Supporting Information

Organo-Photoredox Catalyzed *gem*-Difluoroallylation of Ketone-Derived Dihydroquinazolinonesvia C(sp^3)-C Bond and C(sp^3)-F Bond Cleavage

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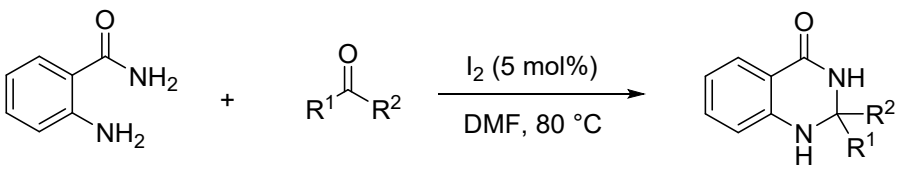
1. General information

All experiments were monitored by analytical thin-layer chromatography (TLC). TLC was performed on pre-coated plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active material. Columns were packed as a slurry of silica gel in petroleum ether (PE) and equilibrated solution using the appropriate solvent system. All reagents were commercially available unless otherwise noted. All reactions were carried out under a nitrogen atmosphere in dried glassware. Air and moisture-sensitive liquids and solutions were transferred via a syringe. All sol-vents were dried and distilled by standard procedures. Solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished on silica gel Si 60® (300-400 mesh). All heating reactions were heated by a metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com). Nuclear magnetic resonance spectra were acquired on a Bruker AMX 400 (400 MHz, and 100 MHz for ^{1}H, and ^{13}C respectively) and Bruker AMX 600 (600 MHz, and 150 MHz for ^{1}H, and ^{13}C respectively). All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CDCl_3$) or 2.50 ppm (DMSO). All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm) or DMSO (35.92 ppm) with ^{1}H -decoupling. Data for ^{1}H-NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s = singlet; brs = broad singlet; vbs = vary broad singlet; d = doublet; t= triplet; q = quartet; quint = quintet; sext = sextet; m = multiplet), coupling constant (Hz), integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ in ppm), multiplicity, coupling constant (Hz). Melting points were measured on a WRS-1A digital.

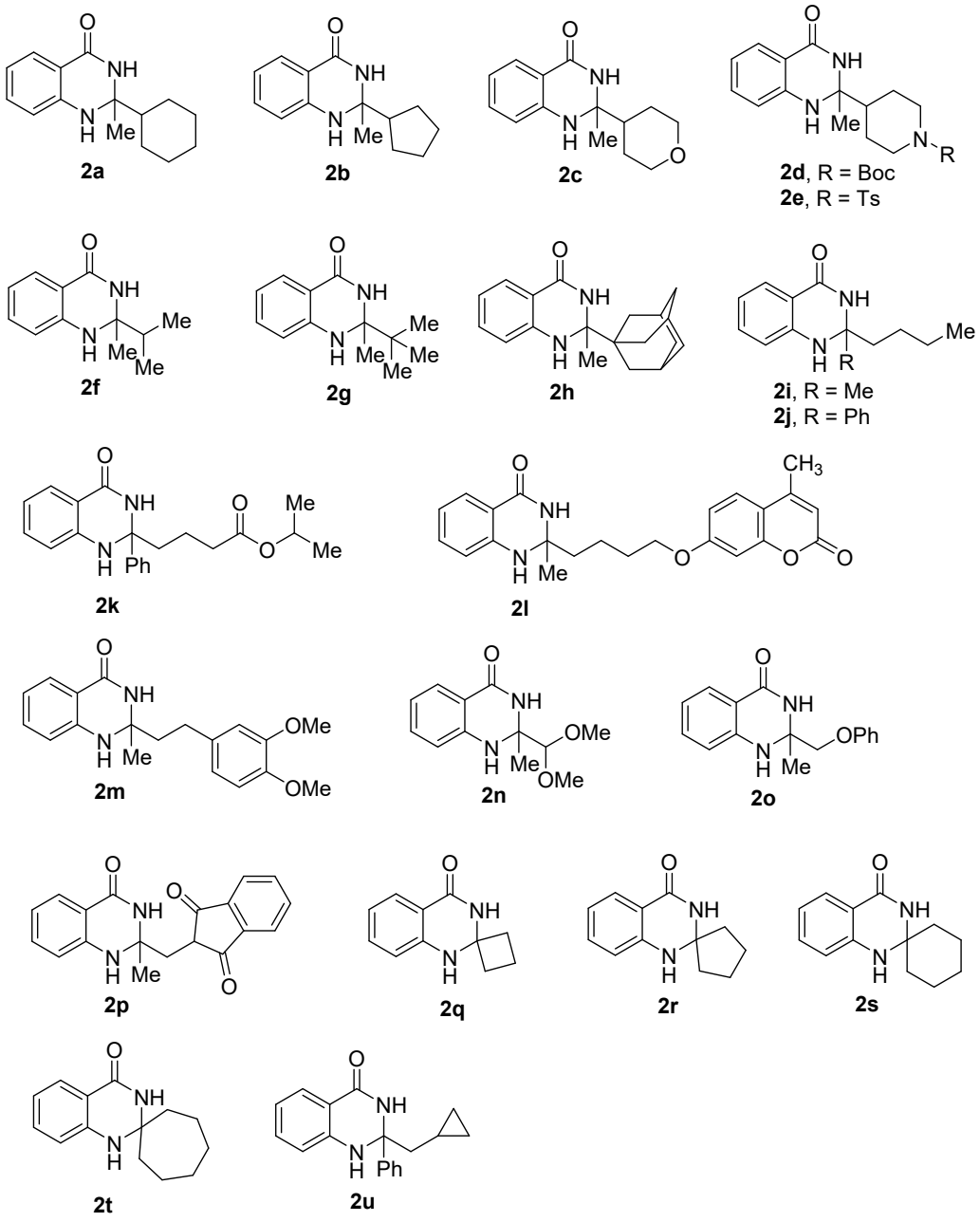
2. General procedures

2.1 General procedure 1 (GP1): synthesis of 2,2-disubstituted dihydroquinazolinones

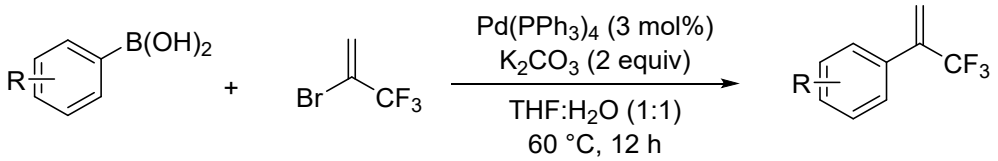


According to literature reports[1, 2], a 100 mL flask containing a stirring bar was charged

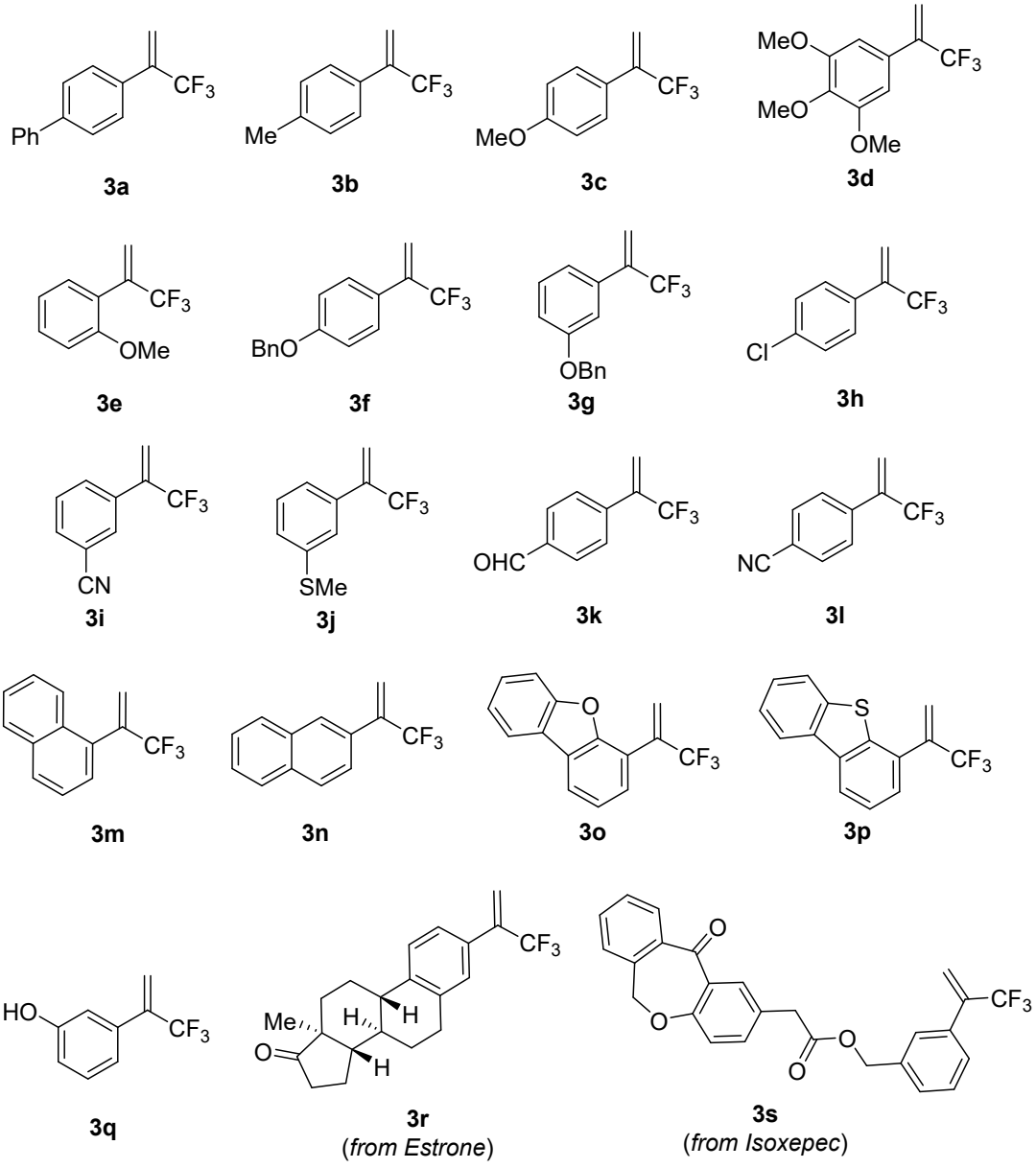
with 2-aminobenzamide (10 mmol, 1.0 equiv.), ketone (10.5 mmol, 1.05 equiv.), iodine (5 mol%) and DMF (0.67 M). The reaction mixture was stirred at 80 °C for 12-36 hours. The reaction was cooled to 20 °C and water (50 mL) was added to the reaction generating precipitate that was collected as crude product by suction filtration. The crude material was washed with water and purified by recrystallization (EtOH) to give targeted product.



2.2 General procedure 2 (GP2): synthesis of aryl trifluoromethyl alkenes

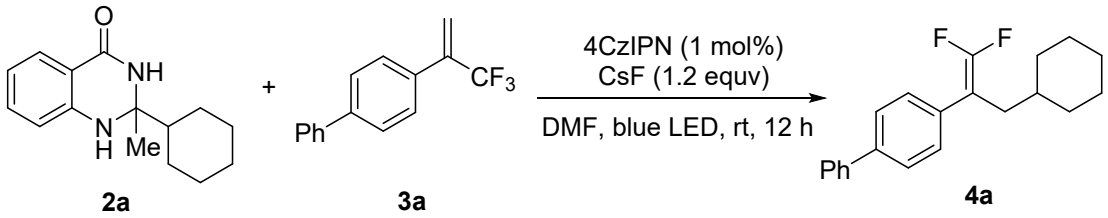


According to literature reports[3-6], to a Schlenk tube equipped with stir bar, boronic acid (1.0 equiv., 10 mmol), K_2CO_3 (2.0 equiv., 20 mmol), and $Pd(PPh_3)_4$ (3 mol%, 0.3 mmol) were added. The vessel was evacuated and filled with nitrogen (three times), and then water (40 mL) and THF (40 mL) were added. After addition of 2- bromo-3,3,3-trifluoro-1-propene (1.5 equiv., 15 mmol), the solution was stirred at 60 ℃ with heating mantle for 12 hours (TLC tracking detection). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene (PE-PE/EA).



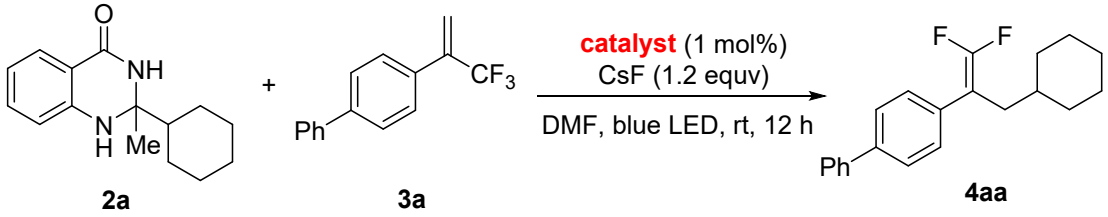
3. Optimization of reaction conditions

Standard condition:



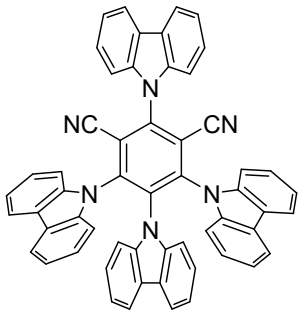
An oven-dried Schlenk tube containing a stirring bar was charged with 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (**2a**, 1.2 equiv.), α-trifluoromethyl alkene (**3a**, 0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), and CsF (1.2 equiv.). The tube was connected to a vacuum line where it was evacuated and back-filled with N_2 for three times. Then DMF (2 mL) was added under N_2 atmosphere. Finally, the reaction mixture in sealed tube was stirred at room temperature for 12 h under continuous light irradiation from 40 W blue LED (λ = 440 nm). The reaction was quenched by the addition of brine solution (2 mL) and then extracted with ethyl acetate (3×5 mL). The combined organic layers were washed once again with water (5 mL), followed by brine (5 mL) and the solvents were removed under reduced pressure. The crude reaction mixture was purified by column chromatography through silica gel (eluent: petroleum ether/ethyl acetate) to afford pure product **4aa**.

Table S1 Screening of catalyst.

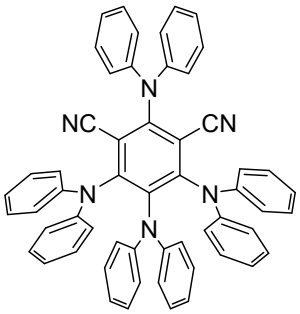


Entry	Variation from the standard conditions	Yield/%
1	4CzIPN	84
2	PC1 instead of 4CzIPN	58
3	PC2 instead of 4CzIPN	0
4	PC3 instead of 4CzIPN	25
5	PC4 instead of 4CzIPN	27
6	PC5 instead of 4CzIPN	61

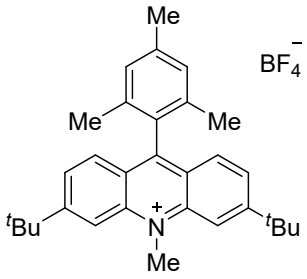
Reactions conditions: **2a** (0.24 mmol, 1.2 equiv.), **3a** (0.2 mmol, 1 equiv.), **catalyst** (1 mol%), CsF (0.24 mmol, 1.2 equiv.), DMF (2 mL), blue LED, rt, 12 h.



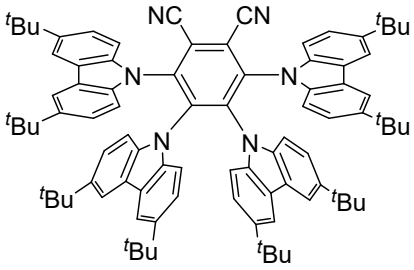
4CzIPN



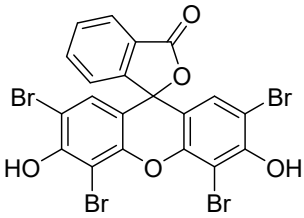
PC1



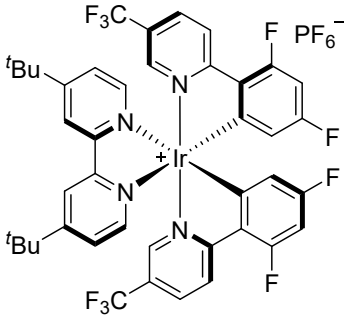
PC2



PC3

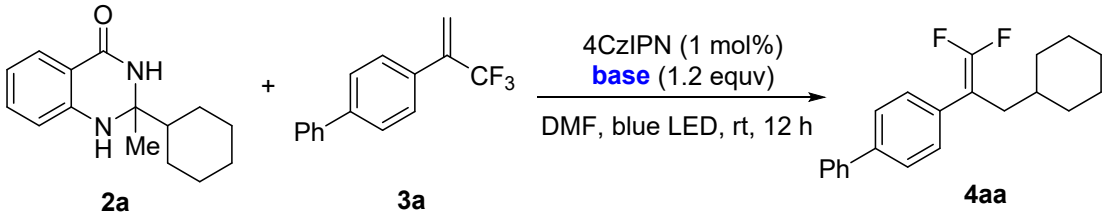


PC4



PC5

Table S2 Screening of base.

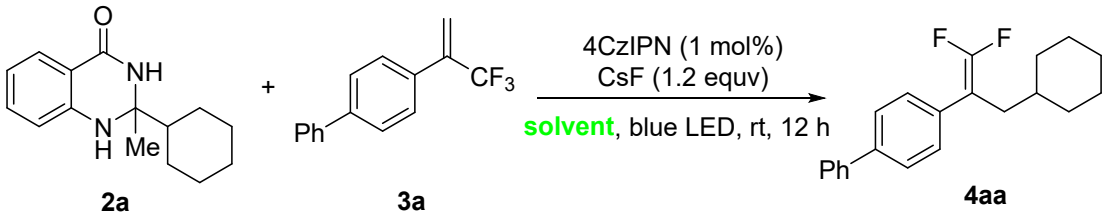


2a **3a** **4aa**

Entry	Variation from the standard conditions	Yield/%
1	CsF	84
2	Na_2CO_3 instead of CsF	81
3	$NaHCO_3$ instead of CsF	82
4	Cs_2CO_3 instead of CsF	49
5	$KHCO_3$ instead of CsF	62
6	K_2CO_3 instead of CsF	76
7	KF instead of CsF	61
8	1.5 equiv CsF instead of 1.2 equiv	83

Reactions conditions: **2a** (0.24 mmol, 1.2 equiv.), **3a** (0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), **base** (0.24 mmol, 1.2 equiv.), DMF (2 mL), blue LED, rt, 12 h.

Table S3 Screening of solvent.

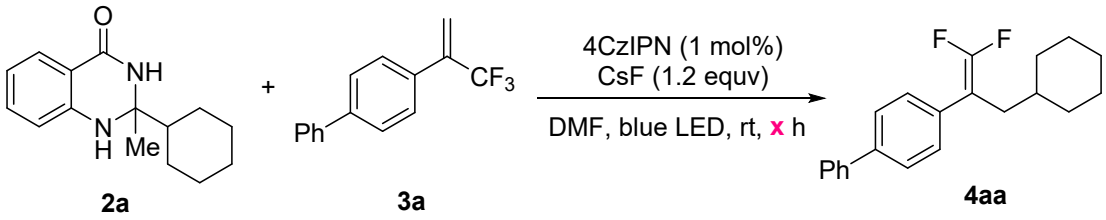


2a **3a** **4aa**

Entry	Variation from the standard conditions	Yield/%
1	DMF	84
2	DMA instead of DMF	52
3	DMSO instead of DMF	39
4	MeCN instead of DMF	14

Reactions conditions: **2a** (0.24 mmol, 1.2 equiv.), **3a** (0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), CsF (0.24 mmol, 1.2 equiv.), solvent (2 mL), blue LED, rt, 12 h

Table S4 Screening of reaction time.

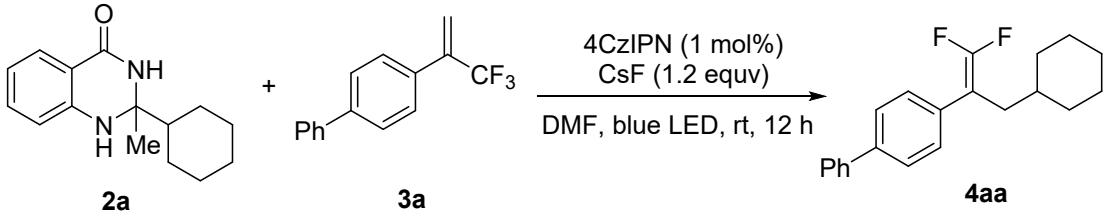


2a **3a** **4aa**

Entry	Variation from the standard conditions	Yield/%
1	12 h	84
2	6 h reaction time instead of 12 h	65

Reactions conditions: **2a** (0.24 mmol, 1.2 equiv.), **3a** (0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), CsF (0.24 mmol, 1.2 equiv.), DMF (2 mL), blue LED, rt, x h.

Table S5 Control experiments.



2a **3a** **4aa**

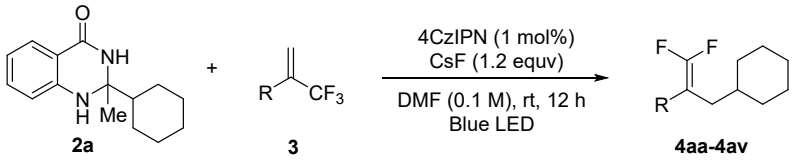
Entry	Variation from the standard conditions	Yield[a]/%
1	**None**	84
2	No photocatalyst	0
3	No light	0

4	No base	40

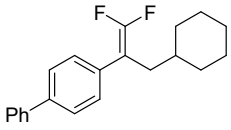
Reactions conditions: **2a** (0.24 mmol, 1.2 equiv.), **3a** (0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), CsF (0.24 mmol, 1.2 equiv.), DMF (2 mL), 40 W blue LED, rt, 12 h.

4. Substrate scopes

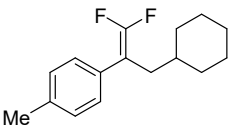
4.1 Substrate scope of α-trifluoromethyl alkenes 3



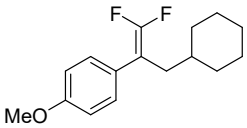
2a + **3** → **4aa-4av**



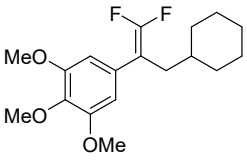
4aa, 84%



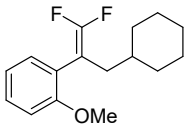
4ab, 90%



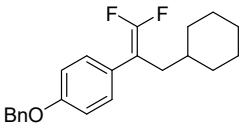
4ac, 74%



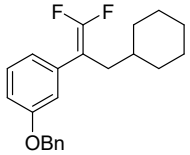
4ad, 55%



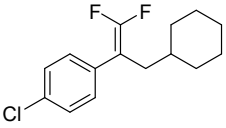
4ae, 38%



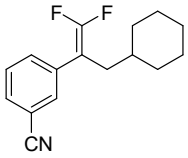
4af, 93%



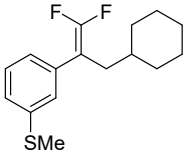
4ag, 60%



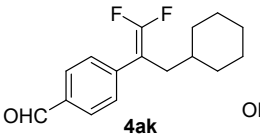
4ah, 71%



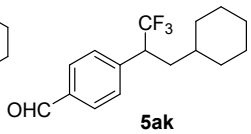
4ai, 92%



4aj, 80%

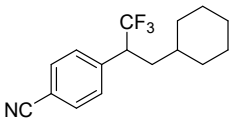


4ak

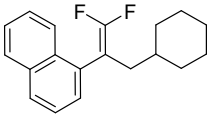


5ak

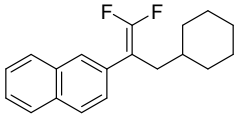
78% total yield, **4ak**:**5ak** = 1:10



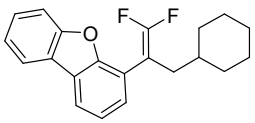
5al, 53%



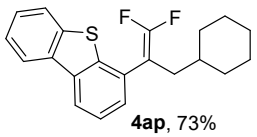
4am, 60%



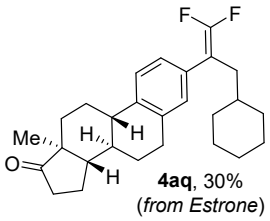
4an, 99%



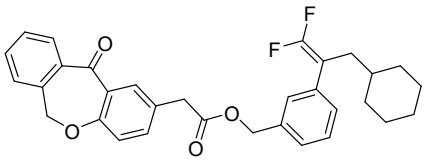
4ao, 66%



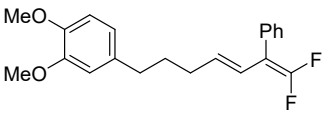
4ap, 73%



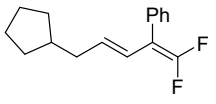
4aq, 30%
(*from Estrone*)



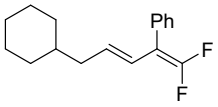
4ar, 35% *(from Isoxepac)*



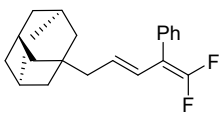
4as, trace



4at, trace

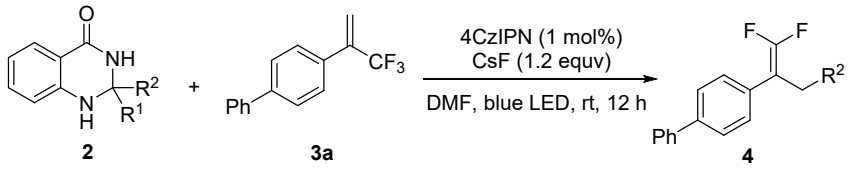


4au, trace

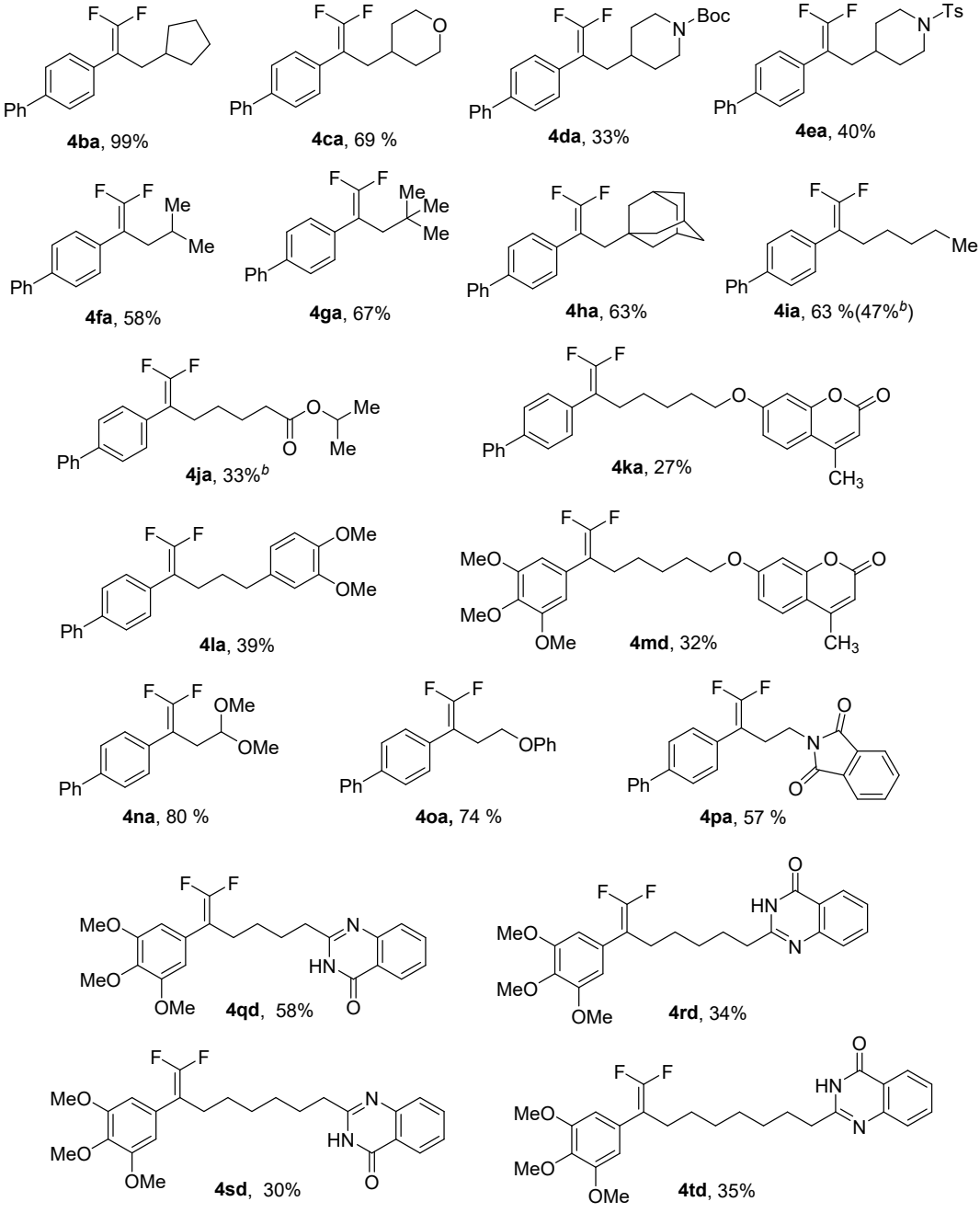


4av, trace

4.2 Substrate scope of ketone-derived dihydroquinazolinone 2



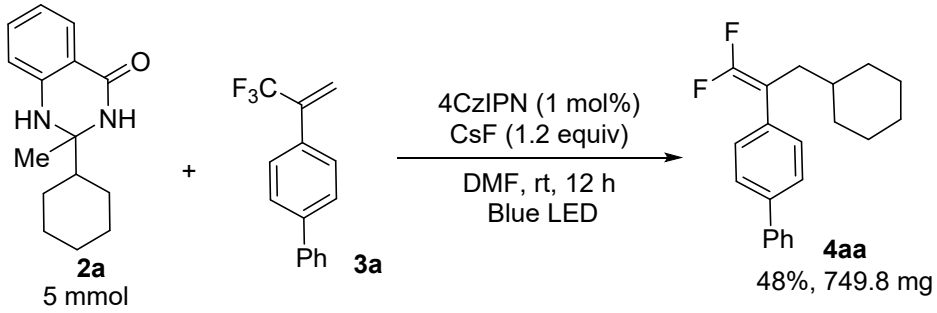
2 **3a** **4**



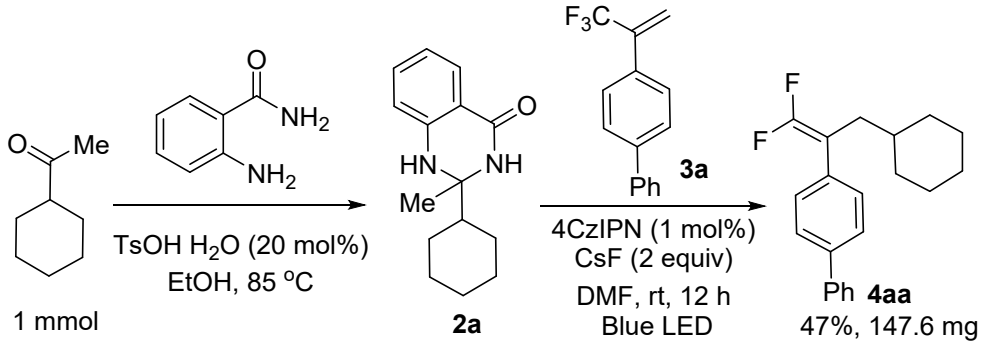
Reactions conditions: [a] **2** (0.24 mmol, 1.2 equiv), **3a** (0.2 mmol, 1.0 equiv), 4CzIPN (1 mol%), CsF (0.24 mmol,1.2 equiv), DMF (2 mL), 40 W blue LED, rt, 12 h. [b] Phenyl-substituted dihydroquinazolinones were used as substrates.

5. Gram-scale and one-pot synthesis of 4aa

5.1 Gram-scale synthesis of 4aa



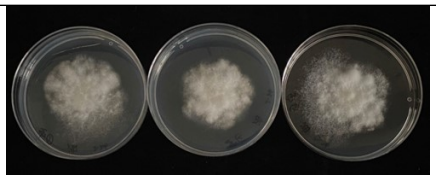
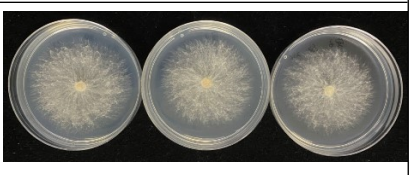
5.2 One-pot reaction

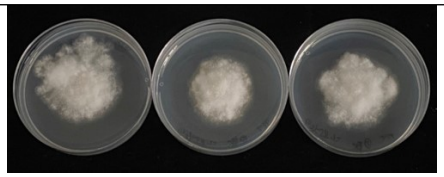
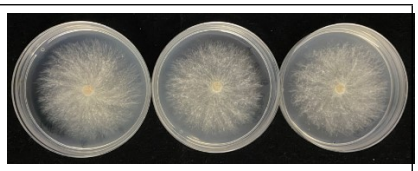
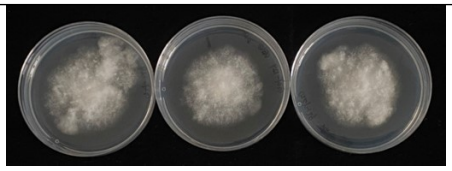
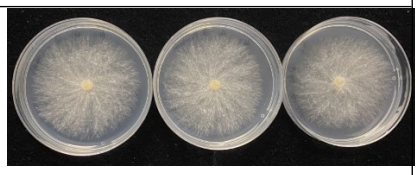
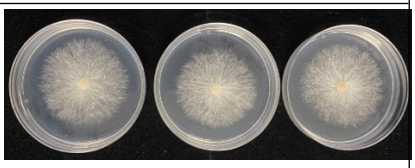
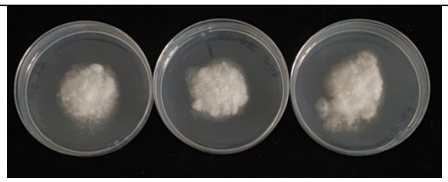
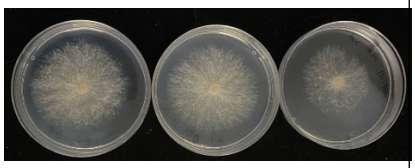


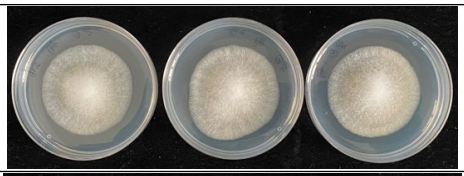
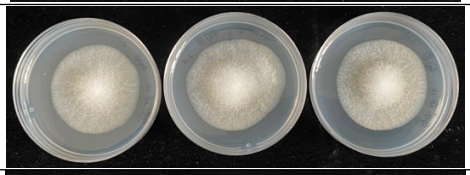
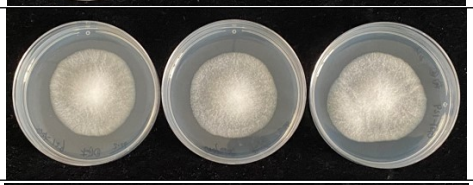
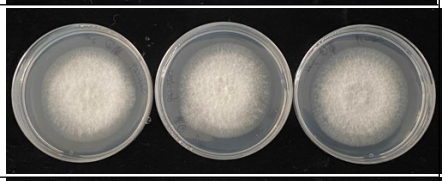
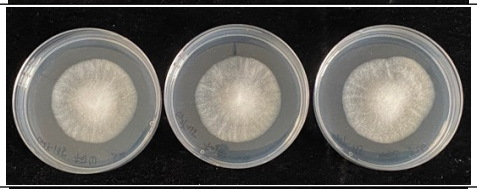
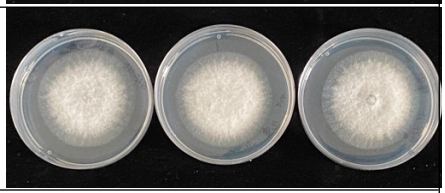
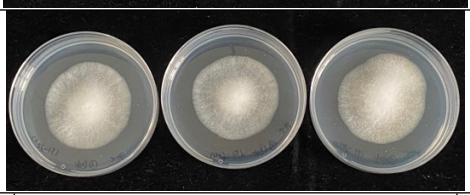
In an oven-dried Schlenk tube equipped with a stirring bar, cyclohexylmethyl ketone (1 mL, 7.5 mmol, 7.5 equiv.), anthranilamide (340.4 mg, 2.5 mmol, 2.5 equiv.) and *p*-toluenesulfonic acid (95.1 mg, 20 mol%) were dissolved in absolute ethanol (2 mL). The reaction mixture was heated at 85 ºC for 36 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure, to provide the crude residue **2a**. Then, 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**3a**, 248.2 mg, 1 mmol, 1 equiv.), 4CzIPN (7.9 mg, 1 mol%), CsF (303.8 mg, 2 mmol, 2 equiv.) and DMF (8 mL) were added to the crude residue in the Schlenk tube under inert atmosphere. The solution was irradiated with 40 W blue LED (λ = 440 nm) at rt for 12 h. The reaction was quenched by the addition of brine solution (10 mL) and then extracted with ethyl acetate (3×15 mL). The combined organic layers were washed once again with water (15 mL), followed by brine (15 mL) and the solvents were removed under reduced pressure. The crude reaction mixture was purified by flash column chromatography through Silica gel (eluent: petroleum ether/ethyl acetate) to afford pure product **4aa** (147.6 mg, 47%) as white solid.

6. In vitro antifungal activities of the target compounds

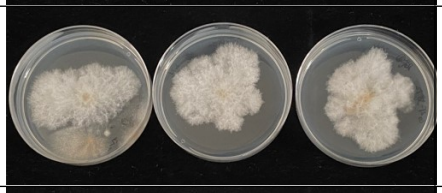
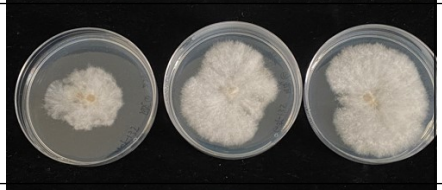
Table S1. In vitro antifungal activity of compounds 4ar, 4md, 4qd and 4rd at 50 μg/mL

Compound	*Sclerotinia sclerotiorum*	*Thanatephorus cucumeris*
Blank		

4ar		
4md		
4qd		
4rd		

Compound	*Colletotrichum acutatum*	*Colletotrichum viniferum*
Blank		
4ar		
4md		
4qd		
4rd		

Compound	*Fusarium equiseti*	

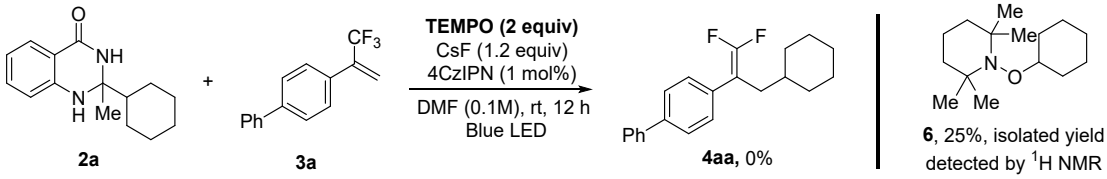
Blank		
4ar		
4md		
4qd		
4rd		

	Fungicidal activity (%) / 50 μg/mL				
Compd.	SS	TC	CA	CV	FE
4ar	14.3	-1.3	0.6	3.3	9.6
4md	0.9	-7.2	6.2	6.0	9.3
4qd	19.4	10.3	7.7	6.0	6.4
4rd	9.1	11.5	8.6	7.5	2.0

7. Mechanistic studies

7.1 Trapping experiment

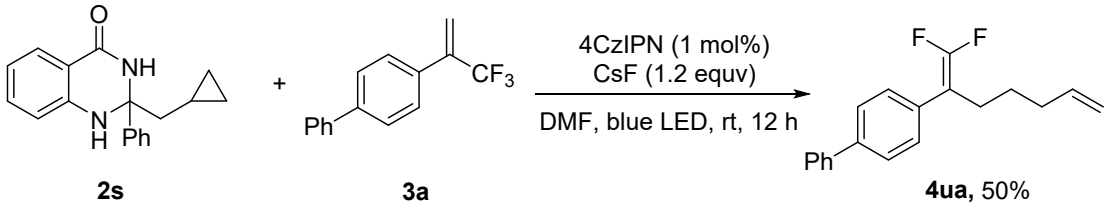
An oven-dried Schlenk tube containing a stirring bar was charged with 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (**2a**, 1.2 equiv.), α-trifluoromethyl alkene (**3a**, 0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), and CsF (1.2 equiv.), **TEMPO** (2 equiv.). The tube was connected to a vacuum line where it was evacuated and back-filled with N_2 for three times. Then DMF (2 mL) was added under N_2 atmosphere. Finally, the reaction mixture in sealed tube was stirred at room temperature for 12 h under continuous light irradiation from 40 W blue LED (λ = 440 nm). The related product **6** was generated by ^{1}H NMR spectroscopy (white solid, 12.0 mg, yield 25%).



7.2 Radical clock experiment

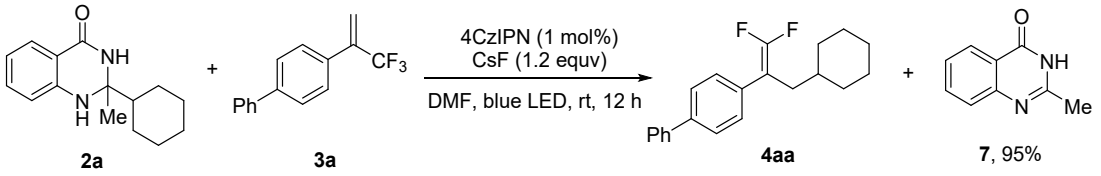
An oven-dried Schlenk tube containing a stirring bar was charged with 2-

(cyclopropylmethyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**2s**, 1.2 equiv.), α-trifluoromethyl alkene (**3a**, 0.2 mmol, 1 equiv.), 4CzIPN (1 mol%), and CsF (1.2 equiv.). The tube was connected to a vacuum line where it was evacuated and back-filled with N_2 for three times. Then DMF (2 mL) was added under N_2 atmosphere. Finally, the reaction mixture in sealed tube was stirred at room temperature for 12 h under continuous light irradiation from 40 W blue LED (λ = 440 nm). The reaction was quenched by the addition of brine solution (2 mL) and then extracted with ethyl acetate (3×5 mL). The combined organic layers were washed once again with water (5 mL), followed by brine (5 mL) and the solvents were removed under reduced pressure. The crude reaction mixture was purified by column chromatography through silica gel (eluent: petroleum ether/ethyl acetate) to afford pure product **4ua** (colorless oil, 28.5 mg, yield 50%).



7.3 Separation of by-products

The by-products **7** can be separated by silica gel column chromatography under standard conditions (white solid, 30.4 mg, yield 95%).



8. Stern-Volmer fluorescence quenching studies

Stern-Volmer quenching experiments were carried by Spectrofluorometer (Edinburgh FS5), using a 5×10^{-4} M solution of 4CzIPN with 0.4 mM of **2a** and **3a** in DMF. Experiments were performed in a screw-capped quartz vial (10×10 mm). All 4CzIPN solutions were excited at 365 nm and emission intensity at 553 nm were collected. Stern-Volmer fluorescence quenching experiments revealed that only dihydroquinazolinones **2a** could quench the excited state of 4CzIPN*. These results support the proposed mechanism.

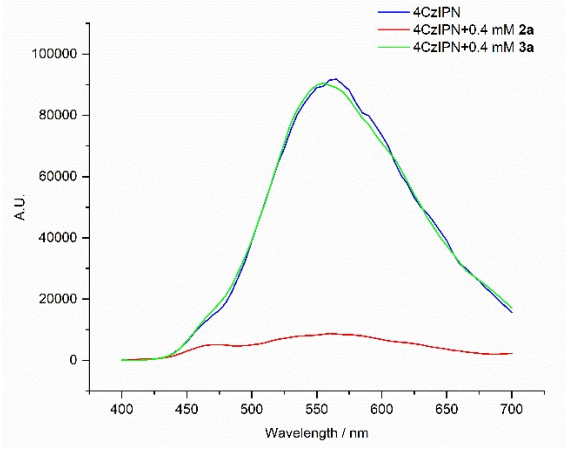
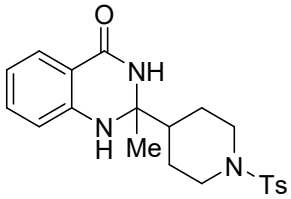


Figure S1 Fluorescence quenching between 4CzIPN and **2a** or **3a**

9. Product characterization

2-methyl-2-(1-tosylpiperidin-4-yl)-2,3-dihydroquinazolin-4(1*H*)-one (2e)



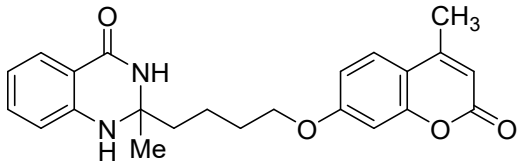
White solid, M. p.: 225-235 ℃.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm) 7.96 (s, 1H), 7.57 (d, J = 6.9 Hz, 2H), 7.50 (d, J = 6.6 Hz, 1H), 7.41 (d, J = 6.5 Hz, 2H), 7.17 (s, 1H), 6.63 (s, 2H), 6.55 (s, 1H), 3.67 (s, 2H), 2.38 (s, 3H), 2.04 – 1.85 (m, 2H), 1.72 (t, J = 12.9 Hz, 2H), 1.50 – 1.29 (m, 3H), 1.26 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm) 163.3, 147.2, 143.9, 133.8, 132.7, 130.2, 127.9, 127.5, 116.5, 114.2, 113.8, 71.0, 46.7, 46.6, 45.6, 25.9, 25.5, 25.2, 21.5.

HRMS (ESI): m/z calc. for ($C_{21}H_{26}N_3O_3S$) $[M+H]^+$: 400.1690, found 400.1688.

2-methyl-2-(4-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)butyl)-2,3-dihydroquinazolin-4(1*H*)-one (2l)



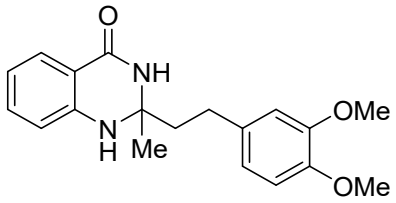
White solid, M. p.: 66-67 ℃.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm) 7.90 (s, 1H), 7.64 (d, J = 8.9 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 6.92 (s, 2H), 6.73 (s, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.57 (t, J = 7.4 Hz, 1H), 6.18 (s, 1H), 4.04 (s, 2H), 2.37 (s, 3H), 1.69 (d, J = 6.9 Hz, 4H), 1.53 (t, J = 8.0 Hz, 2H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ (ppm) 163.6, 162.2, 160.6, 155.2, 153.9, 147.7, 133.6, 127.6, 126.9, 116.5, 114.5, 113.9, 112.9, 111.5, 101.6, 69.6, 68.8, 41.4, 29.0, 28.5, 20.7, 18.6.

HRMS (ESI): m/z calc. for ($C_{23}H_{25}N_2O_4$) $[M+H]^+$: 393.1809, found 393.1808.

2-(3,4-dimethoxyphenethyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (2m)



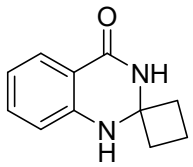
White solid, M. p.: 156-164 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 – 7.80 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 6.75 (dd, J = 14.0, 7.4 Hz, 2H), 6.71 – 6.61 (m, 2H), 6.50 (d, J = 8.0 Hz, 1H), 4.31 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.71 (dd, J = 27.5, 11.9 Hz, 2H), 2.19 – 2.07 (m, 1H), 2.02 (d, J = 6.7 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.9, 147.2, 146.2, 134.0, 133.9, 128.1, 120.1, 118.3, 114.6, 114.3, 111.6, 111.3, 69.9, 55.9, 55.8, 43.7, 30.1, 28.3.

HRMS (ESI): m/z calc. for ($C_{24}H_{24}N_2O_3$) $[M]^+$: 388.1787, found 388.1786.

1'*H*-spiro[cyclobutane-1,2'-quinazolin]-4'(3'*H*)-one (2q)



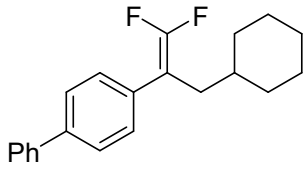
White solid, M. p.: 223-226 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.49 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.16 (s, 1H), 6.71 (d, J = 8.1 Hz, 1H), 6.65 (t, J = 7.4 Hz, 1H), 2.34 – 2.14 (m, 4H), 1.80 – 1.67 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 163.5, 147.4, 133.7, 127.6, 117.4, 115.0, 114.9, 70.3, 38.3, 11.9.

HRMS (ESI): m/z calc. for ($C_{11}H_{13}N_2O$) $[M+H]^+$: 189.1023, found 189.1021.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (4aa)



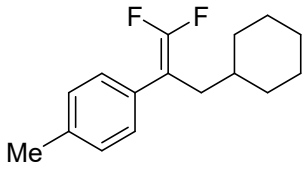
White solid, yield 84% (52.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (dd, J = 13.9, 8.0 Hz, 4H), 7.45 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 2.31 (dt, J = 7.1, 2.2 Hz, 2H), 1.76 – 1.65 (m, 5H), 1.34 – 1.29 (m, 1H), 1.14 (t, J = 8.4 Hz, 3H), 0.94 (dt, J = 11.5, 6.9 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.69 (d, J = 43.2 Hz), -91.24 (d, J = 43.3 Hz).

The analytical data were in good agreement with the literature.[7]

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (4ab)



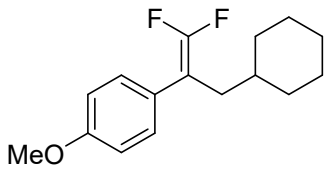
Colorless oil, yield 90% (45.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (q, J = 7.4 Hz, 4H), 2.38 (s, 3H), 2.27 (d, J = 5.1 Hz, 2H), 1.76 – 1.52 (m, 5H), 1.28 (s, 1H), 1.14 (s, 3H), 0.95 (t, J = 8.0 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.87 (d, J = 45.3 Hz), -92.24 (d, J = 45.3 Hz).

The analytical data were in good agreement with the literature.[8]

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methoxybenzene (4ac)



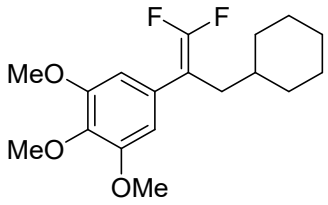
Colorless oil, yield 74% (39.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 3.82 (s, 3H), 2.24 (d, J = 6.5 Hz, 2H), 1.64 (t, J = 16.1 Hz, 5H), 1.26 (s, 1H), 1.12 (s, 3H), 0.99 – 0.84 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -92.36 (d, J = 46.7 Hz), -92.76 (d, J = 46.7 Hz).

The analytical data were in good agreement with the literature.[8]

5-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,2,3-trimethoxybenzene (4ad)



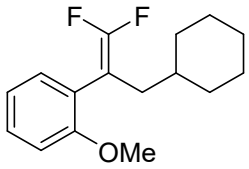
Colorless oil, yield 55% (36.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.50 (s, 2H), 3.86 (s, 9H), 2.23 (d, J = 6.4 Hz, 2H), 1.66 (t, J = 15.4 Hz, 5H), 1.38 – 1.22 (m, 1H), 1.13 (d, J = 6.8 Hz, 3H), 0.95 (dd, J = 22.0, 9.1 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.12 (d, J = 44.7 Hz), -91.49 (d, J = 44.8 Hz).

The analytical data were in good agreement with the literature.[3]

1-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-methoxybenzene (4ae)



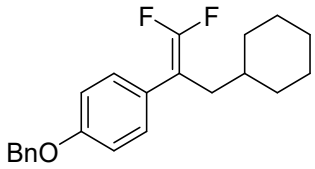
Colorless oil, yield 38% (20.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32 (dd, J = 11.6, 4.2 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 6.96 (dd, J = 16.9, 8.0 Hz, 2H), 3.85 (s, 3H), 2.24 (dd, J = 5.1, 2.0 Hz, 2H), 1.81 – 1.54 (m, 5H), 1.24 – 1.08 (m, 4H), 1.00 – 0.87 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.26 (d, J = 44.8 Hz), -94.07 (d, J = 45.4 Hz).

The analytical data were in good agreement with the literature.[9]

1-(benzyloxy)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (4af)



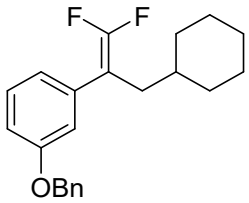
White solid, yield 93% (63.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 – 7.37 (m, 4H), 7.35 (d, J = 6.5 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.9 Hz, 2H), 5.07 (s, 2H), 2.26 (d, J = 6.1 Hz, 2H), 1.65 (d, J = 23.9 Hz, 5H), 1.30 (d, J = 7.9 Hz, 1H), 1.14 (s, 3H), 1.03 – 0.86 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -92.12 (d, J = 46.5 Hz), -92.54 (d, J = 46.5 Hz).

The analytical data were in good agreement with the literature.[3]

1-(benzyloxy)-3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (4ag)



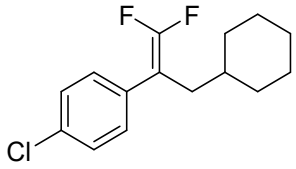
Yellow oil, yield 60% (41.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 – 7.31 (m, 5H), 7.30 – 7.21 (m, 1H), 6.98 – 6.87 (m, 3H), 5.08 (s, 2H), 2.26 (d, J = 5.6 Hz, 2H), 1.63 (dd, J = 35.5, 17.5 Hz, 5H), 1.28 (t, J = 9.8 Hz, 1H), 1.13 (s, 3H), 1.01 – 0.83 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.04 (t, J = 45.2 Hz).

The analytical data were in good agreement with the literature.[10]

1-chloro-4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (4ah)



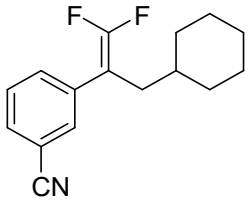
Colorless oil, yield 71% (38.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32 (d, J = 8.0 Hz, 2H), 7.28 – 7.20 (t, J = 8.0 Hz, 2H), 2.24 (d, J = 6.1 Hz, 2H), 1.62 (dd, J = 25.8, 10.2 Hz, 5H), 1.23 (d, J = 16.9 Hz, 1H), 1.11 (s, 3H), 0.91 (t, J = 12.0 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.52 (d, J = 42.5 Hz), -91.08 (d, J = 42.7 Hz).

The analytical data were in good agreement with the literature.[9]

3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzonitrile (4ai)



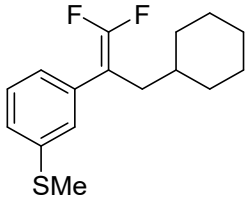
Colorless oil, yield 92% (47.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62 (s, 1H), 7.60 – 7.55 (m, 2H), 7.49 (t, J = 7.7 Hz, 1H), 2.30 (dt, J = 7.2, 2.4 Hz, 2H), 1.73 – 1.62 (m, 5H), 1.25 – 1.18 (m, 1H), 1.15 (d, J = 10.8 Hz, 3H), 0.94 (td, J = 14.5, 4.3 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -88.67 (d, J = 38.9 Hz), -89.79 (d, J = 38.9 Hz).

The analytical data were in good agreement with the literature.[5]

(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)(methyl)sulfane (4aj)



Colorless oil, yield 80% (45.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.24 (t, J = 8.0 Hz, 1H), 7.21 – 7.14 (t, J = 8.0 Hz, 2H), 7.08 (d, J = 7.5 Hz, 1H), 2.50 (s, 3H), 2.26 (d, J = 6.5 Hz, 2H), 1.65 (t, J = 15.4 Hz,

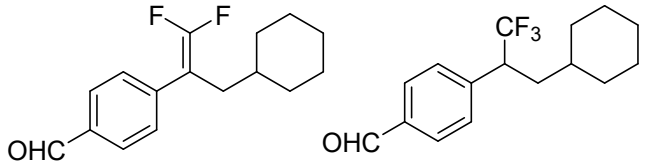
5H), 1.26 (s, 1H), 1.13 (s, 3H), 1.00 – 0.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.0 (dd, J = 290.9, 286.8 Hz), 138.6, 134.8 (t, J = 4.0 Hz), 128.8, 126.4 (t, J = 4.0 Hz), 125.2, 125.1 (t, J = 3.0 Hz), 90.9 (dd, J = 21.2, 13.1 Hz), 35.7, 35.2, 32.9, 26.4, 26.1, 15.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.82 (d, J = 42.9 Hz), -91.06 (d, J = 42.9 Hz).

HRMS (ESI): m/z calc. for ($C_{16}H_{20}F_2S$) $[M]^+$: 282.1254, found 282.1243.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzaldehyde (4ak) and **4-(3-cyclohexyl-1,1,1-trifluoropropan-2-yl)benzaldehyde (5ak)**



Colorless oil, 78% total yield, **4ak**:**5ak** = 1:10.

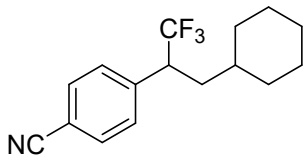
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.04 (d, J = 10.0 Hz, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 3.64 – 3.34 (m, 1H), 2.35 (d, J = 6.7 Hz, 0.2H), 1.98 – 1.80 (m, 2H), 1.79 – 1.59 (m, 5H), 1.18 – 1.07 (m, 3H), 1.06 – 0.83 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.7, 141.9, 136.2, 130.0, 129.8, 128.8, 128.2, 125.4, 47.4 (q, J = 26.3 Hz), 35.9, 34.1, 34.0, 32.8, 31.8, 26.3, 26.0, 25.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -69.46 (s), -88.05 (d, J = 37.1 Hz), -88.91 (d, J = 37.1 Hz).

HRMS (ESI): m/z calc. for ($C_{16}H_{18}F_2O$) $[M]^+$: 264.1326, found 264.1323;
m/z calc. for ($C_{16}H_{19}F_3O$) $[M]^+$: 284.1388, found 284.1384.

4-(3-cyclohexyl-1,1,1-trifluoropropan-2-yl)benzonitrile (5al)



Colorless oil, yield 53% (30.0 mg).

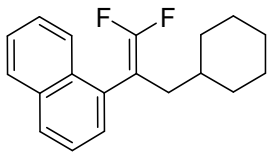
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 3.51 – 3.37 (m, 1H), 1.81 (s, 2H), 1.63 (dt, J = 22.4, 12.9 Hz, 5H), 1.10 (dd, J = 18.7, 10.3 Hz, 3H), 1.00 – 0.83 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 140.5, 132.5, 129.9, 126.6 (q, J = 280.8 Hz), 118.4, 112.3, 47.4 (q, J = 26.3 Hz), 35.8, 34.1, 34.0, 31.7, 26.3, 26.0, 25.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -69.56 (s).

The analytical data were in good agreement with the literature.[5]

1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)naphthalene (4am)



Colorless oil, yield 60% (34.4 mg).

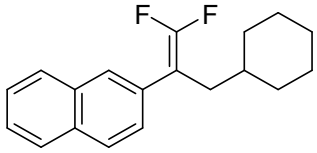
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.80 (m, 3H), 7.60 – 7.44 (m, 3H), 7.36 (d, J = 6.9 Hz, 1H), 2.35 (s, 2H), 1.87 – 1.51 (m, 5H), 1.34 – 1.20 (m, 1H), 1.14 (s, 3H), 1.06 – 0.92

(m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -88.53 (d, J = 43.8 Hz), -92.93 (d, J = 43.9 Hz).

The analytical data were in good agreement with the literature.[11]

2-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)naphthalene (4an)



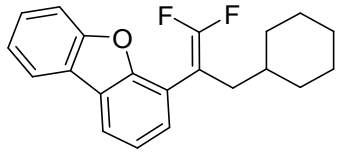
Colorless oil, yield 99% (58.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, J = 7.6 Hz, 3H), 7.76 (s, 1H), 7.52 – 7.38 (m, 3H), 2.38 (d, J = 6.3 Hz, 2H), 1.66 (dd, J = 38.0, 22.5 Hz, 5H), 1.28 (d, J = 9.6 Hz, 1H), 1.08 (dd, J = 20.3, 10.5 Hz, 3H), 0.94 (dd, J = 22.1, 10.8 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.84 (d, J = 43.3 Hz), -91.54 (d, J = 43.4 Hz).

The analytical data were in good agreement with the literature.[8]

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)dibenzo[b,d]furan (4ao)



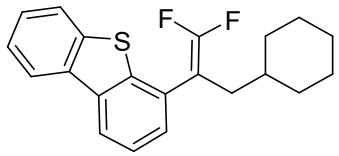
White solid, yield 66% (43.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J = 7.7 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.41 – 7.34 (m, 3H), 2.51 (dd, J = 5.2, 2.0 Hz, 2H), 1.67 (ddd, J = 34.6, 29.4, 11.6 Hz, 5H), 1.27 – 1.17 (m, 1H), 1.17 – 1.03 (m, 3H), 1.02 – 0.91 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -87.98 (d, J = 39.3 Hz), -91.42 (d, J = 39.5 Hz).

The analytical data were in good agreement with the literature.[5]

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)dibenzo[b,d]thiophene (4ap)



Colorless oil, yield 73% (50.3 mg).

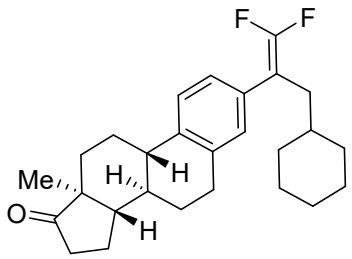
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.17 (dd, J = 16.1, 5.7 Hz, 2H), 7.90 (d, J = 4.3 Hz, 1H), 7.51 (t, J = 6.6 Hz, 3H), 7.35 (d, J = 7.2 Hz, 1H), 2.43 (d, J = 5.2 Hz, 2H), 1.80 (d, J = 12.3 Hz, 2H), 1.66 (d, J = 33.3 Hz, 3H), 1.24 (s, 1H), 1.21 – 1.07 (m, 3H), 1.07 – 0.93 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6 (t, J = 290.9 Hz), 139.8 (d, J = 1.0 Hz), 139.3, 136.0, 135.8, 129.4 (d, J = 5.1 Hz), 127.5, 126.9, 124.7, 124.4, 122.8, 121.7, 120.9, 90.3 (dd, J = 24.2, 15.2 Hz), 35.9, 35.7, 33.0, 26.4, 26.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -86.83 (d, J = 39.1 Hz), -91.55 (d, J = 39.2 Hz).

HRMS (ESI): m/z calc. for ($C_{21}H_{20}F_2S$) $[M]^+$: 342.1254, found 342.1253.

(8*R*,9*S*,13*S*,14*S*)-3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (4aq)



Colorless oil, yield 30% (24.4 mg).

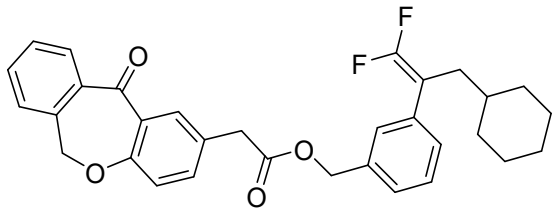
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.04 (s, 1H), 2.91 (s, 2H), 2.58 – 2.39 (m, 2H), 2.32 (d, J = 9.7 Hz, 1H), 2.24 (d, J = 6.2 Hz, 2H), 2.20 – 1.93 (m, 4H), 1.73-1.58 (m, 8H), 1.55-1.40 (m, 3H), 1.26 (s, 1H), 1.13 (s, 3H), 0.92 (s, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 220.8, 154.0 (dd, J = 289.9, 286.8 Hz), 138.7, 136.4, 131.5 (t, J = 4.0 Hz), 128.8 (t, J = 3.0 Hz), 125.7 (t, J = 2.0 Hz), 125.3, 90.7 (dd, J = 22.2, 13.1 Hz), 50.6, 48.0, 44.4, 38.1, 35.9, 35.6, 35.2, 32.9, 31.6, 29.5, 26.5, 26.4, 26.1, 25.6, 21.6, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.47 (d, J = 45.1 Hz), -91.85 (d, J = 45.1 Hz).

HRMS (ESI): m/z calc. for ($C_{27}H_{34}F_2O$) $[M]^+$: 412.2578, found 412.2573.

3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (4ar)



Colorless oil, yield 35% (36.0 mg).

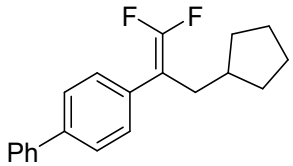
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14 (s, 1H), 7.89 (d, J = 7.5 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 20.4, 8.0 Hz, 2H), 7.36 (dd, J = 12.9, 7.1 Hz, 2H), 7.25 (d, J = 8.9 Hz, 3H), 7.04 (d, J = 8.3 Hz, 1H), 5.18 (d, J = 15.2 Hz, 4H), 3.71 (s, 2H), 2.25 (d, J = 6.5 Hz, 2H), 1.64 (t, J = 15.2 Hz, 5H), 1.40 – 1.17 (m, 1H), 1.11 (s, 3H), 0.92 (t, J = 12.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.9, 171.3, 160.6, 154.0 (dd, J = 291.9, 287.9 Hz), 140.5, 136.4, 135.9, 135.5, 134.5 (t, J = 4.0 Hz), 132.8, 132.6, 129.5, 129.3, 128.7, 128.2 (t, J = 3.0 Hz), 127.9 (t, J = 3.0 Hz), 127.9, 127.6, 126.9, 125.1, 121.1, 90.8 (dd, J = 22.2, 13.1 Hz), 73.6, 66.6, 40.2, 35.7, 35.2, 32.9, 26.4, 26.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.81 (d, J = 43.0 Hz), -91.29 (d, J = 43.0 Hz).

HRMS (ESI): m/z calc. for ($C_{32}H_{31}F_2O_4$) $[M+H]^+$: 517.2185, found 517.2180.

4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (4ba)



White solid, yield 99% (59.4 mg).

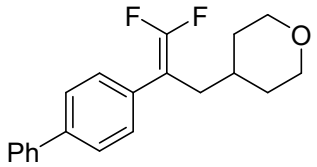
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (t, J = 7.7 Hz, 4H), 7.50 – 7.33 (m, 5H), 2.44 (d, J = 7.2 Hz, 2H), 1.86 (dq, J = 14.5, 7.2 Hz, 1H), 1.78 – 1.57 (m, 4H), 1.52 (d, J = 18.9 Hz, 2H),

1.24 – 1.12 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.53 (d, J = 44.5 Hz), -91.93 (d, J = 44.5 Hz).

The analytical data were in good agreement with the literature.[8]

4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)tetrahydro-2H-pyran (4ca)



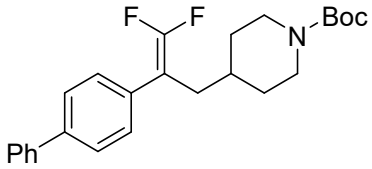
White solid, yield 69% (43.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 – 7.58 (m, 4H), 7.46 (t, J = 7.2 Hz, 2H), 7.38 (dd, J = 16.1, 7.8 Hz, 3H), 3.94 (d, J = 11.1 Hz, 2H), 3.30 (t, J = 11.7 Hz, 2H), 2.41 (d, J = 3.6 Hz, 2H), 1.61 (d, J = 12.6 Hz, 3H), 1.31 (t, J = 8.0 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.11 (d, J = 41.9 Hz), -90.53 (d, J = 41.9 Hz).

The analytical data were in good agreement with the literature.[8]

Tert-butyl 4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)piperidine-1-carboxylate (4da)



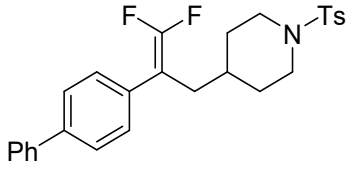
Light yellow solid, yield 33% (26.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 – 7.58 (m, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.37 (dd, J = 14.7, 7.5 Hz, 3H), 4.05 (s, 2H), 2.60 (t, J = 12.0 Hz, 2H), 2.42 – 2.33 (m, 2H), 1.64 (t, J = 11.8 Hz, 1H), 1.52 – 1.46 (m, 1H), 1.45 (s, 9H), 1.15 (dt, J = 11.7, 8.7 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.06 (d, J = 41.7 Hz), -90.53 (d, J = 42.0 Hz).

The analytical data were in good agreement with the literature.[10]

4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)piperidin-1-yl 4-methylbenzenesulfonate (4ea)



Colorless oil, yield 40% (37.2 mg).

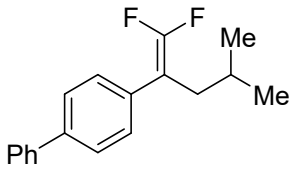
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65 – 7.52 (m, 6H), 7.44 (t, J = 7.5 Hz, 2H), 7.39 – 7.26 (m, 5H), 3.74 (d, J = 11.6 Hz, 2H), 2.39 (s, 3H), 2.36 (d, J = 7.0 Hz, 2H), 2.16 – 2.02 (m, 2H), 1.71 (d, J = 11.4 Hz, 2H), 1.43 – 1.30(m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.1 (dd, J = 291.9, 288.9 Hz), 143.4, 140.4, 140.2, 133.1, 132.3 (t, J = 4.0 Hz), 129.6, 128.9, 128.5 (t, J = 3.0 Hz), 127.7, 127.5, 127.2, 127.0, 90.0 (dd, J = 21.2, 13.1 Hz), 46.3, 33.8, 33.5, 31.2, 21.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -89.86 (d, J = 41.3 Hz), -90.27 (d, J = 40.9 Hz).

HRMS (ESI): m/z calc. for ($C_{27}H_{28}F_2NO_2S$) $[M+H]^+$: 468.1804, found 468.1804.

4-(1,1-difluoro-4-methylpent-1-en-2-yl)-1,1'-biphenyl (4fa)



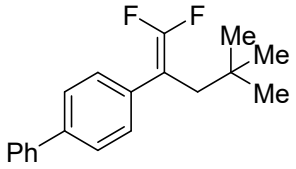
White solid, yield 58% (31.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (dd, J = 11.3, 4.4 Hz, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.44 – 7.35 (m, 3H), 2.41 – 2.28 (m, 1H), 1.12 (d, J = 6.9 Hz, 1H), 0.94 (d, J = 6.7 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.98 (d, J = 43.3 Hz), -91.51 (d, J = 43.6 Hz).

The analytical data were in good agreement with the literature.[8]

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl (4ga)



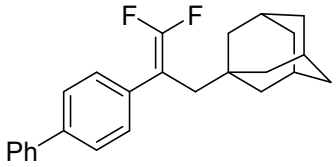
White solid, yield 67% (38.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (dd, J = 13.8, 7.8 Hz, 4H), 7.49 – 7.32 (m, 5H), 2.39 (s, 2H), 0.85 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -89.26 (d, J = 40.3 Hz), -91.95 (d, J = 40.5 Hz).

The analytical data were in good agreement with the literature.[7]

(3*r*,5*r*,7*r*)-1-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)adamantane (4ha)



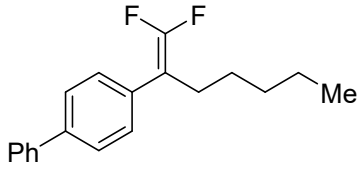
White solid, yield 63% (46.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (dd, J = 17.6, 7.7 Hz, 4H), 7.42 (dd, J = 19.3, 7.7 Hz, 4H), 7.34 (t, J = 7.2 Hz, 1H), 2.24 (s, 2H), 1.88 (s, 2H), 1.73 – 1.60 (m, 3H), 1.55 (d, J = 12.2 Hz, 3H), 1.41 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -88.49 (d, J = 40.2 Hz), -91.65 (d, J = 40.2 Hz).

The analytical data were in good agreement with the literature.[8]

4-1,1-difuorohept-l-en-2-y-1,1' - biphenyl (4ia)



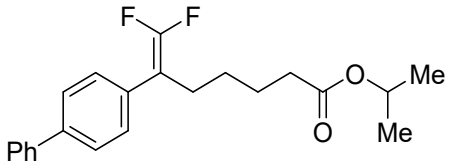
Colorless oil, yield 60% (**4ia**, R^1 = Me, 36.1 mg), yield 47% (**4ia**, R^1 = Ph, 28.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (t, J = 7.4 Hz, 4H), 7.50 – 7.32 (m, 5H), 2.43 (s, 2H), 1.40 (d, J = 5.9 Hz, 2H), 1.29 (d, J = 14.5 Hz, 4H), 0.88 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.34 (d, J = 44.0 Hz), -91.49 (d, J = 44.0 Hz).

The analytical data were in good agreement with the literature.[3]

Isopropyl 6-([1,1'-biphenyl]-4-yl)-7,7-difluorohept-6-enoate (4ja)



Yellow oil, yield 33% (24.0 mg).

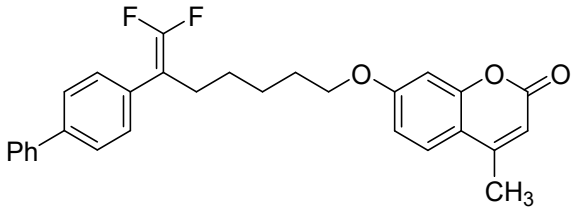
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (d, J = 4.5 Hz, 4H), 7.51 – 7.34 (m, 5H), 5.01 (dt, J = 11.7, 5.7 Hz, 1H), 2.48 (s, 2H), 2.28 (t, J = 7.2 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.54 – 1.41 (m, 2H), 1.22 (d, J = 6.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.1, 153.7 (dd, J = 290.9, 287.9 Hz), 140.6, 140.1, 132.5 (t, J = 2.0 Hz), 128.9, 128.6 (t, J = 3.0 Hz), 127.5, 127.2, 127.1, 91.8 (dd, J = 22.2, 14.1 Hz), 67.5, 34.4, 27.2, 24.4, 21.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.88 (d, J = 43.1 Hz), -91.03 (d, J = 43.1 Hz).

HRMS (ESI): m/z calc. for ($C_{22}H_{25}F_2O_2$) $[M+H]^+$: 359.1817, found 359.1824.

7-((6-([1,1'-biphenyl]-4-yl)-7,7-difluorohept-6-en-1-yl)oxy)-4-methyl-2*H*-chromen-2-one (4ka)



White solid, yield 27% (24.4 mg), M. p.= 95-100 ℃.

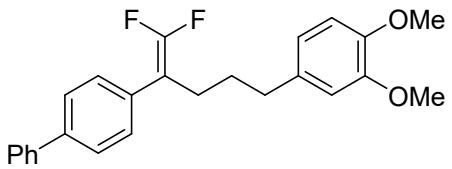
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, J = 5.0 Hz, 4H), 7.44 (t, J = 7.6 Hz, 3H), 7.36 (dd, J = 17.6, 7.9 Hz, 3H), 6.80 (t, J = 8.0 Hz, 1H), 6.12 (s, 1H), 3.97 (t, J = 6.0 Hz, 2H), 2.48 (s, 2H), 2.37 (s, 3H), 1.79 (d, J = 5.6 Hz, 2H), 1.50 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.1, 161.4, 155.3, 153.7 (t, J = 289.9 Hz), 152.6, 140.5, 140.0, 132.5, 128.8, 128.6 (t, J = 3.0 Hz), 127.4, 127.1, 127.0, 125.5, 113.5, 112.7, 111.9, 101.3, 91.1 (t, J = 3.0 Hz), 68.3, 28.6, 27.4, 25.3, 18.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.10 (t, J = 41.5 Hz).

HRMS (ESI): m/z calc. for ($C_{29}H_{27}F_2O_3$) $[M+H]^+$: 461.1923 , found 461.1920.

4-(4-(3,4-dimethoxyphenyl)-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (4la)



Colorless oil, yield 39% (31.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (dd, J = 11.2, 4.7 Hz, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.40 – 7.32 (m, 3H), 6.78 (d, J = 8.1 Hz, 1H), 6.72 – 6.62 (m, 2H), 3.85 (d, J = 7.5 Hz, 6H), 2.63 – 2.54 (m, 2H), 2.53 – 2.41 (m, 2H), 1.79 – 1.67 (m, 2H).

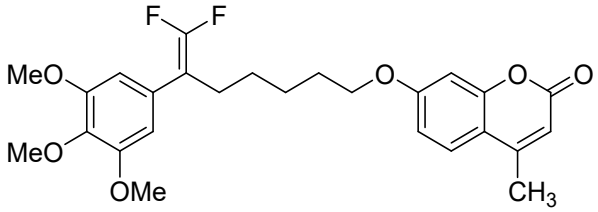
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.7 (dd, J = 291.9, 287.9 Hz), 148.8, 147.2, 140.5, 140.1, 134.4, 132.6 (t, J = 3.0 Hz), 128.9, 128.6 (t, J = 3.0 Hz), 127.5, 127.1, 127.0, 120.2,

111.6, 111.1, 92.0 (dd, J = 22.2, 13.1 Hz), 56.0, 55.8, 34.8, 29.6, 27.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.76 (d, J = 43.0 Hz), -91.01 (d, J = 43.0 Hz).

HRMS (ESI): m/z calc. for ($C_{25}H_{25}F_2O_2$) $[M+H]^+$: 395.1817 , found 395.1815.

7-((7,7-difluoro-6-(3,4,5-trimethoxyphenyl)hept-6-en-1-yl)oxy)-4-methyl-2*H*-chromen-2-one (4md)



Colorless oil, yield 32% (30.4 mg).

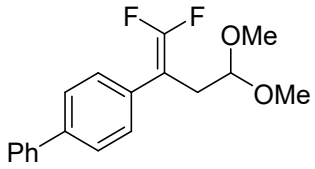
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.77 (s, 1H), 6.49 (s, 2H), 6.12 (s, 1H), 3.98 (s, 2H), 3.84 (s, 9H), 2.38 (s, 5H), 1.79 (s, 2H), 1.46 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.1, 161.4, 153.5 (dd, J = 290.9, 287.9 Hz), 155.3, 152.7, 137.2, 129.2 (t, J = 4.0 Hz), 125.6, 113.5, 112.6, 111.9, 105.5 (t, J = 2.0 Hz), 101.3, 92.4 (dd, J = 21.1, 13.1Hz), 68.4, 60.9, 56.2, 28.7, 27.8, 27.4, 25.4, 18.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.09 (d, J = 44.7 Hz), -91.87 (d, J = 44.6 Hz).

HRMS (ESI): m/z calc. for ($C_{26}H_{29}F_2O_6$) $[M+H]^+$: 475.1927, found 475.1918.

4-(1,1-difluoro-4,4-dimethoxybut-1-en-2-yl)-1,1'-biphenyl (4na)



White solid, yield 80% (48.5 mg), M. p.= 31-36 ℃.

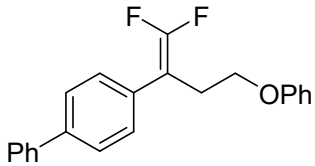
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (d, J = 7.8 Hz, 4H), 7.45 (t, J = 8.3 Hz, 4H), 7.36 (t, J = 7.2 Hz, 1H), 4.40 (t, J = 5.4 Hz, 1H), 3.32 (s, 6H), 2.75 (d, J = 3.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.5 (t, J = 290.9 Hz), 140.5, 140.2, 132.4, 128.8, 128.7 (t, J = 3.0 Hz), 127.5, 127.2, 127.0, 102.5 (t, J = 3.0 Hz), 88.4 (dd, J = 21.2, 17.2 Hz), 53.2, 31.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -89.62 (d, J = 39.6 Hz), -89.78 (d, J = 39.1 Hz).

HRMS (ESI): m/z calc. for ($C_{18}H_{18}F_2O_2$) $[M]^+$: 304.1275, found 304.1273.

4-(1,1-difluoro-4-phenoxybut-1-en-2-yl)-1,1'-biphenyl (4oa)



Colorless oil, yield 74% (47.8 mg).

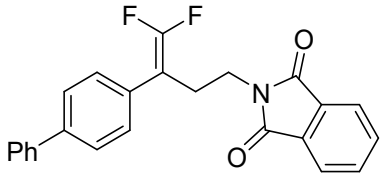
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62 (d, J = 7.5 Hz, 4H), 7.47 (t, J = 7.4 Hz, 4H), 7.38 (t, J = 6.8 Hz, 1H), 7.29 (d, J = 7.5 Hz, 2H), 6.95 (t, J = 7.1 Hz, 1H), 6.87 (d, J = 7.9 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 2.94 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.6, 154.4 (dd, J = 291.9, 289.9 Hz), 140.5, 140.3, 132.1 (t, J = 4.0 Hz), 129.5, 128.9, 128.7 (t, J = 4.0 Hz), 127.5, 127.3, 127.1, 120.9, 114.6, 89.0 (dd, J = 22.2, 15.2 Hz), 65.4 (t, J = 3.0 Hz), 28.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -89.03 (d, J = 38.9 Hz), -89.33 (d, J = 38.9 Hz).

HRMS (ESI): m/z calc. for ($C_{22}H_{18}F_2O$) $[M]^+$: 336.1326, found 336.1322.

2-(3-([1,1'-biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)isoindoline-1,3-dione (4pa)



White solid, yield 57% (44.4 mg), M. p.= 75-80 ℃.

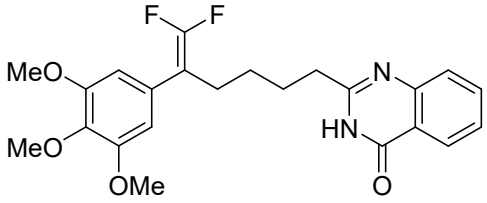
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 2.9 Hz, 2H), 7.62 (d, J = 2.6 Hz, 2H), 7.47 (d, J = 7.5 Hz, 3H), 7.40 (t, J = 10.0 Hz, 4H), 7.33 (t, J = 7.2 Hz, 1H), 3.82 (t, J = 6.3 Hz, 2H), 2.87 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.2, 154.3 (t, J = 291.9 Hz), 140.4, 140.1, 133.9, 131.9, 131.7, 128.7, 125.8 (t, J = 4.0 Hz),127.4, 127.1, 127.0, 123.1, 89.5 (t, J = 18.2 Hz), 36.6, 26.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -89.27 (s).

HRMS (ESI): m/z calc. for ($C_{24}H_{18}F_2NO_2$) $[M+H]^+$: 390.1300, found 390.1302.

2-(6,6-difluoro-5-(3,4,5-trimethoxyphenyl)hex-5-en-1-yl)quinazolin-4(3*H*)-one (4qd)



White solid, yield 58% (49.9 mg), M. p.= 119-125 ℃.

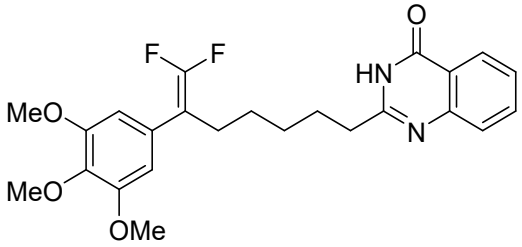
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.25 (s, 1H), 8.24 (d, J = 7.7 Hz, 1H), 7.82 – 7.57 (m, 2H), 7.45 (t, J = 7.0 Hz, 1H), 6.50 (s, 1H), 3.84 (s, 3H), 3.80 (s, 6H), 2.79 (t, J = 6.9 Hz, 2H), 2.46 (s, 2H), 1.93 (s, 2H), 1.58 (d, J = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.5, 156.8, 153.5 (dd, J = 290.9, 287.9 Hz), 153.1, 149.5, 137.2, 134.9, 129.2 (t, J = 4.0 Hz), 127.2, 126.4, 126.2, 120.4, 105.5, 92.4 (dd, J = 22.2, 12.1 Hz), 60.9, 56.1, 35.5, 27.7, 27.4, 26.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -90.82 (d, J = 44.2 Hz), -91.53 (d, J = 44.2 Hz).

HRMS (ESI): m/z calc. for ($C_{23}H_{25}F_2N_2O_4$) $[M+H]^+$: 431.1777, found 431.1768.

2-(7,7-difluoro-6-(3,4,5-trimethoxyphenyl)hept-6-en-1-yl)quinazolin-4(3*H*)-one (4rd)



White solid, yield 34% (30.6 mg), M. p.= 107-117 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.76 (s, 1H), 8.25 (dd, J = 7.9, 1.0 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 6.48 (s, 2H), 3.84 (s, 3H), 3.82 (s,

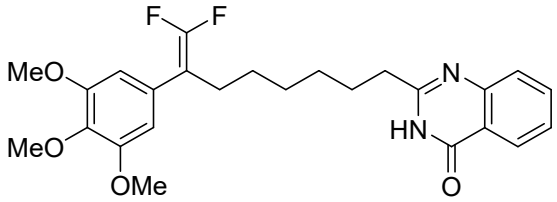
6H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 2H), 1.88 (t, *J* = 8.0 Hz, 2H), 1.53 – 1.42 (t, *J* = 8.0 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.5, 156.8, 153.5 (dd, *J* = 290.9, 287.9 Hz), 153.1, 149.5, 137.2, 134.9, 129.2 (t, *J* = 4.0 Hz), 127.2, 126.4, 126.2, 120.4, 105.5, 92.4 (dd, *J* = 22.2, 12.1 Hz), 60.9, 56.1, 35.8, 28.6, 27.8, 27.4, 27.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.14 (d, *J* = 44.6 Hz), -91.87 (d, *J* = 44.5 Hz).

HRMS (ESI): m/z calc. for ($C_{24}H_{27}F_2N_2O_4$) $[M+H]^+$: 445.1934, found 445.1926.

2-(8,8-difluoro-7-(3,4,5-trimethoxyphenyl)oct-7-en-1-yl)quinazolin-4(3*H*)-one (4sd)



White solid, yield 30% (27.4 mg), M. p.= 123.6-127.3 ℃.

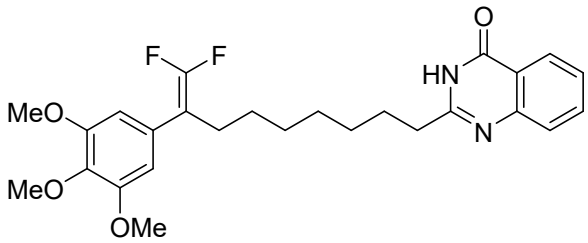
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.26 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.42 (m, 1H), 6.48 (s, 2H), 3.84 (s, 3H), 3.82 (s, 6H), 2.80 – 2.75 (m, 2H), 2.35 (s, 2H), 1.90 – 1.83 (m, 2H), 1.48 – 1.37 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 156.8, 153.5 (dd, *J* = 288.0, 285.0 Hz), 153.1, 149.5, 137.3, 134.8, 129.3 (dd, *J* = 4.5, 3.0 Hz), 127.2, 126.4, 126.2, 120.5, 105.7 (t, *J* = 3.0 Hz), 92.5 (dd, *J* = 22.5, 12.0 Hz), 60.9, 56.2, 35.8, 28.9, 28.7, 27.8, 27.6, 27.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -91.25 (d, *J* = 45.0 Hz), -92.03 (d, *J* = 45.0 Hz).

HRMS (ESI): m/z calc. for ($C_{25}H_{28}F_2N_2O_4$) $[M]^+$: 458.2017, found 458.2014

2-(9,9-difluoro-8-(3,4,5-trimethoxyphenyl)non-8-en-1-yl)quinazolin-4(3*H*)-one (4td)



White solid, yield 35% (32.8 mg), M. p.= 109.9-119.0 ℃.

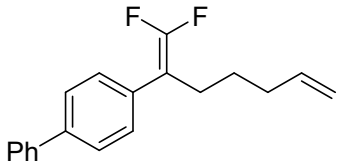
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.02 (s, 1H), 8.26 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.48 (s, 2H), 3.84 (s, 3H), 3.83 (s, 6H), 2.77 (t, *J* = 6.0 Hz, 2H), 2.38 – 2.28 (m, 2H), 1.90 – 1.83 (m, 2H), 1.46 – 1.40 (m, 2H), 1.39 – 1.30 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 157.0, 153.5 (dd, *J* = 288.0, 285.0 Hz), 153.1, 149.5, 137.3, 134.8, 129.4 (t, *J* = 3.0 Hz), 127.2, 126.3, 126.2, 120.5, 105.7, 92.6 (dd, *J* = 22.5, 12.0 Hz), 60.9, 56.2, 35.9, 29.2, 28.9, 28.9, 27.9, 27.7, 27.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -91.31 (d, *J* = 45.8 Hz), -92.08 (d, *J* = 45.4 Hz).

HRMS (ESI): m/z calc. for ($C_{26}H_{30}F_2N_2O_4$) $[M]^+$: 472.2174, found 472.2173.

4-(1,1-difluorohepta-1,6-dien-2-yl)-1,1'-biphenyl (4ua)



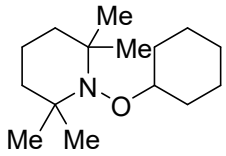
Colorless oil, yield 50% (28.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (t, J = 6.3 Hz, 4H), 7.45 (t, J = 7.3 Hz, 2H), 7.37 (dd, J = 17.8, 7.8 Hz, 3H), 5.79 (td, J = 16.3, 7.6 Hz, 1H), 5.00 (t, J = 15.4 Hz, 2H), 2.46 (s, 2H), 2.09 (q, J = 6.7 Hz, 2H), 1.58 – 1.45 (t, J = 8.0 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) -91.00 (d, J = 43.1 Hz), -91.14 (d, J = 43.2 Hz).

The analytical data were in good agreement with the literature.[8]

1-cyclohexyloxy-2,2,6,6-tetramethylpiperidine (6)

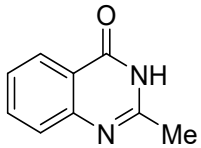


White solid, yield 25% (12.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.64 – 3.52 (m, 1H), 2.04 (s, 2H), 1.74 (s, 2H), 1.57 – 1.42 (m, 6H), 1.29 – 1.16 (m, 6H), 1.12 (s, 13H).

The analytical data were in good agreement with the literature.[12]

2-methyl-4-quinazolone (7)



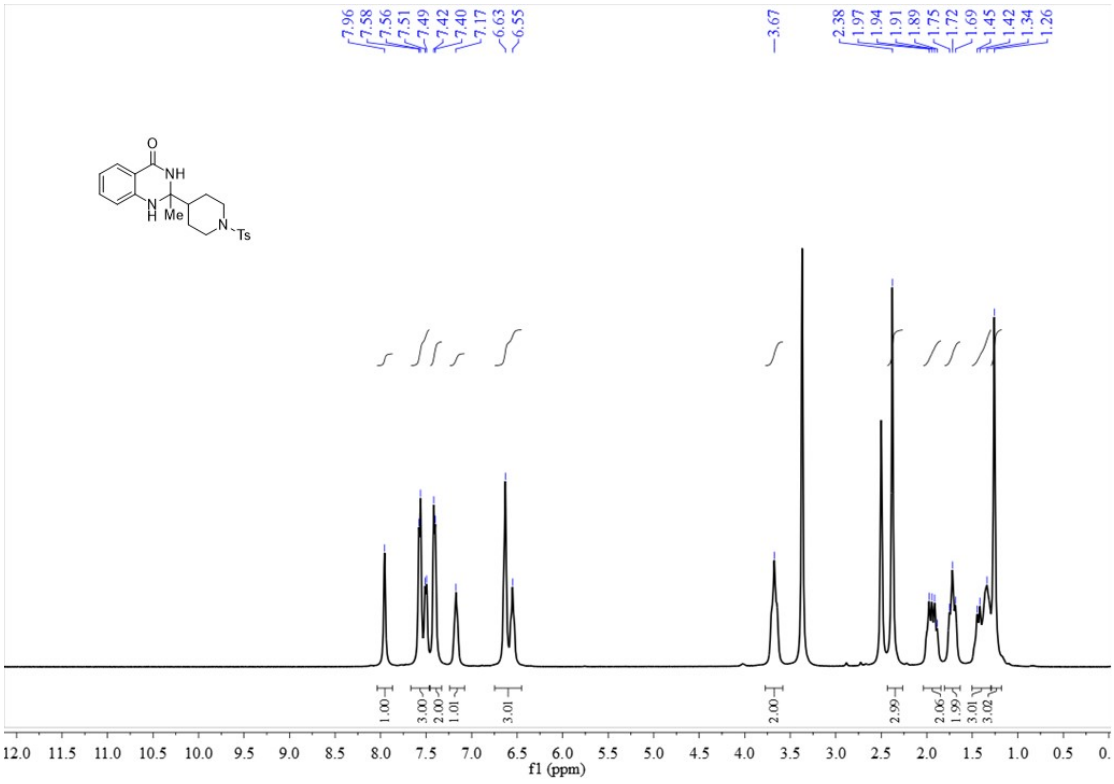
White solid, yield 95% (30.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.61 (s, 1H), 8.29 (dd, J = 8.0, 1.2 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 15.1, 7.2 Hz, 1H), 2.60 (s, 3H).

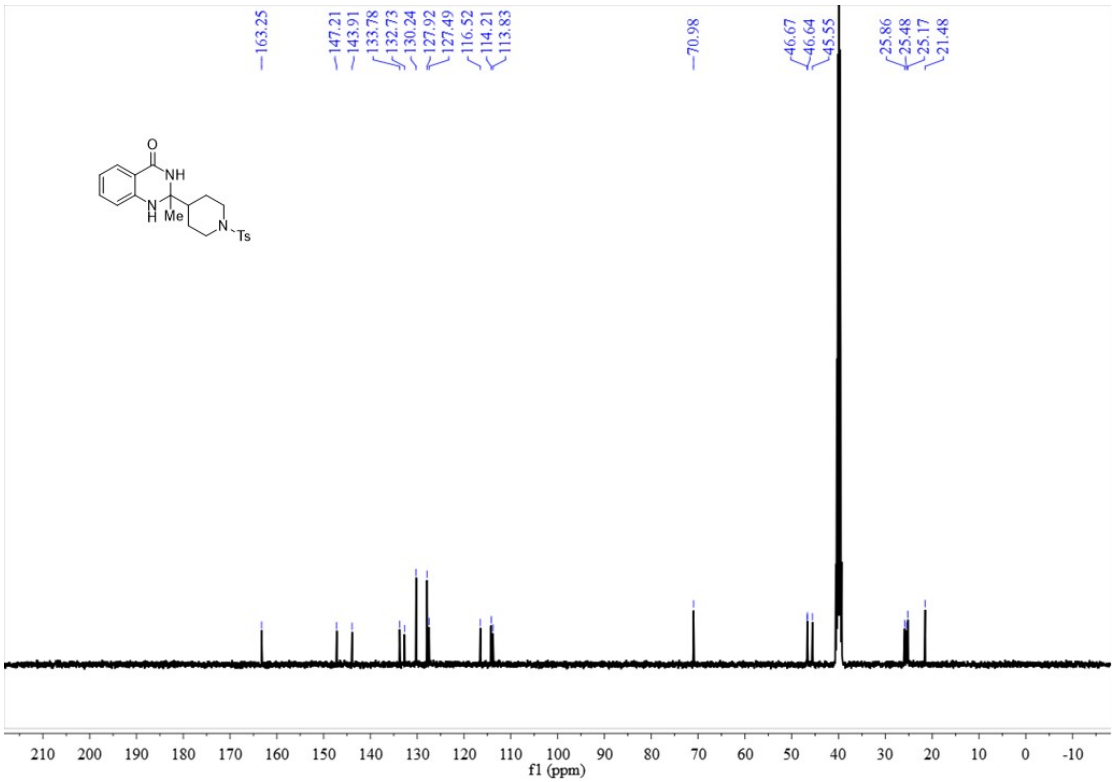
The analytical data were in good agreement with the literature.[13]

10. NMR spectra

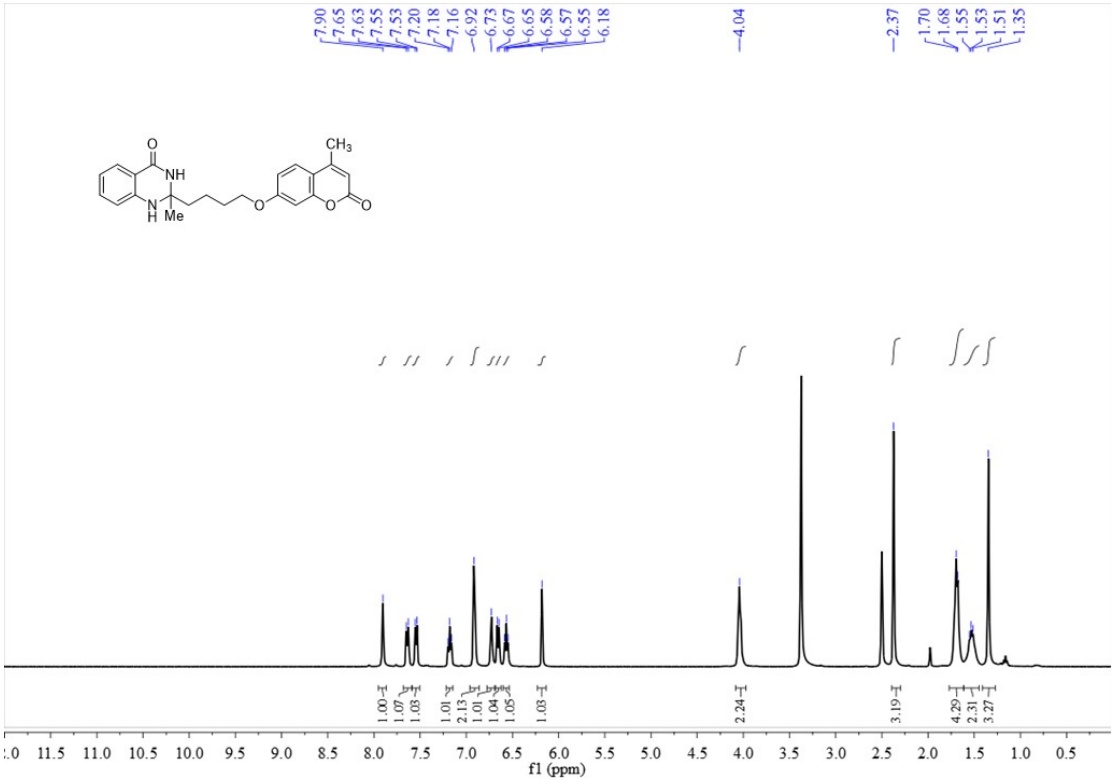
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **2e**



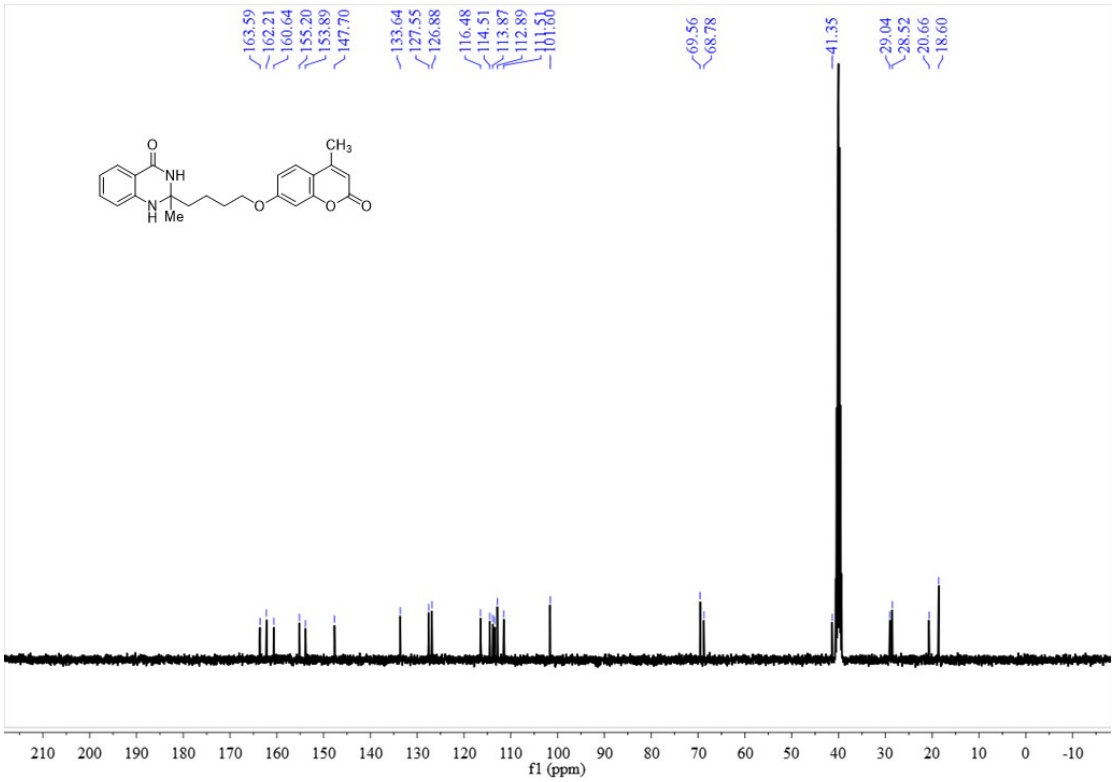
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **2e**



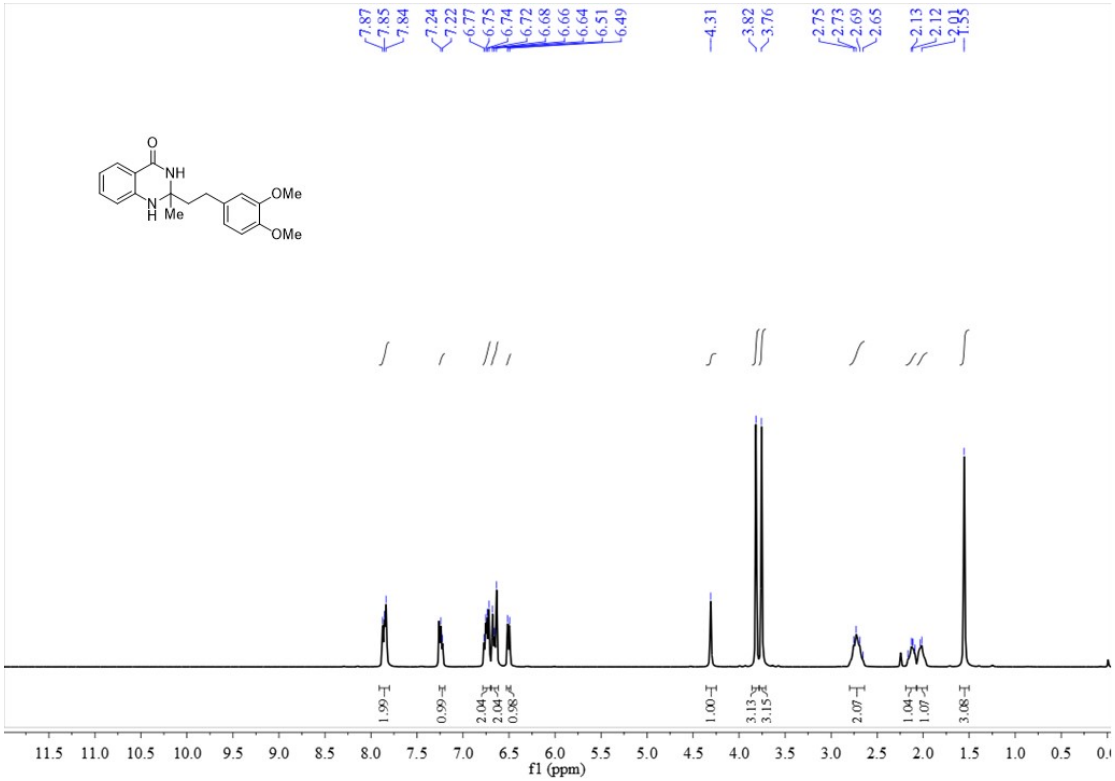
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **2l**



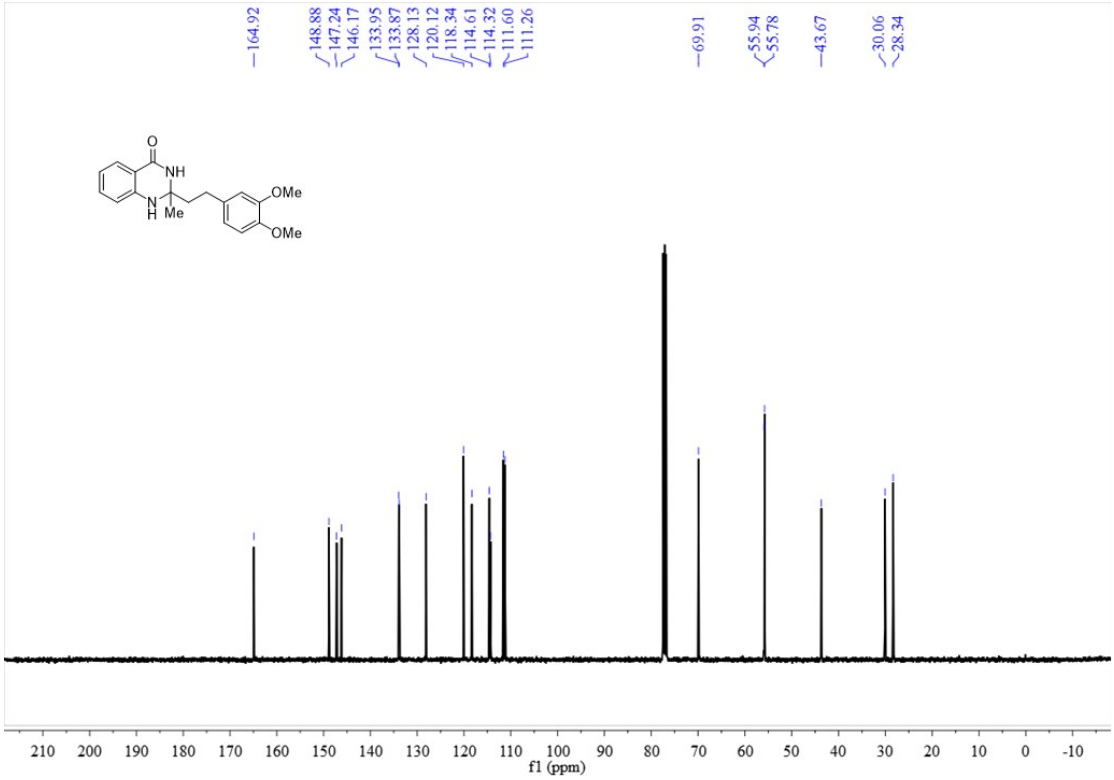
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **2l**



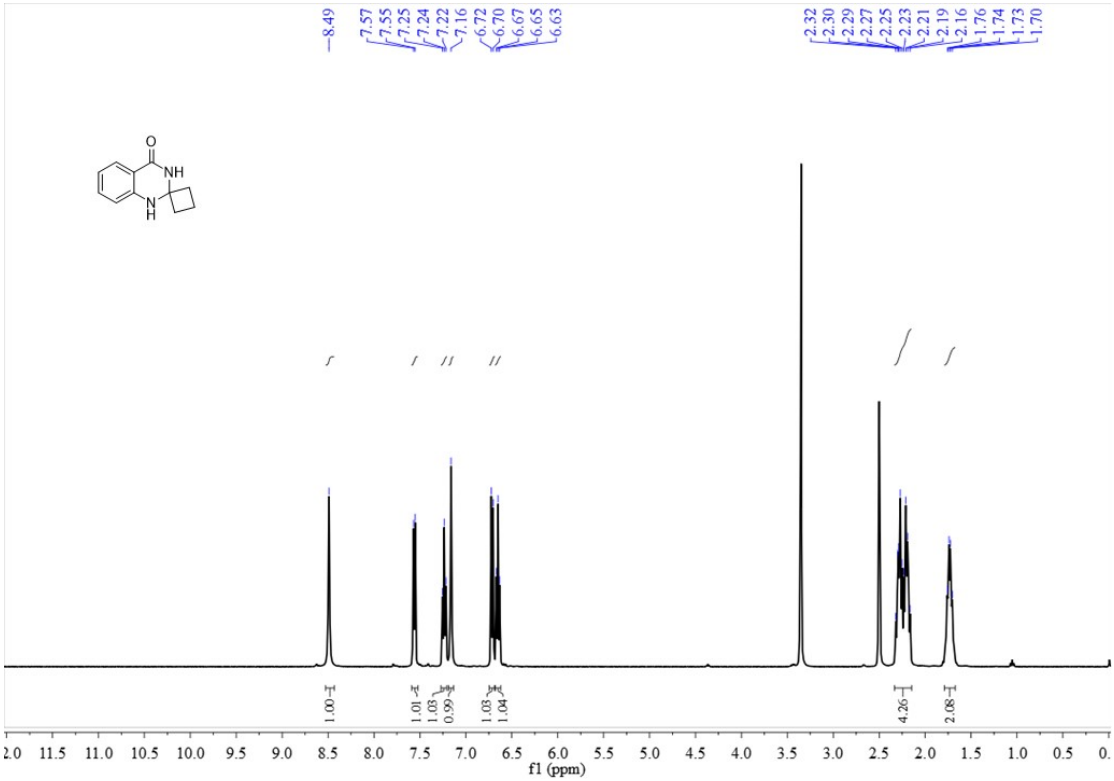
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2m**



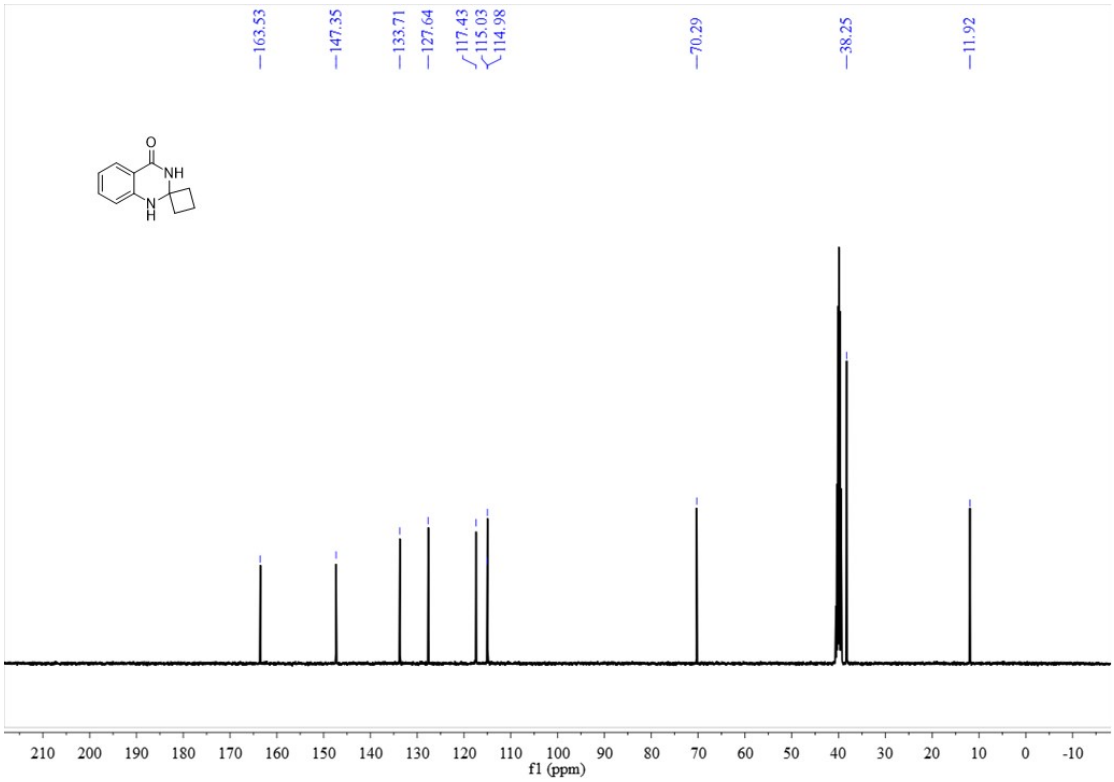
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2m**



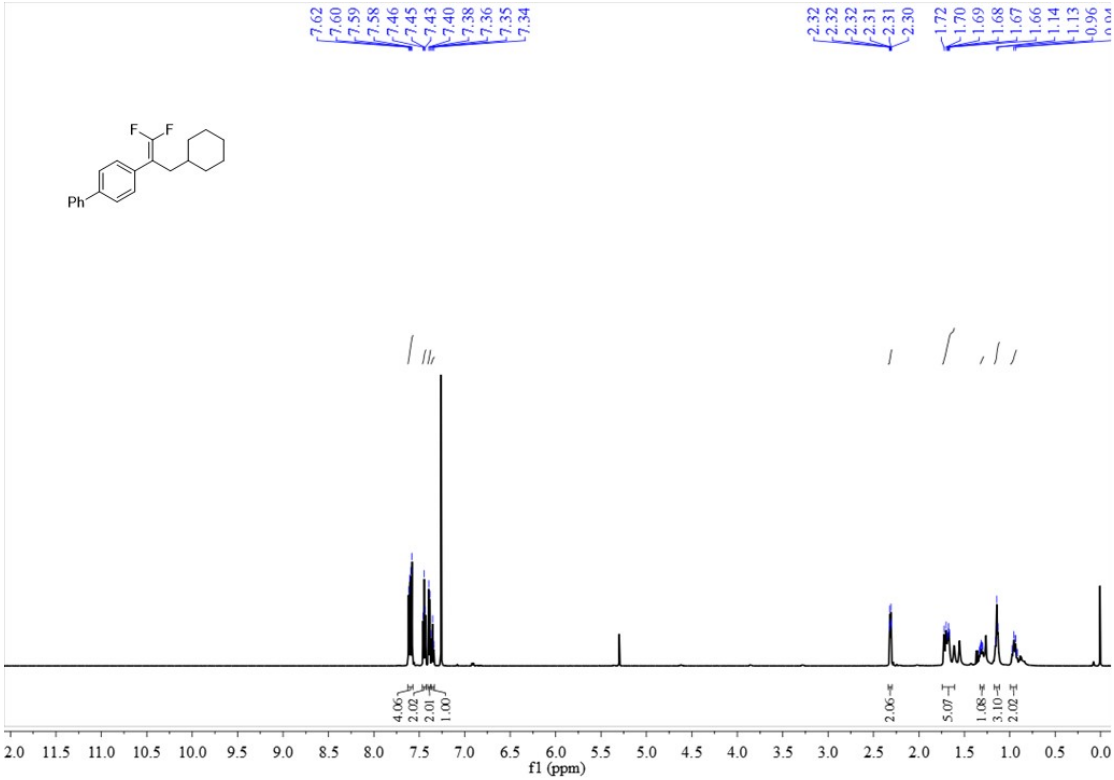
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **2q**



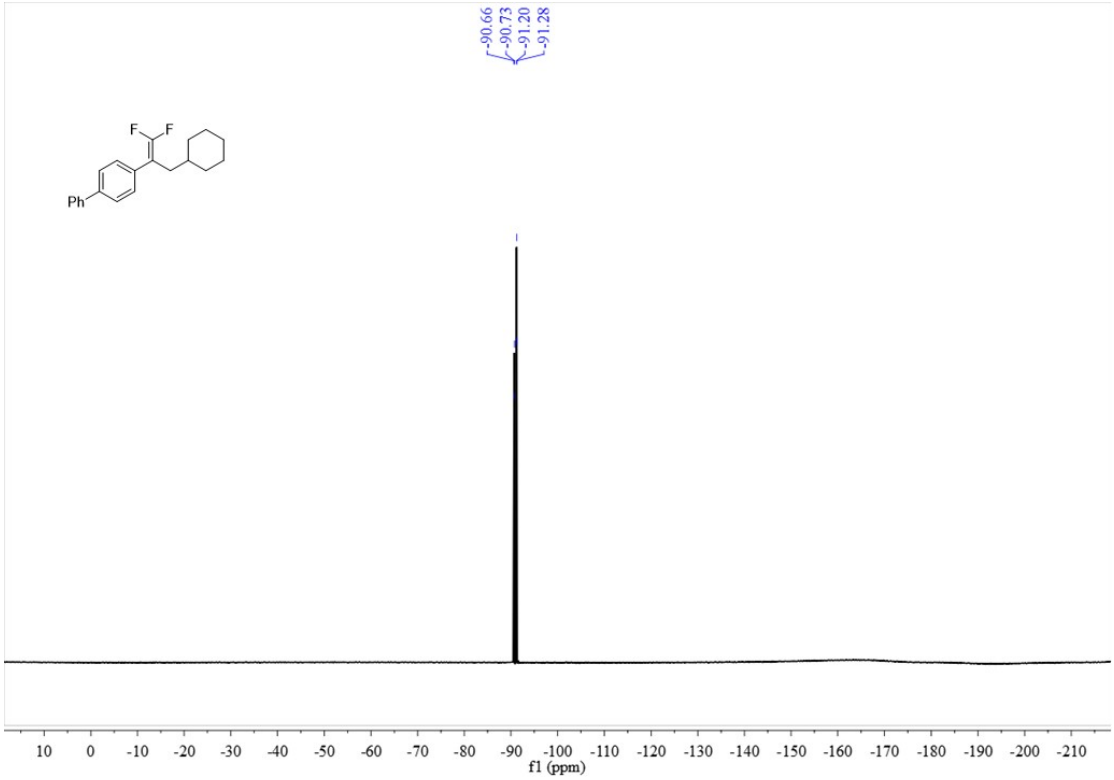
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **2q**



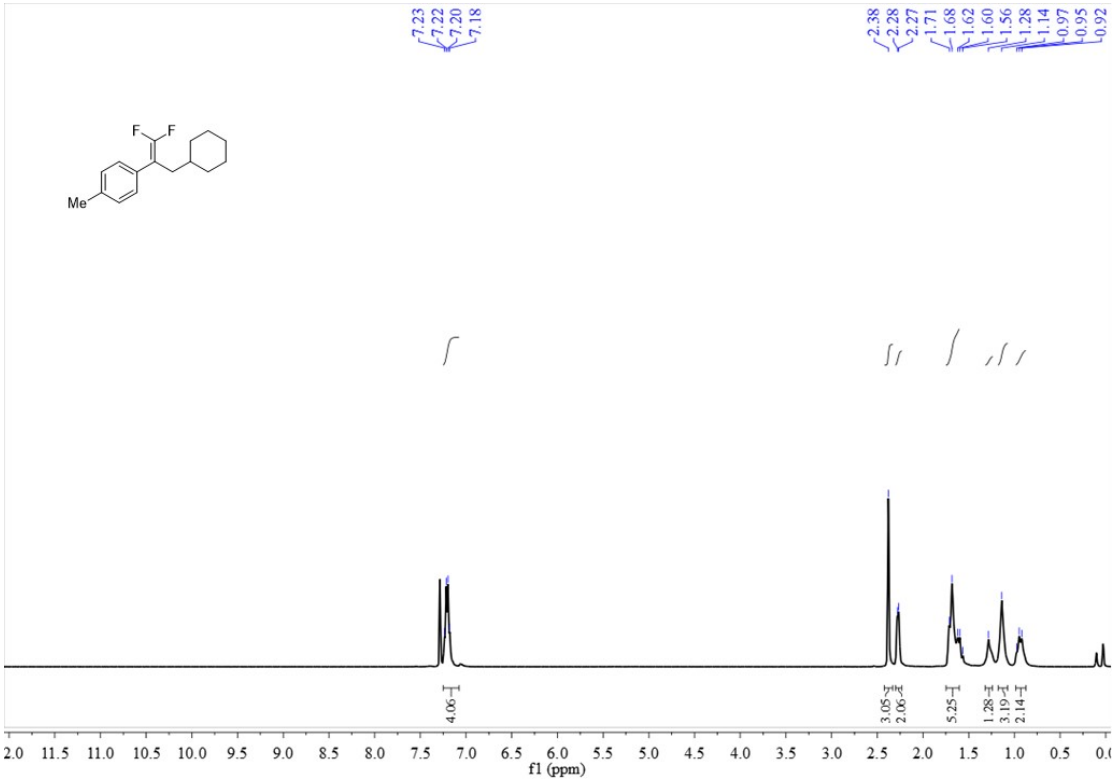
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4aa**



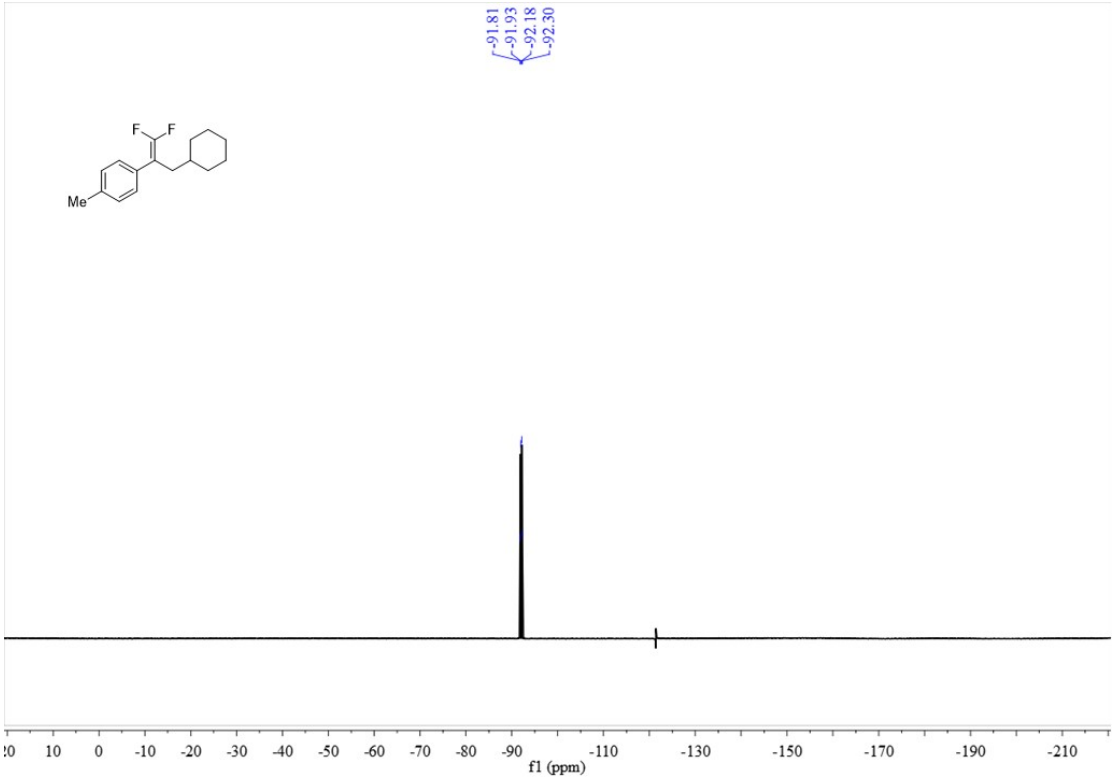
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4aa**



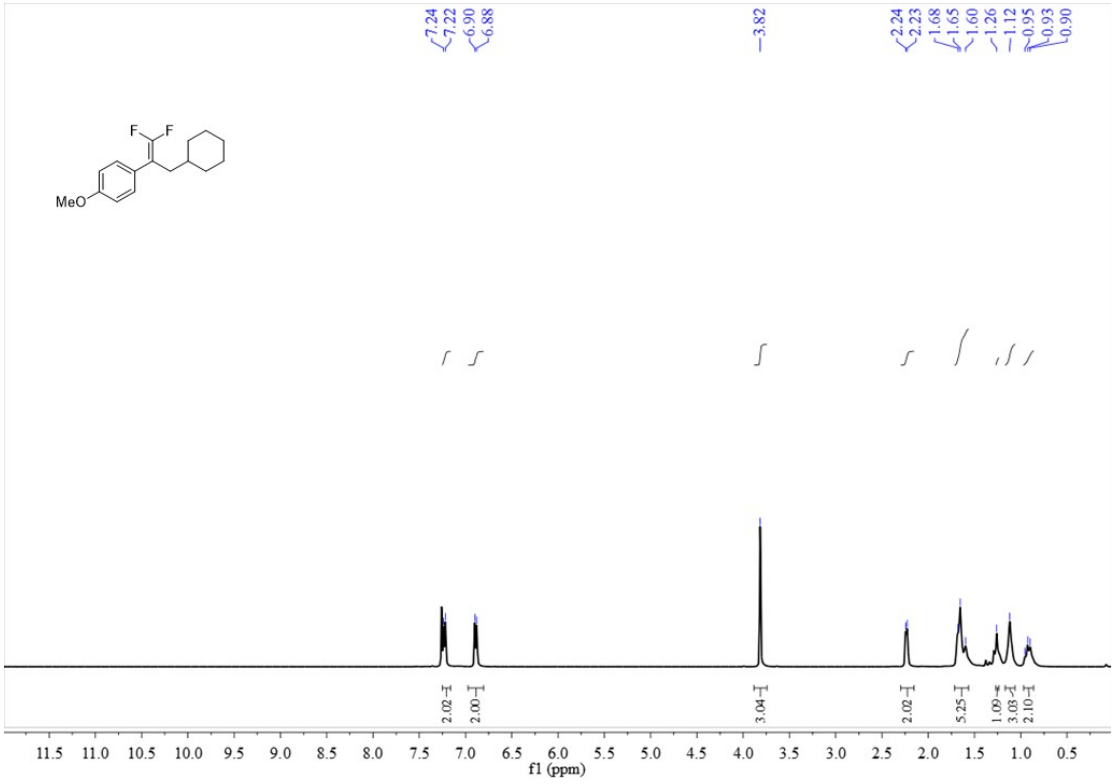
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ab**



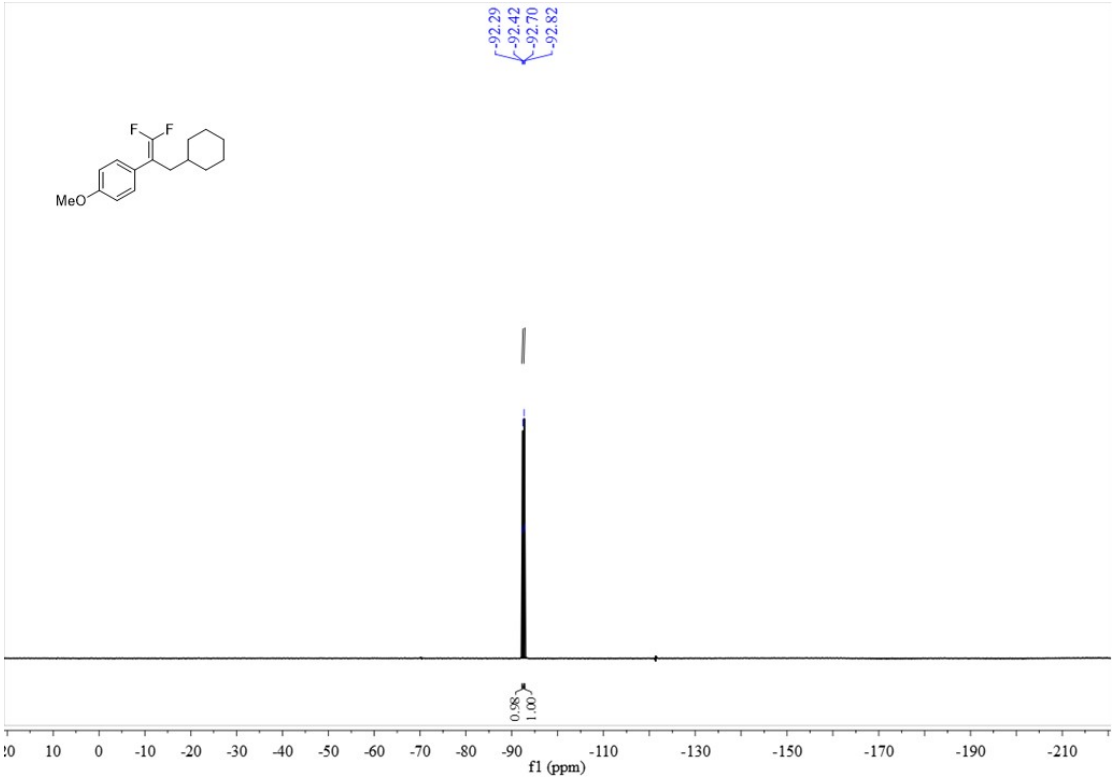
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ab**



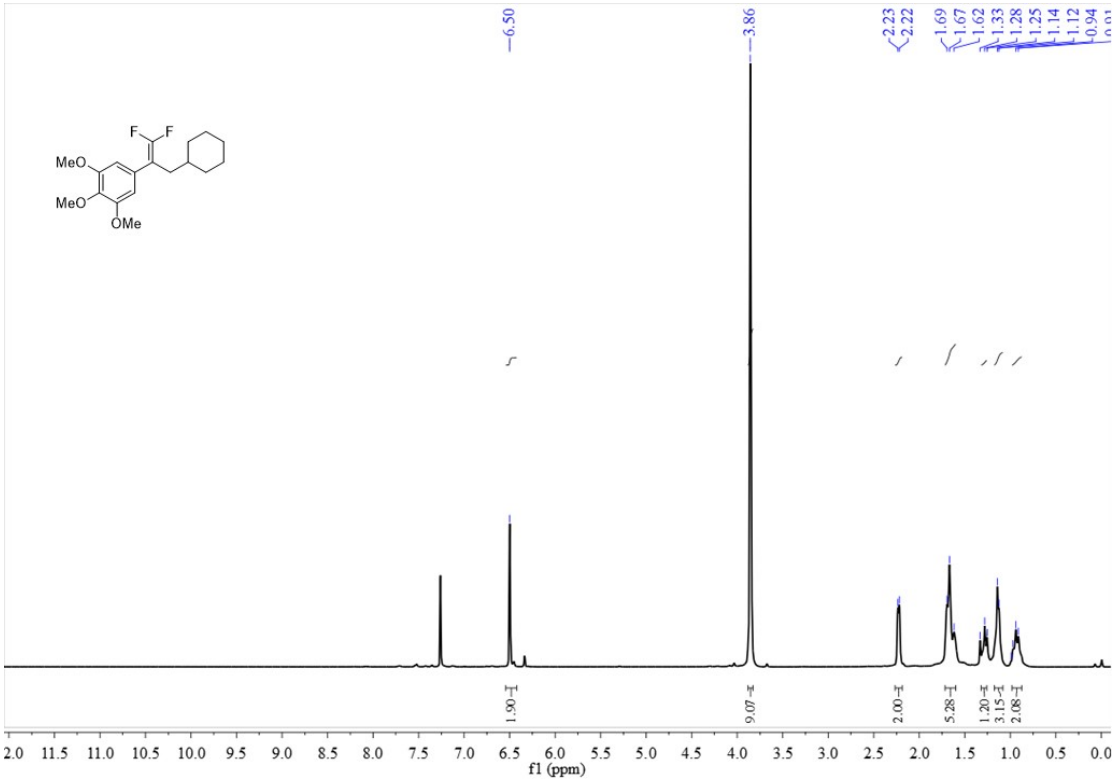
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ac**



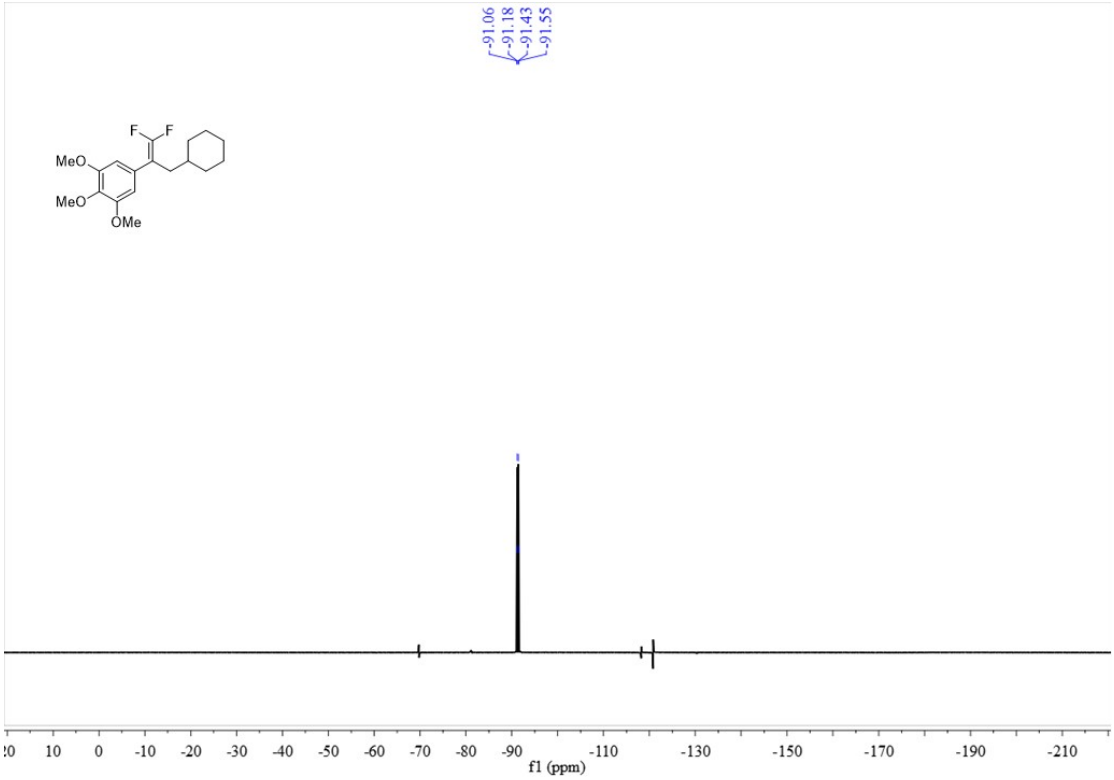
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ac**



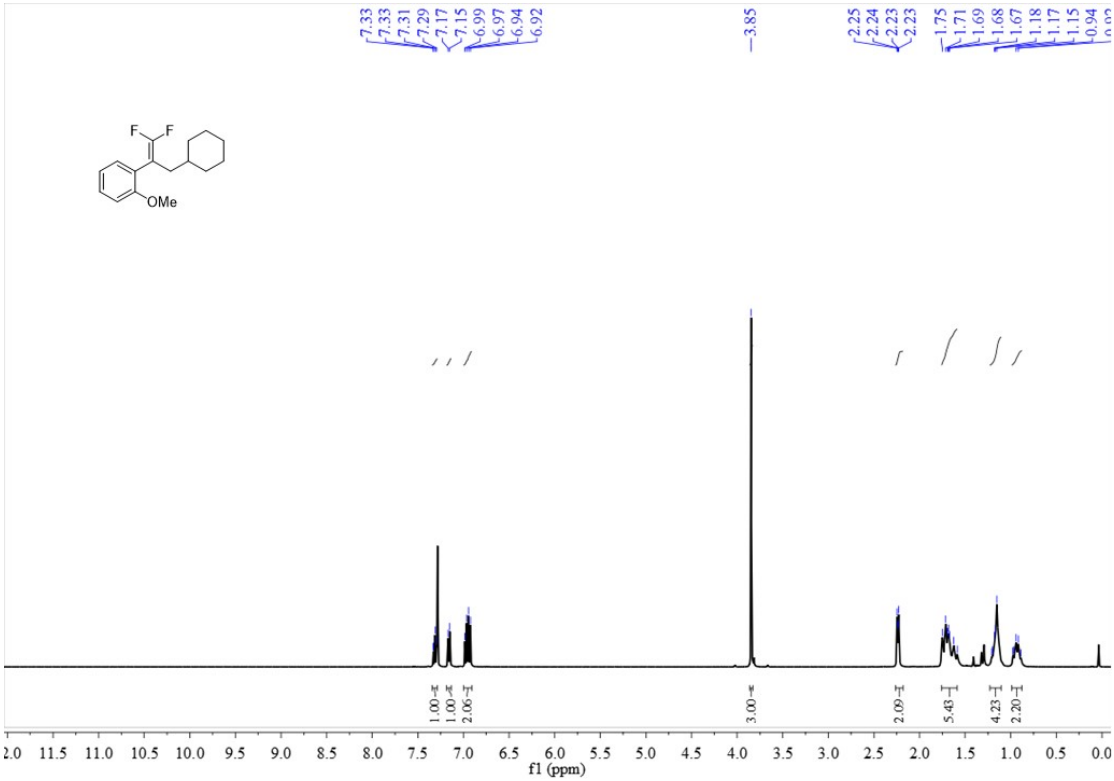
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ad**



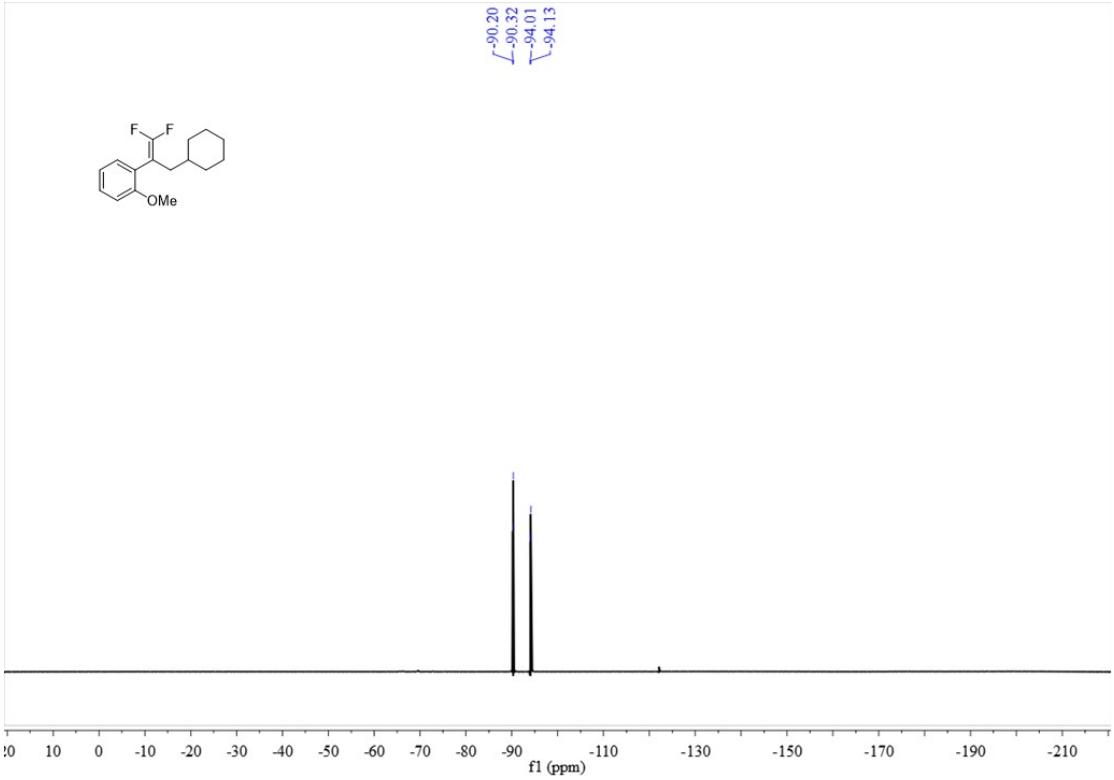
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ad**



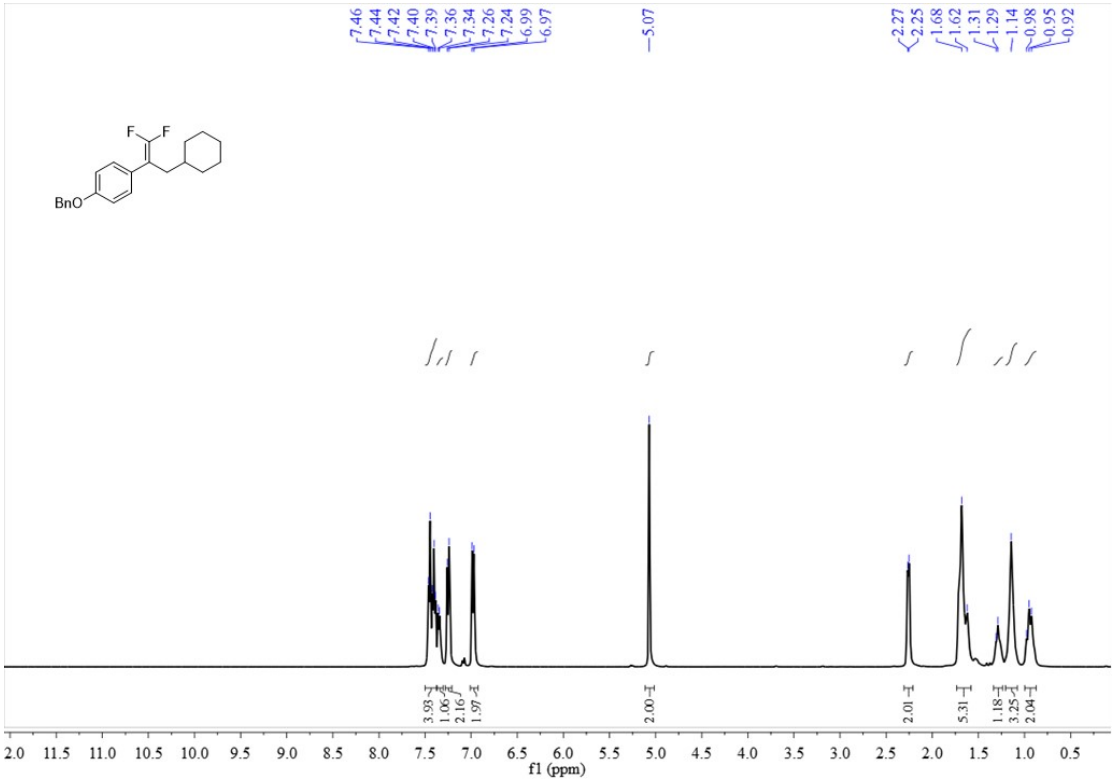
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ae**



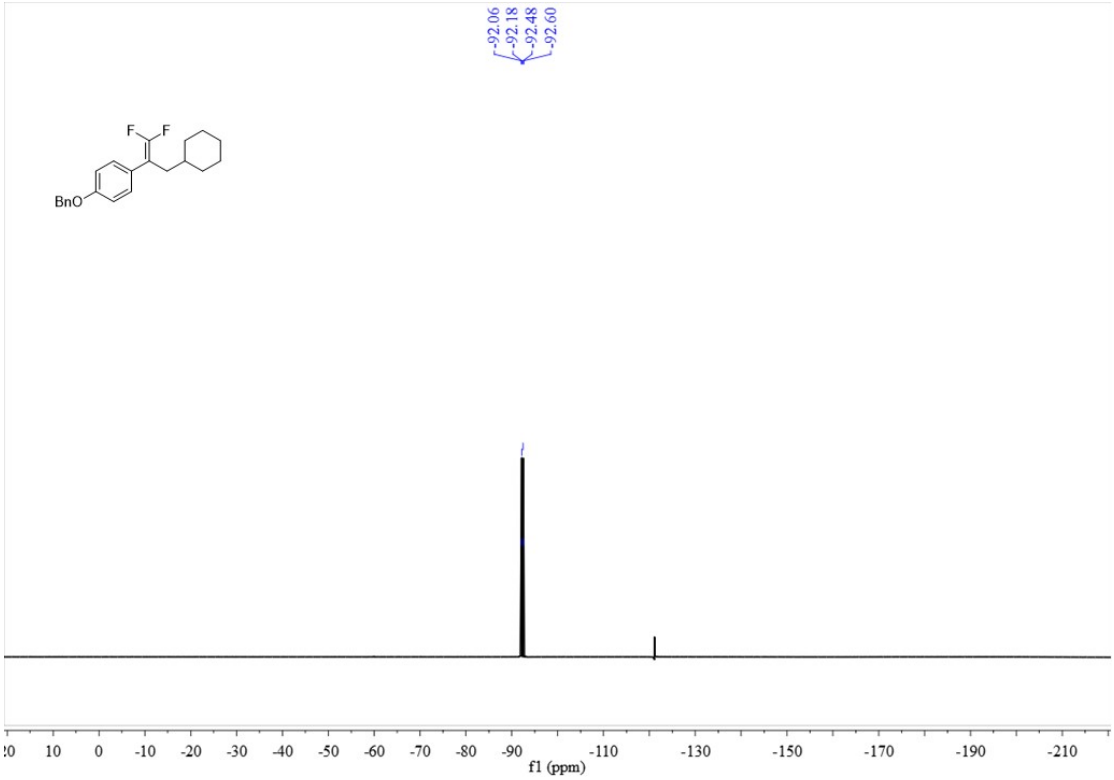
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ae**



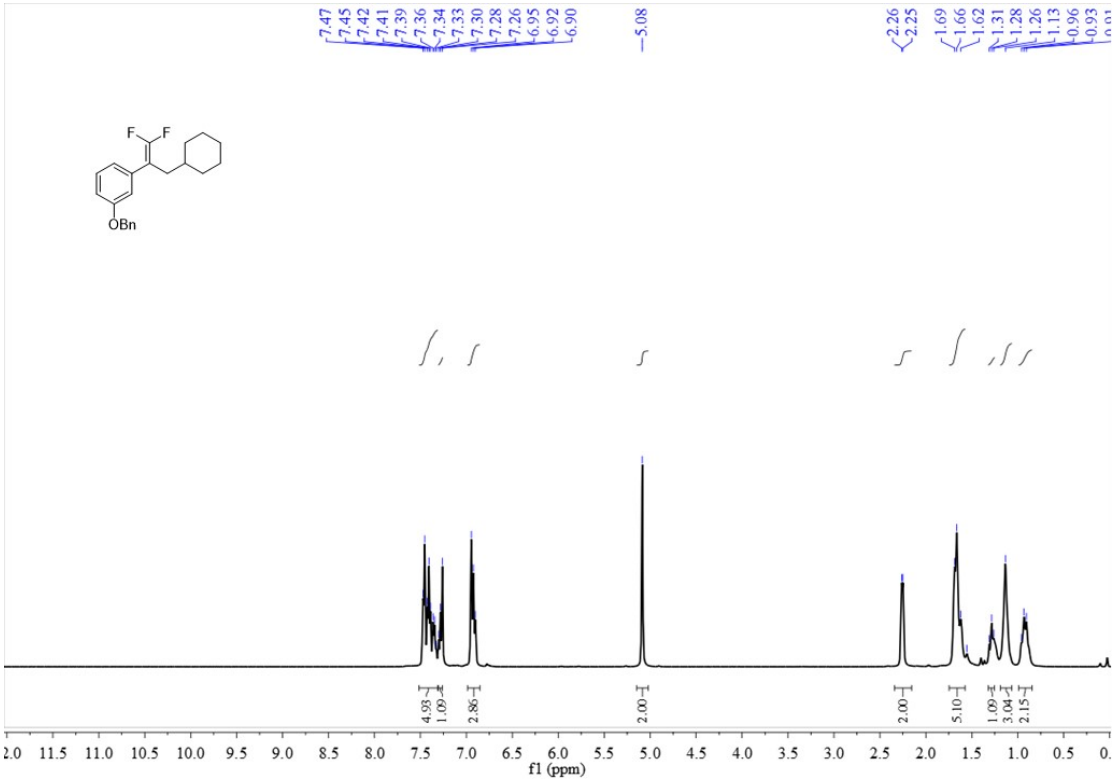
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4af**



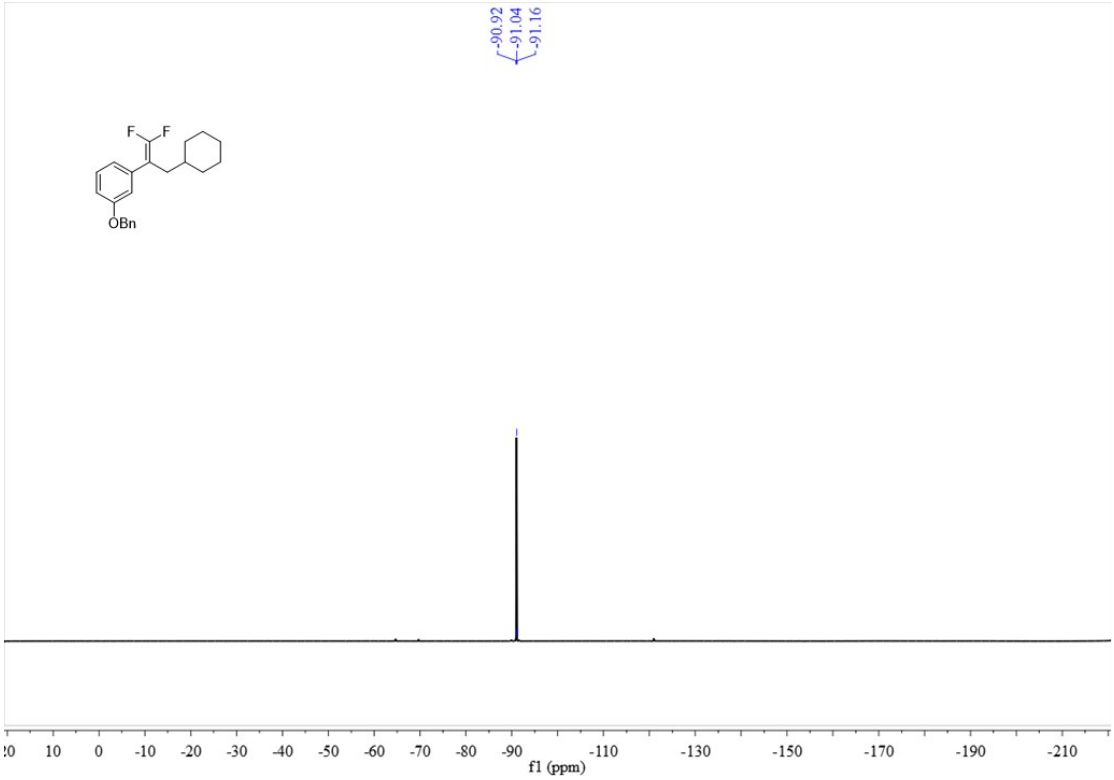
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4af**



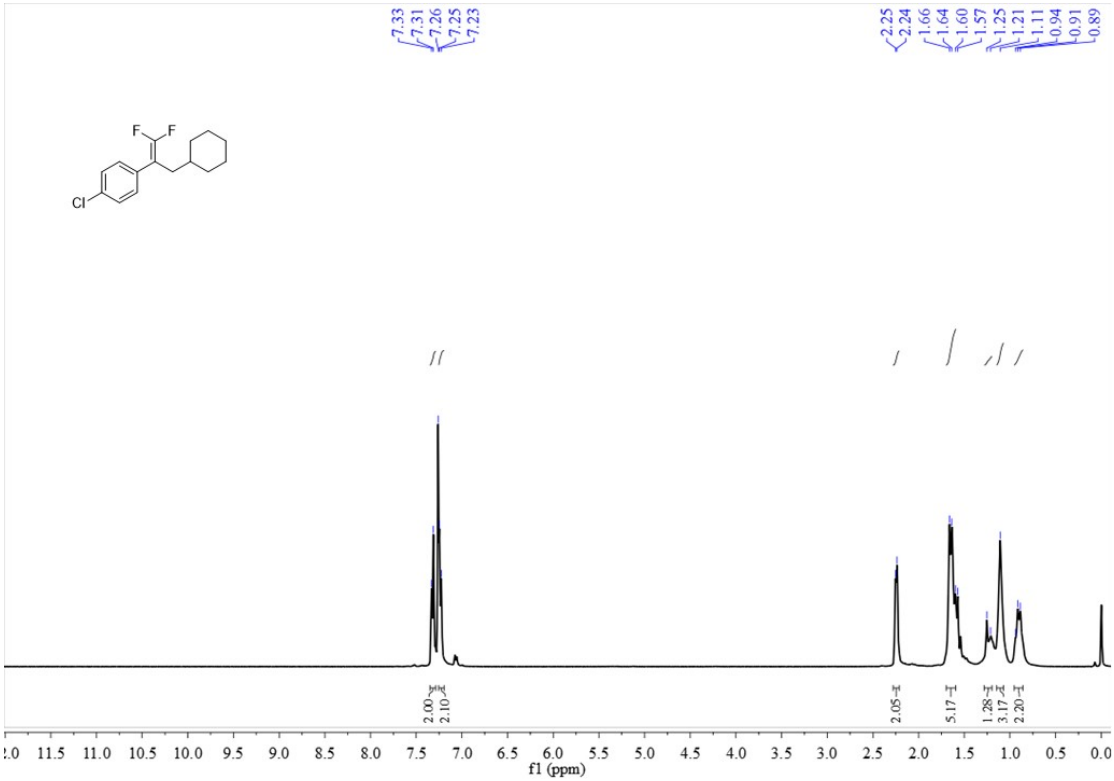
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ag**



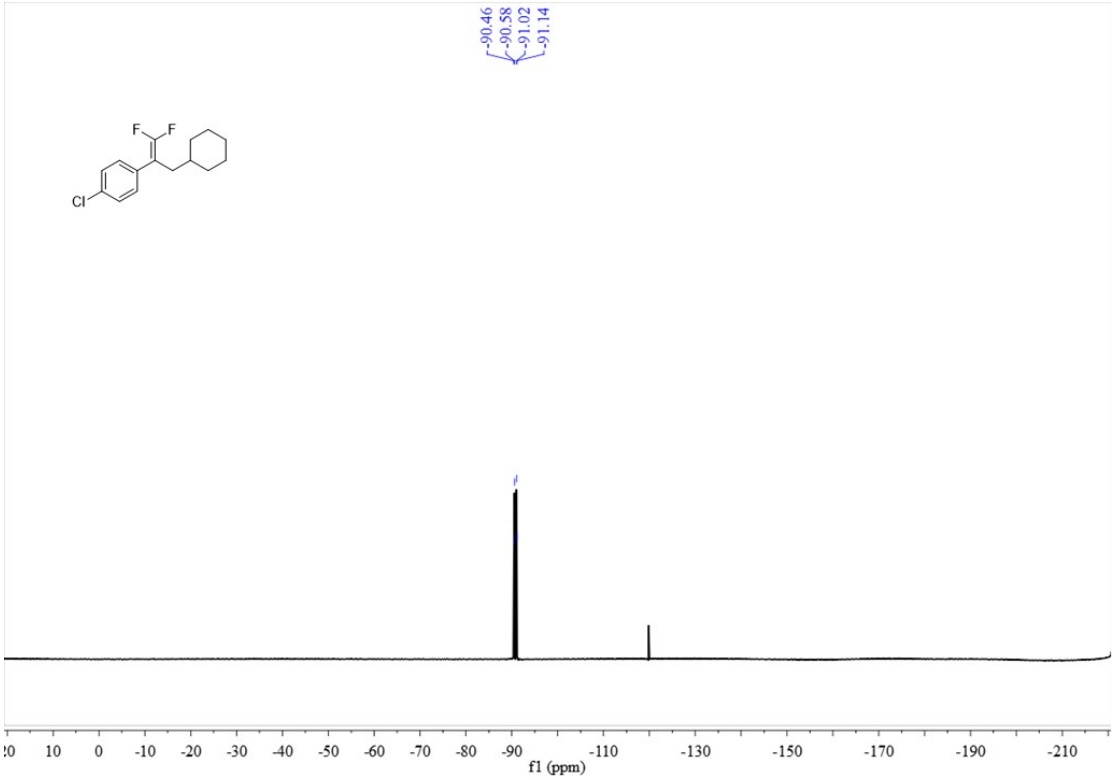
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ag**



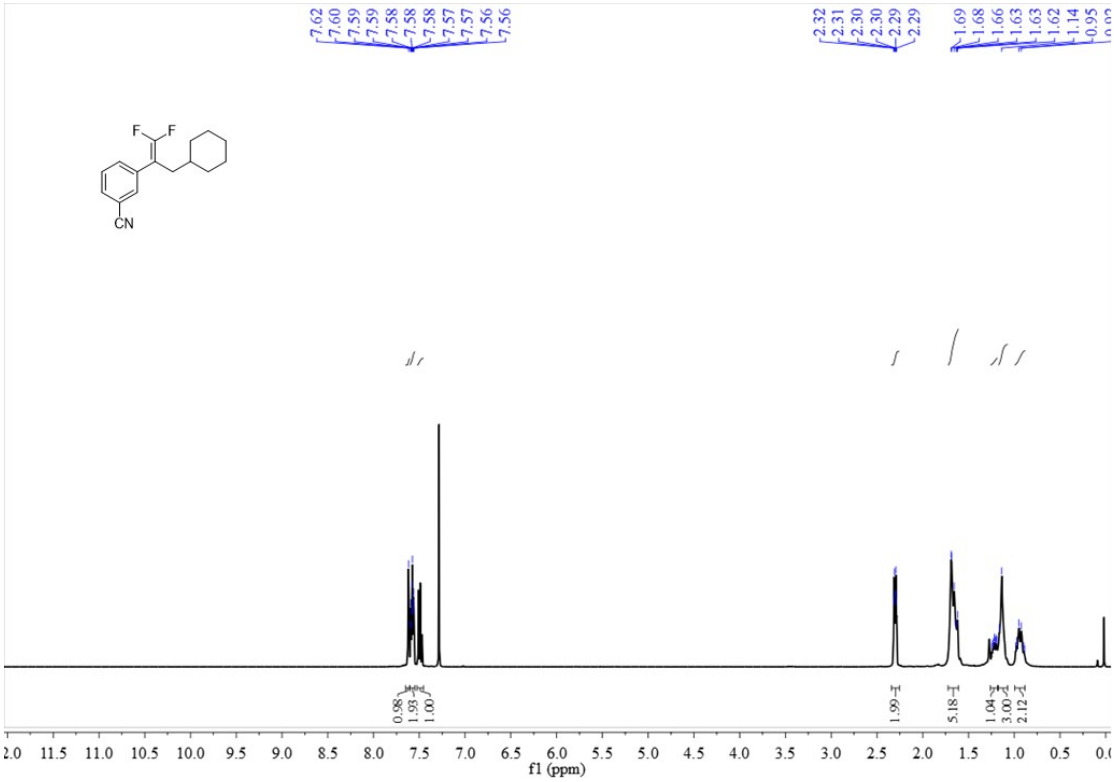
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ah**



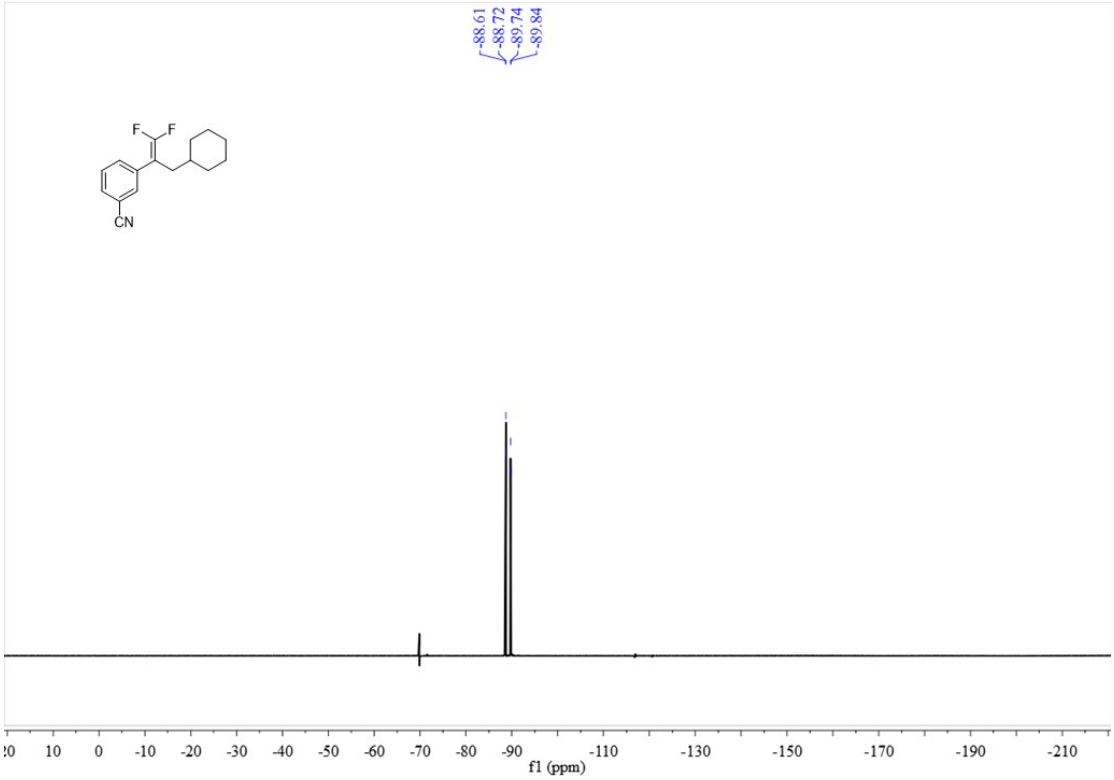
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ah**



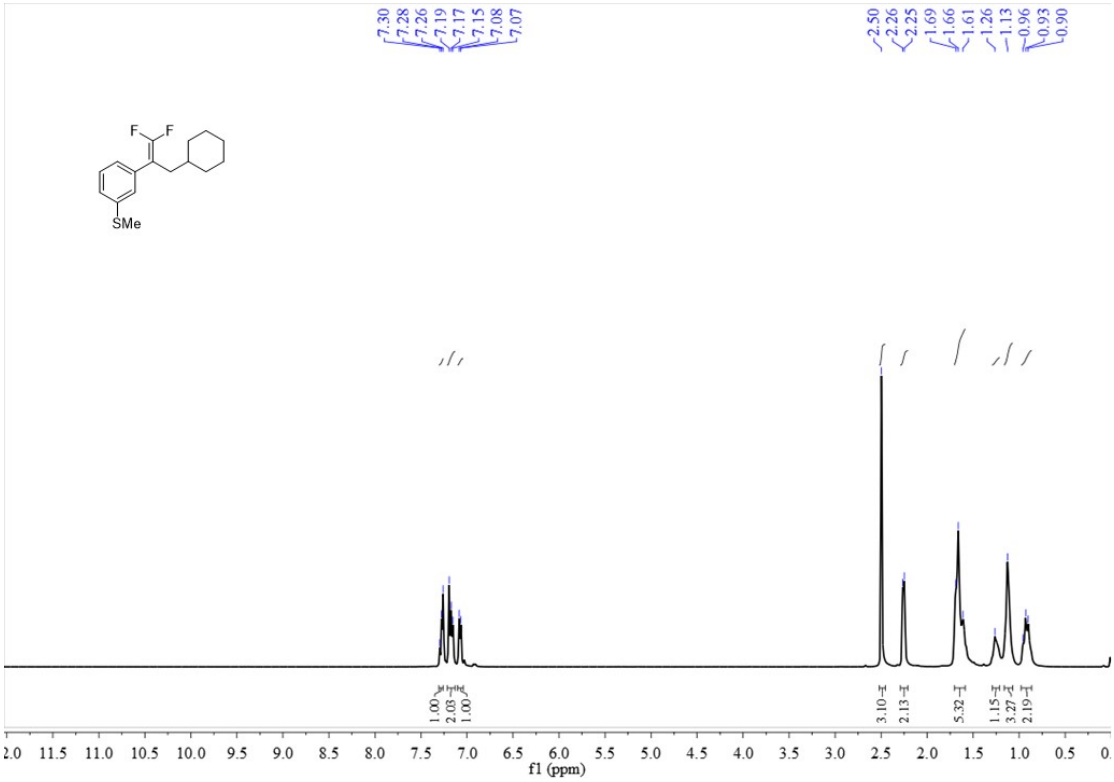
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ai**



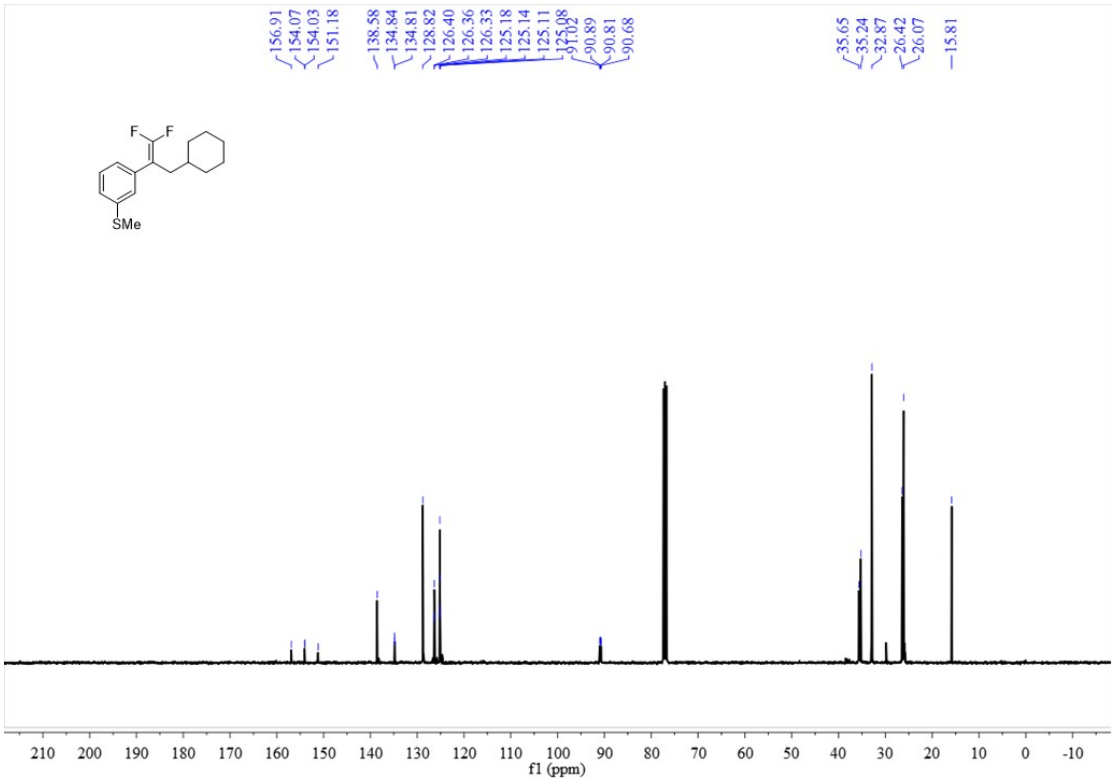
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ai**



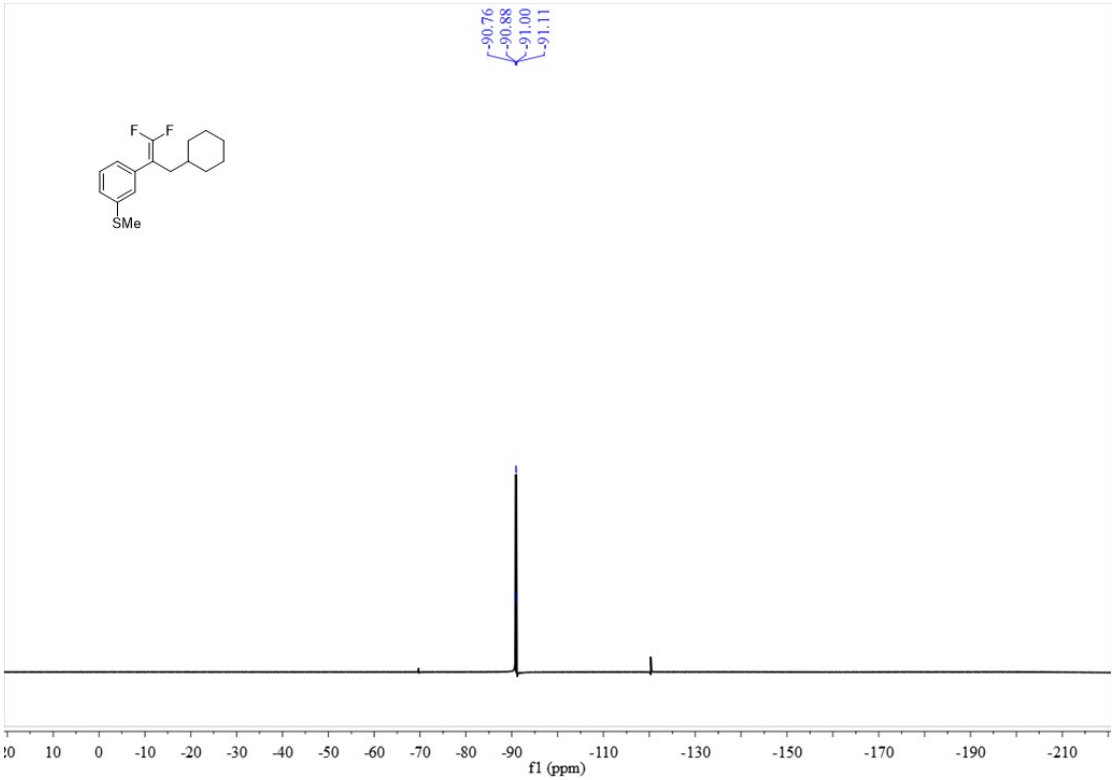
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4aj**



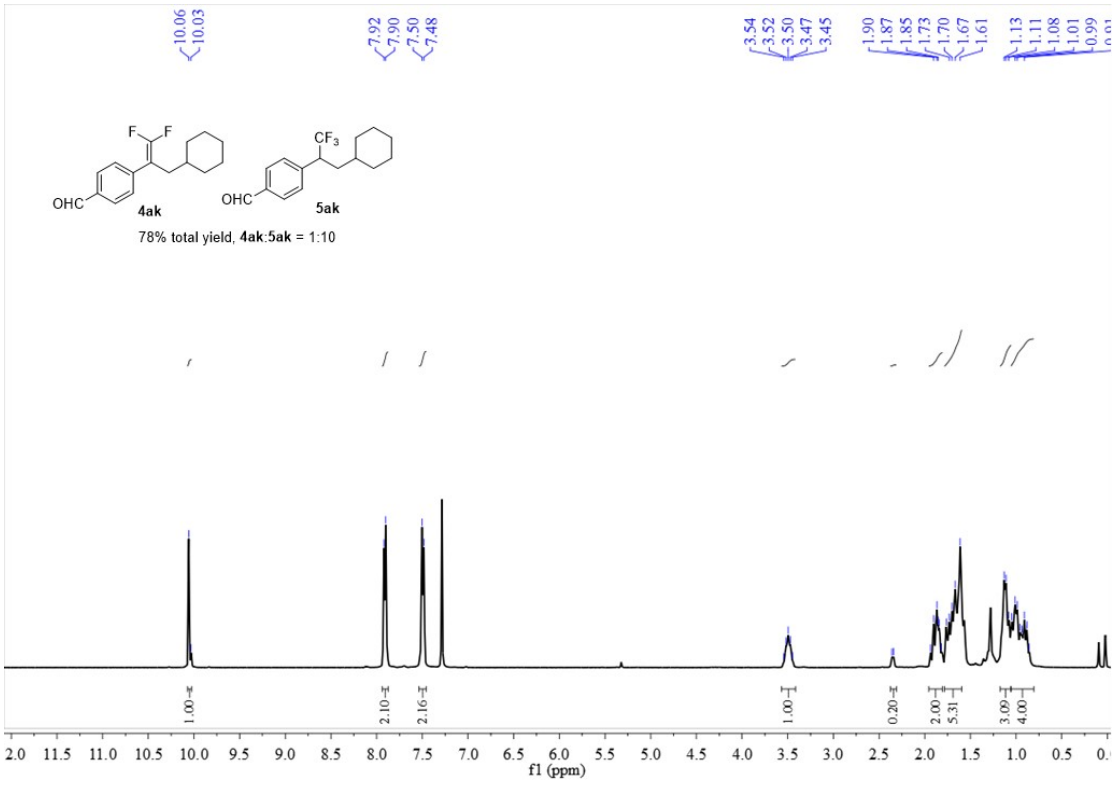
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4aj**



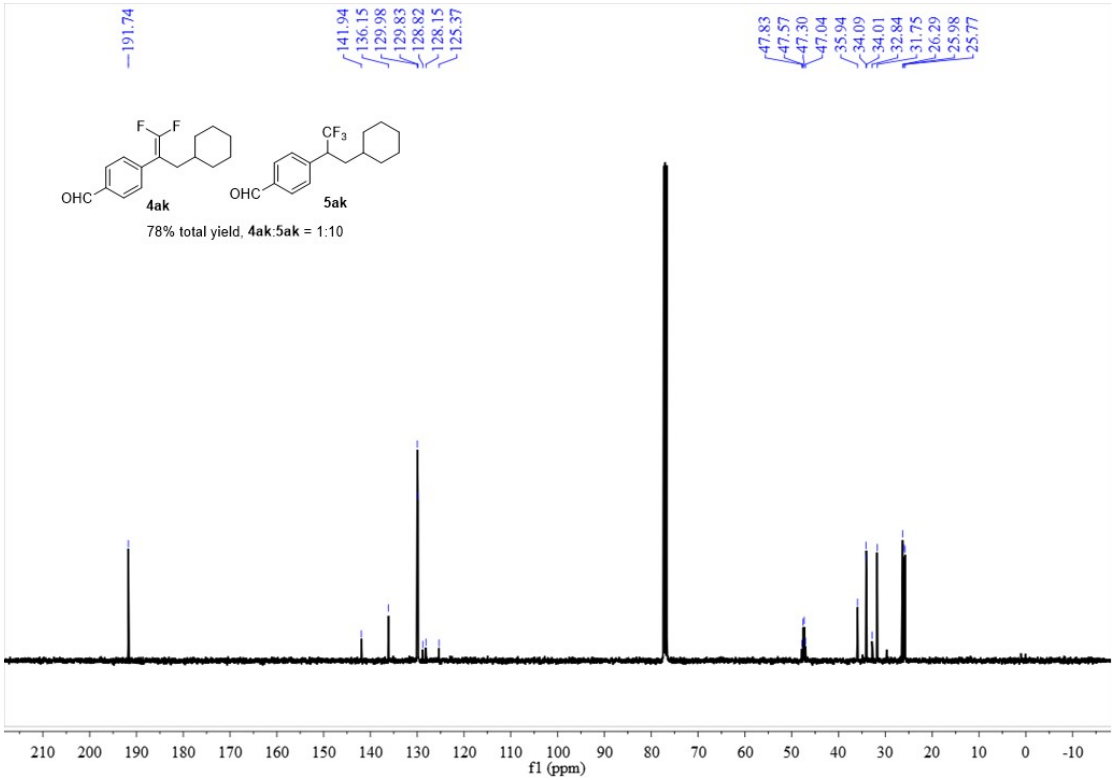
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4aj**



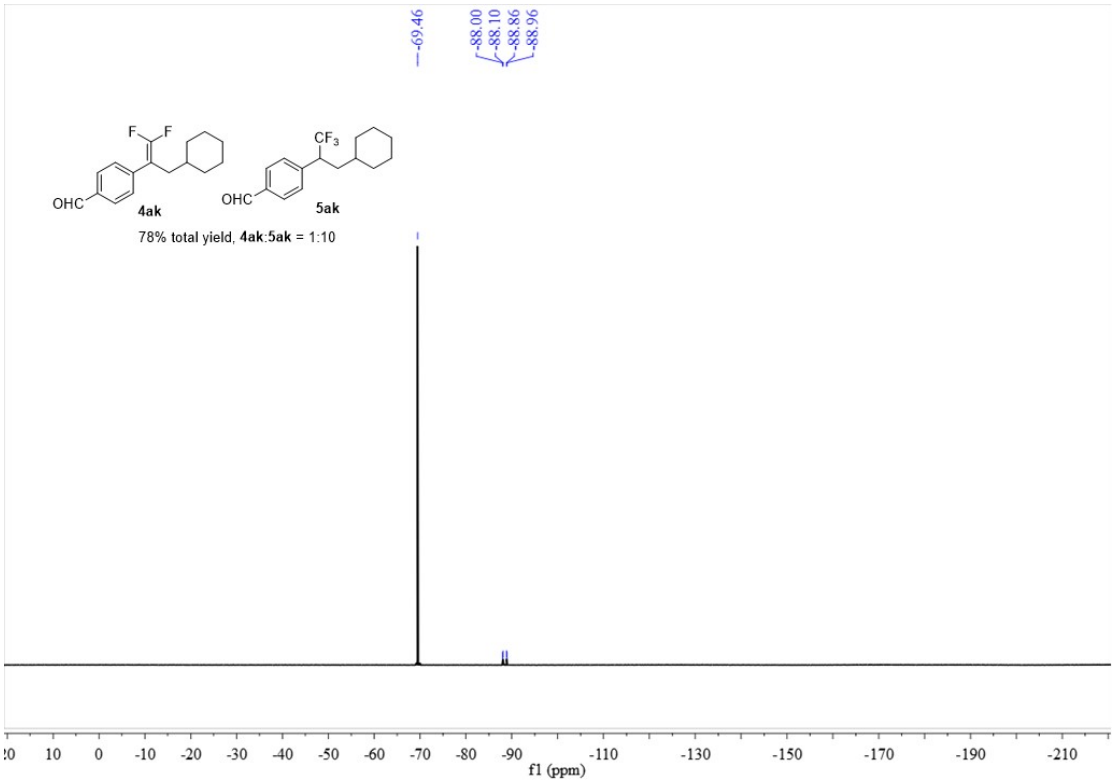
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ak** and **5ak**



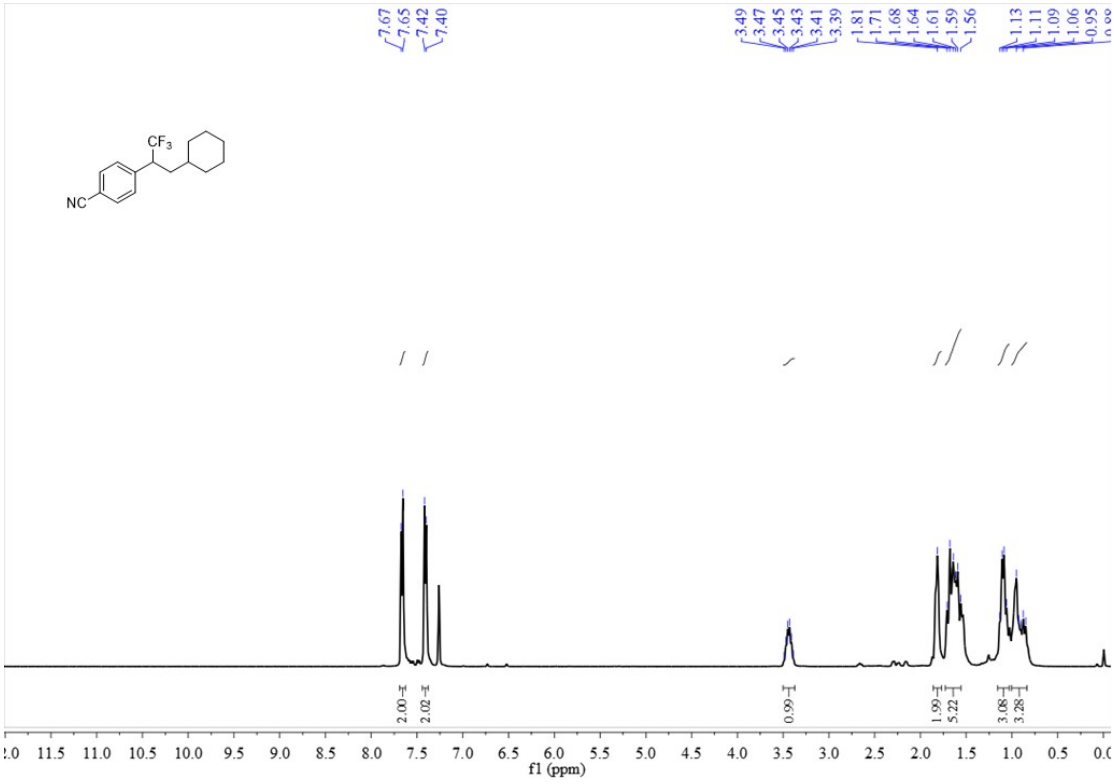
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4ak** and **5ak**



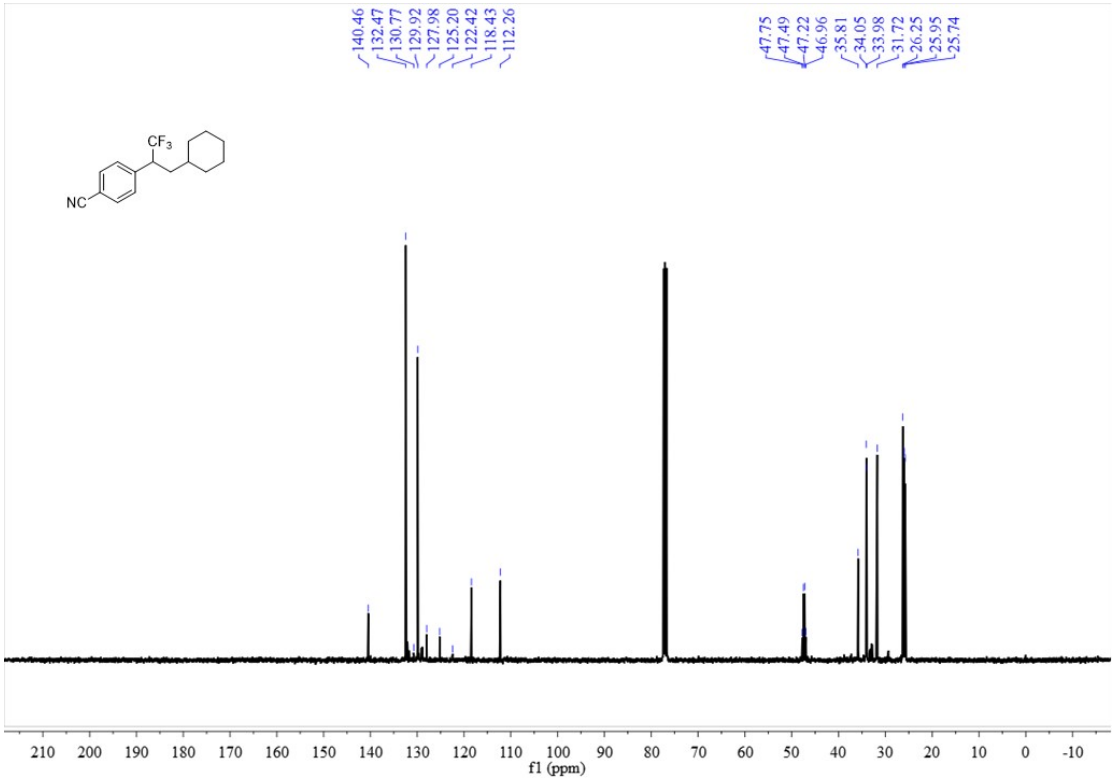
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ak** and **5ak**



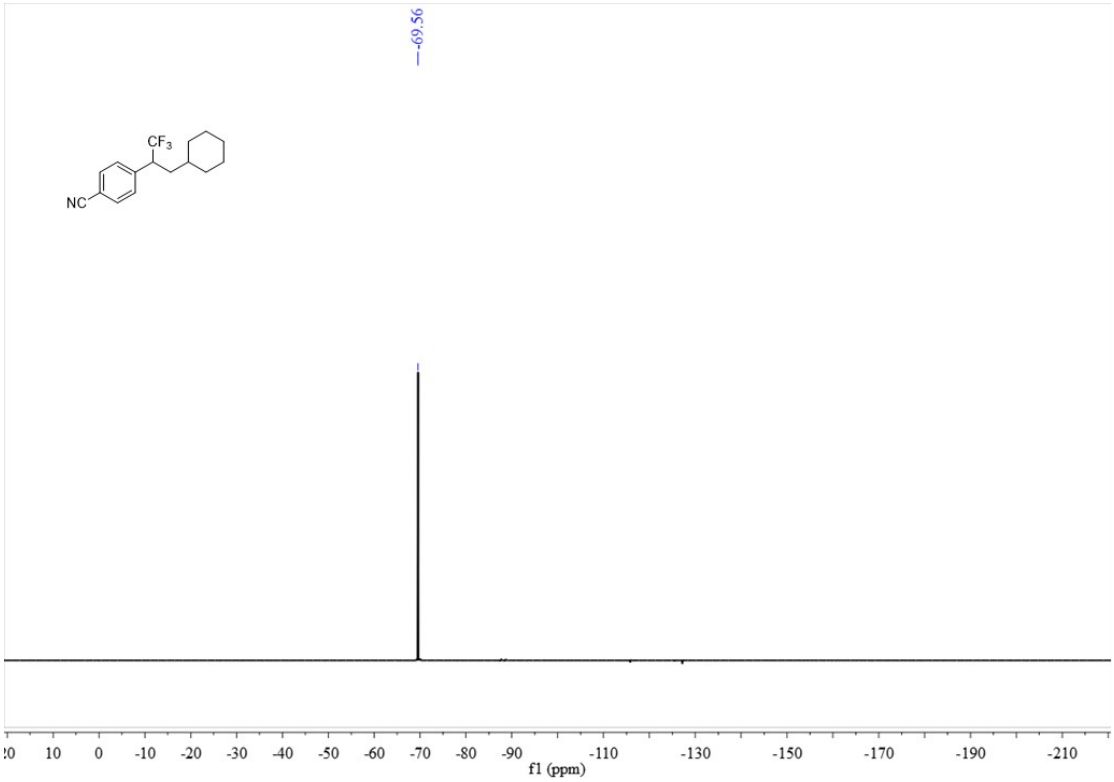
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5al**



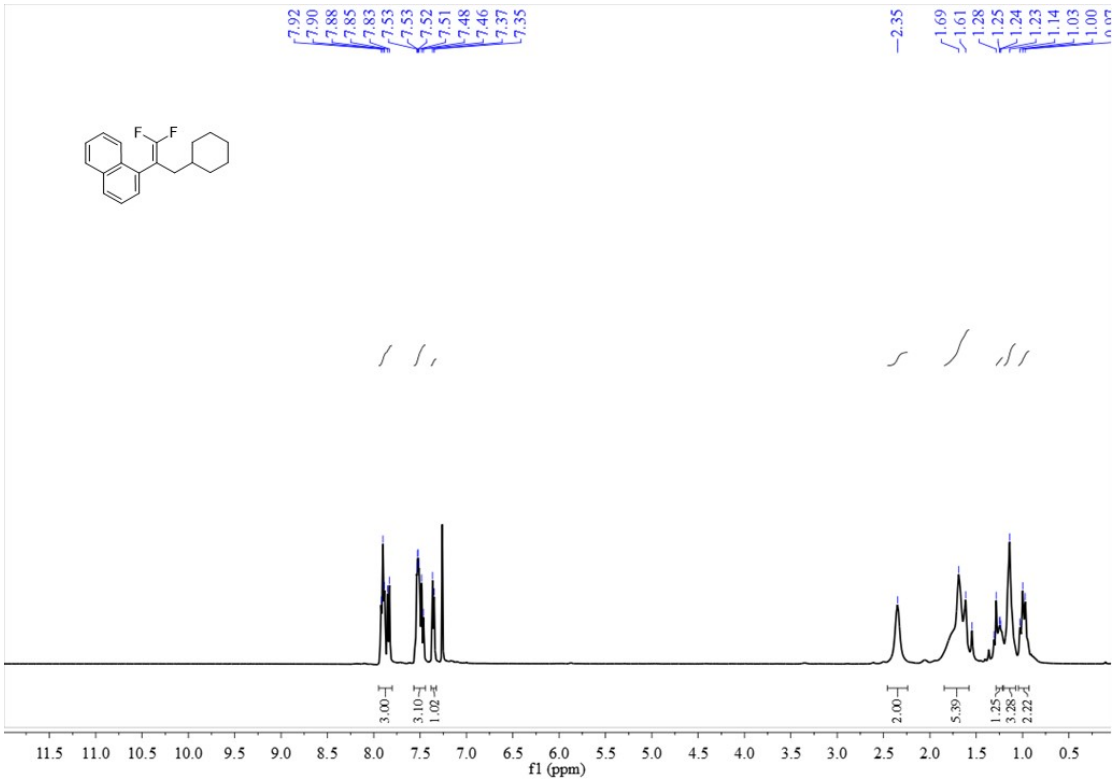
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5al**



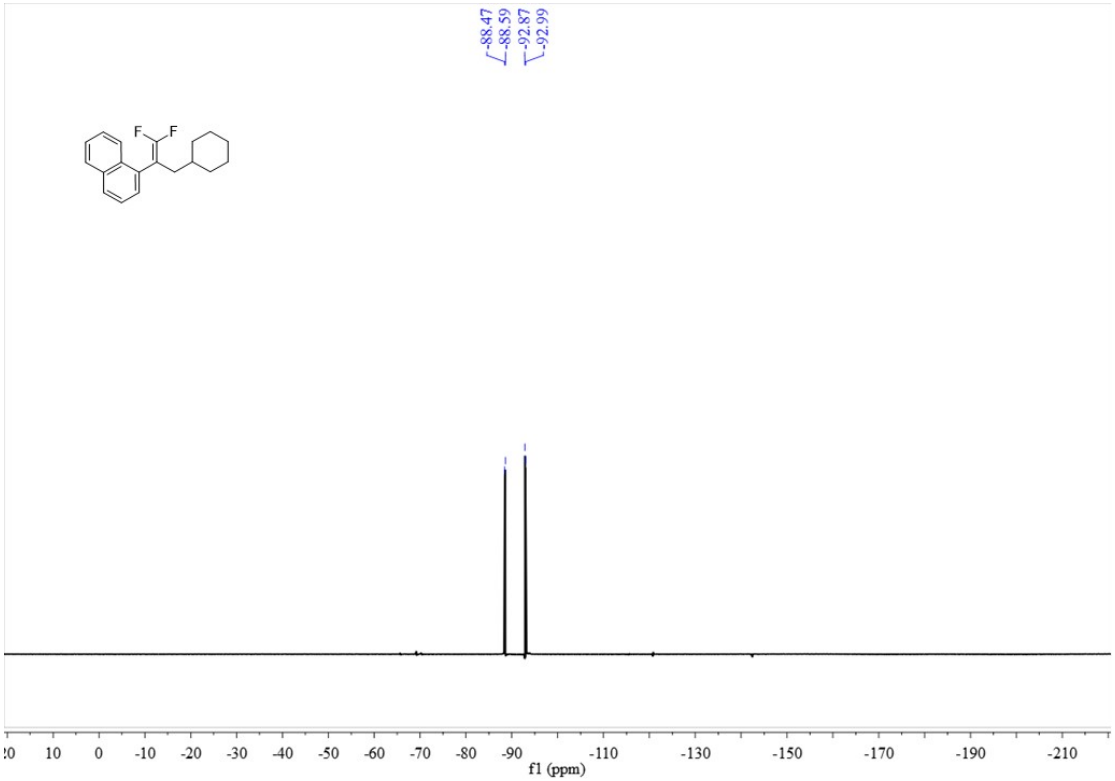
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **5al**



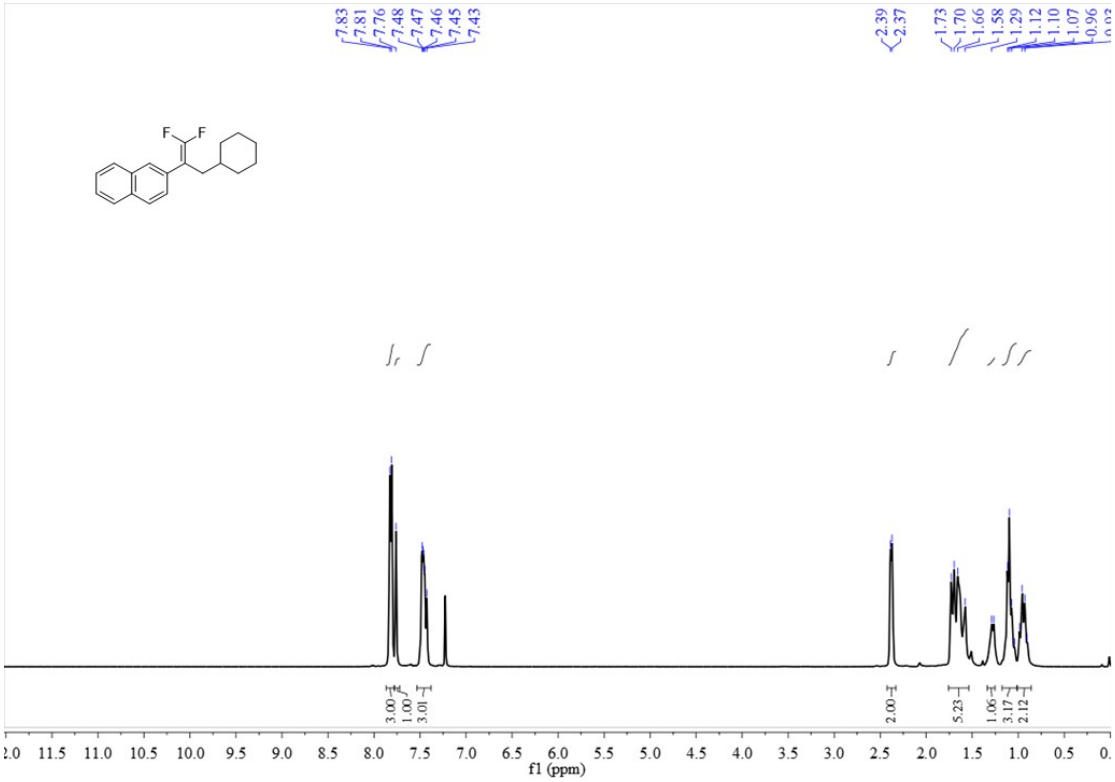
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4am**



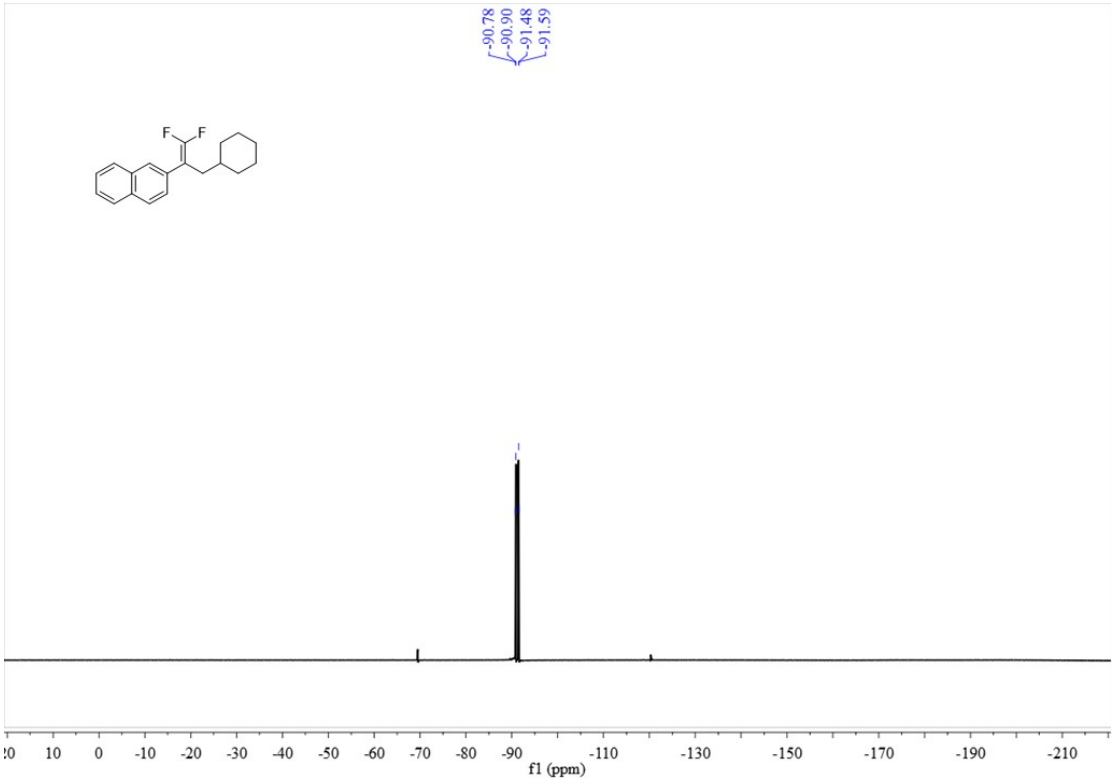
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4am**



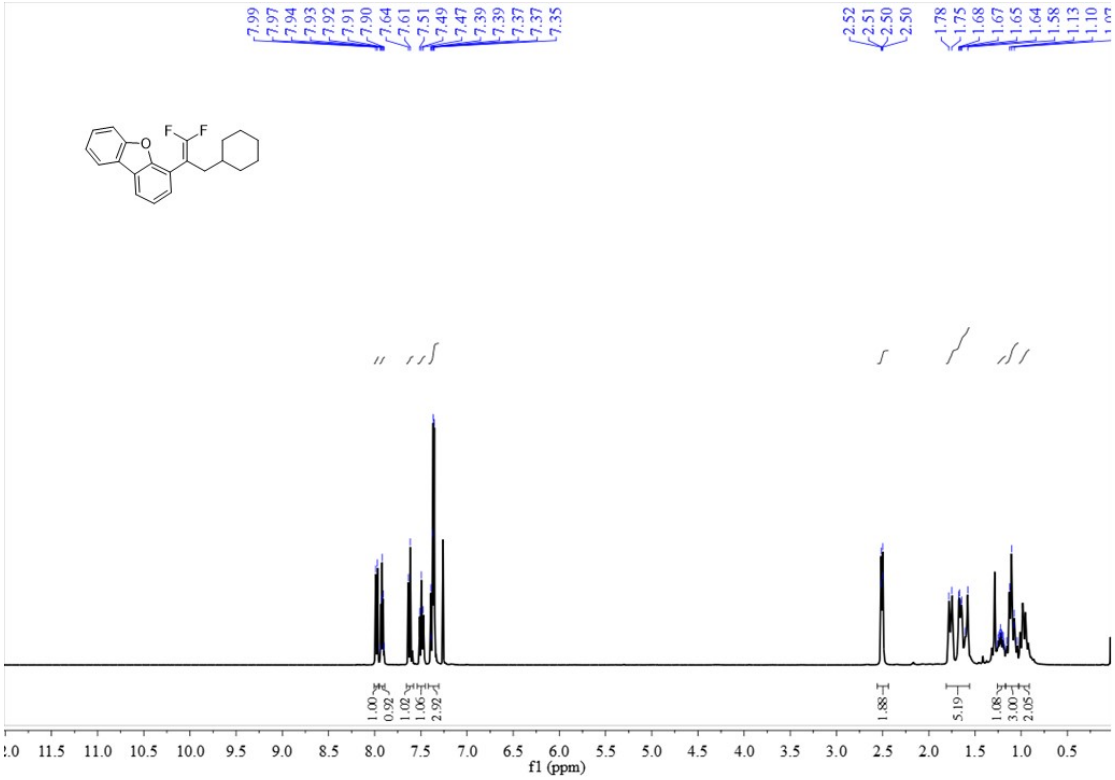
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4an**



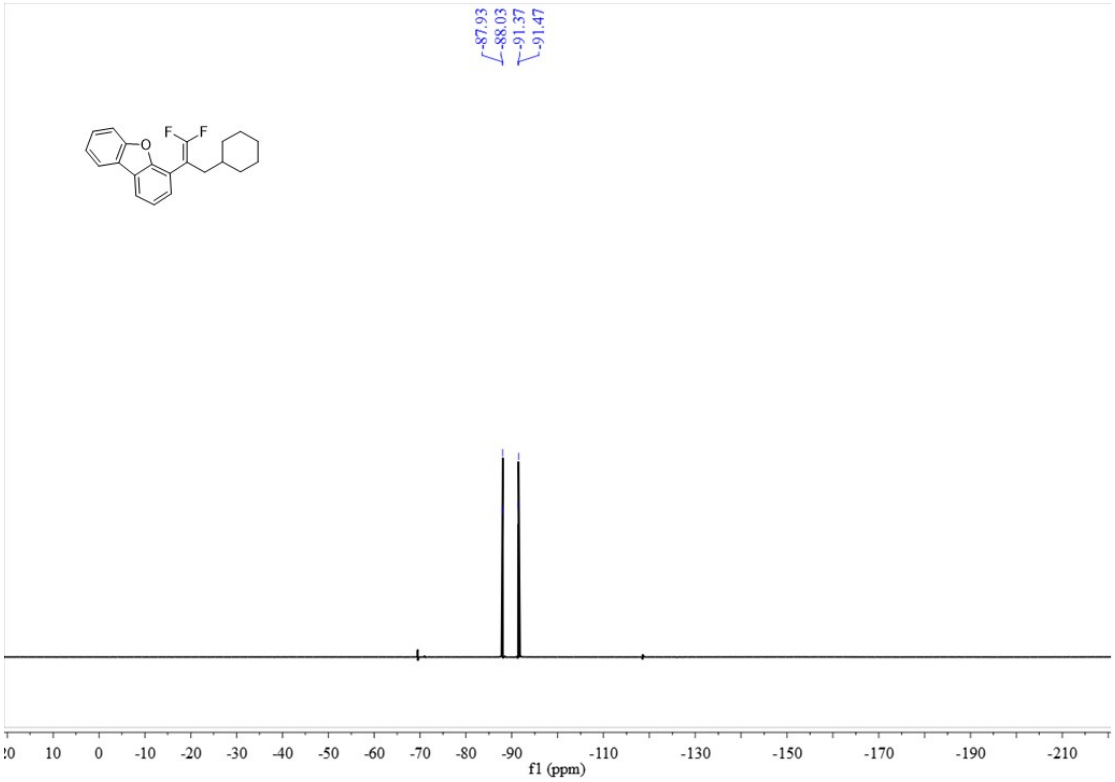
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4an**



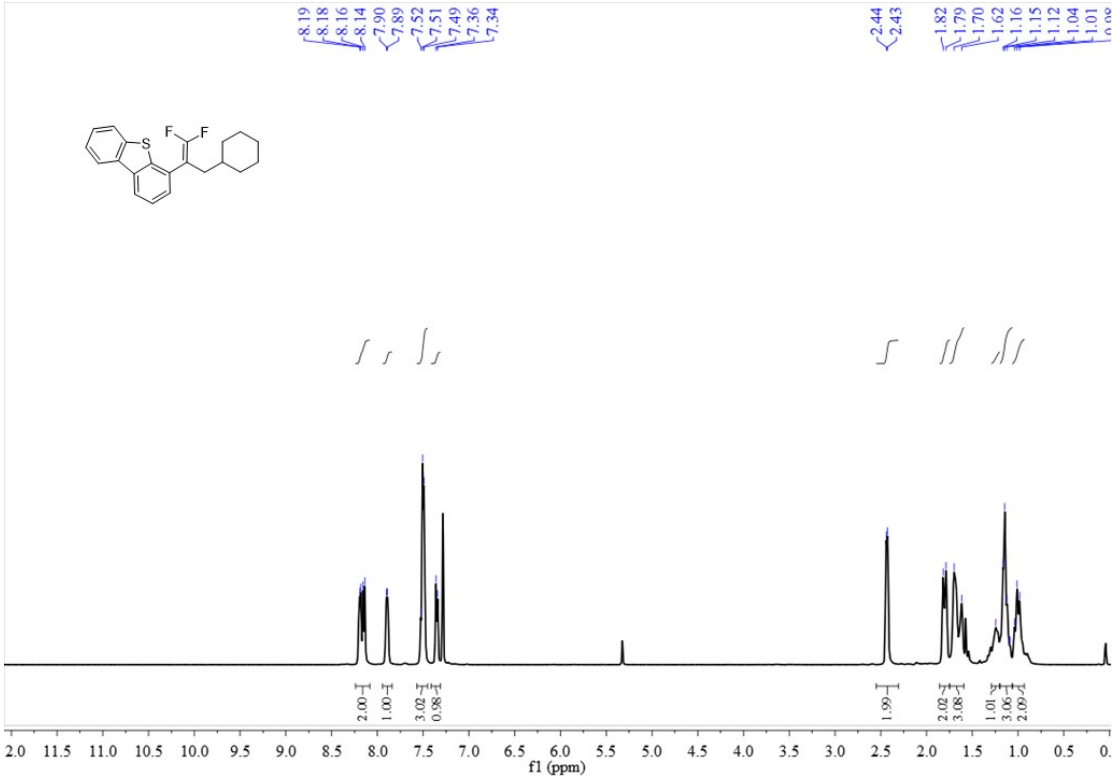
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ao**



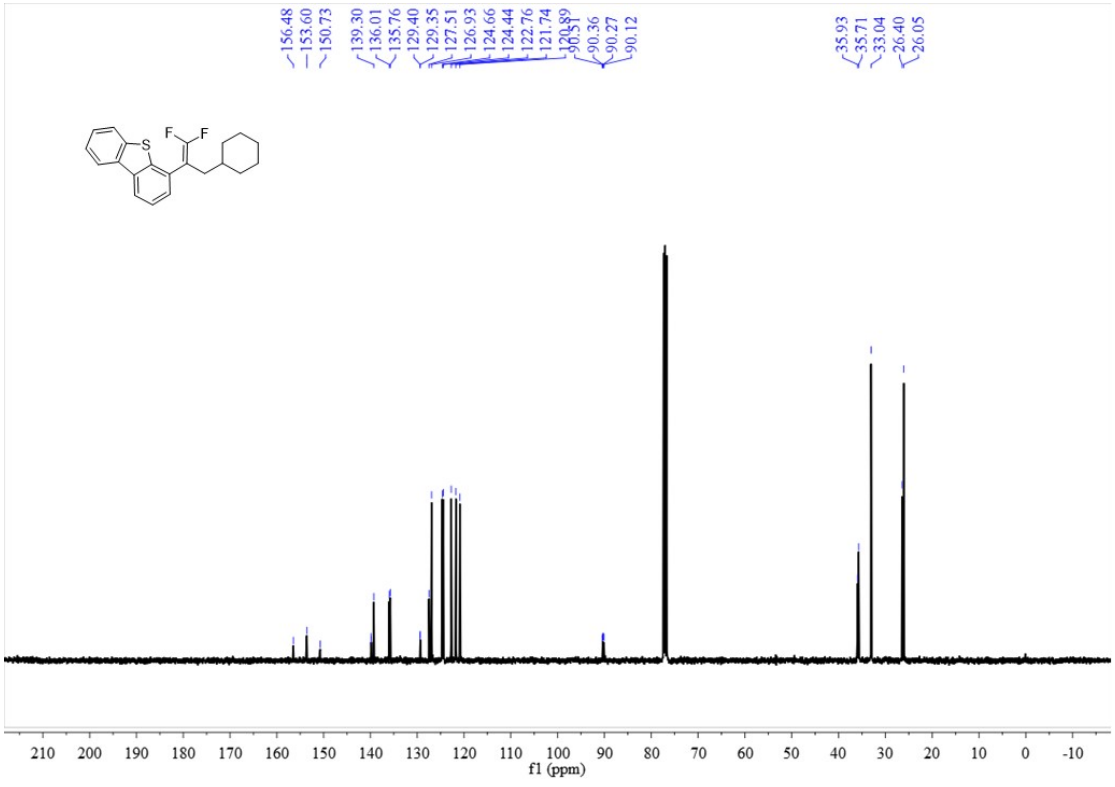
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ao**



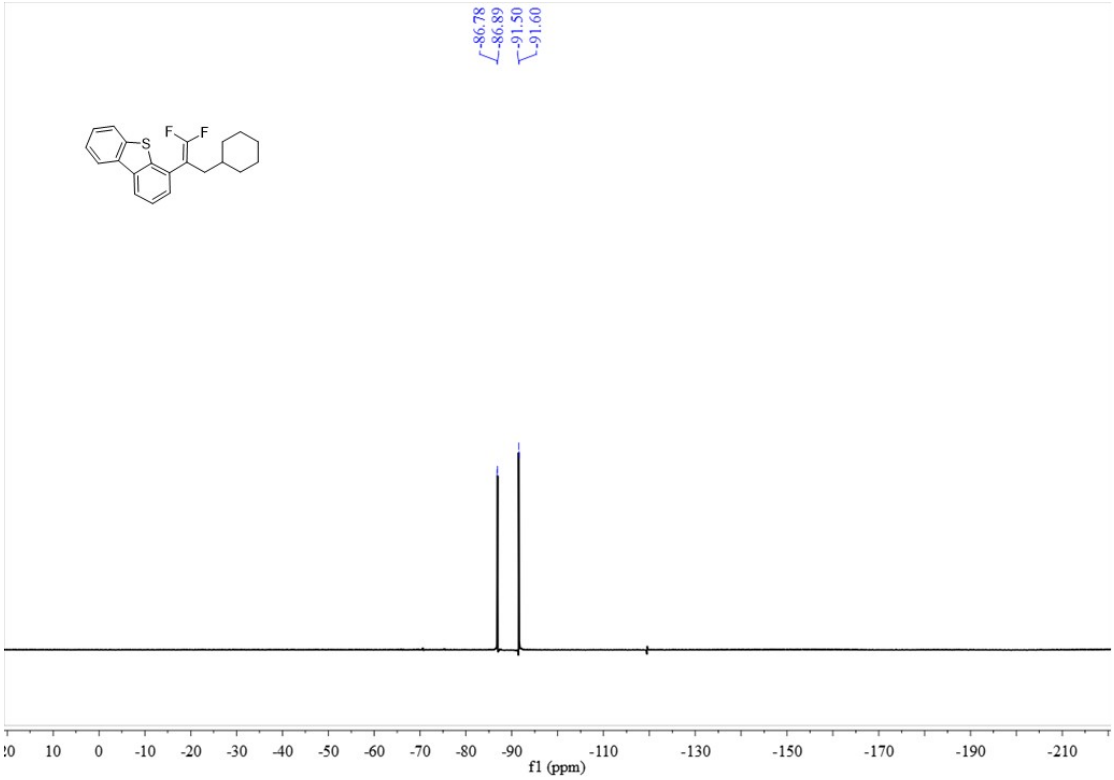
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ap**



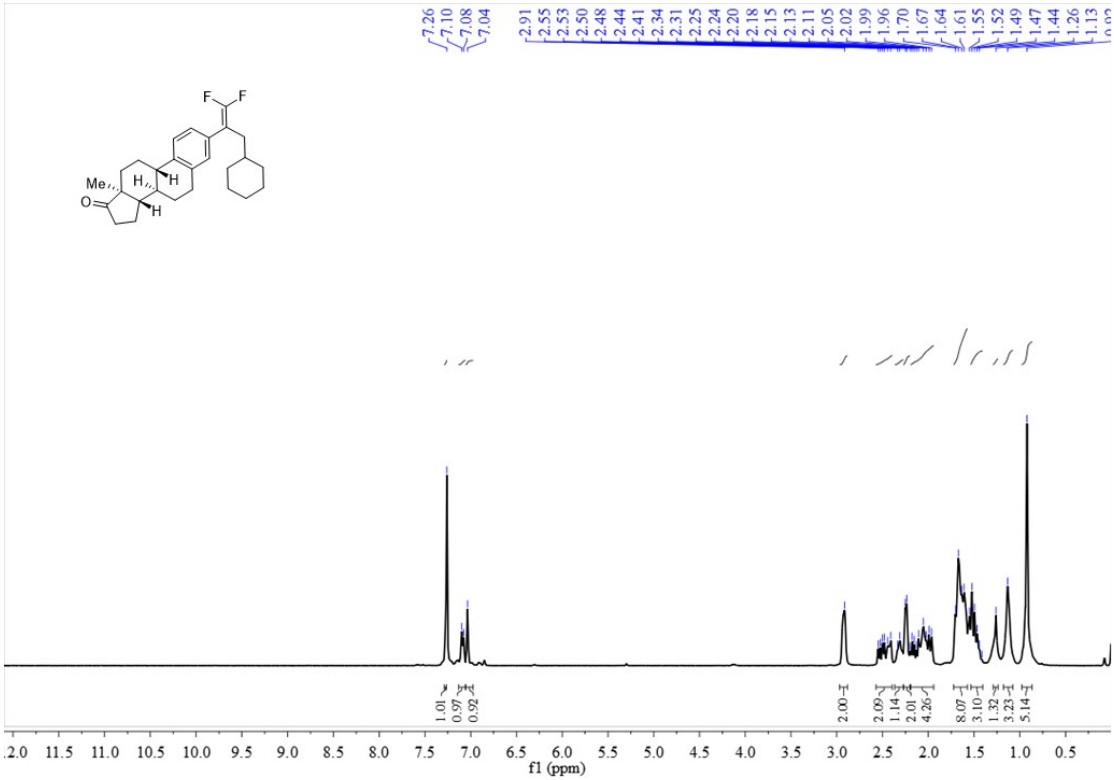
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4ap**



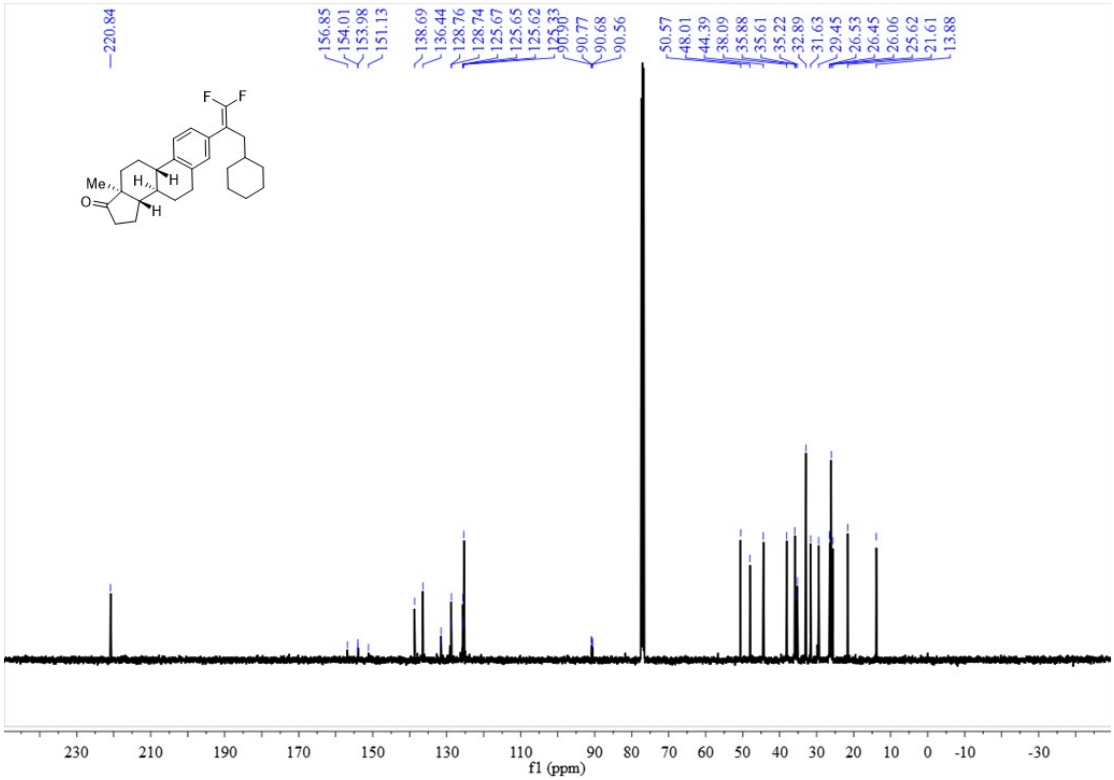
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ap**



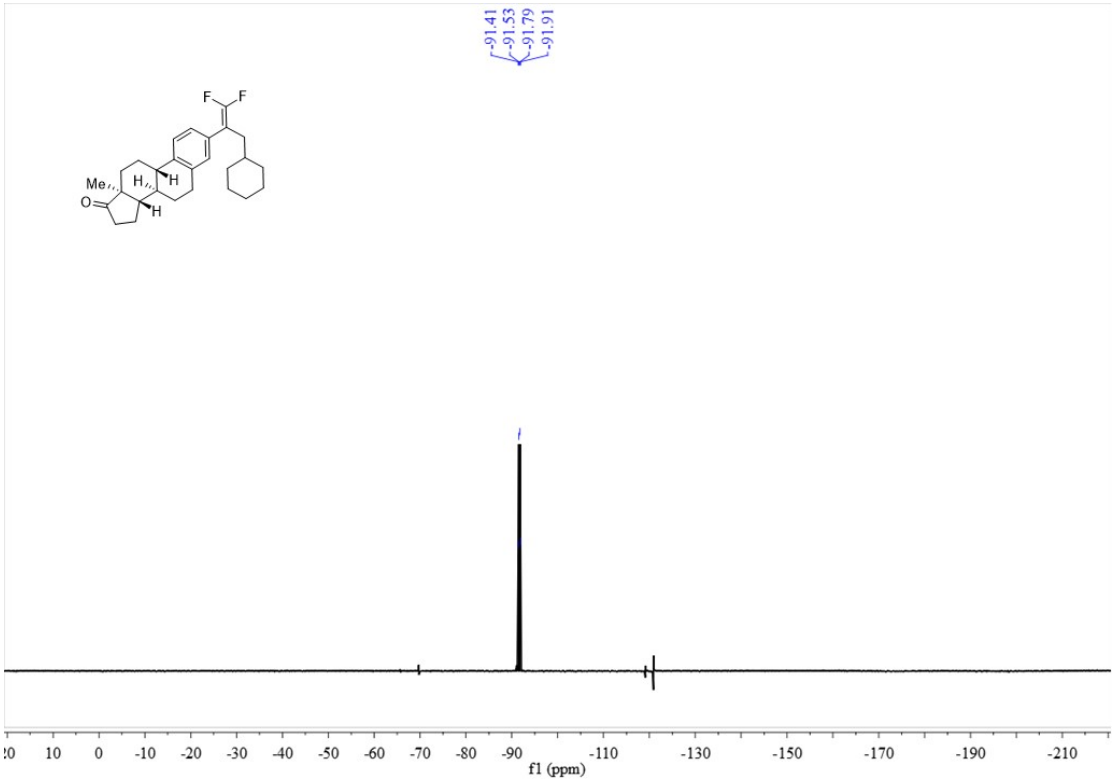
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4aq**



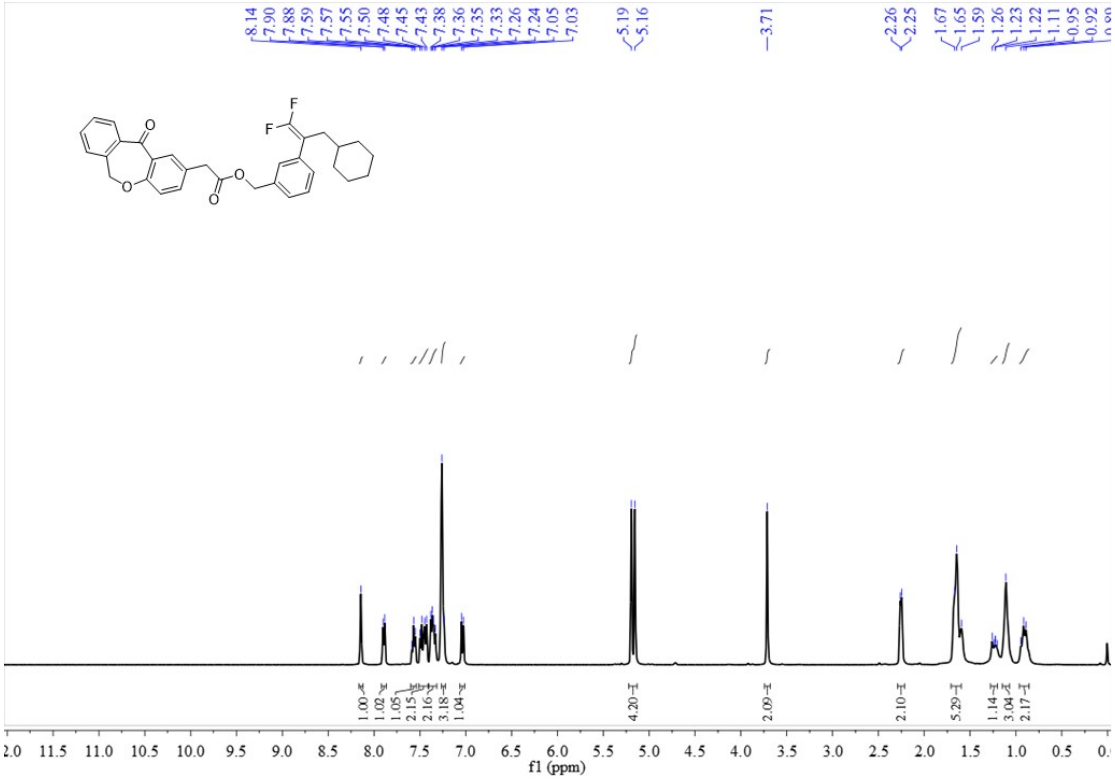
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4aq**



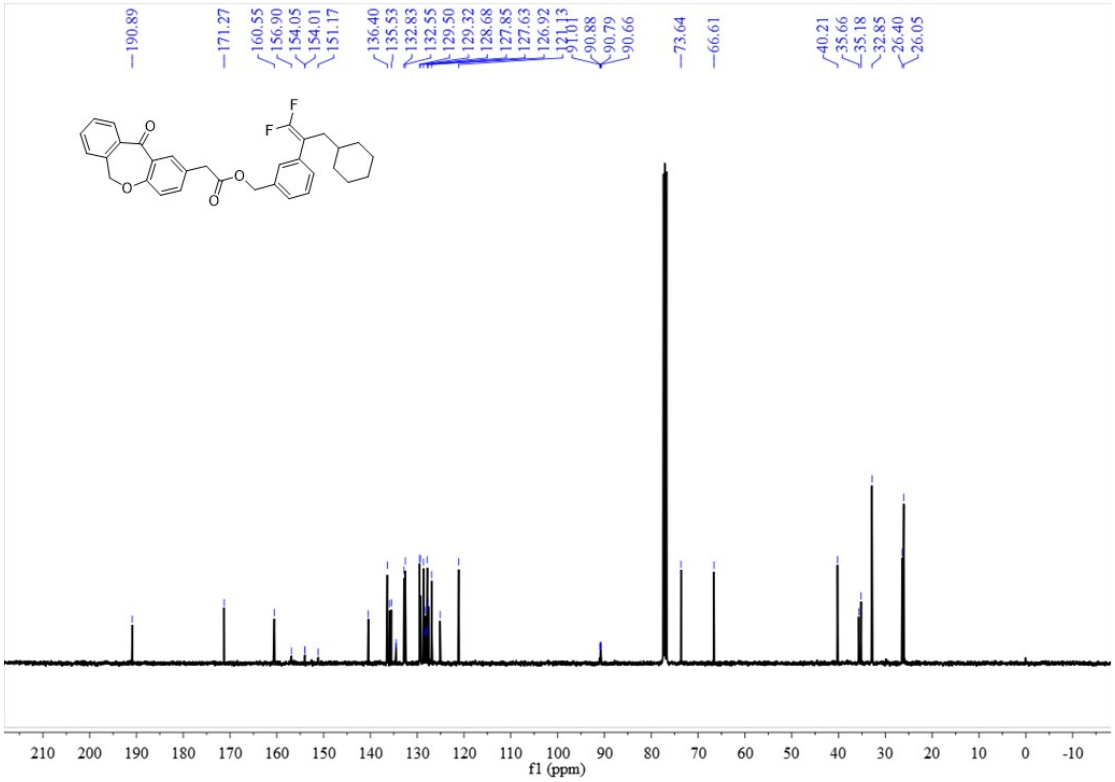
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4aq**



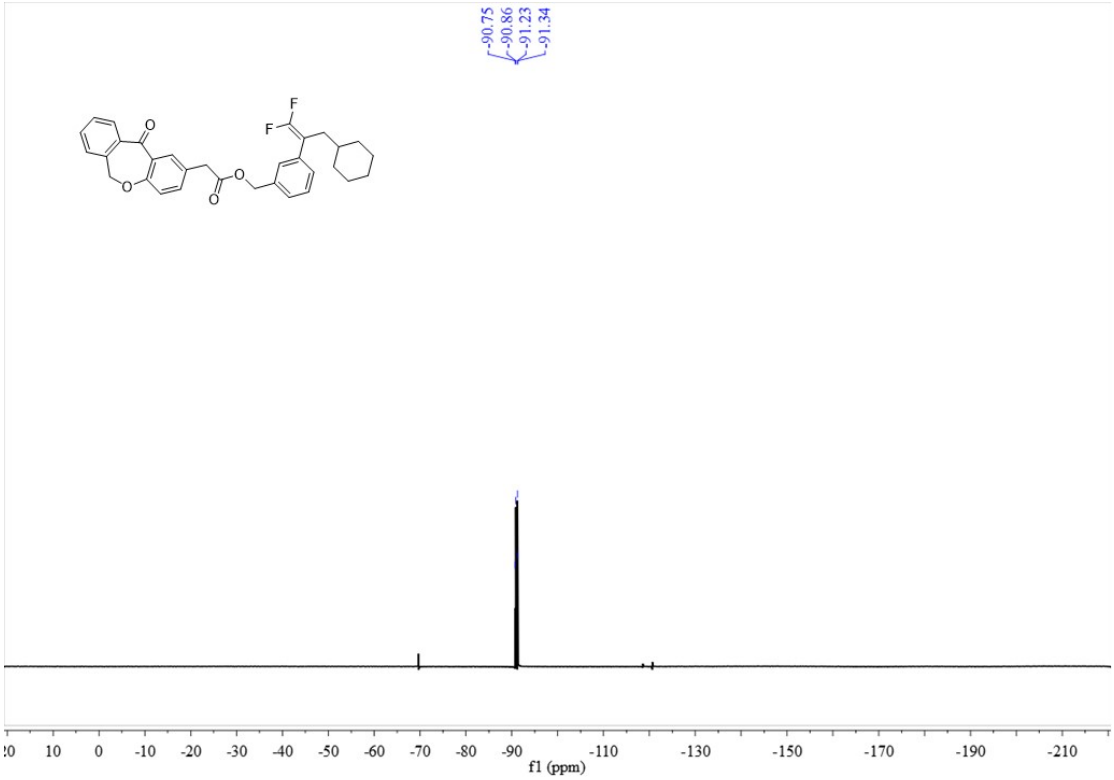
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ar**



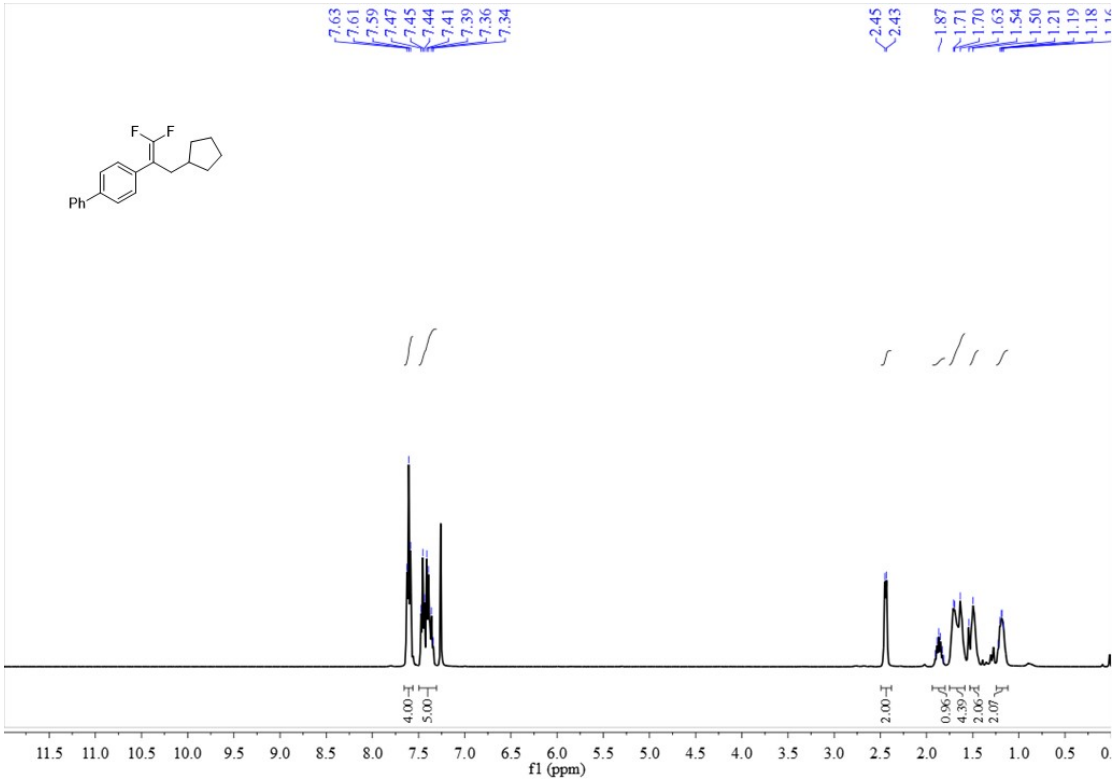
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4ar**



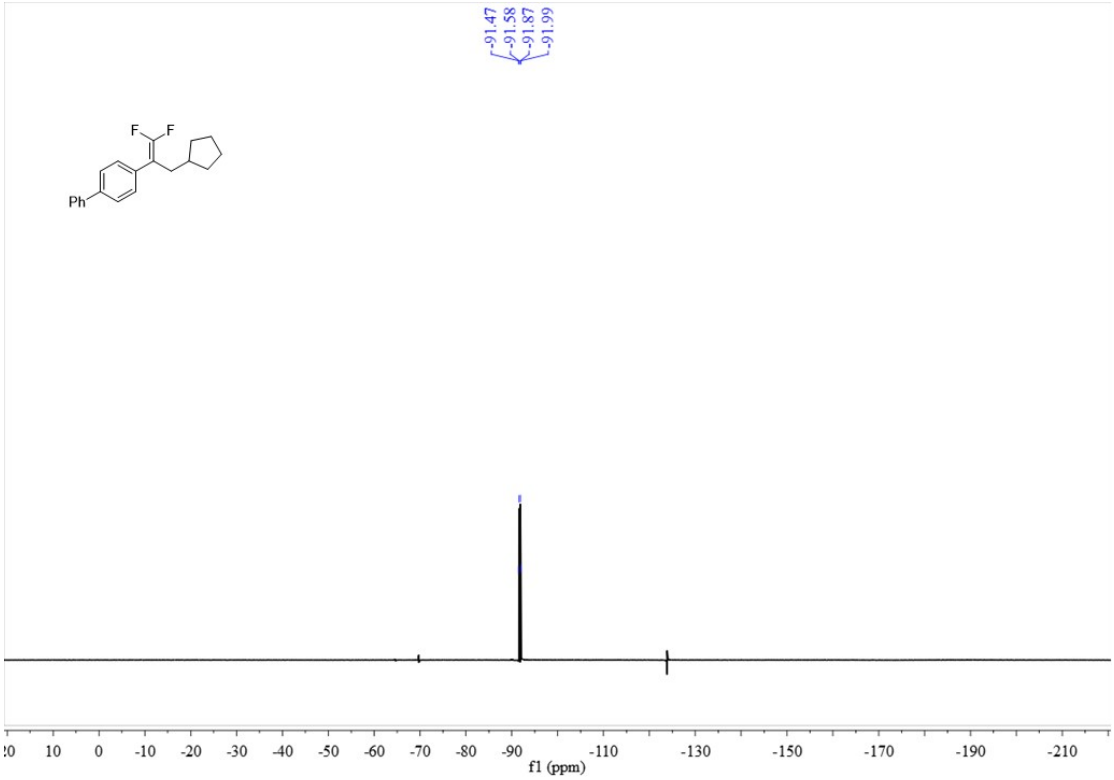
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ar**



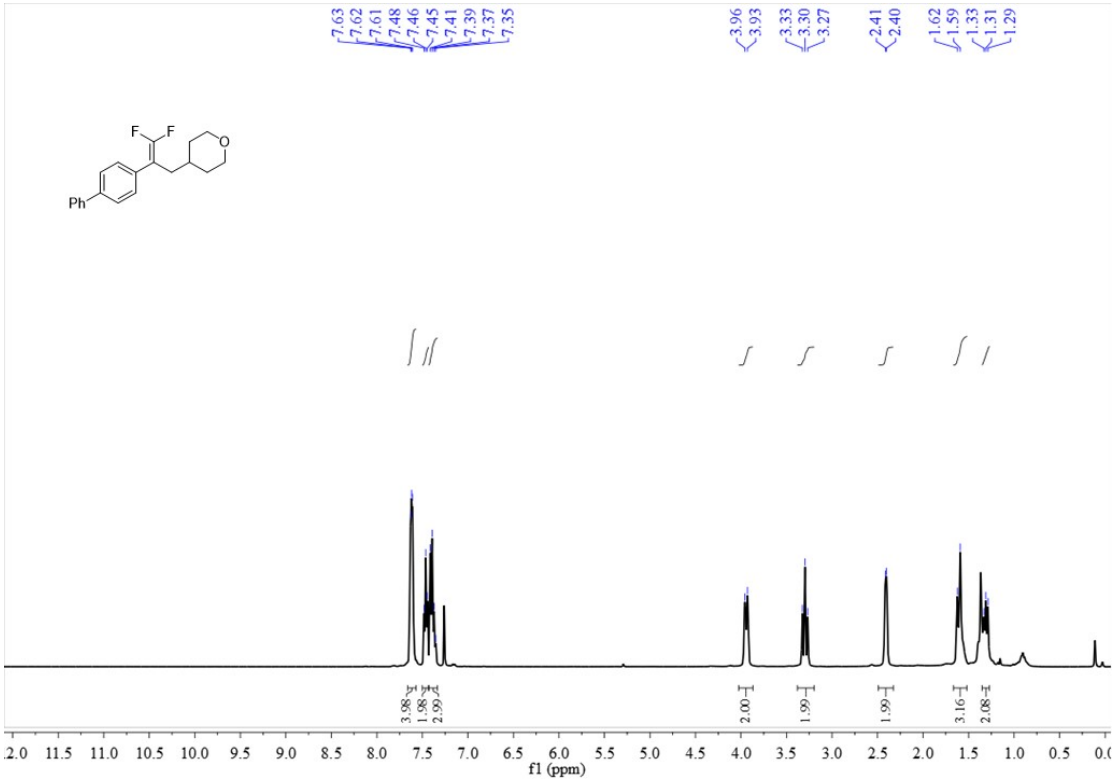
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ba**



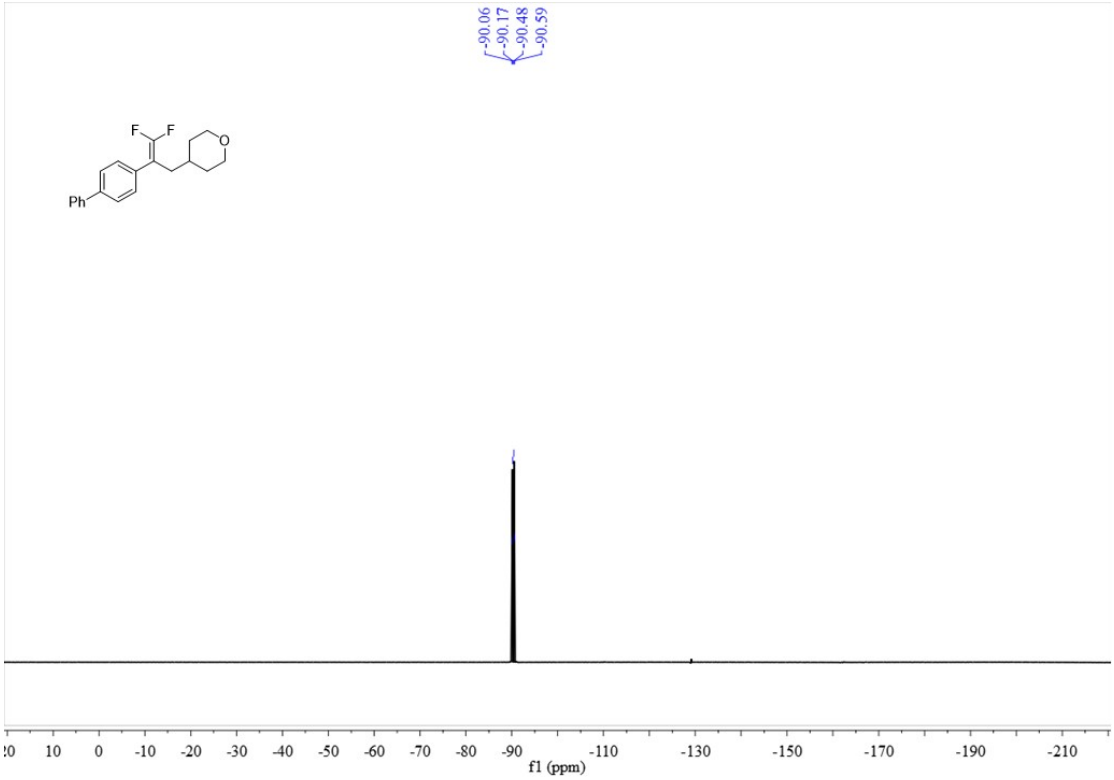
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ba**



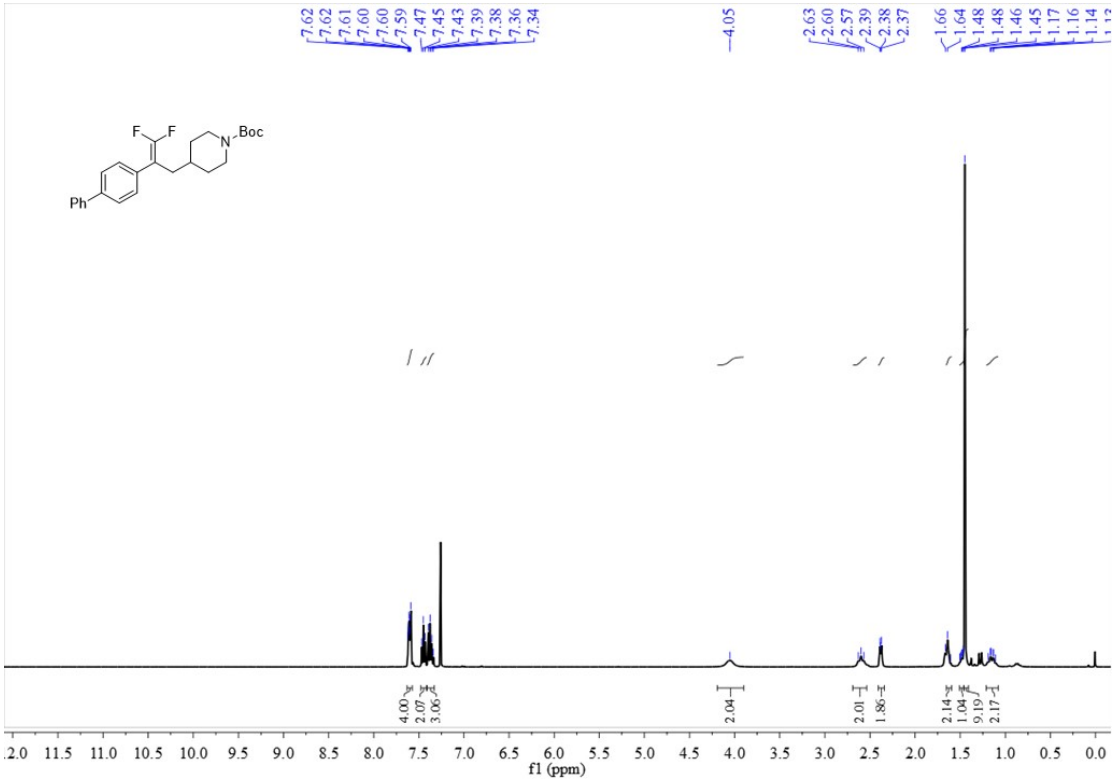
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ca**



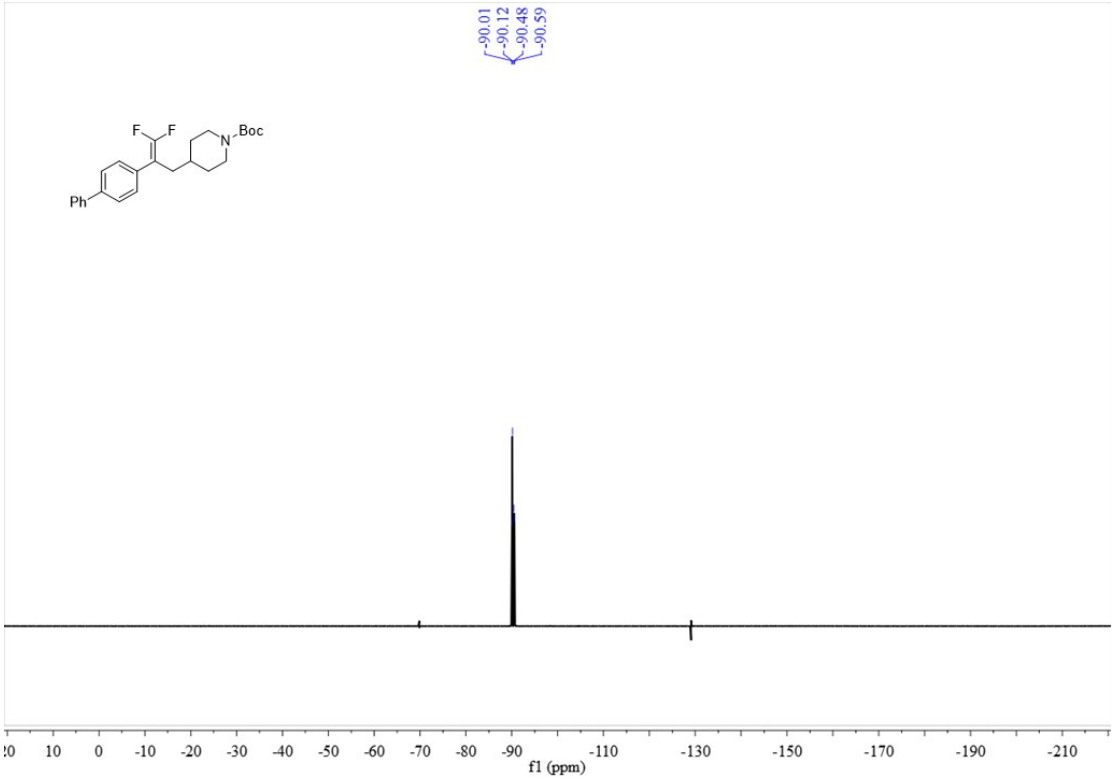
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ca**



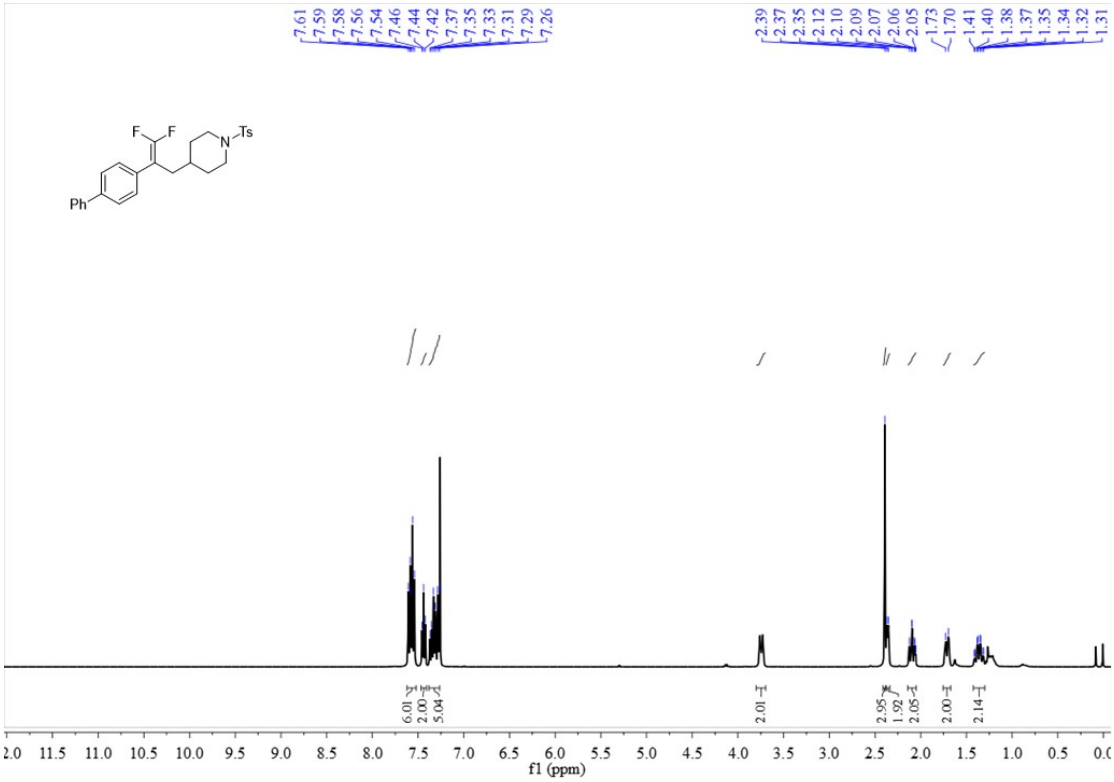
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4da**



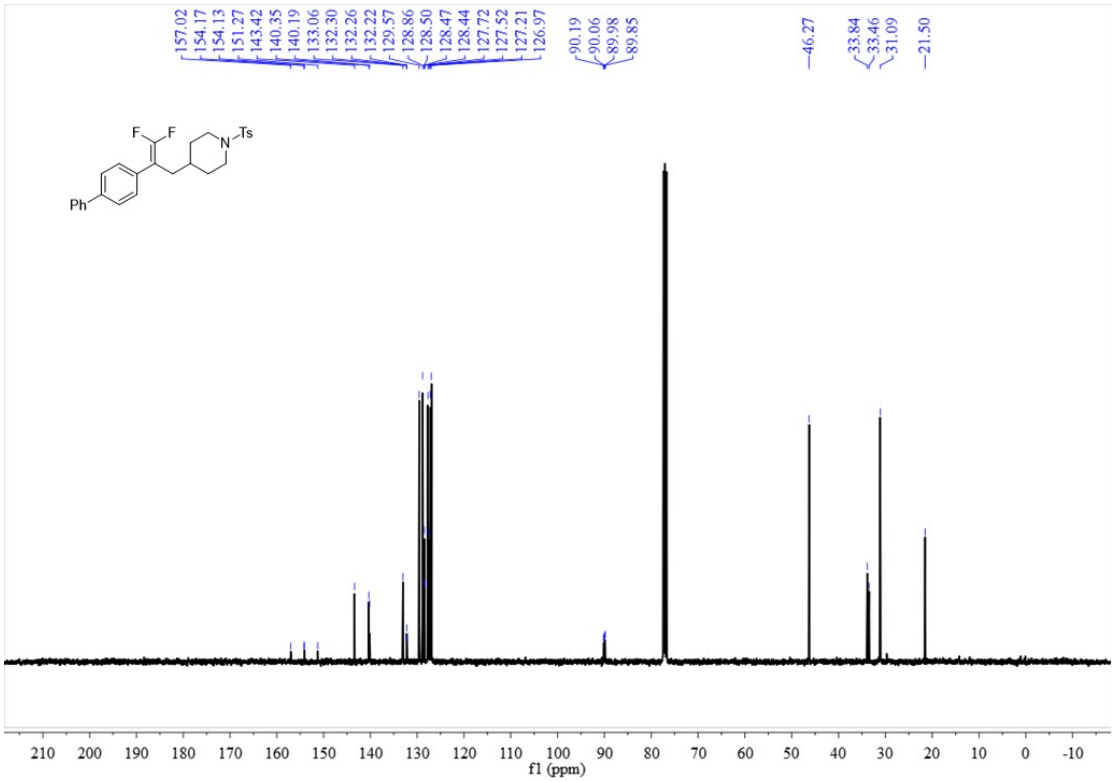
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4da**



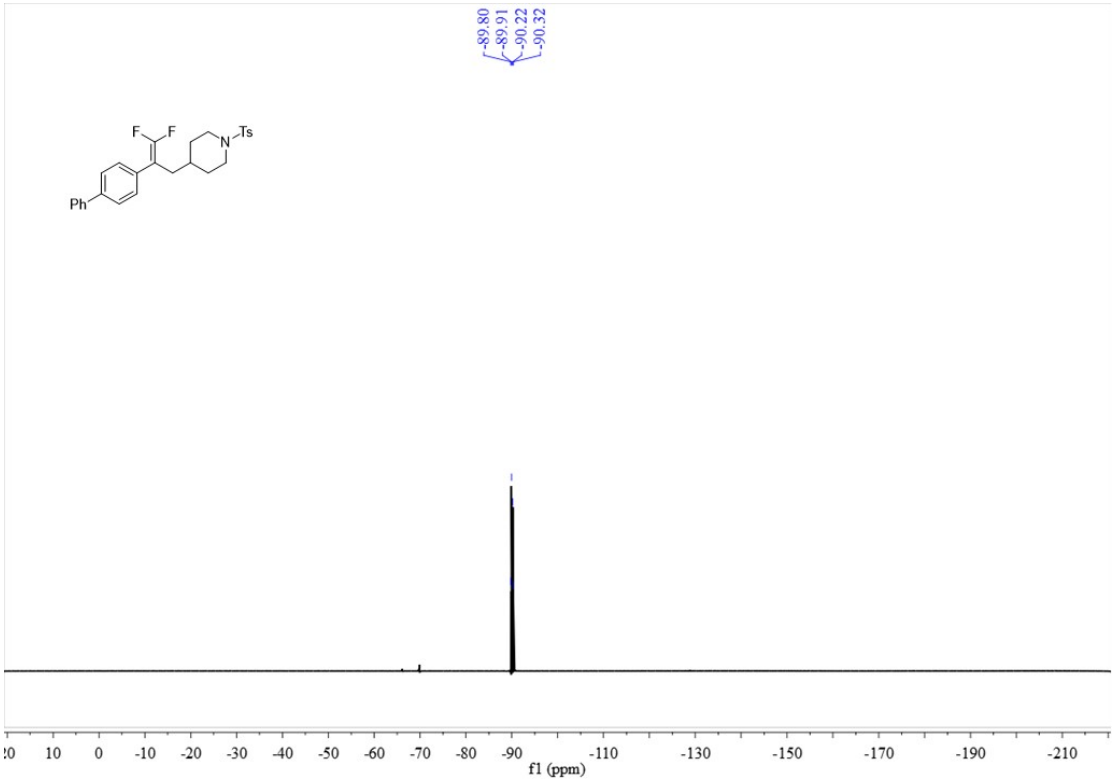
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ea**



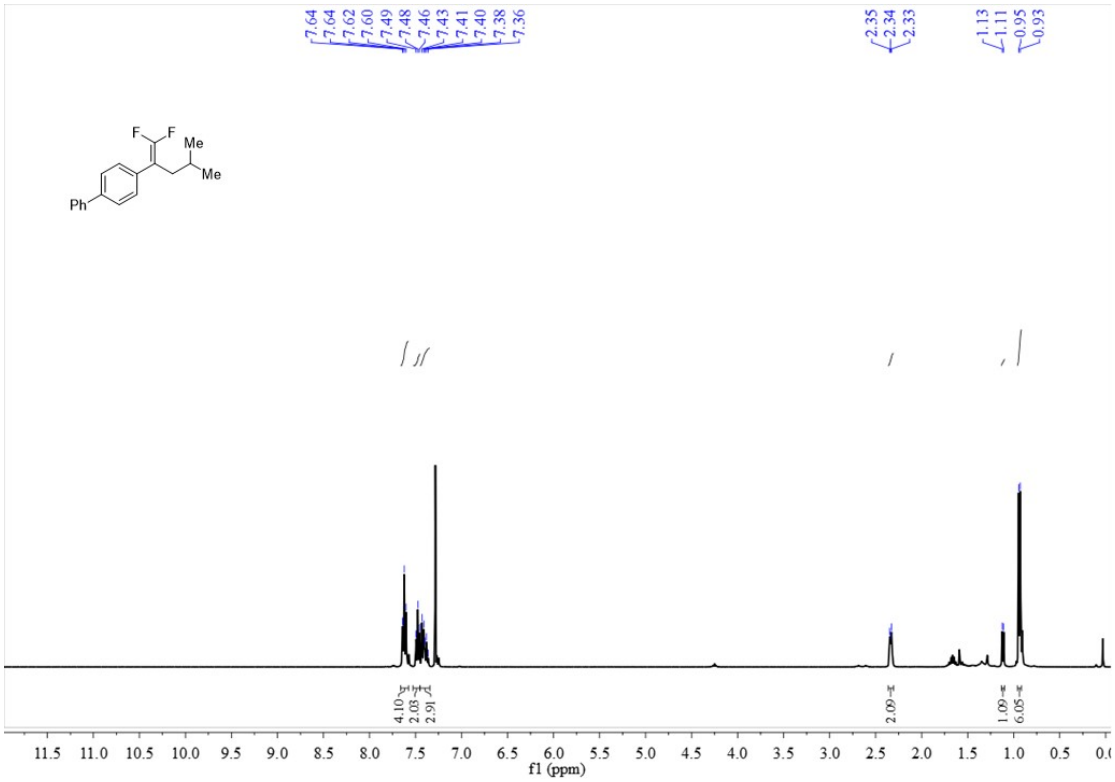
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4ea**



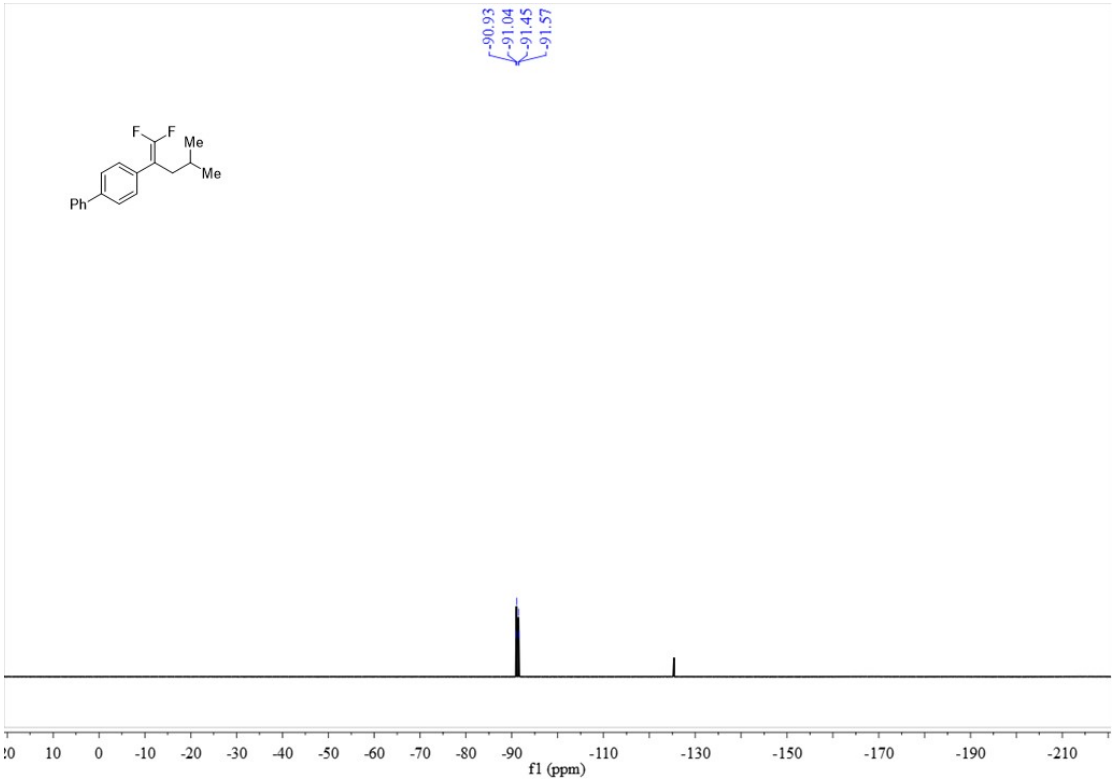
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ea**



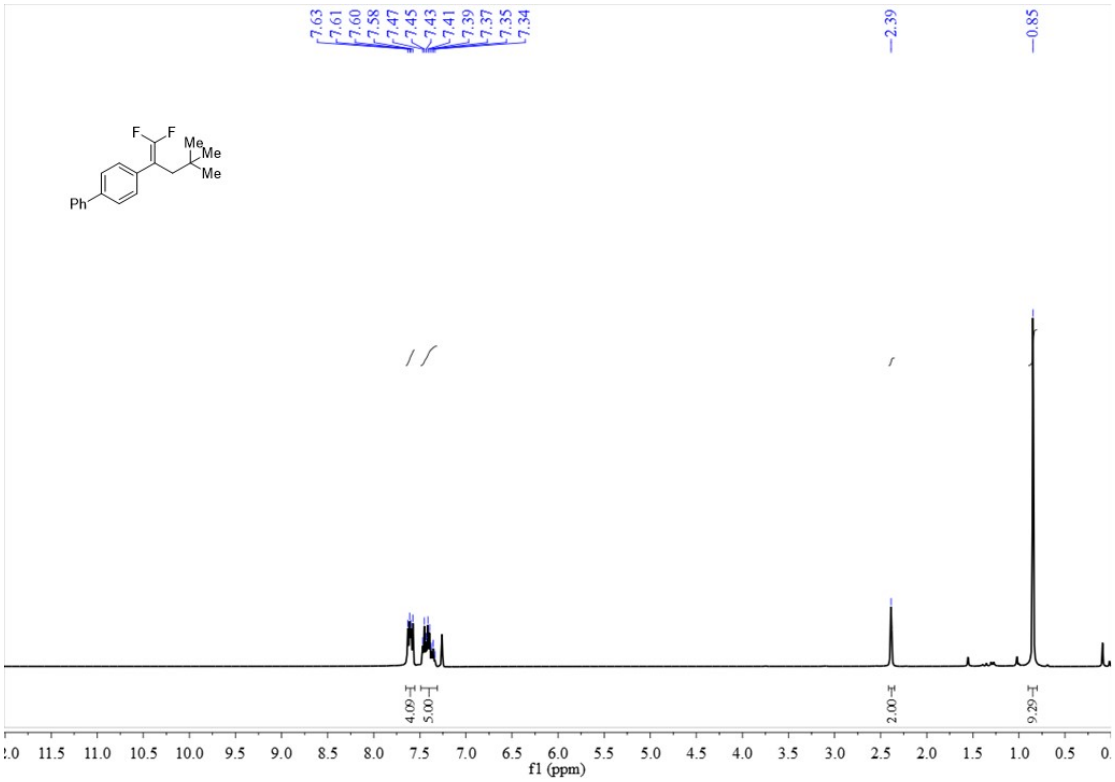
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4fa**



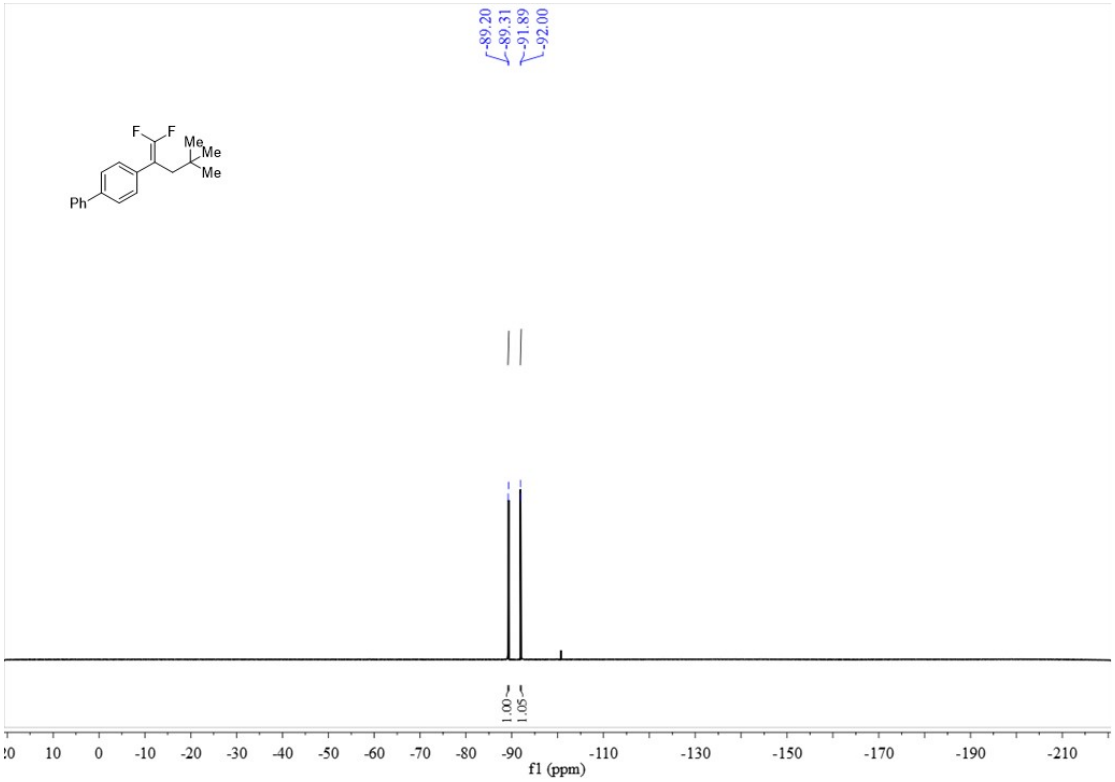
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4fa**



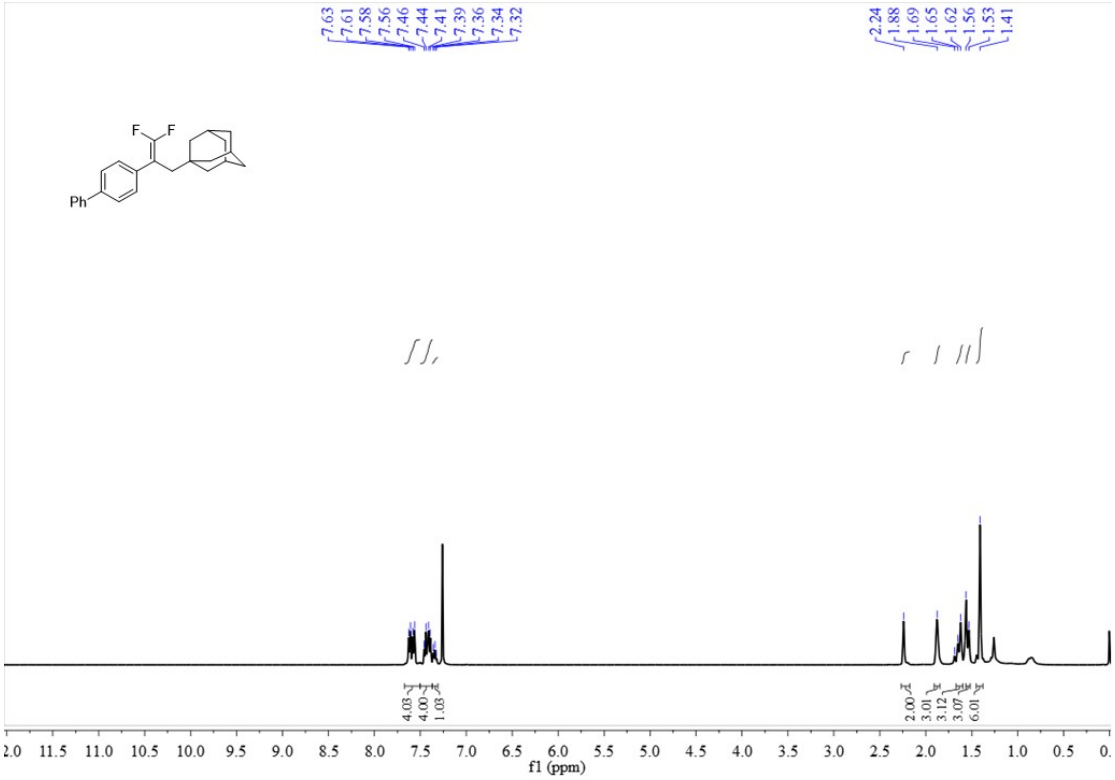
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ga**



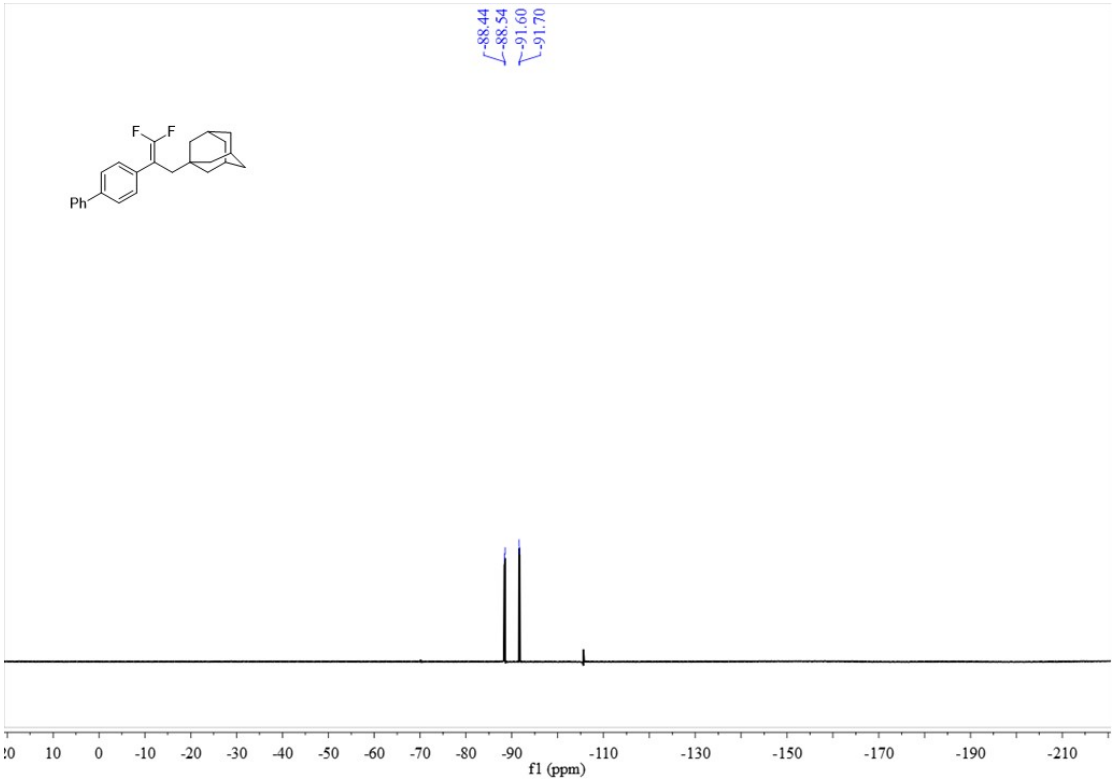
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ga**



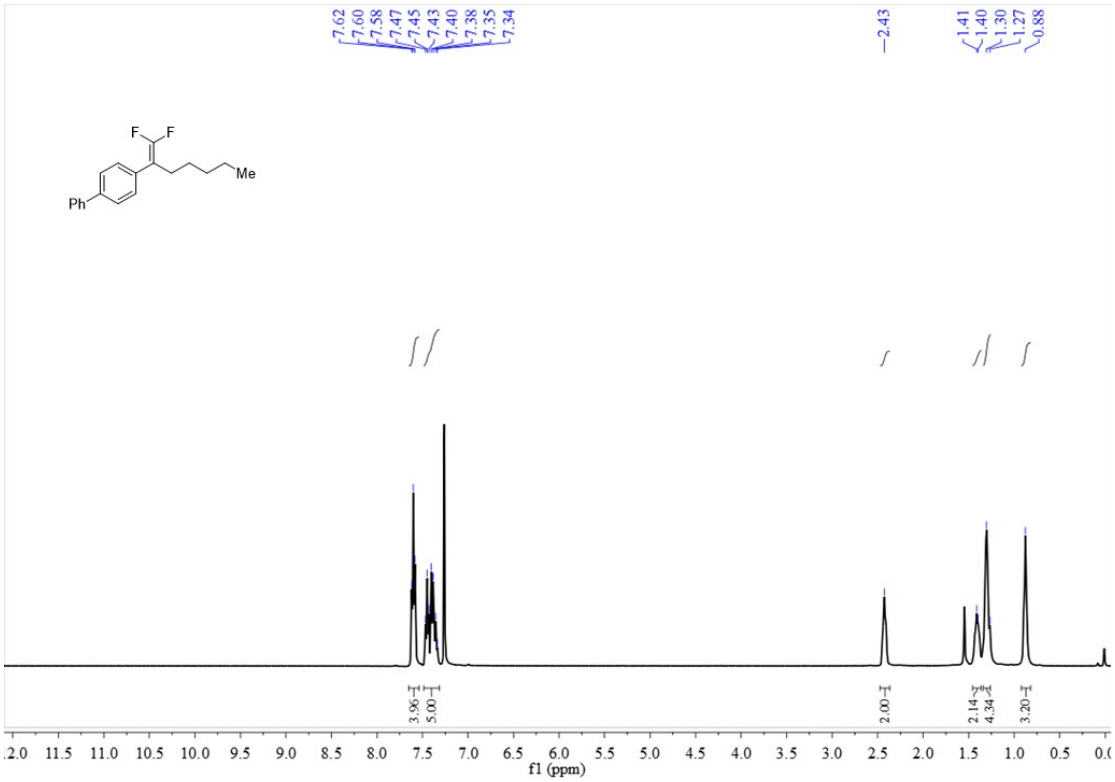
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ha**



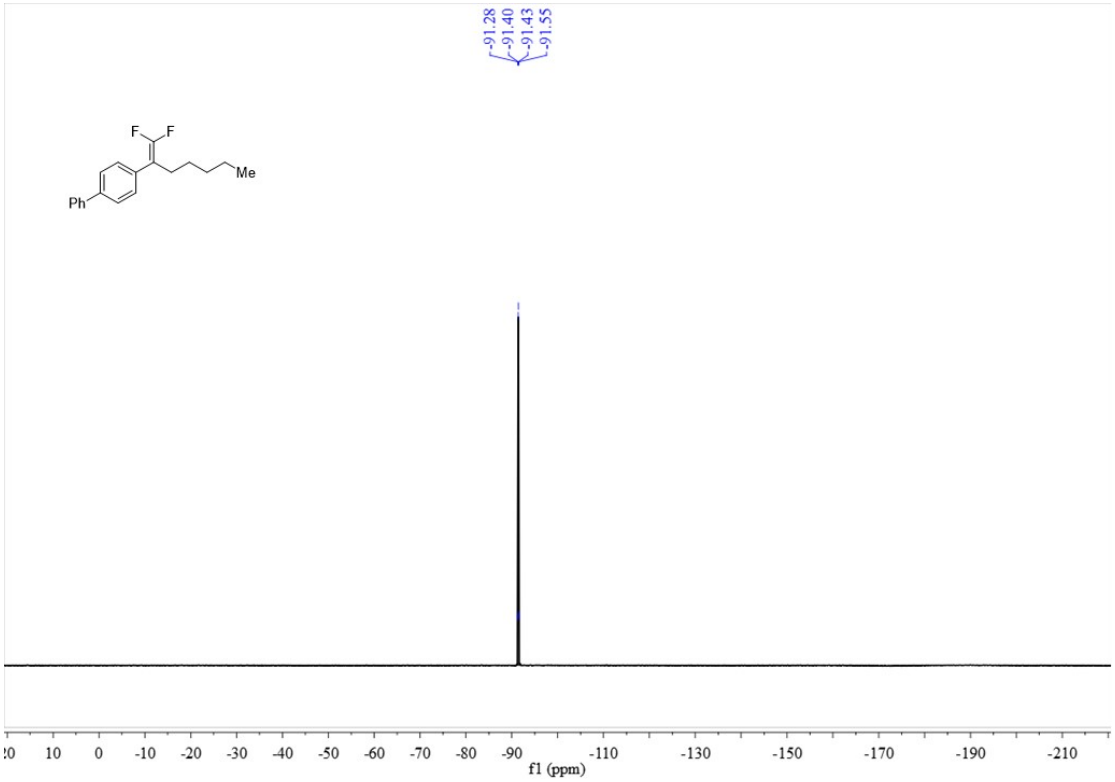
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ha**



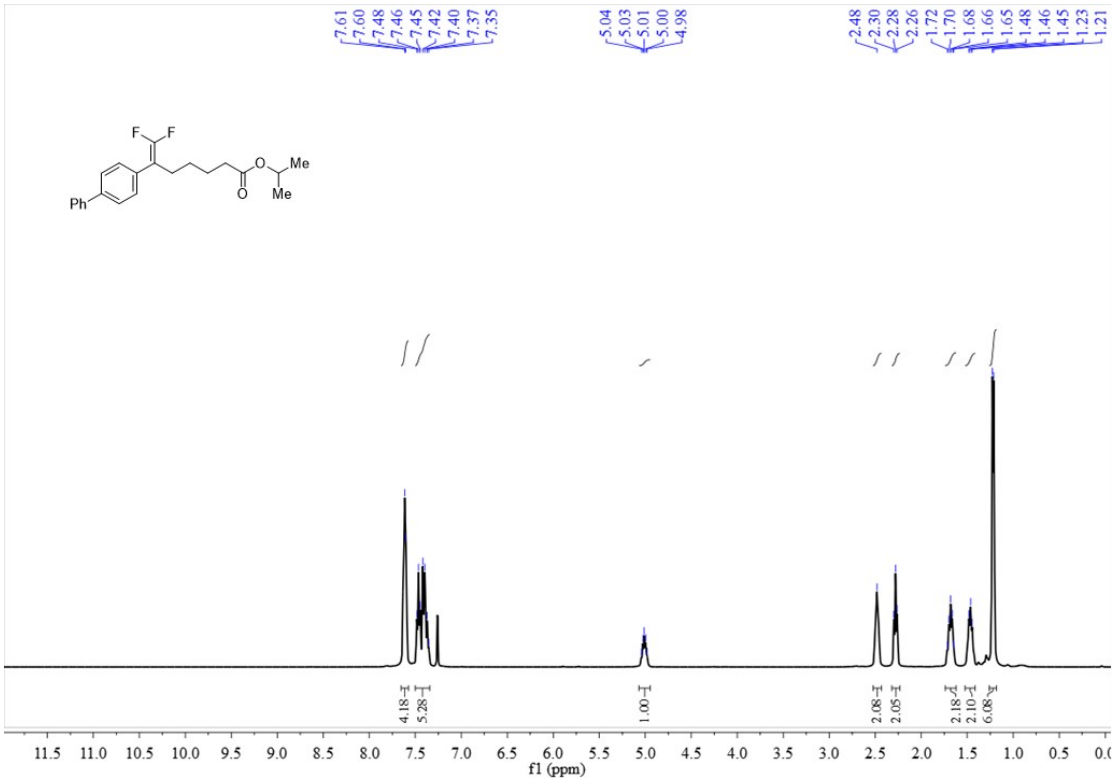
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ia**



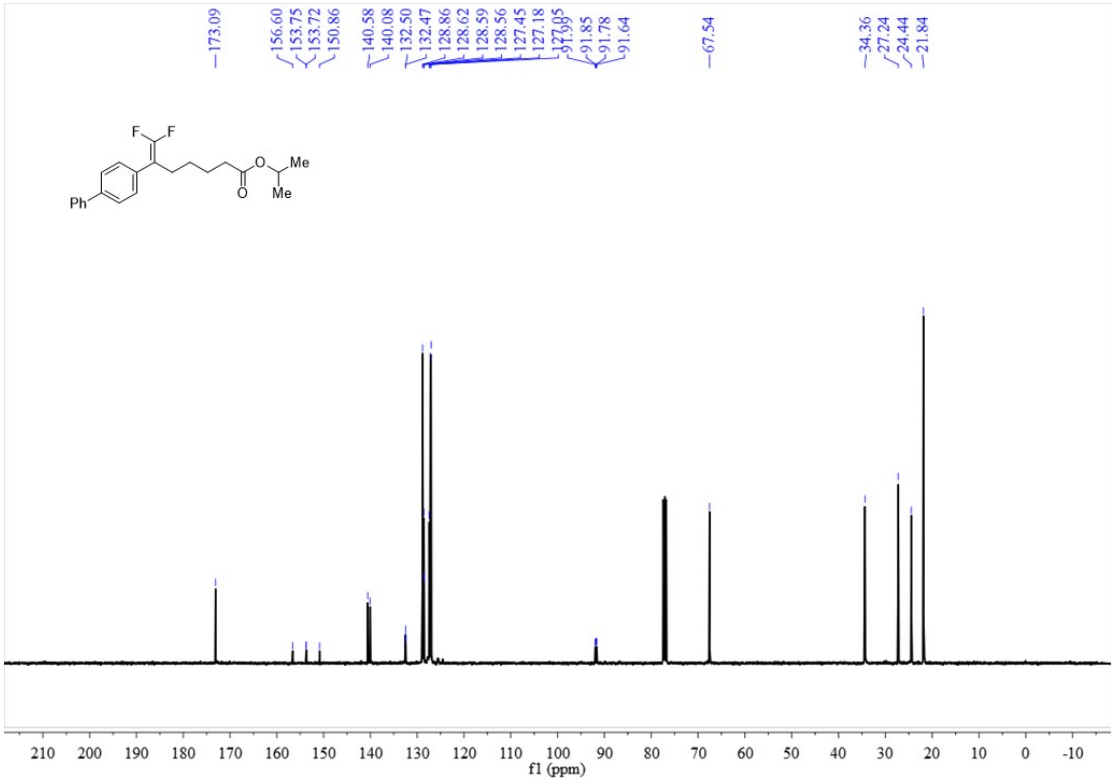
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ia**



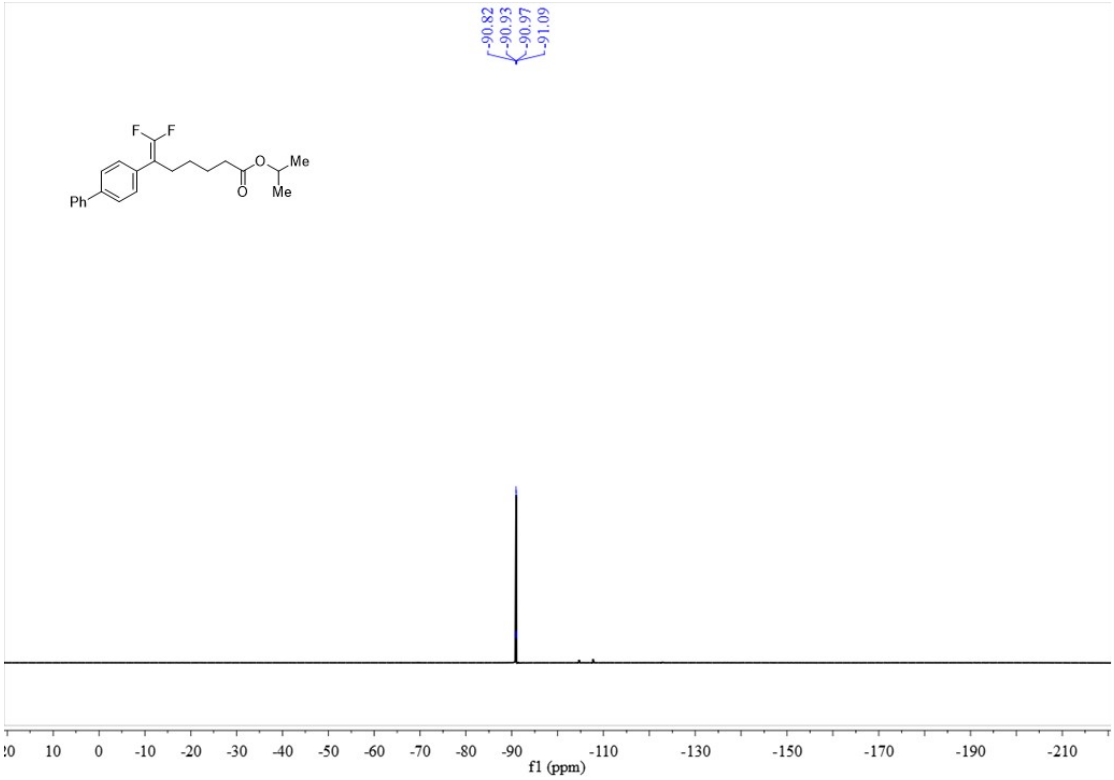
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ja**



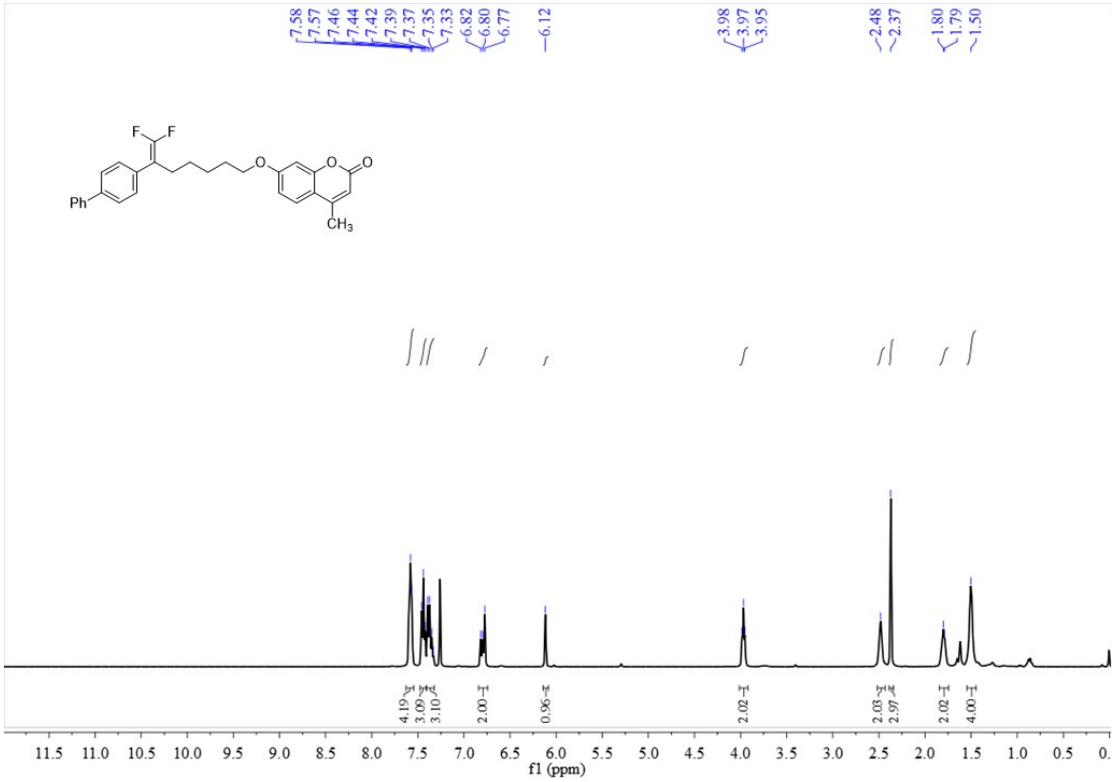
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4ja**



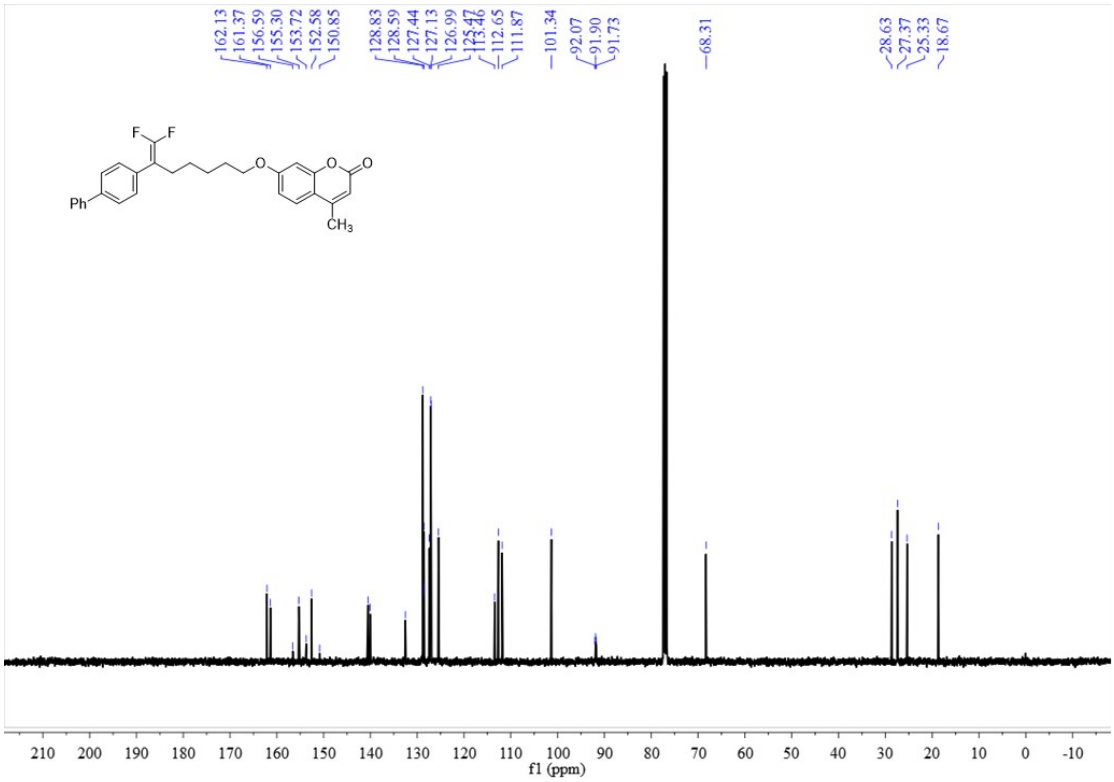
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ja**



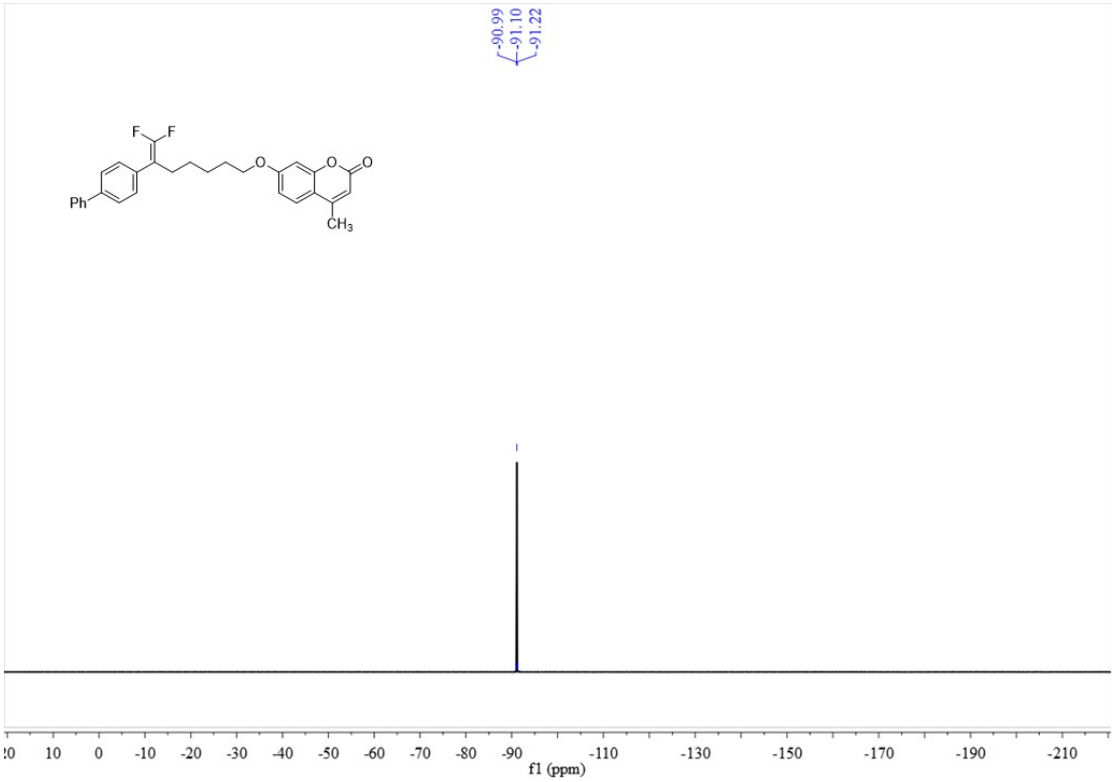
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ka**



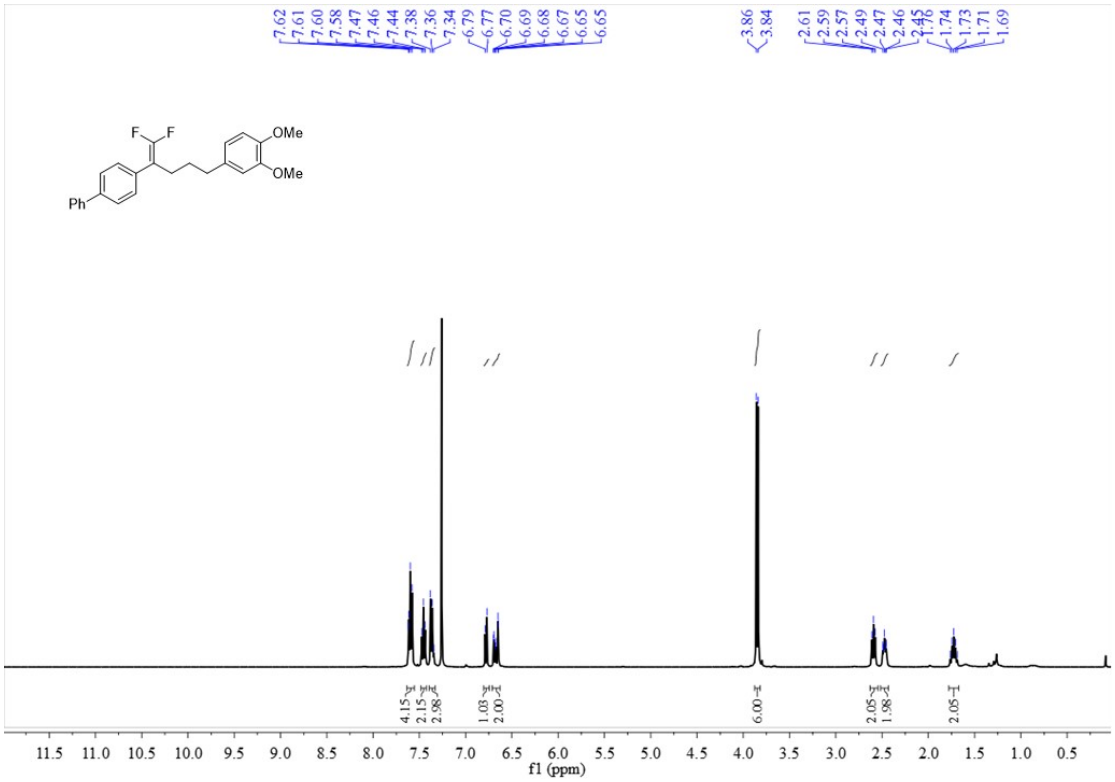
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4ka**



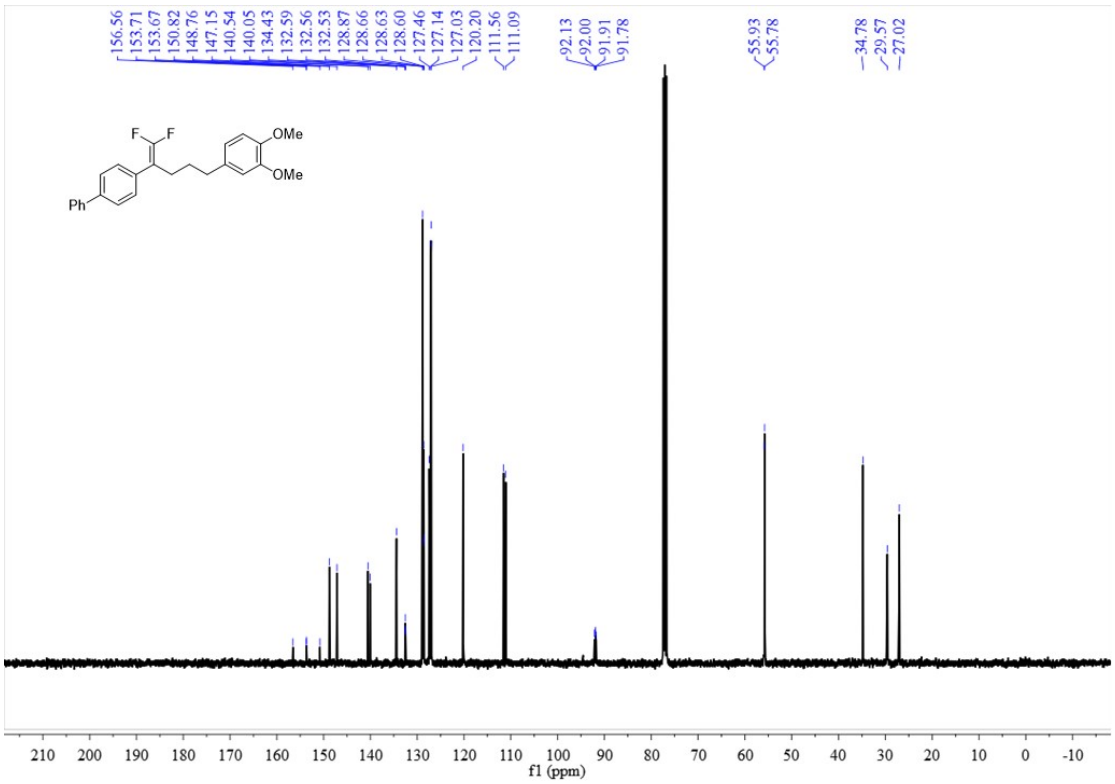
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ka**



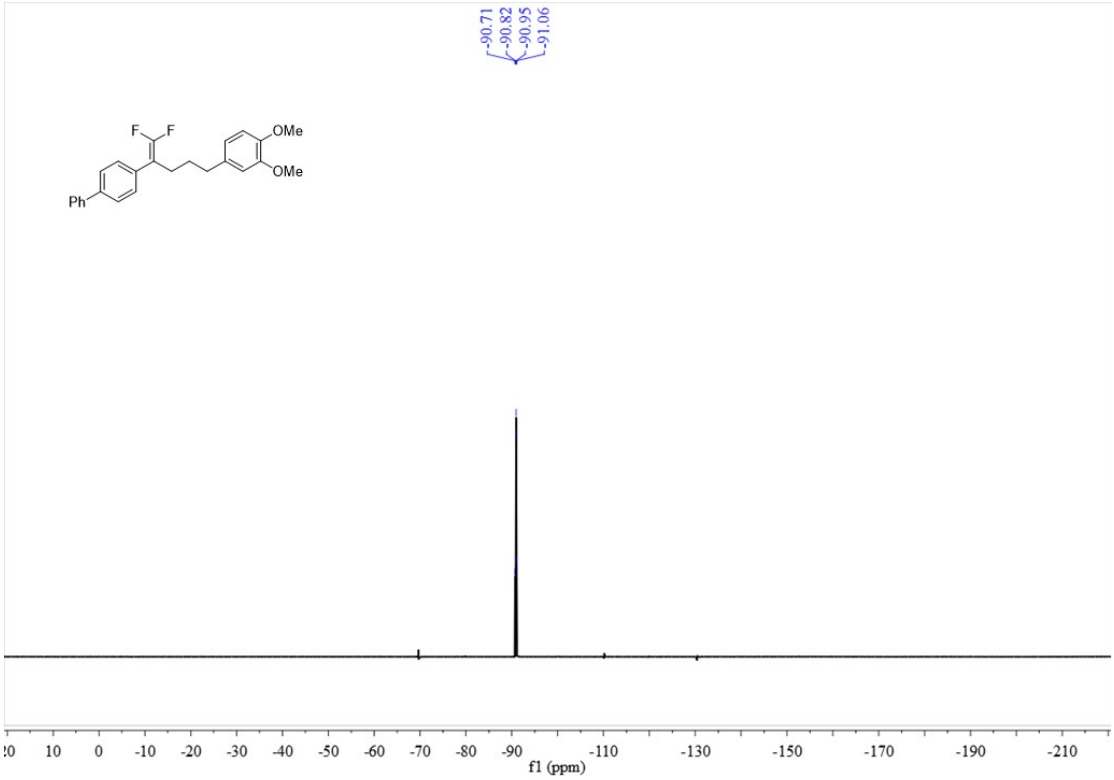
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4la**



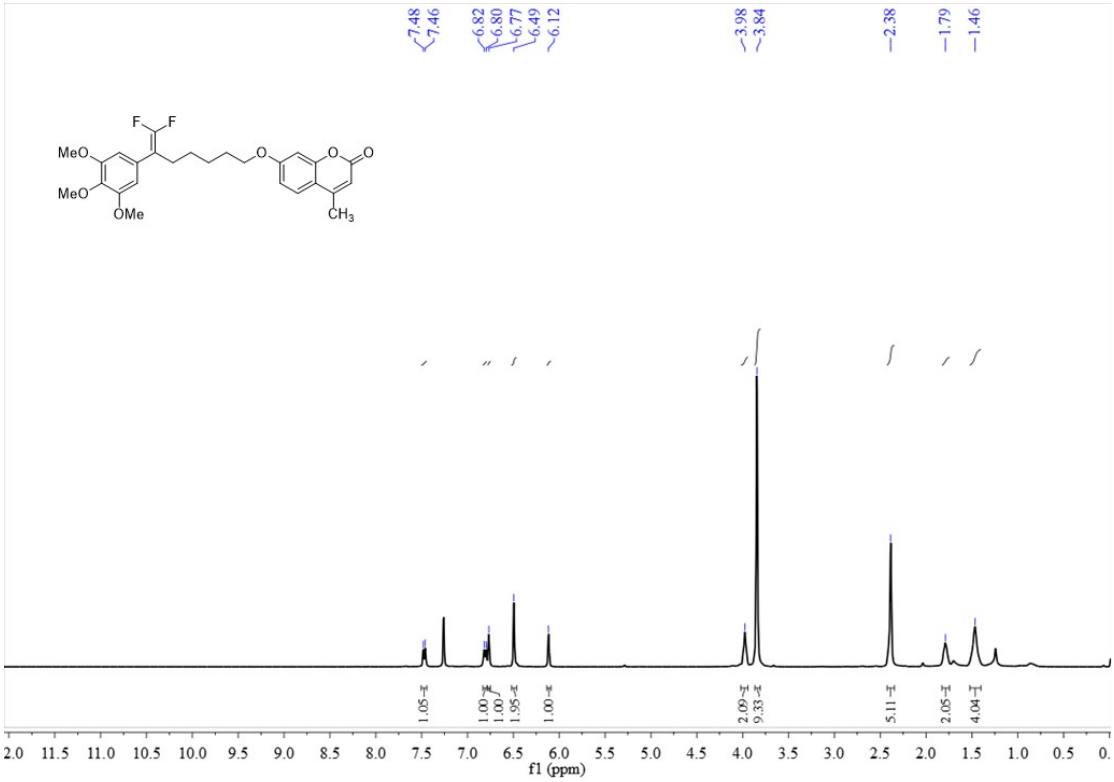
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4la**



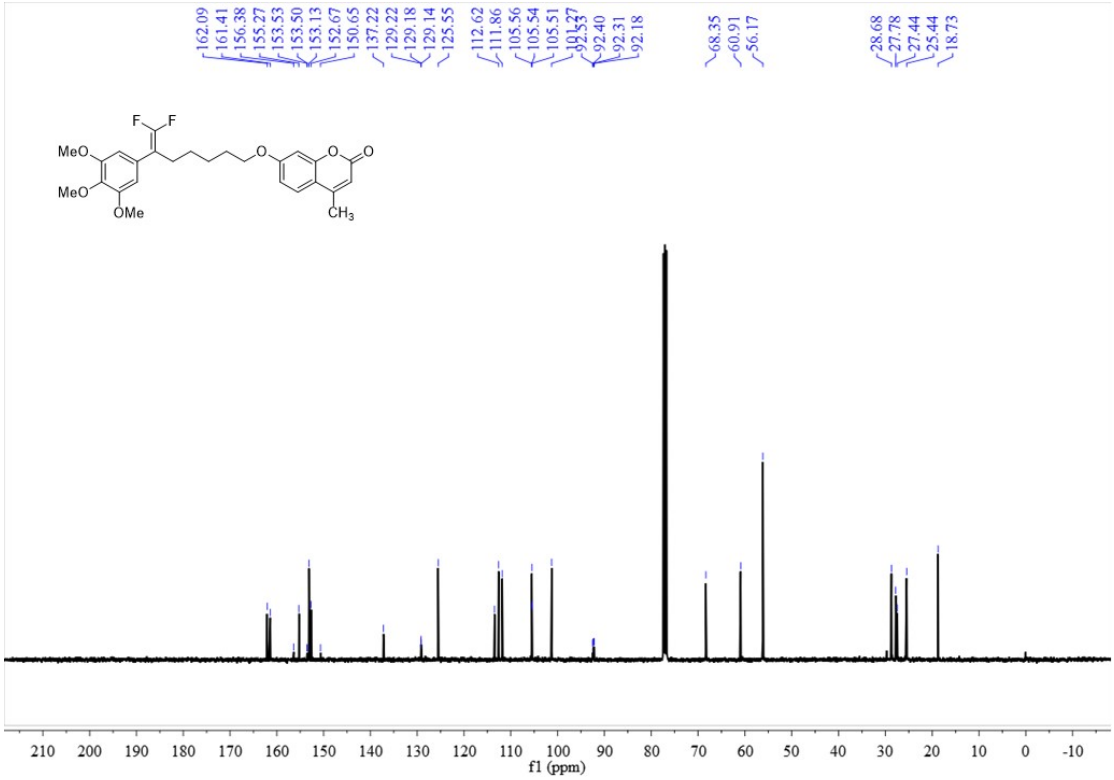
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4la**



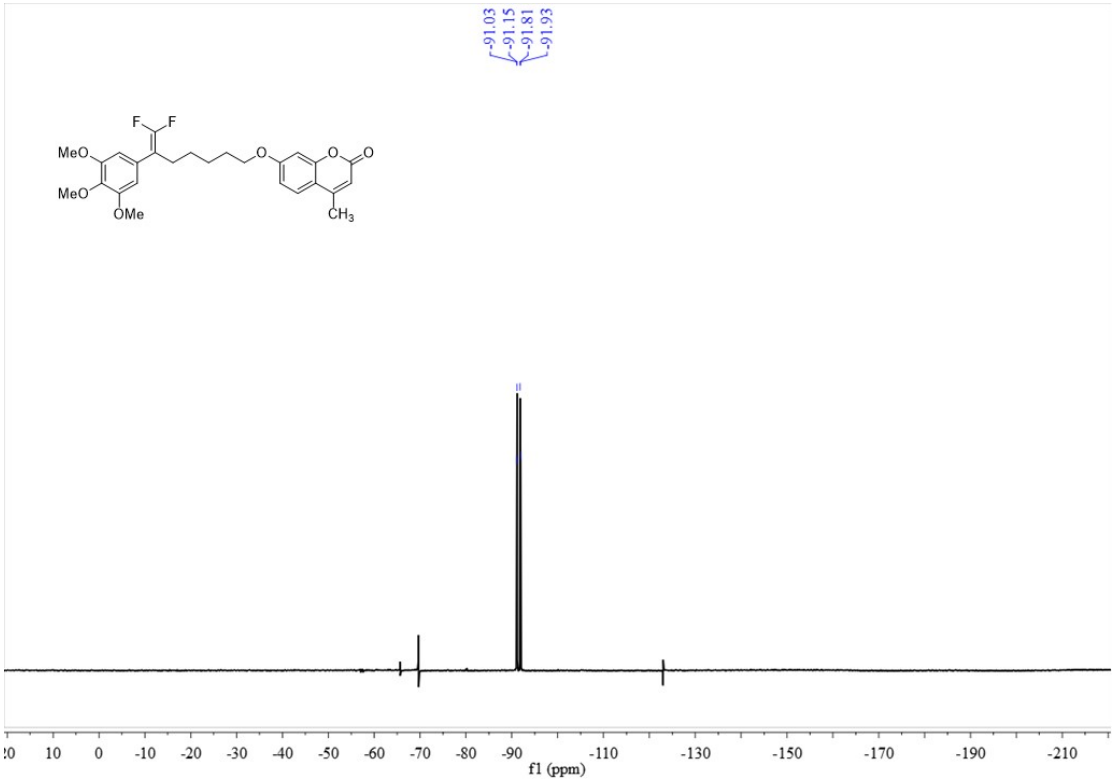
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4md**



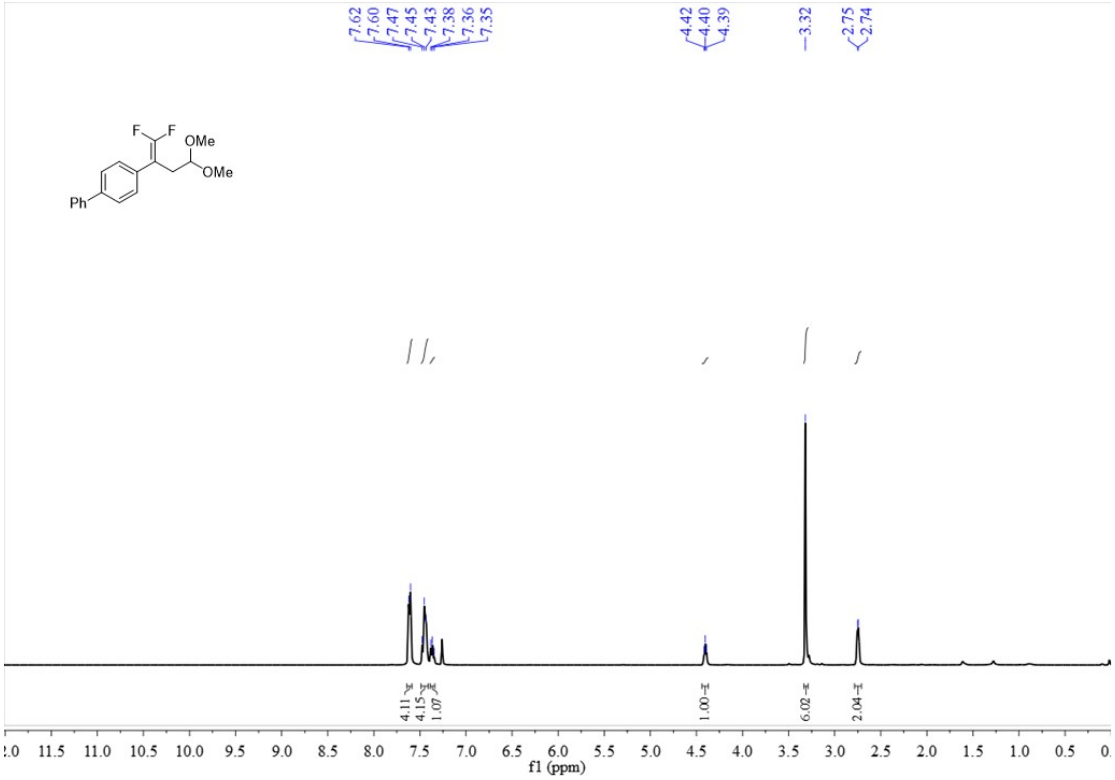
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4md**



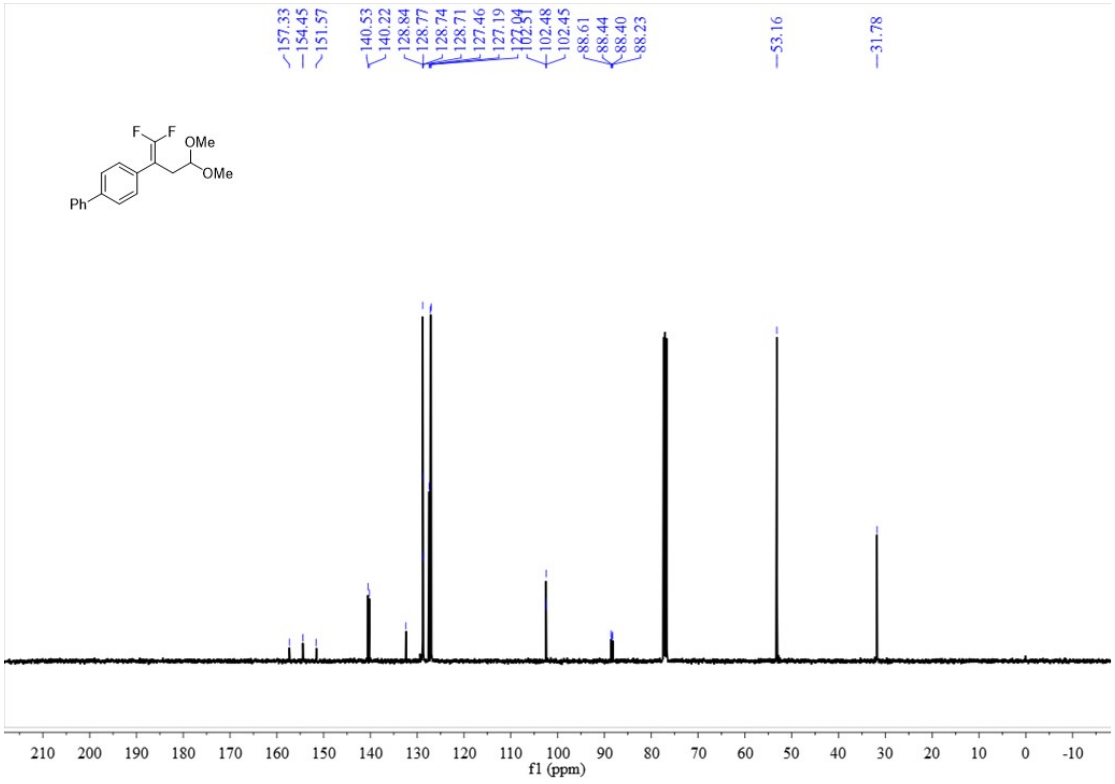
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4md**



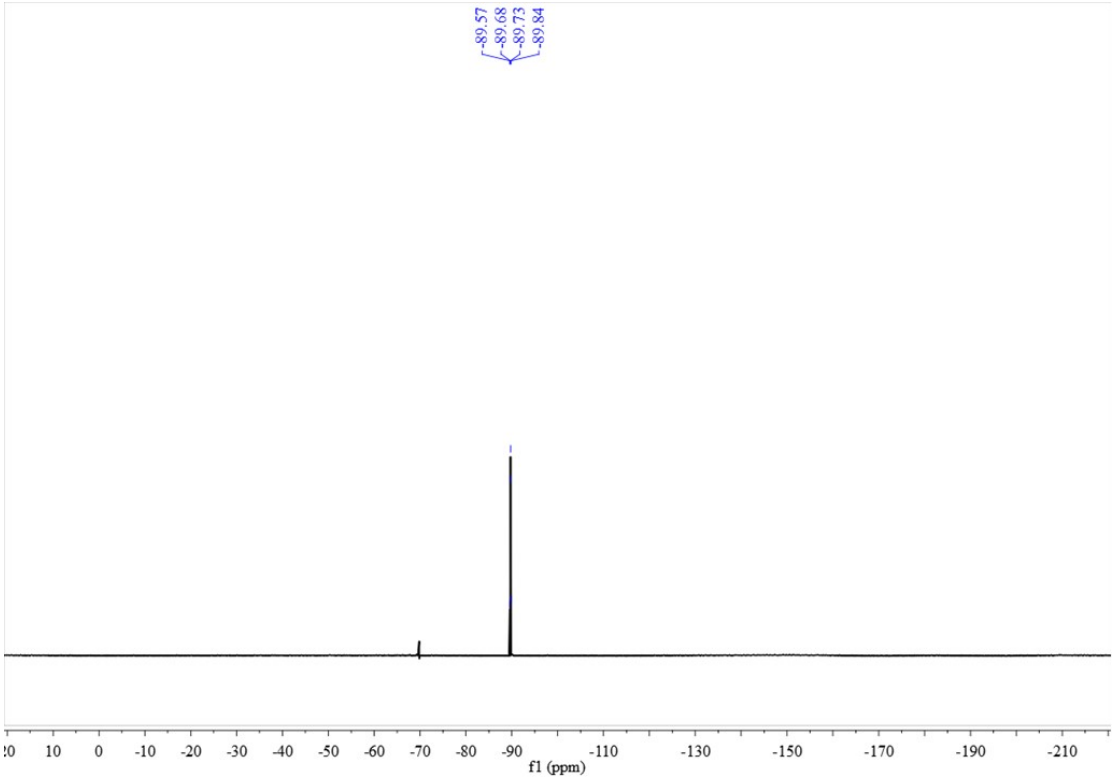
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4na**



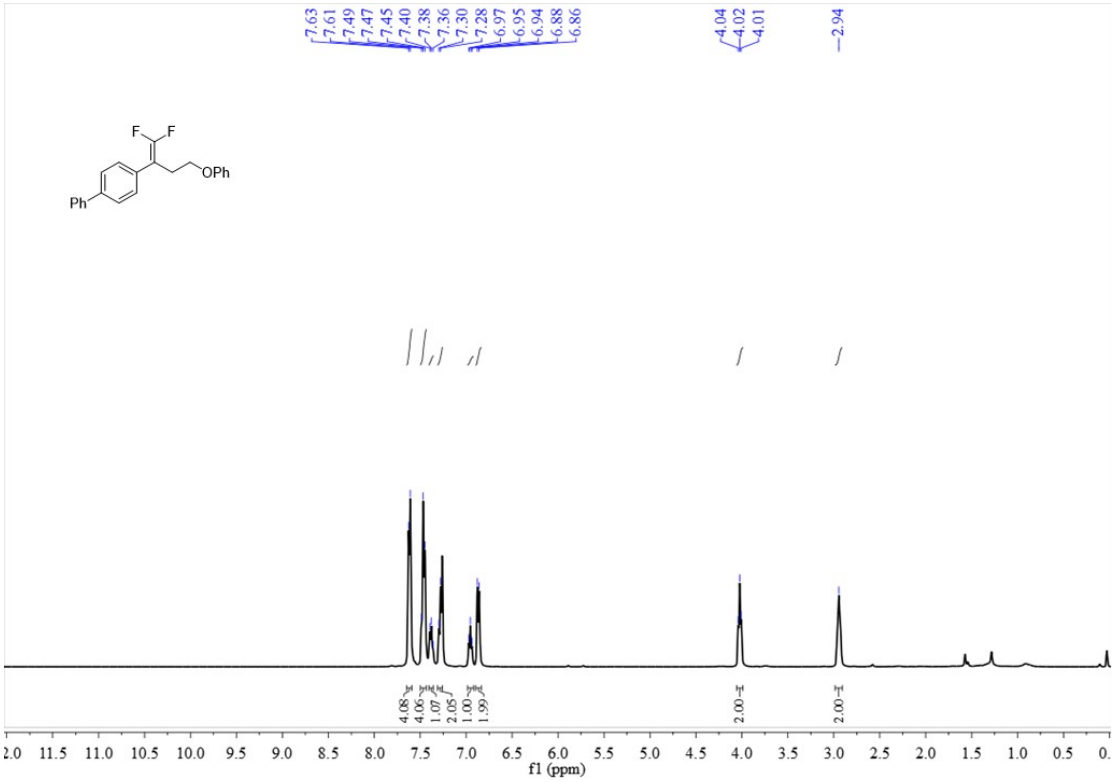
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4na**



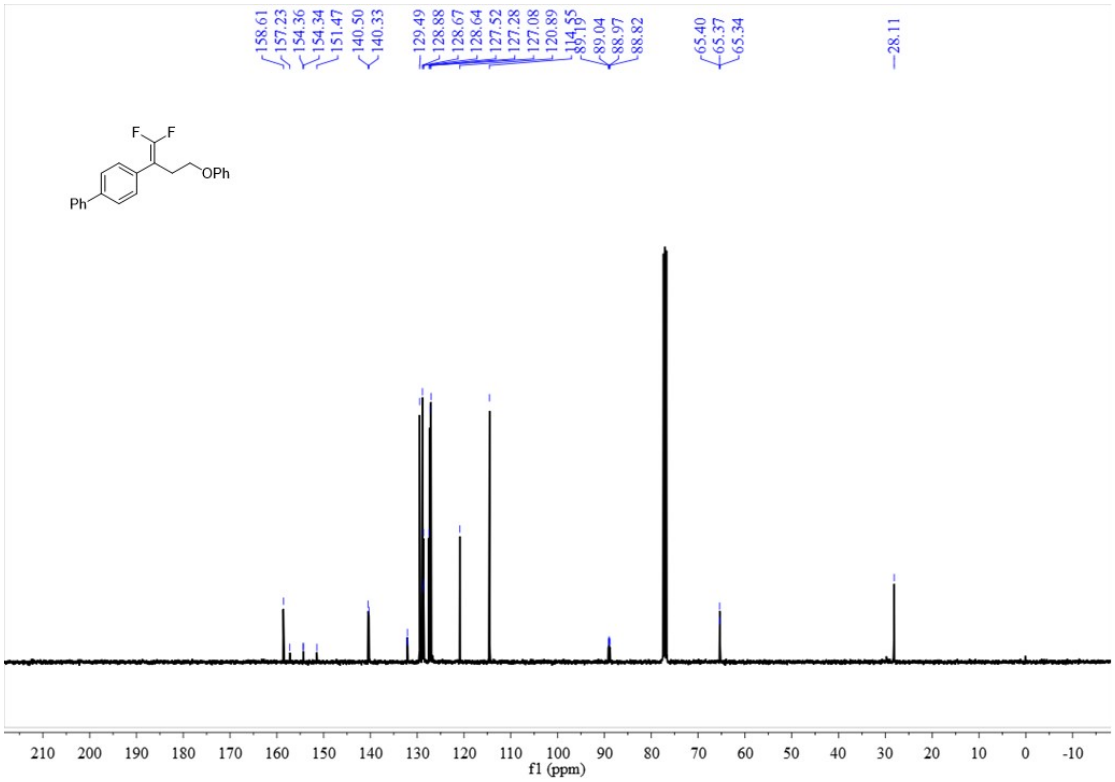
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4na**



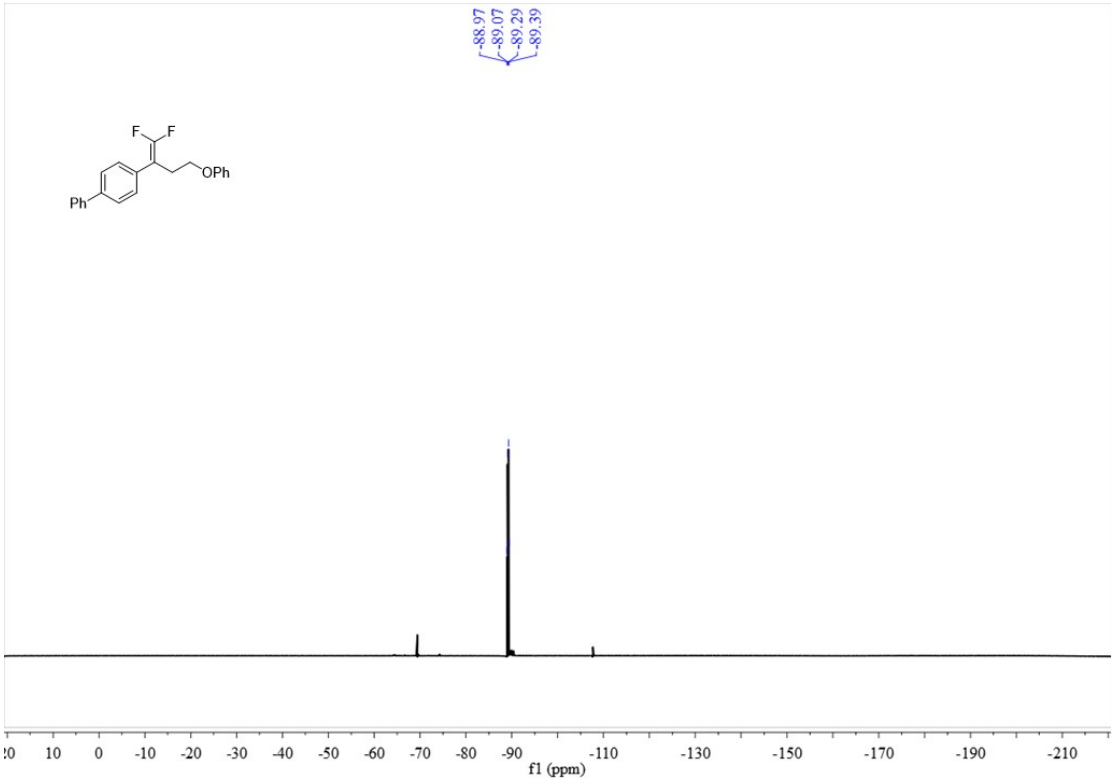
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4oa**



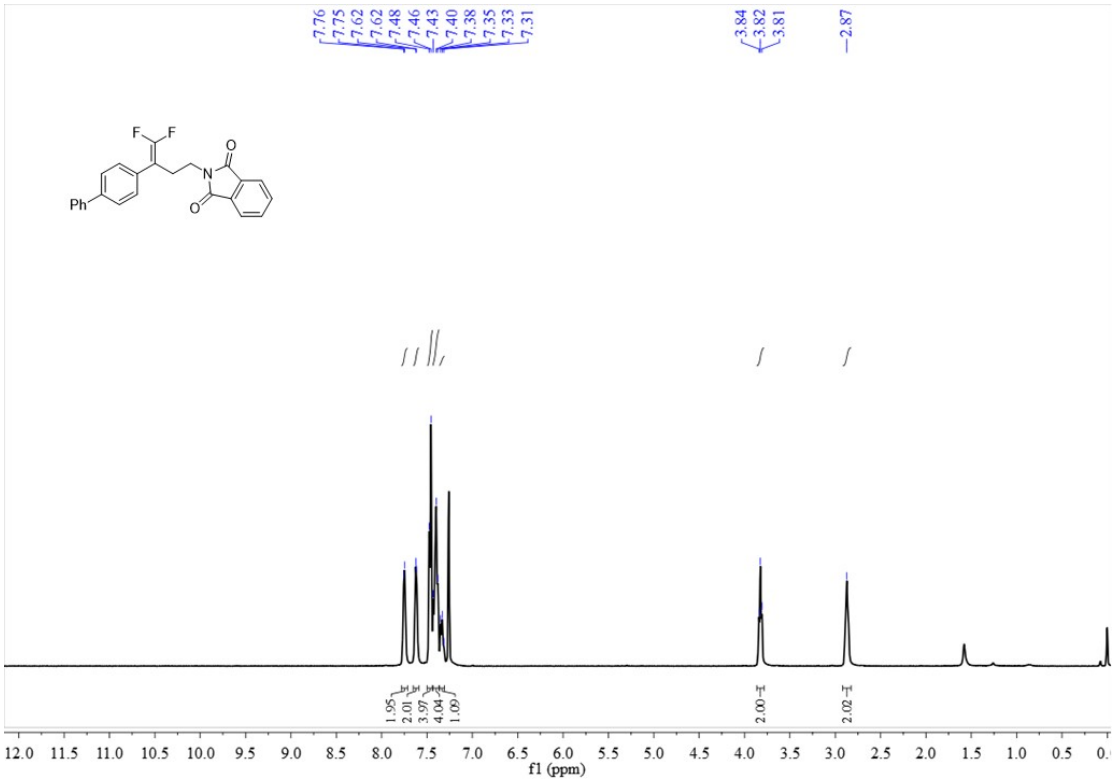
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4oa**



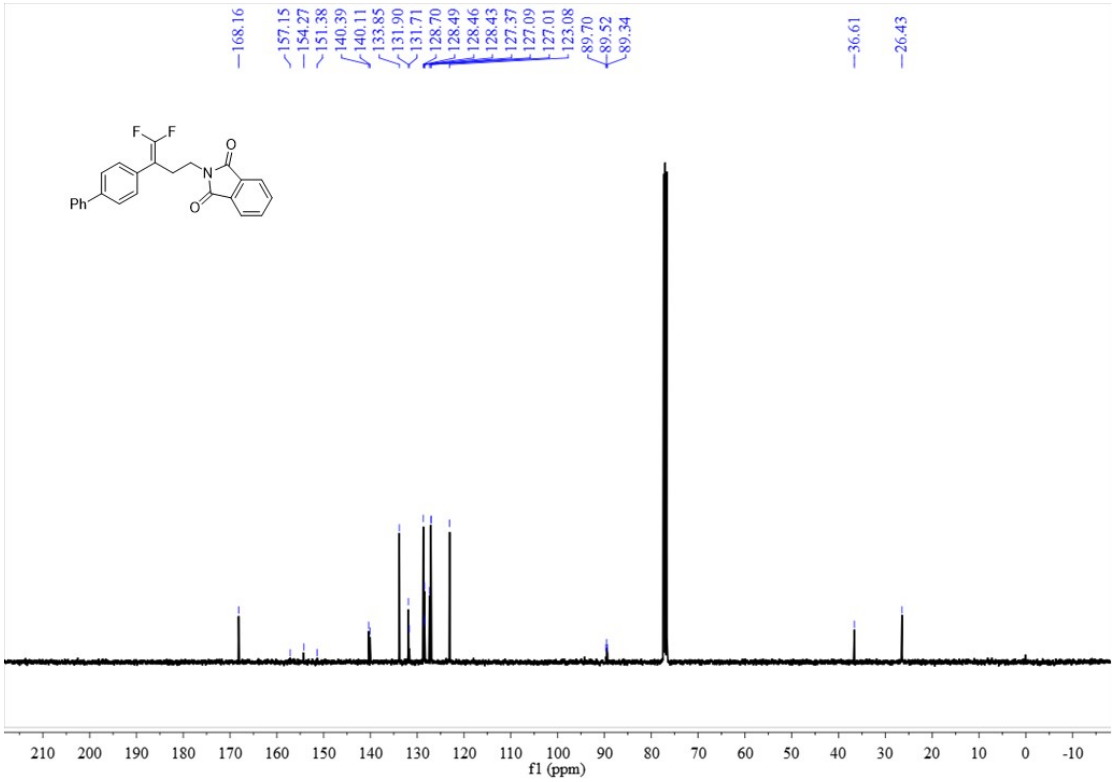
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4oa**



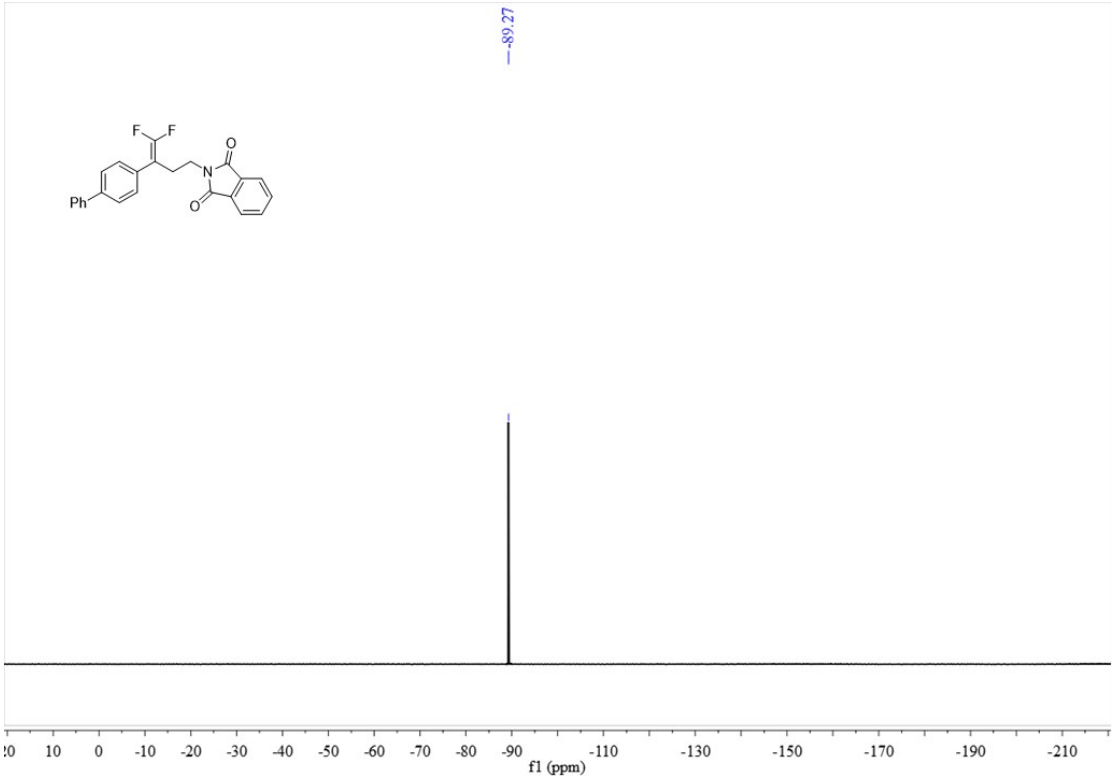
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4pa**



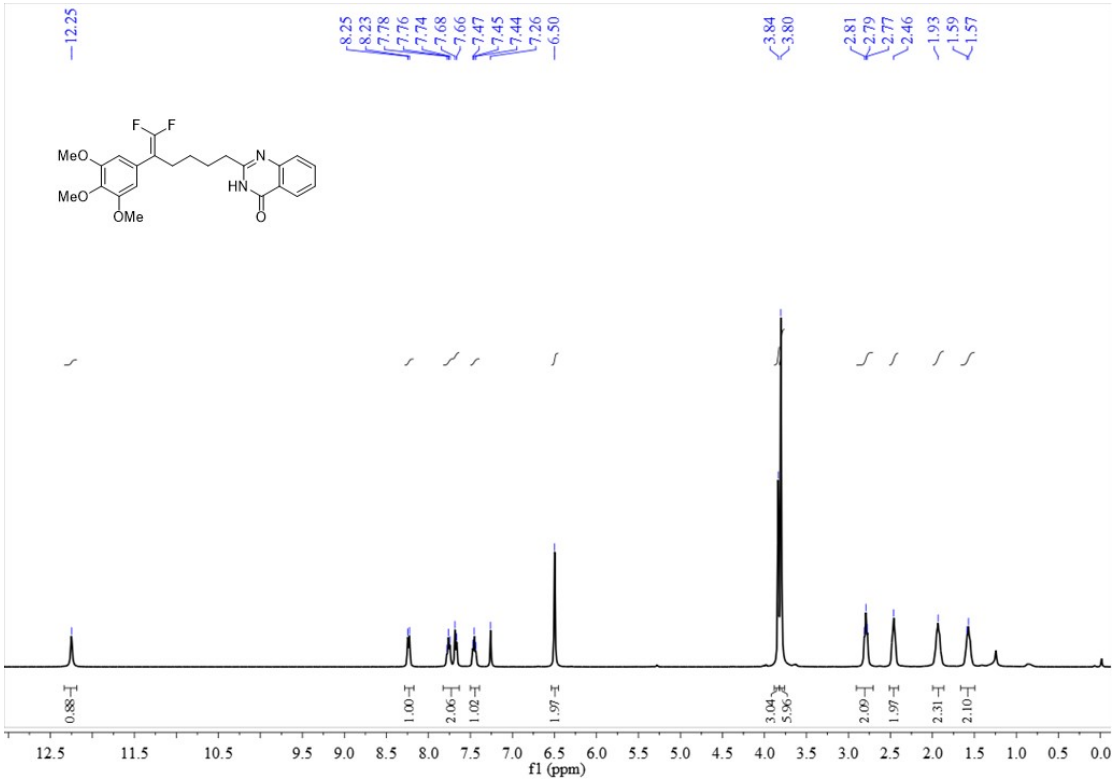
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4pa**



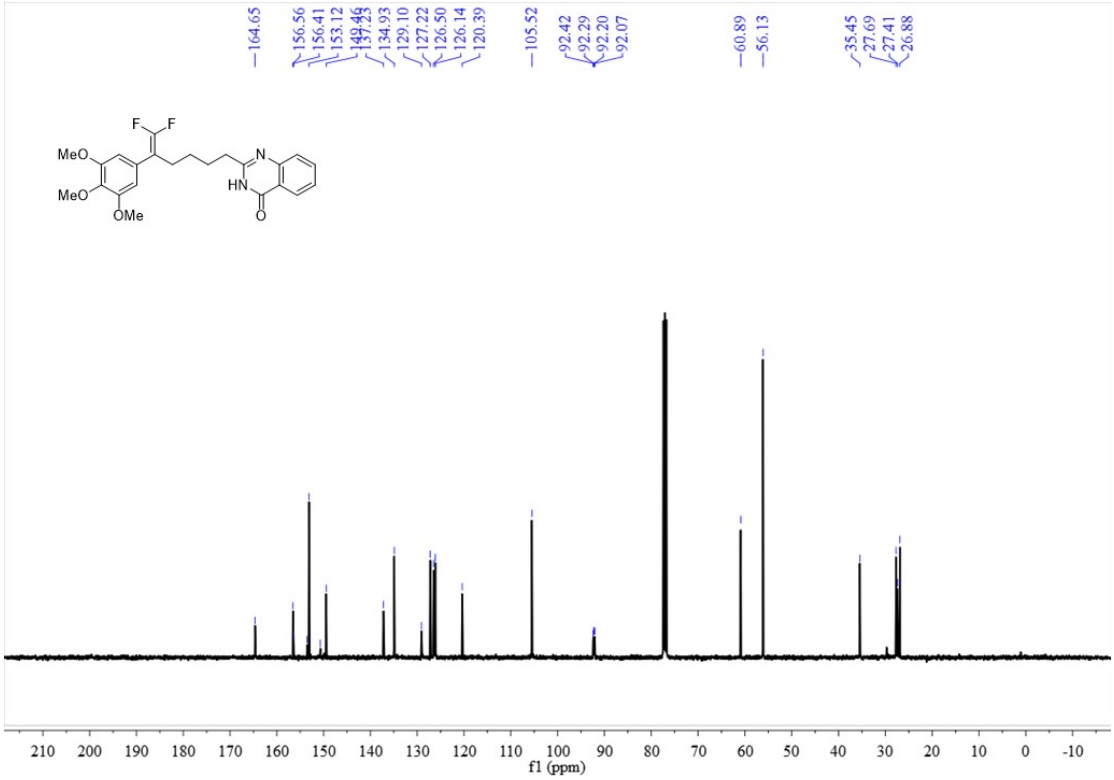
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4pa**



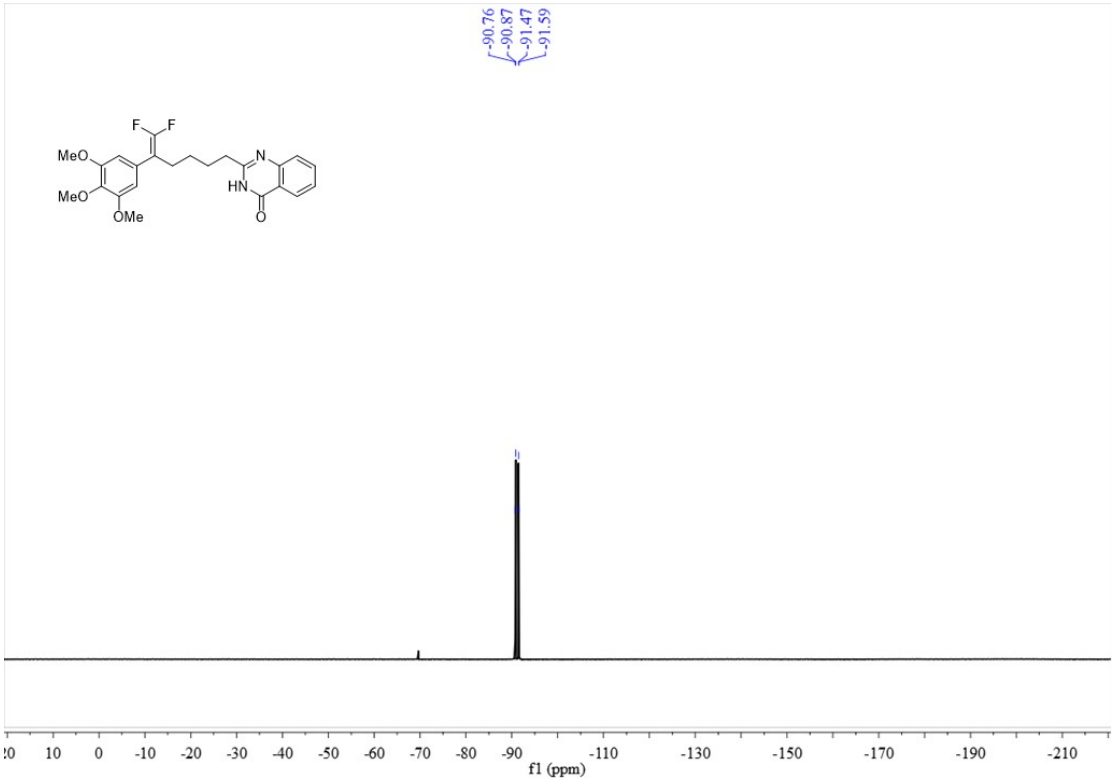
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4qd**



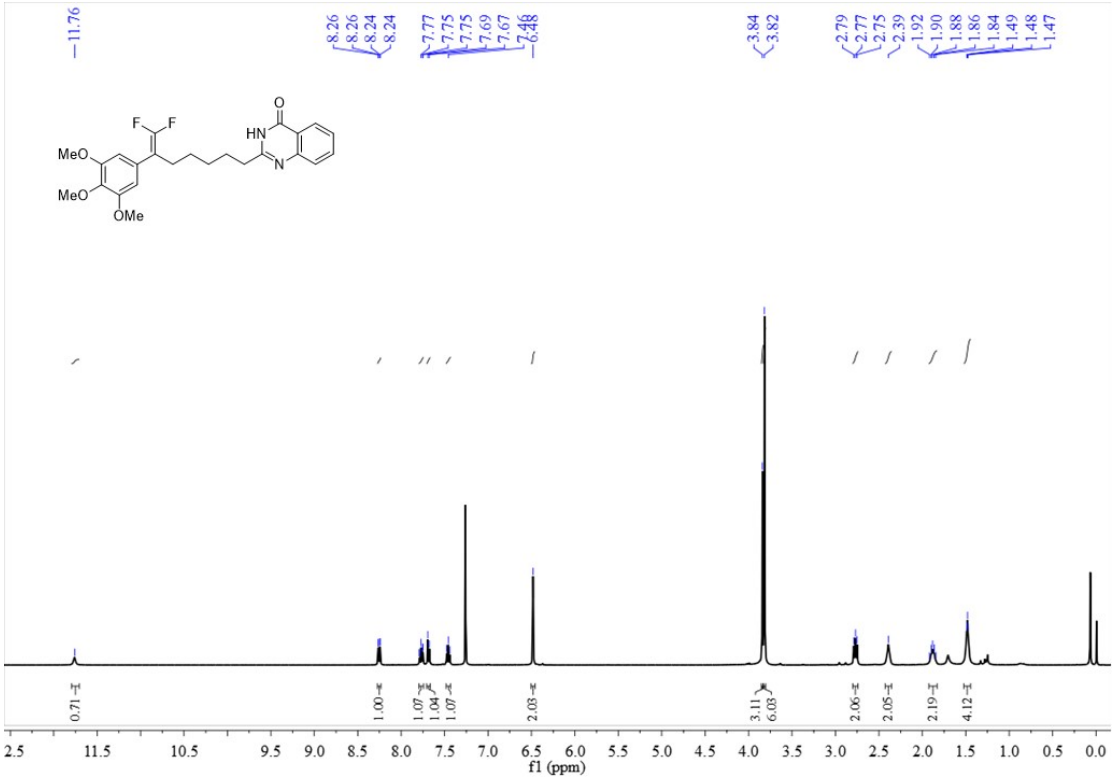
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4qd**



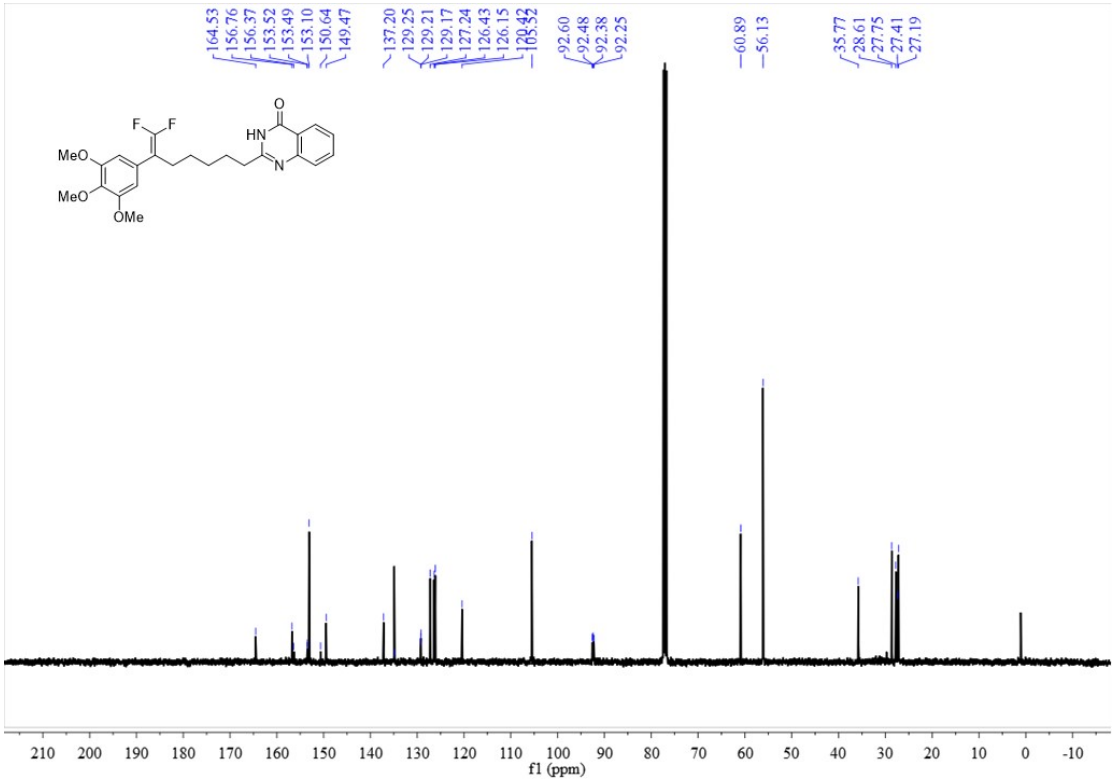
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4qd**



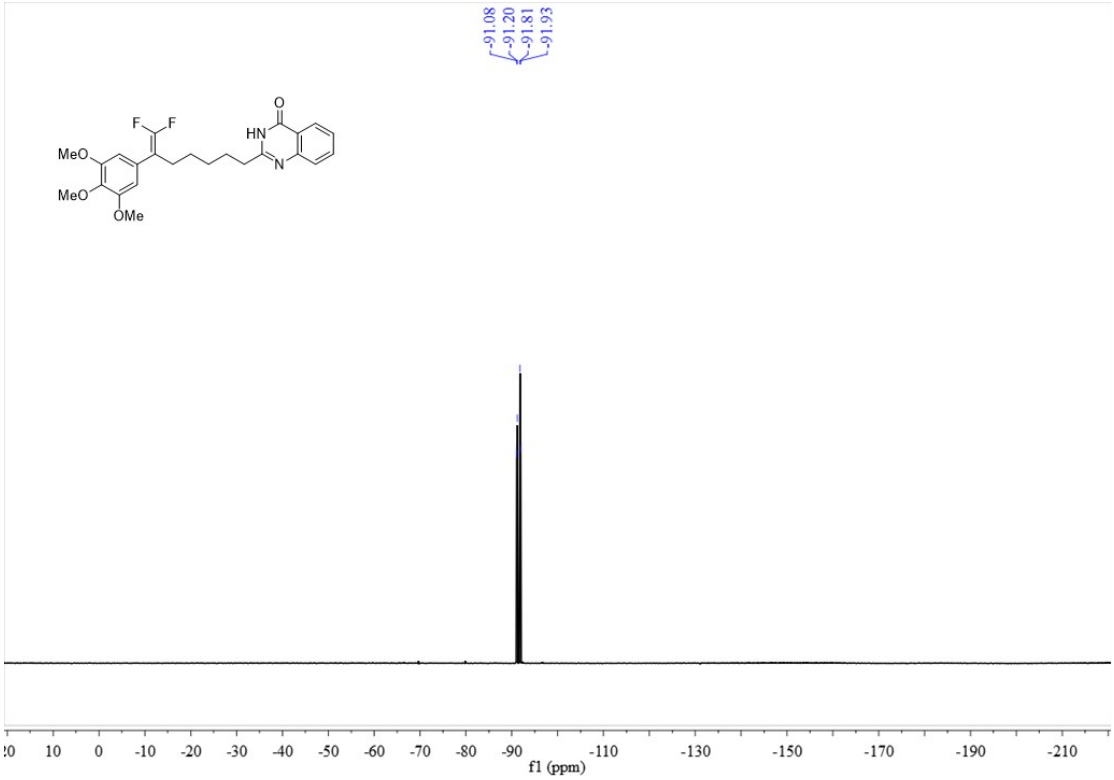
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4rd**



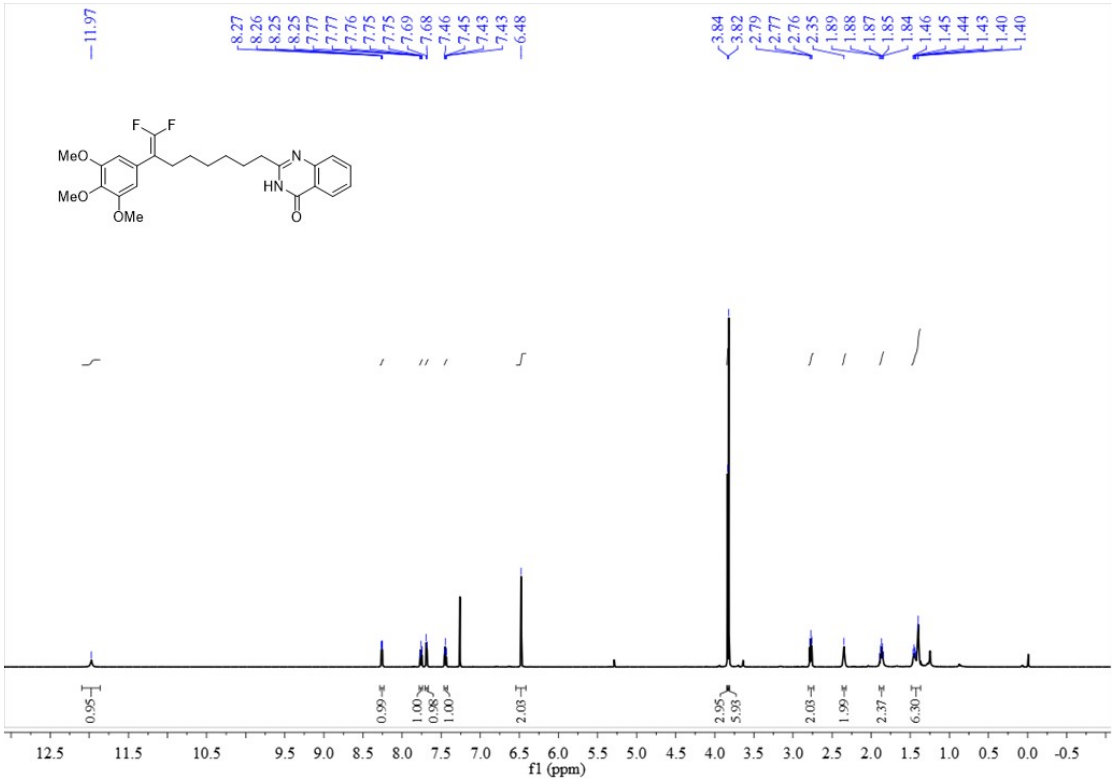
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4rd**



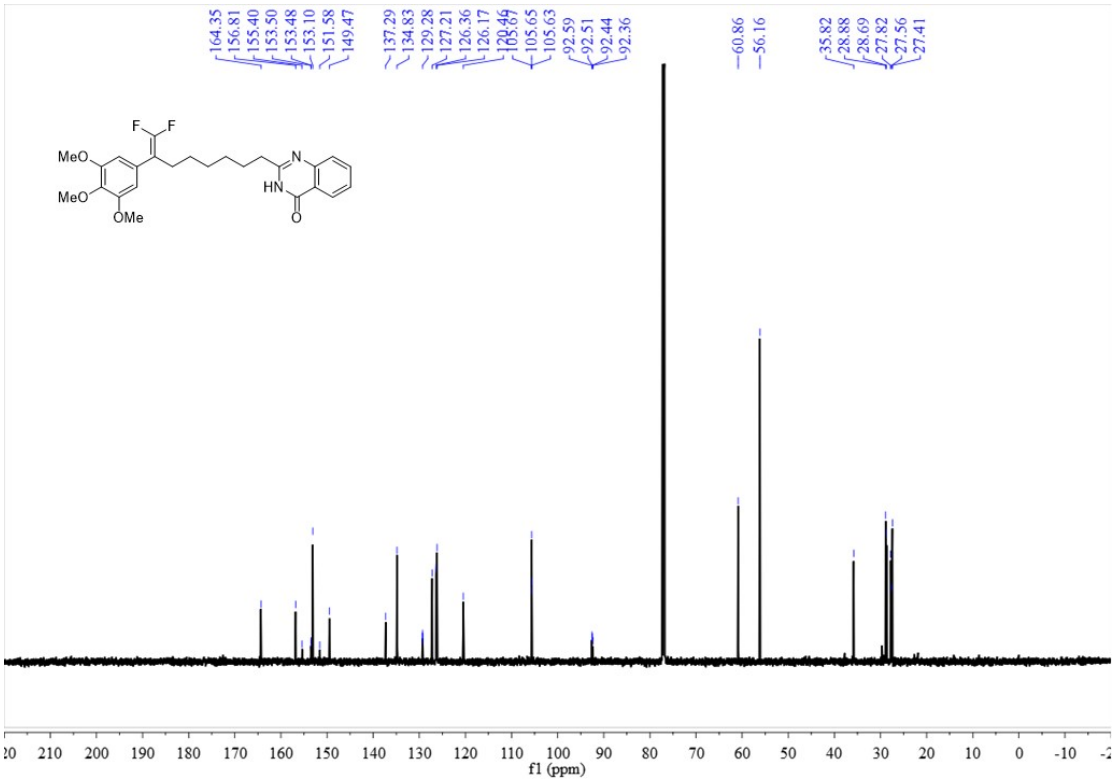
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4rd**



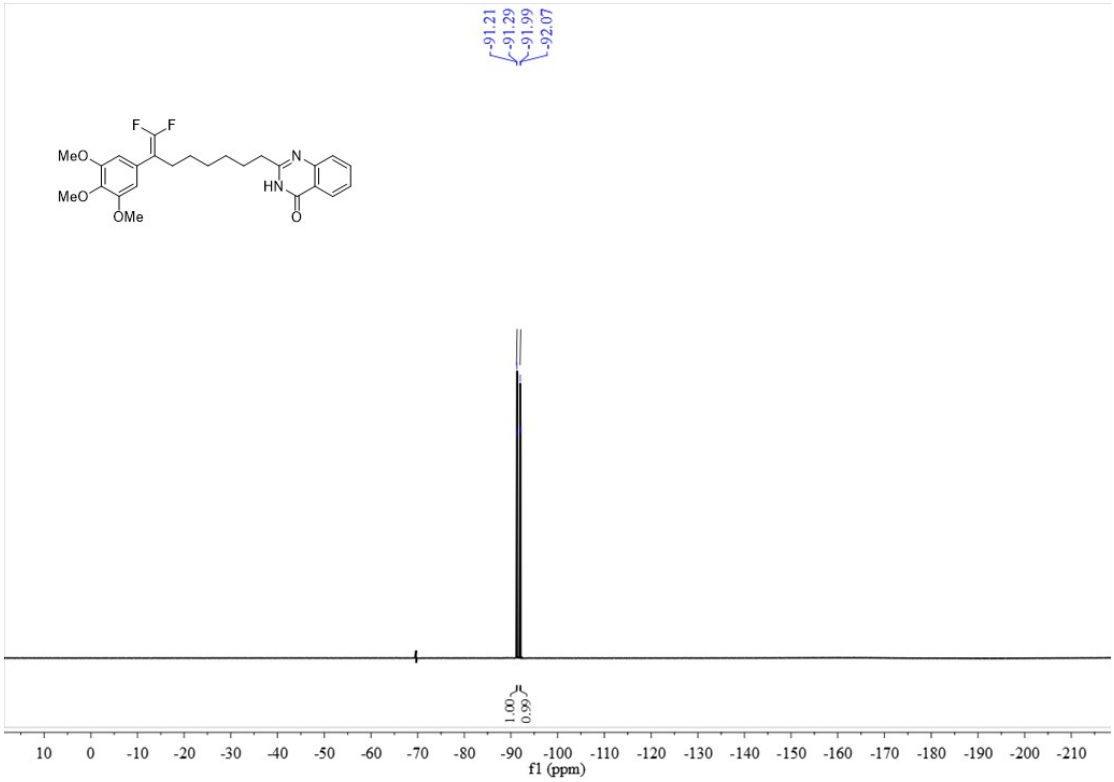
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **4sd**



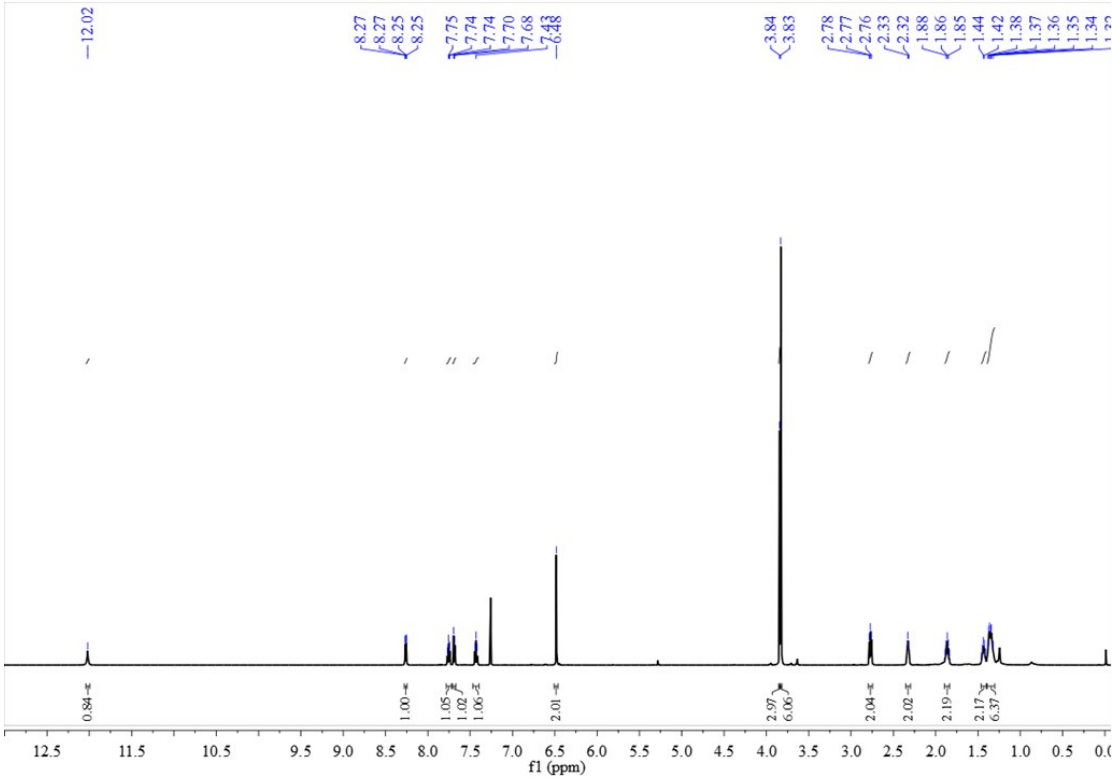
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **4sd**



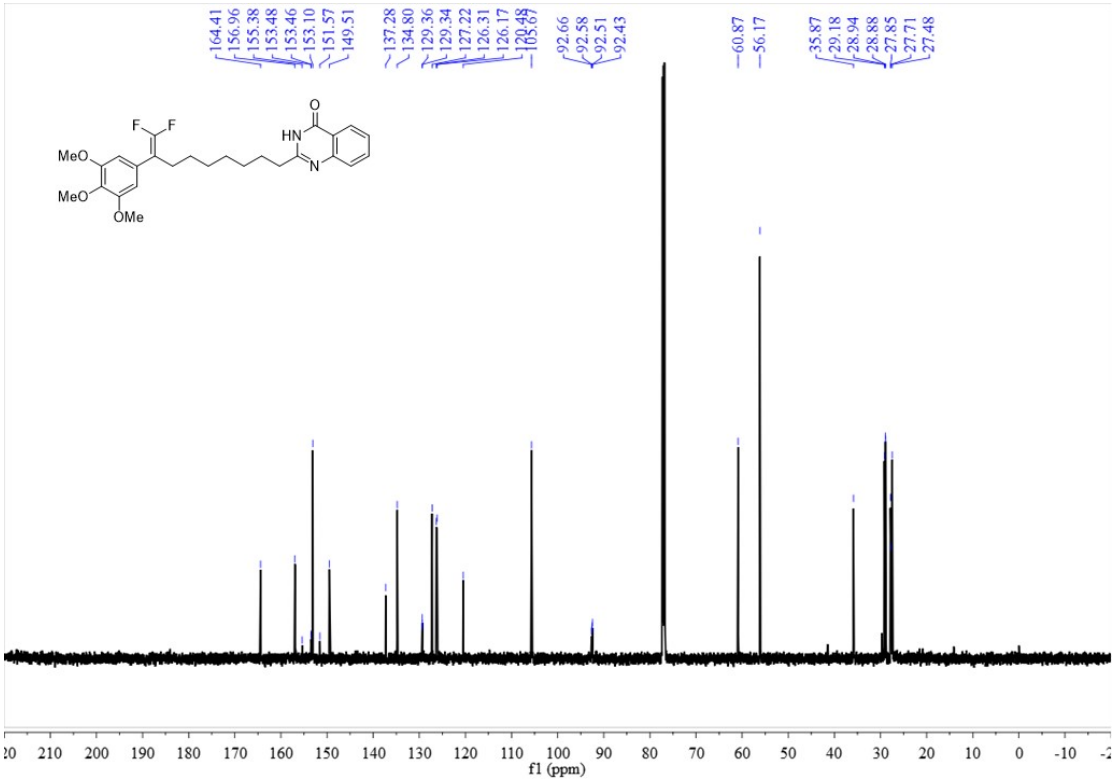
^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **4sd**



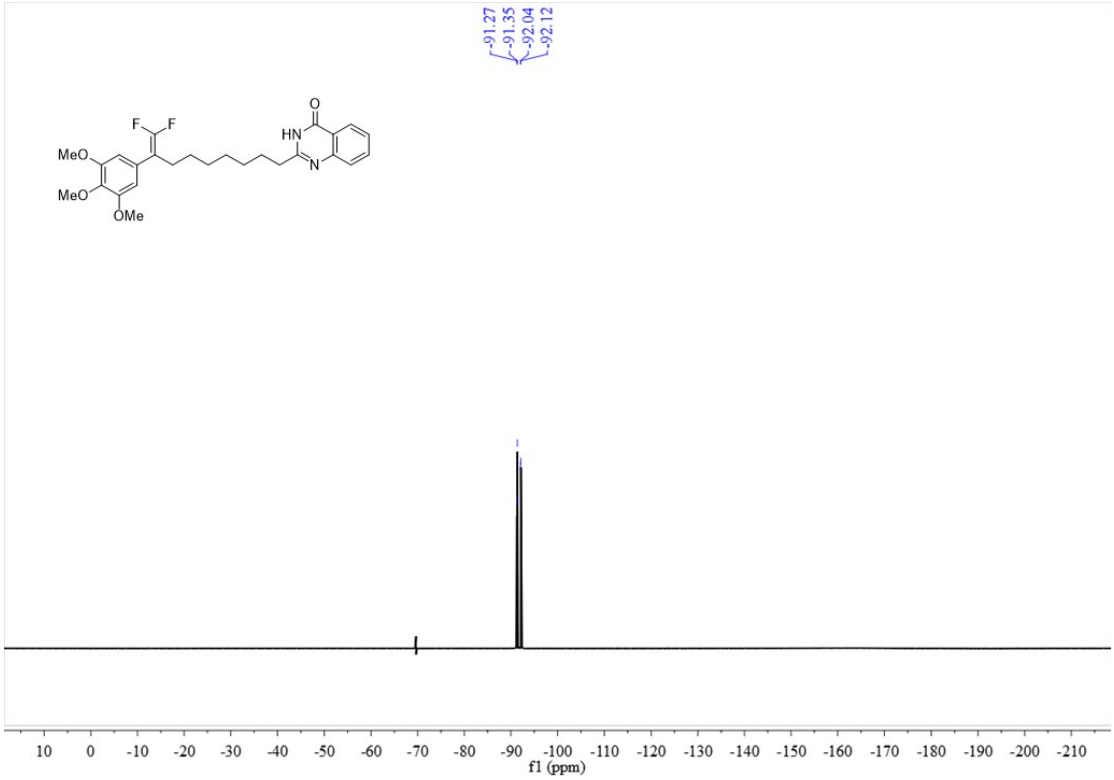
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **4td**



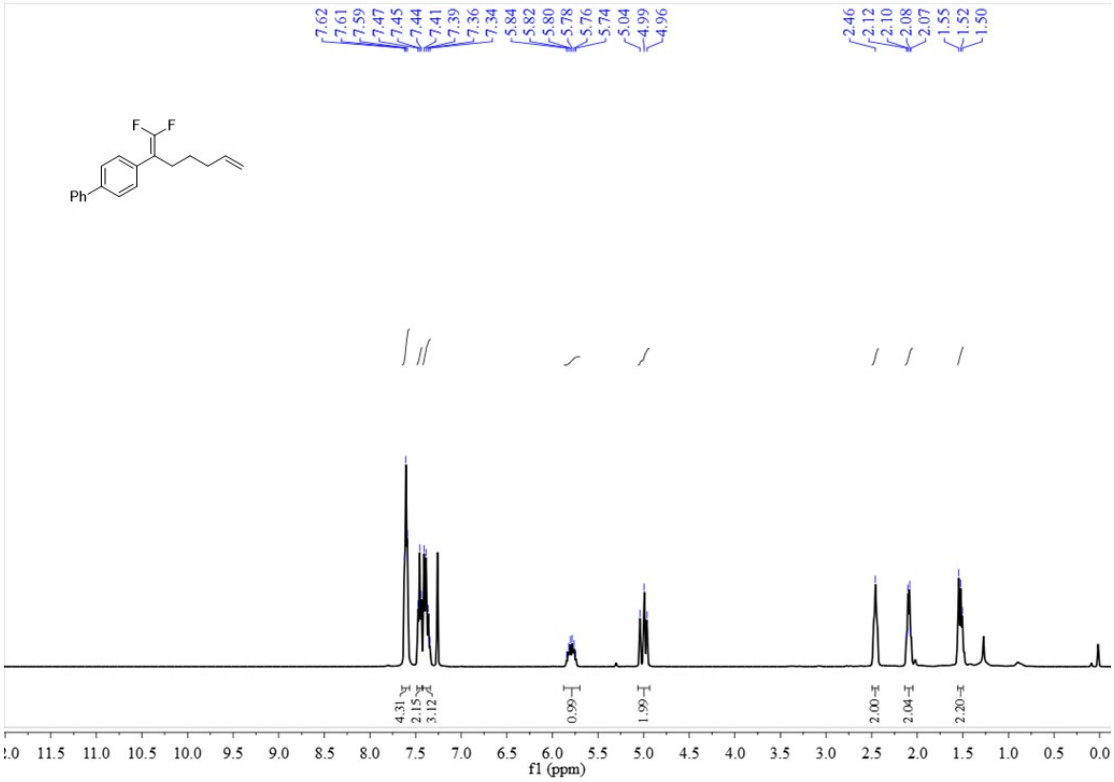
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **4td**



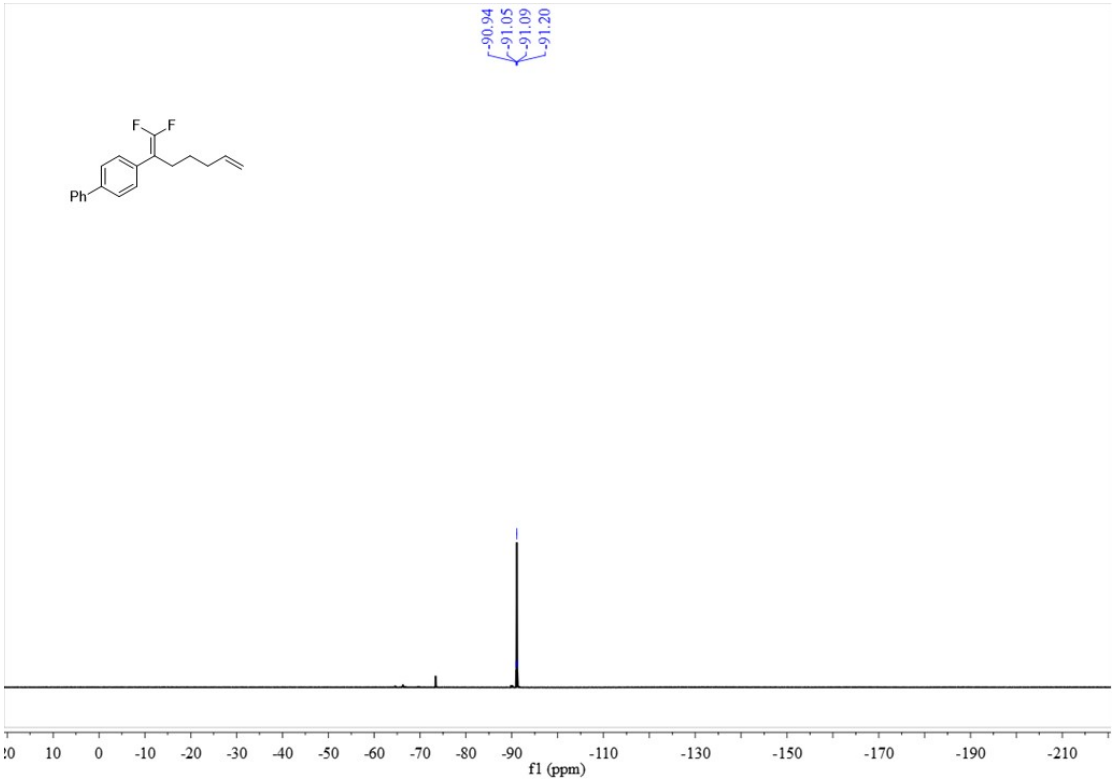
^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **4td**



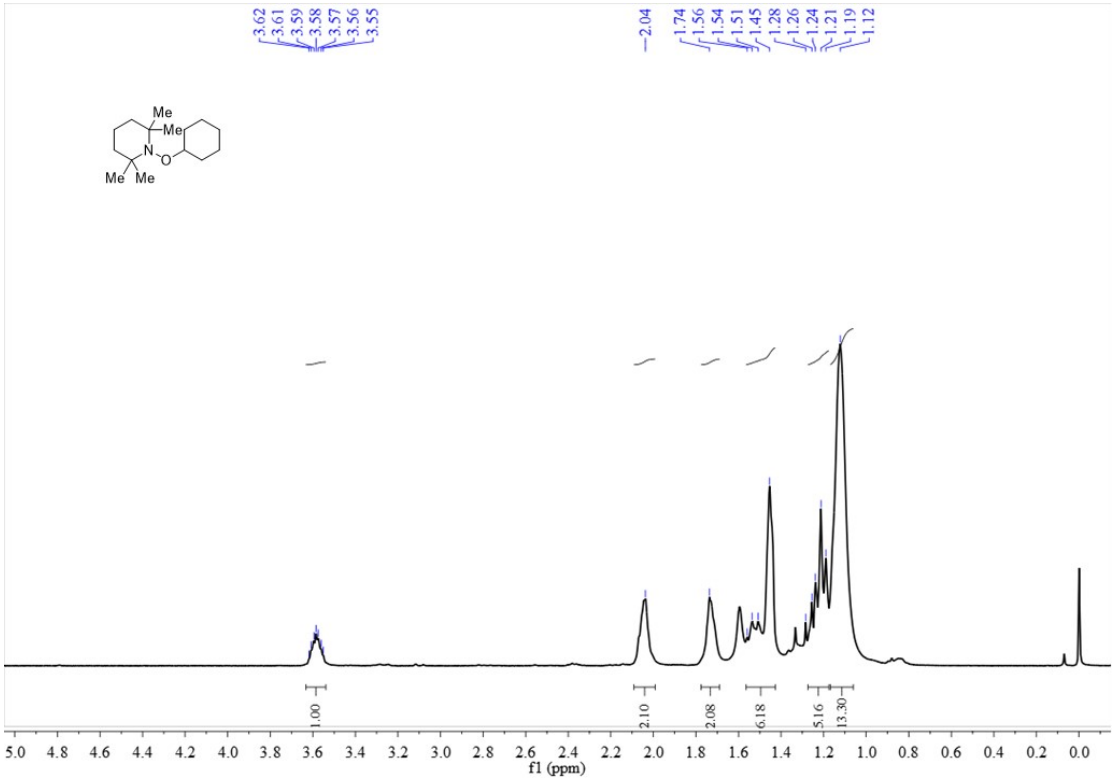
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ua**



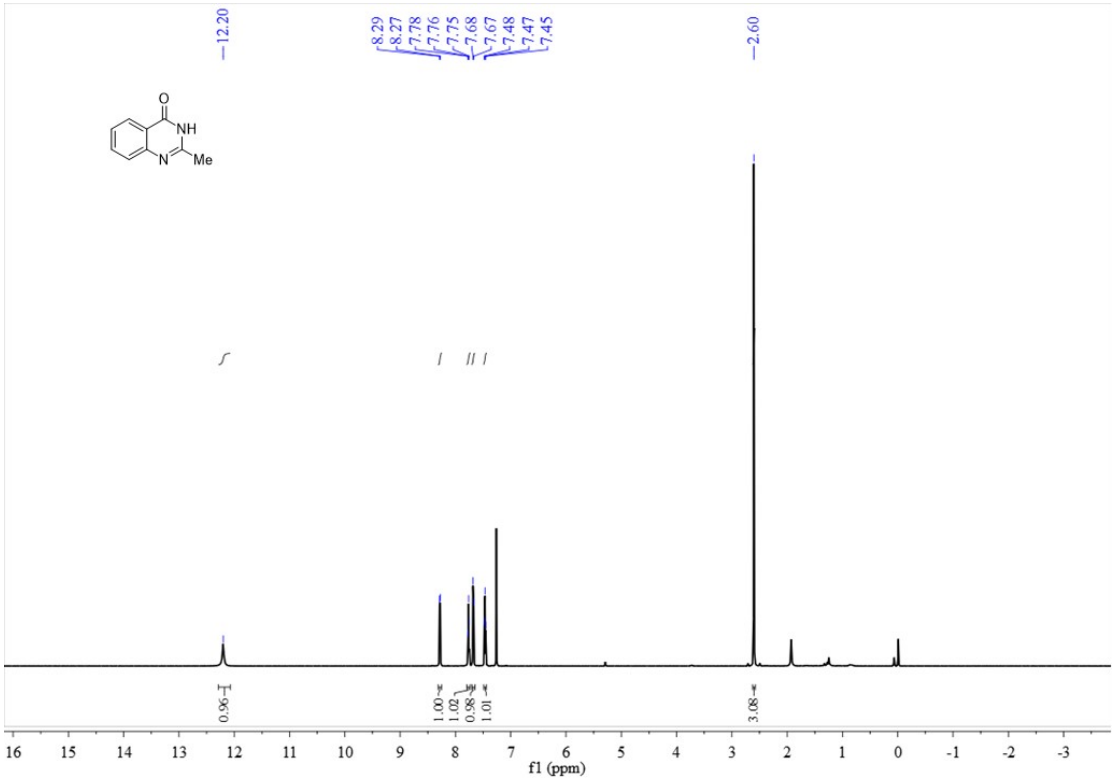
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **4ua**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**



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