Supporting Information

Synthesis of cyclic 3-arylsubstituted 1,2-dicarbonyl compounds via Suzuki cross-coupling reaction

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Table of Contents

Experimental procedure for compounds 1-Cl-b, 2-Br-b and 3-Br-a,b,c,c’,d S2 – S4

$^1$H NMR and $^{13}$C NMR data for compounds 1-Cl-b, 2-Br-b and 3-Br-a,b,c,c’,d S5 – S11

$^1$H NMR and $^{13}$C NMR data for synthesized compounds 5, 6 and 7 S12 – S33
3-Chloro-2-methoxycyclopent-2-en-1-one (1-Cl-b)

To a solution of 1,2-cyclopentanedione (276 mg, 2.8 mmol) in MeCN (28 mL) and water (2.8 mL) NCS (449 mg, 3.36 mmol) was added and the mixture was stirred for 40 h at room temperature. Water (28 mL) was then added and the mixture was extracted with CH₂Cl₂ (2x30 mL and 6x20 mL). The combined extracts were dried (Na₂SO₄) and the solvents were evaporated. Purification of the residue by column chromatography on silica gel (petroleum ether/EtOAc 10:1.5 to 10:2) gave 3-chloro-2-hydroxy-cyclopent-2-enone (351 mg, 94%), that was directly used in the next step.

To a solution of 3-chloro-2-hydroxy-cyclopent-2-enone (351 mg, 2.65 mmol) in DMF (3 mL) NaH (60% in mineral oil, 107 mg, 2.67 mmol) was added at 0°C. After stirring for 30 min at 0°C MeI (0.2 mL, 2.4 mmol) was added, the reaction mixture was warmed up to room temperature and stirred for 2h. Water (20 mL) was added and the mixture was extracted with CH₂Cl₂ (1x20 mL and 2x15 mL). The combined extracts were washed with water (10 mL), brine (10 mL) and dried (Na₂SO₄). The solvents were evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1) to give 1-Cl-b as a colorless oil (274 mg, 71%); ¹H NMR (400 MHz, CDCl₃) δ 4.04 (s, 3H), 2.72–2.69 (M, 2H), 2.51–2.49 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 199.1, 151.3, 144.3, 58.5, 33.7, 28.7; ν_max (neat, cm⁻¹): 2948, 2849, 1710, 1638, 1441, 1407, 1322, 1188, 1154, 1074, 994, 974; m/z (EI) 148 and 146 (M⁺, 30.9 and 100), 116 (58.0), 104 (53.0), 89 (59.7), 83 (93.0); HRMS (ESI) calcd for C₇H₆ClO₂ [M+H]⁺ 147.0207, found 147.0206.

3-Bromo-2-methoxycyclohex-2-en-1-one (2-Br-b)

To a solution of 3-bromo-2-methoxycyclohex-2-en-1-one (458 mg, 2.4 mmol) in DMF (4 mL) NaH (60% in mineral oil, 96 mg, 2.4 mmol) was added at 0°C. After stirring for 30 min at 0°C MeI (0.18 mL, 2.88 mmol) was added, the reaction mixture was warmed up to room temperature and stirred for 2h. Water (15 mL) was added and the mixture was extracted with MTBE (1x20 mL and 2x15 mL). The combined extracts were washed with brine (10 mL) and dried (Na₂SO₄). The solvents were evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/acetone 20:1 to 10:1) to give 2-Br-b as a yellow oil (218 mg, 44%); ¹H NMR (400 MHz, CDCl₃) δ 3.75 (s, 3H), 2.72–2.69 (M, 2H), 2.09 – 1.97 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 192.09, 151.07, 135.27, 59.85, 38.40, 35.87, 22.68.; ν_max (neat, cm⁻¹): 2942, 1730, 1684, 1615, 1429, 1327, 1287, 1133, 984; m/z (EI) 206 and 204 (M⁺, 54.1 and 58.0), 176 (53.4), 174 (52.1), 135 (32.6), 133 (34.7), 125 (95.8), 107 (23.2), 105 (20.3), 95 (79.7), 67 (81.3), 53 (100); HRMS (ESI) calcd for C₁₀H₉BrO₂ [M+H]⁺ 204.9859, found 204.9863.

4-Bromo-3-hydroxyfuran-(5H)-one (3-Br-a)

To a solution of 3-hydroxyfuran-(5H)-one (343 mg, 3.43 mmol) in MeCN (42 mL) and water (4.2 mL) NBS (611 mg, 3.43 mmol) was added and the mixture was stirred for 17 h at room temperature. Water (42 mL) was then added and the mixture was extracted with CH₂Cl₂ (1x40 mL and 5x20 mL). The combined extracts were dried (Na₂SO₄) and the solvents were evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1.5 to 10:2) to give 3-Br-a as a white solid (461 mg, 75%); mp 112-114 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.82 (s, 1H), 4.82 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 140.4, 108.8, 70.6; ν_max (KBr, cm⁻¹): 3326, 1752, 1701, 1378, 1345, 1271, 1170, 1104, 1018,
4-Bromo-3-methoxyfuran-2(5H)-one (3-Br-b)

To a solution of 3-Br-a (153 mg, 0.85 mmol) in CHCl₃ (2mL) Ag₂O (237 mg, 1.02 mmol) and MeI (0.424 mL, 6.8mmol) were added and the mixture was heated at reflux for 45 min. The cooled mixture was filtered through a bed of Celite and the filtrate was evaporated. The residue was purified by column chromatography on silica gel (5-15% EtOAc in petroleum ether) to give 3-Br-b as a white solid (132 mg, 80%); mp 48-49 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.74 (s, 2H), 4.13 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 166.0, 142.9, 112.0, 70.0, 58.9; νmax (KBr, cm⁻¹): 2952, 2926, 2856, 1768, 1672, 1428, 1321, 1184, 1115, 1091, 1029, 969, 908; m/z (EI) 194 and 192 (M⁺, 31.4 and 32.6), 165 (33.1), 163 (35.5), 135 (21.7), 113 (55.6), 107 (43.3), 105 (43.5), 95 (41.3), 85 (97.1), 69 (100); HRMS (ESI) calcd for C₈H₇BrO₃ [M+H⁺] 192.9495, found 192.9493.

4-Bromo-3-((tert-butyldimethylsilyl)oxy)furan-2(5H)-one (3-Br-c)

To a solution of 3-Br-a (461 mg, 2.58 mmol) and imidazole (281 mg, 4.13 mmol) in CH₂Cl₂ (13 mL) TBDMSCl (467 mg, 3.1 mmol) was added. After stirring at room temperature for 30 min, water (25 mL) was added, CH₂Cl₂ layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 x 15 mL). The combined extracts were washed with brine (12 mL), dried (Na₂SO₄) and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 60:1 to 50:1) to give 3-Br-c as a colorless oil, which solidified in refrigerator (687 mg, 91%); ¹H NMR (400 MHz, CDCl₃) δ 4.76 (s, 2H), 0.99 (s, 9H), 0.28 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 167.1, 140.9, 115.7, 69.8, 25.5, 18.3, -4.1; νmax (neat, cm⁻¹): 2933, 2887, 2860, 1778, 1673, 1472, 1317, 1255, 1184, 1089, 1024, 907, 848, 790;; m/z (EI) 237 and 235 (M⁺-57, 100 and 99.9), 139 (94.3), 137 (92.3), 107 (20.3), 105 (18.4), 83 (21.3), 84 (19.9), 73 (56.7); HRMS (ESI) calcd for C₁₆H₁₈BrO₃Si [M+H⁺] 293.0203, found 293.0208.

4-Bromo-3-((tert-butyldiphenylsilyl)oxy)furan-2(5H)-one (3-Br-c ‘)

To a solution of 3-Br-a (290 mg, 1.62 mmol) and imidazole (220 mg, 3.24 mmol) in CH₂Cl₂ (8 mL) TBDPSCI (0.63 mL, 2.43 mmol) was added. After stirring at room temperature for 30 min, water (15 mL) was added, CH₂Cl₂ layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 x 10 mL). The combined extracts were washed with brine (10 mL), dried (Na₂SO₄) and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 50:1) to give 3-Br-c ‘ as a white solid (606 mg, 90%); mp 71-73 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.12 (m, 4H), 7.48-7.37 (m 6H), 4.62 (s, 2H), 1.16 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 166.5, 140.7, 135.6, 131.9, 130.4, 127.8, 116.1, 69.6, 26.7, 19.8; νmax (KBr, cm⁻¹): 2964, 2926, 2856, 1768, 1672, 1428, 1321, 1184, 1115, 1091, 1018, 910, 845, 739, 697; m/z (EI) 361 and 359 (M⁺-57, 66.8 and 65.6), 263 (13.3), 261 (14.7), 207 (10.1), 181 (25.2) 135 (15.6), 115 (14.1), 103 (100); HRMS (ESI) calcd for C₂₀H₂₁BrO₃SiNa [M+Na⁺] 439.0336, found 439.0343.
4-Bromo-3-(methoxymethoxy)furan-2(5H)-one (3-Br-d)

To a solution of 3-Br-a (298 mg, 1.66 mmol) in CHCl$_2$ (8.8 mL) dimetoxymethane (8.8 mL, 99.6 mmol) and P$_2$O$_5$ (1.06 g, 7.47 mmol) were added. After stirring at room temperature for 5 h the reaction mixture was poured into a cold saturated Na$_2$CO$_3$ solution. CH$_2$Cl$_2$ layer was separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (2 x 12 mL). The combined extracts were washed with brine (10 mL), dried (Na$_2$SO$_4$) and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1-10:1.5) to give 3-Br-d as a colorless oil (348 mg, 94%); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.39 (s, 2H), 4.79 (s, 2H), 3.54 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 166.0, 141.1, 119.1, 95.6, 70.3, 57.3; $\nu_{\text{max}}$ (neat, cm$^{-1}$): 2963, 2832, 1774, 1668, 1452, 1352, 1311, 1282, 1213, 1162, 1065, 1025, 926, 882; m/z (EI) 224 and 222 (M$^+$ 1.2 and 1.3), 135 (2.3), 133 (2.7), 107 (2.9), 105 (2.9), 45 (100); HRMS (ESI) calcd for C$_6$H$_8$BrO$_4$ [M+H]$^+$ 222.9600, found 222.9602.
$^1$H NMR and $^{13}$C NMR data for compound 1-Cl-b
$^1$H NMR and $^{13}$C NMR data for compound 2-Br-\textit{b}
$^1$H NMR and $^{13}$C NMR data for compound 3-Br-a
$^1$H NMR and $^{13}$C NMR data for compound 3-Br-b
$^1$H NMR and $^{13}$C NMR data for compound 3-Br-c
$^1\text{H NMR and } ^{13}\text{C NMR data for compound 3-Br-c}^-$
$^1$H NMR and $^{13}$C NMR data for compound **3-Br-d**
$^1$H NMR and $^{13}$C NMR data for compound 5a-b
$^1$H NMR and $^{13}$C NMR data for compound 5b-b
$^1$H NMR and $^{13}$C NMR data for compound 5e-b
$^1$H NMR and $^{13}$C NMR data for compound 5d-b
$^1$H NMR and $^{13}$C NMR data for compound 5e-b
$^1$H NMR and $^{13}$C NMR data for compound 5a-a
$^1$H NMR and $^{13}$C NMR data for compound 6a-b
$^1$H NMR and $^{13}$C NMR data for compound 6f-b
$^1$H NMR and $^{13}$C NMR data for compound 6g-b
$^1$H NMR and $^{13}$C NMR data for compound 7c-b
\(^1\)H NMR and \(^{13}\)C NMR data for compound 7d-d
$\text{H NMR and } ^{13}\text{C NMR data for compound } 7g\cdot d$
$^1$H NMR and $^{13}$C NMR data for compound 7h-d
$^1$H NMR and $^{13}$C NMR data for compound 5a-c
$^1$H NMR and $^{13}$C NMR data for compound 5b-a
$^1$H NMR and $^{13}$C NMR data for compound 5b-c
^1^H NMR and ^13^C NMR data for compound 5i-c
$^1$H NMR and $^{13}$C NMR data for compound 6a-c
$^1$H NMR and $^{13}$C NMR data for compound 6c-c
$^1$H NMR and $^{13}$C NMR data for compound 6h-a
$^1$H NMR and $^{13}$C NMR data for compound 6h-c
$^{1}$H NMR and $^{13}$C NMR data for compound 7a-a