Electronic Supplementary Information

Metal-Free and Site-Selective \( \alpha \)-C-H Functionalization of Tetrahydrofuran Enabled by Photocatalytic Generation of Bromine Radical

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1. Experimental section

1) General information

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Unless stated otherwise, all reactions were carried out under air atmosphere. The substrates N-phenyl-sulfenyl phthalimides (a) and α-trifluoromethyl arylalkenes (c) were synthesized according to the literature methods with slight modification.\textsuperscript{1-5} Irradiation with visible light was performed using blue LEDs (λ = 450 ± 10 nm) illumination instruments (The instruments were designed by ourselves and the actual output power density of the LEDs at 0.5 cm distance is 33.70 mW/cm\textsuperscript{2} detected by CEL-NP2000-10 (Beijing Ceau Light Co. Ltd., China) light power meter). For irradiation, the material of the reaction vessel is common glass; the distance from the light source is about 0.5 cm.

The nuclear magnetic resonance spectra were recorded on the Bruker Ascend\textsuperscript{TM} 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). Cyclic voltammogram experiments were measured on the CHI-Instrument CHI660E.
2) Preparation of N-phenyl-sulfenyl phthalimides\textsuperscript{1-3}  

**Method A:**

\[
\begin{array}{c}
\text{S-S-phenyl} + \text{Phthalimide} \\
\text{1) CH}_3\text{CN, Pyridine} \\
\text{2) Br}_2 (1.2 \text{ equiv}), 0 \text{ °C} \\
\end{array}
\]

A suspension of phthalimide (1.047 g, 10.0 mmol) and diphenyl disulfide (1.30 g, 6.0 mmol) in CH\textsubscript{3}CN (5.0 mL) and pyridine (4.0 mL) were treated with a solution of Br\textsubscript{2} (615 μL in 5.0 mL CH\textsubscript{3}CN, 12.0 mmol, 1.2 equiv) dropwise over 30 mins. Upon complete addition of Br\textsubscript{2} solution, the mixture was stirred for 1 h at 0 °C, and was subsequently quenched by dropwise addition of CH\textsubscript{3}OH (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled CH\textsubscript{3}OH (0 °C, 3 × 10.0 mL). Further purification was achieved by recrystallization in ethyl acetate through hot cooling to room temperature.  

\textit{a1} was prepared according to the above procedure.

**Method B:**

\[
\begin{array}{c}
\text{R-SH-phenyl} + \text{Phthalimide} \\
\text{1) CH}_3\text{CN, Pyridine, 80 °C} \\
\text{2) Br}_2 (1.2 \text{ equiv}), 0 \text{ °C} \\
\end{array}
\]

A suspension of phthalimide (1.047 g, 10.0 mmol) and thiophenols (11.0 mmol, 1.1 equiv) in CH\textsubscript{3}CN (5.0 mL) and pyridine (4.0 mL) was heated to 80 °C and then cooled to room temperature. The mixture was treated with a solution of Br\textsubscript{2} (615 μL in 5.0 mL CH\textsubscript{3}CN, 12.0 mmol, 1.2 equiv) dropwise over 30 mins. Upon complete addition of Br\textsubscript{2} solution, the mixture was stirred for 1 h at 0 °C and was subsequently quenched by dropwise addition of H\textsubscript{2}O (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled CH\textsubscript{3}OH (0 °C, 3 × 10.0 mL). Further purification was achieved by recrystallization in ethyl acetate through hot cooling to room temperature.  

\textit{a2-a29} were prepared according to the above procedure.
Method C:

\[
\text{R-SH} + \text{SO}_2\text{Cl}_2 \xrightarrow{\text{Et}_3\text{N} \quad 0 \degree \text{C to r.t.}} \text{R-SCI} \xrightarrow{\text{Phthalimide, Et}_3\text{N} \quad 0 \degree \text{C to r.t.}} \text{Phthalamide}
\]

Sulfuryl chloride (5 mmol in 10 mL CH₂Cl₂) was added dropwise via a dropping funnel to a solution of thiol (1.0 equiv) in CH₂Cl₂ (1.0 M) and Et₃N (0.1 mL) at 0 °C. After stirring for 15 min, the mixture was warmed to room temperature for 30 mins and then cooled to 0 °C. The resulting solution was transferred dropwise via cannula to a solution of phthalimide (1.0 equiv) in CH₂Cl₂ (1.0 M) and Et₃N (1.3 equiv) at 0 °C and the mixture was then warmed to room temperature over 1 h. The solution was diluted with H₂O, extracted with hot ethyl acetate before being dried over Na₂SO₄, and then concentrated to give crude product that was purified by recrystallization. **a30-a33** were prepared according to the above procedure.
3) Preparation of boronic acid of Estrone

Estrone (10.0 mmol, 1.0 equiv., 2.70 g), and DIPEA (12.0 mmol, 1.2 equiv.) were dissolved in DCM (30.0 mL) in a two-neck flask with a stir bar under argon atmosphere. The reaction mixture was stirred at 0 °C, and Tf₂O (12.0 mmol, 1.2 equiv., 2.0 mL) was dropwise added into reaction system over 5 min. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min. Upon completion, water (50.0 mL) was added to quench the reaction. The reaction mixture was then extracted with ethyl acetate (30.0 mL x 3). The combined organic extracts were dried with anhydrous MgSO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding trifluoromethanesulfonic ester ES-1 (81%, 3.21 g).

Trifluoromethanesulfonic ester ES-1 (5.0 mmol, 1.0 equiv.), B₂pin₂ (10.0 mmol, 2.0 equiv., 2.7 g), Pd(dppf)Cl₂ (0.5 mmol, 10 mol%, 0.367 g), and AcONa (15.0 mmol, 3.0 equiv., 1.5 g) were dissolved in 1,4-dioxane (20.0 mL) in a two-neck flask with a stir bar under argon atmosphere. The reaction mixture was stirred at 120 °C for 8 h. Upon completion, water (50.0 mL) was added to quench the reaction. The reaction mixture was then extracted with ethyl acetate (30.0 mL x 3). The combined organic extracts were dried with anhydrous MgSO₄ and concentrated under vacuum. The desired product ES-2 was obtained through silica gel chromatography.

ES-2 (2.0 mmol, 1.0 equiv., 0.76 g), NH₄OAc (12.0 mmol, 6.0 equiv., 0.92 g) and NaIO₄ (12.0 mmol, 6.0 equiv., 2.57 g) in acetone (50 mL) and water (20 mL) in a 200 mL round-bottom flask with a stir bar under argon atmosphere. Then the reaction...
mixture was stirred at room temperature for 48 h. Upon completion, the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with ethyl acetate (20.0 mL x 3). The combined organic layer was dried with anhydrous MgSO₄ and concentrated under vacuum. The corresponding boronic acid ES-3 was obtained (57% yield) without further purification.
4) Preparation of α-trifluoromethyl arylalkenes

Arylboronic acid (10.0 mmol), Pd(PPh₃)₄ (0.3 mmol, 3 mol%), K₂CO₃ (2.0 M) were dissolved in THF (30.0 mL) in a two-neck flask under argon atmosphere. Then, 2-bromo-3,3,3-trifluoroprop-1-ene (20.0 mmol, 2.1 mL) was added dropwise into the mixture. The mixture was heated to 60 °C in an oil bath for at least 12 h. Then the mixed solution was extracted with ethyl acetate (3 × 15.0 mL). The organic layer was washed with brine (20.0 mL), dried over Na₂SO₄, and then concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 200/1) to afford the desired products.

c₁-c₃₃, c₃⁹ were prepared according to the above procedure.

Carboxylic acid (2.2 mmol in dry DCM) was added dropwise via a dropping funnel to a solution of 4-(3,3,3-trifluoroprop-1-en-2-yl)phenol (2.0 mmol), DCC (2.2 mmol, 1.1 equiv.), DMAP (20 mol%) were dissolved in dry-DCM (10.0 mL) in a two-neck flask under argon atmosphere at 0 °C. After stirring for 5 min, the mixture was allowed to warm to room temperature over 3h. Upon completion, the resulting mixture was filtered through a pad of celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to afford the desired products.

c₃₄-c₃₈ were prepared according to the above procedure.
5) General procedure for the photochemical reactions

\[ \text{General procedure for the photochemical reactions} \]

\[ \text{a (0.2 mmol), tetra-butyl ammonium bromide }^{n}\text{Bu}_{4}\text{NBr (12.9 mg, 20 mol%), 4-CzIPN (3.1 mg, 2.0 mol%) were dissolved in 2.0 mL THF in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (λ = 450 ± 10 nm) at room temperature for 12 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product } \text{b.} \]

\[ \text{c (0.2 mmol), tetra-butyl ammonium bromide }^{n}\text{Bu}_{4}\text{NBr (12.9 mg, 20 mol%), 4-CzIPN (3.1 mg, 2 mol%) were dissolved in 2.0 mL THF in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (λ = 450 ± 10 nm) at room temperature for 12 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product } \text{d.} \]
a (0.2 mmol), tetra-butyl ammonium bromide \(^{\text{Bu}_4 \text{NBr}}\) (12.9 mg, 20 mol%), 4-CzIPN (3.1 mg, 2 mol%) and isochroman (0.3 mmol) were dissolved in 2.0 mL acetone in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (\(\lambda = 450 \pm 10 \text{ nm}\)) at room temperature for 12 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product \(\text{b34}\).

\[
\text{a} + \text{b} \rightarrow \text{c} + \text{d}
\]

\[
\text{PhS} \quad \text{O}
\]

Yield: 52%

\(\text{a}\) (0.2 mmol), tetra-butyl ammonium bromide \(^{\text{Bu}_4 \text{NBr}}\) (12.9 mg, 20 mol%), 4-CzIPN (3.1 mg, 2 mol%) were dissolved in 2.0 mL Diethyl ether in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (\(\lambda = 450 \pm 10 \text{ nm}\)) at room temperature for 12 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product \(\text{b35}\).

\[
\text{c} + \text{e} \rightarrow \text{d} + \text{f}
\]

Yield: 56%

c’ (0.2 mmol), tetra-butyl ammonium bromide \(^{\text{Bu}_4 \text{NBr}}\) (12.9 mg, 20 mol%), 4-CzIPN (3.1 mg, 2 mol%) and Trifluoroacetic acid (1.0 equiv., 20 μL) were dissolved in 2.0 mL THF in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (\(\lambda = 450 \pm 10 \text{ nm}\)) at room temperature for 12 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the desired product \(\text{d}’\).
6) Crystal structure determination of b15

A suitable crystal of b15 was mounted with glue at the end of a glass fiber. Data collection for b15 was performed on a Rigaku OD (Enhance Cu X-ray Source, Ka, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 293 K. Data were processed with the CrysAlisPro 1.171.39.7e (Rigaku Oxford Diffraction, 2015).

Structure was solved by ShelXT6 in Olex2 1.57 and refined on F2 using full-matrix least-squares (SHELXL-2018 in Olex2 1.5). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data and structure refinement parameters are summarized in Table S1. CCDC No. 2161362.

Single crystals of b15 were prepared in acetonitrile solution of b15. Colourless block crystals formed.

**Table S1 Crystal data and structure refinements for b15**

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<th>Compound</th>
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<td>c/Å</td>
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<tr>
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</table>

**Figure S1.** Molecular structure of **b15** with 50% thermal ellipsoid.

**CCDC Number:** 2161362
7) Luminescence quenching experiments

**General procedure:** The luminescence quenching experiments were measured with excitation at 450 nm. A THF solution of $1 \times 10^{-4}$ M 4-CzIPN and $1.0 \times 10^{-1}$ M a1 or $n$Bu$_4$NBr respectively were prepared. The experiments were conducted in 1.25 cm x 1.25 cm x 4.5 cm quartz cuvette at room temperature. Appropriate volume (the whole solution volume change < 5%) of the quencher a1 or $n$Bu$_4$NBr was respectively injected to the THF solution (3.0 mL) of $1 \times 10^{-4}$ M 4-CzIPN in the quartz cuvette by microsyringe.

![Luminescence quenching spectra](image)

**Figure S2.** Luminescence quenching spectra of 4-CzIPN (1.0 x 10^{-4} M) **a)** by various concentration of a1; **b)** by various concentration of $n$Bu$_4$NBr under argon atmosphere; **c)** by various concentration of $n$Bu$_4$NBr under air atmosphere with excitation at 450 nm.
8) Radical inhibition experiment

\[ \text{Radical inhibition experiment} \]

[Chemical structure diagram]

HRMS spectra for Radical inhibition experiment.

**Figure S3.** HRMS spectra for Radical inhibition experiment.
9) Kinetic isotope effect experiment

![Chemical structure diagram](image)

a1 (0.15 mmol), "Bu4NBr (9.7 mg, 20 mol%), 4-CzIPN (2.4 mg, 2.0 mol%) were dissolved in THF/D₈-THF (1.0 mL/1.0 mL) in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (λ = 450 ± 10 nm) at room temperature for 8 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product b1.

\[
k_H / k_D = 0.80/ (1-0.80) = 4.0
\]

Figure S4. ^1^H NMR spectra for kinetic isotope effect experiment.
10) References


2. Characterization data of the products

![Chemical structure](image-b1)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b1** as a colorless oil (33.5 mg, 93% yield).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 7.1$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 5.64 (dd, $J = 7.2$, 3.8 Hz, 1H), 4.04 – 3.91 (m, 2H), 2.39 – 2.29 (m, 1H), 2.04 – 1.92 (m, 2H), 1.90 – 1.79 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) $\delta$ 135.8, 131.0, 128.8, 126.8, 87.1, 67.3, 32.7, 24.9.

**HRMS** (EI) calculated for C$_{10}$H$_{12}$OS [M]$^+$: 180.0604; Found: 180.0605

![Chemical structure](image-b2)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b2** as a colorless oil (30.3 mg, 78% yield).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 6.3$ Hz, 1H), 7.14 (d, $J = 4.7$ Hz, 1H), 7.13 – 7.09 (m, 1H), 5.63 (dd, $J = 7.2$, 3.7 Hz, 1H), 4.04 – 3.91 (m, 2H), 2.38 (s, 3H), 2.37 – 2.30 (m, 1H), 2.06 – 1.97 (m, 2H), 1.91 – 1.82 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) $\delta$ 138.4, 135.2, 130.8, 130.0, 126.7, 126.5, 86.4, 67.4, 32.8, 24.9, 20.8.

**HRMS** (ESI) calculated for C$_{11}$H$_{14}$OS [M+H]$^+$: 195.0839; Found: 195.0841

![Chemical structure](image-b3)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b3** as a pale-yellow oil (33.3 mg, 84% yield).
\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.60 (td, $J = 7.6, 1.8$ Hz, 1H), 7.29 – 7.19 (m, 1H), 7.13 – 7.03 (m, 2H), 5.70 (dd, $J = 7.1, 3.4$ Hz, 1H), 4.07 – 3.93 (m, 2H), 2.42 – 2.33 (m, 1H), 2.12 – 1.97 (m, 2H), 1.93 – 1.84 (m, 1H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 161.5 (d, $J = 245.9$ Hz), 133.9, 129.0 (d, $J = 7.8$ Hz), 124.5 (d, $J = 3.8$ Hz), 122.3 (d, $J = 17.9$ Hz), 115.6 (d, $J = 22.9$ Hz), 86.4 (d, $J = 7.8$ Hz), 67.37, 32.70, 24.62.

\textbf{19F NMR} (376 MHz, CDCl$_3$) $\delta$ -109.35 (s, 1F).

\textbf{HRMS} (ESI) calculated for C$_{10}$H$_{11}$FOS [M+H]$^+$: 199.0588; Found: 199.0592

![b4](image)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b4} as a pale-yellow oil (37.7 mg, 88% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.68 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.35 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.22 (td, $J = 7.6, 1.5$ Hz, 1H), 7.12 (td, $J = 7.6, 1.6$ Hz, 1H), 5.75 (dd, $J = 7.2, 3.6$ Hz, 1H), 4.04 – 3.94 (m, 2H), 2.46 – 2.37 (m, 1H), 2.12 – 2.00 (m, 2H), 1.94 – 1.85 (m, 1H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 135.5, 133.9, 130.7, 129.5, 127.2, 127.2, 85.5, 67.5, 32.6, 24.8.

\textbf{HRMS} (ESI) calculated for C$_{10}$H$_{11}$ClOS [M+H]$^+$: 215.0292; Found: 215.0297

![b5](image)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b5} as a pale-yellow oil (42.8 mg, 83% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.70 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.55 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.29 (td, $J = 7.6, 1.3$ Hz, 1H), 7.06 (td, $J = 7.7, 1.6$ Hz, 1H), 5.78 (dd, $J = 7.3,
3.6 Hz, 1H), 4.11 – 3.94 (m, 2H), 2.52 – 2.38 (m, 1H), 2.15 – 2.00 (m, 2H), 2.01 – 1.84 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.7, 132.8, 130.3, 127.9, 127.2, 123.9, 85.6, 67.5, 32.5, 24.8.

HRMS (ESI) calculated for C$_{10}$H$_{11}$BrOS [M+H]$^+$: 258.9787; Found: 258.9783

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b6 as a colorless oil (42.2 mg, 85% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J$ = 7.9 Hz, 1H), 7.66 (d, $J$ = 7.9 Hz, 1H), 7.50 (t, $J$ = 7.7 Hz, 1H), 7.32 (t, $J$ = 7.7 Hz, 1H), 5.71 (dd, $J$ = 7.2, 3.5 Hz, 1H), 4.10 – 3.96 (m, 2H), 2.48 – 2.36 (m, 1H), 2.13 – 2.01 (m, 2H), 1.97 – 1.86 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 135.6 (d, $J$ = 1.8 Hz), 133.1 (d, $J$ = 3.7 Hz), 132.0 (d, $J$ = 1.9 Hz), 126.5 (q, $J$ = 275.2 Hz), 126.4, 125.2, 122.5, 87.1, 67.4, 32.7, 24.7.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -60.62 (s, 3F).

HRMS (ESI) calculated for C$_{11}$H$_{11}$F$_3$OS [M+H]$^+$: 249.0556; Found: 249.0559

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b7 as a colorless oil (38.6 mg, 81% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, $J$ = 8.7 Hz, 1H), 7.86 (d, $J$ = 8.1 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 1H), 7.18 (t, $J$ = 7.6 Hz, 1H), 5.75 (dd, $J$ = 7.4, 3.9 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.89 (s, 3H), 2.47 – 2.38 (m, 1H), 2.13 – 2.03 (m, 2H), 1.96 – 1.86 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.0, 141.1, 132.4, 130.9, 128.0, 124.6, 122.9, 84.5, 67.6, 52.1, 32.4, 25.1.
**HRMS** (ESI) calculated for C$_{12}$H$_{14}$O$_3$S [M+H]$^+$: 239.0737; Found: 239.0731

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b8 as a colorless oil (32.2 mg, 83% yield).

**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.32 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 7.8$ Hz, 1H), 5.64 (dd, $J = 7.2$, 3.9 Hz, 1H), 4.03 – 3.93 (m, 2H), 2.40 – 2.34 (m, 1H), 2.32 (s, 3H), 2.05 – 1.94 (m, 2H), 1.90 – 1.82 (m, 1H).

**$^{13}$C NMR (101 MHz, CDCl$_3$)** δ 138.6, 135.4, 131.6, 128.7, 128.0, 127.7, 87.1, 67.3, 32.7, 24.9, 21.4.

**HRMS** (ESI) calculated for C$_{11}$H$_{14}$OS [M+H]$^+$: 195.0839; Found: 195.0840

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b9 as a colorless oil (30.9 mg, 77% yield).

**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.25 (d, $J = 2.9$ Hz, 1H), 7.24 (d, $J = 3.1$ Hz, 1H), 7.23 (d, $J = 5.7$ Hz, 1H), 6.94 – 6.85 (m, 1H), 5.68 (dd, $J = 7.3$, 3.9 Hz, 1H), 4.04 – 3.93 (m, 2H), 2.44 – 2.32 (m, 1H), 2.08 – 1.94 (m, 2H), 1.93 – 1.84 (m, 1H).

**$^{13}$C NMR (101 MHz, CDCl$_3$)** δ 162.7 (d, $J = 248.8$ Hz), 138.3 (d, $J = 3.0$ Hz), 130.0 (d, $J = 8.7$ Hz), 125.9 (d, $J = 3.2$ Hz), 117.2 (d, $J = 22.4$ Hz), 113.5(d, $J = 21.2$ Hz), 86.8, 67.4, 32.6, 24.8.

**$^{19}$F NMR (376 MHz, CDCl$_3$)** δ -112.37 (s, 1F).

**HRMS** (ESI) calculated for C$_{10}$H$_{11}$FOS [M+H]$^+$: 199.0588; Found: 199.0581
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b10} as a pale-yellow oil (38.1 mg, 89% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.50 (m, 1H), 7.38 (dt, $J$ = 6.9, 1.9 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.18 (m, 1H), 5.68 (dd, $J$ = 7.3, 3.8 Hz, 1H), 4.05 – 3.96 (m, 2H), 2.44 – 2.34 (m, 1H), 2.09 – 1.95 (m, 2H), 1.94 – 1.85 (m, 1H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 138.0, 134.5, 130.2, 129.8, 128.6, 126.7, 86.9, 67.4, 32.6, 24.8.

\textbf{HRMS} (ESI) calculated for C$_{10}$H$_{11}$ClOS [M+H]$^+$: 215.0292; Found: 215.0297

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b11} as a pale-yellow oil (41.3 mg, 80% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.66 (t, $J$ = 1.8 Hz, 1H), 7.41 (d, $J$ = 8.5 Hz, 1H), 7.34 (d, $J$ = 8.9 Hz, 1H), 7.14 (t, $J$ = 7.9 Hz, 1H), 5.66 (dd, $J$ = 7.3, 3.8 Hz, 1H), 4.03 – 3.95 (m, 2H), 2.41 – 2.33 (m, 1H), 2.08 – 1.93 (m, 2H), 1.93 – 1.83 (m, 1H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 138.3, 133.0, 130.1, 129.7, 129.1, 122.6, 86.9, 67.4, 32.6, 24.8.

\textbf{HRMS} (ESI) calculated for C$_{10}$H$_{11}$BrOS [M+H]$^+$: 258.9787; Found: 258.9778

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1, v/v) afforded \textbf{b12} as a colorless oil (32.6 mg, 84% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 8.2 Hz, 2H), 7.10 (d, $J$ = 7.9 Hz, 2H), 5.57
(dd, J = 7.2, 3.8 Hz, 1H), 4.05 – 3.90 (m, 2H), 2.38 – 2.32 (m, 1H), 2.31 (s, 3H), 2.05 – 1.92 (m, 2H), 1.91 – 1.82 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.0, 131.9, 131.8, 129.6, 87.6, 67.2, 33.6, 24.8, 21.1.

HRMS (ESI) calculated for C$_{11}$H$_{14}$OS [M+H]$^+$: 195.0838; Found: 195.0843

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1, v/v) afforded b13 as a colorless oil (36.1 mg, 86% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.46 (dd, J = 7.2, 3.7 Hz, 1H), 4.06 – 3.96 (m, 1H), 3.92 (td, J = 8.1, 4.1 Hz, 1H), 3.78 (s, 3H), 2.34 – 2.26 (m, 1H), 2.02 – 1.92 (m, 2H), 1.88 – 1.79 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.4, 134.6, 125.6, 114.4, 88.2, 67.2, 55.3, 32.5, 24.8.

HRMS (ESI) calculated for C$_{11}$H$_{14}$O$_2$S [M+H]$^+$: 211.0788; Found: 211.0786

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b14 as a colorless oil (42.5 mg, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 5.61 (dd, J = 7.2, 3.9 Hz, 1H), 4.05 – 3.91 (m, 2H), 2.40 – 2.28 (m, 1H), 2.03 – 1.91 (m, 2H), 1.91 – 1.79 (m, 1H), 1.29 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.2, 132.0, 131.4, 126.0, 87.5, 67.3, 34.6, 32.7, 31.4, 25.0.

HRMS (ESI) calculated for C$_{14}$H$_{20}$OS [M+H]$^+$: 237.1308; Found: 237.1312
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b15 as a white solid (35.3 mg, 69% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (dd, $J = 3.9, 2.4$ Hz, 2H), 7.56 (d, $J = 3.2$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 5.69 (dd, $J = 7.2, 3.8$ Hz, 1H), 4.08 – 3.95 (m, 2H), 2.43 – 2.34 (m, 1H), 2.08 – 1.96 (m, 2H), 1.95 – 1.85 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.6, 139.8, 134.8, 131.4, 128.8, 127.5, 127.4, 127.0, 87.2, 67.4, 32.7, 24.9.

HRMS (ESI) calculated for C$_{16}$H$_{16}$OS [M+H]$^+$: 257.0995; Found: 257.0999

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b16 as a pale-yellow oil (36.4 mg, 92% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (dd, $J = 8.8, 5.3$ Hz, 2H), 7.00 (t, $J = 8.7$ Hz, 2H), 5.54 (dd, $J = 7.2, 3.8$ Hz, 1H), 4.08 – 3.89 (m, 2H), 2.41 – 2.28 (m, 1H), 2.06 – 1.92 (m, 2H), 1.91 – 1.82 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.3 (d, $J = 247.8$ Hz), 134.0 (d, $J = 8.2$ Hz), 130.4 (d, $J = 3.4$ Hz), 115.8 (d, $J = 21.7$ Hz), 87.8, 67.2, 32.5, 24.8.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -114.81 (s, 1F).

HRMS (ESI) calculated for C$_{10}$H$_{11}$FOS [M+H]$^+$: 199.0588; Found: 199.0588
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b17** as a pale-yellow oil (39.4 mg, 92% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (dd, $J = 8.8$, 5.3 Hz, 2H), 6.99 (t, $J = 8.7$ Hz, 2H), 5.53 (dd, $J = 7.2$, 3.8 Hz, 1H), 4.04 – 3.89 (m, 2H), 2.40 – 2.27 (m, 1H), 2.06 – 1.92 (m, 2H), 1.90 – 1.80 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.1, 134.0, 130.5, 116.0, 87.8, 67.2, 32.6, 24.8.

HRMS (ESI) calculated for C$_{10}$H$_{11}$ClOS [M+H]$^+$: 215.0292; Found: 215.0300

![b18](image)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b18** as a pale-yellow oil (47.0 mg, 91% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.7$ Hz, 2H), 5.60 (dd, $J = 7.2$, 3.8 Hz, 1H), 4.03 – 3.92 (m, 2H), 2.42 – 2.29 (m, 1H), 2.06 – 1.93 (m, 2H), 1.92 – 1.83 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.0, 132.6, 131.8, 120.9, 87.1, 67.3, 32.6, 24.8.

HRMS (ESI) calculated for C$_{10}$H$_{11}$BrOS [M+H]$^+$: 258.9787; Found: 258.9785

![b19](image)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b19** as a yellow oil (54.5 mg, 89% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 5.61 (dd, $J = 7.3$, 3.8 Hz, 1H), 4.02 – 3.92 (m, 2H), 2.40 – 2.30 (m, 1H), 2.05 – 1.92 (m, 2H), 1.90 – 1.82 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.6, 136.0, 132.6, 92.1, 87.0, 67.4, 32.6, 24.8.

HRMS (ESI) calculated for C$_{10}$H$_{11}$IOS [M+H]$^+$: 306.9649; Found: 306.9439
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b20} as a colorless oil (43.6 mg, 88% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 8.3$ Hz, 2H), 5.75 (dd, $J = 7.3$, 3.8 Hz, 1H), 4.08 – 3.95 (m, 2H), 2.42 (tdd, $J = 12.0$, 5.2, 3.4 Hz, 1H), 2.10 – 1.97 (m, 2H), 1.96 – 1.86 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.48 (d, $J = 1.5$ Hz), 129.49, 128.2 (d, $J = 32.5$ Hz), 125.5 (q, $J = 3.8$ Hz), 122.8, 86.2, 67.4, 32.6, 24.8.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.49 (s, 3F).

HRMS (ESI) calculated for C$_{11}$H$_{11}$F$_3$OS [M+H]$^+$: 249.0556; Found: 249.0552

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b22} as a colorless oil (36.2 mg, 87% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (s, 2H), 6.85 (s, 1H), 5.65 (dd, $J = 7.3$, 4.0 Hz, 1H), 4.05 – 3.92 (m, 2H), 2.40 – 2.32 (m, 1H), 2.28 (s, 6H), 2.05 – 1.93 (m, 2H), 1.91 – 1.82 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.4, 135.2, 128.7, 128.5, 87.1, 67.3, 32.7, 24.9, 21.3.

HRMS (ESI) calculated for C$_{12}$H$_{16}$OS [M+H]$^+$: 209.0995; Found: 209.0995

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{b23} as a colorless oil (34.1 mg, 82% yield).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 7.9\) Hz, 1H), 7.01 (s, 1H), 6.97 (d, \(J = 8.5\) Hz, 1H), 5.59 (dd, \(J = 7.1, 3.6\) Hz, 1H), 4.08 – 3.94 (m, 2H), 2.37 (s, 3H), 2.36 – 2.30 (m, 1H), 2.28 (s, 3H), 2.08 – 1.95 (m, 2H), 1.91 – 1.80 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 139.1, 137.0, 132.2, 131.2, 131.0, 127.3, 86.9, 67.3, 32.7, 24.9, 21.0, 20.8.

HRMS (ESI) calculated for C\(_{12}\)H\(_{16}\)OS [M+H]\(^+\): 209.0995; Found: 209.1002

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \(\text{b24}\) as a colorless oil (23.1 mg, 52% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.96 (s, 2H), 5.40 – 5.31 (m, 1H), 4.06 – 3.87 (m, 2H), 2.53 (s, 6H), 2.37 – 2.29 (m, 1H), 2.27 (s, 3H), 2.13 – 1.97 (m, 2H), 1.90 – 1.82 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.2, 138.4, 129.1, 129.0, 88.1, 67.3, 32.9, 25.0, 22.3, 21.1.

HRMS (ESI) calculated for C\(_{13}\)H\(_{18}\)OS [M+H]\(^+\): 223.1152; Found: 223.1159

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \(\text{b25}\) as a colorless oil (28.3 mg, 65% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, \(J = 1.9\) Hz, 1H), 7.31 (dd, \(J = 7.9, 1.9\) Hz, 1H), 7.16 (d, \(J = 7.2\) Hz, 1H), 5.62 (dd, \(J = 7.2, 3.8\) Hz, 1H), 4.07 – 3.95 (m, 2H), 2.43 – 2.36 (m, 1H), 2.35 (s, 3H), 2.08 – 1.95 (m, 2H), 1.94 – 1.86 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 134.8, 134.5, 134.2, 131.6, 131.1, 129.7, 87.4, 67.3, 32.6, 24.8, 19.7.

HRMS (ESI) calculated for C\(_{11}\)H\(_{13}\)ClOS [M+H]\(^+\): 229.0449; Found: 229.0439
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b26 as a colorless oil (29.2 mg, 63% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (ddd, $J = 8.0, 6.4, 1.7$ Hz, 1H), 7.28 (ddd, $J = 8.2, 6.8, 1.6$ Hz, 1H), 7.03 (td, $J = 8.0, 1.2$ Hz, 1H), 5.71 (dd, $J = 7.2, 3.4$ Hz, 1H), 4.06 – 3.93 (m, 2H), 2.43 – 2.34 (m, 1H), 2.12 – 1.98 (m, 2H), 1.96 – 1.86 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.7 (d, $J = 247.2$ Hz), 131.6, 124.8, 124.6 (q, $J = 4.5, 3.8$ Hz), 121.4(d, $J = 19.2$ Hz), 86.4, 67.4, 32.7, 24.6.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -110.73 (s, 1F).

HRMS (ESI) calculated for C$_{13}$H$_{18}$OS [M+H]$^+$: 233.0198; Found: 233.0190

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded b27 as a pale-yellow oil (28.1 mg, 61% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (s, 1H), 7.81 (d, $J = 6.8$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.58 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.51 – 7.43 (m, 2H), 5.78 (dd, $J = 7.2, 3.8$ Hz, 1H), 4.12 – 3.98 (m, 2H), 2.49 – 2.37 (m, 1H), 2.11 – 2.00 (m, 2H), 1.98 – 1.87 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.7, 133.2, 132.2, 129.4, 128.7, 128.2, 127.7, 127.4, 126.4, 125.8, 87.2, 67.4, 32.7, 24.9.

HRMS (ESI) calculated for C$_{14}$H$_{14}$OS [M+H]$^+$: 231.0839; Found: 231.0833
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b28** as a colorless oil (17.5 mg, 47% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 5.4$ Hz, 1H), 7.17 (d, $J = 3.5$ Hz, 1H), 7.00 (dd, $J = 5.3$, 3.6 Hz, 1H), 5.43 (dd, $J = 7.2$, 3.0 Hz, 1H), 4.07 – 3.92 (m, 2H), 2.34 – 2.25 (m, 1H), 2.04 – 1.92 (m, 2H), 1.93 – 1.81 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 134.3, 132.4, 129.9, 127.5, 89.5, 67.5, 32.1, 24.6.

**HRMS** (ESI) calculated for C$_8$H$_{10}$OS$_2$ [M+H]$^+$: 187.0246; Found: 187.0247

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b29** as a colorless oil (28.3 mg, 73% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.35 (d, $J = 7.6$ Hz, 2H), 7.30 (d, $J = 7.7$ Hz, 2H), 7.26 (s, 1H), 5.22 (dd, $J = 7.3$, 3.6 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.91 – 3.73 (m, 2H), 2.23 – 2.15 (m, 1H), 2.05 – 1.95 (m, 2H), 1.87 – 1.75 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 138.6, 129.0, 128.6, 126.9, 83.0, 66.8, 36.0, 31.0, 26.2.

**HRMS** (ESI) calculated for C$_{11}$H$_{14}$OS [M+H]$^+$: 195.0839; Found: 195.0833

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b30** as a colorless oil (26.3 mg, 70% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 5.36 (dd, $J = 7.3$, 3.9 Hz, 1H), 3.98 – 3.86 (m, 2H), 2.73 – 2.54 (m, 2H), 2.32 – 2.22 (m, 1H), 2.04 – 1.94 (m, 1H), 1.89 – 1.78 (m, 2H), 1.67 – 1.58 (m, 2H), 1.42 – 1.35 (m, 2H), 1.33 – 1.26 (m, 4H), 0.88 (t, $J = 6.8$ Hz, 3H).

**13C NMR** (101 MHz, CDCl$_3$) δ 84.5, 66.8, 32.7, 31.5, 31.3, 30.0, 28.8, 24.9, 22.6, 14.1.
HRMS (ESI) calculated for C_{10}H_{20}OS [M+H]^+: 189.1308; Found: 189.1308

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b31** as a colorless oil (29.9 mg, 55% yield).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{)}\delta 5.36 (dd, J = 7.3, 3.9 Hz, 1H), 3.97 – 3.86 (m, 2H), 2.74 – 2.53 (m, 2H), 2.33 – 2.20 (m, 1H), 2.03 – 1.94 (m, 1H), 1.88 – 1.78 (m, 2H), 1.67 – 1.59 (m, 2H), 1.41 – 1.33 (m, 2H), 1.31 – 1.23 (m, 16H), 0.92 – 0.82 (t, 3H). \]

\[ ^13\text{C NMR (101 MHz, CDCl}_3\text{)}\delta 84.4, 66.7, 32.6, 31.9, 31.2, 30.0, 29.65, 29.63, 29.60, 29.5, 29.3, 29.2, 29.0, 24.8, 22.3, 14.1. \]

HRMS (ESI) calculated for C_{16}H_{32}OS [M+H]^+: 273.2247; Found: 273.2238

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b34** as a colorless oil (25.2 mg, 52% yield).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{)}\delta 7.60 (d, J = 6.9 Hz, 2H), 7.35 (d, J = 7.0 Hz, 2H), 7.32 (s, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.12 (dd, J = 5.4, 3.6 Hz, 1H), 6.49 (s, 1H), 4.55 (td, J = 11.6, 3.2 Hz, 1H), 4.01 (dd, J = 10.9, 5.7 Hz, 1H), 3.11 (ddd, J = 16.7, 12.3, 6.3 Hz, 1H), 2.70 (dd, J = 16.0, 3.0 Hz, 1H). \]

\[ ^13\text{C NMR (101 MHz, CDCl}_3\text{)}\delta 136.0, 133.9, 133.8, 131.2, 128.9, 128.8, 127.7, 127.2, 127.1, 126.1, 85.9, 58.2, 27.8. \]

HRMS (ESI) calculated for C_{15}H_{14}OS [M+H]^+: 243.0839; Found: 243.0844
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **b35** as a colorless oil (20.4 mg, 56% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, $J = 9.5$ Hz, 2H), 7.30 (d, $J = 6.5$ Hz, 2H), 7.28 (d, $J = 4.5$ Hz, 1H), 4.89 (q, $J = 6.3$ Hz, 1H), 4.02 – 3.90 (m, 1H), 3.56 – 3.44 (m, 1H), 1.50 (d, $J = 6.3$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.8, 128.7, 127.5, 84.5, 63.4, 22.7, 14.9.

HRMS (ESI) calculated for C$_{10}$H$_{14}$OS [M+H]$^+$: 183.0839; Found: 183.0841

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\text{b36}
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Purification by column chromatography on silica gel (hexane/ethyl acetate = 50/1, v/v) afforded **b36** as a colorless oil (23.8 mg, 60% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.46 (m, 2H), 7.31 (dd, $J = 5.1$, 2.0 Hz, 3H), 4.76 (dd, $J = 7.8$, 4.1 Hz, 1H), 3.61 (dd, $J = 10.6$, 4.1 Hz, 1H), 3.56 (s, 3H), 3.53 (dd, $J = 10.6$, 7.8 Hz, 1H), 3.37 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.9, 132.3, 128.8, 127.9, 88.9, 74.7, 59.1, 56.3.

HRMS (ESI) calculated for C$_{10}$H$_{15}$O$_2$S [M+H]$^+$: 199.0787; Found: 199.0788

\[
\text{b37/ b37'}
\]

Due to the minimal polarity difference of **b37** and **b37’**, the isolation is difficult. Therefore, the mixture of **b37** and **b37’** was obtained. Purification by column chromatography on silica gel (hexane/ethyl acetate = 50/1, v/v) afforded the mixture of **b37/ b37’** as a colorless oil (34.5 mg, 89% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.53 (dt, $J = 7.0$, 2.9 Hz, 7H), 7.51 – 7.48 (m, 2H), 7.36 – 7.28 (m, 11H), 7.28 – 7.25 (m, 2H), 7.24 – 7.18 (m, 2H), 5.69 (dd, $J = 7.4$, 4.7 Hz, 1H), 5.48 (dd, $J = 7.1$, 4.0 Hz, 1H), 4.31 (dp, $J = 8.7$, 6.0 Hz, 1H), 4.24 – 4.17
(m, 1H), 4.17 – 4.10 (m, 3H), 4.02 (ddd, $J = 10.1, 7.5, 4.4$ Hz, 3H), 2.47 (dddd, $J = 13.5, 9.7, 7.3, 3.9$ Hz, 1H), 2.39 – 2.29 (m, 1H), 2.22 – 2.14 (m, 3H), 2.11 (ddd, $J = 12.9, 6.6, 3.8$ Hz, 5H), 2.06 – 2.03 (m, 1H), 2.01 – 1.96 (m, 4H), 1.96 – 1.91 (m, 3H), 1.73 – 1.62 (m, 1H), 1.55 (s, 9H), 1.50 – 1.38 (m, 1H), 1.35 (d, $J = 6.2$ Hz, 3H), 1.29 (d, $J = 6.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.1, 135.5, 133.4, 131.6, 130.8, 128.8, 128.5, 128.1, 126.9, 126.6, 95.0, 87.1, 86.8, 74.5, 67.7, 39.5, 33.6, 33.2, 32.5, 28.2, 25.1, 22.0, 20.1.
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{d1} as a colorless oil (24.7 mg, 55% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 4.8$ Hz, 4H), 7.30 – 7.22 (m, 1H), 3.90 – 3.75 (m, 2H), 3.73 – 3.63 (m, 1H), 2.71 (ddt, $J = 14.2$, 6.7, 2.4 Hz, 1H), 2.49 (ddt, $J = 14.2$, 6.8, 2.3 Hz, 1H), 1.93 – 1.84 (m, 2H), 1.83 – 1.75 (m, 1H), 1.52 – 1.43 (m, 1H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 154.3 (t, $J = 286.6$ Hz), 133.6, 128.5, 128.4 (t, $J = 3.2$ Hz), 127.3, 90.1 (dd, $J = 20.1$, 16.6 Hz), 77.0 (t, $J = 3.0$ Hz), 67.8, 33.9, 30.9, 25.6

\textbf{19F NMR} (376 MHz, Chloroform-$d$) $\delta$ -90.80 (s, 1F), -90.81 (s, 1F).

\textbf{19F NMR} (376 MHz, CDCl$_3$) $\delta$ -90.72 (d, $J = 42.8$ Hz, 1F), -90.85 (d, $J = 44.0$ Hz, 1F)

\textbf{HRMS} (ESI) calculated for C$_{13}$H$_{14}$F$_2$O $[M+H]^+$: 225.1086; Found: 225.1081

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{d2} as a colorless oil (40.0 mg, 84% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J = 7.1$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 3.88 – 3.77 (m, 2H), 3.72 – 3.65 (m, 1H), 2.70 (ddt, $J = 14.1$, 6.6, 2.4 Hz, 1H), 2.47 (ddt, $J = 14.2$, 7.0, 2.3 Hz, 1H), 2.34 (s, 3H), 1.93 – 1.84 (m, 2H), 1.83 – 1.75 (m, 1H), 1.53 – 1.43 (m, 1H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 154.3 (t, $J = 289.5$ Hz), 137.2, 130.6, 129.3, 128.3 (t, $J = 3.0$ Hz), 89.9 (dd, $J = 20.9$, 15.4 Hz), 70.1, 67.9, 33.9, 30.9, 25.7, 21.2.

\textbf{19F NMR} (376 MHz, CDCl$_3$) $\delta$ -90.96 (d, $J = 43.2$ Hz, 1F), -91.26 (d, $J = 44.0$Hz, 1F).

\textbf{HRMS} (ESI) calculated for C$_{14}$H$_{16}$F$_2$O $[M+H]^+$: 239.1242; Found: 239.1240
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d3 as a colorless oil (49.3 mg, 88% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.38 (m, 2H), 7.31 (d, \(J = 7.6\) Hz, 2H), 3.95 – 3.81 (m, 2H), 3.78 – 3.68 (m, 1H), 2.74 (ddt, \(J = 14.1, 6.6, 2.5\) Hz, 1H), 2.52 (ddt, \(J = 14.1, 6.9, 2.3\) Hz, 1H), 1.98 – 1.89 (m, 2H), 1.88 – 1.80 (m, 1H), 1.58 – 1.48 (m, 1H), 1.35 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.3 (dd, \(J = 290.9, 287.8\) Hz), 150.2, 130.4, 127.9 (t, \(J = 3.3\) Hz), 125.4, 89.8 (dd, \(J = 20.3, 15.5\) Hz), 77.0, 67.8, 34.5, 33.8, 31.3, 30.9, 25.6.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -90.81 (d, \(J = 41.7\) Hz, 1F), -90.96 (d, \(J = 42.2\) Hz, 1F).

HRMS (ESI) calculated for C\(_{17}\)H\(_{22}\)F\(_2\)O [M+H]: 281.1712; Found: 281.1707

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d4 as a colorless oil (53.9 mg, 90% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 – 7.56 (m, 4H), 7.43 (t, \(J = 7.7\) Hz, 4H), 7.34 (t, \(J = 7.3\) Hz, 1H), 3.91 – 3.83 (m, 2H), 3.70 (td, \(J = 8.1, 5.9\) Hz, 1H), 2.74 (ddt, \(J = 14.3, 6.7, 2.4\) Hz, 1H), 2.53 (ddt, \(J = 14.3, 6.8, 2.3\) Hz, 1H), 1.96 – 1.87 (m, 2H), 1.86 – 1.76 (m, 1H), 1.56 – 1.46 (m, 1H).

\(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 154.4 (t, \(J = 290.1\) Hz), 140.6, 140.1, 132.5, 128.8,
128.7 (t, J = 3.4 Hz), 127.4, 127.2, 127.0, 89.8 (t, J = 17.3 Hz), 67.8, 33.8, 31.0, 25.6.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -90.04 (d, J = 40.6 Hz, 1F), -90.16 (d, J = 40.6 Hz, 1F).

HRMS (ESI) calculated for C$_{19}$H$_{18}$F$_2$O [M+H]$^+$: 301.1399; Found: 301.1392

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d$_5$ as a colorless oil (51.6 mg, 86% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.28 (m, 9H), 3.78 – 3.69 (m, 1H), 3.65 – 3.54 (m, 2H), 2.18 – 2.01 (m, 1H), 1.90 – 1.79 (m, 1H), 1.79 – 1.71 (m, 2H), 1.71 – 1.65 (m, 1H), 1.32 – 1.20 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.3 (t, J = 286.8 Hz), 141.6 (d, J = 2.9 Hz), 141.2, 131.9 (d, J = 4.9 Hz), 131.3, 130.4, 128.6 (d, J = 41.9 Hz), 127.4 (d, J = 5.6 Hz), 125.8, 120.4, 119.4, 110.7, 90.4 (dd, J = 22.0, 17.8 Hz), 67.7, 34.1, 30.9, 25.6.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -89.35 (d, J = 43.1 Hz, 1F), -93.06 (d, J = 42.5 Hz, 1F).

HRMS (ESI) calculated for C$_{19}$H$_{18}$F$_2$O [M+H]$^+$: 301.1399; Found: 301.1392

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d$_6$ as a colorless oil (34.6 mg, 68% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.25 (m, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.89 (s, 1H), 6.82 (dd, J = 8.3, 2.3 Hz, 1H), 3.91 – 3.80 (m, 2H), 3.80 (s, 3H), 3.69 (td, J = 8.1, 5.9 Hz, 1H), 2.69 (ddt, J = 14.2, 6.7, 2.4 Hz, 1H), 2.47 (ddt, J = 14.2, 6.8, 2.4 Hz, 1H),
1.95 – 1.84 (m, 2H), 1.86 – 1.75 (m, 1H), 1.54 – 1.42 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.6, 154.4 (t, $J = 288.4$ Hz), 135.0 (t, $J = 3.8$ Hz), 129.6 (d, $J = 275$ Hz), 120.8 (t, $J = 3.0$ Hz), 114.4 (t, $J = 3.3$ Hz), 112.8, 90.1 (dd, $J = 21.6, 14.5$ Hz), 67.8, 55.3, 33.9, 31.0, 25.6, 8.1.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -90.02 (d, $J = 41.0$ Hz, 1F), -90.54 (d, $J = 40.9$ Hz, 1F).

**HRMS (ESI)** calculated for C$_{14}$H$_{16}$F$_2$O$_2$ [M+H]$^+$: 255.1192; Found: 255.1199

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d7** as a colorless oil (50.0 mg, 79% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, $J = 2.1$ Hz, 1H), 7.31 – 7.27 (m, 2H), 7.27 – 7.21 (m, 1H), 7.12 – 7.04 (m, 2H), 6.96 – 6.92 (m, 2H), 6.90 (dd, $J = 8.2, 1.2$ Hz, 1H), 3.85 – 3.74 (m, 2H), 3.70 – 3.62 (m, 1H), 2.65 (ddt, $J = 14.1, 6.5, 2.2$ Hz, 1H), 2.47 (ddt, $J = 14.1, 7.1, 2.1$ Hz, 1H), 1.91 – 1.82 (m, 2H), 1.81 – 1.72 (m, 1H), 1.50 – 1.41 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.3, 154.9, 153.9 (t, $J = 287.7$ Hz), 131.8 (t, $J = 2.3$ Hz), 129.7, 129.3, 125.4, 123.6, 123.1, 119.3, 118.3, 86.6 (dd, $J = 23.8, 17.6$ Hz), 77.2, 67.7, 34.0, 30.9, 25.6.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -88.47 (d, $J = 40.3$ Hz, 1F), -92.32 (d, $J = 40.2$ Hz, 1F).

**HRMS (ESI)** calculated for C$_{19}$H$_{18}$F$_2$O$_2$ [M+H]$^+$: 317.1348; Found: 317.1346
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d8** as a colorless oil (46.8 mg, 74% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.34 (dd, $J = 8.6$, 7.4 Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 2H), 6.98 (d, $J = 8.7$ Hz, 2H), 3.89 – 3.79 (m, 2H), 3.70 (td, $J = 8.1$, 4.5 Hz, 1H), 2.67 (ddt, $J = 14.2$, 6.8, 2.4 Hz, 1H), 2.48 (ddt, $J = 14.2$, 6.7, 2.4 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.89 – 1.76 (m, 1H), 1.55 – 1.44 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 156.8, 156.6, 154.2 (t, $J = 290.5$ Hz), 129.8, 129.7 (t, $J = 3.2$ Hz), 128.2, 123.5, 119.2, 118.5, 89.5 (dd, $J = 20.2$, 16.6 Hz), 77.0, 67.8, 34.0, 31.0, 25.6.

**19F NMR** (376 MHz, CDCl$_3$) δ -90.88 (d, $J = 42.9$ Hz, 1F), -91.00 (d, $J = 42.1$ Hz, 1F)

**HRMS** (ESI) calculated for C$_{19}$H$_{18}$F$_2$O$_2$ [M+H]$^+$: 317.1348; Found: 317.1343

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d9** as a pale-yellow oil (35.7 mg, 63% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.29 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 2.9$ Hz, 2H), 3.88 – 3.77 (m, 2H), 3.72 – 3.65 (m, 1H), 2.95 (q, $J = 7.4$ Hz, 2H), 2.68 (ddt, $J = 14.3$, 6.7, 2.4 Hz, 1H), 2.48 (ddt, $J = 14.2$, 6.7, 2.4 Hz, 1H), 1.95 – 1.86 (m, 2H), 1.86 – 1.77 (m, 1H), 1.54 – 1.43 (m, 1H), 1.33 (t, $J = 7.3$ Hz, 3H).

**13C NMR** (101 MHz, CDCl$_3$) δ 159.2, 154.3 (t, $J = 290.2$ Hz), 136.0, 130.9, 128.7 (t, $J = 3.6$ Hz), 128.6, 89.6 (t, $J = 18.2$ Hz), 67.8, 33.7, 30.9, 27.4, 25.6, 14.3.
**19F NMR** (376 MHz, CDCl₃) δ -90.15 (s, 2F)

**HRMS (ESI)** calculated for C₁₅H₁₈F₂OS [M+H]⁺: 285.1120; Found: 285.1126

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d10** as a colorless oil (38.3 mg, 76% yield).

**1H NMR** (400 MHz, CDCl₃) δ 6.94 (s, 2H), 6.90 (s, 1H), 3.89 – 3.76 (m, 2H), 3.73 – 3.63 (m, 1H), 2.69 (ddt, J = 14.1, 6.6, 2.5 Hz, 1H), 2.45 (ddt, J = 14.1, 7.1, 2.3 Hz, 1H), 2.30 (s, 6H), 1.94 – 1.85 (m, 2H), 1.84 – 1.74 (m, 1H), 1.55 – 1.40 (m, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 154.2 (dd, J = 289.8, 286.9 Hz), 137.9, 133.3, 129.1, 126.2 (t, J = 3.0 Hz), 90.10 (dd, J = 21.0, 15.0 Hz), 77.0, 67.8, 34.0, 30.9, 25.6, 21.3.

**19F NMR** (376 MHz, CDCl₃) δ -90.86 (d, J = 42.9 Hz, 1F), -91.36 (d, J = 42.9 Hz, 1F).

**HRMS (ESI)** calculated for C₁₅H₁₈F₂O [M+H]⁺: 253.1399; Found: 253.1403

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d11** as a pale-yellow oil (52.6 mg, 70% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.71 (t, J = 1.8 Hz, 1H), 7.64 (d, J = 7.0 Hz, 4H), 7.54 (s, 2H), 7.46 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.3 Hz, 2H), 3.93 – 3.84 (m, 2H), 3.70 (td, J = 8.1, 5.9 Hz, 1H), 2.79 (ddt, J = 14.2, 6.8, 2.3 Hz, 1H), 2.57 (ddt, J = 14.2, 6.7, 2.3 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.86 – 1.76 (m, 1H), 1.57 – 1.47 (m, 1H).
\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 154.56 (t, $J = 289.1$ Hz), 142.1, 140.9, 134.6, 128.9, 127.6, 127.4, 126.3 (t, $J = 3.2$ Hz), 125.31, 90.22 (dd, $J = 21.6, 14.8$ Hz), 77.0, 67.9, 34.1, 31.1, 25.6.

\textbf{19F NMR} (376 MHz, CDCl$_3$) $\delta$ -89.82 (d, $J = 40.6$ Hz, 1F), -90.17 (d, $J = 40.8$ Hz, 1F).

\textbf{HRMS} (ESI) calculated for C$_{25}$H$_{22}$F$_2$O [M+H]$^+$: 377.1712; Found: 377.1718

\begin{center}
\includegraphics[width=0.2\textwidth]{d12.png}
\end{center}

\textbf{d12}

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{d12} as a colorless oil (40.9 mg, 69% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 3.89 – 3.78 (m, 2H), 3.68 (td, $J = 8.1, 6.0$ Hz, 1H), 2.71 (ddt, $J = 14.2, 6.7, 2.4$ Hz, 1H), 2.50 (ddt, $J = 14.2, 6.9, 2.3$ Hz, 1H), 1.93 – 1.85 (m, 2H), 1.83 – 1.74 (m, 1H), 0.26 (s, 9H).

\textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ 154.4 (t, $J = 289.2$ Hz), 139.6, 133.9, 133.5, 127.6 (t, $J = 3.1$ Hz), 90.09 (t, $J = 17.9$ Hz), 77.0, 67.8, 33.8, 30.9, 25.6, -1.2.

\textbf{19F NMR} (376 MHz, CDCl$_3$) $\delta$ -90.34 (s, 2F)

\textbf{HRMS} (ESI) calculated for C$_{16}$H$_{22}$F$_2$OSi [M+H]$^+$: 297.1481; Found: 297.1489

\begin{center}
\includegraphics[width=0.2\textwidth]{d13.png}
\end{center}

\textbf{d13}

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{d13} as a colorless oil (29.5 mg, 61% yield).

\textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.28 (m, 2H), 7.07 – 7.01 (m, 2H), 3.88 – 3.76 (m, 2H), 3.69 (td, $J = 8.1, 5.9$ Hz, 1H), 2.66 (ddt, $J = 14.3, 6.9, 2.3$ Hz, 1H), 2.47 (ddt,
J = 14.3, 6.5, 2.5 Hz, 1H), 1.95 – 1.87 (m,2H), 1.86 – 1.77 (m, 1H), 1.54 – 1.42 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.0 (d, J = 247.1 Hz), 154.3 (t, J = 292.8), 130.17 (dt, J = 7.6, 3.2 Hz), 129.6, 115.5 (d, J = 21.3 Hz), 89.44 (t, J = 18.3 Hz), 77.0, 67.9, 34.1, 31.0, 25.6.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -90.70 (s, 2F), -114.53 (s, 1F).

HRMS (ESI) calculated for C$_{13}$H$_{13}$F$_3$O [M+H]$^+$: 243.0992; Found: 243.0993

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d14 as a colorless oil (28.4 mg, 55% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 9.0 Hz, 2H), 3.87 – 3.76 (m, 2H), 3.68 (td, J = 8.1, 5.9 Hz, 1H), 2.65 (ddt, J = 14.3, 7.0, 2.3 Hz, 1H), 2.48 (ddt, J = 14.3, 6.5, 2.5 Hz, 1H), 1.96 – 1.84 (m, 2H), 1.87 – 1.75 (m, 1H), 1.52 – 1.43 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.3 (t, J = 290.6 Hz), 133.2, 132.1, 129.7 (t, J = 3.3 Hz), 128.6, 89.4 (dd, J = 20.3, 16.5 Hz), 76.90 (t, J = 2.9 Hz), 77.0, 67.8, 33.8, 31.0, 25.6.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -89.85 (d, J = 35.3 Hz, 1F), -89.98 (d, J = 39.9 Hz, 1F).

HRMS (ESI) calculated for C$_{13}$H$_{13}$ClF$_2$O [M+H]$^+$: 259.0696; Found: 259.0690

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d15 as a colorless oil (30.4 mg, 50% yield).
**1H NMR** (400 MHz, CDCl₃) δ 7.48 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 7.6 Hz, 2H), 3.88 – 3.76 (m, 2H), 3.69 (td, J = 8.1, 5.9 Hz, 1H), 2.65 (ddt, J = 14.4, 6.9, 2.3 Hz, 1H), 2.48 (ddt, J = 14.3, 6.4, 2.5 Hz, 1H), 1.95 – 1.86 (m, 2H), 1.86 – 1.77 (m, 1H), 1.52 – 1.43 (m, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 154.2 (dd, J = 290.6, 288.6 Hz), 132.6 (dd, J = 3.5, 1.9 Hz), 131.6, 130.0 (t, J = 3.3 Hz), 121.3, 89.5 (dd, J = 21.0, 15.7 Hz), 77.0, 67.8, 33.7, 31.0, 25.6.

**19F NMR** (376 MHz, CDCl₃) δ -89.68 (d, J = 39.5 Hz, 1F), -89.82 (d, J = 39.9 Hz, 1F).

**HRMS** (ESI) calculated for C₁₃H₁₃BrF₂O [M+H⁺]: 303.0191; Found: 303.0190

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d2** as a pale-yellow oil (37.0 mg, 60% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.38 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 3.88 – 3.77 (m, 2H), 3.70 (td, J = 8.2, 6.0 Hz, 1H), 2.66 (ddt, J = 14.3, 7.1, 2.3 Hz, 1H), 2.50 (ddt, J = 14.4, 6.3, 2.5 Hz, 1H), 1.96 – 1.88 (m, 2H), 1.87 – 1.79 (m, 1H), 1.54 – 1.45 (m, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 154.4 (t, J = 291.6 Hz), 148.2, 132.4, 129.8 (t, J = 3.3 Hz), 121.7, 120.9, 119.2, 89.3 (dd, J = 21.8, 15.1 Hz), 67.8, 33.4, 31.0, 25.6.

**19F NMR** (376 MHz, CDCl₃) δ -57.88 (s, 3F), -89.81 (d, J = 40.1 Hz, 1F), -90.00 (d, J = 40.1 Hz, 1F).

**HRMS** (ESI) calculated for C₁₄H₁₃F₂O₂ [M+H⁺]: 309.0909; Found: 309.0902
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded d17 as a colorless oil (38.5 mg, 56% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.60 (d, J = 7.9 Hz, 2H), 7.40 (t, J = 8.3 Hz, 2H), 4.40 – 4.25 (m, 1H), 3.98 – 3.91 (m, 1H), 3.85 – 3.62 (m, 4H), 2.75 (ddd, J = 13.6, 6.6, 3.0 Hz, 1H), 2.63 (tdd, J = 13.5, 7.0, 3.0 Hz, 1H), 2.11 – 1.98 (m, 2H), 1.94 – 1.76 (m, 5H), 1.59 – 1.39 (m, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 157.0 (d, J = 260.8 Hz), 156.9 (d, J = 260.4 Hz), 141.8 (d, J = 8.1 Hz), 141.3 (d, J = 8.1 Hz), 129.6, 125.4 (t, J = 4.6 Hz), 119.4 (t, J = 18.0 Hz), 74.2 (d, J = 26.9 Hz), 69.1, 67.8 (d, J = 11.7 Hz), 36.4 (d, J = 4.2 Hz), 35.9 (d, J = 4.6 Hz), 31.0 (d, J = 22.6 Hz), 28.5, 26.8, 25.6 (d, J = 9.3 Hz).

**19F NMR** (376 MHz, CDCl₃) δ -62.53 (d, J = 5.9 Hz, 3F), -125.37 (d, J = 29.6 Hz, 0.5F), -126.07 (d, J = 29.9 Hz, 0.5F).

**HRMS** (ESI) calculated for C₁₈H₂₀F₄O₂ [M+H]⁺: 345.1473; Found: 345.1477

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded d18 as a colorless oil (34.7 mg, 52% yield).

**1H NMR** (400 MHz, CDCl₃) δ 8.01 (d, J = 7.9 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 4.43 – 4.28 (m, 1H), 3.98 – 3.93 (m, 1H), 3.92 (s, 3H), 3.86 – 3.81 (m, 1H), 3.80 – 3.76 (m, 1H), 3.75 – 3.60 (m, 2H), 2.77 (ddt, J = 13.3, 6.4, 3.2 Hz, 1H), 2.68 – 2.59 (m, 1H), 2.10 – 1.98 (m, 2H), 1.93 – 1.76 (m, 5H), 1.56 – 1.37 (m, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 166.8 (d, J = 2.4 Hz), 156.8 (d, J = 260.7 Hz), 156.7
(d, \( J = 260.4 \text{ Hz} \)), 142.8 (d, \( J = 8.3 \text{ Hz} \)), 142.3 (d, \( J = 8.1 \text{ Hz} \)), 129.6 (d, \( J = 4.5 \text{ Hz} \)), 129.3, 119.6 (dd, \( J = 18.6, 12.9 \text{ Hz} \)), 74.2 (d, \( J = 27.0 \text{ Hz} \)), 69.1, 67.7 (d, \( J = 11.6 \text{ Hz} \)), 52.2, 36.0 (dd, \( J = 39.5, 4.5 \text{ Hz} \)), 30.9 (d, \( J = 19.6 \text{ Hz} \)), 28.5, 26.8, 25.6 (d, \( J = 8.6 \text{ Hz} \)).

\(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)) \( \delta \) -125.50 (d, \( J = 29.6 \text{ Hz}, 0.5\text{F} \)), -126.20 (d, \( J = 29.7 \text{ Hz}, 0.5\text{F} \)).

HRMS (ESI) calculated for C\(_{19}\)H\(_{23}\)FO\(_4\) [M+H]\(^+\): 335.1654; Found: 335.1661

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d\(_{19}\) as a green oil (39.1 mg, 52% yield).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 7.28 (dd, \( J = 8.5, 7.2 \text{ Hz}, 4\text{H} \)), 7.23 (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.12 (d, \( J = 7.3 \text{ Hz}, 4\text{H} \)), 7.05 (dd, \( J = 8.0, 6.3 \text{ Hz}, 4\text{H} \)), 3.95 – 3.84 (m, 2H), 3.74 (td, \( J = 8.1, 5.9 \text{ Hz}, 1\text{H} \)), 2.69 (ddt, \( J = 14.1, 6.6, 2.5 \text{ Hz}, 1\text{H} \)), 2.50 (ddt, \( J = 14.1, 6.8, 2.3 \text{ Hz}, 1\text{H} \)), 2.00 – 1.92 (m, 2H), 1.91 – 1.81 (m, 1H), 1.58 – 1.49 (m, 1H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \( \delta \) 154.3 (t, \( J = 215.6 \text{ Hz} \)), 147.6, 146.8, 129.3, 129.0 (t, \( J = 3.9 \text{ Hz} \)), 127.05, 127.01, 124.55, 123.08 (d, \( J = 4.5 \text{ Hz} \)), 114.50, 89.6 (dd, \( J = 20.6, 14.6 \text{ Hz} \)), 67.8, 33.8, 31.0, 25.6.

\(^{19}\text{F NMR}\) (376 MHz, Chloroform-d) \( \delta \) -90.70 (d, \( J = 42.8 \text{ Hz}, 1\text{F} \)), -90.89 (d, \( J = 42.9 \text{ Hz}, 1\text{F} \)).

HRMS (ESI) calculated for C\(_{25}\)H\(_{23}\)F\(_2\)NO [M+H]\(^+\): 392.1821; Found: 392.1826
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d20 as a colorless oil (35.6 mg, 65% yield).

\(^{1}\text{H NMR}\) (400 MHz, CDCl\(_{3}\)) \(\delta\) 7.81 (dd, \(J = 8.7, 2.4\) Hz, 4H), 7.50 – 7.44 (m, 3H), 3.89 – 3.79 (m, 2H), 3.67 (td, \(J = 8.1, 6.0\) Hz, 1H), 2.81 (ddt, \(J = 14.3, 6.7, 2.4\) Hz, 1H), 2.59 (ddt, \(J = 14.3, 6.9, 2.3\) Hz, 1H), 1.94 – 1.85 (m, 2H), 1.84 – 1.72 (m, 1H), 1.58 – 1.43 (m, 1H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_{3}\)) \(\delta\) 154.6 (dd, \(J = 290.6, 287.8\) Hz), 133.3, 132.6, 131.0 (t, \(J = 3.5\) Hz), 128.2, 128.0, 127.5 (t, \(J = 3.4\) Hz), 127.5, 126.4, 126.2, 90.2 (dd, \(J = 21.3, 14.8\) Hz), 77.3, 76.8, 67.9, 34.0, 31.0, 25.6.

\(^{19}\text{F NMR}\) (376 MHz, Chloroform-\(d\)) \(\delta\) -90.12 (d, \(J = 40.3\) Hz, 1F), -90.36 (d, \(J = 40.5\) Hz, 1F).

HRMS (ESI) calculated for C\(_{17}\)H\(_{16}\)F\(_2\)O \([\text{M+H}]^+\): 275.1242; Found: 275.1252

\[ \text{d21} \]

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d21 as a colorless oil (46.9 mg, 67% yield).

\(^{1}\text{H NMR}\) (400 MHz, CDCl\(_{3}\)) \(\delta\) 7.95 – 7.82 (m, 3H), 7.51 (d, \(J = 7.0\) Hz, 1H), 7.49 – 7.45 (m, 5H), 7.42 (ddd, \(J = 8.6, 7.0, 1.5\) Hz, 2H), 3.96 – 3.85 (m, 2H), 3.73 (td, \(J = 8.0, 5.9\) Hz, 1H), 2.77 (ddt, \(J = 14.3, 6.8, 2.4\) Hz, 1H), 2.57 (ddt, \(J = 14.3, 6.7, 2.3\) Hz, 1H), 2.00 – 1.89 (m, 2H), 1.89 – 1.80 (m, 1H), 1.61 – 1.48 (m, 1H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_{3}\)) \(\delta\) 154.5 (t, \(J = 290.6\) Hz) 139.8, 139.7, 133.9, 132.5, 131.6, 130.2, 128.4, 128.2 (t, \(J = 3.3\) Hz), 77.1, 127.8, 127.0, 126.1, 126.0, 125.9, 125.4, 90.0 (dd, \(J = 19.4, 16.6\) Hz), 67.9, 33.9, 31.1, 25.7.

\(^{19}\text{F NMR}\) (376 MHz, CDCl\(_{3}\)) \(\delta\) -89.91, -90.01, -90.03, -90.14.

HRMS (ESI) calculated for C\(_{23}\)H\(_{20}\)F\(_2\)O \([\text{M+H}]^+\): 351.1555; Found: 355.1547
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d23 as a colorless oil (32.2 mg, 60% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.83 (s, 1H), 6.79 (s, 2H), 5.96 (s, 2H), 3.90 – 3.78 (m, 2H), 3.69 (td, $J = 8.0$, 5.9 Hz, 1H), 2.63 (ddt, $J = 14.2$, 6.8, 2.4 Hz, 1H), 2.43 (ddt, $J = 14.2$, 6.7, 2.4 Hz, 1H), 1.95 – 1.86 (m, 2H), 1.85 – 1.76 (m, 1H), 1.54 – 1.42 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.2 (t, $J = 289.3$ Hz), 147.8, 146.8, 127.2 (t, $J = 3.7$ Hz), 122.0 (t, $J = 3.2$ Hz), 109.0 (t, $J = 3.3$ Hz), 108.4, 101.2, 89.9 (dd, $J = 22.0$, 14.8 Hz), 77.0, 67.8, 34.2, 31.0, 25.6.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -90.91 (d, $J = 43.4$ Hz, 1F), -91.38 (d, $J = 43.3$ Hz, 1F).

HRMS (ESI) calculated for C$_{14}$H$_{14}$F$_2$O$_3$ [M+H]$^+$: 269.0984; Found: 269.0980

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d23 as a pale-yellow oil (48.7 mg, 70% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.21 (dd, $J = 7.7$, 4.3 Hz, 4H), 8.16 – 8.03 (m, 3H), 8.03 (t, $J = 7.6$ Hz, 2H), 3.93 (dt, $J = 8.5$, 6.6 Hz, 1H), 3.82 (p, $J = 6.6$ Hz, 1H), 3.72 (td, $J = 8.0$, 5.9 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.70 (ddt, $J = 14.0$, 5.9, 2.7 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.83 – 1.71 (m, 1H), 1.59 – 1.46 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.0 (t, $J = 294.1$ Hz), 139.56, 131.29, 131.09, 130.93, 128.04, 127.76, 127.29, 126.14, 125.79, 125.40, 125.28, 124.97, 124.76, 120.32, 119.34, 110.61, 88.6 (dd, $J = 21.9$, 18.7 Hz), 67.71, 36.19, 31.16, 25.62.
$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -87.32 (t, $J = 36.7$ Hz, 1F), -91.84 (d, $J = 40.5$ Hz, 1F).

HRMS (ESI) calculated for C$_{23}$H$_{18}$F$_2$O $[\text{M+H}]^+$: 349.1399; Found: 349.1399

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d24** as a colorless oil (60.2 mg, 93% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (dd, $J = 21.5$, 8.1 Hz, 2H), 8.10 – 7.84 (m, 2H), 7.76 – 7.68 (m, 1H), 7.68 – 7.62 (m, 3H), 7.62 – 7.57 (m, 1H), 3.93 – 3.76 (m, 2H), 3.74 – 3.61 (m, 1H), 2.92 – 2.76 (m, 1H), 2.64 – 2.41 (m, 1H), 1.98 – 1.82 (m, 2H), 1.81 – 1.72 (m, 1H), 1.57 – 1.39 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.4, 130.8, 130.3, 129.1, 128.8, 127.03, 126.9, 126.0, 125.6, 123.2, 123.0, 122.6, 88.2 (dd, $J = 22.0$, 18.9 Hz), 77.0, 67.7, 35.2, 31.2, 25.6.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -87.23 (dd, $J = 135.5$, 41.0 Hz, 1F), -92.14 (dd, $J = 63.1$, 41.0 Hz, 1F).

HRMS (ESI) calculated for C$_{21}$H$_{18}$F$_2$O $[\text{M+H}]^+$: 325.1398; Found: 325.1407

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d25** as a yellow oil (52.0 mg, 65% yield).

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\[ ^1H \text{ NMR} \ (400 \text{ MHz, Chloroform}-d) \delta \ 8.35 \ (d, \ J = 8.8 \text{ Hz}, 1H), 8.08 \ (d, \ J = 8.8 \text{ Hz}, 1H), 7.67 \ (t, \ J = 9.3 \text{ Hz}, 2H), 7.62 - 7.46 \ (m, 5H), 7.43 \ (t, \ J = 7.1 \text{ Hz}, 2H), 7.35 \ (dd, \ J = 8.8, 6.5 \text{ Hz}, 2H), 3.94 \ (td, \ J = 7.8, 5.6 \text{ Hz}, 1H), 3.71 \ (dq, \ J = 14.5, 7.1, 6.3 \text{ Hz}, 2H), 2.99 \ (ddd, \ J = 14.1, 8.3, 2.3 \text{ Hz}, 1H), 2.62 - 2.54 \ (m, 1H), 1.97 - 1.72 \ (m, 3H), 1.55 - 1.39 \ (m, 1H). \]

\[ ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta \ 154.2 \ (dd, \ J = 291.6, 286.7 \text{ Hz}), 138.8, 138.2, 131.3, 131.1, 130.4, 130.1 \ (d, \ J = 3.0 \text{ Hz}), 129.9, 129.7, 129.6 \ (d, \ J = 3.2 \text{ Hz}), 128.4, 128.4, 127.7, 127.6, 127.3, 127.0, 126.1, 125.9, 125.8, 125.4, 125.3, 125.0, 85.9 \ (dd, \ J = 22.1, 19.6 \text{ Hz}), 67.5, 36.6, 31.3, 25.6. \]

\[ ^{19}F \text{ NMR} \ (376 \text{ MHz, Chloroform}-d) \delta \ -85.96 \ (d, \ J = 38.8 \text{ Hz}, 1F), -91.06 \ (d, \ J = 38.8 \text{ Hz}, 1F). \]

HRMS (ESI) calculated for C_{27}H_{22}F_{2}O \ [M+H]^+: 401.1712; Found: 401.1710

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \textbf{d26} as a colorless oil (68.8 mg, 95% yield).

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.51 - 7.44 \ (m, 3H), 7.26 - 7.19 \ (m, 4H), 3.83 \ (q, \ J = 7.2, 6.8 \text{ Hz}, 1H), 3.74 - 3.61 \ (m, 2H), 2.69 \ (dd, \ J = 14.1, 6.5 \text{ Hz}, 1H), 2.49 \ (ddt, \ J = 14.1, 6.8, 2.4 \text{ Hz}, 1H), 1.97 - 1.85 \ (m, 2H), 1.83 - 1.73 \ (m, 1H), 1.58 - 1.45 \ (m, 1H). \]

\[ ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta \ 154.0 \ (t, \ J = 288.4 \text{ Hz}), 136.3 \ (d, \ J = 9.5 \text{ Hz}), 136.1, 135.4, 133.7, 129.5, 128.8, 128.6 \ (d, \ J = 6.9 \text{ Hz}), 127.8 \ (d, \ J = 13.1 \text{ Hz}), 127.3, 88.8 \ (dd, \ J = 23.7, 18.2 \text{ Hz}), 67.7, 34.7, 31.1, 25.6. \]

\[ ^{19}F \text{ NMR} \ (376 \text{ MHz, Chloroform}-d) \delta \ -88.66 \ (d, \ J = 42.8 \text{ Hz}, 1F), -93.11 \ (d, \ J = 42.6 \text{ Hz}, 1F). \]

HRMS (ESI) calculated for C_{19}H_{16}F_{2}OS_{2} \ [M+H]^+: 363.0684; Found: 363.0677
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \( \text{d27} \) as a colorless oil (51.5 mg, 82% yield).

\(^1\)\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.91 (dd, \( J = 20.1, 8.3 \) Hz, 2H), 7.58 (d, \( J = 8.2 \) Hz, 1H), 7.48 – 7.42 (m, 1H), 7.38 (d, \( J = 7.1 \) Hz, 1H), 7.33 (td, \( J = 7.4, 3.2 \) Hz, 2H), 3.85 – 3.73 (m, 2H), 3.64 (tdd, \( J = 8.3, 5.9, 1.5 \) Hz, 1H), 2.93 (ddq, \( J = 14.0, 6.6, 2.4 \) Hz, 1H), 2.72 (ddq, \( J = 14.1, 7.0, 2.4 \) Hz, 1H), 1.93 – 1.81 (m, 2H), 1.79 – 1.70 (m, 1H), 1.56 – 1.43 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 156.1, 154.3 (t, \( J = 290.0 \) Hz), 153.8, 128.0 (t, \( J = 2.5 \) Hz), 127.4, 124.6, 124.1, 122.9 (d, \( J = 4.6 \) Hz), 120.7, 120.2, 118.1, 111.9, 86.0 (dd, \( J = 24.5, 16.6 \) Hz), 77.2 (t, \( J = 3.0 \) Hz), 67.8, 33.7, 30.9, 25.6.

\(^{19}\)F NMR (376 MHz, Chloroform-d) \( \delta \) -87.13 (d, \( J = 36.8 \) Hz, 1F), -90.58 (d, \( J = 36.7 \) Hz, 1F).

HRMS (ESI) calculated for C\(_{19}\)H\(_{16}\)F\(_2\)O\(_2\) [M+H]\(^+\): 315.1192; Found: 315.1189

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded \( \text{d28} \) as a colorless oil (61.4 mg, 93% yield).

\(^1\)\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.15 – 8.06 (m, 2H), 7.87 – 7.80 (m, 1H), 7.50 – 7.41 (m, 3H), 7.36 (d, \( J = 6.2 \) Hz, 1H), 3.87 – 3.72 (m, 2H), 3.66 (td, \( J = 7.9, 6.0 \) Hz, 1H), 2.81 (dddd, \( J = 14.1, 6.7, 2.6, 1.6 \) Hz, 1H), 2.60 (ddt, \( J = 14.1, 6.9, 2.4 \) Hz, 1H), 1.96 – 1.82 (m, 2H), 1.83 – 1.71 (m, 1H), 1.54 – 1.43 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 153.9 (t, \( J = 291.4 \) Hz), 139.8, 139.2, 135.9 (d, \( J =
26.6 Hz), 128.6 (d, J = 4.5 Hz), 127.8 (d, J = 1.9 Hz), 127.0, 124.8, 124.5, 122.8, 121.8, 121.1, 89.2 (dd, J = 23.2, 17.5 Hz), 76.9, 67.8, 34.0, 31.1, 25.6.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -85.80 (d, J = 36.9 Hz, 1F), -90.86 (d, J = 36.3 Hz, 1F).

HRMS (ESI) calculated for C$_{19}$H$_{16}$F$_2$OS [M+H]$^+$: 331.0963; Found: 331.0973

d29

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d29 as a colorless oil (41.1 mg, 61% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 – 8.09 (m, 2H), 7.81 (dd, J = 8.8, 6.5 Hz, 2H), 7.47 – 7.39 (m, 3H), 3.90 – 3.80 (m, 2H), 3.68 (td, J = 8.2, 5.9 Hz, 1H), 2.80 (ddt, J = 14.3, 6.9, 2.3 Hz, 1H), 2.58 (ddt, J = 14.2, 6.6, 2.5 Hz, 1H), 1.96 – 1.83 (m, 2H), 1.83 – 1.74 (m, 1H), 1.55 – 1.45 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.4 (t, J = 288.8 Hz), 139.8, 138.5, 135.8, 135.3, 130.0, 127.0 (t, J = 3.1 Hz), 126.96, 124.5, 122.8, 121.7, 121.6 (t, J = 3.2 Hz), 90.2 (dd, J = 20.1, 16.5 Hz), 77.0 (t, J = 2.9 Hz), 67.8, 34.3, 31.0, 25.6.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -90.55 (d, J = 42.1 Hz, 1F), -90.68 (d, J = 40.8 Hz, 1F).

HRMS (ESI) calculated for C$_{19}$H$_{16}$F$_2$OS [M+H]$^+$: 331.0963; Found: 331.0964

d30

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d30 as a colorless oil (33.0 mg, 60% yield).
$^{1}H$ NMR (400 MHz, Chloroform-$d$) $\delta$ 8.92 (s, 1H), 8.17 – 8.08 (m, 2H), 7.82 (d, $J$ = 8.2 Hz, 1H), 7.72 (t, $J$ = 7.9 Hz, 1H), 7.57 (t, $J$ = 7.6 Hz, 1H), 3.88 – 3.80 (m, 2H), 3.69 (td, $J$ = 8.0, 6.1 Hz, 1H), 2.83 – 2.73 (m, 1H), 2.70 – 2.61 (m, 1H), 1.95 – 1.88 (m, 2H), 1.86 – 1.80 (m, 1H), 1.58 – 1.48 (m, 1H).

$^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 154.8 (t, $J$ = 292.8 Hz), 150.4, 147.1, 135.0, 129.6, 129.2, 127.8, 127.6, 127.0, 87.9 (dd, $J$ = 22.9, 13.6 Hz), 76.9 (t, $J$ = 2.9 Hz), 67.8, 33.7, 31.1, 25.6.

$^{19}F$ NMR (376 MHz, Chloroform-$d$) $\delta$ -88.13 (d, $J$ = 7.3 Hz, 1F), -88.97 (d, $J$ = 7.0 Hz, 1F).

HRMS (ESI) calculated for C$_{16}$H$_{15}$F$_{2}$NO $[M+H]^+$: 276.1195; Found: 276.1189

![d31](image)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded d31 as a colorless oil (53.0 mg, 73% yield).

$^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 7.2 Hz, 1H), 7.51 (d, $J$ = 7.7 Hz, 1H), 7.30 (t, $J$ = 7.1 Hz, 1H), 7.22 (t, $J$ = 7.5 Hz, 1H), 6.55 (s, 1H), 3.88 – 3.79 (m, 2H), 3.69 (td, $J$ = 8.0, 6.0 Hz, 1H), 2.65 (ddddd, $J$ = 14.2, 6.9, 2.5, 1.3 Hz, 1H), 2.42 – 2.32 (m, 1H), 1.97 – 1.86 (m, 2H), 1.85 – 1.77 (m, 1H), 1.63 (s, 9H), 1.53 – 1.43 (m, 1H).

$^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 154.4 (t, $J$ = 290.0 Hz), 149.8, 136.9, 131.0 (d, $J$ = 7.9 Hz), 128.9, 124.5, 122.9, 120.6, 115.7, 111.5, 85.1 (dd, $J$ = 28.3, 17.0 Hz), 84.0, 67.7, 34.6, 31.1, 28.1, 25.6.

$^{19}F$ NMR (376 MHz, Chloroform-$d$) $\delta$ -87.04 (d, $J$ = 36.5 Hz, 1F), -91.30 (d, $J$ = 36.4 Hz, 1F).

HRMS (ESI) calculated for C$_{20}$H$_{23}$F$_{2}$NO$_3$ $[M+H]^+$: 364.1719; Found: 364.1712
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d32** as a colorless oil (35.7 mg, 57% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.30 (dd, $J = 3.3, 1.9$ Hz, 1H), 6.18 – 6.09 (m, 2H), 3.89 – 3.75 (m, 2H), 3.69 (td, $J = 8.0, 6.0$ Hz, 1H), 2.58 (dddd, $J = 14.1, 6.6, 2.6, 1.6$ Hz, 1H), 2.31 (ddt, $J = 14.1, 7.0, 2.4$ Hz, 1H), 1.97 – 1.87 (m, 2H), 1.86 – 1.79 (m, 1H), 1.57 (s, 9H), 1.50 – 1.41 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 154.4 (t, $J = 296.7$ q Hz), 151.4, 148.7, 125.0, 122.4, 115.5, 110.4, 84.0 (dd, $J = 28.6, 17.5$ Hz), 83.9, 67.6, 34.53, 30.92, 27.9, 25.6.

**19F NMR** (376 MHz, Chloroform-$d$) δ -87.47 (d, $J = 37.0$ Hz, 1F), -91.41 (d, $J = 36.9$ Hz, 1F).

**HRMS** (ESI) calculated for C$_{16}$H$_{21}$F$_2$NO$_3$ [M+H]$^+$: 314.1563; Found: 314.1565

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Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **d33** as a colorless oil (20.7 mg, 45% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.31 (dd, $J = 5.1,3.0$ Hz, 2H), 7.19 (ddd, $J = 5.2, 2.3, 1.3$ Hz, 1H), 4.03 – 3.85 (m, 2H), 3.72 (td, $J = 8.0, 6.0$ Hz, 1H), 2.67 (ddt, $J = 14.3, 6.6, 2.6$ Hz, 1H), 2.52 (dddd, $J = 14.3, 6.8, 2.9, 1.4$ Hz, 1H), 2.00 – 1.89 (m, 2H), 1.88 – 1.81 (m, 1H), 1.59 – 1.48 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 154.8 (t, $J = 294.5$ Hz) 133.7, 127.2, 127.1 (dd, $J = 6.4, 2.4$ Hz), 122.2 (t, $J = 5.3$ Hz), 86.4 (t, $J = 13.6$), 67.9, 33.4 (d, $J = 2.1$ Hz), 31.0, 25.6.

**19F NMR** (376 MHz, Chloroform-$d$) δ -86.39 (d, $J = 38.6$ Hz, 1F), -90.68 (d, $J = 39.3$ Hz, 1F).
HRMS (ESI) calculated for C_{13}H_{14}F_{2}O [M+H]^{+}: 231.0650; Found: 231.0640

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded d34 as a colorless oil (48.4 mg, 52% yield).

$^{1}H$ NMR (400 MHz, Chloroform-$d$) δ 7.59 (d, $J = 7.3$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 3H), 7.41 (d, $J = 7.2$ Hz, 1H), 7.37 (d, $J = s 8.5$ Hz, 2H), 7.32 – 7.26 (m, 1H), 7.29 – 7.22 (m, 1H), 7.07 (d, $J = 8.7$ Hz, 2H), 4.03 (q, $J = 7.1$ Hz, 1H), 3.99 – 3.76 (m, 2H), 3.71 (td, $J = 8.1$, 5.8 Hz, 1H), 2.70 (ddt, $J = 14.3$, 6.9, 2.3 Hz, 1H), 2.50 (ddt, $J = 14.2$, 6.5, 2.4 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.88 – 1.78 (m, 1H), 1.69 (d, $J = 7.2$ Hz, 3H), 1.55 – 1.44 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.4, 159.8 (d, $J = 248.8$ Hz), 154.3 (t, $J = 290.4$ Hz), 149.8, 141.2 (d, $J = 7.8$ Hz), 135.4, 131.3, 131.0 (d, $J = 3.8$ Hz), 129.4 (t, $J = 3.3$ Hz), 129.0 (d, $J = 3.0$ Hz), 128.5, 128.2 (d, $J = 13.4$ Hz), 127.8, 123.6 (d, $J = 3.3$ Hz), 121.4, 115.4 (d, $J = 23.8$ Hz), 89.5 (dd, $J = 20.2$, 16.5 Hz), 67.8, 45.2, 33.9, 31.0, 25.6, 18.4.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -90.26 (s, 2F), -117.28 (s, 1F).

HRMS (ESI) calculated for C$_{28}$H$_{25}$F$_{3}$O$_{3}$ [M+H]^{+}: 467.1829; Found: 467.1831

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded d35 as a colorless oil (47.9 mg, 56% yield).

$^{1}H$ NMR (400 MHz, Chloroform-$d$) δ 7.30 (dd, $J = 8.4$, 4.9 Hz, 4H), 7.14 (d, $J = 7.7$ Hz, 1H).
Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 3.93 (q, J = 7.1 Hz, 1H), 3.88 – 3.74 (m, 2H), 3.71 – 3.63 (m, 1H), 2.66 (ddt, J = 16.2, 6.5, 1.9 Hz, 1H), 2.47 (d, J = 7.2 Hz, 3H), 1.94 – 1.78 (m, 4H), 1.60 (d, J = 7.2 Hz, 3H), 1.51 – 1.39 (m, 1H), 0.91 (d, J = 6.6 Hz, 6H).

13C NMR (101 MHz, CDCl3) δ 173.2, 154.3 (t, J = 290.1 Hz), 145.0, 140.9, 137.2, 131.0, 130.8, 129.9, 129.6, 129.39 (t, J = 3.3 Hz), 127.3, 121.5, 89.5 (dd, J = 20.2, 16.5 Hz), 67.8, 45.2 (d, J = 20.8 Hz), 33.9, 31.0, 30.3, 26.7, 25.6, 22.5, 18.6.

19F NMR (376 MHz, Chloroform-d) δ -91.62 (d, J = 44.1 Hz, 1F), -91.78 (d, J = 44.2 Hz, 1F).

HRMS (ESI) calculated for C26H30F2O3 [M+H]+: 429.2236; Found: 429.2233

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded d36 as a pale-yellow oil (47.2 mg, 50% yield).

1H NMR (400 MHz, Chloroform-d) δ 7.33 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.99 (s, 1H), 6.66 (d, J = 7.5 Hz, 1H), 6.62 (s, 1H), 3.98 (s, 2H), 3.88 – 3.77 (m, 2H), 3.68 (td, J = 8.1, 5.8 Hz, 1H), 2.68 (ddt, J = 14.3, 6.9, 2.3 Hz, 1H), 2.47 (ddt, J = 14.2, 6.6, 2.4 Hz, 1H), 2.30 (s, 3H), 2.17 (s, 3H), 1.87 (s, 6H), 1.85 – 1.75 (m, 1H), 1.53 – 1.42 (m, 1H), 1.37 (s, 6H).

13C NMR (101 MHz, CDCl3) δ 176.3, 156.9, 154.4 (t, J = 289.9 Hz), 150.1, 136.6, 131.0, 130.4, 129.5 (t, J = 3.3 Hz), 123.7, 121.6, 120.8, 112.0, 89.6 (t, J = 16.3 Hz), 77.3, 77.0, 67.8 (d, J = 3.2 Hz), 42.5, 37.2, 34.0, 31.0, 29.6 (d, J = 28.6 Hz), 25.6, 25.3 (d, J = 13.3 Hz), 21.5, 15.9.

19F NMR (376 MHz, CDCl3) δ -90.33 (d, J = 41.0 Hz, 1F), -90.40 (d, J = 41.2 Hz, 1F)

HRMS (ESI) calculated for C28H34F2O4 [M+H]+: 473.2498; Found: 473.2450
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded **d37** as a colorless oil (57.2 mg, 55% yield).

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 8.21 (d, \(J = 7.8\) Hz, 1H), 7.63 (dd, \(J = 16.3, 7.9\) Hz, 2H), 7.48 (s, 1H), 7.43 (t, \(J = 7.1\) Hz, 1H), 7.32 (t, \(J = 8.4\) Hz, 3H), 7.26 (s, 1H), 6.98 (d, \(J = 8.4\) Hz, 2H), 4.39 (s, 2H), 3.96 (q, \(J = 7.1\) Hz, 1H), 3.88 – 3.70 (m, 2H), 3.72 – 3.62 (m, 1H), 2.65 (ddt, \(J = 14.2, 6.9, 2.3\) Hz, 1H), 2.46 (ddt, \(J = 14.2, 6.5, 2.4\) Hz, 1H), 1.94 – 1.81 (m, 2H), 1.84 – 1.71 (m, 1H), 1.60 (d, \(J = 7.1\) Hz, 3H), 1.52 – 1.39 (m, 1H), 1.34 – 1.25 (m, 1H).

**13C NMR** (101 MHz, CDCl\(_3\)) \(\delta\) 191.4, 172.4, 154.3 (t, \(J = 290.1\) Hz), 149.7, 142.1, 140.2, 138.2, 136.2, 133.6, 132.6, 131.7 (d, \(J = 15.1\) Hz), 131.2, 130.9, 129.4 (t, \(J = 3.3\) Hz), 128.8, 127.0, 126.4, 125.8, 125.3, 121.4, 89.5 (t, \(J = 18.3\) Hz), 67.8, 51.1, 45.3, 33.9, 31.0, 25.6, 18.6.

**19F NMR** (376 MHz, CDCl\(_3\)) \(\delta\) -90.25 (s, 2F).

**HRMS (ESI)** calculated for C\(_{30}\)H\(_{26}\)F\(_2\)O\(_4\)S [M+Na]\(^+\): 543.1413; Found: 543.1413

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =
afforded d38 as a pale-yellow oil (53.8 mg, 45% yield).

**1H NMR** (400 MHz, Chloroform-<d>) δ 7.35 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 3.90 – 3.76 (m, 2H), 3.74 – 3.56 (m, 1H), 2.73 – 2.54 (m, 1H), 2.53 – 2.41 (m, 1H), 2.02 – 1.72 (m, 3H), 1.69 – 1.57 (m, 1H), 1.55 – 1.45 (m, 1H), 1.39 (q, J = 3.5 Hz, 1H), 1.34 – 1.03 (m, 3H), 0.98 (d, J = 6.2 Hz, 2H), 0.92 (s, 2H), 0.67 (s, 2H).

**13C NMR** (101 MHz, CDCl3) δ 172.7, 154.4, 150.0, 131.0, 129.4 (t, J = 3.3 Hz), 121.6, 89.5 (dd, J = 21.1, 16.2 Hz), 77.3, 76.9, 71.9, 67.8, 56.6, 56.0, 49.2, 42.8, 42.1, 40.5, 40.2, 36.5, 35.9, 35.4, 34.6, 33.9, 31.4, 31.0, 30.6, 28.3, 27.2, 26.5, 25.6, 24.3, 23.4, 20.9, 18.4, 12.1.

**19F NMR** (376 MHz, CDCl3) δ -90.23 (d, J = 41.0 Hz, 1F) -90.36 (d, J = 40.6 Hz, 1F).

**HRMS** (ESI) calculated for C37H52F2O4 [M+H]+: 599.3907; Found: 599.3913

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded d39 as a colorless oil (48.1 mg, 60% yield).

**1H NMR** (400 MHz, Chloroform-<d>) δ 7.27 (d, J = 6.1 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 7.07 (s, 1H), 3.92 – 3.77 (m, 2H), 3.70 (td, J = 8.1, 5.9 Hz, 1H), 2.91 (dd, J = 9.0, 4.3 Hz, 2H), 2.69 (ddt, J = 14.0, 6.6, 2.5 Hz, 1H), 2.55 – 2.40 (m, 3H), 2.30 (td, J = 10.5, 3.8 Hz, 1H), 2.11 – 1.79 (m, 7H), 1.71 – 1.60 (m, 2H), 1.58 – 1.51 (m, 3H), 1.49 – 1.44 (m, 2H), 0.91 (s, 3H).

**13C NMR** (101 MHz, CDCl3) δ 220.9, 154.3 (t, J = 288.6 Hz), 139.0, 136.6, 130.9 (t, J = 3.2 Hz), 128.8, 125.7, 125.5, 110.3, 110.1, 89.8 (dd, J = 21.2, 15.0 Hz), 67.8, 50.6, 48.0, 44.4, 38.1, 35.9, 33.8, 31.6, 31.0, 29.4, 26.5, 25.6 (d, J = 3.0 Hz), 21.6, 13.9.

**19F NMR** (376 MHz, Chloroform-<d>) δ -90.54 (d, J = 43.6 Hz, 1F) -90.78 (d, J = 43.7 Hz, 1F).
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50/1, v/v) afforded **d40** as a colorless oil (44.0 mg, 70% yield).

**1H NMR** (400 MHz, Chloroform-d) δ 7.62 – 7.54 (m, 3H), 7.41 (q, J = 7.0, 6.6 Hz, 3H), 7.32 (t, J = 7.3 Hz, 1H), 3.71 (dq, J = 33.0, 8.1, 7.5 Hz, 2H), 2.65 (q, J = 14.3 Hz, 1H), 1.85 (p, J = 7.1 Hz, 2H), 1.69 (dd, J = 12.5, 7.3 Hz, 1H), 1.51 (dt, J = 12.2, 7.3 Hz, 1H), 1.12 (s, 4H).

**13C NMR** (101 MHz, CDCl₃) δ 154.8 (t, J = 289.5 Hz), 140.6, 139.8, 133.8 (dd, J = 5.0, 3.4 Hz), 128.8 (d, J = 3.6 Hz), 127.4, 127.1 (d, J = 3.7 Hz), 90.0 (dd, J = 21.3, 14.1 Hz), 83.1 (t, J = 3.3 Hz), 67.1, 38.4, 36.6, 26.3, 26.0.

**19F NMR** (376 MHz, Chloroform-d) δ -89.15 (d, J = 38.9 Hz, 1F), -90.66 (d, J = 38.9 Hz, 1F).

**HRMS** (ESI) calculated for C₂₀H₂₀F₂O [M+H]⁺: 315.1555; Found: 315.1558

Purification by column chromatography on silica gel (hexane/ethyl acetate = 50/1, v/v) afforded **d41** as a colorless oil (34.9 mg, 62% yield).

**1H NMR** (400 MHz, Chloroform-d) δ 6.79 (d, J = 9.9 Hz, 3H), 5.95 (s, 2H), 3.82 – 3.64 (m, 2H), 2.61 – 2.48 (m, 2H), 1.95 – 1.80 (m, 2H), 1.65 (dt, J = 12.4, 7.5 Hz, 1H), 1.49 (ddd, J = 12.4, 8.1, 6.5 Hz, 1H), 1.10 (s, 3H).
\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 154.7 (t, \(J = 289.2\) Hz), 147.6, 146.6, 128.5 (d, \(J = 4.2\) Hz), 122.0 (t, \(J = 3.0\) Hz), 109.0 (t, \(J = 3.0\) Hz), 108.2, 101.1, 89.9 (dd, \(J = 21.8, 14.5\) Hz), 82.9 (d, \(J = 3.3\) Hz), 67.0, 38.8, 36.5, 26.2, 25.9.

\(^{19}\text{F NMR}\) (376 MHz, Chloroform-\(d\)) \(\delta\) -90.26 (d, \(J = 40.9\) Hz, 1F), -91.26 (d, \(J = 40.8\) Hz, 1F).

HRMS (ESI) calculated for C\(_{12}\)H\(_{17}\)F\(_2\)O\(_3\) [M+H]\(^+\): 283.1141; Found: 283.1139

Purification by column chromatography on silica gel (hexane/ethyl acetate = 50/1, v/v) afforded \textbf{d42} as a colorless oil (41.3 mg, 60% yield).

\(^1\text{H NMR}\) (400 MHz, Chloroform-\(d\)) \(\delta\) 8.20 – 8.08 (m, 2H), 7.87 – 7.77 (m, 2H), 7.47 – 7.37 (m, 3H), 3.71 (ddt, \(J = 29.1, 8.3, 6.8\) Hz, 2H), 2.80 – 2.63 (m, 2H), 1.83 (p, \(J = 7.1\) Hz, 2H), 1.66 (dt, \(J = 12.3, 7.5\) Hz, 1H), 1.49 (dt, \(J = 12.4, 7.3\) Hz, 1H), 1.11 (s, 3H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 154.9 (t, \(J = 291.6\) Hz), 139.9, 138.3, 135.7, 135.3, 131.3 (dd, \(J = 5.2, 3.3\) Hz), 127.2 (t, \(J = 2.9\) Hz), 126.9, 124.4, 122.9, 122.6, 121.6, 121.5 (t, \(J = 3.0\) Hz), 90.25 (d, \(J = 21.6, 14.3\) Hz), 83.1, 67.1, 39.0, 36.7, 26.3, 25.9.

\(^{19}\text{F NMR}\) (376 MHz, Chloroform-\(d\)) \(\delta\) -89.35 (d, \(J = 39.3\) Hz, 1F), -90.93 (d, \(J = 39.5\) Hz, 1F).

HRMS (ESI) calculated for C\(_{20}\)H\(_{19}\)F\(_2\)OS [M+H]\(^+\): 345.1120; Found: 345.1113
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded f1 as a white solid (38.9 mg, 99% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.32 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.74 – 7.66 (m, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.2, 156.1, 134.8, 126.7, 123.9, 121.8, 118.0.

HRMS (EI) calculated for C$_{13}$H$_8$O [M]$^+$: 196.0519; Found: 196.0519

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded f2 as a white solid (33.4 mg, 93% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.63 (d, $J = 7.3$ Hz, 1H), 7.46 (q, $J = 7.4$ Hz, 2H), 7.27 (td, $J = 7.1, 1.7$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.9, 144.4, 134.7, 134.1, 129.1, 124.3, 120.3.

HRMS (EI) calculated for C$_{13}$H$_8$O [M]$^+$: 180.0570; Found: 180.0570

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded f3 as a white solid (18.3 mg, 62% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.03 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.47 (td, $J = 7.5, 1.5$ Hz, 1H), 7.30 (t, $J = 7.0$ Hz, 1H), 7.25 (d, $J = 7.7$ Hz, 1H), 2.97 (t, $J = 6.1$ Hz, 2H), 2.66 (dd, $J = 7.3, 5.8$ Hz, 2H), 2.14 (p, $J = 6.5$ Hz, 2H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.4, 144.5, 133.4, 132.6, 128.8, 127.2, 126.6, 39.2, 29.7, 23.3.

HRMS (EI) calculated for C$_{10}$H$_{10}$O [M]$^+$: 146.0627; Found: 146.0627

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded f4 as a white solid (16.4 mg, 45% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.81 (d, $J$ = 6.8 Hz, 2H), 7.59 (t, $J$ = 7.4 Hz, 1H), 7.48 (d, $J$ = 15.3 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.8, 137.6, 132.4, 130.1, 128.3.

HRMS (EI) calculated for C$_{13}$H$_{10}$O [M]$^+$: 182.0727; Found: 182.0727
Purification by column chromatography on silica gel (hexane/ethyl acetate = 2/1, v/v) afforded \(d'1\) as a colorless oil (33.5 mg, 83% yield).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.39 (d, \(J = 5.8\) Hz, 1H), 8.16 (d, \(J = 8.4\) Hz, 1H), 7.81 (d, \(J = 8.1\) Hz, 1H), 7.63 (dt, \(J = 31.7, 6.9\) Hz, 1H), 7.51 (d, \(J = 5.8\) Hz, 1H), 3.72 (t, \(J = 6.2\) Hz, 2H), 3.36 (t, \(J = 7.6\) Hz, 2H), 3.28 – 3.03 (1H), 2.00 (p, \(J = 7.3\) Hz, 2H), 1.74 (p, \(J = 6.4\) Hz, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.8, 141.4, 136.3, 130.0, 127.4, 127.2, 127.0, 125.3, 119.4, 62.1, 34.3, 32.4, 25.3.

HRMS (ESI) calculated for C\(_{13}\)H\(_{15}\)NO [M+H]\(^+\): 202.1226; Found: 202.1222

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Purification by column chromatography on silica gel (hexane/ethyl acetate = 3/1, v/v) afforded \(d'2\) as a colorless oil (42.3 mg, 76% yield).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.21 (d, \(J = 7.2\) Hz, 1H), 8.11 (d, \(J = 5.1\) Hz, 2H), 8.00 (d, \(J = 8.5\) Hz, 1H), 7.71 (t, \(J = 6.9\) Hz, 1H), 7.66 (s, 1H), 7.55 – 7.43 (m, 4H), 3.67 (t, \(J = 6.4\) Hz, 2H), 3.10 (t, \(J = 7.7\) Hz, 2H), 2.18 (1H), 1.85 (p, \(J = 7.6\) Hz, 2H), 1.68 (dt, \(J = 13.2, 6.5\) Hz, 2H).
$^1$H NMR (400 MHz, Chloroform-$d$) δ 9.05 (d, $J = 2.3$ Hz, 1H), 8.16 (dd, $J = 8.2$, 2.3 Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 3.69 (t, $J = 6.3$ Hz, 2H), 2.91 (t, $J = 7.7$ Hz, 2H), 2.79 – 2.75 (1H), 2.62 (s, 3H), 1.86 (p, $J = 7.5$ Hz, 2H), 1.65 (dt, $J = 13.0$, 6.5 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.6, 166.9, 149.5, 136.1, 130.2, 122.9, 62.1, 37.8, 32.0, 26.6, 25.6.

HRMS (ESI) calculated for C$_{11}$H$_{15}$NO$_2$ [M+H]$^+$: 194.1176; Found: 194.1170

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded d’4 as a pale-yellow oil (15.5 mg, 34% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.95 (d, $J = 7.0$ Hz, 2H), 7.65 (t, $J = 7.7$ Hz, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.3$ Hz, 1H), 7.08
(d, $J = 7.6$ Hz, 1H), 3.66 (t, $J = 6.4$ Hz, 2H), 2.89 (t, $J = 7.6$ Hz, 2H), 2.57 – 2.28 (1H), 1.88 (p, $J = 7.4$ Hz, 2H), 1.65 (dt, $J = 13.0$, 6.6 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.9, 157.0, 139.7, 137.1, 128.8, 128.7, 127.1, 121.2, 118.1, 62.4, 37.6, 32.0, 25.9.

HRMS (ESI) calculated for C$_{15}$H$_{17}$NO [M+H]$^+$: 228.1383; Found: 228.1375

Purification by column chromatography on silica gel (hexane/ethyl acetate = 2/1, v/v) afforded d'5 as a pale-yellow oil (25.1 mg, 61% yield).

$^1$H NMR (400 MHz, Chloroform- $d$) δ 7.95 (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.44 (dd, $J = 8.3$, 7.1 Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 3.70 (t, $J = 6.3$ Hz, 2H), 3.15 (t, $J = 7.5$ Hz, 2H), 2.63 (1H), 1.98 (p, $J = 7.5$ Hz, 2H), 1.71 (dt, $J = 13.2$, 6.5 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.2, 153.0, 135.0, 126.0, 124.8, 122.4, 121.5, 62.0, 33.8, 32.0, 25.7.

HRMS (ESI) calculated for C$_{11}$H$_{13}$NOS [M+H]$^+$: 208.0791; Found: 208.0795
3. NMR spectra for the products
Due to the minimal polarity difference of \textbf{b37} and \textbf{b37}', the isolation is difficult. Therefore, the mixture of \textbf{b37} and \textbf{b37}' was obtained.