Bridging homogeneous and heterogeneous catalysis with CAN:SiO₂ as solid catalysts for four-component reactions for the synthesis of tetrasubstituted pyrroles.
Bridging homogeneous and heterogeneous catalysis with CAN·SiO₂ as solid catalysts for four-component reactions for the synthesis of tetrasubstituted pyrroles.

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The attractive features of this methodology are newer and greener method, simple procedure, reusability and high efficiency of the catalyst and easy workability.
Abstract
An efficient, and expeditious method has been developed for the synthesis of tetrasubstituted pyrroles via a four component, one-pot cyclocondensation reaction of amines, aldehydes, dialkyl acetylenedicarboxylates and nitroalkanes using silica supported ceric ammonium nitrate as heterogeneous catalyst for the first time. Reusable silica supported ceric ammonium nitrate was found to be a highly efficient and renewable heterogeneous catalyst for the rapid and convenient synthesis of tetrasubstituted pyrroles derivatives. The advantageous features of this novel methodology are high atom-economy, operational simplicity, shorter reaction time, convergence, and facile automation.

Keywords-Silica supported ceric ammonium nitrate, Heterogeneous catalyst, tetrasubstituted pyrroles, Multicomponent reaction.
1. Introduction
Polysubstituted pyrroles represent one of the most important classes of heterocyclic molecules found in numerous natural and biologically active compounds. Polysubstituted pyrroles have received considerable attention in the field of synthetic organic chemistry due to their numerous applications in the pharmaceutical industry. Functionalized pyrroles have shown interesting biological properties such as antibacterial, antiinflammatory, antioxidant, antitumor, antifungal and immune suppressant activities. Highly functionalized pyrroles are subunits of heme, chlorophyll, bile pigments, vitamin B12 and pyrrole alkaloids isolated from marine source. Furthermore, substituted pyrroles are widely used as synthetic building blocks, pharmacophores, and various kinds of functional materials. These compounds have many applications as chemosensors, for laser manufacture, image diagnosis.

The importance of chemical and pharmacological properties of pyrrole derivatives and the development of synthetic methods which enable a facile access to these heterocyclic compounds are desirable. Recently, many efforts have been devoted to develop novel and highly efficient synthetic protocols for the synthesis of functionalized pyrroles such as multicomponent coupling, tandem reactions, transition-metal-catalyzed cyclization, and catalytic C–H bond functionalization strategies have been developed and drawn extensive and enduring attention. In the midst of them, multicomponent processes have received great attention from the chemical community because they address fundamental principles of synthetic efficiency and reaction processing. Multicomponent coupling reactions (MCRs) are known as a powerful tool for the construction of novel and structurally complex molecules in a single pot ensuring high atom economy, good overall yields and high selectivity, lower costs, shorter reaction times, minimizing waste, labor, energy, and avoidance of expensive purification processes.

Recently a four-component reaction of amines, aldehydes, dialkyl acetylenedicarboxylates and nitroalkanes is reported to give diversity oriented pyrroles by using iodine as a catalyst. But unfortunately, they used homogenous catalyst and are not recyclable. The use of homogeneous catalysts has received little attention as alternatives in alleviating some of the limitations. Thus, the search for an inexpensive, readily available, and convenient catalyst is desirable. The use of heterogeneous catalysts has received considerable importance in organic synthesis because of their ease of handling, enhanced reaction rates, greater selectivity, simple work-up, and recoverability of catalysts. Among the various heterogeneous catalysts, particularly, silica gel-supported ceric ammonium nitrate has the advantages of low cost, ease of preparation and catalyst recycling. It is evident from the previous literature that silica gel supported ceric
ammonium nitrate has invoked enormous interest as a green and a potential acid catalyst to construct carbon–carbon and carbon–heteroatom bonds in various organic transformations.\textsuperscript{19}

As part of our ongoing research program for the development of new environmentally benign methodology for the synthesis of a useful precursor in the field of biology, industry, and key intermediate for the multistep synthesis,\textsuperscript{20-23} we decided to investigate the efficiency of silica gel supported ceric ammonium nitrate catalyst for the synthesis of functionalized pyrroles. The reaction is easy to perform and allows synthesizing various multi functionalized derivatives. These reaction workup procedures were simple and we can isolate products with high purity and yields. So herein, we wish to report a tandem synthesis of tetrasubstituted pyrroles derivatives by using CAN-SiO\textsubscript{2} as expeditious reusable catalyst in an excellent yield (Scheme 1).

\textbf{Scheme 1} Synthesis of fully substituted tetrasubstituted pyrroles functionalities catalyzed by CAN-SiO\textsubscript{2}

\section*{2. Results and discussion}
To identify the suitable conditions for the four-component annulation process, a series of catalysts and solvents were screened (Table 1). Initially, in search of the best catalytic system for this one-pot synthesis, optimization of various reaction parameters like different metal Lewis acid catalysts, temperature, and solvent was carried out (Table 1) with the standard reaction of benzaldehyde, aniline, dimethyl acetylenedicarboxylates, and nitromethane. In order to establish the real effectiveness of the catalyst for the synthesis of tetra substituted pyrroles, a test reaction was performed without catalyst using the model reaction at reflux condition. It was found that only a trace amount of product was obtained in the absence of catalyst even after 24 h (Table 1, entry 1).

\textbf{Table 1} Optimization of the formation of tetrasubstituted pyrroles\textsuperscript{a}
In search of effective, eco-friendly, and efficient reusable catalytic system for this reaction, the same test reaction was performed with different metal Lewis acid catalysts such as SiO$_2$, BF$_3$·SiO$_2$, Cu(OTf)$_2$·SiO$_2$, FeCl$_3$·SiO$_2$, TiO$_2$·SiO$_2$, ZnCl$_2$·SiO$_2$, CAN, CAN·SiO$_2$, Zn(OTf)$_2$·SiO$_2$, and P$_2$O$_5$·SiO$_2$ (Table 1). To study the role of SiO$_2$, the reaction was tested with SiO$_2$ (100 mg) only, and we observed comparable good yield as compared to catalyst free reaction (Table 1, entry 2). Among all screened catalysts CAN and CAN·SiO$_2$ gave the best result in view of yield and reaction time (Table 1, entry 8, 9). In contrast BF$_3$·SiO$_2$, Cu(OTf)$_2$·SiO$_2$, FeCl$_3$·SiO$_2$, TiO$_2$·SiO$_2$, ZnCl$_2$·SiO$_2$, Zn(OTf)$_2$·SiO$_2$ and P$_2$O$_5$·SiO$_2$ did not afford the desired product in good
yields (Table 1, entries 3, 4, 5, 6, 7, 10 and 11). The supported Lewis acid catalyst FeCl$_3$·SiO$_2$ shows effective, but required time for the completion of the reaction which is more as compared with CAN·SiO$_2$ catalyst to slightly lower yield (Table 1, entry 5, 9, 12). The reaction was also studied in various solvents such as tetrahydrofuran, dichloromethane, dichloroethane, and toluene; however, the yield of the desired product was decreased. So, in this reaction nitromethane was used both as a solvent and as one of the reactants as well.

Once we found CAN·SiO$_2$ as the best catalyst for this system, the optimization of catalyst loading was done (Table 1, entries 14, 15, 16, and 17). Consequently, the optimum 10 mol % loading of CAN·SiO$_2$ provided the maximum yield in minimum time (Table 1, entry 9), but while loading of the high amount of catalyst, the reaction proceeded quite slowly with lower yield (Table 2, entries 16, 17), on the other hand, a decrease in yield was observed by lowering the amount of catalyst (Table 1, entry 14, 15). So, 10 mol % of catalyst were found to be the optimal quantity and sufficient to push the reaction forward.

To explore the scope of this novel methodology, reactions of several of amines, aldehydes, dialkyl acetylenedicarboxylates and nitromethane in the presence of 10 mol % of CAN·SiO$_2$ were conducted. The results are summarized in Table 2. Thus, we selected the optimized reaction condition to examine the universality of this catalyst application with different electron rich and deficient substrates. It was gratifying to observe that most of the tested substrates exhibited satisfactory reactivity profiles, in all cases leading to a heterocyclization sequence that readily afforded the target structures (Table 2). But, with an aliphatic aldehyde only a trace amount of product was detected (Table 2, entry 29). On the other hand, in the case of amines, both aromatic and aliphatic substrates underwent the conversion smoothly.

Table 2 Synthesis of tetrasubstituted pyrroles by four-component coupling reactions using CAN·SiO$_2$ as catalyst$^a$

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*a*All reactions were carried out using amines (1 mmol), aldehydes (1 mmol), dialkyl acetylenedicarboxylates (1 mmol) and nitromethane (1 ml) under reflux. *b*Isolated yield

A possible mechanism of this one-pot reaction is expected on the basis of reported literature. A possible mechanism for the tetrasubstituted pyrroles ring formation of four-component coupling reactions using CAN·SiO$_2$ as catalyst is outlined in Scheme 2.
The reusability of the CAN-SiO$_2$ catalyst was also examined. The catalyst was reused four times and the results show that silica supported ceric ammonium nitrate can be reused as such without a significant loss in yield (Table 3). The recyclability of the catalyst was checked with the model reaction (Table 3, entries 1–4). Accordingly, after the first fresh run with 93% yield, the catalyst was removed by filtration. The recovered catalyst was dried under vacuum at 120 °C for 12 h and tested up to three more reaction cycles. Recycling and reuse of the catalyst showed minimal decreases in yields. The product was obtained in 93%, 93%, 91%, and 90% yields after successive cycles. (Table 3, entries 1–4), thus proving the catalyst reusability. The catalyst showed excellent recyclability in all these reactions (Table 3), as the reaction times and yield remained almost the same without having a loss of catalytic activity.

The reported as well as synthesized novel compounds were further characterized by their spectral properties ($^1$H, $^{13}$C NMR, and HRMS).

### 3. Conclusion

In summary, an efficient, expeditious, operationally simple, economical, and environmentally friendly method has been developed for the synthesis of tetra-substituted pyroles via a four
component; one-pot reaction of amines, aldehydes, dialkyl acetylenedicarboxylates, and nitromethane using silica supported ceric ammonium nitrate as heterogeneous catalyst. The main advantage of this present methodology is the simple work-up, easy recovery of catalyst, no need for anhydrous condition, no base or any additional activator required. To the best of our knowledge this is the first report for the synthesis of tetra-substituted pyrroles by using silica supported ceric ammonium nitrate as heterogeneous catalyst. Shorter reaction times, excellent yields and more importantly, the recyclability without losing catalytic activity, makes this protocol a good and attractive.

4. Experimental
4.1 Material and methods
Chemicals were purchased from Aldrich and Alfa Aesar chemical companies and used as it is. The NMR spectra were recorded in CDCl$_3$ on a Jeol JNMECP 400 NMR instrument using TMS as an internal standard. The HRMS was recorded on a Jeol JMS-700 mass spectrometer.

4.2 General procedure for the synthesis of silica supported ceric ammonium nitrate catalyst
A silica supported ceric ammonium nitrate catalyst was prepared by adopting the literature procedure.$^{24}$ Neutral silica gel (9.01 g, Merck Kieselgel 60, particle size 0.063–0.200 mm, 70–230 mesh) was mixed with a solution of CAN (1.02 g) in water (2.0 mL). Evaporation of water under reduced pressure gave a dry yellowish powder, which contained 10% (by weight) of CAN. According to Hwu et al., this reagent was found active for at least six months by storage in a well-capped bottle.$^{24}$

4.3 General procedure for the synthesis of fully substituted pyrrole functionalities
To a mixture of amines (1 mmol), aldehydes (1 mmol), dialkyl acetylenedicarboxylates (1 mmol) and nitromethane (1 ml) was added 10 mol % CAN-SiO$_2$ and the reaction mixture was kept for refluxing in a heated oil-bath with constant stirring. After completion of the reaction as monitored by TLC, the reaction mixture was brought to room temperature and the excess nitroalkane was removed on a rotary evaporator. Then, the crude residue was dissolved in 10 mL of dichloromethane and the solid particle was removed by filtration. The precipitate was further washed with 2 mL of dichloromethane. The filtrate was washed with water and dried over anhydrous sodium sulfate. The organic extract was concentrated and the crude residue was finally purified through a silica gel column chromatography. The final product was obtained by eluting with ethyl acetate and hexane mixture.

4.3.1. Dimethyl 4-(phenyl)-1-phenyl-1H-pyrrole-2,3-dicarboxylate
Brown sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.48-7.32 (m, 5H), 7.26-7.15 (m, 5H), 7.02 (s, 1H), 3.82(s, 3H), 3.74 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.52, 160.12, 138.12, 133.20, 129.32, 128.56, 127.66, 127.09, 126.58, 125.45, 121.23, 120.73, 55.23, 53.26; HRMS m/z calcd for C$_{20}$H$_{17}$NO$_4$ [M$^+$] 335.1158, found 335.1153.

4.3.2. Diethyl 1-(2-methylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.47-7.45 (m, 2H), 7.36-7.32 (m, 3H), 7.30-7.20 (m, 4H), 6.88 (s, 1H), 4.34-4.32 (m, 2H), 4.11-4.08 (m 2H), 2.11 (s, 3H), 1.29 (t, $J=12$Hz, 3H), 1.09 (t, $J=12$Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.47, 159.52, 139.11, 135.46, 133.31, 130.42, 128.91, 12852, 127.58, 127.35, 126.99, 126.30, 125.35, 124.60, 123.29, 121.85, 61.32, 60.55, 17.36, 14.06, 13.80; HRMS m/z calcd for C$_{21}$H$_{19}$NO$_5$ [M$^+$] 349.1314, found 349.1315.

4.3.3. Diethyl 1-(4-methoxyphenyl)-4-(2-methyphenyl)-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.27-7.22 (m, 5H), 7.09 (d, $J=4$Hz, 1H), 6.95-6.92 (m, 3H), 4.35-4.29 (m, 2H), 4.19-4.13 (m, 2H), 3.83 (s, 3H), 2.35 (s, 3H), 1.30 (d, $J=12$Hz, 3H), 1.17 (d, $J=12$Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.41, 159.89, 159.48, 138.00, 133.19, 132.55, 128.43, 127.78, 127.45, 126.10, 124.77, 124.48, 123.17, 121.95, 113.90, 61.25, 60.70, 55.50, 21.45, 14.09, 13.95; HRMS m/z calcd for C$_{24}$H$_{25}$NO$_5$ [M$^+$] 407.1733, found 407.1736.

4.3.4. Diethyl 1-(3-methylphenyl)-4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.44 (d, $J=8$Hz, 2H), 7.29 (t, $J=8$Hz, 2H), 7.22 (t, $J=12$Hz, 2H), 7.15 (d, $J=8$Hz, 1H), 7.09 (t, $J=12$Hz, 2H), 6.90 (s, 1H), 4.29-4.26 (m, 2H), 4.14-4.11 (m, 2H), 2.32 (s, 3H), 1.24 (t, $J=12$Hz, 3H), 1.11 (t, $J=12$Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.01, 159.91, 139.42, 138.77, 133.29, 129.05, 128.58, 128.38, 127.74, 126.95, 126.60, 125.50, 124.66, 123.10, 121.71, 61.09, 60.70, 21.14, 13.99, 13.82; HRMS m/z calcd for C$_{23}$H$_{23}$NO$_4$ [M$^+$] 377.1627, found 377.1629.

4.3.5. Diethyl 1-(4-methylphenyl)-4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.43 (t, $J=12$Hz, 2H), 7.28-7.19 (m, 3H), 7.12 (t, $J=8$Hz, 4H), 6.87 (s, 1H), 4.2-4.25 (m, 2H), 4.13-4.10 (m, 2H), 2.29 (s, 3H), 1.23 (t, $J=12$Hz, 3H), 1.11 (t, $J=12$Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.03, 159.87, 138.17, 136.99, 133.33, 129.36, 128.39, 127.71, 126.94, 125.80, 125.63, 124.56, 123.58, 121.76, 61.06, 60.67, 20.97, 14.00, 13.84; HRMS m/z calcd for C$_{23}$H$_{23}$NO$_4$ [M$^+$] 377.1627, found 377.1629.
4.3.6. Diethyl 1-(3-methoxyphenyl)-4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.46-7.44 (m, 2H), 7.37-7.32 (m, 2H), 7.30-7.24 (m, 2H), 6.98 (s, 1H), 9.96-6.92 (m, 2H), 6.89 (t, J=12Hz, 1H), 4.33-4.28 (m, 2H), 4.20-4.14 (m, 2H), 3.80 (s, 3H), 1.27 (t, J=12Hz, 3H), 1.16 (t, J=12Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.09, 159.93, 159.85, 140.58, 133.25, 129.55, 128.45, 127.81, 127.06, 125.51, 124.79, 123.64, 121.76, 118.38, 114.19, 112.03, 61.25, 60.86, 55.44, 14.03, 13.89; HRMS m/z calcd for C$_{25}$H$_{23}$NO$_5$ [M$^+$] 393.4324, found 393.4321.

4.3.7. Dimethyl 1-(4-methylphenyl)-4-(4-hydroxyphenyl)-1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.24-7.22 (m, 3H), 7.20-7.15 (m, 4H), 6.87 (s, 1H), 6.76 (d, J=8Hz, 2H), 3.81 (s, 3H), 3.67 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 167.48, 160.74, 155.72, 138.41, 136.80, 129.48, 128.90, 125.80, 125.71, 124.84, 124.78, 122.93, 121.24, 115.62, 52.50, 51.99, 21.05; HRMS m/z calcd for C$_{23}$H$_{19}$NO$_5$ [M$^+$] 365.1263, found 365.1264.

4.3.8. Diethyl 1-(4-methoxyphenyl)-4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.46-7.43 (m, 2H), 7.35 (t, J=12Hz, 2H), 7.29-7.24 (m, 3H), 6.96-6.92 (m, 3H), 4.34-4.28 (m, 2H), 4.19-4.14 (m, 2H), 3.83 (s, 3H), 1.28 (t, J=12Hz, 3H), 1.17 (t, J=12Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.31, 159.92, 159.49, 133.33, 132.49, 128.47, 127.74, 127.42, 127.00, 126.04, 124.46, 123.41, 121.77, 61.26, 60.74, 55.50, 14.05, 13.95; HRMS m/z calcd for C$_{23}$H$_{23}$NO$_5$ [M$^+$] 393.4324, found 393.4321.

4.3.9. Dimethyl 1-(benzyl)-4-(4-ethoxyphenyl)-1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.30-7.22 (m, 5H), 7.14 (d, J=8Hz, 2H), 6.85 (d, J=12Hz, 2H), 6.83 (s, 1H), 5.46 (s, 2H), 4.01-3.96 (m, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 1.37 (t, J=12Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 167.35, 160.64, 158.12, 137.10, 128.74, 128.53, 127.79, 127.17, 125.62, 125.35, 123.82, 122.07, 120.90, 115.35, 114.59, 63.39, 52.31, 51.71, 14.82; HRMS m/z calcd for C$_{23}$H$_{23}$NO$_5$ [M$^+$] 393.4324, found 393.4323.

4.3.10. Diethyl 1-(2-methoxyphenyl)-4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.43 (d, J=8Hz, 2H), 7.32-7.27 (m, 3H), 7.21-7.18 (m, 2H), 6.95-6.91 (m, 2H), 6.83 (s, 1H), 4.29-4.26 (m, 2H), 4.10-4.06 (m, 2H), 3.64 (s, 3H), 1.24 (t, J=12Hz, 3H), 1.07 (t, J=12Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.36, 159.64, 154.42, 133.46, 129.71, 128.79, 128.40, 127.57, 126.81, 125.56, 124.27, 124.00,
4.3.11. Diethyl 1-(4-chlorophenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.45-7.40 (m, 4H), 7.35 (t, J=12Hz, 2H), 7.29-7.24 (m, 3H), 6.95 (s, 1H), 4.34-4.28 (m, 2H), 4.20-4.14 (m, 2H), 1.28 (t, J=12Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 166.11, 159.67, 138.07, 134.37, 132.97, 129.02, 128.54, 127.66, 127.61, 127.19, 125.70, 125.70, 124.94, 122.99, 122.66, 121.45, 104.60, 61.38, 60.91, 14.03, 13.91; HRMS m/z calcd for C$_{23}$H$_{23}$NO$_5$ [M$^+$] 393.4324, found 393.4321.

4.3.12. Diethyl 1-(4-bromophenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.48 (d, J=8Hz, 2H), 7.41(d, J=8Hz, 2H), 7.29 (t, J=12Hz, 2H), 7.22 (d, J=8Hz, 1H), 7.13 (d, J=12Hz, 2H), 6.90 (s, 1H), 4.29-4.26 (m, 2H), 4.14-4.10 (m, 2H), 1.25 (t, J=12Hz, 3H), 1.14 (t, J=12Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 165.92, 159.52, 138.44, 132.88, 131.87, 128.48, 127.80, 127.54, 127.10, 125.56, 124.82, 122.93, 122.63, 122.12, 61.25, 60.82, 13.98, 13.84; HRMS m/z calcd for C$_{22}$H$_{20}$BrNO$_4$ [M$^+$] 442.3025, found 442.3028.

4.3.13. Dimethyl 1-(4-methoxyphenyl)- 4-(4-fluorophenyl) -1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.05 (d, J=8Hz, 1H), 7.46-7.61 (m, 2H), 7.47-7.44 (m, 1H), 7.36 (d, J=4Hz, 1H), 7.17-7.02 (m, 3H), 6.95-6.91 (m, 1H), 4.02 (s, 3H), 3.93 (m, 3H), 3.72 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 168.25, 166.59, 159.26, 152.73, 144.71, 136.93, 131.40, 130.36, 130.27, 127.22, 124.89, 124.62, 123.45, 115.59, 115.36, 114.03, 55.66, 53.17, 52.78; HRMS m/z calcd for C$_{21}$H$_{18}$FNO$_5$ [M$^+$] 383.1669, found 383.1167.

4.3.14. Diethyl 1-(3, 5-dimethoxyphenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.44 (d, J=8Hz, 2H), 7.33 (t, J=12Hz, 2H), 7.28-7.23 (m, 1H), 6.97 (s, 1H), 6.50 (s, 3H), 4.32-4.27 (m, 2H), 4.21-4.16 (m, 2H), 3.75 (s, 6H), 1.26 (t, J=12Hz, 3H), 1.18 (t, J=12Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm) 165.94, 160.74, 159.99, 141.05, 133.26, 128.42, 127.86, 127.05, 125.29, 124.82, 123.91, 121.45, 104.60, 100.46, 61.19, 60.91, 55.49, 14.02, 13.92; HRMS m/z calcd for C$_{24}$H$_{25}$NO$_6$ [M$^+$] 423.4584, found 423.4582.

4.3.15. Diethyl 1-(3, 4-dimethylphenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.44 (d, J=8Hz, 2H), 7.28 (t, J=12Hz, 2H), 7.21-7.17 (m, 1H), 7.10-7.05 (m, 2H), 7.00 (d, J=8Hz, 1H), 6.89 (s, 1H), 4.28-4.26 (m, 2H),
4.16-4.11 (m, 2H), 2.21 (s, 6H), 1.23 (t, \(J=12\text{Hz}\), 3H), 1.15 (t, \(J=12\text{Hz}\), 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.04, 159.98, 137.21, 137.16, 136.83, 133.39, 129.83, 128.37, 127.75, 126.94, 125.60, 124.55, 123.26, 121.50, 61.03, 60.68, 19.65, 19.33, 14.01, 13.87; HRMS m/z calcld for C\(_{24}\)H\(_{25}\)NO\(_4\) [M\(^{+}\)] 391.4596, found 391.4595.

4.3.16. Dimethyl 1-(benzyl)- 4-(4-bromophenyl)-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.40-7.37 (m, 2H), 7.27-7.19 (m, 5H), 7.11 (d, \(J=8\text{Hz}\), 2H), 6.88 (s, 1H), 5.40 (s, 2H), 3.77 (s, 3H), 3.71 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.82, 160.41, 136.84, 132.21, 131.56, 128.92, 128.70, 127.80, 127.05, 125.57, 122.68, 121.83, 121.52, 120.80, 52.27, 51.74; HRMS m/z calcld for C\(_{21}\)H\(_{18}\)BrNO\(_4\) [M\(^{+}\)] 427.0419, found 427.0416.

4.3.17. Dimethyl 1-(benzyl)- 4-(3-fluorophenyl)-1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.32-7.22 (m, 5H), 7.16-7.12 (m, 3H), 7.09-7.06 (m, 1H), 6.93 (s, 1H), 5.47 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.96, 164.11, 161.67, 160.53, 136.82, 135.51, 130.12, 130.04, 128.82, 127.93, 127.22, 125.77, 122.99, 122.76, 122.13, 121.46, 114.29, 114.07, 113.84, 113.63, 52.43, 51.84; HRMS m/z calcld for C\(_{21}\)H\(_{18}\)FNO\(_4\) [M\(^{+}\)] 367.3703, found 367.3705.

4.3.18. Dimethyl 1-(4-methoxyphenyl)- 4-(3, 4-difluorophenyl)-1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.06 (d, \(J=8\text{Hz}\), 1H), 7.56-7.47 (m, 3H), 7.37-7.32 (m, 2H), 7.27-7.21 (m, 2H), 4.03 (s, 3H), 3.95 (s, 3H), 3.76 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 167.99, 166.47, 159.52, 151.47, 144.69, 137.10, 131.45, 124.89, 124.69, 123.69, 119.76, 117.96, 117.76, 117.36, 117.19, 102.69, 55.72, 53.22, 52.90; HRMS m/z calcld for C\(_{21}\)H\(_{17}\)F\(_2\)NO\(_5\) [M\(^{+}\)] 401.3601, found 401.3603.

4.3.19. Diethyl 1-(3, 5-dimethylphenyl)- 4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.43 (d, \(J=8\text{Hz}\), 2H), 7.27 (t, \(J=12\text{Hz}\), 2H), 7.18 (t, \(J=12\text{Hz}\), 1H), 6.97 (s, 1H), 6.85 (d, \(J=8\text{Hz}\), 3H), 4.28-4.23 (m, 2H), 4.15-4.10 (m, 2H), 2.26 (s, 6H), 1.22 (t, \(J=12\text{Hz}\), 3H), 1.17 (t, \(J=12\text{Hz}\), 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 165.92, 160.01, 139.36, 138.52, 133.40, 129.91, 128.36, 127.80, 126.91, 125.37, 124.65, 123.68, 121.45, 60.99, 60.68, 21.03, 13.99, 13.84; HRMS m/z calcld for C\(_{24}\)H\(_{25}\)NO\(_4\) [M\(^{+}\)] 391.4596, found 391.4597.

4.3.20. Diethyl 1-(2, 5-dimethylphenyl)- 4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.44 (d, \(J=8\) Hz, 2H), 7.27 (t, \(J=12\) Hz, 2H), 7.17 (t, \(J=12\) Hz, 1H), 7.08 (s, 2H), 6.96 (s, 1H), 6.77 (s, 1H), 4.30-4.25 (m, 2H), 4.08-4.03 (m, 2H), 2.26 (s, 3H), 2.00 (s, 3H), 1.23 (t, \(J=12\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.26, 159.43, 138.88, 135.94, 133.37, 132.09, 130.47, 130.17, 129.56, 128.45, 127.82, 127.53, 126.89, 125.30, 124.46, 123.53, 121.71, 61.09, 60.41, 20.59, 16.75, 14.00, 13.75; HRMS m/z calcd for C\(_{24}\)H\(_{25}\)NO\(_4\) [M\(^+\)] 391.1718, found 391.1786.

4.3.21. Dimethyl 1-(3, 4-dimethylphenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.41 (d, \(J=8\) Hz, 2H), 7.29 (t, \(J=8\) Hz, 2H), 7.22-7.19 (m, 1H), 7.11 (d, \(J=8\) Hz, 1H), 7.06 (s, 1H), 7.00 (d, \(J=8\) Hz, 1H), 6.90 (s, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 2.23 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.54, 160.45, 137.29, 137.06, 136.96, 133.24, 129.88, 128.46, 127.65, 126.99, 126.80, 125.85, 124.62, 123.45, 123.19, 121.22, 52.12, 51.78, 19.69, 19.36; HRMS m/z calcd for C\(_{24}\)H\(_{25}\)NO\(_4\) [M\(^+\)] 391.4596, found 391.4598.

4.3.22. Dimethyl 1-(phenyl)- 4-(thiophene) -1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.42–7.32 (m, 4H), 7.26–7.15 (m, 4H), 6.99 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 165.42, 161.34, 139.54, 136.21, 129.57, 129.19, 128.71, 127.93, 126.44, 125.86, 124.56, 124.21, 52.89, 52.21; HRMS m/z calcd for C\(_{18}\)H\(_{15}\)NO\(_4\)S [M\(^+\)] 341.3810, found 341.3812.

4.3.23. Dimethyl 1-(benzyl)- 4-(4-methylphenyl) -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.27–7.17 (m, 5H), 7.14–7.09 (m, 4H), 6.86 (s, 1H), 5.41 (s, 2H), 3.76 (s, 3H), 3.70 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 167.30, 160.56, 137.11, 136.55, 130.33, 129.28, 128.68, 127.73, 127.16, 127.08, 125.60, 123.90, 122.19, 120.93, 52.24, 51.64, 21.03; HRMS m/z calcd for C\(_{22}\)H\(_{21}\)NO\(_4\) [M\(^+\)] 363.4064, found 363.4066.

4.3.24. Diethyl 1-(3, 4-dimethoxyphenyl) - 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.45 (d, \(J=8\) Hz, 2H), 7.34 (t, \(J=12\) Hz, 2H), 7.27 (t, \(J=8\) Hz, 1H), 6.97 (s, 1H), 6.92–6.86 (m, 3H), 4.33–4.28 (m, 2H), 4.19–4.14 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 1.28 (t, \(J=12\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.03, 159.82, 148.95, 148.69, 133.13, 132.41, 128.30, 127.60, 126.87, 125.80, 124.35, 123.56, 121.39, 118.14, 110.49, 110.00, 61.09, 60.66, 55.88, 13.89, 13.82; HRMS m/z calcd for C\(_{22}\)H\(_{21}\)NO\(_6\) [M\(^+\)] 395.4052, found 395.4055.
4.3.25. Diethyl 1-(benzyl)-4-(3-fluorophenyl) -1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.30-7.20 (m, 5H), 7.16-1.09 (m, 4H), 6.92 (s, 1H), 5.46 (s, 2H), 4.30-4.21 (m, 4H), 1.29-1.21 (m, 6H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.51, 164.08, 161.64, 160.14, 137.01, 130.05, 129.96, 128.75, 127.22, 125.66, 123.09, 122.44, 121.51, 114.34, 113.50, 61.35, 60.77, 52.31, 14.01, 13.99; HRMS m/z calcd for C\(_{23}\)H\(_{22}\)FNO\(_4\) [M\(^+\)] 395.4235, found 395.4237.

4.3.26. Dimethyl 1-(5-indane)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.41 (d, \(J=8\)Hz, 2H), 7.29 (t, \(J=12\)Hz, 2H), 7.22-7.16 (m, 2H), 7.11 (s, 1H), 7.01 (d, \(J=8\)Hz, 1H), 6.91 (s, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 2.87 (t, \(J=12\)Hz, 4H), 2.08-2.03 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.53, 160.44, 145.06, 144.55, 137.49, 133.23, 128.39, 127.62, 126.96, 125.96, 124.55, 124.37, 123.82, 121.85, 121.18, 119.13, 52.11, 51.77, 32.74, 32.48, 25.52; HRMS m/z calcd for C\(_{23}\)H\(_{21}\)NO\(_4\) [M\(^+\)] 375.4171, found 375.4173.

4.3.27. Dimethyl 1-(4-methoxyphenyl) - 4-(2, 3-fluorophenyl)-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.07 (d, \(J=8\)Hz, 1H), 7.50-7.47 (m, 1H), 7.40 (t, \(J=12\)Hz, 1H), 7.28-7.16 (m, 5H), 4.04 (s, 3H), 3.94 (s, 3H), 3.77 (s, 3H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.83, 166.76, 159.62, 144.96, 138.31, 131.50, 125.94, 125.07, 124.36, 123.97, 117.83, 117.67, 102.72, 55.73, 53.19, 52.84; HRMS m/z calcd for C\(_{21}\)H\(_{17}\)F\(_2\)NO\(_5\) [M\(^+\)] 401.3602, found 401.3605.

4.3.28. Diethyl 1-(2, 4, 6-trimethylphenyl) – 4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Yellow sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.45 (d, \(J=8\)Hz, 2H), 7.33 (t, \(J=12\)Hz, 2H), 7.25 (d, \(J=8\)Hz, 1H), 6.92 (s, 2H), 6.76 (s, 1H), 4.34-4.28 (m, 2H), 4.13-4.08 (m, 2H), 2.30 (s, 3H), 2.00 (s, 6H), 1.27 (t, \(J=12\)Hz, 3H), 1.10 (t, \(J=12\)Hz, 3H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.37, 159.60, 138.31, 135.91, 135.25, 134.63, 133.47, 129.49, 128.58, 128.43, 127.64, 126.88, 125.03, 124.52, 123.20, 121.30, 61.16, 60.50, 20.89, 17.41, 14.04, 13.79; HRMS m/z calcd for C\(_{25}\)H\(_{27}\)NO\(_4\) [M\(^+\)] 405.4862, found 405.4865.

4.3.30. Dimethyl 1-allyl-4-phenyl-1H-pyrrole-2, 3-dicarboxylate
Brown sticky liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.43 (d, \(J=8\)Hz, 2H), 7.25 (t, \(J=12\)Hz, 2H), 7.20 (d, \(J=8\)Hz, 1H), 6.91 (s, 1H), 6.02 (m, 1H), 5.22 (d, \(J=10\)Hz, 1H), 5.13 (d, \(J=16\)Hz, 1H), 5.01 (d, \(J=5\)Hz, 2H), 3.82 (s, 3H), 3.76 (s, 3H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm) 166.32, 160.51, 133.74, 126.56, 127.21, 126.85, 125.32, 123.87, 122.12, 120.85, 118.75, 53.21, 51.36, 51.01; HRMS m/z calcd for C\(_{17}\)H\(_{17}\)NO\(_4\) [M\(^+\)] 299.3212, found 299.3215.
4.3.31. Diethyl 1-(benzyl) - 4-(4-bromophenyl) -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.50 (d, $J=8$Hz, 2H), 7.41 (d, $J=8$Hz, 1H), 7.34 (m, 4H), 7.15 (d, $J=4$Hz, 2H), 6.90 (s, 1H), 5.47 (s, 2H), 4.30-4.21 (m, 4H), 1.30-1.22 (m, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 166.44, 160.11, 137.62, 137.45, 136.91, 132.53, 131.50, 130.43, 129.01, 128.71, 127.80, 127.19, 126.54, 125.34, 122.58, 122.12, 121.57, 120.76, 61.29, 60.75, 52.27, 14.03, 13.98; HRMS m/z calcd for C$_{25}$H$_{22}$BrNO$_4$ [M$^+$] 456.3291, found 456.3292.

4.3.32. Diethyl 1-(5-indane) - 4-phenyl -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J=4$Hz, 2H), 7.28 (t, $J=12$Hz, 2H), 7.21-7.15 (m, 2H), 7.11 (s, 1H), 7.03-7.00 (m, 1H), 6.91 (s, 1H), 4.30-4.25 (m, 2H), 4.17-4.11 (m, 2H), 2.86 (t, $J=12$Hz, 4H), 2.07-2.01 (m, 2H), 1.24 (t, $J=12$Hz, 3H), 1.13 (t, $J=12$Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) 166.04, 159.97, 144.94, 144.43, 137.65, 133.39, 128.46, 128.36, 128.21, 127.71, 126.88, 125.72, 124.30, 123.90, 121.99, 121.48, 119.07, 61.02, 60.66, 32.73, 32.47, 25.56, 14.00, 13.86; HRMS m/z calcd for C$_{25}$H$_{25}$NO$_4$ [M$^+$] 403.4706, found 403.4706.

References
3 G. Daidone, B. Maggio, D. Schillaci, Pharmazie 1990, 45, 441-442.
9 (a) B. A. Trofimov, N. A. Nedolya, In Comprehensive Heterocyclic Chemistry III; A. R.


