Supporting Information

Synthesis of Mask α, β-Unsaturated Trifluoromethyl Ketones via Iodine(III)-Mediated Double Decarboxylative Trifluoroacetylation

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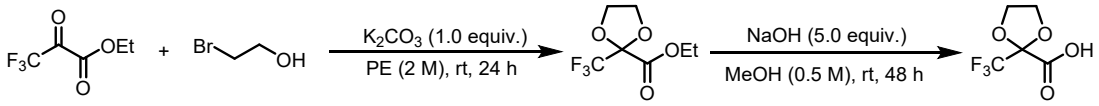
1 Supplemental Methods

1.1 General Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. All heating reaction was placed in an oil bath (Heidolph Hei-Tec Heat Expert). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on BRUKER 400 MHz or Keysight 600 MHz spectrometer in deuterated solvents. ^{1}H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded in deuterated solvent. GC measurements were conducted on Thermo Fisher Trace 1300. HRMS ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (300-400 mesh).

1.2 General procedures for the synthesis of cyclic CF_3-pyruvate acetals



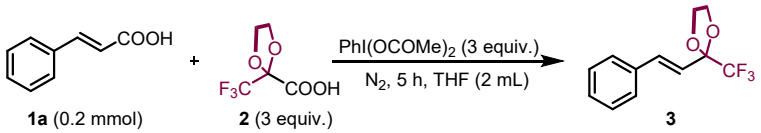
Step 1.[1] Ethyl 2-(trifluoromethyl)-1,3-dioxolane-2-carboxylate was synthesized according to known procedure. A round-bottom flask was charged with ethyl 3,3,3-trifluoro-2-oxopropanoate (10 mL, 76.0 mmol, 1 equiv.) in petroleum ether (38 mL). 2-bromoethanol (5.4 mL, 76.0 mmol, 1 equiv.) was then added dropwise over 15 minutes. The reaction mixture was stirred at room temperature for 30 minutes. Then cooled to 5 °C and K_2CO_3 (10.5 g, 76.0 mmol, 1 equiv.) was added with vigorous stirring. The reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (30 mL) and filtered. The filtrate was concentrated under reduced pressure, and the resulting material was dissolved in diethyl ether (30 mL) and washed saturated aqueous sodium chloride solution. The organic layer was dried with sodium sulfate, filtered and the filtrate was concentrated under reduced pressure to provide the compound colorless oil.

Step 2. 2-(trifluoromethyl)-1,3-dioxolane-2-carboxylic acid was synthesized according to a literature and slightly modified reaction condition. A round-bottom flask was charged with ethyl 2-

(trifluoromethyl)-1,3-dioxolane-2-carboxylate (11.3 g, 52.7 mmol, 1 equiv.) followed by the addition of MeOH (100 mL, 0.5 M). To this solution, NaOH (10.5 g, 263.5 mmol, 5 equiv.) in H_2O (40 mL) was added dropwise. The mixture was stirred vigorously for 5 min at room temperature, and then reaction mixture was allowed to stir at room temperature for 48 h. The reaction was then acidified to pH 2 with aqueous 1 M HCl, then extracted with ethyl acetate. The organic extracts were washed with saturated aqueous sodium chloride solution. The organic layer was dried with sodium sulfate, filtered and the filtrate was concentrated under reduced pressure to give as a white solid.

2 Reaction optimization

2.1 Evaluation of temperature (Table S1)

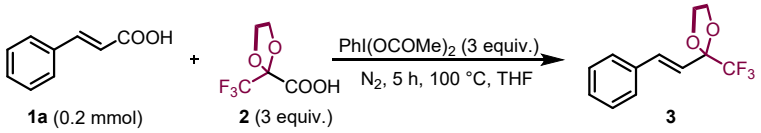


1a (0.2 mmol) **2** (3 equiv.) **3**

Entry	T (°C)	Yield[b] (%)
1	r.t.	25
2	50	35
3	60	47
4	70	43
5	80	58
6	**100**	**72**
7	120	71

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (0.6 mmol, 3 equiv.), $PhI(OCOMe)_2$ (0.6 mmol, 3 equiv.) in THF (2 mL) for 5 h under a nitrogen atmosphere. [b]Yields were determined by GC analysis with Methyl phenylacetate as the internal standard.

2.2 Evaluation of solvent loading (Table S2)

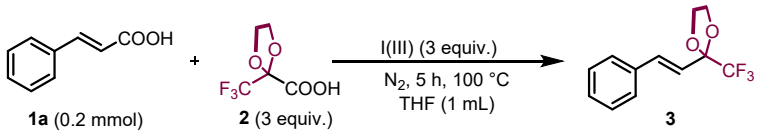


1a (0.2 mmol) **2** (3 equiv.) **3**

Entry	THF (mL)	Yield[b] (%)
1	0.5	70
2	**1**	**84**
3	2	72
4	4	70

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (0.6 mmol, 3 equiv.), $PhI(OCOMe)_2$ (0.6 mmol, 3 equiv.) in THF at 100 ˚C for 5 h under a nitrogen atmosphere. [b]Yields were determined by GC analysis with Methyl phenylacetate as the internal standard.

2.3 Evaluation of different iodine(III) reagents (Table S3)



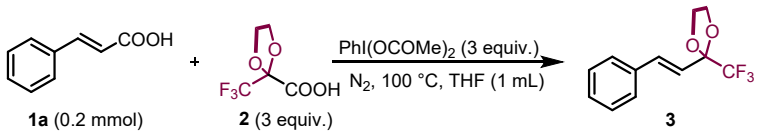
1a (0.2 mmol) **2** (3 equiv.) **3**

Entry	Iodine reagent	Yield[b] (%)
1	**$PhI(OCOMe)_2$**	**84**
2	$PhI(OCOCF_3)_2$	83

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (0.6 mmol, 3 equiv.), iodine reagent (0.6 mmol, 3 equiv.) in THF at 100 ˚C for 5 h under a nitrogen atmosphere. [b]Yields were determined by GC

analysis with Methyl phenylacetate as the internal standard.

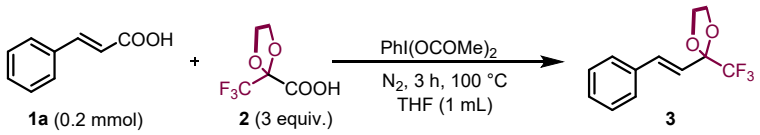
2.4 Evaluation of reaction time (Table S4)



Entry	Time (h)	Yield[b] (%)
1	1	75
2	**3**	**90**
3	5	84
4	8	83
5	12	85

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (0.6 mmol, 3 equiv.), $PhI(OCOMe)_2$ (0.6 mmol, 3 equiv.) in THF at 100 ˚C under a nitrogen atmosphere. [b]Yields were determined by GC analysis with Methyl phenylacetate as the internal standard.

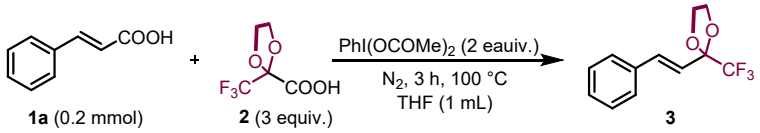
2.5 Evaluation of $Ph(OCOMe)_2$ equivalents (Table S5)



Entry	$PhI(OCOMe)_2$ (equiv)	Yield[b] (%)
1	1	16
2	**2**	**90**
3	3	90
4	5	75

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (0.6 mmol, 3 equiv.), $PhI(OCOMe)_2$ in THF (1 mL) at 100 ˚C for 5 h under a nitrogen atmosphere. [b]Yields were determined by GC analysis with Methyl phenylacetate as the internal standard.

2.6 Control experiments (Table S6)

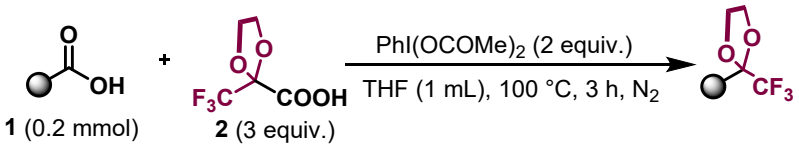


Entry	Deviation from stand condition	Yield[b] (%)
1	**Standard condition**	**90**
2	Without $PhI(OCOMe)_2$	ND
2	In air	trace
3	In the darkness	88

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (0.6 mmol, 3 equiv.), $PhI(OCOMe)_2$ (0.4 mmol, 2 equiv.) in THF (1 mL) at 100 ˚C for 5 h under a nitrogen atmosphere. [b]Yields were determined by GC analysis with Methyl phenylacetate as the internal standard.

3 Experimental procedures and spectral data

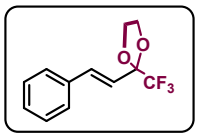
3.1 Experimental procedure for 3-34



To a 25 mL high-pressure nitrogen storage were added α, β-unsaturated carboxylic acids **1** (0.2 mmol, 1.0 equiv.), 2-(trifluoromethyl)-1,3-dioxolane-2-carboxylic acid **2** (111.6 mg, 0.6 mmol, 3.0 equiv.), and $PhI(OCOMe)_2$ (128.8 mg, 0.4 mmol, 2.0 equiv.). The reaction mixture was evacuated and back-filled with nitrogen (three cycles). Under a nitrogen atmosphere, tetrahydrofuran (1 mL) was added via syringe. The mixture was stirred at 100 °C for 3 h. After completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified directly by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluent to afford the target product.

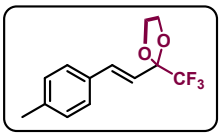
3.2 Spectral data for 3-34

(*E*)-2-styryl-2-(trifluoromethyl)-1,3-dioxolane (3)



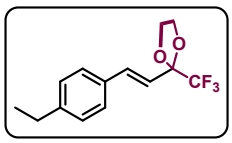
The product (80% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 4.26 – 4.12 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.2, 134.9, 129.0, 128.8, 127.3, 123.0 (q, *J* = 288.4 Hz), 120.3, 104.3 (q, *J* = 32.4 Hz), 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.19. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}F_3O_2^+$ 245.0784; Found 245.0786.

(*E*)-2-(4-methylstyryl)-2-(trifluoromethyl)-1,3-dioxolane (4)



The product (73% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 15.9 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.28 – 4.08 (m, 4H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.0, 134.7, 132.4, 129.5, 127.2, 123.0 (q, *J* = 288.4 Hz), 119.2, 104.4 (q, *J* = 32.4 Hz), 66.8, 21.4. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.22. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3O_2^+$ 259.0941; Found 259.0940.

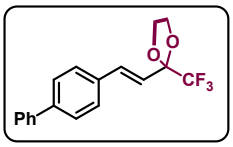
(*E*)-2-(4-ethylstyryl)-2-(trifluoromethyl)-1,3-dioxolane (5)



The product (61% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.21 (d, *J* = 15.9 Hz, 1H), 4.34 – 4.08 (m, 4H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.4, 134.8, 132.7,

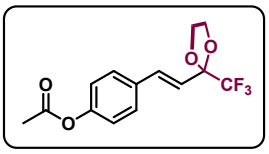
128.3, 127.3, 123.0 (q, J = 288.4 Hz), 119.3, 104.4 (q, J = 32.4 Hz), 66.7, 28.8, 15.6. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.22. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3O_2^+$ 273.1097; Found 273.1093.

(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-2-(trifluoromethyl)-1,3-dioxolane (6)



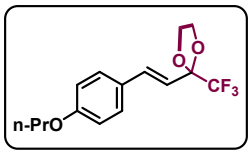
The product (71% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 4H), 7.56 (d, J = 6.7 Hz, 2H), 7.49 (t, J = 6.9 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 16.1 Hz, 1H), 6.34 (d, J = 16.1 Hz, 1H), 4.35 – 4.08 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.7, 140.5, 134.4, 134.2, 129.0, 127.8, 127.7, 127.5, 127.1, 123.0 (q, J = 288.2 Hz), 120.4, 104.3 (q, J = 32.5 Hz), 66.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.04. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}F_3O_2^+$ 321.1097; Found 321.1096.

(*E*)-4-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)phenyl acetate (7)



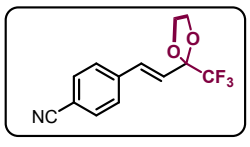
The product (63% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.45 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 16.0 Hz, 1H), 6.24 – 6.16 (m, 1H), 4.26 – 4.17 (m, 2H), 4.11 (d, J = 6.7 Hz, 2H), 2.34 – 2.23 (m, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 169.4, 151.1, 133.8, 133.0, 128.3, 124.8 (q, J = 287.8 Hz), 122.0, 120.6, 104.2 (q, J = 32.5 Hz), 66.7, 21.1. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.19. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}F_3O_4^+$ 303.0839; Found 303.0836.

(*E*)-2-(4-propoxystyryl)-2-(trifluoromethyl)-1,3-dioxolane (8)



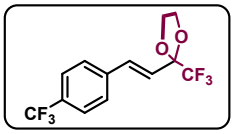
The product (74% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.38 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 15.9 Hz, 1H), 6.88 (d, J = 8.9 Hz, 2H), 6.10 (d, J = 15.8 Hz, 1H), 4.24 – 4.09 (m, 4H), 3.93 (t, J = 6.6 Hz, 2H), 1.82 (h, J = 7.0 Hz, 2H), 1.05 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.9, 134.4, 128.6, 127.8, 123.1 (q, J = 288.6 Hz), 117.8, 114.8, 104.4 (q, J = 32.3 Hz), 69.7, 66.7, 22.6, 10.6. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_3O_3^+$ 303.1203; Found 303.1209.

(*E*)-4-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzonitrile (9)



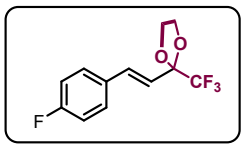
The product (60% yield) was purified with column chromatography (petroleum ether/EtOAc = 10:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 16.0 Hz, 1H), 6.33 (d, J = 15.9 Hz, 1H), 4.29 – 4.12 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.6, 133.2, 132.6, 127.8, 124.2, 122.7 (q, J = 288.6 Hz), 118.7, 112.2, 103.9 (q, J = 32.7 Hz), 66.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.07. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}F_3NO_2^+$ 270.0737; Found 270.0732.

(*E*)-2-(trifluoromethyl)-2-(4-(trifluoromethyl)styryl)-1,3-dioxolane (10)



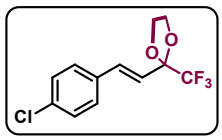
The product (80% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.46 (m, 4H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 4.33 – 4.07 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.7 (d, *J* = 1.5 Hz), 133.6, 130.7 (q, *J* = 32.6 Hz), 127.5, 125.8 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 272.0 Hz), 123.1, 122.9 (d, *J* = 288.6 Hz), 104.1 (q, *J* = 32.6 Hz), 66.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.70, -82.17. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}F_6O_2^+$ 313.0658; Found 313.0662.

(*E*)-2-(4-fluorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (11)



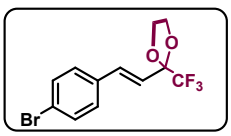
The product (67% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 15.9 Hz, 1H), 6.15 (d, *J* = 15.9 Hz, 1H), 4.40 – 3.94 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 248.5 Hz), 133.7, 131.4 (d, *J* = 3.3 Hz), 129.0 (d, *J* = 8.2 Hz), 123.0 (q, *J* = 288.4 Hz), 120.1 (d, *J* = 2.4 Hz), 115.8 (d, *J* = 21.7 Hz), 104.2 (q, *J* = 32.5 Hz), 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.22, -112.42. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}F_4O_2^+$ 263.0690; Found 263.0699.

(*E*)-2-(4-chlorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (12)



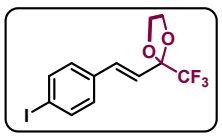
The product (74% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.21 (d, *J* = 16.0 Hz, 1H), 4.25 – 4.10 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 134.7, 133.8, 133.7, 129.0, 128.5, 122.9 (q, *J* = 288.4 Hz), 121.1, 104.2 (q, *J* = 32.5 Hz), 66.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.15. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}ClF_3O_2^+$ 279.0395; Found 279.0398.

(*E*)-2-(4-bromostyryl)-2-((difluoro-λ^3-methyl)-λ^2-fluoraneyl)-1,3-dioxolane (13)



The product (61% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 4.26 – 4.10 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 134.2, 133.7, 132.0, 128.8, 122.9, 122.9 (q, *J* = 193.1 Hz), 121.2, 104.2 (q, *J* = 32.5 Hz), 66.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.13. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}BrF_3O_2^+$ 322.9890; Found 322.9897.

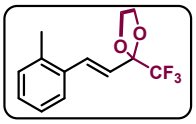
(*E*)-2-(4-iodostyryl)-2-(trifluoromethyl)-1,3-dioxolane (14)



The product (65% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 4.26 – 3.99 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.9, 134.7, 133.8, 129.0, 122.9 (q, *J* = 288.6 Hz), 121.2, 104.1 (q, *J*

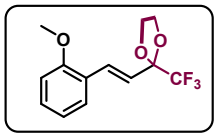
= 32.5 Hz), 94.6, 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.12. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}IF_3O_2^+$ 370.9751; Found 370.9759.

(*E*)-2-(2-methylstyryl)-2-(trifluoromethyl)-1,3-dioxolane (15)



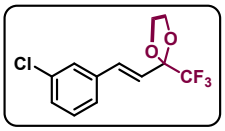
The product (71% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.28 (d, *J* = 4.8 Hz, 2H), 7.16 (d, *J* = 4.4 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 17.6 Hz, 1H), 4.30 – 4.07 (m, 4H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 138.5, 135.2, 135.0, 129.8, 128.7, 128.0, 124.5, 123.0 (q, *J* = 288.1 Hz), 120.2, 104.4 (q, *J* = 32.3 Hz), 66.8, 21.4. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.19. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3O_2^+$ 259.0941; Found 259.0948.

(*E*)-2-(2-methoxystyryl)-2-(trifluoromethyl)-1,3-dioxolane (16)



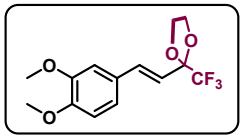
The product (60% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.4, 1.7 Hz, 1H), 7.34 (d, *J* = 15.9 Hz, 1H), 7.29 – 7.22 (m, 3H), 6.18 (d, *J* = 15.9, 1.2 Hz, 1H), 4.30 –4.18 (m, 4H), 2.44 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 136.4, 134.5, 132.8, 130.6, 128.7, 126.3, 126.2, 123.0 (q, *J* = 288.5 Hz), 121.8, 104.4 (q, *J* = 32.4 Hz), 66.8, 19.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.15. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3O_3^+$ 275.0890; Found 275.0894.

(*E*)-2-(3-chlorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (17)



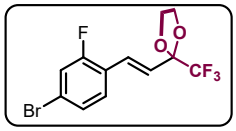
The product (75% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.43 (s, 1H), 7.31 (tt, *J* = 4.2, 2.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 4.26 – 4.09 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 137.1, 134.8, 133.6, 130.1, 128.9, 127.2, 125.5, 123.0 (q, *J* = 288.7 Hz), 122.0, 104.1 (q, *J* = 32.5 Hz), 66.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.15. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}ClF_3O_2^+$ 279.0395; Found 279.0397.

(*E*)-2-(3,4-dimethoxystyryl)-2-(trifluoromethyl)-1,3-dioxolane (18)



The product (70% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.80 (d, *J* = 10.8 Hz, 1H), 6.07 (d, *J* = 15.9 Hz, 1H), 4.21 – 4.05 (m, 4H), 3.87 (d, *J* = 2.4 Hz, 3H), 3.85 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 149.8, 149.1, 134.5, 128.1, 123.0 (q, *J* = 288.6 Hz), 120.9, 118.1, 111.1, 109.2, 104.3 (q, *J* = 32.3 Hz), 66.6, 55.9, 55.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.20. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}F_3O_4^+$ 305.0996; Found 305.0998.

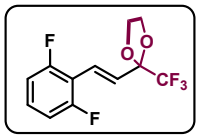
(*E*)-2-(4-bromo-2-fluorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (19)



The product (65% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.11 (d,

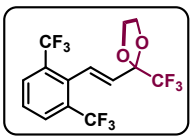
J = 16.2 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 4.31 – 4.09 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.4 (d, *J* = 255.8 Hz), 129.3 (d, *J* = 4.0 Hz), 127.8 (d, *J* = 3.7 Hz), 126.7 (d, *J* = 3.1 Hz), 123.6 (d, *J* = 5.6 Hz), 122.8 (d, *J* = 9.8 Hz), 122.8 (q, *J* = 289.7 Hz), 122.3 (d, *J* = 12.0 Hz), 119.7 (d, *J* = 25.3 Hz), 104.1 (q, *J* = 32.5 Hz), 66.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.14, -113.95. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_9BrF_4O_2^+$ 340.9795; Found 340.9797.

(*E*)-2-(2,6-difluorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (20)



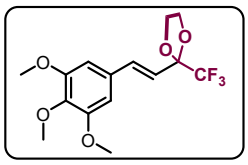
The product (66% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 1H), 7.10 (d, *J* = 16.4 Hz, 1H), 6.90 (t, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 16.5 Hz, 1H), 4.31 – 4.09 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.4 (dd, *J* = 253.2, 7.2 Hz), 129.8 (t, *J* = 10.9 Hz), 126.8 (t, *J* = 8.4 Hz), 122.9 (q, *J* = 289.7 Hz), 121.5, 112.8 (t, *J* = 15.0 Hz), 112.2 – 111.5 (m), 104.2 (q, *J* = 32.6 Hz), 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.17, -112.08. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}F_5O_2^+$ 281.0596; Found 281.0592.

(*E*)-2-(2,6-bis(trifluoromethyl)styryl)-2-(trifluoromethyl)-1,3-dioxolane (21)



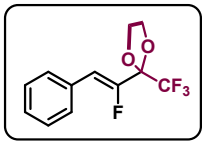
The product (75% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 2H), 7.81 (s, 1H), 7.11 (d, *J* = 14.2 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 4.33 – 4.11 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 137.5, 132.4 (q, *J* = 33.1 Hz), 132.3, 127.2, 124.8, 123.3 (q, *J* = 272.8 Hz), 122.8 (q, *J* = 288.5 Hz), 122.3, 104.0 (q, *J* = 32.9 Hz), 67.0. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -63.20, -82.18 **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}F_9O_2^+$ 381.0532; Found 381.0538.

(*E*)-2-(trifluoromethyl)-2-(3,4,5-trimethoxystyryl)-1,3-dioxolane (22)



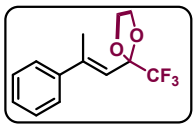
The product (71% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 15.9 Hz, 1H), 6.65 (s, 2H), 6.12 (d, *J* = 15.9 Hz, 1H), 4.30 – 4.05 (m, 4H), 3.87 (s, 6H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.4, 138.8, 134.8, 130.8, 122.9 (q, *J* = 288.5 Hz), 119.7, 104.3, 104.2 (q, *J* = 32.3 Hz), 66.7, 61.0, 56.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.19. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}F_3O_5^+$ 335.1101; Found 335.1107.

(*Z*)-2-(1-fluoro-2-phenylvinyl)-2-(trifluoromethyl)-1,3-dioxolane (23)



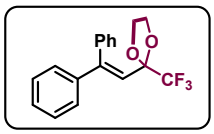
The product (26% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil.**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.28 (m, 3H), 6.27 (d, *J* = 37.3 Hz, 1H), 4.32 – 4.17 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.0 (d, *J* = 273.8 Hz), 131.6 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 7.6 Hz), 128.8, 128.6 (d, *J* = 2.5 Hz), 123.5 – 120.5 (m), 110.3 (d, *J* = 3.8 Hz), 101.8 (q, *J* = 37.1 Hz), 67.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -81.13 (d, *J* = 8.1 Hz), -121.93 (q, *J* = 8.2 Hz). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}F_4O_2^+$ 263.0690; Found 263.0698.

(*E*)-2-(2-phenylprop-1-en-1-yl)-2-(trifluoromethyl)-1,3-dioxolane (24)



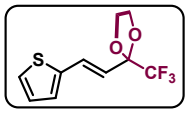
The product (65% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.28 (m, 5H), 5.90 – 5.63 (t, 1H), 4.26 – 4.13 (m, 4H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.2, 143.2, 128.5, 128.1, 126.2, 123.6 (q, *J* = 289.7 Hz), 120.0, 104.9 (q, *J* = 32.4 Hz), 66.5, 17.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -81.90. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3O_2^+$ 259.0941; Found 259.0947.

2-(2,2-diphenylvinyl)-2-(trifluoromethyl)-1,3-dioxolane (25)



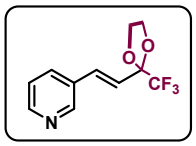
The product (43% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.16 (m, 11H), 6.16 (s, 1H), 3.91 – 3.45 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.6, 141.6, 139.4, 129.2, 128.5, 128.4, 127.7, 127.6, 127.3, 123.3 (q, *J* = 290.3 Hz), 119.2, 104.3 (q, *J* = 31.5 Hz), 66.4. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.60. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}F_3O_2^+$ 321.1097; Found 321.1099.

(*E*)-2-(2-(thiophen-2-yl)vinyl)-2-(trifluoromethyl)-1,3-dioxolane (26)



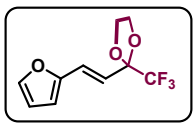
The product (40% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 15.7 Hz, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.05 (d, *J* = 15.7 Hz, 1H), 4.22 – 4.11 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.2, 128.2, 128.0, 127.7, 126.2, 122.9 (q, *J* = 288.4 Hz), 119.5, 104.1 (q, *J* = 32.6 Hz), 66.8. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.22. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}F_3O_2S^+$ 251.0349; Found 251.0343.

(*E*)-3-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)pyridine (27)



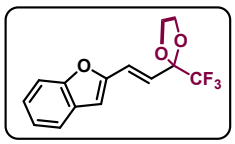
The product (45% yield) was purified with column chromatography (petroleum ether/EtOAc = 10:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.51 (d, *J* = 4.8 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 4.28 – 3.98 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.9, 149.1, 133.6, 131.5, 130.9, 123.7, 122.8 (q, *J* = 288.5 Hz), 122.7, 104.0 (q, *J* = 32.6 Hz), 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.16. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}F_3NO_2^+$ 246.0737; Found 246.0735.

(*E*)-2-(2-(furan-2-yl)vinyl)-2-(trifluoromethyl)-1,3-dioxolane (28)



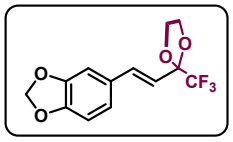
The product (42% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 6.81 (d, *J* = 15.7 Hz, 1H), 6.40 (tt, *J* = 5.4, 2.4 Hz, 2H), 6.15 (d, *J* = 15.7 Hz, 1H), 4.22 – 4.09 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.2, 143.3, 122.9 (q, *J* = 289.5 Hz),122.8, 118.6, 111.7, 111.1, 104.2 (q, *J* = 32.7 Hz), 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.25. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}F_3O_3^+$ 235.0577; Found 235.0572.

(*E*)-2-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzofuran (29)



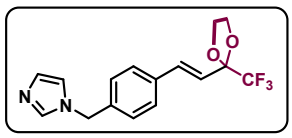
The product (75% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.25 (q, *J* = 6.6 Hz, 1H), 6.98 (d, *J* = 15.7 Hz, 1H), 6.75 (s, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 4.33 – 4.04 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.2, 152.8, 128.6, 125.6, 123.2, 123.1, 122.9 (q, *J* = 289.6 Hz), 122.0, 121.4, 111.3, 107.8, 104.1 (q, *J* = 32.7 Hz), 66.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.06. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}F_3O_3^+$ 285.0734; Found 285.0734.

(*E*)-5-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzo[d][1,3]dioxole (30)



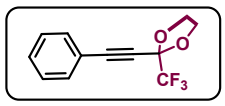
The product (66% yield) was purified with column chromatography (petroleum ether/EtOAc = 20:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.97 (s, 1H), 6.95 – 6.86 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.05 (d, *J* = 15.9 Hz, 1H), 5.97 (s, 2H), 4.24 – 4.09 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.4, 148.3, 134.4, 129.6, 123.0 (q, *J* = 288.5 Hz), 122.6, 118.4, 108.4, 106.2, 104.3 (q, *J* = 32.3 Hz), 101.4, 66.7. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.23. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}F_3O_4^+$ 289.0683; Found 289.0685.

(*E*)-1-(4-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzyl)-1H-imidazole (31)



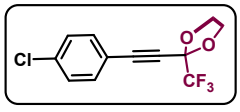
The product (75% yield) was purified with column chromatography (petroleum ether/EtOAc = 10:1) as a colorless oil. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.83 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 6.97 (d, *J* = 16.1 Hz, 1H), 6.94 (s, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 5.21 (s, 2H), 4.25 – 4.02 (m, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 138.6, 137.5, 134.1, 133.9, 128.8, 127.9, 127.7, 122.9 (q, *J* = 289.0 Hz), 120.5, 119.6, 103.5 (q, *J* = 31.8 Hz), 66.6, 49.1.Z**^{19}F NMR** (376 MHz, DMSO-d_6) δ -81.14. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}F_3N_2O_2^+$ 325.1159; Found 325.1158.

2-(phenylethynyl)-2-(trifluoromethyl)-1,3-dioxolane (32)



The product (25% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 4.34 – 4.17 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 132.4, 129.8, 128.5, 121.5 (q, *J* = 288.2 Hz), 120.6, 99.1 (q, *J* = 36.1 Hz), 87.1, 80.3, 67.2. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -82.95. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}F_3O_2^+$ 243.0628; Found 243.0628.

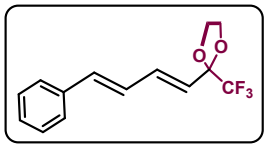
2-((4-chlorophenyl)ethynyl)-2-(trifluoromethyl))-1,3-dioxolane (33)



The product (25% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 5.7 Hz, 2H), 7.32 (d, *J* = 5.3 Hz, 2H), 4.29 – 4.19 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.1, 133.6, 128.9, 121.4 (q, *J* = 287.0 Hz), 119.1, 99.0 (q, *J* = 36.2 Hz), 85.9, 81.2, 67.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.93. **HRMS**

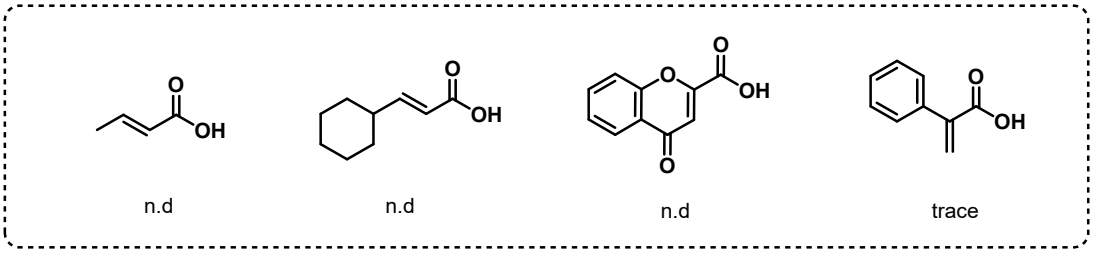
(ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_9ClF_3O_2^+$ 277.0238; Found 277.0239.

2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-2-(trifluoromethyl))-1,3-dioxolane (34)



The product (30% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 1H), 6.85 – 6.75 (m, 2H), 6.75 – 6.65 (m, 1H), 5.91 – 5.76 (m, 1H), 4.28 – 4.04 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.7, 136.4, 135.1, 128.8, 128.4, 126.8, 123.7, 122.9 (d, *J* = 288.5 Hz), 104.1 (d, *J* = 32.4 Hz), 93.1, 66.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -82.20. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}F_3O_2^+$ 271.0941; Found 271.0940.

3.3 Unsuccessful substrates

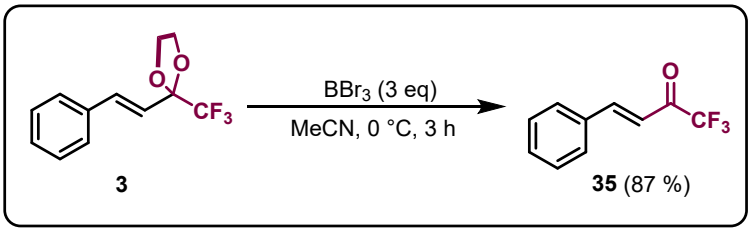


3.4 Scale-up reaction

To a solution of compound **1a** (8 mmol, 1.0 equiv.) and **2** (24 mmol, 3.0 equiv.) in THF (20.0 mL) was added $PhI(OOCMe)_2$ (16 mmol, 2.0 equiv.). The reaction mixture was stirred under a nitrogen atmosphere at 100 °C for 3 h. Upon completion (monitored by TLC), the mixture was cooled to room temperature, diluted with EtOAc (150 mL), and washed with saturated aqueous $NaHCO_3$ solution (3 ×100 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the crude residue was purified directly by silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to afford the product.

3.5 Synthetic application

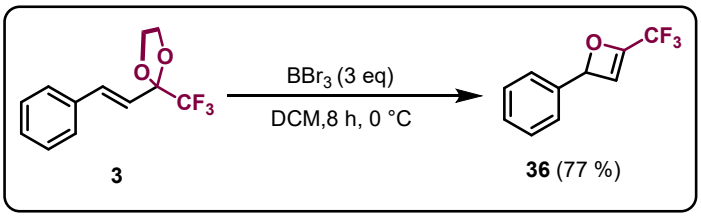
General procedure for deprotection



To a solution of compound **3** (0.3 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added BBr_3 (0.9 mmol, 3.0 equiv.) at 0 °C. The reaction mixture was stirred at this temperature for 3 h. Upon completion

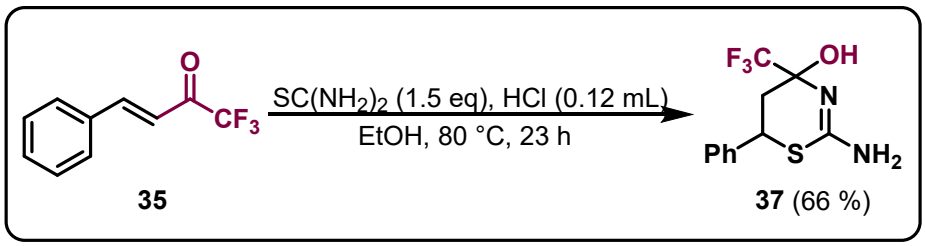
(monitored by TLC), the mixture was carefully poured into water and vigorously shaken to quench the reaction at room temperature. The aqueous mixture was then extracted with ethyl acetate (30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution (3 × 30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified directly by silica gel column chromatography using a gradient of petroleum ether and ethyl acetate as the eluent to afford the desired product.

General procedure for cyclization:



To a solution of compound **3** (0.3 mmol, 1.0 equiv.) in DCM (2.0 mL) was added BBr_3 (0.9 mmol, 3.0 equiv.) at 0 °C. The reaction mixture was stirred at this temperature for 8 h. Upon completion (monitored by TLC), the mixture was carefully poured into water and vigorously shaken to quench the reaction at room temperature. The aqueous mixture was then extracted with ethyl acetate (30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution (3 × 30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified directly by silica gel column chromatography using a gradient of petroleum ether and ethyl acetate as the eluent to afford the desired product.

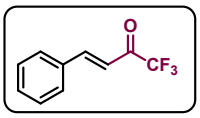
Application after deprotection:



To a solution of compound **35** (0.3 mmol, 1.0 equiv.) in EtOH (1.0 mL) in a 10-mL crimp cap vial equipped with a magnetic stir bar was added a solution of thiourea (0.45 mmol, 1.5 equiv.) in concentrated HCl (0.12 mL) at room temperature. The vial was sealed, and the reaction mixture was stirred under reflux at 80 °C for 23 h. After cooling to room temperature, the mixture was carefully poured into a saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with chloroform (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using a gradient of hexane and ethyl acetate (10:1, v/v) as the eluent to afford compound **37** as a white solid.

3.6 Spectral data for 35-37

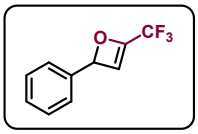
(*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (35)



The product (87% yield) was purified with column chromatography (petroleum ether/EtOAc = 30:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 16.0 Hz, 1H), 7.66 (d, *J* = 1.3 Hz, 2H), 7.56 – 7.42 (m, 3H), 7.03

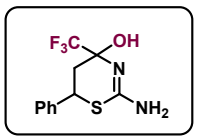
(d, J = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 180.2 (q, J = 35.4 Hz), 150.3, 133.4, 132.5, 129.4, 116.8, 116.5 (q, J = 290.8 Hz). **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -77.6.

2-phenyl-4-(trifluoromethyl)-2H-oxete (36)



The product (77% yield) was purified with column chromatography (petroleum ether/EtOAc = 50:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.34 (m, 5H), 6.92 (d, J = 8.0 Hz, 1H), 5.62 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.1, 139.1 (q, J = 4.4 Hz), 129.1, 128.9, 126.3, 120.3 (q, J = 271.8 Hz), 112.4 (q, J = 38.2 Hz), 72.7. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -67.5.

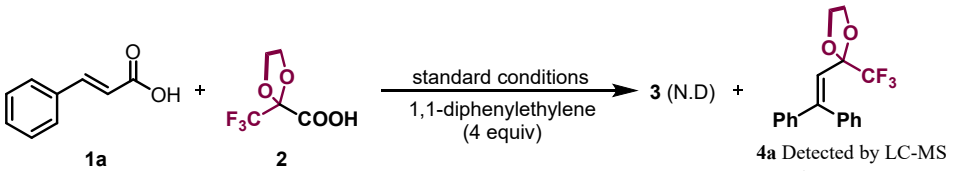
2-amino-6-phenyl-4-(trifluoromethyl)-5,6-dihydro-4H-1,3-thiazin-4-ol (37)



The product (66% yield) was purified with column chromatography (petroleum ether/EtOAc = 10:1) as a white solid. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.39 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 6.61 (s, 2H), 6.45 (s, 1H), 4.58 (dd, J = 12.8, 2.8 Hz, 1H), 2.10 (dd, J = 12.9, 2.9 Hz, 1H), 1.77 (t, J = 12.9 Hz, 1H).**^{13}C NMR** (151 MHz, DMSO-d_6) δ 155.7, 139.6, 129.0, 128.2, 128.0, 125.3 (q, J = 286.4 Hz), 83.1 (q, J = 28.9 Hz), 38.9, 32.2. **^{19}F NMR** (565 MHz, DMSO-d_6) δ -83.8.

4 Mechanistic studies

Radical-trapping experiments



4a Detected by LC-MS
[M+H$^+$] Calcd: 321.1097
Found: 321.1097

1a (0.2 mmol, 1.0 equiv.), **2** (0.6 mmol, 3.0 equiv.), PhI(OCOMe)$_2$ (0.4 mmol, 2.0 equiv.) and 1,1-diphenylethylene (0.8 mmol, 4 equiv.) in THF (1.0 mL) was stirred under nitrogen atmosphere at 100 °C for 3 h. After the reaction was complete (monitored by TLC). In order to ensure whether the related radicals were trapped by 1,1-diphenylethylene, HRMS analysis of the crude reaction mixture was performed (see **Figure S1**). The resulting mass spectrum clearly shows a peak corresponding to the coupled product **4a**.

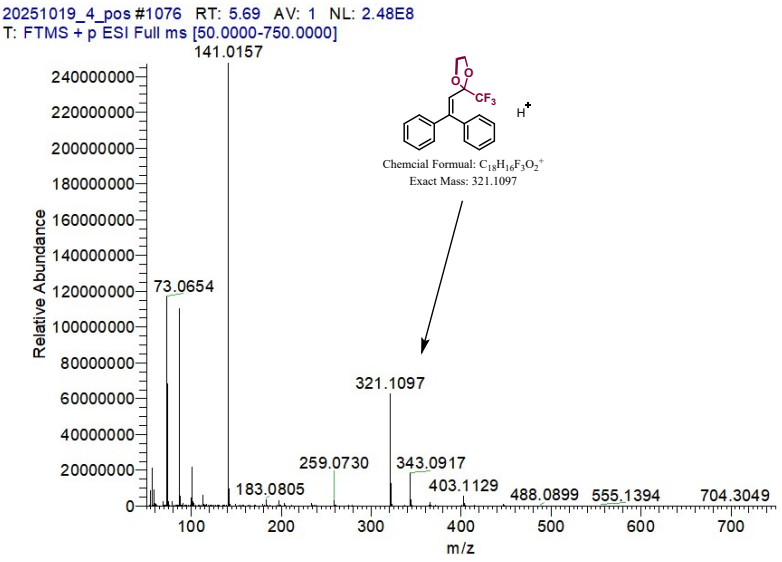
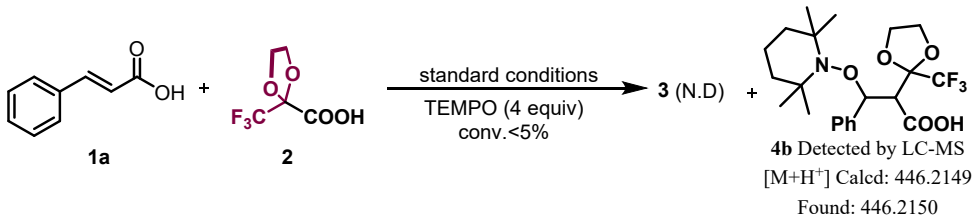


Figure S1. HRMS of 1,1-diphenylethylene-adduct



4b Detected by LC-MS
[M+H$^+$] Calcd: 446.2149
Found: 446.2150

1a (0.2 mmol, 1.0 equiv.), **2** (0.6 mmol, 3.0 equiv.), $PhI(OCOMe)_2$ (0.4 mmol, 2.0 equiv.) and TEMPO (0.8 mmol, 4 equiv.) in THF (1.0 mL) was stirred under nitrogen atmosphere at 100 °C for 3 h. After the reaction was complete (monitored by TLC). In order to ensure whether the related radicals were trapped by TEMPO, HRMS analysis of the crude reaction mixture was performed (see **Figure S2**). The resulting mass spectrum clearly shows a peak corresponding to the coupled product **4b**.

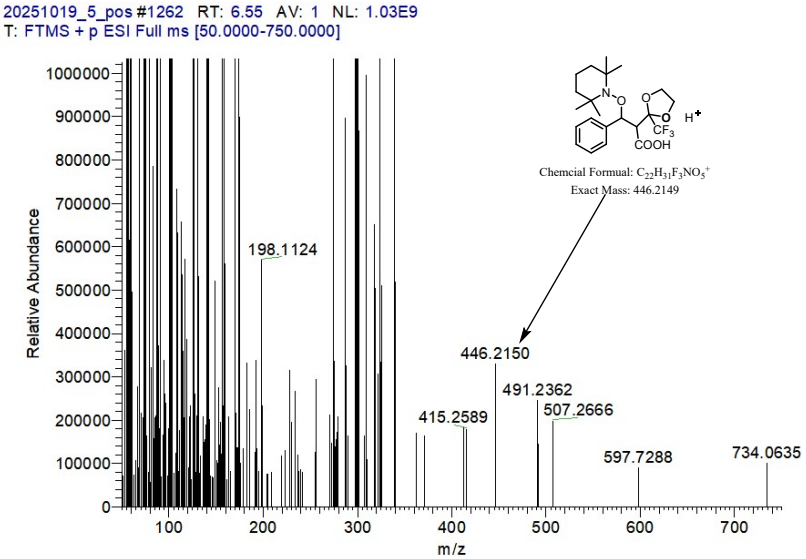


Figure S2. HRMS of TEMPO-adduct

5 References

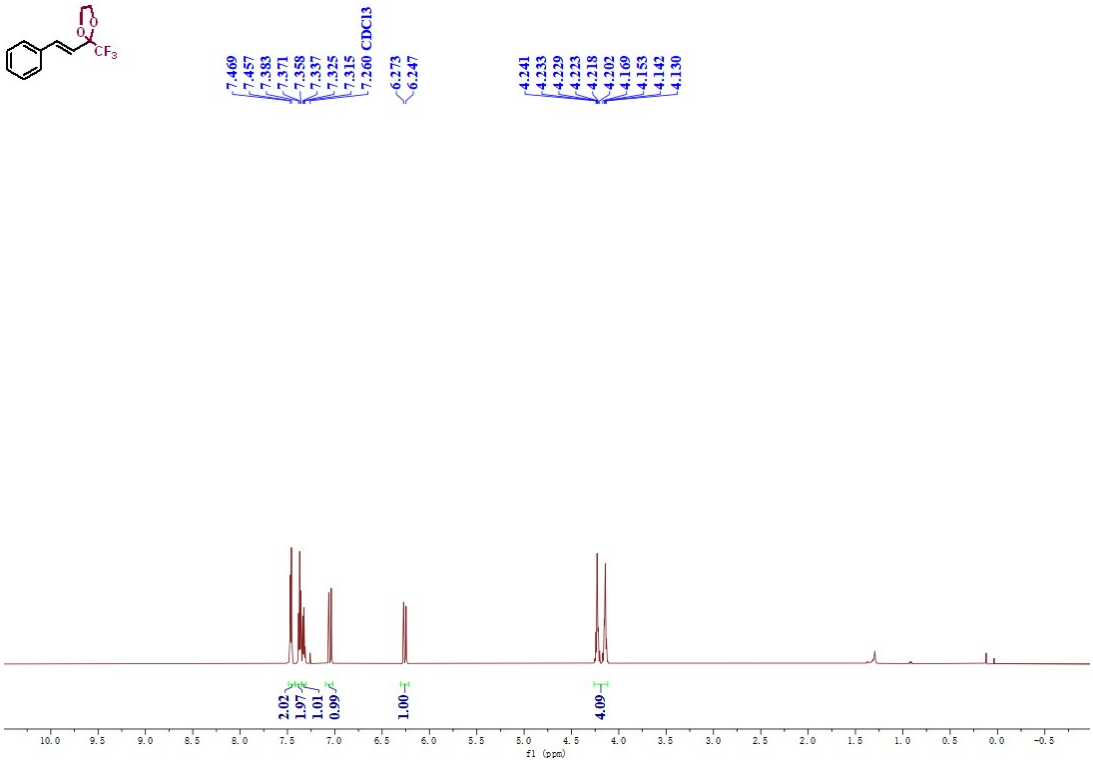
(1) Han, S.; Samony, K. L.; Nabi, R. N.; Bache, C. A.; Kim, D. K., Hydrotrifluoroacetylation of Alkenes via Designer Masked Acyl Reagents. *J. Am. Chem. Soc.* **2023**, *145*, 11530-11536.

(2) Zhang, K.; Rombach, D.; Nötel, N. Y.; Jeschke, G.; Katayev, D., Radical Trifluoroacetylation of Alkenes Triggered by a Visible-Light-Promoted C–O Bond Fragmentation of Trifluoroacetic Anhydride. *Angew. Chem. Int. Ed.* **2021**, *60*, 22487-22495.

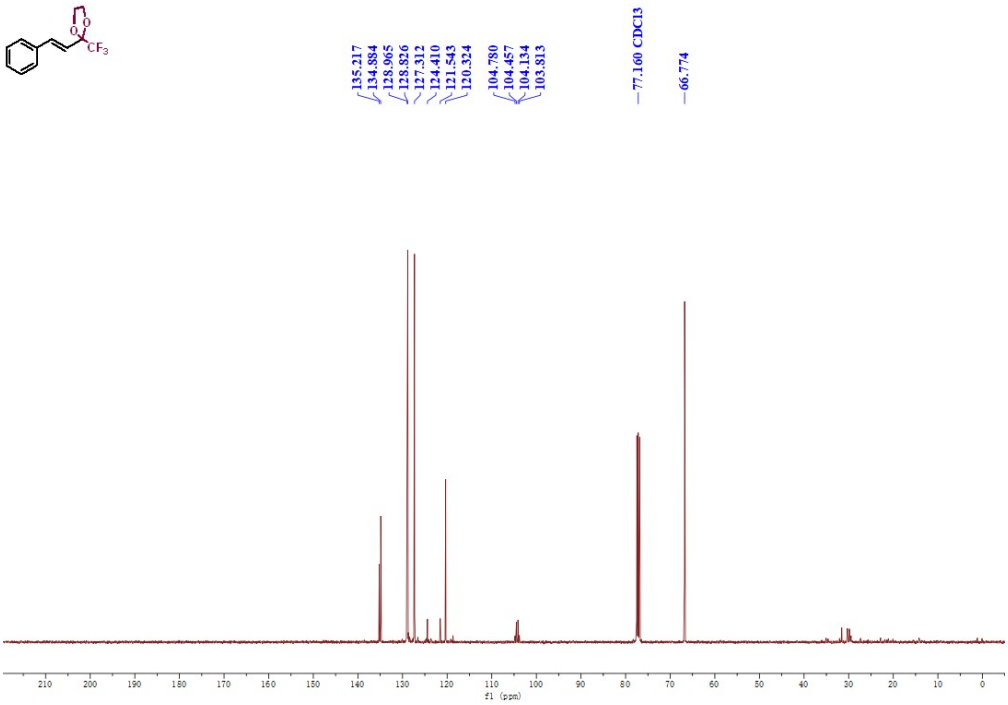
6 ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

(*E*)-2-styryl-2-(trifluoromethyl)-1,3-dioxolane (3)

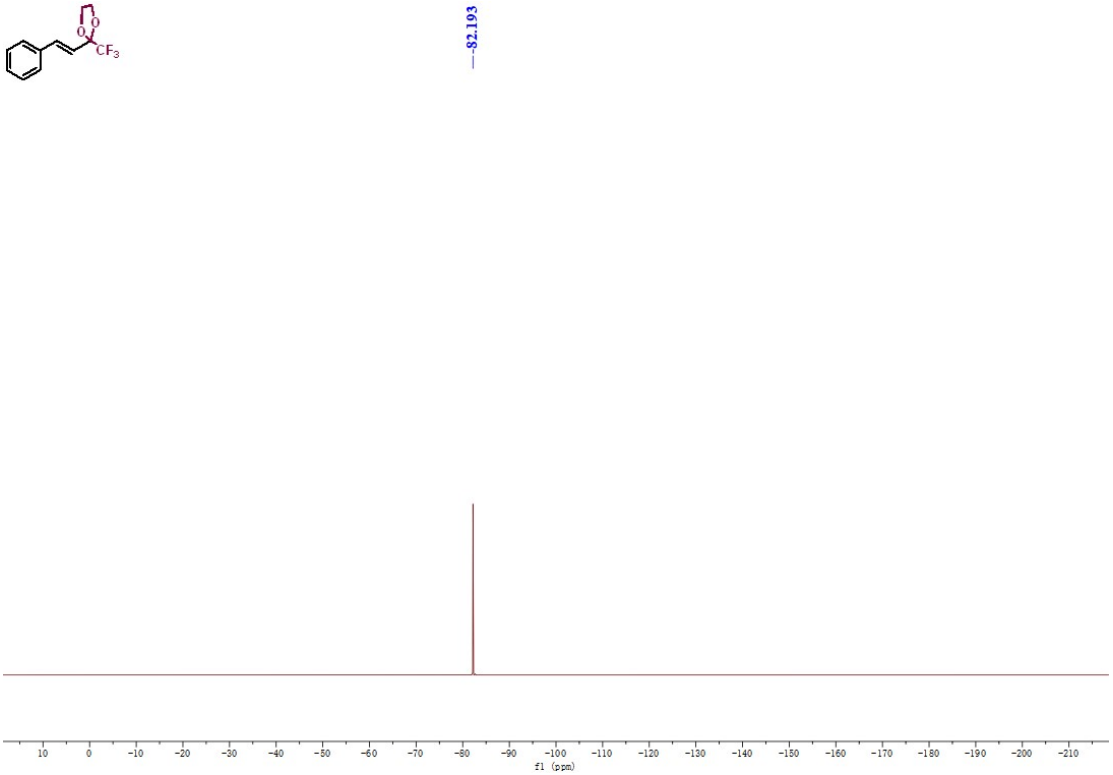
^{1}H NMR of 3



^{13}C NMR of 3

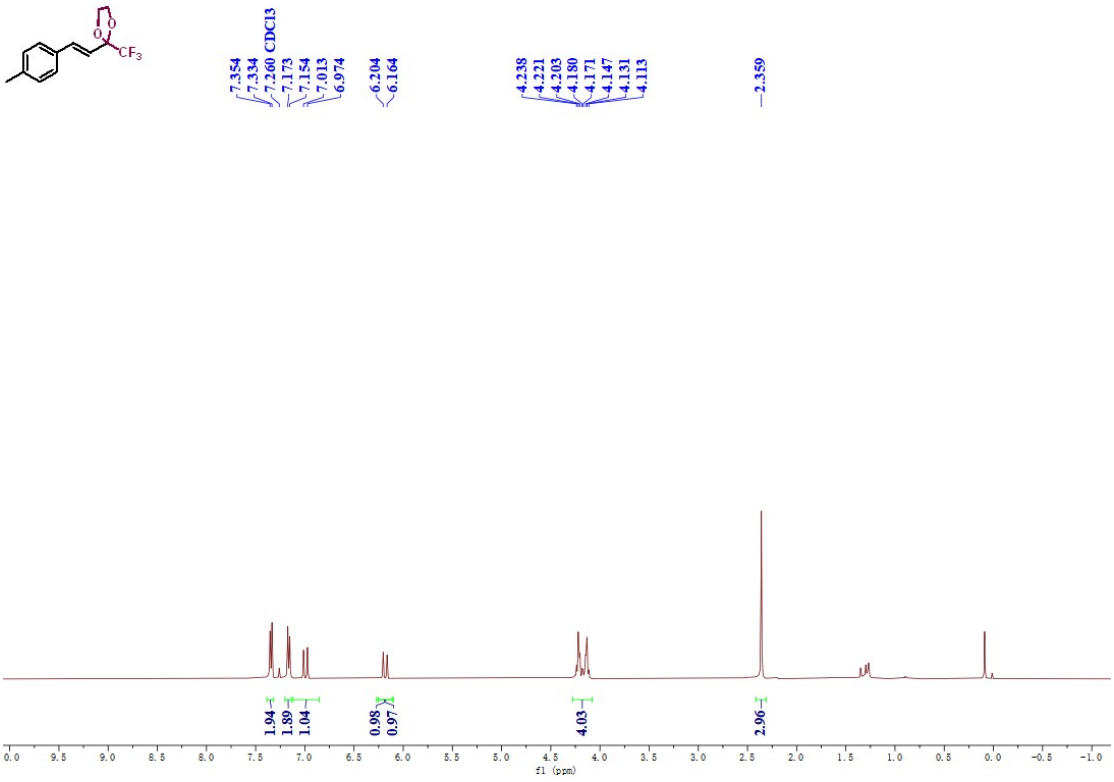


^{19}F NMR of 3

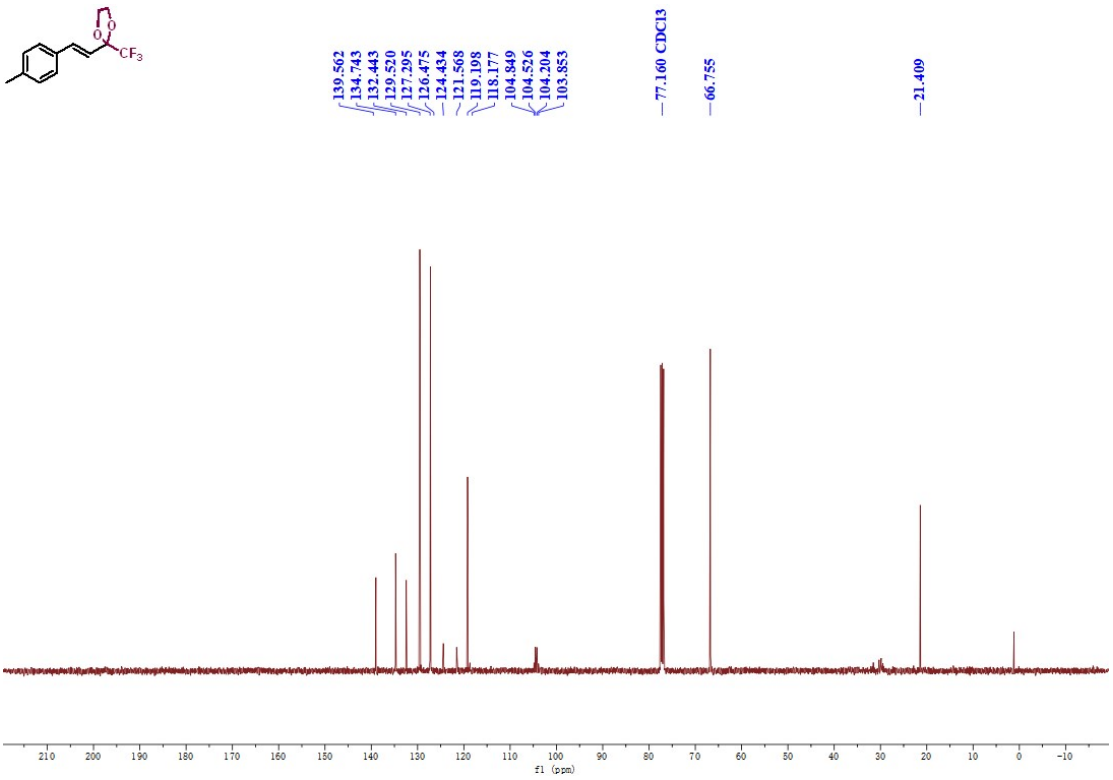


(*E*)-2-(4-methylstyryl)-2-(trifluoromethyl)-1,3-dioxolane (4)

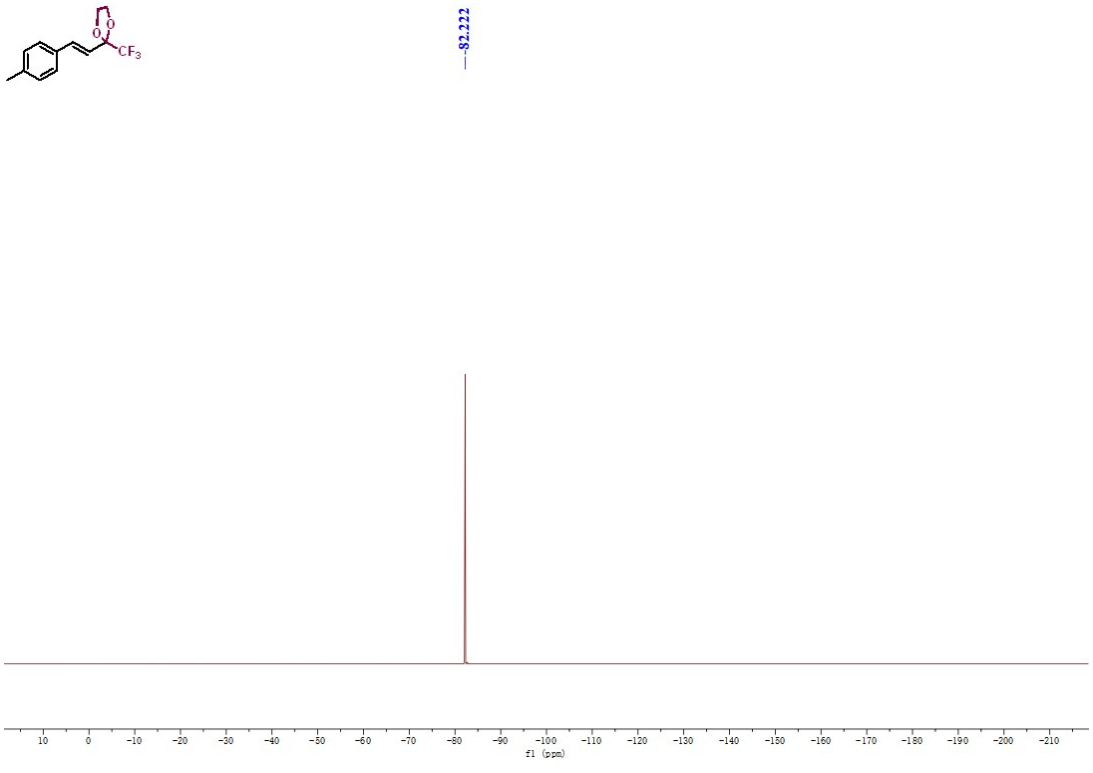
^{1}H NMR of 4



^{13}C NMR of 4

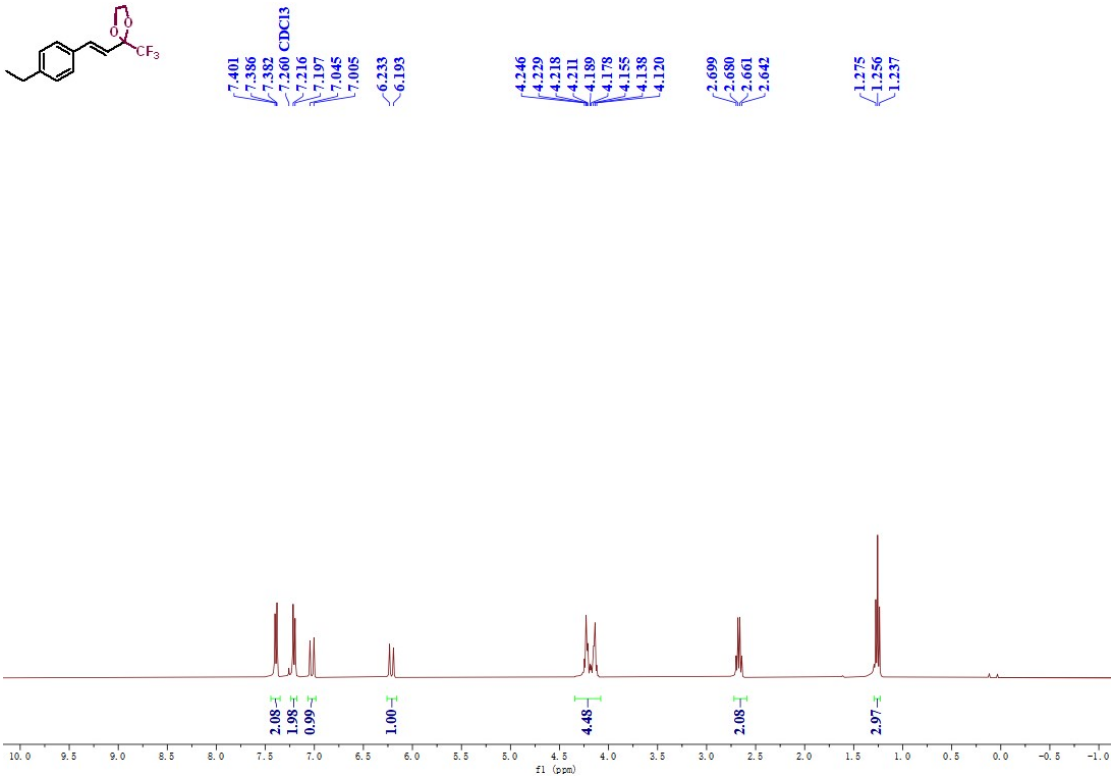


^{19}F NMR of 4

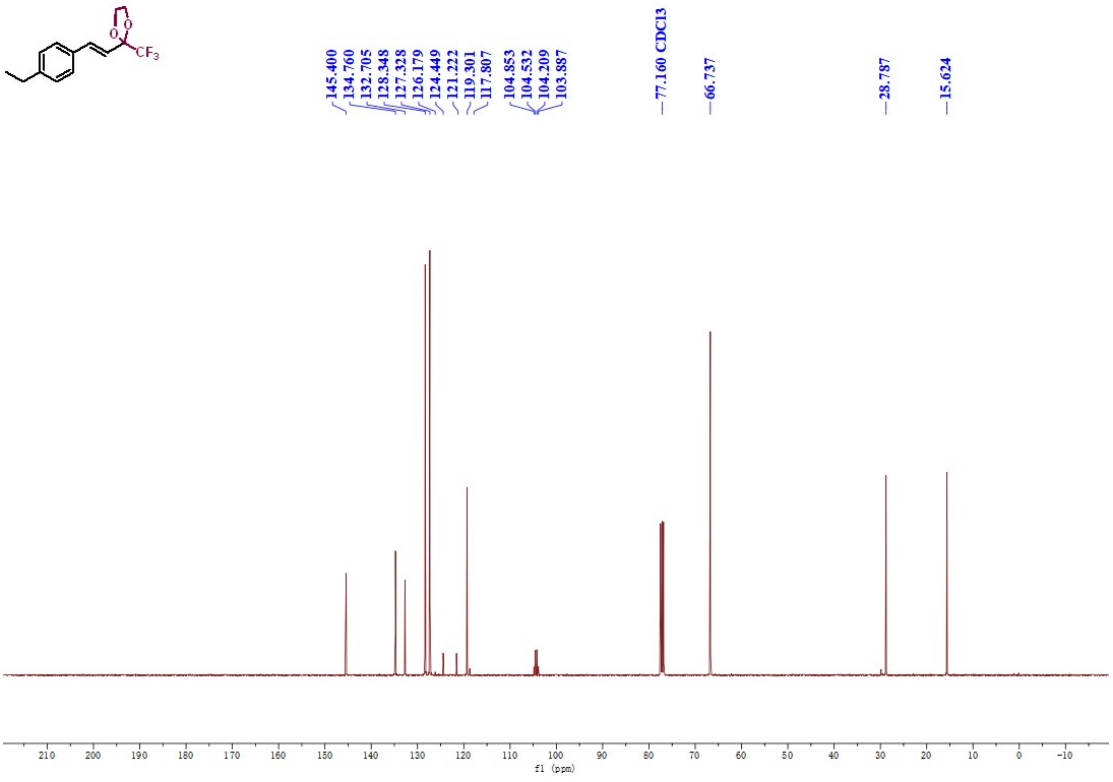


(*E*)-2-(4-ethylstyryl)-2-(trifluoromethyl)-1,3-dioxolane (5)

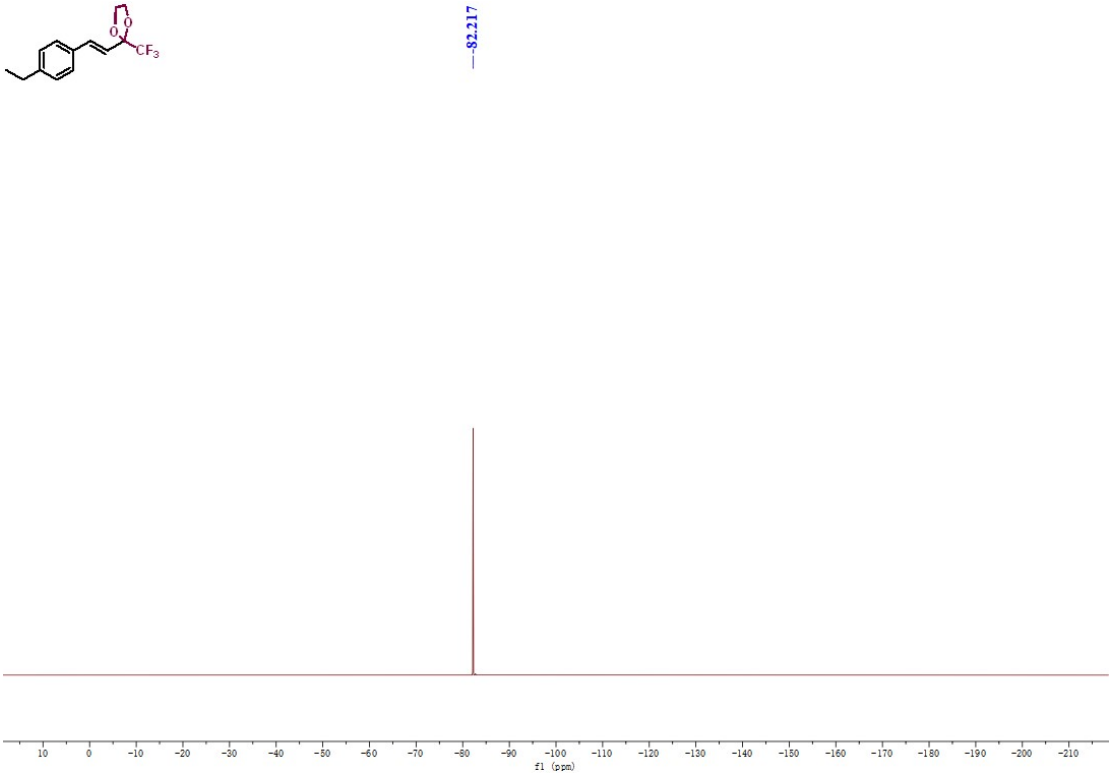
^{1}H NMR of 5



^{13}C NMR of 5

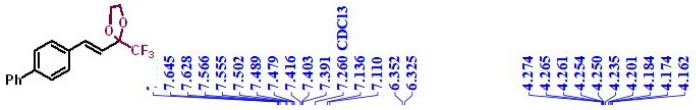


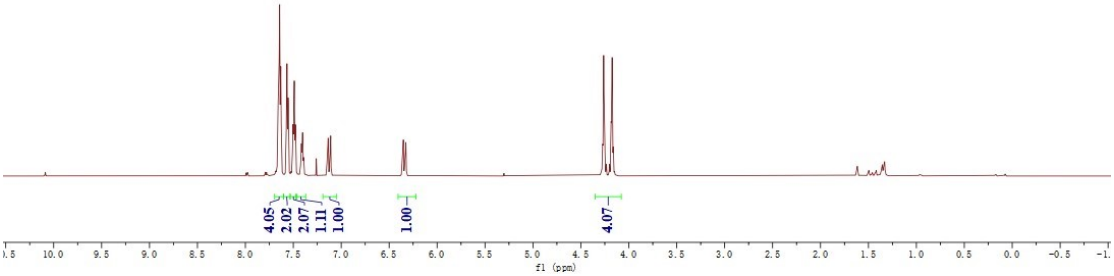
^{19}F NMR of 5



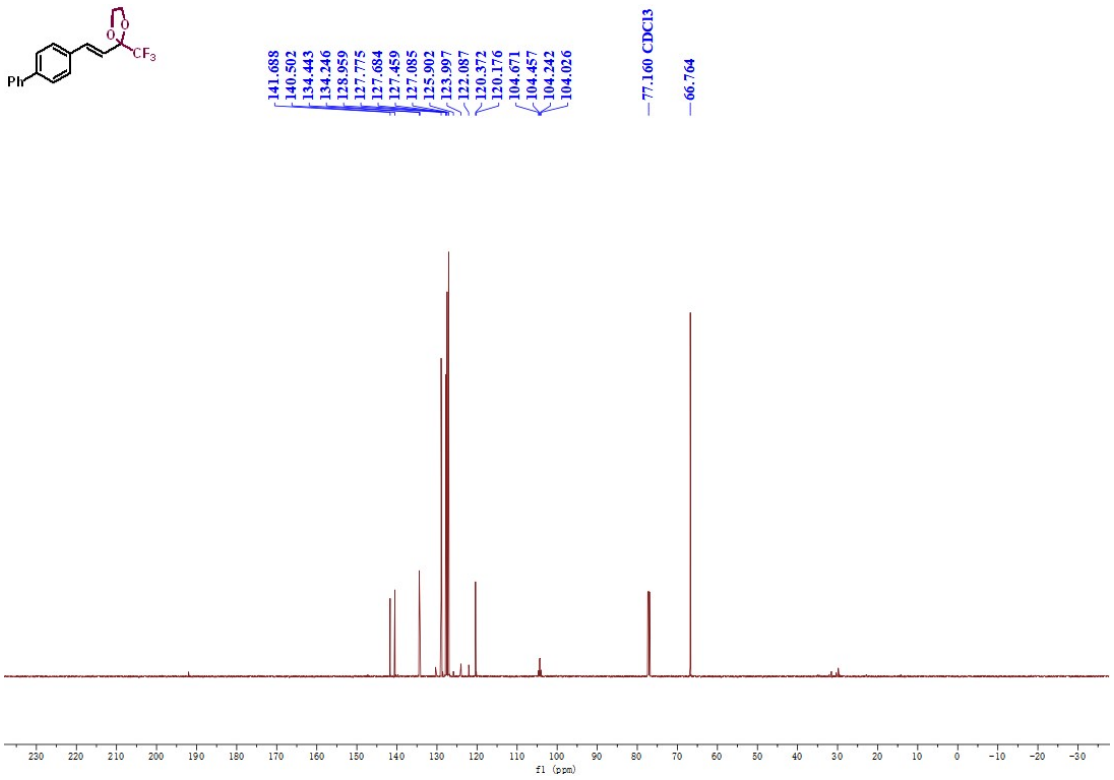
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-2-(trifluoromethyl)-1,3-dioxolane (6)

^{1}H NMR of 6

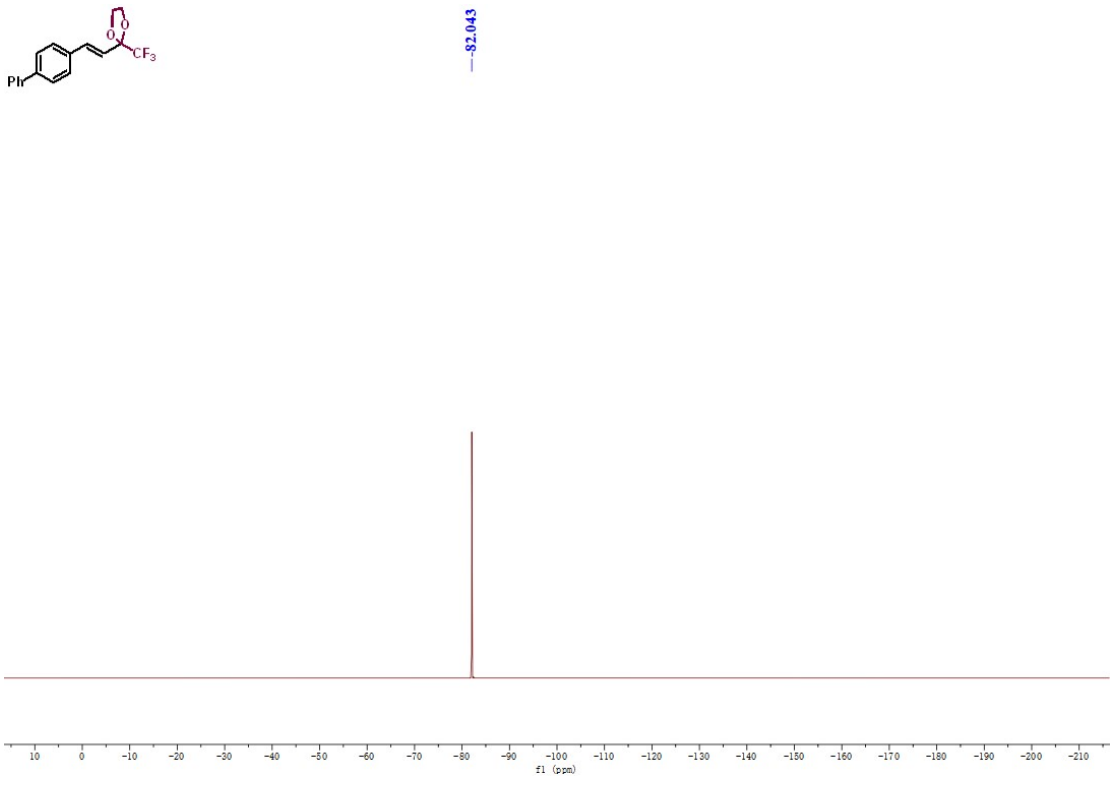




^{13}C NMR of 6

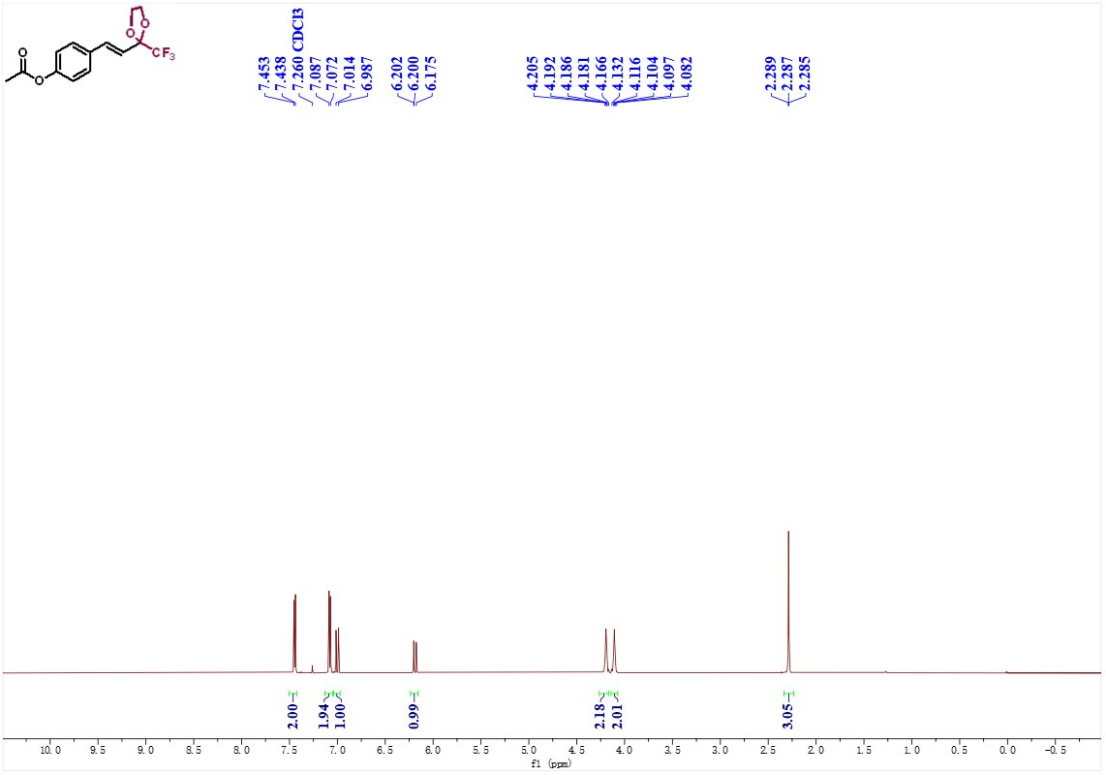


^{19}F NMR of 6

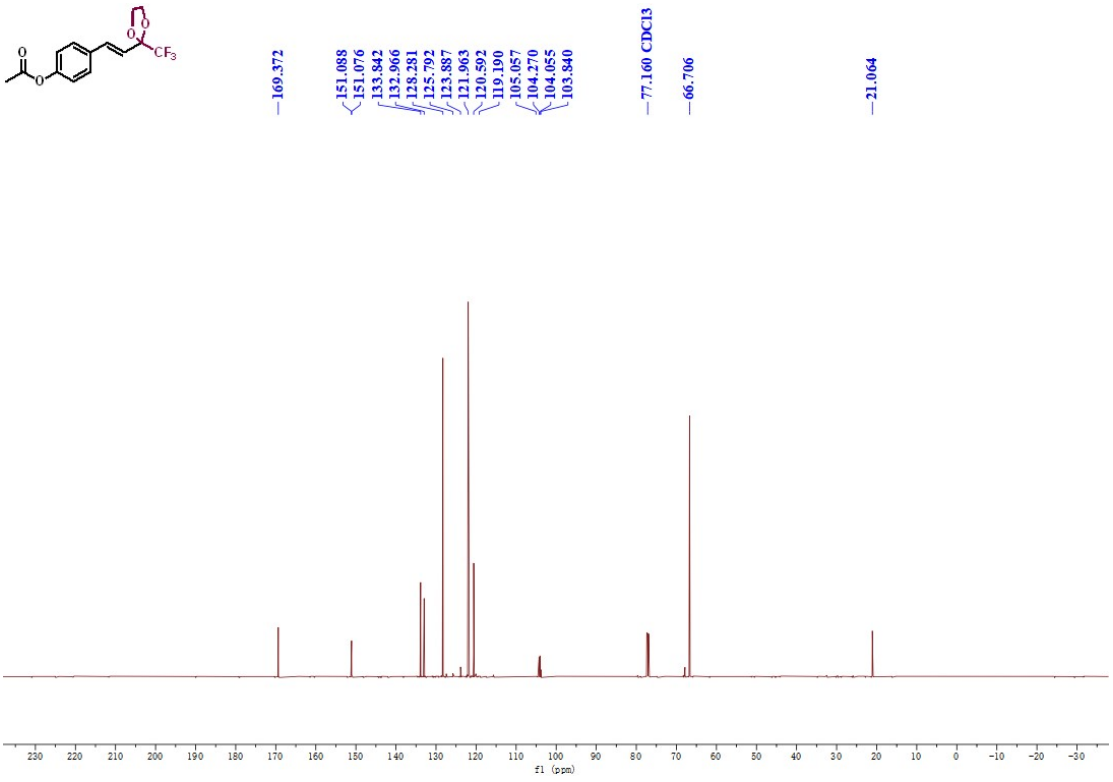


(*E*)-4-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)phenyl acetate (7)

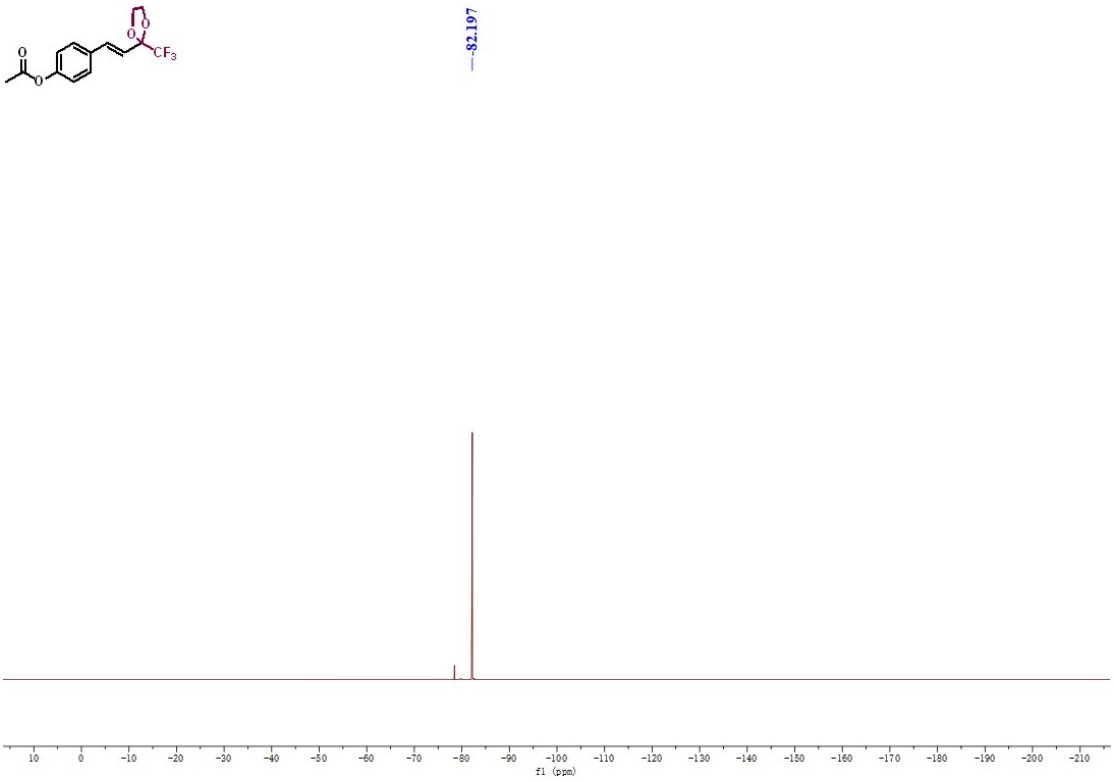
^{1}H NMR of 7



^{13}C NMR of 7

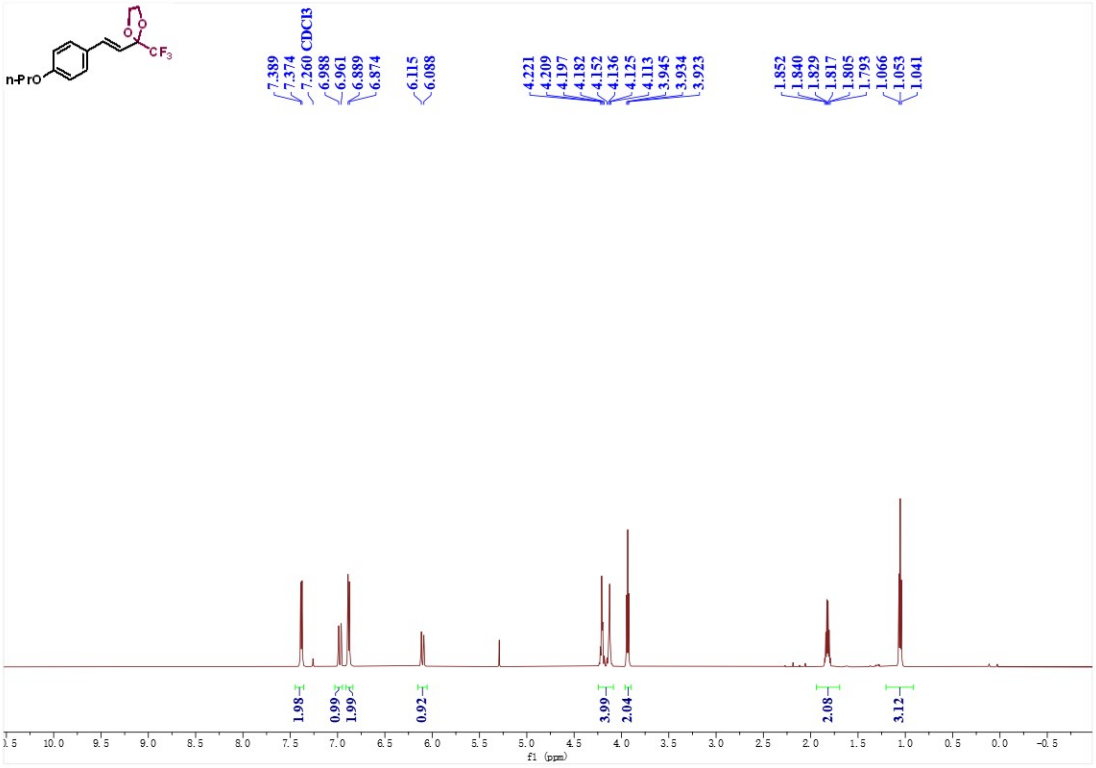


^{19}F NMR of 7

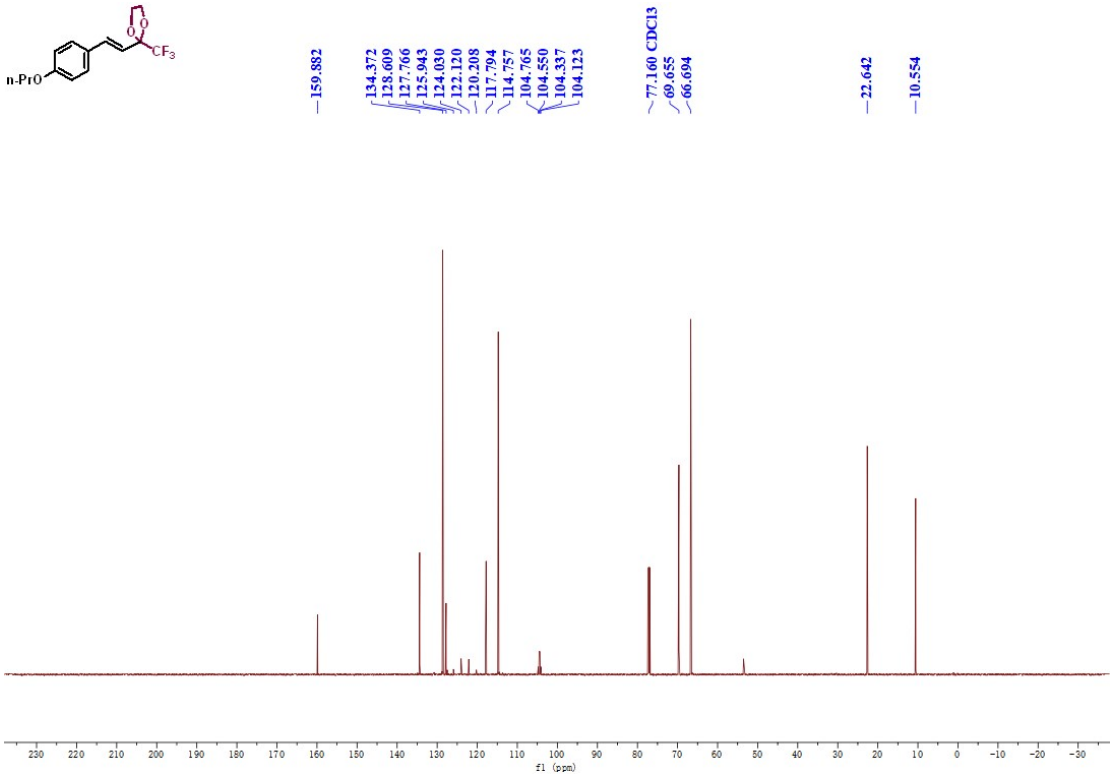


(*E*)-2-(4-propoxystyryl)-2-(trifluoromethyl)-1,3-dioxolane (8)

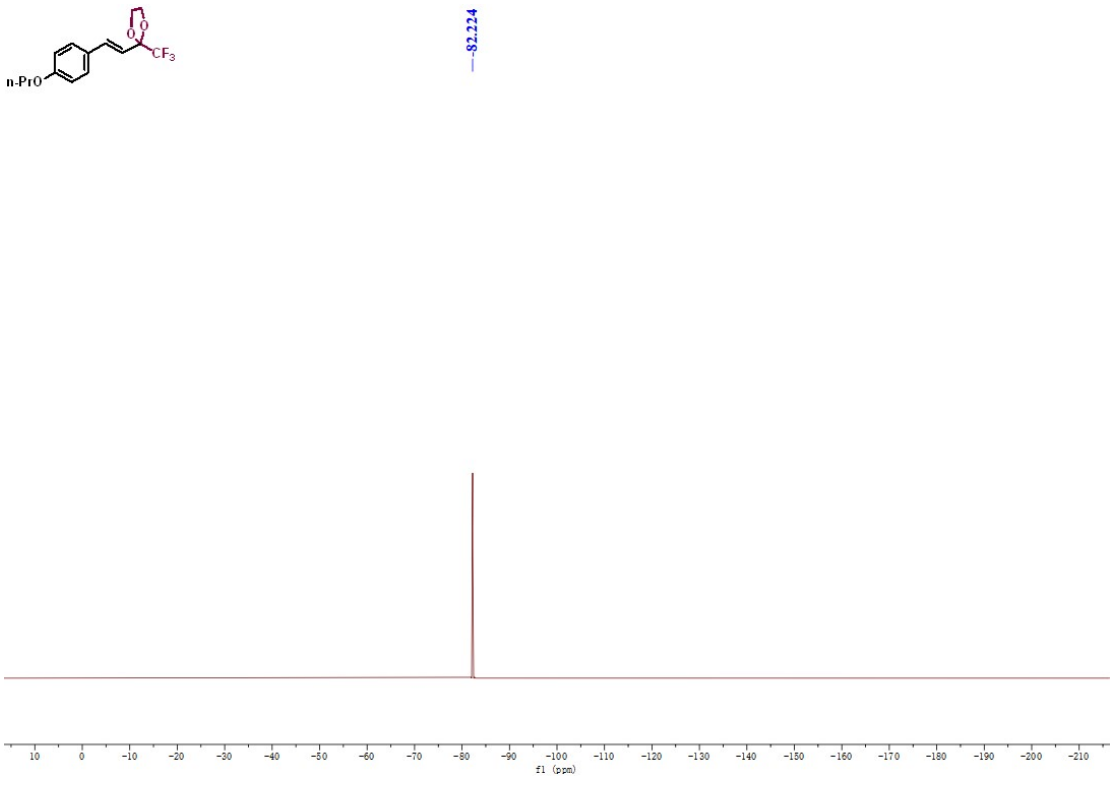
^{1}H NMR of 8



^{13}C NMR of 8

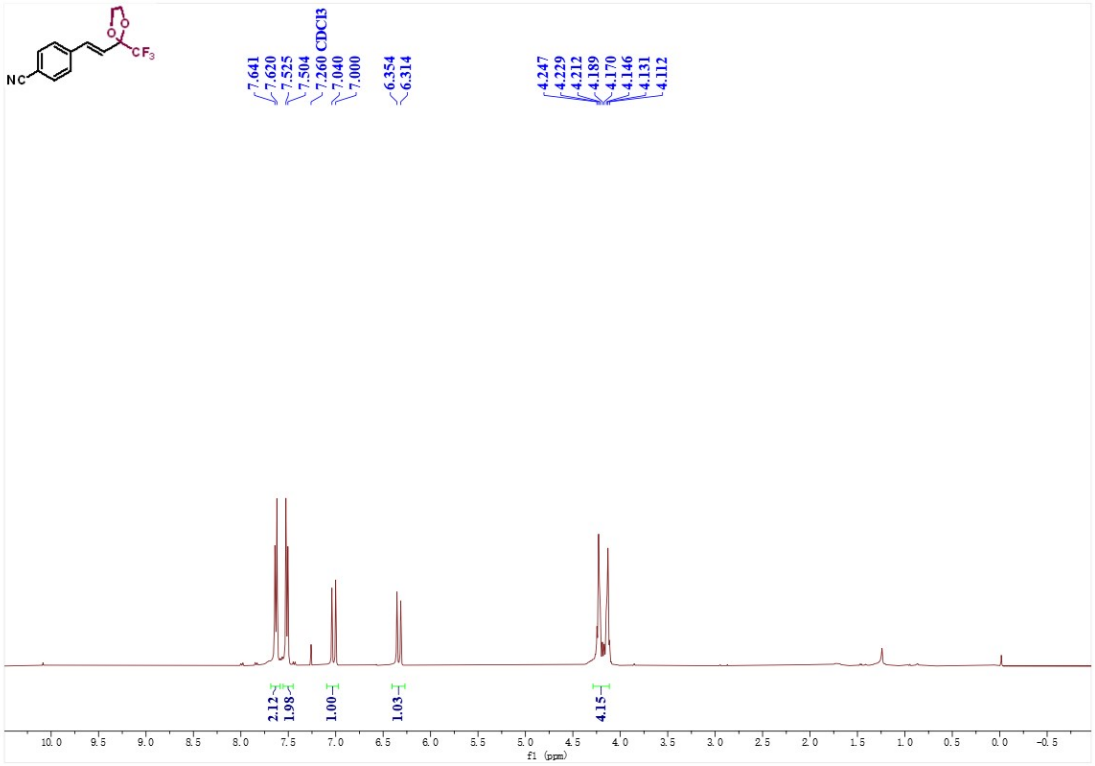


^{19}F NMR of 8

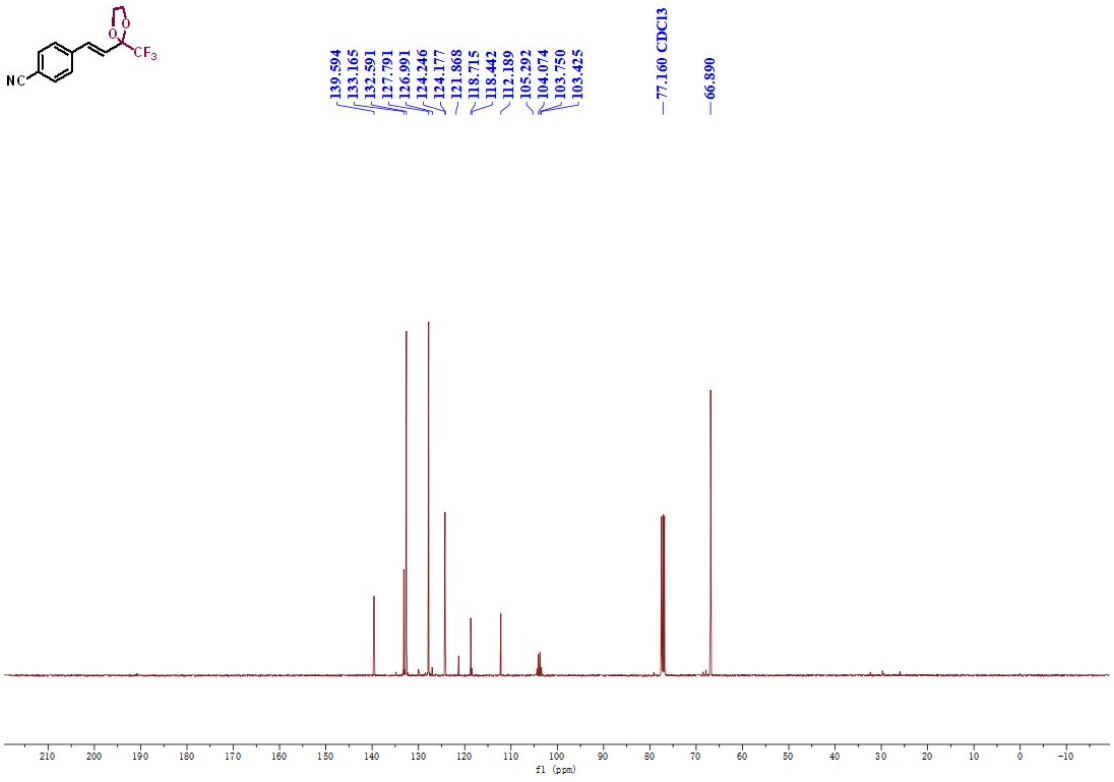


(*E*)-4-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzonitrile (9)

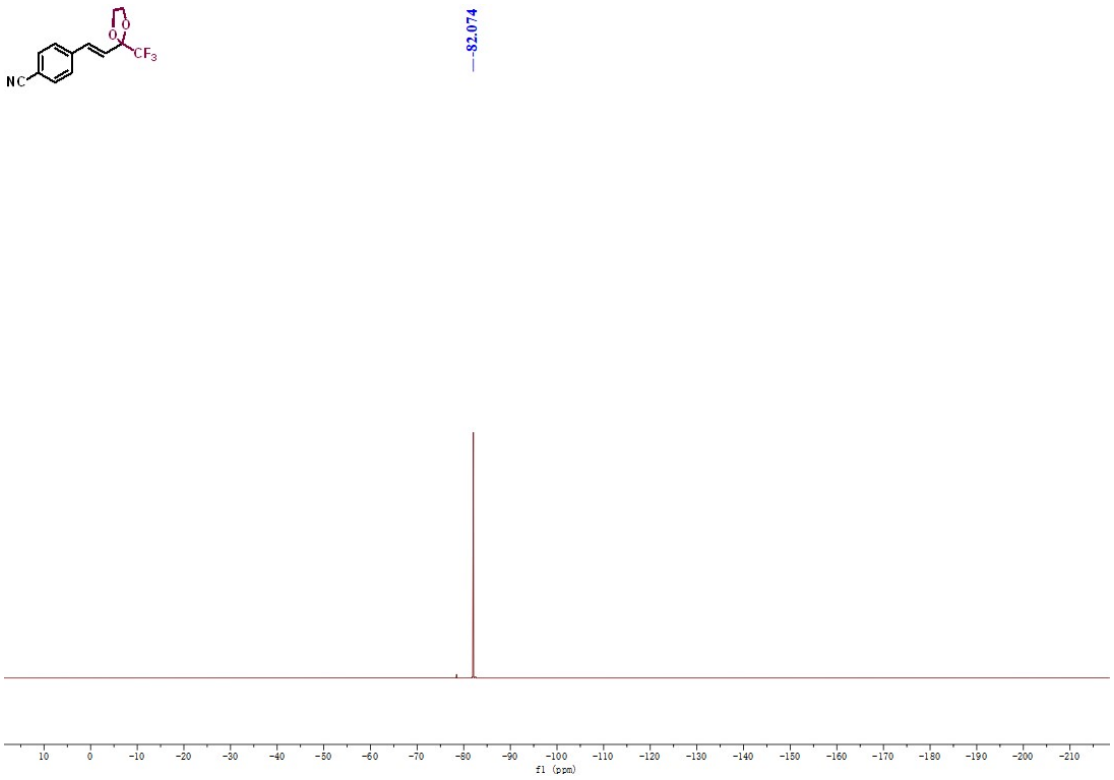
^{1}H NMR of 9



^{13}C NMR of 9

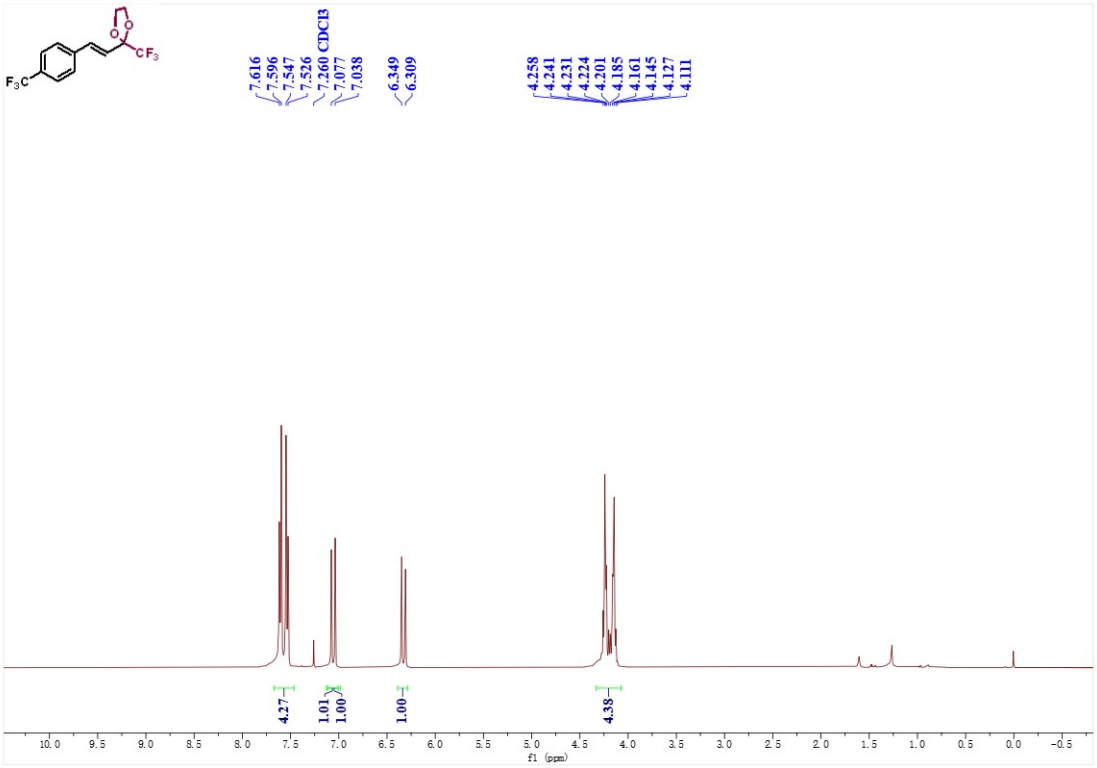


^{19}F NMR of 9

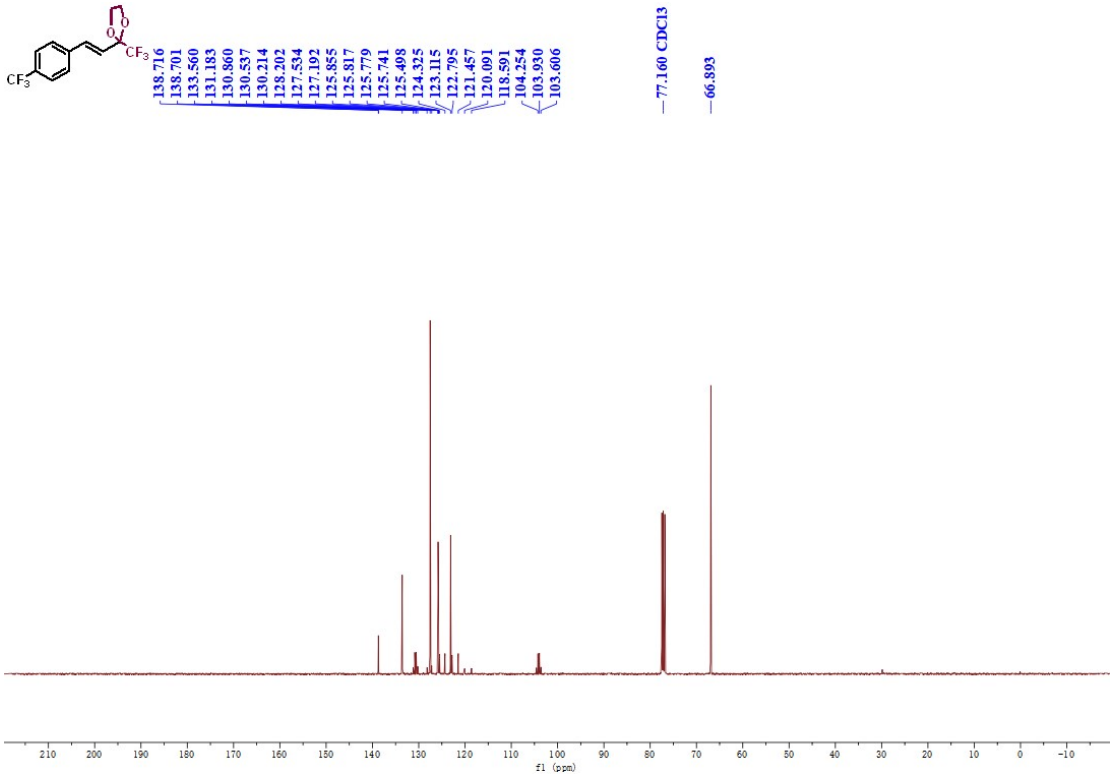


(*E*)-2-(trifluoromethyl)-2-(4-(trifluoromethyl)styryl)-1,3-dioxolane (10)

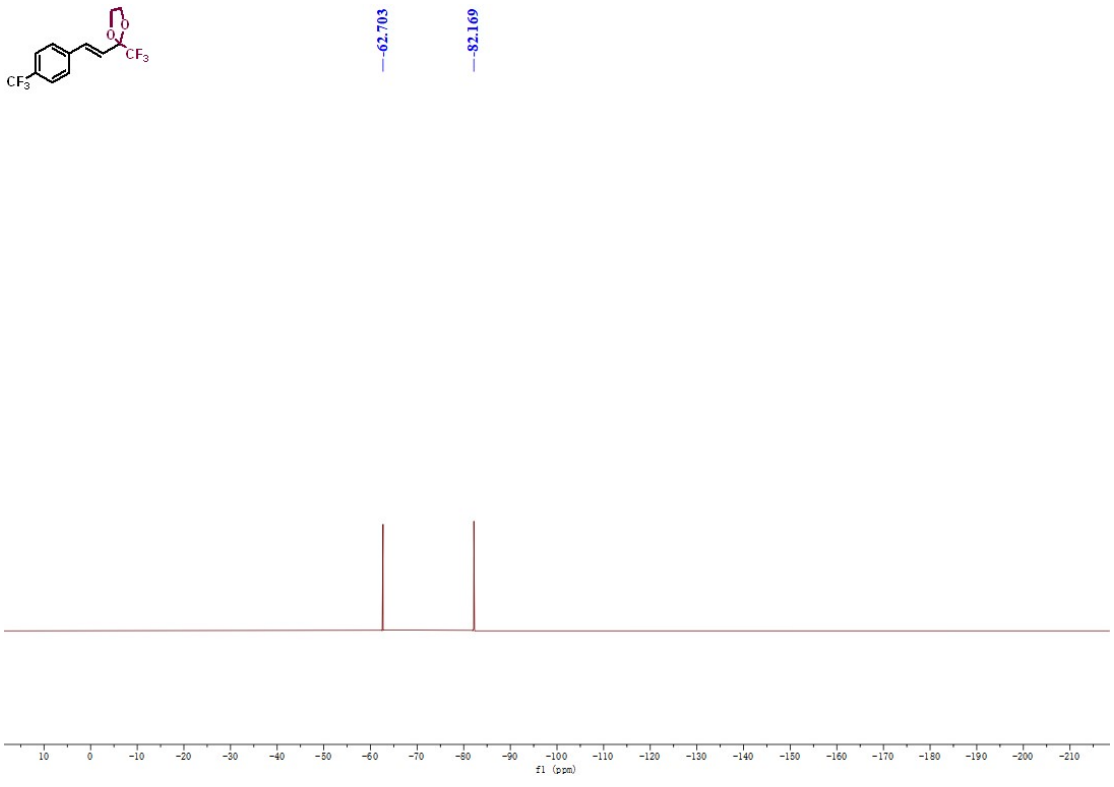
^{1}H NMR of 10



^{13}C NMR of 10

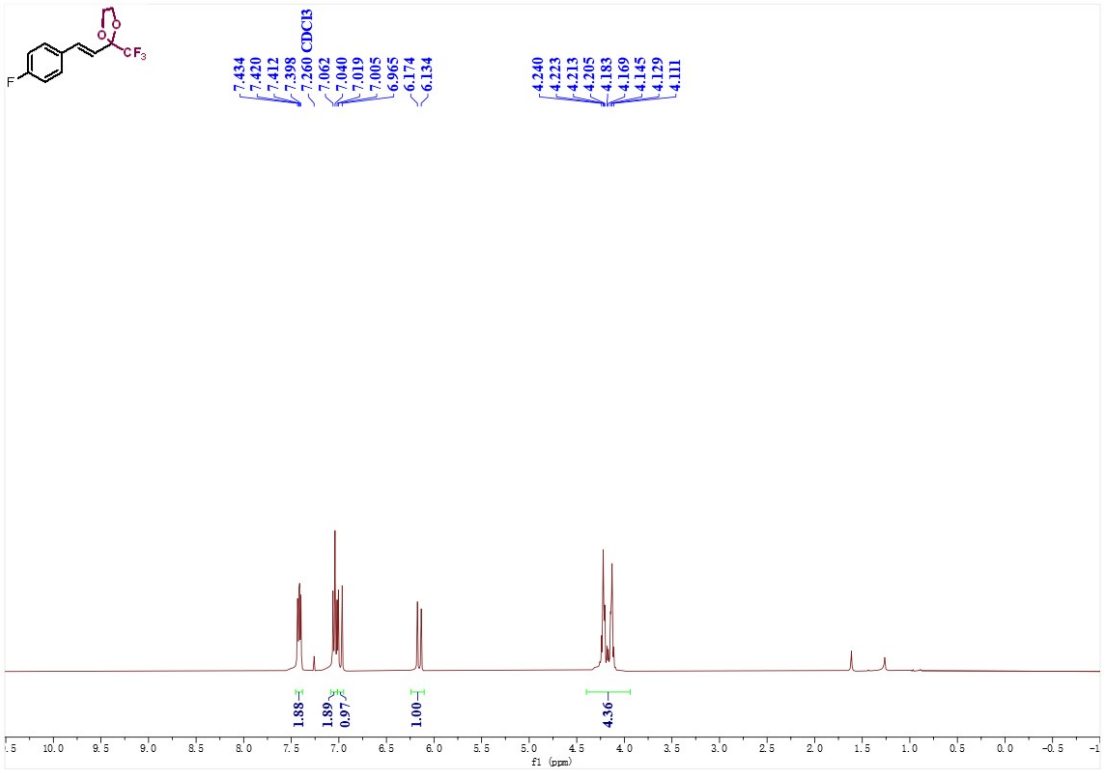


^{19}F NMR of 10

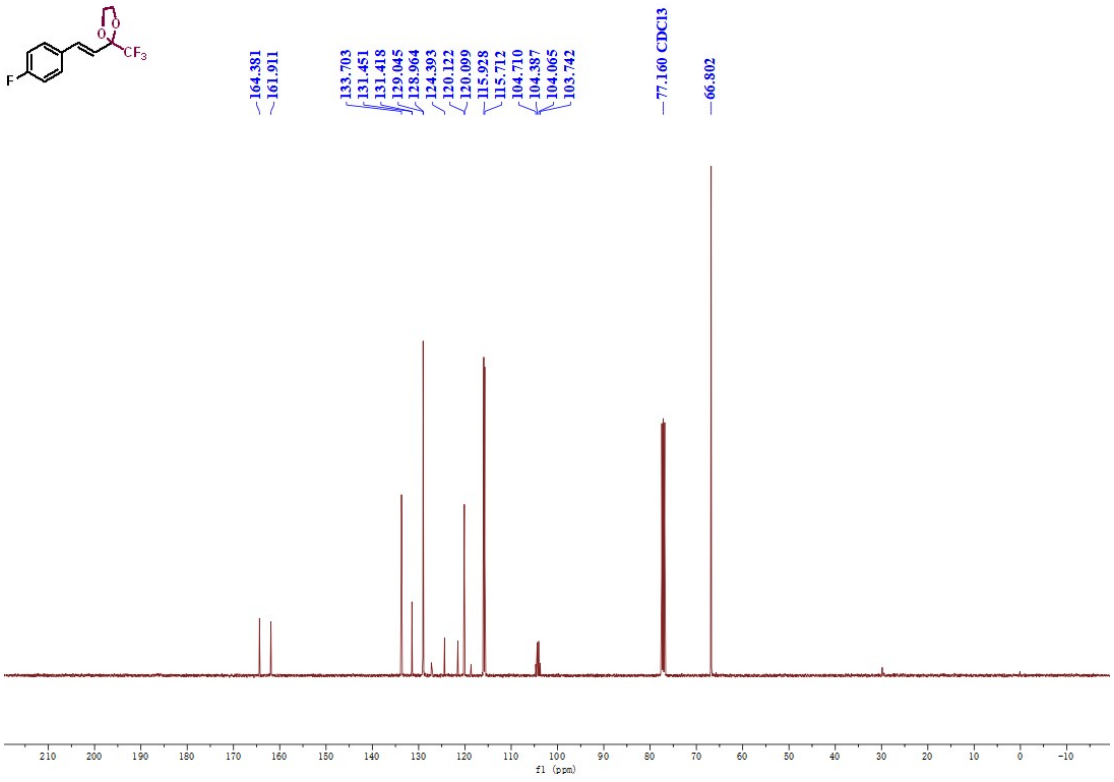


(*E*)-2-(4-fluorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (11)

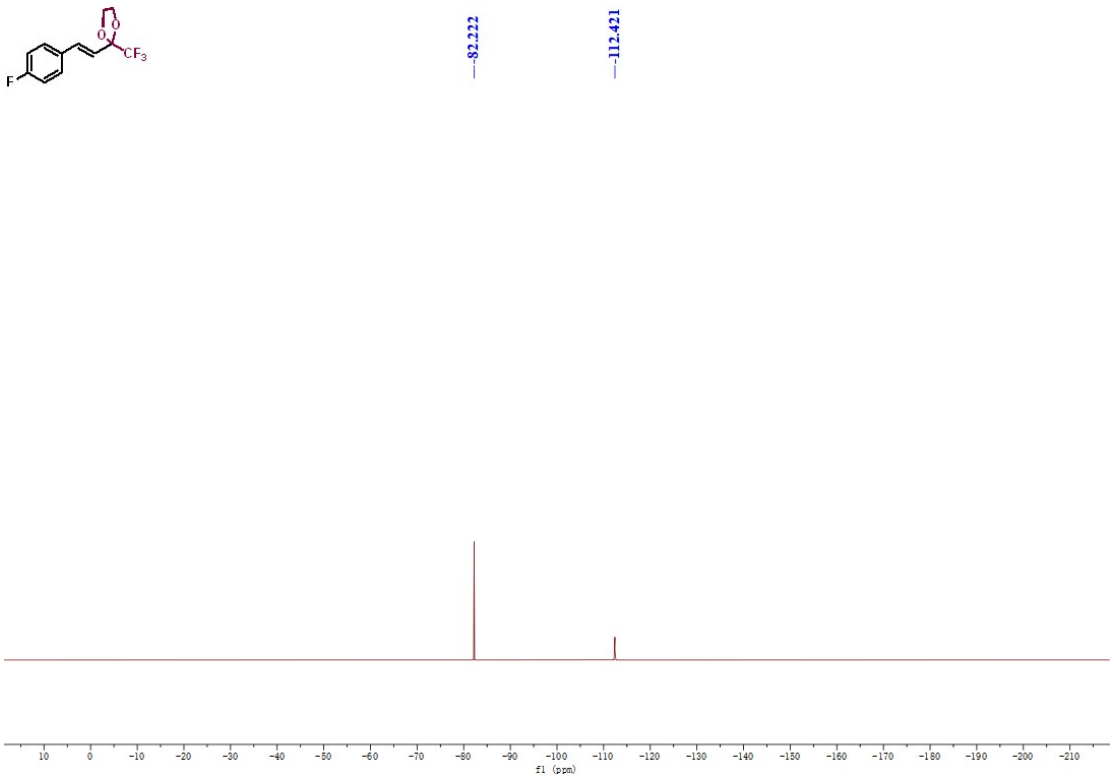
^{1}H NMR of 11



^{13}C NMR of 11

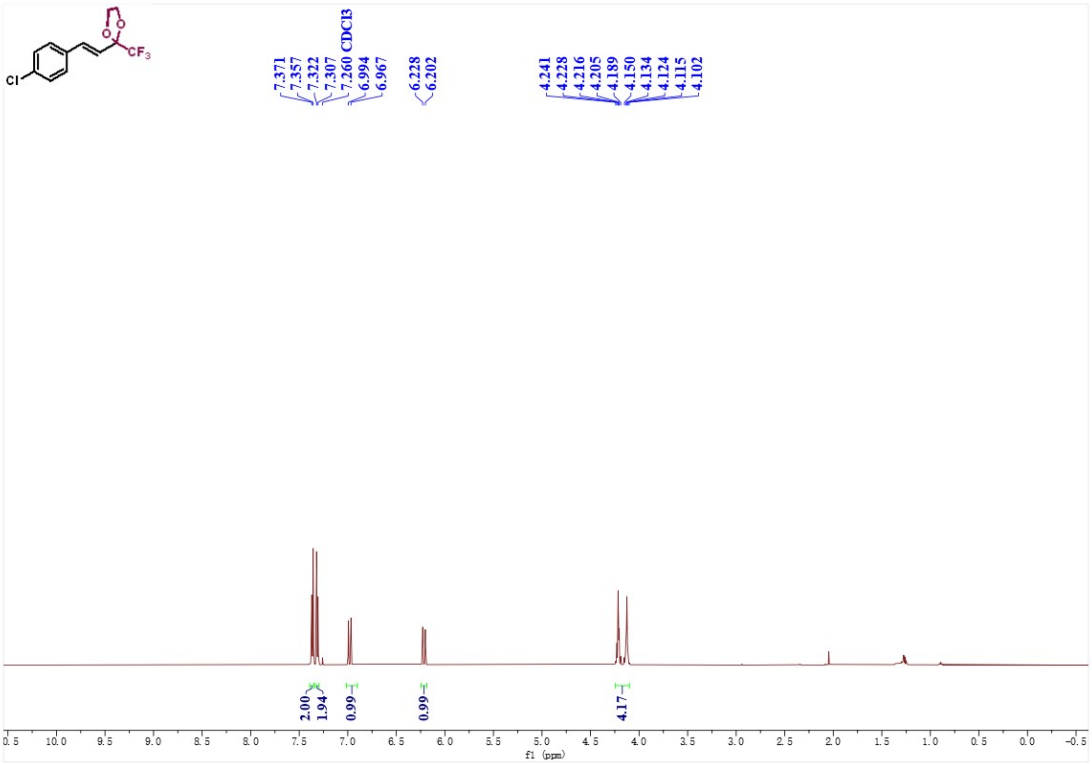


^{19}F NMR of 11

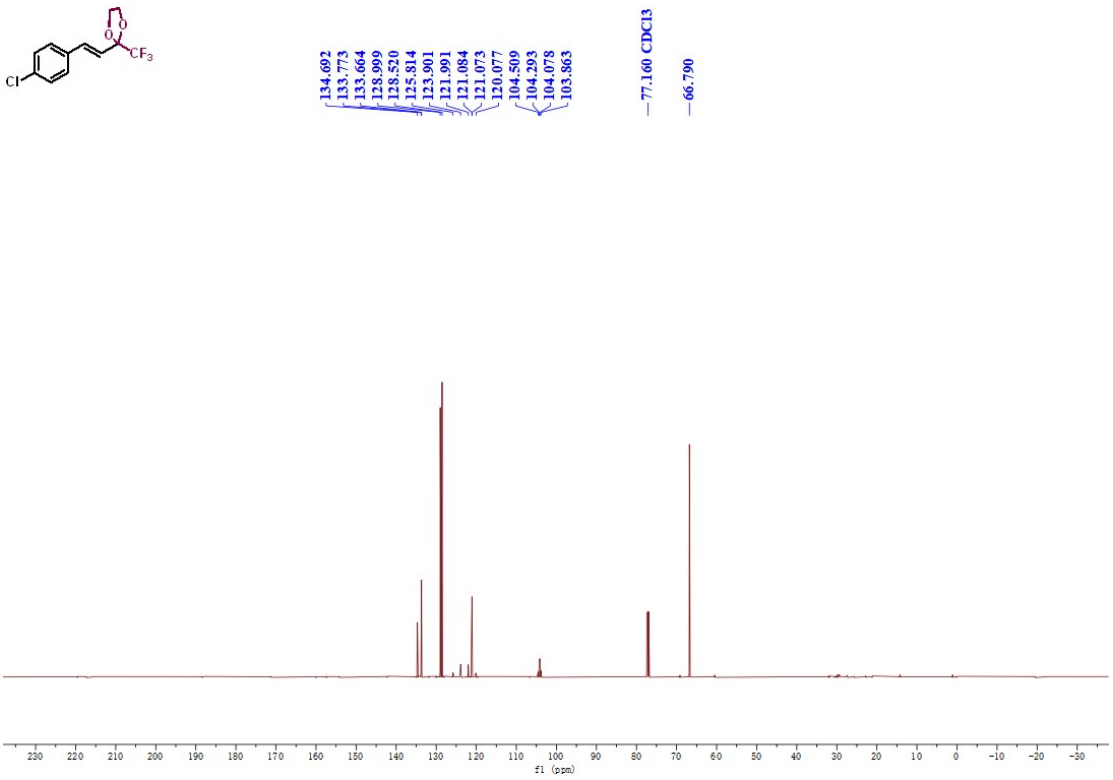


(*E*)-2-(4-chlorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (12)

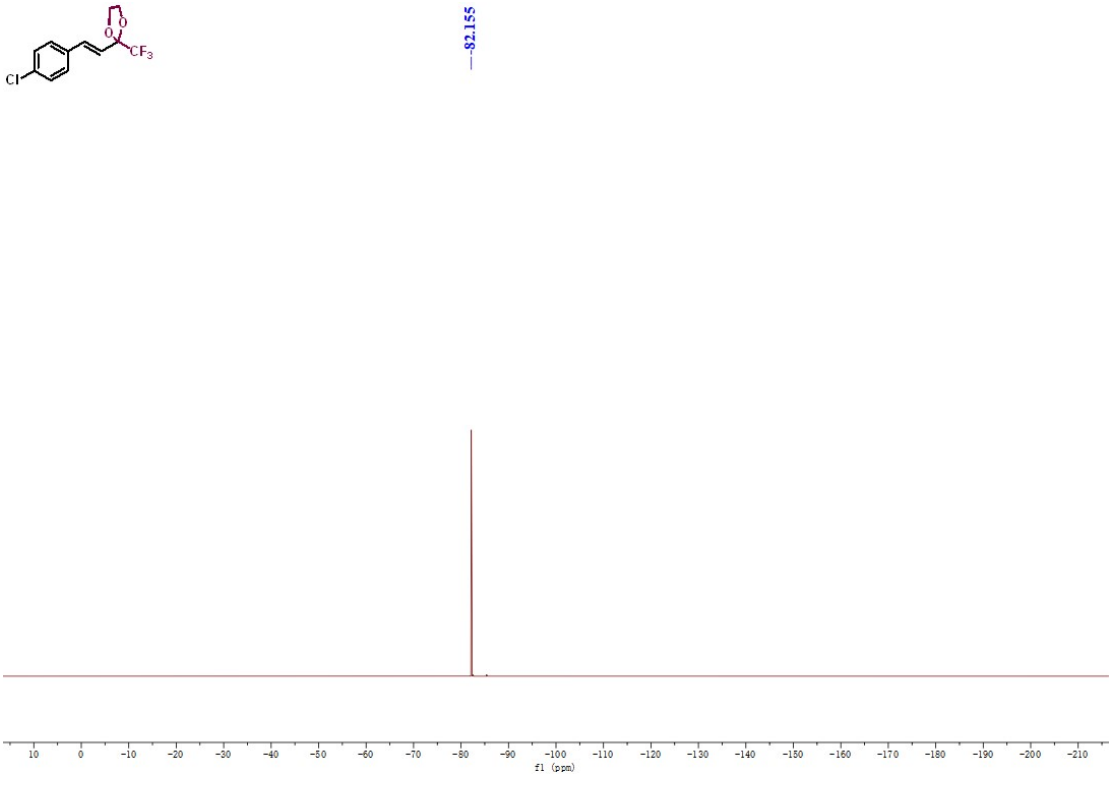
^{1}H NMR of 12



^{13}C NMR of 12

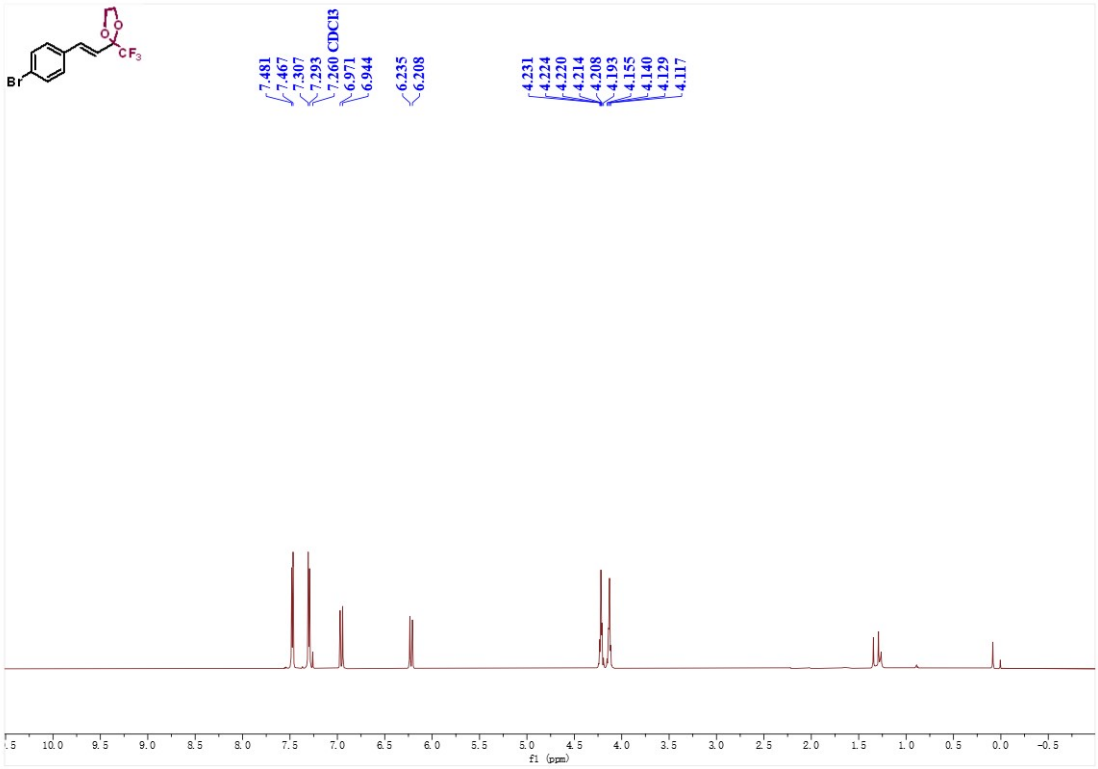


^{19}F NMR of 12

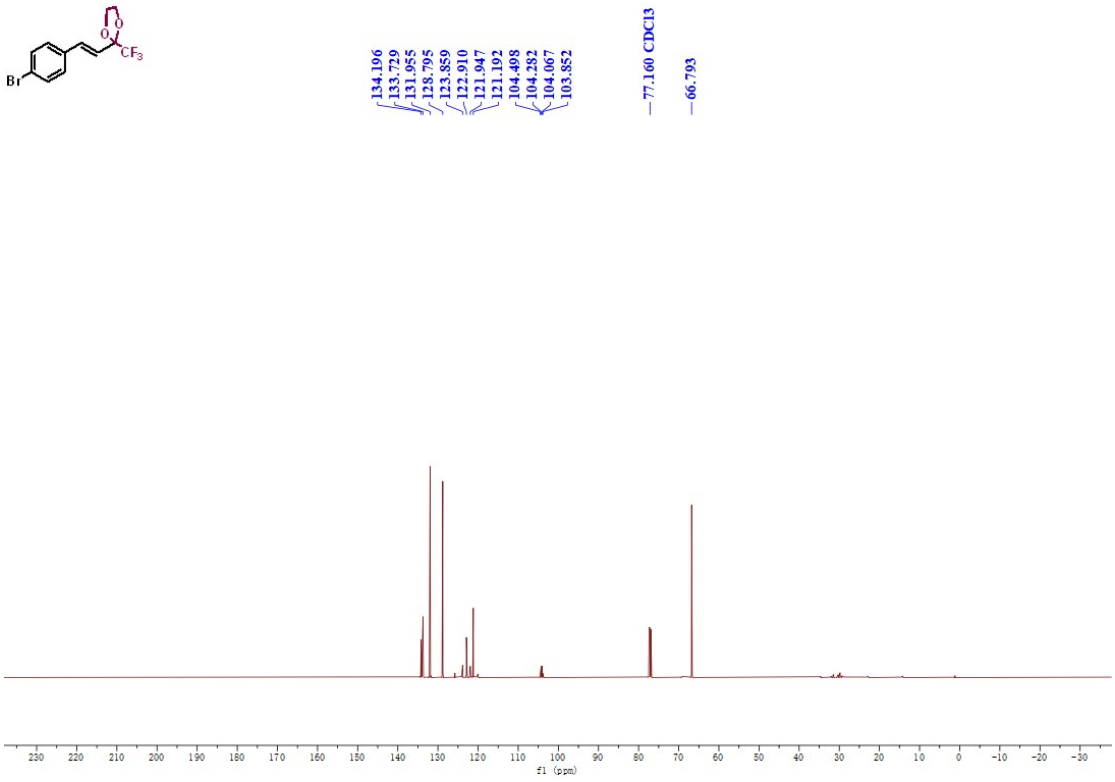


(*E*)-2-(4-bromostyryl)-2-((difluoro-λ^3-methyl)-λ^2-fluoraneyl)-1,3-dioxolane (13)

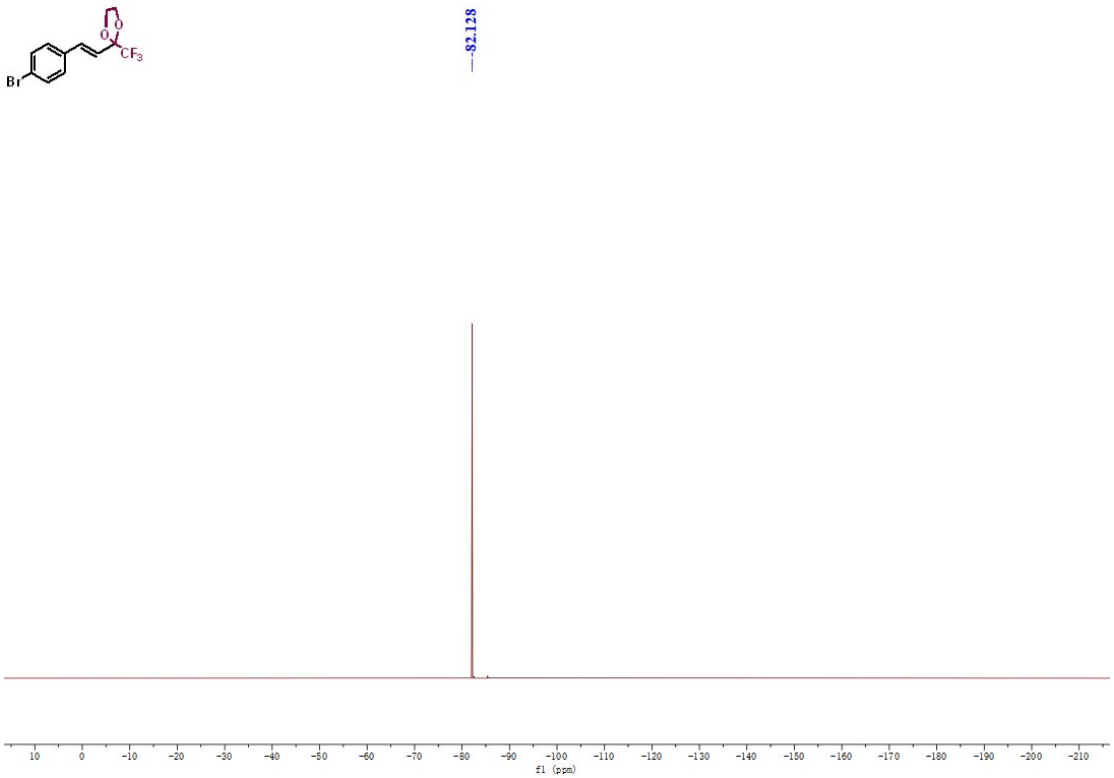
^{1}H NMR of 13



^{13}C NMR of 13

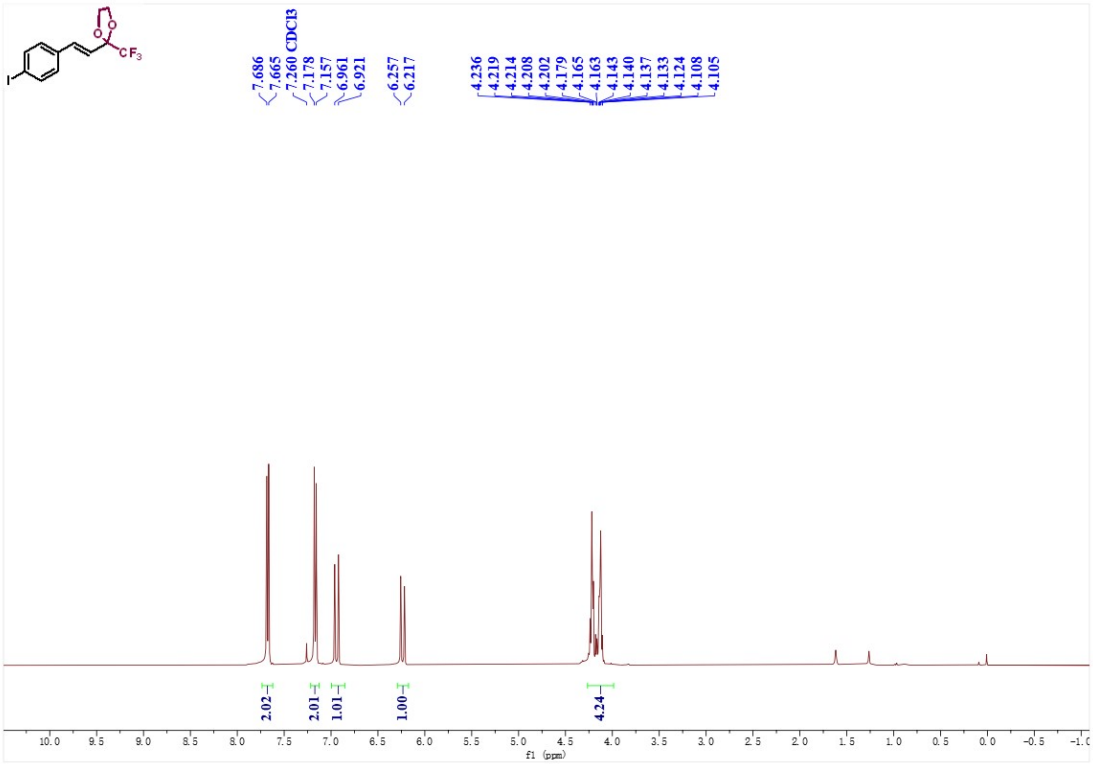


^{19}F NMR of 13

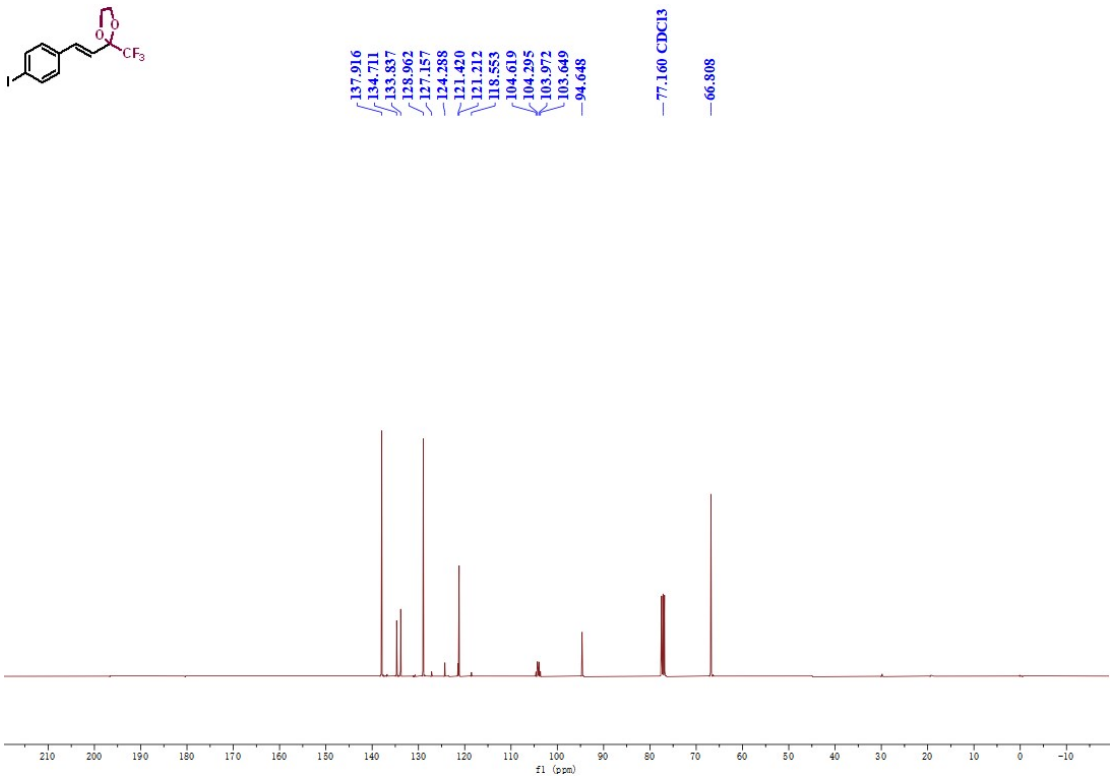


(*E*)-2-(4-iodostyryl)-2-(trifluoromethyl)-1,3-dioxolane (14)

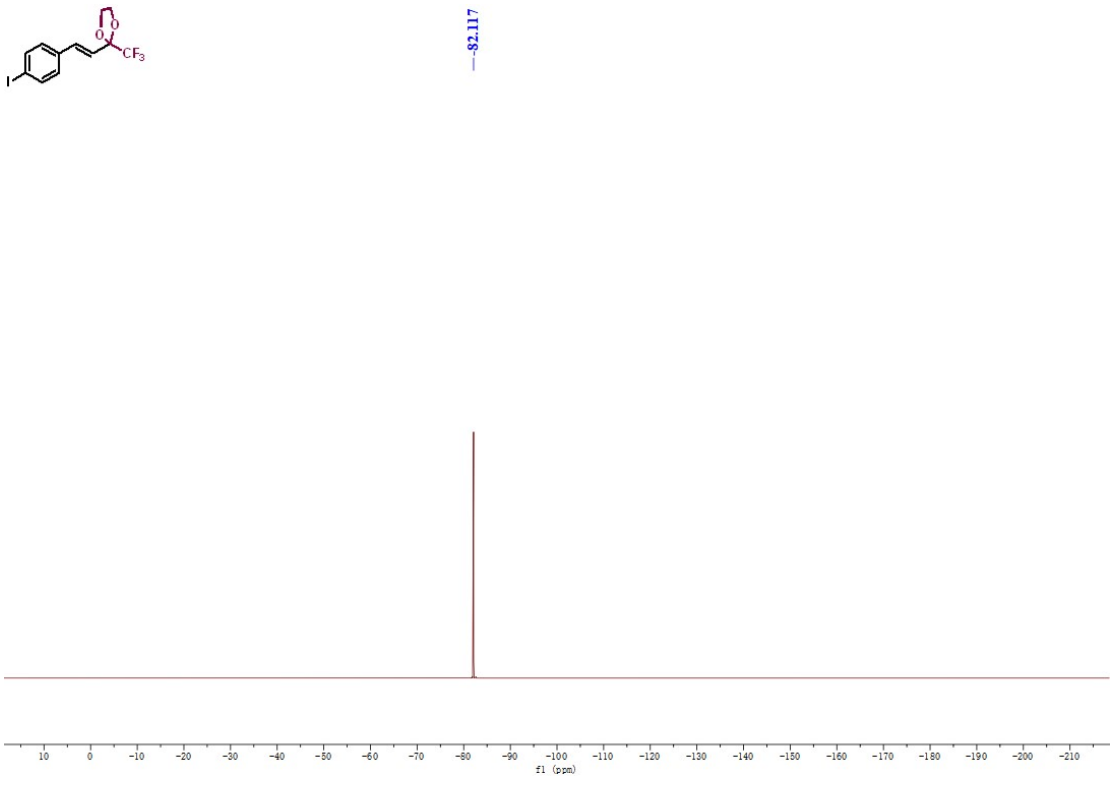
^{1}H NMR of 14



^{13}C NMR of 14

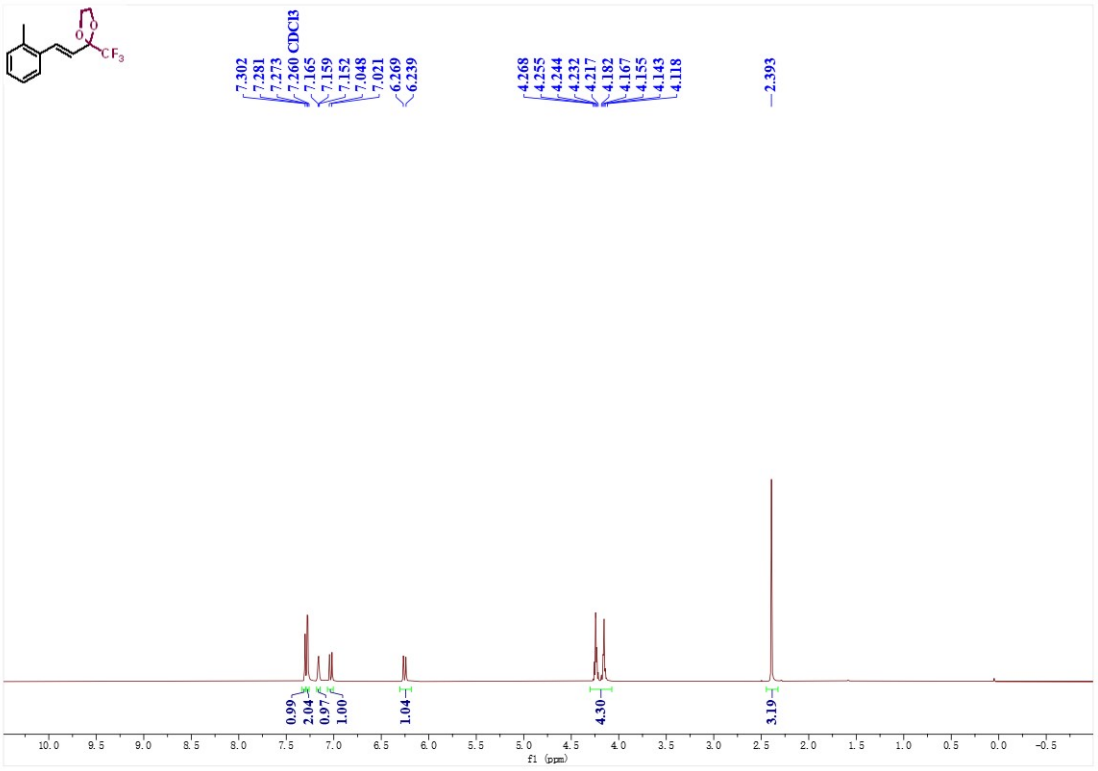


^{19}F NMR of 14

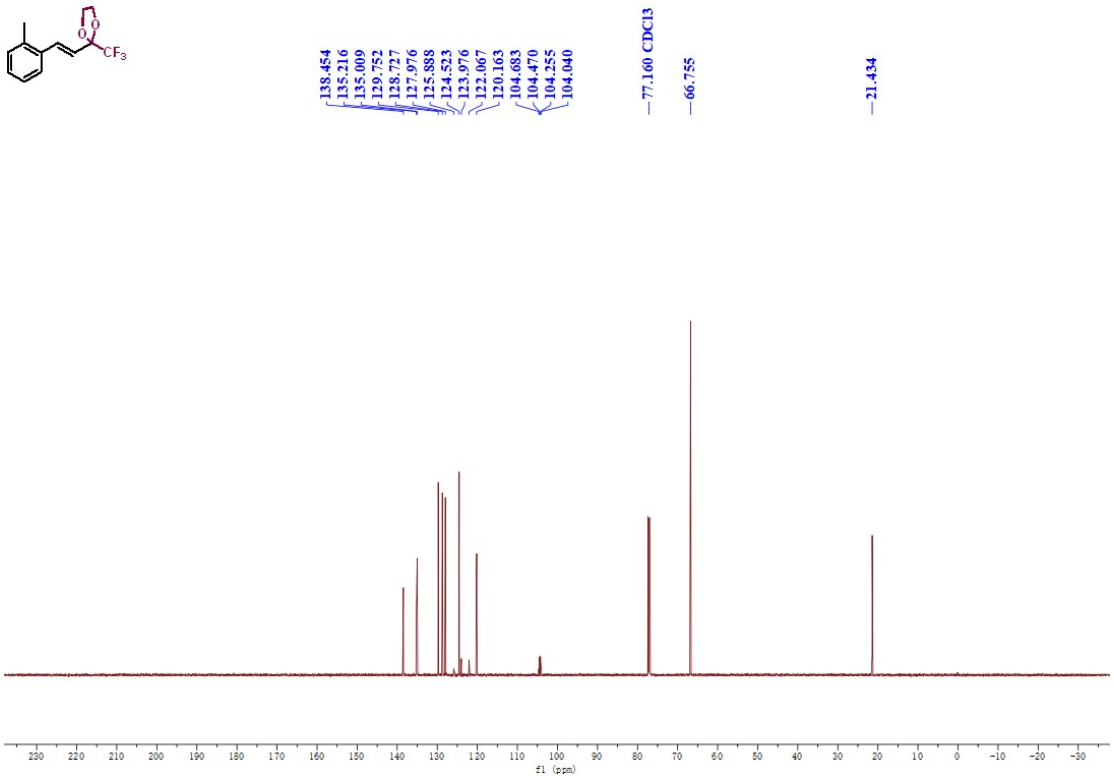


(*E*)-2-(2-methylstyryl)-2-(trifluoromethyl)-1,3-dioxolane (15)

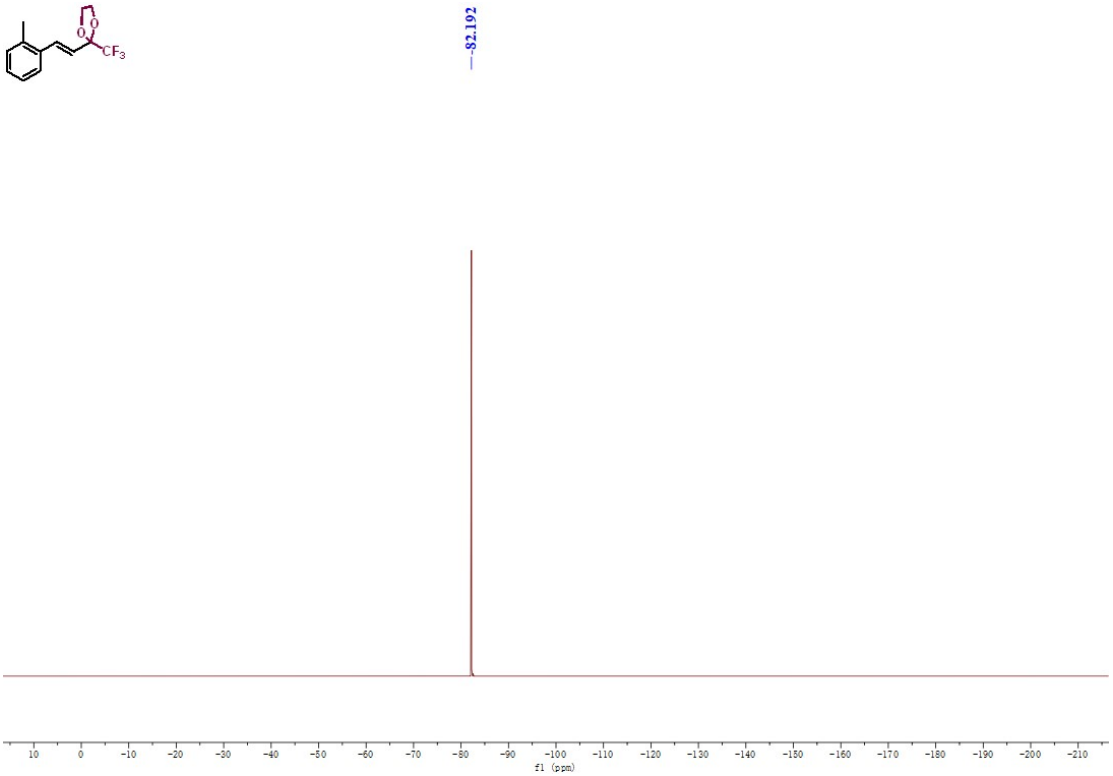
^{1}H NMR of 15



^{13}C NMR of 15

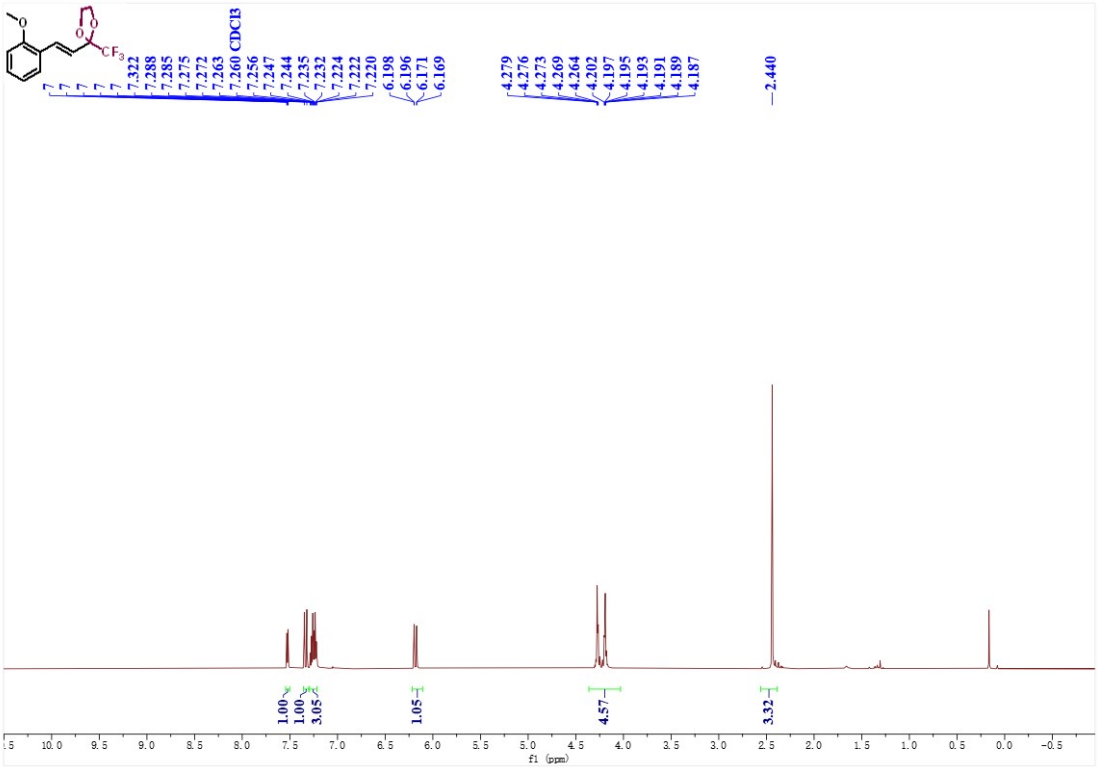


^{19}F NMR of 15

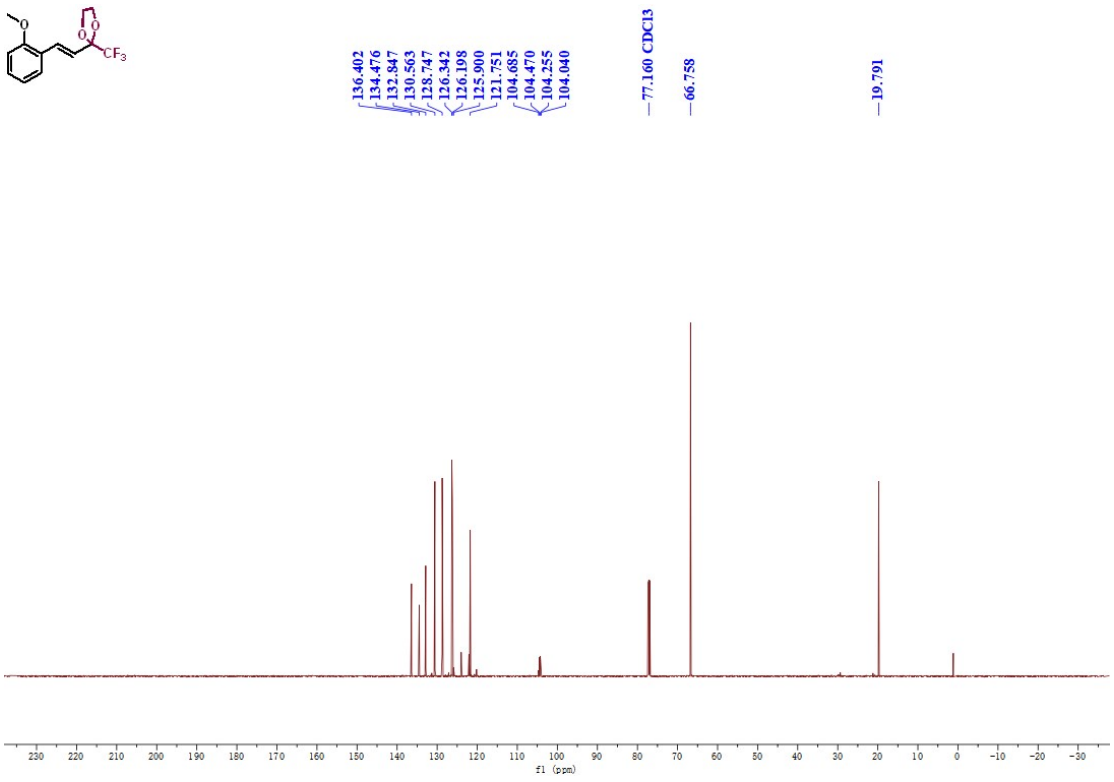


(*E*)-2-(2-methoxystyryl)-2-(trifluoromethyl)-1,3-dioxolane (16)

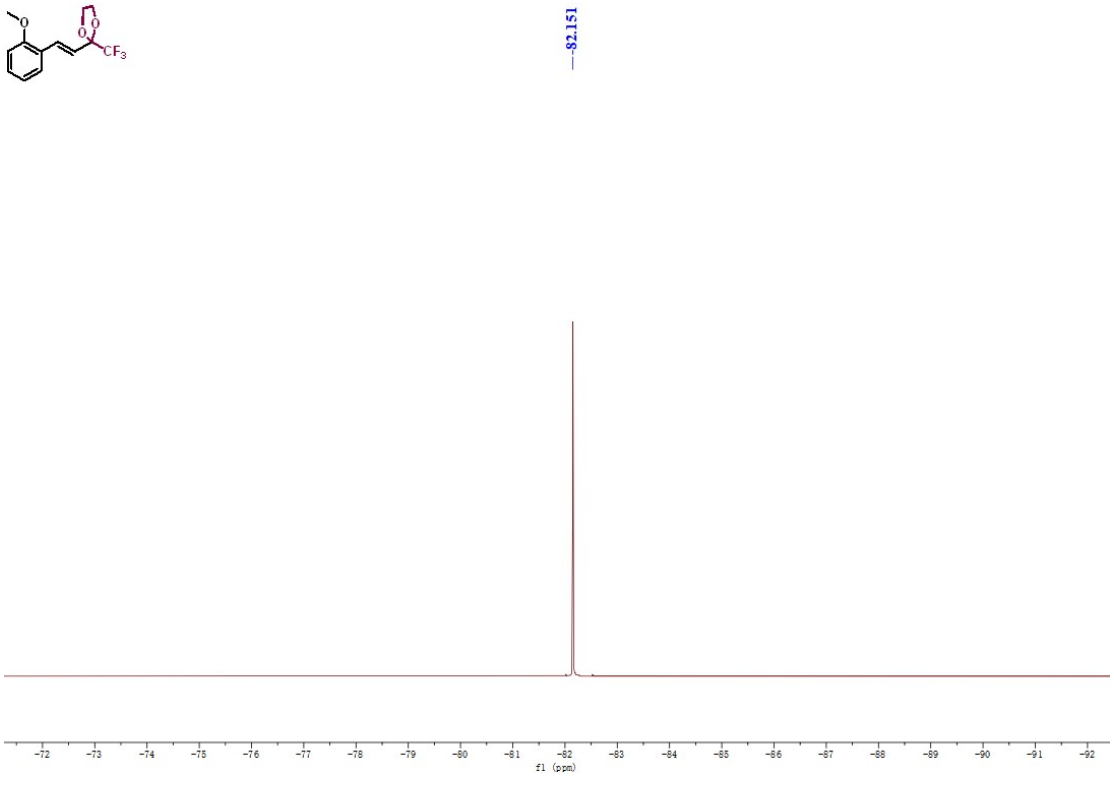
^{1}H NMR of 16



^{13}C NMR of 16

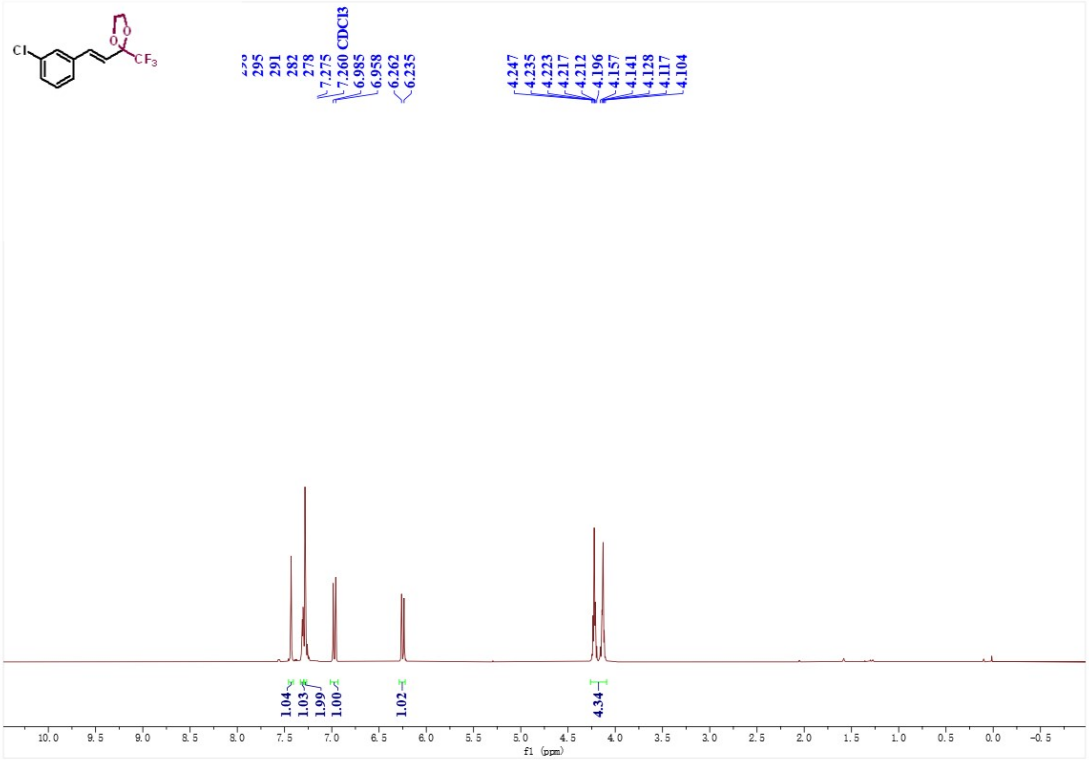


^{19}F NMR of 16

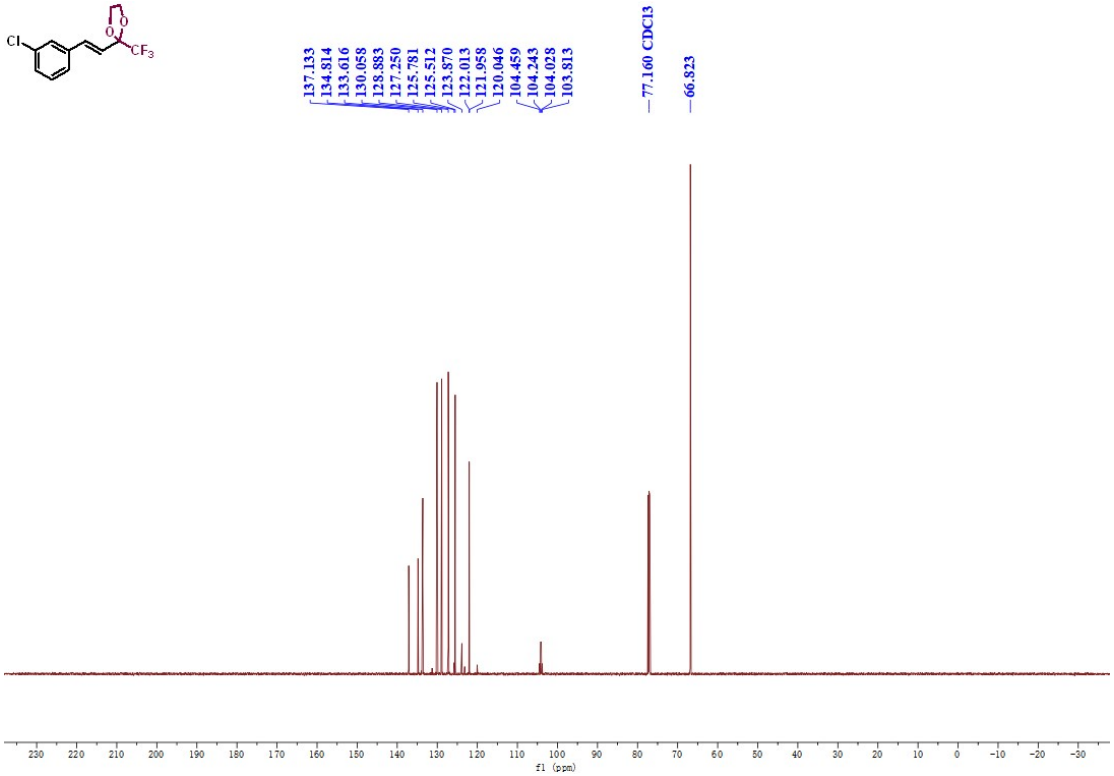


(*E*)-2-(3-chlorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (17)

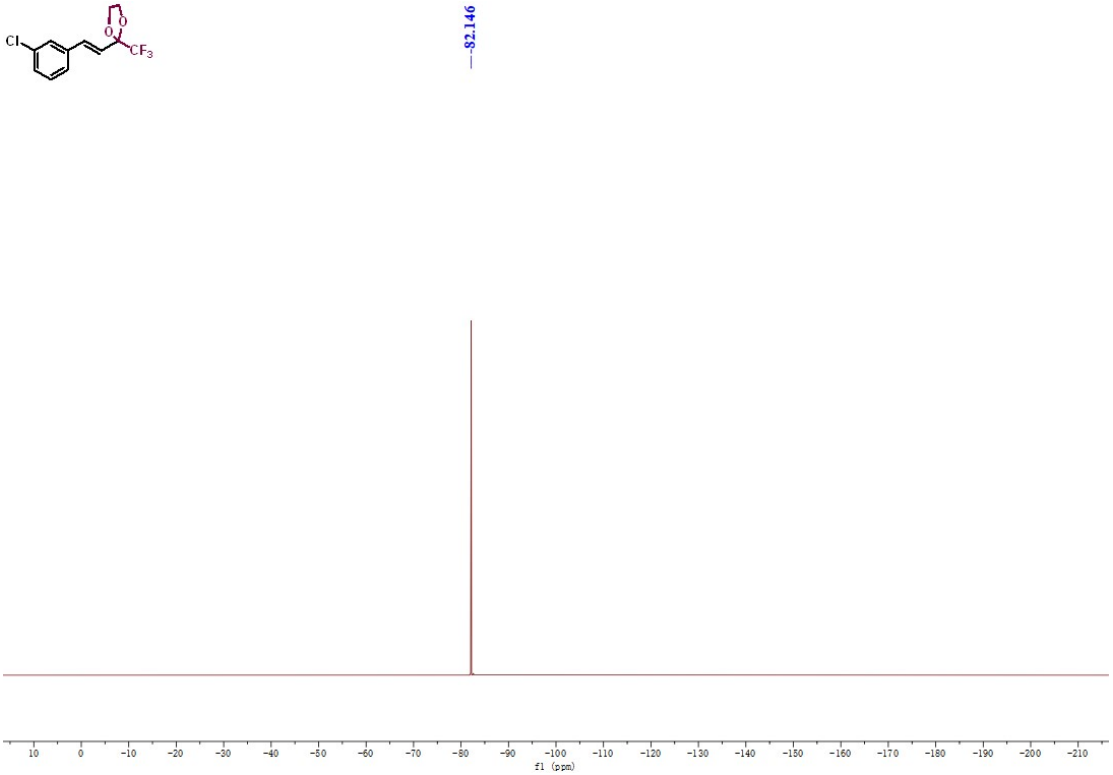
^{1}H NMR of 17



^{13}C NMR of 17

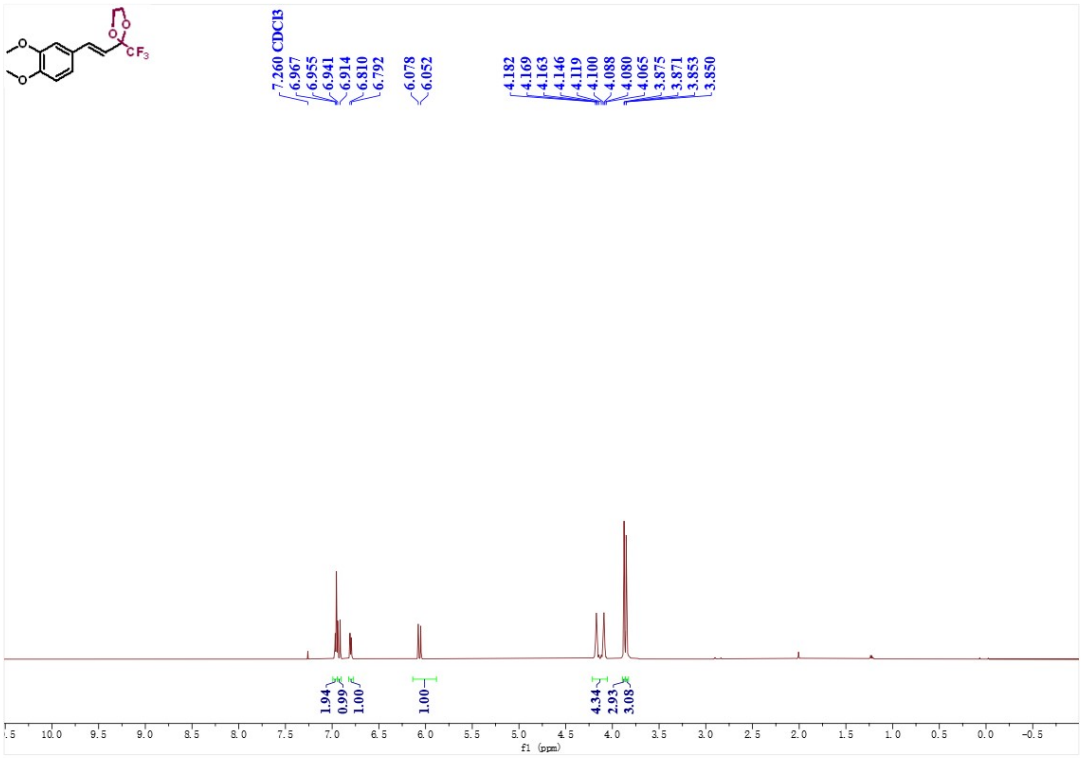


^{19}F NMR of 17

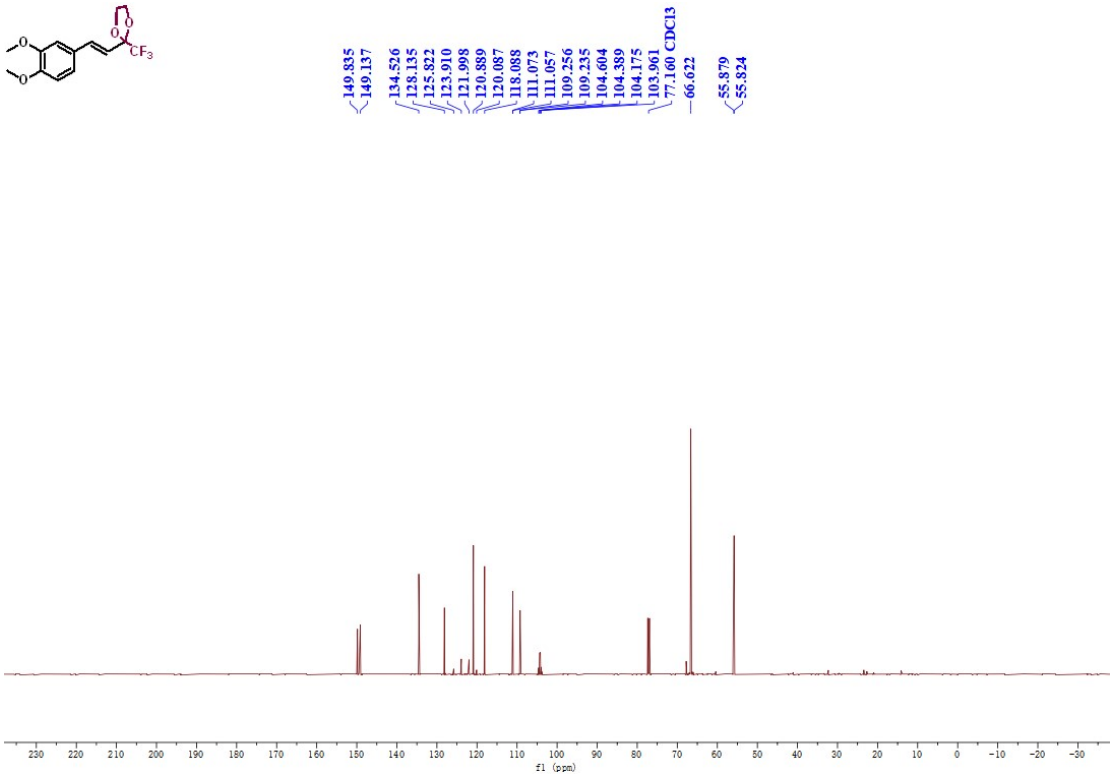


(*E*)-2-(3,4-dimethoxystyryl)-2-(trifluoromethyl)-1,3-dioxolane (18)

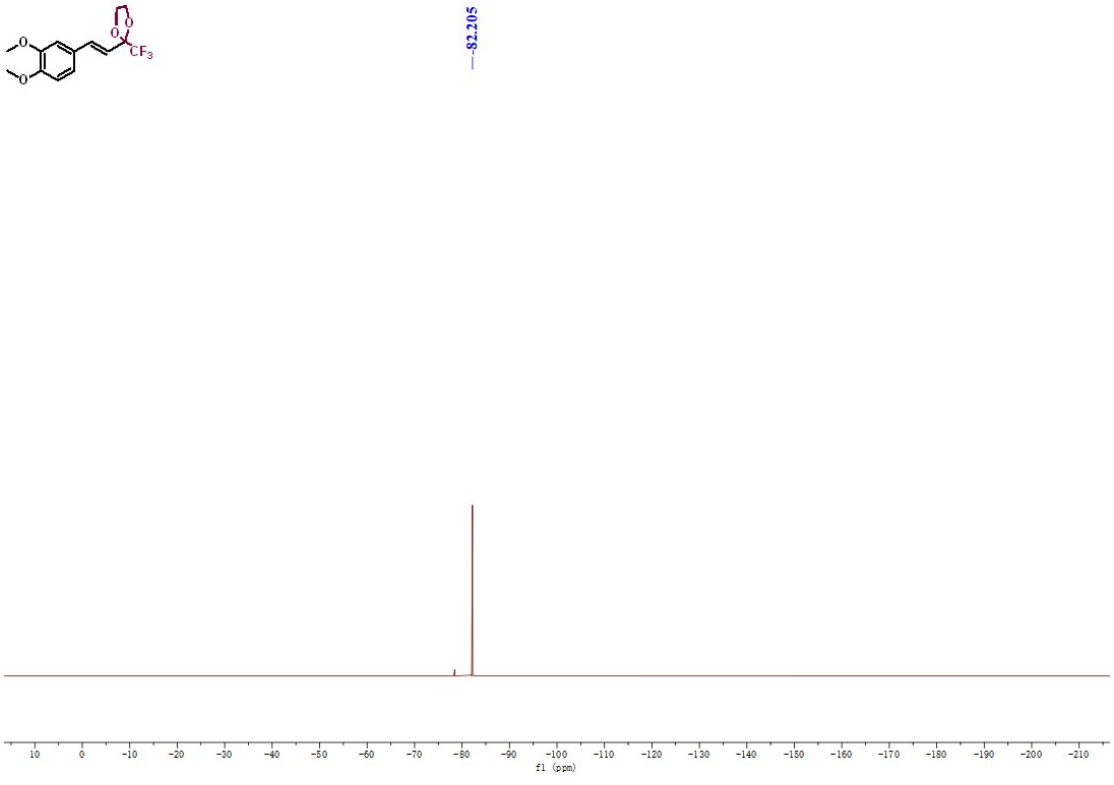
^{1}H NMR of 18



^{13}C NMR of 18

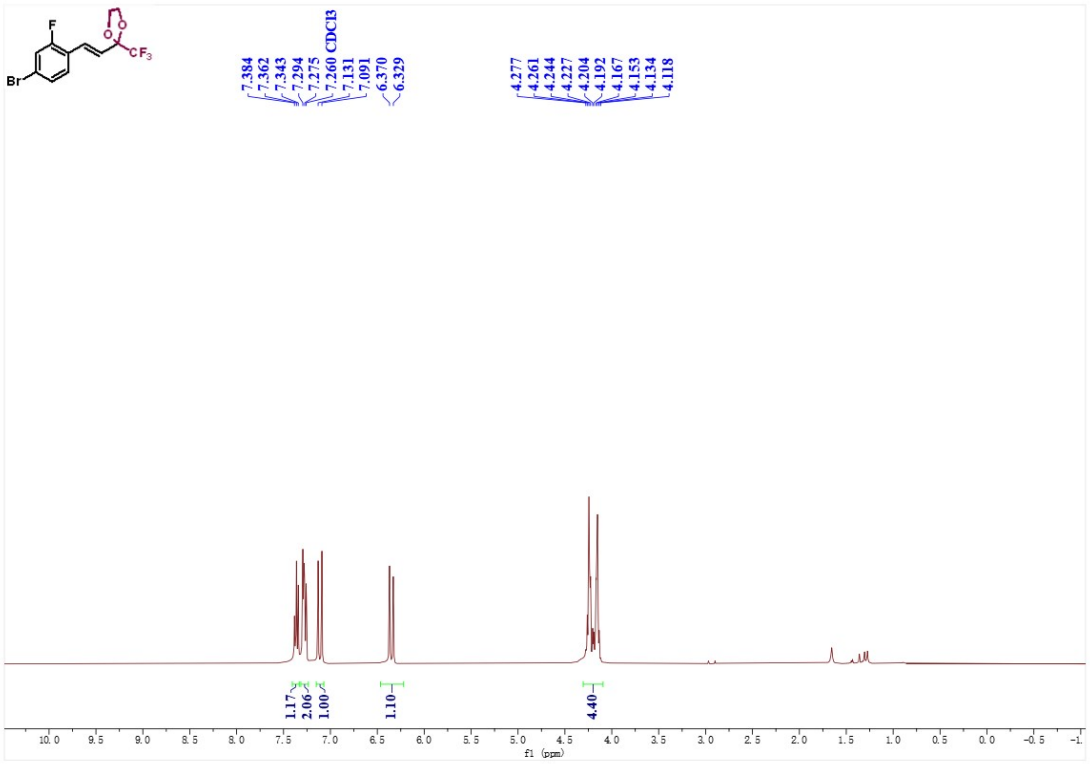


^{19}F NMR of 18

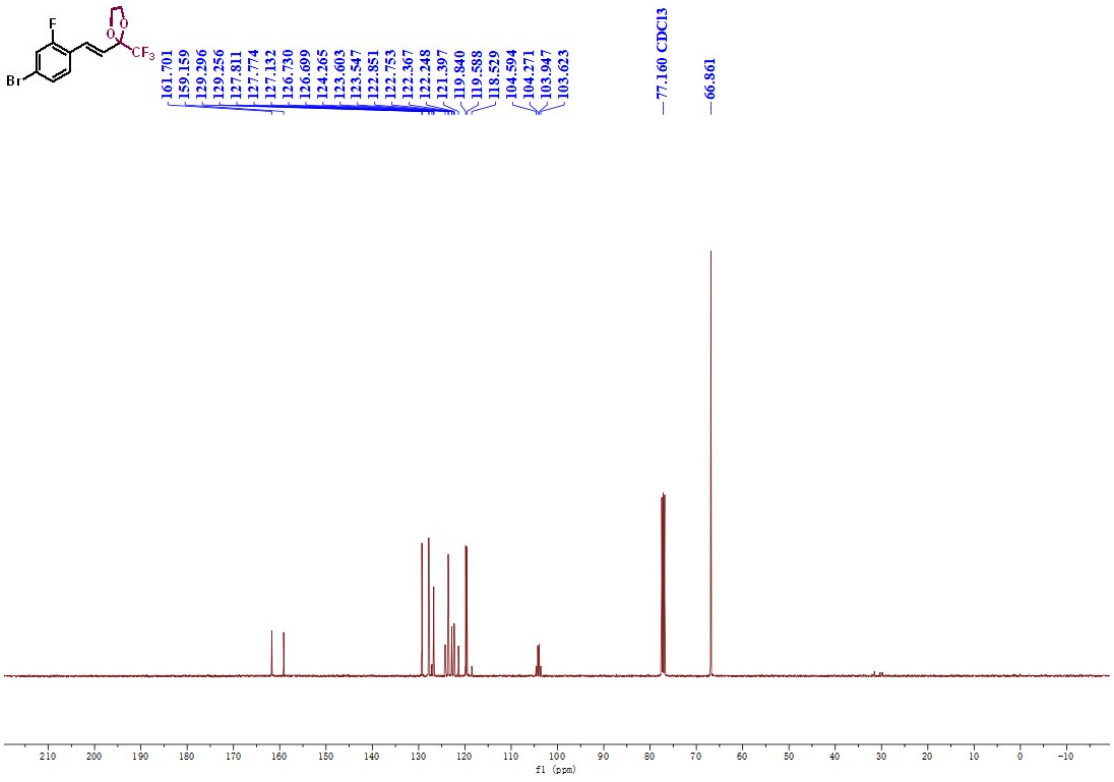


(*E*)-2-(4-bromo-2-fluorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (19)

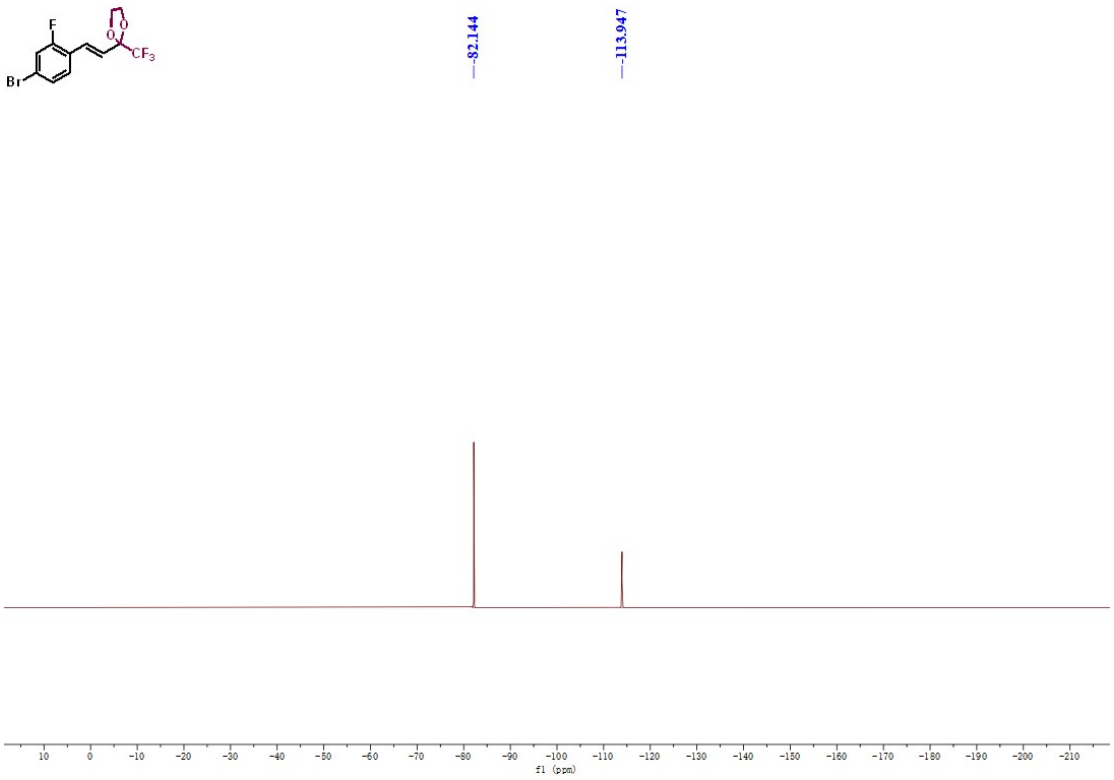
^{1}H NMR of 19



^{13}C NMR of 19

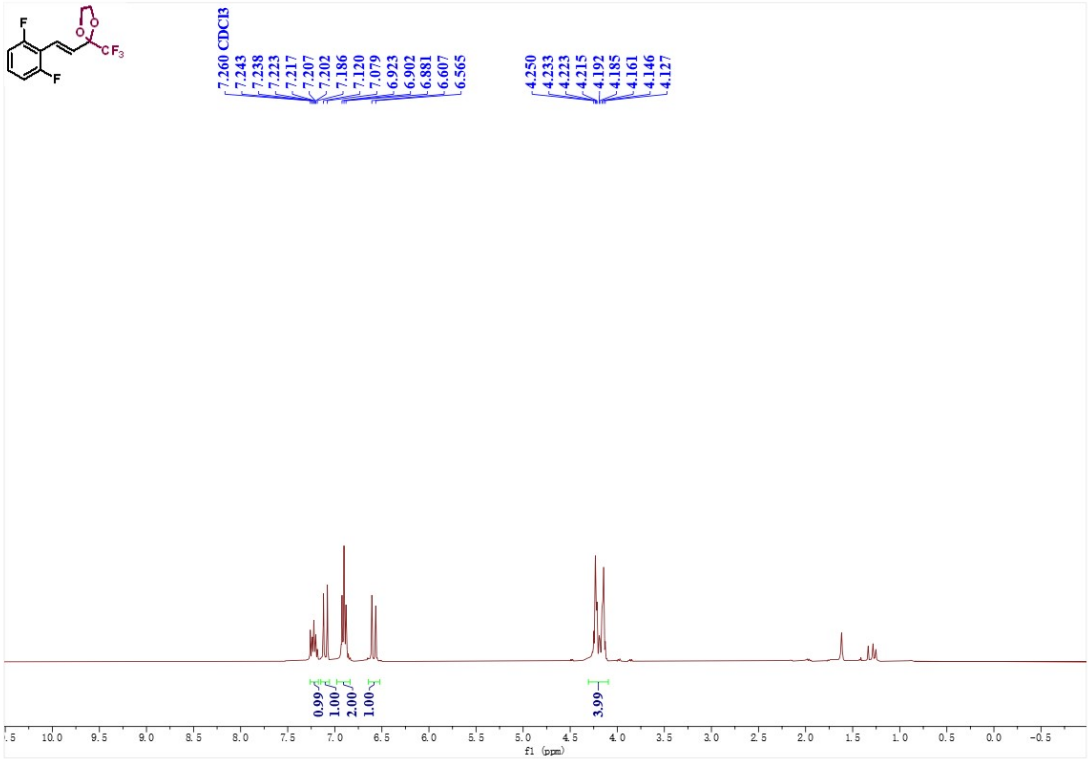


^{19}F NMR of 19

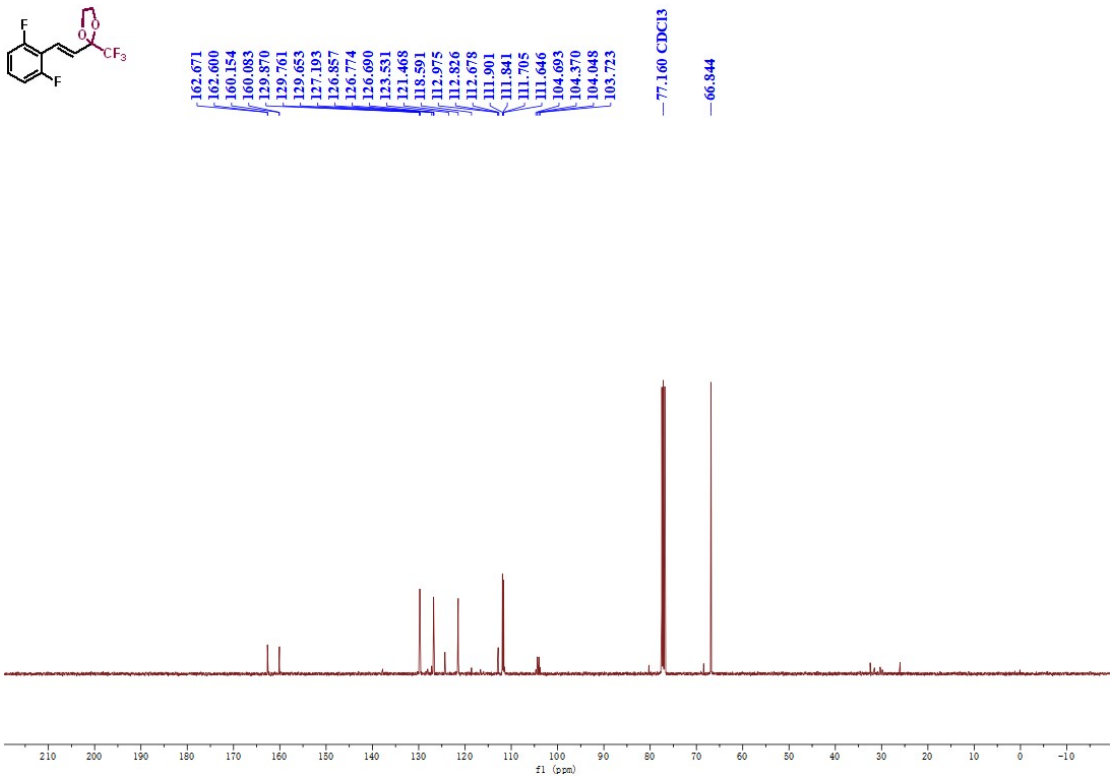


(*E*)-2-(2,6-difluorostyryl)-2-(trifluoromethyl)-1,3-dioxolane (20)

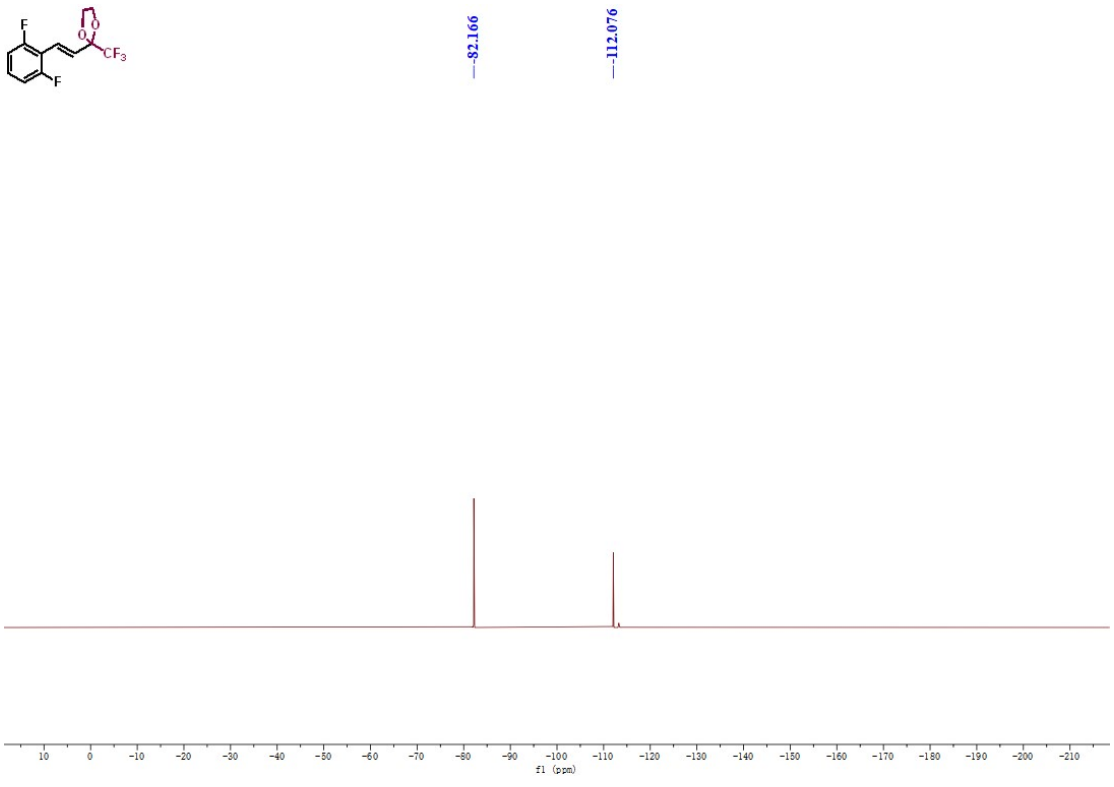
^{1}H NMR of 20



^{13}C NMR of 20

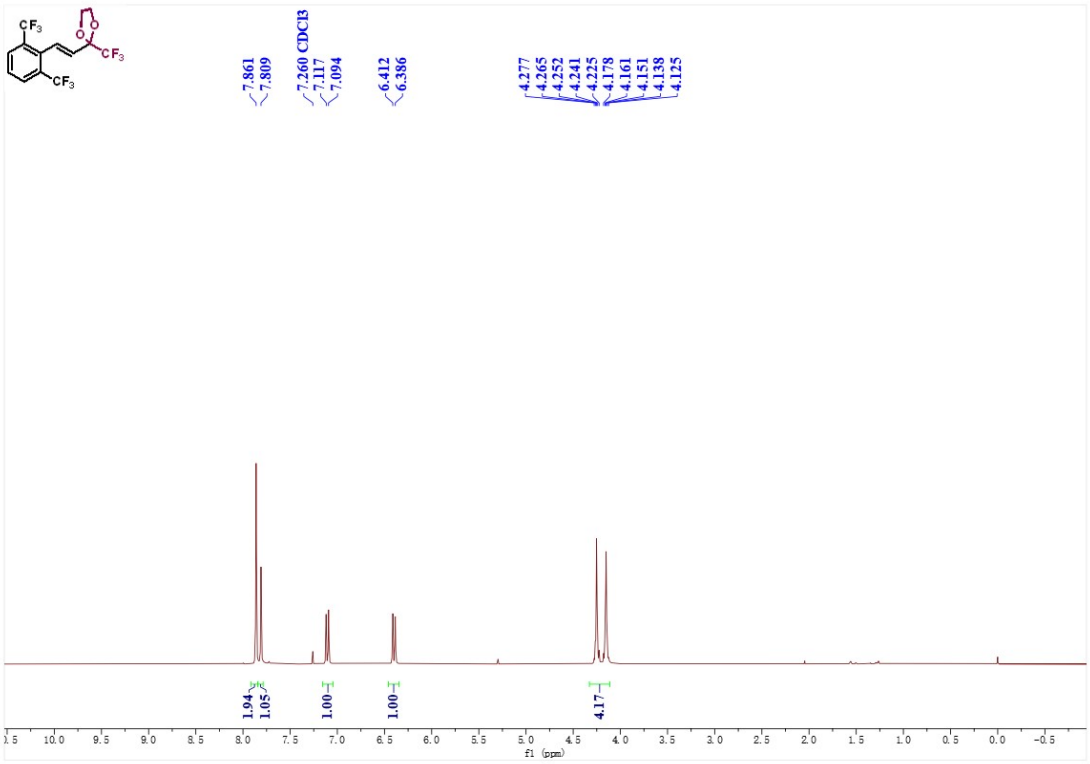


^{19}F NMR of 20

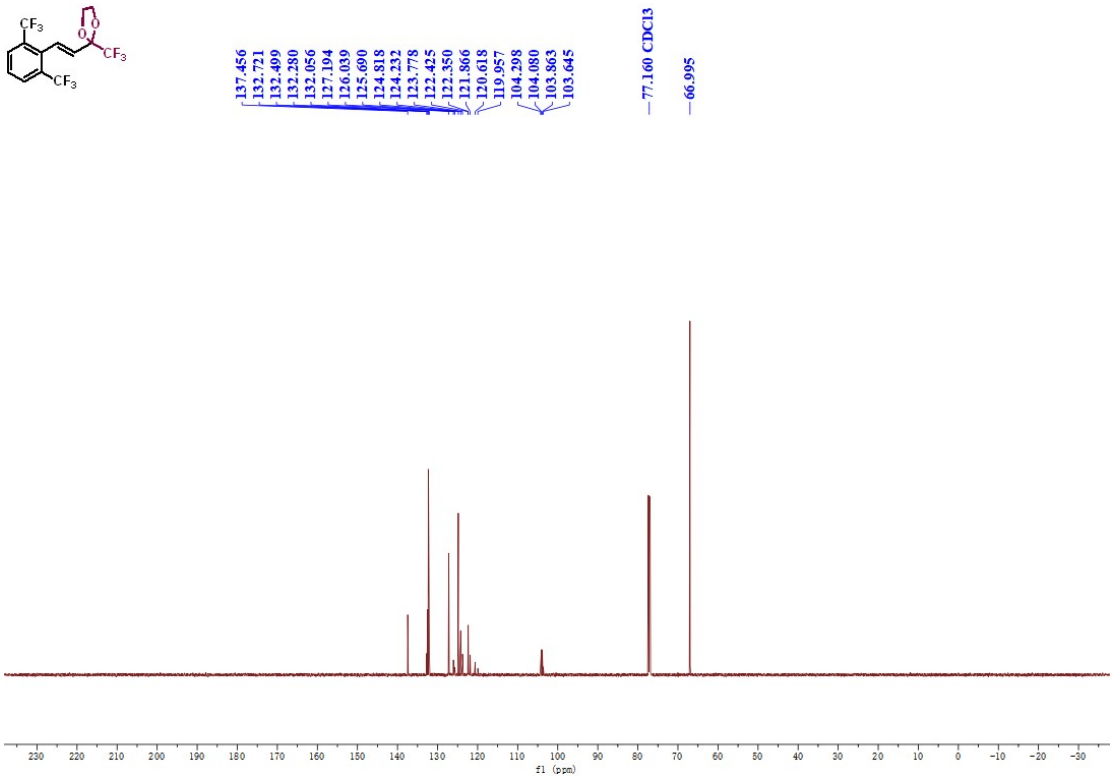


(*E*)-2-(2,6-bis(trifluoromethyl)styryl)-2-(trifluoromethyl)-1,3-dioxolane (21)

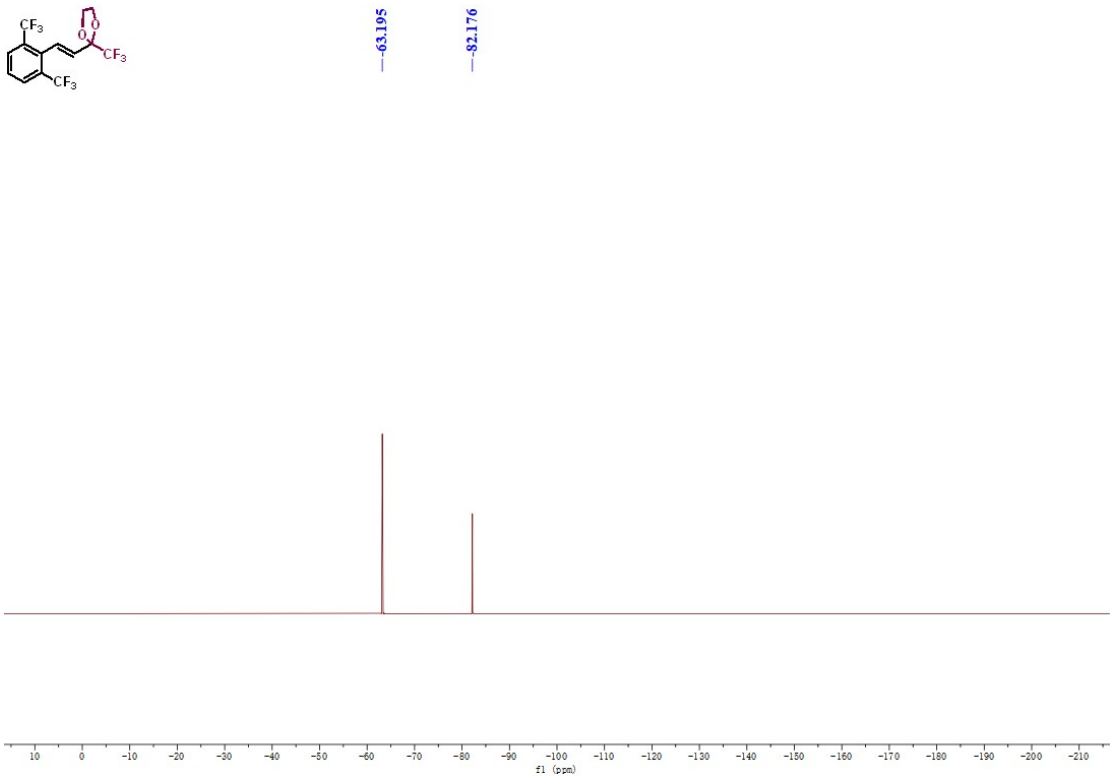
^{1}H NMR of 21



^{13}C NMR of 21

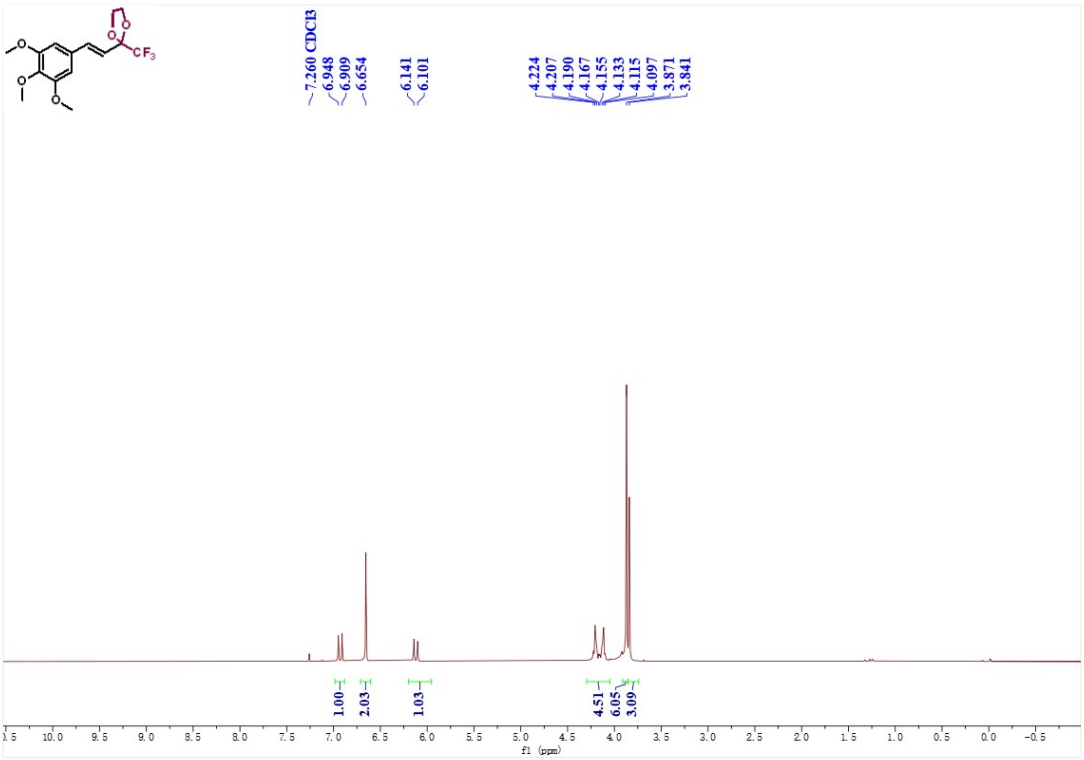


^{19}F NMR of 21

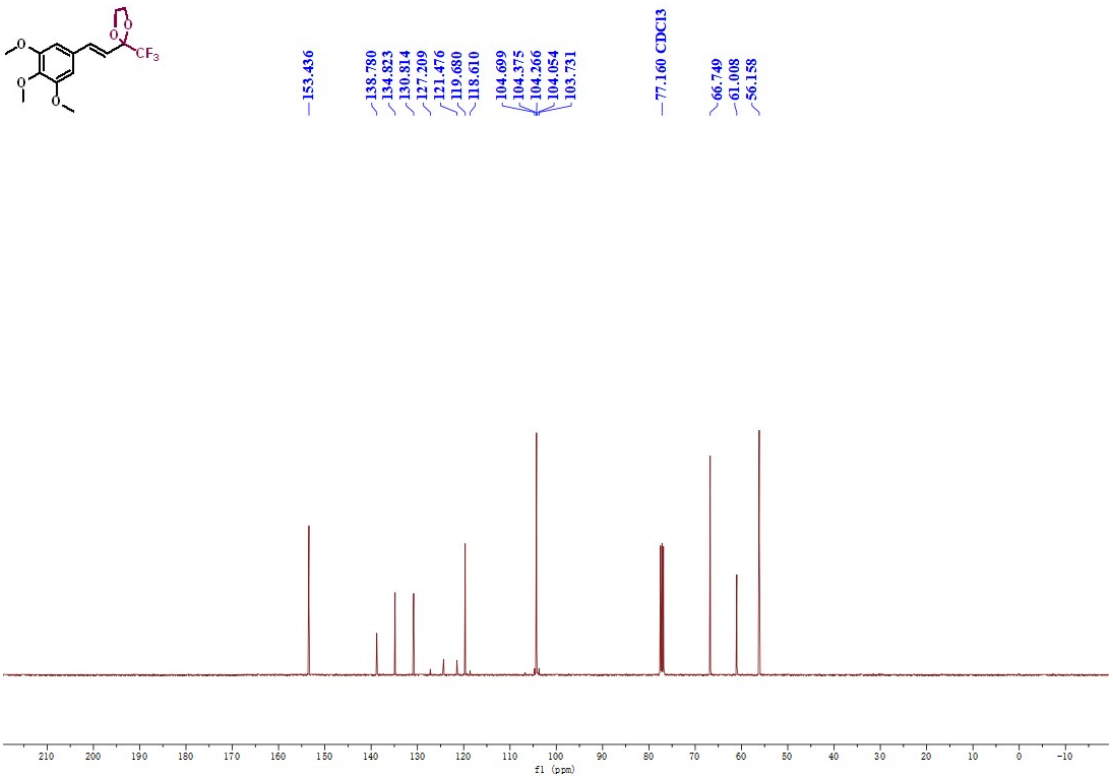


(*E*)-2-(trifluoromethyl)-2-(3,4,5-trimethoxystyryl)-1,3-dioxolane (22)

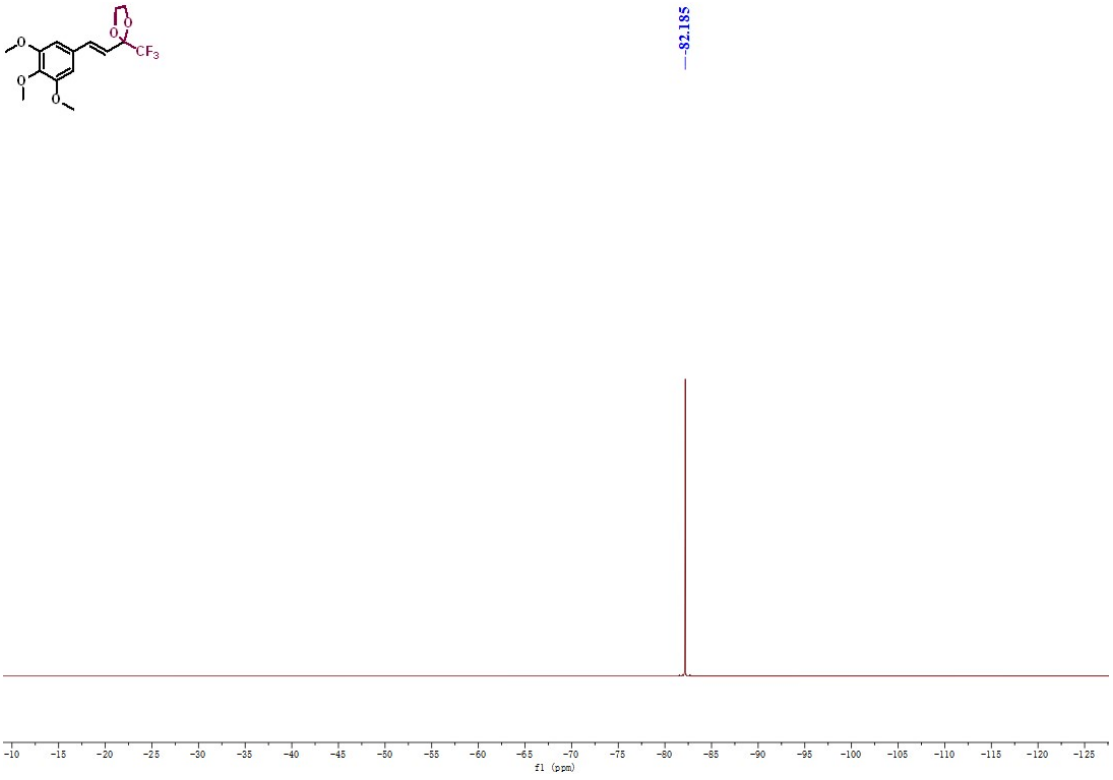
^{1}H NMR of 22



^{13}C NMR of 22

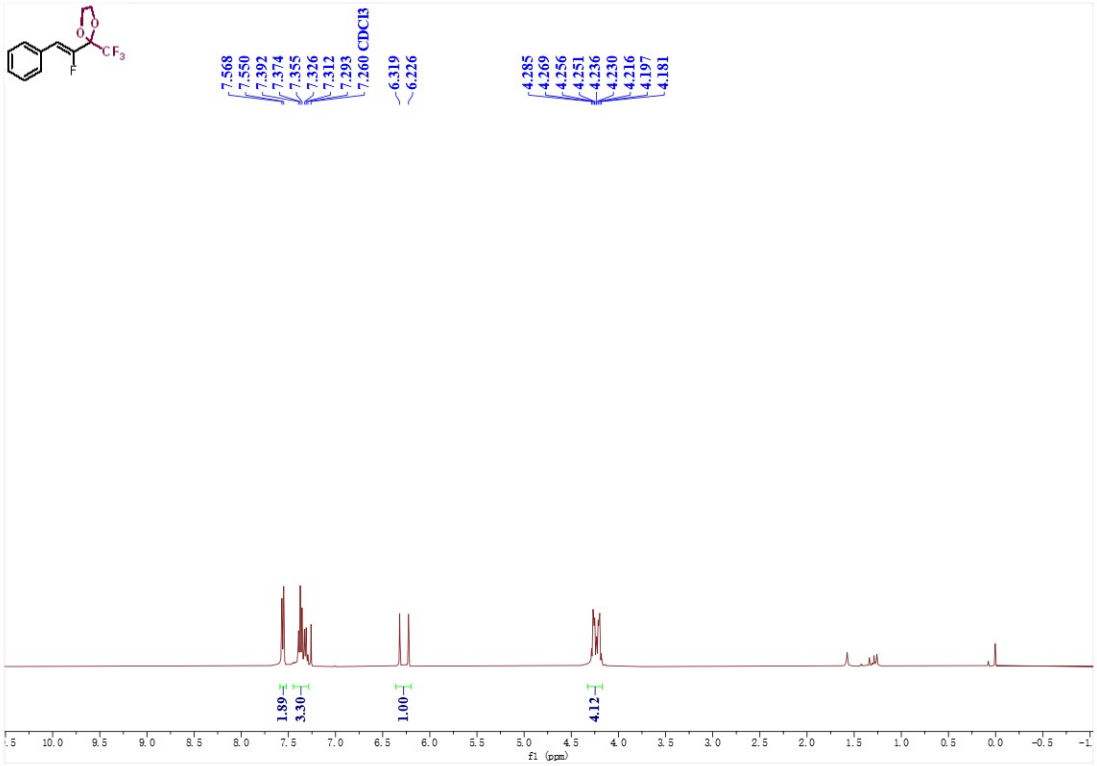


^{19}F NMR of 22

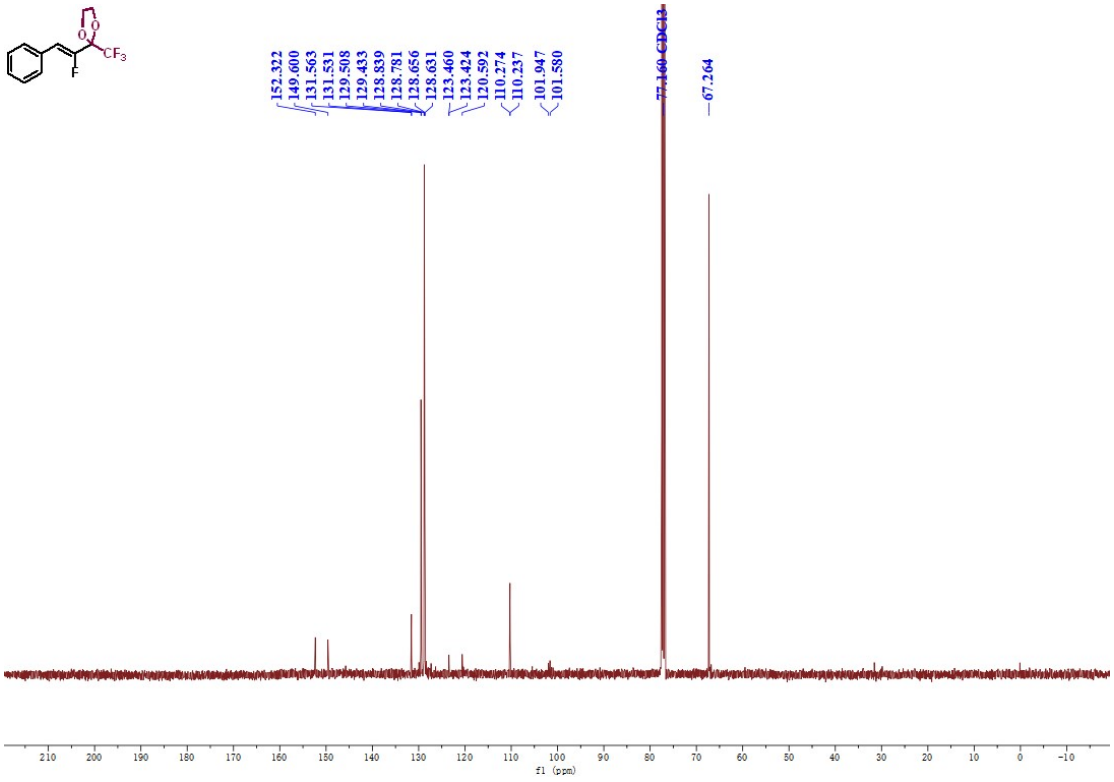


(*Z*)-2-(1-fluoro-2-phenylvinyl)-2-(trifluoromethyl)-1,3-dioxolane (23)

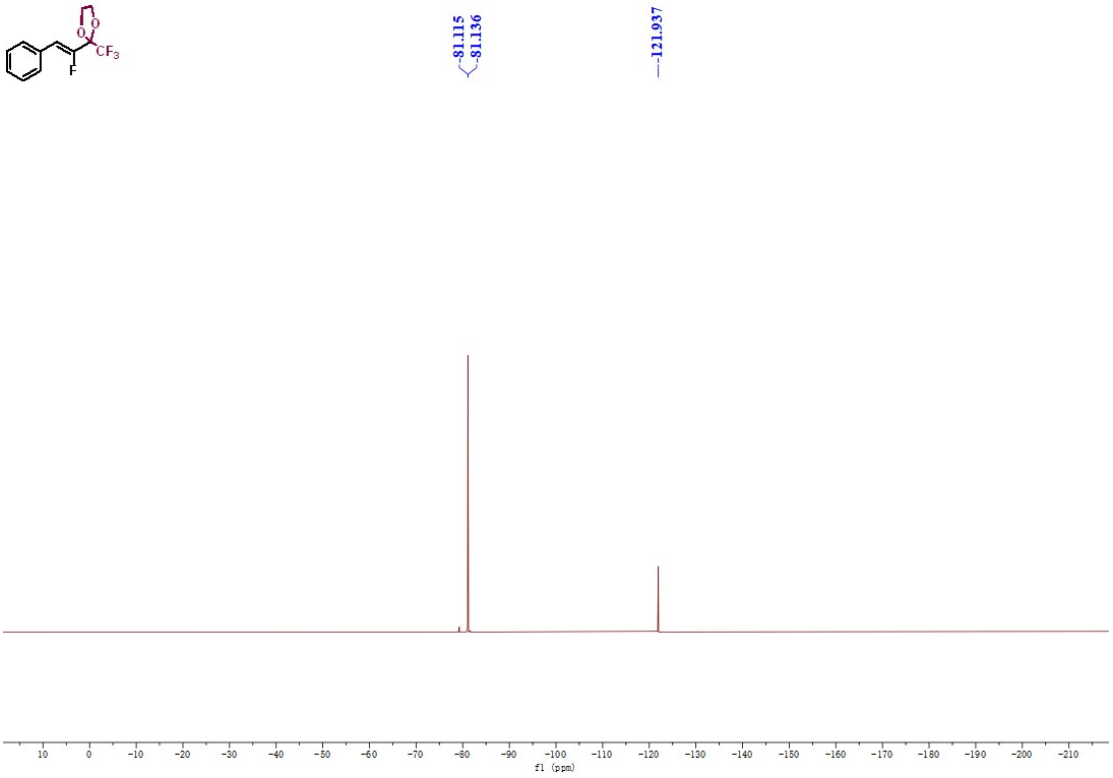
^{1}H NMR of 23



^{13}C NMR of 23

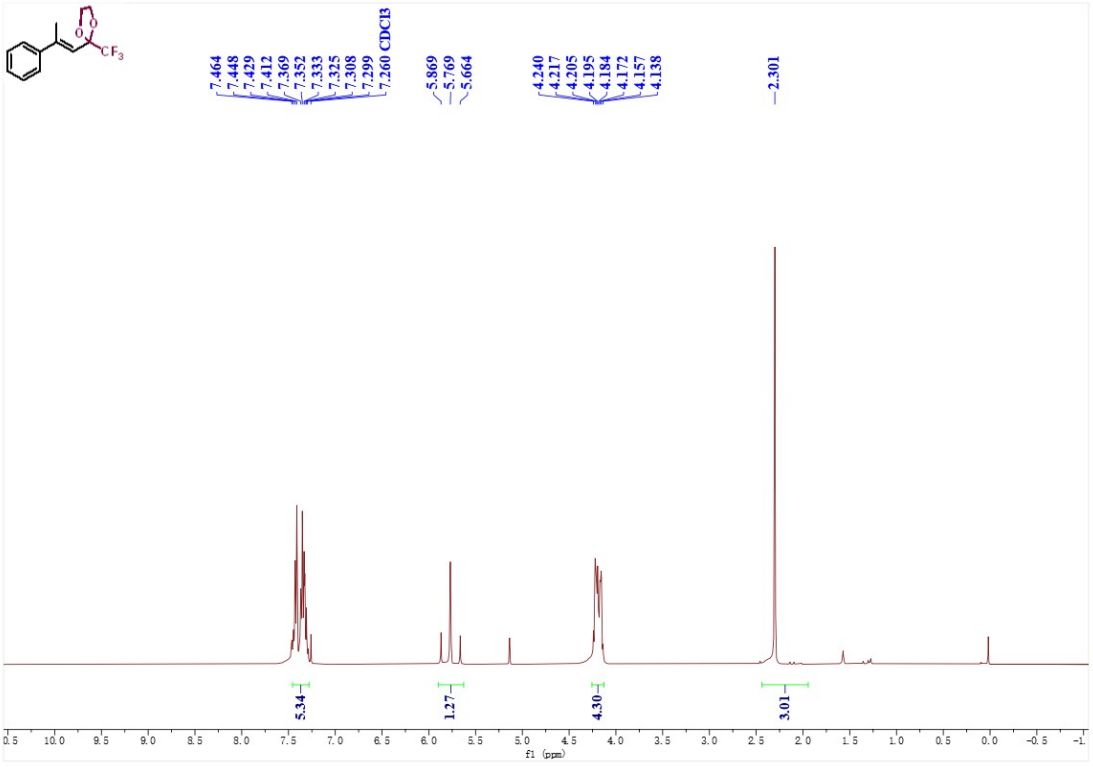


^{19}F NMR of 23

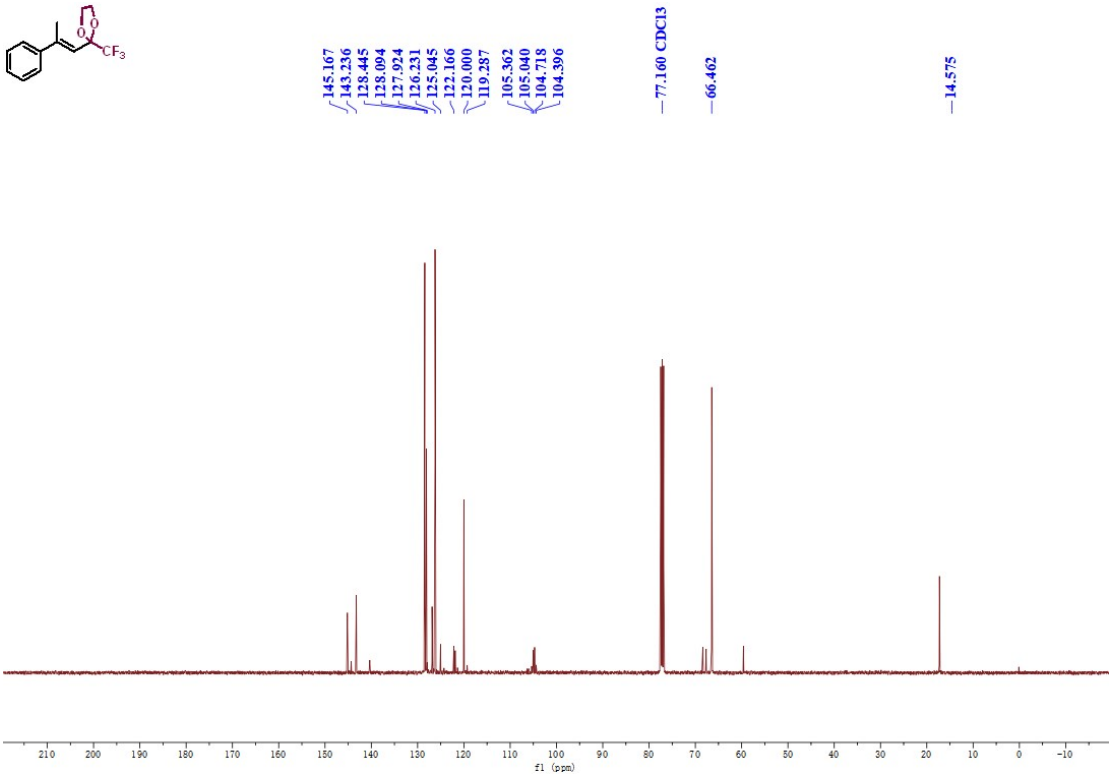


(*E*)-2-(2-phenylprop-1-en-1-yl)-2-(trifluoromethyl)-1,3-dioxolane (24)

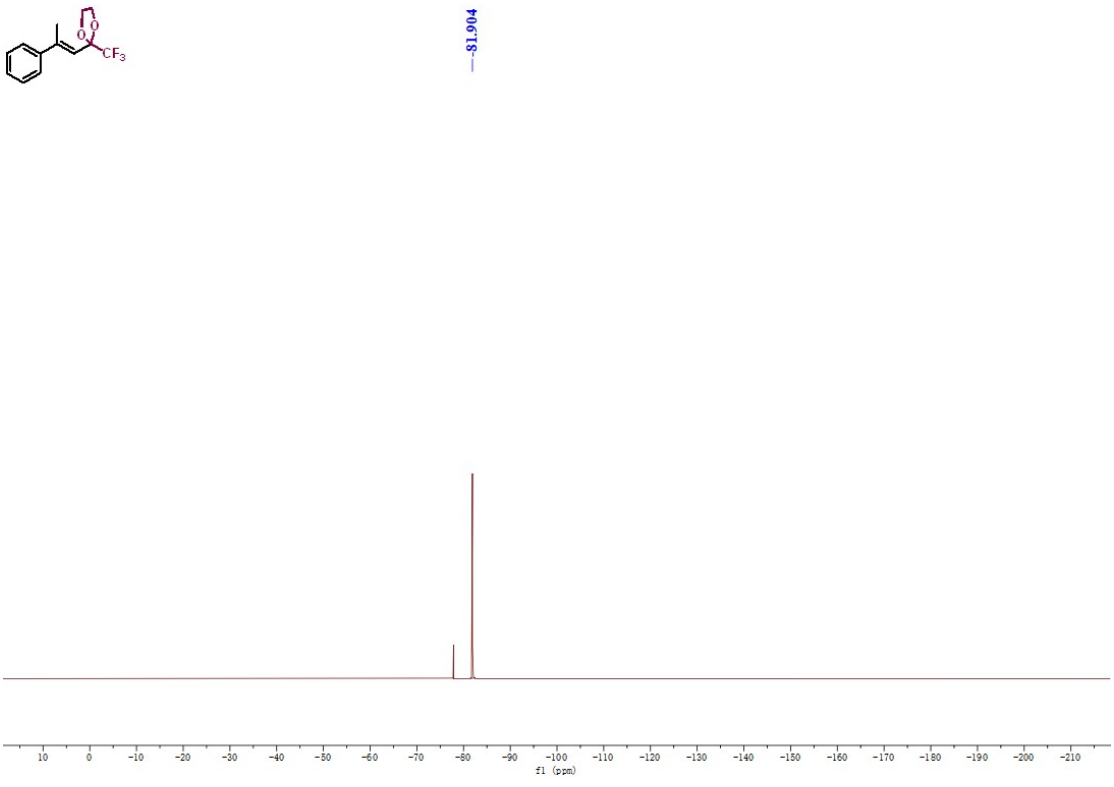
^{1}H NMR of 24



^{13}C NMR of 24

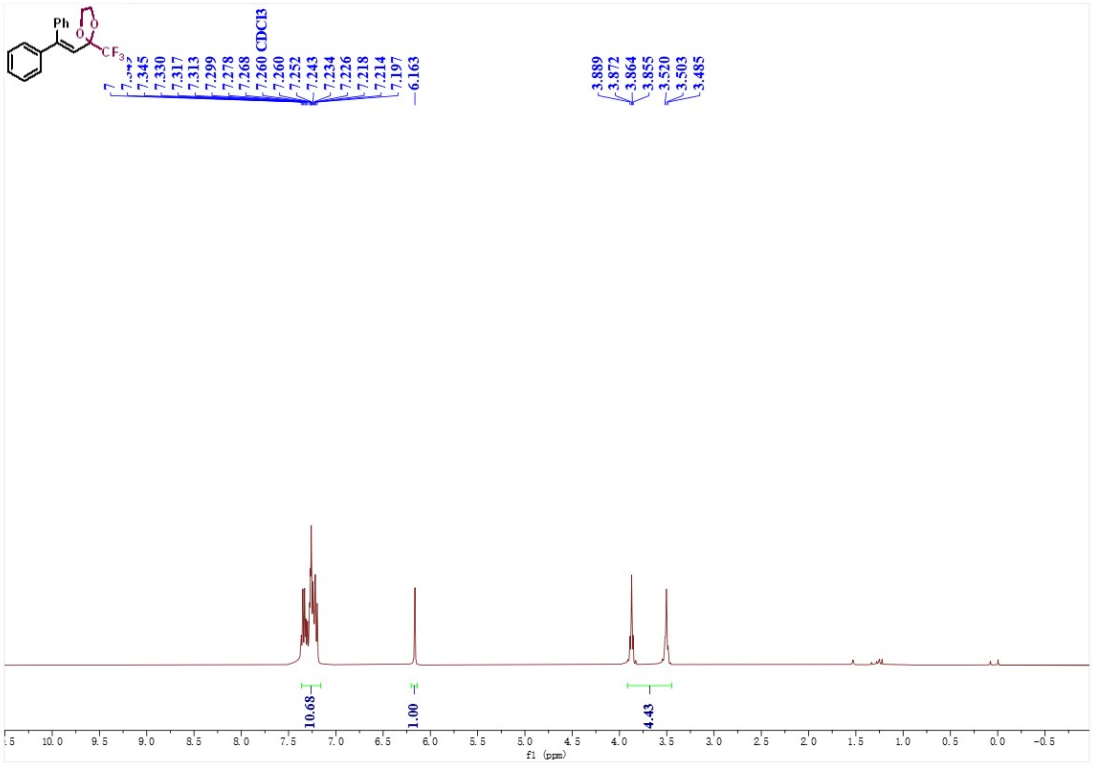


^{19}F NMR of 24

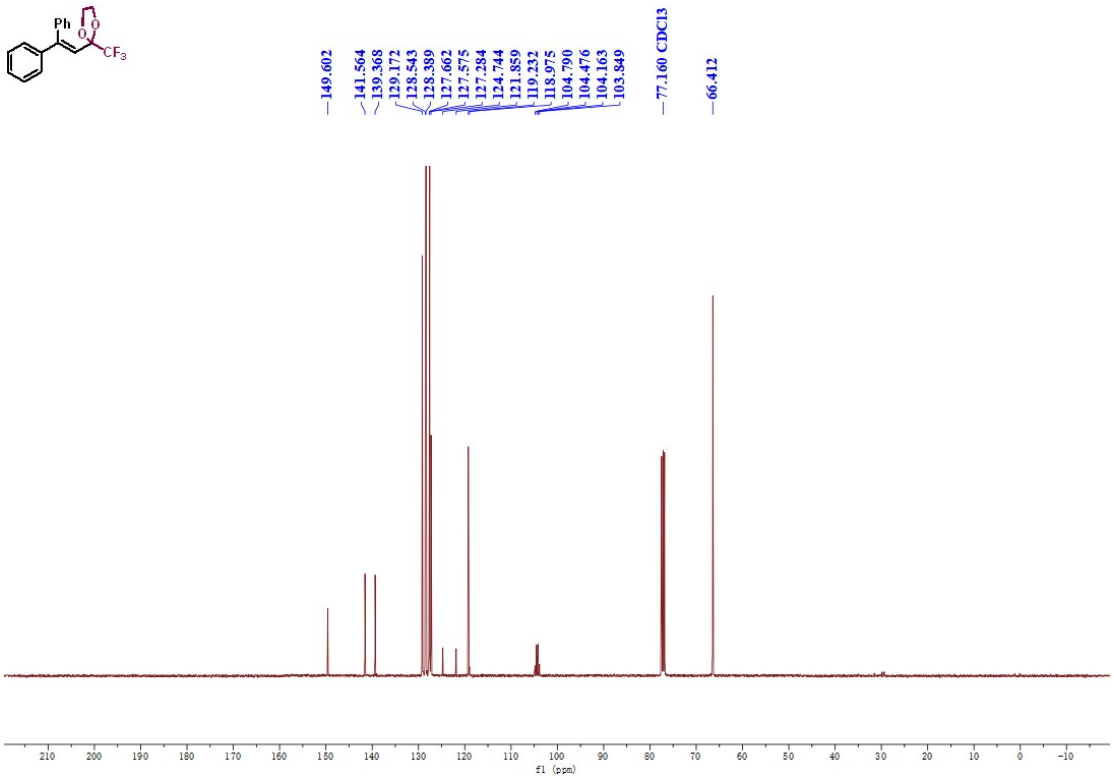


2-(2,2-diphenylvinyl)-2-(trifluoromethyl)-1,3-dioxolane (25)

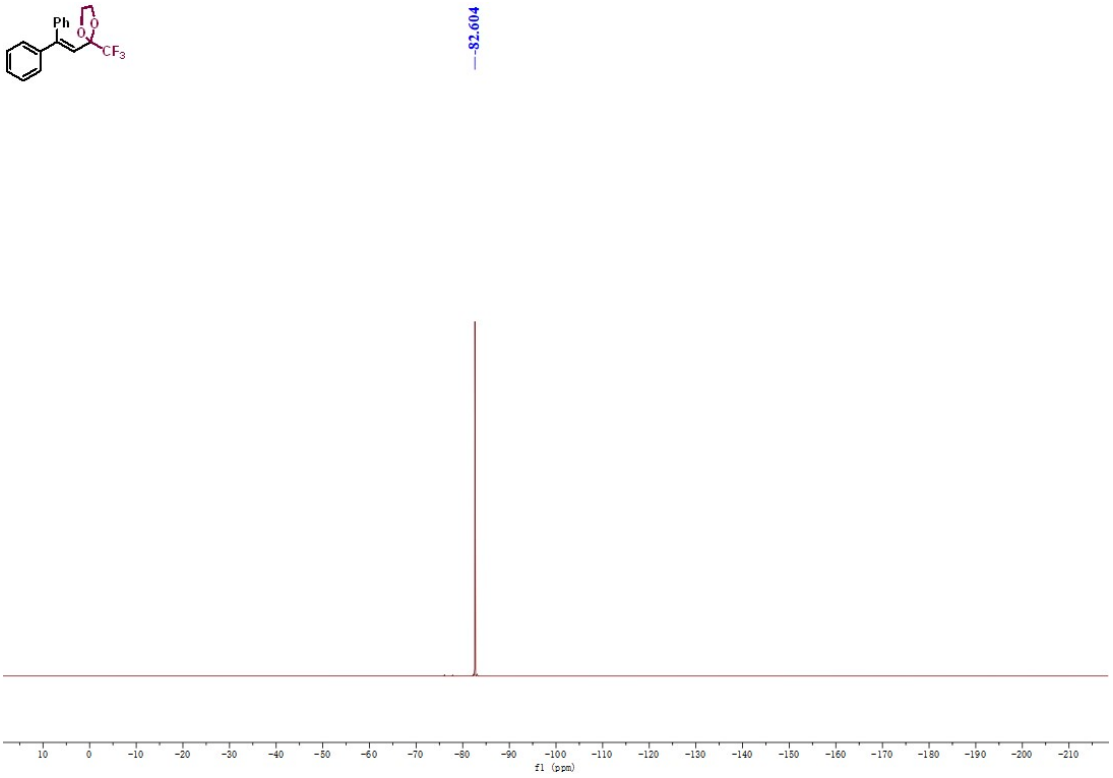
^{1}H NMR of 25



^{13}C NMR of 25

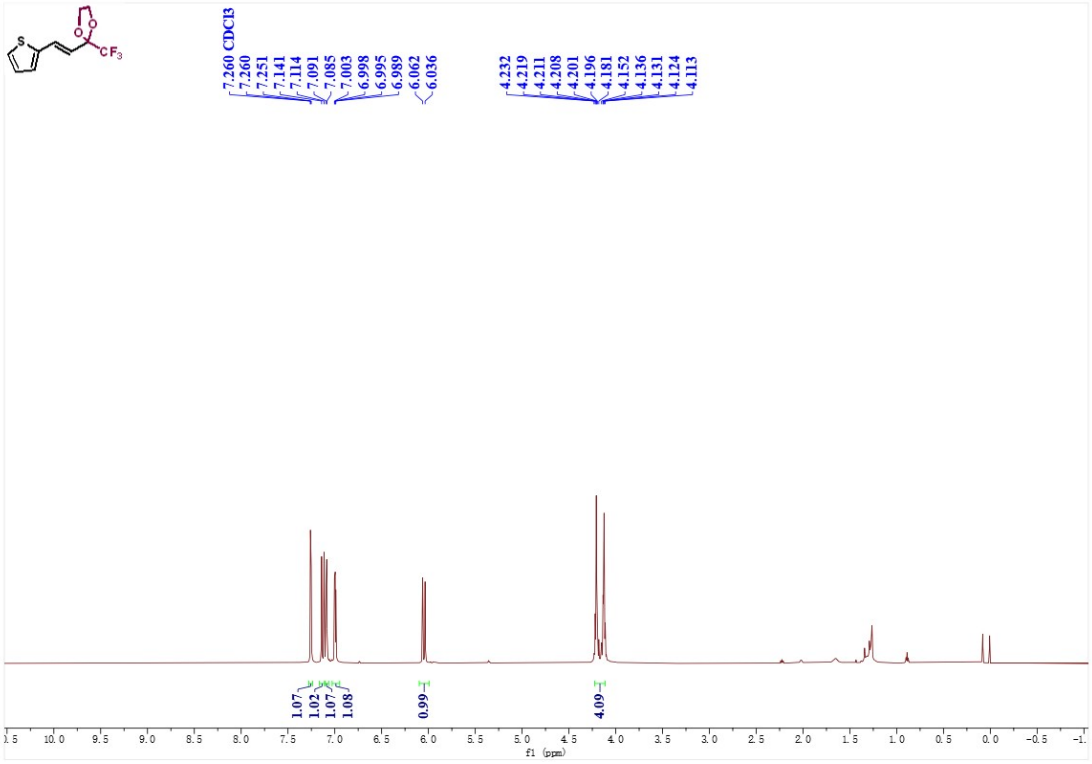


^{19}F NMR of 25

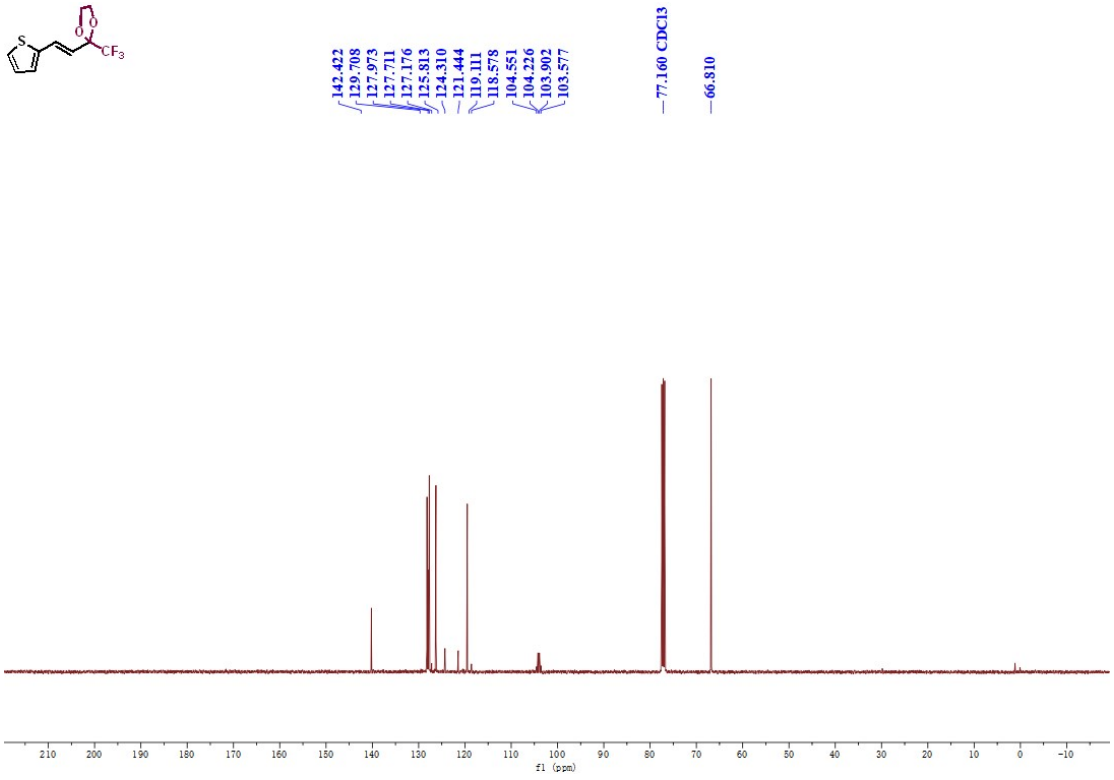


(*E*)-2-(2-(thiophen-2-yl)vinyl)-2-(trifluoromethyl)-1,3-dioxolane (26)

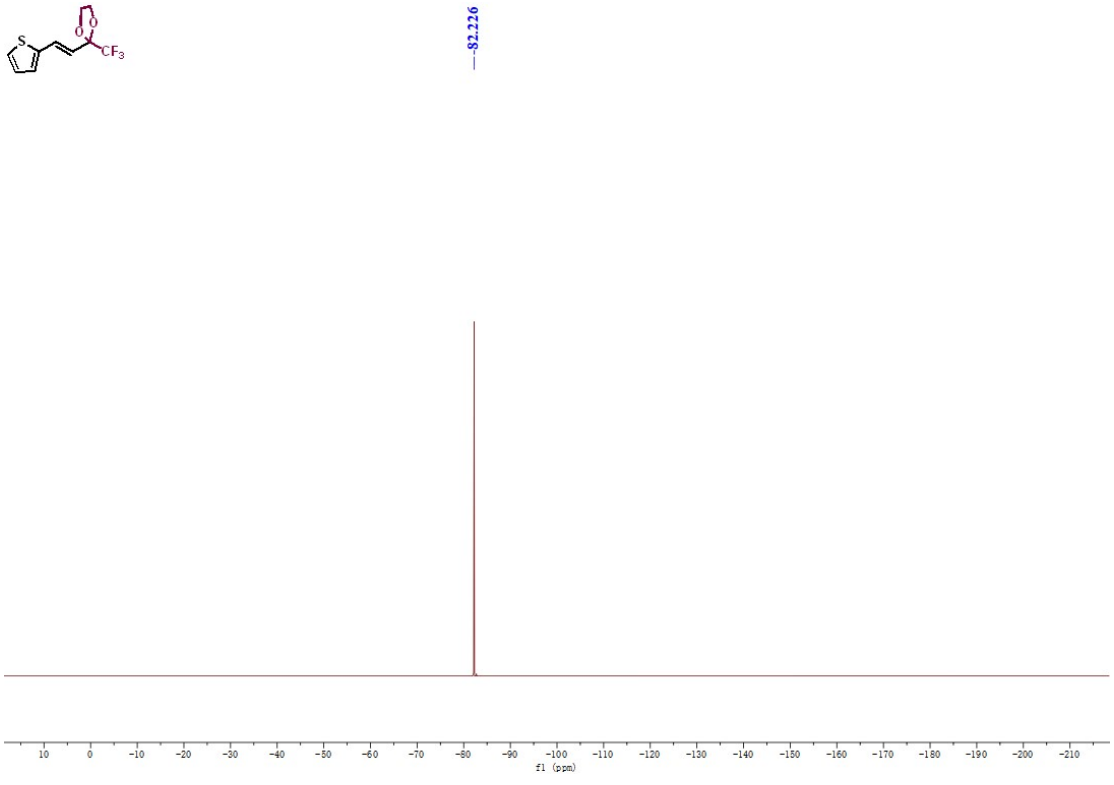
^{1}H NMR of 26



^{13}C NMR of 26

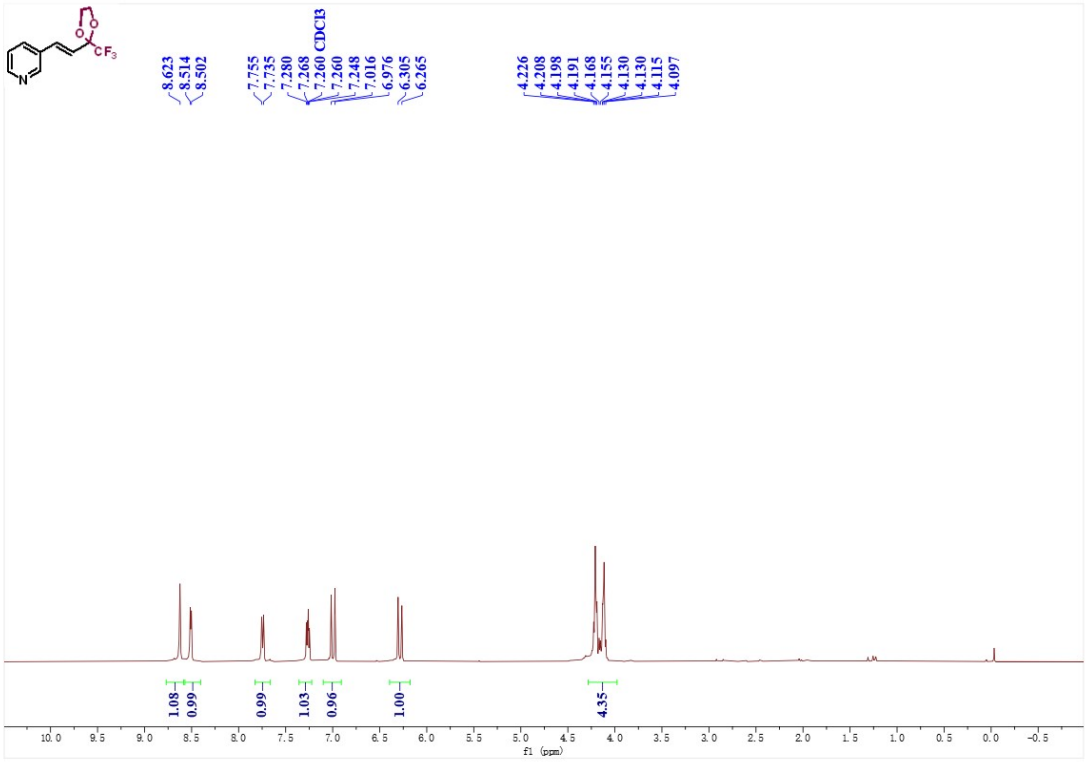


^{19}F NMR of 26

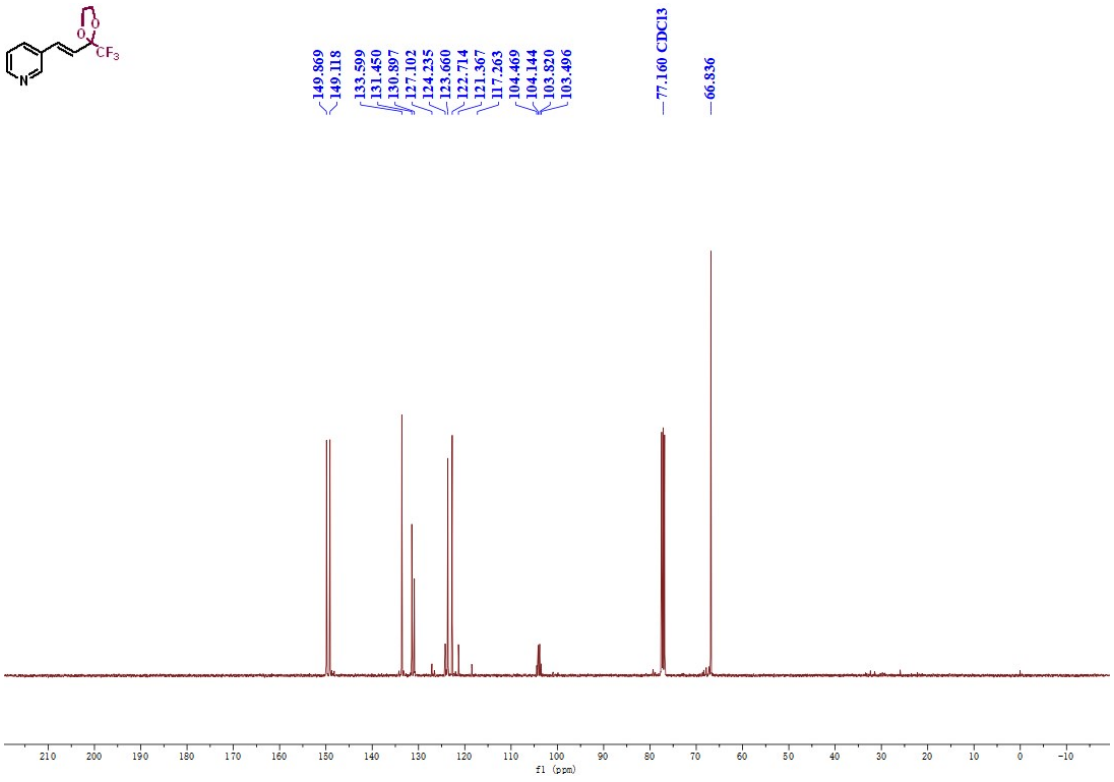


(*E*)-3-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)pyridine (27)

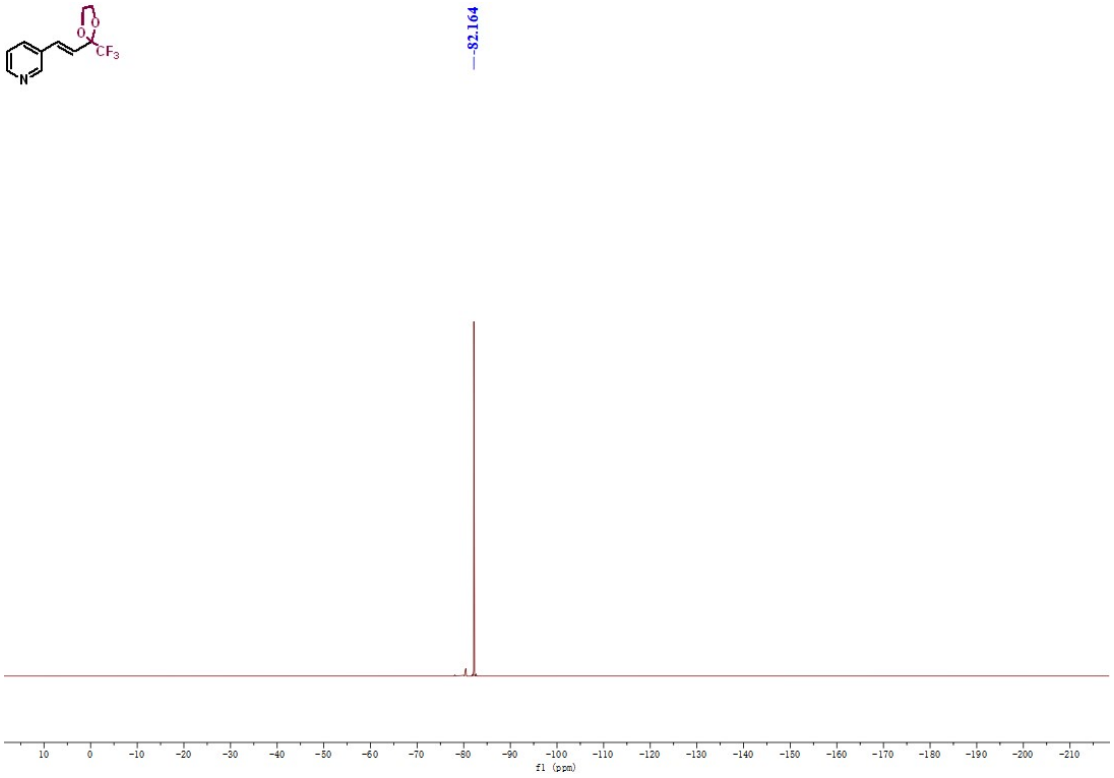
^{1}H NMR of 27



^{13}C NMR of 27

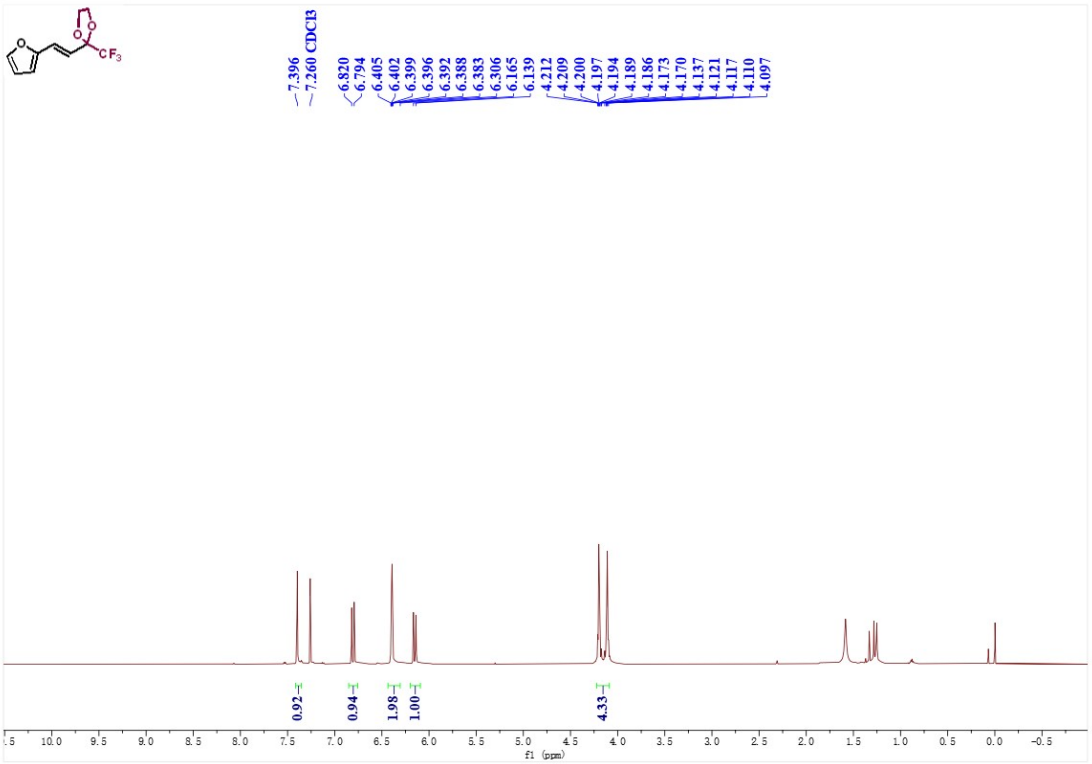


^{19}F NMR of 27

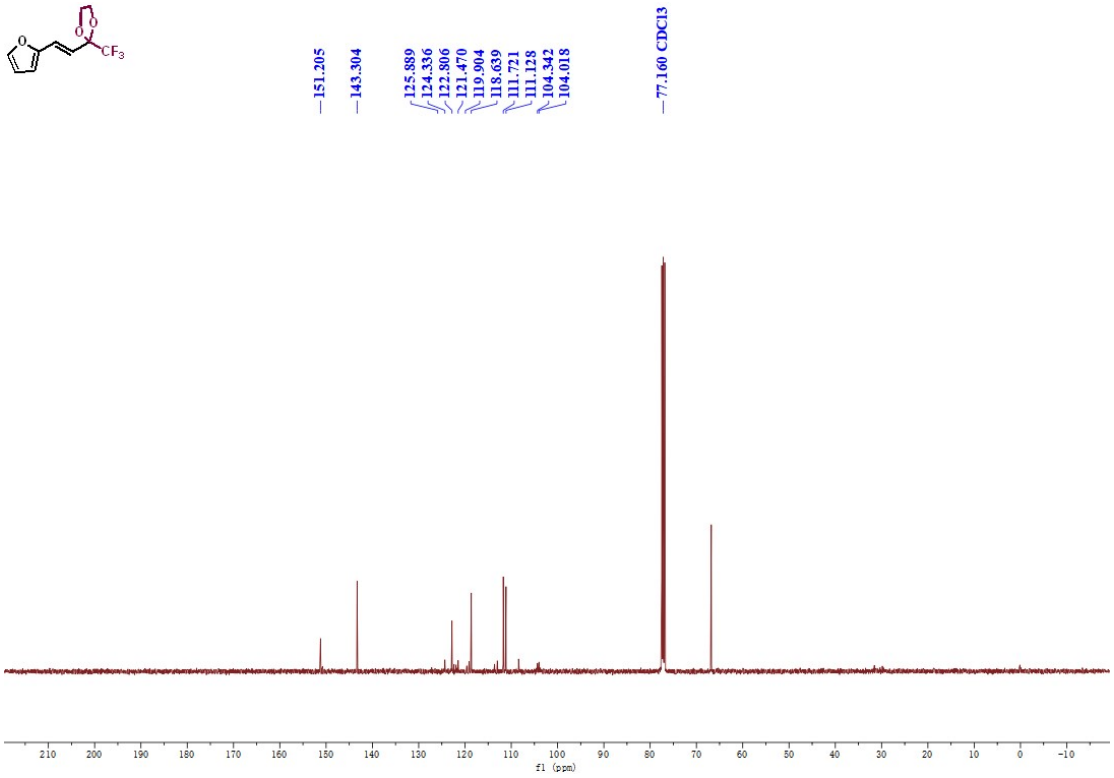


(*E*)-2-(2-(furan-2-yl)vinyl)-2-(trifluoromethyl)-1,3-dioxolane (28)

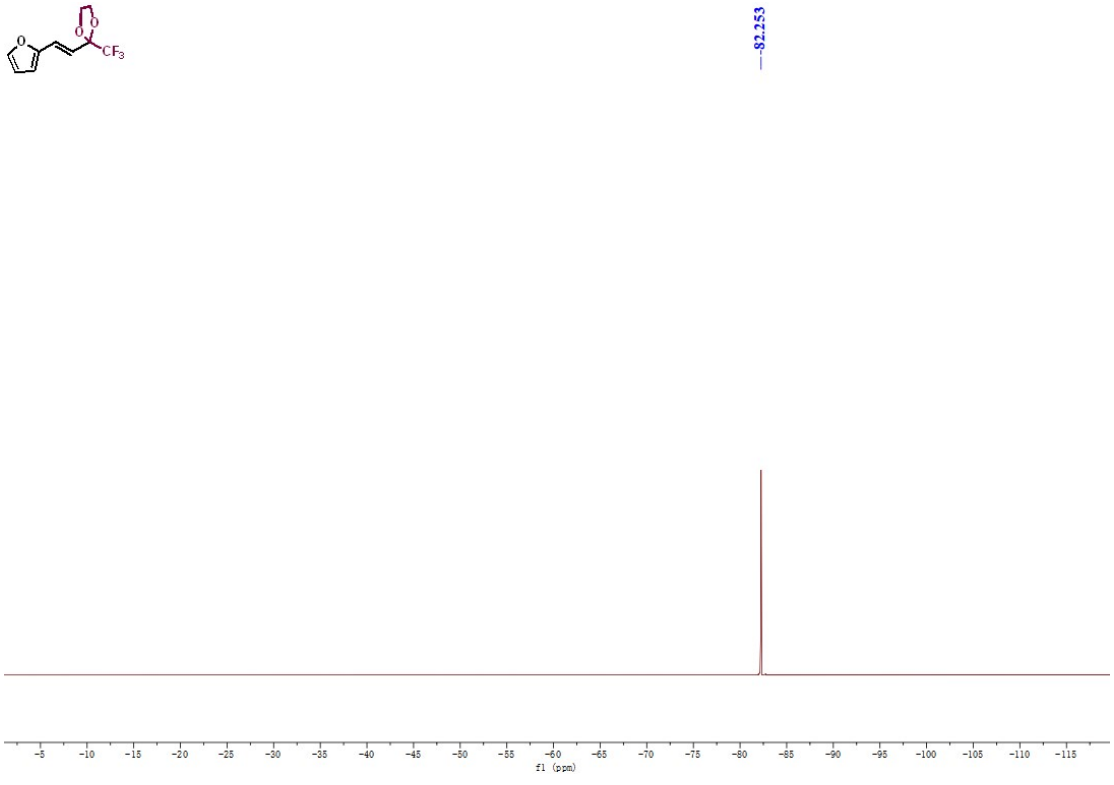
^{1}H NMR of 28



^{13}C NMR of 28

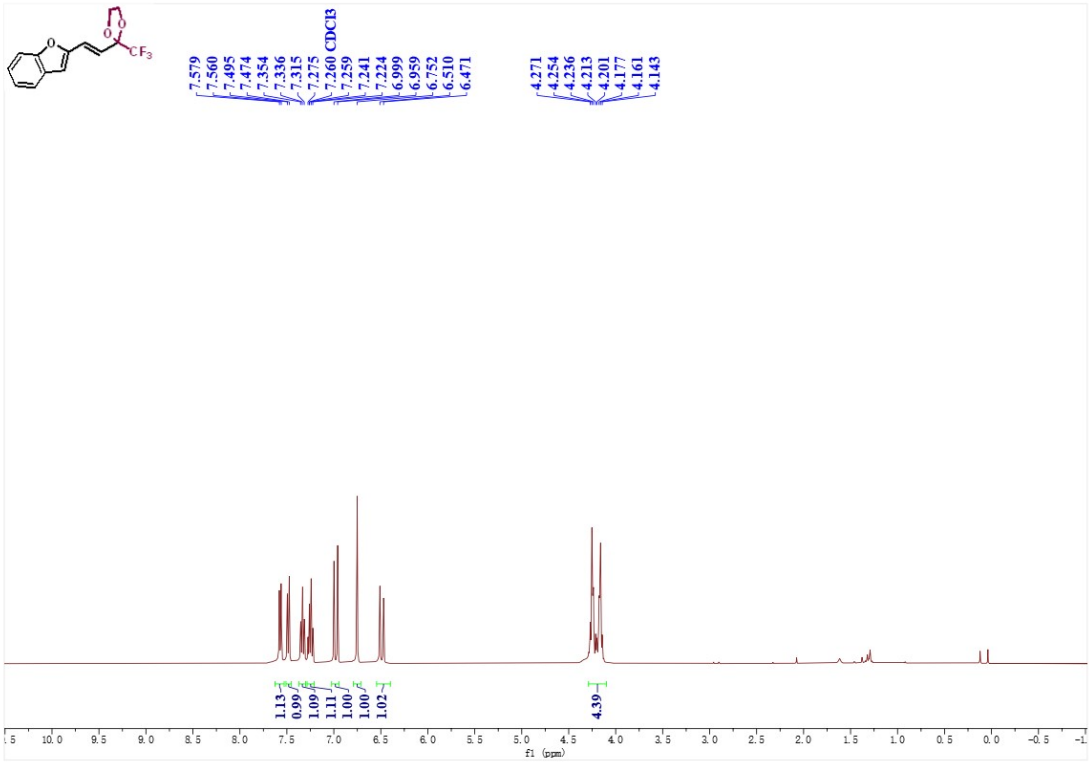


^{19}F NMR of 28

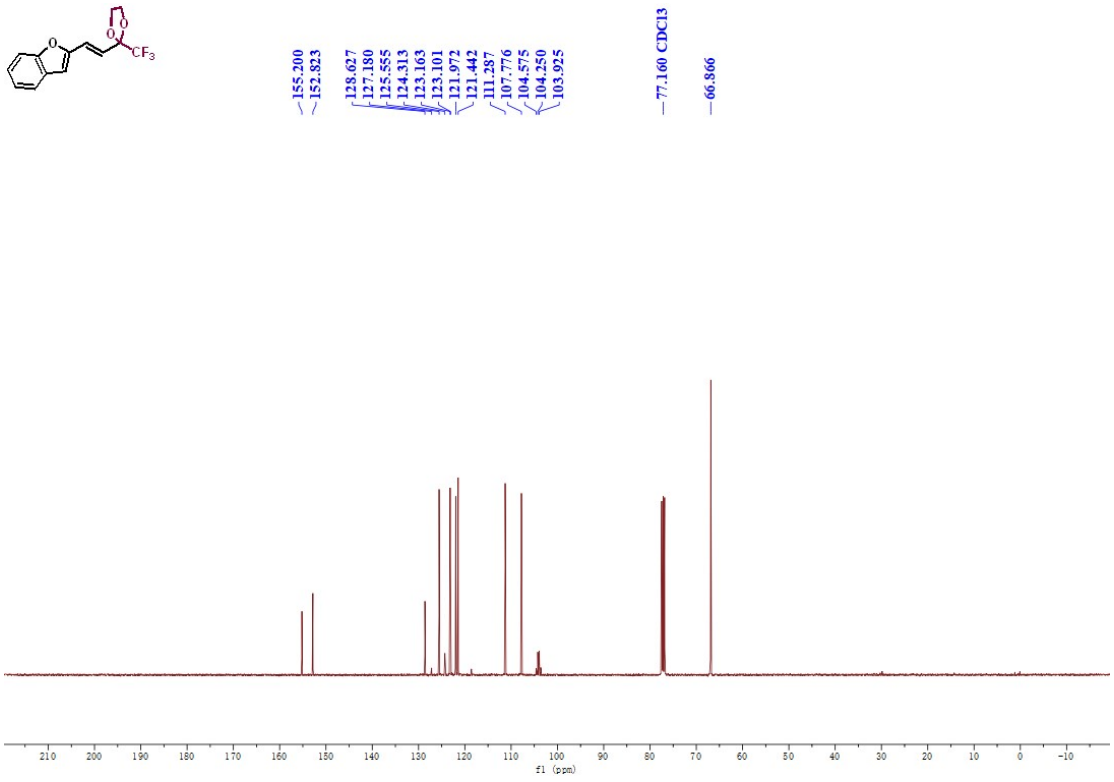


(*E*)-2-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzofuran (29)

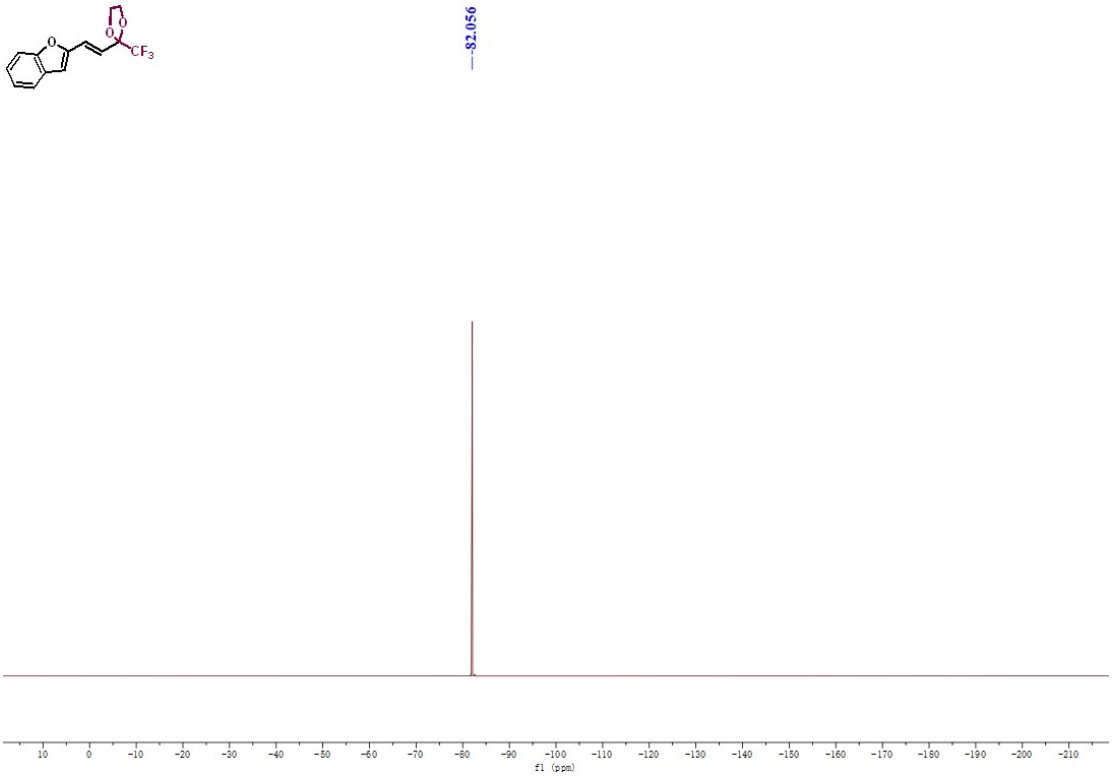
^{1}H NMR of 29



^{13}C NMR of 29

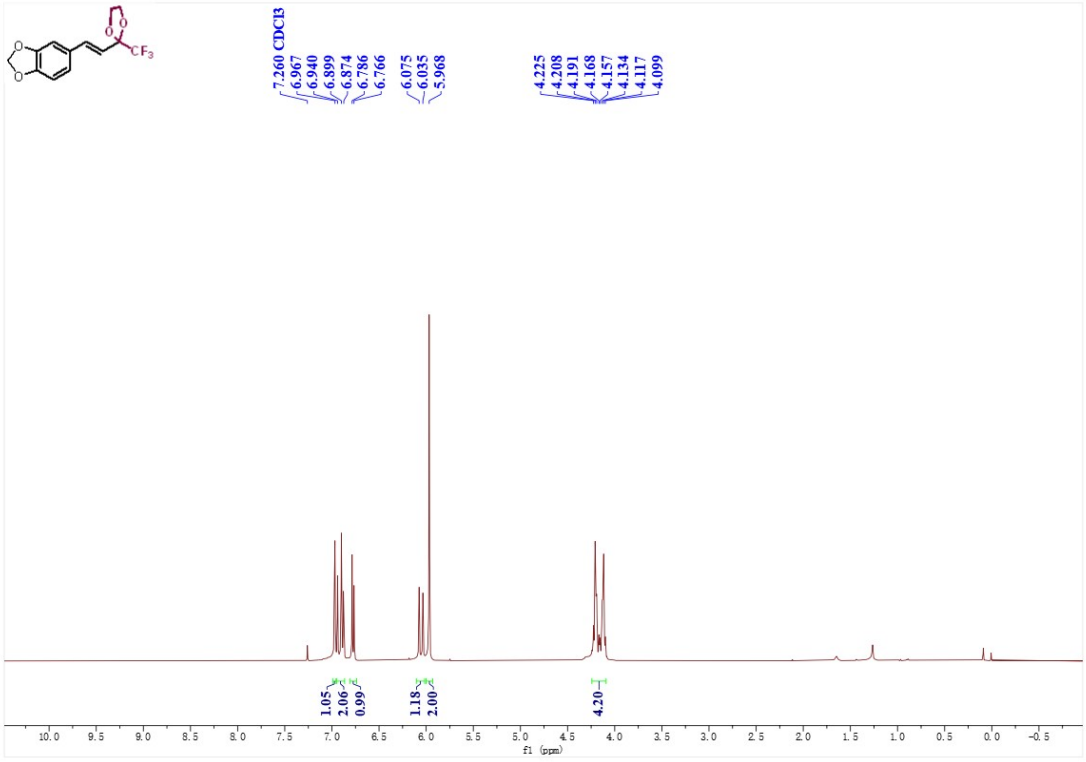


^{19}F NMR of 29

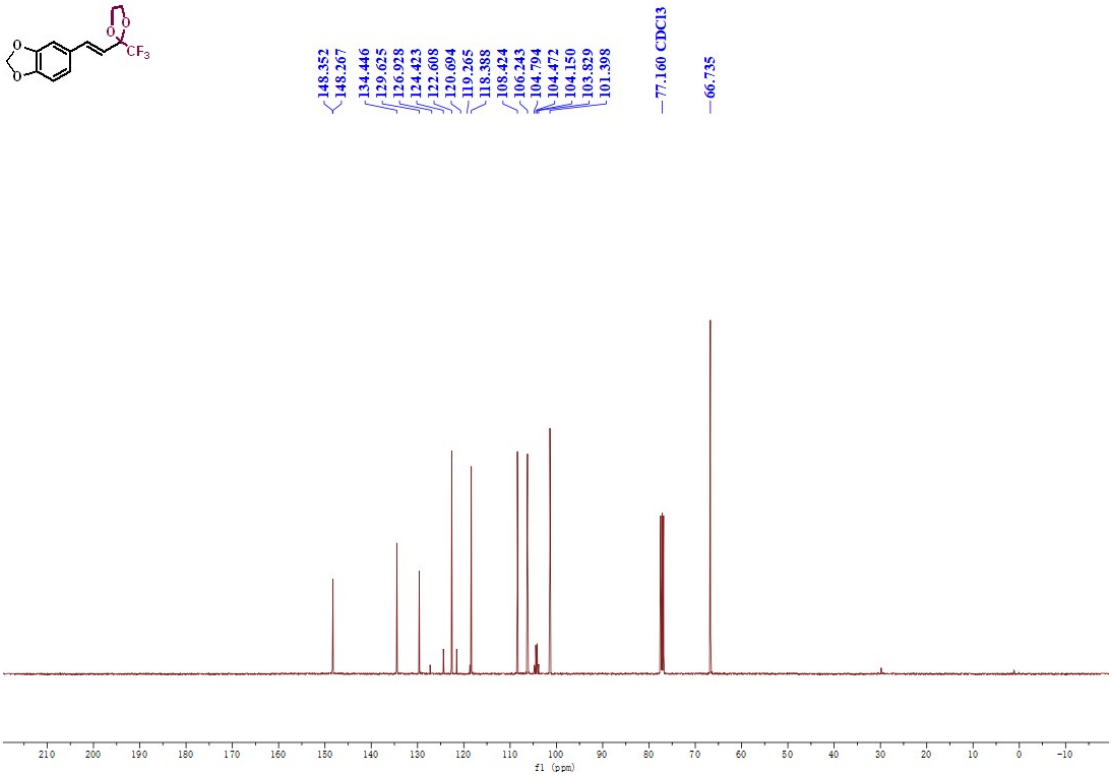


(*E*)-5-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)benzo[d][1,3]dioxole (30)

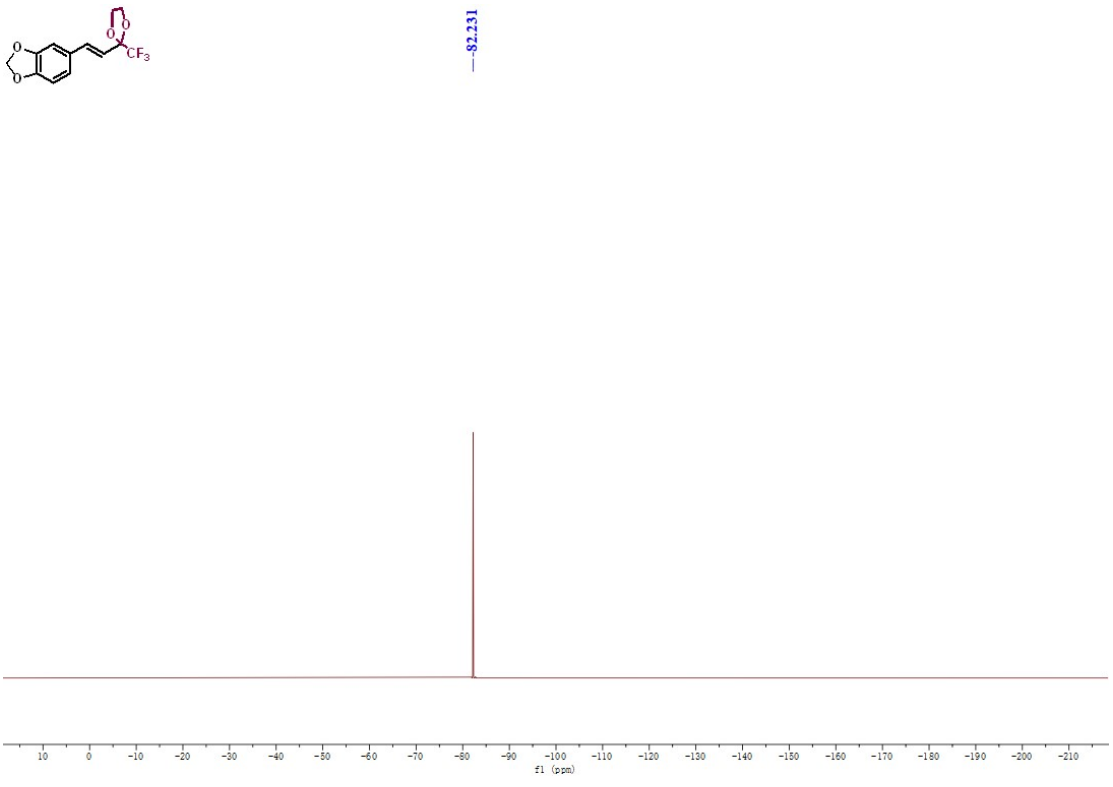
^{1}H NMR of 30



^{13}C NMR of 30

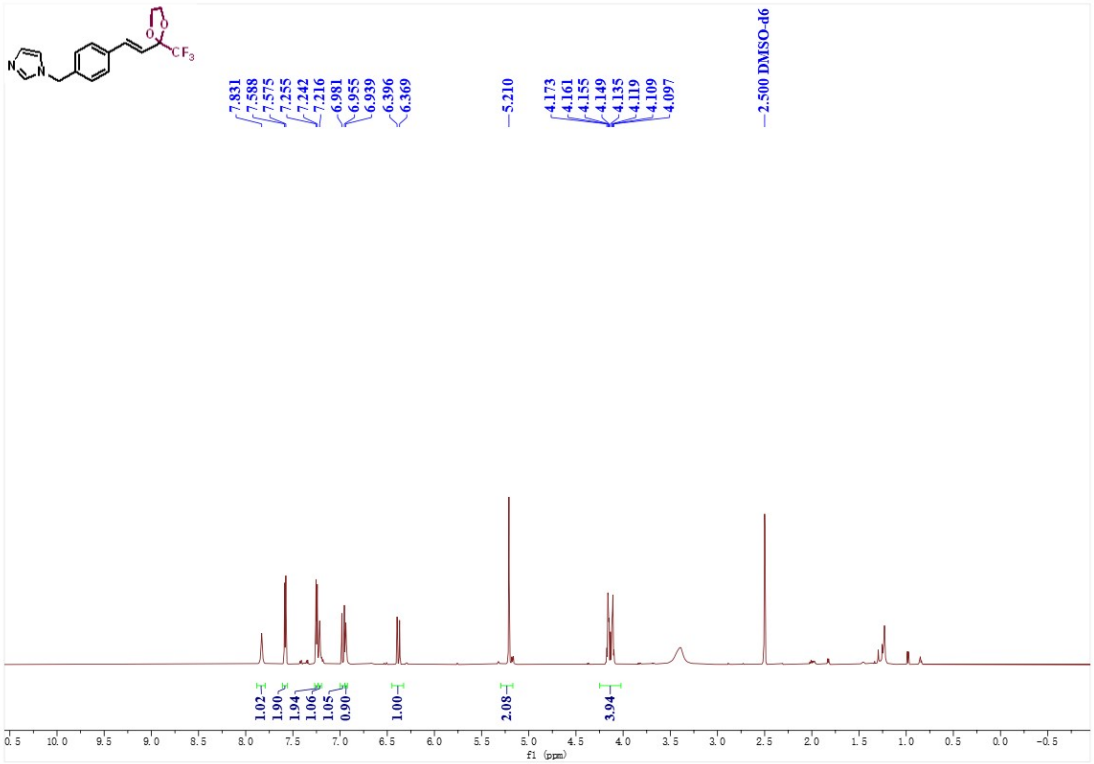


^{19}F NMR of 30

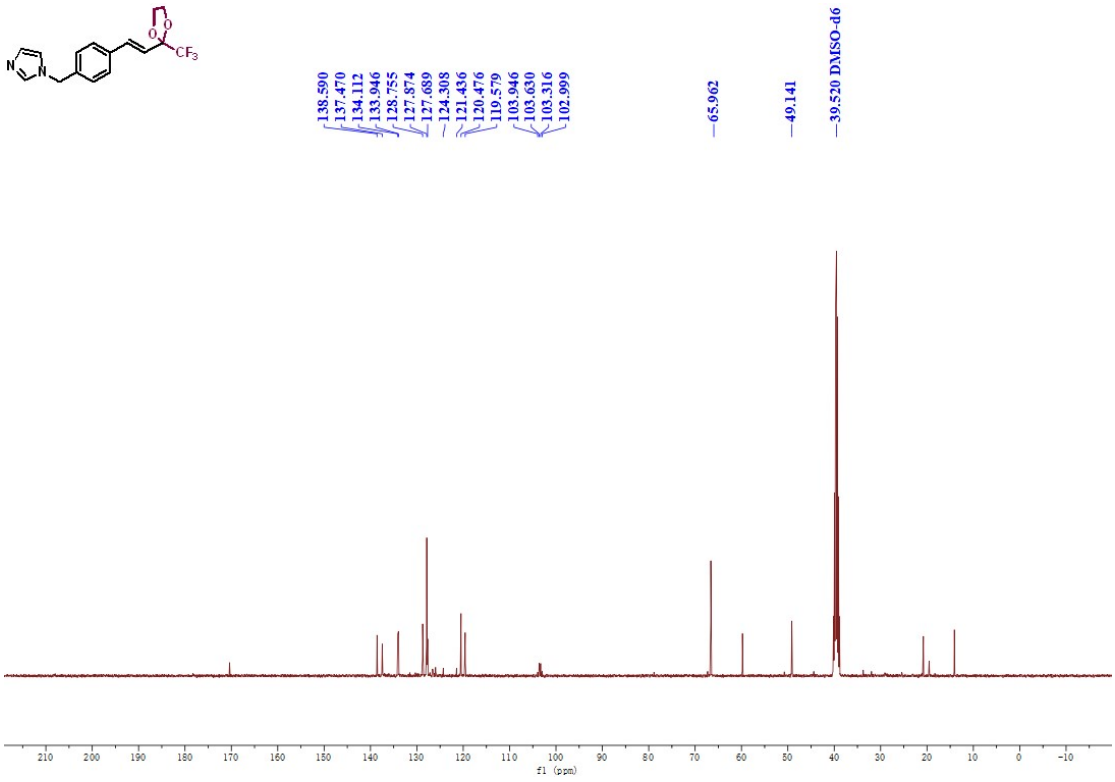


(*E*)-6-(2-(2-(trifluoromethyl)-1,3-dioxolan-2-yl)vinyl)quinoline (31)

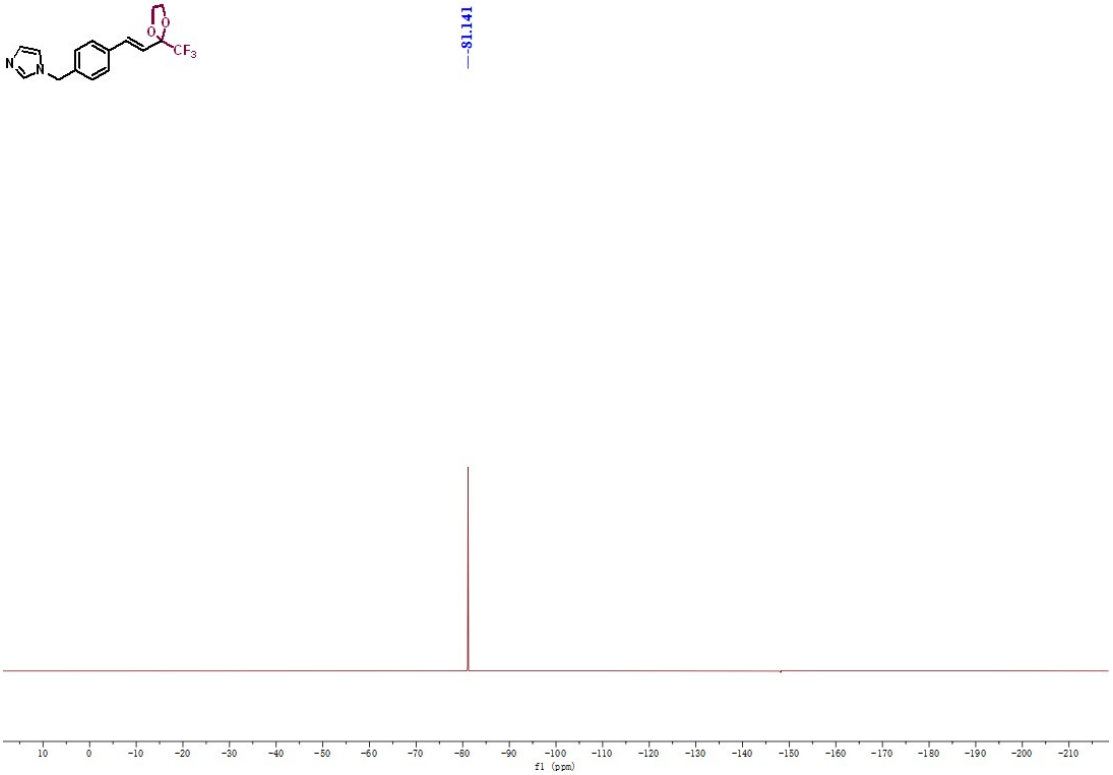
^{1}H NMR of 31



^{13}C NMR of 31

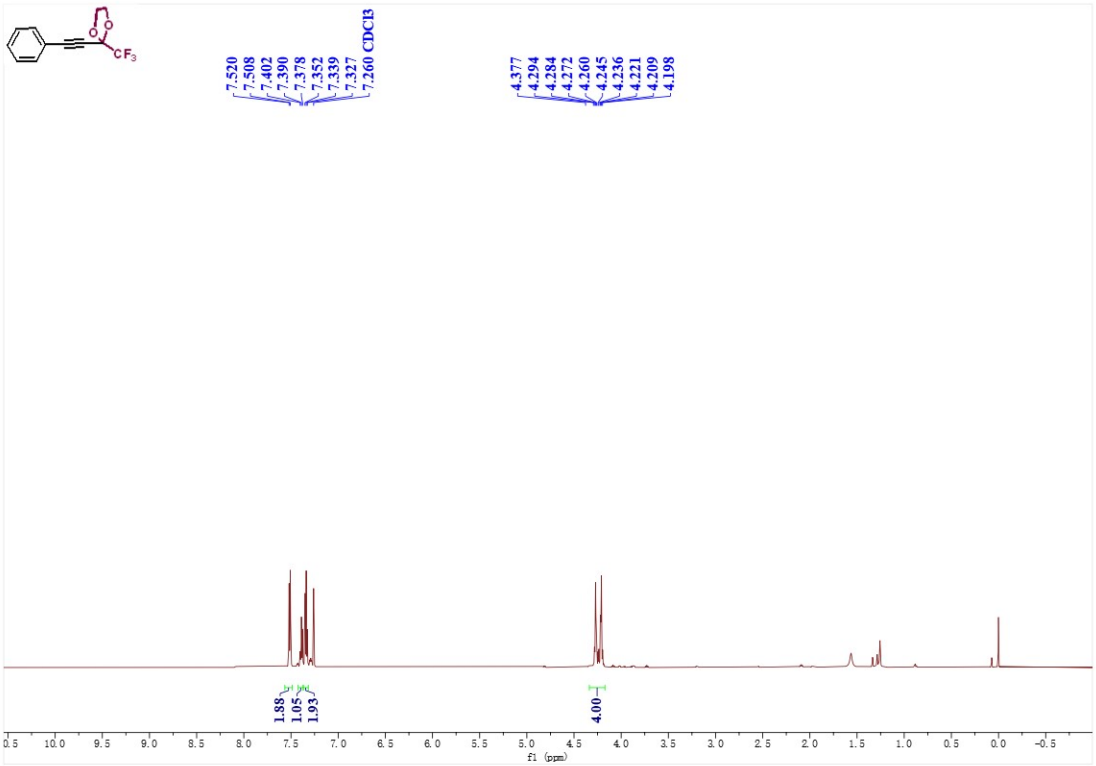


^{19}F NMR of 31

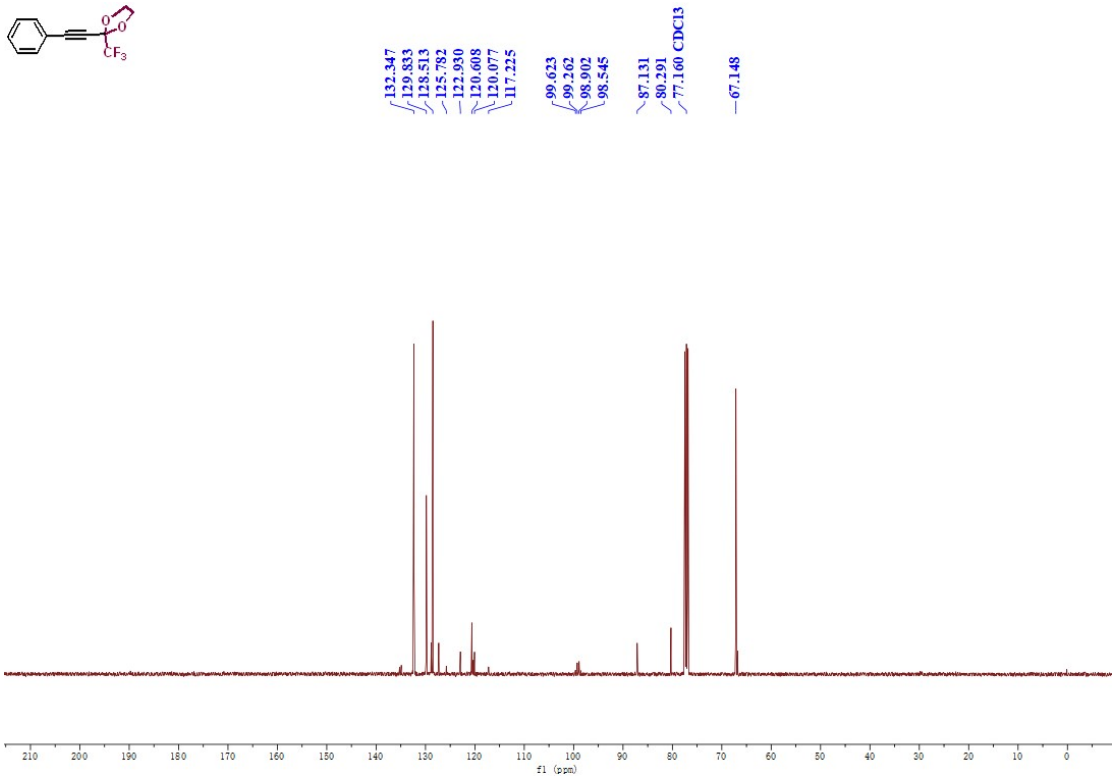


2-(phenylethynyl)-2-(trifluoromethyl)-1,3-dioxolane (32)

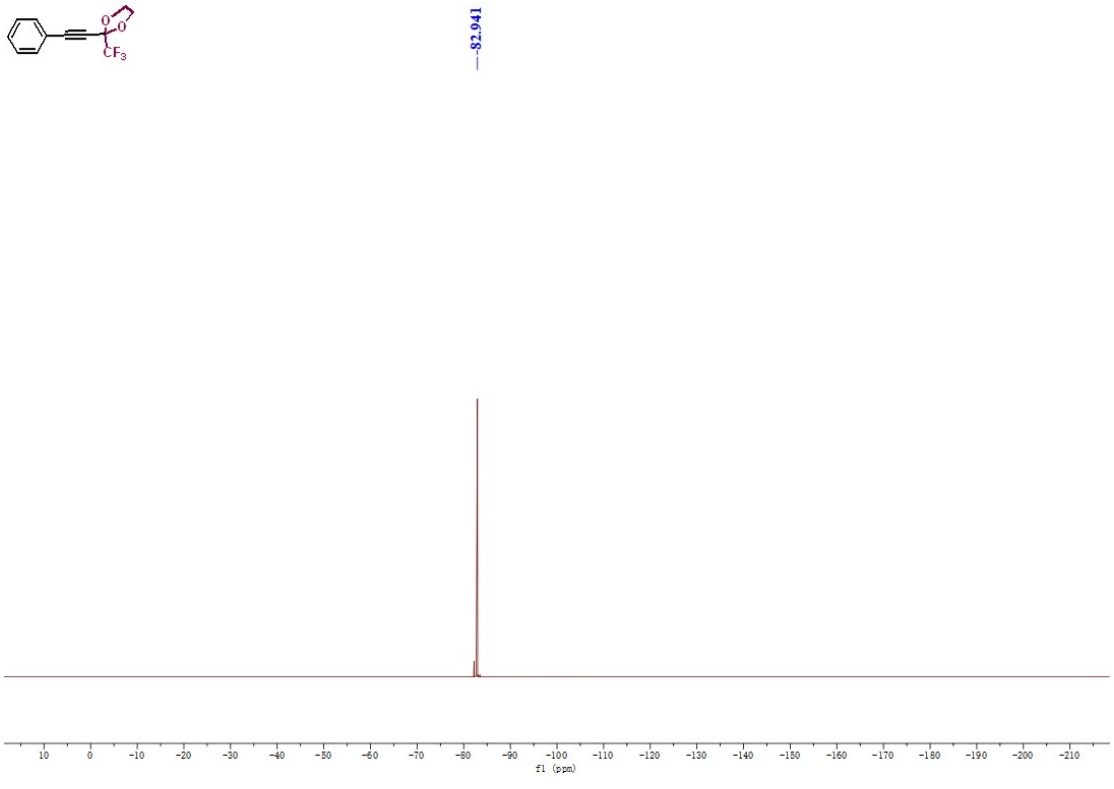
^{1}H NMR of 32



^{13}C NMR of 32

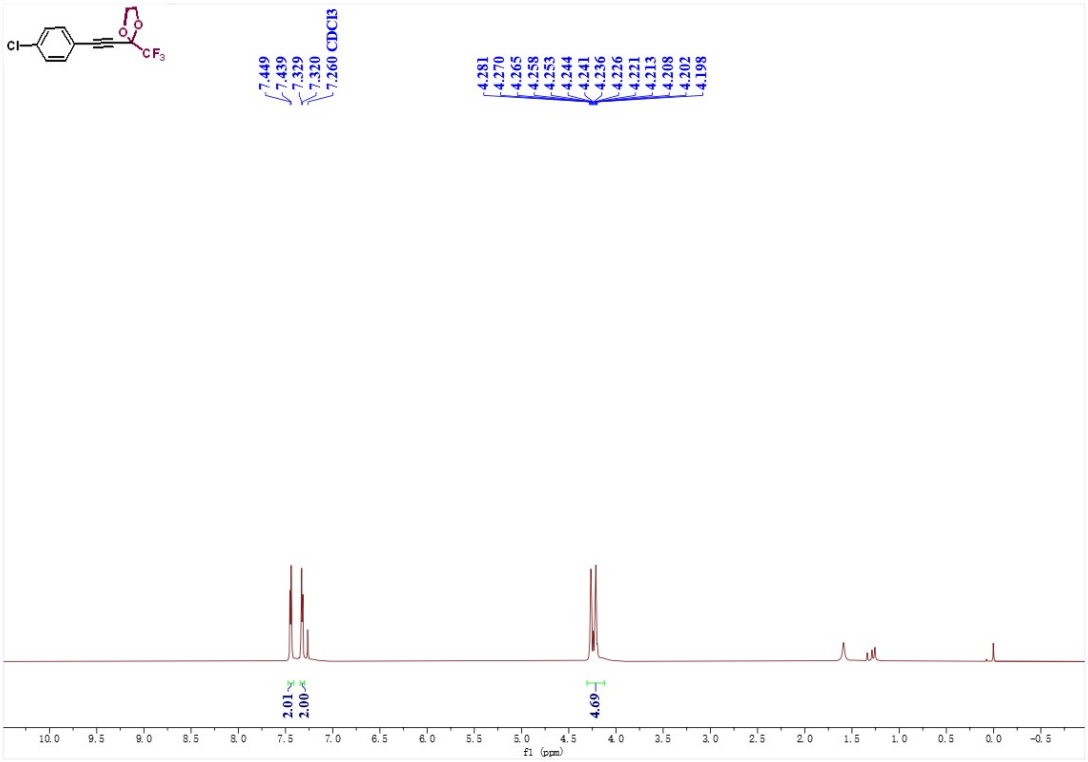


^{19}F NMR of 32

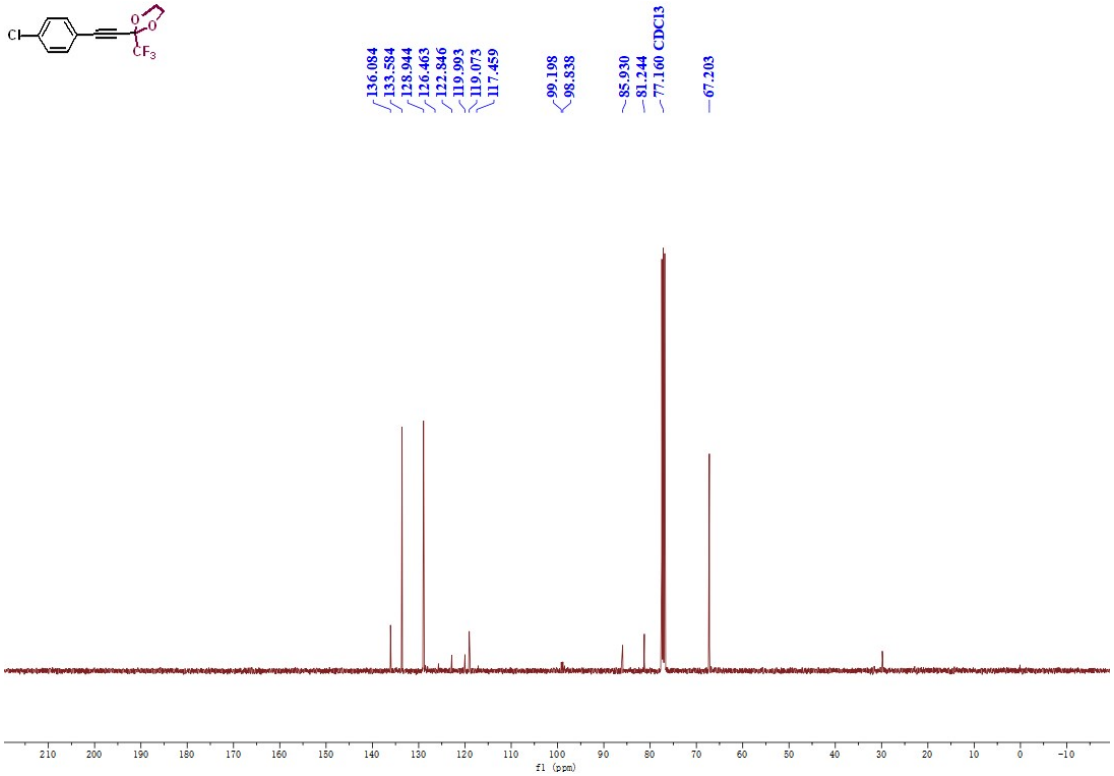


2-((4-chlorophenyl)ethynyl)-2-(trifluoromethyl))-1,3-dioxolane (33)

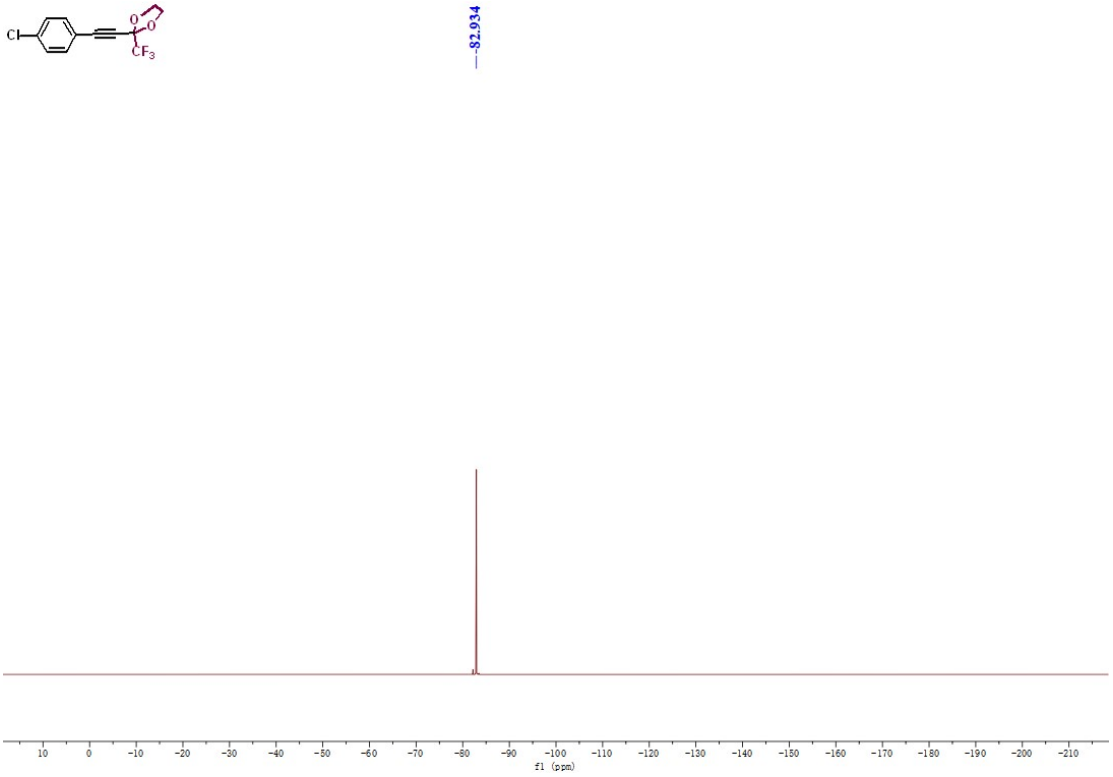
^{1}H NMR of 33



^{13}C NMR of 33

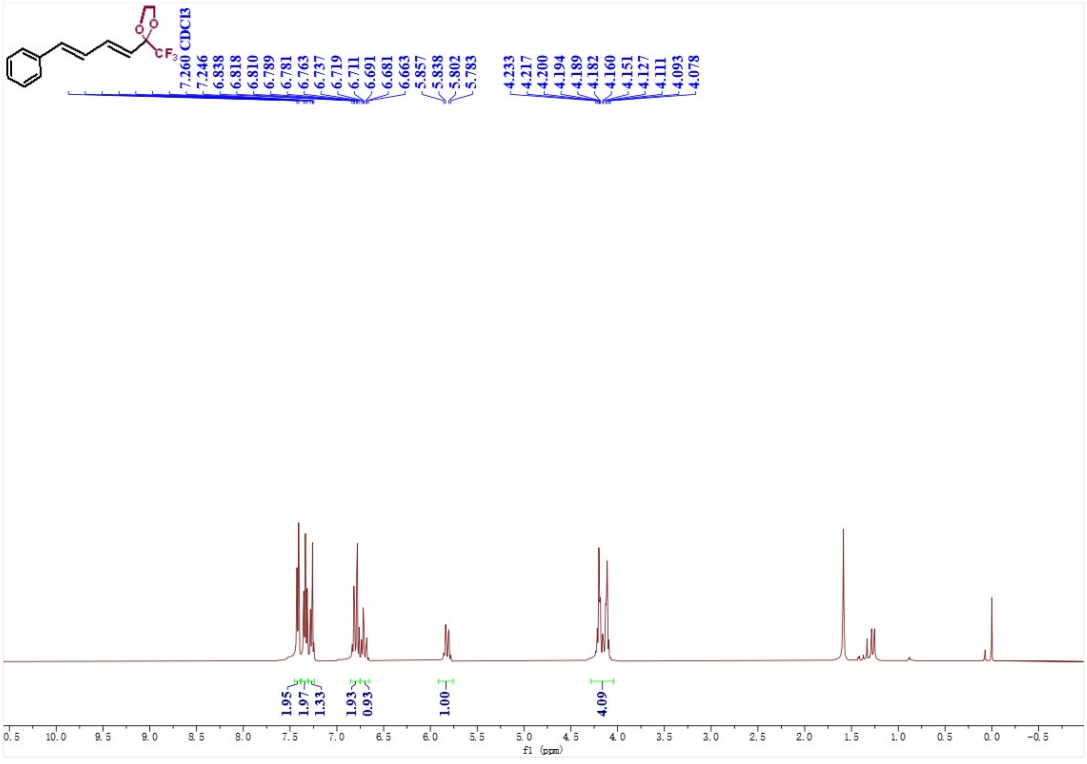


^{19}F NMR of 33

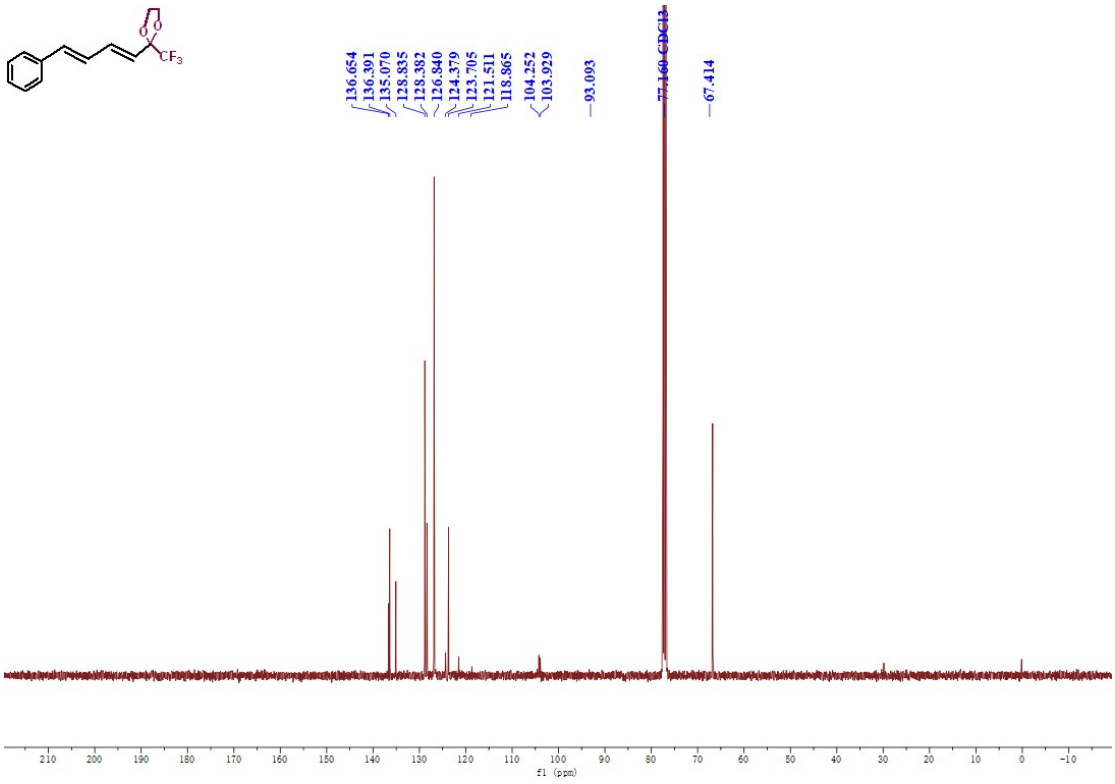


2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-2-(trifluoromethyl))-1,3-dioxolane (34)

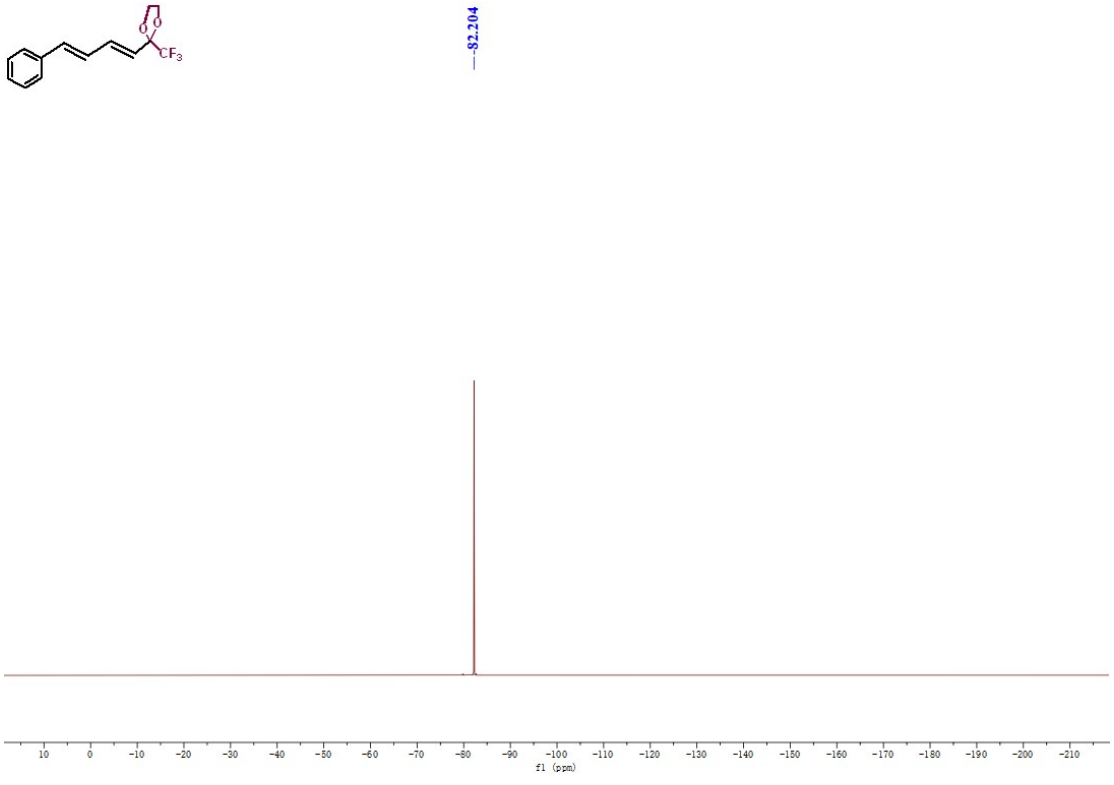
^{1}H NMR of 34



^{13}C NMR of 34

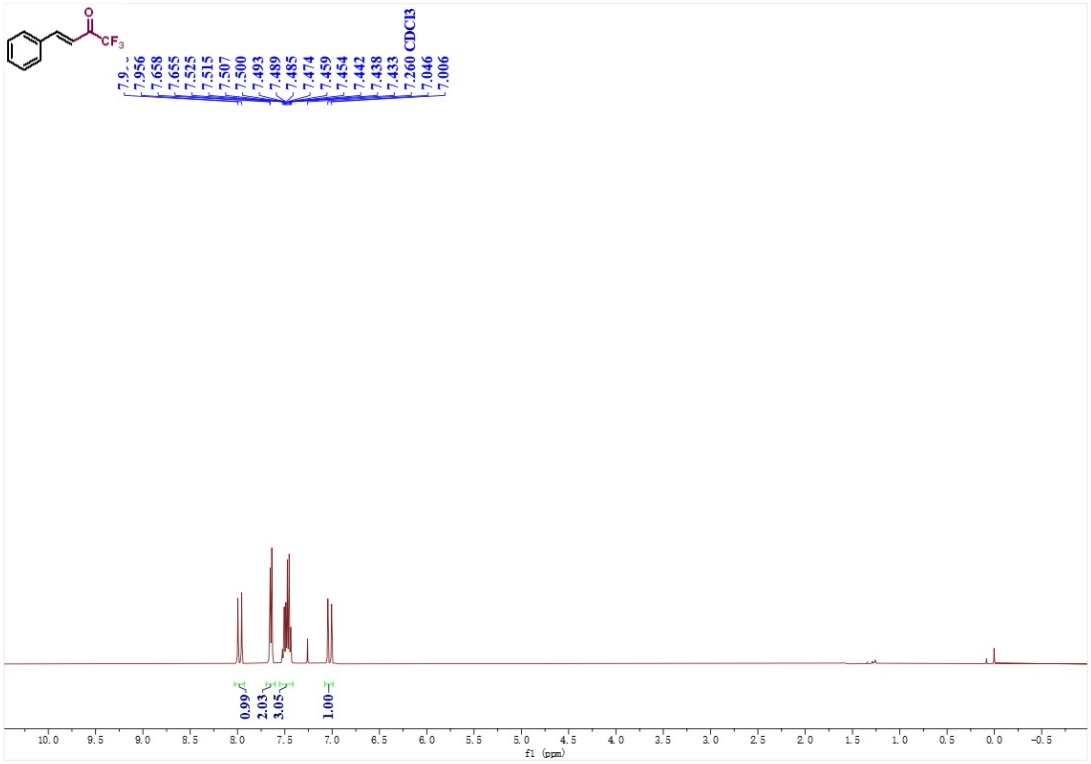


^{19}F NMR of 34

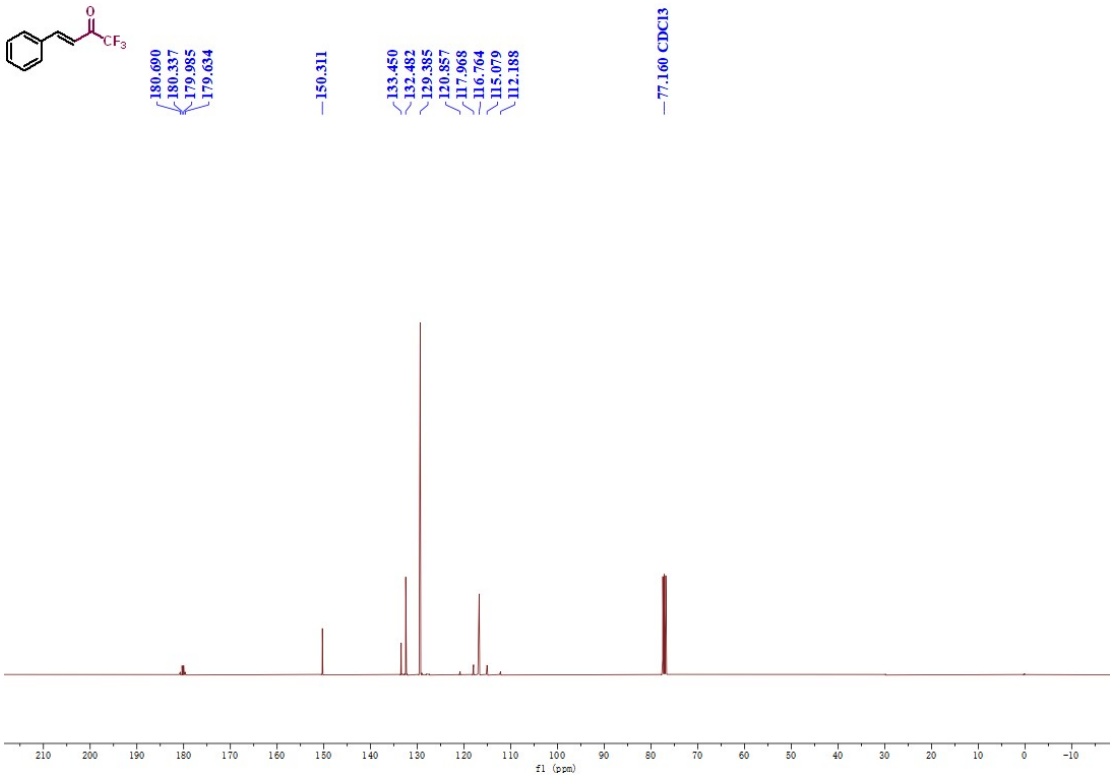


(*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (35)

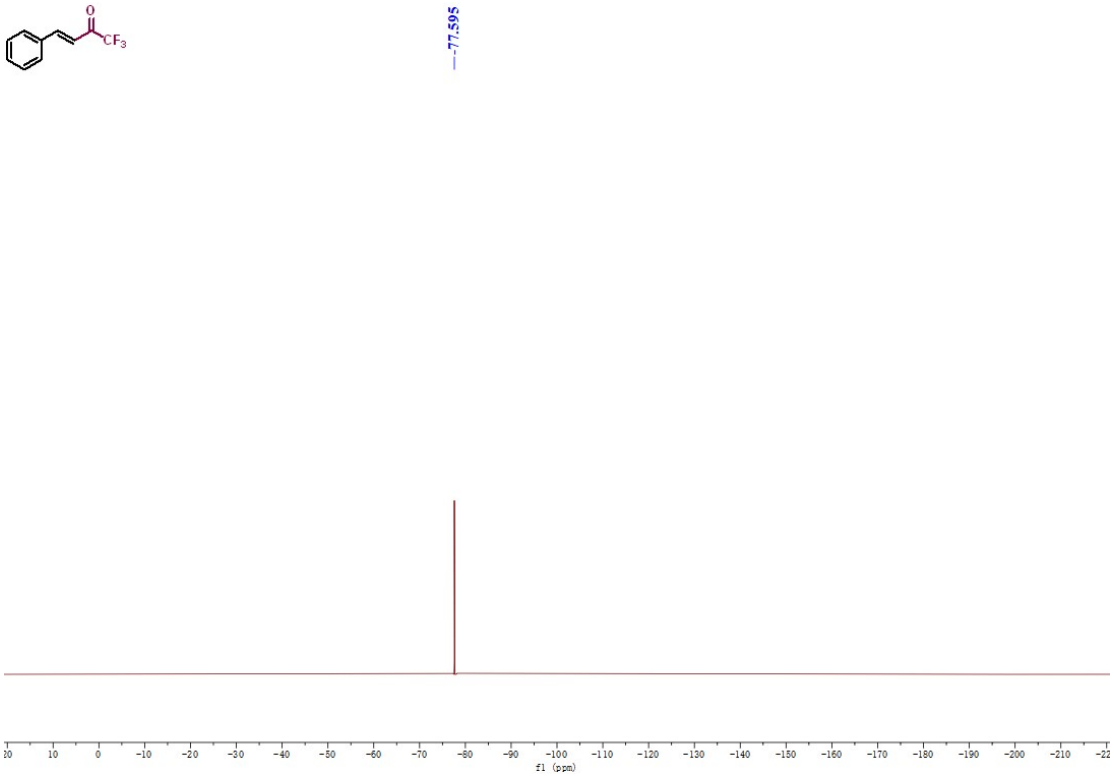
^{1}H NMR of 35



^{13}C NMR of 35

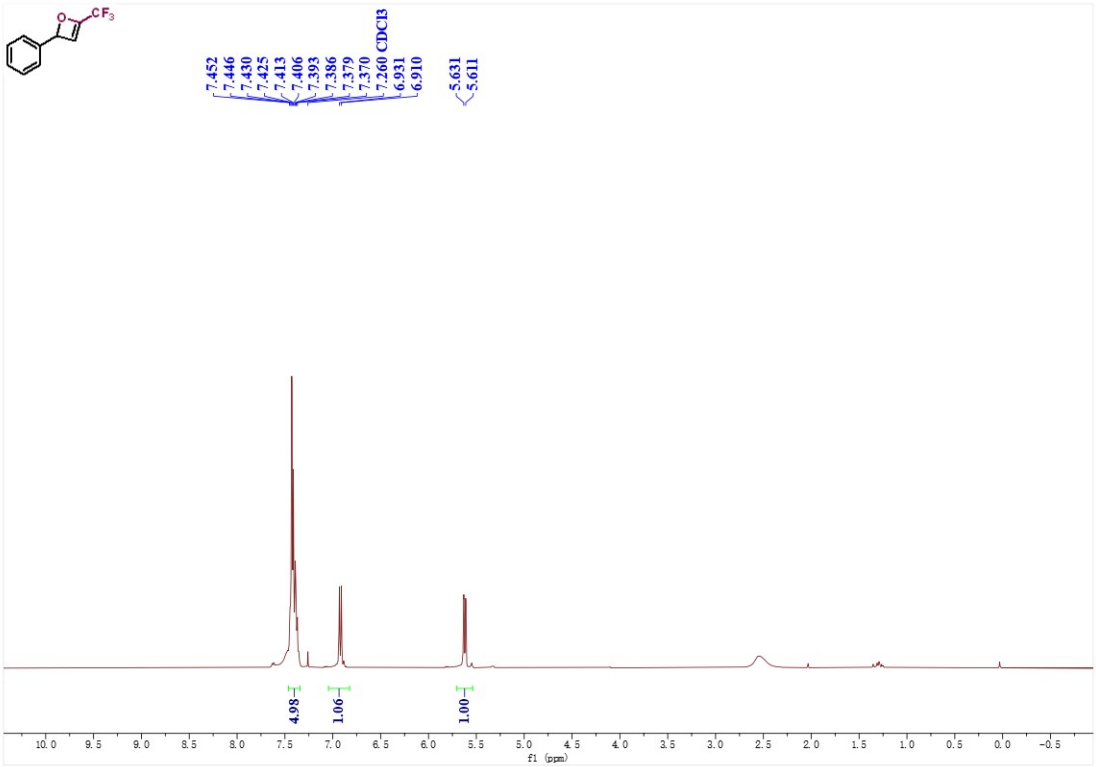


^{19}F NMR of 35

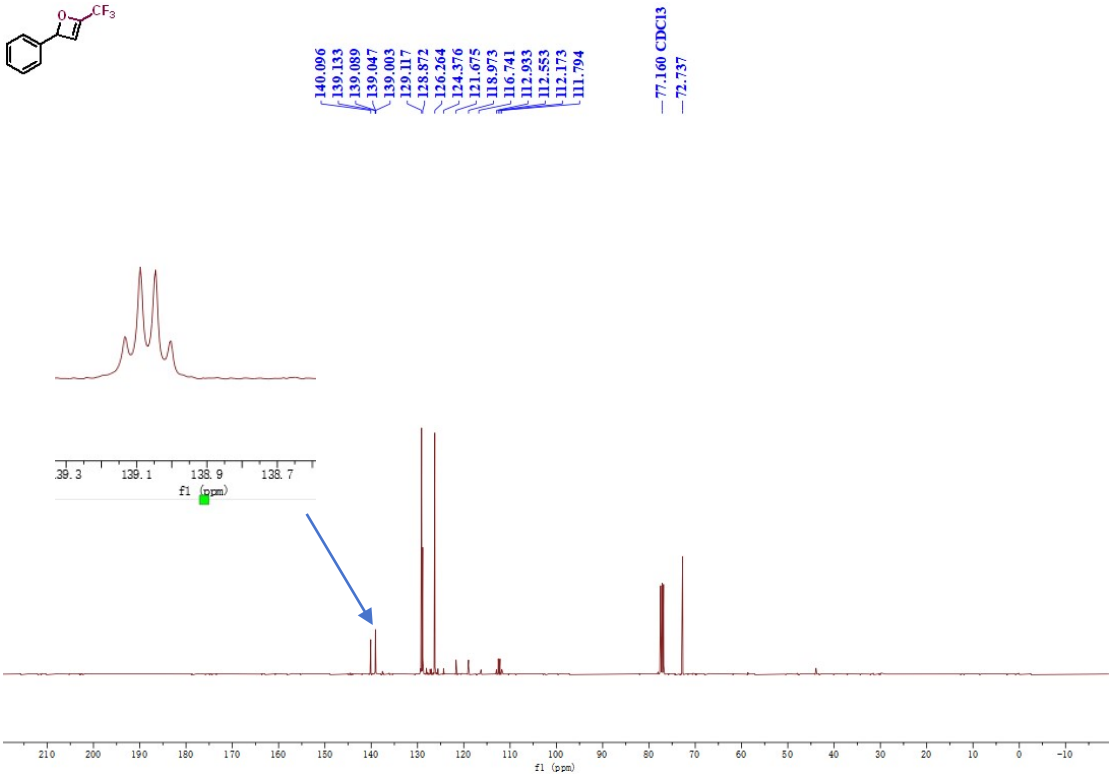


2-phenyl-4-(trifluoromethyl)-2H-oxete (36)

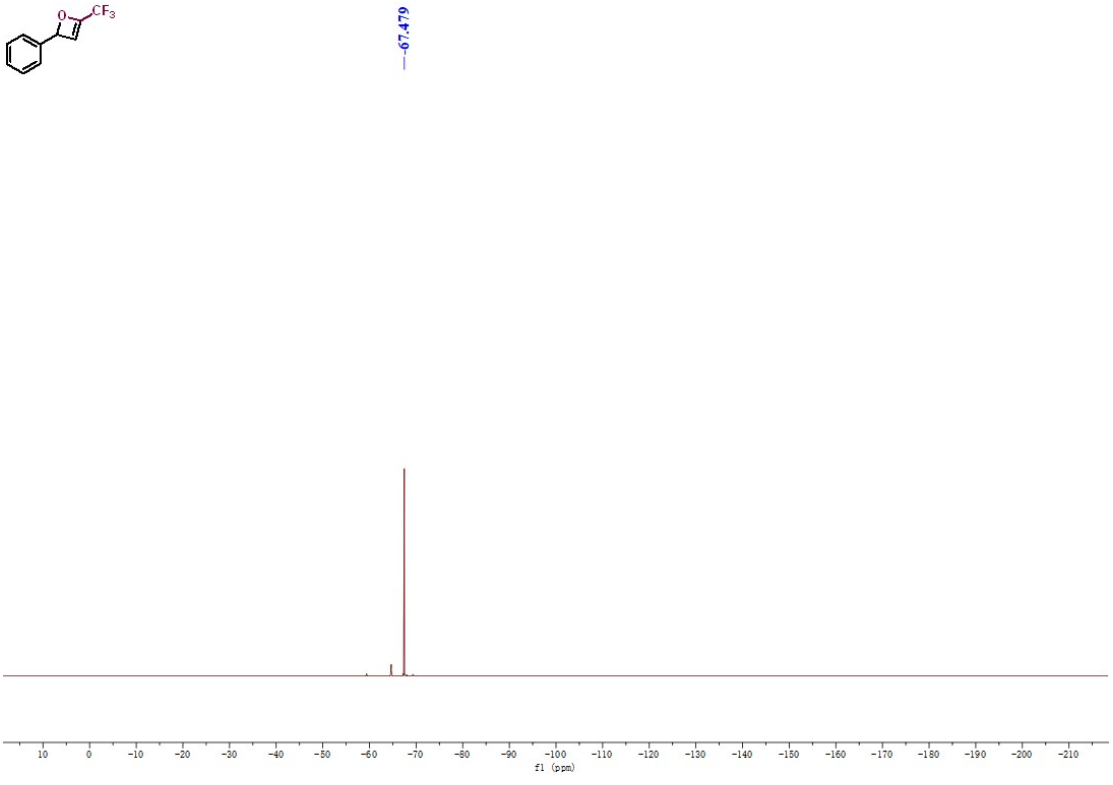
^{1}H NMR of 36



^{13}C NMR of 36

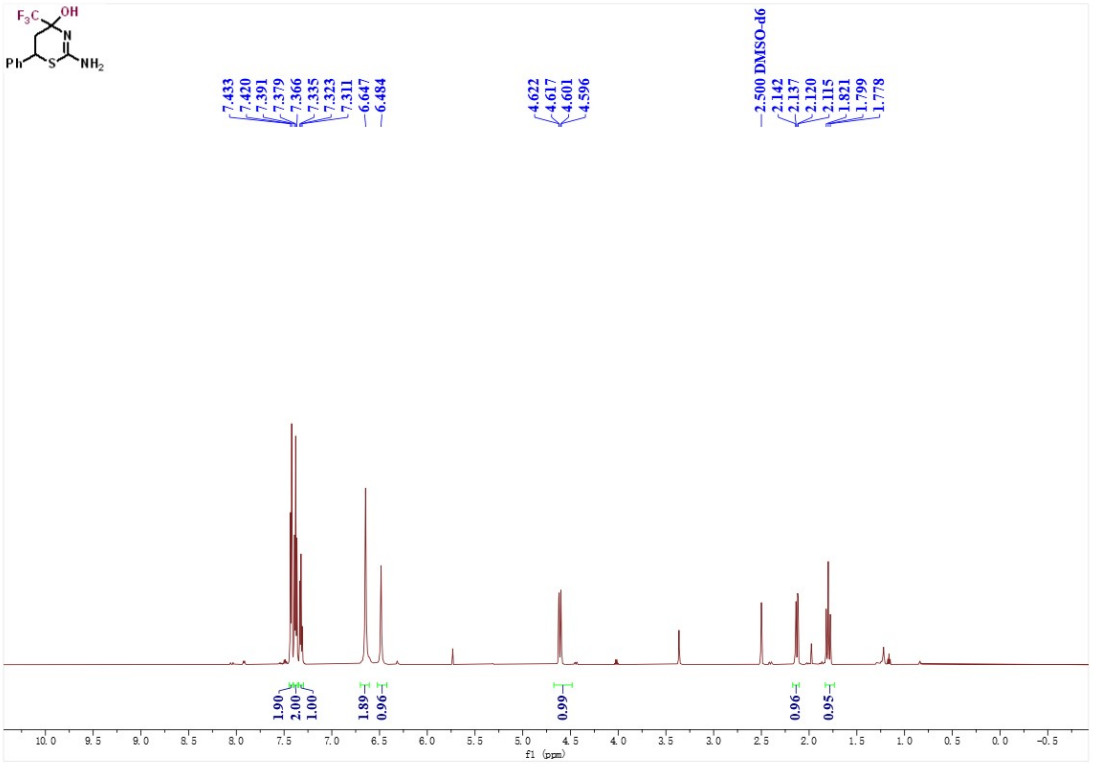


^{19}F NMR of 36

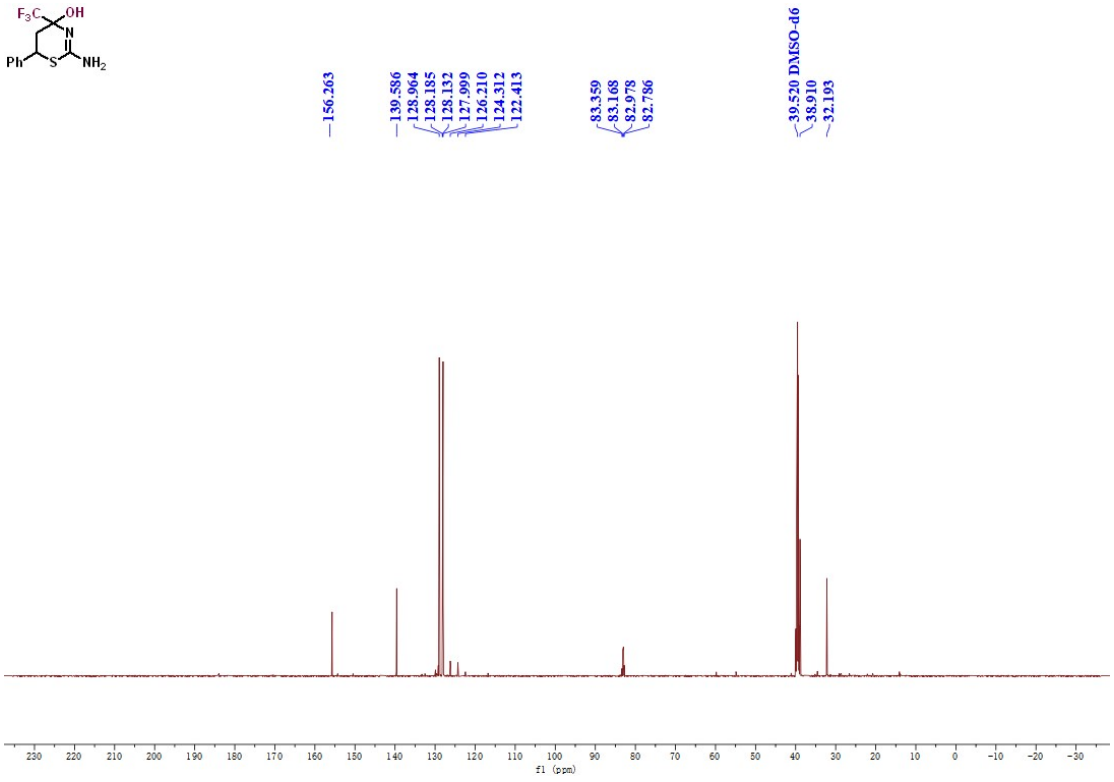


2-amino-6-phenyl-4-(trifluoromethyl)-5,6-dihydro-4H-1,3-thiazin-4-ol (37)

^{1}H NMR of 37

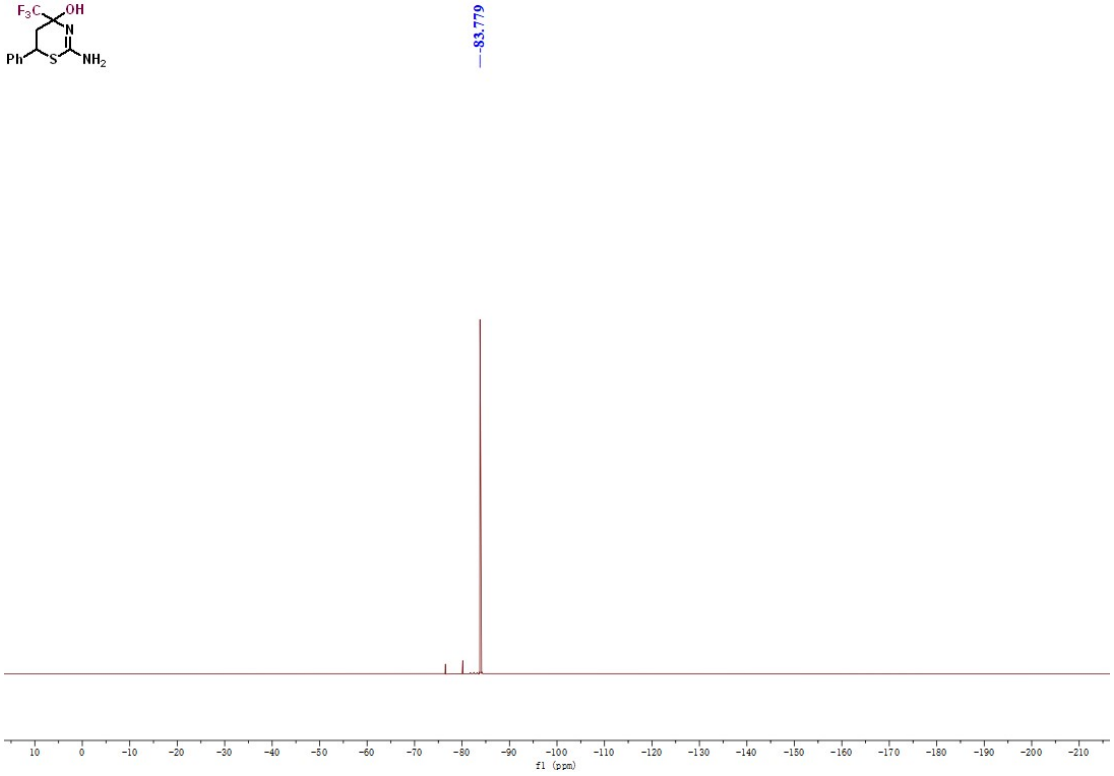


^{13}C NMR of 37



^{19}F NMR of 37

F3C
OH
N
Ph
S
NH2


-83.779
10
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-210
f1 (ppm)