

Supporting Information

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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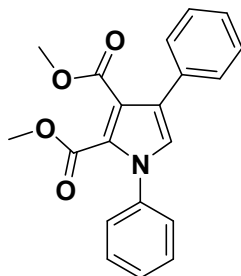
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General procedure for the synthesis of fully substituted pyrrole functionalities

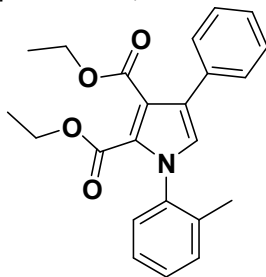
To a mixture of amines (1 mmol), aldehydes (1 mmol), dialkyl acetylenedicarboxylates (1 mmol) and nitromethane (1 ml) was added 10 mol % $\text{CAN}\cdot\text{SiO}_2$ and the reaction mixture was kept for refluxing in a heated oil-bath with constant stirring. After completion of the reaction as monitored 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.

Spectral data of the compounds



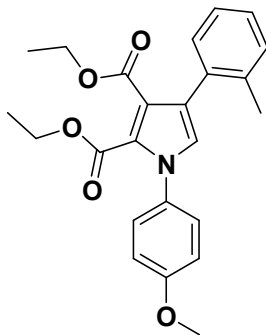
1. Dimethyl 4-(phenyl)-1-phenyl-1H-pyrrole-2,3-dicarboxylate

Brown sticky liquid; ^1H 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 $\text{C}_{20}\text{H}_{17}\text{NO}_4$ [M^+] 335.1158, found 335.1153.



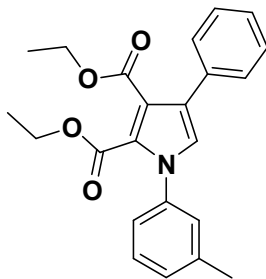
2. Diethyl 1-(2-methylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H 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, $J=12\text{Hz}$, 3H), 1.09 (t, $J=12\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 166.47, 159.52, 139.11, 135.46, 133.31, 130.42, 128.91, 128.52, 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 $\text{C}_{21}\text{H}_{19}\text{NO}_4$ [M^+] 349.1314, found 349.1315.



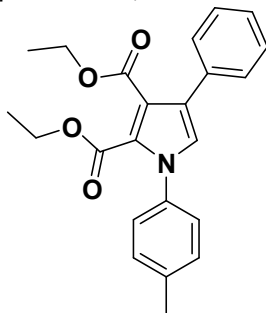
3. Diethyl 1-(4-methoxyphenyl)-4-(2-methylphenyl)-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.27-7.22 (m, 5H), 7.09 (d, $J=4\text{Hz}$, 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, $J=12\text{Hz}$, 3H), 1.17 (d, $J=12\text{Hz}$, 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 $\text{C}_{24}\text{H}_{25}\text{NO}_5$ [M^+] 407.1733, found 407.1736.



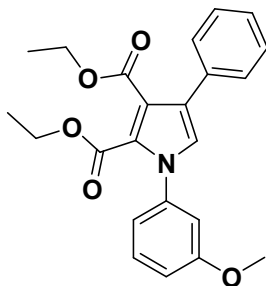
4. Diethyl 1-(3-methylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.44 (d, $J=8\text{Hz}$, 2H), 7.29 (t, $J=8\text{Hz}$, 2H), 7.22 (t, $J=12\text{Hz}$, 2H), 7.15 (d, $J=8\text{Hz}$, 1H), 7.09 (t, $J=12\text{Hz}$, 2H), 6.90 (s, 1H), 4.29-4.26 (m, 2H), 4.14-4.11 (m, 2H), 2.32 (s, 3H), 1.24 (t, $J=12\text{Hz}$, 3H), 1.11 (t, $J=12\text{Hz}$, 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 $\text{C}_{23}\text{H}_{23}\text{NO}_4$ [M^+] 377.1627, found 377.1629.



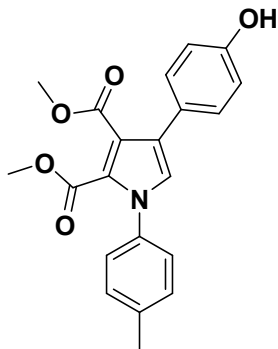
5. Diethyl 1-(4-methylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.43 (t, $J=12\text{Hz}$, 2H), 7.28-7.19 (m, 3H), 7.12 (t, $J=8\text{Hz}$, 4H), 6.87 (s, 1H), 4.2-4.25 (m, 2H), 4.13-4.10 (m, 2H), 2.29 (s, 3H), 1.23 (t, $J=12\text{Hz}$, 3H), 1.11 (t, $J=12\text{Hz}$, 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 $\text{C}_{23}\text{H}_{23}\text{NO}_4$ [M^+] 377.1627, found 377.1629.



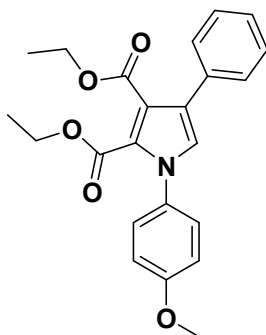
6. Diethyl 1-(3-methoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H 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, $J=12\text{Hz}$, 1H), 4.33-4.28 (m, 2H), 4.20-4.14 (m, 2H), 3.80 (s, 3H), 1.27 (t, $J=12\text{Hz}$, 3H), 1.16 (t, $J=12\text{Hz}$, 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 $\text{C}_{23}\text{H}_{23}\text{NO}_5$ [M^+] 393.4324, found 393.4321.



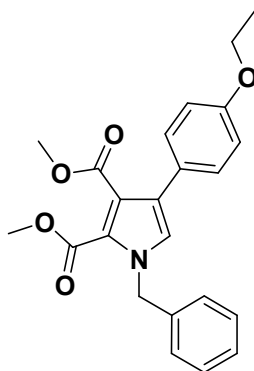
7. Dimethyl 1-(4-methylphenyl)-4-(4-hydroxyphenyl)-1H-pyrrole-2, 3-dicarboxylate

Brown sticky liquid; ^1H 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, $J=8\text{Hz}$, 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 $\text{C}_{21}\text{H}_{19}\text{NO}_5$ [M^+] 365.1263, found 365.1264.



8. Diethyl 1-(4-methoxyphenyl)-4-phenyl-1H-pyrrole-2, 3-dicarboxylate

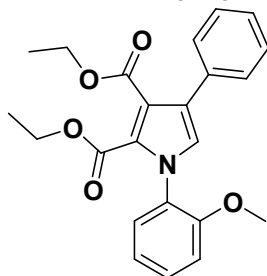
Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.46-7.43 (m, 2H), 7.35 (t, $J=12\text{Hz}$, 2H), 7.29-7.24 (m, 3H), 6.96-6.92 (m, 3H), 4.34-4.28 (m, 2H), 4.19-4.14 (m, 2H), 3.83 (s, 3H), 1.28 (t, $J=12\text{Hz}$, 3H), 1.17 (t, $J=12\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 166.31, 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 $\text{C}_{23}\text{H}_{23}\text{NO}_5$ [M^+] 393.4324, found 393.4321.



9. Dimethyl 1-(benzyl)-4-(4-ethoxyphenyl)-1H-pyrrole-2, 3-dicarboxylate

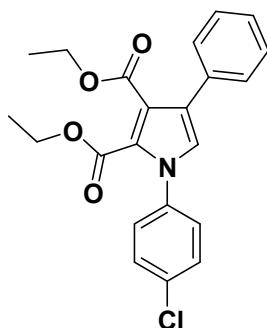
Brown sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.30-7.22 (m, 5H), 7.14 (d, $J=8\text{Hz}$, 2H), 6.85 (d, $J=12\text{Hz}$, 2H), 6.83 (s, 1H), 5.46 (s, 2H), 4.01-3.96 (m, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 1.37 (t, $J=12\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 167.35, 160.64, 158.12,

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.



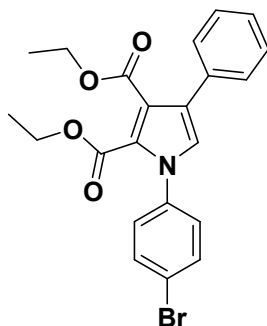
10. Diethyl 1-(2-methoxyphenyl)- 4-phenyl -1*H*-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; 1H 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, 121.51, 120.33, 111.56, 61.10, 60.34, 55.48, 14.00, 13.83; HRMS m/z calcd for $C_{23}H_{23}NO_5$ [M^+] 393.4324, found 393.4321.



11. Diethyl 1-(4-chlorophenyl)- 4-phenyl -1*H*-pyrrole-2, 3-dicarboxylate

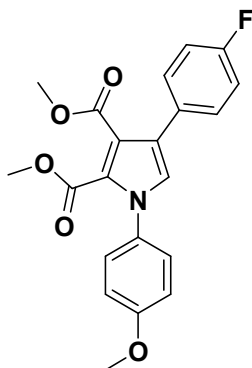
Yellow sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45-7.40 (m, 4H), 7.35 (t, $J=12Hz$, 2H), 7.29-7.24 (m, 3H), 6.95 (s, 1H), 4.34-4.28 (m, 2H), 4.20-4.14 (m, 2H), 1.28 (t, $J=12Hz$, 3H), 1.18 (t, $J=12Hz$, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.11, 159.67, 138.07, 134.37, 132.97, 129.02, 128.54, 127.66, 127.61, 127.19, 125.70, 125.70, 124.94, 122.99, 122.66, 61.38, 60.91, 14.03, 13.91; HRMS m/z calcd for $C_{22}H_{20}ClNO_4$ [M^+] 397.8515, found 397.8519.



12. Diethyl 1-(4-bromophenyl)- 4-phenyl -1*H*-pyrrole-2, 3-dicarboxylate

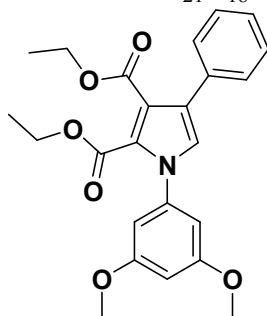
Yellow sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (d, $J=8Hz$, 2H), 7.41(d, $J=8Hz$, 2H), 7.29 (t, $J=12Hz$, 2H), 7.22 (d, $J=8Hz$, 1H), 7.13 (d, $J=12Hz$, 2H), 6.90 (s, 1H), 4.29-4.26 (m, 2H), 4.14-4.10 (m, 2H), 1.25 (t, $J=12Hz$, 3H), 1.14 (t, $J=12Hz$, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 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.



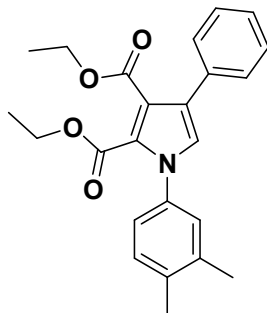
13. Dimethyl 1-(4-methoxyphenyl)-4-(4-fluorophenyl)-1H-pyrrole-2,3-dicarboxylate

Brown sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, $J=8$ Hz, 1H), 7.46-7.61 (m, 2H), 7.47-7.44 (m, 1H), 7.36 (d, $J=4$ Hz, 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 383.1667.



14. Diethyl 1-(3,5-dimethoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

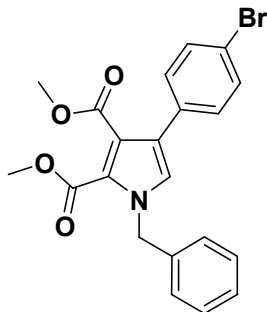
Yellow sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, $J=8$ Hz, 2H), 7.33 (t, $J=12$ Hz, 2H), 7.28-7.23 (m, 1H), 6.97 (s, 1H), 6.50 (s, 3H), 4.32-4.27 (m, 2H), 4.21-4.16 (m, 2H), 3.75 (s, 6H), 1.26 (t, $J=12$ Hz, 3H), 1.18 (t, $J=12$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 165.94, 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.



15. Diethyl 1-(3,4-dimethylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

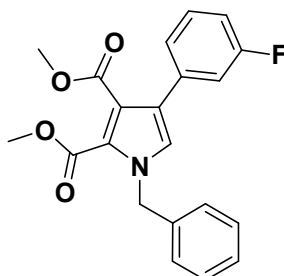
Yellow sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, $J=8$ Hz, 2H), 7.28 (t, $J=12$ Hz, 2H), 7.21-7.17 (m, 1H), 7.10-7.05 (m, 2H), 7.00 (d, $J=8$ Hz, 1H), 6.89 (s, 1H), 4.28-4.26 (m, 2H), 4.16-4.11 (m, 2H), 2.21 (s, 6H), 1.23 (t, $J=12$ Hz, 3H), 1.15 (t, $J=12$ Hz, 3H); ^{13}C NMR ($CDCl_3$,

100 MHz) δ (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 calcd for $C_{24}H_{25}NO_4$ [M^+] 391.4596, found 391.4595.



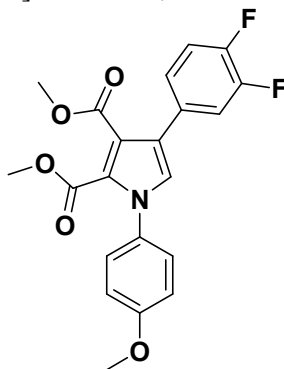
16. Dimethyl 1-(benzyl) - 4-(4-bromophenyl) -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40-7.37 (m, 2H), 7.27-7.19 (m, 5H), 7.11 (d, $J=8$ 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) δ (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 calcd for $C_{21}H_{18}BrNO_4$ [M^+] 427.0419, found 428.0416.



17. Dimethyl 1-(benzyl) - 4-(3-fluorophenyl) -1H-pyrrole-2, 3-dicarboxylate

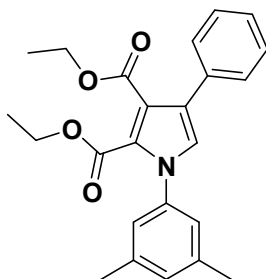
Brown sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32-7.22 (m, 5H), 7.16-7.12 (m, 3H), 7.09-7.06 (m, 1H), 6.93 (s, 1H), 5.47 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 166.96, 164.11, 161.67, 160.53, 136.82, 135.51, 130.12, 130.04, 128.82, 127.93, 127.22, 125.77, 122.99, 122.76, 122.13, 121.46, 114.29, 114.07, 113.84, 113.63, 52.43, 51.84; HRMS m/z calcd for $C_{21}H_{18}FNO_4$ [M^+] 367.3703, found 367.3705.



18. Dimethyl 1-(4-methoxyphenyl)- 4-(3, 4-difluorophenyl) -1H-pyrrole-2, 3-dicarboxylate

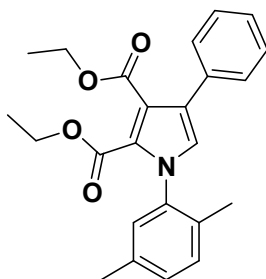
Brown sticky liquid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, $J=8$ Hz, 1H), 7.56-7.47 (m, 3H), 7.37-7.32 (m, 2H), 7.27-7.21 (m, 2H), 4.03 (s, 3H), 3.95 (s, 3H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 167.99, 166.47, 159.52, 151.47, 144.69, 137.10, 131.45, 124.89, 124.69, 123.69, 117.96, 117.76, 117.36, 117.19, 102.69, 55.72, 53.22, 52.90; HRMS m/z calcd

for C₂₁H₁₇F₂NO₅ [M⁺] 401.3601, found 401.3603.



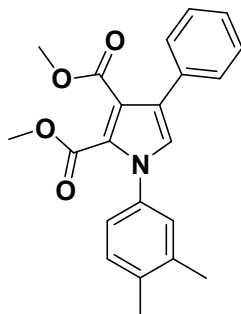
19. Diethyl 1-(3, 5-dimethylphenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43 (d, *J*=8Hz, 2H), 7.27 (t, *J*=12Hz, 2H), 7.18 (t, *J*=12Hz, 1H), 6.97 (s, 1H), 6.85 (d, *J*=8Hz, 3H), 4.28-4.23 (m, 2H), 4.15-4.10 (m, 2H), 2.26 (s, 6H), 1.22 (t, *J*=12Hz, 3H), 1.17 (t, *J*=12Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ (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* calcd for C₂₄H₂₅NO₄ [M⁺] 391.4596, found 391.4597.



20. Diethyl 1-(2, 5-dimethylphenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate

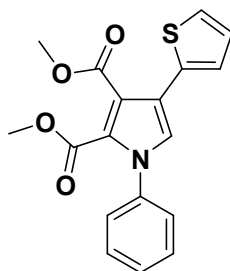
Yellow sticky liquid; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.44 (d, *J*=8Hz, 2H), 7.27 (t, *J*=12Hz, 2H), 7.17 (t, *J*=12Hz, 1H), 7.08 (s, 2H), 6.96 (s, 1H), 6.77 (s, 1H), 4.30-4.25 (m, 2H), 4.08-4.03 (m, 2H), 2.26 (s, 3H), 2.00 (s, 3H), 1.23 (t, *J*=12Hz, 3H), 1.04 (t, *J*=12Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ (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 C₂₄H₂₅NO₄ [M⁺] 391.1718, found 391.1786.



21. Dimethyl 1-(3, 4-dimethylphenyl)- 4-phenyl -1H-pyrrole-2, 3-dicarboxylate

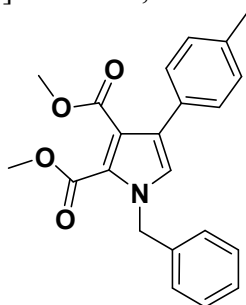
Brown sticky liquid; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.41 (d, *J*=8Hz, 2H), 7.29 (t, *J*=8Hz, 2H), 7.22-7.19 (m, 1H), 7.11 (d, *J*=8Hz, 1H), 7.06 (s, 1H), 7.00 (d, *J*=8Hz, 1H), 6.90 (s, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 2.23 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm) 166.54, 160.45, 137.29, 137.06, 136.96, 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 C₂₄H₂₅NO₄ [M⁺] 391.4596,

found 391.4598.



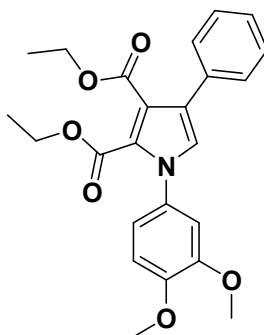
22. Dimethyl 1-(phenyl)- 4-(thiophene) -1H-pyrrole-2, 3-dicarboxylate

Brown sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (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) δ (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 $\text{C}_{18}\text{H}_{15}\text{NO}_4\text{S}$ [M^+] 341.3810, found 341.3812.



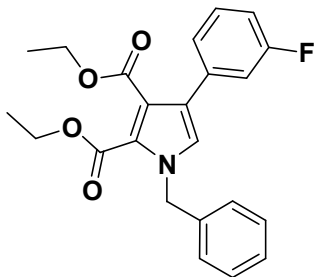
23. Dimethyl 1-(benzyl)- 4-(4-methylphenyl) -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (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) δ (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 $\text{C}_{22}\text{H}_{21}\text{NO}_4$ [M^+] 363.4064, found 363.4066.



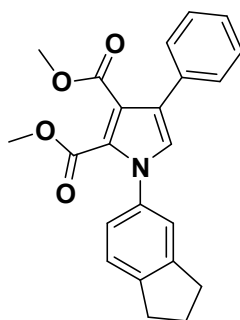
24. Diethyl 1-(3, 4-dimethoxyphenyl) - 4-phenyl -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.45 (d, $J=8\text{Hz}$, 2H), 7.34 (t, $J=12\text{Hz}$, 2H), 7.27 (t, $J=8\text{Hz}$, 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, $J=12\text{Hz}$, 3H), 1.18 (t, $J=12\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{22}\text{H}_{21}\text{NO}_6$ [M^+] 395.4052, found 395.4055.



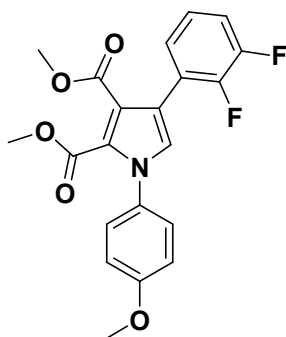
25. Diethyl 1-(benzyl)-4-(3-fluorophenyl)-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (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); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{23}\text{H}_{22}\text{FNO}_4$ [M^+] 395.4235, found 395.4237.



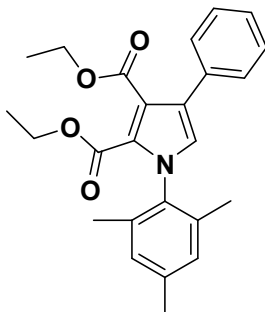
26. Dimethyl 1-(5-indane)-4-phenyl-1H-pyrrole-2,3-dicarboxylate

Brown sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.41 (d, $J=8\text{Hz}$, 2H), 7.29 (t, $J=12\text{Hz}$, 2H), 7.22-7.16 (m, 2H), 7.11 (s, 1H), 7.01 (d, $J=8\text{Hz}$, 1H), 6.91 (s, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 2.87 (t, $J=12\text{Hz}$, 4H), 2.08-2.03 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{23}\text{H}_{21}\text{NO}_4$ [M^+] 375.4171, found 375.4173.



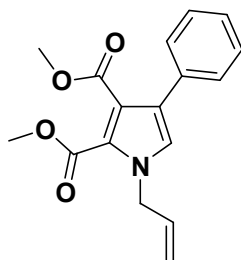
27. Dimethyl 1-(4-methoxyphenyl)-4-(2,3-difluorophenyl)-1H-pyrrole-2,3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.07 (d, $J=8\text{Hz}$, 1H), 7.50-7.47 (m, 1H), 7.40 (t, $J=12\text{Hz}$, 1H), 7.28-7.16 (m, 5H), 4.04 (s, 3H), 3.94 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{21}\text{H}_{17}\text{F}_2\text{NO}_5$ [M^+] 401.3602, found 401.3605.



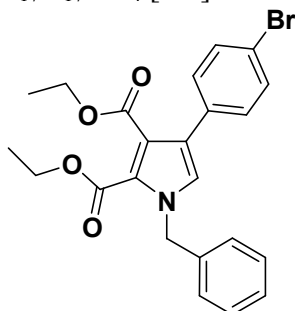
28. Diethyl 1-(2, 4, 6-trimethylphenyl) – 4-phenyl-1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.45 (d, $J=8\text{Hz}$, 2H), 7.33 (t, $J=12\text{Hz}$, 2H), 7.25 (d, $J=8\text{Hz}$, 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, $J=12\text{Hz}$, 3H), 1.10 (t, $J=12\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{25}\text{H}_{27}\text{NO}_4$ [M^+] 405.4862, found 405.4865.



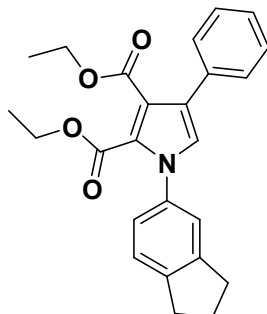
30. Dimethyl 1-allyl-4-phenyl-1H-pyrrole-2, 3-dicarboxylate

Brown sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.43 (d, $J=8\text{Hz}$, 2H), 7.25 (t, $J=12\text{Hz}$, 2H), 7.20 (d, $J=8\text{Hz}$, 1H), 6.91 (s, 1H), 6.02 (m, 1H), 5.22 (d, $J=10\text{Hz}$, 1H), 5.13 (d, $J=16\text{Hz}$, 1H), 5.01 (d, (d, $J=5\text{Hz}$, 2H), 3.82 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{17}\text{H}_{17}\text{NO}_4$ [M^+] 299.3212, found 299.3215.



31. Diethyl 1-(benzyl) - 4-(4-bromophenyl) -1H-pyrrole-2, 3-dicarboxylate

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.50 (d, $J=8\text{Hz}$, 2H), 7.41 (d, $J=8\text{Hz}$, 1H), 7.34 (m, 4H), 7.15 (d, $J=4\text{Hz}$, 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) δ (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 $\text{C}_{23}\text{H}_{22}\text{BrNO}_4$ [M^+] 456.3291, found 456.3292.



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

Yellow sticky liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J=4\text{Hz}$, 2H), 7.28 (t, $J=12\text{Hz}$, 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, $J=12\text{Hz}$, 4H), 2.07-2.01 (m, 2H), 1.24 (t, $J=12\text{Hz}$, 3H), 1.13 (t, $J=12\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (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 $\text{C}_{25}\text{H}_{25}\text{NO}_4$ [M^+] 403.4703, found 403.4706.

^1H and ^{13}C NMR spectra of the compounds

