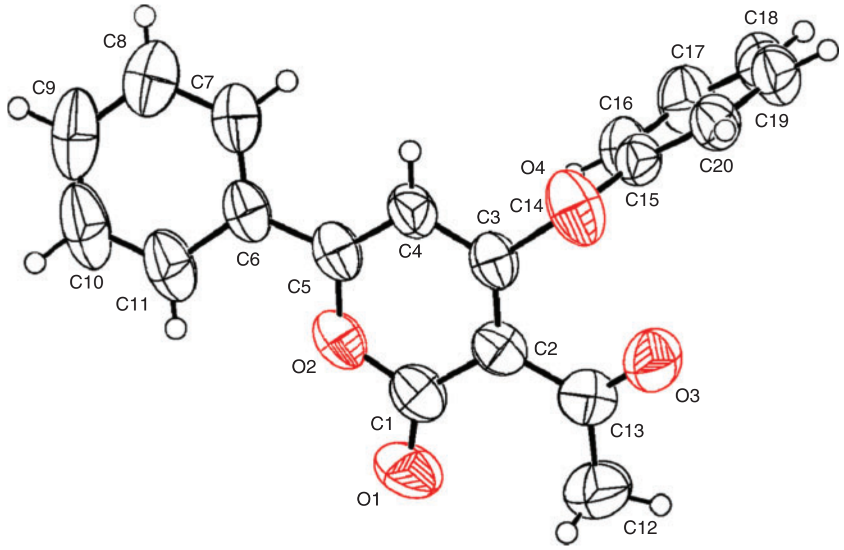


Fig. 2. *ORTEP* diagram of compound **8a**.

organic layer was separated, washed with brine, and then dried over anhydrous Na_2SO_4. Removal of the solvent resulted in the crude product, which was chromatographed over silica gel using petroleum ether and increasing proportions of chloroform as eluent to provide the products **6a**–**s**.

*2-Methyl-4-(2-oxo-2-phenyl-ethyl)-5-phenyl-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (**6a**)*

Light green crystals; yield: 319 mg (96 %); mp 158–160°C, R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3262 (N–H), 1702 (C=O), 1662 (C=O), 1447, 1343, 1261, 1220, 1139, 1095. δ_H (600 MHz, $CDCl_3$) 8.56–8.49 (br s, NH), 8.07 (d, *J* 7.2, 2H, ArH), 7.57 (t, *J* 7.5, 1H, ArH), 7.48 (t, *J* 7.8, 2H, ArH), 7.30–7.22 (m, 5H, ArH), 4.43 (s, 2H, $-C(O)CH_2-$), 3.55 (s, 3H, $-OCH_3$), 2.50 (s, 3H, pyrrole ring 2-CH_3). δ_C (150 MHz, $CDCl_3$) 199.4 ($-CH_2\mathbf{C}(O)Ph$), 166.0 ($-\mathbf{C}(O)OCH_3$), 137.4, 136.5 (2C), 132.8 (ArCH), 132.0, 129.8 (ArCH), 128.9 (2 × ArCH), 128.5 (2 × ArCH), 128.2 (2 × ArCH), 127.3 (ArCH), 127.1 (ArCH), 114.9, 111.4, 50.4 ($-OCH_3$), 36.4 ($-C(O)\mathbf{C}H_2-$), 14.0 (pyrrole ring 2-CH_3). *m*/*z* (ESI) 356 ($[M+Na]^+$). Anal. Calc. for $C_{21}H_{19}NO_3$: C 75.66, H 5.74, N 4.20. Found: C 75.61, H 5.71, N 4.19 %.

*2-Methyl-4-(2-oxo-2-phenyl-ethyl)-5-phenyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6b**)*

CAS Reg. No. 1326822-91-6. White powder; yield: 324 mg (93 %); mp 182–184°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3316 (N–H), 1686 (C=O), 1337, 1266, 1218, 1148, 1100. δ_H (600 MHz, $CDCl_3$) 8.61 (br s, NH), 8.08 (d, *J* 8.1, 2H, ArH), 7.56 (t, *J* 7.5, 1H, ArH), 7.48 (t, *J* 7.8, 2H, ArH), 7.28–7.19 (m, 5H, ArH), 4.45 (s, 2H, $-C(O)CH_2-$), 4.05 (q, *J* 7.0, 2H, $-OCH_2CH_3$), 2.50 (s, 3H, pyrrole ring 2-CH_3), 1.03 (t, *J* 7.2, 3H, $-OCH_2CH_3$). δ_C (150 MHz, $CDCl_3$) 199.1 ($-CH_2\mathbf{C}(O)Ph$), 165.6 ($-\mathbf{C}(O)OCH_2CH_3$), 137.3, 136.6, 132.8 (ArCH), 132.1, 129.7, 128.8 (2 × ArCH), 128.5 (2 × ArCH), 128.2 (2 × ArCH), 127.2 (2 × ArCH), 127.0 (ArCH), 114.6, 111.7, 59.1 ($-O\mathbf{C}H_2CH_3$), 36.6 ($-C(O)\mathbf{C}H_2-$), 14.2, 14.0. *m*/*z* (ESI) 370 ($[M+Na]^+$). Anal. Calc. for $C_{22}H_{21}NO_3$: C 76.06, H 6.09, N 4.03. Found: C 76.02, H 6.07, N 4.01 %.

*2-(4-Acetyl-5-methyl-2-phenyl-1*H*-pyrrol-3-yl)-1-phenyl Ethanone (**6c**)*

Pale yellow powder; yield: 299 mg (94 %); mp 172–174°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3217 (N–H), 1687 (C=O), 1609 (C=O), 1474, 1448, 1419, 1335, 1216. δ_H (600 MHz, $CDCl_3$) 9.14 (br s, NH), 8.07 (d, *J* 7.2, 2H, ArH), 7.55 (t, *J* 7.5, 1H, ArH), 7.46 (t, *J* 7.8, 2H, ArH), 7.24–7.16 (m, 5H, ArH), 4.44 (s, 2H, $-C(O)CH_2-$), 2.37 (s, 3H, $-C(O)CH_3$), 2.27 (s, 3H, pyrrole ring 5-CH_3). δ_C (150 MHz, $CDCl_3$) 199.9, 194.6, 137.5, 135.3, 132.7 (ArCH), 131.7, 130.2, 128.6 (2 × ArCH), 128.5 (2 × ArCH), 128.2 (2 × ArCH), 127.2 (2 × ArCH), 127.0 (ArCH), 121.4, 115.0, 36.8 ($-C(O)\mathbf{C}H_2-$), 30.3 ($-C(O)\mathbf{C}H_3$), 15.4 (pyrrole ring 5-CH_3). *m*/*z* (ESI) 340 ($[M+Na]^+$). Anal. Calc. for $C_{21}H_{19}NO_2$: C 79.47, H 6.03, N 4.41. Found: C 79.42, H 6.00, N 4.51 %.

*2-Methyl-4-(2-oxo-2-*p*-tolyl-ethyl)-5-*p*-tolyl-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (**6d**)*

Pale yellow powder; yield: 340 mg (94 %); mp 136–138°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3329 (N–H), 1683 (C=O), 1657 (C=O), 1448, 1334, 1264, 1181, 1094. δ_H (600 MHz, $CDCl_3$) 8.32 (br s, NH), 7.96 (d, *J* 7.8, 2H, ArH), 7.27 (d, *J* 8.4, 2H, ArH), 7.18 (d, *J* 7.8, 2H, ArH), 7.11 (d, *J* 7.8, 2H, ArH), 4.38 (s, 2H, $-C(O)CH_2-$), 3.56 (s, 3H, $-OCH_3$), 2.52 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H). δ_C (150 MHz, $CDCl_3$) 198.8 ($-CH_2\mathbf{C}(O)Ar$), 166.0 ($-\mathbf{C}(O)OCH_3$), 143.4, 137.0, 136.1, 134.9, 129.8, 129.5 (2 × ArCH), 129.2, 129.1 (2 × ArCH), 128.3 (2 × ArCH), 127.3 (2 × ArCH), 114.7, 111.5, 50.4 ($-OCH_3$), 36.3 ($-C(O)\mathbf{C}H_2-$), 21.6 (Ar-CH_3), 21.2 (Ar-CH_3), 14.0 (pyrrole ring 2-CH_3). *m*/*z* (ESI) 384 ($[M+Na]^+$). Anal. Calc. for $C_{23}H_{23}NO_3$: C 76.43, H 6.41, N 3.88. Found: C 76.39, H 6.38, N 3.86 %.

*2-Methyl-4-(2-oxo-2-*p*-tolyl-ethyl)-5-*p*-tolyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6e**)*

White powder; yield: 345 mg (92 %); mp 248–250°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3347 (N–H), 1691 (C=O), 1655 (C=O), 1446, 1286, 1172, 1094. δ_H (300 MHz, $CDCl_3$) 8.18 (br s, NH), 7.97 (d, *J* 7.7, 2H, ArH), 7.27 (d, *J* 7.7, 2H, ArH), 7.20 (d, *J* 7.7, 2H, ArH), 7.14 (d, *J* 7.7, 2H, ArH), 4.41 (s, 2H, –C(O)CH_2–), 4.08 (q, *J* 7.2, 2H, –OCH_2CH_3), 2.57 (s, 3H), 2.42 (s, 3H), 2.34 (s, 3H), 1.04 (t, *J* 7.2, 3H, –OCH_2CH_3). δ_C (75 MHz, $CDCl_3$) 198.9 (–CH_2**C**(O)Ar), 165.7 (–**C**(O)OCH_2CH_3), 143.5, 136.7, 136.4, 134.8, 129.7, 129.4 (2 × ArCH), 129.3, 129.1 (2 × ArCH), 128.3 (2 × ArCH), 127.1 (2 × ArCH), 114.3, 111.6, 59.0 (–O**C**H_2CH_3), 36.5 (–C(O)**C**H_2–), 21.6, 21.1, 14.2, 14.0. *m/z* (ESI) 398 ($[M + Na]^+$). Anal. Calc. for $C_{24}H_{25}NO_3$: C 76.77, H 6.71, N 3.73. Found: C 76.72, H 6.67, N 3.70 %.

*2-(4-Acetyl-5-methyl-2-*p*-tolyl-1*H*-pyrrol-3-yl)-1-*p*-tolyl Ethanone (**6f**)*

White powder; yield: 325 mg (94 %); mp 170–172°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3216 (N–H), 1681 (C=O), 1606 (C=O), 1471, 1450, 1415, 1337, 1224, 1179. δ_H (300 MHz, $CDCl_3$) 8.25 (br s, NH), 7.98 (d, *J* 8.0, 2H, ArH), 7.27 (d, *J* 8.0, 2H, ArH), 7.21 (d, *J* 7.4, 2H, ArH), 7.1 (d, *J* 7.4, 2H, ArH), 4.40 (s, 2H, –C(O)CH_2–), 2.56 (s, 3H, –C(O)CH_3), 2.41 (s, 3H), 2.35 (s, 6H). δ_C (75 MHz, $CDCl_3$) 200.0, 194.9, 143.8, 137.1, 135.6, 135.4, 130.7, 129.8 (2 × ArCH), 129.6 (2 × ArCH), 129.4, 128.8 (2 × ArCH), 127.6 (2 × ArCH), 121.9, 115.2, 37.1 (–C(O)**C**H_2–), 30.8 (–C(O)**C**H_3), 22.1 (Ar-CH_3), 21.6 (Ar-CH_3), 15.9 (pyrrole ring 5-CH_3). *m/z* (ESI) 368 ($[M + Na]^+$). Anal. Calc. for $C_{23}H_{23}NO_2$: C 79.97, H 6.71, N 4.05. Found: C 79.93, H 6.69, N 4.06 %.

*5-(4-Chloro-phenyl)-4-[2-(4-chloro-phenyl)-2-oxo-ethyl]-2-methyl-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (**6g**)*

White powder; yield: 386 mg (96 %); mp 62–64°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3312 (N–H), 1682 (C=O), 1588 (C=O), 1487, 1450, 1265, 1214, 1142, 1091. δ_H (300 MHz, $CDCl_3$) 9.14 (br s, NH), 8.04 (d, *J* 8.4, 2H, ArH), 7.49 (d, *J* 8.4, 2H, ArH), 7.16 (d, *J* 8.0, 2H, ArH), 7.04 (d, *J* 8.0, 2H, ArH), 4.37 (s, 2H, –C(O)CH_2–), 3.60 (s, 3H, –OCH_3), 2.37 (s, 3H, pyrrole ring 2-CH_3). δ_C (75 MHz, $CDCl_3$) 199.5 (–CH_2**C**(O)Ar), 166.5 (–**C**(O)OCH_3), 140.0, 137.6, 135.9, 133.2, 130.8, 130.1 (2 × ArCH), 129.4 (2 × ArCH), 129.3 (2 × ArCH), 129.2, 128.3 (2 × ArCH), 115.3, 111.5, 50.9 (–C(O)O**C**H_3), 36.8 (–C(O)**C**H_2–), 14.2 (pyrrole ring 2-CH_3). *m/z* (ESI) 424 ($[M + Na]^+$). Anal. Calc. for $C_{21}H_{17}Cl_2NO_3$: C 62.70, H 4.26, N 3.48. Found: C 62.67, H 4.24, N 3.45 %.

*5-(4-Chloro-phenyl)-4-[2-(4-chloro-phenyl)-2-oxo-ethyl]-2-methyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6h**)*

White solid; yield: 380 mg (91 %); mp 174–176°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3311 (N–H), 1680 (C=O), 1487, 1444, 1334, 1263, 1213, 1143, 1091. δ_H (600 MHz, $CDCl_3$) 8.65 (br s, NH), 8.02 (d, *J* 8.4, 2H, ArH), 7.46 (d, *J* 8.4, 2H, ArH), 7.22 (d, *J* 8.4, 2H, ArH), 7.10 (d, *J* 8.4, 2H, ArH), 4.37 (s, 2H, –C(O)CH_2–), 4.09 (q, *J* 7.2, 2H, –OCH_2CH_3), 2.47 (s, 3H, pyrrole ring 2-CH_3), 1.09 (t, *J* 7.2, 3H, –OCH_2CH_3). δ_C (150 MHz, $CDCl_3$) 198.2 (–CH_2**C**(O)Ar), 165.5 (–**C**(O)OCH_2CH_3), 139.5, 136.9, 135.5, 133.0, 130.4, 129.7 (2 × ArCH), 129.0 (2 × ArCH), 128.9 (2 × ArCH), 128.6, 128.2 (2 × ArCH), 114.9, 111.7, 59.2 (–O**C**H_2CH_3), 36.4 (–C(O)**C**H_2–), 14.3, 14.0. *m/z* (ESI) 438 ($[M + Na]^+$). Anal. Calc. for $C_{22}H_{19}Cl_2NO_3$: C 63.47, H 4.60, N 3.36. Found: C 63.42, H 4.57, N 3.34 %.

*2-[4-Acetyl-2-(4-chloro-phenyl)-5-methyl-1*H*-pyrrol-3-yl]-1-(4-chloro-phenyl) Ethanone (**6i**)*

Pale yellow powder; yield: 359 mg (93 %); mp 228–230°C; R_f 0.2 (chloroform/petroleum ether 3 : 1). ν_{max} (KBr)/cm^{-1} 3202 (N–H), 1685 (C=O), 1606 (C=O), 1474, 1451, 1214, 1092. δ_H (600 MHz, $CDCl_3$) 8.38 (br s, NH), 8.02 (d, *J* 8.4, 2H, ArH), 7.45 (d, *J* 8.4, 2H, ArH), 7.30 (d, *J* 8.1, 2H, ArH), 7.22 (d, *J* 7.8, 2H, ArH), 4.34 (s, 2H, –C(O)CH_2–), 2.56 (s, 3H, –C(O)CH_3), 2.37 (s, 3H, pyrrole ring 5–CH_3). δ_C (150 MHz, $CDCl_3$) 199.0, 194.3, 139.2, 135.8, 134.8, 133.5, 130.0, 129.7 (2 × ArCH), 129.3, 129.1 (2 × ArCH), 128.8 (2 × ArCH), 128.6 (2 × ArCH), 121.6, 115.7, 36.4 (–C(O)**C**H_2–), 30.5 (–C(O)**C**H_3), 15.7 (pyrrole ring 5-CH_3). *m/z* (ESI) 408 ($[M + Na]^+$). Anal. Calc. for $C_{21}H_{17}Cl_2NO_2$: C 65.30, H 4.44, N 3.63. Found: C 65.24, H 4.40, N 3.59 %.

*5-(4-Bromo-phenyl)-4-[2-(4-bromo-phenyl)-2-oxo-ethyl]-2-methyl-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (**6j**)*

Pale yellow powder; yield: 457 mg (93 %); mp 156–158°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3313 (N–H), 1685 (C=O), 1660 (C=O), 1483, 1448, 1266, 1095. δ_H (600 MHz, $CDCl_3$) 8.74 (br s, NH), 7.94 (d, *J* 6.6, 2H, ArH), 7.64 (d, *J* 6.6, 2H, ArH), 7.36 (d, *J* 8.4, 2H, ArH), 7.02 (d, *J* 8.4, 2H, ArH), 4.34 (s, 2H, –C(O)CH_2–), 3.59 (s, 3H, –OCH_3), 2.43 (s, 3H, pyrrole ring 2-CH_3). δ_C (150 MHz, $CDCl_3$) 198.9 (–CH_2**C**(O)Ar), 165.9 (–**C**(O)OCH_3), 137.0, 135.9, 131.9 (4 × ArCH), 130.8, 129.8 (2 × ArCH), 128.7 (2 × ArCH), 128.3, 128.2, 121.1, 115.0, 111.3, 50.6 (–C(O)O**C**H_3), 36.3 (–C(O)**C**H_2–), 13.9 (pyrrole ring 2-CH_3). *m/z* (ESI) 514 ($[M + Na]^+$). Anal. Calc. for $C_{21}H_{17}Br_2NO_3$: C 51.35, H 3.49, N 2.85. Found: C 51.39, H 3.45, N 2.81 %.

*5-(4-Bromo-phenyl)-4-[2-(4-bromo-phenyl)-2-oxo-ethyl]-2-methyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6k**)*

White solid; yield: 475 mg (94 %); mp 106–108°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3601 (N–H), 1683 (C=O), 1657 (C=O), 1483, 1266, 1210, 1147, 1098. δ_H (600 MHz, $CDCl_3$) 8.95 (br s, NH), 7.95 (d, *J* 8.4, 2H, ArH), 7.63 (d, *J* 8.4, 2H, ArH), 7.31 (d, *J* 8.4, 2H, ArH), 6.95 (d, *J* 8.4, 2H, ArH), 4.36 (s, 2H, –C(O)CH_2–), 4.09 (q, *J* 7.0, 2H, –OCH_2CH_3), 2.40 (s, 3H, pyrrole ring 2-CH_3), 1.10 (t, *J* 7.2, 3H, –OCH_2CH_3). δ_C (150 MHz, $CDCl_3$) 198.8 (–CH_2**C**(O)Ar), 165.5 (–**C**(O)OCH_2CH_3), 137.2, 135.8, 131.9 (2 × ArCH), 131.8 (2 × ArCH), 130.8, 129.8 (2 × ArCH), 128.6, 128.3, 128.2 (2 × ArCH), 120.9, 114.8, 111.5, 59.2 (–O**C**H_2CH_3), 36.5 (–C(O)**C**H_2–), 14.3, 14.0. *m/z* (ESI) 528 ($[M + Na]^+$). Anal. Calc. for $C_{22}H_{19}Br_2NO_3$: C 52.30, H 3.79, N 2.77. Found: C 52.24, H 3.76, N 2.74 %.

*2-[4-Acetyl-2-(4-bromo-phenyl)-5-methyl-1H-pyrrol-3-yl]-1-(4-bromo-phenyl) Ethanone (**6l**)*

Pale yellow solid; yield: 442 mg (93 %); mp 114–116°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3198 (N–H), 1682 (C=O), 1607 (C=O), 1474, 1451, 1416, 1212, 1072. δ_H (600 MHz, $CDCl_3$) 8.33 (br s, NH), 7.94 (d, *J* 6.9, 2H, ArH), 7.62 (d, *J* 7.2, 2H, ArH), 7.47 (d, *J* 8.4, 2H, ArH), 7.17 (d, *J* 8.4, 2H, ArH), 4.33 (s, 2H, –C(O)CH_2–), 2.57 (s, 3H, –C(O)CH_3), 2.38 (s, 3H, pyrrole ring 5-CH_3). δ_C (150 MHz, $CDCl_3$) 198.3, 194.2, 137.3, 136.6, 132.5 (4 × ArCH), 131.9, 130.9 (2 × ArCH), 130.0 (2 × ArCH), 129.1, 127.6, 121.9, 120.8, 116.0, 37.2 (–C(O)**C**H$_2$–), 31.2 (–C(O)**C**H$_3$), 15.7 (pyrrole ring 5-CH$_3$). *m/z* (ESI) 498 ([M + Na]$^+$). Anal. Calc. for $C_{21}H_{17}Br_2NO_2$: C 53.08, H 3.61, N 2.95. Found: C 53.03, H 3.58, N 2.90 %.

*5-(3-Chloro-4-methyl-phenyl)-4-[2-(3-chloro-4-methyl-phenyl)-2-oxo-ethyl]-2-methyl-1*H*-pyrrole-3-carboxylic Acid Methyl Ester (**6m**)*

White powder; yield: 413 mg (96 %); mp 128–130°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3300 (N–H), 1690 (C=O), 1480, 1444, 1261, 1140, 1096. δ_H (600 MHz, CDCl$_3$) 8.94 (br s, NH), 7.95 (s, 1H, ArH), 7.84 (d, *J* 8.4, 1H, ArH), 7.45 (d, *J* 8.4, 1H, ArH), 7.14 (d, *J* 7.8, 1H, ArH), 6.94 (s, 1H, ArH), 6.88 (d, *J* 7.8, 1H, ArH), 4.35 (s, 2H, –C(O)C*H$_2$*–), 3.60 (s, 3H, –OC*H$_3$*), 2.58 (s, 3H), 2.45 (s, 3H), 2.21 (s, 3H, pyrrole ring 2-CH$_3$). δ_C (150 MHz, CDCl$_3$) 199.3 (–CH$_2$**C**(O)Ar), 165.5 (–**C**(O)OCH$_3$), 139.5, 137.2, 137.0, 136.5, 135.6, 133.0, 130.6 (ArCH), 130.5, 129.5 (ArCH), 129.4 (ArCH), 129.3 (ArCH), 128.7, 127.4 (ArCH), 125.9 (ArCH), 114.8, 111.1, 50.5 (–OCH$_3$), 36.4 (–C(O)CH$_2$–), 20.2 (Ar-CH$_3$), 20.1 (Ar-CH$_3$), 13.8 (pyrrole ring 2-CH$_3$). *m/z* (ESI) 452 ([M + Na]$^+$). Anal. Calc. for $C_{23}H_{21}Cl_2NO_3$: C 64.19, H 4.92, N 3.25. Found: C 64.11, H 4.90, N 3.24 %.

*5-(3-Chloro-4-methyl-phenyl)-4-[2-(3-chloro-4-methyl-phenyl)-2-oxo-ethyl]-2-methyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6n**)*

White powder; yield: 409 mg (92 %); mp 190–192°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3291 (N–H), 1695 (C=O), 1676 (C=O), 1479, 1449, 1262, 1138, 1096. δ_H (600 MHz, CDCl$_3$) 8.97 (br s, NH), 7.95 (s, 1H, ArH), 7.86 (d, *J* 8.4, 1H, ArH), 7.45 (d, *J* 8.4, 1H, ArH), 7.13 (d, *J* 8.4, 1H, ArH), 6.92 (s, 1H, ArH), 6.87 (d, *J* 7.8, 1H, ArH), 4.40 (s, 2H, –C(O)CH$_2$–), 4.10 (q, *J* 7.2, 2H, –OC*H$_2$*CH$_3$), 2.45 (s, 3H), 2.39 (s, 3H), 2.20 (s, 3H), 1.11 (t, *J* 7.2, 3H, –OCH$_2$C*H$_3$*). δ_C (150 MHz, CDCl$_3$) 198.5 (–CH$_2$**C**(O)Ar), 165.5 (–**C**(O)OCH$_2$CH$_3$), 139.6, 137.1, 136.7, 136.1, 135.6, 132.9, 130.6 (ArCH), 130.5, 129.3 (ArCH), 129.2 (ArCH), 129.1 (ArCH), 128.9, 127.4 (ArCH), 125.4 (ArCH), 114.7, 111.3, 59.1 (–O**C**H$_2$CH$_3$), 36.6 (–C(O)**C**H$_2$–), 20.5 (2C), 14.3, 13.9. *m/z* (ESI) 466 ([M + Na]$^+$). Anal. Calc. for $C_{24}H_{23}Cl_2NO_3$: C 64.87, H 5.22, N 3.15. Found: C 64.81, H 5.17, N 3.15 %.

*2-[4-Acetyl-2-(3-chloro-4-methyl-phenyl)-5-methyl-1*H*-pyrrol-3-yl]-1-(3-chloro-4-methyl-phenyl) Ethanone (**6o**)*

White solid; yield: 385 mg (93 %); mp 175–177°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3278 (N–H), 1679 (C=O), 1615 (C=O), 1476, 1446, 1231, 1050. δ_H (600 MHz, CDCl$_3$) 9.10 (br s, NH), 7.95 (s, 1H, ArH), 7.84 (d, *J* 8.4, 1H, ArH), 7.44 (d, *J* 8.4, 1H, ArH), 7.24 (d, *J* 8.4, 1H, ArH), 7.07 (s, 1H, ArH), 7.00 (d, *J* 8.7, 1H, ArH), 4.33 (s, 2H, –C(O)CH$_2$–), 2.49 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 2.03 (s, 3H, pyrrole ring 5-CH$_3$). δ_C (150 MHz, CDCl$_3$) 199.7, 194.4, 139.5, 136.5, 135.9, 135.3, 133.3, 131.1 (ArCH), 130.7, 130.1, 129.4 (ArCH), 129.3 (ArCH), 129.1 (ArCH), 128.9, 127.1 (ArCH), 125.8 (ArCH), 121.4, 115.2, 36.7 (–C(O)**C**H$_2$–), 30.4 (–C(O)**C**H$_3$), 20.4 (Ar-CH$_3$), 20.1 (Ar-CH$_3$), 15.5 (pyrrole ring 5-CH$_3$). *m/z* (ESI) 436 ([M + Na]$^+$). Anal. Calc. for $C_{23}H_{21}Cl_2NO_2$: C 66.67, H 5.11, N 3.38. Found: C 66.62, H 5.08, N 3.33 %.

*4-(2-Oxo-2-phenyl-ethyl)-2,5-diphenyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6p**)*

Light yellow solid; yield: 132 mg (32 %); mp 102–104°C; R_f 0.5 (ethyl acetate/petroleum ether, 1.5 : 8.5). ν_{max} (KBr)/cm^{-1} 3300 (N–H), 2924, 1685 (C=O), 1602 (C=O), 1455. δ_H (600 MHz, CDCl$_3$) 8.41 (br s, NH), 8.09 (d, *J* 7.8, 2H, ArH), 7.61–7.56 (m, 3H, ArH), 7.49 (t, *J* 7.8, 2H, ArH), 7.42–7.30 (m, 8H, ArH), 4.53 (s, 2H, –C(O)CH$_2$–), 4.00 (q, *J* 7.2, 2H, –OC*H$_2$*CH$_3$), 0.92 (t, *J* 7.2, 3H, –OCH$_2$C*H$_3$*). δ_C (150 MHz, CDCl$_3$) 198.4 (–CH$_2$**C**(O)Ph), 165.0 (–**C**(O)OCH$_2$CH$_3$), 137.7, 137.3, 132.9 (ArCH), 132.6, 131.8, 131.7, 129.3 (2 × ArCH), 129.0 (2 × ArCH), 128.5 (2 × ArCH), 128.2 (2 × ArCH), 128.0 (2 × ArCH), 127.7 (2 × ArCH), 127.6 (2 × ArCH), 116.1, 112.5, 59.5 (–O**C**H$_2$CH$_3$), 36.6 (–C(O)**C**H$_2$–), 13.9 (–OCH$_2$**C**H$_3$). *m/z* (ESI) 432 ([M + Na]$^+$). Anal. Calc. for $C_{27}H_{23}NO_3$: C 79.20, H 5.66, N 3.42. Found: C 79.27, H 5.72, N 3.35 %.

*2-(4-Benzoyl-5-methyl-2-phenyl-1*H*-pyrrol-3-yl)-1-phenyl Ethanone (**6q**)*

Yellow solid; yield: 155 mg (41 %); mp 127–129°C; R_f 0.5 (ethyl acetate/petroleum ether, 1 : 9). ν_{max} (KBr)/cm^{-1} 3289 (N–H), 2923, 2854, 1682 (C=O), 1598 (C=O), 1421, 1211. δ_H (600 MHz, CDCl$_3$) 8.51 (br s, NH), 7.99 (d, *J* 7.8, 2H, ArH), 7.64 (d, *J* 7.2, 2H, ArH), 7.52 (t, *J* 7.5, 1H, ArH), 7.45–7.40 (m, 3H, ArH), 7.37 (t, *J* 7.5, 2H, ArH), 7.34–7.23 (m, 5H, ArH), 4.41 (s, 2H, –C(O)CH$_2$–), 1.99 (s, 3H, pyrrole ring 5-CH$_3$). δ_C (150 MHz, CDCl$_3$) 199.0, 194.1, 141.3, 137.3, 134.6, 132.7 (ArCH), 131.9, 131.2 (2 × ArCH), 130.7, 128.8 (2 × ArCH), 128.7 (2 × ArCH), 128.4 (2 × ArCH), 128.3 (2 × ArCH), 128.2 (2 × ArCH), 127.2 (2 × ArCH), 121.7, 114.1, 29.6 (–C(O)**C**H$_2$–), 14.2 (pyrrole ring 5-CH$_3$). *m/z* (EI) 379 (85 %, M$^+$), 274 (100), 259 (12), 230 (8), 196 (7), 105(21), 77 (17). Anal. Calc. for $C_{26}H_{21}NO_2$: C 82.30, H 5.58, N 3.69. Found: C 82.43, H 5.65, N 3.65 %.

*2-Methyl-4-(2-oxo-propyl)-5-phenyl-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6r**)*

Light yellow solid; yield: 103 mg (36 %); mp 138–140°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3311 (N–H), 2924, 1689 (C=O), 1605 (C=O), 1446, 1358, 1263, 1163, 1094. δ_H (600 MHz, CDCl$_3$) 8.44 (br s, NH), 7.33 (t, *J* 7.5, 2H, ArH), 7.28–7.23 (m, 3H, ArH), 4.24 (q, *J* 7.2, 2H, –OC*H$_2$*CH$_3$), 3.85 (s, 2H, –C(O)CH$_2$–), 2.50 (s, 3H, pyrrole ring 2-CH$_3$), 2.27 (s, 3H, –CH$_2$C(O)C*H$_3$*), 1.32 (t, *J* 7.2, 3H, –OCH$_2$C*H$_3$*). δ_C (150 MHz, CDCl$_3$) 208.5 (–CH$_2$**C**(O)CH$_3$), 165.7 (–**C**(O)CH$_2$CH$_3$), 136.1 (pyrrole ring 2-*C*), 131.9, 129.5 (pyrrole ring 4-*C*), 128.8 (2 × ArCH), 127.3 (2 × ArCH), 127.2 (ArCH), 115.0 (pyrrole ring 5-*C*), 111.5 (pyrrole ring 3-*C*), 59.3 (–O**C**H$_2$CH$_3$), 41.1 (–C(O)**C**H$_2$–), 29.8 (–C(O)**C**H$_3$), 14.5 (pyrrole ring 2-CH$_3$), 14.1 (–OCH$_2$**C**H$_3$). *m/z* (ESI) 308 ([M + Na]$^+$). Anal. Calc. for $C_{17}H_{19}NO_3$: C 71.56, H 6.71, N 4.91. Found: C 71.63, H 6.77, N 4.84 %.

*2,5-Dimethyl-4-(2-oxo-2-phenyl-ethyl)-1*H*-pyrrole-3-carboxylic Acid Ethyl Ester (**6s**)*

Yellow solid; yield: 71 mg (25 %); mp 122–124°C; R_f 0.2 (chloroform/petroleum ether, 3 : 1). ν_{max} (KBr)/cm^{-1} 3329 (N–H), 2924, 2855, 1680 (C=O), 1447, 1342, 1267, 1213, 1130. δ_H (600 MHz, CDCl$_3$) 8.14 (br s, NH), 8.08 (d, *J* 7.8, 2H, ArH), 7.55 (t, *J* 7.2, 1H, ArH), 7.47 (t, *J* 7.8, 2H, ArH), 4.35 (s, 2H, –C(O)CH$_2$–), 4.09 (q, *J* 7.2, 2H, –OC*H$_2$*CH$_3$), 2.43 (s, 3H, pyrrole ring 2-CH$_3$), 2.08 (s, 3H, pyrrole ring 5-CH$_3$), 1.09

(t, *J* 7.2, 3H, –OCH$_2$*C*H$_3$). δ_C (150 MHz, CDCl$_3$) 198.5 (–CH$_2$**C**(O)Ph), 165.8 (–**C**(O)CH$_2$CH$_3$), 137.3, 134.5 (pyrrole ring 2-C), 132.7 (ArCH), 128.4 (2 × ArCH), 128.2 (2 × ArCH), 124.3 (pyrrole ring 5-C), 113.1 (pyrrole ring 4-C), 110.3 (pyrrole ring 3-C), 58.9 (–O**C**H$_2$CH$_3$), 35.7 (–C(O)**C**H$_2$–), 14.2 (pyrrole ring 5-CH$_3$), 13.9 (pyrrole ring 2-CH$_3$), 10.7 (–OCH$_2$**C**H$_3$). *m/z* (ESI) 308 ([M + Na]$^+$). Anal. Calc. for $C_{17}H_{19}NO_3$: C 71.56, H 6.71, N 4.91. Found: C 71.65, H 6.80, N 4.81 %.

*General Procedure for the Synthesis of Tri-Substituted 2-Pyrones **8a**–**f***

Anhydrous InCl$_3$ (44 mg, 20 mol %) was added to a mixture of a diaroyl acetylene **4a**–**f** (1 mmol) and β-dicarbonyl **2b** or **2d** (1 mmol) in dry isopropyl alcohol (10 mL). The reaction mixture turned reddish-brown after a few minutes of stirring at 80–85°C; stirring was continued at that temperature for the indicated time (Table 4, entry 1–6). The reaction was monitored by TLC using CHCl$_3$/petroleum ether (3 : 2). The solvent was removed under reduced pressure, water (10 mL) was added, and the reaction mixture was extracted with CHCl$_3$ (3 × 10 mL). The organic layer was washed with water (3 × 10 mL) and then with brine (10 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$. The solvent was removed to give an oily mass, which was chromatographed over silica gel using petroleum ether with an increasing proportion of ethyl acetate as eluent to provide the products **8a**–**f**.

*3-Acetyl-4-benzoyl-6-phenyl-pyran-2-one (**8a**)*

Yellow solid; yield: 273 mg (85 %); mp 134–136°C (Lit.[32] 135–137°C); R_f 0.5 (ethyl acetate/petroleum ether, 4 : 96). ν_{max} (KBr)/cm^{-1} 1733 (C=O), 1665 (C=O), 1605 (C=O), 1484. δ_H (600 MHz, CDCl$_3$) 7.90 (d, *J* 7.8, 2H, ArH), 7.85 (d, *J* 7.2, 2H, ArH), 7.63–7.49 (m, 6H, ArH), 6.68 (s, 1H, pyrone ring 5-CH), 2.64 (s, 3H, 3-C(O)CH$_3$). δ_C (150 MHz, CDCl$_3$) 195.3, 194.0, 165.5 (pyrone ring 2-*C*(O)O–), 160.8, 159.7, 134.3, 134.1 (ArCH), 132.9 (ArCH), 129.8, 129.3 (2 × ArCH), 129.0 (2 × ArCH), 128.7 (2 × ArCH), 126.9 (2 × ArCH), 117.8, 100.9 (pyrone ring 5-CH), 30.7 (3-C(O)**C**H$_3$). *m/z* (ESI) 341 ([M + Na]$^+$). Anal. Calc. for $C_{20}H_{14}O_4$: C 75.46, H 4.43. Found: C 75.41, H 4.45 %.

*3-Acetyl-4-(4-methyl-benzoyl)–6-p-tolyl-pyran-2-one (**8b**)*

Yellow solid; yield: 262 mg (76 %); mp 126–128°C (Lit.[32] 127–130°C); R_f 0.5 (ethyl acetate/petroleum ether, 5 : 95). ν_{max} (KBr)/cm^{-1} 1734 (C=O), 1667 (C=O), 1609 (C=O), 1483. δ_H (300 MHz, CDCl$_3$) 7.81–7.72 (m, 4H, ArH), 7.31–7.26 (m, 4H, ArH), 6.62 (s, 1H, pyrone ring 5-CH), 2.62 (s, 3H, 3-C(O)CH$_3$), 2.43 (s, 6H, Ar-CH$_3$). δ_C (75 MHz, CDCl$_3$) 195.7, 194.1, 166.1 (pyrone ring 2-*C*(O)O–), 161.4, 160.3, 145.5, 144.3, 132.4, 130.5 (2 × ArCH), 130.1 (2 × ArCH), 129.2 (2 × ArCH), 127.6, 127.1 (2 × ArCH), 117.7, 100.8 (pyrone ring 5-CH), 31.0 (3-C(O)**C**H$_3$), 22.2 (Ar-CH$_3$), 22.1 (Ar-CH$_3$). *m/z* (ESI) 369 ([M + Na]$^+$). Anal. Calc. for $C_{22}H_{18}O_4$: C 76.29, H 5.24. Found: C 76.24, H 5.29 %.

*3-Acetyl-4-(4-chloro-benzoyl)-6-(4-chloro-phenyl)-pyran-2-one (**8c**)*

Yellow solid; yield: 275 mg (71 %); mp 244–246°C; R_f 0.5 (ethyl acetate/petroleum ether, 5 : 95). ν_{max} (KBr)/cm^{-1} 1733 (C=O), 1663 (C=O), 1607 (C=O), 1481. δ_H (600 MHz, CDCl$_3$) 7.83–7.76 (m, 4H, ArH), 7.50–7.46 (m, 4H, ArH), 6.61 (s, 1H, pyrone ring 5-CH), 2.63 (s, 3H, 3-C(O)CH$_3$). δ_C (150 MHz, CDCl$_3$) 195.2, 192.6, 164.6 (pyrone ring 2-*C*(O)O–), 160.1, 159.3, 140.7, 139.5, 132.7, 129.9 (2 × ArCH), 129.8 (2 × ArCH), 129.4 (2 × ArCH), 128.1, 127.9 (2 × ArCH), 117.9, 100.7 (pyrone ring 5-CH), 30.6 (3-C(O)**C**H$_3$). *m/z* (ESI) 409 ([M + Na]$^+$). Anal. Calc. for $C_{20}H_{12}Cl_2O_4$: C 62.04, H, 3.12. Found: C 62.10, H 3.09 %.

*3-Acetyl-4-(4-bromo-benzoyl)-6-(4-bromo-phenyl)-pyran-2-one (**8d**)*

Yellow solid; yield: 371 mg (78 %); mp 250–252°C; R_f 0.5 (ethyl acetate/petroleum ether, 5 : 95). ν_{max} (KBr)/cm^{-1} 1728 (C=O), 1663 (C=O), 1605 (C=O), 1483. δ_H (600 MHz, CDCl$_3$) 7.76 (d, *J* 9.0, 2H, ArH), 7.69 (d, *J* 8.4, 2H, ArH), 7.66–7.63 (m, 4H, ArH), 6.62 (s, 1H, pyrone ring 5-CH), 2.63 (s, 3H, 3-C(O)CH$_3$). δ_C (150 MHz, CDCl$_3$) 195.2, 192.8, 164.7 (pyrone ring 2-*C*(O)O–), 160.1, 159.2, 133.1, 132.7 (2 × ArCH), 132.4 (2 × ArCH), 130.0 (2 × ArCH), 129.4, 128.6, 128.1, 128.0 (2 × ArCH), 118.0, 100.7 (pyrone ring 5-CH), 30.6 (3-C(O)**C**H$_3$). *m/z* (ESI) 499 ([M + Na]$^+$). Anal. Calc. for $C_{20}H_{12}Br_2O_4$: C 50.45, H 2.54. Found: C 50.39, H 2.51 %.

*3-Acetyl-4-(3-chloro-4-methyl-benzoyl)-6-(3-chloro-4-methyl-phenyl)-pyran-2-one (**8e**)*

Yellow solid; yield: 258 mg (62 %); mp 170–172°C; R_f 0.5 (ethyl acetate/petroleum ether, 5 : 95). ν_{max} (KBr)/cm^{-1} 1735 (C=O), 1672 (C=O), 1607 (C=O), 1477. δ_H (600 MHz, CDCl$_3$) 7.78 (d, *J* 1.8, 1H, ArH), 7.72 (d, *J* 1.8, 1H, ArH), 7.65 (dd, *J* 8.4, 2.4, 1H, ArH), 7.56 (dd, *J* 8.1, 2.1, 1H, ArH), 7.47 (d, *J* 8.4, 1H, ArH), 7.45 (d, *J* 8.4, 1H, ArH), 6.61 (s, 1H, pyrone ring 5-CH), 2.63 (s, 3H, 3-C(O)CH$_3$), 2.44 (s, 3H, Ar-CH$_3$), 2.43 (s, 3H, Ar-CH$_3$). δ_C (150 MHz, CDCl$_3$) 195.3, 193.0, 164.8 (pyrone ring 2-C(O)O–), 160.4, 159.5, 140.9, 139.7, 137.7, 137.3, 132.7, 130.8 (ArCH), 130.1 (ArCH), 129.8 (ArCH), 128.9 (ArCH), 128.1, 127.3 (ArCH), 125.3 (ArCH), 117.7, 100.8 (pyrone ring 5-CH), 30.7 (3-C(O)**C**H$_3$), 20.2 (2 × ArCH$_3$). *m/z* (ESI) 437 ([M + Na]$^+$). Anal. Calc. for $C_{22}H_{16}Cl_2O_4$: C 63.63, H 3.88. Found: C 63.55, H 3.80 %.

*3,4-Dibenzoyl-6-phenyl-pyran-2-one (**8f**)*

Yellow solid; yield: 242 mg (63 %); mp 156–158°C; R_f 0.5 (ethyl acetate/petroleum ether, 4 : 96). ν_{max} (KBr)/cm^{-1} 1728 (C=O), 1778 (C=O), 1607 (C=O), 1499, 1263. δ_H (300 MHz, CDCl$_3$) 7.89–7.79 (m, 5H, ArH), 7.63–7.39 (m, 10H, ArH), 6.80 (s, 1H, pyrone ring 5-CH). δ_C (75 MHz, CDCl$_3$) 193.2, 191.5, 163.2 (pyrone ring 2-C(O)O–), 159.3, 156.2, 136.3, 134.6 (ArCH), 134.3, 133.8 (ArCH), 132.3 (ArCH), 130.1, 129.6 (2 × ArCH), 129.3 (2 × ArCH), 129.2 (2 × ArCH), 128.9 (2 × ArCH), 128.4 (2 × ArCH), 126.2 (2 × ArCH), 122.2, 100.4 (pyrone ring 5-CH). *m/z* (ESI) 403 ([M + Na]$^+$). Anal. Calc. for $C_{25}H_{16}O_4$: C 78.94, H 4.24. Found: C 79.03, H 4.30 %.

*3-Amino-1,3-diphenylprop-2-en-1-one (**9**)*

White solid; yield: 172 mg (77 %); mp 76–78°C [lit.[31] mp 78–79°C]. δ_H (600 MHz, CDCl$_3$) 10.43 (br s, NH), 7.96–7.94 (m, 2H, ArH), 7.65–7.63 (m, 2H, ArH), 7.52–7.42 (m, 6H, ArH), 6.16 (s, 1H, =CH–), 5.44 (br s, NH). δ_C (150 MHz, CDCl$_3$) 190.2 (Ph**C**(O)CH=), 162.8 (C-NH$_2$), 140.3, 137.6, 131.1 (ArCH), 130.7 (ArCH), 129.1 (2 × ArCH), 128.3 (2 × ArCH), 127.2 (2 × ArCH), 126.3 (2 × ArCH), 91.9 (=CH–). *m/z* (ESI)

246 ($[M+Na]^+$). Anal. Calc. for $C_{15}H_{13}NO$: C 80.69, H 5.87, N 6.27. Found: C 80.61, H 5.94, N, 6.19 %.

Supplementary Material

^{1}H and ^{13}C NMR spectra for compounds **6a**–**s** and **8a**–**f** and *ORTEP* diagrams of **6d**, **6i**, and **6l** are available on the Journal's website. The CCDC numbers of **6a**, **6d**, **6i**, **6l**, and **8a** are 759230, 836577, 836578, 836579, and 869936. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This project was funded by the Council of Scientific and Industrial Research (CSIR), New Delhi, India in the form of Network Project (*ORIGIN*). Author S.K.M. thanks the CSIR, New Delhi, India for award of Senior Research Fellowship (SRF). Thanks are also due to Mr. Partha Mitra of Department of Inorganic Chemistry, IACS, Kolkata, India for his help in refining raw data of X-ray analysis.

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