Supporting Information

Photoredox-Catalyzed Cascade Difluoromethylation/SO_2 Reintegration/Polyfluoroarylation of Conjugated Dienes with a Bifunctional CF_2HSO_2Na Reagent

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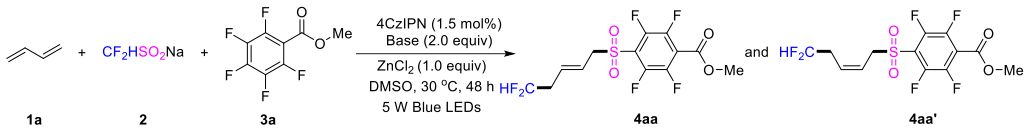
I. General Information

All reactions were carried out under nitrogen atmosphere. Reagents were purchased from commercial sources and used without further purification, unless otherwise noted. All of the solvents were anhydrous according distillation. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm precoated silica gel plates. ^{1}H NMR spectra were recorded at 25 °C on a Bruker 600 MHz or Varian 500 MHz, ^{13}C NMR spectra were recorded at 25 °C on a Bruker 151 MHz, respectively in $CDCl_3$ by using TMS as internal standard. ^{19}F NMR spectra were recorded at 25 °C on a Bruker 565 MHz. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for ^{1}H NMR) and $CDCl_3$ (77.0 ppm for ^{13}C NMR), respectively. Letters m, s, d, t, and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. High-resolution mass spectra (HRMS) were recorded on Bruck microtof. We use RLH-18 8-position Photo Reaction System, which manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This photo reactor we used has equipped 10 blue light 5 W LEDs. This blue light 5 W LED's energy peak wavelength is 453.6 nm, peak width at half-height is 20.4 nm. Another photo reactor we used has equipped 8 blue light 40 W LED. This blue light 40 W LED's energy peak wavelength is 456 nm, peak width at half-height is 20.4 nm. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2 cm and no filter between LED and test tube. The 1,3-butadiene (**1a**) used as a solution in tetrahydrofuran (THF) at a concentration of 2 mol/L.

II. Optimization of the Reaction Conditions

2.1 Optimization of 1,3-butadiene (Table S1-S3)

Table S1. Screen of Bases

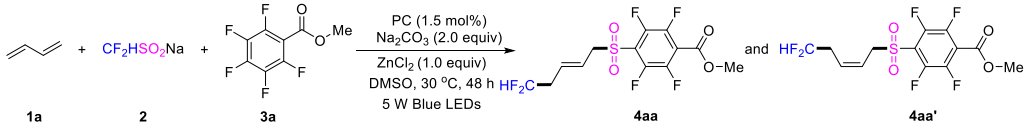


1a 2 3a 4aa 4aa'

Entry	PC	Base	Yield of 4aa (%) [b]	Yield of 4aa' (%) [b]
1	4CzIPN	--	74	12
2	4CzIPN	K_3PO_4	63	10
3	4CzIPN	K_2CO_3	58	7
4	4CzIPN	Na_2CO_3	74	7
5	4CzIPN	Cs_2CO_3	58	12
6	4CzIPN	DABCO	trace	--

[a] Reaction conditions: **1a** (1.0 mmol, 5.0 equiv), **2** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), 4CzIPN (1.5 mol%), $ZnCl_2$ (1.0 equiv), Base (0.4 mmol, 2.0 equiv), DMSO (1.5 mL) at 30 °C, 5 W Blue LEDs, 48 h in nitrogen. [b] Yields refer to isolated products and are based on **3a**. n.d. = not detected.

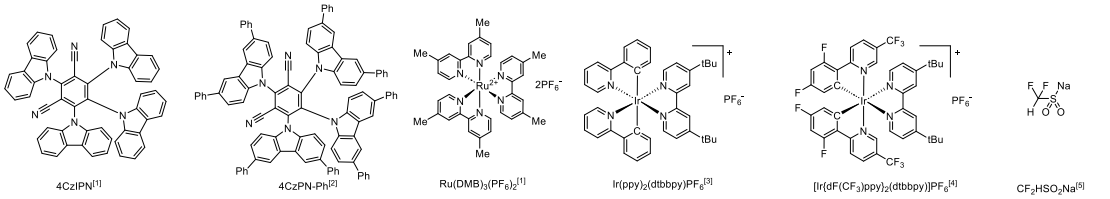
Table S2. Screen of Photocatalysts



1a 2 3a 4aa 4aa'

Entry	PC	Yield of 4aa (%) [b]	Yield of 4aa' (%) [b]
1	4CzIPN	74	7
2	4CzPN-Ph	79	13
3	$Ru(DMB)_3(PF_6)_2$	27	2
4	$Ir[dFppy]_2(dtbbpy)PF_6$	41	7
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	52	11

[a] Reaction conditions: **1a** (1.0 mmol, 5.0 equiv), **2** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), PC (1.5 mol%), $ZnCl_2$ (1.0 equiv), Na_2CO_3 (0.4 mmol, 2.0 equiv), DMSO (1.5 mL) at 30 °C, 5 W Blue LEDs, 48 h in nitrogen. [b] Yields refer to isolated products and are based on **3a**. n.d. = not detected.



4CzIPN[1] — $E_{1/2}^{*PC/PC^-}$ = +1.38 V vs. SCE; $E_{1/2}^{PC/PC^-}$ = -1.21 V vs. SCE

4CzPN-Ph[2] — $E_{1/2}^{*PC/PC^-}$ = +1.21 V vs. SCE; $E_{1/2}^{PC/PC^-}$ = -1.17 V vs. SCE

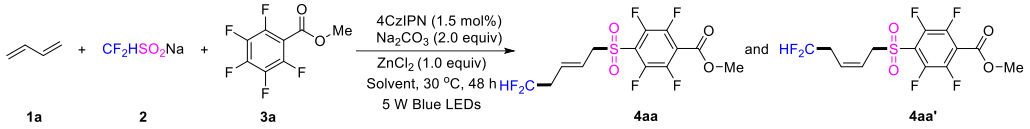
$Ru(DMB)_3(PF_6)_2$[1] — $E_{1/2}^{*PC/PC^-}$ = +1.63 V vs. SCE; $E_{1/2}^{PC/PC^-}$ = -1.43 V vs. SCE

$Ir(ppy)_2(dtbbpy)PF_6$[3] — $E_{1/2}^{*PC/PC^-}$ = +1.48 V vs. SCE; $E_{1/2}^{PC/PC^-}$ = -1.17 V vs. SCE

$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$[4] — $E_{1/2}^{*PC/PC^-}$ = +1.21 V vs. SCE; $E_{1/2}^{PC/PC^-}$ = -0.89 V vs. SCE

CF_2HSO_2Na[5] — E_{OX} = + 0.59 V vs SCE

Table S3. Screen of Solvents

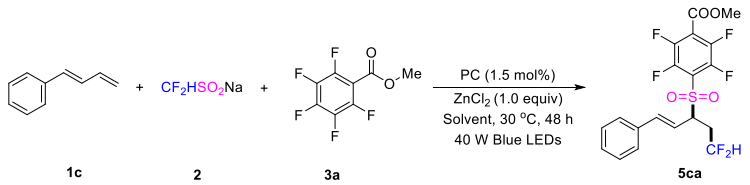


1a 2 3a 4aa 4aa'

Entry	PC	Solvent	Yield of 4aa (%) [b]	Yield of 4aa' (%) [b]
1	4CzIPN	DMSO	74	7
2	4CzIPN	DMF	71	10
3	4CzIPN	DMAc	66	11
4	4CzIPN	CH_3CN	n.d.	--
5	4CzIPN	THF	n.d.	--
6	4CzIPN	DCM	n.d.	--

[a] Reaction conditions: **1a** (1.0 mmol, 5.0 equiv), **2** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), 4CzIPN (1.5 mol%), $ZnCl_2$ (1.0 equiv), Na_2CO_3 (0.4 mmol, 2.0 equiv), Solvent (1.5 mL) at 30 °C, 5 W Blue LEDs, 48 h in nitrogen. [b] Yields refer to isolated products and are based on **3a**. n.d. = not detected.

2.2 Optimization of phenyl-1,3-butadiene (Table S4)



1c 2 3a 5ca

Entry	PC	Solvent	Yield of 5ca (%) [b]
1	4CzIPN	DMSO	38
2[c]	4CzIPN	DMSO	n.d.
3[d]	4CzIPN	DMSO	n.d.
4	4CzIPN	DMF	74
5	4CzIPN	DMAc	61
6	4CzIPN	CH_3CN	n.d.
7	4CzIPN	THF	n.d.
8	4CzIPN	DCM	n.d.
9	4CzPN-Ph	DMF	62
10	4CzTPN	DMF	56
11	$Ir[dFppy]_2(dtbbpy)PF_6$	DMF	14
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMF	5

[a] Reaction conditions: **1c** (0.3 mmol, 1.5 equiv), **2** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), PC (1.5 mol%), $ZnCl_2$ (1.0 equiv), anhydrous solvent (2.0 mL) at 30 °C, 40 W Blue LEDs, 48 h. [b] Yields refer to isolated products and are based on **3a**. [c] Na_2CO_3 (2.0 equiv) was added. [d] DABCO (2.0 equiv) was added. n.d. = not detected.

III. Synthesis of the Starting Materials

3.1 List of substrates 1

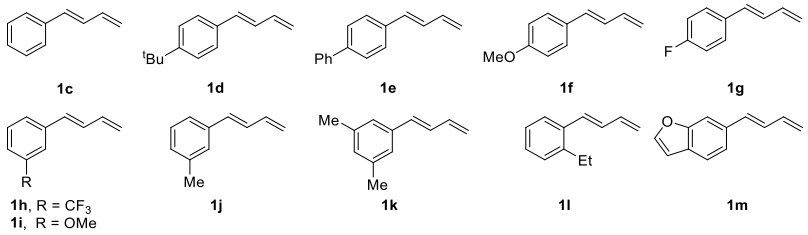
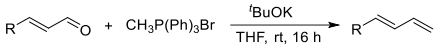


Table **S5** Substrate of 1-Phenyl-1,3-butadiene



To a suspension of methyltriphenylphosphonium bromide (18 mmol, 1.2 equiv.) in anhydrous THF (50 mL) was added potassium tert-butoxide (21 mmol, 1.4 equiv.). After stirring the reaction mixture at room temperature for 30 min, the corresponding aldehyde (15 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room temperature for 16 h, diluted with pentane (20 mL). The mixture was filtered through a silica gel plug, eluting with pentane, and the resulting filtrate concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with pentane, to give the corresponding 1,3-dienes.[6]

3.2 List of substrates 3

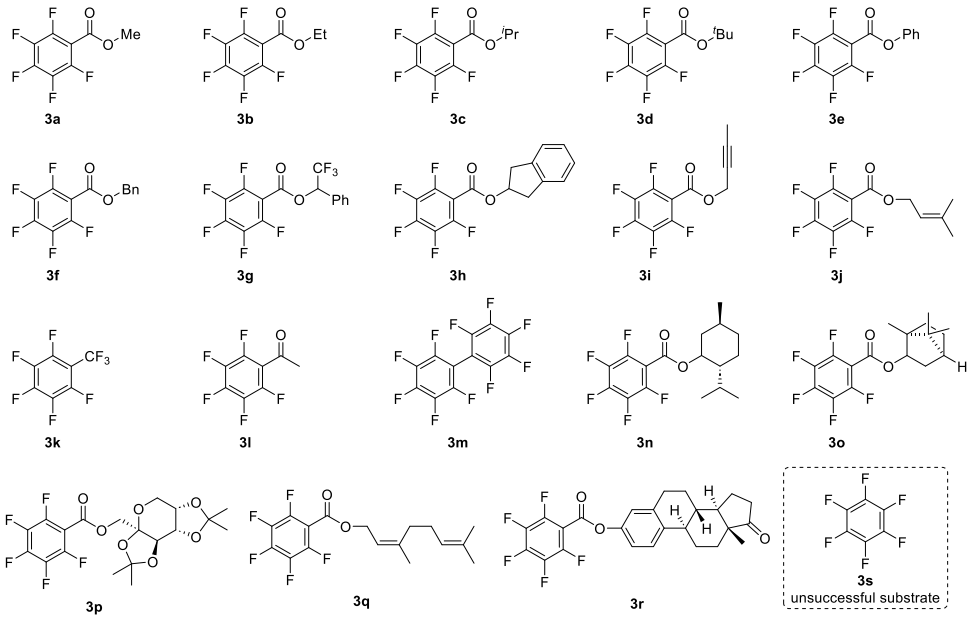
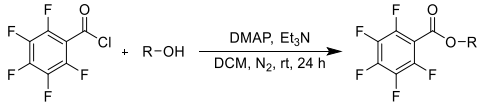


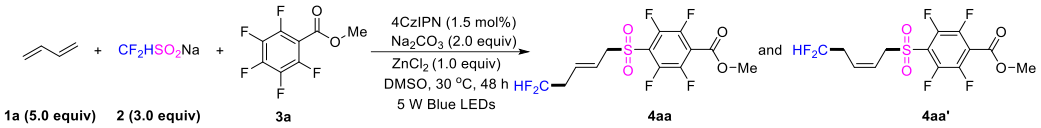
Table **S6** Substrate of polyfluoroaromatics



To a solution of Pentafluorobenzoyl chloride (1.2 g, 5 mmol) in DCM (15 mL) was added Et_3N (1.0 g, 10 mmol), DMAP (61.0 mg, 0.5 mmol), and alcohol (6.0 mmol). The mixture was stirred for 24 h at room temperature. After filtration, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the products.[7]

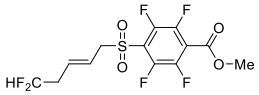
Reagents **3a-3b, 3k-3m, 3s** were purchased from commercial sources.

IV. General Procedure for the Synthesis of Product



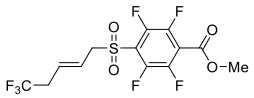
Taking 4aa as an example: In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar were charged with 4CzIPN (2.4 mg, 1.5 mol%) and dry DMSO (1.5 mL). Then buta-1,3-diene **1a** (500 ul, 1.0 mmol), CF_2HSO_2Na **2** (82.8 mg, 3.0 equiv), $ZnCl_2$ (1.0 equiv), Na_2CO_3 (0.4 mmol, 2.0 equiv) and Methyl 2,3,4,5,6-pentafluorobenzoate **3a** (45.2 mg, 1.0 equiv) were added. The reaction mixture was irradiated with 5W Blue LEDs at 30 ℃ for 48 h, until the reaction was complete as indicated by TLC. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered. And the reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1) to obtain product **4aa** and **4aa'**.

V. Characterization Data of Compounds



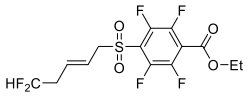
methyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4aa)

The title compound **4aa** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4aa** was obtained as a white solid (56.4 mg, 74%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.6 (m, 3H), 4.07 (d, J = 7.2 Hz, 2H), 4.03 (s, 3H), 2.65 – 2.56 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.67, 144.63 (dm, J = 258.2 Hz), 144.44 (dm, J = 264.2 Hz), 132.39 (t, J = 5.9 Hz), 120.93, 119.81 (t, J = 14.3 Hz), 117.81 (t, J = 16.9 Hz), 114.79 (t, J = 240.7 Hz), 60.99, 53.88, 37.25 (t, J = 22.2 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.96 (t, J = 17.5 Hz), -117.06 (t, J = 17.5 Hz), -134.84 – -135.02 (m), -135.93 – -136.07 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{10}F_6O_4NaS$, ($[M + Na]^+$), 399.0096, found: 399.0098.



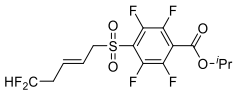
methyl (*E*)-2,3,5,6-tetrafluoro-4-((5,5,5-trifluoropent-2-en-1-yl)sulfonyl)benzoate (4aa'')

The title compound **4aa''** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4aa''** was obtained as a white solid (53.6 mg, 68%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.87 (dt, J = 15.3, 7.5 Hz, 1H), 5.76 – 5.63 (m, 1H), 4.09 (d, J = 7.5 Hz, 2H), 4.03 (s, 3H), 2.92 – 2.82 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.63, 144.69 (dm, J = 262.7 Hz), 144.57 (dm, J = 257.8 Hz), 130.25,124.99 (q, J = 276.8 Hz), 122.68, 119.70 (t, J = 14.8 Hz), 117.97 (t, J = 17.0 Hz), 60.78, 53.94, 37.18 (q, J = 30.4 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -66.41 (t, J = 10.4 Hz), -134.68 – -135.01 (m), -135.64 – -135.98 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_9F_7O_4NaS$, ($[M + Na]^+$), 417.0002, found: 417.0007.



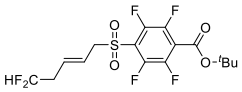
ethyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ab)

The title compound **4ab** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ab** was obtained as a white solid (59.3 mg, 76%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85-5.65 (m, 3H), 4.49 (q, J = 7.0 Hz, 2H), 4.07 (d, J =7.0 Hz, 2H), 2.65-2.58 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.14, 144.56 (dm, J = 261.7 Hz), 144.46 (dm, J = 261.6 Hz), 132.39 (t, J = 6.1 Hz), 120.89, 119.61 (t, J = 14.6 Hz), 118.32 (t, J = 17.3 Hz), 114.81 (t, J = 240.9 Hz), 63.54, 60.97, 37.27 (t, J = 22.2 Hz), 13.98. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.90 (t, J = 17.8 Hz), -117.00 (t, J = 17.8 Hz), -134.95 – 135.09 (m), -136.34 – 136.45 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{12}F_6O_4NaS$, ($[M + Na]^+$), 413.0253, found: 413.0255.



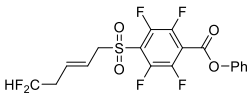
isopropyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ac)

The title compound **4ac** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ac** was obtained as a white solid (72.3 mg, 68%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.65 (m, 3H), 5.38 – 5.30 (m, 1H), 4.06 (d, J = 6.6 Hz, 2H), 2.67 – 2.56 (m, 2H), 1.40 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.64, 144.46 (dm, J = 261.2 Hz), 144.32 (dm, J = 261.2 Hz), 132.39 (t, J = 6.2 Hz), 120.87, 119.42 (t, J = 14.9 Hz), 118.81 (t, J = 17.5 Hz), 114.84 (t, J = 241.0 Hz), 72.09, 60.96, 37.28 (t, J = 22.2 Hz), 21.60. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.86 (t, J = 17.5 Hz), -116.96 (t, J = 17.5 Hz), -135.04 – -135.16 (m), -136.80 – -136.89 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{14}F_6O_4NaS$, ($[M + Na]^+$), 427.0409, found: 427.0399.



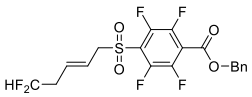
tert-butyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ad)

The title compound **4ad** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ad** was obtained as a white solid (32.6 mg, 40%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.64 (m, 3H), 4.05 (d, J = 7.2 Hz, 2H), 2.66 – 2.56 (m, 2H), 1.61 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.98, 144.50 (dm, J = 259.5 Hz), 144.12(dm, J = 258.0 Hz), 132.36(t, J = 6.0 Hz), 120.91, 119.90 (t, J = 18.4 Hz), 119.00 (t, J = 14.8 Hz), 114.84 (t, J = 239.5 Hz), 86.21, 60.97, 37.33 (t, J = 22.0 Hz), 28.01. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.79 (t, J = 18.1 Hz), -116.89 (t, J = 18.1 Hz), -135.11 – -135.24 (m), -137.66 – -137.78 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{16}F_6O_4NaS$, ($[M + Na]^+$), 441.0566, found: 441.0556.



phenyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ae)

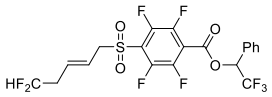
The title compound **4ae** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ae** was obtained as a white solid (54.4 mg, 62%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (t, J = 7.8 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.28 – 7.24 (m, 2H), 5.87 – 5.67 (m, 3H), 4.09 (d, J = 7.2 Hz, 2H), 2.67 – 2.58 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.68, 149.87, 144.85(dm, J = 270.3 Hz), 144.61 (dm, J = 262.7 Hz), 132.48 (t, J = 6.0 Hz), 129.81, 127.02, 121.09, 120.92, 120.34, 117.43 (t, J = 16.7 Hz), 114.78 (t, J = 240.7 Hz), 61.05, 37.28 (t, J = 22.0 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.96 (t, J = 18.1 Hz), -117.05 (t, J = 17.5 Hz), -134.43 – 134.55 (m), -135.33 – -135.45 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{12}F_6O_4NaS$, 461.0253, ($[M + Na]^+$), found: 461.0267.



benzyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4af)

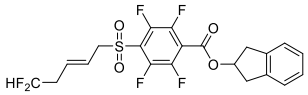
The title compound **4af** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4af** was obtained as a white solid

(67.9 mg, 75%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 5H), 5.83 – 5.63 (m, 3H), 5.43 (s, 2H), 4.05 (d, J = 7.2 Hz, 2H), 2.64 – 2.54 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.04, 144.67 (dm, J =261.2 Hz), 144.5 (dm, J =265.7 Hz), 134.08, 132.40 (t, J = 6.2 Hz), 128.90, 128.76, 128.41, 120.85, 119.85 (t, J = 14.3 Hz), 117.84 (t, J = 16.6 Hz), 114.79 (t, J = 241.0 Hz), 68.98, 60.96, 37.24 (t, J = 22.0 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.87 (t, J = 17.5 Hz), -116.97 (t, J = 18.1 Hz), -134.83 – -134.94 (m), -135.78 – -135.87 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{14}F_6O_4NaS$, 475.0409, ([M + Na]$^+$), found: 475.0419.



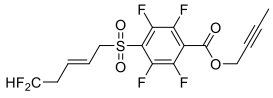
2,2,2-trifluoro-1-phenylethyl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ag)

The title compound **4ag** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ag** was obtained as a white solid (68.7 mg, 66%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 2H), 7.49 – 7.41 (m, 3H), 6.38 – 6.34 (m, 1H), 5.85 – 5.65 (m, 3H), 4.08 (d, J = 7.2 Hz, 2H), 2.67 – 2.54 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.34, 145.09 (dm, J = 259.7 Hz), 144.60 (dm, J = 274.8 Hz), 132.50 (t, J = 6.0 Hz), 130.53, 129.60, 128.95, 128.13, 122.54 (q, J = 278.8 Hz), 120.90, 120.74 (d, J = 14.7 Hz), 116.04 (t, J = 15.5 Hz), 114.74 (t, J = 240.8 Hz), 74.29 (q, J = 34.1 Hz), 61.07, 37.22 (t, J = 22.0 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -76.00 (d, J = 6.2 Hz), -117.18 (t, J = 18.1 Hz), -117.28 (t, J = 18.1 Hz), -134.32 – -134.45 (m), -134.70 – -134.83 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{13}F_9O_4NaS$, ([M + Na]$^+$), 543.0283, found: 543.0271.



2,3-dihydro-1H-inden-2-yl(*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ah)

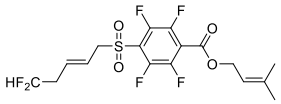
The title compound **4ah** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ah** was obtained as a white solid (58.4 mg, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 – 7.26 (m, 2H), 7.22 – 7.21 (m, 2H), 5.88 – 5.85 (m, 1H), 5.88 – 5.61 (m, 3H), 4.03 (d, J = 7.2 Hz, 2H), 3.46 – 3.43 (m, 2H), 3.18 – 3.16 (m, 2H), 2.62 – 2.55 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.10, 144.53 (dm, J = 261.5 Hz), 144.43 (dm, J = 262.4 Hz), 139.60, 132.45 (t, J = 6.0 Hz), 127.12, 124.69, 120.82, 119.69 (t, J = 14.5 Hz), 118.33 (t, J = 17.2 Hz), 114.83 (t, J = 240.8 Hz), 60.99, 60.41, 53.44, 39.52, 37.31 (t, J = 22.2 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.80 (t, J = 18.1 Hz), -116.90 (t, J = 18.1 Hz), -134.87 – -134.95 (m), -136.34 – -136.45 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{16}F_6O_4NaS$, ([M + Na]$^+$), 501.0566, found: 501.0572.



but-2-yn-1-yl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ai)

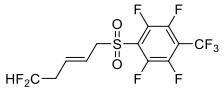
The title compound **4ai** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ai** was obtained as a white solid (33.1 mg, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.86 – 5.66 (m, 3H), 4.97 (d, J = 1.2 Hz, 2H), 4.07 (d, J = 6.6 Hz, 2H), 2.67 – 2.56 (m, 2H), 1.89 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.67, 144.68 (dm, J

= 271.8 Hz), 144.49 (dm, *J* = 268.7 Hz), 132.43 (t, *J* = 6.1 Hz), 120.82, 120.05 (t, *J* = 14.3 Hz), 117.44 (t, *J* = 16.7 Hz), 114.81 (t, *J* = 240.9 Hz), 85.12, 71.48, 60.97, 55.48, 37.26 (t, *J* = 22.0 Hz), 3.60. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.86 (t, *J* = 18.0 Hz), -116.96 (t, *J* = 17.5 Hz), -134.75 – -134.94 (m), -135.51 – -135.72 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{12}F_6O_4NaS$, ($[M + Na]^+$), 437.0253, found: 437.0243.



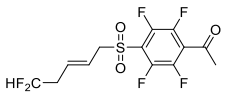
3-methylbut-2-en-1-yl (*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4aj)

The title compound **4aj** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4aj** was obtained as a white solid (29.1 mg, 35%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.65 (m, 3H), 5.44 (t, *J* = 7.8 Hz, 1H), 4.90 (d, *J* = 7.2 Hz, 2H), 4.06 (d, *J* = 7.2 Hz, 2H), 2.68 – 2.54 (m, 2H), 1.80 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.19, 144.54 (dm, *J* = 264.25 Hz), 144.45 (dm, *J* = 261.23Hz), 141.80, 132.40 (t, *J* = 6.0 Hz), 120.88, 119.53 (t, *J* = 14.0 Hz), 118.40 (t, *J* = 17.0 Hz), 116.89, 114.81 (t, *J* = 240.8 Hz), 64.20, 60.98, 37.31 (t, *J* = 22.3 Hz), 25.77, 18.11. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.81 (t, *J* = 17.5 Hz), -116.91 (t, *J* = 17.5 Hz), -134.95 – -135.11 (m), -136.16 – -136.28 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{16}F_6O_4NaS$, ($[M + Na]^+$), 453.0566, found: 453.0576.



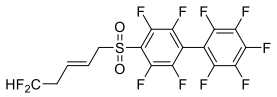
(*E*)-1-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (4ak)

The title compound **4ak** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ak** was obtained as a white solid (50.2 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.65 (m, 3H), 4.09 (d, *J* = 7.2 Hz, 2H), 2.61 – 2.53 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.76 (dm, *J* = 267.2 Hz), 144.53 (dm, *J* = 271.8 Hz), 132.51 (t, *J* = 5.8 Hz), 120.96 (q, *J* = 14.9Hz), 119.98 (q, *J* = 275.1 Hz), 119.07, 118.25, 114.63 (t, *J* = 240.6 Hz), 61.11, 37.14 (t, *J* = 21.8 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -57.00 (t, *J* = 22.0 Hz), -117.59 (t, *J* = 18.6 Hz), -117.69 (t, *J* = 18.6 Hz), -133.92 – -134.03 (m), -136.37 – -136.59 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_7F_9O_2NaS$, ($[M + Na]^+$), 408.9915, found: 408.9924.



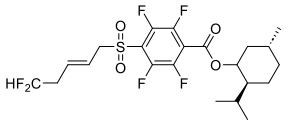
(*E*)-1-(4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorophenyl)ethan-1-one (4al)

The title compound **4al** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4al** was obtained as a white solid (45.4 mg, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.86 – 5.65 (m, 3H), 4.06 (d, *J* = 7.2 Hz, 2H), 2.64 (d, *J* = 1.2 Hz, 3H), 2.62 – 2.56 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.64, 144.56 (dm, *J* = 262.7 Hz), 143.64 (dm, *J* = 261.23 Hz), 132.20 (t, *J* = 5.9 Hz), 124.58 (t, *J* = 18.6 Hz), 121.19, 119.14 (t, *J* = 14.6 Hz), 118.46, 114.80 (t, *J* = 240.7 Hz), 60.99, 37.17 (t, *J* = 21.9 Hz), 32.16. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.22 (t, *J* = 18.1 Hz), -117.32 (t, *J* = 18.1 Hz), -134.57 – -134.70(m), -138.76 – -138.87 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{10}F_6O_3NaS$, ($[M + Na]^+$), 383.0147, found: 383.0146.



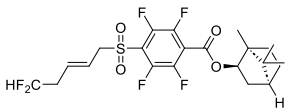
(*E*)-4-((5,5-difluoropent-2-en-1-yl)sulfonyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl (4am)

The title compound **4am** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4am** was obtained as a white solid (78.5 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.87 – 5.62 (m, 3H), 4.11 (d, J = 7.2 Hz, 2H), 2.68 – 2.57 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.57 (dm, J = 261.2 Hz), 144.33 (dm, J = 250.6 Hz), 138.04 (dm, J = 249.7 Hz), 137.88 (dm, J = 252.0 Hz), 132.35 (t, J = 5.8 Hz), 121.21, 119.32 (t, J = 14.8 Hz), 114.72 (t, J = 240.9 Hz), 112.27 (t, J = 18.3 Hz), 101.56, 61.12, 37.27 (t, J = 22.0 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.28 (t, J = 18.0 Hz), -117.38 (t, J = 17.5 Hz), -134.25 – -134.45 (m), -135.18 – -135.30 (m), -136.64 – -136.78 (m), -148.14 (t, J = 20.9 Hz), -159.48 – -159.60 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_7F_{11}O_2NaS$, ($[M + Na]^+$), 506.9883, found: 506.9894.



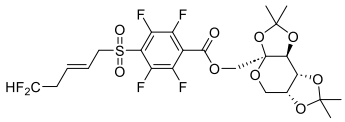
(2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(((*E*)-5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4an)

The title compound **4an** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4an** was obtained as a white solid (52.1 mg, 52%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.84 – 5.64 (m, 3H), 5.02 (td, J = 9.6, 4.2 Hz, 1H), 4.06 (d, J = 7.2 Hz, 2H), 2.66 – 2.57 (m, 2H), 2.20 – 2.12 (m, 1H), 1.99 – 1.89 (m, 1H), 1.77 – 1.69 (m, 2H), 1.59 – 1.52 (m, 1H), 1.52 – 1.45 (m, 1H), 1.19 – 1.06 (m, 2H), 0.96 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 3.6 Hz, 1H), 0.81 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.83, 144.47 (dm, J = 261.2 Hz), 144.21 (dm, J = 261.23 Hz), 132.40 (t, J = 6.2 Hz), 120.89, 119.30 (t, J = 14.8 Hz), 119.01 (t, J = 18.1 Hz), 114.82 (t, J = 241.1 Hz), 78.62, 60.99, 46.80, 40.50, 37.32 (t, J = 22.2 Hz), 33.97, 31.50, 25.98, 23.11, 21.90, 20.70, 15.87. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.83 (t, J = 17.5 Hz), -116.93 (t, J = 18.1 Hz), -134.91 – -135.02 (m), -136.75 – -136.85 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{26}F_6O_4NaS$, ($[M + Na]^+$), 523.1348, found: 523.1337.



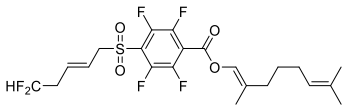
(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl4-(((*E*)-5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ao)

The title compound **4ao** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ao** was obtained as a white solid (47.9 mg, 48%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85-5.65 (m, 3H), 5.23 – 5.20 (m, 1H), 4.07 (d, J = 7.2 Hz, 2H), 2.56 – 2.47 (m, 2H), 2.53 – 2.47 (m, 1H), 1.95 – 1.91 (m, 1H), 1.81 – 1.76 (m, 2H), 1.39 – 1.34 (m, 1H), 1.29 – 1.24 (m, 1H), 1.17 – 1.14 (m, 1H), 0.96 (s, 3H), 0.91 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.49, 144.64 (dm, J = 261.2 Hz), 144.51 (dm, J = 260.9 Hz), 132.42 (t, J = 6.1 Hz), 120.97, 119.49 (t, J = 14.4 Hz), 118.64 (t, J = 17.3 Hz), 114.82 (t, J = 240.9 Hz), 84.21, 61.03, 49.13, 48.01, 44.84, 37.31 (t, J = 22.2 Hz), 36.67, 27.90, 27.03, 19.67, 18.84, 13.34. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.91 (t, J = 17.9 Hz), -117.00 (t, J = 17.9 Hz), -134.96 – -135.11 (m), -136.32 – -136.53 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{24}F_6O_4NaS$, ($[M + Na]^+$), 521.1192, found: 521.1191.



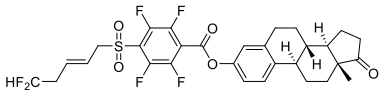
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl4-(((*E*)-5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ap)

The title compound **4ap** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ap** was obtained as a white solid (59.2 mg, 49%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85-5.65 (m, 3H), 4.69 (d, J = 11.4 Hz, 1H), 4.64 (d, J = 7.8 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 4.34 (d, J = 3.0 Hz, 1H), 4.26 (d, J = 9.0 Hz, 1H), 4.07 (d, J = 7.2 Hz, 2H), 3.94 (d, J = 13.0 Hz, 1H), 3.79 (d, J = 13.0 Hz, 1H), 2.61 – 2.57 (m, 2H), 1.55 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.61, 144.73 (dm, J = 262.3 Hz), 144.51 (dm, J = 260.5 Hz), 132.43 (t, J = 6.0 Hz), 120.91, 120.10 (t, J = 14.8 Hz), 117.56 (t, J = 16.8 Hz), 114.78 (t, J = 241.1 Hz), 109.22 (d, J = 4.0 Hz), 100.80, 70.69, 70.52, 69.93, 67.50, 61.50, 61.00, 37.27 (t, J = 22.2 Hz), 26.50, 25.82, 24.92, 24.04. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.89 (t, J = 15.3 Hz), -116.99 (t, J = 18.1 Hz), -134.73 – -134.65 (m), -135.18 – -135.09 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{26}F_6O_9NaS$, ($[M + Na]^+$), 627.1094, found: 627.1074.



(*E*)-2,7-dimethylocta-1,6-dien-1-yl 4-(((*E*)-5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluoro-benzoate (4aq)

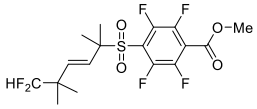
The title compound **4aq** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4aq** was obtained as a white solid (45.9 mg, 46%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.65 (m, 3H), 5.47 – 5.39 (m, 1H), 5.10 – 5.05 (m, 1H), 4.92 (d, J = 7.2 Hz, 2H), 4.06 (d, J = 7.0 Hz, 2H), 2.65 – 2.57 (m, 2H), 2.15 – 2.07 (m, 4H), 1.77 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.18, 145.36 (dm, J = 261.7 Hz), 145.03, 143.62 (dm, J = 262.1 Hz), 132.40 (t, J = 6.1 Hz), 132.03, 123.44, 120.87, 119.58 (t, J = 14.4 Hz), 118.42, 118.37, 116.62, 114.81(t, J = 241.0 Hz), 64.19, 60.98, 39.48, 37.30 (t, J = 22.2 Hz), 26.16, 25.61, 17.65, 16.54. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.81 (t, J = 17.6 Hz), -116.90 (t, J = 17.6 Hz), -134.85 – -135.37 (m), -136.18 – -136.42 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{22}H_{24}F_6O_4NaS$, ($[M + Na]^+$), 521.1192, found: 521.1188.



(8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a] phenanthren-3-yl4-(((*E*)-5,5-difluoropent-2-en-1-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ar)

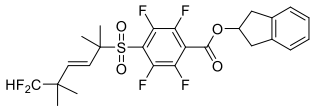
The title compound **4ar** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ar** was obtained as a white solid (47.9 mg, 41%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 9.0 Hz, 1H), 6.99 (s, 1H), 5.87 – 5.67 (m, 3H), 4.09 (d, J = 6.6 Hz, 2H) 2.96 (q, J =4.8 Hz, 2H), 2.65 – 2.57 (m, 2H), 2.54 – 2.50 (m, 1H), 2.45 – 2.42 (m, 1H), 2.34 – 2.30 (m, 1H), 2.21 – 2.12 (m, 1H), 2.11 – 2.02 (m, 2H), 1.99 (m, 1H), 1.68 – 1.61 (m, 2H), 1.56 – 1.50 (m, 3H), 0.93 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 220.52, 156.93, 147.84, 144.87(dm, J = 262.3 Hz), 144.72(dm, J = 260.9 Hz), 138.78, 138.65, 132.49 (t, J = 6.0 Hz), 126.79, 121.05, 120.94, 120.34 (t, J = 14.5 Hz), 118.21, 117.61 (t, J = 16.5 Hz), 114.82 (t, J = 240.8

Hz), 61.09, 50.47, 47.93, 44.20, 37.99, 37.32 (t, J = 22.2 Hz), 35.84, 31.57, 29.44, 26.27, 25.80, 21.61, 13.85. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.91 (t, J = 17.5 Hz), -117.01 (t, J = 17.5 Hz), -134.52 – -134.55 (m), -135.42 – -135.49 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{30}H_{28}F_6O_5NaS$, ($[M + Na]^+$), 637.0485, found: 637.0492.



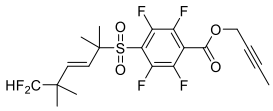
methyl(*E*)-4-((6,6-difluoro-2,5,5-trimethylhex-3-en-2-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4ba)

The title compound **4ba** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4ba** was obtained as a white solid (63.1 mg, 73%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.89 (d, J = 16.2 Hz, 1H), 5.58 (d, J = 16.2 Hz, 1H), 5.37 (t, J = 56.4 Hz, 1H), 4.02 (s, 3H), 1.56 (s, 6H), 1.08 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.78, 145.18 (dm, J = 258.5 Hz), 144.52 (dm, J = 260.2 Hz), 137.21 (t, J = 3.9 Hz), 128.06, 119.06 (t, J = 247.3 Hz), 67.50, 53.84, 41.13 (t, J = 18.7 Hz), 20.42 (t, J = 3.9 Hz), 19.98. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -126.45, -126.55, -130.15 – -130.21 (m), -136.38 – -136.42 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{18}F_6O_4NaS$, ($[M + Na]^+$), 455.0722, found: 455.0713.



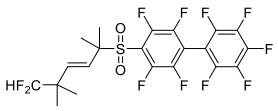
2,3-dihydro-1H-inden-2-yl(*E*)-4-((6,6-difluoro-2,5,5-trimethylhex-3-en-2-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (4bh)

The title compound **4bh** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4bh** was obtained as a white solid (82.3 mg, 77%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 – 7.26 (m, 2H), 7.22 – 7.20 (m, 2H), 5.89 – 5.85 (m, 2H), 5.56 (d, J = 16.2 Hz, 1H), 5.35 (t, J = 57.0 Hz, 1H), 3.47 – 3.43 (m, 2H), 3.19 – 3.15 (m, 2H), 1.54 (s, 6H), 1.06 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.20, 145.13 (dm, J = 262.7 Hz), 144.42 (dm, J = 261.2 Hz), 139.60, 137.24 (t, J = 3.9 Hz), 128.00, 127.11, 124.68, 119.03 (t, J = 247.2 Hz), 78.91, 67.46, 41.14 (t, J = 18.7 Hz), 39.51, 20.41 (t, J = 3.9 Hz), 20.02. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -126.43, -126.53, -130.18 – -130.20 (m), -136.79 – -136.82 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}F_6O_4NaS$, ($[M + Na]^+$), 557.1192, found: 557.1187.



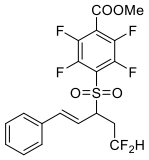
but-2-yn-1-yl(*E*)-4-((6,6-difluoro-2,5,5-trimethylhex-3-en-2-yl)sulfonyl)-2,3,5,6-tetrafluorobenzo-ate (4bi)

The title compound **4bi** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4bi** was obtained as a white solid (48.9 mg, 52%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.89 (d, J = 16.2 Hz, 1H), 5.58 (d, J = 16.2 Hz, 1H), 5.37 (t, J = 56.4 Hz, 1H), 4.96 (s, 2H), 1.89 (s, 3H), 1.56 (s, 6H), 1.08 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.81, 145.18 (dm, J = 262.7 Hz), 144.64 (dm, J = 262.1 Hz), 137.24 (t, J = 3.8 Hz), 128.02, 119.05 (t, J = 247.3 Hz), 85.14, 71.52, 67.50, 55.50, 41.15 (t, J = 18.9 Hz), 20.44 (t, J = 3.6 Hz), 20.00, 3.66. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -126.41, -126.51, -129.41 – -130.06 (m), -135.92 – -135.98 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{20}F_6O_4NaS$, ($[M + Na]^+$), 493.0879, found: 493.0871.



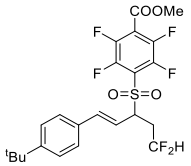
(*E*)-4-((6,6-difluoro-2,5,5-trimethylhex-3-en-2-yl)sulfonyl)-2,2',3,3',4',5,5',6,6'-nonafluoro-1,1'-biphenyl (4bm)

The title compound **4bm** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4bm** was obtained as a white solid (58.4 mg, 54%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.94 (d, *J* = 16.2 Hz, 1H), 5.60 (d, *J* = 16.2 Hz, 1H), 5.37 (t, *J* = 56.7 Hz), 1.61 (s, 6H), 1.08 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.17 (dm, *J* = 277.7Hz), 145.16 (dm, *J* = 277.8 Hz), 144.38 (dm, *J* = 259.1 Hz), 144.37 (dm, *J* = 259.0 Hz), 137.20, 128.21, 119.08 (t, *J* = 247.2 Hz), 108.83 (t, *J* = 22.3 Hz), 67.63, 41.14 (t, *J* = 18.8 Hz), 20.47, 20.02. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -126.52 (d, *J* = 56.8 Hz), -130.49 – -130.82 (m), -134.58 – -134.67 (m), -136.71 – -136.87 (m), -137.62 – -137.65 (m), -148.23 (t, *J* = 20.9 Hz), -159.55 – -159.61 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{15}F_{11}O_2NaS$, ($[M + Na]^+$), 563.0509, found: 563.0506.



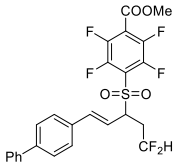
methyl (*E*)-4-((5,5-difluoro-1-phenylpent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5ca)

The title compound **5ca** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ca** was obtained as a white solid (66.9 mg, 74%). **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.34 – 7.30 (m, 5H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.13 – 5.92 (m, 2H), 4.20 (td, *J* = 10.2, 4.2 Hz, 1H), 3.99 (s, 3H), 2.83 – 2.74 (m, 1H), 2.56 – 2.45 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 158.55, 144.78 (dm, *J* = 263.0 Hz), 144.61 (dm, *J* = 254.9 Hz), 140.57, 134.50, 129.51, 128.92, 126.90, 119.22 (t, *J* = 14.5 Hz), 118.16 (t, *J* = 16.8 Hz), 117.57, 114.46 (t, *J* = 241.8 Hz), 66.07 (t, *J* = 4.7 Hz), 53.90, 31.65 (t, *J* = 23.7 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) *δ* -116.35 – -117.16 (m), -133.65 – -133.72 (m), -135.67 – -135.73 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{14}F_6O_4NaS$, ($[M + Na]^+$), 475.0409, found: 475.0412.



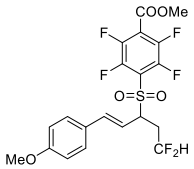
Methyl (*E*)-4-((1-(4-(tert-butyl)phenyl)-5,5-difluoropent-1-en-3-yl)sulfonyl)-2,3,5,6-tetra-fluoro-benzoate (5da)

The title compound **5da** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5da** was obtained as a white solid (74.2 mg, 73%). **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 10.8 Hz, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.10 – 5.90 (m, 2H), 4.20 (td, *J* = 9.6 Hz, 4.2 Hz, 1H), 3.99 (s, 3H), 2.83 – 2.74 (m, 1H), 2.55 – 2.44 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 158.61, 152.98, 144.77 (dm, *J* = 263.0 Hz), 144.71 (dm, *J* = 263.0 Hz), 140.40, 131.72, 126.74, 125.87, 119.36 (t, *J* = 14.8 Hz), 118.06 (t, *J* = 16.6 Hz), 116.51, 114.51 (t, *J* = 241.8 Hz), 66.13 (t, *J* = 6.2 Hz), 53.91, 34.78, 31.63 (t, *J* = 23.9 Hz), 31.17. **^{19}F NMR** (565 MHz, $CDCl_3$) *δ*-115.64 – -117.17 (m), -133.71 – -133.76 (m), -135.61 – -135.64 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}F_6O_4NaS$, ($[M + Na]^+$), 531.1035, found: 531.1022.



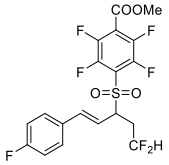
methyl (*E*)-4-((1-([1,1'-biphenyl]-4-yl)-5,5-difluoropent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5ea)

The title compound **5ea** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ea** was obtained as a white solid (42.3 mg, 40%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (t, J = 7.2 Hz, 4H), 7.45 (t, J = 7.2 Hz, 2H), 7.41 – 7.35 (m, 3H), 6.58 (d, J = 16.2 Hz, 1H), 6.17 – 5.94 (m, 2H), 4.23 (td, J = 10.2, 4.2 Hz, 1H), 3.99 (s, 3H), 2.85 – (m, 1H), 2.58 – 2.48 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.57, 144.80 (dm, J = 261.3 Hz), 144.60 (dm, J = 291.1 Hz), 142.36, 140.13, 140.10, 133.41, 128.90, 127.79, 127.58, 127.39, 127.02, 119.27 (t, J = 15.6 Hz), 118.175 (t, J = 16.6 Hz), 117.41, 114.47 (t, J = 241.4 Hz), 66.13, 53.93, 31.69 (t, J = 23.7 Hz).**^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.34 – -117.35 (m), -133.61 – -133.66 (m), -135.51 – -135.57 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{18}F_6O_4NaS$, ($[M + Na]^+$), 551.0722, found: 551.0731.



methyl (*E*)-4-((5,5-difluoro-1-(4-methoxyphenyl)pent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5fa)

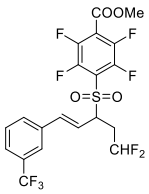
The title compound **5fa** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5fa** was obtained as a white solid (74.3 mg, 77%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 15.6 Hz, 1H), 6.12 – 5.91 (m, 2H), 4.16 (td, J = 10.2, 3.6 Hz, 1H) 3.99 (s, 3H), 3.81 (s, 3H), 2.81 – 2.72 (m, 1H), 2.54 – 2.44 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.69, 158.60, 144.75 (dm, J = 263.1 Hz), 144.43 (dm, J = 260.0 Hz), 140.08, 131.00, 128.35, 127.22, 114.79, 114.72, 114.53 (t, J = 241.4 Hz), 114.32, 66.27, 55.36, 53.90, 31.69 (t, J = 23.9 Hz).**^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.69 – -117.152 (m), -133.67 – -133.74 (m), -135.74 – -135.81 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{16}F_6O_5NaS$, ($[M + Na]^+$), 505.0517, found: 505.0520.



Methyl (*E*)-4-((5,5-difluoro-1-(4-fluorophenyl)pent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5ga)

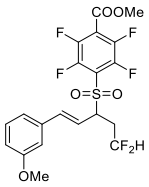
The title compound **5ga** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ga** was obtained as a white solid (69.6 mg, 74%).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.02 (t, J = 8.4 Hz 2H), 6.51 (d, J = 15.6 Hz, 1H), 6.13 – 5.92 (m, 2H), 4.18 (td, J = 10.2, 4.2 Hz, 1H), 4.00 (s, 3H), 2.81 – 2.72 (m, 1H), 2.56 – 2.45 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.20, 162.55, 158.55, 144.78 (dm, J = 262.0 Hz), 144.48 (dm, J = 262.9 Hz), 128.71, 128.66, 128.71, 128.66, 119.22 (dt, J = 14.3, 16.8 Hz), 118.21 (t, J = 17.1 Hz), 116.10, 115.96, 114.43 (t, J = 241.6 Hz), 65.98 (t, J = 4.1 Hz), 53.97, 31.65 (t, J = 23.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.91, -115.49 – 117.24 (m), -133.66 (q, J = 9.6 Hz), -135.64 (q, J = 9.6 Hz). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{13}F_7O_4NaS$, ($[M + Na]^+$), 493.0315, found: 493.0334.



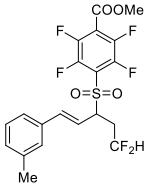
methyl (*E*)-2,3,5,6-tetrafluoro-4-((5,5,5-trifluoro-1-(4-(trifluoromethyl)phenyl)pent-1-en-3-yl) sulfonyl)benzoate (5ha)

The title compound **5ha** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ha** was obtained as a white solid (54.9 mg, 51%).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (d, J = 7.4 Hz, 1H), 7.55 – 7.45 (m, 3H), 6.59 (d, J = 15.8 Hz, 1H), 6.21 (dd, J = 15.9, 9.8 Hz, 1H), 6.05 (tt, J = 55.6, 3.6 Hz, 1H), 4.23 (td, J = 9.9, 4.1 Hz, 1H), 4.00 (s, 3H), 2.84 – 2.75 (m, 1H), 2.61 – 2.45 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.49, 144.71 (dm, J = 283.3 Hz), 144.55 (dm, J = 278.7 Hz), 138.94, 135.24, 131.47 (q, J = 32.4 Hz), 129.81, 129.54, 124.90 (dd, J = 345.7, 3.9 Hz), 123.73 (q, J = 272.6 Hz), 119.78, 118.96 (t, J = 14.3 Hz), 118.39 (t, J = 16.8 Hz), 114.32 (t, J = 241.8 Hz), 65.90 – 65.63 (m), 54.00, 31.65 (t, J = 23.5 Hz), 29.71. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.93, -115.27 – 117.31 (m), -135.57 – 135.59 (m), -135.38 – 135.40 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{12}F_{10}O_4NaS$, ($[M + Na]^+$), 561.0189, found: 561.0194.



methyl (*E*)-4-((5,5-difluoro-1-(3-methoxyphenyl)pent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5ia)

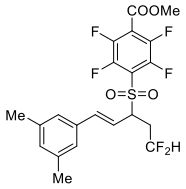
The title compound **5ia** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ia** was obtained as a white solid (50.2 mg, 52%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (t, J = 8.4 Hz, 1H), 6.87 (t, J = 8.4 Hz, 2H), 6.82 (s, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.15 – 5.88 (m, 2H), 4.19 (td, J = 9.6, 4.2 Hz, 1H), 3.99 (s, 3H), 3.81 (s, 3H), 2.82 – 2.74 (m, 1H), 2.57 – 2.44 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.97, 158.55, 144.78 (dm, J = 264.3 Hz), 144.64 (dm, J = 251.3 Hz), 140.49, 135.85, 129.94, 119.50, 119.18 (t, J = 15.0 Hz), 118.16 (t, J = 16.9 Hz), 117.86, 115.32, 114.45 (t, J = 241.6 Hz), 112.01, 66.03, 55.29, 53.91, 31.61 (t, J = 23.9 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.42 – -117.29 (m), -133.67 – -133.71 (m), -135.62 – -135.68 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{16}F_6O_5NaS$, ($[M + Na]^+$), 505.0517, found: 505.0526.



methyl (*E*)-4-((5,5-difluoro-1-(m-tolyl)pent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5ja)

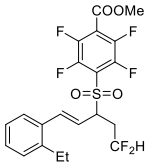
The title compound **5ja** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ja** was obtained as a white solid

(39.2 mg, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 1H), 7.15 – 7.09 (m, 3H), 6.50 (d, J = 15.6 Hz, 1H), 6.12 – 5.92 (m, 2H), 4.19 (td, J = 10.0, 4.2 Hz, 1H), 3.99 (s, 3H), 2.83 – 2.74 (m, 1H), 2.55 – 2.44 (m, 1H), 2.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.58, 144.77 (dm, J = 263.3 Hz), 144.54 (dm, J = 278.3 Hz), 140.74, 138.64, 134.41, 130.33, 128.80, 127.57, 124.10, 119.23 (t, J = 14.5 Hz), 118.12 (t, J = 16.6 Hz) 117.25, 114.48 (t, J = 241.5 Hz), 66.10 (t, J = 6.2 Hz), 53.93, 31.60 (t, J = 24.0 Hz), 21.29. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.45 – -117.93 (m), -133.67 – -133.73 (m), -135.64 – -135.70 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{16}F_6O_4NaS$, ($[M + Na]^+$), 489.0566, found: 489.0556.



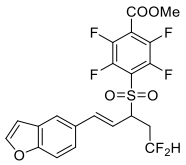
methyl (*E*)-4-((1-(3,5-dimethylphenyl)-5,5-difluoropent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5ka)

The title compound **5ka** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ka** was obtained as a white solid (81.6 mg, 85%).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.91 (s, 2H), 6.45 (d, J = 16.2 Hz, 1H), 6.11 – 5.91 (m, 2H), 4.18 (td, J = 10.2, 3.6 Hz, 1H), 3.99 (s, 3H), 2.82 – 2.73 (m, 1H), 2.55 – 2.44 (m, 1H), 2.29 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.58, 144.77 (dm, J = 262.9 Hz), 144.62 (dm, J = 254.7 Hz), 140.89, 138.50, 134.41, 131.24, 124.78, 119.29 (t, J = 14.2 Hz), 118.09 (t, J = 16.8 Hz), 117.02, 114.50 (t, J = 241.8 Hz), 66.16 (t, J = 4.5 Hz), 53.88, 31.61 (t, J = 23.6 Hz), 21.13.**^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.30 – -117.40 (m), -133.71 – -133.77 (m), -135.70 – -135.76 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}F_6O_4NaS$, ($[M + Na]^+$), 503.0722, found: 503.0734.



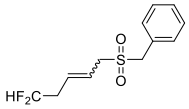
methyl (*E*)-4-((1-(2-ethylphenyl)-5,5-difluoropent-1-en-3-yl)sulfonyl)-2,3,5,6-tetrafluorobenzoate (5la)

The title compound **5la** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5la** was obtained as a white solid (71.1 mg, 74%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (d, J = 7.8 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 3.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 15.6 Hz, 1H), 6.14 – 5.94 (m, 2H), 4.27 (td, J = 10.2, 3.6 Hz, 1H), 3.99 (s, 3H), 2.86 – 2.77 (m, 1H), 2.55 – 2.48 (m, 3H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.50, 144.78 (dm, J = 263.0 Hz), 144.65 (dm, J = 270.7 Hz), 142.10, 138.56, 133.14, 129.54, 128.95, 126.54, 126.31, 119.34 (t, J = 14.8 Hz), 119.24, 118.18 (t, J = 16.9 Hz), 114.54 (t, J = 241.6 Hz), 66.23, 53.92, 31.51 (t, J = 23.6 Hz), 26.17, 15.18.**^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.39 – -117.18 (m), -133.62 – -133.68 (m), -135.64 – -135.70 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}F_6O_4NaS$, ($[M + Na]^+$), 503.0722, found: 503.0724.



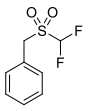
methyl (*E*)-4-((1-(benzofuran-5-yl) -5,5-difluoropent-1-en-3-yl) sulfonyl) -2,3,5,6-tetrafluoroben-zoate (5ma)

The title compound **5ma** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1). **5ma** was obtained as a white solid (56.1 mg, 57%).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.52 (s, 1H), 7.45 (d, J = 9.0 Hz, 1H), 7.26 (d, J = 6.6 Hz, 1H), 6.75 (s, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.14 – 5.94 (m, 2H), 4.21 (td, J = 10.2, 4.2 Hz, 1H), 3.97 (s, 3H), 2.84 – 2.75 (m, 1H), 2.60 – 2.43 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.56, 155.50, 146.07, 144.78 (dm, J = 261.8 Hz), 144.67 (dm, J = 262.3 Hz), 140.82, 129.63, 128.03, 123.17, 120.12, 119.28 (t, J = 14.6 Hz), 118.08 (t, J = 16.9 Hz), 116.24, 114.53 (t, J = 241.6 Hz), 111.90, 106.69, 66.20, 53.89, 31.67 (t, J = 23.6 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.34 – -117.38 (m), -133.69 (q, J = 9.0 Hz), -135.73 (q, J = 9.6 Hz). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{14}F_6O_5NaS$, ([M + Na]$^+$), 515.0358, found: 515.0355.



(((difluoromethyl)sulfonyl)methyl)benzene--(*E)*-(((5,5-difluoropent-2-en-1-yl)sulfonyl) methyl) benzene (4at of 4.5/1)

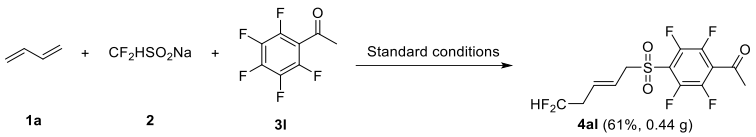
The title compound **4at** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **4at** was obtained as a white solid (21.3 mg, 31%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (s, 6.1H), 6.02 – 5.70 (m, 4H), 4.23 (s, 0.5H), 4.22 (s, 1.9H), 3.62 (d, J = 7.8 Hz, 0.4H), 3.58 (d, J = 5.4 Hz, 2.0H), 2.77 – 2.59 (m, 2.6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 130.73, 130.66, 130.54 (t, J = 6.2 Hz), 129.23, 129.15, 129.14, 129.09, 127.71, 127.58, 122.46, 120.09, 115.49 (t, J = 240.6 Hz), 115.41 (t, J = 240.6 Hz), 58.97, 58.21, 54.95, 50.30, 37.54 (t, J = 22.0 Hz), 33.07 (t, J = 22.4 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.87 (dt, J = 56.4, 17.4 Hz), -116.20 (dt, J = 56.3, 17.6 Hz). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{14}F_2O_2NaS$, ([M + Na]$^+$), 283.0575, found: 283.0571.



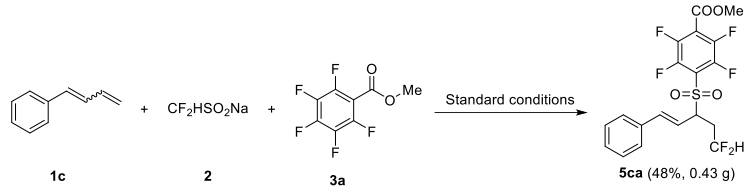
(((difluoromethyl)sulfonyl)methyl)benzene (4at')

The title compound **4at'** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1). **4at'** was obtained as a white solid (25.2 mg, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (s, 5H), 6.11 (t, J = 52.8 Hz, 1H), 4.40 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$)δ 131.26, 129.71, 129.26, 114.57 (t, J = 286.3 Hz), 54.64. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -123.08 (d, J = 52.8 Hz). **HRMS** (ESI-TOF) (m/z): Calcd for $C_8H_8F_2O_2NaS$, ([M + Na]$^+$), 299.0105, found: 299.0110.

VI. Procedure for Large-Scale Synthesis



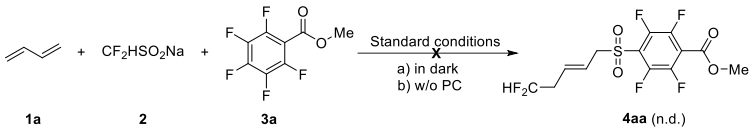
In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar were charged with 4CzIPN (24.0 mg, 1.5 mol%), $ZnCl_2$ (273.0 mg, 1.0 equiv), Na_2CO_3 (212.0 mg, 2.0 equiv) and dry DMSO (10.0 mL). Then **3l** (452.0 mg, 2.0 mmol), **2** (840.0 mg, 3.0 equiv) and **1a** (5000 ul, 5.0 equiv) were added. The reaction mixture was irradiated with Blue LEDs at 30 ℃ for 48 h, until the reaction was complete as indicated by TLC. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered. And the reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1) to obtain product **4al** (0.44 g, 61%).



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar were charged with 4CzIPN (24.0 mg, 1.5 mol%), $ZnCl_2$ (273.0 mg, 1.0 equiv) and dry DMF (10.0 mL). Then **3a** (452.0 mg, 2.0 mmol), **2** (840.0 mg, 3.0 equiv) and **1c** (390.2 mg, 1.5 equiv) were added. The reaction mixture was irradiated with Blue LEDs at 30 ℃ for 48 h, until the reaction was complete as indicated by TLC. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered. And the reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to obtain product **5ca** (0.43 g, 48%).

VII. Mechanistic Studies

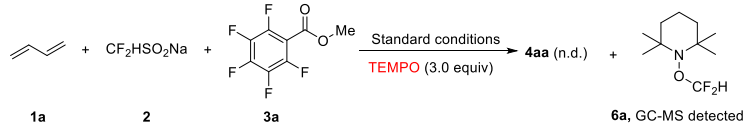
7.1 Control experiment.



a) Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.3 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv) and dry DMSO (1.5 mL). Then **3a** (45.2 mg, 0.2 mmol), **2** (84.0 mg, 3.0 equiv) and **1a** (500 ul, 5.0 equiv) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred in dark at 30 ℃ for 48 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered, then solvent was evaporated under vacuum. The residue was analyzed by ^{1}H NMR, the product **4aa** was not detected.

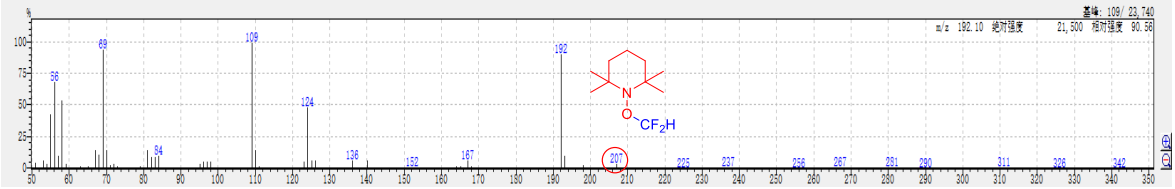
b) Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with $ZnCl_2$ (27.3 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv) and dry DMSO (1.5 mL). Then **3a** (45.2 mg, 0.2 mmol), **2** (84.0 mg, 3.0 equiv) and **1a** (500 ul, 5.0 equiv) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LEDs at 30 ℃ for 48 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered, then solvent was evaporated under vacuum. The residue was analyzed by ^{1}H NMR, the product **4aa** was not detected.

7.2 Radical trapping experiments

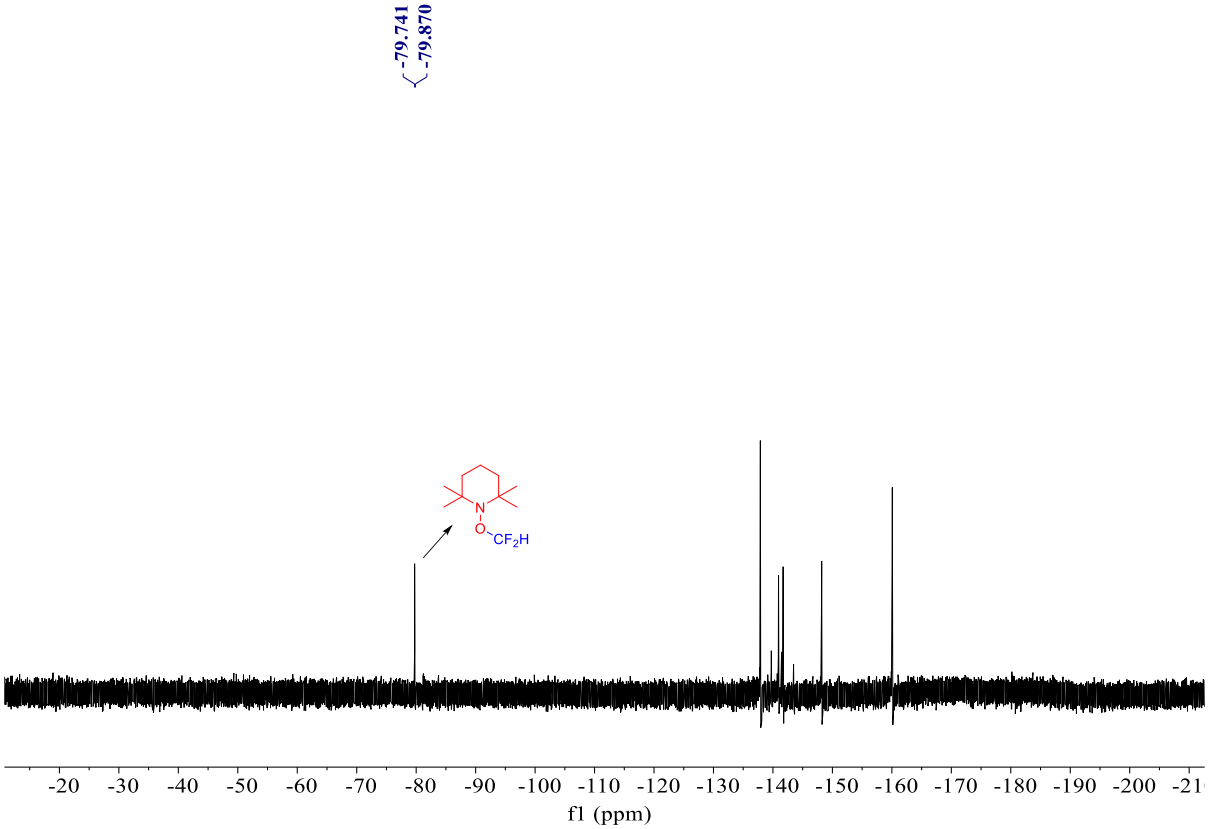


Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.3 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv) and dry DMSO (1.5 mL). Then Methyl pentafluorobenzoate **3a** (45.2 mg, 0.2 mmol), Sodium difluoromethanesulfinate **2** (84.0 mg, 3.0 equiv) and 1,3-Butadiene **1a** (500 ul, 5.0 equiv) were added. Finally, TEMPO (93.8 mg, 3.0 equiv) was added to the mixture. The vial was removed from the glovebox, and then the reaction mixture was irradiated with 5 W Blue LEDs at 30 ℃ for 24 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered, then solvent was evaporated under vacuum. The residue was analyzed by ^{1}H NMR, the product **4aa** was not detected. The details and characterization data of **6a** were stated below.

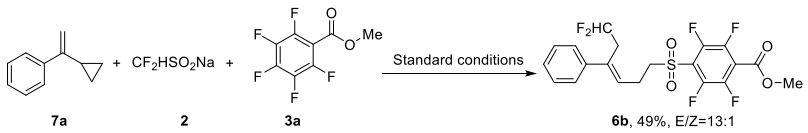
GC-MS of 6a



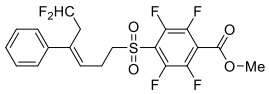
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 6a



7.3 Radical clock Experiment



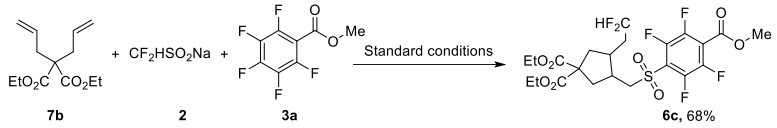
Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.3 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv), and dry DMSO (2.0 mL). Then alkene **7a** (43.3 mg, 0.2 mmol), **2** (84.0 mg, 3.0 equiv) and methyl pentafluorobenzoate **3a** (45.2 mg, 0.2 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred with Blue LEDs at 30 ℃ for 48 hours. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered. And the reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 12:1) to obtain product **6b** (22.9 mg, 49%) as white solid.



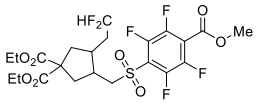
methyl-4-((6,6-difluoro-4-phenylhex-3-en-1-yl)sulfonyl)-2,3,5,6-tetrafluoro-benzoate (6b)

The title compound **6b** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12: 1). **6b** was obtained as a white solid (45.7 mg, 49%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 3H), 7.26 – 7.24 (m, 2H), 5.83 – 5.57 (m, 2H), 4.00 (s, 3H), 3.53 (t, J = 7.2 Hz, 2H), 3.09 (td, J = 16.8, 4.8 Hz, 2H), 2.85 (q, J = 7.2 Hz, 2H),

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.60, 144.73 (dm, J = 261.4), 144.44 (dm, J = 260.2), 140.63, 135.28 (t, J = 5.7 Hz), 128.73, 128.04, 127.39, 126.19, 121.37 (t, J = 14.3 Hz), 117.65 (t, J = 16.8 Hz), 115.37 (t, J = 241.4 Hz), 56.90, 53.88, 35.34 (t, J = 22.8 Hz), 22.29. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.78 (dt, J = 56.4, 16.8 Hz), -135.07 – -135.14 (m), -135.44 – -135.48 (m). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{16}F_6NaO_4S$ ([M + Na]$^+$), 489.0564; found, 489.0569.



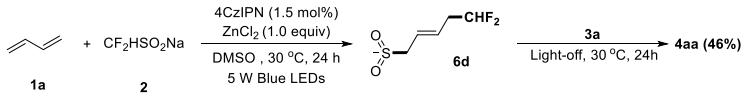
Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.2 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv), and dry DMSO (2.0 mL). Then alkene **7b** (72.0 mg, 0.2 mmol), **2** (84.0 mg, 3.0 equiv) and **3a** (45.2 mg, 0.2 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred with Blue LEDs at 30 ℃ for 48 hours. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered. And the reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to obtain product **6c** (56.3 mg, 68%) as white solid.



diethyl 3-(2,2-difluoroethyl)-4-(((2,3,5,6-tetrafluoro-4-(methoxycarbonyl)phenyl)sulfonyl) methyl) cyclopentane-1,1-dicarboxylate (6c)

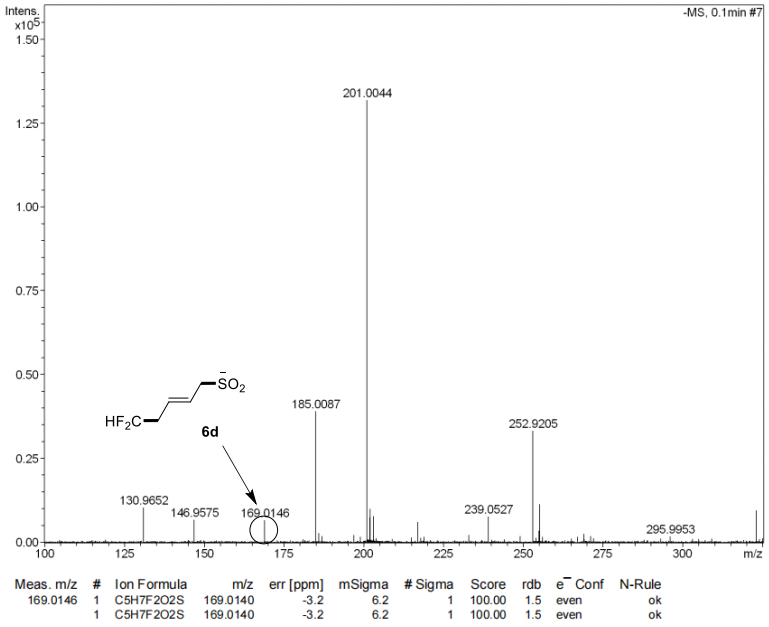
The title compound **6c** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 10: 1). **6c** was obtained as a white solid (76.5 mg, 68%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.88 (tt, J = 56.4, 4.2 Hz, 1H), 4.22 – 4.18 (m, 4H), 4.03 (s, 3H), 3.40 – 3.38 (m, 2H), 2.75 – 2.72 (m, 1H), 2.62 – 2.58 (m, 1H), 2.50 – 2.43 (m, 3H), 2.13 – 2.09 (m, 1H), 1.93 – 1.78 (m, 2H), 1.27 – 1.24 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.43, 171.64, 158.71, 144.76 (dm, J = 261.7 Hz), 121.36 (t, J = 14.4 Hz), 117.94 – 117.83 (m), 116.35, 114.76, 61.94, 61.91, 58.02, 56.93, 53.95, 38.41, 38.32, 36.88 (t, J = 4.6 Hz), 36.55, 33.33 (t, J = 21.1 Hz), 13.97 (d, J = 4.4 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.72 – -116.21 (m), -135.06 – -135.10 (m), -135.55 – -135.62 (m). **HRMS** (ESI-TOF) (m/z): calcd for $C_{22}H_{24}F_6NaO_8S$ ([M + Na]$^+$), 585.0998; found, 585.0992.

7.4 Two-step wise experiment



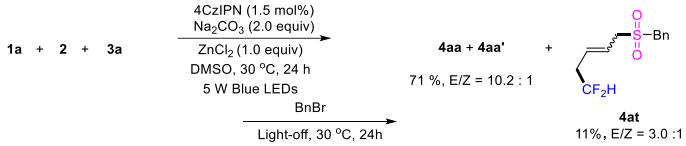
In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.3 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv) and dry DMSO (2.0 mL). Then **2** (84.0 mg, 3.0 equiv) and **1a** (500 ul, 5.0 equiv) were added. The reaction mixture was irradiated with Blue LEDs at 30 ℃ for 24 h. Then **3a** (45.2 mg, 0.2 mmol) was added. The vial was removed from the glovebox, and then the reaction mixture was stirred in the dark at 30 ℃ for 24 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered. And the reaction mixture was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **4aa** (32.7 mg, 46%).

HRMS of 6d

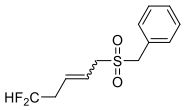


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
169.0146	1	C5H7F2O2S	169.0140	-3.2	6.2	1	100.00	1.5	even	ok
	1	C5H7F2O2S	169.0140	-3.2	6.2	1	100.00	1.5	even	ok

7.5 Accumulation of the sulfinate intermediate



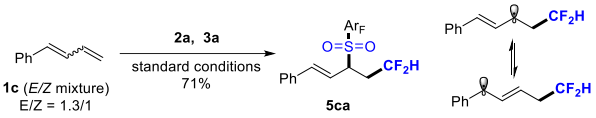
Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.3 mg, 1.0 equiv), Na_2CO_3 (21.2 mg, 2.0 equiv), and dry DMSO (1.5 mL). Then **3a** (45.2 mg, 0.2 mmol), **2** (84.0 mg, 3.0 equiv), and **1a** (500 μL, 5.0 equiv) were added. The vial was removed from the glovebox, and the reaction mixture was irradiated with Blue LEDs at 30 ℃ for 24 h. Benzyl bromide was then added to the mixture, and the reaction was transferred to a dark environment and stirred in the dark for an additional 24 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and the solvent was evaporated under vacuum. The residue was analyzed by ^{1}H NMR, affording **4aa** in 71% yield (E/Z = 10.2:1), together with 11% yield of isolated **4at** (E/Z = 3.0:1).



(((difluoromethyl)sulfonyl)methyl)benzene--(*E*)-(((5,5-difluoropent-2-en-1-yl)sulfonyl) methyl) benzene (**4at of 3.0/1**)

The title compound **4at** was prepared under the optimized conditions and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 12 : 1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (s, 6.6H), 6.00 – 5.72 (m, 4.4H), 4.23 (s, 0.7H), 4.22 (s, 2.0H), 3.62 (d, *J* = 7.8 Hz, 0.7H), 3.57 (d, *J* = 5.6 Hz, 2.0H), 2.74 – 2.61 (m, 2.7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 130.70, 130.62, 130.51 (t, *J* = 6.2 Hz), 129.25, 129.17, 129.15, 129.11, 127.71, 127.58, 122.49, 120.09, 115.36 (t, *J* = 240.8 Hz), 59.03, 58.26, 54.92, 50.27, 37.56 (t, *J* = 22.1 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.89 (dt, *J* = 56.3, 17.4 Hz), -116.21 (dt, *J* = 56.3, 17.8 Hz). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{14}F_2O_2NaS$, ($[M + Na]^+$), 283.0575, found: 283.0579.

7.6 Employment of Z/E mixtured olefins



Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), $ZnCl_2$ (27.3 mg, 1.0 equiv) and dry DMF (2.0 mL). Then **3a** (45.2 mg, 0.2 mmol), **2** (42.0 mg, 1.5 equiv) and the mixed E/Z conjugated alkenes **1c** (39.0 mg, 1.5 equiv) were added. The vial was removed from the glovebox, and the reaction mixture was irradiated with Blue LEDs at 30 °C for 48 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered, then solvent was evaporated under vacuum. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **5ca** (66.4 mg, 71%).

7.7 Emission quenching experiment

Emission intensities were recorded using a spectrofluorometer (Figure **S1**) at ambient temperature. 4CzIPN solutions were excited at 390 nm or 430 nm, and the emission intensity at 550 nm was observed. Firstly, the emission spectrum of a 5 x 10^{-5} M solution of 4CzIPN in DMSO was collected. Then, an appropriate amount of quencher was added to the measured solution, and the emission spectrum of the sample was collected. Stern-Volmer emission quenching studies have shown that only $NaSO_2CF_2H$ **2** can quench the excited photosensitizer.

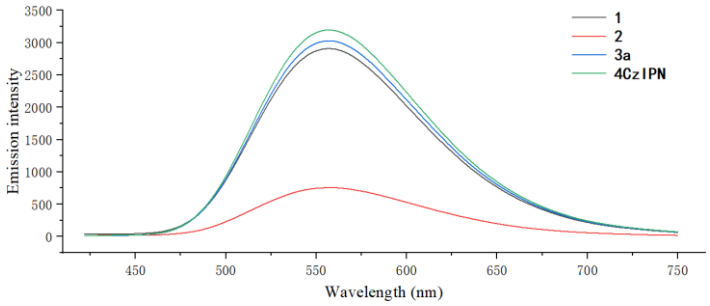


Figure **S1**. 4CzIPN emission quenching by buta-1,3-diene **1a,** $NaSO_2CF_2H$ **2,** methyl pentafluorobenzoate **3a**

7.8 Investigation of the role of $ZnCl_2$

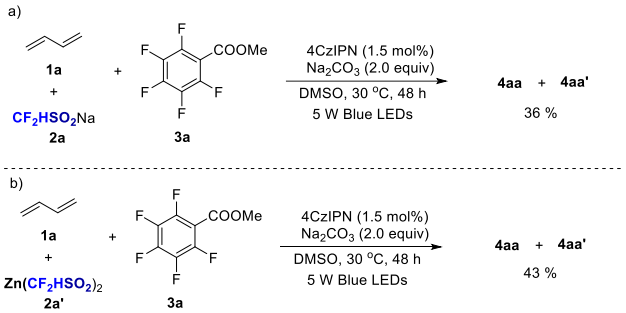


Figure **S2** Investigation of the role of $ZnCl_2$

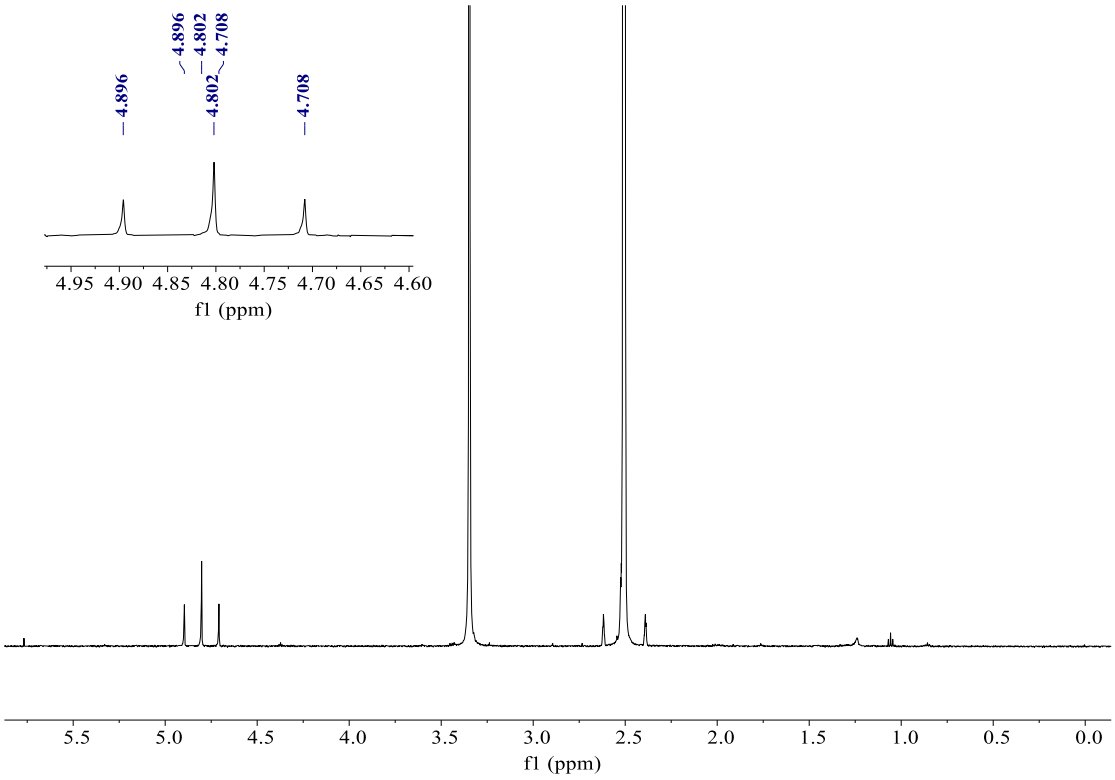
a) Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), Na_2CO_3 (21.2 mg, 2.0 equiv) and dry DMSO (1.5 mL). Then **3a** (45.2 mg, 0.2 mmol), **2a** (84.0 mg, 3.0 equiv) and **1a** (500 µL, 5.0 equiv) were added. The vial was removed from the glovebox, and the reaction mixture was irradiated with Blue LEDs at 30 °C for 48 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried

over Na_2SO_4 and filtered, then solvent was evaporated under vacuum. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **4aa** (27.1 mg, 36%).

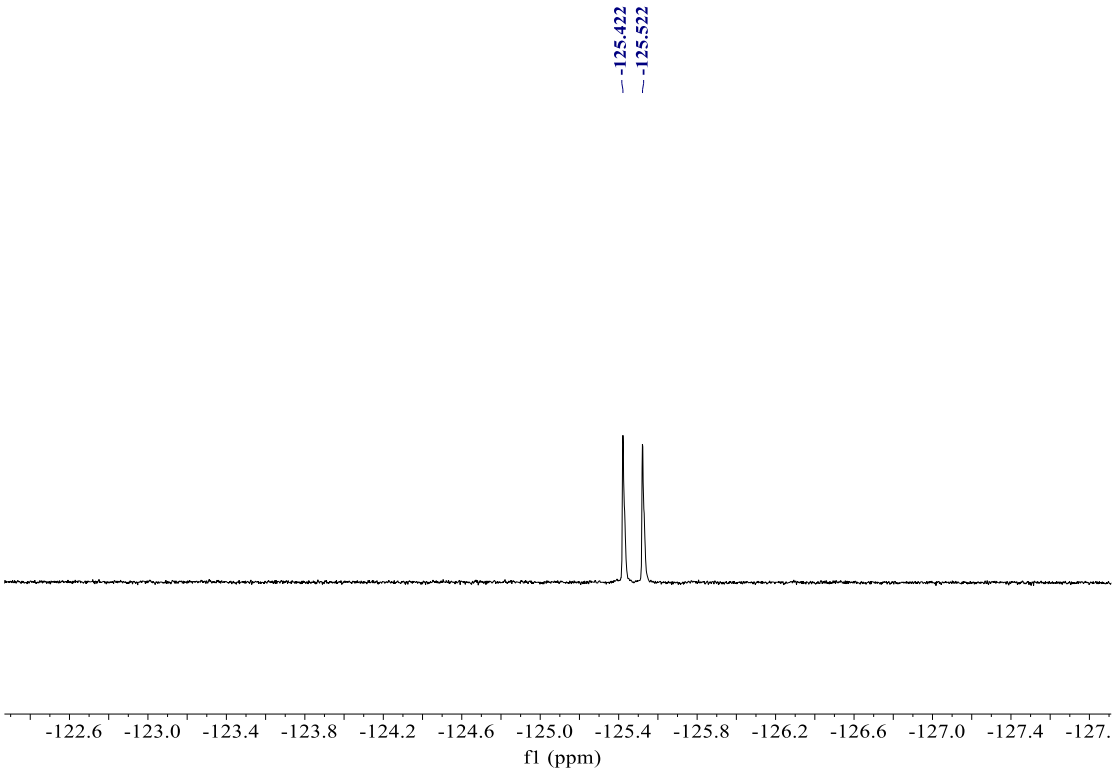
b) Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with 4CzIPN (2.4 mg, 1.5 mol%), Na_2CO_3 (21.2 mg, 2.0 equiv) and dry DMSO (1.5 mL). Then **3a** (45.2 mg, 0.2 mmol), **2a'** (88.8 mg, 1.5 equiv) and **1a** (500 μL, 5.0 equiv) were added. The vial was removed from the glovebox, and the reaction mixture was irradiated with Blue LEDs at 30 ℃ for 48 h. After the reaction, ethyl acetate and water were poured into the mixture. The organic layer was washed with brine, dried over Na_2SO_4 and filtered, then solvent was evaporated under vacuum. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **4aa** (32.4 mg, 43%).

Finally, into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with **2a** (28.0 mg, 0.2 mmol), $ZnCl_2$ (27.3 mg, 1.0 equiv) and dry DMSO-d_6 (2.0 mL). The vial was removed from the glovebox, and then the reaction mixture was stirred in dark at 30 ℃ for 12 h. NMR analysis confirmed the formation of a new species, suggesting the generation of a new intermediate.

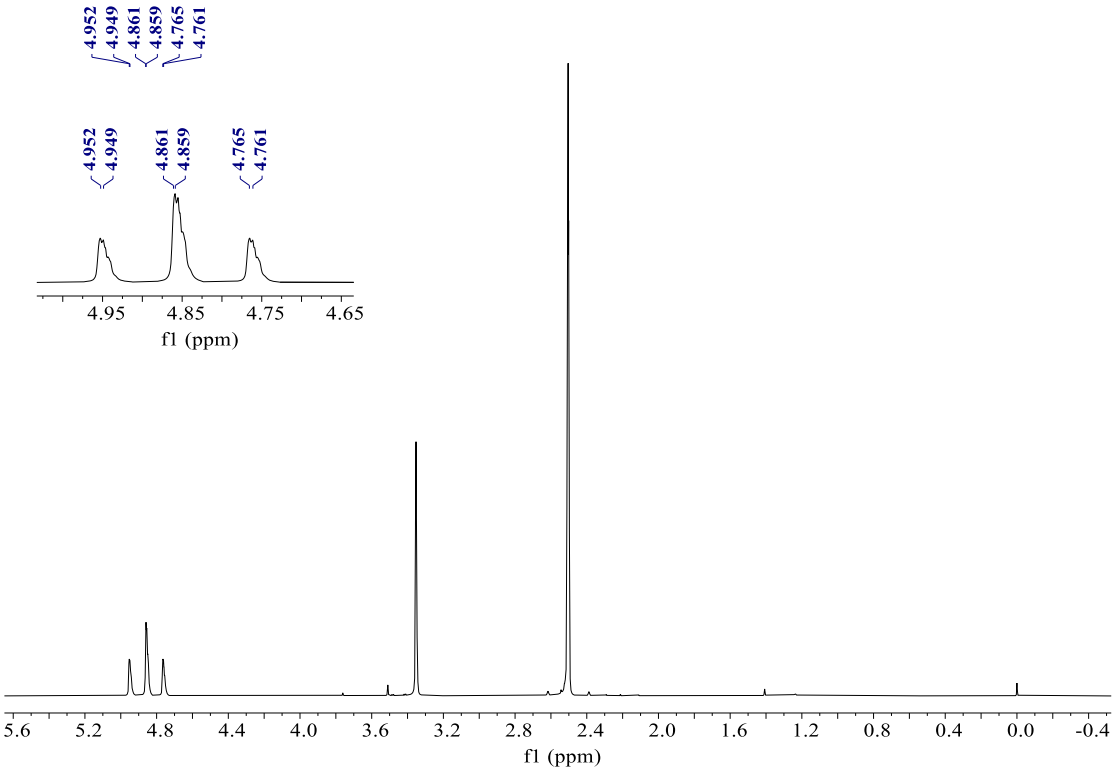
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of CF_2HSO_2Na



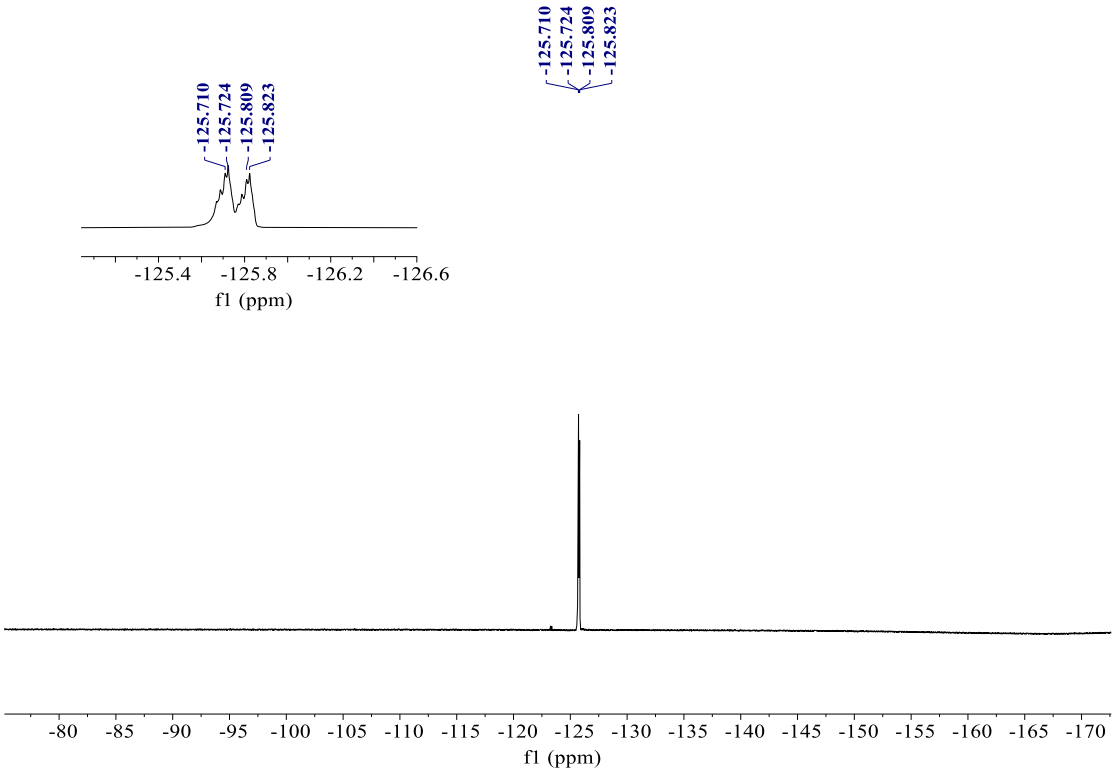
^{19}F NMR (600 MHz, DMSO-d_6) spectrum of CF_2HSO_2Na



^{1}H NMR (600 MHz, DMSO-d_6) spectrum of CF_2HSO_2Na + $ZnCl_2$



^{19}F NMR (565 MHz, DMSO-d_6) spectrum of CF_2HSO_2Na + $ZnCl_2$



VIII. Computational Methodology

All of the calculations were performed using Gaussian 16 program.[8] Geometry optimization were performed in the gas phase using PBE1PBE functional[9] including Grimme empirical dispersion correction (GD3BJ)[10, 11] with a basis set of 6-31G(d)[12, 13] in gas phase. Frequency calculations have been performed to verify the optimized structures as local minima or transition state and to obtain Gibbs free energy at 298.15 K.[14] Intrinsic reaction coordinate (IRC) calculations were carried out to make sure that every transition state links relevant intermediates.[15, 16] The PBE1PBE/6-311+G(d,p) was used for the solution phase single-point energy calculations.[17] The SMD solvation model with DMSO or DMF as the solvent was employed to account for solvation effect.[18, 19] All the geometries were displayed using CYLview software. [20]

8.1 spin density distributions for Int2-a and Int2-b

We have calculated and plotted the spin density distributions for the two key allylic radical intermediates, **Int2-a** and **Int2-b**, derived from 1,3-butadiene. As shown in Figure **S3**, the spin density in **Int2-a** is primarily localized on the terminal carbon atom (C4), with a calculated population of 0.75, compared to a value of 0.71 at the C2 position. This indicates tendency for sulfur dioxide addition at the 4-position, favoring the 1,4-addition pathway over the sterically more hindered or electronically less favorable 1,2-addition. A similar spin density distribution pattern is observed for intermediate **Int2-b**, where the terminal carbon also shows a higher spin population (0.74) than the internal C2 position (0.72). Spin density populations were evaluated with Multiwfn[21], and the pictures of spin density populations were prepared with VMD[22].

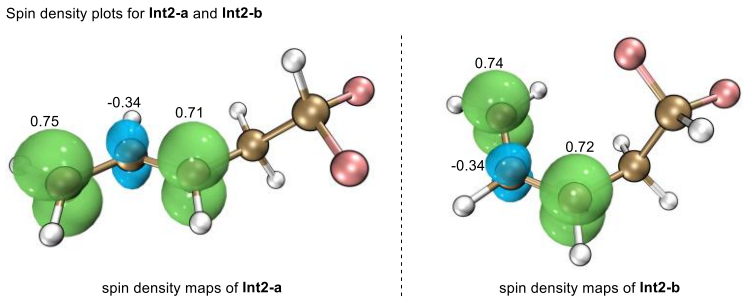


Figure **S3** Spin Density Distribution of Key Allylic Radical Intermediates

8.2 Cartesian Coordinates of reported structures.

A

PBE1PBE /6-31G(d) thermal correction Energy: -0.000678 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -786.543454504 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -786.5441325 a.u.

S	-0.81658400	0.00000000	-0.27875900
O	-1.36023000	-1.29217300	0.17993600
O	-1.36023000	1.29217300	0.17993600
C	0.96760400	0.00000000	0.35794900
H	0.93087100	0.00000000	1.45233800
F	1.56069700	1.09301400	-0.11215900
F	1.56069700	-1.09301400	-0.11216000

SO_2

PBE1PBE /6-31G(d) thermal correction Energy: -0.017169 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -548.3595904 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -548.3767594 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMF: -548.35965 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMF: -548.376819 a.u.

S	0.00000000	0.00000000	0.36855600
O	0.00000000	1.25350800	-0.36855600
O	0.00000000	-1.25350800	-0.36855600

Int1

PBE1PBE /6-31G(d) thermal correction Energy: -0.005491 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -238.1569987 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -238.1624897 a.u.

C	-0.00012700	0.48251800	-0.15166600
H	-0.00009400	1.42879900	0.39405600
F	1.09683900	-0.24018100	0.02865800
F	-1.09674300	-0.24025300	0.02866900

1a

PBE1PBE /6-31G(d) thermal correction Energy: 0.059558 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -155.8400169 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -155.7804589 a.u.

C	1.84233200	-0.10920500	-0.00011900
H	2.72382700	0.52448900	-0.00017300
H	2.01118600	-1.18391200	0.00007300
C	0.60591000	0.40148100	0.00013100
H	0.47059100	1.48329700	0.00056300
C	-0.60577100	-0.40076500	-0.00004400
H	-0.46937700	-1.48248000	0.00042600
C	-1.84258600	0.10873300	-0.00015500
H	-2.01233600	1.18327600	-0.00017400
H	-2.72320300	-0.52613600	0.00041200

TS1

PBE1PBE /6-31G(d) thermal correction Energy: 0.068987 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -393.9997348 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -393.9307478 a.u.

C	1.70573200	0.23281800	0.37887100
H	1.20712700	0.62686600	1.26604000
F	2.20142200	1.17633800	-0.41611800
F	2.61945600	-0.69386200	0.64791200
C	-0.26440000	-0.84717200	-0.94788000
H	0.36554800	-1.73100000	-0.96025100
H	-0.01752300	-0.06195200	-1.65867500
C	-1.37995700	-0.78217900	-0.19333900
H	-1.62466000	-1.60888100	0.47364300
C	-2.28266200	0.34875200	-0.18393800
H	-2.03413600	1.17182400	-0.85493700

C	-3.37825000	0.43517200	0.58424100
H	-3.65778600	-0.36683800	1.26392600
H	-4.02923700	1.30335200	0.55637900

Int2-a

PBE1PBE /6-31G(d) thermal correction Energy: 0.076901 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -394.0767188 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -393.9998178 a.u.

C	-1.41244000	-0.00401400	-0.35385900
H	-1.20044300	-0.01021700	-1.42898200
F	-2.56417200	0.68925400	-0.14930700
F	-1.62868600	-1.28918500	0.03888400
C	-0.29933200	0.60103000	0.47426600
H	-0.65641900	0.58938700	1.51478400
H	-0.18410900	1.65005100	0.17947200
C	0.98474300	-0.14223000	0.33597200
H	0.96888300	-1.20247600	0.58223700
C	2.17337700	0.43399200	-0.08065800
H	2.15768300	1.49829800	-0.32143000
C	3.37438700	-0.23809900	-0.21038700
H	3.45117100	-1.29780500	0.01694800
H	4.27454800	0.26805500	-0.54123600

Int2-b

PBE1PBE /6-31G(d) thermal correction Energy: 0.07773 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -394.0753309 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -393.9976009 a.u.

C	-1.26069700	-0.06721800	-0.33383200
H	-1.46950300	-0.47398600	-1.32994700
F	-0.80372600	1.20314900	-0.48793000
F	-2.43504100	0.00138700	0.35168800
C	-0.26567100	-0.89206300	0.45840400
H	-0.75129700	-1.84823500	0.68339300
H	-0.11624400	-0.37225300	1.41249800
C	1.02848000	-1.12210200	-0.25318600
H	1.10939200	-2.02685600	-0.85067800
C	2.12282800	-0.26634200	-0.21171800
H	3.00951600	-0.59093000	-0.75563800
C	2.19458600	0.94404600	0.44934500
H	1.34374700	1.36177200	0.97624300
H	3.10613900	1.53172400	0.43623000

TS2-a

PBE1PBE /6-31G(d) thermal correction Energy: 0.078722 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -942.4508783 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -942.3721563 a.u.

C	-3.11281900	-0.22147400	-0.39224500

H	-3.02629700	-0.53322700	-1.44005000
F	-3.34894700	1.11517000	-0.36890500
F	-4.18846300	-0.84652300	0.15005900
C	-1.88196500	-0.53886300	0.43237000
H	-1.76954500	-1.63206700	0.44265000
H	-2.07831300	-0.21418600	1.45981500
C	-0.64843500	0.08963000	-0.11078500
H	-0.37127000	-0.15990100	-1.13495700
C	0.16804400	0.92200000	0.59653400
H	-0.07717100	1.13815500	1.63559200
C	1.37480100	1.43359600	0.07332700
H	1.53315200	1.42161200	-1.00330500
H	1.93543300	2.18701400	0.61877100
S	2.94166800	-0.31435000	0.27271100
O	2.16049900	-1.45228900	-0.22842000
O	3.99278500	0.23916800	-0.59251400

TS2-b

PBE1PBE /6-31G(d) thermal correction Energy: 0.080328 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -942.4480953 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -942.3677673 a.u.

C	-2.57445800	-0.17978300	0.02722400
H	-3.39000500	0.54616100	-0.06720800
F	-2.14980500	-0.16029200	1.32041400
F	-3.07198400	-1.41631200	-0.22440400
C	-1.40937100	0.08663700	-0.90716900
H	-1.77281900	-0.06272800	-1.92903200
H	-0.65375300	-0.68405200	-0.72272100
C	-0.83958600	1.46082600	-0.76766000
H	-1.23446600	2.22634900	-1.43215500
C	0.12834300	1.83781000	0.12666000
H	0.48281100	2.86572000	0.07376300
C	0.74563200	0.98820600	1.06408300
H	0.28996000	0.03596200	1.31842200
H	1.41123000	1.40652500	1.81325100
S	2.47107000	-0.18286100	-0.14127700
O	1.75020300	-0.58563500	-1.35544400
O	2.75263000	-1.21197900	0.86584400

TS2-c

PBE1PBE /6-31G(d) thermal correction Energy: 0.080494 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -942.4477903 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -942.3672963 a.u.

C	2.36838200	-0.30395900	0.35591200
H	2.40378500	-0.27348600	1.45077500
F	2.78206800	0.90367300	-0.11271000

F	3.25022400	-1.23966100	-0.07560500
C	0.99435200	-0.62974600	-0.19670600
H	0.72830300	-1.64137900	0.12463900
H	1.08597300	-0.63218700	-1.28920400
C	-0.04334500	0.35233700	0.25374700
H	-0.35902300	0.26681500	1.29558000
C	-0.11438800	1.66060900	-0.31232200
H	0.41414300	1.82930100	-1.24887300
C	-0.84678500	2.66176900	0.23182800
H	-1.41709300	2.51105900	1.14416300
H	-0.90149200	3.64079600	-0.23285800
S	-1.99580500	-0.70191700	-0.35537400
O	-3.00506000	0.23617500	0.15457900
O	-1.80264500	-1.97272700	0.36315200

Int3

PBE1PBE /6-31G(d) thermal correction Energy: 0.082027 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -942.4575138 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -942.3754868 a.u.

C	-3.16611000	-0.13110400	-0.37344300
H	-3.13772100	-0.39851900	-1.43680100
F	-3.24204700	1.22158100	-0.28311400
F	-4.30037800	-0.65013800	0.16354300
C	-1.96868800	-0.63218000	0.40507800
H	-1.99104500	-1.72929800	0.37087200
H	-2.10341600	-0.32812700	1.44869400
C	-0.67614900	-0.12738800	-0.14288700
H	-0.43738300	-0.40234000	-1.17123200
C	0.19487500	0.61576200	0.54362800
H	-0.01571300	0.87620300	1.57965900
C	1.48664800	1.06572300	-0.01828200
H	1.47057500	1.17417600	-1.10775000
H	1.88153100	1.97896600	0.43132900
S	2.84964300	-0.19497600	0.22795600
O	2.35393900	-1.45568700	-0.36177600
O	4.07071800	0.46327300	-0.28453500

Int4

PBE1PBE /6-31G(d) thermal correction Energy: 0.081476 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -942.6215073 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -942.5400313 a.u.

C	-3.10598300	-0.18479400	-0.35664400
H	-2.99388200	-0.55651100	-1.38280600
F	-3.31471700	1.15922400	-0.42268200
F	-4.25169400	-0.73579700	0.15998200
C	-1.92374900	-0.50677200	0.52184900

H	-1.94311900	-1.59484000	0.68499700
H	-2.09997300	-0.02786400	1.49368200
C	-0.61920100	-0.07503800	-0.06675600
H	-0.28841600	-0.57876400	-0.97408200
C	0.20251600	0.82262100	0.49870800
H	-0.10548600	1.26265300	1.45199500
C	1.54764900	1.14198700	0.01008500
H	1.61654900	1.19147200	-1.08052100
H	1.97173800	2.05144700	0.44442700
S	2.85297800	-0.27294500	0.30846000
O	2.18922000	-1.40397200	-0.44257500
O	4.02143700	0.35655500	-0.41395000

4CzIPN·-

PBE1PBE /6-31G(d) thermal correction Energy: 0.645645 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -2479.805277 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -2479.159632 a.u.

C	0.53404500	-0.00002100	0.00001900
C	-0.15259400	-1.16396500	-0.36781400
C	-1.60500800	-1.14692100	-0.42278200
C	-2.28562400	0.00004000	0.00001300
C	-1.60496000	1.14697200	0.42280600
C	-0.15254600	1.16395500	0.36783800
C	-2.31224600	-2.23062100	-0.98623300
C	-2.31215400	2.23070500	0.98625000
N	-2.88756600	-3.13789400	-1.44402500
N	-2.88744300	3.13801200	1.44401200
C	-5.85962800	-0.51065500	0.51017300
C	-4.50579900	-0.80198000	0.79379400
C	-4.14157300	-1.74031700	1.75509700
C	-5.16109400	-2.39834100	2.42876700
C	-6.51055000	-2.12879700	2.15794800
C	-6.86526800	-1.18660100	1.20238900
C	-5.85960500	0.51088400	-0.51015600
C	-4.50576400	0.80215300	-0.79377300
C	-4.14149700	1.74047500	-1.75507600
C	-5.16098800	2.39854100	-2.42874800
C	-6.51045600	2.12905300	-2.15793200
C	-6.86521500	1.18687200	-1.20237400
H	-3.09715600	-1.94856200	1.96162000
H	-4.90447600	-3.14102400	3.17944400
H	-7.28367700	-2.66436700	2.70215100
H	-7.91127300	-0.97367400	0.99607900
H	-3.09707000	1.94867600	-1.96159600
H	-4.90433800	3.14121300	-3.17942500

H	-7.28356000	2.66465500	-2.70213800
H	-7.91123000	0.97398900	-0.99606700
N	-3.69726700	0.00007000	0.00001200
C	4.11376300	0.51315500	-0.50726700
C	2.76002500	0.80175900	-0.79338400
C	2.40015400	1.72885800	-1.76691400
C	3.42016000	2.39406700	-2.43356900
C	4.76853300	2.13291700	-2.15260400
C	5.12041800	1.19004300	-1.19607200
C	4.11376200	-0.51325400	0.50727600
C	2.76002300	-0.80182400	0.79342500
C	2.40015300	-1.72889200	1.76698500
C	3.42015900	-2.39411700	2.43362600
C	4.76853100	-2.13300900	2.15262000
C	5.12041700	-1.19015700	1.19606600
H	1.35926600	1.93531000	-1.98818700
H	3.15979600	3.13754400	-3.18190700
H	5.54323100	2.67295900	-2.69020200
H	6.16573300	0.97816800	-0.98532600
H	1.35926700	-1.93531200	1.98829100
H	3.15979400	-3.13757400	3.18198200
H	5.54323000	-2.67306200	2.69020700
H	6.16573200	-0.97830800	0.98529500
N	1.94895400	-0.00003400	0.00001800
C	2.01607300	-3.79869400	-1.66231000
C	1.45098400	-2.50431300	-1.73706200
C	1.81901300	-1.60129200	-2.72978800
C	2.79247300	-1.99953500	-3.63505800
C	3.37765700	-3.27258200	-3.56692900
C	2.98856600	-4.17759400	-2.58866300
C	1.38318500	-4.46177300	-0.54704900
C	0.46884000	-3.53650100	0.00640300
C	-0.30568200	-3.84760400	1.12158700
C	-0.15078900	-5.10846500	1.68214700
C	0.75243400	-6.03931100	1.14868500
C	1.51966900	-5.72199300	0.03538100
H	1.36541400	-0.61831100	-2.78635400
H	3.10814400	-1.30371500	-4.40767200
H	4.14061200	-3.55145100	-4.28877400
H	3.43434400	-5.16824500	-2.54174500
H	-1.00992200	-3.12839000	1.52739000
H	-0.74864400	-5.37885600	2.54857200
H	0.84785100	-7.01867400	1.60978100
H	2.22274900	-6.44264100	-0.37523600

N	0.52770100	-2.34815600	-0.71086800
C	1.38341400	4.46168100	0.54700500
C	0.46902900	3.53644300	-0.00643900
C	-0.30545200	3.84755600	-1.12164900
C	-0.15048400	5.10839500	-1.68223800
C	0.75277600	6.03921000	-1.14878000
C	1.51997300	5.72188000	-0.03545400
C	2.01625300	3.79859400	1.66229000
C	1.45109600	2.50424500	1.73706300
C	1.81907400	1.60122200	2.72980700
C	2.79254600	1.99943300	3.63507700
C	3.37779200	3.27245100	3.56693100
C	2.98875500	4.17746400	2.58864500
H	-1.00972200	3.12836800	-1.52744700
H	-0.74830800	5.37879500	-2.54868100
H	0.84825200	7.01855600	-1.60989900
H	2.22308400	6.44250100	0.37515700
H	1.36542600	0.61826300	2.78638500
H	3.10817500	1.30361200	4.40770700
H	4.14075400	3.55129500	4.28877900
H	3.43458500	5.16809000	2.54171100
N	0.52780900	2.34811600	0.71086900

4CzIPN

PBE1PBE /6-31G(d) thermal correction Energy: 0.651968 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -2479.691924 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -2479.039956 a.u.

C	-0.51801900	-0.00004700	-0.00011500
C	0.19504800	1.15658800	-0.38539500
C	1.60374000	1.13768300	-0.41045800
C	2.31277400	-0.00018400	-0.00012900
C	1.60363900	-1.13799200	0.41019800
C	0.19493500	-1.15676300	0.38514500
C	2.31683200	2.23946400	-0.97011700
C	2.31662700	-2.23972600	0.97008300
N	2.90125500	3.12481200	-1.44101200
N	2.90098000	-3.12501600	1.44117200
C	5.86873200	0.52397200	0.49828500
C	4.52056600	0.82562300	0.78129100
C	4.15655000	1.77208900	1.73166300
C	5.17949200	2.44473400	2.38870300
C	6.52529000	2.17246300	2.11194000
C	6.87711600	1.21142400	1.17364500
C	5.86876000	-0.52444900	-0.49825500
C	4.52061000	-0.82605400	-0.78138800

C	4.15665200	-1.77248700	-1.73181500
C	5.17963300	-2.44515600	-2.38877000
C	6.52541400	-2.17294000	-2.11187200
C	6.87718400	-1.21192700	-1.17353000
H	3.11492900	1.97401300	1.96189400
H	4.92696100	3.19481700	3.13239100
H	7.30059200	2.71678000	2.64256400
H	7.92175400	0.99301100	0.97043800
H	3.11504700	-1.97436800	-1.96215300
H	4.92714500	-3.19521600	-3.13249700
H	7.30074700	-2.71727400	-2.64243300
H	7.92181000	-0.99354900	-0.97022600
N	3.70755300	-0.00021300	-0.00007200
C	-4.07926300	-0.55221600	-0.46591200
C	-2.73115700	-0.86629900	-0.73474200
C	-2.37389000	-1.85161000	-1.64742000
C	-3.39840700	-2.56367200	-2.25988000
C	-4.74287400	-2.28484500	-1.98627300
C	-5.09001000	-1.27442600	-1.09872100
C	-4.07914000	0.55263000	0.46598900
C	-2.73096300	0.86654200	0.73466200
C	-2.37346400	1.85183500	1.64726900
C	-3.39781800	2.56403700	2.25983600
C	-4.74235300	2.28536900	1.98639900
C	-5.08972100	1.27497800	1.09890500
H	-1.33711100	-2.07177400	-1.87645400
H	-3.14267500	-3.35353000	-2.95995500
H	-5.52052600	-2.86031900	-2.47957000
H	-6.13358700	-1.04541600	-0.90138500
H	-1.33662800	2.07187400	1.87617100
H	-3.14190400	3.35387900	2.95986300
H	-5.51987400	2.86095100	2.47977600
H	-6.13335000	1.04610100	0.90168900
N	-1.91489400	0.00005500	-0.00006800
C	-2.09064700	3.66936500	-1.65221000
C	-1.49746600	2.39385200	-1.72895200
C	-1.89479100	1.45045800	-2.66758900
C	-2.95397100	1.78366800	-3.50244600
C	-3.57756100	3.03502200	-3.42220900
C	-3.14316800	3.98745000	-2.50980100
C	-1.39056900	4.40166100	-0.62036800
C	-0.39066500	3.54862200	-0.11022700
C	0.43930500	3.93331900	0.93672800
C	0.26258100	5.20822800	1.46291500

C	-0.71768100	6.07316600	0.96293400
C	-1.54796100	5.67560100	-0.07692100
H	-1.40753200	0.48530200	-2.74803100
H	-3.30016200	1.05444900	-4.22872200
H	-4.40229600	3.26534800	-4.08998300
H	-3.61325800	4.96576900	-2.46380000
H	1.20535800	3.27419800	1.33178700
H	0.90527300	5.53694700	2.27427800
H	-0.82783300	7.06388900	1.39344600
H	-2.31656600	6.34238000	-0.45759600
N	-0.46841900	2.31796600	-0.78175700
C	-1.39119400	-4.40157400	0.62045200
C	-0.39122300	-3.54872200	0.11012600
C	0.43849800	-3.93359800	-0.93696200
C	0.26147000	-5.20849600	-1.46307500
C	-0.71884700	-6.07325400	-0.96289500
C	-1.54889000	-5.67550800	0.07708000
C	-2.09100200	-3.66911800	1.65236200
C	-1.49760300	-2.39369900	1.72895900
C	-1.89464400	-1.45019400	2.66760300
C	-2.95376500	-1.78318800	3.50262100
C	-3.57757200	-3.03444300	3.42253100
C	-3.14345900	-3.98698800	2.51011100
H	1.20459000	-3.27462400	-1.33218300
H	0.90396900	-5.53735000	-2.27453600
H	-0.82923800	-7.06397400	-1.39335300
H	-2.31755000	-6.34214100	0.45790200
H	-1.40721200	-0.48511600	2.74793400
H	-3.29973700	-1.05387700	4.22891000
H	-4.40225400	-3.26460000	4.09042800
H	-3.61371800	-4.96523000	2.46422000
N	-0.46866300	-2.31802700	0.78163100

TS3-pre

PBE1PBE /6-31G(d) thermal correction Energy: 0.167118 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -2060.360442 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -2060.193324 a.u.

C	2.58260000	0.91523300	0.73840900
C	3.50743500	-0.10307500	0.57247700
C	3.47975000	-0.88256500	-0.57540700
C	2.53040300	-0.64263900	-1.56096400
C	1.61335500	0.37301600	-1.37845200
C	1.60683500	1.17651500	-0.23281500
C	0.53955600	2.18070000	-0.04573400
O	-0.58244700	2.08964800	-0.52451400

O	0.91834300	3.20991200	0.69542200
F	0.71250600	0.57508700	-2.35277300
F	2.62377000	1.60043100	1.87116500
F	4.40693300	-0.34586800	1.51347300
F	2.50427500	-1.38475300	-2.65813600
F	4.35590400	-1.85799800	-0.73106400
S	-0.17113200	-1.31238100	0.96773100
O	-0.38740900	-1.56760700	-0.54260500
O	1.14386600	-1.84368200	1.44731100
C	-1.44795100	-2.49333100	1.66181300
H	-1.48283500	-2.30612000	2.73911000
Na	-1.50274700	0.12352400	-1.24658500
C	-2.72475600	-2.22104400	0.96940600
C	-3.60119300	-1.26935000	1.31842800
H	-2.89573700	-2.77148600	0.04461000
C	-4.81923800	-0.92774000	0.51605200
H	-3.44292500	-0.70450900	2.23851900
H	-5.72165400	-0.91037900	1.14162100
H	-4.98697500	-1.66400000	-0.27909200
C	-0.09367200	4.17935200	0.97284200
H	0.38686200	4.92228000	1.60771400
H	-0.44977600	4.63431800	0.04559500
H	-0.93325200	3.71218600	1.49326800
H	-1.05090000	-3.49384200	1.46899500
C	-4.73177000	0.42720700	-0.13918100
H	-4.48591300	1.24691800	0.54303400
F	-5.87674700	0.72586000	-0.78875100
F	-3.73281200	0.41992100	-1.11178000

TS3

PBE1PBE /6-31G(d) thermal correction Energy: 0.171336 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -2060.330164 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -2060.158828 a.u.

C	-0.90943700	-2.14094700	-0.07217300
C	0.44827200	-2.28201900	0.10312900
C	1.22811800	-1.25061800	0.68333100
C	0.46691100	-0.24269300	1.31736600
C	-0.88825300	-0.10806400	1.15625800
C	-1.64314000	-1.05306400	0.44786000
C	-3.07984700	-0.82918600	0.22006200
O	-3.61614100	0.26080200	0.23364700
O	-3.74802700	-1.96861600	-0.00686200
F	-1.46673200	0.94473200	1.72990000
F	-1.51793600	-3.08523000	-0.78238400
F	1.09270500	-3.30409600	-0.46760000

F	1.15325800	0.72810700	2.00364400
F	2.35103000	-1.64982800	1.46549300
S	2.63497900	-0.47577700	-0.85820100
O	3.37869100	0.67236700	-0.20093400
O	3.47014700	-1.45648000	-1.57796400
C	1.58684600	0.32485000	-2.11819800
H	0.97512000	-0.47057900	-2.55594000
Na	3.41765200	0.37995500	1.92569800
C	0.78212000	1.45488400	-1.58703400
C	-0.55237000	1.49549700	-1.63683500
H	1.34668700	2.27241100	-1.14698000
C	-1.43204800	2.57293800	-1.07971500
H	-1.08323700	0.66744200	-2.10718700
H	-2.30133400	2.10805300	-0.59846000
H	-1.82099000	3.21413300	-1.88302600
C	-5.13475100	-1.79745000	-0.28392000
H	-5.64586300	-1.34868000	0.57186000
H	-5.27857500	-1.15406100	-1.15603500
H	-5.51825400	-2.79901000	-0.47807100
H	2.32906500	0.64335100	-2.86143600
C	-0.77632500	3.46609300	-0.05946100
H	-0.32926600	2.91144400	0.77140200
F	-1.69708400	4.32834000	0.44538900
F	0.20907600	4.22269900	-0.63163300

4aa

PBE1PBE /6-31G(d) thermal correction Energy: 0.171559 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMSO: -2060.361372 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMSO: -2060.189813 a.u.

C	1.72144300	1.47937000	-0.51288500
C	0.36756700	1.77192400	-0.65706500
C	-0.60390800	1.08661600	0.06050500
C	-0.16938500	0.06427000	0.90002000
C	1.17027400	-0.23276200	1.04328100
C	2.15787600	0.46130700	0.33251000
C	3.59242600	0.11985800	0.54112300
O	4.03924900	-0.32209700	1.57164100
O	4.31943600	0.34661400	-0.55804000
F	1.49053600	-1.25575500	1.83243100
F	2.57566300	2.21073500	-1.21631900
F	0.03046000	2.71218600	-1.53907300
F	-1.03625500	-0.67847100	1.60768400
F	-1.56589000	2.11249000	1.88967300
S	-2.33283700	1.34902700	-0.38694000
O	-3.22457300	0.50285000	0.43212500

O	-2.63832000	2.74526100	-0.63414000
C	-2.31231200	0.50771600	-2.00046500
H	-1.54604300	1.01226800	-2.59634600
Na	-2.80290100	0.73295800	2.61471300
C	-2.08127100	-0.95428000	-1.84551500
C	-0.88985900	-1.53785200	-1.99518900
H	-2.93575400	-1.54636300	-1.52693300
C	-0.64646700	-2.99874800	-1.74944100
H	-0.03169800	-0.93005800	-2.28321900
H	0.29190100	-3.32477500	-2.20825300
H	-1.44958700	-3.60921200	-2.17835700
C	5.71256100	0.07343500	-0.41272500
H	6.16115500	0.33203000	-1.37135900
H	6.13976500	0.67960100	0.38997700
H	5.87313100	-0.98297700	-0.18267400
H	-3.29492900	0.74177900	-2.42360600
C	-0.58923200	-3.35616300	-0.27715400
H	0.16834100	-2.81063600	0.29326900
F	-0.33591000	-4.68618800	-0.15613100
F	-1.79900500	-3.11475200	0.29973700

TS2-d

PBE1PBE /6-31G(d) thermal correction Energy: 0.155661 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMF: -1173.31595 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMF: -1173.160289 a.u.

C	-2.88273700	-1.88371200	-0.05765700
H	-2.04711100	-2.50570200	-0.39830900
F	-4.01133500	-2.30119700	-0.68400700
F	-3.04390300	-2.09176100	1.27700600
C	-2.68023900	-0.40640300	-0.31911700
H	-3.58896200	0.10657800	0.01394700
H	-2.58378800	-0.24657500	-1.39817900
C	-1.46738000	0.11220200	0.39904300
H	-1.55913100	0.17045200	1.48400700
C	-0.17069600	-0.20787700	-0.09377500
H	-0.09163900	-0.45490100	-1.15122500
C	0.95433500	-0.08586900	0.67073100
H	0.82015800	0.21272500	1.70972400
C	2.32082300	-0.30368500	0.25380600
C	2.67971400	-0.64422600	-1.06414900
C	3.34453800	-0.16853500	1.20849600
C	4.00736100	-0.84369000	-1.40486000
H	1.91413800	-0.74411800	-1.82743800
C	4.67377000	-0.36819800	0.86515100
H	3.08099800	0.10072500	2.22827900

C	5.01013000	-0.70813100	-0.44314300
H	4.26752300	-1.10246800	-2.42719500
H	5.44959000	-0.25676700	1.61700100
H	6.04987500	-0.86373200	-0.71616700
S	-1.62314200	2.28010900	0.04572200
O	-0.46688900	2.83724200	0.76406800
O	-1.65585500	2.37368400	-1.42533500

TS2-e

PBE1PBE /6-31G(d) thermal correction Energy: 0.156308 a.u.

PBE1PBE /6-311+G(d,p) SCF energy in DMF: -1173.311643 a.u.

PBE1PBE /6-311+G(d,p) Gibbs energy in DMF: -1173.155335 a.u.

C	4.00064400	-1.17927700	0.00797700
H	3.57038700	-2.17271200	-0.16298200
F	5.11461700	-1.32162400	0.77013300
F	4.37963400	-0.67306700	-1.19656300
C	3.04474600	-0.21987800	0.68452600
H	3.60290600	0.71295900	0.84438300
H	2.78021500	-0.62360200	1.66734000
C	1.83134700	0.04868600	-0.13777600
H	2.00166000	0.45892500	-1.13191200
C	0.57278000	-0.16739100	0.27936700
H	0.39173400	-0.54316900	1.28411800
C	-0.59175500	0.14580000	-0.54007600
H	-0.36319600	0.24718700	-1.60273200
C	-1.87700400	-0.51907500	-0.26674800
C	-2.34743100	-0.69631600	1.04178600
C	-2.66650200	-0.95817800	-1.33690300
C	-3.56505700	-1.32336000	1.26882200
H	-1.77462500	-0.30823900	1.87833800
C	-3.88099800	-1.59190500	-1.10687700
H	-2.31395300	-0.81188100	-2.35517200
C	-4.33206300	-1.77811700	0.19761600
H	-3.92255400	-1.45039600	2.28652400
H	-4.47709300	-1.93884900	-1.94596200
H	-5.28367400	-2.26933500	0.37959600
S	-0.89013600	2.19808500	-0.15681900
O	0.31519000	2.83743900	-0.71492400
O	-1.13395600	2.27706500	1.29681800

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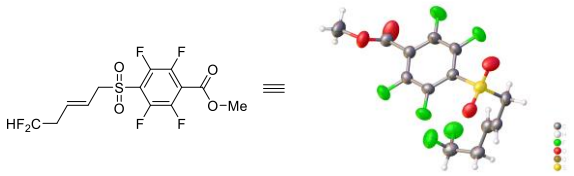
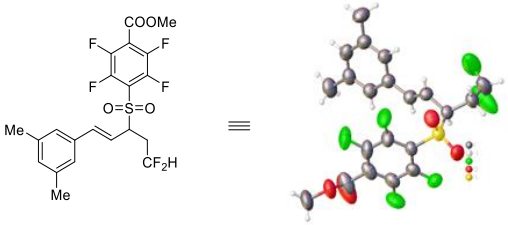
X. X-Ray Crystallographic Data



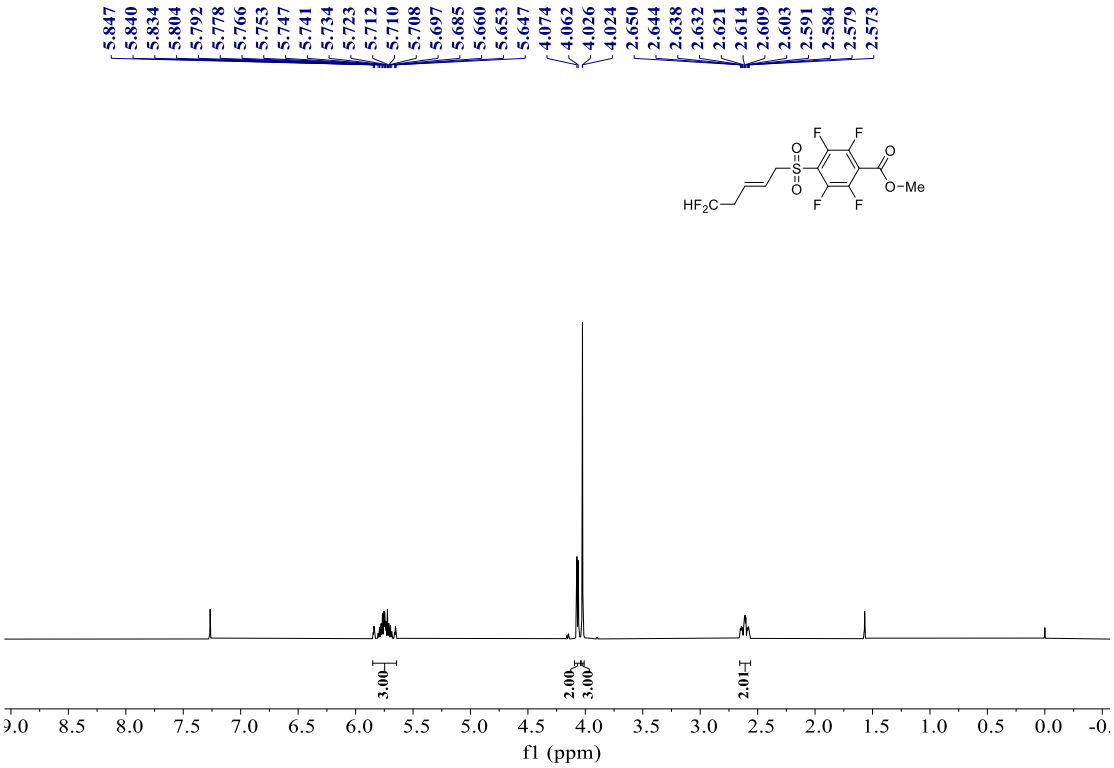
CCDC number	**2350968**
Empirical formula	**$C_{13}H_{10}F_6O_4S$**
Formula weight	**376.27**
Temperature	**172 K**
Wavelength	**0.71073**
Crystal system, space group	**monoclinic, P21/c**
Unit cell dimensions	**a=7.6984(5) alpha=90** **b=24.816(2) beta=101.995(2)** **c=7.9995(7) gamma=90**
Volume	**1494.9(2)**
Z, Calculated density	**4, 1.672 g/cm^3**
Reflections collected / unique	**37779 / 2934[R(int) = 0.0623]**
F(000)	**760**
Absorption correction	**MULTI-SCAN**
Max. and min. transmission	**0.745 and 0.705**
Data / restraints / parameters	**2934/0/218**
Goodness-of-fit on F^2	**1.042**
Final R indices [I>2sigma(I)]	**R_1 = 0.0362, wR_2 = 0.0900**
R indices (all data)	**R_1 = 0.0438, wR_2 = 0.0958**
Largest diff. peak and hole	**0.21 and -0.26 e.A^{-3}**



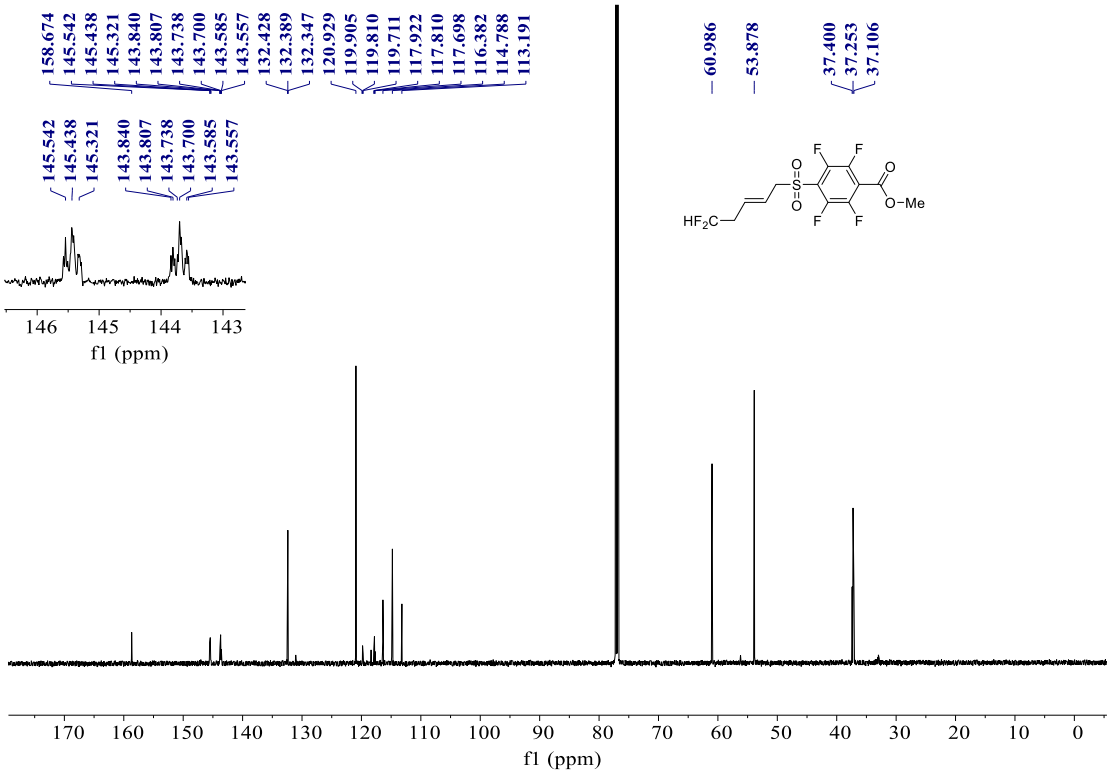
CCDC number	**2456069**
Empirical formula	**$C_{21}H_{18}F_6O_4S$**
Formula weight	**960.83**
Temperature	**293 K**
Wavelength	**0.71073**
Crystal system, space group	**triclinic, $P\bar{1}$**
Unit cell dimensions	**a= 5.6107(4) alpha= 87.148(3)** **b= 10.2669(8) beta= 87.326(2)** **c= 18.5433(15) gamma= 88.241(2)**
Volume	**1065.26(14)**
Z, Calculated density	**1, 1.498 g/cm^3**
Reflections collected / unique	**33827 / 3545 [R(int) = 0.063]**
F(000)	**492**
Absorption correction	**MULTI-SCAN**
Max. and min. transmission	**0.745 and 0.676**
Data / restraints / parameters	**4201/0/292**
Goodness-of-fit on F^2	**1.069**
Final R indices [I>2sigma(I)]	**R_1 = 0.0698, wR_2 = 0.2048**
R indices (all data)	**R_1 = 0.0785, wR_2 = 0.2151**
Largest diff. peak and hole	**0.997 and -0.423 e.A^{-3}**

XI. ^{1}H, ^{13}C and ^{19}F NMR Spectra of New Compounds

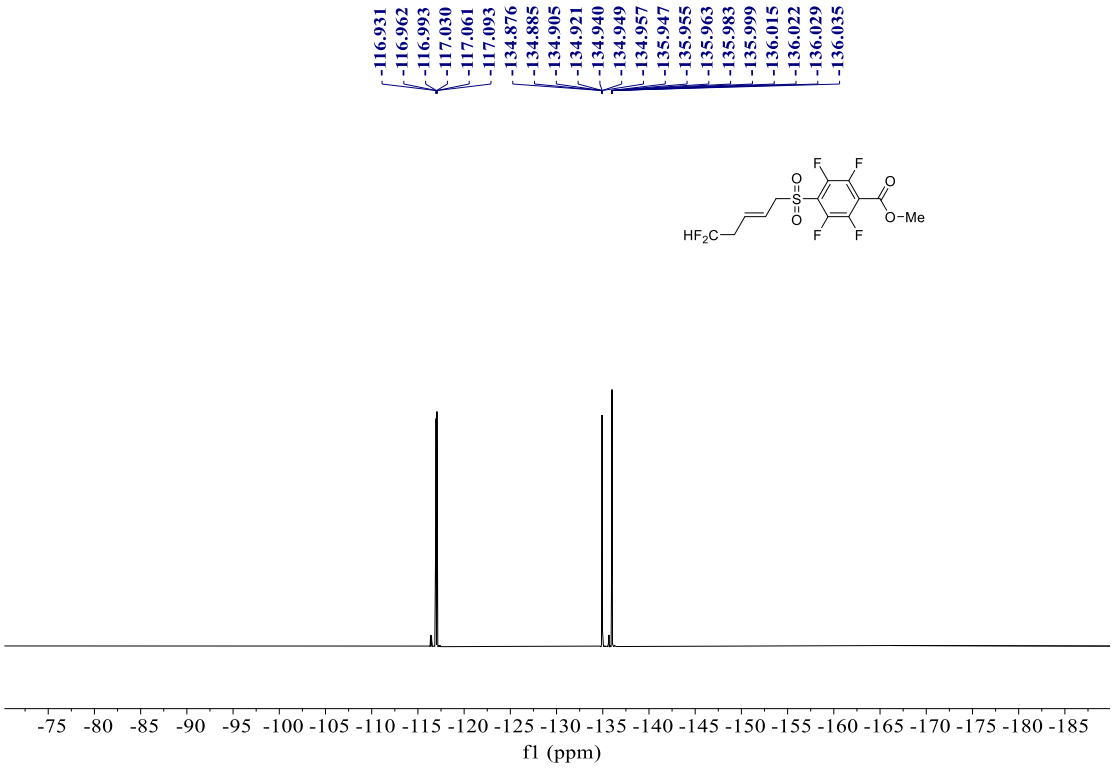
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4aa



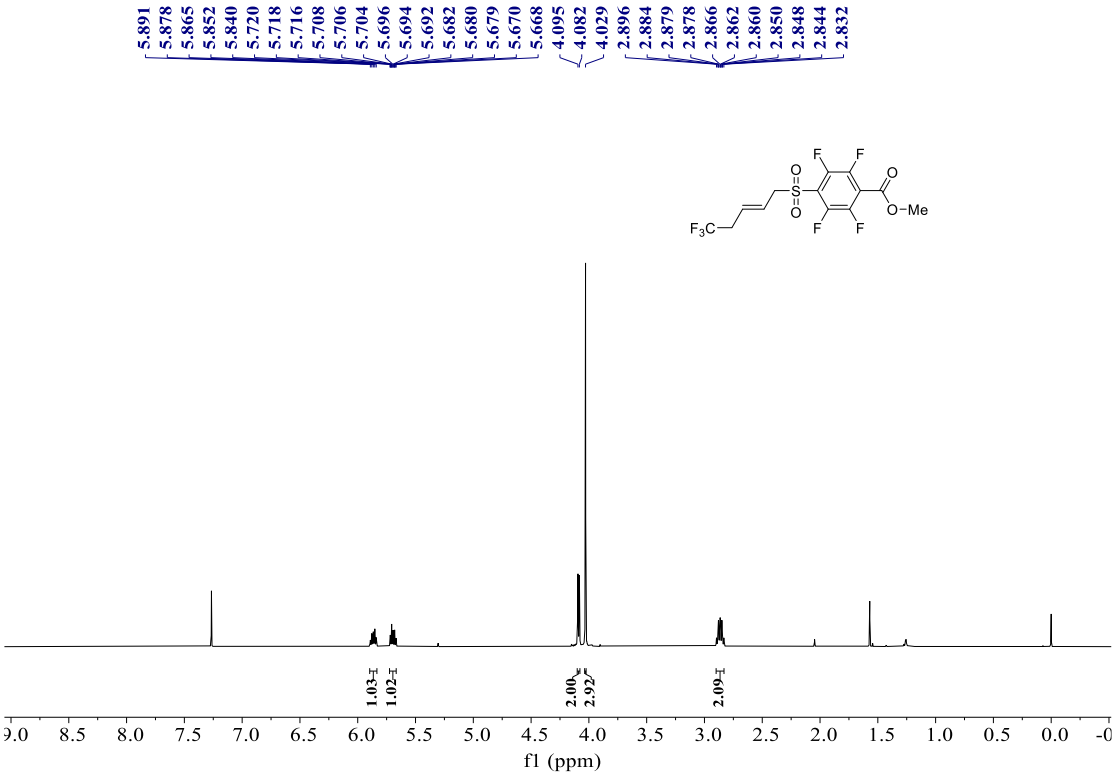
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4aa



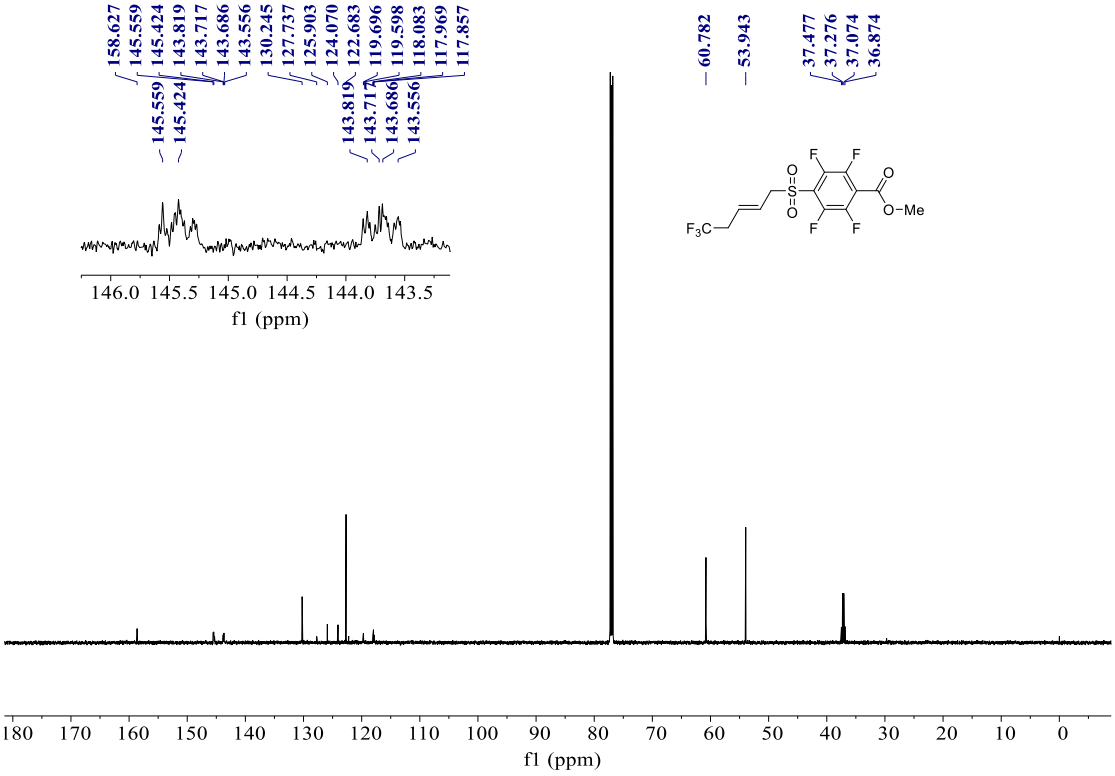
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4aa



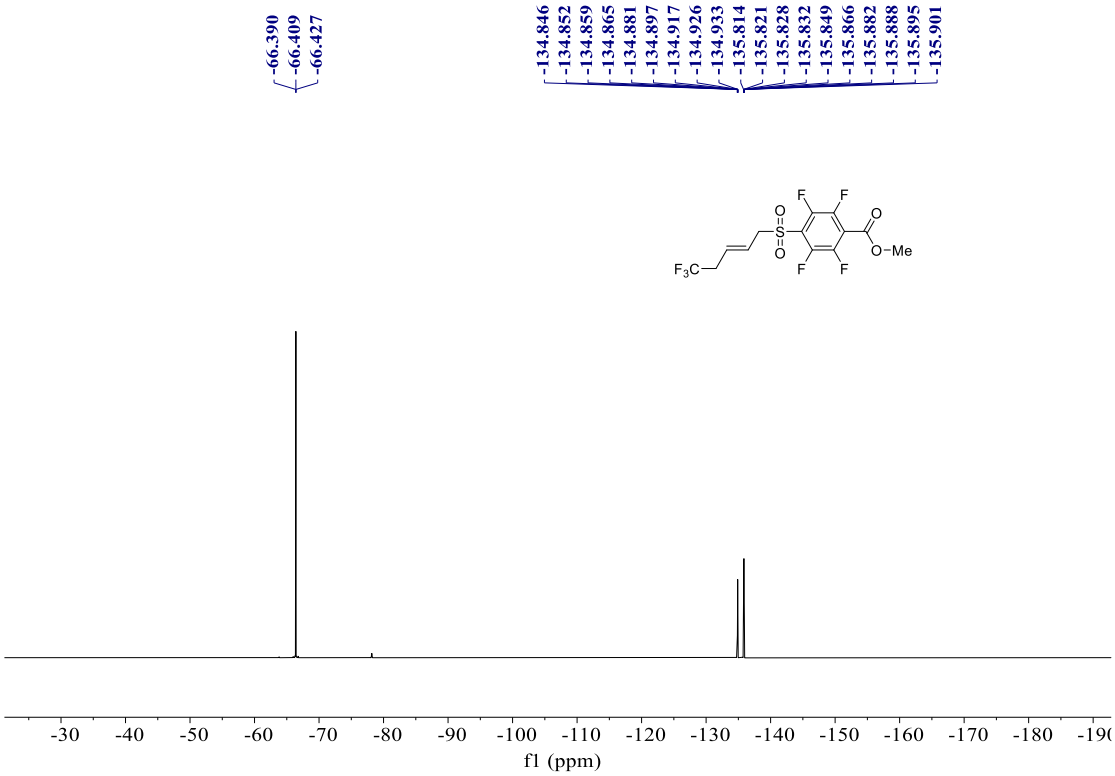
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4aa''



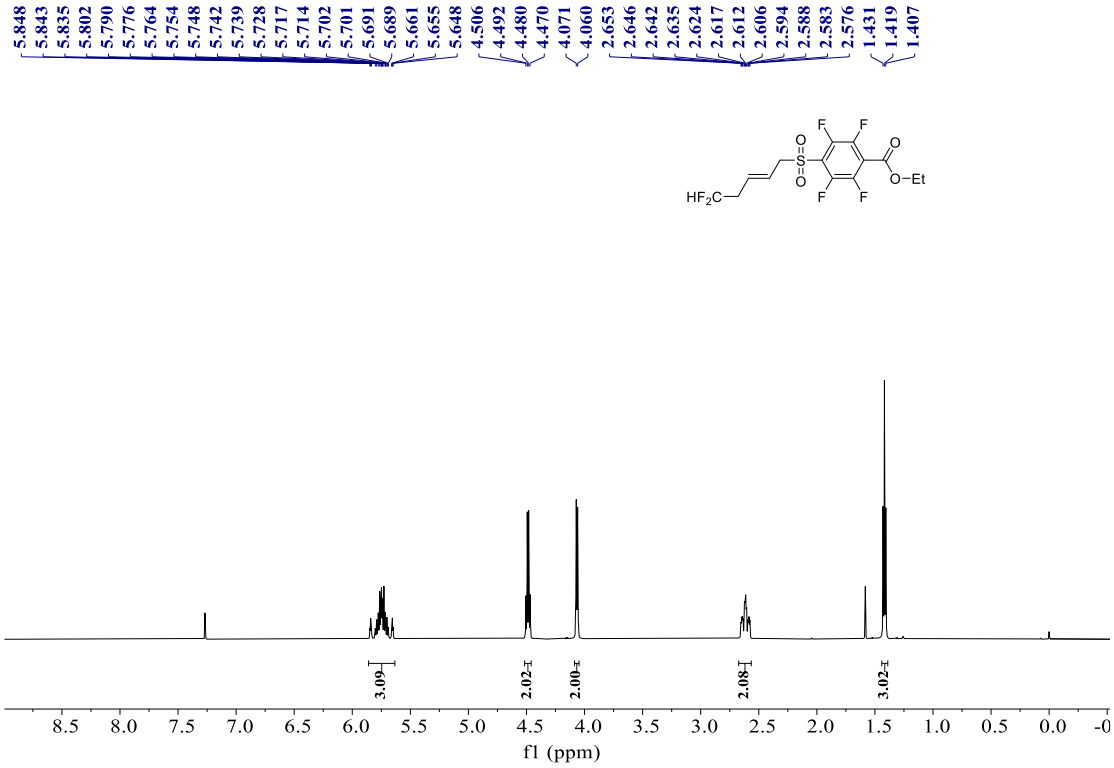
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4aa''



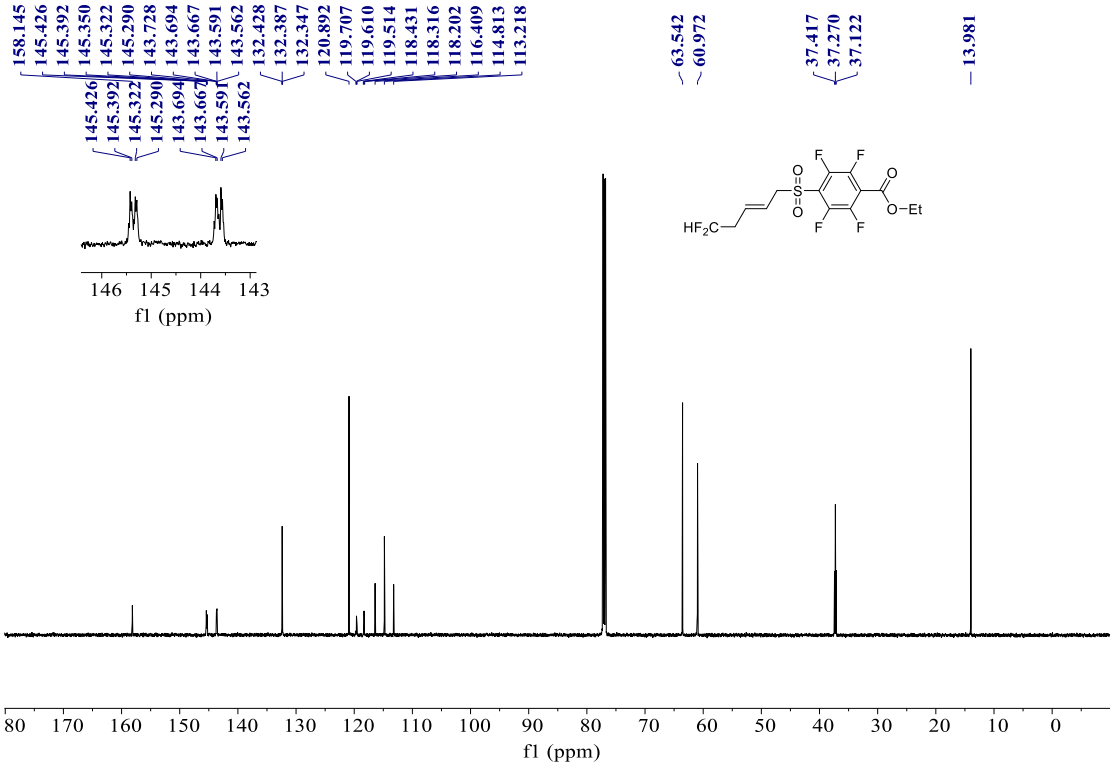
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4aa''



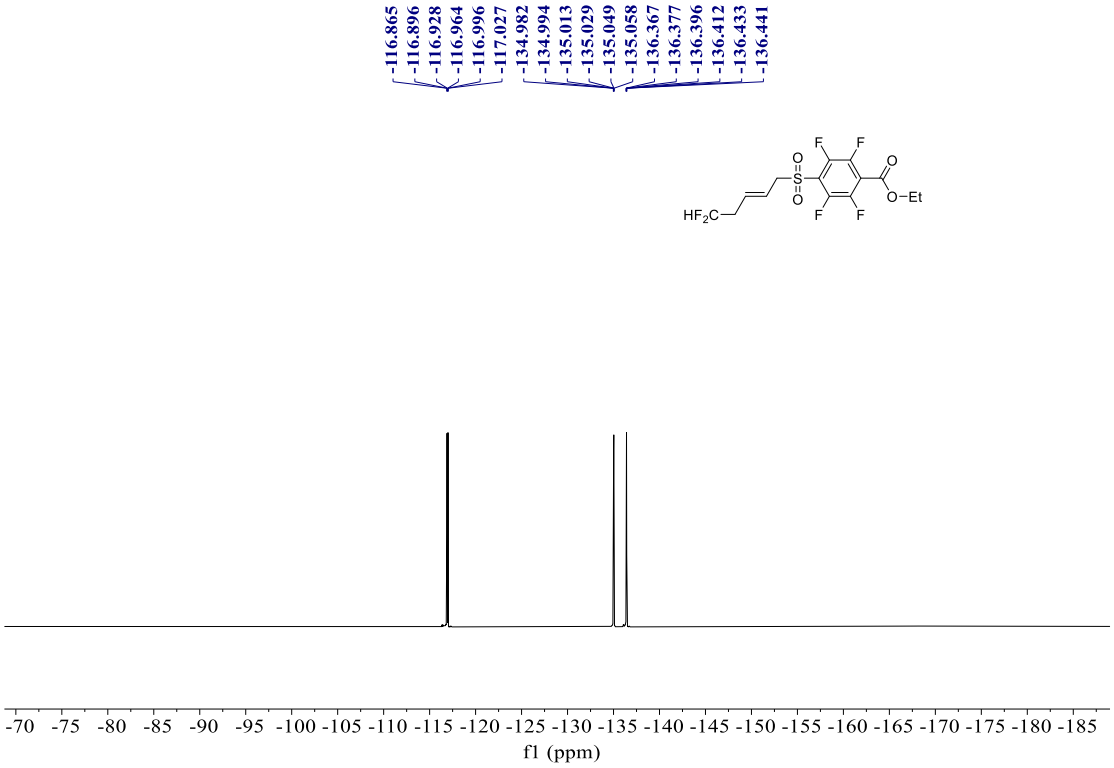
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ab



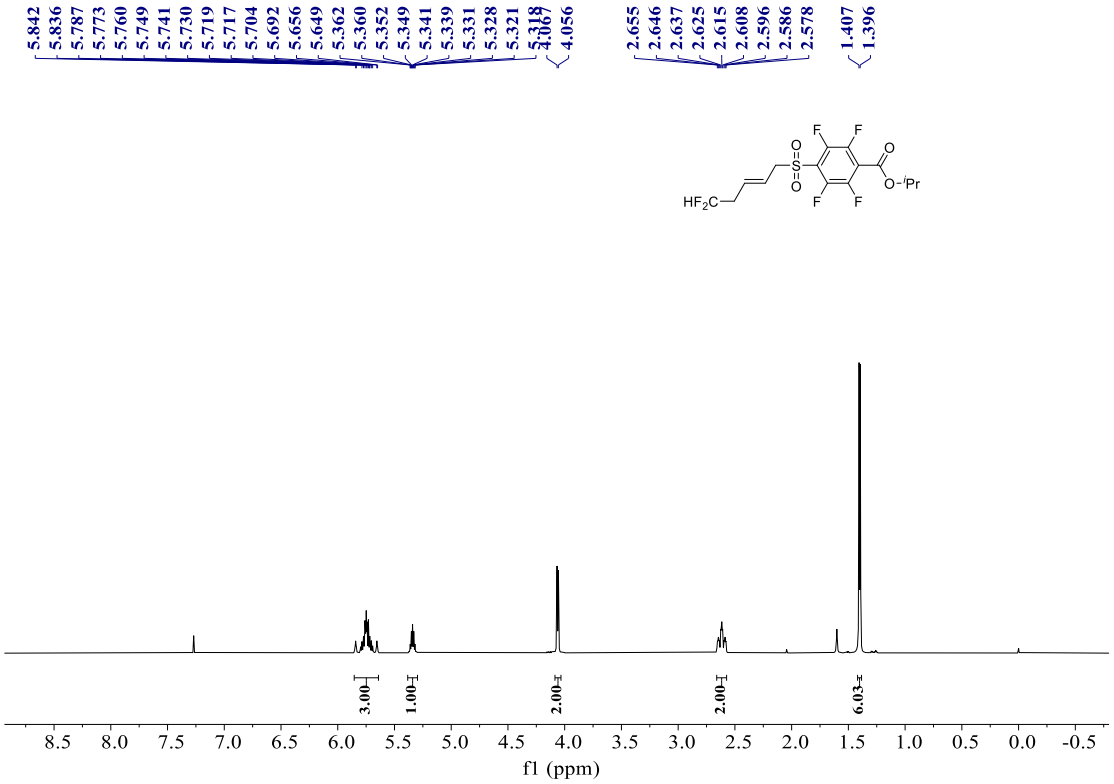
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ab



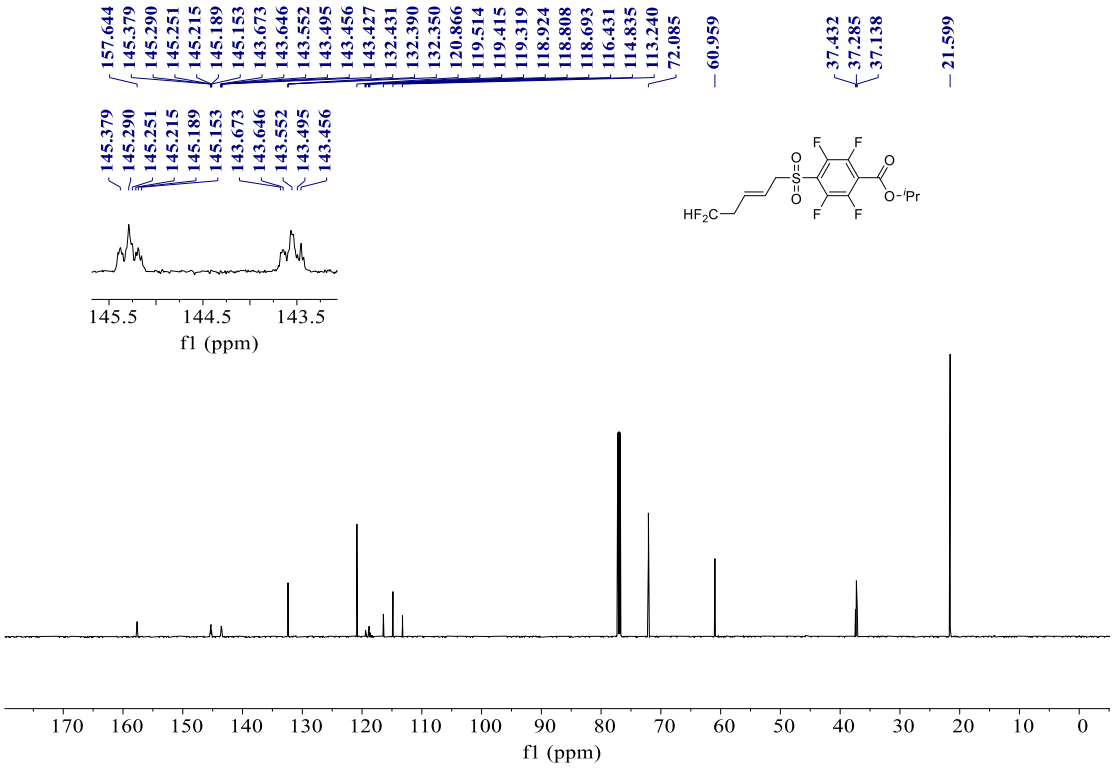
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ab



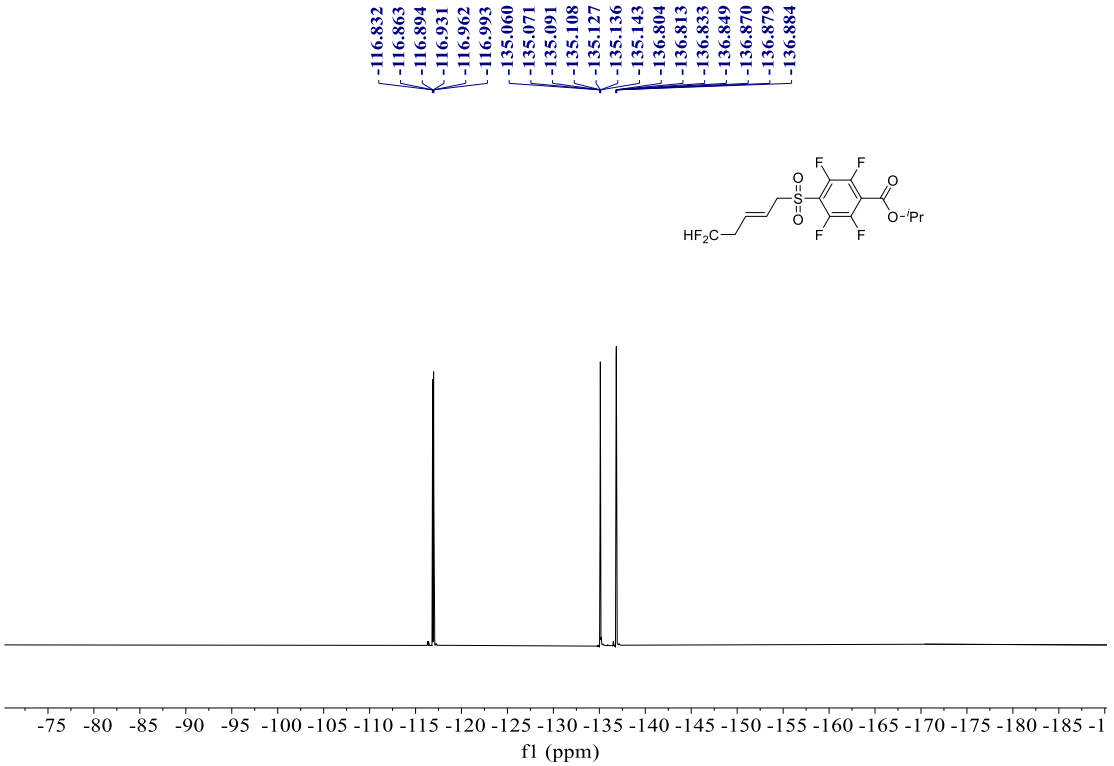
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ac



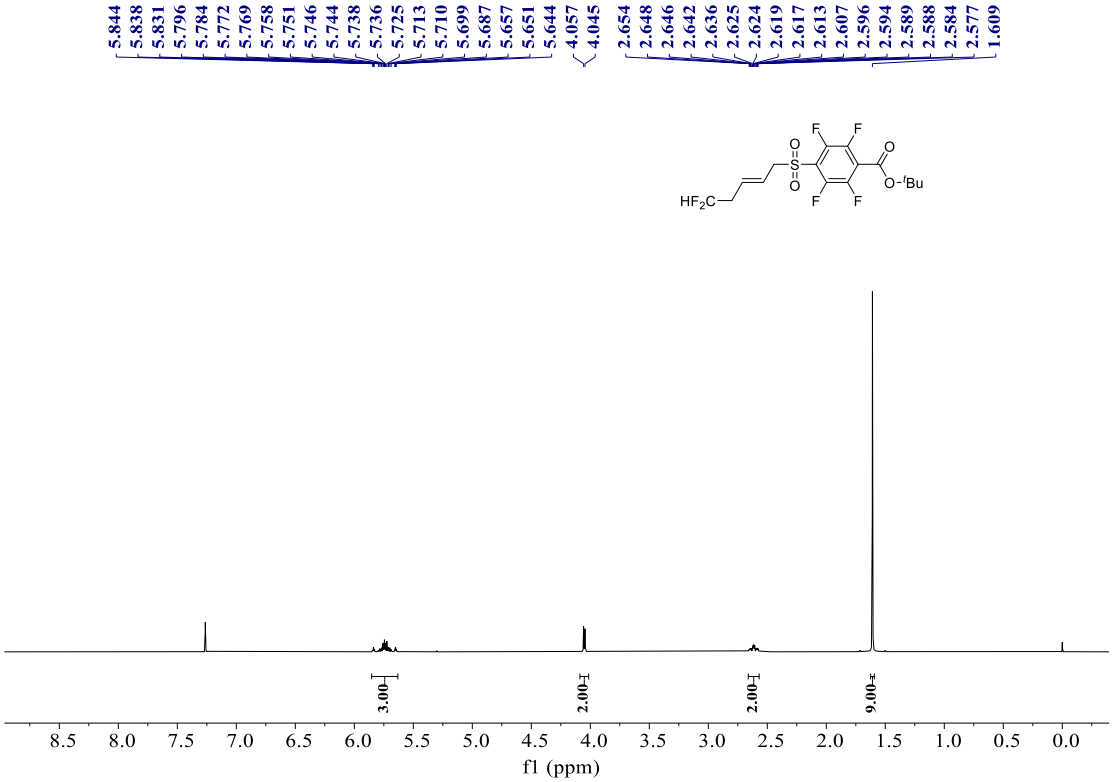
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ac



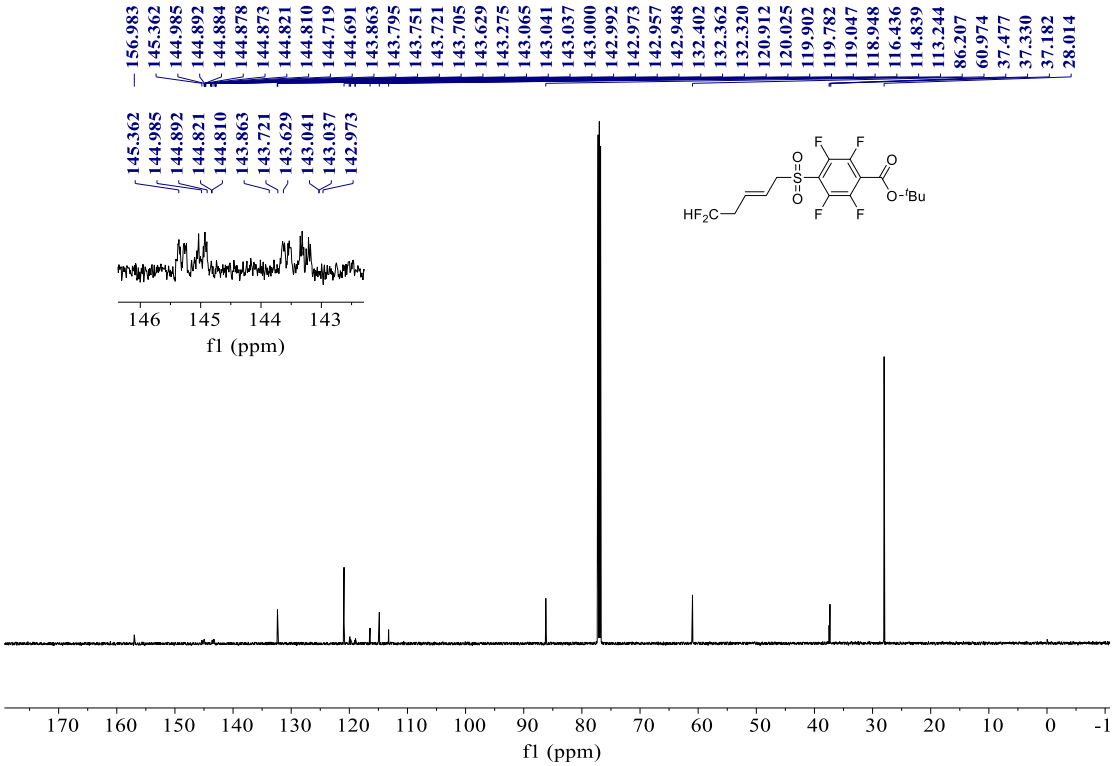
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ac



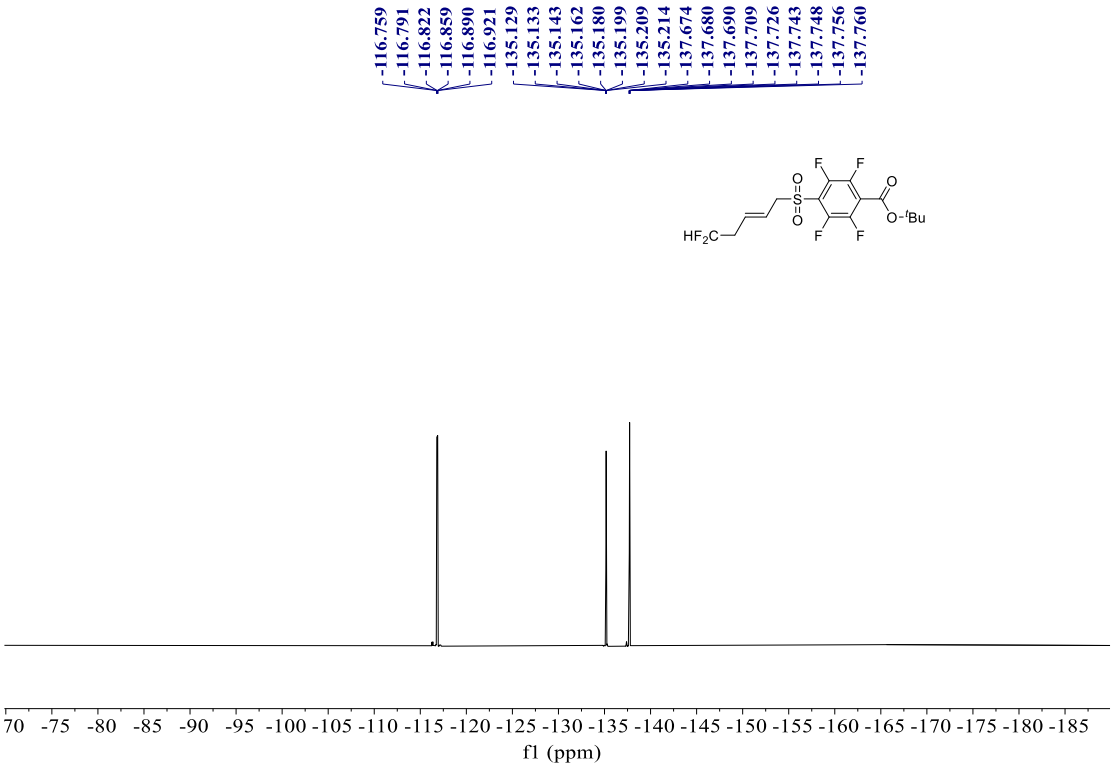
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ad



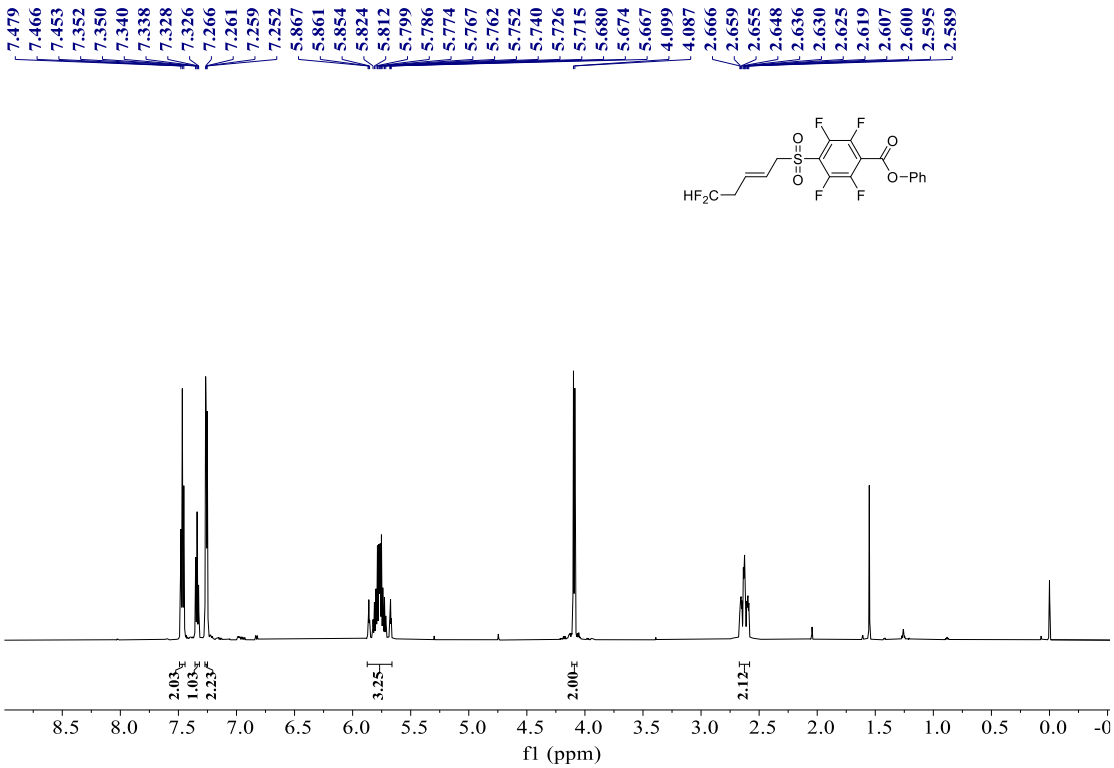
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ad



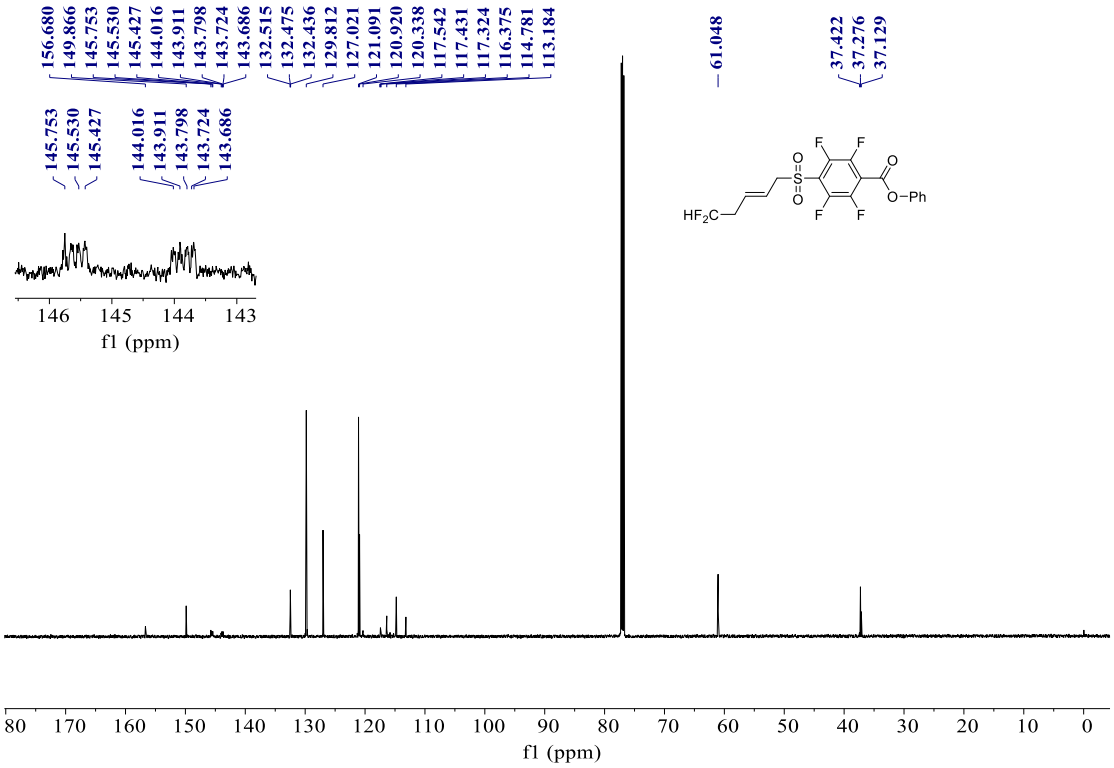
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ad



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ae



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ae



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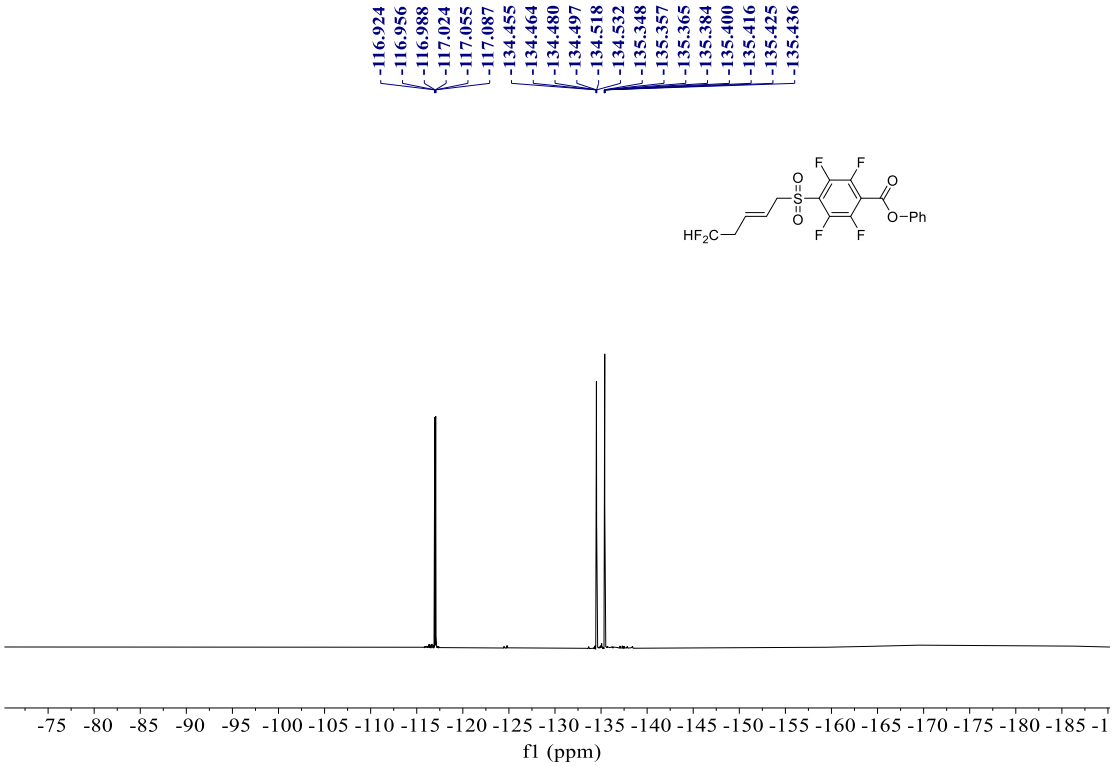
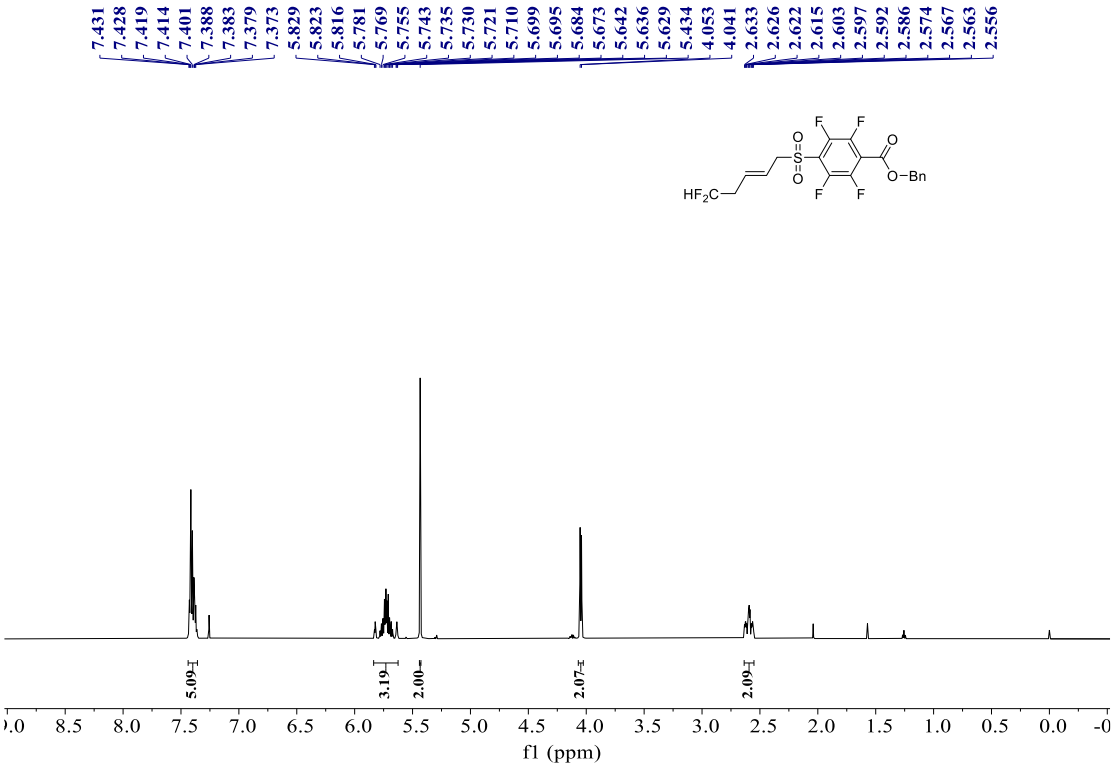
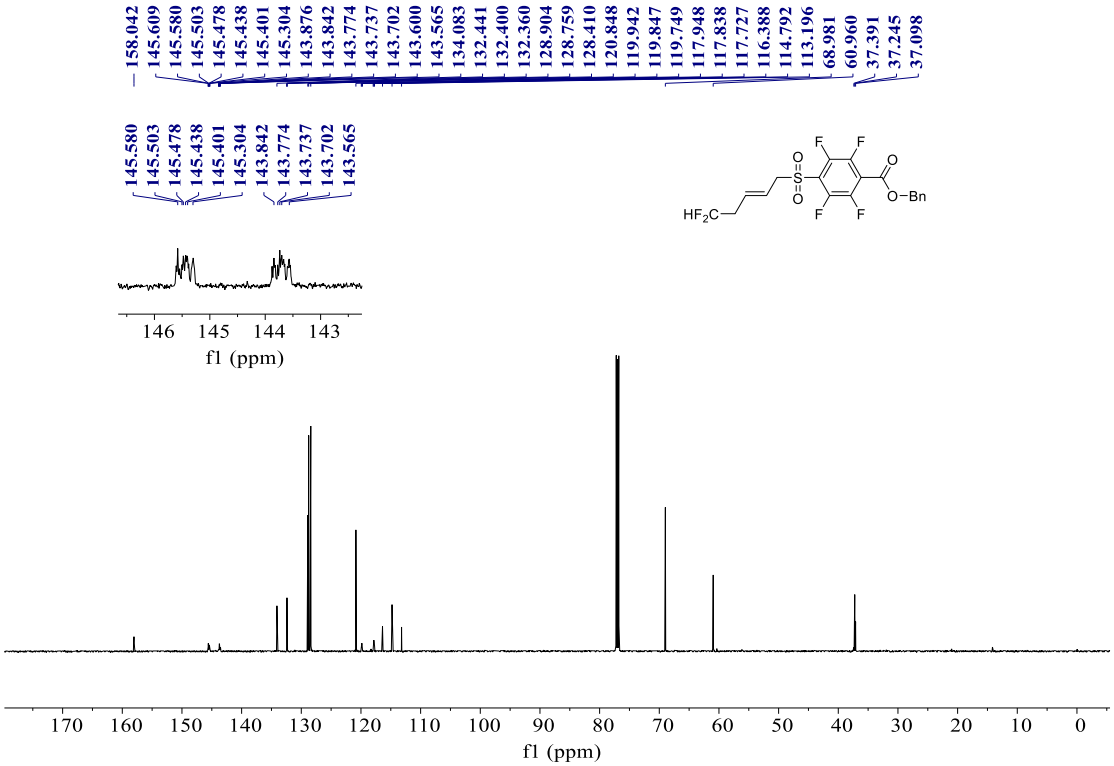


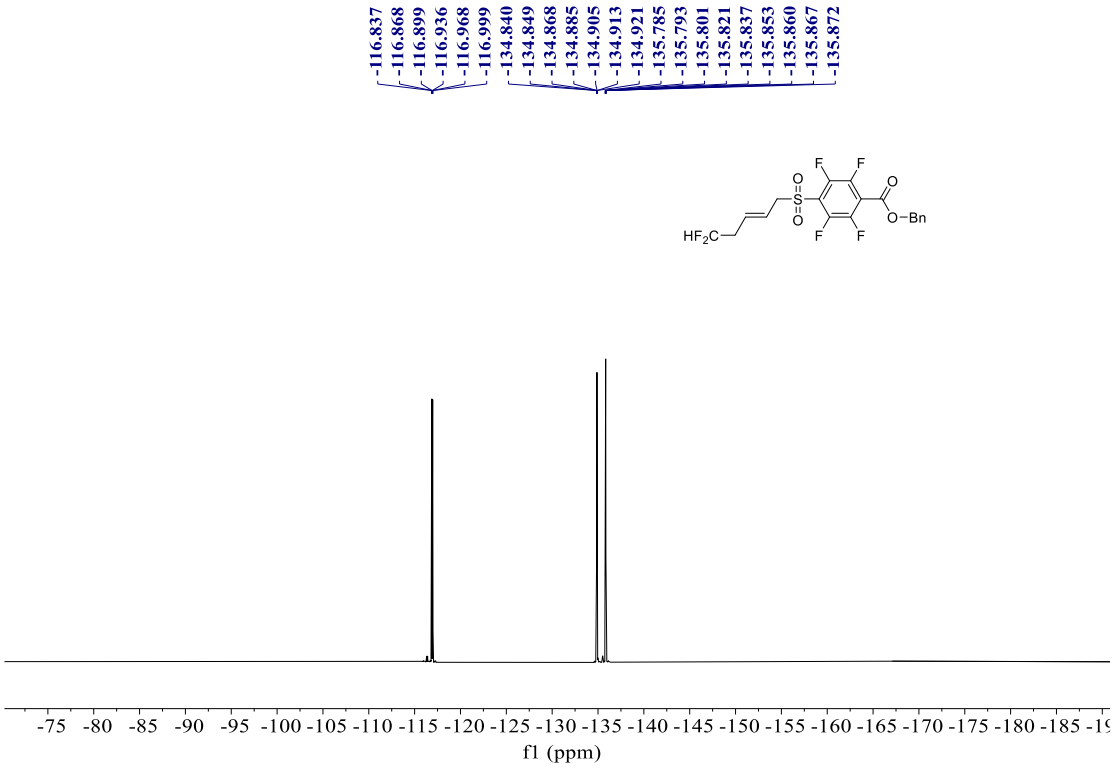
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4af



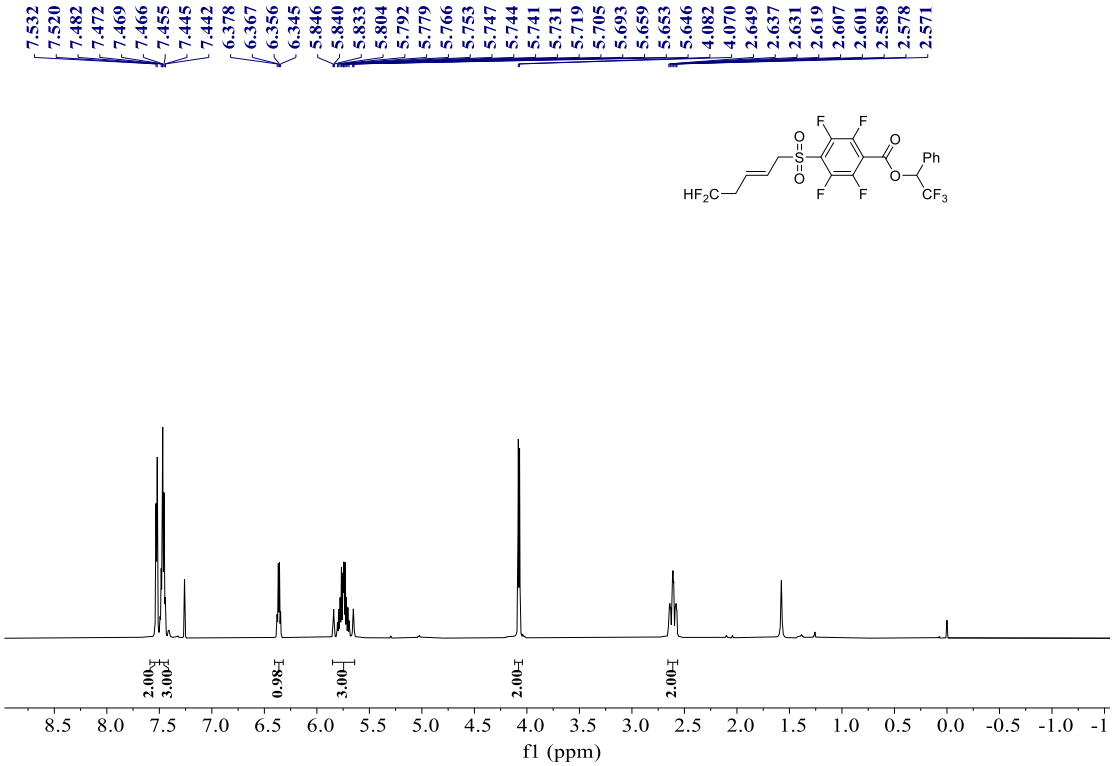
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4af



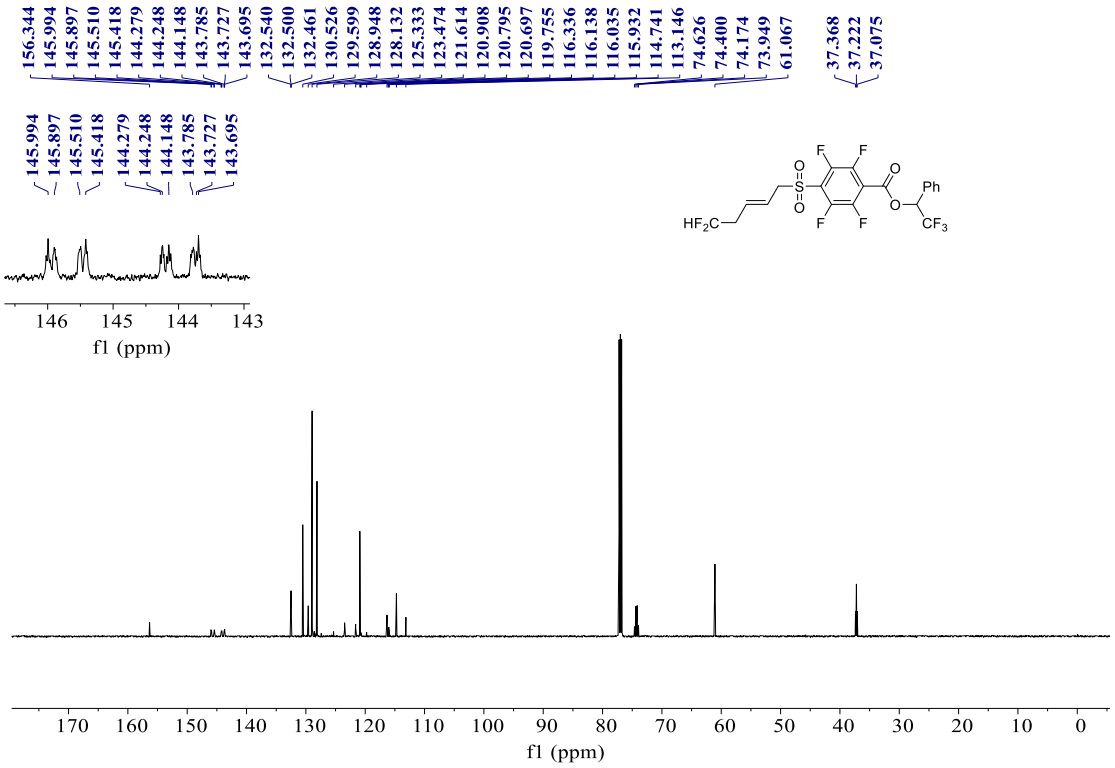
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4af



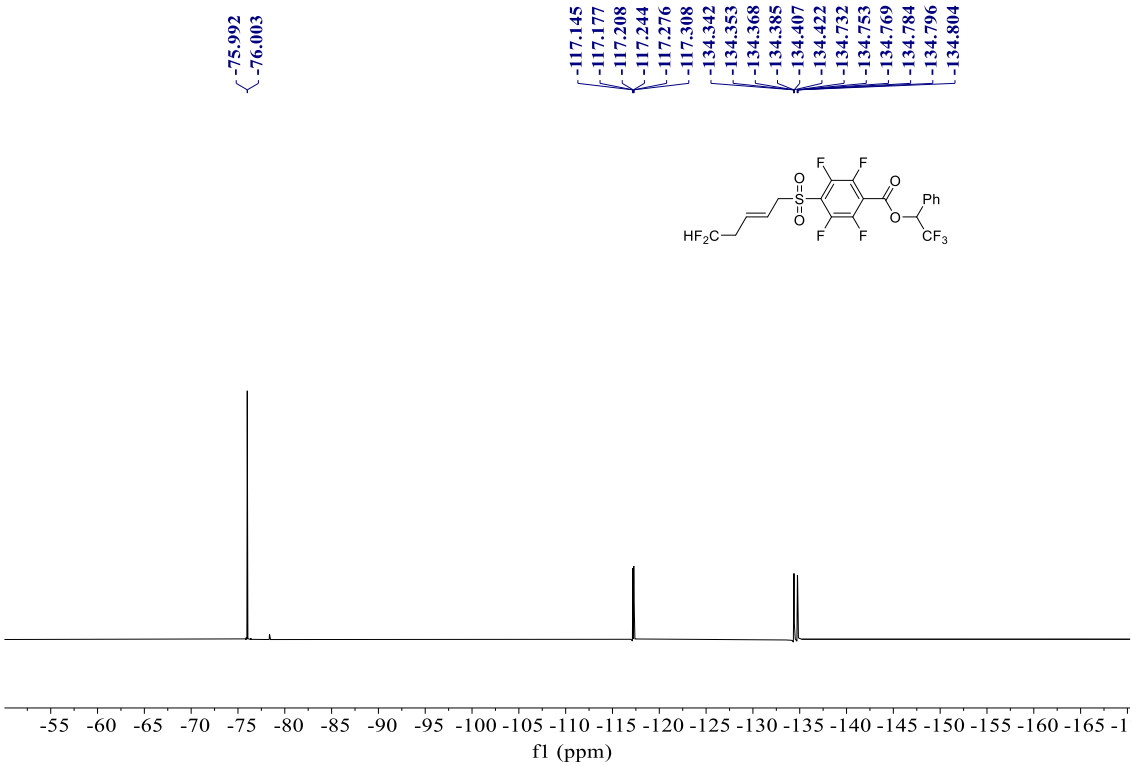
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ag



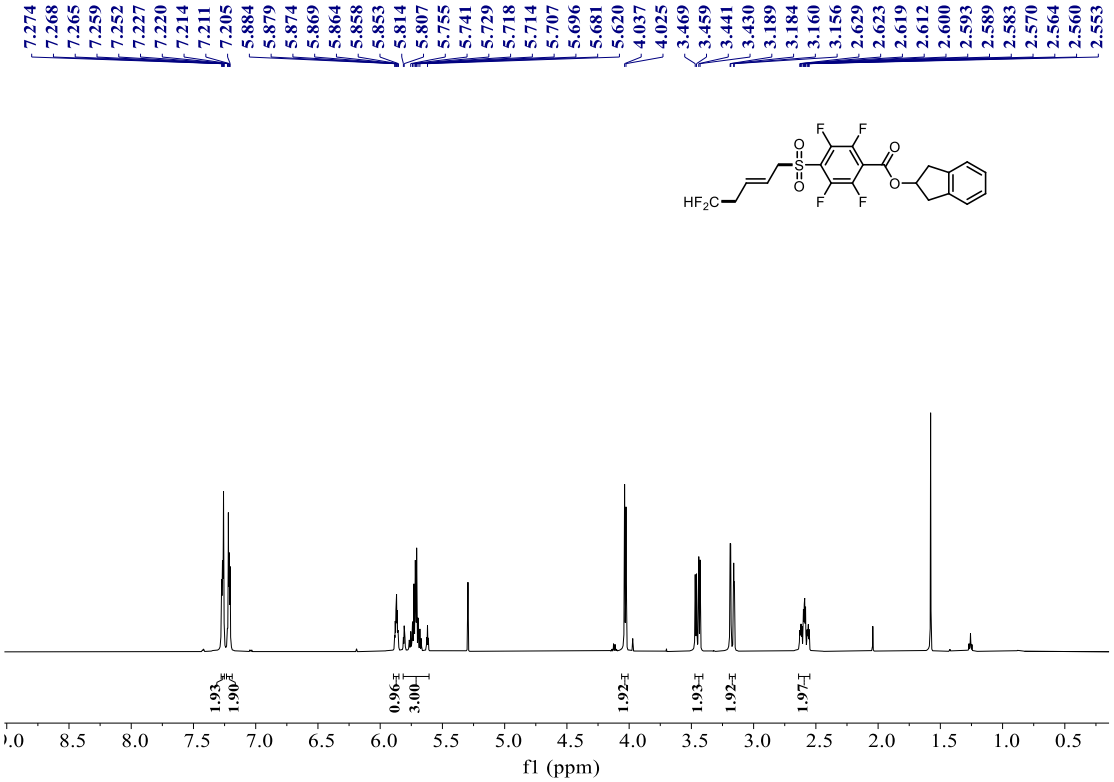
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ag



^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ag



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ah



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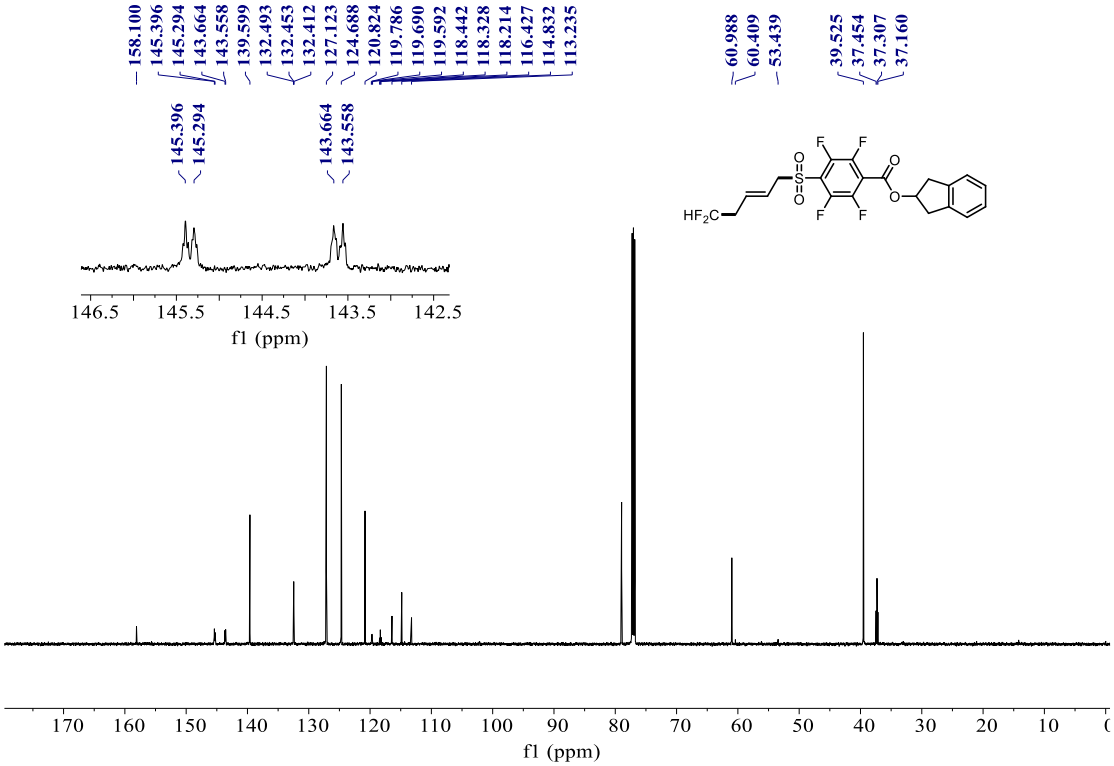
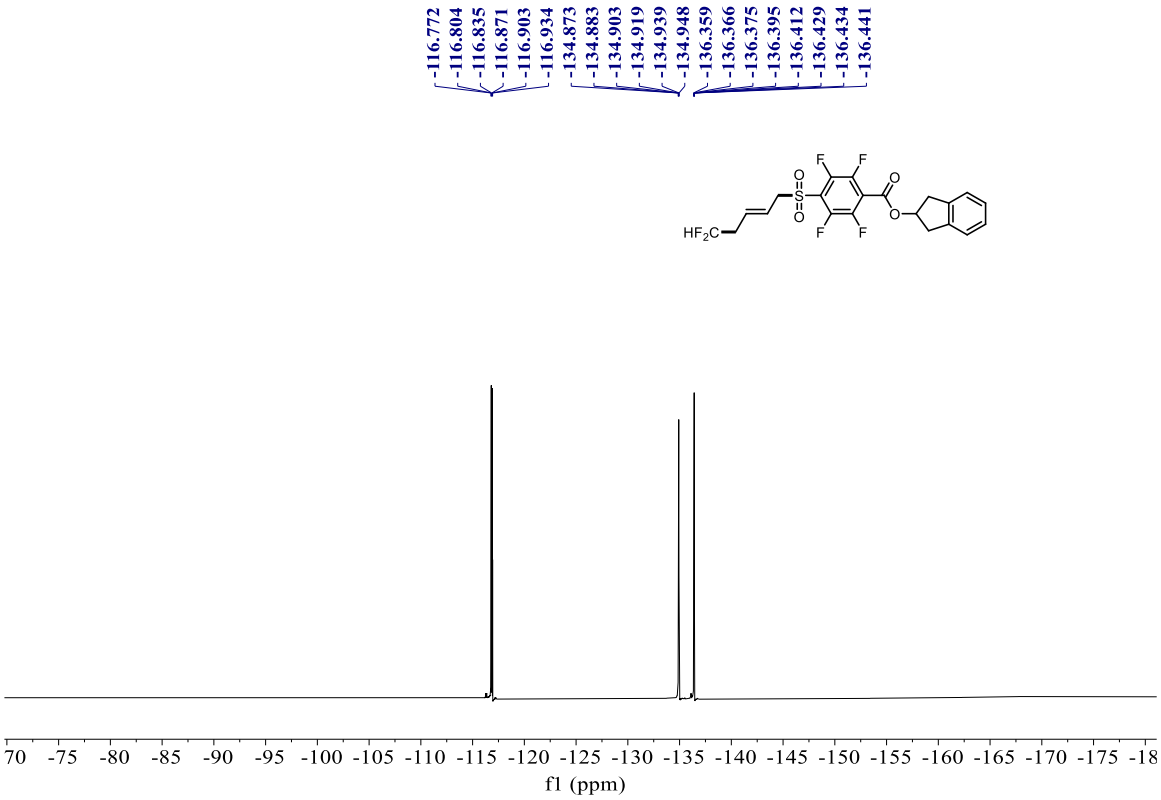
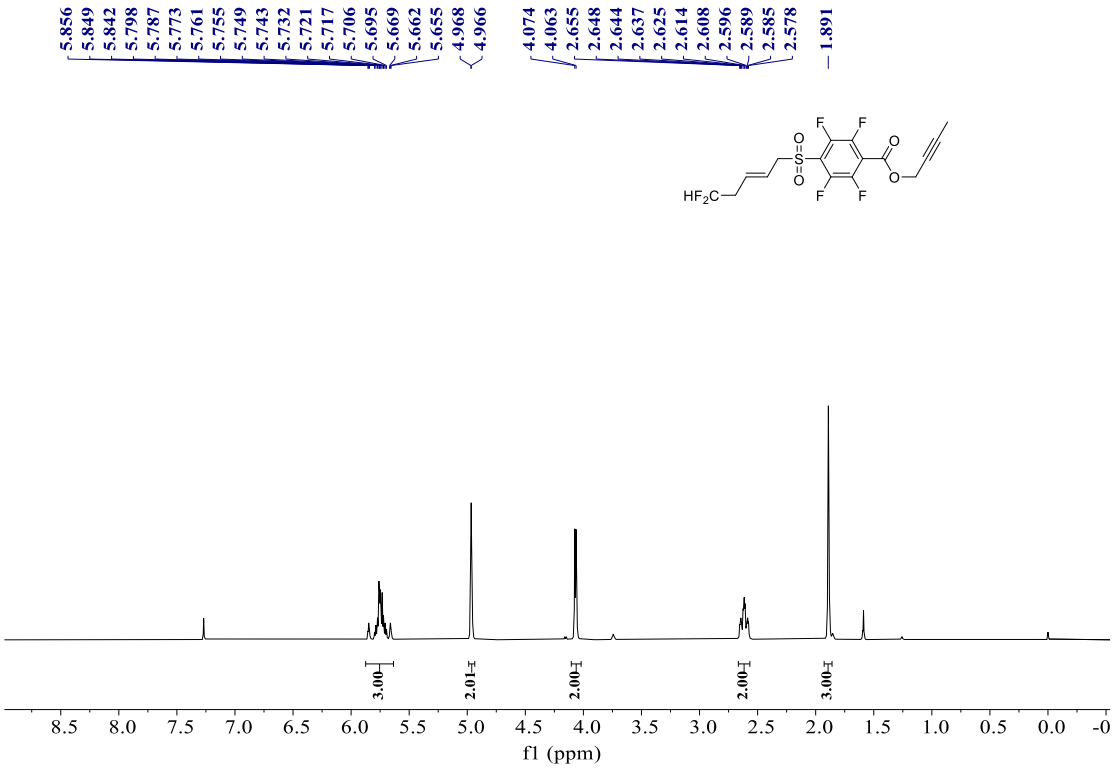


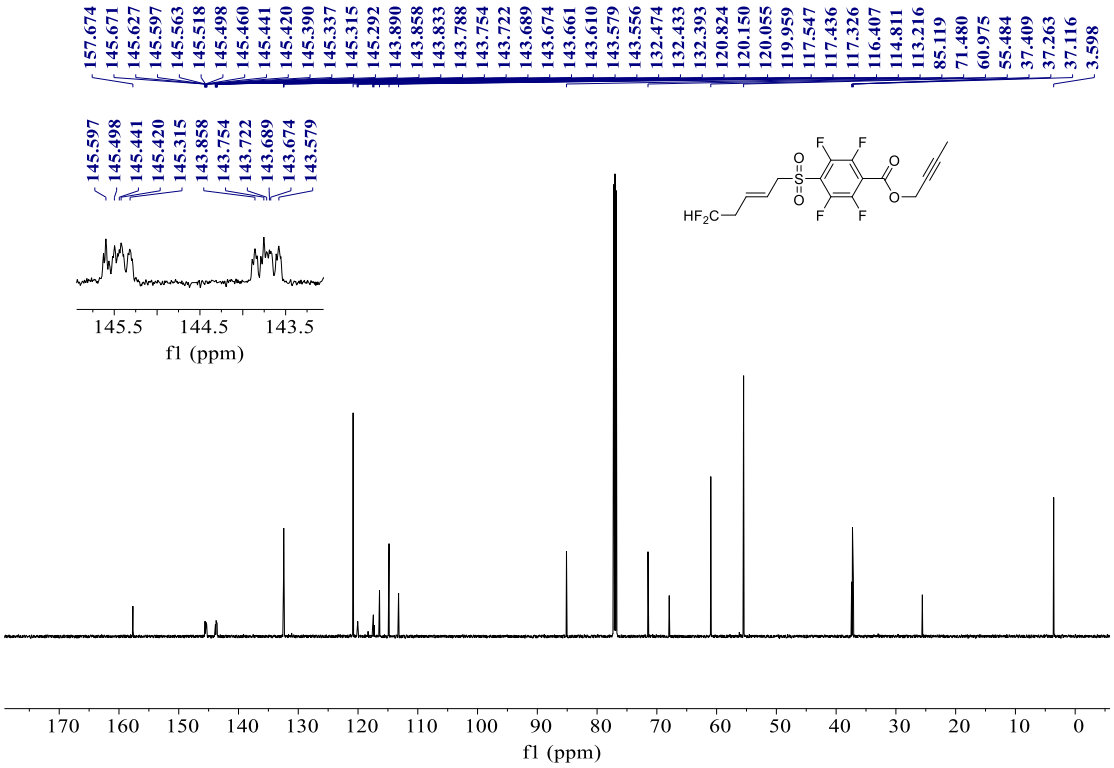
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ah



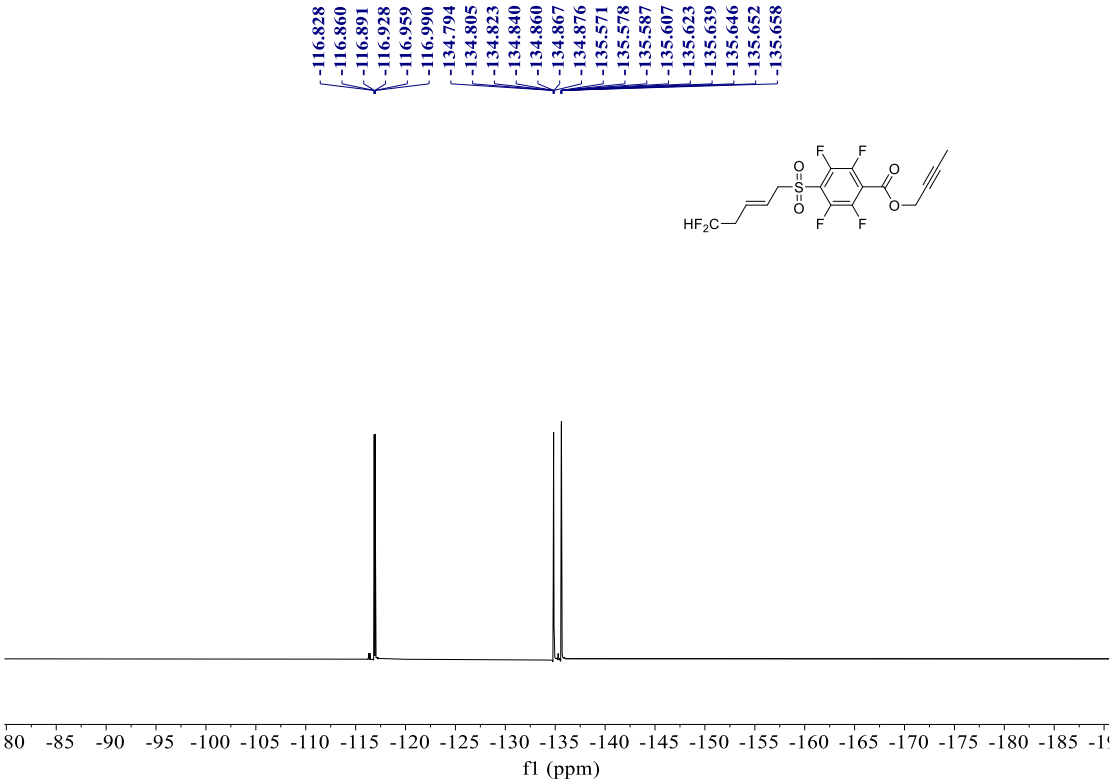
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ai



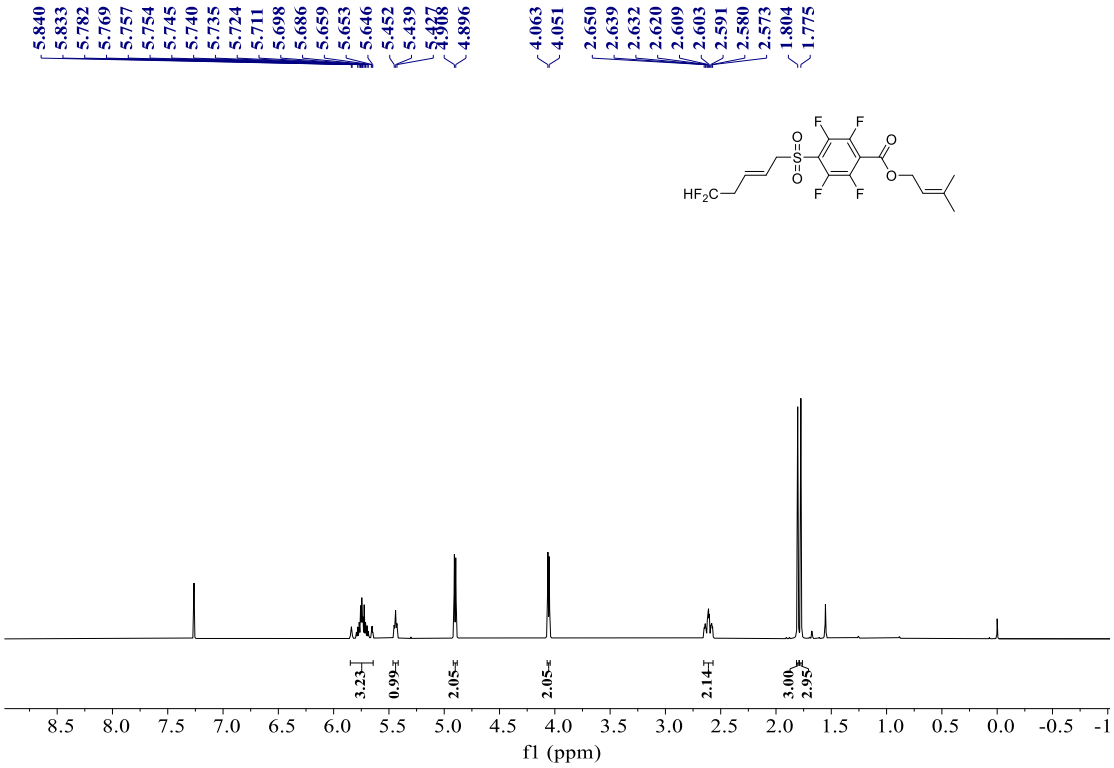
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ai



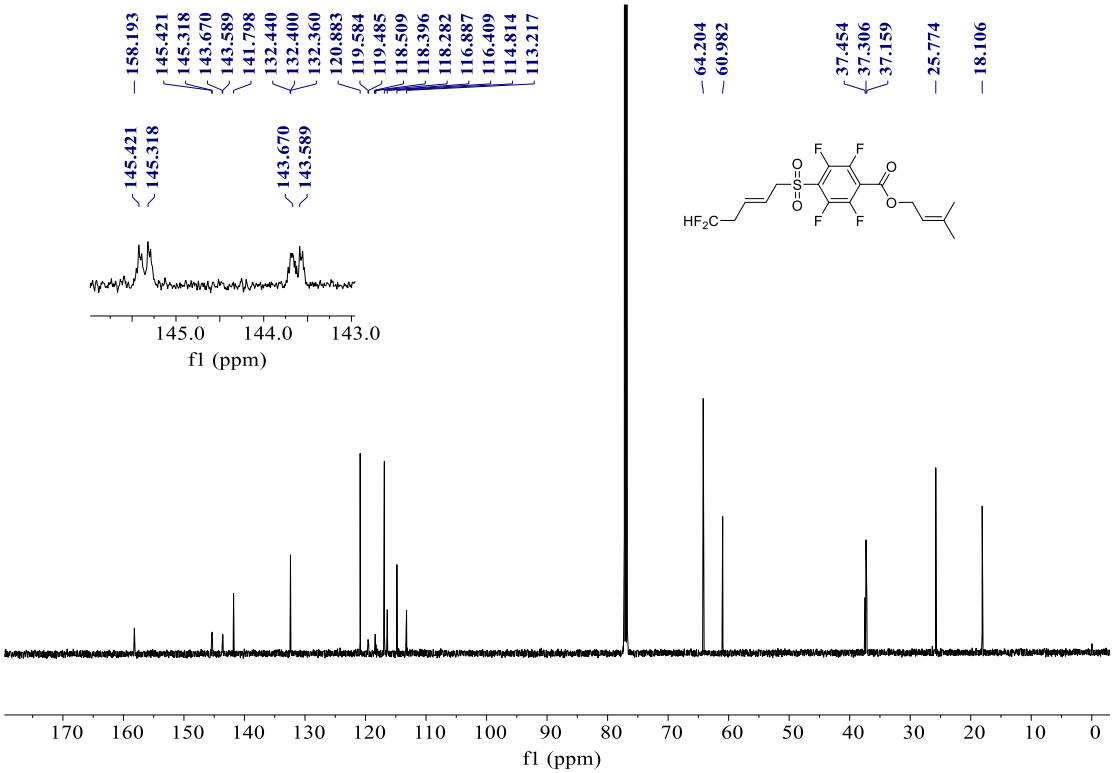
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ai



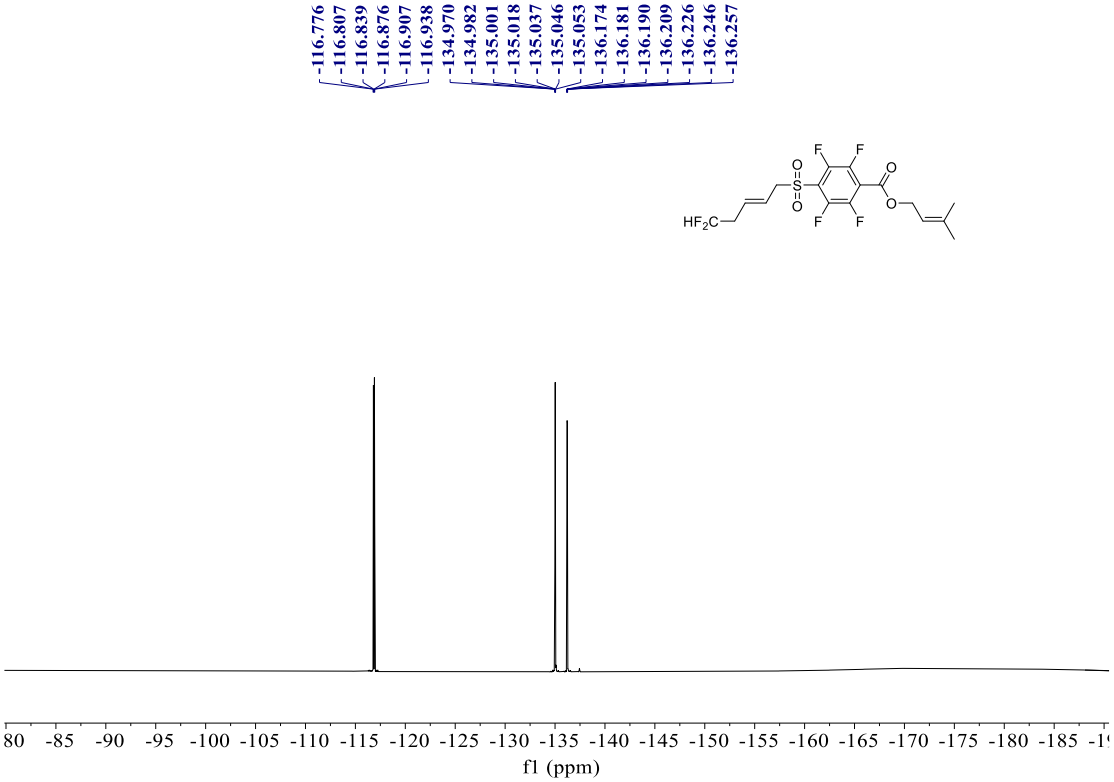
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4aj



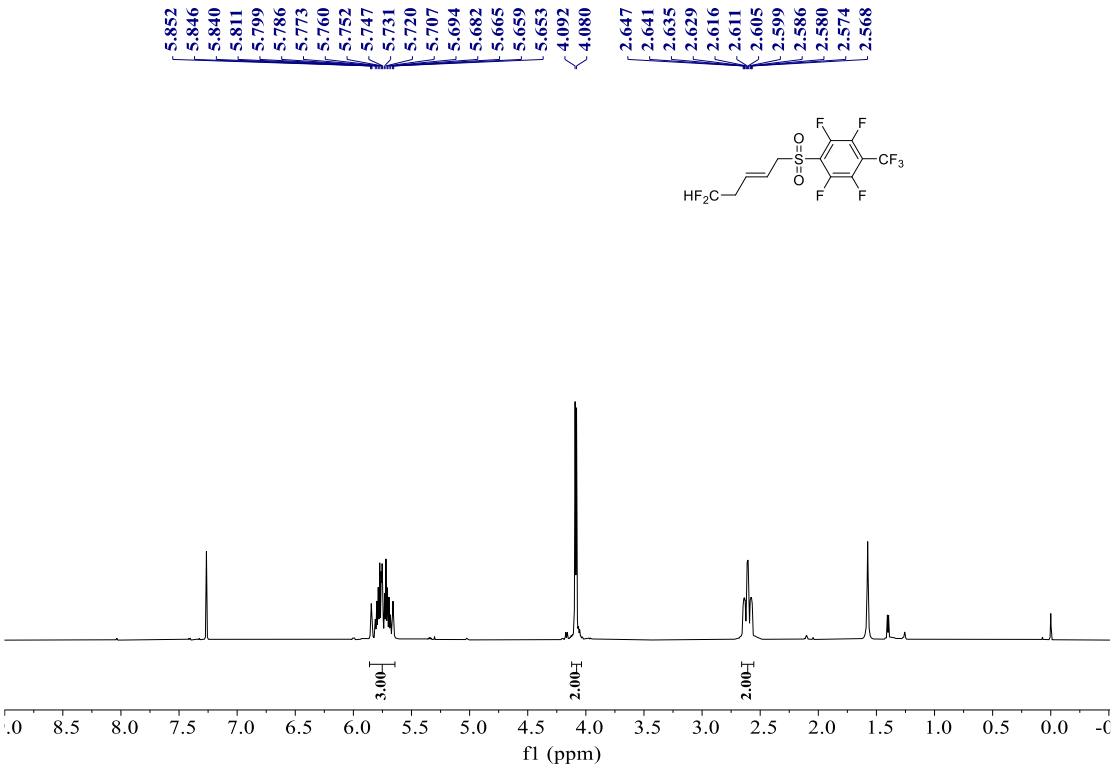
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4aj



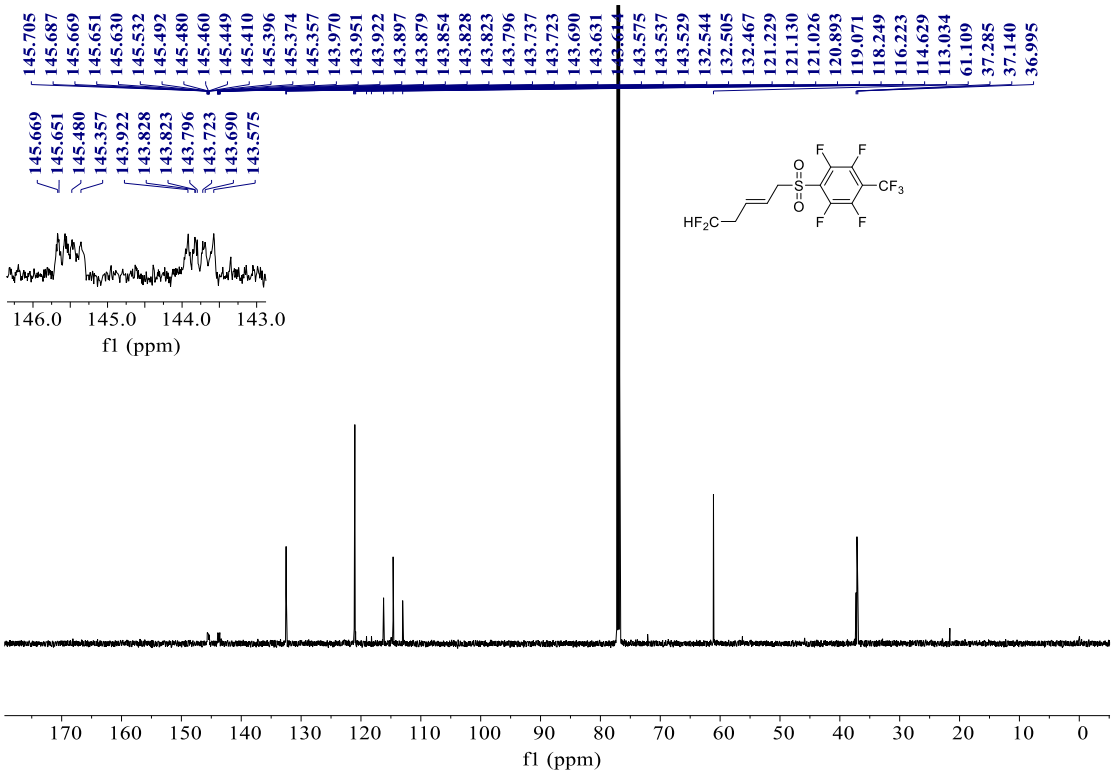
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4aj



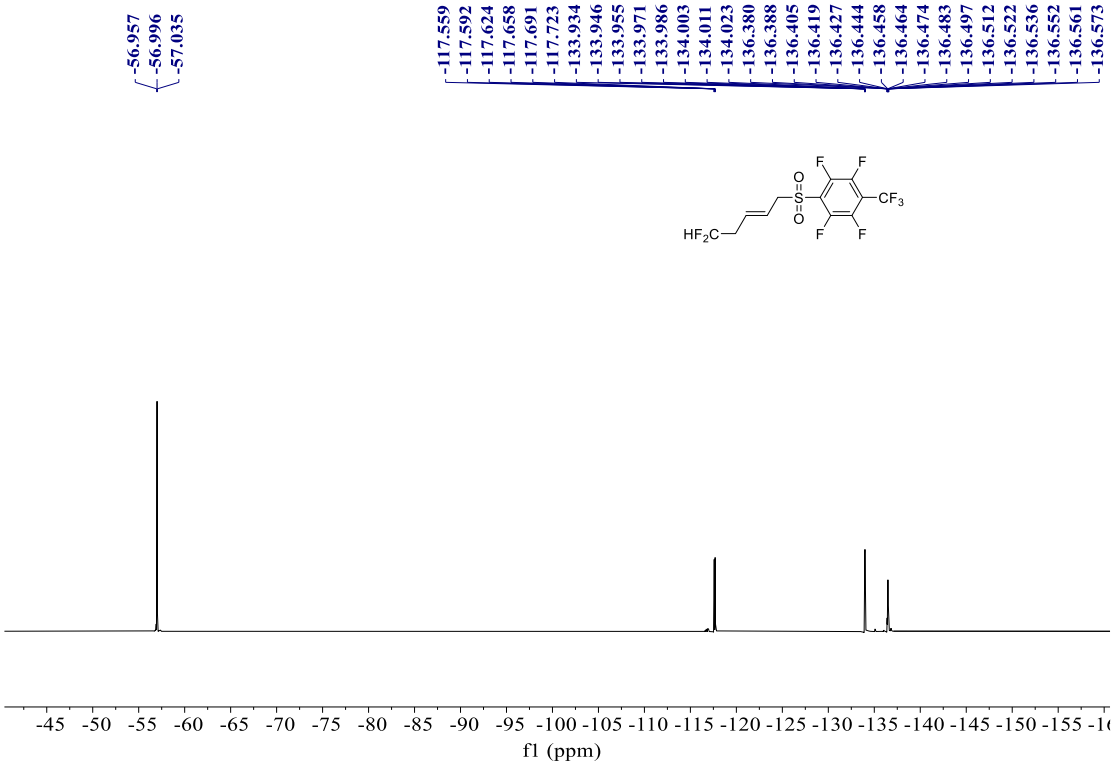
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ak



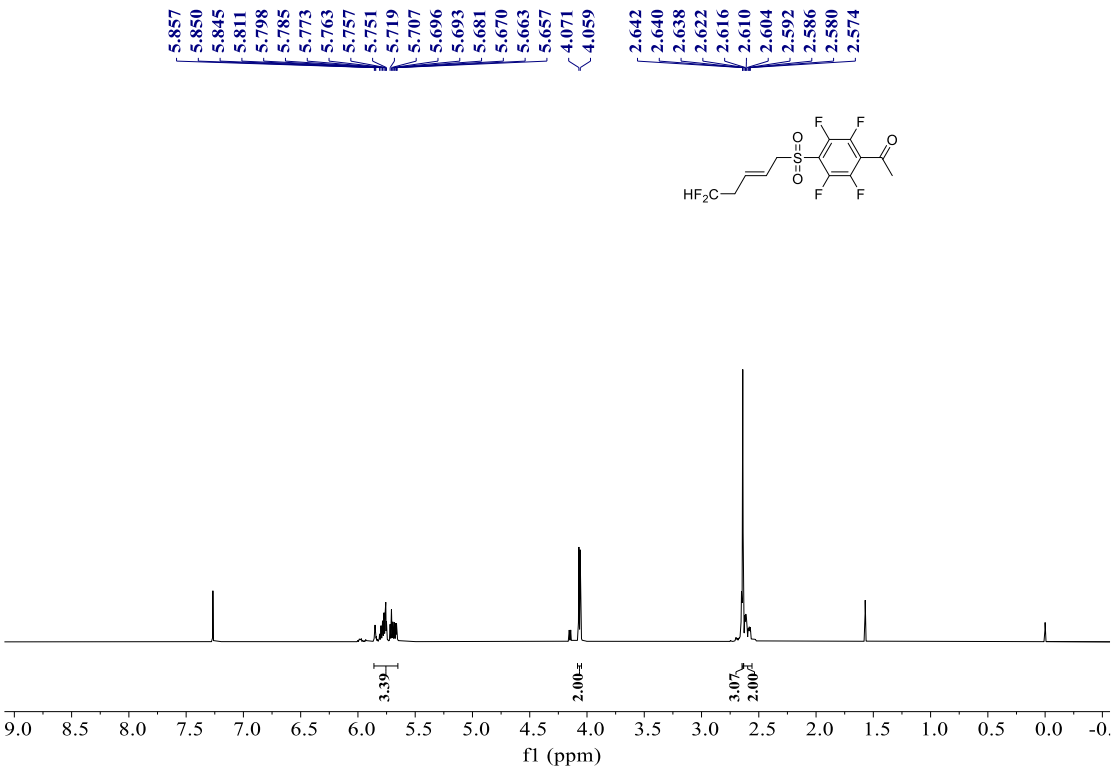
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ak



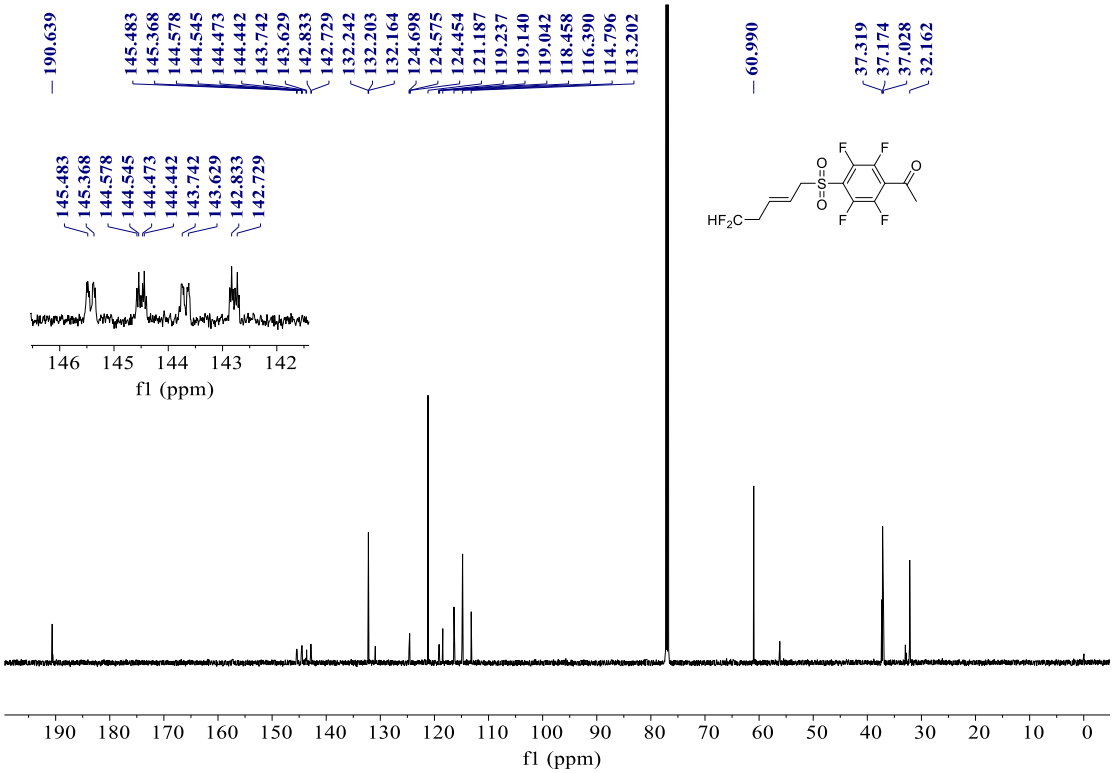
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ak



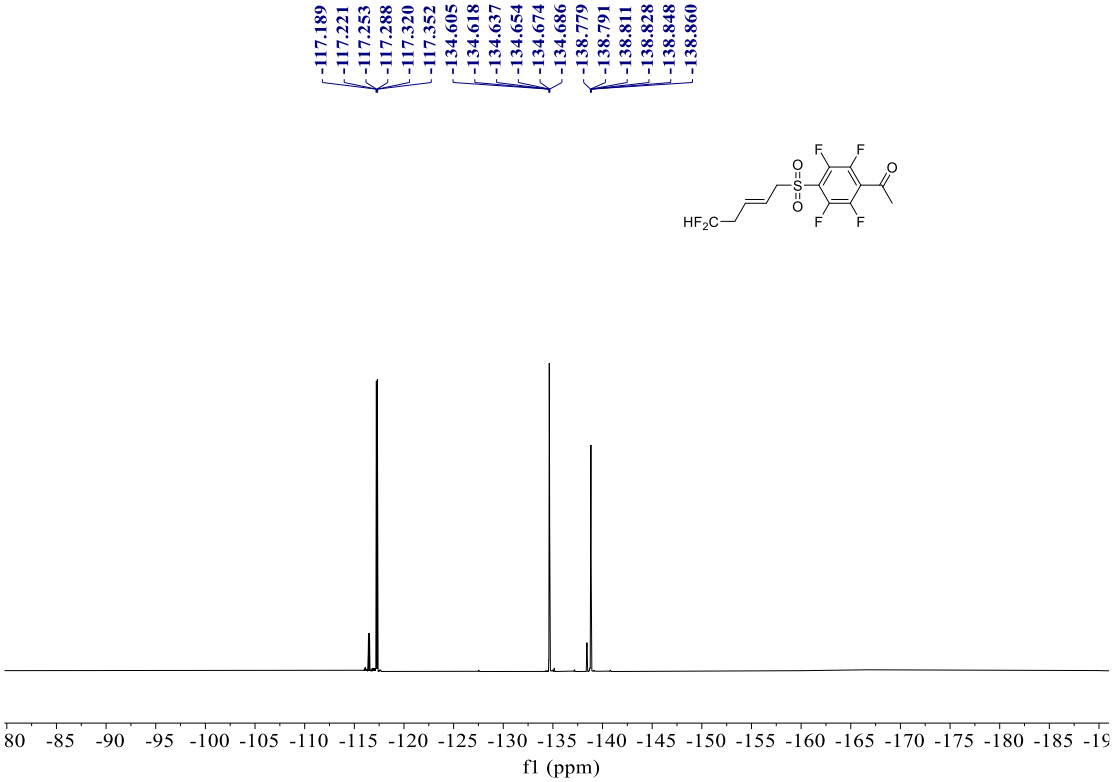
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4al



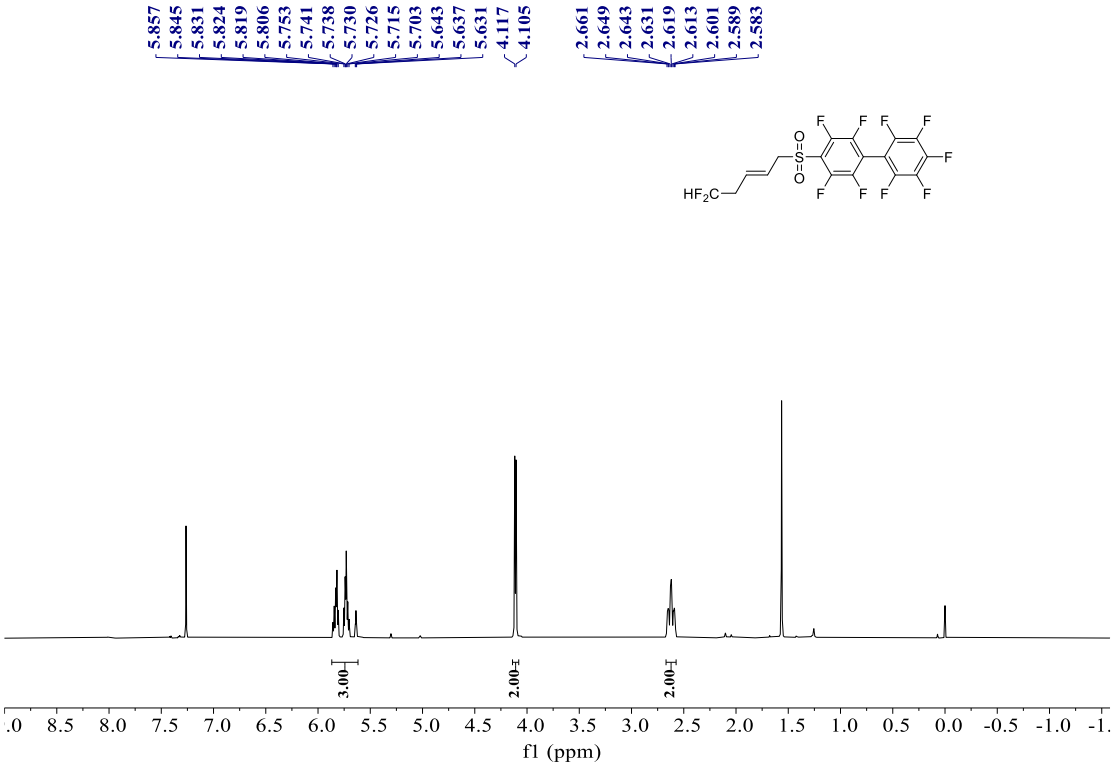
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4al



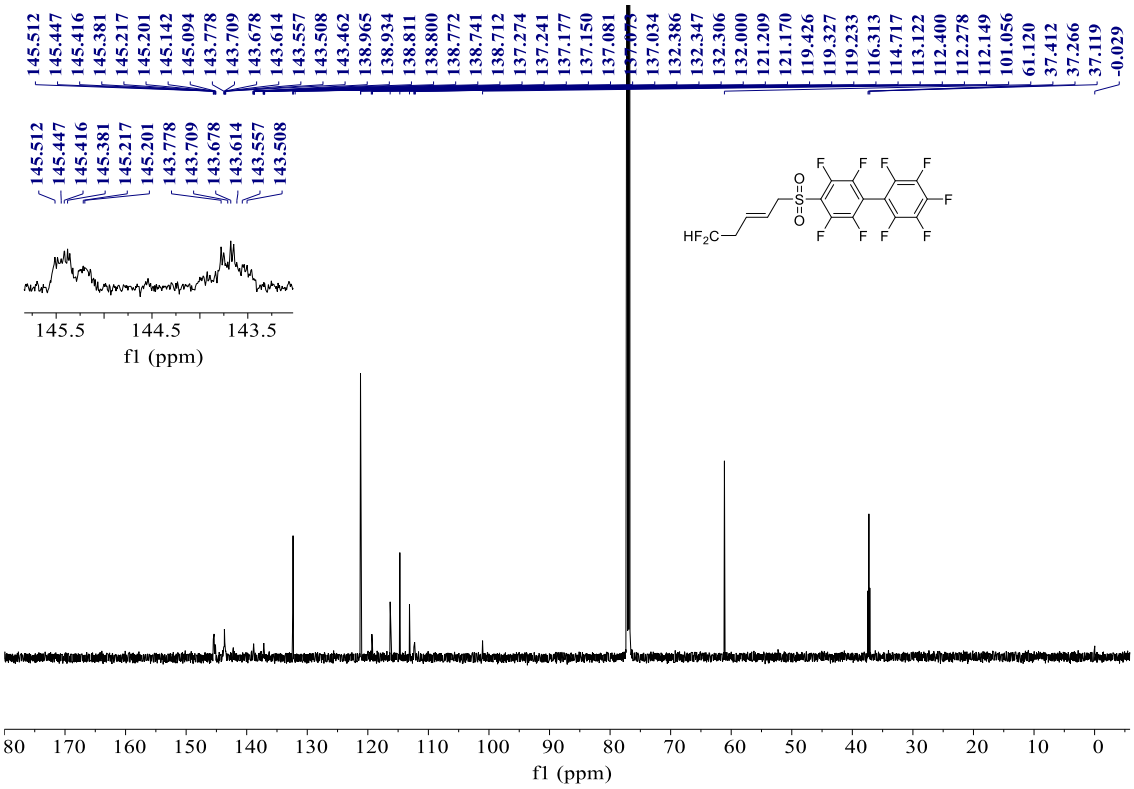
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4al



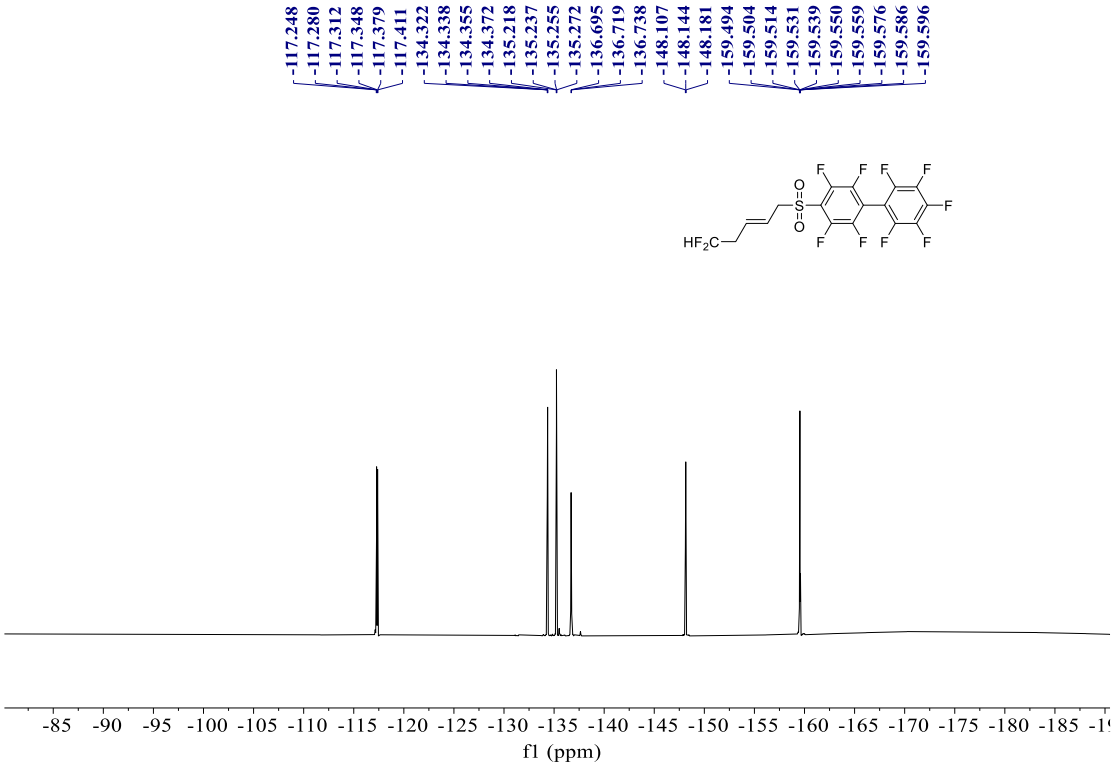
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4am



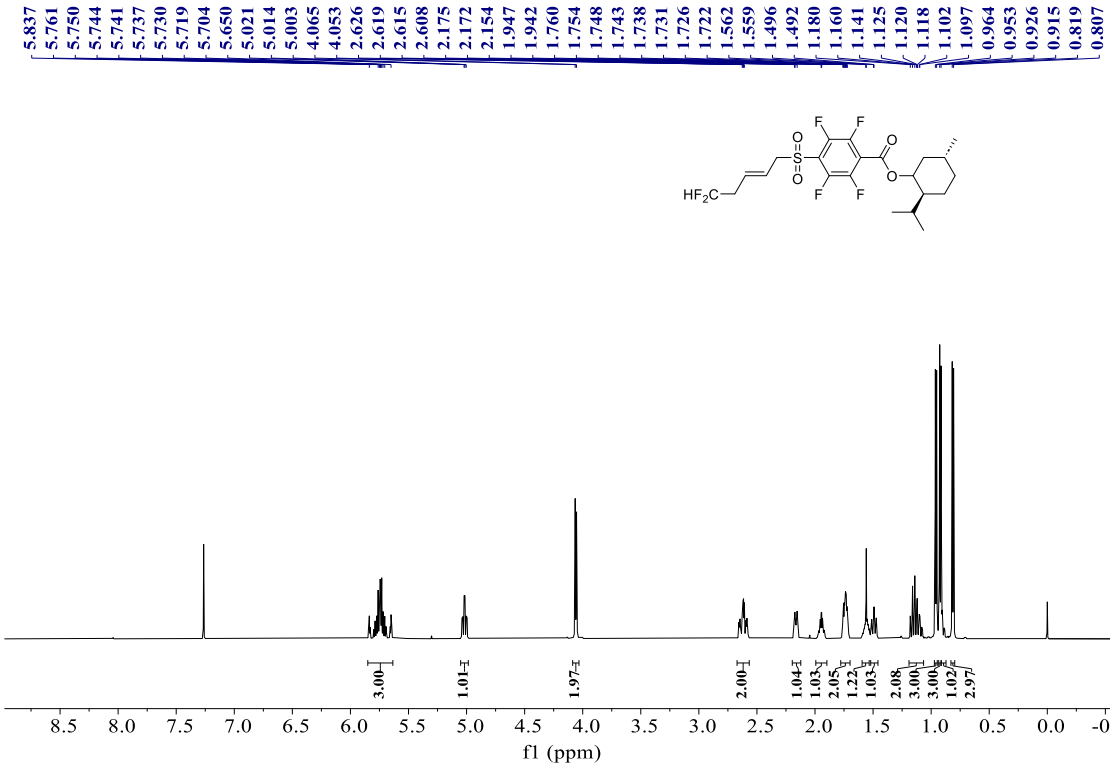
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4am



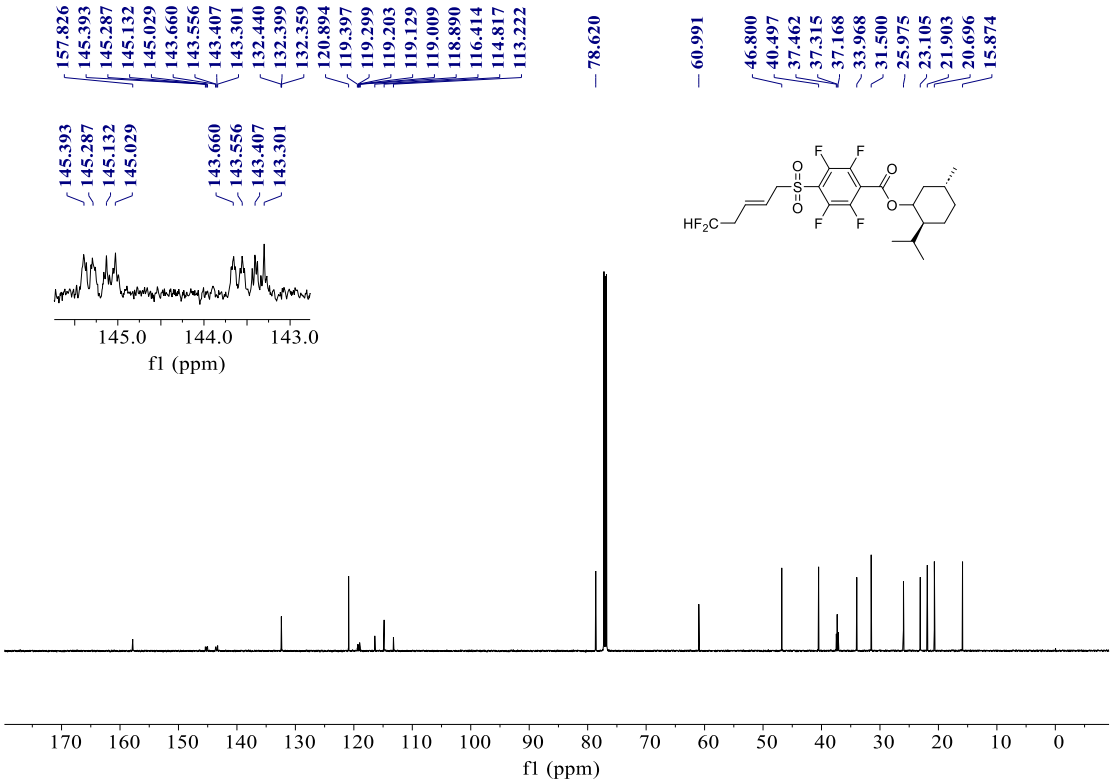
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4am



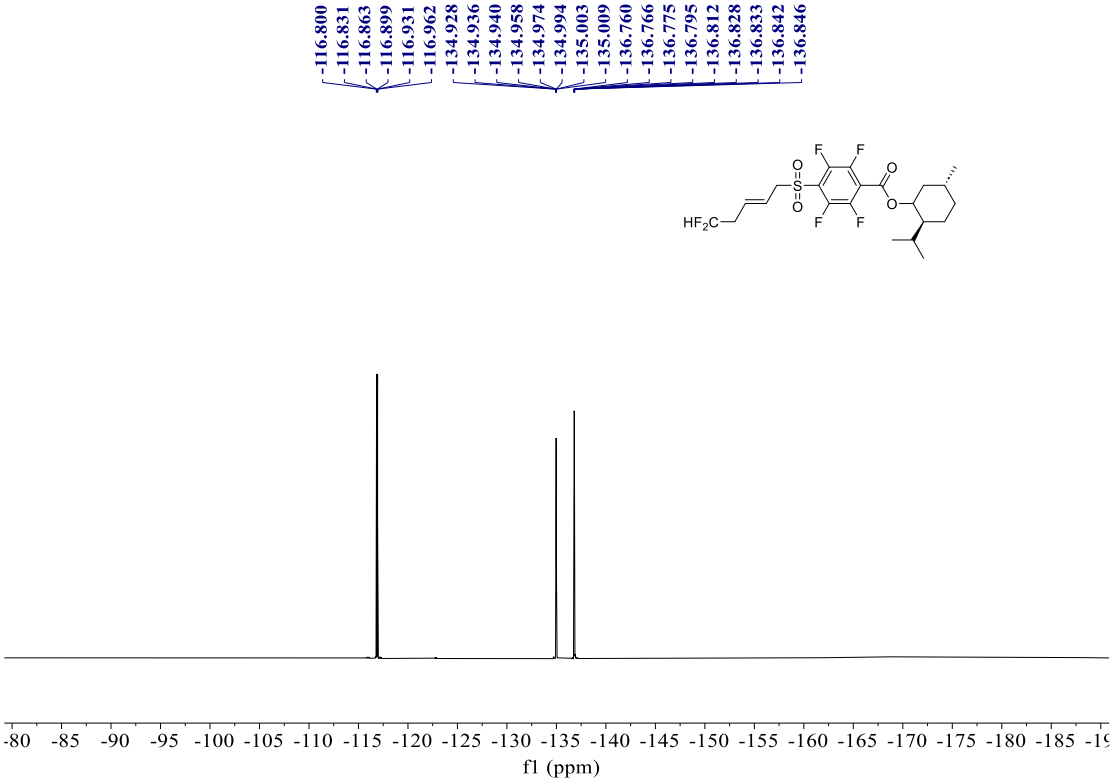
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4an



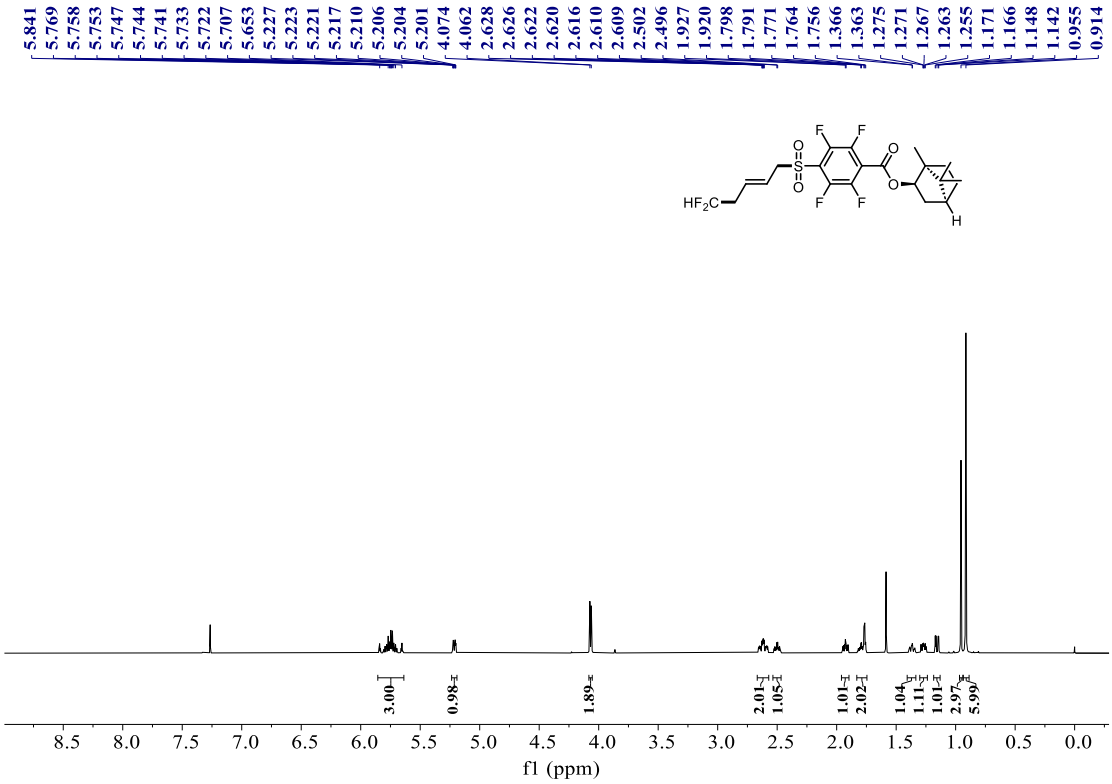
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4an



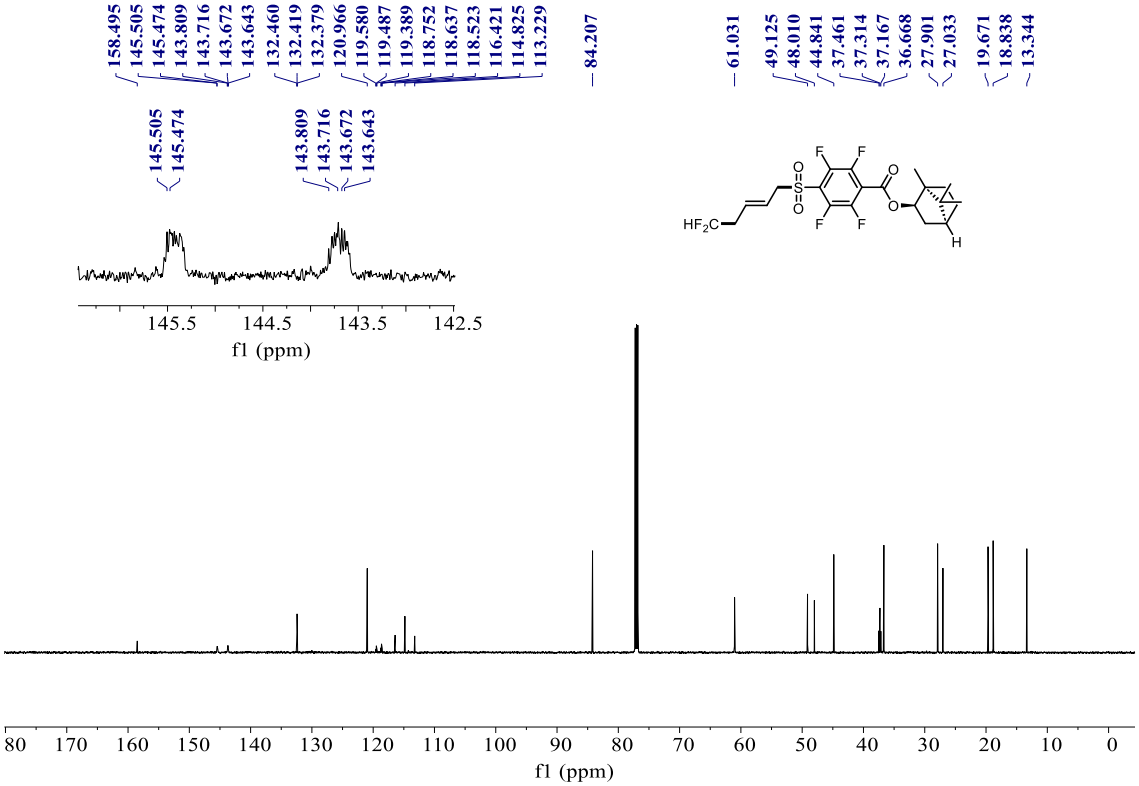
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4an



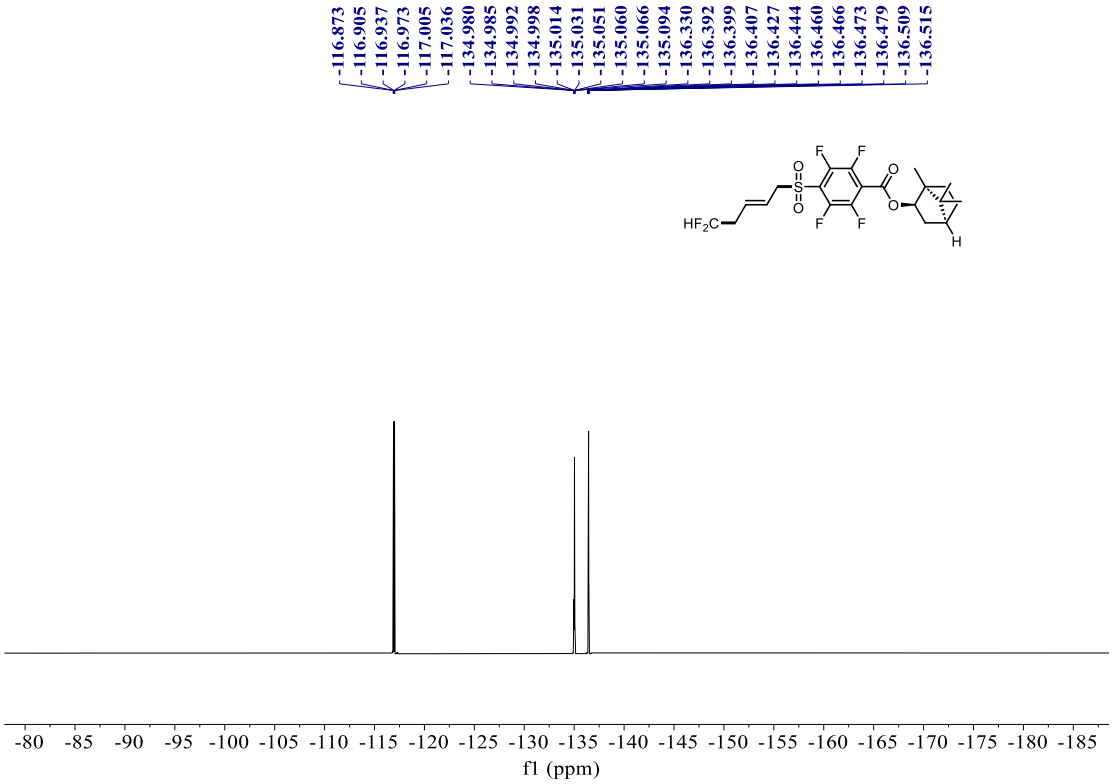
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ao



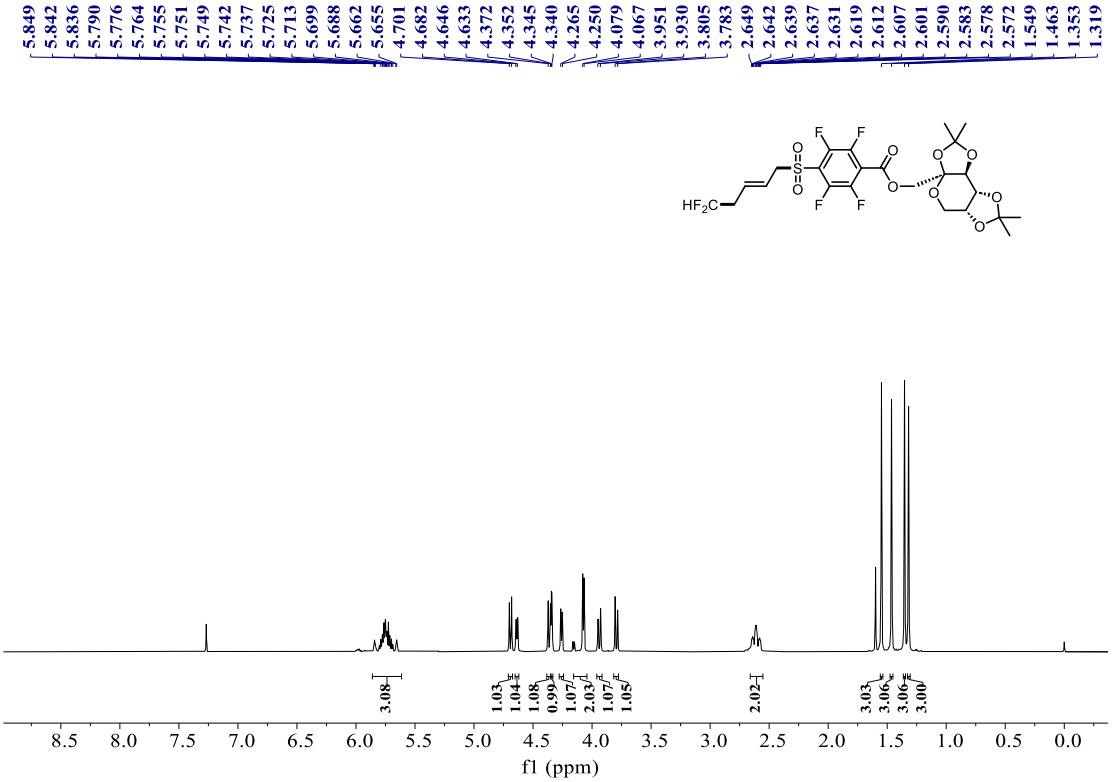
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ao



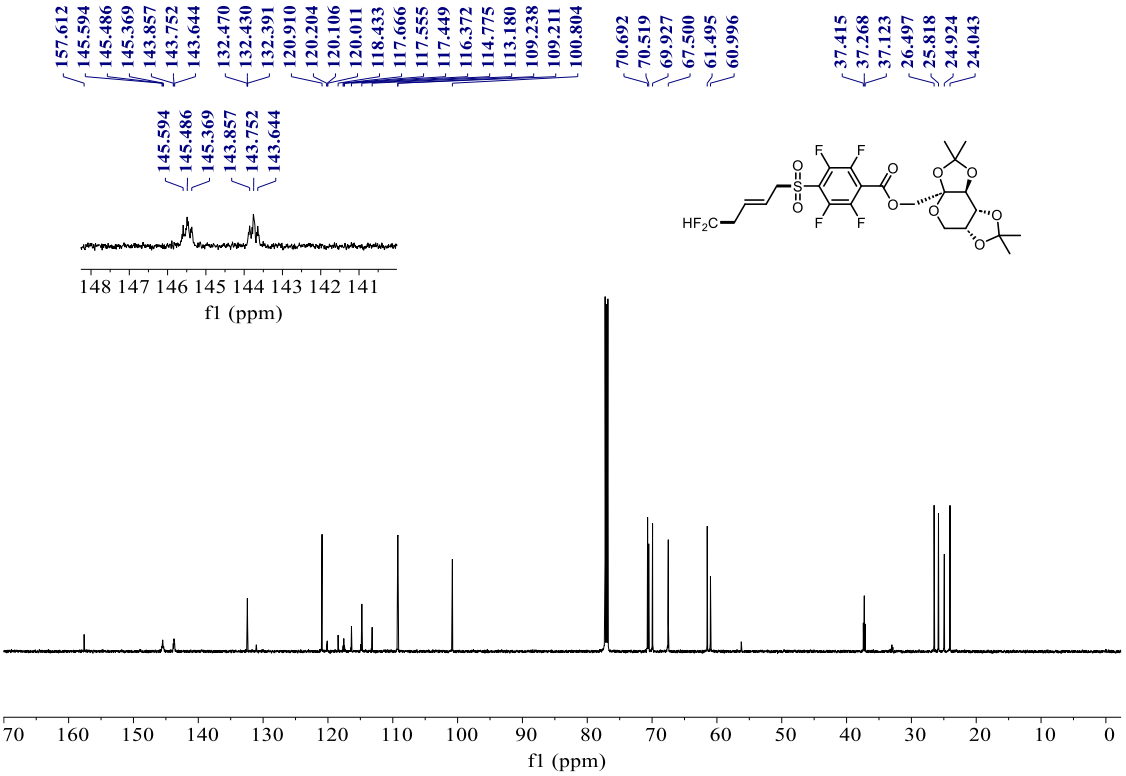
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ao



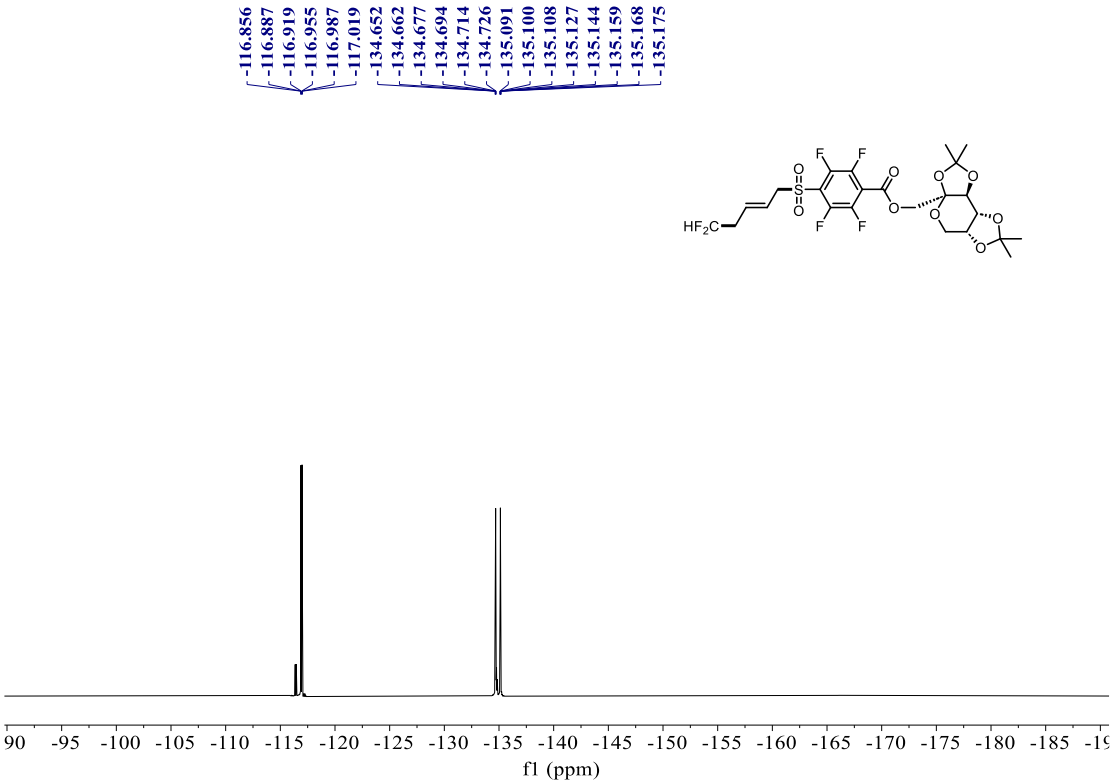
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ap



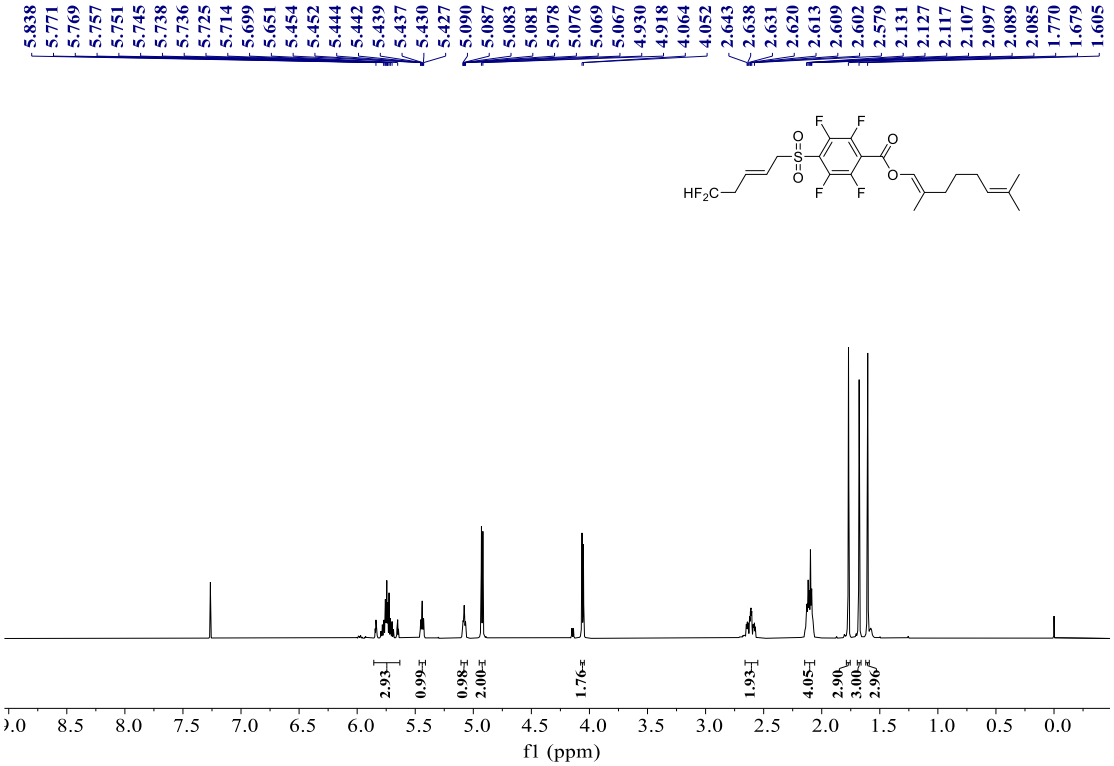
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ap



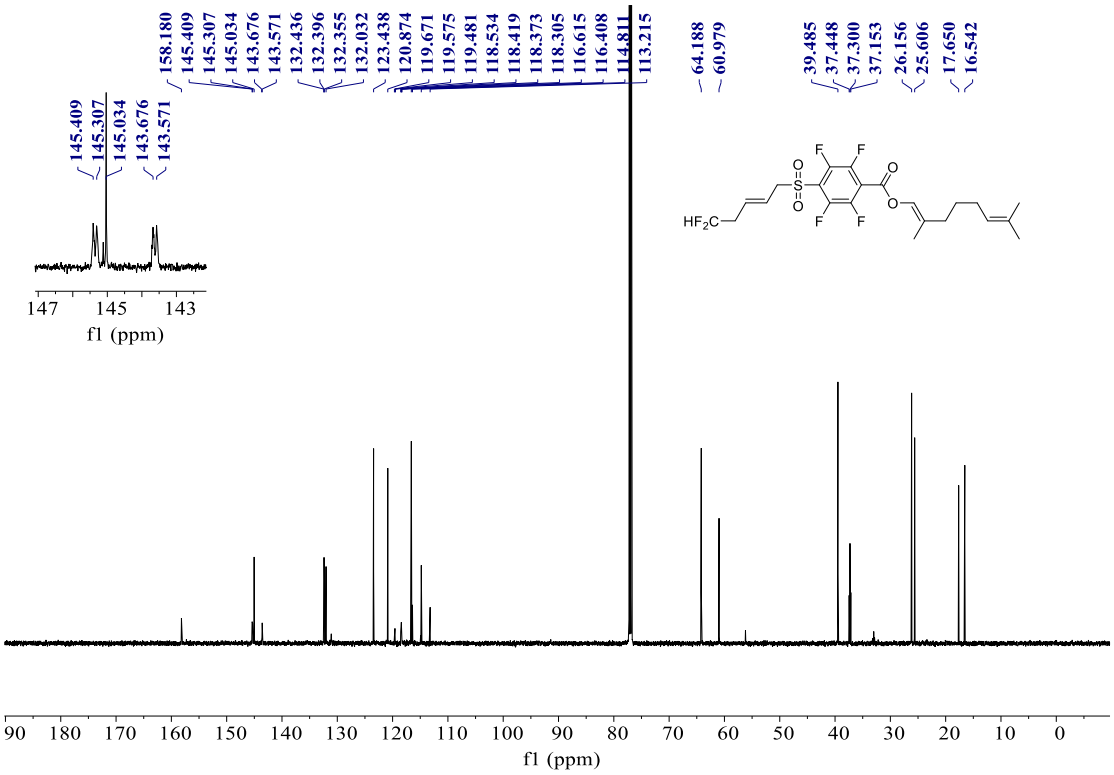
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ap



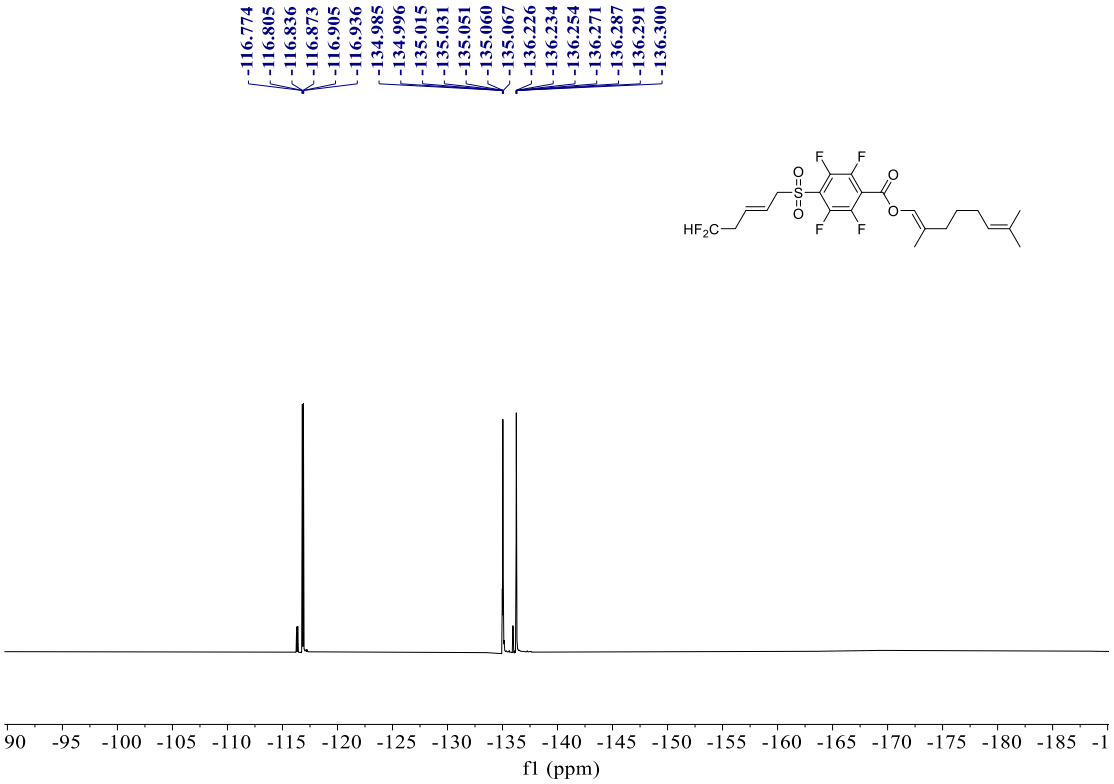
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4aq



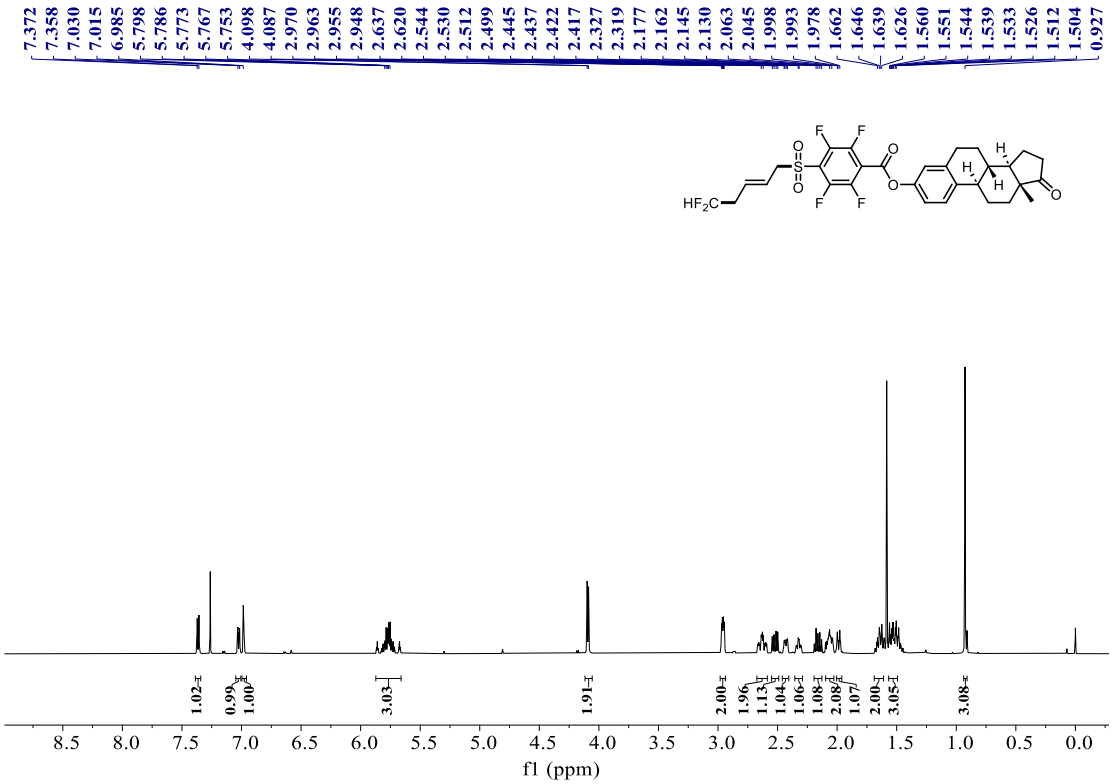
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4aq



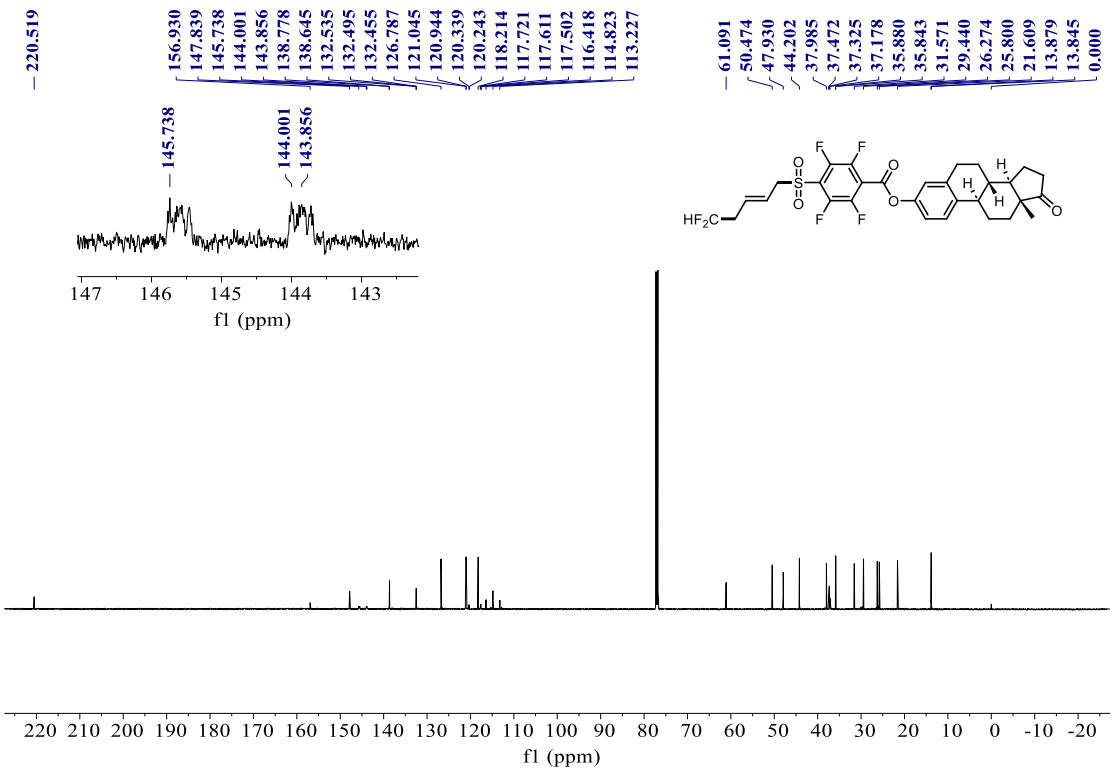
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4aq



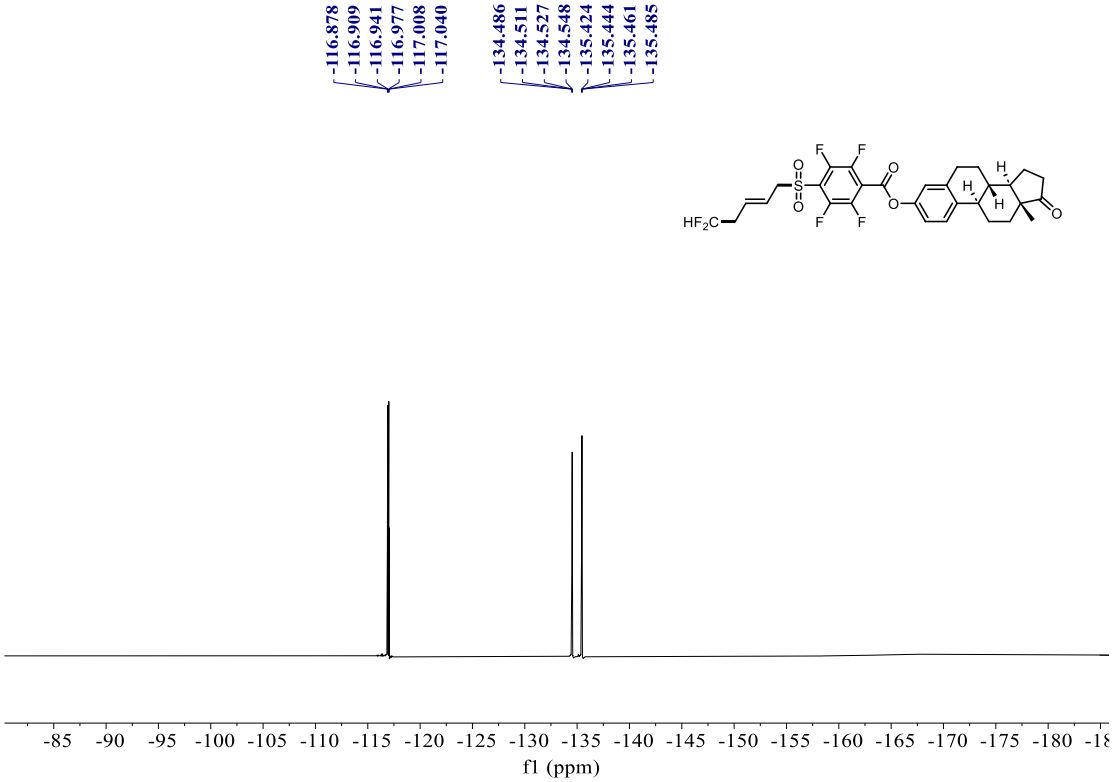
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ar



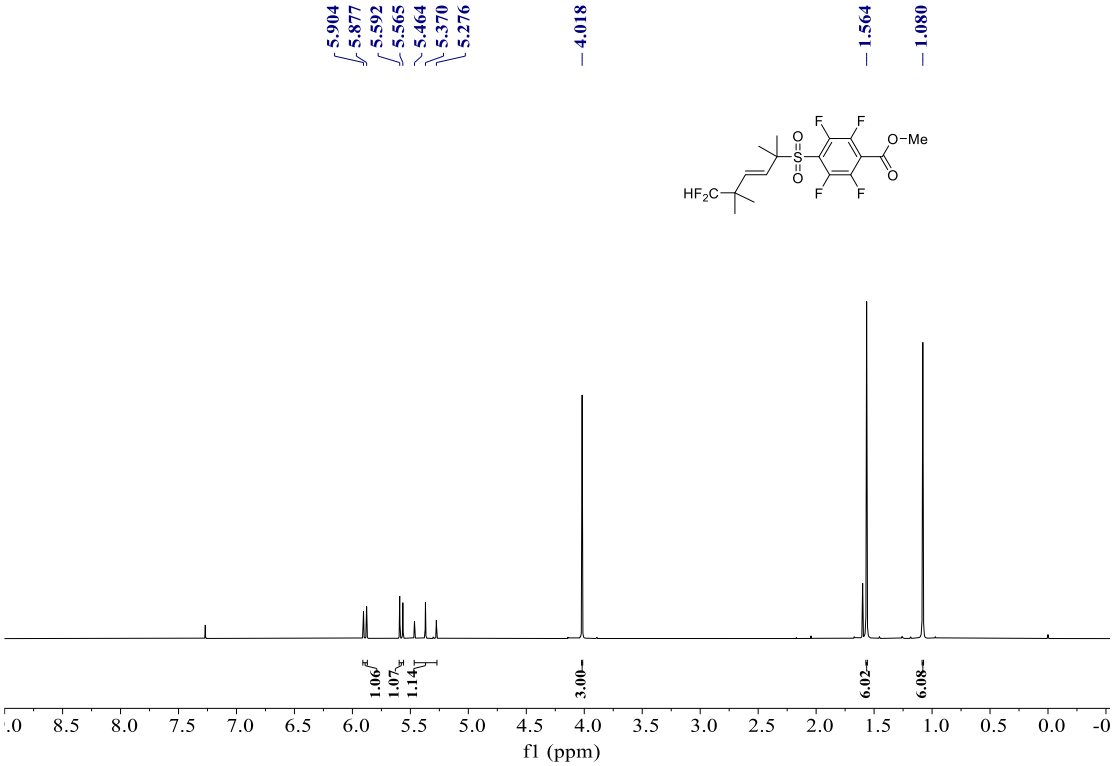
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ar



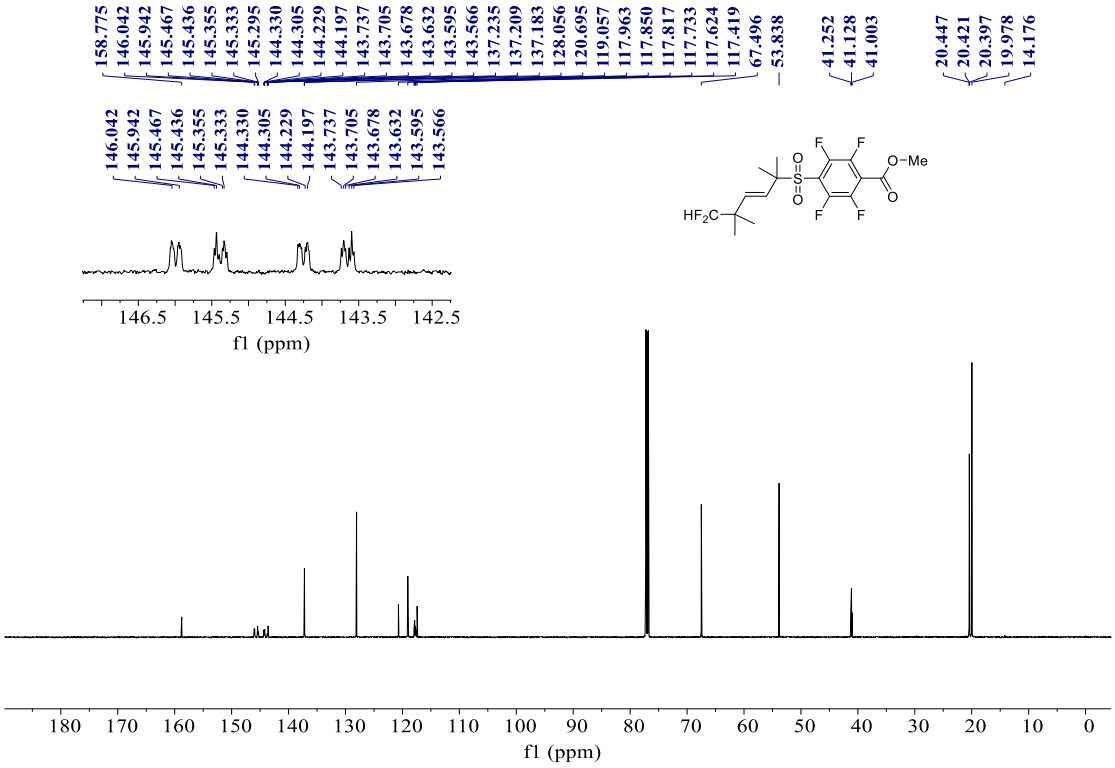
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ar



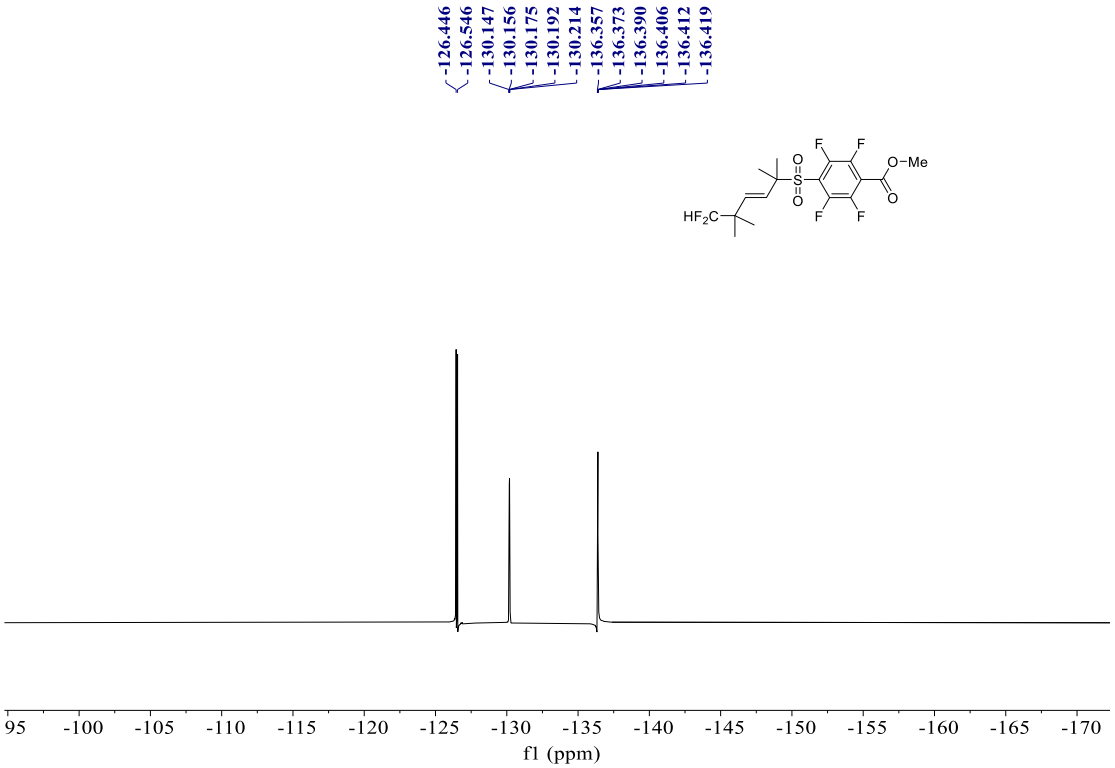
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4ba



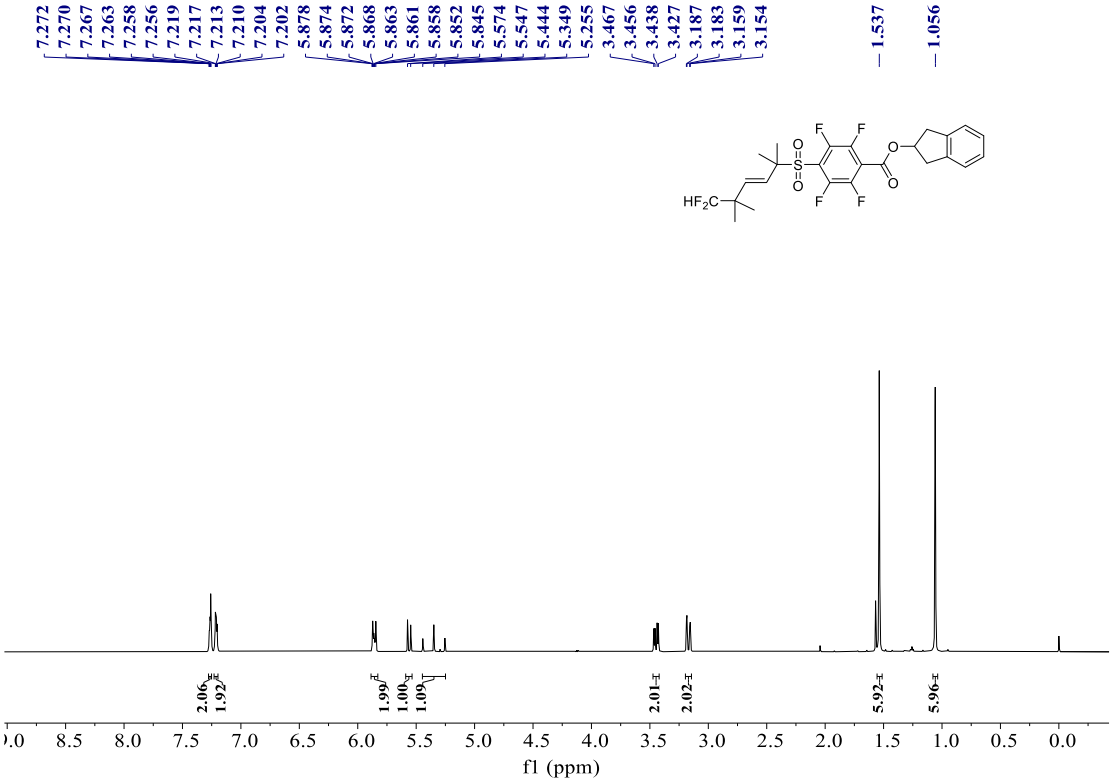
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4ba



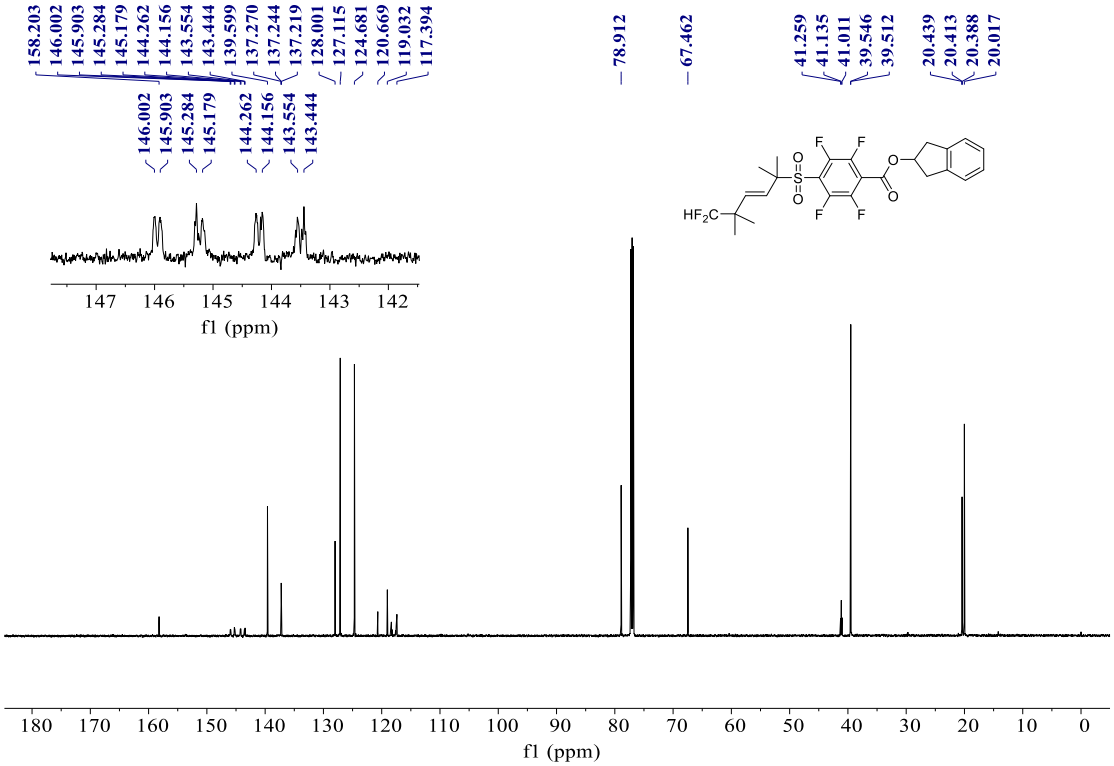
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4ba



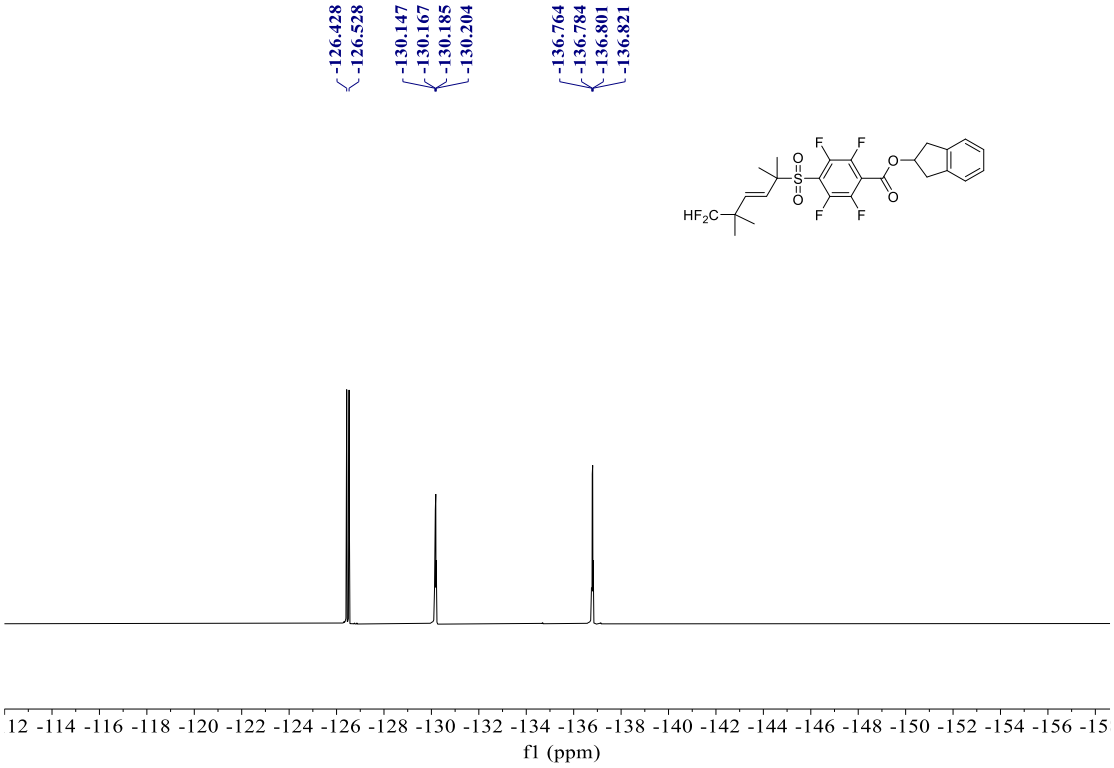
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4bh



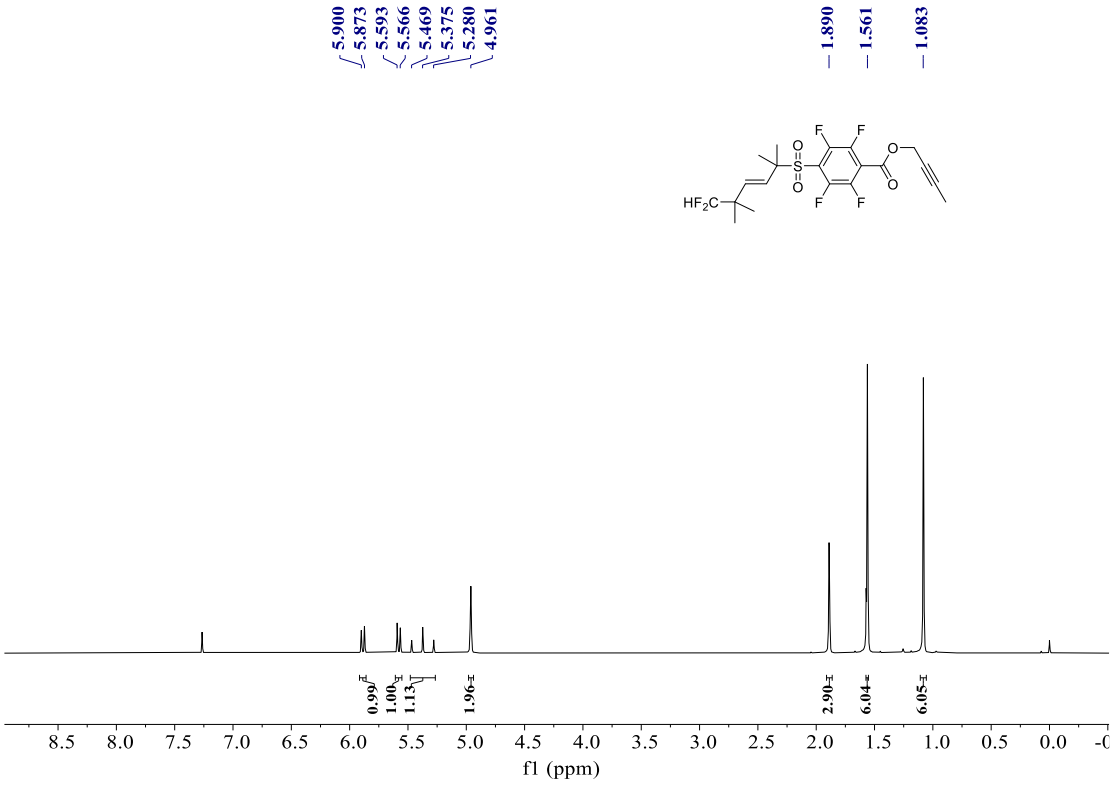
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4bh



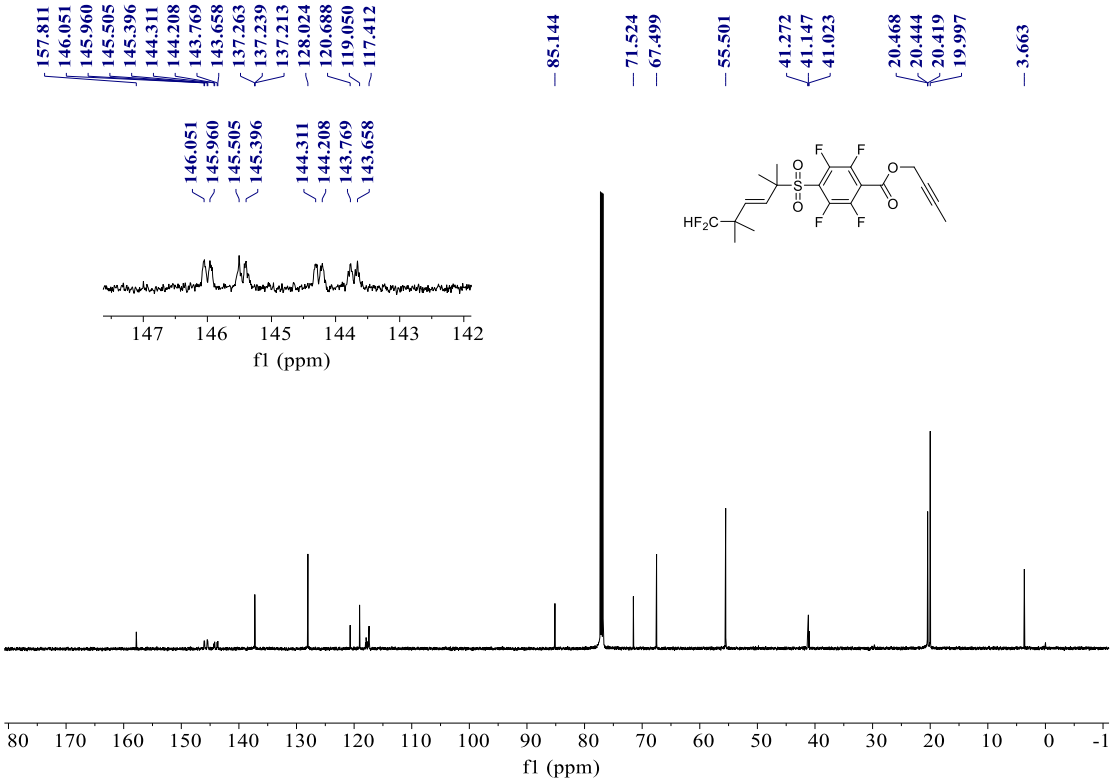
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4bh



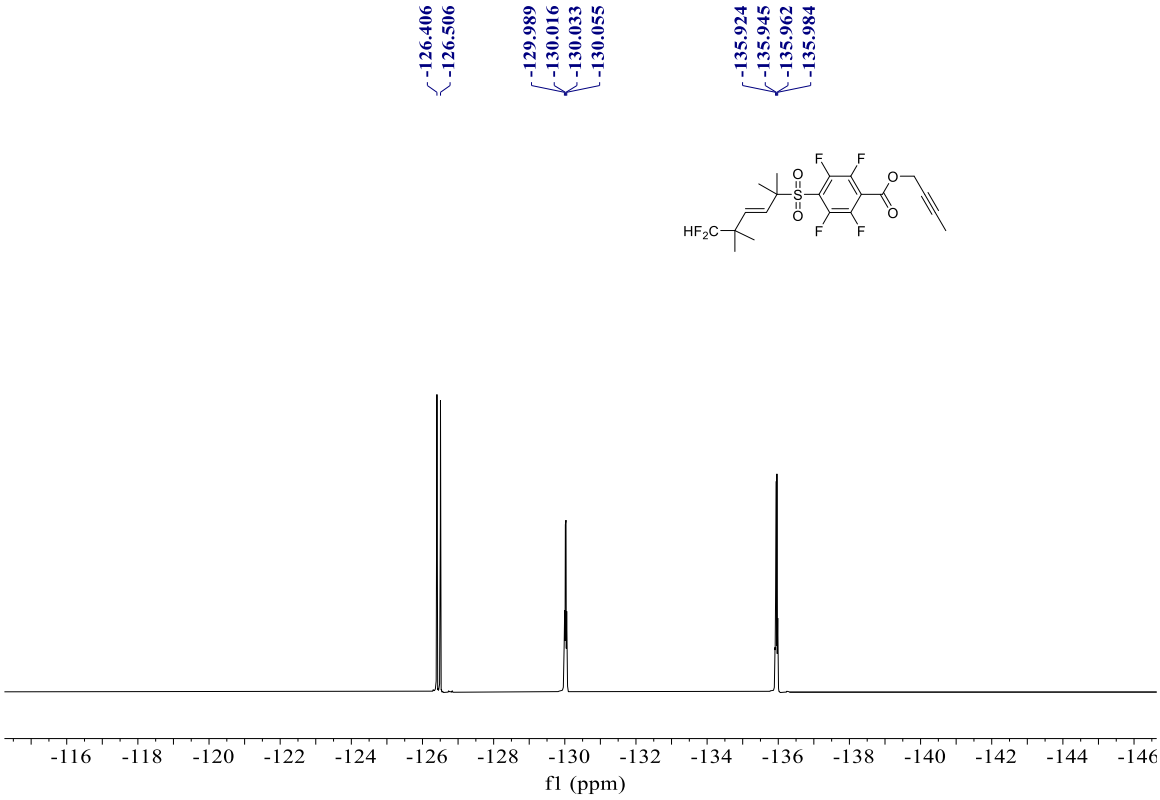
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4bi



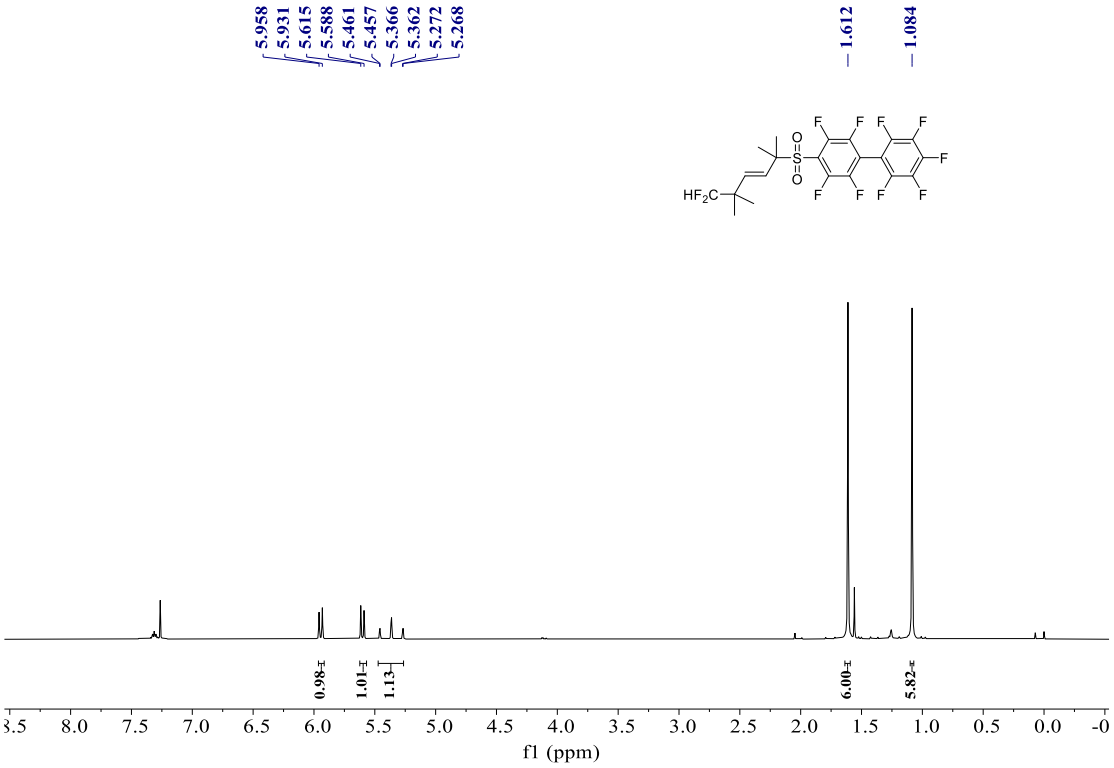
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4bi



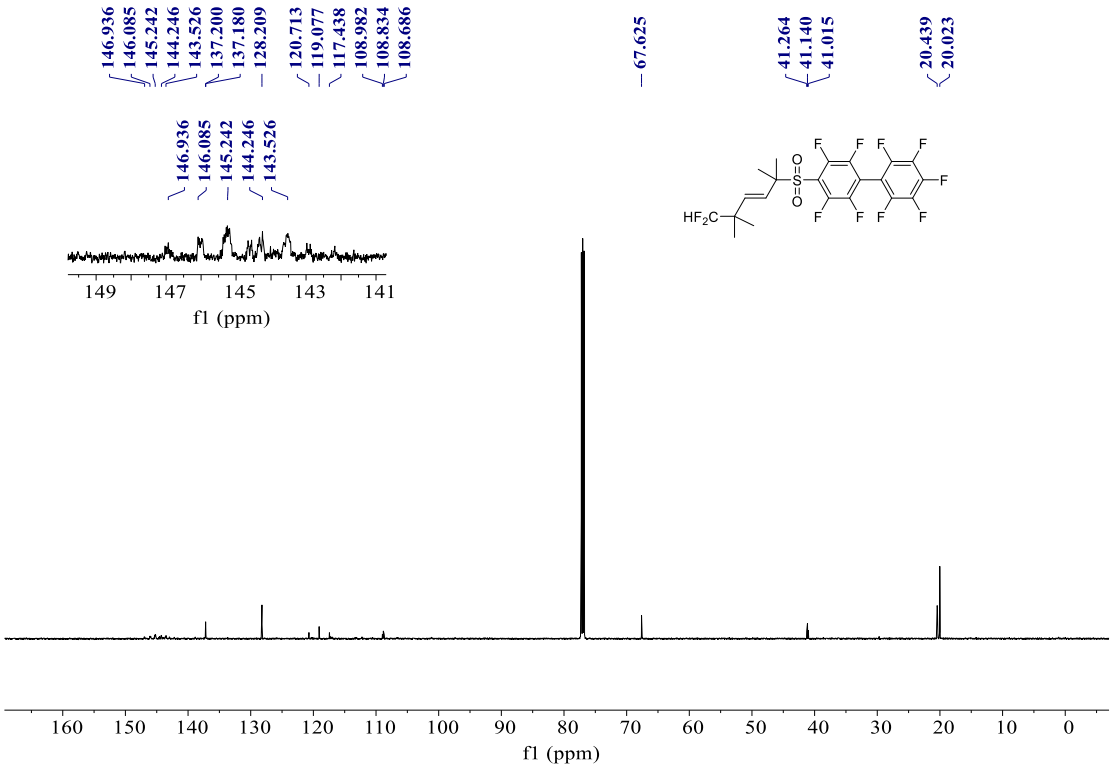
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4bi



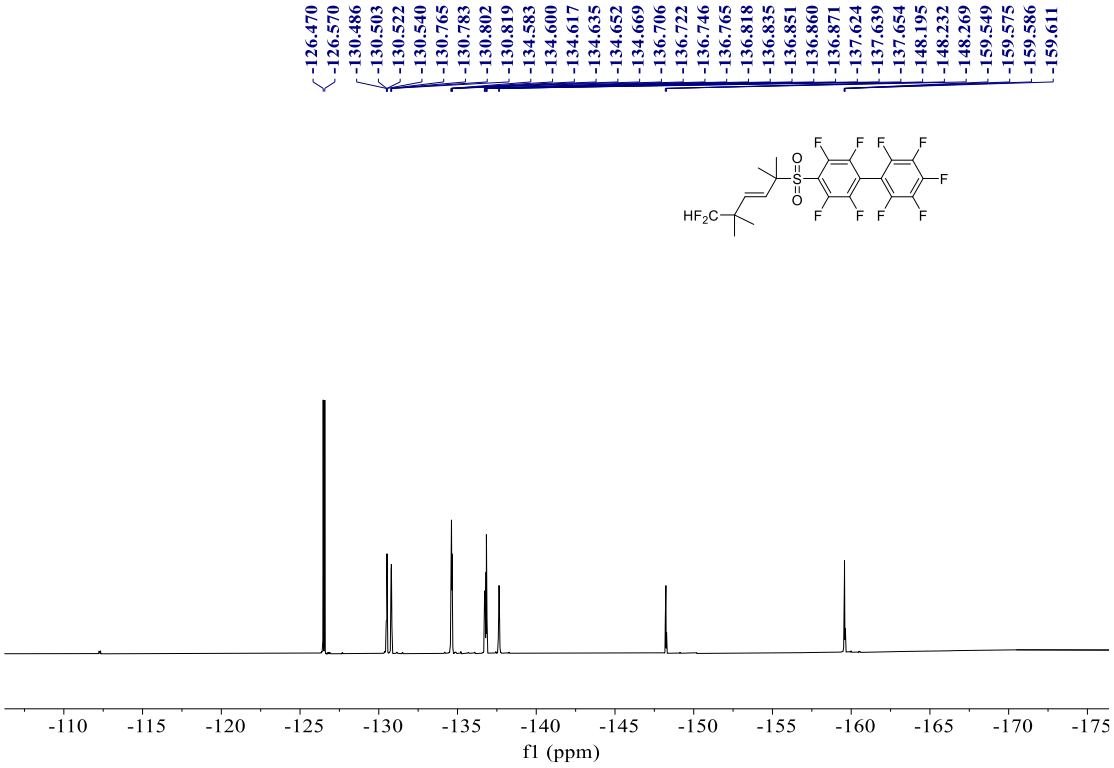
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4bm



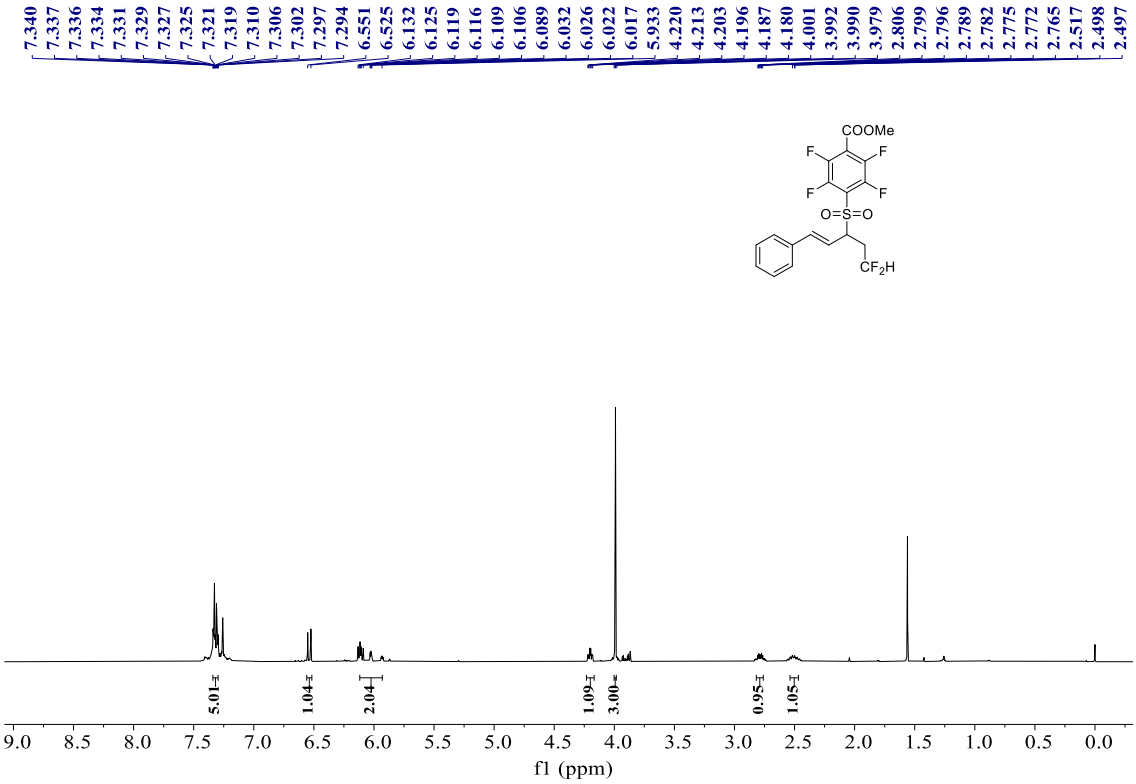
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4bm



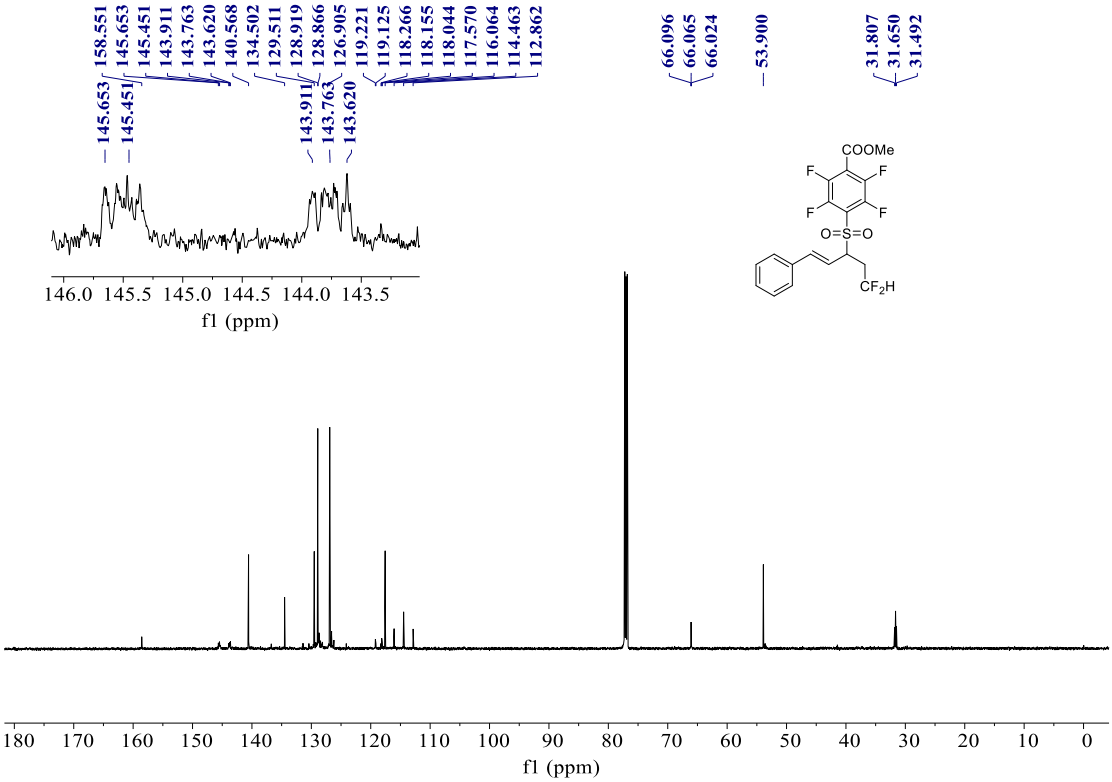
^{19}F NMR (565 MHz, CDCl3) spectrum of 4bm



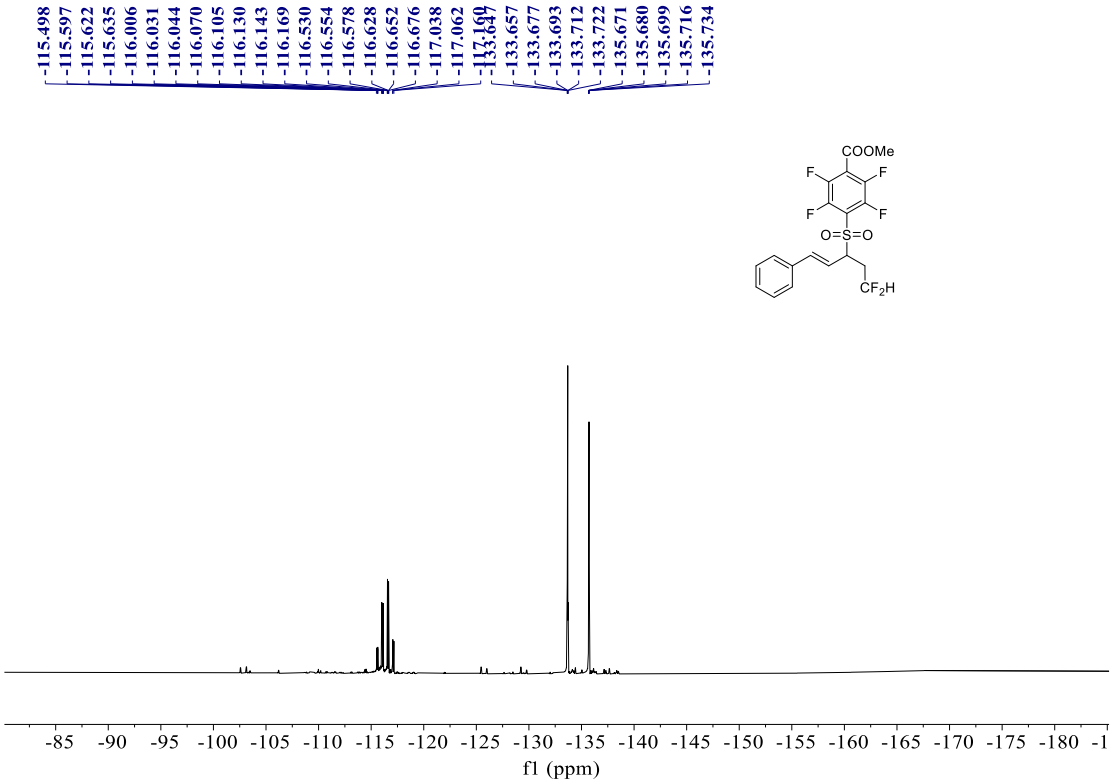
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of 5ca



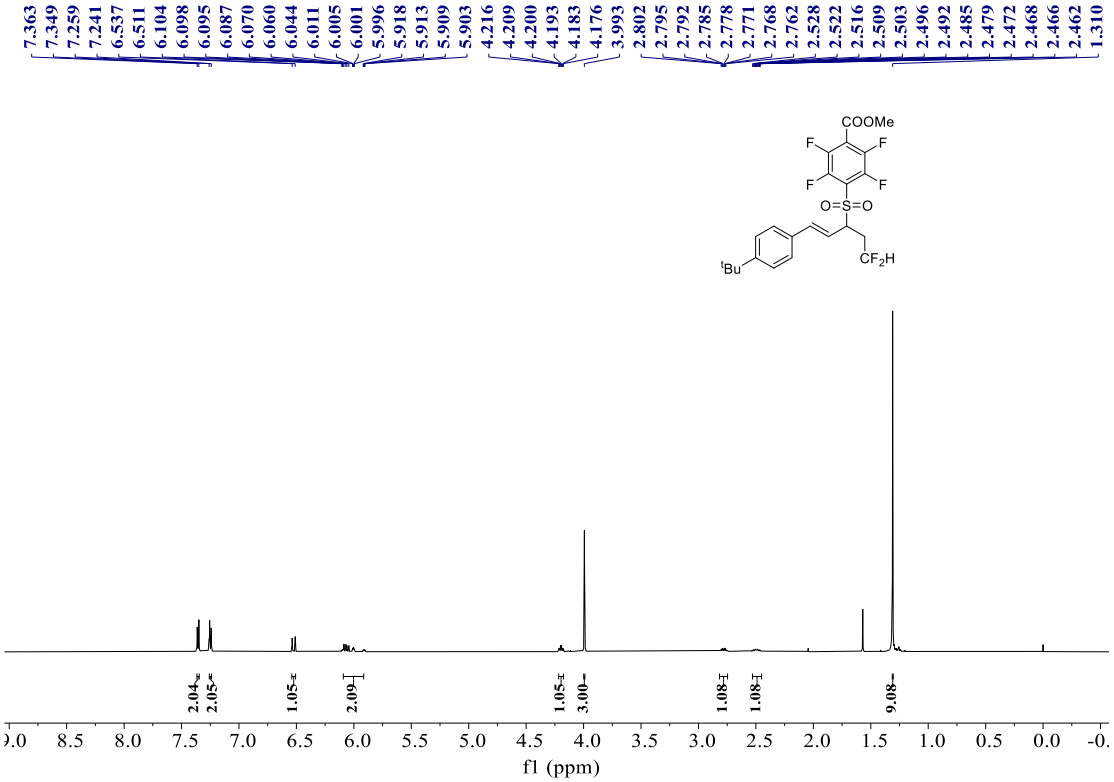
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ca



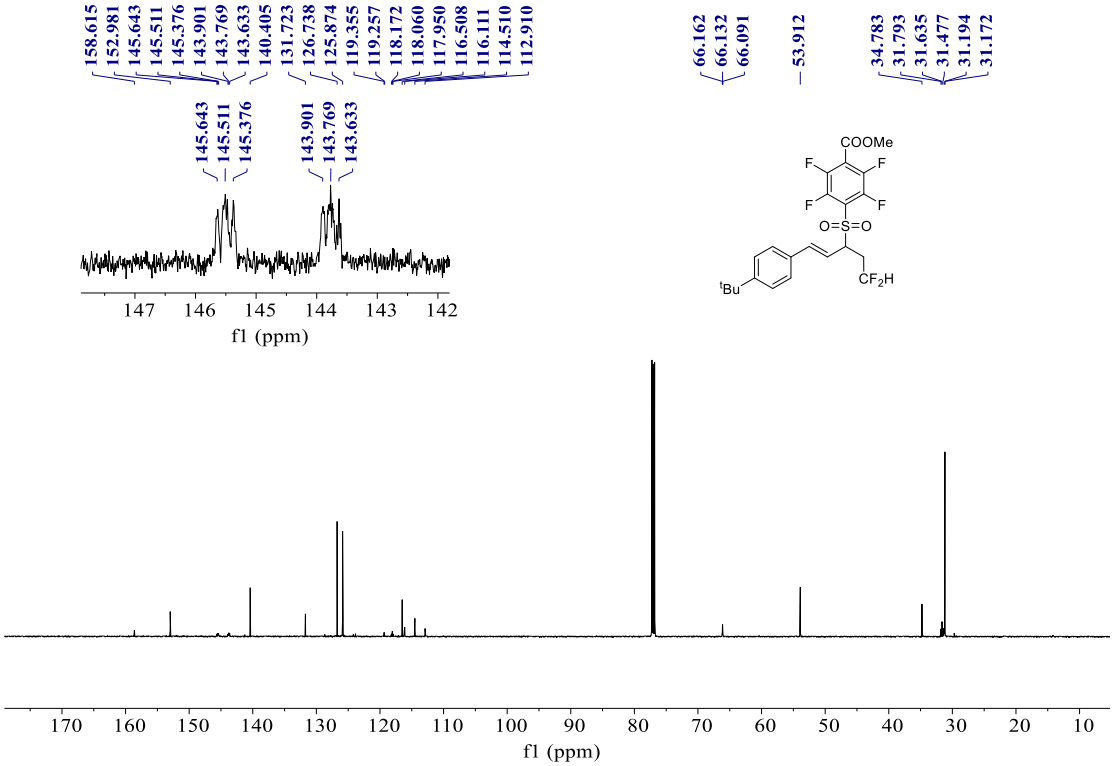
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ca



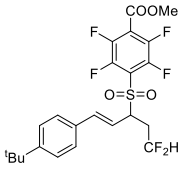
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5da

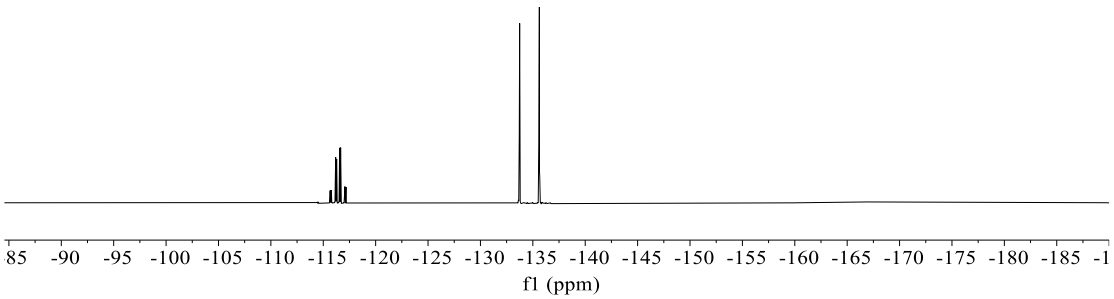


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5da

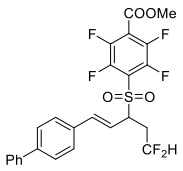


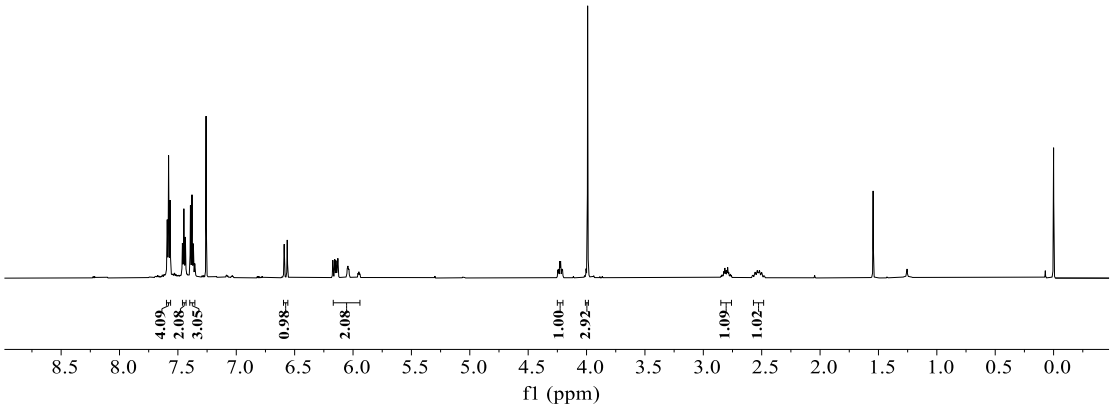
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5da



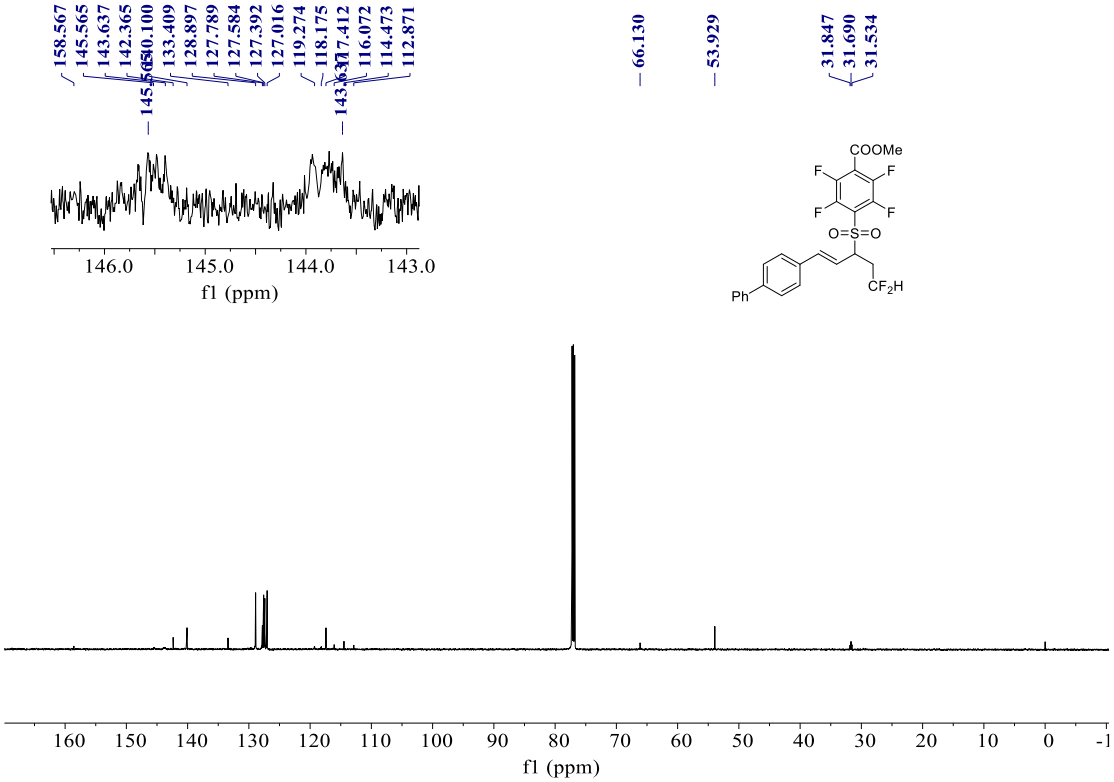


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ea

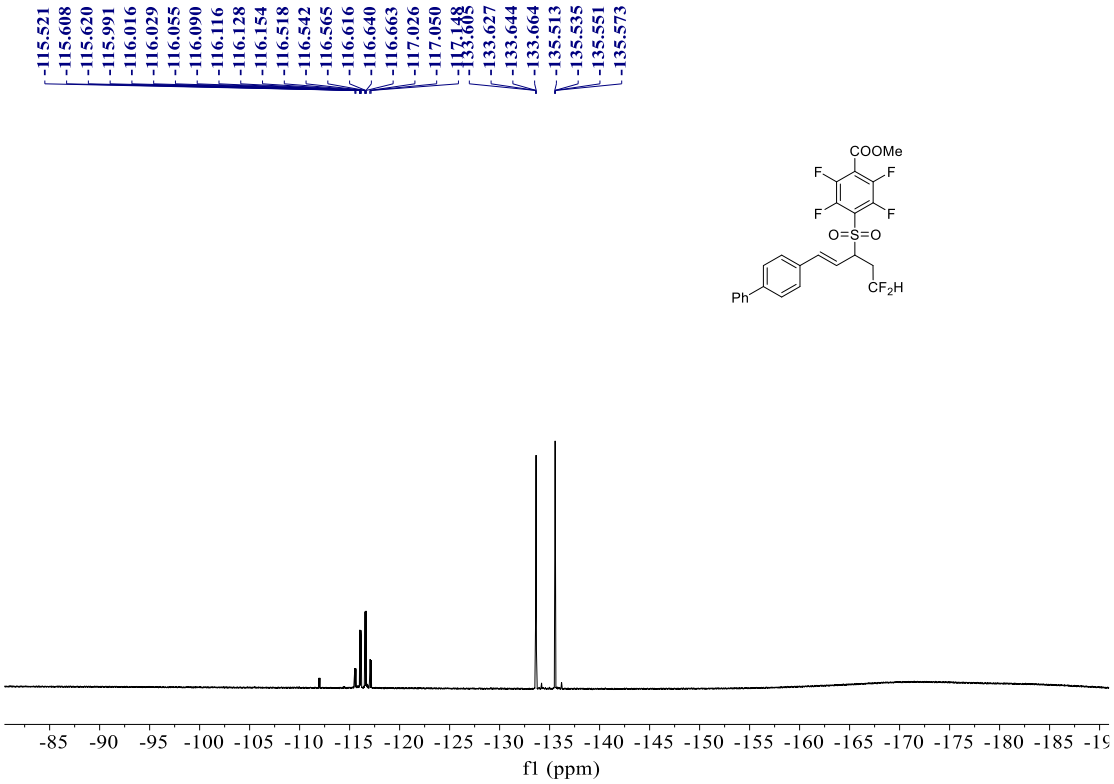




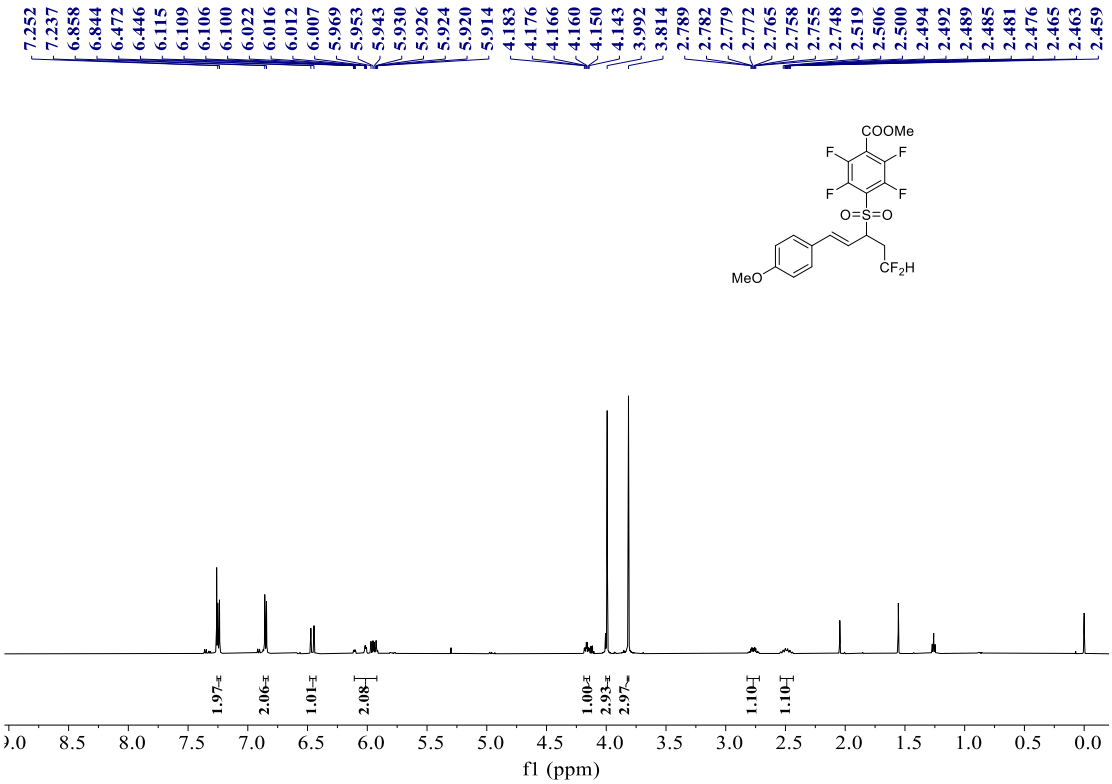
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ea



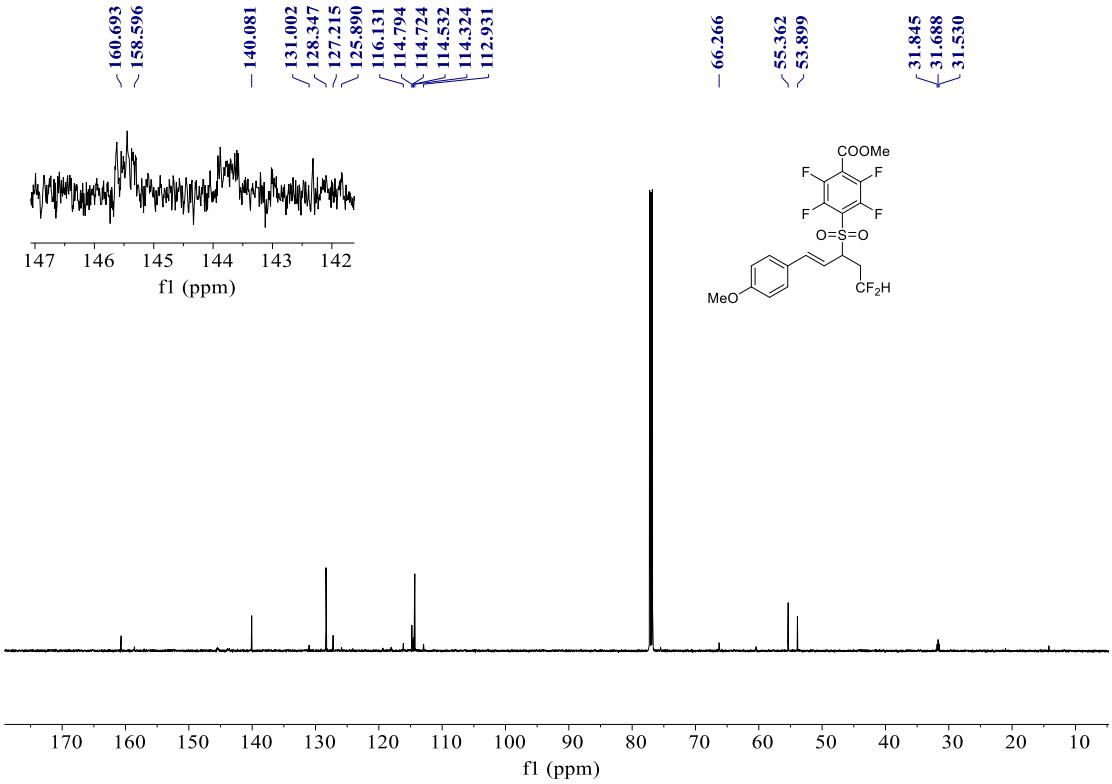
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ea



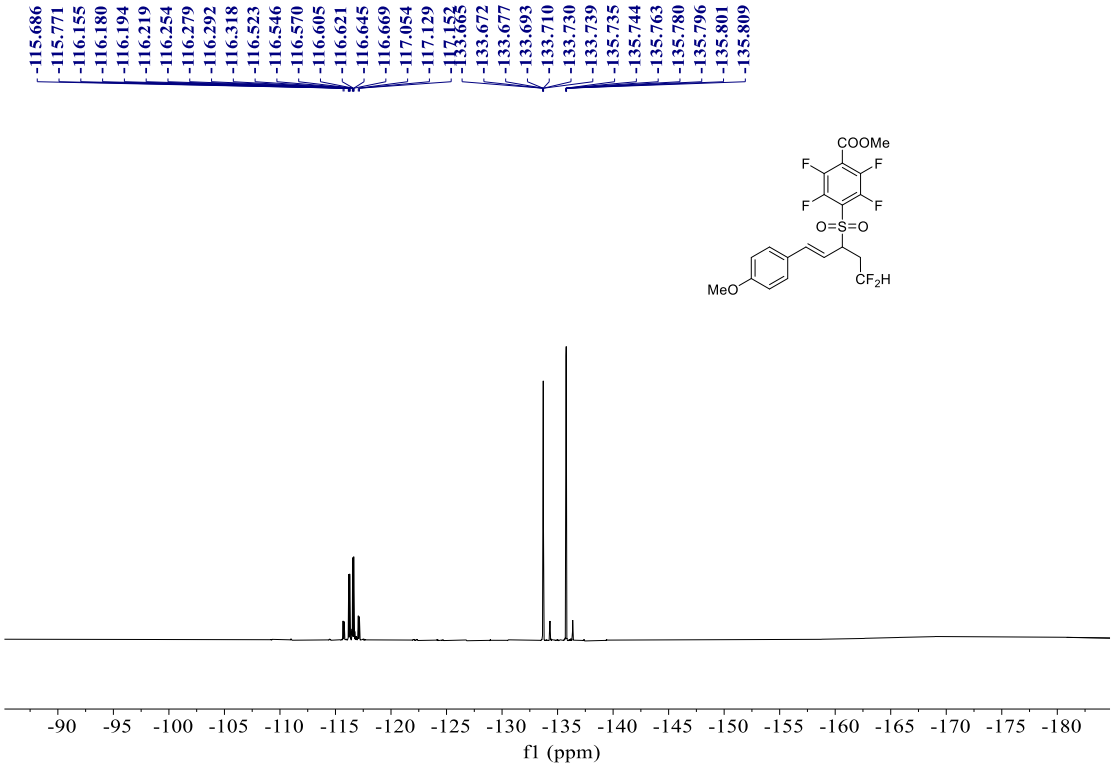
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5fa



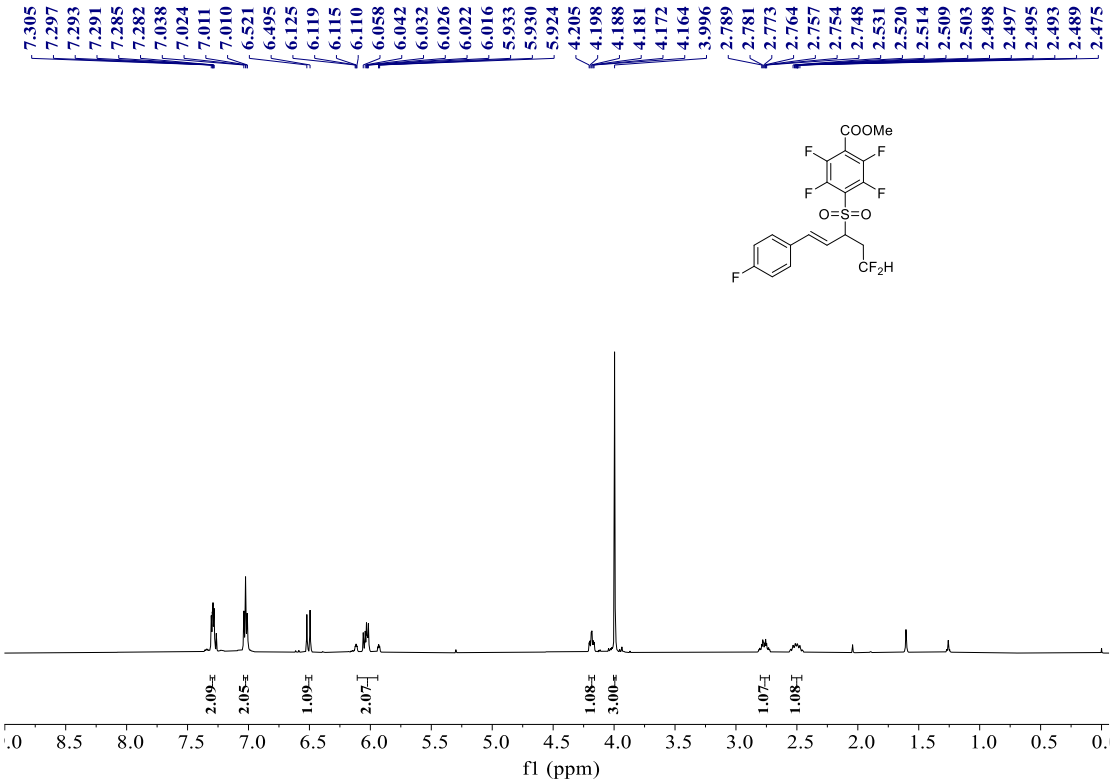
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5fa



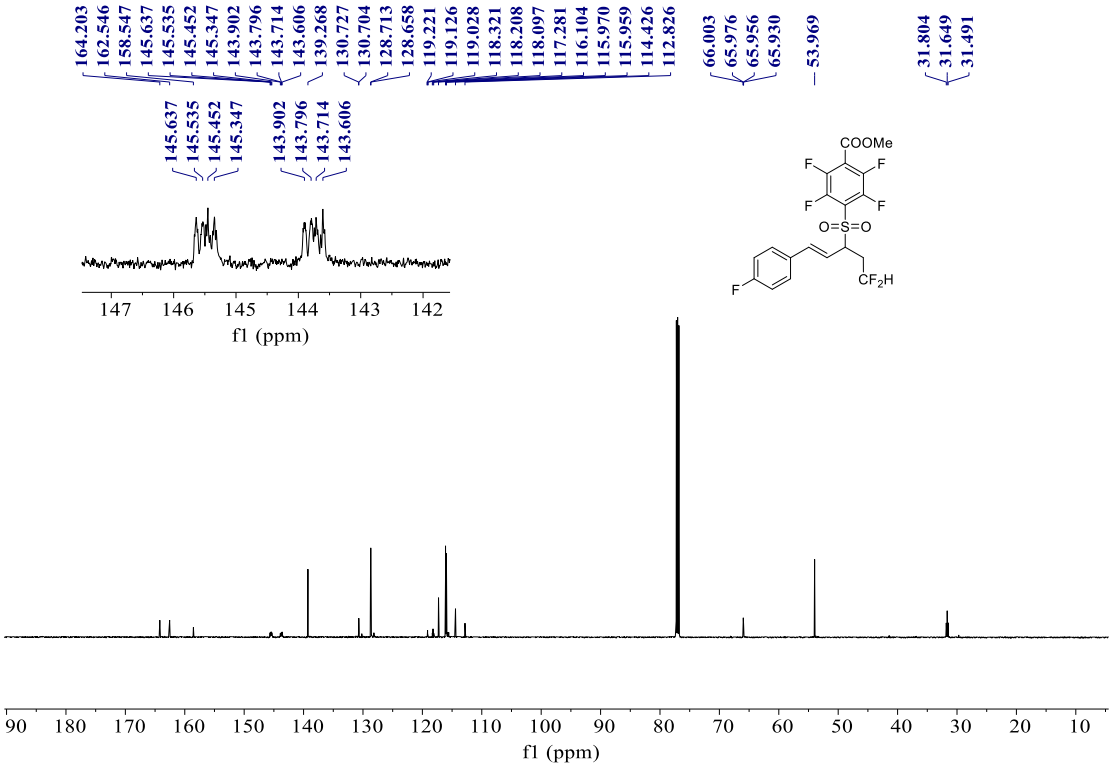
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5fa



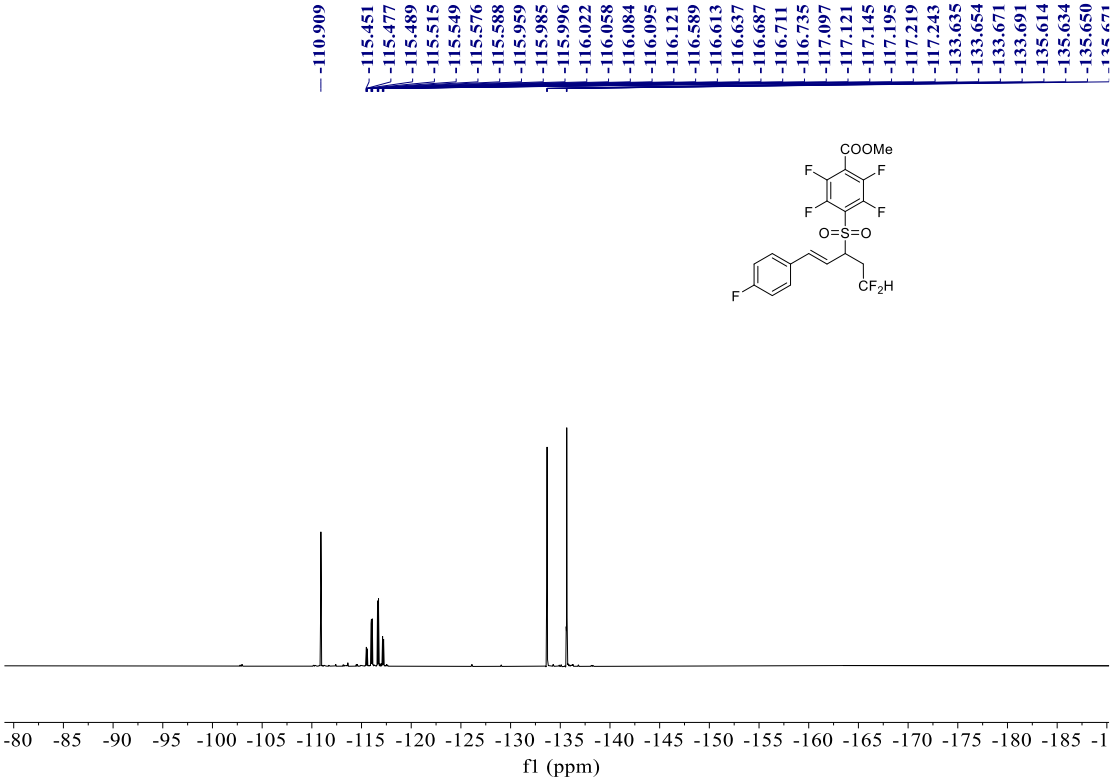
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ga



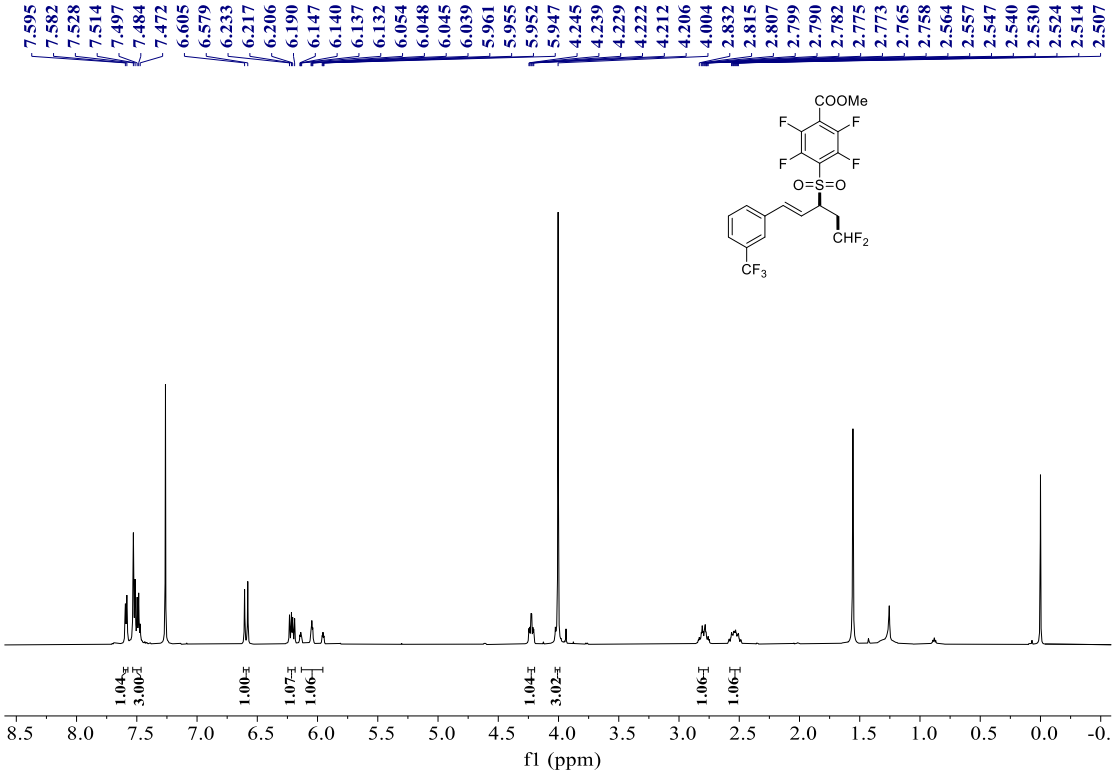
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ga



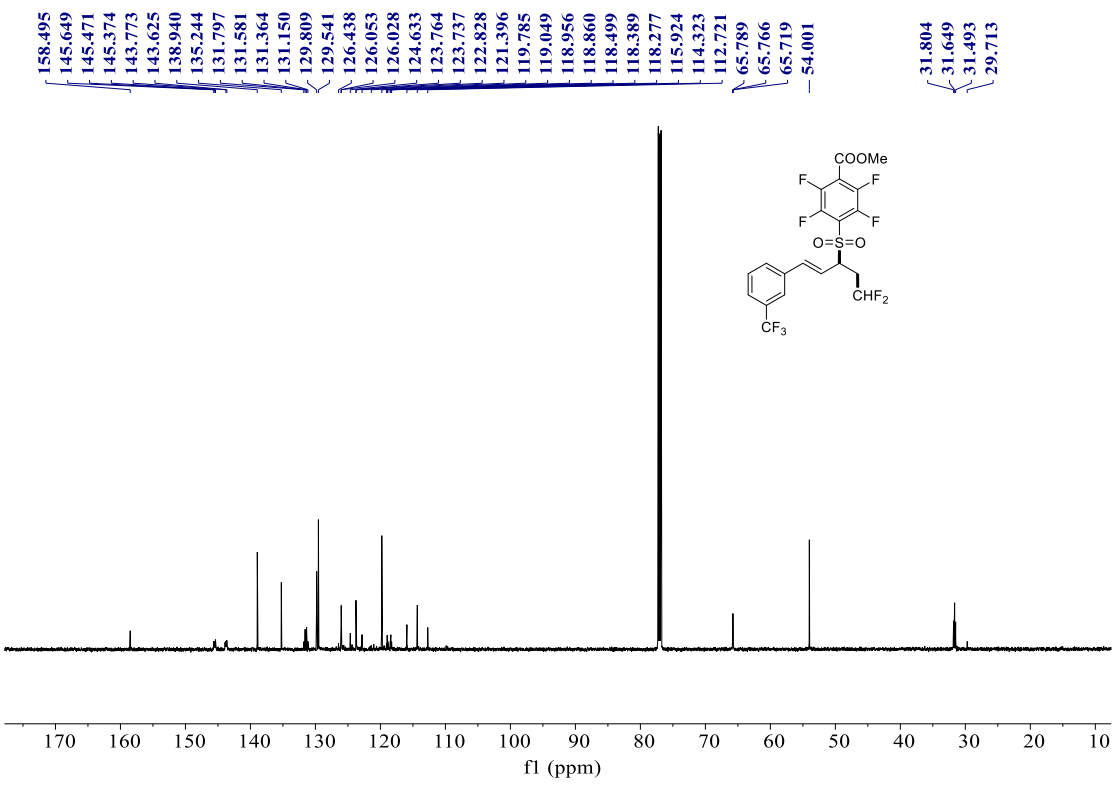
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ga



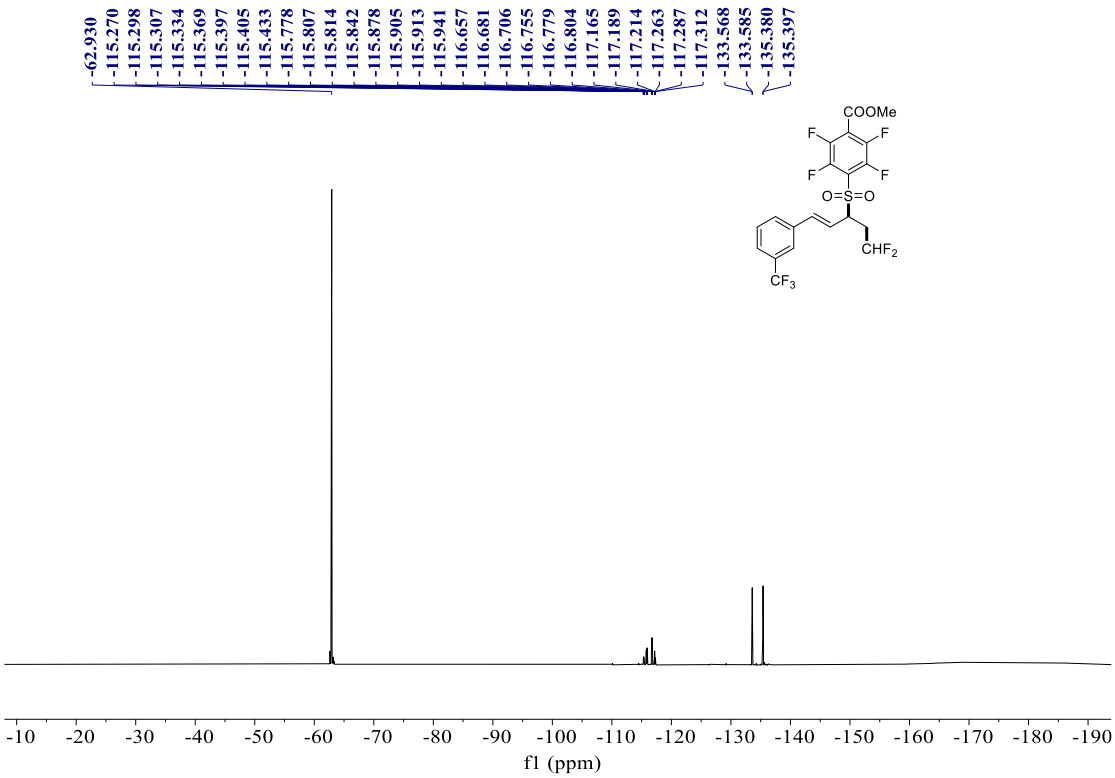
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ha



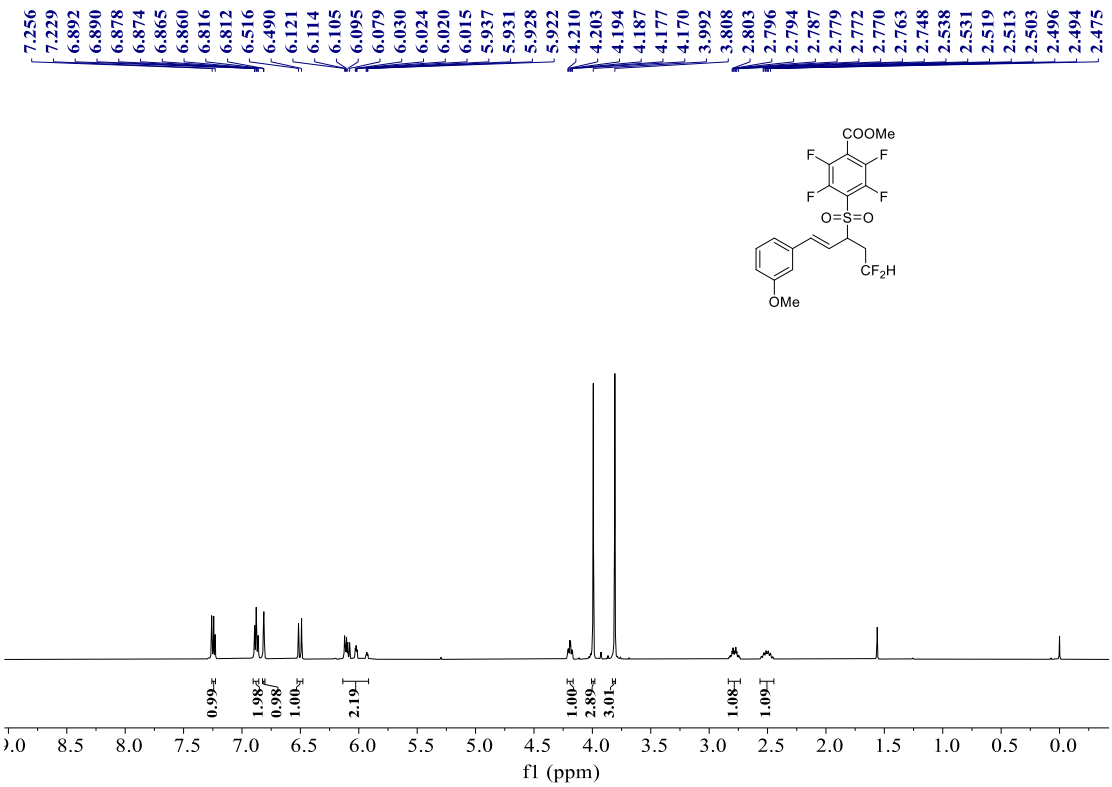
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ha



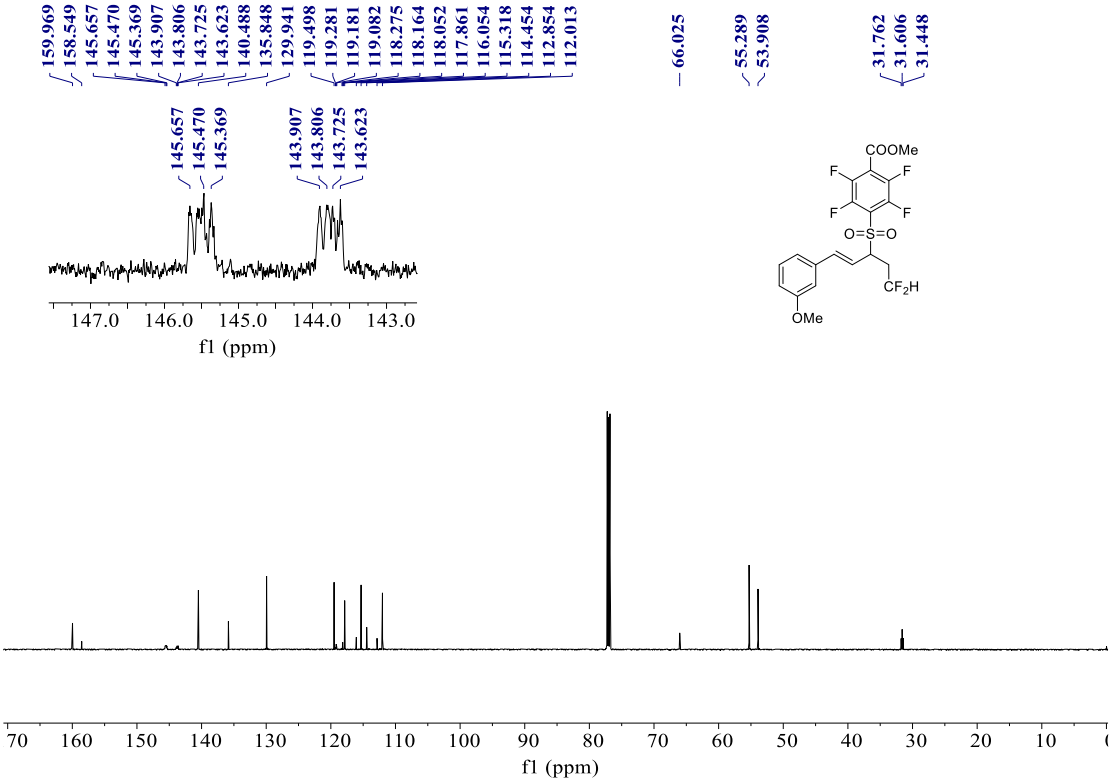
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ha



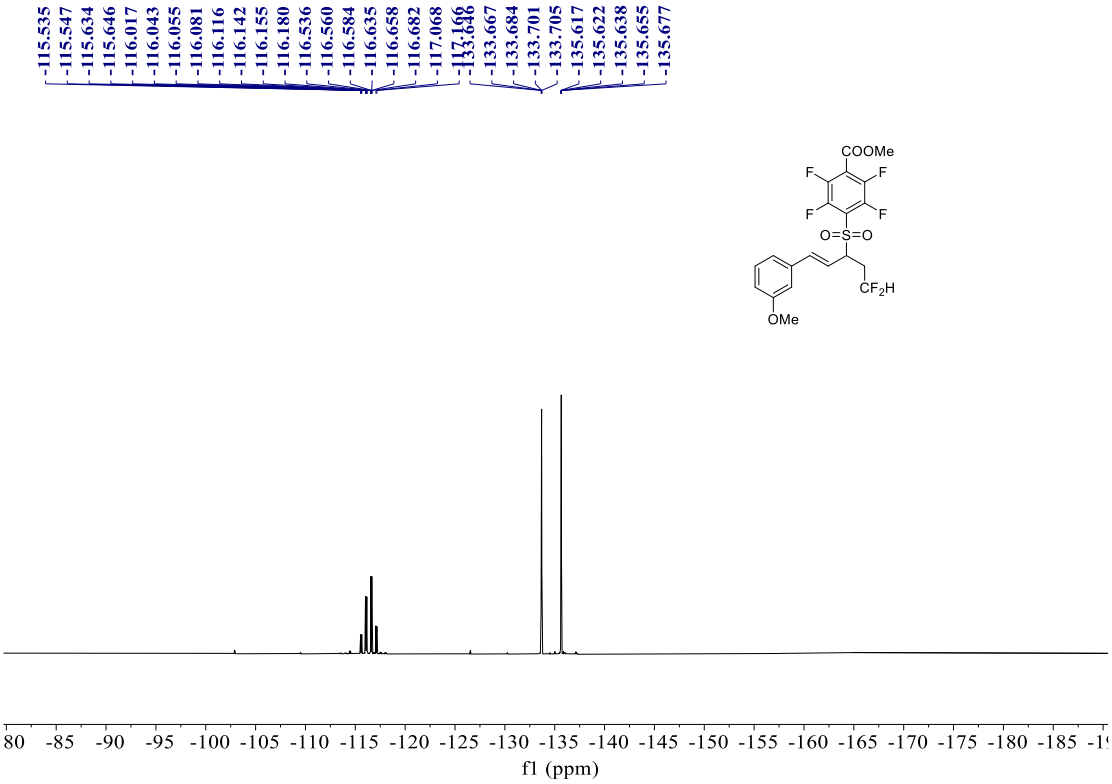
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ia



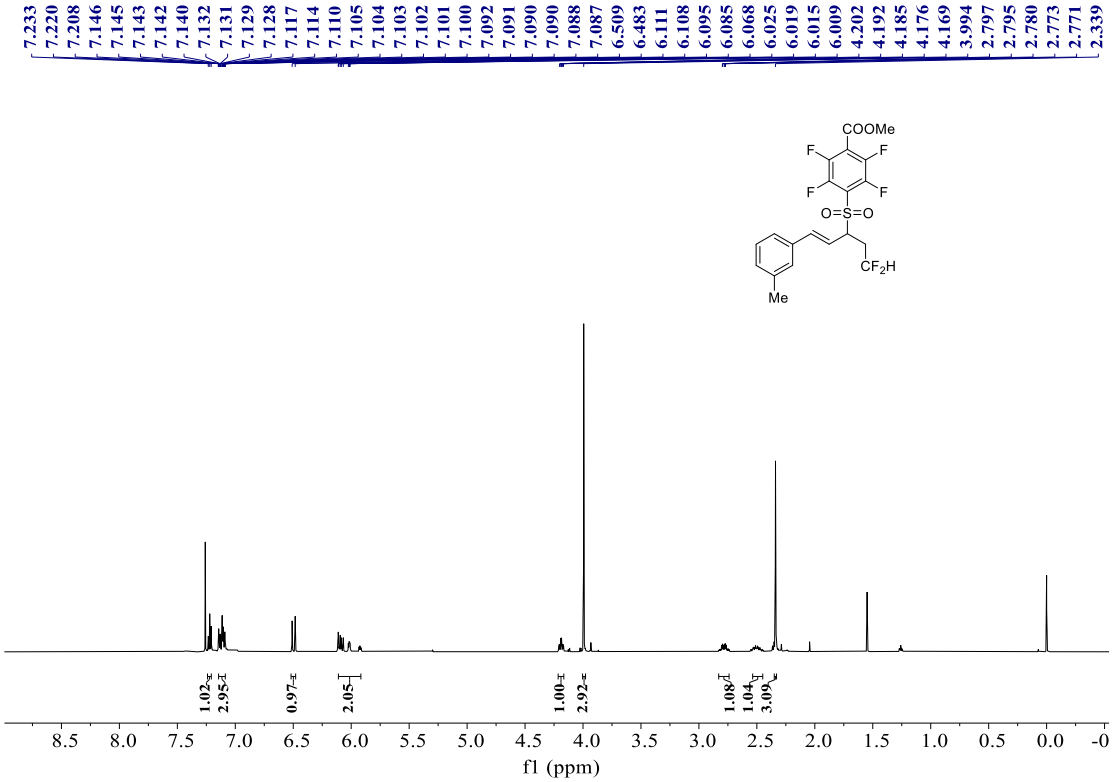
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ia



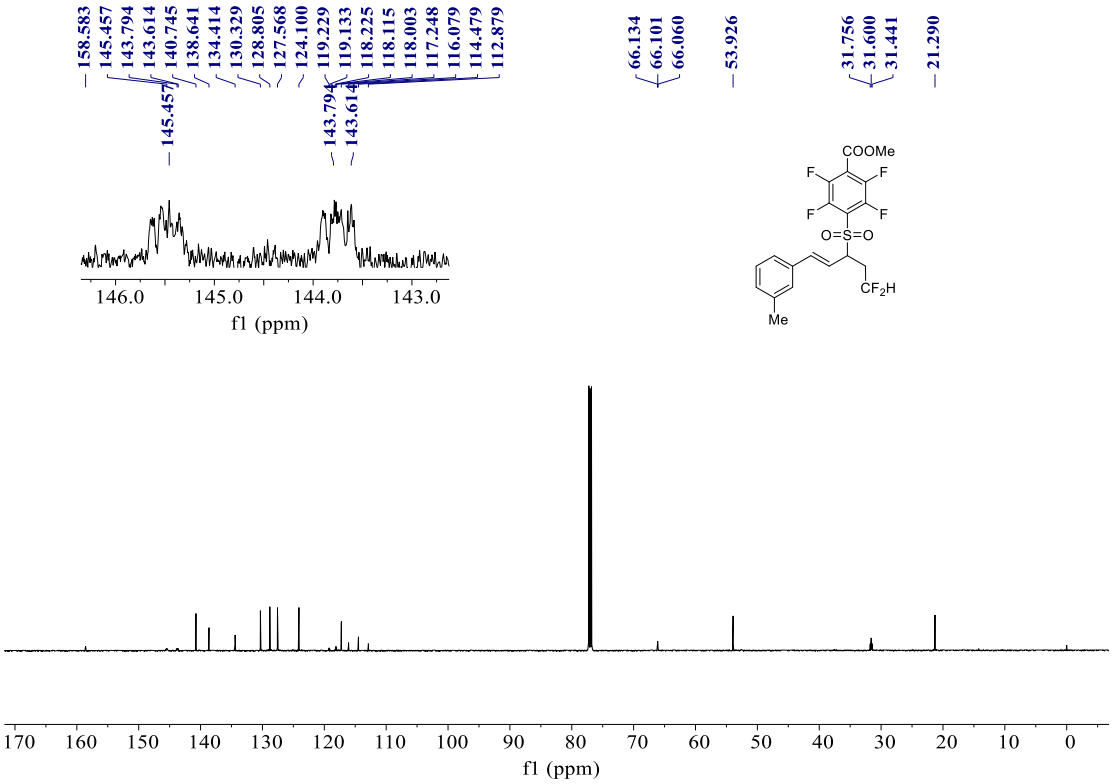
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ia



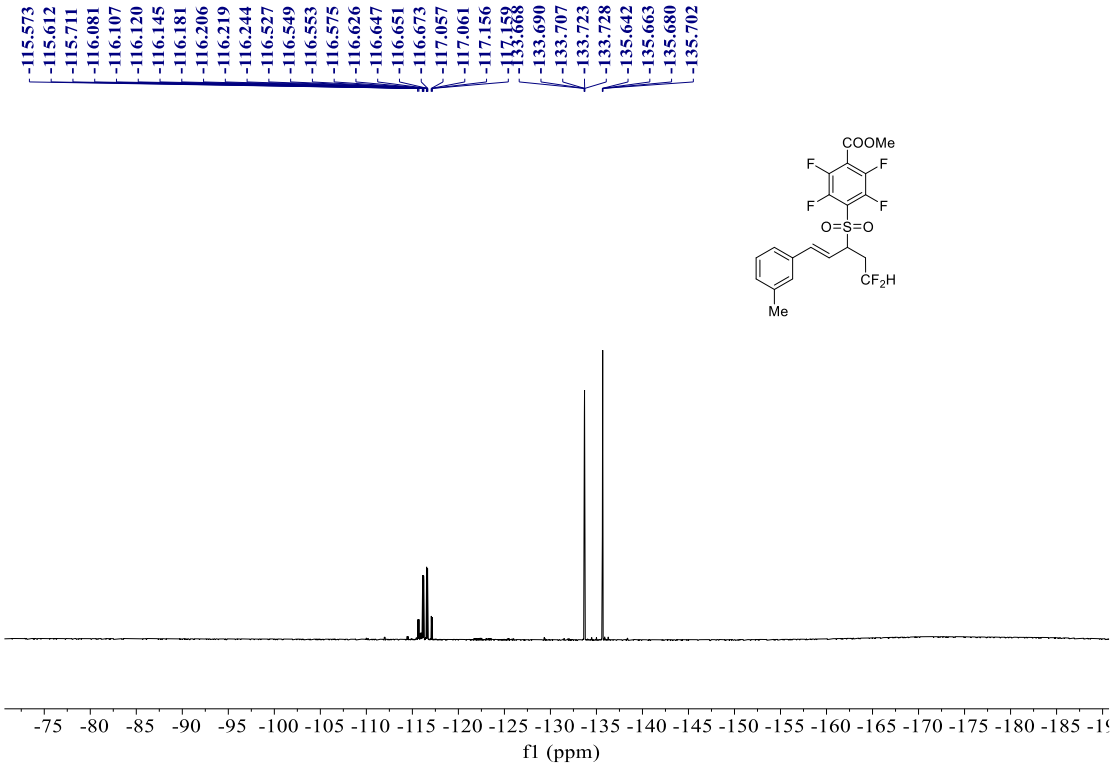
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ja



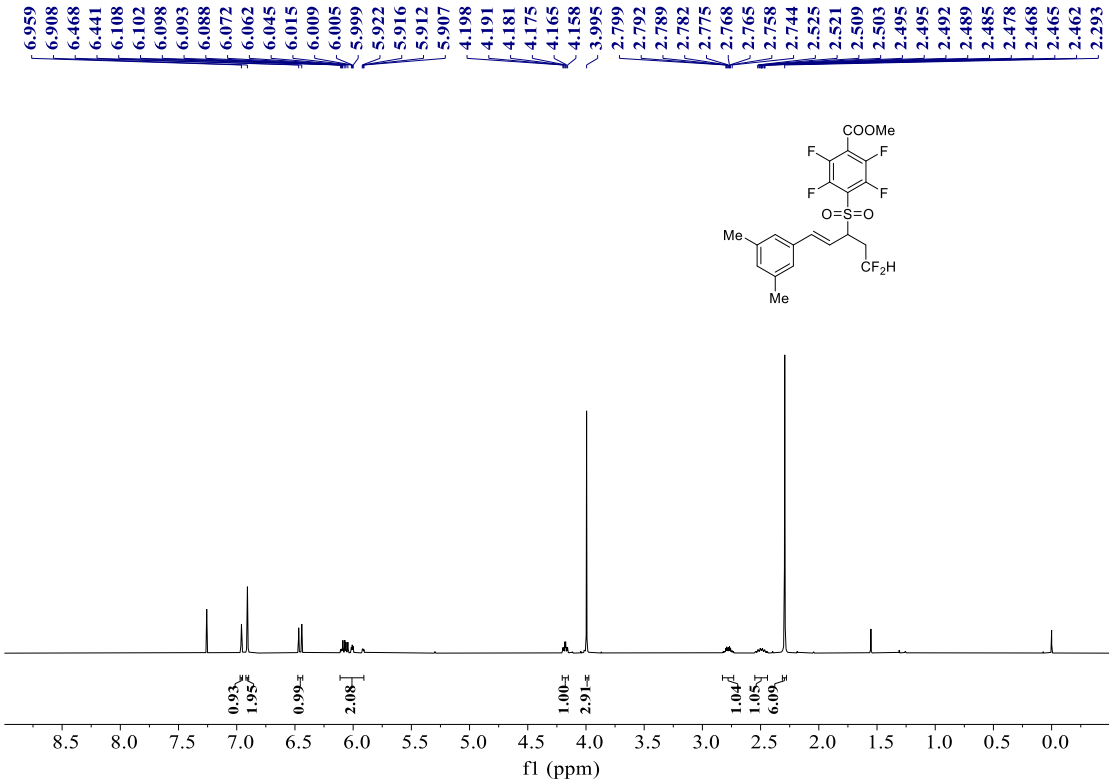
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ja



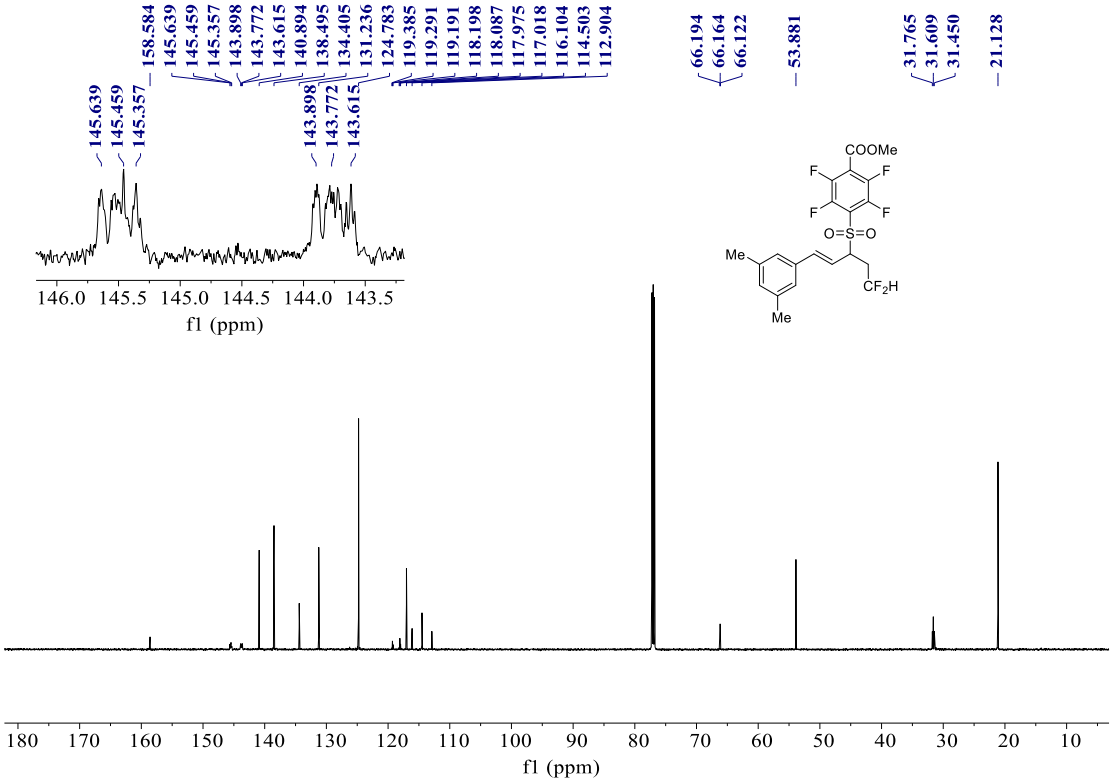
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ja



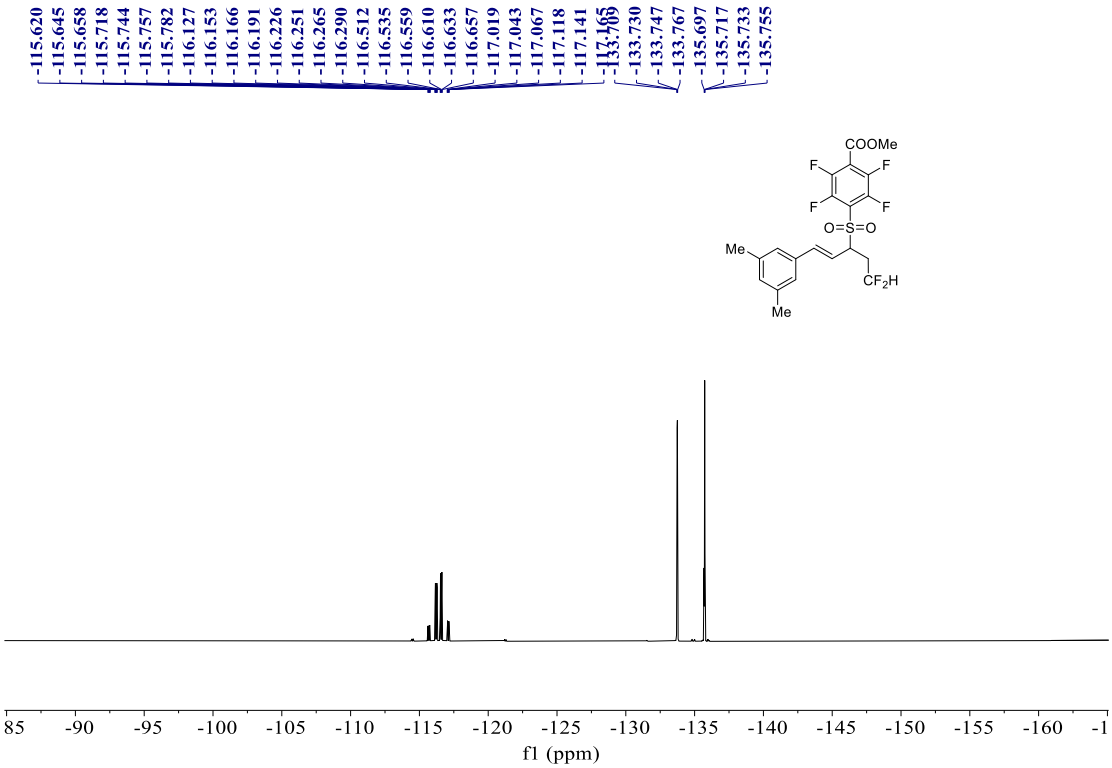
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ka



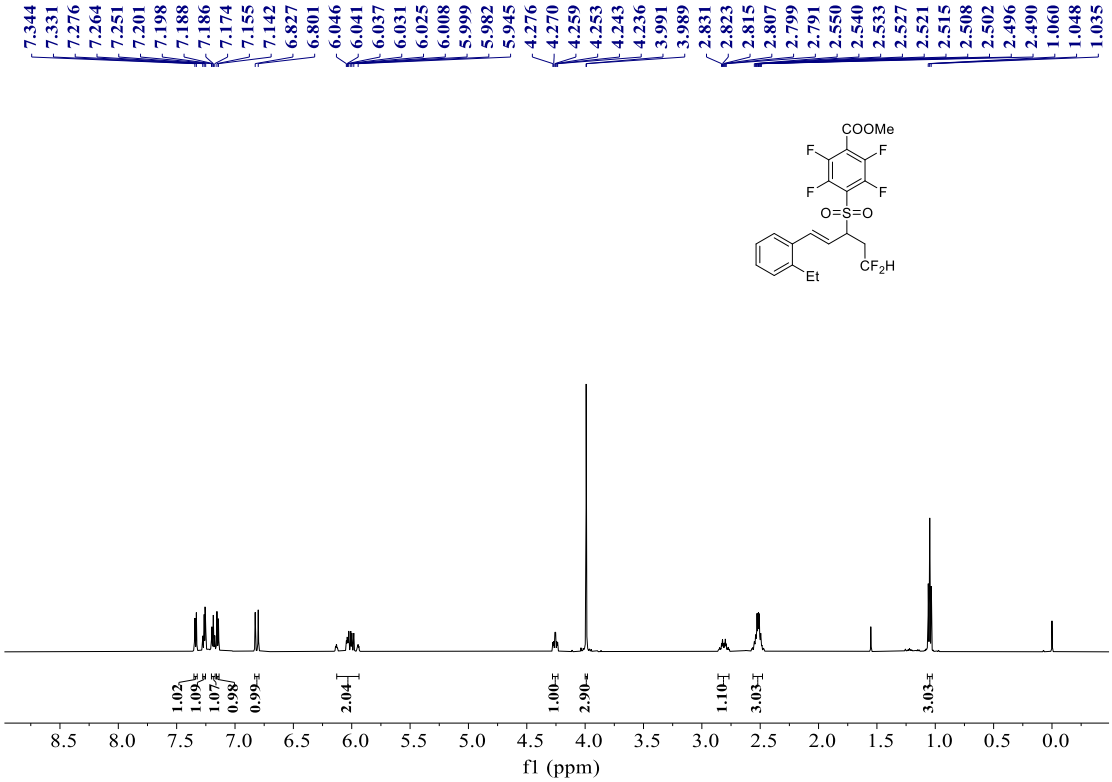
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ka



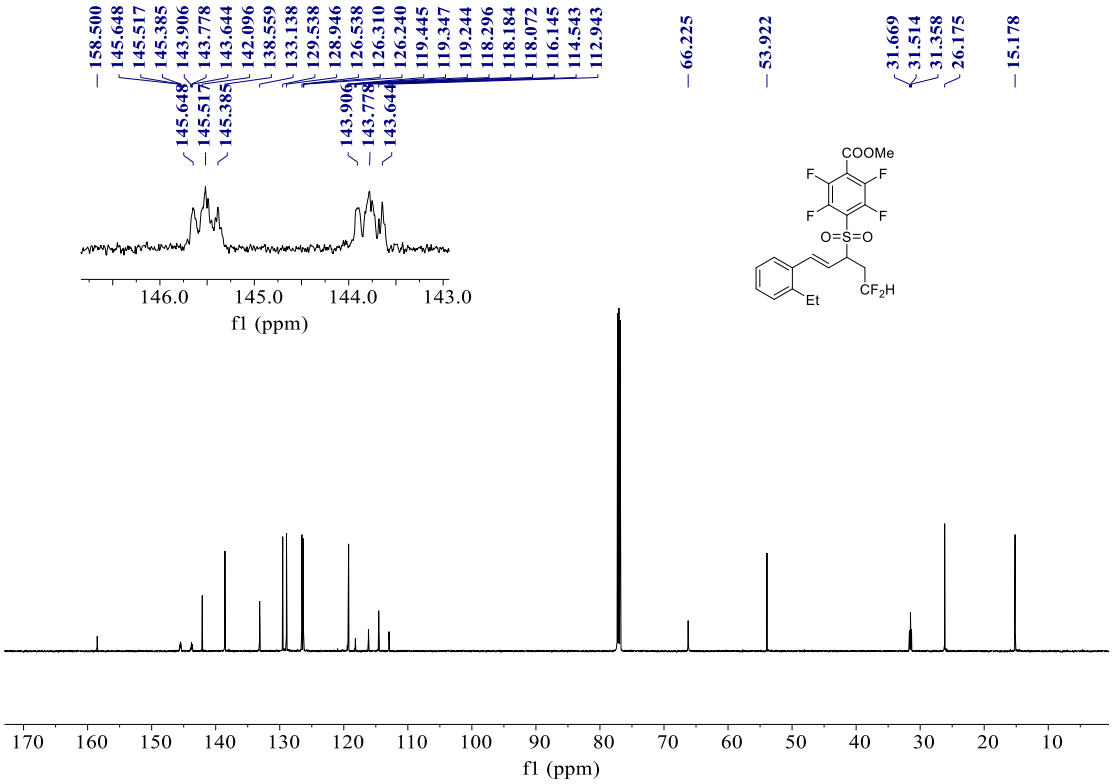
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ka



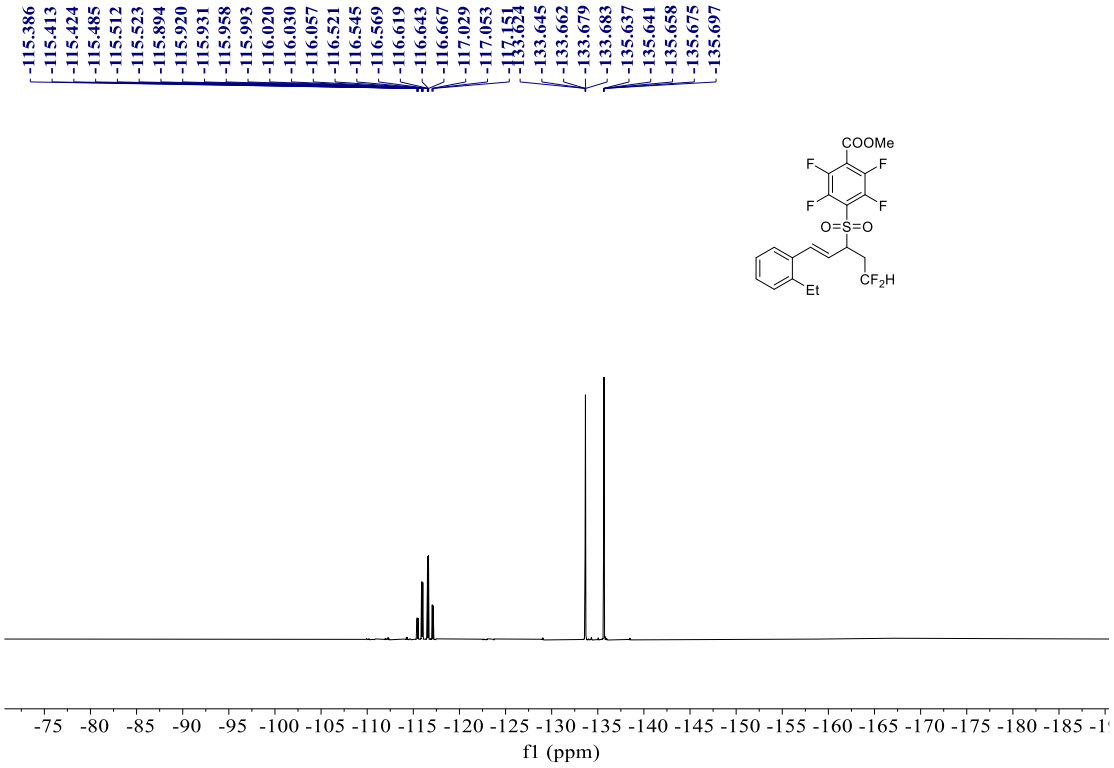
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5la



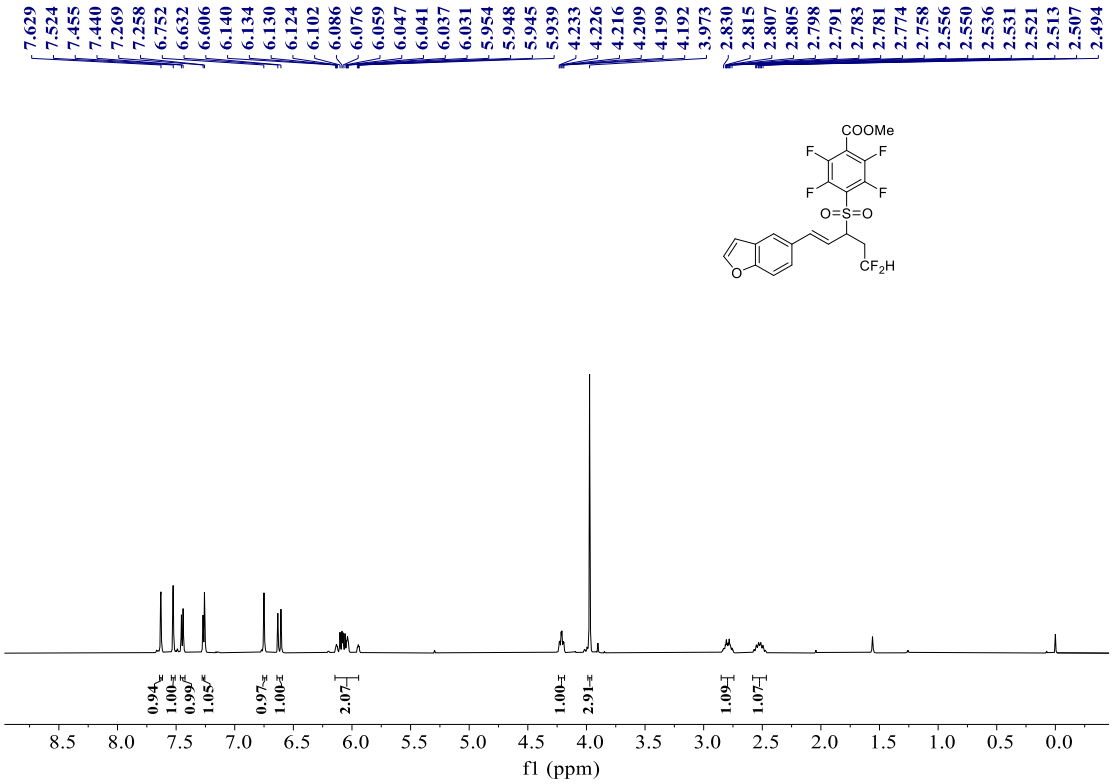
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5la



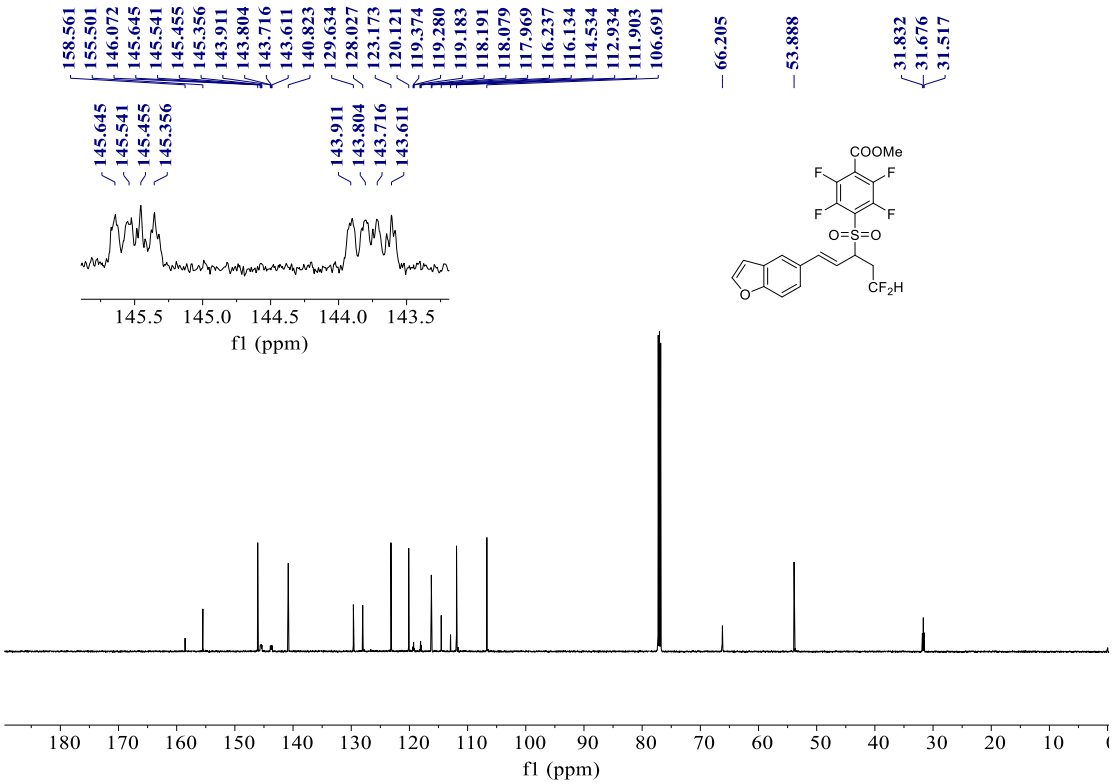
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5la



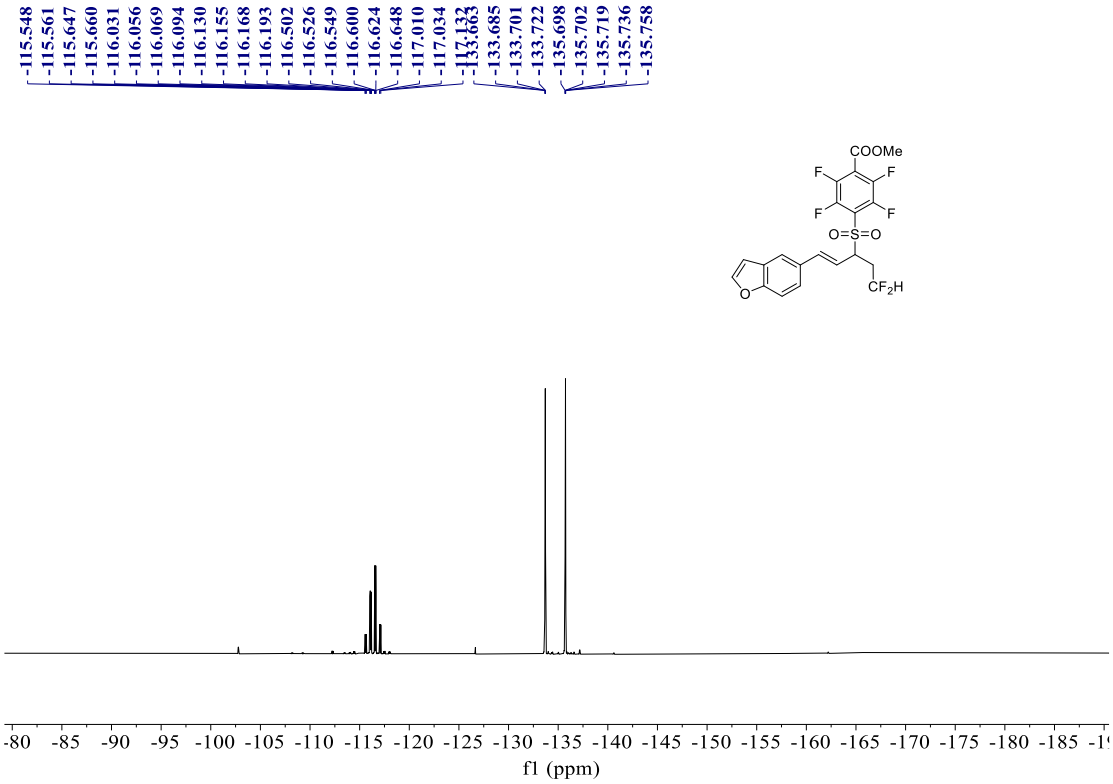
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5ma



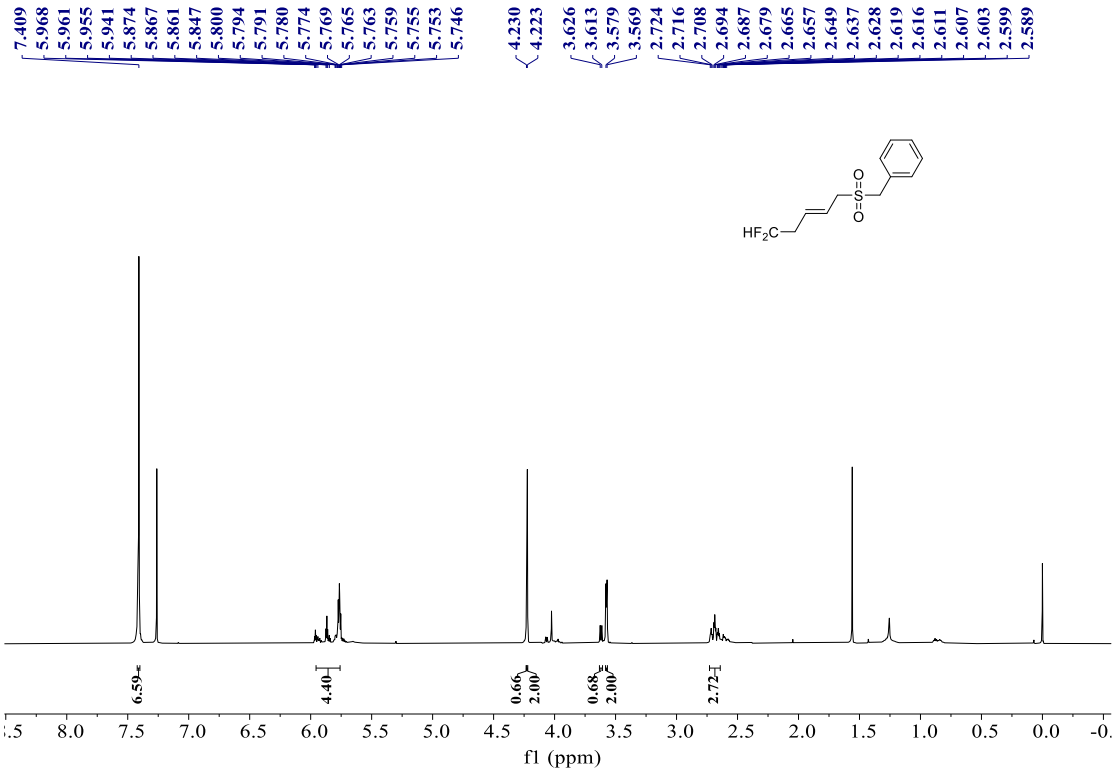
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5ma



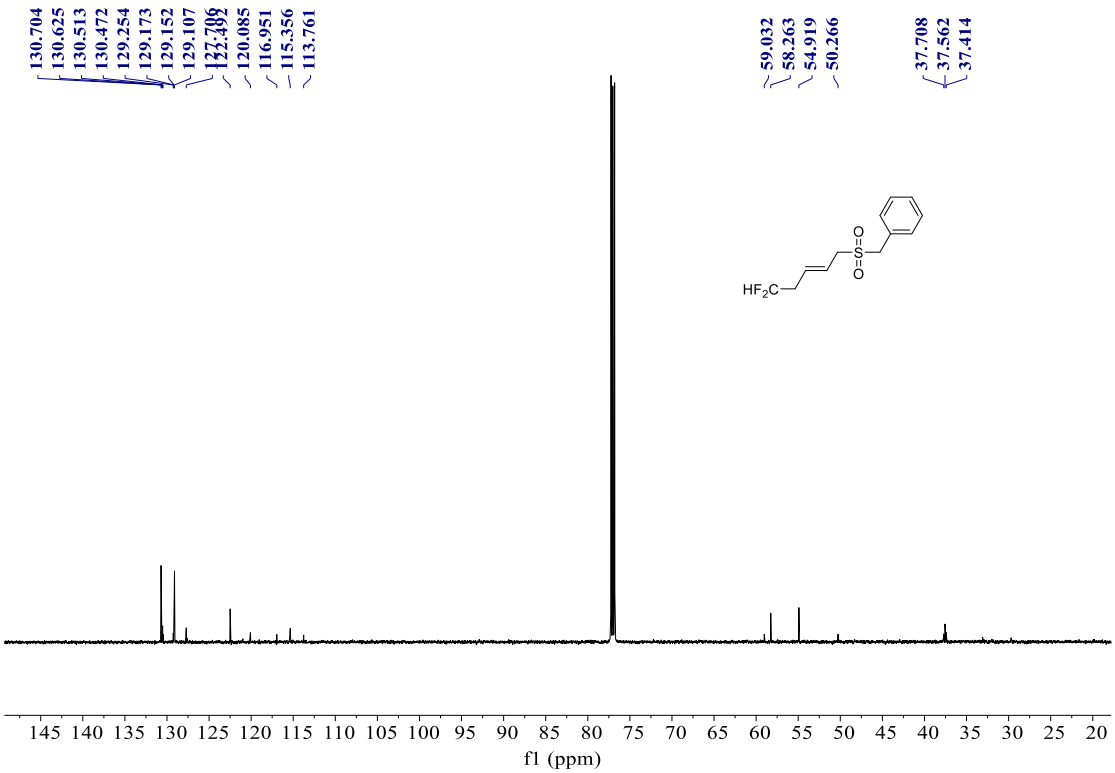
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 5ma



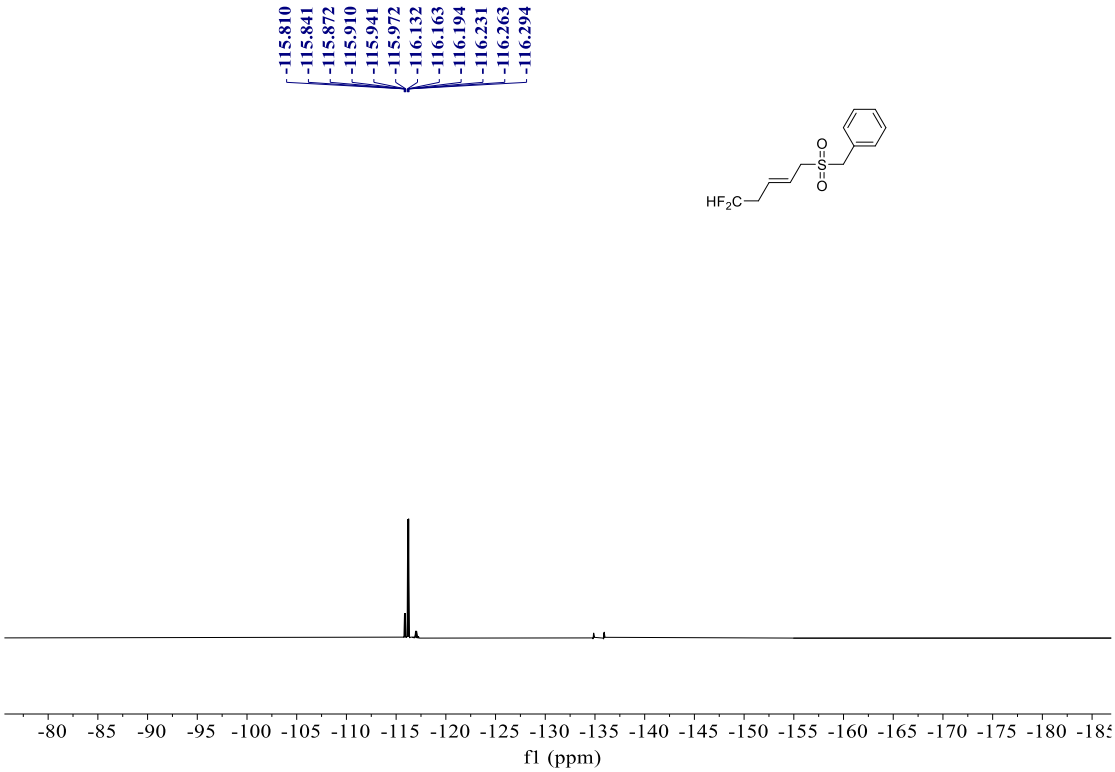
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4at



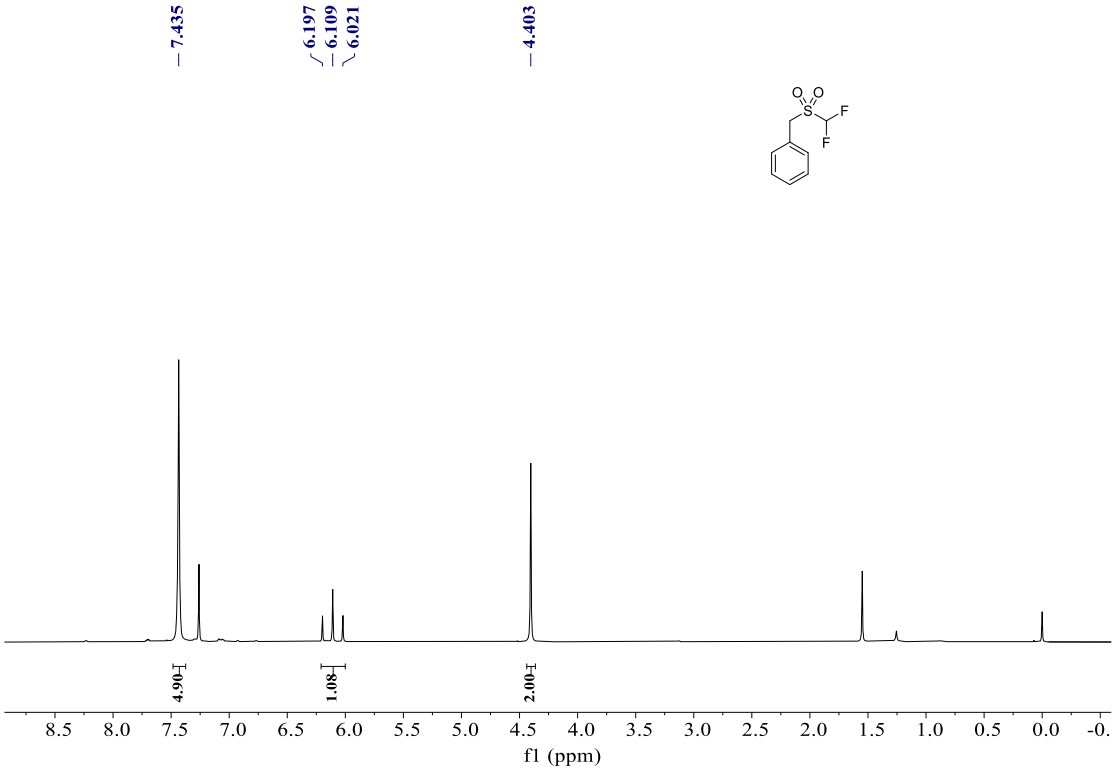
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4at



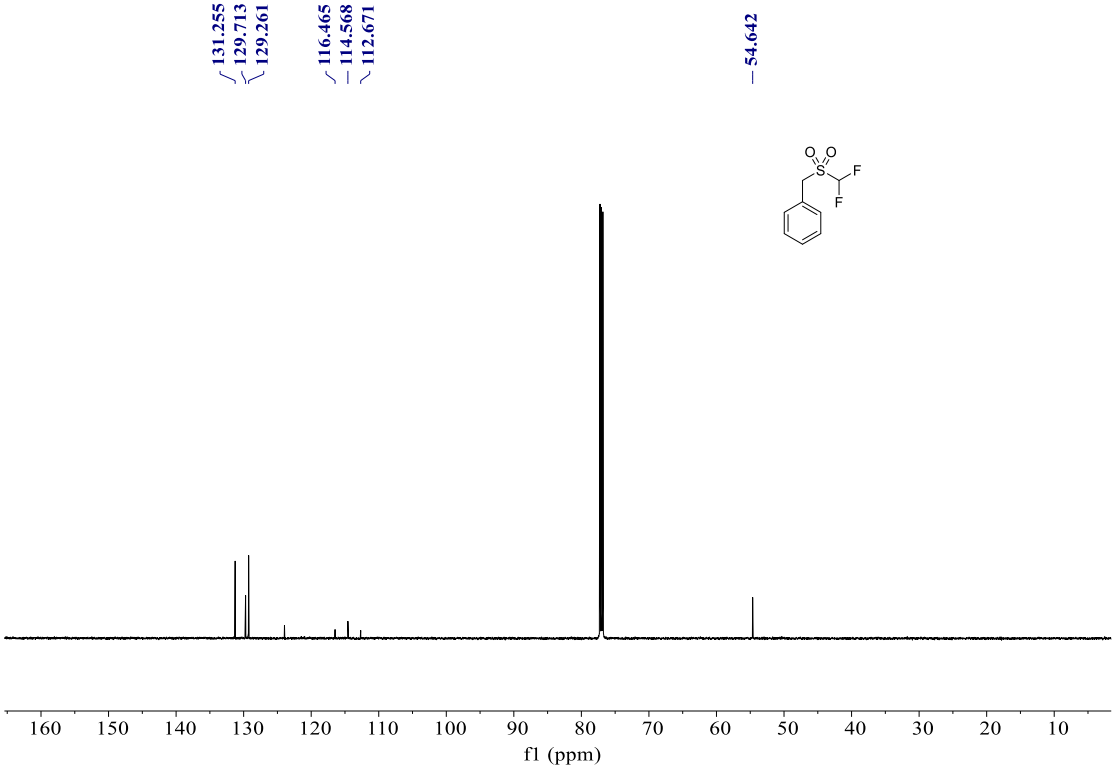
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4at



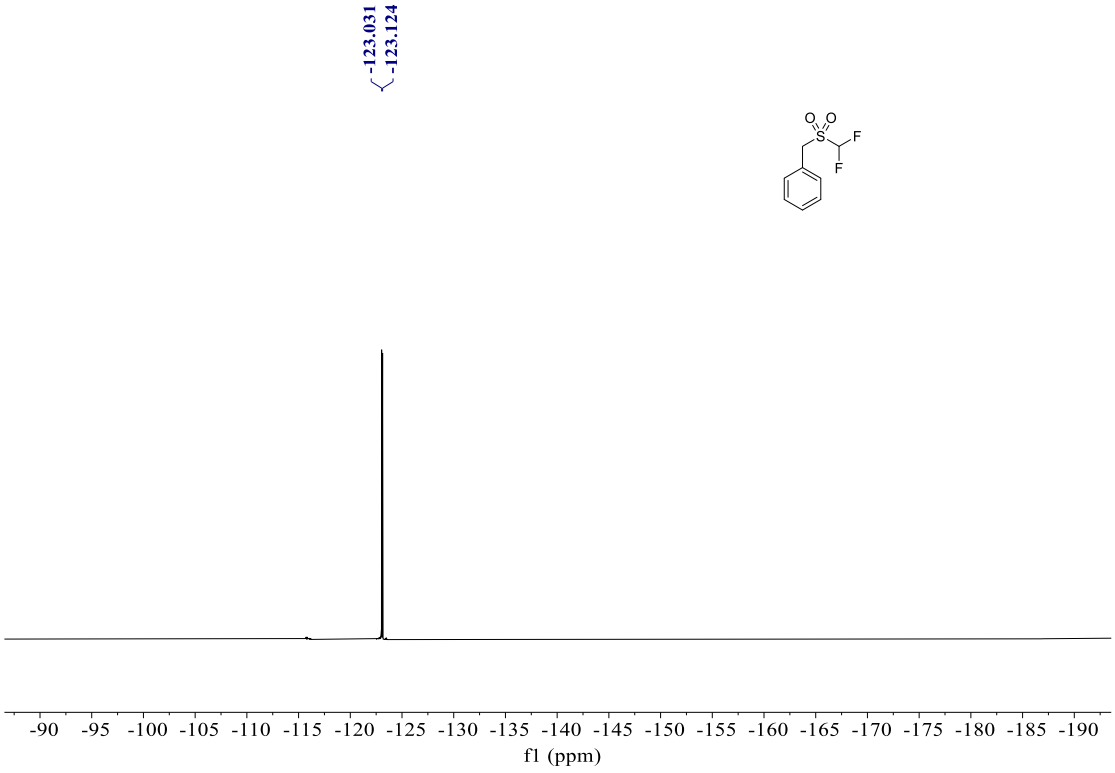
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4at'



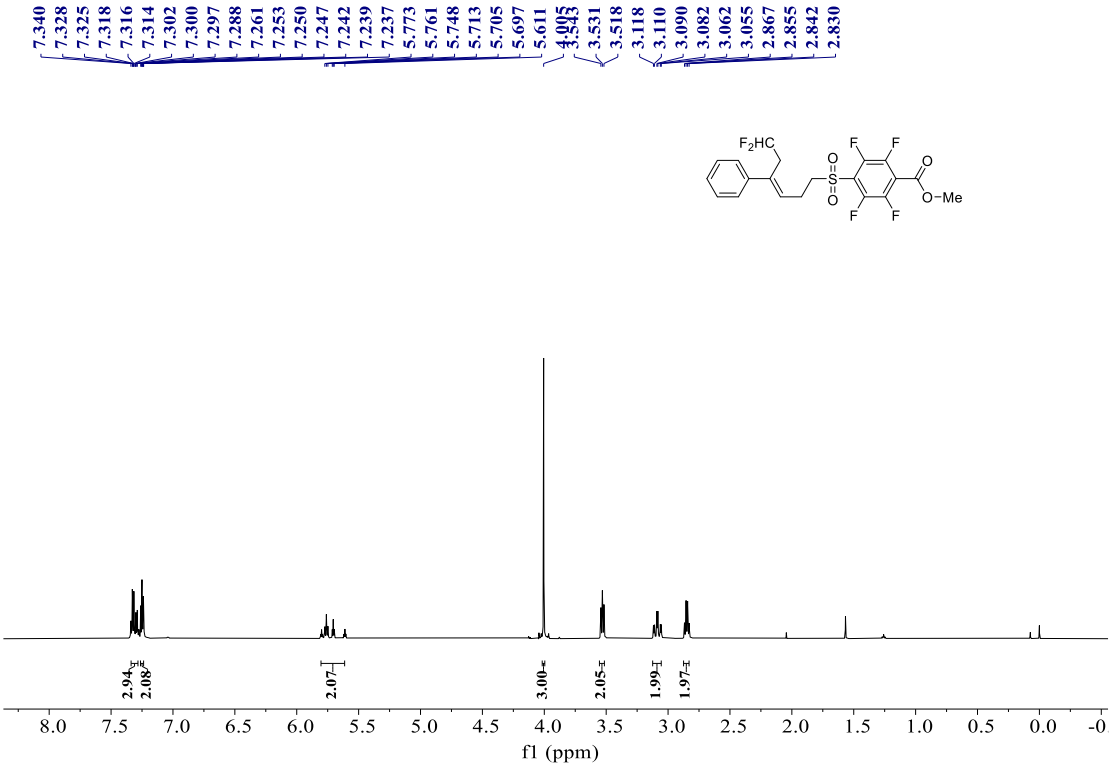
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4at'



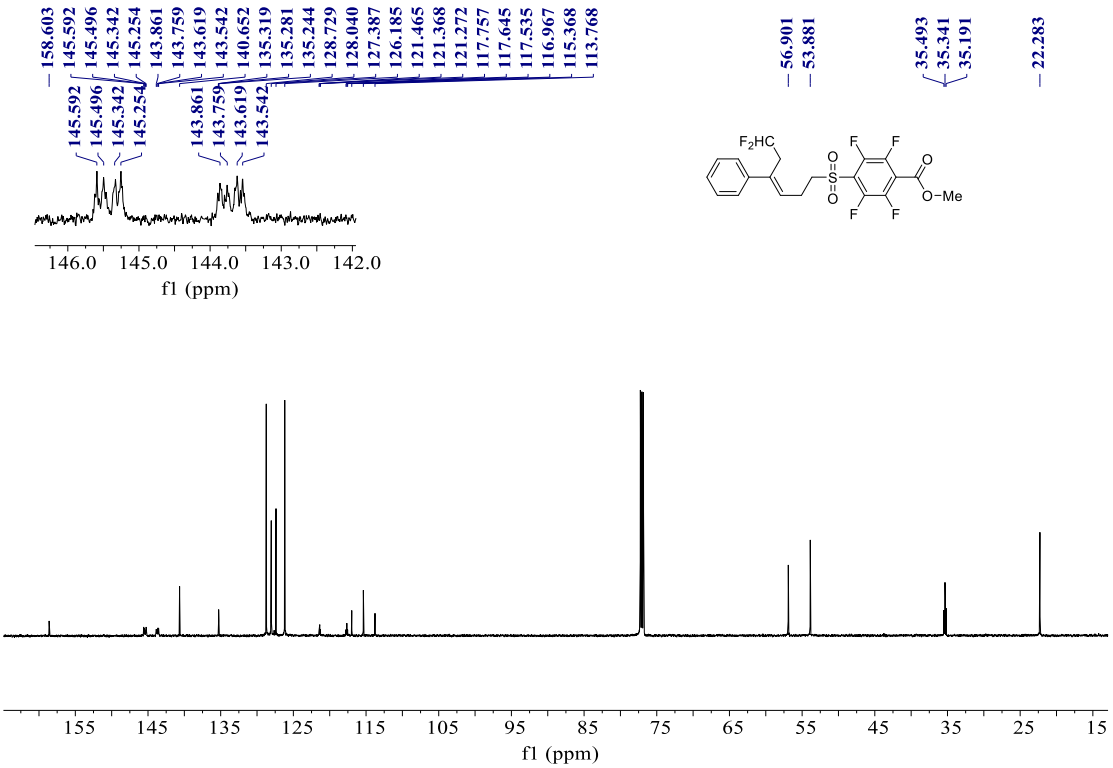
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 4at'



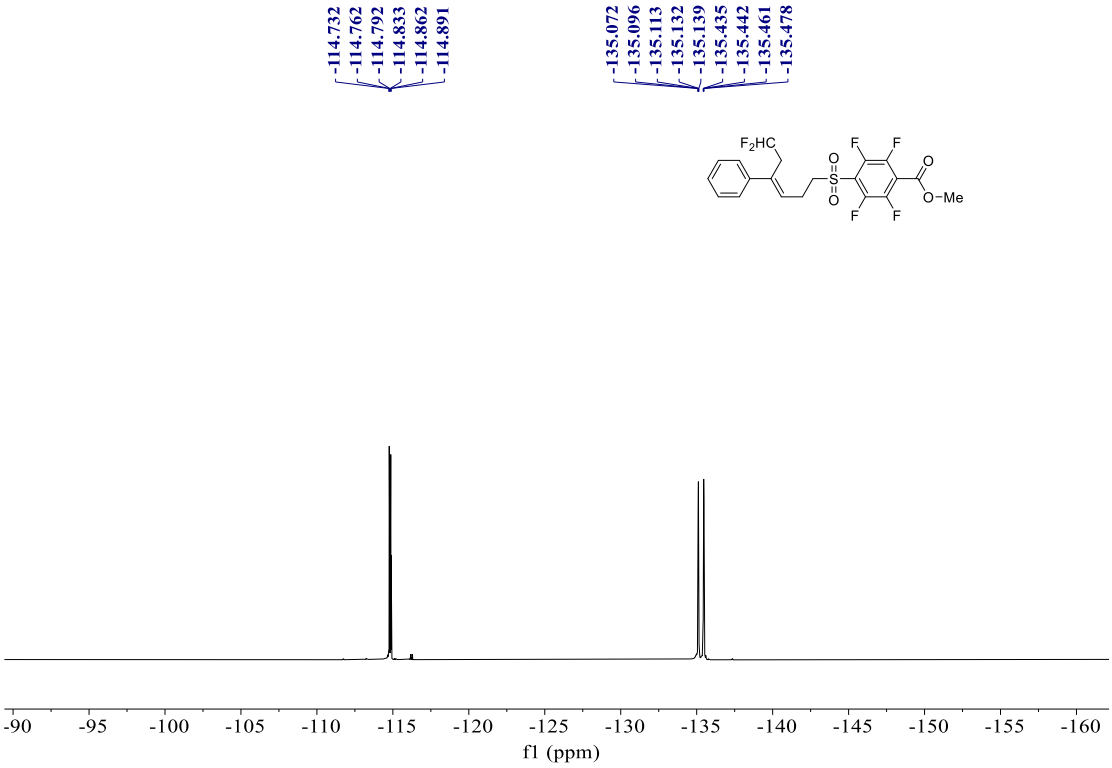
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6b



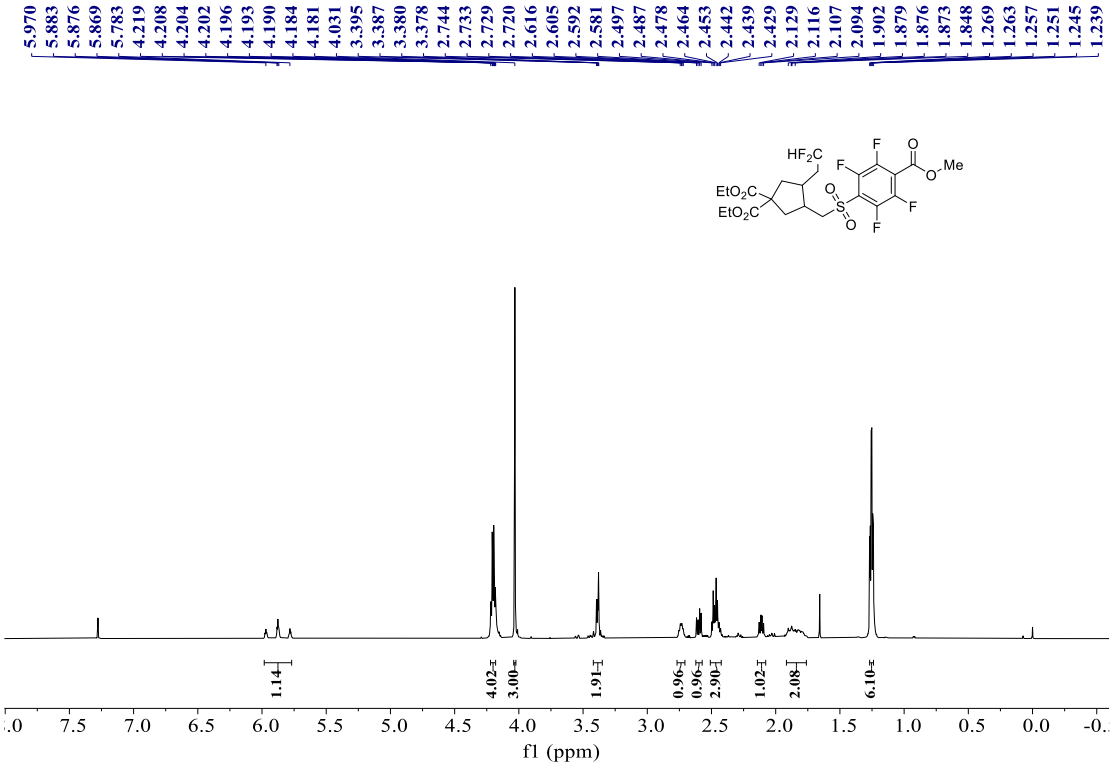
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6b



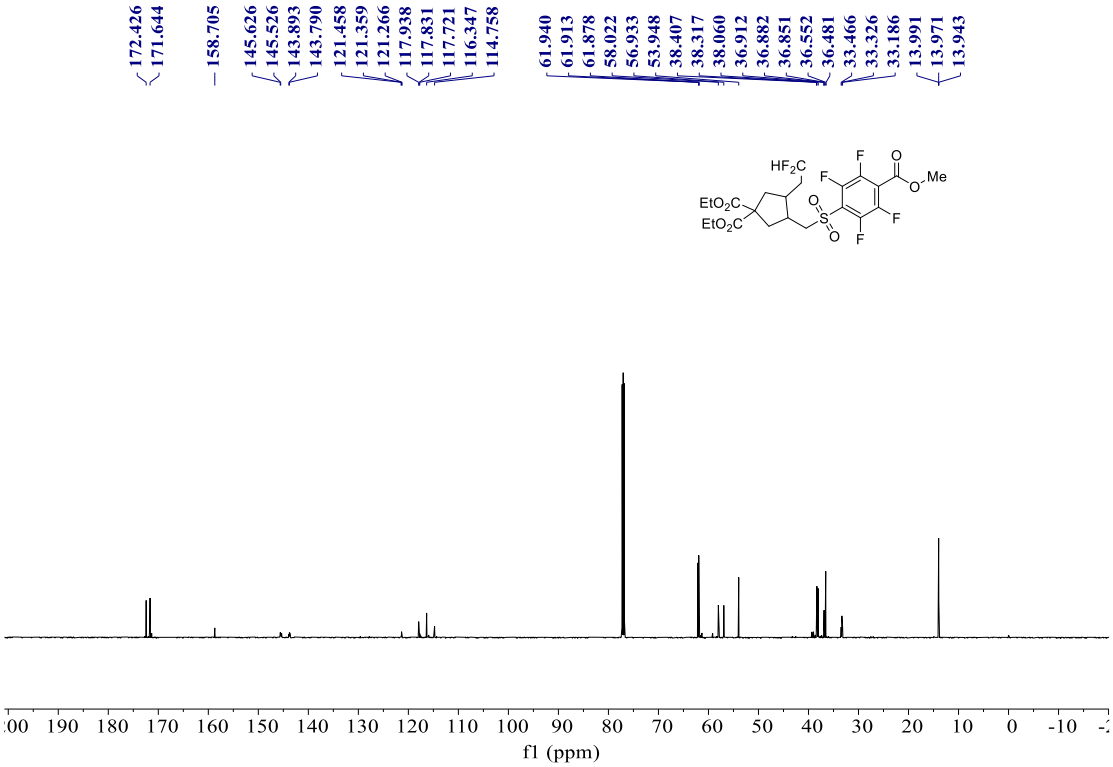
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 6b



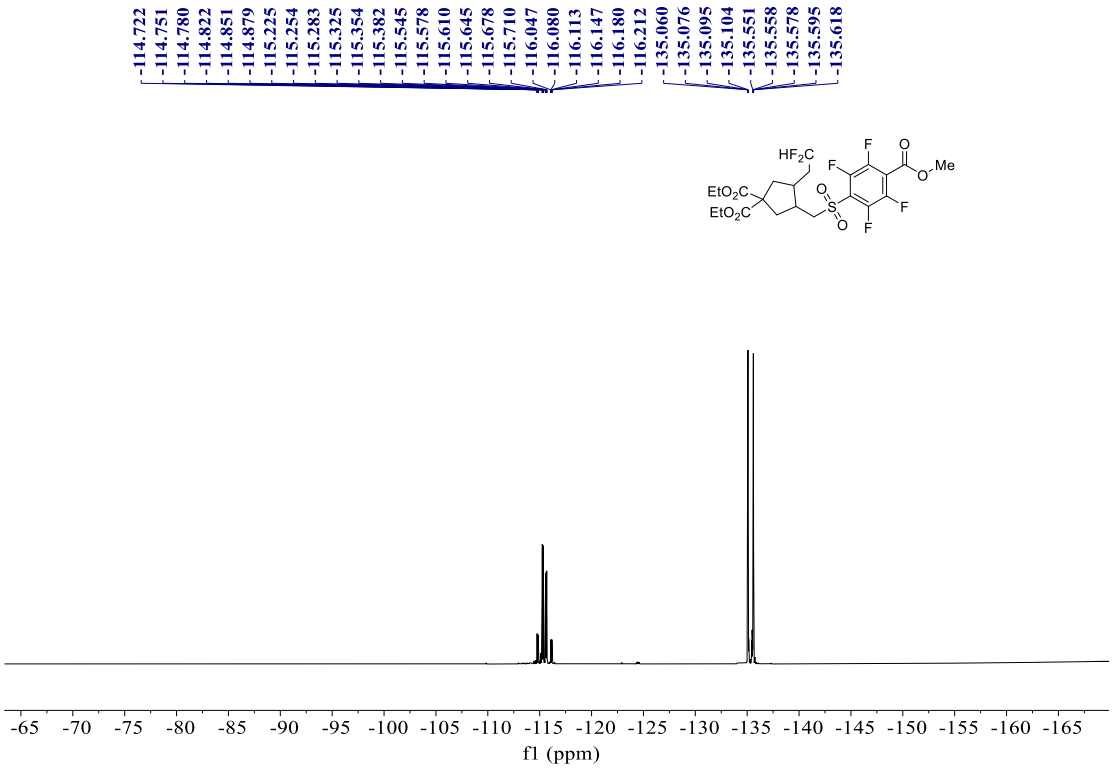
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6c



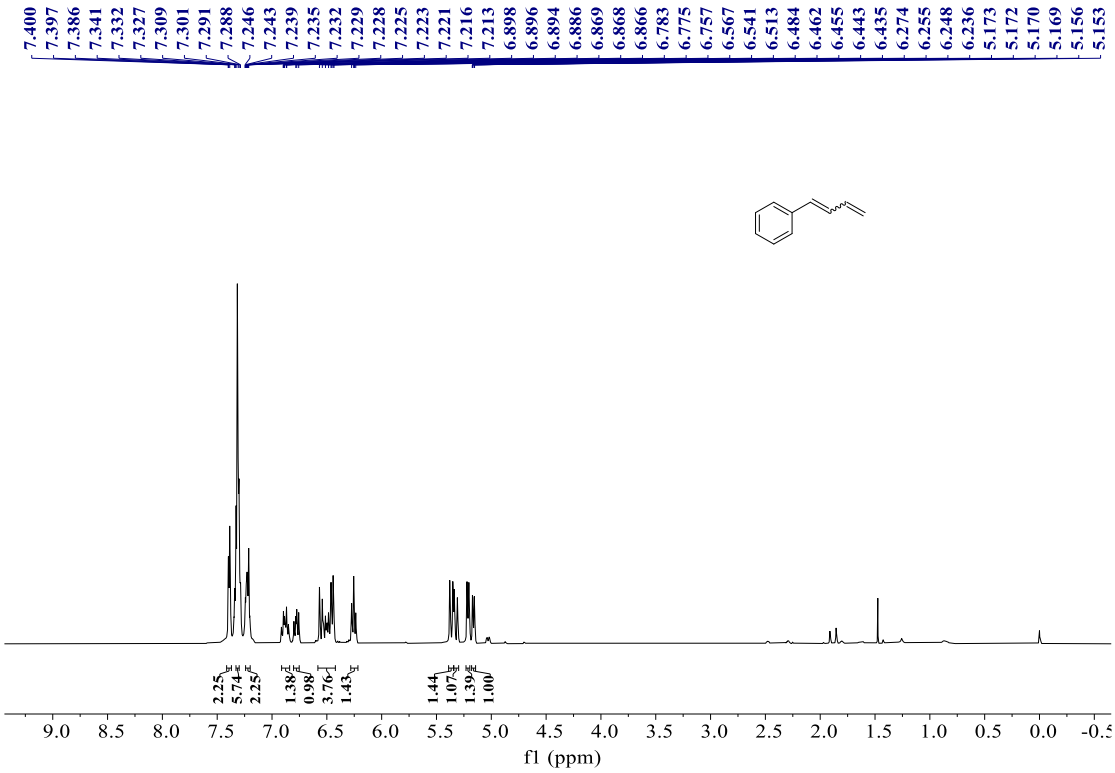
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6c



^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 6c



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the E/Z mixture of buta-1,3-dien-1-ylbenzene.



^{1}H NMR (600 MHz, $CDCl_3$) of the of the *(E)*-buta-1,3-dien-1-ylbenzene.