Zirconocene-catalyzed sequential ethylcarboxylation of alkenes using ethylmagnesium chloride and carbon dioxide†

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1. General Comments

All the reactions were carried out using pre-dried screw capped tube with a Teflon-lined septum under N\textsubscript{2} atmosphere. Ethylmagnesium chloride was obtained from Alfa-aesar. All of the solvents were fresh distilled. Column chromatography was performed using silica gel (particle size 10-40 μm, Ocean Chemical Factory of Yantai, China). \(^{1}\text{H} \text{NMR and} \quad ^{13}\text{C} \text{NMR spectra were recorded using JEOL AL-300MHz or AL-400MHz spectrometer at ambient temperature with CDCl}_3 \text{ and} \quad d^6\text{-DMSO as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of CDCl}_3 \text{ (7.26) and} \quad d^6\text{-DMSO (2.50), to the carbon resonance of CDCl}_3 \text{ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, t, d, s referred to multiplet, triplet, doublet, and singlet. Mass spectra were obtained on a Bruker Esquire ion trap mass spectrometer in positive mode. The reaction progress was monitored by GC-MS if applicable.}
2. Experimental Section

General procedure for the synthesis of product 2

To a solution of Zirconocene dichloride (0.1 mmol) in THF (2 mL) was added EtMgCl (2.7 M THF solution, 3 mmol) at -78 °C. The solution was stirred at room temperature for 1 h, followed by the addition of styrene \( \mathbf{1} \) (1 mmol) via syringe at -78 °C. The mixture was stirred for 1 h at -78 °C, after which, it was warmed to room temperature and was stirred for 24 h. Then the reaction mixture was bubbled with CO\(_2\) for 30 minutes at room temperature. After completion, then H\(_2\)O (2 mL) was added to quench the reaction and the mixture was acidified till pH = 3~4 with HCl (2 M). Then the mixture was extracted with ethyl acetate (5 mL x 3), dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in vacuo, followed by purification on silica gel (petroleum ether/ethyl acetate = 5/1) to give the corresponding product \( \mathbf{2} \).

General procedure for the synthesis of product 3

To a solution of Zirconocene dichloride (0.1 mmol) in THF (2 mL) was added EtMgCl (2.7 M THF solution, 3 mmol) at -78 °C. The solution was stirred at room temperature for 1 h, followed by the addition of styrene \( \mathbf{1} \) (1 mmol) via syringe at -78 °C. The mixture was stirred for 1 h at -78 °C, after which, it was warmed to room temperature and was stirred for 24 h. Then the reaction mixture was bubbled with CO\(_2\) for 30 minutes at room temperature. After that, CuCl (3 mmol) was added and stirred at room temperature for 1 h, followed by the addition of allyl bromide (4 mmol). The mixture was stirred for further 3 h at rt. Then H\(_2\)O (2 mL) was added to quench the reaction and the mixture was extracted with ethyl acetate (5 mL x 3), dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in vacuo, followed by purification on silica gel (petroleum ether/ethyl acetate = 50/1) to give the corresponding product \( \mathbf{3} \).
3. NMR Data of Product

(2a)

2-Phenylpentanoic acid (2a): Colorless oil, 124.6 mg, Yield: 70%; \(^1\)H NMR (\(\text{d}^6\)-DMSO, 400 MHz): \(\delta\) 12.30 (s, 1H), 7.22-7.34 (m, 5H), 3.50 (t, \(J = 8\) Hz, 1H), 1.88-1.97 (m, 1H), 1.59-1.65 (m, 1 H), 1.15-1.27 (m, 2 H), 0.86 (t, \(J = 8\) Hz, 3H); \(^{13}\)C NMR (\(\text{d}^6\)-DMSO, 101 MHz): 14.2, 20.8, 35.7, 51.1, 127.4, 128.3, 128.9, 140.4, 175.4; IR (neat) \(\nu_{\text{max}}\) cm\(^{-1}\) 3027, 2957, 2930, 2872, 1713, 1601, 1495, 1454, 1200, 1178; GC-MS m/z: 178. HRMS (ESI) calcd for C\(_{11}\)H\(_{13}\)O\(_2\): 177.0916; found: 177.0911.

(2b)

2-(p-Tolyl)pentanoic acid (2b): Colorless oil, 144.0 mg, Yield: 75%; \(^1\)H NMR (\(\text{d}^6\)-DMSO, 400 MHz): \(\delta\) 12.22 (s, 1H), 7.16 (d, \(J = 8\) Hz, 2H), 7.11 (d, \(J = 8\) Hz, 2H), 3.44 (t, \(J = 8\) Hz, 1H), 2.26 (s, 3H), 1.85-1.92 (m, 1H), 1.54-1.61 (m, 1H), 1.17-1.23 (m, 2H), 0.85 (t, \(J = 8\) Hz, 3H) ppm; \(^{13}\)C NMR (\(\text{d}^6\)-DMSO, 101 MHz): 14.2, 20.7, 21.1, 35.7, 50.7, 128.2, 129.5, 136.4, 137.3, 175.5 ppm; IR (neat) \(\nu_{\text{max}}\) cm\(^{-1}\) 3020, 2955, 2922, 2870, 1703, 1512, 1447; GC-MS m/z: 192. HRMS (ESI) calcd for C\(_{12}\)H\(_{15}\)O\(_2\): 191.1072; found: 191.1075.

(2c)

2-(m-Tolyl)pentanoic acid (2c): Colorless oil, 115.2 mg, Yield: 60%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 11.47 (s, 1H), 7.06-7.22 (m, 4H), 3.51 (t, \(J = 8\) Hz, 1H), 2.33 (m, 3H), 1.99-2.08 (m, 1H), 1.70-1.79 (m, 1H), 1.25-1.33 (m, 2H), 0.90 (t, \(J = 8\) Hz, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): 13.9, 20.8, 21.5, 35.2, 51.4, 125.2, 128.3, 128.6, 128.9, 138.4, 138.6, 180.7 ppm; GC-MS m/z: 192. HRMS (ESI) calcd for C\(_{12}\)H\(_{15}\)O\(_2\): 191.1072; found: 191.1070.
2-(4-Isopropylphenyl)pentanoic acid (2d): Colorless oil, 173.8 mg, Yield: 79%; \( ^1 \)H NMR (\( d^6 \)-DMSO, 400 MHz) \( \delta \) 12.19 (s, 1H), 7.12-7.17 (m, 4H), 3.42 (t, \( J = 8 \) Hz, 1H), 2.77-2.84 (m, 1H), 1.83-1.92 (m, 1H), 1.52-1.61 (m, 1H), 1.11-1.23 (m, 8H), 0.82 (t, \( J = 8 \) Hz, 3H) ppm; \( ^{13} \)C NMR (\( d^6 \)-DMSO, 101 MHz): 14.2, 20.8, 24.4, 33.6, 35.7, 50.8, 126.8, 128.2, 137.7, 147.4, 175.5 ppm; GC-MS m/z: 220. HRMS (ESI) calcd for \( C_{14}H_{19}O_2 \): 219.1385; found: 219.1381.

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\text{(2d)}
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2-(4-(Tert-butyl)phenyl)pentanoic acid (2e): Colorless oil, 196.6 mg, Yield: 84%; \( ^1 \)H NMR (\( d^6 \)-DMSO, 400 MHz): \( \delta \) 12.23 (s, 1H), 7.33 (d, \( J = 8 \) Hz, 2H), 7.21 (d, \( J = 8 \) Hz, 2H), 3.46 (t, \( J = 8 \) Hz, 1H), 1.87-1.96 (m, 1H), 1.56-1.65 (m, 1H), 1.26, (s, 9H), 1.17-1.24 (m, 2H), 0.86 (t, \( J = 8 \) Hz, 3H) ppm; \( ^{13} \)C NMR (\( d^6 \)-DMSO, 101 MHz): 14.2, 20.8, 31.7, 34.6, 35.7, 50.7, 125.7, 127.9, 137.3, 149.6, 175.5 ppm; GC-MS m/z: 234. HRMS (ESI) calcd for \( C_{15}H_{21}O_2 \): 233.1542; found: 233.1539.

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\text{(2e)}
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2-(4-Methoxyphenyl)pentanoic acid (2f): White solid, m.p. 67-69 °C, 187.2 mg, Yield: 90%; \( ^1 \)H NMR (\( d^6 \)-DMSO, 400 MHz): \( \delta \) 12.20 (s, 1H), 7.20 (d, \( J = 8 \) Hz, 2H), 6.87 (d, \( J = 8 \) Hz, 2H), 3.72, (s, 3H), 3.43 (t, \( J = 8 \) Hz, 1H), 1.84-1.93 (m, 1H), 1.53-1.62 (m, 1H), 1.17-1.25 (m, 2H), 0.85 (t, \( J = 8 \) Hz, 3H) ppm; \( ^{13} \)C NMR (\( d^6 \)-DMSO, 101 MHz): 14.2, 20.7, 35.7, 50.2, 55.5, 114.3, 129.3, 132.3, 175.7 ppm; IR (neat) \( \nu_{\max } \) cm\(^{-1} \) 3031, 2958, 2933, 2873, 1703, 1610, 1584, 1512, 1464, 1249, 1178; GC-MS m/z: 208. HRMS (ESI) calcd for \( C_{12}H_{15}O_2 \): 207.1026.

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\text{(2f)}
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2-(3-Methoxyphenyl)pentanoic acid (2g): Colorless oil, 133.1 mg, Yield: 64%; \( ^1 \)H NMR (\( d^6 \)-DMSO, 400 MHz): \( \delta \) 12.29 (s, 1H), 7.23 (t, \( J = 8 \) Hz, 1H), 6.80-6.87 (m, 3H), 3.73, (s, 3H), 3.47 (t, \( J = 8 \) Hz, 1H), 1.85-1.95 (m, 1H), 1.56-1.64 (m, 1H), 1.16-1.27 (m, 2H), 0.86 (t, \( J = 8 \) Hz, 3H) ppm; \( ^{13} \)C NMR (\( d^6 \)-DMSO, 101 MHz): 14.2, 20.8, 35.7, 51.1, 55.5, 112.6,
114.2, 120.5, 130.0, 141.9, 159.8, 175.3 ppm; IR (neat) \( \nu_{\text{max}} \) cm\(^{-1} \): 3025, 2957, 2933, 2872, 1713, 1599, 1584, 1488, 1258, 1193; GC-MS m/z: 208. HRMS (ESI) calcd for \( \text{C}_{12}\text{H}_{15}\text{O}_2 \): 207.1021; found: 207.1024.

\[ \text{C} \quad \text{O} \quad \text{H} \quad \text{Et} \]

\[ \text{EtO} \quad \text{Me} \]

**2-(2-Methoxyphenyl)pentanoic acid (2h):** Colorless oil, 112.3 mg, Yield: 54%; \(^1\)H NMR (\(d_6\)-DMSO, 400 MHz): \( \delta \) 12.11 (s, 1H), 7.19-7.23 (m, 2H), 6.97 (d, \( J = 8 \) Hz, 1H), 6.91 (t, \( J = 8 \) Hz, 1H), 3.86 (t, \( J = 8 \) Hz, 1H), 3.76 (s, 3H), 1.83-1.92 (m, 1H), 1.53-1.62 (m, 1H), 1.13-1.26 (m, 2H), 0.84 (t, \( J = 8 \) Hz, 3H) ppm; \(^{13}\)C NMR (\(d_6\)-DMSO, 101 MHz): 14.3, 20.9, 34.6, 43.6, 56.0, 111.6, 120.9, 128.4, 128.4, 128.7, 157.1, 175.6 ppm; IR (neat) \( \nu_{\text{max}} \) cm\(^{-1} \): 3035, 2957, 2934, 2872, 2837, 1709, 1599, 1493, 1463, 1243, 1186; GC-MS m/z: 208. HRMS (ESI) calcd for \( \text{C}_{12}\text{H}_{15}\text{O}_2 \): 207.1021; found: 207.1018.

\[ \text{MeO} \quad \text{COOH} \quad \text{Et} \]

**2-(2,5-Dimethoxyphenyl)pentanoic acid (2i):** Colorless oil, 140.4 mg, Yield: 59%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 6.87 (d, \( J = 4 \) Hz, 1H), 6.74-6.82 (m, 2H), 4.01 (t, \( J = 8 \) Hz, 1H), 3.77, 3.75, 3.57, (s, 3H), 1.95-2.05 (m, 1H), 1.69-1.75 (m, 1H), 1.24-1.34 (m, 2H), 0.90 (t, \( J = 8 \) Hz, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): 14.0, 20.8, 34.2, 43.9, 55.8, 56.4, 112.1, 112.5, 114.9, 128.7, 151.4, 153.8, 180.3 ppm; IR (neat) \( \nu_{\text{max}} \) cm\(^{-1} \): 3020, 2957, 2933, 2872, 2835, 1702, 1591, 1498, 1464, 1226, 1178; GC-MS m/z: 238. HRMS (ESI) calcd for \( \text{C}_{13}\text{H}_{17}\text{O}_4 \): 237.1127; found: 237.1122.

\[ \text{O} \quad \text{O} \quad \text{Et} \]

**Allyl 2-(4-isopropylphenyl)pentanoate (3d):** Colorless oil, 174.3 mg, Yield: 67%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.15-7.24 (m, 4H), 5.82-5.90 (m, 1H), 5.16-5.24 (m, 2H), 4.50-4.61 (m, 2H), 3.56 (t, \( J = 8 \) Hz, 2H), 2.84-2.90 (m, 1H), 2.00-2.08 (m, 2H), 1.72-1.75 (m, 2H), 1.23 (d, \( J = 8 \) Hz, 6H), 0.91 (t, \( J = 8 \) Hz, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): 13.9, 20.9, 24.1, 33.8, 35.8, 51.2, 65.2, 118.0, 126.7, 127.9, 132.3, 136.6, 147.8, 174.1 ppm; IR (neat) \( \nu_{\text{max}} \) cm\(^{-1} \)
1 2959, 2927, 2872, 1735, 1511, 1461, 1156; GC-MS m/z: 260  HRMS (ESI Mode) calcd for C_{17}H_{24}O_{2}+H^+ 261.1855; found: 261.1859.

![Structure 2k](image)

### 3-Benzylpentanoic acid (2k):
- Colorless oil, 126.7 mg, Yield: 66%;
- $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ 12.07 (s, 1H), 7.29 (t, $J = 8$ Hz, 2H), 7.18 (t, $J = 8$ Hz, 3H), 2.50-2.60 (m, 2H), 2.06-2.18 (m, 2H), 1.95-2.01 (m, 1H), 1.24-1.32 (m, 1H), 0.86 (t, $J = 8$ Hz, 3H) ppm;
- $^{13}$C NMR ($d^6$-DMSO, 101 MHz): 11.2, 25.9, 38.1, 38.5, 126.4, 128.7, 129.6, 140.9, 174.6 ppm; GC-MS m/z: 192. HRMS (ESI-) calcd for C_{12}H_{15}O_{2} - 191.1072; found: 191.1069.

![Structure 2l](image)

### 3-Ethyl-5-phenylpentanoic acid (2l):
- Colorless oil, 152.4 mg, Yield: 74%;
- $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ 12.01 (s, 1H), 7.13 - 7.28 (m, 5H), 2.56 (t, $J = 8$ Hz, 2H), 2.15-2.25 (m, 2H), 1.70-1.77 (m, 2H), 1.50-1.59 (m, 2H), 1.30-1.41 (m, 2H), 0.84 (t, $J = 8$ Hz, 3H) ppm;
- $^{13}$C NMR ($d^6$-DMSO, 101 MHz): 11.1, 26.1, 32.8, 35.4, 36.0, 38.7, 126.1, 128.7, 128.8, 142.9, 174.7 ppm; IR (neat) $\nu_{\text{max}}$ cm$^{-1}$ 3026, 2961, 2928, 2875, 2859, 1706, 1603, 1496, 1454, 1251, 1192; GC-MS m/z: 206. HRMS (ESI-) calcd for C_{13}H_{17}O_{2} - 205.1229; found: 205.1226.

![Structure 2m](image)

### 3-Ethyl-6-phenylhexanoic acid (2m):
- Colorless oil, 114.4 mg, Yield: 52%;
- $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ 11.98 (s, 1H), 7.15 - 7.26 (m, 5H), 2.54 (t, $J = 8$ Hz, 2H), 2.12 (d, $J = 8$ Hz, 2H), 1.68-1.75 (m, 1H), 1.51-1.58 (m, 2H), 1.23-1.30 (m, 4H), 0.80 (t, $J = 8$ Hz, 6H) ppm;
- $^{13}$C NMR ($d^6$-DMSO, 101 MHz): 11.1, 26.3, 28.6, 33.0, 35.9, 36.1, 38.9, 126.1, 128.7, 128.8, 142.7, 174.8 ppm; GC-MS m/z: 220. HRMS (ESI-) calcd for C_{14}H_{19}O_{2} - 219.1385; found: 219.1381.

![Structure 2n](image)

### 3-Ethyl-5-(4-fluorophenyl)pentanoic acid (2n):
- Colorless oil, 164.0 mg, Yield: 73%;
- $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.10-7.14 (m, 2H), 6.93-6.97 (m, 2H), 2.54 (t, $J = 8$ Hz, 2H), 2.34-2.36 (m, 2H), 1.84-1.90 (m, 1H), 1.59-1.66 (m, 2H), 1.37-1.50 (m, 2H), 0.91 (t, $J = 8$ Hz, 2H), 0.87 (t, $J = 8$ Hz, 3H) ppm.

S7
Hz, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 101MHz): 10.8, 26.2, 32.3, 35.5, 36.0, 38.4, 115.2 (d, $J=21.1$ Hz), 129.7 (d, $J=7.7$ Hz), 138.0, (d, $J=2.9$ Hz), 161.3 (d, $J=243.3$ Hz), 180.0 ppm; IR (neat) $\nu_{\text{max}}$ cm$^{-1}$ 3030, 2962, 2927, 2878, 2862, 1703, 1601, 1509, 1458, 1220, 1157; GC-MS m/z: 224. HRMS (ESI$^-$) calcd for C$_{13}$H$_{16}$FO$_2$: 223.1134; found: 223.1138.

3-Ethylheptanoic acid (2o): Colorless oil, 86.9 mg, Yield: 55%; $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ 11.95 (s, 1H), 2.11 (d, $J=8$ Hz, 2H), 1.64-1.70 (m, 1H), 1.23-1.31 (m, 8H), 0.80-0.88 (m, 6H) ppm; $^{13}$C NMR ($d^6$-DMSO, 101 MHz): 11.2, 14.5, 22.9, 26.3, 28.7, 33.0, 36.2, 38.9, 39.4, 174.8 ppm; GC-MS m/z: 158. HRMS (ESI$^-$) calcd for C$_9$H$_{17}$O$_2$: 157.1229; found: 157.1225.

2-Propylheptanoic acid (2p): Colorless oil, 103.2 mg, Yield: 60%; $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ 11.96 (s, 1H), 2.11 (d, $J=4$ Hz, 2H), 1.65-1.70 (m, 1H), 1.23-1.31 (m, 10H), 0.80-0.87 (m, 6H) ppm; $^{13}$C NMR ($d^6$-DMSO, 101 MHz): 11.1, 14.4, 22.6, 26.2, 26.3, 32.1, 33.3, 36.2, 38.9, 174.8 ppm; GC-MS m/z: 172. HRMS (ESI$^-$) calcd for C$_{10}$H$_{19}$O$_2$: 171.1385; found: 171.1381.

3-Ethynonanoic acid (2q): Colorless oil, 145.1 mg, Yield: 78%; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.28 (d, $J=8$ Hz, 2H), 1.78-1.83 (m, 1H), 1.27-1.42 (m, 12H), 0.88 (t, $J=8$ Hz, 6H) ppm; $^{13}$C NMR (CDCl$_3$, 101 MHz): 10.8, 14.2, 22.7, 26.3, 26.6, 29.6, 31.9, 33.4, 36.3, 38.7, 180.6 ppm; IR (neat) $\nu_{\text{max}}$ cm$^{-1}$ 2959, 2925, 2857, 1705, 1190; GC-MS m/z: 186. HRMS (ESI$^-$) calcd for C$_{11}$H$_{21}$O$_2$: 185.1542; found: 185.1538.

3-(Cyclohexylmethyl)pentanoic acid (2r): Colorless oil, 104.9 mg, Yield: 53%; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 11.7 (s, 1H), 2.26 (t, $J=8$ Hz, 2H), 1.87-1.96 (m, 1H), 1.63-1.70 (m, 5H), 1.06-1.40 (m, 8H), 0.88 (t, $J=8$ Hz, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 101 MHz): 10.7, 26.4, 26.6, 26.8, 33.3, 33.6, 33.6, 34.9, 39.0, 41.6, 180.5 ppm; IR (neat) $\nu_{\text{max}}$ cm$^{-1}$ 2959, 2920, 1704, 1197; GC-MS m/z: 198. HRMS (ESI$^-$) calcd for C$_{12}$H$_{23}$O$_2$: 197.1542; found: 197.1547.
3-Ethyl-5-phenoxypentanoic acid (2s): Colorless oil, 182.0 mg, Yield: 82%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.24-7.28\) (m, 2H), \(6.87-6.94\) (m, 3H), \(4.00\) (t, \(J = 8\) Hz, 1H), \(2.39\) (d, \(J = 8\) Hz, 2H), \(2.04-2.10\) (m, 1H), \(1.77-1.90\) (m, 2H), \(1.41-1.50\) (m, 2H), \(0.93\) (t, \(J = 8\) Hz, 3H) ppm; \(^1^3\)C NMR (CDCl\(_3\), 101 MHz): \(10.9, 26.6, 32.8, 33.8, 38.5, 65.8, 114.5, 120.7, 129.5, 158.9, 179.9\) ppm; IR (neat) \(\nu_{\text{max}}\) cm\(^{-1}\): 3040, 2962, 2929, 1703, 1599, 1586, 1496, 1474, 1241, 1172; GC-MS m/z: 222. HRMS (ESI\(^+\)) calcd for C\(_{13}\)H\(_{17}\)O\(_3\): 221.1178; found: 221.1175.

Allyl 3-ethyl-5-(4-fluorophenyl)pentanoate (3n): Colorless oil, 163.8 mg, Yield: 62%; \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta 7.09-7.14\) (m, 2H), \(6.92-6.98\) (m, 2H), \(5.85-5.98\) (m, 1H), \(5.21-5.34\) (m, 2H), \(5.18\) (d, \(J = 6\) Hz, 2H), \(2.58\) (t, \(J = 9\) Hz, 2H), \(2.32-2.35\) (m, 2H), \(1.84-1.92\) (m, 1H), \(1.56-1.64\) (m, 2H), \(1.35-1.48\) (m, 2H), \(0.90\) (t, \(J = 6\) Hz, 3H) ppm; \(^1^3\)C NMR (CDCl\(_3\), 76 MHz): \(10.8, 26.3, 32.3, 35.5, 36.2, 38.6, 65.1, 115.1\) (d, \(J = 21.1\) Hz), \(118.3, 129.7\) (d, \(J = 7.7\) Hz), \(132.4, 138.1, 161.3\) (d, \(J = 243.2\) Hz), \(173.0\) ppm; IR (neat) \(\nu_{\text{max}}\) cm\(^{-1}\): 2962, 2930, 1733, 1601, 1509, 1458, 1220, 1156; GC-MS m/z: 264. HRMS (ESI Mode) calcd for C\(_{16}\)H\(_{21}\)FO\(_2\)\(^+\): 265.1604; found: 265.1600.
4. $^1$H NMR and $^{13}$C NMR Spectrum

$^1$H NMR for compound 2a

$^{13}$C NMR for compound 2a
$^1$H NMR for compound 2b

$^{13}$C NMR for compound 2b
$^{1}$H NMR for compound 2c

$^{13}$C NMR for compound 2c
$^{1}$H NMR for compound 2e

$^{13}$C NMR for compound 2e
\(^1\)H NMR for compound 2f

\(^1\)C NMR for compound 2f
$^1$H NMR for compound 2g

$^{13}$C NMR for compound 2g
**1H NMR for compound 2h**

**13C NMR for compound 2h**
$^1$H NMR for compound 2i

$^{13}$C NMR for compound 2i
$^1$H NMR for compound 3d

$^{13}$C NMR for compound 3d
$^1$H NMR for compound 21

$^{13}$C NMR for compound 21
\[^1\text{H} \text{NMR for compound 2m}\]

\[^{13}\text{C} \text{NMR for compound 2m}\]
\(^1\)H NMR for compound 2n

\(^13\)C NMR for compound 2n
$^{1}H$ NMR for compound 2o

$^{13}C$ NMR for compound 2o
$^1$H NMR for compound 2p

$^{13}$C NMR for compound 2p
$^{1}$H NMR for compound 2q

$^{13}$C NMR for compound 2q
$^1$H NMR for compound 2r

$^1$C NMR for compound 2r
$^1$H NMR for compound 2s

$^1$C NMR for compound 2s
\(^1\)H NMR for compound 3n

\(^1\)C NMR for compound 3n