

Supplementary Information

for

Native carboxyl group assisted C–H acetoxylation of hydrocinnamic and phenylacetic acids

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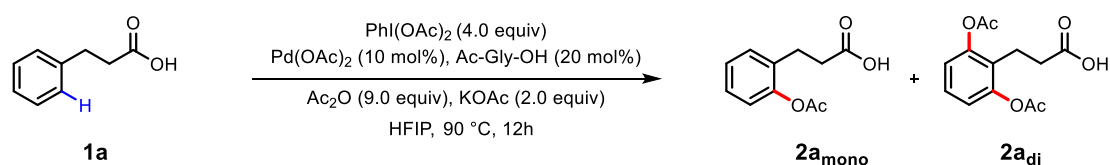
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1. General Information

Unless otherwise noted, commercially available reagents were purchased from commercial suppliers (such as Strem, Alfa Aesar, J&K Chemical Co, Energy Chemical, Sinocompound and Adamas) and used as received. Solvents were generally dried over 4 Å molecular sieves. Hexafluoroisopropanol (HFIP) was dried over 4 Å molecular sieves and distilled before use. The reaction vessels used for C–H functionalization were 15 mL sealed tube or 50 mL Schlenk tube (Synthware). Purification of products was performed by flash chromatography (FC) using silica gel or preparative thin layer chromatography. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz and 101 MHz, respectively). Chemical shifts are reported parts per million (ppm) referenced to CDCl_3 (δ 7.26 ppm) or MeOD (δ 3.10 ppm) or $(\text{CD}_3)_2\text{CO}$ (δ 2.05 ppm), tetramethylsilane (TMS, δ 0.00 ppm) for ^1H NMR; CDCl_3 (δ 77.16 ppm) or MeOD (δ 49.00 ppm) or $(\text{CD}_3)_2\text{CO}$ (δ 29.84 ppm, 206.26 ppm) for ^{13}C NMR. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptaplet, m = multiplet, and br = broad. To distinguish, some ^{13}C NMR chemical shifts retain two decimal places. High-resolution mass spectra (HRMS) were obtained on an Impact II UHR-TOF mass spectrometry equipped with an ESI source from Bruker at Fujian Institute of Research on the Structure of Matter.

2. Experimental Section

2.1 Optimization of reaction conditions substrate **1a**^a

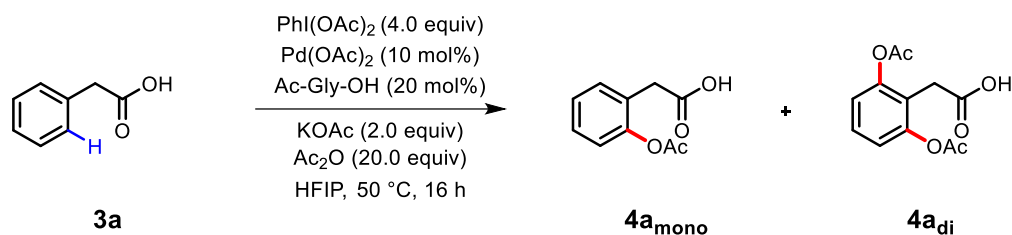


| Entry | Deviation from standard conditions | Yield(%) (mono/di) |
|-------|--|---------------------------|
| 1 | None | 72 [50, 22] |
| 2 | Ac_2O (0 equiv) | 47 [19, 28] |
| 3 | Ac_2O (3.0 equiv) | 60 [33, 27] |
| 4 | Ac_2O (6.0 equiv) | 64 [43, 21] |
| 5 | Ac_2O (12.0 equiv) | 62 [48, 14] |
| 6 | $\text{PhI}(\text{OAc})_2$ (1.0 equiv) | 45 [38, 7] |
| 7 | $\text{PhI}(\text{OAc})_2$ (2.0 equiv) | 57 [43, 14] |
| 8 | $\text{PhI}(\text{OAc})_2$ (3.0 equiv) | 63 [42, 21] |

| | | |
|----|--|-------------|
| 9 | PhI(OAc) ₂ (5.0 equiv) | 66 [52, 14] |
| 10 | KOPiv instead of KOAc | 60 [46, 14] |
| 11 | LiOAc instead of KOAc | 22 [22, 0] |
| 12 | NaOAc instead of KOAc | 55 [48, 7] |
| 13 | CsOAc instead of KOAc | 55 [41, 14] |
| 14 | K ₂ CO ₃ instead of KOAc | 60 [44, 16] |
| 15 | Without KOAc | 12 [12, 0] |
| 16 | 2-Hydroxy-5-bromopyridine instead of Ac-Gly-OH | 16 [16, 0] |
| 17 | 3-nitropyridin-2-ol instead of Ac-Gly-OH | 46 [39, 7] |
| 18 | 2-bromo-3-methylpyridine instead of Ac-Gly-OH | 35 [35, 0] |
| 19 | Fmoc-Gly-OH instead of Ac-Gly-OH | 61 [51, 10] |
| 20 | Ac-DL-Phe-OH instead of Ac-Gly-OH | 62 [53, 9] |
| 21 | Fmoc-L-Phe-OH instead of Ac-Gly-OH | 56 [49, 7] |
| 22 | Fmoc-L-Ile-OH instead of Ac-Gly-OH | 62 [51, 11] |
| 23 | Without Ac-Gly-OH | 57 [44, 13] |
| 24 | Pd(OAc) ₂ (5 mol%) Ac-Gly-OH (10 mol%) | 43 [34, 9] |
| 25 | Pd(OAc) ₂ (5 mol%) | 48 [36, 12] |
| 26 | HFIP 4 mL | 69 [33, 36] |
| 27 | TFE as solvent | 23 [23, 0] |
| 28 | <i>t</i> -BuOH as solvent | N.D. |
| 29 | 1,4-dioxane as solvent | N.D. |
| 30 | MeCN as solvent | N.D. |
| 31 | AcOH as solvent | 5 [5, 0] |
| 32 | 70 °C | 30 [30, 0] |
| 33 | 80 °C | 33 [28, 5] |
| 34 | 100 °C | 59 [46, 13] |
| 35 | 18 h | 64 [44, 20] |
| 36 | 24 h | 60 [42, 18] |

^a Reaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (10 mol %), Ac-Gly-OH (20 mol%), PhI(OAc)₂ (4.0 equiv), Ac₂O (9.0 equiv), HFIP (2 mL), 12 h, 90 °C. Yield was determined by ¹H NMR with CH₂Br₂ as internal standard.

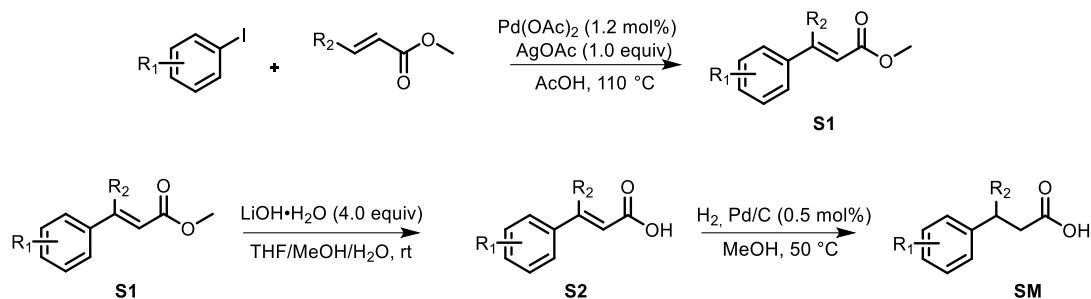
2.2 Optimization of reaction conditions substrate **3a**^a



| Entry | Deviation from standard conditions | Yield(%) (mono/di) |
|-------|--|---------------------------|
| 1 | None | 76 [55, 21] |
| 2 | Ac_2O (0 equiv) | 29 [0, 29] |
| 3 | Ac_2O (5.0 equiv) | 42 [0, 42] |
| 4 | Ac_2O (10.0 equiv) | 60 [15, 45] |
| 5 | Ac_2O (15.0 equiv) | 68 [36, 32] |
| 6 | Ac_2O (25.0 equiv) | 71 [55, 16] |
| 7 | PhI(OAc)_2 (2.0 equiv) | 66 [38, 28] |
| 8 | PhI(OAc)_2 (3.0 equiv) | 68 [42, 26] |
| 9 | PhI(OAc)_2 (5.0 equiv) | 74 [52, 22] |
| 10 | PhI(OAc)_2 (2.0 equiv); Ac_2O (10.0 equiv) | 46 [3, 43] |
| 11 | PhI(OAc)_2 (2.0 equiv); Ac_2O (15.0 equiv) | 48 [15, 33] |
| 12 | PhI(OAc)_2 (3.0 equiv); Ac_2O (10.0 equiv) | 50 [9, 41] |
| 13 | PhI(OAc)_2 (3.0 equiv); Ac_2O (15.0 equiv) | 62 [27, 35] |
| 14 | LiOAc instead of KOAc | 34 [34, 0] |
| 15 | NaOAc instead of KOAc | 52 [41, 11] |
| 16 | CsOAc instead of KOAc | 60 [44, 16] |

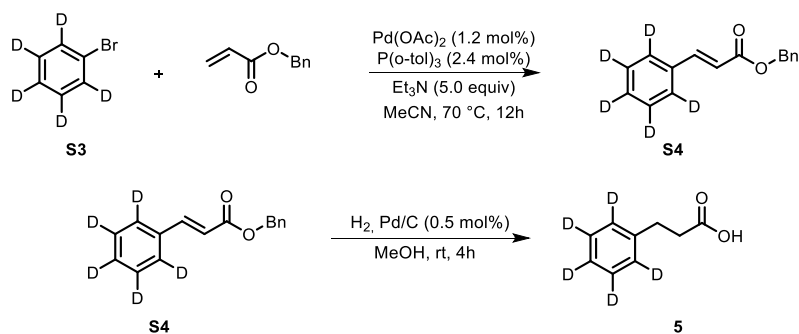
^a Reaction conditions: **3a** (0.2 mmol), Pd(OAc)_2 (10 mol %), Ac-Gly-OH (20 mol%), PhI(OAc)_2 (4.0 equiv), Ac_2O (20.0 equiv), HFIP (2 mL), 16 h, 50 °C. Yield was determined by ¹H NMR with CH_2Br_2 as internal standard.

2.3 General procedures for synthesis of substrates



To a stirred solution of silver acetate (5 mmol) and palladium acetate (0.06 mmol) in acetic acid (10 mL) was added iodobenzene (5 mmol) and ethyl acrylate (6 mmol). The resulting mixture was stirred at 110 °C for 6~12 h^[S1]. After being cooled to room temperature, the reaction mixture was diluted with 15 mL ethyl acetate. The reaction mixture was filtered over a pad of celite, and concentrated under reduced pressure to give the product **S1**. **S1** was then dissolved in a solution of THF (15 mL), EtOH (10 mL) and H₂O (5 mL). The solution was cooled to 0 °C and LiOH H₂O (4.0 equiv) was added. The mixture was stirred at room temperature for 2 h and then H₂O (10 mL) was added. The solution was extracted with Et₂O (20 mL × 2) and the aqueous phase was acidized with 2N HCl (20 mL). The aqueous phase was extracted with DCM (10 mL × 4). The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give compound **S2**. A mixture of **S2** and 60.0 mg of Pd/C (10%) was placed in flask under nitrogen before methanol (30 ml) was carefully added. The resulting suspension was evacuated and then refilled with hydrogen and equipped with a hydrogen balloon, and the reaction mixture was vigorously stirred at room temperature for 4h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography with petroleum ether (PE)/EtOAc (EA) (3/1) to give compound hydrocinnamic acids.

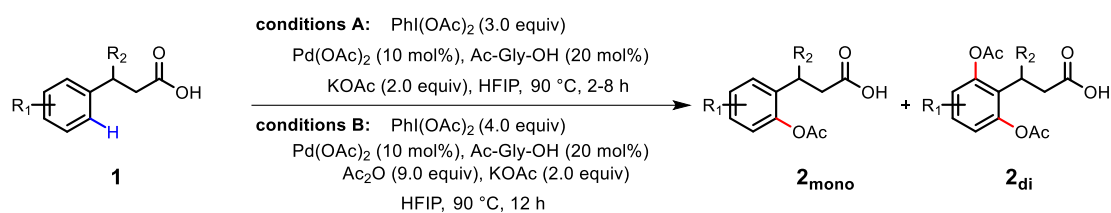
2.4 General procedures for synthesis of substrate 5



Pd(OAc)₂ (13.5 mg, 0.06 mmol), tri(o-tol)phosphine (36.5 mg, 0.12 mmol) and Et₃N (1.4 mL, 10 mmol) were added to a solution of **S3** (0.21 mL, 2.0 mmol) and benzyl acrylate (0.33 mL, 2.2 mmol) in anhydrous MeCN (10.0 mL). The mixture was stirred at 80 °C for 12 h and then cooled to room

temperature. H₂O (10 mL) was added and the aqueous phase was extracted with EA (5 mL × 3). The combined organic phase was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash silica gel chromatography with PE/EA (3/1) to afford **S4**. A mixture of **S4** and 10% palladium over activated charcoal (24.0 mg) was placed under nitrogen before methanol (10 ml) was carefully added. The resulting suspension was placed under vacuum, then under hydrogen (1 atm), and the reaction mixture was vigorously stirred at room temperature for 4h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography with petroleum ether (PE)/EtOAc (EA) (3/1) to give compound **5**.

2.5 General procedures for synthesis of products

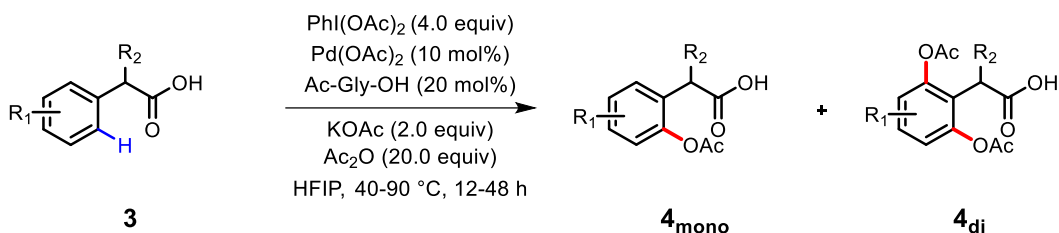


General procedure A

An oven-dried 15 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with compound **1a** (30.0 mg, 0.2 mmol, 1.0 equiv), PhI(OAc)₂ (193 mg, 0.6 mmol, 3.0 equiv), Pd(OAc)₂ (4.6 mg, 0.02 mmol, 10 mol %), ligand (Ac-Gly-OH, 4.7 mg 0.04 mmol, 20 mol %), KOAc (39.2 mg 0.4 mmol, 2.0 equiv) sequentially. HFIP (2.0 mL) was added to the mixture along the inside wall of the tube. The tube was then capped and placed into a preheated oil bath (90 °C) or hotplate (90 °C). [Note: good stirring was important for reproducibility, splashes on the wall of the tube showed adverse effects for the reaction]. The reaction vessel was then cooled to room temperature. Then a 3 N HCl solution (2 mL) was added, and the mixture was extracted with DCM (3 × 5 mL). The organic layers were combined and removed under reduced pressure. The resulting residue was purified by preparative TLC using PE/EA (4/1, with 1% HOAc) as the eluent.

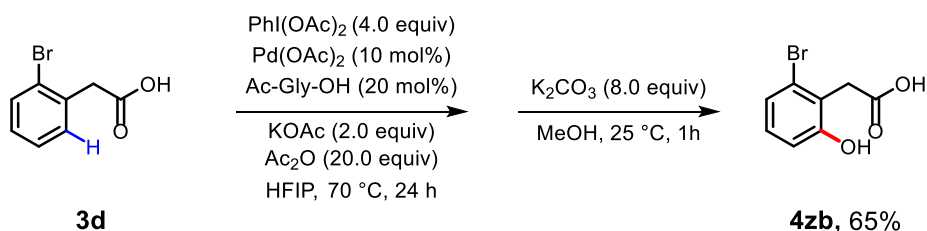
General procedure B

An oven-dried 15 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with compound **1a** (30.0 mg, 0.2 mmol, 1.0 equiv), PhI(OAc)₂ (257 mg, 0.8 mmol, 4.0 equiv), Pd(OAc)₂ (4.6 mg, 0.02 mmol, 10 mol %), ligand (Ac-Gly-OH, 4.7 mg 0.04 mmol, 20 mol %), KOAc (39.2 mg 0.4 mmol, 2.0 equiv) and Ac₂O (0.172 mL 9 equiv) sequentially. HFIP (2.0 mL) was added to the mixture along the inside wall of the tube. The tube was then capped and placed into a preheated oil bath (90 °C) or hotplate (90 °C). [Note: good stirring was important for reproducibility, splashes on the wall of the tube showed adverse effects for the reaction]. The reaction vessel was then cooled to room temperature. Then a 3 N HCl solution (2 mL) was added, and the mixture was extracted with DCM (3 × 5 mL). The organic layers were combined and removed under reduced pressure. The resulting residue was purified by preparative TLC using PE/EA (4/1, with 1% HOAc) as the eluent.



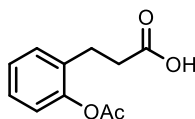
General procedure C

An oven-dried 15 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with compound **3a** (27.6 mg, 0.2 mmol, 1.0 equiv), PhI(OAc)_2 (257 mg, 0.8 mmol, 4.0 equiv), Pd(OAc)_2 (4.6 mg, 0.02 mmol, 10 mol %), ligand (Ac-Gly-OH , 4.7 mg 0.04 mmol, 20 mol %), KOAc (39.2 mg 0.4 mmol, 2.0 equiv) and Ac_2O (0.382 mL 20 equiv) sequentially. HFIP (2.0 mL) was added to the mixture along the inside wall of the tube. The tube was then capped and placed into a preheated oil bath (40- 90 °C) or hotplate (40- 90 °C). [Note: good stirring was important for reproducibility, splashes on the wall of the tube showed adverse effects for the reaction]. The reaction vessel was then cooled to room temperature. Then a 3 N HCl solution (2 mL) was added, and the mixture was extracted with DCM (3 × 5 mL). The organic layers were combined and removed under reduced pressure. The resulting residue was purified by preparative TLC using PE/EA (3/1, with 1% HOAc) as the eluent.



General procedure D

An oven-dried 15 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with compound **3d** (43.0 mg, 0.2 mmol, 1.0 equiv), PhI(OAc)_2 diacetate (257 mg, 0.8 mmol, 4.0 equiv), Pd(OAc)_2 (4.6 mg, 0.02 mmol, 10 mol %), ligand (Ac-Gly-OH , 4.7 mg 0.04 mmol, 20 mol %), KOAc (39.2 mg 0.4 mmol, 2.0 equiv) and Ac_2O (0.382 mL 20 equiv) sequentially. HFIP (2.0 mL) was added to the mixture along the inside wall of the tube. The tube was then capped and placed into a preheated hotplate (70 °C). [Note: good stirring was important for reproducibility, splashes on the wall of the tube showed adverse effects for the reaction]. Volatile matter was removed under reduced pressure and the residue was re-dissolved in methanol (2 mL). To the solution was added K_2CO_3 (219 mg, 1.6 mmol). The reaction was stirred at room temperature for 1 h. A 3.0 N HCl solution (1 mL) was then added, and the mixture was extracted with DCM (3 × 5 mL). The organic layers were combined and removed under reduced pressure. The resulting residue was purified by preparative TLC using PE/EA (2/1, with 1% HOAc) as the eluent.

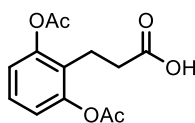


2a_{mono}

2a_{mono}: 3-(2-acetoxyphenyl)propanoic acid

The general procedure **A** was followed (2.5h). Pale yellow oil, 8.3 mg, 20% yield. The general procedure **B** was followed. Pale yellow oil, 20.0 mg, 48% yield.

¹H NMR (600 MHz, CDCl₃) δ 7.29 – 7.20 (m, 2H), 7.18 (td, *J* = 7.5, 1.3 Hz, 1H), 7.03 (dd, *J* = 7.9, 1.4 Hz, 1H). 2.86 (t, *J* = 7.9 Hz, 2H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 179.1, 169.7, 149.1, 132.1, 130.2, 127.9, 126.5, 122.6, 34.3, 25.3, 21.0. HRMS (ESI) *m/z* calcd for C₁₁H₁₂O₄Na⁺ (*M*+Na⁺) 231.0628, found 231.0628.

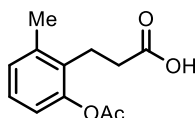


2a_{di}

2a_{di}: 3-(2,6-diacetoxyphenyl)propanoic acid

The general procedure **A** was followed (2.5h). Pale yellow oil, 18.4 mg, 36% yield. The general procedure **B** was followed. Pale yellow oil, 9.9 mg, 19% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.27 (t, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 178.8, 169.4, 149.9, 127.6, 125.4, 120.4, 33.3, 21.0, 20.2. HRMS (ESI) *m/z* calcd for C₁₃H₁₄O₆Na⁺ (*M*+Na⁺) 289.0683, found 289.0684.

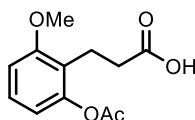


2b

2b: 3-(2-acetoxy-6-methylphenyl)propanoic acid

The general procedure **B** was followed. White solid, 25.3 mg, 57% yield, M. p.: 98.3-100.2 °C.

¹H NMR (400 MHz, MeOD) δ 7.17 – 7.08 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 2.86 (t, *J* = 8.7 Hz, 2H), 2.41 (t, *J* = 8.7 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H). ¹³C NMR (101 MHz, MeOD) δ 176.7, 171.6, 150.7, 139.3, 132.5, 129.0, 127.9, 121.3, 34.5, 23.5, 20.8, 19.4. HRMS (ESI) *m/z* calcd for C₁₂H₁₄O₄Na⁺ (*M*+Na⁺) 245.0784, found 245.0784.

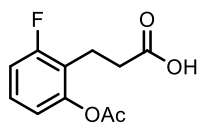


2c

2c: 3-(2-acetoxy-6-methoxyphenyl)propanoic acid

The general procedure **B** was followed. Pale yellow oil, 21.9 mg, 46% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.20 (t, $J = 8.2$ Hz, 1H), 6.76 (d, $J = 8.3$ Hz, 1H), 6.67 (d, $J = 8.1$ Hz, 1H), 3.83 (s, 3H), 2.87 (t, $J = 8.0$ Hz, 2H), 2.56 (t, $J = 8.0$ Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.5, 169.9, 158.6, 149.7, 127.6, 121.2, 114.8, 108.1, 55.8, 33.1, 21.0, 19.6. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{O}_5^-$ ($\text{M}-\text{H}^+$) 237.0768, found 237.0767.

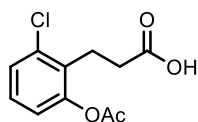


2d

2d: 3-(2-acetoxy-6-fluorophenyl)propanoic acid

The general procedure **A** was followed (4h, HFIP 4 mL). Pale yellow oil, 25.2 mg, 56% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.22 (td, $J = 8.3, 6.3$ Hz, 1H), 6.95 (ddd, $J = 9.4, 8.3, 1.1$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 2.90 (t, $J = 7.8$ Hz, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.8, 169.5, 161.8 (d, $J_{\text{C-F}} = 246.5$ Hz), 149.9 (d, $J_{\text{C-F}} = 7.4$ Hz), 128.0 (d, $J_{\text{C-F}} = 10.0$ Hz), 120.6 (d, $J_{\text{C-F}} = 18.5$ Hz), 118.5 (d, $J_{\text{C-F}} = 3.4$ Hz), 113.2 (d, $J_{\text{C-F}} = 22.3$ Hz), 33.4, 20.9, 19.0 (d, $J_{\text{C-F}} = 3.1$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -115.7. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 249.0534, found 249.0533.

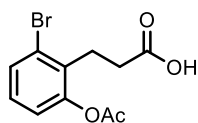


2e

2e: 3-(2-acetoxy-6-chlorophenyl)propanoic acid

The general procedure **A** was followed (3h). Pale yellow solid, 29.1 mg, 60% yield, M. p.: 98.2-100.1 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.28 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.19 (t, $J = 8.1$ Hz, 1H), 6.98 (dd, $J = 8.1, 1.3$ Hz, 1H), 3.02 (t, $J = 8.0$ Hz, 2H), 2.61 (t, $J = 8.0$ Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.8, 169.6, 149.9, 135.3, 130.9, 128.1, 127.5, 121.5, 32.7, 23.1, 21.0. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{ClO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 265.0238, found 265.0239.

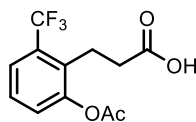


2f

2f: 3-(2-acetoxy-6-bromophenyl)propanoic acid

The general procedure **A** was followed (4h). Pale yellow solid, 37.2 mg, 65% yield, M. p.: 110.2-111.8 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.45 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.13 (t, $J = 8.1$ Hz, 1H), 7.02 (dd, $J = 8.2, 1.2$ Hz, 1H), 3.05 (t, $J = 8.0$ Hz, 2H), 2.61 (t, $J = 8.0$ Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.9, 169.6, 149.7, 132.5, 130.8, 128.6, 125.3, 122.1, 32.8, 25.7, 21.0. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 308.9733, found 308.9737.

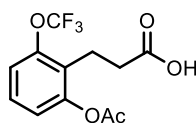


2g

2g: 3-(2-acetoxy-6-(trifluoromethyl)phenyl)propanoic acid

The general procedure **A** was followed (8h ,HFIP 4 mL). Pale yellow solid, 34.8 mg, 63% yield, M. p.: 65.7-67.3 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), δ 7.28 (d, *J* = 8.2 Hz, 1H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.7, 169.4, 150.3, 131.4, 130.52 (q, *J*_{C-F} = 30.3 Hz), 127.8, 126.7, 124.1 (q, *J*_{C-F} = 274.7 Hz), 124.02 (q, *J*_{C-F} = 5.7 Hz), 34.3, 22.4, 21.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -59.5. HRMS (ESI) *m/z* calcd for C₁₂H₁₁F₃O₄Na⁺ (M+Na⁺) 299.0502, found 299.0505.

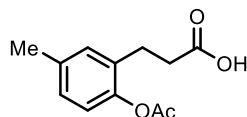


2h

2h: 3-(2-acetoxy-6-(trifluoromethoxy)phenyl)propanoic acid

The general procedure **A** was followed (4.5h ,HFIP 4 mL). Pale yellow oil, 36.2 mg, 62% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.28 (t, *J* = 8.3 Hz, 1H), 7.16 (dt, *J* = 8.4, 1.5 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.1 Hz, 1H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.7, 169.4, 150.1, 148.5 (d, *J*_{C-F} = 1.5 Hz), 128.0, 125.8, 121.2, 120.6 (q, *J*_{C-F} = 259.7 Hz), 117.9 (d, *J*_{C-F} = 1.7 Hz), 33.2, 21.0, 19.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.1. HRMS (ESI) *m/z* calcd for C₁₂H₁₁F₃O₅Na⁺ (M+Na⁺) 315.0451, found 315.0449.

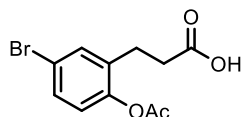


2i

2i: 3-(2-acetoxy-5-methylphenyl)propanoic acid

The general procedure **B** was followed. Pale yellow oil, 24.0 mg, 54% yield.

¹H NMR (400 MHz, MeOD) δ 7.11 (s, 1H), 7.03 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H). ¹³C NMR (101 MHz, MeOD) δ 176.5, 171.5, 148.2, 137.0, 133.6, 131.6, 129.0, 123.2, 35.4, 26.5, 20.9, 20.8. HRMS (ESI) *m/z* calcd for C₁₂H₁₄O₄Na⁺ (M+Na⁺) 245.0784, found 245.0783.

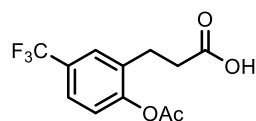


2j

2j: 3-(2-acetoxy-5-bromophenyl)propanoic acid

The general procedure **A** was followed (4h). Pale yellow solid, 23.1 mg, 40% yield, M. p.: 86.5-88.1 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.34 (m, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 2.83 (t, $J = 7.8$ Hz, 2H), 2.63 (t, $J = 7.8$ Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.4, 169.4, 148.1, 134.4, 133.1, 130.9, 124.4, 119.4, 34.0, 25.1, 21.0. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 308.9733, found 308.9737.

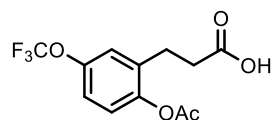


2k

2k: 3-(2-acetoxy-5-(trifluoromethyl)phenyl)propanoic acid

The general procedure **A** was followed (4h, HFIP 4 mL). Pale yellow solid, 29.1 mg, 53% yield, M. p.: 68.8-70.6 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.57 (m, 2H), 7.19 (d, $J = 8.2$ Hz, 1H), 2.92 (t, $J = 7.7$ Hz, 2H), 2.66 (t, $J = 7.7$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.50, 169.13, 151.56, 133.13, 128.62 (q, $J_{\text{C-F}} = 32.7$ Hz), 127.50 (q, $J_{\text{C-F}} = 3.8$ Hz), 125.11 (q, $J_{\text{C-F}} = 3.7$ Hz), 123.89 (q, $J_{\text{C-F}} = 273.2$ Hz), 123.31, 33.96, 25.26, 20.99. ^{19}F NMR (376 MHz, CDCl_3) δ -60.4. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 299.0502, found 299.0506.

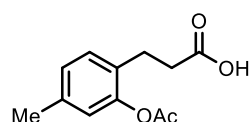


2l

2l: 3-(2-acetoxy-5-(trifluoromethoxy)phenyl)propanoic acid

The general procedure **A** was followed (4h, HFIP 4 mL). Pale yellow oil, 23.3 mg, 40% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.17 – 7.04 (m, 3H), 2.86 (t, $J = 7.7$ Hz, 2H), 2.64 (t, $J = 7.7$ Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.2, 169.4, 147.3, 146.8 (d, $J_{\text{C-F}} = 2.2$ Hz), 134.1, 123.9, 122.8, 120.7, 120.5 (q, $J_{\text{C-F}} = 258.6$ Hz), 33.9, 25.3, 21.0. ^{19}F NMR (376 MHz, CDCl_3) δ -58.0. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_5\text{Na}^+$ ($\text{M}+\text{Na}^+$) 315.0451, found 315.0448.

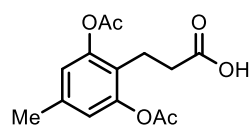


2m_{mono}

2m_{mono}: 3-(2-acetoxy-4-methylphenyl)propanoic acid

The general procedure **B** was followed. Pale yellow oil, 12.9 mg, 29% yield.

^1H NMR (400 MHz, MeOD) δ 7.17 (d, $J = 7.8$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.85 (s, 1H), 2.77 (t, $J = 7.6$ Hz, 2H), 2.51 (t, $J = 7.8$ Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, MeOD) δ 176.6, 171.4, 150.3, 138.8, 130.9, 130.8, 127.9, 124.0, 35.4, 26.20, 20.9, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 245.0784, found 245.0783.

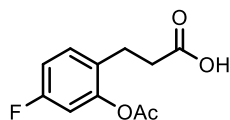


2m_{di}

2m_{di}: 3-(2,6-diacetoxy-4-methylphenyl)propanoic acid

The general procedure **B** was followed. Pale yellow solid, 13.0 mg, 23% yield, M. p.: 87.6-89.3 °C.

¹H NMR (400 MHz, MeOD) δ 6.82 (s, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 6H). ¹³C NMR (101 MHz, MeOD) δ 176.4, 171.1, 151.0, 139.1, 124.2, 122.0, 34.4, 21.1, 20.9, 20.7. HRMS (ESI) *m/z* calcd for C₁₄H₁₆O₆Na⁺ (M+Na⁺) 303.0839, found 303.0839.

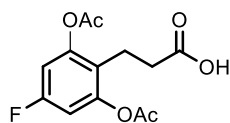


2n_{mono}

2n_{mono}: 3-(2-acetoxy-4-fluorophenyl)propanoic acid

The general procedure **A** was followed (2.5h). Pale yellow oil, 20.4 mg, 45% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, *J* = 8.2, 6.5 Hz, 1H), 6.91 (td, *J* = 8.3, 2.6 Hz, 1H), 6.83 (dd, *J* = 9.1, 2.6 Hz, 1H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.8, 169.2, 161.5 (d, *J*_{C-F} = 248.5 Hz), 149.5 (d, *J*_{C-F} = 10.7 Hz), 130.9 (d, *J*_{C-F} = 9.2 Hz), 127.9 (d, *J*_{C-F} = 3.7 Hz), 113.4 (d, *J*_{C-F} = 21.0 Hz), 110.5 (d, *J*_{C-F} = 24.3 Hz), 34.3, 24.8, 21.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.2. HRMS (ESI) *m/z* calcd for C₁₁H₁₁FO₄Na⁺ (M+Na⁺) 249.0534, found 249.0532.

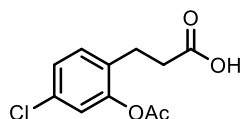


2n_{di}

2n_{di}: 3-(2,6-diacetoxy-4-fluorophenyl)propanoic acid

The general procedure **A** was followed (2.5h). Pale yellow solid, 10.3 mg, 18% yield, M. p.: 113.8-115.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 6.78 (d, *J* = 8.8 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.52 (m, *J* = 8.0 Hz, 2H), 2.33 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.6, 168.9, 159.7, 150.2 (d, *J*_{C-F} = 12.7 Hz), 121.3, 108.6 (d, *J*_{C-F} = 24.4 Hz), 33.2, 21.0, 19.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.1. HRMS (ESI) *m/z* calcd for C₁₃H₁₃FO₆Na⁺ (M+Na⁺) 307.0588, found 307.0581.

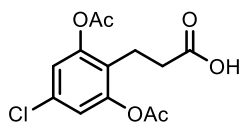


2o_{mono}

2o_{mono}: 3-(2-acetoxy-4-chlorophenyl)propanoic acid

The general procedure **A** was followed (3h). Pale yellow solid, 20.6 mg, 43% yield, M. p.: 85.7-87.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.17 (br s, 1H), 7.24 – 7.12 (m, 2H), 7.08 (s, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.8, 169.3, 149.3, 132., 131.0, 130.8, 126.6, 123.1, 34.2, 24.9, 20.9. HRMS (ESI) *m/z* calcd for C₁₁H₁₁ClO₄Na⁺ (M+Na⁺) 265.0238, found 265.0239.

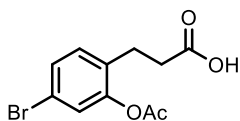


2o_{di}

2o_{di}: 3-(2,6-diacetoxy-4-chlorophenyl)propanoic acid

The general procedure **A** was followed (3h). Pale yellow solid, 16.5 mg, 28% yield, M. p.: 88.3-90.2 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.02 (s, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.51 (t, *J* = 7.8 Hz, 2H), 2.32 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 178.4, 169.0, 150.1, 132.7, 124.3, 121.1, 33.2, 20.9, 20.0. HRMS (ESI) *m/z* calcd for C₁₃H₁₃ClO₆Na⁺ (M+Na⁺) 323.0293, found 323.0291.

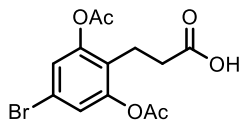


2p_{mono}

2p_{mono}: 3-(2-acetoxy-4-bromophenyl)propanoic acid

The general procedure **A** was followed (2.5h). Pale yellow solid, 22.3 mg, 39% yield, M. p.: 78.1-80.2 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.31 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.23 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.5, 169.2, 149.5, 131.4, 131.3, 129.6, 126.0, 120.33, 34.0, 24.9, 20.9. HRMS (ESI) *m/z* calcd for C₁₁H₁₁BrO₄Na⁺ (M+Na⁺) 308.9733, found 308.9735.

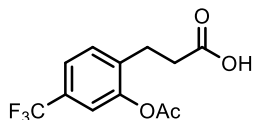


2p_{di}

2p_{di}: 3-(2,6-diacetoxy-4-bromophenyl)propanoic acid

The general procedure **A** was followed (2.5h). Pale yellow solid, 17.87 mg, 26% yield, M. p.: 85.6-87.3 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.17 (s, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.52 (t, *J* = 7.9 Hz, 2H), 2.32 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 178.3, 169.0, 150.2, 124.8, 123.9, 119.8, 33.0, 20.9, 20.0. HRMS (ESI) *m/z* calcd for C₁₃H₁₃BrO₆Na⁺ (M+Na⁺) 366.9788, found 366.9787.



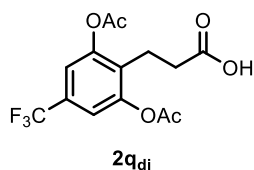
2q_{mono}

2q_{mono}: 3-(2-acetoxy-4-(trifluoromethyl)phenyl)propanoic acid

The general procedure **A** was followed (3h, HFIP 4 mL). Pale yellow solid, 22.8 mg, 41% yield, M. p.: 78.9-81.0 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ

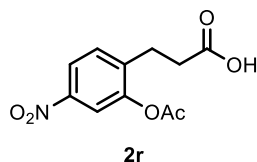
178.4, 169.2, 149.1, 136.4, 130.8, 130.3 (q, $J_{C-F} = 33.3$ Hz), 123.6 (q, $J_{C-F} = 273.7$ Hz), 123.2 (q, $J_{C-F} = 3.7$ Hz), 120.1 (q, $J_{C-F} = 3.7$ Hz), 33.8, 25.2, 20.9. ^{19}F NMR (376 MHz, CDCl_3) δ -62.5. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 299.0502, found 299.0506.



2q_{di}: 3-(2,6-diacetoxy-4-(trifluoromethyl)phenyl)propanoic acid

The general procedure **A** was followed (3h, HFIP 4 mL). Pale yellow solid, 18.8 mg, 28% yield, M. p.: 102.4-104.1 °C.

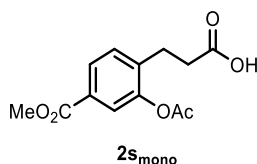
^1H NMR (400 MHz, CDCl_3) δ 7.27 (s, 2H), 2.84 (t, $J = 7.9$ Hz, 2H), 2.56 (t, $J = 7.8$ Hz, 2H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.9, 169.0, 150.1, 130.2 (q, $J_{C-F} = 273.7$ Hz), 129.7, 123.1 (q, $J_{C-F} = 273.7$ Hz), 117.7 (q, $J_{C-F} = 3.6$ Hz), 32.8, 20.9, 20.2. ^{19}F NMR (376 MHz, CDCl_3) δ -62.6. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{F}_3\text{O}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 357.0556, found 357.0554.



2r: 3-(2-acetoxy-4-nitrophenyl)propanoic acid

The general procedure **A** was followed (4.5h, HFIP 4 mL). Pale yellow solid, 22.3 mg, 44% yield, M. p.: 130.7-132.3 °C.

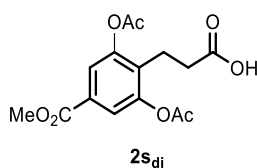
^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.3$ Hz, 1H), 7.97 (s, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 2.95 (t, $J = 7.7$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.8, 168.9, 149.1, 147.3, 140.0, 130.8, 121.3, 118.5, 33.5, 25.3, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 276.0479, found 276.0477.



2s_{mono}: 3-(2-acetoxy-4-(methoxycarbonyl)phenyl)propanoic acid

The general procedure **A** was followed (6h, HFIP 2 mL). Pale yellow oil, 23.7 mg, 45% yield,.

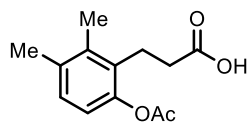
^1H NMR (400 MHz, CDCl_3) δ 7.86 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.72 (d, $J = 1.7$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 3.89 (s, 3H), 2.91 (t, $J = 7.7$ Hz, 2H), 2.65 (t, $J = 7.7$ Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.4, 169.4, 166.2, 148.9, 137.6, 130.2, 130.1, 127.6, 124.0, 52.4, 33.8, 25.4, 21.0. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 289.0683, found 289.0684.



2sai: 3-(2,6-diacetoxy-4-(methoxycarbonyl)phenyl)propanoic acid

The general procedure **A** was followed (6h, HFIP 2 mL). Pale yellow oil, 16.2 mg, 17.3% yield,.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (s, 1H), 3.89 (s, 2H), 2.84 (t, $J = 7.9$ Hz, 1H), 2.55 (t, $J = 7.9$ Hz, 1H), 2.35 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 177.7, 169.2, 165.4, 149.8, 130.8, 130.1, 121.7, 52.6, 32.85, 21.0, 20.4. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_8\text{Na}^+$ ($\text{M}+\text{Na}^+$) 347.0737, found 347.0737.

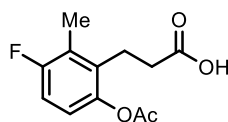


2t

2t: 3-(6-acetoxy-2,3-dimethylphenyl)propanoic acid

The general procedure **B** was followed (HFIP 4 mL). Pale yellow solid, 24.5 mg, 52% yield, M. p.: 58.4-60.2 $^{\circ}\text{C}$.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.06 (d, $J = 8.2$ Hz, 1H), 6.80 (d, $J = 8.2$ Hz, 1H), 2.92 (t, $J = 8.0$ Hz, 2H), 2.50 (t, $J = 8.0$ Hz, 2H), 2.33 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.8, 170.4, 147.4, 136.4, 135.1, 130.3, 128.9, 119.5, 33.7, 22.7, 21.1, 20.7, 15.6. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4^-$ ($\text{M}-\text{H}^+$) 235.0976, found 235.0974.

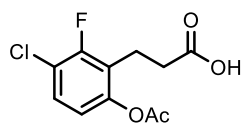


2u

2u: 3-(6-acetoxy-3-fluoro-2-methylphenyl)propanoic acid

The general procedure **A** was followed (3h, HFIP 4 mL). Pale yellow oil, 27.4 mg, 57% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.92 (d, $J = 8.9$ Hz, 1H), 6.85 (dd, $J = 8.9, 4.9$ Hz, 1H), 2.89 (t, $J = 7.9$ Hz, 2H), 2.51 (t, $J = 7.9$ Hz, 2H), 2.33 (s, 3H), 2.25 (d, $J = 2.4$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.5, 170.1, 159.1 (d, $J_{\text{C-F}} = 242.5$ Hz), 144.9 (d, $J_{\text{C-F}} = 2.8$ Hz), 132.7 (d, $J_{\text{C-F}} = 4.4$ Hz), 124.9 (d, $J_{\text{C-F}} = 17.6$ Hz), 120.9 (d, $J_{\text{C-F}} = 9.2$ Hz), 114.0 (d, $J_{\text{C-F}} = 25.4$ Hz), 33.3, 22.6 (d, $J_{\text{C-F}} = 2.2$ Hz), 20.9 (d, $J_{\text{C-F}} = 10.2$ Hz), 11.0 (d, $J_{\text{C-F}} = 5.5$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -117.7. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{FO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 263.0690, found 263.0692.

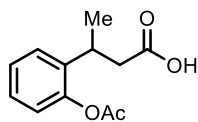


2v

2v: 3-(6-acetoxy-3-chloro-2-fluorophenyl)propanoic acid

The general procedure **A** was followed (4.5 h, HFIP 4 mL). Pale yellow solid, 26.4 mg, 51% yield, M. p.: 83.3-85.3 $^{\circ}\text{C}$.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.05 (d, $J = 8.5$ Hz, 1H), 6.97 (dd, $J = 8.9, 4.5$ Hz, 1H), 3.03 (t, $J = 8.1$ Hz, 2H), 2.61 (t, $J = 8.1$ Hz, 2H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.6, 169.7, 156.3 (d, $J_{\text{C-F}} = 247.0$ Hz), 145.2 (d, $J_{\text{C-F}} = 3.2$ Hz), 132.9, 122.2, 122.0 (d, $J_{\text{C-F}} = 8.1$ Hz), 114.8 (d, $J_{\text{C-F}} = 23.2$ Hz), 32.5, 23.2 (d, $J_{\text{C-F}} = 2.1$ Hz), 20.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -115.1. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{ClFO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 283.0144, found 283.0146.

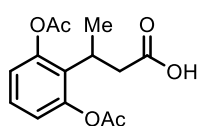


2w_{mono}

2w_{mono}: 3-(2-acetoxyphenyl)butanoic acid

The general procedure **A** was followed (2.5h). Pale yellow oil, 12.6 mg, 28% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 7.07 – 6.99 (m, 1H), 3.44 (dq, *J* = 13.3, 6.8 Hz, 1H), 2.66 (dd, *J* = 15.5, 5.8 Hz, 1H), 2.51 (dd, *J* = 15.5, 8.9 Hz, 1H), 2.34 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.0, 169.9, 148.2, 137.1, 127.5, 127.2, 126.6, 122.8, 41.8, 29.6, 21.1, 20.6. HRMS (ESI) *m/z* calcd for C₁₂H₁₄O₄Na⁺ (*M*+Na⁺) 245.0784, found 245.0785.

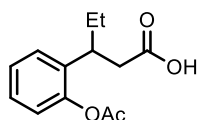


2w_{di}

2w_{di}: 3-(2,6-diacetoxyphenyl)butanoic acid

The general procedure **A** was followed (2.5h). Pale yellow solid, 13.5 mg, 24% yield, *M. p.*: 58.5-60.5 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.54 (dq, *J* = 13.7, 6.8 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.34 (s, 6H), 1.27 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.8, 169.4, 149.6, 129.2, 127.4, 121.0, 39.6, 27.5, 21.3, 19.1. HRMS (ESI) *m/z* calcd for C₁₄H₁₅O₆⁻ (*M*-H⁺) 279.0874, found 279.0874.

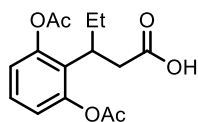


2x_{mono}

2x_{mono}: 3-(2-acetoxyphenyl)pentanoic acid

The general procedure **A** was followed (2.5h). Pale yellow oil, 17.4 mg, 37% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.17 (m, 3H), 7.07 – 7.00 (m, 1H), 3.32 – 3.17 (m, 1H), 2.59 (d, *J* = 7.3 Hz, 2H), 2.32 (s, 3H), 1.80 – 1.54 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.1, 169.8, 148.9, 135.4, 127.7, 127.4, 126.4, 122.8, 40.53, 36.6, 28.2, 21.1, 12.0. HRMS (ESI) *m/z* calcd for C₁₃H₁₅O₄⁻ (*M*-H⁺) 235.0976, found 235.0975.



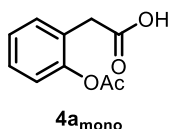
2x_{di}

2x_{di}: 3-(2,6-diacetoxyphenyl)pentanoic acid

The general procedure **A** was followed (2.5h). Pale yellow oil, 19.0 mg, 32% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.25 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.44 – 3.32 (m, 1H), 2.69 (dd, *J* = 7.1, 2.5 Hz, 2H), 2.32 (s, 6H), 1.74 – 1.54 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H). ¹³C

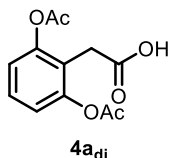
NMR (101 MHz, CDCl₃) δ 178.0, 169.3, 150.0, 127.5, 127.3, 120.9, 38.6, 34.7, 26.8, 21.2, 12.5.
HRMS (ESI) m/z calcd for C₁₅H₁₇O₆⁻ (M-H⁺) 293.1031, found 293.1031.



4a_{mono}: 2-(2-acetoxyphenyl)acetic acid

The general procedure C was followed (50 °C, 16h). Yellow oil, 20.5 mg, 53% yield.

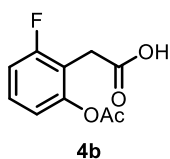
¹H NMR (600 MHz, CDCl₃) δ 7.44 – 7.28 (m, 2H), 7.22 (td, *J* = 7.4, 1.2 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 3.59 (s, 2H), 2.30 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 176.8, 169.4, 149.2, 131.6, 129.0, 126.4, 126.0, 122.7, 36.3, 21.0. HRMS (ESI) *m/z* calcd for C₁₀H₁₁O₄⁺ (M+H⁺) 195.0652, found 195.0645.



4a_{di}: 2-(2,6-diacetoxyphenyl)acetic acid

The general procedure C was followed (50 °C, 16h). Brown oil, 9.1 mg, 18% yield.

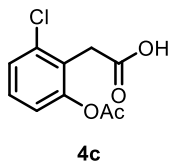
¹H NMR (600 MHz, CDCl₃) δ 7.34 (t, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.55 (s, 2H), 2.31 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 175.1, 169.0, 150.0, 128.6, 120.3, 119.5, 30.4, 21.0. HRMS (ESI) *m/z* calcd for C₁₂H₁₃O₆⁺ (M+H⁺) 253.0707, found 253.0707.



4b: 2-(2-acetoxy-6-fluorophenyl)acetic acid

The general procedure C was followed (70 °C, 24h). Brown oil, 33.4 mg, 79% yield.

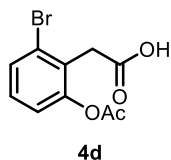
¹H NMR (400 MHz, CDCl₃) δ 9.37 (br s, 1H), 7.36 – 7.20 (m, 1H), 7.06 – 6.84 (m, 2H), 3.65 (s, 2H), 2.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 161.5 (d, *J*_{C-F} = 247.9 Hz), 150.1 (d, *J*_{C-F} = 6.4 Hz), 129.0 (d, *J*_{C-F} = 9.9 Hz), 118.3 (d, *J*_{C-F} = 3.4 Hz), 114.8 (d, *J*_{C-F} = 18.4 Hz), 113.1 (d, *J*_{C-F} = 22.2 Hz), 29.2, 20.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.6. HRMS (ESI) *m/z* calcd for C₁₀H₈FO₄⁻ (M-H⁺) 211.0412, found 211.0411.



4c: 2-(2-acetoxy-6-chlorophenyl)acetic acid

The general procedure C was followed (70 °C, 24h). Brown oil, 37.4 mg, 82% yield.

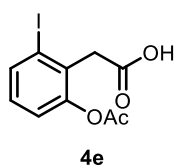
¹H NMR (400 MHz, CDCl₃) δ 9.81 (br s, 1H), 7.38 – 7.20 (m, 2H), 7.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.81 (s, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 150.2, 135.8, 129.0, 127.2, 125.3, 121.3, , 33.4, 20.9. HRMS (ESI) *m/z* calcd for C₁₀H₈ClO₄⁻ (M-H⁺) 227.0117, found 227.0117.



4d: 2-(2-acetoxy-6-bromophenyl)acetic acid

The general procedure **C** was followed (70 °C, 24h). Pale yellow solid, 42.0 mg, 77% yield, M. p.: 119.9-121.7 °C.

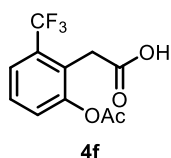
¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.84 (s, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.9, 168.92, 150.0, 130.5, 129.4, 127.0, 126.1, 122.0, 36.1, 20.9. HRMS (ESI) *m/z* calcd for C₁₀H₈BrO₄⁻ (M-H⁺) 272.9757, found 272.9759.



4e: 2-(2-acetoxy-6-iodophenyl)acetic acid

The general procedure **C** was followed (70 °C, 24h). White solid, 35.2 mg, 55% yield, M. p.: 125.5-127.5 °C.

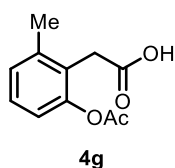
¹H NMR (400 MHz, CDCl₃) δ 7.75 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.12 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 2H), 2.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.0, 168.9, 149.1, 137.2, 130.2, 130.1, 122.9, 102.1, 41.1, 21.0. HRMS (ESI) *m/z* calcd for C₁₀H₁₀IO₄⁺ (M+H⁺) 320.9618, found 320.9617.



4f: 2-(2-acetoxy-6-(trifluoromethyl)phenyl)acetic acid

The general procedure **C** was followed (80 °C, 16h). Pale yellow solid, 39.6 mg, 76% yield, M. p.: 118.2-120.4 °C.

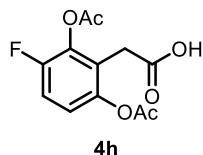
¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 7.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.0, 168.7, 150.5, 130.8 (q, *J*_{C-F} = 30.3 Hz), 128.6, 126.5, 124.8, 123.8 (q, *J*_{C-F} = 274.7 Hz), 123.6 (q, *J*_{C-F} = 5.6 Hz), 32.4, 20.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -59.6. HRMS (ESI) *m/z* calcd for C₁₁H₁₀F₃O₄⁺ (M+H⁺) 263.0537, found 263.0537.



4g: 2-(2-acetoxy-6-methylphenyl)acetic acid

The general procedure **C** was followed (50 °C 16h). White solid, 32.7 mg, 79% yield, M. p.: 84.6-86.7 °C.

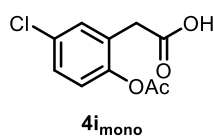
¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 3.62 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 169.5, 149.5, 139.1, 128.2, 128.1, 124.8, 120.2, 32.7, 21.0, 20.0. HRMS (ESI) *m/z* calcd for C₁₁H₁₁O₄⁻ (M-H⁺) 207.0663; found, 207.0664.



4h: 2-(2,6-diacetoxy-3-fluorophenyl)acetic acid

The general procedure **C** was followed (70 °C, 16h). Pale yellow solid, 32.3 mg, 60% yield, M. p.: 123.2-125.1 °C.

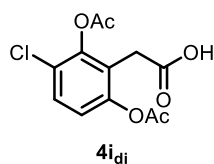
¹H NMR (400 MHz, CDCl₃) δ 7.12 (t, *J* = 9.1 Hz, 1H), 7.02 (dd, *J* = 9.1, 4.3 Hz, 1H), 3.54 (s, 2H), 2.33 (s, 3H), 2.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.2, 169.1, 167.6, 152.2 (d, *J*_{C-F} = 248.3 Hz), 145.2, 137.6 (d, *J*_{C-F} = 15.4 Hz), 121.9, 120.8 (d, *J*_{C-F} = 7.5 Hz), 115.6 (d, *J*_{C-F} = 20.3 Hz), 30.6, 20.8, 20.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -128.7. HRMS (ESI) *m/z* calcd for C₁₂H₁₂FO₆⁺ (M+H⁺) 271.0623, found 271.0617.



4i_{mono}: 2-(2-acetoxy-5-chlorophenyl)acetic acid

The general procedure **C** was followed (70 °C, 16h). White solid, 20.0 mg, 44% yield, M. p.: 98.8-100.3 °C.

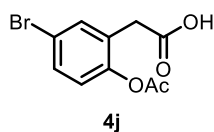
¹H NMR (400 MHz, CDCl₃) δ 8.03 (br s, 1H), 7.33 – 7.27 (m, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 3.55 (s, 2H), 2.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.9, 169.1, 147.7, 131.6, 131.4, 128.9, 127.7, 124.0, 36.0, 20.9. HRMS (ESI) *m/z* calcd for C₁₀H₁₀ClO₄⁺ (M+H⁺) 229.0262, found 229.0265.



4i_{di}: 2-(2,6-diacetoxy-5-chlorophenyl)acetic acid

The general procedure **C** was followed (70 °C, 16h). Pale yellow solid, 19.0 mg, 33% yield, M. p.: 93.5-95.1 °C.

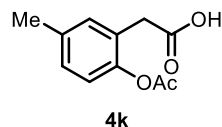
¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 3.54 (s, 2H), 2.36 (s, 3H), 2.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 167.9, 148.4, 146.6, 129.2, 125.0, 122.2, 121.3, 31.1, 20.9, 20.4. HRMS (ESI) *m/z* calcd for C₁₂H₁₂ClO₆⁺ (M+H⁺) 287.0317, found 287.0310.



4j: 2-(2-acetoxy-5-bromophenyl)acetic acid

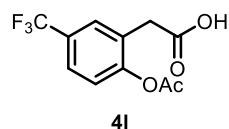
The general procedure **C** was followed (50 °C, 24h). Pale yellow solid, 41.3 mg, 76% yield, M. p.: 108.6-110.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.84 (s, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.1, 148.3, 134.3, 131.8, 128.2, 124.4, 119.2, 36.0, 20.9. HRMS (ESI) *m/z* calcd for C₁₀H₉BrO₄Na⁺ (*M*+Na⁺) 294.9576, found 294.9580.

**4k:** 2-(2-acetoxy-5-methylphenyl)acetic acid

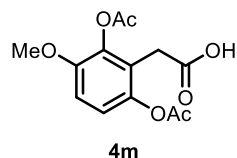
The general procedure **C** was followed (40 °C, 16h). Yellow oil, 33.5 mg, 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.12 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.54 (s, 2H), 2.33 (s, 3H), 2.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.0, 169.6, 146.9, 136.1, 132.1, 129.5, 125.6, 122.4, 36.3, 20.93, 20.90. HRMS (ESI) *m/z* calcd for C₁₁H₁₂O₄Na⁺ (*M*+Na⁺) 231.0628, found 231.0629.

**4l:** 2-(2-acetoxy-5-(trifluoromethyl)phenyl)acetic acid

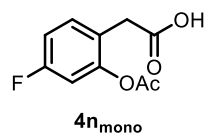
The general procedure **C** was followed (70 °C, 24h). White solid, 33.3 mg, 64% yield, M. p.: 108.8-110.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.60 (m, 2H), 7.36 – 7.17 (m, 1H), 3.65 (s, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.2, 168.7, 151.7, 128.8 (q, *J*_{C-F} = 3.8 Hz), 128.6, 126.9 (q, *J*_{C-F} = 21.7 Hz), 126.2 (q, *J*_{C-F} = 3.9 Hz), 123.8, 123.4 (q, *J*_{C-F} = 181.8 Hz), 36.1, 20.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3. HRMS (ESI) *m/z* calcd for C₁₁H₉F₃O₄Na⁺ (*M*+Na⁺) 285.0345, found 285.0346.

**4m:** 2-(2,6-diacetoxy-3-methoxyphenyl)acetic acid

The general procedure **C** was followed (50 °C, 24h). Yellow oil, 20.9 mg, 37% yield.

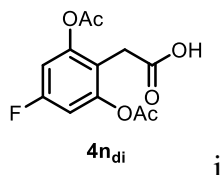
¹H NMR (400 MHz, CDCl₃) δ 7.88 (br s, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.50 (s, 2H), 2.30 (s, 3H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.3, 169.5, 168.4, 149.3, 142.6, 139.0, 121.0, 120.2, 111.3, 56.3, 30.7, 20.8, 20.4.

**4n_{mono}:** 2-(2-acetoxy-4-fluorophenyl)acetic acid

The general procedure **C** was followed (50 °C, 48h). Brown oil, 25.3 mg, 60% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.27 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.70- 6.788 (m, 2H), 3.55 (s, 2H), 2.29 (s,

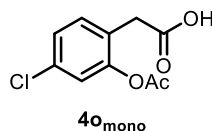
3H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 168.8, 162.2 (d, $J_{\text{C-F}} = 9.8$ Hz) 149.7 (d, $J_{\text{C-F}} = 10.7$ Hz), 132.2 (d, $J_{\text{C-F}} = 9.4$ Hz), 121.8 (d, $J_{\text{C-F}} = 3.7$ Hz), 113.4 (d, $J_{\text{C-F}} = 21.3$ Hz), 110.7 (d, $J_{\text{C-F}} = 24.6$ Hz), 35.6, 20.9. ^{19}F NMR (376 MHz, CDCl_3) δ -111.9. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{FO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 235.0377, found 235.0378.



4n_{di}: 2-(2,6-diacetoxy-4-fluorophenyl)acetic acid

The general procedure **C** was followed (50 $^{\circ}\text{C}$, 48h). White solid, 11.8 mg, 22% yield, M. p.: 117.7-119.9 $^{\circ}\text{C}$.

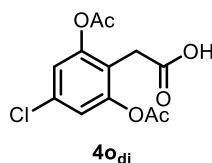
^1H NMR (400 MHz, CDCl_3) δ 6.85 (d, $J = 8.8$ Hz, 2H), 3.50 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 161.4 (d, $J_{\text{C-F}} = 248.3$ Hz), 150.3 (d, $J_{\text{C-F}} = 12.9$ Hz), 115.7, 108.5 (d, $J_{\text{C-F}} = 24.7$ Hz), 30.1, 20.9. ^{19}F NMR (376 MHz, CDCl_3) δ -110.4. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{FO}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 293.0432, found 293.0435.



4o_{mono}: 2-(2-acetoxy-4-chlorophenyl)acetic acid

The general procedure **C** was followed (50 $^{\circ}\text{C}$, 48h). Pale yellow solid, 25.5 mg, 56% yield, M. p.: 73.3-75.1 $^{\circ}\text{C}$.

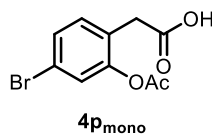
^1H NMR (400 MHz, CDCl_3) δ 7.35 (dd, $J = 8.2, 2.0$ Hz, 1H), 7.31 (s, 1H), 3.54 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 149.5, 134.0, 132.3, 126.6, 124.6, 123.3, 35.8, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{ClO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 251.0082, found 251.0082.



4o_{di}: 2-(2,6-diacetoxy-4-chlorophenyl)acetic acid

The general procedure **C** was followed (50 $^{\circ}\text{C}$, 48h). Pale yellow solid, 15.6 mg, 27% yield, M. p.: 135.8-137.7 $^{\circ}\text{C}$.

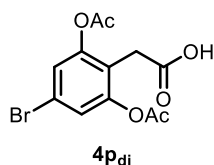
^1H NMR (400 MHz, CDCl_3) δ 7.10 (s, 2H), 3.51 (s, 2H), 2.29 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.4, 150.1, 133.7, 120.9, 118.3, 30.2, 20.8. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{10}\text{ClO}_6^-$ ($\text{M}-\text{H}^+$) 285.0171, found 285.0171.



4p_{mono}: 2-(2-acetoxy-4-bromophenyl)acetic acid

The general procedure **C** was followed (50 $^{\circ}\text{C}$, 48h). Pale yellow solid, 28.0 mg, 52% yield, M. p.: 80.6-82.0 $^{\circ}\text{C}$.

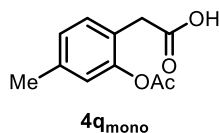
^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.29 (m, 2H), 7.19 (d, $J = 8.2$ Hz, 1H), 3.54 (s, 2H), 2.29 (s, 3H).
 ^{13}C NMR (101 MHz, CDCl_3) δ 176.4, 168.8, 149.6, 132.6, 129.5, 126.1, 125.1, 121.6, 35.8, 20.8.
HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_9\text{BrO}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 294.9576, found 294.9577.



4p_{di}: 2-(2,6-diacetoxy-4-bromophenyl)acetic acid

The general procedure C was followed (50 $^\circ\text{C}$, 48h). Pale yellow solid, 17.4 mg, 26% yield, M. p.: 156.4-158.7 $^\circ\text{C}$.

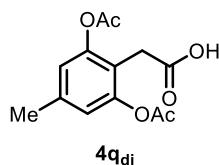
^1H NMR (400 MHz, CDCl_3) δ 7.25 (s, 2H), 3.50 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 175.2, 168.5, 150.2, 123.8, 120.9, 118.9, 30.3, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{BrO}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 352.9631, found 352.9633.



4q_{mono}: 2-(2-acetoxy-4-methylphenyl)acetic acid

The general procedure C was followed (40 $^\circ\text{C}$, 24h). Pale yellow oil, 23.6 mg, 57% yield.

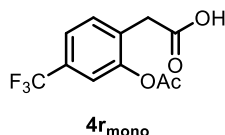
^1H NMR (400 MHz, MeOD) δ 7.20 (d, $J = 7.8$ Hz, 1H), 7.03 (d, $J = 8.6$ Hz, 1H), 6.91 (s, 1H), 3.49 (s, 2H), 2.33 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 174.9, 170.9, 150.5, 139.7, 132.2, 127.8, 125.6, 124.1, 36.8, 21.0, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{O}_4^-$ ($\text{M}-\text{H}^+$) 207.0663; found, 207.0662.



4q_{di}: 2-(2,6-diacetoxy-4-methylphenyl)acetic acid

The general procedure C was followed (40 $^\circ\text{C}$, 24h). Pale yellow solid, 12.6 mg, 24% yield.

^1H NMR (400 MHz, MeOD) δ 6.88 (s, 2H), 3.44 (s, 2H), 2.34 (s, 3H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, MeOD) δ 174.0, 170.6, 151.1, 139.7, 121.8, 119.07, 31.0, 21.1, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{O}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 289.0683, found 289.0683.

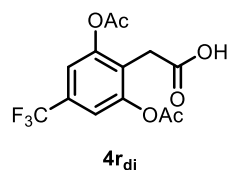


4r_{mono}: 2-(2-acetoxy-4-(trifluoromethyl)phenyl)acetic acid

The general procedure C was followed (60 $^\circ\text{C}$, 24h). White solid, 33.8 mg, 65% yield, M. p.: 111.4-113.1 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.43 (m, 2H), 7.42 (s, 1H), 3.65 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 149.3, 132.2, 131.4 (q, $J_{\text{C-F}} = 33.4$ Hz), 130.1, 123.5, (q, $J_{\text{C-F}} = 273.7$ Hz) 123.1 (q, $J_{\text{C-F}} = 3.6$ Hz), 120.2 (q, $J_{\text{C-F}} = 3.9$ Hz), 119.4, 36.1, 20.8. ^{19}F NMR (376 MHz, CDCl_3) δ

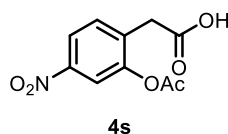
-62.6. HRMS (ESI) m/z calcd for $C_{11}H_9F_3O_4Na^+$ ($M+Na^+$) 285.0345, found 285.0346.



4r_{di}: 2-(2,6-diacetoxy-4-(trifluoromethyl)phenyl)acetic acid

The general procedure **C** was followed (60 °C, 24h). White solid, 8.4 mg, 13% yield, M. p.: 141.2-143.1 °C.

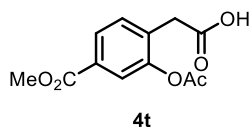
¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 2H), 3.59 (s, 2H), 2.32 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 174.7, 168.5, 150.2, 131.0 (q, J_{C-F} = 34.0 Hz), 123.6, 123.1 (q, J_{C-F} = 273.7 Hz), 117.6 (q, J_{C-F} = 3.8 Hz), 30.5, 20.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.8. HRMS (ESI) m/z calcd for $C_{13}H_{11}F_3O_6Na^+$ ($M+Na^+$) 343.0400, found 343.0401.



4s: 2-(2-acetoxy-4-nitrophenyl)acetic acid

The general procedure **C** was followed (70 °C, 24h). White solid, 21.1 mg, 44% yield, M. p.: 133.6-135.7 °C.

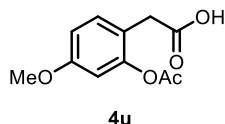
¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, J = 8.4, 2.3 Hz, 1H), 8.04 (d, J = 2.3 Hz, 1H), 7.51 (d, J = 4.0 Hz, 1H), 3.70 (s, 2H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.5, 168.5, 149.4, 148.0, 133.3, 132.2, 121.2, 118.5, 36.1, 20.8. HRMS (ESI) m/z calcd for $C_{10}H_9NO_6Na^+$ ($M+Na^+$) 262.0322, found 262.0322.



4t: 2-(2-acetoxy-4-(methoxycarbonyl)phenyl)acetic acid

The general procedure **C** was followed (50 °C, 16h). Pale yellow oil, 30.0 mg, 61% yield.

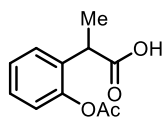
¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, J = 7.9, 1.7 Hz, 1H), 7.79 (d, J = 1.7 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.64 (s, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.1, 169.0, 166.1, 149.1, 131.1, 131.1, 131.0, 127.5, 124.0, 52.5, 36.3, 20.9 (d, J = 6.0 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{12}O_6Na^+$ ($M+Na^+$) 275.0526, found 275.0528.



4u: 2-(2-acetoxy-4-(methoxycarbonyl)phenyl)acetic acid

The general procedure **C** was followed (50 °C, 16h). Pale yellow oil, 12.5 mg, 28% yield.

¹H NMR (600 MHz, (CD₃)₂CO) δ 7.28 (d, J = 8.5 Hz, 1H), 6.80 (dd, J = 8.5, 2.7 Hz, 1H), 6.72 (d, J = 2.6 Hz, 1H), 3.78 (s, 3H), 3.48 (s, 2H), 2.25 (s, 3H). ¹³C NMR (151 MHz, (CD₃)₂CO) δ 172.4, 169.2, 160.4, 151.1, 132.6, 120.4, 112.2, 109.3, 55.8, 35.7, 20.8. HRMS (ESI) m/z calcd for $C_{11}H_{12}O_5Na^+$ ($M+Na^+$) 247.0577, found 247.0578.

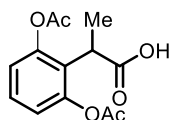


4v_{mono}

4v_{mono}: 2-(2-acetoxyphenyl)propanoic acid

The general procedure **C** was followed (50 °C, 16h). Pale yellow oil, 24.1 mg, 58% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.31 (td, *J* = 7.6, 1.7 Hz, 1H), 7.24 (td, *J* = 7.6, 1.6 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 180.0, 169.5, 148.4, 132.0, 128.7, 128.5, 126.5, 122.8, 39.7, 20.9, 17.1. HRMS (ESI) *m/z* calcd for C₁₁H₁₂O₄Na⁺ (*M*+Na⁺) 231.0628, found 231.0627.

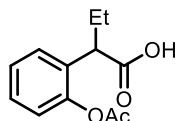


4t_{di}

4t_{di}: 2-(2,6-diacetoxyphenyl)propanoic acid

The general procedure **C** was followed (50 °C, 16h). Pale yellow solid, 16.0 mg, 30% yield, *M. p.*: 101.5-103.7 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 3.90 (q, *J* = 7.1 Hz, 1H), 2.28 (s, 6H), 1.35 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 178.5, 169.0, 149.0, 127.98, 125.9, 120.5, 36.0, 20.8, 15.6. HRMS (ESI) *m/z* calcd for C₁₃H₁₃O₆⁻ (*M*-H⁺) 265.0718, found, 265.0718.

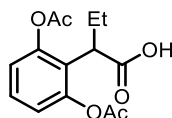


4w_{mono}

4w_{mono}: 2-(2-acetoxyphenyl)butanoic acid

The general procedure **C** was followed (50 °C, 16h). Pale yellow oil, 14.6 mg, 33% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.39 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.30 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 (td, *J* = 7.5, 1.4 Hz, 1H), 7.08 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.63 (t, *J* = 7.6 Hz, 1H), 2.31 (s, 3H), 2.17 – 2.02 (m, 1H), 1.87 – 1.70 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.6, 148.7, 130.6, 129.1, 128.5, 126.5, 122.9, 46.8, 25.2, 21.0, 12.2. HRMS (ESI) *m/z* calcd for C₁₂H₁₃O₄⁻ (*M*-H⁺) 221.0819; found, 221.0819.



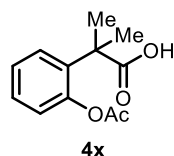
4w_{di}

4w_{di}: 2-(2,6-diacetoxyphenyl)butanoic acid

The general procedure **C** was followed (50 °C, 16h). Yellow solid, 35.3 mg, 63% yield, *M. p.*: 116.2-118.7 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.77 – 3.68 (m, 1H), 2.27 (s, 6H), 2.16 – 2.06 (m, 1H), 1.63 (dt, *J* = 13.8, 7.6 Hz, 1H), 0.82 (t, *J* = 7.5 Hz, 3H). ¹³C NMR

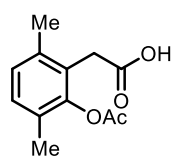
(101 MHz, CDCl₃) δ 178.1, 169.0, 149.4, 128.1, 124.3, 120.6, 43.2, 23.4, 20.9, 12.3. HRMS (ESI) m/z calcd for C₁₄H₁₅O₆⁻ (M-H⁺) 279.0874; found, 279.0874.



4x: 2-(2-acetoxyphenyl)-2-methylpropanoic acid

The general procedure C was followed (50 °C, 16h). White solid, 32.4 mg, 73% yield, M. p.: 122.1-124.0 °C.

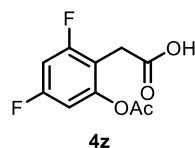
¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.35 – 7.28 (td, $J = 7.9, 2.0$ Hz, 1H), 7.28 – 7.21 (td, $J = 7.9, 1.2$ Hz, 1H), 7.14 (dd, $J = 7.9, 1.5$ Hz, 1H), 2.23 (s, 3H), 1.54 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 183.2, 169.1, 148.0, 136.1, 128.1, 126.2, 126.1, 123.3, 44.5, 25.9, 21.0. HRMS (ESI) m/z calcd for C₁₂H₁₄O₄Na⁺ (M+Na⁺) 245.0784, found 245.0785.



4y: 2-(2-acetoxy-3,6-dimethylphenyl)acetic acid

The general procedure C was followed (70 °C, 16h). White solid, 28.2 mg, 64% yield, M. p.: 128.2-130.4 °C.

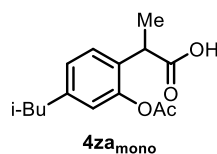
¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, $J = 7.8$ Hz, 1H), 7.02 (d, $J = 7.8$ Hz, 1H), 3.57 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.12 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.0, 169.1, 148.3, 136.4, 130.0, 128.1, 128.1, 125.0, 33.0, 20.6, 19.7, 16.4. HRMS (ESI) m/z calcd for C₁₂H₁₃O₄⁻ (M-H⁺) 221.0819; found, 221.0820.



4z: 2-(2-acetoxy-4,6-difluorophenyl)acetic acid

The general procedure C was followed (90 °C, 12h). Pale yellow solid, 20.7 mg, 45% yield, M. p.: 93.3-95.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.78 (br, 1H), 6.79 – 6.75 (m, 2H), 3.60 (s, 2H), 2.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.9, 168.4, 162.9 (dd, $J_{C-F} = 37.7, 14.9$ Hz), 160.5 (dd, $J_{C-F} = 37.4, 14.7$ Hz), 150.5 (dd, $J_{C-F} = 13.2, 8.5$ Hz), 110.9 (dd, $J_{C-F} = 18.9, 4.4$ Hz), 106.8 (dd, $J_{C-F} = 24.9, 4.0$ Hz), 101.9 (t, $J_{C-F} = 26.0$ Hz), 28.8 (d, $J_{C-F} = 3.2$ Hz), 20.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.4 (d, $J = 6.7$ Hz), -113.4 (d, $J = 7.2$ Hz). HRMS (ESI) m/z calcd for C₁₀H₇F₂O₄⁻ (M-H⁺) 229.0318; found, 229.0317.

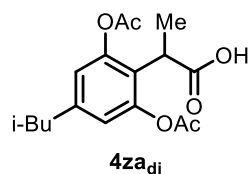


4za_{mono}: 2-(2-acetoxy-4-isobutylphenyl)propanoic acid

The general procedure C was followed (50 °C, 16h). Pale yellow oil, 16.5 mg, 31% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.87 (s, 1H), 3.80 (q, J

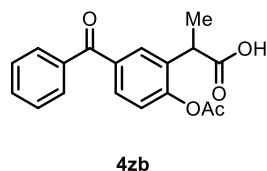
= 7.2 Hz, 1H), 2.45 (d, $J = 7.1$ Hz, 2H), 2.28 (s, 3H), 1.91 – 1.78 (m, 1H), 1.46 (d, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.9, 169.6, 148.1, 142.5, 129.1, 128.2, 127.4, 123.3, 45.0, 39.4, 30.2, 22.5, 21.0, 17.2. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}^+$) 287.1254, found 287.1250.



4za_{dii}: 2-(2,6-diacetoxy-4-isobutylphenyl)propanoic acid

The general procedure C was followed (50 °C, 16h). Pale yellow oil, 29.1 mg, 45% yield.

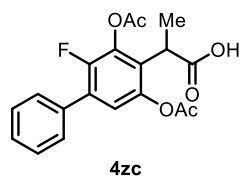
^1H NMR (400 MHz, CDCl_3) δ 6.81 (s, 2H), 3.83 (q, $J = 7.1$ Hz, 1H), 2.45 (d, $J = 7.1$ Hz, 2H), 2.26 (s, 6H), 1.84 (dt, $J = 13.5, 6.8$ Hz, 1H), 1.33 (d, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.7, 169.2 (d, $J = 1.6$ Hz), 148.7, 142.4, 123.0, 121.2, 44.9, 36.0, 30.0, 22.4 (d, $J = 1.6$ Hz), 20.9, 15.7. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_6\text{Na}^+$ ($\text{M}+\text{Na}^+$) 345.1309, found 345.1309.



4zb: 2-(2-acetoxy-5-benzoylphenyl)propanoic acid

The general procedure C was followed (70 °C, 24h). Pale yellow oil, 43.3 mg, 69% yield.

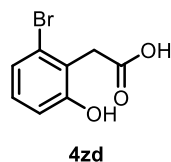
^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.79 (dd, $J = 8.1, 1.3$ Hz, 2H), 7.74 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 1H), 3.93 (q, $J = 7.2$ Hz, 1H), 2.33 (s, 3H), 1.53 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.6, 179.4, 168.8, 151.7, 137.3, 135.5, 132.7, 132.4, 131.0, 130.6, 130.1, 128.5, 122.8, 39.9, 20.9, 16.9. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5^-$ ($\text{M}-\text{H}^+$) 311.0925; found, 311.0918.



4zc: 2-(3,5-diacetoxy-2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid

The general procedure C was followed (70 °C, 16h). Yellow oil, 44.2 mg, 61% yield.

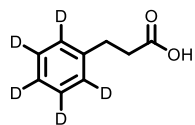
^1H NMR (400 MHz, CDCl_3) δ 7.82 (br, 1H), 7.57 – 7.49 (m, 2H), 7.48 – 7.35 (m, 3H), 7.14 (d, $J = 6.3$ Hz, 1H), 3.94 (q, $J = 7.1$ Hz, 1H), 2.32 (d, $J = 19.6$ Hz, 6H), 1.41 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.1, 169.2, 167.8, 149.5 (d, $J_{\text{C-F}} = 250.5$ Hz), 144.0 (d, $J_{\text{C-F}} = 3.5$ Hz), 137.4 (d, $J_{\text{C-F}} = 16.1$ Hz), 134.0, 129.3 (d, $J_{\text{C-F}} = 13.4$ Hz), 129.1 (d, $J_{\text{C-F}} = 2.8$ Hz), 128.7, 128.5, 127.0, 121.8 (d, $J_{\text{C-F}} = 3.4$ Hz), 36.4, 20.8, 20.2, 15.6. ^{19}F NMR (376 MHz, CDCl_3) δ -133.6. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{FO}_6^-$ ($\text{M}-\text{H}^+$) 359.0936; found, 359.0936.



4zd: 2-(2-bromo-6-hydroxyphenyl)acetic acid

The general procedure **D** was followed. White solid, 29.9 mg, 65% yield, M. p.: 130.1-132.1 °C.

¹H NMR (400 MHz, MeOD) δ 7.04 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 2H). ¹³C NMR (101 MHz, MeOD) δ 173.7, 156.9, 128.7, 125.7, 123.0, 122.2, 113.7, 34.9.



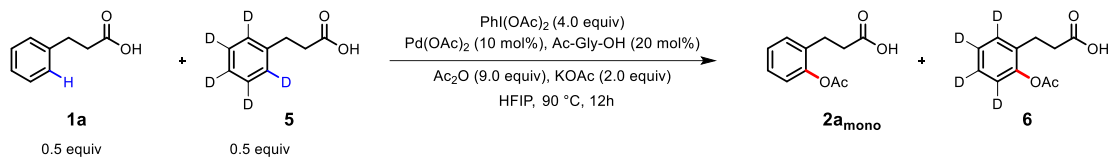
5

5: 3-(phenyl-d5)propanoic acid

¹H NMR (600 MHz, CDCl₃) δ 2.97 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H).

2.6 Mechanistic studies

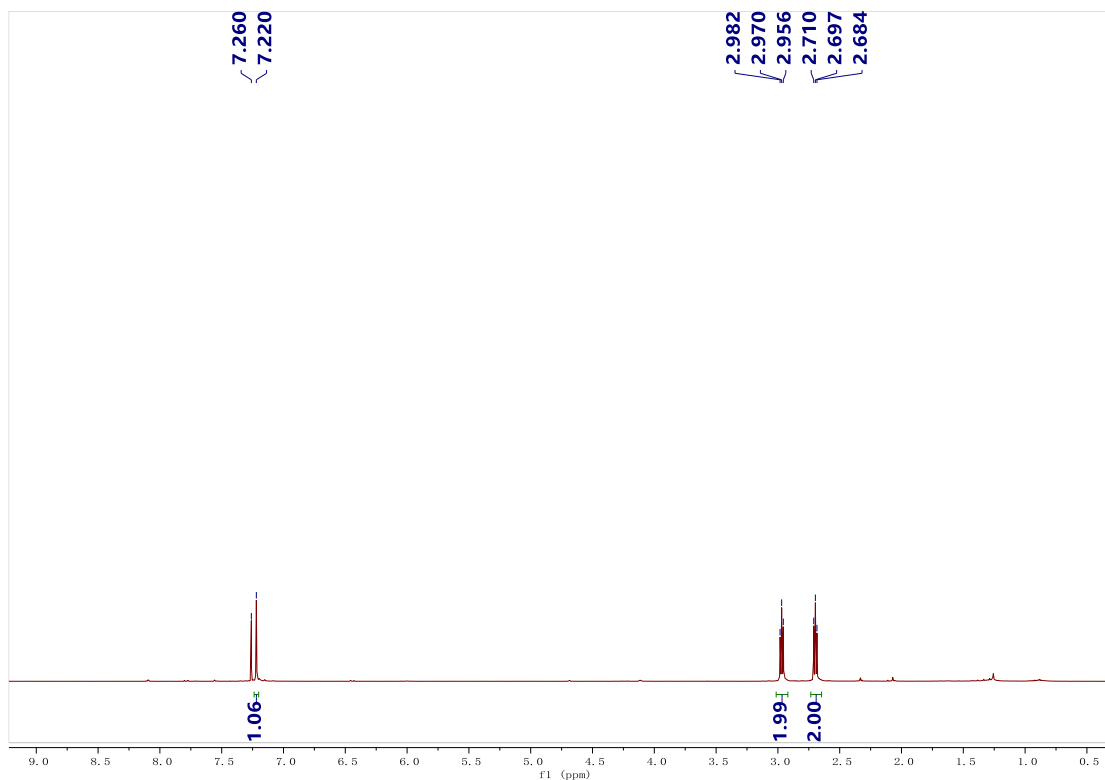
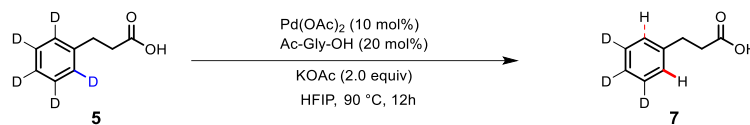
Results from the kinetic isotope experiments with 1a and 5a:

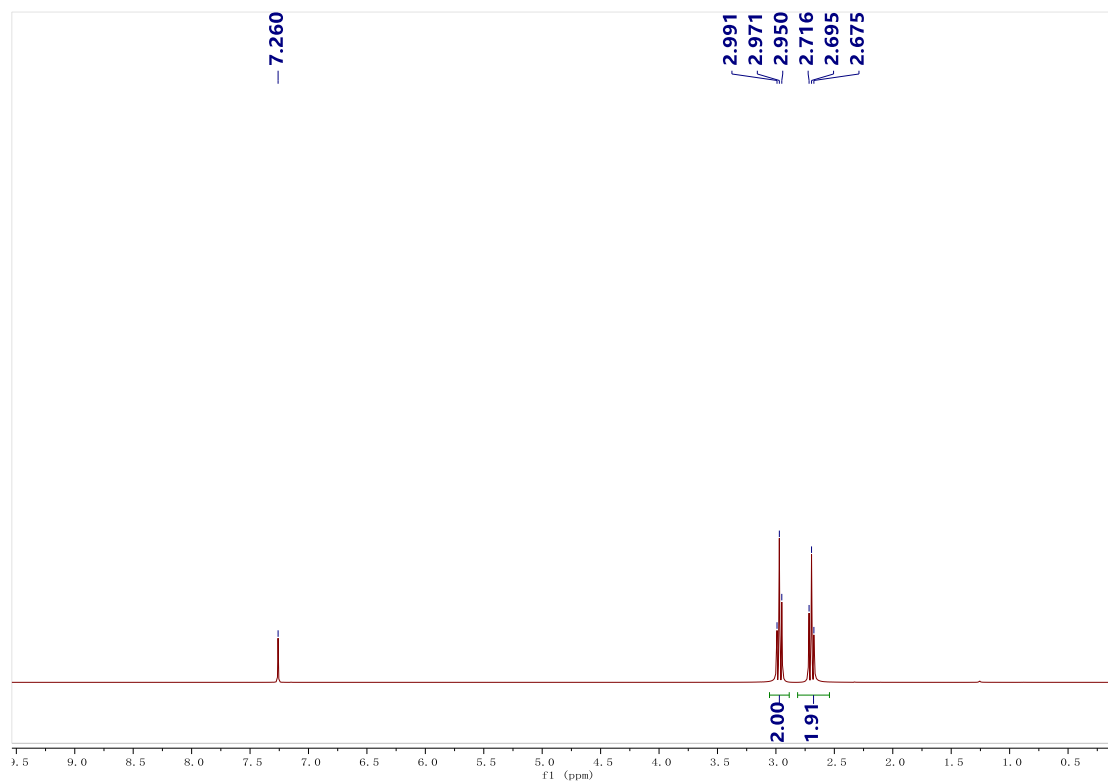
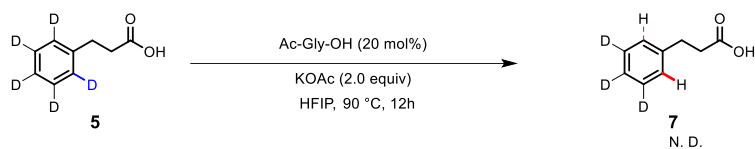


| Entry ^a | Time (min) | % Conv. 2a | % Conv. 2y | k_{H} ([M]/min) | k_{D} ([M]/min) | $k_{\text{H}}/k_{\text{D}}$ |
|--------------------|------------|-------------------|-------------------|--------------------------|--------------------------|-----------------------------|
| 1 | 60 | 20.0 | 6.7 | 3.3×10^{-4} | 1.1×10^{-4} | 2.99 |
| 2 | 60 | 19.0 | 5.7 | 3.2×10^{-4} | 9.5×10^{-5} | 3.33 |
| 3 | 60 | 18.4 | 5.7 | 3.3×10^{-4} | 9.5×10^{-5} | 3.23 |
| Average | | | | | | 3.18 |

^a The conversion was determined by ¹H NMR analysis of the crude reaction mixture, as discussed in the preceding section.

Results from the reversibility experiments of 5:





3. References

¹H Daichao Xu; Chunxin Lu; Wanzhi Chen. *Tetrahedron Lett.* **2012**, 68, 1466.

4. NMR Spectra of Compounds

