Supporting Information

Radical Alkynyl trifluoromethylation of Alkenes Initiated by An Electron-Donor-Acceptor Complex

Heng Jiang, Yanyan He, Yuanzheng Cheng, and Shouyun Yu*

State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.

E-mail: yushouyun@nju.edu.cn
# Table of Contents

1. General Methods ...........................................................................................................S3
2. Structure of Alkenes .................................................................................................S4
3. General Procedure for the Preparation of Acetylenic Triflones \((2a-2n)\) ..................S6
4. Conditions Optimization and Control Experiments ..................................................S8
5. General Procedures A-D and Scale up Reaction .......................................................S10
6. Data of Compounds .................................................................................................S12
7. Synthetic Applications ...............................................................................................S54
8. Mechanistic Studies .................................................................................................S57
9. Reference ....................................................................................................................S59
10. NMR Spectra for All Compounds ............................................................................S60
1. General Methods.

All commercially available reagents were purchased from Sigma-Aldrich, J&K, Alfa Aesar, TCI, Adamas or Acros in the highest purity grade and used without further purification. Extra pure solvents including EtOAc (99.9%) and Dioxane (99.8%) were purchased from J&K and used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300 – 400 Mesh) using a forced flow of 0.5 – 1.0 bar. $^1$H NMR (400 MHz), $^{13}$C NMR (100MHz) and $^{19}$F (376MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm$^{-1}$).
2. Structure of Alkenes
3. General Procedure for the Preparation of Acetylenic Triflones (2a-2n)

Tert-butyldimethyl(((trifluoromethyl)sulfonyl)ethynyl)silane (2a) was prepared according to the literature procedure. To a stirring solution of tert-butyl(ethynyl)dimethylsilane (3.09 g, 22.0 mmol, 1.1 equiv) in dry Et₂O (100 mL) was added n-BuLi (13.8 mL, 1.6 M in hexanes, 1.1 equiv) over 30 min at -78 °C under N₂. After being stirred for 0.5 h at -78 °C, the corresponding lithium acetylide was slowly transferred via a syringe to a solution of triflic anhydride (3.36 mL, 20 mmol, 1.0 equiv) in dry Et₂O (50 mL) at -78 °C. The reaction was stirred at -78 °C for 30 min before being quenched with water. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by fast flash chromatography (petrol ether/EtOAc = 100:0 to 99:1) to afford 2a as a pale yellow oil (3.54 g, 13 mmol) in 65% yield. H NMR (400 MHz, CDCl₃) δ 0.99 (s, 9H), 0.27 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 118.90 (q, J = 323.2 Hz), 111.34, 90.34, 25.71, 16.75, -5.85. ¹⁹F NMR (377 MHz, CDCl₃) δ -79.85. HRMS (ESI) ([M+NH₄]⁺) Calcd. for C₉H₁₉F₃NO₂Si: 290.0852; found: 290.0853.
List of aryl acetylene-derived acetylenic triflones used in this work:

Acetylenic triflones 2b-2m were prepared as the same procedures for 2a from Tf₂O and corresponding alkynes. NMR data are the same as previous reports.²
4. Conditions Optimization and Control Experiments

*Alknyl trifluoromethylation of 1a with silyl alkyne-derived triflone 2a*

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from above</th>
<th>yield (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>96 (92&lt;sup&gt;c&lt;/sup&gt;)</td>
</tr>
<tr>
<td>2</td>
<td>II instead of I</td>
<td>N.D.</td>
</tr>
<tr>
<td>3</td>
<td>III instead of I</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>4&lt;sup&gt;d&lt;/sup&gt;</td>
<td>III instead of I, no NMM</td>
<td>N.D.</td>
</tr>
<tr>
<td>7</td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;N instead of NMM</td>
<td>65</td>
</tr>
<tr>
<td>8</td>
<td>piperidine instead of NMM</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>i-Pr&lt;sub&gt;2&lt;/sub&gt;NH instead of NMM</td>
<td>73</td>
</tr>
<tr>
<td>10&lt;sup&gt;e&lt;/sup&gt;</td>
<td>n-Bu&lt;sub&gt;4&lt;/sub&gt;I instead of NMM</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>11</td>
<td>2.0 mol% I</td>
<td>31</td>
</tr>
<tr>
<td>12</td>
<td>5.0 mol% I</td>
<td>80</td>
</tr>
<tr>
<td>13</td>
<td>no I</td>
<td>N.D.</td>
</tr>
<tr>
<td>14</td>
<td>no NMM</td>
<td>N.D.</td>
</tr>
<tr>
<td>15</td>
<td>under air</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

<sup>a</sup>Standard conditions: 1a (0.2 mmol), 2a (0.24 mmol), Togni’s reagent I (7.5 mol%) and NMM (10 mol%) in dry EtOAc (0.5 mL) at 30 °C for 24 h under N<sub>2</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>c</sup>Isolated yield. <sup>d</sup>60 °C. <sup>e</sup>80 °C.
Alkynyltrifluoromethylation of 1a with phenyl acetylene-derived triflone 2b

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from above</th>
<th>yield (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>90 (89&lt;sup&gt;c&lt;/sup&gt;)</td>
</tr>
<tr>
<td>2</td>
<td>II instead of I</td>
<td>N.D.</td>
</tr>
<tr>
<td>3</td>
<td>III instead of I</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>DMF as solvent</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>MeCN as solvent</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>MeOH as solvent</td>
<td>41</td>
</tr>
<tr>
<td>7</td>
<td>DCM as solvent</td>
<td>82</td>
</tr>
<tr>
<td>8</td>
<td>1,4-Dioxane as solvent</td>
<td>73</td>
</tr>
<tr>
<td>9</td>
<td>DMSO as solvent</td>
<td>N.D.</td>
</tr>
<tr>
<td>10</td>
<td>3 mol% I and 6% NMM</td>
<td>51</td>
</tr>
<tr>
<td>11</td>
<td>2 mol% I and 4% NMM</td>
<td>35</td>
</tr>
<tr>
<td>12</td>
<td>no I</td>
<td>N.D.</td>
</tr>
<tr>
<td>13</td>
<td>no NMM</td>
<td>N.D.</td>
</tr>
<tr>
<td>14</td>
<td>no I and NMM</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 1a (0.24 mmol), 2b (0.2 mmol), Togni’s reagent I (5 mol%) and NMM (10 mol%) in dry EtOAc (0.5 mL) at 30 °C for 24 h under N2. <sup>b</sup>Determined by <sup>1</sup>HNMR analysis using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>c</sup>Isolated yield.
5. General Procedures A-D and scale up reaction

**General Procedure A:** A 10.0 mL microwave tube equipped with magnetic stir bar was charged with alkene 1a (0.2 mmol, 43.1 mg), acetylenic triflone 2a (0.24 mmol, 65.4 mg) and Togni’s reagent (I, 0.015 mmol, 4.8 mg) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). 4-methylmorpholine (NMM, 0.02 mmol, 2.2 μL) and degassed EtOAc (0.5 mL) were added by syringe under N₂. The tube was then sealed with a PTFE lined cap and stirred at 30 °C (oil bath) for 24 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography (petrol ether/EtOAc = 50:1 to 10:1) to give the desired product 3a (77.1 mg, 92%) as a white solid.

**General Procedure B:** A 10.0 mL microwave tube equipped with magnetic stir bar was charged with 4-vinyl-1,1'-biphenyl 1ai (0.2 mmol, 36.1 mg), acetylenic triflone 2a (0.3 mmol, 81.7 mg) and Togni’s reagent (I, 0.02 mmol, 6.4 mg) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). 4-methylmorpholine (NMM, 0.02 mmol, 2.2 μL) and degassed 1,4-dioxane (1.0 mL) were added by syringe under N₂. The tube was then sealed with a PTFE lined cap and stirred at 30 °C (oil bath) for 72 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by preparative TLC (petrol ether as eluent) to give the desired product 3ac (25.6 mg, 33%) as a colorless oil.
**General Procedure C:** A 10.0 mL microwave tube equipped with magnetic stir bar was charged with alkene 1a (0.24 mmol, 51.6 mg), acetylenic triflone 2b (0.2 mmol, 56.2 mg) and Togni’s reagent (I, 0.01 mmol, 3.2 mg) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). 4-methylmorpholine (NMM, 0.02 mmol, 2.2 μL) and degassed EtOAc (0.5 mL) were added by syringe under N₂. The tube was then sealed with a PTFE lined cap and stirred at 30 °C (oil bath) for 24 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography (petrol ether/EtOAc = 50:1 to 10:1) to give the desired product 4a (67.1 mg, 89%) as a colorless oil.

**General Procedure D:** A 10.0 mL microwave tube equipped with magnetic stir bar was charged with acetylenic triflone 2b (0.2 mmol, 46.8 mg) and Togni’s reagent (I, 0.02 mmol, 6.4 mg) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). Styrene 1ag (0.24 mmol, 25.0 mg), 4-methylmorpholine (NMM, 0.02 mmol, 2.2 μL) and degassed 1,4-dioxane (0.5 mL) were added by syringe under N₂. The tube was then sealed with a PTFE lined cap and stirred at 30 °C (oil bath) for 48 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by preparative TLC (petrol ether as eluent) to give the desired product 4t (41.1 mg, 75%) as a colorless oil.

**Scale up Reaction:** A 25 mL round bottom flask equipped with magnetic stir bar was charged
with alkene 1a (2 mmol, 431 mg), acetylenic triflone 2a (24 mmol, 654 mg) and Togni’s reagent (I, 0.15 mmol, 48 mg) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 x 5 min). 4-methylmorpholine (NMM, 0.2 mmol, 22 µL) and degassed EtOAc (5 mL) were added by syringe under N₂. The flask was then sealed and stirred at 30 °C (oil bath) for 24 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography (petrol ether/EtOAc = 50:1 to 10:1) to give the desired product 3a (685 mg, 81%) as a white solid.

6. Data of Compounds

2-(6-(Tert-butyldimethylsilyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (3a): According to General Procedure A, 3a was obtained as a white solid (77.1 mg, 92%) from alkene 1a and acetylenic triflone 2a. ¹H NMR (400 MHz, CDCl₃) δ 1H NMR (400 MHz, CDCl₃) δ 7.86 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 3.72 (t, J = 6.9 Hz, 2H), 2.83 – 2.74 (m, 1H), 2.40 – 2.10 (m, 2H), 2.02 – 1.90 (m, 1H), 1.88 – 1.75 (m, 1H), 1.65 – 1.46 (m, 2H), 0.88 (s, 9H), 0.05 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.34, 133.94, 132.08, 125.99 (q, J = 277.7 Hz), 123.23, 106.62, 85.62, 39.11 (q, J = 27.9 Hz), 37.39, 31.89, 26.43 (q, J = 3.0 Hz), 26.10, 25.96, 16.40, -4.66. ¹⁹F NMR (376 MHz, CDCl₃): δ -64.12. HRMS (ESI) ([M+H]⁺) Calcd. for C₂₂H₂₉F₃NO₂Si: 424.1914; found: 424.1914.
Tert-butyldimethyl(5,5,5-trifluoro-3-phenethylpent-1-yn-1-yl)silane (3b): According to **General Procedure A**, 3b was obtained as a colorless oil (64.5 mg, 95%) from alkene 1b and acetylenic triflone 2a. 1H NMR (400 MHz, CDCl3) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 2.95 – 2.86 (m, 1H), 2.81 – 2.71 (m, 2H), 2.47 – 2.31 (m, 1H), 2.30 – 2.16 (m, 1H), 1.93 – 1.75 (m, 2H), 0.97 (s, 9H), 0.13 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 141.21, 128.50, 128.49, 126.11, 126.06 (q, J = 277.7 Hz), 107.05, 85.69, 39.11 (q, J = 27.8 Hz), 36.50, 33.14, 26.41 (q, J = 2.6 Hz), 26.05, 16.50, -4.54. 19F NMR (376 MHz, CDCl3): δ -63.97. HRMS (ESI) ([M+H]+) Calcd. for C19H28F3Si: 341.1907; found: 341.1906.

7-(Tert-butyldimethylsilyl)-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl 4-bromobenzoate (3c):

According to **General Procedure A**, 3c was obtained as a colorless oil (83.4 mg, 85%) from alkene 1c and acetylenic triflone 2a. 1H NMR (400 MHz, CDCl3) δ 7.83 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 4.27 (t, J = 6.5 Hz, 2H), 2.75 – 2.65 (m, 1H), 2.38 – 2.23 (m, 1H), 2.22 – 2.08 (m, 1H), 1.84 – 1.43 (m, 6H), 0.84 (s, 9H), 0.00 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 165.88, 131.70, 131.09, 129.27, 128.00, 126.07 (q, J = 277.6 Hz), 107.01, 85.29, 65.05, 39.18 (q, J = 27.8 Hz), 34.22, 28.32, 26.75 (q, J = 3.0 Hz), 25.98, 23.50, 16.43, -4.61. 19F NMR (376 MHz, CDCl3): δ -64.05. HRMS (ESI) ([M+H]+) Calcd. for C22H31BrF3O2Si: 491.1223; found: 491.1224.

5-(Tert-butyldimethylsilyl)-3-(2,2,2-trifluoroethyl)pent-4-yn-1-yl thiophene-2-carboxylate (3d): According to **General Procedure A**, 3d was obtained as a colorless oil (58.7 mg, 75%) from alkene 1d and acetylenic triflone 2a. 1H NMR (400 MHz, CDCl3) δ 7.80 (dd, J = 3.7, 1.3 Hz, 1H), 7.56 (dd, J = 5.0, 1.2 Hz, 1H), 7.11 (dd, J = 5.0, 3.8 Hz, 1H), 4.56 – 4.41 (m, 2H), 3.04 – 2.94 (m, 1H), 2.52 – 2.24 (m, 2H), 2.12 – 2.01 (m, 1H), 1.95 – 1.85 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). 13C
NMR (101 MHz, CDCl$_3$) δ 161.99, 133.58, 133.52, 132.50, 127.80, 125.93 (q, $J = 277.6$ Hz), 105.62, 86.28, 62.46, 39.14 (q, $J = 28.1$ Hz), 33.48, 25.98, 24.11 (q, $J = 3.2$ Hz), 16.42, -4.65, -4.66. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.03. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{18}$H$_{26}$F$_3$O$_2$Si: 391.1369; found: 391.1362.

Tert-butyl((7-(tert-butyldimethylsilyl)-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl)oxy)diphenylsilane (3e): According to General Procedure A, 3e was obtained as a colorless oil (101.5 mg, 93%) from alkene 1e and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 – 7.62 (m, 4H), 7.48 – 7.35 (m, 6H), 3.68 (t, $J = 6.0$ Hz, 2H), 2.77 – 2.65 (m, 1H), 2.41 – 2.10 (m, 2H), 1.71 – 1.42 (m, 6H), 1.07 (s, 9H), 0.92 (s, 9H), 0.08 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 135.59, 134.03, 129.56, 127.62, 126.17 (q, $J = 277.8$ Hz), 107.46, 84.87, 63.68, 39.16 (q, $J = 27.7$ Hz), 34.50, 32.14, 26.89, 26.77 (q, $J = 2.7$ Hz), 26.02, 23.25, 19.22, 16.47, -4.57. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.04. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{31}$H$_{46}$F$_3$OSi$_2$: 547.3034; found: 547.3033.

5-(tert-butyldimethylsilyl)-3-(2,2,2-trifluoroethyl)pent-4-yn-1-ol (3f): According to General Procedure A, 3f was obtained as a colorless oil (25.3 mg, 45%) from alkene 1f and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.88 – 3.83 (m, 2H), 3.01 – 2.92 (m, 1H), 2.47 – 2.19 (m, 2H), 1.90 – 1.81 (m, 1H), 1.76 – 1.68 (m, 1H), 0.92 (s, 9H), 0.08 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 125.99 (q, $J = 277.7$ Hz), 106.74, 85.96, 60.51, 39.24 (q, $J = 28.0$ Hz), 37.11, 25.98, 24.00 (q, $J = 2.8$ Hz), 16.42, -4.64. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.03. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{13}$H$_{24}$F$_3$OSi: 281.1543; found: 281.1543.
**benzyl (4-(tert-butyldimethylsilyl)-2-(2,2,2-trifluoroethyl)but-3-yn-1-yl)carbamate (3g):**

According to *General Procedure A*, 3g was obtained as a colorless oil (71.2 mg, 89%) from alkene 1g and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.28 (m, 5H), 5.12 (s, 2H), 5.10 (brs, 1H), 3.53 – 3.36 (m, 1H), 3.33 – 3.24 (m, 1H), 3.03 – 2.88 (m, 1H), 2.40 – 2.19 (m, 2H), 0.92 (s, 9H), 0.09 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.35, 136.27, 128.59, 128.27, 128.12, 125.91 (q, $J = 277.4$ Hz), 104.48, 86.91, 67.02, 44.38, 36.56 (q, $J = 28.6$ Hz), 28.05, 25.97, 16.41, -4.67. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.04. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{20}$H$_{29}$F$_3$NO$_2$Si: 400.1914; found: 400.1913.

**7-(tert-butyldimethylsilyl)-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl (tert-butoxycarbonyl)-L-phenylalaninate (3h):** According to *General Procedure A*, 3h was obtained as a colorless oil (96.8 mg, 87%, d.r. = 1:1) from alkene 1h and acetylenic triflone 2a.

Data of the mixture of diastereoisomers: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.13 (m, 3H), 7.10 – 7.02 (m, 2H), 4.91 (d, $J = 7.4$ Hz, 1H), 4.49 (d, $J = 6.5$ Hz, 1H), 4.10 – 3.92 (m, 2H), 3.00 (s, 2H), 2.63 (s, 1H), 2.36 – 2.03 (m, 2H), 1.63 – 1.39 (m, 6H), 1.34 (s, 9H), 0.84 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.99, 155.07, 136.05, 129.33, 128.53, 127.01, 126.08 (q, $J = 277.4$ Hz), 107.00, 85.26, 79.90, 65.13, 54.48, 39.13 (q, $J = 27.9$ Hz), 38.48, 34.15, 28.30, 28.06, 26.66 (q, $J = 2.9$ Hz), 26.00, 23.26, 16.47, -4.59. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.06. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{29}$H$_{45}$F$_3$NO$_4$Si: 556.3064; found: 556.3063.
(3-(2-bromoethyl)-5,5,5-trifluoropent-1-yn-1-yl)(tert-butyl)dimethylsilane (3i): According to **General Procedure A**, 3i was obtained as a colorless oil (63 mg, 92%) from alkene 1i and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.62 – 3.53 (m, 2H), 3.08 – 2.99 (m, 1H), 2.49 – 2.33 (m, 1H), 2.31 – 2.17 (m, 1H), 2.13 – 1.95 (m, 2H), 0.92 (s, 9H), 0.09 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 125.80 (q, $J = 277.9$ Hz), 105.07, 86.51, 38.85 (q, $J = 28.2$ Hz), 37.23, 30.20, 25.97, 25.87 (q, $J = 3.1$ Hz), 16.42, -4.66. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.03. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_{23}$BrF$_3$Si: 343.0699; found: 343.0672.

7-(tert-butyldimethylsilyl)-5-(2,2,2-trifluoroethyl)hept-6-yn-2-one (3j): According to **General Procedure A**, 3j was obtained as a colorless oil (55.2 mg, 90%) from alkene 1j and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.82 – 2.73 (m, 1H), 2.58 (t, $J = 7.4$ Hz), 2.59 (dd, $J = 8.2, 6.2$ Hz), 2.42 – 2.17 (m, 2H), 2.16 (s, 3H), 1.95 – 1.85 (m, 1H), 1.69 – 1.58 (m, 1H), 0.91 (s, 9H), 0.07 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.67, 125.92 (q, $J = 277.5$ Hz), 106.35, 85.98, 40.71, 39.27 (q, $J = 28.0$ Hz), 30.09, 28.26, 26.13 (q, $J = 3.0$ Hz), 25.97, 16.43, -4.62. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.09. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{15}$H$_{26}$F$_3$OSi: 307.1700; found: 307.1699.

7-(tert-butyldimethylsilyl)-N,N-dimethyl-5-(2,2,2-trifluoroethyl)hept-6-ynamide (3k): According to **General Procedure A**, 3k was obtained as a colorless oil (66.5 mg, 95%) from
alkene 1k and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.99 (s, 3H), 2.93 (s, 3H), 2.78 – 2.69 (m, 1H), 2.41 – 2.14 (m, 4H), 1.92 – 1.69 (m, 2H), 1.66 – 1.47 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.44, 126.10 (q, $J = 277.7$ Hz), 107.14, 85.14, 39.06 (q, $J = 27.8$ Hz), 37.22, 35.37, 34.33, 32.77, 26.61 (q, $J = 3.0$ Hz), 25.98, 22.35, 16.43, -4.60, -4.61. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.09. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{17}$H$_{31}$F$_3$NOSi: 350.2122; found: 350.2123.

6-(tert-butyldimethylsilyl)-4-(2,2,2-trifluoroethyl)hex-5-ynal (3l): According to General Procedure A, 3l was obtained as a colorless oil (42.2 mg, 72%) from alkene 1l and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.82 (t, $J = 1.0$ Hz, 1H), 2.85 – 2.77 (m, 1H), 2.76 – 2.61 (m, 2H), 2.45 – 2.31 (m, 1H), 2.29 – 2.16 (m, 1H), 2.02 – 1.92 (m, 1H), 1.78 – 1.67 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 200.00, 124.85 (q, $J = 277.6$ Hz), 104.97, 85.41, 40.35, 38.21 (q, $J = 28.1$ Hz), 25.79, 25.26 (q, $J = 3.1$ Hz), 24.96, 15.39, -5.68. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.09. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{14}$H$_{24}$F$_3$OSi: 293.1543; found: 293.1544.

ethyl 6-(tert-butyldimethylsilyl)-4-(2,2,2-trifluoroethyl)hex-5-ynoate (3m): According to General Procedure A, 3m was obtained as a colorless oil (59.3 mg, 88%) from alkene 1m and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.14 (q, $J = 7.1$ Hz, 2H), 2.87 – 2.77 (m, 1H), 2.61 – 2.43 (m, 2H), 2.43 – 2.14 (m, 2H), 2.00 – 1.89 (m, 1H), 1.77 – 1.66 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.80, 125.92 (q, $J = 277.6$ Hz), 106.07, 86.04, 60.50, 39.17 (q, $J = 28.0$ Hz), 31.58, 29.62, 26.26 (q, $J = 3.0$ Hz), 25.96, 16.41, 14.16, -4.65. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.12. HRMS (ESI) ([M+H$^+$]) Calcd. for
C_{16}H_{28}F_{3}O_{2}Si: 337.1805; found: 337.1805.

5-(tert-butyldimethylsilyl)-3-(2,2,2-trifluoroethyl)pent-4-yenitrile (3n): According to General Procedure A, 3n was obtained as a colorless oil (42.5 mg, 77%) from alkene 1n and acetylenic triflone 2a. ^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 3.16 – 3.08 (m, 1H), 2.74 – 2.62 (m, 2H), 2.60 – 2.37 (m, 2H), 0.93 (s, 9H), 0.10 (s, 6H). ^13C NMR (101 MHz, CDCl\textsubscript{3}) δ 125.30 (q, J = 277.7 Hz), 116.30, 102.52, 88.42, 37.88 (q, J = 28.9 Hz), 25.93, 24.24 (q, J = 3.1 Hz), 23.61, 16.40, -4.83. ^19F NMR (376 MHz, CDCl\textsubscript{3}): δ -64.15. HRMS (ESI) ([M+H]^+) Calcd. for C\textsubscript{13}H\textsubscript{21}F\textsubscript{3}NSi: 276.1390; found: 276.1390.

tert-butyldimethyl(2-(trifluoromethyl)cyclopentyl)ethynyl)silane (3o): According to General Procedure A, 3o was obtained as a colorless oil (32.3 mg, 55%, d.r. > 20:1) from alkene 1o and acetylenic triflone 2a. ^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 2.84 (q, J = 7.5 Hz, 1H), 2.75 – 2.60 (m, 1H), 2.13 – 1.92 (m, 2H), 1.85 – 1.61 (m, 4H), 0.92 (s, 9H), 0.07 (s, 6H). ^13C NMR (101 MHz, CDCl\textsubscript{3}) δ 127.82 (q, J = 278.3 Hz), 108.77, 83.32, 50.16 (q, J = 26.5 Hz), 34.64, 32.04 (q, J = 2.6 Hz), 26.11 (q, J = 2.3 Hz), 26.00, 24.86, 16.53, -4.59, -4.61. ^19F NMR (376 MHz, CDCl\textsubscript{3}): δ -70.98. HRMS (ESI) ([M+HH\textsubscript{4}]^+) Calcd. for C\textsubscript{14}H\textsubscript{27}F\textsubscript{3}NSi: 294.1859; found: 294.1859.
tert-butyldimethyl((2-(trifluoromethyl)cyclohexyl)ethynyl)silane (3p): According to General Procedure A, 3p was obtained as a colorless oil (45.6 mg, 74%, d.r. > 20:1) from alkene 1p and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.47 (td, $J = 10.3$, 3.9 Hz, 1H), 2.21 – 2.02 (m, 2H), 1.82 – 1.68 (m, 2H), 1.52 – 1.40 (m, 1H), 1.37 – 1.20 (m, 3H), 0.92 (s, 9H), 0.07 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 127.13 (q, $J = 280.9$ Hz), 108.09, 84.14, 45.80 (q, $J = 24.7$ Hz), 32.73, 29.61 (q, $J = 2.1$ Hz), 25.99, 24.48, 24.47 (q, $J = 2.9$ Hz), 23.95, 16.47, -4.60, -4.61. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -69.14. HRMS (ESI) ([M+NH$_4$]$^+$) Calcd. for C$_{15}$H$_{29}$F$_3$N$_3$Si: 308.2016; found: 308.2016.

![3q](image)

tert-butyldimethyl((2-(trifluoromethyl)cycloheptyl)ethynyl)silane (3q): According to General Procedure A, 3q was obtained as a colorless oil (56.1 mg, 87%, d.r. > 20:1) from alkene 1q and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.96 (td, $J = 5.7$, 3.4 Hz, 1H), 2.56 – 2.43 (m, 1H), 1.99 – 1.82 (m, 3H), 1.82 – 1.62 (m, 4H), 1.58 – 1.41 (m, 2H), 1.38 – 1.26 (m, 1H), 0.93 (s, 9H), 0.08 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 128.14 (q, $J = 280.9$ Hz), 110.52, 84.12, 49.50 (q, $J = 23.8$ Hz), 31.01, 30.35 (q, $J = 2.2$ Hz), 30.27, 26.83, 26.05, 25.65 (q, $J = 2.6$ Hz), 24.83, 16.60, -4.54, -4.56. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -71.70. HRMS (ESI) ([M+NH$_4$]$^+$) Calcd. for C$_{16}$H$_{31}$F$_3$NSi: 322.2172; found: 322.2172.

![3r](image)

2-(4-(tert-butyldimethylsilyl)-2-methyl-2-(2,2,2-trifluoroethyl)but-3-yn-1-yl)isoindoline-1,3-dione (3r): According to General Procedure A, 3r was obtained as a colorless oil (35.5 mg, 43%) from alkene 1r and acetylenic triflone 2a. Reaction time: 48 h. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.84 (m, 2H), 7.78 – 7.72 (m, 2H), 3.85 (d, $J = 15.6$ Hz), 3.82 (d, $J = 15.6$ Hz), 2.56 (dq, $J =$...
15.2, 11.2 Hz, 1H), 2.31 (dq, J = 15.2, 10.5 Hz, 1H), 0.84 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.35, 134.21, 131.86, 125.85 (q, $J = 278.5$ Hz), 123.50, 107.23, 86.73, 47.42 (q, $J = 1.1$ Hz), 42.92 (q, $J = 27.3$ Hz), 35.26 (q, $J = 1.9$ Hz), 25.89, 25.19 (q, $J = 1.3$ Hz), 16.34, -4.86. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -59.92. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{21}$H$_{27}$F$_3$NO$_2$Si: 410.1758; found: 410.1756.

tert-butyldimethyl(3-(trifluoromethyl)tetrahydrofuran-2-yl)ethynyl)silane (3s): According to General Procedure A, 3s was obtained as a colorless oil (36.3 mg, 65%, d.r. > 20:1) from alkene 1s and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.69 (d, $J = 5.0$ Hz, 1H), 4.00 (dd, $J = 15.5$, 7.7 Hz, 1H), 3.94 (t, $d$, $J = 8.2$, 5.5 Hz, 1H), 3.07 – 2.95 (m, 1H), 2.32 – 2.22 (m, 1H), 2.09 – 2.00 (m, 1H), 0.93 (s, 9H), 0.11 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 125.51 (q, $J = 277.8$ Hz), 102.06, 88.45, 67.42 (q, $J = 3.2$ Hz), 66.36, 49.71 (q, $J = 27.4$ Hz), 25.29 (q, $J = 1.8$ Hz), 24.95, 15.44, -5.86, -5.87. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -70.57. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_{22}$F$_3$OSi: 279.1387; found: 279.1386.

![3s](image)

tert-butyldimethyl(3-(trifluoromethyl)tetrahydro-2H-pyran-2-yl)ethynyl)silane (3t): According to General Procedure A, 3t was obtained as a colorless oil (43.5 mg, 74%, d.r. = 12:1) from alkene 1t and acetylenic triflone 2a. Data of the major diastereoisomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.38 (d, $J = 7.1$ Hz, 1H), 4.06 – 3.99 (m, 1H), 3.50 (ddd, $J = 11.6$, 8.6, 3.2 Hz, 1H), 2.44 – 2.31 (m, 1H), 2.17 – 2.08 (m, 1H), 1.79 – 1.58 (m, 3H), 0.94 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 126.02 (q, $J = 280.1$ Hz), 101.81, 90.53, 65.98, 65.88 (q, $J = 2.7$ Hz), 44.35 (q, $J = 25.1$ Hz), 25.97, 22.99, 21.32 (q, $J = 2.5$ Hz), 16.45, -4.82, -4.83. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.20. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{14}$H$_{24}$F$_3$OSi: 293.1543; found:
(3-butoxy-5,5,5-trifluoropent-1-yn-1-yl)(tert-butyl)dimethylsilane (3u): According to **General Procedure A**, 3u was obtained as a colorless oil (74.2 mg, 95%) from alkene 1u and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.32 (dd, $J=7.7$, 5.2 Hz, 1H), 3.75 (dt, $J=9.1$, 6.4 Hz, 1H), 3.39 (dt, $J=9.1$, 6.5 Hz, 1H), 2.66 – 2.41 (m, 2H), 1.61 – 1.53 (m, 2H), 1.44 – 1.33 (m, 2H), 0.93 (s, 9H), 0.92 (t, $J=7.4$ Hz, 3H), 0.11 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 125.19 (q, $J=277.4$ Hz), 102.89, 89.72, 68.71, 63.92 (q, $J=3.9$ Hz), 40.32 (q, $J=28.1$ Hz), 31.44, 25.95, 19.18, 16.41, 13.73, -4.81, -4.82. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -63.90. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{15}$H$_{28}$F$_3$OSi: 309.1856; found: 309.1857.

tert-butyldimethyl(5,5,5-trifluoro-3-phenoxy pent-1-yn-1-yl)silane (3v): According to **General Procedure A**, 3v was obtained as a colorless oil (59.9 mg, 91%) from alkene 1v and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.27 (m, 2H), 7.07 – 6.99 (m, 3H), 5.02 (dd, $J=7.8$, 5.0 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.79 – 2.65 (m, 1H), 0.88 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.91, 129.36, 124.97 (q, $J=277.3$ Hz), 122.13, 116.36, 101.57, 91.70, 63.05 (q, $J=3.9$ Hz), 40.43 (q, $J=28.6$ Hz), 25.88, 16.44, -4.95, -4.97. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -63.86. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{24}$F$_3$OSi: 329.1543; found: 329.1542.
1-(tert-butyldimethylsilyl)-5,5,5-trifluoropent-1-yn-3-yl acetate (3w): According to **General Procedure A**, 3w was obtained as a colorless oil (54.9 mg, 93%) from alkene 1w and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.68 (dd, $J = 7.8, 5.1$ Hz, 1H), 2.74 – 2.52 (m, 2H), 2.09 (s, 3H), 0.92 (s, 9H), 0.10 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.16, 123.64 (q, $J = 277.3$ Hz), 99.41, 89.38, 56.89 (q, $J = 3.8$ Hz), 38.24 (q, $J = 28.8$ Hz), 24.89, 19.72, 15.40, -5.97. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.07. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_{22}$F$_3$O$_2$Si: 295.1336; found: 295.1335.

1-(tert-butyldimethylsilyl)-5,5,5-trifluoropent-1-yn-3-yl benzoate (3x): According to **General Procedure A**, 3x was obtained as a colorless oil (65 mg, 91%) from alkene 1x and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 – 8.04 (m, 2H), 7.62 – 7.56 (m, 1H), 7.50 – 7.43 (m, 2H), 5.93 (dd, $J = 7.9, 4.9$ Hz, 1H), 2.92 – 2.67 (m, 2H), 0.93 (s, 9H), 0.11 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.84, 133.45, 129.88, 129.32, 128.48, 124.75 (q, $J = 277.7$ Hz), 100.36, 90.74, 58.58 (q, $J = 3.8$ Hz), 39.39 (q, $J = 28.9$ Hz), 25.93, 16.44, -4.94. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -63.77. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{18}$H$_{24}$F$_3$O$_2$Si: 357.1492; found: 357.1491.

benzyl benzyl(1-(tert-butyldimethylsilyl)-5,5,5-trifluoromethylpent-1-yn-3-yl)carbamate (3y): According to **General Procedure A**, 3y was obtained as a colorless oil (85.3 mg, 87%) from alkene 1y and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.21 (m, 10H), 5.20 (d,
$J = 12.5 \text{ Hz}, \ 1\text{H}), \ 5.14 \ (d, J = 12.5 \text{ Hz}, \ 1\text{H}), \ 5.02 \ (d, J = 16.7 \text{ Hz}, \ 1\text{H}), \ 4.90 \ (d, J = 16.7 \text{ Hz}, \ 1\text{H}), \ 3.48 \ (d, J = 21.1, 10.5 \text{ Hz}, \ 1\text{H}), \ 2.73 \ (d, J = 15.1, 10.5 \text{ Hz}, \ 1\text{H}), \ 1.95 \ (s, \ 3\text{H}), \ 0.90 \ (s, \ 9\text{H}), \ 0.07 \ (s, \ 3\text{H}), \ 0.06 \ (s, \ 3\text{H}). \ ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_{3}) \ \delta \ 155.29, \ 139.39, \ 136.31, \ 128.41, \ 128.15, \ 127.95, \ 127.75, \ 126.66, \ 125.49 \ (q, J = 27\ 8.2 \text{ Hz}), \ 105.34, \ 91.34, \ 67.18, \ 55.69 \ (q, J = 2.1 \text{ Hz}), \ 51.28, \ 42.06 \ (q, J = 26.1 \text{ Hz}), \ 29.31, \ 25.88, \ 16.43, \ -5.03, \ -5.05. \ ^{19}\text{F NMR} \ (376 \text{ MHz, CDCl}_{3}): \ \delta \ -61.53. \ \text{HRMS (ESI) ([M+H]^+) Calcd. for C}_{27}\text{H}_{35}\text{F}_{3}\text{NO}_{2}\text{Si: 490.2384; found: 490.2380.} \n
(4R)-3-(1-(tert-butyldimethylsilyl)-5,5,5-trifluoropent-1-yn-3-yl)-4-isoproplyoxazolidin-2-one (3z): According to General Procedure A, 3z was obtained as a colorless oil (67 mg, 92%, d.r. = 10:1) from alkene 1z and acetylenic triflone 2a. Data of the major diastereoisomer: $^{1}\text{H NMR} \ (400 \text{ MHz, CDCl}_{3}) \ \delta \ 4.91 \ (t, J = 7.3 \text{ Hz}, \ 1\text{H}), \ 4.18 \ (t, J = 8.8 \text{ Hz}, \ 1\text{H}), \ 4.12 \ (dd, J = 8.8, 5.1 \text{ Hz}, \ 1\text{H}), \ 3.86 – 3.79 \ (m, \ 1\text{H}), \ 2.93 – 2.66 \ (m, \ 2\text{H}), \ 2.53 – 2.40 \ (m, \ 1\text{H}), \ 0.94 \ (d, J = 6.8 \text{ Hz}, \ 6\text{H}), \ 0.91 \ (s, \ 9\text{H}), \ 0.08 \ (s, \ 6\text{H}). \ ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_{3}) \ \delta \ 157.60, \ 124.89 \ (q, J = 277.4 \text{ Hz}), \ 100.74, \ 89.00, \ 62.98, \ 58.80, \ 40.70 \ (q, J = 3.7 \text{ Hz}), \ 36.87 \ (q, J = 28.5 \text{ Hz}), \ 27.95, \ 25.90, \ 18.02, \ 16.36, \ 14.30, \ -4.95. \ ^{19}\text{F NMR} \ (376 \text{ MHz, CDCl}_{3}): \ \delta \ -64.47. \ \text{HRMS (ESI) ([M+H]^+) Calcd. for C}_{17}\text{H}_{29}\text{F}_{3}\text{NO}_{2}\text{Si: 364.1914; found: 364.1913.} \n
benzyl 2-((tert-butyldimethylsilyl)ethynyl)-3-(trifluoromethyl)pyrrolidine-1-carboxylate (3aa): According to General Procedure A, 3aa was obtained as a colorless oil (55.2 mg, 67%, d.r. > 20:1) from alkene 1aa and acetylenic triflone 2a. $^{1}\text{H NMR} \ (400 \text{ MHz, CDCl}_{3}) \ \delta \ 7.44 – 7.28 \ (m, \ 5\text{H}), \ 5.29 – 5.08 \ (m, \ 2\text{H}), \ 4.74 \ (s, \ 1\text{H}), \ 3.69 \ (s, \ 1\text{H}), \ 3.60 – 3.50 \ (m, \ 1\text{H}), \ 3.01 \ (s, \ 1\text{H}), \ 2.40 – 2.26 \ (m, \ 1\text{H}), \ 2.18 – 2.06 \ (m, \ 1\text{H}), \ 0.90 \ (s, \ 9\text{H}), \ 0.08 \ (s, \ 6\text{H}). \ ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_{3}) \ \delta \ 153.94, \ 136.45, \ 128.47, \ 127.98, \ 127.64, \ 126.32 \ (q, J = 278.8 \text{ Hz}), \ 103.49, \ 86.81, \ 67.30, \ 50.83 \ (q,
$J = 28.9$ Hz), 48.85, 44.96, 25.99, 23.91, 16.49, -4.81. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -71.42. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{21}$H$_{29}$F$_3$NOSi: 412.1914; found: 412.1912.

(5R,6R)-1-benzyl-6-((tert-butyldimethylsilyl)ethynyl)-5-(trifluoromethyl)piperidin-2-one (3ab): According to General Procedure A, 3ab was obtained as a white solid (71.3 mg, 90%, d.r. > 20:1) from alkene 1ab and acetylenic triflone 2a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.19 (m, 5H), 5.42 (d, $J = 14.8$ Hz, 1H), 4.23 (d, $J = 2.9$ Hz, 1H), 4.06 (d, $J = 14.8$ Hz, 1H), 2.81 – 2.68 (m, 1H), 2.68 – 2.48 (m, 2H), 2.39 – 2.27 (m, 1H), 2.05 – 1.94 (m, 1H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.03, 135.72, 128.63, 128.59, 127.78, 126.05 (q, $J = 280.7$ Hz), 101.91, 89.01, 47.88, 46.56 (q, $J = 3.0$ Hz), 43.07 (q, $J = 27.1$ Hz), 28.86, 26.01, 18.12 (q, $J = 1.9$ Hz), 16.46, -4.82. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -71.42. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{21}$H$_{29}$F$_3$NOSi: 396.1965; found: 396.1966.

(3-([1,1'-biphenyl]-4-yl)-5,5,5-trifluoropent-1-yn-1-yl)(tert-butyl)dimethylsilane (3ac): According to General Procedure B, 3ac was obtained as a colorless oil (25.6 mg, 33%) from alkene 1ai and acetylenic triflone 2a. Reaction time: 72 h. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 – 7.56 (m, 4H), 7.44 (dd, $J = 10.9$, 4.7 Hz, 4H), 7.39 – 7.33 (m, 1H), 4.06 (dd, $J = 9.0$, 5.4 Hz, 1H), 2.74 – 2.44 (m, 2H), 0.97 (s, 9H), 0.13 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.58, 140.49, 138.61, 128.81, 127.80, 127.55, 127.41, 127.09, 125.58 (q, $J = 278.1$ Hz), 105.40, 87.17, 42.48 (q, $J = 27.6$ Hz), 32.56 (q, $J = 3.2$ Hz), 26.05, 16.57, -4.63, -4.64. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$
-64.22. HRMS (ESI) ([M+NH₄⁺]) Calcd. for C₂₃H₃₁F₃N₅Si: 406.2172; found: 406.2172.

![Image of tert-butyldimethyl(5,5,5-trifluoro-3-(4-methoxyphenyl)pent-1-yn-1-yl)silane (3ad)]

tert-butyldimethyl(5,5,5-trifluoro-3-(4-methoxyphenyl)pent-1-yn-1-yl)silane (3ad): According to General Procedure B, 3ad was obtained as a colorless oil (39.1 mg, 57%) from alkene 1aj and acetylenic triflone 2a. Reaction time: 72 h. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.96 (dd, J = 8.8, 5.6 Hz, 1H), 3.81 (s, 3H), 2.67 – 2.52 (m, 1H), 2.51 – 2.37 (m, 1H), 0.95 (s, 9H), 0.11 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 158.91, 131.63, 128.40, 125.58 (q, J = 278.2 Hz), 114.16, 105.89, 86.70, 55.29, 42.60 (q, J = 27.4 Hz), 32.08 (q, J = 3.2 Hz), 26.03, 16.54, -4.64, -4.65. ¹⁹F NMR (376 MHz, CDCl₃): δ -64.25. HRMS (ESI) ([M+H⁺]) Calcd. for C₁₈H₂₆F₃Si: 343.1700; found: 343.1699.

![Image of tert-butyldimethyl((2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)ethynyl)silane (3ae)]

tert-butyldimethyl((2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)ethynyl)silane (3ae): According to General Procedure A, 3ae was obtained as a colorless oil (38.4 mg, 59%, d.r. > 20:1) from alkene 1ax and acetylenic triflone 2a. Reaction time: 72 h. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 7.1 Hz, 1H), 7.32 – 7.20 (m, 3H), 4.26 (d, J = 8.9 Hz, 1H), 3.30 – 3.04 (m, 3H), 0.96 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.97, 139.03, 127.90, 127.55, 127.22 (q, J = 278.8 Hz), 124.51, 124.46, 105.64, 85.26, 51.03 (q, J = 27.2 Hz), 37.87 (q, J = 3.0 Hz), 31.85 (q, J = 2.6 Hz), 26.04, 16.54, -4.60. ¹⁹F NMR (376 MHz, CDCl₃): δ -70.20. HRMS (ESI) ([M+H⁺]) Calcd. for C₁₈H₂₄F₃Si: 325.1594; found: 325.1594.
2-(6-Phenyl-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (4a): According to General Procedure C, 4a was obtained as a colorless oil (67.1 mg, 89%) from alkene 1a and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.80 (m, 2H), 7.74 – 7.67 (m, 2H), 7.42 – 7.33 (m, 2H), 7.31 – 7.23 (m, 3H), 3.77 (t, $J$ = 7.0 Hz, 2H), 3.06 – 2.95 (m, 1H), 2.51 – 2.36 (m, 1H), 2.35 – 2.21 (m, 1H), 2.10 – 1.97 (m, 1H), 1.96 – 1.84 (m, 1H), 1.76 – 1.57 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.40, 133.96, 132.09, 131.65, 128.22, 128.03, 126.09 (q, $J$ = 277.9 Hz), 123.26, 123.09, 89.17, 83.18, 39.16 (q, $J$ = 27.9 Hz), 37.48, 31.96, 26.20, 26.19 (q, $J$ = 3.1 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.11. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{22}$H$_{19}$F$_3$NO$_2$: 386.1362; found: 386.1361.

**Tert-butyldiphenyl((7-phenyl-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl)oxy)silane** (4b): According to General Procedure C, 4b was obtained as a colorless oil (92.6 mg, 91%) from alkene 1e and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 – 7.64 (m, 4H), 7.44 – 7.33 (m, 8H), 7.30 – 7.25 (m, 3H), 3.69 (t, $J$ = 5.9 Hz, 2H), 2.95 – 2.86 (m, 1H), 2.49 – 2.34 (m, 1H), 2.33 – 2.18 (m, 1H), 1.77 – 1.55 (m, 6H), 1.04 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.60, 134.03, 131.63, 129.57, 128.20, 127.91, 127.63, 126.26 (q, $J$ = 277.5 Hz), 123.36, 89.99, 82.67, 63.62, 39.19 (q, $J$ = 27.7 Hz), 34.59, 32.16, 26.88, 26.51 (q, $J$ = 2.9 Hz), 23.38, 19.23. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.08. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{31}$H$_{36}$F$_3$OSi: 509.2482; found: 509.2484.
**Benzyl (4-phenyl-2-(2,2,2-trifluoroethyl)but-3-yn-1-yl)carbamate (4c):** According to *General Procedure C*, 4c was obtained as a colorless oil (47.1 mg, 65%) from alkene 1g and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.26 (m, 10H), 5.22 – 5.14 (m, 1H), 5.13 (s, 2H), 3.58 – 3.47 (m, 1H), 3.43 – 3.34 (m, 1H), 3.21 – 3.10 (m, 1H), 2.50 – 2.30 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.43, 136.22, 131.72, 128.61, 128.42, 128.32, 128.31, 128.23, 126.01 (q, J = 277.6 Hz), 122.55, 87.15, 83.88, 67.12, 44.54, 36.58 (q, J = 28.7 Hz), 27.84 (q, J = 2.9 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.05. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{20}$H$_{19}$F$_3$NO$_2$: 362.1362; found: 362.1362.

**7-Phenyl-5-(2,2,2-trifluoroethyl)hept-6-yn-2-one (4d):** According to *General Procedure C*, 4d was obtained as a colorless oil (47.4 mg, 88%) from alkene 1j and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 3.03 – 2.94 (m, 1H), 2.80 – 2.65 (m, 2H), 2.53 – 2.24 (m, 2H), 2.19 (s, 3H), 2.05 – 1.95 (m, 1H), 1.82 – 1.71 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.66, 131.60, 128.29, 128.18, 126.02 (q, J = 277.7 Hz), 122.97, 88.95, 83.40, 40.87, 39.31 (q, J = 27.9 Hz), 30.13, 28.48, 25.92 (q, J = 3.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.11. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{15}$H$_{16}$F$_3$O: 269.1148; found: 269.1148.
7-Phenyl-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl (tert-butoxycarbonyl)-L-phenylalaninate (4e):

According to **General Procedure C**, 4e was obtained as a colorless oil (82.9 mg, 80%, d.r. = 1:1) from alkene 1h and acetylenic triflone 2b. Data of the mixture of diastereoisomers: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.34 (m, 2H), 7.31 – 7.20 (m, 6H), 7.15 – 7.08 (m, 2H), 4.98 (d, $J$ = 8.0 Hz, 1H), 4.56 (dd, $J$ = 13.8, 6.4 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.13 – 2.98 (m, 2H), 2.96 – 2.86 (m, 1H), 2.52 – 2.36 (m, 1H), 2.35 – 2.21 (m, 1H), 1.73 – 1.45 (m, 6H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.02, 155.09, 136.06, 131.59, 129.31, 128.53, 128.27, 128.05, 127.00, 126.17 (q, $J$ = 277.5 Hz), 123.16, 89.56, 82.91, 79.91, 65.09, 54.52, 39.16 (q, $J$ = 27.8 Hz), 38.49, 34.31, 28.30, 28.14, 26.42 (q, $J$ = 2.9 Hz), 23.43. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.06. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{29}$H$_{35}$F$_3$NO$_4$: 518.2513; found: 518.251.

(3-(2-Bromoethyl)-5,5,5-trifluoropent-1-yn-1-yl)benzene (4f): According to **General Procedure C**, 4f was obtained as a colorless oil (51.9 mg, 85%) from alkene 1i and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 3.64 (dd, $J$ = 7.5, 5.8 Hz, 2H), 3.29 – 3.19 (m, 1H), 2.58 – 2.43 (m, 1H), 2.40 – 2.26 (m, 1H), 2.21 – 2.06 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 131.67, 128.31, 125.91 (q, $J$ = 277.7 Hz), 122.77, 87.77, 83.74, 38.89 (q, $J$ = 28.2 Hz), 37.41, 30.35, 25.60 (q, $J$ = 3.1 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -63.94. HRMS (ESI) ([M+H$^+$]) Calcd. for C$_{13}$H$_{13}$BrF$_3$: 305.0147; found: 305.0148.
N,N-dimethyl-7-phenyl-5-(2,2,2-trifluoroethyl)hept-6-ynamide (4g): According to General Procedure C, 4g was obtained as a colorless oil (44.3 mg, 71%) from alkene 1k and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.35 (m, 2H), 7.31 – 7.24 (m, 3H), 3.00 (s, 3H), 2.99 – 2.92 (m, 1H), 2.95 (s, 3H), 2.52 – 2.25 (m, 4H), 2.02 – 1.78 (m, 2H), 1.77 – 1.59 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.46, 131.61, 128.21, 127.97, 126.21 (q, $J = 277.6$ Hz), 123.24, 89.70, 82.86, 39.09 (q, $J = 27.7$ Hz), 37.21, 35.40, 34.43, 32.75, 26.39 (q, $J = 3.0$ Hz), 22.48. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.10. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{21}$F$_3$NO: 312.1570; found: 312.1569.

(Trans-2-(trifluoromethyl)cyclohexyl)ethynyl)benzene (4h): According to General Procedure C, 4h was obtained as a colorless oil (31.9 mg, 63%, d.r. = 6:1) from alkene 1p and acetylenic triflone 2b. Data of the major diastereoisomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.36 (m, 2H), 7.31 – 7.26 (m, 3H), 2.65 (td, $J = 10.6$, 3.9 Hz, 1H), 2.30 – 2.11 (m, 2H), 2.10 – 1.98 (m, 1H), 1.91 – 1.73 (m, 2H), 1.66 – 1.47 (m, 1H), 1.42 – 1.23 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 131.56, 128.18, 127.77, 127.24 (q, $J = 280.8$ Hz), 123.61, 90.70, 82.02, 46.05 (q, $J = 24.6$ Hz), 32.77, 29.42 (q, $J = 2.0$ Hz), 24.71 (q, $J = 2.7$ Hz), 24.70, 24.12. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -69.38. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{15}$H$_{16}$F$_3$: 253.1199; found: 253.1198.
**Trans-1-(phenylethynyl)-2-(trifluoromethyl)cycloheptane (4i):** According to *General Procedure C*, 4i was obtained as a colorless oil (43.3 mg, 81%, d.r. = 9:1) from alkene 1q and acetylenic triflone 2b. Data of the major diastereoisomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.37 (m, 2H), 7.32 – 7.26 (m, 3H), 3.15 (td, $J = 6.4$, 3.3 Hz, 1H), 2.67 – 2.53 (m, 1H), 2.03 – 1.67 (m, 7H), 1.64 – 1.44 (m, 2H), 1.42 – 1.30 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.54, 128.23 (q, $J = 280.5$ Hz), 128.22, 127.78, 123.65, 93.04, 82.02, 49.57 (q, $J = 23.8$ Hz), 31.33, 30.30, 30.09 (q, $J = 2.2$ Hz), 27.07, 25.66 (q, $J = 2.6$ Hz), 25.02. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -71.63.

HRMS (ESI) ([M+H$^+$]+) Calcd. for C$_{16}$H$_{18}$F$_{3}$: 267.1355; found: 267.1356.

**2-(2-Methyl-4-phenyl-2-(2,2,2-trifluoroethyl)but-3-yn-1-yl)isooindoline-1,3-dione (4j):** According to *General Procedure C*, 4j was obtained as a colorless oil (64.0 mg, 86%) from alkene 1r and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 – 7.85 (m, 2H), 7.77 – 7.71 (m, 2H), 7.41 – 7.34 (m, 2H), 7.30 – 7.23 (m, 3H), 3.94 (s, 2H), 2.63 (dq, $J = 15.2$, 11.2 Hz, 1H), 2.41 (dq, $J = 15.2$, 10.5 Hz, 1H), 1.52 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.49, 134.28, 131.86, 131.61, 128.17, 128.13, 125.98 (q, J = 278.6 Hz), 123.55, 122.88, 90.20, 83.76, 47.64, 42.84 (q, J = 27.3 Hz), 35.07 (q, J = 1.9 Hz), 24.99. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -59.98. HRMS (ESI) ([M+H$^+$]+) Calcd. for C$_{21}$H$_{17}$F$_{3}$NO$_2$: 372.1206; found: 372.1204.
(3-Ethoxy-5,5,5-trifluoropent-1-yn-1-yl)benzene (4k): According to General Procedure C, 4k was obtained as a colorless oil (44.2 mg, 91%) from alkene 1ac and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.41 (m, 2H), 7.37 – 7.29 (m, 3H), 4.58 (dd, $J = 7.4$, 5.5 Hz, 1H), 3.89 (dq, $J = 9.1$, 7.0 Hz, 1H), 3.54 (dq, $J = 9.1$, 7.0 Hz, 1H), 2.76 – 2.53 (m, 2H), 1.26 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 131.77, 128.73, 128.34, 125.25 (q, $J = 277.2$ Hz), 122.12, 86.36, 85.88, 64.61, 63.86 (q, $J = 3.9$ Hz), 40.42 (q, $J = 28.0$ Hz), 14.95. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -63.85. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_4$F$_3$O: 243.0991; found: 243.0991.

5,5,5-Trifluoro-1-phenylpent-1-yn-3-yl acetate (4l): According to General Procedure C, 4l was obtained as a colorless oil (46.3 mg, 90%) from alkene 1w and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 5.92 (dd, $J = 7.8$, 5.0 Hz, 1H), 2.86 – 2.64 (m, 2H), 2.13 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.36, 131.93, 129.10, 128.35, 124.75 (q, $J = 277.0$ Hz), 121.52, 86.33, 83.90, 58.16 (q, $J = 3.9$ Hz), 39.23 (q, $J = 28.8$ Hz), 20.78. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.04. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_{12}$F$_3$O$_2$: 257.0784; found: 257.0784.

Trans-2-(phenylethynyl)-3-(trifluoromethyl)tetrahydrofuran (4m): According to General
**Procedure C**, 4m was obtained as a colorless oil (41.1 mg, 85%, d.r. > 20:1) from alkene 1s and acetylenic triflone 2b. ^1^H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.40 (m, 2H), 7.36 – 7.28 (m, 3H), 4.94 (d, $J = 5.0$ Hz, 1H), 4.12 – 3.97 (m, 2H), 3.21 – 3.08 (m, 1H), 2.38 – 2.28 (m, 1H), 2.16 – 2.06 (m, 1H). ^1^C NMR (101 MHz, CDCl$_3$) $\delta$ 131.80, 128.78, 128.32, 126.62 (q, $J = 278.1$ Hz), 122.01, 86.24, 85.90, 68.66 (q, $J = 3.3$ Hz), 67.56, 50.67 (q, $J = 27.3$ Hz), 26.45 (q, $J = 1.9$ Hz). ^1^9F NMR (376 MHz, CDCl$_3$): $\delta$ -70.48. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_{12}$F$_3$O: 241.0835; found: 241.1836.

(R)-4-isopropyl-3-((R)-5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)oxazolidin-2-one (4n): According to **General Procedure C**, 4n was obtained as a colorless oil (57.4 mg, 88%, d.r. = 10:1) from alkene 1z and acetylenic triflone 2b. Data of the major diastereoisomer: ^1^H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.29 (m, 5H), 5.11 (dd, $J = 8.1$, 6.3 Hz, 1H), 4.23 (t, $J = 8.9$ Hz, 1H), 4.15 (dd, $J = 8.9$, 5.4 Hz, 1H), 3.91 (ddd, $J = 8.9$, 5.4, 3.4 Hz, 1H), 3.00 – 2.80 (m, 2H), 2.53 – 2.41 (m, 1H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 7.0$ Hz, 3H). ^1^C NMR (101 MHz, CDCl$_3$) $\delta$ 157.75, 131.67, 128.95, 128.42, 124.99 (q, $J = 277.4$ Hz), 121.72, 84.92, 84.05, 63.02, 58.97, 40.71 (q, $J = 3.8$ Hz), 36.90 (q, $J = 28.4$ Hz), 28.08, 18.11, 14.24. ^1^9F NMR (376 MHz, CDCl$_3$): $\delta$ -64.53. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{19}$F$_3$NO$_2$: 326.1362; found: 326.1362.

Benzyl Trans-2-(phenylethynyl)-3-(trifluoromethyl)pyrrolidine-1-carboxylate (4o): According to **General Procedure C**, 4o was obtained as a colorless oil (59.1 mg, 79%, d.r. > 20:1) from
alkene 1aa and acetylenic triflone 2b. ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.26 (m, 10H), 5.44 – 4.88 (br. m, 3H), 3.73 (br. s, 1H), 3.65 – 3.56 (br. m, 1H), 3.13 (br. s, 1H), 2.48 – 2.29 (br. m, 1H), 2.24 – 2.10 (br. m, 1H). ¹³C NMR (101 MHz, CDCl₃, lack of 4 carbons due to the rotamer) δ 154.02, 136.49, 131.80, 128.65, 128.49, 128.28, 127.97, 127.77, 127.69, 123.58 (q, J = 286.9 Hz), 86.68, 83.63, 67.31. ¹⁹F NMR (376 MHz, CDCl₃): δ -71.36. HRMS (ESI) ([M+H]+) Calcd. for C₂₁H₁₉F₃NO₂: 374.1362; found: 374.1360.

Trans-1-benzyl-6-(phenylethynyl)-5-(trifluoromethyl)piperidin-2-one (4p): According to General Procedure C, 4p was obtained as a white solid (66.6 mg, 93%, d.r. > 20:1) from alkene 1ab and acetylenic triflone 2b. ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.27 (m, 10H), 5.47 (d, J = 14.8 Hz, 1H), 4.49 (d, J = 3.2 Hz, 1H), 4.18 (d, J = 14.8 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.73 – 2.56 (m, 2H), 2.48 – 2.37 (m, 1H), 2.12 – 2.02 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 169.11, 135.85, 131.77, 129.06, 128.66, 128.65, 128.45, 127.81, 126.11 (q, J = 280.8 Hz), 121.54, 85.26, 85.18, 48.08, 46.67 (q, J = 3.0 Hz), 43.17 (q, J = 27.0 Hz), 28.96, 18.27 (q, J = 1.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -69.70. HRMS (ESI) ([M+H]+) Calcd. for C₂₁H₁₉F₃NO₂: 358.1413; found: 358.1413.

Methyl 4-phenyl-2-(2,2,2-trifluoroethyl)but-3-ynoate (4q): According to General Procedure C, 4q was obtained as a colorless oil (17 mg, 33%) from alkene 1ad and acetylenic triflone 2b. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.27 (m, 5H), 6.70 (t, J = 1.9 Hz, 1H), 3.78 (s, 3H), 3.35 – 3.11 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 214.62, 165.79, 130.70, 128.98, 128.47, 127.71, 125.49 (q, J = 277.5 Hz), 99.69, 94.56 (q, J = 3.3 Hz), 52.86, 33.43 (q, J = 30.1 Hz). ¹⁹F NMR (376 MHz,
N,N-dimethyl-4-phenyl-2-(2,2,2-trifluoroethyl)but-3-ynamide (4r): According to General Procedure C, 4r was obtained as a colorless oil (21 mg, 39%) from alkene 1ae and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 3.91 (dd, J = 7.7, 5.8 Hz, 1H), 3.22 (s, 3H), 3.03 (s, 3H), 3.02 – 2.91 (m, 1H), 2.75 – 2.61 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.01, 131.73, 128.56, 128.30, 126.19 (q, $J = 277.8$ Hz), 122.35, 84.20, 83.67, 37.52, 36.41, 36.09 (q, $J = 28.5$ Hz), 30.15 (q, $J = 3.2$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.87. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{13}$H$_{12}$F$_3$O$_2$: 257.0784; found: 257.0784.

Diethyl (5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)phosphonate (4s): According to General Procedure C, 4s was obtained as a colorless oil (47.6 mg, 71%) from alkene 1af and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 4.33 – 4.20 (m, 4H), 3.34 (ddd, $J = 25.9$, 11.2, 2.9 Hz, 1H), 2.78 – 2.51 (m, 2H), 1.38 (tdd, $J = 7.1$, 1.9, 0.4 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.01, 131.73, 128.56, 128.30, 126.19 (q, $J = 277.8$ Hz), 122.35, 84.20, 83.67, 37.52, 36.41, 36.09 (q, $J = 28.5$ Hz), 30.15 (q, $J = 3.2$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.86. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{14}$H$_{15}$F$_3$O$_3$P: 335.1018; found: 335.1017.
(5,5,5-Trifluoropent-1-yn-1,3-diyl)dibenzene (4t): According to General Procedure D, 4t was obtained as a colorless oil (41.2 mg, 75%) from alkene 1ag and acetylenic triflone 2b. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.48 - 7.41\) (m, 4H), 7.40 - 7.34 (m, 2H), 7.33 - 7.26 (m, 4H), 4.20 (dd, \(J = 9.1, 5.4\) Hz, 1H), 2.80 - 2.65 (m, 1H), 2.64 - 2.50 (m, 1H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 139.77, 131.67, 128.95, 128.28, 128.23, 127.62, 127.41, 125.68\) (q, \(J = 277.9\) Hz), 123.05, 88.46, 84.15, 42.28 (q, \(J = 27.5\) Hz), 32.55 (q, \(J = 3.2\) Hz). \(^1\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -64.75\). HRMS (ESI) ([M+H]^+) Calcd. for C\(_{17}\)H\(_{14}\)F\(_3\): 275.1042; found: 275.1042.

1-Methyl-2-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4u): According to General Procedure D, 4u was obtained as a colorless oil (41 mg, 71%) from alkene 1ah and acetylenic triflone 2b. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.59 - 7.55\) (m, 1H), 7.46 - 7.39 (m, 2H), 7.32 - 7.16 (m, 6H), 4.39 (dd, \(J = 9.7, 4.4\) Hz, 1H), 2.77 - 2.63 (m, 1H), 2.58 - 2.43 (m, 1H), 2.42 (s, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 138.00, 134.78, 131.65, 130.92, 128.25, 128.14, 127.57, 127.51, 126.75, 125.82\) (q, \(J = 278.3\) Hz), 123.15, 88.84, 83.49, 40.89 (q, \(J = 27.6\) Hz), 28.90 (q, \(J = 3.2\) Hz), 19.09. \(^1\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -64.77\). HRMS (ESI) ([M+H]^+) Calcd. for C\(_{18}\)H\(_{16}\)F\(_3\): 289.1199; found: 289.1198.
4-(5,5,5-Trifluoro-1-phenylpent-1-yn-3-yl)-1,1'-biphenyl (4v): According to General Procedure D, 4v was obtained as a white solid (53.3 mg, 76%) from alkene 1ai and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 – 7.55 (m, 4H), 7.54 – 7.49 (m, 2H), 7.48 – 7.40 (m, 4H), 7.39 – 7.27 (m, 4H), 4.25 (dd, $J = 9.0, 5.4$ Hz, 1H), 2.83 – 2.69 (m, 1H), 2.68 – 2.54 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.64, 140.59, 138.77, 131.69, 128.84, 128.29, 128.26, 127.83, 127.67, 127.45, 127.12, 125.69 (q, $J = 278.5$ Hz), 123.03, 88.40, 84.25, 42.24 (q, $J = 27.5$ Hz), 32.24 (q, $J = 3.2$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.26. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{23}$H$_{18}$F$_3$: 351.1355; found: 351.1355.

1-Methoxy-4-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4w): According to General Procedure D. 4w was obtained as a colorless oil (49.4 mg, 81%) from alkene 1aj and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.39 (m, 2H), 7.35 (d, $J = 8.7$ Hz, 2H), 7.32 – 7.25 (m, 3H), 6.90 (d, $J = 8.7$ Hz, 2H), 4.15 (dd, $J = 8.9, 5.6$ Hz, 1H), 3.80 (s, 3H), 2.77 – 2.62 (m, 1H), 2.60 – 2.46 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.01, 131.81, 131.65, 128.43, 128.26, 128.17, 125.69 (q, $J = 277.9$ Hz), 123.12, 114.28, 88.83, 83.94, 55.33, 42.38 (q, $J = 27.3$ Hz), 31.76 (q, $J = 3.2$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.29. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{18}$H$_{16}$F$_3$O: 305.1148; found: 305.1148.
1-Methoxy-2-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4x): According to General Procedure D, 4x was obtained as a colorless oil (42.1 mg, 69%) from alkene 1ak and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.49 – 7.42 (m, 2H), 7.34 – 7.25 (m, 4H), 6.99 (td, $J = 7.5, 1.0$ Hz, 1H), 6.89 (dd, $J = 8.2, 1.3$ Hz, 1H), 4.61 (dd, $J = 9.5, 4.4$ Hz, 1H), 3.87 (s, 3H), 2.69 – 2.46 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.01, 131.68, 128.78, 128.64, 128.23, 128.03, 127.70, 126.04 (q, $J = 277.8$ Hz), 123.37, 120.87, 110.57, 88.68, 83.73, 55.46, 40.07 (q, $J = 27.5$ Hz), 26.50 (q, $J = 3.4$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.46. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{18}$H$_{16}$F$_3$O: 305.1148; found: 305.1148.

1-Methoxy-3-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4y): According to General Procedure D, 4y was obtained as a colorless oil (47 mg, 77%) from alkene 1al and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.40 (m, 2H), 7.33 – 7.26 (m, 4H), 7.05 – 6.98 (m, 2H), 6.86 – 6.80 (m, 1H), 4.16 (dd, $J = 9.2, 5.3$ Hz, 1H), 3.82 (s, 3H), 2.79 – 2.64 (m, 1H), 2.63 – 2.50 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.00, 141.34, 131.67, 129.96, 128.27, 128.22, 125.68 (q, $J = 277.9$ Hz), 123.04, 119.68, 113.35, 112.80, 88.33, 84.20, 55.29, 42.21 (q, $J = 27.7$ Hz), 32.54 (q, $J = 3.2$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.36. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{18}$H$_{16}$F$_3$O: 305.1148; found: 305.1148.
3-(5,5,5-Trifluoro-1-phenylpent-1-yn-3-yl)phenyl acetate (4z): According to General Procedure D, 4z was obtained as a colorless oil (50 mg, 75%) from alkene 1am and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.39 (m, 4H), 7.34 – 7.26 (m, 3H), 7.10 (d, J = 8.6 Hz, 2H), 4.20 (dd, J = 9.1, 5.3 Hz, 1H), 2.78 – 2.64 (m, 1H), 2.62 – 2.48 (m, 1H), 2.30 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.44, 150.02, 137.25, 131.66, 128.49, 128.30, 125.59 (q, J = 278.1 Hz), 122.89, 122.04, 88.11, 84.38, 42.26 (q, J = 27.7 Hz), 32.02 (q, J = 3.3 Hz), 21.13. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.32. HRMS (ESI) ([M+H]^+) Calcd. for C$_{19}$H$_{16}$F$_3$O$_2$: 333.1097; found: 333.1097.

Tert-butyl (4-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)phenyl)carbamate (4aa): According to General Procedure D, 4aa was obtained as a colorless oil (55 mg, 68%) from alkene 1an and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.40 (m, 2H), 7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 6.52 (s, 1H), 4.15 (dd, J = 9.0, 5.5 Hz, 1H), 2.76 – 2.62 (m, 1H), 2.60 – 2.46 (m, 1H), 1.52 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.73, 137.78, 134.24, 131.65, 128.26, 128.19, 127.98, 125.65 (q, J = 278.0 Hz), 123.05, 118.94, 88.57, 84.05, 80.70, 42.22 (q, J = 27.3 Hz), 31.92 (q, J = 3.3 Hz), 28.34. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.27. HRMS (ESI) ([M+HH$_4$]^+) Calcd. for C$_{22}$H$_{26}$F$_3$N$_2$O$_2$: 407.1941; found: 407.1941.
1-Fluoro-4-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4ab): According to General Procedure D, 4ab was obtained as a colorless oil (45.7 mg, 78%) from alkene 1ao and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.38 (m, 4H), 7.34 – 7.26 (m, 3H), 7.06 (t, J = 8.7 Hz, 2H), 4.19 (dd, J = 8.7, 5.8 Hz, 1H), 2.78 – 2.64 (m, 1H), 2.61 – 2.47 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.16 (d, J = 246.3 Hz), 135.47 (d, J = 3.3 Hz), 131.65, 129.02 (d, J = 8.2 Hz), 128.34, 128.31, 125.55 (q, J = 277.8 Hz), 122.84, 115.79 (d, J = 21.6 Hz), 88.20, 84.33, 42.30 (q, J = 27.3 Hz), 31.90 (q, J = 3.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.27 (s, 3F), -114.86 (s, 1F). HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{13}$F$_4$: 293.0948; found: 293.0947.

1-Chloro-4-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4ac): According to General Procedure D, 4ac was obtained as a colorless oil (42 mg, 68%) from alkene 1ap and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.27 (m, 9H), 4.18 (dd, J = 8.6, 5.8 Hz, 1H), 2.79 – 2.64 (m, 1H), 2.61 – 2.47 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.21, 133.50, 131.66, 129.08, 128.81, 128.39, 128.32, 125.51 (q, J = 277.8 Hz), 122.76, 87.88, 84.46,42.10 (q, J = 27.7 Hz), 32.04 (q, J = 3.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.24. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{13}$ClF$_3$: 309.0652; found: 309.0652.
1-Bromo-4-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)benzene (4ad): According to General Procedure D, 4ad was obtained as a colorless oil (41.6 mg, 59%) from alkene 1aq and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, J = 8.5 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.35 – 7.27 (m, 5H), 4.16 (dd, J = 8.6, 5.8 Hz, 1H), 2.78 – 2.64 (m, 1H), 2.61 – 2.47 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.75, 132.05, 131.65, 129.17, 128.39, 128.32, 125.49 (q, J = 278.1 Hz), 122.75, 121.56, 87.79, 84.49, 42.03 (q, J = 27.7 Hz), 32.12 (q, J = 3.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.23. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{17}$H$_{13}$BrF$_3$: 353.0147; found: 353.0147.

1-(5,5,5-Trifluoro-1-phenylpent-1-yn-3-yl)-4-(trifluoromethyl)benzene (4ae): According to General Procedure D, 4ae was obtained as a colorless oil (30.9 mg, 45%) from alkene 1ar and acetylenic triflone 2b. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.37 – 7.27 (m, 3H), 4.26 (dd, J = 8.5, 5.9 Hz, 1H), 2.83 – 2.68 (m, 1H), 2.65 – 2.51 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.67 (q, J = 1.2 Hz), 131.66, 130.05 (q, J = 32.6 Hz), 128.50, 128.34, 127.91, 125.94 (q, J = 3.8 Hz), 125.44 (q, J = 277.9 Hz), 123.99 (q, J = 271.9 Hz), 122.60, 87.37, 84.78, 41.94 (q, J = 28.0 Hz), 32.47 (q, J = 3.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.58 (s, 3F), -64.24 (s, 3F). HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{18}$H$_{15}$F$_6$: 343.0916; found: 343.0916.
2-(5,5,5-Trifluoro-1-phenylpent-1-yn-3-yl)naphthalene (4af): According to *General Procedure D*, 4af was obtained as a colorless oil (41.6 mg, 64%) from alkene 1as and acetylenic triflone 2b. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.81 (m, 4H), 7.58 – 7.42 (m, 5H), 7.35 – 7.27 (m, 3H), 4.37 (dd, $J = 9.0$, 5.5 Hz, 1H), 2.89 – 2.74 (m, 1H), 2.74 – 2.60 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.03, 133.46, 132.77, 131.70, 128.86, 128.29, 128.26, 127.88, 127.71, 126.46, 126.24, 126.17, 125.71 (q, $J = 279.8$ Hz), 125.23, 123.03, 88.44, 84.40, 42.09 (q, $J = 27.3$ Hz), 32.71 (q, $J = 3.3$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.25. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{21}$H$_{16}$F$_3$: 325.1199; found: 325.1198.

Methyl (2S)-2-(((tert-butoxycarbonyl)amino)-3-(4-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)phenyl)propanoate (4ag): According to *General Procedure D*, 4ag was obtained as a colorless oil (72.3 mg, 73%, d.r. = 1:1) from alkene 1at and acetylenic triflone 2b. Data of the mixture of diastereoisomers: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.40 (m, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.33 – 7.26 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 5.00 (d, $J = 8.1$ Hz, 1H), 4.60 (dd, $J = 13.4$, 6.1 Hz, 1H), 4.17 (dd, $J = 9.0$, 5.4 Hz, 1H), 3.71 (d, $J = 2.0$ Hz, 3H), 3.21 – 2.85 (m, 2H), 2.78 – 2.62 (m, 1H), 2.62 – 2.47 (m, 1H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.28, 155.07, 138.45, 135.51, 131.66, 129.88, 128.27, 128.24, 127.58, 125.64 (q, $J = 278.1$ Hz), 122.99, 88.35, 84.17, 54.35, 52.28, 52.26, 42.21 (q, $J = 27.6$ Hz), 38.01, 32.18 (q, $J = 3.2$ Hz), 28.29. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -64.32. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{26}$H$_{29}$F$_3$NO$_4$: 476.2043; found:
4-Methyl-7-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)-2H-chromen-2-one (4ah): According to General Procedure D, 4ah was obtained as a yellow solid (40.7 mg, 57%) from alkene 1au and acetylenic triflone 2b. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 8.2\) Hz, 1H), 7.47 (d, \(J = 1.7\) Hz, 1H), 7.46 – 7.41 (m, 2H), 7.38 (dd, \(J = 8.2, 1.8\) Hz, 1H), 7.36 – 7.28 (m, 3H), 6.30 (q, \(J = 1.2\) Hz, 1H), 4.29 (dd, \(J = 8.2, 6.2\) Hz, 1H), 2.85 – 2.71 (m, 1H), 2.69 – 2.55 (m, 1H), 2.45 (d, \(J = 1.2\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.59, 153.80, 151.98, 144.01, 131.68, 128.55, 128.35, 125.41 (q, \(J = 277.8\) Hz), 125.17, 123.42, 122.47, 119.41, 116.11, 115.20, 87.07, 85.03, 41.81 (q, \(J = 27.9\) Hz), 32.46 (q, \(J = 3.3\) Hz), 18.64. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -64.12. HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{21}\)H\(_{16}\)F\(_3\)O\(_2\): 357.1097; found: 357.1096.

(5,5,5-Trifluoro-3-methylpent-1-yn-1,3-diyl)dibenzene (4ai): According to General Procedure D, 4ai was obtained as a colorless oil (24.3 mg, 42%) from alkene 1av and acetylenic triflone 2b. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.66 – 7.60 (m, 2H), 7.52 – 7.45 (m, 2H), 7.41 – 7.26 (m, 6H), 2.82 – 2.63 (m, 2H), 1.81 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.70, 131.64, 128.51, 128.28, 128.16, 127.18, 125.89, 125.55 (q, \(J = 279.0\) Hz), 123.22, 91.84, 84.88, 46.85 (q, \(J = 26.5\) Hz), 37.25 (q, \(J = 2.1\) Hz), 29.72. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -60.52. HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{18}\)H\(_{16}\)F\(_3\): 289.1199; found: 289.1199.
(5,5,5-Trifluoro-4-methylpent-1-yn-1,3-diyl)dibenzene (4aj): According to General Procedure D, 4aj was obtained as a colorless oil (50.7 mg, 88%, d.r. = 4:1) from alkene 1aw and acetylenic triflone 2b. Data of the major diastereoisomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.51 – 7.43\) (m, 4H), 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 4.43 (d, \(J = 3.3\) Hz, 1H), 2.60 – 2.47 (m, 1H), 1.20 (d, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 138.87, 131.68, 128.67, 128.29, 128.17, 127.97, 127.43, 127.34\) (q, \(J = 280.6\) Hz), 123.23, 86.10, 85.97, 44.69 (q, \(J = 25.4\) Hz), 37.47 (q, \(J = 2.8\) Hz), 8.63 (q, \(J = 2.4\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -71.01\). HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{18}\)H\(_{16}\)F\(_3\): 289.1199; found: 289.1198.

Trans-1-(phenylethynyl)-2-(trifluoromethyl)-2,3-dihydro-1H-indene (4ak): According to General Procedure D, 4ak was obtained as a colorless oil (40.8 mg, 71%, d.r. > 20:1) from alkene 1ax and acetylenic triflone 2b. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.52 – 7.39\) (m, 3H), 7.33 – 7.21 (m, 6H), 4.44 (d, \(J = 8.8\) Hz, 1H), 3.39 – 3.10 (m, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 141.04, 139.09, 131.78, 128.26, 128.18, 128.01, 127.61, 127.30\) (q, \(J = 277.9\) Hz), 124.61, 124.56, 123.09, 88.62, 82.67, 50.92 (q, \(J = 27.2\) Hz), 37.59 (q, \(J = 2.9\) Hz), 31.90 (q, \(J = 2.6\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -70.26\). HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{18}\)H\(_{14}\)F\(_3\): 287.1042; found: 287.1043.
Trans-1-(phenylethynyl)-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene (4al): According to General Procedure D, 4al was obtained as a colorless oil (43.9 mg, 73%, d.r. > 20:1) from alkene 1ay and acetylenic triflone 2b. 1H NMR (400 MHz, CDCl3) δ 7.65 (d, J = 7.5 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.31 – 7.09 (m, 6H), 4.21 (d, J = 8.8 Hz, 1H), 2.89 (t, J = 6.4 Hz, 2H), 2.84 – 2.71 (m, 1H), 2.31 – 2.22 (m, 1H), 1.90 – 1.79 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 135.18, 133.95, 131.66, 129.26, 128.61, 128.23, 128.05, 127.39 (q, J = 280.7 Hz), 127.05, 126.70, 123.29, 90.19, 82.62, 44.89 (q, J = 25.5 Hz), 31.50 (q, J = 2.4 Hz), 27.52, 21.72 (q, J = 2.7 Hz). 19F NMR (376 MHz, CDCl3): δ -70.37. HRMS (ESI) ([M+H]+) Calcd. for C19H16F3: 301.1199; found: 301.1198.

(8R,9S,13S)-13-methyl-3-((6-phenyl-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4am): According to General Procedure C, 4am was obtained as a colorless oil (76.3 mg, 75%, d.r. = 1:1) from alkene 1az and acetylenic triflone 2b. Data of the mixture of diastereoisomers: 1H NMR (400 MHz, CDCl3) δ 7.43 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 7.20 (d, J = 8.5 Hz, 1H), 6.73 (dd, J = 8.6, 2.7 Hz, 1H), 6.66 (d, J = 2.6 Hz, 1H), 4.02 (t, J = 6.2 Hz, 2H), 3.07 – 2.98 (m, 1H), 2.96 – 2.83 (m, 2H), 2.57 – 1.83 (m, 12H), 1.80 – 1.37 (m, 7H), 0.92 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 156.95, 137.79, 132.13, 131.64, 128.26, 128.05, 126.37, 126.18 (q, J = 277.5 Hz), 123.20, 114.60, 114.58, 112.15, 112.14, 89.60, 83.04, 67.22, 50.43, 48.04, 44.01, 39.25 (q, J = 27.8 Hz), 38.40, 35.89, 31.61, 31.47, 29.67, 26.93, 26.57, 26.34 (q, J = 3.0 Hz), 25.95, 21.60, 13.87. 19F NMR (376 MHz, CDCl3): δ
(8R,9S,13S,14S)-13-methyl-3-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4an): According to General Procedure D, 4an was obtained as a colorless oil (65.8 mg, 73%, d.r. = 1:1) from alkene 1ba and acetylenic triflone 2b. Data of the mixture of diastereoisomers: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 – 7.40 (m, 2H), 7.33 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 7.16 (s, 1H), 4.14 (dd, \(J = 9.3\), 5.1 Hz, 1H), 2.93 (dd, \(J = 8.7\), 3.9 Hz, 2H), 2.78 – 2.39 (m, 4H), 2.36 – 2.25 (m, 1H), 2.21 – 1.93 (m, 4H), 1.73 – 1.37 (m, 6H), 0.91 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 220.87, 139.20, 139.17, 137.26, 137.18, 137.16, 131.66, 128.26, 128.16, 127.94, 127.92, 125.99, 125.98, 125.73 (q, \(J = 278.0\) Hz), 124.74, 124.71, 123.15, 88.68, 83.98, 83.94, 50.51, 48.00, 44.33, 42.21 (q, \(J = 27.5\) Hz), 38.11, 35.87, 32.04 (q, \(J = 29.7\) Hz), 31.60, 29.45, 26.46, 25.72, 21.60, 13.86. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -64.33. HRMS (ESI) ([M+H\(^+\]) Calcd. for \(\text{C}_{32}\text{H}_{36}\text{F}_{3}\text{O}_{2}\): 509.2662; found: 509.2660.

(2R)-2,8-dimethyl-6-(5,5,5-trifluoro-1-phenylpent-1-yn-3-yl)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (4ao): According to General Procedure D, 4ao was obtained as a colorless oil (99.1 mg, 85%, d.r. = 1:1) from alkene 1bb and acetylenic triflone 2b. Data of the mixture of diastereoisomers: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 – 7.40 (m, 2H), 7.33 – 7.26 (m, 3H), 6.99 (s, 1H), 6.94 (s, 1H), 4.06 (dd, \(J = 9.6\), 4.9 Hz, 1H), 2.82 – 2.59 (m, 3H), 2.58 – 2.44 (m, 1H), 2.17 (s, 3H), 1.86 – 1.70 (m, 2H), 1.63 – 1.00 (m, 24H), 0.87 (d, \(J = 6.6\) Hz, 6H), 0.85 (t, \(J = 6.4\) Hz, 6H).
\[ ^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 151.51, 131.67, 129.79, 128.22, 128.02, 127.14, 127.13, 126.80, 125.80 (\text{q, } J = 277.8 \text{ Hz}), 125.65, 125.64, 123.37, 120.73, 89.27, 83.66, 42.59 (\text{q, } J = 27.2 \text{ Hz}), 40.27, 40.22, 39.40, 37.47, 37.44, 37.31, 32.82, 32.72, 31.73 (\text{q, } J = 3.2 \text{ Hz}), 31.13, 28.01, 24.83, 24.47, 24.29, 24.26, 22.75, 22.66, 22.40, 21.00, 19.78, 19.68, 16.19. \]

\[ ^{19}\text{F} \text{ NMR} (376 \text{ MHz, CDCl}_3): \delta -64.42. \]

HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{38}\)H\(_{54}\)F\(_3\)O: 583.4121; found: 583.4122.

**5,5,5-Trifluoro-3-methyl-3-((R)-4-methylcyclohex-3-en-1-yl)pent-1-yn-1-yl)benzene (4ap):**

According to General Procedure C, 4ap was obtained as a colorless oil (77.2 mg, 76%, d.r. = 1:1) from alkene 1bc and acetylenic triflone 2b. Data of the mixture of diastereoisomers: \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.41 – 7.35 (m, 2H), 7.31 – 7.25 (m, 3H), 5.42 – 5.37 (m, 1H), 2.58 – 2.25 (m, 2H), 2.24 – 1.92 (m, 5H), 1.86 – 1.62 (m, 4H), 1.53 – 1.43 (m, 1H), 1.42 (d, \( J = 1.1 \text{ Hz, 1.5H}\), 1.40 (d, \( J = 0.9 \text{ Hz, 1.5H}\)). \(^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 133.98, 133.97, 131.59, 128.18, 127.82, 127.81, 126.54 (\text{q, } J = 278.8 \text{ Hz}), 126.51 (\text{q, } J = 278.8 \text{ Hz}), 123.52, 123.50, 120.23, 120.20, 92.60, 92.42, 82.98, 82.85, 42.91, 42.69, 42.05 (\text{q, } J = 26.4 \text{ Hz}), 41.73 (\text{q, } J = 26.3 \text{ Hz}), 35.92 (\text{q, } J = 1.8 \text{ Hz}), 35.79 (\text{q, } J = 1.8 \text{ Hz}), 30.90, 30.87, 27.32, 27.00, 24.73, 24.28, 23.88 (\text{q, } J = 1.4 \text{ Hz}), 23.75 (\text{q, } J = 1.4 \text{ Hz}), 23.24. \(^{19}\text{F} \text{NMR} (376 \text{ MHz, CDCl}_3): \delta -59.58, -59.60. \) HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{19}\)H\(_{22}\)F\(_3\): 509.2662; found: 509.2660.

**4R,4aS,6R)-4,4a-dimethyl-6-(5,5,5-trifluoro-3-methyl-1-phenylpent-1-yn-3-yl)-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (4aq):** According to General Procedure C, 4aq was obtained as a colorless oil (55.2 mg, 71%, d.r. = 1:1) from alkene 1bd and acetylenic triflone 2b. Data of the mixture of diastereoisomers: \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.42 – 7.34 (m, 2H), 7.33 – 7.27 (m,
3H), 5.78 (s, 1H), 2.58 – 1.89 (m, 10H), 1.44 (d, J = 0.8 Hz, 1.5 H), 1.42 (s, 1.5 H), 1.41 – 1.32 (m, 1H), 1.28 – 1.14 (m, 1H), 1.11 (s, 3H), 1.00 (d, J = 6.8 Hz, 1.5H), 0.99 (d, J = 6.8 Hz, 1.5H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 199.46, 199.44, 169.76, 169.74, 131.55, 131.53, 128.30, 128.29, 128.10, 126.31 (q, J = 278.3 Hz), 124.66, 124.64, 123.11, 123.09, 91.95, 91.85, 83.70, 83.60, 42.02, 41.93 (q, J = 26.3 Hz), 41.85 (q, J = 26.6 Hz), 41.33, 41.22, 40.53, 40.49, 40.15, 39.62, 39.27, 36.01 (q, J = 1.7 Hz), 35.87 (q, J = 1.7 Hz), 32.72, 32.68, 28.13, 27.73, 24.18, 23.99, 16.94, 16.88, 15.04. HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{24}\)H\(_{28}\)F\(_3\)O: 389.2087; found: 389.2086.

![5a](image)

2-(6-(4-Methoxyphenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione  (5a):

According to General Procedure C, 5a was obtained as a colorless oil (59.1 mg, 71%) from alkene 1a and acetylenic triflone 2c. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 7.31 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 3.76 (t, J = 7.1 Hz, 2H), 3.03 – 2.94 (m, 1H), 2.50 – 2.35 (m, 1H), 2.34 – 2.20 (m, 1H), 2.10 – 1.97 (m, 1H), 1.96 – 1.83 (m, 1H), 1.75 – 1.56 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 168.41, 159.39, 133.96, 133.01, 132.09, 126.12 (q, J = 277.7 Hz). 123.25, 115.24, 113.84, 87.66, 82.94, 55.27, 39.24 (q, J = 27.7 Hz), 37.51, 32.02, 26.21, 26.20 (q, J = 2.9 Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -70.37. HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{23}\)H\(_{21}\)F\(_3\)NO: 416.1468; found: 416.1470.
2-(6-(4-(Tert-butyl)phenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5b): According to General Procedure C, 5b was obtained as a colorless oil (66.1 mg, 75%) from alkene 1a and acetylenic triflone 2d. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 7.35 – 7.27 (m, 4H), 3.76 (t, $J = 7.0$ Hz, 2H), 3.04 – 2.95 (m, 1H), 2.51 – 2.35 (m, 1H), 2.35 – 2.20 (m, 1H), 2.10 – 1.97 (m, 1H), 1.96 – 1.83 (m, 1H), 1.75 – 1.57 (m, 2H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.40, 151.24, 133.95, 132.09, 131.35, 126.11 (q, $J = 277.6$ Hz), 125.21, 123.25, 120.07, 88.46, 83.20, 39.21 (q, $J = 27.8$ Hz), 37.50, 34.71, 32.00, 31.17, 26.21 (q, $J = 2.9$ Hz), 26.20. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.10. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{26}$H$_{27}$F$_3$NO$_2$: 442.1988; found: 442.1989.

2-(6-([1,1'-Biphenyl]-4-yl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5c): 5c was obtained as a colorless oil (76.7 mg, 83%) from alkene 1a and acetylenic triflone 2e. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.81 (m, 2H), 7.73 – 7.67 (m, 2H), 7.59 – 7.49 (m, 4H), 7.47 – 7.40 (m, 4H), 7.37 – 7.31 (m, 1H), 3.77 (t, $J = 7.0$ Hz, 2H), 3.08 – 2.97 (m, 1H), 2.53 – 2.38 (m, 1H), 2.37 – 2.23 (m, 1H), 2.11 – 1.99 (m, 1H), 1.98 – 1.85 (m, 1H), 1.77 – 1.59 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.43, 140.79, 140.42, 133.98, 132.09, 132.08, 128.85, 127.58, 127.02, 126.92,
126.11 (q, J = 277.9 Hz), 123.27, 122.02, 89.87, 83.06, 39.17 (q, J = 27.8 Hz), 37.51, 31.98, 26.29 (q, J = 3.0 Hz), 26.23. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.07. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{28}$H$_{23}$F$_3$NO$_2$: 462.1675; found: 462.1674.

2-(6-(4-Chlorophenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5d): 5d was obtained as a colorless oil (64.7 mg, 77%) from alkene 1a and acetylenic triflone 2f. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.81 (m, 2H), 7.74 – 7.69 (m, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.26 (t, J = 7.0 Hz, 2H), 3.04 – 2.95 (m, 1H), 2.49 – 2.35 (m, 1H), 2.35 – 2.21 (m, 1H), 2.08 – 1.96 (m, 1H), 1.95 – 1.83 (m, 1H), 1.75 – 1.57 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.40, 134.03, 134.00, 132.88, 132.06, 128.54, 126.02 (q, J = 277.3 Hz), 123.27, 121.56, 90.19, 82.14, 39.06 (q, J = 27.9 Hz), 37.44, 31.87, 26.20 (q, J = 3.2 Hz), 26.16. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.15. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{22}$H$_{18}$ClF$_3$NO$_2$: 420.0973; found: 420.0971.

2-(6-(3-Chlorophenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5e): 5e was obtained as a colorless oil (58.8 mg, 70%) from alkene 1a and acetylenic triflone 2g. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 7.36 (t, J = 1.6 Hz, 1H), 7.28 – 7.18 (m, 3H), 3.77 (t, J = 7.0 Hz, 2H), 3.04 – 2.96 (m, 1H), 2.49 – 2.35 (m, 1H), 2.35 – 2.21 (m, 1H), 2.08 – 1.96 (m, 1H), 1.95 – 1.83 (m, 1H), 1.75 – 1.58 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$)
δ 168.41, 134.02, 134.00, 132.05, 131.52, 129.82, 129.45, 128.35, 126.00 (q, J = 277.7 Hz), 124.76, 123.28, 90.49, 81.90, 39.03 (q, J = 27.9 Hz), 37.42, 31.84, 26.18 (q, J = 3.0 Hz), 26.15.

19F NMR (376 MHz, CDCl3): δ -64.16. HRMS (ESI) (M+H)+ Calcd. for C22H18ClF3NO2: 420.0973; found: 420.0972.

2-(6-(2-Chlorophenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5f): 5f was obtained as a colorless oil (70.6 mg, 84%) from alkene 1a and acetylenic triflone 2h. 1H NMR (400 MHz, CDCl3) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 7.44 – 7.39 (m, 1H), 7.37 – 7.33 (m, 1H), 7.24 – 7.15 (m, 2H), 3.78 (t, J = 6.9 Hz, 2H), 3.11 – 3.03 (m, 1H), 2.55 – 2.40 (m, 1H), 2.38 – 2.24 (m, 1H), 2.16 – 2.04 (m, 1H), 2.00 – 1.88 (m, 1H), 1.78 – 1.61 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 168.41, 135.95, 133.96, 133.36, 132.08, 129.15, 129.06, 126.35, 126.03 (q, J = 277.6 Hz), 123.26, 122.93, 94.72, 80.02, 39.05 (q, J = 28.0 Hz), 37.44, 31.94, 26.39 (q, J = 3.0 Hz), 26.22. 19F NMR (376 MHz, CDCl3): δ -64.13. HRMS (ESI) (M+H)+ Calcd. for C22H18ClF3NO2: 420.0973; found: 420.0972.

2-(6-(4-Bromophenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5g): 5g was obtained as a colorless oil (65 mg, 70%) from alkene 1a and acetylenic triflone 2i. 1H NMR (400 MHz, CDCl3) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6
Hz, 2H), 3.76 (t, J = 7.0 Hz, 2H), 3.03 – 2.94 (m, 1H), 2.49 – 2.35 (m, 1H), 2.35 – 2.21 (m, 1H), 2.08 – 1.96 (m, 1H), 1.95 – 1.83 (m, 1H), 1.75 – 1.57 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 168.40, 134.00, 133.11, 132.05, 131.46, 126.02 (q, J = 278.8 Hz), 123.27, 122.22, 122.03, 90.40, 82.21, 39.02 (q, J = 27.9 Hz), 37.44, 31.84, 26.22 (q, J = 3.0 Hz), 26.16. 19F NMR (376 MHz, CDCl3): δ -64.14. HRMS (ESI) ([M+H]+) Calcd. for C22H18BrF3NO2: 464.0468; found: 464.0470

2-(4-(2,2,2-Trifluoroethyl)-6-(4-(trifluoromethyl)phenyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5h): 5h was obtained as a colorless oil (81.7 mg, 90%) from alkene 1a and acetylenic triflone 2j. 1H NMR (400 MHz, CDCl3) δ 7.88 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 3.77 (t, J = 7.0 Hz, 2H), 3.07 – 2.98 (m, 1H), 2.51 – 2.37 (m, 1H), 2.37 – 2.23 (m, 1H), 2.09 – 1.97 (m, 1H), 1.96 – 1.85 (m, 1H), 1.78 – 1.60 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 168.37, 133.98, 132.04, 131.88, 129.80 (q, J = 32.7 Hz), 126.87 (q, J = 1.2 Hz), 125.96 (q, J = 277.5 Hz), 125.13 (q, J = 3.9 Hz), 123.92 (q, J = 273.71 Hz), 123.25, 91.79, 82.03, 38.97 (q, J = 28.0 Hz), 37.40, 31.79, 26.22 (q, J = 3.0 Hz), 26.13. 19F NMR (376 MHz, CDCl3): δ -62.82 (s, 3F), -64.19 (s, 3F). HRMS (ESI) ([M+H]+) Calcd. for C23H18F6NO2: 454.1236; found: 454.1233.
2-(6-(4-Fluorophenyl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5i): 5i was obtained as a colorless oil (65.4 mg, 81%) from alkene 1a and acetylenic triflone 2k. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.80 (m, 2H), 7.75 – 7.68 (m, 2H), 7.36 (d, $J$ = 8.8 Hz, 1H), 7.35 (d, $J$ = 8.8 Hz, 1H), 6.97 (t, $J$ = 8.8 Hz, 2H), 3.77 (t, $J$ = 7.0 Hz, 2H), 3.03 – 2.94 (m, 1H), 2.49 – 2.35 (m, 1H), 2.35 – 2.20 (m, 1H), 2.08 – 1.96 (m, 1H), 1.96 – 1.83 (m, 1H), 1.75 – 1.57 (m, 2H). 

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.41, 162.35 (d, $J$ = 248.9 Hz), 133.99, 133.50 (d, $J$ = 8.3 Hz), 132.07, 126.05 (q, $J$ = 277.8 Hz), 123.26, 119.14 (d, $J$ = 3.5 Hz), 115.45 (d, $J$ = 22.0 Hz), 88.82 (d, $J$ = 1.3 Hz), 82.15, 39.12 (q, $J$ = 27.8 Hz), 37.46, 31.92, 26.17, 26.15 (q, $J$ = 2.9 Hz). 

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.15 (s, 3F), -111.49 (s, 1F). HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{22}$H$_{18}$F$_4$NO$_2$: 404.1268; found: 404.1267.

2-(6-(Thiophen-3-yl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5j): 5j was obtained as a colorless oil (45.4 mg, 58%) from alkene 1a and acetylenic triflone 2l. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 7.37 (dd, $J$ = 3.0, 1.1 Hz, 1H), 7.23 (dd, $J$ = 5.0, 3.0 Hz, 1H), 7.05 (dd, $J$ = 5.0, 1.2 Hz, 1H), 3.76 (t, $J$ = 7.1 Hz, 2H), 3.02 – 2.94 (m, 1H), 2.50 – 2.35 (m, 1H), 2.34 – 2.20 (m, 1H), 2.08 – 1.96 (m, 1H), 1.95 – 1.83 (m, 1H), 1.74 – 1.57 (m, 2H). 

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.41, 133.98, 132.08, 129.95, 128.42, 126.06 (q, $J$ = 277.9 Hz), 125.13, 123.26, 122.05, 88.73, 78.25, 39.11 (q, $J$ = 27.9 Hz), 37.48, 31.90, 26.21 (q, $J$ = 3.2 Hz), 26.17. 

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.15. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{20}$H$_{17}$F$_3$NO$_2$S: 392.0927; found: 392.0926.
2-(6-(6-Methoxynaphthalen-2-yl)-4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (5k): 5k was obtained as a colorless oil (58.7 mg, 63%) from alkene 1a and acetylenic triflone 2m. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.80 (m, 3H), 7.72 – 7.67 (m, 2H), 7.66 (d, $J = 8.8$ Hz, 1H), 7.63 (d, $J = 8.8$ Hz, 1H), 7.39 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.13 (dd, $J = 8.9$, 2.5 Hz, 1H), 7.08 (d, $J = 2.4$ Hz, 1H), 3.91 (s, 3H), 3.79 (t, $J = 7.0$ Hz, 2H), 3.09 – 2.99 (m, 1H), 2.54 – 2.39 (m, 1H), 2.38 – 2.24 (m, 1H), 2.14 – 2.01 (m, 1H), 2.00 – 1.87 (m, 1H), 1.78 – 1.60 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.44, 158.17, 133.99, 133.96, 132.09, 131.20, 129.24, 129.13, 128.44, 126.70, 126.14 (q, $J = 277.7$ Hz), 123.26, 119.30, 117.99, 105.76, 88.76, 83.61, 55.32, 39.24 (q, $J = 27.7$ Hz), 37.53, 32.04, 26.31 (q, $J = 3.0$ Hz), 26.25. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.06. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{27}$H$_{23}$F$_3$NO$_3$: 466.1625; found: 466.1626.
7. Synthetic Applications

To a solution of 3a (42.4 mg, 0.1 mmol) in THF (0.5 mL) was added TBAF (1.0 M in THF, 150 μL, 0.15 mmol) at 0 °C. The mixture was stirred for 12 h at 0 °C and further 12 h at room temperature. The reaction was quenched by addition of water (1.0 mL) and extracted with EtOAc. The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 20:1 to 5:1) to give 6 (27.5 mg, 89%) as a white solid.

2-(4-(2,2,2-trifluoroethyl)hex-5-yn-1-yl)isoindoline-1,3-dione (6): ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.80 (m, 2H), 7.75 – 7.68 (m, 2H), 3.72 (t, J = 7.1 Hz), 2.82 – 2.72 (m, 1H), 2.43 – 2.28 (m, 1H), 2.27 – 2.15 (m, 1H), 2.13 (d, J = 2.4 Hz, 1H), 2.04 – 1.90 (m, 1H), 1.88 – 1.75 (m, 1H), 1.66 – 1.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.39, 133.99, 132.06, 125.93 (q, J = 277.2 Hz), 123.27, 83.79, 71.10, 38.94 (q, J = 28.2 Hz), 37.37, 31.69, 26.00, 25.36 (q, J = 3.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃); δ -64.29. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₆H₁₅F₃NO₂: 310.1049; found: 310.1049.

To a 10 mL flask was added 4a (38.5 mg, 0.1 mmol) and Pd/C (7.1 mg, 0.01 mmol, 15% Pd) under N₂. The mixture was then evacuated and backfilled with H₂ for 3 times, following the addition of 1.0 mL MeOH by syringe. The mixture was then stirred at room temperature under 1
atm H₂ (H₂ balloon) for 2 h and filtered to remove insoluble materials. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel column chromatography (hexane/AcOEt = 20:1 to 5:1) to give 7 (38.5 mg, 99%) as a colourless oil.

![Image of compound 7]

2-(6,6,6-trifluoro-4-phenethylhexyl)isoindoline-1,3-dione (7): ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 7.30 – 7.22 (m, 2H), 7.20 – 7.12 (m, 3H), 3.68 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 8.2 Hz, 2H), 2.17 – 2.01 (m, 2H), 1.90 – 1.79 (m, 1H), 1.76 – 1.63 (m, 4H), 1.55 – 1.44 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.40, 141.71, 133.97, 132.09, 128.44, 128.28, 127.19 (q, J = 277.3 Hz), 125.93, 123.24, 37.95, 37.25 (q, J = 27.1 Hz), 35.18, 32.53, 31.76, 30.46, 25.22. ¹⁹F NMR (376 MHz, CDCl₃): δ -63.28. HRMS (ESI) ([M+H]⁺) Calcd. for C₂₂H₂₃F₃NO₂: 390.1675; found: 390.1675.

![Image of reaction scheme]

Compound 8 was prepared according to the method reported by Li and co-workers.³ To a solution of 4a (38.5 mg, 0.1 mmol) in 0.5 mL CF₃CH₂OH was added H₂O (4 µL, 0.2 mmol, 2 equiv) and CF₃SO₂H (2 µL, 0.02 mmol, 0.2 equiv). The mixture was stirred at 50 °C for 72 h and concentrated under reduced pressure to remove the volatile. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 20:1 to 5:1) to give 8 (37.1 mg, 92%) as a colourless oil.
2-(6,6,6-trifluoro-4-(2-oxo-2-phenylethyl)hexyl)isoindoline-1,3-dione (8): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 – 7.88 (m, 2H), 7.87 – 7.80 (m, 2H), 7.75 – 7.67 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 3.69 (t, $J = 7.2$ Hz, 2H), 3.10 (dd, $J = 17.5$, 6.3 Hz, 1H), 3.04 (dd, $J = 17.5$, 6.2 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.35 – 2.14 (m, 2H), 1.80 – 1.69 (m, 2H), 1.61 – 1.53 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.35, 168.35, 136.88, 133.94, 133.25, 132.08, 128.67, 127.94, 127.05 (q, $J = 278.7$ Hz), 123.23, 41.76, 37.78, 36.88 (q, $J = 27.4$ Hz), 30.98, 28.51 (q, $J = 2.2$ Hz), 25.72. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.88. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{22}$H$_{21}$F$_3$NO$_3$: 404.1468; found: 404.1467.
8. Mechanistic Studies

Radical clock experiment:

According to general procedure 1, a 10.0 mL microwave tube equipped with magnetic stir bar was charged with β-pinene 9 (0.2 mmol, 27.3 mg), acetylenic triflone 2a (0.24 mmol, 65.4 mg) and Togni’s reagent (I, 0.015 mmol, 4.8 mg) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). 4-methylmorpholine (NMM, 0.02 mmol, 2.2 μL) and degassed EtOAc (0.5 mL) were added by syringe under N₂. The tube was then sealed with a PTFE lined cap and stirred at 30 °C (oil bath) for 12 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography (petrol ether as eluent) to give the desired product 10 (53.1 mg, 77%) as a colorless oil.

tert-butyldimethyl(3-methyl-3-(4-(2,2,2-trifluoroethyl)cyclohex-3-en-1-yl)but-1-yn-1-yl)silane (10): ¹H NMR (400 MHz, CDCl₃) δ 128.93, 127.33 (q, J = 2.6 Hz), 126.24 (q, J = 277.6 Hz), 114.00, 82.26, 43.05, 41.76 (q, J = 28.8 Hz), 34.85, 29.70 (q, J = 0.9 Hz), 27.59, 27.25, 26.91, 26.09, 24.49, 16.56, -4.37. ¹³C NMR (101 MHz, CDCl₃) δ 168.44, 158.17, 133.99, 133.96, 132.09,
$^{13}$C labeling experiment:

$^{13}$C-labeled acetylenic triflone $2b'$ was prepared according to the previous report.\textsuperscript{4}

According to General Procedure 3: A 10.0 mL microwave tube equipped with magnetic stir bar was charged with alkene $1a$ (0.24 mmol, 51.6 mg), acetylenic triflone $2b'$ (0.2 mmol, 56.5 mg) and Togni’s reagent (I, 0.01 mmol, 3.2 mg) under air. The tube was evacuated and backfilled with N$_2$ for 3 times (3 × 5 min). 4-methylmorpholine (NMM, 0.02 mmol, 2.2 μL) and degassed EtOAc (0.5 mL) were added by syringe under N$_2$. The tube was then sealed with a PTFE lined cap and stirred at 30 °C (oil bath) for 12 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography (petrol ether/EtOAc = 50:1 to 10:1) to give the desired product $11a$ (62 mg, 81%) as a colorless oil.
(400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.81 (m, 2H), 7.74 – 7.67 (m, 2H), 7.42 – 7.34 (m, 2H), 7.32 – 7.24 (m, 3H), 3.77 (t, $J$ = 7.0 Hz, 2H), 3.05 – 2.95 (m, 1H), 2.51 – 2.36 (m, 1H), 2.35 – 2.21 (m, 1H), 2.10 – 1.98 (m, 1H), 1.96 – 1.84 (m, 1H), 1.76 – 1.58 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.42, 133.98, 132.08, 131.65 (d, $J$ = 1.8 Hz), 128.22 (d, $J$ = 5.6 Hz), 128.04 (d, $J$ = 1.5 Hz), 126.09 (q, $J$ = 277.1 Hz), 123.26, 123.08 (d, $J$ = 90.3 Hz), 89.28 (d, $J$ = 178.9 Hz), 83.17, 39.15 (qd, $J$ = 27.8, 1.9 Hz), 37.48, 31.95 (d, $J$ = 1.0 Hz), 26.21, 26.19 (dq, $J$ = 10.8, 3.1 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.10. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{21}$H$_{19}$F$_3$NO$_2$: 387.1396; found: 387.1394.

9. Reference.


10. NMR Spectra for All Compounds.
3x

O

O

Ph

CF₃

TBS

\[ \text{f1 (ppm)} \]

9.5  8.5  7.5  6.5  5.5  4.5  3.5  2.5  1.5  0.5  0.0  -0.5  -1.0

190 170 150 130 110  90  70  50  30  10  0

O

O

Ph

CF₃

TBS

3x

\[ \text{f1 (ppm)} \]
S106
S127