Supporting Information

Aerobic, copper-catalyzed desulfitative C–C bond-forming reaction of ketene dithioacetals/vinylogous thioesters and arylboronic acids

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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. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded at 25°C on a Varian 500 MHz and 125 MHz or a Bruker 100 MHz, respectively, and using TMS as internal standard. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400–4000 cm\(^{-1}\). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). Melting points were uncorrected. The substrates, \(1a\text{--}i, 1a\text{,}1j\) and \(1k, 1b\) were prepared according to the procedures in our previously reported papers.

II. Preparation of ketene dithioacetals 1a–k

General procedure for the synthesis of ketene dithioacetals 1a–i (taking 1a as example): To a well-stirred suspension of diethyl malonate (15.2 mL, 100 mmol), K\(_2\)CO\(_3\) (30.4 g, 220 mmol) and DMF (40 mL) at room temperature was added CS\(_2\) (6.6 mL, 110 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 0.5 h, PhCH\(_2\)Br (26.2 mL, 220 mmol) was added dropwise within 15 min. The mixture was allowed to warm to room temperature and stirred for 8.0 h, and then poured into ice-water (200 mL) under stirring and neutralized with dilute HCl. The resulting mixture was extracted with CH\(_2\)Cl\(_2\) (3 × 80 mL). The combined organic phase was washed with water (5 × 80 mL), dried over anhydrous MgSO\(_4\), filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/diethyl ether 20/1, V/V) to give diethyl 2-(bis(benzylthio)methylene)malonate 1a (38.9 g, 93%) as a yellow crystal.

General procedure for the synthesis of ketene dithioacetals 1j and 1k (taking 1j as an example): To a solution of 3-(bis(methylthio)methylene)pentane-2,4-dione (1.02 g, 5.0 mmol) in 50 mL of CH\(_2\)Cl\(_2\) was added concentrated H\(_2\)SO\(_4\) (1.1 mL, 20 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 10 h, and then poured onto saturated NaCl ice-water (50 mL) under stirring. The mixture was neutralized with aqueous Na\(_2\)CO\(_3\), and extracted with CH\(_2\)Cl\(_2\) (3 × 20 mL). The combined organic phase was washed with water (3 × 15 mL), dried over MgSO\(_4\) and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/diethyl ether 20/1, V/V) to give 4,4-bis(methylthio)but-3-en-2-one 1j (770 mg, 95%) as a white solid.

III. Synthesis and analytical data of 3a–o

General Procedure for the reaction of ketene dithioacetals 1a–e and boronic acids 2 leading to
3a–l (taking the reaction of 1a and 2a as an example): To a solution of 1a (208 mg, 0.5 mmol) and 4-chlorophenylboronic acid 2a (234 mg, 1.5 mmol) in DMF (4.0 mL) was added Cu(OAc)$_2$ (27 mg, 0.15 mmol). The reaction mixture was allowed to stir at 130°C for 60 h and monitored by TLC. Then the mixture was cooled to room temperature and poured into the saturated aqueous NaCl solution (50 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over anhydrous MgSO$_4$, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography using petroleum ether/diethyl ether (100:1, V/V) as eluent to give diethyl 2-(benzylthio(4-chlorophenyl)methylene)malonate 3a (142 mg, 70%), benzyl(4-chlorophenyl)sulfane (83 mg, 71%) and 4,4'-dichlorobiphenyl (42 mg).

General Procedure for the reaction of ketene dithioacetals 1f–h with boronic acid 2a leading to 3m–o (taking the reaction of 1f and 2a as an example): To a solution of 1f (117 mg, 0.5 mmol) and PhB(OH)$_2$ 2b (183 mg, 1.5 mmol) in DMF (4.0 mL) was added Cu(OAc)$_2$ (27 mg, 0.15 mmol). The reaction mixture was allowed to stir at 110°C for 50 h and monitored by TLC. Then the mixture was cooled to room temperature and poured into the saturated aqueous NaCl solutions (50 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over anhydrous MgSO$_4$, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography using petroleum ether/diethyl ether (50:1, V/V) as eluent to give 3m as a mixture of two isomers (79 mg, 60% yield, The molar ratio of two isomers were 3.5 to 1 based on $^1$H NMR).

Diethyl 2-(benzylthio(4-chlorophenyl)methylene)malonate (3a)

![Structure of 3a](image)

Yellowish viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.96 (t, $J$ = 7.0 Hz, 3H), 1.30 (t, $J$ = 7.0 Hz, 3H), 3.49 (s, 2H), 3.91 (q, $J$ = 7.0 Hz, 2H), 4.28 (q, $J$ = 7.0 Hz, 2H), 7.02-7.04 (m, 2H), 7.11-7.12 (m, 2H), 7.21 (d, $J$ = 6.5 Hz, 3H), 7.32-7.33 (m, 2H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.8, 14.3, 37.6, 61.4, 61.5, 122.7, 127.6, 128.6 (2C), 128.7 (2C), 129.0 (2C), 129.8 (2C), 134.1, 135.2, 135.9, 159.5, 164.0, 164.8; IR (KBr): 3061, 2924, 2854, 1728, 1245 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{21}$H$_{21}$ClO$_4$SNa$^+$ ([M+Na$^+$]) 427.0741, found 427.0730; Anal. calcd for C$_{21}$H$_{21}$ClO$_4$S: C, 62.29; H, 5.23. Found: C, 62.18; H, 5.29.
Diethyl 2-(benzylthio(phenyl)methylene)malonate (3b)

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.89 (t, $J$ = 7.0 Hz, 3H), 1.30 (t, $J$ = 7.0 Hz, 3H), 3.47 (s, 2H), 3.86 (q, $J$ = 7.0 Hz, 2H), 4.28 (q, $J$ = 7.0 Hz, 2H), 7.01-7.03 (m, 2H), 7.18-7.21 (m, 5H), 7.34-7.37 (m, 3H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.5, 14.1, 37.4, 61.0, 61.1, 121.8, 127.2, 128.1 (2C), 128.2 (2C), 128.3 (2C), 128.8 (2C), 128.9, 135.5, 135.9, 161.1, 163.9, 165.0; IR (KBr): 3084, 3028, 2989, 1720, 1285 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{21}$H$_{22}$O$_4$SNa$^+$ ([M+Na]$^+$) 393.1131, found 393.1125.

Diethyl 2-(benzylthio(3-nitrophenyl)methylene)malonate (3c)

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.96 (t, $J$ = 7.0 Hz, 3H), 1.34 (t, $J$ = 7.0 Hz, 3H), 3.52 (s, 2H), 3.90 (q, $J$ = 7.0 Hz, 2H), 4.33 (q, $J$ = 7.0 Hz, 2H), 6.97 (t, $J$ = 8.0 Hz, 1H), 7.18-7.19 (m, 3H), 7.48-7.55 (m, 2H), 7.94 (s, 1H), 8.20 (d, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.7, 14.1, 37.3, 61.3, 61.6, 123.5, 123.6, 123.8, 127.6, 128.5 (2C), 128.6 (2C), 129.2, 134.2, 135.4, 136.9, 147.7, 156.9, 163.7, 163.8; IR (KBr): 3055, 2980, 1726, 1245 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{21}$H$_{21}$NO$_6$SNa$^+$ ([M+Na]$^+$) 438.0982, found 438.0973; Anal. calcd for C$_{21}$H$_{21}$NO$_6$S: C, 60.71; H, 5.09; N, 3.37. Found: C, 60.80; H, 5.01; N, 3.39.

Diethyl 2-(benzylthio(p-tolyl)methylene)malonate (3d)

White semi-solid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.93 (t, $J$ = 7.0 Hz, 3H), 1.29 (t, $J$ = 7.0 Hz, 3H), 2.37 (s, 3H), 3.48 (s, 2H), 3.89 (q, $J$ = 7.0 Hz, 2H), 4.27 (q, $J$ = 7.0 Hz, 2H), 7.04-7.05 (m, 2H),
7.09 (d, $J = 8.5$ Hz, 2H), 7.16-7.20 (m, 5H); $^{13}$C NMR (125 Hz, CDCl$_3$) $\delta$ 13.6, 14.2, 21.3, 37.5, 61.0, 61.1, 121.7, 127.3, 128.1 (2C), 128.4 (2C), 128.9 (2C), 129.0 (2C), 132.7, 136.0, 138.9, 161.5, 164.0, 165.1; IR (KBr): 3064, 2923, 2854, 1728, 1244, 1079 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{22}$H$_{24}$O$_4$SNa$^+$ ([M+Na]$^+$) 407.1288, found 407.1302.

**Diethyl 2-(benzylthio(m-tolyl)methylene)malonate (3e)**

![Chemical structure of 3e]

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) $\delta$ 0.89 (t, $J = 7.0$ Hz, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 2.31 (s, 3H), 3.48 (s, 2H), 3.87 (q, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.0$ Hz, 2H), 6.93 (s, 1H), 6.99-7.02 (m, 3H), 7.14-7.20 (m, 4H); $^{13}$C NMR (125 Hz, CDCl$_3$) $\delta$ 13.5, 14.1, 21.2, 37.4, 60.8, 61.0, 121.8, 125.3, 127.2, 128.1, 128.3 (2C), 128.9 (3C), 129.5, 135.5, 136.2, 137.9, 161.2, 163.9, 164.9; IR (KBr): 3032, 2926, 2856, 1728, 1245 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{22}$H$_{24}$O$_4$SNa$^+$ ([M+Na]$^+$) 407.1288, found 407.1293.

**Diethyl 2-(benzylthio(o-tolyl)methylene)malonate (3f)**

![Chemical structure of 3f]

Yellow semi-solid; $^1$H NMR (500 Hz, CDCl$_3$) $\delta$ 0.93 (t, $J = 7.0$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H), 2.37 (s, 3H), 3.48 (s, 2H), 3.89 (q, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.0$ Hz, 2H), 7.04-7.05 (m, 2H), 7.09 (d, $J = 8.5$ Hz, 2H), 7.16-7.20 (m, 5H); $^{13}$C NMR (125 Hz, CDCl$_3$) $\delta$ 13.6, 14.1, 21.3, 37.5, 60.9, 61.0, 127.2, 127.7, 128.2 (2C), 128.4 (2C), 129.0 (4C), 132.8, 136.2, 138.9, 161.2, 164.0, 165.0; IR (KBr): 3028, 2925, 1727, 1690, 1243, cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{22}$H$_{24}$O$_4$SNa$^+$ ([M+Na]$^+$) 407.1288, found 407.1296.

**Diethyl 2-(benzylthio(biphenyl-4-yl)methylene)malonate (3g)**

![Chemical structure of 3g]
Yellowish viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.90 (t, $J = 7.0$ Hz, 3H), 1.31 (t, $J = 7.0$ Hz, 3H), 3.55 (s, 2H), 3.90 (q, $J = 7.0$ Hz, 2H), 4.29 (q, $J = 7.0$ Hz, 2H), 7.03-7.05 (m, 2H), 7.18-7.20 (m, 3H), 7.25-7.26 (m, 2H), 7.38 (t, $J = 7.0$ Hz, 1H), 7.45-7.48 (m, 2H), 7.59 (t, $J = 9.0$ Hz, 4H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.6, 14.2, 37.5, 61.1, 61.2, 122.0, 126.8 (2C), 127.0 (2C), 127.3, 127.8, 128.4 (2C), 128.7 (2C), 128.8 (2C), 128.9 (2C), 134.4, 136.0, 140.1, 141.7, 160.9, 163.9, 165.0; IR (KBr): 3029, 2926, 2855, 1725, 1245, 1083 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{27}$H$_{27}$O$_4$S$^+$ ([M+H]$^+$) 447.1625, found 447.1630; Anal. Calcd for C$_{27}$H$_{26}$O$_4$S: C, 72.62; H, 5.87. Found: C, 72.73; H, 5.84.

**Diethyl 2-(benzylthio(naphthalen-2-yl)methylene)malonate (3h)**

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.75 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 3.47 (s, 2H), 3.79 (q, $J = 7.0$ Hz, 2H), 4.30 (q, $J = 7.0$ Hz, 2H), 6.94-6.96 (m, 2H), 7.13-7.14 (m, 3H), 7.36 (d, $J = 8.5$ Hz, 1H), 7.51-7.54 (m, 2H), 7.60 (s, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.5, 14.2, 37.5, 61.0, 61.2, 122.2, 125.8, 126.7, 127.0, 127.3, 127.5, 127.7, 128.1, 128.3 (2C), 128.8, 128.9 (2C), 130.9, 132.6, 133.0, 135.9, 161.1, 163.9, 165.0; IR (KBr): 3058, 2928, 1725, 1232 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{25}$H$_{24}$O$_4$SNa$^+$ ([M+Na]$^+$) 443.1288, found 443.1297.

**Diethyl 2-(methylthio(phenyl)methylene)malonate (3i)**

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H),
1.80 (s, 3H), 3.87 (q, J = 7.0 Hz, 2H), 4.30 (q, J = 7.0 Hz, 2H), 7.19 (d, J = 7.0 Hz, 2H), 7.35-7.30 (m, 3H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.5, 14.2, 16.1, 61.0, 61.1, 121.4, 127.9 (2C), 128.3 (2C), 128.7, 135.4, 162.7, 163.9, 165.2; IR (KBr): 3056, 2927, 1727, 1242 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{15}$H$_{18}$O$_4$SNa$^+$ ([M+Na]$^+$) 317.0818, found 317.0830.

**Diethyl 2-(ethylthio(phenyl)methylene)malonate (3j)**

![Diethyl 2-(ethylthio(phenyl)methylene)malonate (3j)](image)

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 0.90 (t, J = 7.0 Hz, 3H), 1.07 (t, J = 7.5 Hz, 3H), 1.32 (t, J = 7.0 Hz, 3H), 2.24 (q, J = 7.5 Hz, 2H), 3.87 (q, J = 7.0 Hz, 2H), 4.30 (q, J = 7.0 Hz, 2H), 7.24 (d, J = 7.0 Hz, 2H), 7.36 (m, 3H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 13.5, 14.0, 14.1, 26.9, 60.9, 61.0, 121.7, 128.0 (2C), 128.1 (2C), 128.7, 135.7, 161.7, 164.0, 165.1; IR (KBr): 3010, 2925, 1731, 1235 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{16}$H$_{20}$O$_4$SNa$^+$ ([M+Na]$^+$) 331.0975, found 331.0991.

**Dimethyl 2-(benzylthio(phenyl)methylene)malonate (3k)**

![Dimethyl 2-(benzylthio(phenyl)methylene)malonate (3k)](image)

Yellow viscous liquid; $^1$H NMR (500 Hz, CDCl$_3$) δ 3.38 (s, 3H), 3.48 (s, 2H), 3.81 (s, 3H), 7.01-7.03 (m, 2H), 7.19 (t, J = 6.5 Hz, 5H), 7.37 (d, J = 4.5 Hz, 3H); $^{13}$C NMR (125 Hz, CDCl$_3$) δ 37.5, 52.0, 52.1, 121.1, 127.3, 128.0 (2C), 128.3 (2C), 128.4 (2C), 128.9 (3C), 135.5, 135.8, 162.2, 164.2, 165.5; IR (KBr): 3026, 2950, 2852, 1735, 1247, 1085 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{19}$H$_{18}$O$_4$SNa$^+$ ([M+Na]$^+$) 365.0818, found 365.0826; Anal. calcd for C$_{19}$H$_{18}$O$_4$S: C, 66.65; H, 5.30. Found: C, 66.73; H, 5.25.

**3-(Benzylthio(phenyl)methylene)pentane-2,4-dione (3l)**

![3-(Benzylthio(phenyl)methylene)pentane-2,4-dione (3l)](image)
Yellow solid, mp 75-76 °C; $^1$H NMR (500 Hz, CDCl$_3$) 1.69 (s, 3H), 2.28 (s, 3H), 3.50 (s, 2H), 6.98 (d, $J = 6.0$ Hz, 2H), 7.21 (d, $J = 6.0$ Hz, 3H), 7.25-7.26 (m, 2H ), 7.42-7.44 (m, 3H ); $^{13}$C NMR (125 Hz, CDCl$_3$) 30.1, 31.1, 37.6, 127.3, 128.4 (2C), 128.8 (2C), 128.9 (2C), 129.2 (2C), 129.8, 135.5, 136.3, 140.6, 155.3, 197.1, 210.7; IR (KBr): 3058, 2961, 2855, 1680, 1474, 1233 cm$^{-1}$. HRMS (ESI-TOF) calcd for C$_{19}$H$_{19}$O$_2$S$^+$ ([M+H]$^+$) 311.1100, found 311.1117.

($E$) and ($Z$)-Ethyl 2-(benzylthio(phenyl)methylene)-3-oxobutanoate (3m)

Yellow solid; **One of two isomers:** $^1$H NMR (500 Hz, CDCl$_3$) 0.83 (t, $J = 7.0$ Hz, 3H), 1.77 (s, 3H), 2.35 (s, 3H), 3.83 (q, $J = 7.0$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 2H), 7.30-7.43 (m, 3H); $^{13}$C NMR (125 Hz, CDCl$_3$) 13.4, 16.4, 29.1, 60.9, 127.8 (2C), 128.3 (2C), 128.6, 129.0, 135.9, 164.0, 167.2, 193.8; **The other one:** $^1$H NMR (500 Hz, CDCl$_3$) 1.32 (t, $J = 7.0$ Hz, 3H), 1.81 (s, 3H), 1.96 (s, 3H), 4.30 (q, $J = 7.0$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 2H), 7.30-7.43 (m, 3H); $^{13}$C NMR (125 Hz, CDCl$_3$) 14.1, 15.9, 30.9, 60.9, 127.8 (2C), 128.3 (2C), 128.6, 129.9, 135.1, 159.8, 164.3, 198.9; HRMS: calcd. For C$_{14}$H$_{17}$O$_3$S$^+$ ([M+H]$^+$) 265.0893, found 265.0911.

($E$) and ($Z$)-2-(Benzylthio(phenyl)methylene)-1-phenylbutane-1,3-dione (3n)

Yellow viscous liquid; **One of two isomers:** $^1$H NMR (500 Hz, CDCl$_3$) 2.23 (s, 3H), 3.46 (s, 2H), 7.00-7.02 (m, 2H), 7.07-7.15 (m, 2H), 7.20-7.22 (m, 2H ), 7.23-7.26 (m, 1H ), 7.38-7.43 (m, 2H), 7.47-7.49 (m, 2H ), 7.56-7.59 (m, 2H ), 7.90 (d, $J = 8.0$ Hz, 2H ); $^{13}$C NMR (125 Hz, CDCl$_3$) 29.7, 37.8, 127.3, 128.2 (2C), 128.4 (2C), 128.6 (2C), 128.8 (2C), 129.0 (2C), 129.1 (2C), 129.4, 130.2, 133.1, 133.3, 135.1, 136.1, 137.8, 194.5, 196.5; **The other one:** $^1$H NMR (500 Hz, CDCl$_3$) 1.80 (s, 3H), 3.46 (s, 2H), 6.69 (d, $J = 4.5$ Hz, 2H), 7.00-7.02 (m, 2H), 7.07-7.15 (m, 2H), 7.20-7.22 (m, 2H ), 7.23-7.26 (m, 2H ), 7.38-7.43 (m, 2H), 7.56-7.59 (m, 1H ), 7.90 (d, $J = 8.0$ Hz, 2H ); $^{13}$C NMR (125 Hz, CDCl$_3$) 29.6, 37.2, 127.2, 128.1 (2C), 128.3 (2C), 128.6 (2C), 128.8 (2C), 129.0 (2C), 129.1 (2C), 129.4, 130.2, 133.1, 133.3, 135.1, 136.1, 137.8, 194.5, 196.5; HRMS (ESI-TOF)
calcd for C_{24}H_{21}O_{2}S^+ ([M+H]^+) 373.1257, found 373.1273.

**(E) and (Z)-Ethyl 3-(methylthio)-2-nitro-3-phenylacrylate (3o)**

Yellow liquid; **One of two isomers:** ¹H NMR (500 Hz, CDCl₃) δ 0.93 (t, J = 7.0 Hz, 3H), 1.88 (s, 3H), 3.97 (q, J = 7.0 Hz, 2H), 7.18-7.23 (m, 2H), 7.43-7.48 (m, 3H); ¹³C NMR (125 Hz, CDCl₃) δ 13.4, 16.6, 62.2, 121.0, 128.4 (2C), 128.8 (2C), 129.3, 132.2, 159.5, 160.6. **The other one:** ¹H NMR (500 Hz, CDCl₃) δ 1.34 (t, J = 7.0 Hz, 3H), 1.84 (s, 3H), 4.35 (q, J = 7.0 Hz, 2H), 7.18-7.23 (m, 2H), 7.43-7.48 (m, 3H); ¹³C NMR (125 Hz, CDCl₃) δ 14.0, 16.3, 62.3, 122.0, 127.8, 128.6 (2C), 128.9 (2C), 131.9, 159.4, 160.1; HRMS (ESI-TOF) calcd for C_{12}H_{13}NO_{4}SNa^+ ([M+Na]^+) 290.0457, found 290.0470.

**IV. Synthesis and analytical data of 4a–e**

**General Procedure for the synthesis of Compound 4a–e** (taking 4a as an example): To a solution of 3b (185 mg, 0.5 mmol) and PhB(OH)₂ (183 mg, 1.5 mmol) in DMF (4.0 mL) was added Cu(OAc)₂ (27 mg, 0.15 mmol). The reaction mixture was allowed to stir at 130°C for 30 h and monitored by TLC. Then, the reaction mixture was cooled to room temperature and poured into saturated NaCl solution (50 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography using petroleum ether/diethyl ether (50:1, V/V) as eluent to give diethyl 2-(diphenylmethylene)malonate 4a (76 mg, 47%), benzyl(phenyl)sulfane (45 mg, 45%) and biphenyl (62 mg).

**Diethyl 2-(diphenylmethylene)malonate (4a)**

White solid, mp: 69-71 °C (lit. 41-41.5 °C); ¹H NMR (500 Hz, CDCl₃) δ 1.02 (t, J = 7.0 Hz, 6H), 4.07 (q, J = 7.0 Hz, 4H), 7.18-7.20 (m, 4H), 7.31-7.36 (m, 6H); ¹³C NMR (125 Hz, CDCl₃) δ 13.6 (2C), 61.2 (2C), 128.1 (4C), 129.1 (7C), 140.2 (2C), 155.6, 165.9 (2C); IR (KBr): 3050, 2925, 2853,
1723, 1302, 1285 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{20}$H$_{20}$O$_4$Na$^+$ ([M+Na]$^+$) 347.1254, found 347.1261.

**Dimethyl 2-(diphenylmethylene)malonate (4b)**

![Chemical Structure](image)

White solid, mp: 115-116 °C (lit. 119-121 °C); $^1$H NMR (500 Hz, CDCl$_3$) $\delta$ 3.61 (s, 6H), 7.18 (d, $J = 6.5$ Hz, 4H), 7.32-7.37 (m, 6H); $^{13}$C NMR (125 Hz, CDCl$_3$) $\delta$ 52.2 (2C), 128.2 (5C), 129.0 (4C), 129.3 (2C), 139.9 (2C), 156.5, 166.4 (2C); IR (KBr): 3028, 2950, 1735, 1247 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{18}$H$_{16}$O$_4$Na$^+$ ([M+Na]$^+$) 319.0941, found 319.0949.

**3-(Diphenylmethylene)pentane-2,4-dione (4c)**

![Chemical Structure](image)

White solid, mp: 116-118 °C (lit. 120-121 °C); $^1$H NMR (500 Hz, CDCl$_3$) $\delta$ 1.94 (s, 6H), 7.18-7.20 (m, 4H), 7.35-7.38 (m, 4H), 7.40-7.42 (m, 2H); $^{13}$C NMR (125 Hz, CDCl$_3$) $\delta$ 31.3 (2C), 128.6 (4C), 129.8 (2C), 130.0 (4C), 139.3 (2C), 143.1, 149.2, 203.6 (2C); IR (KBr): 3061, 3028, 2923, 2852, 1695, 12873 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{18}$H$_{16}$O$_2$Na$^+$ ([M+Na]$^+$) 287.1043, found 287.1046.

**Diethyl 2-((4-chlorophenyl)(phenyl)methylene)malonate (4d)**

![Chemical Structure](image)

White solid, mp: 89-90 °C; $^1$H NMR (500 Hz, CDCl$_3$) $\delta$ 1.02 (t, $J = 7.0$ Hz, 3H), 1.09 (t, $J = 7.0$ Hz, 3H), 4.05-4.13 (m, 4H), 7.12-7.18 (m, 4H), 7.30-7.37 (m, 5H); $^{13}$C NMR (125 Hz, CDCl$_3$) $\delta$ 13.6, 13.7, 61.3, 61.4, 126.9, 128.2 (2C), 128.4 (2C), 129.1 (2C), 129.3, 130.5 (2C), 135.4, 138.5, 139.7, 154.2, 165.6, 165.7; IR (KBr): 3021, 2980, 29312, 1725, 1296 cm$^{-1}$; HRMS (ESI-TOF) calcd for C$_{20}$H$_{19}$ClO$_4$Na$^+$ ([M+Na]$^+$) 381.0864, found 381.0869; Anal. calcd for C$_{20}$H$_{19}$ClO$_4$: C, 66.95; H, 5.34. Found: C, 66.81; H, 5.39.
Dimethyl 2-((4-chlorophenyl)(phenyl)methylene)malonate (4e)

White solid, mp: 82-83 °C; \(^1^H\) NMR (500 Hz, CDCl\(_3\)) \(\delta\) 3.61 (s, 3H), 3.65 (s, 3H), 7.11-7.16 (m, 4H), 7.30-7.37 (m, 5H); \(^{13}\) C NMR (125 Hz, CDCl\(_3\)) \(\delta\) 52.2, 52.3, 127.3, 128.3 (2C), 128.5 (2C), 129.0 (2C), 129.5, 130.4 (2C), 135.5, 138.3, 139.6, 155.1, 166.0, 166.1; IR (KBr): 3025, 2946, 1746, 1285 cm\(^{-1}\); HRMS (ESI-TOF) calcd for C\(_{18}\)H\(_{16}\)ClO\(_4\) \([\text{M+H}]^+\) 331.0732, found 331.0735; Anal. calcd for C\(_{18}\)H\(_{15}\)ClO\(_4\): C, 65.36; H, 4.57. Found: C, 65.43; H, 4.47.

V. References


VI. Copies of NMR spectra for compounds 3a–l and 4a–e

3a
3h
petrolatum ether
3m