Supporting Information

Visible Light-Induced Aryltrifluoromethylation of Hydroxy Alkenes via Radical Trifluoromethylation-Triggered Aryl and Heteroaryl Migration

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1. General methods.

DMSO was dried according to Purification of Common Laboratory Chemicals. Other reagents were 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 phosphomolybdc 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.

**Reaction Apparatus**

Photochemical reaction was carried out under visible light irradiation by a 48W blue lamp at room temperature (about 25 ºC).
2. General procedure for the difunctionalization of olefins

General Procedure. A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with 1a (0.2 mmol, 1.0 equiv), IV (0.4 mmol, 2.0 equiv) and K₂HPO₄ (0.3 mmol, 1.5 equiv). The flask was evacuated and backfilled with nitrogen for 3 times, DMSO (2.0 mL, 0.1 M) were added with a syringe under nitrogen. The mixture was then irradiated by a 48W blue lamp. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 20 mL of H₂O and 20 mL of Et₂O. The layers were separated and the aqueous layer was extracted with Et₂O (2 × 20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product 2a.
The structures of substrates 1

1a: $R' = H$
1b: $R' = \text{Me}$
1c: $R' = \text{OME}$
1d: $R' = \text{F}$
1e: $R' = \text{Cl}$
1f: $R' = \text{CO}_2\text{Et}$
1g: $R' = \text{CONET}_2$
1h: $R' = O\text{N' Me}$

1i
1j

1k

1l

1m

1n: $R' = H$
1o: $R' = F$
1p: $R' = \text{Cl}$

1q

1r

1s: $R' = \text{CF}_3$
1t: $R' = \text{CN}$

1u

1v

1w

1x
3. Scale-up Experiment

A 100 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with 1s (1.11g, 4 mmol, 1.0 equiv), IV (5.51g, 8.0 mmol, 2.0 equiv) and K2HPO4 (1.05g, 6.0 mmol, 1.5 equiv). The flask was evacuated and backfilled with nitrogen for 3 times, DMSO (40.0 mL, 0.1 M) were added with a syringe under nitrogen. The mixture was then irradiated by a 96 W blue lamps( two 48 W blue lamps). After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 100 mL of H2O and 100 mL of Et2O. The layers were separated and the aqueous layer was extracted with Et2O (2 × 100 mL). The combined organic layers were dried over Na2SO4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product 2s in 90% yield (1.25g).
4. EPR Experiment.

Line A: A 10 mL round bottom flask equipped magnetic stir bar was charged with PBN (0.2 mmol) and DMSO (1 mL). EPR spectrum was recorded by Bruker EMX-10/12 EPR spectrometer immediately.

Line B: A 10 mL round bottom flask equipped magnetic stir bar was charged with PBN (0.2mmol), IV (0.2mmol), DMSO (1 mL) and was irradiated with 48W blue lamp for 1 hour. EPR spectrum was recorded by Bruker EMX-10/12 EPR spectrometer immediately.

Line C: A 10 mL round bottom flask equipped magnetic stir bar was charged with PBN (0.2mmol), IV (0.2mmol), DMSO (1 mL) and was in the dark condition for 1 hour. EPR spectrum was recorded by Bruker EMX-10/12 EPR spectrometer immediately.
5. Characterization of products

![Structure of 2a](image)

**4,4,4-trifluoro-1,2-diphenylbutan-1-one (2a):** According to the general procedure: 1a (0.2 mmol, 42.0 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2a (44.4 mg, 80%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.97-7.94 (m, 2H), 7.52-7.48 (m, 1H), 7.40 (dd, $J = 8.3, 6.9$ Hz, 2H), 7.30 (d, $J = 4.3$ Hz, 4H), 7.26-7.21 (m, 1H), 4.91 (dd, $J = 7.7, 5.4$ Hz, 1H), 3.31 (dd, $J = 15.0, 10.8, 7.7$ Hz, 1H), 2.54 (dd, $J = 15.1, 10.7, 5.5$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.61. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.73, 137.42, 135.70, 133.36, 129.34, 128.82, 128.67, 128.05, 126.40 (q, $J = 277.3$ Hz), 47.20 (q, $J = 2.5$ Hz), 37.38 (q, $J = 28.2$ Hz).

![Structure of 2b](image)

**4,4,4-trifluoro-1,2-di-p-tolylbutan-1-one (2b):** According to the general procedure: 1b (0.2 mmol, 47.6 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2b (49.3 mg, 81%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.86 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 3.2$ Hz,2H), 7.17 (d, $J = 3.1$ Hz, 2H), 6.69 (d, $J = 7.6$ Hz, 2H).

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2H), 7.10 (d, $J = 7.9$ Hz, 2H), 4.84 (dd, $J = 7.6$, 5.5 Hz, 1H), 3.34-3.20 (m, 1H), 2.51 (dqd, $J = 15.0$, 10.8, 5.5 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.55. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.42, 144.21, 137.50, 134.65, 133.17, 129.97, 129.34, 128.96, 128.87, 126.40 (q, $J = 277.3$ Hz), 46.63 (q, $J = 2.6$ Hz), 37.34 (q, $J = 28.0$ Hz), 6.93, 21.61, 21.02.

4,4,4-trifluoro-1,2-bis(4-methoxyphenyl)butan-1-one (2c): According to the general procedure: $1c$ (0.2 mmol, 54.0 mg), $IV$ (0.4 mmol, 175.3 mg), $K_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2c (42.1 mg, 62%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.94 (d, $J = 9.0$ Hz, 2H), 7.21 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 4.82-4.79 (m, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.24 (dqd, $J = 15.0$, 10.9, 7.5 Hz, 1H), 2.57-2.44 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.50. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.37, 163.61, 159.04, 131.15, 129.82, 129.05, 128.59, 126.53 (q, $J = 277.4$ Hz), 114.65, 113.85, 55.44, 55.21, 45.95 (q, $J = 2.5$ Hz), 37.39 (q, $J = 27.9$ Hz).

4,4,4-trifluoro-1,2-bis(4-fluorophenyl)butan-1-one (2d): According to the general procedure: 1d (0.2 mmol, 49.2 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2d (44.2 mg, 70%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 7.99-7.95 (m, 2H), 7.28-7.25 (m, 2H), 7.10-7.06 (m, 2H), 7.03-6.99 (m, 2H), 4.85 (dd, $J$ = 7.4, 5.9 Hz, 1H), 3.24 (dqd, $J$ = 15.1, 10.7, 7.4 Hz, 1H), 2.53 (dqd, $J$ = 15.0, 10.6, 5.8 Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.50, -104.01, -113.80. $^{13}$C NMR (101 MHz, Chloroform-d) δ 195.07, 165.86 (d, $J$ = 256.2 Hz), 162.31 (d, $J$ = 247.6 Hz), 132.93 (d, $J$ = 3.0 Hz), 131.81 (d, $J$ = 2.9 Hz), 131.48 (d, $J$ = 9.5 Hz), 129.63 (d, $J$ = 8.2 Hz), 126.25 (d, $J$ = 277.2 Hz), 116.42 (d, $J$ = 21.6 Hz), 115.95 (d, $J$ = 21.9 Hz), 46.35 (d, $J$ = 2.8 Hz), 37.39 (q, $J$ = 28.3 Hz).

1,2-bis(4-chlorophenyl)-4,4,4-trifluorobutan-1-one (2e): According to the general procedure: 1e (0.2 mmol, 55.6 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2e (55.3 mg, 80%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 7.87-7.85 (m, 2H), 7.39-7.37 (m, 1H), 7.30-7.27 (m, 2H), 7.23-7.21 (m, 2H), 4.82 (dd, $J$ = 7.3, 6.0 Hz, 1H), 3.24 (dqd, $J$ = 15.1, 10.7, 7.3 Hz, 1H), 2.53 (dqd, $J$ = 15.0, 10.6, 5.9 Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.45. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.22, 140.17, 135.48, 134.13, 133.65, 130.16, 129.67, 129.33, 129.13, 126.19 (d, $J$ = 277.3 Hz), 46.58 (q, $J$ = 2.7 Hz), 37.20 (q, $J$ = 28.3 Hz).
diethyl 4,4’-(4,4,4-trifluoro-1-oxobutane-1,2-diyl)dibenzoate (2f): According to the general procedure: 1f (0.2 mmol, 70.8 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2f (50.6 mg, 60%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. 

$^1$H NMR (400 MHz, Chloroform-d) δ 8.06 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 2H), 7.96 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H), 4.96 (t, $J = 6.6$ Hz, 1H), 4.40-4.32 (m, 3H), 3.37-3.23 (m, 1H), 2.66-2.52 (m, 1H), 1.40-1.34 (m, 6H). $^{19}$F NMR (376 MHz, CDCl₃) δ -64.41. $^{13}$C NMR (101 MHz, CDCl₃) δ 195.81, 165.84, 165.39, 141.60, 138.51, 134.65, 130.65, 130.35, 129.87, 128.64, 128.12, 126.16 (d, $J = 277.3$ Hz), 61.51, 61.13, 47.65, 37.05 (q, $J = 28.6$ Hz), 14.27, 14.23. HRMS (DART Positive) ([M+H]^+) Calcd for C₂₂H₂₂F₃O₅: 423.1414; found: 423.1413.

4,4’-(4,4,4-trifluoro-1-oxobutane-1,2-diyl)bis(N,N-diethylbenzamide) (2g): According to the general procedure: 1g (0.2 mmol, 81.6 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2g (92.8 mg, 97%) as a white solid after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. m.p. 135-136 °C. $^1$H NMR (400 MHz, Chloroform-d) δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.36-7.33 (m, 4H), 4.94 (dd, $J = 7.8$, 5.4 Hz,
1H), 3.56-3.51 (m, 4H), 3.38-3.26 (1H), 3.24-3.16 (4H), 2.62-2.49 (1H), 1.27-1.21 (m, 6H), 1.13-1.07 (m, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.55. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.68, 170.44, 169.82, 142.17, 137.92, 136.97, 135.66, 129.07, 128.15, 127.43, 126.61, 126.20 (d, $J = 277.2$ Hz), 46.92 (d, $J = 2.9$ Hz), 43.28, 43.19, 39.25, 37.19 (q, $J = 28.3$ Hz), 14.17, 12.81. HRMS (DART Positive) ([M+H]$^+$) Calcd for C$_{26}$H$_{32}$F$_3$N$_2$O$_3$: 477.2360; found: 477.2356.

4,4'-((4,4,4-trifluoro-1-oxobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2h): According to the general procedure: 1a (0.2 mmol, 76.8 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2h (88.7 mg, 98%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.98 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 4.95 (dd, $J = 7.6$, 5.6 Hz, 1H), 3.50 (s, 6H), 3.34 (s, 3H), 3.33-3.24 (m, 4H), 2.64-2.51 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.50. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.80, 168.99, 168.53, 139.34, 138.85, 136.71, 133.80, 129.32, 128.47, 128.42, 127.78, 126.19 (d, $J = 277.2$ Hz), 61.30, 61.08, 47.18 (q, $J = 2.3$ Hz), 37.16 (q, $J = 28.5$ Hz), 33.57, 33.30. HRMS (DART Positive) ([M+Na]$^+$) Calcd for C$_{26}$H$_{31}$F$_3$N$_2$O$_3$Na: 475.1451; found: 475.1452.
1,2-bis(3-chlorophenyl)-4,4,4-trifluorobutan-1-one (2i): According to the general procedure: 1i (0.2 mmol, 55.6 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2i (54.6 mg, 79%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 7.91 (t, $J = 1.9$ Hz, 1H), 7.80 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.51 (ddd, $J = 8.0, 2.1, 1.1$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.29-7.23 (m, 3H), 7.19 (dt, $J = 6.9, 1.9$ Hz, 1H), 4.81 (dd, $J = 7.7, 5.5$ Hz, 1H), 3.26 (dqd, $J = 15.0, 10.6, 7.6$ Hz, 1H), 2.60-2.47 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.59. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.01, 138.67, 136.91, 135.30, 135.25, 133.61, 130.73, 130.10, 128.87, 128.44, 128.04, 127.44, 126.80, 126.26, 126.07 (d, $J = 277.1$ Hz), 46.90 (q, $J = 2.5$ Hz), 37.28 (q, $J = 28.6$ Hz).

1,2-bis(2-chlorophenyl)-4,4,4-trifluorobutan-1-one (2j): According to the general procedure: 1j (0.2 mmol, 55.6 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2j (49.2 mg, 71%) as a colorless oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 7.35-7.15 (m, 8H), 5.39 (t, $J = 6.5$ Hz, 1H), 3.31 (dqd, $J = 15.1, 10.7, 6.7$ Hz, 1H), 2.56 (dqd, $J = 15.1, 10.6, 6.4$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.57. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.43, 137.63, 134.22,
133.75, 131.96, 131.28, 130.55, 130.23, 129.39, 129.30, 129.00, 127.61, 126.61, 126.23 (d, \( J = 277.2 \) Hz), 35.33 (q, \( J = 29.0 \) Hz).

**4,4,4-trifluoro-1,2-di(thiophen-2-yl)butan-1-one (2k):** According to the general procedure: 1k (0.2 mmol, 44.4 mg), IV (0.4 mmol, 175.3 mg), \( \text{K}_2\text{HPO}_4 \) (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2k (30.1 mg, 52%) a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. \( ^1\text{H} \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.82 (dd, \( J = 3.9, 1.1 \) Hz, 1H), 7.67 (dd, \( J = 4.9, 1.1 \) Hz, 1H), 7.22 (dd, \( J = 5.1, 1.2 \) Hz, 1H), 7.12 (dd, \( J = 4.9, 3.9 \) Hz, 1H), 6.99 (ddd, \( J = 3.5, 1.3, 0.6 \) Hz, 1H), 6.93 (dd, \( J = 5.1, 3.5 \) Hz, 1H), 5.01 (dd, \( J = 8.3, 5.0 \) Hz, 1H), 3.37-3.23 (m, 1H), 2.70-2.57 (m, 1H). \(^{19}\text{F} \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -64.86. \(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 188.34, 142.10, 139.18, 135.05, 133.14, 128.37, 127.31, 126.38, 125.89 (d, \( J = 277.4 \) Hz), 125.82, 43.21, 37.82 (q, \( J = 28.6 \) Hz). HRMS (DART Positive) ([M+H]+) Calcd for C\(_{12}\)H\(_{10}\)F\(_3\)O\(_2\): 291.0120; found: 291.0118.

**4,4,4-trifluoro-1,2-di(pyridin-2-yl)butan-1-one (2l):** According to the general procedure: 1l (0.2 mmol, 42.4 mg), IV (0.4 mmol, 175.3 mg), \( \text{K}_2\text{HPO}_4 \) (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2l (33.9 mg, 61%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. \( ^1\text{H} \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 8.64 (ddd, \( J = 4.8, 1.7, 0.9 \) Hz, 1H), 8.49 (ddd, \( J = 4.8, 1.9, 1.0 \) Hz, 1H), 8.05 (m, 1H), 7.78 (td, \( J = 7.7, 1.7 \) Hz, 1H), 7.59 (td, \( J = 7.6, 1.8 \) Hz, 1H), 7.40 (s, 1H), 4.18 (s, 1H).
Hz, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.41 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 7.09 (ddd, J = 7.4, 4.8, 1.4 Hz, 1H), 5.88 (t, J = 6.6 Hz, 1H), 3.27 (dqd, J = 15.2, 11.0, 6.7 Hz, 1H), 2.90 (dqd, J = 15.2, 10.9, 6.5 Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.50. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.80, 156.95, 151.97, 149.66, 148.81, 136.94, 136.67, 127.27, 126.84 (d, J = 276.8 Hz), 124.97, 123.11, 122.11, 47.29 (q, J = 2.4 Hz), 35.00 (q, J = 28.6 Hz). HRMS (DART Positive) ([M+Na$^+$]) Calcd for Chemical Formula: C$_{14}$H$_{11}$F$_3$N$_2$O$_x$Na: Exact Mass: 303.0716; found: 303.0709.

4,4,4-trifluoro-2-methyl-1,2-diphenylbutan-1-one (2m):$^5$ According to the general procedure: 1m (0.2 mmol, 44.8 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2m (29.5 mg, 50%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 7.42-7.31 (m, 8H), 7.24-7.20 (m, 2H), 3.06 (dq, J = 15.5, 11.1 Hz, 1H), 2.83 (dq, J = 15.5, 11.2 Hz, 1H), 1.82 (d, J = 1.4 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -58.58. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 201.42, 140.81, 136.04, 131.85, 129.34, 129.26, 128.10, 127.77, 126.43 (d, J = 277.2 Hz), 126.30, 51.88, 43.41 (q, J = 26.8 Hz), 22.02.

phenyl(2-phenyl-3-(trifluoromethyl)tetrahydro-2H-pyran-2-yl)methanone (2n):$^3$ According to the general procedure: 1n (0.2 mmol, 53.2 mg), IV (0.4 mmol, 175.3

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mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2n (44.3 mg, 66%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 7.94 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.48-7.44 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.27 (m, 5H), 3.85-3.80 (m, 1H), 3.55 (ddd, $J = 12.3, 8.9, 3.6$ Hz, 1H), 3.09-2.99 (m, 1H), 2.22-2.12 (m, 1H), 2.07-1.99 (m, 1H), 1.87-1.80 (m, 1H), 1.76-1.65 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -60.08. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.31, 139.88, 135.19, 132.71, 130.44, 128.44, 128.28, 127.92, 126.87, 126.30 (d, $J = 281.6$ Hz), 86.27, 64.15, 49.95 (q, $J = 25.9$ Hz), 23.61, 21.00 (q, $J = 3.2$ Hz).

(4-fluorophenyl)(2-(4-fluorophenyl)-3-(trifluoromethyl)tetrahydro-2H-pyran-2-yl)methanone (2o): According to the general procedure: 1o (0.2 mmol, 60.4 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2o (33.9 mg, 46%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. $^1$H NMR (400 MHz, Chloroform-d) δ 8.02-7.98 (m, 2H), 7.35 (dd, $J = 8.6, 5.2$ Hz, 2H), 7.04-6.96 (m, 4H), 3.84 (dt, $J = 12.2, 4.6, 1.1$ Hz, 1H), 3.52 (ddd, $J = 12.5, 9.5, 3.5$ Hz, 1H), 2.92 (pd, $J = 10.0, 3.9$ Hz, 1H), 2.16 (dt, $J = 14.3, 10.0, 4.5$ Hz, 1H), 2.06-1.99 (m, 1H), 1.87-1.79 (m, 1H), 1.78-1.69 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -60.25, -104.77, -113.27. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.27, 165.48 (d, $J = 255.6$ Hz), 162.47 (d, $J = 248.2$ Hz), 135.72 (d, $J = 3.5$ Hz), 133.32 (d, $J = 9.3$ Hz), 131.13 (d, $J = 3.2$ Hz), 128.63 (d, $J = 8.4$ Hz), 126.07 (d, $J = 281.3$ Hz), 115.46 (d, $J = 21.7$ Hz), 115.17 (d, $J = 21.7$ Hz), 85.76, 64.37, 23.77, 20.97 (q, $J = 2.7$ Hz).
(4-chlorophenyl)(2-(4-chlorophenyl)-3-(trifluoromethyl)tetrahydro-2H-pyran-2-yl)methanone (2p): According to the general procedure: 1p (0.2 mmol, 66.8 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2p (33.0 mg, 41%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. ¹H NMR (400 MHz, Chloroform-d) δ 7.89 (d, J = 8.7 Hz, 1H), 7.34-7.28 (m, 6H), 3.84 (dt, J = 12.1, 4.7 Hz, 1H), 3.53 (ddd, J = 12.4, 9.2, 3.5 Hz, 1H), 2.93 (pd, J = 9.9, 3.9 Hz, 1H), 2.21-2.11 (m, 1H), 2.05-1.98 (m, 1H), 1.89-1.81 (m, 1H), 1.78-1.67 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -60.17. ¹³C NMR (101 MHz, CDCl₃) δ 197.58, 139.52, 138.28, 134.46, 133.03, 131.94, 128.75, 128.41, 128.21, 126.03 (d, J = 281.5 Hz), 85.75, 64.36, 50.19 (q, J = 26.0 Hz), 23.60, 20.89 (q, J = 2.8 Hz).

4,4,4-trifluoro-1-(4-methoxyphenyl)-2-phenylbutan-1-one (2q): According to the general procedure: 1q (0.2 mmol, 48.0 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2q, 2q* (48.6 mg, 79%, 5:1) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. ¹H NMR (400 MHz, Chloroform-d) δ 7.96 (d, J = 8.9 Hz, 2H), 7.32-7.20 (m, 5H), 6.87 (d, J = 8.9 Hz, 2H), 4.86 (dd, J = 7.6, 5.5 Hz, 1H), 3.81 (s, 3H), 3.29 (dqd, J = 15.0, 10.9, 7.6 Hz, 1H), 2.53 (dqd, J = 15.0, 10.8, 5.5 Hz, 1H). ¹⁹F NMR (376 MHz,
CDCl₃ δ -64.57. ¹³C NMR (101 MHz, CDCl₃) δ 195.16, 163.68, 137.91, 131.19, 129.26, 128.56, 127.96, 127.71, 126.47 (d, J = 277.2 Hz), 113.87, 55.46, 46.80 (q, J = 2.5 Hz), 37.37 (q, J = 28.1 Hz).

According to the general procedure: 1r (0.2 mmol, 42.2 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2r, 2r' (52.0 mg, 93%, 3:1) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. ¹H NMR (400 MHz, Chloroform-d) δ 8.65 (d, J = 2.4 Hz, 1H), 8.51 (dd, J = 4.8, 1.6 Hz, 1H), 7.97-7.94 (m, 2H), 7.62 (dt, J = 8.0, 2.0 Hz, 1H), 7.57-7.52 (m, 1H), 7.45-7.41 (m, 2H), 7.27-7.23 (m, 1H), 4.97 (t, J = 6.7 Hz, 1H), 3.27 (dqd, J = 15.1, 10.6, 7.2 Hz, 1H), 2.59 (dqd, J = 15.1, 10.5, 6.2 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -64.39. ¹³C NMR (101 MHz, CDCl₃) δ 196.13, 149.78, 149.34, 135.08, 135.08, 133.84, 133.14, 128.90, 128.78, 126.14 (q, J = 277.2 Hz), 124.05, 44.40 (q, J = 2.7 Hz), 37.18 (q, J = 28.5 Hz).

According to the general procedure: 1s (0.2 mmol, 55.6 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2s (58.1 mg, 84%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction
time: 10 h. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.96-7.93 (m, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.54-7.52 (m, 1H), 7.46-7.41 (m, 4H), 4.99 (t, $J = 6.6$ Hz, 1H), 3.29 (dqd, $J = 15.1$, 10.7, 7.3 Hz, 1H), 2.58 (dqd, $J = 15.0$, 10.6, 5.9 Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.77, -64.50. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.14, 141.28, 135.29, 133.78, 130.22 (q, $J = 32.7$ Hz), 128.86, 128.79, 128.50, 126.30 (q, $J = 3.8$ Hz), 126.19 (q, $J = 277.2$ Hz), 123.81 (q, $J = 272.2$ Hz), 46.85 (q, $J = 2.6$ Hz), 37.28 (q, $J = 28.6$ Hz).

![ Molecular structure of 2t ]

4-(4,4,4-trifluoro-1-oxo-1-phenylbutan-2-yl)benzonitrile (2t):$^1$ According to the general procedure: 1t (0.2 mmol, 47.0 mg), IV (0.4 mmol, 175.3 mg), K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2t (46.1 mg, 76%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10h. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.93 (dd, $J = 8.4$, 1.3 Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.58-7.53 (m, 1H), 7.47-7.41 (m, 4H), 4.99 (t, $J = 6.7$ Hz, 1H), 3.32-3.18 (m, 1H), 2.66-2.53 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.33. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.80, 142.46, 135.10, 133.96, 133.07, 128.96, 128.93, 128.77, 126.10 (d, $J = 277.2$ Hz), 118.20, 112.06, 47.00 (q, $J = 2.7$ Hz), 37.16 (q, $J = 28.6$ Hz).

![ Molecular structure of 2u ]
4-(benzo[d]thiazol-2-yl)-6,6,6-trifluoro-1-phenylhexan-1-one (2u): According to the general procedure: 1u (0.2 mmol, 59.0 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2u (64.1 mg, 88%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. 

1H NMR (400 MHz, Chloroform-d) δ 7.99 (dd, J = 8.2, 1.1 Hz, 1H), 7.87-7.84 (m, 3H), 7.54-7.46 (m, 2H), 7.42-7.36 (m, 3H), 3.75-3.65 (m, 1H), 3.03-2.88 (m, 3H), 2.70-2.57 (m, 1H), 2.47-2.28 (m, 2H). 19F NMR (376 MHz, CDCl₃) δ -64.05. 13C NMR (101 MHz, CDCl₃) δ 198.62, 172.04, 153.07, 136.56, 134.67, 133.21, 128.59, 127.96, 126.23, 126.12 (d, J = 277.4 Hz), 125.24, 123.00, 121.74, 39.35 (q, J = 28.5 Hz), 37.96 (q, J = 2.7 Hz), 35.28, 30.00.

6,6,6-trifluoro-1-phenyl-4-(thiazol-2-yl)hexan-1-one (2v): According to the general procedure: 1v (0.2 mmol, 49.0 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2v (58.9 mg, 94%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h. 

1H NMR (400 MHz, Chloroform-d) δ 7.88-7.85 (m, 2H), 7.74 (d, J = 3.3 Hz, 1H), 7.56-7.52 (m, 1H), 7.45-7.41 (m, 2H), 7.25 (d, J = 3.3 Hz, 1H), 3.67-3.60 (m, 1H), 2.93-2.88 (m, 2H), 2.87-2.77 (m, 1H), 2.64-2.51 (m, 1H), 2.39-2.19 (m, 2H). 19F NMR (376 MHz, CDCl₃) δ -64.10. 13C NMR (101 MHz, CDCl₃) δ 198.73, 171.11, 142.74, 136.60, 133.19, 128.60, 127.93, 126.14 (d, J = 277.4 Hz), 118.55, 39.61 (q, J = 28.3 Hz), 36.90 (q, J = 2.7 Hz), 35.24, 30.27.

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6,6,6-trifluoro-1-phenyl-4-(pyridin-2-yl)hexan-1-one (2w):⁴ According to the general procedure: 1w (0.2 mmol, 47.8 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2w (42.4 mg, 69%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h.¹H NMR (400 MHz, Chloroform-d) δ 8.60 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H), 7.85-7.82 (m, 2H), 7.61 (td, J = 7.6, 1.9 Hz, 1H), 7.55-7.51 (m, 1H), 7.44-7.39 (m, 2H), 7.18-7.12 (m, 2H), 3.26-3.19 (m, 1H), 2.91-2.71 (m, 3H), 2.54-2.40 (m, 1H), 2.22 (q, J = 7.4 Hz, 2H).¹⁹F NMR (376 MHz, CDCl₃) δ -64.02.¹³C NMR (101 MHz, CDCl₃) δ 199.31, 161.32, 149.81, 136.69, 136.56, 133.08, 128.56, 127.94, 126.66 (q, J = 277.3 Hz), 123.55, 122.05, 40.64, 38.96 (q, J = 27.6 Hz), 35.61, 29.85.

13-(2,2,2-trifluoroethyl)-6,7,8,13-tetrahydro-5H-dibenzo[a,d][9]annulen-5-one (2x):⁵ According to the general procedure: 1x (0.2 mmol, 52.8 mg), IV (0.4 mmol, 175.3 mg), K₂HPO₄ (0.3 mmol, 52.3 mg) in DMSO (2.0 mL) afforded 2x (23.2 mg, 35%) as a yellow oil after purification on silica gel (Petroleum ether: EtOAc = 10:1). Reaction time: 10 h.¹H NMR (400 MHz, Chloroform-d) δ 7.44 (dd, J = 7.4, 1.6 Hz, 1H), 7.32 (td, J = 7.4, 1.7 Hz, 1H), 7.28 (dd, J = 7.5, 1.4 Hz, 1H), 7.25-7.19 (m, 1H), 7.18-7.11 (m, 4H), 3.36-3.30 (m, 2H), 3.25-3.11 (m, 2H), 2.93-2.85 (m, 1H).

2.74-2.64 (m, 2H), 2.54-2.31 (m, 3H), 1.72-1.63 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -64.15. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 206.91, 141.90, 140.37, 139.48, 137.64, 131.20, 130.89, 130.73, 129.23, 127.24, 126.94, 126.03 (q, $J = 277.6$ Hz), 125.45, 44.27, 39.84 (q, $J = 27.5$ Hz), 38.09, 36.24 (q, $J = 2.4$ Hz), 29.17, 26.77.
6. NMR spectra for all compounds
2r

-64.3868

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