One-pot metal-free synthesis of highly substituted pyrroles from 2-acetyl-3-methylene-1,4-dicarbonyl compounds and primary amines via TBHP and activated carbon oxidative aromatization of dihydropyrrole

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(A) General Information

The reagents (chemicals) were purchased from commercial sources, and used without further purification. The activated carbon was purchased from Sigma-Aldrich (DARCO®, powder; particle size, 100 mesh). Toluene used in reactions was reagent grade and distilled from Na. Analytical thin-layer chromatography (TLC) was performed on HSGF 254 (0.15-0.2 mm thickness), visualized by irradiation with UV light (254 nm). All products were characterized by their NMR and MS SPECTRA. ¹H and ¹³C NMR spectra were recorded in deuterchloroform (CDCl₃) on a 400MHz or 500MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns were described as singlet(s), doublet (d), triplet (t), quartet (q), multiple (m), and broad (br). Low-and high-resolution mass spectra (LRMS and HRMS) were measured on spectrometer.

(B) General procedure for the synthesis of substrate 1a, 1u-y.¹²

(Z)-3-(1-hydroxyethylidene)-4-methylenehexane-2,5-dione 1a

2, 4-Pentanedione (1.0 mmol) was added to a vigorously stirred solvent of Ph₃P (0.1 mmol, 0.1 equiv) in CH₂Cl₂ (4 mL) at room temperature under N₂ atmosphere. Immediately, 3-butyn-2-one (1.5 mmol) was added. The solution became deep red. The mixture was stirred for 3 h and was concentrated. Purification by flash chromatography [silica gel; petroleum ether/ethyl acetate (10/1)] gave pure product
(120 mg; 71% yield). The spectroscopic data were in accordance with those reported in literature.¹

(Z)-4-(1-hydroxypropylidene)-3-methyleneheptane-2,5-dione 1z

(Z)-4-(1-hydroxypropylidene)-3-methyleneheptane-2,5-dione was prepared similarly to the 1a. And the spectroscopic data were in accordance with those reported in literature.¹

3-Benzoyl-4-methylenehexane-2,5-dione 1aa

3-benzoyl-4-methylenehexane-2,5-dione was prepared similarly to the 1a. And the spectroscopic data were in accordance with those reported in literature.¹

Ethyl 2-acetyl-3-methylene-4-oxopentanoate 1ab

Ethyl 2-acetyl-3-methylene-4-oxopentanoate was prepared similarly to the 1a. And the spectroscopic data were in accordance with those reported in literature.¹

(Z)-3-(1-hydroxyethylidene)-2-methylene-1-phenylpentane-1,4-dione 1ac
(Z)-3-(1-hydroxyethylidene)-2-methylene-1-phenylpentane-1,4-dione was prepared similarly to the 1a. And the spectroscopic data were in accordance with those reported in literature.¹

(Z)-ethyl 3-acetyl-4-hydroxy-2-methylenepent-3-enoate 1ad

![1ad](image)

Under argon atmosphere, a mixture of 2,4-pentanedione (1 g, 10 mmol), triphenylphosphine (262 mg, 1 mmol), and sodium acetate (410 mg, 5 mmol) in toluene (20 mL) was heated to reflux. After introduction of acetic acid (300 mg; 5 mmol) in one portion, ethyl propiolate (981 mg, 10 mmol) was added dropwise. The resulting mixture was stirred under reflux for 0.5 h, filtered, and concentrated. Purification by flash chromatography (silica gel; hexane/ethyl acetate (90/10)) gave pure product (1.74 g; 88% yield). The spectroscopic data were in accordance with those reported in literature.²

(C) General procedures for the synthesis of polysubstituted pyrrole derivatives 3.

![Reaction Scheme](image)

To a solution of substrate 1 (0.25 mmol), and amines 2 (0.5 mmol) in toluene (1 mL) was added 150 μL TBHP in decane solution (5.5 M), followed by 36 mg activated
carbon, then the reaction mixture was stirred at RT for 18h. The substrate 1 was consumed completely monitored by TLC. The mixture was filtered through celite, washed with methanol, then the filtration was concentrated, and the residue was purified by column chromatography, hexane/EtOAc (v/v, 10/1 then 4/1) as eluent, giving the desired pyrroles derivatives 3.

(D) Proton and Carbon NMR spectra for all compounds

1, 1’-(2-Methyl-1-phenyl-1H-pyrrole-3,4-diyl)dienethanone 3a

Isolated yield 93% $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.50-7.36 (m, 3H), 7.22 (d, $J$ = 7.6 Hz, 2H), 7.19 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.12 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 200.2, 192.84, 137.98, 134.85, 129.64, 128.91, 127.93, 126.21, 124.65, 123.56, 31.40, 27.72, 11.81 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{15}$H$_{15}$NO$_2$Na: 264.1000, found: 264.1002.

1, 1’-(1-(3-Ethylphenyl)-2-methyl-1H-pyrrole-3,4-diyl)dienethanone 3b

Isolated yield 80% , $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.39-7.35 (t, $J$ = 7.6 Hz, 1H), 7.28-7.26 (m, 1H), 7.23 (s, 1H), 7.08-7.05 (m, 2H), 2.72-2.66 (q, $J$ = 7.6 Hz, 2H), 2.476 (s, 3H) 2.41 (s, 3H), 2.16 (s, 3H), 1.26-1.22 (t, $J$ = 7.6 Hz, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 200.09, 192.78, 146.14, 137.97, 134.88, 129.43, 128.45, 127.97,

1, 1'- (2-Methyl-1-(p-tolyl)-1H-pyrrole-3,4-diyl) diethanone 3c

Isolated yield 80%, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.29-7.28 (dd, \(J = 8.0\) Hz, 2H), 7.22 (s, 1H), 7.16-7.14 (dd, \(J = 8.0\) Hz, 2H), 2.49 (s, 3H), 2.42 (s, 6H), 2.16 (s, 3H) ppm. \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\): 199.60, 192.30, 138.52, 134.95, 134.49, 129.66, 127.519, 125.50, 124.03, 122.93, 30.87, 27.20, 20.66, 11.25 ppm. HRMS (ESI) calcd for [M+Na]^+ C_{16}H_{17}NO_2Na: 278.1157, found: 278.1158.

1, 1'- (2-Methyl-1-(o-tolyl)-1H-pyrrole-3, 4-diyl) diethanone 3d

Isolated yield 85%, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.40-7.37 (t, \(J = 7.0, 7.5\) Hz, 1H), 7.34-7.33 (d, \(J = 7.5\) Hz, 1H), 7.31-7.28 (t, \(J_1 = 7.0, 7.5\) Hz, 1H), 7.15-7.14 (d, \(J = 7.5\) Hz, 1H), 7.13 (s, 1H), 2.51 (s, 3H), 2.50 (s, 3H), 2.41 (s, 3H), 2.41 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H) ppm. \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\): 199.85, 192.88, 136.93, 135.74, 135.58, 131.20, 129.65, 127.72, 127.62, 127.04, 124.64, 122.75, 31.37, 27.77, 17.25, 11.21 ppm. HRMS (ESI) calcd for [M+Na]^+ C_{16}H_{17}NO_2Na: 278.1157, found: 278.1157.
1, 1’-(1-(4-Methoxyphenyl)-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3e

Isolated yield 80%, $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.19 (s, 1H), 7.17-7.150 (d, $J = 8.8$ Hz, 2H), 6.97-6.95 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H), 2.12 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 200.05, 192.74, 159.71, 135.17, 130.68, 128.14, 127.39, 124.34, 123.19, 114.60, 55.58, 31.29, 27.64, 11.62 ppm.

HRMS (ESI) calcd for [M+Na]$^+$ C$_{16}$H$_{18}$NO$_3$: 272.1287, found: 272.1285.

1, 1’-(2-Methyl-1-(naphthalen-2-yl)-1H-pyrrole-3, 4-diyl)diethanone 3f

Isolated yield 78%, $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.98-7.96(dd, $J = 11.5$ Hz, 1H), 7.94-7.92 (m, 1H), 7.90-7.88 (m, 1H), 7.77 (d, $J = 2$ Hz, 1H), 7.61-7.58 (m, 2H), 7.38-7.36 (dd, $J = 9$, 2Hz 1H), 7.34 (s, 1H), 2.54(s, 3H), 2.46 (s, 3H), 2.24(s, 3H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) δ: 200.20, 192.86, 135.38, 135.11, 133.14, 132.78, 129.75, 128.12, 128.02, 127.96, 127.49, 127.33, 124.91, 124.77, 123.90, 123.69, 31.45, 27.79, 11.95 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{19}$H$_{17}$NO$_2$Na: 314.1157, found: 314.1158.

1, 1’-(1-(3, 4-Dimethylphenyl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3g

Isolated yield 75%, $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.22-7.20 (dd, $J = 8.0$ Hz, 1H), 7.20 (s, 1H), 7.02 (s, 1H), 6.98-6.96 (dd, $J = 2.0$, 8.0Hz, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H), 2.29 (s, 3H), 2.15 (s, 3H). ppm $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 200.15,
192.84, 138.22, 137.65, 135.63, 135.05, 130.50, 128.13, 127.12, 124.37, 123.40, 123.27, 31.36, 27.70, 19.87, 19.51, 11.78 ppm. HRMS (ESI) calcd for [M+H]$^+$ C$_{17}$H$_{20}$NO$_2$: 270.1494, found: 270.1487.

1, 1'-(1-(2, 4-Dimethylphenyl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3h

Isolated yield 85%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.13 (br, 1H), 7.10 (s, 1H), 7.09-7.07 (m, 1H), 7.02-7.00 (dd, $J$ = 8 Hz, 1H), 2.49 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 199.84, 192.89, 139.68, 135.91, 135.13, 134.36, 131.77, 127.85, 127.62, 127.42, 124.52, 122.66, 31.34, 27.74, 21.12, 17.15, 11.20 ppm. HRMS (ESI) calcd for [M+H]$^+$ C$_{17}$H$_{20}$NO$_2$: 270.1494, found: 270.1493.

1, 1'-(1-(4-Fluoro-2-methylphenyl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3i

Isolated yield 93%, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.15-7.12 (dd, $J$ = 5, 8.5Hz, 1H), 7.10 (s, 1H), 7.04-7.02 (dd, $J$=2.5, 9 Hz, 1H), 6.99-6.96 (dt, $J$ = 2.5, 8.5 Hz, 1H), 2.47 (s,3H), 2.40 (s, 3H), 2.01 (s, 3H), 1.20 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 199.79, 192.84, 163.63, 161.65, 138.32, 138.25, 135.67, 132.92, 132.90, 129.46, 129.39, 127.66, 124.77, 122.89, 117.87, 117.70, 114.07, 113.89, 31.32, 27.74, 17.44, 11.12 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{16}$H$_{16}$FNO$_2$Na: 296.1063, found: 296.1069.
1, 1’-(1-(Benzo[d][1,3]dioxol-5-yl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3j

Isolated yield 52%, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.19 (s, 1H) 6.87-6.86 (d, $J = 8.5$ Hz, 1H), 6.74-6.71 (m, 2H), 6.06(s, 2H), 2.48(s, 3H), 2.41 (s, 3H), 2.15(s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 200.17, 192.80, 148.31, 148.06, 135.17, 131.74, 128.14, 124.42, 123.30, 119.95, 108.44, 107.44, 102.17, 31.37, 27.72, 11.69 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{16}$H$_{15}$NO$_4$Na: 308.0899, found: 308.0898.

1, 1’-(1-(4-Bromophenyl)-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3k

Isolated yield 80%, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.63-7.61 (d, $J = 8.0$ Hz, 2H), 7.21 (s, 1H), 7.17-7.16 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 2.16 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 200.08, 192.74, 136.98, 134.52, 132.85, 127.80, 127.56, 124.93, 123.87, 122.87, 31.38, 27.74, 11.75 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{15}$H$_{14}$NO$_2$BrNa: 342.0106, found: 342.0109.

1, 1’-(1-(3-Ethynylphenyl)-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3l

Isolated yield 76%, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.59-7.57 (d, $J = 8$Hz, 1H), 7.49-7.46(t, $J = 8$ Hz, 1H), 7.42-7.42 (d, $J = 2$Hz, 1H), 7.30-7.27 (m, 1H), 7.25 (s, 1H), 3.20 (s, 1H), 2.50 (s, 3H), 2.44 (s, 3H), 2.19 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$)

1, 1’-(1-(3-Chlorophenyl)-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3m

Isolated yield 80%, ¹H NMR (500 MHz, CDCl₃) δ: 7.45-7.44 (m, 2H), 7.31-7.30 (m, 1H), 7.23 (s, 1H), 7.20-7.18 (m, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 2.18 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ: 200.10, 192.75, 139.02, 135.26, 134.51, 130.67, 129.16, 127.58, 126.53, 124.94, 124.50, 123.88, 31.39, 27.72, 11.77 ppm. HRMS (ESI) calcd for [M+Na]⁺ C₁₅H₁₄NO₂ClNa: 298.0611, found: 298.0609.

Ethyl 4-(3, 4-diacetyl-2-methyl-1H-pyrrol-1-yl)benzoate 3n

Isolated yield 50%, ¹H NMR (500 MHz, CDCl₃) δ: 8.12-8.11 (d, J = 8.5 Hz, 2H), 7.31-7.29 (d, J = 8.5 Hz, 2H), 7.20 (s, 1H), 4.37-4.32 (q, J = 7.0 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H), 2.14 (s, 3H), 1.36-1.33 (t, J = 7.0 Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ: 200.07, 192.72, 165.40, 141.64, 134.33, 131.01, 130.83, 127.35, 125.97, 125.18, 124.23, 61.55, 31.39, 27.72, 14.31, 11.87 ppm. HRMS (ESI) calcd for [M+H]⁺ C₁₈H₂₀NO₄: 314.1392, found: 314.1393.
N-(4-(3, 4-diacetyl-2-methyl-1H-pyrro1-yl)phenyl)acetamide 3o

Isolated yield 70%, $^1$H NMR (500 MHz, MeOD) $\delta$: 7.76-7.74 (d, $J = 8.5$ Hz, 2H), 7.63 (s, 1H), 7.34-7.33 (d, $J = 8.5$ Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H) ppm. $^{13}$C NMR (126 MHz, MeOD) $\delta$: 201.31, 194.50, 170.49, 139.28, 135.15, 133.33, 129.56, 126.51, 124.15, 122.78, 120.26, 30.03, 26.24, 22.52, 10.42 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{17}$H$_{18}$N$_2$O$_3$Na: 321.1215, found: 321.1213.

1, 1’-(1-(4-Aminophenyl)-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3p

Isolated yield 56%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.18 (s, 1H), 7.03-7.01 (d, $J = 8.8$ Hz, 2H), 6.74-6.71 (d, $J = 8.8$ Hz, 2H), 3.93 (br, 2H), 2.50 (s, 3H), 2.42 (s, 3H), 2.15 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 199.78, 192.40, 146.61, 135.03, 128.10, 127.89, 126.82, 123.74, 122.59, 114.66, 30.90, 27.24, 11.23. HRMS (ESI) calcd for [M+Na]$^+$ C$_{15}$H$_{16}$N$_2$O$_2$Na: 279.1109, found: 279.1116.

1, 1’-(1-(3, 4-Dichlorophenyl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3q

Isolated yield 62%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.60-7.58 (d, $J = 8.5$ Hz, 1H), 7.44-7.43 (d, $J = 2.4$ Hz, 1H), 7.21 (s, 1H), 7.18-7.15 (d, $J = 8.5$, 2.5 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.19 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 199.92, 192.65, 137.21, 134.32, 133.70, 133.42, 131.31, 128.17, 127.35, 125.54, 125.13, 124.08,
31.35, 27.71, 11.69 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{15}$H$_{13}$NO$_2$Cl$_2$Na: 332.0221, found: 332.0224.

1, 1'-(1-Isopentyl-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3s

Isolated yield 40%, $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.09 (s, 1H), 3.82-3.79 (t, $J = 8.0$ Hz, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 1.63-1.58 (m, 3H), 0.96-0.95 (d, $J = 6.0$ Hz, 6H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 200.30, 192.57, 134.16, 126.88, 123.82, 123.16, 45.55, 39.60, 31.34, 27.65, 25.72, 22.37, 10.57 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{14}$H$_{21}$NO$_2$Na: 258.1470, found: 258.1472.

1, 1'-(1-Benzyl-2-methyl-1H-pyrrole-3, 4-diyl)diethanone 3t

Isolated yield 46%, $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.38-7.31 (m, 3H), 7.14 (s, 1H), 7.06-7.03(d, $J = 8.0$ Hz, 2H), 5.04 (s, 2H), 2.47 (s, 3H), 2.39 (s, 3H), 2.21 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 199.72, 192.14, 135.15, 134.15, 128.66, 127.76, 127.10, 126.14, 123.64, 123.10, 50.41, 30.91, 27.21, 10.22 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{16}$H$_{17}$NO$_2$Na: 278.1157, found: 278.1152.

1,1'-(1-Butyl-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3u
Isolated yield 32%, $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.10 (s, 1H), 3.85-3.81 (t, $J = 7.4$ Hz, 2H), 2.48 (s, 3H), 2.42 (s, 3H), 2.30 (s, 3H), 1.77-1.67 (m, 2H), 1.43-1.33(m, $J = 14.9$, 7.4 Hz, 2H), 1.00-0.96 (t, $J = 7.3$ Hz, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 199.71, 192.03, 133.68, 126.49, 123.29, 122.65, 46.45, 32.20, 30.82, 27.12, 19.33, 13.12, 10.07 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{13}$H$_{19}$NO$_2$Na: 244.1313, found:244.1312.

1,1’-(1-Allyl-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3v

Isolated yield 35%, $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.09 (s, 1H), 5.90 (m, $J = 17.0$, 10.3, 5.1 Hz, 1H), 5.26 (dd, $J = 10.3$, 0.7 Hz, 1H), 5.00 (dd, $J = 17.0$, 0.7 Hz, 1H), 4.43 (dt, $J = 5.1$, 1.7 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 199.67, 192.08, 133.98, 131.74, 126.68, 123.53, 122.88, 117.81, 49.00, 30.89, 27.19, 9.96 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{12}$H$_{15}$NO$_2$Na: 228.1000, found: 228.1000.

1,1’-(1-(3-Methoxypropyl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3w

Isolated yield 25%, $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.10 (s,1H), 3.94 (t, $J = 7.0$ Hz, 2H), 3.33 (s, 3H), 3.31 (t, $J =5.6$ Hz, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H), 1.93 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 199.71, 192.06, 133.86, 126.89, 123.43,
122.72, 67.83, 58.25, 43.33, 30.88, 30.05, 27.18, 10.00 ppm. HRMS (ESI) calcd for [M+Na]^+ C_{13}H_{19}NO_3Na: 260.1263, found: 228.1256.

1,1’-(1-Isopropyl-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3x
Isolated yield 18%, ^1H NMR (400 MHz, CDCl_3) δ: 7.18 (s, 1H), 4.31 (hept, J = 6.8 Hz, 1H), 2.46 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H), 1.44 (d, J = 6.8 Hz, 6H) ppm. ^13C NMR (101 MHz, CDCl_3) δ: 200.09, 192.04, 132.96, 123.75, 122.68, 122.15, 47.14, 30.96, 27.15, 22.86, 9.97 ppm. HRMS (ESI) calcd for [M+Na]^+ C_{12}H_{17}NO_2Na: 230.1157, found: 230.1159.

1,1’-(1-(Tert-butyl)-2-methyl-1H-pyrrole-3,4-diyl)diethanone 3y
Isolated yield 10%, ^1H NMR (400 MHz, CDCl_3) δ: 7.30 (s, 1H), 2.46 (s, 6H), 2.40 (s, 3H), 1.65 (s, 9H) ppm. ^13C NMR (101 MHz, CDCl_3) δ: 201.21, 191.87, 132.67, 125.35, 124.42, 121.88, 57.28, 31.28, 30.01, 26.82, 13.46 ppm. HRMS (ESI) calcd for [M+Na]^+ C_{13}H_{19}NO_2Na: 244.1313, found: 244.1307.

1-(4-Acetyl-2-ethyl-1-phenyl-1H-pyrrol-3-yl)propan-1-one 3z
Isolated yield 82%, ^1H NMR (500 MHz, CDCl_3) δ: 7.51 - 7.47 (m, 3H), 7.31 -7.29 (m, 2H), 7.20 (s, 1H), 2.84-2.80 (q, J = 7.5 Hz, 2H), 2.58-2.53 (q, J = 7.5 Hz, 2H),
2.40 (s, 3H), 1.18-1.15 (t, J = 7.5 Hz, 3H), 0.93-0.90 (t, J = 7.5 Hz, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 204.43, 192.72, 139.40, 138.22, 129.58, 129.02, 127.96, 126.56, 124.32, 122.92, 36.93, 27.41, 18.17, 14.74, 8.87 ppm. HRMS (ESI) calcd for [M+H]$^+$ C$_{16}$H$_{18}$NO$_3$: 272.1281, found: 272.1279.

1-(4-Benzoyl-5-methyl-1-phenyl-1H-pyrrol-3-yl)ethanone 3aa

Isolated yield 80%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.88-7.86 (m, 2H), 7.54-7.47 (m, 4H), 7.44-7.40 (m, 2H), 7.37-7.34 (m, 3H), 2.25 (s, 3H), 2.13 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 194.07, 191.74, 138.78, 137.75, 133.03, 132.12, 129.16, 128.73, 128.30, 127.82, 126.28, 125.67, 125.56, 121.19, 27.05, 11.08 ppm. HRMS (ESI) calcd for [M+H]$^+$ C$_{20}$H$_{18}$NO$_2$: 304.1332, found: 304.1331.

Ethyl 4-acetyl-2-methyl-1-phenyl-1H-pyrrole-3-carboxylate 3ab

Isolated yield 76%, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.49-7.43 (m, 3H), 7.26-7.25 (d, J = 7.5Hz, 2H), 7.17 (s, 1H), 4.36-4.32 (q, J = 7.5 Hz, 2H), 2.45 (s, 3H), 2.28 (s, 3H), 1.37-1.34(t, J = 7.5 Hz, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 194.51, 165.60, 138.13, 135.92, 129.57, 128.77, 126.29, 126.21, 125.89, 113.37, 60.57, 34.45, 29.09, 23.82, 14.24, 11.97 ppm. HRMS (ESI) calcd for [M+H]$^+$ C$_{16}$H$_{18}$NO$_3$: 270.1489, found: 270.1488.
1-(4-Benzoyl-2-methyl-1-phenyl-1H-pyrrol-3-yl)ethanone 3ac

Isolated yield 80%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.94-7.92 (m, 2H), 7.58-7.54 (m, 1H), 7.51-7.45 (m, 5H), 7.32-7.28 (m, 2H), 7.00 (s, 1H), 2.40 (s, 3H), 2.32 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 197.76, 190.30, 138.73, 137.46, 135.71, 131.96, 129.125, 129.00, 128.40, 128.11, 127.94, 125.79, 123.63, 123.61, 30.62, 11.77 ppm. HRMS (ESI) calcd for [M+Na]$^+$ C$_{20}$H$_{17}$NO$_2$Na: 326.1157, found: 326.1156.

Ethyl 4-acetyl-5-methyl-1-phenyl-1H-pyrrole-3-carboxylate 3ad

Isolated yield 30%, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.48-7.44 (m, 3H), 7.29 (s, 1H), 7.27-7.25 (m, 2H), 4.32-4.26 (q, $J = 7.2$ Hz, 2H), 2.57 (s, 3H), 2.22 (s, 3H), 1.34-1.31 (t, $J = 7.2$ Hz, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 198.57, 163.69, 137.62, 134.30, 129.06, 128.26, 127.14, 125.72, 123.23, 114.51, 59.82, 31.08, 13.87, 11.69 ppm. HRMS (ESI) calcd for [M+H]$^+$ C$_{16}$H$_{18}$NO$_3$: 272.1281, found: 272.1284.

1, 1’-(1-(4-Methoxyphenyl)-5-methyl-2,3-dihydro-1H-pyrrole-3,4-diyl)diethanone 3e’

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.04 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 4.09 (dd, $J = 11.2$, 5.4 Hz, 1H), 3.96 (t, $J = 11.0$ Hz, 1H), 3.86 (dd, $J = 10.9$, 5.4 Hz, 2H),
$^1$H), 3.78 (s, 3H), 2.28 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$)

δ: 210.14, 190.79, 160.29, 158.44, 133.02, 127.18, 114.74, 113.14, 57.04, 55.52, 52.21, 28.59 (2× CH$_3$), 14.77. HRMS (ESI) calcd for [M+H]$^+$ C$_{16}$H$_{20}$NO$_3$: 274.1443, found: 274.1440.
$^{13}$C NMR (125 MHz, CDCl$_3$): δ 189.946, 182.850, 157.218, 154.931, 153.702, 138.642, 131.308, 128.174, 127.529, 123.542, 121.139, 120.679, 31.752, 27.798, 11.495
Reference:
