Supporting Information

Chromium-Catalyzed Selective Cross-Electrophile-Coupling between Unactivated C(aryl)–F and C(aryl)–O Bonds

Fei Fan,† Lixing Zhao,† Meiming Luo,* and Xiaoming Zeng*

*E-mail: luomm@scu.edu.cn
*E-mail: zengxiaoming@scu.edu.cn

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

Table of Contents

1. Materials and Methods .............................................................................................................. S2
2. Optimizing Reaction Parameters ............................................................................................ S3
3. Procedure for the Preparation of Substrates .......................................................................... S6
4. General Procedure for Cr-Catalyzed Reductive Cross-Coupling of Unactivated C(aryl)–F/C(aryl)–O Bonds .............................................................................................................. S6
5. General Procedure for Chromium Catalysis for Forming Polyfluoro-Substituted Molecules ..................................................................................................................... S29
6. Mechanistic Studies ................................................................................................................ S35
7. Synthetic Application ............................................................................................................... S52
8. Supplementary References .................................................................................................... S56
9. ¹H, ¹³C and ¹⁹F NMR Spectra .................................................................................................. S57
1. Materials and Methods

**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. $^1$H NMR spectra were recorded at 400 MHz in CDCl$_3$ and $d_8$-THF were referenced internally to tetramethysilane as a standard, and $^{13}$C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300. X-ray photoelectron spectroscopy (XPS) data were collected with a Thermo Fisher ESCALAB Xi+ spectrometer equipped with monochromatic Al Kα radiation. The analyzer was in the constant analyzer energy (CAE) mode at a pass energy of 20 eV for all the valence-band XPS measurements. The binding energies were measured with an accuracy of 0.1 eV. The binding energy scales were calibrated using the C1s peak at 284.8 eV from carbon contamination. Elemental analyses were tested on a Flash EA 112 elemental analyzer.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas-beta®, Energy Chemical and other commercial suppliers and used as received. Solvents were dried over sodium (for THF and ether) by refluxing for overnight and freshly distilled prior to use. Metallic magnesium turnings (≥99.99%) were purchased
from Adamas-beta. CrCl₂ (99.99%), CrCl₃ (99.99%), CoCl₂ (99.9%), and FeCl₂ (98%) were purchased from Aldrich Inc. and used as received. Cr(acac)₃ (97%), Cr(CO)₆ (97%), CrCl₂ (97%), NiCl₂ and NiCl₃ were purchased from Alfa Aesar and used as received.

2. Optimizing Reaction Parameters

Table S1. Studying the Effect of Ligands on the Cr-Catalyzed Reductive Cross-Coupling of Unactivated C(aryl)–F/C(aryl)–O Bonds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield (3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>2%</td>
</tr>
<tr>
<td>2</td>
<td>L1</td>
<td>ndᵇ</td>
</tr>
<tr>
<td>3</td>
<td>L2</td>
<td>ndᵇ</td>
</tr>
<tr>
<td>4</td>
<td>L3 (dtbpy)</td>
<td>82%</td>
</tr>
<tr>
<td>5</td>
<td>L4</td>
<td>54%</td>
</tr>
<tr>
<td>6</td>
<td>L5 (dnbpy)</td>
<td>87%</td>
</tr>
<tr>
<td>7</td>
<td>L6</td>
<td>ndᵇ</td>
</tr>
<tr>
<td>8</td>
<td>L7</td>
<td>ndᵇ</td>
</tr>
<tr>
<td>9</td>
<td>L8</td>
<td>ndᵇ</td>
</tr>
<tr>
<td>10</td>
<td>L9</td>
<td>62%</td>
</tr>
</tbody>
</table>

*b* Conditions: 1a (0.2 mmol), 2a (0.3 mmol), CrCl₂ (10 mol %), ligand (10 mol %), metallic magnesium (0.3 mmol), THF (0.1 M), 40 °C, 24 h. Isolated yields were given.
\[ \text{Table S2. Studying the Effect of Reductant on the Cross-Coupling}^a \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reductant</th>
<th>Yield (3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na</td>
<td>nd(^b)</td>
</tr>
<tr>
<td>2</td>
<td>Mg</td>
<td>87%</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td>nd(^b)</td>
</tr>
<tr>
<td>4</td>
<td>Zn</td>
<td>nd(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Reactions were carried out using 1a (0.2 mmol), 2a (0.3 mmol), CrCl\(_2\) (10 mol %), dnbpy (10 mol %), reductant (0.3 mmol), THF (0.1 M). Isolated yields were given.

\(^b\)Not detected.

\[ \text{Table S3. Studying the Effect of First-Row Metal Salts on the Cross-Coupling}^a \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal Salts</th>
<th>Yield (3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CrCl(_3) + THF</td>
<td>52%</td>
</tr>
<tr>
<td>2</td>
<td>Cr(CO)(_6)</td>
<td>nd(^b)</td>
</tr>
<tr>
<td>3</td>
<td>Cr(acac)(_3)</td>
<td>nd(^b)</td>
</tr>
<tr>
<td>4</td>
<td>FeCl(_2)</td>
<td>nd(^b)</td>
</tr>
<tr>
<td>5</td>
<td>CoCl(_2)</td>
<td>nd(^b)</td>
</tr>
<tr>
<td>6</td>
<td>NiCl(_2)</td>
<td>nd(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Reactions were carried out using 1a (0.2 mmol), 2a (0.3 mmol), metal salt (10 mol %), dnbpy (10 mol %), metallic magnesium (0.3 mmol), THF (0.1 M). Isolated yields were given.
yields were given. \(^{b}\)Not detected.

**Table S4. Studying the Effect of Directing Groups on the Cross-Coupling**

\[ \text{DG} + \text{PivO} \rightarrow \text{DG} \]

\[ 2a (1.5 \text{ equiv}) \]

\[ \begin{array}{c}
\text{CrCl}_2/\text{dnbpy} \\
(10 \text{ mol %}) \\
\text{THF, 40 °C, 24 h} \\
\text{Mg (1.5 equiv) then HCl (aq)}
\end{array} \]

\[ \]

\[ \begin{array}{c}
\text{nd} \\
\text{nd} \\
\text{nd} \\
\text{nd} \\
\text{trace (< 5%)} \\
\text{nd}
\end{array} \]

\(^{b}\)Reactions were carried out using 2a (0.3 mmol), aryl fluoride derivative (0.2 mmol), CrCl\(_2\) (10 mol %), dnbpy (10 mol %), metallic magnesium (0.3 mmol), THF (0.1 M) at 40 °C for 24 h. nd = Not detected.

**Table S5. Studying the Effect of Ester Groups on the Cross-Coupling**

\[ \begin{array}{c}
\text{CHO} \\
\text{3a}
\end{array} \]

\[ \begin{array}{c}
\text{H} \\
\text{N'Bu} \\
\text{F}
\end{array} \]

\[ \begin{array}{c}
\text{CH}_2 \text{CO} \\
\text{O} \\
\text{(1-Ad)}
\end{array} \]

\[ \begin{array}{c}
\text{ND}
\end{array} \]

\[ \begin{array}{c}
\text{15%}
\end{array} \]

\[ \begin{array}{c}
\text{OAc} \\
\text{ND}
\end{array} \]

\[ \begin{array}{c}
\text{OTf} \\
\text{ND}
\end{array} \]

\[ \begin{array}{c}
\text{OTs} \\
\text{ND}
\end{array} \]

\[ \begin{array}{c}
\text{OBz} \\
\text{ND}
\end{array} \]

\[ \text{the effect of leaving group} \]

\(^{b}\)Reactions were carried out using aniline (0.2 mmol), aryl ester (0.3 mmol), CrCl\(_2\) (10 mol %), dnbpy (10 mol %), metallic magnesium (0.3 mmol), THF (0.1 M) at 40 °C for 24 h. Isolated yields were given.
3. Procedure for the Preparation of Substrates

General procedure A: Synthesis of N-tert-butyl-substituted ortho-fluoro-bearing aromatic imines

In a 25 mL screw-capped vial with a stirring bar, the ortho-fluoro-substituted aromatic aldehyde (5 mmol) was treated with tert-butylamine (25 mmol). The vial was then sealed and the mixture was stirred in reflux for 6 h. After cooling to room temperature, the excess tert-butylamine was evaporated under a reduced pressure. The corresponding imine product was generally obtained in very high purity and employed without further purification.

General procedure B: Synthesis of aryl esters

A round bottom flask was charged with the corresponding arenil derivate (1.0 equiv) and dissolved with CH$_2$Cl$_2$ (3–5 mL/mmol). Triethylamine (1.2 equiv) and acetyl chloride derivative (1.1 equiv) were subsequently added dropwise to the reaction vessel at 0 ºC. The mixture was then allowed to warm to room temperature and stirred for 3-4 hours. The mixture was then quenched with 1M HCl and extracted several times with CH$_2$Cl$_2$. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography.

4. General Procedure for Cr-Catalyzed Reductive Cross-Coupling of Unactivated C(aryl)–F/C(aryl)–O Bonds.

In a dried Schlenk tube were placed magnesium (8 mg, 0.3 mmol) and CrCl$_2$ (3 mg, 0.02 mmol). The tube was heated to around 400 ºC under vacuum for 5 min using a
heat gun. After cooling to room temperature, a mixture of dnbpy (8 mg, 0.02 mmol), the corresponding aniline 1 (0.2 mmol) and aryl ester 2 (0.3 mmol) in dry THF solution (2 mL) was added and stirred at 40 or 60 °C (adamantane-1-carboxylate) for 24 h. The mixture was then treated with a solution of aqueous HCl (3 M, 2 mL) and stirred at room temperature for 0.5 h. After neutralization with saturated aqueous solution of NaHCO₃, the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired coupling product.

![Naphthalen-2-ylbenzaldehyde (3a)](image)

**2-(Naphthalen-2-yl)benzaldehyde (3a)**

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (41 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ = 10.09 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.92–7.86 (m, 3H), 7.82 (s, 1H), 7.66–7.62 (m, 1H), 7.58–7.50 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 191.9, 145.5, 134.8, 133.6, 133.2, 132.7, 132.4, 130.7, 129.2, 127.9, 127.87, 127.53, 127.5, 127.46, 127.4, 126.5, 126.4. GC-MS (EI): calcd for C₁₇H₁₂O [M⁺] 232.09, found 232.07. Spectroscopic data are in accordance with those described in the literature.¹

![Fluoro-2-(naphthalen-2-yl)benzaldehyde (3b)](image)

**3-Fluoro-2-(naphthalen-2-yl)benzaldehyde (3b)**

The general procedure was applied to
2,3-Difluorobenzylidene-2-methylpropan-2-amine (1b) (40 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (41 mg, 81% yield). Melting point: 80–82 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.87\) (s, 1H), 7.98–7.88 (m, 4H), 7.84 (s, 1H), 7.60–7.56 (m, 2H), 7.55–7.49 (m, 2H), 7.43 (td, \(J = 8.0, 1.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 191.0\) (d, \(J = 4.0\) Hz), 158.6 (d, \(J = 247.0\) Hz), 136.0 (d, \(J = 2.0\) Hz), 133.0 (d, \(J = 4.0\) Hz), 132.8 (d, \(J = 2.0\) Hz), 130.6, 129.2, 129.1, 128.1, 127.9, 127.8, 126.9, 126.8, 123.3 (d, \(J = 4.0\) Hz), 121.0, 120.8; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): \(\delta = -116.0\). HRMS (ESI\(^+\)): calcd for C\(_{17}\)H\(_{12}\)FO \([\text{M+H}]^+\) 251.0867, found 251.0868.

![Chemical Structure](image)

**4-Fluoro-2-(naphthalen-2-yl)benzaldehyde (3c)**

The general procedure was applied to 2,4-Difluorobenzylidene-2-methylpropan-2-amine (1c) (40 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (42 mg, 83% yield). Melting point: 89–91 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.96\) (d, \(J = 0.4\) Hz, 1H), 8.14–8.10 (m, 1H), 7.98–7.89 (m, 3H), 7.84 (s, 1H), 7.60–7.56 (m, 2H), 7.51 (dd, \(J = 8.4, 1.6\) Hz, 1H), 7.27–7.20 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 190.7, 164.2\) (d, \(J = 255.0\) Hz), 148.7 (d, \(J = 9.3\) Hz), 133.9 (d, \(J = 1.4\) Hz), 132.9 (d, \(J = 3.8\) Hz), 130.7, 130.6, 130.5 (d, \(J = 2.8\) Hz), 129.4, 128.4, 128.2, 127.8, 127.2, 127.0, 126.9, 117.5 (d, \(J = 21.9\) Hz), 115.2 (d, \(J = 21.9\) Hz); \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): \(\delta = -103.6\). HRMS (ESI\(^+\)): calcd for C\(_{17}\)H\(_{11}\)FONa \([\text{M+Na}]^+\) 273.0692, found 273.0696.
The general procedure was applied to 2,5-Difluorobenzylidene-2-methylpropan-2-amine (1d) (40 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (45 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.97$ (d, $J = 3.2$ Hz, 1H), 7.98–7.86 (m, 3H), 7.80 (s, 1H), 7.75 (dd, $J = 8.8$, 2.8 Hz, 1H), 7.60–7.51 (m, 3H), 7.50 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.38 (td, $J = 8.4$, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 191.1$ (d, $J = 1.0$ Hz), 161.0 (d, $J = 248.0$ Hz), 142.0 (d, $J = 3.0$ Hz), 134.1, 133.0, 132.9, 132.7, 129.5, 128.3, 128.1, 127.7, 127.6, 126.9, 126.8, 120.7 (d, $J = 23.0$ Hz), 113.6 (d, $J = 22.0$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -113.0$. GC-MS (EI): calcd for C$_{17}$H$_{11}$FO [M$^+$] 250.08, found 250.11. Spectroscopic data are in accordance with those described in the literature.$^1$

The general procedure was applied to 2-Fluoro-5-(trifluoromethyl)benzylidene-2-methylpropan-2-amine (1e) (50 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (45 mg, 75% yield). Melting point: 83–84 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.05$ (s, 1H), 8.35 (d, $J = 0.8$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.97–7.88 (m, 3H), 7.84 (s, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.63–7.57 (m, 2H), 7.52 (dd, $J = 8.4$, 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 190.9, 148.8, 134.1, 133.7, 133.0, 132.9, 131.7, 130.3$ (q, $J = 33.0$ Hz), 129.7 (q, $J = 3.5$ Hz), 129.6, 128.6,
128.2, 127.8, 127.1, 124.9 (q, J = 3.5 Hz), 122.3; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): δ = -62.7. HRMS (ESI\(^{+}\)): calcd for C\(_{18}\)H\(_{11}\)F\(_3\)O [M] 300.0762, found 300.0758.

4-Chloro-2-(naphthalen-2-yl)benzaldehyde (3f)

The general procedure was applied to 4-Chloro-2-fluorobenzylidene-2-methylpropan-2-amine (1f) (43 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (35 mg, 66% yield). Melting point: 97–98 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 9.97 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.97–7.86 (m, 3H), 7.82 (d, J = 1.2 Hz, 1H), 7.60–7.53 (m, 3H), 7.51 (d, J = 1.6 Hz, 1H), 7.49 (d, J = 1.6 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ = 191.1, 147.2, 139.8, 133.7, 132.9, 132.2, 130.8, 129.4, 129.2, 128.4, 128.2, 128.1, 127.8, 127.3, 127.0, 126.9. HRMS (ESI\(^{+}\)): calcd for C\(_{17}\)H\(_{11}\)ClONa [M+Na]\(^+\) 289.0391, found 289.0395.

5-Chloro-2-(naphthalen-2-yl)benzaldehyde (3g)

The general procedure was applied to 5-Chloro-2-fluorobenzylidene-2-methylpropan-2-amine (1g) (43 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (44 mg, 82% yield). Melting point: 96–98 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 9.97 (s, 1H), 8.04 (d, J = 2.4 Hz, 1H), 7.98–7.86 (m, 3H), 7.80 (s, 1H), 7.64 (dd, J = 8.4, 2.4 Hz, 1H), 7.60–7.54 (m, 2H), 7.52–7.46 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ = 191.0, 144.1, 134.9, 134.4, 133.9, 133.4, 132.9,
HRMS (ESI$^+$): calcd for C$_{17}$H$_{11}$ClONa [M+Na]$^+$ 289.0391, found 289.0390.

5-Methyl-2-(naphthalen-2-yl)benzaldehyde (3h)

The general procedure was applied to 2-Fluoro-5-methylbenzylidene-2-methylpropan-2-amine (1h) (39 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (42 mg, 85% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.01$ (s, 1H), 7.94–7.82 (m, 4H), 7.78 (s, 1H), 7.55–7.44 (m, 4H), 7.42 (d, $J = 8.0$ Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.6$, 143.2, 137.8, 135.1, 134.4, 133.6, 133.0, 132.6, 130.9, 129.3, 128.0, 127.8, 127.7, 126.7, 126.5, 21.0. GC-MS (El): calcd for C$_{18}$H$_{14}$O [M$^+$] 246.10, found 246.08. Spectroscopic data are in accordance with those described in the literature.$^1$

2-Methyl-6-(naphthalen-2-yl)benzaldehyde (3i)

The general procedure was applied to 2-Fluoro-6-methylbenzylidene-2-methylpropan-2-amine (1i) (39 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless oil (39 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.02$ (s, 1H), 7.95–7.84 (m, 3H), 7.79 (s, 1H), 7.59–7.52 (m, 2H), 7.50 (d, $J = 7.2$ Hz, 2H), 7.38 (d, $J = 7.2$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 2.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 194.5$, 147.0, 140.1, 136.3, 132.9, 132.8, 132.7, 132.1, 131.1,
129.3, 128.8, 128.1, 128.0, 127.8, 127.7, 126.7, 126.5, 21.5. GC-MS (EI): calcd for C_{18}H_{14}O [M^+] 246.10, found 246.11. Spectroscopic data are in accordance with those described in the literature.  

4-(Naphthalen-2-yl)-4'-(trimethylsilyl)-[1,1'-biphenyl]-3-carbaldehyde (3j)

The general procedure was applied to (4-Fluoro-4'-(trimethylsilyl)-[1,1'-biphenyl]-3-yl)methylene-2-methylpropan-2-amine (1j) (65 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (64 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.10\) (s, 1H), 8.33 (d, \(J = 2.0\) Hz, 1H), 7.99–7.89 (m, 4H), 7.88 (d, \(J = 1.2\) Hz, 1H), 7.73–7.63 (m, 5H), 7.60–7.55 (m, 3H), 0.33 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 192.4, 144.7, 140.7, 140.3, 139.8, 134.9, 134.2, 134.0, 133.0, 132.8, 132.0, 131.6, 129.5, 128.3, 128.2, 127.8, 127.7, 126.9, 126.7, 126.4, 126.0, −1.1. GC-MS (EI): calcd for C\(_{26}\)H\(_{24}\)OSi [M^+] 380.16, found 380.13. Spectroscopic data are in accordance with those described in the literature.  

4'-(Methylthio)-4-(naphthalen-2-yl)-[1,1'-biphenyl]-3-carbaldehyde (3k)

The general procedure was applied to (4-Fluoro-4'-(methylthio)-[1,1'-biphenyl]-3-yl)methylene-2-methylpropan-2-amine (1k) (60 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (60 mg, 85% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.09\) (s, 1H), 8.29 (d, \(J = 2.0\) Hz, 1H), 7.99–7.88 (m, 4H), 7.86 (s, 1H), 7.67–7.61 (m, 3H), 7.60–7.54 (m, 3H), 7.40–7.35 (m, 2H), 2.55 (s, 3H); \(^{13}\)C
NMR (100 MHz, CDCl$_3$): $\delta = 192.4, 144.6, 140.1, 138.7, 136.1, 134.8, 134.2, 133.0, 132.8, 131.6, 129.4, 128.3, 128.2, 127.8, 127.7, 127.4, 126.9, 126.7, 125.6, 125.0, 124.0, 123.8, 123.0, 122.8, 122.6, 121.8 (q, $J = 258.0$ Hz), 121.4; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -57.7$. GC-MS (EI): calcd for C$_{24}$H$_{19}$F$_3$O$_2$ [M$^+$] 392.10, found 392.12. Spectroscopic data are in accordance with those described in the literature.$^1$

4-(Naphthalen-2-yl)-4’-(trifluoromethoxy)-[1,1’-biphenyl]-3-carbaldehyde (3l)
The general procedure was applied to 3-((Tert-butylimino)methyl)-N,N-dimethyl-4’-(trifluoromethoxy)-[1,1’-biphenyl]-4-amine (11) (72 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (64 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.10$ (s, 1H), 8.28 (d, $J = 2.0$ Hz, 1H), 8.00–7.86 (m, 5H), 7.74–7.69 (m, 2H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.60–7.55 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.2, 149.2, 145.0, 139.3, 138.2, 134.6, 134.2, 133.0, 132.8, 131.8, 131.7, 129.5, 128.5, 128.3, 128.1, 127.8, 127.6, 126.9, 126.8, 126.0, 121.8 (q, $J = 258.0$ Hz), 121.4; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -57.7$. GC-MS (EI): calcd for C$_{24}$H$_{19}$F$_3$O$_2$ [M$^+$] 392.10, found 392.12. Spectroscopic data are in accordance with those described in the literature.$^1$

4-Methoxy-2-(naphthalen-2-yl)benzaldehyde (3m)
The general procedure was applied to 2-Fluoro-4-methoxybenzylidene-2-methylpropan-2-amine (1m) (42 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title...
compound as a white solid (47 mg, 89% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.90$ (s, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.95–7.88 (m, 3H), 7.84 (d, $J = 1.2$ Hz, 1H), 7.58–7.52 (m, 3H), 7.06–7.03 (m, 1H), 6.98 (d, $J = 2.4$ Hz, 1H), 3.93 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 191.0, 163.5, 148.4, 135.2, 132.9, 132.8, 130.1, 129.2, 128.1, 128.0, 127.8, 127.6, 127.56, 126.8, 126.6, 115.5, 114.0, 55.6. GC-MS (EI): calcd for C$_{13}$H$_{14}$O$_2$ [M$^+$] 262.10, found 262.08. Spectroscopic data are in accordance with those described in the literature.$^1$

5-Methoxy-2-(naphthalen-2-yl)benzaldehyde (3n)

The general procedure was applied to 2-Fluoro-5-methoxybenzylidene-2-methylpropan-2-amine (1n) (42 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (46 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.99$ (s, 1H), 7.94–7.82 (m, 3H), 7.77 (s, 1H), 7.56–7.51 (m, 3H), 7.51–7.43 (m, 2H), 7.22 (dd, $J = 8.8, 2.8$ Hz, 1H), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.3, 159.2, 139.0, 134.8, 134.7, 133.0, 132.5, 132.3, 129.4, 128.1, 128.0, 127.9, 127.7, 126.7, 126.5, 121.4, 110.0, 55.6. GC-MS (EI): calcd for C$_{18}$H$_{14}$O$_2$ [M$^+$] 262.10, found 262.09. Spectroscopic data are in accordance with those described in the literature.$^1$

4-((2-Methylallyl)oxy)-2-(naphthalen-2-yl)benzaldehyde (3o)

The general procedure was applied to 2-Fluoro-4-((2-methylallyl)oxy)benzylidene-2-methylpropan-2-amine (1o) (50 mg,
0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (52 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.90 (s, 1H), 8.06 (d, $J$ = 8.8 Hz, 1H), 7.95–7.88 (m, 3H), 7.84 (d, $J$ = 1.2 Hz, 1H), 7.59–7.49 (m, 3H), 7.07–7.04 (m, 1H), 7.01 (d, $J$ = 2.4 Hz, 1H), 5.13 (s, 1H), 5.04 (s, 1H), 4.56 (s, 2H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 191.0, 162.7, 148.4, 139.9, 135.2, 132.9, 132.8, 130.1, 129.2, 128.1, 128.0, 127.7, 127.6, 127.6, 126.8, 126.6, 116.3, 114.5, 113.4, 72.0, 19.3. GC-MS (EI): calcd for C$_{21}$H$_{18}$O$_2$ [M$^+$] 302.13, found 302.10. Spectroscopic data are in accordance with those described in the literature.$^1$

![5-Butylbenzylbenzaldehyde](image)

5-(Benzo[d][1,3]dioxol-5-yl)-2-(naphthalen-2-yl)benzaldehyde (3p)

The general procedure was applied to 5-(Benzo[d][1,3]dioxol-5-yl)-2-fluorobenzylidene-2-methylpropan-2-amine (1p) (60 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (58 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.09 (s, 1H), 8.23 (d, $J$ = 2.0 Hz, 1H), 7.99–7.88 (m, 3H), 7.87–7.79 (m, 2H), 7.60–7.55 (m, 4H), 7.19–7.16 (m, 2H), 6.95–6.89 (m, 1H), 6.03 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.4, 148.4, 147.6, 144.3, 140.4, 134.8, 134.1, 133.7, 133.0, 132.7, 131.6, 131.5, 129.4, 128.2, 128.1, 127.7, 127.6, 126.8, 126.6, 125.6, 120.8, 108.7, 107.5, 101.3. GC-MS (EI): calcd for C$_{24}$H$_{16}$O$_3$ [M$^+$] 352.11, found 352.13. Spectroscopic data are in accordance with those described in the literature.$^1$

![5-Butylbenzylbenzaldehyde](image)
5-(Furan-3-yl)-2-(naphthalen-2-yl)benzaldehyde (3q)
The general procedure was applied to 2-Fluoro-5-(furan-3-yl)benzylidene-2-methylpropan-2-amine (1q) (49 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (50 mg, 84% yield). Melting point: 134–135 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.07$ (s, 1H), 8.18 (d, $J = 1.6$ Hz, 1H), 7.98–7.86 (m, 4H), 7.84 (s, 1H), 7.79 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.60–7.53 (m, 5H), 6.82 (dd, $J = 1.6$, 0.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.4$, 144.4, 144.1, 139.2, 134.8, 134.2, 133.0, 132.8, 132.2, 131.6, 130.7, 129.4, 128.2, 128.1, 127.8, 127.7, 126.8, 126.7, 125.2, 124.6, 108.7. HRMS (ESI$^+$): calcd for C$_{21}$H$_{14}$O$_2$ [M] 298.0994, found 298.0989.

![Chemical structure]

2-(Naphthalen-2-yl)-5-(thiophen-3-yl)benzaldehyde (3r)
The general procedure was applied to 2-Fluoro-5-(thiophen-3-yl)benzylidene-2-methylpropan-2-amine (1r) (52 mg, 0.2 mmol) and Naphthalen-2-yl pivalate (2a) (68 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (54 mg, 86% yield). Melting point: 136–137 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.08$ (s, 1H), 8.30 (d, $J = 2.0$ Hz, 1H), 7.99–7.88 (m, 4H), 7.85 (s, 1H), 7.63–7.60 (m, 1H), 7.60–7.54 (m, 4H), 7.51 (dd, $J = 4.8$, 1.2 Hz, 1H), 7.46 (dd, $J = 4.8$, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.4$, 144.4, 140.7, 135.4, 134.8, 134.2, 133.0, 132.8, 131.6, 131.2, 129.4, 128.2, 128.1, 127.8, 127.7, 126.8, 126.8, 126.7, 126.1, 125.2, 121.4. HRMS (ESI$^+$): calcd for C$_{21}$H$_{14}$OS [M] 314.0765, found 314.0764.
The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 6-(4-Fluorophenyl)naphthalen-2-yl pivalate (2b) (97 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (59 mg, 91% yield). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 10.06 \) (s, 1H), 8.11–8.04 (m, 2H), 8.00–7.94 (m, 2H), 7.75 (s, 1H), 7.77 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 7.73–7.67 (m, 3H), 7.59–7.52 (m, 3H), 7.23–7.16 (m, 2H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 192.4, 163.9 \) (d, \( J = 246.0 \) Hz), 145.7, 138.4, 136.9 (d, \( J = 3.0 \) Hz), 135.3, 133.9, 133.6, 133.0, 132.0, 131.0, 129.2, 129.0, 128.9, 128.7, 128.4, 128.3, 127.9, 127.8, 126.4, 125.4, 115.9 (d, \( J = 21.0 \) Hz); \( ^{19} \)F NMR (377 MHz, CDCl\(_3\)): \( \delta = -115.09 \). GC-MS (EI): calcd for C\(_{23}\)H\(_{15}\)FO \([M^+\)] 326.11, found 326.08. Spectroscopic data are in accordance with those described in the literature.\(^1\)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 6-(4-Chlorophenyl)naphthalen-2-yl pivalate (2c) (101 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (52 mg, 76% yield). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 10.06 \) (s, 1H), 8.09 (d, \( J = 7.2 \) Hz, 2H), 8.00–7.95 (m, 2H), 7.85 (s, 1H), 7.78 (dd, \( J = 8.4, 1.6 \) Hz, 1H), 7.72–7.65 (m, 3H), 7.59–7.52 (m, 3H), 7.48 (d, \( J = 8.8 \) Hz, 2H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 192.4, 145.7, 139.2, 138.1, 135.5, 133.9, 133.7, 133.60, 132.9, 132.2, 131.0, 129.2, 129.1, 128.8, 128.6, 128.4, 128.36, 127.9, 127.8, 126.2, 126.5. GC-MS (EI): calcd for C\(_{23}\)H\(_{15}\)ClO
Spectroscopic data are in accordance with those described in the literature.\textsuperscript{1}

\[
\text{CHO} \quad \begin{array}{c}
\text{CF}_3 \\
\end{array} \\
\text{CHO} \quad \begin{array}{c}
\text{Si} \\
\end{array}
\]

\textbf{2-(6-(4-(Trifluoromethyl)phenyl)naphthalen-2-yl)benzaldehyde (3u)}

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 6-(4-(Trifluoromethyl)phenyl)naphthalen-2-yl pivalate (2d) (112 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (48 mg, 64\% yield). Melting point: 147–148 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} = 10.06 (s, 1H), 8.14 (d, \textit{J} = 1.2 Hz, 1H), 8.11–8.07 (m, 1H), 8.04–7.97 (m, 2H), 7.88–7.80 (m, 4H), 7.77 (d, \textit{J} = 8.4 Hz, 2H), 7.73–7.67 (m, 1H), 7.61–7.53 (m, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{\delta} = 192.3, 145.6, 137.9, 135.8, 133.9, 133.6, 132.9, 132.5, 131.0, 129.2, 129.0, 128.6, 128.5, 128.0, 127.8, 127.7, 126.2 (d, \textit{J} = 4.0 Hz), 125.9 (d, \textit{J} = 4.0 Hz); \textsuperscript{19}F NMR (377 MHz, CDCl\textsubscript{3}): \textit{\delta} = -62.4. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{24}H\textsubscript{15}F\textsubscript{3}O [M] 376.1075, found 376.1077.

\textbf{2-(6-(Trimethylsilyl)naphthalen-2-yl)benzaldehyde (3v)}

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 6-(Trimethylsilyl)naphthalen-2-yl pivalate (2e) (90 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a yellow oil (51 mg, 84\% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} = 10.05 (s, 1H), 8.09 (dd, \textit{J} = 7.6, 0.8 Hz, 2H), 7.96 (d, \textit{J} = 8.4 Hz, 1H), 7.88 (d, \textit{J} = 8.4 Hz, 1H), 7.82 (s, 1H), 7.72–7.66 (m, 2H), 7.57–7.52 (m, 3H), 0.40 (s, 9H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{\delta} = 192.4, 145.9, 139.2, 135.5,
GC-MS (EI): calcd for C\textsubscript{20}H\textsubscript{20}O\textsubscript{Si} [M\textsuperscript{+}] 304.13, found 304.10. Spectroscopic data are in accordance with those described in the literature.\textsuperscript{1}

(E)-2-(6-Styrylnaphthalen-2-yl)benzaldehyde (3w)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and (E)-6-Styrylnaphthalen-2-yl pivalate (2f) (99 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (54 mg, 81\% yield).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 10.02\) (s, 1H), 8.08–8.02 (m, 1H), 7.91–7.87 (m, 2H), 7.56–7.48 (m, 5H), 7.37 (t, \(J = 7.6\) Hz, 2H), 7.31–7.20 (m, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 192.4\), 145.8, 137.2, 135.7, 135.1, 133.9, 133.6, 133.0, 132.5, 130.9, 129.6, 129.3, 128.7, 128.5, 128.4, 128.23, 128.2, 127.8, 127.7, 126.6, 126.3, 124.5. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{25}H\textsubscript{18}O [M] 334.1358, found 334.1359.

4-(6-(2-Formylphenyl)naphthalen-2-yl)phenyl pivalate (3x)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 4-(6-(Pivaloyloxy)naphthalen-2-yl)phenyl pivalate (2g) (121 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (53 mg, 65\% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 10.06\) (s, 1H), 8.11–8.06 (m, 2H), 8.01–7.95 (m, 2H), 7.85 (s, 1H), 7.80 (dd, \(J = 8.4\), 2.0 Hz, 1H), 7.77–7.72 (m, 2H), 7.69 (td, \(J = 7.6\), 1.2 Hz, 1H), 7.58–7.55 (m, 3H), 7.23–7.18 (m, 2H), 1.41 (s, 9H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 192.4\), 177.1, 150.8, 145.8, 138.6, 138.3, 135.3, 133.9, 133.6,
133.0, 132.1, 131.0, 129.2, 128.7, 128.4, 128.35, 128.3, 127.9, 127.7, 126.5, 125.5, 122.0, 39.1, 27.2. GC-MS (EI): calcd for C_{28}H_{24}O_{3} [M⁺] 408.17, found 408.14. Spectroscopic data are in accordance with those described in the literature.²

2-(7-(Benzyloxy)naphthalen-2-yl)benzaldehyde (3y)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 7-(Benzyloxy)naphthalen-2-yl pivalate (2h) (100 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (52 mg, 77% yield). 

\(^1\)H NMR (400 MHz, CDCl₃): δ = 10.02 (s, 1H), 8.08–8.03 (m, 1H), 7.86–7.80 (m, 2H), 7.70–7.62 (m, 2H), 7.53–7.48 (m, 4H), 7.43–7.27 (m, 5H), 7.26–7.22 (m, 1H), 5.19 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl₃): δ = 192.5, 157.5, 146.0, 136.6, 135.7, 134.1, 133.9, 133.5, 130.9, 129.3, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 125.6, 119.9, 107.3, 70.1. GC-MS (EI): calcd for C_{24}H_{18}O_{2} [M⁺] 338.13, found 338.10. Spectroscopic data are in accordance with those described in the literature.²

2-(7-((Tert-butyldimethylsilyloxy)naphthalen-2-yl)benzaldehyde (3z)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 7-((Tert-butyldimethylsilyloxy)naphthalen-2-yl pivalate (2i) (107 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a yellow oil (57 mg, 79% yield). 

\(^1\)H NMR (400 MHz, CDCl₃): δ = 10.05 (s, 1H), 8.07 (dd, J = 8.0, 0.8 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.70–7.63 (m, 2H), 7.58–7.49
(m, 2H), 7.38 (dd, \(J = 8.0, 2.0\) Hz, 1H), 7.24 (d, \(J = 2.4\) Hz, 1H), 7.16 (dd, \(J = 8.8, 2.4\) Hz, 1H), 1.04 (s, 9H), 0.28 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 192.6, 154.4, 146.1, 135.5, 134.3, 133.9, 133.5, 130.9, 129.2, 128.5, 128.2, 127.8, 127.8, 127.6, 125.7, 122.9, 115.0, 25.7, 18.3, -4.3.\) GC-MS (EI): calcd for C\(_{23}\)H\(_{26}\)O\(_2\)Si [M\(^+\)] 362.17, found 362.14. Spectroscopic data are in accordance with those described in the literature.\(^1\)

![Chemical Structure](attachment://chemical_image.png)

**2-(7-((2-Methylallyl)oxy)naphthalen-2-yl)benzaldehyde (3aa)**

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 7-((2-Methylallyl)oxy)naphthalen-2-yl pivalate (2j) (89 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (51 mg, 85% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.04\) (s, 1H), 8.07 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.87–7.80 (m, 2H), 7.71–7.64 (m, 2H), 7.56–7.51 (m, 2H), 7.38 (dd, \(J = 8.4, 2.0\) Hz, 1H), 7.26 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.18 (d, \(J = 2.4\) Hz, 1H), 5.17 (s, 1H), 5.04 (s, 1H), 4.58 (s, 2H), 1.89 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 192.6, 157.5, 146.1, 140.6, 135.6, 134.1, 133.9, 133.5, 130.9, 129.2, 128.4, 128.3, 127.9, 127.8, 127.6, 125.6, 119.9, 112.9, 107.2, 71.8, 19.4.\) HRMS (ESI\(^+\)): calcd for C\(_{21}\)H\(_{18}\)O\(_2\) [M] 302.1307, found 302.1306.

![Chemical Structure](attachment://chemical_image.png)

**2-(7-(Cyclopropylmethoxy)naphthalen-2-yl)benzaldehyde (3ab)**

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 7-(Cyclopropylmethoxy)naphthalen-2-yl pivalate (2k)
(89 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a yellow oil (45 mg, 75% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.03 (s, 1H), 8.06 (dd, $J$ = 8.0, 0.8 Hz, 1H), 7.83 (m, 2H), 7.67 (td, $J$ = 8.0, 1.6 Hz, 2H), 7.57–7.49 (m, 2H), 7.37 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.25 (dd, $J$ = 8.8, 2.4 Hz, 1H), 7.14 (d, $J$ = 2.0 Hz, 1H), 3.94 (d, $J$ = 7.2 Hz, 2H), 1.40–1.30 (m, 1H), 0.74–0.64 (m, 2H), 0.43–0.40 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.6, 157.8, 146.1, 135.6, 134.2, 133.9, 133.5, 130.9, 129.2, 128.4, 128.2, 127.9, 127.8, 127.6, 125.5, 120.0, 106.8, 72.9, 10.2, 3.3. GC-MS (EI): calcd for C$_{21}$H$_{18}$O$_2$ [M$^+$] 302.13, found 302.10. Spectroscopic data are in accordance with those described in the literature.$^1$

![Chemical structure of 2-(8-(Dimethylamino)naphthalen-2-yl)benzaldehyde (3ac)]

2-(8-(Dimethylamino)naphthalen-2-yl)benzaldehyde (3ac)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 8-(Dimethylamino)naphthalen-2-yl pivalate (2I) (81 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a yellow oil (48 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.07 (s, 1H), 8.24–8.21 (m, 1H), 8.08 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.68 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.59–7.45 (m, 5H), 7.15 (dd, $J$ = 7.6, 0.8 Hz, 1H), 2.89 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.6, 151.2, 146.5, 134.4, 134.1, 134.0, 133.5, 131.2, 128.6, 128.4, 127.7, 127.6, 127.5, 126.7, 126.1, 122.6, 114.9, 45.2. HRMS (ESI$^+$): calcd for C$_{19}$H$_{18}$NO [M+H]$^+$ 276.1383, found 276.1381.
2-(9-Methyl-9H-carbazol-2-yl)benzaldehyde (3ad)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 9-Methyl-9H-carbazol-2-yl pivalate (2m) (84 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a slight yellow solid (35 mg, 62% yield). Melting point: 102–104 °C; ¹H NMR (400 MHz, CDCl₃): δ = 10.05 (s, 1H), 8.16 (t, J = 8.4 Hz, 2H), 8.07 (dd, J = 7.6, 1.2 Hz, 1H), 7.68 (td, J = 7.6, 1.6 Hz, 1H), 7.61–7.58 (m, 1H), 7.56–7.51 (m, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 0.8 Hz, 1H), 7.31–7.25 (m, 2H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 192.9, 147.0, 141.6, 140.9, 135.3, 134.0, 133.4, 131.1, 127.6, 127.4, 126.2, 122.6, 122.3, 121.3, 120.5, 120.1, 119.3, 110.2, 108.7, 29.2. HRMS (ESI⁺): calcd for C₂₀H₁₆NO [M+H]⁺ 286.1226, found 286.1226.

![2-(9-Methyl-9H-carbazol-2-yl)benzaldehyde (3ad)](image)

2-(Anthracen-2-yl)benzaldehyde (3ae)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and Anthracen-2-yl pivalate (2n) (83 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (37 mg, 66% yield). Melting point: 146–148 °C; ¹H NMR (400 MHz, CDCl₃): δ = 10.10 (s, 1H), 8.50 (s, 1H), 8.48 (s, 1H), 8.13–8.08 (m, 2H), 8.07–8.01 (m, 2H), 7.97 (s, 1H), 7.71 (td, J = 7.6, 1.2 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.58–7.48 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 192.4, 145.9, 134.6, 134.0, 133.6, 132.2, 132.2, 131.0, 130.9, 130.7, 129.8, 128.6, 128.2, 127.9, 127.8, 127.4, 126.8, 126.3, 125.8. HRMS (ESI⁺): calcd for C₂₁H₁₄O [M] 282.1045, found 282.1041.
2-(Phenanthren-9-yl)benzaldehyde (3af)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and Phenanthren-9-yl pivalate (2o) (83 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (38 mg, 68% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.73$ (s, 1H), 8.81–8.75 (m, 2H), 8.15 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.90 (d, $J = 7.2$ Hz, 1H), 7.76–7.60 (m, 6H), 7.56–7.49 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.0$, 144.2, 135.0, 134.1, 133.8, 131.9, 131.7, 131.0, 130.3, 129.1, 128.7, 128.3, 127.2, 127.2, 127.15, 127.1, 126.9, 126.8, 123.0, 122.6. GC-MS (EI): calcd for C$_{21}$H$_{14}$O [M$^+$] 282.10, found 282.11. Spectroscopic data are in accordance with those described in the literature.$^1$

2-(Naphthalen-1-yl)benzaldehyde (3ag)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and Naphthalen-1-yl adamantane-1-carboxylate (2p) (92 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (38 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.64$ (s, 1H), 8.13 (dd, $J = 8.0$, 0.8 Hz, 1H), 7.97–7.92 (m, 2H), 7.71 (td, $J = 7.6$, 1.6 Hz, 1H), 7.62–7.56 (m, 2H), 7.55–7.47 (m, 3H), 7.46–7.41 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.0$, 144.2, 135.4, 134.1, 133.8, 131.7, 131.0, 130.3, 129.6, 128.7, 128.3, 127.2, 127.2, 127.15, 127.1, 126.9, 126.8, 123.0, 122.6. GC-MS (EI): calcd for C$_{17}$H$_{12}$O [M$^+$] 232.09, found 232.05. Spectroscopic data are in accordance with those described in the literature.$^1$
The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and Phenyl adamantane-1-carboxylate (2q) (77 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (19 mg, 52% yield). 

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta = 9.99 \text{ (s, 1H), 8.04 (dd, } J = 8.0, 0.2 \text{ Hz, 1H), 7.64 (td, } J = 7.6, 1.6 \text{ Hz, 1H), 7.53–7.44 (m, 5H), 7.41–7.37 (m, 2H); } \] 

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3\text{): } \delta = 192.4, 159.9, 145.6, 133.7, 133.5, 130.7, 130.4, 128.4, 128.1, 127.7, 127.5. \] 

GC-MS (EI): calcd for C\text{13H10O} [M+] 182.07, found 182.11. Spectroscopic data are in accordance with those described in the literature.\(^1\)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 4-Methoxyphenyl adamantane-1-carboxylate (2r) (86 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a colorless oil (15 mg, 35% yield). 

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta = 10.00 \text{ (s, 1H), 8.01 (dd, } J = 7.6, 1.2 \text{ Hz, 1H), 7.62 (td, } J = 7.2, 1.2 \text{ Hz, 1H), 7.50–7.41 (m, 2H), 7.34–7.28 (m, 2H), 7.03–6.98 (m, 2H), 3.88 (s, 3H); } \] 

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3\text{): } \delta = 192.7, 159.7, 145.6, 133.7, 133.5, 131.3, 130.8, 130.0, 127.6, 127.4, 113.9, 55.4. \] 

GC-MS (EI): calcd for C\text{14H12O2} [M+] 212.08, found 212.11. Spectroscopic data are in accordance with those described in the literature.\(^3\)
4'-{(Trifluoromethoxy)-[1,1'-biphenyl]-2-carbaldehyde (3aj)}

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 4-{(Trifluoromethoxy)phenyl adamantan-1-carboxylate (2a) (102 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (35 mg, 66% yield). ^1H NMR (400 MHz, CDCl₃): δ = 9.98 (s, 1H), 8.04 (dd, J = 8.0, 0.8 Hz, 1H), 7.66 (m, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.43–7.40 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl₃): δ = 191.8, 149.2 (q, J =1.6 Hz), 144.3, 136.5, 133.7, 131.4, 130.7, 128.2, 127.9, 121.7 (q, J = 256.1 Hz), 120.8, ^19F NMR (377 MHz, CDCl₃): δ = –57.8. HRMS (ESI⁺): calcd for C₁₄H₉F₃O₂ [M] 266.0555, found 266.0550.

![4'-{(Trifluoromethoxy)-[1,1'-biphenyl]-2-carbaldehyde (3aj)}](image)

4'-{(Tert-butyl)-[1,1'-biphenyl]-2-carbaldehyde (3ak)}

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 4-{(Tert-butyl)phenyl adamantan-1-carboxylate (2a) (94 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (20 mg, 41% yield). ^1H NMR (400 MHz, CDCl₃): δ = 10.02 (s, 1H), 8.03 (dd, J = 7.6, 0.8 Hz, 1H), 7.63 (td, J = 7.6, 1.6 Hz, 1H), 7.52–7.44 (m, 4H), 7.35–7.30 (m, 2H), 1.39 (s, 9H); ^13C NMR (100 MHz, CDCl₃): δ = 192.7, 151.2, 146.0, 134.7, 133.8, 133.5, 130.8, 129.8, 127.5, 127.4, 125.4, 34.6, 31.3. HRMS (ESI⁺): calced for C₁₇H₁₉O [M+H]⁺ 239.1430, found 239.1424.

![4'-{(Tert-butyl)-[1,1'-biphenyl]-2-carbaldehyde (3ak)}](image)

4'-{(Dimethylamino)-[1,1'-biphenyl]-2-carbaldehyde (3al)}

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine
(1a) (36 mg, 0.2 mmol) and 4-(Dimethylamino)phenyl adamantane-1-carboxylate (2u) (90 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a yellow oil (18 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.02 (s, 1H), 7.98 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.59 (td, $J$ = 7.6, 1.6 Hz, 1H), 7.47–7.37 (m, 2H), 7.29–7.23 (m, 2H), 6.83–6.77 (m, 2H), 3.02 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.1, 150.3, 146.3, 133.6, 133.4, 131.1, 130.6, 127.5, 126.6, 125.2, 112.0, 40.4. GC-MS (EI): calcd for C$_{15}$H$_{15}$NO [M$^+$] 225.12, found 225.10. Spectroscopic data are in accordance with those described in the literature.$^3$

![3'-Methyl-[1,1'-biphenyl]-2-carbaldehyde (3am)](image)

**3'-Methyl-[1,1'-biphenyl]-2-carbaldehyde (3am)**

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and $m$-Tolyl adamantane-1-carboxylate (2v) (81 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless oil (19 mg, 48% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.99 (s, 1H), 8.02 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.63 (td, $J$ = 8.8, 1.6 Hz, 1H), 7.51–7.42 (m, 2H), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.28–7.25 (m, 1H), 7.20–7.17 (m, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.6, 146.2, 138.1, 137.7, 133.7, 133.5, 130.8, 130.7, 128.8, 128.3, 127.6, 127.4, 127.2, 21.4. GC-MS (EI): calcd for C$_{14}$H$_{13}$O [M$^+$] 196.09, found 196.11. Spectroscopic data are in accordance with those described in the literature.$^3$

![1,1':4',1''-Terphenyl]-2-carbaldehyde (3an)

**[1,1':4',1''-Terphenyl]-2-carbaldehyde (3an)**

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and [1,1'-Biphenyl]-4-yl pivalate (2w) (76 mg, 0.3 mmol).
The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (32 mg, 62% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.08$ (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.73--7.70 (m, 2H), 7.68--7.65 (m, 3H), 7.53--7.46 (m, 6H), 7.42--7.37 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.4$, 145.5, 141.0, 140.3, 136.6, 133.6, 130.7, 130.5, 128.9, 127.8, 127.7, 127.6, 127.1. GC-MS (EI): calcd for C$_{19}$H$_{14}$O [M$^+$] 258.10, found 258.12. Spectroscopic data are in accordance with those described in the literature.$^1$

4''-(Trifluoromethoxy)-[1,1':4',1''-terphenyl]-2-carbaldehyde (3ao)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 4'-Trifluoromethoxy-[1,1'-biphenyl]-4-yl adamantane-1-carboxylate (2x) (125 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (47 mg, 68% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.06$ (s, 1H), 8.06 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.69--7.66 (m, 5H), 7.56--7.46 (m, 4H), 7.33 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.3$, 149.0, 145.3, 139.6, 139.0, 137.1, 133.8, 133.6, 130.7, 130.66, 128.5, 128.0, 127.8, 127.1, 121.8 (q, $J = 256.0$ Hz), 121.4. $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -57.8$. GC-MS (EI): calcd for C$_{20}$H$_{13}$F$_3$O$_2$ [M$^+$] 342.09, found 342.11. Spectroscopic data are in accordance with those described in the literature.$^1$

2-(2-Methylquinolin-6-yl)benzaldehyde (3ap)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and 2-Methylquinolin-6-yl adamantane-1-carboxylate (2y) (49 mg, 0.3 mmol). The crude product was purified by column chromatography on
silica gel (EtOAc/PE = 1/10) to afford the title compound as a slight yellow oil (38 mg, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.00 (s, 1H), 8.13–8.03 (m, 3H), 7.74–7.69 (m, 2H), 7.69–7.64 (m, 1H), 7.56–7.49 (m, 2H), 7.35 (d, $J$ = 8.4 Hz, 1H), 2.77 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.1, 159.9, 147.3, 145.1, 136.2, 135.0, 133.8, 133.6, 131.1, 130.9, 128.9, 128.8, 128.0, 127.8, 126.0, 122.8, 25.4. HRMS (ESI$^+$): calcd for C$_{17}$H$_{14}$NO [M+H]$^+$ 248.1070, found 248.1070.

2-(Benzo[d][1,3]dioxol-5-yl)benzaldehyde (3aq)

The general procedure was applied to 2-Fluorobenzylidene-2-methylpropan-2-amine (1a) (36 mg, 0.2 mmol) and Benzo[d][1,3]dioxol-5-yl adamantane-1-carboxylate (2z) (90 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (20 mg, 45% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.00 (s, 1H), 7.99 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.60 (td, $J$ = 7.6, 1.6 Hz, 1H), 7.49–7.43 (m, 1H), 7.41 (dd, $J$ = 7.6, 0.8 Hz, 1H), 6.90–6.87 (m, 2H), 6.79 (dd, $J$ = 8.0, 2.0 Hz, 1H), 6.03 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.4, 147.8, 147.7, 145.5, 133.8, 133.5, 131.5, 130.6, 127.6, 127.5, 124.1, 110.2, 108.2, 101.4. HRMS (ESI$^+$): calcd for C$_{14}$H$_{10}$O$_3$ [M] 226.0630, found 226.0626.

5. General Procedure for Chromium Catalysis for Forming Polyfluoro-Substituted Molecules

In a dried Schlenk tube were placed magnesium (8 mg, 0.3 mmol) and CrCl$_2$ (5 mg, 0.04 mmol). The tube was heated to around 400 °C under vacuum for 5 min using a
heat gun. After cooling to room temperature, a mixture of dnbpy (16 mg, 0.04 mmol), the corresponding aniline 1 (0.2 mmol) and aryl ester 2 (0.3 mmol) in dry THF solution (2 mL) was added and stirred at 60 °C for 24 h. The mixture was then treated with a solution of aqueous HCl (3 M, 2 mL) and stirred at room temperature for 0.5 h. After neutralization with saturated aqueous solution of NaHCO₃, the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired coupling product.

![Chemical structure of 3',4',5',6-Tetrafluoro-[1,1'-biphenyl]-2-carbaldehyde (4a)](image)

**3',4',5',6-Tetrafluoro-[1,1'-biphenyl]-2-carbaldehyde (4a)**

The general procedure was applied to 2,3-Difluorobenzylidene-2-methylpropan-2-amine (1b) (39 mg, 0.2 mmol) and 3,4,5-Trifluorophenyl adamantane-1-carboxylate (2aa) (93 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (34 mg, 68% yield). Melting point: 97–98 °C; 

**1H NMR (400 MHz, CDCl₃):** δ = 9.85 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.58–7.52 (m, 1H), 7.45–7.38 (m, 1H), 7.06–6.96 (m, 2H); 

**13C NMR (100 MHz, CDCl₃):** δ = 189.7, 160.7, 158.2, 151.0 (ddd, J = 250.0, 10.0, 4.0 Hz), 140.0 (dt, J = 252.0, 15.0 Hz), 135.5, 130.4 (d, J = 8.0 Hz), 129.3 (d, J = 17.0 Hz), 126.7–126.5 (m), 124.3 (d, J = 3.0 Hz), 121.3, 121.1, 115.2 (dd, J = 16.0, 7.0 Hz); 

**19F NMR (377 MHz, CDCl₃):** δ = -115.3, -133.4, -133.5, -159.5 (t, J = 20.7 Hz). GC-MS (EI): calcd for C₁₃H₆F₄O [M⁺] 254.04, found 254.01.
3',4',5',5'-Tetrafluoro-[1,1'-biphenyl]-2-carbaldehyde (4b)

The general procedure was applied to 2,4-Difluorobenzylidene-2-methylpropan-2-amine (1c) (39 mg, 0.2 mmol) and 3,4,5-Trifluorophenyl adamantane-1-carboxylate (2aa) (93 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (38 mg, 75 yield). Melting point: 98–99 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.91\) (s, 1H), 8.07 (dd, \(J = 8.4, 5.6\) Hz, 1H), 7.25 (td, \(J = 8.8, 2.8\) Hz, 1H), 7.13–6.99 (m, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 189.3, 166.6, 164.1, 151.0\) (ddd, \(J = 250.0, 10.0, 4.0\) Hz), 145.0 (d, \(J = 10.0\) Hz), 140.0 (dt, \(J = 253.0, 15.0\) Hz), 132.8–132.6 (m), 131.6 (d, \(J = 10.0\) Hz), 130.2 (d, \(J = 3.0\) Hz), 117.6 (d, \(J = 23.0\) Hz), 116.4 (d, \(J = 22.0\) Hz), 114.1 (dd, \(J = 16.0, 7.0\) Hz); \(^19\)F NMR (377 MHz, CDCl\(_3\)): \(\delta = -112.6, -132.9, -133.0, -159.7\) (t, \(J = 20.7\) Hz). GC-MS (EI): calcd for C\(_{13}\)H\(_6\)F\(_4\)O [M\(^+\)] 254.04, found 254.00.

![Chemical structure](image)

3',4',4',5'-Tetrafluoro-[1,1'-biphenyl]-2-carbaldehyde (4c)

The general procedure was applied to 2,5-Difluorobenzylidene-2-methylpropan-2-amine (1d) (39 mg, 0.2 mmol) and 3,4,5-Trifluorophenyl adamantane-1-carboxylate (2aa) (93 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (40 mg, 78 yield). Melting point: 98–100 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.92\) (d, \(J = 2.8\) Hz, 1H), 7.71–7.65 (m, 1H), 7.42–7.33 (m, 2H), 7.04–6.95 (m, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 189.7\) (d, \(J = 2.0\) Hz), 164.0, 161.4, 151.0 (ddd, \(J = 251.0, 10.0, 4.0\) Hz), 139.9 (dt, \(J = 253.0, 15.0\) Hz), 138.4 (d, \(J = 2.0\) Hz), 135.3, 135.2, 133.0–132.8 (m), 132.6 (d, \(J = 7.0\) Hz), 121.2 (d, \(J = 22.0\) Hz), 114.7, 114.4 (dd, 15.0, 6.0 Hz); \(^19\)F NMR (377 MHz, CDCl\(_3\)): \(\delta = -111.0, -133.0, -133.05, -160.2\) (t, \(J = 20.7\) Hz). GC-MS (EI): calcd for C\(_{13}\)H\(_6\)F\(_4\)O [M\(^+\)] 254.04, found 254.00.
254.04, found 254.06.

3',4',5,5',6-Pentafluoro-[1,1'-biphenyl]-2-carbaldehyde (4d)
The general procedure was applied to 2-Methyl-N-(2,3,4-trifluorobenzylidene)propan-2-amine (1s) (43 mg, 0.2 mmol) and 3,4,5-Trifluorophenyl adamantane-1-carboxylate (2aa) (93 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (38 mg, 70% yield). Melting point: 104–106 °C; 1H NMR (400 MHz, CDCl3): δ = 9.77 (d, J = 0.4 Hz, 1H), 7.84 (ddd, J = 8.8, 4.8, 1.6 Hz, 1H), 7.42–7.33 (m, 1H), 7.08–6.98 (m, 2H); 13C NMR (100 MHz, CDCl3): δ = 188.4 (d, J = 3.0 Hz), 154.1 (dd, J = 259.0, 14.0 Hz), 151.2 (ddd, J = 251.0, 10.0, 4.0 Hz), 147.6 (dd, J = 249.0, 13.5 Hz), 140.4 (dt, J = 254.0, 15.0 Hz), 131.8 (d, J = 13.0 Hz), 130.8 (d, J = 4.0 Hz), 125.4–125.3 (m), 117.9 (d, J = 17.0 Hz), 115.1 (dd, J = 17.0, 7.0 Hz); 19F NMR (377 MHz, CDCl3): δ = -126.2 (d, J = 22.6 Hz), -132.7, -132.8, -138.9 (d, J = 18.8 Hz), -159.7 (t, J = 20.7 Hz). GC-MS (EI): calcd for C₁₃H₃F₄O [M⁺] 272.03, found 272.01.

3',4,4',5',6-Pentafluoro-[1,1'-biphenyl]-2-carbaldehyde (4e)
The general procedure was applied to 2-Methyl-N-(2,3,5-trifluorobenzylidene)propan-2-amine (1t) (43 mg, 0.2 mmol) and 3,4,5-Trifluorophenyl adamantane-1-carboxylate (2aa) (93 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (39 mg, 71% yield). Melting point: 105–106
°C; ¹H NMR (400 MHz, CDCl₃): δ = 9.81 (d, J = 3.2 Hz, 1H), 7.54 (ddd, J = 8.0, 2.4, 1.2 Hz, 1H), 7.20–7.15 (m, 1H), 7.05–6.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 188.3, 163.9 (d, J = 12.0 Hz), 161.4–161.2 (m), 158.8 (d, J = 12.0 Hz), 151.1 (ddd, J = 251.0, 10.0, 4.0 Hz), 140.2 (dt, J = 254.0, 15.0 Hz), 136.4 (dd, J = 7.0, 2.0 Hz), 125.9–125.6 (m), 115.4 (dd, J = 16.0, 7.0 Hz), 110.8 (dd, J = 22.0, 4.0 Hz), 109.5 (t, J = 26.0 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ = -106.5 (d, J = 7.5 Hz), -110.4 (d, J = 11.3 Hz), -132.9 (d, J = 18.8 Hz), -158.8 (t, J = 20.7 Hz). GC-MS (EI): calcd for C₁₃H₁₃F₅O [M⁺] 272.03, found 272.00.

3',4,4',5,5'-Pentafluoro-[1,1'-biphenyl]-2-carbaldehyde (4f)
The general procedure was applied to 2-Methyl-N-(2,4,5-trifluorobenzylidene)propan-2-amine (1u) (43 mg, 0.2 mmol) and 3,4,5-Trifluorophenyl adamantane-1-carboxylate (2aa) (93 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (45 mg, 82% yield). Melting point: 103–105 °C; ¹H NMR (400 MHz, CDCl₃): δ = 9.85 (d, J = 3.2 Hz, 1H), 7.87–7.83 (m, 1H), 7.28–7.18 (m, 1H), 7.06–6.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 188.3, 185.7 (d, J = 13.0 Hz), 152.4 (dd, J = 10.0, 5.0 Hz), 152.0 (dd, J = 13.0, 6.0 Hz), 149.9 (dd, J = 10.0, 4.0 Hz), 149.4 (d, J = 13.0 Hz), 140.2 (dt, J = 254.0, 15.0 Hz), 139.9–139.8 (m), 131.8–131.6 (m), 130.6 (t, J = 3.5 Hz), 119.6 (d, J = 19.0 Hz), 117.4 (dd, J = 18.0, 2.0 Hz), 114.3 (dd, J = 15.0, 24.5 Hz); ¹⁹F NMR (377 MHz, CDCl₃): δ = -126.6 (d, J = 21.9 Hz), -132.3 (d, J = 20.7 Hz), -159.0 (d, J = 22.2 Hz), -159.1 (t, J = 20.4 Hz). GC-MS (EI): calcd for C₁₃H₁₃F₅O [M⁺] 272.03, found 272.05.
3',4,4',5-Tetrafluoro-[1,1'-biphenyl]-2-carbaldehyde (4g)

The general procedure was applied to 2-Methyl-N-(2,4,5-trifluorobenzylidene)propan-2-amine (1u) (43 mg, 0.2 mmol) and 3,4-Difluorophenyl adamantane-1-carboxylate (2ab) (88 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (37 mg, 73% yield). Melting point: 115–117 °C; ^1H NMR (400 MHz, CDCl$_3$): $\delta = 9.84$ (d, $J = 2.8$ Hz, 1H), 7.87–7.82 (m, 1H), 7.33–7.19 (m, 3H), 7.12–7.06 (m, 1H); ^13C NMR (100 MHz, CDCl$_3$): $\delta = 188.9$, 154.6 (d, $J = 13.0$ Hz), 152.1–151.4 (m), 149.6–148.9 (m), 141.0–140.9 (m), 132.5 (t, $J = 4.5$ Hz), 130.6 (t, $J = 4.0$ Hz), 126.3 (dd, $J = 6.0$, 4.0 Hz), 119.6 (d, $J = 18.0$ Hz), 118.3 (dd, $J = 118.0$, 17.0 Hz), 117.0 (dd, $J = 18.0$, 2.0 Hz); ^19F NMR (377 MHz, CDCl$_3$): $\delta = -127.0$ (d, $J = 22.6$ Hz), -135.9 (dd, $J = 22.6$, 15.1 Hz), -136.7 (d, $J = 18.8$ Hz). HRMS (ESI$^+$): calcd for C$_{13}$H$_6$F$_4$O [M] 254.0355, found 254.0351.

3',4,5,5'-Tetrafluoro-[1,1'-biphenyl]-2-carbaldehyde (4h)

The general procedure was applied to 2-Methyl-N-(2,4,5-trifluorobenzylidene)propan-2-amine (1u) (43 mg, 0.2 mmol) and 3,5-Difluorophenyl adamantane-1-carboxylate (2ac) (88 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a white solid (38 mg, 75% yield). Melting point: 108–109 °C; ^1H NMR (400 MHz, CDCl$_3$): $\delta = 9.86$ (d, $J = 2.8$ Hz, 1H), 7.88–7.83 (m, 1H), 7.28–7.21 (m, 1H), 6.99–6.87 (m, 3H); ^13C NMR (100 MHz, CDCl$_3$): $\delta = 188.6$, 162.9 (dd, $J = 250.0$, 12.9 Hz), 152.0 (dd, $J = 524.4$, 13.4 Hz), 151.9 (t, $J = 13.0$ Hz), 151.0 (dd, $J = 118.0$, 17.0 Hz), 117.0 (dd, $J = 18.0$, 2.0 Hz), 116.9 (d, $J = 18.0$ Hz), 116.8 (d, $J = 118.0$, 17.0 Hz), 116.3 (dd, $J = 22.6$, 15.1 Hz), -135.9 (dd, $J = 22.6$, 15.1 Hz), -136.7 (d, $J = 18.8$ Hz). HRMS (ESI$^+$): calcd for C$_{13}$H$_6$F$_4$O [M] 254.0355, found 254.0351.
140.8–140.6 (m), 138.7 (t, $J = 9.3$ Hz), 130.6 (t, $J = 3.8$ Hz), 119.4 (d, $J = 18.8$ Hz), 117.0 (dd, $J = 18.1, 2.2$ Hz), 113.2 (dd, $J = 18.5, 7.6$ Hz), 104.4 (t, $J = 25.4$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -108.1, -126.9$ (d, $J = 18.8$ Hz), -135.3 (d, $J = 22.6$ Hz).

GC-MS (EI): calcd for C$_{13}$H$_6$F$_4$O [M$^+$] 254.04, found 254.01.

6. Mechanistic Studies

In two dried Schlenk tubes were placed magnesium (15 mg, 0.6 mmol) and CrCl$_2$ (10 mg, 0.08 mmol). The tubes were heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, aniline 1a (0.4 mmol) and dry THF (2 mL) was added under nitrogen atmosphere and the resulting mixture was stirred at 40 °C for 24 h. One of the two reactions was treated with D$_2$O (1 mL, 56 mmol) and then the mixture was stirred at rt for 1 h. The other reaction was treated with 2a (18 mg, 0.08 mmol) and the resulting mixture was stirred at 40 °C for 12 h. Both reactions were quenched with HCl (aq) (3 M, 2 mL) and then neutralized with saturated aqueous solution of NaHCO$_3$. The aqueous mixture was then extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the organic solvent was removed under reduced pressure. The residue was purified by column chromatography.
Figure S1. $^1$H NMR spectrum of compound 5.

[1,1'-Biphenyl]-2,2'-dicarbaldehyde (6)

A colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.84$ (d, $J = 0.4$ Hz, 2H), 8.07 (dd, $J = 7.8$, 1.4 Hz, 2H), 7.67 (td, $J = 7.2$, 1.2 Hz, 2H), 7.63–7.57 (m, 2H), 7.38–7.33 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 191.0$, 141.2, 134.6, 133.4, 131.7, 128.8, 128.6. HRMS (ESI$^+$): calcd for C$_{14}$H$_{11}$O$_2$ [M+H]$^+$ 211.0754, found 211.0754.
Figure S2. $^1$H and $^{13}$C NMR spectra of compound 6.
Synthesis of Cyclochromate Species I

In a dried Schlenk tube were placed magnesium (15 mg, 0.6 mmol) and CrCl₂ (10 mg, 0.08 mmol). The tube was heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, aniline 1a (0.4 mmol) in dry THF solution (2 mL) was added and stirred at 40 °C for 24 h, then dnbpy (0.08 mmol) was introduced. After stirring for another 1 h, the THF solution was filtered and the solvent was removed in vacuum. The purple solid was washed with hexane (3 × 5 mL) to afford a black powder (50 mg, 90% based on CrCl₂). HRMS (ESI⁺): calcd for C₄₃H₆₇CrN₃O [M+H]⁺ 693.4684, found 693.4686. Elemental analysis calcd (%) for C₄₃H₆₆CrN₃O: C, 74.52; H, 9.60; O, 2.31; N, 6.07. Found: C, 74.88; H, 9.88; O, 2.41; N, 6.57.

**HRMS analysis of cyclochromate species I (ESI⁺):**

![HRMS spectra](image1.png)

**Figure S3.** Images for HRMS analysis of cyclochromate species I.
**XPS analysis of cyclochromate species I:**

![XPS spectra diagram](image)

**Figure S4.** Binding energies of XPS spectra for the analysis of valent states of cyclochromate species.

**Magnetic Measurements of Cyclochromate Species I:**

Magnetic measurements were performed on polycrystalline samples sealed in polyethylene film. Data were collected using a Quantum Design MPMS-XL7 SQUID magnetometer from 2.0 to 300 K at applied dc field of 1000 Oe. Dc susceptibility data were corrected for diamagnetic contributions from the sample holder and for the core diamagnetism of each sample estimated using Pascal’s constants.

\[ M(300 \, K) = 3.93 \, \mu_B \]
**Figure S5.** Magnetic measurement of cyclochromate species I.

**Elemental analysis of cyclochromate species I:**

```
<table>
<thead>
<tr>
<th>Group</th>
<th>Sample name</th>
<th>Filename</th>
<th>Inj Date</th>
<th>Inj Time</th>
<th>Type</th>
<th>Weight (mg)</th>
<th>Humidity %</th>
<th>Nitrogen</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FF-1</td>
<td>Fea027</td>
<td>01/14/2022</td>
<td>19:13</td>
<td>UNK</td>
<td>2.603</td>
<td>0.9633</td>
<td>74.0821</td>
<td>5.8734</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

```

**Figure S6.** Images for elemental analysis of cyclochromate species I.
**Cyclochromate Species I-Catalyzed Cross-Coupling Reaction:**

In a dried Schlenk tube were placed metallic magnesium (8 mg, 0.3 mmol) and heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, a mixture of cyclochromate (0.02 mmol), the corresponding aniline 1a (0.2 mmol) and aryl ester 2a (0.3 mmol) in dry THF solution (2 mL) was added and stirred at 40 °C for 24 h. The mixture was then treated with a solution of aqueous HCl (3 M, 2 mL) and stirred at room temperature for 0.5 h. After neutralization with saturated aqueous solution of NaHCO₃, the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the coupling product 3a in 83%.

---

**Procedure for eq 1:** According to the procedure of synthesis of cyclochromate species, the complex was prepared. Which was isolated and further treated with Naphthalen-2-yl pivalate (2a) (18 mg, 0.08 mmol) in dry THF (2 mL) at 40 °C for 12 h. The mixture was then treated with 1 mL of D₂O or a solution of aqueous HCl (3 N, 2 mL) for 0.5 h. The mixture was then extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the coupling product 3a in 83%.

---

**Procedure for eq 2:**

---

**Procedure for eq 3:**

---

*GC yield based on 2a. GC yield based on 1a.*
2 mL) and stirred at room temperature for 0.5 h. After neutralization with saturated aqueous solution of NaHCO₃, the mixture was detected by GC/MS analysis using tridecane as internal standard.

Procedure for eqs 2-3: In a dried Schlenk tube were placed metallic magnesium (15 mg, 0.6 mmol) and CrCl₂ (10 mg, 0.08 mmol). The tube was heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, dn bpy (32 mg, 0.08 mmol) and dry THF (2 mL) was added. After stirring at 40 °C for 24 h, the mixture was filtrated and the corresponding substrates (0.4 mmol) was added stirred at 40 °C for another 2 h. The mixture was then treated with 1 ml of D₂O and stirred at room temperature for 0.5 h. After hydrolysis with HCl (aq) and neutralization with saturated aqueous solution of NaHCO₃, the mixture was detected by GC/MS analysis using tridecane as internal standard.

\[ \text{N-(2-fluorobenzyl)-2-methylpropan-2-amine} \]

A colorless oil. \(^1\)H NMR (400 MHz, \(d_8\)-THF): \(\delta = 7.52–7.47 \text{ (m, 1H)}, 7.20–7.13 \text{ (m, 1H)}, 7.06 \text{ (td, } J = 7.6, 1.2 \text{ Hz, 1H}), 7.00–6.94 \text{ (m, 1H)}, 3.77 \text{ (s, 2H)}, 1.14 \text{ (s, 10H)}; \(^{13}\)C NMR (100 MHz, \(d_8\)-THF): \(\delta = 160.9 \text{ (d, } J = 243.0 \text{ Hz), 130.0 \text{ (d, } J = 5.0 \text{ Hz), 129.2 \text{ (d, } J = 15.0 \text{ Hz), 127.6 \text{ (d, } J = 9.0 \text{ Hz), 123.6 \text{ (d, } J = 3.0 \text{ Hz), 114.2 \text{ (d, } J = 22.0 \text{ Hz), 50.1, 39.5 \text{ (d, } J = 3.0 \text{ Hz), 28.4; }^{19}\)F NMR (377 MHz, \(d_8\)-THF): \(\delta = -121.2. \text{ HRMS (ESI⁺): calcd for C}_{11}H_{17}FN [M+H]^+ 182.1340, found 182.1340.} \]
Figure S7. $^1$H, $^{13}$C and $^{19}$F NMR spectra of amine.

Table S6. Time course for the Cr-catalyzed C(aryl)–F/C(aryl)–O bond coupling.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>3a (%)</th>
<th>Recovery of 1a (%)</th>
<th>Recovery of 2a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ~ 8</td>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>88</td>
<td>92</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>80</td>
<td>87</td>
</tr>
<tr>
<td>11</td>
<td>21</td>
<td>75</td>
<td>76</td>
</tr>
<tr>
<td>12</td>
<td>38</td>
<td>57</td>
<td>68</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>45</td>
<td>51</td>
</tr>
<tr>
<td>14</td>
<td>62</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>15</td>
<td>79</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>T (h)</td>
<td>Yield (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reaction profile for the formation of 3a**

**Reaction profile for the recovery of 1a**
Figure S8. Reaction profile for the Cr-catalyzed C(aryl)–F/C(aryl)–O bond coupling.
Experiments of Kinetic Studies

A. Procedure for determining the order in 1a:

In a dried Schlenk tube were placed metallic magnesium (0.6 mmol) and CrCl$_2$ (0.04 mmol). The tube was heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, a mixture of dnbpy (0.04 mmol), different amounts of 1a (0.2, 0.3, 0.4, 0.5, 0.6 mmol) and 2a (0.6 mmol) were placed in the dried Schlenk tube, followed by the addition of $n$-tridecane (0.2 mmol, an internal standard for GC analysis) in dry THF solution (4 mL). After stirring the mixture for 8 hours at 40 °C, periodic aliquots (30 µL) were removed by a syringe and quenched by an aqueous solution of HCl (3 N, 0.5 mL) for a continuous stirring for another 0.5 h. After neutralization with saturated aqueous solution of NaHCO$_3$, the resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using $n$-tridecane as the internal standard. The concentrations of the products were plotted to yield the initial rates for the formation of 3a (with a maximum of 20% conversion).

Table S7. Initial Rate Data Obtained by Varying the Concentration of 1a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>1a [M]</th>
<th>2a [M]</th>
<th>Initial rate [M/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>0.15</td>
<td>2.27×10$^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.075</td>
<td>0.15</td>
<td>1.93×10$^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.15</td>
<td>1.83×10$^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>0.15</td>
<td>1.50×10$^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>0.150</td>
<td>0.15</td>
<td>1.38×10$^{-4}$</td>
</tr>
</tbody>
</table>
Figure S9. Plot of the initial rate vs the initial concentration of fluoroarene 1a.

B. Procedure for determining the order in 2a:

\[
y = -0.0009x + 0.0003 \\
R^2 = 0.97099
\]

\[
y = -0.4516x - 4.2211 \\
R^2 = 0.94206
\]

In a dried Schlenk tube were placed metallic magnesium (0.6 mmol) and CrCl₂ (0.04 mmol). The tube was heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, a mixture of dnbp (0.04 mmol), 1a (0.4 mmol), and Mg (1.5 equiv) in THF, 40 °C, and then HCl (aq).
mmol) and different amounts of 2a (0.2, 0.4, 0.6, 0.8, 1.0 mmol) were placed in the dried Schlenk tube, followed by the addition of n-tridecane (0.2 mmol, an internal standard for GC analysis) in dry THF solution (4 mL). After stirring the mixture for 8 hours at 40 °C, periodic aliquots (30 µL) were removed by a syringe and quenched by an aqueous solution of HCl (3 N, 0.5 mL) for a continuous stirring for another 0.5 h. After neutralization with saturated aqueous solution of NaHCO₃, the resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using n-tridecane as the internal standard. The concentrations of the products were plotted to yield the initial rates for the formation of 3a (with a maximum of 20% conversion).

**Table S8. Initial Rate Data Obtained by Varying the Concentration of 2a.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>1a [M]</th>
<th>2a [M]</th>
<th>Initial rate [M/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.050</td>
<td>1.14×10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.100</td>
<td>1.56×10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.150</td>
<td>1.83×10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>0.100</td>
<td>0.200</td>
<td>2.20×10⁻⁴</td>
</tr>
<tr>
<td>5</td>
<td>0.100</td>
<td>0.250</td>
<td>2.60×10⁻⁴</td>
</tr>
</tbody>
</table>
C. Procedure for determining the order in CrCl\(_2\)/dnbpy:

In a dried Schlenk tube were placed metallic magnesium (0.6 mmol) and different amount of CrCl\(_2\) (0.02, 0.04, 0.06, 0.08 mmol). The tube was heated to around 400 °C under vacuum for 5 min using a heat gun. After cooling to room temperature, a mixture of dnbpy (the amount is equal to that of CrCl\(_2\)), 1a (0.4 mmol) and 2a (0.4, 0.6 mmol) were placed in the dried Schlenk tube, followed by the addition of n-tridecane (0.2 mmol, an internal standard for GC analysis) in dry THF solution (4 mL). After stirring the mixture for 8 hours at 40 °C, periodic aliquots (30 µL) were removed by a syringe and quenched by an aqueous solution of HCl (3 N, 0.5 mL) for a continuous stirring for another 0.5 h. After neutralization with saturated aqueous solution of NaHCO\(_3\), the resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using n-tridecane as the internal standard. The concentrations of the products were plotted to yield the initial rates for the formation of 3a (with a maximum of 20% conversion).
Table S9. Initial Rate Data Obtained by Varying the Concentration of CrCl\(_2\)/dnbpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>mol %</th>
<th>CrCl(_2)/dnbpy [M]</th>
<th>Initial rate [M/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0.005</td>
<td>7.81 × 10(^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.010</td>
<td>1.83 × 10(^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>0.015</td>
<td>2.34 × 10(^{-4})</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.020</td>
<td>3.06 × 10(^{-4})</td>
</tr>
</tbody>
</table>

Figure S11. Plot of the initial rate vs the initial concentration of CrCl\(_2\)/dnbpy.
7. Synthetic Application

Using fluoro-bearing benzaldehyde as precursor in the cross-coupling

In a dried Schlenk tube were placed 2,4,5-Trifluorobenzaldehyde 7 (0.8 g, 5 mmol) and 2-Methylpropan-2-amine (6 mmol, 1.2 equiv) in reflux for 6 h. After removal of the volatiles under vacuum, CrCl₂ (1 mmol), dnbp (1 mmol), 3,4,5-Trifluorophenyl adamantane-1-carboxylate (3.1 g, 10 mmol), metallic magnesium (240 mg, 10 mmol) (disposed with a heat gun heated to around 400 °C under vacuum for 5 min) and dry THF (5 mL) were added in glove box and the resulting mixture was stirred at 60 °C for 48 h. The mixture was then treated with a solution of aqueous HCl (3 M, 4 mL) and stirred at room temperature for 0.5 h. After neutralization with saturated aqueous solution of NaHCO₃, the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford a white solid 4f (0.8 g, 59% yield).

Synthesis of

N-(tert-butyl)-N-((3',4,4',5,5'-pentafluoro-[1,1'-biphenyl]-2-yl)methyl)-4-(4-pentyl cyclohexyl)benzamide (8)

According to the procedure of using fluoro-bearing benzaldehyde as precursor in the
cross-coupling, the crude product imine of 4f was collected, THF solution was filtrated and the solvent was removed in vacuum. MeOH (10 mL) was added and stirred at room temperature for 5 min, then NaBH₄ (190 mg, 5 mmol) was added in sequential at 0 °C, the resulting mixture was warm to room temperature stirring for another 2 h. The mixture was filtrated and removed the volatiles under vacuum, Et₃N (5 mmol), CH₂Cl₂ (10 mL) were added and corresponding acetyl chloride (5 mmol) was added dropwise by a syringe at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 3-4 hours, aqueous solution of NaHCO₃ was added and extracted several times with CH₂Cl₂. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude residue was purified by flash chromatography to afford a white solid 8 (1.6 g, 92% base on 4f).

\[
N\text{-}(\text{tert-butyl})\text{-}N\text{-}((3',4,4',5,5'\text{-}pentafluoro\text{-}[1,1'\text{-}biphenyl]-2-yl)methyl)\text{-}4\text{-}(4\text{-}pentylcyclohexyl)benzamide (8)
\]

Melting point: 118–120 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.40 (dd, J = 11.2, 8 Hz, 1H), 7.12 (s, 4H), 6.89 (dd, J = 10.4, 7.6 Hz, 1H), 6.47–6.42 (t, J = 7.2 Hz, 2H), 4.29 (s, 2H), 2.48–2.42 (m, 1H), 1.87 (s, 2H), 1.84 (s, 2H), 1.45 (s, 9H), 1.40 (s, 1H), 1.34–1.16 (m, 10H), 1.07–0.98 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 174.0, 152.2 (dd, J = 10.0, 4.0 Hz), 150.3 (dd, J = 249.0, 12.0 Hz), 149.9–149.6 (m), 149.2, 147.3 (d, J = 12.0 Hz), 139.5 (dt, J = 252.0, 15.0 Hz), 136.3, 135.1 (t, J = 4.0 Hz), 134.0 (dd, J = 13.0, 8.0 Hz), 133.1, 126.9, 125.7, 118.7 (d, J = 17.0 Hz), 116.3 (d, J = 19.0 Hz), 113.1 (dd, J = 15.0, 6.0 Hz), 57.9, 48.5, 44.4, 37.3,
37.2, 34.1, 33.4, 32.2, 28.6, 26.6, 22.7, 14.0; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -132.9$
(d, $J = 18.8$ Hz), -136.3 (d, $J = 22.6$ Hz), -139.6 (d, $J = 18.8$ Hz), -160.6 (t, $J = 20.7$
Hz). HRMS (ESI$^+$): calec for C$_{35}$H$_{41}$F$_5$NO [M+H]$^+$ 586.3103, found 586.3111.

Synthesis of 2-(2,2-Difluorovinyl)-3',4,4',5,5'-pentafluoro-1,1'-biphenyl (9)
In a 25 mL of screw-capped vial with stirring bar, the
3',4,4',5,5'-Pentafluoro-[1,1'-biphenyl]-2-carbaldehyde (4f) (82 mg, 0.3 mmol),
ClCF$_2$CO$_2$Na (61 mg, 0.4 mmol), PPh$_3$ (125 mg, 0.5 mmol) and 5 mL of DMF were
added. The reaction mixture stirred at 110 °C for 2 h. Water was then added and the
mixture was extracted three times with ethyl acetate. The organic phases were
collected, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The
product was purified by column chromatography on silica gel (hexane) to afford the
title compound as a white solid (74 mg, 81% yield).

2-(2,2-Difluorovinyl)-3',4,4',5,5'-pentafluoro-1,1'-biphenyl (9)
Melting point: 65–67 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$ (dd, $J = 11.6$, 8.0 Hz,
1H), 7.07 (dd, $J = 10.4$, 8.0 Hz, 1H), 6.96–6.88 (m, 2H), 5.06 (dd, $J = 24.8$, 3.6 Hz,
1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 159.4$, 156.4 (dd, $J = 8.0$, 2.0 Hz), 153.5 (d, $J$
= 2.0 Hz), 151.1 (ddd, J = 250.0, 10.0, 4.0 Hz), 150.0 (dd, J = 248.5, 12.5 Hz), 149.8 (dd, J = 12.0, 5.0 Hz), 148.9 (dd, J = 250.0, 13.0 Hz), 139.7 (dt, J = 252.0, 15.0 Hz), 134.8–134.5 (m), 125.0–124.8 (m), 117.2 (dd, J = 18.5, 9.5 Hz), 117.0 (d, J = 18.0 Hz), 113.8 (dd, J = 15.5, 6.5 Hz), 79.0 (dd, J = 32.0, 13.0 Hz); 19F NMR (377 MHz, CDCl3): δ = -80.8 (d, J = 26.4 Hz), -82.6 (d, J = 26.4 Hz), -133.2 (d, J = 22.6 Hz), -136.8 (d, J = 22.6 Hz), -137.8 (dd, J = 22.6, 3.8 Hz), -160.7 (t, J = 20.7 Hz). GC-MS (EI): calcd for C14H3F7 [M+] 306.03, found 306.05.

Synthesis of N-methyl-1-(3',4,4',5,5'-pentafluoro-[1,1'-biphenyl]-2-yl)methanamine (10)

In a dried Schlenk tube were placed 3',4,4',5,5'-Pentafluoro-[1,1'-biphenyl]-2-carbaldehyde (4f) (82 mg, 0.3 mmol) and Methanamine (0.6 mmol, 0.6 mL, 1 M in MeOH) in reflux for 6 h. After removal of the volatiles under vacuum, MeOH (10 mL) was added and stirred at room temperature for 5 min, then NaBH₄ (23 mg, 0.6 mmol) was added in sequential at 0 °C, After stirring the mixture at room temperature for 2 h, saturated aqueous solution of NH₄Cl was added and stirred for another 5 min. The mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford a yellow oil 10 (77 mg, 89% yield).

N-methyl-1-(3',4,4',5,5'-pentafluoro-[1,1'-biphenyl]-2-yl)methanamine (10)

1H NMR (400 MHz, d8-THF): δ = 7.48 (dd, J = 12.0, 8.4 Hz, 1H), 7.41–7.33 (m, 2H), 7.23 (dd, J = 11.2, 8.0 Hz, 1H), 3.54 (s, 2H), 2.35 (s, 3H), 1.87 (s, 1H); 13C NMR (100 MHz, d8-THF): δ = 150.6 (ddd, J = 234.0, 10.0, 4.0 Hz), 150.4 (dd, J = 125.0, 13.0 Hz), 147.9 (dd, J = 123.0, 12.5 Hz), 139.2 (dt, J = 249.0, 15.5 Hz), 135.9–135.4 (m),

S55
118.2 (dd, $J = 37.0$, 18.0 Hz), 113.8 (dd, $J = 16.0$, 6.0 Hz), 52.5, 35.3; $^{19}$F NMR (377 MHz, $d_8$-THF): $\delta = -136.5$ (d, $J = 18.8$ Hz), -140.6 (d, $J = 22.6$ Hz), -142.1 (d, $J = 18.8$ Hz), -164.5 (t, $J = 20.7$ Hz). HRMS (ESI$^+$): calcd for C$_{14}$H$_{11}$F$_5$N [M+H]$^+$ 288.0806, found 288.0805.

8. Supplementary References


9. $^1\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra

\begin{figure}
\centering
\includegraphics[width=\textwidth]{nmr_spectra.png}
\caption{$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra for compound 3a}
\end{figure}
Figure S13. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3b
Figure S14. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3e
Figure S15. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3d
Figure S16. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3e
Figure S17. $^1$H and $^{13}$C NMR Spectra for compound 3f
Figure S18. $^1$H and $^{13}$CNMR Spectra for compound 3g
Figure S19. $^1$H and $^{13}$CNMR Spectra for compound 3h
Figure S20. $^1$H and $^{13}$C NMR Spectra for compound 3i
Figure S21. $^1$H and $^{13}$CNMR Spectra for compound 3j
Figure S22. $^1$H and $^{13}$CNMR Spectra for compound 3k
Figure S23. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 31
Figure S24. $^1$H and $^{13}$C NMR Spectra for compound 3m
Figure S25. $^1$H and $^{13}$C NMR Spectra for compound 3n
**Figure S26.** $^1$H and $^{13}$C NMR Spectra for compound 3o
Figure S27. $^1$H and $^{13}$C NMR Spectra for compound 3p
Figure S28. $^1$H and $^{13}$C NMR Spectra for compound 3q
Figure S29. $^1$H and $^{13}$C NMR Spectra for compound 3r
Figure S30. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3s
Figure S31. $^1$H and $^{13}$C NMR Spectra for compound 3t
Figure S32. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3u
Figure S33. $^1$H and $^{13}$C NMR Spectra for compound 3v
Figure S34. $^1$H and $^{13}$C NMR Spectra for compound 3w
Figure S35. $^1$H and $^{13}$C NMR Spectra for compound 3x
Figure S36. $^1$H and $^{13}$C NMR Spectra for compound 3y
Figure S37. $^1$H and $^{13}$C NMR Spectra for compound 3z
Figure S38. $^1$H and $^{13}$C NMR Spectra for compound 3aa
Figure S39. $^1$H and $^{13}$C NMR Spectra for compound 3ab
Figure S40. $^1$H and $^{13}$C NMR Spectra for compound 3ac
Figure S41. $^1$H and $^{13}$C NMR Spectra for compound 3ad
Figure S42. $^1$H and $^{13}$C NMR Spectra for compound 3ae
Figure S43. $^1$H and $^{13}$C NMR Spectra for compound 3af
Figure S44. $^1$H and $^{13}$C NMR Spectra for compound 3ag
Figure S45. $^1$H and $^{13}$C NMR Spectra for compound 3ah
Figure S46. $^1$H and $^{13}$C NMR Spectra for compound 3ai
Figure S47. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 3aj
Figure S48. $^1$H and $^{13}$C NMR Spectra for compound 3ak
Figure S49. $^1$H and $^{13}$C NMR Spectra for compound 3al
Figure S50. $^1$H and $^{13}$C NMR Spectra for compound 3am
Figure S51. $^1$H and $^{13}$C NMR Spectra for compound 3an
Figure S52. \(^1\)H, \(^{13}\)C and \(^{19}\)F NMR Spectra for compound 3ao
Figure S53. $^1$H and $^{13}$C NMR Spectra for compound 3ap
Figure S54. $^1$H and $^{13}$C NMR Spectra for compound 3aq
Figure S55. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4a
Figure S56. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4b
Figure S57. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4c
Figure S58. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4d
Figure S59. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4e
Figure S60. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4f
Figure S61. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4g
Figure S62. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 4h
Figure S63. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 8
Figure S64. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 9
Figure S65. $^1$H, $^{13}$C and $^{19}$F NMR Spectra for compound 10