Electronic Supplementary Information

Acid/Halide Co-Mediated Transesterification of Unactivated Carboxylic Esters with O-H Nucleophiles

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1. General information

All starting materials reported in the manuscript have been previously described in literature or prepared by the method reported previously. Esters were prepared by standard methods. The reactions were carried out in Schlenk tubes of 25 mL under N₂ atmosphere. All heating and stirring were conducted on the IKA (Model: RCT B S025). Reagents were used as received unless otherwise noted, and solvents were purified according to standard operation procedure. Column chromatography was performed using Silica Gel 60 (300–400 mesh). The reactions were monitored by GC and GC-MS. GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2010 plus. The ¹H, and ¹³C NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz, and 100 MHz respectively, and chemical shifts were reported in parts per million (ppm) with deuterated chloroform as solvent. The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI. All solvents and reagents were purchased from Energy Chemical, Alfa Aesar, and Aladdin.

2. Experimental procedure





Scheme S1. Ester substrates



Scheme S2. OH nucleophiles

2.1 Preparation of the starting materials



Representative procedure for the synthesis of ester substrates I-V (synthesis of ester I is used as an example).



- 1) A 100 mL round-bottom flask was charged with 2-naphthic acid (10.0 mmol). Then thionyl chloride (15.0 mmol, 1.5 equiv) was added dropwise to the reaction mixture and stirred at 85 °C for 5 h. After cooling down to room temperature, the resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.
- 2) Methanol (20.0 mL) added to an oven-dried round-bottom flask (100.0 mL), which was equipped a stirring bar and ice bath. Dissolved acyl chloride (10.0 mmol) in CH₂Cl₂ (0.5 ml), which was added dropwise to the flask at 0 °C. Then the base triethylamine (3 drops), solvent acetonitrile (10.0 ml) was added and the reaction mixture was stirred at room temperature overnight. After completion of the reaction, the reaction mixture was washed with HCl (1.0 M, 15 mL), brine (20 mL × 3), dried over anhydrous NaSO₄, and concentrated under *vacuo*. The crude product was purified by column chromatography over silica gel (300-400 mesh) using petroleum ether : ethyl acetate (100: 1) as eluent to give analytical product.

Procedure for the synthesis of ester substrates (VI-VIII) come as follows:



Dissolved benzoyl chloride (10.0 mmol) in CH₂Cl₂ (10 ml), which was added dropwise to a rapidly stirred solution of the corresponding alcohol (1.2 equiv) and DMAP (1.0 equiv) in 20.0 mL of CH₃CN at 0 °C. Then the reaction mixture was stirred at room temperature overnight. After completion of the reaction, the reaction mixture was washed with HCl (1.0 M, 15 mL), brine (20 mL \times 3), dried over anhydrous Na₂SO₄, and concentrated under *vacuo*. The crude product was purified by column chromatography over silica gel (300-400 mesh) using petroleum ether : ethyl acetate (100: 1) as eluent to give analytical product VI-VIII.

2.2 General experimental procedure for the synthesis of aromatic esters.



An oven dried 25 mL Schlenk tube with 4Å MS (90 mg) were charged with ester **a** (0.2 mmol), phenol **b** (0.4 mmol, 2.0 equiv.) and KF (0.2 mmol, 1.0 equiv.). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and solvent (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether as eluent. The crude product was purified by PTLC eluting with petroleum ether.

| 2.3 | General | experimental | procedure for | r the synthesis | of alkyl esters. |
|-----|---------|--------------|---------------|-----------------|-----------------------|
| | | | | | • • • • • • • • • • • |

| | O OMe | + H0 | `Ме | Acid, Salt | o o n-hexyl 3a | | |
|---|-----------------|----------------------|------|----------------------|-------------------------|--|--|
| | 1a | (1.2 equiv) 2a | | Solvent Temp, 24h | | | |
| | entry | acid | salt | solvent | yield (%) ^f | | |
| | 1 | TfOH | | Су | 63 | | |
| | 2 | TfOH | KF | Су | 50 | | |
| | 3 | TfOH | KCI | Су | 94 | | |
| | 4 | TfOH | KBr | Су | 90 | | |
| | 5 | TfOH | KI | Су | 81 | | |
| | 6 | TfOH | NaCl | Су | 61 | | |
| | 7 | Benzenesulfonic acid | KCI | Су | 8 | | |
| | 8 | TFA | KCI | Су | N.D. | | |
| | 9 | PivOH | KCI | Су | N.D. | | |
| | 10 | Methanesolfonic acid | KCI | Су | Trace | | |
| | 11 | | KCI | Су | N.D. | | |
| | 12 | | | Су | N.D. | | |
| | 13 | TfOH | KCI | Hexane | 58 | | |
| | 14 | TfOH | KCI | toluene | 40 | | |
| | 15 | TfOH | KCI | <i>p</i> -xylene | 46 | | |
| | 16 | TfOH | KCI | PhOMe | 37 | | |
| | 17 | TfOH | KCI | dioxane | N.D. | | |
| | 19 | TfOH | KCI | THF | N.D. | | |
| | 20 | TfOH | KCI | MeCN | N.D. | | |
| | 21 | TfOH | KCI | DMF | N.D. | | |
| | 22 | TfOH | KCI | DMSO | N.D. | | |
| | 23 ^b | TfOH | KCI | Су | 90 | | |
| | 24 ^c | TfOH | KCI | Су | 90 | | |
| | 25 ^d | TfOH | KCI | Су | 72 | | |
| - | 26 ^e | TfOH | KCI | Су | 68 | | |

^{*a*} Reaction conditions: a mixture of **1a** (0.2 mmol), **2a** (0.24 mmol, 1.2 equiv), acid (0.14 mmol, 0.7 equiv), and salt (0.2 mmol) in a solvent (2 mL) was heated at 130 °C for 24 h under N₂; ^{*b*} acid (0.8 mmol, 0.4 equiv); ^{*c*} 90 °C; ^{*d*} 1 h; ^{*e*} no 4Å MS; ^{*f*} GC yield using tridecane as an internal standard.

$$\begin{array}{c} O \\ R_1 \\ O \\ O \\ O \\ R_1 \end{array} + HO - R_2 \xrightarrow{\text{TfOH, KCl}} O \\ 4 \text{Å MS, solvent, 130 °C, 24 h} \\ \textbf{a} \\ \textbf{b} \\ \textbf{c} \end{array}$$

An oven dried 25 mL Schlenk tube with 4Å MS (150 mg) were charged with ester **a** (0.2 mmol), alcohol **b** (0.24 mmol, 1.2 equiv.) and KCl (0.2 mmol, 1.0 equiv.). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and solvent (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether as eluent. The crude product was purified by PTLC eluting with petroleum ether.

2.4 Substituent effect at benzene ring of ester.



A typical experimental procedure (taking the reaction of methyl 4-methoxybenzoate 7a with phenol 8b as an example): An oven dried 25 mL Schlenk tube with 4Å MS (90 mg) was charged with methyl 4-methoxybenzoate 7a (0.2 mmol), phenol 8b (2 equiv) and KF (1 equiv). Subsequently, HOTf (2 equiv) and cyclohexane (2 mL) was added under N₂. The reaction mixture was allowed to react at 150 °C for 1.5 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard.

| 2.5 | Su | bsti | tuent | eff | ect | at | benzene | ring | of | pheno | ls. |
|-----|----|------|-------|-----|-----|----|---------|------|----|-------|-----|
|-----|----|------|-------|-----|-----|----|---------|------|----|-------|-----|

| | O OMe | + R [] | HOTf 0.4 KF 0.2 <u>4Å MS</u> Cy, N ₂ , 150 | | | |
|--------|----------|-----------------|--|-----|-----|--------|
| 0.2 mn | nol | 2 equiv | | | | |
| 3a | | b | | | (| |
| R | OMe | ^t Bu | Ме | Н | CI | CF_3 |
| Yield | 14% | 18% | 20% | 27% | 35% | 42% |

A typical experimental procedure (taking the reaction of methyl benzoate **3a** with 4-methoxyphenol **7b** as an example): An oven dried 25 mL Schlenk tube with 4Å MS (90 mg) was charged with methyl benzoate **3a** (0.2 mmol), 4-methoxyphenol **7b** (2 equiv) and KF (1 equiv). Subsequently, HOTf (2 equiv) and cyclohexane (2 mL) was added under N₂. The reaction mixture was allowed to react at 150 °C for 1.5 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.

3. Characterization data of the products



p-tolyl (*3r*,5*r*,7*r*)-adamantane-1-carboxylate (1c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), *p*-cresol (43.2 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure 1c in 93% isolated yield (50.2 mg); white solid; mp 104-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 2.33 (s, 3H), 2.08-2.04 (m, 9H), 1.80-1.73 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 176.4, 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.



o-tolyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (2c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), *o*-cresol (26.0 mg, 0.24 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **2c** in 95% isolated yield (51.5 mg); white solid; mp 78-79 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.22-7.17 (m, 2H), 7.12 (dd, *J*₁ = *J*₂ = 7.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 2.16 (s, 3H), 2.09 (b, 9H), 1.81-1.75 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 175.8, 149.5, 131.0, 130.1, 126.8, 125.7, 121.8, 41.1, 38.9, 36.4, 27.9, 16.2. MS (EI): m/z = 270.1. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₂₂O₂ 271.1693; Found 271.1692.



2,6-dimethylphenyl (*3r,5r,7r*)-adamantane-1-carboxylate (3c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 2,6-dimethylphenol (36.6 mg, 0.3 mmol) and KF (17.4 mg, 0.3 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **3c** in 87% isolated yield (49.5 mg); white solid; mp 81-82 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.06-7.01 (m, 3H), 2.12 (b, 15H), 1.78 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 175.1, 148.1, 130.1, 128.5, 125.5, 41.3, 39.0, 36.5, 28.0, 16.3. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₂₄O₂ 285.1849; Found 285.1849.



4-ethylphenyl (3r,5r,7r)-adamantane-1-carboxylate (4c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 4-ethylphenol (36.6 mg, 0.3 mmol) and KF (17.4 mg, 0.3 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **4c** in 93% isolated yield (52,8 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.08-2.05 (m, 9H), 1.80-1.73 (m, 6H), 1.22 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 176.4, 149.0, 141.4, 128.6, 121.2, 41.0, 38.8, 36.5, 28.3, 27.9, 15.6. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₂₄O₂ 285.1849; Found 285.1849.



4-(tert-butyl)phenyl (3*r***,5***r***,7***r***)-adamantane-1-carboxylate (5c). ^[1] The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 4-(***tert***-butyl)phenol (60.1 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure 5c** in 73% isolated yield (45.5 mg); white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 2.08-2.05 (m, 9H), 1.80-1.73 (m, 6H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 176.3, 148.7, 148.2, 126.2, 120.8, 41.0, 38.7, 36.4, 34.4, 31.4, 27.9. GC-MS (EI): m/z = 312.1 ([M + H]⁺, 2), 165.1 (11), 135.1 (100), 79 (10), 135 (100), 107 (6), 93 (8), 79 (10), 67 (3), 55 (2). This compound is known.



4-methoxyphenyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (6c).^[2] The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 4-methoxyphenol (37.2 mg, 0.3 mmol) and KF (17.4 mg, 0.3 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **6c** in 84% isolated yield (48.1 mg); white solid. ¹H NMR (400 MHz, CDCl₃): δ 6.95 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.79, (s, 3H), 2.08-2.04 (m, 9H), 1.80-1.32 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 176.5, 157.0, 144.5, 122.2, 114.3, 55.6, 40.9, 38.8, 36.4, 27.9. GC-MS (EI): m/z = 287 ([M + H]⁺, 1), 286 (M⁺, 6), 258 (5), 163 (4), 135 (100), 124 (5), 107 (9), 93 (13), 79 (13), 67 (5), 55 (3). This compound is known.



phenyl (*3r*,5*r*,7*r*)-adamantane-1-carboxylate (8c).^[1] The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), phenol (28.2 mg, 0.3 mmol) and KF (17.4 mg, 0.3 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **8c** in 69% isolated yield (35.3 mg); white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.36 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 2.08-2.06 (m, 9H), 1.80-1.74 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 176.2, 151.1, 129.3, 125.5, 121.6, 41.0, 38.8, 36.5, 27.9. GC-MS (EI): m/z = 256 (M⁺, 2), 228 (1), 163 (24), 135 (100), 107 (10), 93 (17), 79 (18), 77 (7), 67 (6), 55 (3). This compound is known.



[1,1'-biphenyl]-2-yl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (9c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 2-phenylphenol (68.1 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **9c** in 80% isolated yield (53.1 mg); white solid; mp 108-109 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.32 (m, 7H), 7.29-7.28 (m, 1H), 7.07-7.05 (m, 1H), 1.97 (b, 3H), 1.80 (b, 6H), 1.72-1.63 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 176.0, 148.1, 137.5, 135.2, 130.8, 129.2, 128.4, 128.0, 127.3, 126.0, 122.8, 40.8, 38.5, 36.4, 27.8. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₂₄O₂ 333.1849; Found 333.1849.



4-chlorophenyl (*3r*,*5r*,*7r*)-adamantane-1-carboxylate (10c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 4-chlorophenol (38.5 mg, 0.3 mmol) and KF (15.1 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **10c** in 76% isolated yield (44.0 mg); white solid; mp 79-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 2.08-2.04 (m, 9H), 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 291.1146.



4-bromophenyl (3*r***,5***r***,7***r***)-adamantane-1-carboxylate (11c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 4-bromophenol (51.9 mg, 0.3 mmol) and KF (15.1 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure 11c** in 80% isolated yield (53.4 mg); white solid; mp 104-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 2.08-2.03 (m, 9H), 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 335.0641.



2,4,6-tribromophenyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (12c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 2,4,6-tribromophenol (132.3 mg, 0.4 mmol) and KF (5.8 mg, 0.1 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **12c** in 65% isolated yield (63.6 mg); white solid; mp 108-109 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (s, 2H), 2.15-2.10 (m, 9H), 1.82-1.75 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 173.3, 145.9, 134.8, 119.4, 118.5, 41.5, 38.8, 36.4, 27.8. HRMS (APCI-TOF) m/z: [M + K]⁺ Calcd for C₁₇H₁₇Br₃O₂ 582.8410; Found 582.8410.



2,3,5,6-tetrafluorophenyl (*3r,5r,7r*)-adamantane-1-carboxylate (13c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 2,3,5,6-tetrafluorophenol (66.4 mg, 0.4 mmol) and KF (5.8 mg, 0.1 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **13c** in 60% isolated yield (39.3 mg); white solid; mp 71-72 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.00-6.92 (m, 1H), 2.10 (b, 9H), 1.82-1.75 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 173.5, 146.0 (dddd, *J*₁ = 4.2 Hz, *J*₂ = *J*₃ = 12.1, Hz, *J*₄ = 246.4 Hz), 140.6 (dddd, *J*₁ = 2.2 Hz, *J*₂ = 4.6 Hz, *J*₃ = 15.2 Hz, *J*₄ = 248.2 Hz), 130.2 (dddd, *J*₁ = *J*₂ = 3.7 Hz, *J*₃ = *J*₄ = 18.0 Hz), 102.8 (tb, *J* = 22.9 Hz), 41.4, 38.6, 36.2, 27.7; ¹⁹F NMR (376 MHz, CDCl₃): δ

-139.43 (dd, *J*₁ = 9.8 Hz, *J*₂ = 21.8 Hz), -153.73 (dd, *J*₁ = 9.8 Hz, *J*₂ = 21.4 Hz). HRMS (ESI-TOF) m/z: [M - H]⁻ Calcd for C₁₇H₁₆F₄O₂ 327.1014; Found 327.1036.



3-(trifluoromethyl) phenyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (14c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 3-trifluoromethylphenol (64.8 mg, 0.4 mmol) and KF (15.1 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **14c** in 65% isolated yield (42.1 mg); white solid; mp 90-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.46 (m, 2H), 7.32 (b, 1H), 7.26-7.24 (m, 1H), 2.10-2.06 (m, 9H), 1.81-1.74 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 175.8, 151.2, 131.8 (q, *J* = 32.7 Hz), 129.8, 125.2, 123.6 (q, *J* = 270.8 Hz), 122.3 (q, *J* = 3.7 Hz), 118.9 (q, *J* = 3.8 Hz), 41.1, 38.7, 36.4, 27.8; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.65. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₈H₁₉F₃O₂ 325.1410; Found 325.1410.



p-tolyl pivalate (15c).^[2] The title compound was prepared according to the general procedure: methyl pivalate (23.2 mg, 0.2 mmol), *p*-cresol (43.2 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **15c** in 67% isolated yield (25.8 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.16 (d, *J* = 8.2 Hz, 2H), 6.97 - 6.88 (m, 2H), 2.33 (s, 3H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 177.30 (s), 148.88 (s), 135.16 (s), 129.86 (s), 121.16 (s), 39.04 (s), 27.18 (s), 20.88 (s). This compound is known.



4-(trifluoromethoxy) phenyl hexanoate (16c). The title compound was prepared according to the general procedure: methyl hexanoate (26.0 mg, 0.2 mmol), *p*-trifluoromethoxy phenol (71.2 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **16c** in 65% isolated yield (35.9 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.79-1.72 (m, 2H), 1.42-1.37 (m, 4H), 0.93 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.0, 149.0, 146.5, 122.9, 122.0, 120.4 (q, *J* = 255.8 Hz), 34.3, 31.2, 24.5, 22.3, 13.9; ¹⁹F NMR (376 MHz, CDCl₃): δ -58.14. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₃H₁₅F₃O₃ 277.1046; Found 277.1046.



naphthalen-2-yl hexanoate (17c).^[3] The title compound was prepared according to the general procedure: methyl hexanoate (26.0 mg, 0.2 mmol), 2-naphthol (57.7 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **17c** in 83% isolated yield (40.1 mg); white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.82 (m, 2H), 7.80-7.78 (m, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.50-7.43 (m, 2H), 7.22 (dd, *J*₁ = 2.4 Hz, *J*₂ = 8.8 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.84-1.76 (m, 2H), 1.46-1.37 (m, 4H), 0.95 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 148.4, 133.8, 131.4, 129.3, 127.7, 127.6, 126.5, 125.6, 121.2, 118.5, 34.4, 31.3, 24.7, 22.3, 13.9. GC-MS (EI): m/z = 243 ([M + H]⁺, 1), 242 (7), 144 (100), 127 (3), 115 (15), 99 (2), 89 (2), 71 (4), 63 (1), 55 (3). This compound is known.



p-tolyl 4-methoxybenzoate (18c).^[4] The title compound was prepared according to the general procedure: methyl anisate (33.2 mg, 0.2 mmol), *p*-cresol (43.2 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **18c** in 81% isolated yield (39.2 mg); white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.0, 163.8, 148.8, 135.2, 132.2, 129.9, 121.9, 121.4, 113.7, 55.4, 20.8. GC-MS (EI): m/z = 242 (M⁺, 4), 135 (100), 107 (9), 92 (8), 77 (16), 64 (5), 51 (2). This compound is known.



p-tolyl [1,1'-biphenyl]-4-carboxylate (19c). The title compound was prepared according to the general procedure: methyl [1,1'-biphenyl]-4-carboxylate (42.4 mg, 0.2 mmol), *p*-cresol (43.2 mg, 0.4 mmol) and KF (15.1 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **19c** in 77% isolated yield (44.3 mg); white solid; mp 128-129 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.50-7.39 (m, 3H), 7.24-7.10 (m, 4H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.3, 148.7, 146.2, 139.9, 135.5, 130.7, 130.0, 129.0, 128.4, 128.3, 127.3, 127.2, 121.4, 20.9. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₁₆O₂ 289.1223; Found 289.1223.



p-tolyl 4-fluorobenzoate (20c).^[5] The title compound was prepared according to the general procedure: methyl 4-fluorobenzoate (30.8 mg, 0.2 mmol), *p*-cresol (43.2 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **20c** in 50% isolated yield (23.0 mg); white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.22 (dd, *J*₁ = 5.2 Hz, *J*₂ = 8.4 Hz, 2H), 7.23-7.16 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1 (d, *J* = 253.6 Hz), 164.4, 148.6, 135.6, 132.7 (d, *J* = 9.4 Hz), 130.0, 125.9 (d, *J* = 2.8 Hz), 121.3, 115.7 (d, *J* = 22.1 Hz), 20.9; ¹⁹F NMR (376 MHz, CDCl₃): δ -104.65. GC-MS (EI): m/z = 231 ([M + H]⁺, 1), 230 (M⁺, 9), 123 (100), 95 (31), 75 (8), 69 (1), 51 (2). This compound is known.



3,5-dimethylphenyl 4-fluorobenzoate (21c). The title compound was prepared according to the general procedure: methyl 4-fluorobenzoate (30.8 mg, 0.2 mmol), 3,5-dimethylphenol (48.9 mg, 0.4 mmol) and KF (15.2 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.6 mmol, 3.0 equiv.) and hexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **21c** in 60% isolated yield (29.3 mg); white solid; mp 34-35 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.22-8.19 (m, 2H), 7.20-7.15 (m, 2H), 6.91-6.78 (m, 3H), 2.34 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1 (d, *J* = 253.4 Hz), 164.4, 150.7, 139.4, 132.7 (d, *J* = 9.3 Hz), 127.7, 126.0 (d, *J* = 3.0 Hz), 119.2, 115.7 (d, *J* = 22.0 Hz), 21.2; ¹⁹F NMR (376 MHz, CDCl₃): δ -104.70. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₃FO₂ 245.0972; Found 245.0972.



3,5-dimethylphenyl 4-chlorobenzoate (22c). The title compound was prepared according to the general procedure: methyl 4-chlorobenzoate (34.1 mg, 0.2 mmol), 3,5-dimethylphenol (48.9 mg, 0.4 mmol) and KF (15.2 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.6 mmol, 3.0 equiv.) and hexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **22c** in 65% isolated yield (33.9 mg); white solid; mp 93-94 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.91 (s, 1H), 6.82 (s, 2H), 2.34 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 164.6, 150.6, 140.0, 139.4, 131.5, 128.9, 128.2, 127.8, 119.1, 21.2. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₃ClO₂ 261.0677; Found 261.0677.



3,5-dimethylphenyl thiophene-3-carboxylate (23c). The title compound was prepared according to the general procedure: methyl thiophene-3-carboxylate (28.4 mg, 0.2 mmol), 3,5-dimethylphenol (48.9 mg, 0.4 mmol) and KCl (19.4 mg, 0.26 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 140 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **23c** in 56% isolated yield (26.0 mg); white solid; mp 58-59 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.28 (dd, $J_1 = 1.2$ Hz, $J_2 = 3.2$ Hz, 1H), 7.65 (dd, $J_1 = 1.2$ Hz, $J_2 = 5.2$ Hz, 1H), 7.37 (dd, $J_1 = 2.8$ Hz, $J_2 = 4.8$ Hz, 1H), 6.90 (s, 1H), 6.81 (s, 2H), 2.38 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 161.3, 150.6, 139.3, 133.8, 133.1, 128.2, 127.6, 126.2, 119.2, 21.2. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₃H₁₂O₂S 233.0631; Found 233.0631.



hexyl benzoate (24c).^[6] The title compound was prepared according to the general procedure: methyl benzoate (27.2 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **24c** in 90% isolated yield (37.1 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.43 (dd, *J*₁ = *J*₂ = 7.6 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.80-1.73 (m, 2H), 1.48-1.41 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 132.7, 130.5, 129.5, 128.3, 65.1, 31.4, 28.6, 25.7, 22.5, 14.0. GC-MS (EI): m/z = 206 (M⁺, 1). 123 (100), 105 (92), 84 (14), 77 (42), 69 (12), 56 (25), 51 (9). This compound is known.



(1r,3r,5r,7r)-adamantan-2-yl benzoate (25c).^[16] The title compound was prepared according to the general procedure: methyl benzoate (27.2 mg, 0.2 mmol), (1r,3r,5r,7r)-adamantan-2-ol (36.5 mg, 0.24 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **25c** in 71% isolated yield (36.4 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.12–8.07 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.19 (s, 1H), 2.17 (d, *J* = 15.0 Hz, 4H), 1.94–1.81 (m, 6H), 1.78 (s, 2H), 1.64 (d, *J* = 11.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 165.86 (s), 132.72 (s), 131.16 (s), 129.57 (s), 128.33 (s), 37.42 (s), 36.38 (s), 32.07 (s), 27.36 (s), 27.05 (s). This compound is known.



hexyl 4-methylbenzoate (27c).¹⁶¹ The title compound was prepared according to the general procedure: methyl 4-methylbenzoate (30.0 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **27c** in 83% isolated yield (36.5 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 1H), 1.79-1.72 (m, 2H), 1.48-1.40 (m, 2H), 1.36-1.31 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 143.4, 129.5, 129.0, 127.8, 64.9, 31.4, 28.7, 25.7, 22.5, 21.6, 14.0. GC-MS (EI): m/z = 220 (M⁺, 2), 137 (82), 136 (72), 119 (100), 107 (1), 91 (53), 84 (6), 77 (2), 65 (19), 56 (13). This compound is known.



hexyl 3-methylbenzoate (28c).^[6] The title compound was prepared according to the general procedure: methyl 3-methylbenzoate (30.0 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **28c** in 98% isolated yield (43.1 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.83 (m, 2H), 7.37-7.30 (m, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.80-1.73 (m, 2H), 1.48-1.41 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 138.0, 133.5, 130.4, 130.0, 128.2, 126.6, 65.0, 31.4, 28.7, 25.7, 22.5, 21.2, 14.0. GC-MS (EI): m/z = 220 (M⁺, 5), 149 (1), 137 (81), 136 (88), 119 (100), 93 (16), 92 (16), 91 (65), 84 (8), 77 (2), 69 (7), 65 (18), 56 (18), 55 (10). This compound is known.



hexyl 2-methylbenzoate (29c).^[6] The title compound was prepared according to the general procedure: methyl 2-methylbenzoate (30.0 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **29c** in 75% isolated yield (33.0 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.91 (dd, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 11H), 7.41-7.37 (m, 11H), 7.25-7.23 (m, 2H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.60 (s, 3H), 1.79-1.72 (m, 2H), 1.48-1.41 (m, 2H), 1.36-1.32 (m, 4H), 0.904 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.8, 140.0, 131.8, 131.6, 130.5, 123.0, 125.6, 64.9, 31.4, 28.7, 25.8, 22.5, 21.7, 14.0. GC-MS (EI): m/z = 221 ([M + H⁺], 2), 220 (M⁺, 15), 137 (40), 136 (80), 119 (65), 118 (100), 107 (1), 91 (48), 90 (11), 84 (5), 69 (4), 65 (17), 56 (8), 55 (7). This compound is known.



hexyl 4-methoxybenzoate (**30c**).^[6] The title compound was prepared according to the general procedure: methyl 4-methoxybenzoate (33.2 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **30c** in 85% isolated yield (40.1 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 1.78-1.71 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.4, 163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 31.5, 28.7, 25.7, 22.5, 14.0. GC-MS (EI): m/z = 237 ([M + H]⁺, 1), 236 (M⁺, 3), 152 (100), 135 (65), 107 (9), 92 (9), 77 (15), 64 (4), 55 (4). This compound is known.



hexyl 3,4,5-trimethoxybenzoate (31c).^[7] The title compound was prepared according to the general procedure: methyl 3,4,5-trimethoxybenzoate (45.2 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **31c** in 80% isolated yield (47.3 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.31 (s, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 3.91 (b, 9H), 1.81-1.74 (m, 2H), 1.44 (b, 2H), 1.35-1.34 (m, 4H), 0.92-0.89 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 152.7, 141.9, 125.4, 106.6, 65.1, 60.7, 56.0, 31.3, 28.5, 25.5, 22.4, 13.8. GC-MS (EI): m/z = 297 ([M + H]⁺, 9), 296 (M⁺ 52), 225 (2), 212 (100), 197 (30), 195 (28), 169 (5), 154 (4), 93 (7), 77 (3), 55 (4). This compound is known.



hexyl [1,1'-biphenyl]-4-carboxylate (32c). The title compound was prepared according to the general procedure: methyl [1,1'-biphenyl]-4-carboxylate (42.4 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **32c** in 93% isolated yield (52.5 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.46 (dd, *J*₁ = *J*₂ = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 4.34 (t, *J* = 6.8 Hz, 3H), 1.82-1.74 (m, 2H), 1.50-1.42 (m, 2H), 1.37-1.34 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 145.5, 140.0, 130.0, 129.2, 128.9, 128.1, 127.2, 127.0, 65.1, 31.5, 28.7, 25.7, 22.6, 14.0. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₂₂O₂ 283.1693; Found 283.1693.



hexyl 4-fluorobenzoate (33c).^[6] The title compound was prepared according to the general procedure: methyl 4-fluorobenzoate (30.8 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **33c** in 86% isolated yield (38.5 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (dd, $J_1 = 5.6$ Hz, $J_2 = 9.2$ Hz, 2H), 7.11 (dd, $J_1 = J_2 = 8.8$ Hz, 2H), 4.30 (t, J = 6.4 Hz, 2H), 1.79-1.72 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.7, 165.6 (d, J = 252.0Hz), 132.0 (d, J = 9.3 Hz), 126.7 (d, J = 2.9 Hz), 115.4 (d, J = 22.0 Hz), 65.3, 31.4, 28.6, 25.7, 22.5, 14.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -106.07. GC-MS (EI): m/z = 224 (M⁺, 1), 141 (62), 140 (15), 123 (100), 95 (38), 84 (27), 75 (12), 69 (17), 56 (38), 55 (15). This compound is known.



hexyl 3-fluorobenzoate (34c). The title compound was prepared according to the general procedure: methyl 3-fluorobenzoate (30.8 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **34c** in 85% isolated yield (38.1 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.82 (m, 1H), 7.74-7.70 (m, 1H), 7.44-7.39 (m, 1H), 7.28-7.23 (m, 1H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.80-1.73 (m, 2H), 1.48-1.40 (m, 2H), 1.36-1.32 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.5 (d, *J* = 3.0 Hz), 162.5 (d, *J* = 245.5 Hz), 132.7 (d, *J* = 7.3 Hz), 129.9 (d, *J* = 7.8 Hz), 125.2 (d, *J* = 2.9 Hz), 119.8 (d, *J* = 21.2 Hz), 1 16.4 (d, *J* = 22.7 Hz), 65.5, 31.4, 28.6, 25.6, 22.5, 14.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -112.51. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₃H₁₇FO₂ 225.1285; Found 225.1286.



hexyl 4-chlorobenzoate (35c).¹⁶¹ The title compound was prepared according to the general procedure: methyl 4-chlorobenzoate (34.1 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **35c** in 90% isolated yield (43.2 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 1.79-1.72 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.31 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.7, 139.1, 130.8, 128.9, 128.6, 65.3, 31.4, 28.6, 25.6, 22.5, 13.9. GC-MS (EI): m/z = 240 (M⁺, 2), 159 (25), 158 (22), 157 (³⁷Cl, 74), 156 (52), 141 (³⁷Cl, 32), 139 (³⁵Cl, 100), 113 (³⁷Cl, 19), 111 (³⁵Cl, 41), 84 (52), 75 (20), 69 (29), 56 (74), 55 (26). This compound is known.



hexyl 4-bromobenzoate (36c).¹⁶¹ The title compound was prepared according to the general procedure: methyl 4-bromobenzoate (43.0 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **36c** in 89% isolated yield (50.5 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 1.79-1.72 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 131.6, 131.1, 129.40 127.9, 65.4, 31.4, 28.6, 25.7, 22.5, 14.0. GC-MS (EI): m/z = 286 (M⁺, ⁸¹Br, 2), 284 (M⁺, ⁷⁹Br, 2), 202 (⁸¹Br, 72), 201 (⁸¹Br, 81), 200 (⁷⁹Br, 81), 199 (⁷⁹Br, 78), 184 (⁸¹Br, 97), 182 (⁷⁹Br, 100), 157 (⁸¹Br, 41), 155 (⁷⁹Br, 36), 104 (10), 84 (79), 77 (11), 76 (39), 69 (42), 56 (97), 55 (37). This compound is known.



hexyl 2-bromobenzoate (37c).^[8] The title compound was prepared according to the general procedure: methyl 2-bromobenzoate (43.0 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **37c** in 80% isolated yield (45.4 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (dd, $J_1 = 2.0$ Hz, $J_2 = 7.6$ Hz, 1H), 7.65 (dd, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz, 1H), 7.38-7.29 (m, 2H), 4.34 (t, J = 6.8 Hz, 2H), 1.80-1.73 (m, 2H), 1.49-1.41 (m, 2H), 1.36-1.31 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 134.2, 132.6, 132.3, 131.1, 127.1, 121.5, 65.8, 31.4, 28.5, 25.6, 22.5, 14.0. GC-MS (EI): m/z = 286 (M⁺, ⁸¹Br, 3), 284 (M⁺, ⁷⁹Br, 3), 202 (⁸¹Br, 97), 201 (⁸¹Br, 63), 200 (⁷⁹Br, 100), 199 (⁷⁹Br, 57), 184 (⁸¹Br, 84), 182 (⁷⁹Br, 88), 156 (⁸¹Br, 23), 154 (⁷⁹Br, 10), 84 (18), 76 (8), 76 (23), 75 (17), 69 (18), 56 (42), 55 (24). This compound is known.



hexyl 4-iodobenzoate (38c).^[9] The title compound was prepared according to the general procedure: methyl 4-iodobenzoate (52.4 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **38c** in 85% isolated yield (56.4 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 1.79-1.72 (m, 2H), 1.46-1.39 (m, 2H), 1.36-1.31 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 137.7, 131.0, 130.0, 100.6, 65.4, 31.5,

28.6, 25.7, 22.6, 14.0. GC-MS (EI): m/z = 332 (M⁺, 6), 248 (31), 247 (100), 230 (50), 202 (17), 121 (5), 104 (9), 84 (10), 76 (29), 56 (20), 55 (11). This compound is known.



hexyl 4-iodo-3-methylbenzoate (39c). The title compound was prepared according to the general procedure: methyl 3-iodo-4-methylbenzoate (55.2 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **39c** in 86% isolated yield (59.5 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.90-7.87 (m, 2H), 7.50 (dd, $J_1 = 1.6$ Hz, $J_2 = 8.0$ Hz, 1H), 4.30 (t, J = 6.8 Hz, 2H), 2.47 (s, 3H), 1.79-1.72 (m, 2H), 1.46-1.39 (m, 2H), 1.36-1.31 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 141.7, 139.1, 130.5, 130.2, 128.0, 107.2, 65.3, 31.4, 28.6, 28.0, 25.6, 22.5, 14.0. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₄H₁₉IO₂ 347.0503; Found 347.0503.



hexyl 4-(trifluoromethyl) benzoate (40c).^[6] The title compound was prepared according to the general procedure: methyl 4-trifluoromethylbenzoate (40.8 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure 40c in 87% isolated yield (47.6 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 6.4 Hz, 2H), 1.82-1.75 (m, 2H), 1.48-1.41 (m, 2H), 1.37-1.32 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 134.3 (q, *J* = 32.4 Hz), 133.7, 129.9, 125.3 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 270.9 Hz), 65.7, 31.4, 28.6

25.6, 22.5, 14.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -63.09. GC-MS (EI): m/z = 256 ([M + H]⁺ - F, 1), 255 (M⁺ - F, 8), 191 (41), 173 (100), 145 (56), 144 (2), 125 (7), 95 (9), 84 (64), 69 (35), 56 (84), 55 (29). This compound is known.



hexyl 4-nitrobenzoate (41c).^[6] The title compound was prepared according to the general procedure: methyl 4-nitrobenzoate (36.2 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **41c** in 77% isolated yield (38.6 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.29 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 4.37 (t, *J* = 6.8 Hz, 2H), 1.83-1.76 (m, 2H), 1.49-1.42 (m, 2H), 1.37-1.34 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.7, 150.4, 135.9, 130.6, 123.5, 66.1, 31.4, 28.5, 25.6, 22.5, 14.0. MS (EI): m/z = 235 ([M⁺ - O], 1), 221 (1), 169 (13), 168 (24), 151 (17), 150 (62), 120 (19), 104 (36), 92 (20), 84 (54), 83 (25), 76 (32), 75 (10), 69 (43), 65 (11), 56 (100), 55 (43), 50 (10). This compound is known.



hexyl 2-naphthoate (42c).^[6] The title compound was prepared according to the general procedure: methyl 2-naphthoate (37.2 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **42c** in 83% isolated yield (42.5 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.60 (s, 1H), 8.07 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.60-7.52 (m, 2H), 4.38 (t, J = 6.8 Hz, 2H), 1.85-1.78 (m, 2H), 1.52-1.45 (m, 2H), 1.39-1.35 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 135.5, 132.5, 130.9, 129.3, 128.1, 128.1, 127.8, 127.7, 126.6, 125.3, 65.3, 31.5, 28.7, 25.7, 22.6, 14.0. GC-MS (EI): m/z = 257 ([M + H]⁺, 3), 256 (17), 172 (100), 155 (40), 127 (38), 101 (2), 77 (4), 55 (3). This compound is known.



hexyl 1-naphthoate (43c).^[10] The title compound was prepared according to the general procedure: methyl 1-naphthoate (37.2 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **43c** in 87% isolated yield (44.6 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.90 (d, *J* = 8.8 Hz, 1H), 8.18 (dd, *J*₁ = 1.2 Hz, *J*₂ = 7.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.88, (d, *J* = 7.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.55-7.48 (m, 2H), 4.41 (t, *J* = 6.8 Hz, 2H), 1.86-1.79 (m, 2H), 1.53-1.46 (m, 2H), 1.40-1.33 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.7, 133.8, 133.2, 131.3, 130.0, 128.5, 127.6, 127.5, 126.1, 125.8, 124.5, 65.3, 31.5, 28.7, 25.8, 22. 6, 14.0. GC-MS (EI): m/z = 257 ([M + H]⁺, 3), 256 (17), 172 (100), 155 (45), 144 (1), 127 (44), 101 (2), 77 (5), 55 (3). This compound is known.

hexyl 2-phenylacetate (44c).^[11] The title compound was prepared according to the general procedure: methyl 2-phenylacetate (30.0 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **44c** in 93% isolated yield (40.9 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.23 (m, 5H), 4.08 (t, *J* = 6.8 Hz, 2H), 3.60 (s, 2H), 1.63-1.56 (m, 2H), 1.33-1.24 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 171.6, 134.2, 129.2, 128.5, 127.0, 65.0, 41.4, 31.3, 28.4, 25.4, 22.4, 13.9. GC-MS (EI): m/z = 220 (M⁺, 3), 137 (23), 136 (49), 129 (28), 119 (6), 92 (41), 91 (100), 85 (7), 65 (16), 57 (20), 51 (2). This compound is known.



hexyl 2,2-diphenylacetate (45c).^[12] The title compound was prepared according to the general procedure: methyl 2,2-diphenylacetate (45.2 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure 45c in 80% isolated yield (47.4 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.30 (m, 8H), 7.28-7.22 (m, 2H), 5.01 (s, 1H), 4.14 (t, *J* = 6.8 Hz, 2H), 1.64-1.57 (m, 2H), 1.30-1.24 (m, 6H), 0.85 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 138.8, 128.6, 128.5, 127.2, 65.3, 57.2, 31.3, 28.4, 25.4, 22.4, 13.9. GC-MS (EI): m/z = 297 ([M + H]⁺, 1), 296 (M⁺, 5), 168 (16), 167 (100), 165 (15), 152 (9), 85 (1), 57 (2). This compound is known.



hexyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (46c).^[13] The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 1-hexanol (24.5 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **46c** in 85% isolated yield (44.9 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 4.04 (t, *J* = 6.8 Hz, 2H), 2.01 (b, 3H), 1.88 (d, *J* = 3.2 Hz, 6H), 1.75-1.68 (m, 6H), 1.64-1.57 (m, 2H), 1.37-1.28 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 177.8, 64.2, 40.7, 38.9, 36.6, 31.4, 28.6, 28.0, 25.6, 22.5, 14.0. GC-MS (EI): m/z = 181 (100), 163 (1), 135 (99), 121 (4), 107 (12), 93 (18), 84 (6), 79 (19), 67 (6), 55 (7). This compound is known.



(1*R*,3*R*,5*R*,7*R*)-adamantan-2-yl (3*R*,5*R*,7*R*)-adamantane-1-carboxylate (47c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 2-adamantanol (60.9 mg, 0.4 mmol) and KF (11.6 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (90 mg). After charging N₂ for three times, TfOH (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 150 °C for 10 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **47c** in 70% isolated yield (43.9 mg); white solid; mp 261-263 °C. ¹H NMR (400 MHz, CDCl₃): δ 4.88 (t, *J* = 2.8 Hz, 1H), 2.02 (b, 5H), 1.96 (b, 2H), 1.92 (b, 6H), 1.86-1.83 (m, 4H), 1.78 (b, 2H), 1.73 (b, 8H), 1.57 (b, 1H), 1.54 (b, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 177.0, 76.0, 40.9, 39.0, 37.4, 36.6, 36.3, 31.9, 31.8, 28.0, 27.3, 27.0. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₂₁H₃₀O₂ 315.2319; Found 315.2319.

3-cyclohexylpropyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (48c). The title compound was prepared according to the general procedure: adamantan-1-carboxylic acid methyl ester (38.9 mg, 0.2 mmol), 3-cyclohexyl-1-propanol (34.1 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **48c** in 84% isolated yield (51.2 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 3.95 (t, *J* = 6.8 Hz, 2H), 1.94 (b, 3H), 1.81 (d, *J* = 2.8 Hz, 6H), 1.68-1.60 (m, 9H), 1.57-1.53 (m, 4H), 1.18-1.10 (m, 6H), 0.85-0.76 (m, 2H); ¹³C NMR (100

MHz, CDCl₃): δ 177.8, 64.5, 40.7, 38.9, 37.3, 36.5, 33.6, 33.3, 28.0, 26.6, 26.3, 26.0. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₂₀H₃₂O₂ 305.2475; Found 305.2475.



phenethyl 2-naphthoate (49c).^[14] The title compound was prepared according to the general procedure: methyl 2-naphthoate (37.2 mg, 0.2 mmol), phenethyl alcohol (29.3 mg, 0.24 mmol) and KCl (14.9 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **49c** in 80% isolated yield (44.1 mg); white solid; mp 68-69 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.57 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.60-7.51 (m, 2H), 7.36-7.31 (m, 4H), 7.26-7.24 (m, 1H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 137.9, 135.5, 132.4, 131.0, 129.3, 129.0, 128.5, 128.2, 128.1, 127.7, 127.5, 126.6, 125.2, 65.6, 35.3. MS (EI): m/z = 276 (M⁺, 3), 173 (13), 172 (100), 155 (41), 127 (46), 104 (36), 91 (2), 77 (8). This compound is known.



hexyl cinnamate (50c).¹⁶¹ The title compound was prepared according to the general procedure: methyl cinnamate (32.4 mg, 0.2 mmol), 1-hexanol (40.9 mg, 0.4 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **50c** in 90% isolated yield (41.7 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.39-7.37 (m, 3H), 6.45 (d, *J* = 16.4 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 1.74-1.67 (m, 2H), 1.44-1.31 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 144.5, 134.4, 130.2, 128.8, 128.0, 118.2, 64.7, 31.4, 28.6, 25.6, 22.5, 14.0. GC-MS (EI): m/z = 233 ([M + H]⁺, 2), 232 (M⁺,

11), 189 (13), 149 (26), 148 (89), 147 (67), 132 (11), 131 (100), 104 (13), 103 (57), 102 (11), 77 (34), 56 (11), 55 (10). This compound is known.



hexyl 2-(4-isobutylphenyl) propanoate (51c).^[15] The title compound was prepared according to the general procedure: methyl 2-(4-isobutylphenyl) propanoate (44.1 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **51c** in 83% isolated yield (48.1 mg); colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.89-1.79 (m, 1H), 1.59-1.52 (m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.28-1.24 (m, 6H), 0.89 (d, *J* = 6.4 Hz, 6H), 0.85 (t, *J* = 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 7.40.4, 137.9, 129.2, 127.1, 64.8, 45.2, 45.0, 31.3, 30.2, 28.5, 25.4, 22.5, 22.4, 18.4, 13.9. GC-MS (EI): m/z = 291 ([M + H]⁺, 2), 290 (9), 206 (8), 162 (15), 161 (100), 119 (19), 117 (10), 105 (6), 91 (10), 83 (3), 57 (9), 55 (6). This compound is known.



hexyl 4-(*N***,***N***-dipropylsulfamoyl) benzoate (52c).** The title compound was prepared according to the general procedure: methyl 4-(*N*,*N*-dipropylsulfamoyl) benzoate (59.8 mg, 0.2 mmol), 1-hexanol (30.6 mg, 0.3 mmol) and KBr (23.8 mg, 0.2 mmol) were added to a 25 mL Schlenk tube with 4Å MS (150 mg). After charging N₂ for three times, TfOH (0.14 mmol, 0.7 equiv.) and cyclohexane (2 mL) were added. The reaction mixture was heated at 130 °C for 24 hours. After completion, the reaction mixture was concentrated under vacuum. The crude product was purified by PTLC eluting with petroleum ether to afford analytically pure **52c** in 80% isolated yield (59.1 mg); colorless liquid. ¹H NMR (400 MHz,

CDCl₃): δ 8.16 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 4.35 (t, J = 6.4 Hz, 2H), 3.10 (t, J = 7.6 Hz, 4H), 1.82-1.75 (m, 2H), 1.60-1.50 (m, 4H), 1.48-1.41 (m, 2H), 1.37-1.32 (m, 4H), 0.93-0.85 (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 144.1, 133.8, 130.4, 127.0, 65.8, 49.9, 31.4, 28.6, 25.7, 22.6, 22.0, 14.0, 11.2. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₃₁O₄SN 370.2047; Found 370.2047.

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

¹H NMR Spectrum of *p*-tolyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (1c)


















¹H NMR Spectrum of phenyl (3r,5r,7r)-adamantane-1-carboxylate (8c)























¹³C NMR Spectrum of 2,3,5,6-tetrafluorophenyl (3r,5r,7r)-adamantane-1-carboxylate (13c)



¹⁹F NMR Spectrum of 2,3,5,6-tetrafluorophenyl (3r,5r,7r)-adamantane-1-carboxylate (13c)

| 389 | 415 | 447 | 474 | 691 | 717 | 748 | 775 |
|------|------|------|------|------|------|------|------|
| 139. | 139. | 139. | 139. | 153. | 153. | 153. | 153. |
| Ľ | Ľ | 4 | - | Ľ | 4 | Ż | 1 |







20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)



¹H NMR Spectrum of 4-(trifluoromethoxy)phenyl hexanoate (16c)



¹⁹F NMR Spectrum of 4-(trifluoromethoxy)phenyl hexanoate (16c)













20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)

























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¹⁹F NMR Spectrum of hexyl 3-fluorobenzoate (34c)



¹³C NMR Spectrum of hexyl 4-chlorobenzoate (35c)



¹³C NMR Spectrum of hexyl 4-bromobenzoate (36c)














¹H NMR Spectrum of hexyl 4-nitrobenzoate (41c)



¹H NMR Spectrum of hexyl 2-naphthoate (42c)







¹H NMR Spectrum of hexyl 2-phenylacetate (44c)







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H NMR Spectrum of (1R,3R,5R,7R)-adamantan-2-yl (3R,5R,7R)-adamantane-1-carboxylate (47c)



¹³C NMR Spectrum of (1R,3R,5R,7R)-adamantan-2-yl (3R,5R,7R)-adamantane-1-carboxylate (47)









¹H NMR Spectrum of hexyl cinnamate (50c)







¹H NMR Spectrum of hexyl 4- (N,N-dipropylsulfamoyl) benzoate (52c)