Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Pd-Catalyzed *gem*-Difluoroallylation of Arylboronic Acids with γ,γ-Difluoroallylic Acetates

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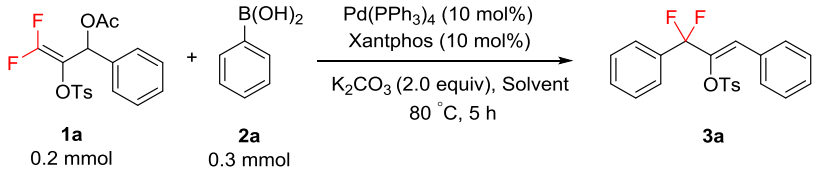
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400, AM500, Agilent MR300 spectrometer. ^{19}F NMR was recorded on a Bruker AM400 and Agilent MR300 spectrometer ($CFCl_3$ as an outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air, and backfilled with an inert atmosphere of N_2 at room temperature. All solvents were distilled before use.

Table S1. Solvent Effect on Pd-Catalyzed *gem*-Difluoroallylation of Phenylbronic Acid 2a with 3,3-Difluoro-1-Phenyl-2-(Tosyloxy) Allyl Acetate 1a.[a]

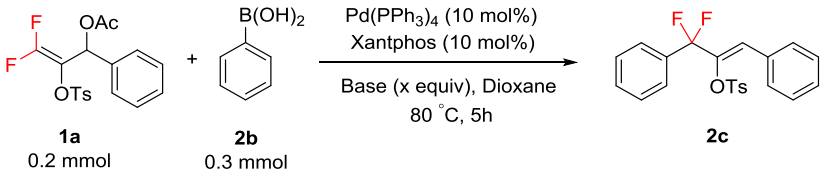


1a 0.2 mmol **2a** 0.3 mmol **3a**

Entry	Solvent	Yield (%)[b]
1	Dioxane	57
2	THF	50
3	Toluene	38
4	CH_3CN	/
5	DCE	/
6	CCl_4	/

[a]Solvent (1.5 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

Table S2. Base Effect on Pd-Catalyzed *gem*-Difluoroallylation of Phenylbronic Acid 2a with 3,3-Difluoro-1-Phenyl-2-(Tosyloxy) Allyl Acetate 1a.[a]

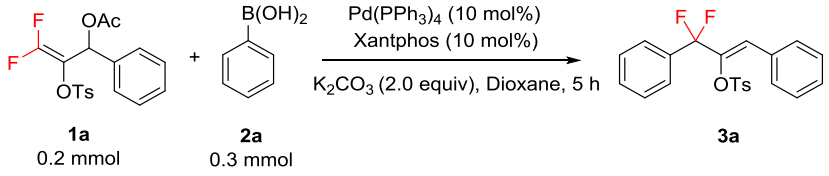


1a 0.2 mmol **2b** 0.3 mmol **2c**

Entry	Base (x)	yield (%)[a]
1	Na_2CO_3 (2.0)	ND
2	Cs_2CO_3 (2.0)	30
3	K_3PO_4 (2.0)	40
4	NaOAc (2.0)	10
5	KF (2.0)	48
6	K_2CO_3 (2.0)	57
7	K_2CO_3 (0.5)	10
8	K_2CO_3 (1.0)	23
9	K_2CO_3 (1.5)	35
10	K_2CO_3 (3.0)	41

[a]Solvent (1.5 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

Table S3. Screening Reaction Temperature for Pd-Catalyzed *gem*-Difluoroallylation of Phenylbronic Acid 2a with 3,3-Difluoro-1-Phenyl-2-(Tosyloxy) Allyl Acetate 1a.[a]

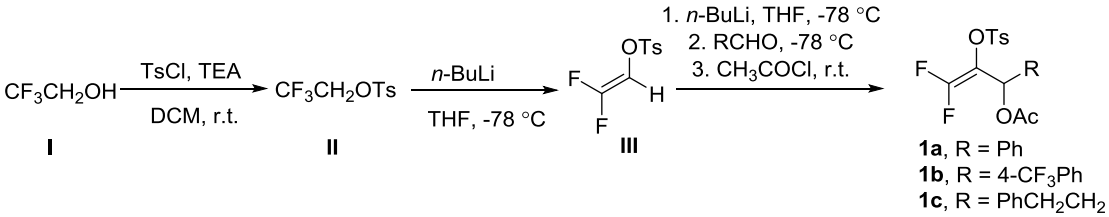


1a 0.2 mmol **2a** 0.3 mmol **3a**

Entry	Temp. (℃)	Yield (%)[a]
1	r.t.	Trace
2	40	15
3	60	65
4	80	57 (60)
5	100	64 (62)

[a]Solvent (1.5 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield**.**

General Procedure for the Synthesis of Compounds 1:

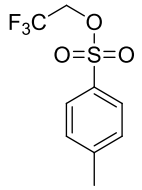


I II III

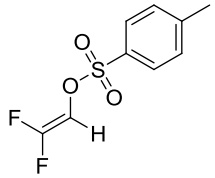
General Procedure: 4-Methylbenzenesulfonate (**III**) was prepared according to the procedure reported by Troels Skrydstrup *et. al.*[1] 3,3-Difluoro-2-(tosyloxy) allyl acetates **1** were synthesized from compound **III** with different aldehydes and acetyl chloride in one pot via three steps.

Typical Procedure for the Synthesis of Compound 1a: To a stirred solution of 2,2-difluorovinyl-4-methylbenzenesulfonate (**III**) (1.87 g, 8.0 mmol) in THF (100 mL) was added *n*-BuLi (2.5 M, 3.2 mL, 8.0 mmol) dropwise under N_2 at -78 ºC. After stirring for 1.5 h, the corresponding benzaldehyde (0.85 g, 8.0 mmol) was added and the resulting reaction mixture was stirred for another 1.5 h at same temperature. Acetyl acetate (0.79 g, 10.0 mmol) was then added, the resulting mixture was warmed to room temperature and stirred for another 1 h. The mixture was quenched with the slow addition of aqueous solution of HCl (10 mL, 1.0 M). The reaction mixture

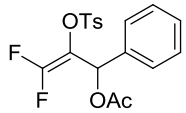
was extracted with EtOAc (50 mL × 3). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The residue was purified with silica gel chromatography (petroleum/ethyl acetate = 18 : 1) to give compound **1a** in 77% yield.



2,2,2-Trifluoroethyl 4-methylbenzenesulfonate (**II**).[1] White solid (m.p. 52 °C), 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.31 (q, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.1 (t, *J* = 8.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 131.5, 130.1, 127.9, 121.8 (q, *J* = 278.9 Hz), 64.5 (q, *J* = 38.2 Hz), 21.4.

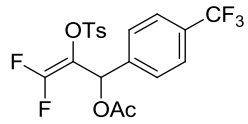


2,2-Difluorovinyl 4-methylbenzenesulfonate (III).[1] Colorless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.03 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.41 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -90.8 (dd, *J* = 50.8, 14.4 Hz), -109.4 (d, *J* = 50.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (dd, *J* = 296.4, 285.6 Hz), 146.1, 130.9, 129.9, 128.2, 100.8 (dd, *J* = 60.2, 15.2 Hz), 21.5.

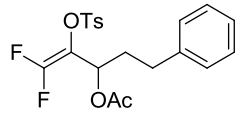


3,3-Difluoro-1-phenyl-2-(tosyloxy)allyl acetate (1a). The product (2.36 g, 77% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 18 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.28 (m, 7H), 6.56 (t, *J* = 0.8 Hz, 1H), 2.45 (s, 3H), 2.20 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.5 (d, *J* = 36.4 Hz, 1F), -99.8 (dd, *J* = 36.4, 2.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 156.1 (dd, *J* = 299.4, 293.4 Hz), 145.6, 134.7 (t, *J* = 2.0 Hz), 133.2, 129.7, 128.7, 128.5, 128.1 (d, *J* = 0.8 Hz), 126.7, 111.5 (dd, *J* = 42.4, 15.4 Hz), 69.0

(t, *J* = 2.8 Hz), 21.7, 20.9. IR (thin film): ν_{max} 3034, 1764, 1597, 1450 cm^{-1}. MS (MALDI): *m/z* (%) 428 (M^+ + 2Na), 409 (100), 405 (M^+ + Na), 381 (M^+ - H), 346. HRMS: Calculated for $C_{18}H_{16}F_2O_5S$: 382.0687; Found: 405.0578 (M^+ + Na).

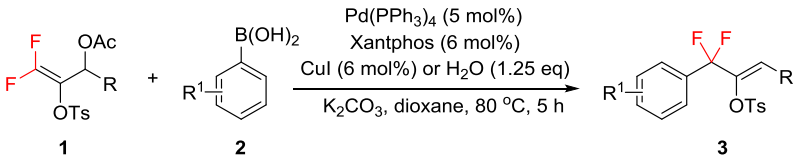


3,3-Difluoro-2-(tosyloxy)-1-(4-(trifluoromethyl)phenyl)allyl acetate (1b). The product (3.06 g, 85% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 10.4 Hz, 2H), 7.60 (d, *J* = 10.8 Hz, 2H), 7.46 (d, *J* = 10.4 Hz, 2H), 7.32 (d, *J* = 10.4 Hz, 2H), 6.59 (s, 1H), 2.45 (s, 3H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F), -87.5 (d, *J* = 34.6 Hz, 1F), -99.0 (dd, *J* = 34.0, 2.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 156.3 (dd, *J* = 298.9, 293.7 Hz), 145.8, 138.7, 133.0, 130.9 (q, *J* = 33.3 Hz), 129.8, 128.1, 127.1, 125.6 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.8 Hz), 111.0 (dd, *J* = 42.5, 16.0 Hz), 68.5 (t, *J* = 3.0 Hz), 21.7, 20.8. IR (thin film): ν_{max} 3040, 1767, 1598, 1417 cm^{-1}. MS (MALDI): *m/z* (%) 473 (M^+ + Na), 449 (M^+ - H), 444 (100). HRMS: Calculated for $C_{19}H_{15}F_5O_5S$: 450.0560; Found: 473.0458 (M^+ + Na).



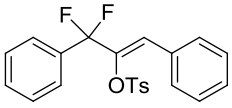
1,1-Difluoro-5-phenyl-2-(tosyloxy)pent-1-en-3-yl acetate (1c). The product (1.97 g, 60% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.25 (m, 2H),, 7.19 (t, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.46 – 5.39 (m, 1H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 2.21 – 2.11 (m, 1H), 2.09 (s, 3H), 2.09 – 1.95 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.3 (d, *J* = 35.3 Hz, 1F), -99.0 (dd, *J* = 35.3, 2.6 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 156.2 (dd, *J* = 298.2, 292.4 Hz), 145.7, 140.1, 133.2, 129.8, 128.4, 128.2, 128.0, 126.2, 110.9 (dd, *J* = 43.4, 14.8 Hz), 67.4 (t, *J* = 2.9 Hz), 31.8, 31.2, 21.6, 20.8. IR (thin film): ν_{max} 3064, 1763, 1598, 1496 cm^{-1}. MS (MALDI): *m/z* (%) 433 (M^+ + Na), 410 (M^+), 409(100, M^+ - H). HRMS: Calculated for $C_{20}H_{20}F_2O_5S$: 410.1000; Found: 433.0895 (M^+ + Na).

General Procedure for the Synthesis of Compounds 3:



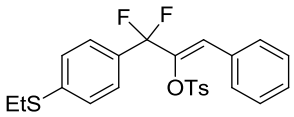
Method A (CuI was used as an additive): To a Schlenk tube was charged with $Pd(PPh_3)_4$ (46.4 mg, 0.04 mmol), Xantphos (27.8 mg, 0.048 mmol), CuI (9.2 mg, 0.048 mmol), arylboronic acid **2** (0.6 mmol), K_2CO_3 (110 mg, 0.8 mmol), **1** (0.4 mmol), and dioxane (2 mL) under N_2. The tube was then screwed capped and the reaction mixture was stirred at 80 °C for 5 h. The resulting mixture was cooled to room temperature, and filtrated through a silica gel pad. After concentrated under reduced pressure, the residue was subjected to purification on silica gel chromatography to give desired product.

Method B (H_2O was used as an additive): To a Schlenk tube was charged with $Pd(PPh_3)_4$ (46.4 mg, 0.04 mmol), Xantphos (27.8 mg, 0.048 mmol), arylboronic acid **2** (0.6 mmol), K_2CO_3 (110 mg, 0.8 mmol), **1** (0.4 mmol), H_2O (9 μL, 0.5 mmol) and dioxane (2 mL). The tube was screwed capped and the reaction mixture was stirred at 80 °C for 5 h. The resulting mixture was cooled to room temperature, and filtrated through a silica gel pad. After concentrated under reduced pressure, the residue was subjected to purification on silica gel chromatography to give desired product.

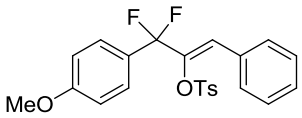


***(Z)*-3,3-Difluoro-1,3-diphenylprop-1-en-2-yl-4-methylbenzenesulfonate (3a).** Method A. The product (136 mg, 85% yield) as a faint yellow solid (m.p. 76 °C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.49 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.46 – 7.36 (m, 5H), 7.31 – 7.23 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 2.42 (s, 1H).^{19}F NMR (376 MHz, $CDCl_3$) δ -95.3 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 140.5 (t, *J* = 31.8 Hz), 134.3 (t, *J* = 26.8 Hz), 134.0, 131.2, 130.4, 129.6, 129.2, 129.1, 128.4, 128.3, 128.1, 125.9 (t, *J* = 5.6 Hz), 124.7 (t, *J* = 5.4

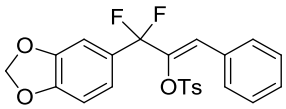
Hz), 117.2 (t, *J* = 244.7 Hz), 21.6. IR (thin film): ν_{max} 3062, 2926, 1667, 1595, 1495 cm^{-1}. MS (EI): *m/z* (%) 400 (M^+), 127 (100). HRMS: Calculated for $C_{22}H_{18}F_2O_3S$: 400.0945; Found: 400.0942.



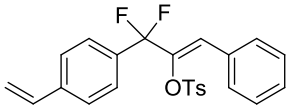
***(Z)*-3-(4-(Ethylthio)phenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3b).** Method B. The product (149 mg, 81% yield) as a red-brown sticky oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 18 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.32 – 7.25 (m, 7H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 2.99 (q, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.36 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.9 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 140.6, 140.4 (t, *J* = 32.2 Hz), 134.0, 131.2, 131.1 (t, *J* = 27.3 Hz), 129.6, 129.2, 129.1, 128.4, 128.1, 127.2, 126.4 (t, *J* = 5.5 Hz), 124.63 (t, *J* = 5.4 Hz), 117.1 (t, *J* = 244.7 Hz), 26.6, 21.6, 14.0. IR (thin film): ν_{max} 3042, 2980, 2933, 2873, 1679, 1597, 1493 cm^{-1}. MS (EI): *m/z* (%) 460 (M^+), 187 (100). HRMS: Calculated for $C_{24}H_{22}F_2O_3S$: 460.0978; Found: 460.0981.



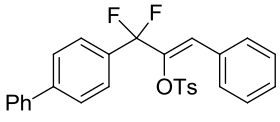
***(Z)*-3,3-Difluoro-3-(4-methoxyphenyl)-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3c).** Method B. The product (156 mg, 91% yield) as a red-brown oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.30-7.26 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 1H), 3.84 (s, 3H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.8 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 144.9, 140.7 (t, *J* = 32.4 Hz), 134.0, 131.3, 129.6, 129.2, 129.0, 128.4, 128.0, 127.5 (t, *J* = 5.5 Hz), 126.3 (t, *J* = 27.3 Hz), 124.6 (t, *J* = 5.4 Hz), 117.4 (t, *J* = 244.0 Hz), 113.6, 55.3, 21.5. IR (thin film): ν_{max} 3059, 3029, 2936, 1668, 1597, 1496 cm^{-1}. MS (EI): *m/z* (%) 430 (M^+), 157 (100). HRMS: Calculated for $C_{23}H_{20}F_2O_4S$: 430.1050; Found: 430.1046.



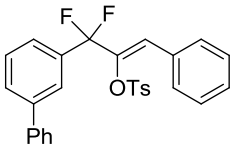
***(Z)*-3-(Benzo[*d*][1,3]dioxol-5-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3d).** Method B. The product (119 mg, 68% yield) as a faint yellow solid (m.p. 75 ºC) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.31 – 7.28 (m, 2H), 7.28 – 7.26 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.88 (m, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.01 (s, 2H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.3 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 147.6, 145.0, 140.4 (t, *J* = 32.4 Hz), 134.0, 131.2, 129.6, 129.2, 129.1, 128.4, 128.1, 127.9 (t, *J* = 27.4 Hz), 124.5 (t, *J* = 5.4 Hz), 120.3 (t, *J* = 6.2 Hz), 117.1 (t, *J* = 244.9 Hz), 108.0, 106.5 (t, *J* = 5.7 Hz), 101.6, 21.5. IR (thin film): ν_{max} 3048, 2909, 1664, 1593, 1493 cm^{-1}. MS (EI): *m/z* (%) 444 (M^+), 171 (100). HRMS: Calculated for $C_{23}H_{18}F_2O_5S$: 444.0843; Found: 444.0848.



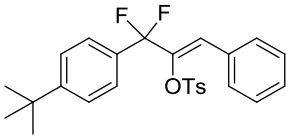
***(Z)*-3,3-Difluoro-1-phenyl-3-(4-vinylphenyl)prop-1-en-2-yl-4-methylbenzenesulfonate (3e).** Method B. The product (136 mg, 80% yield) as a light yellow oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.33 (m, 2H), 7.30 – 7.24 (m, 3H), δ 7.18 (d, *J* = 8.0 Hz, 2H), 6.77 – 6.70 (m, 1H), 6.68 (s, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.1 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 140.4 (t, *J* = 32.1 Hz), 139.6, 135.8, 134.0, 133.5 (t, *J* = 26.8 Hz), 131.2, 129.6, 129.2, 129.1, 128.4, 128.1, 126.2 (t, *J* = 5.6 Hz), 126.1, 124.7 (t, *J* = 5.4 Hz), 117.2 (t, *J* = 244.7 Hz), 115.7, 21.6. IR (thin film): ν_{max} 3060, 2929, 1669, 1598, 1450 cm^{-1}. MS (EI): *m/z* (%) 426 (M^+), 153 (100). HRMS: Calculated for $C_{24}H_{20}F_2O_3S$: 426.1101; Found: 426.1104.



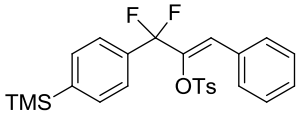
***(Z)*-3-([1,1'-Bphenyl]-4-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3f).** Method B. The product (128 mg, 67% yield) as a red-brown sticky oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.55 – 7.44 (m, 6H), 7.43 – 7.35 (m, 1H), 7.32 – 7.26 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.72 (s, 1H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.9 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.2, 140.4 (t, *J* = 32.1 Hz), 139.9, 134.0, 133.1 (t, *J* = 27.0 Hz), 131.2, 129.7, 129.2, 129.1, 128.8, 128.4, 128.1, 127.9, 127.1, 127.0, 126.4 (t, *J* = 5.5 Hz), 124.7 (t, *J* = 5.2 Hz), 117.3 (t, *J* = 244.8 Hz), 21.5. IR (thin film): ν_{max} 3058, 3031, 2924, 1669, 1597, 1488 cm^{-1}. MS (EI): *m/z* (%) 476 (M^+), 203 (100). HRMS: Calculated for $C_{28}H_{22}F_2O_3S$: 476.1258; Found: 476.1256.



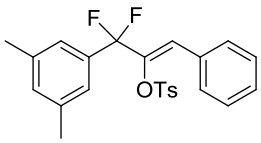
***(Z)*-3-([1,1'-Biphenyl]-3-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3g).** Method B. The product (137 mg, 72% yield) as a red-brown sticky oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.50 (m, 5H), 7.45 – 7.39 (m, 5H), 7.38 – 7.30 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 2.26 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.3 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 141.3, 140.2 (t, *J* = 31.6 Hz), 140.0, 134.8 (t, *J* = 26.8 Hz), 133.9, 131.2, 129.7, 129.21, 129.17, 129.0, 128.85, 128.80, 128.4, 128.0, 127.7, 127.0, 124.8 (t, *J* = 5.4 Hz), 124.5 (t, *J* = 5.4 Hz), 124.4 (t, *J* = 5.6 Hz), 117.15 (t, *J* = 245.5 Hz), 21.4. ν_{max} 3059, 3034, 2963, 1668, 1598, 1496 cm^{-1}. MS (EI): *m/z* (%) 476 (M^+), 203 (100). HRMS: Calculated for $C_{28}H_{22}F_2O_3S$: 476.1258; Found: 476.1260.



***(Z)*-3-(4-(*tert*-Butyl)phenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3h).** Method A. The product (151 mg, 83% yield) as a white solid (m.p. 94 ^{o}C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.37 (dd, *J* = 25.2, 8.4 Hz, 4H), 7.30 – 7.26 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 2.42 (s, 3H), 1.34 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.6 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 144.8, 140.7 (t, *J* = 32.3 Hz), 134.1, 131.4 (t, *J* = 27.1 Hz), 131.3, 129.7, 129.2, 129.1, 128.4, 128.2, 125.7 (t, *J* = 5.5 Hz), 125.3, 124.6 (t, *J* = 5.4 Hz), 117.4 (t, *J* = 245.4 Hz), 34.8, 31.2, 21.6. IR (thin film): ν_{max} 3058, 3032, 2907, 1661, 1597, 1494 cm^{-1}. MS (EI): *m/z* (%) 456 (M^+), 183 (100). HRMS: Calculated for $C_{26}H_{26}F_2O_3S$: 456.1571; Found: 456.1574.

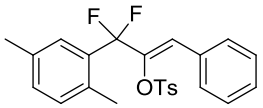


***(Z)*-3,3-Difluoro-1-phenyl-3-(4-(trimethylsilyl)phenyl)prop-1-en-2-yl-4-methylbenzenesulfonate (3i).** Method A. The product (142 mg, 75% yield) as a red-brown solid (m.p. 77 ^{o}C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 2.42 (s, 3H), 0.29 (s, 9H). ^{19}F NMR (400 MHz, $CDCl_3$) δ -95.5 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.5, 140.5 (t, *J* = 31.9 Hz), 134.6 (t, *J* = 27.0 Hz), 133.9, 133.2, 131.2, 129.6, 129.2, 129.0, 128.4, 128.1, 125.0 (t, *J* = 5.4 Hz), 124.6 (t, *J* = 5.2 Hz), 117.2 (t, *J* = 244.7 Hz), 21.5, -1.3. IR (thin film): ν_{max} 3028, 2956, 1670, 1598, 1496 cm^{-1}. MS (EI): *m/z* (%) 472 (M^+), 197 (100). HRMS: Calculated for $C_{25}H_{26}F_2O_3SSi$: 472.1340; Found: 472.1343.

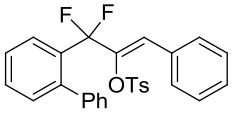


***(Z)*-3-(3,5-Dimethylphenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3j).**

Method B. The product (127 mg, 68% yield) as a claybank solid (m.p. 108 °C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.32 – 7.29 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 1H), 6.92 (s, 2H), 6.68 (s, 1H), 2.44 (s, 3H), 2.30 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.1 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 140.4 (t, *J* = 31.4 Hz), 137.9, 134.1, 134.0 (t, *J* = 26.5 Hz), 132.0, 131.3, 129.7, 129.2, 129.1, 128.4, 128.1, 124.4 (t, *J* = 5.4 Hz), 123.5 (t, *J* = 5.5 Hz), 117.3 (t, *J* = 244.5 Hz), 21.5, 21.2. IR (thin film): ν_{max} 3062, 3025, 2922, 1668, 1599, 1495 cm^{-1}. MS (EI): *m/z* (%) 428 (M^+), 155 (100). HRMS: Calculated for $C_{24}H_{22}F_2O_3S$: 428.1258; Found: 428.1261.

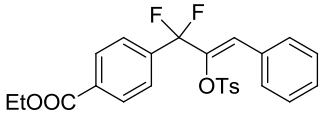


***(Z)*-3-(2,5-Dimethylphenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3k).** Method B. The product (103 mg, 60% yield) as a gray white solid (m.p. 81 °C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.32 – 7.28 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 19.2, 7.6 Hz, 2H), 7.06 (s, 1H), 6.53 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.5 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 140.2 (t, *J* = 30.8 Hz), 135.2, 134.2, 133.4 (t, *J* = 2.9 Hz), 131.8, 131.7 (t, *J* = 24.1 Hz), 131.4, 131.1, 129.6, 129.3, 129.2, 128.5, 128.2, 127.3 (t, *J* = 8.1 Hz), 125.5 (t, *J* = 5.5 Hz), 118.1 (t, *J* = 241.9 Hz), 21.6, 20.9, 19.6. IR (thin film): ν_{max} 3061, 3023, 2923, 1668, 1595, 1450 cm^{-1}. MS (EI): *m/z* (%) 428 (M^+), 155 (100). HRMS: Calculated for $C_{24}H_{22}F_2O_3S$: 428.1258; Found: 428.1254.

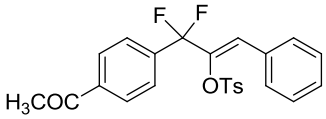


***(Z)*-3-([1,1'-Biphenyl]-2-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3l).** Method B. he product (105 mg, 55% yield) as a red-brown solid (m.p. 94 °C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.26 – 7.19 (m, 7H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.19 (s, 1H), 2.44 (s, 3H). ^{19}F NMR

(376 MHz, $CDCl_3$) δ -88.2 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 141.6 (t, *J* = 3.6 Hz), 140.0, 139.4 (t, *J* = 31.6 Hz), 133.6, 131.6, 131.44 (t, *J* = 25.1 Hz), 131.42, 129.9, 129.6, 129.4, 129.1, 128.8, 128.2, 128.1, 127.22, 127.21, 127.0, 126.5 (t, *J* = 8.1 Hz), 124.5 (t, *J* = 5.1 Hz), 116.9 (t, *J* = 245.8 Hz), 21.6. IR (thin film): ν_{max} 3069, 3028, 2926, 1669, 1597, 1445 cm^{-1}. MS (EI): *m/z* (%) 476 (M^+), 183 (100). HRMS: Calculated for $C_{28}H_{22}F_2O_3S$: 476.1258; Found: 476.1261.

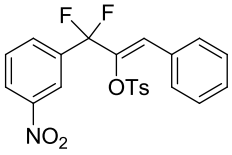


***(Z)*-Ethyl 4-[1,1-difluoro-3-phenyl-2-(tosyloxy)allyl]benzoate (3m).** Method B. The product (87 mg, 46% yield) as a claybank oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 18 : 1). This compound is unknown. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.32 – 7.24 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.70 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.9 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 145.1, 139.8 (t, *J* = 31.7 Hz), 138.4 (t, *J* = 27.0 Hz), 133.8, 132.4, 131.0, 129.6, 129.5, 129.3, 129.2, 128.4, 128.1, 126.0 (t, *J* = 5.5 Hz), 124.8 (t, *J* = 5.2 Hz), 116.7 (t, *J* = 245.7 Hz), 61.3, 21.6, 14.2. IR (thin film): ν_{max} 3053, 2929, 1764, 1722, 1660, 1593, 1451 cm^{-1}. MS (EI): *m/z* (%) 472 (M^+), 199 (100). HRMS: Calculated for $C_{25}H_{22}F_2O_5S$: 472.1156; Found: 472.1152.

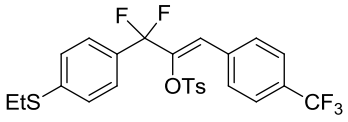


***(Z)*-3-(4-Acetylphenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3n).** Method B. The product (76 mg, 43% yield) as a faint yellow oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 15 : 1). This compound is unknown. ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.31 – 7.19 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.69 (s, 1H), 2.61 (s, 3H), 2.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.1 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 145.2, 139.8 (t, *J* = 31.5 Hz), 138.7 (t, *J* = 27.2 Hz), 138.5, 133.8, 131.0, 129.6, 129.31, 129.26, 128.5, 128.3, 128.1, 126.4 (t, *J* = 5.5 Hz), 124.8 (t, *J* = 5.4 Hz), 116.7 (t, *J* = 245.9 Hz), 26.7, 21.6. IR (thin film):

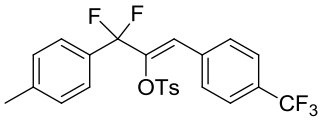
ν_{max} 3044, 2922, 1686, 1605, 1592, 1453 cm^{-1}. MS (EI): *m/z* (%) 442 (M^+), 169 (100). HRMS: Calculated for $C_{24}H_{20}F_2O_4S$: 442.1050; Found: 442.1053.



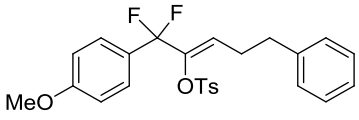
***(Z)*-3,3-Difluoro-3-(3-nitrophenyl)-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3o).** Method B. The product (71 mg, 40% yield) as a faint yellow solid (m.p. 75 ^oC) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 15 : 1). This compound is unknown. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.49 (d, *J* = 6.0 Hz, 2H), 7.32 – 7.21 (m, 4H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.84 (s, 1H), 2.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.6 (s, 2F). ^{13}C NMR NMR (101 MHz, $CDCl_3$) δ 148.0, 145.6, 138.9 (t, *J* = 31.4 Hz), 136.3 (t, *J* = 28.4 Hz), 133.5, 132.1 (t, *J* = 5.2 Hz), 130.8, 129.7, 129.5, 129.4, 128.6, 128.0, 125.3, 124.8 (t, *J* = 5.4 Hz), 121.1 (t, *J* = 6.1 Hz), 115.9 (t, *J* = 246.5 Hz), 21.6. IR (thin film): ν_{max} 3059, 2926, 1614, 1515, 1496 cm^{-1}. MS (EI): *m/z* (%) 445 (M^+), 172, 155, 91 (100). HRMS: Calculated for $C_{22}H_{17}F_2NO_5S$: 445.0795; Found: 445.0798.



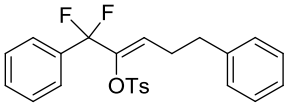
***(Z)*-3-[4-(Ethylthio)phenyl]-3,3-difluoro-1-[4-(trifluoromethyl)phenyl]prop-1-en-2-yl-4-methylbenzenesulfonate (3p).** Method B. The product (164 mg, 78% yield) as a red-brown solid (m.p. 93 ^oC) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20 : 1). This compound is unknown. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 23.2, 8.4 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 3.00 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.2 (s, 3F), -96.3 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 142.4 (t, *J* = 32.4 Hz), 140.9, 134.9, 133.9, 130.6 (t, *J* = 27.2 Hz), 130.3, 129.7, 129.3, 127.8, 127.0, 126.3 (t, *J* = 5.5 Hz), 125.2 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.9 Hz), 122.8 (t, *J* = 4.8 Hz), 116.8 (t, *J* = 245.4 Hz), 26.4, 21.4, 13.9. IR (thin film): ν_{max} 3042, 2980, 2933, 1679, 1597, 1449 cm^{-1}. MS (EI): *m/z* (%) 528 (M^+), 187 (100). HRMS: Calculated for $C_{25}H_{21}F_5O_3S_2$: 528.0852; Found: 528.0851.



***(Z)*-3,3-Difluoro-3-(p-tolyl)-1-[4-(trifluoromethyl)phenyl]prop-1-en-2-yl-4-methylbenzenesulfonate (3q).** Method A. The product (139 mg, 72% yield) as a gray white solid (m.p. 89 ^{o}C) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 26.4, 8.0 Hz, 4H), 7.28 (dd, *J* = 48.8, 8.0 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 2.44 – 2.38 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s, 3F), -95.8 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 142.8 (t, *J* = 32.6 Hz), 140.8, 135.0, 134.1, 131.1 (t, *J* = 26.8 Hz), 130.6 (q, *J* = 32.6 Hz), 129.8, 129.3, 129.1, 127.9, 125.9 (t, *J* = 5.6 Hz), 125.2 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.2 Hz), 122.9 (t, *J* = 5.4 Hz), 117.1 (t, *J* = 245.0 Hz), 21.5, 21.3. IR (thin film): ν_{max} 3064, 2928, 1919, 1678, 1597, 1449 cm^{-1}. MS (EI): *m/z* (%) 428 (M^+), 155, 141 (100), 91. HRMS: Calculated for $C_{24}H_{19}F_5O_3S$: 482.0975; Found: 482.0978.

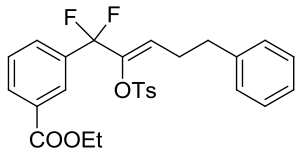


***(Z)*-1,1-Difluoro-1-(4-methoxyphenyl)-5-phenylpent-2-en-2-yl-4-methylbenzenesulfonate (3r).** Method B. The product (152 mg, 83% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 25 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.27 (m, 4H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.82 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.4 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 144.9, 141.8 (t, *J* = 32.6 Hz), 140.6, 134.1, 129.5, 128.4, 128.0, 127.4 (t, *J* = 5.4 Hz), 126.9 (t, *J* = 4.5 Hz), 126.3 (t, *J* = 27.1 Hz), 126.1, 117.0 (t, *J* = 241.6 Hz), 113.5, 55.3, 34.3, 28.0, 21.7. IR (thin film): ν_{max} 3070, 2926, 1684, 1597, 1453 cm^{-1}. MS (MALDI): *m/z* (%) 481 (100, M^+ + Na), 439 (M^+ + F). HRMS: Calculated for $C_{25}H_{24}F_2O_4S$: 458.1363; Found: 481.1261 (M^+ + Na).



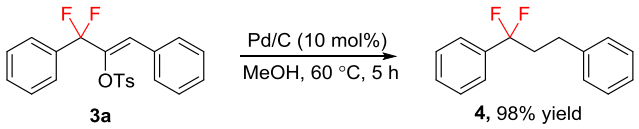
***(Z)*-1,1-Difluoro-1,5-diphenylpent-2-en-2-yl-4-methylbenzenesulfonate (3s).** Method A. The

product (120 mg, 70% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.4 Hz, 2H), 7.45 – 7.37 (m, 1H), 7.37 – 7.26 (m, 6H), 7.26 – 7.21 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 2H), 5.87 (t, *J* = 7.4 Hz, 1H), 2.84 – 2.73 (m, 2H), 2.73 – 2.62 (m, 2H), 2.45 (d, *J* = 1.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.8 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 141.6 (t, *J* = 31.8 Hz), 140.5, 134.1 (t, *J* = 26.3 Hz), 134.0, 130.2, 129.5, 128.4, 128.2, 127.9, 127.1 (t, *J* = 4.7 Hz), 126.1, 125.8 (t, *J* = 5.7 Hz), 116.8 (t, *J* = 244.1 H), 34.2, 28.0, 21.6. IR (thin film): ν_{max} 3070, 2925, 1680, 1597, 1456 cm^{-1}. MS (MALDI): *m/z* (%) 474 (M^+ + 2Na), 451 (M^+ + Na), 446 (100, M^+ + H_2O), 427 (M^+ - H). HRMS: Calculated for $C_{24}H_{22}F_2O_3S$: 428.1258; Found: 451.1151 (M^+ + Na).



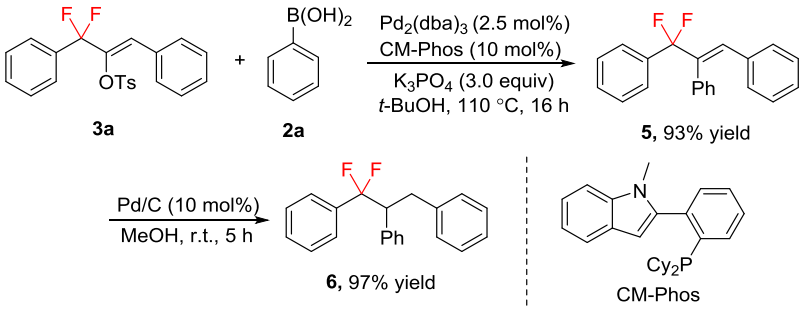
***(Z)*-Ethyl-3-(1,1-difluoro-5-phenyl-2-(tosyloxy)pent-2-en-1-yl)benzoate (3t)**. Method B. The product (76 mg, 38% yield) as a colorless oil was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30 : 1). This compound is unknown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.93 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.31 (m, 2H), 7.31 – 7.22 (m, 4H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.88 (t, *J* = 7.4 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.1 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 145.1, 141.1 (t, *J* = 32.0 Hz), 140.4, 134.7 (t, *J* = 27.4 Hz), 133.9, 131.4, 130.8, 130.2 (t, *J* = 5.4 Hz), 129.6, 128.42, 128.40, 127.9, 127.3 (t, *J* = 4.7 Hz), 126.9 (t, *J* = 5.7 Hz), 126.1, 116.3 (t, *J* = 244.8 Hz), 61.3, 34.2, 28.1, 21.6, 14.3. IR (thin film): ν_{max} 3064, 2931, 1720, 1671, 1597, 1450 cm^{-1}. MS (MALDI): *m/z* (%) 523 (M^+ + Na), 518 (100, M^+ + H_2O), 501 (M^+ + H). HRMS: Calculated for $C_{24}H_{22}F_2O_3S$: 500.1469; Found: 523.1360 (M^+ + Na).

Procedure for the Synthesis of Compound 4:



To a 25 mL of round-bottle flask was charged with 10% Pd/C (10.6 mg, 0.01 mmol), *(Z)*-3,3-difluoro-1,3-diphenylprop-1-en-2-yl-4-methylbenzenesulfonate **3a** (40 mg, 0.1 mmol), and MeOH (10 mL). The reaction was evacuated and backfilled with H_2 (three times). The reaction mixture was stirred at 60 ºC for 5 h. The resulting mixture was cooled to room temperature, and filtrated through a silica gel pad. After concentrated under reduced pressure, the residue was subjected to purification on silica gel chromatography using petroleum (100%) to give product **4** as a colorless oil (23 mg, 98% yield). Compound **4** is known[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.48 – 7.40 (m, 3H), 7.31 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 2.81 – 2.75 (m, 2H), 2.51 – 2.37 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.3 (t, *J* = 16.0 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.2 (t, *J* = 26.7 Hz), 129.7, 128.5, 128.4, 128.2, 126.2, 124.9 (t, *J* = 6.2 Hz), 121.3 (t, *J* = 243.8 Hz), 40.9 (t, *J* = 27.7 Hz), 28.8 (t, *J* = 4.2 Hz).

Procedure for the Synthesis of Compounds 5 and 6:

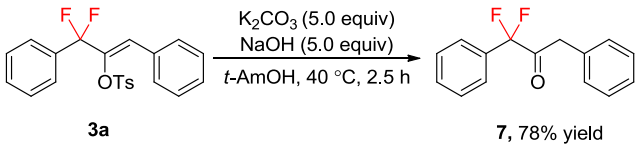


Synthesis of compound 5: To a Schlenk tube was charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), CM-Phos (4.0 mg, 0.01 mmol), K_3PO_4 (64mg, 0.2mmol), phenylboronic acid **2a** (24.5 mg, 0.2 mmol), **3a** (40 mg, 0.1 mmol), and *t*-BuOH (1 mL) under N_2. The tube was screwed capped and the reaction mixture was stirred at 110 ºC for 16 h. The resulting mixture was cooled to room

temperature, and filtrated through a silica gel pad. After concentrated under reduced pressure, the residue was subjected to purification on silica gel chromatography using pure petroleum to give desired product **5** as a faint yellow solid (28 mg, 93% yield, m.p. 78 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.4 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.35 – 7.24 (m, 3H), 7.19 – 7.05 (m, 6H), 6.96 (d, *J* = 6.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.3 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8 (t, *J* = 25.7 Hz), 136.3 (t, *J* = 28.4 Hz), 134.9 (t, *J* = 1.3 Hz), 134.7, 130.8 (t, *J* = 8.5 Hz), 130.2, 129.8, 129.7 (t, *J* = 1.6 Hz), 128.4, 128.1, 128.03, 128.01, 127.9, 126.0 (t, *J* = 5.7 Hz), 120.7 (t, *J* = 244.6 Hz). IR (thin film): ν_{max} 3055, 3026, 2924, 2851, 1647, 1598, 1449 cm^{-1}. MS (EI): *m/z* (%) 306 (M^+), 179 (100). HRMS: Calculated for $C_{21}H_{16}F_2$: 306.1220; Found: 306.1217.

Synthesis of compound 6: To a 25 mL of round-bottle flask was charged with 10% Pd/C (10.6 mg, 0.01 mmol), compound **5** (30.6 mg, 0.1 mmol), and MeOH (10 mL). The reaction was evacuated and backfilled with H_2 (three times). The reaction mixture was stirred at 60 ^{o}C for 5 h. The resulting mixture was cooled to room temperature, and filtrated through a silica gel pad. After concentrated under reduced pressure, the residue was subjected to purification on silica gel chromatography using pure petroleum to give desired product **6** as a colorless oil (30 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 6H), 7.20 – 7.15 (m, 3H), 7.14-7.10 (m, 2H), 7.08 – 7.05 (m, 2H), 6.95 (d, *J* = 6.8 Hz, 2H), 3.64 – 3.49 (m, 1H), 3.48 – 3.43 (m, 1H), 3.20 – 3.11 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.4 (dd, *J* = 242.2, 11.8 Hz, 1F), -102.34 (dd, *J* = 242.4, 18.3 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 129.9, 129.8, 129.4, 128.9, 128.1, 127.93, 127.91, 127.0, 126.6, 126.0, 125.6 (t, *J* = 6.4 Hz), 123.1 (t, *J* = 249.0 Hz) , 56.8 (t, *J* = 25.9 Hz), 35.3 (t, *J* = 3.7 Hz). IR (thin film): ν_{max} 3062, 3028, 2927, 2854, 1717, 1601, 1541, 1453 cm^{-1}. MS (EI): *m/z* (%) 308(M^+), 181 (100). HRMS: Calculated for $C_{21}H_{16}F_2$: 308.1377; Found: 308.1380.

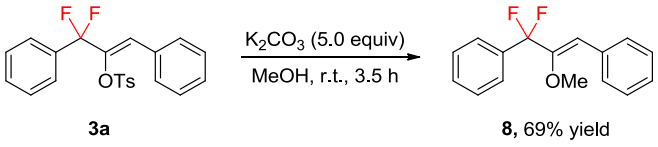
Procedure for the Synthesis of Compound 7:



3a **7**, 78% yield

To a 25 mL of Schlenk tube were charged with **3a** (80 mg, 0.2 mmol), K_2CO_3 (138 mg, 1 mmol), NaOH (40 mg, 1 mmol) and *t*-AmOH (3 mL). The reaction was monitored by ^{19}F NMR. After stirring for 2.5 h, the reaction mixture was filtered through a celite pad. The filtrate was concentrated, the residue was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50 : 1) to give product **7** as a light yellow oil (38 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.38 (m, 3H), 7.33 – 7.22 (m, 3H), 7.10 (d, *J* = 7.1 Hz, 2H), 3.98 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.0 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 (t, *J* = 32.2 Hz), 131.84, 131.81 (t, *J* = 25.2 Hz), 131.0 (t, *J* = 1.8 Hz), 129.6, 128.7, 128.6, 127.3, 125.6 (t, *J* = 6.3 Hz), 116.1 (t, *J* = 254.8 Hz), 43.1. IR (thin film): ν_{max} 3066, 3034, 1747, 1604, 1496, 1452 cm^{-1}. MS (EI): *m/z* (%) 246 (M^+), 127, 91 (100). HRMS: Calculated for $C_{16}H_{14}F_2O$: 246.0856; Found: 246.0859.

Procedure for the Synthesis of Compound 8:

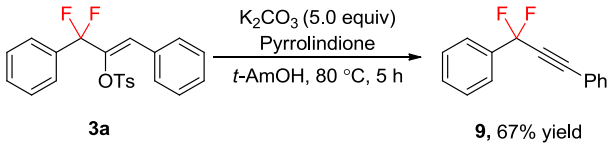


3a **8**, 69% yield

To a 25 mL of Schlenk tube were charged with **3a** (80 mg, 0.2 mmol), K_2CO_3 (138 mg, 1 mmol) and MeOH (4 mL). The reaction was monitored by ^{19}F NMR. After the reaction mixture was stirred for 3.5 h, the resulting mixture was filtered through a celite pad. The filtrate was concentrated, the residue was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50 : 1) to give product **8** as a light green oil (36 mg, 69% yield). **Note:** This compound is unstable. It can slowly decompose on the silica gel column. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.53 (m, 4H), 7.51 – 7.40 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 6.33 (s, 1H), 3.65 (s, 3H). ^{19}F NMR (376

MHz, $CDCl_3$) δ -96.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4 (t, *J* = 27.5 Hz), 135.6 (t, *J* = 27.3 Hz), 133.3, 130.1 (t, *J* = 1.8 Hz), 129.2, 128.5, 128.4, 128.0, 125.9 (t, *J* = 5.7 Hz), 118.6 (t, *J* = 244.3 Hz), 115.6 (t, *J* = 5.7 Hz), 60.2. IR (thin film): ν_{max} 3064, 2941, 1664, 1494, 1451 cm^{-1}. MS (EI): *m/z* (%) 260 (M^+), 198, 127 (100). HRMS: Calculated for $C_{16}H_{14}F_2O$: 260.1613; Found: 260.1017.

Procedure for the Synthesis of Compound 9:



3a **9**, 67% yield

To a 25 mL of Schlenk tube were charged with **3a** (80 mg, 0.2 mmol), K_2CO_3 (138 mg, 1 mmol), pyrrolindione (2 mL) and *t*-AmOH (1 mL). The reaction was monitored by ^{19}F NMR. After the reaction was stirred for 5 h, the resulting mixture was washed by water (20 mL × 3), dried over Na_2SO_4, filtered, and concentrated. The residue was purified with silica gel chromatography (petroleum ether 100%) to give product **9** as a colorless oil (30 mg, 67% yield). This compound is known[3]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.45 (m, 3H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.41 – 7.34 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2 (t, *J* = 28.2 Hz), 132.1 (t, *J* = 2.2 Hz), 130.7 (t, *J* = 1.7 Hz), 130.0, 128.5, 128.5, 125.4 (t, *J* = 4.6 Hz), 120.1, 112.7 (t, *J* = 231.2 Hz), 88.7 (t, *J* = 6.1 Hz), 81.8 (t, *J* = 41.8 Hz).

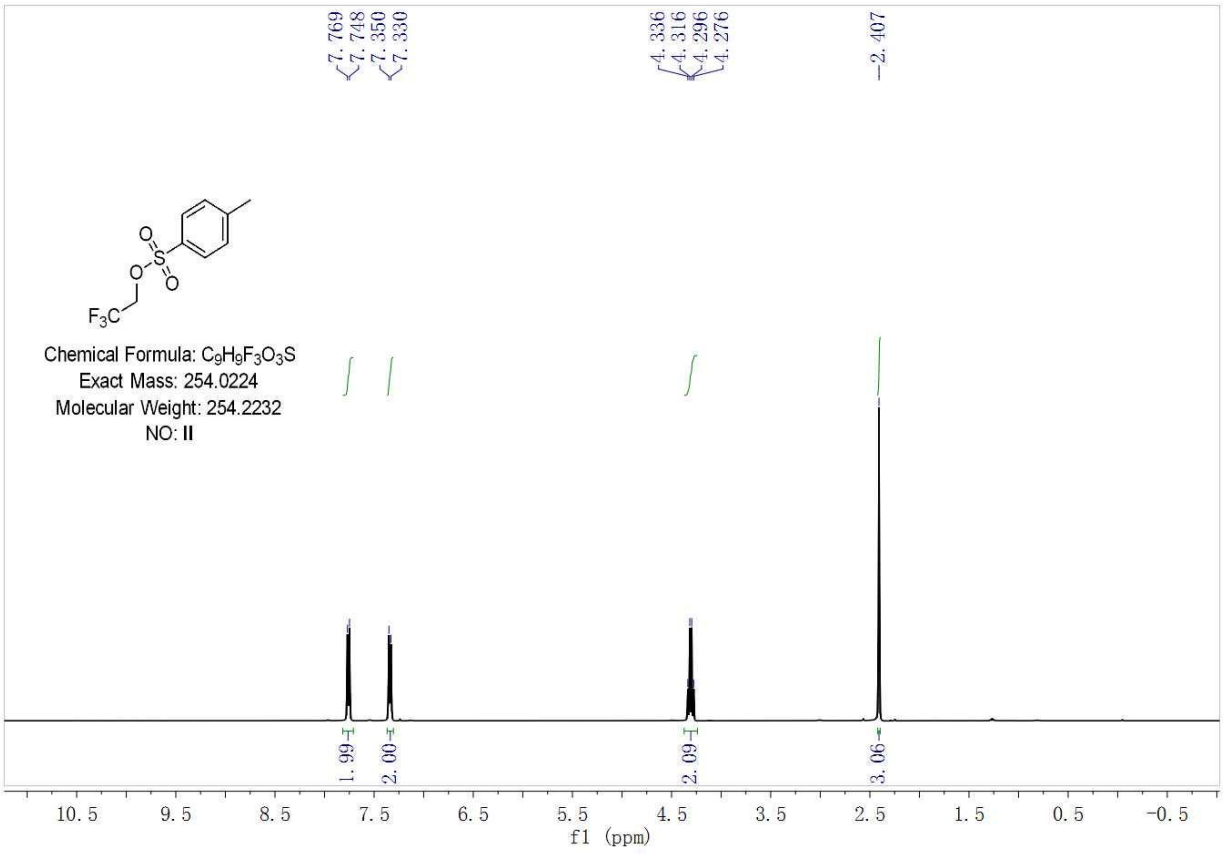
References:

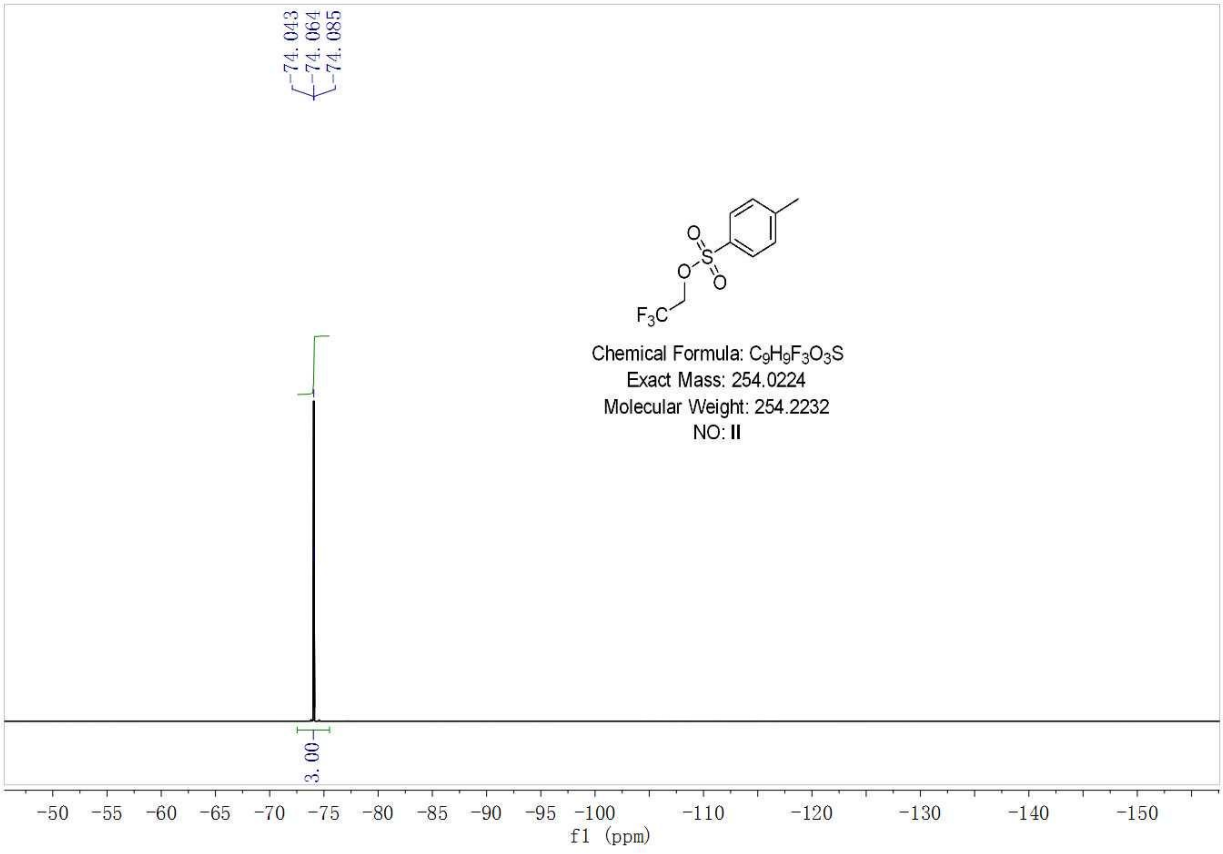
(1) T. M. Gøgsig, L. S. Søbjerg, A. T. Lindhardt, K. L. Jensen and T. Skrydstrup, *J. Org. Chem.*, 2008, **73**, 3404.

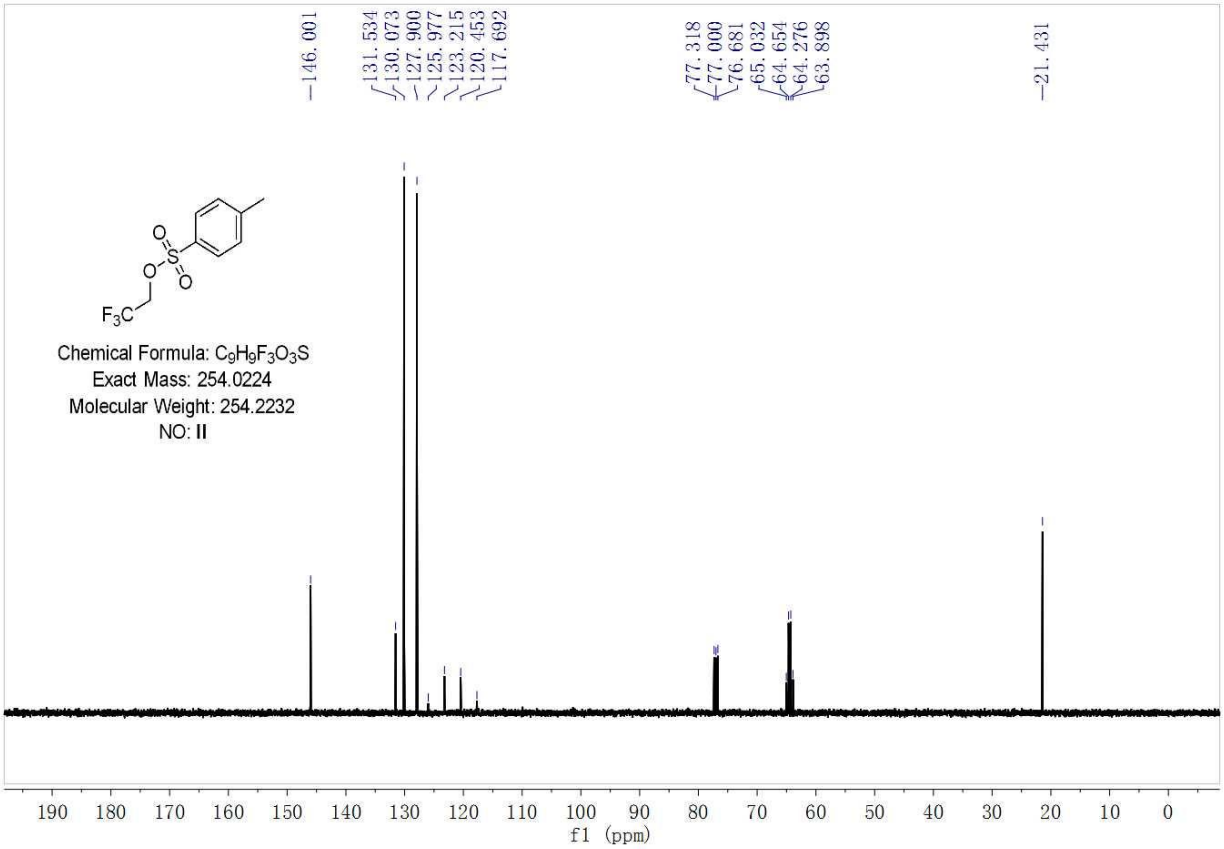
(2) Y. Masato, S. Daiki and I. Masahiko, *Chem. Lett.*, 1994, **12**, 2357.

(3) Y.-B. Yu, G.-Z. He and X. Zhang, *Angew. Chem., Int. Ed.* 2014, **53**, 10457.

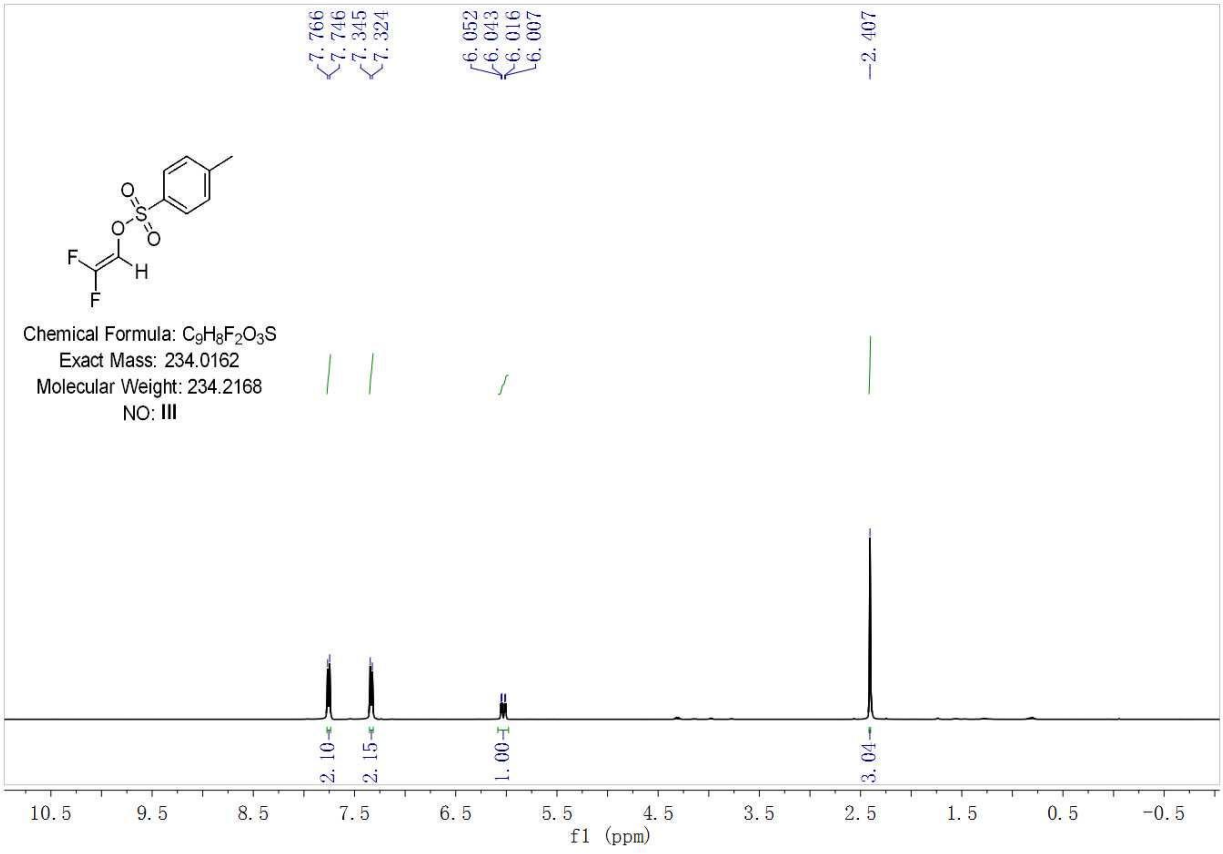
2,2,2-Trifluoroethyl 4-methylbenzenesulfonate (II)

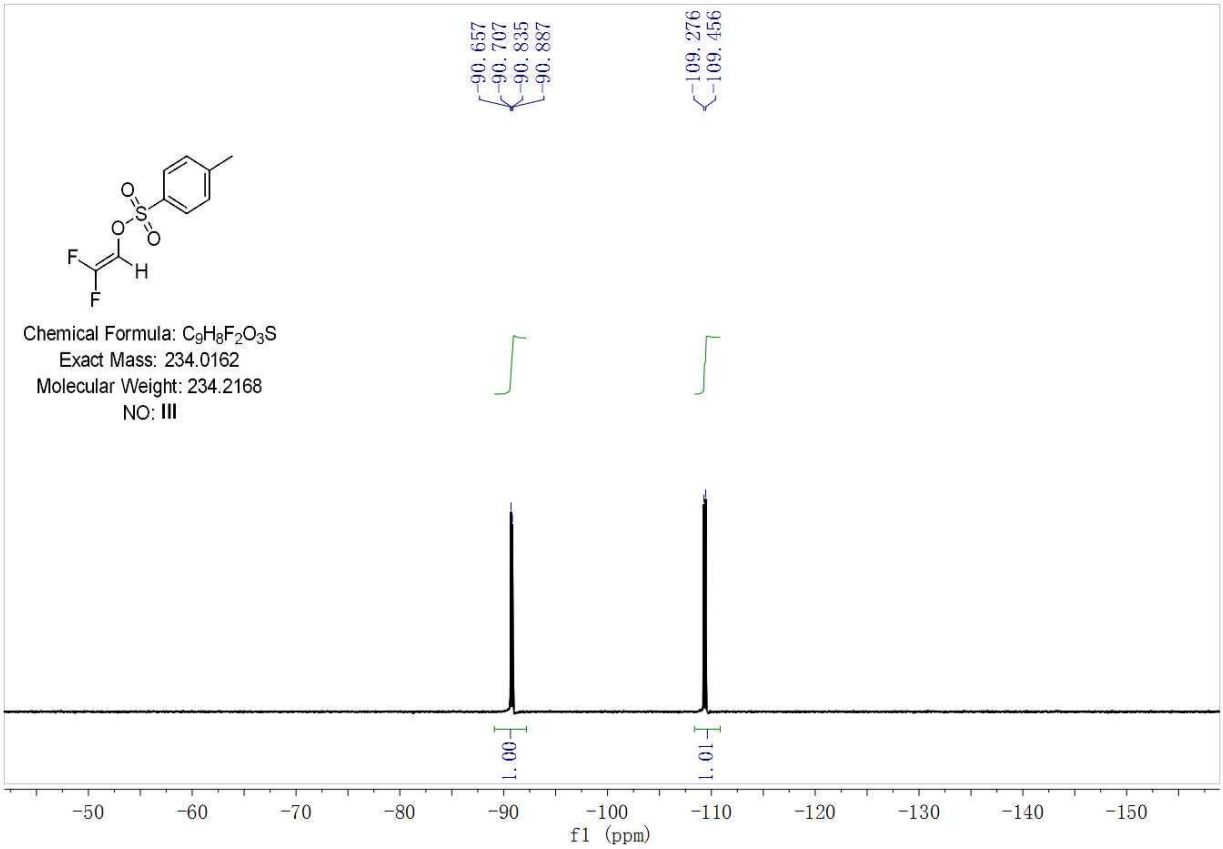






2,2-Difluorovinyl 4-methylbenzenesulfonate (III)

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-90.835
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-109.276
-109.456
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1.00
1.01
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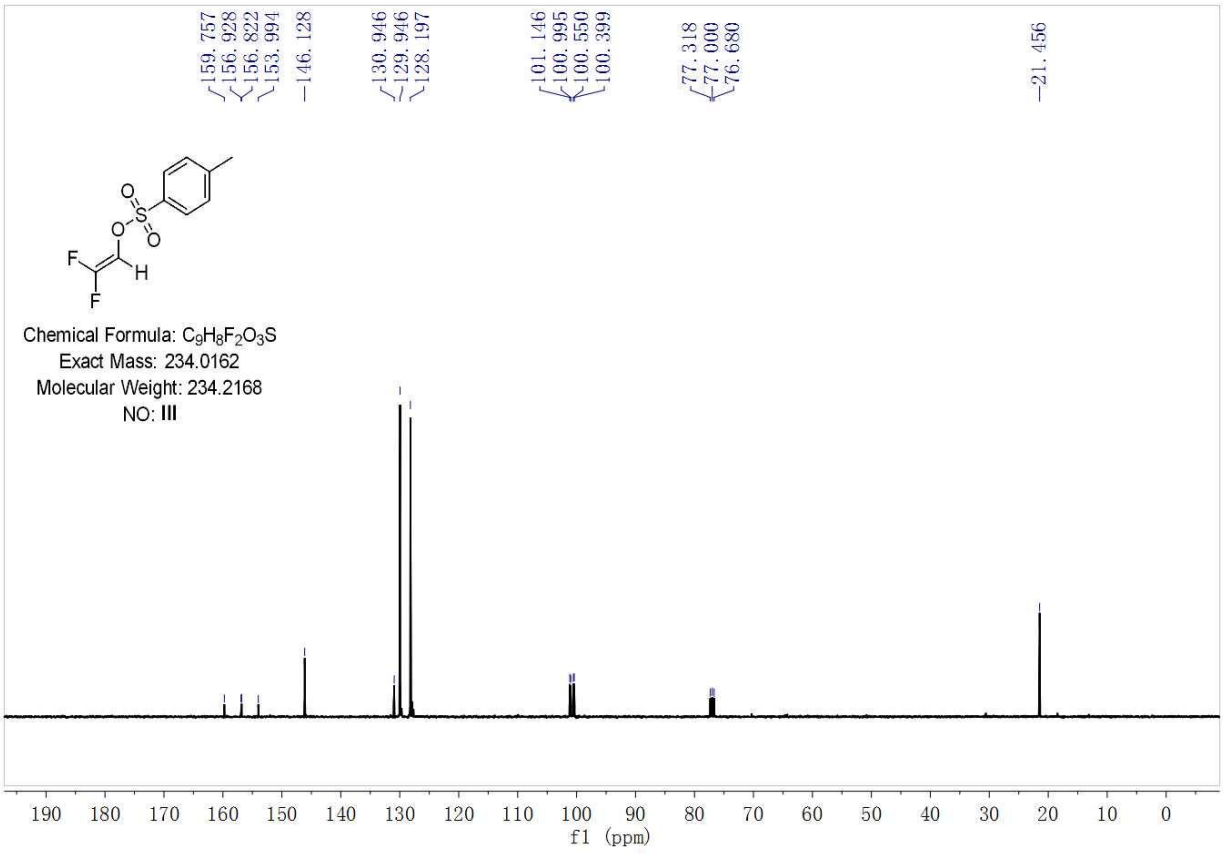
f1 (ppm)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77.000
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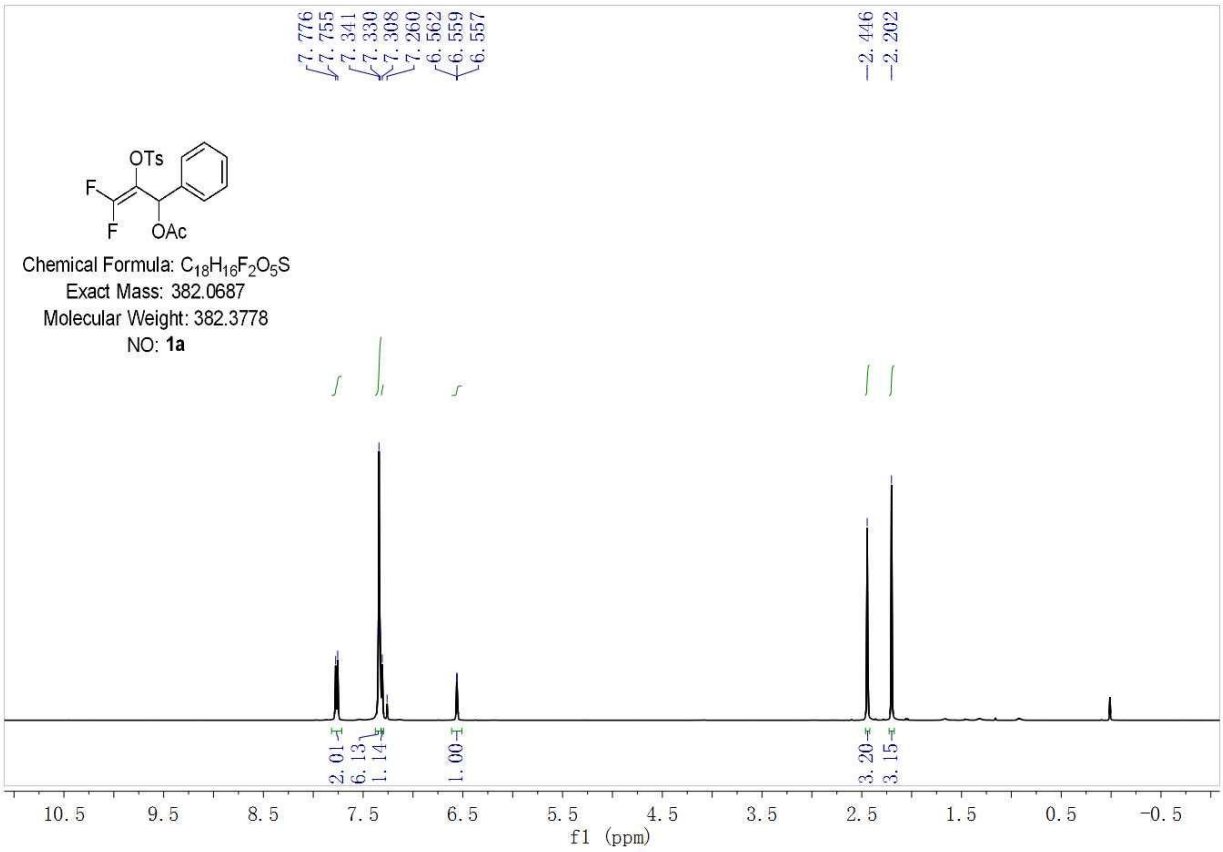
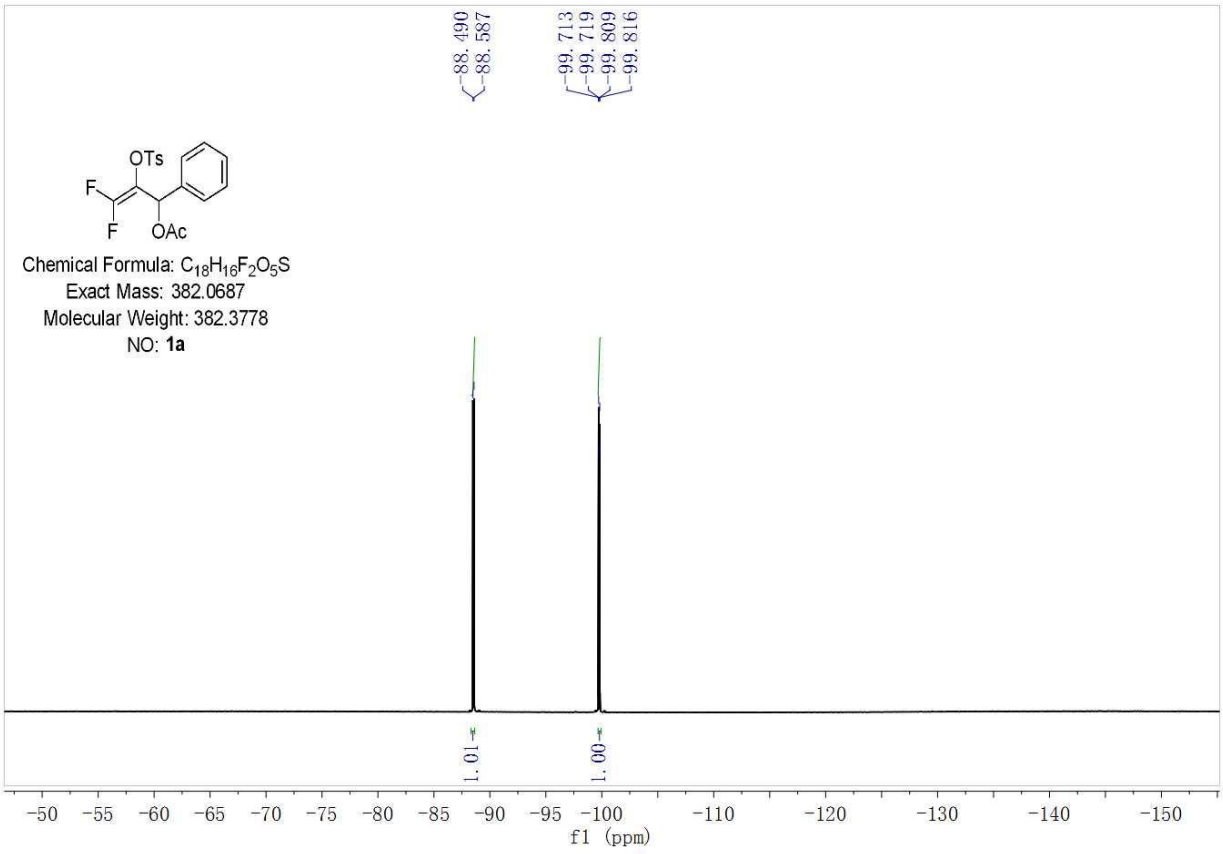
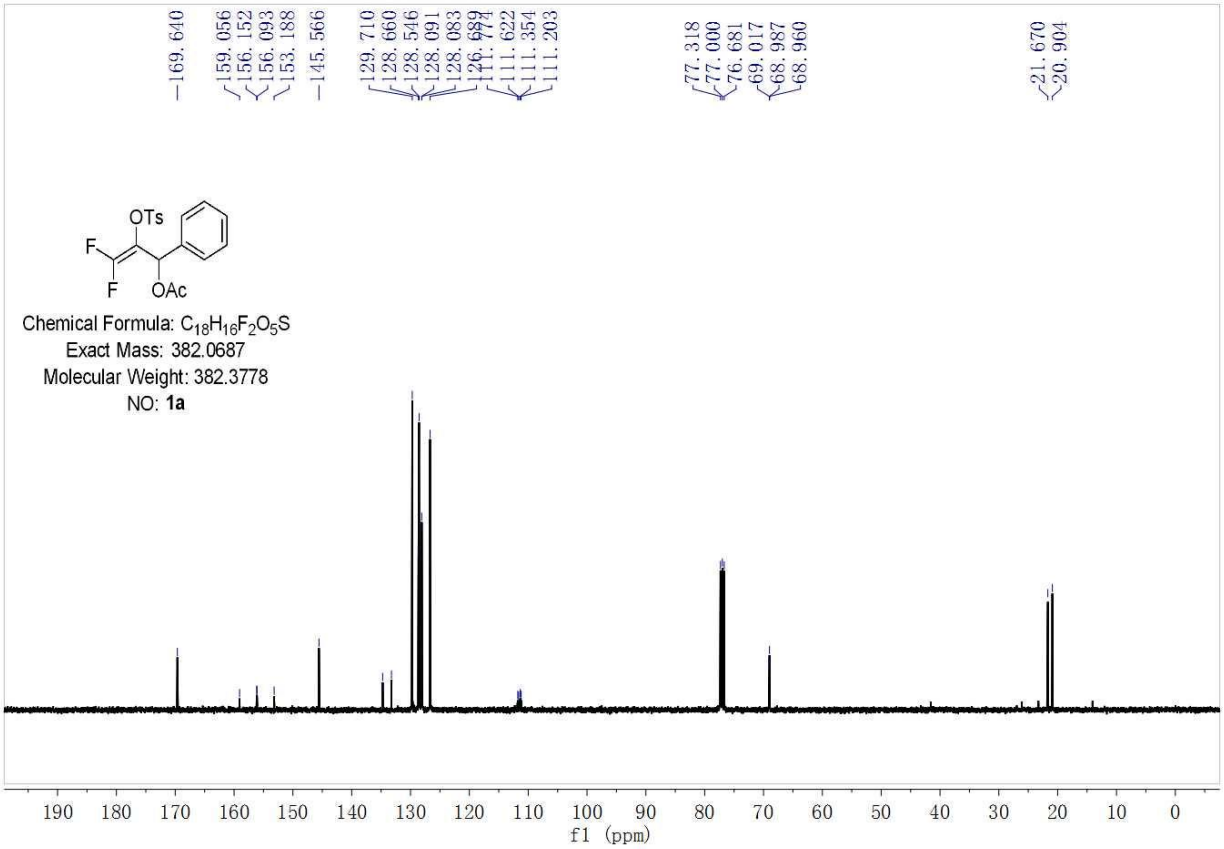
21.456
Chemical Formula: C9H8F2O3S
Exact Mass: 234.0162
Molecular Weight: 234.2168
NO: III
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

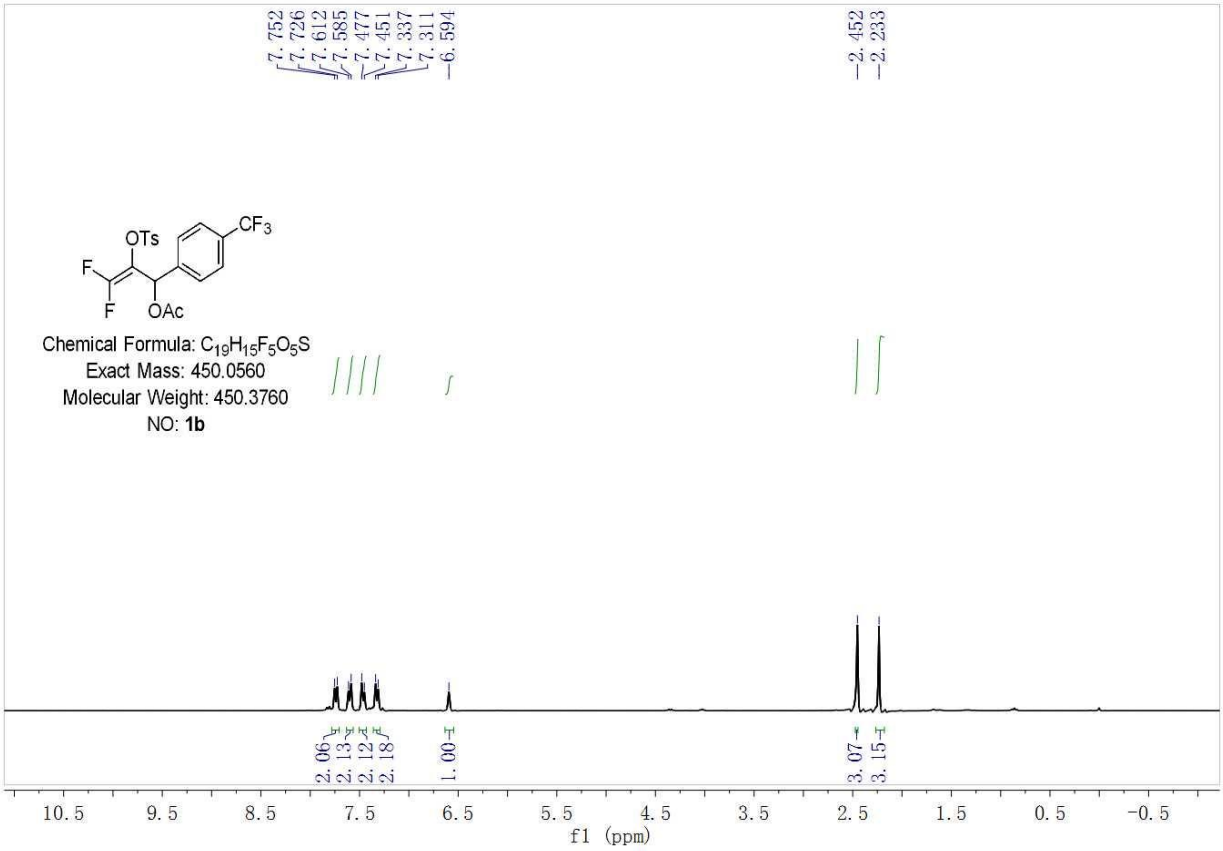
3,3-Difluoro-1-phenyl-2-(tosyloxy)allyl acetate (1a)

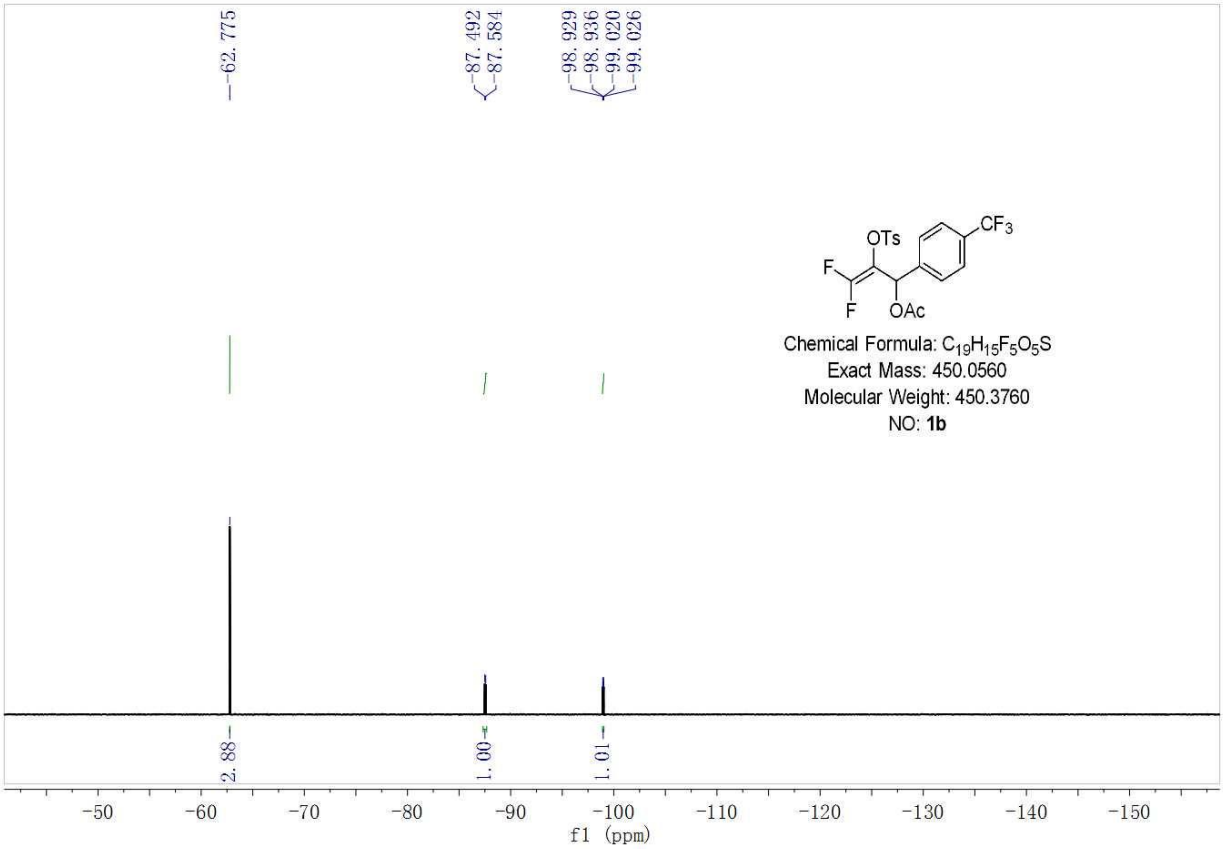


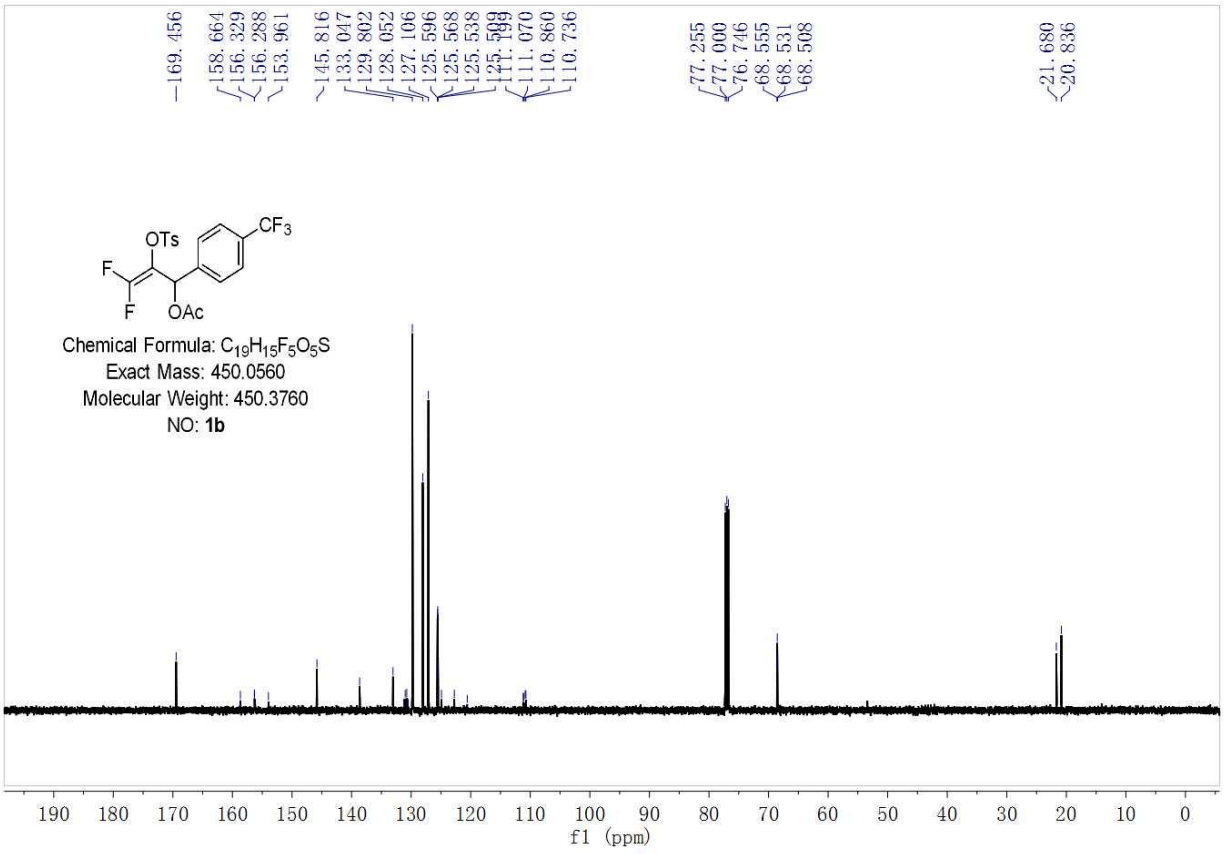




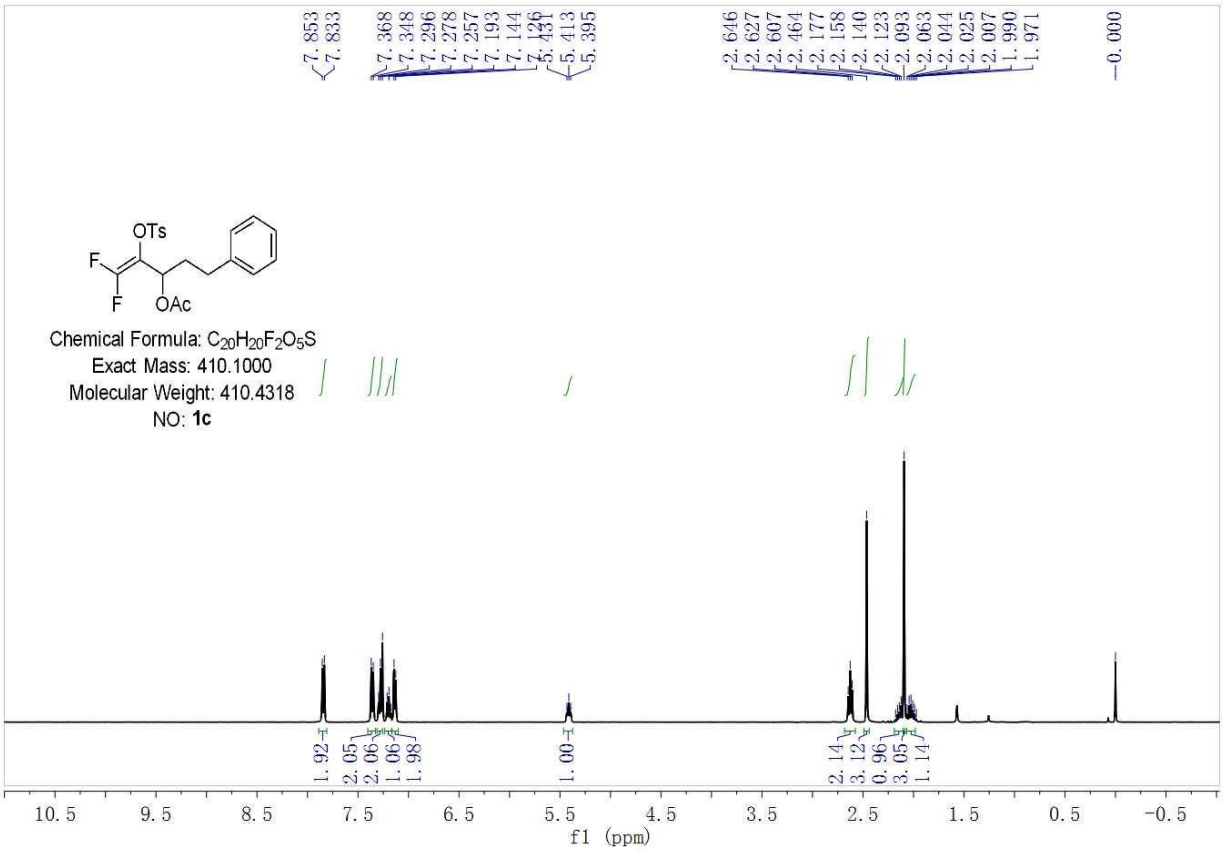
3,3-Difluoro-2-(tosyloxy)-1-(4-(trifluoromethyl)phenyl)allyl acetate (1b)

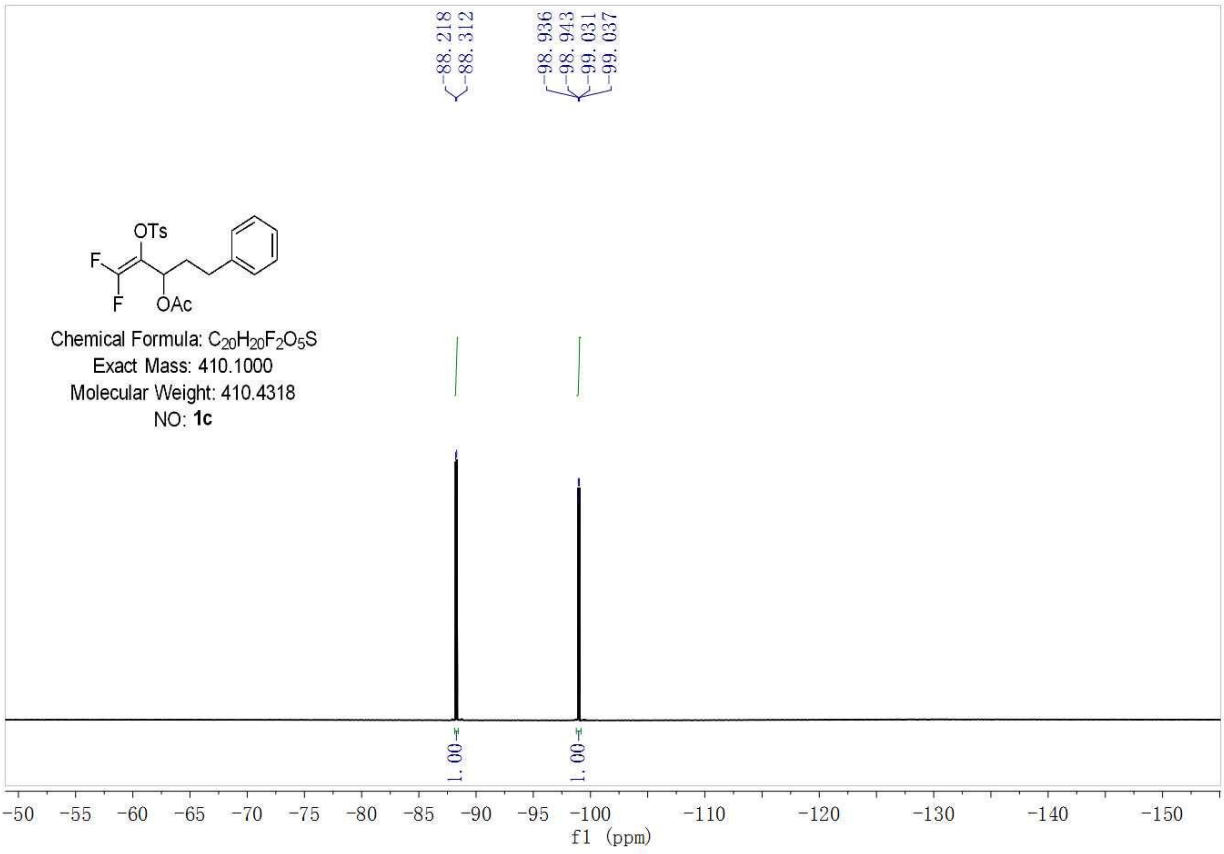


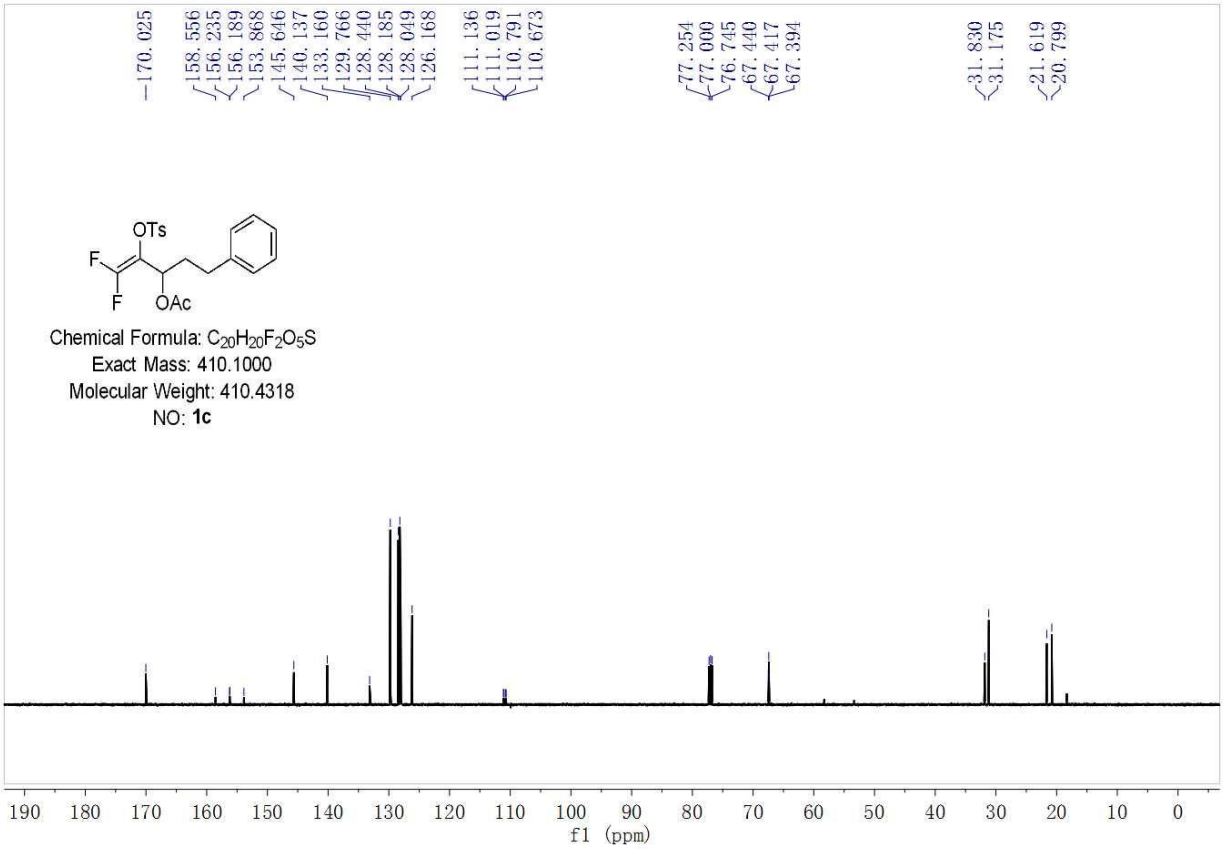

-62.775
-87.492
-87.584
-98.929
-98.936
-99.020
-99.026
OTs
CF3
F
F
OAc
Chemical Formula: C19H15F5O5S
Exact Mass: 450.0560
Molecular Weight: 450.3760
NO: 1b
2.88
1.00
1.01
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


-169.456
158.664
156.329
156.288
153.961
145.816
133.047
129.802
128.052
127.106
125.596
125.568
125.538
111.670
110.860
110.736
77.255
77.000
76.746
68.555
68.531
68.508
21.680
20.836
OTs
CF3
F
F
OAc
Chemical Formula: C19H15F5O5S
Exact Mass: 450.0560
Molecular Weight: 450.3760
NO: 1b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

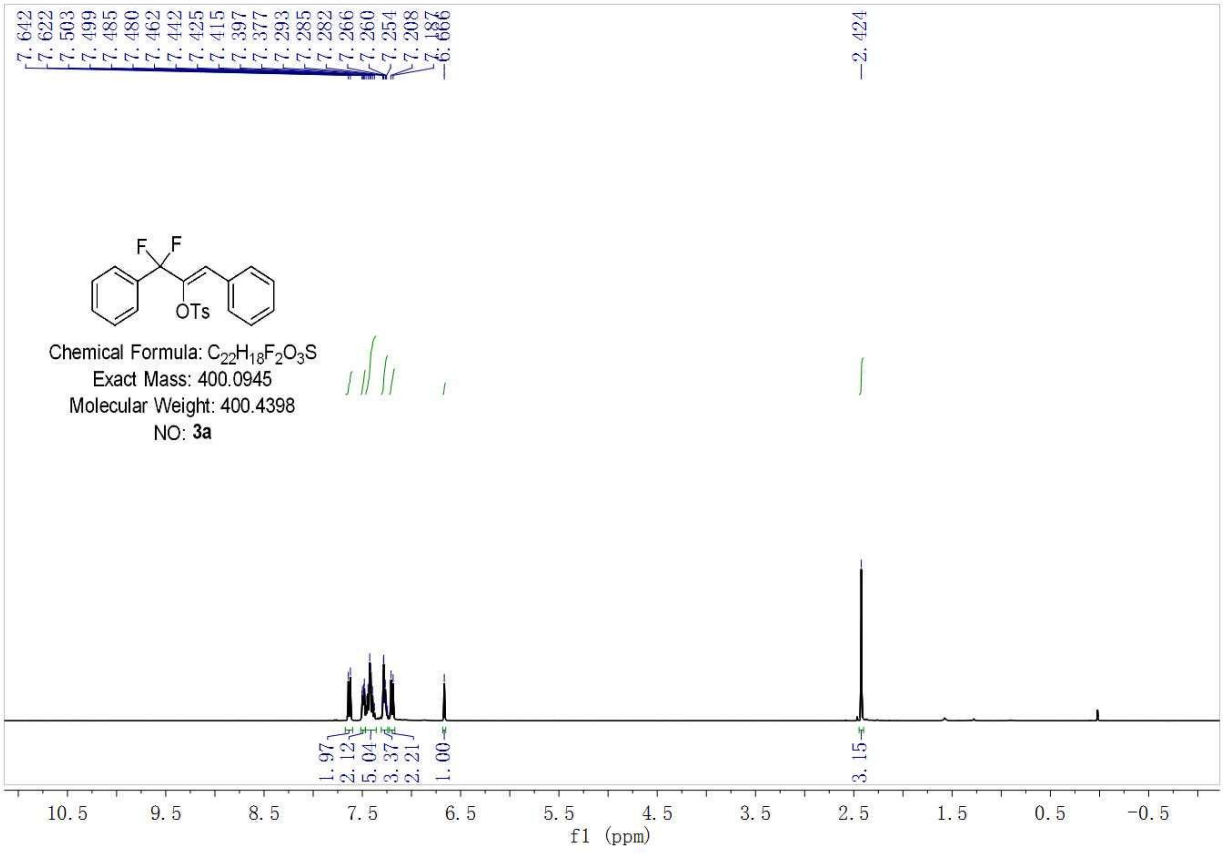
1,1-Difluoro-5-phenyl-2-(tosyloxy)pent-1-en-3-yl acetate (1c)

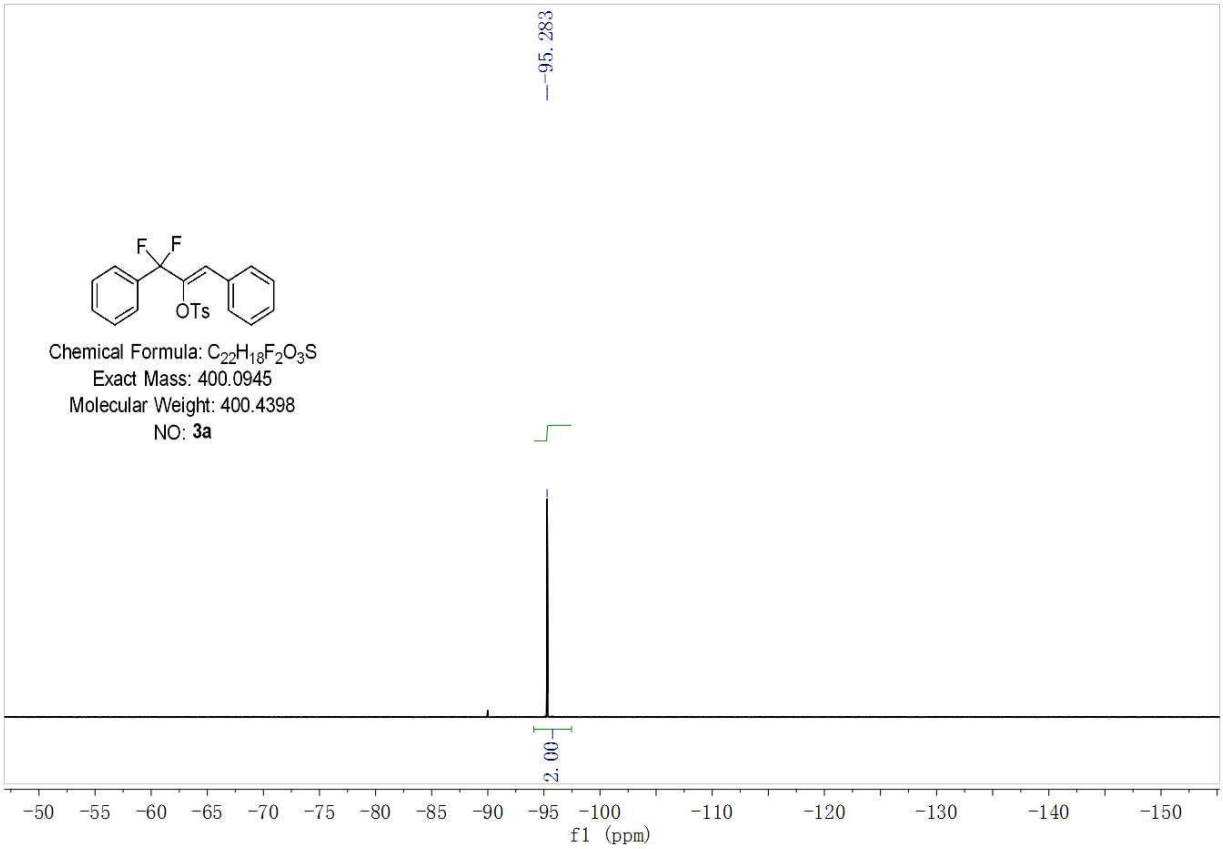


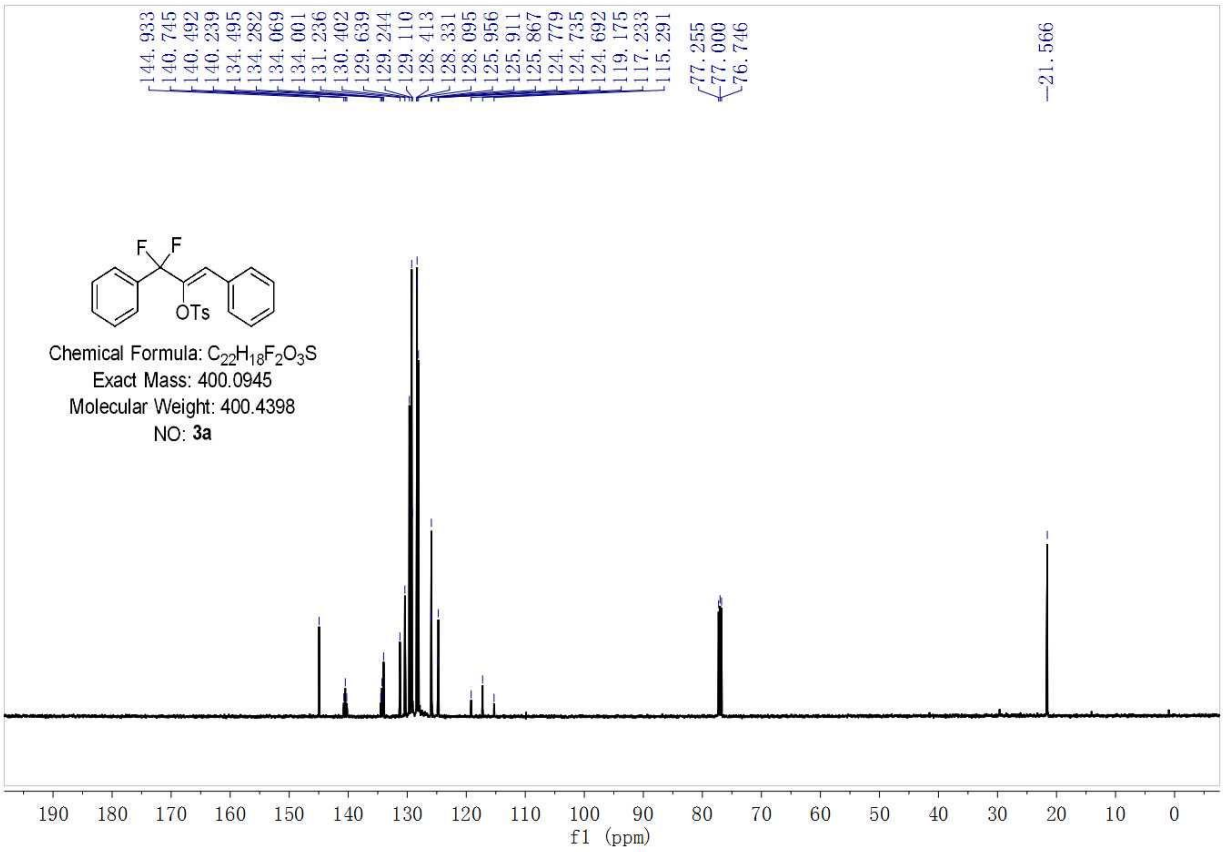




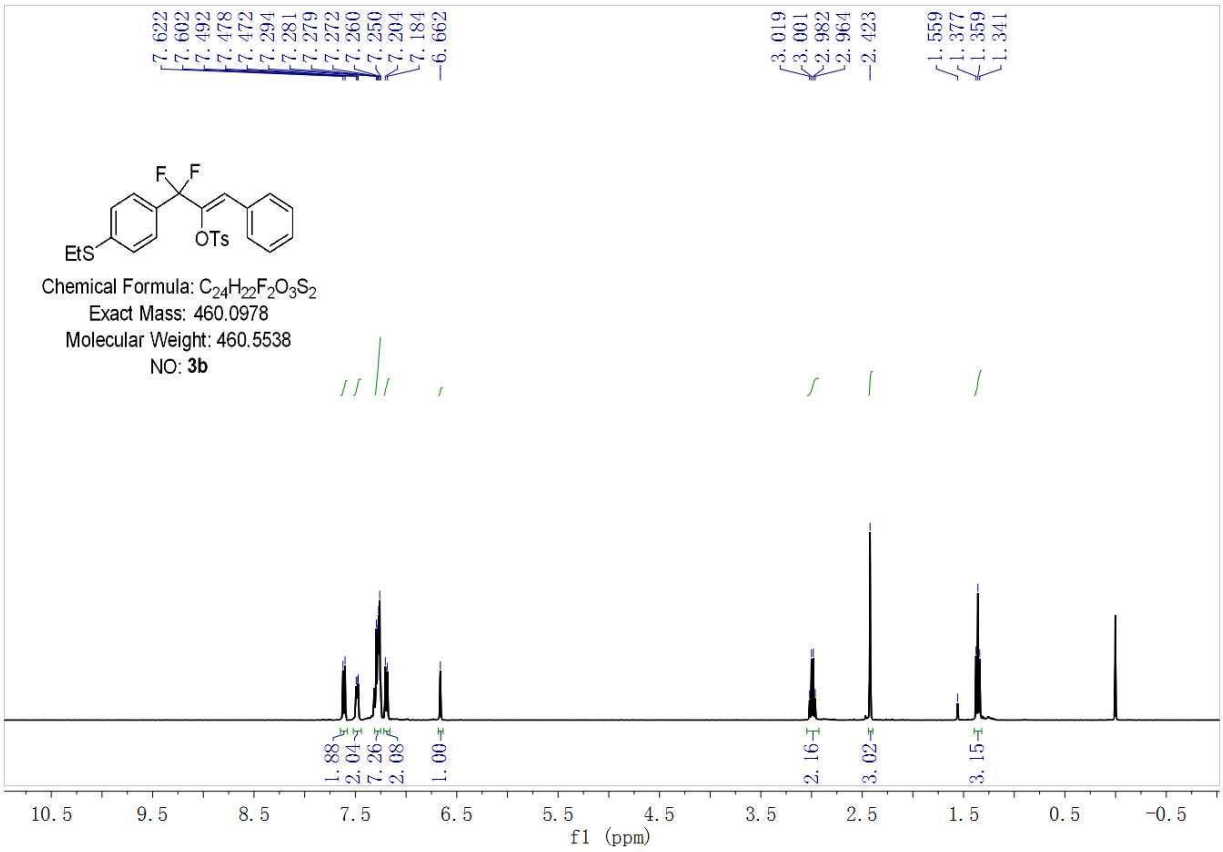
***(Z)*-3,3-Difluoro-1,3-diphenylprop-1-en-2-yl-4-methylbenzenesulfonate (3a)**

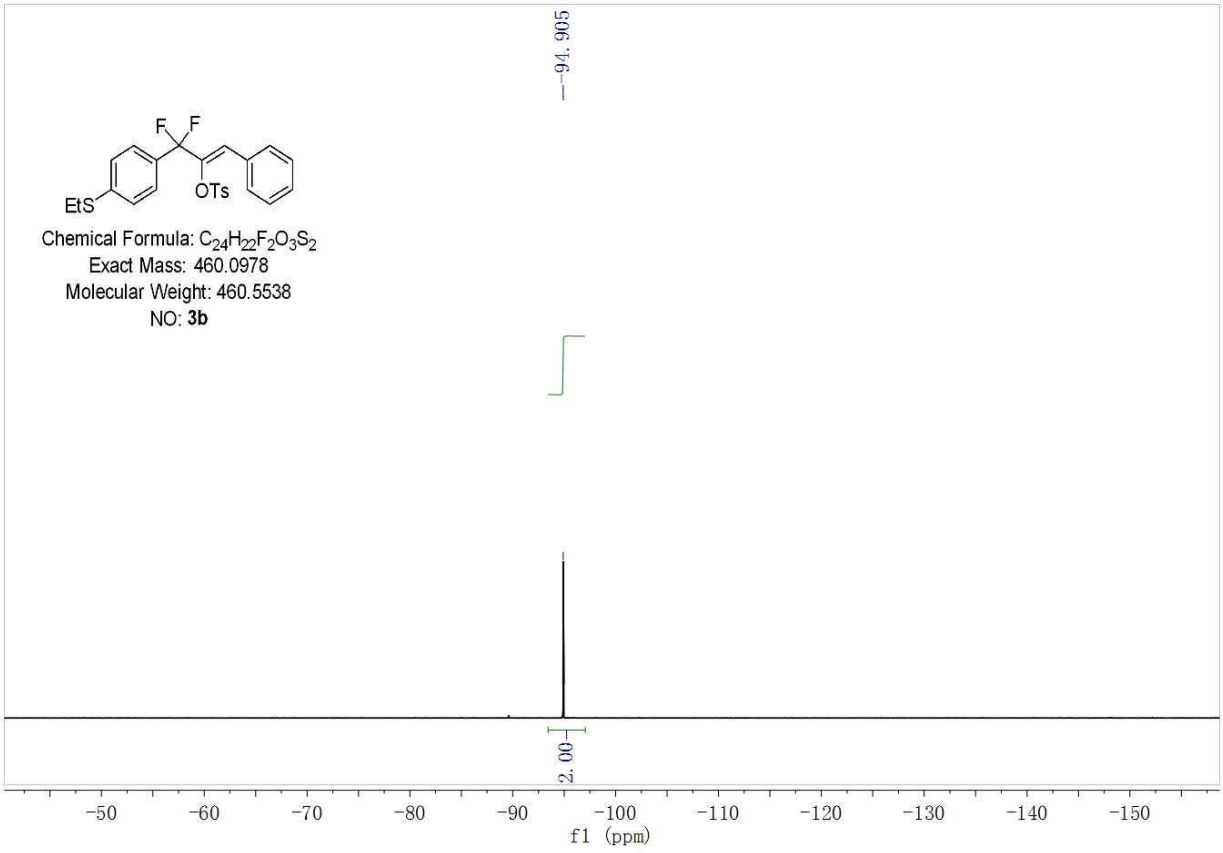


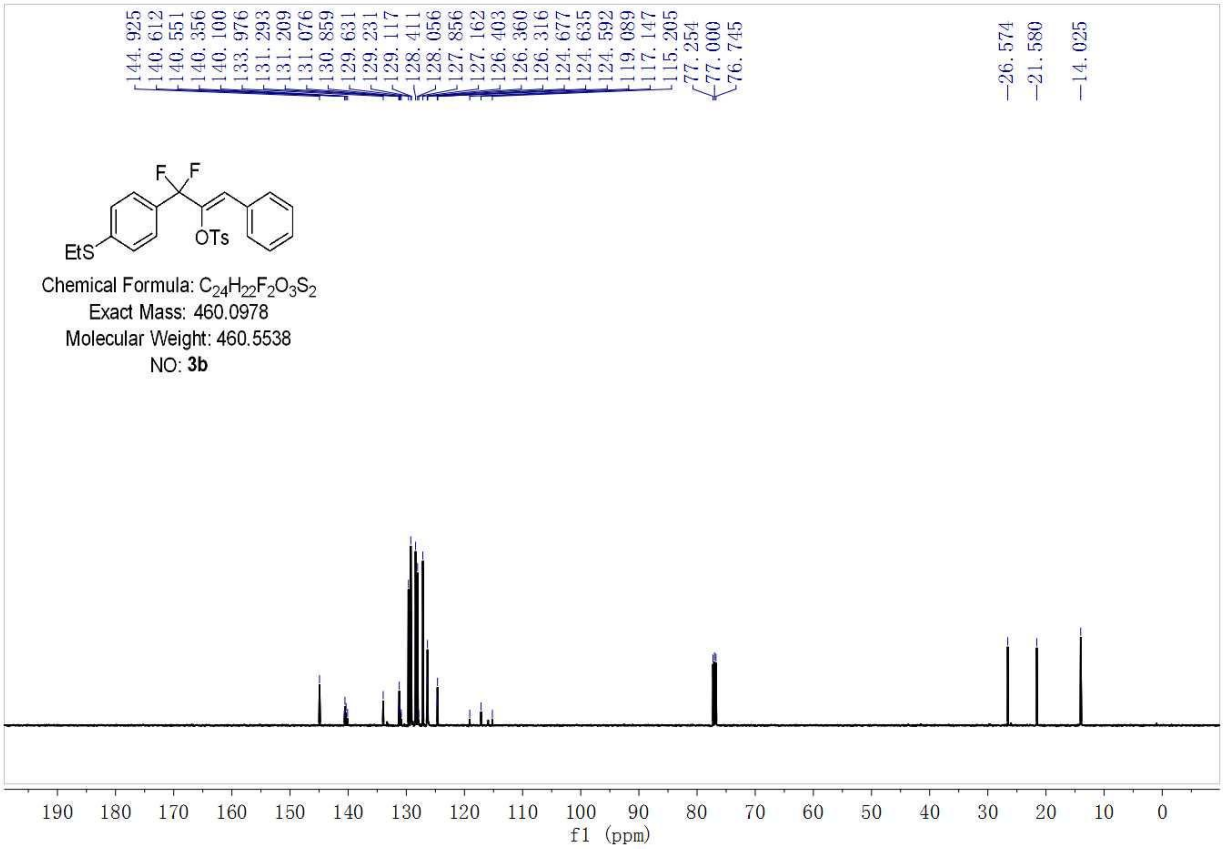

-95.283
F
F
OTs
Chemical Formula: C22H18F2O3S
Exact Mass: 400.0945
Molecular Weight: 400.4398
NO: 3a
2.00
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150
f1 (ppm)


144.933
140.745
140.492
140.239
134.495
134.282
134.069
134.001
131.236
130.402
129.639
129.244
129.110
128.413
128.331
128.095
125.956
125.911
125.867
124.779
124.735
124.692
119.175
117.233
115.291
77.255
77.000
76.746
-21.566
F
F
OTs
Chemical Formula: C22H18F2O3S
Exact Mass: 400.0945
Molecular Weight: 400.4398
NO: 3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

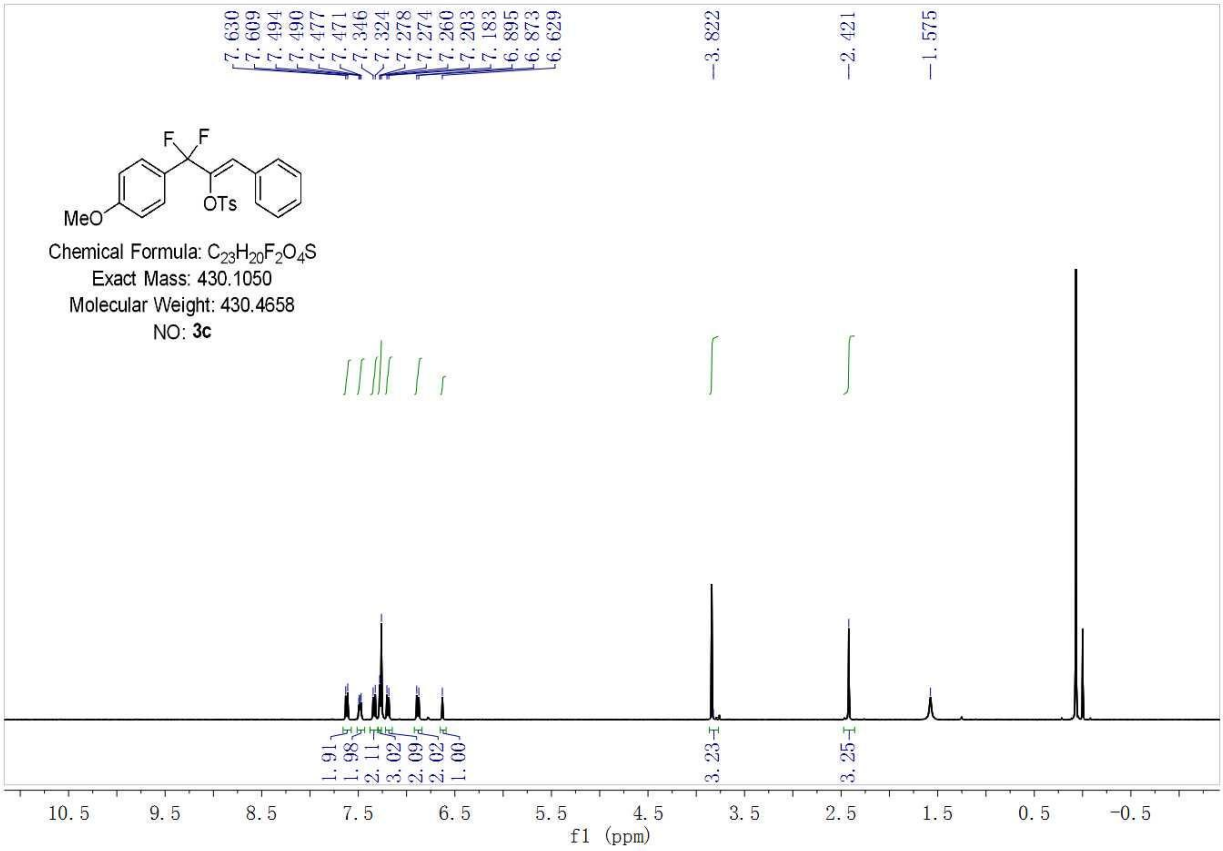
(Z)-3-(4-(Ethylthio)phenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3b)

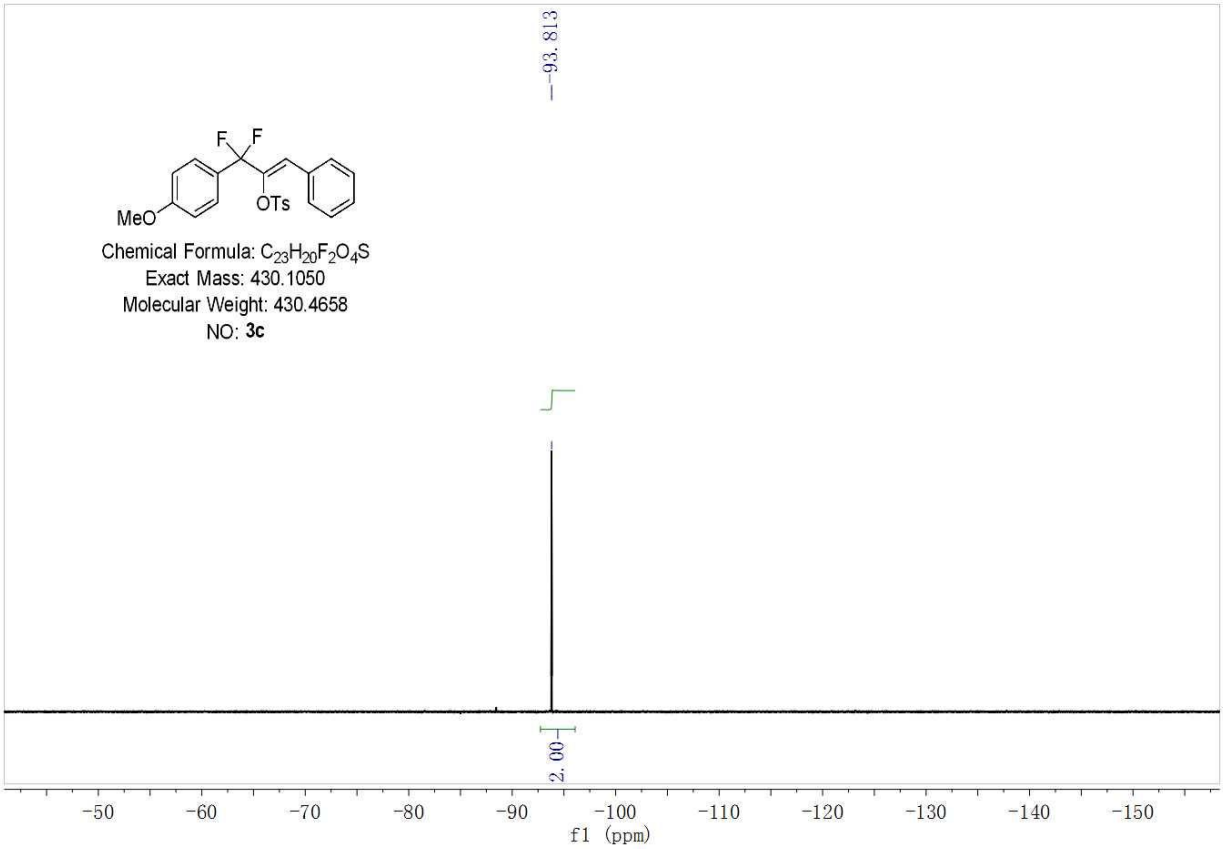


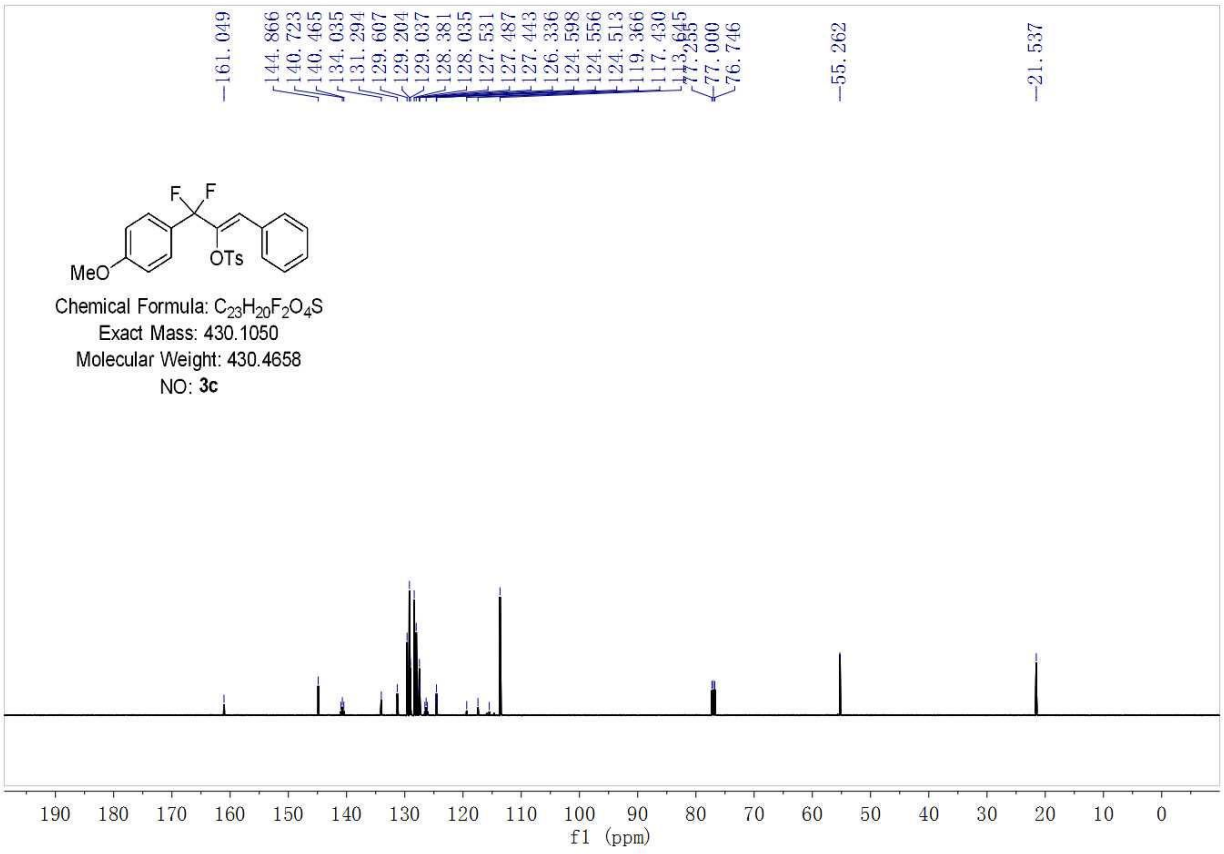




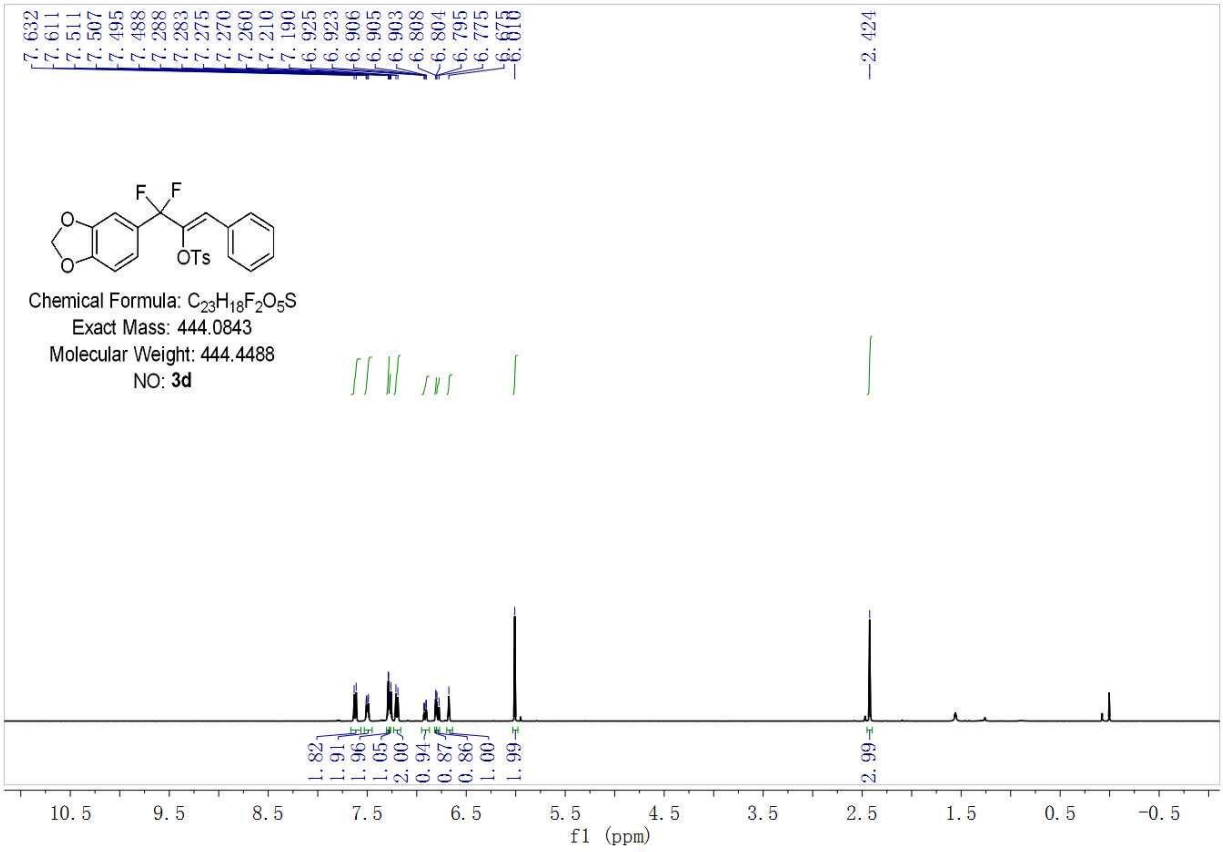
***(Z)*-3,3-Difluoro-3-(4-methoxyphenyl)-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3c)**

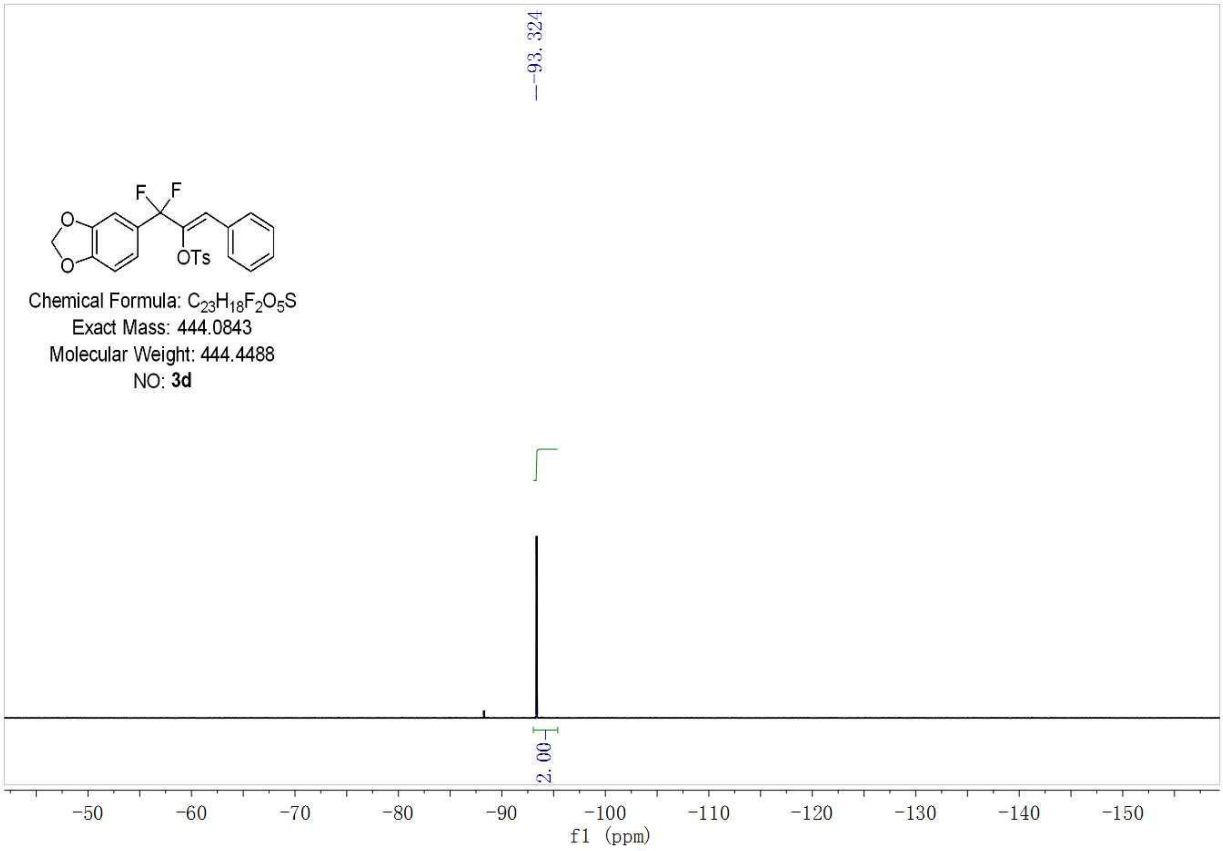


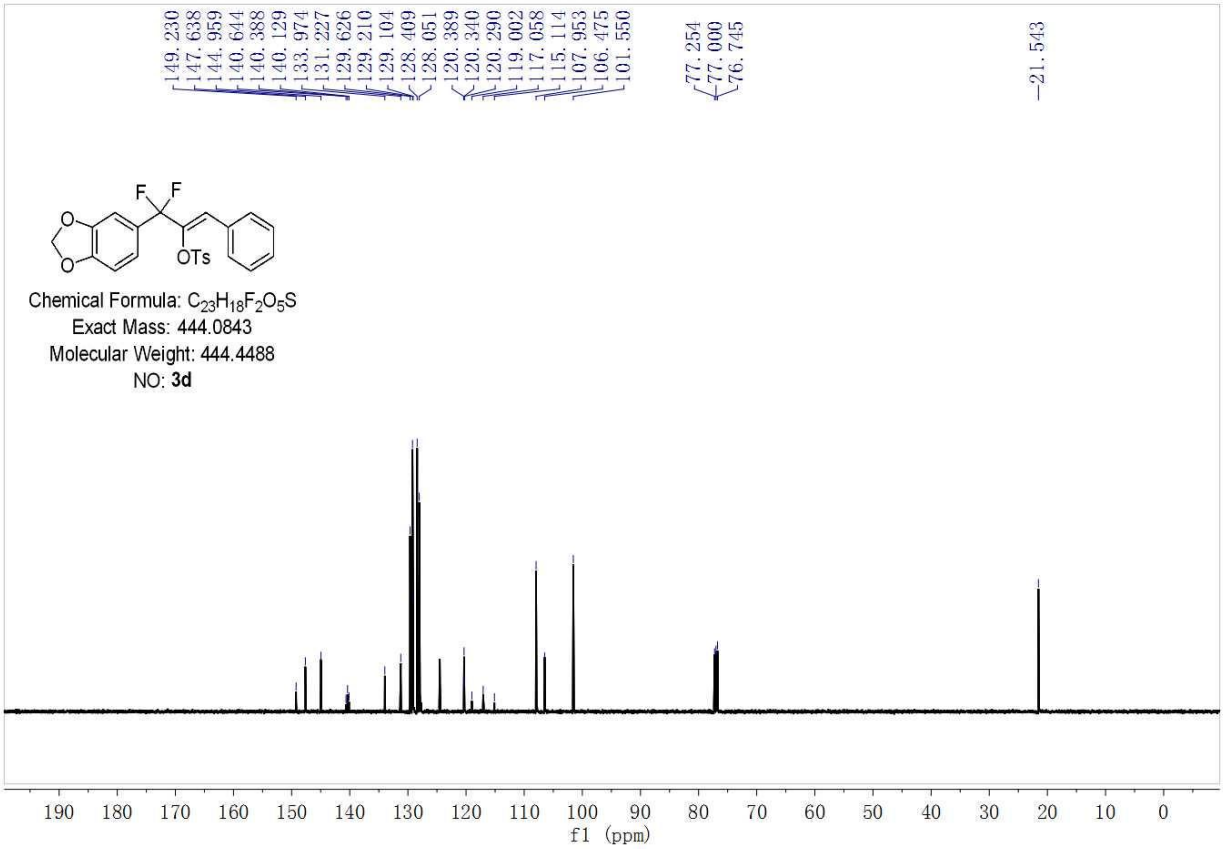

-93.813
F
F
MeO
OTs
Chemical Formula: C23H20F2O4S
Exact Mass: 430.1050
Molecular Weight: 430.4658
NO: 3c
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


-161.049
144.866
140.723
140.465
134.035
131.294
129.607
129.204
129.037
128.381
128.035
127.531
127.487
127.443
126.336
124.598
124.556
124.513
119.366
117.430
113.645
77.255
77.000
76.746
-55.262
-21.537
F
F
MeO
OTs
Chemical Formula: C23H20F2O4S
Exact Mass: 430.1050
Molecular Weight: 430.4658
NO: 3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

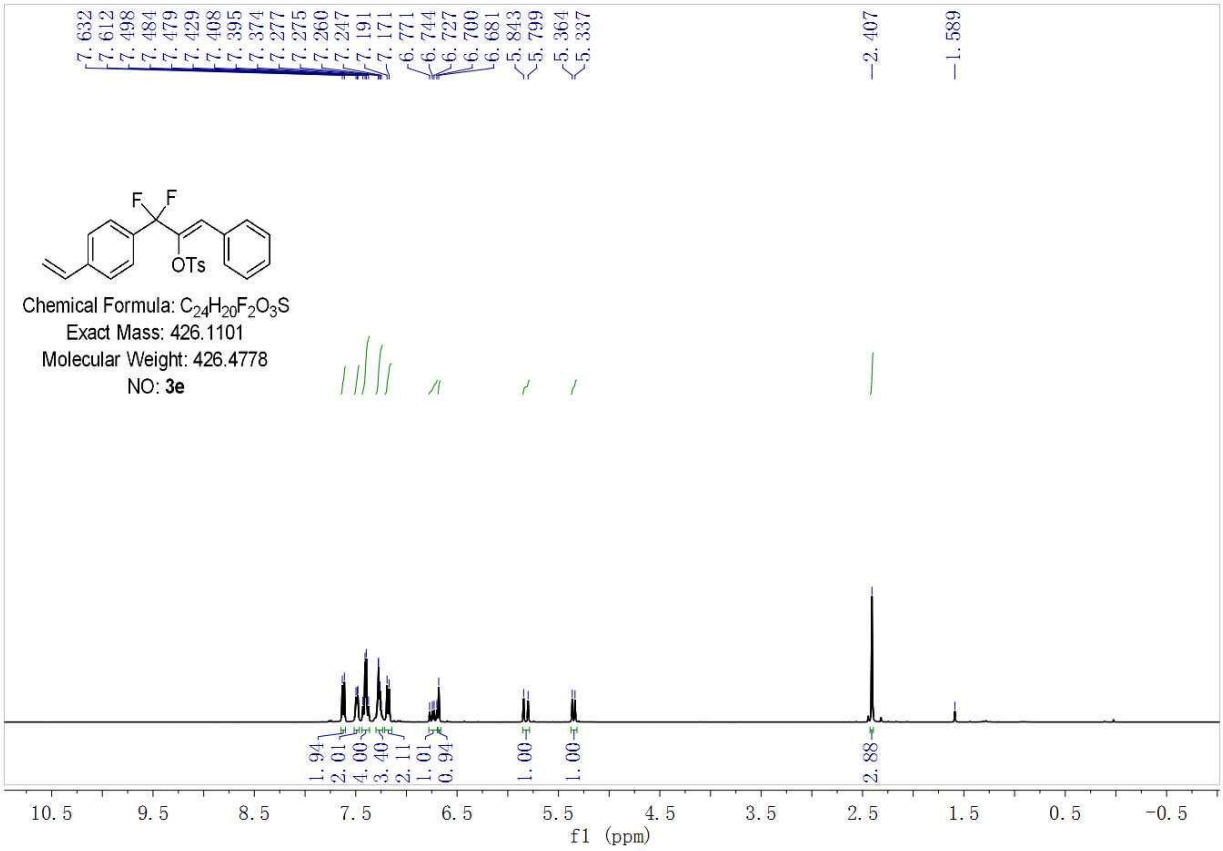
***(Z)*-3-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3d)**

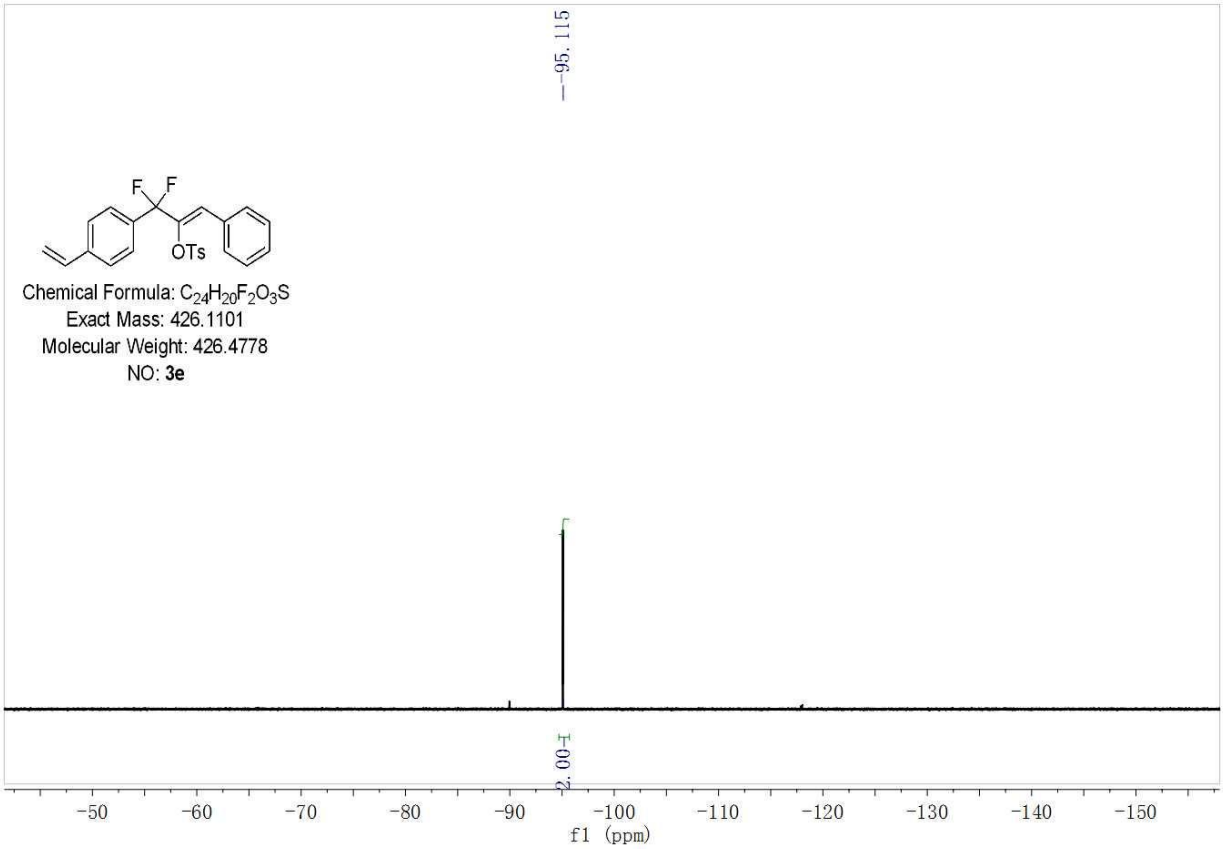


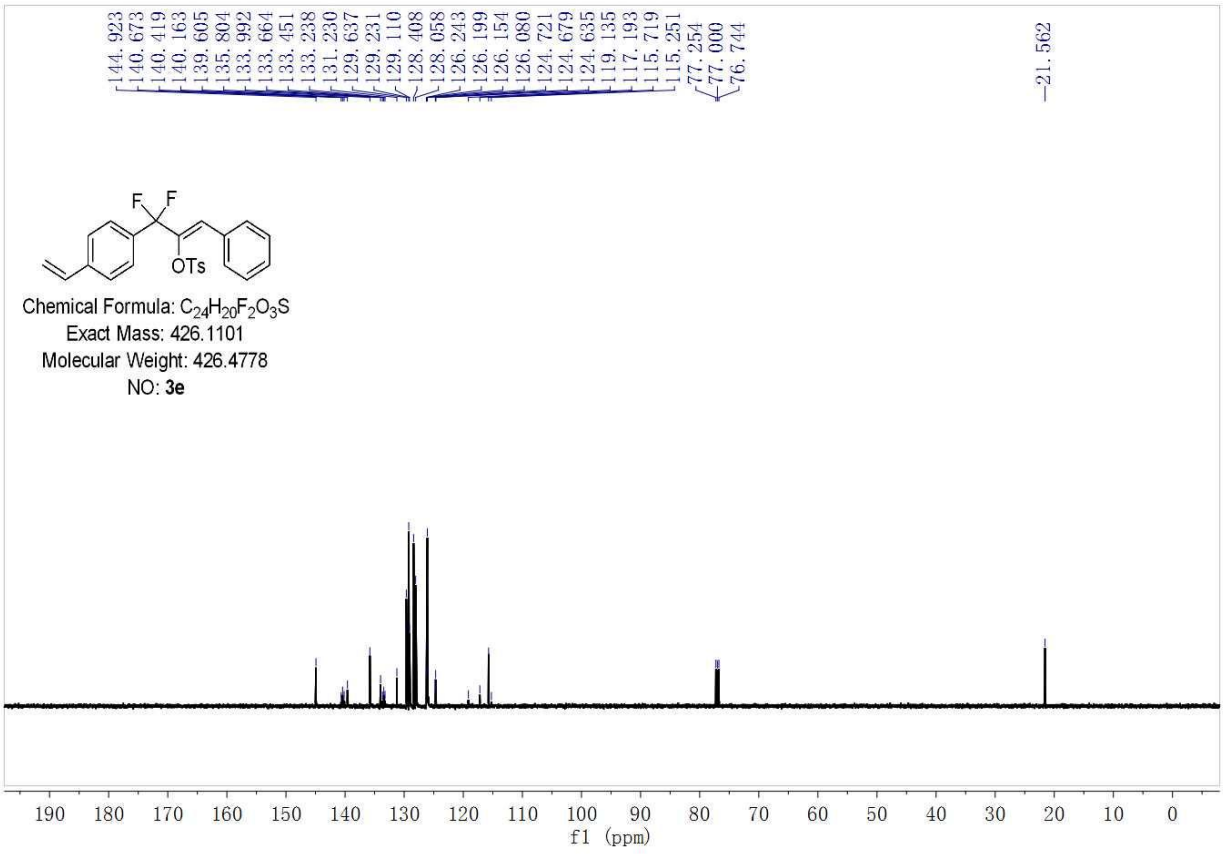




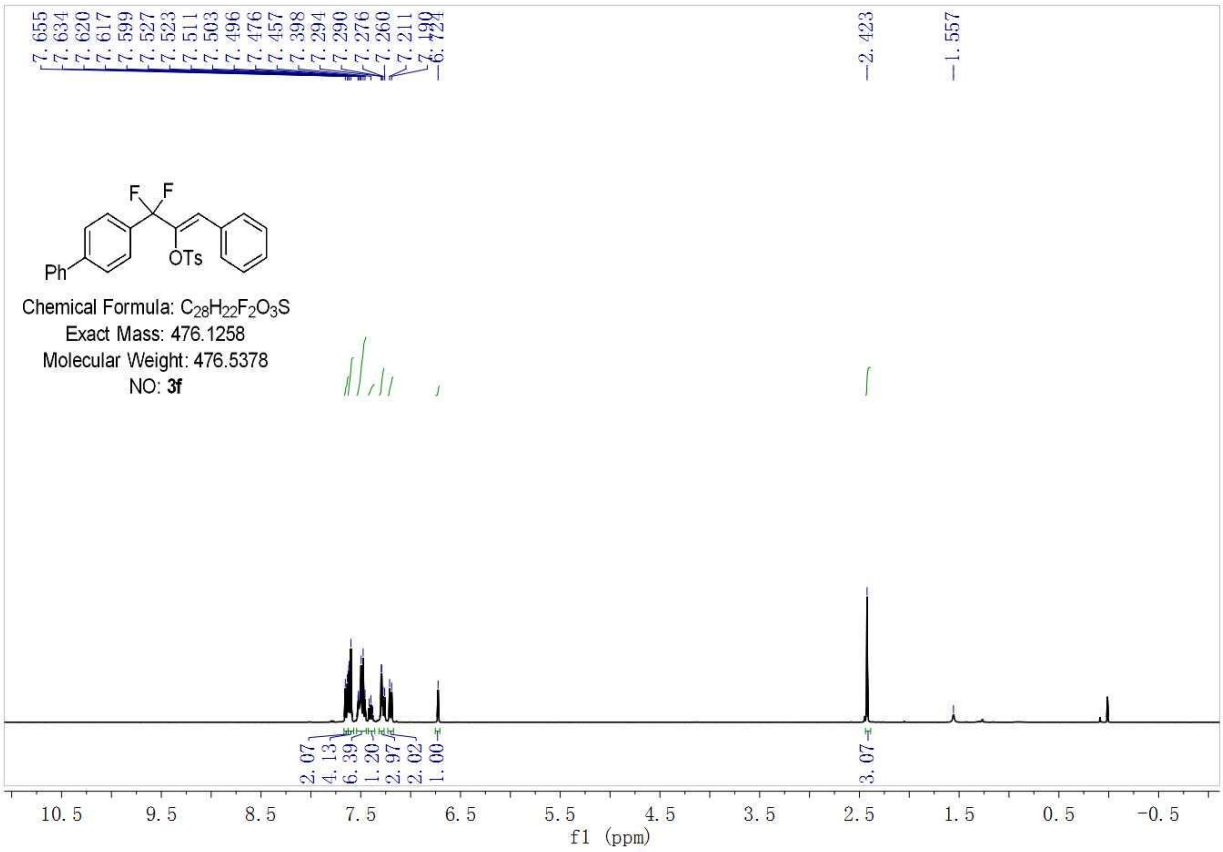
***(Z)*-3,3-Difluoro-1-phenyl-3-(4-vinylphenyl)prop-1-en-2-yl-4-methylbenzenesulfonate (3e)**

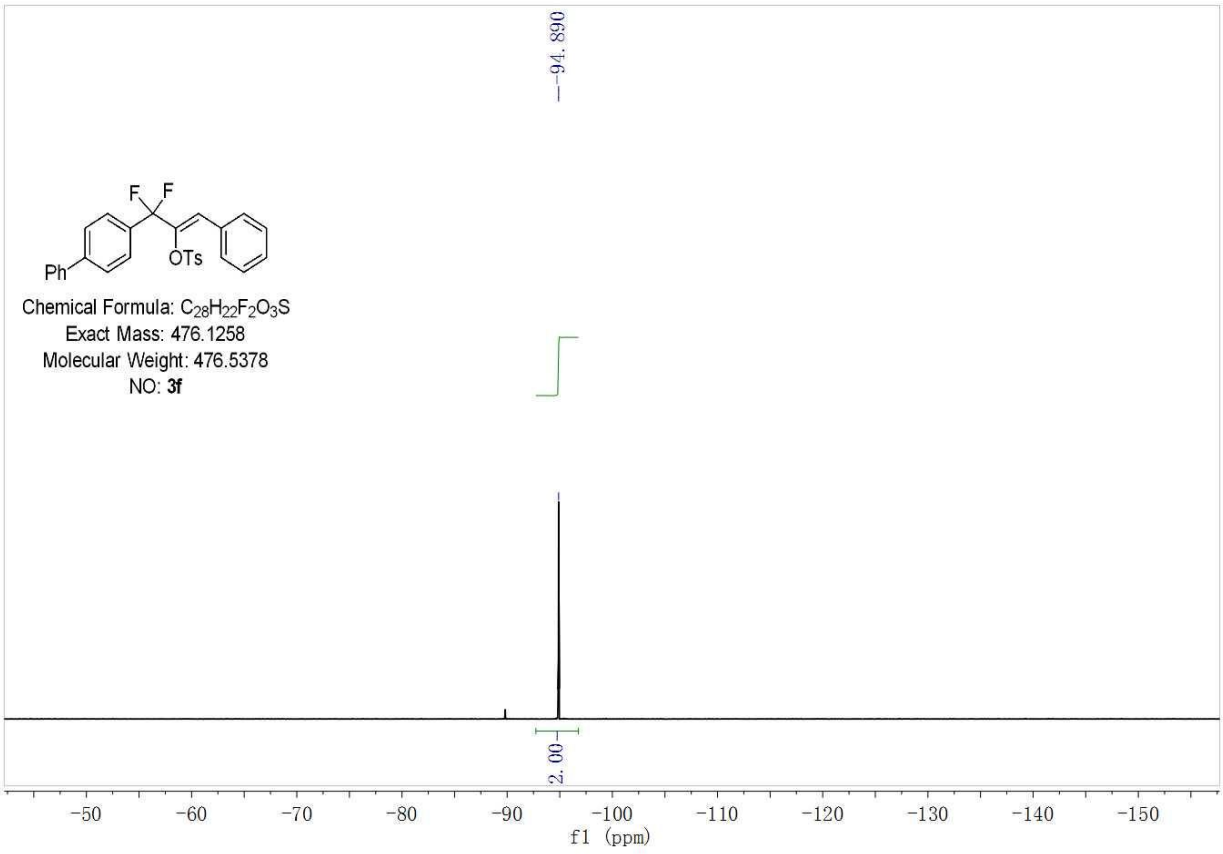


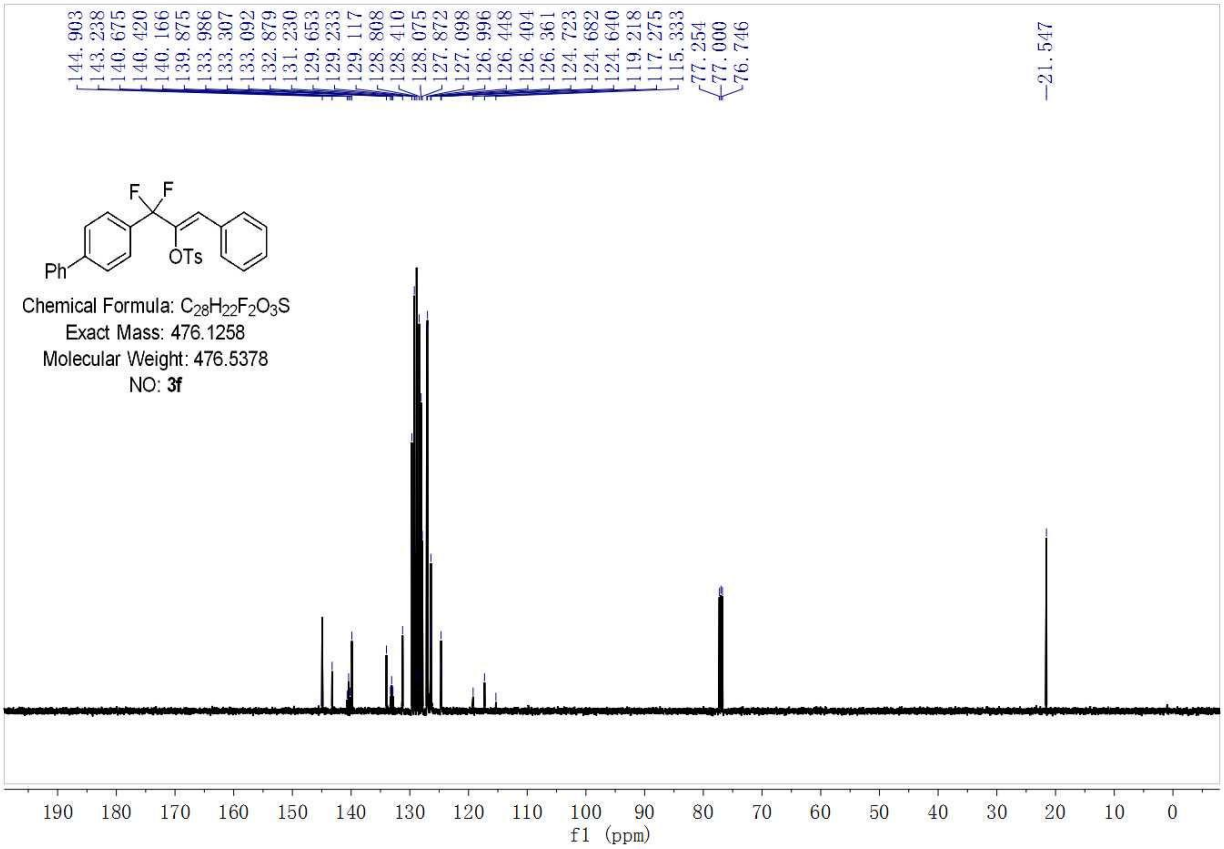

-95.115
F
F
OTs
Chemical Formula: C24H20F2O3S
Exact Mass: 426.1101
Molecular Weight: 426.4778
NO: 3e
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


144.923
140.673
140.419
140.163
139.605
135.804
133.992
133.664
133.451
133.238
131.230
129.637
129.231
129.110
128.408
128.058
126.243
126.199
126.154
126.080
124.721
124.679
124.635
119.135
117.193
115.719
115.251
77.254
77.000
76.744
21.562
F
F
OTs
Chemical Formula: C24H20F2O3S
Exact Mass: 426.1101
Molecular Weight: 426.4778
NO: 3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

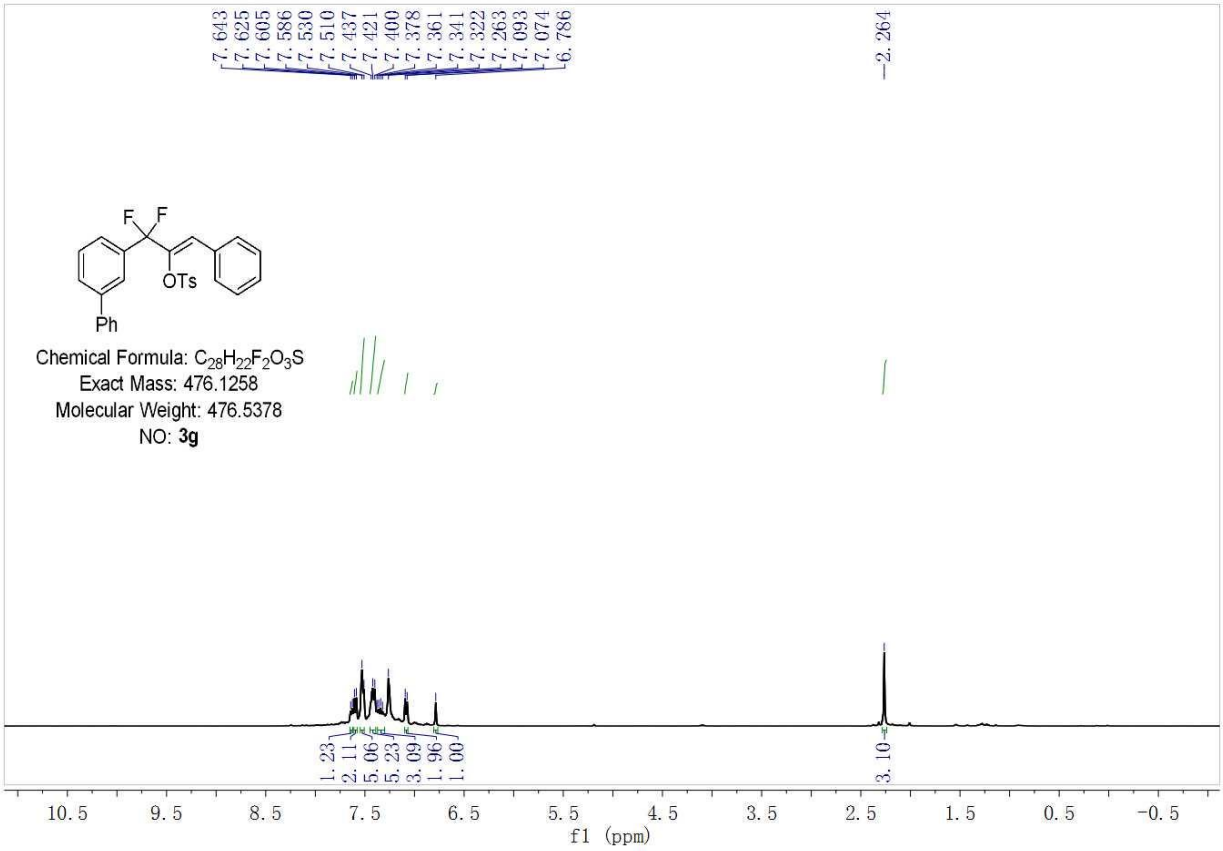
(Z)-3-([1,1'-Biphenyl]-4-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3f)

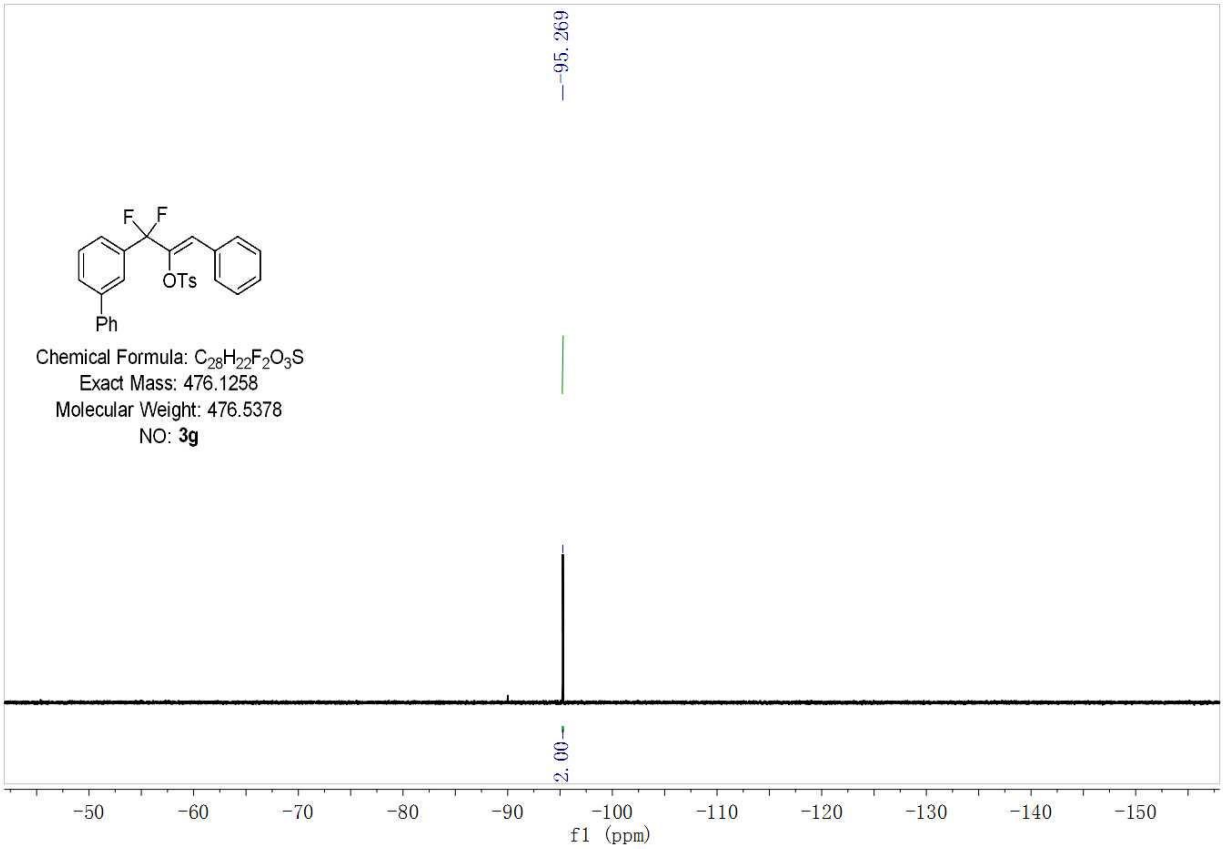


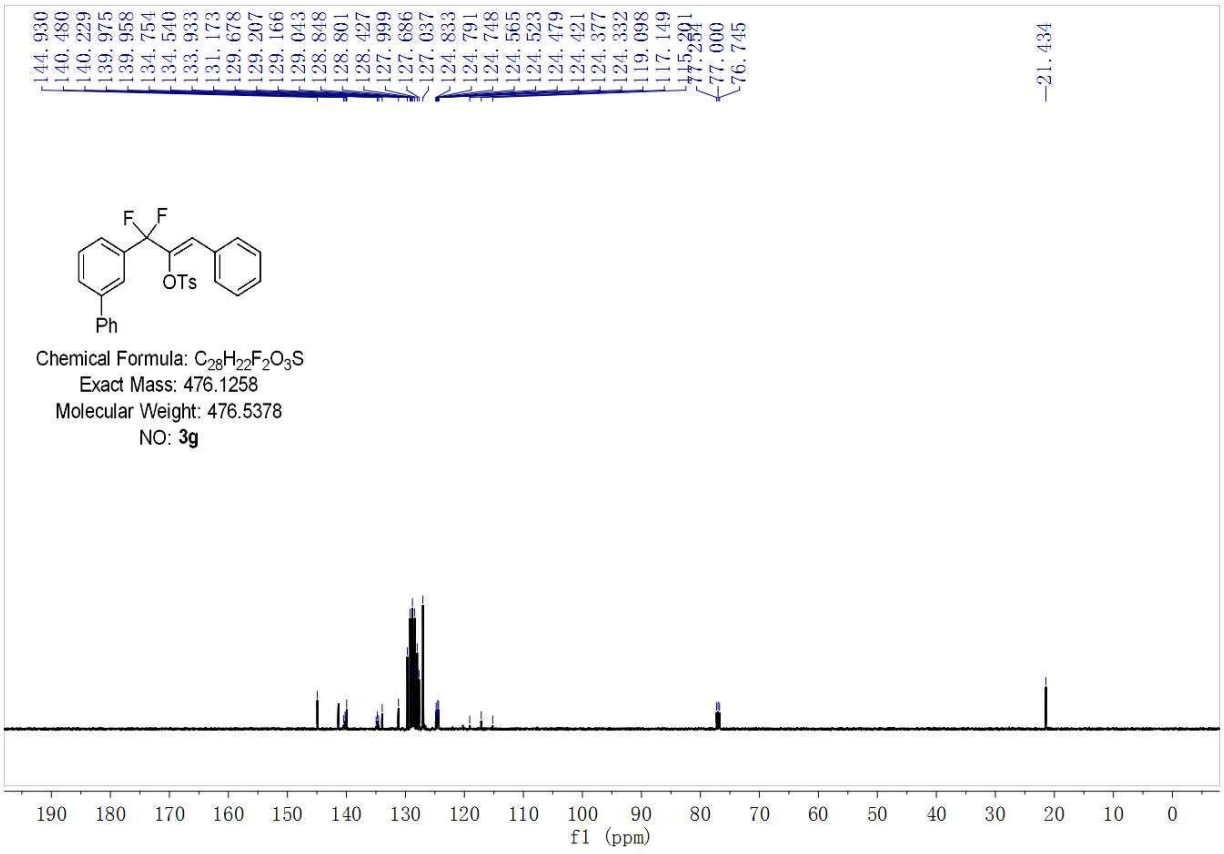




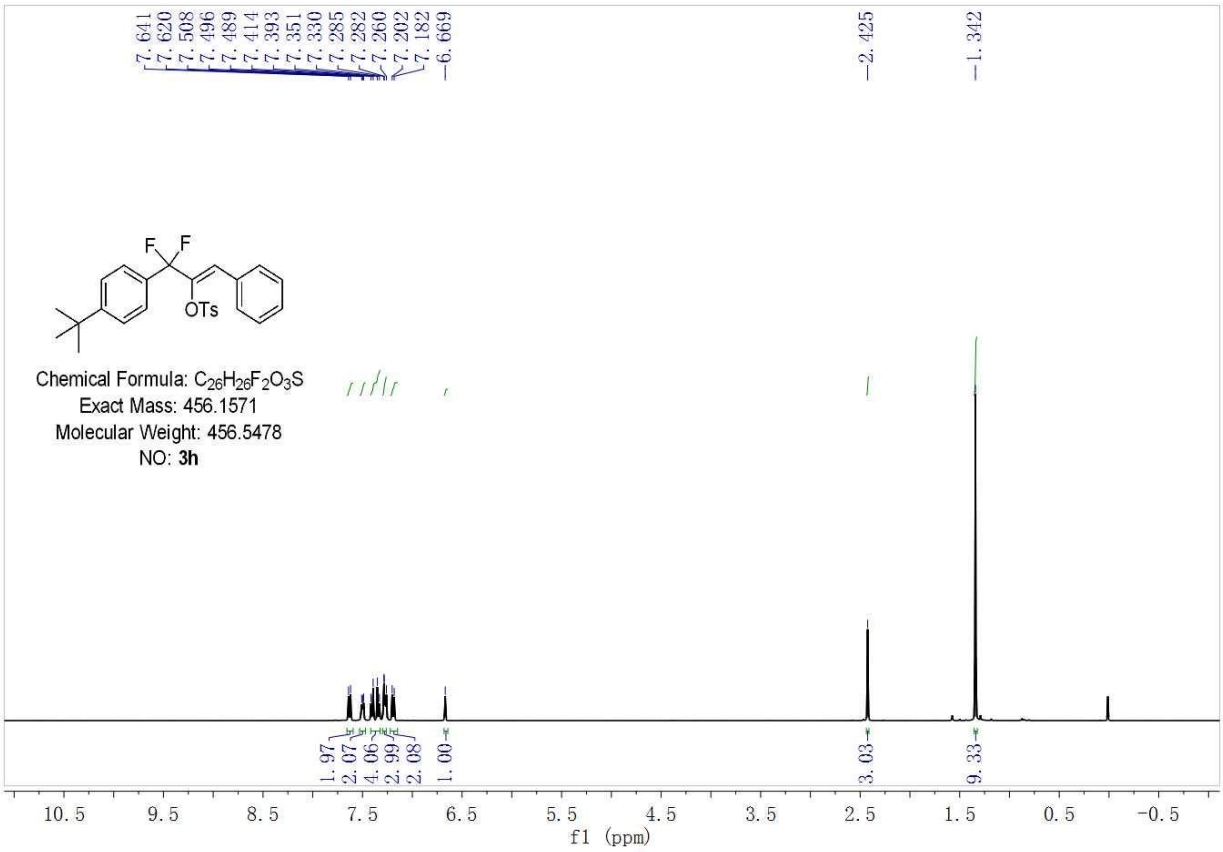
***(Z)*-3-([1,1'-Biphenyl]-3-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3g)**

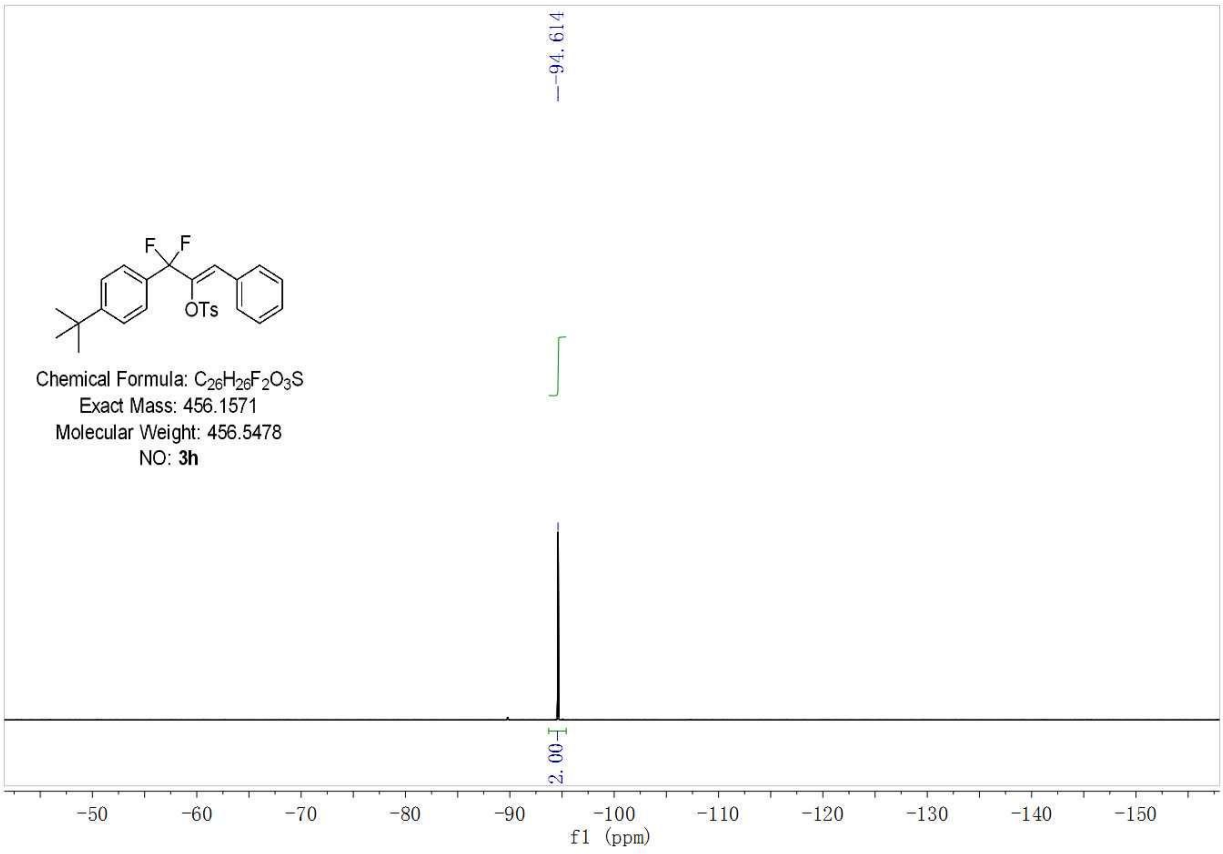


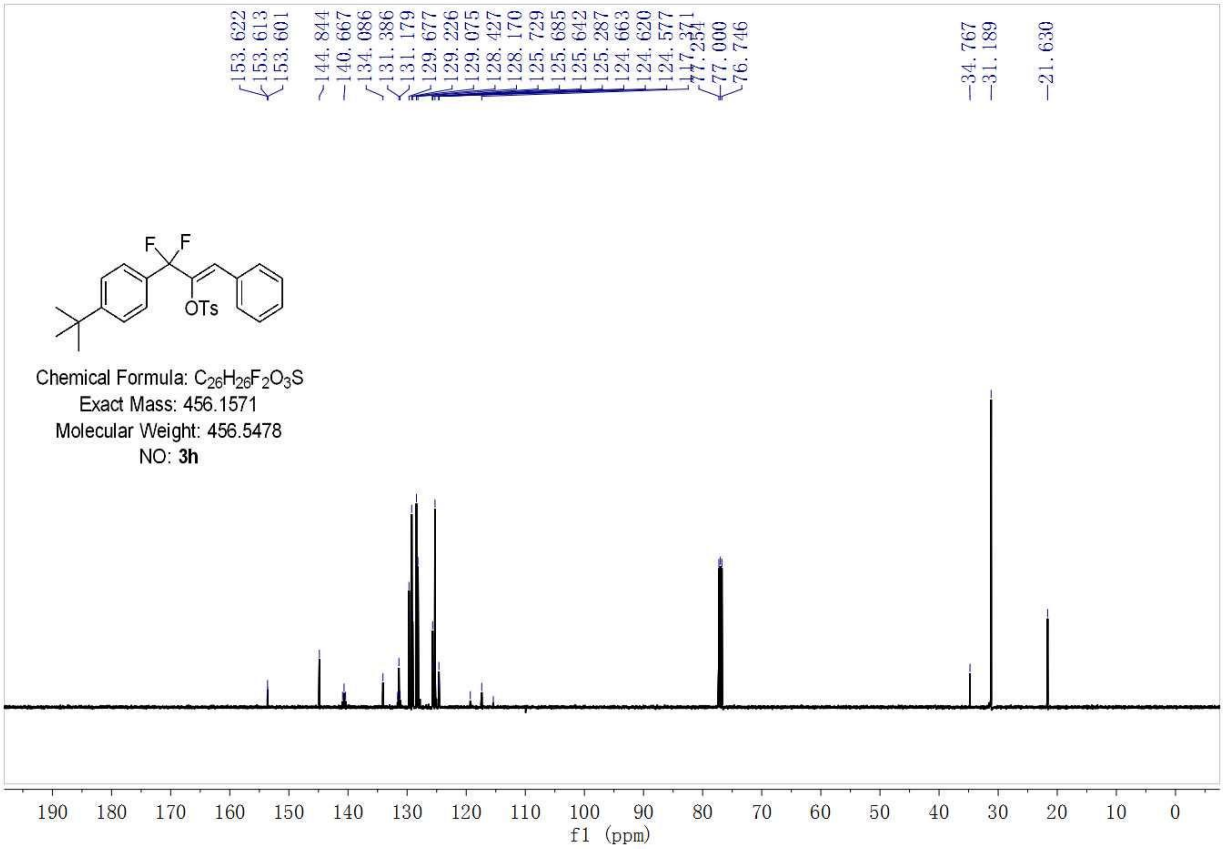

-95.269
F
F
OTs
Ph
Chemical Formula: C28H22F2O3S
Exact Mass: 476.1258
Molecular Weight: 476.5378
NO: 3g
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


144.930
140.480
140.229
139.975
139.958
134.754
134.540
133.933
131.173
129.678
129.207
129.166
129.043
128.848
128.801
128.427
127.999
127.686
127.037
124.833
124.791
124.748
124.565
124.523
124.479
124.421
124.377
124.332
119.098
117.149
115.201
77.000
76.745
-21.434
F
F
OTs
Ph
Chemical Formula: C28H22F2O3S
Exact Mass: 476.1258
Molecular Weight: 476.5378
NO: 3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

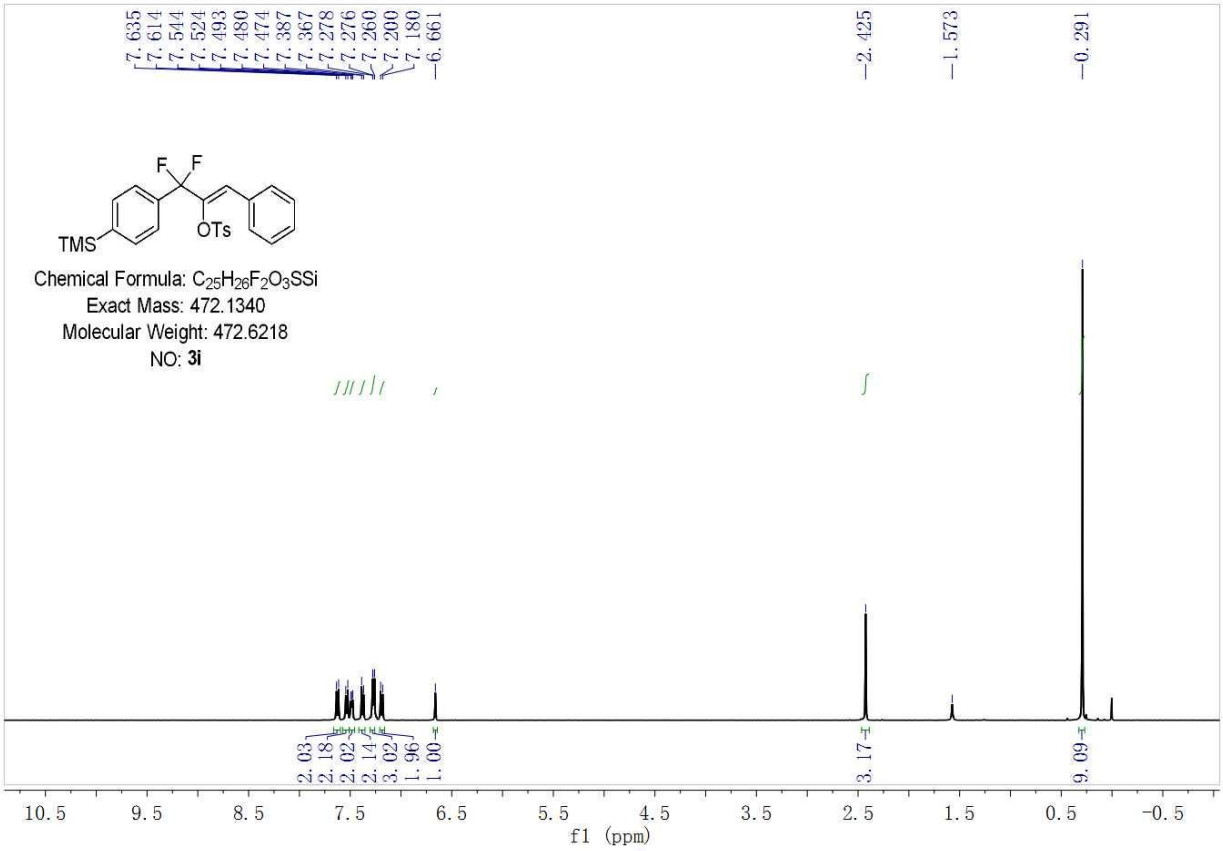
***(Z)*-3-(4-(*tert*-Butyl)phenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3h)**

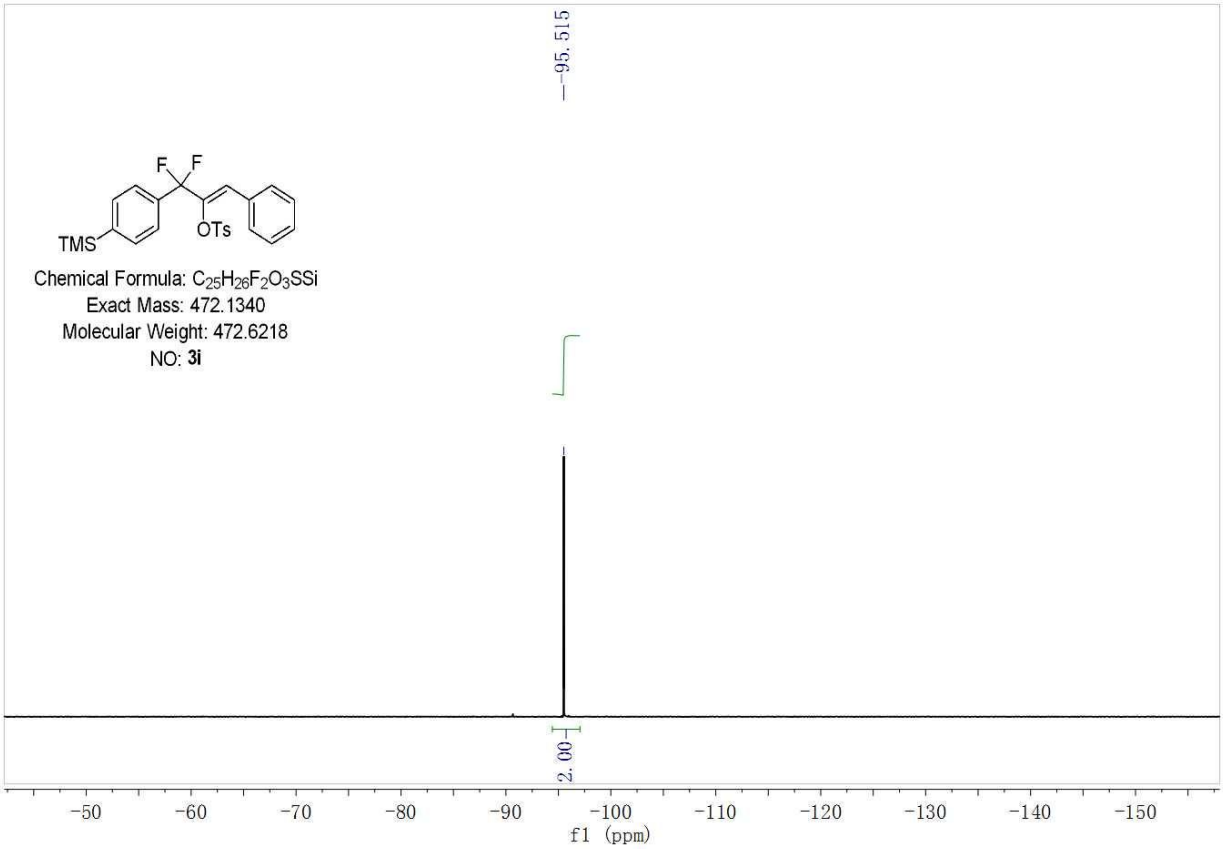


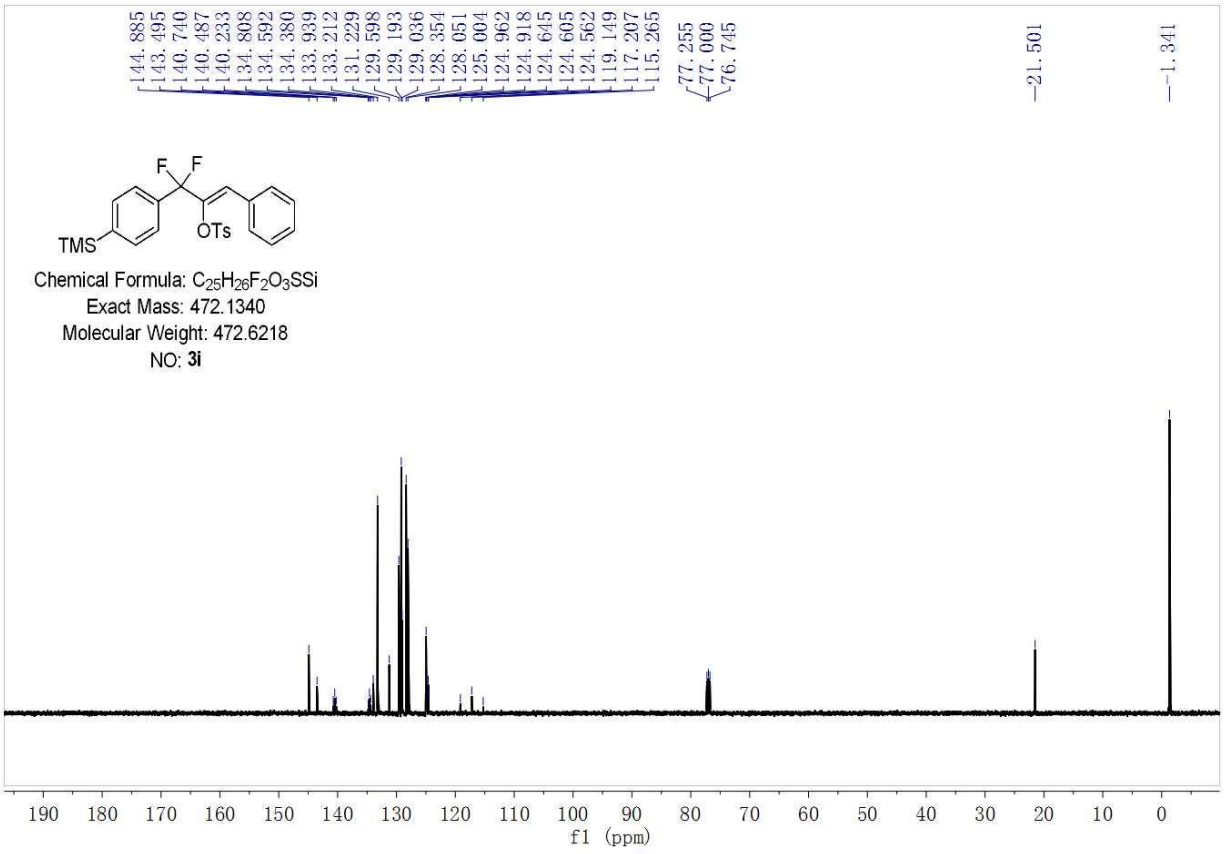




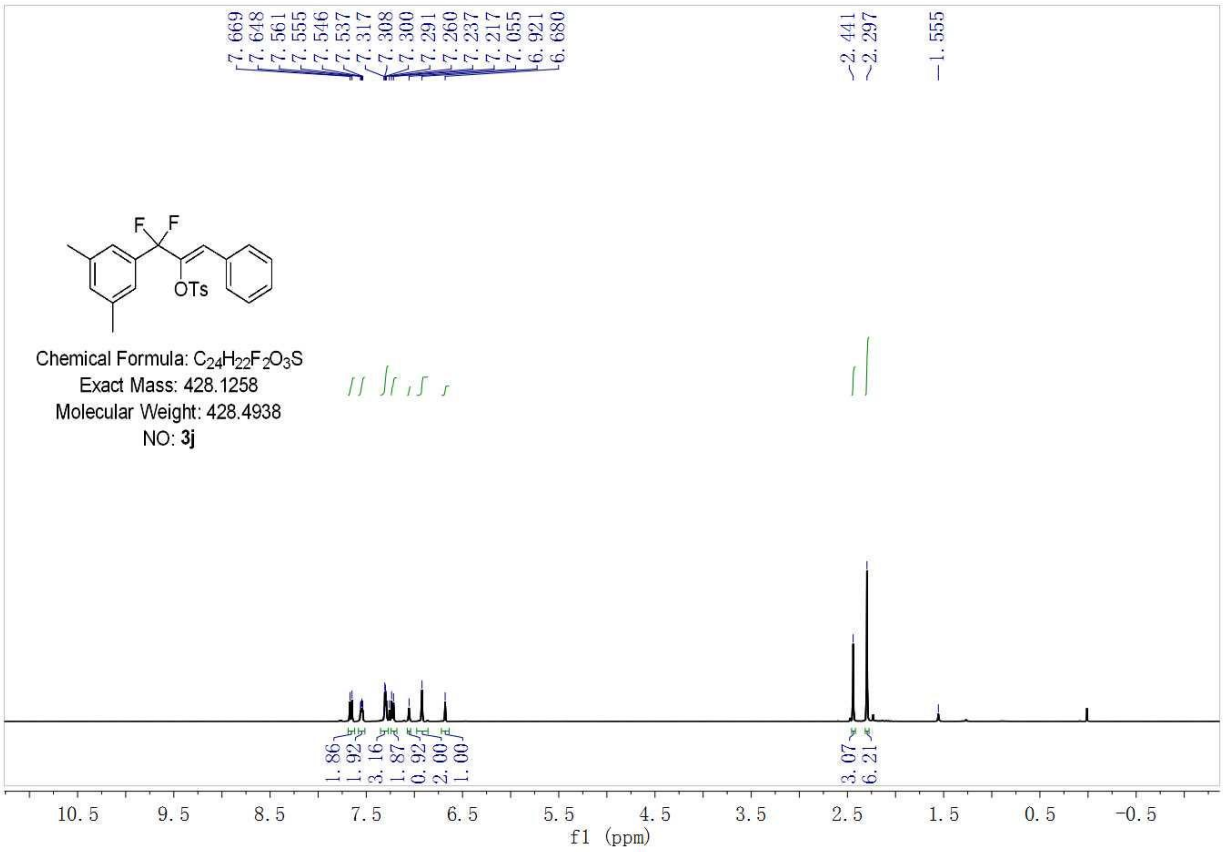
***(Z)*-3,3-Difluoro-1-phenyl-3-(4-(trimethylsilyl)phenyl)prop-1-en-2-yl-4-methylbenzenesulfonate (3i)**

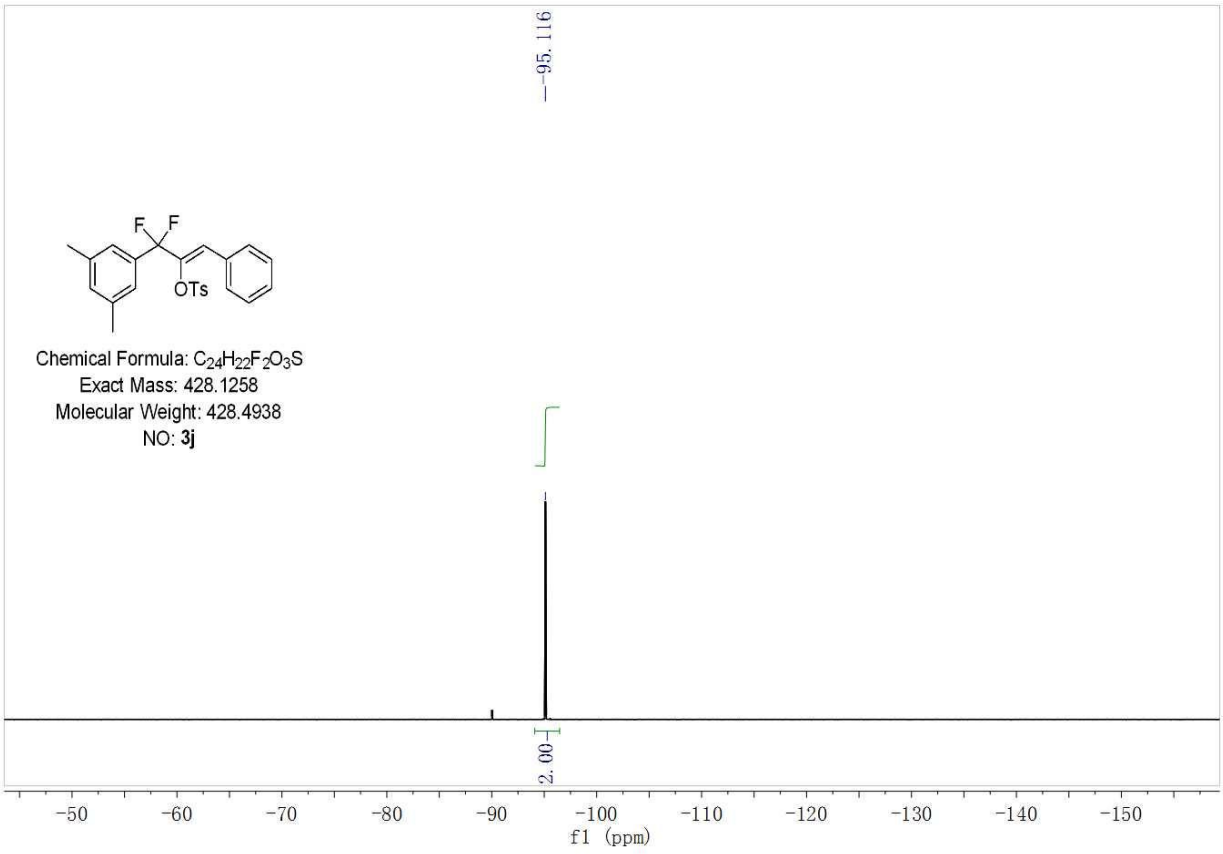


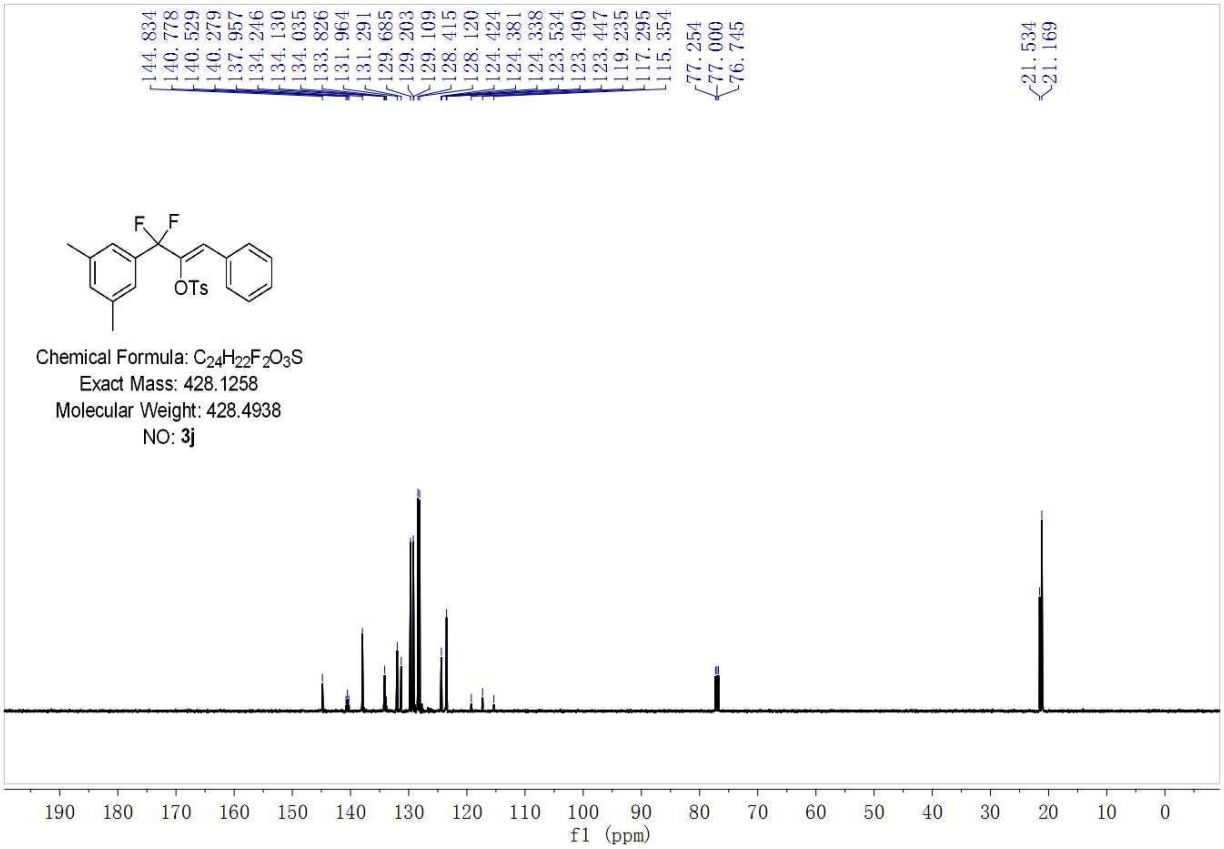

-95.515
F F
TMS
OTs
Chemical Formula: C25H26F2O3SSi
Exact Mass: 472.1340
Molecular Weight: 472.6218
NO: 3i
2.00
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


144.885
143.495
140.740
140.487
140.233
134.808
134.592
134.380
133.939
133.212
131.229
129.598
129.193
129.036
128.354
128.051
125.004
124.962
124.918
124.645
124.605
124.562
119.149
117.207
115.265
77.255
77.000
76.745
-21.501
-1.341
F F
TMS
OTs
Chemical Formula: C25H26F2O3SSi
Exact Mass: 472.1340
Molecular Weight: 472.6218
NO: 3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

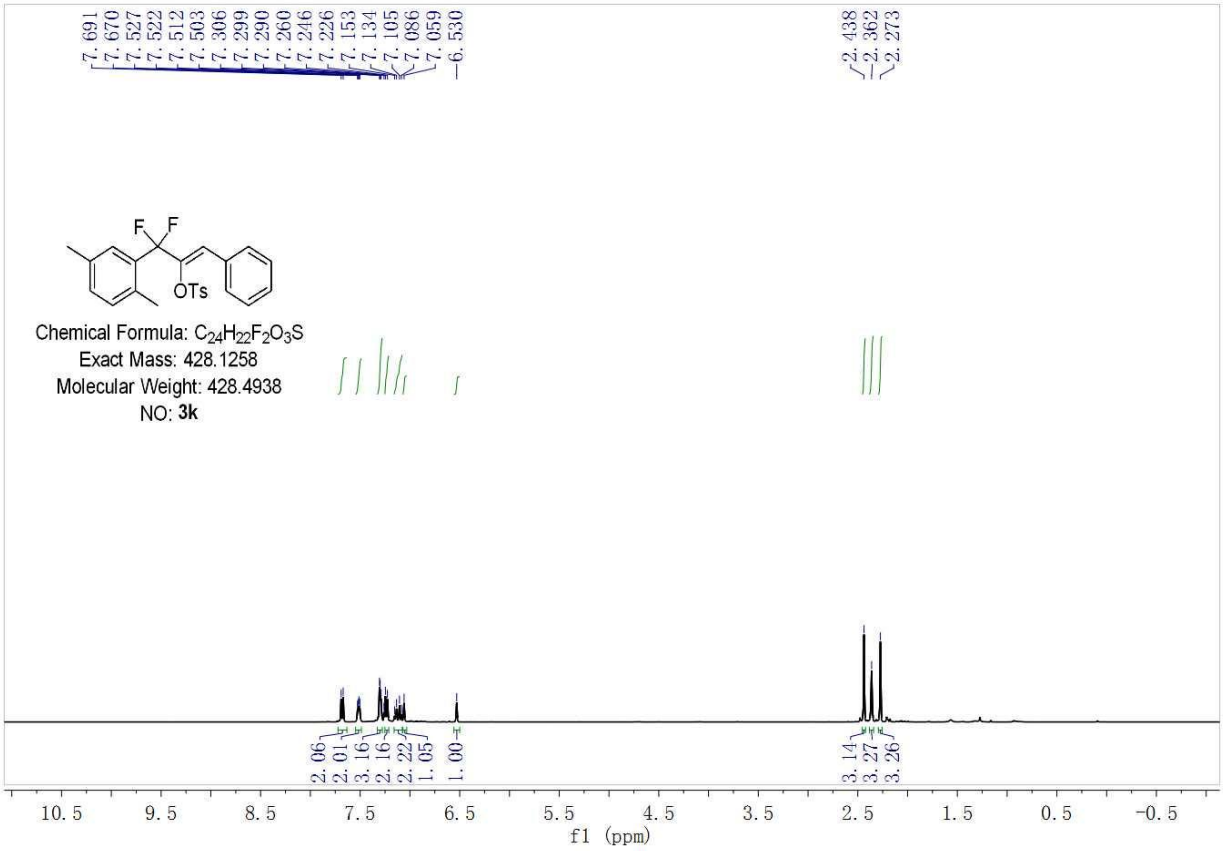
(Z)-3-(3,5-Dimethylphenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3j)

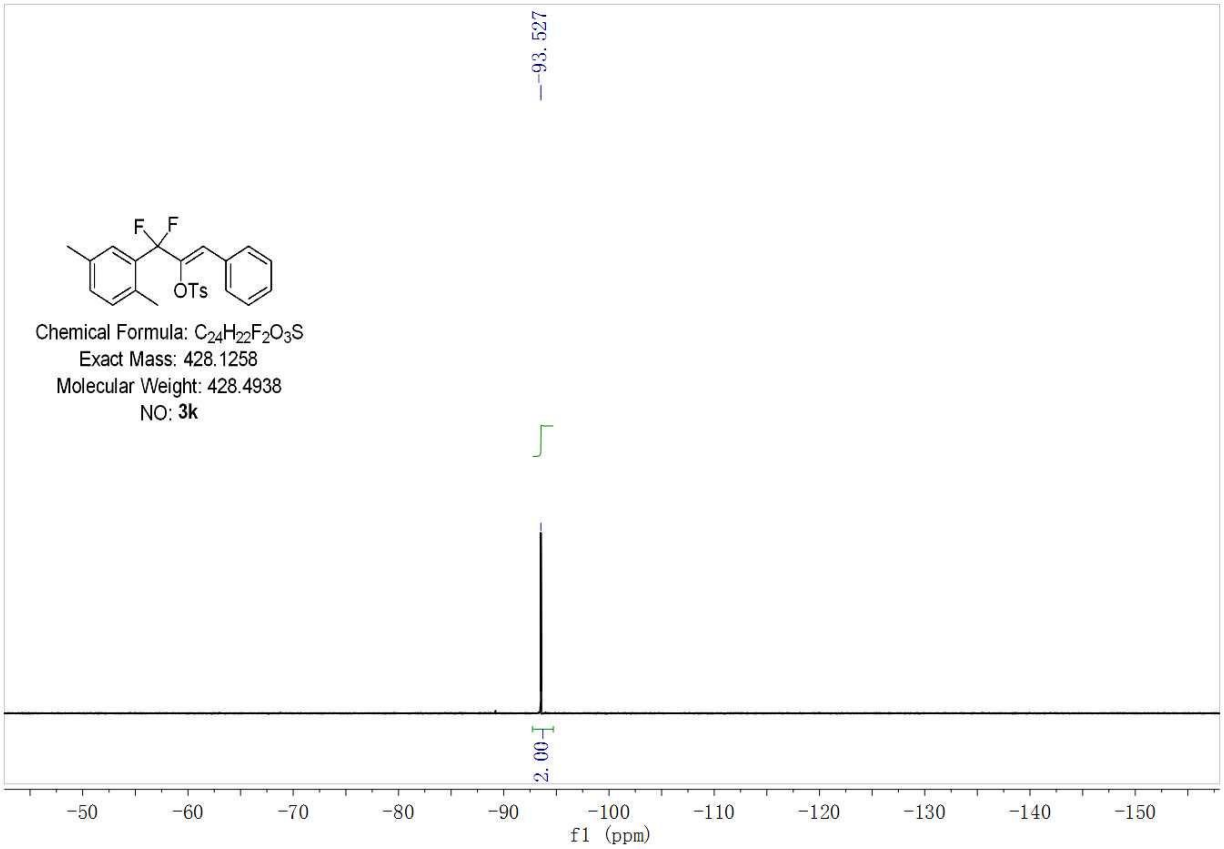


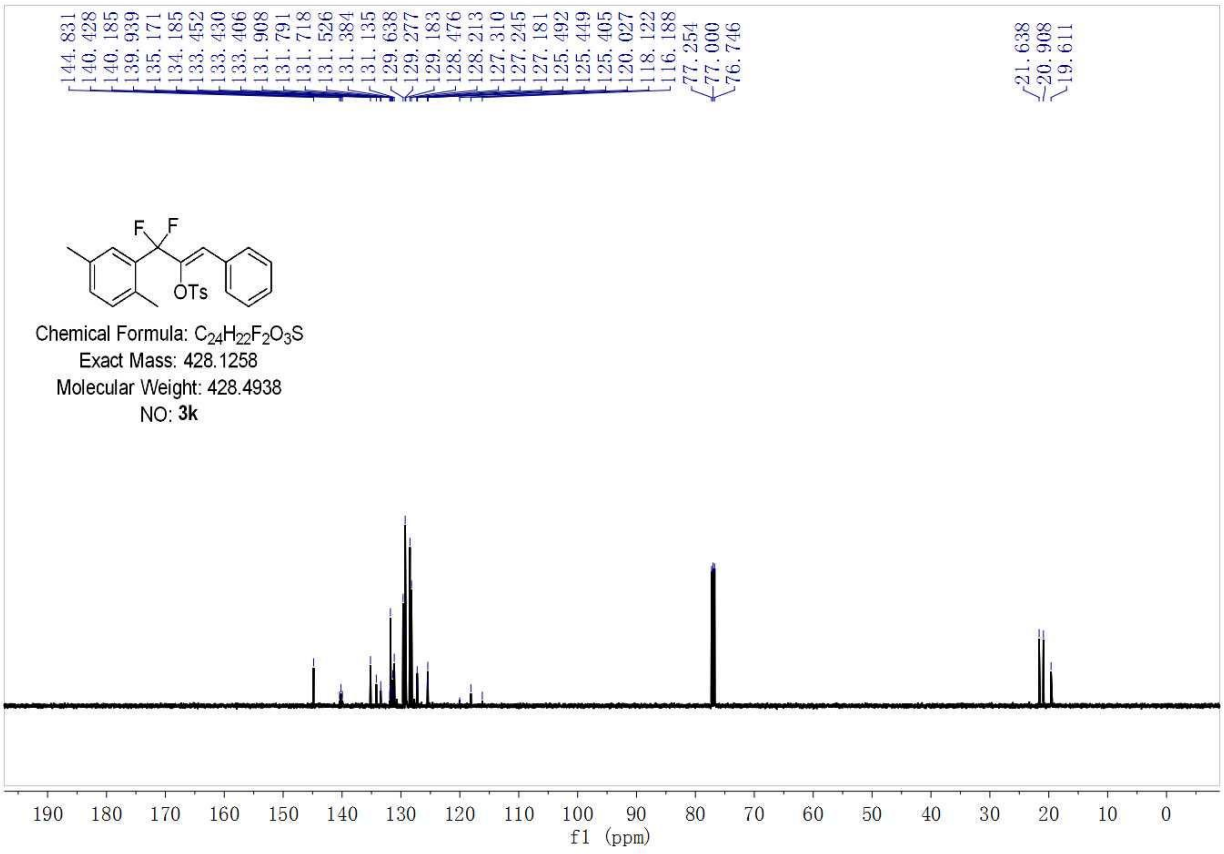




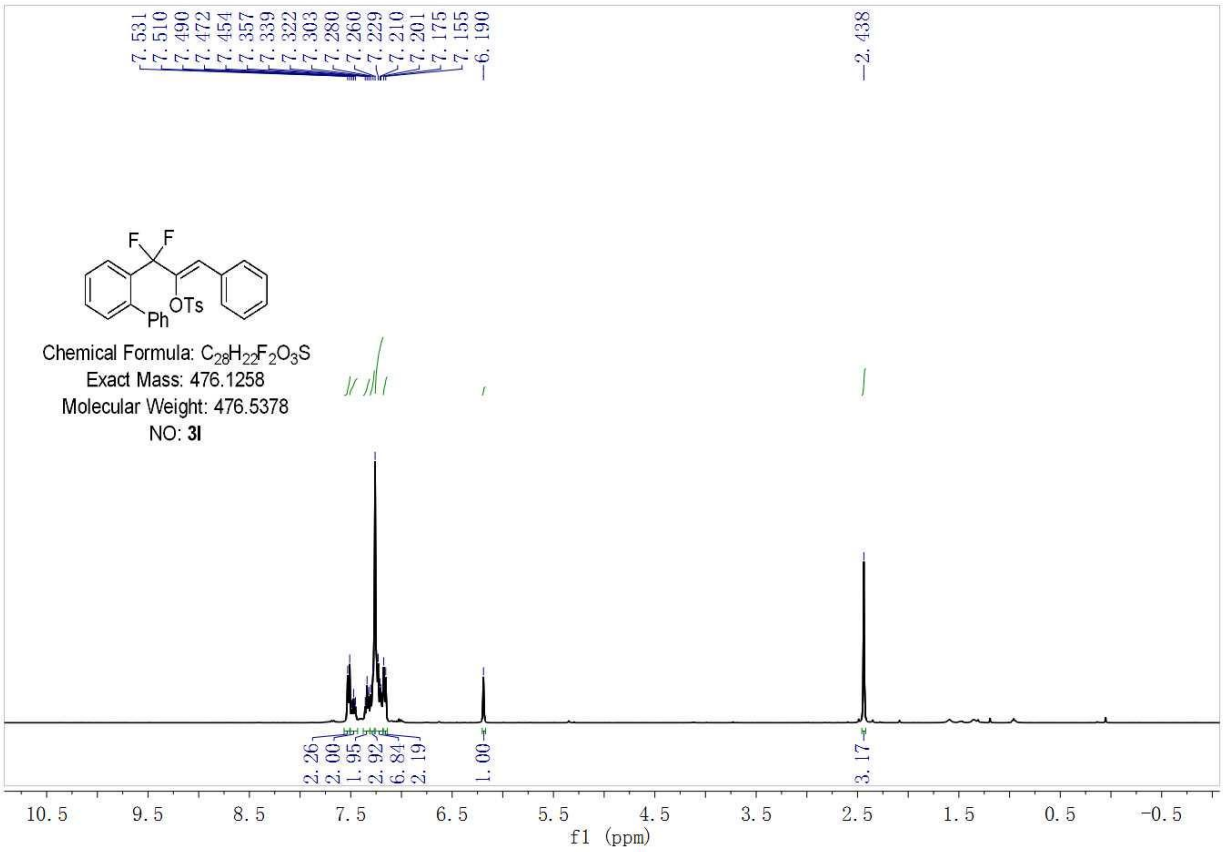
***(Z)*-3-(2,5-Dimethylphenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3k)**

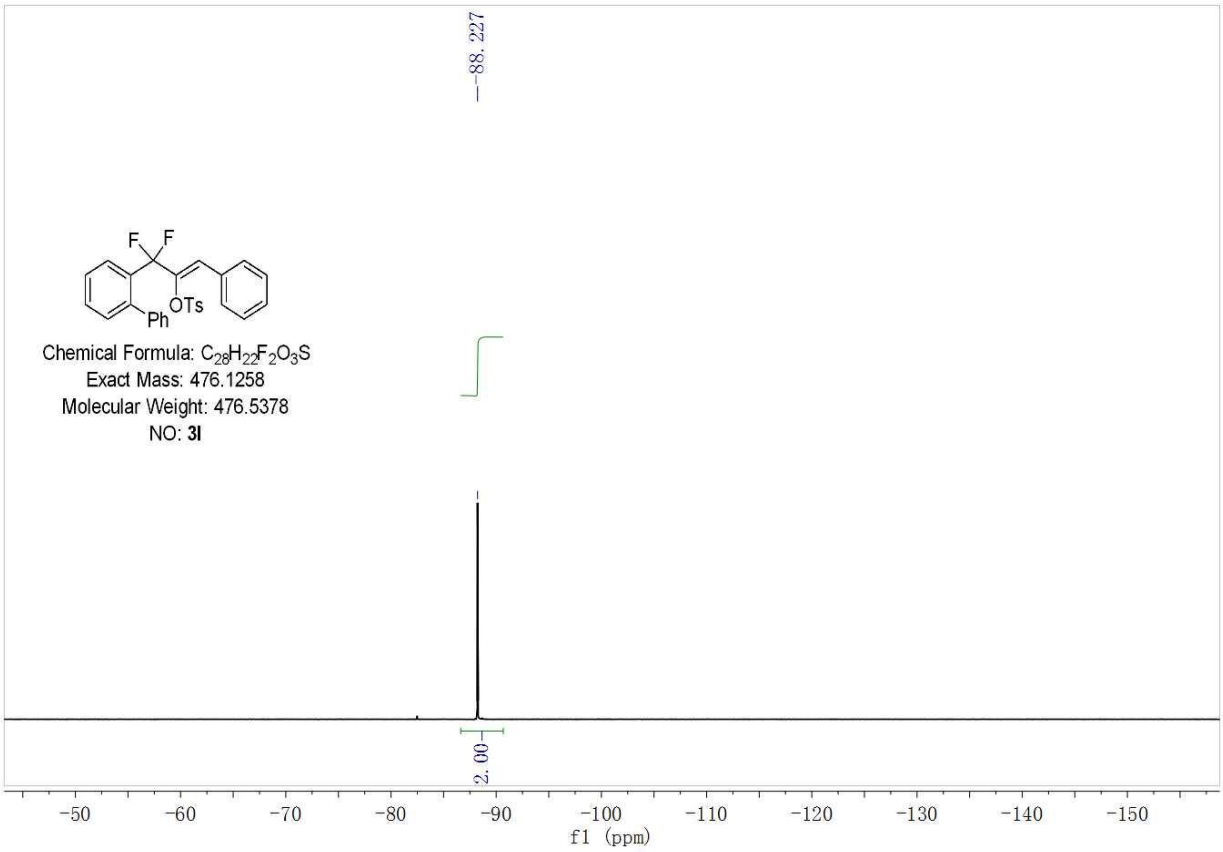


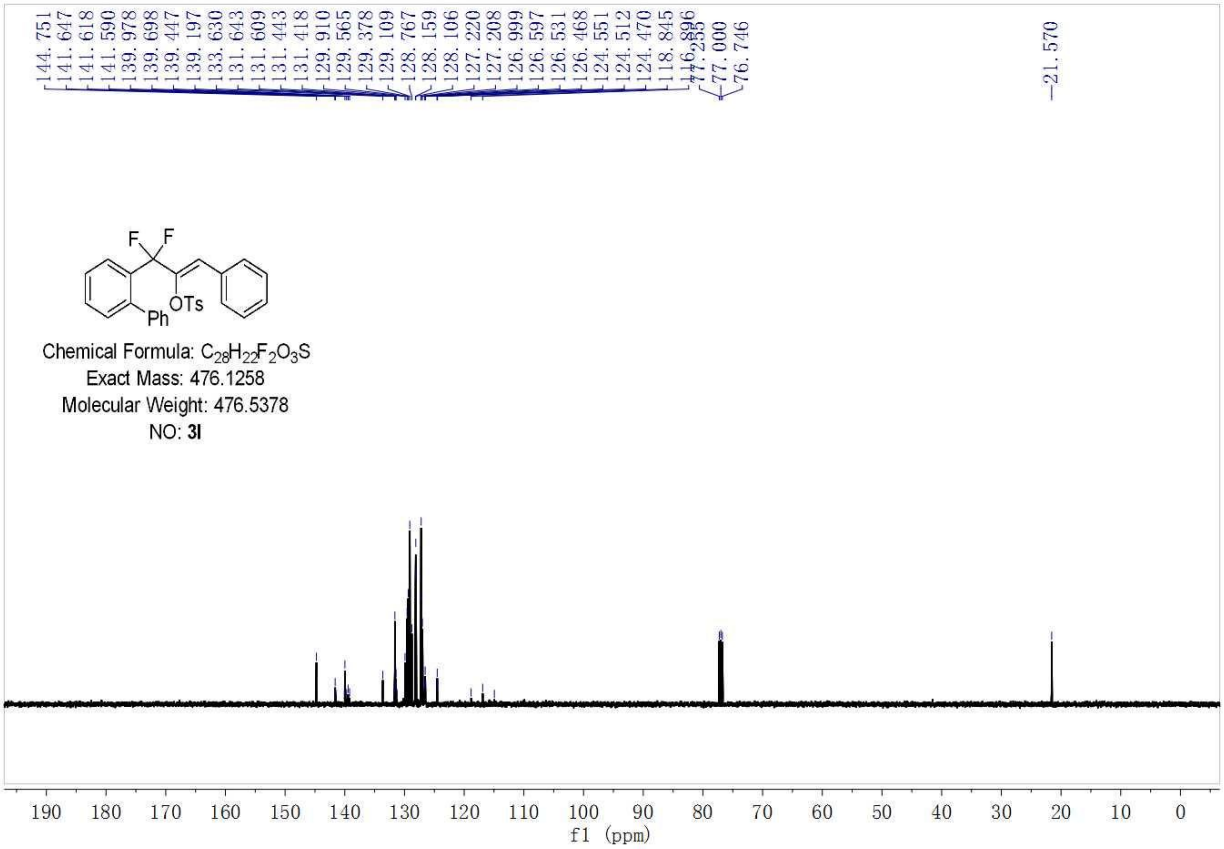

-93.527
F
F
OTs
Chemical Formula: C24H22F2O3S
Exact Mass: 428.1258
Molecular Weight: 428.4938
NO: 3k
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


144.831
140.428
140.185
139.939
135.171
134.185
133.452
133.430
133.406
131.908
131.791
131.718
131.526
131.384
131.135
129.638
129.277
129.183
128.476
128.213
127.310
127.245
127.181
125.492
125.449
125.405
120.627
118.122
116.188
77.254
77.000
76.746
21.638
20.908
19.611
F
F
OTs
Chemical Formula: C24H22F2O3S
Exact Mass: 428.1258
Molecular Weight: 428.4938
NO: 3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

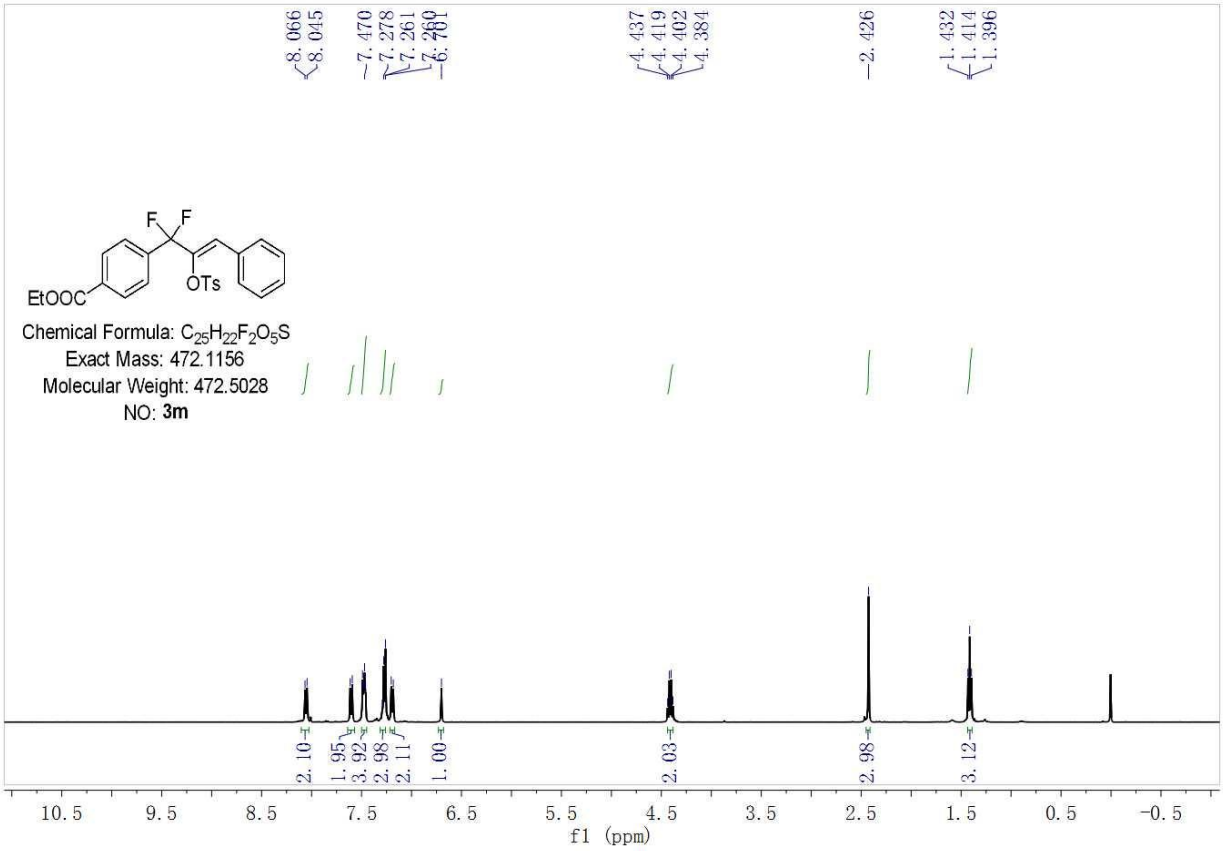
(*Z*)-3-([1,1'-Biphenyl]-2-yl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3l)

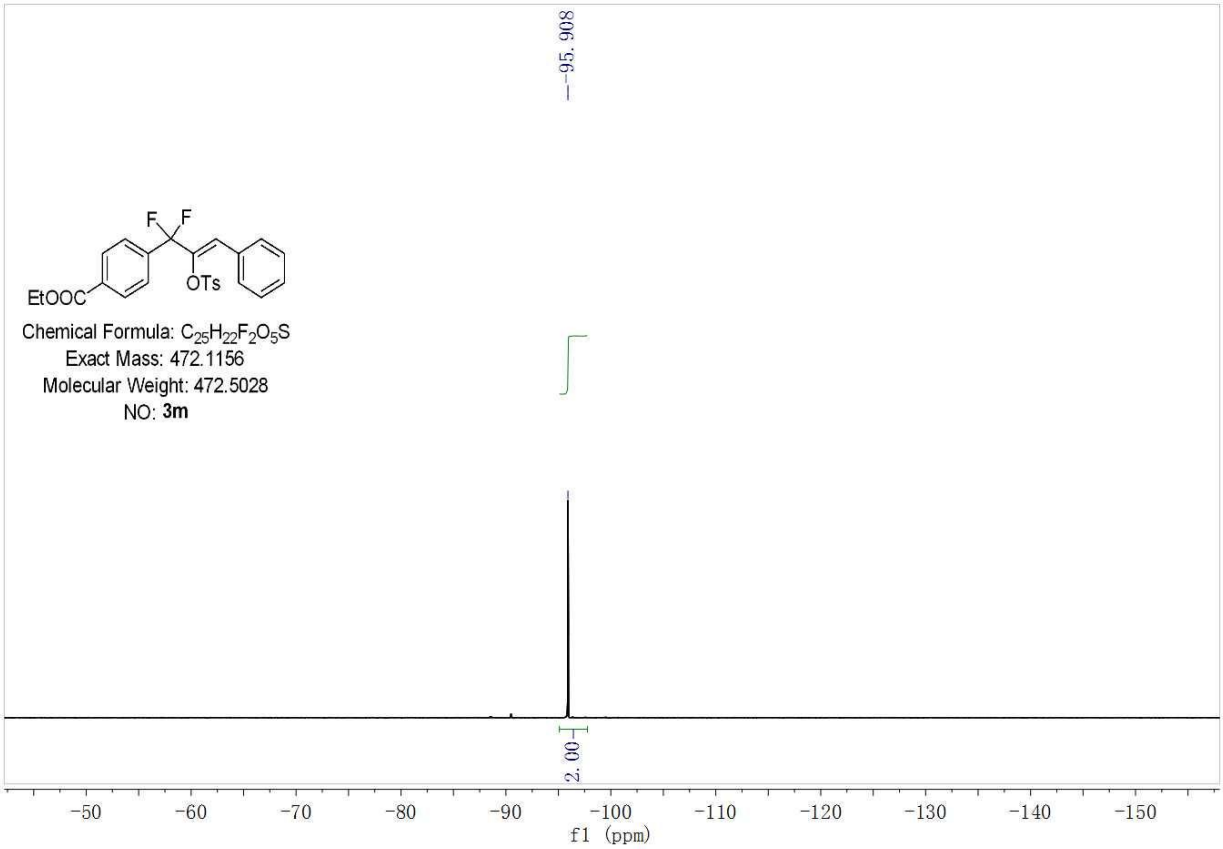


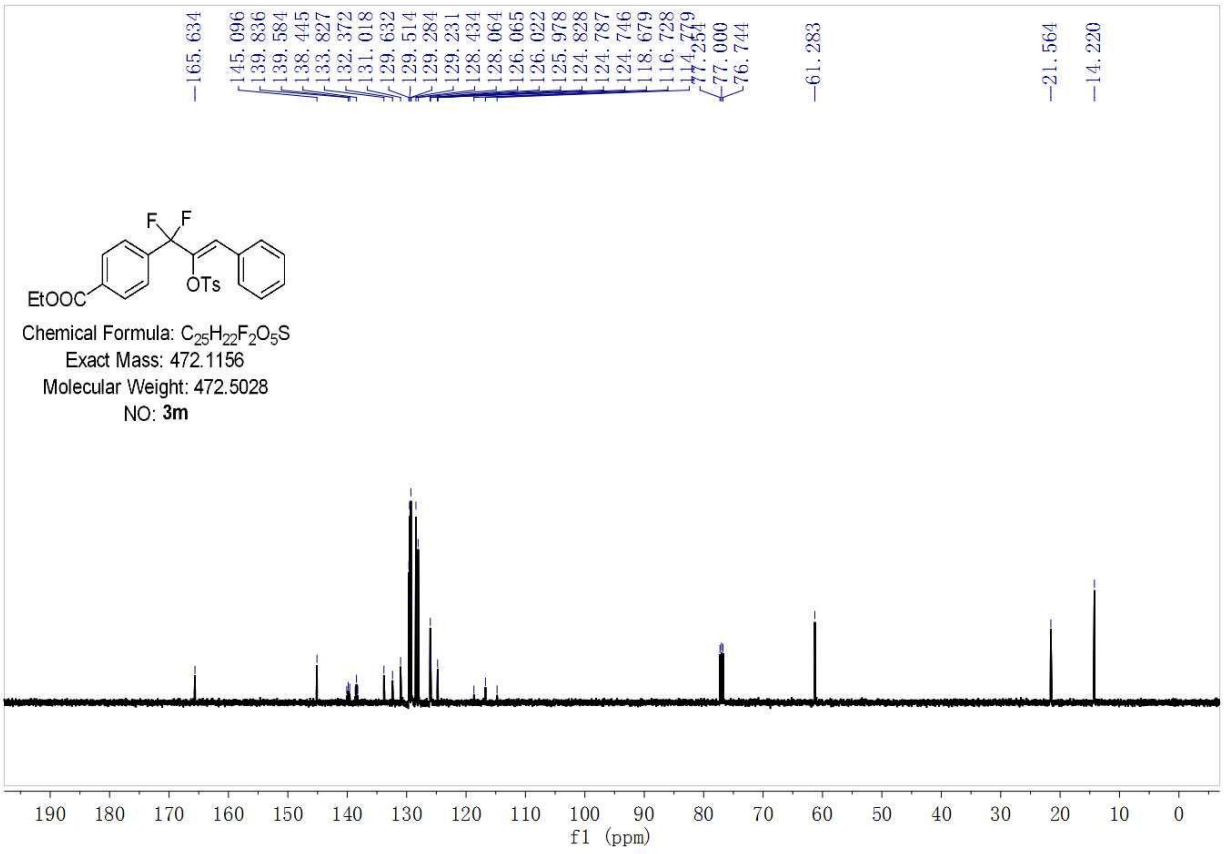




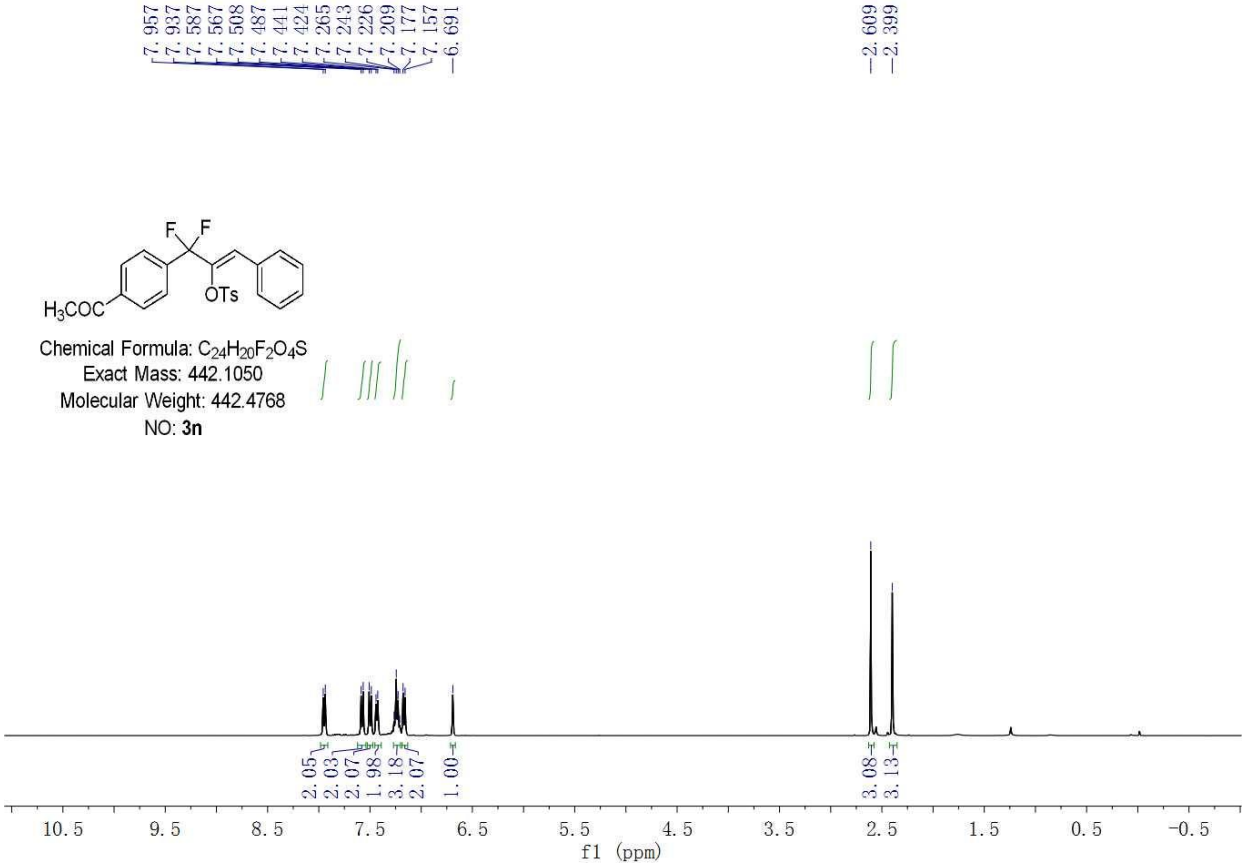
(Z)-Ethyl 4-[1,1-difluoro-3-phenyl-2-(tosyloxy)allyl]benzoate (3m)

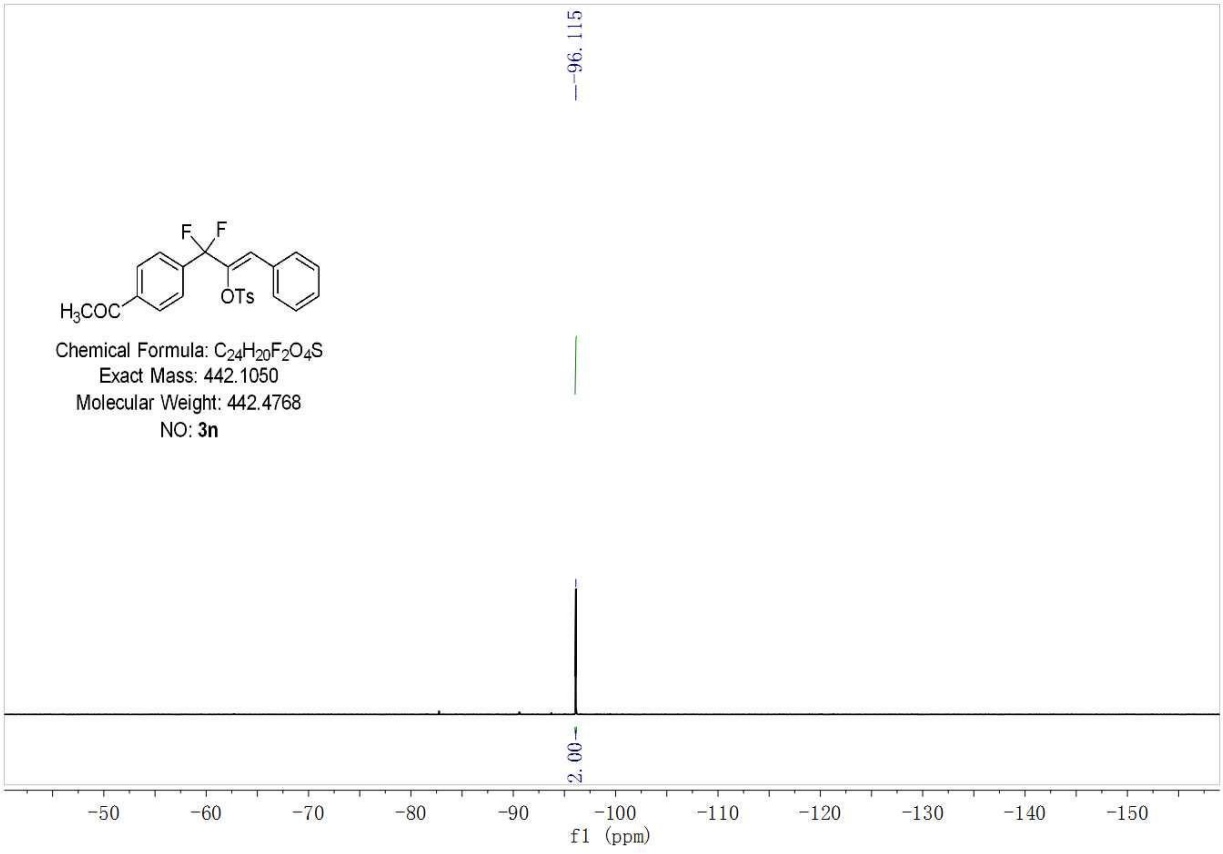


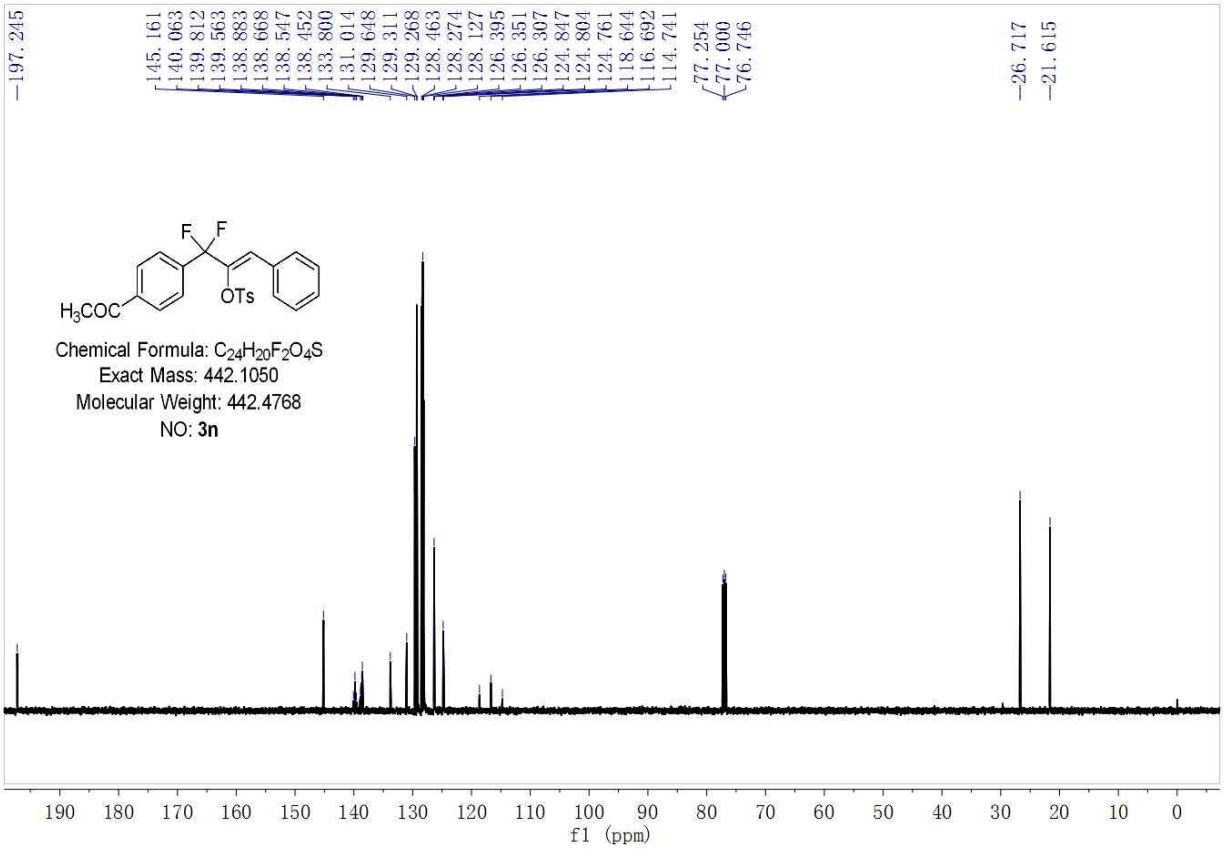

-95.908
F
F
OTs
EtOOC
Chemical Formula: C25H22F2O5S
Exact Mass: 472.1156
Molecular Weight: 472.5028
NO: 3m
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


-165.634
145.096
139.836
139.584
138.445
133.827
132.372
131.018
129.632
129.514
129.284
129.231
128.434
128.064
126.065
126.022
125.978
124.828
124.787
124.746
118.679
116.728
114.779
77.254
77.000
76.744
-61.283
-21.564
-14.220
F
F
OTs
EtOOC
Chemical Formula: C25H22F2O5S
Exact Mass: 472.1156
Molecular Weight: 472.5028
NO: 3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

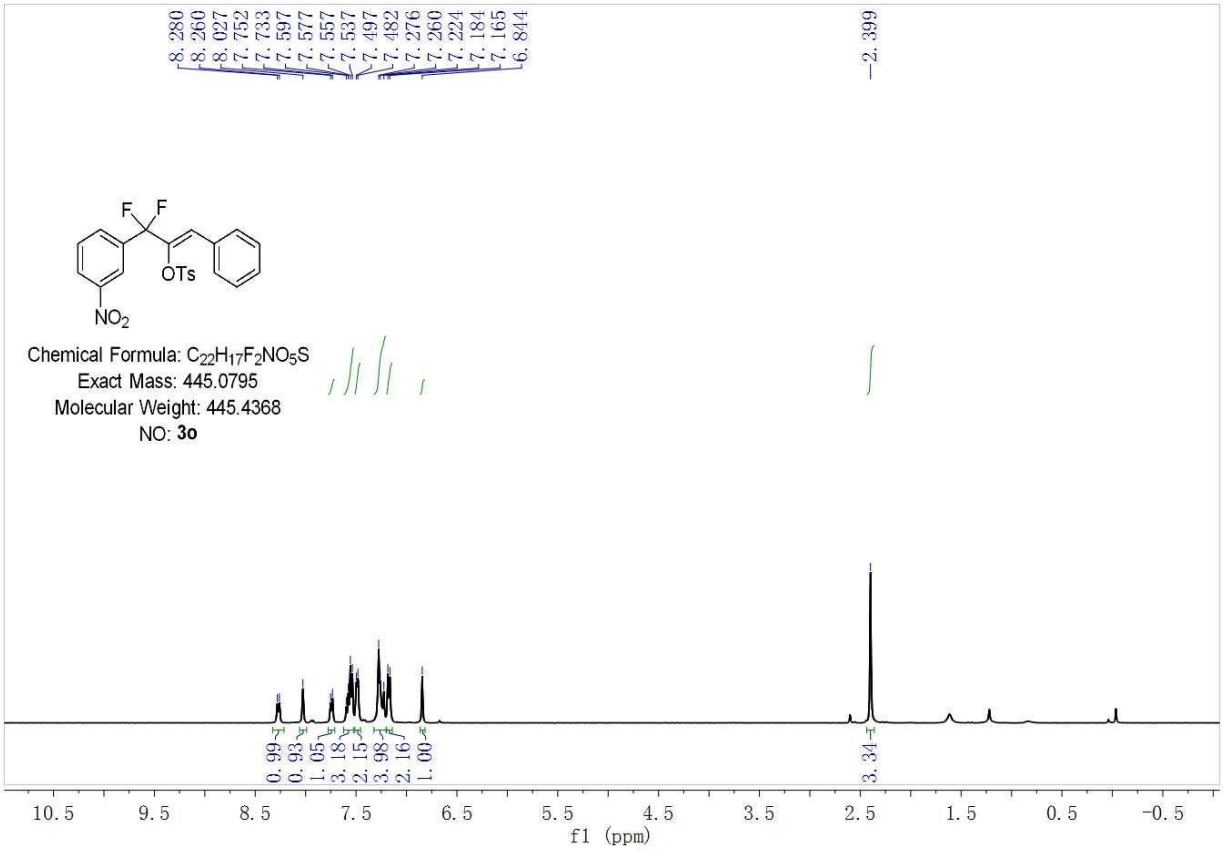
(Z)-3-(4-Acetylphenyl)-3,3-difluoro-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3n)

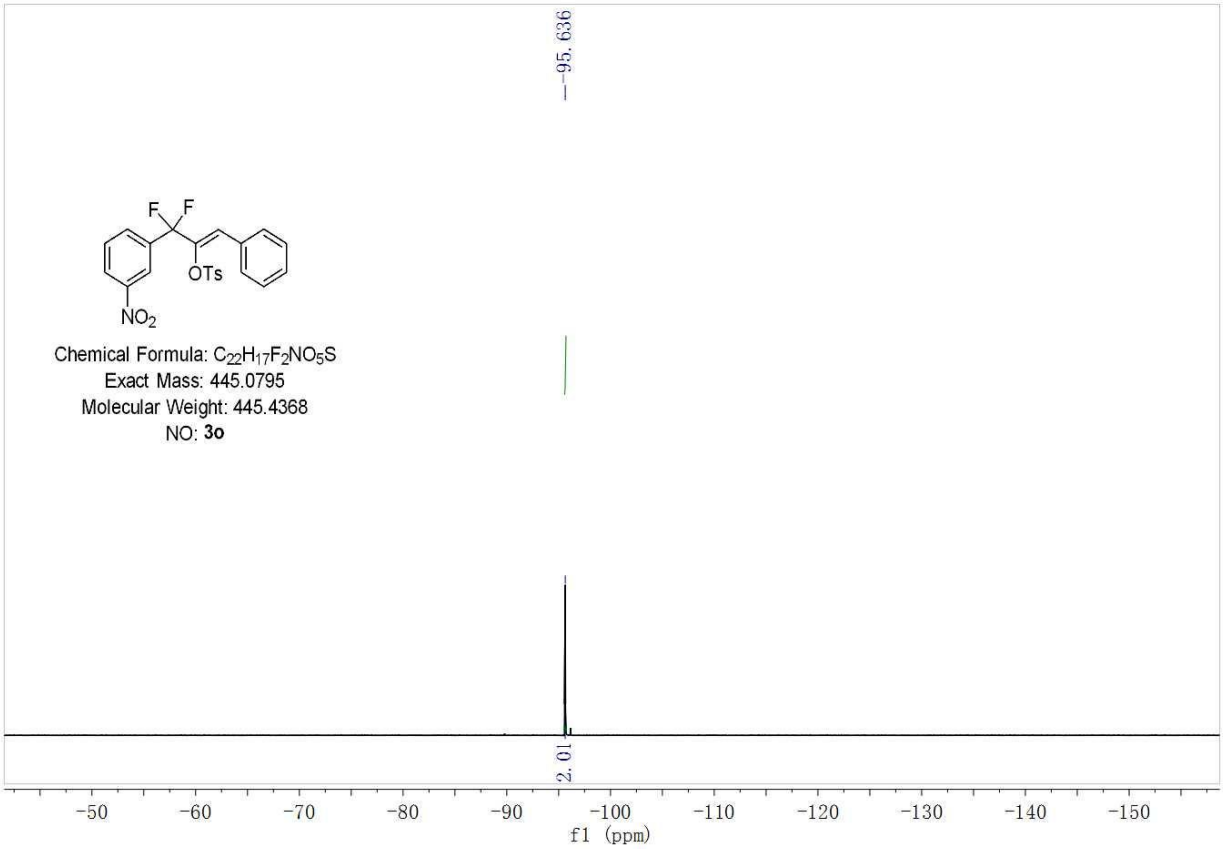


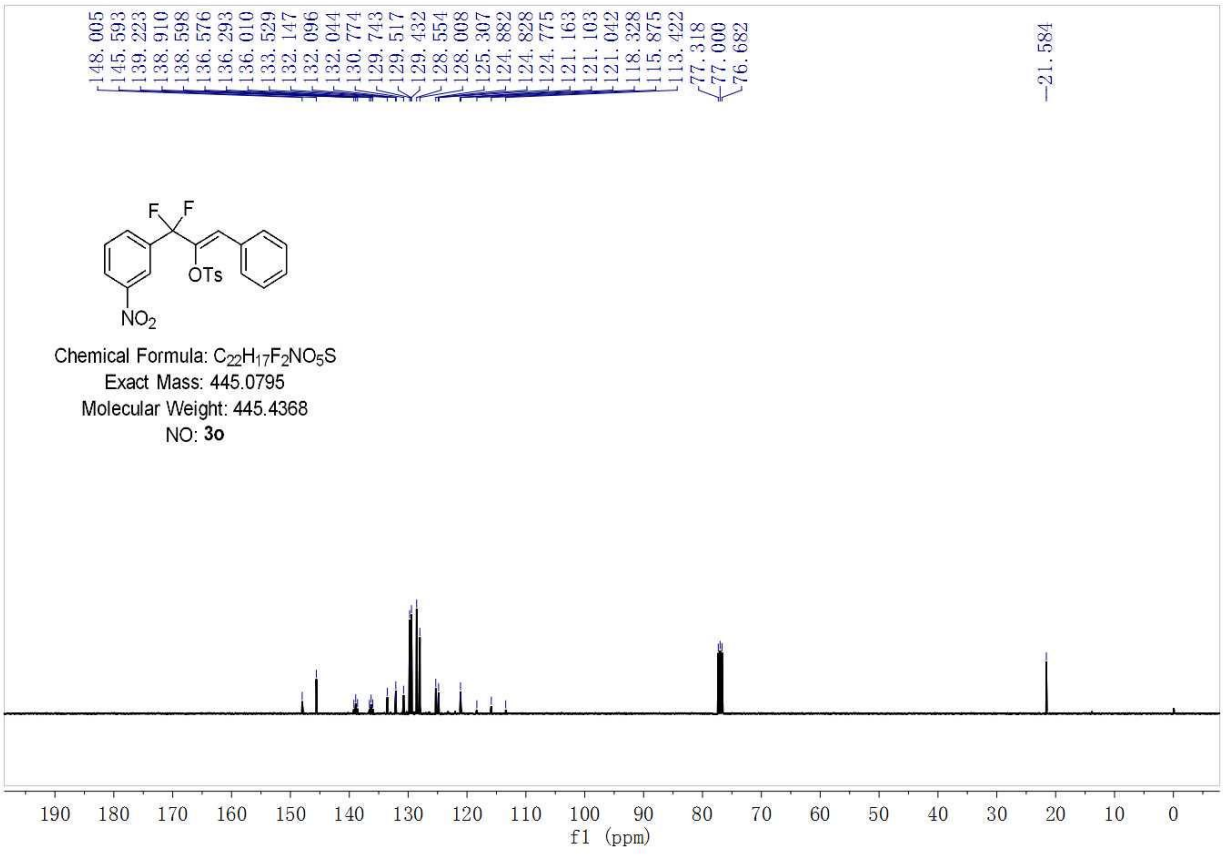




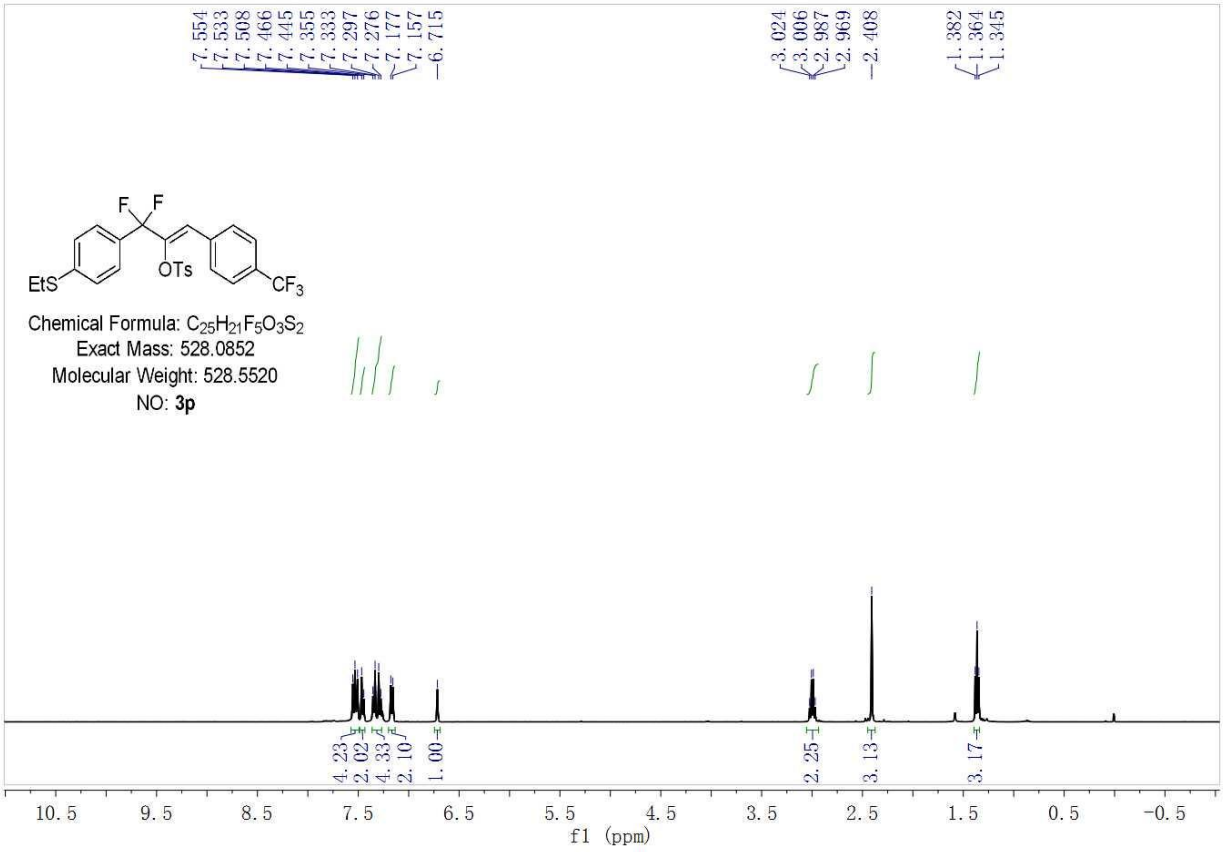
***(Z)*-3,3-Difluoro-3-(3-nitrophenyl)-1-phenylprop-1-en-2-yl-4-methylbenzenesulfonate (3o)**

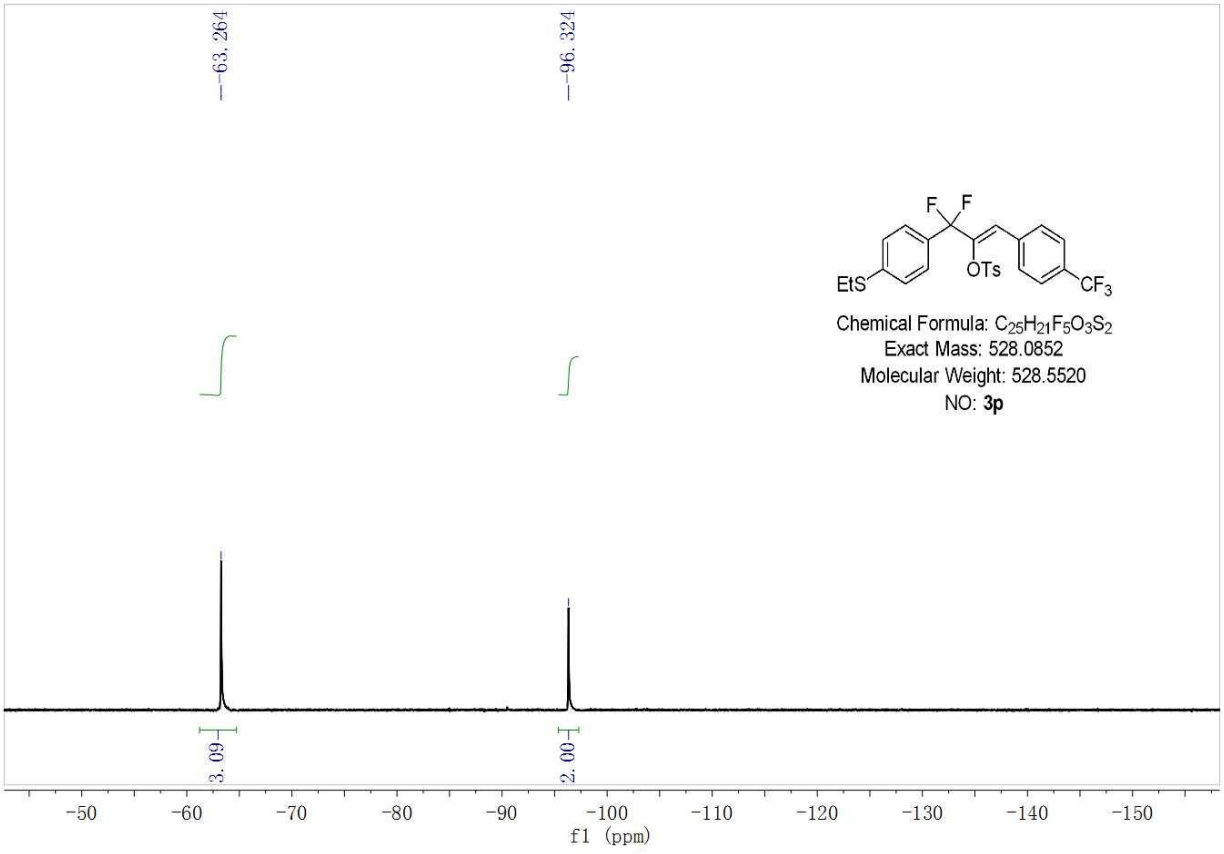


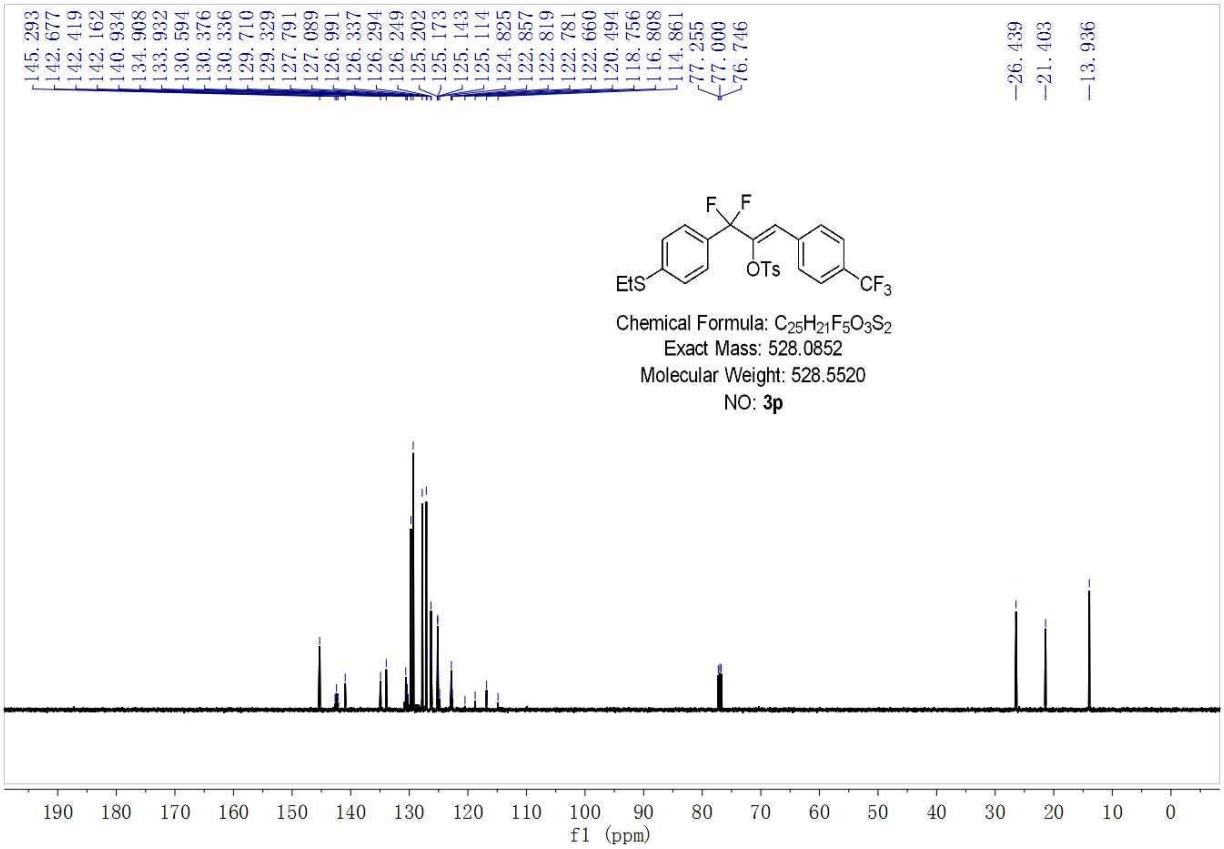

-95.636
F
F
OTs
NO2
Chemical Formula: C22H17F2NO5S
Exact Mass: 445.0795
Molecular Weight: 445.4368
NO: 3o
2.01
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


148.005
145.593
139.223
138.910
138.598
136.576
136.293
136.010
133.529
132.147
132.096
132.044
130.774
129.743
129.517
129.432
128.554
128.008
125.307
124.882
124.828
124.775
121.163
121.103
121.042
118.328
115.875
113.422
77.318
77.000
76.682
-21.584
F
F
OTs
NO2
Chemical Formula: C22H17F2NO5S
Exact Mass: 445.0795
Molecular Weight: 445.4368
NO: 3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

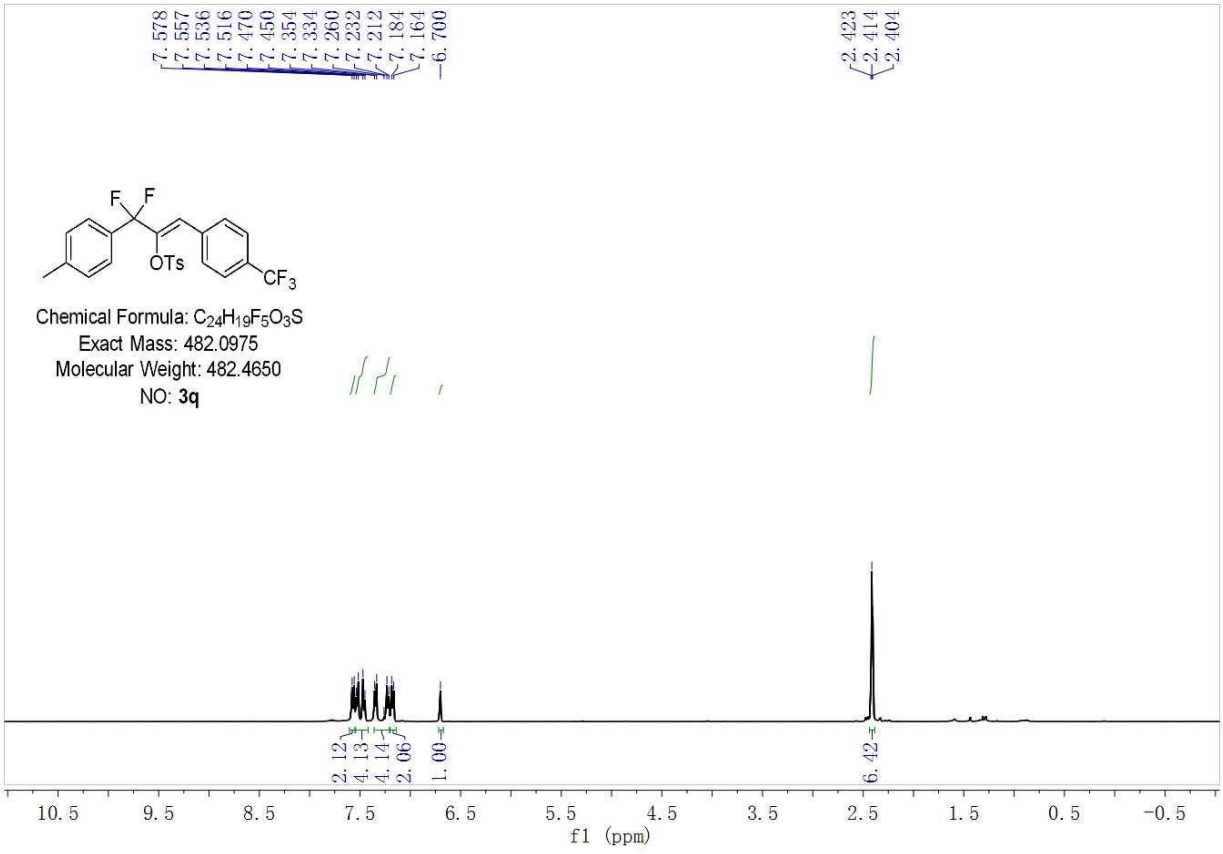
***(Z)*-3-[4-(Ethylthio)phenyl]-3,3-difluoro-1-[4-(trifluoromethyl)phenyl]prop-1-en-2-yl-4-methylbenzenesulfonate (3p)**

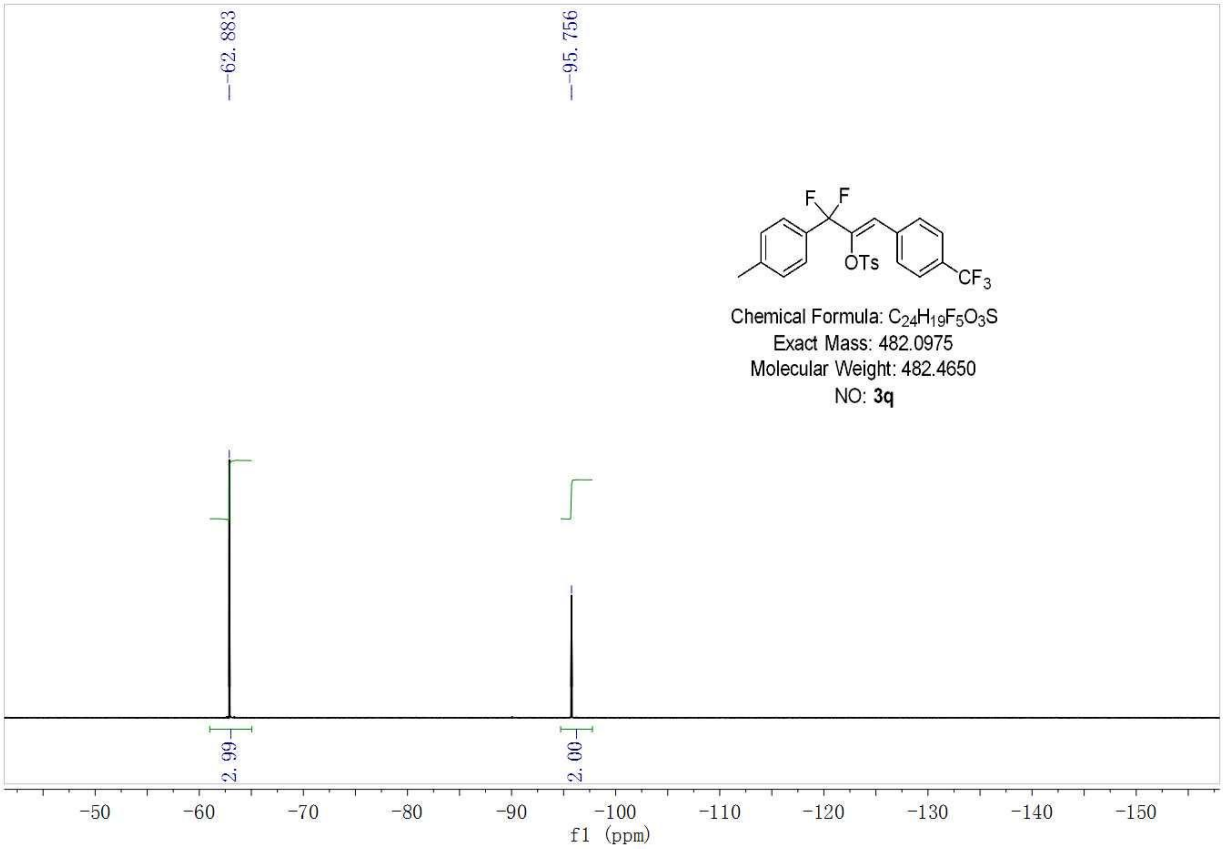


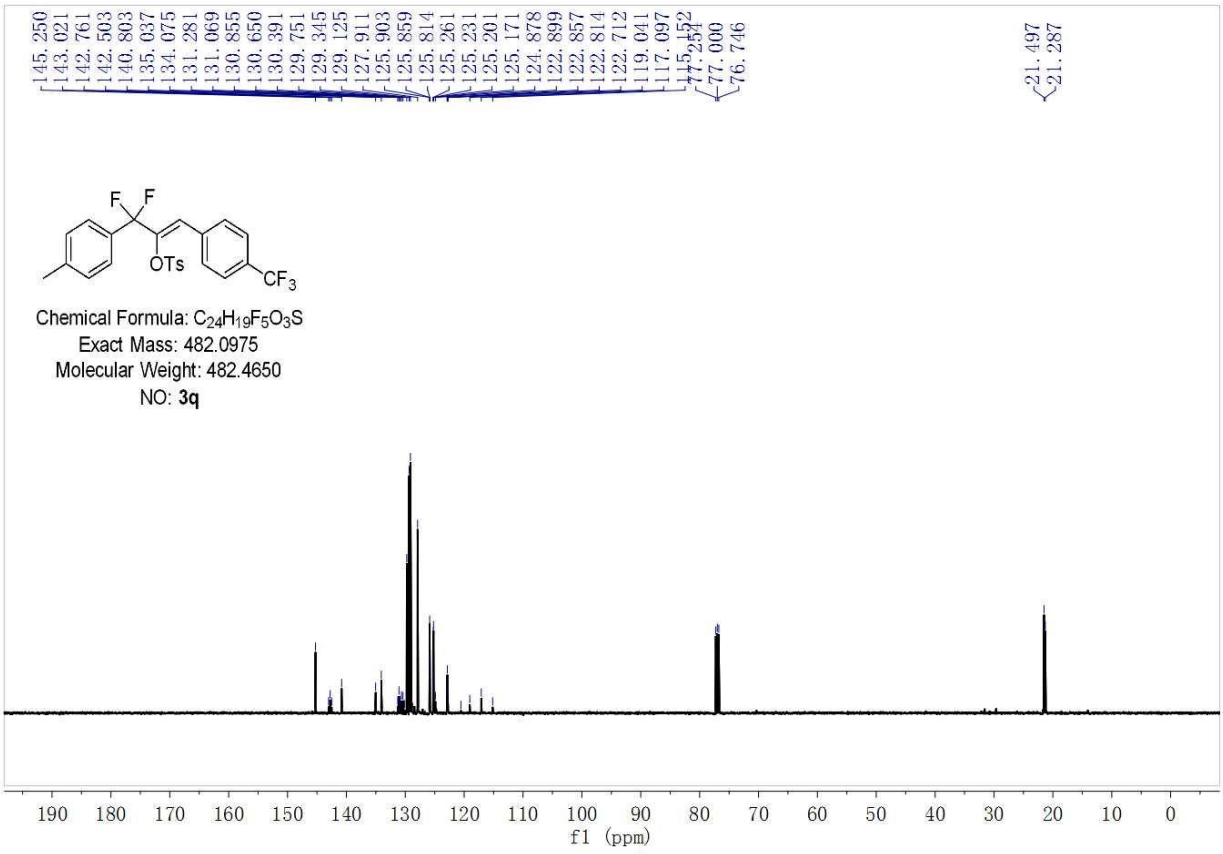




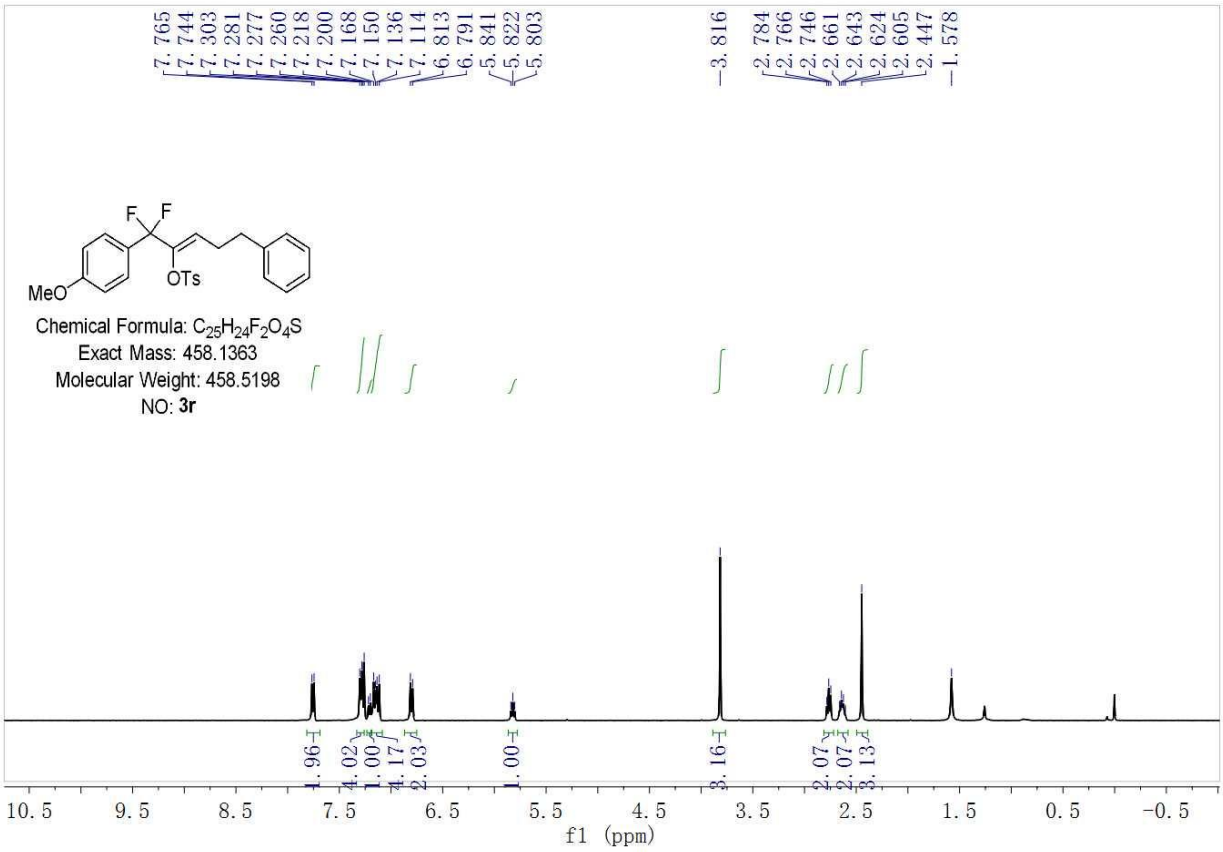
***(Z)*-3,3-Difluoro-3-(p-tolyl)-1-[4-(trifluoromethyl)phenyl]prop-1-en-2-yl-4-methylbenzenesulfonate (3q)**

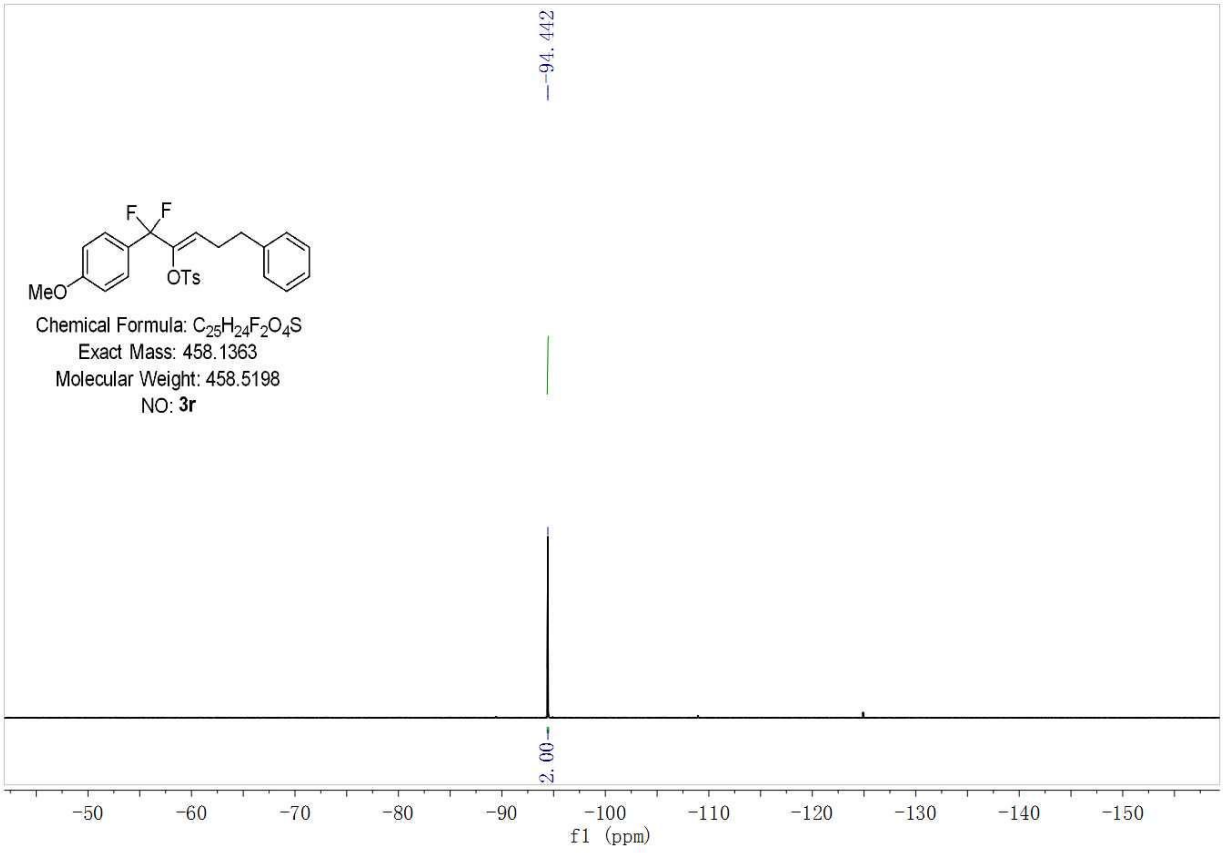


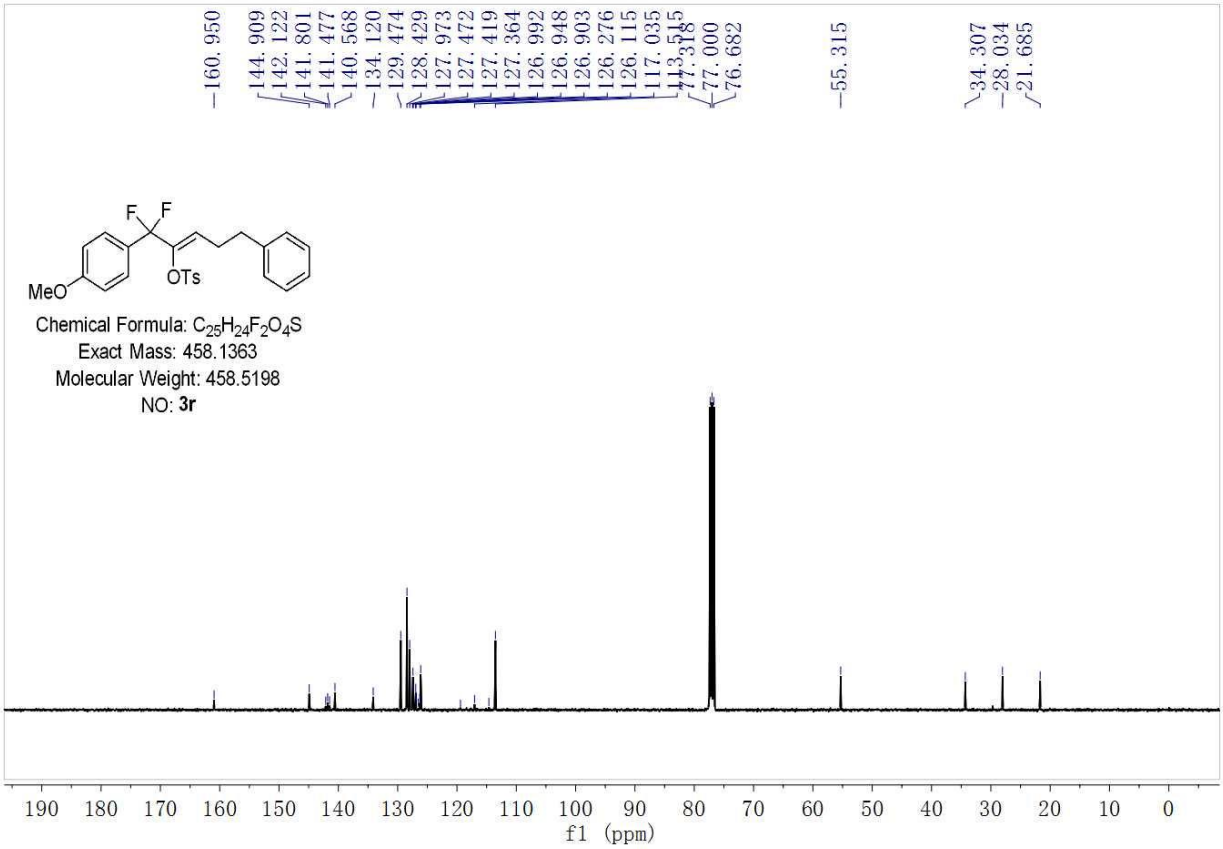

-62.883
-95.756
F
F
OTs
CF3
Chemical Formula: C24H19F5O3S
Exact Mass: 482.0975
Molecular Weight: 482.4650
NO: 3q
2.99
2.00
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


145.250
143.021
142.761
142.503
140.803
135.037
134.075
131.281
131.069
130.855
130.650
130.391
129.751
129.345
129.125
127.911
125.903
125.859
125.814
125.261
125.231
125.201
125.171
124.878
122.899
122.857
122.814
122.712
119.041
117.097
77.254
77.000
76.746
21.497
21.287
F
F
OTs
CF3
Chemical Formula: C24H19F5O3S
Exact Mass: 482.0975
Molecular Weight: 482.4650
NO: 3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

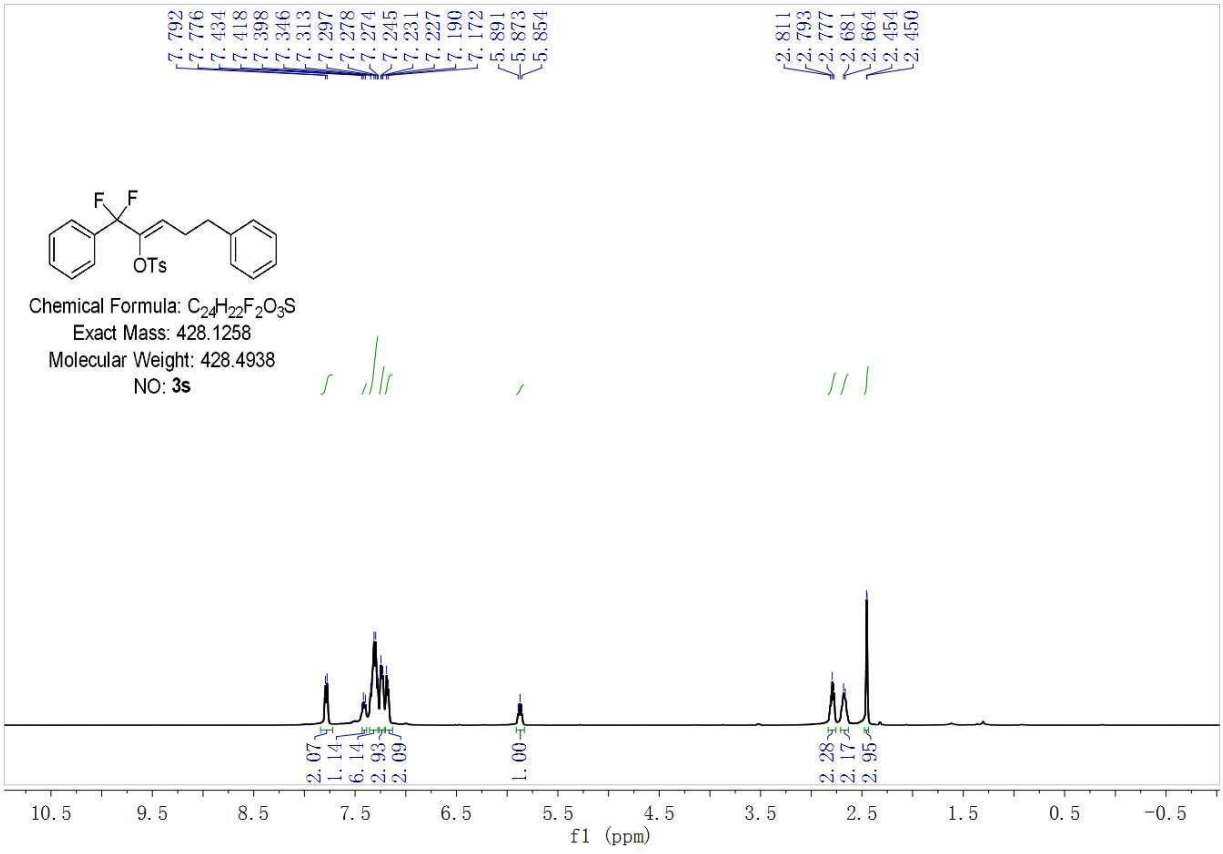
(Z)-1,1-Difluoro-1-(4-methoxyphenyl)-5-phenylpent-2-en-2-yl-4-methylbenzenesulfonate (3r)

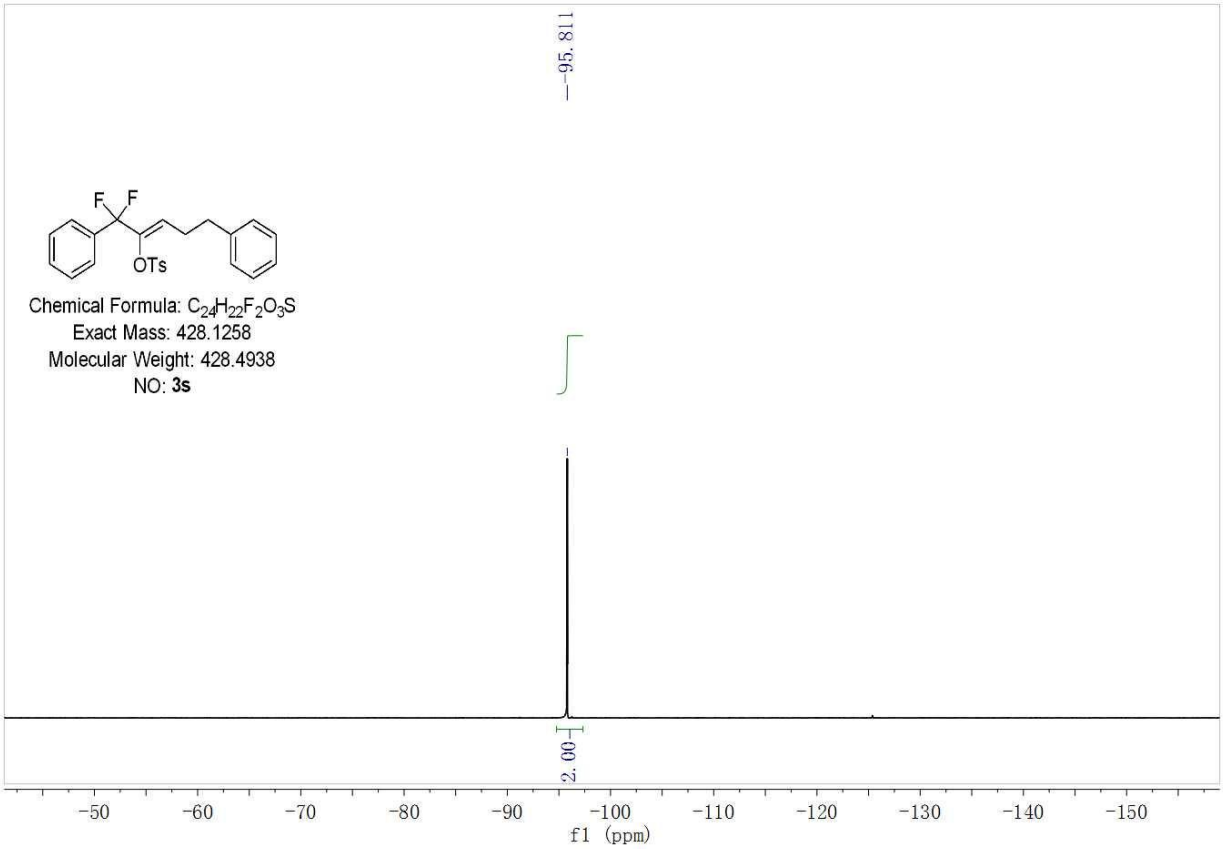


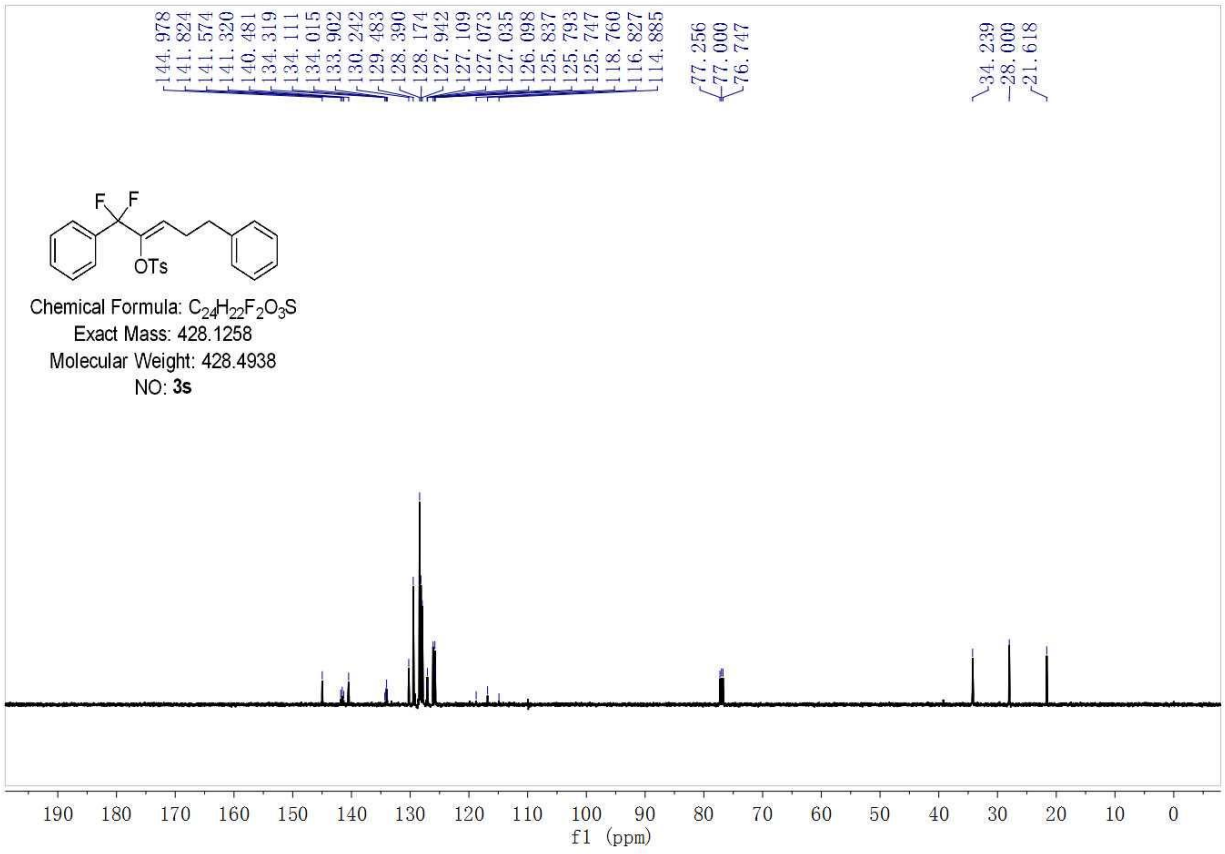




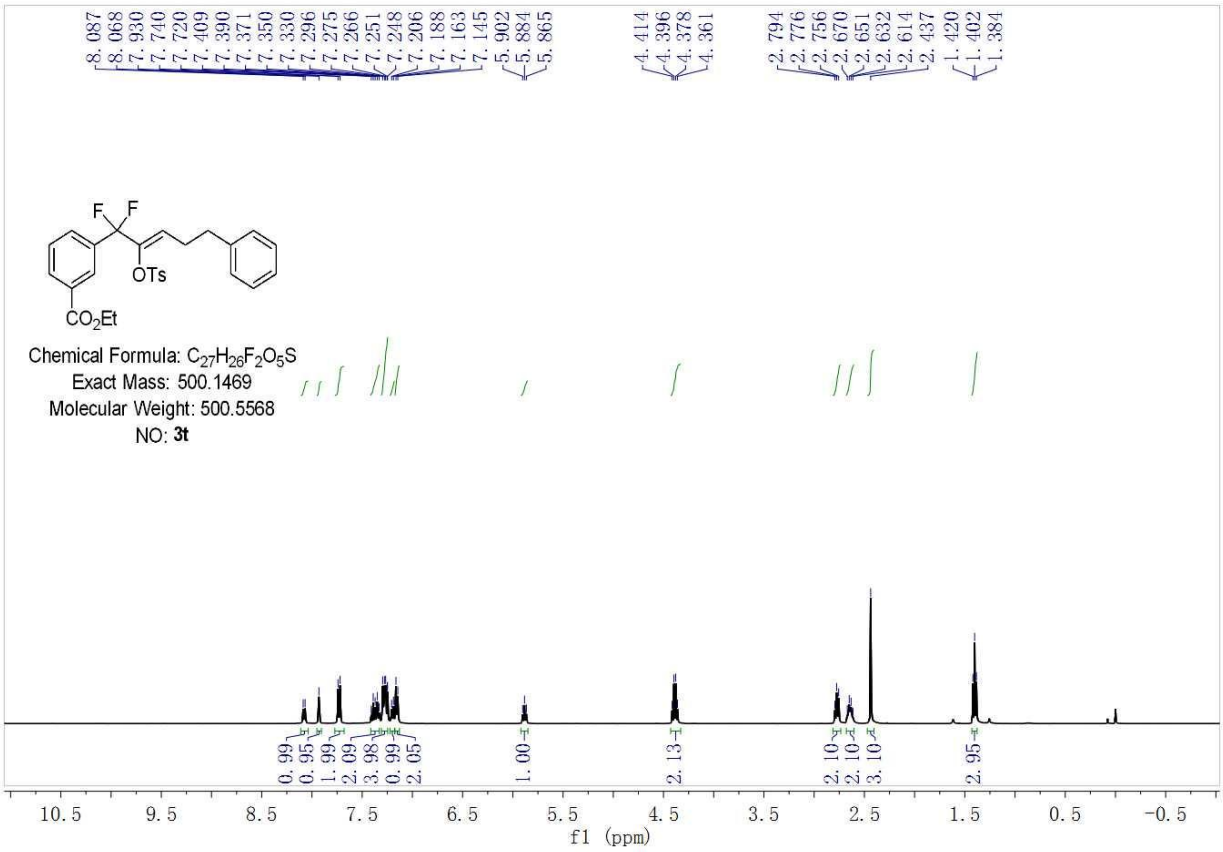
***(Z)*-1,1-Difluoro-1,5-diphenylpent-2-en-2-yl-4-methylbenzenesulfonate (3s)**

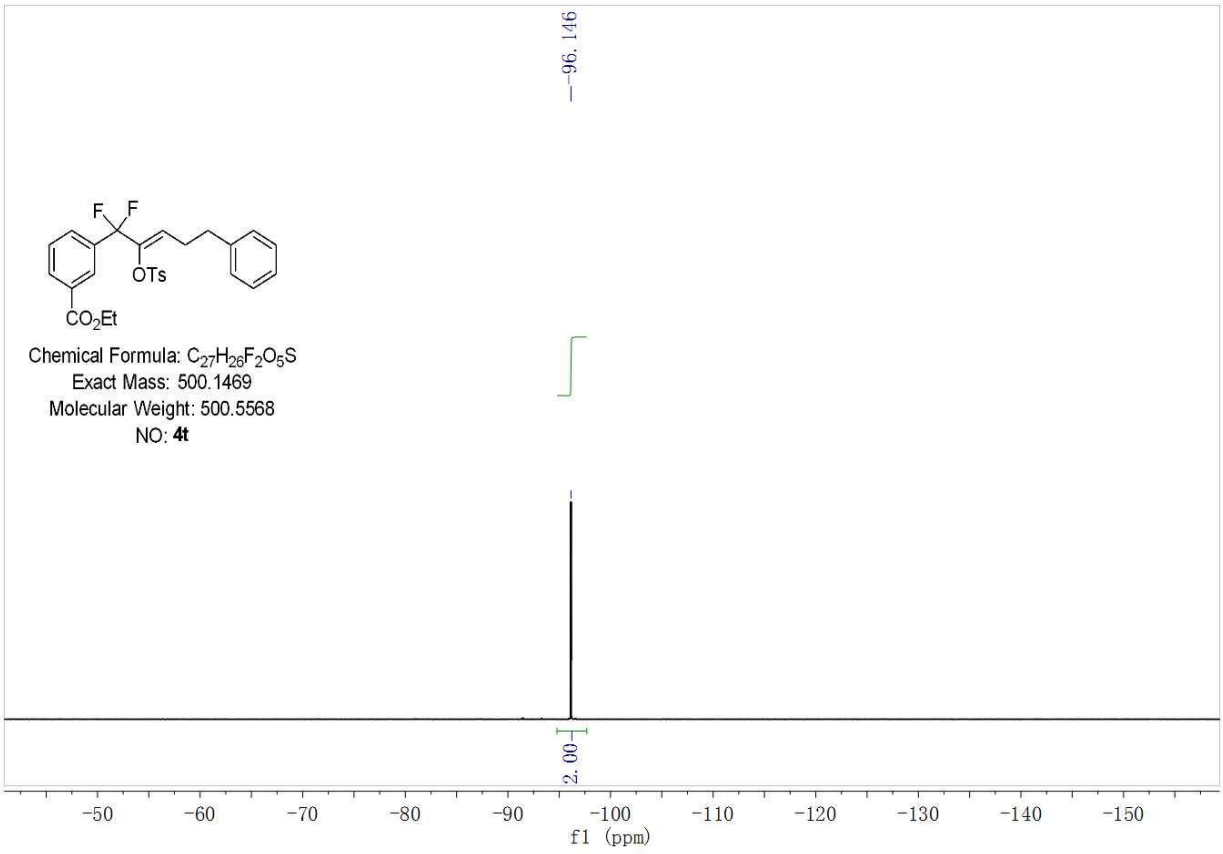


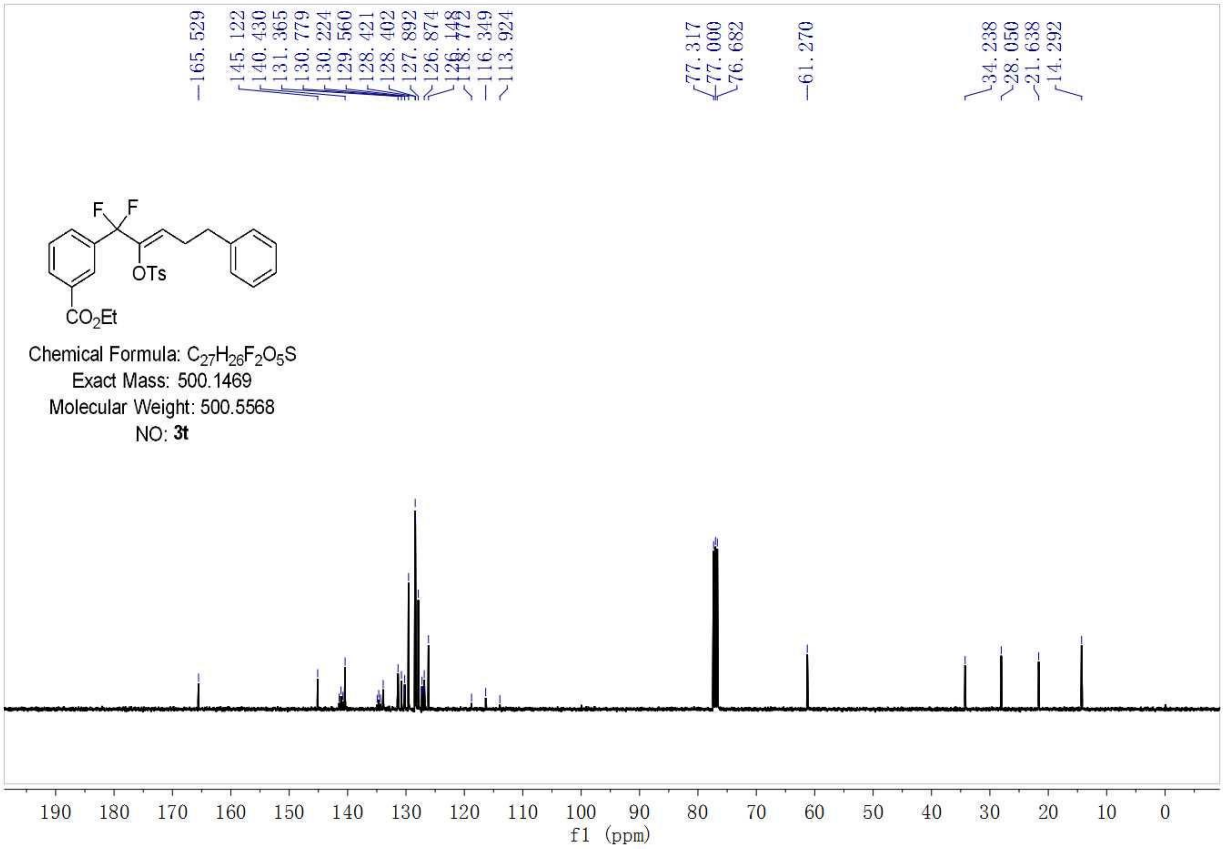

-95.811
F F
OTs
Chemical Formula: C24H22F2O3S
Exact Mass: 428.1258
Molecular Weight: 428.4938
NO: 3s
2.00
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


144.978
141.824
141.574
141.320
140.481
134.319
134.111
134.015
133.902
130.242
129.483
128.390
128.174
127.942
127.109
127.073
127.035
126.098
125.837
125.793
125.747
118.760
116.827
114.885
77.256
77.000
76.747
34.239
28.000
21.618
F F
OTs
Chemical Formula: C24H22F2O3S
Exact Mass: 428.1258
Molecular Weight: 428.4938
NO: 3s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

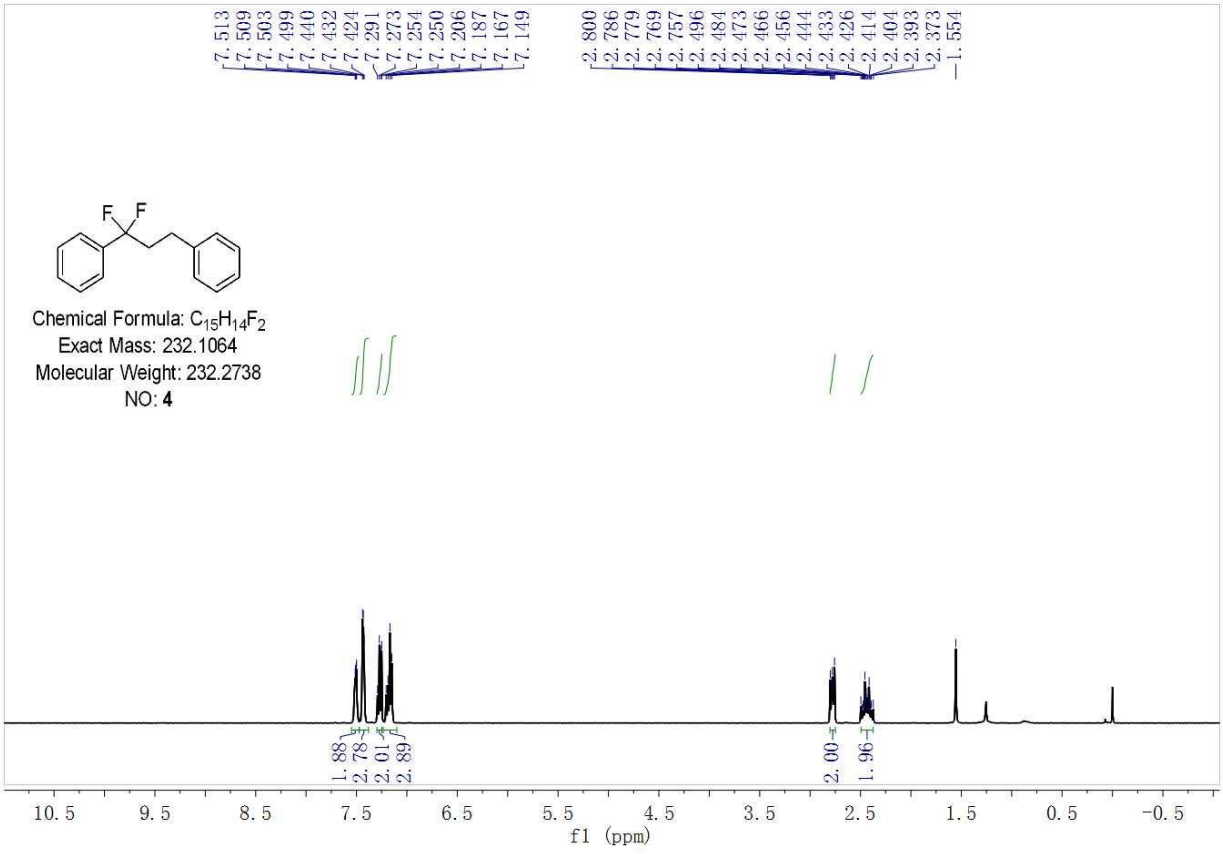
(Z)-Ethyl-3-(1,1-difluoro-5-phenyl-2-(tosyloxy)pent-2-en-1-yl)benzoate (3t)

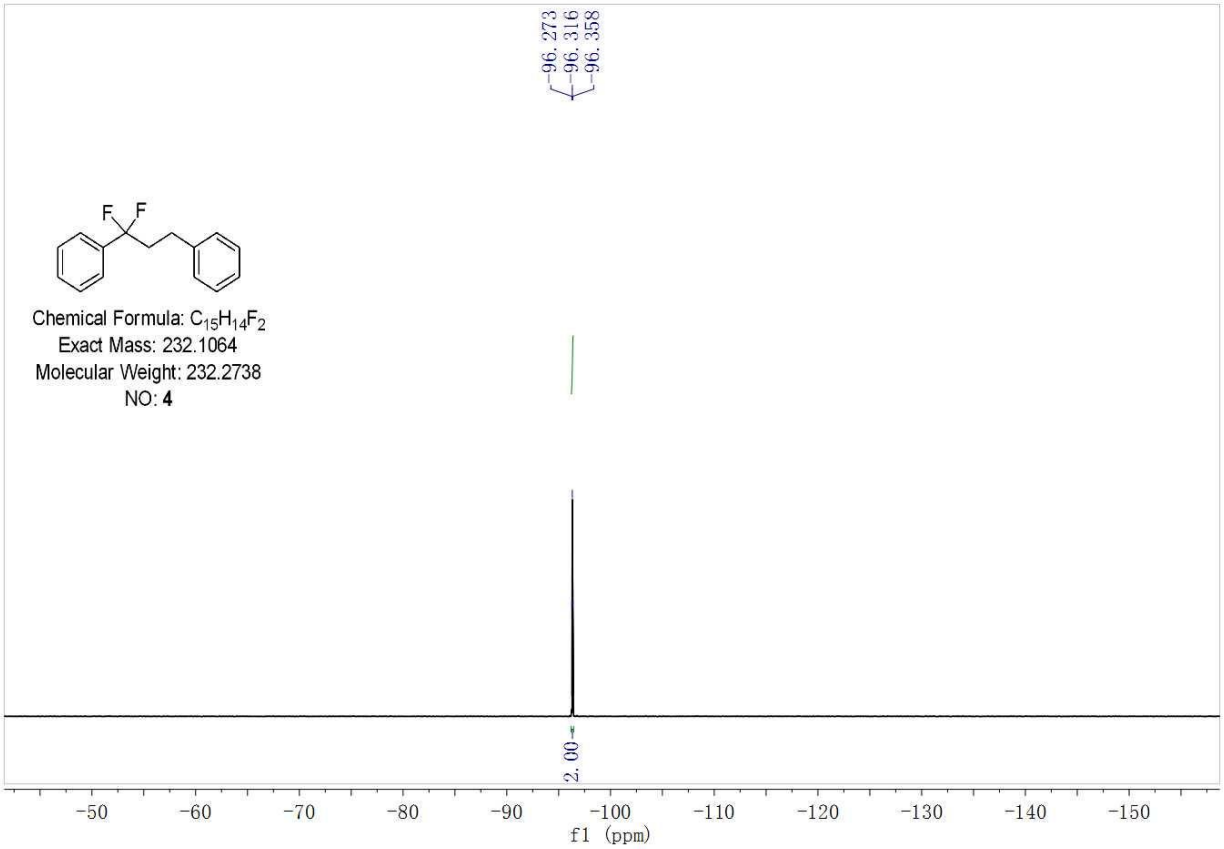


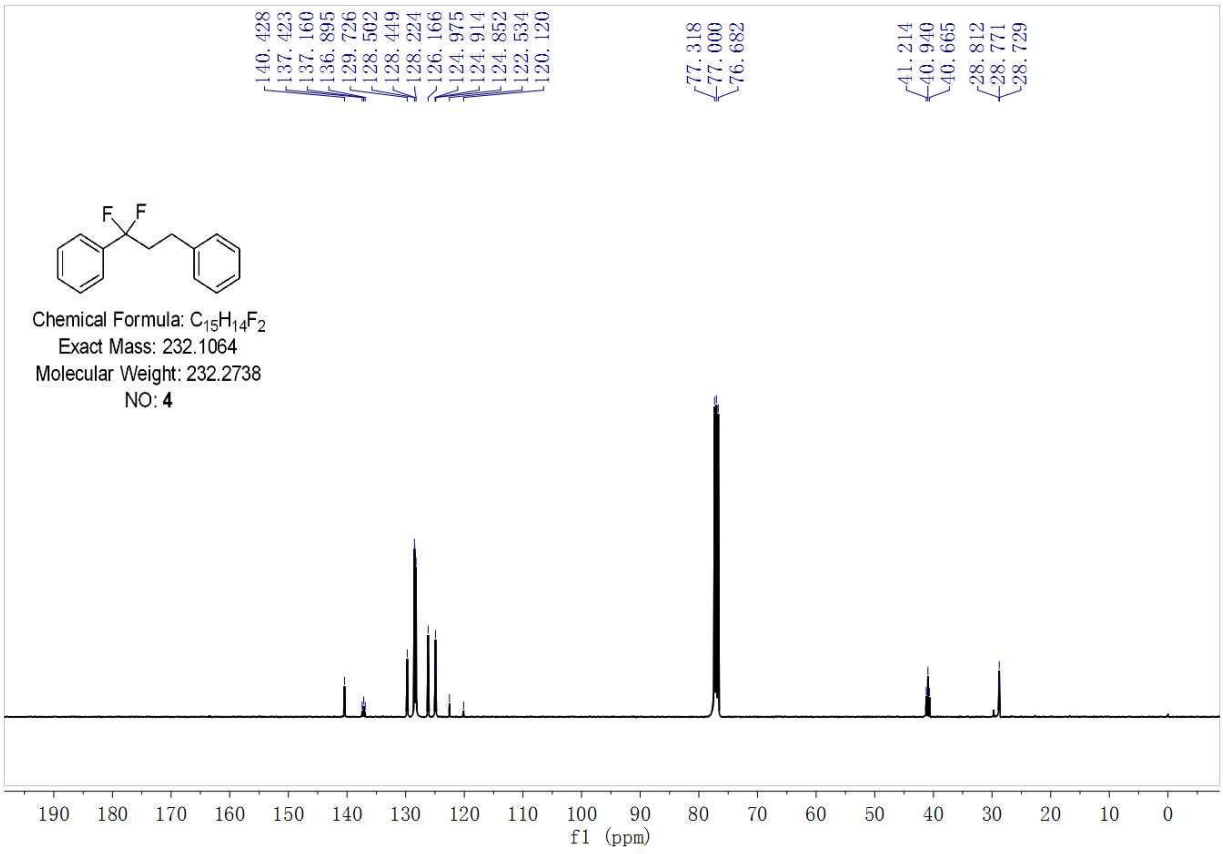




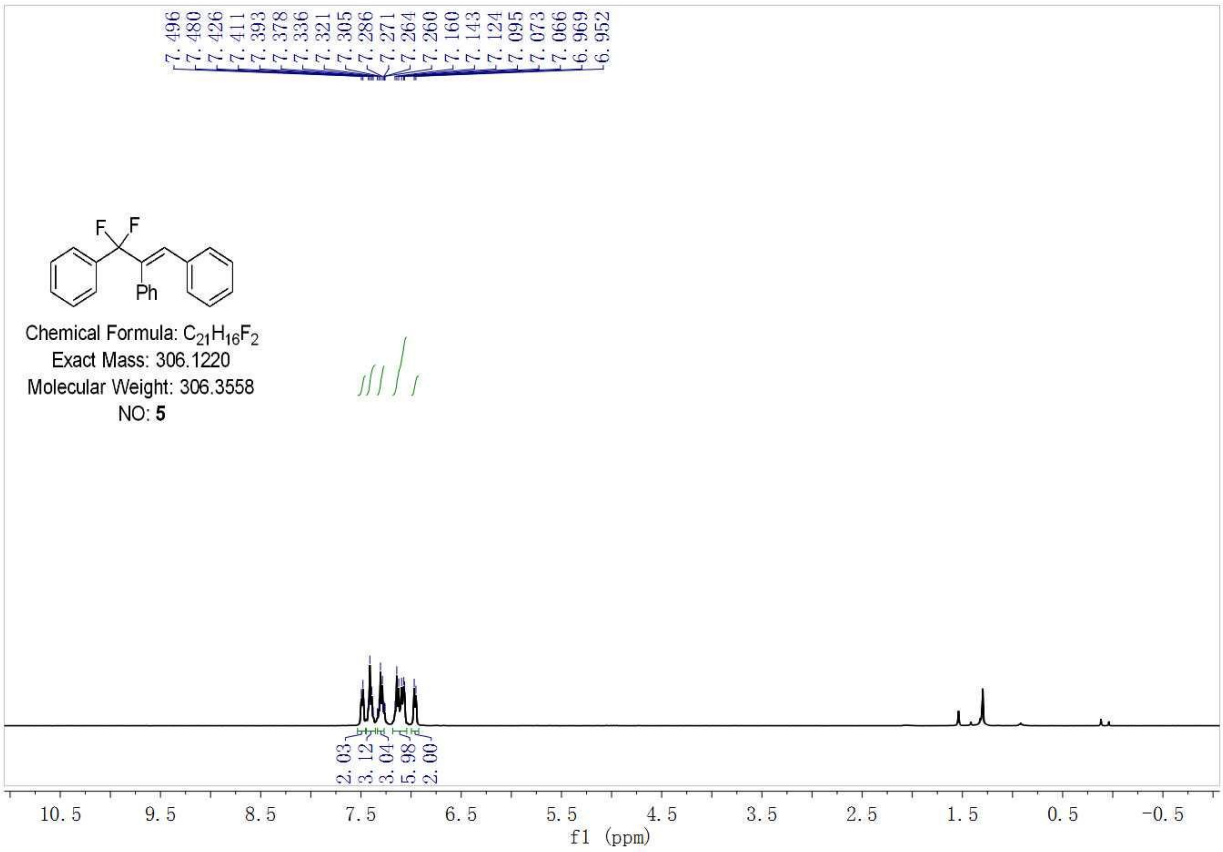
(1,1-Difluoropropane-1,3-diyl)dibenzene (4)

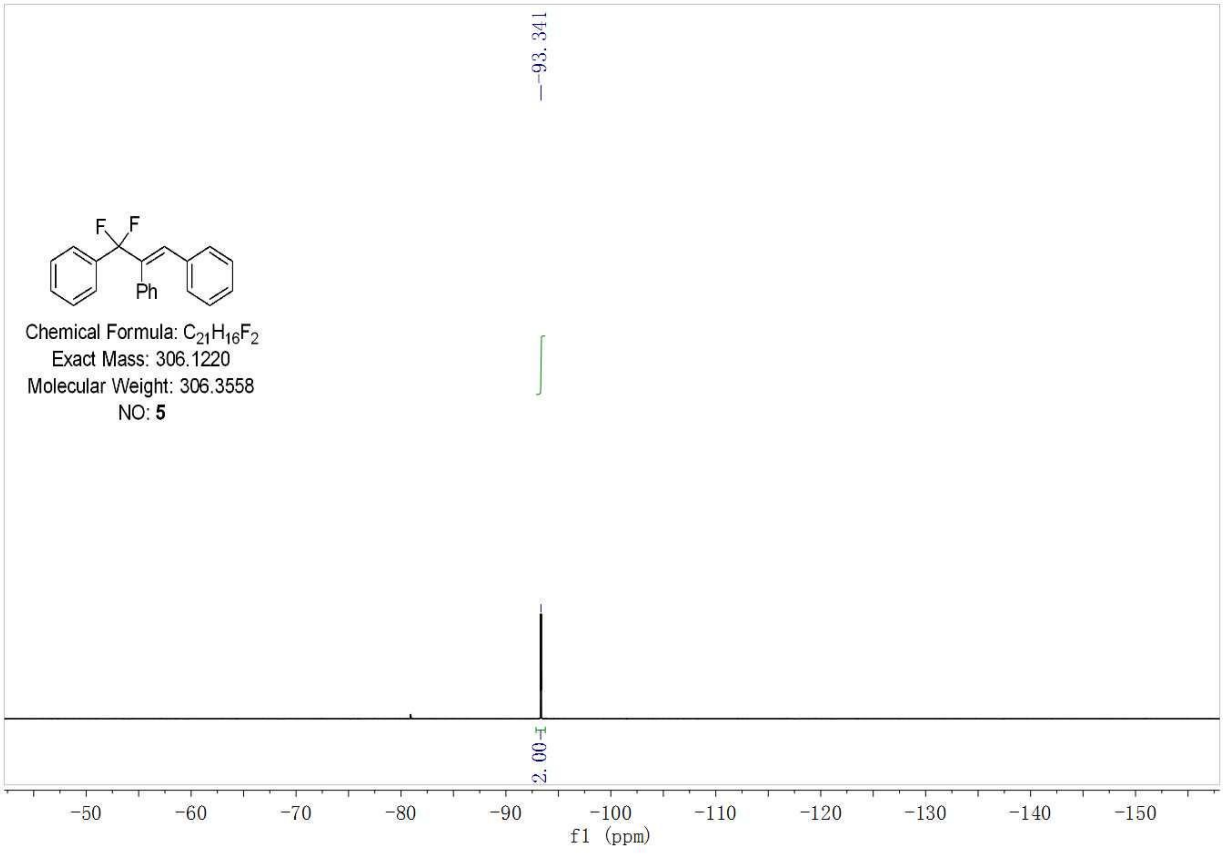


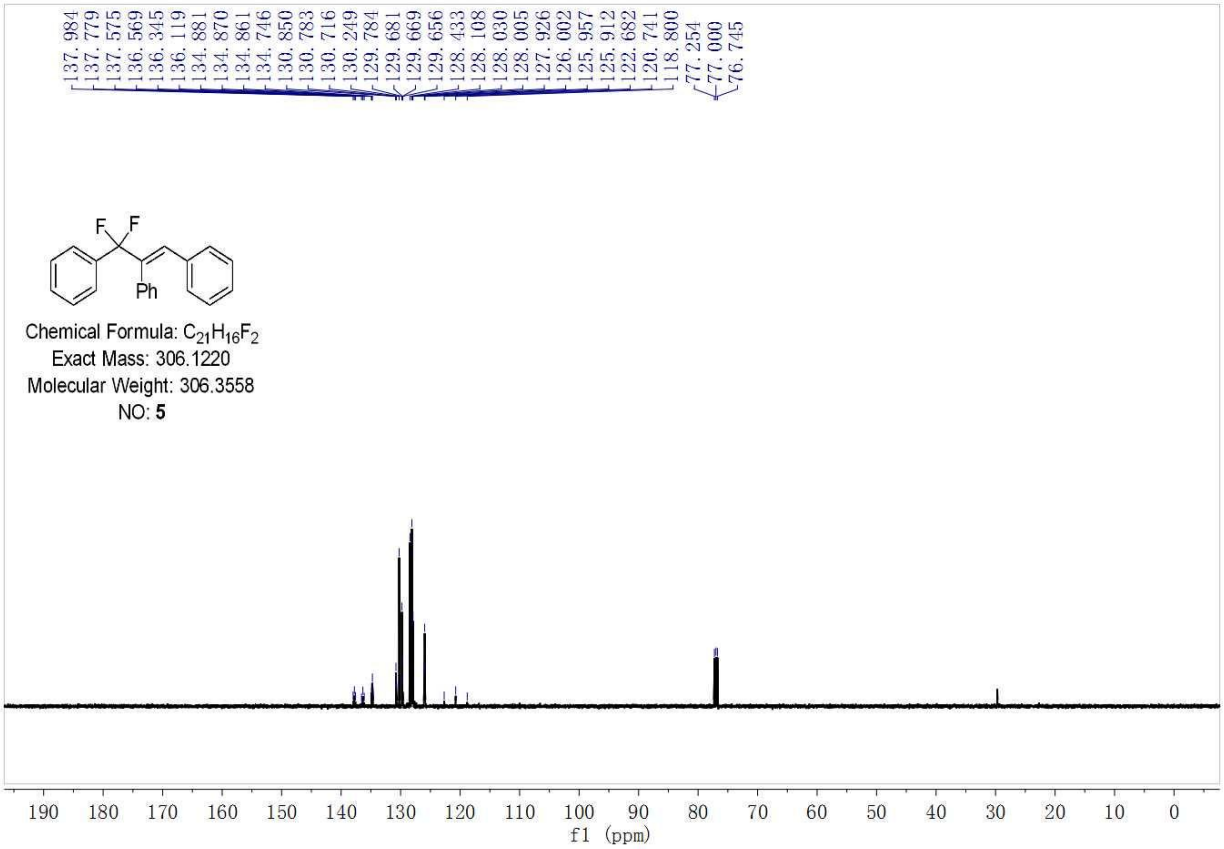

96.273
96.316
96.358
F F
Chemical Formula: C15H14F2
Exact Mass: 232.1064
Molecular Weight: 232.2738
NO: 4
2.00
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


140.428
137.423
137.160
136.895
129.726
128.502
128.449
128.224
126.166
124.975
124.914
124.852
122.534
120.120
77.318
77.000
76.682
41.214
40.940
40.665
28.812
28.771
28.729
F F
Chemical Formula: C15H14F2
Exact Mass: 232.1064
Molecular Weight: 232.2738
NO: 4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

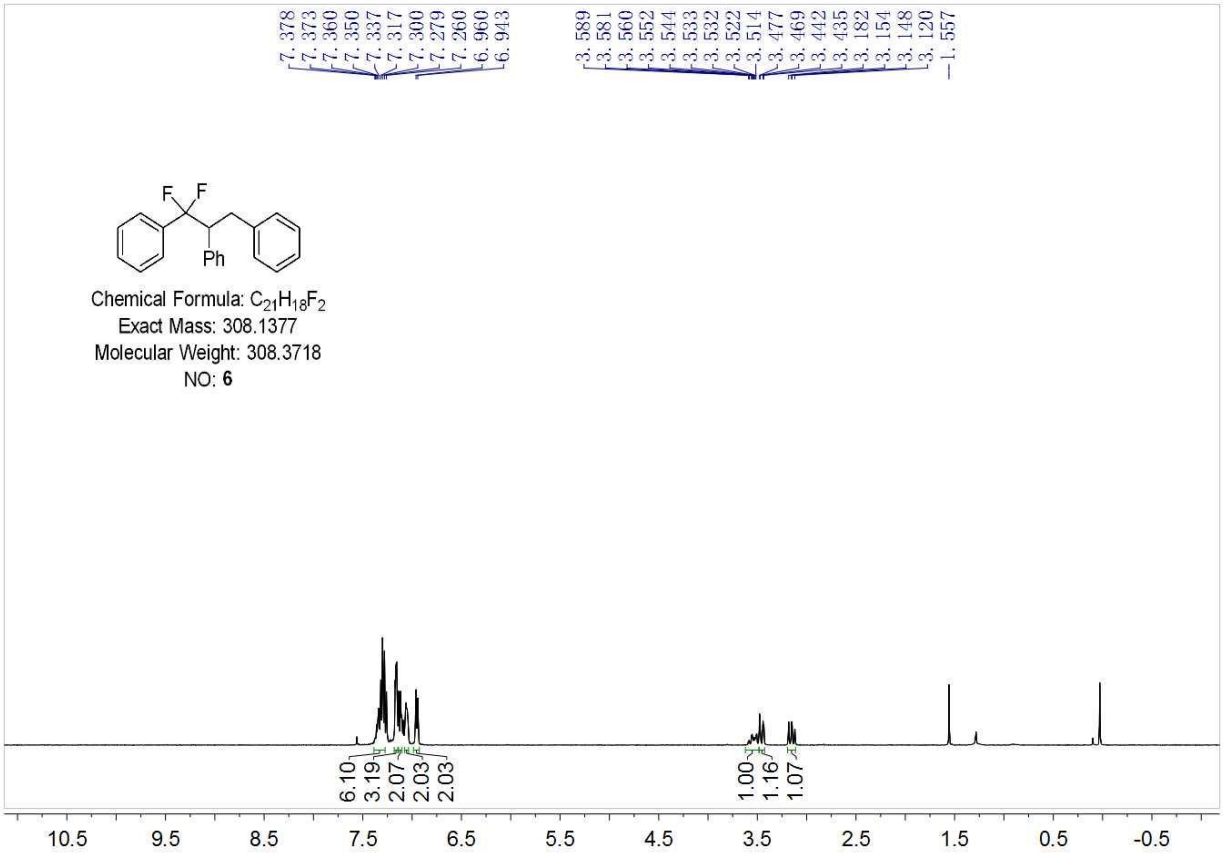
(E)-(3,3-Difluoroprop-1-ene-1,2,3-triyl)tribenzene (5)

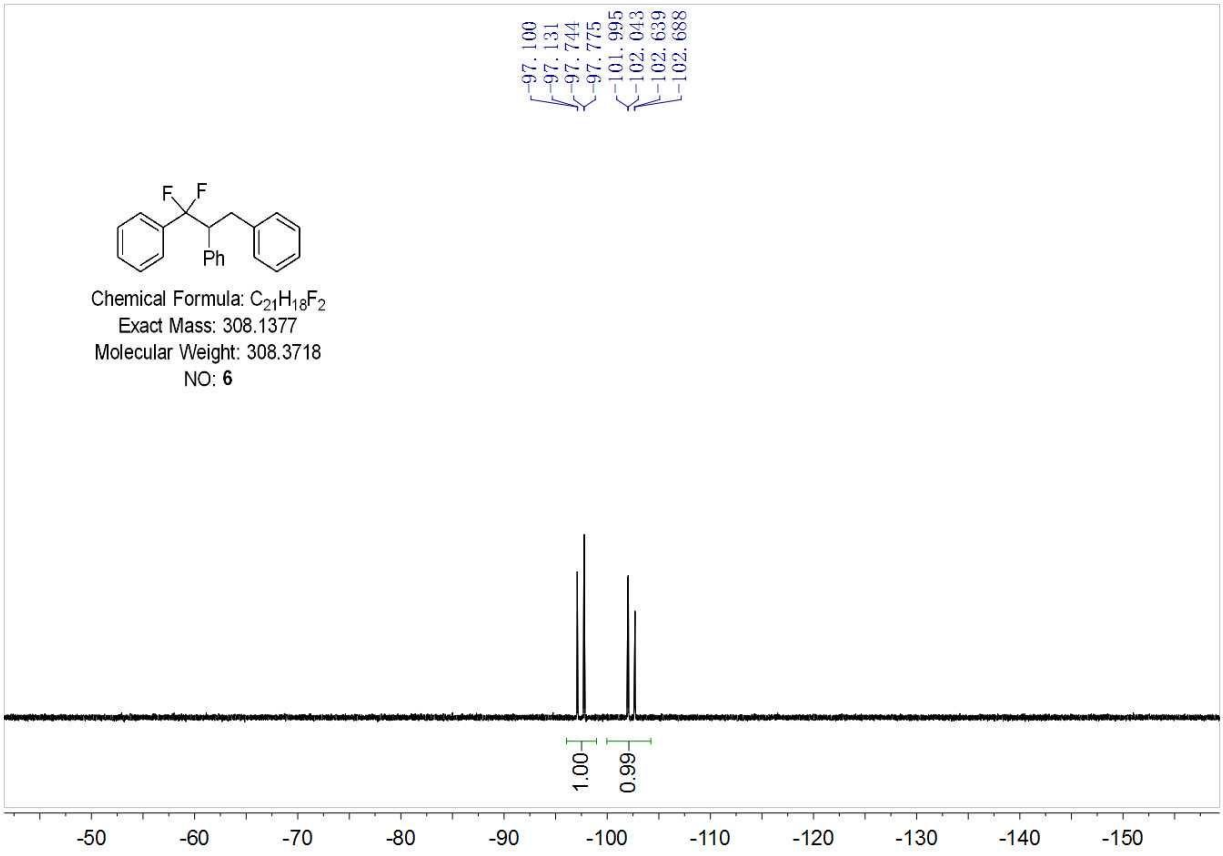


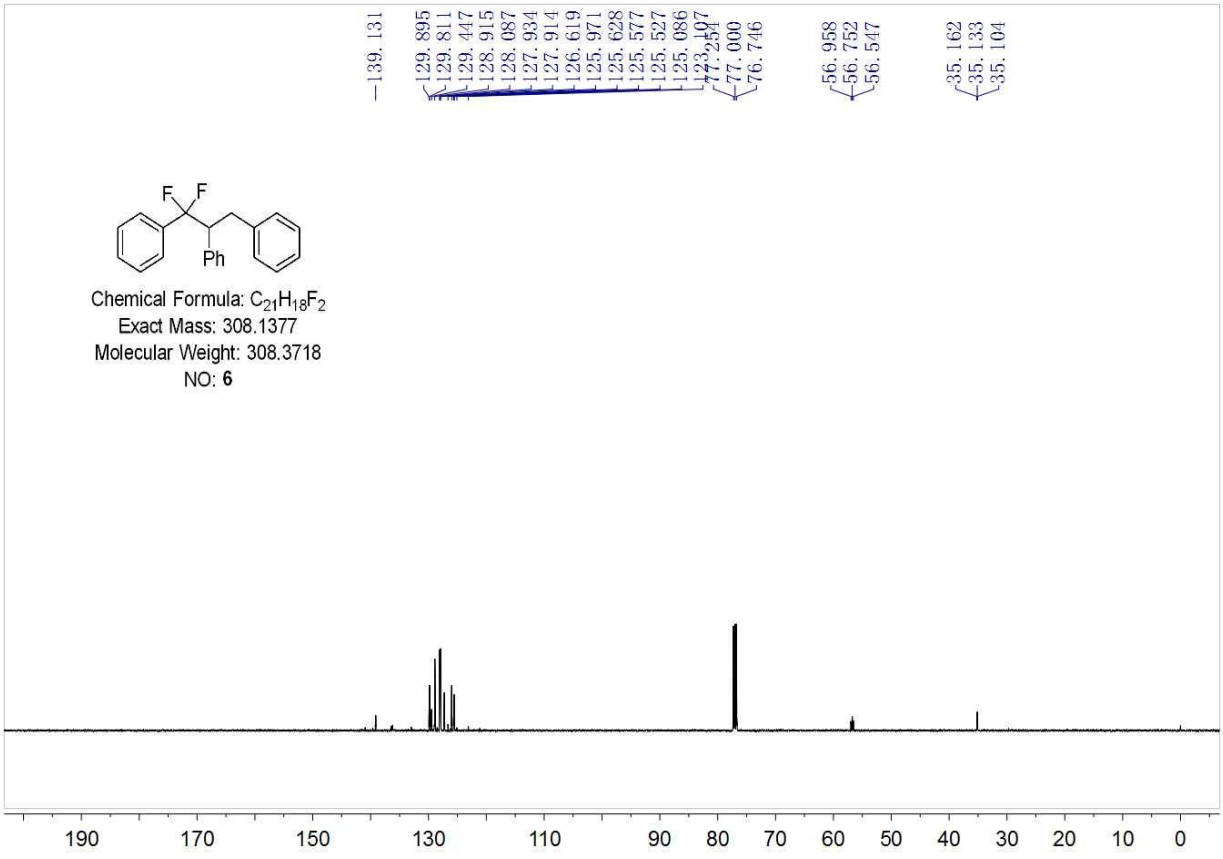




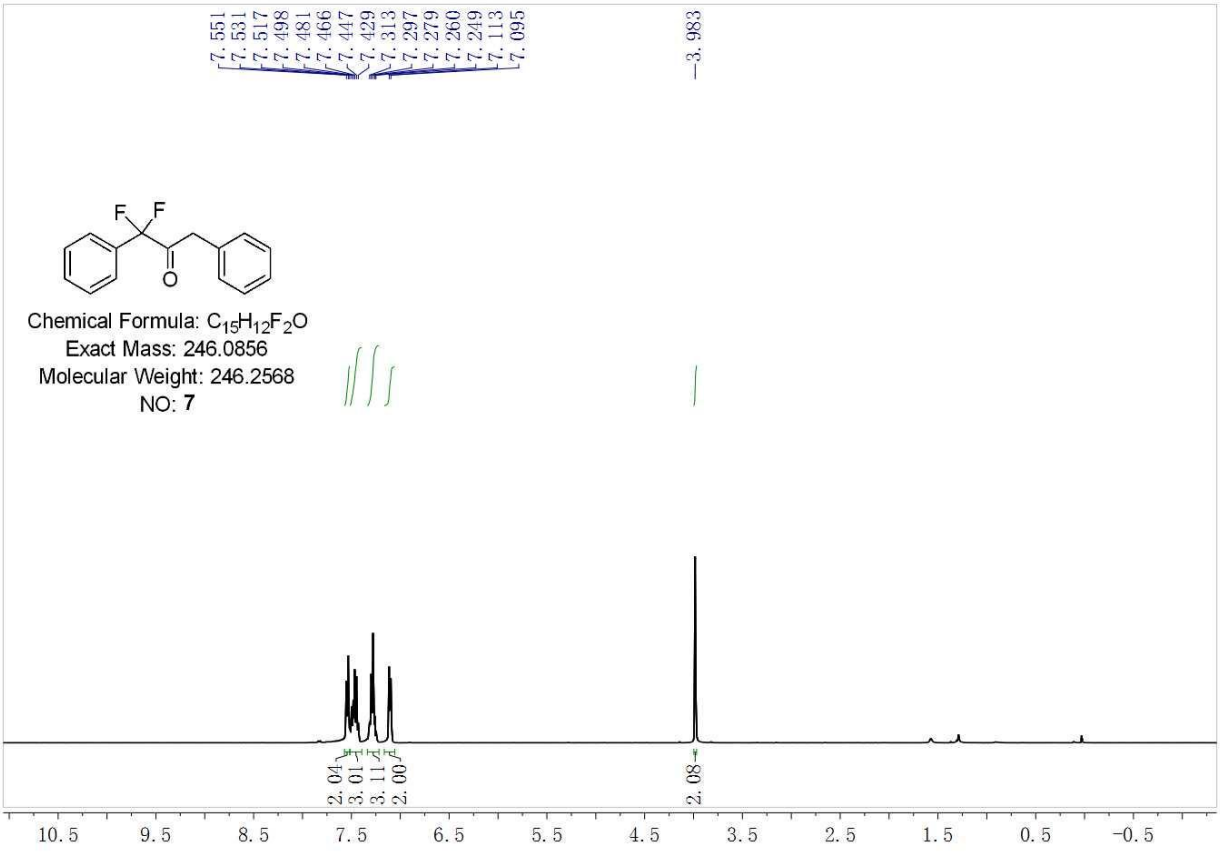
(1,1-Difluoropropane-1,2,3-triyl)tribenzene (6)

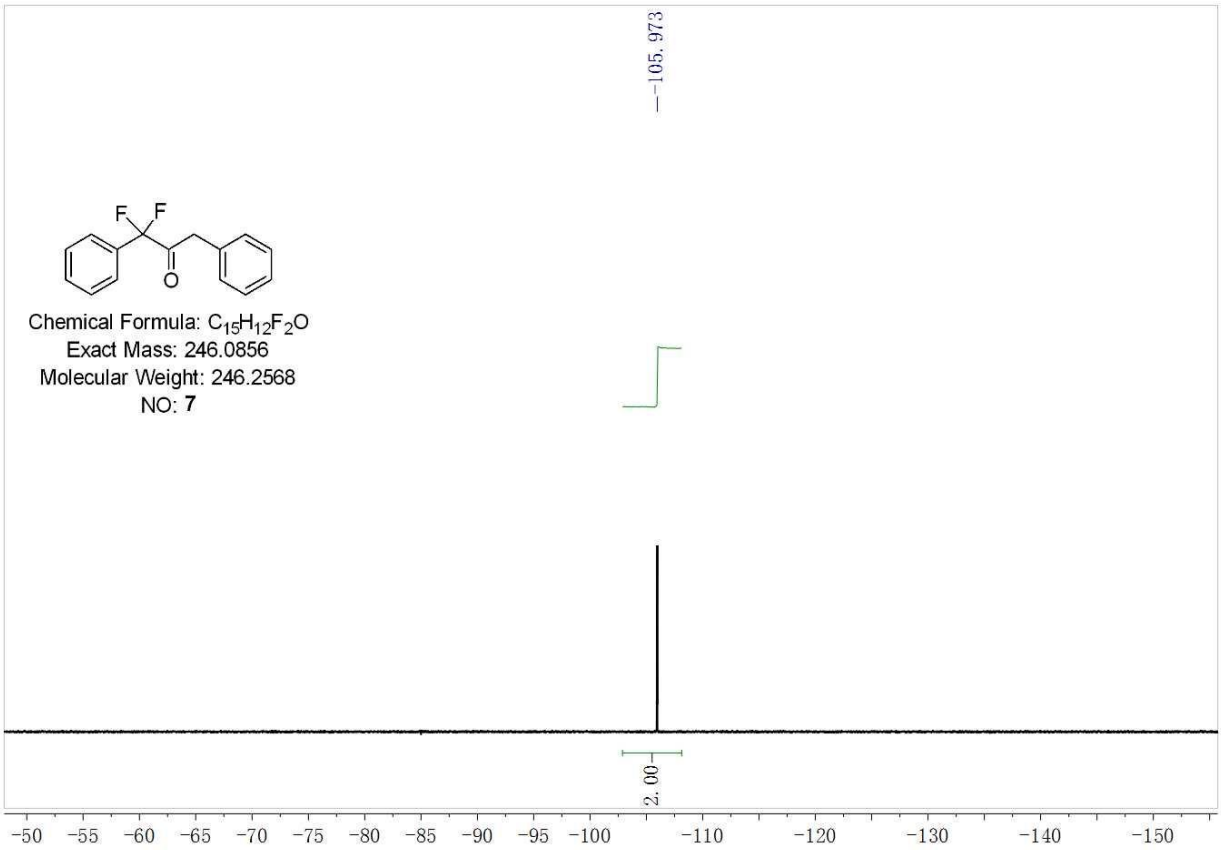


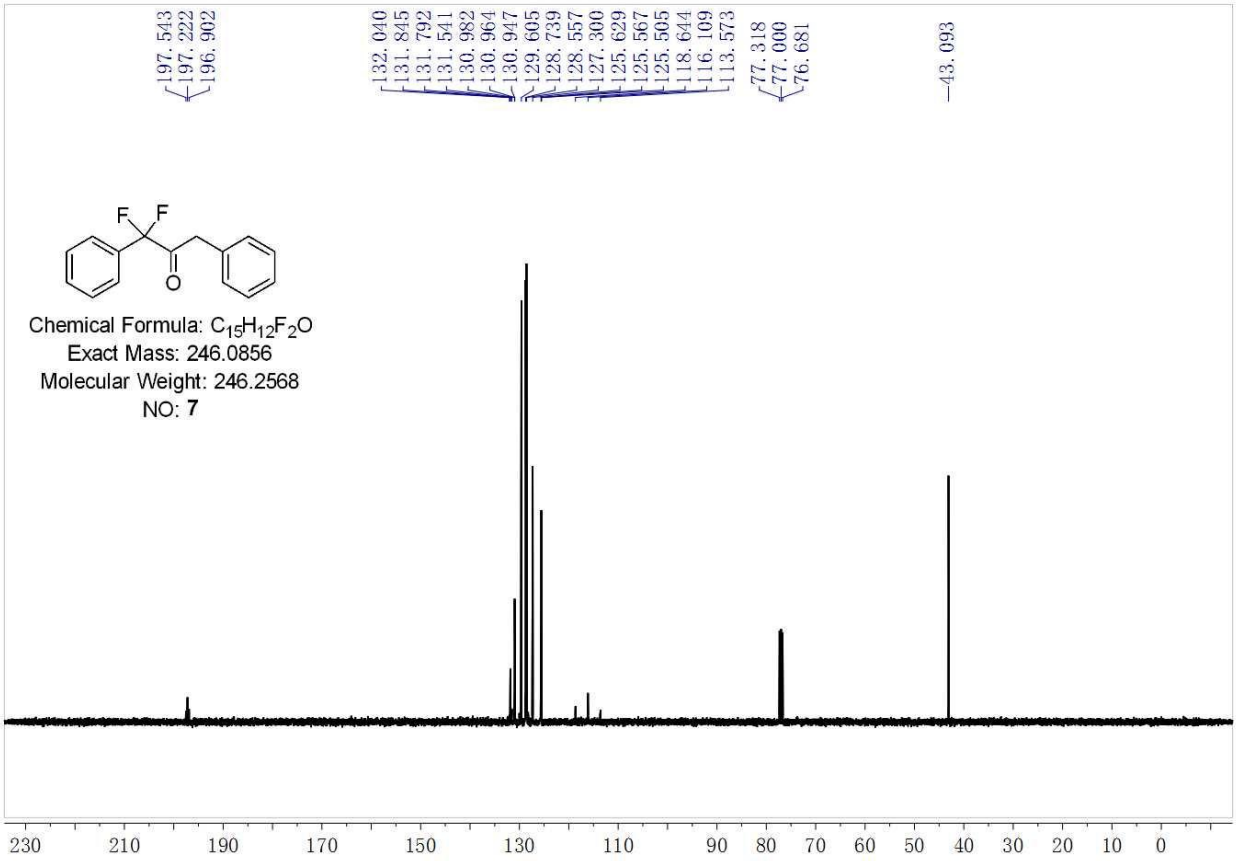

-97.100
-97.131
-97.744
-97.775
-101.995
-102.043
-102.639
-102.688
F
F
Ph
Chemical Formula: $C_{21}H_{18}F_2$
Exact Mass: 308.1377
Molecular Weight: 308.3718
NO: 6
1.00
0.99
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150


139.131
129.895
129.811
129.447
128.915
128.087
127.934
127.914
126.619
125.971
125.628
125.577
125.527
125.086
123.107
77.294
77.000
76.746
56.958
56.752
56.547
35.162
35.133
35.104
F
F
Ph
Chemical Formula: $C_{21}H_{18}F_2$
Exact Mass: 308.1377
Molecular Weight: 308.3718
NO: 6
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

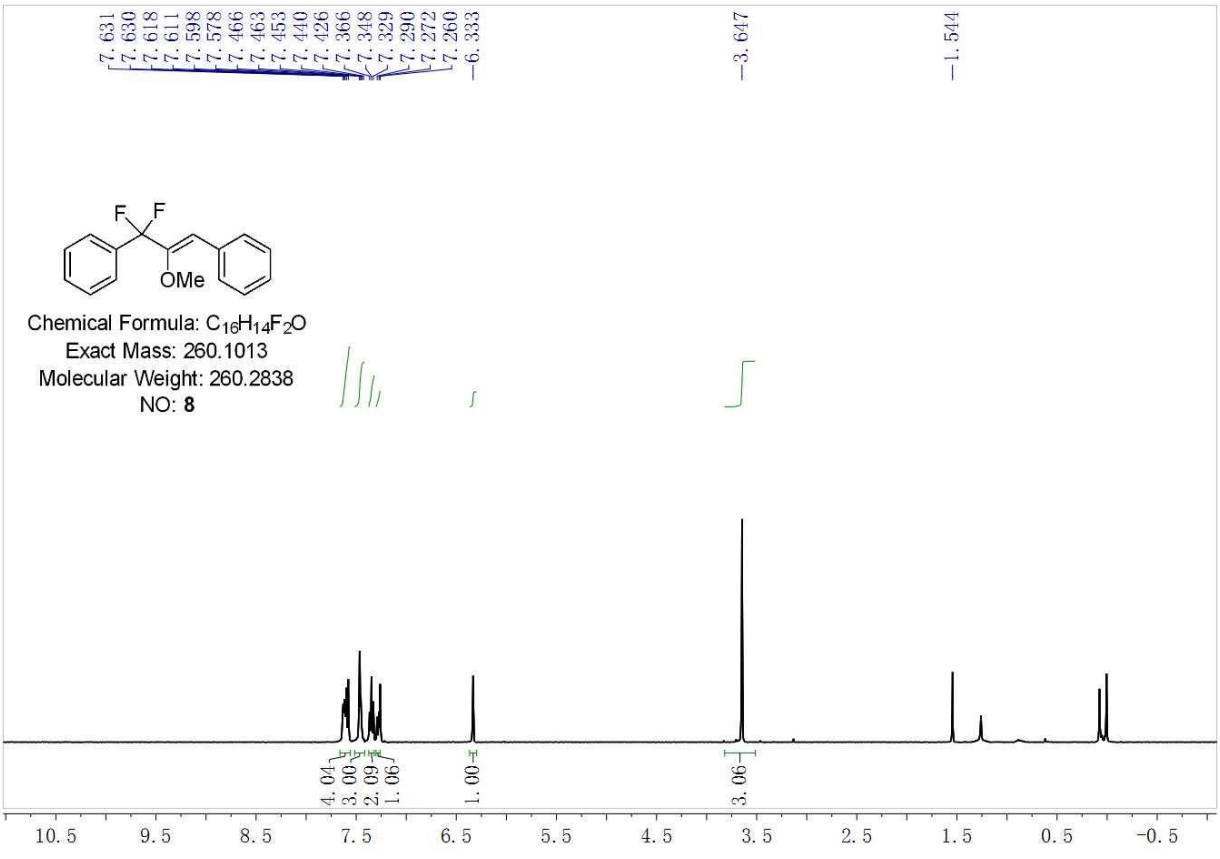
1,1-Difluoro-1,3-diphenylpropan-2-one (7)

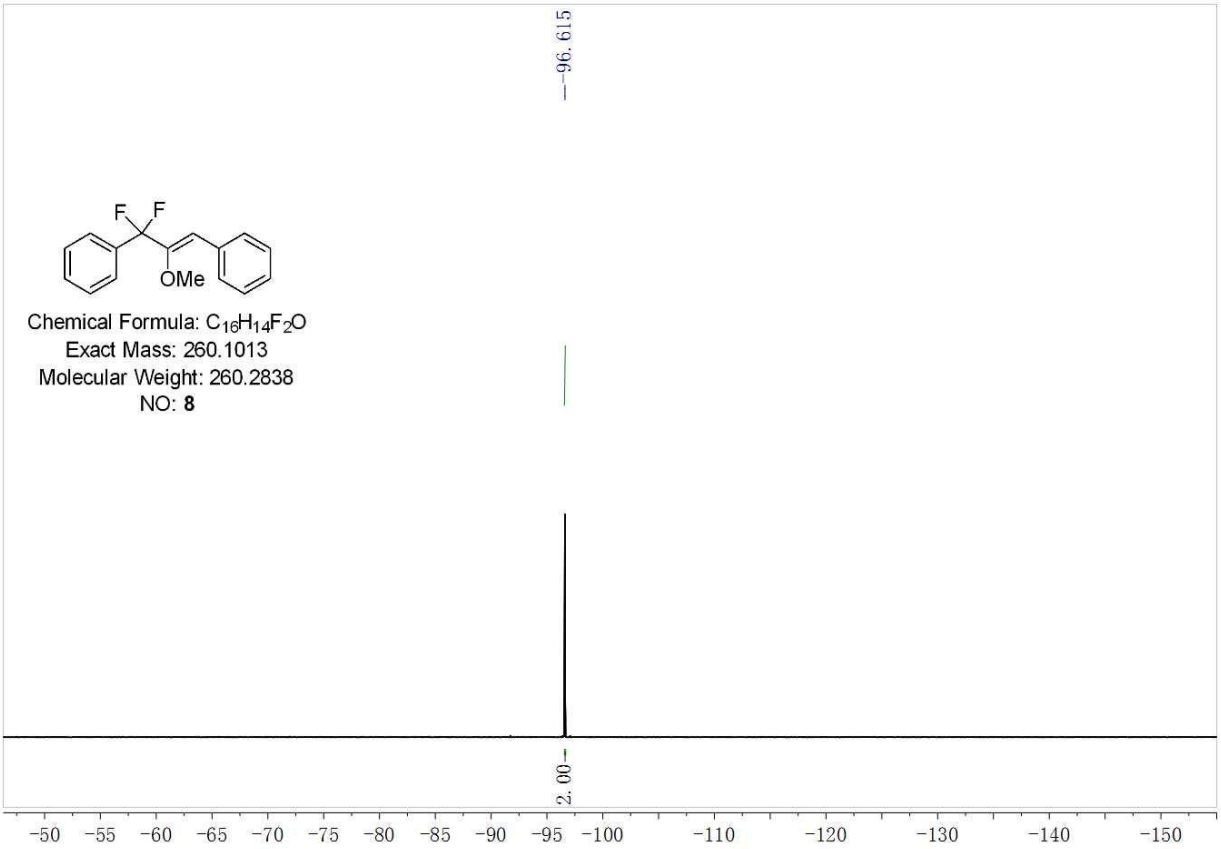


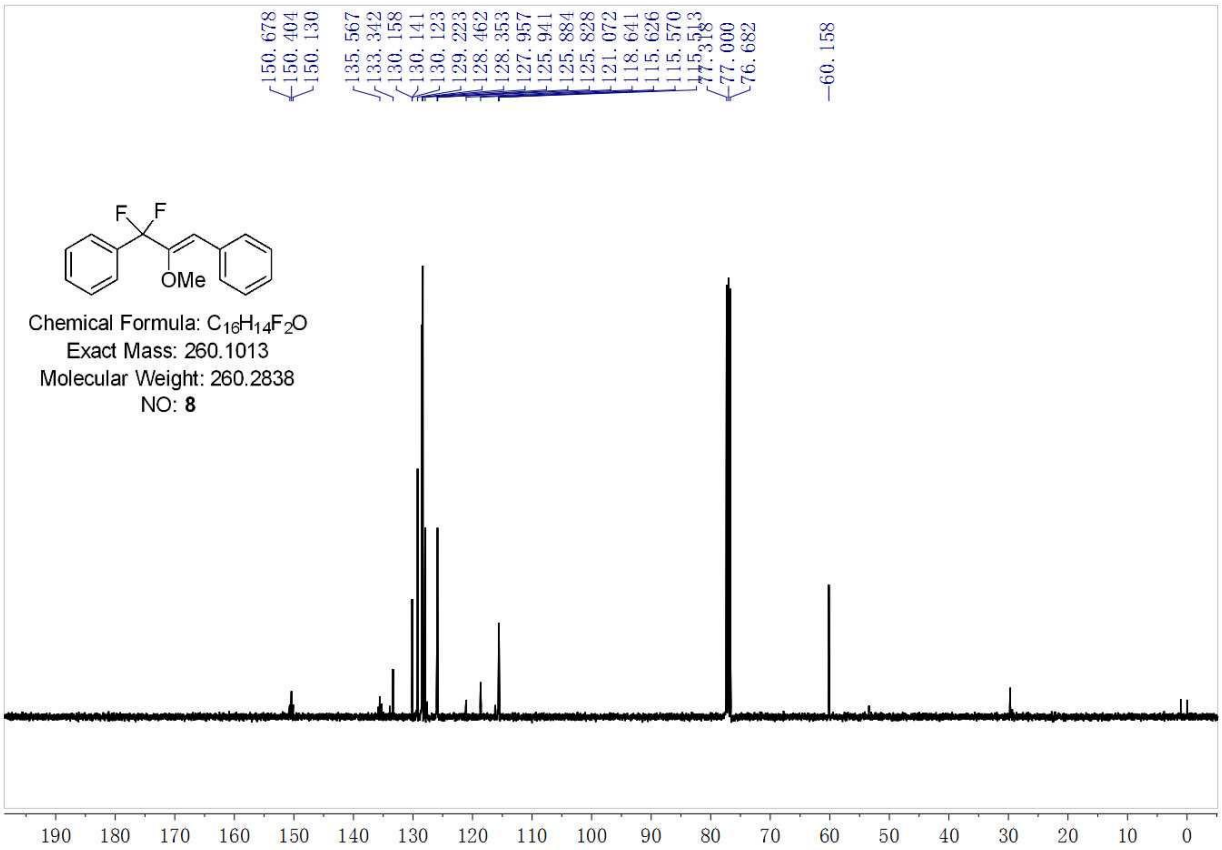




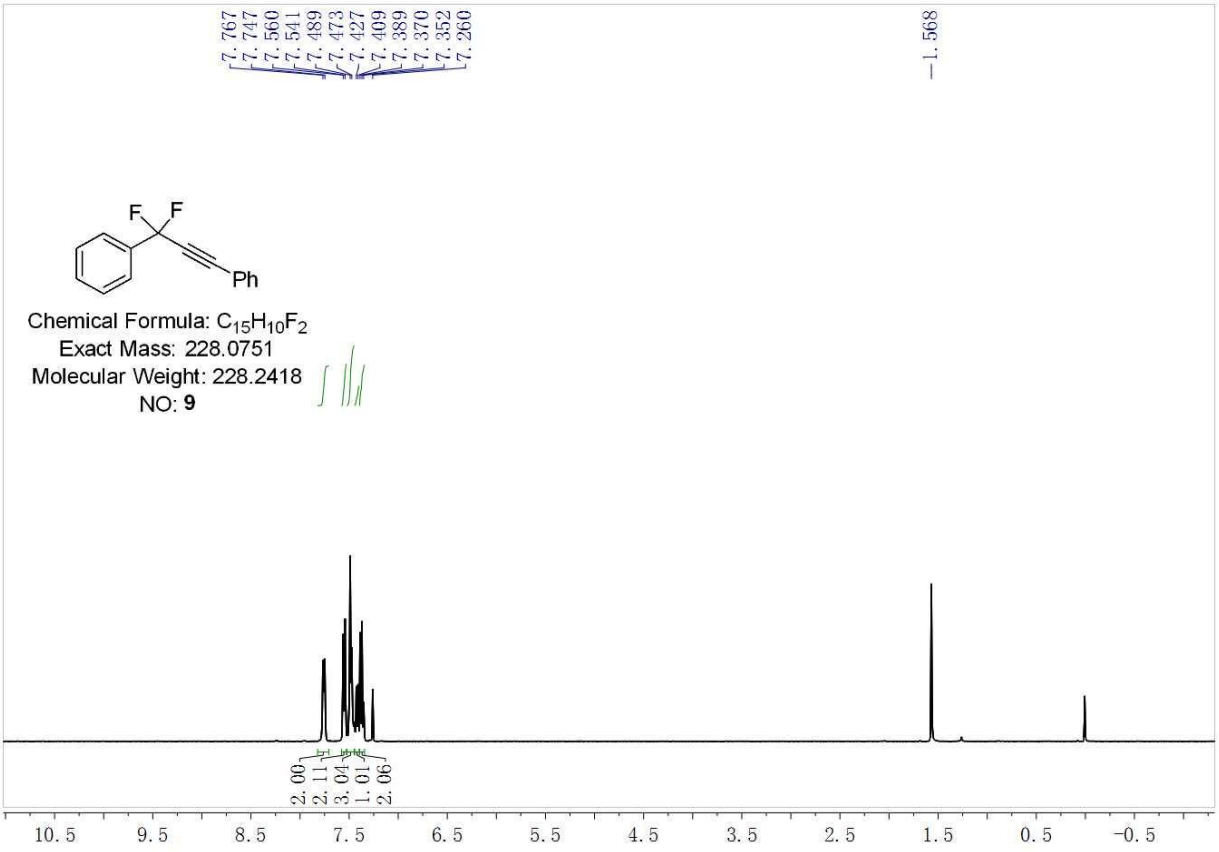
***(Z)*-(3,3-Difluoro-2-methoxyprop-1-ene-1,3-diyl)dibenzene (8)**

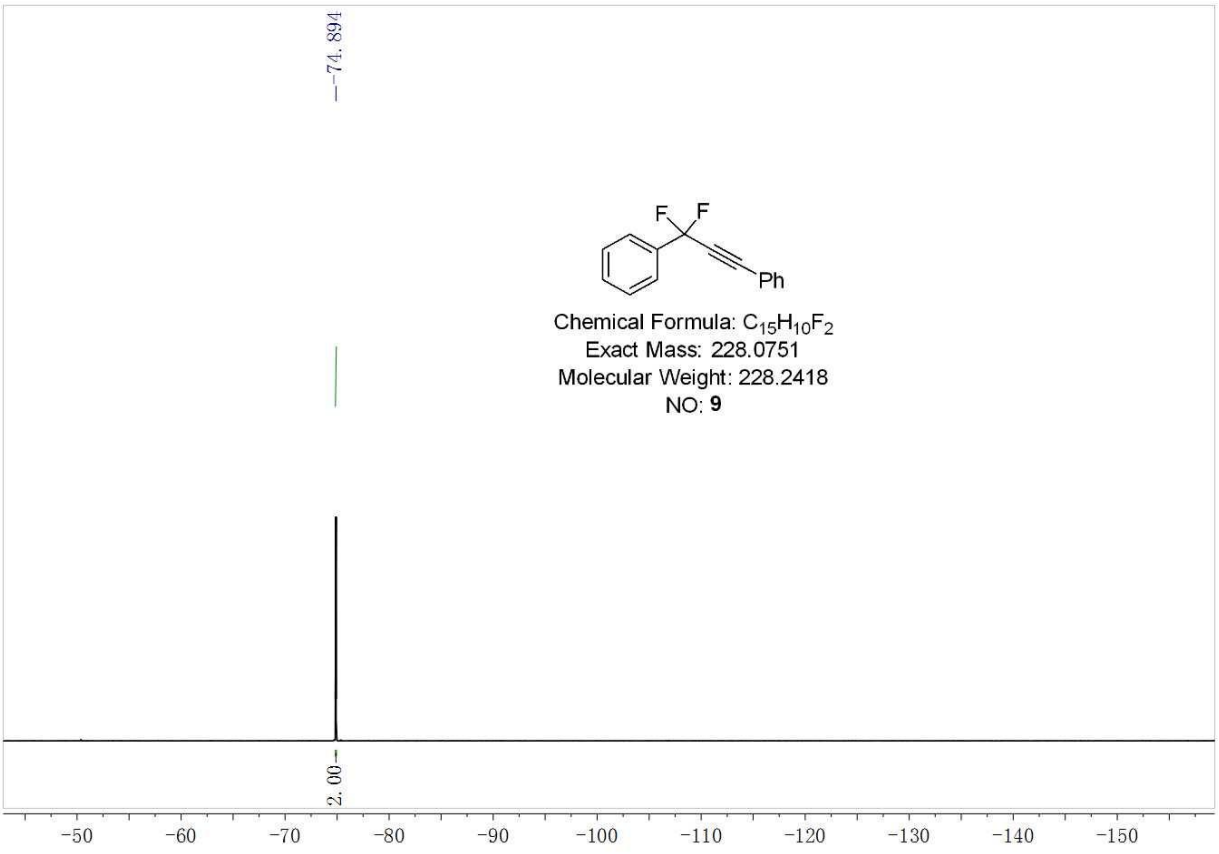


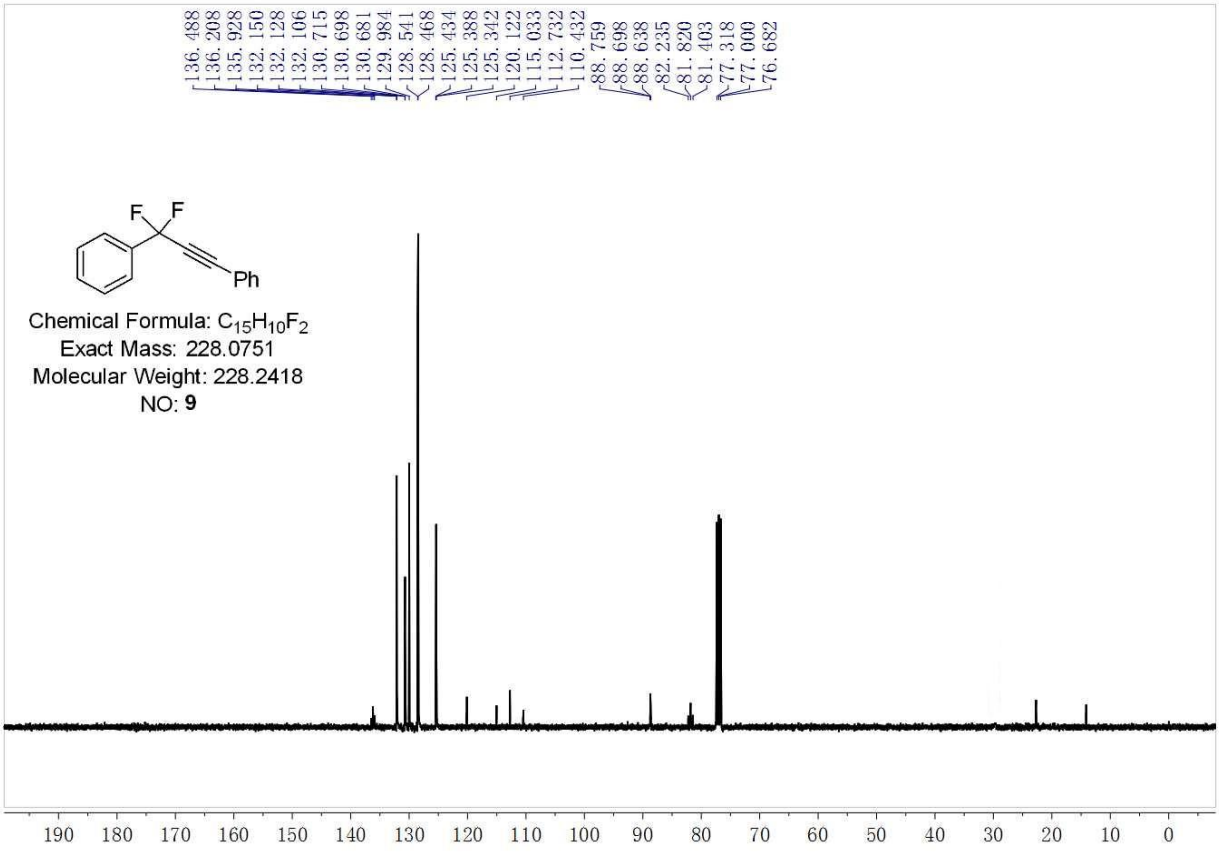

-96.615
F
F
OMe
Chemical Formula: C16H14F2O
Exact Mass: 260.1013
Molecular Weight: 260.2838
NO: 8
2.00
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150


150.678
150.404
150.130
135.567
133.342
130.158
130.141
130.123
129.223
128.462
128.353
127.957
125.941
125.884
125.828
121.072
118.641
115.626
115.570
115.513
77.318
77.000
76.682
-60.158
F
F
OMe
Chemical Formula: C16H14F2O
Exact Mass: 260.1013
Molecular Weight: 260.2838
NO: 8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

(3,3-Difluoroprop-1-yne-1,3-diyl)dibenzene (9)



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136.208
135.928
132.150
132.128
132.106
130.715
130.698
130.681
129.984
128.541
128.468
125.434
125.388
125.342
120.122
115.033
112.732
110.432
88.759
88.698
88.638
82.235
81.820
81.403
77.318
77.000
76.682
F
F
Ph
Chemical Formula: C15H10F2
Exact Mass: 228.0751
Molecular Weight: 228.2418
NO: 9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0