Supporting Information

Cooperation of *Cis* Vicinal Acceptors for Donor–Acceptor Cyclopropane Activation: TfOH-Promoted Ring-Opening/Aryl Shift

Rearrangement to 3- and 5-Ylidenebutenolides

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1. General information

All reactions were carried out under dry argon atmosphere. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures. All glassware was oven-dried before use.

NMR spectra were recorded on a Brucker 500 MHz (¹H: 500 MHz, ¹³C: 125 MHz and ¹⁹F: 470 MHz) or Brucker 600 MHz (¹H: 600 MHz, ¹³C: 150 MHz) in CDCl₃ at 298 K. ¹H and ¹³C NMR spectra in CDCl₃ were internally referenced to the proton (¹H) of the internal TMS signal at 0.00 ppm and the residual carbon nuclei (¹³C) of the solvent signal at 77.16 ppm, respectively. ¹⁹F NMR spectra were referenced to external standard CFCl₃ at 0.00 ppm. The data are reported in ppm as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br s = broad singlet, coupling constant(s) in Hz, integration). High resolution mass spectra were determined on a Brucker MAXIS impact mass spectrometer (ESI) or a Waters GCT Premier micromass spectrometer (EI). Melting points were obtained by SGW X4 Micro Melting Point Apparatus.

Substituted methyl benzoylformates¹ and 2-acylcyclopropane-1-carboxylates² were prepared according to the procedures reported in the literatures.

2. Preparation of new DACs

Method A:



A modified procedure according to the literature:^{2a} To a stirred solution of α , β unsaturated ketone **5a** (500.1 mg, 2.252 mmol, 1.0 equiv) and methyl benzoylformate **6a** (425.7 mg, 2.593 mmol, 1.2 equiv) in DCM (6.0 mL) cooled at -78 °C, was added dropwise P(NMe₂)₃ (496.1 mg, 3.040 mmol, 1.3 equiv) via microsyringe. Upon complete addition of P(NMe₂)₃, the solution was warmed to rt and vigorously stirred at rt. After the reaction was completed as monitored by TLC, the mixture was concentrated under vacuum and purified by flash column chromatography on silica gel eluted with PE/Et₂O/DCM (40/0.5/1 to 7/0.5/1, v/v/v) to afford the corresponding products **1a** (518.3 mg, 62%) and *trans*-**1a** (294.5 mg, 35%).

Method B:



The same procedure as reported in the literature:^{2b} To a solution of α -Ketoester **S1** (360.9 mg, 2.025 mmol, 2.0 equiv) and dimethyl phosphite phosphite (0.18 mL, 2.0 mmol, 2.0 equiv) in THF (6.0 mL) cooled at -15 °C, was added dropwise 1.0 M LiHMDS in THF (2.0 mL, 2.0 mmol) at -15 °C. After additional 10 min, a solution of α , β -unsaturated ketone **S2** (222.6 mg, 1.001 mmol, 1.0 equiv) in THF (3.0 mL) was added dropwise. The reaction was stirred at the same temperature and was monitored by TLC. Once the α , β -unsaturated ketone was fully consumed (2 h), the reaction mixture was quenched with saturated aqueous ammonium chloride. After being warmed to rt, the mixture was extracted with ethyl acetate. The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (30/1 to 10/1, v/v) to give the product **1c** (338.7 mg, 88%).



Known compound.^{2b}

Method A: 459.3 mg, 62% (based on **5a**: 500.1 mg, 2.252 mmol).

Colorless solid. $PE/Et_2O/DCM = 40/0.5/1$ to 7/0.5/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.99 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.21 (br s, 5H), 7.14-7.11 (m, 3H), 6.92-6.90 (m, 2H), 3.79 (d, J = 6.5 Hz, 1H), 3.73 (d, J = 6.5 Hz, 1H), 3.65 (s, 3H), 2.44 (s, 3H) ppm.



trans**-1a**

Method A: 276.1 mg, 35% (based on 5a: 500.1 mg, 2.252 mmol).

Single-crystals for X-ray analysis were obtained from PE and EA at rt.

Colorless crystals. M.p. 158.2-159.1 °C. PE/Et₂O/DCM = 40/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.35-7.30 (m, 4H), 7.28-7.22 (m, 6H), 4.41 (d, *J* = 7.0 Hz, 1H), 3.99 (d, *J* = 7.0 Hz, 1H), 3.42 (s, 3H), 2.45 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 193.6, 170.1, 144.4, 135.6, 135.4, 134.9, 130.2, 129.6, 128.9, 128.7, 128.5, 128.0, 127.4, 52.9, 48.8, 35.5, 35.3, 21.9 ppm.

IR (neat): 3062 (w), 2952 (w), 1719 (s), 1672 (s), 1449 (m), 1428 (s), 1266 (s), 1207 (s), 1183 (s), 1162 (s), 806 (m), 745 (m), 716 (m), 698 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₂₂O₃Na 393.1461; Found 393.1462.



Method B: 338.7 mg, 88% (based on α , β -unsaturated ketone: 222.6 mg, 1.001 mmol). Colorless solid. M.p. 113.9-114.2 °C. PE/EA = 30/1 to 10/1.

¹**H** NMR (500 MHz, CDCl₃): δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.5 Hz, 2H), 3.74 (d, *J* = 6.5 Hz, 1H), 3.66 (d, *J* = 6.5 Hz, 1H), 3.64 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 196.1, 170.9, 137.7, 136.5, 133.4, 132.1, 131.3, 130.5, 129.3, 128.8, 128.4, 128.1, 52.9, 47.7, 37.3, 37.2, 21.3, 21.1 ppm.

IR (neat): 2946 (w), 1736 (s), 1661 (s), 1517 (m), 1451 (m), 1263 (s), 1152 (s), 1026 (m), 818 (s), 805 (s), 700 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₂₄O₃Na 407.1618; Found 407.1614.



Method B: 385.9 mg, 75% (based on α , β -unsaturated ketone: 286.9 mg, 0.9990 mmol). Colorless solid. M.p. 103.7-104.5 °C. PE/EA = 30/1 to 10/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.74 (d, *J* = 6.5 Hz, 1H), 3.64 (s, 3H), 3.62 (d, *J* = 7.0 Hz, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 195.1, 170.0, 137.2, 133.8, 133.7, 133.1, 132.3, 131.9, 131.5, 129.8, 129.0, 128.4, 122.5, 121.3, 53.1, 47.1, 36.9, 36.5 ppm.

Note: The crystals contain ca. 0.25 *mol/mol of cyclohexane* (δ 1.43 ppm and 27.0 ppm). **HRMS (ESI)** m/z: [M+Na]⁺ Calcd for C₂₄H₁₈Br₂O₃Na 534.9515; Found 534.9517.



Method B: 366.3 mg, 79% (based on α , β -unsaturated ketone: 242.7 mg, 1.000 mmol). Colorless solid. M.p. 102.6-103.8 °C. PE/EA = 30/1 to 10/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.05 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0

Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.76 (d, *J* = 7.0 Hz, 1H), 3.64 (s, 3H), 3.63 (d, *J* = 7.0 Hz, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 195.2, 170.1, 137.3, 134.3, 133.7, 133.3, 133.1, 132.6, 132.0, 129.4, 129.01, 128.98, 128.6, 128.4, 53.1, 47.0, 36.9, 36.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈Cl₂O₃Na 447.0525; Found 447.0524.



Method B: 330.7 mg, 84% (based on α , β -unsaturated ketone: 226.1 mg, 0.9992 mmol). Colorless solid. M.p. 153.6-155.7 °C. PE/EA = 30/1 to 10/1.

¹**H NMR** (600 MHz, CDCl₃): δ 8.06 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.18-7.16 (m, 2H), 6.92 (t, *J* = 8.4 Hz, 2H), 6.89-6.84 (m, 4H), 3.77 (d, *J* = 6.6 Hz, 1H), 3.65 (s, 3H), 3.63 (d, *J* = 7.2 Hz, 1H) ppm.

¹³**C** NMR (125 MHz, CDCl₃): δ 195.4, 170.4, 162.4 (C-F, ¹*J*_{C-F} = 246.4 Hz), 162.0 (C-F, ¹*J*_{C-F} = 244.6 Hz), 137.4, 133.6, 132.4 (C-F, ³*J*_{C-F} = 8.1 Hz), 130.5 (C-F, ⁴*J*_{C-F} = 2.8 Hz), 130.0 (C-F, ⁴*J*_{C-F} = 2.8 Hz), 129.6 (C-F, ³*J*_{C-F} = 8.1 Hz), 129.0, 128.4, 115.7 (C-F, ²*J*_{C-F} = 21.8 Hz), 115.3 (C-F, ²*J*_{C-F} = 20.8 Hz), 53.0, 46.9, 37.1, 36.4 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –113.4, –115.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈F₂O₃Na 415.1116; Found 415.1118.



Method A: 276.1 mg, 56% (based on α , β -unsaturated ketone: 276.4 mg, 1.000 mmol). Colorless solid. M.p. 90.5-91.3 °C. PE/Et₂O/DCM = 30/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.89 (d, *J* = 7.0 Hz, 1H), 3.76 (d, *J* = 6.5 Hz, 1H), 3.67 (s, 3H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 194.8, 169.6, 138.7, 137.9, 137.1, 133.9, 131.0, 130.6 (C-F, ²*J*_{C-F} = 32.6 Hz), 129.6 (C-F, ²*J*_{C-F} = 32.4 Hz), 129.1, 128.5, 128.4, 125.8 (C-F, ³*J*_{C-F} = 4.4 Hz), 125.4 (C-F, ³*J*_{C-F} = 4.4 Hz), 124.1 (C-F, ¹*J*_{C-F} = 270.8 Hz), 123.9 (C-F, ¹*J*_{C-F} = 269.7 Hz) ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –62.6, –62.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₁₈F₆O₃Na 515.1052; Found 515.1054.



Method A: 313.0 mg, 30% (based on α , β -unsaturated ketone: 574.7 mg, 2.001 mmol). Colorless solid. M.p. 132.7-133.3 °C. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.41 (s, 1H), 7.39-7.37 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.13-7.08 (m, 3H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.75 (d, *J* = 7.0 Hz, 1H), 3.67 (d, *J* = 7.0 Hz, 1H) 3.66 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 195.0, 169.8, 137.2, 137.0, 136.1, 133.8, 133.6, 131.5, 131.4, 130.4, 130.1, 129.8, 129.3, 129.0, 128.5, 126.6, 122.6, 122.4, 53.2, 47.2, 36.54, 36.49 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈Br₂O₃Na 534.9515; Found 534.9526.



Method A: 601.1 mg, 77% (based on α , β -unsaturated ketone: 452.4 mg, 1.999 mmol). Colorless solid. M.p. 131.1-132.2°C. PE/Et₂O/DCM = 30/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.10 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.0 Hz, 1H), 7.20 (q, J = 6.5 Hz, 1H), 7.12 (q, J = 6.5 Hz, 1H), 7.03-6.97 (m, 2H), 6.89 (t, J = 9.0 Hz, 1H), 6.83 (t, J = 7.0 Hz, 1H), 6.66 (t, J = 7.5 Hz, 1H), 4.09 (d, J = 7.5 Hz, 1H), 3.83 (d, J = 7.5 Hz, 1H), 3.64 (s, 3H) ppm. ¹³**C NMR** (125 MHz, CDCl₃): δ 194.6, 169.8, 162.3 (C-F, ¹ $J_{C-F} = 246.4$ Hz), 162.1

(C-F, ${}^{1}J_{C-F} = 248.1$ Hz), 137.1, 133.6, 131.8 (C-F, ${}^{3}J_{C-F} = 3.6$ Hz), 130.0 (C-F, {}^{3}J_{C-F} = 3.6 Hz), 130.0 (C-F, {}^{3}

8.1 Hz), 128.9, 128.8 (C-F, ${}^{3}J_{C-F} = 8.3$ Hz), 128.6, 127.9 (C-F, ${}^{4}J_{C-F} = 2.6$ Hz), 124.1 (C-F, ${}^{4}J_{C-F} = 2.8$ Hz), 123.6 (C-F, ${}^{3}J_{C-F} = 3.6$ Hz), 122.1 (C-F, ${}^{2}J_{C-F} = 13.5$ Hz), 122.0 (C-F, ${}^{2}J_{C-F} = 12.6$ Hz), 115.7 (C-F, ${}^{2}J_{C-F} = 21.6$ Hz), 115.5 (C-F, ${}^{2}J_{C-F} = 21.6$ Hz), 53.0, 41.1, 35.9, 30.5 (d, J = 4.5 Hz) ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –113.3, –116.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈F₂O₃Na 415.1116; Found 415.1118.



Method B: 218.7 mg, 50% (based on α , β -unsaturated ketone: 289.8 mg, 1.009 mmol). Colorless solid. M.p. 157.4-158.8 °C. PE/EA = 40/1 to 10/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.12 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.56-7.51 (m, 3H), 7.29-7.28 (m, 2H), 7.18-7.17 (m, 3H), 7.00-6.98 (m, 2H), 6.67-6.65 (m, 1H), 4.11 (d, *J* = 7.5 Hz, 1H), 3.84 (d, *J* = 7.5 Hz, 1H), 3.64 (s, 3H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 195.2, 170.4, 137.4, 134.5, 134.2, 133.6, 133.0, 130.0, 129.0, 128.6, 128.5, 128.4, 128.0, 127.9, 127.0, 126.8, 52.9, 46.7, 37.6, 35.6 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₉BrO₃Na 457.0410; Found 457.0407.



Method A: 317.0 mg, 37% (based on α , β -unsaturated ketone: 551.3 mg, 1.997 mmol). Colorless solid. M.p. 103.9-104.4 °C. PE/Et₂O/DCM = 40/1/1 to 10/1/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.64 (d, *J* = 7.0 Hz, 1H), 7.49-7.44 (m, 2H), 7.42-7.39 (m, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.21-7.20 (m, 2H), 7.14-7.13 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.07 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 6.5 Hz, 1H), 3.73 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 198.5, 170.2, 139.6, 136.0, 134.0, 132.8, 132.3, 131.3, 130.6, 130.0, 129.9, 129.6, 128.40, 128.36, 128.1, 128.0, 127.4, 126.3, 53.1, 48.9, 38.3, 36.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈Cl₂O₃Na 447.0525; Found 447.0519.



Method B: 272.3 mg, 76% (based on α , β -unsaturated ketone: 242.6 mg, 1.000 mmol). Colorless oil. PE/Et₂O/DCM = 30/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.05 (s, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.22 (br s, 5H), 7.13 (br s, 3H), 6.91 (br s, 2H), 3.80 (d, *J* = 6.5 Hz, 1H), 3.67 (d, *J* = 6.0 Hz, 1H), 3.65 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 194.8, 170.4, 139.1, 135.3, 134.7, 134.0, 133.4, 130.6, 130.2, 128.6, 128.5, 128.19, 128.15, 128.1, 127.1, 126.5, 53.0, 48.5, 37.6, 36.8 ppm.
HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₉ClO₃Na 413.0915; Found 413.0906.



Method B: 336.1 mg, 77% (based on α , β -unsaturated ketone: 287.7 mg, 1.002 mmol). Colorless oil. PE/Et₂O/DCM = 30/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.20 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.22 (br s, 5H), 7.14-7.13 (m, 3H), 6.91-6.90 (m, 2H), 3.80 (d, *J* = 7.0 Hz, 1H), 3.67 (d, *J* = 7.0 Hz, 1H), 3.65 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 194.7, 170.4, 139.3, 136.3, 134.7, 134.0, 131.5, 130.6, 130.5, 128.6, 128.21, 128.16, 128.1, 127.1, 127.0, 123.3, 53.0, 48.5, 37.6, 36.8 ppm.
HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₉BrO₃Na 457.0410; Found 457.0400.



Method A: 222.4 mg, 29% (based on α , β -unsaturated ketone: 456.1 mg, 2.016 mmol). Colorless solid. M.p. 106.4-107.5 °C. PE/Et₂O/DCM = 30/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.85 (t, J = 7.5 Hz, 1H), 7.57 (q, J = 6.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.25-7.24 (m, 2H), 7.20-7.19 (m, 4H), 7.11-7.10 (m, 3H), 6.91-6.90 (m, 2H), 3.87 (dd, J = 6.5, 1.5 Hz, 1H), 3.81 (d, J = 6.5 Hz, 1H), 3.67 (s, 3H) ppm. ¹³**C NMR** (125 MHz, CDCl₃): δ 194.9 (C-F, ³*J*_{C-F} = 2.6 Hz), 170.5, 162.0 (C-F, ¹*J*_{C-F} = 251.9 Hz), 135.1, 134.9 (C-F, ³*J*_{C-F} = 9.0 Hz), 134.1, 131.0 (C-F, ³*J*_{C-F} = 2.8 Hz), 130.6, 128.5, 128.2, 128.02, 127.96, 126.9, 126.7 (C-F, ${}^{2}J_{C-F} = 12.6$ Hz), 124.8 (C-F, ${}^{4}J_{C-F} = 2.8$ Hz), 116.8 (C-F, ${}^{2}J_{C-F} = 23.5$ Hz), 52.9, 49.7, 39.8 (C-F, ${}^{4}J_{C-F} = 8.1$ Hz), 38.1 ppm. ¹⁹F NMR (470 MHz, CDCl₃): δ –110.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₉FO₃Na 397.1210; Found 397.1212.



Method B: 269.7 mg, 68% (based on α,β-unsaturated ketone: 246.5 mg, 1.016 mmol). Colorless solid. M.p. 95.8-96.5 °C. PE/Et₂O/DCM = 30/0.5/1 to 10/0.5/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.18 (br s, 5H), 7.11 (br s, 3H), 6.89 (br s, 2H), 3.79 (d, *J* = 6.5 Hz, 1H), 3.74 (d, *J* = 6.5 Hz, 1H), 3.71 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 199.1, 170.3, 139.7, 134.8, 133.9, 132.3, 131.5, 130.6, 130.5, 129.8, 128.5, 128.2, 128.1, 128.0, 127.3, 126.9, 53.0, 49.9, 39.9, 38.8 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₉ClO₃Na 413.0915; Found 413.0917.



Method B: 333.7 mg, 76% (based on α,β-unsaturated ketone: 289.3 mg, 1.007 mmol). Colorless solid. M.p. 96.3-97.1 °C. PE/Et₂O/DCM = 30/0.5/1 to 10/0.5/1. ¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.18 (br s, 5H), 7.11 (br s, 3H), 6.90 (br s, 2H), 3.81 (d, J = 6.0 Hz, 1H), 3.72 (s, 3H), 3.70 (d, J = 7.0 Hz, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 199.8, 170.3, 141.9, 134.8, 133.9, 133.8, 132.2, 130.5, 129.5, 128.5, 128.2, 128.1, 127.8, 127.0, 119.3, 53.0, 50.1, 39.7, 38.8 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₉BrO₃Na 457.0410; Found 457.0404.



Method A: 297.5 mg, 39% (based on α , β -unsaturated ketone: 474.7 mg, 2.009 mmol).

Colorless oil. $PE/Et_2O/DCM = 40/0.5/1$ to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.69 (s, 2H), 7.25-7.22 (m, 6H), 7.13-7.12 (m, 3H), 6.93-6.91 (m, 2H), 3.78 (d, *J* = 6.5 Hz, 1H), 3.73 (d, *J* = 7.0 Hz, 1H), 3.65 (s, 3H), 2.39 (s, 6H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 196.3, 170.7, 138.5, 137.8, 135.20, 135.15, 134.4, 130.6, 128.5, 128.2, 128.1, 128.0, 126.9, 126.2, 52.9, 48.3, 37.4, 36.8, 21.4 ppm.
HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₂₄O₃Na 407.1618; Found 407.1615.



Method B: 316.5 mg, 82% (based on α , β -unsaturated ketone: 238.0 mg, 1.007 mmol). Colorless solid. M.p. 91.2-92.3 °C. PE/Et₂O/DCM = 30/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.20 (br s, 5H), 7.13-7.11 (m, 5H), 6.89-6.88 (m, 2H), 3.77 (d, *J* = 6.0 Hz, 1H), 3.66 (s, 3H), 3.60 (d, *J* = 6.5 Hz, 1H), 2.51 (s, 3H), 2.38 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 198.9, 170.7, 142.3, 138.8, 135.7, 135.2, 134.3, 132.9, 130.6, 129.3, 128.5, 128.2, 128.1, 127.9, 126.9, 126.6, 52.9, 48.7, 39.1, 37.6, 21.6. 21.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₂₄O₃Na 407.1618; Found 407.1617.



Method A: 478.1 mg, 52% (based on α , β -unsaturated ketone: 614.4 mg, 2.013 mmol). Colorless solid. M.p. 97.0-98.4 °C. PE/Et₂O/DCM = 30/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 8.31-8.30 (m, 1H), 8.05-8.03 (m, 1H), 7.25-7.19 (m, 6H), 7.15-7.14 (m, 3H), 6.91-6.90 (m, 2H), 3.79 (d, *J* = 6.5 Hz, 1H), 3.66 (s, 3H), 3.62 (d, *J* = 6.5 Hz, 1H) ppm.

¹³**C** NMR (125 MHz, CDCl₃): δ 193.3, 170.4, 162.3 (C-F, ¹*J*_{C-F} = 253.6 Hz), 135.0 (C-F, ³*J*_{C-F} = 3.6 Hz), 134.6, 134.3 (C-F, unresolved), 133.9, 130.6, 129.6 (C-F, ³*J*_{C-F} = 8.1 Hz), 128.6, 128.2, 128.14, 128.12, 127.2, 116.9 (C-F, ²*J*_{C-F} = 22.5 Hz), 110.2 (C-F, ²*J*_{C-F} = 21.6 Hz), 53.0, 48.3, 37.5, 36.7 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –98.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈BrFO₃Na 475.0316; Found 475.0321.



Method A: 250.2 mg, 39% (based on α , β -unsaturated ketone: 348.5 mg, 2.000 mmol). Colorless solid. M.p. 74.7-75.2 °C. PE/EA = 40/1 to 20/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.19-7.11 (m, 5H), 7.11-7.09 (m, 3H), 6.85-6.83 (m, 2H), 3.65 (s, 3H), 3.57 (d, J = 6.5 Hz, 1H), 3.15 (d, J = 6.5 Hz, 1H), 2.96 (hept, J = 7.0 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H), 1.23 (d, J = 7.0 Hz, 3H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 209.8, 170.4, 135.1, 134.2, 130.5, 128.5, 128.1, 128.04, 127.99, 126.8, 52.8, 48.6, 42.3, 37.6, 36.8, 18.3, 18.0 ppm.

IR (neat): 2977 (w), 1729 (s), 1703 (s), 1432 (m), 1256 (s), 1188 (m), 1153 (s), 1069 (m), 1059 (m), 695 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₂O₃Na 345.1461; Found 345.1455.



Method A: 174.9 mg, 27% (based on α , β -unsaturated ketone: 348.5 mg, 2.000 mmol). Colorless oil. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.35-7.24 (m, 10H), 3.80 (d, *J* = 7.5 Hz, 1H), 3.73 (d, *J* = 7.0 Hz, 1H), 3.36 (s, 3H), 2.83 (hept, *J* = 7.0 Hz, 1H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 207.7, 169.9, 135.2, 135.0, 130.2, 128.7, 128.5, 128.0, 127.4, 52.7, 48.8, 42.6, 36.6, 36.1, 17.9, 17.8 ppm.

IR (neat): 2968 (w), 1727 (s), 1703 (s), 1447 (m), 1253 (s), 1207 (s), 1156 (s), 1050 (m), 717 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₂O₃Na 345.1461; Found 345.1461.



Method B: 273.3 mg, 81% (based on α , β -unsaturated ketone: 174.5 mg, 1.002 mmol). Colorless oil. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.11-7.10 (m, 3H), 7.04 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.86-6.84 (m, 2H), 3.64 (s, 3H), 3.55 (d, J = 6.5 Hz, 1H), 3.12 (d, J = 6.5 Hz, 1H), 2.95 (hept, J = 7.0 Hz, 1H), 2.25 (s, 3H), 1.30 (d, J = 7.0 Hz, 3H), 1.22 (d, J = 6.5 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.9, 170.5, 137.8, 135.3, 131.1, 130.4, 129.2, 128.1, 128.0, 126.8, 52.8, 48.4, 42.4, 37.8, 36.8, 21.3, 18.3, 18.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1616.



Method A: 321.3 mg, 40% (based on α , β -unsaturated ketone: 349.2 mg, 2.004 mmol). Colorless oil. PE/Et₂O/DCM = 30/0.5/1 to 10/0.5/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.31 (d, J = 8.5 Hz, 2H), 7.15-7.12 (m, 3H), 7.01 (d, J = 8.5 Hz, 2H), 6.86-6.84 (m, 2H), 3.66 (s, 3H), 3.57 (d, J = 6.5 Hz, 1H), 3.09 (d, J = 6.5 Hz, 1H), 2.95 (hept, J = 7.0 Hz, 1H), 1.29 (d, J = 6.5 Hz, 3H), 1.22 (d, J = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.4, 170.0, 134.7, 133.4, 132.3, 131.7, 128.3, 128.1, 127.1, 122.3, 53.0, 47.7, 42.3, 37.5, 36.8, 18.3, 18.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₁BrO₃Na 423.0566; Found 423.0561.



Method B: 326.5 mg, 81% (based on α,β-unsaturated ketone: 255.2 mg, 1.008 mmol). Colorless solid. M.p. 72.9-74.0 °C. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.23-7.20 (m, 5H), 7.16-7.13 (m, 2H), 6.69 (d, J = 8.5 Hz, 2H), 3.65 (s, 3H), 3.51 (d, J = 6.5 Hz, 1H), 3.09 (d, J = 6.0 Hz, 1H), 2.95 (hept, J = 7.0 Hz, 1H), 1.30 (d, J = 7.0 Hz, 3H), 1.22 (d, J = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.4, 170.1, 134.3, 133.8, 131.2, 130.4, 129.7, 128.7, 128.2, 120.8, 52.9, 48.6, 42.4, 37.7, 36.1, 18.2, 18.0 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₁H₂₁BrO₃Na 423.0566; Found 423.0561.



Method B: 239.2 mg, 67% (based on α , β -unsaturated ketone: 174.3 mg, 1.001 mmol). Colorless solid. M.p. 64.7-66.1 °C. PE/EA = 40/1 to 20/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.16-7.12 (m, 5H), 7.07 (d, J = 9.0 Hz, 2H), 6.86-6.84 (m, 2H), 3.66 (s, 3H), 3.57 (d, J = 6.5 Hz, 1H), 3.10 (d, J = 6.5 Hz, 1H), 2.95 (hept, J = 7.0 Hz, 1H), 1.29 (d, J = 7.5 Hz, 3H), 1.22 (d, J = 7.5 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.5, 170.1, 134.7, 134.0, 132.8, 131.9, 128.8, 128.3, 128.1, 127.1, 53.0, 47.6, 42.3, 37.6, 36.8, 18.3, 18.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₁ClO₃Na 379.1071; Found 379.1074.



Method A: 77.1 mg, 23% (based on α , β -unsaturated ketone: 175.0 mg, 1.005 mmol). Colorless oil. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.13-7.10 (m, 5H), 6.88-6.83 (m, 4H), 3.66 (s, 3H), 3.56 (d, J = 6.5 Hz, 1H), 3.10 (d, J = 6.5 Hz, 1H), 2.95 (hept, J = 7.0 Hz, 1H), 1.30 (d, J = 7.0 Hz, 3H), 1.22 (d, J = 7.0 Hz, 3H) ppm.

¹³**C** NMR (125 MHz, CDCl₃): δ 209.6, 170.3, 162.4 (C-F, ¹*J*_{C-F} = 246.4 Hz), 134.8, 132.3 (C-F, ³*J*_{C-F} = 8.1 Hz), 130.1 (C-F, ⁴*J*_{C-F} = 3.6 Hz), 128.2, 128.1, 127.0, 115.5 (C-F, ²*J*_{C-F} = 21.6 Hz), 52.9, 47.6, 42.3, 37.8, 36.8, 18.3, 18.0 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –113.6 ppm.

HRMS(ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₁FO₃Na 363.1367; Found 363.1368.



Method B: 250.1 mg, 74% (based on α , β -unsaturated ketone: 175.1 mg, 1.005 mmol). Colorless oil. PE/EA = 40/1 to 20/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.12-7.09 (m, 3H), 7.06 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.96 (s, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.85-6.83 (m, 2H), 3.65 (s, 3H), 3.55 (d, J = 6.5 Hz, 1H), 3.13 (d, J = 6.5 Hz, 1H), 2.97 (hept, J = 7.0 Hz, 1H), 2.21 (s, 3H), 1.30 (d, J = 7.0 Hz, 3H), 1.22 (d, J = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.9, 170.5, 138.1, 135.2, 134.0, 131.2, 128.8, 128.3, 128.1, 128.0, 127.6, 126.8, 52.8, 48.5, 42.3, 37.7, 36.9, 21.4, 18.3, 18.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1619.



Method B: 263.4 mg, 73% (based on α , β -unsaturated ketone: 210.1 mg, 1.008 mmol). Colorless solid. M.p. 69.2-70.3 °C. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.22-7.20 (m, 3H), 7.17-7.15 (m, 2H), 7.09-7.06 (m, 1H), 7.02 (t, J = 8.5 Hz, 1H), 6.83 (t, J = 1.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 3.65 (s, 3H), 3.53 (d, J = 6.5 Hz, 1H), 3.13 (d, J = 6.0 Hz, 1H), 2.97 (hept, J = 7.0 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H), 1.23 (d, J = 6.5 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.4, 170.0, 137.4, 134.0, 133.7, 130.4, 129.2, 128.7, 128.3, 127.0, 126.2, 52.9, 48.6, 42.4, 37.5, 36.1, 18.2, 18.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₁ClO₃Na 379.1071; Found 379.1074.



Method B: 199.4 mg, 59% (based on α , β -unsaturated ketone: 190.1 mg, 1.010 mmol). Colorless oil. PE/EA = 40/1 to 20/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.12-7.11 (m, 4H), 7.09-7.06 (m, 2H), 7.02 (td, J = 7.5, 1.0 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 3.69 (s, 3H), 3.63 (d, J = 7.0 Hz, 1H), 3.34 (d, J = 6.5 Hz, 1H), 2.99 (hept, J = 7.0 Hz, 1H), 2.58 (s, 3H), 1.32 (d, J = 7.0 Hz, 3H), 1.26 (d, J = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 210.0, 170.6, 138.4, 134.3, 132.9, 130.2, 129.5, 128.3, 127.8, 127.0, 126.0, 125.4, 52.8, 48.1, 42.5, 35.6, 35.5, 20.1, 18.3, 18.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1615.



Method B: 282.1 mg, 81% (based on α , β -unsaturated ketone: 195.5 mg, 1.017 mmol). Colorless solid. M.p. 95.6-96.2 °C. PE/EA = 40/1 to 20/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.18-7.16 (m, 5H), 7.08 (dd, J = 8.5, 6.5 Hz, 1H), 6.96 (t, J = 9.0 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.54 (dd, J = 7.5, 6.5 Hz, 1H), 3.75 (d, J = 6.5 Hz, 1H), 3.68 (s, 3H), 3.27 (d, J = 7.0 Hz, 1H), 2.99 (hept, J = 7.0 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H), 1.26 (d, J = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 209.4, 170.2, 162.0 (C-F, ¹*J*_{C-F} = 245.5 Hz), 134.2, 129.9, 128.61 (C, ³*J*_{C-F} = 8.1 Hz), 130.59 (C-F, ⁴*J*_{C-F} = 3.6 Hz), 128.5, 128.0, 123.5 (C-F, ³*J*_{C-F} = 3.5 Hz), 122.5 (C-F, ²*J*_{C-F} = 13.5 Hz), 115.4 (C-F, ²*J*_{C-F} = 21.6 Hz), 52.9, 47.4, 42.3, 35.9 (C-F, ⁴*J*_{C-F} = 1.8 Hz), 30.7 (C-F, ³*J*_{C-F} = 4.5 Hz), 18.2, 18.0 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –115.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₁FO₃Na 363.1367; Found 363.1368.



Method B: 259.2 mg, 68% (based on α , β -unsaturated ketone: 174.2 mg, 1.000 mmol). Colorless oil. PE/EA = 40/1 to 15/1.

¹**H NMR** (600 MHz, CDCl₃): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.11-

7.10 (m, 3H), 6.85-6.83 (m, 2H), 3.86 (s, 3H), 3.66 (s, 3H), 3.61 (d, J = 6.0 Hz, 1H), 3.18 (d, J = 6.6 Hz, 1H), 2.98 (hept, J = 6.6 Hz, 1H), 1.30 (d, J = 6.6 Hz, 3H), 1.23 (d, J = 6.6 Hz, 3H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 209.4, 169.9, 166.8, 139.4, 134.5, 130.6, 129.7, 128.3, 128.0, 127.1, 53.0, 52.3, 48.0, 42.3, 37.3, 36.9, 18.2, 18.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₂₄O₅Na 403.1516; Found 403.1519.



Method B: 179.8 mg, 46% (based on α , β -unsaturated ketone: 176.3 mg, 1.012 mmol). Colorless oil. PE/EA = 40/1 to 10/1.

¹**H NMR** (600 MHz, CDCl₃): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.13-7.12 (m, 3H), 6.85-6.84 (m, 2H), 3.67 (s, 3H), 3.62 (d, *J* = 6.6 Hz, 1H), 3.15 (d, *J* = 6.6 Hz, 1H), 2.97 (hept, *J* = 7.2 Hz, 1H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H) ppm.

¹³**C** NMR (125 MHz, CDCl₃): δ 209.3, 169.8, 138.4, 134.4, 131.0, 130.1 (C-F, ²*J*_{C-F} = 26.3 Hz), 128.3, 128.0, 127.2, 125.4 (C-F, ³*J*_{C-F} = 3.6 Hz), 124.0 (C-F, ¹*J*_{C-F} = 270.8 Hz), 53.0, 47.7, 42.3, 37.3, 36.8, 18.2, 18.0 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –62.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₁F₃O₃Na 413.1335; Found 413.1336.



Method B: 322.7 mg, 82% (based on α , β -unsaturated ketone: 243.5 mg, 1.005 mmol). Colorless oil. PE/Et₂O/DCM = 40/1 to 10/1.

¹**H NMR** (600 MHz, CDCl₃): δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.23-7.19 (m, 3H), 7.16-7.14 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 3.66 (s, 3H), 3.61 (d, *J* = 6.0 Hz, 1H), 3.17 (d, *J* = 6.6 Hz, 1H), 2.97 (hept, *J* = 7.2 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 7.2 Hz, 3H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 209.3, 169.9, 139.5, 133.6, 130.4, 129.1 (C-F, ²*J*_{C-F} =

32.6 Hz), 128.8, 128.4, 125.0 (C-F, ³*J*_{C-F} = 3.3 Hz), 124.2 (C-F, ¹*J*_{C-F} = 269.6 Hz), 53.0, 48.9, 42.4, 37.8, 36.1, 18.2, 18.0 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –62.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₁F₃O₃Na 413.1335; Found 413.1340.



Method B: 256.6 mg, 74% (based on α , β -unsaturated ketone: 210.0 mg, 0.9202 mmol). Colorless solid. M.p. 119.6-120.6 °C. PE/EA = 40/1 to 20/1.

¹**H** NMR (500 MHz, CDCl₃): δ 7.26-7.22 (m, 3H), 7.16-7.15 (m, 2H), 6.45 (dd, J = 9.0, 6.5 Hz, 2H), 3.65 (s, 3H), 3.48 (d, J = 6.5 Hz, 1H), 3.05 (d, J = 6.5 Hz, 1H), 2.96 (hept, J = 7.0 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H), 1.23 (d, J = 7.0 Hz, 3H) ppm.

¹³**C** NMR (125 MHz, CDCl₃): δ 208.8, 169.6, 150.9 (C-F, ¹*J*_{C-F} = 248.1 Hz, ²*J*_{C-F} = 9.9 Hz, ³*J*_{C-F} = 4.5 Hz), 138.7 (C-F, ¹*J*_{C-F} = 250.0 Hz, ²*J*_{C-F} = 15.4 Hz), 133.2, 131.9 (C-F, m), 130.1, 128.9, 128.6, 112.2 (C-F, ²*J*_{C-F} = 16.3 Hz, ³*J*_{C-F} = 5.4 Hz), 53.0, 48.7, 42.4, 37.5, 35.3, 18.2, 17.9 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –134.6 (d, *J* = 21.6 Hz, 2F), –162.4 (t, *J* = 21.6 Hz, 1F) ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₁₉F₃O₃Na 399.1178; Found 399.1177.



Method A: 193.9 mg, 30% (bsed on α , β -unsaturated ketone: 350.9 mg, 2.014 mmol). Colorless oil. PE/Et₂O/DCM = 10/0.5/1 to 7/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.20-7.13 (m, 5H), 7.10-7.09 (m, 3H), 6.83-6.81 (m, 2H), 3.65 (s, 3H), 3.59 (d, *J* = 6.5 Hz, 1H), 3.09 (d, *J* = 6.5 Hz, 1H), 2.82-2.69 (m, 2H), 1.79-1.71 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 206.4, 170.4, 135.1, 134.1, 130.6, 128.5, 128.1, 128.04, 128.00, 126.8, 52.9, 48.4, 46.5, 39.1, 36.6, 17.5, 13.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₂O₃Na 345.1461; Found 345.1464.



Method A: 245.2 mg, 36% (based on α , β -unsaturated ketone: 378.7 mg, 2.011 mmol). Colorless oil. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.20-7.13 (m, 5H), 7.10-7.09 (m, 3H), 6.83-6.81 (m, 2H), 3.65 (s, 3H), 3.58 (d, *J* = 6.5 Hz, 1H), 3.08 (d, *J* = 6.5 Hz, 1H), 2.70-2.60 (m, 2H), 2.33-2.25 (m, 1H), 1.01 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 206.1, 170.3, 135.1, 134.1, 130.6, 128.5, 128.3, 128.03, 127.99, 126.8, 53.6, 52.8, 48.5, 39.3, 36.8, 24.9, 22.8, 22.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1618.



Method A: 183.8 mg, 31% (based on α , β -unsaturated ketone: 295.3 mg, 2.020 mmol). Colorless solid. M.p. 149.7-150.7 °C. PE/Et₂O/DCM = 40/0.5/1 to 10/0.5/1.

¹H NMR (500 MHz, CDCl₃): δ 7.20-7.13 (m, 5H), 7.11-7.09 (m, 3H), 6.83-6.81 (m, 2H), 3.66 (s, 3H), 3.60 (d, *J* = 6.5 Hz, 1H), 3.10 (d, *J* = 6.5 Hz, 1H), 2.49 (s, 3H) ppm.
¹³C NMR (125 MHz, CDCl₃): δ 204.0, 170.4, 134.9, 134.0, 130.7, 128.5, 128.10, 128.05, 128.0, 126.9, 53.0, 48.5, 39.8, 36.7, 31.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₁₈O₃Na 317.1148; Found 317.1147.



Method B: 274.6 mg, 81% (based on α , β -unsaturated ketone:189.3 mg, 1.005 mmol). Colorless solid. M.p. 100.7-101.3 °C. PE/EA = 40/1 to 20/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.19-7.09 (m, 8H), 6.86-6.84 (m, 2H), 3.66 (s, 3H), 3.55 (d, *J* = 6.0 Hz, 1H), 3.32 (d, *J* = 6.0 Hz, 1H), 1.33 (s, 9H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 210.9, 170.4, 135.2, 134.4, 130.4, 128.5, 128.09, 128.05, 128.0, 126.8, 52.8, 48.7, 44.7, 37.0, 34.7, 26.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1628.

3. Condition optimization



General procedure: To a dry Schlenk tube equipped with a high vacuum valve, **1a** (55.3 mg, 0.149 mmol) was dissolved in 2.0 mL of dry solvent with a stir bar. A certain equivalent of TfOH was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred overnight or about 14 h at rt, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL \times 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (50/1 to 30/1, v/v) to afford the product **3a** as orange solid. Single-crystals for X-ray analysis were obtained from PE and EA at rt.

entry	solvent	TfOH (equiv)	3a (%) (isolated)
1	DCM	2.0	53
2	DCM	3.0	89
3	DCM	3.5	99
4	DCM	5.0	83
5	DCE	3.5	75
6	PhMe	3.5	36
7	CH ₃ CN	3.5	18

Table S1. Condition Optimization



Yield: 50.1 mg, 99% (based on 1a: 55.3 mg, 0.149 mmol).

Orange crystals. M.p. 150.1-152.3 °C. PE/EA = 50/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.42-7.37 (m, 6H), 7.34-7.31 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 2.38 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.9, 154.5, 152.3, 141.5, 140.4, 138.5, 130.9, 130.8, 129.63, 129.56, 128.5, 128.1, 125.7, 125.1, 124.5, 102.8, 21.7 ppm.

IR (neat): 3027 (w), 2921 (w), 1762 (s), 1616 (m), 1508 (m), 1443 (m), 1282 (m), 1206 (s), 1057 (m), 1008 (s), 890 (s), 830 (s), 809 (s), 758 (s), 698 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₂Na 361.1199; Found 361.1207.

4. TfOH-promoted transformation of DACs



Representative procedure for 3: To a dry Schlenk tube equipped with a high vacuum valve, **1a** (55.3 mg, 0.149 mmol) was dissolved in DCM (2.0 mL) with a stir bar. TfOH (46.5 μ L, 0.525 mmol) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred overnight at rt, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (50/1 to 30/1, v/v) to afford the product **3a** (50.1 mg, 99%) as orange solid.



Yield: 38.4 mg, 75% (based on1b: 56.2 mg, 0.158 mmol).

Orange crystals. M.p. 163.9-165.8 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.68 (d, *J* = 7.0 Hz, 2H), 7.43-7.38 (m, 9H), 7.35-7.31 (m, 4H), 6.57 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.7, 154.3, 153.1, 141.4, 138.4, 130.88, 130.86, 130.0, 129.8, 129.7, 128.9, 128.54, 128.49, 128.1, 125.1, 124.3, 103.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₆O₂Na 347.1043; Found 347.1050.



Yield: 42.4 mg, 81% (based on 1c: 57.4 mg, 0.149 mmol).

Orange crystals. M.p. 164.5-164.7 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.66 (d, *J* = 7.0 Hz, 2H), 7.41-7.35 (m, 3H), 7.25-7.18 (m, 8H), 6.55 (s, 1H), 2.42 (s, 3H), 2.40 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 167.0, 153.8, 153.5, 140.15, 140.07, 138.8, 135.6, 131.1, 131.0, 129.8, 129.2, 128.8, 128.7, 125.0, 123.4, 104.1, 21.7, 21.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₂₀O₂Na 375.1356; Found 375.1352.



Yield: 67.1 mg, 92% (based on 1d: 77.8 mg, 0.151 mmol).

Orange crystals. M.p. 196.3-197.5 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H** NMR (500 MHz, CDCl₃): δ 7.68-7.67 (m, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.42-7.41 (m, 3H), 7.20 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.50 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ166.4, 155.1, 149.7, 139.8, 136.7, 132.5, 132.3, 132.0, 131.6, 130.5, 129.0, 128.1, 125.3, 124.9, 124.6, 124.4, 103.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₄Br₂O₂Na 502.9253; Found 502.9243.



Yield: 56.6 mg, 96% (based on 1e: 64.0 mg, 0.150 mmol).

Orange crystals. M.p. 174.5-175.9 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (600 MHz, CDCl₃): δ 7.68-7.67 (m, 2H), 7.42-7.40 (m, 5H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 166.4, 155.0, 149.7, 139.4, 136.3, 136.11, 136.07, 132.3, 132.1, 130.4, 129.03, 128.99, 128.6, 128.1, 125.2, 124.9, 103.1 ppm.
HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₄Cl₂O₂Na 415.0263; Found 415.0260.



Yield: 53.7 mg, 99% (based on 1f: 59.3 mg, 0.151 mmol).

Orange crystals. M.p. 150.7-152.3 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (600 MHz, CDCl₃): δ 7.68-7.66 (m, 2H), 7.42-7.39 (m, 3H), 7.33-7.28 (m, 4H), 7.13 (t, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 6.51 (s, 1H) ppm.

¹³**C** NMR (150 MHz, CDCl₃): δ 166.6, 163.8 (C-F, ¹*J*_{C-F} = 249.2 Hz), 163.6 (C-F, ¹*J*_{C-F} = 250.2 Hz), 154.6, 150.4, 137.3 (C-F, ⁴*J*_{C-F} = 3.3 Hz), 134.1 (C-F, ⁴*J*_{C-F} = 3.3 Hz), 133.0 (C-F, ³*J*_{C-F} = 7.7 Hz), 132.8 (C-F, ³*J*_{C-F} = 8.7 Hz), 130.3, 129.0, 128.3, 125.2, 124.4, 115.9 (C-F, ²*J*_{C-F} = 21.8 Hz), 115.4 (C-F, ²*J*_{C-F} = 21.6 Hz), 103.3 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –110.0, –110.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₄F₂O₂Na 383.0854; Found 383.0853.



Yield: 33.3 mg, 48% (based on 1g: 73.8 mg, 0.150 mmol).

Orange crystals. M.p. 153.8-155.7 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.71-7.69 (m, 4H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.45-7.42 (m, 7H), 6.52 (s, 1H) ppm.

¹³**C** NMR (150 MHz, CDCl₃): δ 166.0, 156.4, 148.0, 144.2, 141.2, 131.6 (C-F, ²*J*_{C-F} = 32.6 Hz), 131.5 (C-F, ²*J*_{C-F} = 32.6 Hz), 131.0, 130.88, 130.86, 129.1, 127.8, 126.6,

125.8 (C-F, ${}^{3}J_{C-F} = 3.3 \text{ Hz}$), 125.5, 125.4 (C-F, ${}^{3}J_{C-F} = 3.3 \text{ Hz}$), 124.1 (C-F, ${}^{1}J_{C-F} = 270.8 \text{ Hz}$), 123.9 (C-F, ${}^{1}J_{C-F} = 269.3 \text{ Hz}$), 102.5 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –62.77, –62.85 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₁₄F₆O₂Na 483.0790; Found 483.0798.



Yield: 60.4 mg, 83% (based on 1h: 77.8 mg, 0.151 mmol).

Orange crystals. M.p. 156.7-158.9 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.70-7.68 (m, 2H), 7.59-7.56 (m, 2H), 7.43-7.42 (m, 5H), 7.33-7.28 (m, 3H), 7.24-7.23 (m, 1H), 6.51 (s, 1H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 166.1, 155.7, 148.4, 142.7, 139.7, 133.25, 133.17, 132.82, 132.78, 130.6, 130.3, 129.9, 129.3, 129.2, 129.0, 128.0, 125.9, 125.4, 123.0, 122.4, 102.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₄Br₂O₂Na 502.9253; Found 502.9256.



Yield: 44.1 mg, 82% (based on 1i: 59.0 mg, 0.150 mmol).

Yellow crystals. M.p. 122.5-123.8 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (600 MHz, CDCl₃): δ 7.69-7.68 (m, 2H), 7.44-7.37 (m, 5H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.18-7.12 (m, 4H), 6.34 (d, *J* = 1.8 Hz, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 165.5, 160.4 (C-F, ¹*J*_{C-F} = 248.3 Hz), 159.8 (C-F, ¹*J*_{C-F} = 250.0 Hz), 155.7, 137.6, 131.8 (C-F, ⁴*J*_{C-F} = 2.6 Hz), 131.4, 131.3 (C-F, ³*J*_{C-F} = 3.6 Hz), 131.1 (C-F, ³*J*_{C-F} = 8.1 Hz), 130.5, 128.9, 128.4, 128.2, 127.9 (C-F, ²*J*_{C-F} = 13.6 Hz), 125.9 (C-F, ²*J*_{C-F} = 14.4 Hz), 125.5, 124.4 (C-F, ³*J*_{C-F} = 3.6 Hz), 124.0 (C-F, ³*J*_{C-F} = 3.5 Hz), 116.6 (C-F, ²*J*_{C-F} = 21.6 Hz), 115.8 (C-F, ²*J*_{C-F} = 21.6 Hz), 102.6 (C-F, ⁴*J*_{C-F} = 1.9 Hz) ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –111.6, –112.7 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₃H₁₄F₂O₂Na 383.0854; Found 383.0853.



Yield: 50.7 mg, 83% (based on 1j: 65.8 mg, 0.151 mmol).

Yellow solid. PE/EA = 40/1 to 20/1.

The major isomer. Yellow crystals. M.p. 142.0-143.8 °C. Crystals were obtained from PE and EA at rt.

¹**H NMR** (600 MHz, CDCl₃): δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.42-7.38 (m, 9H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 166.1, 156.0, 149.1, 140.0, 139.2, 133.3, 130.8, 130.4, 130.1, 129.7, 129.0, 128.7, 128.3, 127.7, 126.1, 125.4, 123.2, 101.9 ppm.

130.1, 129.7, 129.0, 120.7, 120.3, 127.7, 120.1, 125.4, 125.2, 101.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅BrO₂Na 425.0148; Found 425.0136.



Yield: 54.7 mg, 93% (based on 1k: 64.0 mg, 0.150 mmol).

Yellow crystals. M.p. 127.1-128.8 °C. PE/EA = 40/1 to 20/1. Single-crystals for X-ray analysis were obtained from PE and EA at rt.

¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, *J* = 6.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41-7.39 (m, 5H), 7.37-7.30 (m, 5H), 7.25-7.23 (m, 1H) ppm.
¹³C NMR (125 MHz, CDCl₃): δ 165.3, 152.1, 149.6, 139.3, 137.9, 133.3, 132.2, 131.2, 130.9, 130.6, 130.12, 130.08, 130.01, 129.96, 129.2, 128.8, 127.2, 127.0, 126.7, 126.0, 108.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₄Cl₂O₂Na 415.0263; Found 415.0261.



Yield: 57.2 mg, 94% (based on 11: 65.9 mg, 0.151 mmol).

Orange crystals. M.p. 165.1-167.3 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.53 (s, 4H), 7.44-7.38 (m, 6H), 7.34-7.30 (m, 4H), 6.56 (s, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 166.4, 153.9, 153.2, 141.3, 138.3, 132.2, 130.9, 130.8, 129.9, 129.8, 128.6, 128.2, 127.4, 126.5, 124.2, 124.1, 104.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅BrO₂Na 425.0148; Found 425.0142.



Yield: 52.1 mg, 97% (based on 1m: 58.6 mg, 0.150 mmol).

Orange crystals. M.p. 173.3-174.2 °C. PE/EA = 40/1 to 20/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.44-7.37 (m, 8H), 7.35-7.30 (m, 4H), 6.55 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.4, 153.8, 153.1, 141.3, 138.3, 135.9, 130.9, 130.8, 129.9, 129.8, 129.2, 128.6, 128.1, 127.0, 126.3, 124.1, 104.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅ClO₂Na 381.0653; Found 381.0648.



Yield: 50.5 mg, 98% (based on **1n**: 56.2 mg, 0.150 mmol).

Orange crystals. M.p. 209.9-212.2 °C. PE:EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.68-7.65 (m, 2H), 7.45-7.38 (m, 6H), 7.35-7.30 (m, 4H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.50 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.6, 163.7 (C-F, ¹*J*_{C-F} = 250.0 Hz), 153.3 (C-F, ⁴*J*_{C-F} = 6.3 Hz), 141.4, 138.3, 130.9, 130.8, 129.8, 129.7, 128.6, 128.1, 127.1 (C-F, ³*J*_{C-F} = 8.1 Hz), 124.9, 124.8, 124.2, 116.1 (C-F, ²*J*_{C-F} = 22.6 Hz), 103.3 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –109.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅FO₂Na 365.0948; Found 365.0951.



Yield: 48.3 mg, 87% (based on **1o**: 60.7 mg, 0.151 mmol).

Orange crystals. M.p. 167.4-168.3 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.50-7.40 (m, 6H), 7.36-7.31 (m, 4H), 6.75 (s, 1H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 165.8, 156.9, 151.7, 148.1, 141.0, 137.9, 134.3, 131.02, 131.01, 130.5, 130.4, 128.7, 128.2, 125.6, 124.3, 123.6, 107.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅NO₄Na 392.0893; Found 392.0884.



Yield: 24.6 mg, 46% (based on 1p: 58.4 mg, 0.151 mmol).

Orange crystals. M.p. 157.4-158.2 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.41-7.37 (m, 6H), 7.34-7.31 (m, 4H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.44 (s, 1H), 3.85 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 167.0, 161.2, 154.3, 151.5, 141.6, 138.6, 130.9, 130.8, 129.54, 129.46, 128.5, 128.1, 126.8, 124.5, 121.2, 114.4, 101.7, 55.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₄H₁₈O₃Na 377.1148; Found 377.1148.



Yield: 49.4 mg, 98% (based on 1q: 55.3 mg, 0.149 mmol).

Orange crystals. M.p. 106.1-107.4 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹H NMR (500 MHz, CDCl₃): δ 7.50 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.43-7.37 (m, 6H), 7.35-7.27 (m, 5H), 7.19 (d, J = 7.5 Hz, 1H), 6.54 (s, 1H), 2.37 (s, 3H) ppm.
¹³C NMR (125 MHz, CDCl₃): δ 166.8, 154.4, 152.8, 141.5, 138.6, 138.4, 130.91, 130.88, 130.86, 129.7, 129.6, 128.8, 128.5, 128.4, 128.1, 125.7, 124.4, 122.3, 103.5, 21.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₂Na 361.1199; Found 361.1191.



Yield: 53.3 mg, 99% (based on 1r: 58.5 mg, 0.150 mmol).

Orange crystals. M.p. 130.2-132.8 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.65 (s, 1H), 7.55-7.54 (m, 1H), 7.44-7.38 (m, 6H), 7.35-7.33 (m, 4H), 7.31-7.30 (m, 2H), 6.57 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.3, 154.4, 152.7, 141.2, 138.2, 135.1, 130.91, 130.88, 130.3, 130.2, 130.0, 129.93, 129.89, 128.6, 128.2, 125.1, 123.9, 123.2, 104.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅ClO₂Na 381.0653; Found 381.0651.



Yield: 59.9 mg, 95% (based on 1s: 68.3 mg, 0.157 mmol).

Orange crystals. M.p. 150.6-151.8 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.81 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.44-7.38 (m, 6H), 7.35-7.27 (m, 5H), 6.57 (s, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 166.3, 154.5, 152.6, 141.2, 138.2, 132.8, 130.91, 130.88, 130.5, 130.4, 130.0, 129.9, 128.6, 128.2, 127.9, 123.9, 123.6, 123.1, 104.8 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅BrO₂Na 425.0148; Found 425.0135.



Yield: 50.2 mg, 99% (based on 55.6 mg, 0.150 mmol).

Orange crystals. M.p. 154.7-156.3 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.71 (d, *J* = 7.0 Hz, 1H), 7.43-7.38 (m, 6H), 7.36-7.32 (m, 4H), 7.31-7.23 (m, 3H) , 6.43 (s, 1H) 2.47 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.5, 154.3, 153.3, 141.4, 138.4, 136.6, 131.6, 130.9, 130.8, 129.8, 129.7, 128.5, 128.1, 128.0, 127.9, 126.3, 124.3, 107.8, 22.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₁₈O₂Na 361.1199; Found 361.1201.



Yield: 50.2 mg, 97% (based on 1u: 56.6 mg, 0.151 mmol).

Orange crystals. M.p. 129.5-130.1 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H** NMR (500 MHz, CDCl₃): δ 7.79 (t, *J* = 7.5 Hz, 1H), 7.43-7.38 (m, 6H), 7.35-7.31 (m, 5H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13-7.09 (m, 1H), 6.78 (d, *J* = 1.5 Hz, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.1, 160.6 (C-F, ¹*J*_{C-F} = 252.8 Hz), 154.5, 148.7 (C-F, ³*J*_{C-F} = 3.6 Hz), 141.2, 138.4, 131.0, 130.9, 129.9, 128.5, 128.1, 127.5, 124.7 (C-F, ⁴*J*_{C-F} = 2.8 Hz), 124.1, 117.1 (C-F, ³*J*_{C-F} = 10.9 Hz), 116.1 (C-F, ²*J*_{C-F} = 21.6 Hz), 109.3 (C-F, ²*J*_{C-F} = 15.4 Hz) ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –111.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅FO₂Na 365.0948; Found 365.0952.



Yield: 47.9 mg, 89% (based on 1v: 58.5 mg, 0.150 mmol).

Orange crystals. M.p. 187.3-187.6 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.45-7.39 (m, 7H), 7.36-7.33 (m, 5H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.12 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 165.9, 155.0, 150.5, 141.1, 138.3, 131.9, 131.2, 131.01, 130.97, 130.2, 130.0, 129.0, 128.5, 128.1, 127.2, 126.8, 124.1, 110.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅ClO₂Na 381.0653; Found 381.0646.



Yield: 46.7 mg, 77% (based on 1w: 65.9 mg, 0.151 mmol).

Orange crystals. M.p. 193.9-195.2 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.45-7.39 (m, 7H), 7.37-7.33 (m, 4H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.18 (s, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 166.0, 155.0, 151.6, 141.2, 138.3, 134.7, 131.03, 130.98, 130.5, 130.0, 129.5, 128.8, 128.5, 128.1, 127.7, 123.9, 120.9, 110.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₅BrO₂Na 425.0148; Found 425.0151.



Yield: 46.7 mg, 88% (based on 1x: 57.9 mg, 0.151 mmol).

Orange crystals. M.p. 182.6-183.5 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.43-7.37 (m, 6H), 7.35-7.30 (m, 6H), 7.02 (s, 1H), 6.52 (s, 1H), 2.33 (s, 6H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.8, 154.6, 152.6, 141.5, 138.50, 138.47, 131.9, 130.9, 130.8, 129.7, 129.6, 128.5, 128.3, 128.1, 124.4, 122.9, 103.3, 21.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₂₀O₂Na 375.1356; Found 375.1350.



Yield: 49.7 mg, 94% (based on **1y**: 57.8 mg, 0.150 mmol).

Orange crystals. M.p. 165.8-167.3 °C. PE/EA = 40/1 to 20/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.41-7.37 (m, 6H), 7.35-7.32 (m, 4H), 7.07-7.05 (m, 2H), 6.38 (s, 1H), 2.43 (s, 3H), 2.34 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.6, 154.5, 152.6, 141.5, 140.0, 138.5, 136.4, 132.5, 130.9, 130.8, 129.7, 129.6, 128.5, 128.1, 127.8, 127.1, 125.2, 124.5, 107.0, 22.2, 21.4 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₂₀O₂Na 375.1356; Found 375.1359.



Yield: 59.7 mg, 94% (based on 1z: 68.1 mg, 0.150 mmol).

Orange crystals. M.p. 158.7-160.3 °C. PE/EA = 50/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (600 MHz, CDCl₃): δ 7.8 (dd, *J* = 6.6, 2.4 Hz, 1H), 7.59 (ddd, *J* = 8.4, 4.2, 1.8 Hz, 1H), 7.45-7.42 (m, 4H), 7.41-7.38 (m, 2H), 7.34-7.33 (m, 2H), 7.31-7.29 (m, 2H), 7.15 (t, *J* = 8.4 Hz, 1H), 6.51 (s, 1H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 166.2, 159.9 (C-F, ¹*J*_{C-F} = 250.0 Hz), 154.5, 151.8, 141.2, 138.2, 130.9, 130.8, 130.3, 130.0, 129.9, 128.6, 128.2, 126.3 (C-F, ³*J*_{C-F} = 3.6 Hz), 125.8 (C-F, ³*J*_{C-F} = 7.3 Hz), 123.8, 117.1 (C-F, ²*J*_{C-F} = 23.5 Hz), 110.0 (C-F, ²*J*_{C-F} = 21.6 Hz), 104.3 (C-F, ⁴*J*_{C-F} = 1.9 Hz) ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –104.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₄BrFO₂Na 443.0053; Found 443.0050.



Representative procedure for 4: To a dry Schlenk tube equipped with a high vacuum valve, **1**^R**a** (48.6 mg, 0.151 mmol) was dissolved in DCM (2.0 mL) with a stir bar. TfOH (47.0 μ L, 0.525 mmol) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred overnight at rt, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (20 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (40/1 to 30/1, v/v) to afford the product **4a** (42.6 mg, 97%) as colorless solid.



Yield: 42.6 mg, 97% (based on **1^Ra**: 48.6 mg, 0.151 mmol).

Colorless crystals. M.p. 121.0-121.8 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H NMR** (600 MHz, CDCl₃): δ 7.32 (t, *J* = 7.2 Hz, 4H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 4H), 7.04 (d, *J* = 0.6 Hz, 1H), 5.27 (s, 1H), 1.99 (s, 3H), 1.86 (s, 3H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 170.0, 144.8, 141.1, 136.0, 135.0, 128.8, 128.7, 127.1, 122.3, 47.9, 18.9, 18.7 ppm.

IR (neat): 2918 (w), 1754 (s), 1493 (m), 1447 (m), 1162 (m), 1047 (s), 899 (m), 827 (m), 748 (s), 700 (s) cm⁻¹.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₀H₁₈O₂Na 313.1199; Found 313.1198.



Yield: 46.2 mg, 99% (based on 1^Rb: 51.5 mg, 0.153 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.05-7.04 (m, 3H), 5.23 (s, 1H), 2.32 (s, 3H), 1.99 (s, 3H), 1.85 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 170.0, 144.8, 141.3, 138.1, 136.7, 135.9, 135.2, 129.5, 128.8, 128.7, 128.6, 127.0, 122.1, 47.6, 21.2, 18.9, 18.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₀O₂Na 327.1356; Found 327.1352.



Yield: 54.9 mg, 98% (based on 1^Rc: 61.0 mg, 0.152 mmol); 54.8 mg, 99% (based on 1^Rc': 60.3 mg, 0.150 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.34-7.31 (m, 2H), 7.28-7.25 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.05-7.03 (m, 3H), 5.22 (s, 1H), 2.00 (s, 3H), 1.87 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.8, 144.7, 140.5, 140.1, 136.1, 134.4, 131.9, 130.5, 129.0, 128.6, 127.4, 122.8, 121.1, 47.4, 18.9, 18.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₇BrO₂Na 391.0304; Found 391.0300.



Yield: 45.1 mg, 92% (based on 1^Rd: 53.8 mg, 0.151 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.34-7.25 (m, 5H), 7.13 (d, J = 7.0 Hz, 2H), 7.10 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 1.5 Hz, 1H) 5.24 (s, 1H), 2.00 (s, 3H), 1.87 (s, 3H) ppm. ¹³**C NMR** (125 MHz, CDCl₃): δ 169.8, 144.7, 140.6, 139.6, 136.1, 134.5, 133.0, 130.1, 128.99, 128.96, 128.6, 127.3, 122.8, 47.4, 18.9, 18.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₇ClO₂Na 347.0809; Found 347.0807.



Yield: 45.0 mg, 97% (based on 1^Re: 51.2 mg, 0.150 mmol).

S33

Colorless oil. PE/EA = 50/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.28-7.26 (m, 1H), 7.15-7.11 (m, 4H), 7.02-6.99 (m, 3H), 5.25 (s, 1H), 2.00 (s, 3H), 1.86 (s, 3H) ppm.

¹³**C** NMR (125 MHz, CDCl₃): δ 169.8, 161.9 (C-F, ¹*J*_{C-F} = 244.5 Hz), 144.7, 140.9, 136.8 (C-F, ⁴*J*_{C-F} = 3.6 Hz), 136.0, 134.8, 130.2 (C-F, ³*J*_{C-F} = 7.3 Hz), 128.9, 128.6, 127.3, 122.6, 115.7 (C-F, ²*J*_{C-F} = 21.6 Hz), 47.2, 18.9, 18.7 ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ –115.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₇FO₂Na 331.1105; Found 331.1110.



Yield: 42.5 mg, 92% (based on 1^Rf: 51.0 mg, 0.152 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 6.97 (s, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 5.23 (s, 1H), 2.31 (s, 3H), 1.99 (s, 3H), 1.86 (s, 3H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 170.0, 144.8, 141.2, 140.9, 138.5, 135.9, 135.1, 129.5, 128.8, 128.73, 128.67, 127.9, 127.1, 125.7, 122.1, 47.9, 21.6, 18.9, 18.7 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₁H₂₀O₂Na 327.1356; Found 327.1357.



Yield: 47.7 mg, 97% (based on 1^Rg': 54.0 mg, on 0.151 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.33 (t, *J* = 7.0 Hz, 2H), 7.29-7.24 (m, 3H), 7.15-7.14 (m, 3H), 7.07-7.04 (m, 2H), 5.24 (s, 1H), 2.00 (s, 3H), 1.87 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.7, 144.7, 143.0, 140.3, 136.2, 134.7, 134.2, 130.1, 129.0, 128.7, 128.6, 127.4, 127.0, 122.9, 47.6, 18.9, 18.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₇ClO₂Na 347.0809; Found 347.0808.


Yield: 42.4 mg, 93% (based on $1^{R}h'$: 50.5 mg, 0.150 mmol). Colorless oil. PE/EA = 40/1 to 30/1. ¹H NMR (500 MHz, CDCl₃): δ 7.33-7.30 (m, 2H), 7.26-7.24 (m, 1H), 7.18-7.11 (m, 5H), 6.95-6.94 (m, 2H), 5.40 (s, 1H), 2.27 (s, 3H), 1.99 (s, 3H), 1.84 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 169.9, 144.8, 140.6, 139.1, 136.6, 136.4, 135.0, 131.0, 128.9, 128.8, 128.0, 127.2, 127.0, 126.1, 122.0, 44.6, 19.9, 18.9, 18.7 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₀O₂Na 327.1356; Found 327.1352.



Yield: 43.6 mg, 94% (based on **1^Ri'**: 51.2 mg, 0.150 mmol).

Colorless crystals. M.p. 133.9-135.4 °C. PE/EA = 40/1 to 30/1. Single-crystals for X-ray analysis were obtained from PE and EA at rt.

¹**H** NMR (500 MHz, CDCl₃): δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.11-7.05 (m, 4H), 5.51 (s, 1H), 2.00 (s, 3H), 1.86 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.7, 160.7 (C-F, ¹*J*_{C-F} = 246.4 Hz), 144.7, 139.7, 136.2, 133.7, 129.9 (C-F, ³*J*_{C-F} = 3.6 Hz), 129.0 (C-F, ³*J*_{C-F} = 8.1 Hz), 128.9, 128.6, 128.2 (C-F, ²*J*_{C-F} = 14.5 Hz), 127.3, 124.3 (C-F, ⁴*J*_{C-F} = 2.8 Hz), 122.5, 115.9 (C-F, ²*J*_{C-F} = 21.8 Hz), 41.4 (C-F, ³*J*_{C-F} = 2.6 Hz), 18.9, 18.7 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –116.0 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₇FO₂Na 331.1105; Found 331.1107.



Yield: 40.2 mg, 77% (based on 1_Rj : 57.2 mg, 0.150 mmol). Colorless oil. PE/EA = 40/1 to 10/1. ¹**H NMR** (600 MHz, CDCl₃): δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.34-7.32 (m, 2H), 7.29-7.24 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.03 (s, 1H), 5.32 (s, 1H), 3.90 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 169.7, 166.9, 146.2, 144.7, 140.3, 136.2, 134.1, 130.1, 129.1, 129.0, 128.8, 128.7, 127.4, 123.0, 52.2, 47.9, 29.8, 18.9, 18.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₀O₄Na 371.1254; Found 371.1252.



Yield: 16.7 mg, 31% (based on **1^Rk**: 59.3 mg, 0.152 mmol); 40.6 mg, 76% (based on **1^Rk'**: 58.1 mg, 0.149 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.36-7.33 (m, 2H), 7.30-7.28 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.05 (s, 1H), 5.32 (s, 1H), 2.01 (s, 3H), 1.88 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.7, 145.1, 144.6, 140.2, 136.2, 134.1, 129.5 (C-F, ²*J*_{C-F} = 31.5 Hz), 129.09, 129.07, 128.7, 127.5, 125.8 (C-F, ³*J*_{C-F} = 3.6 Hz), 124.2 (C-F, ¹*J*_{C-F} = 267.1 Hz) (partially overlapped with the signal at 123.2 ppm), 123.2, 47.8, 19.0, 18.8 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –62.5 ppm.

HRMS (ESI) m/z: Calcd for C₂₁H₁₇F₃O₂Na 381.1073; Found 381.1078.



Yield: 41.8 mg, 80% (based on 1^Rl': 56.8 mg, 0.151 mmol).

Colorless oil. PE/EA = 40/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.05 (s, 1H), 6.78 (t, *J* = 7.5 Hz, 2H), 5.18 (s, 1H), 2.02 (s, 3H), 1.89 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.5, 151.4 (C-F, ¹*J*_{C-F} = 249.0 Hz, ²*J*_{C-F} =15.0 Hz, ³*J*_{C-F} = 3.6 Hz), 144.6, 139.6, 137.4 (C-F, m), 136.3, 133.5, 129.2, 128.6, 127.8, 123.8, 112.8 (C-F, ²*J*_{C-F} = 16.3 Hz, ³*J*_{C-F} = 4.5 Hz), 47.2, 19.0, 18.8 ppm.

¹⁹**F NMR** (470 MHz, CDCl₃): δ –133.6 (d, *J* = 17.9 Hz, 2F), –162.2 (t, *J* = 17.9 Hz, 1F) ppm.

HRMS (ESI) m/z: Calcd for C₂₀H₁₅F₃O₂Na 367.0916; Found 367.0909.



Yield: 46.5 mg, 94% (based on 1^Rm: 53.4 mg, 0.150 mmol).

Colorless crystals. M.p. 152.1-152.5 °C. PE/EA = 40/1 to 30/1. Crystals were obtained from PE and EA at rt.

¹**H** NMR (500 MHz, CDCl₃): δ 7.32 (t, *J* = 7.5 Hz, 4H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.17 (d, *J* = 7.0 Hz, 4H), 7.07 (d, *J* = 1.5 Hz, 1H), 5.27 (s, 1H), 2.50 (t, *J* = 5.5 Hz, 2H), 2.24 (t, *J* = 5.5 Hz, 2H), 1.66-1.61 (m, 4H), 1.57-1.56 (m, 2H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 170.1, 142.3, 141.1, 135.6, 134.9, 130.4, 128.8, 128.7, 127.1, 48.0, 29.3, 28.8, 28.1, 27.3, 26.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₂₂O₂Na 353.1512; Found 353.1508.



Yield: 31.5 mg, 72% (based on $1^{R}n$: 48.2 mg, 0.150 mmol).

Colorless oil. PE/EA = 50/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.31 (t, *J* = 7.5 Hz, 4H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 4H), 6.78 (s, 1H), 5.25 (s, 1H), 5.16 (t, *J* = 7.5 Hz, 1H), 2.40 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3 H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.6, 148.0, 140.8, 139.8, 136.1, 128.9, 128.7, 127.2, 118.0, 47.9, 19.9, 13.7 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈O₂Na 313.1199; Found 313.1200.



Figure S1. NOESY spectrum of 4n (600 MHz, CDCl₃).



Yield: 10.0 mg, 23% (based on 1^Rn: 48.2 mg, 0.150 mmol).

Colorless oil. PE/EA = 50/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.33 (t, *J* = 7.5 Hz, 4H), 7.28-7.25 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 4H), 7.05 (s, 1H), 5.69 (t, *J* = 8.0 Hz, 1H), 5.27 (s, 1H), 2.21 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3 H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.5, 148.2, 140.7, 137.1, 135.3, 128.9, 128.7, 127.2, 117.3, 48.1, 20.2, 14.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈O₂Na 313.1199; Found 313.1196.



Figure S2. NOESY spectrum of 4n' (600 MHz, CDCl₃).



Yield: 34.2 mg, 74% (based on **1^Ro**: 51.0 mg, 0.152 mmol).

Colorless oil. PE/EA = 50/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.32 (t, *J* = 7.5 Hz, 4H), 7.26-7.23 (m, 2H), 7.17-7.15 (m, 4H), 6.77 (d, *J* = 1.5 Hz, 1H), 5.25 (s, 1H), 5.02 (d, *J* = 10.0 Hz, 1H), 3.04-2.97 (m, 1H), 1.08 (s, 3H), 1.07 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.7, 146.7, 140.8, 140.1, 136.0, 128.9, 128.7, 127.2, 123.3, 48.0, 26.5, 22.7 ppm.

IR (neat): 2959 (m), 1774 (s), 1495 (m), 1447 (m), 1301 (m), 1076 (m), 1037 (s), 964 (s), 779 (s), 699 (s) cm⁻¹.

HRMS (ESI) m/z: Calcd for C₂₁H₂₀O₂Na 327.1356; Found 327.1356.



Yield: 11.0 mg, 24% (based on **1^Ro**: 51.0 mg, 0.152 mmol).

Colorless oil. PE/EA = 50/1 to 30/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.33 (t, *J* = 7.5 Hz, 4H), 7.28-7.25 (m, 2H), 7.17-7.16 (m, 4H), 7.05 (s, 1H), 5.55 (d, *J* = 11.0 Hz, 1H), 5.26 (s, 1H), 2.61-2.54 (m, 1H), 1.08 (s, 3H), 1.07 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 169.5, 147.1, 140.7, 137.2, 135.4, 128.9, 128.7, 127.2, 122.6, 48.2, 26.9, 23.6 ppm.

IR (neat): 2958 (m), 2920 (m), 2867 (m), 1763 (s), 1603 (m), 1494 (s), 1445 (m), 1304 (m), 1192 (m), 1077 (m), 1043 (s), 973 (s), 744 (s), 700 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₀O₂Na 327.1356; Found 327.1350.



To a dry Schlenk tube equipped with a high vacuum valve, $1^{R}p$ (117.5 mg, 0.3991 mmol) was dissolved in DCM (4.5 mL) with a stir bar. TfOH (124.0 μ L, 1.401 mmol) was

added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred overnight at rt, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (50 mL \times 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (40/1 to 6/1, v/v) to afford the product **4p** (16.8 mg, 16%) as light yellow solid and **7** (64.5 mg, 61%) as colorless solid.



Yield: 16.8 mg, 16% (based on 1^Rp: 117.5 mg, 0.3991 mmol).

Light yellow crystals. M.p. 89.1-90.3 °C. PE/EA = 40/1 to 6/1. Crystals were obtained from PE and EA at rt.

¹**H** NMR (600 MHz, CDCl₃): δ 7.33 (t, *J* = 7.8 Hz, 4H), 7.27-7.25 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 4H), 6.85 (s, 1H), 5.25 (s, 1H), 5.17 (s, 1H), 4.79 (s, 1H) ppm.

¹³**C NMR** (150 MHz, CDCl₃): δ 169.3, 153.8, 140.4, 139.2, 139.0, 128.9, 128.7, 127.3, 97.1, 48.0 ppm.

HRMS (ESI) m/z: Calcd for C₁₈H₁₄O₂Na 285.0886; Found 285.0886.



Yield: 64.5 mg, 62% (based on 1^Rp: 117.5 mg, 0.3991 mmol).

Colorless crystals. M.p. 124.3-125.1 °C. PE/EA = 40/1 to 6/1. Single-crystals for X-ray analysis were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.36-7.23 (m, 10H), 7.25-7.22 (m, 2H), 7.17-7.15 (m, 8H), 7.12 (d, *J* = 1.5 Hz, 1H), 6.80 (d, *J* = 1.5 Hz, 1H), 5.30 (s, 1H), 5.23 (s, 1H), 5.15 (s, 1H), 1.73 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 171.4, 168.1, 153.0, 147.9, 140.6, 140.5, 140.08, 140.06, 140.0, 138.2, 136.1, 129.0, 128.94, 128.89, 128.7, 128.6, 127.5, 127.25, 127.20, 111.8, 84.2, 48.2, 47.9, 25.9 ppm.

IR (neat): 3028 (w), 1778 (s), 1752 (s), 1672 (m), 1494 (m), 1449 (m), 1219 (m), 1099

(m), 1022 (s), 927 (s), 758 (s), 697 (s) cm⁻¹. **HRMS (ESI)** m/z: [M+Na]⁺ Calcd for C₃₆H₂₈O₄Na 547.1880; Found 547.1879.



To a dry Schlenk tube equipped with a high vacuum valve, $1^{R}q$ (101.2 mg, 0.301 mmol) was dissolved in DCM (4.0 mL) with a stir bar. TfOH (93.0 µL, 1.051 mmol) was added dropwise via microsyringe to the solution at 0 °C. The reaction mixture was stirred overnight at rt, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (40 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (40/1 to 10/1, v/v) to afford the product **8** (41.8 mg, 46%) as yellow solid and **9** (52.5 mg, 52%) as colorless solid.



Known compouds.³ Yield: 41.8 mg, 46% (based on $1^{R}q$: 101.2 mg, 0.301 mmol). Yellow solid. M.p. 170.0-171.2 °C. PE/EA = 40/1 to 10/1.

¹**H NMR** (600 MHz, CDCl₃): δ 7.38-7.35 (m, 6H), 7.29-7.28 (m, 2H), 7.25-7.24 (m, 2H), 5.82 (s, 1H), 1.22 (s, 9H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 167.4, 166.5, 151.5, 141.4, 138.6, 130.57, 130.55, 129.4, 129.3, 128.4, 128.1, 124.4, 101.2, 32.8, 27.5 ppm.

HRMS (ESI) m/z: Calcd for C₂₁H₂₀O₂Na 327.1356; Found 327.1357.



Yield: 52.5 mg, 52% (based on 1^Rq: 101.2 mg, 0.301 mmol).

Colorless crystals. M.p. 79.4-80.2 °C. PE/EA = 40/1 to 10/1. Single-crystals for X-ray analysis were obtained from PE and EA at rt.

¹**H NMR** (500 MHz, CDCl₃): δ 7.35-7.31 (m, 4H), 7.28-7.24 (m, 2H), 7.18-7.15 (m, 4H), 6.54 (d, *J* = 1.5 Hz, 1H), 5.25 (s, 1H), 3.18 (s, 3H), 0.99 (s, 9H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 170.3, 147.5, 142.1, 140.5, 140.4, 129.0, 128.9, 128.6, 127.30, 127.28, 113.1, 51.3, 48.3, 38.7, 25.2 ppm.

IR (neat): 2965 (w), 1760 (s), 1672 (m), 1492 (m), 1450 (m), 1279 (m), 1246 (m), 1210 (m), 1117 (s), 1075 (m), 959 (s), 706 (s), 699 (s) cm⁻¹.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1622.



Procedure for 1.0 mmol scale reaction: To a dry Schlenk tube equipped with a high vacuum valve, $1^{R}a$ (322.2 mg, 0.999 mmol) was dissolved in DCM (22.0 mL) with a stir bar. Neat TfOH (0.31 mL, 3.5 mmol) was added quickly via syringe to the solution at 0 °C. The reaction mixture was stirred overnight at rt, which was then neutralized with saturated NaHCO₃. The mixture was extracted with DCM (60 mL × 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with PE/EA (50/1 to 30/1, v/v) to afford the product **3a** (277.9 mg, 96%) as orange solid.

5. Reduction of **3a** and **4a** by $LiAlH_4$



To a dry Schlenk tube with a stir bar, **4a** (58.2 mg, 0.200 mmol) was dissolved in dry ether (4.0 mL). To the solution cooled at 0 °C for 10 min, was added LiAlH4 (23.0 mg, 0.606 mmol). After stirred at 0 °C for 1 h, the reaction was quenched with 1.0 M HCl and stirred overnight at rt. The mixture was extracted with Et₂O (20 mL \times 3). The combined organics were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and purified by flash column chromatography on silica gel eluted with PE/EA (100/1, v/v) to afford the product **11** (41.6 mg, 75%) as colorless oil.



Yield: 27.2 mg, 42% (based on **3a**: 67.7 mg, 0.200 mmol). Colorless oil. PE/EA = 100/1.

¹**H NMR** (500 MHz, CDCl₃): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.32-7.29 (m, 4H), 7.25-7.21 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 1H), 6.44 (s, 1H), 5.29 (s, 1H), 2.34 (s, 3H) ppm.

¹³C NMR (150 MHz, CDCl₃): δ 154.7, 143.6, 140.3, 137.3, 130.4, 129.4, 128.9, 128.6, 128.3, 126.7, 123.8, 106.2, 48.5, 21.4 ppm.

IR (neat): 3027 (w), 2992 (w), 1771 (m), 1736 (m), 1493 (m), 1450 (m), 1239 (m), 1029 (m), 916 (m), 818 (s), 748 (s), 698 (s) cm⁻¹.

HRMS (EI) m/z: M⁺ Calcd for C₂₄H₂₀O 324.1514; Found 324.1510.



Yield: 41.6 mg, 75% (based on **4a**: 58.2 mg, 0.200 mmol). Colorless oil. PE/EA = 100/1. ¹**H NMR** (600 MHz, CDCl₃): δ 7.31-7.28 (m, 4H), 7.23-7.21 (m, 6H), 6.79 (s, 1H), 5.82 (s, 1H), 5.22 (s, 1H), 2.92-2.85 (m, 1H), 1.22 (s, 3H), 1.21 (s, 3H) ppm.

¹³**C NMR** (125 MHz, CDCl₃): δ 162.4, 143.9, 139.2, 128.9, 128.7, 128.4, 126.5, 104.7, 48.7, 28.0, 21.2 ppm.

IR (neat): 2962 (w), 1609 (m), 1547 (m), 1494 (s), 1450 (s), 1260 (m), 1129 (m), 1091 (m), 1032 (m), 933 (s), 799 (s), 728 (s), 696 (s) cm⁻¹.

HRMS (EI) m/z: M⁺ Calcd for C₂₀H₂₀O 276.1514; Found 276.1516.

6. X-ray crystallographic data



Crystal data and structure refinement for trans-1a:		
Empirical formula	C25H22O3	
Formula weight	370.42	
Temperature	170.03 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	$a = 13.0124(2)$ Å, $\alpha = 90^{\circ}$	
	$b = 9.00140(10)$ Å, $\beta = 101.7520(10)^{\circ}$	
	$c = 17.0056(3) \text{ Å}, \gamma = 90^{\circ}$	
Volume	1950.11(5) Å ³	
Z	4	
Density (calculated)	1.262 mg/m^3	
Absorption coefficient	0.418 mm ⁻¹	
F(000)	784	
Crystal size	$0.12\times0.08\times0.06\ mm^3$	
Theta range for data collection	3.406 to 54.921°	
Index ranges	$-13 \le h \le 15, -10 \le k \le 10, -20 \le l \le 20$	
Reflections collected	20216	
Independent reflections	3681 [R(int) = 0.0363]	
Completeness to theta = 53.594°	99.3 %	
Max. and min. transmission	0.7508 and 0.6385	
Data / restraints / parameters	3681 / 0 / 255	
Goodness-of-fit on F ²	1.051	
Final R indices [I>2sigma(I)]	$R_1 = 0.0401, wR_2 = 0.0973$	
R indices (all data)	$R_1 = 0.0467, wR_2 = 0.1029$	
Largest diff. peak and hole	0.206 and –0.207 $e {\rm \AA}^{-3}$	



Crystal data and structure refinement for 3a:

Empirical formula	$C_{24}H_{18}O_{2}$
	220.20
–	338.38
Temperature	170.01 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	$a = 10.9549(2)$ Å, $\alpha = 90^{\circ}$
	$b = 8.6376(2) \text{ Å}, \beta = 97.0550(10)^{\circ}$
	$c = 19.2969(4) \text{ Å}, \gamma = 90^{\circ}$
Volume	1812.13(7) Å ³
Z	4
Density (calculated)	1.240 mg/m^3
Absorption coefficient	0.394 mm ⁻¹
F(000)	712
Crystal size	$0.15\times0.12\times0.08\ mm^3$
Theta range for data collection	4.886 to 54.873°
Index ranges	$-13 \le h \le 13, -8 \le k \le 10, -23 \le l \le 23$
Reflections collected	18563
Independent reflections	3392 [R(int) = 0.0299]
Completeness to theta = 53.594°	98.7 %
Max. and min. transmission	0.7508 and 0.6421
Data / restraints / parameters	3392 / 0 / 236
Goodness-of-fit on F ²	1.040
Final R indices [I>2sigma(I)]	$R_1 = 0.0359, wR_2 = 0.0902$
R indices (all data)	$R_1 = 0.0374, wR_2 = 0.0916$
Largest diff. peak and hole	0.210 and $-0.183 \text{ e}\text{\AA}^{-3}$



Crystal data and structure refinement for 3k:

Empirical formula	$C_{23}H_{14}O_2Cl_2$
Formula weight	393.24
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	$a = 9.4518(2) \text{ Å}, \alpha = 90^{\circ}$
	$b = 17.1313(2) \text{ Å}, \beta = 109.841(2)^{\circ}$
	$c = 12.0812(3) \text{ Å}, \gamma = 90^{\circ}$
Volume	1840.08(7) Å ³
Z	4
Density (calculated)	1.419 mg/m^3
Absorption coefficient	3.297 mm^{-1}
F(000)	808.0
Crystal size	$0.32 \times 0.26 \times 0.18 \text{ mm}^3$
Theta range for data collection	9.338 to 134.068°
Index ranges	$-11 \le h \le 11, -20 \le k \le 20, -14 \le l \le 14$
Reflections collected	40415
Independent reflections	3157 [R(int) = 0.0638]
Data / restraints / parameters	3157 / 14 / 232
Goodness-of-fit on F ²	1.036
Final R indices [I>2sigma(I)]	$R_1 = 0.0925, wR_2 = 0.2334$
R indices (all data)	$R_1 = 0.0951, wR_2 = 0.2357$
Largest diff. peak and hole	2.98 and $-0.91 \text{ e}\text{\AA}^{-3}$





Crystal data and structure refinement for 4i:

Empirical formula	$C_{20}H_{16}O_2F$
Formula weight	307.33
Temperature	100.00 (10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 8.9779(2) \text{ Å}, \alpha = 90^{\circ}$
	$b = 17.0515(3) \text{ Å}, \beta = 92.520(2)^{\circ}$
	$c = 10.1052(2) \text{ Å}, \gamma = 90^{\circ}$
Volume	1545.48(5) Å ³
Z	4
Density (calculated)	1.321 mg/m^3
Absorption coefficient	0.754 mm^{-1}
F(000)	644.0
Crystal size	$0.32 \times 0.26 \times 0.12 \text{ mm}^3$
Theta range for data collection	9.862 to 134.108°
Index ranges	$-10 \le h \le 10, -17 \le k \le 20, -7 \le l \le 12$
Reflections collected	14704
Independent reflections	2743 [R(int) = 0.0404]
Data / restraints / parameters	2743 / 0 / 219
Goodness-of-fit on F ²	1.101
Final R indices [I>2sigma(I)]	$R_1 = 0.0429, wR_2 = 0.1057$
R indices (all data)	$R_1 = 0.0460, wR_2 = 0.1075$
Largest diff. peak and hole	0.19 and $-0.18 \text{ e}\text{\AA}^{-3}$





Crystal data and structure refinement for 7:

Empirical formula	C36H28O4
Formula weight	524.58
Temperature	293.74(10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 9.47360(10)$ Å, $\alpha = 90^{\circ}$
	b = 16.7897(2) Å, β = 96.2320(10)°
	$c = 17.7289(3) \text{ Å}, \gamma = 90^{\circ}$
Volume	2803.27(7) Å ³
Z	4
Density (calculated)	1.243 mg/m^3
Absorption coefficient	0.638 mm^{-1}
F(000)	1104.0
Crystal size	$0.32\times0.28\times0.11~mm^3$
Theta range for data collection	7.272 to 134.116°
Index ranges	$-8{\leqslant}h{\leqslant}11,-20{\leqslant}k{\leqslant}20,-21{\leqslant}l{\leqslant}21$
Reflections collected	29794
Independent reflections	4998 [R(int) = 0.0428]
Data / restraints / parameters	4998 / 0 / 363
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	$R_1 = 0.0382, wR_2 = 0.0955$
R indices (all data)	$R_1 = 0.0455, wR_2 = 0.0966$
Largest diff. peak and hole	0.21 and $-0.14 \text{ e}\text{\AA}^{-3}$



Crystal data and structure refinement for 9:

Empirical formula	C22H24O3
Formula weight	336.41
Temperature	100.00(10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	$a = 11.1433(2)$ Å, $\alpha = 90^{\circ}$
	$b = 9.4429(2) \text{ Å}, \beta = 97.0790(10)^{\circ}$
	$c = 17.7217(3)$ Å, $\gamma = 90^{\circ}$
Volume	1850.55(6) Å ³
Z	4
Density (calculated)	1.207 mg/m^3
Absorption coefficient	0.628 mm^{-1}
F(000)	720.0
Crystal size	$0.42\times0.26\times0.12\ mm^3$
Theta range for data collection	8.906 to 134.118°
Index ranges	$-13 \le h \le 13, -11 \le k \le 11, -21 \le l \le 21$
Reflections collected	39794
Independent reflections	3292 [R(int) = 0.1005]
Data / restraints / parameters	3292 / 0 / 230
Goodness-of-fit on F ²	1.084
Final R indices [I>2sigma(I)]	$R_1 = 0.0601, wR_2 = 0.1588$
R indices (all data)	$R_1 = 0.0626, wR2 = 0.1613$
Largest diff. peak and hole	0.65 and $-0.24 \text{ e}\text{\AA}^{-3}$

7. References

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8. NMR spectra of new compounds




































































































































































































































































































































































































