Supporting Information

Protection of COOH and OH Groups in Acid, Base and Salt Free Reactions

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Materials and methods

All reactions were carried out under an atmosphere of air in glassware with magnetic stirring unless otherwise indicated. Commercially purchased reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC data were recorded on Thermo TRACE 1300. GC-MS data were recorded on Thermo ISQ QD. $^1$H and $^{13}$C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for $^1$H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity (m), coupling constant (Hz), and integration. Data for $^{13}$C NMR spectra are reported relative to chloroform as an internal standard (77.23 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Thermo Finnigan Impact II UHR-TOF. Melting point was obtained from Shanghai Shengguang SGW X-4.
General procedure

General procedure A for Table 1: Catalyst, benzoic acid (0.4 mmol, 1.0 equiv.), and MTBE (1.0 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 °C for 8 hours. The mixture was filtered by a short silica gel column (about 3 g) or a short activated carbon column (about 2 g), which was washed by EA (10 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product 3a could be detected by GC analysis.

General procedure B for Table 2: Fe(OTf)₃ (0.05 mmol, 1 mol%), carboxylic acid 1 (5.0 mmol, 1.0 equiv.), and MTBE 2 (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 °C for 48 hours. The mixture was filtered by a short silica gel column (about 5 g) or a short activated carbon column (about 3 g), which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and products 3 were attained directly without further purification.

General procedure C for Table 2: Fe(OTf)₃ (0.01 mmol, 0.1 mol%), phenol 4 (10 mmol, 1.0 equiv.) and IPA 5 (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature for 5 hours. The mixture was filtered by a short silica gel column (about 5 g) or a short activated carbon column (about 2 g), which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and products 6 were attained directly without further purification.

General procedure D for Table 3: Fe(OTf)₃ (0.025 mmol, 0.5 mol%), alcohol 4 (5 mmol, 1.0 equiv.) and IPA 5 (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature for 5 hours. The solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel to give the product 6.
Efficiency of catalyst

Figure S1:

![Reaction Scheme](image)

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$^a$ Reaction conditions: benzoic acid 1a (20 mmol, 1 equiv), MTBE, 48 h. $^b$ Yields of product 3a were determined by GC analysis with 1,4-dimethoxybenzene as the internal standard.

**General procedure for Figure S1:** Fe(OTf)$_3$, benzoic acid 1a (20.0 mmol, 1.0 equiv.), and MTBE 2 were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 °C for 48 hours. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product methyl benzoate 3a could be detected by GC analysis.
Figure S2:

![Chemical Reaction Diagram]

### General Procedure for Figure S2:

Fe(O Tf)$_3$, phenol 4a (20 mmol, 1.0 equiv) and IPA 5 were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product methyl benzoate 6a could be detected by $^1$H NMR.

### Table

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$^a$ Reaction conditions: phenol 4a (20 mmol, 1 equiv), IPA 5, room temperature. $^b$ Yields of product 6a were determined by $^1$H NMR analysis with 1,4-dimethoxybenzene as the internal standard. $^c$ Phenol 4a (1 mmol, 1 equiv), IPA 5 (2.5 mL), room temperature, 24 h.
Characterization data for the products

3b

Following the general procedure B (967.5 mg, 90% yield, a pale yellow solid (m.p.: 75.1-75.6 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 7.7$ Hz, 2H), 7.58 (d, $J = 6.8$ Hz, 2H), 3.91 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.36, 131.71, 131.11, 166.96, 141.32, 135.07, 132.66, 130.95, 127.90, 94.10, 52.52.

3c

Following the general procedure B (2.0 mmol, Fe(OTf)$_3$ (5 mol %), MTBE (2.0 mL), 445.4 mg, 85% yield, product 3c was chromatographed on silica gel as a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 7.9$ Hz, 1H), 7.80 (d, $J = 7.7$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.15 (t, $J = 8.4$ Hz, 1H), 3.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.96, 141.32, 135.07, 132.66, 130.95, 127.90, 94.10, 52.52.

3d

Following the general procedure B (853.6 mg, 88% yield, a white solid (m.p.: 64.0-64.6 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.68 (t, $J = 1.8$ Hz, 1H), 8.22 (dd, $J = 7.8, 1.8$ Hz, 2H), 7.53 (t, $J = 7.8$ Hz, 1H), 3.95 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.18, 133.76, 130.67, 130.56, 128.59, 52.33.

3e

Following the general procedure B (2.0 mmol, Fe(OTf)$_3$ (5 mol %), MTBE (2.0 mL), 333.1 mg, 92% yield, product 3e was chromatographed on silica gel as a white solid (m.p.: 91.5-92.2 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.29 (d, $J = 6.2$ Hz, 2H), 8.22 (d,
$J = 6.3 \text{ Hz, 2H}$, \(3.99 \text{ (s, 3H)}\). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.15, 150.51, 135.47, 130.70, 123.53, 52.83.

![Structure 3f]

Following the general procedure B (2.0 mmol, Fe(OTf)$_3$ (5 mol %), MTBE (2.0 mL), 288.8 mg, 87% yield, product 3f was chromatographed on silica gel as a white solid (m.p.: 44.0-44.8 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.87, 163.31, 131.58, 122.58, 113.59, 55.42, 51.88.

![Structure 3g]

Following the general procedure B (676.4 mg, 89% yield, a white solid (m.p.: 66.9-68.0 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 – 7.55 (m, 2H), 7.31 (t, $J = 7.8$ Hz, 1H), 6.44 (br, 1H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.49, 155.96, 131.25, 129.76, 121.86, 120.41, 116.40, 52.43. Compound 3g is commercially available.

![Structure 3h]

Following the general procedure B (2.0 mmol, Fe(OTf)$_3$ (5 mol %), MTBE (2.0 mL), 275.4 mg, 85% yield, product 3h was chromatographed on silica gel as a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 2H), 6.75 (dd, $J = 17.6$, 10.9 Hz, 1H), 5.86 (d, $J = 17.6$ Hz, 1H), 5.38 (d, $J = 10.9$ Hz, 1H), 3.91 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.87, 141.91, 136.01, 129.89, 129.26, 126.11, 116.49, 52.10.

![Structure 3f]

Following the general procedure B (729.0 mg, 90% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 16.0$ Hz, 1H), 7.55 – 7.45 (m, 2H), 7.37 (t, $J = 3.8$ Hz,
3H, 6.44 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.41, 144.87, 134.38, 130.30, 128.89, 128.07, 117.80, 51.70.

3f

Following the general procedure B (541.8 mg, 86% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (dd, J = 15.3, 9.8 Hz, 1H), 6.30 – 6.06 (m, 2H), 5.78 (d, J = 15.4 Hz, 1H), 3.73 (s, 3H), 1.85 (d, J = 5.5 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.64, 145.12, 139.37, 129.72, 118.50, 51.34, 18.58.

3k

Following the general procedure B (1097.5 mg, 98% yield, a white solid (m.p.: 34.7-35.4 °C)). $^1$H NMR (400 MHz, CDCl$_3$) δ 6.82 – 6.77 (m, 1H), 6.77 – 6.70 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.67 (s, 3H), 2.90 (t, J = 7.8 Hz, 2H), 2.66 – 2.57 (t, J = 7.8 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.39, 148.83, 147.45, 133.11, 120.06, 111.57, 111.22, 55.89, 55.80, 51.63, 36.01, 30.60. HRMS (ESI) m/z calcd. for (C$_{12}$H$_{16}$O$_4$) [M+ Na]$^+$: 247.0941, found: 247.0942.

3m

Following the general procedure B (598.0 mg, 92% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.60 (s, 3H), 2.70 (m, 2H), 2.51 (t, J = 6.1 Hz, 2H), 2.12 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.62, 173.12, 51.65, 37.81, 29.70, 27.62.

3n

Following the general procedure B (809.1 mg, 93% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.67 (s, 6H), 2.40 – 2.28 (m, 4H), 1.72 – 1.59 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.61, 51.39, 33.52, 24.25.
Following the general procedure B (762.6 mg, 93% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.26 (m, 4H), 7.26 – 7.19 (m, 1H), 3.71 (q, $J = 7.2$ Hz, 1H), 3.63 (s, 3H), 1.49 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.99, 140.60, 128.68, 127.50, 127.18, 52.02, 45.44, 18.65.

Following the general procedure B (644.0 mg, 92% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.75 – 5.58 (m, 2H), 3.69 (s, 3H), 2.62 – 2.51 (m, 1H), 2.30 – 2.21 (m, 2H), 2.15 – 2.05 (m, 2H), 2.05 – 1.95 (m, 1H), 1.75 – 1.61 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.24, 126.61, 125.14, 51.57, 39.18, 27.42, 25.05, 24.41. Compound 3o is commercially available.

Following the general procedure B (1303.5 mg, 79% yield, product 3p was chromatographed on silica gel as a white solid (m.p.: 116.5-117.2 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.73 (s, 1H), 3.68 (s, 3H), 2.48 – 2.24 (m, 5H), 2.21 – 2.10 (m, 1H), 2.08 – 1.98 (m, 2H), 1.91 – 1.67 (m, 4H), 1.64 – 1.50 (m, 2H), 1.48 – 1.38 (m, 1H), 1.35 – 1.23 (m, 2H), 1.19 (s, 3H), 1.16 – 1.02 (m, 2H), $\delta$ 1.02 – 0.93 (m, 1H), 0.71 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.40, 174.31, 170.99, 123.88, 55.24, 55.06, 53.69, 51.27, 43.87, 38.59, 38.02, 35.70, 35.68, 33.93, 32.78, 31.91, 24.42, 23.57, 20.85, 17.35, 13.43.

Following the general procedure B (911.8 mg, 94% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.65 (s, 3H), 2.05 – 1.97 (m, 3H), 1.93 – 1.84 (m, 6H), 1.77 – 1.65 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.18, 51.52, 40.68, 38.84, 36.48, 27.93.
Following the general procedure C (10 mmol, 1361.5 mg, 99% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.31 (m, 2H), 7.22 – 7.16 (m, 1H), 7.10 – 7.03 (m, 2H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.52, 150.74, 129.48, 125.87, 121.64, 21.14.

Following the general procedure C (10 mmol, 2150.5 mg, 99% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.25 (m, 1H), 7.20 (t, $J$ = 2.1 Hz, 1H), 7.15 (t, $J$ = 8.1 Hz, 1H), 6.98 – 6.92 (m, 1H), 2.19 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.98, 151.18, 130.49, 129.01, 125.12, 122.35, 120.50, 21.03. Compound 6b is commercially available.

Following the general procedure C (10 mmol, 2939.4 mg, 99% yield, a white solid (m.p.: 48.7-49.2 $^\circ$C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (t, $J$ = 1.7 Hz, 1H), 7.16 (d, $J$ = 1.7 Hz, 2H), 2.20 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.52, 151.38, 131.65, 124.13, 122.75, 20.96. Compound 6c is commercially available.

Following the general procedure C (1801.6 mg, 99% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.76 (d, $J$ = 8.3 Hz, 1H), 6.60 (d, $J$ = 2.3 Hz, 1H), 6.51 (dd, $J$ = 8.4, 2.3 Hz, 1H), 5.95 (s, 2H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.79, 147.99, 145.35, 144.99, 113.91, 107.96, 103.73, 101.71, 20.98.
Following the general procedure C (5 mmol, Fe(OTf)$_3$ (0.2 mol %), IPA (2.5 mL), 931.1 mg, 99% yield, a white solid (m.p.: 62.3-63.5 °C)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.74 (m, 3H), 7.55 (d, $J = 2.4$ Hz, 1H), 7.52 – 7.40 (m, 2H), 7.22 (dd, $J = 8.9$, 2.3 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.68, 148.34, 133.77, 131.49, 129.44, 127.79, 127.67, 126.58, 125.74, 121.15, 118.56, 21.23.

![Image](image-url)

Following the general procedure C (5 mmol, Fe(OTf)$_3$ (0.2 mol %), IPA (2.5 mL), DCM (1.0 mL) 1251.3 mg, 99% yield, a white solid (m.p.: 118.4-119.2 °C)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J = 15.9$ Hz, 1H), 7.14 – 7.08 (m, 2H), 7.04 (d, $J = 8.3$ Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.77, 167.23, 151.36, 144.13, 141.40, 133.31, 123.23, 121.18, 117.99, 111.24, 55.86, 51.74, 20.63.

![Image](image-url)

Following the general procedure C (5 mmol, Fe(OTf)$_3$ (0.2 mol %), IPA (2.5 mL), 1562.0 mg, 99% yield, a white solid (m.p.: 142.5-143.7 °C)). $^1$H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.27 (m, 1H), 6.85 (dd, $J = 8.4$, 2.7 Hz, 1H), 6.81 (d, $J = 2.6$ Hz, 1H), 2.95 – 2.87 (m, 2H), 2.51 (dd, $J = 18.8$, 8.4 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.33 – 2.24 (m, 4H), 2.20 – 1.94 (m, 4H), 1.69 – 1.41 (m, 6H), 0.91 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 220.75, 169.84, 148.56, 138.02, 137.41, 126.42, 121.60, 118.76, 50.44, 47.95, 44.16, 38.00, 35.87, 31.56, 29.41, 26.35, 25.75, 21.60, 21.14, 13.84.

![Image](image-url)

Following the general procedure D (5 mmol, Fe(OTf)$_3$ (0.5 mol %), IPA (2.5 mL), 0.83 g, 94% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 6.64 (dt, $J = 15.8$, 1.3 Hz, 1H), 6.27 (dt, $J = 15.9$, 6.4 Hz, 1H), 4.72 (dd, $J = 6.4$, 1.4 Hz, 2H), 2.08 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.81, 168.22, 134.20, 128.62, 128.08, 126.62, 123.19, 65.08, 20.99.
Following the general procedure D (5 mmol, Fe(OTf)₃ (0.5 mol %), IPA (2.5 mL), 0.78 g, 95% yield, a clear oil). ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 4.26 (t, J = 7.1 Hz, 2H), 2.91 (t, J = 7.1 Hz, 2H), 1.99 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.98, 137.86, 128.93, 128.54, 126.60, 64.96, 35.12, 20.96.

Following the general procedure D (5 mmol, Fe(OTf)₃ (0.5 mol %), IPA (2.5 mL), 0.78 g, 92% yield, a clear oil). ¹H NMR (400 MHz, CDCl₃) δ 5.77 – 5.62 (m, 1H), 5.63 – 5.58 (m, 1H), 5.20 – 5.11 (m, 2H), 5.08 (d, J = 10.5 Hz, 1H), 1.99 (s, 3H), 1.61 – 1.46 (m, 2H), δ 1.29 – 1.19 (m, 6H), 0.80 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.30, 136.63, 116.43, 74.83, 34.12, 31.52, 24.69, 22.48, 21.19, 13.94.

Following the general procedure D (2.5 mmol, Fe(OTf)₃ (1.0 mol %), IPA (2.5 mL), 0.50 g, 66% yield, a clear oil). ¹H NMR (400 MHz, CDCl₃) δ 8.84 (br, 1H), 6.82 (s, 1H), 5.71 (s, 1H), 5.34 – 5.14 (m, 2H), 2.86 (d, J = 18.9 Hz, 1H), 2.39 (d, J = 18.8 Hz, 1H), 2.10 – 1.99 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 177.00, 170.14, 170.07, 169.84, 134.66, 130.75, 67.54, 66.77, 66.03, 28.07, 20.95, 20.72, 20.70.

Following the general procedure D (2.5 mmol, Fe(OTf)₃ (1.0 mol %), IPA (2.5 mL), 0.86 g, 90% yield, a white solid (m.p.: 142.2-143.1 °C)). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 1H), 6.84 (dd, J = 8.4, 2.7 Hz, 1H), 6.79 (d, J = 2.6 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.85 – 2.73 (m, 1H), 2.63 (s, 1H), 2.43 – 2.32 (m, 1H), 2.33 – 2.22 (m, 4H), 2.13 – 1.97 (m, 5H), 1.94 – 1.78 (m, 3H), 1.80 – 1.67 (m, 1H), 1.59 – 1.34 (m,
4H), 0.90 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.86, 169.60, 148.45, 138.17, 137.78, 126.45, 121.52, 118.62, 84.45, 83.37, 74.95, 47.87, 47.84, 43.63, 38.78, 37.37, 33.12, 29.54, 27.11, 26.18, 23.32, 21.47, 21.15, 13.41.

Following the general procedure D (2.5 mmol, Fe(OTf)$_3$ (1.0 mol %), IPA (2.5 mL), 0.86 g, 87% yield, a white solid). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.70 (s, 1H), 5.39 (t, $J = 5.2$, 1H), 2.79 – 2.70 (m, 1H), 2.60 (s, 1H), 2.52 – 2.41 (m, 1H), 2.24 – 2.11 (m, 5H), 2.07 – 2.02 (m, 4H), 1.92 – 1.82 (m, 2H), 1.78 – 1.66 (m, 5H), 1.64 – 1.50 (m, 2H), 1.39 – 1.31 (m, 2H), 1.12 – 1.01 (m, 4H), 0.92 – 0.88 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.61, 169.37, 147.07, 139.39, 123.44, 116.91, 84.50, 83.36, 74.85, 49.20, 47.55, 47.52, 34.91, 33.76, 32.91, 32.16, 31.42, 28.80, 21.46, 21.10, 20.84, 18.87, 13.43. MS (EI): 396 [M$^+$].

Following the general procedure D (2.5 mmol, Fe(OTf)$_3$ (1.0 mol %), IPA (2.5 mL), 0.93 g, 70% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.10 (d, $J = 2.9$ Hz, 1H), 4.91 (q, $J = 3.1$ Hz, 1H), 4.58 (tt, $J = 11.3$, 4.3 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.29 – 2.20 (m, 1H), 2.14 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.02 – 1.75 (m, 7H), 1.74 – 1.29 (m, 13H), 1.17 – 1.03 (m, 2H), 0.92 (s, 3H), 0.82 (d, $J = 6.3$ Hz, 3H), 0.73 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.68, 170.68, 170.63, 170.52, 75.41, 74.13, 70.74, 47.32, 45.05, 43.39, 40.90, 37.71, 34.67, 34.59, 34.54, 34.32, 31.23, 30.83, 30.53, 28.88, 27.16, 26.88, 25.57, 22.79, 22.57, 21.65, 21.52, 21.46, 17.48, 12.24. HRMS (ESI) m/z calcd. for (C$_{36}$H$_{46}$O$_6$Na)[M+Na]$^+$: 557.3085, found: 557.3081.
Following the general procedure D (2.5 mmol, Fe(OTf)₃ (1.0 mol %), IPA (2.5 mL), 0.81 g, 90% yield, a white solid (m.p.: 144.0-144.9 °C)). ¹H NMR (400 MHz, CDCl₃) δ 5.35 (d, J = 3.8 Hz, 1H), 4.64 – 4.52 (m, 1H), 2.51 (t, J = 8.8 Hz, 1H), 2.35 – 2.25 (m, 2H), 2.23 – 2.13 (m, 1H), 2.10 (s, 3H), 2.05 – 1.93 (m, 5H), 1.85 (d, J = 11.3 Hz, 2H), 1.72 – 1.54 (m, 5H), 1.52 – 1.42 (m, 3H), 1.24 – 1.11 (m, 3H), 1.04 – 0.94 (m, 4H), 0.61 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 209.49, 170.51, 139.65, 122.32, 73.83, 63.67, 56.83, 49.89, 43.97, 38.79, 38.07, 37.00, 36.60, 31.82, 31.76, 31.54, 27.73, 24.48, 22.83, 21.42, 21.03, 19.30, 13.22.

Following the general procedure D (2.5 mmol, Fe(OTf)₃ (1.0 mol %), IPA (2.5 mL), 0.93 g, 87% yield, a clear oil). ¹H NMR (400 MHz, CDCl₃) δ 6.15 (d, J = 11.2 Hz, 1H), 5.96 (d, J = 11.4 Hz, 1H), 4.99 (d, J = 2.4 Hz, 1H), 4.87 (tt, J = 8.0, 3.9 Hz, 1H), 4.77 (d, J = 2.4 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.50 (dd, J = 13.5, 4.1 Hz, 1H), 2.37 – 2.25 (m, 2H), 2.18 – 2.12 (m, 1H), 1.97 (s, 3H), 1.91 – 1.77 (m, 3H), 1.71 – 1.60 (m, 2H), 1.50 – 1.37 (m, 4H), 1.32 – 1.16 (m, 9H), 1.10 – 1.02 (m, 3H), 0.85 (d, J = 6.4 Hz, 3H), 0.80 (d, J = 1.9 Hz, 3H), 0.79 (d, J = 1.9 Hz, 3H), 0.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.65, 144.62, 142.50, 134.30, 122.46, 117.46, 112.74, 71.81, 56.59, 56.38, 45.93, 42.15, 40.55, 39.51, 36.15, 32.20, 31.98, 29.73, 29.08, 28.04, 27.69, 23.88, 23.59, 22.85, 22.59, 22.24, 21.44, 18.86, 12.00.
Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 160 mg, 41% yield, a white solid (m.p.: 97.6-99.2 °C)). $^1$H NMR (400 MHz, CDCl$_3$) δ 6.33 (d, $J = 3.7$ Hz, 1H), 5.51 – 5.44 (m, 1H), 5.18 – 5.07 (m, 2H), 4.30 – 4.24 (m, 1H), 4.16 – 4.07 (m, 2H), 2.19 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.59, 170.18, 169.63, 169.37, 168.73, 89.02, 69.79, 69.16, 67.85, 61.43, 20.83, 20.65, 20.62, 20.52, 20.41.

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 156.5 mg, 91% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.78 – 5.73 (m, 2H), 4.68 (d, $J = 5.2$ Hz, 4H), 2.07 (s, 6H).

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 178.4 mg, 90% yield, a clear oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 4.76 – 4.58 (m, 1H), 2.03 (s, 3H), 2.01 – 1.94 (m, 1H), 1.91 – 1.82 (m, 1H), 1.73 – 1.62 (m, 2H), 1.54 – 1.42 (m, 1H), 1.40 – 1.30 (m, 1H), 1.26 (d, $J = 4.2$ Hz, 1H), 1.13 – 1.02 (m, 1H), 1.01 – 0.94 (m, 1H), 0.91 (d, $J = 2.4$ Hz, 3H), 0.89 (d, $J = 2.9$ Hz, 3H), 0.77 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.56, 74.07, 46.97, 40.90, 34.23, 31.33, 26.28, 23.46, 21.96, 21.23, 20.68, 16.33.

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 0.5 h, 146.2 mg, 58% yield, a white solid (m.p.: 104.5-101.9 °C)). $^1$H NMR (400 MHz, CDCl$_3$) δ 6.84 (s, 3H), 2.27 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.59, 151.09, 112.78, 21.07.

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 24 h, 114.8 mg, 85% yield, a pale yellow solid (m.p.: 114.8-145.7 °C)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (s, 1H), 7.53 – 7.46 (m, 2H), 7.35 – 7.27 (m, 2H), 7.14 – 7.05 (m, 2H).
1H), 2.16 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.59, 137.94, 128.97, 124.31, 119.98, 24.55. Compound 6q is commercially available.

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 24 h, 119.0 mg, 73% yield, a pale yellow solid (m.p.: 49.5-50.5 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 5.66 (s, 1H), 3.51 (td, $J$ = 7.0, 5.7 Hz, 2H), 2.81 (t, $J$ = 7.0 Hz, 2H), 1.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.15, 138.89, 128.74, 128.64, 126.52, 40.69, 35.63, 23.30. Compound 6r is commercially available.

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 24 h, 82.0 mg, 55% yield, a pale yellow solid (m.p.: 99.3-100.2 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 7.23 – 7.16 (m, 2H), 3.27 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.58, 144.62, 129.73, 127.71, 127.08, 37.17, 22.42. Compound 6s is commercially available.

Following the general procedure D (1.0 mmol, Fe(OTf)$_3$ (10 mol %), IPA (2.5 mL), 24 h, 151.0 mg, 74% yield, a yellow solid (m.p.: 94.1-94.9 °C)). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.25 (m, 2H), 6.97 – 6.88 (m, 3H), 3.77 (t, $J$ = 5.2 Hz, 2H), 3.61 (t, $J$ = 5.2 Hz, 2H), 3.16 (dt, $J$ = 13.1, 5.3 Hz, 4H), 2.14 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.02, 150.92, 129.25, 120.56, 116.67, 49.70, 49.37, 46.23, 41.35, 21.36. Compound 6t is commercially available.
Sequential protection of COOH and OH in a one-pot reaction

Fe(OTf)$_3$ (0.05 mmol, 10 mol%), lithocholic acid 7 (0.5 mmol, 1.0 equiv.), and MTBE (1 mL) were added into the Schlenk tube with a stirring bar. The reaction mixture was heated for 5 hours, and then cooled to room temperature. After remove the solvent under vacuum, IPA (1 mL) were added into the Schlenk tube. The reaction mixture was stirred at room temperature for 30 minutes. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel to give the product 8 (164.4 mg, 76% yield, a white solid (m.p.: 126.5-126.9 °C)).

Fe(OTf)$_3$ (0.05 mmol, 10 mol%), deoxycholic acid 9 (0.5 mmol, 1.0 equiv.), and MTBE (1 mL) were added into the Schlenk tube with a stirring bar. The reaction mixture was heated for 5 hours, and then cooled to room temperature. After remove the solvent under vacuum, IPA (1 mL) were added into the Schlenk tube. The reaction mixture was stirred at room temperature for 30 minutes. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). The solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel to give the product 10 (168.7 mg, 69% yield, a clear oil).
$^1$H NMR (400 MHz, CDCl$_3$) δ 5.11 – 5.05 (m, 1H), 4.76 – 4.64 (m, 1H), 3.66 (s, 3H), 2.39 – 2.28 (m, 1H), 2.25 – 2.15 (m, 1H), 2.10 (s, 3H), 2.03 (s, 3H), 1.93 – 1.76 (m, 4H), 1.74 – 1.53 (m, 8H), 1.51 – 1.23 (m, 9H), 1.22 – 1.01 (m, 3H), 0.91 (s, 3H), 0.81 (d, $J = 6.4$ Hz, 3H), 0.73 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.56, 170.53, 170.44, 75.88, 74.17, 51.48, 49.43, 47.56, 44.99, 41.81, 35.66, 34.71, 34.69, 34.38, 34.02, 32.24, 30.95, 30.82, 27.33, 26.87, 26.61, 25.85, 25.63, 23.42, 23.06, 21.44, 21.35, 17.49, 12.39. HRMS (ESI) m/z calcd. for (C$_{29}$H$_{46}$O$_6$Na) [M+Na]$^+$: 513.3187, found: 513.3185.
Mechanistic study

(a)

Fe(OTf)$_3$ (0.1 mmol, 10 mol%), benzoic acid (1.0 mmol, 1.0 equiv.), and MTBE (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was heated at 90 °C for 1 hour. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product 3a could be detected by GC-MS. Isobutene (MS (Ion trap, EI): m/z (%) = 56.07 [M$^+$] (100.00)) and H$_2$O (MS (Ion trap, EI): m/z (%) = 18.07 [M$^+$] (100.00)) could be detected by GC-MS.

(b)

Fe(OTf)$_3$ (0.1 mmol, 10 mol%), phenol (1.0 mmol, 1.0 equiv.) and IPA (2.5 mL) were added into the Schlenk tube with a stirring bar, and then the reaction mixture was stirred at room temperature for 10 minutes. The reaction mixture was stirred at room temperature for 10 minutes. The mixture was filtered by a short silica gel column, which was washed by EA (30 mL). After added the 1,4-dimethoxybenzene into the solvent as the internal standard, the yield of product 3a could be detected by GC-MS. Acetone (MS (Ion trap, EI): m/z (%) = 58.04 [M$^+$] (100.00)) could be detected by GC-MS.
References


3o
$6b$