

**Supporting information.** Experimental procedures and full characterization for compounds (**1,2, 4-10**) IR, <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR spectra and analysis are available.

Experimental procedures and full characterization.

[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)OH]-**1**

A solution of EtMgBr (0.89 g, 36.6 mmol) in THF (120 mL) was added to a THF (20 mL) solution of 1-hexyne (2.54 g, 31 mmol) at room temperature. Further, the mixture was heated to 40°C. After one hour, at -78°C a THF solution (100mL) of 5.8 g (33.6 mmol) phenyl trifluoro methyl ketone was added dropwise in 1.5 hours, then stirred for 1.5 hours at 0°C. After hydrolysis by an aqueous NH<sub>4</sub>Cl solution, the organic phase was extracted by Et<sub>2</sub>O, then dried over MgSO<sub>4</sub>. After removing of the solvent and chromatography on silica gel column (Et<sub>2</sub>O, pentane 2:8) 7.1g of **1** were obtained (90% yield).

IR (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3486, 2966, 2940, 2878, 2238.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -80.8 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.94 (t, J = 7.0 Hz, 3 H), 1.51 (m, 4H), 2.32 (t, J = 7.0Hz, 2H), 7.5 (m, 5H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.4, 18.3, 21.8, 30.1, 72.7 (q, <sup>2</sup>J<sub>CF</sub> = 32.0Hz), 89.4, 99.9, 123.4 (q, <sup>1</sup>J<sub>CF</sub> = 285.0Hz), 121.1, 127.2, 127.9, 129.1, 135.9.

Analysis for C<sub>14</sub>H<sub>15</sub>OF<sub>3</sub> calcd. C 65.62, H 5.9; found C 64.69, H 5.58.

[(Co<sub>2</sub>(CO)<sub>6</sub>)[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)OH]]-**2**

To a solution of Co<sub>2</sub>(CO)<sub>8</sub> (2.67 g, 7.8 mmol) in 50 mL Et<sub>2</sub>O was added 2g (7.8 mmol) of **1** at room temperature. In one hour, the reaction was complete. After removing of the solvent, the residue was chromatographed on silica gel column (Et<sub>2</sub>O, pentane 1:9) and 4.1 g of **2** were obtained in 97% yield.

IR (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3612, 3073, 2940, 2086, 2046, 2018, 1721.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -73.9 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.99 (t, J=7.0Hz, 3H), 1.62 (m, 4H), 2.80 (m, 2H), 7.32 (m, 3H), 7.69 (m, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.8, 22.6, 32.7, 33.9, 78.9 (q, <sup>2</sup>J<sub>CF</sub> = 29.0Hz), 96.9, 101.3, 125.0 (q, <sup>1</sup>J<sub>CF</sub> = 287.6Hz), 125.1, 125.2, 128.6, 129.0, 139.8, 203.1.

Analysis for C<sub>20</sub>H<sub>15</sub>O<sub>7</sub>F<sub>3</sub>Co<sub>2</sub> calcd. C 44.31, H 2.80; found C 44.09, H 2.91.

[(Co<sub>2</sub>(CO)<sub>6</sub>)[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)]]BF<sub>4</sub> -**3**

To a solution of **2** (0.5g, 9.2 mmol) in 10 mL Et<sub>2</sub>O, was added at -20°C 1 mL of the complex HBF<sub>4</sub>/Et<sub>2</sub>O. The mixture was left to attain room temperature and stirred for 1 hour. The insoluble red-brown formed oil was washed five times with Et<sub>2</sub>O and dried under vacuum leading to **3** (0.39 g, 70% yield). The ethereal layer contains 0.15 g of **2**.

The carbenium ion **3** is very sensitive to moisture, in presence of water it leads to the starting material **2**.

<sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ ppm: -58.5 (s), -151.6 (m).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ ppm: 2.96 (m, 3H), 3.51 (m, 2H), 3.83 (m, 2H), 4.90 (m, 2H), 9.50 (m, 5H).

[(Co<sub>2</sub>(CO)<sub>6</sub>)[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)NHCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>]]-**4**

To a solution of the carbenium ion **3** (4 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 0.178 g (2 mmol) of methyl glycinate. The reaction was achieved in 5 mn, after hydrolysis and extraction by Et<sub>2</sub>O, the organic layer was dried under MgSO<sub>4</sub>. Two products were recovered by chromatography on silica gel column (Et<sub>2</sub>O, pentane, 1:9) the less polar (0.038g, 8%yield) was identified as: [(Co<sub>2</sub>(CO)<sub>6</sub>)[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)H]]-**10**. The more polar (0.35g, 61% yield) as [(Co<sub>2</sub>(CO)<sub>6</sub>)[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)NHCH<sub>2</sub>CO<sub>2</sub>Me]]-**4**

compound **4**: IR (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3441, 2085, 2066, 2048, 2021, 1751.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -64.2 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.94 (t, J = 7.1Hz, 3H), 1.44 (m, 2H), 1.53 (m, 2H), 2.53 (d, J = 6.2Hz, 1H), 2.63 (m, 2H), 3.53 (d, J = 6.2Hz, 2H), 3.75 (s, 3H), 7.29-7.66 (m, 5H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.8, 22.5, 32.8, 33.8 (q, <sup>6</sup>J<sub>CF</sub> = 6.2Hz), 45.3, 52.0, 68.3 (q, <sup>2</sup>J<sub>CF</sub> = 26.0Hz), 84.7, 100.5, 126.3 (q, <sup>1</sup>J<sub>CF</sub> = 283.0Hz), 126.7, 128.8, 138.2, 178.1.

Analysis for C<sub>23</sub>H<sub>20</sub>NO<sub>3</sub>F<sub>3</sub>Co<sub>2</sub> calcd. C 45.05, H 3.29, N 2.28; found C 44.11, H 3.89, N 1.88.

[(Co<sub>2</sub>(CO)<sub>6</sub>)[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)NHCH(CH<sub>3</sub>)(C<sub>2</sub>O<sub>2</sub>CH<sub>3</sub>)]]-**5**

The same procedure was used as for product **4** using methyl alaninate. Two fractions were separated by column chromatography on silica gel (Et<sub>2</sub>O, pentane, 1:9). The less polar (9% yield) was identified as **10**, the more polar was obtained in 52% yield as a mixture of diastereomers **5a**, **5b**.

(**5a+5b**): IR (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 2083, 2047, 2020, 1736.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -65.2 (s), -64.9 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.94 (t, J = 7.0Hz, 3H), 1.33 (d, J = 7.0Hz, 3H), 1.42-1.60 (m, 4H), 2.40 (d, J = 7.0Hz, 1H), 2.67 (m, 2H), 3.48 (m, 1H), 3.68 (s, 3H), 7.32 (m, 3H), 7.54 (m, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.9, 22.6, 32.7, 33.8, 54.1, 84.8 (q, <sup>2</sup>J<sub>CF</sub> = 26.0Hz), 94.3, 101.1, 125.4 (q, <sup>1</sup>J<sub>CF</sub> = 292.0Hz), 126.1, 128.7, 128.9, 137.7, 177.6, 202.2.

Analysis for C<sub>24</sub>H<sub>22</sub>O<sub>8</sub>NF<sub>3</sub>Co<sub>2</sub> calcd. C 45.95, H 3.54, N 2.24 found C 46.41, H 3.61, N 2.15.

[(Co<sub>2</sub>(CO)<sub>6</sub>][CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)NHCH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)]-**6a**, **6b**

The same procedure was used as for product **4**, using (S)-(+)-methyl-benzyl-amine. Three products were separated by column chromatography on silica gel (Et<sub>2</sub>O, pentane, 1:9). The less polar (10% yield) was identified as **10**. Two diastereomers were separated, the less polar **6a** in 24% yield, the most polar **6b** in 30% yield.

compound **6a**:

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -64.5 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.95 (t, J = 7.0Hz, 3H), 1.44 (d, J = 6.7Hz, 3H), 1.45 (m, 2H), 1.50 (m, 2H), 2.10 (d, J = 6.6Hz, 1H), 2.65 (m, 2H), 3.95 (qd, J = 6.7, 6.6Hz, 1H), 7.09-7.41 (m, 10H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.7, 22.4, 32.9, 33.4, 53.3, 70.3 (q, <sup>2</sup>J<sub>CF</sub> = 30.1Hz), 98.6, 102.1, 125.4, 125.7, 126.7, 127.9, 136.3 (q, <sup>1</sup>J<sub>CF</sub> = 271.1Hz), 138.7, 148.1.

Analysis for C<sub>28</sub>H<sub>24</sub>O<sub>6</sub>NF<sub>3</sub>Co<sub>2</sub> calcd. C 52.11, H 3.75, N 2.17; found C 52.41, H 3.95, N 2.07.

[α]<sub>D</sub> = +18.2 (c = 0.55, CH<sub>2</sub>Cl<sub>2</sub>).

compound **6b**:

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -63.6 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.95 (t, J = 7.0Hz, 3H), 1.35 (d, J = 6.7Hz, 3H), 1.40-1.60 (m, 4H), 2.32 (d, J = 6.8Hz, 1H), 2.67 (m, 2H), 3.96 (qd, J = 6.7, 6.8Hz, 1H), 7.20-7.81 (m, 10H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.7, 24.6, 26.9, 33.6, 54.1, 70.6 (q, <sup>2</sup>J<sub>CF</sub> = 27.0Hz), 93.5, 99.4, 125.8, 127.0, 128.2, 132.9 (q, <sup>1</sup>J<sub>CF</sub> = 277.0Hz), 135.9, 145.3, 186.2.

Analysis for C<sub>28</sub>H<sub>24</sub>O<sub>6</sub>NF<sub>3</sub>Co<sub>2</sub> calcd. C 52.11, H 3.75, N 2.17; found C 51.13, H 4.06, N 2.04.

[α]<sub>D</sub> = -14.5 (c = 0.55, CH<sub>2</sub>Cl<sub>2</sub>).

CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)NHCH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)]-**7a**, **7b**

0.1g (0.18 mmol) of **6a** or **6b**, 1.5 g of silica gel and 0.1 g of ceric ammonium nitrate were mixed in 10 mL of methanol at -78°C and stirred for two hours at -20°C. After addition of water, the mixture was filtered under celite. The filtrate was extracted with Et<sub>2</sub>O. The organic layer was washed and dried under MgSO<sub>4</sub>. After removing of the solvent and chromatography on silica gel plates (Et<sub>2</sub>O, pentane 2:8) 0.046g of **7a** (83% yield) or 0.048 g of **7b** (87% yield) was obtained.

compound **7a**:

IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 3266, 3109, 2968, 2878, 2234.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -77.5 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.90 (t, J = 7.1Hz, 3H), 1.20 (d, J = 6.8Hz, 3H), 1.40-1.60 (m, 4H), 1.45 (broad, 1H), 2.07 (t, J = 6.8Hz, 2H), 3.96 (q, J = 6.8Hz, 1H), 7.10-7.60 (m, 10H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.6, 18.3, 21.9, 25.7, 30.3, 54.1, 65.0, 75.0, 90.4, 124.4 (q, <sup>1</sup>J<sub>CF</sub> = 285.0Hz), 126.0, 126.3, 126.5, 127.9, 128.1, 128.6, 128.9, 129.1, 129.2, 129.4, 136.2, 146.5.

Analysis for C<sub>22</sub>H<sub>24</sub>NF<sub>3</sub> calcd. C 73.52, H 6.73; found C 72.35, H 6.81.

[α]<sub>D</sub> = +22.2 (c = 0.55, CH<sub>2</sub>Cl<sub>2</sub>).

compound **7b**:

IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 3266, 3109, 2968, 2878, 2234.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -77.6 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.97 (t, J = 7.3Hz, 3H), 1.40-1.60 (m, 4H), 1.47 (d, J = 6.8Hz, 3H), 1.83 (broad, 1H), 2.37 (t, J = 7.1Hz, 2H), 3.93 (q, J = 6.8Hz, 1H), 7.10-7.60 (m, 10H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.6, 18.5, 22.0, 25.7, 30.5, 53.9, 65.0, 76.6, 89.3, 125.4 (q, <sup>1</sup>J<sub>CF</sub> = 284.6Hz), 126.2, 126.4, 127.5, 127.7, 128.1, 128.6, 128.9, 129.1, 129.2, 129.4, 134.6, 146.7.

Analysis for C<sub>22</sub>H<sub>24</sub>NF<sub>3</sub> calcd. C 73.52, H 6.73; found C 73.21, H 6.63.

[α]<sub>D</sub> = -25.2 (c = 0.55, CH<sub>2</sub>Cl<sub>2</sub>).

[(Co<sub>2</sub>(CO)<sub>6</sub>][CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)CH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>)]-**8**

To a solution of the carbenium ion **3** (4 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> at -10°C was added 0.38 g (0.2 mmol) of 1-phenyl-1-(trimethylsilyloxy)-ethylene in 5 mL CH<sub>2</sub>Cl<sub>2</sub>. After stirring ten minutes and hydrolysis, the organic layer was washed and dried under MgSO<sub>4</sub>. The crude product was

chromatographed on silica gel plates (Et<sub>2</sub>O, pentane 1:9) leading to 0.35 g (60% yield) of the product **8**.

IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 2084, 2041, 2013, 1705.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -62.5 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.98 (t, J = 7.0Hz, 3H), 1.56 (m, 4H), 2.81 (m, 2H), 4.07 (d, J = 17.8Hz, 1H), 4.27 (d, J = 17.8Hz, 1H), 7.46 (m, 8H), 7.95 (m, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.9, 22.6, 33.6, 34.0, 44.6, 55.2 (q, <sup>2</sup>J<sub>CF</sub> = 24.4Hz), 127.2 (q, <sup>1</sup>J<sub>CF</sub> = 285.4Hz), 127.9, 128.0, 128.4, 128.3, 137.0, 138.9, 193.4.

Analysis for C<sub>28</sub>H<sub>21</sub>O<sub>7</sub>F<sub>3</sub>Co<sub>2</sub> calcd. C 52.20, H 3.29; found C 53.10, H 3.31.

[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)CH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>]-**9**

The same procedure was used as for **7**, product **9** was obtained in 88% yield starting from **8**.

IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 3266, 3109, 2968, 2878, 2234. 1685.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -74.3 (s).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.88 (t, J = 7.2Hz, 3H), 1.39 (sx, J = 7.2Hz, 2H), 1.48 (qui, J = 7.2Hz, 2H), 2.33 (t, J = 7.0Hz, 2H), 3.92 (d, J = 16.8Hz, 1H), 3.98 (d, J = 16.8Hz, 1H), 7.45-7.95 (m, 10H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.5, 18.4, 21.8, 30.4, 42.1, 48.8, 75.3, 88.2, 125.6 (q, <sup>1</sup>J<sub>CF</sub> = 283.0Hz), 127.9, 128.1, 128.2, 128.5, 133.2, 134.7, 137.1, 193.3.

Analysis for C<sub>22</sub>H<sub>21</sub>OF<sub>3</sub> calcd. C 73.73, H 5.91; found C 73.59, H 5.78.

[Co<sub>2</sub>(CO)<sub>6</sub>CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CC(C<sub>6</sub>H<sub>5</sub>)(CF<sub>3</sub>)H]-**10**

IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 2085, 2043, 2011.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ ppm: -65.7 (d, <sup>2</sup>J<sub>FH</sub> = 9.0Hz).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.89 (t, J = 7.2Hz, 3H), 1.39-1.54 (m, 4H), 2.67 (m, 2H), 4.54 (q, J = 9.0Hz, 1H), 7.31 (s, 5H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 13.8, 22.6, 33.0, 33.7, 53.7 (q, <sup>2</sup>J<sub>CF</sub> = 27.0Hz), 94.64, 101.2, 126.3 (q, <sup>1</sup>J<sub>CF</sub> = 276.0Hz), 128.5, 128.9, 136.2.

Analysis for C<sub>20</sub>H<sub>15</sub>F<sub>3</sub>Co<sub>2</sub> calcd. C 55.84, H 3.51; found C 55.32, H 3.46.