

## Supporting Information

### A modular synthesis of $\alpha$ -aryl $\beta$ -perfluoroalkyl ketones via *N*-heterocyclic carbene catalysis

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## General Information:

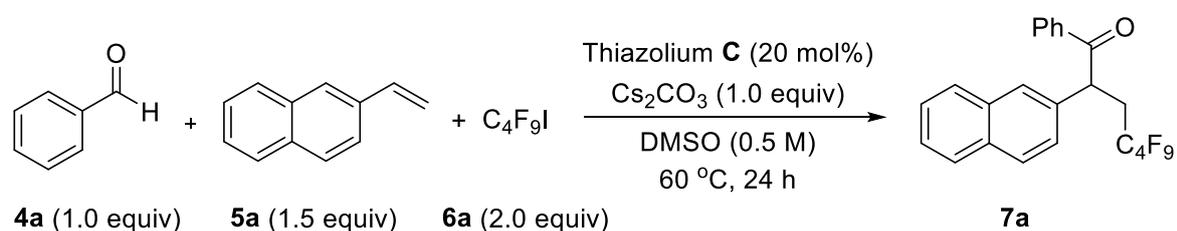
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker AVANCE III 400 MHz Superconducting Fourier and were internally referenced to residual protio solvent signal (note:  $\text{CDCl}_3$  referenced at  $\delta$  7.26 ppm for  $^1\text{H}$  NMR and  $\delta$  77.16 ppm for  $^{13}\text{C}$  NMR, respectively). Data for  $^1\text{H}$  NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Thermo-Fisher Nicolet 6700 spectrometer. High-resolution mass spectrometry data were recorded on an Thermo Scientific Q Exactive instrument using direct injection of samples in dichloromethane into the electrospray source (ESI) or atmosphere pressure chemical ionization (APCI) with positive or negative ionization.

All reactions were carried out under an inert atmosphere of nitrogen in oven dried or flame dried glassware with magnetic stirring, unless otherwise noted. DMSO, aldehyde, alkene and perfluoroalkyl reagent were used as obtained from commercial sources, unless otherwise indicated. Trifluoromethyl iodide ( $\text{CF}_3\text{I}$ ) was purchased as a 3 M solution in DMSO. Thiazoliums **C1-C3** were prepared according to literature.<sup>1</sup> Reactions were monitored by thin-layer chromatography (TLC) and carried out on 0.25 mm coated commercial silica gel plates using UV light as visualizing agent. Flash chromatography was performed on silica gel (Silicycle, SiliaFlash P60, 200-300 mesh).

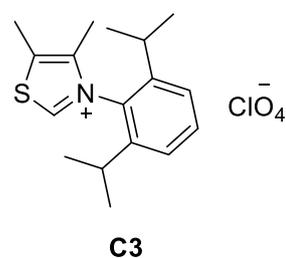
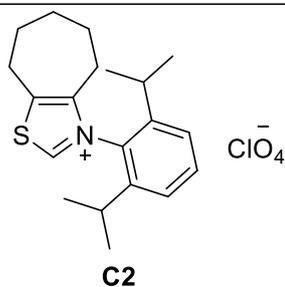
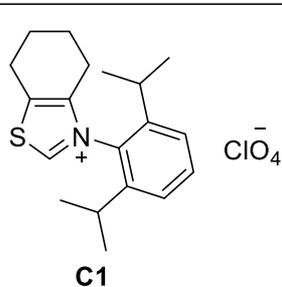
## Optimization details:

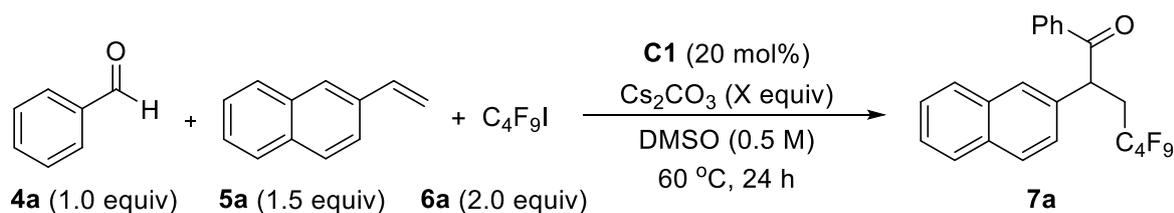
To an 8-mL glass vial equipped with magnetic stir bar were sequentially added benzaldehyde **4a** (0.2 mmol, 1.0 equiv), 2-vinylnaphthalene **5a** (0.3 mmol, 1.5 equiv), thiazolium **C** (5-25 mol%) and perfluorobutyl iodide **6a** (0.4 mmol, 2.0 equiv) and DMSO (0.4 mL). The vial was sealed with a Teflon septum and then the resulting mixture was degassed via “freeze, pump, thaw” operation. The glass vial was brought into a glove box and Cs<sub>2</sub>CO<sub>3</sub> (0.1-2.0 equiv) was added. Sealed the glass vial and took the vial out from the glove box. The reaction mixture was stirred at specified temperature for 24 h. After 24 h, the yield was determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. The results were summarized in **Table S1-S7**.

**Table S1** Screening of thiazolium **C**

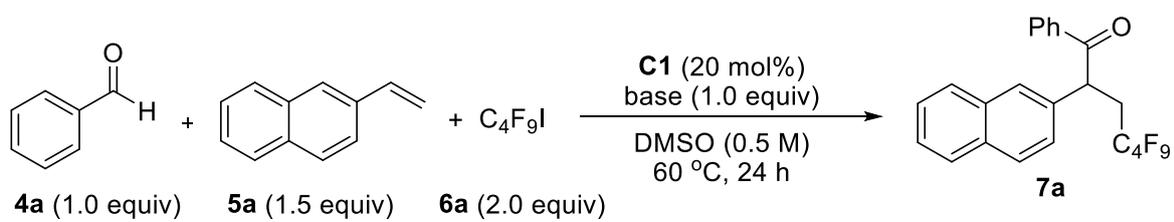


Thiazolium <b>C</b> (20 mol%)	Conv ( <b>4a</b> , %)	yield ( <b>7a</b> , %)
<b>C1</b>	97	72
<b>C2</b>	100	53
<b>C3</b>	100	54

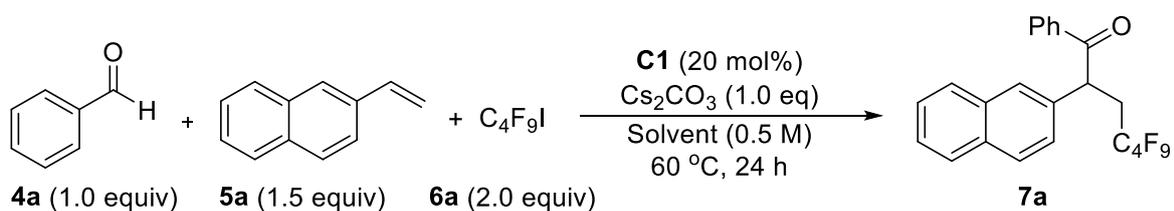


**Table S2** Screening of Cs<sub>2</sub>CO<sub>3</sub> equivalent

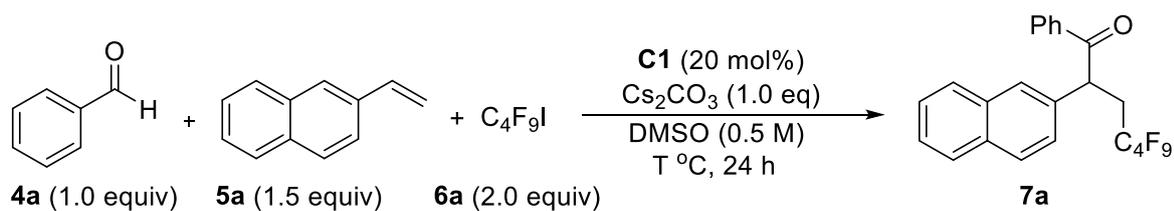
Cs <sub>2</sub> CO <sub>3</sub> (X equiv)	Conv ( <b>4a</b> , %)	yield ( <b>7a</b> , %)
0.1	27	8
0.5	75	45
<b>1.0</b>	<b>97</b>	<b>72</b>
1.5	96	65
2.0	97	62

**Table S3** Screening of base

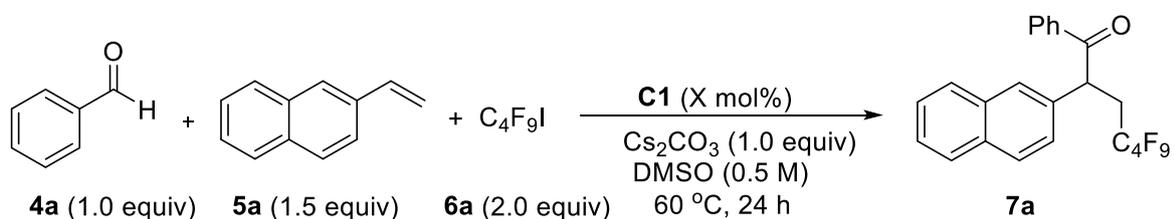
base (1.0 equiv)	Conv ( <b>4a</b> , %)	yield ( <b>7a</b> , %)
<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>97</b>	<b>72</b>
K <sub>2</sub> CO <sub>3</sub>	99	59
Na <sub>2</sub> CO <sub>3</sub>	99	30

**Table S4** Screening of solvent

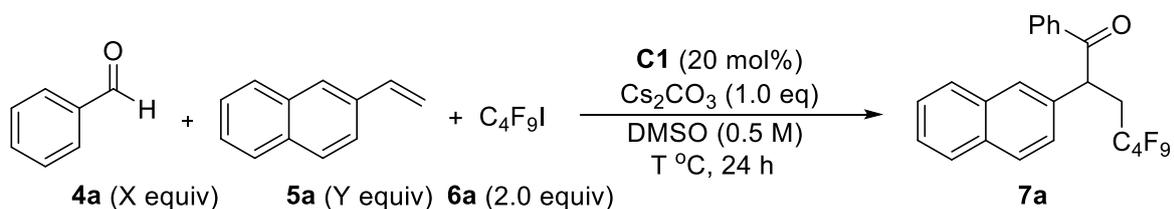
Solvent (0.5 M)	Conv ( <b>4a</b> , %)	yield ( <b>7a</b> , %)
<b>DMSO</b>	<b>97</b>	<b>72</b>
NMP	97	63
DMF	97	60
CH <sub>3</sub> CN	97	24

**Table S5** Screening of temperature

T (°C)	Conv ( <b>4a</b> , %)	yield ( <b>7a</b> , %)
20	88	66
40	92	70
<b>60</b>	<b>97</b>	<b>72</b>
80	94	59

**Table S6** Screening of **C1** loading

<b>C1</b> loading (X mol%)	Conv ( <b>4a</b> , %)	yield ( <b>7a</b> , %)
5%	50	27
10%	76	57
<b>20%</b>	<b>97</b>	<b>72</b>
25%	98	79

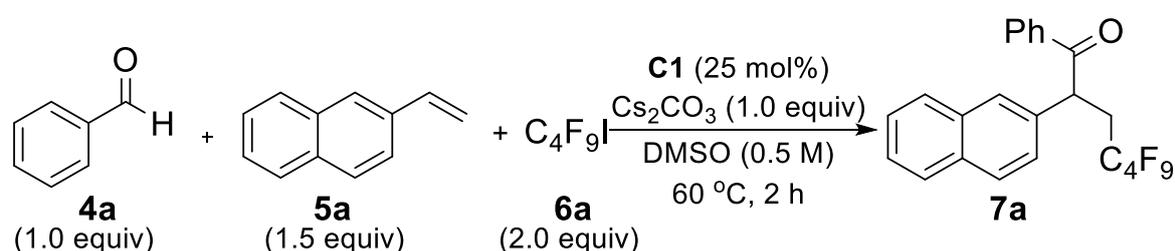
**Table S7** Comparison between aldehyde and alkene as limiting reagent

<b>4a</b> (X equiv) and <b>5a</b> (Y equiv)	Conv ( <b>4a</b> or <b>5a</b> , %)	yield ( <b>7a</b> , %)
<b>4a</b> (1.0 equiv) and <b>5a</b> (1.5 equiv)	<b>97</b>	<b>72</b>
<b>4a</b> (1.5 equiv) and <b>5a</b> (1.0 equiv)	100	36

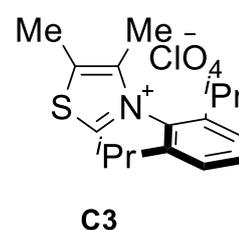
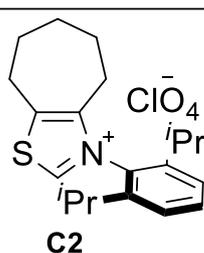
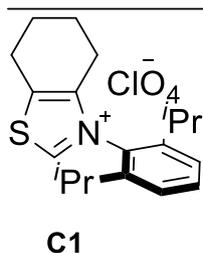
## Control experiments:

To an 8-mL glass vial equipped with magnetic stir bar were sequentially added benzaldehyde **4a** (0.2 mmol, 1.0 equiv), 2-vinylnaphthalene **5a** (0.3 mmol, 1.5 equiv), thiazolium **C** (25 mol%) and perfluorobutyl iodide **6a** (0.4 mmol, 2.0 equiv) and DMSO (0.4 mL). The vial was sealed with a Teflon septum and then the resulting mixture was degassed via “freeze, pump, thaw” operation. The glass vial was brought into a glove box and Cs<sub>2</sub>CO<sub>3</sub> (1.0 equiv) was added. Sealed the glass vial and took the vial out from the glove box. The reaction mixture was stirred at 60 °C for 2 h. After 2 h, the yield was determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. The results were summarized in **Table S8**.

**Table S8** Control experiments

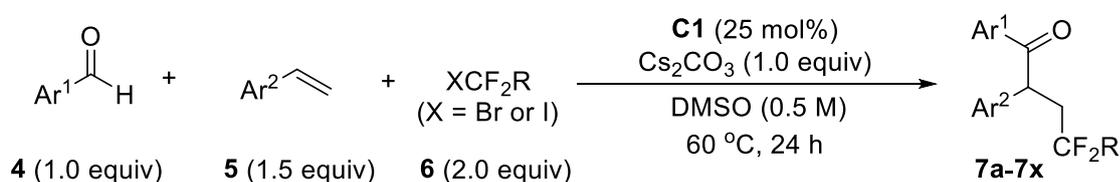


Entry	Variation from "standard" conditions	Conv. ( <b>4a</b> , %)	Yield ( <b>7a</b> , %)
1	none	97	80 (78)
2	0.5 eq base	63	45
3	K <sub>2</sub> CO <sub>3</sub>	77	41
4	<b>C2</b>	98	53
5	<b>C3</b>	98	70
6	10% of <b>C1</b>	65	44
7	CH <sub>3</sub> CN	69	27



## Synthesis and Characterization of products:

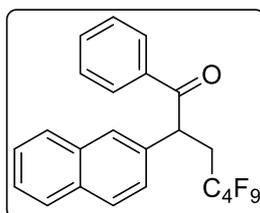
### General Procedure



General Procedure: To an 8-mL glass vial equipped with magnetic stir bar were sequentially added **4** (0.2 mmol, 1.0 equiv), **5** (0.3 mmol, 1.5 equiv), thiazolium **C1** (0.05 mmol, 1.0 equiv), perfluoroalkyl reagent (0.4 mmol, 2.0 equiv,  $\text{CF}_3\text{I}$  used as a 3 M solution in DMSO (133  $\mu\text{L}$ )) and DMSO (0.4 mL, 267  $\mu\text{L}$  of DMSO was used for  $\text{CF}_3\text{I}$ ). The vial was sealed with a Teflon septum. The resulting mixture was degassed via “freeze, pump, thaw” operation. The glass vial was brought into a glove box and  $\text{Cs}_2\text{CO}_3$  (65 mg, 0.2 mmol) was added. Sealed the glass vial and took the vial out from the glove box. The mixture was then stirred at 60 °C for 24 h. The mixture was diluted with dichloromethane (20 mL) and washed with  $\text{H}_2\text{O}$  (20 mL  $\times$  3). The organic phase was concentrated under reduced pressure and purified by flash column chromatography to afford the **7w-7x**. (Note: The product in reaction mixture will not decompose over time, so the reaction time was fixed to be 24 h for removing the trouble of repeatedly monitoring the reaction.)

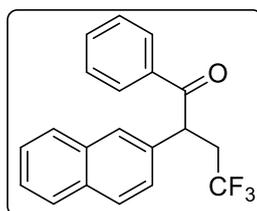
### Characterization Data

#### 4, 4, 5, 5, 6, 6, 7, 7, 7-Nonafluoro-2-(naphthalen-2-yl)-1-phenylheptan-1-one (**7a**)



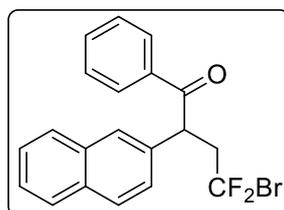
Prepared according to General Procedure using 2-vinylnaphthalene, benzaldehyde and perfluorobutyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7a** (75.0 mg, 78% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19-7.94 (m, 2H), 7.93-7.70 (m, 4H), 7.67-7.31 (m, 6H), 5.21 (dd,  $J$  = 8.2, 4.2 Hz, 1H), 3.73-3.36 (m, 1H), 2.71-2.32 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.70, 135.75, 135.17, 133.73, 133.56, 132.83, 129.60, 129.01, 128.85, 127.99, 127.83, 127.34, 126.73, 126.57, 125.70, 45.87, 34.51 (t,  $J$  = 20.9 Hz), Signals corresponding to the perfluorobutyl moiety were not resolvable due to their anticipated weak intensity;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -(79.27-82.19) (m, 3F), -(110.91-114.57) (m, 2F), -(124.27-124.38) (m, 2F), -(125.29-126.97) (m, 2F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{14}\text{F}_9\text{O}$  (M-H) $^-$  477.09064, found 477.09042.

#### 4,4,4-Trifluoro-2-(naphthalen-2-yl)-1-phenylbutan-1-one (7b)



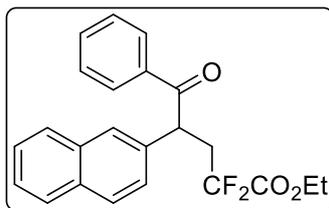
Prepared according to General Procedure using 2-vinylnaphthalene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7b** (53.0 mg, 81% yield), IR (film) 3321, 2842, 1669, 1236, 1051, 958, 732, 688, 541  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.01 (m, 2H), 7.85-7.79 (m, 4H), 7.51-7.38 (m, 6H), 5.11 (dd,  $J = 7.6, 5.5$  Hz, 1H), 3.50-3.36 (m, 1H), 2.74-2.60 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.78, 135.81, 134.94, 133.70, 133.51, 132.81, 129.47, 128.98, 128.80, 127.96, 127.80, 127.36, 126.66, 126.58 (q,  $J = 276.0$  Hz), 126.49, 125.70, 47.45 (q,  $J = 2.0$  Hz), 37.53 (q,  $J = 28.3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.45 (t,  $J = 10.8$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{14}\text{F}_3\text{O}$  (M-H) $^-$  327.10022, found 327.10014.

#### 4-Bromo-4, 4-difluoro-2-(naphthalen-2-yl)-1-phenylbutan-1-one (7c)



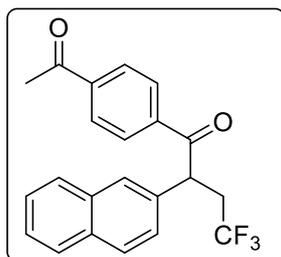
Prepared according to General Procedure using 2-vinylnaphthalene, benzaldehyde and dibromodifluoromethane as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7c** (31.0 mg, 40% yield), IR (film) 2863, 1745, 1142, 1084, 978, 747, 630, 548, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.00 (m, 2H), 7.83-7.76 (m, 4H), 7.52-7.38 (m, 6H), 5.18 (dd,  $J = 7.6, 4.5$  Hz, 1H), 3.86-3.74 (m, 1H), 2.97-2.85 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.74, 135.93, 134.92, 133.69, 133.51, 132.80, 129.49, 129.01, 128.83, 127.97, 127.80, 127.40, 126.67, 126.50, 125.79, 121.77 (t,  $J = 304.7$  Hz), 48.97 (t,  $J = 2.3$  Hz), 47.66 (t,  $J = 21.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -(42.18-43.73) (m, 2F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{16}\text{BrF}_2\text{O}$  (M+H) $^+$  389.03471, found 389.03418.

#### Ethyl 2,2-difluoro-4-(naphthalen-2-yl)-5-oxo-5-phenylpentanoate (7d)



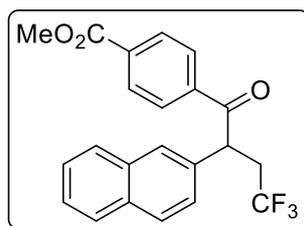
Prepared according to General Procedure using 2-vinylnaphthalene, benzaldehyde and ethyl bromodifluoroacetate as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/25) to afford **7d** (47.4 mg, 62% yield), IR (film) 1711, 1312, 1164, 955, 732, 697, 594, 516  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-7.98 (m, 2H), 7.84-7.74 (m, 4H), 7.40-7.34 (m, 6H), 5.15 (dd,  $J = 7.9, 4.9$  Hz, 1H), 4.17-3.94 (m, 2H), 3.46-3.31 (m, 1H), 2.72-2.59 (m, 1H), 1.18 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.31, 163.88 (t,  $J = 32.5$  Hz), 135.91, 135.29, 133.63, 133.35, 132.72, 129.29, 128.97, 128.73, 127.91, 127.74, 127.50, 126.59, 126.41, 125.94, 115.45 (t,  $J = 250.7$  Hz), 63.03, 47.14 (t,  $J = 3.8$  Hz), 38.33 (t,  $J = 23.4$  Hz), 13.77;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -(103.40-105.05) (m, 2F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{20}\text{F}_2\text{O}_3\text{Na}$  ( $\text{M}+\text{Na}$ ) $^+$  405.12727, found 405.12695.

#### 1-(4-Acetylphenyl)-4,4,4-trifluoro-2-(naphthalen-2-yl)butan-1-one (**7e**)



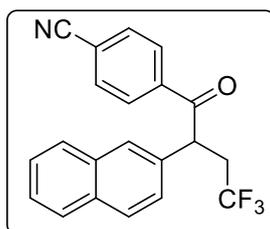
Prepared according to General Procedure using 2-vinylnaphthalene, 4-acetylbenzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford **7e** (41.0 mg, 55% yield), IR (film) 1654, 1376, 1063, 916, 852, 617, 571, 524  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.5$  Hz, 2H), 7.93 (d,  $J = 8.5$  Hz, 2H), 7.85-7.76 (m, 3H), 7.73 (d,  $J = 1.8$  Hz, 1H), 7.52-7.43 (m, 2H), 7.41 (dd,  $J = 8.5, 1.9$  Hz, 1H), 5.06 (dd,  $J = 7.6, 5.5$  Hz, 1H), 3.49-3.33 (m, 1H), 2.74-2.59 (m, 1H), 2.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.33, 196.28, 140.35, 139.01, 134.27, 133.68, 132.86, 129.69, 129.15, 128.62, 127.94, 127.83, 127.48, 126.81, 126.68, 126.45 (q,  $J = 275.5$  Hz), 125.54, 47.96 (q,  $J = 2.2$  Hz), 37.39 (q,  $J = 28.4$  Hz), 26.93;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.48 (t,  $J = 10.7$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{16}\text{F}_3\text{O}_2$  ( $\text{M}-\text{H}$ ) $^-$  369.11079, found 369.11130.

#### Methyl 4-(4,4,4-trifluoro-2-(naphthalen-2-yl)butanoyl)benzoate (**7f**)



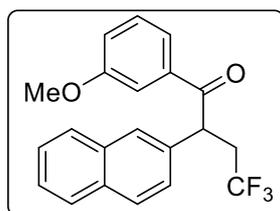
Prepared according to General Procedure using 2-vinylnaphthalene, methyl 4-formylbenzoate and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/25) to afford **7f** (41.7 mg, 54% yield), IR (film) 2815, 1545, 1269, 984, 798, 635, 598, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10-8.00 (m, 4H), 7.83-7.74 (m, 4H), 7.48-7.40 (m, 3H), 5.07 (dd,  $J = 7.6, 5.5$  Hz, 1H), 3.89 (s, 3H), 3.48-3.33 (m, 1H), 2.73-2.59 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.33, 166.05, 139.06, 134.28, 134.16, 133.66, 132.84, 130.59, 129.96, 129.65, 128.83, 126.46 (q,  $J = 276.1$  Hz), 127.92, 127.81, 126.78, 126.64, 125.53, 52.54, 47.91 (q,  $J = 2.5$  Hz), 37.41 (q,  $J = 28.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.47 (t,  $J = 10.6$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{16}\text{F}_3\text{O}_3$  (M-H) $^-$  385.1057, found 385.10638.

#### 4-(4,4,4-Trifluoro-2-(naphthalen-2-yl)butanoyl)benzonitrile (**7g**)



Prepared according to General Procedure using 2-vinylnaphthalene, 4-cyanobenzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/20) to afford **7g** (30.2 mg, 39% yield),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11-8.01 (m, 2H), 7.88-7.75 (m, 3H), 7.74-7.63 (m, 3H), 7.54-7.44 (m, 2H), 7.39 (dd,  $J = 8.5, 1.9$  Hz, 1H), 5.01 (dd,  $J = 7.6, 5.3$  Hz, 1H), 3.49-3.32 (m, 1H), 2.76-2.57 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.49, 138.85, 133.78, 133.67, 132.92, 132.64, 129.90, 129.30, 127.92, 127.87, 127.48, 126.96, 126.85, 126.34 (q,  $J = 275.5$  Hz), 125.36, 117.80, 116.70, 48.02 (q,  $J = 2.4$  Hz), 37.36 (q,  $J = 28.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.51 (t,  $J = 10.6$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{13}\text{F}_3\text{NO}$  (M-H) $^-$  352.09547, found 352.09604.

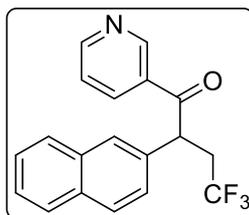
#### 4,4,4-Trifluoro-1-(3-methoxyphenyl)-2-(naphthalen-2-yl)butan-1-one (**7h**)



Prepared according to General Procedure using 2-vinylnaphthalene, 3-methoxybenzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/25) to afford **7h** (50.9 mg, 71% yield), IR (film) 2843, 1695, 1302, 944, 896, 748, 691, 528, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.68 (m, 4H), 7.58-7.52 (m, 1H), 7.51-7.47 (m, 1H), 7.46-7.36 (m, 3H), 7.30-7.17 (m, 1H), 7.02-6.94 (m, 1H), 5.06-4.98 (m, 1H), 3.74 (s, 3H), 3.44-3.27 (m, 1H), 2.70-2.52 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.59, 159.95, 137.13, 134.95, 133.69, 132.81, 129.76, 129.47, 127.96, 127.80, 127.31, 126.66, 126.49, 126.55 (q,  $J = 275.7$  Hz), 125.69, 121.51, 119.98, 113.39, 55.47, 47.57 (q,  $J = 2.2$  Hz), 37.55 (q,  $J = 28.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 3F)  $\delta$  -(64.40-64.54) (m, 3F) HRMS (APCI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{F}_3\text{O}_2$  (M-H) $^-$  357.11078, found 357.11087.

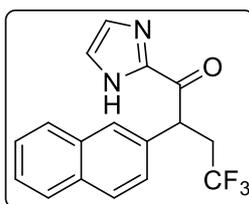
Scale-up experiment: The reaction was set up in 25 ml reaction tube and operated according to General Procedure; 1.84 mmol of 3-methoxybenzaldehyde was used and **7h** was obtained in 62% isolated yield (0.41 g).

#### 4,4,4-Trifluoro-2-(naphthalen-2-yl)-1-(pyridin-3-yl)butan-1-one (**7i**)



Prepared according to General Procedure using 2-vinylnaphthalene, 3-pyridinecarboxaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/3) to afford **7i** (39.2 mg, 60% yield), IR (film), 2945, 1615, 1124, 994, 737, 728, 685, 614, 548, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.95-9.05 (brs, 1H), 9.07-8.35 (brs, 1H), 8.33-8.20 (m, 1H), 7.88-7.72 (m, 4H), 7.56-7.27 (m, 4H), 5.05-4.99 (m, 1H), 3.50-3.31 (m, 1H), 2.76-2.57 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.72, 136.21, 133.92, 133.68, 132.92, 129.82, 127.96, 127.84, 127.56, 126.87, 126.75, 126.38 (q,  $J = 275.3$  Hz), 125.42, 48.07 (q,  $J = 2.7$  Hz), 37.21 (q,  $J = 28.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -(64.43-64.56) (m, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{15}\text{F}_3\text{NO}$  (M+H) $^+$  330.11002, found 330.10976.

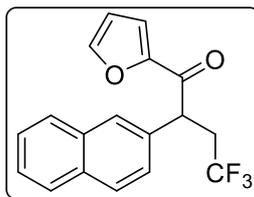
#### 4,4,4-Trifluoro-1-(1H-imidazol-2-yl)-2-(naphthalen-2-yl)butan-1-one (**7j**)



Prepared according to General Procedure using 2-vinylnaphthalene, imidazole-2-carboxaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/5) to afford **7j** (40.8 mg, 64% yield),

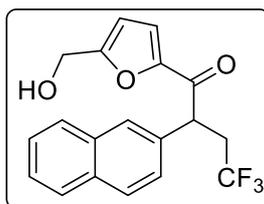
IR (film) 2982, 1734, 1372, 963, 903, 842, 647, 627, 524  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.88 (brs, 1H), 7.89 (s, 1H), 7.83-7.72 (m, 3H), 7.56 (d,  $J = 8.3$  Hz, 1H), 7.46-7.43 (m, 2H), 7.25 (brs, 2H), 5.60 (dd,  $J = 9.1, 4.7$  Hz, 1H), 3.48-3.36 (m, 1H), 2.74-2.64 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.43, 144.03, 134.20, 133.54, 132.86, 128.98, 128.02, 127.82, 127.74, 126.51, 126.43, 126.36 (q,  $J = 275.7$  Hz), 126.03, 45.91 (q,  $J = 2.9$  Hz), 36.37 (q,  $J = 28.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.73 (t,  $J = 10.6$  Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2$  (M+H) $^+$  319.10527, found 319.10492.

#### 4,4,4-Trifluoro-1-(furan-2-yl)-2-(naphthalen-2-yl)butan-1-one (7k)



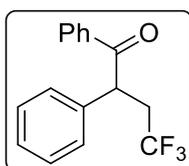
Prepared according to General Procedure using 2-vinylnaphthalene, furfural and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/70) to afford **7k** (48.0 mg, 75% yield), IR (film) 2904, 1615, 1389, 954, 816, 673, 574, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.78 (m, 4H), 7.56-7.52 (m, 1H), 7.51-7.45 (m, 3H), 7.26-7.22 (m, 1H), 6.46 (dd,  $J = 3.7, 1.7$  Hz, 1H), 4.92 (dd,  $J = 7.9, 5.5$  Hz, 1H), 3.45-3.31 (m, 1H), 2.74-2.58 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  185.65, 151.69, 147.03, 134.56, 133.60, 132.88, 129.18, 127.97, 127.79, 127.46, 126.61, 126.47, 126.46 (q,  $J = 272.4$  Hz), 125.77, 118.83, 112.70, 47.48 (q,  $J = 2.5$  Hz), 36.53 (q,  $J = 28.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.67 (t,  $J = 10.6$  Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{O}_2$  (M-H) $^-$  317.07949, found 317.07938.

#### 4,4,4-Trifluoro-1-(5-(hydroxymethyl)furan-2-yl)-2-(naphthalen-2-yl)butan-1-one (7l)



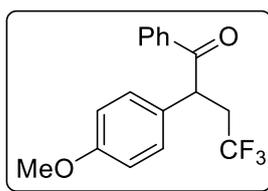
Prepared according to General Procedure using 2-vinylnaphthalene, 5-(hydroxymethyl) furan-2-carbaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/2) to afford **7l** (30.0 mg, 43% yield), IR (film) 2948, 1635, 1138, 836, 747, 684, 605, 581  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.77 (m, 4H), 7.50-7.42 (m, 3H), 7.18 (d,  $J = 3.6$  Hz, 1H), 6.33 (d,  $J = 3.5$  Hz, 1H), 4.83 (dd,  $J = 7.9, 5.5$  Hz, 1H), 4.60 (s, 2H), 3.42-3.28 (m, 1H), 2.68-2.55 (m, 1H), 2.39 (brs, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  185.44, 159.58, 150.87, 134.61, 133.58, 132.86, 129.22, 127.93, 127.79, 127.38, 126.67, 126.51, 126.39 (q,  $J = 275.5$  Hz), 125.64, 120.19, 110.09, 57.68, 47.45 (q,  $J = 2.5$  Hz), 36.47 (q,  $J = 28.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.63 (t,  $J = 10.6$  Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{O}_3$  (M+H) $^+$  349.10460, found 349.10443.

#### 4,4,4-Trifluoro-1,2-diphenylbutan-1-one (7m)



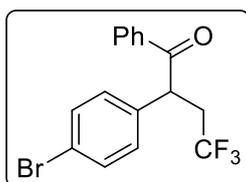
Prepared according to General Procedure using styrene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/25) to afford **7m** (52.2 mg, 83% yield), IR (film) 2973, 1641, 1239, 1204, 984, 892, 728, 648, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94-7.89 (m, 2H), 7.47-7.41 (m, 1H), 7.38-7.30 (m, 2H), 7.30-7.22 (m, 4H), 7.22-7.14 (m, 1H), 4.86 (dd,  $J = 7.7, 5.4$  Hz, 1H), 3.35-3.18 (m, 1H), 2.59-2.42 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.86, 137.54, 135.81, 133.48, 129.45, 128.94, 128.78, 128.16, 127.96, 126.53 (q,  $J = 275.5$  Hz), 47.31 (q,  $J = 2.5$  Hz), 37.49 (q,  $J = 28.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.57 (t,  $J = 10.8$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{12}\text{F}_3\text{O}$  (M-H) $^-$  277.08457, found 277.08464.

#### 4,4,4-Trifluoro-2-(4-methoxyphenyl)-1-phenylbutan-1-one (7n)



Prepared according to General Procedure using 4-methoxystyrene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7n** (51.8 mg, 84% yield), IR (film) 3006, 1715, 1180, 826, 728, 695, 626, 549, 521  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.3$  Hz, 2H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 2H), 7.23-7.21 (m, 2H), 6.86-6.83 (m, 2H), 4.88 (t,  $J = 6.6$  Hz, 1H), 3.74 (s, 3H), 3.32-3.23 (m, 1H), 2.60-2.47 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.02, 159.26, 135.84, 133.38, 129.39, 129.26, 128.91, 128.76, 126.59 (q,  $J = 275.5$  Hz), 114.84, 55.30, 46.47 (q,  $J = 2.6$  Hz), 37.50 (q,  $J = 28.0$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.49 (t,  $J = 10.7$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{F}_3\text{O}_2$  (M+H) $^+$  309.10969, found 309.10962.

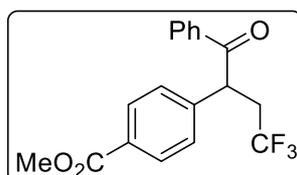
#### 2-(4-Bromophenyl)-4,4,4-trifluoro-1-phenylbutan-1-one (7o)



Prepared according to General Procedure using 4-bromostyrene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/25) to afford **7o** (58.9 mg, 82% yield), IR (film)

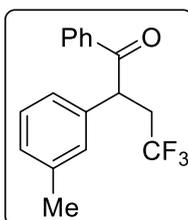
2973, 1696, 1357, 1094, 924, 732, 625, 587, 524 $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96-7.93 (m, 2H), 7.55-7.40 (m, 5H), 7.21-7.18 (m, 2H), 4.89 (dd,  $J = 7.3, 6.0$  Hz, 1H), 3.31-3.19 (m, 1H), 2.57-2.51 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.46, 136.47, 135.50, 133.73, 132.62, 129.86, 128.90, 126.39 (q,  $J = 325.5$  Hz), 122.15, 46.66 (q,  $J = 2.5$  Hz), 37.34 (q,  $J = 28.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 3F)  $\delta$  -64.41 (t,  $J = 10.8$  Hz). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{11}\text{BrF}_3\text{O}$  (M-H) $^-$  354.99508, found 354.99499.

#### Methyl 4-(4,4,4-trifluoro-1-oxo-1-phenylbutan-2-yl)benzoate (7p)



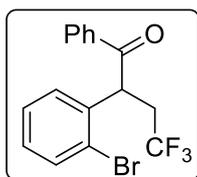
Prepared according to General Procedure using methyl 4-vinylbenzoate, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford **7p** (40.3 mg, 55% yield), IR (film) 2866, 1329, 1044, 984, 736, 712, 689, 604, 548, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.92 (m, 4H), 7.54-7.50 (m, 1H), 7.43-7.38 (m, 4H), 4.97 (t,  $J = 6.6$  Hz, 1H), 3.88 (s, 3H), 3.33-3.25 (m, 1H), 2.64-2.51 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.30, 166.59, 142.46, 135.53, 133.78, 130.72, 129.94, 128.93, 128.91, 128.29, 126.38 (q,  $J = 275.5$  Hz), 52.33, 47.30 (q,  $J = 2.3$  Hz), 37.33 (q,  $J = 28.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.46 (t,  $J = 10.8$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_3\text{O}_3$  (M-H) $^-$  335.09005, found 335.09067.

#### 4,4,4-Trifluoro-1-phenyl-2-(m-tolyl)butan-1-one (7q)



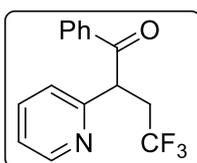
Prepared according to General Procedure using 3-methylstyrene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7q** (43.1.0 mg, 74% yield), IR (film) 2981, 1715, 1399, 1204, 934, 803, 624, 518, 502  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86-7.84 (m, 2H), 7.40-7.36 (m, 1H), 7.30-7.27 (m, 2H), 7.10-7.06 (m, 1H), 7.01-6.98 (m, 2H), 6.94-6.91 (m, 1H), 4.76 (dd,  $J = 7.9, 5.1$  Hz, 1H), 3.27-3.13 (m, 1H), 2.45-2.34 (m, 1H), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.90, 139.24, 137.47, 135.89, 133.44, 129.30, 128.96, 128.77, 128.75, 128.63, 126.54 (q,  $J = 275.5$  Hz), 125.16, 47.23 (q,  $J = 2.4$  Hz), 37.54 (q,  $J = 28.3$  Hz), 21.50;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.66 (t,  $J = 10.8$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{O}$  (M-H) $^-$  291.10022, found 291.10076.

#### 2-(2-Bromophenyl)-4,4,4-trifluoro-1-phenylbutan-1-one (7r)



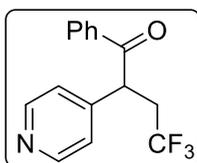
Prepared according to General Procedure using 2-bromostyrene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7r** (53.0 mg, 74% yield), IR (film) 2976, 2845, 1633, 1084, 813, 757, 663, 518, 501  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.97 (m, 2H), 7.63 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.54-7.50 (m, 1H), 7.43-7.39 (m, 2H), 7.23-7.17 (m, 2H), 7.14-7.08 (m, 1H), 5.45 (dd,  $J$  = 8.5, 4.4 Hz, 1H), 3.37-3.23 (m, 1H), 2.49-2.36 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.59, 136.98, 135.55, 133.99, 133.73, 129.60, 128.88, 128.87, 128.47, 126.16 (q,  $J$  = 285.5 Hz), 124.32, 46.07 (q,  $J$  = 2.4 Hz), 36.65 (q,  $J$  = 28.8 Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.73 (t,  $J$  = 10.6 Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{11}\text{BrF}_3\text{O}$  (M-H) $^-$  354.99509, found 354.99591.

#### 4,4,4-Trifluoro-1-phenyl-2-(pyridin-2-yl)ethan-1-one (**7s**)



Prepared according to General Procedure using 3-vinylpyridine, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford **7s** (50.8 mg, 91% yield), IR (film) 2856, 1445, 1199, 1044, 984, 747, 604, 548, 531  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (d,  $J$  = 4.8 Hz, 1H), 8.04-8.02 (m, 2H), 7.63-7.58 (m, 1H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 2H), 7.30-7.28 (m, 1H), 7.21-7.12 (m, 1H), 5.17 (t,  $J$  = 6.6 Hz, 1H), 3.34-3.21 (m, 1H), 2.84-2.71 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.02, 157.10, 150.16, 137.34, 135.73, 133.57, 129.15, 128.77, 126.56 (q,  $J$  = 275.4 Hz), 122.86, 122.71, 50.03 (q,  $J$  = 2.2 Hz), 36.08 (q,  $J$  = 28.6 Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.44 (t,  $J$  = 10.7 Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}$  (M+H) $^+$  280.09439, found 280.09412.

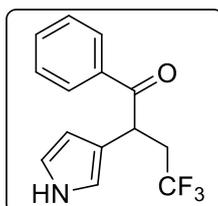
#### 1-Phenyl-2-(3-(2,2,2-trifluoroethyl)pyridin-4-yl)ethan-1-one (**7t**)



Prepared according to General Procedure using 4-vinylpyridine, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/3) to afford **7t** (36.9 mg, 66% yield), IR (film) 3021, 2873, 1715, 1349, 768, 604, 538, 511  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41-8.40

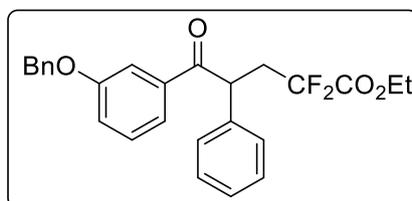
(m, 2H), 7.79-7.77 (m, 2H), 7.40 (t,  $J = 7.4$  Hz, 1H), 7.28 (t,  $J = 7.7$  Hz, 2H), 7.11 (d,  $J = 5.1$  Hz, 2H), 4.76 (t,  $J = 6.6$  Hz, 1H), 3.16-3.07 (m, 1H), 2.47-2.38 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.71, 150.69, 146.31, 135.20, 134.05, 129.00, 128.85, 126.17 (q,  $J = 274.9$  Hz), 123.28, 46.54 (q,  $J = 2.5$  Hz), 37.01 (q,  $J = 28.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.47 (t,  $J = 10.5$  Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}$  ( $\text{M}+\text{H}$ ) $^+$  280.09439, found 280.09409.

#### 4,4,4-Trifluoro-1-phenyl-2-(1H-pyrrol-3-yl)butan-1-one (7u)



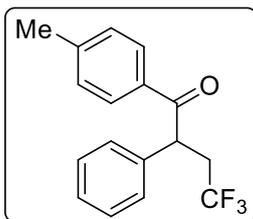
Prepared according to General Procedure using 2-vinyl-pyrrole, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/20) to afford **7u** (42.1 mg, 58% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (brs, 1H), 8.04-7.97 (m, 2H), 7.61-7.53 (m, 1H), 7.46 (t,  $J = 7.8$  Hz, 2H), 6.78-6.67 (m, 1H), 6.19-6.09 (m, 2H), 5.11 (dd,  $J = 8.8, 4.9$  Hz, 1H), 3.31-3.13 (m, 1H), 2.69-2.50 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.44, 135.74, 133.90, 128.94, 128.85, 126.22 (q,  $J = 275.7$  Hz), 125.82, 119.18, 109.18, 108.14, 40.07 (q,  $J = 2.9$  Hz), 37.40 (q,  $J = 28.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.97 (t,  $J = 10.6$  Hz, 3F).

#### Ethyl 5-(3-(benzyloxy)phenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate (7v)



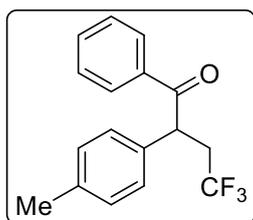
Prepared according to General Procedure using styrene, 3-benzyloxybenzaldehyde and ethyl bromodifluoroacetate as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/20) to afford **7v** (59.0 mg, 67% yield),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.42 (m, 2H), 7.35-7.06 (m, 11H), 7.04-6.95 (m, 1H), 4.94 (s, 2H), 4.87-4.79 (m, 1H), 4.12-3.87 (m, 2H), 3.26-3.05 (m, 1H), 2.52-2.35 (m, 1H), 1.11 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.14, 163.84 (t,  $J = 32.6$  Hz), 159.04, 137.85, 137.26, 136.55, 129.75, 129.31, 128.75, 128.33, 128.24, 127.79, 127.63, 121.74, 120.59, 115.38 (t,  $J = 249.1$  Hz), 114.36, 70.26, 63.02, 47.07 (t,  $J = 4.0$  Hz), 38.28 (t,  $J = 23.4$  Hz), 13.83;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -(103.41-105.21) (m, 2F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{24}\text{NaF}_2\text{O}_4$  ( $\text{M}+\text{Na}$ ) $^+$  461.15349, found 461.15323.

#### 4,4,4-Trifluoro-2-phenyl-1-(p-tolyl)butan-1-one (7w)



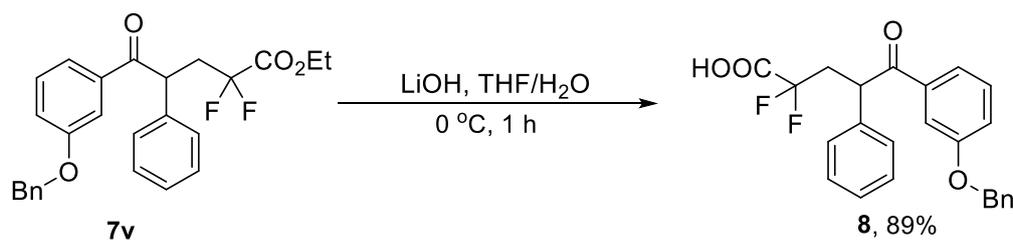
Prepared according to General Procedure using styrene, *p*-tolualdehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7w** (37.0 mg, 63% yield), IR (film) 2996, 2845, 1689, 1519, 1134, 1084, 886, 747, 684, 568, 533  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90-7.88 (m, 2H), 7.33-7.32 (m, 4H), 7.28-7.21 (m, 3H), 4.93-4.90 (m, 1H), 3.37-3.28 (m, 1H), 2.60-2.52 (m, 1H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.44, 144.44, 137.81, 133.27, 129.50, 129.41, 129.10, 128.15, 127.87, 126.58 (q,  $J = 275.5$  Hz), 47.14 (q,  $J = 2.4$  Hz), 37.48 (q,  $J = 28.2$  Hz), 21.74;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.58 (t,  $J = 10.9$  Hz, 3F). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{O}$  (M-H) $^-$  291.10022, found 291.10062.

#### 4,4,4-Trifluoro-1-phenyl-2-(*p*-tolyl)butan-1-one (**7x**)



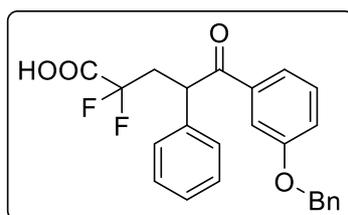
Prepared according to General Procedure using 4-methylstyrene, benzaldehyde and trifluoromethyl iodide as the substrates. The crude residue was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford **7x** (40.0 mg, 68% yield),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.96 (m, 2H), 7.53-7.48 (m, 1H), 7.42-7.38 (m, 2H), 7.20 (d,  $J = 7.8$  Hz, 2H), 7.12 (d,  $J = 7.9$  Hz, 2H), 4.89 (t,  $J = 6.6$  Hz, 1H), 3.35-3.26 (m, 1H), 2.54-2.50 (m, 1H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.97, 137.74, 135.86, 134.50, 133.40, 130.15, 128.94, 128.76, 128.02, 126.59 (q,  $J = 275.6$  Hz), 46.94 (q,  $J = 2.5$  Hz), 36.50 (q,  $J = 28.0$  Hz), 21.13;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.56 (t,  $J = 10.8$  Hz, 3F). HRMS (APCI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{O}$  (M-H) $^-$  291.10022, found 291.10074.

## Hydrolysis of 7v



The reaction was performed according to literature.<sup>2</sup> To compound **7v** (59 mg, 0.1346 mmol, 1.0 equiv) in THF (0.7 mL) was added a aqueous solution of LiOH (2.7 M, 10 equiv) at 0 °C. The mixture was stirred for 1 h and then concentrated hydrochloric acid was added to neutralize the solution (pH = 1). The mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford the difluorinated analogue of compound **1** (51.4 mg, 89% yield). Note: Compound **8** contains THF and MeOH, the yield was calculated on deducting the solvent residual via <sup>1</sup>H NMR spectra analysis.

### 5-(3-(Benzyloxy)phenyl)-2,2-difluoro-5-oxo-4-phenylpentanoic acid (**8**)



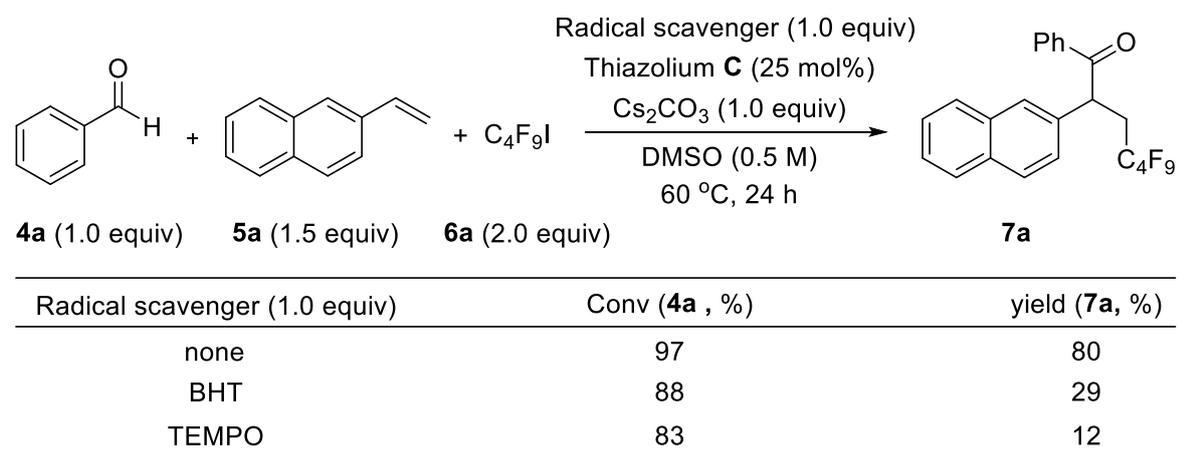
Compound **8** (51.4 mg, 89% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59-7.57 (m, 2H), 7.43-7.20 (m, 11H), 7.13-7.11 (m, 1H), 5.05 (s, 2H), 4.97 (dd, *J* = 8.4, 4.6 Hz, 1H), 3.41-3.27 (m, 1H), 2.63-2.48 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.92, 166.37 (t, *J* = 32.6 Hz), 159.02, 137.80, 137.26, 136.52, 129.79, 129.35, 128.75, 128.29, 128.25, 127.83, 127.67, 121.84, 120.75, 115.30 (t, *J* = 250.5 Hz), 114.38, 70.28, 47.06 (t, *J* = 3.5 Hz), 38.08 (t, *J* = 22.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -(103.99-106.00) (m, 2F). HRMS (APCI) *m/z* calcd for C<sub>24</sub>H<sub>19</sub>F<sub>2</sub>O<sub>4</sub> (M-H)<sup>-</sup> 409.12560, found 409.12631.

## Mechanism studies

To an 8-mL glass vial equipped with magnetic stir bar were sequentially added benzaldehyde **4a** (0.2 mmol, 1.0 equiv), 2-vinylnaphthalene **5a** (0.3 mmol, 1.5 equiv), thiazolium **C1** (0.05 mmol, 1.0 equiv), perfluorobutyl iodide **6a** (0.4 mmol, 2.0 equiv), TEMPO (0.2 mmol, 1.0 equiv, or BHT) and DMSO (0.4 mL). The vial was sealed with a Teflon septum. The resulting mixture was degassed via “freeze, pump, thaw” operation. The glass vial was brought into a glove box and Cs<sub>2</sub>CO<sub>3</sub> (1.0 equiv) was added. Sealed the glass vial and took the vial out from the glove box. The reaction mixture was stirred at 60 °C for 2 h. After 2 h, the yield was determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. The results were summarized in **Table S9**.

The addition of TEMPO and BHT inhibited the reaction, which indicated that a radical intermediate may be involved in mechanism pathway.

**Table S9** Experiment of probing mechanism



## References

1. a) I. Piel, M. D. Pawelczyk, K. Hirano, R. Frohlich and F. Glorius, *Eur. J. Org. Chem.* **2011**, 5475.
2. X. Liu, H. Chen, E. Laurini, Y. Wang, V. D. Col, P. Posocco, F. Ziarelli, M. Fermeglia, C. -C. Zhang, S. Priel, L. Peng, *Org. Lett.* **2011**, *13*, 2924-2927

# $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR Spectra of Products

