

Supporting Information

Synthesis of C3-alkenylated 2, 3, 4-trisubstituted pyrrole derivatives through cyclization of methylene isocyanides and Ene-yne-ketones

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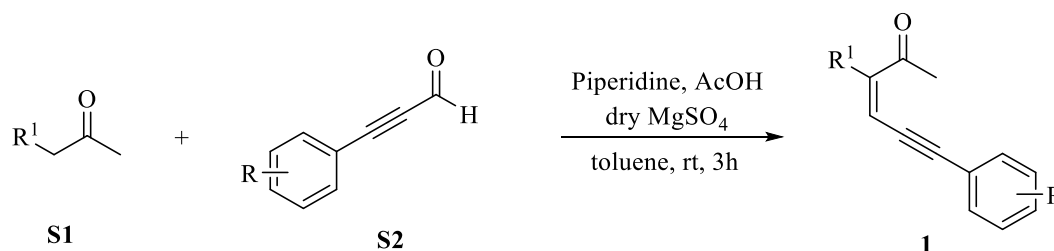
Table of contents

1. Experimental (General procedures and characterization data for target compounds)
2. X-ray crystallography data of compounds (*E*)-3n and (*Z*)-3n
3. ¹H and ¹³C NMR spectra for target products

1. Experimental

General. All reactions were carried out in test tube under air atmosphere. Chemicals were purchased from commercial suppliers and used without further purification. Purification of reaction products were carried out by chromatography using silica gel (200-300 mesh). High resolution MS data were recorded on a Agilent 6200 Series TOF spectrometer. NMR spectra were recorded on AVIII for ^1H NMR at 400 MHz and for ^{13}C NMR at 100 MHz. For ^1H NMR, tetramethylsilane (TMS) was served as internal standard (δ). The spectra data presented here are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hertz. For ^{13}C NMR TMS was used as internal standard and spectra were obtained with complete proton decoupling. The starting materials ene-yne-ketones (**1**) were prepared according to literature with modification (*Chem. Commun.*, **2017**, 53, 640-643).

General procedure for the synthesis of ene-yne-ketones (**1**)

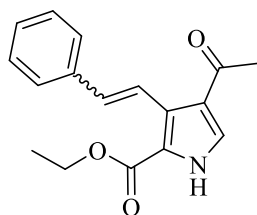


To a round bottom flask, a mixture of **S1** (10 mmol), AcOH (0.1 equiv), piperidine (0.1 equiv) in 40 mL of toluene was added propionaldehyde **S2** (1.1 equiv) and dry MgSO_4 (1.2 equiv). The reaction was carried out at room temperature for 3h. After completion of the reaction, the mixture was dried under reduced pressure to give the crude product. The ene-yne-ketone was purified by chromatography on silica gel in 70-95% yields.

General procedure for the preparation of target compounds **3**

A mixture of corresponding ene-yne-ketone (0.5 mmol), methylene isocyanide (0.75 mmol, 1.5 equiv) and DBU (0.75 mmol, 1.5 equiv) was stirred in DCM (2 mL) at room temperature for 1 h. The reaction was monitored with TLC. After completion, the solvent was removed in vacuo, and purification of the crude product by chromatography with silica gel afforded target compounds **3**.

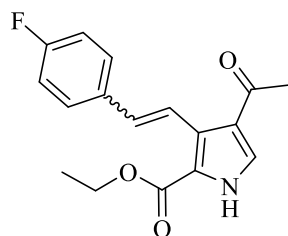
Characterization data for target compounds 3



ethyl 4-acetyl-3-styryl-1H-pyrrole-2-carboxylate (**3a**)

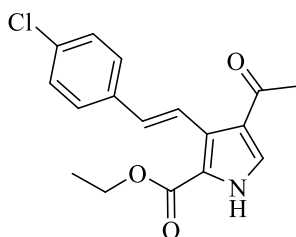
(*E*)-isomer: White solid; 34%; ^1H NMR (400 MHz, CDCl_3): δ 9.39 (1H, s), 7.78 (1H, d, $J = 20.0$ Hz), 7.56-7.45 (4H, m), 7.35 (2H, t, $J = 8.0$ Hz), 7.25-7.23 (1H, m), 4.38 (2H, q, $J = 8.0$ Hz), 2.48 (3H, s), 1.26 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.95, 161.10, 137.88, 135.64, 128.68, 128.57, 127.63, 126.76, 125.38, 121.14, 119.47, 61.02, 28.89, 14.41; HRMS calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 284.3350, found 284.3348.

(*Z*)-isomer: Colorless oil; 34%; ^1H NMR (400 MHz, CDCl_3): δ 9.71 (1H, s), 7.54 (1H, d, $J = 4.0$ Hz), 7.14-7.07 (5H, m), 6.72 (2H, q, $J = 16.0$ Hz), 4.14 (2H, q, $J = 8.0$ Hz), 2.32 (3H, s), 1.19 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 194.01, 161.17, 137.35, 132.71, 128.35, 128.07, 127.12, 126.92, 126.42, 126.15, 122.06, 120.69, 60.87, 28.53, 14.12; HRMS calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 284.3350, found 284.3352.



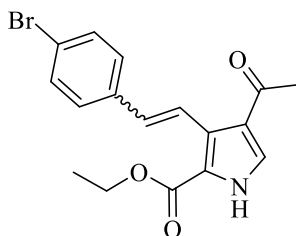
ethyl 4-acetyl-3-(4-fluorostyryl)-1H-pyrrole-2-carboxylate (**3b**)

White solid; 62%; ^1H NMR (400 MHz, CDCl_3): δ 9.68 (0.43H, s), 9.60 (1H, s), 7.70 (1H, d, $J = 16.0$ Hz), 7.53-7.46 (4.33H, m), 7.07-7.01 (2.81H, m), 6.82 (0.84H, t, $J = 8.0$ Hz), 6.68 (0.84H, q, $J = 12.0$ Hz), 4.37 (2H, q, $J = 8.0$ Hz), 4.16 (0.86H, q, $J = 8.0$ Hz), 2.47 (3H, s), 2.32 (1.26H, s), 1.38 (3H, t, $J = 8.0$ Hz), 1.20 (1.28H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.95, 193.79, 161.24, 161.07, 134.32, 134.13, 133.60, 131.43, 129.97, 129.89, 128.26, 127.95, 127.02, 126.04, 125.14, 121.87, 121.12, 120.70, 119.25, 115.60, 115.38, 115.07, 114.86, 61.03, 60.89, 28.82, 28.43, 14.40, 14.14; HRMS calcd. for $\text{C}_{17}\text{H}_{16}\text{FNO}_3$ $[\text{M}+\text{H}]^+$ 302.3254, found 302.3262.



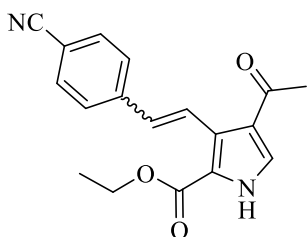
ethyl 4-acetyl-3-(4-chlorostyryl)-1H-pyrrole-2-carboxylate (**3c**)

White solid; 69%; ^1H NMR (400 MHz, CDCl_3): δ 9.55 (1H, s), 7.77 (1H, d, $J = 16.0$ Hz), 7.51-7.46 (4H, m), 7.30 (2H, d, $J = 8.0$ Hz), 4.39 (2H, q, $J = 8.0$ Hz), 2.47 (3H, s), 1.38 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.88, 160.98, 136.49, 134.17, 133.22, 128.73, 128.43, 127.92, 127.90, 125.16, 121.26, 120.09, 61.07, 28.81, 14.40; HRMS calcd. for $\text{C}_{17}\text{H}_{16}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$ 318.7770, found 318.7764.



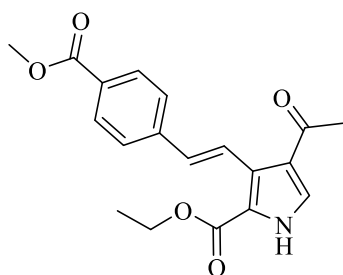
ethyl 4-acetyl-3-(4-bromostyryl)-1H-pyrrole-2-carboxylate (**3d**)

White solid; 53%; ^1H NMR (400 MHz, CDCl_3): δ 9.43 (1.39H, s), 7.79 (1H, d, $J = 16.0$ Hz), 7.54-7.40 (6.39H, m), 7.26-7.24 (0.84H, m), 6.95 (0.86H, t, $J = 8.0$ Hz), 6.77 (0.45H, d, $J = 12.0$ Hz), 6.63 (0.45H, d, $J = 12.0$ Hz), 4.38 (2H, q, $J = 8.0$ Hz), 4.16 (0.85H, q, $J = 8.0$ Hz), 2.48 (3H, s), 2.33 (1.26H, s), 1.38 (3H, t, $J = 8.0$ Hz), 1.20 (1.30H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.80, 193.52, 160.93, 160.75, 136.93, 136.41, 134.25, 131.67, 131.43, 131.18, 129.87, 128.39, 128.24, 127.81, 126.87, 126.04, 125.94, 125.22, 122.87, 121.41, 121.27, 120.89, 120.70, 120.17, 61.08, 60.92, 28.83, 28.41, 14.41, 14.18; HRMS calcd. for $\text{C}_{17}\text{H}_{16}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$ 363.2310, found 363.2319.



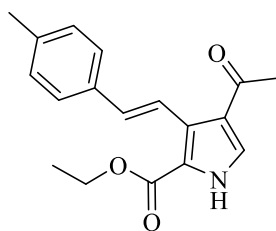
ethyl 4-acetyl-3-(4-cyanostyryl)-1H-pyrrole-2-carboxylate (**3e**)

White solid; 48%; ^1H NMR (400 MHz, CDCl_3): δ 9.61 (2.1H, s), 7.95 (1H, d, $J = 16.0$ Hz), 7.64-7.60 (5H, m), 7.55-7.53 (2.11H, m), 7.42 (2.20H, d, $J = 8.0$ Hz), 7.18 (2.20H, d, $J = 8.0$ Hz), 6.92 (1.10H, d, $J = 12.0$ Hz), 6.69 (1.10H, d, $J = 12.0$ Hz), 4.39 (2H, q, $J = 8.0$ Hz), 4.14 (2.28H, q, $J = 8.0$ Hz), 2.49 (3H, s), 2.34 (3.33H, s), 1.39 (3H, t, $J = 8.0$ Hz), 1.19 (3.42H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.70, 193.16, 160.68, 160.49, 142.69, 142.39, 133.36, 132.39, 131.80, 130.72, 128.76, 128.07, 127.71, 127.16, 127.11, 125.80, 125.63, 125.34, 125.17, 123.23, 121.75, 120.78, 119.20, 118.97, 110.47, 110.14, 61.20, 60.99, 28.78, 28.23, 14.41, 14.15; HRMS calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 309.3450, found 309.3455.



ethyl 4-acetyl-3-(4-(methoxycarbonyl)styryl)-1H-pyrrole-2-carboxylate (**3f**)

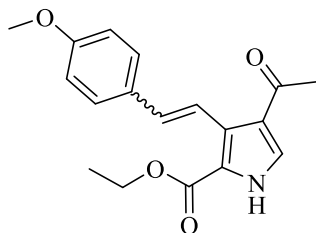
White solid; 72%; ^1H NMR (400 MHz, CDCl_3): δ 9.57 (1H, s), 8.01 (2H, d, $J = 8.0$ Hz), 7.91 (1H, d, $J = 16.0$ Hz), 7.61-7.56 (3H, m), 7.51 (1H, d, $J = 4.0$ Hz), 4.38 (2H, q, $J = 8.0$ Hz), 3.92 (3H, s), 2.48 (3H, s), 1.38 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.80, 167.07, 160.91, 142.58, 134.29, 129.93, 128.89, 128.10, 127.96, 126.55, 125.24, 122.10, 121.57, 61.14, 52.04, 28.80, 14.38; HRMS calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_5$ $[\text{M}+\text{H}]^+$ 342.3710, found 342.3716.



ethyl 4-acetyl-3-(4-methylstyryl)-1H-pyrrole-2-carboxylate (**3g**)

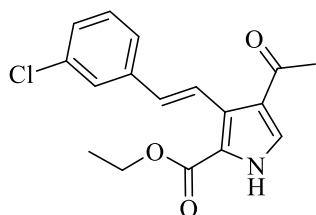
White solid; 59%; ^1H NMR (400 MHz, CDCl_3): δ 9.42 (1H, s), 7.73 (1H, d, $J = 16.0$ Hz), 7.48-7.43 (4H, m), 7.15 (2H, d, $J = 8.0$ Hz), 4.37 (2H, q, $J = 8.0$ Hz), 2.47 (3H, s), 2.35 (3H, s), 1.38 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 194.05, 161.18, 137.59, 135.62, 135.08, 129.31, 128.92, 127.71, 126.69, 125.31, 120.99, 118.48, 60.99, 28.91, 21.29, 14.42; HRMS calcd.

for $C_{18}H_{19}NO_3$ $[M+H]^+$ 298.3620, found 298.3615.



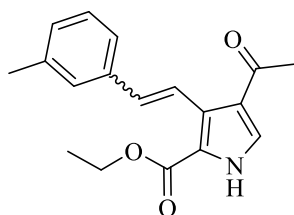
ethyl 4-acetyl-3-(4-methoxystyryl)-1H-pyrrole-2-carboxylate (**3h**)

White solid; 65%; 1H NMR (400 MHz, $CDCl_3$): δ 9.32 (1H, s), 7.66 (1H, d, $J = 16.0$ Hz), 7.51-7.43 (4H, m), 6.89 (2H, d, $J = 8.0$ Hz), 4.38 (2H, q, $J = 8.0$ Hz), 3.83 (3H, s), 2.48 (3H, s), 1.39 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.00, 161.11, 159.42, 135.28, 130.70, 129.14, 128.01, 127.64, 125.25, 120.82, 117.30, 114.03, 60.95, 55.31, 28.91, 14.43; HRMS calcd. for $C_{18}H_{19}NO_4$ $[M+H]^+$ 314.3610, found 314.3617.



ethyl 4-acetyl-3-(3-chlorostyryl)-1H-pyrrole-2-carboxylate (**3i**)

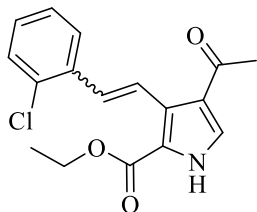
White solid; 54%; 1H NMR (400 MHz, $CDCl_3$): δ 9.53 (1H, s), 7.79 (1H, d, $J = 16.0$ Hz), 7.53-7.40 (4H, m), 7.27-7.20 (2H, m), 4.38 (2H, q, $J = 8.0$ Hz), 2.48 (3H, s), 1.39 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.88, 160.99, 139.89, 134.55, 134.01, 129.78, 128.17, 127.97, 127.52, 126.56, 125.20, 124.94, 121.43, 120.90, 61.15, 28.84, 14.41; HRMS calcd. for $C_{17}H_{16}ClNO_3$ $[M+H]^+$ 318.7770, found 318.7774.



ethyl 4-acetyl-3-(3-methylstyryl)-1H-pyrrole-2-carboxylate (**3j**)

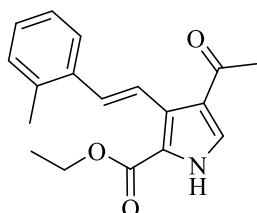
White solid; 67%; 1H NMR (400 MHz, $CDCl_3$): δ 9.55 (1H, s), 7.76 (1H, d, $J = 16.0$ Hz),

7.49-7.42 (2H, m), 7.37-7.34 (2H, m), 7.25-7.21 (1H, m), 7.07 (1H, d, $J=8.0$ Hz), 4.37 (2H, q, $J=8.0$ Hz), 2.47 (3H, s), 2.36 (3H, s), 1.39 (3H, t, $J=8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 194.08, 161.18, 138.08, 137.80, 135.76, 128.83, 128.52, 128.46, 127.83, 127.44, 125.29, 123.95, 121.09, 119.28, 61.01, 28.89, 21.43, 14.41; HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 298.3620, found 298.3627.



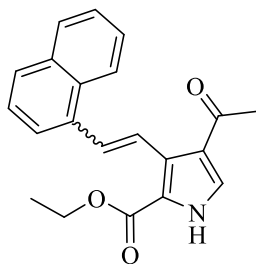
ethyl 4-acetyl-3-(2-chlorostyryl)-1H-pyrrole-2-carboxylate (**3k**)

White solid; 47%; ^1H NMR (400 MHz, CDCl_3): δ 9.53 (1H, s), 7.89-7.75 (3H, m), 7.56-7.47 (1H, m), 7.38-7.33 (1H, m), 7.20-7.16 (2H, m), 4.39 (2H, q, $J=8.0$ Hz), 2.49 (3H, s), 1.37 (3H, t, $J=8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.97, 161.13, 135.96, 133.56, 131.48, 129.71, 128.56, 128.19, 127.69, 126.89, 126.77, 125.44, 122.08, 121.37, 61.18, 28.83, 14.39; HRMS calcd. for $\text{C}_{17}\text{H}_{16}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$ 318.7770, found 318.7776.



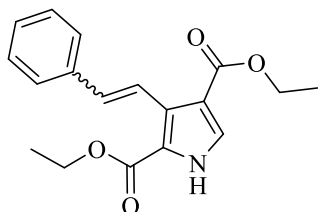
ethyl 4-acetyl-3-(2-methylstyryl)-1H-pyrrole-2-carboxylate (**3l**)

White solid; 56%; ^1H NMR (400 MHz, CDCl_3): δ 9.38 (1H, s), 7.83 (1H, d, $J=16.0$ Hz), 7.69-7.65 (2H, m), 7.56-7.51 (1H, m), 7.25-7.17 (3H, m), 4.40 (2H, q, $J=8.0$ Hz), 2.49 (3H, s), 2.46 (3H, s), 1.38 (3H, t, $J=8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.85, 161.02, 136.95, 136.28, 133.66, 130.29, 129.11, 127.82, 127.55, 126.09, 125.52, 125.33, 121.25, 120.41, 61.01, 28.98, 19.98, 14.46; HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 298.3620, found 298.3624.



ethyl 4-acetyl-3-(2-(naphthalen-1-yl)vinyl)-1H-pyrrole-2-carboxylate (**3m**)

Pale yellow oil; 45%; ^1H NMR (400 MHz, CDCl_3): δ 9.48 (1H, s), 9.33 (1H, s), 8.43 (1H, d, $J = 16.0$ Hz), 8.38 (1H, d, $J = 8.0$ Hz), 8.10 (1H, d, $J = 8.0$ Hz), 7.87-7.77 (5H, m), 7.63 (1H, d, $J = 8.0$ Hz), 7.53-7.44 (6H, m), 7.38 (1H, d, $J = 4.0$ Hz), 7.32 (1H, d, $J = 12.0$ Hz), 7.16 (1H, t, $J = 8.0$ Hz), 7.07 (2H, t, $J = 8.0$ Hz), 4.41 (2H, q, $J = 8.0$ Hz), 3.97 (2H, q, $J = 8.0$ Hz), 2.52 (3H, s), 2.20 (3H, s), 1.39 (3H, t, $J = 8.0$ Hz), 1.07 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 193.84, 161.06, 161.05, 135.70, 134.22, 133.74, 133.52, 132.84, 131.72, 131.59, 130.42, 129.07, 128.39, 128.06, 127.98, 127.41, 126.44, 126.41, 126.33, 126.16, 126.11, 125.74, 125.72, 125.60, 125.27, 125.01, 124.41, 124.28, 123.93, 123.56, 122.01, 121.42, 120.97, 61.09, 60.79, 28.95, 28.30, 14.46, 14.09; HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 314.3610, found 314.3617.

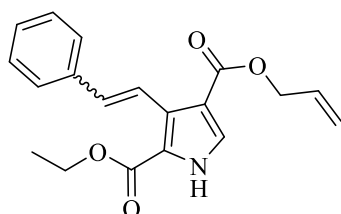


diethyl 3-styryl-1H-pyrrole-2,4-dicarboxylate (**3n**)

(*E*)-isomer: White solid; 42%; ^1H NMR (400 MHz, CDCl_3): δ 9.44 (1H, s), 7.79 (1H, d, $J = 16.0$ Hz), 7.61-7.54 (4H, m), 7.34 (2H, t, $J = 8.0$ Hz), 7.26-7.23 (1H, m), 4.38 (2H, q, $J = 8.0$ Hz), 4.30 (2H, q, $J = 8.0$ Hz), 1.41-1.34 (6H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 164.31, 161.02, 138.01, 135.27, 129.26, 128.55, 127.59, 126.69, 120.62, 119.05, 116.13, 60.94, 60.11, 14.44; HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 314.3610, found 314.3617.

(*Z*)-isomer: White solid; 42%; ^1H NMR (400 MHz, CDCl_3): δ 9.47 (1H, s), 7.54 (1H, d, $J = 4.0$ Hz), 7.15-7.09 (5H, m), 6.69 (2H, q, $J = 12.0$ Hz), 4.15-4.07 (4H, m), 1.22-1.16 (6H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 163.88, 161.03, 137.75, 132.27, 128.25, 127.90, 127.24, 127.10, 126.87, 121.33, 120.41, 117.08, 60.76, 59.95, 14.20, 14.11; HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$

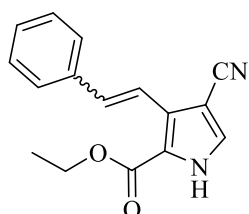
314.3610, found 314.3614.



4-allyl 2-ethyl 3-styryl-1H-pyrrole-2,4-dicarboxylate (**3o**)

(*E*)-isomer: White solid; 34%; ^1H NMR (400 MHz, CDCl_3): δ 9.42 (1H, s), 9.78 (1H, d, $J = 16.0$ Hz), 7.62-7.54 (4H, m), 7.34 (2H, t, $J = 8.0$ Hz), 7.26-7.22 (1H, m), 6.07-5.97 (1H, m), 5.38 (1H, dd, $J = 16.0, 4.0$ Hz), 5.25 (1H, dd, $J = 12.0, 4.0$ Hz), 4.76 (2H, d, $J = 4.0$ Hz), 4.38 (2H, q, $J = 8.0$ Hz), 1.39 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 163.82, 160.98, 138.01, 135.41, 132.58, 129.42, 128.54, 128.04, 127.61, 126.74, 120.72, 118.07, 115.77, 64.79, 60.96, 14.43; HRMS calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 326.3720, found 326.3725.

(*Z*)-isomer: White solid; 34%; ^1H NMR (400 MHz, CDCl_3): δ 9.32 (1H, s), 7.56 (1H, d, $J = 4.0$ Hz), 7.12-7.07 (5H, m), 6.69 (2H, q, $J = 12.0$ Hz), 5.90-5.82 (1H, m), 5.28 (1H, dq, $J = 20.0, 4.0$ Hz), 5.18 (1H, dq, $J = 12.0, 4.0$ Hz), 4.55 (2H, dt, $J = 4.0, 1.0$ Hz), 4.12 (2H, q, $J = 8.0$ Hz), 1.18 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 163.42, 160.88, 137.71, 132.50, 132.47, 128.26, 127.90, 127.28, 127.13, 126.90, 121.20, 120.54, 117.69, 116.80, 64.65, 60.76, 14.11; HRMS calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 326.3720, found 326.3723.

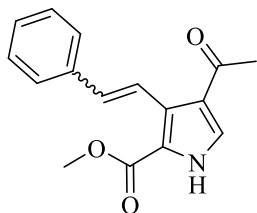


ethyl 4-cyano-3-styryl-1H-pyrrole-2-carboxylate (**3p**)

White solid; 62%; ^1H NMR (400 MHz, CDCl_3): δ 9.72 (0.62H, s), 9.63 (1H, s), 7.72 (1H, d, $J = 16.0$ Hz), 7.63-7.54 (3H, m), 7.39-7.35 (3H, m), 7.31-7.29 (1.6H, m), 7.23-7.16 (3H, m), 6.83 (0.6H, d, $J = 12.0$ Hz), 6.63 (0.6H, d, $J = 12.0$ Hz), 4.42 (2H, q, $J = 8.0$ Hz), 4.32 (1.2H, q, $J = 8.0$ Hz), 1.44 (3H, t, $J = 8.0$ Hz), 1.34 (1.8H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 160.41, 137.01, 136.72, 134.43, 133.05, 129.60, 129.48, 129.44, 128.74, 128.43, 128.31, 128.28, 127.65,

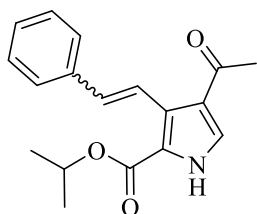
126.79, 120.86, 120.43, 119.10, 118.41, 116.06, 114.26, 96.41, 92.97, 61.42, 61.37, 14.41, 14.28;

HRMS calcd. for $C_{16}H_{14}N_2O_2$ $[M+H]^+$ 267.3080, found 267.3089.



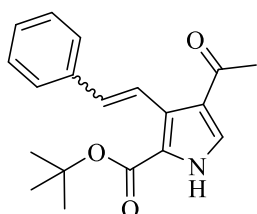
methyl 4-acetyl-3-styryl-1H-pyrrole-2-carboxylate (**3q**)

White solid; 70%; 1H NMR (400 MHz, $CDCl_3$): δ 9.58 (1.72H, m), 7.76 (1H, d, $J = 16.0$ Hz), 7.57-7.47 (4.81H, m), 7.36-7.33 (2.23H, m), 7.26-7.08 (3.6H, m), 6.73 (1.19H, q, $J = 12.0$ Hz), 3.90 (3H, s), 3.66 (1.81H, s), 2.47 (3H, s), 2.31 (1.78H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.09, 194.02, 161.55, 161.45, 137.87, 137.39, 135.72, 132.88, 128.99, 128.59, 128.30, 128.07, 127.74, 127.14, 127.09, 126.82, 126.50, 126.13, 125.24, 121.93, 120.85, 120.58, 119.42, 51.92, 51.70, 28.91, 28.48; HRMS calcd. for $C_{16}H_{15}NO_3$ $[M+H]^+$ 270.3080, found 270.3082.



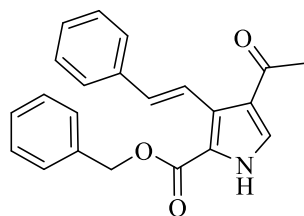
isopropyl 4-acetyl-3-styryl-1H-pyrrole-2-carboxylate (**3r**)

White solid; 61%; 1H NMR (400 MHz, $CDCl_3$): δ 9.51 (1H, s), 7.54 (1H, d, $J = 4.0$ Hz), 7.14-7.10 (5H, m), 6.70 (2H, q, $J = 12.0$ Hz), 5.06-5.00 (1H, m), 2.32 (3H, s), 1.15 (6H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.94, 160.59, 137.38, 132.61, 128.43, 128.07, 127.10, 126.57, 126.31, 126.26, 122.16, 120.96, 68.67, 28.53, 21.70; HRMS calcd. for $C_{18}H_{19}NO_3$ $[M+H]^+$ 298.3620, found 298.3625.



tert-butyl 4-acetyl-3-styryl-1H-pyrrole-2-carboxylate (**3s**)

White solid; 64%; ^1H NMR (400 MHz, CDCl_3): δ 9.64 (0.53H, s), 9.53 (0.86H, s), 7.73 (1H, d, $J = 20.0$ Hz), 7.55-7.52 (2.57H, m), 7.47 (1H, d, $J = 4.0$ Hz), 7.39-7.32 (3H, m), 7.26-7.22 (2.78H, m), 6.68 (1.16H, q, $J = 12.0$ Hz), 2.46 (3H, s), 2.33 (1.73H, s), 1.58 (9H, s), 1.37 (5.25H, s); ^{13}C NMR (100 MHz, CDCl_3): δ 194.12, 194.02, 160.80, 160.59, 137.91, 137.36, 135.26, 132.18, 128.54, 128.44, 128.07, 127.69, 127.55, 127.30, 127.08, 126.67, 126.39, 126.11, 125.76, 125.32, 122.56, 121.79, 119.84, 82.29, 82.00, 28.89, 28.54, 28.46, 27.99; HRMS calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 312.3890, found 312.3896.



benzyl 4-acetyl-3-styryl-1H-pyrrole-2-carboxylate (**3t**)

White solid; 60%; ^1H NMR (400 MHz, CDCl_3): δ 9.58 (1H, s), 7.73 (1H, d, $J = 16.0$ Hz), 7.48-7.34 (9H, m), 7.30-7.20 (3H, m), 5.33 (2H, s), 2.45 (3H, s); ^{13}C NMR (100 MHz, CDCl_3): δ 1194.00, 161.02, 137.74, 135.80, 135.36, 129.06, 128.74, 128.59, 128.53, 128.50, 128.14, 127.66, 126.81, 125.33, 120.90, 119.43, 66.99, 28.92; HRMS calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 346.4060, found 346.4065.

2. X-ray crystallography data of compounds (*E*)-**3n** and (*Z*)-**3n**

Crystals of compounds (*E*)-**3n** (CCDC No. 2035580) and (*Z*)-**3n** (CCDC No. 2035586) were measured on a Rigaku RAXIS-RAPID single-crystal diffractometer. The recrystallization solvent was MeOH.

Crystal structure of (*E*)-**3n** (two molecular of *E*-**3n**)

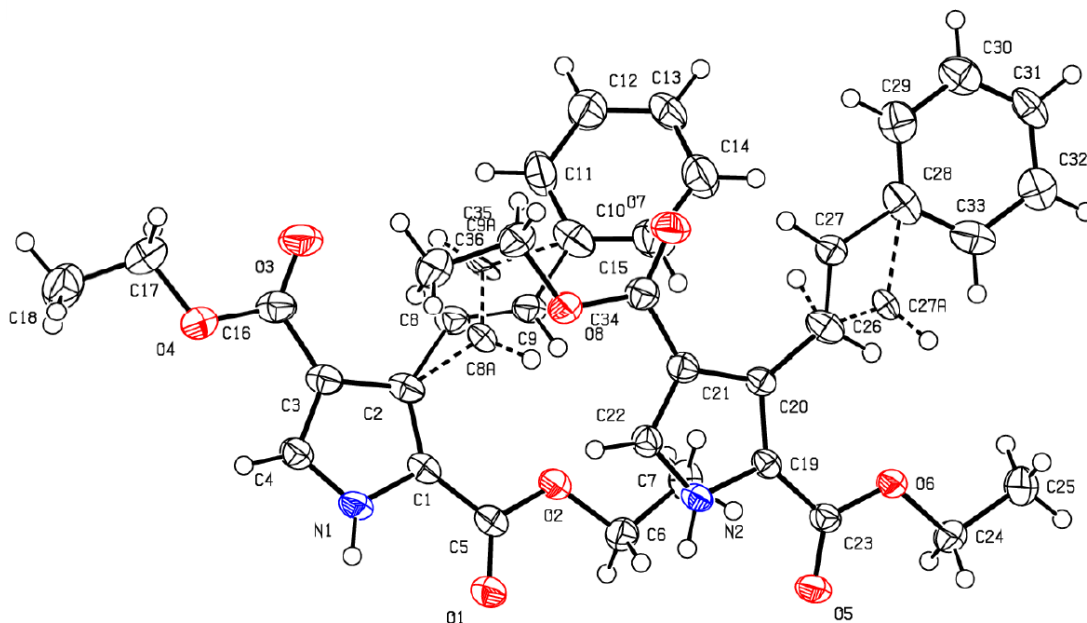


Table S1 X-ray crystallography data of (*E*)-**3n**

Formula moiety	C ₁₈ H ₁₉ NO ₄
Formula sum	C ₁₈ H ₁₉ NO ₄
Formula weight	313.34
Temperature	170 K
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a=12.567(3) Å b=14.560(3) Å c=18.343(5) Å alpha=90 deg. beta=104.458(8) deg. gamma=90 deg.
Volume	3250.0(14) Å ³
Z	8
Calculated density	1.281 g/cm ³
Absorption coefficient	0.091
F(000)	1328.0 mm ⁻¹
Crystal size	0.42×0.32×0.26 mm
Theta range for data collection	2.293 to 27.075 deg.
Reflections collected / unique	5830/7119 [R(int) = 0.0486]
Data / restraints / parameters	7119/73/448
Goodness-of-fit on F ²	1.048
Final R indices [I>2sigma(I)]	R1=0.0486, wR2 = 0.1159
R indices (all data)	R1 = 0.0603, wR2 = 0.1244

Crystal structure of (Z)-3n (six molecular of Z-3n)

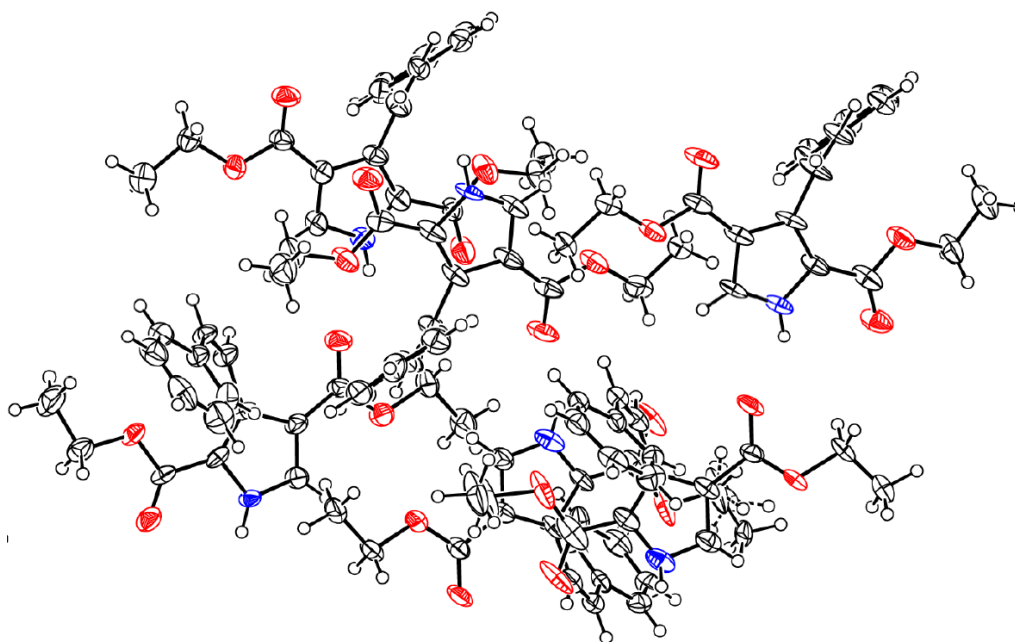


Table S2 X-ray crystallography data of (Z)-3n

Formula moiety	C ₁₈ H ₁₉ NO ₄
Formula sum	C ₁₈ H ₁₉ NO ₄
Formula weight	313.34
Temperature	170 K
Crystal system	monoclinic
Space group	P 1 c 1
Unit cell dimensions	a=12.8475(15) Å
	b=13.2526(18) Å
	c=29.650(4) Å
	alpha=90 deg. beta=102.492(5) deg. gamma=90 deg.
Volume	4928.8(11) Å ³
Z	12
Calculated density	1.267 g/cm ³
Absorption coefficient	0.090
F(000)	1992.0 mm ⁻¹
Crystal size	0.36×0.26×0.23 mm
Theta range for data collection	2.236 to 26.430 deg.
Reflections collected / unique	13233/18954 [R(int) = 0.0663]
Data / restraints / parameters	18954/35/1266
Goodness-of-fit on F ²	1.035
Final R indices [I>2sigma(I)]	R1=0.0663, wR2 = 0.1595
R indices (all data)	R1 = 0.0990, wR2 = 0.1870

3. ^1H and ^{13}C NMR spectra for target compounds 3

