[5+1] Annulation: A New Synthetic Strategy for Highly Substituted Phenols and Cyclohexenones

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I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 25°C on a Varian 500 MHz and 125 MHz, respectively, and TMS as internal standard. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400–4000 cm^{-1} . Elemental analyses were measured on a PE-2400 analyzer (Perkin-Elmer). Mass spectra were recorded on Agilent 1100 LCMsD mass spectrometer.

II. Preparation of Substrates

1. Preparation of α -acyl ketene-*S,S*-acetals **A**₁–**A**₅.

Entry	R ₂	R ₁	Product	Y (%) ^a
1	4-ClC ₆ H ₄ NHCO	Et	A ₁	98
2	2-MeC ₆ H ₄ NHCO	Et	A ₂	96
3	PhCO	Et	A ₃	96
4	4-ClC ₆ H ₄ NHCO	Me	A ₄	quant.
5	4-ClC ₆ H ₄ NHCO	n-Bu	A ₅	95

^a Isolated yields.

Typical procedure for the preparation of **A**₁–**A**₅ (with **A**₁ as an example): To a well-stirred suspension of *N*-(4-chlorophenyl)-3-oxobutanamide (21.2 g, 100 mmol) and anhydrous K₂CO₃ (35.0 g, 250 mmol) in DMF (150 mL) at 0 °C was added CS₂ (7.2 mL, 120 mmol). After the reaction mixture was stirred at 0 °C for 1.0 h, bromoethane (16.4 mL, 220 mmol) was added dropwise within 15 min. The mixture was allowed to warm to room temperature and stirred for 6 h, and then poured onto ice-water (800 mL) under stirring. The precipitated solid was collected by filtration, washed with water (3 × 200 mL), and dried in *vacuo* to afford the product **A**₁ (33.7 g, 98%) as a yellowish solid.

A₁ Yellowish solid, m.p. 132–133 °C. ^1H NMR (CDCl₃, 500 MHz), δ 1.29–1.32 (m, 6H), 2.50 (s, 3H), 2.93–2.97 (m, 4H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 8.47 (br s, 1H). IR (KBr, cm^{-1}) 3227, 1640, 1599, 1543, 1486, 1397, 1322, 1254, 1202, 1091, 831. MS (*m/z*): 344.6 [(*M* + 1)]⁺. Anal. Calcd for C₁₅H₁₈ClNO₂S₂: C, 52.39; H, 5.28; N, 4.07; Found: C, 52.55; H, 5.34; N, 4.09.

A₂ Yellow solid, m.p. 100-101 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.31-1.34 (m, 6H), 2.31 (s, 3H), 2.53 (s, 3H), 2.94-2.99 (m, 4H), 7.06-7.07 (m, 1H), 7.18-7.23 (m, 2H), 8.00 (d, J = 8.0 Hz, 1H), 8.22 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 199.4, 162.4, 149.5, 141.6, 135.8, 130.7 (2C), 128.9, 126.9 (2C), 125.3, 31.1, 30.9, 29.6, 18.2, 14.9 (2C). IR (KBr, cm⁻¹) 3369, 1674, 1656, 1529, 1453, 1307. MS (*m/z*): 324.5 [(*M* + 1)]⁺.

A₃ Light yellow liquid. ¹H NMR (CDCl₃, 500 MHz) δ 1.01 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H), 2.28 (s, 3H), 2.70 (q, J = 7.0 Hz, 2H), 2.99 (q, J = 7.0 Hz, 2H), 7.45-7.48 (m, 2H), 7.56-7.59 (m, 1H), 7.91 (d, J = 7.5 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 194.7, 193.9, 150.3, 143.8, 137.3, 133.7, 129.4 (2C), 128.8 (2C), 30.7, 30.3 (2C), 28.4, 14.8, 14.3. IR (KBr, cm⁻¹) 2967, 2927, 1660, 1482, 1448, 1259, 1210, 845, 691. MS (*m/z*): 295.0 [(*M* + 1)]⁺. Anal. Calcd for C₁₅H₁₈O₂S₂: C, 61.19; H, 6.16; Found: C, 61.33; H, 6.20.

A₄ Yellowish solid, m.p. 154-156 °C. ¹H NMR (CDCl₃, 500 MHz) δ 2.46 (s, 3H), 2.48 (s, 6H), 7.29 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 8.46 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 198.5, 162.7, 138.0, 136.5, 129.8, 129.3 (2C), 121.3 (2C), 30.5, 18.6. IR (KBr, cm⁻¹) 3274, 1652, 1551, 1492, 1092, 826. MS (*m/z*): 338.8 [(*M* + 23)]⁺. Anal. Calcd for C₁₃H₁₄ClNO₂S₂: C, 49.44; H, 4.47; N, 4.43; Found: C, 49.54; H, 4.40; N, 4.47.

A₅ Yellowish solid, m.p. 82-83 °C. ¹H NMR (CDCl₃, 500 MHz) δ 0.88-0.92 (m, 6H), 1.37-1.42 (m, 4H), 1.59-1.63 (m, 4H), 2.47 (s, 3H), 2.90-2.93 (m, 4H), 7.29 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 8.58 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 198.8, 162.7, 152.7, 140.2, 136.5, 129.7, 129.2 (2C), 121.2 (2C), 35.3, 30.7 (2C), 31.9, 22.1 (2C), 13.7 (2C). IR (KBr, cm⁻¹) 3330, 2957, 2928, 1677, 1659, 1598, 1491, 1397, 1312, 1196, 1089, 841. MS (*m/z*): 401.3 [(*M* + 1)]⁺. Anal. Calcd for C₁₉H₂₆ClNO₂S₂: C, 57.05; H, 6.55; N, 3.50; Found: C, 57.34; H, 6.61; N, 3.55.

2. Preparation of α-alkenoyl ketene-S,S-acetals **1a-l**. These compounds were synthesized *via* the Claisen-Schmidt condensation of α-acyl ketene-S,S-acetals **A₁-A₅** with aromatic aldehydes or trans-cinnamaldehyde, respectively.

Key: (a) NaH (2.0 eq.), DMSO, 0~70 °C, 1.0~2.0 h.

Entry	A	R ₃	Product	Y (%) ^a
1	A₁	4-MeC ₆ H ₄	1a	96
2	A₁	3,4-O ₂ CH ₂ C ₆ H ₃	1b	98
3	A₁	4-ClC ₆ H ₄	1c	95
4	A₁	4-FC ₆ H ₄	1d	96

5	A ₁	2-thienyl	1e	93
6	A ₁	2-furyl	1f	95
7	A ₁	PhCH=CH	1g	88
8	A ₂	4-MeC ₆ H ₄	1h	94
9	A ₃	4-MeC ₆ H ₄	1i	90
10	A ₃	PhCH=CH	1j	93
11	A ₄	4-MeC ₆ H ₄	1k	96
12	A ₅	4-MeC ₆ H ₄	1l	93

^a Isolated yields.

Typical procedure for the preparation of **1a-l** (with **1a** as an example): To a solution of α -acyl ketene-*S,S*-acetals **A₁** (1670 mg, 5.0 mmol) and *p*-tolualdehyde (0.8 mL, 6.5 mmol) in DMSO (6.0 mL) at 0 °C was added NaH (240 mg, 10.0 mmol) in one portion. The reaction mixture was stirred at 0 °C for 10 min, then heated and kept at 70 °C for 0.5 h. After the starting material **A₁** was consumed as indicated by TLC, the resulting mixture was then allowed to cool down to room temperature and poured onto ice-water (250 mL) under stirring. The precipitated solid was collected by filtration, washed with water (3 $\times$ 30 mL), and dried in *vacuo* to afford the product **1a** (2100 mg, 96%) as a yellow solid.

1a Yellow solid, m.p. 151-152 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.28-1.32 (m, 6H), 2.38 (s, 3H), 2.92-2.97 (m, 4H), 7.02 (d, *J* = 16.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 16.0 Hz, 1H), 8.82 (br s, 1H). IR (KBr, cm⁻¹) 3292, 1669, 1652, 1594, 1490, 1308, 1178, 814. MS (*m/z*): 447.0 [(*M* + 1)]⁺. Anal. Calcd for C₂₃H₂₄ClNO₂S₂: C, 61.94; H, 5.42; N, 3.14; Found: C, 61.35; H, 5.60; N, 3.21.

1b Yellow solid, m.p. 134-136 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.28-1.31 (m, 6H), 2.93-2.95 (m, 4H), 6.02 (s, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 7.05-7.06 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 16.0 Hz, 1H), 8.80 (br s, 1H). IR (KBr, cm⁻¹) 3225, 3105, 1665, 1641, 1544, 1488, 1397, 1327, 1205, 1091, 861.

1c Yellow solid, m.p. 135-136 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.28-1.31 (m, 6H), 2.93-2.97 (m, 4H), 7.03 (d, *J* = 15.5 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 15.5 Hz, 1H), 8.85 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 192.0, 161.3, 153.5, 142.5, 138.5, 136.8, 136.5, 133.1, 129.7 (2C), 129.1 (2C), 127.2, 121.2 (2C), 29.9 (2C), 14.9 (2C). IR (KBr, cm⁻¹) 3296, 1649, 1592, 1529, 1490, 1398, 1313, 1092, 1012, 824. MS (*m/z*): 467.3 [(*M* + 1)]⁺. Anal. Calcd for C₂₂H₂₁Cl₂NO₂S₂: C, 56.65; H, 4.54; N, 3.00; Found: C, 56.80; H, 4.44; N, 3.04.

1d Yellow solid, m.p. 147-148°. ¹H NMR (CDCl₃, 500 MHz) δ 1.28-1.32 (m, 6H), 2.94-2.97 (m, 4H), 7.00 (d, J = 16.0 Hz, 1H), 7.07-7.10 (m, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.52-7.57 (m, 4H), 7.62 (d, J = 16.0 Hz, 1H), 8.82 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 192.3, 165.4, 163.4, 161.3, 153.1, 143.0, 138.7, 136.5, 130.9, 130.7, 130.6, 129.5, 129.2 (2C), 126.6, 121.2 (2C), 116.5, 116.3, 29.9 (2C), 14.9 (2C). IR (KBr, cm⁻¹) 3298, 1668, 1644, 1595, 1507, 1232, 1157, 829. MS (*m/z*): 473.1 [(M + 23)]⁺. Anal. Calcd for C₂₂H₂₁ClFNO₂S₂: C, 58.72; H, 4.70; N, 3.11; Found: C, 58.89; H, 4.82; N, 3.08.

1e Yellow solid, m.p. 142-143°. ¹H NMR (CDCl₃, 500 MHz) δ 1.30-1.33 (m, 6H), 2.93-2.96 (m, 4H), 6.86 (d, J = 15.5 Hz, 1H), 7.07 (dd, J = 3.5, 5.0 Hz, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 3.5 Hz, 1H), 7.42 (d, J = 5.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 15.5 Hz, 1H), 8.92 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 191.8, 161.3, 153.0, 140.1, 138.8, 136.6, 132.3, 129.7, 129.4, 129.2, 129.1 (2C), 128.6, 15.8, 121.2 (2C), 29.8 (2C), 14.9 (2C). IR (KBr, cm⁻¹) 3310, 2966, 2925, 1663, 1641, 1582, 1533, 1490, 1397, 1315, 1165, 968, 830, 702. MS (*m/z*): 439.1 [(M + 1)]⁺. Anal. Calcd for C₂₀H₂₀ClNO₂S₃: C, 54.84; H, 4.60; N, 3.20; Found: C, 54.99; H, 4.66; N, 3.32.

1f Yellow solid, m.p. 137-138°. ¹H NMR (CDCl₃, 500 MHz) δ 1.30-1.33 (m, 6H), 2.90-2.96 (m, 4H), 6.50 (d, J = 3.0 Hz, 1H), 6.50 (s, 1H), 6.70 (d, J = 3.0 Hz, 1H), 6.97 (d, J = 15.5 Hz, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 15.5 Hz, 1H), 7.51 (s, 1H), 7.56 (d, J = 8.5 Hz, 2H), 8.87 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 192.1, 161.1, 152.9, 140.1, 138.7, 136.5, 132.3, 129.6, 129.4, 129.1 (2C), 128.6, 125.9, 121.2 (2C), 29.8 (2C), 14.9 (2C). IR (KBr, cm⁻¹) 3296, 1666, 1639, 1593, 1534, 1490, 1313, 1260, 1160, 1018, 831.

1g Yellow solid, m.p. 125-127°. ¹H NMR (DMSO, 500 MHz) δ 1.23 (br s, 6H), 2.89-2.95 (m, 4H), 6.63 (d, J = 15.0 Hz, 1H), 7.14-7.19 (m, 1H), 7.25 (d, J = 15.0 Hz, 1H), 7.33-7.45 (m, 6H), 7.60 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H). IR (KBr, cm⁻¹) 3446, 1652, 1646, 1558, 1533, 1490, 1456. MS (*m/z*): 459.0 [(M + 1)]⁺. Anal. Calcd for C₂₀H₂₀ClNO₃S₂: C, 56.93; H, 4.78; N, 3.32; Found: C, 56.99; H, 4.74; N, 3.40.

1h Yellow semisolid. ¹H NMR (CDCl₃, 500 MHz) δ 1.29-1.32 (m, 6H), 2.32 (s, 3H), 2.38 (s, 3H), 2.91-2.96 (m, 4H), 7.02-7.05 (m, 2H), 7.16-7.21 (m, 4H), 7.46 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 16.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.66 (br s, 1H). IR (KBr, cm⁻¹) 3308, 2965, 2925, 1668, 1588, 1530, 1455, 1255, 1179, 753.

1i Yellow solid, m.p. 86-87°. ¹H NMR (CDCl₃, 500 MHz) δ 1.05 (t, J = 7.0 Hz, 3H), 1.13 (t, J = 7.0 Hz, 3H), 2.36 (s, 3H), 2.73 (q, J = 7.0 Hz, 2H), 2.94 (q, J = 7.0 Hz, 2H), 6.95 (d, J = 16.0 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.41-7.48 (m, 4H), 7.55-7.58 (m, 1H), 7.72 (d, J = 16.0 Hz, 1H), 7.99 (d, J = 7.5 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 193.4, 188.5, 147.3, 141.4, 137.4, 133.6, 132.1, 129.8 (4C), 128.8 (2C), 128.7 (2C), 124.4, 29.8, 28.7, 21.7, 15.1, 14.6. IR (KBr, cm⁻¹) 1668, 1589, 1330, 1256, 1185, 809. MS (*m/z*): 397.2 [(M + 1)]⁺. Anal. Calcd for C₂₃H₂₄O₂S₂: C, 69.66; H, 6.10; Found: C, 69.75; H, 6.12.

1j Yellow solid, m.p. 78-80°. ¹H NMR (DMSO, 500 MHz) δ 0.95 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H), 2.73 (q, J = 7.0 Hz, 2H), 2.94 (q, J = 7.0 Hz, 2H), 6.63 (d, J = 15.0 Hz, 1H), 7.25-7.37 (m, 2H), 7.33-7.45 (m, 4H), 7.54-7.57 (m, 2H), 7.61 (d, J = 7.5 Hz, 2H), 7.66-7.69 (m, 1H), 7.89 (d, J = 8.0 Hz, 2H). IR (KBr, cm⁻¹) 1659, 1639, 1575, 1268, 1144, 1007, 688.

1k Yellow solid, m.p. 151-152°. ¹H NMR (CDCl₃, 500 MHz) δ 2.38 (s, 3H), 2.45 (s, 6H), 7.03 (d, J = 16.0 Hz, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 16.0 Hz, 1H), 8.97 (br s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 192.6, 161.3, 157.3, 144.2, 141.7, 136.6, 136.4, 131.8 (2C), 130.0, 129.4 (2C), 128.8 (2C), 126.0, 121.3 (2C), 21.7, 18.7. IR (KBr, cm⁻¹) 3292, 1652, 1594, 1490, 1249, 1037, 827. MS (*m/z*): 419.0 [(M + 1)]⁺. Anal. Calcd for C₂₁H₂₀ClNO₂S₂: C, 60.34; H, 4.82; N, 3.35; Found: C, 60.55; H, 4.96; N, 3.32.

1l Yellow solid, m.p. 99-100°. ¹H NMR (CDCl₃, 500 MHz) δ 0.85-0.92 (m, 6H), 1.36-1.42 (m, 4H), 1.56-1.62 (m, 4H), 2.38 (s, 3H), 2.90-2.94 (m, 4H), 7.02 (d, J = 16.0 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H), 7.27 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.63 (d, 16.0 Hz, 1H), 8.81 (br s, 1H). IR (KBr, cm⁻¹) 3294, 1646, 1594, 1491, 1310, 1159, 827.

III. Preparation of 3a-l, 5m and 5n

Typical procedure (**3a** as an example): To the mixture of **1a** (450 mg, 1.0 mmol) and nitroethane **2a** (0.22 mL, 3.0 mmol) in DMF (5 mL) was added 1,8-diazabicyclo [5.4.0.]undec-7-ene (DBU, 0.15 mL, 1.0 mmol) in dry THF (2 mL) within 5 min at room temperature. The starting material **1a** was quickly consumed as indicated by TLC within 0.5 h. Then brine (30 mL) was added into the reaction mixture which was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over MgSO₄, filtered and concentrated in *vacuo*. The crude product was purified by flash chromatography (silica gel, diethylether : acetone = 4: 1) to give **3a** (404 mg, 88%).

3a White solid, m.p. 182-183°. ¹H NMR (CDCl₃, 500 MHz) δ 1.23 (t, J = 7.5 Hz, 3H), 1.77 (s, 3H), 2.34 (s, 3H), 2.87 (dd, J = 4.0, 17.5 Hz, 1H), 2.98-3.04 (m, 3H), 4.14 (dd, J = 4.0, 13.5 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 8.41 (br s, 1H). IR (KBr, cm⁻¹) 3336, 1628, 1541, 1491, 1402, 1246, 1092, 828. MS (*m/z*): 459.1 [(M + 1)]⁺. Anal. Calcd for C₂₃H₂₃ClN₂O₄S: C, 60.19; H, 5.05; N, 6.10; Found: C, 60.33; H, 5.00; N, 6.19.

3b White solid, m.p. 162-164°. ¹H NMR (CDCl₃, 500 MHz) δ 1.23 (t, J = 7.5 Hz, 3H), 1.79 (s, 3H), 2.87 (dd, J = 4.0, 17.0 Hz, 1H), 2.90 (dd, J = 13.0, 17.0 Hz, 1H), 2.99 (q, J = 7.5 Hz, 2H), 4.10 (dd, J = 4.0, 13.0 Hz, 1H), 5.98 (s, 2H), 6.54 (d, J = 8.0 Hz, 1H), 6.57 (s, 1H), 6.77 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 8.40 (br s, 1H). IR (KBr, cm⁻¹) 3431, 1678, 1548, 1491, 1445, 1260, 1039, 932, 818.

3c White solid, m.p. 203-204°. ¹H NMR (DMSO, 500 MHz) δ 1.14 (t, J = 7.5 Hz, 3H), 1.72 (s, 3H), 2.70 (dd, J = 3.5, 17.0 Hz, 1H), 2.93 (q, J = 7.5 Hz, 2H), 3.40 (dd, J = 14.5, 17.0 Hz, 1H), 4.27 (dd, J = 3.5, 14.5 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 10.52 (br s, 1H). ¹³C NMR (DMSO, 125 MHz) δ 197.6, 168.6, 159.7, 146.8, 143.8, 141.2, 139.7, 136.8 (2C), 135.4 (2C), 135.1 (2C), 134.0, 127.3 (2C), 104.3, 54.2, 45.2, 36.1, 23.8, 20.9. IR (KBr, cm⁻¹) 3395, 1670, 1549, 1491, 1314, 1092, 825. MS (*m/z*): 480.0 [(M + 1)]⁺. Anal. Calcd for C₂₂H₂₀Cl₂N₂O₄S: C, 55.12; H, 4.21; N, 5.84; Found: C, 55.56; H, 4.34; N, 5.80.

3d White solid, m.p. 143-145°. ¹H NMR (DMSO, 500 MHz) δ 1.14 (t, J = 7.5 Hz, 3H), 1.72 (s, 3H), 2.70 (dd, J =

3.0, 17.0 Hz, 1H), 2.94 (q, $J = 7.5$ Hz, 2H), 3.41 (dd, $J = 14.5, 17.0$ Hz, 1H), 4.27 (dd, $J = 3.0, 14.5$ Hz, 1H), 7.22-7.25 (m, 4H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 10.52 (s, 1H). ^{13}C NMR (DMSO, 125 MHz) δ 197.7, 168.6, 167.5, 159.7, 146.8, 138.5, 137.1, 137.0, 135.4 (2C), 134.0, 127.3 (2C), 122.0, 121.8, 104.3, 54.0, 36.1 (2C), 23.8, 20.9 (2C). IR (KBr, cm^{-1}) 3446, 1682, 1548, 1492, 1319, 1093, 1014, 832. MS (m/z): 486.5 [(M + 23)] $^{+}$. Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{ClFN}_2\text{O}_4\text{S}$: C, 57.08; H, 4.35; N, 6.05; Found: C, 57.27; H, 4.39; N, 6.03.

3e White solid, m.p. 137-138 $^{\circ}$. ^1H NMR (DMSO, 500 MHz) δ 1.14 (t, $J = 7.5$ Hz, 3H), 1.77 (s, 3H), 2.85 (dd, $J = 3.0, 13.5$ Hz, 1H), 2.94 (q, $J = 7.5$ Hz, 2H), 3.26 (dd, $J = 14.0, 16.5$ Hz, 1H), 4.62 (dd, $J = 3.0, 14.0$ Hz, 1H), 7.03 (s, 1H), 7.06-7.08 (m, 1H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 4.0$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 2H), 10.48 (br s, 1H). IR (KBr, cm^{-1}) 3425, 1548, 1492, 1293, 1093, 818, 706.

3f White solid, d.p. 186-188 $^{\circ}$. ^1H NMR (DMSO, 500 MHz) δ 1.14 (t, $J = 7.5$ Hz, 3H), 1.68 (s, 3H), 2.83 (dd, $J = 4.0, 17.0$ Hz, 1H), 2.91 (q, $J = 7.5$ Hz, 2H), 3.13 (dd, $J = 14.5, 17.0$ Hz, 1H), 4.46 (dd, $J = 4.0, 14.5$ Hz, 1H), 6.40 (s, 1H), 6.47 (d, $J = 1.5$ Hz, 1H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.68 (s, 1H), 10.46 (s, 1H). ^{13}C NMR (DMSO, 125 MHz) δ 196.8, 168.6, 159.2, 156.4, 149.9, 146.8, 143.8, 135.4 (2C), 134.0, 127.2 (2C), 117.1, 115.6, 102.5, 48.9, 43.5, 36.0, 24.4, 20.9. IR (KBr, cm^{-1}) 3419, 1683, 1596, 1549, 1512, 1319, 1236, 840. MS (m/z): 435.5 [(M + 1)] $^{+}$. Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{ClN}_2\text{O}_5\text{S}$: C, 55.24; H, 4.40; N, 6.44; Found: C, 55.33; H, 4.26; N, 6.50.

3g White solid, m.p. 122-123 $^{\circ}$. ^1H NMR (CDCl_3 , 500 MHz) δ 1.23 (t, $J = 7.5$ Hz, 3H), 2.03 (s, 3H), 2.71 (dd, $J = 4.0, 17.5$ Hz, 1H), 2.80-2.83 (m, 1H), 2.94 (dd, $J = 14.0, 17.5$ Hz, 1H), 3.14 (q, $J = 7.5$ Hz, 2H), 5.78 (dd, $J = 8.5, 16.0$ Hz, 1H), 6.61 (d, $J = 16.0$ Hz, 1H), 7.30-7.35 (m, 7H), 7.63 (d, $J = 8.0$ Hz, 2H), 9.45 (br s, 1H). IR (KBr, cm^{-1}) 3446, 1683, 1541, 1456, 832.

3h White solid, m.p. 168-169 $^{\circ}$. ^1H NMR (DMSO, 500 MHz) δ 1.18 (t, $J = 7.5$ Hz, 3H), 1.72 (s, 3H), 2.29 (s, 6H), 2.64 (dd, $J = 3.5, 17.5$ Hz, 1H), 3.00-3.06 (m, 6H), 3.41 (dd, $J = 14.5, 17.5$ Hz, 1H), 4.21 (dd, $J = 3.5, 14.5$ Hz, 1H), 7.07 (d, $J = 7.5$ Hz, 2H), 7.12-7.27 (m, 5H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.98 (s, 1H). IR (KBr, cm^{-1}) 3421, 1683, 1549, 1456, 1316.

3i White solid, m.p. 171-172 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.11 (t, J = 7.5 Hz, 3H), 1.79 (s, 3H), 2.35 (s, 3H), 2.72-2.80 (m, 2H), 2.87 (dd, J = 4.0, 17.0 Hz, 1H), 3.06 (dd, J = 14.5, 17.0 Hz, 1H), 4.32 (dd, J = 4.0, 14.5 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.52-7.55 (m, 2H), 7.63-7.66 (m, 1H), 8.04 (d, J = 7.5 Hz, 1H). IR (KBr, cm⁻¹) 1686, 1548, 1451, 1290, 1232, 1178, 826.

3j White solid, m.p. 101-102 °C. ¹H NMR (CDCl₃, 500 MHz) δ 1.12 (t, J = 7.5 Hz, 3H), 1.97 (s, 3H), 2.68-2.79 (m, 3H), 2.87 (dd, J = 4.5, 17.5 Hz, 1H), 3.84-3.89 (m, 1H), 6.04 (dd, J = 8.5, 16.0 Hz, 1H), 6.56 (d, J = 16.0 Hz, 1H), 7.28-7.37 (m, 5H), 7.50-7.53 (m, 2H), 7.62-7.65 (m, 1H), 7.99 (d, J = 7.5 Hz, 2H). ¹³C NMR (DMSO, 125 MHz) δ 203.1, 202.7, 164.2, 153.5, 146.3, 145.7, 145.0, 144.7, 139.7 (2C), 139.4 (2C), 139.2 (2C), 138.7, 137.2 (2C), 135.0, 108.0, 58.0, 41.5, 27.9, 24.9 (2C). IR (KBr, cm⁻¹) 1685, 1596, 1546, 1449, 1291, 1229, 753, 691. MS (*m/z*): 444.0 [(M + 23)]⁺. Anal. Calcd for C₂₄H₂₃NO₄S: C, 68.39; H, 5.50; N, 3.32; Found: C, 68.36; H, 5.67; N, 3.33.

3k White solid, m.p. 147-148 °C. ¹H NMR (DMSO, 500 MHz) δ 1.73 (s, 3H), 2.30 (s, 3H), 2.43 (s, 3H), 2.65 (dd, J = 3.0, 17.0 Hz, 1H), 3.38 (dd, J = 14.5, 17.0 Hz, 1H), 4.17 (dd, J = 3.0, 14.5 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 10.53 (s, 1H). ¹³C NMR (DMSO, 125 MHz) δ 197.8, 168.7, 161.2, 145.9, 144.3, 143.8, 139.1, 135.6 (2C), 135.3 (2C), 134.8 (2C), 134.0, 127.3 (2C), 104.2, 54.6, 37.1, 27.1, 24.4, 24.0. IR (KBr, cm⁻¹) 3423, 1685, 1565, 1458, 1416, 1292, 1116, 738.

3l White solid, m.p. 136-137 °C. ¹H NMR (DMSO, 500 MHz) δ 0.74 (t, J = 7.5 Hz, 3H), 1.15-1.20 (m, 2H), 1.44-1.49 (m, 2H), 1.71 (s, 3H), 2.29 (s, 3H), 2.66 (dd, J = 3.0, 17.0 Hz, 1H), 2.92 (q, J = 7.5 Hz, 2H), 3.38 (dd, J = 15.5, 17.0 Hz, 1H), 4.20 (dd, J = 3.0, 15.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 10.52 (br s, 1H). IR (KBr, cm⁻¹) 3307, 1651, 1549, 1491, 1320, 1092, 825.

5m Yellowish solid, m.p. 166-167 °C. ¹H NMR (CDCl₃, 500 MHz) δ 0.82 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.5 Hz, 6H), 1.43-1.48 (s, 1H), 1.78-1.85 (m, 1H), 2.12 (s, 3H), 2.83-2.93 (m, 4H), 3.20 (dd, J = 4.0, 16.0 Hz, 1H), 3.36 (dd, J =

10.5, 16.0 Hz, 1H), 3.66-3.71 (m, 1H), 4.51-4.56 (m, 1H), 6.96 (d, $J = 7.5$ Hz, 2H), 7.02 (d, $J = 7.5$ Hz, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.86 (s, 1H). IR (KBr, cm^{-1}) 3310, 2972, 1653, 1595, 1548, 1490, 1451, 1397, 1247, 819. MS (m/z): 536.0 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{ClN}_2\text{O}_4\text{S}_2$: C, 58.36; H, 5.84; N, 5.23; Found: C, 58.54; H, 5.85; N, 5.26.

5n Yellowish solid, m.p. 175-176°. ^1H NMR (CDCl_3 , 500 MHz) δ 1.06 (t, $J = 7.0$ Hz, 3H), 1.24-1.29 (m, 6H), 2.17 (s, 3H), 2.88-2.92 (m, 4H), 3.39 (dd, $J = 4.5, 17.5$ Hz, 1H), 3.48 (dd, $J = 9.0, 17.5$ Hz, 1H), 4.01-4.07 (m, 2H), 4.29 (m, 1H), 5.38 (d, $J = 8.5$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 9.0$ Hz, 2H), 7.94 (s, 1H). IR (KBr, cm^{-1}) 3292, 2980, 1747, 1653, 1560, 1516, 1490, 1397, 1310, 1247, 1092, 828.

IV. Preparation of phenols 4a-n

Typical procedure (**4a** as an example): To the mixture of **1a** (450 mg, 1.0 mmol) and nitroethane **2a** (0.22 mL, 3.0 mmol) in DMF (5 mL) was added 1,8-diazabicyclo [5.4.0.]undec-7-ene (DBU, 0.15 mL, 1.0 mmol) in dry THF (2 mL) within 5 min. The mixture was stirred at room temperature for 0.5 h, and then was heated in an oil bath at 70° for another 0.5 h. The resulting mixture was then allowed to cool down to ambient temperature, brine (30 mL) was added and the solution was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with water (3×20 mL), dried over MgSO_4 , filtered and concentrated in *vacuo*. The crude product was purified by flash chromatography (silica gel, petroleum: diethylether = 4: 1) to give phenol **4a** (280 mg, 67%).

4a White solid, m.p. 180-181°. ^1H NMR (CDCl_3 , 500 MHz) δ 1.22 (t, $J = 7.5$ Hz, 3H), 2.38 (s, 3H), 2.41 (s, 3H), 2.83 (q, $J = 7.5$ Hz, 4H), 6.94 (s, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 11.54 (br s, 1H), 12.26 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 168.7, 160.7, 148.1, 138.5, 137.5, 136.1, 132.6, 131.6, 130.3, 129.4, (2C), 129.1 (2C), 128.8 (2C), 122.2 (2C), 121.2, 116.5, 32.2, 21.4, 19.8, 14.5. IR (KBr, cm^{-1}) 3430, 1633, 1539, 1492, 1399, 1246, 830. MS (m/z): 411.7 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{ClNO}_2\text{S}$: C, 67.06; H, 5.38; N, 3.40; Found: C, 67.46; H, 5.50; N, 3.44.

4b White solid, m.p. 160-161°. ^1H NMR (CDCl_3 , 500 MHz) δ 1.22 (t, $J = 7.5$ Hz, 3H), 2.39 (s, 3H), 2.83 (q, 2H), 6.02 (s, 2H), 6.73-6.75 (m, 2H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.93 (s, 1H), 7.37 (d, $J = 9.0$ Hz, 2H), 7.64 (d, $J = 9.0$ Hz, 2H), 11.52 (br s, 1H), 12.25 (s, 1H). IR (KBr, cm^{-1}) 3113, 1638, 1600, 1537, 1490, 1243, 1039, 815.

4c White solid, m.p. 168-169°. ¹H NMR (CDCl₃, 500 MHz) δ 1.21 (t, J = 7.5 Hz, 3H), 2.35 (s, 3H), 2.83 (q, J = 7.5 Hz, 2H), 6.91 (s, 1H), 7.21 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 9.0 Hz, 2H), 7.39 (d, J = 9.0 Hz, 2H), 7.64 (d, J = 9.0 Hz, 2H), 11.50 (br s, 1H), 12.26 (s, 1H). IR (KBr, cm⁻¹) 3119, 1640, 1548, 1455, 1236, 825. MS (ESI): *m/z* 433.1 [(M + 1)]⁺

4d White solid, m.p. 161-162°. ¹H NMR (CDCl₃, 500 MHz) δ 1.22 (t, J = 7.5 Hz, 3H), 2.36 (s, 3H), 2.84 (q, J = 7.5 Hz, 2H), 6.92 (s, 1H), 7.10-7.14 (m, 2H), 7.19-7.25 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 11.49 (br s, 1H), 12.23 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 168.5, 160.7, 146.9, 137.3, 136.0, 132.5, 131.8, 130.6, 130.5, 130.4, 129.5 (2C), 122.2 (2C), 121.2, 116.8, 115.5, 115.4, 32.2, 19.8, 14.6. IR (KBr, cm⁻¹) 3304, 2926, 1640, 1597, 1533, 1452, 1237, 1093, 833. MS (*m/z*): 416.4 [(M + 1)]⁺. Anal. Calcd for C₂₂H₁₉ClFNO₂S: C, 63.53; H, 4.60; N, 3.37; Found: C, 63.50; H, 4.76; N, 3.45.

4e White solid, m.p. 140-141°. ¹H NMR (CDCl₃, 500 MHz) δ 1.22 (t, J = 7.5 Hz, 3H), 2.56 (s, 3H), 2.83 (q, J = 7.5 Hz, 2H), 7.07 (dd, J = 1.0, 3.5 Hz, 1H), 7.10-7.11 (m, 1H), 7.11 (s, 1H), 7.38 (d, J = 9.0 Hz, 2H), 7.40 (dd, J = 1.0, 5.0 Hz, 1H), 7.64 (d, J = 9.0 Hz, 2H), 11.49 (br s, 1H), 12.18 (s, 1H). IR (KBr, cm⁻¹) 3403, 1638, 1593, 1537, 1491, 1243, 828.

4f White solid, m.p. 135-137°. ¹H NMR (CDCl₃, 500 MHz) δ 1.20 (t, J = 7.5 Hz, 3H), 2.67 (s, 3H), 2.83 (q, J = 7.5 Hz, 2H), 6.53 (d, J = 1.5 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 7.36 (s, 1H), 7.37 (d, J = 9.0 Hz, 2H), 7.55 (s, 1H), 7.62 (d, J = 9.0 Hz, 2H), 11.45 (br s, 1H), 12.18 (s, 1H). IR (KBr, cm⁻¹) 3118, 1635, 1593, 1539, 1492, 1400, 1247, 828, 741.

4g White solid, m.p. 138-139°. ¹H NMR (CDCl₃, 500 MHz) δ 1.19 (t, J = 7.5 Hz, 3H), 2.61 (s, 3H), 2.79 (q, J = 7.5 Hz, 2H), 7.04 (d, J = 16.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.30-7.33 (m, 2H), 7.35-7.39 (m, 3H), 7.38 (d, J = 16.0 Hz, 1H), 7.39 (s, 1H), 7.54 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 11.59 (br s, 1H), 12.38 (s, 1H). IR (KBr, cm⁻¹) 3439, 1634, 1533, 1492, 1449, 1244, 823. MS (*m/z*): 425.0 [(M + 1)]⁺. Anal. Calcd for C₂₄H₂₂ClNO₂S: C, 67.99; H, 5.23; N, 3.30; Found: C, 68.12; H, 5.33; N, 3.32.

4h Colorless semisolid. ^1H NMR (CDCl_3 , 500 MHz) δ 1.26 (t, $J = 7.5$ Hz, 3H), 2.41 (s, 9H), 2.90 (q, $J = 7.5$ Hz, 2H), 6.96 (s, 1H), 7.16-7.20 (m, 3H), 7.24-7.31 (m, 4H), 7.90 (d, $J = 7.5$ Hz, 1H), 11.23 (br s, 1H), 12.54 (s, 1H). IR (KBr, cm^{-1}) 3200, 2925, 1636, 1532, 1456, 1250, 822, 752.

4i White solid, m.p. 170-171 $^\circ$. ^1H NMR (CDCl_3 , 500 MHz) δ 0.97 (t, $J = 7.5$ Hz, 3H), 2.35 (s, 3H), 2.42 (s, 3H), 2.56 (q, $J = 7.5$ Hz, 4H), 6.89 (s, 1H), 7.01 (br s, 1H), 7.22-7.26 (m, 4H), 7.43-7.46 (m, 2H), 7.55-7.58 (m, 1H), 7.79 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 198.4, 152.8, 146.4, 139.3, 138.7, 137.3, 133.9, 133.1, 132.8, 129.4, 129.1, 129.0, 128.6, 118.9, 31.3, 21.4, 18.2, 14.4. IR (KBr, cm^{-1}) 33325, 2968, 2933, 1658, 1586, 1448, 1394, 1309, 1229, 977, 827, 681.

4j White solid, m.p. 100-101 $^\circ$. ^1H NMR (CDCl_3 , 500 MHz) δ 0.96 (t, $J = 7.5$ Hz, 3H), 2.51 (q, $J = 7.5$ Hz, 2H), 2.58 (s, 3H), 7.05 (d, $J = 16.0$ Hz, 1H), 7.25 (s, 1H), 7.26 (d, $J = 7.5$ Hz, 1H), 7.30-7.33 (m, 1H), 7.36-7.45 (m, 4H), 7.54-7.56 (m, 3H), 7.40 (d, $J = 8.0$ Hz, 2H). IR (KBr, cm^{-1}) 3431, 1653, 1540, 1399, 1232, 1090, 692.

4k White solid, m.p. 156-157 $^\circ$. ^1H NMR (CDCl_3 , 500 MHz) δ 2.37 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H), 6.94 (s, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 11.36 (s, 1H), 12.10 (s, 1H). IR (KBr, cm^{-1}) 3336, 1674, 1628, 1541, 1491, 1444, 1401, 1317, 1247, 821.

4l White solid, m.p. 137-139 $^\circ$. ^1H NMR (CDCl_3 , 500 MHz) δ 0.84 (t, $J = 7.5$ Hz, 3H), 1.33-1.37 (m, 2H), 1.50-1.55 (m, 2H), 2.38 (s, 3H), 2.41 (s, 3H), 2.79 (q, $J = 7.5$ Hz, 2H), 6.93 (s, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 11.51 (br s, 1H), 12.22 (s, 1H). IR (KBr, cm^{-1}) 3431, 1637, 1536, 1492, 1398, 1245, 824. MS (m/z): 440.8 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{ClNO}_2\text{S}$: C, 68.24; H, 5.96; N, 3.18; Found: C, 68.57; H, 6.02; N, 3.18.

4m White solid, m.p. 176-178°. ¹H NMR (CDCl₃, 500 MHz) δ 1.03 (t, J = 7.5 Hz, 3H), 1.21 (t, J = 7.5 Hz, 3H), 2.41 (s, 3H), 2.79-2.85 (m, 4H), 6.88 (s, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 9.0 Hz, 2H), 11.34 (br s, 1H), 12.01 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 168.5, 160.3, 148.0, 138.9, 138.5, 137.3, 136.1, 131.4, 130.3, 129.4 (2C), 129.0 (2C), 128.5 (2C), 122.0 (2C), 121.3, 116.6, 32.8, 25.1, 21.4, 16.5, 14.4. IR (KBr, cm⁻¹) 3306, 2967, 1638, 1533, 1457, 1176, 825. MS (*m/z*): 425.1 [(M + 1)]⁺. Anal. Calcd for C₂₄H₂₄ClNO₂S: C, 67.67; H, 5.68; N, 3.29; Found: C, 67.81; H, 5.77; N, 3.26.

4n White solid, m.p. 166-167°. ¹H NMR (CDCl₃, 500 MHz) δ 1.12 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.5 Hz, 3H), 2.39 (s, 3H), 2.91 (q, J = 7.5 Hz, 2H), 4.15 (q, J = 7.5 Hz, 2H), 7.06 (s, 1H), 7.21 (d, J = 7.0 Hz, 2H), 7.31 (d, J = 7.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 11.39 (s, 1H), 12.77 (s, 1H). IR (KBr, cm⁻¹) 3445, 1717, 136, 1540, 1452, 1247, 1111, 825.

V. Copies of NMR spectra for compounds **3a-l**, **4a-n**, **5m** and **5n**