

Supporting Information to

**Nickel-Catalyzed Remote Arylation of Alkenyl Aldehydes Initiated by Radical
Alkylation with Tertiary α -Carbonyl Alkyl Bromides**

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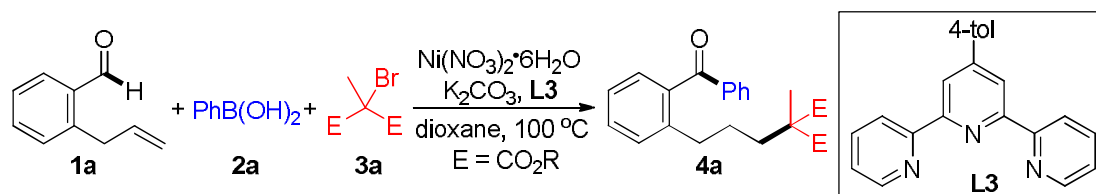
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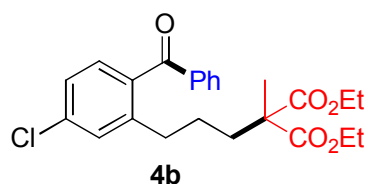
General information:

Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a 600 or 400 MHz NMR spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with ESI source. Column chromatography was performed using silica gel (300–400 mesh).

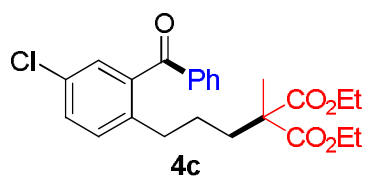
General Procedure for the Nickel-Catalyzed Remote Arylation of Aldehydes Initiated by Radical Alkylation of Unactivated Olefins:



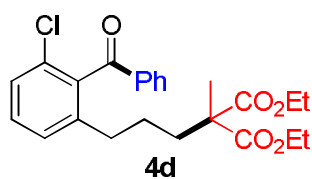
To a mixture of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.8 mg, 0.02 mmol), **L3** (6.8 mg, 0.02 mmol), PhB(OH)_2 (73 mg, 0.6 mmol), and K_2CO_3 (138 mg, 0.8 mmol) was added a solution of **1a** (29.2 mg, 0.20 mmol) and **3a** (151.2 mg, 0.6 mmol) in 2 mL of 1,4-dioxane under a nitrogen atmosphere. After stirring at 100°C for 12 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated. Column chromatography on silica gel (petroleum ether/EtOAc = 20:1) gave 57 mg of **4a** (75% yield) as a colorless oil. Starting from **1a** (292 mg, 2.0 mmol) and following the general procedure, 562 mg (71% yield) of **4a** was obtained as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.82–7.77 (m, 2H), 7.60–7.56 (m, 1H), 7.46–7.43 (m, 2H), 7.42–7.40 (m, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.28–7.23 (m, 2H), 4.11–4.07 (m, 4H), 2.71–2.65 (m, 2H), 1.84–1.80 (m, 2H), 1.53–1.46 (m, 2H), 1.30 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.4, 172.2, 140.8, 138.4, 137.7, 133.1, 130.2, 130.1, 130.0, 128.5, 128.3, 125.3, 61.0, 53.4, 35.2, 33.3, 26.3, 19.6, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{28}\text{O}_5$ ($\text{M} + \text{Na}$) $^+$ 419.1829 found 419.1825.



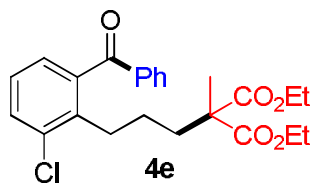
Compound 4b: 60 mg, 70% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.77–7.76 (m, 2H), 7.61–7.58 (m, 1H), 7.47–7.45 (m, 2H), 7.31 (d, $J = 1.4$ Hz, 1H), 7.25–7.21 (m, 2H), 4.13–4.08 (m, 4H), 2.65 (t, $J = 7.9$ Hz, 2H), 1.82–1.79 (m, 2H), 1.52–1.47 (m, 2H), 1.31 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.4, 172.1, 143.2, 137.5, 136.7, 136.2, 133.4, 130.1, 130.0, 130.0, 128.5, 125.6, 61.1, 53.4, 35.2, 33.2, 26.1, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{Cl}$ ($\text{M}+\text{Na}$) $^+$ 453.1439, found 453.1434.



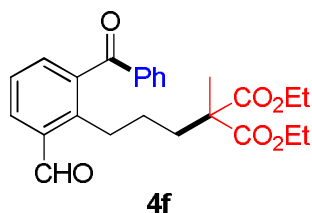
Compound 4c: 50 mg, 58% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 7.2$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.39–7.37 (m, 1H), 7.27–7.25 (m, 2H), 4.12–4.08 (m, 4H), 2.61 (t, $J = 7.8$ Hz, 2H), 1.80–1.77 (m, 2H), 1.50–1.46 (m, 2H), 1.30 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.8, 172.1, 140.0, 139.1, 137.0, 133.6, 131.4, 131.3, 130.1, 130.1, 128.6, 128.0, 61.1, 53.4, 35.1, 32.7, 26.1, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{Cl}$ ($\text{M}+\text{Na}$) $^+$ 453.1439, found 453.1436.



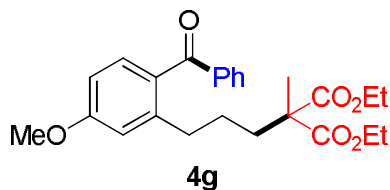
Compound 4d: 22 mg, 25% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 7.2$ Hz, 2H), 7.62–7.59 (m, 1H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.35–7.31 (m, 1H), 7.29–7.28 (m, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 4.13–4.10 (m, 4H), 2.45 (t, $J = 7.8$ Hz, 2H), 1.77–1.74 (m, 2H), 1.46–1.41 (m, 2H), 1.27 (s, 3H), 1.20 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.0, 172.1, 141.1, 138.2, 136.5, 133.9, 130.5, 130.0, 129.5, 128.8, 127.6, 127.1, 61.1, 53.4, 35.1, 33.4, 25.7, 19.6, 14.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{Cl}$ ($\text{M}+\text{Na}$) $^+$ 453.1439, found 453.1434.



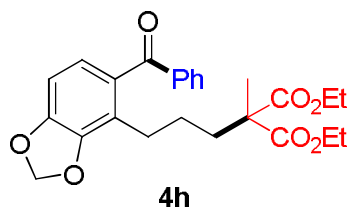
Compound 4e: 73 mg, 85% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.79–7.77 (m, 2H), 7.61–7.58 (m, 1H), 7.48–7.45 (m, 3H), 7.20 (t, J = 7.8 Hz, 1H), 7.15–7.14 (m, 1H), 4.11 (q, J = 7.1 Hz, 4H), 2.72 (t, J = 8.2 Hz, 2H), 1.85 (t, J = 8.4 Hz, 2H), 1.51–1.46 (m, 2H), 1.31 (s, 3H), 1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.1, 172.2, 140.7, 138.2, 137.1, 135.4, 133.6, 131.2, 130.2, 128.5, 126.5, 126.4, 61.1, 53.5, 35.4, 30.9, 24.8, 19.6, 14.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{Cl}$ ($\text{M}+\text{Na}$) $^+$ 453.1439, found 453.1434.



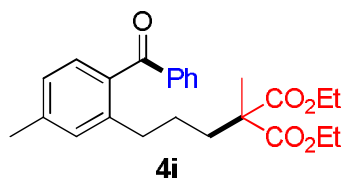
Compound 4f: 48 mg, 57% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 10.33 (s, 1H), 7.98–7.97 (m, 1H), 7.79–7.77 (m, 2H), 7.63–7.60 (m, 1H), 7.49–7.45 (m, 4H), 4.10 (q, J = 7.1 Hz, 4H), 2.99 (t, J = 8.2 Hz, 2H), 1.88 (t, J = 8.3 Hz, 2H), 1.52–1.46 (m, 2H), 1.29 (s, 3H), 1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.4, 191.5, 172.1, 143.0, 140.8, 137.1, 134.4, 133.8, 133.1, 132.8, 130.1, 128.7, 126.1, 61.2, 53.4, 35.4, 29.2, 27.8, 19.6, 14.0; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{O}_6$ ($\text{M}+\text{Na}$) $^+$ 447.1778, found 447.1780.



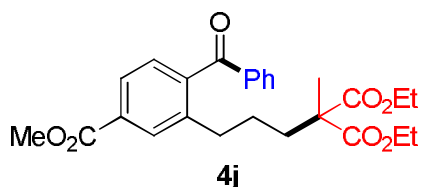
Compound 4g: 72 mg, 84% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 2.5 Hz, 1H), 6.75–6.73 (m, 1H), 4.12–4.08 (m, 4H), 3.86 (s, 3H), 2.76 (t, J = 7.8 Hz, 2H), 1.87–1.84 (m, 2H), 1.54–1.50 (m, 2H), 1.33 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.7, 172.3, 161.2, 144.5, 138.7, 132.6, 132.0, 130.5, 130.0, 128.2, 116.0, 110.0, 61.1, 55.3, 53.5, 35.3, 33.7, 26.4, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_6$ ($\text{M}+\text{Na}$) $^+$ 449.1935, found 449.1938.



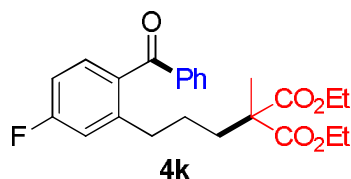
Compound 4h: 77 mg, 88% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 6.03 (s, 2H), 4.10 (q, J = 7.1 Hz, 4H), 2.74 (t, J = 7.8 Hz, 2H), 1.88–1.85 (m, 2H), 1.54–1.50 (m, 2H), 1.33 (s, 3H), 1.18 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.9, 172.2, 148.9, 146.7, 138.6, 132.6, 132.3, 130.1, 128.2, 125.3, 124.1, 105.1, 101.3, 61.0, 53.5, 35.2, 26.8, 24.8, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{O}_7$ ($\text{M}+\text{Na}$) $^+$ 463.1727, found 463.1730.



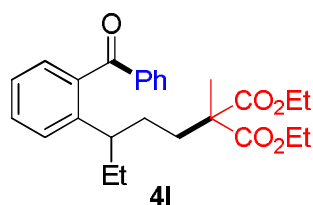
Compound 4i: 57 mg, 70% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.78–7.77 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.18 (d, J = 7.7 Hz, 1H), 7.12 (s, 1H), 7.04 (d, J = 7.7 Hz, 1H), 4.12–4.08 (m, 4H), 2.67 (t, J = 7.9 Hz, 2H), 2.39 (s, 3H), 1.84–1.81 (m, 2H), 1.50–1.47 (m, 2H), 1.31 (s, 3H), 1.18 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.4, 172.3, 141.4, 140.5, 138.2, 135.4, 132.9, 130.9, 130.1, 129.2, 128.3, 125.9, 61.0, 53.5, 35.3, 33.4, 26.5, 21.4, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 433.1985, found 433.1980.



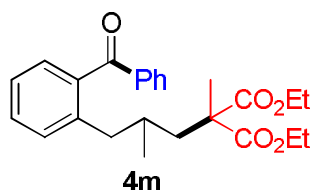
Compound 4j: 35 mg, 38% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.99 (s, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 7.9 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.33 (d, J = 7.9 Hz, 1H), 4.12–4.08 (m, 4H), 3.96 (s, 3H), 2.67 (t, J = 7.9 Hz, 2H), 1.82–1.79 (m, 2H), 1.53–1.48 (m, 2H), 1.30 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.7, 172.1, 166.5, 142.7, 140.8, 137.0, 133.6, 131.4, 131.0, 130.0, 128.6, 128.1, 126.7, 61.1, 53.4, 52.3, 35.2, 33.2, 26.2, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{O}_7$ ($\text{M}+\text{Na}$) $^+$ 477.1884, found 477.1887.



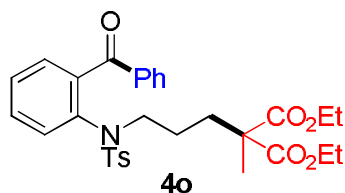
Compound 4k: 48mg, 58% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 7.4$ Hz, 2H), 7.60–7.58 (m, 1H), 7.47–7.45 (m, 2H), 7.30–7.28 (m, 1H), 7.03–7.01 (m, 1H), 6.95–6.92 (m, 1H), 4.13–4.09 (m, 4H), 2.70 (t, $J = 7.8$ Hz, 2H), 1.83–1.81 (m, 2H), 1.54–1.48 (m, 2H), 1.32 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.3, 172.1, 163.6 (d, $J = 250.8$ Hz), 144.6 (d, $J = 7.8$ Hz), 137.8, 134.4, 133.2, 131.1 (d, $J = 9.0$ Hz), 130.1, 128.4, 116.8 (d, $J = 21.2$ Hz), 112.3 (d, $J = 21.5$ Hz), 61.1, 53.4, 35.1, 33.3, 26.0, 19.7, 13.9; ^{19}F NMR (565 MHz, CDCl_3) δ -109.7; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{F}$ ($\text{M}+\text{Na}$) $^+$ 437.1735, found 437.1736.



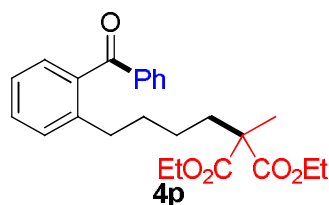
Compound 4l: 44 mg, 52% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.81–7.80 (m, 2H), 7.59–7.56 (m, 1H), 7.47–7.44 (m, 3H), 7.34 (d, $J = 7.9$ Hz, 1H), 7.24–7.23 (m, 2H), 4.15–4.08 (m, 4H), 2.71–2.66 (m, 1H), 1.75–1.72 (m, 1H), 1.66–1.50 (m, 5H), 1.30 (s, 3H), 1.20–1.18 (m, 6H), 0.71 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.7, 172.2, 144.1, 139.8, 137.9, 133.2, 130.2, 130.1, 128.3, 127.8, 126.5, 125.1, 61.0, 61.0, 53.5, 42.5, 33.4, 30.7, 29.5, 19.8, 14.0, 14.0, 11.9; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{32}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 447.2142, found 447.2144.



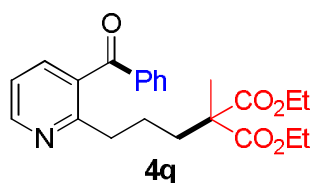
Compound 4m: 36mg, 44% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.80–7.78 (m, 2H), 7.59–7.57 (m, 1H), 7.45 (t, $J = 8.0$ Hz, 2H), 7.42–7.40 (m, 1H), 7.28–7.25 (m, 3H), 4.15–4.04 (m, 4H), 2.75–2.72 (m, 1H), 2.48–2.45 (m, 1H), 1.93–1.90 (m, 1H), 1.82–1.75 (m, 2H), 1.28 (s, 3H), 1.21–1.17 (m, 6H), 0.70 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.5, 172.7, 139.8, 139.0, 137.8, 133.2, 131.0, 130.2, 130.0, 128.5, 128.4, 125.4, 61.2, 61.1, 53.1, 41.7, 41.5, 31.2, 19.9, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 433.1985, found 433.1989.



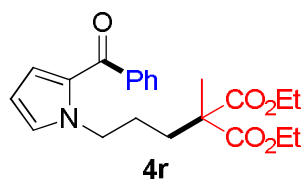
Compound 4o: 34 mg, 30% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.46–7.36 (m, 7H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.13 (q, $J = 7.2$ Hz, 4H), 3.60 (brs, 2H), 2.30 (s, 3H), 1.80–1.78 (m, 2H), 1.55 (brs, 2H), 1.34 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 195.0, 172.1, 143.3, 140.4, 137.5, 137.0, 135.8, 132.9, 130.7, 130.5, 130.5, 130.0, 129.3, 128.0, 127.8, 127.4, 61.2, 53.3, 52.5, 32.6, 23.4, 21.4, 19.8, 14.0; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{35}\text{O}_7\text{NS}$ ($\text{M}+\text{Na}$) $^+$ 588.2026, found 588.2030.



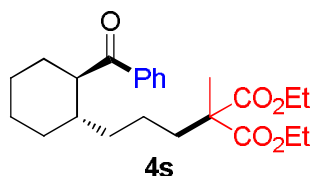
Compound 4p: 52 mg, 64% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.79–7.78 (m, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.42–7.39 (m, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.27–7.23 (m, 2H), 4.14 (q, $J = 7.1$ Hz, 4H), 2.65 (t, $J = 8.0$ Hz, 2H), 1.80–1.77 (m, 2H), 1.58–1.53 (m, 2H), 1.33 (s, 3H), 1.22–1.17 (m, 8H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.6, 172.3, 141.3, 138.4, 137.8, 133.1, 130.1, 130.1, 130.0, 128.5, 128.4, 125.2, 61.0, 53.5, 35.1, 33.0, 31.8, 24.1, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 433.1985, found 433.1985.



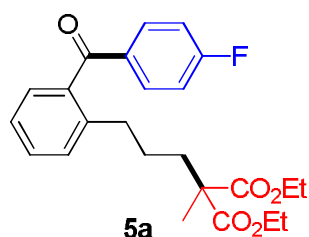
Compound 4q: 48 mg, 61% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.67–7.66 (m, 1H), 7.78–7.77 (m, 2H), 7.65–7.59 (m, 2H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.23–7.21 (m, 1H), 4.14–4.08 (m, 4H), 2.81 (t, $J = 7.9$ Hz, 2H), 1.86–1.83 (m, 2H), 1.67–1.62 (m, 2H), 1.33 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.7, 172.2, 159.6, 150.4, 137.0, 136.0, 133.9, 133.7, 130.0, 128.6, 120.3, 61.1, 53.4, 36.1, 35.1, 24.6, 19.6, 13.9; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{27}\text{O}_5\text{N}$ ($\text{M}+\text{Na}$) $^+$ 420.1781, found 420.1786.



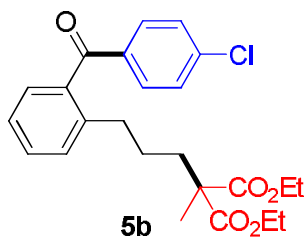
Compound 4r: 40 mg, 52% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 7.1$ Hz, 2H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 2H), 6.98 (t, $J = 1.9$ Hz, 1H), 6.73–6.72 (m, 1H), 6.16–6.15 (m, 1H), 4.41 (t, $J = 7.0$ Hz, 2H), 4.15 (q, $J = 7.1$ Hz, 4H), 1.91–1.88 (m, 2H), 1.82–1.77 (m, 2H), 1.39 (s, 3H), 1.21 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 186.0, 172.1, 140.1, 131.2, 130.6, 129.7, 129.1, 127.9, 123.5, 108.2, 61.2, 53.3, 49.5, 32.4, 26.6, 19.8, 14.0; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{27}\text{O}_5\text{N}$ ($\text{M}+\text{Na}$) $^+$ 408.1781, found 408.1786.



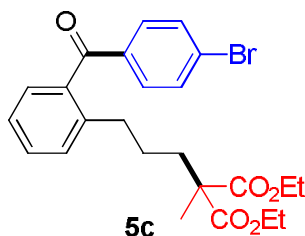
Compound 4s: 36 mg, 45% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, $J = 7.4$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 4.14–4.09 (m, 4H), 3.14–3.10 (m, 1H), 1.95–1.68 (m, 7H), 1.33 (s, 3H), 1.29–1.27 (m, 4H), 1.22–1.18 (m, 6H), 1.18–0.98 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 204.7, 172.4, 137.4, 132.9, 128.6, 128.1, 61.0, 61.0, 53.6, 50.8, 38.5, 35.5, 35.2, 31.1, 30.9, 26.0, 25.7, 21.3, 19.8, 14.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{34}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 425.2298, found 425.2302.



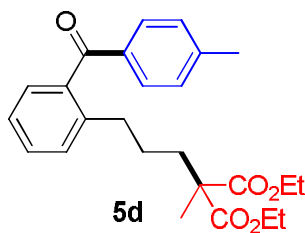
Compound 5a: 55 mg, 66% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.84–7.81 (m, 2H), 7.42–7.40 (m, 1H), 7.31 (d, $J = 7.7$ Hz, 1H), 7.26–7.25 (m, 2H), 7.14–7.11 (m, 2H), 4.13–4.09 (m, 4H), 2.66 (t, $J = 7.8$ Hz, 2H), 1.83–1.80 (m, 2H), 1.51–1.48 (m, 2H), 1.31 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.8, 172.2, 165.8 (d, $J = 255.6$ Hz), 140.7, 138.1, 134.1 (d, $J = 2.8$ Hz), 132.8 (d, $J = 9.4$ Hz), 130.3, 130.1, 128.3, 125.4, 115.5 (d, $J = 21.9$ Hz), 61.0, 53.4, 35.2, 33.3, 26.3, 19.7, 13.9; ^{19}F NMR (565 MHz, CDCl_3) δ -104.8; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{F}$ ($\text{M}+\text{Na}$) $^+$ 437.1735, found 437.1740.



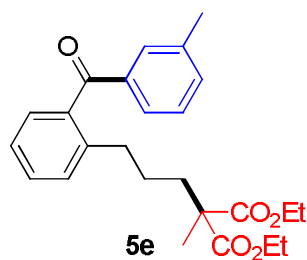
Compound 5b: 65 mg, 76% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, J = 8.5 Hz, 2H), 7.43–7.41 (m, 3H), 7.31 (d, J = 7.7 Hz, 1H), 7.27–7.25 (m, 2H), 4.12–4.09 (m, 4H), 2.66 (t, J = 7.9 Hz, 2H), 1.83–1.80 (m, 2H), 1.51–1.47 (m, 2H), 1.31 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.1, 172.2, 140.9, 139.7, 137.9, 136.1, 131.5, 130.5, 130.2, 128.7, 128.4, 125.4, 61.1, 53.4, 35.2, 33.3, 26.4, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{Cl}$ ($\text{M}+\text{Na}$) $^+$ 453.1439, found 453.1445.



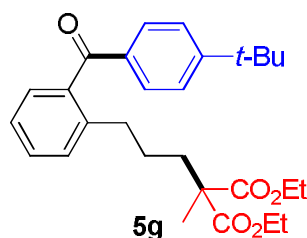
Compound 5c: 64 mg, 67% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.67–7.65 (m, 2H), 7.60–7.59 (m, 2H), 7.44–7.41 (m, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.25–7.24 (m, 2H), 4.12–4.09 (m, 4H), 2.66 (t, J = 7.8 Hz, 2H), 1.83–1.80 (m, 2H), 1.50–1.48 (m, 2H), 1.31 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.2, 172.1, 140.9, 137.8, 136.5, 131.7, 131.6, 130.4, 130.1, 128.4, 125.4, 61.0, 53.4, 35.2, 33.3, 26.3, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{Br}$ ($\text{M}+\text{Na}$) $^+$ 497.0934, found 497.0937.



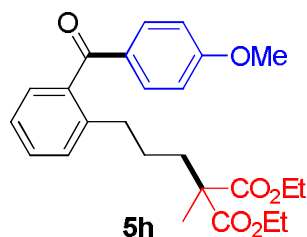
Compound 5d: 58 mg, 71% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.69 (d, J = 8.2 Hz, 2H), 7.41–7.38 (m, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.25–7.23 (m, 4H), 4.11–4.08 (m, 4H), 2.65 (t, J = 7.9 Hz, 2H), 2.42 (s, 3H), 1.82–1.80 (m, 2H), 1.51–1.46 (m, 2H), 1.30 (s, 3H), 1.18 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.2, 172.2, 144.1, 140.6, 138.8, 135.2, 130.3, 130.0, 129.9, 129.1, 128.3, 125.3, 61.0, 53.5, 35.2, 33.3, 26.3, 21.6, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 433.1985, found 433.1988.



Compound 5e: 53 mg, 65% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.63 (s, 1H), 7.54 (d, $J = 8.3$ Hz, 1H), 7.42–7.38 (m, 2H), 7.33–7.30 (m, 2H), 7.27–7.23 (m, 2H), 4.12–4.08 (m, 4H), 2.67 (t, $J = 7.8$ Hz, 2H), 2.39 (s, 3H), 1.83–1.80 (m, 2H), 1.52–1.47 (m, 2H), 1.30 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.7, 172.2, 140.7, 138.6, 138.2, 137.8, 133.9, 130.4, 130.1, 129.9, 128.4, 128.2, 127.6, 125.3, 61.0, 53.5, 35.2, 33.3, 26.3, 21.2, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 433.1985, found 433.1989.

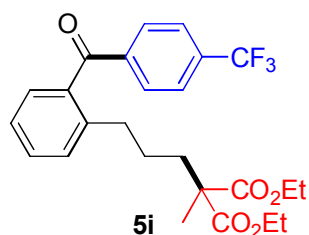


Compound 5g: 71 mg, 78% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.41–7.39 (m, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.27–7.22 (m, 2H), 4.11–4.06 (m, 4H), 2.66 (t, $J = 7.9$ Hz, 2H), 1.83–1.80 (m, 2H), 1.51–1.45 (m, 2H), 1.34 (s, 9H), 1.29 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.1, 172.2, 157.0, 140.6, 138.8, 135.1, 130.2, 130.0, 129.9, 128.3, 125.4, 125.3, 61.1, 53.5, 35.3, 35.1, 33.3, 31.1, 26.3, 19.7, 14.0; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{36}\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 475.2455, found 475.2455.

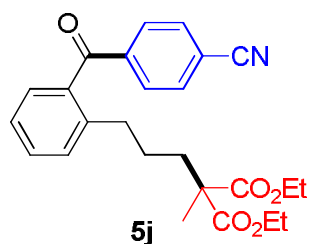


Compound 5h: 46 mg, 54% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.9$ Hz, 2H), 7.40–7.37 (m, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.25–7.24 (m, 2H), 6.92 (d, $J = 8.9$ Hz, 2H), 4.12–4.08 (m, 4H), 3.87 (s, 3H), 2.64 (t, $J = 7.9$ Hz, 2H), 1.82–1.79 (m, 2H), 1.50–1.47 (m, 2H), 1.30 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.1, 172.2, 163.6, 140.3, 138.9, 132.5, 130.6, 129.8, 129.7, 128.0, 125.3, 113.6, 61.0, 55.4, 53.4, 35.2, 33.2, 26.2, 19.6, 13.9;

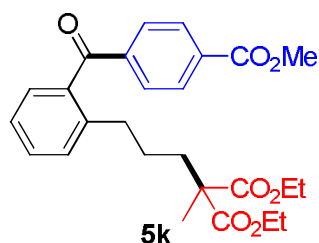
HRMS (ESI) calcd for C₂₅H₃₀O₆ (M+Na)⁺ 449.1935, found 449.1933.



Compound 5i: 65 mg, 70% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.46–7.44 (m, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 3.3 Hz, 2H), 4.12–4.08 (m, 4H), 2.69 (t, *J* = 7.8 Hz, 2H), 1.84–1.81 (m, 2H), 1.53–1.48 (m, 2H), 1.32 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 197.1, 172.2, 141.4, 140.7 (q, *J* = 1.0 Hz), 137.4, 134.3 (q, *J* = 32.6 Hz), 130.9, 130.4, 130.4, 128.8, 125.5, 125.4 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.9 Hz), 61.1, 53.4, 35.2, 33.4, 26.5, 19.7, 13.9; ¹⁹F NMR (565 MHz, CDCl₃) δ -63.1; HRMS (ESI) calcd for C₂₅H₂₇O₅F₃ (M+Na)⁺ 487.1703, found 487.1700.

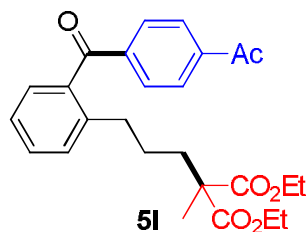


Compound 5j: 46 mg, 55% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.48–7.45 (m, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.29–7.24 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 4H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.84–1.81 (m, 2H), 1.54–1.48 (m, 2H), 1.32 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 196.6, 172.1, 141.5, 141.1, 136.9, 132.2, 131.1, 130.4, 130.3, 128.8, 125.5, 117.9, 116.2, 61.1, 53.3, 35.2, 33.3, 26.4, 19.7, 13.9; HRMS (ESI) calcd for C₂₅H₂₇O₅N (M+Na)⁺ 444.1781, found 444.1776.

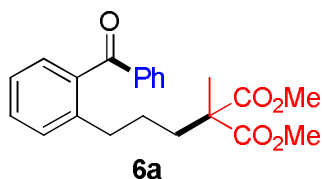


Compound 5k: 62 mg, 68% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.46–7.43 (m, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.28–7.26 (m, 2H), 4.12–4.09 (m, 4H), 3.96 (s, 3H), 2.69 (t, *J* = 7.8 Hz, 2H), 1.84–1.81 (m, 2H), 1.53–1.49 (m, 2H), 1.31 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 197.7, 172.2, 166.2, 141.3,

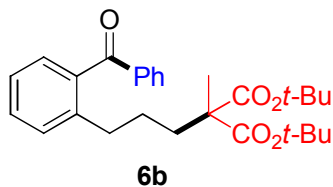
141.2, 137.6, 133.8, 130.7, 130.3, 129.9, 129.6, 128.8, 125.4, 61.1, 53.4, 52.4, 35.2, 33.4, 26.4, 19.7, 13.9; HRMS (ESI) calcd for $C_{26}H_{30}O_7 (M+Na)^+$ 477.1884, found 477.1889.



Compound 5I: 39 mg, 45% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.46–7.43 (m, 1H), 7.34 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 4.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 4H), 2.70–2.66 (m, 5H), 1.84–1.81 (m, 2H), 1.54–1.48 (m, 2H), 1.31 (s, 3H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 197.5, 172.1, 141.3, 141.2, 140.0, 137.6, 130.7, 130.2, 130.2, 128.8, 128.2, 125.4, 61.0, 53.4, 35.2, 33.3, 26.9, 26.4, 19.7, 13.9; HRMS (ESI) calcd for $C_{26}H_{30}O_6 (M+Na)^+$ 461.1935, found 461.1937.

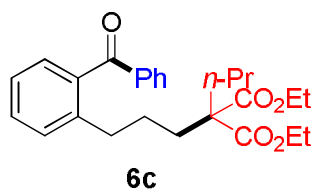


Compound 6a: 68 mg, 92% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46–7.40 (m, 3H), 7.31 (d, J = 7.8 Hz, 1H), 7.28–7.23 (m, 2H), 3.63 (s, 6H), 2.67 (t, J = 7.8 Hz, 2H), 1.83–1.80 (m, 2H), 1.51–1.45 (m, 2H), 1.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 172.6, 140.7, 138.4, 137.7, 133.1, 130.2, 130.1, 130.0, 128.5, 128.4, 125.3, 53.5, 52.3, 35.4, 33.3, 26.4, 19.8; HRMS (ESI) calcd for $C_{22}H_{24}O_5 (M+Na)^+$ 391.1516, found 391.1515.

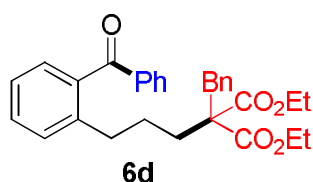


Compound 6b: 36 mg, 40% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45–7.40 (m, 3H), 7.31 (d, J = 7.7 Hz, 1H), 7.28–7.27 (m, 1H), 7.25–7.23 (m, 1H), 2.67 (t, J = 7.9 Hz, 2H), 1.75–1.72 (m, 2H), 1.50–1.48 (m, 2H), 1.39 (s, 18H), 1.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 171.6, 141.0, 138.4, 137.8, 133.1, 130.2, 130.2, 130.1, 128.5, 128.4, 125.3, 80.8, 54.4, 35.2, 33.5, 27.8, 26.2, 19.5; HRMS (ESI) calcd for

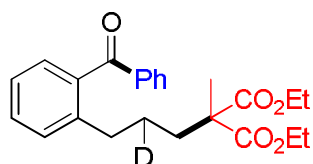
$C_{28}H_{36}O_5$ ($M+Na$)⁺ 475.2455, found 475.2454.



Compound 6c: 57 mg, 67% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.79–7.78 (m, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.42–7.39 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.28–7.23 (m, 2H), 4.11–4.07 (m, 4H), 2.67 (t, J = 7.8 Hz, 2H), 1.85–1.82 (m, 2H), 1.75–1.72 (m, 2H), 1.43–1.38 (m, 2H), 1.18 (t, J = 7.1 Hz, 6H), 1.09–1.03 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 171.7, 140.9, 138.4, 137.7, 133.1, 130.2, 130.1, 130.0, 128.5, 128.4, 125.3, 60.9, 57.3, 34.3, 33.3, 32.0, 26.1, 17.3, 14.3, 14.0; HRMS (ESI) calcd for $C_{26}H_{32}O_5$ ($M+Na$)⁺ 447.2142, found 447.2142.

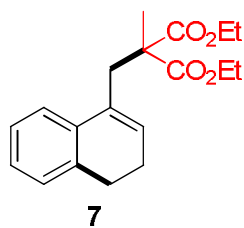


Compound 6d: 57 mg, 60% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.80–7.79 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45–7.40 (m, 3H), 7.31–7.25 (m, 3H), 7.18–7.17 (m, 3H), 6.95–6.93 (m, 2H), 4.09 (q, J = 7.1 Hz, 4H), 3.13 (s, 2H), 2.66 (t, J = 7.8 Hz, 2H), 1.76–1.73 (m, 2H), 1.58–1.52 (m, 2H), 1.17 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 171.0, 140.8, 138.5, 137.7, 136.0, 133.2, 130.2, 130.1, 129.8, 128.5, 128.4, 128.1, 126.7, 125.3, 61.1, 58.6, 37.7, 33.2, 31.3, 26.6, 13.9; HRMS (ESI) calcd for $C_{30}H_{32}O_5$ ($M+Na$)⁺ 495.2142, found 495.2138.



Compound 4a-d: 34 mg, 43% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.43–7.40 (m, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.28–7.23 (m, 2H), 4.11–4.07 (m, 4H), 2.66 (d, J = 7.8 Hz, 2H), 1.81 (d, J = 8.6 Hz, 2H), 1.50–1.46 (m, 1H), 1.30 (s, 3H), 1.18 (t, J = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.5, 172.2, 140.8, 138.4, 137.7, 133.2, 130.2, 130.1, 130.0, 128.5, 128.4, 125.3, 61.1, 53.4, 35.1, 33.2, 26.0 (t, J = 19.5 Hz), 19.7, 14.0; HRMS (ESI) calcd for $C_{24}H_{27}O_5D$ ($M+Na$)⁺ 420.1892, found

420.1893.



Compound 7: 32 mg, 10% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.27 (d, $J = 6.6$ Hz, 1H), 7.17–7.09 (m, 3H), 5.90 (t, $J = 4.6$ Hz, 1H), 4.08–4.01 (m, 4H), 3.13 (s, 2H), 2.68 (t, $J = 7.9$ Hz, 2H), 2.21–2.17 (m, 2H), 1.32 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 172.1, 136.6, 135.0, 132.1, 129.8, 127.5, 126.7, 126.0, 122.8, 61.1, 54.1, 36.4, 28.5, 23.2, 20.3, 13.9; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4(\text{M}+\text{Na})^+$ 339.1567, found 339.1565.

