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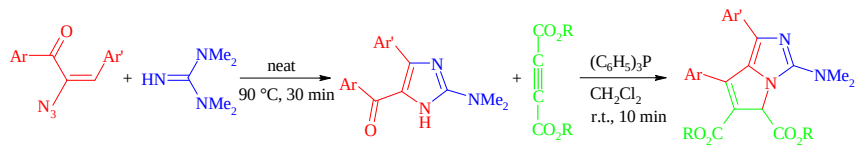

A new synthetic strategy towards 2,4,5-trisubstituted 1*H*-imidazoles and highly substituted pyrrolo[1,2-*c*]imidazoles by use of α-azidochalcones *via* Michael addition-cyclization followed by Wittig reaction

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Abstract

Efficient and facile protocols for the preparation of highly functionalized 1*H*-imidazoles and 5*H*-pyrrolo[1,2-*c*]imidazoles are described. Heating a mixture of an α-azidochalcones and *N*,*N*,*N'*,*N'*-tetramethyl guanidine under neat conditions gave the corresponding 2,4,5-trisubstituted 1*H*-imidazole *via* Michael addition-cyclization in excellent yields. Subsequently, the prepared 1*H*-imidazoles undergo addition-Wittig reaction with acetylenic esters in presence of triphenylphosphine in dichloromethane to afford 5*H*-pyrrolo[1,2-*c*]imidazoles in high yields.

Keywords: α-Azidochalcones, *N*,*N*,*N'*,*N'*-tetramethyl guanidine, 2,4,5-trisubstituted 1*H*-imidazoles, 5*H*-pyrrolo[1,2-*c*]imidazoles, Michael addition-cyclization-Wittig reaction.

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1. Introduction

2-Aminoimidazoles are valuable scaffolds in pharmaceutical chemistry. They exhibit different biological effects resulting in their extensive use as human *β*-secretase and biofilm formation inhibitory activity, antibacterial, antimicrobial, anticancer, anti-inflammatory, and antagonists of serotonergic and histaminergic receptors.[1] Thus, great attention has been focused for development of new approaches towards these compounds.[2]

Pyrrolo[1,2-*c*]imidazoles have attracted great attention as common structural motifs in naturally occurring compounds and pharmacologically important synthetic compounds.[3] Compounds having the pyrrolo[1,2-*c*]imidazole scaffold have been shown to possess a broad range of biological activities including cardiotonic, neuroprotective, antinociceptive, tissue-selective agonist of androgen receptor, anxiolytic, antiviral, antibacterial, antifungal, and herbicidal properties.[4]

Over the last decade, α-azidochalcones have got one of the fascinating synthons in organic synthesis. They have been widely applied to synthesize various nitrogen containing five- or six-memebered rings such as pyrroles,[5] indoles,[6] pyrazoles,[7] imidazoles,[8] oxazoles,[9] thiazoles,[10] triazolines,[5c,11] pyridines and pyrimidines,[12] isoquinolines,[13] pyrrolo[1,2-*a*]pyrazines[14] and imidazo[1,2-*a*]pyridines.[15]

In 2014, a direct synthesis of 2-aminoimidazoles was reported by Yu and co-workers. Heating a mixture of a vinyl azide and cyanamide in the presence of Et_3N in ethanol afforded the corresponding 2-aminoimidazoles in good yields.[8b]

Very recently, Guchhait and co-workers have reported an imidazole synthesis by treating guanidine derivatives and 2-bromo-2-alkenones which afforded the corresponding 2-aminoimidazoles.[16]

It has been reported that three-component reactions between triphenylphosphine, acetylenic esters and various NH-acids such as 2-pyrrolylglyoxalate, 2-indolecarboxaldehyde or imidazole-4-carbaldehyde afforded the corresponding phosphorus ylides. The phosphorane intermediates underwent smooth intramolecular Wittig reaction to afford 1*H*-pyrrolizines,[17a] 3*H*-pyrrolo[1,2-*a*]indoles[17b] and pyrrolo[1,2-*c*]imidazoles,[17c] respectively, among other mono- and bicyclo azaheterocyclic compounds.

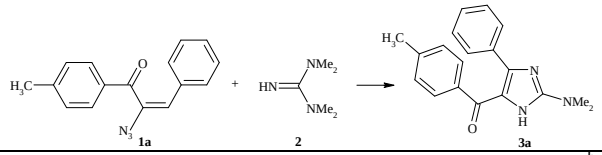
As part of our ongoing effort to develop efficient strategies for the preparation of biologically active heterocyclic compounds from readily accessible precursors,[18] herein, we describe efficient synthetic routes leading to highly functionalized 1*H*-

imidazoles and 5*H*-pyrrolo[1,2-*c*]imidazoles. This proposed protocol involves Michael addition-cyclization of α-azidochalcones with *N*,*N*,*N'*,*N'*-tetramethyl guanidine (TMG) giving 2,4,5-trisubstituted 1*H*-imidazoles, which subsequently will be treated with acetylenic esters in the presence of triphenylphosphine through addition-intramolecular Wittig reaction to produce fully substituted 5*H*-pyrrolo[1,2-*c*]imidazoles.

2. Result and discussion

First, to achieve the best conditions for synthesis of 2,4,5-trisubstituted 1*H*-imidazoles **3**, α-azidochalcone **1a**[19] was selected as model substrate and the effects of several solvents, reaction temperature and time as well as different equivalents of TMG were investigated (Table 1). Initially, the reaction was carried out in the presence of **2** (1.0 equiv) in acetonitrile at ambient temperature for 30 min and 1*H*-imidazole **3a** was detected in 10% yield (entry 1). By rising the temperature to 50 °C and then refluxing acetonitrile, 1*H*-imidazole **3a** obtained in 20 and 37% yields, respectively (entries 2 and 3). However, increasing the time to 40 and 60 min had no effect on the yield (entries 4 and 5). Subsequently, different quantities of **2** were evaluated to improve the yield (entries 6–8). Increasing the amount of **2** to 1.5 and 2 equiv, led to the desired product **3a** in 45 and 62% yields, respectively (entries 6 and 7). However, applying more quantities of **2** was ineffective (entry 8). By carrying out the reaction in other solvents such as DMF, toluene (both at 80 and 100 °C), acetone (reflux) and EtOH (reflux), **3a** obtained in 25–68% yields (entries 9–14). The effect of neat conditions at different temperatures and times with the optimized ratios was also tested (entries 15–17). It could be seen that the best result was attained at 90 °C after 30 with a 1:2 molar ratios, in which **3a** was obtained in 95% yield (entry 17). Carrying out the reaction at this temperature beyond 30 min or at higher temperatures, led to lower yields of **3a** (entries 18 and 19). Thus, the optimal conditions for the formation of 1*H*-imidazole **3a** were determined: TMG **2** (2 equiv), under neat conditions (no solvent) at 90 °C for 30 min (entry 17).

Table 1. Condition screening for the reaction between α-azidochalcone **1a** and TMG **2**[a]

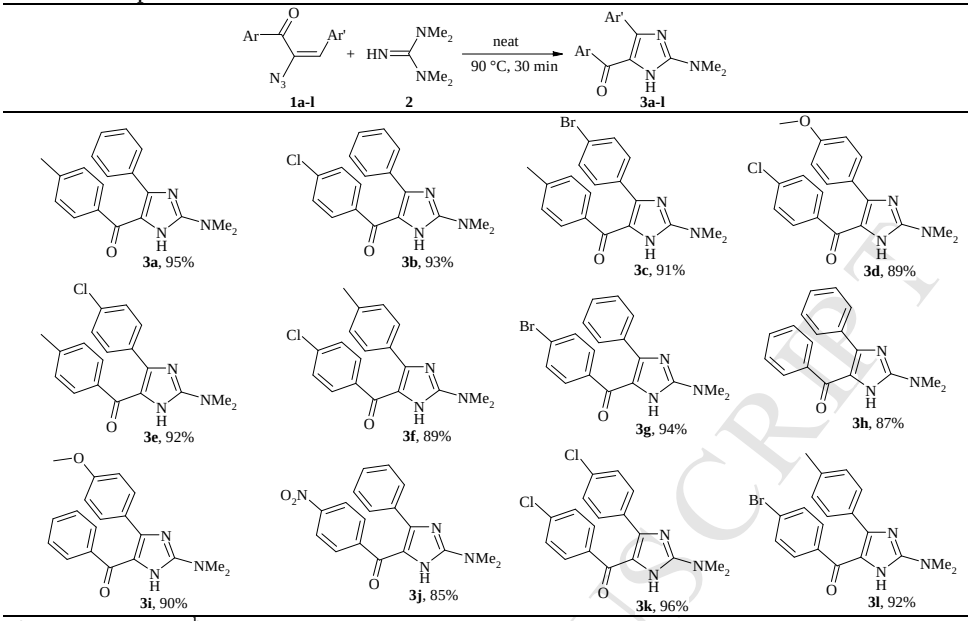


Entry	Solvent	TMG (equiv)	temp (°C)	Time (min)	Yield (%)[b]
1	CH_3CN	1	25	30	10
2	CH_3CN	1	50	30	20
3	CH_3CN	1	Reflux	30	37
4	CH_3CN	1	Reflux	40	37
5	CH_3CN	1	Reflux	60	37
6	CH_3CN	1.5	Reflux	30	45
7	CH_3CN	2	Reflux	30	62
8	CH_3CN	2.5	Reflux	30	62
9	DMF	2	80	30	68
10	DMF	2	100	30	68
11	Toluene	2	80	30	32
12	Toluene	2	100	30	25
13	Acetone	2	Reflux	30	40
14	EtOH	2	Reflux	30	53
15	—	2	50	30	64
16	—	2	75	30	82
17	—	2	90	30	95
18	—	2	90	40	86
19	—	2	110	30	80

[a]Reaction conditions: α-azidochalcones (0.5 mmol), solvent (1.5 mL). [b]Isolated yields.

After optimization of the reaction conditions, with the purpose of extending this reaction, a series of different α-azidochalcones with electron-donating alkyl or methoxy groups as well as electron-withdrawing chlorine, bromine and nitro groups (**1a–l**) treated with TMG **2** in a 1:2 molar ratio under neat conditions at 90 °C. All the reactions went to completion within 30 min. TLC and NMR analysis of the reaction mixtures clearly indicated the formation of the corresponding 2,4,5-trisubstituted 1*H*-imidazole **3a–l** in excellent yields. The results are summarized in Table 2. The structures of the isolated products were deduced on the basis of their IR, ^{1}H, and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

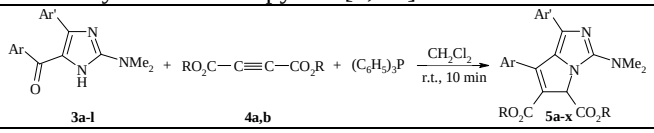
Table 2. Substrate scope for the synthesis of 2,4,5-trisubstituted 1*H*-imidazole **3a–l** under the optimized conditions[a,b]



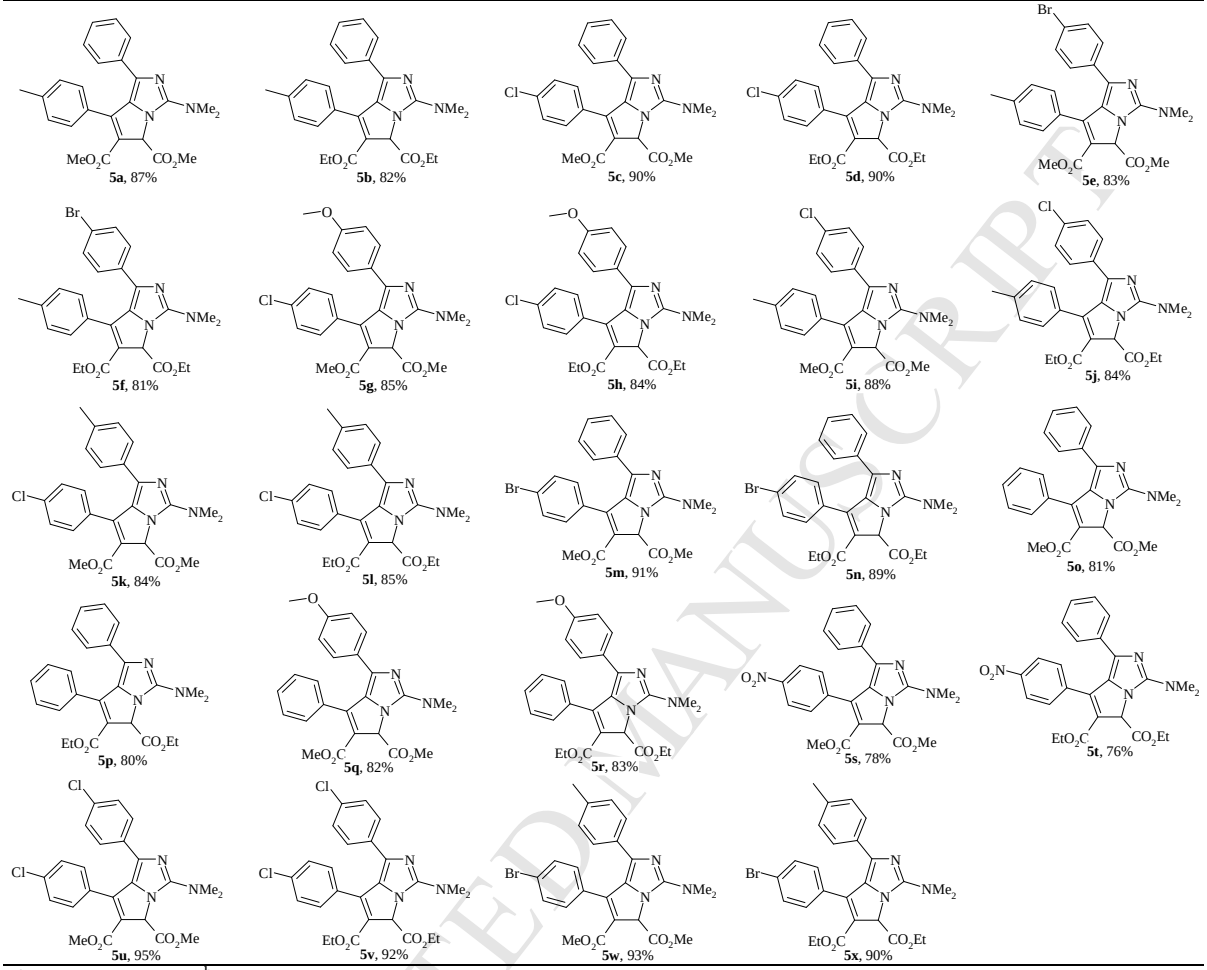
[a]Isolated yields. [b]All products were purified by recrystallization from EtOAc.

The presence of appropriately positioned NH and carbonyl functionalities in the prepared 2,4,5-trisubstituted 1*H*-imidazoles **3** encouraged us to use these entities for the preparation of bridgehead bicyclic 5:5 ring systems 5*H*-pyrrolo[1,2-*c*]imidazoles **5** through an intramolecular Wittig reaction. The reaction of 1*H*-imidazoles **3a–l** with acetylenic esters **4a**,**b** in the presence of triphenylphosphine proceeded smoothly in dichloromethane to afford highly substituted 5*H*-pyrrolo[1,2-*c*]imidazoles **5a–x** in high yields. The reactions were carried out at ambient temperature and completed within 10 min. TLC and ^{1}H NMR analysis of the reaction mixtures clearly indicated formation of 5*H*-pyrrolo[1,2-*c*]imidazoles **5**. Any product other than **5** and triphenylphosphine oxide could not be detected by NMR spectroscopy. The results are summarized in Table 3. Structure **5** was assigned to the isolated products on the basis of their elemental analyses, mass spectrometry, as well as their ^{1}H and ^{13}C NMR and IR spectral data.

Table 3. Substrate scope for the synthesis of 5*H*-pyrrolo[1,2-*c*]imidazoles **5a–x**[a–c]



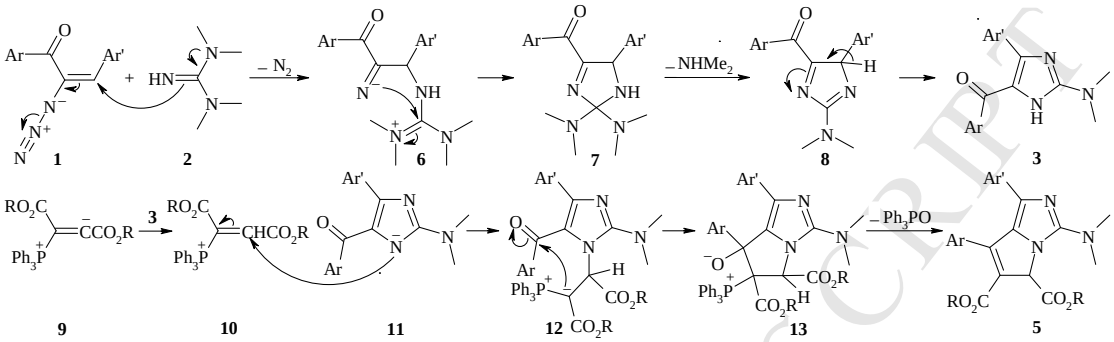
3a-l **4a,b** **5a-x**



[a]Isolated yields. [b]In the case of compounds **5d**, **5n** and **5o**, at first most of the by-product PPh_3O was separated by nucleation of its crystals into a 2:3 *n*-hexane/EtOAc solution of the reaction mixture, followed by decreasing the polarity of the mother liquor to 1:1 *n*-hexane/EtOAc, from which the product was crystallized. Other products were purified by crystallization from 1:1 *n*-hexane/EtOAc. [c]All products were subjected to a further recrystallization from 1:1 *n*-hexane/EtOAc for data collection.

A plausible mechanism for the formation of 1*H*-imidazoles **3** and *5H*-pyrrolo[1,2-*c*]imidazoles **5** is outlined in Scheme 1. The reaction is initiated by Michael addition of TMG **2** to α-azidochalcone **1** by removal of a nitrogen molecule and formation of intermediate **6**. Intramolecular nucleophilic attack of *N*-atom to the adjacent iminium give the 2,3-dihydro-1*H*-imidazole intermediate **7**, which may undergo elimination of dimethylamine as well as a proton shift to afford 5-aroyl-4-aryl-2-(dimethylamino)-1*H*-imidazole **3** through **8**. On the other hand, the 1:1 zwitter ionic intermediate **9** generated from the initial addition of triphenylphosphine to the acetylenic ester **4** may be protonated by the NH-acid **3**. Then, the positively charged ion **10** may be attacked

by the conjugate base of NH-acid **11** to form the phosphorus ylide **12**. Phosphorane **12** undergoes an intramolecular Wittig reaction to afford the bridgehead bicyclic system 5*H*-pyrrolo[1,2-*c*]imidazole-5,6-dicarboxylate **5** through betaine intermediate **13**.



Scheme 1 Proposed reaction mechanism.

3. Conclusion

In conclusion, we have developed new strategies for the preparation of two valuable aza-heterocycles 1*H*-imidazoles and 5*H*-pyrrolo[1,2-*c*]imidazoles by use of α-azidochalcones. The use of easily available starting materials, efficiency and facility of operation, short reaction times, catalyst-free and mild conditions, easy work-up without any need to chromatography purification processes as well as high yields of the products are the main advantages of the strategy.

4. Experimental

4.1. General

All chemicals were purchased from Merck (Germany) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on an Agilent Technologies (HP) 5973 mass spectrometer operating at an ionization potential of 20 eV. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured ($CDCl_3$ solution) with Bruker DRX-300 (at 300.1 and 75.5 MHz) and Bruker DRX-500 AVANCE (at 500.1 and 125.8 MHz) instruments.

4.2. General procedure for the preparation of dibromochalcones: To a suspension of the corresponding chalcone (50.0 mmol) in ether (200 mL) was added dropwise

bromine (50.0 mmol) at 0 °C, which was stirred at the same temperature. After completion of the reaction (monitored by TLC), the precipitate was filtered off and washed with cold water. The products were enough pure that were used for the next reaction without further purification.[19]

4.3. General procedure for the preparation of vinyl azides: To a solution of a dibromochalcone (10.0 mmol) in DMF (45 mL) was added sodium azide (37.3 mmol) at ambient temperature. It took nearly 3h that all the starting materials were disappeared. Then the reaction mixture was poured into water and extracted with dichloromethane. The organic extracts were washed with brine (2 × 40 mL), water (40 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was crystallized from *n*-hexane to afford the corresponding vinyl azides.[19]

4.4. General procedure for the preparation of 2,4,5-trisubstituted 1*H*-imidazoles (3a–l): A mixture of the appropriate α-azidochalcone **1** (1 mmol) and *N*,*N*,*N*′,*N*′-tetramethyl guanidine **2** (2 mmol) was stirred at 90 °C for 30 min. After completion the reaction, as was indicated by TLC monitoring, the mixture was cooled to ambient temperature and the residue was recrystallized from EtOAc.

*4.4.1. 2-(Dimethylamino)-5-(4-methylbenzoyl)-4-phenyl-1H-imidazole (**3a**)*

Yellow crystals, mp 174 °C, yield: 0.290 g, 95%. IR (KBr) (ν_{max}/cm^{-1}): 3135 (NH), 1610 (C=O), 1526, 1487, 1438, 1375, 1348, 1322, 1301, 1278, 1230, 1173, 1074, 1042, 1013, 911, 855, 827, 780, 749, 697. EI-MS, *m/z* (%): 305 (M^+, 100), 290 (9), 276 (20), 261 (8), 213 (8), 198 (37), 185 (17), 170 (15), 156 (20), 142 (6), 129 (5), 119 (40), 103 (6), 91 (45), 77 (6), 65 (16), 56 (11), 42 (6). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.22 (s, 3H, CH_3), 3.15 (s, 6H, NMe_2), 6.83 (d, J = 8.0 Hz, 2H, 2CH), 7.01 (t, J = 7.5 Hz, 2H, 2CH), 7.09 (t, J = 7.5 Hz, 1H, CH), 7.19 (dd, J = 8.1, 1.3 Hz, 2H, 2CH), 7.31 (d, J = 8.0 Hz, 2H, 2CH), 10.25–10.95 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.4 (CH_3), 38.3 ($2NCH_3$), 124.2 (C), 127.4 (2CH), 127.5 (CH), 128.1 (2CH), 129.4 (2CH), 129.8 (2CH), 134.6, 135.6 and 141.3 (3C), 151.6 (CN_3), 154.5 (C), 184.6 (C=O). Anal. Calcd for $C_{19}H_{19}N_3O$ (305.37): C, 74.73; H, 6.27; N, 13.76. Found: C, 74.59; H, 6.14; N, 13.55%.

*4.4.2. 2-(Dimethylamino)-5-(4-chlorobenzoyl)-4-phenyl-1H-imidazole (**3b**)*

Yellow crystals, mp 176–177 °C, yield: 0.302 g, 93%. IR (KBr) (ν_{max}/cm^{-1}): 3237 (NH), 1620 (C=O), 1546, 1483, 1373, 1322, 1277, 1233, 1173, 1080, 1011, 910, 835, 756, 695, 676, 617. EI-MS, *m/z* (%): 327 ($M^{+\ 37}$Cl, 35), 325 ($M^{+\ 35}$Cl, 100), 312 (10), 310 (30), 296 (44), 283 (5), 281 (14), 240 (16), 214 (15), 198 (54), 186 (9), 170 (15),

159 (19), 139 (56), 129 (8), 111 (45), 102 (19), 89 (29), 71 (17), 57 (16), 43 (12). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.17 (s, 6H, NMe_2), 7.00 (d, J = 8.2 Hz, 2H, 2CH), 7.06 (dd, J = 8.1, 7.5 Hz, 2H, 2CH), 7.15 (t, J = 7.5 Hz, 1H, CH), 7.16 (d, J = 8.0 Hz, 2H, 2CH), 7.30 (d, J = 8.2 Hz, 2H, 2CH), 9.20–10.75 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.0 ($2NCH_3$), 123.3 (C), 127.29 (2CH), 127.34 (2CH), 127.9 (CH), 129.4 (2CH), 130.1 (2CH), 132.8, 136.1 and 136.7 (3C), 150.7 (CN_3), 153.6 (C), 182.6 (C=O). Anal. Calcd for $C_{18}H_{16}ClN_3O$ (325.79): C, 66.36; H, 4.95; N, 12.90. Found: C, 66.30; H, 5.03; N, 12.86%.

*4.4.3. 4-(4-Bromophenyl)-2-(dimethylamino)-5-(4-methylbenzoyl)-1H-imidazole (**3c**)*

Yellow crystals, mp 208 °C, yield: 0.349 g, 91%. IR (KBr) (ν_{max}/cm^{-1}): 3245 (NH), 1614 (C=O), 1571, 1543, 1481, 1443, 1375, 1317, 1231, 1170, 1104, 1069, 1009, 916, 826, 794, 760, 677. EI-MS, *m/z* (%): 385 (M^{+} ^{81}Br, 85), 383 (M^{+} ^{79}Br, 92), 354 (8), 304 (12), 276 (13), 264 (8), 250 (7), 237 (10), 196 (12), 184 (37), 169 (25), 119 (93), 102 (17), 91 (100), 65 (25). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.29 (s, 3H, CH_3), 3.16 (s, 6H, NMe_2), 6.90 (d, J = 7.9 Hz, 2H, 2CH), 7.06 (d, J = 8.6 Hz, 2H, 2CH), 7.16 (d, J = 8.6 Hz, 2H, 2CH), 7.28 (d, J = 8.1 Hz, 2H, 2CH), 9.77–9.92 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.4 (CH_3), 38.2 ($2NCH_3$), 121.9 and 124.0 (2C), 128.3 (2CH), 129.2 (2CH), 130.5 (2CH), 131.2 (2CH), 133.4, 135.3 and 141.8 (3C), 149.7 (CN_3), 154.1 (C), 184.3 (C=O). Anal. Calcd for $C_{19}H_{18}BrN_3O$ (384.27): C, 59.39; H, 4.72; N, 10.94. Found: C, 59.31; H, 4.68; N, 10.79%.

*4.4.4. 5-(4-Chlorobenzoyl)-2-(dimethylamino)-4-(4-methoxyphenyl)-1H-imidazole (**3d**)*

Yellow crystals, mp 216–218 °C, yield: 0.316 g, 89%. IR (KBr) (ν_{max}/cm^{-1}): 3248 (NH), 1608 (C=O), 1576, 1542, 1495, 1443, 1380, 1321, 1237, 1169, 1085, 1011, 913, 841, 798, 762, 719, 666. EI-MS, *m/z* (%): 357 (M^{+} ^{37}Cl, 32), 355 (M^{+} ^{35}Cl, 100), 340 (29), 326 (32), 311 (8), 285 (4), 270 (9), 244 (12), 228 (35), 216 (35), 200 (18), 186 (15), 159 (17), 139 (74), 111 (47), 75 (17), 56 (8), 42 (8). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.14 (s, 6H, NMe_2), 3.71 (s, 3H, OCH_3), 6.57 (d, J = 8.7 Hz, 2H, 2CH), 7.02 (d, J = 8.4 Hz, 2H, 2CH), 7.08 (d, J = 8.7 Hz, 2H, 2CH), 7.30 (d, J = 8.4 Hz, 2H, 2CH), 9.60–10.85 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 37.9 ($2NCH_3$), 54.9 (OCH_3), 112.8 (2CH), 123.3 and 125.7 (2C), 127.3 (2CH), 130.1 (2CH), 130.7 (2CH), 136.36 and 136.41 (2C), 151.6 (CN_3), 154.0 and 159.3 (2C), 182.3 (C=O). Anal. Calcd for $C_{19}H_{18}ClN_3O_2$ (355.82): C, 64.13; H, 5.10; N, 11.81. Found: C, 63.89; H, 5.05; N, 11.70%.

*4.4.5. 4-(4-Chlorophenyl)-2-(dimethylamino)-5-(4-methylbenzoyl)-1H-imidazole (**3e**)*

Yellow crystals, mp 209–210 °C, yield: 0.312 g, 92%. IR (KBr) (ν_{max}/cm^{-1}): 3170 (NH), 1614 (C=O), 1549, 1523, 1481, 1378, 1342, 1307, 1229, 1171, 1089, 1049, 1012, 958, 912, 828, 795, 759, 735, 706, 672. EI-MS, *m/z* (%): 341 (M^{+} ^{37}Cl, 34), 339 (M^{+} ^{35}Cl, 100), 324 (13), 310 (27), 295 (10), 248 (12), 232 (53), 219 (18), 204 (19), 193 (14), 184 (44), 150 (14), 137 (15), 119 (90), 91 (73), 82 (8), 65 (23), 56 (10), 42 (7). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.28 (s, 3H, CH_3), 3.16 (s, 6H, NMe_2), 6.89 (d, J = 8.0 Hz, 2H, 2CH), 7.00 (d, J = 8.5 Hz, 2H, 2CH), 7.12 (d, J = 8.5 Hz, 2H, 2CH), 7.28 (d, J = 8.0 Hz, 2H, 2CH), 9.30–10.80 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.0 (CH_3), 38.0 ($2NCH_3$), 123.6 (C), 127.2 (2CH), 127.9 (2CH), 128.9 (2CH), 130.6 (2CH), 131.9, 133.4, 134.8 and 141.6 (4C), 148.5 (CN_3), 153.5 (C), 184.1 (C=O). Anal. Calcd for $C_{19}H_{18}ClN_3O$ (339.82): C, 67.15; H, 5.34; N, 12.37. Found: C, 67.04; H, 5.41; N, 12.16%.

*4.4.6. 5-(4-Chlorobenzoyl)-2-(dimethylamino)-4-(4-methylphenyl)-1H-imidazole (**3f**)*

Yellow crystals, mp 221–222 °C, yield: 0.302 g, 89%. IR (KBr) (ν_{max}/cm^{-1}): 3246 (NH), 1617 (C=O), 1576, 1542, 1498, 1444, 1376, 1320, 1228, 1173, 1084, 1010, 913, 848, 825, 762, 726, 670. EI-MS, *m/z* (%): 341 (M^{+} ^{37}Cl, 34), 339 (M^{+} ^{35}Cl, 100), 324 (23), 310 (33), 295 (9), 228 (12), 212 (38), 200 (22), 184 (23), 170 (18), 139 (61), 130 (22), 111 (45), 102 (38), 91 (7), 75 (16), 65 (3), 56 (6), 42 (8). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.25 (s, 3H, CH_3), 3.15 (s, 6H, NMe_2), 6.86 (d, J = 7.9 Hz, 2H, 2CH), 7.01 (d, J = 8.5 Hz, 2H, 2CH), 7.04 (d, J = 7.9 Hz, 2H, 2CH), 7.30 (d, J = 8.5 Hz, 2H, 2CH), 9.51–10.85 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.1 (CH_3), 38.3 ($2NCH_3$), 123.7 (C), 127.6 (2CH), 128.3 (2CH), 129.6 (2CH), 130.4 (2CH), 130.6, 136.6, 136.9 and 138.1 (4C), 151.9 (CN_3), 154.2 (C), 182.9 (C=O). Anal. Calcd for $C_{19}H_{18}ClN_3O$ (339.82): C, 67.15; H, 5.34; N, 12.37. Found: C, 67.09; H, 5.28; N, 12.08%.

*4.4.7. 5-(4-Bromobenzoyl)-2-(dimethylamino)-4-phenyl)-1H-imidazole (**3g**)*

Yellow crystals, mp 189 °C, yield: 0.347 g, 94%. IR (KBr) (ν_{max}/cm^{-1}): 3228 (NH), 1616 (C=O), 1546, 1483, 1373, 1320, 1277, 1232, 1173, 1066, 1008, 908, 832, 755, 698, 672. EI-MS, *m/z* (%): 371 (M^{+} ^{81}Br, 96), 369 (M^{+} ^{79}Br, 100), 356 (14), 354 (15), 342 (21), 340 (22), 214 (12), 198 (46), 185 (40), 170 (12), 155 (28), 129 (6), 116 (11), 103 (14), 89 (25), 76 (19), 56 (11), 42 (5). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.16 (s, 6H, NMe_2), 7.05 (dd, J = 7.6, 7.0 Hz, 2H, 2CH), 7.14−7.17 (m, 5H, 5CH), 7.23 (d, J = 8.5 Hz, 2H, 2CH), 9.10–10.80 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.3

(2NCH_3), 123.8 and 125.5 (2C), 127.6 (2CH), 128.2 (CH), 129.7 (2CH), 130.59 (2CH), 130.64 (2CH), 133.4 and 136.9 (2C), 151.7 (CN_3), 154.2 (C), 183.0 (C=O). Anal. Calcd for $C_{18}H_{16}BrN_3O$ (370.24): C, 58.39; H, 4.36; N, 11.35. Found: C, 58.14; H, 4.44; N, 11.18%.

*4.4.8. 5-Benzoyl-2-(dimethylamino)-4-phenyl-1H-imidazole (**3h**)*

Yellow crystals, mp 179–180 °C, yield: 0.253 g, 87%. IR (KBr) (ν_{max}/cm^{-1}): 3258 (NH), 1609 (C=O), 1554, 1489, 1444, 1377, 1325, 1240, 1171, 1071, 1013, 913, 850, 782, 726, 691, 654. EI-MS, *m/z* (%): 291 (M^+, 100), 276 (40), 262 (60), 247 (16), 214 (24), 198 (50), 186 (17), 178 (8), 170 (15), 159 (23), 142 (8), 129 (8), 116 (14), 105 (62), 89 (33), 77 (70), 67 (8), 51 (16), 42 (7). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.17 (s, 6H, NMe_2), 6.99–7.10 (m, 5H, 5CH), 7.16−7.24 (m, 3H, 3CH), 7.39 (dd, J = 8.1, 1.3 Hz, 2H, 2CH), 9.60–10.80 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.0 (2NCH_3), 123.6 (C), 127.08 (2CH), 127.10 (2CH), 127.5 (CH), 128.7 (2CH), 129.4 (2CH), 130.5 (CH), 133.4 and 137.8 (2C), 150.9 (CN_3), 153.8 (C), 184.2 (C=O). Anal. Calcd for $C_{18}H_{17}N_3O$ (291.35): C, 74.20; H, 5.88; N, 14.42. Found: C, 74.03; H, 5.64; N, 14.26%.

*4.4.9. 5-Benzoyl-2-(dimethylamino)-4-(4-methoxyphenyl)-1H-imidazole (**3i**)*

Yellow crystals, mp 176 °C, yield: 0.289 g, 90%. IR (KBr) (ν_{max}/cm^{-1}): 3220 (NH), 1604 (C=O), 1549, 1494, 1442, 1375, 1312, 1289, 1234, 1170, 1106, 1071, 1026, 912, 836, 788, 748, 720, 687, 635. EI-MS, *m/z* (%): 321 (M^+, 100), 306 (34), 292 (36), 277 (14), 244 (12), 228 (25), 216 (31), 200 (13), 186 (10), 159 (8), 146 (37), 133 (10), 119 (30), 105 (69), 90 (7), 77 (63), 67 (7), 51 (11), 42 (6). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.15 (s, 6H, NMe_2), 3.69 (s, 3H, OCH_3), 6.54 (d, J = 8.7 Hz, 2H, 2CH), 7.06 (t, J = 7.6 Hz, 2H, 2CH), 7.11 (d, J = 8.7 Hz, 2H, 2CH), 7.22 (t, J = 7.4 Hz, 1H, CH), 7.40 (d, J = 7.0 Hz, 2H, 2CH), 9.60–10.72 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.3 (2NCH_3), 55.1 (OCH_3), 113.0 (2CH), 123.6 and 126.3 (2C), 127.5 (2CH), 129.1 (2CH), 130.8 (CH), 131.0 (2CH), 138.3 (C), 151.2 (CN_3), 154.1 and 159.3 (2C), 184.3 (C=O). Anal. Calcd for $C_{19}H_{19}N_3O_2$ (321.37): C, 71.01; H, 5.96; N, 13.08. Found: C, 70.89; H, 5.81; N, 13.00%.

*4.4.10. 2-(Dimethylamino)-5-(4-nitrobenzoyl)-4-phenyl-1H-imidazole (**3j**)*

Yellow crystals, mp 206 °C, yield: 0.286 g, 85%. IR (KBr) (ν_{max}/cm^{-1}): 3223 (NH), 1614 (C=O), 1547, 1440, 1381, 1317, 1236, 1176, 1107, 1070, 1010, 913, 880, 845, 777, 729, 666. EI-MS, *m/z* (%): 336 (M^+, 100), 321 (57), 307 (63), 289 (13), 275 (12), 261 (15), 246 (8), 214 (14), 198 (24), 186 (19), 171 (8), 159 (20), 150 (19), 129

(8), 116 (12), 104 (31), 89 (26), 76 (27), 67 (6), 56 (12), 44 (6). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.21 (s, 6H, NMe_2), 7.02 (t, J = 7.5 Hz, 2H, 2CH), 7.11–7.15 (m, 3H, 3CH), 7.47 (d, J = 8.6 Hz, 2H, 2CH), 7.87 (d, J = 8.6 Hz, 2H, 2CH), 9.00–10.52 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): 38.5 ($2NCH_3$), 122.7 (2CH), 123.8 (C), 127.8 (CH + 2CH), 128.8 (C), 129.8 (2 × 2CH), 132.6 and 143.8 (2C), 148.6 (CN_3), 153.9 (C), 181.4 (C=O). Anal. Calcd for $C_{18}H_{16}N_4O_3$ (336.35): C, 64.28; H, 4.79; N, 16.66. Found: C, 64.04; H, 4.58; N, 16.51%.

*4.4.11. 5-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-2-(dimethylamino)-1H-imidazole (**3k**)*

Yellow crystals, mp 214–216 °C, yield: 0.345 g, 96%. IR (KBr) (ν_{max}/cm^{-1}): 3247 (NH), 1619 (C=O), 1575, 1535, 1486, 1442, 1379, 1315, 1227, 1172, 1088, 1010, 912, 832, 763, 673, 625. EI-MS, *m/z* (%): 363 (M^{+} $^{37}Cl_2$, 10), 361 (M^{+} $^{37}Cl^{35}Cl$, 68), 359 (M^{+} $^{35}Cl_2$, 100), 344 (15), 330 (23), 248 (8), 232 (35), 220 (12), 204 (8), 184 (16), 163 (8), 150 (12), 139 (58), 123 (24), 111 (43), 100 (1), 87 (3), 75 (19), 56 (8), 42 (7). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.16 (s, 6H, NMe_2), 7.05 (d, J = 8.6 Hz, 2H, 2CH), 7.07 (d, J = 8.4 Hz, 2H, 2CH), 7.11 (d, J = 8.6 Hz, 2H, 2CH), 7.31 (d, J = 8.4 Hz, 2H, 2CH), 9.26–10.80 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.3 ($2NCH_3$), 123.8 (C), 127.8 (2CH), 127.9 (2CH), 130.4 (2CH), 131.0 (2CH), 132.0, 134.3, 136.4 and 137.5 (4C), 150.1 (CN_3), 154.1 (C), 182.8 (C=O). Anal. Calcd for $C_{18}H_{15}Cl_2N_3O$ (360.24): C, 60.01; H, 4.20; N, 11.66. Found: C, 59.84; H, 4.13; N, 11.51%.

*4.4.12. 5-(4-Bromobenzoyl)-2-(dimethylamino)-4-(4-methylphenyl)-1H-imidazole (**3l**)*

Yellow crystals, mp 232 °C, yield: 0.352 g, 92%. IR (KBr) (ν_{max}/cm^{-1}): 3235 (NH), 1616 (C=O), 1573, 1541, 1497, 1443, 1380, 1318, 1226, 1172, 1107, 1065, 1007, 911, 847, 824, 760, 721, 669, 635. 373 371. EI-MS, *m/z* (%): 385 (M^{+} ^{81}Br, 95), 383 (M^{+} ^{79}Br, 100), 368 (13), 356 (17), 354 (18), 341 (4), 339 (5), 228 (9), 212 (25), 200 (18), 185 (35), 173 (12), 155 (27), 130 (12), 116 (9), 103 (28), 90 (5), 76 (10), 56 (6), 42 (5). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 3.17 (s, 6H, NMe_2), 6.87 (d, J = 8.0 Hz, 2H, 2CH), 7.03 (d, J = 8.0 Hz, 2H, 2CH), 7.18 (d, J = 8.7 Hz, 2H, 2CH), 7.22 (d, J = 8.7 Hz, 2H, 2CH), 8.81–10.58 (br, 1H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.1 (CH_3), 38.4 ($2NCH_3$), 123.5 and 125.5 (C), 128.3 (2CH), 129.6 (2CH), 129.9 (C), 130.5 (2CH), 130.6 (2CH), 136.8 and 138.4 (2C), 151.9 (CN_3), 153.6 (C), 183.0 (C=O). Anal. Calcd for $C_{19}H_{18}BrN_3O$ (384.27): C, 59.39; H, 4.72; N, 10.94. Found: C, 59.16; H, 4.53; N, 10.75%.

4.5. General procedure for the preparation of pyrrolo[1,2-*c*]imidazoles (5a–x): To a magnetically stirred solution of triphenylphosphine (1 mmol) and the appropriate imidazole **1** (1 mmol) in CH_2Cl_2 (1 mL) at 25 °C was added dropwise a solution of the appropriate dialkyl acetylenedicarboxylate (1 mmol) in CH_2Cl_2 (1 mL) over 2 min. The mixture was stirred at 25 °C for 10 min. The solvent was removed and the product was purified by recrystallization from *n*-hexane/EtOAc (1:1).

*4.5.1. Dimethyl 3-(dimethylamino)-7-(4-methylphenyl)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5a**)*

Orange crystals, mp 162–163 °C, yield: 0.375 g, 87%. IR (KBr) (ν_{max}/cm^{-1}): 1744 and 1707 (C=O), 1597, 1546, 1489, 1426, 1357, 1309, 1206, 1169, 1114, 1069, 983, 953, 924, 858, 768, 698. EI-MS, *m/z* (%): 431 (M^+, 55), 372 (100), 356 (6), 312 (5), 298 (7), 270 (7), 255 (5), 242 (12), 227 (11), 215 (8), 202 (5), 189 (3), 170 (6), 156 (6), 148 (7), 84 (12), 77 (7), 59 (16). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 3.10 (s, 6H, NMe_2), 3.64 and 3.80 (2s, 6H, 2OCH_3), 5.64 (s, 1H, NCH), 6.92–7.02 (m, 2H, 2CH), 7.03–7.12 (m, 5H, 5CH), 7.17 (d, J = 8.1 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.4 (CH_3), 39.3 (2NCH_3), 51.4 and 53.3 (2OCH_3), 63.7 (CH), 121.8 (C), 127.3 (CH), 127.5 (2CH), 128.3 (2CH), 128.4 (C), 128.7 (2CH), 128.8 (2CH), 131.9, 132.8, 135.2, 139.0 and 146.3 (5C), 150.1 (CN_3), 163.0 and 167.9 (2C=O). Anal. Calcd for $C_{25}H_{25}N_3O_4$ (431.48): C, 69.59; H, 5.84; N, 9.74. Found: C, 69.50; H, 5.71; N, 9.66%.

*4.5.2. Diethyl 3-(dimethylamino)-7-(4-methylphenyl)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5b**)*

Orange crystals, mp 120–121 °C, yield: 0.376 g, 82%. IR (KBr) (ν_{max}/cm^{-1}): 1741 and 1709 (C=O), 1577, 1548, 1484, 1426, 1353, 1307, 1191, 1156, 1066, 1024, 951, 903, 834, 768, 744, 696, 655. EI-MS, *m/z* (%): 459 (M^+, 30), 405 (5), 386 (100), 358 (29), 312 (7), 298 (5), 269 (6), 255 (4), 241 (5), 227 (7), 215 (5), 202 (5), 170 (4), 127 (4), 119 (4), 105 (4), 84 (7), 77 (5). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.13 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.37 (s, 3H, CH_3), 3.08 (s, 6H, NMe_2), 4.08 and 4.12 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.25 and 4.29 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.60 (s, 1H, NCH), 6.95–7.02 (m, 2H, 2CH), 7.04–7.12 (m, 4H, 4CH), 7.19 (d, J = 8.0 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 (2OCH_2CH_3), 21.3 (CH_3), 39.2 (2NCH_3), 60.2 and 62.1 (2OCH_2CH_3), 63.7 (CH), 122.3 (C), 127.0 (CH), 127.4 (2CH), 128.1 (2CH), 128.6 (2CH), 128.8 (2CH), 128.9, 132.6, 133.1, 135.5, 138.7 and 146.2 (6C), 150.4 (CN_3),

162.7 and 167.4 (2C=O). Anal. Calcd for $C_{27}H_{29}N_3O_4$ (459.54): C, 70.57; H, 6.36; N, 9.14. Found: C, 70.42; H, 6.39; N, 8.97%.

*4.5.3. Dimethyl 7-(4-chlorophenyl)-3-(dimethylamino)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5c**)*

Orange crystals, mp 132 °C, yield: 0.406 g, 90%. IR (KBr) (ν_{max}/cm^{-1}): 1746 and 1706 (C=O), 1586, 1541, 1485, 1427, 1358, 1303, 1211, 1169, 1083, 985, 955, 925, 850, 836, 808, 766, 699, 655. EI-MS, *m/z* (%): 453 (M^+ ^{37}Cl, 10), 451 (M^+ ^{35}Cl, 26), 394 (36), 392 (100), 376 (4), 318 (4), 290 (4), 255 (4), 227 (14), 214 (4), 200 (5), 180 (5), 162 (4), 139 (5), 105 (4), 77 (7), 59 (14), 42 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.11 (s, 6H, NMe_2), 3.64 and 3.81 (2s, 6H, $2OCH_3$), 5.65 (s, 1H, NCH), 7.00–7.15 (m, 5H, 5CH), 7.23 (d, J = 8.7 Hz, 2H, 2CH), 7.25 (d, J = 8.7 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.3 ($2NCH_3$), 51.6 and 53.4 ($2OCH_3$), 63.7 (CH), 122.2 (C), 127.6 (3CH), 128.2 (4CH), 129.7 (C), 130.4 (2CH), 131.8, 132.3, 135.0, 135.7 and 144.7 (5C), 150.3 (CN_3), 162.9 and 167.7 (2C=O). Anal. Calcd for $C_{24}H_{22}ClN_3O_4$ (451.90): C, 63.79; H, 4.91; N, 9.30. Found: C, 63.60; H, 4.68; N, 9.14%.

*4.5.4. Diethyl 7-(4-chlorophenyl)-3-(dimethylamino)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5d**)*

Orange crystals, mp 114 °C, yield: 0.431 g, 90%. IR (KBr) (ν_{max}/cm^{-1}): 1741 and 1701 (C=O), 1611, 1544, 1486, 1419, 1359, 1307, 1215, 1206, 1140, 1124, 1090, 1062, 1020, 975, 952, 922, 880, 835, 803, 771, 744, 695. EI-MS, *m/z* (%): 481 (M^+ ^{37}Cl, 4), 479 (M^+ ^{35}Cl, 14), 408 (36), 406 (100), 380 (6), 378 (17), 307 (5), 261 (6), 227 (11), 202 (5), 189 (5), 139 (6), 113 (7), 99 (5), 85 (5), 77 (6), 57 (7), 43 (9). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.13 (d, J = 7.1 Hz, 3H, OCH_2CH_3), 1.29 (d, J = 7.1 Hz, 3H, OCH_2CH_3), 3.10 (s, 6H, NMe_2), 4.08 and 4.13 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.27 and 4.30 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.59 (s, 1H, NCH), 7.00–7.15 (m, 5H, 5CH), 7.25 (d, J = 8.8 Hz, 2H, 2CH), 7.27 (d, J = 8.8 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 39.1 ($2NCH_3$), 60.3 and 62.2 ($2OCH_2CH_3$), 63.7 (CH), 122.5 (C), 127.2 (CH), 127.6 (2CH), 128.0 (2CH), 128.1 (2CH), 130.0 (C), 130.4 (2CH), 132.8, 132.9, 134.7, 136.5 and 144.7 (5C), 150.8 (CN_3), 162.6 and 167.3 (2C=O). Anal. Calcd for $C_{26}H_{26}ClN_3O_4$ (479.96): C, 65.06; H, 5.46; N, 8.76. Found: C, 64.77; H, 5.51; N, 8.60%.

*4.5.5. Dimethyl 1-(4-bromophenyl)-3-(dimethylamino)-7-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5e**)*

Orange crystals, mp 148–150 °C, yield: 0.422 g, 83%. IR (KBr) (ν_{max}/cm^{-1}): 1744 and 1712 (C=O), 1601, 1550, 1500, 1432, 1361, 1314, 1294, 1246, 1201, 1167, 1112, 1069, 1017, 996, 954, 912, 830, 796, 768, 733, 683, 630. EI-MS, *m/z* (%): 511 (M^+ ^{81}Br, 13), 509 (M^+ ^{79}Br, 14), 452 (98), 450 (100), 371 (8), 296 (8), 269 (7), 241 (15), 227 (8), 215 (7), 196 (6), 169 (6), 155 (6), 141 (5), 127 (7), 59 (31), 42 (5). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 3.05 (s, 6H, NMe_2), 3.63 and 3.79 (2s, 6H, $2OCH_3$), 5.60 (s, 1H, NCH), 6.94 (d, J = 8.6 Hz, 2H, 2CH), 7.11 (d, J = 8.6 Hz, 2H, 2CH), 7.15 (d, J = 8.4 Hz, 2H, 2CH), 7.19 (d, J = 8.4 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.4 (CH_3), 39.1 ($2NCH_3$), 51.3 and 53.2 ($2OCH_3$), 63.5 (CH), 121.0 and 122.0 (2C), 128.63 (2CH), 128.64 (C), 128.8 (2CH), 129.5 (2CH), 130.5 (2CH), 132.1, 133.4, 134.9, 139.0 and 146.2 (5C), 150.7 (CN_3), 163.1 and 167.9 (2C=O). Anal. Calcd for $C_{25}H_{24}BrN_3O_4$ (510.38): C, 58.83; H, 4.74; N, 8.23. Found: C, 58.94; H, 4.58; N, 8.07%.

*4.5.6. Diethyl 1-(4-bromophenyl)-3-(dimethylamino)-7-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5f**)*

Orange crystals, mp 157–158 °C, yield: 0.435 g, 81%. IR (KBr) (ν_{max}/cm^{-1}): 1745 and 1707 (C=O), 1584, 1547, 1505, 1478, 1427, 1355, 1308, 1209, 1187, 1156, 1125, 1110, 1064, 1023, 973, 902, 880, 831, 768, 745, 717, 677, 648. EI-MS, *m/z* (%): 539 (M^+ ^{81}Br, 13), 537 (M^+ ^{79}Br, 14), 466 (98), 464 (100), 438 (20), 436 (20), 393 (4), 385 (4), 312 (4), 269 (5), 241 (9), 227 (5), 215 (4), 127 (5), 42 (9). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.11 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.27 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.40 (s, 3H, CH_3), 3.05 (s, 6H, NMe_2), 4.07 and 4.11 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.25 and 4.29 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.57 (s, 1H, NCH), 6.96 (d, J = 8.6 Hz, 2H, 2CH), 7.11 (d, J = 8.6 Hz, 2H, 2CH), 7.15 (d, J = 8.4 Hz, 2H, 2CH), 7.18 (d, J = 8.4 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 21.4 (CH_3), 39.1 ($2NCH_3$), 60.2 and 62.2 ($2OCH_2CH_3$), 63.7 (CH), 120.8 and 122.8 (2C), 128.6 (2CH), 128.7 (2CH), 128.9 (C), 129.5 (2CH), 130.5 (2CH), 132.2, 133.6, 134.6, 138.8 and 146.0 (5C), 150.6 (CN_3), 162.6 and 167.3 (2C=O). Anal. Calcd for $C_{27}H_{28}BrN_3O_4$ (538.44): C, 60.23; H, 5.24; N, 7.80. Found: C, 60.01; H, 5.13; N, 7.79%.

*4.5.7. Dimethyl 7-(4-chlorophenyl)3-(dimethylamino)-1-(4-methoxyphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5g**)*

Orange crystals, mp 158 °C, yield: 0.409 g, 85%. IR (KBr) (ν_{max}/cm^{-1}): 1749 and 1718 (C=O), 1574, 1545, 1507, 1477, 1434, 1357, 1313, 1197, 1165, 1113, 1064,

1000, 949, 860, 831, 791, 772, 744, 717, 681, 650. EI-MS, *m/z* (%): 483 (M^+ ^{37}Cl, 4), 481 (M^+ ^{35}Cl, 13), 424 (34), 422 (100), 357 (8), 355 (23), 340 (4), 320 (4), 258 (7), 242 (4), 228 (5), 214 (8), 195 (9), 139 (11), 111 (7), 84 (9), 59 (15), 43 (5). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.06 (s, 6H, NMe_2), 3.62, 3.73 and 3.79 (3s, 9H, $3OCH_3$), 5.60 (s, 1H, NCH), 6.58 (d, J = 8.9 Hz, 2H, 2CH), 7.00 (d, J = 8.9 Hz, 2H, 2CH), 7.24 (d, J = 8.8 Hz, 2H, 2CH), 7.29 (d, J = 8.7 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.0 ($2NCH_3$), 51.3, 53.2 and 55.1 ($3OCH_3$), 63.4 (CH), 113.0 (2CH), 121.0 and 125.6 (2C), 128.2 (2CH), 129.3 (2CH), 130.3 (C), 130.4 (2CH), 131.9, 134.8, 136.8 and 145.0 (4C), 150.8 (CN_3), 159.0 (C), 163.1 and 168.0 (2C=O). Anal. Calcd for $C_{25}H_{24}ClN_3O_5$ (481.94): C, 62.31; H, 5.02; N, 8.72. Found: C, 61.20; H, 4.92; N, 8.57%.

*4.5.8. Diethyl 7-(4-chlorophenyl)3-(dimethylamino)-1-(4-methoxyphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5h**)*

Orange crystals, mp 165–166 °C, yield: 0.428 g, 84%. IR (KBr) (ν_{max}/cm^{-1}): 1752 and 1704 (C=O), 1601, 1545, 1498, 1441, 1365, 1297, 1249, 1172, 1093, 1065, 1021, 978, 926, 903, 837, 797, 728, 686, 633. EI-MS, *m/z* (%): 511 (M^+ ^{37}Cl, 5), 509 (M^+ ^{35}Cl, 12), 438 (34), 436 (100), 410 (7), 408 (18), 258 (5), 237 (12), 222 (6), 214 (5), 195 (5), 135 (7), 119 (4), 105 (7), 77 (8), 42 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.13 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.29 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.12 (s, 6H, NMe_2), 3.74 (s, 3H, OCH_3), 4.08 and 4.12 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.27 and 4.30 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.62 (s, 1H, NCH), 6.58 (d, J = 8.8 Hz, 2H, 2CH), 7.03 (d, J = 8.8 Hz, 2H, 2CH), 7.23 (d, J = 8.5 Hz, 2H, 2CH), 7.28 (d, J = 8.5 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 39.4 ($2NCH_3$), 55.1 (OCH_3), 60.4 and 62.4 ($2OCH_2CH_3$), 64.0 (CH), 113.1 (2CH), 122.5 and 125.8 (2C), 128.2 (2CH), 129.6 (2CH), 130.0 (C), 130.4 (2CH), 131.6, 132.4, 134.9 and 144.4 (4C), 150.3 (CN_3), 159.2 (C), 162.4 and 167.1 (2C=O). Anal. Calcd for $C_{27}H_{28}ClN_3O_5$ (509.98): C, 63.59; H, 5.53; N, 8.24. Found: C, 63.36; H, 5.40; N, 8.19%.

*4.5.9. Dimethyl 1-(4-chlorophenyl)-3-(dimethylamino)-7-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5i**)*

Orange crystals, mp 175 °C, yield: 0.409 g, 88%. IR (KBr) (ν_{max}/cm^{-1}): 1740 and 1711 (C=O), 1580, 1543, 1481, 1427, 1356, 1319, 1281, 1201, 1151, 1114, 1062, 1004, 962, 877, 831, 773, 728, 683, 647. EI-MS, *m/z* (%): 467 (M^+ ^{37}Cl, 11), 465 (M^+ ^{35}Cl, 31), 408 (34), 406 (100), 304 (4), 269 (4), 241 (9), 227 (4), 215 (4), 196 (4), 187

(4), 169 (6), 155 (4), 139 (4), 127 (4), 59 (18), 42 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 3.09 (s, 6H, NMe_2), 3.64 and 3.81 (2s, 6H, $2OCH_3$), 5.64 (s, 1H, NCH), 6.96 (d, J = 8.6 Hz, 2H, 2CH), 7.01 (d, J = 8.6 Hz, 2H, 2CH), 7.12 (d, J = 8.2 Hz, 2H, 2CH), 7.17 (d, J = 8.2 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.4 (CH_3), 39.3 ($2NCH_3$), 51.5 and 53.4 ($2OCH_3$), 63.8 (CH), 122.4 (C), 127.6 (2CH), 128.2 (C), 128.6 (2CH), 128.8 (2CH), 129.4 (2CH), 130.6, 133.00, 133.04, 133.9, 139.2 and 146.0 (6C), 150.1 (CN_3), 162.9 and 167.7 (2C=O). Anal. Calcd for $C_{25}H_{24}ClN_3O_4$ (465.94): C, 64.44; H, 5.19; N, 9.02. Found: C, 64.39; H, 5.01; N, 8.78%.

*4.5.10. Diethyl 1-(4-chlorophenyl)-3-(dimethylamino)-7-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5j**)*

Orange crystals, mp 162–163 °C, yield: 0.414 g, 84%. IR (KBr) (ν_{max}/cm^{-1}): 1748 and 1699 (C=O), 1593, 1547, 1483, 1421, 1355, 1302, 1206, 1098, 1067, 1018, 955, 903, 829, 774, 718, 682, 649. EI-MS, *m/z* (%): 495 (M^{+} ^{37}Cl, 5), 493 (M^{+} ^{35}Cl, 15), 422 (34), 420 (100), 394 (6), 392 (18), 348 (5), 303 (4), 279 (4), 269 (4), 241 (7), 227 (4), 215 (4), 187 (4), 169 (4), 139 (5), 128 (4), 69 (2), 43 (2). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.11 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.27 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.40 (s, 3H, CH_3), 3.05 (s, 6H, NMe_2), 4.06 and 4.11 (2dq, ^{2}J = 10.8, ^{3}J = 7.1 Hz, 2H, OCH_2CH_3), 4.25 and 4.28 (2dq, ^{2}J = 10.8, ^{3}J = 7.1 Hz, 2H, OCH_2CH_3), 5.57 (s, 1H, NCH), 6.95 (d, J = 8.6 Hz, 2H, 2CH), 7.01 (d, J = 8.6 Hz, 2H, 2CH), 7.14 (d, J = 8.2 Hz, 2H, 2CH), 7.18 (d, J = 8.2 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 21.4 (CH_3), 39.1 ($2NCH_3$), 60.2 and 62.1 ($2OCH_2CH_3$), 63.7 (CH), 122.7 (C), 127.5 (2CH), 128.6 (2CH), 128.7 (2CH), 128.9 (C), 129.2 (2CH), 131.7, 132.5, 133.5, 134.6, 138.8 and 146.0 (6C), 150.6 (CN_3), 162.6 and 167.3 (2C=O). Anal. Calcd for $C_{27}H_{28}ClN_3O_4$ (493.98): C, 65.65; H, 5.71; N, 8.51. Found: C, 65.48; H, 5.56; N, 8.25%.

*4.5.11. Dimethyl 7-(4-chlorophenyl)-3-(dimethylamino)-1-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5k**)*

Orange crystals, mp 150–152 °C, yield: 0.391 g, 84%. IR (KBr) (ν_{max}/cm^{-1}): 1749 and 1711 (C=O), 1606, 1576, 1542, 1497, 1439, 1358, 1318, 1209, 1172, 1114, 1086, 1008, 960, 913, 825, 795, 764, 725, 676, 638. EI-MS, *m/z* (%): 467 (M^{+} ^{37}Cl, 4), 465 (M^{+} ^{35}Cl, 13), 408 (35), 406 (100), 341 (33), 339 (93), 324 (12), 310 (17), 237 (26), 222 (11), 212 (17), 200 (10), 184 (9), 169 (8), 139 (29), 111 (22), 77 (15), 59 (12), 43 (12). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 3.07 (s, 6H, NMe_2), 3.64

and 3.80 (2s, 6H, $2OCH_3$), 5.61 (s, 1H, NCH), 6.85 (d, J = 8.1 Hz, 2H, 2CH), 6.96 (d, J = 8.1 Hz, 2H, 2CH), 7.26 (d, J = 8.3 Hz, 2H, 2CH), 7.30 (d, J = 8.6 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.1 (CH_3), 39.1 ($2NCH_3$), 51.3 and 53.2 ($2OCH_3$), 63.4 (CH), 121.4 (C), 127.9 (2CH), 128.2 (2CH), 128.3 (2CH), 129.9 and 130.3 (2C), 130.4 (2CH), 132.3, 134.8, 137.0, 137.1 and 145.1 (5C), 150.8 (CN_3), 163.1 and 168.0 (2C=O). Anal. Calcd for $C_{25}H_{24}ClN_3O_4$ (465.93): C, 64.44; H, 5.19; N, 9.02. Found: C, 64.56; H, 5.02; N, 8.77%.H, 4.38.

*4.5.12. Diethyl 7-(4-chlorophenyl)-3-(dimethylamino)-1-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5l**)*

Orange crystals, mp 138 °C, yield: 0.419 g, 85%. IR (KBr) (ν_{max}/cm^{-1}): 1746 and 1705 (C=O), 1602, 1572, 1543, 1494, 1430, 1355, 1304, 1211, 1185, 1163, 1118, 1111, 1089, 1066, 1021, 972, 959, 904, 879, 849, 826, 766, 726, 683, 646. EI-MS, *m/z* (%): 495 (M^+ ^{37}Cl, 4), 493 (M^+ ^{35}Cl, 13), 422 (34), 420 (100), 394 (6), 392 (18), 332 (4), 242 (8), 227 (4), 213 (4), 187 (4), 169 (4), 139 (4), 4 (8), 43 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.12 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.25 (s, 3H, CH_3), 3.07 (s, 6H, NMe_2), 4.07 and 4.11 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.26 and 4.29 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.58 (s, 1H, NCH), 6.85 (d, J = 8.0 Hz, 2H, 2CH), 6.97 (d, J = 8.1 Hz, 2H, 2CH), 7.26 (d, J = 8.7 Hz, 2H, 2CH), 7.29 (d, J = 8.7 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 21.1 (CH_3), 39.1 ($2NCH_3$), 60.2 and 62.1 ($2OCH_2CH_3$), 63.6 (CH), 122.2 (C), 127.8 (2CH), 128.1 (2CH), 128.3 (2CH), 130.1 (C), 130.4 (2CH), 130.6, 132.4, 134.7, 136.7, 137.0 and 144.8 (6C), 150.8 (CN_3), 162.6 and 167.4 (2C=O). Anal. Calcd for $C_{27}H_{28}ClN_3O_4$ (493.98): C, 65.65; H, 5.71; N, 8.51. Found: C, 65.53; H, 5.58; N, 8.29%.

*4.5.13. Dimethyl 7-(4-bromophenyl)-3-(dimethylamino)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5m**)*

Orange crystals, mp 129–131 °C, yield: 0.450 g, 91%. IR (KBr) (ν_{max}/cm^{-1}): 1745 and 1698 (C=O), 1613, 1538, 1487, 1440, 1396, 1362, 1249, 1226, 1204, 1160, 1066, 1009, 910, 827, 773, 726, 697, 646. EI-MS, *m/z* (%): 497 (M^+ ^{81}Br, 12), 495 (M^+ ^{79}Br, 13), 469 (6), 467 (7), 438 (98), 436 (100), 410 (16), 408 (16), 357 (13), 330 (16), 296 (32), 272 (8), 256 (10), 242 (12), 228 (25), 214 (21), 189 (8), 175 (44), 148 (9), 127 (11), 113 (10), 105 (69), 77 (57), 59 (32), 44 (14). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.10 (s, 6H, NMe_2), 3.64 and 3.81 (2s, 6H, $2OCH_3$), 5.64 (s, 1H, NCH), 7.00–7.13 (m, 5H, 5CH), 7.16 (d, J = 8.4 Hz, 2H, 2CH), 7.42 (d, J = 8.4 Hz, 2H, 2CH). ^{13}C NMR

(75.5 MHz, $CDCl_3$): δ 39.2 ($2NCH_3$), 51.5 and 53.3 ($2OCH_3$), 63.7 (CH), 122.1 and 123.2 (2C), 127.5 (CH), 127.6 (2CH), 128.2 (2CH), 130.4 (C), 130.6 (2CH), 131.2 (2CH), 132.0, 132.3, 136.0 and 144.7 (4C), 150.5 (CN_3), 162.9 and 167.7 (2C=O). Anal. Calcd for $C_{24}H_{22}BrN_3O_4$ (496.35): C, 58.07; H, 4.47; N, 8.47. Found: C, 56.82; H, 4.29; N, 8.35%.

*4.5.14. Diethyl 7-(4-bromophenyl)-3-(dimethylamino)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5n**)*

Orange crystals, mp 115 °C, yield: 0.465 g, 89%. IR (KBr) (ν_{max}/cm^{-1}): 1738 and 1708 (C=O), 1609, 1548, 1487, 1454, 1418, 1359, 1334, 1278, 1208, 1147, 1120, 1066, 1014, 970, 919, 873, 832, 772, 689. EI-MS, *m/z* (%): 525 (M^{+} ^{81}Br, 14), 523 (M^{+} ^{79}Br, 15), 452 (98), 450 (100), 424 (16), 422 (17), 371 (10), 343 (4), 298 (4), 282 (4), 255 (9), 228 (24), 202 (7), 162 (4), 141 (4), 128 (3), 114 (3), 77 (4), 42 (4).^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.22 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.38 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.17 (s, 6H, NMe_2), 4.18 and 4.21 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.36 and 4.39 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.68 (s, 1H, NCH), 7.12–7.21 (m, 5H, 5CH), 7.27 (d, J = 8.4 Hz, 2H, 2CH), 7.52 (d, J = 8.4 Hz, 2H, 2CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.17 and 14.25 ($2OCH_2CH_3$), 39.3 ($2NCH_3$), 60.6 and 62.5 ($2OCH_2CH_3$), 63.9 (CH), 122.7 and 123.2 (2C), 127.5 (CH), 127.8 (2CH), 128.3 (2CH), 130.9 (2CH), 131.1 (C), 131.3 (2CH), 132.9, 133.0, 136.7 and 144.9 (4C), 151.1 (CN_3), 162.8 and 167.6 (2C=O). Anal. Calcd for $C_{26}H_{26}BrN_3O_4$ (524.41): C, 59.55; H, 5.00; N, 8.01. Found: C, 59.63; H, 5.12; N, 7.72%.

*4.5.15. Dimethyl 3-(dimethylamino)-1,7-diphenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5o**)*

Orange crystals, mp 98–99 °C, yield: 0.338 g, 81%. IR (KBr) (ν_{max}/cm^{-1}): 1746 and 1709 (C=O), 1587, 1544, 1488, 1430, 1415, 1358, 1283, 1242, 1207, 1114, 1071, 1005, 986, 960, 920, 874, 764, 732, 692, 644. EI-MS, *m/z* (%): 417 (M^{+}, 18), 358 (100), 256 (6), 228 (11), 202 (6), 163 (6), 141 (4), 114 (4), 82 (3), 77 (5), 59 (13). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.08 (s, 6H, NMe_2), 3.61 and 3.80 (2s, 6H, $2OCH_3$), 5.64 (s, 1H, NCH), 6.92–7.10 (m, 5H, 5CH), 7.27–7.40 (m, 5H, 5CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.2 ($2NCH_3$), 51.3 and 53.2 ($2OCH_3$), 63.6 (CH), 121.9 (C), 127.1 (CH), 127.5 (2CH), 128.0 (2CH), 128.1 (2CH), 128.75 (2CH), 128.83 (CH), 131.7, 132.5, 132.9, 136.1 and 146.2 (5C), 150.5 (CN_3), 163.1 and 167.9 (2C=O). Anal. Calcd for $C_{24}H_{23}N_3O_4$ (417.46): C, 69.05; H, 5.55; N, 10.07. Found: C, 68.76; H, 5.41; N, 9.83%.

*4.5.16. Diethyl 3-(dimethylamino)-1,7-diphenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5p**)*

Orange crystals, mp 136–138 °C, yield: 0.356 g, 80%. IR (KBr) (ν_{max}/cm^{-1}): 1738 and 1705 (C=O), 1585, 1545, 1488, 1437, 1422, 1355, 1311, 1268, 1240, 1199, 1151, 1113, 1071, 1019, 953, 920, 877, 843, 767, 691. EI-MS, *m/z* (%): 445 (M^+, 15), 372 (100), 344 (20), 298 (6), 284 (4), 255 (7), 228 (9), 202 (9), 163 (4), 141 (3), 128 (4), 105 (14), 77 (9). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.09 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.29 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.08 (s, 6H, NMe_2), 4.06 and 4.11 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.27 and 4.30 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.60 (s, 1H, NCH), 6.92–7.10 (m, 5H, 5CH), 7.28–7.40 (m, 5H, 5CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 39.2 ($2NCH_3$), 60.2 and 62.2 ($2OCH_2CH_3$), 63.7 (CH), 122.5 (C), 126.9 (CH), 127.5 (2CH), 127.9 (2CH), 128.0 (2CH), 128.6 (CH), 128.8 (2CH), 132.2, 133.0, 133.2, 136.2 and 146.1 (5C), 150.8 (CN_3), 162.8 and 167.5 (2C=O). Anal. Calcd for $C_{26}H_{27}N_3O_4$ (445.51): C, 70.09; H, 6.11; N, 9.43. Found: C, 69.88; H, 5.93; N, 9.14%.

*4.5.17. Dimethyl 3-(dimethylamino)-1-(4-methoxyphenyl)-7-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5q**)*

Orange crystals, mp 142–143 °C, yield: 0.367 g, 82%. IR (KBr) (ν_{max}/cm^{-1}): 1747 and 1711 (C=O), 1580, 1543, 1494, 1432, 1360, 1320, 1245, 1200, 1166, 1120, 1068, 1033, 985, 948, 922, 859, 833, 774, 727, 692, 645. EI-MS, *m/z* (%): 447 (M^+, 14), 388 (100), 286 (4), 243 (4), 237 (7), 215 (4), 178 (8), 135 (3), 105 (5), 77 (5), 59 (8), 43 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.10 (s, 6H, NMe_2), 3.62, 3.71 and 3.81 (3s, 9H, $3OCH_3$), 5.64 (s, 1H, NCH), 6.53 (d, J = 8.8 Hz, 2H, 2CH), 7.00 (d, J = 8.8 Hz, 2H, 2CH), 7.27–7.42 (m, 5H, 5CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.3 ($2NCH_3$), 51.3, 53.3 and 55.1 ($3OCH_3$), 63.7 (CH), 113.0 (2CH), 121.5 and 124.5 (2C), 128.0 (2CH), 128.7 (2CH), 128.9 (CH), 129.5 (2CH), 131.6, 131.9, 135.5 and 146.1 (4C), 150.1 (CN_3), 159.0 (C), 163.0 and 167.9 (2C=O). Anal. Calcd for $C_{25}H_{25}N_3O_5$ (447.48): C, 67.10; H, 5.63; N, 9.39. Found: C, 66.85 H, 5.46; N, 9.21%.

*4.5.18. Diethyl 3-(dimethylamino)-1-(4-methoxyphenyl)-7-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5r**)*

Orange crystals, mp 130 °C, yield: 0.394 g, 83%. IR (KBr) (ν_{max}/cm^{-1}): 1739 and 1707 (C=O), 1579, 1545, 1495, 1442, 1362, 1304, 1247, 1193, 1164, 1107, 1066, 1025, 954, 897, 834, 772, 730, 690. EI-MS, *m/z* (%): 475 (M^+, 15), 402 (100), 374 (20), 330 (8), 286 (6), 243 (5), 217 (7), 190 (6), 178 (10), 135 (7), 72 (6). ^{1}H NMR

(300.1 MHz, $CDCl_3$): δ 1.08 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.06 (s, 6H, NMe_2), 3.71 (s, 3H, OCH_3), 4.05 and 4.10 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.26 and 4.29 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.58 (s, 1H, NCH), 6.52 (d, J = 8.9 Hz, 2H, 2CH), 6.99 (d, J = 8.9 Hz, 2H, 2CH), 7.20–7.40 (m, 5H, 5CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.8 and 14.0 ($2OCH_2CH_3$), 39.1 ($2NCH_3$), 55.1 (OCH_3), 60.1 and 62.1 ($2OCH_2CH_3$), 63.6 (CH), 112.9 (2CH), 121.8 and 125.9 (2C), 127.9 (2CH), 128.6 (CH), 128.7 (2CH), 129.2 (2CH), 132.3, 132.5, 136.2 and 146.1 (4C), 150.7 (CN_3), 158.7 (C), 162.8 and 167.6 (2C=O). Anal. Calcd for $C_{27}H_{29}N_3O_5$ (475.54): C, 68.19; H, 6.15; N, 8.84. Found: C, 67.86; H, 5.91; N, 8.70%.

*4.5.19. Dimethyl 3-(dimethylamino)-7-(4-nitrophenyl)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5s**)*

Orange crystals, mp 148–149 °C, yield: 0.360 g, 78%. IR (KBr) (ν_{max}/cm^{-1}): 1746 and 1703 (C=O), 1588, 1536, 1521, 1487, 1422, 1341, 1310, 1221, 1168, 1113, 1072, 978, 952, 924, 851, 804, 767, 730, 697. EI-MS, *m/z* (%): 462 (M^+, 16), 403 (100), 357 (23), 255 (5), 227 (9), 216 (4), 200 (4), 175 (4), 105 (3), 84 (5), 59 (11), 43 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.09 (s, 6H, NMe_2), 3.63 and 3.83 (2s, 6H, $2OCH_3$), 5.66 (s, 1H, NCH), 6.95–7.12 (m, 5H, 5CH), 7.47 (d, J = 8.8 Hz, 2H, 2CH), 8.14 (d, J = 8.8 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.0 ($2NCH_3$), 51.6 and 53.3 ($2OCH_3$), 63.5 (CH), 122.4 (C), 123.1 (2CH), 127.6 (2CH), 127.7 (CH), 128.0 (2CH), 130.1 (2CH), 132.0, 132.5, 137.4, 138.8, 143.5 and 147.9 (6C), 151.1 (CN_3), 162.7 and 167.7 (2C=O). Anal. Calcd for $C_{24}H_{22}N_4O_6$ (462.46): C, 62.33; H, 4.79; N, 12.12. Found: C, 62.14; H, 4.70; N, 11.94%.

*4.5.20. Dimethyl 3-(dimethylamino)-7-(4-nitrophenyl)-1-phenyl-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5t**)*

Orange crystals, mp 138 °C, yield: 0.372 g, 76%. IR (KBr) (ν_{max}/cm^{-1}): 1748 and 1703 (C=O), 1585, 1548, 1522, 1486, 1448, 1425, 1346, 1310, 1220, 1188, 1173, 1110, 1072, 1020, 952, 919, 850, 774, 711, 646. EI-MS, *m/z* (%): 490 (M^+, 13), 417 (100), 389 (15), 371 (6), 343 (18), 330 (4), 298 (8), 255 (13), 228 (11), 200 (4), 189 (4), 152 (4), 127 (2), 105 (4), 77 (5), 43 (4). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.11 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.30 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.09 (s, 6H, NMe_2), 4.07 and 4.11 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.27 and 4.32 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.63 (s, 1H, NCH), 6.95–7.13 (m, 5H, 5CH), 7.48 (d, J = 8.7 Hz, 2H, 2CH), 8.15 (d, J = 8.7 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz,

$CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 39.0 ($2NCH_3$), 60.5 and 62.4 ($2OCH_2CH_3$), 63.7 (CH), 123.0 (2CH), 123.1 (C), 127.58 (CH), 127.64 (2CH), 127.9 (2CH), 130.1 (2CH), 132.2, 132.6, 137.0, 139.1, 143.3 and 147.8 (6C), 151.1 (CN_3), 162.3 and 167.1 (2C=O). Anal. Calcd for $C_{26}H_{26}N_4O_6$ (490.51): C, 63.66; H, 5.34; N, 11.42. Found: C, 63.51; H, 5.15; N, 11.13%.

*4.5.21. Dimethyl 1,7-bis(4-chlorophenyl)-3-(dimethylamino)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5u**)*

Orange crystals, mp 163 °C, yield: 0.461 g, 95%. IR (KBr) (ν_{max}/cm^{-1}): 1743 and 1706 (C=O), 1578, 1536, 1483, 1426, 1353, 1279, 1234, 1204, 1149, 1119, 1092, 1063, 1004, 963, 876, 832, 775, 743, 683. EI-MS, *m/z* (%): 489 (M^+ $^{37}Cl_2$, 1.5), 487 (M^+ $^{37}Cl^{35}Cl$, 9), 485 (M^+ $^{35}Cl_2$, 14), 430 (11), 428 (67), 426 (100), 391 (3), 343 (2), 341 (13), 339 (18), 289 (4), 262 (6), 227 (7), 197 (6), 179 (6), 139 (5), 113 (4), 84 (7), 59 (15). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.07 (s, 6H, NMe_2), 3.63 and 3.80 (2s, 6H, $2OCH_3$), 5.62 (s, 1H, NCH), 7.00 (s, 4H, 4CH), 7.23 (d, J = 8.3 Hz, 2H, 2CH), 7.31 (d, J = 8.6 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.1 ($2NCH_3$), 51.5 and 53.4 ($2OCH_3$), 63.6 (CH), 122.5 (C), 127.8 (2CH), 128.4 (2CH), 129.3 (2CH), 129.9 (C), 130.3 (2CH), 131.0, 132.6, 133.1, 134.8, 135.1 and 144.4 (6C), 150.6 (CN_3), 162.8 and 167.7 (2C=O). Anal. Calcd for $C_{24}H_{21}Cl_2N_3O_4$ (486.35): C, 59.27; H, 4.35; N, 8.64. Found: C, 59.06; H, 4.16; N, 8.59%.

*4.5.22. Diethyl 1,7-bis(4-chlorophenyl)-3-(dimethylamino)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5v**)*

Orange crystals, mp 155 °C, yield: 0.472 g, 92%. IR (KBr) (ν_{max}/cm^{-1}): 1745 and 1708 (C=O), 1612, 1588, 1539, 1482, 1428, 1396, 1353, 1306, 1211, 1189, 1159, 1090, 1066, 1019, 973, 902, 879, 837, 768, 747, 723, 678, 641. EI-MS, *m/z* (%): 517 (M^+ $^{37}Cl_2$, 1), 515 (M^+ $^{37}Cl^{35}Cl$, 9), 513 (M^+ $^{35}Cl_2$, 13), 444 (11), 442 (66), 440 (100), 416 (2), 414 (13), 412 (21), 261 (8), 227 (9), 200 (5), 139 (7), 113 (5), 69 (5), 57 (5), 43 (7). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.11 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.05 (s, 6H, NMe_2), 4.07 and 4.11 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 4.26 and 4.29 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 5.58 (s, 1H, NCH), 7.00 (s, 4H, 4CH), 7.24 (d, J = 8.6 Hz, 2H, 2CH), 7.31 (d, J = 8.6 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2CH_3$), 39.0 ($2NCH_3$), 60.4 and 62.3 ($2OCH_2CH_3$), 63.7 (CH), 123.1 (C), 127.7 (2CH), 128.3 (2CH), 129.1 (2CH), 130.3 (2CH), 130.4, 131.5, 132.88, 132.94, 134.9, 135.0 and

144.3 (7C), 150.8 (CN_3), 162.4 and 167.2 (2C=O). Anal. Calcd for $C_{26}H_{25}Cl_2N_3O_4$ (514.40): C, 60.71; H, 4.90; N, 8.17. Found: C, 60.33; H, 4.58; N, 7.87%.

*4.5.23. Dimethyl 7-(4-bromophenyl)-3-(dimethylamino)-1-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5w**)*

Orange crystals, mp 138–139 °C, yield: 0.473 g, 93%. IR (KBr) (ν_{max}/cm^{-1}): 1741 and 1704 (C=O), 1567, 1539, 1499, 1427, 1356, 1331, 1307, 1278, 1242, 1199, 1147, 1115, 1066, 1004, 960, 876, 824, 782, 716, 683, 642. EI-MS, *m/z* (%): 511 (M^+ ^{81}Br, 15), 509 (M^+ ^{79}Br, 16), 452 (98), 450 (100), 371 (9), 286 (7), 269 (7), 243 (24), 237 (45), 222 (13), 215 (6), 194 (6), 162 (6), 105 (15), 77 (15), 59 (34), 42 (7). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 3.20 (s, 6H, NMe_2), 3.66 and 3.84 (2s, 6H, $2OCH_3$), 5.72 (s, 1H, NCH), 6.87 (d, J = 8.1 Hz, 2H, 2CH), 7.01 (d, J = 8.1 Hz, 2H, 2CH), 7.15 (d, J = 8.5 Hz, 2H, 2CH), 7.44 (d, J = 8.4 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.3 (CH_3), 39.7 ($2NCH_3$), 51.3 and 53.2 ($2OCH_3$), 63.4 (CH), 122.3 and 123.0 (2C), 127.8 (2CH), 128.3 (2CH), 130.1 (C), 130.6 (2CH), 131.11 (2CH), 131.13, 132.4, 136.9, 137.0 and 144.8 (5C), 150.8 (CN_3), 163.1 and 167.9 (2C=O). Anal. Calcd for $C_{25}H_{24}BrN_3O_4$ (510.38): C, 58.83; H, 4.74; N, 8.23. Found: C, 58.57; H, 4.48; N, 8.05%.

*4.5.24. Dimethyl 7-(4-bromophenyl)-3-(dimethylamino)-1-(4-methylphenyl)-5H-pyrrolo[1,2-c]imidazole-5,6-dicarboxylate (**5x**)*

Orange crystals, mp 148–149 °C, yield: 0.483 g, 90%. IR (KBr) (ν_{max}/cm^{-1}): 1742 and 1697 (C=O), 1597, 1583, 1569, 1539, 1501, 1419, 1360, 1324, 1295, 1212, 1190, 1103, 1067, 1016, 966, 906, 879, 820, 753, 719, 683, 632. EI-MS, *m/z* (%): 539 (M^+ ^{81}Br, 16), 537 (M^+ ^{79}Br, 16), 466 (97), 464 (100), 436 (20), 434 (21), 385 (7), 269 (7), 242 (23), 227 (8), 215 (7), 169 (5), 119 (5), 91 (5), 69 (4), 42 (10). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.12 (t, J = 7.1 Hz, 3H, $OCH_2C\mathit{H}_3$), 1.28 (t, J = 7.1 Hz, 3H, $OCH_2C\mathit{H}_3$), 2.25 (s, 3H, CH_3), 3.06 (s, 6H, NMe_2), 4.07 and 4.11 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, $OC\mathit{H}_2CH_3$), 4.26 and 4.29 (2dq, ^2J = 10.8, ^3J = 7.1 Hz, 2H, $OC\mathit{H}_2CH_3$), 5.57 (s, 1H, NCH), 6.85 (d, J = 8.1 Hz, 2H, 2CH), 6.97 (d, J = 7.9 Hz, 2H, 2CH), 7.19 (d, J = 8.3 Hz, 2H, 2CH), 7.45 (d, J = 8.4 Hz, 2H, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($2OCH_2\mathit{C}H_3$), 21.1 (CH_3), 39.1 ($2NCH_3$), 60.3 and 62.2 ($2O\mathit{C}H_2CH_3$), 63.6 (CH), 122.2 and 122.9 (2C), 127.8 (2CH), 128.3 (2CH), 130.0 (C), 130.6 (2CH), 131.10 (2CH), 131.12, 132.4, 136.7, 137.0 and 144.8 (5C), 150.8 (CN_3), 162.6 and 167.4 (2C=O). Anal. Calcd for $C_{27}H_{28}BrN_3O_4$ (538.43): C, 60.23; H, 5.24; N, 7.80. Found: C, 59.87; H, 5.11; N, 7.66%.

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