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Supporting Information

Highly Efficient Esterification of Carboxylic Acids with O-H Nucleophiles through Acid/lodide

Cooperative Catalysis

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1. General Information

All experiments were carried out under nitrogen atmosphere using standard Schlenk techniques or in a dry glovebox. All heating (heating module) and stirring were conducted on the IKA (Model: RCT B S025). Solvents were dried over Na metal or CaH₂, and were distilled under nitrogen prior to use. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin. Column chromatography was performed using Silica Gel 60 (300-400 mesh). The reactions were monitored by GC and GC-MS, GC-MS data were recorded on GC-MS QP 2010 plus, and GC analysis was performed on GC 2014. The ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, and 100 MHz respectively, and chemical shifts were reported in parts per million (ppm). The All solvents and reagents were purchased from Energy Chemical, Alfa Aesar, Heowns, Meryer and Aladdin.

2. Optimization of Conditions for Reaction

Competition experiments and time course experiments.^a

ОН	+ He OH	50 mol% TfOH 10 mol% KI Hexane, 100 °C,Time	Me Me
1a , 0.2 mmol	2a , 1.2 equiv.		3a
Entry	Time (h)	3 Yield% ^b	3 Yield% ^{b,c}
1	0.5	50	21
2	1.0	71	35
3	1.5	81	49
4	2.0	89	57
5	2.5	95	64
6	3.0	99	71
7	3.5	99	77
8	4.0	99	71

^{*a*}Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol, 1.2 equiv), TfOH (0.10 mmol, 50 mol%), KI (0.02 mmol, 10 mol%), *n*-hexane (2 mL), 100 °C, N₂ atmosphere. ^{*b*}GC yield using tridecane as an internal standard. ^cNo KI.

3. Experimental Procedure

General procedure for the esterification reaction:



An oven dried 25 mL Schlenk tube was charged with carboxylic acid 1 (0.20 mmol), phenol 2 (0.24 mmol, 1.2 equiv) and KI (0.02 mmol, 10 mol%). Subsequently, TfOH (0.10 mmol, 50 mol%) and *n*-hexane (2 mL) was added under N₂. The reaction mixture was allowed to react at 100 °C for 4 h. After completion of the reaction, the reaction mixture was then cooled down to room temperature, added by water (5 mL) and extracted with EtOAc (5 mL×3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate= 50/1) provided the product **3**.

4. Gram-scale Reaction.



An oven dried 250 mL Schlenk flask was charged with 1-adamantanecarboxylic acid **1a** (1.80 g, 10 mmol), *p*-cresol **2a** (1.30 g, 12 mmol) and KI (0.17 g, 1 mmol, 10 mol%). Subsequently, TfOH (0.75 g, 5 mmol, 50 mol%) and *n*-hexane (100 mL) was added under N₂. The reaction mixture was allowed to react at 100 °C for 4 h. After completion of the reaction, the reaction mixture was then cooled down to room temperature, added by water (30 mL) and extracted with EtOAc (30 mL×3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 50/1) provided the product **3a** in 90% yield (2.43 g).

5. Measurement of Acyl Iodide by MALDI-TOF MS



Experimental procedure: An oven dried 25 mL Schlenk tube was charged with carboxylic acid 1adamantanecarboxylic acid **1a** (0.02 mmol), and KI (30 equiv). Subsequently, HOTf (25 equiv) and hexane (3 mL) was added under N₂, the reaction mixture was allowed to react at 100 °C for 4 h. After the completion of the reaction, the reaction mixture was cooled down to RT. Then, MeCN was added to dilute and dissolve the excess TfOH. The intermediate acyl iodide was determined by MALDI-TOF MS analysis using α -cyano-4-hydroxycinnamic acid (CHCA) as the matrix material.



6. Characterization of the products

p-tolyl (3r,5r,7r)-adamantane-1-carboxylate (3a)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3a** in 99% (53.4 mg) as a white solid, mp: 104-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.09-2.07 (m, 9H), 1.82-1.75 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 176.3, 148.8, 135.0, 129.8, 121.2, 40.9, 38.7, 36.4, 27.9, 20.8. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 271.1693; Found 271.1693.

4-methoxyphenyl (3r,5r,7r)-adamantane-1-carboxylate (3b)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound 3b in 90% (51.4 mg) as a white solid, mp: 64-65 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.95 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 2H), 3.79 (s, 3H), 2.08 (s, 3H), 2.05-2.04 (m, 9H), 1.80-1.73 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 176.5, 157.0, 144.5, 122.2, 114.4, 55.6, 40.9, 38.8, 36.4, 27.9. HRMS (APCI-TOF) m/z: [M + H]+ Calcd for C₁₈H₂₂O₃ 287.1642; Found 287.1641.

phenyl (3r,5r,7r)-adamantane-1-carboxylate (3c)

The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound 3c in 88% (45.0 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.35 (dd, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 2.07-2.04 (m, 9H), 1.79-1.92 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 176.2, 151.0, 129.3, 125.5, 121.5, 41.0, 38.7, 36.4, 27.9. HRMS (APCI-TOF) m/z: [M + H]+ Calcd for C₁₇H₂₀O₂ 257.1536; Found 257.1533.

4-chlorophenyl (3r,5r,7r)-adamantane-1-carboxylate (3d)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound 3d in 83% (48.0 mg) as a white solid, mp: 79-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 2.08 (br, 3H), 2.04-2.03 (m, 6H), 1.80-1.73 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 175.9, 149.6, 130.8, 129.3, 122.9, 41.0, 38.7, 36.4, 27.8. HRMS (APCI-TOF) m/z: [M + H]+ Calcd for C₁₇H₁₉ClO₂ 291.1146; Found 291.1144.

4-bromophenyl (3r,5r,7r)-adamantane-1-carboxylate (3e)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3e** in 85% (56.5 mg) as a white solid, mp: 104-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 9.2 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 2.08 (br, 3H), 2.04-2.03 (m, 6H), 1.80-1.73 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 175.9, 150.1, 132.3, 123.4, 118.5, 41.0, 38.7, 36.4, 27.8. HRMS (APCI-TOF) m/z: [M + H]+ Calcd for C₁₇H₁₉BrO₂ 335.0641; Found 335.0640.

3-(trifluoromethyl)phenyl (3r,5r,7r)-adamantane-1-carboxylate (3f)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3f** in 67% (43.1 mg) as a white solid, mp: 90-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.49 (m, 2H), 7.36 (s, 1H), 7.30-7.27 (m, 1H), 2.13-2.09 (m, 9H), 1.84-1.77 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 175.7, 151.2, 131.8 (q, *J*_{C-F} = 32.7 Hz), 129.8, 125.2 (q, *J*_{C-F} = 1.2 Hz), 123.6 (q, *J*_{C-F} = 270.7 Hz), 122.3 (d, *J*_{C-F} = 3.9 Hz), 118.9 (d, *J*_{C-F} = 3.7 Hz), 41.1, 38.7, 36.4, 27.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.64. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₁₉F₃O₂ 325.1410; Found 325.1407.

[1,1'-biphenyl]-2-yl (3r,5r,7r)-adamantane-1-carboxylate (3g)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3g** in 90% (59.5 mg) as a white soild, mp: 108-109 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.33 (m,, 7H), 7.30 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.0, 1.2 Hz, 1H), 1.99 (br, 3H), 1.81 (m 6H), 1.73-1.64 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 175.9, 148.1, 137.5, 135.2, 130.8, 129.2, 128.4, 128.0, 127.3, 125.9, 122.8, 40.8, 38.5, 36.4, 27.8. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₄O₂ 333.1849; Found 333.1848.

ethyl (3r,5r,7r)-adamantane-1-carboxylate (3h)

An oven dried 25 mL Schlenk tube was charged with carboxylic acid **1a** (0.20 mmol), ethanol **2h** (0.30 mmol, 1.5 equiv) and KI (0.02 mmol, 10 mol%). Subsequently, TfOH (0.10 mmol, 50 mol%) and *n*-hexane (2 mL) was added under N₂. The reaction mixture was allowed to react at 100 °C for 4 h. After completion of the reaction, the reaction mixture was then cooled down to room temperature, added by water (5 mL) and extracted with EtOAc (5 mL×3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuo. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3h** in 80% (33.0 mg) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ 4.10 (q, *J* = 7.2 Hz, 2H), 2.00 (br, 3H), 1.87-1.86 (m, 6H), 1.73-1.66 (m, 6H), 1.22 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 177.7, 60.0, 40.5, 38.8, 36.5, 27.9, 14.2. This compound is known.¹

phenethyl (3r,5r,7r)-adamantane-1-carboxylate (3i)

The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3i** in 99% (56.0 mg) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (dd, *J* = 8.0 Hz, 2H), 7.24-7.21 (m, 3H), 4.26 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H), 2.00 (br, 3H), 1.85-1.84 (m, 6H), 1.74-1.66 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 177.6, 138.0, 129.0, 128.4, 126.4, 64.6, 40.6, 38.8, 36.5, 35.2, 27.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 285.1849; Found 285.1847.

isopropyl (3r,5r,7r)-adamantane-1-carboxylate (3j)

An oven dried 25 mL Schlenk tube was charged with carboxylic acid **1a** (0.20 mmol), isopropyl alcohol **2i** (0.30 mmol, 1.5 equiv) and KI (0.02 mmol, 10 mol%). Subsequently, TfOH (0.10 mmol,

50 mol%) and *n*-hexane (2 mL) was added under N₂. The reaction mixture was allowed to react at 100 °C for 4 h. After completion of the reaction, the reaction mixture was then cooled down to room temperature, added by water (5 mL) and extracted with EtOAc (5 mL×3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuo. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3j** in 78% (34.4 mg) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ 5.00-4.90 (m, 1H), 2.00 (br, 3H), 1.86-1.85 (m, 6H), 1.73-1.66 (m, 6H), 1.19 (d, *J* = 6.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 177.2, 66.8, 40.5, 38.7, 36.5, 28.0, 21.7. This compound is known.²

(3S,5S,7S)-adamantan-1-yl (3R,5R,7R)-adamantane-1-carboxylate (3k)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 25/1) provided the title compound **3k** in 62% (38.5 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 2.15-1.99 (m, 8H), 1.83-1.60 (m, 14H), 1.42-1.26 (m, 8H). ¹³C NMR (100 MHz, CDCl₃): δ 177.0, 79.3, 41.3, 41.1, 38.9, 36.6, 36.3, 30.8, 28.1. This compound is known.³

p-tolyl hexanoate (31)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **31** in 55% (22.4 mg) as a colourless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.16 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.79-1.72 (m, 2H), 1.42-1.35 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 148.5, 135.3, 129.9, 121.2, 34.4, 31.3, 24.6, 22.3, 20.8, 13.9. This compound is known.⁴

p-tolyl 2,2-diphenylacetate (3m)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3m** in 80% (48.1 mg) as a white solid, mp: 97-98 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.42 (m, 4H), 7.40-7.36 (m, 4H), 7.33-7.29 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 148.5, 138.2, 135.5, 129.8, 128.7, 128.6, 127.4, 121.0, 57.0, 20.8. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 303.1380; Found 303.1379.

p-tolyl (E)-2,3-diphenylacrylate (3n)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3n** in 85% (53.1 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (s, 1H), 7.43-7.40 (m, 3H), 7.37-7.35 (m, 2H), 7.28-7.19 (m, 5H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.5, 148.9, 141.8, 135.5, 135.3, 134.4, 132.0, 130.7, 129.8, 129.8, 129.3, 128.7, 128.2, 128.0, 121.2, 20.8. This compound is known.⁵

p-tolyl benzoate (30)

Me

The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the S13

title compound **30** in 85% (35.9 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (d, J = 6.8 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.51 (dd, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 148.7, 135.5, 133.5, 130.1, 130.0, 129.7, 128.5, 121.4, 20.9. This compound is known.⁶

p-tolyl 4-methylbenzoate (3p)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3p** in 80% (35.9 mg) as a white solid, mp: 91-92 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 148.8, 144.3, 135.4, 130.2, 123.0, 129.2, 126.9, 121.4, 21.7, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₄O₂ 227.1067; Found 227.1066.

p-tolyl 4-(tert-butyl)benzoate (3q)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3q** in 70% (37.2 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H), 1.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 157.3, 148.8, 135.4, 130.0, 129.9, 126.8, 125.5, 121.4, 35.2, 31.1, 20.9. This compound is known.⁷

p-tolyl 4-cyclohexylbenzoate (3r)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3r** in 72% (42.0 mg) as a white solid, mp: 108-109 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 2.63-2.56 (m, 1H), 2.37 (s, 3H), 1.92-1.76 (m, 5H), 1.48-1.28 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 154.2, 148.8, 135.4, 130.3, 130.0, 127.2, 127.0, 121.4, 44.8, 34.1, 26.7, 26.0, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 295.1693; Found 295.1691.

p-tolyl 4-methoxybenzoate (3s)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3s** in 81% (39.1 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.0, 163.7, 148.7, 135.2, 132.2, 129.9, 121.9, 121.4, 113.7, 55.4, 20.8. This compound is known.⁷

p-tolyl 4-phenoxybenzoate (3t)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3t** in 74% (44.5 mg) as a white solid, mp: 113-114 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.41 (dd, *J* = 7.6 Hz, 2H), 7.23-7.20 (m, 3H), 7.11-7.03 (m, 6H), 2.37 (s,

3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.9, 162.3, 155.5, 148.7, 135.4, 132.3, 130.1, 130.0, 124.6, 123.8, 121.4, 120.2, 117.3, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 305.1172; Found 305.1169.

p-tolyl 4-fluorobenzoate (3u)

The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3u** in 75% (34.4 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (dd, J = 8.8, 5.6 Hz, 2H), 7.23-7.15 (m, 4H), 7.08 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.0 (d, $J_{C-F} = 253.2$ Hz), 164.4, 148.5, 135.6, 132.7 (d, $J_{C-F} = 9.4$ Hz), 130.0, 125.8 (d, $J_{C-F} = 2.8$ Hz), 121.2, 115.7 (d, $J_{C-F} = 21.9$ Hz), 20.8. ¹⁹F NMR (377 MHz, CDCl₃): δ -78.29. This compound is known.⁷

p-tolyl 4-chlorobenzoate (3v)

The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3v** in 67% (32.5 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.5, 148.5, 140.0, 135.7, 131.5, 130.0, 128.9, 128.1, 121.2, 20.9. This compound is known.⁷

p-tolyl 4-bromobenzoate (3w)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3w** in 60% (34.4 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.7, 148.5, 135.7, 131.9, 131.6, 130.0, 128.7, 128.6, 121.2, 20.9. This compound is known.⁷

p-tolyl 4-iodobenzoate (3x)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3x** in 67% (44.9 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.91-7.86 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.9, 148.5, 137.9, 135.7, 131.5, 130.0, 129.2, 121.2, 101.4, 20.9. This compound is known.⁸

p-tolyl 4-(trifluoromethoxy)benzoate (3y).



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3y** in 70% (41.2 mg) as a white solid, mp: 120-121 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.1, 153.0, 148.5, 135.7, 132.1, 130.0, 128.1, 121.2, 120.3, 120.3 (q, *J*_{C-F} = 257.3 Hz), 20.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -57.37. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 297.0733; Found 297.0731.

p-tolyl 2,4-dimethylbenzoate (3z)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3z** in 71% (33.9 mg) as a white solid, mp: 85-86 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.13-7.12 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.64 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 148.7, 143.3, 141.4, 135.3, 132.7, 131.3, 129.9, 126.6, 125.7, 121.5, 21.9, 21.5, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₆H₁₆O₂ 241.1196; Found 241.1195.

p-tolyl 4-chloro-2-methylbenzoate (3aa)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3aa** in 65% (33.6 mg) as a white solid, mp: 95-96 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.65-7.63 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 2.99 (s, 3H), 2.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.2, 148.4, 143.3, 138.7, 135.6, 132.6, 131.8, 130.0, 127.0, 126.1, 121.4, 21.8, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 261.0677; Found 261.0673.

p-tolyl [1,1'-biphenyl]-4-carboxylate (3ab)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 50/1) provided the title compound **3ab** in 79% (45.0 mg) as a white solid, mp: 128-129 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.51 (dd, *J* =

6.8 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.2, 148.7, 146.2, 139.8, 135.5, 130.6, 130.0, 128.9, 128.3, 128.2, 127.3, 127.1, 121.3, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₁₆O₂ 289.1223; Found 289.1221.

p-tolyl 1-naphthoate (3ac)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3ac** in 76% (39.7 mg) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 9.03 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 7.2 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 7.2 Hz, 1H), 7.59-7.55 (m, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 148.7, 135.6, 134.2, 133.9, 131.7, 131.1, 130.0, 128.6, 128.1, 126.4, 126.0, 125.8, 124.5, 121.5, 20.9. This compound is known.⁷

p-tolyl 2-naphthoate (3ad)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3ad** in 80% (41.5 mg) as a white solid. ¹H NMR (400 MHz, CDCl3): δ 8.79 (s, 1H), 8.20 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.65-7.55 (m, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.6, 148.8, 135.8, 135.5, 132.5, 131.8, 130.0, 129.5, 128.6, 128.3, 127.8, 126.9, 126.8, 125.5, 121.4, 20.9. This compound is known.⁷

p-tolyl 6-methoxy-2-naphthoate (3ae)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3ae** in 75% (43.1 mg) as a white solid, mp: 96-97 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.70 (s, 1H), 8.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.25-7.19 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 3H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.7, 159.8, 148.8, 137.5, 135.4, 131.6, 131.0, 130.0, 127.9, 127.0, 126.2, 124.6, 121.4, 119.8, 105.7, 55.4, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 293.1172; Found 293.1172.

p-tolyl 6-bromo-2-naphthoate (3af)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3af** in 65% (43.8 mg) as a white solid, mp: 101-102 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.73 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.08 (s, 1H), 7.86-7.83 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.2, 148.7, 136.6, 135.6, 131.7, 130.9, 130.9, 130.3, 130.0, 130.0, 127.4, 127.3, 126.6, 123.0, 121.3, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 341.0172; Found 341.0171.

p-tolyl benzo[b]thiophene-2-carboxylate (3ag)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3ag** in 60% (31.8 mg) as a white solid, mp: 76-77 °C. ¹H NMR (400 MHz,

CDCl₃): δ 8.25 (s, 1H), 7.94-7.90 (m, 2H), 7.52-7.42 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 161.4, 148.3, 142.6, 138.6, 135.8, 132.8, 131.8, 130.0, 127.2, 125.7, 125.0, 122.8, 121.2, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 269.0631; Found 269.0630.

phenethyl benzoate(3ah)

The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3ah** in 90% (40.5 mg) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 8.0 Hz, 2H), 7.36-7.24 (m, 5H), 4.54 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 166.5, 137.9, 132.9, 130.2, 129.5, 128.9, 128.5, 128.3, 126.6, 65.4, 35.2. This compound is known.⁹

p-tolyl 2-(4-isobutylphenyl)propanoate (3ai)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3ai** in 71% (41.7 mg) as a colourless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.15-7.11 (m, 4H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.92 (q, *J* = 7.2 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.92-1.82 (m, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 173.4, 148.6, 140.7, 137.3, 135.3, 129.8, 129.5, 127.2, 121.0, 45.2, 45.0, 30.2, 22.4, 20.8, 18.6. This compound is known.¹⁰

p-tolyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3aj)



The representative general procedure mentioned above was followed. Purification by preparative thin-layer chromatography (PTLC) on silica gel (petroleum ether/ethyl acetate = 100/1) provided the title compound **3aj** in 65% (48.6 mg) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 4H), 2.38 (s, 3H), 1.59-1.52 (m, 4H), 0.88 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 164.1, 148.4, 144.8, 136.0, 133.0, 130.8, 130.1, 127.1, 121.1, 49.9, 21.9, 20.9, 11.2. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 376.1577; Found 376.1577.

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8. Copies of ¹H, ¹³C and ¹⁹F NMR Spectra of the Products

¹H NMR of compound **3a** (400 MHz, CDCl₃).



 $^1\mathrm{H}$ NMR of compound $\mathbf{3b}$ (400 MHz, CDCl_3).



¹³C NMR of compound **3b** (100 MHz, CDCl₃).

¹H NMR of compound 3c (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3c (100 MHz, CDCl_3).



 1 H NMR of compound **3d** (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3d (100 MHz, CDCl₃).



¹H NMR of compound **3e** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound **3e** (100 MHz, CDCl₃).



¹H NMR of compound **3f** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound **3f** (100 MHz, CDCl₃).



 ^{19}F NMR of compound **3f** (376 MHz, CDCl₃).



 1 H NMR of compound **3g** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound 3g (100 MHz, CDCl_3).



 1 H NMR of compound **3h** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3h** (100 MHz, CDCl₃).



¹H NMR of compound **3i** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound 3i (100 MHz, CDCl_3).



 1 H NMR of compound **3j** (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3j (100 MHz, CDCl_3).



¹H NMR of compound 3k (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3k (100 MHz, CDCl₃).



 1 H NMR of compound **3l** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3l** (100 MHz, CDCl₃).



¹H NMR of compound 3m (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3m (100 MHz, CDCl₃).



 $^1\mathrm{H}$ NMR of compound 3n (400 MHz, CDCl_3).



 ^{13}C NMR of compound **3n** (100 MHz, CDCl₃).



 1 H NMR of compound **30** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound **30** (100 MHz, CDCl_3).



¹H NMR of compound 3p (400 MHz, CDCl₃).



 ^{13}C NMR of compound $\boldsymbol{3p}$ (100 MHz, CDCl_3).



 1 H NMR of compound **3q** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3q** (100 MHz, CDCl₃).



¹H NMR of compound 3r (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3r (100 MHz, CDCl_3).



¹H NMR of compound **3s** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound 3s (100 MHz, CDCl_3).



¹H NMR of compound 3t (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3t** (100 MHz, CDCl₃).



¹H NMR of compound **3u** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3u** (100 MHz, CDCl₃).



 ^{19}F NMR of compound $\boldsymbol{3u}$ (376 MHz, CDCl_3).



 1 H NMR of compound **3v** (400 MHz, CDCl₃).



¹³C NMR of compound **3v** (100 MHz, CDCl₃).



¹H NMR of compound 3w (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3w (100 MHz, CDCl₃).



¹H NMR of compound 3x (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3x** (100 MHz, CDCl₃).



 1 H NMR of compound **3**y (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound 3y (100 MHz, CDCl_3).



 ^{19}F NMR of compound **3y** (376 MHz, CDCl₃).



¹H NMR of compound 3z (400 MHz, CDCl₃).



¹³C NMR of compound **3z** (100 MHz, CDCl₃).



¹H NMR of compound **3aa** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3aa** (100 MHz, CDCl₃).



¹H NMR of compound **3ab** (400 MHz, CDCl₃).



 ^{13}C NMR of compound 3ab (100 MHz, CDCl_3).



 1 H NMR of compound **3ac** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3ac** (100 MHz, CDCl₃).



¹H NMR of compound **3ad** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3ad** (100 MHz, CDCl₃).



¹H NMR of compound **3ae** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3ae** (100 MHz, CDCl₃).



¹H NMR of compound **3af** (400 MHz, CDCl₃).



 ^{13}C NMR of compound **3af** (100 MHz, CDCl₃).



 1 H NMR of compound **3ag** (400 MHz, CDCl₃).



 ^{13}C NMR of compound $\boldsymbol{3ag}$ (100 MHz, CDCl_3).



 1 H NMR of compound **3ah** (400 MHz, CDCl₃).



¹³C NMR of compound **3ah** (100 MHz, CDCl₃).



¹H NMR of compound **3ai** (400 MHz, CDCl₃).



¹³C NMR of compound **3ai** (100 MHz, CDCl₃).



¹H NMR of compound **3aj** (400 MHz, CDCl₃).



 $^{13}\mathrm{C}$ NMR of compound **3aj** (100 MHz, CDCl₃).

