

Supporting Information

Regioselective C5 alkenylation of 2-acylpyrroles via Pd(II)-catalyzed C-H bond activation

Jian-Hua Duan, Rui-Jie Mi, Jing Sun*, Ming-Dong Zhou*

School of Chemistry and Materials Science, Liaoning Shihua University, Dandong Road 1, Fushun 113001, P. R. China. E-mail:sunjing@lnpu.edu.cn; mingdong.zhou@lnpu.edu.cn.

Fax: +86 24 56863837; Tel: +86 24 56863837

Table of Contents

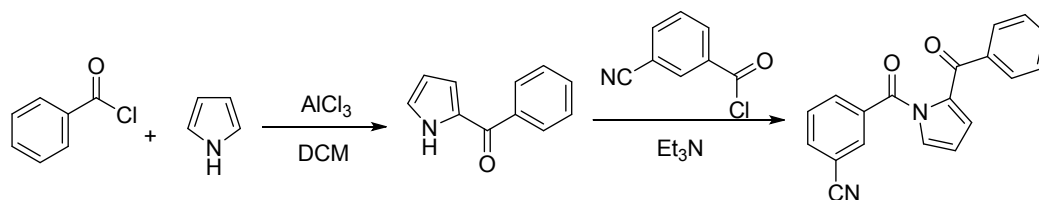
1. General Information	S2
2. Experimental Section	S2
2.1 Typical procedure for the preparation of 2-acylpyrroles	S2
2.2 Characteristic data of 2-acylpyrrole substrates	S3
2.3 General procedure for Pd(II)-catalyzed alkenylation of 2-acylpyrroles	S11
2.4 Characteristic data of alkenylated products	S11
2.5 The procedure for the removal of protecting group	S24
3. NMR spectra	S25

1. General Information

All manipulations were performed in sealing tubes; NMR spectra were obtained on Bruker Ascend HD 500 (^1H NMR, 500 MHz; ^{13}C NMR, 125 MHz) or Bruker Ascend HD 600 (^1H NMR, 600 MHz; ^{13}C NMR, 150 MHz) or Bruker Ascend HD 400 (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz) instrument; High-resolution mass spectra (HRMS) were recorded on a Q-TOF micromass (YA-105) and Bruker Maxis Impact system (282001.00081) mass spectrometer in positive ESI mode; Melting points were measured on a Shanghai Shen Guang WRS-3 melting point instrument; All reagents of analytic grade were used without further purification.

2. Experimental Section

2.1 Typical procedure for the preparation of pyrroles

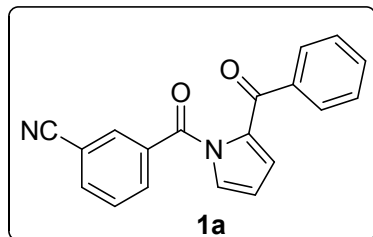


(Step 1) Phenyl(1*H*-pyrrol-2-yl)methanone: A 500 mL Schlenk flask was charged with pyrrole (40 mmol), benzoyl chloride (40 mmol), AlCl_3 (80 mmol), dichloromethane (250 mL). The reaction mixture was stirred at room temperature for 8 h. The resulting mixture was quenched with H_2O (50 mL) and then extraction with saturated aqueous solution of NaOH (3×100 mL). The organic layer was dried over anhydrous MgSO_4 , filtrated and then evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate=5:1).

(Step 2) 3-(2-Benzoyl-1*H*-pyrrole-1-carbonyl)benzonitrile: A 100 mL Schlenk flask was charged with phenyl(1*H*-pyrrol-2-yl)methanone (20 mmol), 3-cyanobenzoyl chloride (20 mmol), Et_3N (20 mmol), N,N -dimethylpyridin-4-amine (2 mmol), CH_2Cl_2 (30 mL). The reaction mixture was stirred at room temperature for 10 h, extraction filtration, and then evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate=5:1).

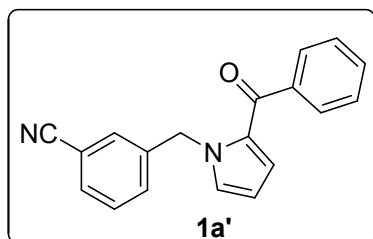
2.2 Characteristic data of pyrrole substrates.

3-(2-Benzoyl-1*H*-pyrrole-1-carbonyl)benzonitrile (**1a**)



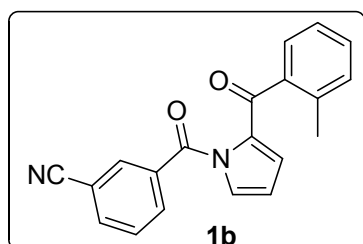
White solid; yield: 2.4245 g (81%); m.p. 100-101 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.10-7.95 (m, 2H), 7.85-7.80 (m, 2H), 7.78-7.74 (m, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 8.5 Hz, 1H), 7.48-7.43 (m, 3H), 6.96-6.92 (m, 1H), 6.42 (t, *J* = 3.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 184.15, 166.76, 136.91, 136.00, 135.06, 134.02, 133.02, 132.84, 132.51, 129.55, 129.05, 128.92, 128.45, 124.63, 117.32, 113.02, 111.47; HRMS (ESI): calcd for C₁₉H₁₃N₂O₂ [M+H⁺] 301.0972, found 301.0973.

3-((2-Benzoyl-1*H*-pyrrol-1-yl)methyl)benzonitrile (**1a'**)



¹H NMR (400 MHz, CDCl₃) δ 7.78-7.72 (m, 2H), 7.56-7.50 (m, 2H), 7.46-7.40 (m, 4H), 7.37 (s, 1H), 7.06-7.01 (m, 1H), 6.85-6.81 (m, 1H), 6.30-6.26 (m, 1H), 5.68 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 186.12, 140.10, 139.48, 131.65, 131.32, 131.16, 130.92, 130.21, 129.90, 129.42, 129.15, 128.09, 123.83, 118.67, 112.78, 109.33, 51.75; HRMS (ESI): calcd for C₁₉H₁₅N₂O [M+H⁺] 287.1179, found 287.1168.

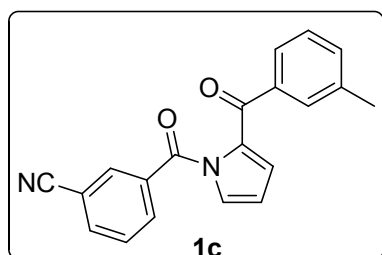
3-(2-(2-Methylbenzoyl)-1*H*-pyrrole-1-carbonyl)benzonitrile (**1b**)



Gray solid; yield: 2.4785 g (79%); m.p. 109-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.6, 1H), 7.96 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H),

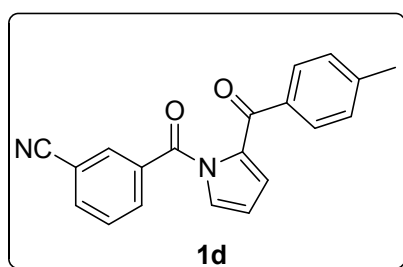
7.52-7.44 (m, 2H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.28-7.20 (m, 2H), 6.80-6.74 (m, 1H), 6.40 (t, $J = 3.2$ Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.93, 167.24, 137.81, 137.01, 136.12, 135.40, 135.39, 133.07, 132.42, 131.35, 131.05, 129.65, 129.44, 128.79, 125.24, 117.44, 113.12, 111.61, 19.80; HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 315.1128, found 315.1132.

3-(2-(3-Methylbenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1c)



Red liquid; yield: 2.4619 g (78%); ^1H NMR (500 MHz, CDCl_3) δ 8.00-7.95 (m, 2H), 7.77-7.72 (m, 1H), 7.64-7.58 (m, 2H), 7.54-7.50 (m, 1H), 7.48-7.44 (m, 1H), 7.40-7.32 (m, 2H), 6.96-6.92 (m, 1H), 6.42 (t, $J = 3.5$ Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 184.35, 166.80, 138.37, 136.95, 135.91, 135.12, 134.13, 133.63, 132.95, 132.44, 129.52, 129.47, 128.80, 128.27, 126.29, 124.50, 117.32, 112.97, 111.43, 21.16; HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 315.1128, found 315.1126.

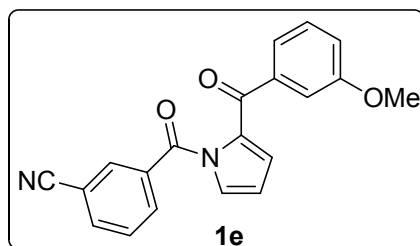
3-(2-(4-Methylbenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1d)



White solid; yield: 2.8145 g (89%); m.p. 125-126 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.50-7.47 (m, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 6.93-6.91 (m, 1H), 6.41 (t, $J = 3.5$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 183.99, 167.33, 143.90, 137.76, 134.34, 134.20, 132.27, 130.57, 129.46, 129.35, 129.23, 129.00, 128.71, 124.32, 117.62, 116.35, 111.44, 21.63; HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 315.1128, found

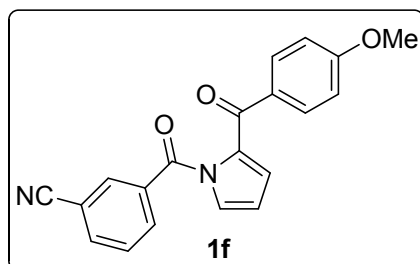
315.1129.

3-(2-(3-Methoxybenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1e)



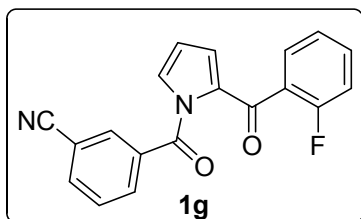
Brown solid; yield: 1.9835 g (60%); ^1H NMR (500 MHz, CDCl_3) δ 8.02-7.96 (m, 2H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.49-7.46 (m, 1H), 7.43 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.30-7.28 (m, 1H), 7.14-7.10 (m, 1H), 6.98-6.95 (m, 1H), 6.43 (t, $J = 3.5$ Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 183.96, 166.80, 159.63, 138.25, 136.02, 135.11, 134.05, 133.03, 132.53, 129.59, 129.46, 128.96, 124.66, 121.70, 119.31, 117.36, 113.39, 113.08, 111.52, 55.34; HRMS (EI): calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3$: 330.1004, found: 330.1000.

3-(2-(4-Methoxybenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1f)



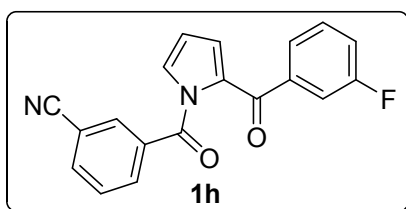
Brown solid; yield: 2.0825 g (63%); m.p. 116-120 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.01-7.96 (m, 2H), 7.86-7.81 (m, 2H), 7.78-7.73 (m, 1H), 7.53 (t, $J = 8.0$ Hz, 1H), 7.45-7.42 (m, 1H), 6.97-6.92 (m, 2H), 6.92-6.89 (m, 1H), 6.41 (t, $J = 3.5$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 183.11, 166.78, 163.50, 135.94, 135.18, 134.21, 133.09, 132.52, 131.43, 129.70, 129.54, 128.29, 123.67, 117.39, 113.78, 112.99, 111.35, 55.44; HRMS (EI): calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3$: 330.1004, found: 330.1001.

3-(2-(2-Fluorobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1g)



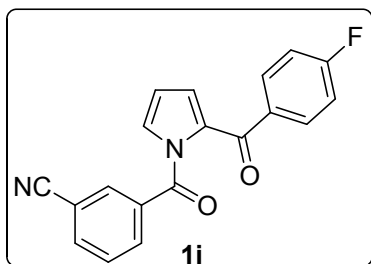
Brown solid; yield: 2.3665 g (74%); m.p. 66-67 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.05-7.99 (m, 2H), 7.83-7.78 (m, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.54-7.48 (m, 3H), 7.24-7.19 (m, 1H), 7.18-7.12 (m, 1H), 6.93-6.89 (m, 1H), 6.43 (t, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 180.76, 167.02, 160.09 (d, $J = 251$ Hz), 136.15, 135.21, 134.88, 133.65 (d, $J = 9.1$ Hz), 133.15, 132.56, 130.53 (d, $J = 1.9$ Hz), 129.70 (d, $J = 19.9$ Hz), 126.0 (d, $J = 13.6$ Hz), 125.15 (d, $J = 2.8$ Hz), 124.38 (d, $J = 3.6$ Hz), 117.43, 116.49, 116.32, 113.12, 111.84; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{12}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 319.0877, found 319.0887.

3-(2-(3-Fluorobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1h)



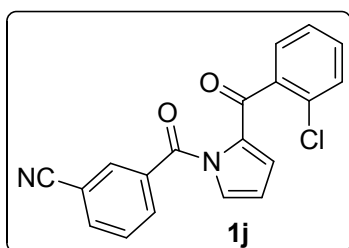
Brown oil; yield: 2.2495 g (71%); ^1H NMR (500 MHz, CDCl_3) δ 8.03-7.99 (m, 2H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 7.5$ Hz, 1H), 7.58 (t, $J = 8.0$ Hz, 1H), 7.52-7.47 (m, 1H), 7.47-7.42 (m, 2H), 7.32-7.26 (m, 1H), 7.00-6.96 (m, 1H), 6.45 (t, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.67 (d, $J = 1.9$ Hz), 166.61, 162.49 (d, $J = 247.4$ Hz), 138.92 (d, $J = 6.4$ Hz), 136.23, 134.86, 133.57, 133.16, 132.66, 130.24 (d, $J = 7.1$ Hz), 129.68, 129.42, 124.99, 124.92 (d, $J = 3.6$ Hz), 119.94 (d, $J = 20.9$ Hz), 117.35, 115.92 (d, $J = 22.6$ Hz), 113.16, 111.66; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{12}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 319.0877, found 319.0876.

3-(2-(4-Fluorobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1i)



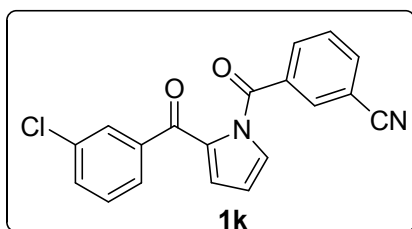
Brown solid; yield: 2.3295 g (73%); m.p. 98-99 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.02-7.98 (m, 2H), 7.92-7.84(m, 2H), 7.80-7.76 (m, 1H), 7.59-7.51 (m, 1H), 7.46-7.42 (m, 1H), 7.14 (t, J = 8.4 Hz, 2H), 6.95-6.90 (m, 1H), 6.42 (t, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.65, 166.79, 165.41 (d, J = 230.4 Hz), 136.11, 134.87, 133.75, 133.21 (d, J = 3.0 Hz), 133.13, 132.60, 131.67 (d, J = 9.5 Hz), 129.61, 128.99, 124.42, 117.30, 115.65 (d, J = 21.9 Hz), 113.07, 111.49; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{12}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 319.0877, found 319.0876.

3-(2-(2-Chlorobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (**1j**)



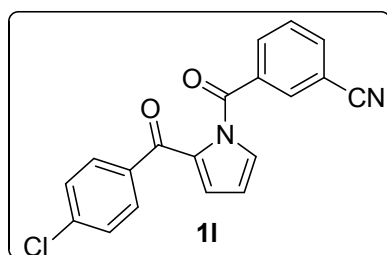
Brown solid; yield: 2.7725 g (83%); m.p. 134-135 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.12-8.08 (m, 1H), 7.99 (s, 1H), 7.85-7.81 (m, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.39 (d, J = 7.5 Hz, 1H), 7.36-7.30 (m, 1H), 6.81-6.78 (m, 1H), 6.43 (t, J = 3.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.79, 167.35, 137.03, 136.24, 135.20, 134.09, 133.33, 132.56, 131.79, 131.54, 130.42, 130.36, 129.75, 129.67, 126.73, 126.18, 117.53, 113.07, 112.00; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{12}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 335.0582, found 335.0584.

3-(2-(3-Chlorobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (**1k**)



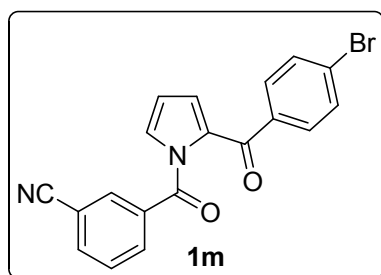
Brown oil; yield: 2.4422 g (73%); ^1H NMR (500 MHz, CDCl_3) δ 8.03-7.97 (m, 2H), 7.84-7.76 (m, 2H), 7.74-7.70 (m, 1H), 7.75-7.70 (m, 2H), 7.60-7.52 (m, 1H), 7.49-7.38 (m, 1H), 6.99-6.95 (m, 1H), 6.45 (t, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.67, 166.62, 138.57, 136.26, 134.93, 134.82, 133.59, 133.17, 132.87, 132.69, 129.89, 129.72, 129.46, 129.13, 127.25, 125.02, 117.35, 113.26, 111.73; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{12}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 335.0582, found 335.0591.

3-(2-(4-Chlorobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1l)



Brown oil; yield: 2.3455 g (70%); ^1H NMR (500 MHz, CDCl_3) δ 8.02-7.98 (m, 2H), 7.80 (d, $J = 8.5$ Hz, 3H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.47-7.42 (m, 3H), 6.95-6.92 (m, 1H), 6.43 (t, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.80, 166.52, 139.27, 136.15, 135.16, 134.77, 133.60, 133.11, 132.59, 130.47, 129.62, 129.21, 128.78, 124.65, 117.29, 113.05, 111.55; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{12}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$ 335.0582, found 335.0578.

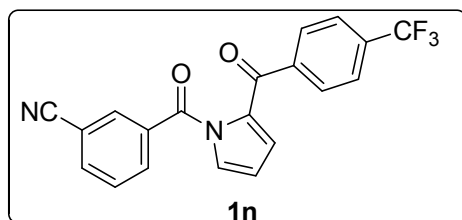
3-(2-(4-Bromobenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1m)



Yellow solid; yield: 2.7929 g (74%); m.p. 154-159 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.02-7.98 (m, 2H), 7.95-7.92 (m, 1H), 7.84-7.80 (m, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.73-7.69 (m, 1H), 7.58 (t, $J = 8.0$ Hz, 1H), 7.48-7.44 (m, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 6.98-6.95 (m, 1H), 6.45 (t, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.64, 166.62, 138.81, 136.26, 135.78, 134.95, 133.57, 133.16, 132.69, 132.04, 130.13, 129.72, 129.45, 127.69, 125.00, 122.81, 117.35, 113.29, 111.75; HRMS (ESI):

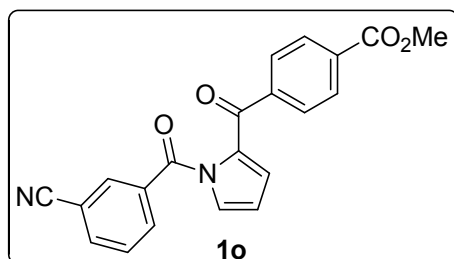
calcd for $C_{19}H_{11}BrN_2NaO_2$ $[M+Na^+]$ 400.9896, found 400.9913.

3-(2-(4-(Trifluoromethyl)benzoyl)-1*H*-pyrrole-1-carbonyl)benzonitrile (1n)



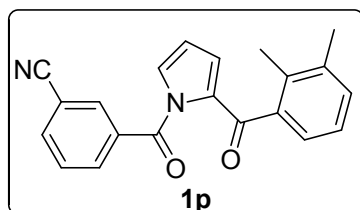
Yellow oil; yield: 2.7965 g (76%); 1H NMR (500 MHz, $CDCl_3$) δ 8.11-7.98 (m, 4H), 7.88-7.80 (m, 2H), 7.66-7.56 (m, 2H), 7.49-7.44 (m, 1H), 7.00-6.94 (m, 1H), 6.46 (t, J = 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.62, 166.52, 137.60, 136.34, 134.76, 133.46, 133.24, 132.77, 132.28, 129.75, 129.62, 129.31 (q, J = 3.6 Hz), 129.23, 126.96 (q, J = 4.5 Hz), 124.31 (q, J = 270.8 Hz), 117.29, 113.29, 111.83; HRMS (ESI): calcd for $C_{20}H_{12}F_3N_2O_2$ $[M+H^+]$ 369.0845, found 369.0840.

Methyl 4-(1-(3-cyanobenzoyl)-1*H*-pyrrole-2-carbonyl)benzoate (1o)



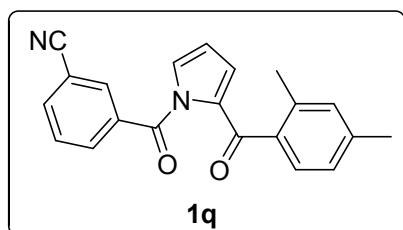
Yellow solid; yield: 2.9765 g (83%); m.p. 135-136 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2H), 8.02-7.98 (m, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.50-7.46 (m, 1H), 6.98-6.92 (m, 1H), 6.45 (t, J = 3.2 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.25, 166.57, 165.99, 140.42, 136.18, 134.82, 133.70, 133.61, 133.10, 132.62, 129.64, 129.61, 129.49, 128.93, 125.06, 117.27, 113.14, 111.67, 52.38; HRMS (ESI): calcd for $C_{21}H_{14}N_2NaO_4$ $[M+Na^+]$ 381.0846, found 381.0862.

3-(2-(2,3-Dimethylbenzoyl)-1*H*-pyrrole-1-carbonyl)benzonitrile (1p)



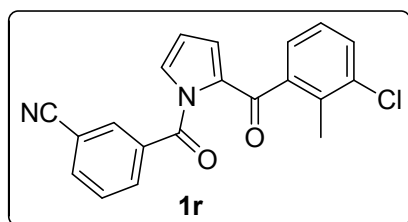
White solid; yield: 2.4848 g (76%); m.p. 99-100 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, J = 8.0 Hz, 1H), 7.95 (s, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.48–7.43 (m, 2H), 7.08-7.02 (m, 2H), 6.79–6.74 (m, 1H), 6.39 (t, J = 3.5 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.80, 167.25, 141.70, 138.26, 136.05, 135.67, 135.45, 134.17, 133.05, 132.39, 132.30, 129.62, 129.39, 129.07, 125.86, 124.83, 117.48, 113.08, 111.51, 21.37, 19.90; HRMS (EI): calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$: 328.1212, found: 328.1216.

3-(2-(2,4-Dimethylbenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1q)



Yellow solid; yield: 2.3541 g (72%); m.p. 89-90 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.02–7.96 (m, 1H), 7.96-7.92 (m, 1H), 7.80–7.74 (m, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.48–7.42 (m, 2H), 7.08-7.02 (m, 2H), 6.78–6.74 (m, 1H), 6.38 (t, J = 3.5 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.77, 167.20, 141.64, 138.19, 136.00, 135.65, 135.42, 134.20, 133.00, 132.38, 132.26, 129.58, 129.33, 129.02, 125.83, 124.73, 117.43, 113.07, 111.47, 21.31, 19.84; HRMS (EI): Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$: 328.1212, found: 328.1205.

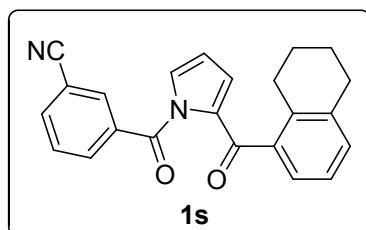
3-(2-(3-Chloro-2-methylbenzoyl)-1H-pyrrole-1-carbonyl)benzonitrile (1r)



White solid; yield: 2.8185 g (81%); m.p. 111-114 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.05-8.01 (m, 1H), 7.97 (s, 1H), 7.86-7.81 (m, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.35 (d, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.78-6.75 (m, 1H), 6.41 (t, J = 3.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 184.83, 167.09, 139.30, 136.25, 136.05, 135.24, 135.13, 134.89, 133.08, 132.38, 131.57, 130.09, 129.71, 126.59, 126.20, 125.80, 117.37, 113.11, 111.79, 16.82; HRMS (EI): calcd for

C₂₀H₁₄ClN₂O₂: 349.0738, found: 349.0740

3-(2-(5,6,7,8-Tetrahydronaphthalene-1-carbonyl)-1H-pyrrole-1-carbonyl)benzonitrile (1s)



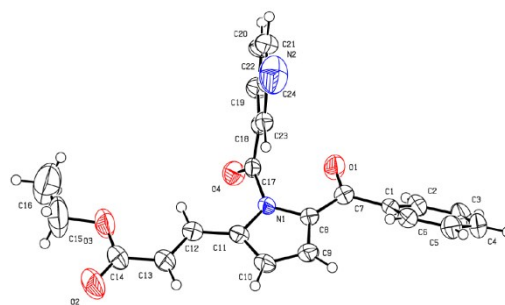
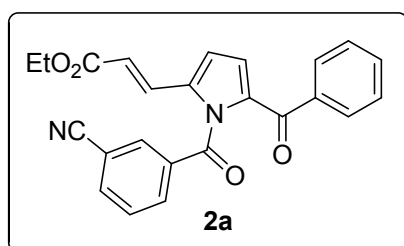
Gray solid; yield: 2.8565 g (81%); m.p. 125-126 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 1H), 7.30-7.24 (m, 1H), 7.21-7.11 (m, 2H), 6.79–6.74 (m, 1H), 6.39 (t, *J* = 3.5 Hz, 1H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 1.78–1.64 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 186.26, 167.40, 138.41, 137.05, 136.52, 136.02, 135.53, 135.50, 132.97, 132.27, 132.16, 129.59, 129.46, 126.10, 125.27, 124.64, 117.46, 113.01, 111.56, 29.78, 26.80, 22.77, 22.39; HRMS (EI): calcd for C₂₃H₁₈N₂O₂: 354.1362, found : 354.1368.

2.3 General procedure for Pd(II)-catalyzed alkenylation of pyrroles

10 mL sealing tube was charged **1** (0.1 mmol), ethyl acrylate (0.15 mmol), Pd(OAc)₂ (20 mol%), AgOAc (0.3 mmol), and PhCF₃ (1 mL). The reaction mixture was stirred at 100 °C for 12 h. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=5/1).

2.4 Characteristic data of alkenylated products

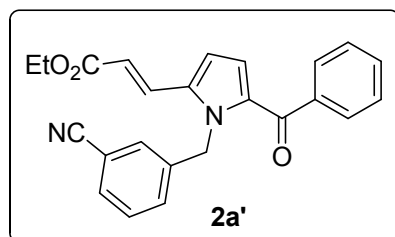
(E)-ethyl 3-(5-benzoyl-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (2a)



¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.83-7.75 (m, 3H), 7.61-7.52 (m, 2H), 7.50-7.44 (m, 3H), 6.97 (d, *J* = 4.0 Hz, 1H), 6.87 (d, *J* = 4.0

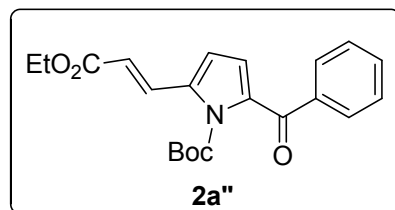
Hz, 1H), 6.45 (d, $J = 15.5$ Hz, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 183.74, 167.74, 165.87, 137.28, 136.77, 136.69, 135.67, 135.55, 133.08, 132.94, 132.38, 130.19, 129.98, 128.95, 128.63, 122.39, 121.89, 117.37, 113.46, 112.39, 60.86, 14.20; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 421.1159, found 421.1169.

(E)-ethyl 3-(5-benzoyl-1-(3-cyanobenzyl)-1H-pyrrol-2-yl)acrylate (2a')



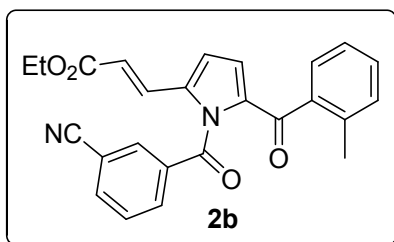
^1H NMR (500 MHz, CDCl_3) δ 7.78-7.73 (m, 2H), 7.57-7.52 (m, 2H), 7.50-7.40 (m, 4H), 7.38-7.34 (m, 1H), 7.27-7.24 (m, 1H), 6.85 (d, $J = 4.0$ Hz, 1H), 6.75 (d, $J = 4.5$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 5.83 (s, 2H), 4.23 (q, $J = 7.0$ Hz, 2H), 1.31 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.23, 166.34, 139.58, 139.20, 136.77, 132.72, 132.07, 131.21, 130.88, 130.64, 130.17, 129.56, 129.28, 128.22, 123.53, 120.70, 118.60, 113.00, 110.64, 60.79, 47.73, 14.22; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}^+]$ 385.1547, found 385.1547.

(E)-ethyl 3-(5-benzoyl-1-(3-cyanobenzyl)-1H-pyrrol-2-yl)acrylate (2a'')



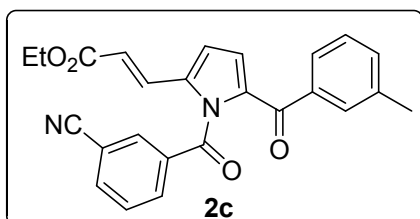
^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 16.0$ Hz, 1H), 7.89 (d, $J = 7.2$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 6.68-6.62 (m, 2H), 6.39 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 1.50 (s, 9H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.10, 166.35, 148.50, 137.39, 135.40, 135.20, 132.84, 132.35, 129.39, 128.43, 120.47, 120.15, 111.49, 86.22, 27.26, 14.23; HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{23}\text{NNaO}_5$ $[\text{M}+\text{Na}^+]$ 392.1468, found 392.1850.

(E)-ethyl 3-(1-(3-cyanobenzoyl)-5-(2-methylbenzoyl)-1H-pyrrol-2-yl)acrylate (2b)



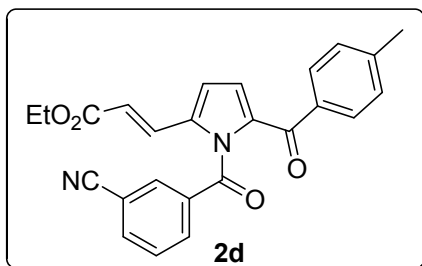
^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 2H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.50 (d, $J = 15.6$ Hz, 1H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.28-7.22 (m, 2H), 6.84 (d, $J = 4.2$ Hz, 1H), 6.74 (d, $J = 4.2$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.25 (s, 3 H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 185.72, 167.87, 165.86, 137.50, 137.46, 136.80, 136.71, 136.43, 135.60, 133.06, 132.31, 131.39, 131.08, 130.08, 129.98, 128.44, 125.27, 122.83, 122.05, 117.39, 113.41, 112.33, 60.89, 19.63, 14.20; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 435.1315, found 435.1318.

(E)-ethyl 3-(1-(3-cyanobenzoyl)-5-(3-methylbenzoyl)-1H-pyrrol-2-yl)acrylate (2c)



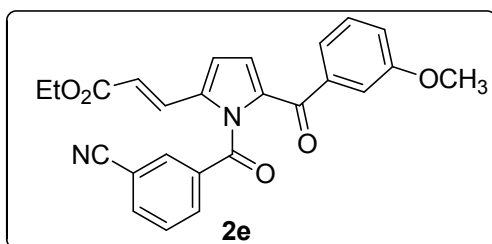
^1H NMR (600 MHz, CDCl_3) δ 8.00 (d, $J = 8.4$ Hz, 1H), 7.85 (s, 1H), 7.82-7.78 (m, 1H), 7.61-7.54 (m, 3H), 7.51 (d, $J = 16.2$ Hz, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 3.6$ Hz, 1H), 6.88 (d, $J = 4.2$ Hz, 1H), 6.46 (d, $J = 16.2$ Hz, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.40 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 183.94, 167.75, 165.91, 138.64, 137.21, 136.73, 136.70, 135.79, 135.60, 133.77, 133.08, 132.34, 130.24, 129.98, 129.43, 128.45, 126.18, 122.34, 121.79, 117.41, 113.41, 112.37, 60.87, 21.30, 14.21; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 435.1315, found 435.1339.

(E)-ethyl 3-(1-(3-cyanobenzoyl)-5-(4-methylbenzoyl)-1H-pyrrol-2-yl)acrylate (2d)



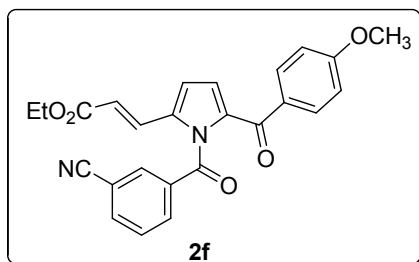
^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, $J = 7.2$ Hz, 1H), 7.70-7.64 (m, 4H), 7.62-7.54 (m, 2H), 7.23 (d, $J = 7.8$ Hz, 2H), 6.91-6.86 (m, 2H), 6.48 (d, $J = 15.6$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.40 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 183.70, 166.84, 166.00, 143.83, 137.82, 137.60, 136.13, 134.53, 134.14, 132.97, 132.57, 130.75, 130.42, 129.28, 129.24, 123.12, 121.85, 115.88, 112.70, 112.03, 60.82, 21.59, 14.12; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_4$ [$\text{M}+\text{Na}^+$] 435.1315, found 435.1331.

(E)-ethyl 3-(1-(3-cyanobenzoyl)-5-(3-methoxybenzoyl)-1H-pyrrol-2-yl)acrylate (2e)



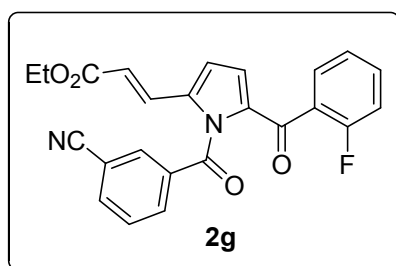
^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.0$ Hz, 1H), 7.88 (s, 1H), 7.82-7.78 (m, 1H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 15.5$ Hz, 1H), 7.42-7.34 (m, 2H), 7.25-7.23 (m, 1H), 7.14 - 7.10 (m, 1H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.88 (d, $J = 4.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 4.22 (q, $J = 7.0$ Hz, 2H), 3.82 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 183.46, 167.70, 165.84, 159.71, 137.90, 137.28, 136.75, 135.63, 135.48, 133.00, 132.39, 130.16, 129.96, 129.56, 122.40, 121.86, 121.44, 119.34, 117.34, 113.43, 113.34, 112.37, 60.83, 55.37, 14.16; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_5$ [$\text{M}+\text{Na}^+$] 451.1264, found 451.1266.

(E)-ethyl 3-(1-(3-cyanobenzoyl)-5-(4-methoxybenzoyl)-1H-pyrrol-2-yl)acrylate (2f)



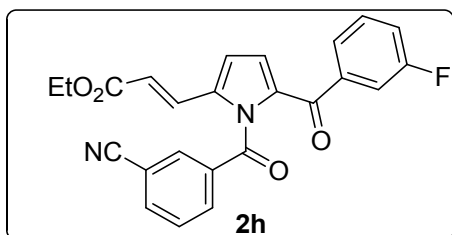
^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, J = 8.4 Hz, 1H), 7.85 (s, 1H), 7.82-7.77 (m, 3H), 7.56 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 16.2 Hz, 1H), 6.97-6.93 (m, 3H), 6.87 (d, J = 4.2 Hz, 1H), 6.43 (d, J = 16.2 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 182.48, 167.75, 165.96, 163.61, 136.73, 136.67, 135.97, 135.63, 133.08, 132.35, 131.32, 130.90, 130.37, 129.95, 129.31, 128.80, 121.55, 121.40, 117.42, 113.93, 113.35, 112.33, 60.82, 55.51, 14.20; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}_5$ $[\text{M}+\text{Na}^+]$ 451.1264, found 451.1285.

(*E*)-ethyl 3-(1-(3-cyanobenzoyl)-5-(2-fluorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (2g)



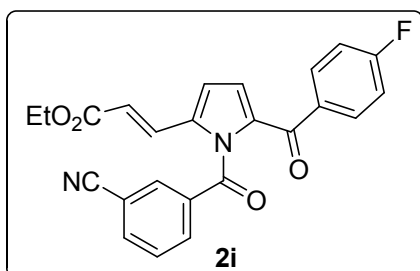
^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, J = 7.8 Hz, 1H), 7.91 (s, 1H), 7.85-7.81 (m, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.56-7.35 (m, 3H), 7.22 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.91- 6.85 (m, 2H), 6.48 (d, J = 16.2 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 180.50, 167.57, 165.80, 159.84 (d, J = 209.9 Hz), 137.84, 136.86, 136.26, 135.33, 133.70 (d, J = 6.4 Hz), 133.18, 132.54, 130.39 (d, J = 1.9 Hz), 130.05, 129.95, 125.53 (d, J = 11.9 Hz), 124.47 (d, J = 3.6 Hz), 122.74 (d, J = 4.3 Hz), 122.37, 117.35, 116.45 (d, J = 18.2 Hz), 113.46, 112.46, 60.89, 14.19; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{FN}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 439.1065, found 439.1090.

(*E*)-ethyl 3-(1-(3-cyanobenzoyl)-5-(3-fluorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (2h)



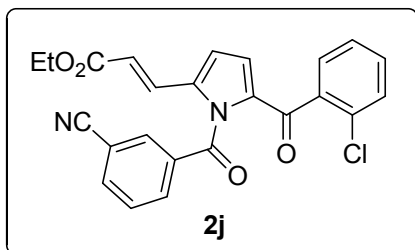
^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.88 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 8.0$ Hz, 2H), 7.52-7.42 (m, 3H), 7.31-7.25 (m, 1H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.89 (d, $J = 4.0$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.22 (q, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.15, 167.60, 165.77, 162.32 (d, $J = 247.4$ Hz), 138.60 (d, $J = 7.3$ Hz), 137.68, 136.88, 135.35, 135.07, 133.01, 132.43, 130.35 (d, $J = 8.1$ Hz), 129.99 (d, $J = 5.4$ Hz), 124.66 (d, $J = 2.8$ Hz), 122.55, 122.26, 120.00, 119.82, 115.87, 115.69, 113.52, 112.43, 60.88, 14.14; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{FN}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 439.1065, found 439.1071.

(E)-ethyl 3-(1-(3-cyanobenzoyl)-5-(4-fluorobenzoyl)-1H-pyrrol-2-yl)acrylate (2i)



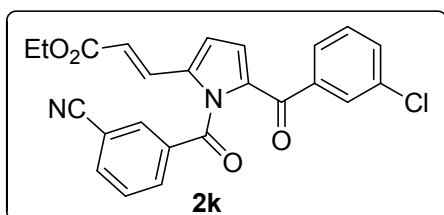
^1H NMR (500 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 1H), 7.87-7.80 (m, 4H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 16.0$ Hz, 1H), 7.16 (t, $J = 8.5$ Hz, 2H), 6.96 (d, $J = 4.0$ Hz, 1H), 6.88 (d, $J = 4.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 4.22 (q, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.21, 167.66, 165.83, 165.61 (d, $J = 253.6$ Hz), 137.39, 136.87, 135.44, 135.34, 133.12, 132.93 (d, $J = 3.6$ Hz), 132.40, 131.55, 131.48, 130.06 (d, $J = 4.5$ Hz), 128.81, 122.12 (d, $J = 20.8$ Hz), 117.35, 115.89 (d, $J = 21.8$ Hz), 113.48, 112.38, 60.90, 14.19; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{FN}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 439.1065, found 439.1085.

(E)-ethyl 3-(5-(2-chlorobenzoyl)-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (2j)



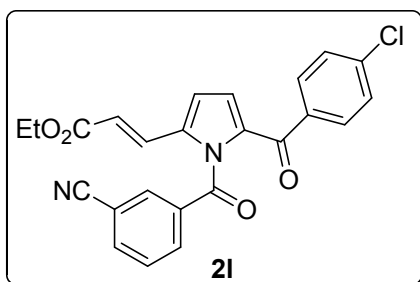
^1H NMR (600 MHz, CDCl_3) δ 8.09 (d, $J = 7.8$ Hz, 1H), 7.88-7.84 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.51 (d, $J = 16.2$ Hz, 1H), 7.43-7.40 (m, 2H), 7.37-7.31 (m, 2H), 6.85 (d, $J = 4.2$ Hz, 1H), 6.74 (d, $J = 4.2$ Hz, 1H), 6.48 (d, $J = 16.2$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 182.67, 167.72, 165.78, 138.14, 136.95, 136.55, 135.50, 135.17, 133.44, 132.68, 131.85, 131.40, 130.91, 130.35, 129.97, 129.44, 128.82, 126.82, 123.41, 122.60, 117.40, 113.40, 60.95, 14.20; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{ClN}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 455.0769, found 455.0793.

(E)-ethyl 3-(5-(3-chlorobenzoyl)-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (2k)



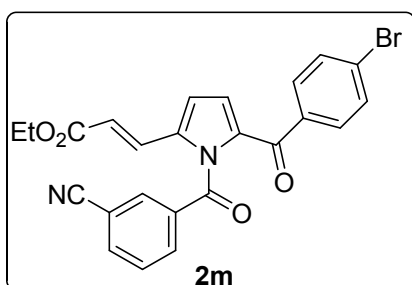
^1H NMR (600 MHz, CDCl_3) δ 7.98 (d, $J = 7.8$ Hz, 1H), 7.88-7.84 (m, 1H), 7.84-7.80 (m, 1H), 7.76-7.72 (m, 1H), 7.69-7.64 (m, 1H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.57-7.54 (m, 1H), 7.48 (d, $J = 15.6$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 4.2$ Hz, 1H), 6.89 (d, $J = 4.2$ Hz, 1H), 6.47 (d, $J = 15.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 182.15, 167.61, 165.77, 138.27, 137.78, 136.97, 135.39, 135.04, 134.92, 133.11, 132.91, 132.51, 130.10, 130.01, 128.98, 127.06, 122.65, 122.42, 117.31, 113.59, 112.51, 60.97, 14.24; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{ClN}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 455.0769, found 455.0799.

(E)-ethyl 3-(5-(4-chlorobenzoyl)-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (2l)



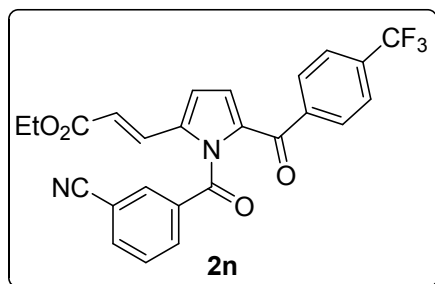
^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.0$ Hz, 1H), 7.88-7.82 (m, 2H), 7.76 (d, $J = 8.5$ Hz, 2H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.52-7.44 (m, 3H), 6.97 (d, $J = 4.0$ Hz, 1H), 6.90 (d, $J = 4.0$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.24 (q, $J = 7.5$ Hz, 2H), 1.32 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.40, 167.64, 165.82, 139.48, 137.56, 136.91, 135.40, 135.24, 134.97, 133.13, 132.41, 130.33, 130.06, 130.03, 129.01, 122.32, 122.19, 117.35, 113.51, 112.41, 60.94, 14.20; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{ClN}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 455.0769, found 455.0766.

(E)-ethyl 3-(5-(4-bromobenzoyl)-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (2m)



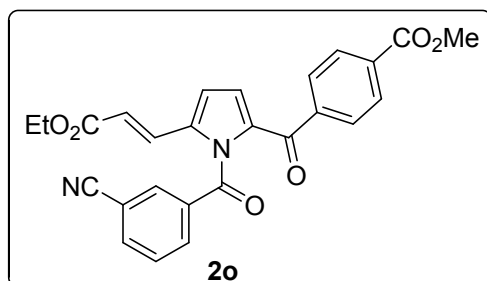
^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.0$ Hz, 1H), 7.92-7.82 (m, 3H), 7.74-7.68 (m, 2H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 16.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 4.0$ Hz, 1H), 6.89 (d, $J = 4.0$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.03, 167.61, 165.78, 138.44, 137.79, 136.94, 135.79, 135.35, 134.97, 133.05, 132.45, 131.83, 130.20, 130.07, 129.96, 127.45, 122.86, 122.65, 122.37, 117.33, 113.53, 112.47, 60.94, 14.20; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{18}\text{BrN}_2\text{O}_4$ $[\text{M}+\text{H}^+]$ 477.0444, found 477.0447.

(E)-ethyl-3-(1-(3-cyanobenzoyl)-5-(4-(trifluoromethyl)benzoyl)-1H-pyrrol-2-yl)acrylate (2n)



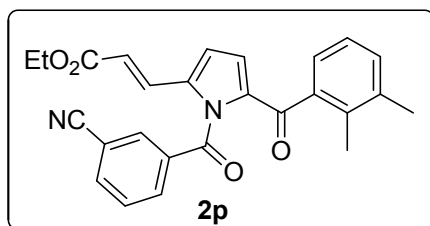
^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.0$ Hz, 1H), 7.91-7.86 (m, 2H), 7.85-7.82 (m, 1H), 7.74-7.69 (m, 2H), 7.60 (t, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 16.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 4.0$ Hz, 1H), 6.90 (d, $J = 4.0$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 182.02, 167.70, 165.78, 138.40, 137.77, 136.95, 135.78, 135.32, 134.94, 133.04, 132.43, 131.81, 130.20, 130.07, 129.94, 127.45, 122.85, 122.67, 122.35, 117.34, 113.54, 112.47, 60.94, 14.19; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_4$ $[\text{M}+\text{H}^+]$ 467.1213, found 467.1208.

(E)-ethyl-4-(1-(3-cyanobenzoyl)-5-(3-ethoxy-3-oxoprop-1-en-1-yl)-1H-pyrrole-2-carbonyl)benzoate (2o)



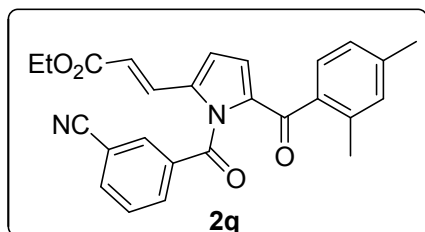
^1H NMR (600 MHz, CDCl_3) δ 8.13 (d, $J = 8.4$ Hz, 2H), 8.00-7.97 (m, 1H), 7.90-7.80 (m, 4H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.48 (d, $J = 15.6$ Hz, 1H), 6.98 (d, $J = 4.2$ Hz, 1H), 6.90 (d, $J = 4.2$ Hz, 1H), 6.48 (d, $J = 15.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 3.95 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 182.84, 167.61, 165.97, 165.71, 140.16, 137.76, 136.92, 135.27, 135.13, 133.66, 133.03, 132.41, 130.04, 129.87, 129.73, 128.78, 122.73, 122.36, 117.28, 113.50, 112.45, 60.88, 52.47, 14.14; HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{NaO}_6$ $[\text{M}+\text{Na}^+]$ 479.1214, found 479.1227.

(E)-ethyl-3-(1-(3-cyanobenzoyl)-5-(2,3-dimethylbenzoyl)-1H-pyrrol-2-yl)acrylate (2p)



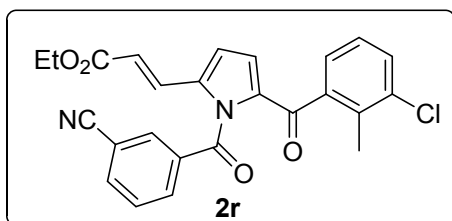
^1H NMR (600 MHz, CDCl_3) δ 8.00 (d, $J = 7.8$ Hz, 1H), 7.85-7.80 (m, 2H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.51 (d, $J = 15.6$ Hz, 1H), 7.40 (d, $J = 7.8$ Hz, 1H), 7.08-7.02 (m, 2H), 6.83 (d, $J = 4.2$ Hz, 1H), 6.74 (d, $J = 4.2$ Hz, 1H), 6.45 (d, $J = 15.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 185.63, 167.88, 165.91, 141.72, 137.88, 137.22, 137.05, 136.73, 135.67, 133.60, 133.06, 132.30, 130.21, 129.95, 128.97, 125.89, 122.52, 121.78, 117.42, 113.37, 112.29, 60.86, 21.36, 19.69, 14.21; HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 449.1472, found 449.1494.

(E)-ethyl-3-(1-(3-cyanobenzoyl)-5-(2,4-dimethylbenzoyl)-1H-pyrrol-2-yl)acrylate (2q)



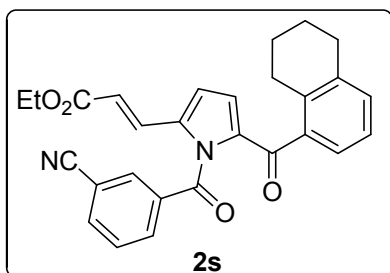
^1H NMR (500 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 1H), 7.85-7.79 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.51 (d, $J = 15.5$ Hz, 1H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.08-7.02 (m, 2H), 6.83 (d, $J = 4.0$ Hz, 1H), 6.74 (d, $J = 4.0$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 4.22 (q, $J = 7.0$ Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.63, 167.88, 165.92, 141.71, 137.88, 137.23, 137.06, 136.72, 135.70, 133.64, 133.07, 132.30, 130.22, 129.94, 128.97, 125.90, 122.50, 121.79, 117.41, 113.39, 112.29, 60.86, 21.37, 19.69, 14.22; HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}^+]$ 427.1652, found 427.1649.

(E)-ethyl-3-(5-(3-chloro-2-methylbenzoyl)-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (2r)



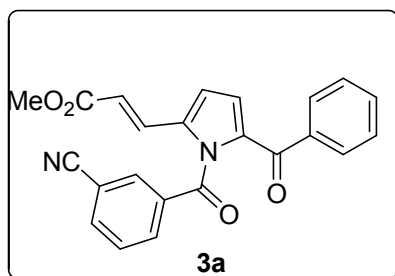
^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, $J = 7.8$ Hz, 1H), 7.88-7.85 (m, 1H), 7.82 (s, 1H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.50- 7.45 (m, 2H), 7.29- 7.26 (m, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 6.84 (d, $J = 4.2$ Hz, 1H), 6.71 (d, $J = 4.2$ Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.23 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 184.76, 167.78, 165.76, 138.68, 138.03, 136.97, 136.18, 135.45, 135.00, 133.13, 132.29, 131.65, 130.08, 129.84, 126.36, 126.34, 123.18, 122.58, 117.34, 113.50, 112.40, 60.97, 16.85, 14.20; HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}^+]$ 447.1106, found 447.1103.

(*E*)-ethyl-3-(1-(3-cyanobenzoyl)-5-(5,6,7,8-tetrahydronaphthalene-1-carbonyl)-1*H*-pyrrol-2-yl)acrylate (2s)



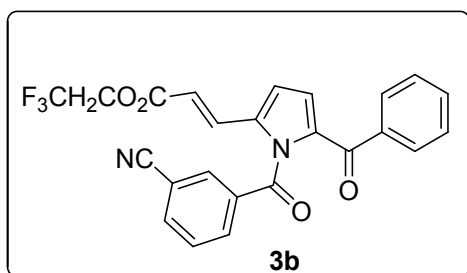
^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 7.8$ Hz, 1H), 7.83 (t, $J = 7.8$ Hz, 2H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.50 (d, $J = 16.2$ Hz, 1H), 7.24-7.12 (m, 3H), 6.83 (d, $J = 4.2$ Hz, 1H), 6.73 (d, $J = 4.2$ Hz, 1H), 6.45 (d, $J = 16.2$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.78 (t, $J = 5.4$ Hz, 2H), 2.62 (t, $J = 6.0$ Hz, 2H), 1.77-1.67 (m, 4H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 186.24, 167.92, 165.89, 138.57, 137.45, 136.95, 136.75, 136.48, 136.28, 135.66, 133.11, 132.28, 132.20, 130.14, 129.96, 125.80, 124.74, 122.80, 121.97, 117.42, 113.36, 112.31, 60.89, 29.78, 26.79, 22.73, 22.42, 14.21; HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}^+]$ 475.1628, found 475.1641.

(*E*)-methyl 3-(5-benzoyl-1-(3-cyanobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3a)



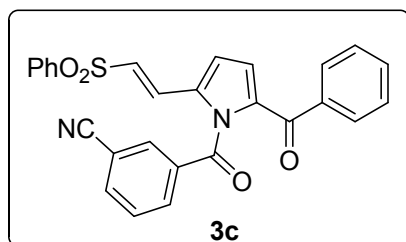
^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 7.6 Hz, 1H), 7.87 (m, 1H), 7.82-7.76 (m, 3H), 7.60-7.52 (m, 2H), 7.50-7.42 (m, 3H), 6.98 (d, J = 4.0 Hz, 1H), 6.89 (d, J = 4.0 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.75, 167.73, 166.28, 137.15, 136.79, 136.66, 135.71, 135.52, 133.06, 132.96, 132.37, 130.44, 129.99, 128.94, 122.35, 121.36, 117.35, 113.46, 112.47, 51.92; HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}^+]$ 385.1183, found 385.1340.

(E)-2,2,2-trifluoroethyl 3-(5-benzoyl-1-(3-cyanobenzoyl)-1H-pyrrol-2-yl)acrylate (3b)



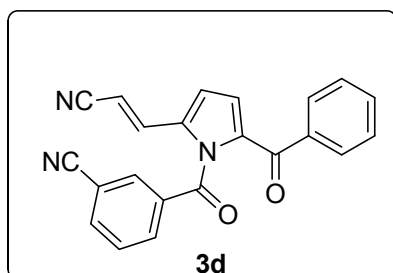
^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.82-7.76 (m, 3H), 7.64-7.52 (m, 3H), 7.50-7.44 (m, 2H), 7.00-6.92 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 4.55 (q, J = 8.4 Hz, 2H), 5.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.80, 167.55, 164.17, 136.84, 136.49, 136.46, 136.14, 135.39, 133.08, 133.00, 132.59, 132.35, 130.01, 129.95, 128.65, 122.84 (q, J = 275.6 Hz), 122.25, 118.97, 118.71, 117.27, 113.47, 113.16, 60.44 (q, J = 36.4 Hz); HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_4$ $[\text{M}+\text{H}^+]$ 453.1057, found 453.1121.

(E)-3-(2-benzoyl-5-(2-(phenylsulfonyl)vinyl)-1H-pyrrole-1-carbonyl)benzonitrile (3c)



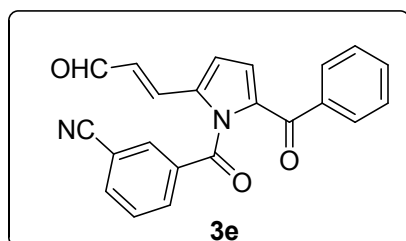
^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.92-7.84 (m, 3H), 7.84-7.74 (m, 3H), 7.66-7.50 (m, 6H), 7.50-7.42 (m, 2H), 6.94 (d, $J = 4.0$ Hz, 1H), 6.87 (d, $J = 15.2$ Hz, 1H), 6.82 (d, $J = 4.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.83, 167.38, 139.89, 136.93, 136.41, 136.37, 135.25, 134.64, 133.72, 133.21, 133.06, 132.40, 130.11, 130.06, 129.45, 128.99, 128.69, 128.62, 127.75, 122.06, 117.25, 113.85, 113.52; HRMS (ESI): calcd for $\text{C}_{27}\text{H}_{19}\text{SN}_2\text{O}_4$ $[\text{M}+\text{H}^+]$ 467.1060, found 467.1282.

(E)-3-(2-benzoyl-5-(2-cyanovinyl)-1H-pyrrole-1-carbonyl)benzonitrile (3d)



^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.0$ Hz, 1H), 7.85-7.75 (m, 4H), 7.64-7.54 (m, 2H), 7.50-7.44 (m, 2H), 7.34-7.25 (m, 1H), 6.98 (d, $J = 4.0$ Hz, 1H), 6.89 (d, $J = 4.0$ Hz, 1H), 5.92 (d, $J = 16.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.86, 167.45, 136.97, 136.38, 136.35, 136.27, 135.83, 133.26, 132.97, 132.24, 130.10, 128.96, 128.74, 122.16, 117.21, 117.18, 113.55, 112.50, 99.24; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}^+]$ 352.1081, found 352.1263.

(E)-3-(2-benzoyl-5-(3-oxoprop-1-en-1-yl)-1H-pyrrole-1-carbonyl)benzonitrile (3e)



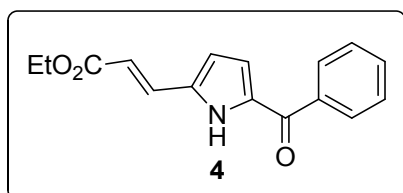
^1H NMR (400 MHz, CDCl_3) δ 9.60 (d, $J = 7.6$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.91 (s, 1H), 7.83-7.77 (m, 3H), 7.64-7.54 (m, 2H), 7.52-7.45 (m, 2H), 7.42 (d, $J = 16.0$ Hz

1H), 7.04-7.96 (m, 2H), 6.71 (dd, $J = 16.0, 7.6$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.53, 183.87, 167.67, 137.17, 136.86, 136.67, 136.62, 136.37, 135.44, 133.19, 132.86, 132.27, 130.71, 130.03, 128.93, 128.69, 122.37, 117.20, 113.73, 113.50; HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}^+]$ 355.1077, found 355.1461.

2.5 The procedure for the removal of N protecting group.

A 10 mL tube sealing was charged with **2a** (0.1 mmol) and HCl/EtOH (1:5) (6 mL). After stirring at 90 °C for 3 h, the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **4**.

(*E*)-ethyl 3-(5-benzoyl-1H-pyrrol-2-yl)acrylate (**4**)



^1H NMR (500 MHz, CDCl_3) δ 10.82 (s, 1H), 7.95 (d, $J = 7.0$ Hz, 2H), 7.67 (d, $J = 16.0$ Hz, 1H), 7.63-7.57 (m, 1H), 7.52 (t, $J = 7.5$ Hz, 2H), 6.92-6.88 (m, 1H), 6.64-6.60 (m, 1H), 6.53 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.5$ Hz, 2H), 1.33 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.26, 166.79, 137.92, 134.68, 133.11, 133.00, 132.34, 129.25, 128.49, 120.85, 118.12, 114.30, 60.70, 14.38; HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}^+]$ 270.1125, found 270.1139.

3. NMR spectra

