Supporting Information

Difluoromethanesulfonyl Hypervalent Iodonium Ylides for Electrophilic Difluoromethylthiolation Reactions under Copper Catalysis

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1. General Information

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All solvents were purified by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light or KMnO₄ in water/heat. All of the reaction products were purified by Column chromatography. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 mm. The ¹⁹F NMR (282 MHz) and ¹H NMR (300 MHz) in CDCl₃, (CD₃)₂CO or (CD₃)₂SO were recorded on a Varian Mercury 300. ¹³C NMR (125 MHz) spectra for solution in CDCl₃, CD₃CN or (CD₃)₂SO were recorded on a BRUKER Advance 500. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00) or C₆F₆ [δ = -162.2 (CDCl₃) or -163.5 ((CD₃)₂CO)] as an internal standard. Coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020 (ESI-MS and APCI-MS). Infrared spectra were recorded on JASCO FT/IR-200 or a JASCO FT/IR-4100 spectrometer.

2. Preparation of Reagent 2a-d and Starting Materials

Synthesis of Reagent 2a-d

Scheme S1. Synthesis of reagent 2a-d
Synthesis of 1-phenyl-2-[(difluoromethyl)sulfonyl]ethanone:

A mixture of 2-bromoacetophenone (4.38 g, 22.0 mmol) and sodium difluoromethanesulfinate (3.34 g, 24.2 mmol) in DMAc (100 mL) was stirred at 50 °C for 20 h. Then water (50 mL) was added to the mixture at room temperature. The resulting mixture was extracted with Et₂O and organic layer was washed with water 2 times, brine for once then dried over magnesium sulfate. The solvent was removed by rotary evaporation to give a crude product then the crude product was purified by flash column chromatography on silica gel (eluent: ethyl acetate/hexane =1/4, Rf = 0.2 - 0.3). A light yellow solid (1-phenyl-2-[(difluoromethyl)sulfonyl]ethanone) was afforded (4.1 g, 79%). Mp: 106-107 °C.

\[ \text{1H NMR (300 MHz, CDCl}_3\text{): } \delta \text{ ppm 7.95 (d, } J = 7.5 \text{ Hz, 2H), 7.71-7.68 (m, 1H), 7.58-7.53 (m, 2H), 6.67 (t, } J = 54.0 \text{ Hz, 1H), 4.83 (s, 2H).} \]

\[ \text{19F NMR (282 MHz, CDCl}_3\text{): } \delta \text{ ppm -125.35 (d, } J = 53.3 \text{ Hz, 2F).} \]

\[ \text{13C NMR (125 MHz, CDCl}_3\text{): } \delta \text{ ppm 187.65, 135.22, 134.77, 129.19, 128.92, 114.32 (t, } J = 284 \text{ Hz), 56.87. IR (KBr): } \nu = 3036, 2958, 2915, 1681, 1452, 1336, 1154, 1108 \text{ cm}^{-1}. \]

\[ \text{MS (ESI): 257 (M+Na). HRMS (ESI) } C_{9}H_{8}F_{2}NaO_{3}S \text{ (M+Na) for Calcd: 257.0060, Found: 257.0059.} \]

**Synthesis of reagent 2a:**
To a mixture of 1-phenyl-2-[(difluoromethyl)sulfonyl]ethanone (3.22 g 13.7 mmol) and KOH (1.16 g, 20.6 mmol) in MeCN (100 mL), PIDA (4.87 g, 15.1 mmol) was added. After stirring for 5 h at room temperature, cold water (200 mL) was added to the mixture and the reaction mixture was stirred continuously for 0.5 h. The precipitate was filtered and washed with water and Et₂O then dried under vacuum. A white solid (reagent 2a) was afforded (4.26 g, 71%). Mp: 72-73ºC (decomposed).

**1H NMR** (300 MHz, (CD₃)₂SO): δ ppm 7.85 (d, J = 7.8 Hz, 2H), 7.62-7.57 (m, 1H), 7.53-7.47 (m, 2H), 7.39-7.29 (m, 5H), 6.70 (t, J = 53.1 Hz, 1H).  
**19F NMR** (282 MHz, CDCl₃): δ ppm -120.86 (d, J = 52.4 Hz, 2F).  
**13C NMR** (125 MHz, CDCl₃): δ ppm 186.53, 137.47, 134.56, 132.58, 131.87, 130.37, 127.98, 127.60, 114.54 (t, J = 281 Hz), 94.37. IR (KBr): ν = 3056, 1685, 1523, 1444, 1325, 1279, 1154, 1092 cm⁻¹. MS (ESI): 475 (M+K). HRMS (EI) C₁₅H₁₁F₂INaO₃S (M+Na) for Calcd: 458.9339, Found: 458.9340.

**Synthesis of reagent 2c:**

To a mixture of 1-phenyl-2-[(difluoromethyl)sulfonyl]ethanone (0.50 g 2.1 mmol) and KOH (0.18 g, 3.2 mmol) in MeCN (10 mL), iodomesitylene diacetate (0.85 g, 2.3 mmol) was added. After stirring at room temperature for 1 h, cold water (20 mL) was added to the mixture and the reaction mixture was stirred continuously for 0.1 h. The precipitate was filtered and washed with cold water and Et₂O then dried under vacuum. A white solid (reagent 2c) was afforded (0.40 g, 39%). Mp: 58-59ºC (decomposed).  
**1H NMR** (300 MHz, CDCl₃): δ ppm 7.49 (d, J = 6.2 Hz, 2H), 7.40-7.33 (m, 3H), 7.06 (s, 2H), 5.92 (t, J = 55.2 Hz, 1H), 2.72 (s, 6H), 2.37 (s, 3H).  
**19F NMR** (282 MHz, CDCl₃): δ ppm -120.9 (d, J = 54.4 Hz, 2F).  
**13C NMR** (125 MHz, CD₃CN): δ ppm 187.24, 144.34, 143.35, 140.10, 130.64, 130.40, 128.79, 128.41, 123.06, 115.44 (t, J = 278 Hz), 73.46, 26.58, 20.92. IR (KBr): ν = 2970, 2943, 2916, 1688, 1600, 1448, 1363, 1170, 1127, 1004 cm⁻¹. MS (ESI): 479 (M+H). HRMS (EI) C₁₈H₁₇F₂INaO₃S (M+Na) for Calcd: 500.9809, Found: 500.9816.

**Synthesis of 1-(4-nitrophenyl)-2-[(difluoromethyl)sulfonyl]ethanone:**
A mixture of 2-bromo-4’-nitroacetophenone (2.00 g, 8.2 mmol) and sodium difluoromethanesulfinate (1.25 g, 9.1 mmol) in DMAc (70 mL) was stirred at 50 ºC for 20 h. Then water (50 mL) was added to the mixture at room temperature. The resulting mixture was extracted with Et₂O and organic layer was washed with water 2 times, brine for once then dried over magnesium sulfate. The solvent was removed by rotary evaporation to give a crude product then the crude product was purified by flash column chromatography on silica gel (eluent: ethyl acetate/hexane =1/1, Rf = 0.5 - 0.6). A yellow solid (1-(4-nitrophenyl)-2-[([difluoromethyl]sulfonyl]ethanone was afforded (1.7 g, 76%). Mp: 83-84 ºC.

1H NMR (300 MHz, CDCl₃): δ ppm 8.41 (d, J = 7.5 Hz, 2H), 8.15 (d, J = 7.2, 2H), 6.55 (t, J = 53.1 Hz, 1H), 4.85 (s, 2H). 19F NMR (282 MHz, CDCl₃): δ ppm -124.0 (d, J = 53.6 Hz, 2F). 13C NMR (125 MHz, CDCl₃): δ ppm 186.15, 151.29, 139.05, 130.05, 124.33, 114.44 (t, J = 285 Hz), 56.81. IR (KBr): ν = 3110, 2970, 1584, 1511, 1329, 1275, 1143, 1092 cm⁻¹. MS (ESI): 117 (M-NO₂-SO₂CF₂H). HRMS (EI) C₉H₇F₂NO₅S for Calcd: 279.0013, Found: 279.0013.

Synthesis of reagent 2b:

To a mixture of 1-(4-nitrophenyl)-2-[([difluoromethyl]sulfonyl]ethanone (0.50 g 1.8 mmol) and KOH (0.15 g, 2.7 mmol) in MeCN (10 mL), PIDA (0.64 g, 2.0 mmol) was added. After stirring at room temperature for 5 h, water (50 mL) was added to the mixture and the reaction mixture was stirred continuously for 0.5 h. The precipitate was filtered and washed with water and Et₂O then dried under vacuum. A white solid (reagent 2b) was afforded (0.73g, 85%). Mp: 101-102 ºC (decomposed).

1H NMR (300 MHz, (CD₃)₂SO): δ ppm 8.19 (d, J = 6.6 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 7.64-7.49 (m, 5H), 6.70 (t, J = 54.0 Hz, 1H). 19F NMR (282 MHz, (CD₃)₂CO): δ ppm -121.6 (d, J = 51.3 Hz, 2F). 13C NMR (125 MHz, (CD₃)₂SO): δ ppm 183.87, 147.40, 146.27, 133.20, 133.20, 131.16, 128.23, 122.75, 117.97, 114.28 (t, J = 280 Hz), 76.50. IR (KBr): ν = 3063, 2970, 1696, 1592, 1507, 1333, 1271, 1139, 1085 cm⁻¹. MS (ESI): 504 (M+Na). HRMS (EI) C₁₅H₁₀F₂INaO₅S (M+Na) for Calcd: 503.9190, Found: 503.9191.
Synthesis of reagent 2d:

To a mixture of 1-(4-nitrophenyl)-2-[(difluoromethyl)sulfonyl]ethanone (0.50 g 1.8 mmol) and KOH (0.15 g, 2.7 mmol) in MeCN (10 mL), iodosmesitylene diacetate (0.72 g, 2.0 mmol) was added. After stirring at room temperature for 5 h, water (50 mL) was added to the mixture and the reaction mixture was stirred continuously for 0.5 h. The precipitate was filtered and washed with water and Et2O then dried under vacuum. A white solid (reagent 2d) was afforded (0.87g, 93%). Mp: 113-114 ºC (decomposed).

1H NMR (300 MHz, (CD3)2SO): δ ppm 8.16 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.12 (s, 2H), 6.50 (t, J = 53.4 Hz, 1H), 2.59 (s, 6H), 2.30 (s, 3H). 19F NMR (282 MHz, CDCl3): δ ppm -120.2 (d, J = 55.5 Hz, 2F). 13C NMR (125 MHz, (CD3)2SO): δ ppm 183.43, 147.28, 146.42, 141.77, 141.63, 128.97, 128.46, 124.14, 122.57, 114.25 (t, J = 280 Hz), 74.65, 26.01, 20.48. IR (KBr): ν = 2970, 2370, 1584, 1511, 1329, 1275, 1143, 1092 cm⁻¹. MS (ESI): 555 (M+MeOH). HRMS (EI) C18H16F2INaO5S (M+Na) for Calcd: 545.9660, Found: 545.9658.

Preparation of Starting Materials
Sodium difluoromethanesulfinate was prepared by the reported procedure. [1]
All starting materials were known compounds. Enamine 3, [2-4] 3z, indole 5, pyrrole 7 [5] and allyl alcohol 11 [6] were commercially available or synthesized by the reported procedure.

3. Experimental Details

(A) General procedure for difluoromethylthiolation of enamines 3, indoles 5 and pyrroles 7.
To a mixture of enamine 3, indole 5 or pyrrole 7 (0.2 mmol) and Cu(I)Br (0.04 mmol) in 1,4-dioxane (2.5 mL), reagent 2a (0.4 mmol) or 2d (0.4 mmol) was added at room temperature under N2. The resulting mixture was stirred at room temperature for 5 h and then filtered through a short plug of celite. The filtrate was concentrated under reduced pressure and purified through flash column chromatography on silica gel (ethyl acetate/hexane) to afforded the target product.
(B) General procedure for difluoromethylthiolation of β-keto esters 9
To a mixture of β-keto ester 9 (0.2 mmol) Cu(I)Br (0.04 mmol) and K₂CO₃ (0.08 mmol) in 1,4-dioxane (2.5 mL), reagent 2d (0.4 mmol) was added at room temperature under N₂. The resulting mixture was stirred at room temperature for 24 h and then filtered through a short plug of celite. The filtrate was concentrated under reduced pressure and purified through flash column chromatography on silica gel (ethyl acetate/hexane) to afforded the target product.

(C) General procedure for reaction of ally alcohols 11 with reagent 2.
To a mixture of allyl alcohol (0.20 mmol) and CuF₂ (0.04 mmol) in DMAc (2.5 mL), reagent 2a (0.4 mmol) was added at room temperature under N₂. After stirring at room temperature for 24 h, water (2.0 mL) was added to the mixture. The resulting mixture was extracted with ethyl acetate, the organic phase was washed with water 2 times and saturated sodium bicarbonate solution over 5 times to remove the starting material and brine once then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified through flash column chromatography on silica gel (ethyl acetate/hexane) to afforded the target product.

(D) General procedure for Enamine method: Two step, one-pot synthesis of difluoromethylthiolated β-keto esters and 1,3-diketones 10p-y.
To a mixture of enamine 3p-y (0.2 mmol) and Cu(I)Br (0.04 mmol) in 1,4-dioxane (2.5 mL), reagent 2a (0.4 mmol) or 2d (0.4 mmol) was added at room temperature under N₂. After stirring at room temperature for 5 h, 1N-HCl aq (1.0 mL) was added to the reaction mixture. The resulting mixture was continuously stirred for 12 h (for 24 h when 3q or 3r was a starting material), then extracted with ethyl acetate, the organic phase was washed with water 2 times and brine once then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified through flash column chromatography on silica gel (ethyl acetate/hexane) to afforded the target product.

(E) General procedure for reaction of β-keto esters with reagent 2.
To a mixture of β-keto esters (0.2 mmol), CuF₂ (0.04 mmol) and Potassium carbonate (0.04 mmol) in DMAc (2.5 mL), reagent 2d (0.4 mmol) was added at room temperature under N₂. After stirring at room temperature for 18 h or 16 h. The resulting mixture was then extracted with ethyl acetate, the organic phase was washed with water and brine once then dried over magnesium sulfate. The solvent was removed by rotary
evaporation and purified through flash column chromatography on silica gel (DCM/hexane) to afforded the target product.

(F) General procedure for reaction of silyl enol ether 9d with reagent 2.

To a mixture of silyl enol ether (0.20 mmol) and CuBr (0.04 mmol) in 1,4-dioxane (2.5 mL), reagent 2d (0.4 mmol) was added at room temperature under N₂. After stirring at room temperature for 18 h, 1 N HClaq (1.0 mL) was added to the mixture and stirring at room temperature for 30 min. The resulting mixture was extracted with ethyl acetate, the organic phase was washed with water 2 times and brine once then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified through flash column chromatography on silica gel (DCM/hexane) to afforded the target product.

Table S1. Stability of Reagent 2a-d

| run | reagent | residual rate (%)<sup>b</sup> | 1 h | 5 h | 10 h | 24 h |
|-----|---------|-------------------------------|-----|-----|------|------|
| 1   | 2a      |                               | 91  | 66  | 42   | 0    |
| 2   | 2b      |                               | 95  | 97  | 92   | 52   |
| 3   | 2c      |                               | 94  | 2   | 0    | 0    |
| 4   | 2d      |                               | 99  | 100 | 100  | 100  |

<sup>a</sup> Conditions: 2 (0.1 mmol), rt, under air atmosphere.  
<sup>b</sup> Residual rate were determined by <sup>19</sup>F NMR spectroscopy with PhF as an internal standard.

Reagent 2a-d (0.1 mmol, respectively) was put into a glass tube at room temperature in air atmosphere. After 1 h, 5 h, 10 h and 24 h respectively, CDCl₃ and PhF (0.2 mmol: an internal standard) were added to the resulting reagent. The residual rate of reagent was immediately analyzed by <sup>19</sup>F NMR spectroscopy.

Scheme S2. Reaction of 3m with Reagent 2a under Different conditions
(1): To a mixture of enamine 3m (0.1 mmol) and Cu(I)Br (2.9 mg, 0.02 mmol) in 1,4-dioxane (1.3 mL), reagent 2a (174.5 mg, 0.2 mmol) was added at room temperature under N₂. The resulting mixture was stirred at room temperature for 5 h and then filtered through a short plug of celite. The filtrate was concentrated under reduced pressure then analyzed by ¹⁹F NMR spectroscopy with PhF (18.4 μL, 0.2 mmol) as an internal standard.

(2): The mixture of Cu(I)Br (2.9 mg, 0.02 mmol), 2a (174.5 mg, 0.2 mmol) and 1,4-dioxane (1.3 mL) was stirred at room temperature for 20 min under N₂. 3m was added to the resulting mixture and then stirred for 5 h. The reaction mixture was filtered through a short plug of celite. The filtrate was concentrated under reduced pressure then analyzed by ¹⁹F NMR spectroscopy with PhF (18.4 μL, 0.2 mmol) as an internal standard.

Scheme S3. GCMS Analysis of Difluoromethylthiolation of 3m with 2d

To a mixture of enamine 3m (18.9 mg, 0.1 mmol) and Cu(I)Br (2.8 mg, 0.02 mmol) in 1,4-dioxane (1.3 mL), reagent 2d (104.7 mg, 0.2 mmol) was added at room temperature under N₂. The resulting mixture was stirred at room temperature for 5 h and then filtered through a short plug of celite. The filtrate 0.1 mL was added into CH₂Cl₂ 1.5 mL then the resulting mixture 5 μL was analyzed by GCMS.

GCMS analytical data of the reaction mixture of 3m, CuBr and reagent 2d.
All peak data (Peak 1-3)
Peak 1 data (RT=3.98 min)

Chemical Formula: C9H11I
Exact Mass: 245.9905

Peak 2 data (RT=5.15 min)

Chemical Formula: C7H5NO3
Exact Mass: 151.0269
Peak 3 data (RT=7.80 min)

GCMS analytical data of authentic sample Mesityl-I and p-NO₂PhC(O)H under same measurement condition.

All peak data

Mesityl-I peak (RT=3.97 min)
Instrument conditions GCMS (SHIMADZU GCMS-QP5050A)
(GC)
Colum: HYDRODEX-B-TBDAc  25 m × 0.25 mm, film thickness: 0.25 μm
Carrier gas: helium
The gradient of temperature: 50~230 °C (40°C/min)
Flow rate: 2 mL/min
(MS)
Temperature of interface: 230 °C
Scan (m/z): 50 ~ 800

4. Optimization of Conditions
Table S2. Optimization of the Difluoromethylthiolation of Enamine 3a
| run | 2a (equiv) | CuX      | temp. (°C) | time (h) | solvent | yield (%) |
|-----|-----------|----------|------------|----------|---------|-----------|
| 1   | 2.0       | CuF₂     | 0→rt       | 5        | DMAc    | 50        |
| 2   | 2.0       | CuCl     | rt         | 5        | 1,4-dioxane | 82        |
| 3   | 2.0       | CuCl₂    | rt         | 5        | 1,4-dioxane | 71        |
| 4   | 2.0       | CuBr     | rt         | 5        | 1,4-dioxane | 94        |
| 5   | 2.0       | CuI      | rt         | 5        | 1,4-dioxane | 82        |
| 6   | 2.0       | CuF₂     | rt         | 5        | 1,4-dioxane | 78        |
| 7   | 2.0       | CuOAc    | rt         | 5        | 1,4-dioxane | 73        |
| 8   | 2.0       | Cu(OAc)₂ | rt         | 5        | 1,4-dioxane | 81        |
| 9   | 2.0       | CuBr     | rt         | 5        | THF     | 74        |
| 10  | 2.0       | CuBr     | rt         | 5        | MeCN    | 38        |
| 11  | 2.0       | CuBr     | rt         | 5        | DMF     | 48        |
| 12  | 2.0       | CuBr     | rt         | 5        | DMAc    | 42        |
| 13  | 2.0       | CuBr     | rt         | 5        | DMSO    | 16        |
| 14  | 2.0       | CuBr     | rt         | 5        | PhMe    | 60        |
| 15  | 2.0       | CuBr     | rt         | 5        | EtOH    | 77        |
| 16  | 1.1       | CuBr     | rt         | 5        | 1,4-dioxane | 58        |
| 17  | 2.0       | -        | rt         | 5        | 1,4-dioxane | 0         |
| 18  | 2.0       | CuBr     | rt         | 1        | 1,4-dioxane | 89        |
| 19  | 2.0       | CuBr     | rt         | 10       | 1,4-dioxane | 91        |
| 20  | 2.0       | CuBr     | rt         | 24       | 1,4-dioxane | 84        |
| 22  | 2.0       | CuBr     | 50         | 5        | 1,4-dioxane | 78        |
| 23³ | 2.0       | CuBr     | rt         | 5        | 1,4-dioxane | 94        |

a Reaction conditions: 3a (0.1 mmol), 2a (0.2 mmol) and CuX (20 mol%) in solvent (1.25 mL) under N₂ atmosphere. b ¹⁹F NMR yields with PhF as an internal standard. c 100 mol% of CuBr was used.

Table S3. Optimization of the Difluoromethylthiolation of Pyrrole 7a

| run | CuX (mol%) | solvent   | time (h) | yield (%) |
|-----|------------|-----------|----------|-----------|
| 1   | CuCl (20)  | 1,4-dioxane | 24       | 51        |
| 2   | CuCl (50)  | 1,4-dioxane | 24       | 46        |
| 3   | CuCl (100) | 1,4-dioxane | 24       | 42        |
4  -  1,4-dioxane  24  0
5\textsuperscript{c}  CuCl (20)  1,4-dioxane  24  38
6  CuBr (20)  1,4-dioxane  24  \textbf{58}
7  CuF\textsubscript{2} (20)  DMAC  24  27
8  CuBr (20)  1,4-dioxane  5  \textbf{58}
9\textsuperscript{d}  CuBr (20)  1,4-dioxane  5  46
10\textsuperscript{e}  CuBr (20)  1,4-dioxane  5  47
11\textsuperscript{f}  CuBr (20)  1,4-dioxane  5  \textbf{57}

\textsuperscript{a} Reaction conditions: 7a (0.1 mmol), 2a (0.2 mmol) in solvent (1.25 mL) under N\textsubscript{2} atmosphere. \textsuperscript{b} \textsuperscript{19}F NMR yields with PhF as an internal standard. \textsuperscript{c} PhNMe\textsubscript{2} (20 mol\%) was added. \textsuperscript{d} 2b (0.2 mmol) was used instead of 2a. \textsuperscript{e} 2c (0.2 mmol) was used instead of 2a. \textsuperscript{f} 2d (0.2 mmol) was used instead of 2a.

### Table S4. Optimization of the Reaction Conditions of Allyl Alcohol 11a

| run | CuX          | solvent | yield (\%)\textsuperscript{b} |
|-----|--------------|---------|-------------------------------|
| 1   | CuBr         | 1,4-dioxane | 27                            |
| 2   | CuF\textsubscript{2} | DMAC   | \textbf{50}                      |

\textsuperscript{a} Reaction conditions: 11a (0.1 mmol), 2a (0.2 mmol) in solvent (1.25 mL) under N\textsubscript{2} atmosphere. \textsuperscript{b} \textsuperscript{19}F NMR yields with PhF as an internal standard.

5. Analytical Data

\textit{(E)-Methyl 3-(benzylamino)-2-[(difluoromethyl)thio]but-2-enoate (4a)}

![Image of analytical data](image)

\textbf{4a} was prepared according to the \textbf{General procedure (A)}. Yellow oil (46.8 mg, 81%). Eluent: ethyl acetate/hexane =1/7, Rf = 0.4.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \textit{\delta} ppm 10.61 (brs, 1H), 7.37-7.33 (m, 5H), 6.53 (t, \textit{J} = 58.5 Hz, 1H), 4.53 (d, \textit{J} = 5.7 Hz, 2H), 3.74 (s, 3H), 2.39 (s, 3H). \textsuperscript{19}F NMR (282 MHz,
CDCl₃: δ ppm -96.85 (d, J = 58.3 Hz, 2F). ¹³C NMR (125 MHz, CDCl₃): δ ppm 171.23, 170.94, 137.03, 128.96, 127.76, 126.85, 121.56 (t, J = 274 Hz), 76.29 (t, J = 3.75 Hz), 51.51, 48.25, 17.89. IR (neat): ν = 3263, 2947, 1638, 1580, 1441, 1255, 1065, 1027 cm⁻¹. MS (EI): 287 (M). HRMS (ESI) C₁₃H₁₅F₂NNaO₂S (M+Na) for Calcd: 310.0689, Found: 310.0695.

(E)-Methyl 3-[(4-methoxybenzyl) amino]-2-[(difluoromethyl)thio]but-2-enoate (4b)

4b was prepared according to the General procedure (A).
Yellow solid (49.6 mg, 78%). Mp: 48 ~ 49 ºC. Eluent: ethyl acetate/hexane =1/7, Rf = 0.5.
¹H NMR (300 MHz, CDCl₃): δ ppm 10.52 (brs, 1H), 7.19 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.53 (t, J = 58.2 Hz, 1H), 4.45 (d, J = 5.4 Hz, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 2.40 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -96.85 (d, J = 58.4 Hz, 2F). ¹³C NMR (125 MHz, CDCl₃): δ ppm 171.22, 170.76, 159.17, 128.93, 128.31, 121.60 (t, J = 274 Hz), 114.35, 76.04 (t, J = 3.75 Hz), 55.27, 51.48, 47.84, 17.92. IR (KBr): ν = 3129, 2951, 1882, 1580, 1514, 1444, 1242, 1062 cm⁻¹. MS (ESI): 335 (M+NH₄). HRMS (ESI) C₁₄H₁₇F₂NNaO₃S (M+Na) for Calcd: 340.0795, Found: 340.0791.

(E)-Methyl 3-[(4-bromobenzyl) amino]-2-[(difluoromethyl)thio]but-2-enoate (4c)

4c was prepared according to the General procedure (A).
Pale yellow solid (62.0 mg, 85%: using 2a, 62.1 mg, 85%: using 2d). Mp: 77-78 ºC. Eluent: ethyl acetate/hexane =1/7, Rf = 0.3.
¹H NMR (300 MHz, CDCl₃): δ ppm 10.60 (brs, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.53 (t, J = 58.2 Hz, 1H), 4.48 (d, J = 5.4 Hz, 2H), 3.74 (s, 3H), 2.37 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -96.86 (d, J = 58.7 Hz, 2F). ¹³C NMR (125 MHz, CDCl₃): δ ppm 171.26, 170.83, 136.15, 132.11, 128.53, 121.71, 121.41 (t, J = 275 Hz), 76.79 (t, J = 3.75 Hz), 51.60, 47.62, 17.90. IR (KBr): ν = 3198, 3125, 2954, 1514, 1444, 1317, 1274, 1069 cm⁻¹. MS (ESI): 365 (M+H). HRMS (ESI) C₁₃H₁₄BrF₂NNaO₂S (M+Na) for Calcd: 387.9794, Found: 387.9787.
(E)-Methyl 3-(butylamino)-2-[(difluoromethyl)thio]but-2-enoate (4d)

4d was prepared according to the General procedure (A).
Yellow oil (42.8 mg, 84%). Eluent: ethyl acetate/hexane =1/7, Rf = 0.6.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 10.26 (brs, 1H), 6.51 (t, $J = 58.8$ Hz, 1H), 3.73 (s, 3H), 3.31 (d, $J = 6.0$ Hz, 2H), 2.37 (s, 3H), 1.64-1.59 (m, 2H), 1.47-1.42 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -97.9 (d, $J = 57.5$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 171.38, 170.78, 121.73 (t, $J = 274$ Hz), 74.89 (t, $J = 3.75$ Hz), 51.41, 44.30, 31.75, 20.00, 17.74, 13.69. IR (neat): $\nu = 3129$, 2958, 2877, 1638, 1588, 1448, 1248, 1065 cm$^{-1}$. MS (ESI): 292 (M+K). HRMS (ESI) C$_{10}$H$_{17}$F$_2$NNaO$_2$S (M+Na) for Calcd: 276.0846, Found: 276.0852.

(E)-Methyl 3-(phenylamino)-2-[(difluoromethyl)thio]but-2-enoate (4e)

4e was prepared according to the General procedure (A).
Yellow solid (47.6 mg, 87%). Mp: 46-47 °C. Eluent: ethyl acetate/hexane =1/7, Rf = 0.5.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 10.84 (brs, 1H), 7.39-7.36 (m, 2H), 7.29-7.26 (m, 1H), 7.12 (d, $J = 6.9$ Hz, 2H), 6.61 (t, $J = 58.5$ Hz, 1H), 3.79 (s, 3H), 2.34 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -96.24 (d, $J = 58.4$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 171.08, 169.16, 138.41, 129.27, 126.69, 15.77, 121.50 (t, $J = 274$ Hz), 76.68 (t, $J = 3.75$ Hz), 51.76, 19.51. IR (KBr): $\nu = 3156$, 2954, 1638, 1569, 1437, 1309, 1248, 1065, 1011 cm$^{-1}$. MS (ESI): 305 (M+MeOH). HRMS (ESI) C$_{12}$H$_{13}$F$_2$NNaO$_2$S (M+Na) for Calcd: 296.0533, Found: 296.0535.

(E)-Methyl 3-(p-tolylamino)-2-[(difluoromethyl)thio]but-2-enoate (4f)

4f was prepared according to the General procedure (A).
Pale yellow solid (51.6 mg, 90%). Mp: 58-59 °C. Eluent: ethyl acetate/hexane =1/7, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 11.75 (brs, 1H), 7.18 (d, $J = 7.5$ Hz, 2H), 7.00 (d, $J = 7.5$ Hz, 2H), 6.60 (t, $J = 58.2$ Hz, 1H), 3.79 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H).  $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -96.26 (d, $J = 58.4$ Hz, 2F).  $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 171.11, 169.47, 136.66, 135.79, 129.83, 125.71, 121.58 (t, $J = 275$ Hz), 78.13 (t, $J = 3.75$ Hz), 51.70, 20.95, 19.45. IR (KBr): ν = 3168, 3098, 2950, 1627, 1565, 1433, 1309, 1255, 1015 cm$^{-1}$. MS (ESI): 310 (M+Na).

HRMS (ESI) C$_{13}$H$_{15}$F$_2$NNaO$_2$S (M+Na) for Calcd: 310.0689, Found: 310.0695.

$(E)$-Methyl 3-(benzylamino)-3-phenyl-2-[(difluoromethyl)thio]acrylate (4g)

4g was prepared according to the General procedure (A).

Colorless oil (58.7 mg, 84%). Eluent: ethyl acetate/hexane =1/7, Rf = 0.4.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 10.44 (brs, 1H), 7.42 (brs, 3H), 7.31-7.28 (m, 2H), 7.12 (brs, 5H), 6.42 (t, $J = 58.2$ Hz, 1H), 4.13 (d, $J = 5.7$ Hz, 2H), 3.80 (s, 3H).  $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -97.26 (d, $J = 58.4$ Hz, 2F).  $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 172.19, 171.24, 137.56, 134.28, 129.02, 128.73, 128.37, 127.72, 127.61, 126.99, 121.21 (t, $J = 275$ Hz), 78.01 (t, $J = 3.75$ Hz), 51.70, 49.44. IR (neat): ν = 3233, 3033, 2945, 1646, 1565, 1444, 1263, 1158, 1065 cm$^{-1}$. MS (ESI): 372 (M+Na). HRMS (ESI) C$_{18}$H$_{17}$F$_2$NNaO$_2$S (M+Na) for Calcd: 372.0846, Found: 372.0850.

$(E)$-Ethyl 3-(benzylamino)-3-phenyl-2-[(difluoromethyl)thio]acrylate (4h)

4h was prepared according to the General procedure (A).

Colorless oil (58.7 mg, 81%). Eluent: ethyl acetate/hexane =1/7, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 10.43 (brs, 1H), 7.42 (brs, 3H), 7.30-7.28 (m, 2H), 7.12 (brs, 4H), 6.43 (t, $J = 58.2$ Hz, 1H), 4.26 (q, $J = 6.9$ Hz, 2H), 4.12 (d, $J = 5.7$ Hz, 2H), 1.34 (t $J = 6.9$ Hz, 3H).  $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -97.15 (d, $J = 58.3$ Hz, 2F).  $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 171.97, 170.82, 137.67, 134.44, 128.96, 128.72, 128.36, 127.74, 127.58, 127.02, 121.33 (t, $J = 274$ Hz), 78.40 (t, $J = 3.75$ Hz), 78.01 (t, $J = 3.75$ Hz), 51.70, 49.44, 47.22. IR (KBr): ν = 3233, 3033, 2945, 1646, 1565, 1444, 1263, 1158, 1065 cm$^{-1}$. MS (ESI): 325 (M+Na). HRMS (ESI) C$_{17}$H$_{16}$F$_2$NNaO$_2$ (M+Na) for Calcd: 325.0517, Found: 325.0519.
60.36, 49.42, 14.42. IR (neat): v = 3229, 2981, 1642, 1565, 1433, 1255, 1158, 1062 cm\(^{-1}\). MS (ESI): 386 (M+Na). HRMS (ESI) \(C_{19}H_{19}F_2NaO_2S\) (M+Na) for Calcd: 386.1002, Found: 386.1016.

\((E)\)-Methyl 3-(benzylamino)-3-(2-methoxyphenyl)-2-[(difluoromethyl)thio]acrylate (4i)

![Image of 4i](image_url)

4i was prepared according to the General procedure (A).
White solid (57.5 mg, 76%). Mp: 70-71 °C. Eluent: ethyl acetate/hexane =1/7, Rf = 0.3. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ ppm 10.40 (brs, 1H), 7.41 (brs, 1H), 7.29-7.26 (m, 3H), 7.12 (d, \(J = 6.3 \) Hz, 2H), 7.02 (brs, 2H), 6.93 (d, \(J = 6.3 \) Hz, 1H), 6.45 (t, \(J = 58.5 \) Hz, 1H), 4.14 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ ppm -96.6 (dd, \(J = 58.4, 242 \) Hz, 1F), -96.6 (dd, \(J = 58.4, 242 \) Hz, 1F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ ppm 171.25, 169.67, 155.50, 137.50, 128.96, 128.58, 127.50, 127.27, 123.31, 122.73 (t, \(J = 273 \) Hz), 120.46, 110.69, 78.41 (t, \(J = 3.75 \) Hz), 55.22, 51.60, 49.40. IR (KBr): ν = 3233, 2947, 1642, 1565, 1499, 1437, 1263, 1158, 1058 cm\(^{-1}\). MS (ESI): 380 (M+H). HRMS (ESI) \(C_{20}H_{21}F_2NaO_3S\) (M+Na) for Calcd: 402.0951, Found: 402.0949.

\((E)\)-Methyl 3-(benzylamino)-3-(3-methoxyphenyl)-2-[(difluoromethyl)thio]acrylate (4j)

![Image of 4j](image_url)

4j was prepared according to the General procedure (A).
Pale yellow oil (60.9 mg, 80%). Eluent: ethyl acetate/hexane =1/7, Rf = 0.4. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ ppm 10.41 (brs, 1H), 7.33-7.26 (m, 4H), 7.13-7.11 (m, 2H), 6.95 (d, \(J = 6.6 \) Hz, 1H), 6.72 (d, \(J = 8.1 \) Hz, 1H), 6.64 (s, 1H), 6.45 (t, \(J = 58.5 \) Hz, 1H), 4.14 (s, 2H), 3.80 (s, 3H), 3.74 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ ppm -95.6 (dd, \(J = 58.4, 13.8 \) Hz, 2F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ ppm 171.86, 171.15, 159.39, 137.68, 135.40, 129.55, 128.68, 127.54, 126.95, 121.23 (t, \(J = 275 \) Hz), 119.77, 114.82, 113.07, 77.84 (t, \(J = 3.75 \) Hz), 55.14, 51.65, 49.35. IR (neat): ν = 3233, 2951, 1646, 1565, 1460, 1437, 1267, 1224, 1042 cm\(^{-1}\). MS (ESI): 380 (M+H). HRMS (ESI)
(E)-Methyl 3-(benzylamino)-3-(4-methoxyphenyl)-2-[(difluoromethyl)thio]acrylate (4k)

4k was prepared according to the General procedure (A).
White solid (64.5 mg, 85%). Mp: 57-58 °C. Eluent: ethyl acetate/hexane =1/7, Rf = 0.4. 
\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 10.44 (brs, 1H), 7.33-7.26 (m, 3H), 7.13-7.04 (m, 4H), 6.93 (d, \(J = 8.4\) Hz, 2H), 6.43 (t, \(J = 58.2\) Hz, 1H), 4.16 (d, \(J = 5.7\) Hz, 2H), 3.84 (s, 3H), 3.79 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -97.28 (d, \(J = 58.4\) Hz, 2F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 172.30, 171.28, 159.92, 137.71, 129.24, 128.72, 127.55, 126.96, 126.46, 121.28 (t, \(J = 275\) Hz), 113.71, 78.19 (t, \(J = 3.75\) Hz), 55.19, 51.67, 49.41. IR (KBr): \(\nu = 3233, 2951, 2843, 1642, 1565, 1441, 1252, 1162, 1062\) cm\(^{-1}\). MS (ESI): 380 (M+H). HRMS (ESI) \(\text{C}_{19}\text{H}_{19}\text{F}_{2}\text{NNaO}_{3}\text{S}\) (M+Na) for Calcd: 402.0951, Found: 402.0960

(\(E\))-Methyl 3-(benzylamino)-3-(4-bromophenyl)-2-[(difluoromethyl)thio]acrylate (4l)

4l was prepared according to the General procedure (A).
White solid (71.7 mg, 84%). Mp: 72-73 °C. Eluent: ethyl acetate/hexane =1/7, Rf = 0.3. 
\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 10.42 (brs, 1H), 7.55 (d, \(J = 8.4\) Hz, 2H), 7.32-7.26 (m, 3H), 7.09 (d, \(J = 6.0\) Hz, 2H), 7.00 (d, \(J = 8.4\) Hz, 2H), 6.43 (t, \(J = 58.8\) Hz, 1H), 4.13 (d, \(J = 5.7\) Hz, 2H), 3.80 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -97.40 (d, \(J = 57.2\) Hz, 2F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 171.06, 171.01, 137.37, 133.06, 131.65, 129.53, 128.80, 127.70, 126.87, 123.35, 120.82 (t, \(J = 275\) Hz), 78.25 (t, \(J = 3.75\) Hz), 51.78, 49.41. IR (KBr): \(\nu = 3237, 3033, 2951, 1646, 1565, 1441, 1263, 1154, 1065\) cm\(^{-1}\). MS (ESI): 450 (M+Na). HRMS (ESI) \(\text{C}_{19}\text{H}_{16}\text{BrF}_{2}\text{NNaO}_{2}\text{S}\) (M+Na) for Calcd: 449.9951, Found: 449.9948
(E)-4-(Benzylationo)-3-[(difluoromethyl)thio]pent-3-en-2-one (4m)

4m was prepared according to the General procedure (A).
Yellow oil (48.7 mg, 90%). Eluent: ethyl acetate/hexane = 1/7, Rf = 0.3.

\[ ^1 \text{H NMR} (300 \text{ MHz, CDCl}_3): \delta \text{ ppm 12.86 (brs, 1H)}, 7.37-7.30 (m, 5H), 6.50 (t, J = 56.7 Hz, 1H), 4.55 (d, J = 5.7 Hz, 2H), 2.43 (s, 3H), 2.37 (s, 3H). \]

\[ ^{19} \text{F NMR} (282 \text{ MHz, CDCl}_3): \delta \text{ ppm -95.54 (dd, J = 57.5, 10.9 Hz, 2F)}. \]

\[ ^{13} \text{C NMR} (125 \text{ MHz, CDCl}_3): \delta \text{ ppm 199.83, 171.75, 136.56, 128.99, 127.81, 126.87, 121.40 (t, J = 274 Hz), 88.33 (t, J = 3.75 Hz), 48.28, 29.45, 18.02. IR (neat): v = 3033, 2958, 1577, 1452, 1356, 1263, 1031 cm}^{-1}. \]

\[ \text{MS (ESI): 272 (M+H). HRMS (ESI) C}_{13}\text{H}_{16}\text{F}_{2}\text{NOS (M+H) for Calcd: 272.0921, Found: 272.0925}. \]

(E)-3-(Benzylationo)-1-phenyl-2-[(difluoromethyl)thio]but-2-en-1-one (4n)

4n was prepared according to the General procedure (A).
Yellow solid (61.5 mg, 92%). Mp: 59-60 °C. Eluent: ethyl acetate/hexane = 1/7, Rf = 0.3.

\[ ^1 \text{H NMR} (300 \text{ MHz, CDCl}_3): \delta \text{ ppm 13.01 (brs, 1H)}, 7.40-7.34 (m, 10H), 6.25 (t, J = 56.7 Hz, 1H), 4.64 (d, J = 5.4 Hz, 2H), 2.49 (s, 3H). \]

\[ ^{19} \text{F NMR} (282 \text{ MHz, CDCl}_3): \delta \text{ ppm -96.68 (dd, J = 57.5, 13.8 Hz, 2F)}. \]

\[ ^{13} \text{C NMR} (125 \text{ MHz, CDCl}_3): \delta \text{ ppm 197.41, 173.63, 142.46, 136.15, 129.03, 128.77, 127.91, 127.44, 127.30, 126.99, 121.00 (t, J = 274 Hz), 87.54 (t, J = 3.75 Hz), 48.51, 18.41. IR (KBr): v = 3033, 2958, 1577, 1553, 1456, 1317, 1294, 1131, 1054 cm}^{-1}. \]

\[ \text{MS (ESI): 351 (M+NH}_4). \text{ HRMS (ESI) C}_{18}\text{H}_{17}\text{F}_2\text{NNaOS (M+Na) for Calcd: 356.0897, Found: 356.0895}. \]

3-(Phenylamino)-2-[(difluoromethyl)thio]cyclohex-2-enone (4o)

4o was prepared according to the General procedure (A).
Brown oil (13.2 mg, 25%). Eluent: ethyl acetate/hexane = 1/1, Rf = 0.4.

\[ ^1 \text{H NMR} (300 \text{ MHz, CDCl}_3): \delta \text{ ppm 8.33 (brs, 1H)}, 7.43-7.33 (m, 3H), 7.16 (d, J = 7.2 \]
Hz, 2H), 6.75 (t, J = 58.8 Hz, 1H), 2.63-2.53 (m, 4H), 1.97 (t, J = 5.7 Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -93.55 (d, J = 59.5 Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 192.84, 169.14, 136.98, 129.54, 127.32, 125.90, 120.27 (t, J = 275 Hz), 94.38 (t, J = 2.5 Hz), 37.15, 28.02, 21.01. IR (neat): ν = 3319, 3245, 2951, 1634, 1553, 1390, 1189, 1065 cm$^{-1}$. MS (ESI): 292 (M+Na). HRMS (ESI) C$_{13}$H$_{13}$F$_2$NaOS (M+Na) for Calcd: 292.0584, Found: 292.0597.

$(E)$-Ethyl 3-amino-3-phenyl-2-[(difluoromethyl)thio]acrylate (4p)

4p was prepared according to the General procedure (A).

White solid (44.8 mg, 83%). Mp: 61-62 ºC. Eluent: ethyl acetate/hexane = 1/9, Rf = 0.3. $^1$H NMR (300 MHz, CDCl$_3$): δ ppm 9.35 (brs, 1H), 7.44-7.41 (m, 2H), 7.39-7.32 (m, 3H), 6.50 (t, J = 58.5 Hz, 1H), 5.38 (brs, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.35 (t J = 6.9 Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -97.08 (d, J = 58.4 Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 170.21, 170.12, 137.80, 129.51, 128.22, 127.87, 121.22 (t, J = 274 Hz), 79.38 (t, J = 3.75 Hz), 60.56, 14.39. IR (KBr): ν = 3408, 3296, 2997, 2954, 1650, 1596, 1479, 1317, 1263, 1027 cm$^{-1}$. MS (ESI): 296 (M+Na). HRMS (ESI) C$_{12}$H$_{13}$F$_2$NNaO$_2$S (M+Na) for Calcd: 296.0533, Found: 296.0524.

3-[(Difluoromethyl)thio]-1H-indole (6a)

6a was prepared according to the General procedure (A).

Orange oil (22.3 mg, 56%). Eluent: ethyl acetate/hexane = 1/4, Rf = 0.5. $^1$H NMR (300 MHz, CDCl$_3$): δ ppm 8.46 (brs, 1H), 7.80 (s, J = 7.8 Hz, 1H), 7.48 (d, J = 2.7 Hz, 1H), 7.42 (d, J = 6.6 Hz, 1H), 7.31-7.24 (m, 2H), 6.88 (t, J = 57.0 Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.6 (d, J = 57.2 Hz, 2F). MS (ESI): 200 (M+H). HRMS (ESI) for C$_9$H$_6$F$_2$NS (M-H) Calcd: 198.0189, Found: 198.0185. The product was identified by comparison of the spectral data with the report data. Reference: Zhu D, Gu, Lu, Shen Q. 2015 N-Difluoromethylthiophthalimide: A Shelf-Stable, Electrophilic Reagent for Difluoromethylthiolation. J. Am. Chem. Soc. 137, 10547-10553. (doi:10.1021/jacs.5b03170)
3-[(Difluoromethy)thio]-2-methyl-1H-indole (6b)

6b was prepared according to the General procedure (A). White solid (36.3 mg, 85%). Mp: 59-60 °C. Eluent: ethyl acetate/hexane = 1/4, Rf = 0.4.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 8.23 (brs, 1H), 7.71-7.68 (m, 1H), 7.34-7.31 (m, 1H), 7.23-7.19 (m, 2H), 6.63 (t, $J = 57.3$ Hz, 1H), 2.57 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.5 (d, $J = 57.5$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 142.61, 135.05, 130.79, 122.37, 121.20 (t, $J = 275$ Hz), 121.01, 118.61, 110.65, 93.46 (t, $J = 3.75$ Hz), 12.13. IR (KBr): ν = 3377, 3060, 2966, 1542, 1456, 1406, 1309, 1069, 1023 cm$^{-1}$. MS (ESI): 231 (M+NH$_4$). HRMS (ESI) C$_{10}$H$_8$F$_2$NS (M-H) for Calcd: 212.0346, Found: 212.0347.

3-[(Difluoromethy)thio]-2-phenyl-1H-indole (6c)

6c was prepared according to the General procedure (A). Yellow solid (30.3 mg, 55%). Mp: 84-85 °C. Eluent: ethyl acetate/hexane = 1/4, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 8.56 (brs, 1H), 7.85-7.79 (m, 3H), 7.54-7.42 (m, 4H), 7.32-7.28 (m, 2H), 6.71 (t, $J = 57.3$ Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.1 (d, $J = 57.5$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 143.26, 135.39, 131.69, 130.97, 129.00, 128.78, 128.63, 123.62, 122.50, 121.42 (t, $J = 275$ Hz), 119.71, 93.72 (t, $J = 3.75$ Hz). IR (KBr): ν = 3419, 2958, 1546, 1398, 1313, 1227, 1058, 1027 cm$^{-1}$. MS (ESI): 298 (M+Na). HRMS (ESI) C$_{15}$H$_{10}$F$_2$NS (M-H) for Calcd: 274.0502, Found: 274.0490.

3-[(Difluoromethy)thio]-5-methyl-1H-indole (6d)

6d was prepared according to the General procedure (A). Yellow solid (32.4 mg, 75%). Mp: 43-44 °C. Eluent: ethyl acetate/hexane = 1/4, Rf = 0.5.
\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 8.39 (brs, 1H), 7.57 (s, 1H), 7.43 (d, \(J = 2.7\) Hz, 1H), 7.31 (d, \(J = 8.1\) Hz, 1H), 7.1 (dd, \(J = 8.1, 1.5\) Hz, 1H), 6.67 (t, \(J = 57.9\) Hz, 1H), 2.49 (s, 3H). \(^1\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -92.8 (d, \(J = 57.5\) Hz, 2F). \(^1\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 134.32, 131.85, 130.81, 129.86, 124.87, 121.08 (t, \(J = 276\) Hz), 118.80, 111.24, 95.99 (t, \(J = 3.77\) Hz), 21.48. IR (KBr): \(\nu = 3403, 3141, 2916, 2370, 1677, 1483, 1456, 1100, 1054, 1035\) cm\(^{-1}\). MS (ESI): 236 (M+Na).

HRMS (ESI) C\(_{10}\)H\(_8\)F\(_2\)NS (M-H) for Calcd: 212.0346, Found: 212.0355

3-[(Difluoromethy)thio]-7-methyl-1H-indole (6e)

\(6e\) was prepared according to the General procedure (A).

Yellow solid (32.4 mg, 75%). Mp: 45-46 °C. Eluent: ethyl acetate/hexane =1/4, Rf = 0.5.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 8.40 (brs, 1H), 7.64 (d, \(J = 7.8\) Hz, 1H), 7.48 (d, \(J = 2.7\) Hz, 1H), 7.18 (t, \(J = 7.5\) Hz, 1H), 7.08 (d, \(J = 7.2\) Hz, 1H), 6.67 (t, \(J = 57.6\) Hz, 1H), 2.51 (s, 3H). \(^1\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -92.6 (d, \(J = 57.2\) Hz, 2F). \(^1\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 135.64, 131.49, 129.25, 123.74, 123.19, 121.46, 121.00 (t, \(J = 274\) Hz), 120.78, 97.09 (t, \(J = 3.75\) Hz), 16.33. IR (KBr): \(\nu = 3404, 2974, 2370, 1495, 1414, 1286, 1058\) cm\(^{-1}\). MS (ESI): 245 (M+MeOH). HRMS (ESI) C\(_{10}\)H\(_8\)F\(_2\)NS (M-H) for Calcd: 212.0346, Found: 212.0340.

3-[(Difluoromethy)thio]-5-methoxy-1H-indole (6f)

\(6f\) was prepared according to the General procedure (A).

White solid (33.9 mg, 74%). Mp: 95-96 °C. Eluent: ethyl acetate/hexane =1/4, Rf = 0.3.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 8.40 (brs, 1H), 7.44 (d, \(J = 2.7\) Hz, 1H), 7.31 (d, \(J = 8.7\) Hz, 1H), 7.21 (d, \(J = 2.1\) Hz, 1H), 6.93 (dd, \(J = 8.7, 2.4\) Hz, 1H), 6.67 (t, \(J = 57.6\) Hz, 1H), 3.90 (s, 3H). \(^1\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -92.5 (d, \(J = 57.2\) Hz, 2F). \(^1\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 155.36, 132.32, 130.91, 130.46, 121.08 (t, \(J = 274\) Hz), 113.80, 112.44, 100.44, 96.07 (t, \(J = 3.75\) Hz), 55.78. IR (KBr): \(\nu = 3381, 3152, 3005, 2831, 1584, 1483, 1286, 1204, 1058, 1023\) cm\(^{-1}\). MS (ESI): 230 (M+H). HRMS (ESI) C\(_{10}\)H\(_8\)F\(_2\)NOS (M-H) for Calcd: 228.0295, Found: 228.0307.
3-[(Difluoromethy)thio]-6-chloro-1H-indole (6g)

6g was prepared according to the **General procedure (A)**.
Brown solid (19.6 mg, 42%: using 1d, 14.5 mg, 31%: using 1a). Mp: 45-46 ºC. Eluent: ethyl acetate/hexane =1/4, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 8.48 (brs, 1H), 7.69 (d, $J = 8.1$ Hz, 1H), 7.47-7.41 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 1H), 6.67 (t, $J = 57.3$ Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -92.5 (d, $J = 57.5$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): 136.37, 132.38, 129.29, 128.39, 122.15, 120.60 (t, $J = 275$ Hz), 120.40, 111.52, 97.04 (t, $J = 3.75$ Hz). IR (KBr): $\nu = 3427, 3144, 2924, 1615, 1503, 1441, 1313, 1227, 1065, 1027$ cm$^{-1}$. MS (ESI): 251 (M+NH$_4$). HRMS (ESI) C$_9$H$_5$ClF$_2$NS (M-H) for Calcd: 231.9799, Found: 231.9797.

3-[(Difluoromethy)thio]-1-methyl-1H-indole (6h)

6h was prepared according to the **General procedure (A)**.
White solid (35.4 mg, 83%). Mp: 45-46 ºC. Eluent: ethyl acetate/hexane =1/9, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.78 (d, $J = 7.5$ Hz, 1H), 7.39-7.31 (m, 2H), 6.65 (t, $J = 57.6$ Hz, 1H), 3.83 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -92.6 (d, $J = 57.5$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): 137.18, 136.09, 130.38, 122.72, 121.03 (t, $J = 275$ Hz), 120.88, 119.37, 109.75, 94.12 (t, $J = 3.75$ Hz), 33.18. IR (KBr): $\nu = 3121, 3056, 2958, 1615, 1503, 1441, 1313, 1227, 1065, 1023$ cm$^{-1}$. MS (ESI): 252 (M+K). HRMS (EI) C$_{10}$H$_9$F$_2$NS for Calcd: 213.0424, Found: 213.0431.

3-[(Difluoromethy)thio]-1-benzyl-1H-indole (6i)

6i was prepared according to the **General procedure (A)**.
Purple solid (28.9 mg, 50%). Mp: 54-55 ºC. Eluent: ethyl acetate/hexane =1/9, Rf = 0.6.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.81-7.78 (m, 1H), 7.39 (s, 1H), 7.34-7.31 (m, 3H), 7.29-7.25 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 1H), 6.67 (t, $J = 57.3$ Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -92.5 (d, $J = 57.5$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): 137.18, 136.09, 130.38, 122.72, 121.03 (t, $J = 275$ Hz), 120.88, 119.37, 109.75, 94.12 (t, $J = 3.75$ Hz), 33.18. IR (KBr): $\nu = 3121, 3056, 2958, 1615, 1503, 1441, 1313, 1227, 1065, 1023$ cm$^{-1}$. MS (ESI): 252 (M+K). HRMS (EI) C$_{10}$H$_9$F$_2$NS for Calcd: 213.0424, Found: 213.0431.
7.28-7.24 (m, 3H), 7.14 (d, J = 6.9 Hz, 2H), 6.67 (t, J = 57.6 Hz, 1H), 5.34 (s, 2H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -92.7 (d, J = 57.2 Hz, 2F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 136.78, 136.24, 135.46, 130.60, 128.94, 128.02, 126.97, 122.93, 121.11, 121.02 (t, J = 274 Hz), 119.53, 110.28, 95.13 (t, J = 3.75 Hz), 50.51. IR (KBr): \(\nu = 3113, 3063, 3029, 1604, 1495, 1452, 1309, 1065, 1035\) cm\(^{-1}\). MS (ESI): 290 (M+H). HRMS (EI) \(\text{C}_{16}\text{H}_{13}\text{F}_{2}\text{NS}\) for Calcd: 289.0737, Found: 289.0756.

2-[(Difluoromethy)thio]-5-phenyl-1H-pyrrole (8a)

8a was prepared according to the General procedure (A). Purple solid (24.6 mg, 55%: using 2d, 20.6 mg, 46%: using 2a). Mp: 30-31°C. Eluent: ethyl acetate/hexane =1/9, Rf = 0.6.\(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 8.54 (brs, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 6.67 (t, J = 57.3 Hz, 1H), 6.61 (s, 1H), 6.55 (s, 1H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -92.8 (d, J = 57.5 Hz, 2F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 137.02, 131.50, 129.01, 127.35, 124.20, 121.58, 120.32 (t, J = 276 Hz), 109.82 (t, J = 3.75 Hz), 107.99. IR (KBr): \(\nu = 3419, 3129, 2974, 1725, 1607, 1495, 1456, 1286, 1042\) cm\(^{-1}\). MS (ESI): 257 (M+MeOH). HRMS (ESI) \(\text{C}_{11}\text{H}_{8}\text{F}_{2}\text{NS}\) (M-H) for Calcd: 224.0346, Found: 224.0340.

2-[(Difluoromethy)thio]-5-(p-tolyl)-1H-pyrrole (8b)

8b was prepared according to the General procedure (A). Purple solid (22.1 mg, 46%: using 2d, 13.4 mg, 28%: using 2a). Mp: 45-46 °C. Eluent: ethyl acetate/hexane =1/9, Rf = 0.6. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 8.53 (brs, 1H), 7.38 (d, J = 7.5 Hz, 2H), 7.20 (t, J = 7.2 Hz, 2H), 6.66 (t, J = 57.9 Hz, 1H), 6.60 (s, 1H), 6.50 (s, 1H), 2.37 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) ppm -92.8 (d, J = 57.5 Hz, 2F). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) ppm 137.25, 137.21, 129.68, 128.78, 124.16, 121.54, 120.40 (t, J = 276 Hz), 109.31 (t, J = 3.75 Hz), 107.52, 21.27. IR (KBr): \(\nu = 3404, 3129, 2974, 1725, 1607, 1495, 1456, 1286, 1042\) cm\(^{-1}\). MS (ESI): 262 (M+Na). HRMS (ESI) \(\text{C}_{12}\text{H}_{10}\text{F}_{2}\text{NS}\) (M-H) for Calcd: 238.0502, Found: 238.053.

2-[(Difluoromethy)thio]-5-(4-bromophenyl)-1H-pyrrole (8c)

25
8c was prepared according to the **General procedure (A).**
Purple solid (34.0 mg, 51%; using 2d, 25.3 mg, 38%; using 2a). Mp: 55 °C. Eluent: ethyl acetate/hexane =1/9, Rf = 0.5.

\( ^1H \text{NMR (300 MHz, CDCl}_3 \): \( \delta \) ppm 8.54 (brs, 1H), 7.51 (d, \( J = 8.4 \text{ Hz, 1H} \)), 6.67 (t, \( J = 57.3 \text{ Hz, 1H} \)), 6.61 (t, \( J = 3.0 \text{ Hz, 1H} \)), 6.53 (t, \( J = 3.0 \text{ Hz, 1H} \)).

\( ^19F \text{NMR (282 MHz, CDCl}_3 \): \( \delta \) ppm -92.8 (d, \( J = 57.5 \text{ Hz, 2F} \)).

\( ^13C \text{NMR (125 MHz, CDCl}_3 \): \( \delta \) ppm 135.83, 132.12, 130.42, 125.68, 121.72, 121.06, 120.12 (t, \( J = 275 \text{ Hz} \)), 110.46 (t, \( J = 3.75 \text{ Hz} \)), 108.43. IR (neat): \( \nu = 3403, 2312, 1487, 1421, 1286, 1166, 1085, 1131 \text{ cm}^{-1} \). MS (ESI): 304 (M+H). HRMS (ESI) C\(_{11}\)H\(_7\)BrF\(_2\)NS (M-H) for Calcd: 301.9451, Found: 301.9455.

3-Acetyl-5-[(difluoromethyl)thio]-2,4-dimethyl-1H-pyrrole (8d)

8d was prepared according to the **General procedure (A).**
White solid (28.1 mg, 64%; using 2d, 11.4 mg, 26%; using 2a). Mp: 134-135°C. Eluent: ethyl acetate/hexane =1/4, Rf = 0.3.

\( ^1H \text{NMR (300 MHz, CDCl}_3 \): \( \delta \) ppm 8.43 (brs, 1H), 6.56 (t, \( J = 57.3 \text{ Hz, 1H} \)), 2.53 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H).

\( ^19F \text{NMR (282 MHz, CDCl}_3 \): \( \delta \) ppm -92.8 (d, \( J = 57.5 \text{ Hz, 2F} \)).

\( ^13C \text{NMR (125 MHz, CDCl}_3 \): \( \delta \) ppm 194.96, 138.68, 130.81, 122.71, 119.87 (t, \( J = 276 \text{ Hz} \)), 106.08 (t, \( J = 3.75 \text{ Hz} \)), 30.96, 15.23, 13.03. IR (KBr): \( \nu = 3175, 3106, 3048, 2370, 2312, 1619, 1471, 1054 \text{ cm}^{-1} \). MS (ESI): 242 (M+Na). HRMS (ESI) C\(_9\)H\(_{10}\)F\(_2\)NOS (M-H) for Calcd: 218.0451, Found: 218.0438.

**Ethyl 5-[(difluoromethyl)thio]-2,4-dimethyl-1H-pyrrole-3-carboxylate (8e)**

8e was prepared according to the **General procedure (A).**
White solid (45.4 mg, 91%). Mp: 114-115 °C. Eluent: ethyl acetate/hexane =1/9, Rf = 0.4.

\( ^1H \text{NMR (300 MHz, CDCl}_3 \): \( \delta \) ppm 8.22 (brs, 1H), 6.55 (t, \( J = 57.3 \text{ Hz, 1H} \)), 4.28 (q, \( J \)
1H NMR (300 MHz, CDCl₃): δ ppm 8.00 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 6.9 Hz, 1H), 7.54-7.43 (m, 2H), 7.07 (t, J = 56.1 Hz, 0.8H) (ketone), 6.58 (t, J = 57.3 Hz, 0.1H) (enol), 5.51 (s, 0.7H) (ketone), 4.39 (q, J = 6.9 Hz, 0.5H) (enol), 4.24 (q, J = 7.2 Hz, 1.5H) (ketone), 1.40 (t, J = 7.2 Hz, 0.7 H) (enol), 1.22 (t, J = 7.2 Hz, 2.4H) (ketone). ¹⁹F NMR (282 MHz, CDCl₃): δ ppm -92.9 (d, J = 56.4 Hz, 2F) MS (ESI): 281 (M+MeOH). The product was identified by comparison of the spectral data with the report data. Reference: Zhu D, Gu, Lu, Shen Q. 2015 N-Difluoromethylthiophthalimide: A Shelf-Stable, Electrophilic Reagent for Difluoromethylthiolation. J. Am. Chem. Soc. 137, 10547-10553. (doi:10.1021/jacs.5b03170)

Ethyl 3-oxo-3-phenyl-2-[(difluoromethyl)thio]propanoate (10a) (10p)

10a (10p) was prepared according to the General procedure (B) and (D).
Brown oil (10a: 19.8 mg, 36%, 10p: 40.2 mg, 73%). Eluent: ethyl acetate/hexane =1/5. Rf = 0.3.

Ethyl 3-oxo-3-phenyl-2-[(difluoromethyl)thio]propanoate (10a) (10p)

10q was prepared according to the General procedure (D).
Yellow oil (36.3 mg, 63%). Eluent: ethyl acetate/hexane = 1/7, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 7.90 (d, J = 8.1 Hz, 1.7H) (ketone), 7.56 (d, J = 8.1 Hz, 0.3H) (enol), 7.32-7.24 (m, 2H), 7.06 (t, J = 56.7 Hz, 0.7H) (ketone), 6.59 (t, J = 57.6 Hz, 0.1H) (enol), 5.48 (s, 0.7H) (ketone), 4.38 (q, J = 6.9 Hz, 0.3H) (enol), 4.25 (q, J = 6.9 Hz, 1.7H) (ketone), 2.44 (s, 2.6H) (ketone), 2.41 (s, 0.5H) (enol), 1.40 (t, J = 7.2 Hz, 0.5H) (enol), 1.22 (t, J = 6.9 Hz, 2.5H) (ketone).

$^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.62 (dd, J = 55.5, 244 Hz, 1F) (ketone), -94.30 (dd, J = 55.5, 244 Hz, 1F) (ketone), -96.19 (d, J = 57.5 Hz, 2F) (enol). 83% of ketone, 17% of enol form.

$^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 189.15 (ketone), 182.69 (enol), 173.34 (enol), 166.89 (ketone), 145.61 (ketone), 141.24 (enol), 131.61 (ketone), 131.26 (enol), 129.65 (ketone), 129.17 (enol), 129.11 (ketone), 128.47 (enol), 120.46 (t, J = 276 Hz) (enol), 119.49 (t, J = 273 Hz) (ketone), 86.53 (t, J = 3.75 Hz) (enol), 62.95 (ketone), 62.29 (enol), 51.31 (t, J = 2.50 Hz) (ketone), 21.76 (ketone), 21.50 (enol), 14.10 (enol), 13.77 (ketone). IR (neat): ν = 2958, 1742, 1685, 1607, 1267, 1185, 1073, 1031 cm$^{-1}$. MS (ESI): 287 (M-H). HRMS (ESI) C$_{13}$H$_{14}$F$_2$NaO$_3$S (M+Na) for Calcd: 311.0529, Found: 311.0530.

Ethyl 3-oxo-(4-chlorophenyl)-2-[(difluoromethyl)thio]propanoate (10r)

10r was prepared according to the General procedure (D).

Brown oil (40.8 mg, 66%). Eluent: ethyl acetate/hexane = 1/7, Rf = 0.6.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 7.95 (d, J = 8.4 Hz, 1.1H) (ketone), 7.61 (d, J = 8.4 Hz, 0.9H) (enol), 7.49 (d, J = 8.4 Hz, 1.2H) (ketone), 7.41 (d, J = 8.4 Hz, 0.8H) (enol), 7.05 (t, J = 55.8 Hz, 0.5H) (ketone), 6.59 (t, J = 57.6 Hz, 0.2H) (enol), 5.45 (s, 0.5H) (ketone), 4.39 (q, J = 7.2 Hz, 0.8H) (enol), 4.26 (q, J = 7.1 Hz, 1.2H) (ketone), 1.40 (t, J = 6.9 Hz, 1.1H) (enol), 1.23 (t, J = 6.9 Hz, 1.9H) (ketone). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.71 (dd, J = 55.5, 244 Hz, 1F) (ketone), -94.00 (dd, J = 55.5, 244 Hz, 1F) (ketone), -96.21 (d, J = 57.2 Hz, 2F) (enol). 54% of ketone, 46% of enol form.

$^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 189.59 (ketone), 181.26 (enol), 173.13 (enol), 166.49 (ketone), 141.06 (enol or ketone), 136.90 (enol or ketone), 132.47 (enol or ketone), 132.41 (enol or ketone), 130.64 (enol or ketone), 130.37 (enol or ketone), 129.33 (enol or ketone), 128.13 (enol or ketone), 120.08 (t, J = 276 Hz) (enol), 119.31 (t, J = 274 Hz) (ketone), 87.23 (t, J = 3.75 Hz) (enol), 63.18 (ketone), 62.52 (enol), 51.21 (t,
$J = 2.50 \text{ Hz}$ (ketone), 14.08 (enol), 13.78 (ketone). IR (neat): $\nu = 2985, 1739, 1688, 1592, 1487, 1263, 1092, 1031 \text{ cm}^{-1}$. MS (ESI): 307 (M-H). HRMS (ESI) $C_{12}H_{11}ClF_{2}NaO_{3}S$ (M+Na) for Calcd: 330.9983, Found: 330.9986.

**Methyl 3-oxo-(4-bromophenyl)-2-((difluoromethyl)thio)propanoate (10s)**

10s was prepared according to the General procedure (D).

Colorless oil (45.8 mg, 68%). Eluent: ethyl acetate/hexane = 1/9, Rf = 0.4.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.87 (d, $J = 8.4 \text{ Hz}, 1\text{H}$) (ketone), 7.66 (d, $J = 8.4 \text{ Hz}, 1\text{H}$) (enol), 7.55 (brs, 2H), 7.04 (t, $J = 55.8 \text{ Hz}, 0.5\text{H}$) (ketone), 6.59 (t, $J = 57.6 \text{ Hz}, 0.4\text{H}$) (enol), 5.48 (s, 0.5H) (ketone), 3.93 (s, 1.4H) (enol), 3.79 (s, 1.6H) (ketone).

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -92.87 (dd, $J = 55.3, 243 \text{ Hz}, 1\text{F}$) (ketone), -94.00 (dd, $J = 55.3, 243 \text{ Hz}, 1\text{F}$) (ketone), -96.34 (d, $J = 57.5 \text{ Hz}, 2\text{F}$) (enol).

51% of ketone, 49% of enol form.

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 188.73 (ketone), 181.49 (enol), 173.52 (enol), 166.97 (ketone), 132.80 (enol), 132.71 (enol), 132.38 (ketone), 132.14 (enol), 131.12 (ketone), 130.80 (ketone), 130.42 (ketone), 130.12 (ketone), 130.42 (ketone), 129.98 (enol), 119.93 (t, $J = 276 \text{ Hz}$) (enol), 119.22 (t, $J = 273 \text{ Hz}$) (ketone), 86.99 (t, $J = 3.75 \text{ Hz}$) (enol), 53.89 (ketone), 53.25 (enol), 50.78 (t, $J = 2.50 \text{ Hz}$) (ketone).

IR (neat): $\nu = 2958, 1746, 1685, 1584, 1483, 1437, 1263, 1073 \text{ cm}^{-1}$. MS (ESI): 337 (M-H). HRMS (ESI) $C_{11}H_{9}BrF_{2}NaO_{3}S$ (M+Na) for Calcd: 360.9322, Found: 360.9319.

**1-Phenyl-2-[(difluoromethyl)thio]-1,3-butanedioin (10t)**

10t was prepared according to the General procedure (D).

Orange oil (34.9 mg, 71%). Eluent: ethyl acetate/hexane = 1/5, Rf = 0.6.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.63 (d, $J = 7.5 \text{ Hz}, 2\text{H}$), 7.49-7.43 (m, 3H), 6.37 (t, $J = 56.4 \text{ Hz}, 1\text{H}$), 2.55 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -95.26 (d, $J = 56.4 \text{ Hz}, 2\text{F}$).

100% of enol form.

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 201.72, 194.01, 135.94, 131.03, 128.71, 127.79, 119.94 (t, $J = 276 \text{ Hz}$), 94.99 (t, $J = 3.75 \text{ Hz}$), 25.60. IR (KBr): $\nu = 3063, 2966, 1542, 1398, 1073, 1035 \text{ cm}^{-1}$. MS (ESI): 267 (M+Na). HRMS (ESI) $C_{11}H_{10}F_{2}NaO_{2}S$ (M+Na) for Calcd: 267.0267, Found: 267.0276.
1-(p-Bromophenyl)-2-[(difluoromethyl)thio]-1,3-butanedion (10u)

10u was prepared according to the General procedure (D).

Yellow oil (32.5 mg, 50%). Eluent: ethyl acetate/hexane = 1/9, Rf = 0.4.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 7.59-7.51 (m, 4H), 6.39 (t, $J = 55.8$ Hz, 1H), 2.55 (s, 3H).

$^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -95.26 (d, $J = 56.4$ Hz, 2F). 100% of enol form.

$^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 201.59, 193.06, 135.94, 131.09, 130.42, 125.72, 119.65 (t, $J = 276$ Hz), 94.75 (t, $J = 2.5$ Hz), 25.49. IR (neat): ν = 2962, 1592, 1398, 1069, 1035, 1011 cm$^{-1}$. MS (ESI): 321 (M-H). HRMS (ESI) C$_{11}$H$_9$BrF$_2$NaO$_2$S (M+Na) for Calcd: 344.9372, Found: 344.9377

1,3-Diphenyl-2-[(difluoromethyl)thio]-1,3-propanedion (10v)

10v was prepared according to the General procedure (D).

Colorless oil (42.9 mg, 70%). Eluent: ethyl acetate/hexane = 1/4, Rf = 0.6.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 8.00 (d, $J = 6.9$ Hz, 3H), 7.76-7.44 (m, 7H), 7.03 (t, $J = 55.5$ Hz, 0.9H) (ketone), 6.28 (s, 1H) (ketone), 6.14 (t, $J = 56.7$ Hz, 0.2H) (enol), 3.71 (s, 0.2H) (enol).

$^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.88 (d, $J = 56.4$ Hz, 2F) (ketone), -96.32 (d, $J = 56.4$ Hz, 2F) (enol). 84% of ketone, 16% of enol form.

$^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 201.59 (enol), 190.97 (ketone), 136.25 (enol), 134.32 (ketone), 131.40 (enol), 129.19 (enol), 129.15 (ketone), 129.01 (ketone), 127.86 (ketone), 119.52 (t, $J = 273$ Hz) (ketone), 93.65 (t, $J = 3.75$ Hz) (enol), 55.46 (ketone). IR (neat): ν = 3063, 2927, 2324, 1700, 1673, 1596, 1448, 1282, 1185, 1073 cm$^{-1}$. MS (ESI): 329 (M+Na). HRMS (ESI) C$_{16}$H$_{12}$F$_2$NaO$_2$S (M+Na) for Calcd: 329.0424, Found: 329.0424.

Methyl 2-[(difluoromethyl)thio]-6-methyl-1-oxo-2,3-dihydro-1H-indane-2-carboxylate (10b) (10w)

10b (10w) was prepared according to the General procedure (B), (D) and (E).
Yello solid (10b: 23.5 mg, 41%, 58% (Synthesized by general procedure E and yield was calculated by \(^{19}\)F NMR with PhF as an internal standard.), 10w: 36.6 mg, 64%). Eluent: DCM/hexane = 4/1, Rf = 0.7

\(^1\)H NMR (300 MHz, CDCl\(_3\)): δ ppm 7.64 (s, 1H), 7.51 (t, J = 55.5 Hz, 1H), 7.50 (brs, 1H), 7.36 (d, J = 7.5 Hz, 1H), 3.98 (d, J = 17.7 Hz, 1H), 3.81 (s, 3H), 3.22 (d, J = 18.0 Hz, 1H), 2.43 (s, 3H).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ ppm -92.06 (dd, J = 55.3, 250 Hz, 1F), -93.48 (dd, J = 55.5, 250 Hz, 1F).

**Allyl 2-[(difluoromethyl)thio]-6-methyl-1-oxo-2,3-dihydro-1H-indane-2-carboxylate (10c)**

\(\text{10c} \) was prepared according to the **General procedure (E)**.

Yellow oil (44.7 mg, 75%). Eluent: DCM/hexane = 4/1, Rf = 0.7.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): δ ppm 7.85 (d, J = 7.5 Hz, 1H), 7.519 (t, J = 55.7 Hz, 1H) 7.716 ~ 7.666 (m, 1H), 7.469 (t, J = 6.8 Hz, 2H), 5.948 ~ 5.817 (m, 1H), 5.345 ~ 5.240 (m, 2H), 4.703 (d, J = 5.4 Hz, 2H), 4.046 (d, 17.7 Hz, 1H), 3.27 (d, J = 18 Hz, 1H).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ ppm 91.9 (dd, J = 55.6 Hz, 250 Hz, 1F), 93.3 Hz (dd, J = 58.8 Hz, 252 Hz).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ ppm 196.66, 167.98, 150.49, 136.29, 132.97, 130.71, 128.61, 126.25, 125.84, 120.26 (t, J = 269 Hz, 1C), 119.48, 67.55, 58.46, 39.44. IR (neat): ν = 3083, 2951, 1746, 1719, 1607, 1464, 1433, 1275, 1239, 1185, 1065, 1042 cm\(^{-1}\). MS (ESI): 321 (M+Na).

**1-phenyl-2-[(difluoromethyl)thio]-Ethanone (10d)**

\(\text{10d} \) was prepared according to the **General procedure (F)**.

Pale yellow solid (13.7 mg, 35%). Mp: 33 ~ 34 ºC. Eluent: DCN/hexane =3/1, Rf = 0.6.
$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 7.99 ~ 7.96 (m, 2H), 7.66 ~ 7.60 (m, 1H), 7.53 ~ 7.48 (m, 2H), 6.95 (t, $J = 56.4$ Hz, 1H), 4.330 (s, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -94.52 (d, $J = 56.4$ Hz, 2F). $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 193.19, 128.48, 128.88, 119.6 (t, $J = 273$ Hz), 134.97, 133.99, 34.42 (t, $J = 3.1$ Hz). IR (KBr): ν = 3334, 2947, 2920, 1673, 1596, 1580, 1448, 1390, 1329, 1313, 1204, 1085, 1023, 1004 cm$^{-1}$. MS (ESI): 225 (M+Na). HRMS (ESI) C$_9$H$_8$F$_2$OS (M+Na) for Calcd: 225.0162, Found: 225.0157.

Methyl 2-[(difluoromethyl)thio]-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (10x)

10x was prepared according to the General procedure (D).
White solid (41.3 mg, 68%). Mp: 65 ~ 66 ºC Eluent: DCM/hexane = 1/4, Rf = 0.3.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 7.50 (t, $J = 55.7$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.29 (d, $J = 10.5$ Hz, 2H), 3.95 (d, $J = 17.7$ Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.20 (d, $J = 17.7$ Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ ppm -92.07 (dd, $J = 55.3$, 250 Hz, 1F), -93.49 (dd, $J = 56.4$, 250, 1F). $^{13}$C NMR (125 MHz, CDCl$_3$): δ ppm 196.73, 168.82, 160.21, 143.43, 134.23, 126.95, 125.92, 106.55, 120.22 (t, $J = 269$ Hz), 59.18, 55.70, 53.98, 38.93. IR (KBr): ν = 3071, 3024, 2962, 2842, 1746, 1707, 1494, 1301, 1259, 1069, 1038 cm$^{-1}$. MS (ESI): 325 (M+Na). HRMS (ESI) C$_{13}$H$_{13}$F$_2$NaO$_4$S (M+Na) for Calcd: 325.0322, Found: 325.0320.

Methyl 2-[(difluoromethyl)thio]-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10y)

10y was prepared according to the General procedure (D).
Pale yellow solid (32.1 mg, 56%). Mp: 50 ºC Eluent: ethyl acetate/hexane = 1/4, Rf = 0.4.

$^1$H NMR (300 MHz, CDCl$_3$): δ ppm 8.08 (d, $J = 7.5$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.36 (t, $J = 49.2$ Hz, 1H), 7.38 (t, $J = 2.6$ Hz, 1H), 7.26 ~ 7.25 (m, 1H), 3.81 (s, 3H), 3.13 ~ 3.01 (m, 2H), 2.98 ~ 2.91 (m, 1H), 2.43 ~ 2.34 (m, 1H). $^{19}$F NMR (282 MHz,
CDCl$_3$: $\delta$ ppm -91.88 (dd, $J = 57.8$, 254 Hz, 1F), -94.48 (dd, $J = 55.5$, 254 Hz, 1F). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 190.15, 169.17, 142.24, 134.48, 130.19, 128.73 (d, $J = 2.5$ Hz), 122.89, 120.75 (t, $J = 239$ Hz), 120.73, 61.27 (d, $J = 1.3$ Hz), 53.76, 32.47, 25.82.

IR (KBr): $\nu = 3361, 3071, 2969, 1726, 1688, 1599, 1436, 1297, 1251, 1069, 1034$ cm$^{-1}$. MS (ESI): 309 (M+Na). HRMS (ESI) C$_{13}$H$_{13}$F$_2$NaO$_3$S (M+Na) for Calcd: 309.0373, Found: 309.0381.

(E)-3-[(Difluoromethyl)-sulfinyl]prop-1-enyl]benzene (12a)

12a was prepared according to the General procedure (C). White solid (20.0 mg, 46%). Mp: 58ºC. Eluent: ethyl acetate/hexane =1/4, Rf = 0.4.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.43-7.32 (m, 5H), 6.80 (d, $J = 15.9$ Hz, 1H), 6.20 (t, $J = 54.0$ Hz, 1H), 6.20-6.14 (m, 1H), 4.07 (d, $J = 7.8$ Hz, 2H).

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -123.28 (d, $J = 52.5$ Hz, 2F).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 141.03, 135.13, 129.06, 128.78, 126.87, 114.83 (t, $J = 285$ Hz), 111.04, 52.94. IR (KBr): $\nu = 3082, 2989, 2915, 1491, 1452, 1410, 1340, 1154, 1096$ cm$^{-1}$. MS (EI): 117 (M-S(O)CF$_2$H).

HRMS (EI) C$_9$H$_9$ (M-S(O)CF$_2$H) for Calcd: 117.0704, Found:117.0682.

1-Chloro-4-[(E)-3-[(difluoromethyl)-sulfinyl]prop-1-enyl]benzene (12b)

12b was prepared according to the General procedure (C). White solid (25.1 mg, 50%). Mp: 61-62 ºC. Eluent: ethyl acetate/hexane =1/4, Rf = 0.5.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.39-7.29 (m, 4H), 6.75 (d, $J = 15.9$ Hz, 1H), 6.20 (t, $J = 52.8$ Hz, 1H), 6.17-6.09 (m, 1H), 4.06 (d, $J = 6.6$ Hz, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ ppm -122.91 (d, $J = 52.4$ Hz, 2F).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 139.73, 134.84, 133.61, 128.99, 128.06, 114.96 (t, $J = 285$ Hz), 111.71, 52.71. IR (KBr): $\nu = 2993, 2935, 2370, 1491, 1340, 1306, 1119, 1092$ cm$^{-1}$. MS (EI): 151 (M-S(O)CF$_2$H).

HRMS (EI) C$_9$H$_9$ (M-S(O)CF$_2$H) for Calcd: 151.0315, Found:151.0300.

4-[(E)-3-[(difluoromethyl)-sulfinyl]prop-1-enyl]-1-methoxy-benzene (12c)

12c was prepared according to the General procedure (C).
Yellow solid (20.1 mg, 41%). Mp: 57-58°C. Eluent: ethyl acetate/hexane =1/9, Rf = 0.2. 

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm 7.36 (d, \(J = 8.4\) Hz, 2H), 6.88 (d, \(J = 8.4\) Hz, 2H), 6.21 (t, \(J = 52.5\) Hz, 1H), 6.06-5.98 (m, 1H), 4.04 (d, \(J = 6.9\) Hz, 2H), 3.82 (s, 3H).

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm -123.56 (d, \(J = 52.4\) Hz, 2F).

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm 7.3 (m, 2H), 7.0 (s, 1H), 6.6 (t, \(J = 57.3\) Hz, 1H).

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm 149.79, 142.63, 129.30, 129.21, 128.69, 128.13, 119.92 (t, \(J = 275\) Hz), 98.27. IR (KBr): \(\nu = 3168, 3101, 3063, 3016, 2951, 2873, 1317, 1069, 1031\) cm\textsuperscript{-1}. MS (EI): 249 (M+Na). HRMS (ESI) \(\text{C}_{10}\text{H}_{7}\text{F}_{2}\text{N}_{2}\text{S}\) (M-H) for Calcd: 225.0298, Found: 225.0297.

4-(Difluoromethyl)thio-3-phenyl-1H-pyrazole (13)

To a mixture of enamine 3z (35.2 mg, 0.2 mmol, 1.0 equiv) and Cu(I)Br (5.7 mg, 0.04 mmol, 20 mol%) in 1,4-dioxane (2.5 ml), reagent 2a (174.5 mg, 0.4 mmol, 2.0 equiv) was added at room temperature. After stirring at room temperature for 5 h, hydrazine monohydrate (48.6 \(\mu\)L, 1.0 mmol, 5.0 equiv) was added to the reaction mixture. The resulting mixture was continuously stirred at 90 °C for 5 h, then 2 mL of water was added and extracted with ethyl acetate, the organic phase was washed with water 2 times and brine once then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified through flash column chromatography on silica gel (eluent: ethyl acetate/hexane =1/4, Rf = 0.3-0.4) to afforded the target product 13.

Yellow solid (30.8 mg, 68%). Mp: 61-62°C. 

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm 7.77-7.74 (m, 2H), 7.70 (s, 1H), 7.45-7.43 (m, 3H), 6.60 (t, \(J = 57.3\) Hz, 1H).

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm -93.5 (d, \(J = 57.2\) Hz, 2F).

\[^1^H\]NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) ppm 149.79, 142.63, 129.30, 129.21, 128.69, 128.13, 119.92 (t, \(J = 275\) Hz), 98.27. IR (KBr): \(\nu = 3168, 3101, 3063, 3016, 2951, 2873, 1317, 1069, 1031\) cm\textsuperscript{-1}. MS (EI): 249 (M+Na). HRMS (ESI) \(\text{C}_{10}\text{H}_{7}\text{F}_{2}\text{N}_{2}\text{S}\) (M-H) for Calcd: 225.0298, Found: 225.0297.

5-(Difluoromethyl)thio-4-phenyl-2-(tert-butyl)-pyrimidine (14)

To a mixture of enamine 3z (35.2 mg, 0.2 mmol, 1.0 equiv) and Cu(I)Br (5.7 mg, 0.04 mmol, 20 mol%) in 1,4-dioxane (2.5 ml), reagent 2a (174.5 mg, 0.4 mmol, 2.0 equiv) was added at room temperature. After stirring at room temperature for 5 h, tert-butylcarbamidine hydrochloride (136.6 mg, 1.0 mmol, 5.0 equiv), sodium
methoxide (67.0 mg, 1.24 mmol, 6.2 equiv) and EtOH (2.0 ml) were added to the reaction mixture. The resulting mixture was continuously stirred at 80 °C for 20 h, then 2 mL of water was added and extracted with ethyl acetate, the organic phase was washed with water 2 times and brine once then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified through flash column chromatography on silica gel (eluent: ethyl acetate/hexane =1/9, Rf = 0.6) to afforded the target product 14.

Colorless oil (38.3 mg, 65%). 1H NMR (300 MHz, CDCl3): δ ppm 8.90 (s, 1H), 7.77 (brs, 2H), 7.50 (brs, 3H), 6.60 (t, J = 56.1 Hz, 1H), 1.46 (s, 9H) 19F NMR (282 MHz, CDCl3): δ ppm -91.8 (d, J = 56.4 Hz, 2F). 13C NMR (125 MHz, CDCl3): 178.06, 168.11, 163.30, 137.26, 130.00, 129.90, 128.10, 119.45 (t, J = 276 Hz), 116.15 (t, J = 2.5 Hz), 39.59, 29.50. IR (neat): ν = 3063, 3029, 2958, 1557, 1519, 1421, 1321, 1185, 1061, 1035 cm⁻¹. MS (EI): 294.

Methyl 6-methoxy-1-amino-1H-indene-2-carboxylate (3x)

3x was prepared according to the reported procedure.

White solid (491.7 mg, 99%). Mp = 127 ~ 128 °C. Eluent: ethyl acetate/hexane = 1/2, Rf = 0.4. 1H NMR (300 MHz, CDCl3): δ ppm 7.36 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.91 (s, 1H), 5.93 (brs, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.49 (s, 2H) 13C NMR (125 MHz, CDCl3): δ ppm 168.12, 158.76, 156.06, 139.16, 136.30, 125.30, 115.26, 103.81, 99.08, 55.49, 50.50, 33.73. IR (KBr): ν = 3431, 3327, 3229, 3160, 2951, 2889, 2835, 1646, 1631, 1542, 1444, 1336, 1313, 1248, 1204, 1100, 1027. MS (ESI): 220 (M+H). HRMS (ESI) C12H16F3N2S (M+Na) for Calcd: 242.0793, Found: 242.0775

6. X-ray structure of 4c
Figure S1. X-ray structure of 4c

7. References and Notes
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8. $^{19}\text{F}$, $^1\text{H}$, $^{13}\text{C}$ NMR Spectra of Corresponding Compounds

$^{19}\text{F}$ NMR (282 MHz, CDCl$_3$)
$^1\text{H}$ NMR (300 MHz, CDCl$_3$)
$^{13}\text{C}$ NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, (CD$_3$)$_2$SO)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^19\text{F} \text{ NMR (282 MHz, CDCl}_3\text{)}$

$^1\text{H} \text{ NMR (300 MHz, CDCl}_3\text{)}$

$^{13}\text{C} \text{ NMR (125 MHz, CD}_3\text{CN)}$
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, (CD$_3$)$_2$CO)

$^1$H NMR (300 MHz, (CD$_3$)$_2$SO)

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, (CD$_3$)$_2$SO)
$^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^{1}$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl₃)
$^1$H NMR (300 MHz, CDCl₃)
$^{13}$C NMR (125 MHz, CDCl₃)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
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$^1$H NMR (300 MHz, CDCl$_3$)
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$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$\text{SCF}_{\text{H}}$

$\text{6e}$

$^{19}\text{F NMR (282 MHz, CDCl}_3)$

$^1\text{H NMR (300 MHz, CDCl}_3)$

$^{13}\text{C NMR (125 MHz, CDCl}_3)$
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^1$H NMR (125 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
8a

$^1$H NMR (282 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}F$ NMR (282 MHz, CDCl$_3$)
$^1H$ NMR (300 MHz, CDCl$_3$)
$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl₃)
$^{1}$H NMR (300 MHz, CDCl₃)
$^{13}$C NMR (125 MHz, CDCl₃)
$^{1}$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl₃)
$^1$H NMR (300 MHz, CDCl₃)
$^{13}$C NMR (125 MHz, CDCl₃)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
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$^{13}$C NMR (125 MHz, CDCl$_3$)
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$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
