Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photoredox-Catalyzed Halotrifluoromethylations of Alkynes with Triethylammonium halides: Synthesis of Tetrasubstituted Alkenes Containing CF_3 and Halogens

I. General Information

Material and Methods:

Reaction was checked on thin-layer chromatography plates (TLC plates). And TLC plates were carried out on pre-coated silica gel 0.25 mm TLC plates with F254 (Merck, art. 5715). The crude reaction mixture analysis use 1,1,2,2-tetrachloroethane as the internal standard at ^{1}H NMR. All new compounds were characterized by ^{1}H, ^{13}C, ^{19}F-NMR spectroscopy which were recorded on a Bruker Avance. 300 MHz, 400 MHz, or 500 MHz. NMR solvents were used with trimethylsilane (TMS, 0.0 ppm), $CDCl_3$ (7.26 ppm or 77.16 ppm for ^{1}H and ^{13}C respectively), $(CD_3)_2CO$ (2.05 ppm or 29.84 ppm for ^{1}H and ^{13}C respectively) CD_3OD (3.31 ppm or 49.00 ppm for ^{1}H and ^{13}C respectively). Column chromatography was performed on silica-cartridge which to use for MPLC (Puchem Flash Column or Biotage ZIP KP-Sil). In addition, High resolution mass spectra were obtained on a JEOL JMS-700 with Electron Impact (EI) ionization mode spectrometer at 70 eV, Resolution 5000. Fourier Transform Infrared spectra (FT-IR, Smiths Identify IR) and Melting points (M.P.) were recorded on a Mettler Toledo MP50. Single crystal X-ray analysis data were collected at 50 kV and 30 mA using a Bruker SMART APEX II X-ray Diffractometer equipped with a Mo tube, graphite-monochromator, and CCD area-detector. And structure analyzed with Bruker SHELXTL software. (When the diffraction intensity is weak, it is measured at 50 kV and 40 mA.)

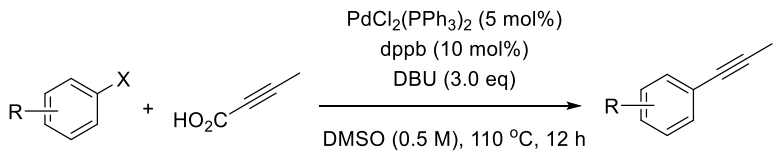
Reagents Information:

All the chemicals used are either prepared as mention in this supporting information (*vide-infra*) or else purchased commercially. Commercial chemical reagents were purchased from Aldrich, Alfa Aesar and TCI and photoredox-catalysts used are purchased as follows: $Ru(bpy_3)Cl_2$ (Aldrich), *fac*-$Ir(ppy)_3$ (TCI), $[Ir(bpy)(ppy)_2][PF_6]$ (TCI), Umemoto's reagent (Aldrich), Togni reagent I and II (TCI), $Et_3N{\cdot}3HF$ (Aldrich), $Et_3N{\cdot}HCl$ (Aldrich), $Et_3N{\cdot}HBr$ (Alfa).

II. Synthesis of Substrates

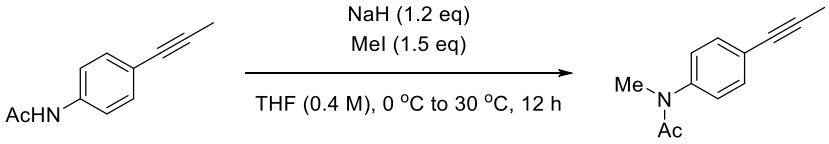
II.1 Procedures for the synthesis of aryl alkynes in Table 2

II.1.1 General Procedure



A round bottom flask equipped with a magnetic stir bar was charged with aryl halide (1.0 equiv.), 2-butynoic acid (1.5 equiv.), 1,4-Bis(diphenylphosphino)butane (10 mol%), $PdCl_2(PPh_3)_2$ (5 mol%) in DMSO (0.5 M). To the resulting solution was added DBU (3 equiv.). under the nitrogen atmosphere for 12 h at 110 ℃. After the reaction was completed, saturated aq NH_4Cl was poured into the reaction mixture and the aqueous layer was extracted with EtOAc. The organic layer was separated and washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was purified by column chromatography using ethyl acetate/hexane as an eluent.

II.1.2 Synthesis procedure of *N*-methyl-*N*-(4-(prop-1-yn-1-yl)phenyl)acetamide (1d)



A solution of *N*-(4-(prop-1-yn-1-yl)phenyl)acetamide (500 mg, 2.9 mmol) was dissolved in THF (3.6 mL, 0.8 M) and added dropwise to a suspension NaH (60% in paraffin oil, 138 mg, 3.6 mmol) in THF (3.6 mL, 0.8 M). The reaction mixture was stirred at 0 ℃ for 30 minutes and MeI (0.27 mL, 4.3 mmol) was added dropwise. After stirring for 12 hours at 30 ℃, water was added to the reaction media and extracted with EtOAc (3 times). The organic layer was separated and dried over $MgSO_4$, filtered and concentrated. The crude mixture was purified by column chromatography using ethyl acetate/hexane as an eluent to get the product 237 mg (50%) as yellow solid.

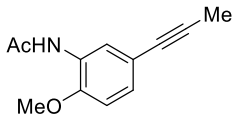
* Reported substrates and references

1a, **1b**, **1c** : *Org. Lett.* **2018**, 20, 7509.

1d, 1h : *Org. Lett.* **2018**, 20, 1693.

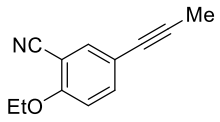
1l : *Chem. Sci.* **2019**, 10, 6311.

N-(2-methoxy-5-(prop-1-yn-1-yl)phenyl)acetamide (1e)



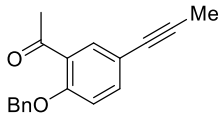
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 3.89 (s, 3H), 2.21 (s, 3H), 2.06 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.07, 147.10, 127.51, 124.77, 119.27, 118.90, 112.82, 85.01, 79.69, 55.72, 24.95, 4.30. **IR (neat)** 3297, 1664, 1589, 1520, 1371, 1294, 1254, 1124, 1033, 962, 827 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{12}H_{13}NO_2$ $[M]^+$ 203.0946, found 203.0946.

2-ethoxy-5-(prop-1-yn-1-yl)benzonitrile (1f)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 2.1 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.50 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.72, 137.27, 136.63, 116.89, 115.84, 112.18, 102.30, 86.23, 64.90, 14.48, 4.24. **IR (neat)** 2988, 2227, 1602, 1491, 1465, 1393, 1274, 1170, 1125, 1035, 923, 730 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{12}H_{11}NO$ $[M]^+$ 185.0840, found 185.0840.

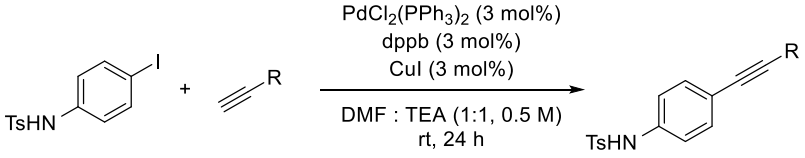
1-(2-(benzyloxy)-5-(prop-1-yn-1-yl)phenyl)ethan-1-one (1g)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 2.2 Hz, 1H), 7.47 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.45 – 7.37 (m, 5H), 6.96 (d, *J* = 8.6 Hz, 1H), 5.18 (s, 2H), 2.60 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.10, 157.15, 141.63, 136.28, 135.93, 133.67, 128.75, 128.35, 127.56, 116.89, 112.88, 85.23, 78.47, 70.83, 31.96, 4.26. **IR (neat)** 3039, 1645, 1598, 1556, 1490, 1399, 1285, 1212, 1145, 990, 822, 759 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{18}H_{16}O_2$ $[M]^+$ 264.1150, found 264.1150

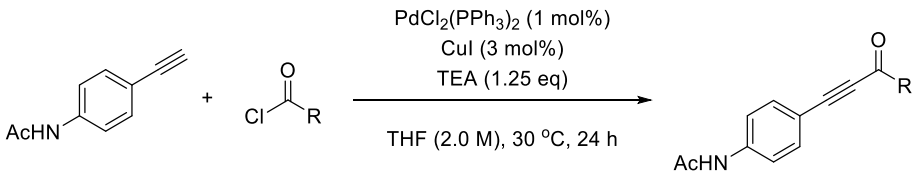
II.2 Procedures for the synthesis of aryl alkynes in Table 3

II.2.1 General Procedure



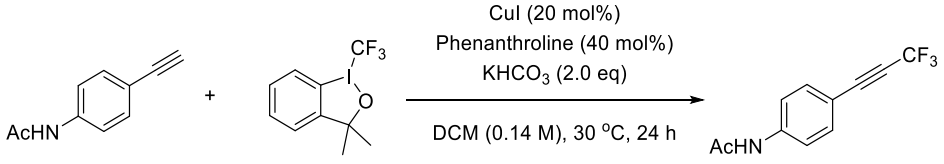
A dried round bottom flask equipped with a magnetic stir bar was charged with *N*-(4-iodophenyl)-4-methylbenzenesulfonamide (1.0 equiv), $PdCl_2(PPh_3)_2$ (3 mol%), 1,4-Bis(diphenylphosphino)butane (3 mol%), CuI (3 mol%) and 1-hexyne (1.5 equiv). After the flask was sealed with a septum, it was evacuated and backfilled with N_2 gas, before DMF : TEA (1:1, 0.5 M) was added. The resulting mixture was stirred at room temperature until the TLC analysis shows the completion of starting materials (12-24 hours). When the reaction completes, saturated aq NH_4Cl was poured into the reaction mixture and extracted with EtOAc. The organic layer was separated and washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude mixture was purified by column chromatography using ethyl acetate/hexane as an eluent.

II.2.2 Synthesis procedure of 4f and 4g



N-(4-ethynylphenyl)acetamide (crude, 1.0 equiv) in THF (2.0 M), acyl chloride (1.5 equiv) was added under N_2. To this $PdCl_2(PPh_3)_2$ (1 mol%), CuI (3 mol%) were added and stirred at 30 ℃ for 15 minute. To this freshly distilled dry TEA (1.25 equiv) was added and the reaction mass was stirred at 30 ℃ until the TLC analysis shows completion of the starting material. The reaction mass was diluted with diethyl ether and washed with water. The aqueous layer was then extracted with DCM (3 times) and combined organic layers were dried over anhydride. $MgSO_4$. The crude mixture was purified by column chromatography using ethyl acetate/hexane as an eluent to afford the desired products

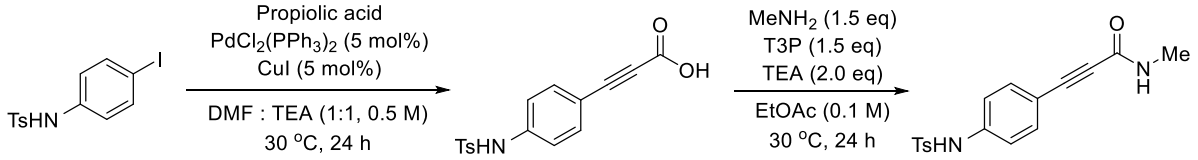
II.2.3 Synthesis procedure of 4d



Dissolve *N*-(4-ethynylphenyl)acetamide (300 mg, 1.8 mmol) in DCM (12.8 mL) were added Togni I (891 mg, 2.7 mmol), CuI (68 mg, 0.36 mmol), 1, 10-phenanthroline (129 mg, 0.72 mmol), $KHCO_3$ (360 mg, 3.6 mmol). The mixture was stirred at room temperature for 24 hours. The reaction mixture was washed with water and extracted with DCM (2 times). And combined organic layers were dried over anhydrous $MgSO_4$. The crude mixture was purified by column chromatography using ethyl acetate/hexane as an eluent to afford the product

147 mg (50%).

II.2.4 Synthesis procedure of 4h



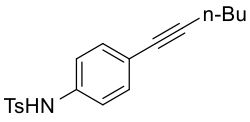
Step 1: To a solution of *N*-(4-iodophenyl)acetamide (1.0 g, 2.68 mmol), $PdCl_2(PPh_3)_2$ (94 mg, 5 mol%), CuI (25 mg, 5 mol%) in DMF (2.7 mL, 1.0 M) and TEA (2.7 mL, 1.0 M) was added propiolic acid (0.25 mL, 4.2 mmol). The mixture was stirred at 30 ℃ for 24 h. Subsequently, the residue was washed with sat. $NaHCO_3$ and acidified with 1N HCl. The crude product was used for next step.

Step 2: 3-(4-((4-methylphenyl)sulfonamido)phenyl)propiolic acid (1.09 g, crude), T3P (50 % in EtOAc, 1.5 mL, 5.1 mmol), TEA (0.95 mL, 6.8 mmol) in EtOAc (11 ml, 0.3 M) was added $MeNH_2$ (2 M in THF, 0.18 mL, 5.1 mmol) in a dried round bottom flask. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. Subsequently, the residue was purified by column chromatography to obtain the product as a yellow solid 119 mg (10%).

* Reported substrates and references

4b, 4d, 4f : *Org. Lett.* **2018**, 20, 1693.

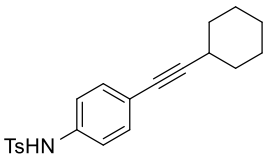
N-(4-(hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (4a)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, J = 8.0 Hz, 2H), 7.30 – 7.17 (m, 4H), 6.99 (d, J = 8.2 Hz, 2H), 6.88 (s, 1H), 2.37 (s, 5H), 1.59 – 1.51 (m, 2H), 1.51 – 1.39 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ δ 144.05, 135.82, 135.67, 132.55, 129.71, 127.27, 121.12, 121.06, 95.01, 79.25, 33.88, 30.75, 25.05, 21.54.

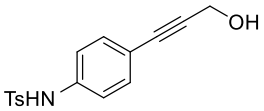
IR (neat) 3275, 3155, 3099, 2750, 1620, 1550, 1540, 1421, 1355, 1022, 821, 755 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{19}H_{21}NO_2S$ $[M]^+$ 327.1293, found 327.1295.

N-(4-(cyclohexylethynyl)phenyl)-4-methylbenzenesulfonamide (4c)



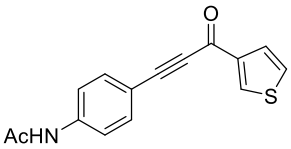
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, J = 7.8 Hz, 2H), 7.26 (dd, J = 15.6, 7.8 Hz, 4H), 7.01 (d, J = 8.1 Hz, 2H), 2.57 (s, 1H), 2.40 (s, 3H), 1.85 (s, 2H), 1.75 (d, J = 5.6 Hz, 2H), 1.59 – 1.44 (m, 3H), 1.43 – 1.27 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.06, 135.79, 135.72, 132.59, 129.73, 127.29, 121.02, 120.97, 94.84, 79.70, 32.68, 29.66, 25.89, 24.91, 21.55. **IR (neat)** 3290, 3170, 3100, 2850, 1595, 1540, 1430, 1360, 837, 745 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{21}H_{23}NO_2S$ $[M]^+$ 353.1449, found 353.1440.

N-(4-(3-hydroxyprop-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (4e)



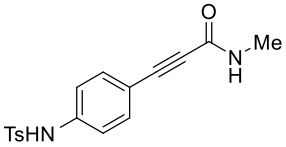
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.62 (m, 2H), 7.29 – 7.19 (m, 4H), 7.02 (dd, J = 8.5, 1.7 Hz, 2H), 4.46 (d, J = 1.6 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.22, 136.87, 135.79, 132.80, 129.80, 127.25, 120.55, 119.07, 87.42, 85.00, 51.61, 21.56. **IR (neat)** 3035, 2175, 1741, 1650, 1577, 1548, 1482, 1354, 1215, 1187, 1126, 954, 867, 729 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{16}H_{15}NO_3S$ $[M]^+$ 301.0772, found 301.0772.

N-(4-(3-oxo-3-(thiophen-3-yl)prop-1-yn-1-yl)phenyl)acetamide (4g)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.75 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.32j (s, 2H), 7.22 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.80, 145.03, 140.28, 135.11, 134.93, 134.28, 128.33, 119.32, 86.62, 24.81, 4.86. **IR (neat)** 3326, 2198, 1694, 1615, 1498, 1490, 1308, 1256, 1231, 1087, 1045, 864 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{15}H_{11}NO_2S$ $[M]^+$ 269.0510, found 269.0513

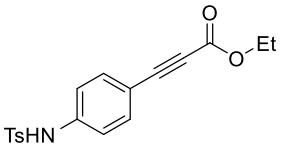
N-methyl-3-(4-((4-methylphenyl)sulfonamido)phenyl)propiolamide (4h)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.27

(d, *J* = 8.7 Hz, 2H), 7.15 (s, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 2.93 (d, J = 5.0 Hz, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.04, 144.36, 138.44, 135.90, 133.73, 129.85, 127.23, 120.04, 116.30, 84.12, 83.12, 26.66, 21.57. **IR (neat)** 2853, 2227, 2196, 1624, 1558, 1507, 1328, 1224, 1182, 1151, 1087, 1017, 908, 836, 728 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{17}H_{16}N_2O_3S$ $[M]^+$ 328.0881, found 328.0881

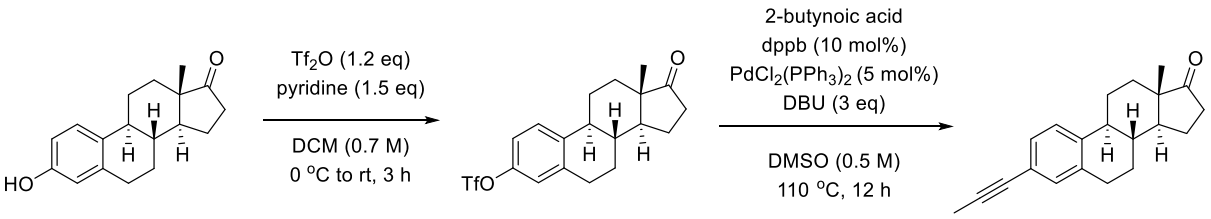
Ethyl 3-(4-((4-methylphenyl)sulfonamido)phenyl)propiolate (4i)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.05, 144.48, 138.93, 135.78, 134.33, 129.90, 127.24, 119.79, 115.64, 85.53, 80.97, 62.13, 21.57, 14.08. **IR (neat)** 3254, 2199, 2177, 1700, 1684, 1602, 1507, 1459, 1364, 1289, 1195, 1149, 1014, 911, 840, 707 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{18}H_{17}NO_4S$ $[M]^+$ 343.0878, found 343.0873

II.3 Synthesis procedure of scheme 3

II.3.1. Synthesis procedure of 7

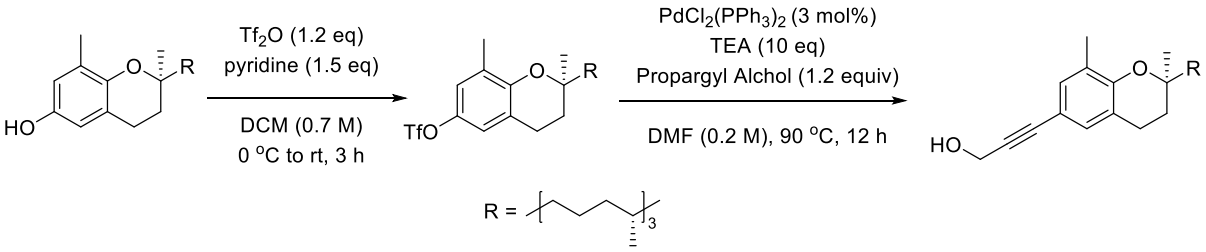


Step 1: A solution of estrone (270 mg, 1.0 mmol) in dichloromethane (1.4 mL, 0.7 M) was added pyridine (0.12 mL, 1.5 mmol). The reaction mixture was cooled to 0 ℃ and trifluoromethane sulfonic anhydride (0.2 mL, 1.2 mmol) was added dropwise. The reaction mixture was allowed to warm to 30 ℃ and stirred 3 hours. The resulting solution was quenched with saturated aqueous $NaHCO_3$, extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified over flash silica gel column chromatography using 10% EtOAc in hexanes afforded the desired the pure product 300 mg (74%) as white solid.

Step 2: Prepared according to $PdCl_2(PPh_3)_2$ (25 mg, 5 mol%), 1,4-bis(diphenylphosphino)butane (31 mg, 10 mol%) in DMSO (1.5 mL, 0.5 M). To the resulting solution was added triflated Estrone (300 mg, 0.74 mmol), 2-butynoic acid (93 mg, 1.1

mmol), and DBU (0.33 mL, 2.2 mmol). The reaction mixture was stirred for 12 h at 110 °C. After the reaction was completed, saturated aq NH_4Cl was poured into the reaction mixture and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography using 2% EtOAc in hexanes afforded the desired the pure product as white solid 120 mg (55%).

II.3.2 Synthesis procedure of 9



Step 1: A solution of δ-tocopherol (400 mg, 1.0 mmol) in dichloromethane (1.4 mL, 0.7 M) was added pyridine (0.12 mL, 1.5 mmol). The reaction mixture was cooled to 0 ℃ and trifluoromethane sulfonic anhydride (0.2 mL, 1.2 mmol) was added dropwise. The reaction mixture was allowed to warm to 30 ℃ and stirred 3 hours. The mixture was neutralized with sat. $NaHCO_3$ solution. The layers were seperated and the organic layer was dried $MgSO_4$, filtered and concentrated. The compound was used in the next step without additional purification.

Step 2: To a degassed solution of the triflated δ-tocoperol (318 mg, 0.59 mmol) in DMF (3.0 mL, 0.2 M) and TEA (0.82 mL, 5.9 mmol), premixed $PdCl_2(PPh_3)_2$ (12 mg, 3 mol%) were added. Obtained reaction mass was degassed, stirred for another 5 minutes, followed by the addition of propargyl alcohol (0.04 mL, 0.7 mmol). The reaction mass was stirred for 12 hours. The reaction mixture was washed with water and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by column chromatography using ethyl acetate/hexane as an eluent to afford the product 61 mg (23%) as a yellow oil.

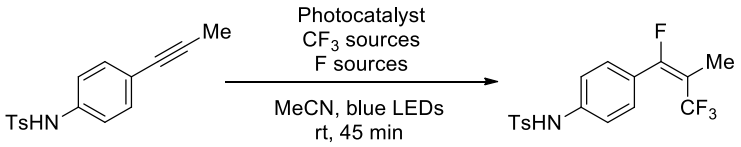
* Reported substrates and references

7 : *Org. Lett.* **2018**, 20, 2530.

9 : *Angew. Chem. Int. Ed.* **2019**, 58, 307.

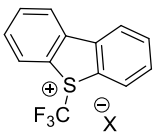
III. Optimization of Reaction Conditions

Table 1. Optimization of the reaction conditions[a]

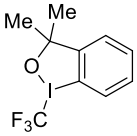


1a **3a**

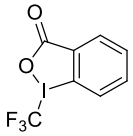
Entry	Photocatalyst	CF_3 sources	F sources	Yield (%)[b]
1[d, e, f]	$Ir(ppy)_3$	**2a**	AgF	44
2[d, e, f]	$Ir(ppy)_3$	**2a**	RbF	26
3[d, e, f]	$Ir(ppy)_3$	**2a**	NFSI	49
4[d, e, f, g]	$Ir(ppy)_3$	**2a**	$Et_3N•3HF$	54
5[e, f, g]	$Ir(ppy)_3$	**2a**	$Et_3N•3HF$	58
6[f, g]	$Ir(ppy)_3$	**2a**	$Et_3N•3HF$	75
7[g]	$Ir(ppy)_3$	**2a**	$Et_3N•3HF$	76(67[c])
8[g]	$Ir(ppy)_3$	**2b**	$Et_3N•3HF$	54
9[g]	$Ir(ppy)_3$	**2c**	$Et_3N•3HF$	n.r.
10[g]	$Ir(ppy)_3$	**2d**	$Et_3N•3HF$	n.r.
11[g]	$Ru(bpy_3)Cl_2$	**2a**	$Et_3N•3HF$	n.r.
12[g]	$[Ir(bpy)(ppy)_2][PF_6]$	**2a**	$Et_3N•3HF$	34
13[g]	-	**2a**	$Et_3N•3HF$	n.r.
14[h]	$Ir(ppy)_3$	**2a**	$Et_3N•3HF$	n.r.



Umemoto reagent
X = BF_4, **2a**
X = OTf, **2b**



Togni I reagent
2c



Togni II reagent
2d

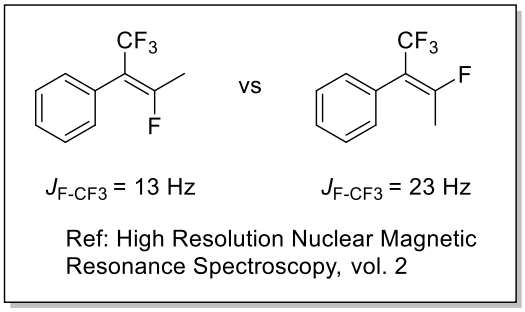
[a] Reactions were run with **1a** (0.2 mmol), $Ir(ppy)_3$ (4 mol%), CF_3 sources (1.5 equiv), and F sources (3.0 equiv) in MeCN (0.05 M) under nitrogen. [b] ^1H NMR yields, n.r. = no reaction. [c] Isolated yield. [d] 2 mol% of photocatalyst. [e] With Li_2CO_3. [f] 0.6 mmol of **2a** was added. [g] 15 equiv of $Et_3N·3HF$. [h] Without light.

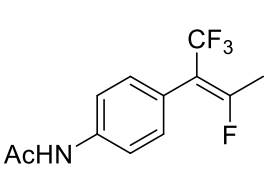
IV. General Procedure for Halotrifluorometylation of Aryl Alkynes

IV.1 The General Procedure for Fluorotrifluoromethylation

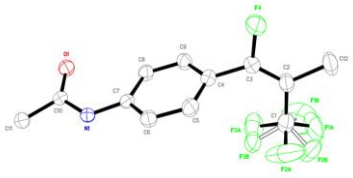
To an 8 mL vial equipped with a stir bar was added Alkyne (0.2 mmol, 1 equiv) was added Umemoto reagent (0.3 mmol, 1.5 equiv), $Ir(ppy)_3$ (0.008 mmol, 4 mol%), $Et_3N{\cdot}3HF$ (3.0 mmol, 15 equiv, Initially 2.0 mmol was added. After 30 min, another 1.0 mmol of was added.) in MeCN (4 ml, 0.05 M) under N_2 gas. The mixture was stirred and turn on blue LEDs (with cooling fan to keep the reaction at room temperature) for 45 min. The reaction mixture was filtered through a Celite pad and washed with DCM. And then filtrate was quenched with aqueous HCl (1.0 M, 50 mL) and extracted with DCM. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica column chromatography using ethyl acetate/hexane as an eluent.

IV.2 The E/Z structure determination procedure

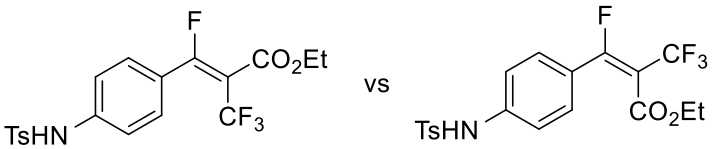




$J_{F\text{-}CF3}$ = 11 Hz



The X-ray crystallographic data was matched with NMR coupling constant



$J_{F\text{-}CF3}$ = 11 Hz $J_{F\text{-}CF3}$ = 21 Hz

E/Z ratio was determined based on the integration value of F NMR

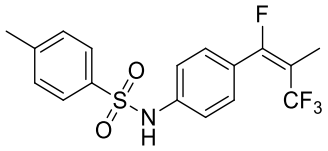
IV.3 The General Procedure for Chloro- and Bromotrifluoromethylation

To an 8 mL vial equipped with a stir bar was added Alkyne (0.2 mmol, 1 equiv) was added

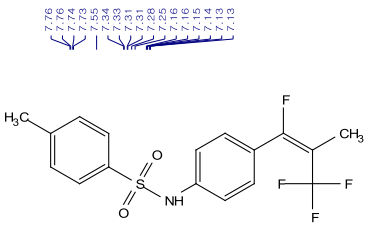
Umemoto reagent (0.3 mmol, 1.5 equiv), $Ir(ppy)_3$ (0.008 mmol, 4 mol%), $Et_3N{\cdot}HX$ (3.0 equiv) in MeCN (4 ml, 0.05 M) under N_2 gas. The mixture was stirred and turn on blue LEDs (with cooling fan to keep the reaction at room temperature) for 45 min. The reaction mixture was filtered through a Celite pad and washed with DCM. And then filtrate was quenched with aqueous HCl (1.0 M, 50 mL) and extracted with DCM. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica column chromatography using ethyl acetate/hexane as an eluent.

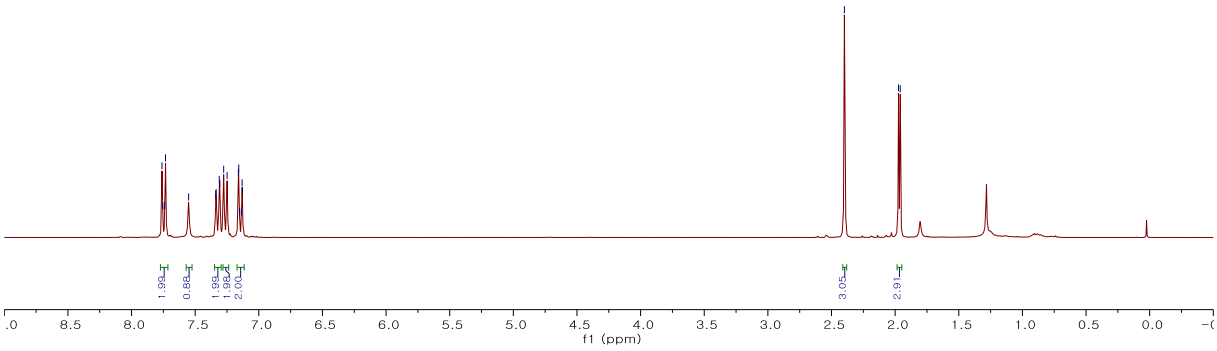
V. Characterization of Products

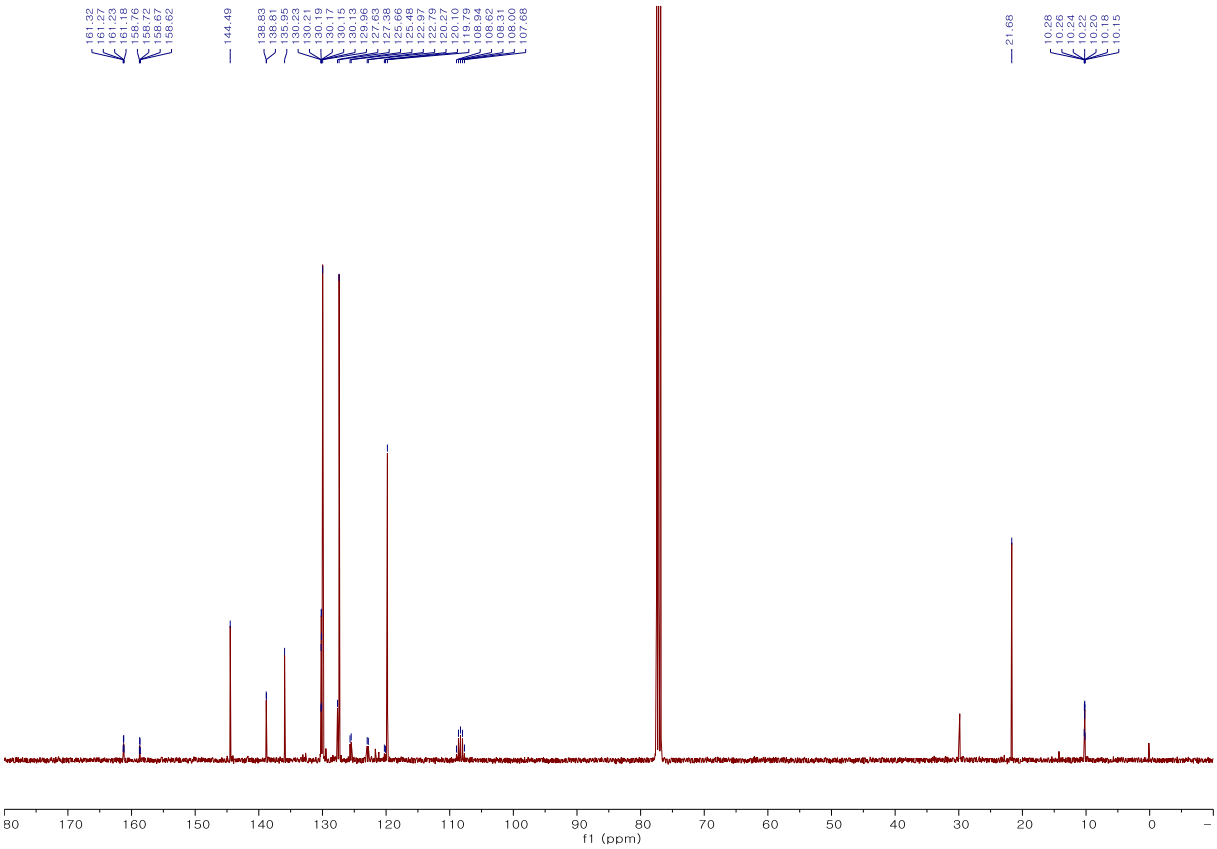
(*E*)-4-methyl-*N*-(4-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)phenyl)benzenesulfonamide (3a)

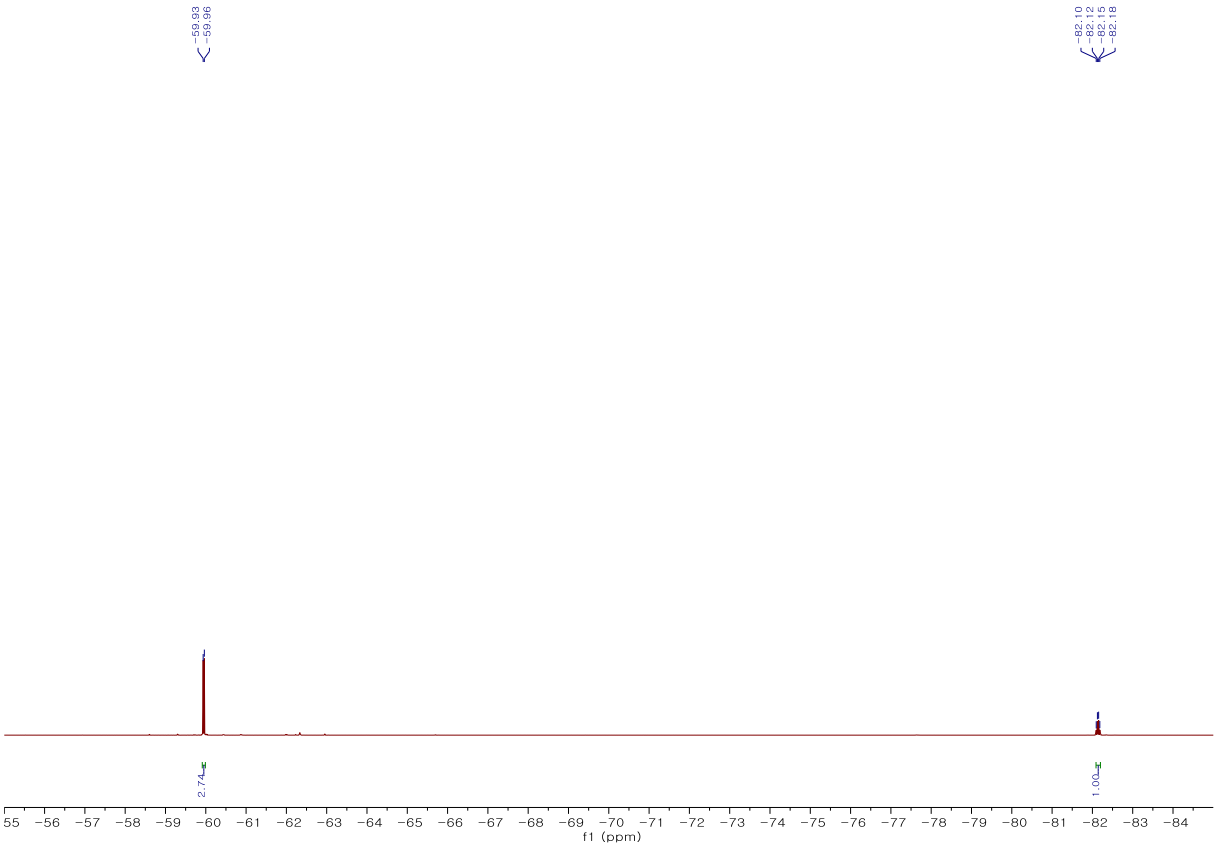


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.77–7.71 (m, 2H), 7.55 (s, 1H), 7.32 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.17–7.12 (m, 2H), 2.40 (s, 3H), 1.97 (d, *J* = 4.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.72 (dq, *J* = 258.5, 5.0 Hz), 144.36, 138.69 (d, *J* = 2.4 Hz), 135.82, 130.05 (dq, *J* = 3.9, 1.9 Hz), 129.96, 127.63, 127.38, 124.22 (qd, *J* =18.1, 271.6 Hz), 119.66, 108.94–108.68 (m, *J* = 31.7 Hz), 21.54, 10.23–10.15 (m). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.95 (d, *J* = 11.0 Hz), -82.14 (q, *J* = 11.0 Hz). **IR (neat)** 3227, 3049, 2925, 2857, 2688, 1918, 1800, 1693, 1610, 1513, 1468, 1403, 1341, 1305, 1228, 1189, 1155, 1111, 1059, 995, 915, 842, 812, 699, 666, 592, 570, 544, 492, 475, 421 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{17}H_{15}F_4NO_2S$ $[M]^+$ 373.0760, found 373.0760. **M.P.** 106.2 ℃. **Appearance** White solid. **Amount** 50 mg. **Yield** 67%.

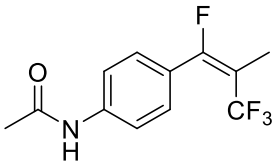




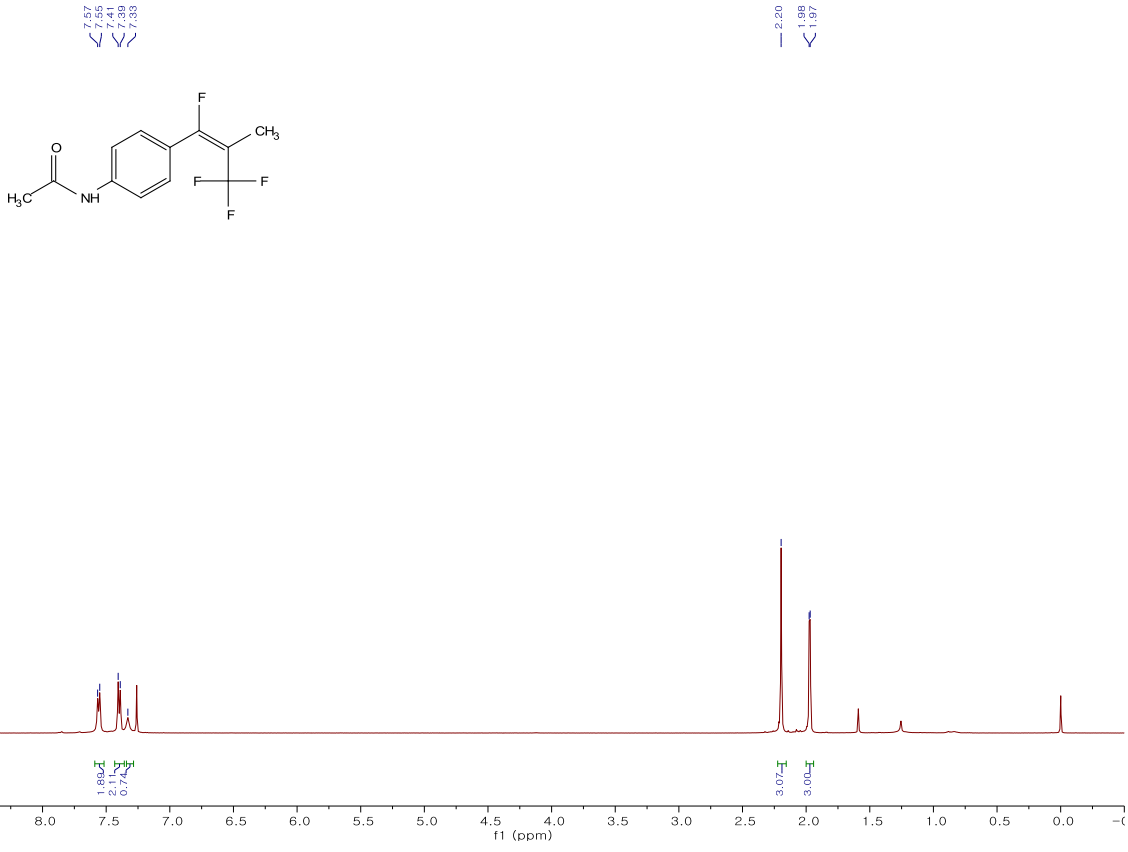

161.32
161.27
161.23
161.18
158.76
158.72
158.67
158.62
144.49
138.83
138.81
135.95
130.23
130.21
130.19
130.17
130.15
130.13
129.96
127.63
127.58
125.66
125.48
122.97
122.79
120.27
120.10
119.79
108.94
108.62
108.31
108.00
107.68
21.68
10.28
10.26
10.24
10.22
10.20
10.18
10.15
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

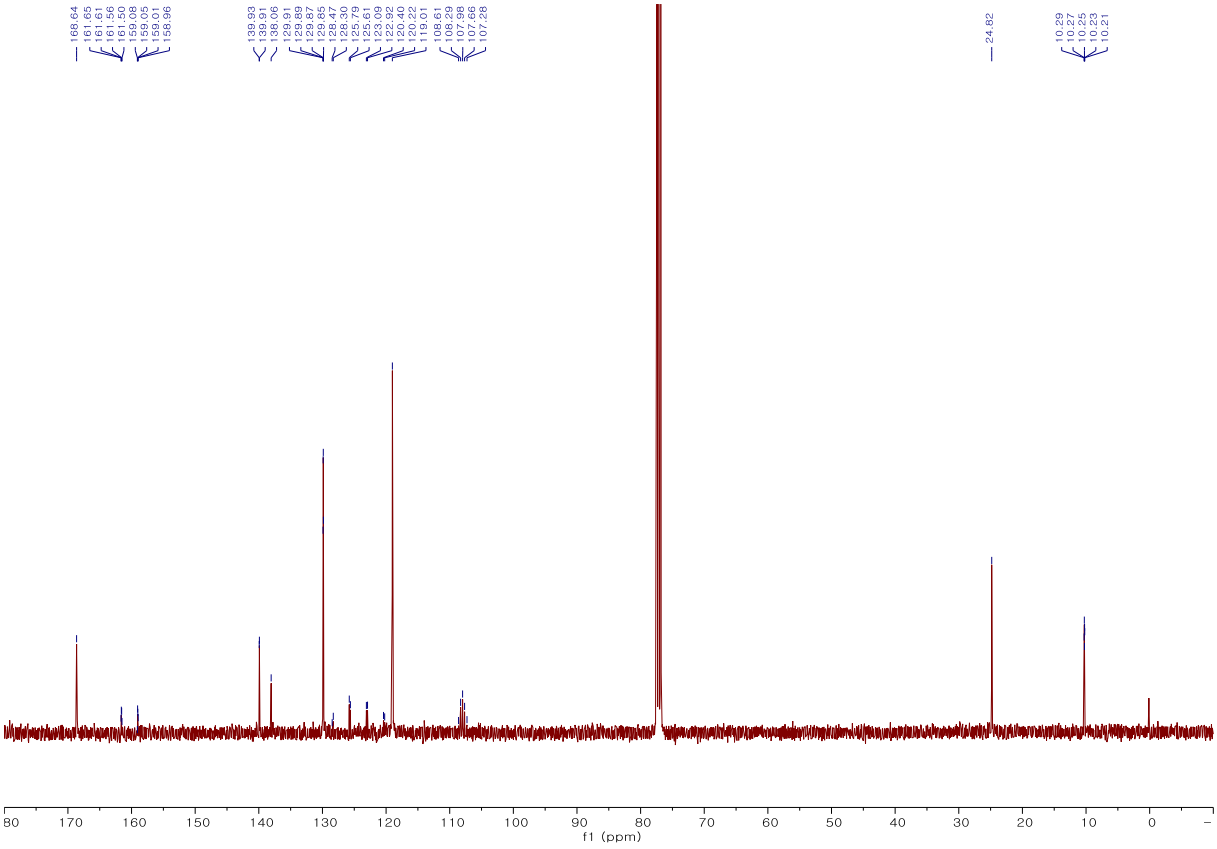

-59.93
-59.96
-82.10
-82.12
-82.15
-82.18
2.74
1.00
55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84
f1 (ppm)

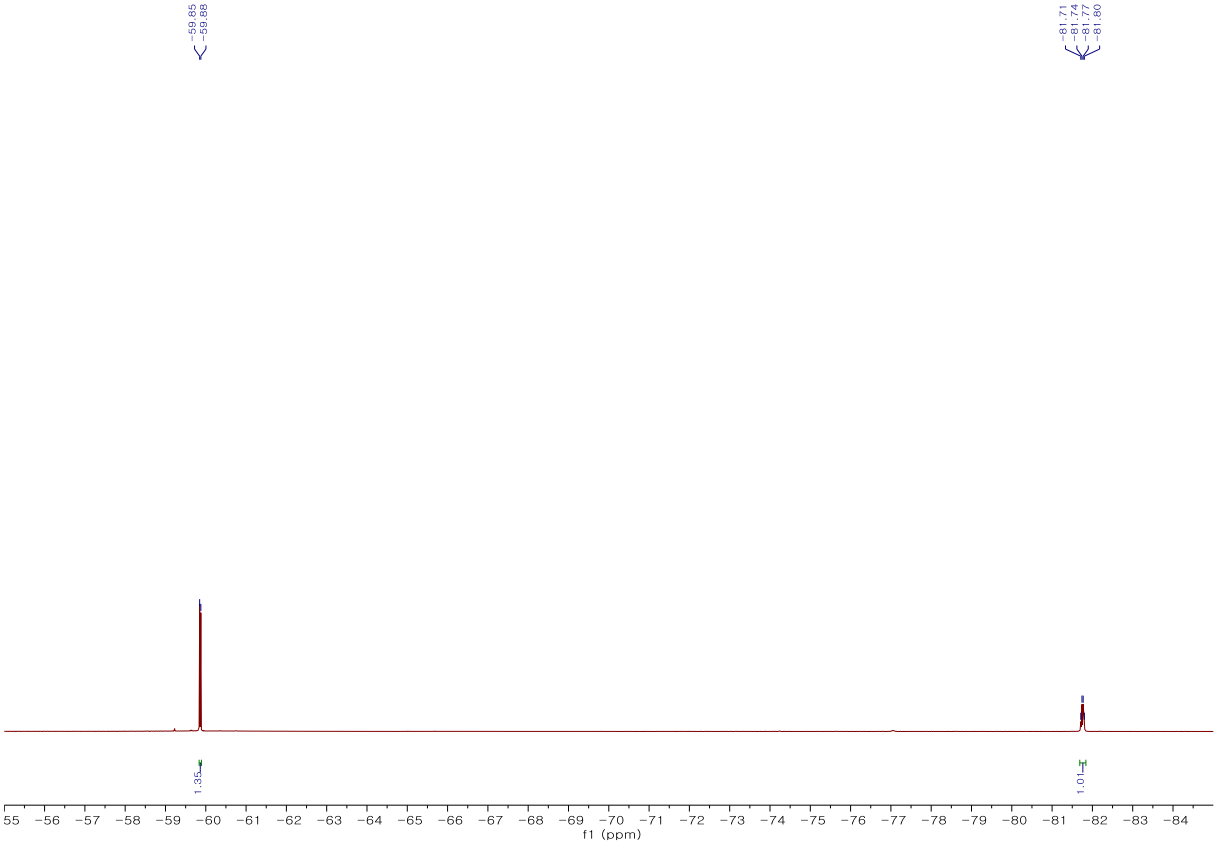
(*E*)-*N*-(4-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)phenyl)acetamide (3b)



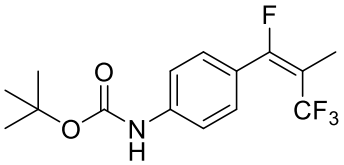
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.50–7.45 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 2.22 (s, 3H), 1.99 (d, *J* = 4.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.64 (C=O), 160.20 (dq, *J* = 288.8, 5.0 Hz), 139.92 (d, *J* = 3.0 Hz), 138.06, 129.89 (q, *J* = 2.0 Hz), 124.35 (qd, *J* = 272.7, 18.0 Hz), 119.01, 108.61–107.28 (m, *J* = 31.5 Hz), 24.82, 10.28–10.21 (m). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.86 (d, *J* = 11.0 Hz), -81.76 (q, *J* = 11.0 Hz). **IR (neat)** 3294, 3183, 3110, 2936, 1914, 1702, 1666, 1605, 1547, 1514, 1448, 1403, 1345, 1321, 1266, 1185, 1117, 1064, 995, 968, 841, 762, 729, 673, 604, 573, 546, 464 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{12}H_{11}F_4NO$ $[M]^+$ 261.0774, found 261.0777. **M.P.** 170.1 ℃. **Appearance** White solid. **Amount** 34 mg. **Yield** 64%.



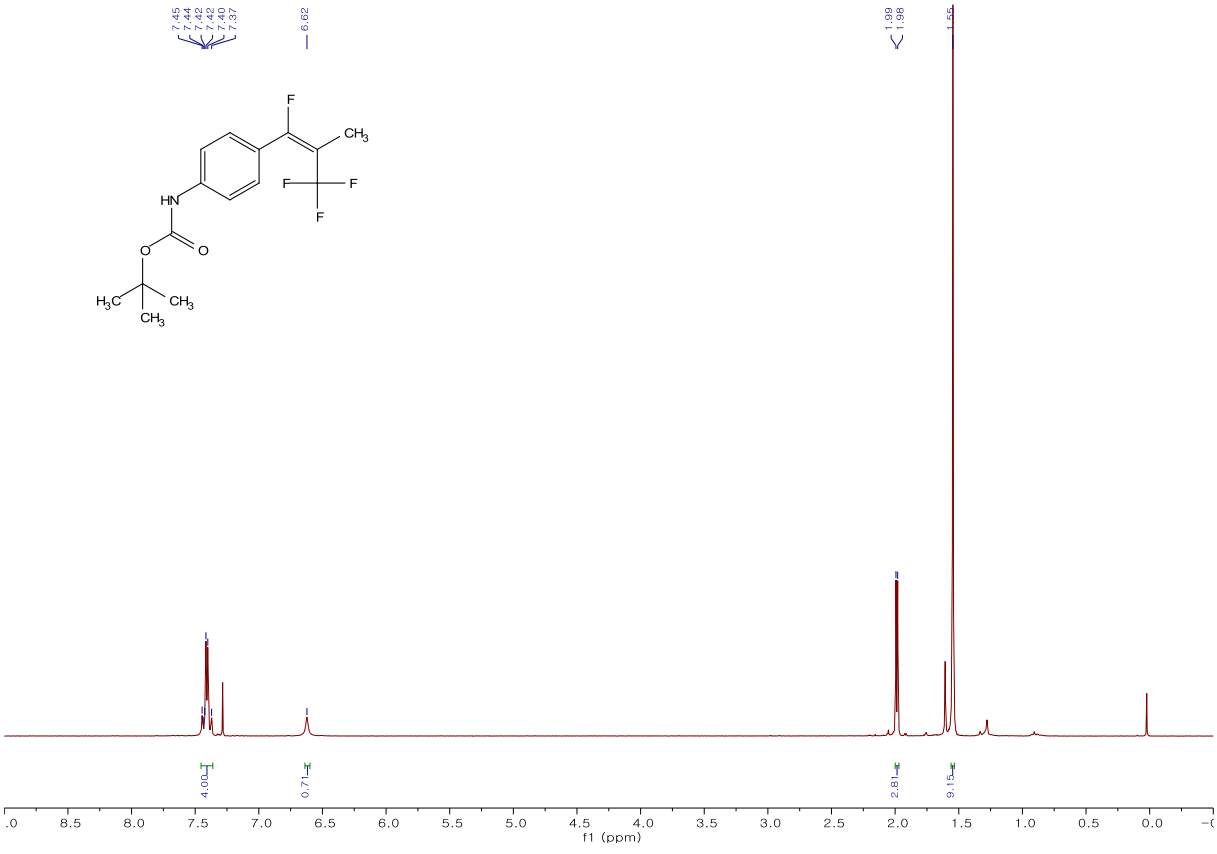

168.64
161.65
161.61
161.56
161.52
159.08
159.05
159.01
158.96
139.93
139.91
138.06
129.91
129.89
129.87
129.85
124.77
123.30
125.79
125.61
123.09
123.02
122.40
120.22
119.01
108.61
108.29
107.98
107.66
107.28
24.82
10.29
10.27
10.25
10.23
10.21
f1 (ppm)

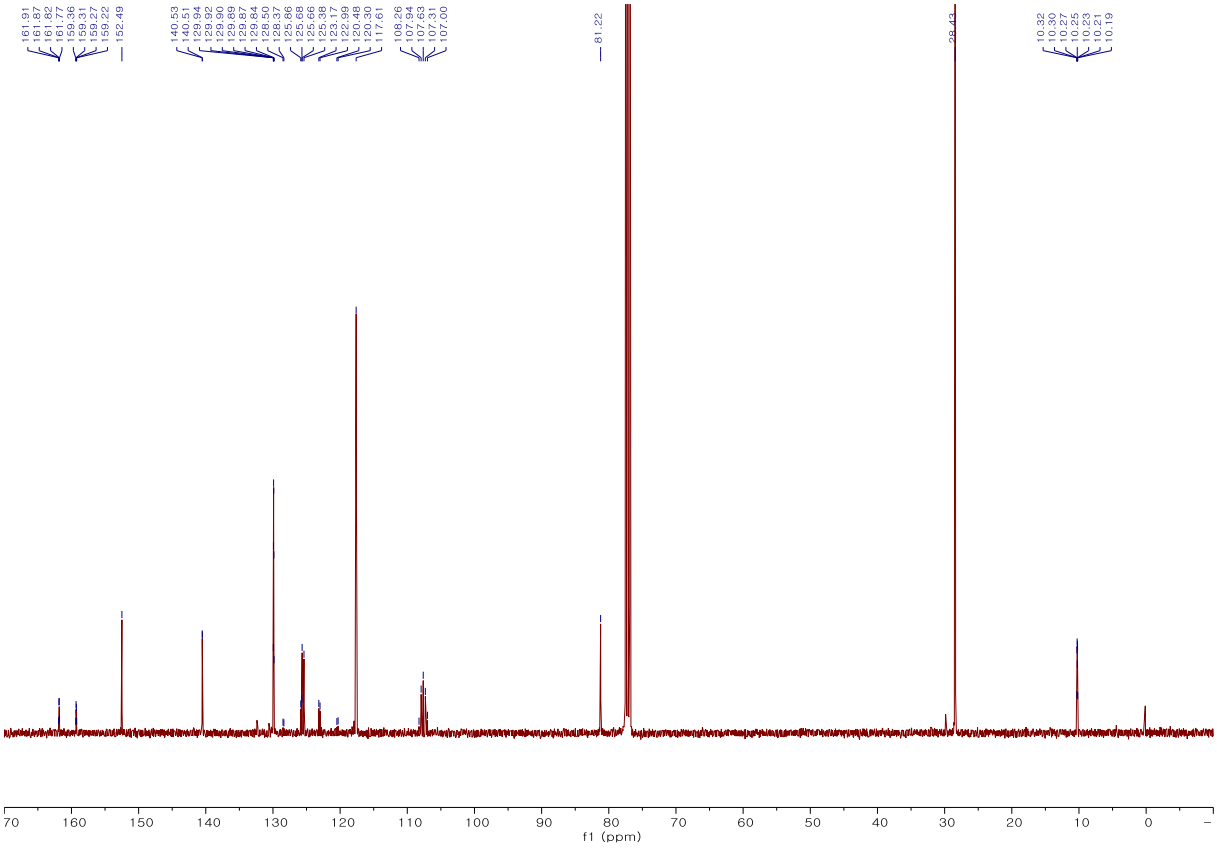

-59.85
-59.88
-81.71
-81.74
-81.77
-81.80
1.35
1.01
f1 (ppm)

(*E*)-tert-butyl (4-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)phenyl)carbamate (3c)



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.4–7.36 (m, 4H), 6.62 (s, 1H), 1.99 (d, *J* = 4.1 Hz, 3H), 1.55 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.70 (dq, *J* = 257.1, 4.7 Hz), 152.49 (C=O), 140.52 (d, *J* = 2.2 Hz), 129.89 (dd, *J* = 3.9, 2.1 Hz), 125.52 (d, *J* = 27.6 Hz), 123.08 (qd, *J* = 270.7, 18.0 Hz), 117.61, 107.94–107.00 (m, *J* = 31.6 Hz), 81.22, 28.43, 10.11 (dq, *J* = 6.7, 2.3 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.84 (d, *J* = 11.3 Hz), -81.52 (q, *J* = 11.1 Hz). **IR (neat)** 3298, 3176, 3107, 3014, 2982, 2934, 2872, 2770, 1916, 1692, 1592, 1529, 1454, 1406, 1369, 1343, 1316, 1245, 1157, 1106, 1060, 1028, 995, 904, 842, 777, 761, 717, 689, 635, 592, 550, 466 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{15}H_{17}F_4NO_2$ $[M]^+$ 319.1199, found 310.1195. **M.P.** 103.0 ℃. **Appearance** White solid. **Amount** 43 mg. **Yield** 69%.




161.91
161.87
161.82
161.77
159.36
159.31
159.27
159.22
152.49
140.53
140.51
129.94
129.92
129.90
129.89
129.87
129.84
128.50
128.37
125.86
125.68
125.66
125.38
123.17
123.09
120.48
120.30
117.61
108.26
107.94
107.63
107.31
107.00
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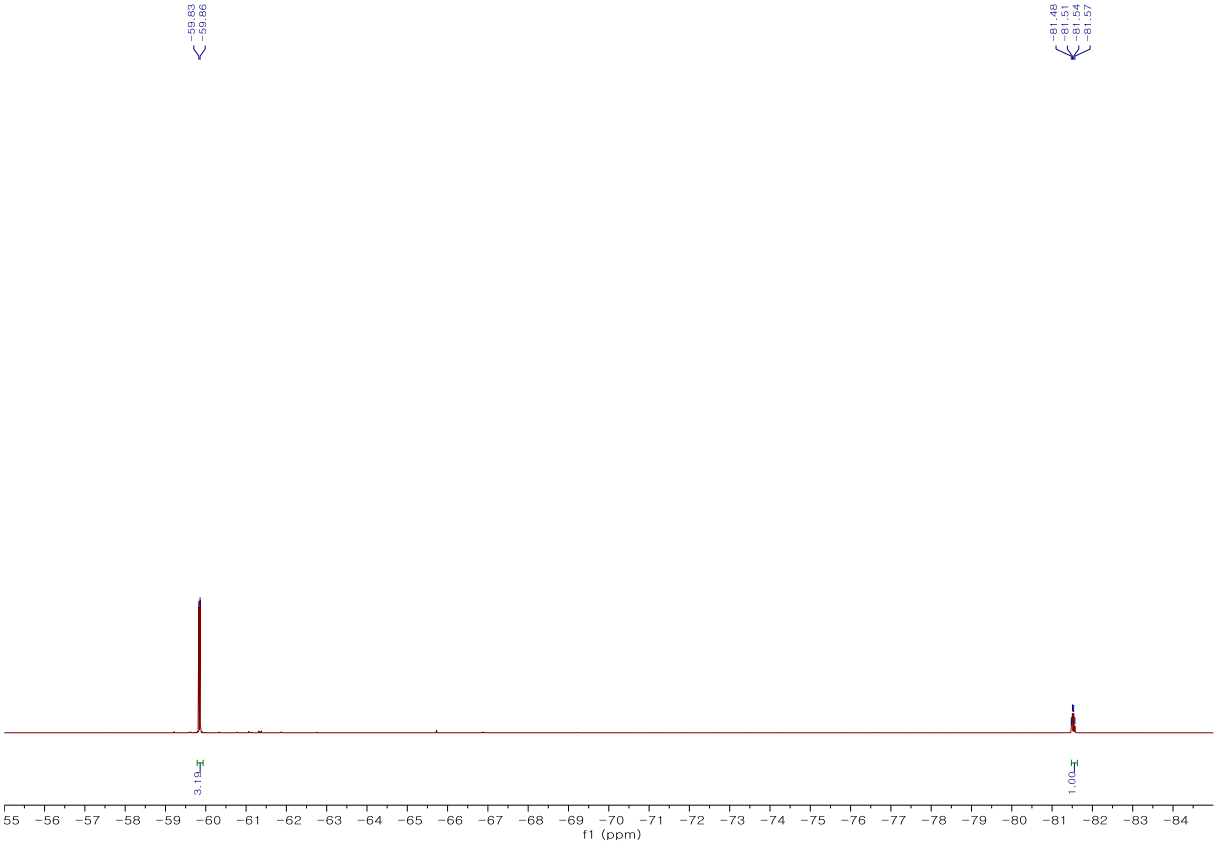
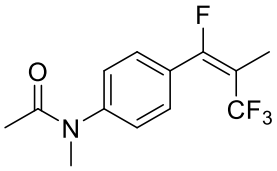
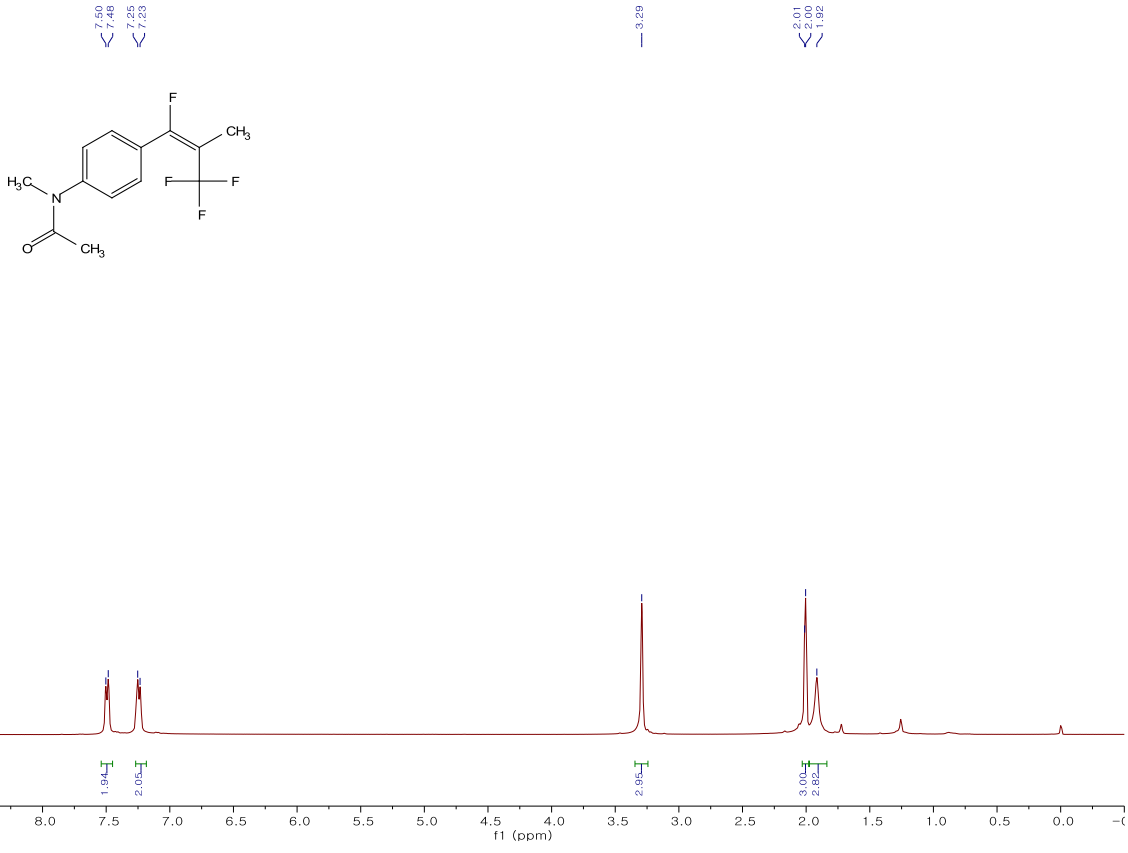
28.43
10.32
10.30
10.27
10.25
10.23
10.21
10.19
f1 (ppm)

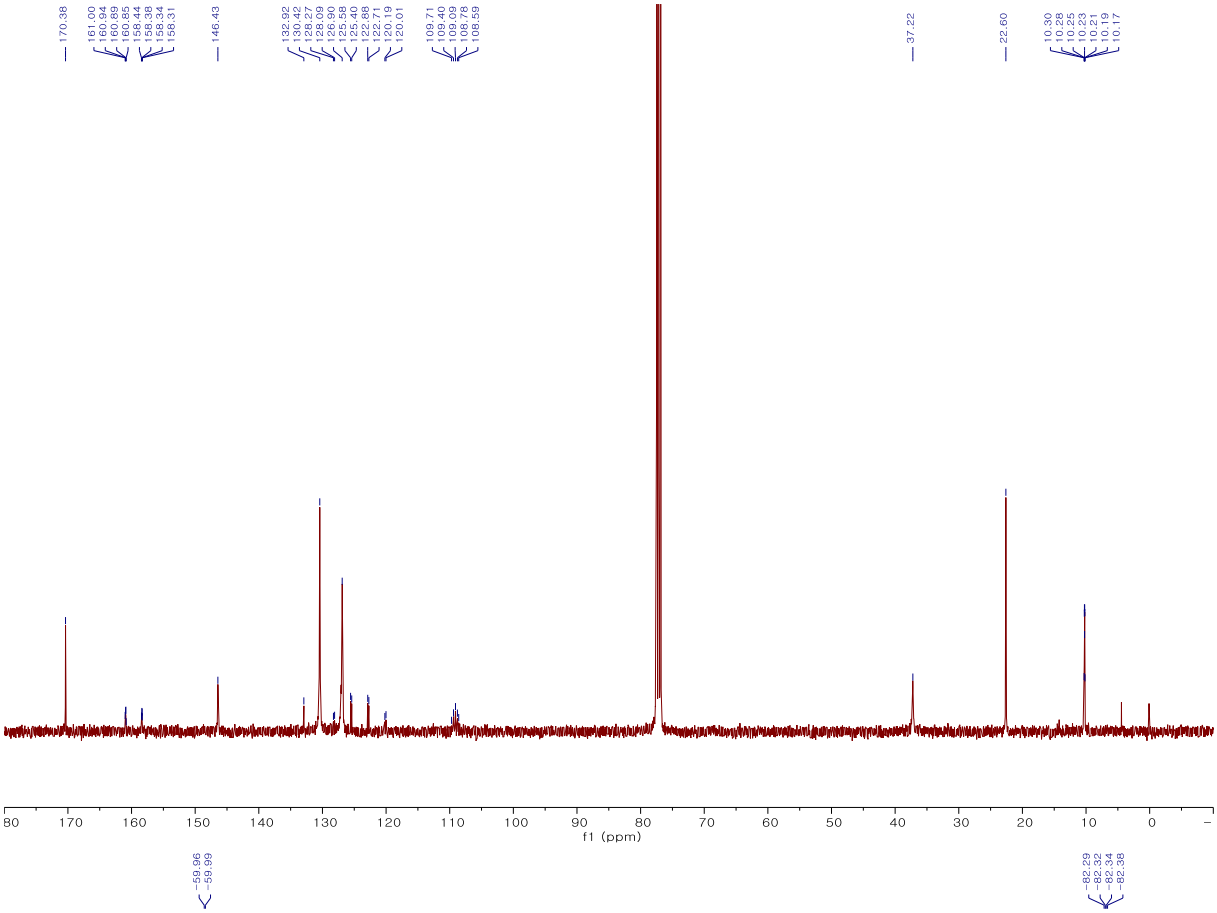

-59.83
-59.86
-81.48
-81.51
-81.54
-81.57
3.16
1.00
f1 (ppm)

(*E*)-*N*-methyl-*N*-(4-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)phenyl)acetamide (3d)

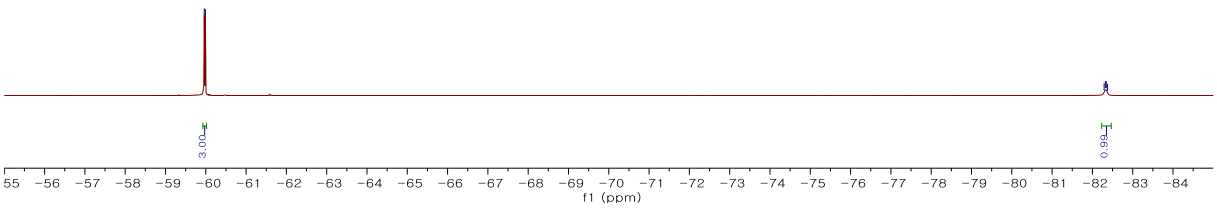


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.31 (s, 3H), 2.02 (d, *J* = 4.1 Hz, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.38 (C=O), 159.66 (dq, *J* = 257.4, 3.0 Hz), 146.43, 132.92, 130.42, 126.90, 124.14 (qd, *J* = 271.0, 17.8 Hz), 109.74–108.72 (m, *J* = 41.4 Hz), 37.22, 22.60, 10.23 (dq, *J* = 6.6, 2.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.98 (d, *J* = 10.9 Hz), -82.33 (q, *J* = 7.5 Hz). **IR (neat)** 3465, 3054, 2935, 1703, 1657, 1604, 1513, 1423, 1382, 1344, 1302, 1264, 1185, 1123, 1067, 996, 973, 854, 754, 705, 639, 603, 575, 501, 445 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{13}H_{13}F_4NO$ $[M]^+$ 275.0925, found 275.0933. **M.P.** 66.2 ℃. **Appearance** Light yellow solid. **Amount** 33 mg. **Yield** 60%.

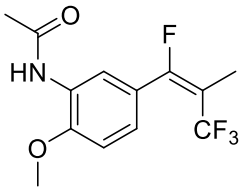



170.38
161.00
160.94
160.89
160.85
158.44
158.38
158.34
158.31
146.43
132.92
130.42
128.27
128.09
127.99
125.58
125.40
122.86
122.71
120.19
120.01
109.71
109.40
109.09
108.78
108.59
37.22
22.60
10.30
10.28
10.25
10.23
10.21
10.19
10.17
f1 (ppm)

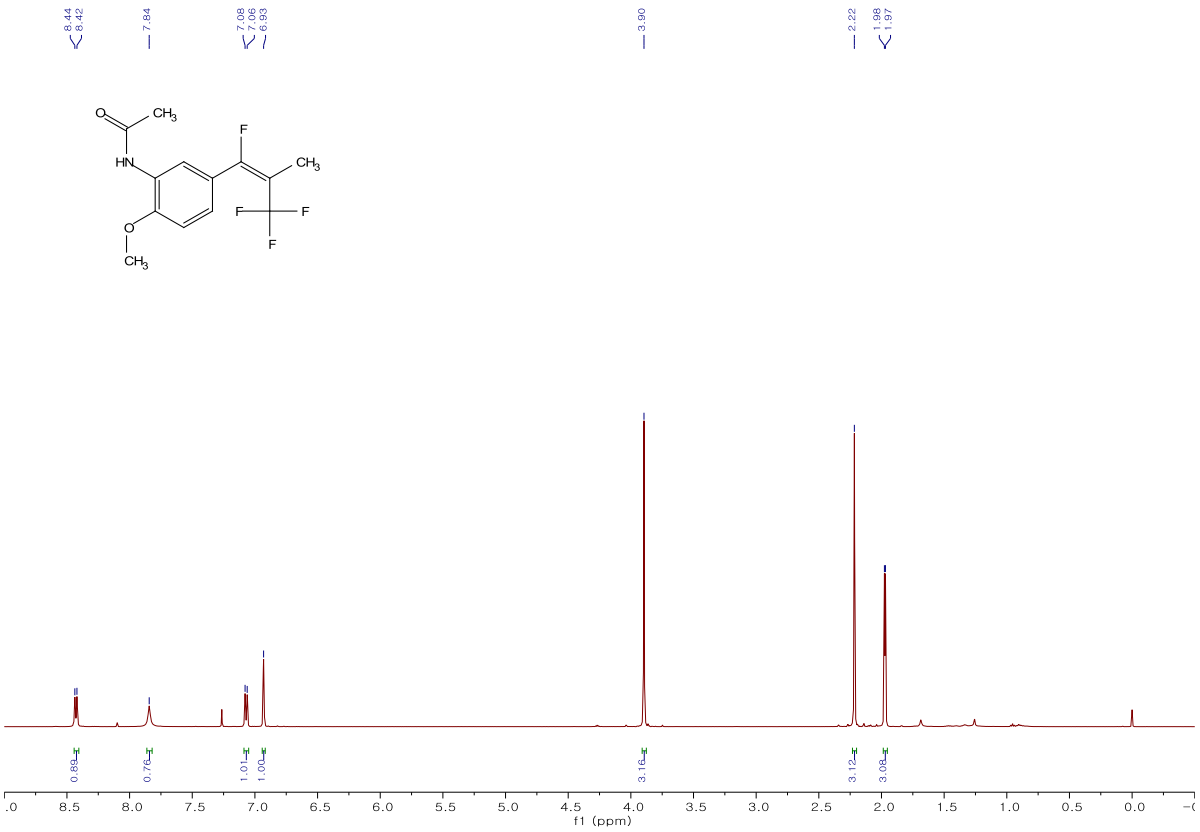
-59.96
-59.99
-82.29
-82.32
-82.34
-82.38

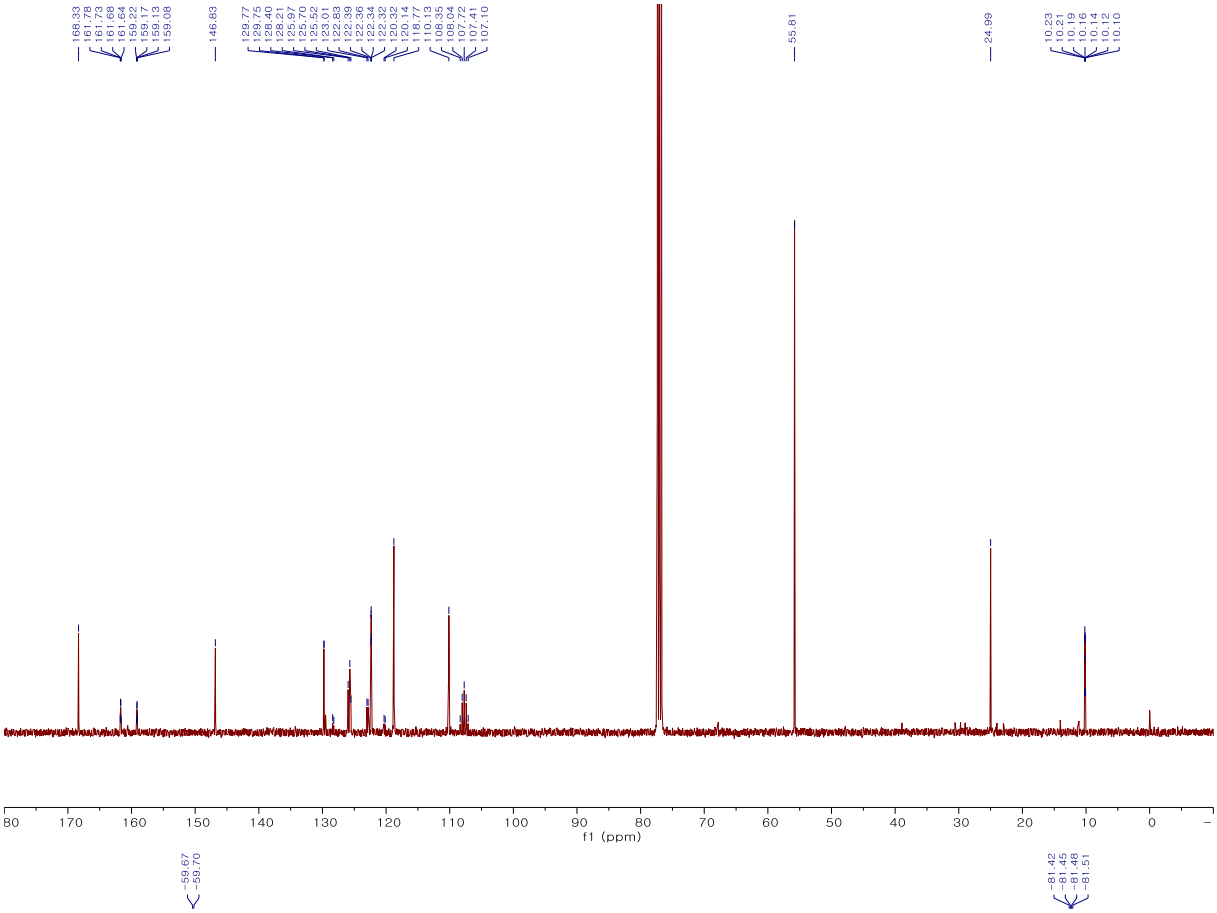

3.00
0.99
f1 (ppm)

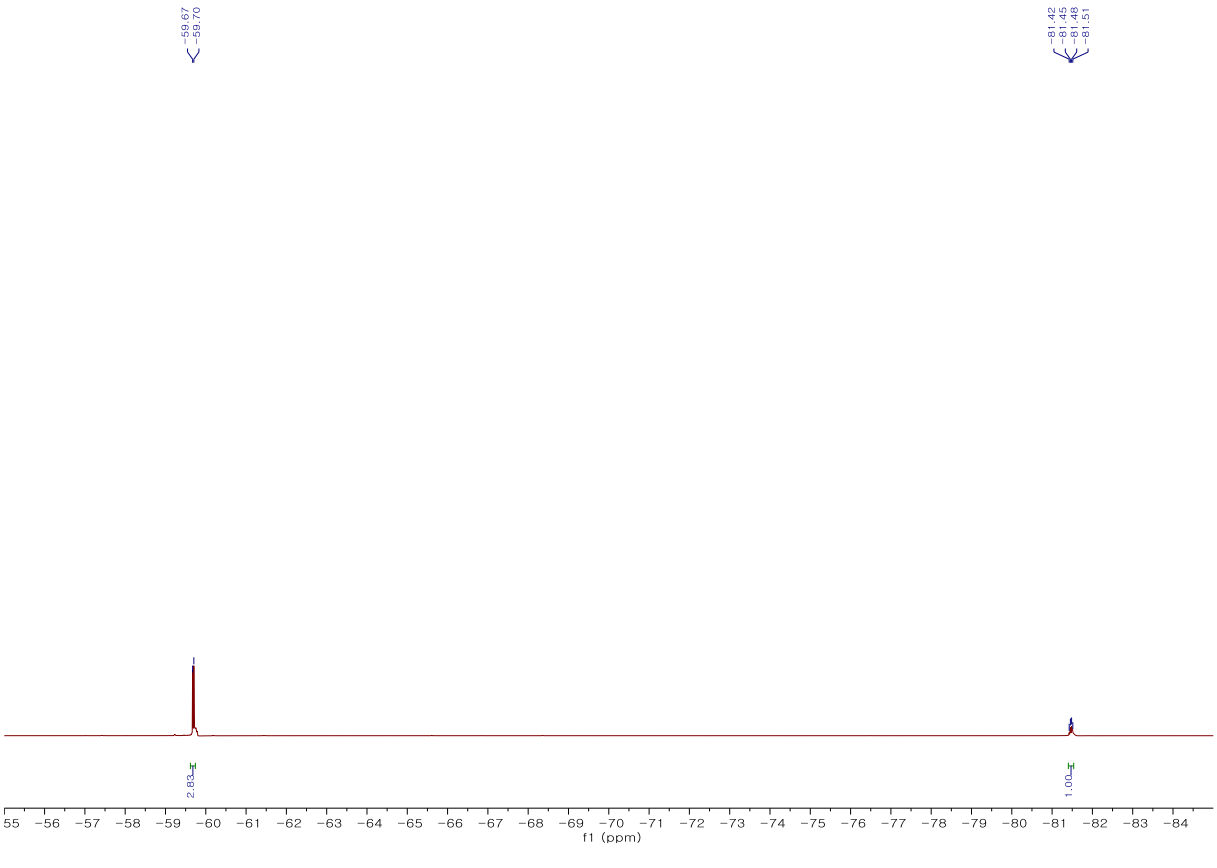
(*E*)-*N*-(2-methoxy-5-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)phenyl)acetamide (3e)



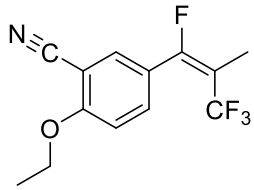
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 1H), 3.90 (s, 3H), 2.22 (s, 3H), 1.97 (d, *J* = 4.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.45 (C=O), 160.55 (dq, *J* = 261.7, 5.0 Hz), 146.95, 129.88 (d, *J* = 2.5 Hz) 125.95 (d, *J* = 27.0 Hz), 124.36 (qd, *J* = 271.6, 17.9 Hz), 122.47 (dd, *J* = 4.4, 2.2 Hz), 118.90, 110.25, 108.47–107.21 (m, *J* = 31.5 Hz), 55.92, 25.11, 10.28 (dq, *J* = 6.7, 2.4 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.69 (d, *J* = 11.3 Hz), -81.47 (q, *J* = 11.3 Hz). **IR (neat)** 3309, 3086, 3017, 2976, 2941, 2870, 1706, 1672, 1604, 1540, 1540, 1500, 1463, 1407, 1346, 1289, 1268, 1213, 1180, 1107, 1063, 1043, 1017, 968, 908, 850, 802, 721, 670, 596, 533, 477, 451 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{15}H_{17}F_4NO_2$ $[M]^+$ 319.1199, found 310.1195. **M.P.** 89.7 ℃. **Appearance** Yellow solid. **Amount** 34 mg. **Yield** 59%.



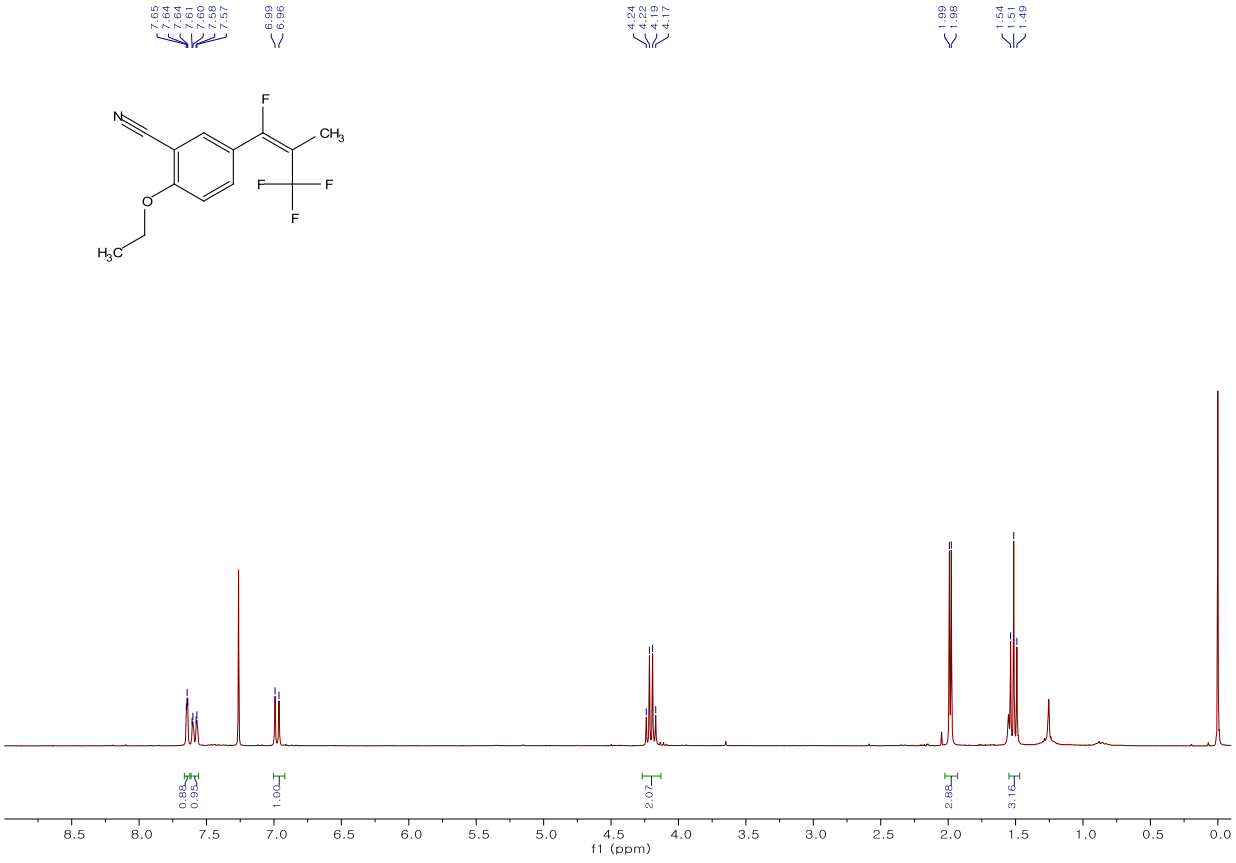

168.33
161.78
161.73
161.68
161.64
159.22
159.17
159.13
159.08
146.83
129.77
129.75
128.40
128.21
125.97
125.70
125.52
123.01
122.83
122.39
122.36
122.34
122.32
120.32
120.14
118.77
110.13
108.35
108.04
107.72
107.41
107.10
55.81
24.99
10.23
10.21
10.19
10.16
10.14
10.12
10.10
f1 (ppm)

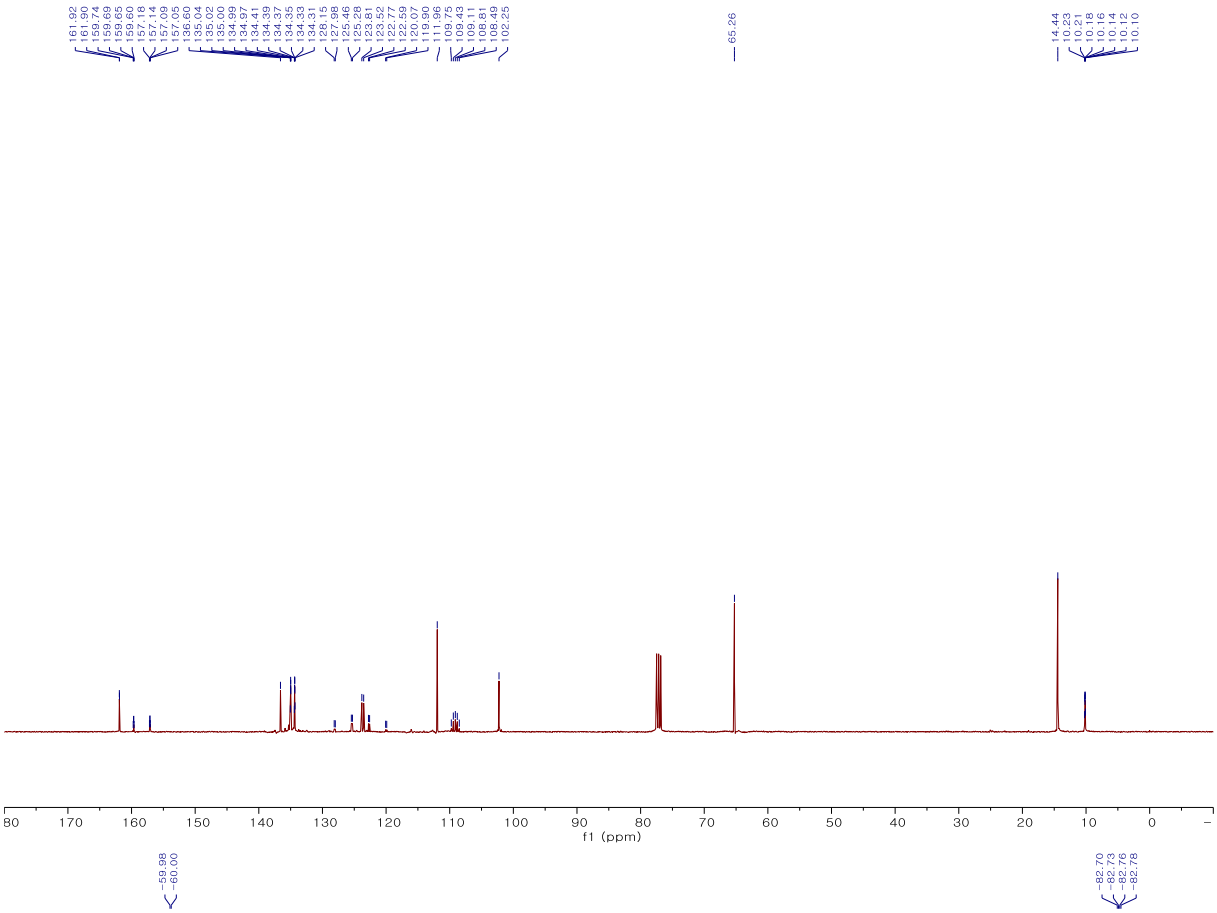

-59.67
-59.70
-81.42
-81.45
-81.48
-81.51
2.83
1.00
f1 (ppm)

(*E*)-2-ethoxy-5-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)benzonitrile (3f)

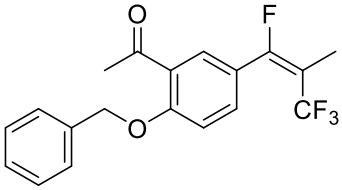


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 1.98 (d, *J* = 4.2 Hz, 3H), 1.51 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.91 (d, *J* = 1.8 Hz), 158.39 (dq, *J* = 256.8, 4.7 Hz), 136.60, 135.00 (dt, *J* = 3.3, 2.0 Hz), 134.36 (dq, *J* = 4.0, 2.1 Hz), 124.03 (qd, *J* = 271.0, 17.6 Hz), 123.66 (d, *J* = 28.9 Hz), 111.96 (C≡N), 109.78–108.44 (m, *J* = 17.6 Hz), 102.25, 65.26, 14.44, 10.16 (dq, *J* = 6.5, 2.3 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.99 (d, *J* = 11.2 Hz), -82.74 (q, *J* = 11.1 Hz). **IR (neat)** 3427, 2989, 2934, 2230, 1702, 1609, 1505, 1474, 1401, 1343, 1282, 1188, 1121, 1069, 1038, 900, 815, 762, 740, 716, 680, 641, 581, 510, 465 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{19}H_{16}F_4O_2$ $[M]^+$ 352.1092, found 352.1086. **M.P.** 77.4 ℃. **Appearance** White solid. **Amount** 27 mg. **Yield** 50%.

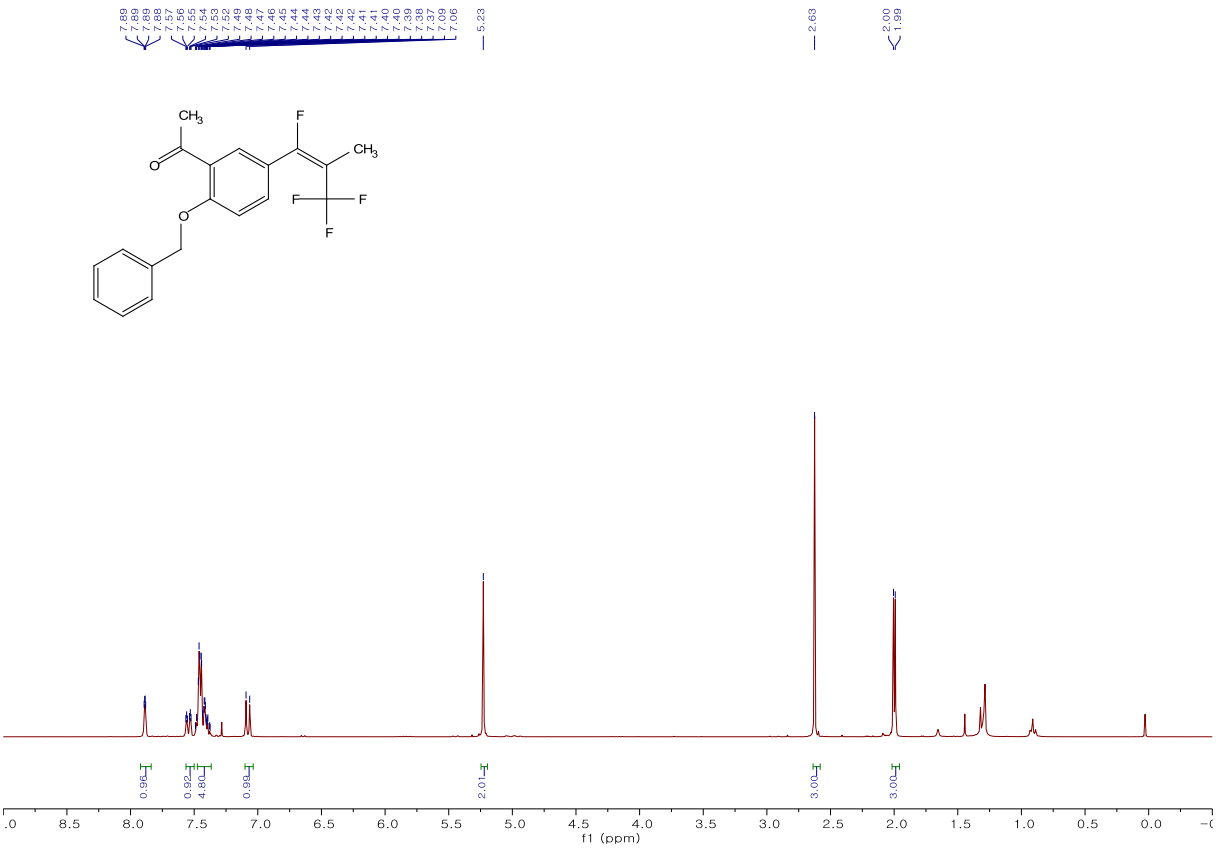


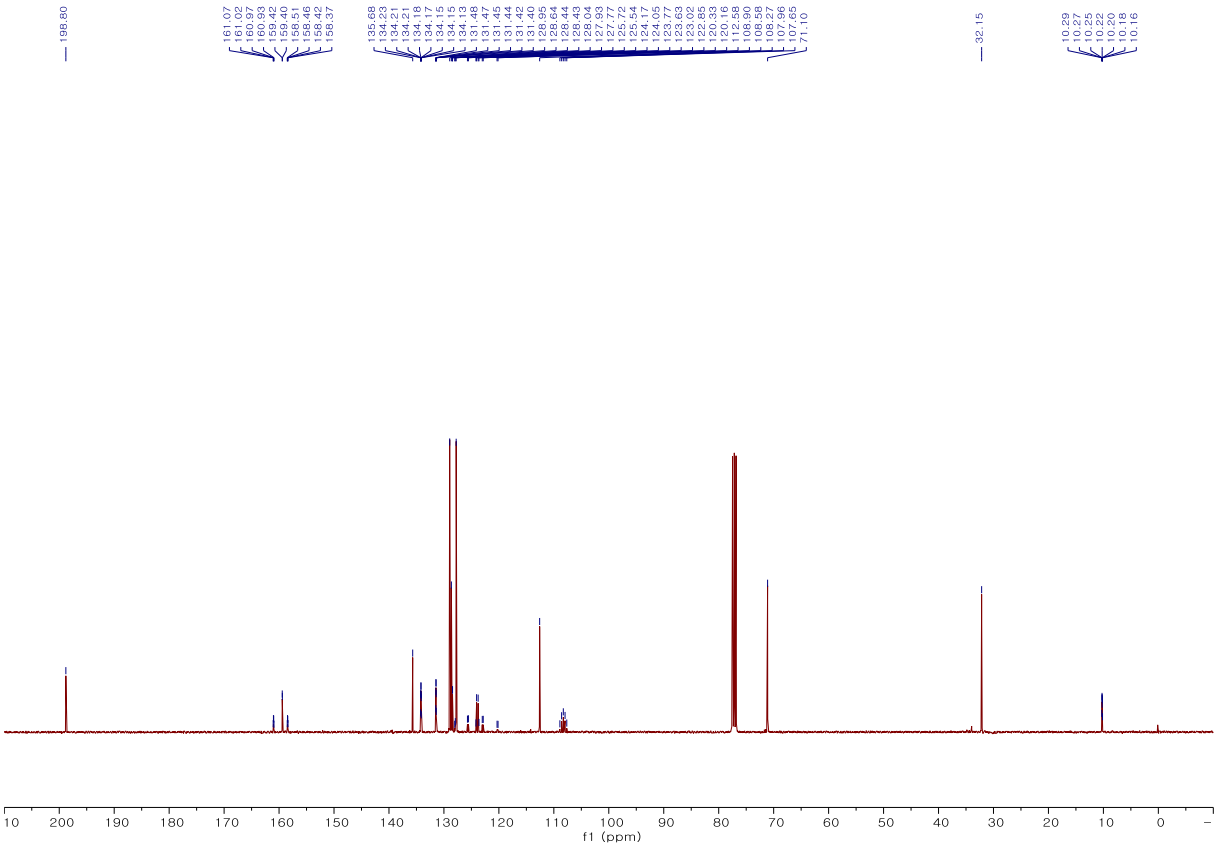

161.92
161.90
159.74
159.68
159.65
159.60
157.18
157.14
157.09
157.05
136.60
135.04
135.02
134.99
134.97
134.41
134.39
134.37
134.35
134.33
134.31
128.15
127.98
125.46
125.28
123.81
123.52
122.77
122.69
120.07
119.90
111.96
109.75
109.43
109.11
108.81
108.49
102.25
65.26
14.44
10.23
10.21
10.18
10.16
10.14
10.12
10.10
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 –
f1 (ppm)
-59.98
-60.00
-82.70
-82.73
-82.76
-82.78
3.15
1.00
−57 −58 −59 −60 −61 −62 −63 −64 −65 −66 −67 −68 −69 −70 −71 −72 −73 −74 −75 −76 −77 −78 −79 −80 −81 −82 −83 −84
f1 (ppm)

(*E*)-1-(2-(benzyloxy)-5-(1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)phenyl)ethanone (3g)



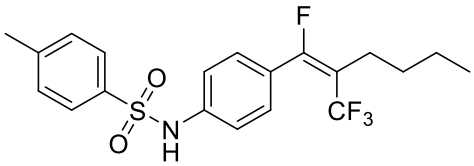
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.56–7.50 (m, 1H), 7.47–7.37 (m, 5H), 7.08 (d, *J* = 8.6 Hz, 1H), 5.23 (s, 2H), 2.63 (s, 3H), 2.00 (d, *J* = 4.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.80 (C=O), 159.72 (dq, *J* = 257.4, 4.7 Hz), 159.41 (d, *J* = 2.1 Hz), 135.68, 134.83–133.15 (m), 131.44 (dq, *J* = 3.3, 1.6 Hz), 128.95, 128.64, 128.43, 127.77, 124.78 (qd, *J* = 270.8, 17.8 Hz), 124.28–123.45 (m), 112.58, 108.27 (m), 71.10, 32.15, 10.22 (dq, *J* = 6.5, 2.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.95 (d, *J* = 10.9 Hz), -81.71 (q, *J* = 11.0 Hz). IR (neat) 3109, 3010, 2928, 2868, 1947, 1662, 1598, 1568, 1500, 1457, 1409, 1343, 1314, 1266, 1221, 1183, 1157, 1132, 1102, 1066, 1011, 971, 931, 906, 888, 835, 732, 696, 652, 599, 569, 473, 435 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{19}H_{16}F_4O_2$ $[M]^+$ 352.1092, found 352.1086**. M.P.** >300 ℃. **Appearance** White solid. **Amount** 35 mg. **Yield** 50%.



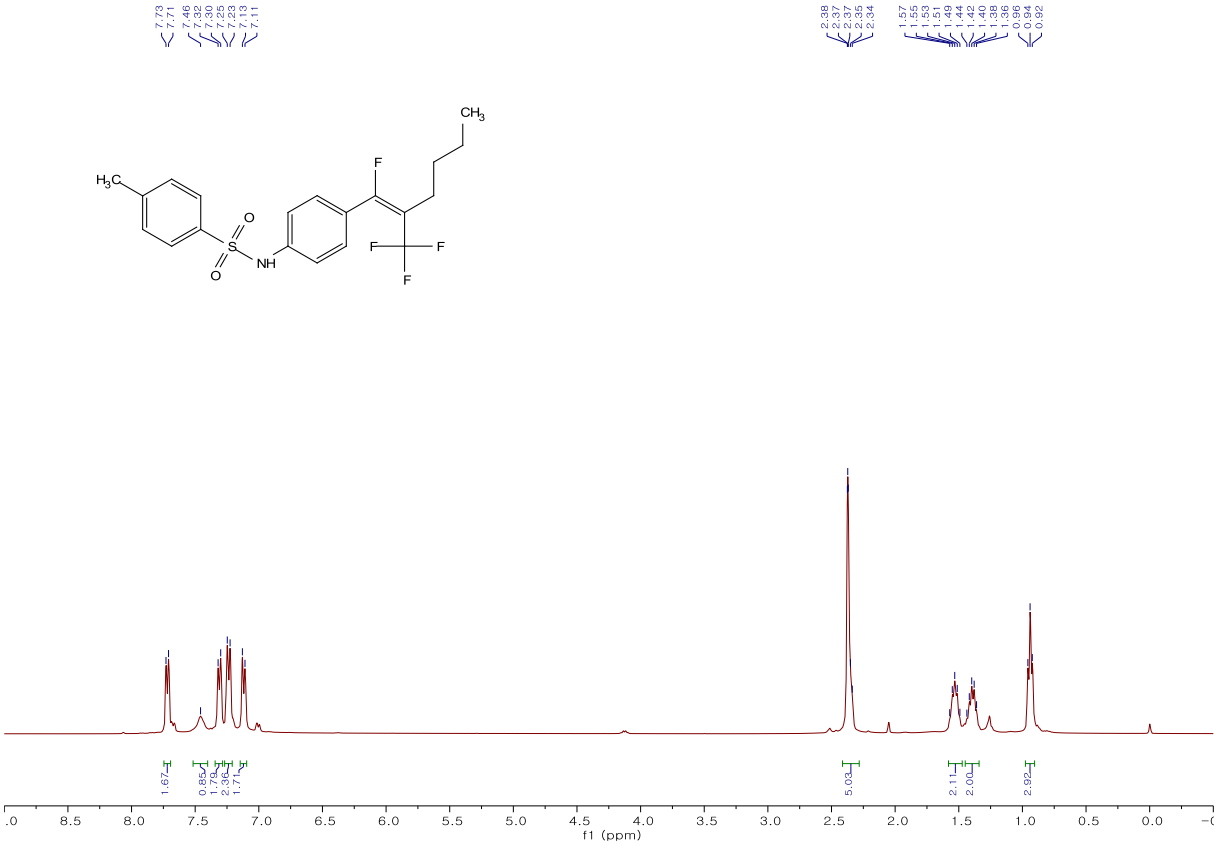

198.80
161.07
161.02
160.97
160.93
159.42
159.40
158.51
158.46
158.42
158.37
135.68
134.23
134.21
134.21
134.18
134.17
134.15
134.15
134.13
131.48
131.47
131.45
131.44
131.42
131.40
128.65
128.64
128.44
128.43
128.04
127.93
127.77
125.72
125.54
124.17
124.05
123.77
123.63
123.02
122.85
120.33
120.16
112.58
108.90
108.59
108.27
107.66
107.65
71.10
32.15
10.29
10.27
10.25
10.22
10.20
10.18
10.16
f1 (ppm)

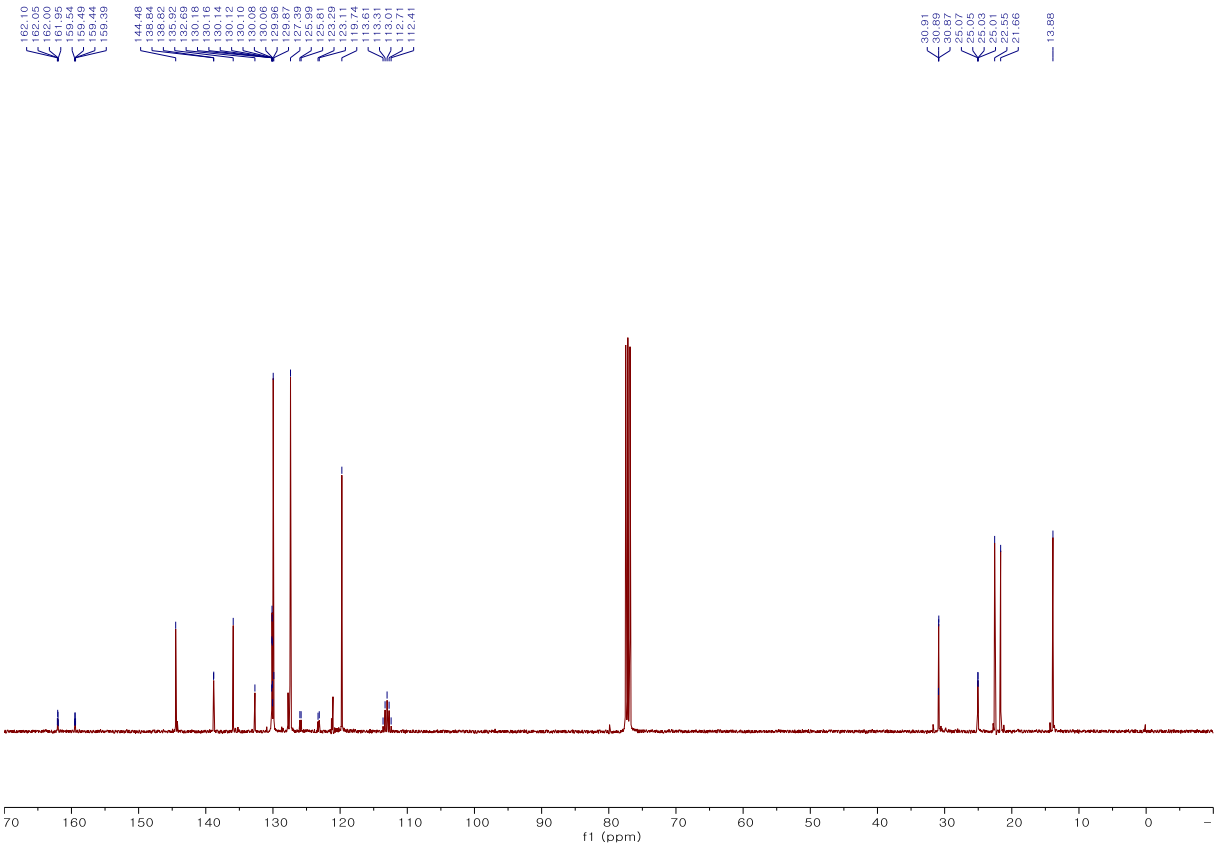

-59.93
-59.96
-81.67
-81.70
-81.73
-81.76
2.90
1.00
f1 (ppm)

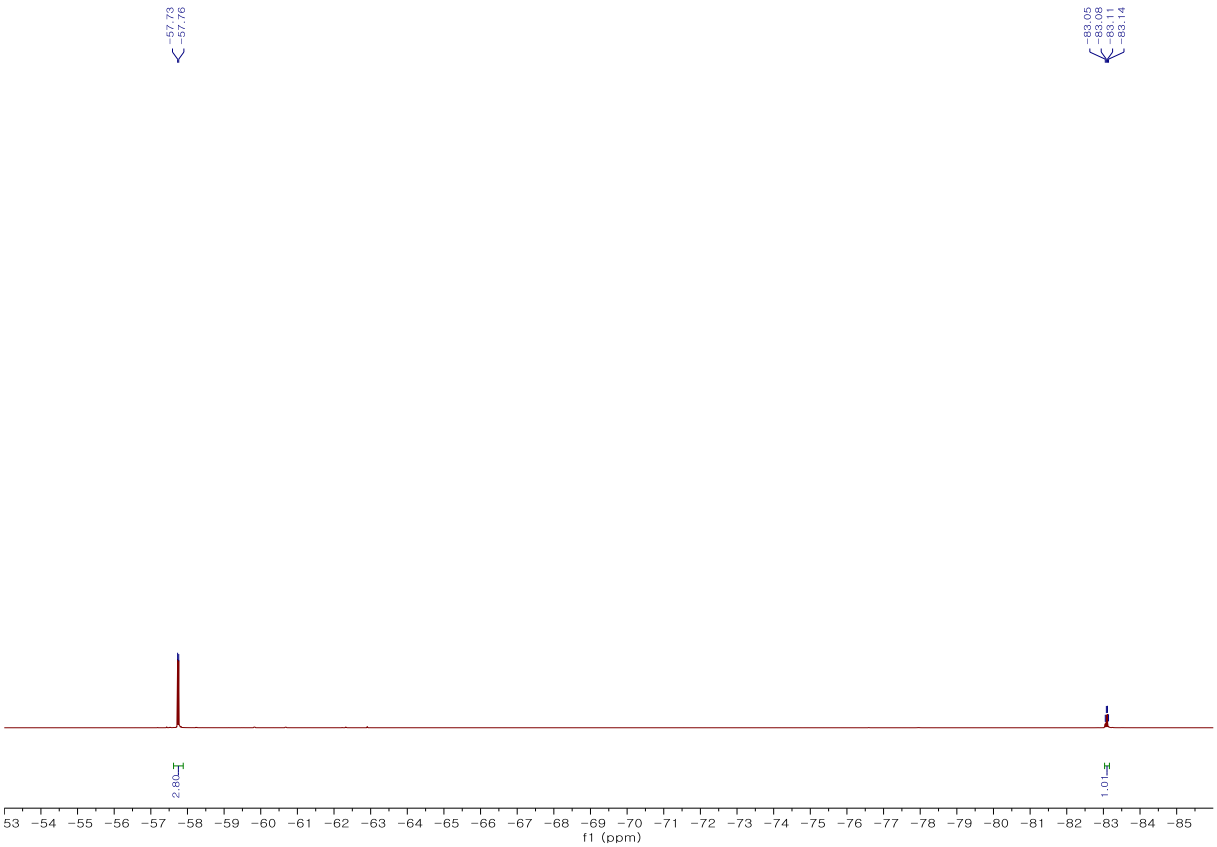
(*E*)-*N*-(4-(1-fluoro-2-(trifluoromethyl)hex-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5a)



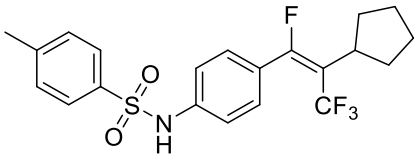
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.46 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 2.41–2.28 (m, 5H), 1.53 (p, *J* = 8.2 Hz, 2H), 1.40 (p, *J* = 7.6 Hz, 2H), 0.94 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.75 (dq, *J* = 257.3, 5.0 Hz), 144.48, 138.83 (d, *J* = 2.5 Hz), 135.92, 132.69, 130.13 (dq, *J* = 4.0, 2.1 Hz), 129.96, 127.39, 124.52 (qd, *J* = 272.7, 18.3 Hz), 119.74, 113.61–112.41 (m), 30.88 (d, *J* = 2.1 Hz), 25.04 (dd, *J* = 4.4, 1.9 Hz), 22.55, 21.66, 13.88. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.74 (d, *J* = 11.1 Hz), -83.14 (q, *J* = 11.3 Hz). **IR (neat)** 3743, 3312, 3046, 2958, 2931, 2869, 2697, 2522, 1918, 1695, 1613, 1515, 1468, 1405, 1342, 1293, 1230, 1182, 1157, 1112, 1028, 1012, 93, 930, 831, 735, 704, 659, 609, 578, 544, 493, 454 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{20}H_{21}F_4NO_2S$ $[M]^+$ 415.1214, found 415.1229. **M.P.** 103.8 ℃. **Appearance** White solid. **Amount** 67 mg. **Yield** 81%.



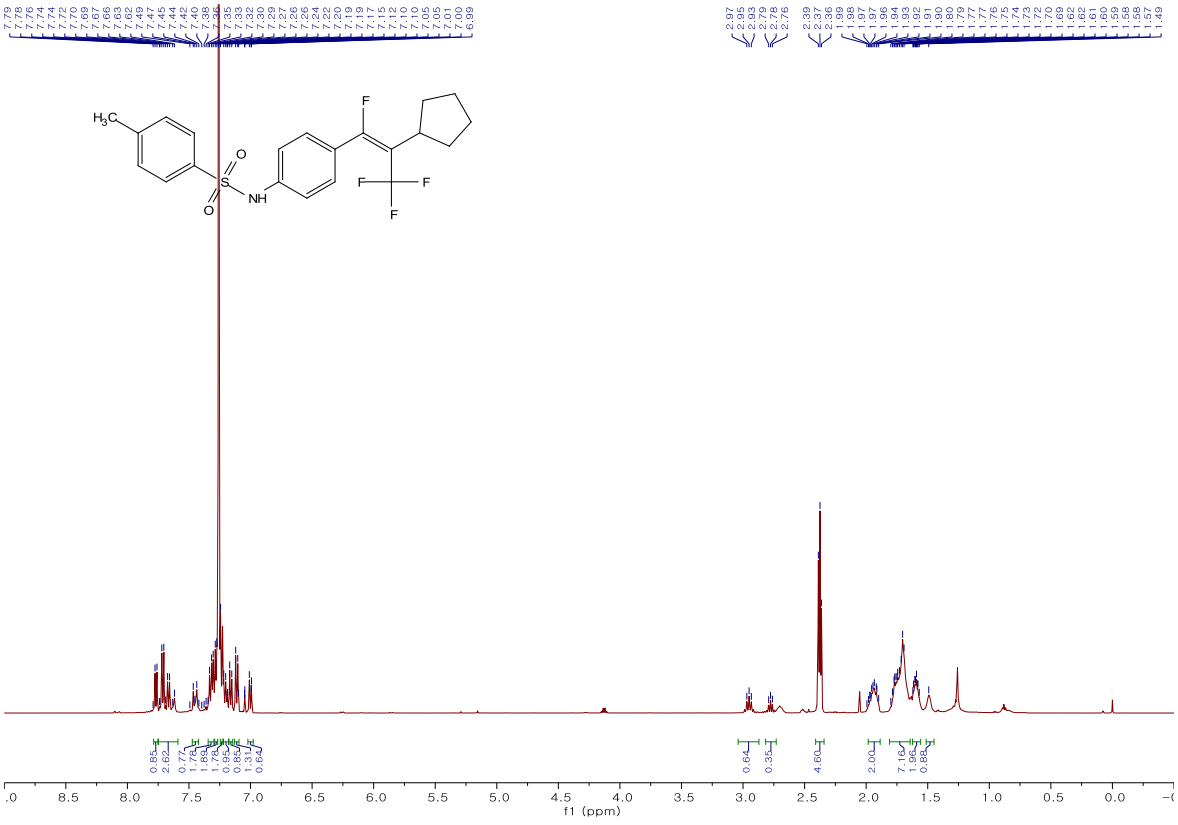

162.10
162.05
162.00
161.95
159.54
159.49
159.44
159.39
144.48
138.84
138.82
135.92
132.69
130.18
130.15
130.14
130.12
130.10
130.08
130.06
129.96
128.87
127.39
125.99
125.61
123.09
123.11
119.74
113.61
113.31
113.01
112.71
112.41
30.91
30.89
30.87
25.07
25.05
25.03
25.01
22.55
21.66
13.88
f1 (ppm)

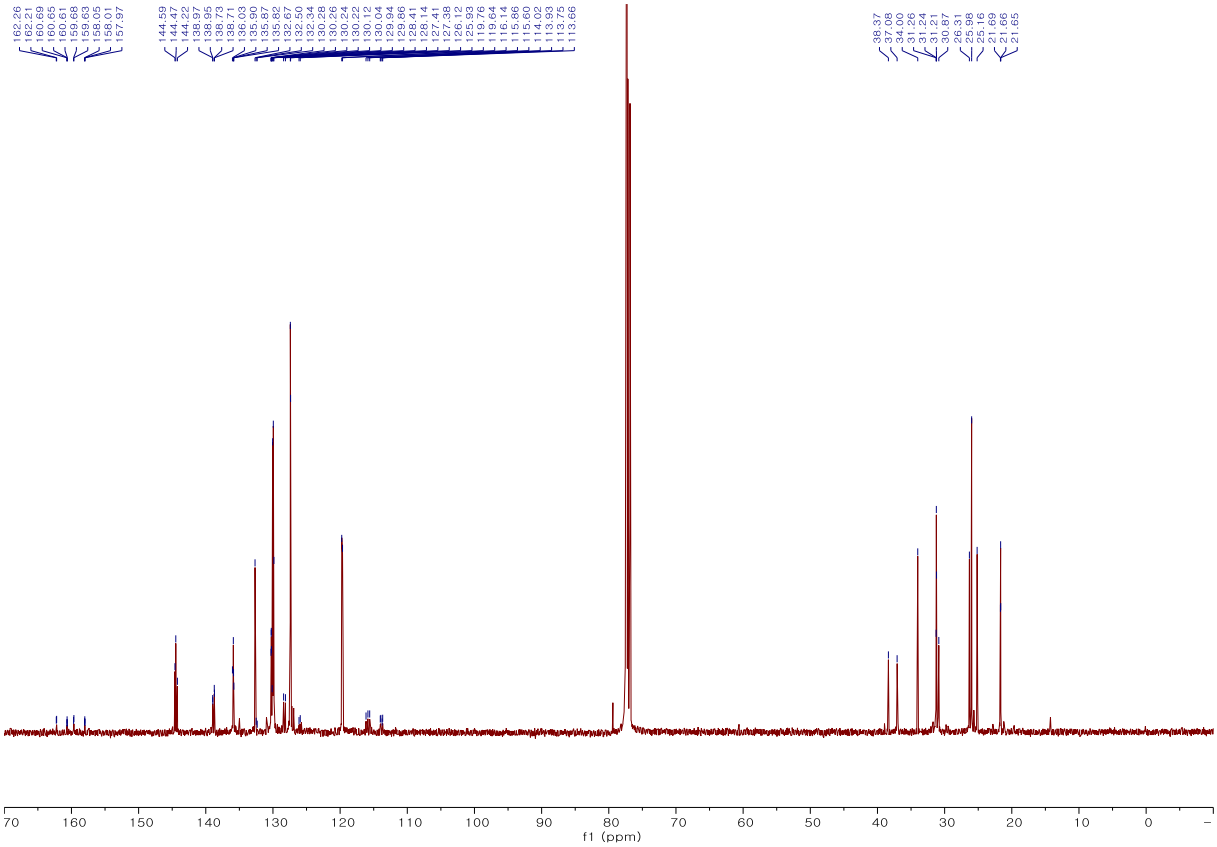

-57.73
-57.76
-83.05
-83.08
-83.11
-83.14
2.80
1.01
f1 (ppm)

(*E*)-*N*-(4-(2-cyclopentyl-1,3,3,3-tetrafluoroprop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5b)

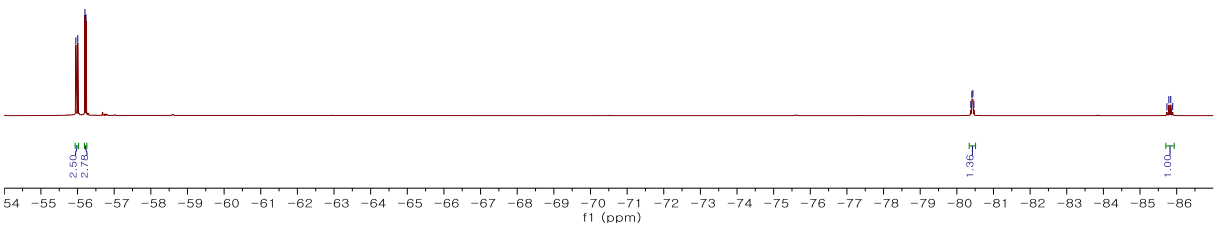


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.75–7.59 (m, 3H), 7.45 (d, *J* = 14.3 Hz, 1H), 7.34–7.30 (m, 2H), 7.28 (d, *J* = 6.4 Hz, 2H), 7.24 (s, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.02–6.98 (m, 1H), 2.95 (t, *J* = 9.1 Hz, 1H), 2.38 (t, *J* = 6.2 Hz, 5H), 1.98–1.89 (m, 2H), 1.80–1.69 (m, 7H), 1.62–1.57 (m, 2H), 1.49 (s, 1H). **^{13}C NMR** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.95 (dd, *J* = 258.7, 5.0 Hz), 159.33 (dt, *J* = 265.6, 4.4 Hz), 144.59, 144.47, 144.22, 138.96 (d, *J* = 1.6 Hz), 138.72 (d, *J* = 2.6 Hz), 135.96 (d, *J* = 13.2 Hz), 135.85 (d, *J* = 4.7 Hz), 132.67, 130.25 (dd, *J* = 3.9, 2.2 Hz), 130.07–129.83 (m), 129.23 (qd, *J* =273.7, 27.7 Hz), 127.40 (d, *J* = 3.2 Hz), 119.70 (d, *J* = 11.7 Hz), 116.27–115.34 (m, *J* = 26.3 Hz), 115.19–113.36 (m), 38.37, 37.08, 34.00, 31.26–31.21 (m), 30.87, 26.31, 25.98, 25.16, 21.90–21.55 (m). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -55.98 (d, *J* = 19.7 Hz), -56.22 (d, *J* = 10.8 Hz), -80.42 (q, *J* = 10.5 Hz), -85.82 (q, *J* = 19.8 Hz). **IR (neat)** 3258, 3050, 2958, 2873, 1916, 1669, 1609, 1511, 1457, 1397, 1335, 1298, 1229, 1160, 1114, 1044, 1015, 915, 838, 814, 704, 665, 576, 546 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{21}H_{21}F_4NO_2S$ $[M]^+$ 427.1227, found 427.1229. **Appearance** Colorless oil. **Amount** 68 mg. **Yield** 80%. (*E*/*Z*=1.7:1)

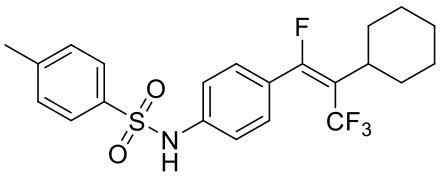



162.26
162.21
160.69
160.65
160.61
159.68
159.63
158.05
158.01
157.97
144.59
144.47
144.22
138.97
138.95
138.73
138.71
136.03
135.90
135.87
135.82
132.67
132.50
132.34
130.28
130.26
130.24
130.22
130.12
130.04
129.84
129.66
128.41
128.14
127.41
127.38
125.72
125.93
119.76
119.64
116.14
115.66
115.60
114.02
113.93
113.75
113.66
38.37
37.08
34.00
31.26
31.24
31.21
30.87
26.31
25.98
25.16
21.69
21.66
21.65
f1 (ppm)

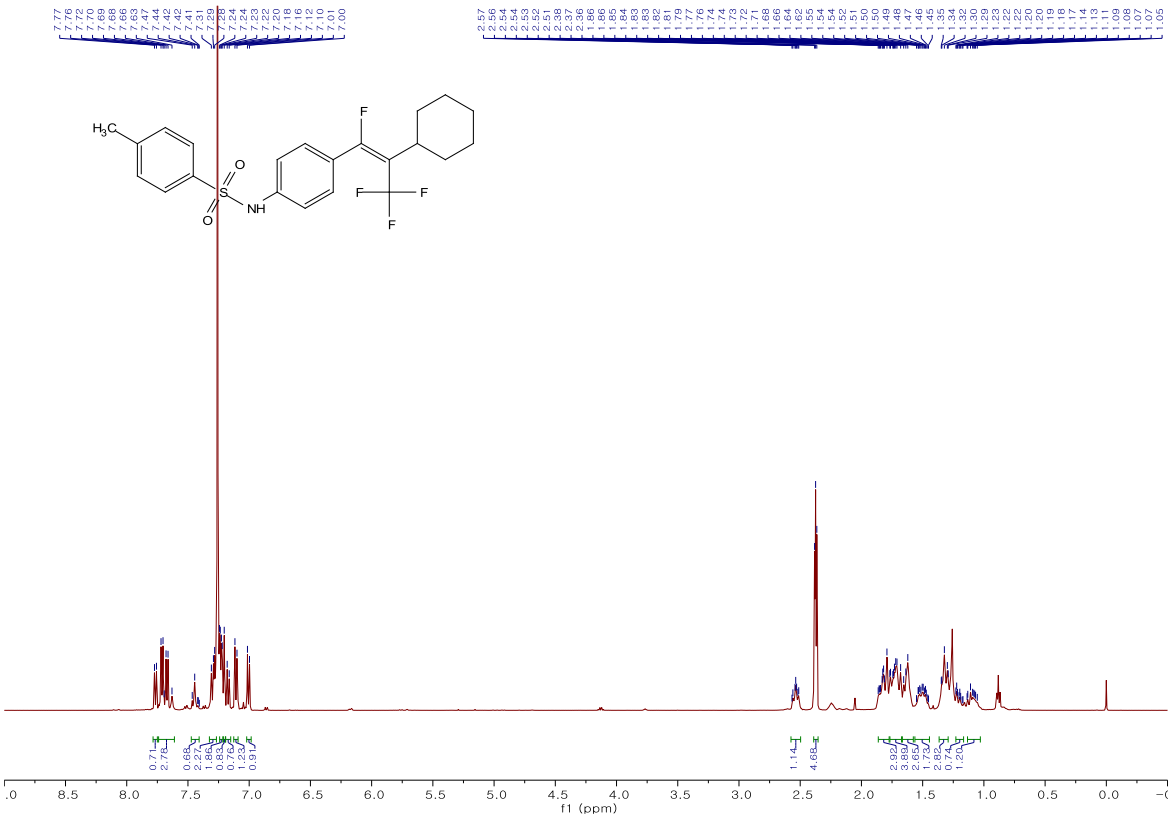

-55.95
-56.01
-56.20
-56.23
-80.38
-80.41
-80.44
-80.47
-85.73
-85.79
-85.84
-85.89

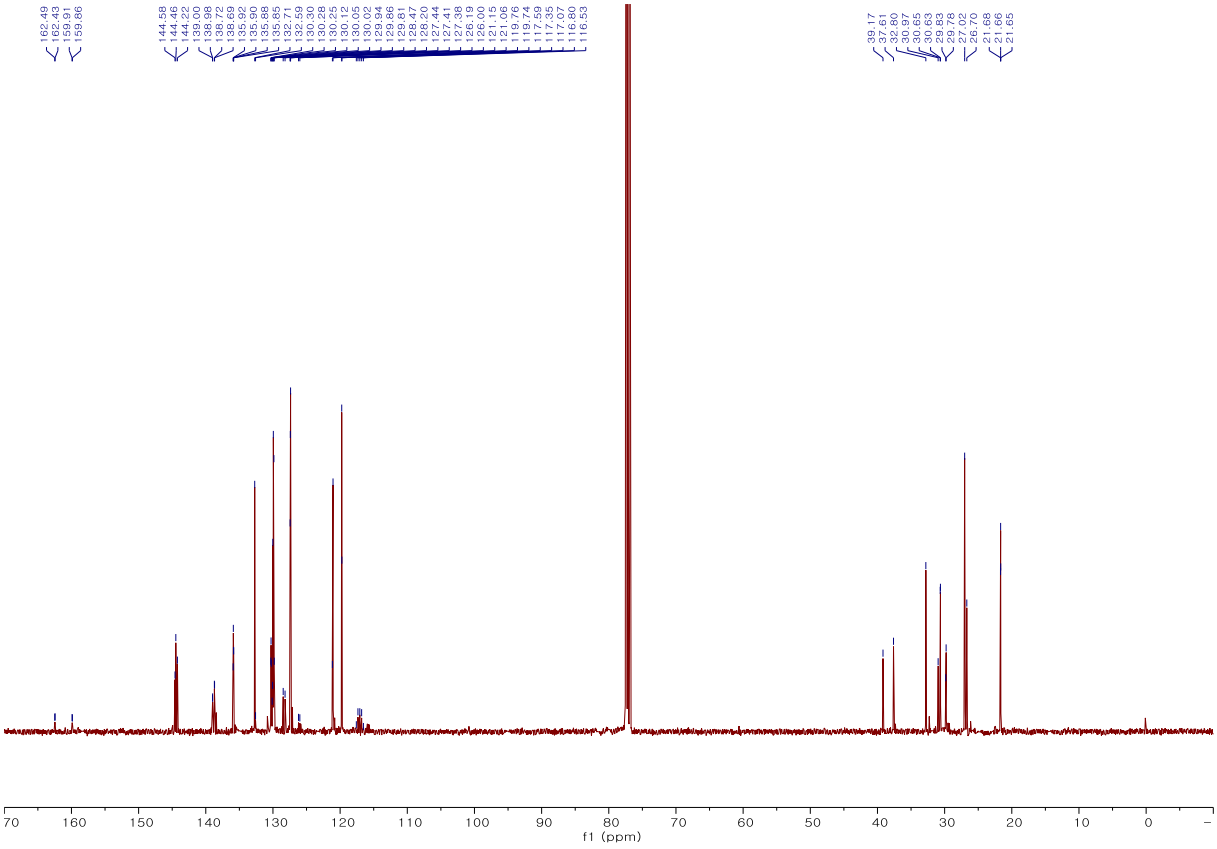

2.50
2.78
1.36
1.00
f1 (ppm)

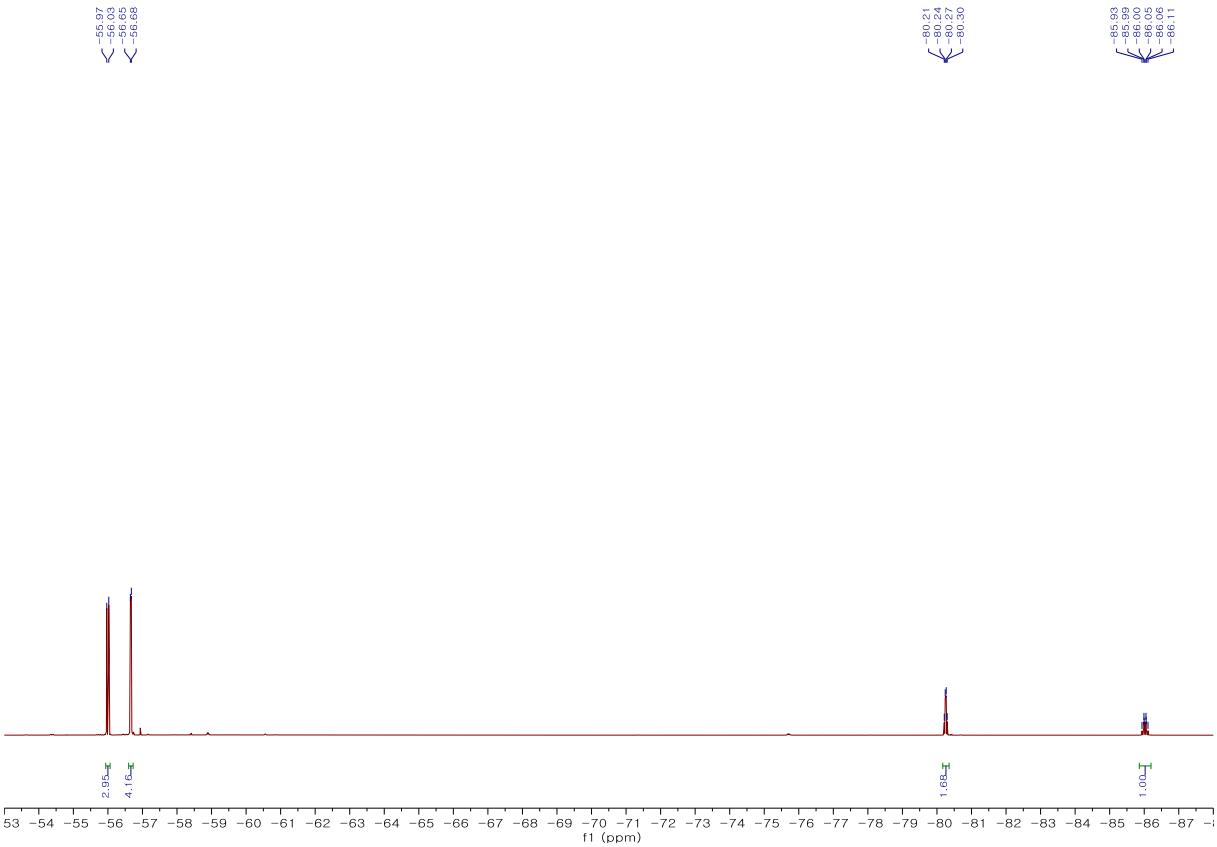
(*E*)-*N*-(4-(2-cyclohexyl-1,3,3,3-tetrafluoroprop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5c)



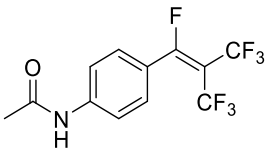
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.74–7.61 (m, 3H), 7.47–7.41 (m, 1H), 7.32–7.27 (m, 2H), 7.24–7.22 (m, 2H), 7.20 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 2.57–2.51 (m, 1H), 2.40–2.35 (m, 5H), 1.86–1.77 (m, 3H), 1.76–1.67 (m, 4H), 1.66–1.54 (m, 3H), 1.52–1.45 (m, 2H), 1.37–1.29 (m, 3H), 1.23–1.17 (m, 1H), 1.13–1.03 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.17 (dd, *J* = 259.2, 5.1 Hz), 144.58, 144.46, 144.22, 138.99 (d, *J* = 1.8 Hz), 138.71 (d, *J* = 2.7 Hz), 135.88 (dd, *J* = 4.8, 2.6 Hz), 132.71, 130.31–130.14 (m), 120.09–129.76 (m), 129.51 (qd, *J* = 230.2, 19.7 Hz), 127.52–127.23 (m), 121.06, 119.75 (d, *J* = 1.8 Hz), 117.68–116.44 (m), 39.17, 37.61, 32.80, 30.97, 30.65, 30.64 (d, *J* = 2.9 Hz), 29.80 (d, *J* = 5.4 Hz), 27.02, 26.70, 21.68–21.65 (m). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -56.00 (d, *J* = 21.9 Hz), -56.66 (d, *J* = 10.3 Hz), -80.25 (q, *J* = 10.4 Hz), -86.02 (q, *J* = 22.5 Hz). **IR (neat)** 3259, 3048, 2927, 2854, 2232, 1915, 1671, 1609, 1512, 1456, 1398, 1337, 1300, 1232, 1160, 1112, 1092, 1044, 1018, 984, 915, 836, 813, 704, 664, 574, 544 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{21}H_{23}F_4NO_2S$ $[M]^+$ 441.1370, found 441.1386. **M.P.** 76.8 ℃. **Appearance** White solid. **Amount** 61 mg. **Yield** 70%. (*E*/*Z*=1.3:1)



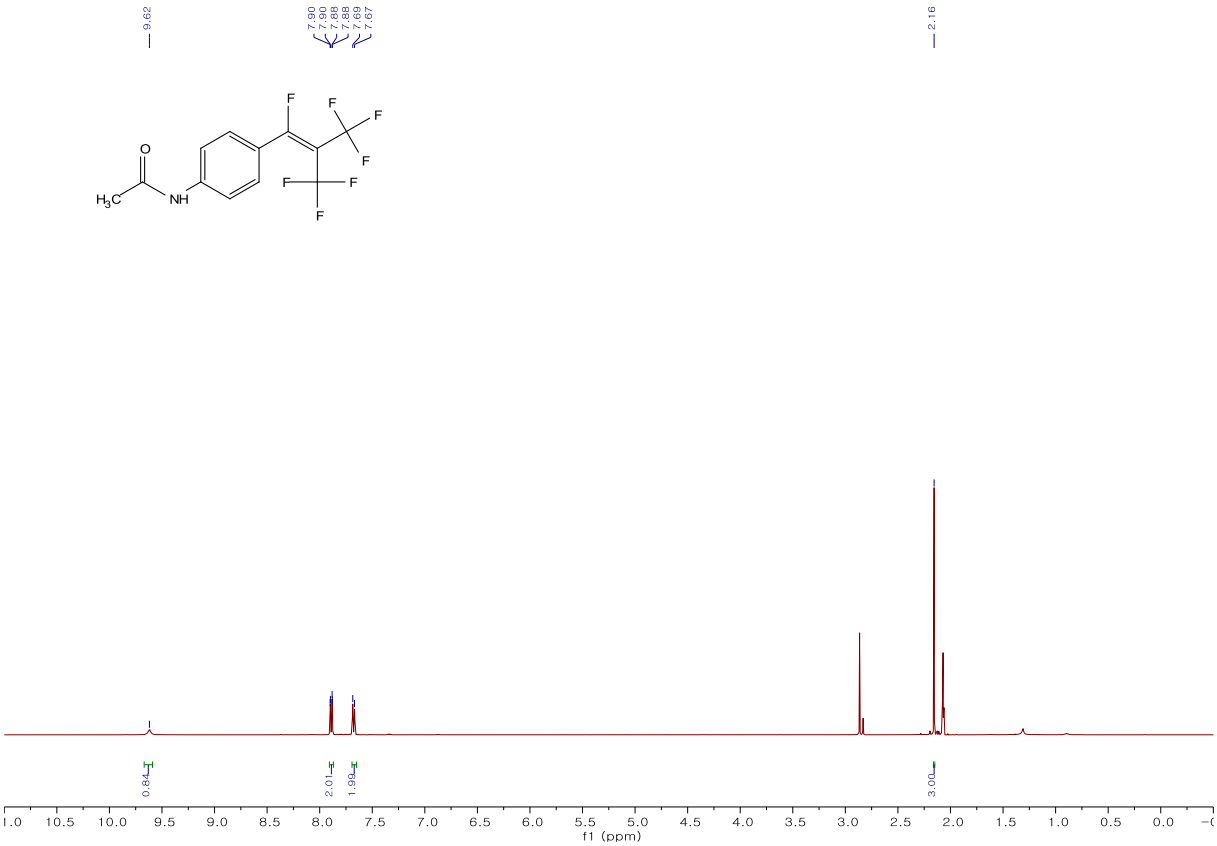

162.49
162.43
159.91
159.86
144.58
144.46
144.22
139.00
138.96
138.72
138.69
135.92
135.90
135.88
135.85
132.71
132.59
130.30
130.28
130.15
130.12
130.05
130.02
129.94
129.86
129.81
128.47
128.20
127.44
127.41
127.18
126.19
126.00
121.15
121.06
119.76
119.74
117.59
117.35
117.07
116.89
116.83
39.17
37.61
32.60
30.97
30.65
30.63
29.83
29.78
27.02
26.70
21.68
21.66
21.65
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

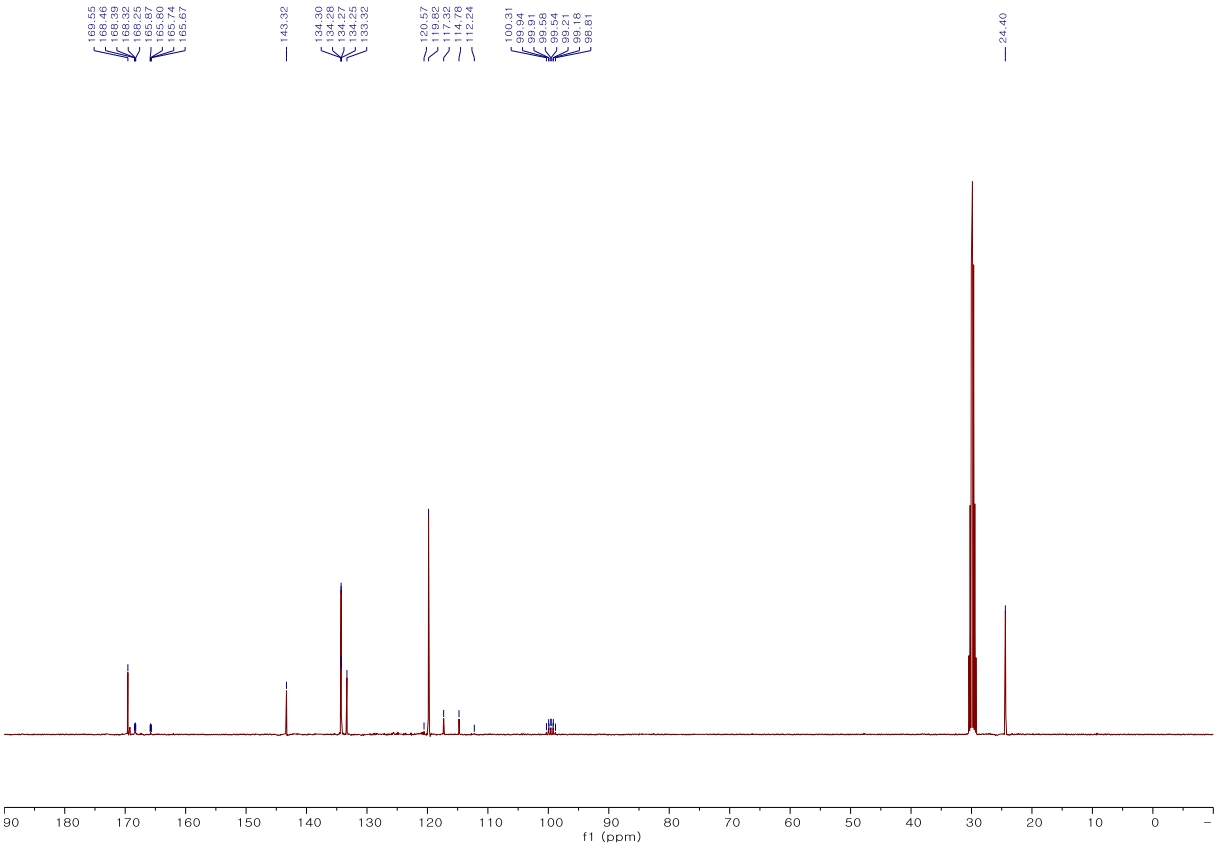

-55.97
-56.03
-56.65
-56.68
-80.21
-80.24
-80.27
-80.30
-85.93
-85.99
-86.00
-86.05
-86.06
-86.11
2.95
4.16
1.68
1.00
53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87
f1 (ppm)

***N*-(4-(1,3,3,3-tetrafluoro-2-(trifluoromethyl)prop-1-en-1-yl)phenyl)acetamide (5d)**

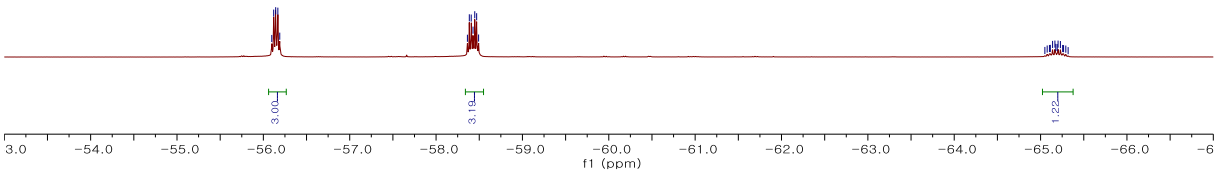


^{1}H NMR (500 MHz, Acetone-d_6) δ 9.62 (s, 1H), 7.91–7.87 (m, 2H), 7.68 (d, J = 8.5 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.55 (C=O), 167.06 (dq, J = 259.8, 6.6 Hz), 143.32, 134.28 (d, J = 1.5 Hz), 133.32, 119.82, 116.05 (q, J = 255.3 Hz), 100.91–98.45 (m), 24.40. **^{19}F NMR** (376 MHz, Chloroform-d) δ -56.07 – -56.21 (m), -58.43 (dq, J = 24.4, 8.4 Hz), -65.18 (dq, J = 33.8, 9.8 Hz). **IR (neat)** 3382, 3313, 3194, 3116, 2925, 2855, 2349, 2253, 1922, 1680, 1597, 1529, 1410, 1360, 1319, 1284, 1258, 1212, 1182, 1144, 1079, 1038, 1010, 985, 874, 834, 747, 713, 678, 632, 598, 546, 525, 470 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{12}H_8F_7NO$ $[M]^+$ 315.0507, found 315.0494. **M.P.** 93.4 ℃. **Appearance** Yellow solid. **Amount** 44 mg. **Yield** 70%.

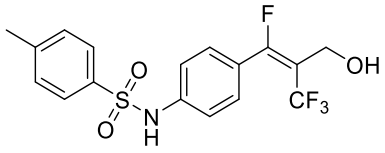



169.55
168.46
168.39
168.32
165.85
165.67
165.80
165.74
165.67
143.32
134.30
134.28
134.27
134.25
133.32
120.57
119.82
117.32
117.28
112.24
100.31
99.94
99.91
99.58
99.54
99.21
99.18
98.81
24.40
f1 (ppm)

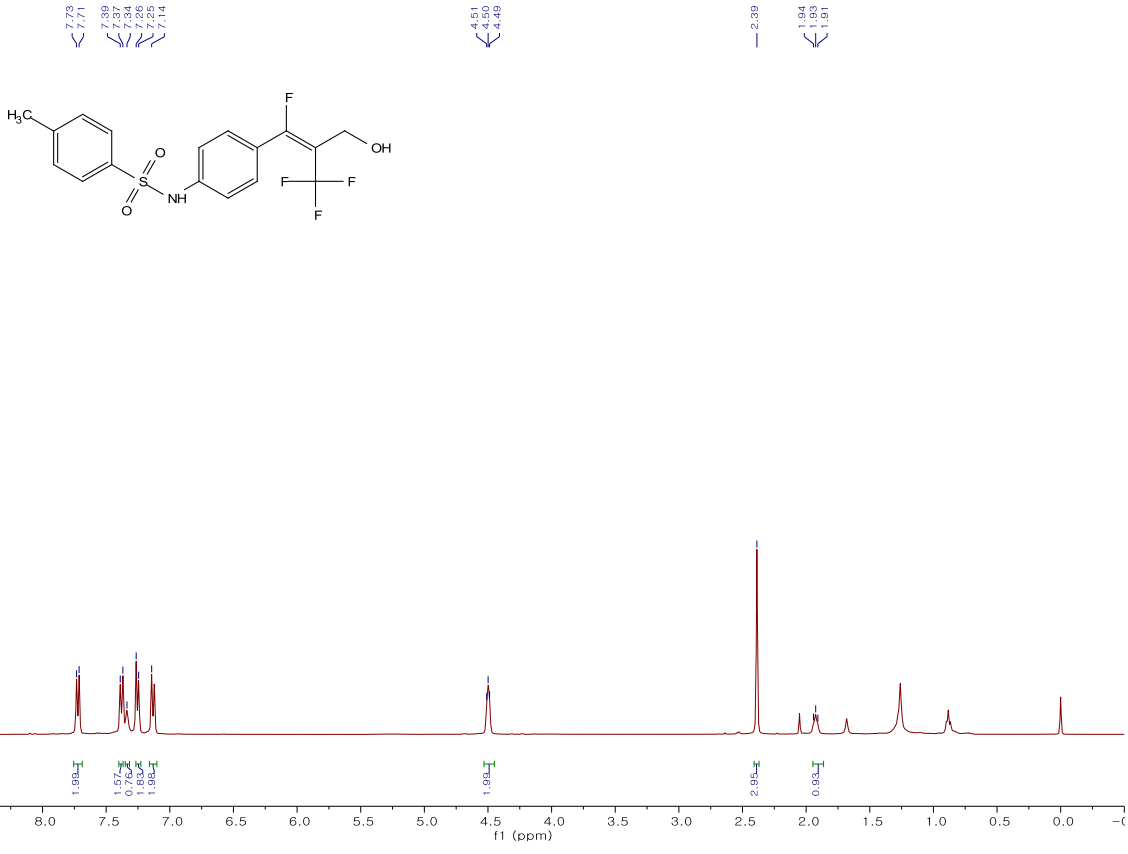

-56.10
-56.12
-56.14
-56.17
-56.19
-58.36
-58.38
-58.41
-58.43
-58.45
-58.47
-58.49
-65.05
-65.08
-65.10
-65.11
-65.14
-65.17
-65.18
-65.19
-65.20
-65.23
-65.26
-65.27
-65.29
-65.32

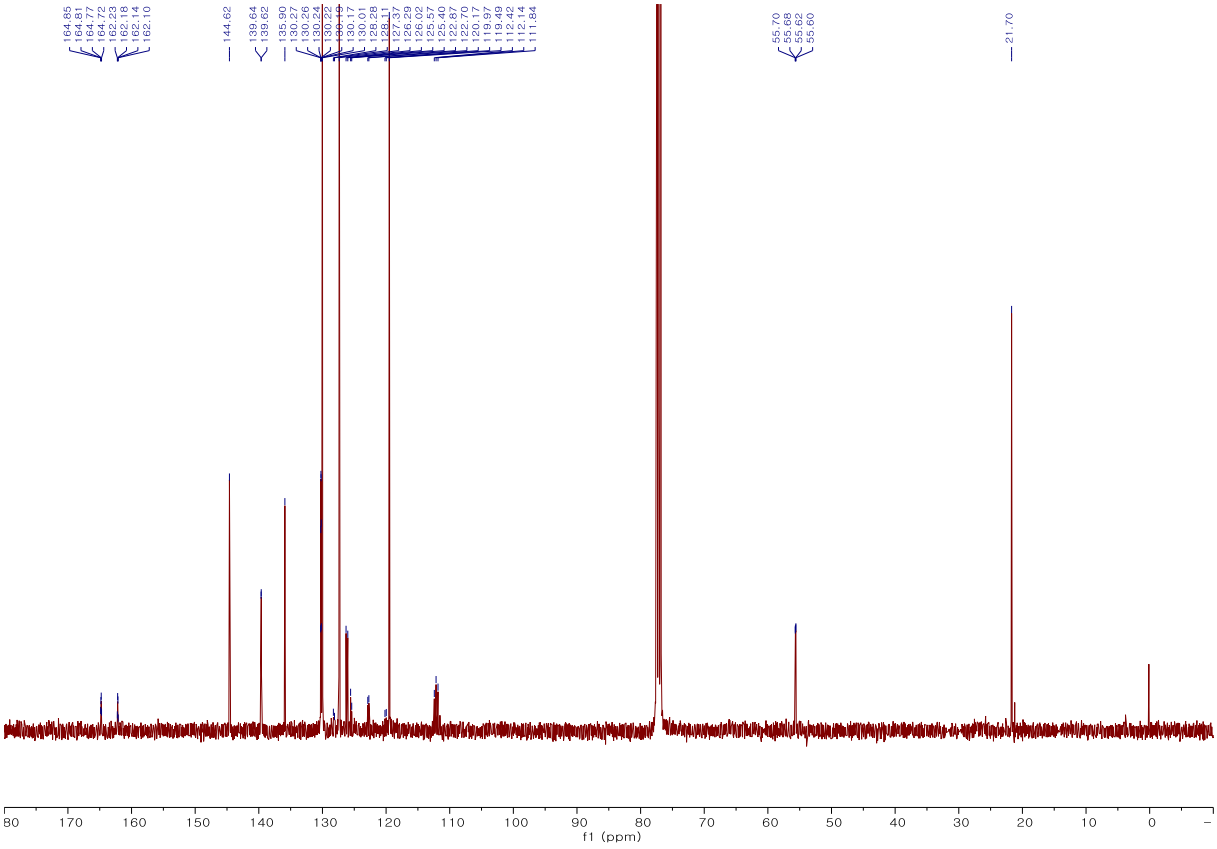

3.00
3.19
1.22
f1 (ppm)

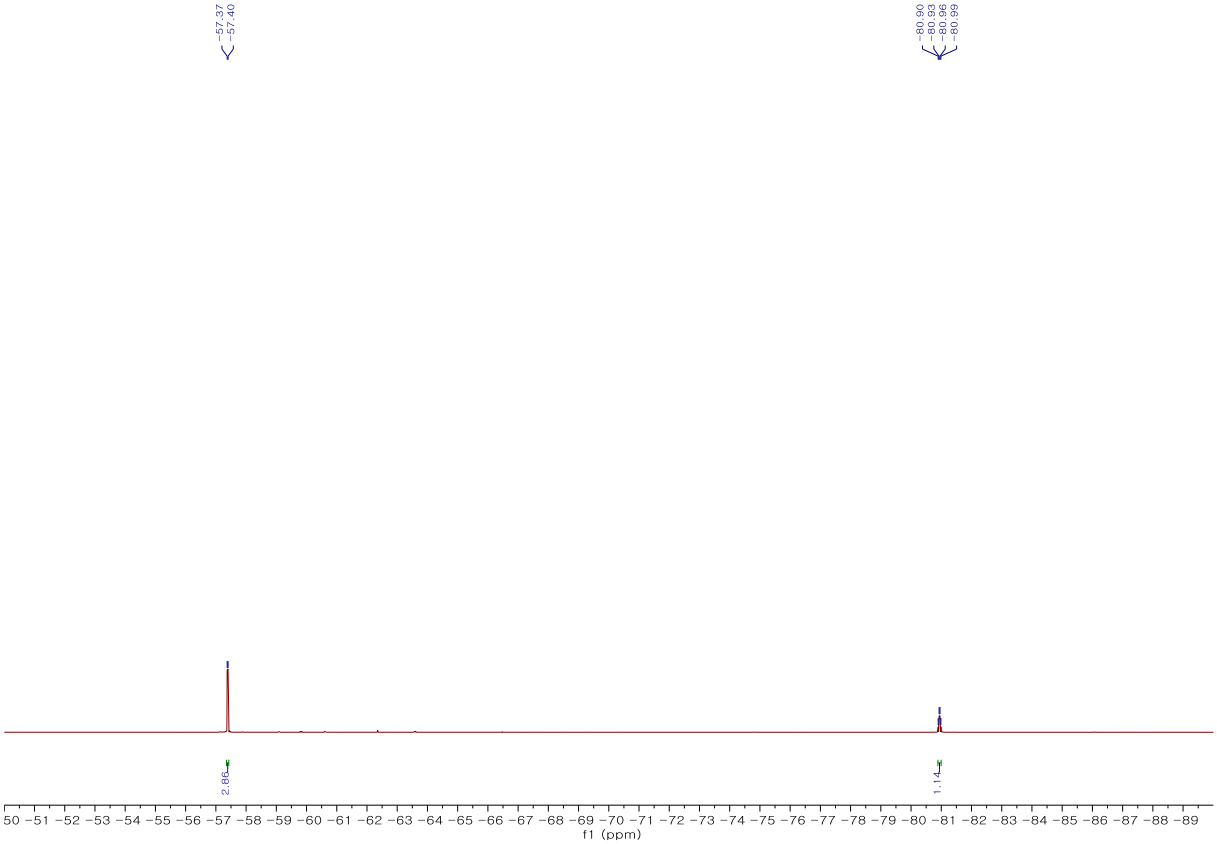
(*E*)-4-methyl-*N*-(4-(1,3,3,3-tetrafluoro-2-(hydroxymethyl)prop-1-en-1-yl)phenyl)benzenesulfonamide (5e)



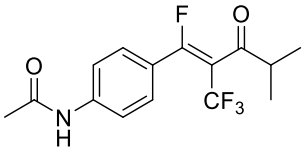
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.34 (s, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.14 (s, 2H), 4.50 (t, *J* = 4.6 Hz, 2H), 2.39 (s, 3H), 1.92 (t, *J* = 6.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.67 (dq, *J* = 264.3, 4.4 Hz), 144.62, 139.63 (d, *J* = 2.2 Hz), 135.90, 130.23 (dq, *J* = 4.2, 1.7 Hz), 130.01, 127.37, 126.15 (d, *J* = 27.5 Hz), 124.14 (qd, *J* =272.7, 17.0 Hz), 119.49, 112.44–111.84 (m, *J* = 30.5 Hz), 55.65 (dd, *J* = 8.1, 2.2 Hz), 21.70. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.39 (d, *J* = 10.9 Hz), -80.94 (q, *J* = 11.0 Hz). **IR (neat)** 3745, 3481, 3257, 3052m 2967, 2925, 2855, 2527, 2313, 1918, 1681, 1610, 1514, 1463, 1402, 1342, 1302, 1234, 1186, 1159, 1113, 1092, 1040, 976, 917, 840, 814, 748, 704, 662, 611, 573, 544, 424 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{17}H_{15}F_4NO_3S$ [M]$^+$ 389.0711, found 389.0709. **M.P.** 288.2 ℃. **Appearance** White solid. **Amount** 50 mg. **Yield** 64%.



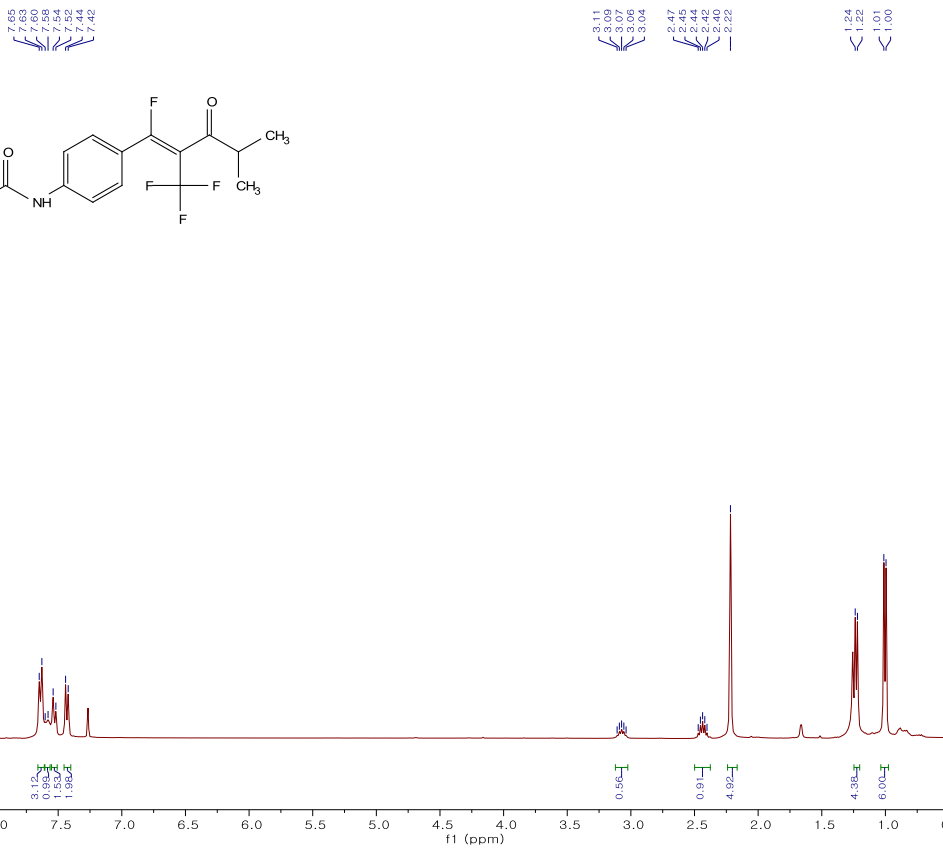

164.85
164.81
164.77
164.72
162.23
162.18
162.14
162.10
144.62
139.64
139.62
135.90
130.27
130.26
130.22
130.19
130.17
130.01
128.28
128.11
127.37
126.29
126.02
125.57
125.40
122.87
122.70
120.17
119.97
119.49
112.42
112.14
111.84
55.70
55.68
55.62
55.60
21.70
f1 (ppm)

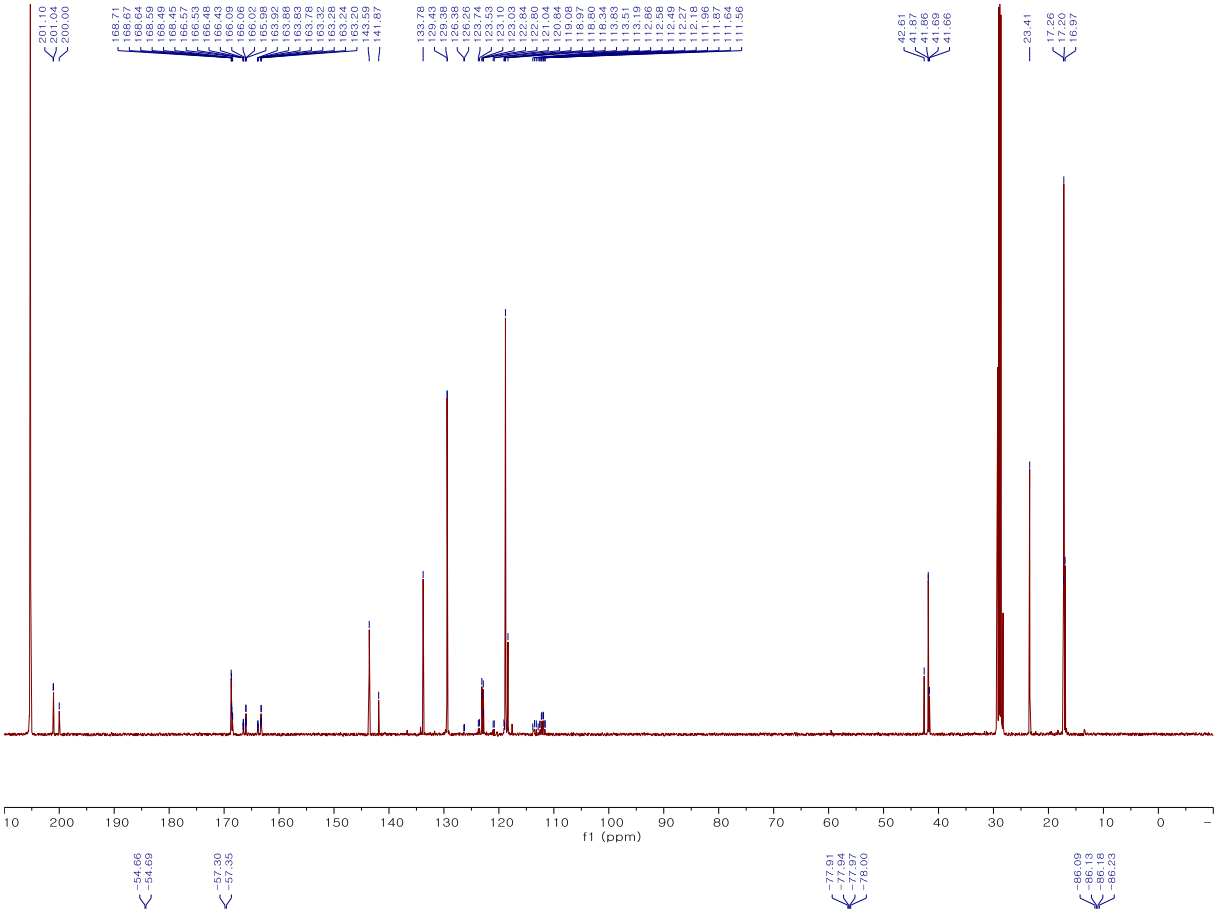

-57.37
-57.40
-80.90
-80.93
-80.96
-80.99
2.86
1.14
f1 (ppm)

(*E*)-*N*-(4-(1-fluoro-4-methyl-3-oxo-2-(trifluoromethyl)pent-1-en-1-yl)phenyl)acetamide (5f)

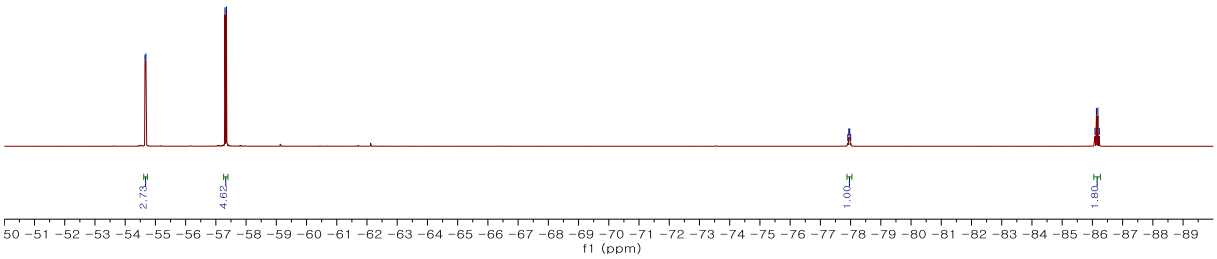


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 4H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.47–7.42 (m, 2H), 3.14–3.04 (m, 1H), 2.49–2.41 (m, 1H), 2.23 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 201.07 (d, *J* = 6.1 Hz), 200.00, 168.69 (d, *J* = 4.0 Hz), 168.54 (dd, *J* = 14.5, 4.3 Hz), 165.18 (dq, *J* = 279.4, 4.8 Hz), 164.65 (dq, *J* = 279.4, 3.9 Hz), 143.59, 141.87, 133.78, 129.41 (d, *J* = 5.4 Hz), 123.20–122.74 (m), 121.19 (dq, *J* = 271.4, 20.6 Hz), 118.80, 118.34, 113.35 (q, *J* = 32.5 Hz), 112.07 (qd, *J* = 31.3, 8.2 Hz), 42.61, 41.98–41.80 (m), 41.67 (d, *J* = 3.0 Hz), 23.41, 17.26, 17.20, 16.97. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -54.67 (d, *J* = 11.9 Hz), -57.32 (d, *J* = 18.2 Hz), -77.93 (q, *J* = 12.0 Hz), -86.13 (q, *J* = 18.0 Hz). **IR (neat)** 3372, 3308, 3183, 3105, 3049, 2972, 2927, 2872, 2791, 2557, 2282, 2189, 1921, 1703, 1667, 1651, 1593, 1532, 1465, 1407, 1371, 1323, 1260, 1160, 1134, 1096, 1054, 1017, 964, 930, 849, 832, 755, 718, 692, 655, 626, 595, 543, 522, 464 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{15}H_{15}F_4NO_2$ $[M]^+$ 317.1021, found 317.1039. **M.P.** 187.3 ℃. **Appearance** Yellow solid. **Amount** 59 mg. **Yield** 70%. (*E*/*Z*=1:1.8)

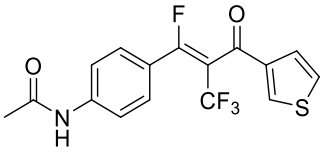



201.10
200.04
200.00
168.71
168.67
168.64
168.59
168.49
168.45
166.57
166.53
166.48
166.43
166.09
166.06
166.02
163.88
163.83
163.78
163.32
163.28
163.24
163.20
143.59
141.87
133.78
129.43
128.38
126.26
123.74
123.53
123.10
123.03
122.84
122.80
121.04
120.84
120.08
118.97
118.80
118.34
113.63
113.31
113.19
112.86
112.58
112.49
112.27
112.18
111.96
111.87
111.64
111.56
42.61
41.87
41.86
41.69
41.66
23.41
17.26
17.20
16.97
f1 (ppm)

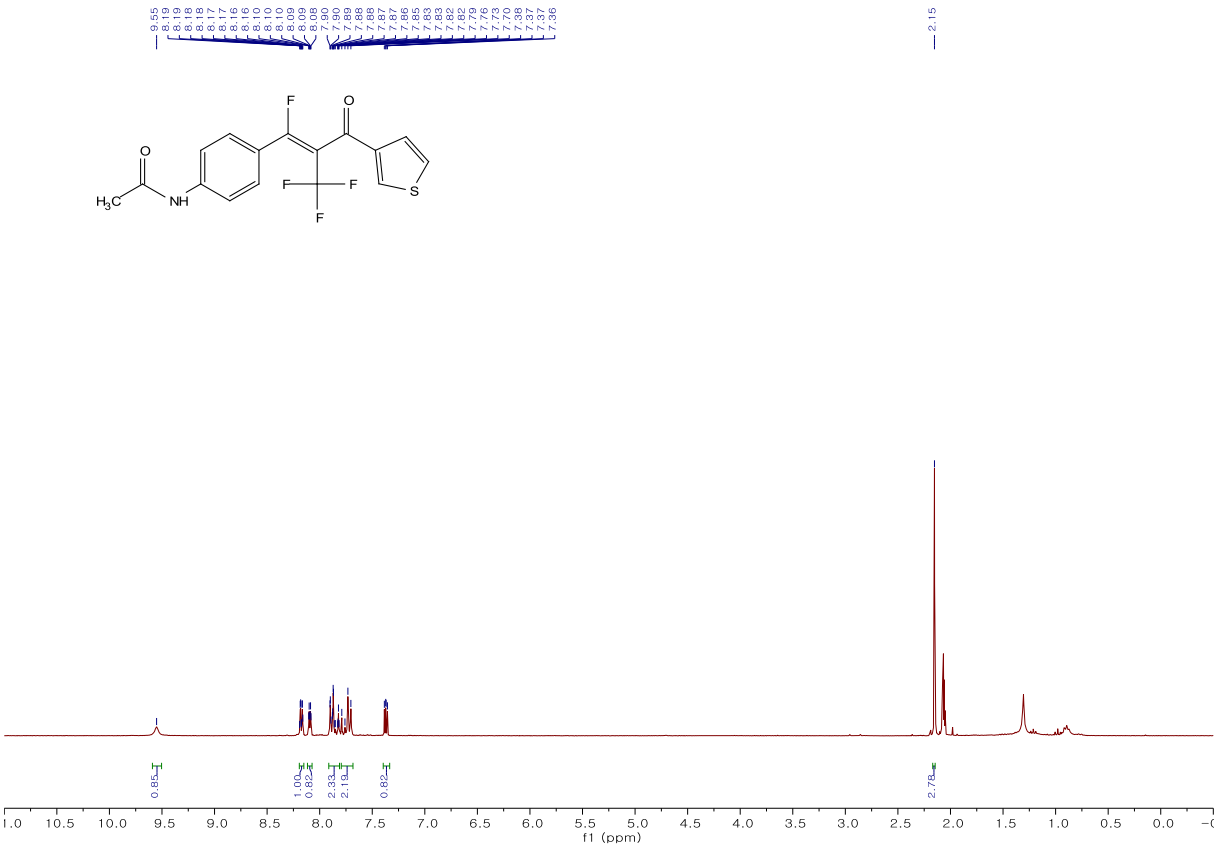
-54.66
-54.69
-57.30
-57.35
-77.91
-77.94
-77.97
-78.00
-86.09
-86.13
-86.18
-86.23

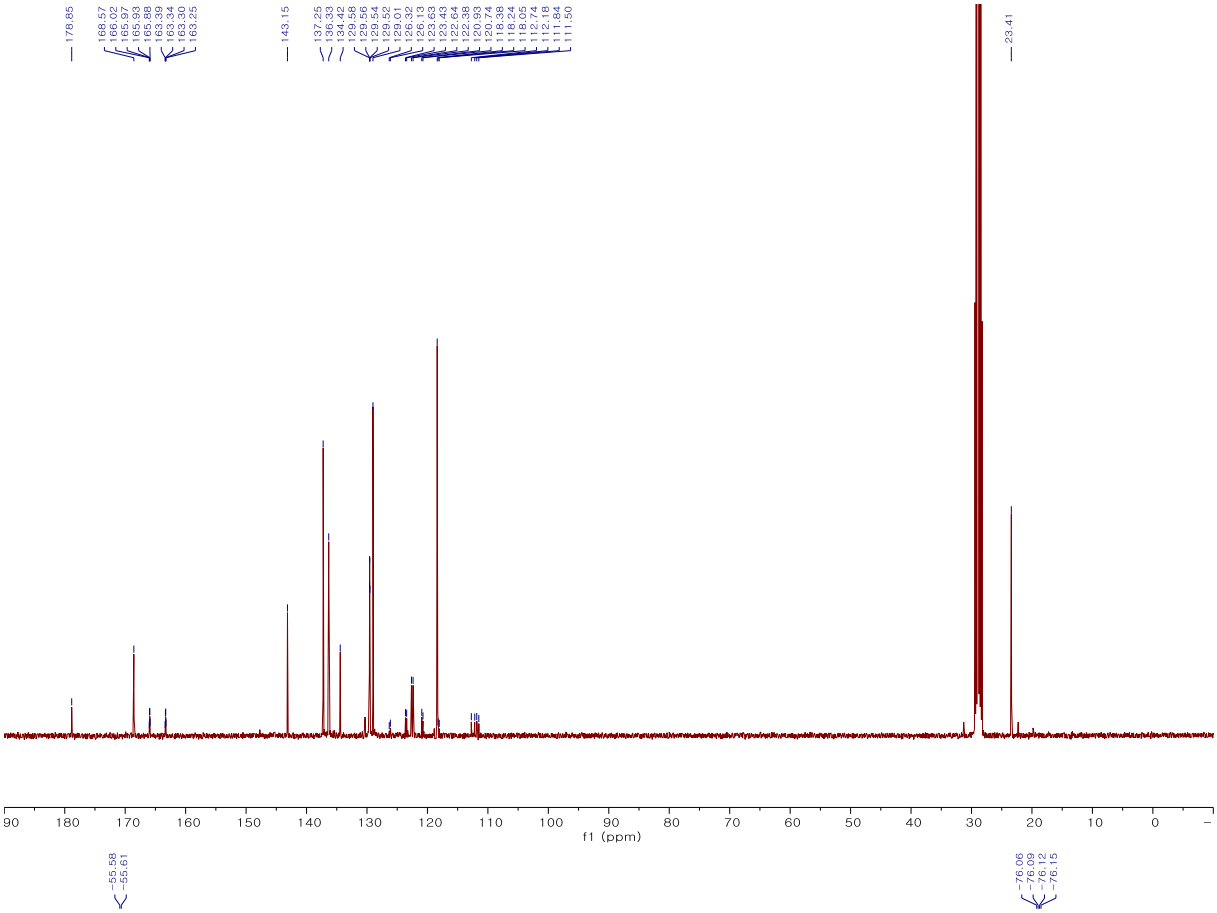

2.73
4.62
1.00
1.80
f1 (ppm)

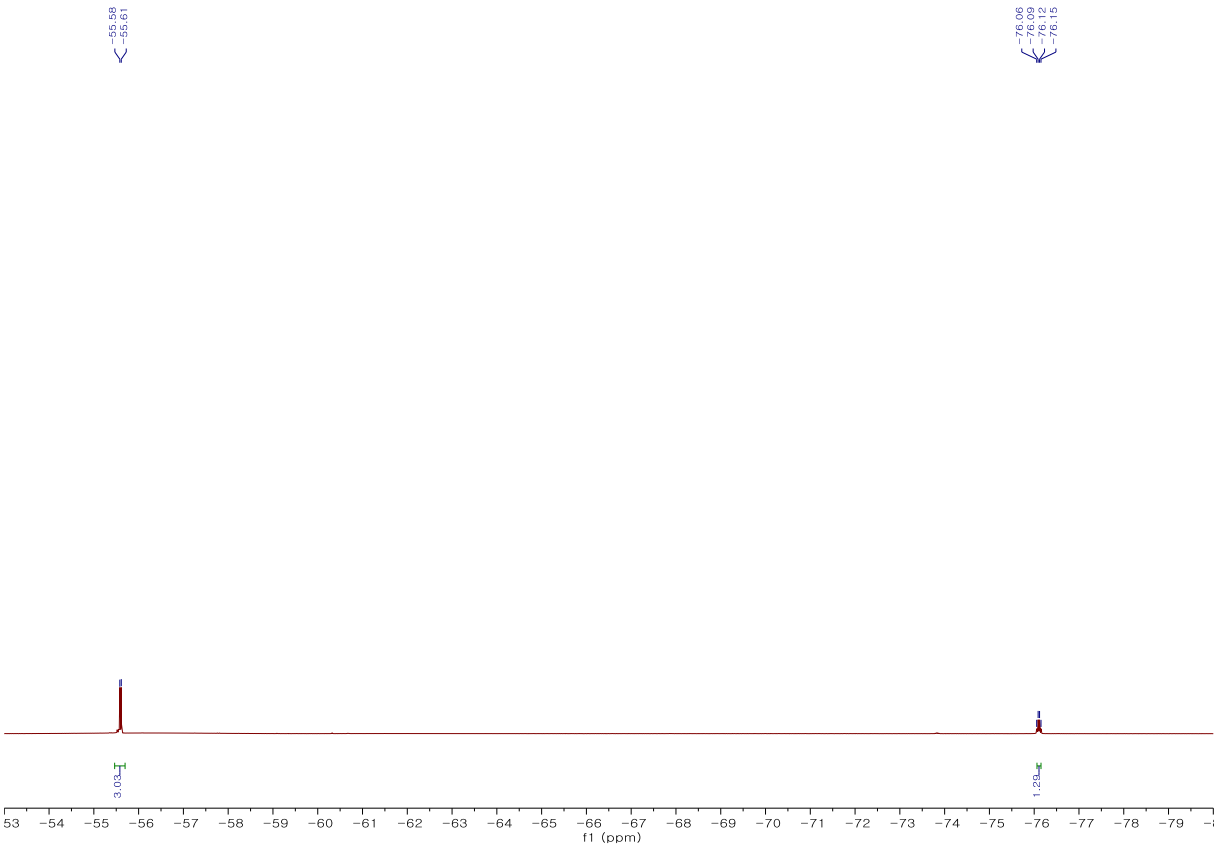
(*E*)-*N*-(4-(1,3,3,3-tetrafluoro-2-(thiophene-3-carbonyl)prop-1-en-1-yl)phenyl)acetamide (5g)



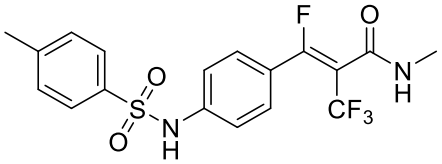
^{1}H NMR (300 MHz, Acetone-d_6) δ 9.55 (s, 1H), 8.19–8.15 (m, 1H), 8.09 (dt, *J* = 3.9, 1.2 Hz, 1H), 7.91–7.81 (m, 2H), 7.75 (dd, *J* = 17.2, 8.7 Hz, 2H), 7.37 (dd, *J* = 5.0, 3.9 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 178.85 (C=O), 168.57 (C=O), 164.63 (dq, *J* = 264.5, 4.6 Hz), 143.15, 137.25, 136.33, 134.42, 129.55 (dd, *J* = 4.6, 2.1 Hz), 129.01, 122.51 (d, *J* = 26.9 Hz), 122.18 (qd, *J* = 270.8, 19.4 Hz), 118.38, 113.73–110.62 (m), 23.41. **^{19}F NMR** (376 MHz, Acetone-d_6) δ -55.60 (d, *J* = 12.3 Hz), -76.10 (q, *J* = 12.1 Hz). **IR (neat)** 3312, 3185, 3098, 2926, 2854, 2192, 1671, 1595, 1524, 1409, 1360, 1324, 1283, 1262, 1180, 1125, 1056, 1011, 966, 914, 837, 793, 727, 686, 646, 595, 573, 537, 511 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{16}H_{11}F_4NO_2S$ $[M]^+$ 357.0451, found 357.0447. **M.P.** 189.7 ℃. **Appearance** Light yellow solid. **Amount** 21 mg. **Yield** 23%.



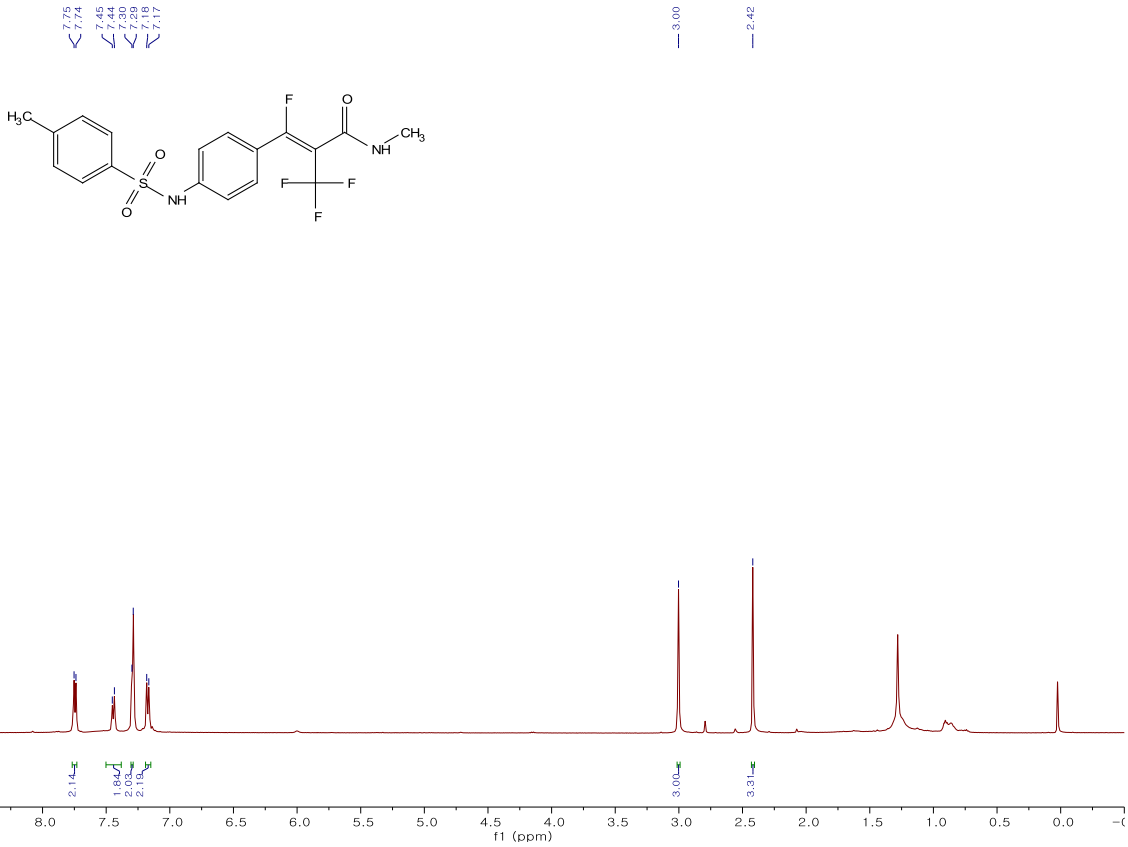

178.85
168.57
166.02
165.97
165.93
165.88
163.39
163.34
163.30
163.25
143.15
137.25
136.33
134.42
129.58
129.56
128.64
128.52
128.01
126.32
126.13
123.63
123.43
122.64
122.38
120.93
120.74
118.48
118.24
118.05
112.74
112.18
111.84
111.50
23.41
f1 (ppm)

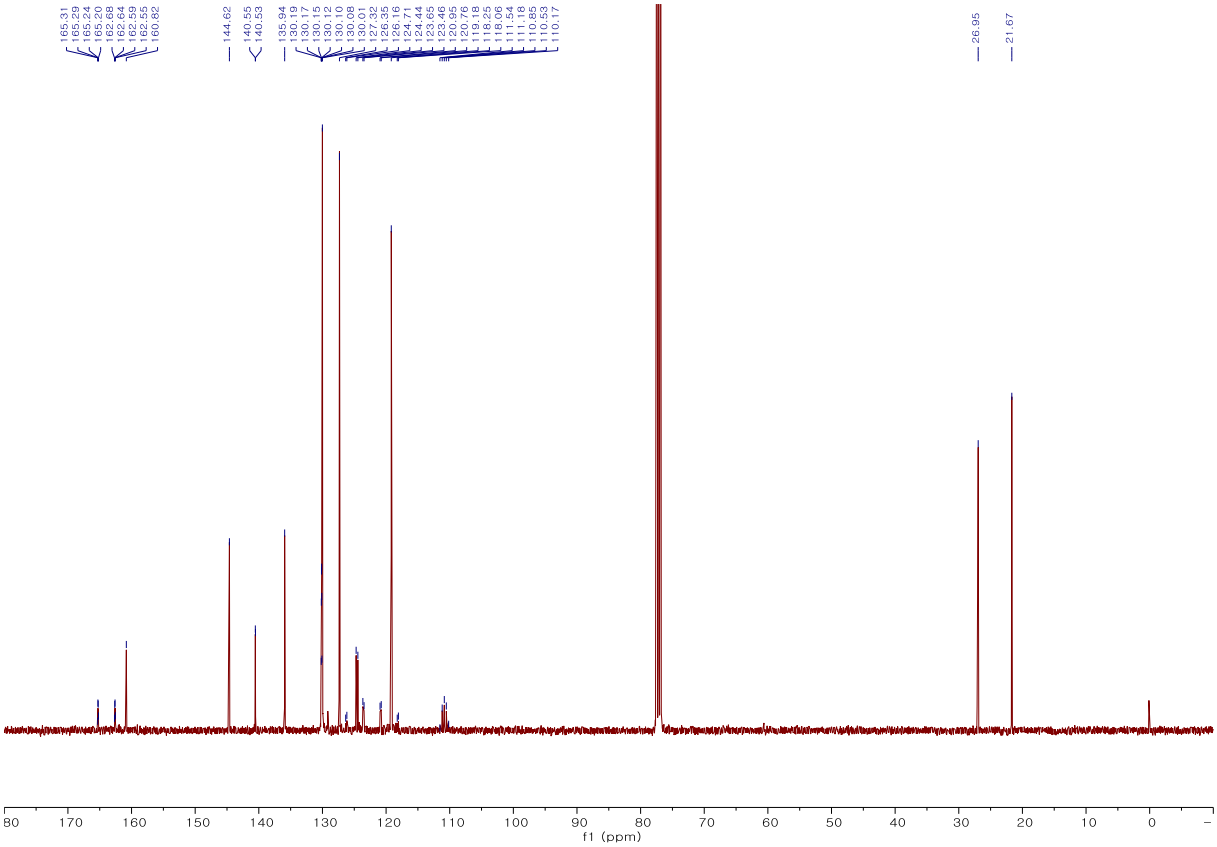

-55.58
-55.61
-76.06
-76.09
-76.12
-76.15
3.03
1.28
f1 (ppm)

(*E*)-3-fluoro-*N*-methyl-3-(4-(4-methylphenylsulfonamido)phenyl)-2-(trifluoromethyl)acrylamide (5h)



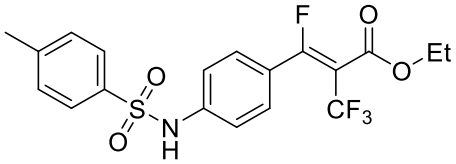
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.00 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.66 (dq, *J* = 267.65, 4.4 Hz), 160.82 (C=O), 144.62, 140.54 (d, *J* = 2.1 Hz), 135.94, 130.14 (dd, *J* = 4.8, 2.3 Hz), 130.01, 127.32, 124.57 (d, *J* = 27.3 Hz), 122.20 (qd, *J* = 271.7, 18.5 Hz), 119.18, 111.54–110.17 (m, *J* = 31.7 Hz), 26.95, 21.67. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -55.75 (d, *J* = 11.1 Hz), -77.36 (q, *J* = 11.0 Hz). **IR (neat)** 3371, 3270, 2925, 2855, 1661, 1609, 1549, 1513, 1463, 1408, 1341, 1301, 1236, 1186, 1160, 1120, 1091, 1047, 1018, 965, 918, 842, 814, 710, 663, 616, 572, 454 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{18}H_{16}F_4N_2O_3S$ $[M]^+$ 416.0821, found 416.0818. **M.P.** >300 ℃. **Appearance** White solid. **Amount** 51 mg. **Yield** 62%.



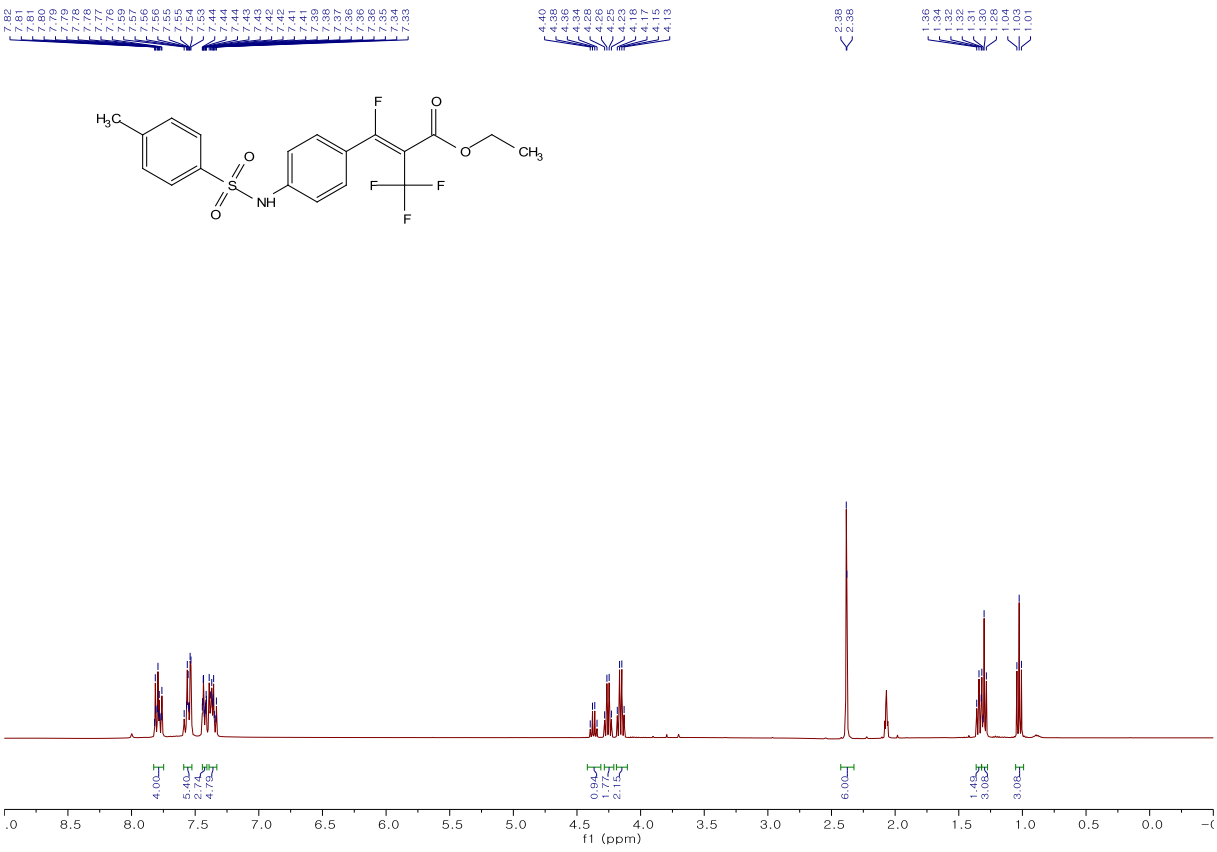

165.31
165.29
165.24
165.20
162.68
162.64
162.59
162.55
160.82
144.62
140.55
140.53
135.94
130.19
130.17
130.15
130.12
130.10
130.08
130.01
127.22
126.35
126.16
124.71
124.44
123.65
123.46
120.95
120.76
119.18
118.95
118.05
111.54
111.18
110.85
110.53
110.17
26.95
21.67
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

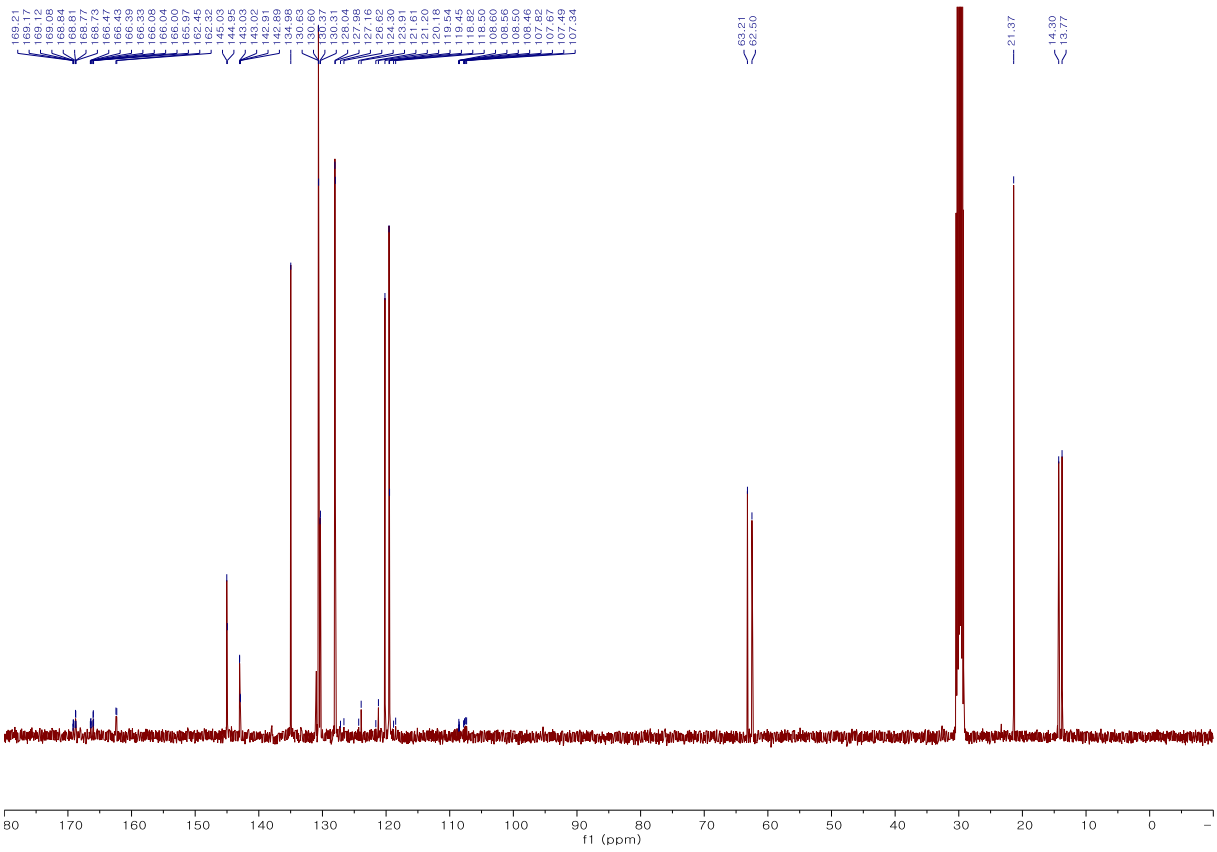

55.74
55.77
77.32
77.35
77.38
77.41
3.00
1.28
53 −54 −55 −56 −57 −58 −59 −60 −61 −62 −63 −64 −65 −66 −67 −68 −69 −70 −71 −72 −73 −74 −75 −76 −77 −78 −79 −80 −81
f1 (ppm)

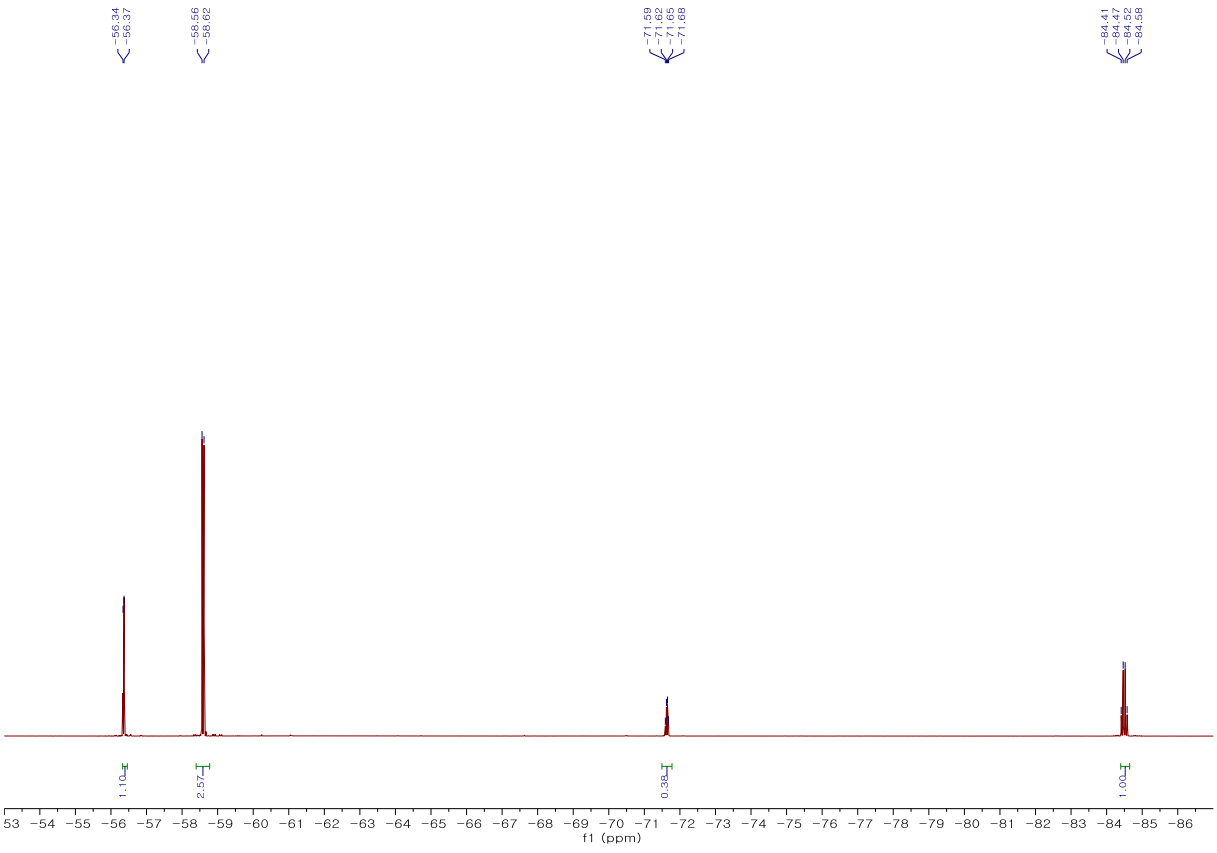
(*E*)-ethyl 3-fluoro-3-(4-(4-methylphenylsulfonamido)phenyl)-2-(trifluoromethyl)acrylate (5i)



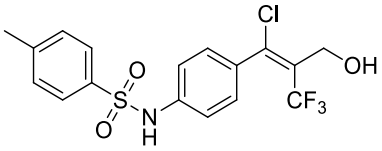
^{1}H NMR (400 MHz, Acetone-*d6*) δ 7.82–7.76 (m, 4H), 7.59–7.53 (m, 5H), 7.45–7.40 (m, 3H), 7.39–7.32 (m, 5H), 4.37 (q, J = 7.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 2.38 (d, J = 1.8 Hz, 6H), 1.34 (t, J = 7.1 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 167.57 (dq, *J* = 276.9, 4.6 Hz), 167.40 (dq, *J* = 278.3, 3.4 Hz) 162.45 (C=O), 162.32 (C=O), 143.02 (d, *J* = 1.1 Hz), 142.9 (d, *J* = 2.0 Hz), 135.01, 134.94 (m), 130.63, 130.60, 130.37, 130.31, 128.04, 127.98, 122.98 (q, *J* = 287.8 Hz), 122.56 (q, *J* = 272.6 Hz), 120.18, 119.54, 119.45, 108.60–108.46 (m), 107.82–107.34 (m), 63.21, 62.50, 21.37, 14.30, 13.77. **^{19}F NMR** (376 MHz, Acetone-*d6*) δ -56.35 (d, J = 11.0 Hz), -58.56, -71.64 (q, J = 11.2 Hz), -84.49 (q, J = 20.8 Hz). **IR (neat)** 3437, 3260, 2924, 2854, 2210, 1915, 1732, 1706, 165, 1605, 1510, 1460, 1376, 1341, 1304, 1161, 1134, 1090, 913, 844, 813, 703, 665, 573, 546 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{19}H_{17}F_4NO_4S$ $[M]^+$ 431.0822, found 431.0814. **M.P.** >300 ℃. **Appearance** White solid. **Amount** 45 mg. **Yield** 70%. (*E*/*Z*=1:2.5)



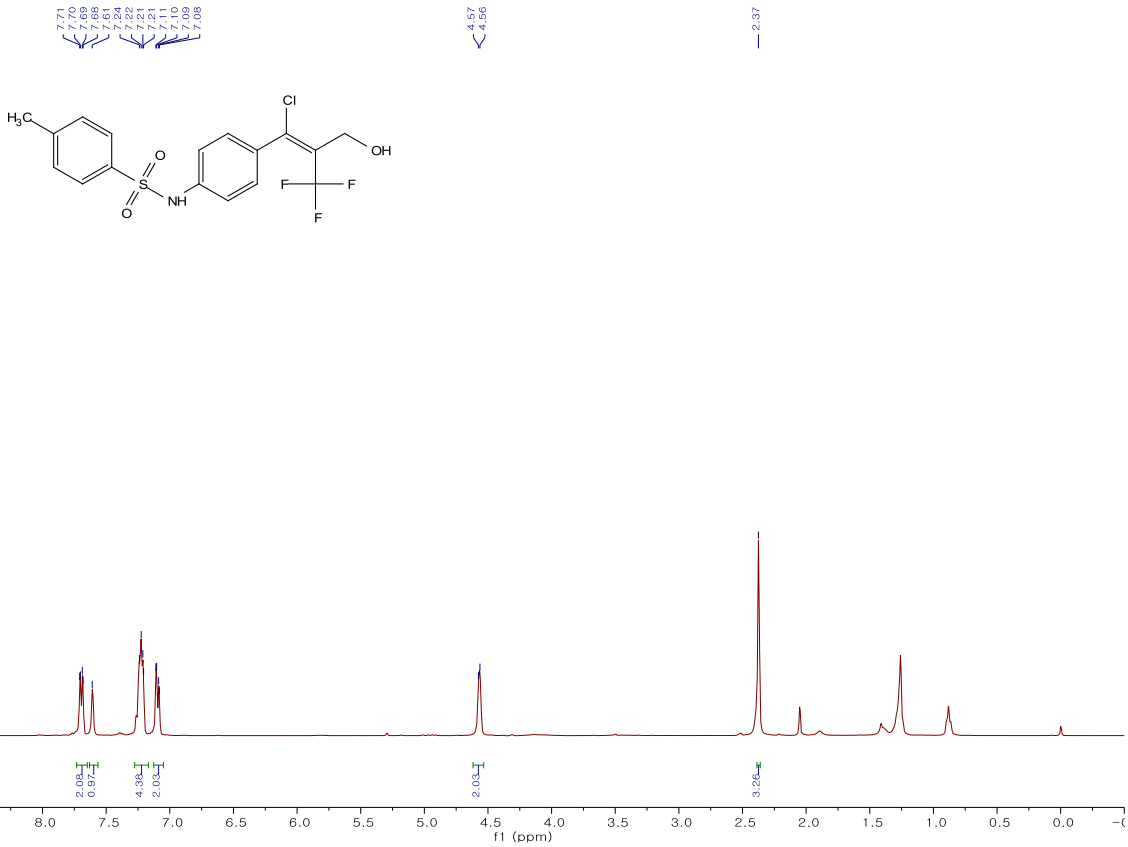

169.21
169.17
169.12
169.08
168.84
168.81
168.77
168.73
168.47
166.43
166.39
166.33
166.08
166.04
166.00
165.97
162.45
162.32
145.03
144.95
143.03
143.02
142.91
142.89
134.98
130.63
130.60
130.37
130.31
130.04
127.98
127.16
126.62
124.30
123.91
121.61
121.20
120.16
119.54
119.45
118.82
118.50
108.60
108.56
108.50
108.46
107.82
107.67
107.49
107.34
63.21
62.50
21.37
14.30
13.77
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

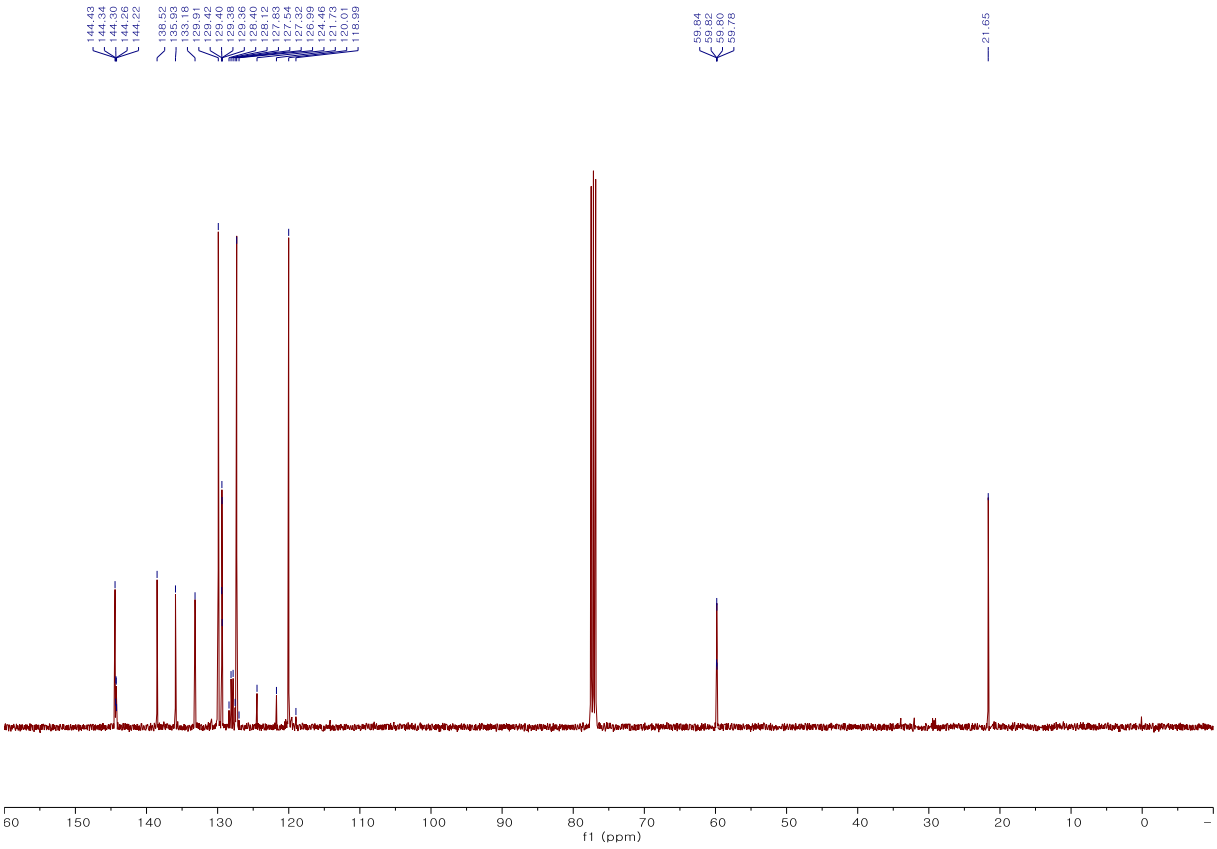

-56.34
-56.37
-58.56
-58.62
-71.59
-71.62
-71.65
-71.68
-84.41
-84.47
-84.52
-84.58
1.10
2.57
0.38
1.00
53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
-80
-81
-82
-83
-84
-85
-86
f1 (ppm)

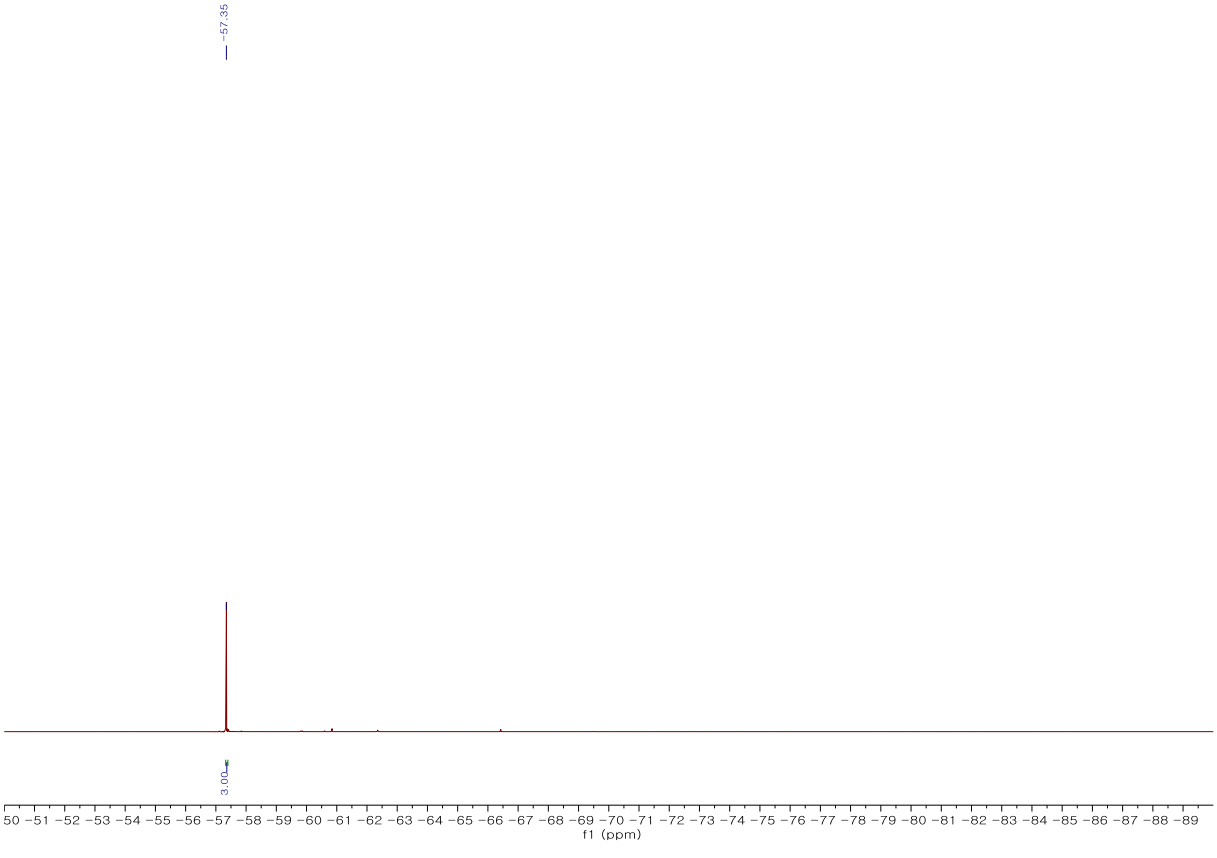
(*E*)-*N*-(4-(1-chloro-3,3,3-trifluoro-2-(hydroxymethyl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (6a)



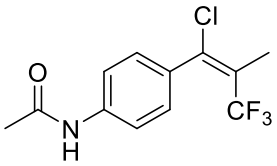
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.61 (s, 1H), 7.24–7.21 (m, 4H), 7.10 (dd, *J* = 8.7, 2.4 Hz, 2H), 4.57 (d, *J* = 4.8 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.43, 144.28 (q, *J* = 4.2 Hz), 138.52, 135.93, 133.18, 129.91, 129.39 (q, *J* = 1.9 Hz), 127.97 (q, *J* = 28.8 Hz), 127.32, 121.73 (q, *J* = 275.7 Hz), 118.99, 59.81 (q, *J* = 1.9 Hz), 21.65. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.35. **IR (neat)** 3478, 3257, 3049, 2924, 2855, 1916, 1643, 1607, 1509, 1462, 1399, 1326, 1233, 1160, 1126, 1090, 1018, 979, 919, 898, 841, 808, 665, 590, 567, 544, 430 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{17}H_{15}ClF_3NO_3S$ $[M]^+$ 405.0409, found 405.0413. **M.P.** 80.4 ℃. **Appearance** Yellow solid. **Amount** 61 mg. **Yield** 75%.



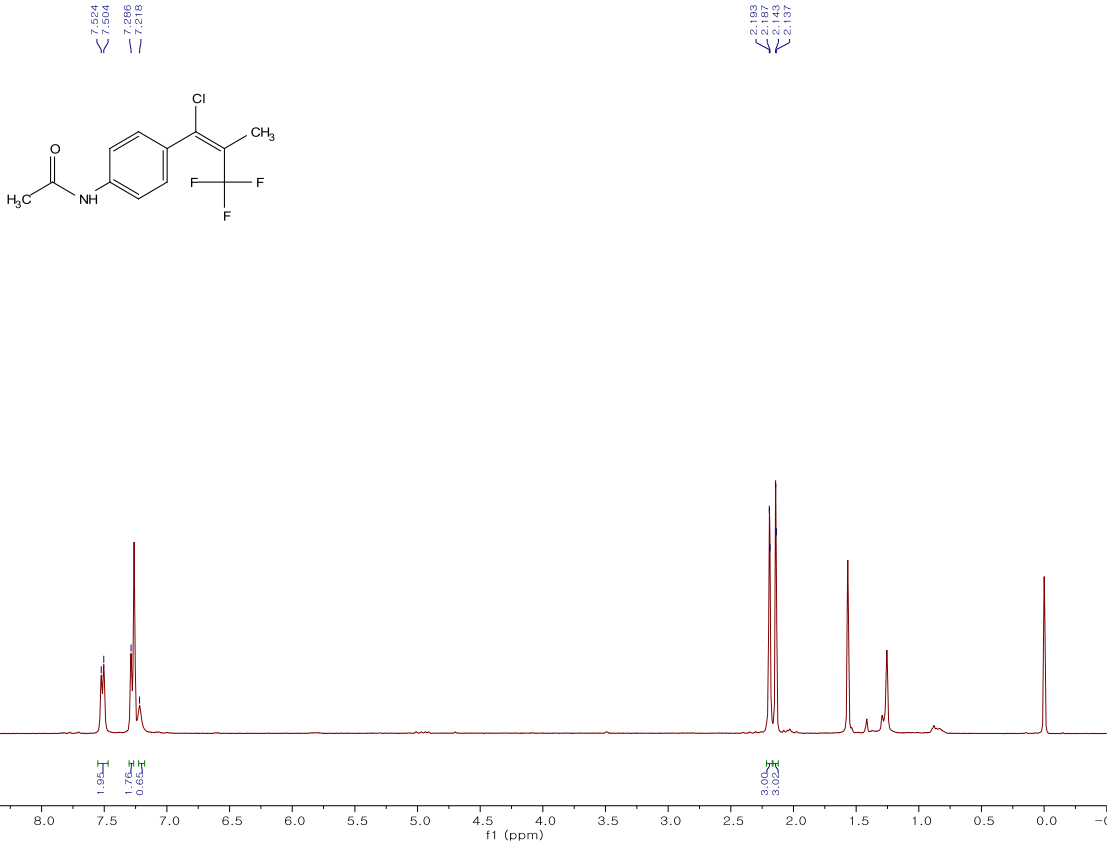

144.43
144.34
144.30
144.25
144.22
138.52
135.93
133.18
129.91
129.42
129.40
129.38
129.36
128.40
128.12
127.83
127.54
127.32
126.99
124.46
121.73
120.01
118.99
59.84
59.82
59.80
59.78
21.65
f1 (ppm)

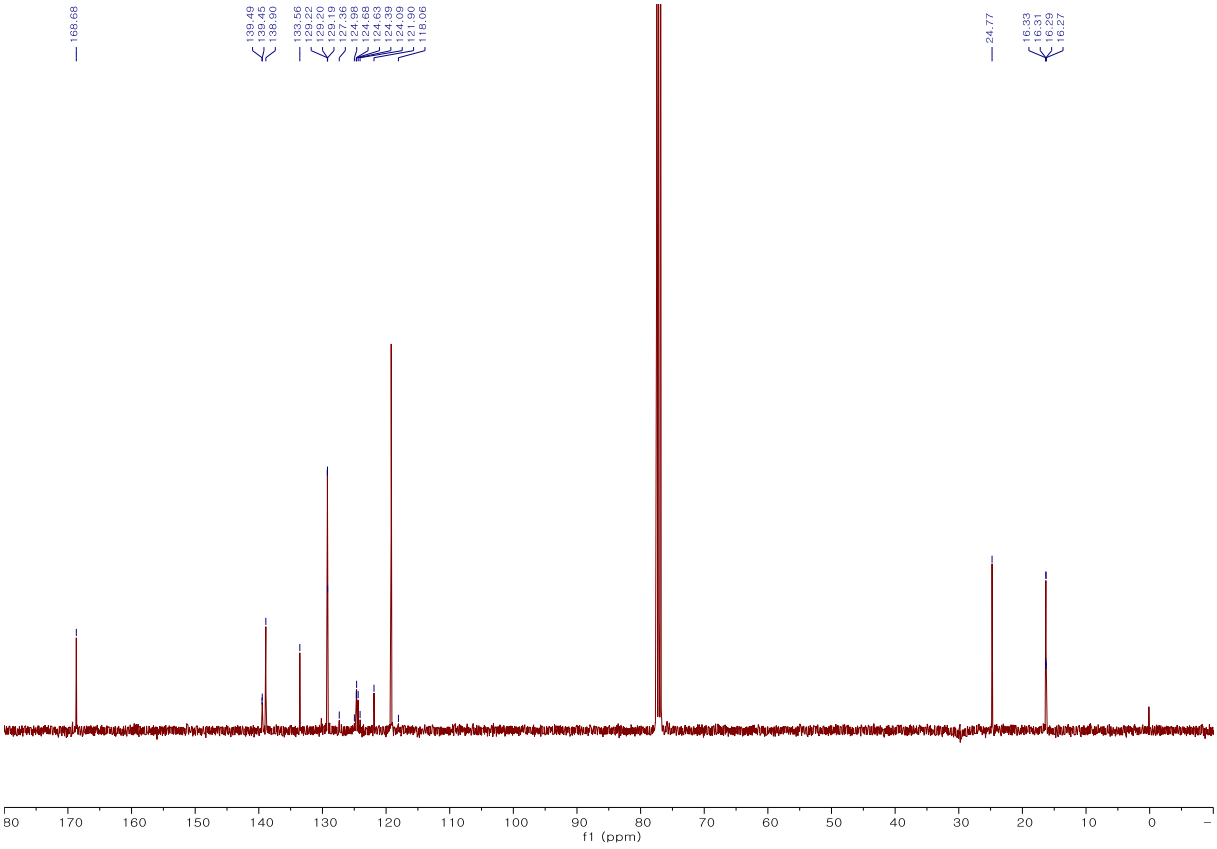

-57.35
3.00
f1 (ppm)

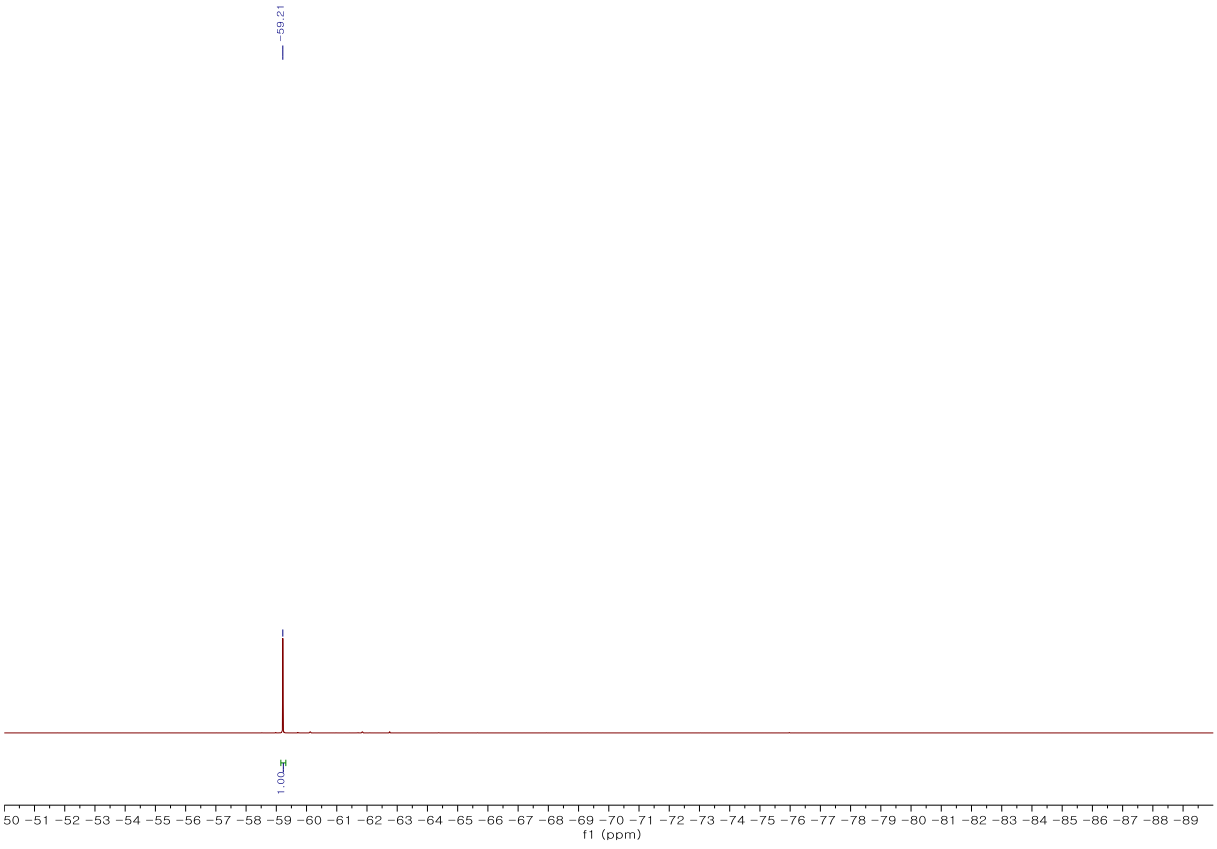
(*E*)-*N*-(4-(1-chloro-3,3,3-trifluoro-2-methylprop-1-en-1-yl)phenyl)acetamide (6b)



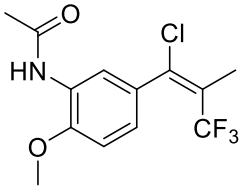
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.22 (s, 1H), 2.19 (d, *J* = 2.4 Hz, 3H), 2.14 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.68 (C=O), 139.47 (d, *J* = 4.0 Hz), 138.90, 133.56, 129.38-128.83 (m), 124.53 (q, *J* = 31.4 Hz), 123.27 (q, *J* = 274.4), 119.19, 24.77, 16.30 (q, *J* = 2.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-d) δ -59.21. IR (neat) 3296, 3257, 3185, 3113, 3056, 2927, 2855, 1909, 1672, 1606, 1545, 1440, 1402, 1319, 1262, 1177, 1111, 1015, 968, 898, 842, 802, 749, 693, 661, 600, 540, 457, 412 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{12}H_{11}ClF_3NO$ $[M]^+$ 277.0475, found 277.0481. **M.P.** 180.1 ℃. **Appearance** White solid. **Amount** 31 mg. **Yield** 57%.



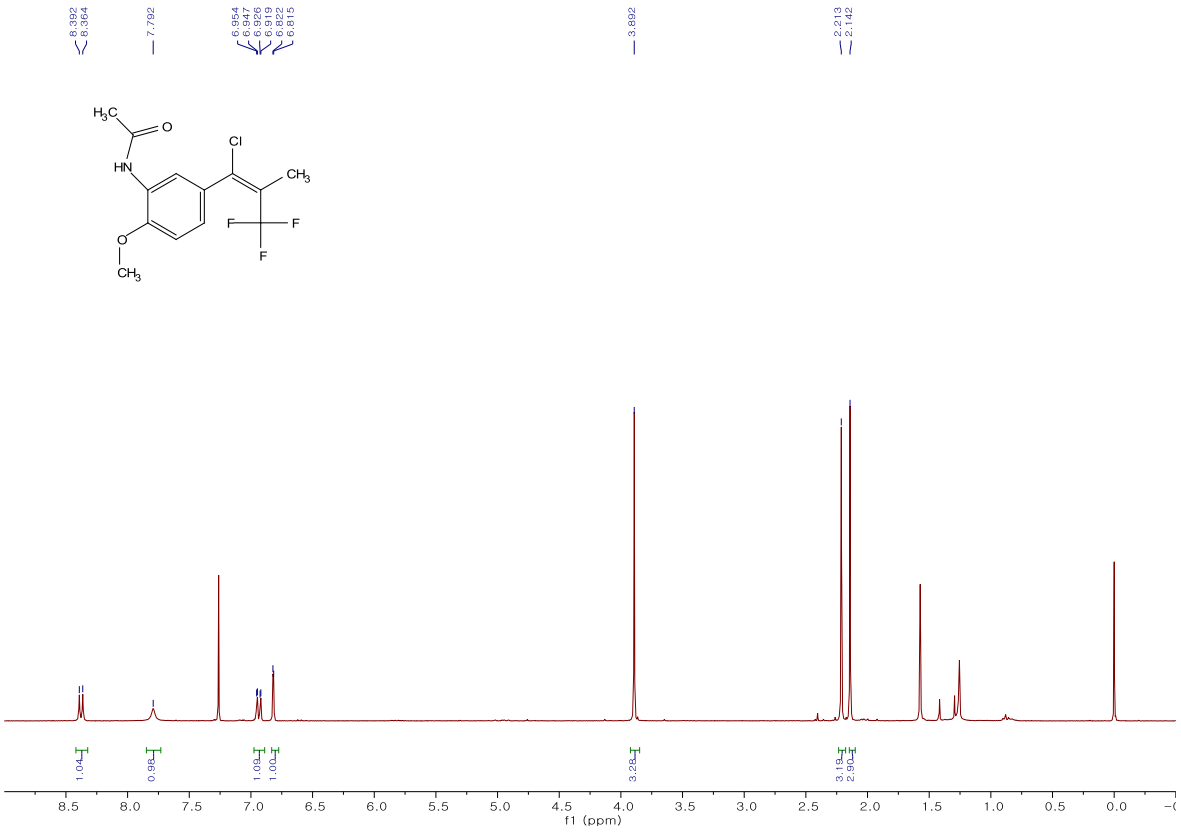

168.68
139.49
139.45
138.90
133.56
129.22
129.20
127.19
127.36
124.98
124.68
124.63
124.49
124.09
121.90
118.06
24.77
16.33
16.31
16.29
16.27
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

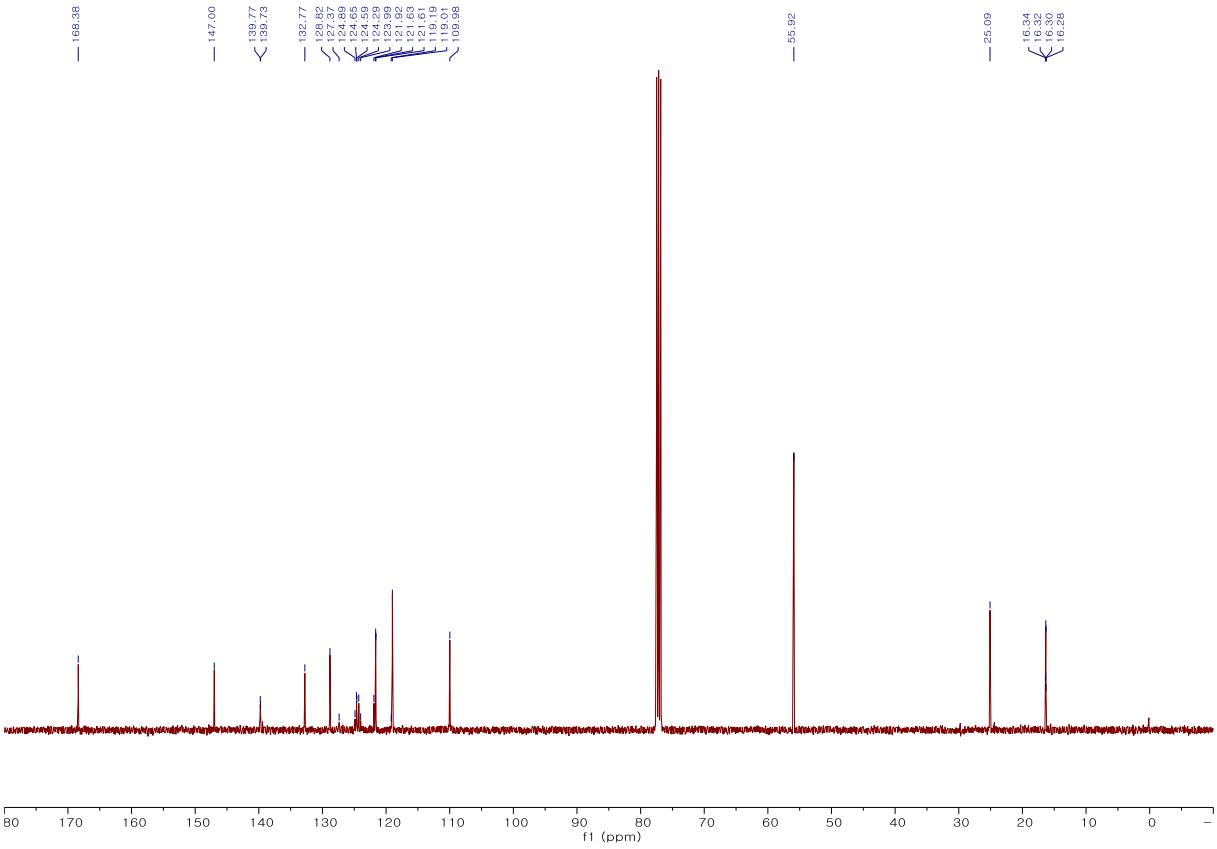

-59.21
1.00
50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87 -88 -89
f1 (ppm)

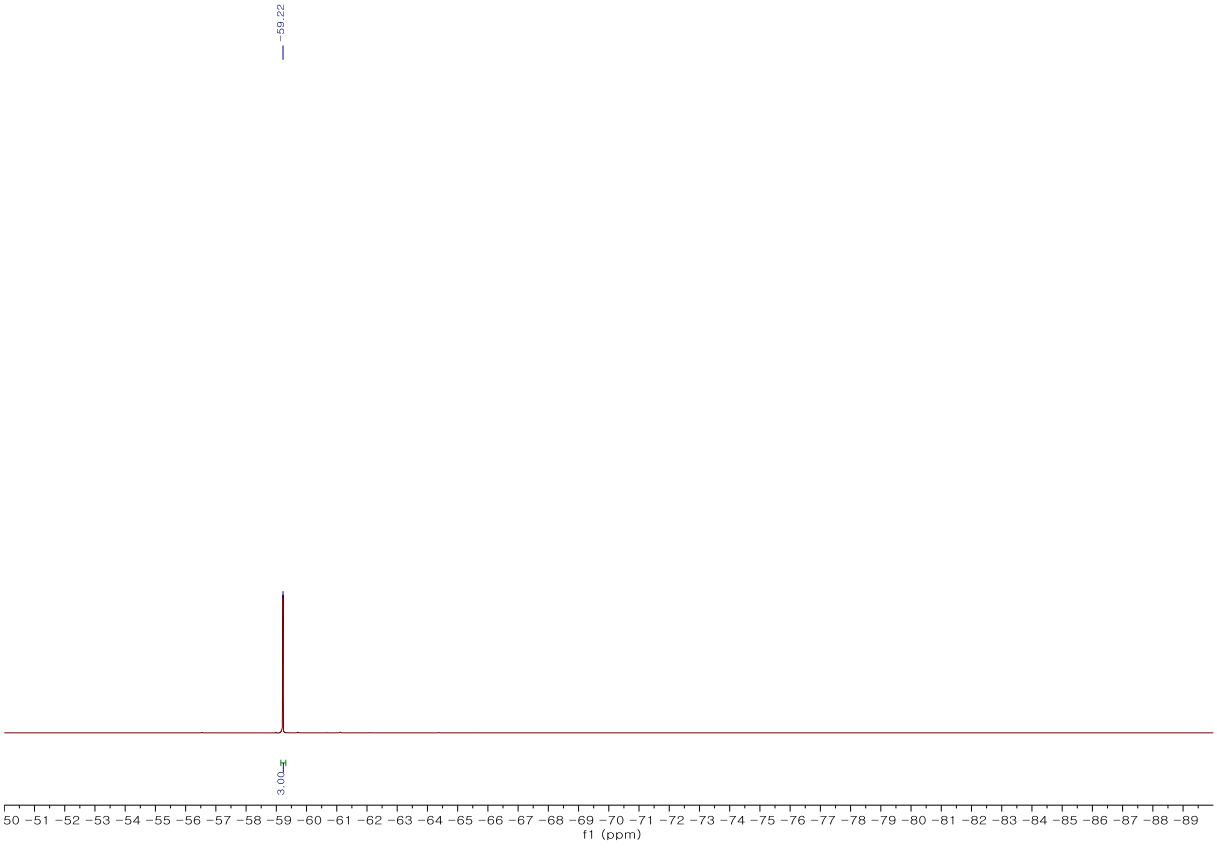
(*E*)-*N*-(5-(1-chloro-3,3,3-trifluoro-2-methylprop-1-en-1-yl)-2-methoxyphenyl)acetamide (6c)



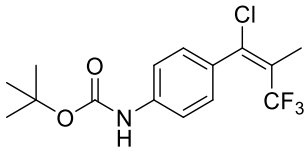
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.79 (s, 1H), 6.94 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 3.89 (s, 3H), 2.21 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.38 (C=O), 147.00, 139.75 (d, *J* = 4.6 Hz), 132.77, 128.82, 124.44 (q, *J* = 30.1 Hz), 123.28 (q, *J* = 275.7 Hz), 121.62 (d, *J* = 2.4 Hz), 119.01, 109.98, 55.92, 25.09, 16.31 (q, *J* = 2.1 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.22. **IR (neat)** 3342, 3010, 2926, 2856, 1668, 1602, 1534, 1494, 1465, 1409, 1314, 1283, 1260, 1200, 1180, 1166, 1103, 1031, 966, 861, 805, 671, 587, 535 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{13}H_{13}ClF_3NO_2$ $[M]^+$ 307.0589, found 307.0587. **M.P.** 121.6 ℃. **Appearance** White solid. **Amount** 26 mg. **Yield** 43%.



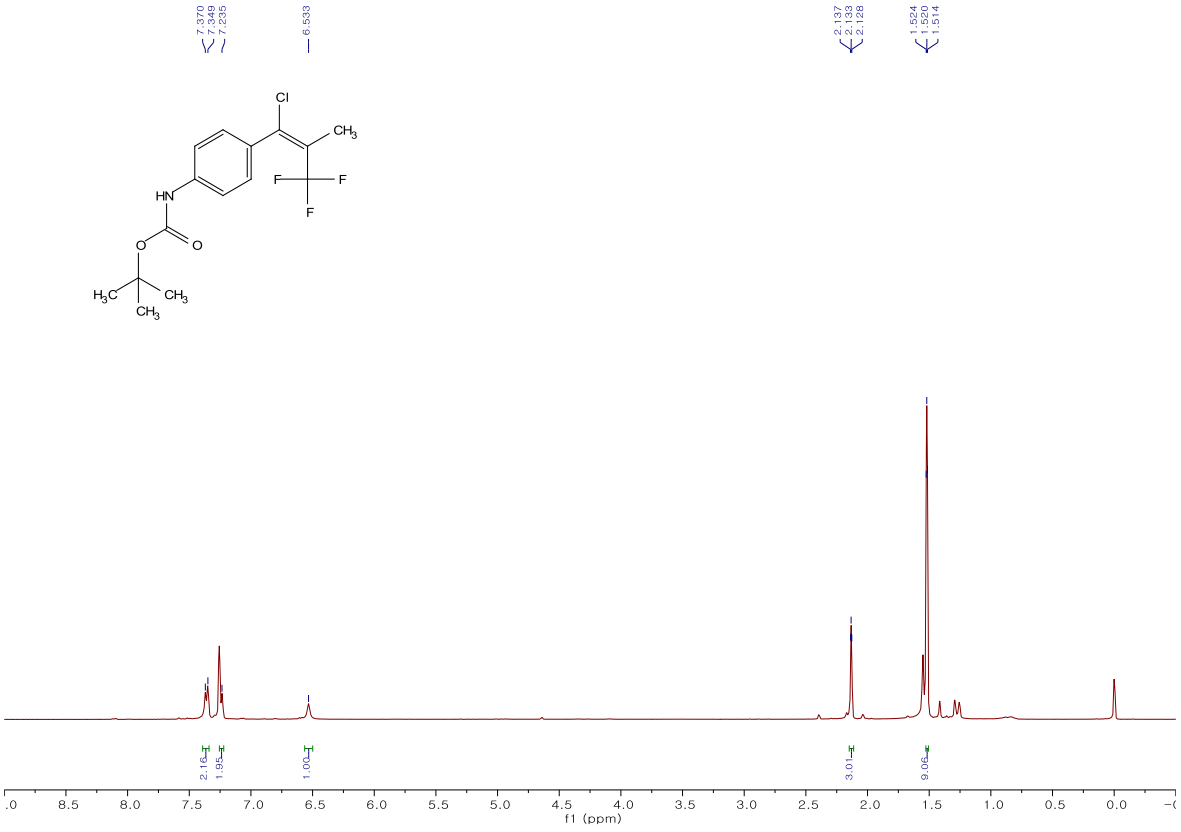

168.38
147.00
139.77
139.73
132.77
128.82
127.37
124.89
124.65
124.59
124.49
123.89
121.92
121.63
121.61
119.19
115.01
109.98
55.92
25.09
16.34
16.32
16.30
16.28
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 –
f1 (ppm)

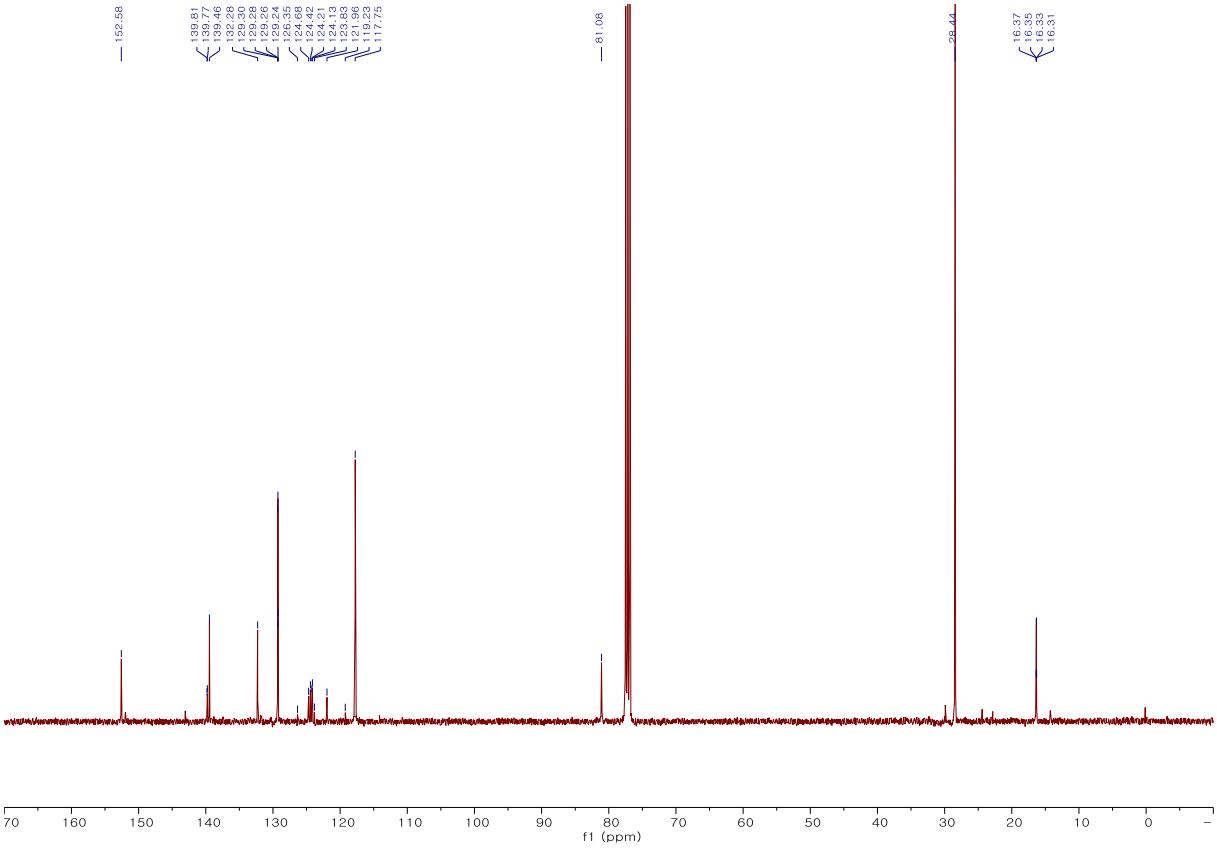

-59.22
3.00
50 –51 –52 –53 –54 –55 –56 –57 –58 –59 –60 –61 –62 –63 –64 –65 –66 –67 –68 –69 –70 –71 –72 –73 –74 –75 –76 –77 –78 –79 –80 –81 –82 –83 –84 –85 –86 –87 –88 –89
f1 (ppm)

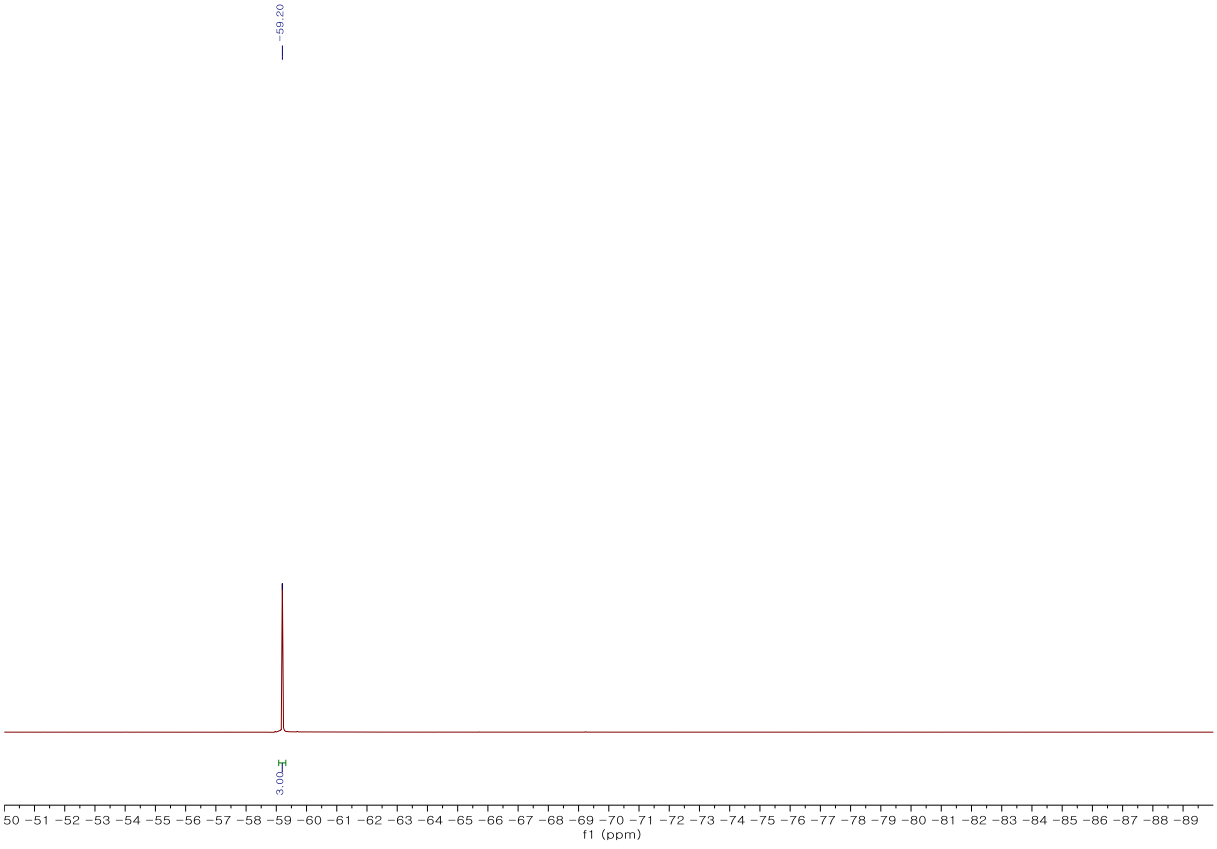
(*E*)-tert-butyl (4-(1-chloro-3,3,3-trifluoro-2-methylprop-1-en-1-yl)phenyl)carbamate (6d)



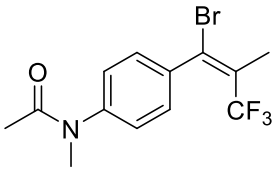
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.3 Hz, 1H), 7.46 (d, J = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.19 (qd, *J* = 7.0, 2.3 Hz, 2H), 2.15 (s, 3H), 1.50 (td, *J* = 7.1, 2.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.58 (C=O), 139.79 (d, *J* = 4.3 Hz), 139.46, 132.28, 129.26 (t, *J* = 2.1 Hz), 124.68–123.83 (m, *J* = 30.0 Hz), 123.04 (q, *J* = 219.17 Hz), 117.75, 81.08, 28.44, 16.34 (q, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.20. **IR (neat)** 3311, 3180, 3110, 3044, 2982, 2928, 2856, 2297, 1918, 1695, 1656, 1594, 1529, 1454, 1408, 1369, 1318, 1270, 1244, 1160, 1126, 1112, 1059, 1017, 952, 899, 844, 826, 805, 774, 684, 624, 567, 536 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{15}H_{17}ClF_3NO_2$ $[M]^+$ 335.0895, found 335.0900. **M.P.** 133.6 ℃. **Appearance** White solid. **Amount** 28 mg. **Yield** 41%.



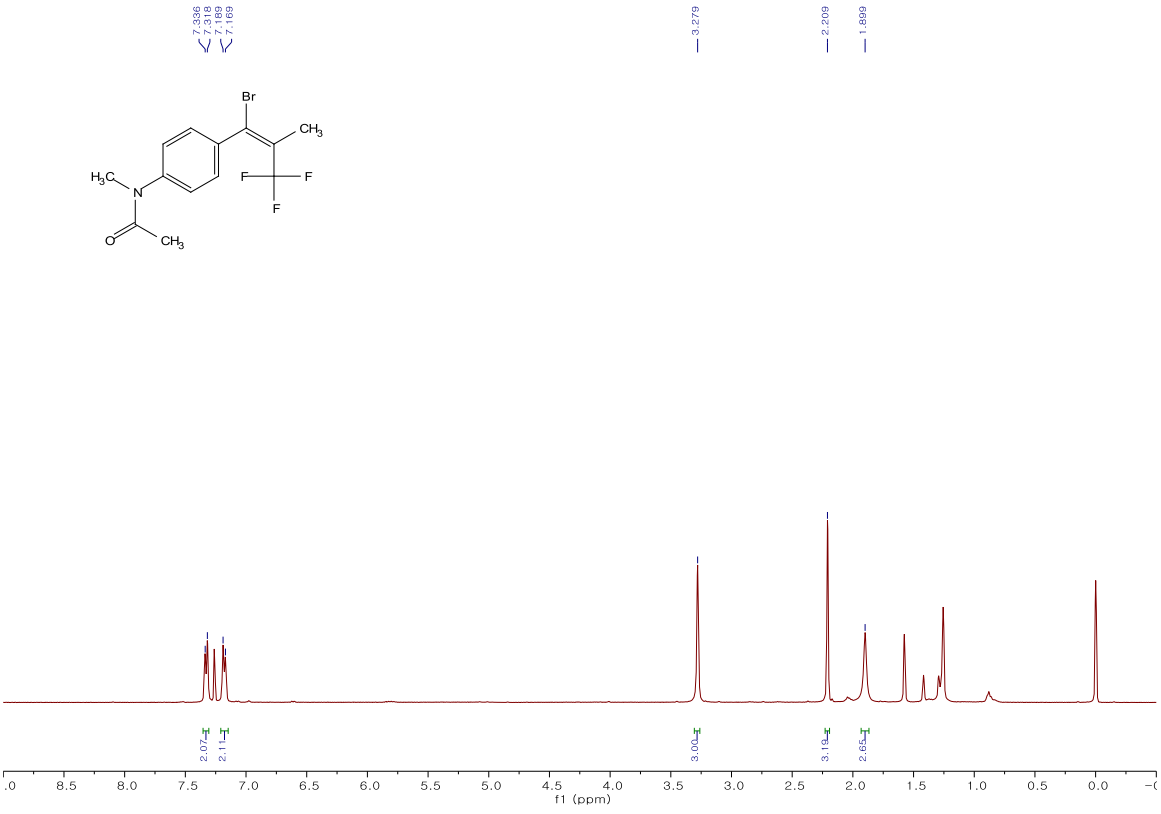

152.58
139.81
139.77
139.46
132.28
129.30
129.28
129.26
129.24
126.35
124.68
124.42
124.21
124.13
123.83
121.96
119.23
117.75
81.08
28.44
16.37
16.35
16.33
16.31
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 –
f1 (ppm)

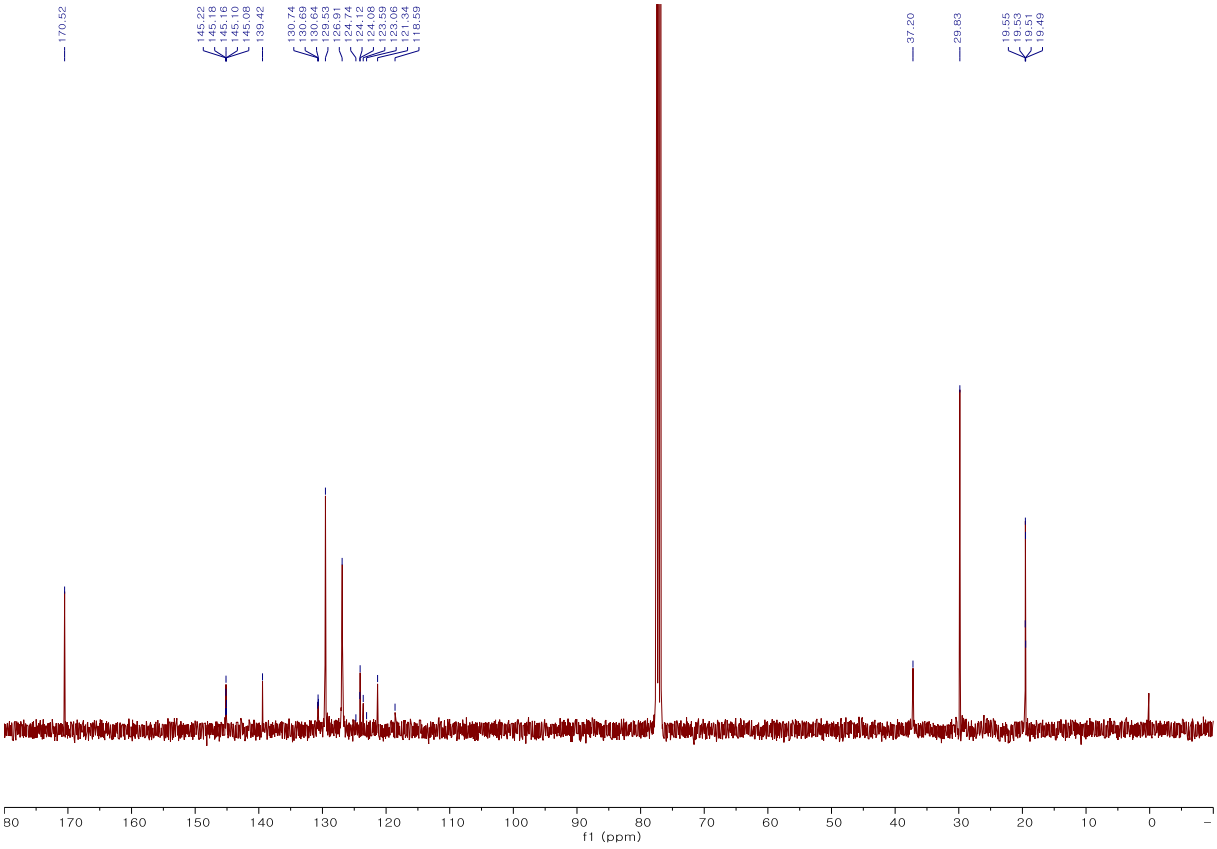

-59.20
3.00
50 –51 –52 –53 –54 –55 –56 –57 –58 –59 –60 –61 –62 –63 –64 –65 –66 –67 –68 –69 –70 –71 –72 –73 –74 –75 –76 –77 –78 –79 –80 –81 –82 –83 –84 –85 –86 –87 –88 –89
f1 (ppm)

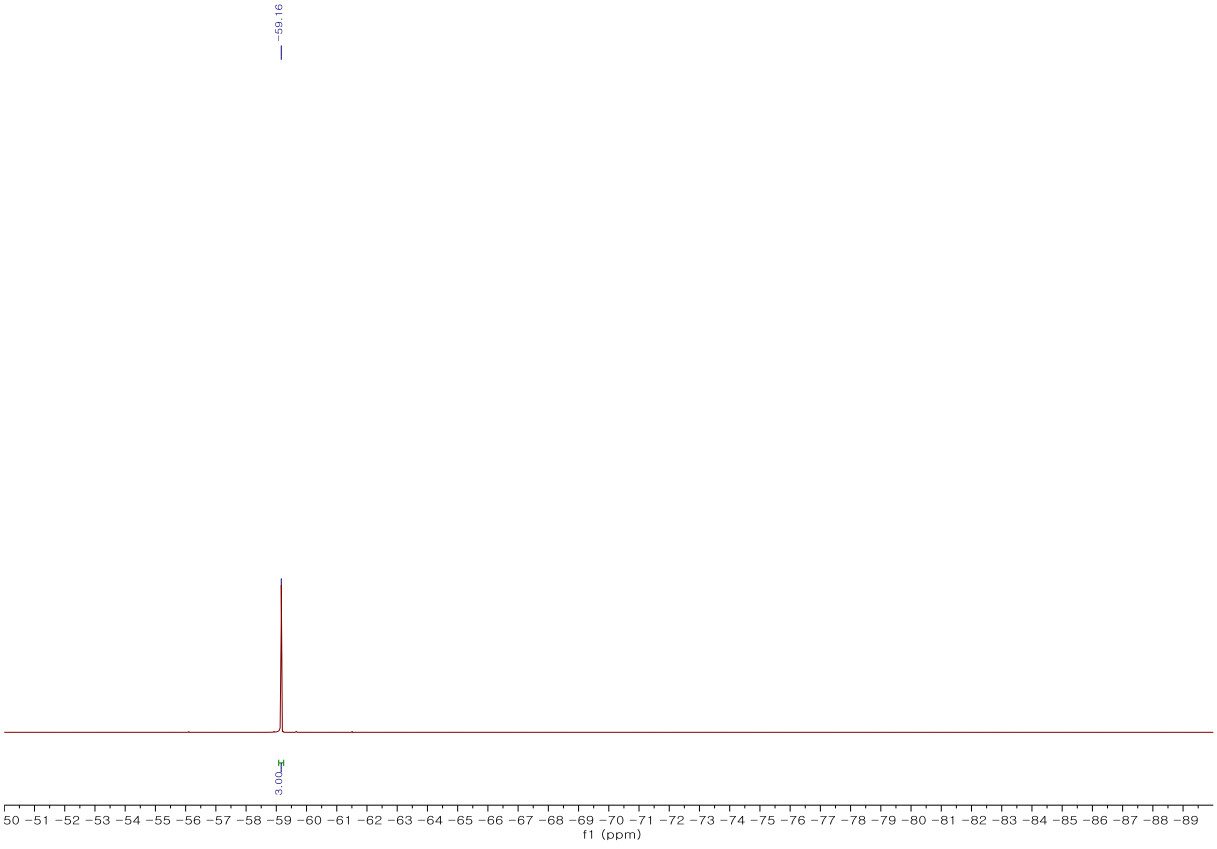
(*E*)-*N*-(4-(1-bromo-3,3,3-trifluoro-2-methylprop-1-en-1-yl)phenyl)-*N*-methylacetamide (6e)



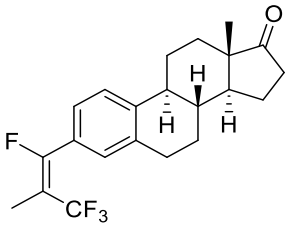
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.28 (s, 3H), 2.21 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.52 (C=O), 145.28–145.03 (m), 139.42, 130.78–130.62 (m), 129.53, 126.91, 123.93 (m, *J* = 53.5 Hz), 121.34 (q, *J* = 276.7 Hz), 37.20, 29.83, 19.52 (q, *J* = 2.0 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.16. **IR (neat)** 3449, 3037, 2926, 2855, 1945, 1653, 1600, 1507, 1424, 1378, 1351, 1306, 1225, 1175, 1110, 1018, 974, 921, 882, 852, 793, 715, 651, 630, 598, 576 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{13}H_{13}BrF_3NO$ $[M]^+$ 334.0131, found 335.0133. **M.P.** 55.9 ℃. **Appearance** White solid. **Amount** 23 mg. **Yield** 34%.



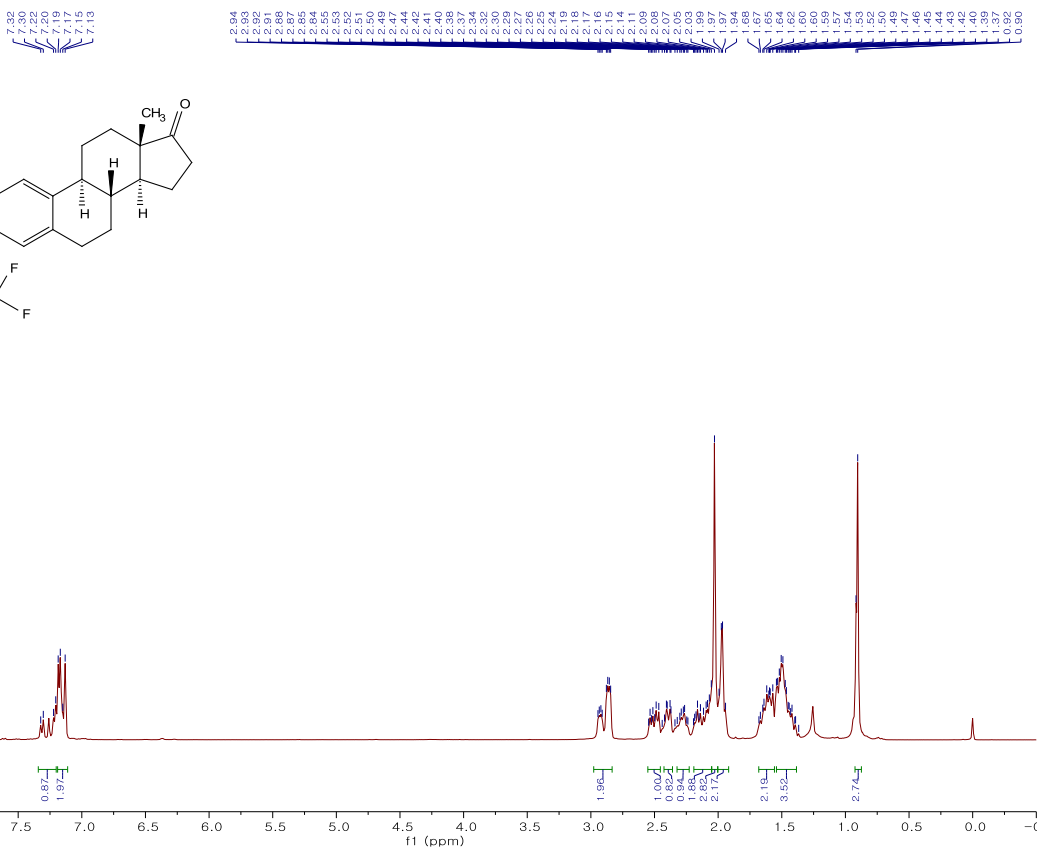

170.52
145.22
145.18
145.16
145.10
145.08
139.42
130.74
130.69
130.64
129.53
126.91
124.74
124.72
124.08
123.59
123.06
121.34
116.59
37.20
29.83
19.55
19.53
19.51
19.49
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

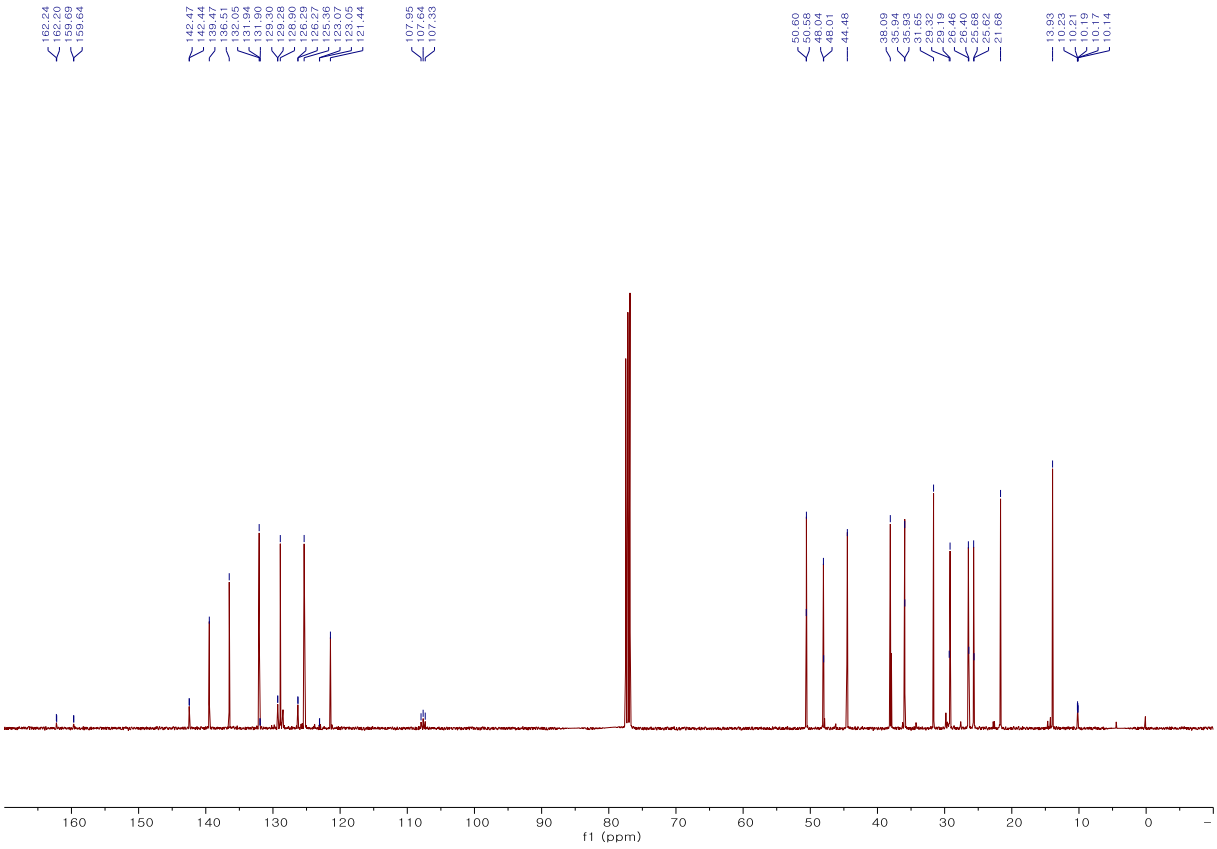

-59.16
3.00
50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87 -88 -89
f1 (ppm)

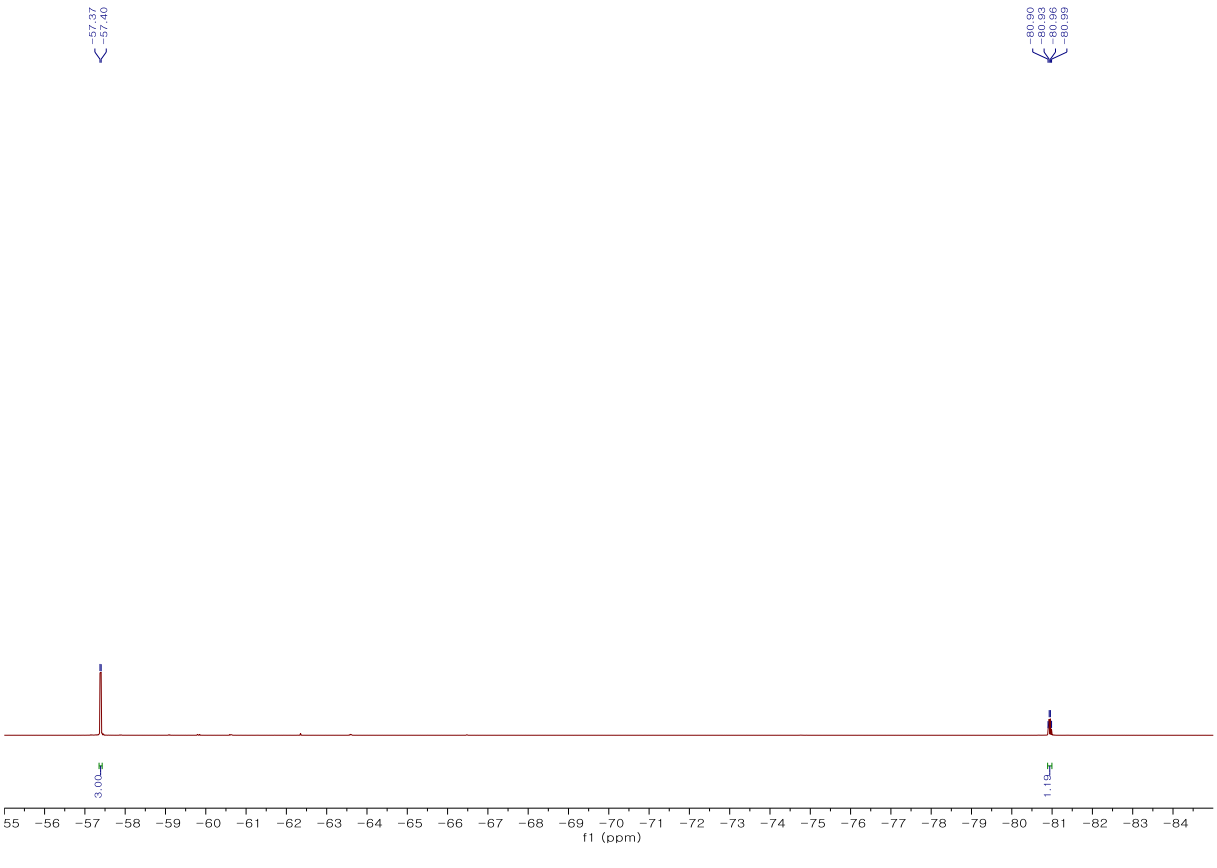
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((*E*)-1,3,3,3-tetrafluoro-2-methylprop-1-en-1-yl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[a]phenanthren-17(14*H*)-one (7a)



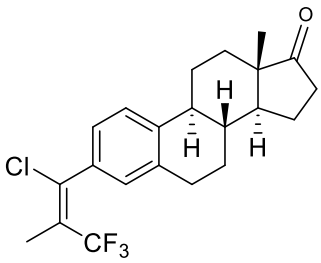
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.11 (m, 2H), 2.94–2.84 (m, 2H), 2.55–2.45 (m, 1H), 2.43–2.36 (m, 1H), 2.32–2.23 (m, 1H), 2.19–2.05 (m, 2H), 2.03 (s, 3H), 1.96 (t, *J* = 6.6 Hz, 2H), 1.68–1.56 (m, 2H), 1.54–1.37 (m, 4H), 0.91 (d, *J* = 5.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.94 (dd, *J* = 257.0, 4.8 Hz), 142.46 (d, *J* = 2.6 Hz, C=O), 139.47, 136.51, 132.05, 128.90, 127.79 (qd, *J* = 303.4, 3.9 Hz), 125.36, 121.44, 107.64 (m, *J* = 31.4 Hz), 50.59 (d, *J* = 2.1 Hz), 48.03 (d, *J* = 3.2 Hz), 44.48, 38.09, 35.94 (d, *J* = 1.5 Hz), 31.65, 29.25 (d, *J* = 12.7 Hz), 26.43 (d, *J* = 6.6 Hz), 25.65 (d, *J* = 5.9 Hz), 21.68, 13.93, 10.35–9.96 (m). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.39 (d, *J* = 10.9 Hz), -80.94 (q, *J* = 11.0 Hz). **IR (neat)** 3746, 3448, 3068, 2933, 2872, 2228, 1913, 1822, 1733, 1606, 1549, 1495, 1453, 1430, 1403, 1370, 1340, 1289, 1256, 1218, 1116, 1065, 1004, 966, 913, 841, 825, 825, 778, 724, 575, 519, 492, 443 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{22}H_{24}F_4O$ $[M]^+$ 380.1763, found 380.1763. **M.P.** 225.3 ℃. **Appearance** White solid. **Amount** 43 mg. **Yield** 56.%.



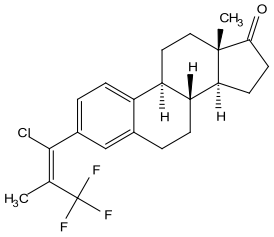

162.24
162.20
159.69
159.64
142.47
142.44
139.47
138.51
131.95
131.94
131.90
129.30
129.28
128.90
128.89
126.27
125.36
123.07
123.05
121.44
107.95
107.64
107.33
50.60
50.58
48.04
48.01
44.48
38.09
35.94
35.93
31.65
29.32
29.19
26.46
26.40
25.68
25.62
21.68
13.93
10.23
10.21
10.19
10.17
10.14
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

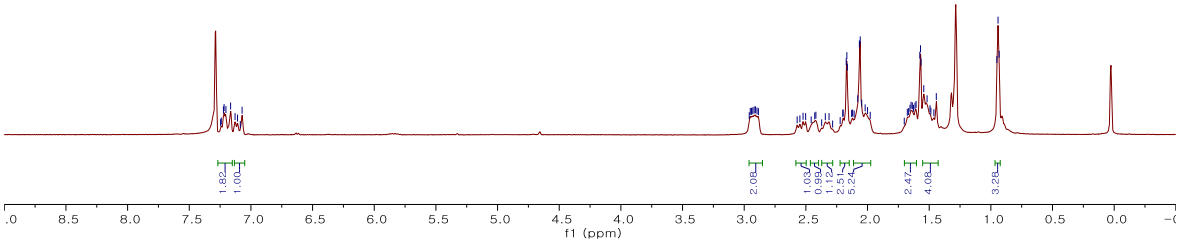

-57.37
-57.40
-80.90
-80.93
-80.96
-80.99
3.00
1.18
55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84
f1 (ppm)

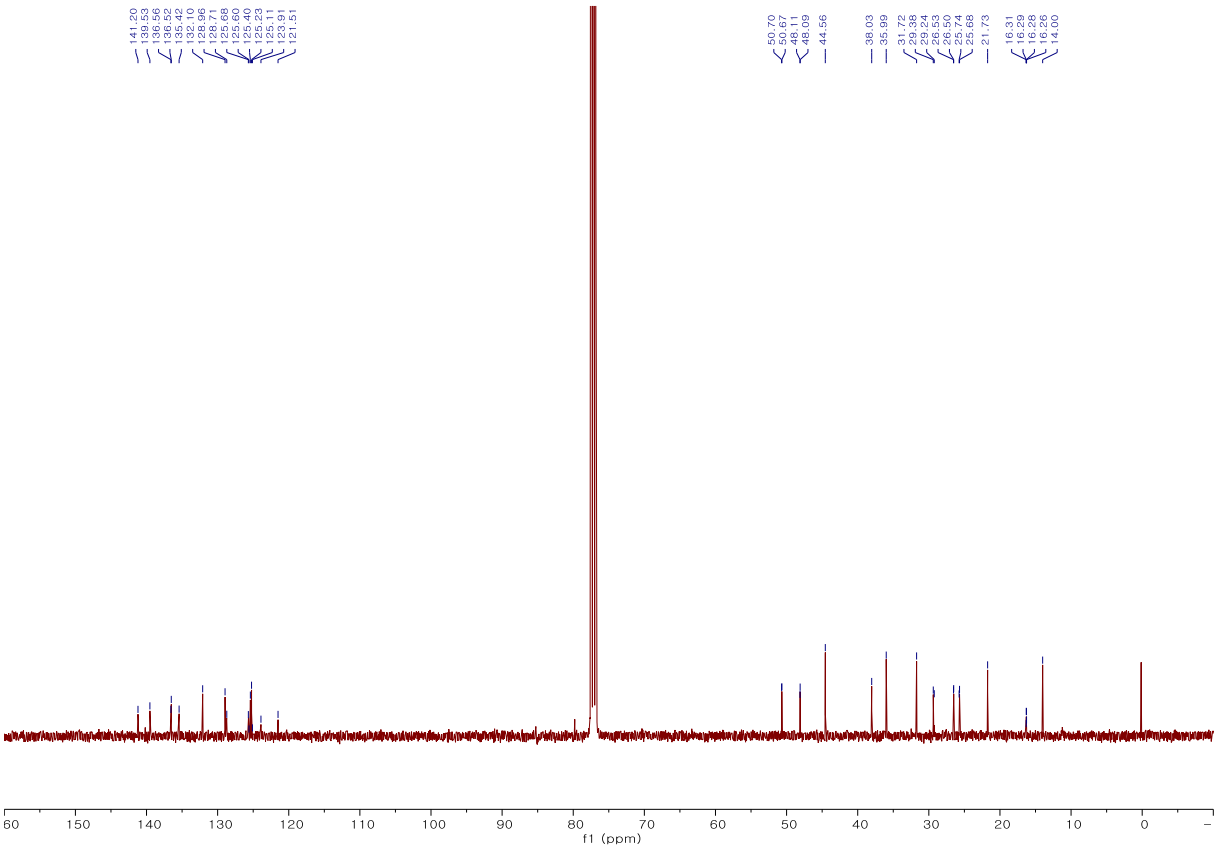
(8*R*,9*S*,13*S*,14*S*)-3-((*E*)-1-chloro-3,3,3-trifluoro-2-methylprop-1-en-1-yl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[a]phenanthren-17(14*H*)-one (7b)

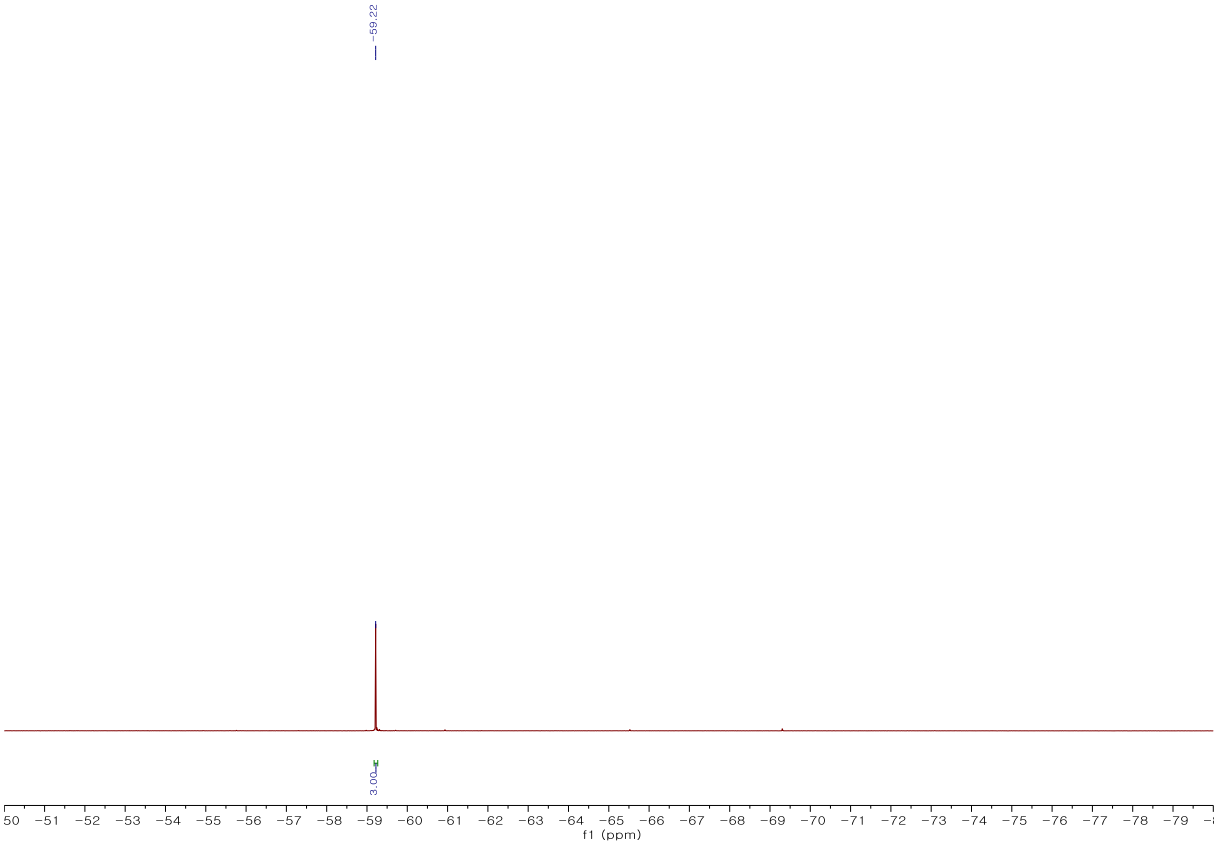


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25–7.20 (m, 2H), 7.13–7.05 (m, 1H), 2.96–2.88 (m, 2H), 2.57–2.50 (m, 1H), 2.46–2.40 (m, 1H), 2.33 (d, *J* = 12.0 Hz, 1H), 2.22–2.15 (m, 3H), 2.04 (m, 5H), 1.70–1.57 (m, 2H), 1.55–1.43 (m, 4H), 0.94 (d, *J* = 3.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.20 (C=O), 139.53, 136.54 (d, *J* = 4.5 Hz), 135.42, 132.10, 128.96, 127.20 (q, *J* = 305.2 Hz), 125.32 (m, *J* = 17.1 Hz), 123.91, 121.51, 50.68 (d, *J* = 2.8 Hz), 48.10 (d, *J* = 1.4 Hz), 44.56, 38.03, 35.99, 31.72, 29.31 (d, *J* = 13.8 Hz), 26.52 (d, *J* = 2.5 Hz), 25.71 (d, *J* = 5.9 Hz), 21.73, 16.29 (q, *J* = 1.7 Hz), 14.00. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -59.22. **IR (neat)** 3448, 2932, 2872, 2227, 2192, 1913, 1823, 1734, 1657, 1600, 1529, 1496, 1455, 1403, 1371, 1317, 1256, 1217, 1083, 1051, 1005, 965, 914, 823, 777, 713, 687, 575, 444 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{22}H_{24}ClF_3O$ $[M]^+$ 396.1478, found 396.1468. **M.P.** 225.6 ℃. **Appearance** White solid. **Amount** 30 mg. **Yield** 38%.

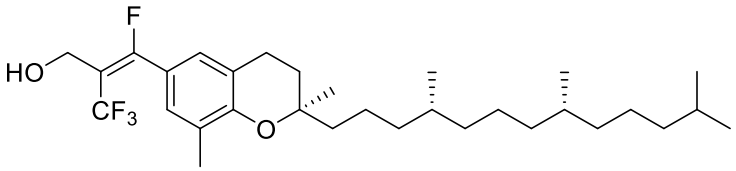




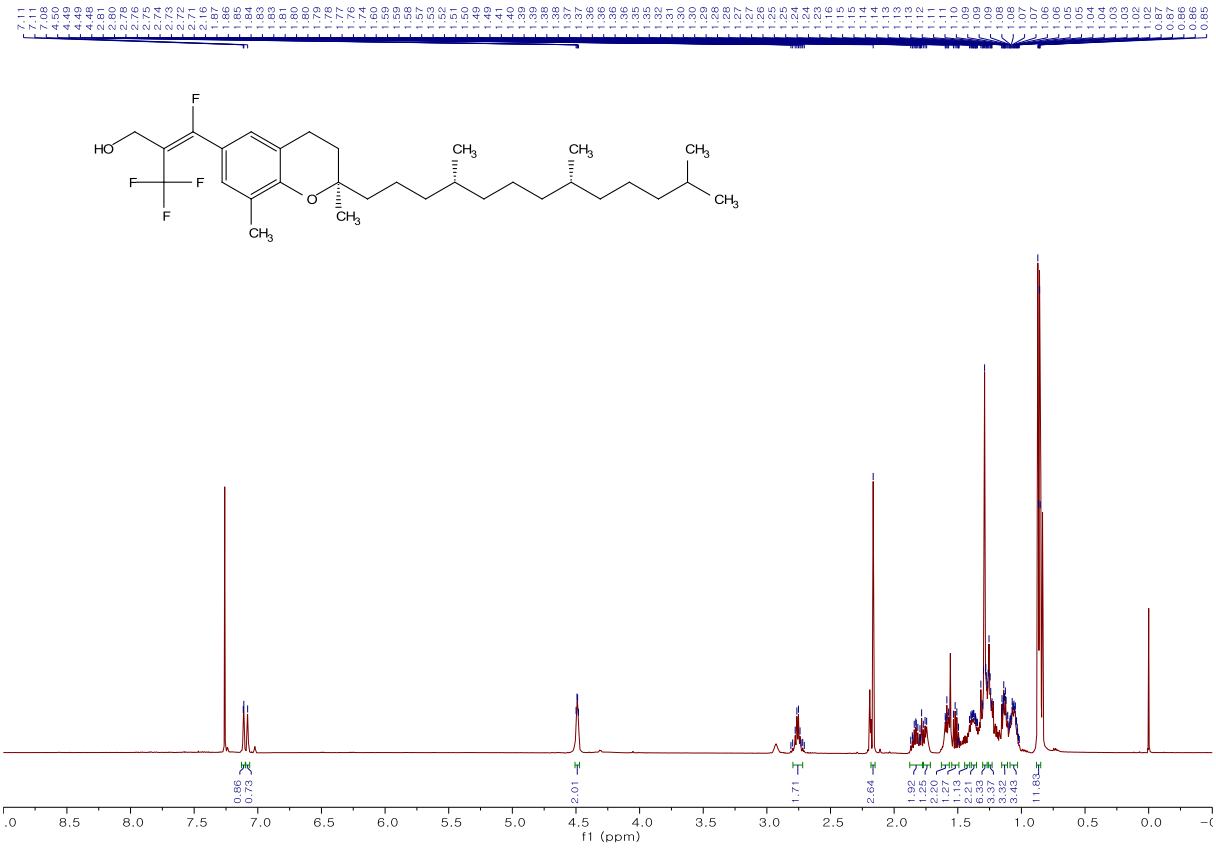

141.20
139.53
136.56
136.52
135.42
132.10
128.96
128.71
125.68
125.60
125.40
125.23
125.11
123.91
121.51
50.70
50.67
48.11
48.09
44.56
38.03
35.99
31.72
29.38
29.24
28.53
28.50
25.74
25.68
21.73
16.31
16.29
16.28
16.26
14.00
f1 (ppm)

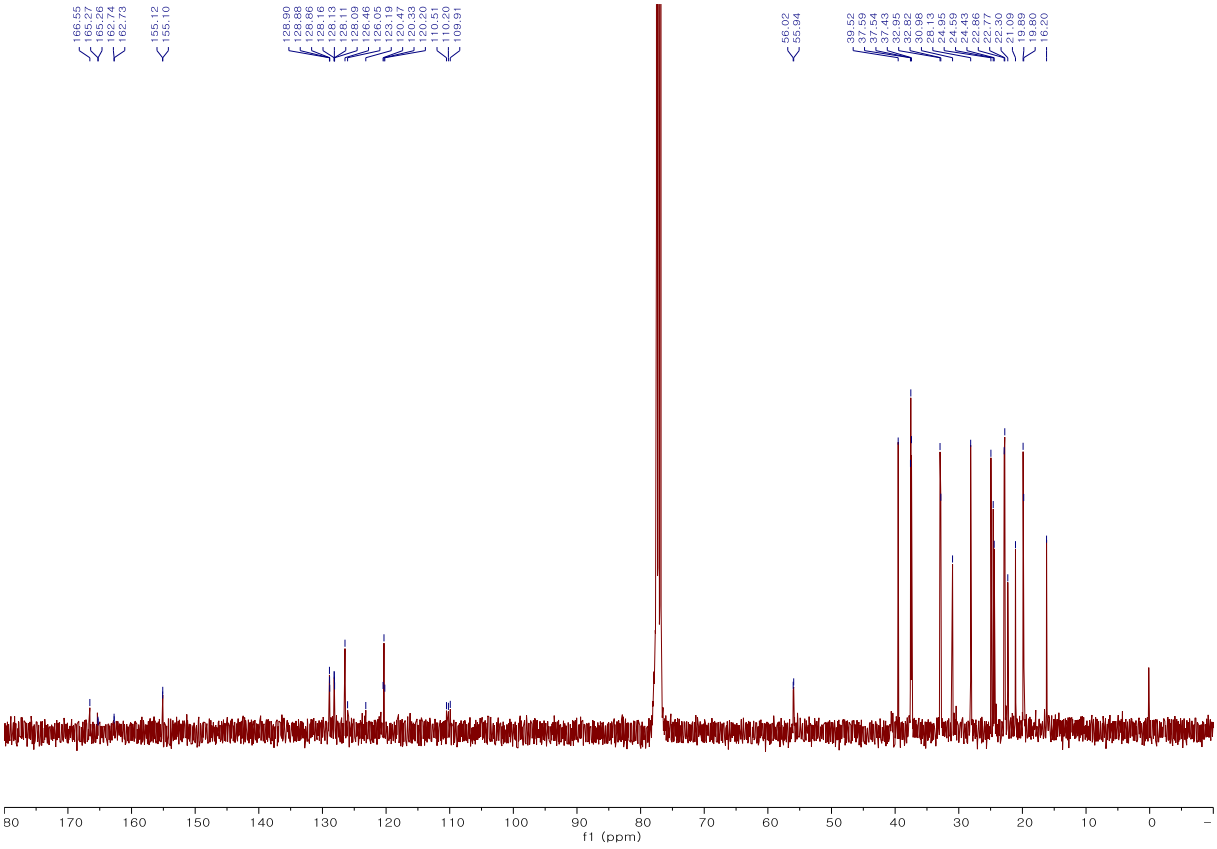

-59.22
3.00
f1 (ppm)

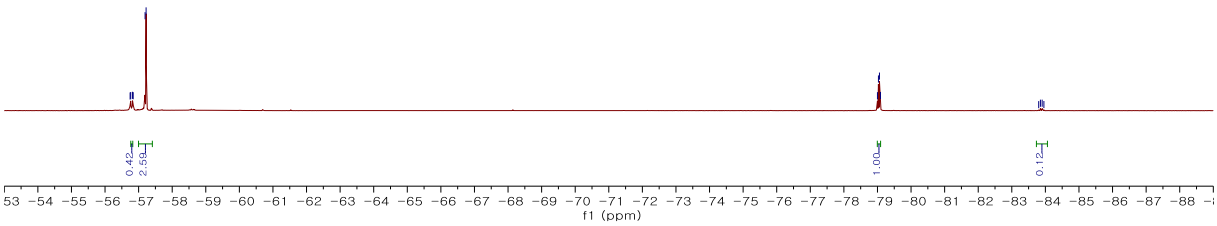
(*E*)-3-((*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)-3-fluoro-2-(trifluoromethyl)prop-2-en-1-ol (7c)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (s, 1H), 7.08 (s, 1H), 4.51–4.47 (m, 2H), 2.76 (q, *J* = 6.4 Hz, 2H), 2.16 (s, 3H), 1.88–1.78 (m, 2H), 1.75 (d, *J* = 6.3 Hz, 1H), 1.62–1.56 (m, 2H), 1.55–1.49 (m, 1H), 1.45–1.41 (m, 1H), 1.40–1.35 (m, 2H), 1.30–1.27 (m, 6H), 1.26–1.23 (m, 3H), 1.16–1.10 (m, 3H), 1.06–1.01 (m, 3H), 0.88–0.85 (m, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.55, 164.00 (dd, *J* = 254.5, 1.7 Hz), 155.11 (d, *J* = 2.2 Hz), 129.43–128.33 (m), 128.53–127.47 (m), 126.46, 124.62 (q, *J* = 287.9 Hz), 120.33 (t, *J* = 13.6 Hz), 110.95–109.16 (m, *J* = 31.3 Hz), 55.98 (d, *J* = 8.1 Hz), 39.52, 37.96–37.17 (m), 32.88 (d, *J* = 12.6 Hz), 30.98, 28.13, 24.95, 24.51 (d, *J* = 15.3 Hz), 22.82 (d, *J* = 9.3 Hz), 22.30, 21.09, 19.84 (d, *J* = 9.5 Hz), 16.20. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -56.79 (dd, *J* = 27.2, 6.8 Hz), -57.21 (d, *J* = 11.5 Hz), -79.04 (q, *J* = 11.2 Hz), -83.88 (q, *J* = 19.3 Hz). **IR (neat)** 3411, 2927, 2867, 1677, 1608, 1479, 1407, 1355, 1284, 1251, 1190, 1157, 1127, 1041, 1005, 967, 940, 895, 740, 692, 660, 529, 456 cm^{-1}. **HRMS (EI)** m/z Calcd. for $C_{31}H_{48}F_4O_2$ $[M]^+$ 528.3584, found 528.3590. **Appearance** Colorless oil. **Amount** 21 mg. **Yield** 41%.




166.55
165.27
165.26
162.74
162.73
155.12
155.10
128.90
128.88
128.86
128.16
128.13
128.11
128.09
126.46
126.05
125.19
120.47
120.33
120.20
110.51
110.20
109.91
56.02
55.94
39.52
37.59
37.54
37.43
32.95
32.82
32.62
30.88
28.13
24.95
24.59
24.43
22.86
22.77
22.30
21.09
19.89
19.80
16.20
f1 (ppm)
-56.75
-56.77
-56.82
-56.84
-57.19
-57.22
-79.00
-79.03
-79.06
-79.09
-83.80
-83.85
-83.90
-83.96


0.42
2.59
1.00
0.12
f1 (ppm)

VI. X-ray Structure of Compound **3b**

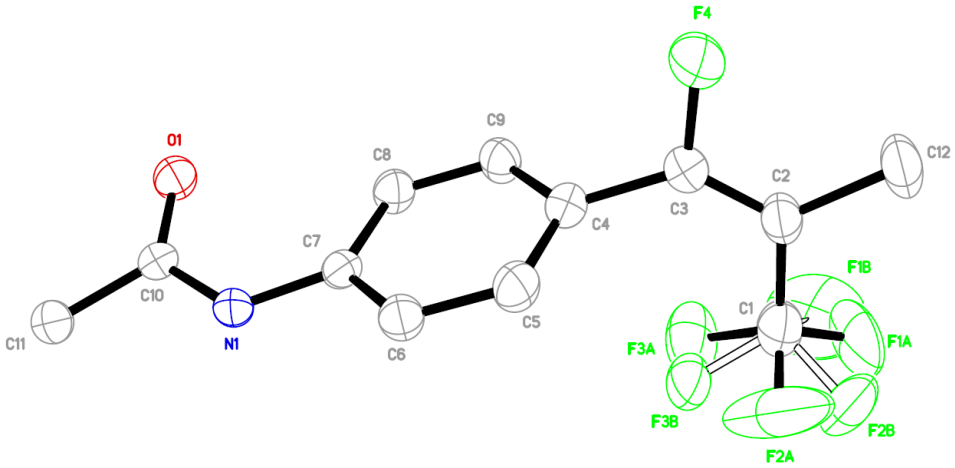


Table 1. Crystal data and structure refinement for **3b**

Identification code	20190611	
Empirical formula	C12 H11 F4 N O	
Formula weight	261.22	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.1815(8) Å	α= 90°.
	b = 9.5647(4) Å	β= 90.801(3)°.
	c = 7.4675(3) Å	γ = 90°.
Volume	1227.06(9) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	536	
Crystal size	0.40 x 0.24 x 0.06 mm^3	
Theta range for data collection	2.37 to 27.87°	
Index ranges	0<=h<=22, -12<=k<=0, -9<=l<=9	
Reflections collected	2880	
Independent reflections	2880 [R(int) = 0.0000]	
Completeness to theta = 27.87°	98.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9922 and 0.9493	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2880 / 0 / 191	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0674, wR2 = 0.2119	
R indices (all data)	R1 = 0.0913, wR2 = 0.2321	
Largest diff. peak and hole	0.273 and -0.275 $e.Å^{-3}$	

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1A)	6177(8)	10780(20)	5440(20)	206(10)
F(2A)	6454(17)	11904(11)	7840(18)	229(8)
F(3A)	7221(6)	10420(20)	6692(18)	154(6)
F(1B)	6472(13)	10310(20)	5306(16)	243(9)
F(2B)	6130(4)	11844(11)	6740(30)	170(7)
F(3B)	7157(8)	11114(16)	7440(30)	146(6)
F(4)	6088(1)	7992(3)	10257(4)	142(1)
O(1)	10095(1)	7334(2)	11727(3)	69(1)
N(1)	9573(1)	9487(2)	12083(3)	53(1)
C(1)	6473(2)	10703(4)	6994(6)	96(1)
C(2)	6101(1)	9624(3)	8089(4)	68(1)
C(3)	6488(1)	8974(3)	9361(4)	67(1)
C(4)	7290(1)	9095(3)	10047(3)	59(1)
C(5)	7515(2)	10198(3)	11145(4)	71(1)
C(6)	8262(1)	10283(2)	11822(4)	64(1)
C(7)	8817(1)	9286(2)	11394(3)	50(1)
C(8)	8595(1)	8168(2)	10309(3)	57(1)
C(9)	7841(1)	8076(3)	9664(3)	60(1)
C(10)	10159(1)	8548(2)	12220(3)	53(1)
C(11)	10904(1)	9102(3)	13034(4)	67(1)
C(12)	5252(2)	9362(4)	7642(5)	92(1)

Table 3. Bond lengths [Å] and angles [°] for **3b**.

F(1A)-C(1)	1.264(10)
F(2A)-C(1)	1.312(10)
F(3A)-C(1)	1.336(12)
F(1B)-C(1)	1.317(14)
F(2B)-C(1)	1.254(8)
F(3B)-C(1)	1.278(12)
F(4)-C(3)	1.348(3)
O(1)-C(10)	1.224(3)
N(1)-C(10)	1.351(3)
N(1)-C(7)	1.404(3)
N(1)-H(1A)	0.8600
C(1)-C(2)	1.468(5)
C(2)-C(3)	1.309(4)
C(2)-C(12)	1.513(4)
C(3)-C(4)	1.468(3)
C(4)-C(5)	1.388(4)
C(4)-C(9)	1.391(3)
C(5)-C(6)	1.375(4)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.389(3)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.392(3)
C(8)-C(9)	1.378(3)
C(8)-H(8A)	0.9300
C(9)-H(9A)	0.9300
C(10)-C(11)	1.505(3)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(10)-N(1)-C(7)	128.43(18)
C(10)-N(1)-H(1A)	115.8
C(7)-N(1)-H(1A)	115.8
F(2B)-C(1)-F(1A)	67.9(9)

F(2B)-C(1)-F(3B)	101.6(9)
F(1A)-C(1)-F(3B)	125.1(11)
F(2B)-C(1)-F(2A)	45.3(7)
F(1A)-C(1)-F(2A)	112.2(11)
F(3B)-C(1)-F(2A)	68.6(17)
F(2B)-C(1)-F(1B)	96.2(10)
F(1A)-C(1)-F(1B)	30.9(14)
F(3B)-C(1)-F(1B)	108.9(15)
F(2A)-C(1)-F(1B)	135.5(9)
F(2B)-C(1)-F(3A)	127.0(8)
F(1A)-C(1)-F(3A)	103.5(12)
F(3B)-C(1)-F(3A)	39.0(8)
F(2A)-C(1)-F(3A)	106.8(17)
F(1B)-C(1)-F(3A)	76.6(13)
F(2B)-C(1)-C(2)	119.4(5)
F(1A)-C(1)-C(2)	112.4(6)
F(3B)-C(1)-C(2)	118.6(6)
F(2A)-C(1)-C(2)	109.5(7)
F(1B)-C(1)-C(2)	109.6(8)
F(3A)-C(1)-C(2)	112.3(7)
C(3)-C(2)-C(1)	121.1(3)
C(3)-C(2)-C(12)	124.1(3)
C(1)-C(2)-C(12)	114.8(3)
C(2)-C(3)-F(4)	115.7(2)
C(2)-C(3)-C(4)	132.9(2)
F(4)-C(3)-C(4)	111.4(2)
C(5)-C(4)-C(9)	118.0(2)
C(5)-C(4)-C(3)	121.2(2)
C(9)-C(4)-C(3)	120.8(2)
C(6)-C(5)-C(4)	120.9(2)
C(6)-C(5)-H(5A)	119.6
C(4)-C(5)-H(5A)	119.6
C(5)-C(6)-C(7)	121.0(2)
C(5)-C(6)-H(6A)	119.5
C(7)-C(6)-H(6A)	119.5
C(6)-C(7)-C(8)	118.6(2)
C(6)-C(7)-N(1)	117.19(19)
C(8)-C(7)-N(1)	124.2(2)
C(9)-C(8)-C(7)	120.1(2)
C(9)-C(8)-H(8A)	120.0

C(7)-C(8)-H(8A)	120.0
C(8)-C(9)-C(4)	121.5(2)
C(8)-C(9)-H(9A)	119.3
C(4)-C(9)-H(9A)	119.3
O(1)-C(10)-N(1)	123.0(2)
O(1)-C(10)-C(11)	121.9(2)
N(1)-C(10)-C(11)	115.1(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2x10^3$) for **3b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1A)	154(8)	300(20)	165(12)	143(13)	-118(9)	-106(10)
F(2A)	420(20)	80(6)	188(10)	27(5)	-35(12)	-55(9)
F(3A)	69(3)	240(14)	154(8)	95(8)	6(4)	-15(7)
F(1B)	340(20)	289(15)	105(7)	32(8)	46(10)	-66(14)
F(2B)	114(5)	119(6)	276(17)	101(8)	-23(6)	23(4)
F(3B)	78(5)	150(9)	209(13)	116(8)	-49(7)	-36(5)
F(4)	84(1)	157(2)	185(2)	93(2)	-26(1)	-40(1)
O(1)	68(1)	50(1)	90(1)	-5(1)	-14(1)	10(1)
N(1)	55(1)	41(1)	64(1)	-1(1)	-10(1)	0(1)
C(1)	77(2)	105(3)	104(3)	27(2)	-21(2)	-3(2)
C(2)	51(1)	73(2)	79(2)	-5(1)	-10(1)	4(1)
C(3)	55(1)	66(2)	80(2)	8(1)	-5(1)	-5(1)
C(4)	58(1)	57(1)	62(1)	5(1)	-7(1)	3(1)
C(5)	63(2)	56(1)	93(2)	-8(1)	-10(1)	15(1)
C(6)	64(1)	46(1)	82(2)	-12(1)	-14(1)	8(1)
C(7)	57(1)	42(1)	51(1)	4(1)	-5(1)	2(1)
C(8)	59(1)	52(1)	60(1)	-8(1)	-5(1)	8(1)
C(9)	60(1)	58(1)	63(1)	-10(1)	-9(1)	1(1)
C(10)	56(1)	45(1)	58(1)	7(1)	-4(1)	0(1)
C(11)	56(1)	62(1)	82(2)	9(1)	-10(1)	-3(1)
C(12)	52(1)	111(3)	113(2)	-9(2)	-21(2)	1(2)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for **3b**.

	x	y	z	U(eq)
H(1A)	9677	10314	12468	64
H(5A)	7156	10888	11426	85
H(6A)	8397	11020	12578	77
H(8A)	8956	7483	10018	68
H(9A)	7698	7315	8956	72
H(11A)	11284	8368	13087	100
H(11B)	10807	9438	14222	100
H(11C)	11095	9855	12312	100
H(12A)	5053	8652	8422	139
H(12B)	5202	9057	6421	139
H(12C)	4962	10210	7800	139

Table 6. Torsion angles [°] for **3b**.

F(2B)-C(1)-C(2)-C(3)	-132.6(11)
F(1A)-C(1)-C(2)-C(3)	151.1(13)
F(3B)-C(1)-C(2)-C(3)	-7.9(13)
F(2A)-C(1)-C(2)-C(3)	-83.6(15)
F(1B)-C(1)-C(2)-C(3)	118.0(12)
F(3A)-C(1)-C(2)-C(3)	34.9(10)
F(2B)-C(1)-C(2)-C(12)	46.5(12)
F(1A)-C(1)-C(2)-C(12)	-29.9(14)
F(3B)-C(1)-C(2)-C(12)	171.1(12)
F(2A)-C(1)-C(2)-C(12)	95.4(14)
F(1B)-C(1)-C(2)-C(12)	-63.0(12)
F(3A)-C(1)-C(2)-C(12)	-146.1(9)
C(1)-C(2)-C(3)-F(4)	-179.1(3)
C(12)-C(2)-C(3)-F(4)	2.0(4)
C(1)-C(2)-C(3)-C(4)	1.2(5)
C(12)-C(2)-C(3)-C(4)	-177.8(3)
C(2)-C(3)-C(4)-C(5)	76.1(4)
F(4)-C(3)-C(4)-C(5)	-103.6(3)
C(2)-C(3)-C(4)-C(9)	-106.2(4)
F(4)-C(3)-C(4)-C(9)	74.1(3)
C(9)-C(4)-C(5)-C(6)	0.4(4)
C(3)-C(4)-C(5)-C(6)	178.2(3)
C(4)-C(5)-C(6)-C(7)	1.5(4)
C(5)-C(6)-C(7)-C(8)	-2.1(4)
C(5)-C(6)-C(7)-N(1)	177.4(2)
C(10)-N(1)-C(7)-C(6)	163.3(2)
C(10)-N(1)-C(7)-C(8)	-17.2(4)
C(6)-C(7)-C(8)-C(9)	0.8(4)
N(1)-C(7)-C(8)-C(9)	-178.6(2)
C(7)-C(8)-C(9)-C(4)	1.1(4)
C(5)-C(4)-C(9)-C(8)	-1.7(4)
C(3)-C(4)-C(9)-C(8)	-179.5(2)
C(7)-N(1)-C(10)-O(1)	0.0(4)
C(7)-N(1)-C(10)-C(11)	-179.8(2)

Symmetry transformations used to generate equivalent atoms: