Pd-Catalyzed Carbonylation for the Construction of Tertiary and Quaternary Carbon Centers with sp³ Carbon Partners

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1. General information

Flash chromatography was performed with freshly distilled solvents. \(^1\)H NMR (400 MHz) and \(^13\)C NMR (100 MHz) spectra were recorded using CDCl\(_3\) as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Toluene was dried over sodium for 4 h, and distilled under N\(_2\) atmosphere.

2. General procedures

2.1 Pd-catalyzed carbonylation for the tertiary and quaternary carbon centers

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. \(t\)-BuOLi (0.5 mmol) and carbon nucleophiles (0.5 mmol) were placed in a 10 mL Teflon reaction tube and then solvent (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic (0.25 mmol) and oxidant (0.5 mmol) were added to the tube, to which was added 2 mL solvent with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to 5 atm with CO at room temperature and heated in an oil bath at 80 °C for 12 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO in a fume hood. Water (10 mL) was added, and the product was extracted with ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the carbonylation products.
2.2 Synthesis of indazole 5

\[ \text{B(OH)}_2 + \text{CO} + \text{our method} \rightarrow \text{indazole} 5 \]

1,3,3'-Triketone 3a (1 mmol) and hydrazine hydrate (2 mmol) were added to a 25 mL round bottom flask, which was evacuated and refilled with N₂ for 3 times. After the addition, the sealed tube was placed in an oil bath and stirred at 25°C for 4 h. After completion, the reaction mixture was quenched by water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine (1 x 45 mL), and dried over MgSO₄. After the evaporation, the residue was purified with silica gel chromatography with petroleum ether/ethyl acetate as eluent to afford product 5.

2.3 Kinetic Experiments

2.3.1 Variation of yield with time in the carbonylation of phenyl boronic acid.

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. t-BuOLi (0.5 mmol) and cyclohexane-1, 3-dione(0.5 mmol) were placed in a 10 mL Teflon reaction tube, and then toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic (0.25 mmol) and oxidant (0.5 mmol) were added in the tube, to which was added 2 mL toluene with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to 5 atm at room temperature and heated in an oil bath at 80 °C with the time shown in Fig 1. The autoclave was then cooled to room temperature and vented to discharge the excess CO in a fumehood. Water (10 mL) was added, and the product
was extracted with ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na₂SO₄, and evaporated. The conversion was determined by ¹H NMR with 1, 3, 5-trimethoxybenzene as internal standard.

2.3.2 Variation of yield with the amount of base in the carbonylation of phenyl boronic acid.

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. t-BuOLi, cyclohexane-1, 3-dione was placed in a 10 mL Teflon reaction tube, then toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic acid (0.25 mmol) and oxidant (0.5 mmol) were added in the tube, which was added 2 mL toluene with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, then pressurized to 1 or 5 atm at room temperature and heated in an oil bath at 80 °C for 10 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na₂SO₄, and evaporated. The conversion was determined by ¹H NMR with 1, 3, 5-trimethoxybenzene as internal standard.

2.3.3 Variation of yield with CO pressure in the carbonylation of phenyl boronic acid

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. t-BuOLi (0.5 mmol), cyclohexane-1, 3-dione (0.5 mmol) was placed in a 10 mL Teflon reaction tube, then toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic (0.25 mmol) and oxidant (0.5 mmol) were added in the tube, which was added 2 mL toluene with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to the pressure shown in Fig 3 at room temperature and heated in an oil bath at 80 °C for 10 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with Ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na₂SO₄,
and evaporated. The conversion was determined by $^1$H NMR with 1,3,5-trimethoxybenzene as internal standard.

3. Data for products

Diethyl 2-benzoylmalonate (2a)

![Structure](structure.png)

Colorless oil; $R_f = 0.3$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.91 (d, $J = 7.2$ Hz, 2H), 7.60 (q, $J = 7.2$ Hz, 1H), 7.49 (q, $J = 7.6$ Hz, 2H), 5.28 (s, 1H), 4.27 (q, $J = 6.9$ Hz, 4H), 1.25 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 189.0, 164.9, 135.4, 134.0, 128.9, 128.5, 62.4, 61.8, 13.9; IR (KBr): 3209, 2992, 1796, 1765, 1693, 787, 695, 643 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 287.0890; found 287.0893.

Diethyl 2-(4-fluorobenzoyl)malonate (2b)

![Structure](structure.png)

Colorless oil; $R_f = 0.2$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.96-7.93 (m, 2H), 7.27-7.14 (m, 2H), 5.22 (s, 1H), 4.29 (q, $J = 7.2$ Hz, 4H), 1.26-1.24 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 187.4, 164.9, 163.7, 131.9, 131.3, 131.2, 130.0, 116.2, 116.0, 62.5, 61.9, 61.3, 13.9, 13.7; IR (KBr): 3070, 2870, 1753, 1733, 1692, 852, 796, 685 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 305.0796; found 305.0790.

Diethyl 2-(4-chlorobenzoyl)malonate (2c)

![Structure](structure.png)

Colorless oil; $R_f = 0.2$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.85 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 5.21 (s, 1H), 4.27 (q, $J = 6.8$ Hz, 4H), 1.26 (t, $J = 6.8$ Hz 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 187.8, 168.4, 133.8, 129.9, 128.6,
62.5, 61.4, 14.1, 14.0; IR (KBr): 3210, 2983, 1768, 1752, 1695, 960, 823, 702 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 321.0500; found 321.0497.

**Diethyl 2-(4-methoxybenzoyl)malonate (2d)**

```
    O     O
  /       |
/        |
  O      Et
\        |
  \       |
    O     Et
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Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 10:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.89 (d, J = 9.2 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 5.24 (s, 1H), 4.27 (q, J = 7.2 Hz, 4H), 3.88 (s, 3H), 1.26 (t, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 187.3, 165.0, 164.2, 130.9, 128.5, 114.1, 62.3, 61.7, 55.6, 13.9; IR (KBr): 3165, 2960, 1764, 1745, 1698, 783, 721, 696 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 317.0996; found 317.0991.

**Diethyl 2-(4-methylbenzoyl)malonate (2e)**

```
    O     O
  /       |
/        |
  O      Et
\        |
  \       |
    O     Et
```

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 10:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.82 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 9.2 Hz, 2H), 5.25 (s, 1H), 4.29 (q, J = 6.8 Hz, 4H), 2.42 (s, 3H), 1.27 (t, J = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 188.5, 164.9, 145.1, 133.0, 129.6, 128.6, 62.3, 61.9, 21.7, 13.9; IR (KBr): 3132, 2983, 1782, 1765, 1687, 792, 765, 721, 684 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 301.1046; found 301.1043.

**Diethyl 2-(4-ethylbenzoyl)malonate (2f)**

```
    O     O
  /       |
/        |
  O      Et
\        |
  \       |
    O     Et
```

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 10:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.83 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.26 (s, 1H), 4.30-4.18 (m, 4H), 2.74-2.67 (m, 2H), 1.28-1.25 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 188.5, 165.0, 133.2, 128.8, 128.4, 114.3, 62.3, 61.8, 29.0, 15.0, 13.9; IR (KBr): 3132, 2983, 1792, 1721, 1695, 831, 797, 758, 693, 684 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 315.1203; found 315.1208.
Diethyl 2-(4-propylbenzoyl)malonate (2g)

\[
\begin{array}{c}
\text{O} \\
\text{OEt} \\
\text{O} \\
\text{OEt}
\end{array}
\]

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.84 (d, \(J = 8.4\) Hz, 2H), 7.29 (d, \(J = 8.4\) Hz, 2H), 5.26 (s, 1H), 4.29 (m, 4H), 2.67 (t, \(J = 7.2\) Hz, 2H), 1.69 (t, \(J = 7.6\) Hz, 2H), 1.27 (t, \(J = 7.2\) Hz, 6H), 1.06 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 188.5, 165.0, 149.7, 133.2, 129.0, 128.7, 127.6, 62.3, 61.8, 38.0, 24.1, 13.9, 13.7; IR (KBr): 3021, 2967, 1795, 1743, 1695, 821, 786, 762, 731, 693, 684 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 329.1359; found 329.1352.

Diethyl 2-(4-(tert-butyl)benzoyl)malonate (2h)

\[
\begin{array}{c}
\text{O} \\
\text{OEt} \\
\text{O} \\
\text{OEt}
\end{array}
\]

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.86 (d, \(J = 8.8\) Hz, 2H), 7.50 (d, \(J = 8.8\) Hz, 2H), 5.27 (s, 1H), 4.30 (m, 4H), 1.32 (s, 9H), 1.28 (t, \(J = 7.2\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 188.5, 165.0, 158.0, 132.9, 128.5, 125.9, 62.3, 61.8, 35.2, 31.0, 13.9; IR (KBr): 3024, 2983, 1786, 1745, 1683, 824, 786, 697, 674 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 343.1516; found 343.1519.

Diethyl 2-[(1, 1'-biphenyl)-4-carbonyl]malonate (2i)

\[
\begin{array}{c}
\text{O} \\
\text{OEt} \\
\text{O} \\
\text{OEt}
\end{array}
\]

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.96 (d, \(J = 8.4\) Hz, 2H), 7.71 (d, \(J = 8.4\) Hz, 2H), 7.64 (q, \(J = 6.6\) Hz, 2H), 7.48 (t, \(J = 7.2\) Hz, 2H), 5.31 (s, 1H), 4.32-4.26 (m, 4H), 1.27 (t, \(J = 7.2\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 188.5, 164.9, 146.7, 139.5, 134.2, 129.1, 128.2, 128.5, 127.5, 127.3, 62.4, 62.0, 13.9; IR (KBr): 3024, 2986, 2893, 1786, 1745, 1683, 835, 798, 692 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 363.1203; found 363.1211.
Diethyl 2-(3-chlorobenzoyl)malonate (2j)

![Chemical Structure](image)

Colorless oil; Rf = 0.2 (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.99 (d, $J$ = 8.4 Hz, 2H), 7.27-7.14 (m, 2H), 5.22 (s, 1H), 4.29 (q, $J$ = 7.2 Hz, 4H), 1.26-1.24 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 187.4, 164.5, 163.7, 137.0, 135.4, 133.9, 130.2, 128.6, 126.6, 62.6, 61.9, 54.3, 13.9; IR (KBr): 3075, 2982, 1752, 1730, 1690, 740, 682, 615 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 321.0500; found 321.0493.

Diethyl 2-(3-fluorobenzoyl)malonate (2k)

![Chemical Structure](image)

Colorless oil; Rf = 0.2(petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.68-7.61 (m, 2H), 7.47 (m, 1H), 5.22 (s, 1H), 4.28 (t, $J$ = 7.2 Hz, 4H), 1.30-1.24 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 187.8, 168.4, 137.5 (d, $J_{CF}$ = 6.5 Hz), 130.6 (d, $J_{CF}$ = 7.2Hz), 124.2 (d, $J_{CF}$ = 3.1 Hz), 121.2(d, $J_{CF}$ = 21.3 Hz), 115.4(d, $J_{CF}$ = 22.6 Hz), 62.5, 61.4, 13.9; IR (KBr): 3132, 2995, 1797, 1765, 1697, 754, 694, 635 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 305.0796; found 305.0791.

Diethyl 2-(3-methoxybenzoyl)malonate (2l)

![Chemical Structure](image)

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 15:1); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.45 (t, $J$ = 7.8 Hz, 2H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 1H), 5.26 (s, 1H), 4.27(t, $J$ = 7.2 Hz, 4H), 3.85 (s, 3H), 1.26 (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 188.8, 164.8, 160.1, 129.8, 121.0, 120.8, 116.4, 112.6, 62.4, 55.5, 13.9; IR (KBr): 3055, 2992, 1742, 1720, 1690, 832, 764, 696, 654 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 317.0996; found 317.0991.
Diethyl 2-(3-methylbenzoyl)malonate (2m)

Colorless oil; R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate 15:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.73-7.68 (m, 2H), 7.43-7.28 (m, 2H), 5.28 (s, 1H), 4.7 (q, J = 5.2 Hz, 4H), 2.41 (s, 3H), 1.25 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 189.0, 164.9, 138.8, 135.5, 134.8, 129.0, 128.7, 125.7, 62.3, 61.9, 21.3, 13.9; IR (KBr): 3043, 2983, 1765, 1732, 1698, 798, 764, 696, 654 cm<sup>-1</sup>; HRMS (ESI): calc. for (M + Na<sup>+</sup>) 301.1046; found 301.1041.

Diethyl 2-(2-naphthoyl)malonate (2n)

Colorless oil; R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate 10:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.31 (s, 1H), 7.99 (t, J = 8.8 Hz, 2H), 7.96-7.85 (m, 2H), 7.66-7.56 (m, 2H), 5.45 (s, 1H), 4.28 (q, J = 4.0 Hz, 4H), 1.27 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 188.9, 164.9, 135.9, 132.9, 132.4, 130.5, 129.8, 129.1, 128.9, 127.8, 127.1, 123.8, 62.4, 62.0, 54.4, 13.9; IR (KBr): 3055, 2992, 2897, 1745, 1730, 1696, 764, 696, 663 cm<sup>-1</sup>; HRMS (ESI): calc. for (M + Na<sup>+</sup>) 337.1046; found 337.1041.

Dimethyl 2-benzoylmalonate (2o)

Colorless oil; R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate 10:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.92-7.90 (m, 2H), 7.51-7.46 (m, 3H), 5.34 (s, 1H), 3.81 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 188.6, 165.8, 135.3, 133.6, 130.5, 130.2, 127.6, 61.4; IR (KBr): 3035, 2987, 1787, 1769, 1698, 832, 764, 696, cm<sup>-1</sup>; HRMS (ESI) calc. for (M + Na<sup>+</sup>) 259.0577; found 259.0571.
2-benzylocyclohexane-1,3-dione (3a)

Light yellow oil; Rf = 0.3 (petroleum ether/ethyl acetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.09 (d, $J$ = 7.2 Hz, 2H), 7.65 (t, $J$ = 7.4 Hz, 1H), 7.50 (t, $J$ = 7.8 Hz, 2H), 6.05 (s, 1H), 6.09 (t, $J$ = 5.6 Hz, 2H), 2.47 (t, $J$ = 6.8 Hz, 2H), 2.17-2.10 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 199.4, 170.1, 163.2, 134.1, 130.2, 128.7, 117.9, 36.8, 28.4, 21.4; IR (KBr): 2950, 2928, 1740, 1738, 1669, 1635, 1125, 968, 748, 700 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 239.0679; found 239.0674.

2-(4-Methylbenzoyl) cyclohexane-1,3-dione (3b)

Light yellow oil; Rf = 0.3 (petroleum ether/ethyl acetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.97 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 6.04 (s, 1H), 2.70-2.66 (m, 2H), 2.48-2.44 (m, 5H), 2.16-2.09 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 199.5, 170.3, 163.2, 145.1, 130.3, 129.4, 125.9, 117.8, 36.8, 28.5, 21.8, 21.4; IR (KBr): 2956, 2926, 1740, 1769, 1679, 1127, 966, 745, 689 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 253.0835; found 253.0839.

2-(4-Methoxybenzoyl) cyclohexane-1,3-dione (3c)

Light yellow oil; Rf = 0.3 (petroleum ether/ethyl acetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.03 (d, $J$ = 8.8 Hz, 2H), 6.97 (d, $J$ = 8.8 Hz, 2H), 6.03 (s, 1H), 6.28 (s, 3H), 2.69 (m, 2H), 2.61 (t, $J$ = 6.8 Hz, 2H), 2.12 (t, $J$ = 6.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 199.6, 170.4, 164.3, 162.9, 132.4, 120.9, 117.8, 114.0, 55.6, 36.8, 28.5, 21.4; IR (KBr): 2956, 2924, 1755, 1711, 1597, 1129, 968, 748, 700 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 269.0784; found 269.0790.
2-(4-Ethylbenzoyl) cyclohexane-1,3-dione (3d)

Light yellow oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 8.00 (d, \( J = 8.4 \) Hz, 2H), 7.32 (d, \( J = 8.0 \) Hz, 2H), 6.03 (s, 1H), 2.76-2.66 (m, 4H), 2.46 (t, \( J = 6.8 \) Hz, 2H), 2.16-2.09 (m, 2H), 1.27 (t, \( J = 7.6 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 199.5, 170.3, 163.3, 151.3, 130.4, 128.3, 126.1, 117.8, 36.8, 29.1, 28.5, 21.4, 15.2; IR (KBr): 2957, 2921, 1743, 1680, 1125, 967, 855, 759 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 267.0992; found 267.0996.

2-(4-Propylbenzoyl) cyclohexane-1,3-dione (3e)

Light yellow oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.98 (d, \( J = 8.4 \) Hz, 2H), 7.29 (d, \( J = 8.0 \) Hz, 2H), 6.02 (s, 1H), 2.68-2.64 (m, 4H), 2.46 (t, \( J = 6.8 \) Hz, 2H), 2.15-2.09 (m, 2H), 1.70-1.64 (m, 2H), 0.95 (t, \( J = 7.4 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 199.5, 170.3, 163.3, 149.8, 130.3, 128.9, 126.1, 117.8, 36.8, 28.5, 24.2, 21.4, 13.7; IR (KBr): 2959, 2924, 1755, 1711, 1158, 847, 800, 710, 513 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 281.1148; found 281.1152.

2-(4-[Tert-butyl] benzoyl) cyclohexane (3f)

Light yellow oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 8.01 (d, \( J = 8.4 \) Hz, 2H), 7.51 (d, \( J = 8.4 \) Hz, 2H), 6.03 (s, 1H), 2.68 (t, \( J = 6.2 \) Hz, 2H), 2.46 (t, \( J = 6.8 \) Hz, 2H), 2.13 (q, \( J = 6.5 \) Hz, 2H), 1.35 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 199.5, 170.3, 163.2, 158.1, 130.2, 125.7, 117.8, 36.8, 35.3, 31.1, 28.5, 21.4; IR (KBr): 2964, 2929, 1740, 1679, 1611, 1064, 966, 853, 757, 699 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 295.1305; found 295.1309.
2-[[1,1'-Biphenyl]-4-carbonyl]cyclohexane-1,3-dione (3g)

Light yellow oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 8.15 (d, \( J = 8.4 \) Hz, 2H), 7.72 (d, \( J = 8.0 \) Hz, 2H), 7.64 (d, \( J = 7.2 \) Hz, 2H), 7.49 (t, \( J = 7.4 \) Hz, 2H), 7.44 (d, \( J = 7.2 \) Hz, 2H), 2.71 (t, \( J = 6.0 \) Hz, 2H), 2.48 (t, \( J = 6.6 \) Hz, 2H), 2.15-2.11 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 199.4, 170.2, 163.1, 146.9, 139.6, 130.8, 129.0, 128.5, 127.4, 127.3, 117.9, 36.8, 28.5, 21.4; IR (KBr): 2955, 2926, 1739, 1668, 1630, 1123, 948, 776, 761 cm\(^{-1}\); HRMS (ESI): calc. for \((M + Na^+)\) 315.0992; found 315.0995.

2-(4-[Trifluoromethyl] benzoyl) cyclohexane-1,3-dione (3h)

Light yellow oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 8.13 (d, \( J = 8.0 \) Hz, 2H), 7.69 (d, \( J = 8.0 \) Hz, 2H), 5.99 (s, 1H), 2.63 (q, \( J = 5.8 \) Hz, 2H), 2.41 (t, \( J = 6.8 \) Hz, 2H), 2.11-2.04 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 199.1, 169.6, 162.0, 135.5, 131.9, 130.6, 125.8, 125.8 (t, \( J_{CF} = 3.6 \) Hz), 118.1, 36.8, 28.3, 21.3; IR (KBr): 2955, 2927, 1748, 1680, 1648, 1127, 967, 862, 769, 698 cm\(^{-1}\); HRMS (ESI): calc. for \((M + Na^+)\) 307.0552; found 307.0554.

2-(3-Methylbenzoyl) cyclohexane-1,3-dione (3i)

Light yellow oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.87 (d, \( J = 8.0 \) Hz, 2H), 7.44 (d, \( J = 7.6 \) Hz, 1H), 7.37 (t, \( J = 7.8 \) Hz, 1H), 6.03 (s, 1H), 2.67 (t, \( J = 6.2 \) Hz, 2H), 2.46 (t, \( J = 6.6 \) Hz, 2H), 2.42 (s, 3H), 2.12 (t, \( J = 6.2 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 199.5, 170.3, 163.4, 138.6, 134.9, 130.7, 128.6, 128.6, 127.4, 117.9, 36.8, 28.5, 21.4, 21.6; IR (KBr): 2958, 2924, 1748, 1766, 1672, 1123, 966, 753, 695.
IR (KBr): 2958, 2924, 1748, 1766, 1672, 1123, 966, 753, 695 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 253.0835; found 253.0838.

2-(3-Fluorobenzoyl) cyclohexane-1, 3-dione (3j)

![Structure of 3j](image)

Colorless oil; Rf = 0.2 (petroleum ether/ethyl acetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.88-7.87 (m, 1H), 7.78-7.75 (m, 1H), 7.52-7.46 (m, 1H), 7.38-7.32 (m, 1H), 6.05 (s, 1H), 2.68 (t, J = 6.2 Hz, 2H), 2.46 (t, J = 6.2 Hz, 2H), 2.17-2.11 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 199.3, 169.7, 161.7 (d, Jₐ⁻⁻F = 70 Hz), 130.5 (d, Jₐ⁻⁻F = 7.5 Hz), 126.0 (d, Jₐ⁻⁻F = 3.2 Hz), 121.4 (d, Jₐ⁻⁻F = 21.1 Hz), 118.1, 117.2 (d, Jₐ⁻⁻F = 23.2 Hz), 36.8, 28.4, 21.3; IR (KBr): 2967, 2926, 1746, 1693, 845, 738 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 257.0584; found 257.0581.

2-(3-Chlorobenzoyl) cyclohexane-1, 3-dione (3k)

![Structure of 3k](image)

Colorless oil; Rf = 0.3 (petroleum ether/ethyl acetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.05 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.62-7.60 (m, 1H), 7.44 (d, J = 7.2 Hz, 1H), 6.04 (s, 1H), 2.67 (t, J = 6.2 Hz, 2H), 2.47 (t, J = 6.6 Hz, 2H), 2.16-2.10 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 199.2, 169.7, 161.7, 135.0, 134.1, 130.2, 130.0, 128.3, 118.1, 36.8, 28.4, 21.3; IR (KBr): 2968, 2928, 1748, 1678, 1576, 1126, 968, 881, 739 cm⁻¹; HRMS (ESI): calc. for (M + Na⁺) 273.0289; found 273.0294.

2-(3, 4-Difluorobenzoyl) cyclohexane-1, 3-dione (3l)

![Structure of 3l](image)

Colorless oil; Rf = 0.2 (petroleum ether/ethyl acetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86-7.80 (m, 2H), 7.26-7.19 (m, 1H), 5.97 (s, 1H), 2.62-2.58 (m, 2H), 2.40 (t, J = 6.8 Hz, 2H), 2.10-2.03 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 199.2, 169.5, 161.3, 155.6 (d, Jₐ⁻⁻F = S12
12.5 Hz), 152.6 (dd, J_CF = 228, 13.1 Hz), 149.0 (d, J_CF = 12.9 Hz), 127.4 (t, J_CF = 3.8 Hz), 125.7 (t, J_CF = 2.1 Hz), 119.6 (t, J_CF = 17.6 Hz), 118.1 (d, J_CF = 18 Hz), 36.8, 28.3, 21.3; IR (KBr): 2958, 2932, 1745, 1677, 1617, 1124, 934, 774, 752 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 275.0490; found 275.0498.

**2-(2-Naphthoyl) cyclohexane-1, 3-dione (3m)**

![2-(2-Naphthoyl) cyclohexane-1, 3-dione (3m)](image)

White solid; m.p = 101-102 °C, Rf = 0.2 (petroleum ether/ethyl acetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.59 (s, 1H), 8.00-7.98 (m, 1H), 7.91 (t, J = 8.0 Hz, 1H), 7.86-7.82 (m, 2H), 7.57-7.51 (m, 2H), 6.03 (s, 1H), 2.67 (t, J = 6.2 Hz, 2H), 2.42 (t, J = 6.8 Hz, 2H), 2.11-2.05 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 199.5, 170.3, 163.4, 136.0, 132.4, 132.3, 129.5, 129.0, 128.6, 127.9, 127.1, 125.8, 125.2, 117.9, 36.8, 28.5, 21.4; IR (KBr): 2960, 2926, 1745, 1677, 1617, 1124, 934, 774, 752 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 289.0835; found 289.840.

**2-(Thiophene-3-carbonyl) cyclohexane-1, 3-dione (3n)**

![2-(Thiophene-3-carbonyl) cyclohexane-1, 3-dione (3n)](image)

Colorless oil; Rf = 0.2 (petroleum ether/ethyl acetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.23 (d, J = 2.0 Hz, 1H), 7.57 (d, J = 4.8 Hz, 1H), 7.37 (t, J = 2.0 Hz, 1H), 6.03 (s, 1H), 2.66 (t, J = 6.0 Hz, 2H), 2.45 (t, J = 6.6 Hz, 2H), 2.15-2.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 199.4, 169.8, 158.9, 134.8, 132.0, 128.1, 126.7, 117.8, 36.8, 28.5, 21.4; IR (KBr): 2958, 2926, 1745, 1677, 1617, 1124, 934, 774, 752 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 245.0243; found 245.0251.

**2-(4-Methylbenzoyl) cyclopentane-1, 3-dione (3o)**

![2-(4-Methylbenzoyl) cyclopentane-1, 3-dione (3o)](image)
Colorless oil; $R_f = 0.2$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.00 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 6.37 (s, 1H), 2.91-2.88 (m, 2H), 2.52-2.50 (m, 2H), 2.44 (s, 3H); $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 206.8, 180.1, 162.2, 145.6, 130.5, 129.6, 125.3, 116.6, 33.4, 28.9, 21.8; IR (KBr): 2958, 2924, 17405, 1768, 1674, 1123, 968, 755, 684 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 239.0679; found 239.0672.

**3-(4-Methylbenzoyl) pentane-2, 4-dione (3p)**

Colorless oil; $R_f = 0.2$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.79 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H), 2.00 (s, 6H); $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 195.3, 192.1, 144.8, 136.2, 129.5, 127.1, 115.5, 24.6, 21.7; IR (KBr): 2958, 2924, 17405, 1768, 1674, 1123, 968, 755, 684 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 239.0679; found 239.0672.

**Diethyl 2-benzoyl-2-methylmalonate (4a)**

Colorless oil; $R_f = 0.3$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.82 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 4.25 (q, $J = 5.2$ Hz, 4H), 1.84 (s, 3H), 1.20 (t, $J = 6.8$ Hz, 6H); $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 193.5, 168.9, 135.3, 132.9, 129.0, 128.3, 62.6, 62.2, 20.2, 13.8. IR (KBr): 3051, 2972, 1764, 1726, 1675, 887, 792, 687, 646 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 301.1046; found 301.1041.

**Diethyl 2-methyl-2-(4-methylbenzoyl)malonate (4b)**

Colorless oil; $R_f = 0.3$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.71 (d, $J = 8.0$ Hz, 2H), 7.21 (t, $J = 8.0$ Hz, 2H), 4.28-4.19 (m, 4H), 2.40 (s, 3H), 1.83 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 6H); $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 193.0, 169.0,
143.8, 132.6, 129.2, 129.0, 65.6, 62.2, 21.6, 20.2, 13.8; IR (KBr): 3044, 2965, 1767, 1731, 1699, 862, 792, 681, 654 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 315.1203; found 315.1210.

**Diethyl 2-methyl-2-(4-propylbenzoyl)malonate (4c)**

![diagram]

Colorless oil. $R_f = 0.3$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.73 (d, $J = 7.2$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 2H), 4.27-4.19 (m, 4H), 2.62 (t, $J = 7.4$ Hz, 2H), 1.83 (s, 3H), 1.65 (q, $J = 7.2$ Hz, 2H), 1.19 (t, $J = 7.0$ Hz, 6H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 193.1, 169.0, 148.4, 132.8, 129.2, 128.4, 65.6, 62.2, 38.0, 24.1, 20.1, 13.8, 13.7; IR (KBr): 3042, 2978, 1761, 1744, 1691, 916, 877, 768, 657, 632 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 343.1516; found 343.1519.

**Diethyl 2-ethyl-2-(4-ethylbenzoyl)malonate (4d)**

![diagram]

Colorless oil. $R_f = 0.2$ (petroleum ether/ethyl acetate 10:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.85 (d, $J = 7.2$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.43-7.41 (m, 2H), 4.22-4.16 (m, 4H), 2.34 (q, $J = 7.2$ Hz, 2H), 1.13 (t, $J = 7.2$ Hz, 6H), 1.05 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 192.2, 167.9, 136.2, 132.8, 128.6, 128.3, 68.9, 61.8, 27.9, 13.8, 9.5. IR (KBr): 3042, 2968, 1769, 1728, 1694, 856, 783, 685, 662 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 314.1125; found 314.1131.

**Diethyl 2-ethyl-2-(4-methylbenzoyl)malonate (4e)**

![diagram]

Colorless oil. $R_f = 0.3$ (petroleum ether/ethyl acetate 20:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.75 (d, $J = 6.8$ Hz, 2H), 7.20 (d, $J = 7.2$ Hz, 2H), 4.18 (q, $J = 6.5$ Hz, 4H), 2.83 (s, 3H), 2.32 (t, $J = 7.3$ Hz, 2H), 1.14 (t, $J = 7.2$ Hz, 6H) 1.03 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 191.7, 168.1, 143.7, 133.3, 129.0, 128.9, 68.8, 61.8, 27.9, 21.6, 13.8, 9.5; IR
(KBr): 3054, 2982, 1762, 1684, 842, 761, 687, 654 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 329.1359; found 329.1353.

**Diethyl 2-ethyl-2-(4-propylbenzoyl)malonate (4f)**

Colorless oil. 

\[ R_f = 0.3 \text{ (petroleum ether/ethyl acetate 10:1)} \]

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.76 (d, \( J = 8.4 \) Hz, 2H), 7.20 (t, \( J = 8.4 \) Hz, 2H), 4.21-4.18 (m, 4H), 2.62 (t, \( J = 7.6 \) Hz, 2H), 2.33 (t, \( J = 7.5 \) Hz, 2H), 1.69-1.60 (m, 2H), 1.13 (t, \( J = 7.2 \) Hz, 6H), 1.65 (q, \( J = 7.2 \) Hz, 2H), 1.19 (t, \( J = 7.0 \) Hz, 6H), 1.04 (t, \( J = 7.4 \) Hz, 3H); 13C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 191.8, 168.0, 148.3, 133.7, 128.8, 128.4, 68.8, 61.8, 37.9, 27.9, 24.1, 13.8, 13.7, 9.5; IR (KBr): 3041, 2975, 1768, 1749, 1698, 873, 762, 677, 642 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 357.1672; found 357.1679.

**Diethyl 2-ethyl-2-(3-methylbenzoyl)malonate (4g)**

Colorless oil; 

\[ R_f = 0.2 \text{ (petroleum ether/ethyl acetate 5:1)} \]

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.67 (s, 1H), 6.96 (d, \( J = 8.8 \) Hz, 2H), 5.24 (s, 1H), 4.22-4.17 (m, 4H), 2.38 (s, 3H), 2.34 (d, \( J = 7.6 \) Hz, 2H), 1.62 (t, \( J = 7.2 \) Hz, 6H), 1.06 (t, \( J = 7.2 \) Hz, 3H); 13C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm): 192.5, 168.0, 138.2, 136.2, 133.6, 129.2, 128.1, 125.8, 61.8, 28.0, 21.4, 13.8, 9.5; IR (KBr): 3046, 2976, 1768, 1727, 1684, 851, 766, 682, 651 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 328.1281; found 328.1275.

**Diethyl 2-benzoyl-2-propylmalonate (4h)**
Colorless oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 20:1); \(^1\)H NMR (400 MHz, CDCl\(_3\) ) \( \delta \) (ppm): 7.83 (d, \( J = 7.6 \) Hz, 2H), 7.52 (t, \( J = 7.4 \) Hz, 1H), 7.40 (t, \( J = 7.2 \) Hz, 1H), 4.21-4.15 (m, 4H), 2.23 (t, \( J = 7.6 \) Hz, 2H), 1.44 (t, \( J = 7.5 \) Hz, 2H), 1.12 (t, \( J = 7.0 \) Hz, 6H), 0.93 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\) ) \( \delta \) (ppm): 192.2, 168.2, 136.1, 132.8, 128.6, 128.3, 68.5, 61.9, 36.6, 18.3, 14.4, 13.8; IR (KBr): 3051, 2972, 1763, 1721, 1674, 857, 786, 692, 656 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 329.1359; found 329.1352.

**Diethyl 2-(4-methylbenzoyl)-2-propylmalonate (4i)**

![Diethyl 2-(4-methylbenzoyl)-2-propylmalonate (4i)](image)

Colorless oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 20:1); \(^1\)H NMR (400 MHz, CDCl\(_3\) ) \( \delta \) (ppm): 7.68 (d, \( J = 8.4 \) Hz, 2H), 7.13 (d, \( J = 8.4 \) Hz, 2H), 4.11 (q, \( J = 6.9 \) Hz, 4H), 2.32 (s, 3H), 2.18-2.14 (m, 2H), 1.36 (t, \( J = 7.7 \) Hz, 2H), 1.07 (t, \( J = 7.2 \) Hz, 6H), 0.86 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\) ) \( \delta \) (ppm): 191.6, 168.1, 143.7, 133.4, 129.0, 128.8, 68.4, 61.8, 36.6, 21.6, 18.3, 14.4, 13.8; IR (KBr): 3052, 2976, 1767, 1726, 1682, 841, 763, 684, 643 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 343.1516; found 343.1512.

**Diethyl 2-benzoyl-2-benzylocetate (4j)**

![Diethyl 2-benzoyl-2-benzylocetate (4j)](image)

Colorless oil; \( R_f = 0.3 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (400 MHz, CDCl\(_3\) ) \( \delta \) (ppm): 7.85 (d, \( J = 6.8 \) Hz, 2H), 7.51 (d, \( J = 6.8 \) Hz, 1H), 7.39 (t, \( J = 6.8 \) Hz, 2H), 7.25-7.22 (m, 5H), 4.11-4.01 (m, 4H), 3.67 (s, 2H), 0.99 (t, \( J = 7.2 \) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\) ) \( \delta \) (ppm): 191.3, 167.2, 136.0, 135.6, 132.9, 130.5, 128.8, 128.3, 128.3, 127.1, 69.7, 61.9, 40.0, 13.6; IR (KBr): 3046, 2968, 1764, 1734, 1695, 912, 867, 798, 687, 656 cm\(^{-1}\); HRMS (ESI): calc. for (M + Na\(^+\)) 377.1359; found 377.1354.
Diethyl 2-benzyl-2-(4-methylbenzoyl) malonate (4k)

Colorless oil; Rf = 0.2 (petroleum ether/ethyl acetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.76 (d, $J = 8.4$ Hz, 2H), 7.23-7.17 (m, 7H), 4.11-4.02 (m, 4H), 3.66 (s, 2H), 2.38 (s, 3H), 1.02 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 190.6, 167.3, 143.8, 135.8, 133.3, 130.5, 129.0, 128.5, 128.0, 127.1, 61.8, 40.0, 21.6, 13.6; IR (KBr): 3047, 2978, 1767, 1724, 1698, 887, 795, 688, 646 cm$^{-1}$; HRMS (ESI): calc. for (M + Na$^+$) 390.1438; found 390.1443.

3-Phenyl-6,7-dihydro-1H-indazol-4(5H)-one (5)

White solid; Rf = 0.2 (petroleum ether/ethyl acetate 1:1); 9.40 (s, 1H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.530 (d, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 2H), 5.16 (s, 1H), 5.485 (s, 1H), 2.45 (s, 2H), 2.31 (t, $J = 5.6$ Hz, 2H), 2.00 (t, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 197.6, 165.7, 163.4, 131.5, 130.3, 127.7, 126.5, 98.0, 35.5, 25.5, 20.7.

4. References.

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No reference was found via SCI finder.

5. Copies of the $^1$H NMR and $^{13}$C NMR spectra of products

![NMR Spectra](image-url)
2k

2k
$\text{F}_3\text{C}$

3h

$\text{F}_3\text{C}$

3h
3n

1.250 1.607 2.084 2.099 2.116 2.132 2.148 2.437 2.454 2.470 2.647 2.662 2.677

3n