Supporting Information

Aryltrifluoromethylative Cyclization of Unactivated Alkenes by the Use of PhICF₃Cl under Catalyst-Free Condition

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I. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. PIFA and TMSCF$_3$ were purchased from Energy Chemical Co. Ltd., Anhydrous MeCN, THF (Tetrahydrofuran), DMF (N, N-dimethylformamide), 1,4-dioxane were purchased from Innochem Co. Ltd., DCM (dichloromethane) was distilled over CaH$_2$ before use. The products were purified by column chromatography over silica gel (particle size 300-400 mesh ASTM, purchased from Taizhou, China). $^1$H NMR, $^{13}$C NMR spectra were recorded at 25 ºC on a Bruker 600 MHz or Varian 500 MHz, 400 MHz, and 151 MHz or 125 MHz spectrometer, respectively by using TMS as internal standard. $^{19}$F-NMR were recorded at 25 ºC on a Bruker 565 MHz or Varian 470 MHz spectrometer by using (trifluoromethyl)benzene (δ -63.2 ppm) as external standard. Data for $^1$H, $^{13}$C, $^{19}$F were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focus spectrometer (ESI). Melting points were uncorrected. PhICF$_3$Cl reagent was prepared according to literature procedures.[1]

II. Screen of Reaction Conditions

Table S1. Screen of solvents.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of 2a [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>NMP</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>1,4-dioxane</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>DCM</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>85</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), PhICF$_3$Cl (0.15 mmol), solvent (1 mL).
[b] $^{19}$F NMR yields using PhCF$_3$ as an internal standard.

Table S2. Screen of temperature.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>T [ºC]</th>
<th>Yield of 2a [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>98</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), PhICF$_3$Cl (0.15 mmol), DMF (1 mL).
[b] $^{19}$F NMR yields using PhCF$_3$ as an internal standard.

Table S3. Screen of time.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>T [ºC]</th>
<th>Yield of 2a [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>98</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), PhICF$_3$Cl (0.15 mmol), DMF (1 mL).
[b] $^{19}$F NMR yields using PhCF$_3$ as an internal standard.
**Supporting Information**

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>t</th>
<th>Yield of 2a [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2h</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>4h</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>6h</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>8h</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>10h</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>12h</td>
<td>98</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), PhICF₃Cl (0.15 mmol), DMF (1 mL).
[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

### Table S4. Screen of reaction atmosphere

<table>
<thead>
<tr>
<th>Entry</th>
<th>N₂ or Air</th>
<th>Yield of 2a [%]</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>N₂</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>Air</td>
<td>51</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), PhICF₃Cl (0.15 mmol), DMF (1 mL).
[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

### Table S5. Screen of the ratio of 1a / PhICF₃Cl

<table>
<thead>
<tr>
<th>Entry</th>
<th>1a : PhICF₃Cl</th>
<th>Yield of 2a [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 1.2</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>1 : 1.5</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>1 : 2.0</td>
<td>98</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), PhICF₃Cl (x mmol), DMF (1 mL).
[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

### Table S6. Catalyst-free trifluoromethylation-carbocyclizations using Togni’s reagent

<table>
<thead>
<tr>
<th>Yield of 2a [%]</th>
<th>Recovery of Togni’s reagent II [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>95</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), **Togni’s reagent II** (0.15 mmol), DMF (1 mL).
[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

### Table S7. Catalyst-free trifluoromethylation-carbocyclizations using Umemoto’s reagent

<table>
<thead>
<tr>
<th>Yield of 2a [%]</th>
<th>Recovery of Umemoto’s reagent [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>95</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.1 mmol), **Umemoto’s reagent** (0.15 mmol), DMF (1 mL).
[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.
### III. Procedures for the synthesis of substrates

1. **Synthesis of substrates 1.**

   Substrates 1a-1q were synthesized according to the literature, and the NMR spectroscopy were consistent with reported data.[2,3] Substrates 1c, 1e-1i, 1l-1n were new compounds synthesized according to the literature.[2] The NMR spectroscopy were as follow:

#### Synthesis of substrates 1a-1k (taking 1c as an example):

A 15 mL Schlenk tube was charged with a stir bar. The tube was evacuated and backfilled with N₂ (3 times). Diethyl malonate (0.92 mL, 6.0 mmol) was added drop-wise to a suspension of NaH (0.24 g, 60%, 6.0 mmol) in THF (5 mL) at 0 °C and was stirred for 15 min. 1-(Bromomethyl)-4-methylbenzene (0.92 g, 5.0 mmol) was then added in one portion and the resulting milky mixture was stirred at reflux for 1 h. The reaction was then cooled and quenched by the addition of H₂O. THF was removed under reduced pressure and the resulting crude was dissolved in Et₂O and washed with water. The aqueous layer was extracted with Et₂O (3×10 mL), and the combined organics were washed with brine, dried over anhydrous MgSO₄ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 15/1, v/v) to give 1.02 g (77%) of benzylated intermediate as a colourless oil. The NMR spectroscopy were consistent with reported data.[2]

A 15 mL Schlenk tube was charged with a stir bar. The tube was evacuated and backfilled with N₂ (3 times). NaH (0.06 g, 60%, 1.5 mmol) was dissolved in dry THF (5 mL) under N₂ atmosphere. The benzylated intermediate (0.27 g, 1.0 mmol) was added slowly. The suspension was stirred 0.5 h at room temperature and 3-bromo-2-methylprop-1-ene (0.13 mL 1.5 mmol) was added. Two hours later, the reaction was quenched with sat. NH₄Cl (10 mL). The reaction mixture was extracted with Et₂O (3×10 mL) and brine (3×10 mL), dried over anhydrous MgSO₄ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 15/1, v/v) to give 1c as a colourless oil.
Diethyl-2-(2-methylallyl)-2-(4-methylbenzyl)malonate (1c). 254.6 mg, 80% yield. Colourless oil. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.03 (dd, $J$ = 22.2 Hz, 7.8 Hz, 4H), 4.91 (s, 1H), 4.81 (s, 1H), 4.11 - 4.19 (m, 4H), 3.27 (s, 2H), 2.62 (s, 2H), 2.30 (s, 3H), 1.72 (s, 3H), 1.22 (t, $J$ = 7.2 Hz, 6H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 171.2, 171.1, 141.2, 136.3, 133.3, 130.0, 130.0, 128.9, 128.8, 114.9, 61.2, 60.2, 58.5, 40.1, 38.4, 38.2, 23.8, 21.0, 13.9. HRMS (ESI): Calcd for [C$_{19}$H$_{26}$O$_4$, M+Na]$^+$: 341.1723, measured: 341.1730.

Diethyl-2-(4-tert-butylbenzyl)-2-(2-methylallyl)malonate (1e). 281.2 mg, 78% yield. Light yellow oil. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.25 (d, $J$ = 8.4 Hz, 2H), 7.06 (d, $J$ = 8.4 Hz, 2H), 4.91 (t, $J$ = 1.2 Hz, 1H), 4.81 (s, 1H), 4.09 - 4.17 (m, 4H), 3.27 (s, 2H), 2.64 (s, 2H), 1.73 (s, 3H), 1.28 (s, 9H), 1.20 (t, $J$ = 7.2 Hz, 6H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 171.3 (2C), 149.6, 141.1, 133.3, 129.8 (2C), 125.0 (2C), 115.0, 61.2 (2C), 58.5, 40.3, 38.2, 34.4, 31.3 (3C), 23.8, 13.9 (2C). HRMS (ESI): Calcd for [C$_{22}$H$_{32}$O$_4$, M+Na]$^+$: 383.2193, measured: 383.2191.

Diethyl-2-[[1,1'-biphenyl]-4-ylmethyl]-2-(2-methylallyl)malonate (1f). 323.5 mg, 85% yield. Colourless oil. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.56 (d, $J$ = 8.4 Hz, 2H), 7.48 (d, $J$ = 7.8 Hz, 2H), 7.42 (t, $J$ = 7.8 Hz, 1H), 7.33 (d, $J$ = 7.2 Hz, 1H), 7.21 (d, $J$ = 7.8 Hz, 2H), 4.94 (s, 1H), 4.84 (s, 1H), 4.12 - 4.20 (m, 4H), 3.34 (s, 2H), 2.68 (s, 2H), 1.75 (s, 3H), 1.22 (t, $J$ = 7.2 Hz, 6H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 171.2 (2C), 141.1, 140.9, 139.7, 135.6, 130.5 (2C), 128.7 (2C), 127.2, 127.0 (2C), 126.8 (2C), 115.0, 61.2 (2C), 58.5, 40.4, 38.4, 23.8, 14.0 (2C). HRMS (ESI): Calcd for [C$_{24}$H$_{28}$O$_4$, M+Na]$^+$: 403.1880, measured: 403.1868.

Diethyl-2-(4-chlorobenzyl)-2-(2-methylallyl)malonate (1g). 254.0 mg, 75% yield. White solid. mp: 46-47 ºC. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 7.54 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 4.94 (s, 1H), 4.80 (s, 1H), 4.08 - 4.18 (m, 4H), 3.27 (s, 2H), 2.66 (s, 2H), 1.71 (s, 3H), 1.20 (t, $J$ = 7.2 Hz, 6H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 170.7 (2C), 142.5, 140.5, 131.8 (2C), 131.0 (2C), 115.3, 61.5 (2C), 58.2, 41.0, 38.8, 23.5, 13.9 (2C). HRMS (ESI): Calcd for [C$_{18}$H$_{22}$ClO$_4$, M+Na]$^+$: 361.1177, measured: 361.1180.

Diethyl-2-(2-methylallyl)-2-(4-nitrobenzyl)malonate (1h). 262.0 mg, 75% yield. White solid. mp: 38-39 ºC. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ = 8.11 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 4.95 (s, 1H), 4.81 (s, 1H), 4.09 - 4.19 (m, 4H), 3.36 (s, 2H), 2.67 (s, 2H),
1.72 (s, 3H), 1.20 (t, J = 7.2 Hz, 6H). \(^{13}\text{C-NMR}\) (151 MHz, CDCl\(_3\)): δ = 170.7 (2C), 147.0, 144.6, 140.5, 131.1 (2C), 123.2 (2C), 115.5, 61.6 (2C), 58.2, 41.0, 38.6, 23.5, 13.9 (2C).

**HRMS (ESI):** Calcd for \([\text{C}_{18}\text{H}_{23}\text{NO}_6], \text{M+Na}^+\]: 372.1418, measured: 372.1423.

Diethyl-2-allyl-2-(4-nitrobenzyl) malonate (1i). 251.4 mg, 75 % yield. White solid. mp: 66-67 ºC. \(^1\text{H-NMR}\) (600 MHz, CDCl\(_3\)): δ = 8.13 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.69 - 5.76 (m, 1H), 5.16 - 5.21 (m, 2H), 4.13 - 4.23 (m, 4H), 3.32 (s, 2H), 2.58 (d, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 6H). \(^{13}\text{C-NMR}\) (151 MHz, CDCl\(_3\)): δ = 170.2 (2C), 147.1, 144.2, 132.0, 131.0 (2C), 123.4 (2C), 119.8, 61.6 (2C), 58.6, 38.1, 37.0, 14.0 (2C).

**HRMS (ESI):** Calcd for \([\text{C}_{17}\text{H}_{21}\text{NO}_6], \text{M+Na}^+\]: 358.1261, measured: 358.1265.

Diethyl-2-(3-methoxybenzyl)-2-(2-methylallyl)malonate (1l). 260.6 mg, 78 % yield. Colourless oil. \(^1\text{H-NMR}\) (600 MHz, CDCl\(_3\)): δ = 7.15 (t, J = 7.8 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.71 (d, J = 9.0 Hz, 2H), 4.92 (s, 1H), 4.82 (s, 1H), 4.11 - 4.19 (m, 4H), 3.76 (s, 3H), 3.28 (s, 2H), 2.65 (s, 2H), 1.73 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H). \(^{13}\text{C-NMR}\) (151 MHz, CDCl\(_3\)): δ = 171.2 (2C), 159.3, 141.1, 137.9, 129.0, 122.5, 115.9, 114.9, 112.2, 61.3 (2C), 58.3, 55.1, 40.1, 38.6, 23.8, 14.0 (2C).

**HRMS (ESI):** Calcd for \([\text{C}_{19}\text{H}_{26}\text{O}_5], \text{M+Na}^+\]: 357.1672, measured: 357.1679.

Diethyl-2-(2-chlorobenzyl)-2-(2-methylallyl)malonate (1m). 1m can't be completely separated from the reaction mixture. 202.9 mg, 60 % yield. Colourless oil. \(^1\text{H-NMR}\) (600 MHz, CDCl\(_3\)): δ = 7.34 - 7.35 (m, 1H), 7.30 - 7.32 (m, 1H), 7.12 - 7.17 (m, 2H), 4.89 (s, 1H), 4.77 (s, 1H), 4.07 - 4.18 (m, 4H), 3.50 (s, 2H), 2.73 (s, 2H), 1.72 (s, 3H), 1.17 (t, J = 7.2 Hz, 6H). \(^{13}\text{C-NMR}\) (151 MHz, CDCl\(_3\)): δ = 171.1 (2C), 141.1, 135.2, 134.9, 131.8, 129.4, 128.0, 126.4, 114.6, 61.4 (2C), 57.7, 41.4, 35.5, 23.9, 13.8 (2C).

**HRMS (ESI):** Calcd for \([\text{C}_{18}\text{H}_{23}\text{ClO}_4], \text{M+Na}^+\]: 361.1177, measured: 361.1174.

Diethyl-2-(2-methylallyl)-2-(naphthalen-1-ylmethyl)malonate (1n). 301.3 mg, 85% yield. Colourless oil. \(^1\text{H-NMR}\) (600 MHz, CDCl\(_3\)): δ = 8.07 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 9.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.40 - 7.46 (m, 3H), 7.36 (t, J = 8.4 Hz, 1H), 4.94
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(2, 1H), 3.96 - 4.02 (m, 2H), 3.87 - 3.93 (m, 2H), 3.83 (s, 2H), 2.76 (s, 2H), 1.73 (s, 3H), 1.05 (t, J = 7.2 Hz, 6H). 

$^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 171.4 (2C), 141.4, 133.8, 133.2, 132.9, 128.7, 128.1, 127.5, 125.6, 125.4, 125.1, 124.0, 114.3, 61.3 (2C), 58.3, 41.1, 34.2, 24.0, 13.7 (2C).


Synthesis of substrates 1o-1q:


Substrates 3a-3e were synthesized according to the literature, and the NMR spectroscopy were consistented with reported data.[2]


Substrates 5a-5i were synthesized according to the literature, and the NMR spectroscopy were consistented with reported data.[4,5,6,7] Substrates 5d-5f were new compounds synthesized according to the literature.[5] The NMR spectroscopy were as follow:

Synthesis of substrates 5a-5c:

Synthesis of substrate 5d-5g (taking 5d as an example):

A solution of p-toluidine (0.54g, 5.0 mmol) and di-tert-butyl dicarbonate (1.28 mL, 6.0 mmol) in 20 mL of dry THF was stirred for 12 h at room temperature. The crude mixture was concentrated under reduced pressure, and purified by silica column chromatography (eluents: petroleum ether/EtOAc = 9/1, v/v) to give 0.88 g (85%) of tert-butyl p-tolylcarbamate as a white solid. The yield and NMR spectroscopy were consistented with reported data.[5]

A solution of tert-butyl p-tolylcarbamate (0.83 g, 4.0 mmol) and NaH (0.19 g, 60%, 4.8 mmol) in 15 mL of dry THF was stirred at 0 ºC under N$_2$ for 15 min. 3-Bromo-2-methylprop-1-ene (0.60 mL, 6.0 mmol) was added and the reaction was stirred at room temperature for 12 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were rinsed with brine, dried over anhydrous MgSO$_4$ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluents: petroleum ether/EtOAc = 15/1, v/v) to give 5d as a colourless oil.
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Tert-butyl (2-methylallyl)(p-tolyl)carbamate (5d). 835.7 mg, 80 % yield. Colourless oil. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.10 - 7.13$ (m, 4H), 4.83 (s, 1H), 4.80 (s, 1H), 4.14 (s, 2H), 2.31 (s, 3H), 1.74 (s, 3H), 1.44 (s, 9H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 154.8, 141.7, 140.3, 135.2, 129.1$ (2C), 125.9 (2C), 111.3, 80.2, 55.9, 28.3 (3C), 20.9, 20.1. HRMS (ESI): Calcd for [C$_{16}$H$_{23}$NO$_2$, M+Na]$^+$: 284.1621, measured: 284.1630.

Tert-butyl (4-chlorophenyl)(2-methylallyl)carbamate (5e). 865.8 mg, 77 % yield. Colourless oil. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.25 - 7.26$ (m, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 4.86 (s, 1H), 4.78 (s, 1H), 4.14 (s, 2H), 1.74 (s, 3H), 1.44 (s, 9H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 154.4, 141.4, 130.9, 128.6$ (2C) 127.2, 111.6, 80.7, 55.7, 28.2 (3C), 20.1. HRMS (ESI): Calcd for [C$_{15}$H$_{20}$ClNO$_2$, M+Na]$^+$: 304.1075, measured: 304.1084.

Tert-butyl (4-methoxyphenyl)(2-methylallyl)carbamate (5f). 909.1 mg, 82 % yield. Colourless oil. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta = 7.13$ (s, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 4.83 (s, 1H), 4.79 (s, 1H), 4.12 (s, 2H), 3.78 (s, 3H), 1.75 (s, 3H), 1.43 (s, 9H). $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta = 157.3, 155.0, 141.7, 135.8, 127.5$ (2C), 113.7 (2C), 111.6, 80.1, 56.2, 55.4, 28.3 (3C), 20.1. HRMS (ESI): Calcd for [C$_{16}$H$_{23}$NO$_3$, M+Na]$^+$: 300.1570, measured: 300.1578.

Synthesis of substrate 5h:[6]

\[
\begin{array}{c}
\text{Br} \quad \text{MeC} \quad \text{N} \\
\text{Ph} \quad \text{Ph} \\
\end{array}
\]

\[
\text{K$_2$CO$_3$, TBAI, MeCN, reflux, 24h}
\]

Synthesis of substrate 5i:[7]

\[
\begin{array}{c}
\text{Br} \quad \text{MeC} \quad \text{N} \\
\text{Bz} \quad \\
\end{array}
\]

IV. Synthetic Procedures and Analytical Data

Typical procedures for catalyst-free intramolecular aryltrifluoromethylation of unactivated alkenes (taking 1a as an example):
To a dried polytetrafluoroethene (PTFE) sealed pressure tube was added 1a (91.3 mg, 0.3 mmol), PhICl (138.6 mg, 4.5 mmol) and anhydrous DMF (3.0 mL) in sequence under N\textsubscript{2}. After the reaction mixture was stirred at 60 °C for 12 h, PhCF\textsubscript{3} (30 μL, 0.2436 mmol) was added as the internal standard and the NMR yield of 2a was calculated from $^{19}$F-NMR integrals. Then the mixture was washed with water and brine, extracted by CH\textsubscript{2}Cl\textsubscript{2}. The combined organic phase was dried over anhydrous MgSO\textsubscript{4} and concentrated under reduce pressure. The residue was purified by silica column chromatography (eluent: petroleum ether/EtOAc = 20/1 to 15/1, v/v) to give 2a as a yellow oil.[8]

### Analytical data for compounds 2a-2o:

**Diethyl-4-methyl-4-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (2a).** 100.5 mg, 90% yield. Colourless oil.[8]

$^{1}$H-NMR (600 MHz, CDCl\textsubscript{3}): $\delta$ = 7.24 (d, $J$ = 7.8 Hz, 1H), 7.19 - 7.22 (m, 1H), 7.14 - 7.17 (m, 2H), 4.06 - 4.24 (m, 4H), 3.32 (d, $J$ = 16.2 Hz, 1H), 3.32 (d, $J$ = 16.2 Hz, 1H), 2.65 (d, $J$ = 15.0 Hz, 1H), 2.47 - 2.56 (m, 1H), 2.34 - 2.44 (m, 2H), 1.42 (s, 3H), 1.26 (t, $J$ = 7.2 Hz, 3H), 1.19 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C-NMR (151 MHz, CDCl\textsubscript{3}): $\delta$ = 171.7, 171.2, 140.8, 133.2, 129.1, 126.9, 126.8, 126.4 (q, $J$ = 277.5 Hz), 126.0, 61.7, 61.5, 52.5, 45.9 (q, $J$ = 25.7 Hz), 39.7, 35.2, 35.1, 29.6 (q, $J$ = 0.9 Hz), 13.9, 13.9.

$^{19}$F-NMR (565 MHz, CDCl\textsubscript{3}): $\delta$ = -58.8 (t, $J$ = 11.3 Hz). HRMS (ESI): Calcd for [C\textsubscript{19}H\textsubscript{23}F\textsubscript{3}O\textsubscript{4}, M+Na\textsuperscript{+}]: 395.1441, measured: 395.1421.

**Diethyl-4-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (2b).** 91.3 mg, 85% yield. Yellow oil.[8]

$^{1}$H-NMR (600 MHz, CDCl\textsubscript{3}): $\delta$ = 7.13 - 7.21 (m, 4H), 4.20 - 4.24 (m, 2H), 4.06 - 4.15 (m, 2H), 3.32 - 3.37 (m, 2H), 3.19 (d, $J$ = 15.6 Hz, 1H), 2.84 (dd, $J$ = 13.8 Hz, 6.0 Hz, 1H), 2.72 - 2.79 (m, 1H), 2.23 - 2.33 (m, 1H), 1.97 (dd, $J$ = 13.8 Hz, 10.2 Hz, 1H), 1.27 (t, $J$ = 7.2 Hz, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C-NMR (151 MHz, CDCl\textsubscript{3}): $\delta$ = 171.5, 170.3, 136.2, 134.1, 129.3, 127.3 (q, $J$ = 277.7 Hz), 126.9, 126.8, 126.7, 61.8, 61.4, 53.7, 40.9 (q, $J$ = 27.3 Hz), 35.2, 34.8, 30.5 (q, $J$ = 2.6 Hz), 14.0, 13.9.$^{19}$F-NMR (565 MHz, CDCl\textsubscript{3}): $\delta$ = -63.5 (t, $J$ = 10.7 Hz). HRMS (ESI): Calcd for [C\textsubscript{18}H\textsubscript{21}F\textsubscript{3}O\textsubscript{4}, M+Na\textsuperscript{+}]: 381.1284, measured: 381.1294.

**Diethyl 6-bromo-4-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (2k).** 65.6 mg, 50% yield. Yellow oil.[8]

$^{1}$H-NMR (600 MHz, CDCl\textsubscript{3}): $\delta$ = 7.28 - 7.30 (m, 2H), 7.02 (d, $J$ = 7.8 Hz, 1H), 4.22 (q, $J$ = 7.2 Hz, 2H), 4.07 - 4.17 (m, 2H), 3.28 - 3.32 (m, 2H), 3.19 (d, $J$ = 15.6 Hz, 1H), 2.84 (dd, $J$ = 13.8 Hz, 6.0 Hz, 1H), 2.72 - 2.79 (m, 1H), 2.23 - 2.33 (m, 1H), 1.97 (dd, $J$ = 13.8 Hz, 10.2 Hz, 1H), 1.27 (t, $J$ = 7.2 Hz, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H), 1.05 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C-NMR (151 MHz, CDCl\textsubscript{3}): $\delta$ = 171.5, 170.3, 136.2, 134.1, 129.3, 127.3 (q, $J$ = 277.7 Hz), 126.9, 126.8, 126.7, 61.8, 61.4, 53.7, 40.9 (q, $J$ = 27.3 Hz), 35.2, 34.8, 30.5 (q, $J$ = 2.6 Hz), 14.0, 13.9.$^{19}$F-NMR (565 MHz, CDCl\textsubscript{3}): $\delta$ = -63.5 (t, $J$ = 10.7 Hz). HRMS (ESI): Calcd for [C\textsubscript{18}H\textsubscript{21}F\textsubscript{3}O\textsubscript{4}, M+Na\textsuperscript{+}]: 381.1284, measured: 381.1294.
(m, 2H), 3.11 (d, J = 16.2 Hz, 7.2 Hz, 1H), 2.68 - 2.76 (m, 1H), 2.24 - 2.33 (m, 1H), 1.95 (dd, J = 13.2 Hz, 3.0 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H). ¹³C-NMR (151 MHz, CDCl₃): δ = 171.2, 170.1, 138.5, 133.2, 130.9 129.9, 129.8, 126.6 (q, J = 277.8 Hz), 120.5, 61.9, 61.6, 53.4, 40.6 (q, J = 27.6 Hz), 34.7, 34.4, 30.5 (q, J = 2.3 Hz), 14.0, 13.9. ¹⁹F-NMR (565 MHz, CDCl₃): δ = -63.4 (t, J = 10.7 Hz). HRMS (ESI): Calcd for [C₁₈H₂₀BrF₃O₄, M+Na]⁺: 459.0389, measured: 459.0381.

¹-(2,2,2-Trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (2m). 2m was volatile and difficult to be isolated from the reaction mixture. ¹⁹F-NMR yield: 80%. Colorless oil. Its NMR spectroscopy were consistented with the literature data.¹⁹¹H-NMR (600 MHz, CDCl₃): δ = 6.99 - 7.06 (m, 4H), 3.12 - 3.14 (m, 1H), 2.64 - 2.74 (m, 2H), 2.24 - 2.43 (m, 2H), 1.84 - 1.90 (m, 1H), 1.77 - 1.83 (m, 1H), 1.70 - 1.76 (m, 2H). ¹⁹F-NMR (565 MHz, CDCl₃): δ = -63.8 (t, J = 11.3 Hz).

7-Fluoro-¹-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (2n). 2n was volatile and difficult to be isolated from the reaction mixture. ¹⁹F-NMR yield: 71%. Colorless oil. Its NMR spectroscopy were consistented with the literature data.¹⁹¹H-NMR (600 MHz, CDCl₃): δ = 7.02 - 7.04 (m, 1H), 6.82 - 6.85 (m, 2H), 3.16 - 3.20 (m, 1H), 2.67 - 2.78 (m, 2H), 2.33 - 2.48 (m, 2H), 1.92 - 1.97 (m, 1H), 1.77 - 1.87 (m, 3H). ¹³C-NMR (151 MHz, CDCl₃): δ = 161.1 (d, J = 343.7 Hz), 140.4, 132.6, 130.7 (d, J = 7.7 Hz), 126.8 (q, J = 277.7 Hz), 114.7 (d, J = 20.8 Hz), 113.5 (d, J = 21.1 Hz), 40.7 (q, J = 27.0 Hz), 32.4, 28.6, 27.5, 19.1. ¹⁹F-NMR (565 MHz, CDCl₃): δ = -63.9 (t, J = 10.8 Hz, 3F), -117.0 (q, J = 7.1 Hz, 1F).

7-Methoxy-¹-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (2o). 2o was volatile and difficult to be isolated from the reaction mixture. ¹⁹F-NMR yield: 89%. Colorless oil. Its NMR spectroscopy were consistented with the literature data.¹⁹¹H-NMR (600 MHz, CDCl₃): δ = 6.82 - 6.86 (m, 1H), 6.72 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.66 (d, J = 2.4 Hz, 1H), 3.78 (s, 3H), 3.15 - 3.19 (m, 1H), 2.65 - 2.75 (m, 2H), 2.32 - 2.50 (m, 2H), 1.90 - 1.96 (m, 1H), 1.83 - 1.87 (m, 1H), 1.73 - 1.80 (m, 2H). ¹⁹F-NMR (565 MHz, CDCl₃): δ = -63.9 (t, J = 12.2 Hz).
**Supporting Information**

Analytical data for compounds 4a-4f:

![Diagram of 4a](image)

**Diethyl-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-indene-1,1-dicarboxylate (4a).** 69.2 mg, 67% yield. Colourless oil. **$^1$H-NMR** (600 MHz, CDCl$_3$): $\delta = 7.61$ (d, $J = 7.2$ Hz, 1H), 7.30 - 7.37 (m, 2H), 7.20 (d, $J = 7.2$ Hz, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 4.14 - 4.24 (m, 2H), 3.60 - 3.65 (m, 1H), 3.49 - 3.54 (m, 1H), 3.09 (dd, $J = 13.8$ Hz, 7.8 Hz, 1H), 2.66 - 2.75 (m, 1H), 2.45 (dd, $J = 13.2$ Hz, 7.2 Hz, 1H), 2.23 - 2.33 (m, 1H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 3H). **$^{13}$C-NMR** (151 MHz, CDCl$_3$): $\delta = 170.5$, 170.1, 144.8, 139.0, 129.0, 127.7, 127.0, 126.7 (q, $J = 275.6$ Hz), 123.4, 64.8, 61.9, 61.8, 40.6, 39.2 (q, $J = 27.8$ Hz). **$^{19}$F-NMR** (565 MHz, CDCl$_3$): $\delta = -64.4$ (t, $J = 10.7$ Hz). HRMS (ESI): Calcd for [C$_{17}$H$_{21}$F$_3$O$_4$, M+Na]$^+$: 367.1128, measured: 367.1135.

![Diagram of 4c](image)

**Diethyl-5-methoxy-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-indene-1,1-dicarboxylate (4c).** 4c can’t be completely separated from 3c. **$^{19}$F-NMR yield:** 72%. Colorless oil. **$^1$H-NMR** (600 MHz, CDCl$_3$): $\delta = 7.49$ (d, $J = 9.0$ Hz, 1H), 6.85 - 6.87 (m, 1H), 4.22 - 4.27 (m, 2H), 4.15 - 4.21 (m, 2H), 3.81 (s, 3H), 3.55 - 3.60 (m, 1H), 3.07 (dd, $J = 13.8$ Hz, 7.8 Hz, 1H), 2.62 - 2.71 (m, 1H), 2.45 (dd, $J = 13.8$ Hz, 7.8 Hz, 1H), 2.23 - 2.33 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 3H). **$^{13}$C-NMR** (151 MHz, CDCl$_3$): $\delta = 170.7$, 170.4, 160.7, 146.4, 131.0, 128.5 (q, $J = 277.2$ Hz), 127.7, 113.9, 108.6, 64.0, 61.8, 61.8, 55.5, 40.9, 39.1 (q, $J = 28.7$ Hz), 37.0 (q, $J = 2.7$ Hz). **$^{19}$F-NMR** (565 MHz, CDCl$_3$): $\delta = -64.4$ (t, $J = 11.3$ Hz). HRMS (ESI): Calcd for [C$_{18}$H$_{23}$F$_3$O$_5$, M+Na]$^+$: 367.1128, measured: 367.1135.

![Diagram of 4e](image)

**Diethyl-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-cyclopenta[a]naphthalene-1,1-dicarboxylate (4e).** 76.9 mg, 65% yield. Yellow oil. **$^1$H-NMR** (600 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.53 (d, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 7.2$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 4.26 - 4.30 (m, 1H), 4.15 - 4.20 (m, 1H), 3.46 - 3.50 (m, 1H), 3.10 (dd, $J = 13.2$ Hz, 3.6 Hz, 1H), 2.97 - 3.06 (m, 1H), 2.51 (t, $J = 12.0$ Hz, 1H), 2.37 - 2.46 (m, 1H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H). **$^{13}$C-NMR** (151 MHz, CDCl$_3$): $\delta = 171.3$, 170.2, 143.7, 134.0, 130.2, 128.8, 128.6, 127.6, 127.0 (q, $J = 275.7$ Hz), 126.3, 125.5, 125.3, 122.3, 62.1, 62.1, 59.7, 38.1 (q, $J = 27.6$ Hz), 34.9, 30.4 (q, $J = 2.4$ Hz), 14.0, 13.9. **$^{19}$F-NMR** (565 MHz, CDCl$_3$): $\delta = -62.8$ (t, $J = 11.3$ Hz). HRMS (ESI): Calcd for [C$_{21}$H$_{25}$F$_3$O$_4$, M+Na]$^+$: 417.1284, measured: 417.1291.
**Supporting Information**

*Tert-butyl-5-methyl-3-(2,2,2-trifluoroethyl)indoline-1-carboxylate (6g)*. 60.5 mg, 64% yield. Colorless oil. ¹H-NMR (600 MHz, CDCl₃): δ = 7.36 - 7.74 (br. 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.94 (s, 1H), 4.20 (s, 1H), 3.74 (s, 1H), 3.57 - 3.61 (m, 1H), 2.56 - 2.65 (m, 1H), 2.26 - 2.35 (m, 4H), 1.56 (s, 9H).

13C-NMR (151 MHz, CDCl₃): δ = 152.2, 132.1, 129.0, 127.1, 126.5 (q, J = 277.5 Hz), 124.3, 124.2, 114.7, 81.4, 65.9, 53.8, 39.2 (q, J = 27.6 Hz), 28.5 (3C), 20.9. ¹⁹F-NMR (470 MHz, CDCl₃): δ = -64.8 (t, J = 11.3 Hz). HRMS (ESI): Calcd for [C₁₆H₂₀F₃NO₂, M+Na]⁺: 338.1338, measured: 338.1346.

**V. Mechanistic Study**

**Experimental Procedures:** To a dried polytetrafluoroethene (PTFE) sealed pressure tube was added alkene 1h (67.1 mg, 0.2 mmol), PhICF₃Cl (92.4 mg, 0.3 mmol), TEMPO/BHT and anhydrous DMF (2 mL) in sequence under N₂. The reaction mixture was stirred at 60 °C for 12 h, monitored by ¹⁹F NMR using PhCF₃ as the internal standard.

<table>
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<th>Entry</th>
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<th>Yield of 2h [%]</th>
<th>TEMPO-CF₃ [%]</th>
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</thead>
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<td>--</td>
<td>91</td>
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</tr>
<tr>
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<td>0</td>
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<tr>
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<td>BHT</td>
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<td>90</td>
<td>--</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1h (0.2 mmol), PhICF₃Cl (0.30 mmol), DMF (2 mL)

[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

**Plausible mechanistic:**

Based on the above experimental results (Table S7), an ionic process is proposed as shown in Scheme SI. The unactivation of the alkene double bond of 1h by [PhICF₃⁺] affords iodonium complex I. Then exo-cyclization occurs via an attack of the aryl group affording...
cyclic intermediate II. Finally, the deprotonation of II gives trifluoromethylated product 2h along with the elimination of PhI.

VI. References


VIII. NMR Spectra
1. NMR Spectra of New Substrates
1H-NMR Spectra of 1c
$\text{SUPPORTING INFORMATION}$

$\text{C-NMR Spectra of 1c}$

$\text{H-NMR Spectra of 1e}$
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 1e

$^1$H-NMR Spectra of 1f
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 1g

$^1$H-NMR Spectra of 1h
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 1h

$^1$H-NMR Spectra of 1i
SUPPORTING INFORMATION

$^1$C-NMR Spectra of 1l

$^1$H-NMR Spectra of 1m
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of $1m$

$^1$H-NMR Spectra of $1n$
$^{13}$C-NMR Spectra of 1n

$^1$H-NMR Spectra of 5d
$^{13}$C-NMR Spectra of 5d

$^1$H-NMR Spectra of 5e
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 5e

$^1$H-NMR Spectra of 5f
2. NMR Spectra of Products

1H-NMR Spectra of 2a
$^{13}$C-NMR Spectra of 2a

$^{19}$F-NMR Spectra of 2a
**1H-NMR Spectra of 2b**

**13C-NMR Spectra of 2b**
**$^1$H-NMR Spectra of 2b**

**$^{19}$F-NMR Spectra of 2c**
$^{13}$C-NMR Spectra of 2c

$^{19}$F-NMR Spectra of 2c
**Supporting Information**

### 19F-NMR Spectra of 2d

- Peaks at 63.176 ppm
- Peaks at 63.195 ppm
- Peaks at 63.215 ppm

### 1H-NMR Spectra of 2e
SUPPORTING INFORMATION

$^{19}$F-NMR Spectra of 2e

$^{13}$C-NMR Spectra of 2e
SUPPORTING INFORMATION

$^{19}$F-NMR Spectra of 2f

$^1$H-NMR Spectra of 2g
**Supporting Information**

$^1$H-NMR Spectra of 2h

$^13$C-NMR Spectra of 2h
**SUPPORTING INFORMATION**

**19F-NMR Spectra of 2h**

**1H-NMR Spectra of 2i**
Supporting Information

$^{1}H$-NMR Spectra of 2j

$^{13}C$-NMR Spectra of 2j
$^{19}$F-NMR Spectra of 2j

$^1$H-NMR Spectra of 2k
$^{13}$C-NMR Spectra of 2k

$^{19}$F-NMR Spectra of 2k
**SUPPORTING INFORMATION**

**1H-NMR Spectra of 2l**

**13C-NMR Spectra of 2l**
**Supporting Information**

$^1$H-NMR Spectra of 2l

$^1$H-NMR Spectra of 2l’
$^{13}$C-NMR Spectra of 2l'

$^{19}$F-NMR Spectra of 2l'
**SUPPORTING INFORMATION**

\[ \text{H-NMR Spectra of 2m} \]

\[ \text{C-NMR Spectra of 2m} \]
**SUPPORTING INFORMATION**

$^{19}$F-NMR Spectra of Zm

$^{1}$H-NMR Spectra of Zn
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 2n

$^{19}$F-NMR Spectra of 2n
**Supporting Information**

**$^1$H-NMR Spectra of 4a**

**$^{13}$C-NMR Spectra of 4a**
SUPPORTING INFORMATION

{\H H-NMR Spectra of 4b}

{\H H-NMR Spectra of 4b}
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 4b

$^{19}$F-NMR Spectra of 4b
SUPPORTING INFORMATION

$^1$H-NMR Spectra of 4c

$^{13}$C-NMR Spectra of 4c
**SUPPORTING INFORMATION**

### 19F-NMR Spectra of 4c

![19F-NMR Spectra of 4c](image)

### 1H-NMR Spectra of 4d

![1H-NMR Spectra of 4d](image)
SUPPORTING INFORMATION

\(^{13}\)C-NMR Spectra of 4d

\(^{19}\)F-NMR Spectra of 4d
$^1$H-NMR Spectra of 4e

$^{13}$C-NMR Spectra of 4e
**SUPPORTING INFORMATION**

**$^{19}$F-NMR Spectra of 4e**

**$^1$H-NMR Spectra of 6a**
**SUPPORTING INFORMATION**

\[ \text{\[^{13}C\text{-NMR Spectra of 6a}} \]

\[ \text{\[^{19}F\text{-NMR Spectra of 6a}} \]

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**S56**
**SUPPORTING INFORMATION**

**H-NMR Spectra of 6b**

![H-NMR Spectra of 6b](image)

**C-NMR Spectra of 6b**

![C-NMR Spectra of 6b](image)
**SUPPORTING INFORMATION**

**$^{19}$F-NMR Spectra of 6b**

![F-NMR Spectra of 6b](image)

**$^1$H-NMR Spectra of 6c**

![H-NMR Spectra of 6c](image)
SUPPORTING INFORMATION

13C-NMR Spectra of 6c

19F-NMR Spectra of 6c
SUPPORTING INFORMATION

$^{1}$$H$-NMR Spectra of 6d

$^{13}$$C$-NMR Spectra of 6d
SUPPORTING INFORMATION

\[19F\text{-NMR Spectra of 6d}\]

\[1^1H\text{-NMR Spectra of 6e}\]
SUPPORTING INFORMATION

$^{13}$C-NMR Spectra of 6e

$^{19}$F-NMR Spectra of 6e
H-NMR Spectra of 6f

13C-NMR Spectra of 6f
$^{19}$F-NMR Spectra of 6f

$^1$H-NMR Spectra of 6g
$^{13}$C-NMR Spectra of 6g

$^{19}$F-NMR Spectra of 6g
SUPPORTING INFORMATION

$^1$H-NMR Spectra of 6h

$^{13}$C-NMR Spectra of 6h
**SUPPORTING INFORMATION**

**19F-NMR Spectra of 6h**

-60.229
-60.255
-60.282

**1H-NMR Spectra of 6i**
$^1$H-NMR Spectra of 6i

$^{13}$C-NMR Spectra of 6i

$^1$H-NMR Spectra of 6i

$^{13}$C-NMR Spectra of 6i