**Supporting Information**

Magnetically Recoverable Cu\(^0\)/Fe\(_3\)O\(_4\) Catalyzed Highly Regioselective Synthesis of 2,3,4-Trisubstituted Pyrroles From Unactivated Terminal Alkynes and Isocyanides

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**1. General Techniques:**

All reagents were purchased from Sigma Aldrich and Alfa Aesar and were used without further purification. All experiments were carried out under nitrogen atmosphere. All the solvents used for the reaction were distilled before use. The product purification by column chromatography was accomplished using silica gel 100-200 mesh. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. Infrared spectra were recorded using a FT-IR spectrophotometer and values reported in cm\(^{-1}\). \(^1\)H and \(^13\)C NMR spectra were recorded with 300, 400 and 500 MHz NMR instruments with trimethylsilane (TMS) as an internal standard. High-resolution mass spectra (ESI-HRMS) were recorded on ESI-QTOP mass spectrometer. Chemical shifts (\(\delta =\))
are reported in ppm using TMS as an internal standard, and spin-spin coupling constants (J) are given in Hz. Multiplicities in the $^1$H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were recorded on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units. All the melting points are uncorrected. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about $10^{-9}$ Torr. The particle size and external morphology of the samples were observed on a JEOL JEM-2100 high resolution transmission electron microscope (HRTEM). Auger electron spectroscopic (AES) analysis is conducted, at a base pressure of $10^{-10}$ Torr, within the K.E. range of 110-700 eV (beam voltage of 3 kV, eV/step 1 eV, time/step 50 ms). X-ray absorption spectra were recorded using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan).

2. Synthesis of copper nanoparticles on Fe$_3$O$_4$:

The stable copper nanoparticles on Fe$_3$O$_4$, Cu(0)/Fe$_3$O$_4$ were synthesized from copper-Iron hydrotalcite successively by coprecipitation and Hydrothermal methods followed reduction by with Hydrogen gas. The detailed procedure is provided in our experimental procedure.

**Copper- Iron Hydrotalcite Cu- Fe HT (Cu-Fe HT):**

In a 250 mL four necked round bottomed flask with an overhead stirrer a mixture of copper nitrate trihydrate (0.0375 mole, 9.03 gm) and FeNO$_3$.9H$_2$O (0.15 moles, 6.06 gm) metal nitrates. NaOH (1.5 moles, 6.0 gm) and Na$_2$CO$_3$ (0.5 moles, 5.5 gm) were added from their respective additional burettes into the flask under stirring condition and precipitated at pH 8 with continuous stirring condition. After complete addition of metal nitrates, the greenish brown coloured precipitate was obtained which was aged at 333 K for 2h followed by filtration, washing with copious amount of distilled water to make the solid catalyst free from base and then dried in an oven at 383 K for 12h. The dried catalyst is then crushed into fine powder to obtain copper iron hydrotalcite Cu Fe HT.
**Synthesis of calcined copper iron hydrotalcite (CuO/ Fe$_3$O$_4$)**

5.0 gm of Cu Fe HT catalyst was taken in a tubular furnace and calcined in a static of air at 200 °C for a period of 5h. Calcined copper iron hydrotalcite CuO/Fe$_3$O$_4$ is obtained as a grey powder.

**Synthesis of copper nanoparticles Cu(0)/ Fe$_3$O$_4$:**

2.0 gm of calcined CuO/Fe$_3$O$_4$ was placed in the sample holder of the closed furnace. The furnace was facilitated with gas inlet and outlet. The inlet was connected to hydrogen gas with the flow rate 1 mL/ min. The furnace was slowly heated to 250 °C and CuO/Fe$_3$O$_4$ was kept at this temperature for 2 h. CuO/Fe$_3$O$_4$ which was in grey colour was reduced to Cu(0)/Fe$_3$O$_4$ (black powder). The furnace was cooled to room temperature under the N$_2$ flow (for 6-7h).

Iron ratio (Cu:Fe) in the synthesized catalysts was determined by Inductively Coupled Plasma-Atomic Optical Emission Spectroscopy (ICP-OES) and it is found to be 3:1 and showed 8 wt % of copper in Cu(0)/Fe$_3$O$_4$.

Cu/α-Al$_2$O$_3$, Cu/La$_2$O$_3$, Cu/Y$_2$O$_3$, Cu/CeO$_2$, Cu/ZrO$_2$, Cu/TiO$_2$, Cu/Nb$_2$O$_5$, Cu/SnO$_2$ with same 8 wt % of copper (ICP-OES) was reduced in same procedure as Cu(0)/Fe$_3$O$_4$. Copper nanoparticles on Fe$_3$O$_4$ Cu(0)/Fe$_3$O$_4$ was characterized and confirmed by various XRD, XPS, OES, and BET analytical methods.

3. **Characterizations of Cu(0)/Fe$_3$O$_4$:**
**Figure S1:** FE-SEM images of Cu(0)/Fe$_3$O$_4$

**Figure S2:** Energy dispersive X-ray spectrum of Cu(0)/Fe$_3$O$_4$
Figure S3: Wide angle powder X-ray diffraction pattern of Cu(0)/Fe₃O₄

Figure S4: XPS spectra of Cu 2p region (A) and Fe 2p region (B) of Cu(0)/Fe₃O₄

4. Reusability of Cu(0)/Fe₃O₄:
Magnetic separation is a more attractive and simple technique than the filtration or centrifugation techniques as it prevents the loss of the catalyst and increases the reusability of the catalyst. Due to the superparamagnetic nature of Fe₃O₄ nanoparticles at room temperature, separation of the Cu(0)/Fe₃O₄ nanocatalyst from the reaction mixture becomes very easy. In
the magnetic separation technique the catalyst became adsorbed onto the magnetic stirring bar when the stirring was stopped. Then the catalyst was washed with diethyl ether, oven dried at 100 °C and then directly used for the next cycle reaction without further purification. A recyclability test was performed under optimised conditions using fresh phenyl acetylene, isocyanides and anhydrous K₂CO₃. Recyclable potential plot of Cu(0)/Fe₃O₄ nanocatalyst suggested that the nanocatalyst can be effectively reused for five consecutive catalytic cycles (ESI, Fig. XX) without significant loss in catalytic activity. A slight drop in the conversion (%) from the 5th to 6th cycles is observed which is due to the clogging of some catalytic active sites with organic reagents during the course of reaction. In every case our recovery of catalyst from the reaction mixture is almost 100%. We have also provided the distribution of product yield which remains consistent in each catalytic cycle.

**Figure S5**: Recycling efficiency of Cu(0)/Fe₃O₄ nanocatalyst for five reaction cycles.
5. General Procedure of synthesis of 4-ethynyl-1,1'-biphenyl: (3f)

To a stirred solution of [1,1'-biphenyl]-4-carbaldehyde (2.55 g, 14.0 mmol) and carbon tetrabromide (9.27 g, 28.0 mmol) in anhydrous dichloromethane (40 mL) was added triphenylphosphine (14.6 g, 56.0 mmol,) in portions over a period of 30 mins at 0 °C temperature under inert atmosphere. The reaction mixture was turned brown that was allowed to stir at 0 °C temperature for 2 h. After completion of reaction (monitored by TLC), reaction mixture was quenched with water (30 mL). The reaction mixture was extracted with dichloromethane (2 x 60 mL); organic layers were washed with brine (20 mL). The organic layers were dried over anhydrous Na₂SO₄; solvent was evaporated under reduced pressure to afford a crude residue. The crude was purified on silica-gel (100 - 200 mesh) to give the dibromo compounds as white solid (3.4 g, 72 % yield). mp. 106-108 °C.; ¹H NMR (300 MHz, CDCl₃) δ 7.69 – 7.57 (m, 6H), 7.52 (s, 1H), 7.45 (t, J = 7.3 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), ¹³C NMR (75 MHz, CDCl₃) δ = 141.32, 140.35, 136.50, 134.22, 128.87, 127.67, 127.05, 89.50.

To a stirred solution of dibromoalkene (3.38 g, 10.0 mmol) in anhydrous CH₃CN (25 mL) was added DBU (5.9 mL, 40.0 mmol, 4 equiv) drop wise over a period of 10 mins at ambient temperature (25-30 °C). The reaction mixture was allowed to stir at ambient temperature for 16 h. After completion of reaction (monitored by TLC), reaction mixture was cooled at 15 °C and quenched by drop wise addition of 5N aqueous HCl (50 mL) over a period of 15 mins then continued stirring for 5 mins. The reaction mixture was extracted with EtOAc/hexane (1:1, 2 x 40 mL); organic layers were washed with water (50 mL). The organic layers were dried over anhydrous K₂CO₃, solvent was evaporated under reduced pressure, and resulting residues were dried in high vacuum to afford the analytically pure 3f as white solid (1.4 g, 78 % yield). ¹H NMR (500 MHz, CDCl₃) δ = 7.61 – 7.54 (m, 6H), 7.45 (dd, J = 10.7, 4.5 Hz, 2H), 7.42 – 7.33 (m, 1 H), 3.13 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ = 141.60, 140.27, 132.57, 128.89, 127.75, 127.08, 127.03, 120.99, 83.57, 77.76.
6. **General experimental Procedure for the synthesis of 2,3,4-trisubstituted pyrroles (3aa-3vb):**

\[
\text{R} \equiv \text{H} + \text{C}=\text{N} \rightarrow \text{COOR'} \xrightarrow{\text{Cu(0)/Fe}_3\text{O}_4, \text{DMSO, 100°C, 90%}} \text{COOR'} \quad \text{3aa-3vb}
\]

To a solution of alkynes (1.0 mmol), isocyanides (2.0 mmol) and anhydrous K\textsubscript{2}CO\textsubscript{3} (3.0 mmol) in dry DMSO (4.0 mL) was added Cu(0)/Fe\textsubscript{3}O\textsubscript{4} nano catalyst (30 mg, 8%, 3.3 mol%) at room temperature under argon atmosphere. The reaction temperature was increased up to 100 °C and stirred for 1 h. The reaction mixture was then allowed to attain room temperature and diluted with ethyl acetate (50 mL). The catalyst was recovered magnetically and the organic layer was washed with successively with water (20 mL) and brine (20 mL). The organic layer was further dried over anhydrous sodium sulphate and evaporation of solvent under reduced pressure produced crude product which was purified by column chromatography using 100-200 mesh silica gel.

7. **Spectral Data of compounds (3aa-3vb)**

**Dimethyl 3-benzyl-1H-pyrrole-2,4-dicarboxylate (3aa)**

**Yield:** 85%; White solid, **M.p.** 120 – 122 °C; **\textsuperscript{1}H NMR** (500 MHz, CDCl\textsubscript{3}) \(\delta = 9.38\) (s, 1H), 7.51 (d, \(J = 3.5\) Hz, 1H), 7.28 – 7.25 (m, 2H), 7.22 (dd, \(J = 10.3, 4.9\) Hz, 2H), 7.14 – 7.11 (m, 1H), 4.52 (s, 2H), 3.86 (s, 3H), 3.77 (s, 3H); **\textsuperscript{13}C NMR** (100 MHz, CDCl\textsubscript{3}) \(\delta = 164.58, 161.58, 141.17, 132.09, 128.55, 128.06, 127.46, 125.64, 121.02, 116.50, 51.62, 51.04, 30.34;**

**IR** (neat): 3300, 1714, 1697, 1559, 1277 1147 cm\textsuperscript{-1}; **HRMS** (ESI, Orbitrap) calcd for C\textsubscript{15}H\textsubscript{16}NO\textsubscript{4} [M+H] is 274.10738 and found 274.10752.
Diethyl 3-benzyl-1H-pyrrole-2,4-dicarboxylate (3ab):

Yield: 89%; Yellow solid, M.p. 95 – 97 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.51 (s, 1H), 7.53 (d, $J$ = 3.5 Hz, 1H), 7.24 - 7.19 (m, 4H), 7.12 (t, $J$ = 7.0 Hz, 1H), 4.53 (s, 2H), 4.32 (q, $J$ = 7.1 Hz, 2H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ = 164.32, 161.35, 141.24, 131.63, 128.51, 127.99, 127.40, 125.54, 121.27, 116.89, 60.73, 59.85, 30.38, 14.37; IR (neat): 3228, 2952, 1724, 1673, 1441, 1278 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{17}$H$_{20}$NO$_4$ [M+H] is 302.13868 and found 302.13814.

Di-tert-butyl 3-benzyl-1H-pyrrole-2,4-dicarboxylate (3ac):

Yield: 86%; White solid; M.p. 96 – 98 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.44 (s, 1H), 7.46 (d, $J$ = 3.4 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.14 – 7.08 (m, 1H), 4.51 (s, 2H), 1.48 (s, 9H), 1.44 (s, 9H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ = 163.98, 161.06, 141.40, 129.61, 128.93, 128.16, 127.84, 126.79, 125.29, 122.48, 118.68, 81.85, 80.24, 30.25, 28.33, 28.28; IR (neat): 3284, 2926, 1702, 1670, 1295, 1150 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{21}$H$_{28}$NO$_4$ [M+H] is 358.20128 and found 358.20158.

Dimethyl 3-(4-methylbenzyl)-1H-pyrrole-2,4-dicarboxylate (3ba):

Yield: 81%; Colourless thick oil; $^1$H (500 MHz, CDCl$_3$) $\delta$ = 9.23 (s, 1H), 7.51 (d, $J$ = 3.5 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.03 (d, $J$ = 7.9 Hz, 2H), 4.47 (s, 2H), 3.86 (s, 3H), 3.77 (s,
3H), 2.28 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ = 164.56, 161.55, 138.10, 135.04, 132.40, 128.78, 128.42, 127.36, 120.92, 116.47, 51.62, 51.04, 29.72, 21.02; IR (neat): 3218, 2923, 1699, 1277, 768 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{16}$H$_{18}$NO$_4$ [M+H] is 288.12303 and found 288.12341.

**Diethyl 3-(4-methylbenzyl)-1H-pyrrole-2,4-dicarboxylate (3bb):**

![Diagram](3bb)

**Yield:** 82%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ = 9.31 (s, 1H), 7.51 (d, $J = 3.5$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 2H), 4.48 (s, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.27 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ = 164.28, 161.28, 138.17, 134.93, 132.01, 128.70, 128.42, 127.25, 121.14, 116.85, 60.70, 59.82, 29.89, 21.01, 14.39; IR (neat): 3295, 2927, 1693, 1271, 1083 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{18}$H$_{22}$NO$_4$ [M+H] is 316.15433 and found 316.15483.

**Diethyl 3-(4-ethylbenzyl)-1H-pyrrole-2,4-dicarboxylate (3bb):**

![Diagram](3ca)

**Yield:** 82%; Yellow thick oil; $^1$H NMR (500 MHz, CDCl$_3$) δ = 9.30 (s, 1H), 7.50 (d, $J = 3.5$ Hz, 1H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 2H), 4.48 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.58 (q, $J = 7.6$ Hz, 2H), 1.19 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 164.60, 161.60, 141.42, 138.35, 132.41, 128.47, 127.57, 127.40, 120.93, 118.23, 116.47, 51.62, 51.04, 29.91, 28.42, 15.56; IR (neat): 3296, 2958, 1700, 1438, 1274, 1020 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{17}$H$_{20}$NO$_4$ [M+H] is 306.13868 and found 306.138647.

**Diethyl 3-(4-ethylbenzyl)-1H-pyrrole-2,4-dicarboxylate (3cb):**
Yield: 81%; Sticky solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.29$ (s, 1H), 7.51 (d, $J = 3.5$ Hz, 1H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 4.49 (s, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.58 (q, $J = 7.6$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.29$, 161.26, 141.00, 138.44, 128.47, 127.49, 127.21, 121.16, 116.91, 60.69, 59.82, 29.91, 28.42, 15.59, 14.41, 14.38; IR (KBr): 3271, 2965, 1701, 1451, 1271, 998 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{19}$H$_{24}$NO$_4$ [M+H$^+$] is 330.16998 and found 330.17014.

**Dimethyl 3-(4-(tert-butyl)benzyl)-1H-pyrrole-2,4-dicarboxylate (3da):**

Yield: 79%; Colourless liquid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.26$ (s, 1H), 7.51 (d, $J = 3.4$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 4.48 (s, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.27 (s, 9H); $^{13}$C NMR (125MHz, CDCl$_3$) $\delta = 164.43$, 161.56, 148.27, 132.40, 128.20, 127.32, 124.99, 120.93, 116.53, 51.61, 51.04, 34.31, 31.42, 29.79; IR (neat): 3299, 2957, 1701, 1272, 1022 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{19}$H$_{24}$NO$_4$ [M+H$^+$] is 330.16998 and found 330.170574.

**Diethyl 3-(4-(tert-butyl)benzyl)-1H-pyrrole-2,4-dicarboxylate (3db):**

Yield: 76%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.29$ (s, 1H), 7.51 (d, $J = 3.4$ Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.5$ Hz, 2H), 4.49 (s, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.27 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.31$, 161.29,
148.18, 138.20, 132.02, 128.18, 127.21, 124.90, 121.16, 116.92, 60.69, 59.82, 34.30, 31.43, 29.80, 14.38; IR (neat): 3291, 2945, 1685, 1445, 1265, 1029 cm\(^{-1}\); HRMS (ESI, Orbitrap) calcd for C\(_{21}\)H\(_{28}\)NO\(_4\) [M+H] is 358.20128 and found 358.20170.

**Dimethyl 3-(4-methoxybenzyl)-1H-pyrrole-2,4-dicarboxylate (3ea):**

![Image of structure 3ea]

**Yield:** 71%; White solid; M.p. 136 – 138 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.55\) (s, 1H), 7.49 (d, \(J = 3.5\) Hz, 1H), 7.20 (d, \(J = 8.5\) Hz, 2H), 6.78 – 6.76 (m, 2H), 4.45 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 164.67, 161.67, 157.61, 133.43, 132.76, 129.50, 127.64, 120.79, 116.22, 113.51, 55.21, 51.61, 51.05, 29.41; IR (KBr): 3358, 3299, 2956, 1680, 1509, 1436, 1278, 1020 cm\(^{-1}\); HRMS (ESI, Orbitrap) calcd for C\(_{16}\)H\(_{18}\)NO\(_5\) [M+H] is 304.11795 and found 304.11815.

**Diethyl 3-(4-methoxybenzyl)-1H-pyrrole-2,4-dicarboxylate (3eb):**

![Image of structure 3eb]

**Yield:** 73%; Sticky solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.44\) (s, 1H), 7.51 (d, \(J = 3.5\) Hz, 1H), 7.20 (d, \(J = 8.7\) Hz, 2H), 6.78 – 6.75 (m, 2H), 4.46 (s, 2H), 4.33 (q, \(J = 7.1\) Hz, 2H), 4.25 (q, \(J = 7.1\) Hz, 2H), 3.75 (s, 3H), 1.33 (t, \(J = 7.2\) Hz, 3H), 1.29 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 164.31, 161.31, 157.57, 133.48, 132.30, 129.47, 127.35, 121.05, 116.73, 113.43, 60.72, 59.84, 55.22, 29.42, 14.41; IR (neat): 3257, 2930, 1718, 1423, 1280 cm\(^{-1}\); HRMS (ESI, Orbitrap) calcd for C\(_{18}\)H\(_{22}\)NO\(_5\) [M+H] is 332.14925 and found 332.14963.

**Dimethyl 3-([1,1’-biphenyl]-4-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3fa):**
Yield: 86%; Colourless liquid, $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.30$ (s, 1H), 7.57 – 7.51 (m, 3H), 7.47 – 7.45 (m, 2H), 7.40 (dd, $J = 10.5$, 4.9 Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.32 – 7.27 (m, 1H), 4.56 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta =$ 164.54, 161.46, 141.25, 140.32, 138.57, 132.02, 128.95, 128.65, 127.38, 127.00, 126.86, 121.04, 116.54, 51.67, 51.09, 29.99; IR (neat): 3266, 2961, 1705, 1438, 1266 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{21}$H$_{20}$NO$_4$ [M+H] is 350.13868 and found 350.13692.

Diethyl 3-([1,1'-biphenyl]-4-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3fb):

Yield: 84%; Colourless liquid, $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.44$ (s, 1H), 7.56 – 7.53 (m, 3H), 7.47 – 7.44 (m, 2H), 7.40 (dd, $J = 10.5$, 4.9 Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.29 (ddd, $J = 8.5$, 2.3, 1.2 Hz, 1H), 4.57 (s, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 164.28, 161.22, 141.28, 140.42, 138.47, 131.60, 128.94, 128.66, 127.30, 127.00, 126.88, 126.78, 121.28, 116.92, 60.77, 59.90, 30.03, 14.43; IR (neat): 3290, 2975, 1705, 1438, 1271 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{23}$H$_{24}$NO$_4$ [M+H] is 378.16998 and found 378.16994.

Dimethyl 3-(3-nitrobenzyl)-1H-pyrrole-2,4-dicarboxylate (3ga):

Yield: 93%; White solid, M.p. 124 – 126 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 9.58 (s, 1H), 8.11 (bs, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 7.4$ Hz, 1H), 7.56 (d, $J = 3.4$ Hz, 1H),
7.48 – 7.37 (m, 1H), 4.62 (s, 2H), 3.90 (s, 3H), 3.80 (s, 3H); ^13^C NMR (75 MHz, CDCl$_3$) δ = 164.42, 161.20, 148.16, 144.19, 143.19, 135.04, 130.42, 128.84, 127.66, 123.41, 121.16, 120.93, 116.25, 51.82, 51.21, 30.02; IR (KBr): 3275, 2966, 1715, 1675, 1531, 1275 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{15}$H$_{15}$N$_2$O$_6$ [M+H] is 319.09246 and found 319.09195.

**Diethyl 3-(3-nitrobenzyl)-1H-pyrrole-2,4-dicarboxylate (3gb):**

![Chemical Structure](image)

**Yield:** 91%; White solid, M.p. 95 - 97 °C; ^1^H NMR (400 MHz, CDCl$_3$) δ = 9.50 (s, 1H), 8.11 (bs, 1H), 8.00 (dd, J = 8.2, 1.3 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 3.5 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 4.62 (s, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^13^C NMR (75 MHz, CDCl$_3$) δ = 164.11, 160.95, 148.15, 143.30, 135.02, 129.96, 128.79, 127.54, 123.38, 121.38, 120.87, 116.63, 60.96, 60.03, 30.06, 14.34; IR (KBr): 3228, 2926, 1717, 1677, 1531, 1350, 1275 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{17}$H$_{19}$N$_2$O$_6$ [M+H] is 347.12376 and found 347.12313.

**Dimethyl 3-(4-cyanobenzyl)-1H-pyrrole-2,4-dicarboxylate (3ha):**

![Chemical Structure](image)

**Yield:** 91%; White solid, M.p. 109 – 111 °C; ^1^H NMR (500 MHz, CDCl$_3$) δ = 9.29 (s, 1H), 7.53 (d, J = 3.5 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 4.57 (s, 2H), 3.86 (s, 3H), 3.77 (s, 3H); ^13^C NMR (125 MHz, CDCl$_3$) δ = 164.30, 161.00, 146.80, 131.95, 130.51, 129.33, 127.35, 121.15, 119.31, 116.43, 109.48, 51.75, 51.17, 30.51; IR (KBr): 3305, 2954, 2224, 1719, 1680, 1453, 1283 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{16}$H$_{15}$N$_2$O$_4$ [M+H] is 299.10263 and found 299.10295.

**Diethyl 3-(4-cyanobenzyl)-1H-pyrrole-2,4-dicarboxylate (3hb):**
**Yield:** 92%; Crystalline solid; **M.p.** 101 – 103 °C; **¹H NMR** (500 MHz, CDCl₃) δ = 9.66 (s, 1H), 7.55 (d, J = 3.5 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 4.59 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.29 (dt, J = 14.2, 7.1 Hz, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ = 164.13, 161.02, 147.05, 132.66, 131.87, 129.98, 129.26, 125.44, 121.40, 119.32, 112.47, 109.24, 60.85, 59.97, 30.63, 14.35; **IR** (KBr): 3301, 2967, 2258, 1715, 1684, 1283 cm⁻¹; **HRMS** (ESI, Orbitrap) calcd for C₁₈H₁₉N₂O₄ [M+H] is 327.13393 and found 327.13441.

**Dimethyl 3-(4-bromobenzyl)-1H-pyrrole-2,4-dicarboxylate (3ia):**

![Diagram of 3ia](image)

**Yield:** 87%; Semi solid, **¹H NMR** (500 MHz, CDCl₃) δ = 9.28 (s, 1H), 7.51 (d, J = 3.5 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 4.46 (s, 2H), 3.86 (s, 3H), 3.77 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ = 164.40, 161.27, 140.14, 139.74, 131.08, 130.33, 127.35, 120.97, 119.45, 116.39, 51.68, 51.10, 29.73; **IR** (neat): 3415, 2927, 1701, 1438, 1279 cm⁻¹; **HRMS** (ESI, Orbitrap) calcd for C₁₅H₁₅BrNO₄ [M+H] is 352.01790 and found 352.01835.

**Diethyl 3-(4-bromobenzyl)-1H-pyrrole-2,4-dicarboxylate (3ib):**

![Diagram of 3ib](image)

**Yield:** 88%; Brown oil, **¹H NMR** (500 MHz, CDCl₃) δ = 930 (s, 1H), 7.45 (d, J = 3.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 4.40 (s, 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ = 163.13, 160.07, 139.20, 130.07, 129.99, 129.27, 126.32, 120.20, 118.32,
115.74, 59.79, 58.89, 28.78, 13.35; **IR** (neat): 3411, 2937, 1698, 1430, 1271, 1020 cm\(^{-1}\); **HRMS** (ESI, Orbitrap) calcd for C\(_{17}\)H\(_{19}\)BrNO\(_4\) [M+H] is 380.04920 and found 380.04969.

**Dimethyl 3-(4-fluorobenzyl)-1H-pyrrole-2,4-dicarboxylate (3ja):**

![Chemical Structure of 3ja]

**Yield:** 90%; White solid, **M.p.** 84 – 86 °C; **\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta = 9.45\) (s, 1H), 7.51 (d, \(J = 3.5\) Hz, 1H), 7.22 (dd, \(J = 8.1, 2.5\) Hz, 2H), 6.92 – 6.87 (m, 2H), 4.47 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H); **\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta = 164.51, 162.13, 161.40, 160.20, 136.81, 132.17, 129.94, 129.87, 127.47, 120.88, 116.31, 114.82, 114.65, 51.65, 51.08, 29.48; **IR** (KBr): 3310, 2925, 1697, 1508, 1275, 1150 cm\(^{-1}\); **HRMS** (ESI, Orbitrap) calcd for C\(_{15}\)H\(_{15}\)FNO\(_4\) [M+H] is 292.09796 and found 292.09856.

**Diethyl 3-(4-fluorobenzyl)-1H-pyrrole-2,4-dicarboxylate (3jb):**

![Chemical Structure of 3jb]

**Yield:** 88%; White solid, **M.p.** 83 – 84 °C; **\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta = 9.46\) (s, 1H), 7.22 (dd, \(J = 8.6, 5.6\) Hz, 2H), 6.91 – 6.87 (m, 1H), 4.49 (s, 3H), 4.33 (q, \(J = 7.1\) Hz, 3H), 4.25 (q, \(J = 7.1\) Hz, 3H), 1.30 (dt, \(J = 14.2, 7.1\) Hz, 6H); **\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta = 164.21, 162.09, 161.14, 160.16, 136.85, 131.68, 129.87, 129.81, 127.34, 121.15, 116.73, 114.74, 114.57, 60.76, 59.88, 29.53, 14.37; **IR** (KBr): 3300, 2932, 1699, 1520, 1292, 1158 cm\(^{-1}\); **HRMS** (ESI, Orbitrap) calcd for C\(_{17}\)H\(_{19}\)FNO\(_4\) [M+H] is 320.12926 and found 320.12988.

**Dimethyl 3-(3-(trifluoromethyl)benzyl)-1H-pyrrole-2,4-dicarboxylate (3ka):**
Yield: 87%; White solid, M.p. 134 – 136 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.57$ (s, 1H), 7.72 – 7.53 (m, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.7$ Hz, 1H), 4.72 (s, 2H), 3.75 (s, 3H), 3.68 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 164.43$, 161.60, 139.82, 131.59, 128.97, 128.32, 127.69, 125.56, 125.44, 122.10, 117.55, 51.71, 51.09, 27.21; IR (KBr): 3290, 2925, 1718, 1687, 1315, 1119 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{16}$H$_{15}$F$_3$NO$_4$ [M+H] is 342.09477 and found 342.09539.

**Diethyl 3-(3-(trifluoromethyl)benzyl)-1H-pyrrole-2,4-dicarboxylate (3kb):**

Yield: 89%; White solid M.p. 118 – 120 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.53$ (s, 1H), 7.66 (d, $J = 3.5$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 4.76 (s, 2H), 4.20 (t, $J = 7.1$ Hz, 2H), 4.14 (q, $J = 7.1$ Hz, 2H), 1.12 (t, $J = 7.1$ Hz, 3H), 1.09 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 164.18$, 161.39, 139.99, 131.54, 128.36, 128.23, 127.73, 126.22, 125.53, 125.48, 125.34, 122.34, 117.93, 60.81, 59.91, 27.33, 14.02, 13.97; IR (KBr): 3290, 2915, 1716, 1321, 1110 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{16}$H$_{19}$F$_3$NO$_4$ [M+H] is 370.12607 and found 370.12607.

**Dimethyl 3-(4-(methoxycarbonyl)benzyl)-1H-pyrrole-2,4-dicarboxylate (3la)**

Yield: 86%; White solid, M.p. 155 – 157 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.30$ (s, 1H), 7.89 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 3.4$ Hz, 1H), 7.30 (d, $J = 8.2$ Hz, 2H), 4.57 (s, 2H), 3.87
(s, 3H), 3.85 (s, 3H), 3.76 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 167.29, 164.43, 161.30, 146.71, 131.01, 129.46, 128.49, 127.59, 127.44, 121.16, 116.51, 51.94, 51.67, 51.09, 30.48; IR (KBr): 3303, 2951, 1710, 1608, 1437, 1138, 1007 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{17}$H$_{18}$NO$_6$ [M+H] is 332.11286 and found 332.11292.

**Diethyl 3-(3-ethynylbenzyl)-1H-pyrrole-2,4-dicarboxylate (3mb):**

Yield: 86%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 9.62 (s, 1H), 7.54 (d, $J = 3.5$ Hz, 1H), 7.35 (s, 1H), 7.26 (dd, $J = 9.8$, 5.5 Hz, 2H), 7.17 (t, $J = 7.7$ Hz, 1H), 4.51 (s, 2H), 4.32 (q, $J = 7.1$ Hz, 2H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.00 (s, 1H), 1.30 (t, $J = 7.3$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 164.31, 161.37, 144.10, 141.45, 132.12, 130.80, 129.44, 129.26, 127.97, 127.64, 121.57, 121.38, 116.78, 84.17, 60.82, 59.92, 30.15, 14.34; IR (neat): 3283, 2987, 1698, 1667, 1419, 1285 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{19}$H$_{20}$NO$_4$ [M+H] is 326.13868 and found 326.13776.

**Dimethyl 3-pentyl-1H-pyrrole-2,4-dicarboxylate (3na):**

Yield: 72%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 9.27 (s, 1H), 7.47 (d, $J = 3.5$ Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.08 (t, $J = 7.3$ Hz, 2H), 1.59 – 1.51 (m, 2H), 1.39 – 1.30 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 164.80, 161.92, 135.39, 127.43, 120.27, 115.99, 51.49, 50.98, 31.93, 30.84, 24.99, 22.48, 14.08; IR (neat): 3300; 2938, 1694, 1557, 1438, 1280, 1105 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{13}$H$_{20}$NO$_4$ [M+H] is 254.13868 and found 254.13875.

**Diethyl 3-pentyl-1H-pyrrole-2,4-dicarboxylate (3nb):**
Yield: 70%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.65$ (s, 1H), 7.43 (d, $J = 3.9$ Hz, 1H), 4.29 q, $J = 7.1$ Hz, 2H), 4.23 q, $J = 7.1$ Hz, 2H), 3.04 – 2.98 (m, 2H), 1.56 – 148 (m, 2H), 1.32 – 1.218 (m, 9H), 0.82 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.56$, 161.74, 134.99, 127.39, 120.50, 116.35, 60.55, 59.73, 32.12, 30.98, 25.23, 22.59, 14.39, 14.37, 14.13; IR (neat): 3308; 2945, 1699, 1441, 1267, 1098 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{13}$H$_{24}$NO$_4$ [M+H] is 282.1699 and found 282.16107.

**Dithyl 3-hexyl-1H-pyrrole-2,4-dicarboxylate (3oa):**

Yield: 71%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.30$ (s, 1H), 7.48 (d, $J = 3.5$ Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.10 – 3.06 (m, 2H), 1.60 – 1.51 (m, 2H), 1.40 – 135 (m, 2H), 1.33 – 1.25 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.80$, 161.92, 135.38, 127.44, 120.26, 115.98, 51.47, 50.96, 31.67, 31.13, 29.43, 25.07, 22.67, 14.12; IR (neat): 3295, 2931, 1701, 1576, 1420, 1296, 1101 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{14}$H$_{22}$NO$_4$ [M+H] is 258.15433 and found 258.15493.

**Diethyl 3-hexyl-1H-pyrrole-2,4-dicarboxylate (3ob):**

Yield: 69%; Colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.26$ (s, 1H), 7.48 (d, $J = 3.5$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 3.08 (t, $J = 6.8$ Hz, 2H), 1.59 – 1.49 (m, 2H), 1.41 – 1.33 (m, 8H), 1.33 – 1.27 (m, 3H), 0.88 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.61$, 161.86, 135.00, 127.59, 120.48, 116.20, 60.51, 59.70, 31.78, 31.28, 29.60, 25.31, 22.70, 14.37, 14.08; IR (neat): 3299, 2923, 1703, 1556, 1438, 1301,
1099 cm⁻¹; HRMS (ESI, Orbitrap) calcd for C₁₆H₂₆NO₄ [M+H] is 296.18563 and found 296.18591.

**Dimethyl 3-(naphthalen-1-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3pa):**

![Diagram of 3pa](Image)

Yield: 90%; crystalline solid, M.p. 165 – 166 °C; ¹H NMR (400 MHz, CDCl₃) δ = 9.73 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.9 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.52 – 7.46 (m, 1H), 7.26 – 7.22 (m, 1H), 6.78 (dd, J = 7.1, 0.7 Hz, 1H), 4.96 (s, 2H), 3.66 (s, 3H), 3.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 164.49, 161.69, 137.11, 133.59, 132.11, 130.69, 128.61, 127.59, 126.14, 125.73, 125.43, 125.34, 123.85, 123.50, 121.99, 117.38, 51.68, 51.05, 27.26; IR (KBr): 3282, 2923, 1724, 1673, 1441, 1279, 1018 cm⁻¹; HRMS (ESI, Orbitrap) calcd for C₁₉H₁₈NO₄ [M+H] is 324.12303 and found 324.12251.

**Diethyl 3-(naphthalen-1-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3pb):**

![Diagram of 3pb](Image)

Yield: 89%; White Solid, M.p. 115 – 118 °C; ¹H NMR (400 MHz, CDCl₃) δ = 9.83 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.64 (dd, J = 8.8, 2.3 Hz, 2H), 7.55 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.25 (dd, J = 9.3, 6.0 Hz, 1H), 6.78 (dd, J = 7.2, 1.0 Hz, 1H), 4.98 (s, 2H), 4.13 (q, J = 7.1 Hz, 2H), 4.07 (q, J = 7.1 Hz, 2H), 0.99 – 0.95 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 164.33, 161.47, 137.28, 133.53, 132.14, 130.30, 128.57, 127.62, 126.00, 125.66, 125.43, 125.28, 123.79, 123.42, 122.21, 117.81, 60.63, 59.79, 27.54, 14.01; IR (KBr): 3290, 2929, 1721, 1675, 1436, 1288, 1001 cm⁻¹; HRMS (ESI, Orbitrap) calcd for C₂₁H₂₂NO₄ [M+H] is 352.15433 and found 352.15374.

**Diethyl 3-(phenanthren-9-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3qb):**
Yield: 91%; Brown solid, M.p. 120 – 122 °C; $^1$H NMR (500 MHz, CDCl$_3$) \( \delta = 9.55 \) (s, 1H), 8.77 – 8.71 (m, 1H), 8.63 (d, \( J = 8.2 \) Hz, 1H), 8.35 – 8.28 (m, 1H), 7.71 - 7.67 (m, 3H), 7.61 (d, \( J = 7.8 \) Hz, 1H), 7.57 – 7.52 (m, 1H), 7.48 (dd, \( J = 10.9, 3.9 \) Hz, 1H), 6.96 (s, 1H), 4.84 (s, 2H), 4.13 (q, \( J = 7.1 \) Hz, 2H), 4.06 (q, \( J = 7.1 \) Hz, 2H), 0.99 (t, \( J = 7.7 \) Hz, 3H), 0.96 (t, \( J = 7.7 \) Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) \( \delta = 164.29, 161.43, 135.56, 131.97, 131.77, 130.34, 129.93, 129.44, 128.22, 127.63, 126.55, 126.05, 125.64, 124.05, 123.84, 123.01, 122.33, 117.85, 60.65, 59.80, 28.02, 14.00; IR (KBr): 3258, 2924, 1707, 1658, 1383, 1284, 1161 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{25}$H$_{24}$NO$_4$ [M+H$^+$] is 402.16998 and found 402.16934.

**Dimethyl 3-(pyren-1-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3ra):**

Yield: 85%; White solid, M.p. 182 – 184 °C; $^1$H NMR (500 MHz, CDCl$_3$) \( \delta = 9.50 \) (s, 1H), 8.55 (d, \( J = 9.3 \) Hz, 1H), 8.18 (dd, \( J = 8.4, 5.5 \) Hz, 2H), 8.15 (d, \( J = 7.6 \) Hz, 1H), 8.02 – 7.95 (m, 4H), 7.66 (s, 1H), 7.43 (d, \( J = 7.9 \) Hz, 1H), 5.25 (s, 2H), 3.67 (s, 3H), 3.58 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) \( \delta = 164.52, 161.61, 135.14, 131.52, 131.01, 129.44, 128.61, 127.59, 127.12, 126.41, 125.69, 125.08, 124.78, 124.72, 124.65, 123.40, 122.06, 117.49, 51.70, 51.09, 27.54; IR (KBr): 3320, 2924, 1718, 1675, 1435, 1281, 1016 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{25}$H$_{20}$NO$_4$ [M+H$^+$] is 398.13868 and found 398.13896.

**Diethyl 3-(pyren-1-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3rb):**
Yield: 84%; White solid, M.p. 207 – 209 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.52$ (s, 1H), 8.52 (d, $J = 9.2$ Hz, 1H), 8.23 – 8.12 (m, 3H), 8.04 – 7.93 (m, 4H), 7.68 (d, $J = 3.5$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 5.26 (s, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 4.05 (q, $J = 7.1$ Hz, 2H), 0.96 (td, $J = 7.1$, 1.6 Hz, 7H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.30$, 161.38, 135.30, 131.53, 131.02, 130.49, 129.38, 128.58, 127.62, 127.08, 126.33, 125.66, 125.01, 124.92, 124.75, 124.69, 124.66, 123.33, 117.89, 77.32, 77.07, 76.81, 60.67, 59.83, 27.90, 14.07; IR (KBr) 3310, 2931, 1714, 1663, 1287, 1007 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{27}$H$_{24}$NO$_4$ [M+H]$^+$ is 426.16998 and found 426.17039.

**Dimethyl 3-(thiophen-2-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3sa):**

Yield: 88%; Brown liquid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.29$ (s, 1H), 7.49 (d, $J = 3.5$ Hz, 1H), 7.16 (dd, $J = 4.9$, 3.0 Hz, 1H), 7.06 – 7.02 (m, 2H), 4.49 (s, 2H), 3.89 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta = 164.52$, 161.40, 141.28, 132.25, 128.65, 127.25, 124.56, 120.94, 116.18, 51.63, 51.07, 25.35; IR (neat): 3345, 3014, 1701, 1691, 1410, 1274, 950 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{13}$H$_{14}$NO$_4$S [M+H]$^+$ is 280.06381 and found 280.06353.

**Dimethyl 3-(pyridin-3-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3ta)**
**Yield:** 88%; White solid, **m.p.** 105 – 107 °C; ¹H NMR (400 MHz, CDCl₃) δ = 10.11 (bs, 1H), 8.50 (bs, 1H), 7.51 (bs, 2H), 7.05 (d, J = 13.7 Hz, 2H), 4.75 (s, 2H), 3.73(s, 3H), 3.69 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 164.52, 161.46, 160.97, 148.71, 136.23, 129.40, 127.57, 122.24, 121.86, 120.74, 118.82, 77.30, 77.05, 76.79, 51.52, 50.99, 33.46; IR (KBr) 3075, 2967, 1718, 1414, 1301, 1176 cm⁻¹; HRMS (ESI, Orbitrap) calcd for C₁₄H₁₅N₂O₄ [M+H] is 275.10263 and found 275.10301.

**Diethyl 3-(pyridin-2-ylmethyl)-1H-pyrrole-2,4-dicarboxylate (3tb):**

Yield: 89%; White solid, **m.p.** 134 – 136 °C; ¹H NMR (500 MHz, CDCl₃) δ = 9.78 (s, 1H), 8.50 (d, J = 4.3 Hz, 1H), 7.56 (s, 1H), 7.51 (dd, J = 10.8, 4.6 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.96 (d, J = 7.8 Hz, 1H), 4.76 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 1.18 (t, J = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ = 164.21, 161.09, 161.13, 148.69, 136.12, 128.94, 127.37, 121.97, 120.61, 117.06, 60.60, 59.78, 33.55, 14.21, 14.14; IR (KBr): 3052, 2985, 2701, 1713, 1566, 1415, 1299 cm⁻¹; HRMS (ESI, Orbitrap) calcd for C₁₆H₁₉N₂O₄ [M+H] is 303.13393 and found 303.13415.

**Dimethyl 3-((1-tosyl-1H-pyrrol-2-yl)methyl)-1H-pyrrole-2,4-dicarboxylate (3ua):**

Yield: 81%; Colourless oil; ¹H NMR (500 MHz, CDCl₃) δ = 9.44 (s, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 3.2 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.23 (s, 1H), 6.05 (t, J = 3.3 Hz, 1H), 5.37 – 5.32 (m, 1H), 4.55 (s, 2H), 3.67 (s, 3H), 3.60 (s, 3H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ = 164.18, 161.42, 156.36, 144.55, 136.73, 134.92, 129.92, 128.15, 127.26, 127.14, 121.82, 117.05, 111.57, 111.23, 51.63, 50.96, 23.90, 21.64; IR (KBr): 3301, 2936, 1705, 1354, 1289, 1171 cm⁻¹; HRMS (ESI, Orbitrap) calcd for C₂₀H₂₁N₂O₄S [M+H] is 417.11148 and found 417.11152.
**Diethyl 3-((1-tosyl-1H-pyrrol-2-yl)methyl)-1H-pyrrole-2,4-dicarboxylate (3ub):**

**Yield:** 82%; Colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 9.50 (s, 1H), 7.81 (d, $J$ = 8.3 Hz, 2H), 7.55 (d, $J$ = 3.4 Hz, 1H), 7.33 (d, $J$ = 8.2 Hz, 2H), 7.26 – 7.24 (m, 1H), 6.05 (t, $J$ = 3.3 Hz, 1H), 5.36 (dd, $J$ = 3.2, 1.6 Hz, 1H), 4.57 (s, 2H), 4.16 (q, $J$ = 7.1 Hz, 2H), 4.09 (q, $J$ = 7.1 Hz, 2H), 2.42 (s, 3H), 1.11 (q, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 163.96, 161.11, 144.57, 136.69, 135.07, 129.92, 127.82, 127.14, 121.69, 117.49, 111.68, 111.21, 60.66, 59.77, 23.94, 21.61, 14.14; IR (KBr): 3298, 2928, 1700, 1367, 1277, 1175 1032 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{22}$H$_{25}$N$_2$O$_6$ [M+H] is 445.14278 and found 445.14301.

**diethyl 3-(3-(2-(methoxycarbonyl)-1H-pyrrol-3-yl)benzyl)-1H-pyrrole-2,4-dicarboxylate (3vb):**

**Yield:** 82%; colourless liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.50 (s, 1H), 9.28 (s, 1H), 7.52 (d, $J$ = 3.4 Hz, 1H), 7.41 (s, 1H), 7.37 – 7.31 (m, 1H), 7.25 – 7.19 (m, 2H), 6.91 (t, $J$ = 2.8 Hz, 1H), 6.28 (t, $J$ = 2.7 Hz, 1H), 4.57 (s, 2H), 4.32 (q, $J$ = 7.1 Hz, 2H), 4.24 (q, $J$ = 7.1 Hz, 2H), 3.69 (s, 3H), 1.30 (t, $J$ = 6.9 Hz, 3H), 1.27 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 164.33, 161.85, 161.39, 140.64, 134.73, 132.46, 131.70, 129.67, 127.35, 126.84, 121.86, 121.30, 117.81, 116.98, 112.67, 60.73, 59.83, 51.21, 30.33, 14.36; IR (KBr): 3319, 2928, 1692, 1441, 1276, 1143, 1029 cm$^{-1}$; HRMS (ESI, Orbitrap) calcd for C$_{23}$H$_{25}$N$_2$O$_6$ [M+H] is 425.17071 and found 425.17099.

8. **Soft copy of $^1$H and $^{13}$C NMR of compounds (3aa-3vb):**
\begin{align*}
\text{\textsuperscript{1}H NMR, 400 MHz,} & \quad \text{CDCl}_3, \text{ 3ea} \\
\text{\textsuperscript{13}C NMR, CDCl}_3, & \quad 125 \text{ MHz, 3ea}
\end{align*}
$^1$H NMR, 500 MHz, CDCl$_3$, 3ha

$^{13}$C NMR, CDCl$_3$, 125 MHz, 3ha
$^1$H NMR, 500 MHz, CDCl$_3$, 3ib

$^{13}$C NMR, CDCl$_3$, 100 MHz, 3ib
$^1$H NMR, 400 MHz, CDCl$_3$, 3ja

$^{13}$C NMR, CDCl$_3$, 125 MHz, 3ja
$^1$H NMR, CDCl$_3$, 400 MHz, 3ka

$^{13}$C NMR, CDCl$_3$, 125 MHz, 3ka
$^{1}H$ NMR, CDCl$_3$, 400 MHz, 3kb

$^{13}C$ NMR, CDCl$_3$, 100 MHz, 3kb
9. X-ray Data of Sample code BA-88 Compound No (3pa)

X-ray data were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program. The structures were solved by Direct Methods using SHELXS and refinement was carried out by full-matrix least-squares technique using SHELXL. Anisotropic displacement parameters were included for all non-hydrogen atoms. The hydrogen atom attached to nitrogen atom was located in a difference density map and refined isotropically. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for BA88: C_{19}H_{17}NO_{4} (M =323.33): triclinic, space group P-1 (no. 2), a = 8.9379(13) Å, b = 10.7203(16) Å, c = 11.0337(16) Å, α = 118.687(2)°, β = 110.073(2)°, γ = 93.964(2)°, V = 835.3(2) Å³, Z = 2, T = 294.15 K, μ(MoKα) = 0.091 mm⁻¹, D_{calc} = 1.286 g/mm³, 9679 reflections measured (4.414 ≤ 2Θ ≤ 56.942), 3904 unique (R_{int} = 0.0210) which were used in all calculations. The final R₁ was 0.0580 (I > 2σ(I)) and wR₂ was 0.2191 (all data). CCDC 1442529 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or
from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk.

10. References:

