Supporting Information

Synthesis of Multisubstituted Furans, Pyrroles and Thiophenes via Ynolates

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Materials. Dry tetrahydrofuran was purchased and used without further purification. *tert*-Butyllithium was titrated with diphenylacetic acid. Dibromoesters were prepared according to the references.¹

General Procedures. ¹H-NMR were measured in CDCl₃ solution and referenced to TMS (0.00 ppm). ¹³C-NMR were measured in CDCl₃ solution and referenced to CDCl₃ (77.0 ppm). Column chromatography was performed on silica gel. Melting points are uncorrected. All reactions were performed in oven-dried glassware under positive pressure of argon, unless otherwise noted. Reaction mixtures were stirred magnetically. Solutions of alkylolithium reagents were transferred by syringe or cannula and were introduced into reaction vessels through septum rubber.

Preparation of α -Acyloxy Ketones (5)

Typical Procedure for Preparation of α -Acyloxy ketones

To a solution of 2-hydroxy-1-propanone (1.0 g, 6.7 mmol)² and pyridine (2.7 mL, 33 mmol) in CH₂Cl₂ (6.7 mL), was added isobutyryl chloride (1.1 g, 10 mmol) and 4-DMAP (0.81 g, 6.7 mmol) at 0 °C, and the solution was stirred for 1.5 h at room temperature. Saturated aqueous NaHCO₃ solution was added to the mixture, which was extracted with ethyl acetate. The organic layer was washed with water and brine, dried over MgSO₄, and concentrated. The residue was purified by bulb-bulb distillation (130 °C, 1.1 mmHg) to provide **5a** (1.18 g, 80%) as a pale yellow oil.

1-Methyl-2-oxo-2-phenylethyl isobutyrate (**5a**):

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.20 (dd, $J=2.6, 7.0$ Hz, 6H), 1.53 (d, $J=7.2$ Hz, 3H), 2.65 (sept, $J=6.8$ Hz, 1H), 5.95 (q, $J=6.8$ Hz, 1H), 7.48 (t, $J=7.6$ Hz, 2H), 7.59 (tt, $J=1.2, 7.6$ Hz, 1H), 7.93 (dd, $J=1.4, 8.6$ Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 17.0(q), 18.8 (q), 18.9 (q), 33.7 (d), 71.0 (d), 128.3 (d), 128.6 (d), 133.3 (d), 134.4 (s), 176.3 (s), 196.9 (s); IR(neat): 1737, 1699 cm^{-1} ; MS (EI): m/z 220 (M^+), 45 (100%); HRMS(APCI) Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3$ ($\text{M}+\text{H}$): 221.1178, found 221.1198.

1-Methyl-2-oxo-2-phenylethyl acetate (5b)³:

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.53 (d, $J = 7.2$ Hz, 3H), 2.14 (s, 3H), 5.97 (q, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.59 (tt, $J=1.2, 7.4$ Hz, 1H), 7.94 (dd, $J = 1.4, 8.6$ Hz, 2H); IR (neat): 1740, 1700 cm^{-1}

1-Methyl-2-oxo-2-phenylethyl benzoate (5c)³

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.67 (d, $J=7.2$ Hz, 3H), 6.21 (q, $J=7.2$ Hz, 1H), 7.42-7.50 (m, 4H), 7.55-7.61 (m, 2H), 7.99-8.01 (m, 2H), 8.08-8.10 (m, 2H); IR (0.2mm KBr, CHCl_3): 1718, 1698 cm^{-1}

1-Methyl-2-oxo-2-phenylethyl 5-hexenoate (5d)

To a solution of 2-hydroxy-1-propanone (1.58 g, 10.5 mmol) and 5-hexenoic acid (1.00 g, 8.76 mmol) in CH₂Cl₂ (18 mL) was added EDCI (3.12 g, 10.5 mmol) and 4-DMAP (53 mg, 0.44 mmol) at room temperature. After being stirred for 1 h, water was added to the mixture, which was then extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried over MgSO₄, and concentrated. The residue was purified with column chromatography (5% EtOAc/hexane) to give 1.43 g (66%) of **5d** as a yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ: 1.53 (d, *J* = 6.8 Hz, 3H), 1.75 (quint, *J* = 7.6 Hz, 2H), 2.10 (q, *J* = 6.8 Hz, 2H), 2.42 (dt, *J* = 3.6, 7.6 Hz, 2H), 4.98 (d, *J* = 11.6 Hz, 1H), 5.02 (d, *J* = 18 Hz, 1H), 5.77 (ddt, *J* = 6.8, 11.6, 18 Hz, 1H), 5.97 (q, *J* = 6.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ: 17.1 (q), 23.9 (t), 32.9 (t), 33.2 (t), 71.2 (d), 115.3 (t), 128.3 (d), 128.6 (d), 133.4 (d), 134.3 (s), 137.5 (d), 172.8 (s), 196.7 (s); IR (neat): 1738, 1699 cm⁻¹; HRMS (APCI); Calcd for C₁₆H₁₉O₃ (M+H): 247.1334, found 247.1343.

2-Oxo-1,2-diphenylethyl benzoate (**5e**)⁴

mp. 125-126 °C (lit 123-124 °C), ¹H-NMR (400 MHz, CDCl₃) δ: 7.09 (s, 1H), 7.34-8.13 (m, 15H); IR (0.2mm KBr, CHCl₃): 1718, 1698 cm⁻¹

Preparation of α-Acylthio Ketones

S-1-Methyl-2-oxo-2-phenylethyl thioacetate (**5f**)⁵

colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.56 (d, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 5.29

(q, $J = 7.1$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.97 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7, 30.2, 42.3, 128.6, 128.7, 133.6, 134.9, 194.0, 197.3; IR (neat) 1682, 952 cm^{-1} ; MS (EI) m/z 208 (M^+); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}$ (M^+): 208.0558. found: 208.0559.

S-1-Methyl-2-oxo-2-phenylethyl thiobenzoate (5g)⁶

colorless prism (methanol, mp. 40-41.8 °C). ^1H NMR (400 MHz, CDCl_3) δ : 1.66 (d, $J = 7.2$ Hz, 3H), 5.51 (q, $J = 6.9$ Hz, 1H), 7.43-7.49 (m, 4H), 7.56-7.60 (m, 2H), 7.96 (d, $J = 7.7$ Hz, 2H), 8.04 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.7, 42.3, 127.3, 128.5, 128.6, 128.7, 133.5, 133.7, 134.9, 136.1, 190.0, 197.4; IR (neat) 1663, 1686 cm^{-1} ; MS (EI) m/z 270 (M^+).

S-2-Oxo-2-phenylethyl thioacetate (5h)⁷

pale yellow prism (methanol, mp. 43.8-44.2 °C). ^1H NMR (270 MHz, CDCl_3) δ : 2.41 (s, 3H), 4.41 (s, 2H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 8.00 (d, $J = 7.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 30.0, 36.4, 128.2, 128.5, 133.5, 135.3, 192.9, 193.9; IR (neat) 1682 cm^{-1} ; MS (EI) m/z 194 (M^+).

S-1-Methyl-2-oxo-2-phenylethyl thiophene-2-carbothioate (5i)

To a CH_2Cl_2 solution (50 ml) of 2-mercapto-1-phenylpropanone (996 mg, 6 mmol)⁸ was added pyridine (1.42 g, 18 mmol) and thiophene-2-carbonyl chloride (1.76 g, 12 mmol) at 0°C under argon. After being stirred at 0°C for 2 hr, H_2O (50 mL) was added and the resulting mixture was washed with a saturated NaHCO_3 solution, brine, dried over MgSO_4 , filtered and concentrated to afford a brown oil (2.60 g), which was chromatographed over silica gel (ethyl acetate/ hexane, 3%) to yield 1.45 g (85%) of **5i** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.66 (d, $J = 7.2$ Hz, 3H), 5.51 (q, $J = 7.9$ Hz, 1H), 7.11 (t, $J = 4.3$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.65 (d, $J = 4.8$ Hz, 1H) 7.80 (d, $J = 2.9$ Hz, 1H) 8.04 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.9, 42.4, 128.0, 128.6, 128.7, 131.7, 133.4, 133.6, 134.7, 140.9, 182.1, 197.2; IR (neat) $1651, 1684\text{ cm}^{-1}$; MS (EI) m/z 276 (M^+); HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}_2$ (M^+): 276.0279. found: 276.0277.

(E)-S-1-Methyl-2-oxo-2-phenylethyl thiocinnamate (5j)

colorless plate (AcOEt-hexane, mp. $76.1\text{--}77.0^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3) δ : 1.63 (d, $J = 6.8$ Hz, 3H), 5.45 (q, $J = 6.9$ Hz, 1H), 6.69 (d, $J = 15.5$ Hz, 1H), 7.26–7.60 (m, 8H), 7.66 (d, $J = 15.9$ Hz, 1H), 8.02 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.7, 42.0, 123.9, 128.4, 128.5, 128.6, 128.9, 130.8, 133.5, 133.7, 134.8, 141.7, 187.7, 197.3; IR (neat) $1614, 1674\text{ cm}^{-1}$; MS (EI) m/z : 296 (M^+), 191 (M-PhCO); Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}$: C, 72.94; H, 5.44. Found: C, 72.95; H, 5.48.

S-1-Methyl-2-oxo-butyl thiobenzoate (5k)

colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.10 (t, $J = 7.2$ Hz, 3H), 1.51 (d, $J = 7.2$ Hz, 3H), 2.53-2.63 (m, 1H), 2.72-2.82 (m, 1H), 4.53 (q, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H) 7.60 (t, $J = 7.7$ Hz, 2H) 7.96 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 7.8, 16.1, 33.3, 45.9, 127.2, 128.5, 133.6, 136.0, 190.2, 208.0; IR (neat) 908, 1665, 1717 cm^{-1} ; MS (EI) m/z 222 (M^+); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}$ (M^+): 222.0715. found: 222.0712.

S-1-Methyl-2-oxo-2-(2-thienyl)ethylthiobenzoate (5l)

colorless prism (AcOEt-hexane, mp. $64.8\text{--}65.2\text{ }^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3) δ 1.67 (d, $J = 7.2$ Hz, 3H), 5.35 (q, $J = 7.1$ Hz, 1H), 7.13-7.15 (m, 1H) 7.45 (t, $J = 7.7$ Hz, 2H) 7.58 (t, $J = 7.5$ Hz, 1H), 7.67-7.69 (m, 1H), 7.91-7.97 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.8, 43.0, 127.3, 128.3, 128.6, 132.8, 133.8, 134.7, 136.0, 141.9, 189.9, 190.3; IR (neat) $1651, 1672\text{ cm}^{-1}$; MS (EI) m/z : 276 (M^+), 277 ($\text{M}+1$); Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}_2$: C, 60.84; H, 4.38. Found: C, 60.87; H, 4.34.

Representative Procedure of Synthesis of Furans (Method A in Table 1)

2,3,5-Trimethyl-4-phenyl-furan (10)⁹: To a solution of ethyl 2,2-dibromopropionate (312 mg, 1.2 mmol) in THF (8 mL) was added *t*-BuLi (3.18 mL, 4.8 mmol, 1.51 M in pentane) at -78 °C. After being stirred for 3 h, the mixture was allowed to warm to 0 °C and stirred for 0.5 h. After cooled to -78 °C, a solution of **5b** (192 mg, 1.0 mmol) in THF was added and the mixture was stirred for 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl, and was extracted with EtOAc. The organic layer was washed by saturated NaHCO₃, brine and dried over MgSO₄ and concentrated to give a yellow oil (277 mg). The residue and *p*-toluenesulfonic acid monohydrate (19 mg, 0.1 mmol) was dissolved in benzene (25 mL) and the solution was heated under reflux for 5 h. To the reaction was added saturated NaHCO₃ solution, and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified with column chromatography (SiO₂, 1% EtOAc/hexane) to afford the furan **9** (131 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 1.90 (s, 3H), 2.23 (s, 3H), 2.26 (s, 3H), 7.25-7.30 (m, 3H), 7.39(t, *J* = 7.6 Hz, 2H); IR(neat): 1607, 1252, 1197, 1006, 994, 700 cm⁻¹; MS(EI): *m/z* 186 (M⁺), 43(100%).

Isolation of β-lactone intermediate (**8**):

The crude product was recrystallized from ethanol/pentane to give colorless prisms: mp. 142.1-143.2 °C; ¹H NMR (400 MHz, CDCl₃) δ: 1.10 (dd, *J*=3.2, 6.8 Hz, 6H), 1.17 (d, *J* = 7.2 Hz, 3H), 1.34 (s, 3H), 2.30 (s, 1H), 2.30 (sept, *J* = 6.8 Hz, 1H), 4.55 (q, *J* = 7.3 Hz, 1H), 7.26-7.45 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ: 13.0 (q), 16.7 (q), 17.6 (q), 20.7

(q), 35.5 (d), 72.8 (s), 81.4 (d), 94.0 (s), 107.9 (s), 126.9 (d), 128.1 (d), 128.3 (d), 132.6 (s), 170.5 (s); IR (CHCl₃): 1825 cm⁻¹; MS (EI): *m/z* 275 (M⁺-1), 161 (100%); Anal. Calcd for C₁₆H₂₀O₄: C, 69.54 ; H, 7.30, found: C, 69.34 ; H, 7.23.

2-Isopropyl-3,5-dimethyl-4-phenylfuran (9)

¹H-NMR (400 MHz, CDCl₃) δ: 1.26 (d, *J*=7.2 Hz, 6H), 1.91 (s, 3H), 2.26 (s, 3H), 3.01 (quint, *J*=6.8 Hz, 1H), 7.25-7.29 (m, 3H), 7.38 (t, *J*=7.8 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ: 9.0 (q), 12.4 (q), 21.6 (q), 26.3 (d), 111.8 (s), 122.4 (s), 126.1 (d), 128.1 (d), 129.3 (d), 134.3 (s), 145.0 (s), 153.3 (s); IR(neat): 1253 cm⁻¹; MS (EI): *m/z* 214 (M⁺), 200 (100%); HRMS (APCI): Calcd for C₁₆H₁₉O (M+H): 215.1436, found 215.1479.

2, 4-Dimethyl-3, 5-diphenyl-furan (11), One-pot procedure (Method B in Table 1):

To a solution of ethyl 2,2-dibromopropionate (312 mg, 1.2 mmol) in THF (6 mL) was added *t*-BuLi (3.08 mL, 4.8 mmol, 1.56 M in pentane) at -78 °C. After being stirred for 3 h, the mixture was allowed to warm to 0 °C and stirred for 0.5 h. After cooled to -78 °C, a solution of **5c** (1.0 mmol) in THF (2 mL) was added and the mixture was stirred for 0.5 h. A suspension of TsOH·H₂O (475 mg, 2.5 mmol) in benzene (15 mL) was added to the reaction mixture. The THF was removed in vacuo at 40 °C and the residual benzene solution was reflux for 1 h. The reaction mixture was treated with saturated

aqueous NaHCO₃, and was extracted with EtOAc. The organic layer was washed with brine and dried over MgSO₄ and concentrated. The residue was purified with column chromatography (SiO₂, hexane) to afford the furan **9** (191 mg, 77%) as a pale yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ: 2.20 (s, 3H), 2.36 (s, 3H), 7.23-7.34 (m, 4H), 7.39-7.45 (m, 4H), 7.64-7.66 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ: 10.9 (q), 12.5 (q), 116.3 (s), 124.7 (s), 125.2 (d), 126.3 (d), 126.6 (d), 128.3 (d), 128.4 (d), 129.6 (d), 131.9 (s), 133.5 (s), 146.8 (s), 147.1 (s); IR (neat): 2919, 1597, 1496, 1443, 1249, 1219, 1015, 1006 cm⁻¹; MS (EI): *m/z* 248 (M⁺), 205 (100%); HRMS (APCI): Calcd for C₁₈H₁₇O (M+H): 249.1279, found 249.1304.

2,4-Dimethyl-5-(4-pentenyl)-3-phenyl-furan (12)

¹H-NMR (400 MHz, CDCl₃) δ: 1.74 (quint, *J*=7.6 Hz, 2H), 1.90 (s, 3H), 2.12 (q, *J*=7.2 Hz, 2H), 2.26 (s, 3H), 2.58 (t, *J*=7.6 Hz, 2H), 4.98 (br d, *J*=10 Hz, 1H), 5.04 (br dd, *J*=1.6, 17.2 Hz, 1 H), 5.79-5.89 (m, 1H), 7.24-7.40 (m, 5H); ¹³C-NMR (100 MHz, CDCl₃) δ: 9.2 (q), 12.4 (q), 25.5 (t), 27.9 (t), 33.3 (t), 113.8 (s), 114.7 (t), 122.4 (s), 126.1 (d), 128.1 (d), 129.2 (d), 134.3 (s), 138.4 (d), 145.4 (s), 148.8 (s); IR (neat): 3078, 1587, 1496, 1441, 1385, 1372, 1073 cm⁻¹; MS (EI): *m/z* 240 (M⁺); HRMS (APCI): Calcd for C₁₇H₂₁O (M+H): 241.1592, found 241.1630.

3-Methyl-2, 4, 5-triphenylfuran (13)

^1H -NMR (400 MHz, CDCl_3) δ : 2.15 (s, 3H), 7.17-7.77 (m, 15H); ^{13}C -NMR (100 MHz, CDCl_3) δ : 10.5 (q), 118.8 (s), 125.4 (d), 125.5 (d), 125.9 (s), 126.8 (d), 126.9 (d), 127.3 (d), 128.2 (d), 128.5 (d), 128.7 (d), 130.1 (d), 131.0 (s), 131.6 (s), 133.8 (s), 147.1 (s), 147.6 (s); IR(CHCl_3): 1597, 1493, 1466, 1445, 1097 cm^{-1} ; HRMS (APCI): Calcd for $\text{C}_{23}\text{H}_{18}\text{O}$ (M+H): 311.1436, found 311.1442.

3-Butyl-2,5-dimethyl-4-phenylfuran (14)

^1H NMR (400 MHz, CDCl_3) δ : 0.78 (t, $J = 7.2$ Hz, 3H), 1.15-1.28 (m, 4H), 2.22 (s, 3H), 2.24 (s, 3H), 2.31 (t, $J = 7.2$ Hz, 2H), 7.22-7.25 (m, 2H), 7.26-7.29 (m, 1H), 7.37 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 11.7 (q), 12.2 (q), 13.8 (q), 22.4 (d), 23.3 (t), 32.5 (t), 119.1 (s), 122.3 (s), 126.2 (d), 128.2 (d), 129.3 (d), 134.5 (s), 145.0 (s), 145.3 (s); IR(neat): 3056, 3033, 1607, 1588, 1496, 1444, 1379 cm^{-1} ; MS (EI): m/z 228 (M^+), 128 (100%); HRMS (APCI): Calcd for $\text{C}_{16}\text{H}_{21}\text{O}$ (M+H): 229.1592, found 229.1591.

General procedure for synthesis of thiophenes (Method C in Table 1)

To a solution of α,α -dibromoester (156 mg, 0.6 mmol) in THF (4 mL) was added *t*-butyllithium (1.7 mL, 2.4 mmol, 1.43 M in pentane) at -78°C under argon. After being stirred at -78°C for 1 h, the solution was allowed to warm to 0°C and was stirred for

0.5 h. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of thioester **5** ($\text{X} = \text{S}$, 0.5 mmol) in THF (1.5 mL) was added. After being stirred at $-78\text{ }^{\circ}\text{C}$ for 0.5 h, the mixture was quenched with a solution of acetic acid (0.343 mL, 6 mmol) in THF (2 mL) at $-78\text{ }^{\circ}\text{C}$, and then saturated aqueous NaHCO_3 solution was added at room temperature. The mixture was then extracted with ethyl acetate, and the combined organic extracts were washed with a saturated aqueous NaHCO_3 solution, brine, dried over MgSO_4 , filtered and concentrated in vacuo. The residue was chromatographed over silica gel (ethyl acetate/hexane, 5%) to yield the pure β -lactone.

To a toluene solution (5 mL) of the β -lactone (0.1 mmol) was added $\text{TsOH}\cdot\text{H}_2\text{O}$ (19 mg, 0.1 mmol), and the mixture was refluxed for 1-4 h. The mixture was quenched with a saturated NaHCO_3 solution. The mixture was extracted with ethyl acetate, and the organic extracts were washed with brine, dried over MgSO_4 , filtered and concentrated to afford a brown oil, which was chromatographed over silica gel (ethyl acetate/hexane, 3%) to yield the thiophene.

2,3,5-Trimethyl-4-phenylthiophene (15**)¹⁰**

Colorless prism (hexane, mp. $37\text{--}37.3\text{ }^{\circ}\text{C}$). ^1H NMR (400 MHz, CDCl_3) δ : 1.92 (s, 3H), 2.25 (s, 3H), 2.34 (s, 3H), 7.20 (d, $J = 7.5\text{ Hz}$, 2H), 7.31 (t, $J = 7.5\text{ Hz}$, 2H), 7.40 (t, $J = 7.5\text{ Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 13.2, 13.4, 13.7, 126.7, 128.1, 128.7, 129.9, 130.5, 132.3, 137.4, 140.0; IR (neat) 1069, 1151, 1441, 1481, 1506, 2855, 2912 cm^{-1} ; MS (EI) m/z : 202 (M^+), 187 ($\text{M}-\text{CH}_3$); Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{S}$: C, 77.18; H, 6.97. Found: C, 77.14; H, 6.97.

2,4-Dimethyl-3,5-diphenylthiophene (16)¹¹

Colorless prism (hexane, mp. 45.2-45.7 °C). ¹H NMR (400 MHz, CDCl₃) δ 2.08 (s, 3H), 2.33 (s, 3H), 7.25-7.49 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.9, 126.9, 128.2, 128.3, 128.4, 129.2, 130.0, 132.6, 133.7, 134.3, 135.1, 137.1, 141.1; IR (neat) 1076, 1439, 1485, 1599 cm⁻¹; MS (EI) m/z: 264 (M⁺), 249 (M-CH₃); Anal. Calcd for C₁₈H₁₆S: C, 81.77; H, 6.10. Found: C, 81.75; H, 5.97.

4-Hydroxy-2,5-dimethyl-1,4-diphenyl-7-oxa-3-thiabicyclo[3.2.0]heptan-6-one (an intermediate for entry 8 in Table 1)

Colorless prism (AcOEt, decomposition point: 156-157 °C). ¹H NMR (400 MHz, CDCl₃) δ: 1.12 (s, 3H), 1.39 (d, *J* = 7.2 Hz, 3H), 2.48-2.50 (m, 1H), 3.93 (q, *J* = 7.6 Hz, 1H), 7.38-7.45 (m, 8H), 7.72-7.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 12.4, 23.1, 52.1, 78.2, 94.6, 96.4, 126.8, 127.0, 128.1, 128.2, 128.4, 129.0, 134.2, 137.5, 169.4; IR (neat) 1800, 3418 cm⁻¹; MS (FAB) m/z: 327 (M+H), Anal. Calcd for C₁₉H₁₈O₃S: C, 69.91; H, 5.56. Found: C, 69.79; H, 5.58.

The stereochemistry was determined by X-ray crystal structure analysis: CCDC 635505 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2,3-Dimethyl-4-phenylthiophene (17)¹⁰

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 2.11 (s, 3H), 2.41 (s, 3H), 6.95 (s, 1H), 7.31-7.41 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 13.1, 13.8, 118.4, 126.8, 128.2, 128.6, 131.5, 133.6, 137.8, 143.7; IR (neat) 1443, 1501, 1601, 2860, 2918, 2945, 3024, 3059 cm⁻¹; MS (EI) *m/z* 188 (M⁺), 173 (M⁺-CH₃); HRMS (EI) *m/z* calcd for C₁₂H₁₂S (M⁺): 188.0660. found: 188.0657.

2-(3,5-Dimethyl-4-phenylthiophen-2-yl)thiophene (18)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 2.14 (s, 3H), 2.30 (s, 3H), 7.05-7.13 (m, 2H), 7.23-7.29 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 13.9, 15.1, 124.7, 125.3, 127.0, 127.30, 127.31, 128.3, 129.9, 133.5, 133.8, 136.8, 137.0, 141.3; IR (neat) 1381, 1421, 1441, 1526, 1601, 2916, 3024, 3059 cm⁻¹; MS (EI) *m/z* 270 (M⁺), 255 (M⁺-CH₃); HRMS (EI) *m/z* calcd for C₁₆H₁₄S₂ (M⁺): 270.0537. found: 270.0533.

2,4-Dimethyl-3-phenyl-5-styrylthiophene (19)

Pale yellow prism (AcOEt-hexane, mp. 80.3-81.0 °C). ¹H NMR (400 MHz, CDCl₃) δ

2.10 (s, 3H), 2.30 (s, 3H),), 6.82 (d, $J = 15.9$ Hz, 1H), 7.20-7.29 (m, 4H), 7.34 (t, $J = 7.7$ Hz, 3H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.47 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 14.2, 120.6, 126.1, 126.8, 127.0, 127.1, 128.3, 128.6, 129.9, 133.0, 133.5, 135.3, 136.6, 137.6, 141.1; IR (neat) 1385, 1443, 1468, 1493, 1595, 1622, 2334, 2914, 3024 cm^{-1} ; MS (EI) m/z : 290 (M^+), 275 ($\text{M}-\text{CH}_3$); Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{S}$: C, 82.71; H, 6.25. Found: C, 82.58; H, 6.13.

3-Ethyl-2,4-dimethyl-5-phenylthiophene (20)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.12 (t, $J = 7.7$ Hz, 3H), 2.20 (s, 3H), 2.39 (s, 3H), 2.54 (q, $J = 7.6$ Hz, 2H), 7.25-7.42 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ : 12.9, 13.6, 14.2, 20.6, 126.7, 128.3, 129.2, 131.3, 132.5, 133.8, 135.3, 140.3; IR (neat) 1450, 1464, 1504, 1599, 2870, 2930, 2964, 3024, 3059 cm^{-1} ; MS (EI) m/z 216 (M^+), 201 (M^+-CH_3); HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{S}$ (M^+): 216.0973. found: 216.0970.

2-(2,4-Dimethyl-5-phenylthiophen-3-yl)thiophene (21)

To a solution of ethyl 2,2-dibromopropionate (624 mg, 2.4 mmol) in THF (13 mL) was added *t*-butyllithium (6 mL, 9.6 mmol, 1.61 M in pentane) at -78 $^{\circ}\text{C}$ under argon. After being stirred at -78 $^{\circ}\text{C}$ for 0.5 h, the solution was allowed to warm to 0 $^{\circ}\text{C}$ and was stirred for 0.5 h. The solution was cooled to -78 $^{\circ}\text{C}$ and a solution of thioester **5** ($\text{X} = \text{S}$,

553 mg, 2.0 mmol) in THF (2 mL) was added. After being stirred at -78 °C for 1 h, the mixture was quenched with a solution of acetic acid (1.4 ml, 24 mmol) in THF (2 ml) at -78 °C, and then saturated aqueous NaHCO₃ solution was added at room temperature. The mixture was then extracted with ethyl acetate, and the combined organic extracts were washed with a saturated aqueous NaHCO₃ solution, brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was chromatographed over silica gel (ethyl acetate/ hexane, 5%) to yield the pure thiophene **21** (385 mg, 71%).

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 2.16 (s, 3H), 2.41 (s, 3H), 6.95 (d, *J* = 3.4 Hz, 1H), 7.11-7.13 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.37-7.47 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 14.9, 125.5, 126.9, 127.0, 127.3, 128.4, 129.2, 133.2, 134.2, 134.9, 136.4, 137.5; IR (neat) 1381, 1439, 1472, 1495, 1599, 2856, 2916 cm⁻¹; MS (EI) *m/z* 270 (M⁺), 255 (M⁺-CH₃); HRMS (EI) *m/z* calcd for C₁₆H₁₄S₂ (M⁺): 270.0537. found: 270.0541.

Pyrroles

Preparation of α-Acylamino Ketones

A solution of the α-bromoketone (2.35 mmol) and amine (5.1 mmol) in DME (10 mL) was refluxed for 1.5 h. After addition of saturated aqueous NaHCO₃ solution, the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc) to yield α-amino ketone. To a solution of α-amino ketone (2.65 mmol) and pyridine (7.9 mmol) in CH₂Cl₂ (5 mL) was added acid chloride

(3.2 mmol) dropwise at 0 °C, and the mixture was stirred for 3 h at room temperature. Saturated aqueous NaHCO₃ solution was added and the mixture was extracted with CH₂Cl₂. The organic extract was washed with water, brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified with silica gel column chromatography (hexane/EtOAc) to yield α -acylaminoketone.

***N*-(1-methyl-2-oxo-2-phenylethyl)-*N*-(4-methoxyphenyl)benzamide (22a)**

Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 1.35 (d, J = 7.2 Hz, 3H), 3.69 (s, 3H), 6.36 (q, J = 7.1 Hz 1H), 6.64 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 7.11-7.17 (m, 5H), 7.50-7.59 (m, 3H), 8.10 (d, J = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 14.9, 55.2, 56.2, 113.8, 127.6, 128.17, 127.18, 128.4, 128.7, 129.2, 131.0, 132.3, 133.19, 136.0, 158.6, 170.7, 199.0; IR (neat) 1691, 1637 cm⁻¹; MS (EI) m/z : 359 (M⁺); HRMS (EI) calcd for C₂₃H₂₁NO₃ (M⁺): 359.1521. found: 359.1523.

***N*-Benzyl-*N*-(1-methyl-2-oxo-2-phenylethyl)benzamide (22b)¹²**

Colorless needles (hexane/EtOAc), mp. 96.5-98.0 °C. ¹H NMR (600 MHz, CDCl₃) δ : 1.40 (d, J = 7.2 Hz, 3H), 4.52 (dd, J = 107.6, 16.5 Hz, 2H), 5.56 (m, 1H), 7.36-7.64 (m, 15H); ¹³C NMR (150 MHz, CDCl₃) δ : 14.4, 50.8, 55.1, 126.3, 126.9, 127.3, 128.1, 128.3, 128.4, 128.5, 129.4, 132.9, 135.9, 137.5, 172.3, 199.2; MS (FAB) m/z : 344

(M+1); HRMS (FAB) m/z calcd for $C_{23}H_{21}NO_2$ ($M^+ + H$): 343.1572. found: 344.1654.

***N*-Benzyl-*N*-(1-methyl-2-oxo-2-phenylethyl)isobutyramide (22c)**

Colorless prisms (hexane/EtOAc), mp. 92.0-93.0 °C. 1H NMR (400 MHz, $CDCl_3$) δ 1.00 (dd, $J = 19.1, 6.5$ Hz, 6H), 1.31 (d, $J = 7.2$ Hz, 3H), 2.55-2.62 (m, 1H), 4.45 (s, 1H), 4.59 (d, $J = 17.9$ Hz, 1H), 6.18 (q, $J = 7.1$ Hz, 1H), 7.08-7.56 (m, 8H), 7.93 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 19.4, 30.9, 47.8, 53.8, 125.6, 127.1, 128.2, 128.4, 128.5, 133.0, 135.5, 138.0, 178.0, 199.8; IR (neat) 1687, 1639 cm^{-1} ; MS (EI) m/z : 309 (M^+); Anal. Calcd for $C_{20}H_{23}O_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.57; H, 7.48; N, 4.54.

***N*-Benzyl-2,2,2-trifluoro-*N*-(1-methyl-2-oxo-2-phenylethyl)acetamide (22d)**

Colorless prisms (hexane/EtOAc), mp. 69.0-70.0 °C. 1H NMR (600 MHz, $CDCl_3$) δ : 1.34 (d, $J = 7.2$ Hz, 2.4H), 1.49 (d, $J = 6.9$ Hz, 0.6H), 4.46 (d, $J = 16.2$ Hz, 0.2H), 4.68 (d, $J = 17.2$ Hz, 0.8H), 4.85 (d, $J = 17.2$ Hz, 0.8H), 5.23 (d, $J = 15.8$ Hz, 0.2H), 5.61 (q, $J = 7.1$ Hz, 0.8H), 5.70 (q, $J = 7.1$ Hz, 0.2H), 7.16-7.33 (m, 5H), 7.41 (t, $J = 7.7$ Hz, 1.6H), 7.47 (t, $J = 7.7$ Hz, 0.4H), 7.55 (t, $J = 7.7$ Hz, 0.8H), 7.59 (t, $J = 7.7$ Hz, 0.2H), 7.75 (d, $J = 7.6$ Hz, 1.6H), 7.83 (d, $J = 7.6$ Hz, 0.4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ : 14.2, 17.0, 48.7, 49.4, 57.0, 116.2 ($J_{CF_3} = 285$ Hz), 126.8, 127.0, 127.1, 127.9, 127.9, 128.0, 128.5, 128.6, 128.9, 133.2, 133.8, 135.2, 135.6, 157.8 ($J_{CCF_3} = 36$ Hz),

197.0, 197.3; IR (neat) 1685, 1685 cm^{-1} ; MS m/z : 336 (M^+); Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NO}_2$: C, 64.47; H, 4.81; N, 4.18. Found: C, 64.46; H, 4.83; N, 4.16.

***N*-Allyl-*N*-(1-methyl-2-oxo-2-phenylethyl)pivalamide (22e)**

Colorless prisms (hexane/EtOAc), mp. 89.0-90.0 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 1.12 (s, 9H), 1.45 (d, $J = 6.8$ Hz, 3H), 4.19 (d, $J = 34.3$ Hz, 2H), 5.00 (s, 1H), 5.26 (t, $J = 13.8$ Hz, 2H), 5.84-5.90 (m, 1H), 7.39-7.47 (m, 3H), 7.77 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 13.8, 28.0, 38.7, 49.9, 58.0, 118.1, 127.5, 127.9, 128.4, 131.8, 135.0, 176.9, 199.7; IR (neat) 1687, 1639 cm^{-1} ; MS m/z : 274 (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.76; H, 8.38; N, 5.08.

***N*-(4-Methoxyphenyl)-*N*-(1-ethyl-2-oxopentyl)benzamide (22f)**

Pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.87-1.00 (m, 6H), 1.63-2.03 (m, 4H), 2.57-2.85 (m, 2H), 3.70 (s, 3H), 4.99 (dt, $J = 25.0, 7.1$ Hz, 1H), 6.69 (d, $J = 8.7$ Hz, 2H), 7.05-7.22 (m, 7H); ^{13}C NMR (150 MHz, CDCl_3) δ : 7.4, 11.3, 13.5, 13.6, 16.8, 19.8, 20.9, 29.9, 33.1, 41.9, 54.9, 66.3, 68.0, 113.6, 113.7, 127.4, 128.0, 129.1, 129.5, 129.6, 133.7, 133.8, 135.9, 157.9, 170.6, 170.7, 207.8, 208.4; IR (neat) 1718, 1641 cm^{-1} ; MS (EI) m/z 339 (M^+); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_3$ (M^+): 339.1834. found: 339.1837.

***N*-Benzyl-*N*-(2-oxocyclohexyl)benzamide (22g)**

To a cooled (-78 °C) solution of oxalyl chloride (0.15 mL, 1.75 mmol) in dry CH₂Cl₂ (5 mL) was added DMSO (0.23 mL, 3.14 mmol). After 30 min at -78 °C, a solution of *N*-benzyl-*N*-benzoyl cyclohexanol¹³ (309 mg, 1.0 mmol) in dry CH₂Cl₂ was added. The mixture was stirred at -78 °C for 1 h and triethylamine (0.74 mL, 5.3 mmol) was added. The solution was stirred at -78 °C for 15 min and then allowed to warm to room temperature. After addition of saturated aqueous NaHCO₃, the reaction mixture was extracted with CH₂Cl₂ and the organic layer was washed with brine, dried over Na₂SO₄ and concentrated to afford a yellow oil, which was chromatographed over silica gel (hexane-EtOAc 9:1) to yield 300 mg (98%) of **22g**. Colorless needles (hexane/EtOAc), mp. 99.0-100.7 °C. ¹H NMR (600 MHz, CDCl₃) δ: 1.24-2.63 (m, 8H), 3.93 (d, *J* = 15.8 Hz, 0.3H), 4.44-4.47 (m, 1.7H), 4.65 (d, *J* = 17.2 Hz, 0.7H), 5.54 (d, *J* = 15.5 Hz, 0.3H), 7.23-7.47 (m, 10H); ¹³C NMR (150 MHz, CDCl₃) δ: 22.5, 24.5, 25.3, 26.0, 30.7, 33.1, 41.1, 47.7, 52.9, 63.9, 68.2, 125.8, 126.4, 126.5, 126.7, 127.2, 128.2, 128.5, 129.5, 136.1, 137.9, 139.1, 172.6, 205.2, 206.7; IR (neat) 1718, 1639 cm⁻¹; MS (EI) *m/z* 307 (M⁺); Anal. Calcd for C₂₀H₂₁O₂: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.19; H, 6.82; N, 4.54.

Ethyl (*N*-allyl-*N*-(1-methyl-2-oxo-2-phenylethyl)carbamoyl)formate (22h)

Pale yellow oil. ¹H NMR (600 MHz, CDCl₃) δ: 1.31 (t, *J* = 7.0 Hz, 3H), 1.46 (d, *J* = 6.9

Hz, 3H), 3.79-3.82 (m, 0.2H), 3.89-3.97 (m, 1.6H), 4.11-4.13 (m, 0.2H), 4.24-4.30 (m, 1.8H), 4.34-4.36 (m, 0.2H), 5.05-5.08 (m, 2H), 5.34 (q, $J = 6.9$ Hz, 0.2H), 5.60-5.64 (m, 0.8H), 5.67-5.73 (m, 0.2H), 6.03 (q, $J = 7.0$ Hz, 0.8H), 7.46-7.60 (m, 3H), 7.95 (dd, $J = 12.4, 7.2$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 13.7, 13.8, 14.1, 16.2, 45.6, 47.3, 52.8, 57.3, 62.1, 62.3, 117.6, 118.3, 128.3, 128.3, 128.7, 128.8, 132.5, 133.6, 133.6, 133.7, 134.9, 161.9, 162.2, 162.8, 196.5, 197.7; IR (neat) 1737, 1693, 1658 cm^{-1} ; MS (EI) m/z 289 (M^+); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4$ (M^+): 289.1314. found: 289.1316.

***N*-(2-Methoxyphenyl)-*N*-(1-methyl-2-oxo-2-phenylethyl)benzamide (22i)**

^1H NMR (400 MHz, CDCl_3) δ : 1.20 (d, $J = 6.8$ Hz, 2.4H), δ 1.47 (d, $J = 6.8$ Hz, 0.6H), 3.20 (s, 0.6H), 3.61 (s, 2.4H), 6.36 (q, $J = 7.2$ Hz, 1H), 6.66-6.78 (m, 2H), 7.05-7.53 (m, 10H), 8.10 (d, $J = 7.7$ Hz, 0.4H), 8.18 (d, $J = 7.7$ Hz, 1.6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 13.3, 14.6, 54.0, 54.8, 55.1, 55.6, 111.1, 111.2, 120.0, 120.3, 126.9, 127.1, 127.2, 127.5, 128.0, 128.1, 128.3, 128.5, 129.1, 129.2, 129.3, 130.6, 130.7, 132.3, 132.9, 135.8, 136.0, 136.1, 136.5, 154.7, 155.5, 171.0, 171.6, 196.8, 199.2; IR (neat) 1693, 1645 cm^{-1} ; MS (EI) m/z : 359 (M^+); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$ (M^+): 359.1521. found: 359.1521.

***N*-(4-Methoxyphenyl)-*N*-(2-oxo-2-phenylethyl)benzamide (22j)**

Colorless prisms (hexane/EtOAc), mp. 113.0-114.0 °C. ^1H NMR (400 MHz, CDCl_3) δ : 3.70 (s, 3H), 5.29 (s, 2H), 6.70 (d, $J = 8.7$ Hz, 2H), 7.10-7.59 (m, 10H), 7.98-8.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 55.2, 57.1, 114.1, 127.6, 127.9, 128.6, 128.7, 128.8, 129.5, 133.4, 135.1, 135.4, 136.8, 158.0, 170.6, 193.5 ; IR (neat) 1699, 1645 cm^{-1} ; Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{O}_3$: C, 76.50; H, 5.54; N, 4.06. Found: C, 76.40; H, 5.38; N, 4.04.

General Procedure for the Synthesis of Pyrroles

To a solution of ethyl 2,2-dibromopropionate (156 mg, 0.6 mmol) in THF (4 ml), cooled to -78 °C under argon, was added dropwise a solution of *tert*-butyllithium (1.66 mL, 2.4 mmol, 1.45M in pentane). The yellow solution was stirred for 1 h at -78 °C and allowed to warm to 0 °C. After 30 min, a solution of α -acylamino ketone (133.7 mg, 0.5 mmol) in THF (1 ml) was added at -20 °C. After 2 h, a saturated NH_4Cl solution (10 ml) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with water, a saturated NaHCO_3 solution, brine, dried over Na_2SO_4 , filtered and concentrated. The residue was chromatographed over silica gel to yield pyrrole.

1-(4-Methoxyphenyl)-2,4-dimethyl-3,5-diphenyl-1H-pyrrole (26)

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ : 2.12 (s, 3H), 2.14 (s, 3H), 3.78 (s, 3H),

6.82 (m, $J = 6.7, 2.2$ Hz, 2H), 7.06-7.12 (m, 5H), 7.19 (dd, $J = 9.8, 5.3$ Hz, 2H), 7.26-7.28 (m, 1H), 7.25 (d, $J = 4.1$ Hz, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ : 11.3, 12.0, 55.3, 113.9, 115.4, 122.9, 125.5, 125.7, 127.1, 127.6, 128.0, 129.4, 130.1, 130.2, 130.6, 132.2, 133.0, 136.5, 158.2; IR (neat) 1602, 1514 cm^{-1} ; MS (EI) m/z 353 (M^+); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{NO}$ (M^+): 353.1780. found: 353.1782.

1-Benzyl-2,4-dimethyl-3,5-diphenyl-1H-pyrrole (27)

Pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 2.05 (s, 3H), 2.21 (s, 3H), 6.93 (d, $J = 7.7$ Hz, 2H), 7.22-7.34 (m, 13H); ^{13}C NMR (150 MHz, CDCl_3) δ : 109, 11.0, 47.8, 114.7, 122.6, 125.4, 125.6, 125.7, 126.8, 126.8, 127.9, 128.1, 128.5, 130.1, 130.5, 130.7, 133.0, 136.7, 139.1; IR (neat) 1602 cm^{-1} ; MS (EI) m/z 337 (M^+); Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{N}$: C, 72.93; H, 5.51; N, 4.25. Found: C, 73.14; H, 5.19; N, 4.43.

1-Benzyl-2-isopropyl-3,5-dimethyl-4-phenyl-1H-pyrrole (28)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.11 (d, $J = 7.2$ Hz, 6H), 1.98 (s, 3H), 2.01 (s, 3H), 2.84-2.91 (m, 1H), 4.97 (s, 2H), 6.80 (d, $J = 8.2$ Hz, 2H), 7.07-7.09 (m, 2H), 7.14-7.20 (m, 4H), 7.24 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 109, 11.0, 47.8, 114.7, 122.6, 125.4, 125.6, 125.7, 126.8, 126.8, 127.9, 128.1, 128.5, 130.1, 130.5, 130.7, 133.0, 136.7, 139.1; IR (neat) 1602 cm^{-1} ; MS (EI) m/z : 303 (M^+); HRMS (EI)

calcd for C₂₂H₂₅N (M⁺): 337.1830. found: 337.1822.

1-Benzyl-2-(trifluoromethyl)-3,5-dimethyl-4-phenyl-1H-pyrrole (29)

Colorless prisms (hexane), mp. 69.1-70.0 °C. ¹H NMR (600 MHz, CDCl₃) δ: 2.04 (s, 3H), 2.16 (s, 3H), 5.22 (s, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 7.23-7.41 (m, 8H); ¹³C NMR (150 MHz, CDCl₃) δ: 10.3, 10.5, 48.4, 116.2 (*J*_{CCF₃} = 36 Hz), 120.5 (*J*_{CCCF₃} = 3 Hz), 123.0 (*J*_{CF₃} = 270 Hz), 123.5, 125.4, 126.2, 127.1, 128.1, 128.6, 130.4, 130.5, 135.0, 137.7; IR (neat) 1604 cm⁻¹; MS (EI) *m/z* 329 (M⁺); HRMS (EI) calcd for C₂₀H₁₈F₃N (M⁺): 337.1830. found: 337.1822.

2-*tert*-butyl-1-allyl-3,5-dimethyl-4-phenyl-1H-pyrrole (30)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 1.46 (s, 9H), 2.07 (s, 3H), 2.12 (s, 3H), 4.67-4.68 (m, 2H), 4.79-4.81 (m, 1H), 5.15-5.17 (m, 1H), 5.91-5.94 (m, 1H), 7.22 (m, 3H), 7.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 10.8, 13.6, 32.4, 34.1, 47.9, 111.6, 115.7, 123.2, 125.2, 125.6, 127.6, 131.1, 133.4, 135.4, 137.2; IR (neat) 1604 cm⁻¹; MS (EI) *m/z* 267 (M⁺); HRMS (EI) calcd for C₁₉H₂₅N (M⁺): 267.1987. found: 267.1986.

3-Isopropyl-1-(4-methoxyphenyl)-5-methyl-2,4-diphenyl-1H-pyrrole (31)

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ : 1.05 (d, $J = 6.9$, 6H), 1.94 (d, $J = 1.0$ Hz, 3H), 2.91-2.96 (m, 1H), 3.76 (s, 3H), 6.76 (t, $J = 4.5$, 2H), 7.04 (d, $J = 8.9$ Hz, 2H), 7.13-7.19 (m, 5H), 7.28-7.30 (m, 1H), 7.38-7.41 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ : 11.5, 24.3, 26.0, 55.2, 113.5, 121.8, 125.8, 126.3, 126.3, 126.7, 127.4, 127.7, 129.5, 129.6, 131.2, 131.5, 132.1, 134.1, 137.9, 158.0; IR (neat) 1604, 1514 cm^{-1} ; MS (EI) m/z 381 (M^+); HRMS (EI) calcd for $\text{C}_{27}\text{H}_{27}\text{NO}$ (M^+): 381.2093. found: 381.2089.

1-(4-Methoxyphenyl)-2-methyl-3,4,5-triphenyl-1H-pyrrole (32)

Colorless oil, ^1H NMR (600 MHz, CDCl_3) δ : 2.16 (s, 3H), 3.80 (s, 3H), 6.83-6.85 (m, 2H), 6.94-6.96 (m, 4H), 7.04-7.05 (m, 6H), 7.11-7.19 (m, 6H), 7.25 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ : 11.6, 55.3, 113.8, 121.3, 122.0, 125.1, 125.4, 126.0, 127.4, 127.7, 128.8, 129.5, 129.9, 130.6, 130.8, 131.0, 131.1, 131.8, 132.5, 135.6, 136.1, 158.5; IR (neat) 1514 cm^{-1} ; MS (FAB) m/z : 415 ($\text{M}+1$); HRMS (EI) calcd for $\text{C}_{30}\text{H}_{25}\text{NO}$ (M^+): 415.1936. found: 415.1938.

2-Ethyl-1-(4-methoxyphenyl)-4-methyl-5-phenyl-3-propyl-1H-pyrrole (33)

Pale yellow oil. ^1H NMR (600 MHz, CDCl_3) δ : 0.77 (dd, $J = 8.9, 5.5$ Hz, 1H), 0.89 (dd, $J = 8.9, 5.8$ Hz, 2H), 1.02 (dd, $J = 8.9, 5.8$ Hz, 2H), 1.19 (q, $J = 6.6$ Hz, 1H), 1.28-1.30 (m, 1H), 1.58-1.61 (m, 1H), 2.11 (d, $J = 8.9$ Hz, 3H), 2.42-2.54 (m, 4H), 3.75 (s, 3H), 6.76-6.78 (m, 2H), 7.00-7.05 (m, 5H), 7.13-7.14 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 10.3, 14.5, 15.3, 18.0, 24.8, 27.3, 55.2, 113.6, 115.8, 119.5, 125.3, 127.4, 129.7, 129.9, 130.2, 130.9, 132.6, 133.3, 158.1; IR (neat) 1602, 1514 cm^{-1} ; MS (EI) m/z : 333 (M^+); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{27}\text{NO}$ (M^+): 333.2093. found: 333.2090.

1-Benzyl-3-methyl-2-phenyl-1H-indole (34)

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ : 1.78 (m, 4H), 2.01 (s, 3H), 2.38 (s, 2H), 2.50 (s, 2H), 4.95 (s, 2H), 6.90 (d, $J = 7.2$ Hz, 2H), 7.18-7.25 (m, 6H), 7.30 (dd, $J = 9.6, 5.5$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 9.6, 21.6, 22.2, 23.4, 47.2, 114.2, 117.3, 125.8, 126.4, 126.7, 128.1, 128.2, 128.4, 129.8, 130.3, 133.1, 139.5; IR (neat) 1604, 1494 cm^{-1} ; MS (EI) m/z 301 (M^+); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{23}\text{N}$ (M^+): 301.1830. found: 301.1830.

Ethyl 1-allyl-3,5-dimethyl-4-phenyl-1H-pyrrole-2-carboxylate (35)

Pale yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 1.28 (t, $J = 7.0$ Hz, 3H), 2.09 (s, 3H), 2.18 (s, 3H), 4.23 (q, $J = 7.2$ Hz, 2H), 4.78 (dd, $J = 17.2, 1.4$ Hz, 1H), 4.91 (m, 2H),

5.04 (dd, $J = 10.3, 1.4$ Hz, 1H) 5.90-5.93 (m, 1H), 7.14 (dd, $J = 5.2, 3.1$ Hz, 2H), 7.19-7.22 (m, 1H), 7.31 (dd, $J = 10.7, 4.8$ Hz, 1H), 7.31 (dd, $J = 10.7, 4.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 10.6, 12.5, 14.4, 47.6, 59.4, 115.3, 118.2, 124.1, 126.1, 127.4, 128.0, 130.5, 133.2, 134.7, 135.3, 162.1; IR (neat) 1687 cm^{-1} ; MS (EI) m/z : 283 (M^+); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ (M^+): 283.1572. found: 283.1570.

1-(2-Methoxyphenyl)-2,4-dimethyl-3,5-diphenyl-1H-pyrrole (36)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 2.07 (s, 3H), 2.16 (s, 3H), 3.74 (s, 3H), 6.84-6.86 (m, 1H), 6.93 (d, $J = 8.2$ Hz, 1H), 7.00-7.01 (m, 1H), 7.07-7.19 (m, 5H), 7.23-7.27 (m, 7H), 7.39-7.46 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.2, 11.4, 55.4, 111.5, 115.2, 120.4, 122.6, 125.3, 125.6, 127.4, 127.8, 128.1, 128.7, 129.5, 130.0, 130.4, 130.6, 133.2, 136.6, 155.5; IR (neat) $1600, 1504\text{ cm}^{-1}$; MS (EI) m/z : 353 (M^+); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{NO}$ (M^+): 353.1780. found: 353.1781.

1-(4-Methoxyphenyl)-3-methyl-2,4-diphenyl-1H-pyrrole (37)

To a solution of phenyl 2,2-dibromopropionate (185 mg, 0.6 mmol) in THF (4 ml), cooled to $-78\text{ }^\circ\text{C}$ under argon, was added dropwise a solution of *tert*-butyllithium (1.5 mL, 2.4 mmol, 1.76M in pentane). The yellow solution was stirred for 3 h at $-78\text{ }^\circ\text{C}$ and allowed to warm to $0\text{ }^\circ\text{C}$. After 30 min, a solution of α -acylamino ketone **22j** (180 mg,

0.5 mmol) in THF(1 ml) was added at -20 °C. After 15 min, butyllithium (0.2 mL, 0.5 mmol, 2.63M in hexane) was added a saturated NH₄Cl solution (10 ml) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with water , a saturated NaHCO₃ , solution, brine, dried over Na₂SO₄ , filtered and concentrated. The residue was chromatographed over silica gel to yield pyrrole.

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 3.78 (s, 3H), 6.79 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz ,2H), 7.17-7.26 (m, 6H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 55.3, 113.9, 116.3, 120.6, 125.6, 126.4, 126.5, 127.8, 127.9, 128.3, 130.4, 131.5, 132.5, 133.6, 136.1, 157.8; IR (neat) 1600, 1514 cm⁻¹; MS (EI) *m/z*: 339 (M⁺); HRMS (EI) calcd for C₂₄H₂₁NO (M⁺): 339.1623. found: 339.1624.

2,4-Dimethyl-3,5-diphenyl-1H-pyrrole (**38**)¹⁴

To 20 mL of distilled liq ammonia was added sodium (8 mg, 0.36 mmol), and the mixture was stirred for 10min at -78 °C. To the resulting blue solution was added N-benzylpyrrole **27** (30 mg, 0.089 mmol) in THF (1 mL) and the mixture was stirred for 1 h. After removal of ammonia at room temperature, the residue was diluted with EtOAc and the organic phase was washed with brine and concentrated in vacuo. The residue was purified with silica gel column chromatography to yield 20 mg of **38**.

¹H NMR (600 MHz, CDCl₃) δ 2.21 (s, 3H), 2.29 (s, 3H), 7.19-7.44 (m, 10H); ¹³C NMR (150 MHz, CDCl₃) δ 11.4, 11.9, 114.8, 123.6, 124.7, 125.6, 125.7, 126.3, 126.7, 128.0,

128.6, 129.9, 133.7; MS (EI) m/z: 247 (M^+); HRMS (EI) calcd for $C_{18}H_{17}N$ (M^+):
247.1361. found: 247.1365.

ORTEP drawing of Xray crystal structure for the intermediate of entry 8 in Table 1.
(CCDC 635505)

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5a**¹H-NMR (400M)**

5a

¹³C-NMR (100M, CDCl₃)

S33

ph 4

5d

¹³C-NMR (100M, CDCl₃)

5i

¹H-NMR (400M, CDCl₃)

S36

5i

¹³C-NMR (100M, CDCl₃)

HSB-1-078b2-d, CDCl₃, 400MHz, 5j

C:\609lima NMR 1\35c1078b2-d.h1non.E6.ALS

5j

¹H-NMR (400M, CDCl₃)

S38

HSB-1-078b2-d, CDCl₃, 400MHz, 5j

C:\606jima NMR 1\35c1078b2-d.ctbom.E28.ALS

5j
¹³C-NMR (100M, CDCl₃)

HSB-1-167b1-d,CDCl3,400MHz,5k

C:\soelim\ima NMR 2\校正済\35c1167b1-d.h1 non_E5.als

S40

5k

¹³C-NMR (100M, CDCl₃)

S41

5I

¹H-NMR (400M, CDCl₃)

5I

¹³C-NMR (100M, CDCl₃)

8

^{13}C -NMR (100M, CDCl_3)

9
¹H-NMR (400M, CDCl₃)

9

^{13}C -NMR (100M, CDCl_3)

11
¹H-NMR (400M, CDCl₃)

11

¹³C-NMR (100M, CDCl₃)

12
¹H-NMR (400M, CDCl₃)

12

¹³C-NMR (100M, CDCl₃)

552

13
1H-NMR (400M, CDCl₃)

13

^{13}C -NMR (100M, CDCl_3)

14
1H-NMR (400M, CDCl₃)

14

¹³C-NMR (100M, CDCl₃)

18

^{13}C -NMR (100M, CDCl_3)

19

¹H-NMR (400M, CDCl₃)

S58

19

¹³C-NMR (100M, CDCl₃)

20

¹³C-NMR (100M, CDCl₃)

21

¹H-NMR (400M, CDCl₃)

21

^{13}C -NMR (100M, CDCl_3)

22c¹H-NMR (400M, CDCl₃)

22c¹³C-NMR (100 M, CDCl₃)

22d¹H-NMR (600M, CDCl₃)

22d¹³C-NMR (150M, CDCl₃)

22e¹H-NMR (400M, CDCl₃)

22f**¹H-NMR (400M, CDCl₃)**

22f¹³C-NMR (100M, CDCl₃)

22g**¹H-NMR (600M, CDCl₃)**

22g¹³C-NMR (150M, CDCl₃)

22h¹H-NMR (600M, CDCl₃)

22i
 $^1\text{H-NMR}$ (400M, CDCl_3)

22i ^{13}C -NMR (100M, CDCl_3)

$^1\text{H-NMR}$ (400M, CDCl_3)

26¹H-NMR (600M, CDCl₃)

26

$^{13}\text{C-NMR}$ (150M, CDCl_3)

27¹H-NMR (400 M, CDCl₃)

^{13}C -NMR (100M, CDCl_3)

28¹H-NMR (400M, CDCl₃)

28¹³C-NMR (100M, CDCl₃)

29¹H-NMR (600M, CDCl₃)

^{13}C -NMR (150M, CDCl_3)

30¹³C-NMR (100M, CDCl₃)

¹H-NMR (600M, CDCl₃)

^{13}C -NMR (150M, CDCl_3)

¹H-NMR (600M, CDCl₃)

$^{13}\text{C-NMR}$ (150M, CDCl_3)

34¹H-NMR (600M, CDCl₃)

34

^{13}C -NMR (150M, CDCl_3)

S100

35¹³C-NMR (150 M, CDCl₃)

¹H-NMR (400M, CDCl₃)

^{13}C -NMR (100M, CDCl_3)

$^1\text{H-NMR}$ (400M, CDCl_3)

^{13}C -NMR (100M, CDCl_3)

HSB-1-162b1-d-2,CDCl3,400MHz,b-lactone

C:\soelim\ima NMR 2\校正済\35c1162b1-d-2.h1non.E4.sis

β-lactone

¹H-NMR (400M, CDCl₃)

β -lactone

^{13}C -NMR (100M, CDCl_3)