

Visible-Light-Promoted Defluorinative-Alkylation/Arylation of α -Trifluoromethyl Alkenes with Thianthrenium Salts

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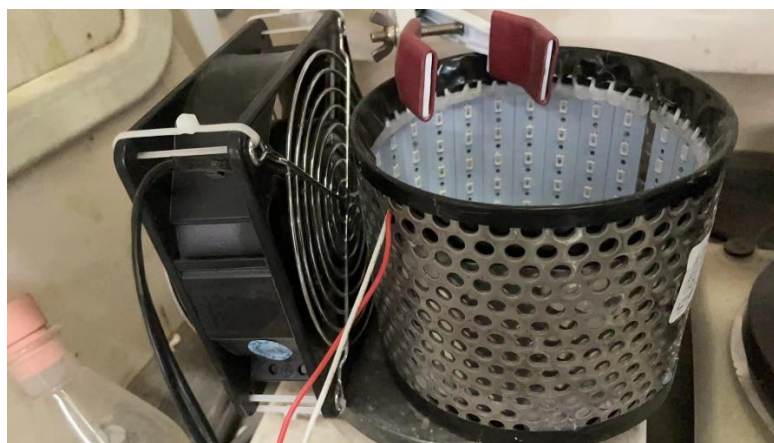
^d

Supporting Information

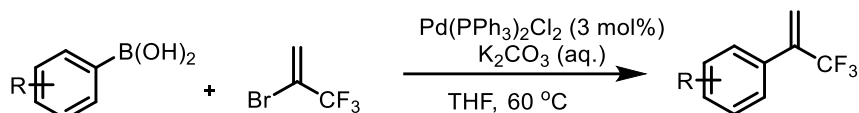
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1. General Information

Reagents were purchased from commercial sources and were used as received. Nuclear magnetic resonance (NMR) spectra for ^1H NMR (400 MHz and 600 MHz), ^{13}C NMR (150 MHz) and ^{19}F NMR (376 MHz) were taken on Bruker Avance 400 MHz and 600 MHz spectrometer in Chloroform-*d* solution with TMS as internal standard. High resolution mass spectra (HRMS) were recorded with an Agilent 6520 Q-TOF LC/MS instrument (Agilent Technologies Inc. State of California, United States of America). The melting points of new compounds were determined on an X-4 digital display micro melting point apparatus (Henan Gongyi Yingyi Yuhua Instrument Co., Ltd.) and temperature was uncorrected. The crystal structure was recorded on a Rigaku 007 Saturn 70 diffractometer (Rigaku, Tokyo, Japan). Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (36 W, $\lambda_{\text{max}} = 470 \text{ nm}$) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature. Photocatalyst 4CzIPN is commercially available.

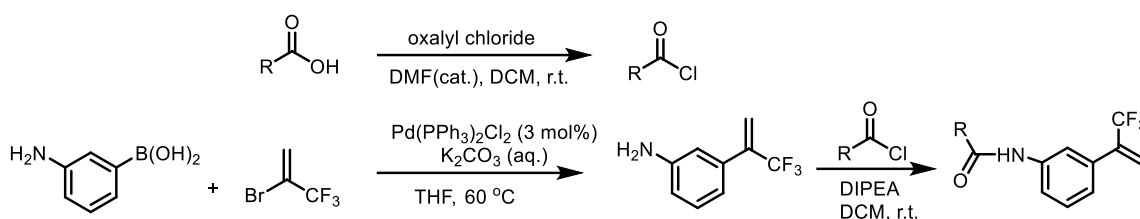


2. General Procedure for the Synthesis of (3,3,3-Trifluoroprop-1-en-2-yl)benzenes



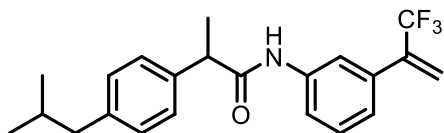
According to literature reports.¹⁻³ A Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv, 3 mmol) and Pd(PPh₃)₂Cl₂ (3 mol%, 0.09 mmol, 63.2 mg) were added. The vessel was evacuated and filled with argon, and then aqueous K₂CO₃ (2.0 M, 6 mL) and THF (9 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1.5 equiv, 4.5 mmol, 470 μL), the solution was stirred at 60 °C 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 alkenes.

3. General Procedure for the CF₃-Styrene Derivatives



According to the reported procedure⁴, to a mixture of acid (5.0 mmol, 1.0 equiv) and oxalyl chloride (847 μL, 10 mmol, 2.0 equiv) in dry CH₂Cl₂ (20 mL) was added dropwise DMF (39 μL, 10 mol%). The reaction mixture was stirred at room temperature for 6 hours. Removal of the solvent in vacuo afforded the desired acid chloride which was used in the next step without further purification. To a mixture of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (940.0 mg, 5.0 mmol, 1.0 equiv) and K₂CO₃ (690.0 mg, 5.0 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise a solution of the freshly prepared acid chloride (5.0 mmol, 1.0 equiv) in dry THF (10 mL). This mixture was stirred at room temperature for 6 hours before water was added to quench the reaction. The resultant mixture was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel (Hexane/EtOAc) to give the desired trifluoromethyl alkenes.

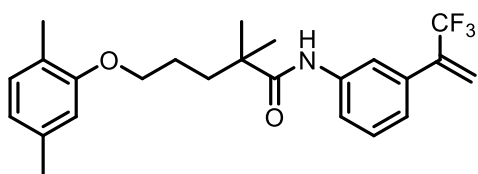
2-(4-Isobutylphenyl)-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)propanamide (1-4a)



¹H NMR (600 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 16.4, 8.1 Hz, 3H), 7.03 (t, *J* = 6.8 Hz, 3H), 5.78 (s, 1H), 5.59 (s, 1H), 3.61 (q, *J* = 7.1 Hz, 1H), 2.36 (s, 2H), 1.75 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.46 (s, 3H), 0.79 (s, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 172.2, 140.0, 137.4 (q, *J* = 30.2 Hz), 137.3, 136.9, 133.2, 128.8, 128.0, 126.3, 122.2 (q, *J* = 274.8 Hz), 122.0, 119.8 (q, *J* = 5.8 Hz), 119.3, 117.8, 46.6, 44.0, 29.1, 21.3, 17.5. The spectral data are consistent with the literature data.⁴

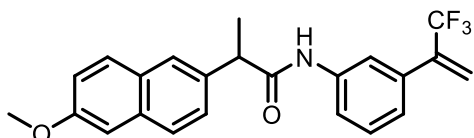
5-(2,5-Dimethylphenoxy)-2,2-dimethyl-N-(3-(3,3,3-trifluoroprop-1-en-2-

yl)phenyl)pentanamide (1-4b)



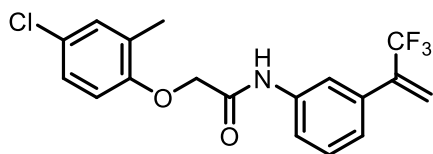
$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.54 (d, $J = 8.1$ Hz, 1H), 7.43 (s, 1H), 7.32 (t, $J = 7.9$ Hz, 1H), 7.19 (d, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.65 (d, $J = 7.4$ Hz, 1H), 6.60 (s, 1H), 5.95 (s, 1H), 5.77 (s, 1H), 3.94 (s, 2H), 2.28 (s, 3H), 2.16 (s, 3H), 1.83 (s, 4H), 1.34 (s, 6H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 175.9, 156.8, 138.2, 136.6, 134.4, 130.4, 129.2, 123.5, 123.26, 123.25 (q, $J = 273.9$ Hz), 121.0 (q, $J = 5.8$ Hz), 120.9, 120.7, 119.1, 112.2, 67.8, 42.9, 37.7, 25.6, 25.2, 21.4, 15.8. The spectral data are consistent with the literature data.⁴

2-(6-Methoxynaphthalen-2-yl)-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)propenamide (1-4c)



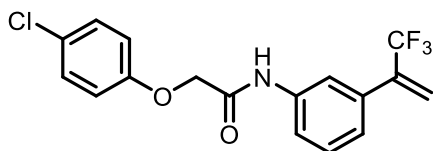
$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.76–7.69 (m, 3H), 7.56 (s, 1H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.31 (s, 1H), 7.24 (t, $J = 7.4$ Hz, 1H), 7.17 (d, $J = 9.0$ Hz, 1H), 7.13 (d, $J = 6.1$ Hz, 2H), 5.90 (s, 1H), 5.71 (s, 1H), 3.91 (s, 3H), 3.84 (q, $J = 7.0$ Hz, 1H), 1.64 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 172.7, 157.9, 138.2, 135.8, 134.4, 133.9, 129.3, 129.1, 129.0, 127.9, 126.4, 126.1, 123.19 (q, $J = 274.0$ Hz), 123.17, 121.0 (q, $J = 5.7$ Hz), 120.3, 119.4, 118.8, 105.7, 55.4, 48.1, 18.6. The spectral data are consistent with the literature data.⁴

2-(4-Chloro-2-methylphenoxy)-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)acetamide (1-4d)



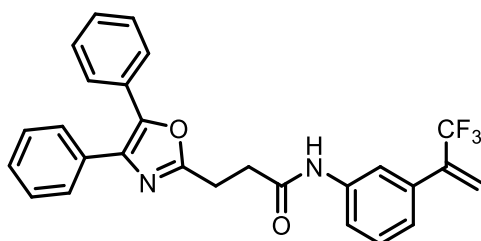
$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.68 (s, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.25 (d, $J = 7.6$ Hz, 1H), 7.19 (s, 1H), 7.15 (d, $J = 8.6$ Hz, 1H), 6.76 (d, $J = 8.6$ Hz, 1H), 5.99 (s, 1H), 5.81 (s, 1H), 4.57 (s, 2H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 166.1, 153.8, 124.0, 138.4 (q, $J = 30.3$ Hz), 137.0, 134.7, 131.1, 129.4, 127.2, 127.0, 124.0, 123.2 (q, $J = 273.9$ Hz), 121.3 (q, $J = 5.7$ Hz), 120.6, 119.0, 113.2, 68.1, 16.3. The spectral data are consistent with the literature data.⁴

2-(4-Chlorophenoxy)-N-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)acetamide (1-4e)



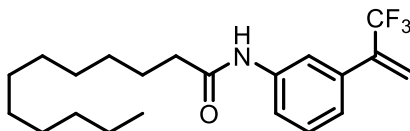
¹H NMR (600 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.66 (d, $J = 7.0$ Hz, 3H), 7.36 (t, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.8$ Hz, 3H), 7.24 (d, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 8.9$ Hz, 3H), 5.98 (s, 1H), 5.80 (s, 1H), 4.56 (s, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 166.0, 155.5, 138.3 (q, $J = 30.1$ Hz), 137.0, 134.6, 129.9, 129.4, 127.6, 124.0, 123.2 (q, $J = 274.0$ Hz), 121.2 (q, $J = 5.7$ Hz), 120.8, 119.1, 116.2, 67.8. The spectral data are consistent with the literature data.⁴

3-(4,5-Diphenyloxazol-2-yl)-*N*-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)propenamide (1-4f)



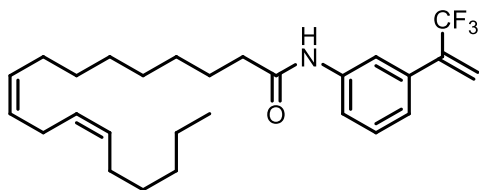
¹H NMR (600 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 7.62 (d, $J = 7.0$ Hz, 3H), 7.57–7.51 (m, 3H), 7.33 (dt, $J = 14.6, 7.5$ Hz, 6H), 7.29–7.24 (m, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 5.87 (s, 1H), 5.64 (s, 1H), 3.27 (t, $J = 6.8$ Hz, 2H), 2.95 (t, $J = 6.8$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 170.1, 162.6, 145.8, 138.5, 134.7, 134.3, 132.1, 129.2, 128.7 (d, $J = 2.0$ Hz), 128.3, 127.9, 126.5, 123.2 (q, $J = 273.9$ Hz), 123.0, 120.8 (q, $J = 5.8$ Hz), 120.3, 118.6, 34.1, 24.0. The spectral data are consistent with the literature data.⁴

***N*-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)dodecanamide (1-4g)**



¹H NMR (600 MHz, Chloroform-*d*) δ 7.61 (s, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.50 (s, 1H), 7.31 (t, $J = 7.9$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 5.94 (s, 1H), 5.77 (s, 1H), 2.36 (t, $J = 7.6$ Hz, 2H), 1.71 (dt, $J = 15.1, 7.5$ Hz, 2H), 1.30–1.22 (m, 16H), 0.88 (t, $J = 7.0$ Hz, 3H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 171.8, 138.3, 134.3, 129.2, 123.2 (q, $J = 273.3$ Hz), 123.1, 120.9 (q, $J = 5.6$ Hz), 120.4, 118.7, 37.8, 31.9, 29.62, 29.61, 29.49, 29.39, 29.34, 29.28, 25.6, 22.7, 14.1. The spectral data are consistent with the literature data.⁴

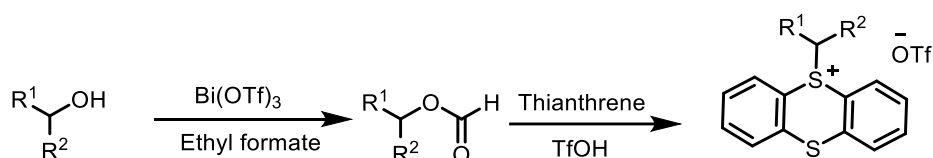
(9*Z*,12*Z*)-*N*-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)octadeca-9,12-dienamide (1-4h)



$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.51 (d, $J = 7.9$ Hz, 1H), 7.43 (d, $J = 10.5$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 5.86 (s, 1H), 5.69 (s, 1H), 5.28 (dq, $J = 16.0$, 10.2, 9.7 Hz, 4H), 2.69 (t, $J = 6.6$ Hz, 2H), 2.28 (t, $J = 7.4$ Hz, 2H), 2.00–1.95 (m, 4H), 1.68–1.59 (m, 2H), 1.25 (dd, $J = 22.5$, 6.7 Hz, 14H), 0.81 (t, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 170.7, 137.2, 133.3, 129.2, 129.0, 128.3 (q, $J = 273.3$ Hz), 128.2, 127.80, 127.04, 126.86, 122.07, 119.85 (q, $J = 5.7$ Hz), 119.35, 117.71, 36.7, 30.5, 28.6, 28.32, 28.27, 28.21, 28.1, 26.18, 26.16, 24.6, 21.6, 13.1. The spectral data are consistent with the literature data.⁴

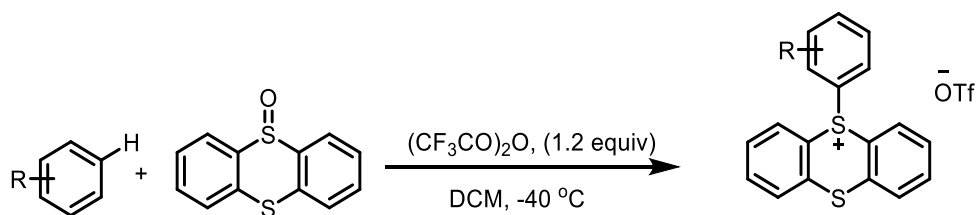
4. Preparation of Thianthrenium Salts

4.1 Preparation of alkyl thianthrenium salts



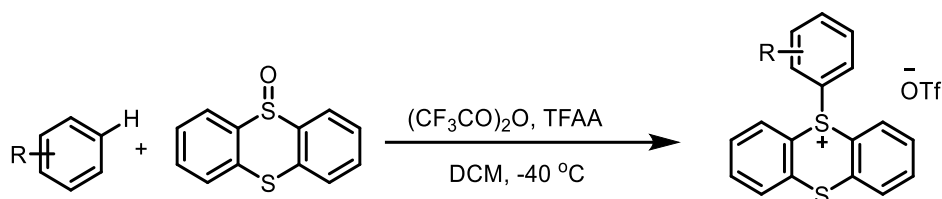
Substrates **2a-2ae** were synthesized following the reported procedures in the literature.⁵ A solution of alcohol (1.0 equiv) in ethyl formate (2.0 equiv) was treated with 2 mol% of $\text{Bi}(\text{OTf})_3$. The reaction mixture was stirred under reflux conditions for 5 h. Evaporation of the solvent followed by silica-gel chromatography gave the pure formate. To a stirred mixture of thianthrene (0.5 equiv) and formate (1.0 equiv), cooled in an ice-bath, was dropwise added trifluoromethanesulfonic acid (0.25 equiv). The mixture was removed from the ice-bath and stirred for 10 h at room temperature, then was poured into proper amount of water. The resulting suspension was extracted with DCM. The collected organic layers were dried over Na_2SO_4 , filtered and concentrated under reduced pressure and purified by precipitation with $\text{Et}_2\text{O}/\text{DCM}$ to afford alkyl thianthrenium salts (**2a-2ae**).

4.2 Preparation of aryl thianthrenium salts

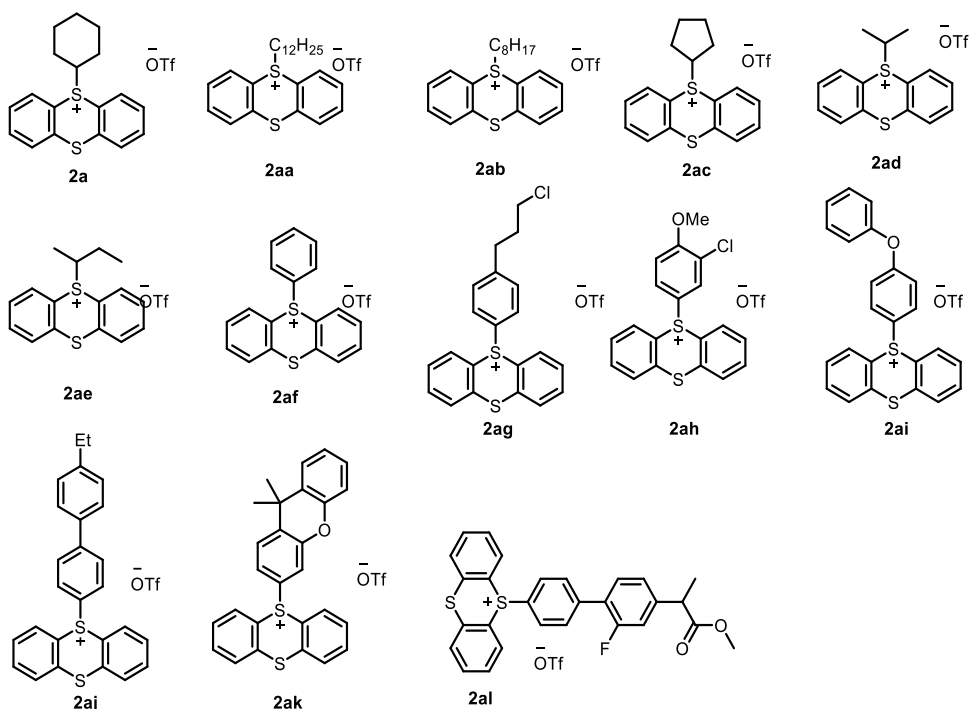


Substrates **2af**, **2ag**, **2ai** were synthesized following the reported procedures in the literature.^{5c}
⁶ A 100 mL schlenk tube was charged with thianthrene S-oxide (TTSO) (5.5 mmol, 1.1 equiv.), CH_2Cl_2 (25 mL, 0.2 M) and arene (5 mmol, 1.0 equiv.) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. TF_2O (6 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at -40 °C for 30 min, and then allowed to stir at ambient temperature (23 °C) for 12 h, neutralized by a saturated aqueous NaHCO_3 solution, and extracted with DCM (3 x 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4

and concentrated under reduced pressure, purified by precipitation with Et₂O/DCM to afford aryl thianthrenium salts (**2af**, **2ag**, **2ai**).

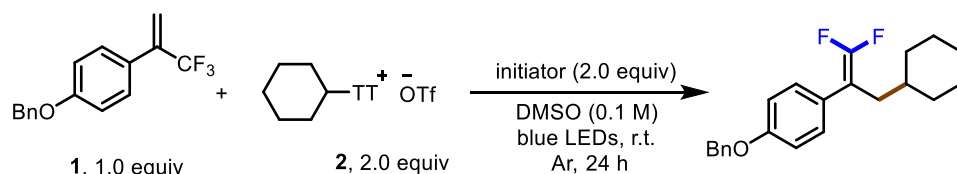


Substrates **2ah**, **2aj**, **2ak**, **2al** were synthesized following the reported procedures in the literature.⁷ A 25 mL schlenk tube was charged with thianthrene S-oxide (2.0 mmol, 1.0 equiv), DCM (5 mL) and arenes (2.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Trifluoroacetic anhydride (TFAA, 6.0 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 3.0 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at -40 °C for 30 min, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous NaHCO₃ solution, and extracted with DCM. The combined organic layers were washed with aqueous NaOTf solution (3 × 20 mL, 5% (w/w)), dried over anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/Et₂O system to afford aryl thianthrenium salts (**2ah**, **2aj**, **2ak**, **2al**).



5. Investigation of the Key Reaction Parameters

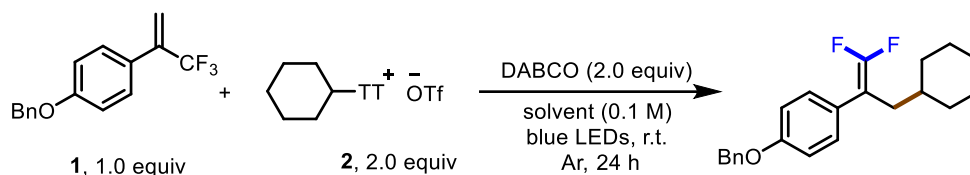
Table S1 Screening of different initiator^a



Entry	Initiator	Yield (%) ^b
1	HE	17
2	TMEDA	20
3	DABCO	33
4	DBU	NR
5	DMAP	NR
6	Et ₃ N	24
7	TMG	12
8	Triphenylamine	14
9	—	NR

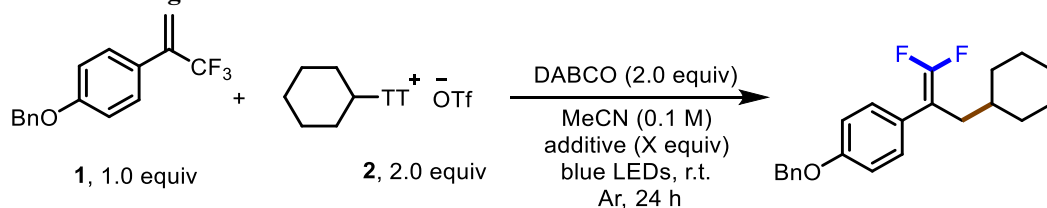
^a Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), initiator (0.4 mmol), DMSO (2 mL), rt, Ar atmosphere, 24 h. ^b Yields were determined by ¹⁹F NMR spectroscopy with fluorobenzene as an internal standard. NR = no reaction

Table S2 Screening of Different Solvents^a



Entry	Solvent	Yield (%) ^b
1	DMSO	33
2	MeCN	43
3	DMF	25
4	Acetone	Trace
5	DCM	Trace
6	EtOH	Trace
7	DCE	20

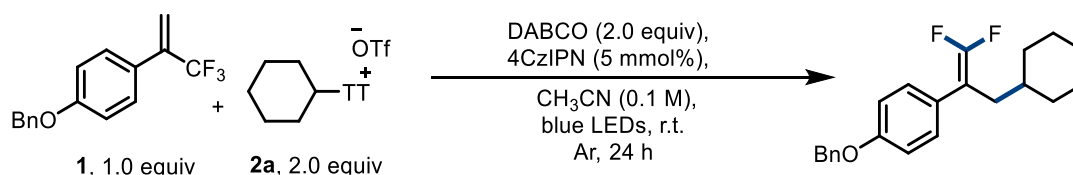
^a Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), DABCO (0.4 mmol), solvent (2 mL), rt, Ar atmosphere, 24 h. ^b Yields were determined by ¹⁹F NMR spectroscopy with fluorobenzene as an internal standard.

Table S3 Screening of Different Additive ^a

Entry	Additive	X equiv	Yield (%) ^b
1	K ₂ CO ₃	2.0	44
2	Cs ₂ CO ₃	2.0	47
3	K ₃ PO ₄	2.0	42
4	CH ₃ COONa	2.0	51
5	KOH	2.0	53
6	NaHCO ₃	2.0	47
7	4CzIPN	0.05	85
8 ^c	KOH	2.0	75

^a Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), DABCO (0.4 mmol), additive (X equiv), MeCN (2 mL), rt, Ar atmosphere, 24 h. ^b Yields were determined by ¹⁹F NMR spectroscopy with fluorobenzene as an internal standard. ^c 48h.

6. Gram-scale Synthesis of 1-(Benzyloxy)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (**3a**)

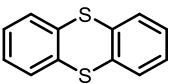


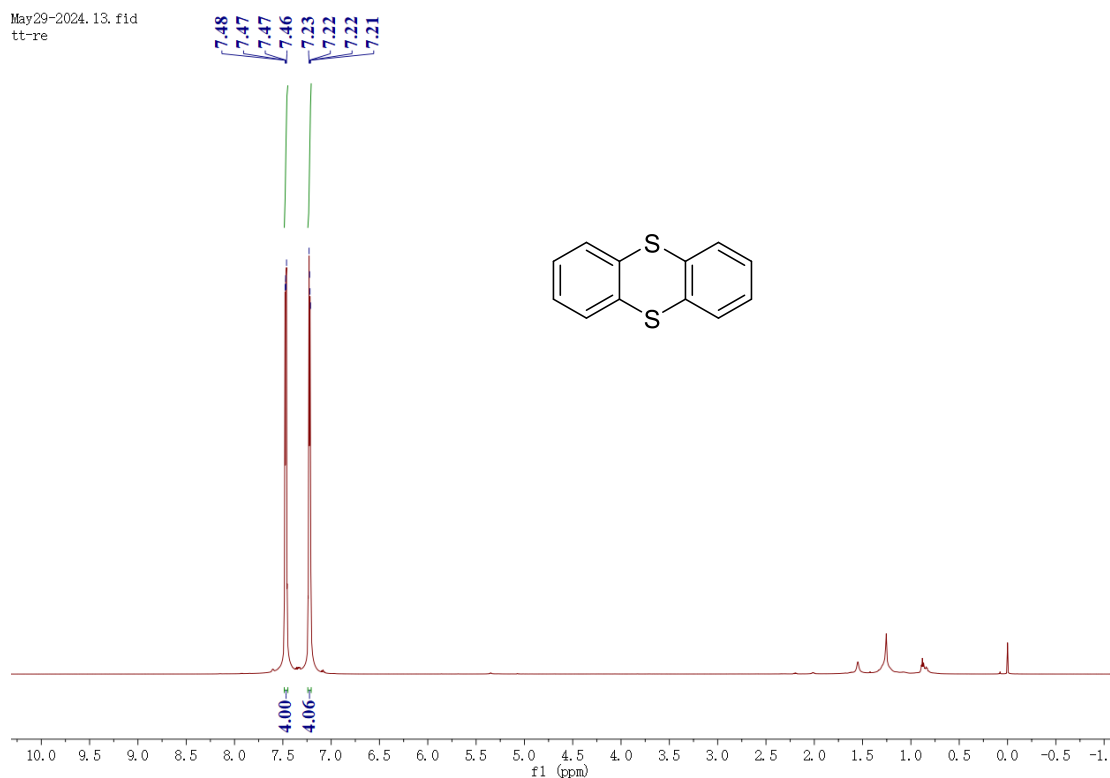
To a 10 mL glass vial was added 4CzIPN (0.215 mmol, 5 mol %), α -trifluoromethyl arylalkene (1.6 g, 4.3 mmol, 1.0 equiv), alkyl thianthrenium salt (8.6 mmol, 2.0 equiv), DABCO (8.6 mmol, 2.0 equiv) and 43 mL of solvent. The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with DCM (3 \times 50 mL). The combined organic extracts were washed with brine (100 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product 1-(benzyloxy)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (**3a**), 1.05g, 71% yield.

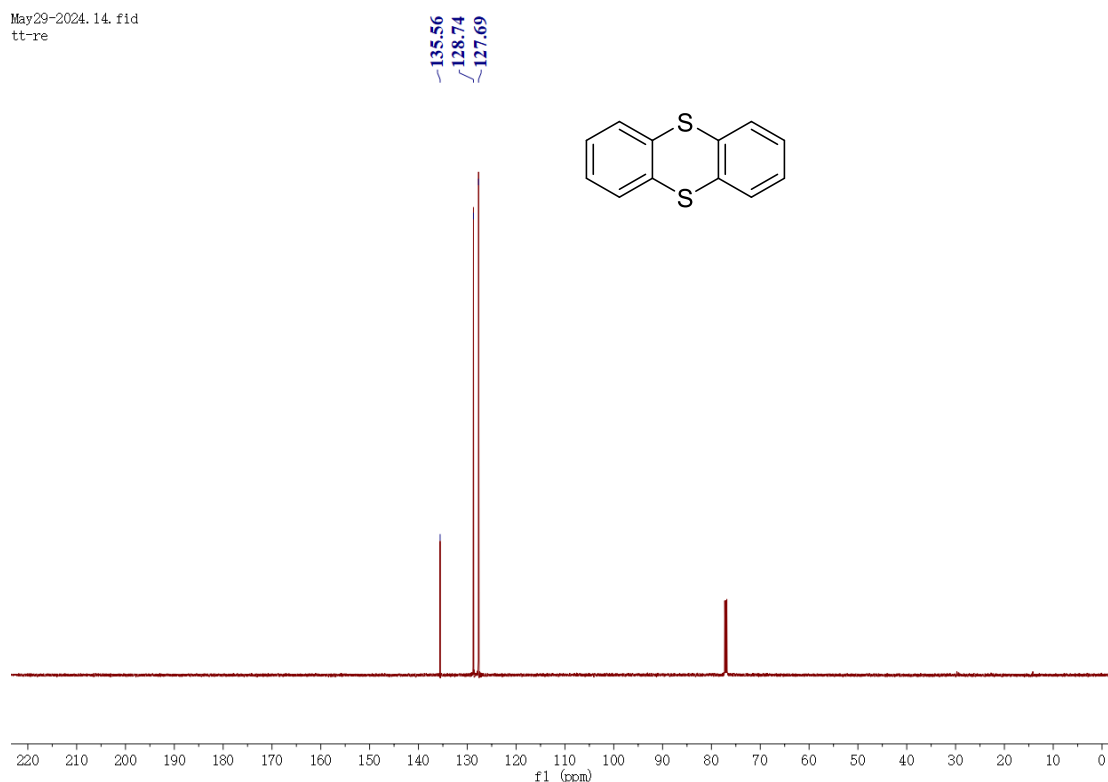
7. Recovery of Thianthrene



To a 10 mL glass vial was added α -trifluoromethyl arylalkene (55.6 mg, 0.2 mmol, 1.0 equiv), aryl thianthrenium salt (202.4 mg, 0.4 mmol, 2.0 equiv), DABCO (44.9 mg, 0.4 mmol, 2.0 equiv) and 2.0 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with EA (3 \times 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product. thianthrene (84.7 mg, 98% yield) as a white solid and 56.0 mg (70% yield) of **3ah** as a yellow oil.

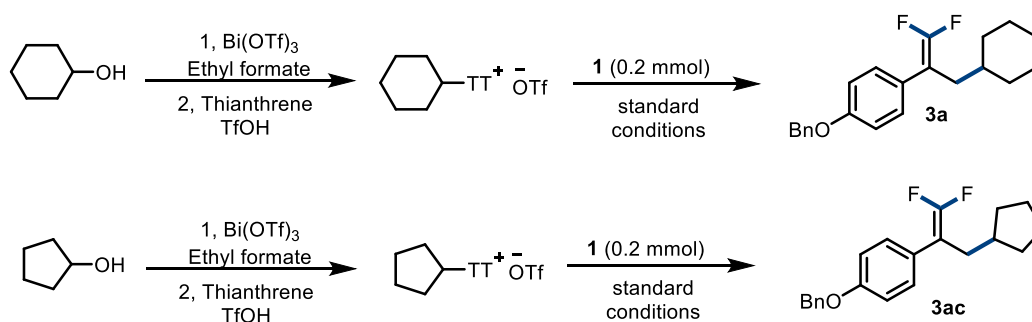
 ¹H NMR (600 MHz, Chloroform-*d*) δ 7.47 (dd, $J = 5.7, 3.4$ Hz, 4H), 7.22 (dd, $J = 5.8, 3.4$ Hz, 4H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 135.6, 128.7, 127.7.





¹³C NMR (150 MHz, Chloroform-*d*) spectrum of thianthrene.

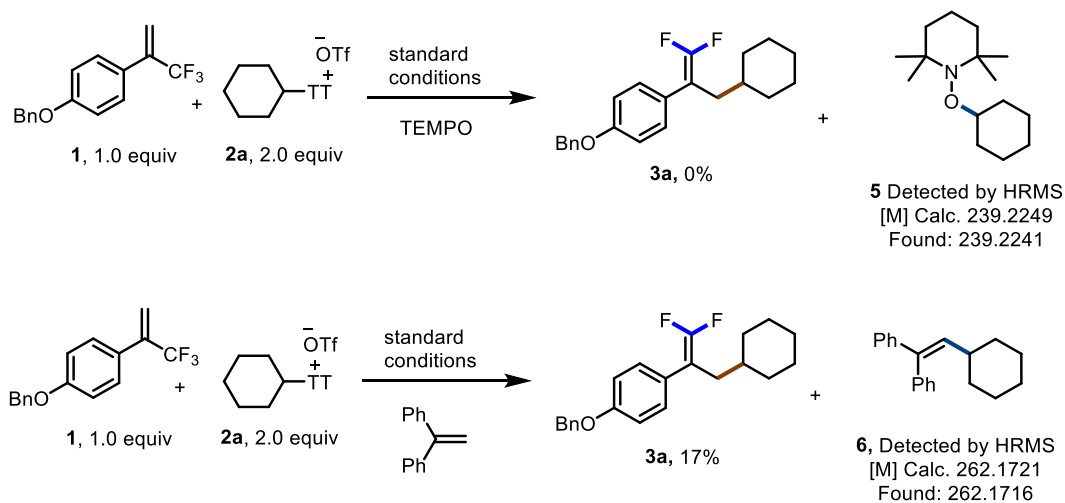
8. One-Pot Procedure for the Synthesis of 3a and 3ac



A solution of alcohol (0.4 mmol) in ethyl formate (37.3 equiv) was treated with Bi(OTf)₃ (0.02 equiv). The reaction mixture was stirred under reflux conditions for 5 h. Then thianthrene (2.0 equiv), 0.25 mL of trifluoromethanesulfonic acid were added to the solution. The mixture was removed from the ice-bath and stirred for 10 h at room temperature, then was poured into 10 ml of water. The resulting suspension was extracted with DCM. The collected organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. α -Trifluoromethyl arylalkene **1** (0.1 mmol, 1.0 equiv), DABCO (0.6 mmol), 4CzIPN (5 mol %) were then added under nitrogen atmosphere, followed by the addition of 2.0 mL of CH₃CN. The mixture was stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with DCM (3 \times 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to give the corresponding products **3**.

9. Investigation of the Mechanism

9.1 TEMPO and 1,1-diphenylethylene were used as radical scavengers



To a 10 mL glass vial was added 4CzIPN (7.9 mg, 0.01 mmol, 5 mol %), α -trifluoromethyl arylalkene (0.2 mmol, 1.0 equiv), alkyl thianthrenium salt (0.4 mmol, 2.0 equiv), DABCO (44.9 mg, 0.4 mmol, 2.0 equiv), TEMPO (117 mg, 0.75 mmol, 2.5 equiv), or 1,1-diphenylethylene (135.0 mg, 0.75 mmol, 2.5 equiv) and 2.0 mL of solvent. The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The yields of corresponding alkylated products **3** were determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard. The corresponding product of radical trapping, 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine or (2-cyclohexylethene-1,1-diyl)dibenzene was detected by HRMS.

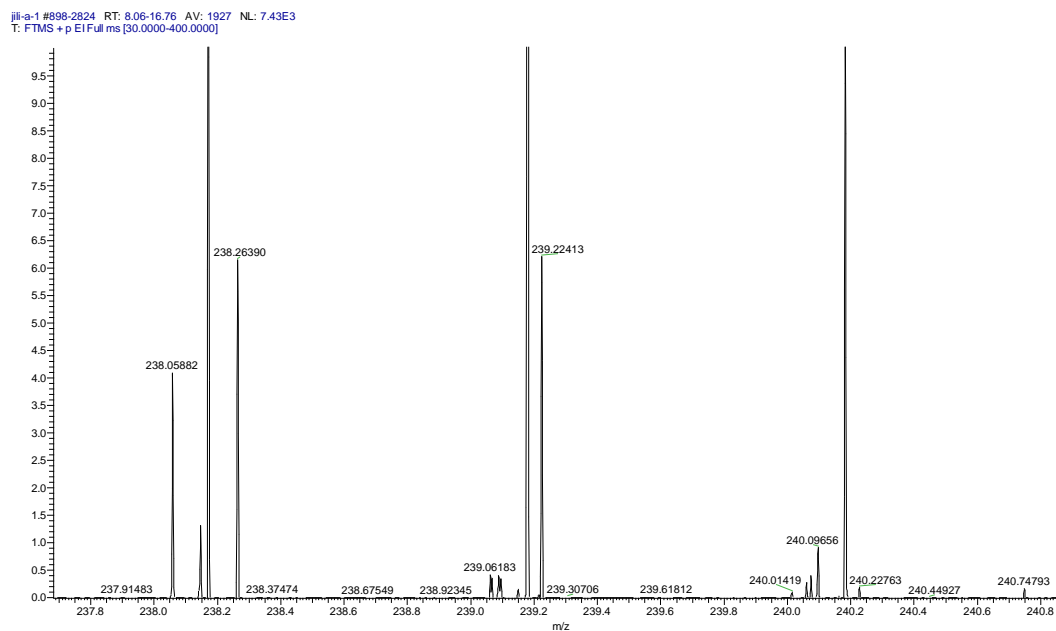


Figure S1. HR-ESI mass spectrum of 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine.

iji-a-2#2408 RT: 14.88 AV: 1 NL: 4.42E4
T: FTMS + p EtFull.ms [30.0000-400.0000]

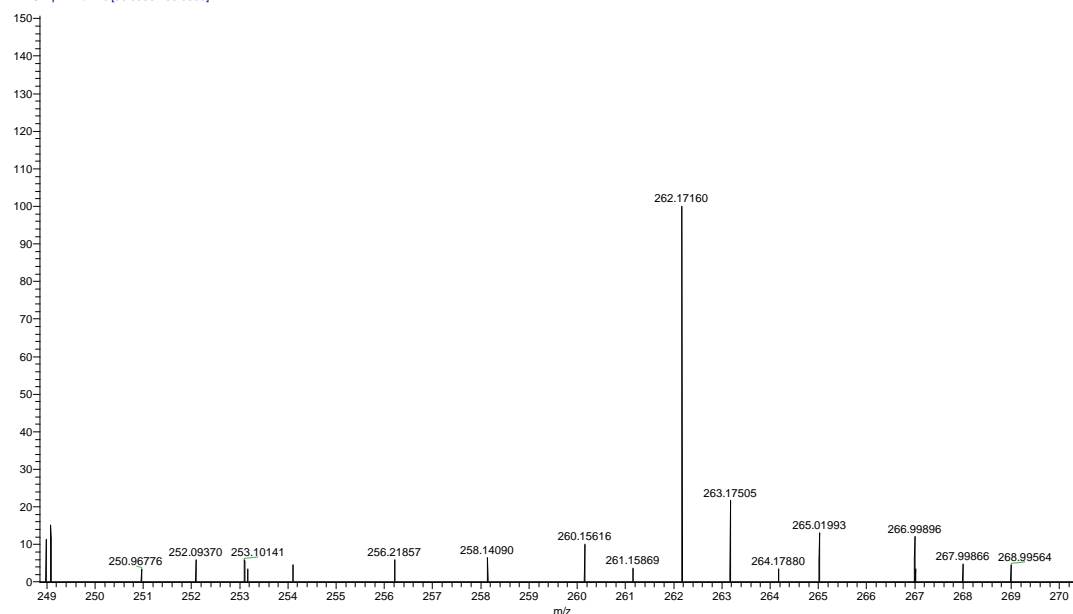
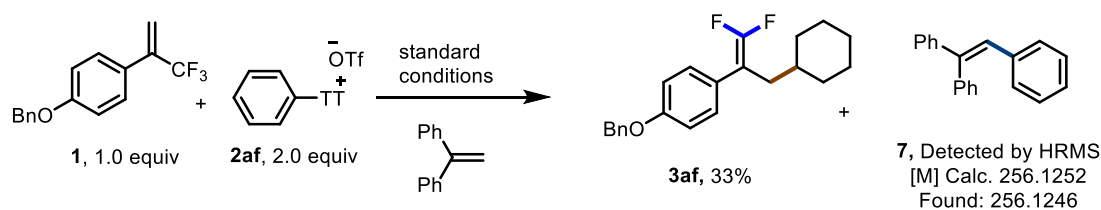


Figure S2. HR-ESI mass spectrum of (2-cyclohexylethene-1,1-diyl)dibenzene.



To a 10 mL glass vial was added α -trifluoromethyl arylalkene (0.2 mmol, 1.0 equiv), aryl thianthrenium salt (0.4 mmol, 2.0 equiv), DABCO (44.9 mg, 0.4 mmol, 2.0 equiv), 1,1-diphenylethene (135.0 mg, 0.75 mmol, 2.5 equiv) and 2.0 mL of solvent. The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The yields of corresponding alkylated products 3 were determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard. The corresponding product of radical trapping, ethene-1,1,2-triyltribenzene was detected by HRMS.

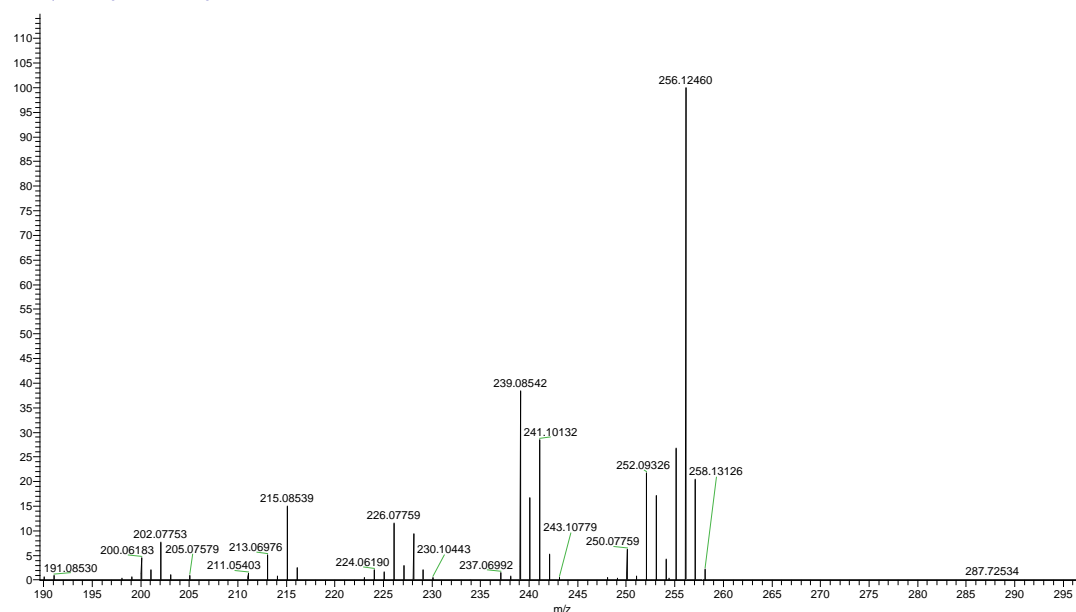


Figure S3. HR-ESI mass spectrum of ethene-1,1,2-triyltribenzene.

9.2 Light/dark experiment

Eight standard reaction mixtures in 10 mL glass vials were charged with 4CzIPN (7.9 mg, 0.01 mmol, 5 mol %), α -trifluoromethyl arylalkene (0.2 mmol, 1.0 equiv), alkyl thianthrenium salt (0.4 mmol, 2.0 equiv), DABCO (44.9 mg, 0.4 mmol, 2.0 equiv) and 2.0 mL of solvent. The reaction mixtures were degassed by bubbling with argon for 15 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yield was determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard.

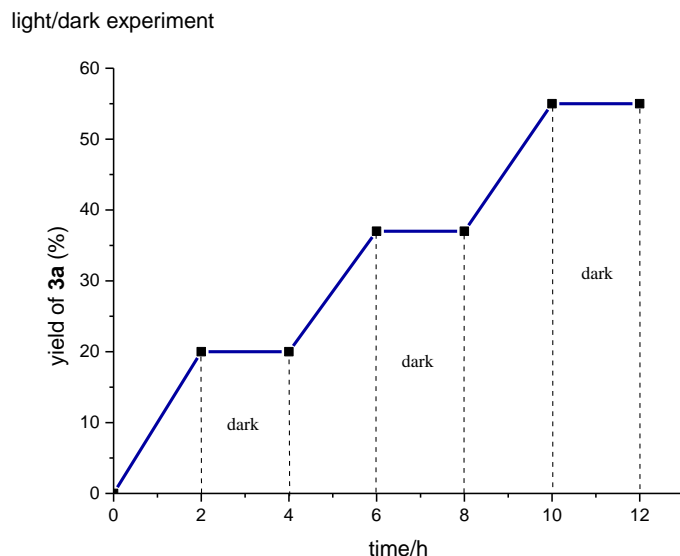


Figure S4. Light/dark experiment.

9.3 UV-vis absorbance experiment

UV-vis absorbance experiments have been carried out for confirming the formation of EDA complex as illustrated below in Figure S5. In Figure S5, the orange UV absorbance line came from compound **2a** solution, the red one came from DABCO solution, and the blue one came from the mixed solution of compound **2a** and DABCO. UV-vis spectra revealed that upon mixing compound **2a** with DABCO, an obvious bathochromic shift of the UV-vis absorbance was observed, strongly suggesting that cyclohexyl thianthrenium salt **2a**-DABCO EDA complex might indeed be formed in the mixed solution.

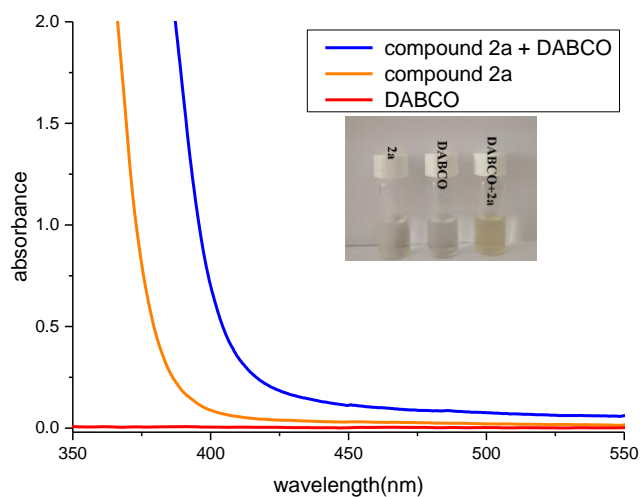


Figure S5. UV-vis absorption spectra. Orange line: compound **2a** (0.1 mmol) in 2 mL MeCN; Red line: DABCO (0.1 mmol) in 2 mL MeCN; Blue line: compound **2a** (0.1 mmol) and DABCO (0.1 mmol) in 2 mL MeCN.

9.4 Determination of binding stoichiometry of EDA complex

The binding stoichiometry between methylbenzene-derived sulfonium salt and DABCO was evaluated using Job's plot analysis: ^1H NMR spectra of mixtures of benzene-derived sulfonium salt and DABCO in CDCl_3 were recorded at 298 K. CDCl_3 ($\delta = 7.2600$) was used as an internal standard. The total volume of the mixture was 0.5 mL, and the total amount of benzene-derived sulfonium salt and DABCO was kept constant at 0.1 mmol (0.2 M), while the amount of benzene-derived sulfonium salt was varied from 0 to 0.1 mmol (0-0.2 M). The molar ratios of [benzene-derived sulfonium salt]/[benzene-derived sulfonium salt + DABCO] were 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0. ^1H NMR for each sample was recorded and the changes of chemical shift ($\Delta\delta$) for ArH in benzene-derived sulfonium salt were used to draw the plot.⁸ These data are consistent with Yu's work, thus the results indicate that the formation of EDA complex of benzene-derived sulfonium salt with DABCO in a binding stoichiometry of 1:1.

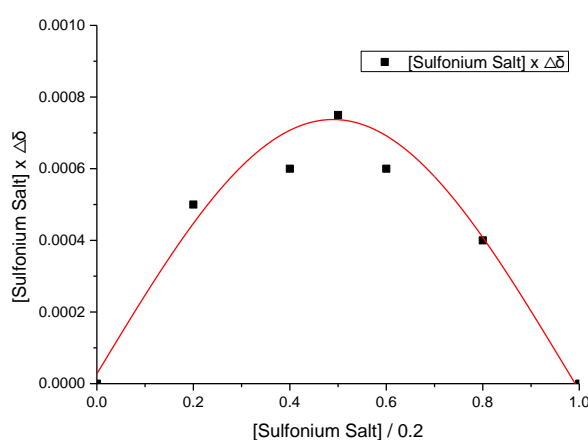


Figure S6. Job's plot

10. Green Chemistry Metrics Calculations

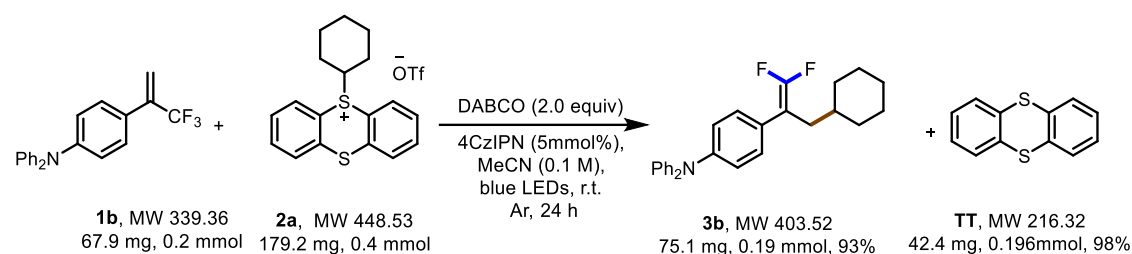
In order to assess the Green Metrics of our process compared to more approaches for *gem*-difluoroalkene syntheses, the accessible green chemistry metrics such as atom economy (AE), atom efficiency (AEf), carbon efficiency (CE) and environmental factor (E-Factor) were performed. The Green Metrics analysis is calculated based on the compound with the highest yielding in each protocol. The present green process for the synthesis of product **3b** has a 78.7% atom economy, 73.1% atom efficiency, 61.9% carbon efficiency, and an E-factor of 14.9 kg waste/1 kg product (Table S4). The present green process for the synthesis of product **3af** has a 76.5% atom economy, 63.5% atom efficiency, 56.4% carbon efficiency, and an E-factor of 24.2 kg waste/1 kg product. Compared with Zhang's^{9a} and Fu's^{9b} work for constructing *gem*-difluoroalkenes via EDA complexes, our protocol displays the better green chemistry metrics, such as higher atom economy, carbon efficiency and lower E-Factor values. Compared with Molander's^{9c}, Patureau's^{9d} and Wang's^{9e} photocatalytic strategy to afford the *gem*-difluoroalkene products, the green chemistry metrics in our protocol (**3b**), such as AE, AEf and CE, are comparable to those in Patureau's approach, but are better than those in Molander's and Wang's protocols. The E-Factor is a useful indicator to measure the amount of wastes generated by a process in the attempt to optimize the reaction.¹⁰ Among all of these *gem*-difluoroalkene syntheses protocols, the synthesis of product **3b** via our protocol has the lowest E-Factor (Table S4).

Table S4. Green metrics (AE, AEf, CE, E-factor)

Entry	Solvent	GHS pictogram hierarchy ^a	Yield (%)	AE	AEf	CE	E-Factor
This work (3b)	MeCN	F, Xi, Xn, T	93	78.7	73.1	61.9	14.9
This work (3af)	DMSO	Xi	83	76.5	63.5	56.4	24.2
Zhang's work	DMA	T, N	91	42.1	38.3	31.0	38.7
Fu's work	DMA	T, N	94	68.2	64.1	55.6	24.5
Molander's work	DMF	T	96	43.6	41.8	34.4	36.9
Patureau's work	MeCN	F, Xi, Xn, T	89	84.2	74.9	61.1	17.3
Wang's work	MeCN	F, Xi, Xn, T	82	71.6	57.9	50.0	42.1

^aF→Highly Flammable; Xn→Harmful; Xi→Irritant; T→ Toxic; N → Dangerous for the environment.

10.1 This work for the synthesis of compound **3b**



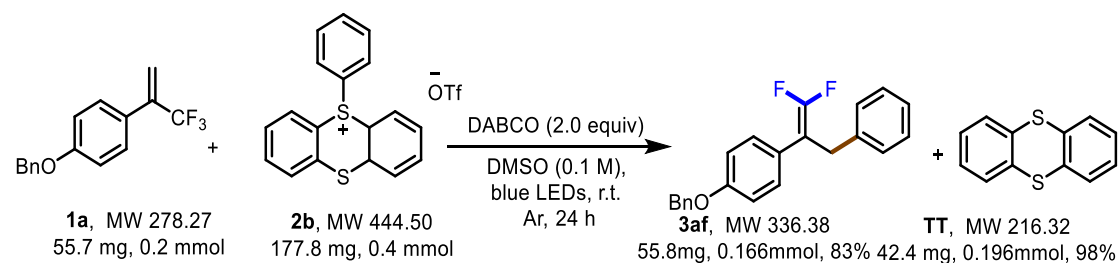
$$AE = \frac{403.52 + 216.32}{339.36 + 448.53} * 100 = 78.7$$

$$AEf = \frac{78.7}{100} * 93 = 73.1$$

$$CE = \frac{27 * 0.000186 + 12 * 0.000196}{21 * 0.0002 + 19 * 0.0004} * 100 = 61.9$$

$$E - factor = \frac{67.9 + 179.2 + 44.9 + 7.9 + 1571.4 - 75.1 - 42.4}{75.1 + 42.4} = 14.9$$

10.2 This work for the synthesis of compound **3af**



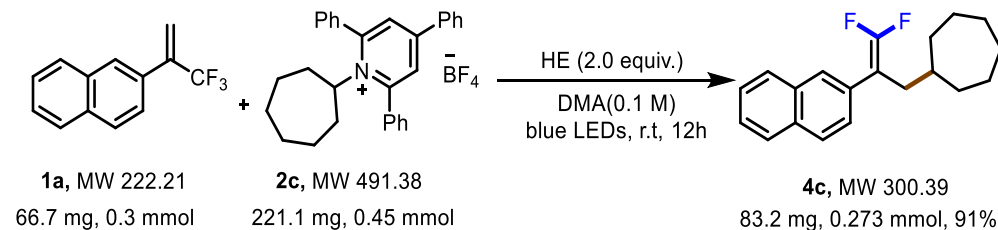
$$AE = \frac{336.38 + 216.32}{278.27 + 444.50} * 100 = 76.5$$

$$AEf = \frac{76.5}{100} * 83 = 63.5$$

$$CE = \frac{22 * 0.00017 + 12 * 0.000196}{16 * 0.0002 + 19 * 0.0004} * 100 = 56.4$$

$$E - \text{Factor} = \frac{55.7 + 177.8 + 44.9 + 2200.0 - 55.8 - 42.4}{55.8 + 42.4} = 24.2$$

10.3 Zhang's work (*Green Chem.*, 2022, 24, 6830–6835.)



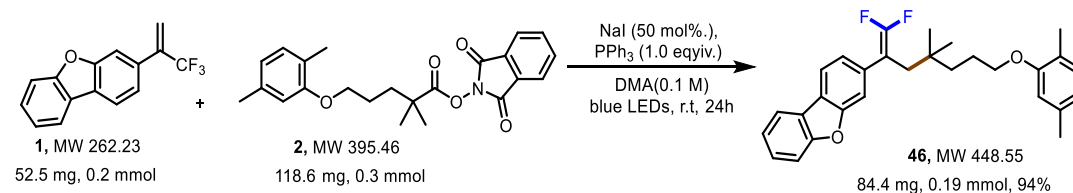
$$AE = \frac{300.39}{222.21 + 491.38} * 100 = 42.1$$

$$AEf = \frac{42.1}{100} * 91 = 38.3$$

$$CE = \frac{20 * 0.00027}{13 * 0.0003 + 30 * 0.00045} * 100 = 31.0$$

$$E - \text{factor} = \frac{66.7 + 221.1 + 152.0 + 2868.0 - 83.2}{83.2} = 38.7$$

10.4 Fu's work (*Adv. Sci.* 2024, 11, 2307241)



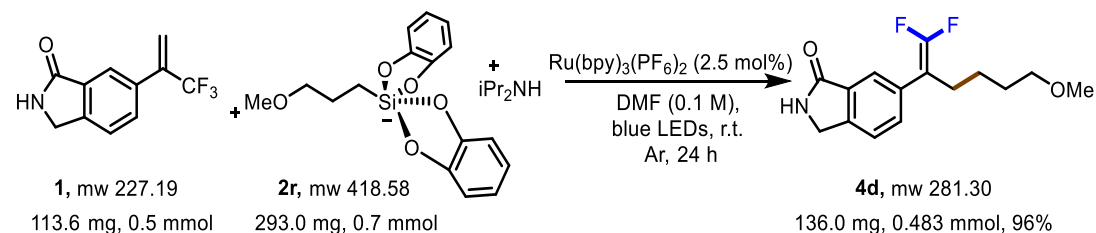
$$AE = \frac{448.55}{262.23 + 395.46} * 100 = 68.2$$

$$AEf = \frac{68.2}{100} * 94 = 64.1$$

$$CE = \frac{29 * 0.00019}{15 * 0.0002 + 23 * 0.0003} * 100 = 55.6$$

$$E - \text{factor} = \frac{52.5 + 118.6 + 14.9 + 52.5 + 1912.0 - 84.4}{84.4} = 24.5$$

10.5 Molander work (*Angew. Chem. Int. Ed.* 2017, 56, 15073–15077.)



$$AE = \frac{281.30}{227.19 + 418.58} * 100 = 43.6$$

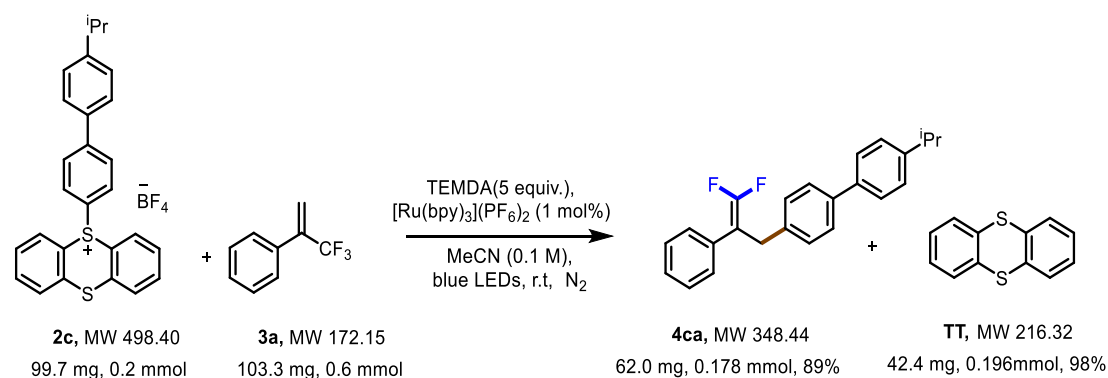
$$AEf = \frac{43.6}{100} * 96 = 41.8$$

$$CE = \frac{15 * 0.00048}{11 * 0.0005 + 22 * 0.0007} * 100 = 34.4$$

$$E - \text{factor} = \frac{113.6 + 293.0 + 11.0 + 4740.0 - 136.0}{136.0} = 36.9$$

10.6 Patureau's work (*Org. Lett.* 2022, 24, 8753-8758.)

The recovery yield of thianthrenium salt was not mentioned in Patureau's work, so we calculated it according to this manuscript.



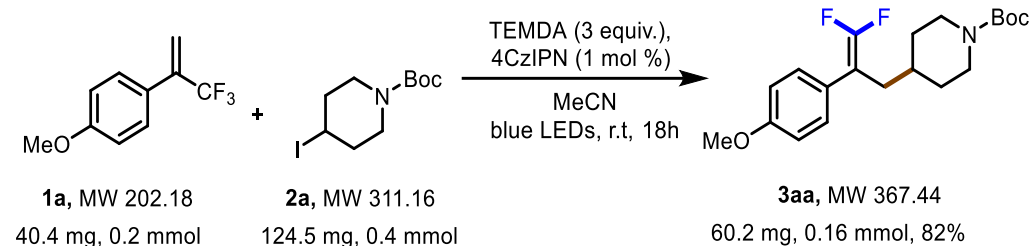
$$AE = \frac{348.44 + 216.32}{498.40 + 172.15} * 100 = 84.2$$

$$AEf = \frac{84.2}{100} * 89 = 74.9$$

$$CE = \frac{24 * 0.00018 + 12 * 0.00019}{27 * 0.0002 + 9 * 0.0006} * 100 = 61.1$$

$$E - \text{factor} = \frac{99.7 + 103.3 + 116.2 + 17.2 + 1571.4 - 62.0 - 42.4}{62.0 + 42.4} = 17.3$$

10.7 Wang's work (*J. Org. Chem.* 2022, 87, 1574-1584.)



$$AE = \frac{367.44}{202.18 + 311.16} * 100 = 71.6$$

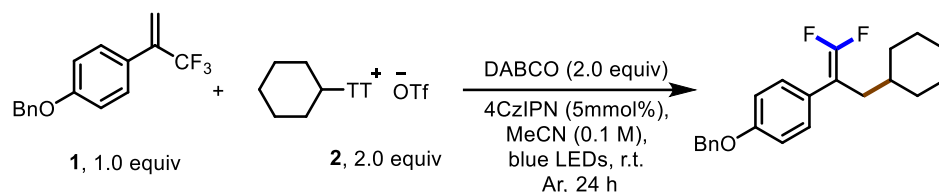
$$AEf = \frac{71.6}{100} * 82 = 57.9$$

$$CE = \frac{20 * 0.00016}{10 * 0.0002 + 11 * 0.0004} * 100 = 50.0$$

$$E - \text{Factor} = \frac{40.4 + 124.5 + 1.6 + 69.7 + 2357.1 - 60.2}{60.2} = 42.1$$

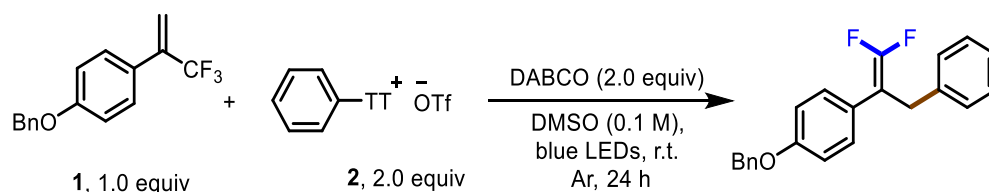
11. Experimental Procedures and Product Characterization

11.1 Procedure A



To a 10 mL glass vial was added 4CzIPN (7.9 mg, 0.01 mmol, 5 mol %), α -trifluoromethyl arylalkene (0.2 mmol, 1.0 equiv), alkyl thianthrenium salt (0.4 mmol, 2.0 equiv), DABCO (44.9 mg, 0.4 mmol, 2.0 equiv) and 2.0 mL of solvent. The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with DCM (3 \times 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product

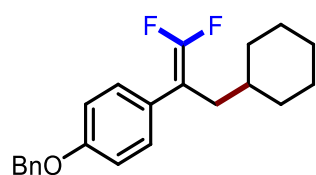
11.2 Procedure B



To a 10 mL glass vial was added α -trifluoromethyl arylalkene (0.2 mmol, 1.0 equiv), aryl thianthrenium salt (0.4 mmol, 2.0 equiv), DABCO (44.9 mg, 0.4 mmol, 2.0 equiv) and 2.0 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 10 mL of H₂O, and extracted with EA (3 \times 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

11.3 Product Characterization

1-(Benzyloxy)-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (3a)



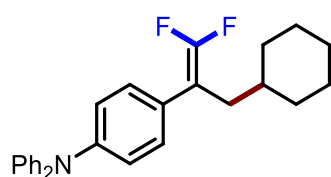
According to the *general procedure A*.

Yellow oil (58.2mg, 85%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.05 (s, 2H), 2.23 (s, 2H), 1.66 (d, *J* = 11.9 Hz, 4H), 1.59 (s, 1H), 1.26 (s, 1H), 1.11 (s, 3H), 0.91 (q, *J* = 10.2, 9.2 Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.8, 153.9 (dd, *J* = 285.4, 283.5 Hz), 137.0, 129.4 (t, *J* = 3.1 Hz), 128.6, 128.0, 127.6, 126.5 (t, *J* = 4.5 Hz), 114.7, 90.5 (dd, *J* = 22.2, 12.8 Hz), 70.0, 35.7, 35.3, 32.9, 26.5, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -92.15 (d, *J* = 46.3 Hz), -92.58 (d, *J* = 46.4 Hz). **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₂₂H₂₄F₂O 342.1795; found 342.1795.

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-N,N-diphenylaniline (3b)



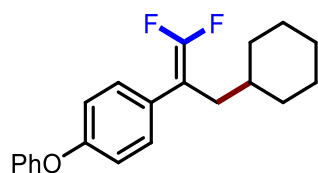
According to the *general procedure A*.

Yellow oil (75.0 mg, 93%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 7.6 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 4H), 7.01 (t, *J* = 8.3 Hz, 4H), 2.23 (d, *J* = 6.2 Hz, 2H), 1.68 (t, *J* = 11.1 Hz, 4H), 1.61 (s, 1H), 1.37–1.28 (m, 1H), 1.15 (t, *J* = 8.9 Hz, 3H), 0.94 (t, *J* = 11.1 Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 154.1 (dd, *J* = 290.2, 285.7 Hz), 147.6, 146.6, 129.3, 128.9 (t, *J* = 3.3 Hz), 127.7 (t, *J* = 3.9 Hz), 124.6, 123.0 (d, *J* = 2.3 Hz), 90.6 (dd, *J* = 22.1, 12.1 Hz), 35.8, 35.1, 32.9, 26.5, 26.2. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.18 (d, *J* = 45.3 Hz), -91.64 (d, *J* = 45.0 Hz). **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₂₇H₂₇F₂N 403.2112; found 403.2117.

1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-phenoxybenzene (3c)



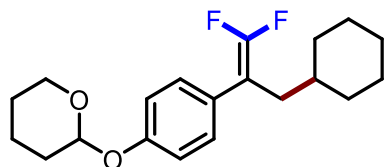
According to the *general procedure A*.

Yellow oil (53.8 mg, 82%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 2.27–2.22 (m, 2H), 1.68 (d, *J* = 11.6 Hz, 4H), 1.61 (s, 1H), 1.30–1.23 (m, 1H), 1.13 (s, 3H), 0.92 (q, *J* = 10.5, 9.8 Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 156.9, 156.4, 154.0 (d, *J* = 3.9 Hz), 129.8, 129.6 (t, *J* = 3.2 Hz), 128.9–128.7 (m), 123.5, 119.2, 118.5, 90.5 (dd, *J* = 22.4, 12.6 Hz), 35.7, 35.3 (t, *J* = 1.9 Hz), 32.9, 26.5, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.53 (d, *J* = 45.3 Hz), -92.02 (d, *J* = 45.0 Hz). **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₂₁H₂₂F₂O 328.1639; found 328.1633.

2-(4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenoxy)tetrahydro-2H-pyran (3d)



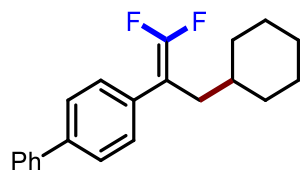
According to the *general procedure A*.

Yellow oil (49.7 mg, 74%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, $J = 8.5$ Hz, 2H), 6.95 (d, $J = 8.5$ Hz, 2H), 5.34 (s, 1H), 3.89–3.80 (m, 1H), 3.54 (dd, $J = 9.6, 5.2$ Hz, 1H), 2.15 (d, $J = 7.0$ Hz, 2H), 1.97–1.89 (m, 1H), 1.78 (dd, $J = 8.6, 4.1$ Hz, 2H), 1.59 (d, $J = 12.1$ Hz, 6H), 1.52 (s, 2H), 1.21–1.15 (m, 1H), 1.04 (s, 3H), 0.83 (q, $J = 10.4, 9.3$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 155.1, 152.8 (dd, $J = 289.1, 285.3$ Hz), 128.3 (t, $J = 3.1$ Hz), 126.11–126.00 (m), 115.2, 95.3, 89.5 (dd, $J = 22.1, 12.8$ Hz), 61.1, 34.6 (t, $J = 1.9$ Hz), 34.3, 31.8 (d, $J = 2.2$ Hz), 29.4, 25.4, 25.1, 24.2, 17.8. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -92.25 (d, $J = 46.5$ Hz), -92.61 (d, $J = 46.3$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₂₀H₂₆F₂O₂ 336.1901; found 336.1901.

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (3e)



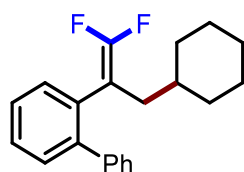
According to the *general procedure A*.

Yellow oil (31.2mg, 50%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, $J = 13.7, 7.8$ Hz, 4H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.38 (d, $J = 7.7$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 2.31 (d, $J = 7.1$ Hz, 2H), 1.74–1.64 (m, 4H), 1.60 (s, 1H), 1.33–1.27 (m, 1H), 1.13 (s, 3H), 0.95 (d, $J = 20.8$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 154.10 (dd, $J = 290.6, 286.3$ Hz), 140.6, 139.9, 133.1 (t, $J = 6.0$ Hz), 128.8, 128.6 (t, $J = 3.2$ Hz), 127.4, 127.1, 127.0, 90.8 (dd, $J = 22.3, 12.2$ Hz), 35.8, 35.2, 32.9, 26.5, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.63 (d, $J = 43.3$ Hz), -91.20 (d, $J = 43.2$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₂₁H₂₁F₂ 312.1690; found 312.1694.

2-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (3f)



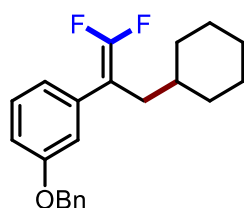
According to the *general procedure A*.

Yellow oil (46.8 mg, 75%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.36 (q, $J = 6.4, 5.5$ Hz, 3H), 7.32 (t, $J = 6.3$ Hz, 5H), 7.25 (d, $J = 7.6$ Hz, 1H), 1.66–1.52 (m, 5H), 1.47 (d, $J = 19.8$ Hz, 2H), 1.06–0.96 (m, 4H), 0.73 (q, $J = 11.1$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 153.98 (dd, $J = 286.8, 285.4$ Hz), 141.6 (d, $J = 3.0$ Hz), 141.4, 133.0 (d, $J = 4.8$ Hz), 131.0 (t, $J = 2.2$ Hz), 130.4, 128.7, 128.1, 127.8, 127.2, 127.1, 91.3 (dd, $J = 22.6, 15.5$ Hz), 35.6, 35.3 (t, $J = 2.3$ Hz), 32.9, 26.4, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.25 (d, $J = 45.6$ Hz), -93.80 (d, $J = 45.7$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₂₁H₂₂F₂ 312.1690; found 312.1684.

1-(Benzyloxy)-3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (3g)



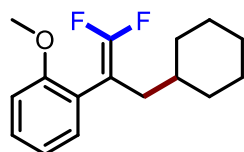
According to the *general procedure A*.

Yellow oil (61.6 mg, 90%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.42 (d, $J = 7.6$ Hz, 2H), 7.37 (t, $J = 7.4$ Hz, 2H), 7.31 (d, $J = 7.3$ Hz, 1H), 7.24 (t, $J = 7.9$ Hz, 1H), 6.92 (s, 1H), 6.89 (dd, $J = 17.4, 8.0$ Hz, 2H), 5.04 (s, 2H), 2.23 (d, $J = 7.0$ Hz, 2H), 1.65 (d, $J = 11.6$ Hz, 4H), 1.58 (s, 1H), 1.24 (dd, $J = 14.9, 7.4$ Hz, 1H), 1.10 (s, 3H), 0.89 (q, $J = 10.5, 9.8$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 158.8, 154.1 (dd, $J = 289.4, 287.1$ Hz), 137.0, 135.6 (d, $J = 2.7$ Hz), 129.4, 128.7, 128.1, 127.6, 121.1 (t, $J = 3.1$ Hz), 115.3 (t, $J = 3.2$ Hz), 113.4, 91.1 (dd, $J = 19.9, 14.7$ Hz), 70.1, 35.7 (t, $J = 1.9$ Hz), 35.3, 32.9, 26.5, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.97 (d, $J = 4.6$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₂₂H₂₄F₂O 342.1795; found 342.1788.

1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-methoxybenzene (3h)



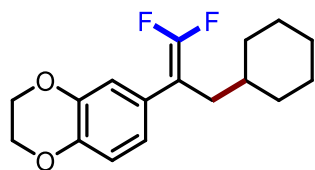
According to the *general procedure A*.

Yellow oil (33.0 mg, 62%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.27 (t, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 7.4$ Hz, 1H), 6.93 (t, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 8.3$ Hz, 1H), 3.81 (s, 3H), 2.20 (d, $J = 7.1$ Hz, 2H), 1.70 (d, $J = 12.8$ Hz, 2H), 1.65 (dd, $J = 8.8, 4.2$ Hz, 2H), 1.59 (s, 1H), 1.16–1.08 (m, 4H), 0.90 (q, $J = 11.0$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.4 (d, $J = 2.5$ Hz), 153.4 (t, $J = 286.0$ Hz), 131.0 (t, $J = 3.0$ Hz), 128.9, 123.2 (dd, $J = 5.1, 1.7$ Hz), 120.4, 111.0, 87.8 (dd, $J = 16.5$ Hz, 15 Hz), 55.5, 35.7, 35.6, 33.0, 26.5, 26.2. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.27 (d, $J = 44.9$ Hz), -94.07 (d, $J = 44.9$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₁₆H₂₀F₂O 266.1482; found 266.1476.

6-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine (3i)



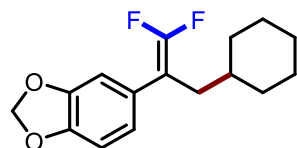
According to the *general procedure A*.

Yellow oil (42.4 mg, 72%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 6.83 (d, $J = 8.5$ Hz, 2H), 6.78 (d, $J = 8.3$ Hz, 1H), 4.26 (s, 4H), 2.20 (d, $J = 6.9$ Hz, 2H), 1.67 (d, $J = 9.9$ Hz, 4H), 1.60 (s, 1H), 1.28–1.24 (m, 1H), 1.16–1.10 (m, 3H), 0.94–0.86 (m, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 153.9 (dd, $J = 289.4, 285.5$ Hz), 143.3, 142.6, 127.3 (dd, $J = 4.1, 2.7$ Hz), 121.4 (t, $J = 3.0$ Hz), 117.1 (t, $J = 3.0$ Hz), 90.4 (dd, $J = 22.0, 13.0$ Hz), 64.4, 35.6, 35.3, 32.9, 26.4, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.74 (d, $J = 43.4$ Hz), -91.29 (d, $J = 43.5$ Hz). HRMS (EI-TOF) m/z : $[M]^+$ Calcd for C₁₇H₂₀F₂O₂ 294.1431; found 294.1425.

5-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (3j)



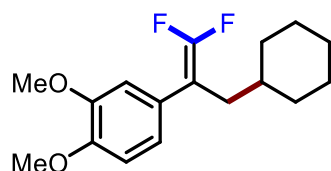
According to the *general procedure A*.

Yellow oil (35.9 mg, 64%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 6.79 (d, $J = 7.4$ Hz, 2H), 6.75 (d, $J = 8.2$ Hz, 1H), 5.95 (s, 2H), 2.20 (d, $J = 7.0$ Hz, 2H), 1.66 (d, $J = 9.6$ Hz, 4H), 1.60 (s, 1H), 1.29–1.21 (m, 1H), 1.12 (s, 3H), 0.94–0.85 (m, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 153.9 (t, $J = 285.0$ Hz), 147.6, 146.6, 127.8 (d, $J = 2.2$ Hz), 121.8 (t, $J = 3.1$ Hz), 108.8 (t, $J = 3.2$ Hz), 108.2, 101.1, 90.8 (dd, $J = 15.1, 18.0$ Hz), 35.6, 35.5, 32.9, 26.4, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -92.08. HRMS (EI-TOF) m/z : $[M]^+$ Calcd for C₁₆H₁₈F₂O₂ 280.1275; found 280.1268.

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,2-dimethoxybenzene (3k)



According to the *general procedure A*.

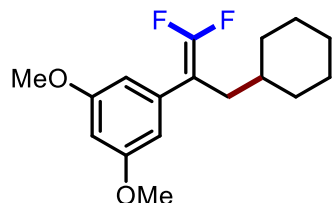
Yellow oil (29.6 mg, 50%);

Rf 0.50 (Petroleum ether/EtOAc, 20/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 6.85 (s, 2H), 6.82 (s, 1H), 3.89 (s, 6H), 2.24 (d, $J = 7.1$ Hz, 2H), 1.68 (d, $J = 12.7$ Hz, 4H), 1.60 (s, 1H), 1.29–1.24 (m, 1H), 1.13 (s, 3H), 0.92 (q, $J = 10.7, 10.1$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 153.9 (dd, $J = 288.3, 286.3$ Hz), 148.7, 148.1, 126.6

(d, $J = 2.8$ Hz), 120.7 (t, $J = 3.1$ Hz), 111.6 (t, $J = 3.4$ Hz), 111.0, 90.8 (dd, $J = 20.0, 14.9$ Hz), 55.9, 55.8, 35.7 (t, $J = 3.0$ Hz), 35.4, 32.9, 26.4, 26.1. ^{19}F NMR (376 MHz, Chloroform- d) δ -92.13 (d, $J = 4.3$ Hz). HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_2\text{O}_2$ 296.1588; found 296.1586.

1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-3,5-dimethoxybenzene (3l)



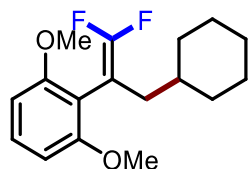
According to the *general procedure A*.

Yellow oil (54.4 mg, 93%);

R_f 0.50 (Petroleum ether/EtOAc, 20/1).

^1H NMR (600 MHz, Chloroform- d) δ 6.46 (s, 2H), 6.39 (s, 1H), 3.78 (s, 6H), 2.23 (s, 2H), 1.75–1.64 (m, 4H), 1.60 (s, 1H), 1.28 (s, 1H), 1.13 (s, 3H), 0.92 (s, 2H). ^{13}C NMR (150 MHz, Chloroform- d) δ 160.6, 153.9 (dd, $J = 283.5$ Hz, 285.0 Hz), 136.1 (t, $J = 3.0$ Hz), 106.7 (t, $J = 3.0$ Hz), 98.9, 91.2 (dd, $J = 22.5, 12.3$ Hz), 55.3, 35.7, 35.3, 32.9, 26.4, 26.1. ^{19}F NMR (376 MHz, Chloroform- d) δ -90.57 (d, $J = 43.3$ Hz), -91.07 (d, $J = 43.4$ Hz). HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_2\text{O}_2$ 296.1588; found 296.1586.

2-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,3-dimethoxybenzene (3m)



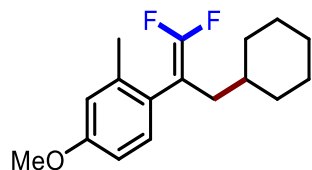
According to the *general procedure A*.

Yellow oil (32.6 mg, 55%);

R_f 0.50 (Petroleum ether/EtOAc, 20/1).

^1H NMR (600 MHz, Chloroform- d) δ 7.23 (t, $J = 8.0$ Hz, 1H), 6.55 (d, $J = 8.1$ Hz, 2H), 3.79 (s, 6H), 2.16–2.10 (m, 2H), 1.76 (d, $J = 12.3$ Hz, 2H), 1.66 (s, 2H), 1.59 (s, 1H), 1.11 (s, 4H), 0.88 (d, $J = 10.5$ Hz, 2H). ^{13}C NMR (150 MHz, Chloroform- d) δ 158.5, 153.1 (t, $J = 283.5$ Hz), 129.1, 111.7 (t, $J = 7.1$ Hz), 106.2, 103.8, 83.3 (dd, $J = 26.0, 17.3$ Hz), 55.7, 36.2, 35.3, 33.1, 26.6, 26.3. ^{19}F NMR (376 MHz, Chloroform- d) δ -89.43 (d, $J = 44.3$ Hz), -94.27 (d, $J = 44.3$ Hz). HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_2\text{O}_2$ 296.1588; found 296.1584.

1-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4-methoxy-2-methylbenzene (3o)



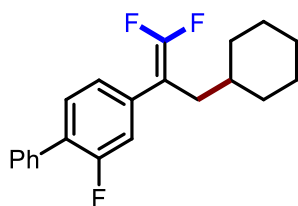
According to the *general procedure A*.

Yellow oil (28.0 mg, 50%);

Rf 0.50 (Petroleum ether/EtOAc, 40/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 8.4 Hz, 1H), 6.75 (s, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 2.25 (s, 3H), 2.12 (d, *J* = 6.6 Hz, 2H), 1.69 (t, *J* = 11.3 Hz, 4H), 1.62 (s, 1H), 1.22–1.18 (m, 1H), 1.15 (t, *J* = 8.5 Hz, 3H), 0.97–0.89 (m, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 158.9, 154.1 (dd, *J* = 289.4, 287.1 Hz), 138.2 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 3.0 Hz), 126.0 (d, *J* = 5.1 Hz), 115.6, 111.2, 89.3 (dd, *J* = 21.9, 16.9 Hz), 55.1, 36.9, 35.5 (t, *J* = 3.0 Hz), 33.2, 26.5, 26.1, 19.8. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.13 (d, *J* = 46.2 Hz), -94.42 (d, *J* = 46.3 Hz). **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₁₇H₂₂F₂O 280.1639; found 280.1631.

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-fluoro-1,1'-biphenyl (3o)



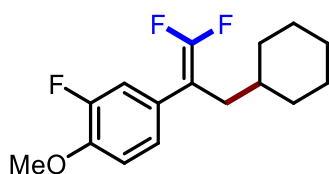
According to the *general procedure A*.

Yellow oil (58.8 mg, 89%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.46–7.42 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 12.1 Hz, 1H), 2.29 (d, *J* = 6.2 Hz, 2H), 1.69 (t, *J* = 11.6 Hz, 4H), 1.62 (s, 1H), 1.35–1.28 (m, 1H), 1.15 (t, *J* = 8.7 Hz, 3H), 0.97–0.90 (m, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 160.4, 158.8, 154.3 (dd, *J* = 292.0, 287.0 Hz), 135.4, 135.2 (dt, *J* = 8.3, 4.2 Hz), 130.6 (d, *J* = 4.1 Hz), 129.0 (d, *J* = 2.9 Hz), 128.5, 127.8, 124.2 (q, *J* = 3.3 Hz), 115.9 (dt, *J* = 24.2, 3.7 Hz), 90.3 (dd, *J* = 23.1, 11.6 Hz), 35.8, 34.9, 32.9, 26.4, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -89.29 (d, *J* = 40.4 Hz), -89.78 (d, *J* = 40.3 Hz), -117.85–117.95 (m). **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₂₁H₂₁F₃ 330.1595; found 330.1591.

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-2-fluoro-1-methoxybenzene (3p)



According to the *general procedure A*.

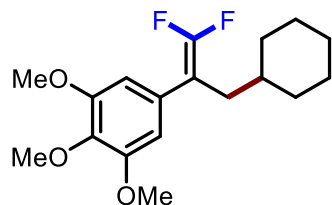
Yellow oil (33.8 mg, 60%);

Rf 0.50 (Petroleum ether/EtOAc, 40/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 16.2, 11.0 Hz, 2H), 6.93 (t, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 2.22 (d, *J* = 6.2 Hz, 2H), 1.66 (d, *J* = 9.4 Hz, 4H), 1.60 (s, 1H), 1.27–1.22 (m, 1H), 1.12 (s, 3H), 0.91 (q, *J* = 10.9 Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 154.0 (dd, *J* = 290.2, 286.0 Hz), 152.1 (d, *J* = 245.3 Hz), 146.6 (d, *J* = 10.6 Hz), 127.0–126.8 (m), 124.1 (q, *J* = 3.4 Hz), 116.0 (dt, *J* = 19.1, 3.4 Hz), 113.2 (d, *J* = 2.3 Hz), 90.0 (ddd, *J* = 22.7, 12.0, 1.5 Hz), 56.2, 35.7, 35.1, 32.8, 26.4, 26.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.06 (d, *J* = 44.0 Hz), -91.53 (d, *J* =

44.0 Hz), -135.24 (dd, $J = 12.0, 9.1$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for $C_{16}H_{19}F_3O$ 284.1388; found 284.1385.

5-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,2,3-trimethoxybenzene (3q)



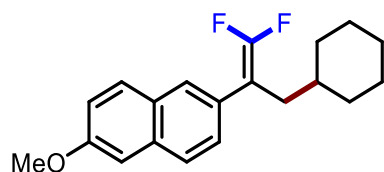
According to the *general procedure A*.

Yellow oil (60.0 mg, 92%);

Rf 0.50 (Petroleum ether/EtOAc, 20/1).

1H NMR (600 MHz, Chloroform-*d*) δ 6.51 (s, 2H), 3.86 (s, 9H), 2.23 (d, $J = 6.8$ Hz, 2H), 1.69 (d, $J = 12.2$ Hz, 5H), 1.62 (s, 1H), 1.38–1.22 (m, 2H), 1.14 (q, $J = 9.1$ Hz, 3H), 0.97–0.89 (m, 2H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.9 (dd, $J = 289.5, 286.0$ Hz), 153.1, 137.2, 129.7 (dd, $J = 4.7, 2.8$ Hz), 105.7 (t, $J = 3.0$ Hz), 91.2 (dd, $J = 22.5, 12.6$ Hz), 60.8, 56.2, 35.8, 35.5, 32.9, 26.4, 26.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -91.17 (d, $J = 44.7$ Hz), -91.55 (d, $J = 44.8$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for $C_{18}H_{24}F_2O_3$ 326.1694; found 326.1690.

2-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-6-methoxynaphthalene (3r)



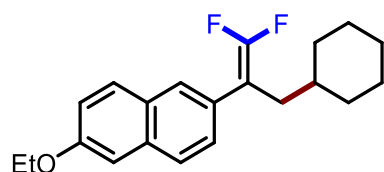
According to the *general procedure A*.

Yellow oil (44.3 mg, 70%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

1H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, $J = 8.6$ Hz, 2H), 7.68 (s, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 8.9$ Hz, 1H), 7.12 (s, 1H), 3.92 (s, 3H), 2.35 (d, $J = 7.0$ Hz, 2H), 1.70 (d, $J = 12.5$ Hz, 2H), 1.64 (d, $J = 6.8$ Hz, 2H), 1.57 (s, 1H), 1.28–1.26 (m, 1H), 1.09 (t, $J = 10.3$ Hz, 3H), 0.94 (q, $J = 11.7$ Hz, 2H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 157.2, 154.1 (dd, $J = 289.9, 285.9$ Hz), 133.5, 129.5, 129.3–129.2 (m), 128.7, 127.1 (t, $J = 3.2$ Hz), 126.8, 126.8, 119.4, 106.3, 91.1 (dd, $J = 22.2, 12.5$ Hz), 63.5, 35.7, 35.3, 32.9, 26.4, 26.1, 14.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -91.37 (d, $J = 44.7$ Hz), -92.04 (d, $J = 44.6$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for $C_{20}H_{22}F_2O$ 316.1639; found 316.1645.

2-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-6-ethoxynaphthalene (3s)



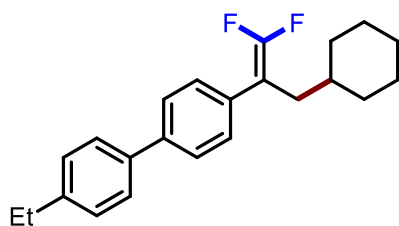
According to the *general procedure A*.

Yellow oil (47.5 mg, 72%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.74–7.68 (m, 2H), 7.67 (s, 1H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 10.6$ Hz, 1H), 7.11 (s, 1H), 4.14 (q, $J = 6.9$ Hz, 2H), 2.35 (d, $J = 7.0$ Hz, 2H), 1.70 (d, $J = 12.7$ Hz, 2H), 1.64 (d, $J = 9.1$ Hz, 2H), 1.57 (s, 1H), 1.48 (t, $J = 6.9$ Hz, 3H), 1.30–1.26 (m, 1H), 1.16–1.04 (m, 3H), 0.93 (q, $J = 11.7$ Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.2, 154.1 (dd, $J = 289.9, 285.9$ Hz), 133.6, 129.4, 129.1 (t, $J = 3.1$ Hz), 128.7, 127.1 (t, $J = 3.2$ Hz), 126.7 (t, $J = 3.0$ Hz), 126.7, 119.4, 106.3, 91.1 (dd, $J = 22.2, 12.5$ Hz), 63.5, 35.7, 35.3, 32.9, 26.4, 26.1, 14.8. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.41 (d, $J = 44.9$ Hz), -92.07 (d, $J = 44.8$ Hz). **HRMS** (EI-TOF) m/z : [M]⁺ Calcd for C₂₁H₂₄F₂O 330.1795; found 330.1790.

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-4'-ethyl-1,1'-biphenyl (3t)



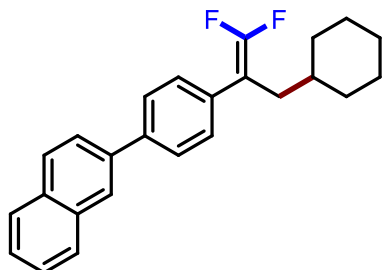
According to the *general procedure A*.

Yellow oil (30.6 mg, 45%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 7.9$ Hz, 2H), 2.69 (q, $J = 7.6$ Hz, 2H), 2.30 (d, $J = 7.0$ Hz, 2H), 1.73–1.63 (m, 4H), 1.62–.57 (m, 1H), 1.34–1.30 (m, 1H), 1.27 (t, $J = 7.6$ Hz, 3H), 1.13 (t, $J = 7.7$ Hz, 3H), 0.99–0.89 (m, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 154.1 (dd, $J = 290.6, 286.2$ Hz), 143.5, 139.8, 138.0, 132.8 (t, $J = 4.4$ Hz), 128.6 (t, $J = 3.2$ Hz), 128.3, 126.93, 126.89, 90.8 (dd, $J = 22.2, 12.2$ Hz), 35.8, 35.2, 32.9, 28.6, 26.5, 26.1, 15.6. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.76 (d, $J = 43.4$ Hz), -91.30 (d, $J = 43.5$ Hz). **HRMS** (EI-TOF) m/z : [M]⁺ Calcd for C₂₃H₂₆F₂ 340.2003; found 340.2001.

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



According to the *general procedure A*.

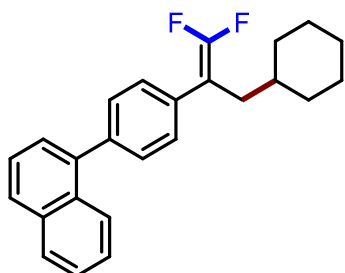
Yellow oil (42.0 mg, 58%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.93–7.88 (m, 2H), 7.86 (d, $J = 7.7$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 7.9$ Hz, 2H), 7.49 (p, $J = 6.8$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H),

2.33 (d, $J = 6.9$ Hz, 2H), 1.74–1.66 (m, 4H), 1.62–1.58 (m, 1H), 1.35–1.30 (m, 1H), 1.15 (t, $J = 8.4$ Hz, 3H), 0.95 (q, $J = 9.8, 8.6$ Hz, 2H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 154.1 (dd, $J = 290.7, 286.4$ Hz), 139.8, 137.9, 133.7, 133.2 (t, $J = 4.5$ Hz), 132.7, 128.7 (t, $J = 3.2$ Hz), 128.5, 128.2, 127.7, 127.3, 126.3, 126.0, 125.7, 125.4, 90.8 (dd, $J = 22.2, 12.2$ Hz), 35.8, 35.1, 32.9, 26.4, 26.1. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -90.60 (d, $J = 43.1$ Hz), -91.15 (d, $J = 43.2$ Hz). **HRMS** (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{25}\text{H}_{24}\text{F}_2$ 362.1846; found 362.1853.

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



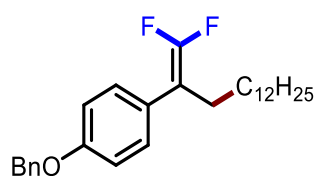
According to the *general procedure A*.

Yellow oil (45.6 mg, 63%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.94 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.85 (d, $J = 8.3$ Hz, 1H), 7.51 (d, $J = 8.1$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 3H), 7.46–7.41 (m, 4H), 2.35 (d, $J = 6.9$ Hz, 2H), 1.75 (d, $J = 12.9$ Hz, 2H), 1.70 (d, $J = 9.3$ Hz, 2H), 1.64 (s, 1H), 1.44–1.34 (m, 1H), 1.17 (q, $J = 12.2$ Hz, 3H), 0.97 (q, $J = 10.9, 10.3$ Hz, 2H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 154.2 (dd, $J = 290.7, 286.2$ Hz), 139.8, 139.5, 133.9, 133.1 (t, $J = 4.5$ Hz), 131.6, 130.1, 128.3, 128.1 (t, $J = 3.3$ Hz), 127.7, 127.0, 126.1, 126.0, 125.8, 125.4, 90.9 (dd, $J = 22.2, 12.1$ Hz), 35.81, 35.23, 32.96, 26.49, 26.13. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -90.48 (d, $J = 43.2$ Hz), -91.14 (d, $J = 43.2$ Hz). **HRMS** (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{25}\text{H}_{24}\text{F}_2$ 362.1846; found 362.1843.

1-(Benzyloxy)-4-(1,1-difluoropentadec-1-en-2-yl)benzene (3aa)



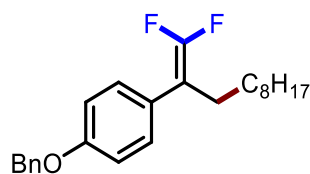
According to the *general procedure A*.

Yellow oil (52.2 mg, 61%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.43 (d, $J = 7.1$ Hz, 2H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.32 (t, $J = 7.0$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 6.95 (d, $J = 7.9$ Hz, 2H), 5.05 (s, 2H), 2.34 (s, 2H), 1.24 (d, $J = 11.7$ Hz, 22H), 0.88 (t, $J = 6.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 157.8, 153.5 (t, $J = 287.3$ Hz), 136.9, 129.4 (t, $J = 3.2$ Hz), 128.6, 128.0, 127.5, 126.3, 114.7, 91.9 (t, $J = 17.4$ Hz), 70.0, 32.0, 29.72, 29.69, 29.65, 29.60, 29.4, 29.3, 29.1, 27.76, 27.75, 27.72, 22.7, 14.2. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -92.83. **HRMS** (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{F}_2\text{O}$ 428.2891; found 428.2898.

1-(Benzyloxy)-4-(1,1-difluoroundec-1-en-2-yl)benzene (3ab)



According to the *general procedure A*.

Yellow oil (41.7 mg, 56%);

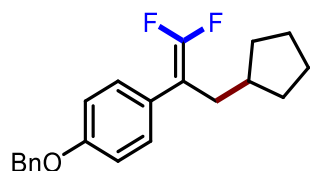
Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26–7.18 (m, 4H), 7.15 (d, *J* = 6.9 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 4.87 (s, 2H), 2.16 (s, 2H), 1.10 (s, 14H), 0.69 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (150 MHz, Chloroform-*d*) δ 157.8, 153.5 (t, *J* = 287.3 Hz), 136.9, 129.4 (t, *J* = 3.1 Hz), 128.6, 128.0, 127.5, 126.3, 91.9 (t, *J* = 17.3 Hz), 70.0, 31.9, 29.6, 29.4, 29.3, 29.0, 27.8, 27.7, 22.7, 14.2.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -92.84. **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₂₄H₃₀F₂O 372.2265; found 372.2263.

1-(Benzyloxy)-4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)benzene (3ac)



According to the *general procedure A*.

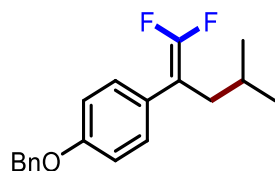
Yellow oil (34.1 mg, 52%);

Rf 0.50 (Petroleum ether/EtOAc, 50/1).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27–7.18 (m, 4H), 7.15 (d, *J* = 6.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.87 (s, 2H), 2.16 (d, *J* = 6.9 Hz, 2H), 1.61 (dt, *J* = 15.1, 7.5 Hz, 1H), 1.49–1.37 (m, 4H), 1.31–1.22 (m, 2H), 0.95 (dq, *J* = 14.0, 7.6 Hz, 2H).

¹³C NMR (150 MHz, Chloroform-*d*) δ 157.9, 153.8 (dd, *J* = 283.5, 286.5 Hz), 136.9, 129.5 (t, *J* = 3.0 Hz), 128.6, 128.1, 127.6, 126.5 (dd, *J* = 4.2, 2.7 Hz), 91.8 (dd, *J* = 22.0, 13.1 Hz), 70.0, 38.2, 33.7, 32.1, 25.0. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -92.93 (d, *J* = 47.4 Hz), -93.26 (d, *J* = 47.4 Hz). **HRMS** (EI-TOF) *m/z*: [M]⁺ Calcd for C₂₂H₂₄F₂O 342.1795; found 342.1795.

1-(Benzyloxy)-4-(1,1-difluoro-4-methylpent-1-en-2-yl)benzene (3ad)



According to the *general procedure A*.

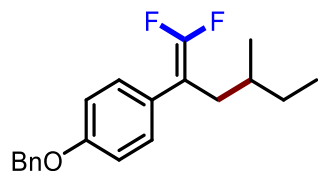
Yellow oil (50.1 mg, 83%);

Rf 0.60 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 2H), 2.22 (d, *J* = 6.3 Hz,

2H), 1.57 (dt, $J = 13.5, 6.7$ Hz, 1H), 0.87 (d, $J = 6.7$ Hz, 6H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 157.9, 154.0 (dd, $J = 288.9, 285.5$ Hz), 136.9, 129.4 (t, $J = 3.1$ Hz), 128.6, 128.0, 127.5, 126.4 (dd, $J = 4.5, 2.8$ Hz), 114.7, 91.1 (dd, $J = 22.0, 13.0$ Hz), 70.0, 36.8, 26.4 (t, $J = 2.3$ Hz), 22.1. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -92.43 (d, $J = 46.5$ Hz), -92.84 (d, $J = 46.3$ Hz). **HRMS** (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{F}_2\text{O}$ 328.1639; found 328.1635.

(S)-1-(Benzyloxy)-4-(1,1-difluoro-4-methylhex-1-en-2-yl)benzene (3ae)



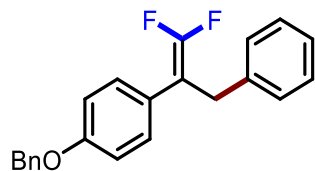
According to the *general procedure A*.

Yellow oil (56.9 mg, 90%);

Rf 0.60 (Petroleum ether/EtOAc, 100/1).

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.42 (d, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.3$ Hz, 2H), 7.31 (t, $J = 7.1$ Hz, 1H), 7.22 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 8.1$ Hz, 2H), 5.04 (s, 2H), 2.34 (d, $J = 13.8$ Hz, 1H), 2.16 (dd, $J = 13.7, 8.0$ Hz, 1H), 1.35 (dt, $J = 12.1, 6.5$ Hz, 2H), 1.13 (dt, $J = 14.8, 7.5$ Hz, 1H), 0.88 – 0.78 (m, 6H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 157.9, 153.9 (dd, $J = 288.7, 285.6$ Hz), 137.0, 129.5 (t, $J = 3.0$ Hz), 128.7, 128.1, 127.6, 126.4 (dd, $J = 4.2, 2.6$ Hz), 114.8, 91.0 (dd, $J = 21.6, 13.3$ Hz), 70.1, 34.7, 32.6 (t, $J = 2.3$ Hz), 29.1, 18.6, 11.3. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -92.42 (d, $J = 46.7$ Hz), -92.66 (d, $J = 47.3$ Hz). **HRMS** (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{O}$ 316.1639; found 316.1634.

1-(Benzyloxy)-4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzene (3af)



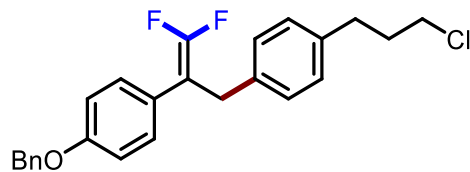
According to the *general procedure B*.

White oil (55.79 mg, 83%);

Rf 0.60 (Petroleum ether/EtOAc, 100/1).

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.37 (dt, $J = 14.5, 7.2$ Hz, 4H), 7.31 (t, $J = 6.8$ Hz, 1H), 7.23 (t, $J = 7.3$ Hz, 2H), 7.16 (dd, $J = 15.5, 7.7$ Hz, 5H), 6.88 (d, $J = 7.9$ Hz, 2H), 5.00 (s, 2H), 3.69 (s, 2H). $^{13}\text{C NMR}$ (150 MHz, Chloroform- d) δ 157.9, 154.3 (dd, $J = 290.8, 286.8$ Hz), 138.6 (t, $J = 2.6$ Hz), 136.9, 129.5 (t, $J = 3.5$ Hz), 128.6, 128.5, 128.3, 128.0, 127.5, 126.4, 126.0 (t, $J = 3.8$ Hz), 114.7, 91.1 (dd, $J = 21.5, 13.8$ Hz), 70.0, 34.0. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -91.26 (d, $J = 42.2$ Hz), -91.70 (d, $J = 42.4$ Hz). **HRMS** (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{O}$ 336.1326; found 336.1321.

1-(Benzyloxy)-4-(3-(4-(3-chloropropyl)phenyl)-1,1-difluoroprop-1-en-2-yl)benzene (3ag)



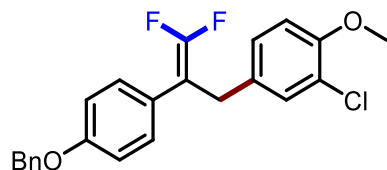
According to the *general procedure B*.

Yellow oil (45.3 mg, 55%);

Rf 0.60 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.40 (t, *J* = 7.6 Hz, 3H), 7.36 (s, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.07 (s, 4H), 6.89 (d, *J* = 7.8 Hz, 2H), 5.02 (s, 2H), 3.67 (s, 2H), 3.50 (t, *J* = 6.0 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 2.04 (p, *J* = 6.5 Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.9, 154.3 (dd, *J* = 291.0, 286.9 Hz), 138.7, 136.8, 136.4 (t, *J* = 2.7 Hz), 129.4 (t, *J* = 3.5 Hz), 128.7, 128.6, 128.4, 128.0, 127.5, 126.0 (t, *J* = 3.8 Hz), 114.7, 91.1 (dd, *J* = 21.5, 13.5 Hz), 70.0, 44.3, 34.0, 33.6, 32.3. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.25 (d, *J* = 42.2 Hz), -91.72 (d, *J* = 42.5 Hz). **HRMS** (EI-TOF) *m/z*: [*M*]⁺ Calcd for C₂₅H₂₃ClF₂O₂ 412.1405; found 412.1414.

4-(2-(4-(Benzyloxy)phenyl)-3,3-difluoroallyl)-2-chloro-1-methoxybenzene (3ah)



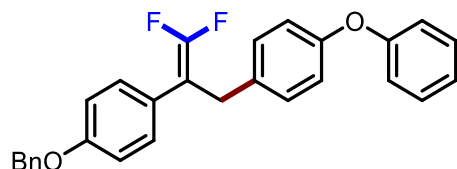
According to the *general procedure B*.

Yellow oil (56.0 mg, 70%);

Rf 0.60 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 6.7 Hz, 2H), 7.39 (s, 2H), 7.33 (d, *J* = 6.7 Hz, 1H), 7.16 (d, *J* = 5.9 Hz, 3H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.03 (s, 2H), 3.84 (s, 3H), 3.61 (s, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 158.0, 155.5, 154.2 (dd, *J* = 291.0, 287.2 Hz), 136.8, 131.7 (t, *J* = 2.8 Hz), 130.0, 129.4 (t, *J* = 3.4 Hz), 128.6, 128.0, 127.5, 127.4, 125.6 (t, *J* = 3.3 Hz), 122.3, 114.8, 112.0, 91.0 (dd, *J* = 20.8, 14.2 Hz), 70.0, 56.1, 32.9. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.29 (d, *J* = 41.8 Hz), -91.45 (d, *J* = 42.3 Hz). **HRMS** (ESI) *m/z*: [*M*+Na]⁺ Calcd for C₂₃H₁₉ClF₂NaO₂⁺ 423.0934; found 423.0923.

1-(Benzyloxy)-4-(1,1-difluoro-3-(4-phenoxyphenyl)prop-1-en-2-yl)benzene (3ai)



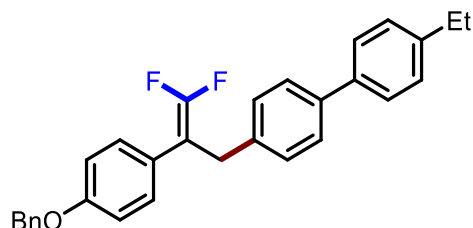
According to the *general procedure B*.

Yellow oil (62.5 mg, 73%);

Rf 0.60 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, J = 7.5 Hz, 2H), 7.37 (s, 2H), 7.31 (d, J = 7.7 Hz, 3H), 7.19 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 7.1 Hz, 1H), 6.97 (d, J = 8.1 Hz, 2H), 6.92–6.88 (m, 4H), 5.02 (s, 2H), 3.67 (s, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.9, 157.3, 155.7, 154.2 (dd, J = 290.8, 287.0 Hz), 136.8, 133.4, 129.7, 129.54, 129.45 (t, J = 3.5 Hz), 128.7, 128.0, 127.5, 123.1, 119.0, 118.72, 114.8, 91.2 (dd, J = 21.3, 13.7 Hz), 70.0, 33.3. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.40 (d, J = 42.6 Hz), -91.72 (d, J = 42.5 Hz). **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₈H₂₂F₂NaO₂⁺ 451.1480; found 451.1470.

4-(2-(4-(Benzyloxy)phenyl)-3,3-difluoroallyl)-4'-ethyl-1,1'-biphenyl (3aj)



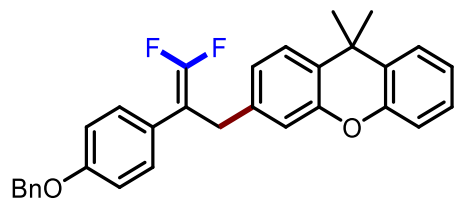
According to the *general procedure B*.

Yellow oil (33.5 mg, 38%);

R_f 0.60 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.47 (t, J = 7.5 Hz, 4H), 7.40 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 7.0 Hz, 1H), 7.25 (s, 2H), 7.21 (t, J = 7.8 Hz, 4H), 6.90 (d, J = 8.6 Hz, 2H), 5.02 (s, 2H), 3.73 (s, 2H), 2.70–2.66 (m, 2H), 1.26 (s, 3H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.9, 154.3 (dd, J = 291.0, 287.0 Hz), 143.3, 139.2, 138.2, 137.3 (t, J = 2.6 Hz), 136.8, 129.4 (t, J = 3.5 Hz), 128.6, 128.6, 128.3, 128.0, 127.5, 127.0, 126.9, 114.8, 91.1 (dd, J = 21.4, 13.7 Hz), 70.0, 33.6, 28.5, 15.6. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.18 (d, J = 42.5 Hz), -91.59 (d, J = 42.5 Hz). **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₃₀H₂₇F₂O⁺ 441.2024; found 441.2035.

3-(2-(4-(Benzyloxy)phenyl)-3,3-difluoroallyl)-9,9-dimethyl-9H-xanthene (3ak)



According to the *general procedure B*.

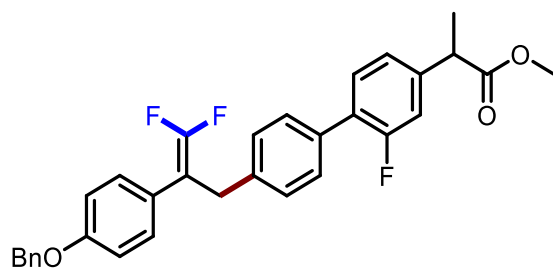
Yellow oil (37.5 mg, 40%);

R_f 0.60 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, J = 8.1 Hz, 2H), 7.37–7.34 (m, 3H), 7.31 (d, J = 6.6 Hz, 1H), 7.17–7.13 (m, 3H), 7.09 (s, 1H), 7.04 (d, J = 7.0 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 5.01 (s, 2H), 3.66 (s, 2H), 1.53 (s, 6H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.9, 154.1 (dd, J = 291.1, 288.4 Hz), 150.4, 148.9, 136.8, 132.9, 129.9, 129.8, 129.62, 129.60, 129.58, 128.6, 128.0, 127.34, 127.28, 126.1, 126.0, 123.0, 116.34, 116.30, 114.7, 91.5 (dd, J = 20.3, 14.9 Hz), 70.0, 33.9, 33.7, 32.3. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -92.02, -92.04.

Methyl 2-(4'-(2-(4-(benzyloxy)phenyl)-3,3-difluoroallyl)-2-fluoro-[1,1'-biphenyl]-4-

yl)propanoate (3al)



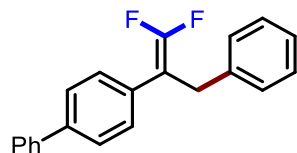
According to the *general procedure B*.

Yellow oil (56.8 mg, 55%);

Rf 0.4 (Petroleum ether/EtOAc, 20/1).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.93 (d, $J = 7.8$ Hz, 1H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 3.6$ Hz, 1H), 7.42 (d, $J = 7.4$ Hz, 4H), 7.36 (d, $J = 7.2$ Hz, 2H), 7.32 (d, $J = 7.5$ Hz, 1H), 7.22 (s, 2H), 7.10 (dd, $J = 13.6, 10.2$ Hz, 3H), 6.91 (d, $J = 8.6$ Hz, 2H), 5.02 (s, 2H), 3.74 (s, 2H), 3.69 (s, 3H), 1.51 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 174.5, 160.5, 158.9, 157.9, 154.4 (dd, $J = 291.2, 287.0$ Hz), 141.7 (d, $J = 7.7$ Hz), 141.4, 138.1 (t, $J = 2.7$ Hz), 136.8, 133.6, 130.7 (d, $J = 4.0$ Hz), 129.9, 129.4 (t, $J = 3.5$ Hz), 129.0 (d, $J = 2.3$ Hz), 128.6, 128.44, 128.35, 128.0, 127.5, 125.9 (t, $J = 3.8$ Hz), 125.5, 124.5, 123.5 (d, $J = 3.2$ Hz), 115.2 (d, $J = 23.7$ Hz), 114.8, 90.9 (dd, $J = 21.5, 13.7$ Hz), 70.0, 52.2, 44.9, 33.7, 18.4. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -91.01 (d, $J = 42.0$ Hz), -91.45 (d, $J = 42.0$ Hz), -117.48.

4-(1,1-Difluoro-3-phenylprop-1-en-2-yl)-1,1'-biphenyl (3am)



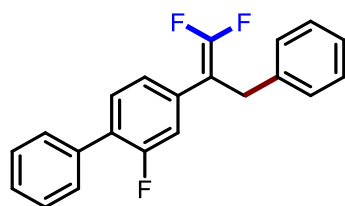
According to the *general procedure B*.

Yellow oil (45.9 mg, 75%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.54 (d, $J = 7.4$ Hz, 2H), 7.50 (d, $J = 7.9$ Hz, 2H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.31 (s, 1H), 7.24 (d, $J = 7.3$ Hz, 2H), 7.21–7.16 (m, 3H), 3.76 (s, 2H). $^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 154.6 (dd, $J = 292.4, 287.8$ Hz), 140.5, 140.0, 138.5 (t, $J = 2.6$ Hz), 132.5 (t, $J = 4.0$ Hz), 128.8, 128.63, 128.60, 128.3, 127.4, 127.1, 127.0, 126.5, 91.4 (dd, $J = 21.5, 13.2$ Hz), 33.8. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -89.54 (d, $J = 39.0$ Hz), -90.11 (d, $J = 38.9$ Hz). HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{16}\text{F}_2$ 306.1220; found 306.1213.

4-(1,1-Difluoro-3-phenylprop-1-en-2-yl)-4'-ethyl-1,1'-biphenyl (3an)



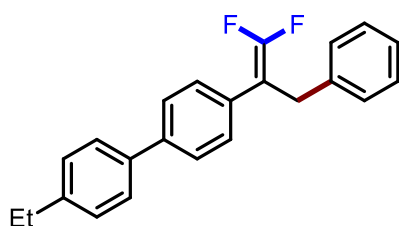
According to the *general procedure B*.

Yellow oil (48.6 mg, 75%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, $J = 6.3$ Hz, 2H), 7.43–7.39 (m, 2H), 7.36–7.32 (m, 2H), 7.29–7.24 (m, 2H), 7.19 (s, 3H), 7.11 (dd, $J = 19.0, 9.7$ Hz, 2H), 3.75 (s, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 160.3, 158.7, 154.8 (dd, $J = 293.7, 288.6$ Hz), 138.1, 135.3, 134.5 (dt, $J = 8.5, 4.0$ Hz), 130.6 (d, $J = 4.5$ Hz), 128.9 (d, $J = 2.9$ Hz), 128.7, 128.5, 128.2, 127.8, 126.6, 124.1 (q, $J = 3.4$ Hz), 115.9 (dt, $J = 24.6, 3.9$ Hz), 90.9 (dd, $J = 22.1, 12.7$ Hz), 33.5. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -88.35 (d, $J = 36.1$ Hz), -88.68 (d, $J = 36.1$ Hz), -117.73. **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₂₁H₁₅F₃ 324.1126; found 324.1120.

4-(1,1-Difluoro-3-phenylprop-1-en-2-yl)-4'-ethyl-1,1'-biphenyl (3ao)



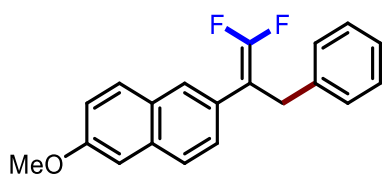
According to the *general procedure B*.

Yellow oil (46.1 mg, 69%);

Rf 0.50 (Petroleum ether/EtOAc, 100/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.49 (dd, $J = 13.1, 8.0$ Hz, 4H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.8$ Hz, 4H), 7.19 (d, $J = 6.8$ Hz, 3H), 3.76 (s, 2H), 2.67 (q, $J = 7.5$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 154.6 (dd, $J = 292.4, 287.7$ Hz), 143.6, 140.0, 138.5 (t, $J = 2.6$ Hz), 137.9, 132.2 (t, $J = 4.0$ Hz), 128.6, 128.5, 128.33, 128.28, 126.90, 126.88, 126.5, 91.4 (dd, $J = 21.5, 13.2$ Hz), 33.8, 28.5, 15.6. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -89.67 (d, $J = 39.3$ Hz), -90.23 (d, $J = 39.1$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for C₂₃H₂₀F₂ 334.1533; found 334.1529.

2-(1,1-Difluoro-3-phenylprop-1-en-2-yl)-6-methoxynaphthalene (3ap)



According to the *general procedure B*.

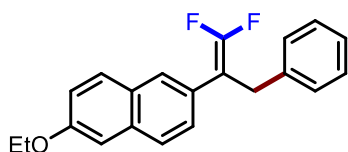
Yellow oil (22.1 mg, 35%);

Rf 0.70 (Petroleum ether/EtOAc, 20/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.67–7.62 (m, 3H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.25 (s, 1H), 7.22 (d, $J = 7.4$ Hz, 2H), 7.19–7.15 (m, 3H), 7.11 (d, $J = 9.8$ Hz, 1H), 7.07 (s, 1H), 3.90 (s, 3H), 3.81 (s, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.9, 154.5 (dd, $J = 291.6, 287.5$ Hz), 138.6, 133.6, 129.5, 128.7, 128.5, 128.3, 127.3 (t, $J = 3.6$ Hz), 126.8, 126.7–126.5 (m), 126.4, 119.1, 105.5, 91.8 (dd, $J = 21.4, 13.4$ Hz), 55.3, 34.0. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.31 (d, $J = 40.3$

Hz), -91.10 (d, $J = 40.6$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for $C_{20}H_{16}F_2O$ 310.1169; found 310.1164.

2-(1,1-Difluoro-3-phenylprop-1-en-2-yl)-6-ethoxynaphthalene (3aq)



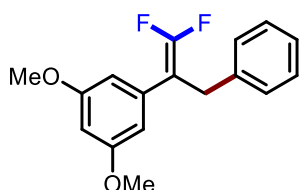
According to the *general procedure B*. The spectral data is consistent with the literature data¹¹.

Yellow oil (37.6 mg, 58%);

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, $J = 8.5$ Hz, 3H), 7.34 (d, $J = 8.3$ Hz, 1H), 7.21 (d, $J = 7.3$ Hz, 2H), 7.19–7.15 (m, 3H), 7.11–7.09 (m, 1H), 7.05 (s, 1H), 4.10 (q, $J = 6.8$ Hz, 2H), 3.80 (s, 2H), 1.45 (t, $J = 6.9$ Hz, 3H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 157.2, 154.5 (dd, $J = 291.5$, 287.4 Hz), 138.62, 138.60, 138.59, 133.6, 129.5, 128.6, 128.5, 128.3, 127.3 (t, $J = 3.4$ Hz), 126.8, 126.6 (t, $J = 3.4$ Hz), 126.4, 119.4, 106.3, 91.8 (dd, $J = 21.4$, 13.4 Hz), 63.5, 34.0, 14.8. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.32 (d, $J = 40.4$ Hz), -91.10 (d, $J = 40.5$ Hz).

1-(1,1-Difluoro-3-phenylprop-1-en-2-yl)-3,5-dimethoxybenzene (3ar)



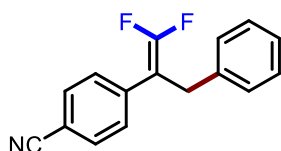
According to the *general procedure B*.

Yellow oil (46.4 mg, 80%);

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.24 (d, $J = 7.0$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 3H), 6.40 (s, 2H), 6.35–6.31 (m, 1H), 3.70 (s, 6H), 3.69 (s, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 160.6, 154.4 (dd, $J = 292.1$, 287.3 Hz), 138.5 (t, $J = 2.6$ Hz), 135.5 (t, $J = 2.6$ Hz), 128.5, 128.3, 126.4, 106.7 (t, $J = 3.5$ Hz), 91.9 (dd, $J = 21.7$, 13.3 Hz), 55.3, 34.0. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -89.64 (d, $J = 39.0$ Hz), -90.04 (d, $J = 38.9$ Hz). **HRMS** (EI-TOF) m/z : $[M]^+$ Calcd for $C_{17}H_{16}F_2O_2$ 290.1118; found 290.1107.

4-(1,1-Difluoro-3-phenylprop-1-en-2-yl)benzonitrile (3as)



According to the *general procedure B*.

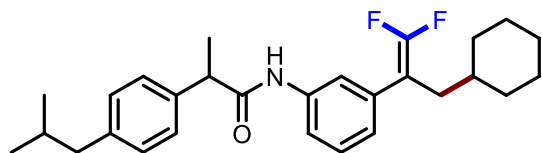
Yellow oil (35.7 mg, 70%);

R_f 0.70 (Petroleum ether/EtOAc, 20/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, $J = 7.4$ Hz, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.25 (d, $J = 6.8$ Hz, 2H), 7.21–7.18 (m, 1H), 7.13 (d, $J = 7.3$ Hz, 2H), 3.75 (s, 2H). **¹³C NMR** (150MHz,

Chloroform-*d*) δ 154.8 (dd, $J = 294.9, 290.0$ Hz), 138.5 (t, $J = 4.3$ Hz), 137.5 (t, $J = 2.6$ Hz), 132.2, 128.9 (t, $J = 2.6$ Hz), 128.7, 128.1, 126.8, 118.6, 91.2 (dd, $J = 22.7, 12.4$ Hz), 33.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -86.84 (d, $J = 32.6$ Hz), -87.55 (d, $J = 32.4$ Hz). HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{11}\text{F}_2\text{N}$ 255.0860; found 255.0850.

N-(3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(4-isobutylphenyl)propanamide (4a)



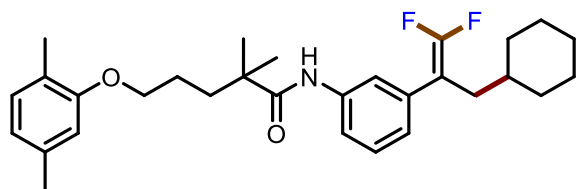
According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

White solid (66.7 mg, 76%); m.p.: 67-69 °C

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

^1H NMR (600 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.28–7.23 (m, 3H), 7.16 (d, $J = 7.8$ Hz, 2H), 7.07 (s, 1H), 6.99 (d, $J = 7.5$ Hz, 1H), 3.69 (q, $J = 7.1$ Hz, 1H), 2.47 (d, $J = 7.2$ Hz, 2H), 2.22 (d, $J = 5.0$ Hz, 2H), 1.90–1.83 (m, 1H), 1.64 (s, 4H), 1.59 (d, $J = 7.1$ Hz, 4H), 1.24–1.17 (m, 1H), 1.10 (s, 3H), 0.91 (d, $J = 6.6$ Hz, 8H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 172.6, 153.9 (dd, $J = 290.2, 286.4$ Hz), 141.2, 138.02, 137.98, 135.0, 129.9, 128.9, 127.5, 124.2, 119.4, 118.5, 90.9 (dd, $J = 22.1, 13.0$ Hz), 47.8, 45.0, 35.6, 35.2, 32.8, 30.2, 26.4, 26.0, 22.4, 18.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.09 (d, $J = 43.2$ Hz), -91.30 (d, $J = 43.1$ Hz).

N-(3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (4b)



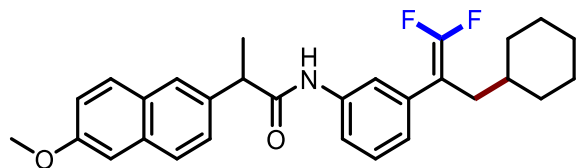
According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

Yellow oil (72.5 mg, 75%);

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

^1H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, $J = 8.0$ Hz, 1H), 7.43 (s, 1H), 7.36 (s, 1H), 7.29 (t, $J = 7.7$ Hz, 1H), 7.03 (d, $J = 7.3$ Hz, 1H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.66 (d, $J = 7.4$ Hz, 1H), 6.61 (s, 1H), 3.95 (s, 2H), 2.29 (s, 3H), 2.25 (d, $J = 6.6$ Hz, 2H), 2.17 (s, 3H), 1.83 (s, 4H), 1.66 (t, $J = 10.6$ Hz, 4H), 1.59 (s, 1H), 1.34 (s, 7H), 1.11 (s, 3H), 0.94 – 0.85 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.7, 156.8, 154.0 (dd, $J = 290.1, 286.4$ Hz), 138.0, 136.6, 135.1 (dd, $J = 4.4, 2.4$ Hz), 130.3, 129.0, 124.3 (t, $J = 2.7$ Hz), 123.5, 120.9, 119.9 (t, $J = 3.2$ Hz), 119.0, 112.2, 91.0 (dd, $J = 12.1, 12.0$ Hz), 67.9, 42.9, 37.7, 35.7, 35.2, 32.9, 26.4, 26.1, 25.7, 25.2, 21.4, 15.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -91.11 (d, $J = 43.2$ Hz), -91.31 (d, $J = 43.4$ Hz).

N-(3-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(6-methoxynaphthalen-2-yl)propanamide (4c)



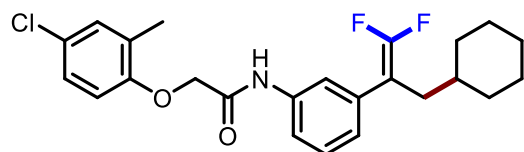
According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

White solid (46.3 mg, 50%); m.p.: 55-57 °C

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.78–7.71 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.14 (s, 1H), 7.10 (s, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 3.93 (s, 3H), 3.85 (q, *J* = 7.0 Hz, 1H), 2.20 (d, *J* = 7.0 Hz, 2H), 1.67 (d, *J* = 7.1 Hz, 3H), 1.62 (s, 3H), 1.57 (s, 1H), 1.24–1.16 (m, 1H), 1.09 (d, *J* = 5.9 Hz, 3H), 0.90–0.84 (m, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 172.4, 155.8, 153.9 (dd, *J* = 289.9, 286.5 Hz), 138.0, 135.9, 135.0, 133.9, 129.3, 129.0, 128.9, 127.9, 126.4, 126.2, 124.2 (t, *J* = 3.0 Hz), 119.5 (t, *J* = 3.0 Hz), 119.4, 118.5, 105.7, 90.9 (dd, *J* = 21.7, 13.4 Hz), 55.4, 48.2, 35.6, 35.2, 32.8, 26.4, 26.0, 18.6. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -91.13 (d, *J* = 43.1 Hz), -91.30 (d, *J* = 43.2 Hz).

2-(4-Chloro-2-methylphenoxy)-N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)acetamide (4d)



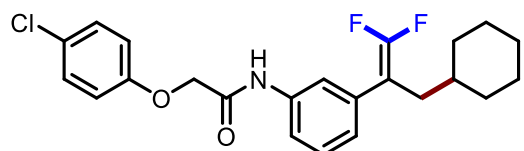
According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

White solid (59.8 mg, 69%); m.p. 60-62 °C

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.56–7.47 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.19 (s, 1H), 7.15 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 4.58 (s, 2H), 2.34 (s, 3H), 2.27 (d, *J* = 7.1 Hz, 2H), 1.74–1.63 (m, 4H), 1.60 (s, 1H), 1.29–1.24 (m, 1H), 1.12 (s, 3H), 0.92 (q, *J* = 10.5, 10.0 Hz, 2H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 166.0, 156.0, 154.0 (dd, *J* = 290.4, 286.5 Hz), 154.0, 136.9, 135.3 (dd, *J* = 4.6, 2.8 Hz), 131.1, 129.2, 128.5, 127.1, 127.0, 125.0 (t, *J* = 3.0 Hz), 119.8 (t, *J* = 3.0 Hz), 118.8, 113.2, 90.8 (dd, *J* = 22.5, 12.6 Hz), 68.1, 35.7, 35.2, 32.9, 26.4, 26.1, 16.3. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.60 (d, *J* = 42.7 Hz), -90.86 (d, *J* = 42.5 Hz).

2-(4-Chlorophenoxy)-N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)acetamide (4e)



According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

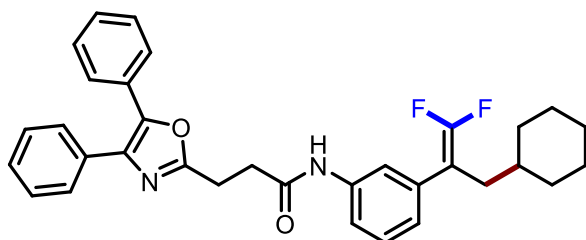
White solid (67.0 mg, 80%); m.p. 55-57 °C

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.62–7.46 (m, 2H), 7.38–7.26 (m, 3H), 7.10 (d,

$J = 7.6$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 2H), 4.56 (s, 2H), 2.26 (s, 2H), 1.73–1.62 (m, 4H), 1.59 (s, 1H), 1.26 (s, 1H), 1.11 (s, 3H), 0.92 (s, 2H). ^{13}C NMR (150 MHz, Chloroform- d) δ 165.8, 155.6, 154.0 (dd, $J = 291.0$ Hz, 285.0 Hz), 136.9, 135.3–135.2 (m), 129.8, 129.1, 127.5, 125.0 (d, $J = 3.0$ Hz), 120.1–119.9 (m), 119.0, 116.2, 90.9 (dd, $J = 22.4$, 12.4 Hz), 67.9, 35.7, 35.2, 32.9, 26.4, 26.1. ^{19}F NMR (376 MHz, Chloroform- d) δ -90.68 (d, $J = 42.8$ Hz), -90.98 (d, $J = 42.7$ Hz).

N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-3-(4,5-diphenyloxazol-2-yl)propanamide (4f)



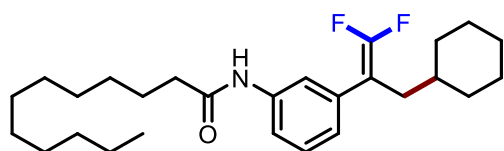
According to the *general procedure A*. The spectral data are consistent with the literature data¹¹

White solid (57.8 mg, 55%); m.p.: 60–62 °C

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

^1H NMR (600 MHz, Chloroform- d) δ 8.82 (s, 1H), 7.65 (d, $J = 7.3$ Hz, 2H), 7.57 (s, 3H), 7.36 (dq, $J = 23.0$, 7.6, 7.1 Hz, 6H), 7.30 (s, 1H), 7.26 (s, 1H), 7.00 (d, $J = 7.6$ Hz, 1H), 3.29 (t, $J = 6.1$ Hz, 2H), 2.98 (t, $J = 6.1$ Hz, 2H), 2.17 (d, $J = 6.5$ Hz, 2H), 1.61 (d, $J = 12.0$ Hz, 4H), 1.57 (s, 1H), 1.22–1.16 (m, 1H), 1.09 (d, $J = 6.3$ Hz, 3H), 0.89–0.83 (m, 2H). ^{13}C NMR (150 MHz, Chloroform- d) δ 169.8, 162.6, 153.9 (dd, $J = 290.0$, 286.5 Hz), 145.8, 138.3, 135.0, 134.6, 132.0, 129.0, 128.71, 128.69, 128.5, 128.4, 127.8, 126.5, 124.0, 119.4–119.3 (m), 118.5, 90.9 (dd, $J = 21.7$, 13.8 Hz), 35.6, 35.2, 34.2, 32.8, 26.4, 26.0, 24.1. ^{19}F NMR (376 MHz, Chloroform- d) δ -91.25 (d, $J = 43.3$ Hz), -91.40 (d, $J = 43.4$ Hz).

4-(3-Cyclohexyl-1,1-difluoroprop-1-en-2-yl)-N-undecylbenzamide (4g)



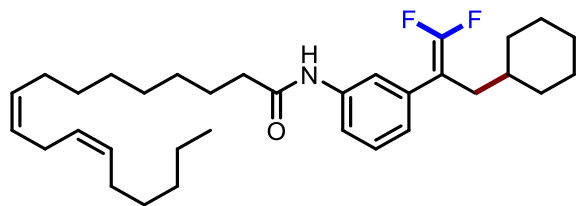
According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

Yellow oil (58.9 mg, 68%);

Rf 0.50 (Petroleum ether/EtOAc, 3/1).

^1H NMR (600 MHz, Chloroform- d) δ 7.71 (s, 1H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.46 (s, 1H), 7.26 (t, $J = 7.8$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 2.35 (t, $J = 7.5$ Hz, 2H), 2.23 (d, $J = 6.8$ Hz, 2H), 1.74–1.68 (m, 3H), 1.65 (d, $J = 12.5$ Hz, 5H), 1.58 (s, 1H), 1.37–1.32 (m, 3H), 1.25 (s, 13H), 1.10 (s, 3H), 0.88 (t, $J = 6.9$ Hz, 4H). ^{13}C NMR (150 MHz, Chloroform- d) δ 171.8, 154.0 (dd, $J = 290.4$, 286.2 Hz), 138.2, 134.9 (t, $J = 3.0$ Hz), 128.9, 124.1, 119.6, 118.7, 90.9 (dd, $J = 22.3$, 12.4 Hz), 37.8, 35.7, 35.2, 32.8, 31.9, 29.7, 29.6, 29.5, 29.43, 29.36, 29.33, 26.4, 26.0, 25.7, 22.7, 14.1. ^{19}F NMR (376 MHz, Chloroform- d) δ -90.15 (d, $J = 41.8$ Hz), -90.85 (d, $J = 41.8$ Hz).

(9Z,12Z)-N-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)octadeca-9,12-dienamide (4h)



According to the *general procedure A*. The spectral data is consistent with the literature data¹¹

Yellow oil (53.4 mg, 52%);

R_f 0.50 (Petroleum ether/EtOAc, 3/1).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, $J = 7.8$ Hz, 1H), 7.42 (s, 1H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.15 (s, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 5.41–5.30 (m, 4H), 2.77 (t, $J = 6.7$ Hz, 2H), 2.35 (t, $J = 7.5$ Hz, 2H), 2.25 (d, $J = 7.1$ Hz, 2H), 2.05 (q, $J = 6.9$ Hz, 4H), 1.78–1.71 (m, 2H), 1.67 (d, $J = 13.0$ Hz, 4H), 1.59 (s, 2H), 1.42–1.22 (m, 18H), 1.11 (s, 3H), 0.89 (t, $J = 6.8$ Hz, 5H). **¹³C NMR** (150 MHz, Chloroform-*d*) δ 171.3, 154.0 (dd, $J = 283.5, 285.0$ Hz), 138.0, 135.0 (t, $J = 4.5$ Hz), 130.2, 130.0, 129.0, 128.1, 127.9, 124.1, 119.5, 118.6, 90.91 (dd, $J = 22.5, 12.7$ Hz), 37.9, 35.7, 35.2, 32.8, 31.5, 29.6, 29.4, 29.3, 29.1, 27.2, 26.4, 26.0, 25.6, 25.6, 22.6, 14.1. **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -90.98 (d, $J = 43.2$ Hz), -91.25 (d, $J = 43.2$ Hz).

References

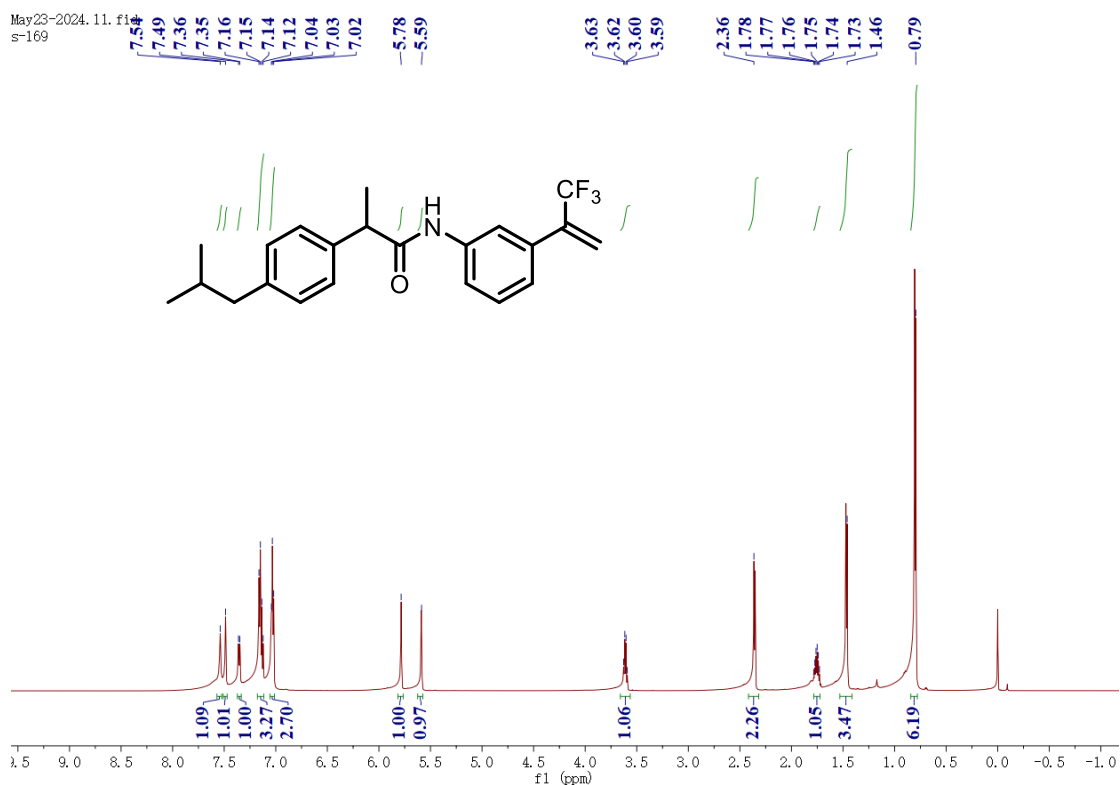
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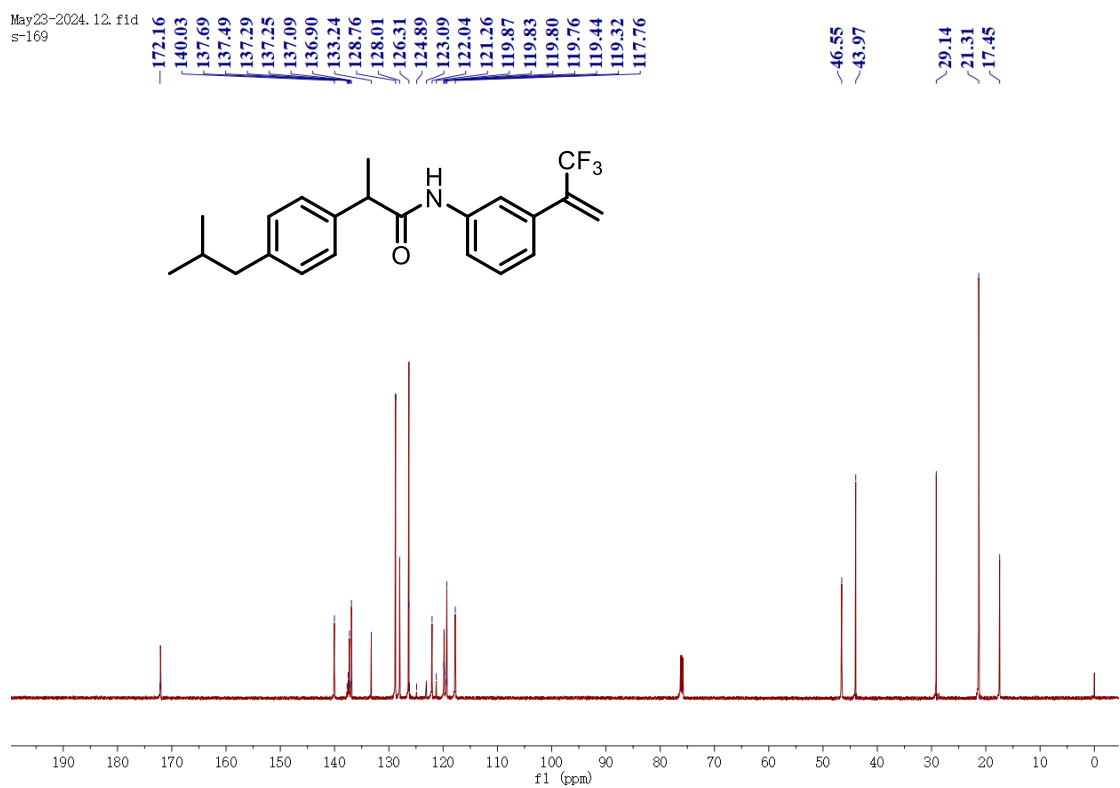
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NMR Spectra

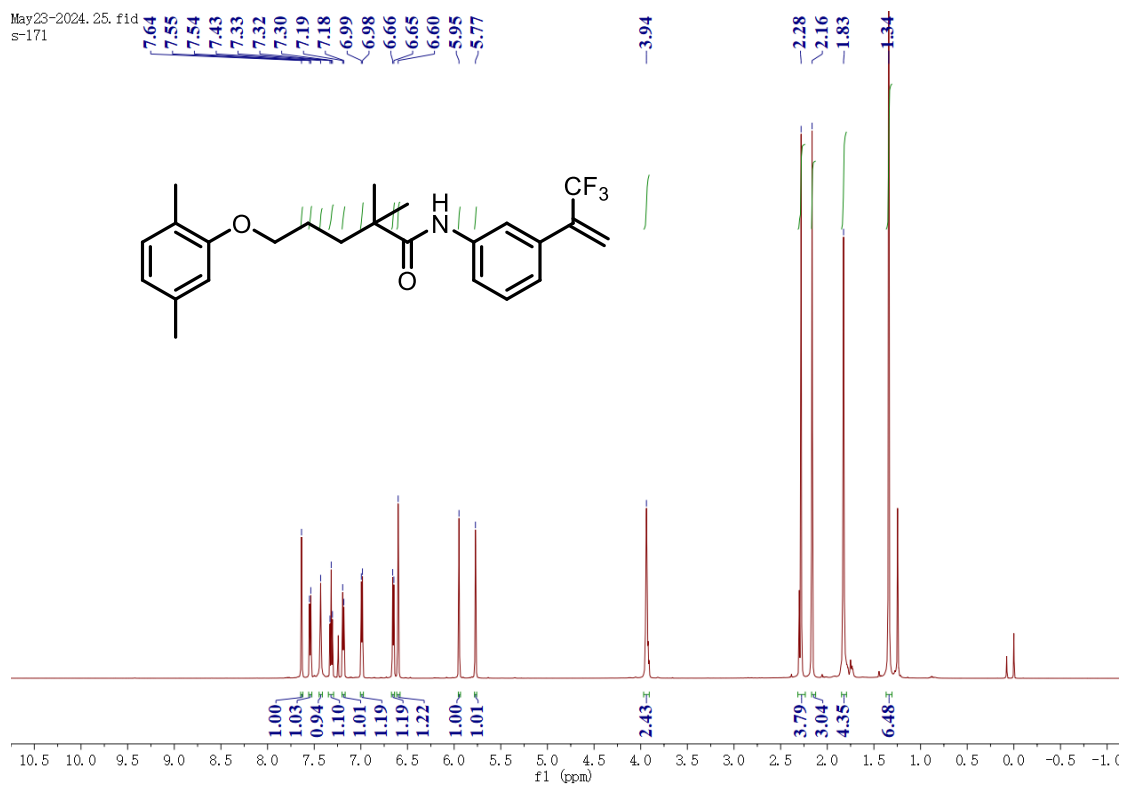


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 1-4a.



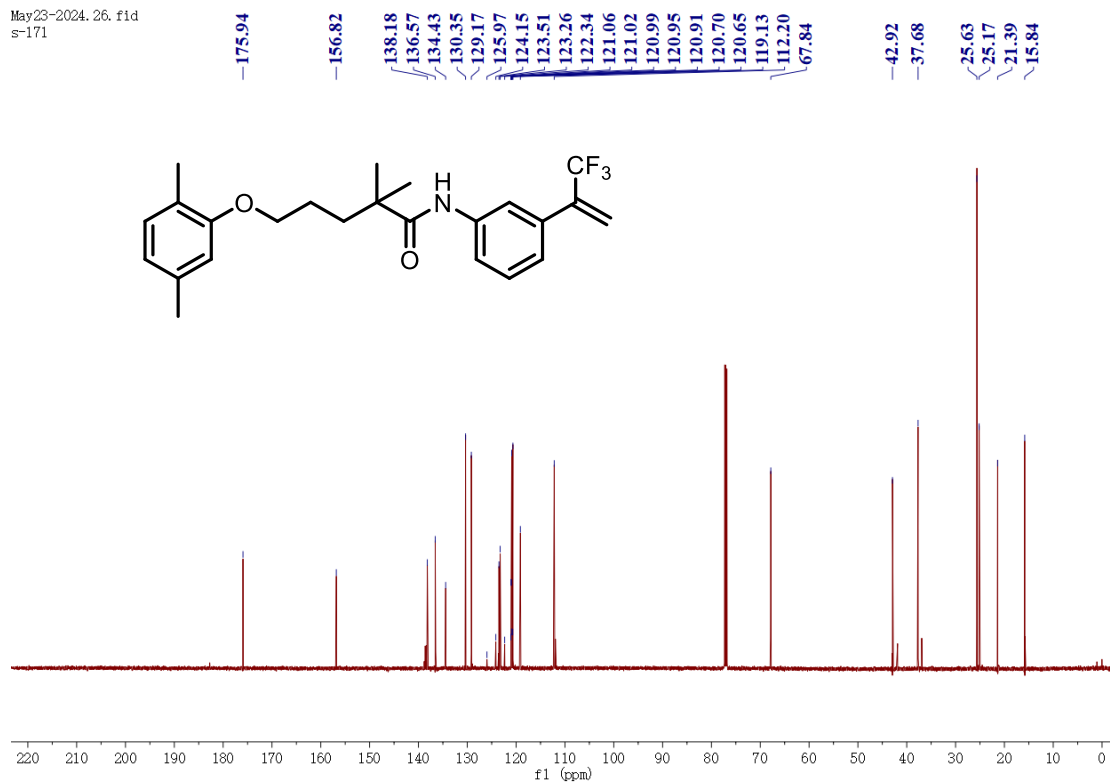
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May23-2024. 25. f1d
s-171

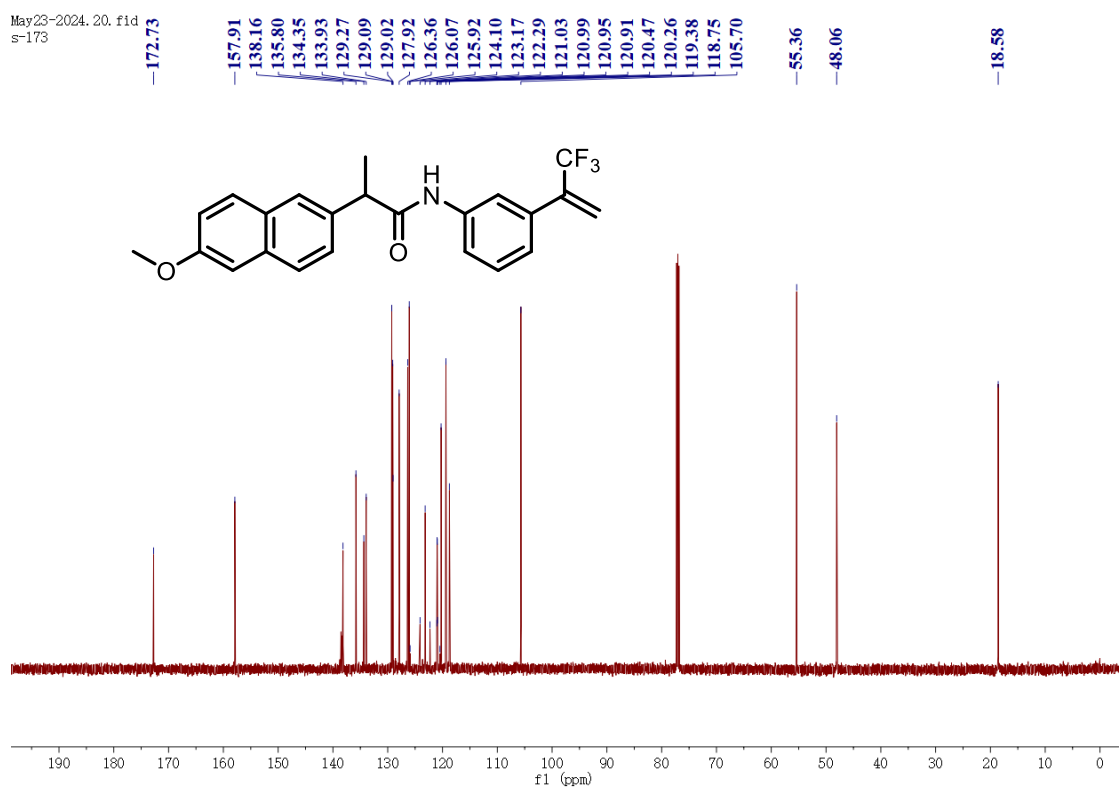
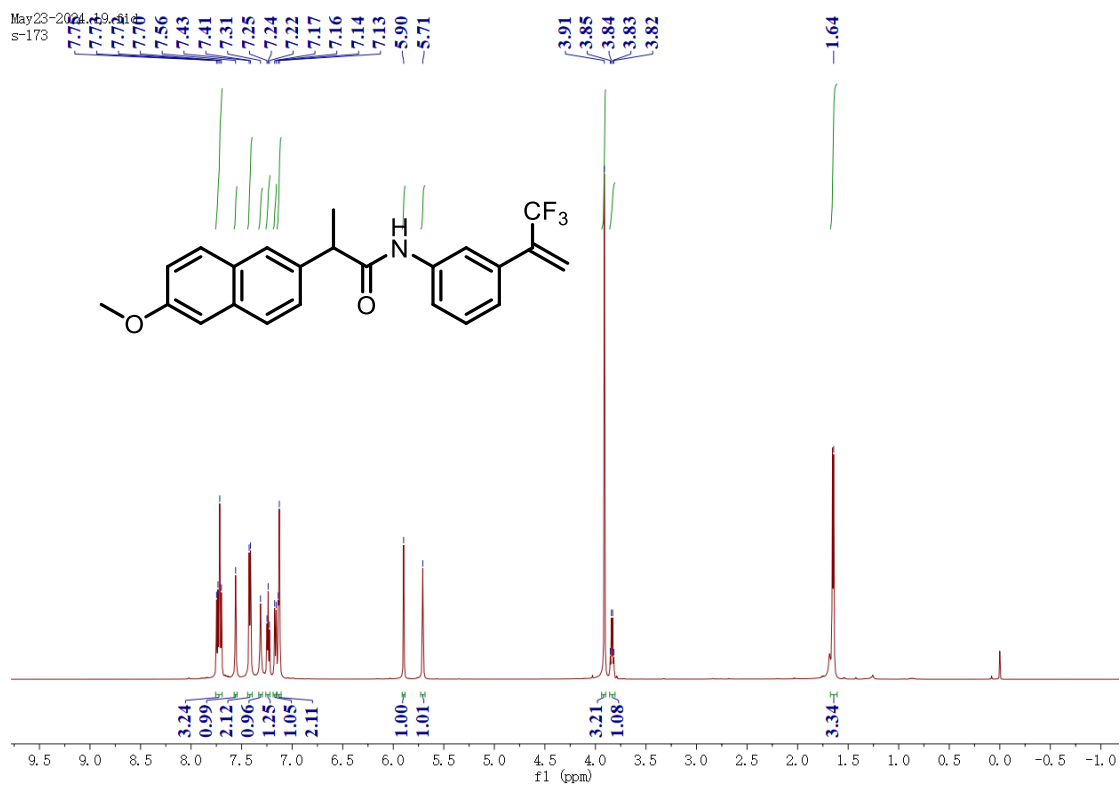


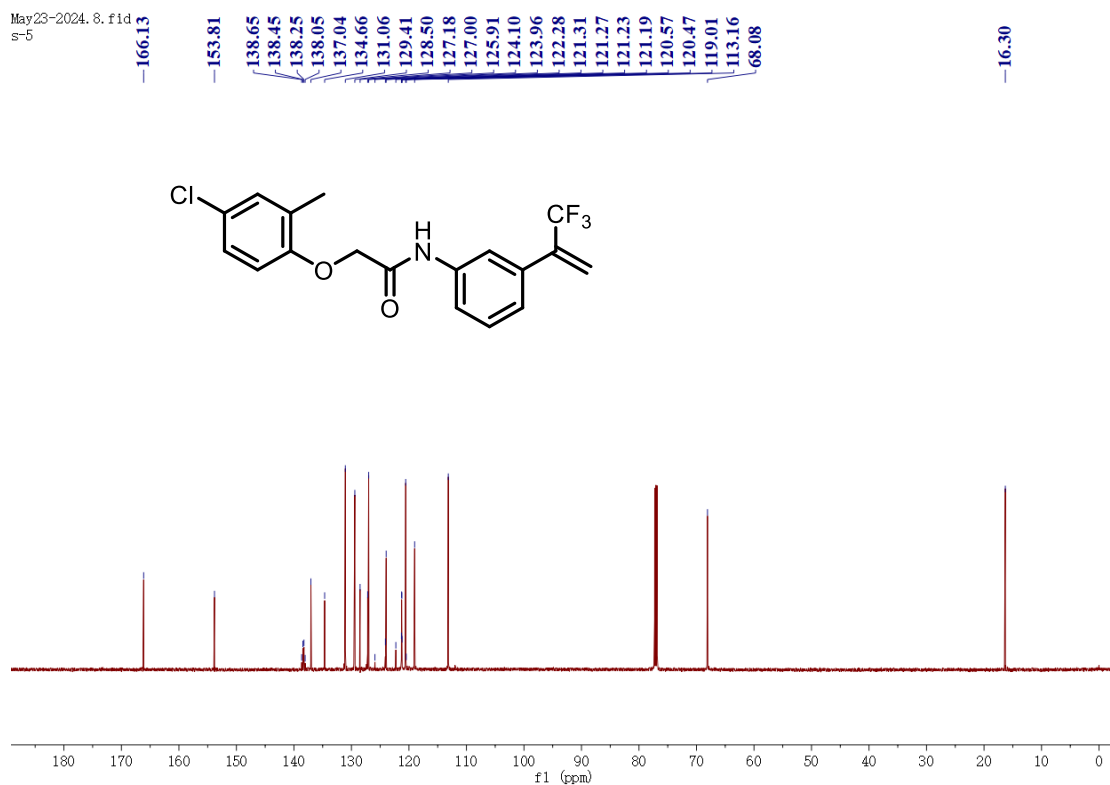
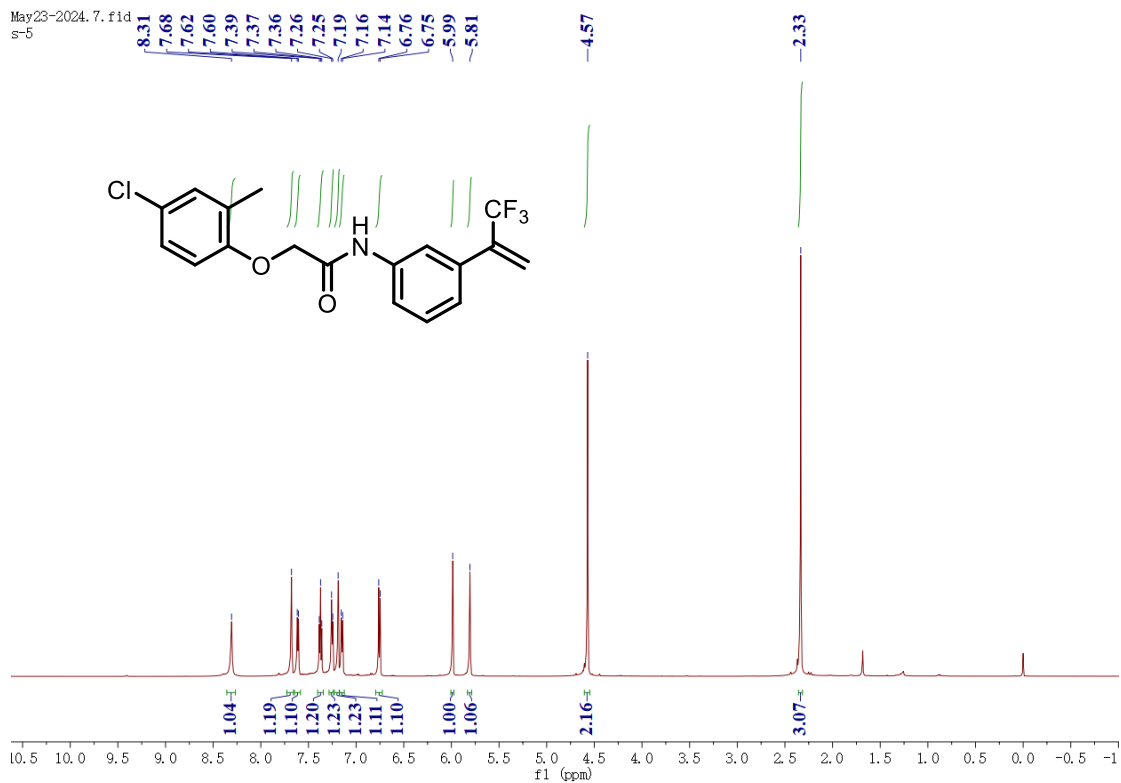
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **1-4b**.

May23-2024. 26. f1d
s-171

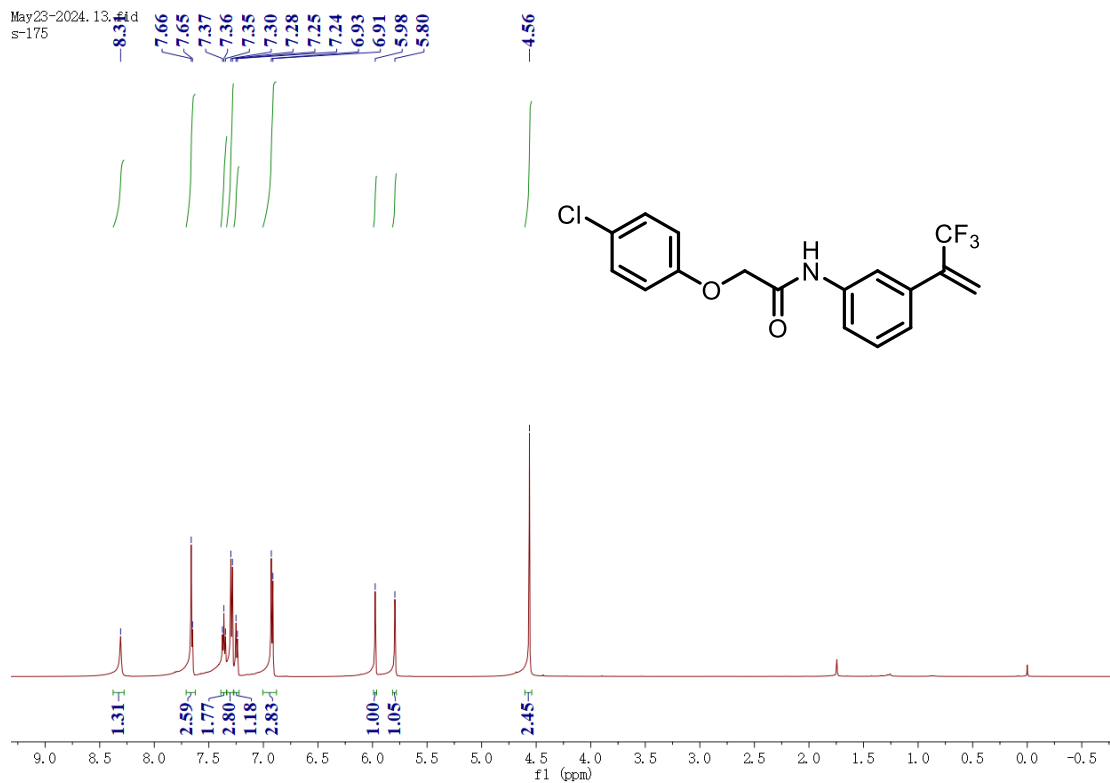


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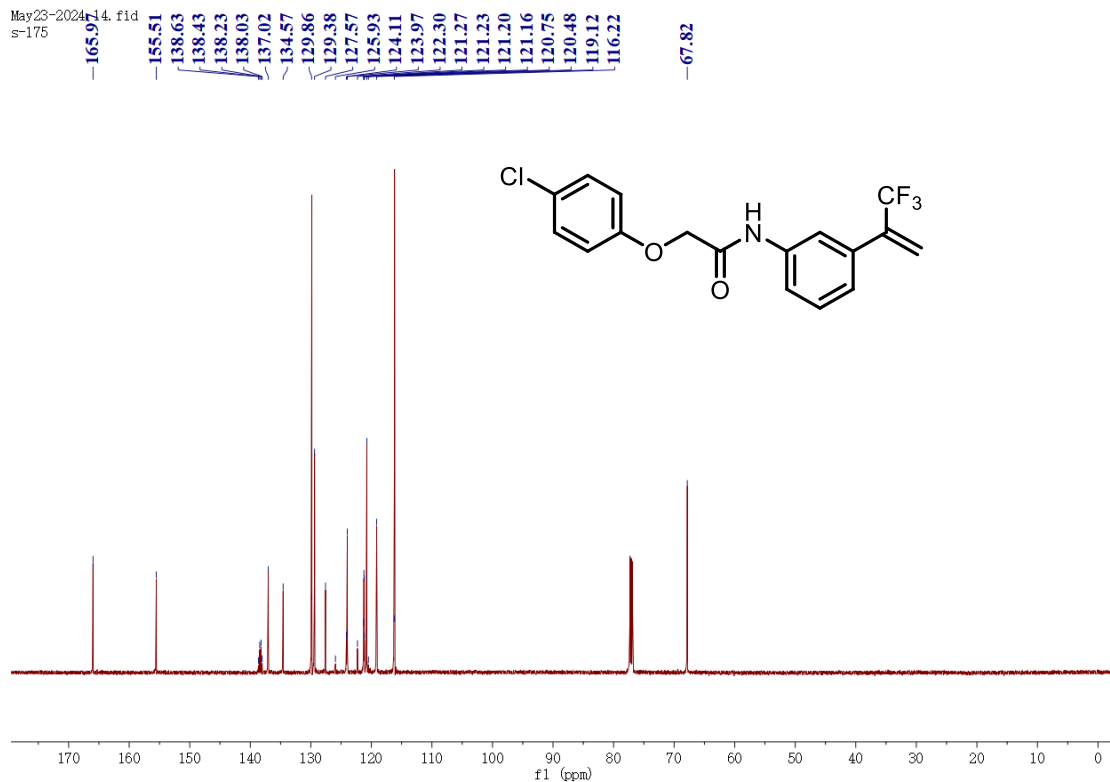


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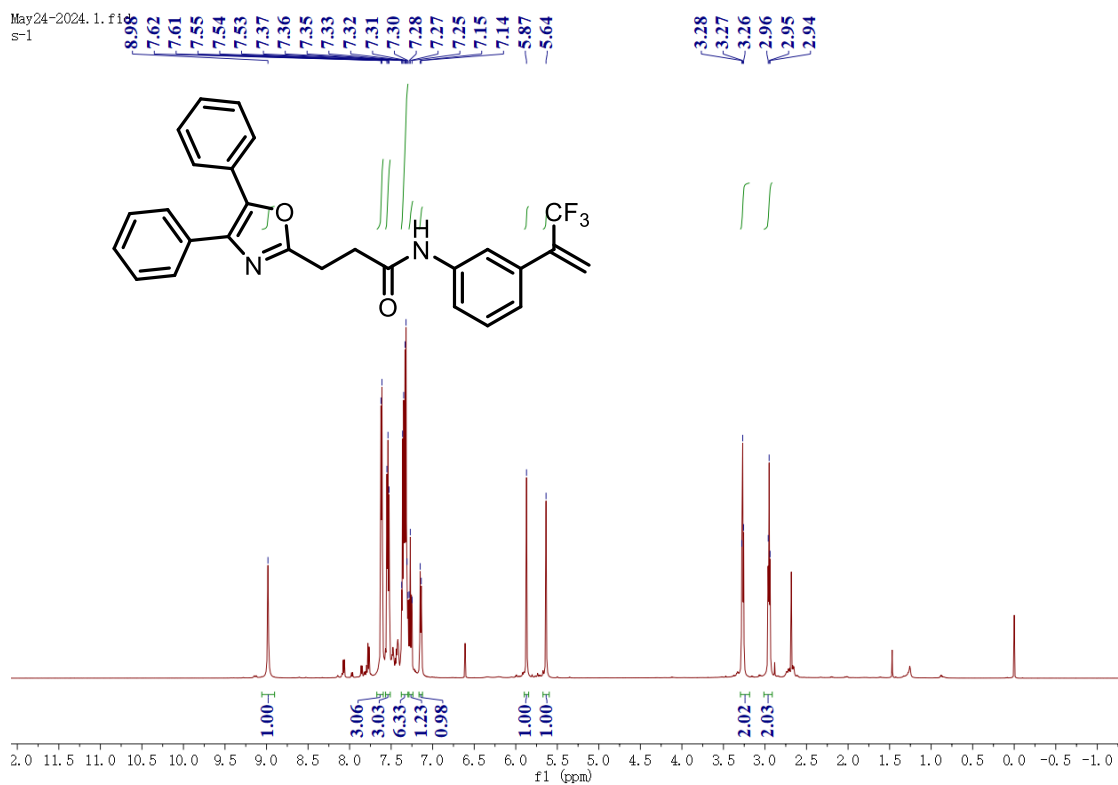


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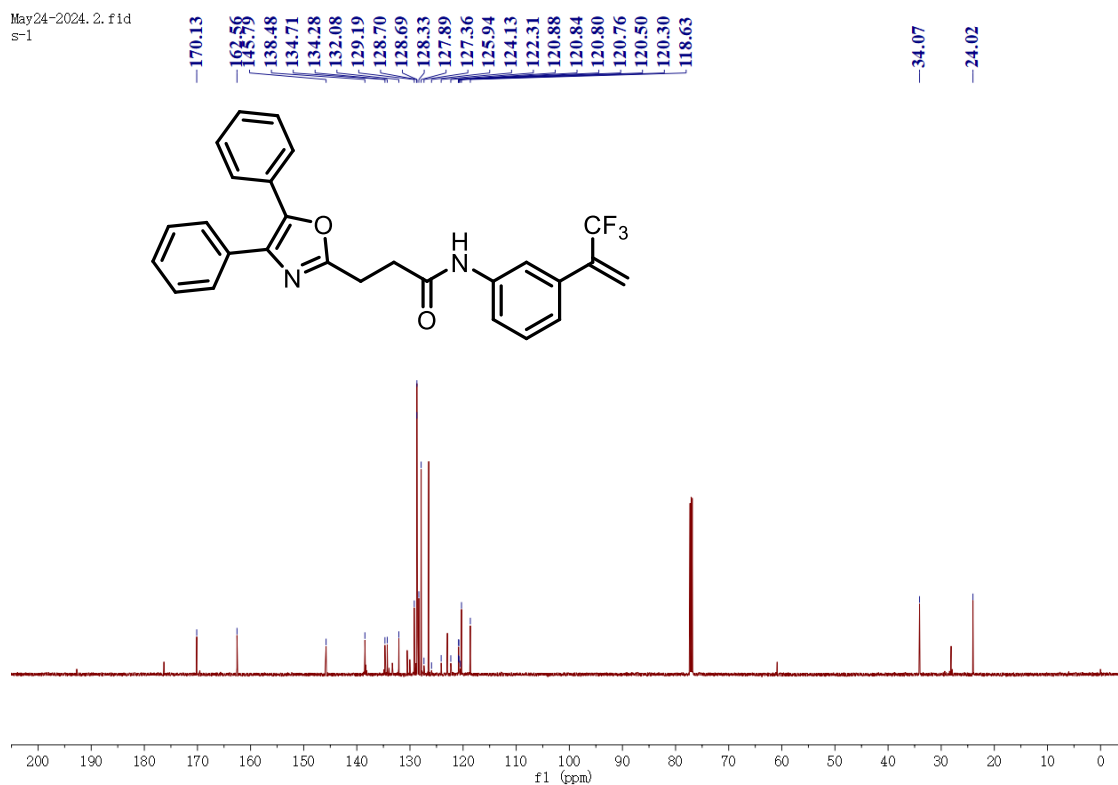
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s-175



¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **1-4e**.

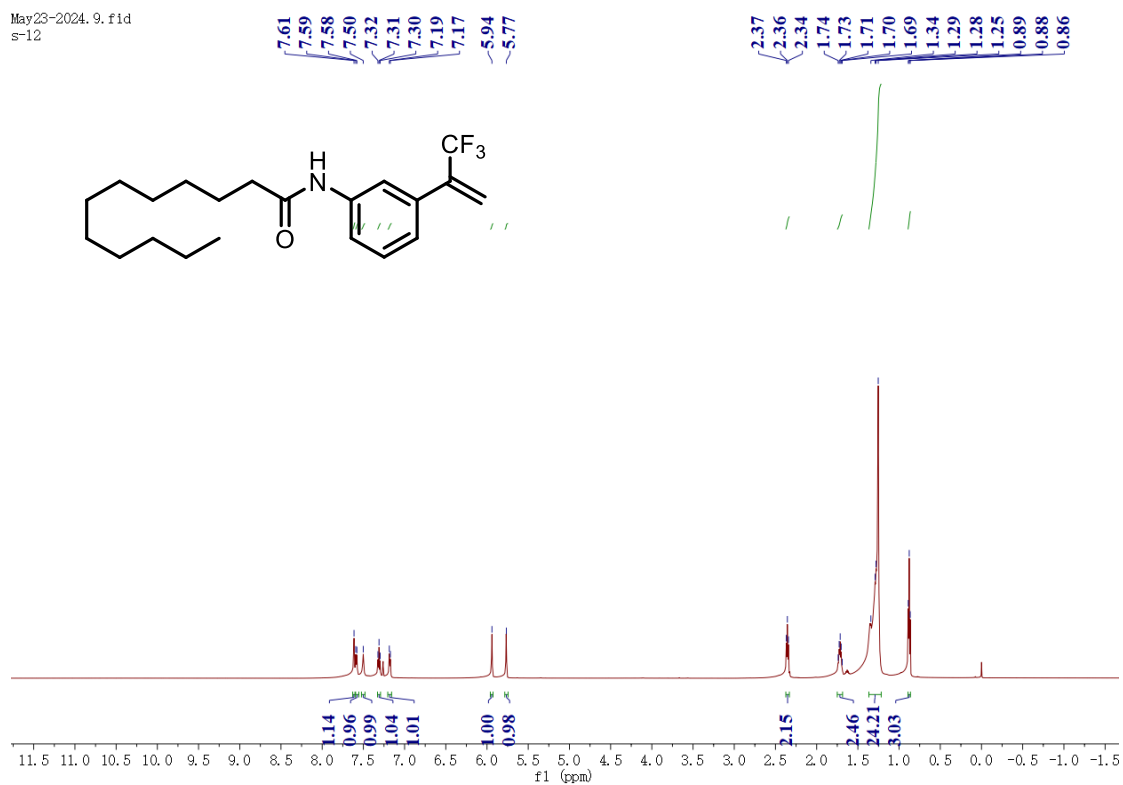


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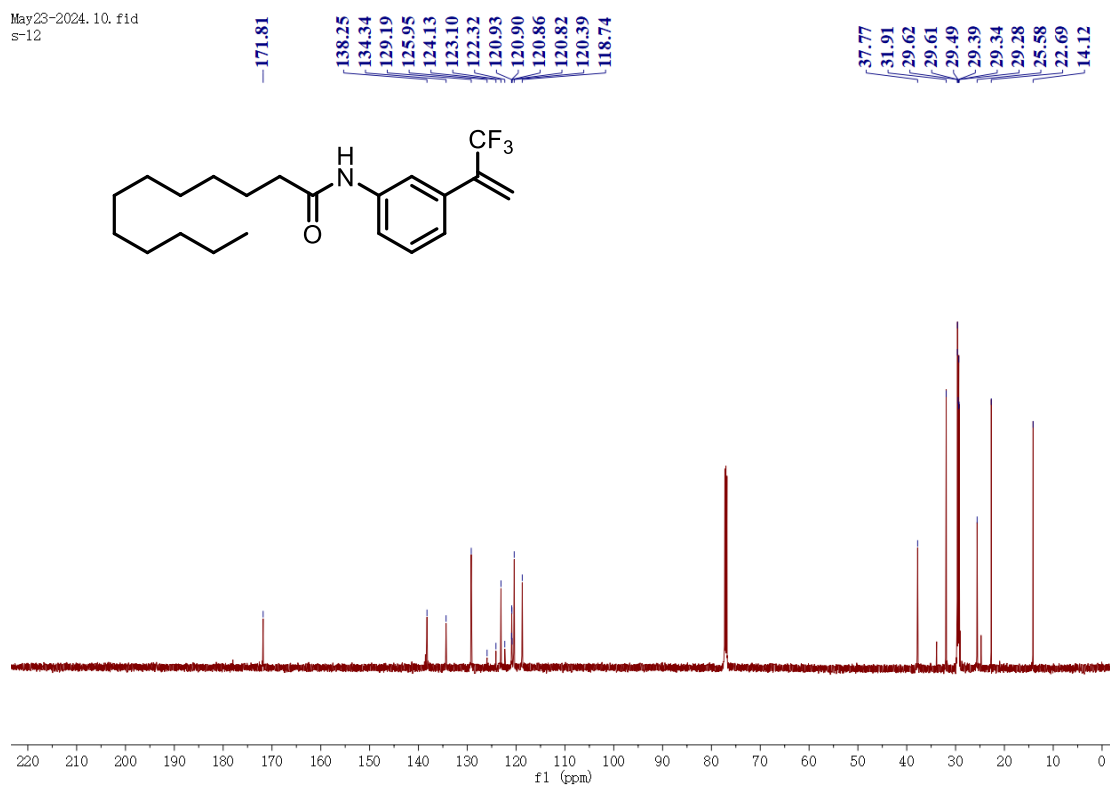
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May23-2024. 9. fid
s-12

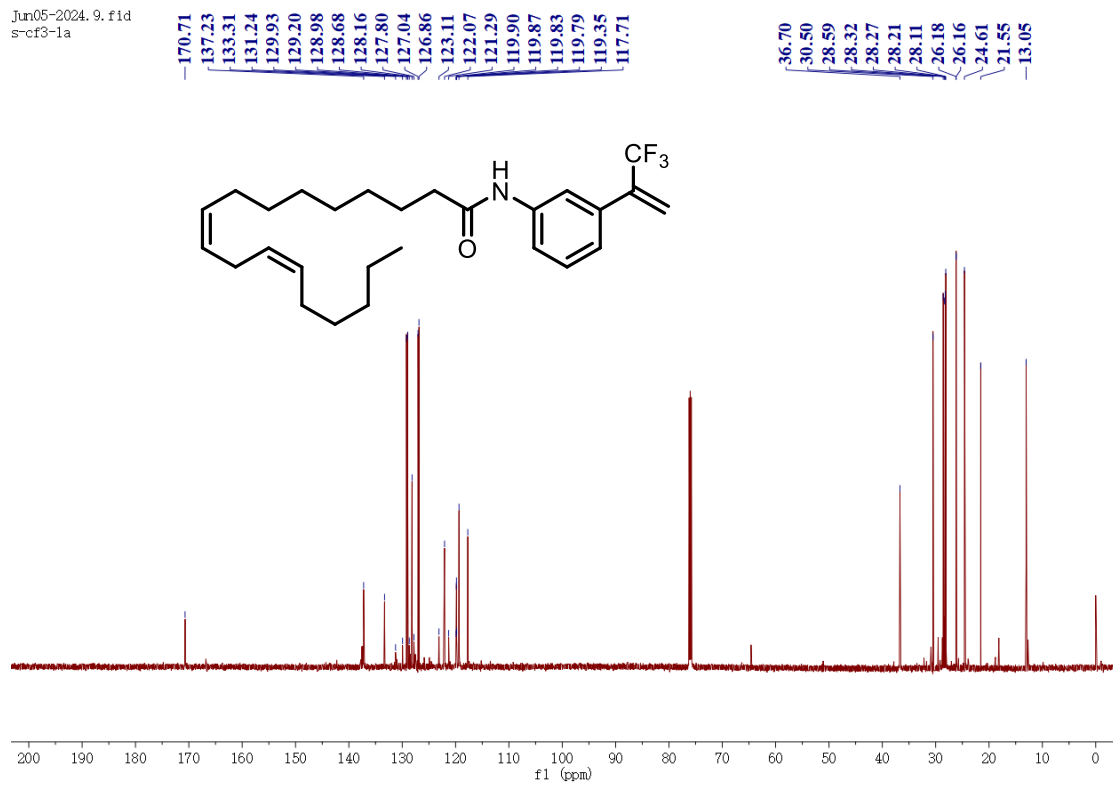
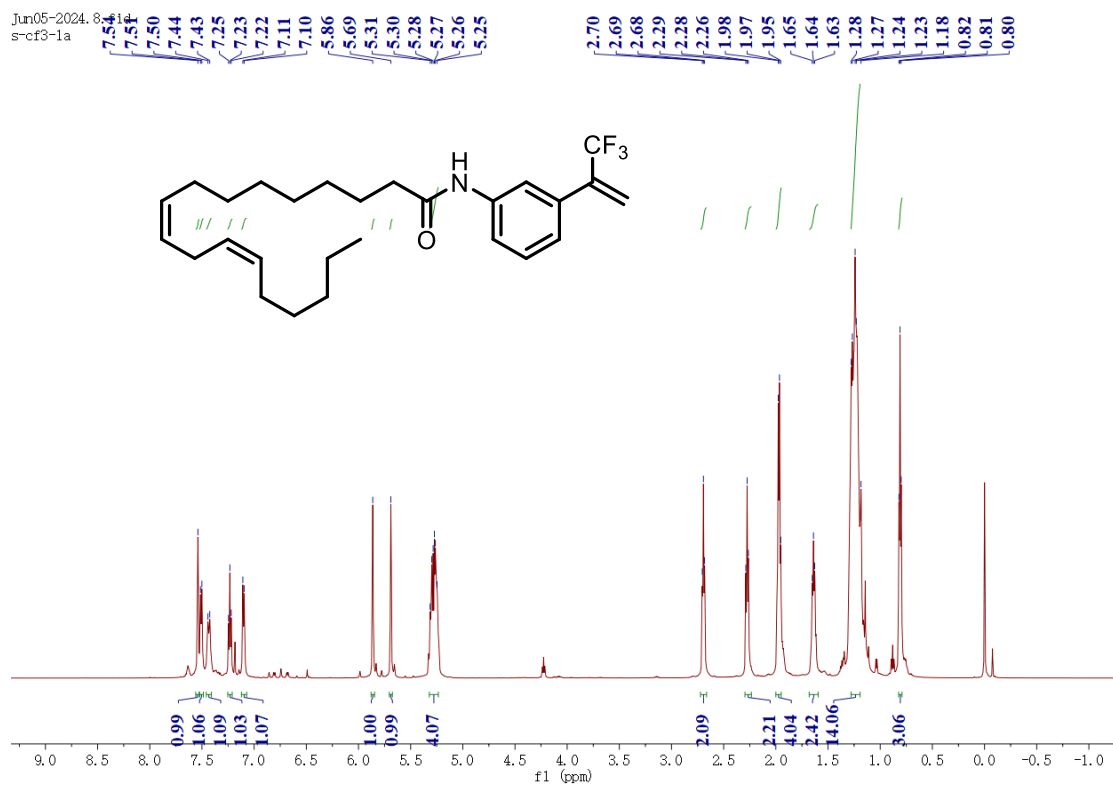


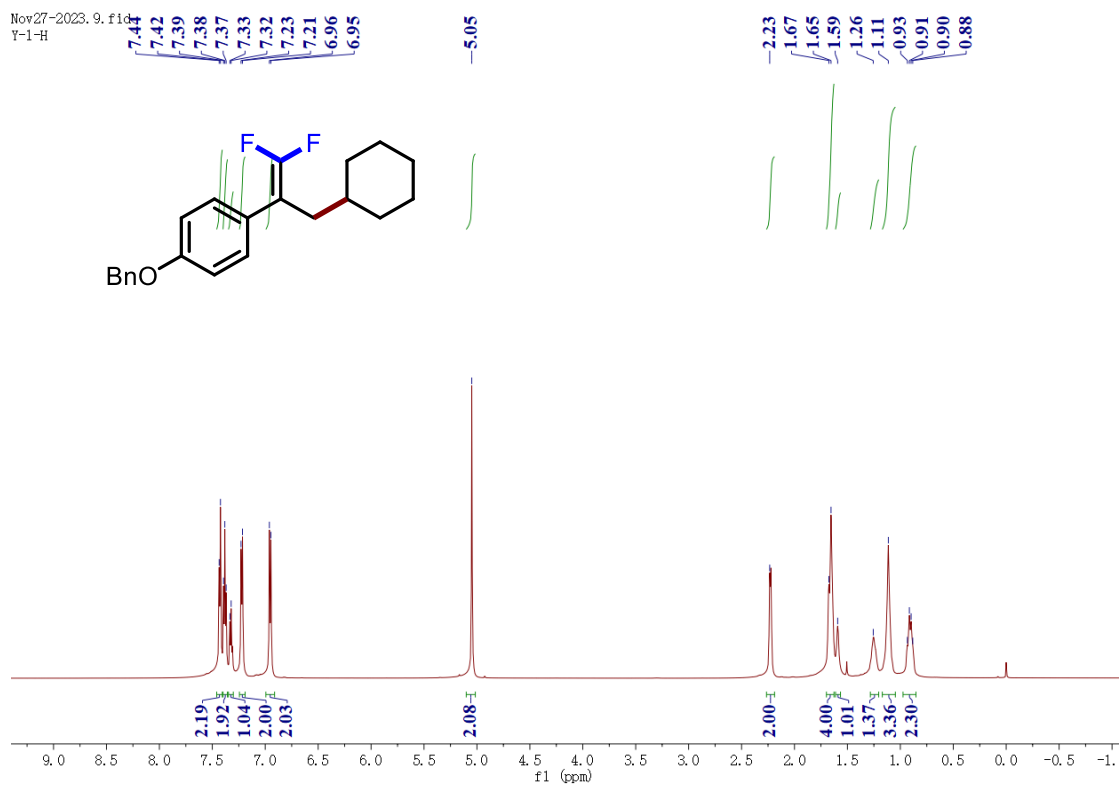
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **1-4g**.

May23-2024. 10. fid
s-12

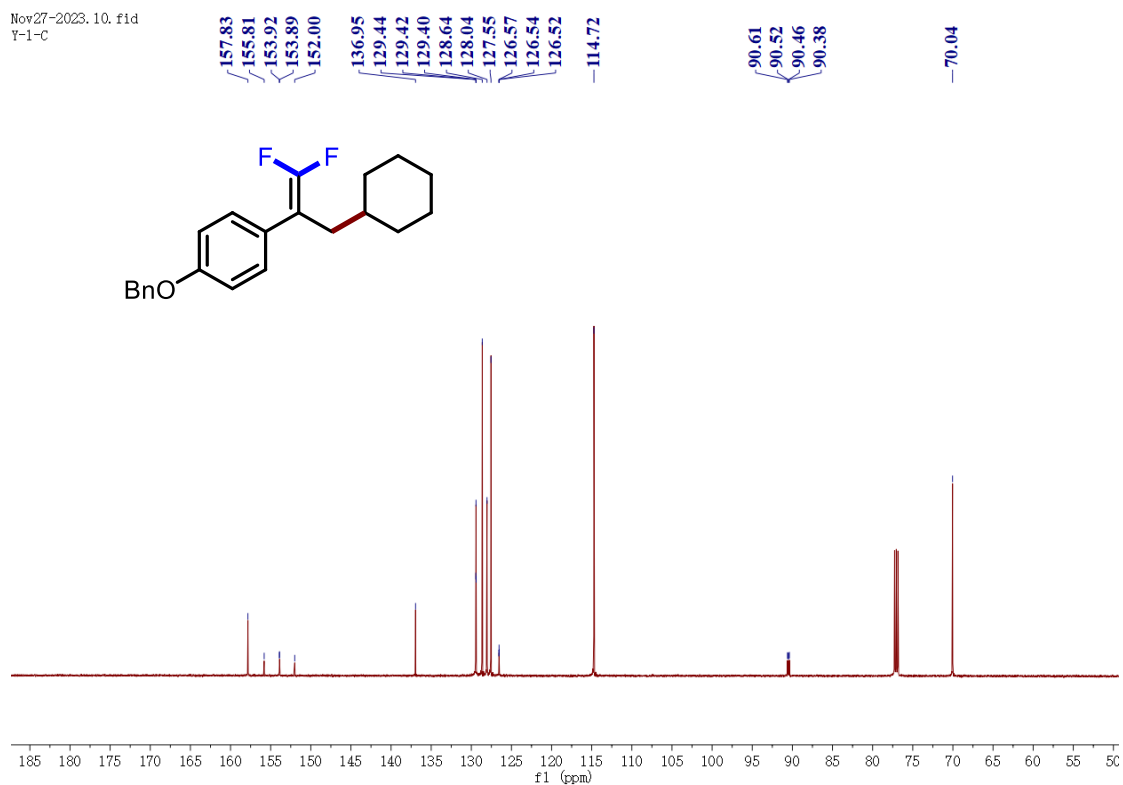


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **1-4g**.



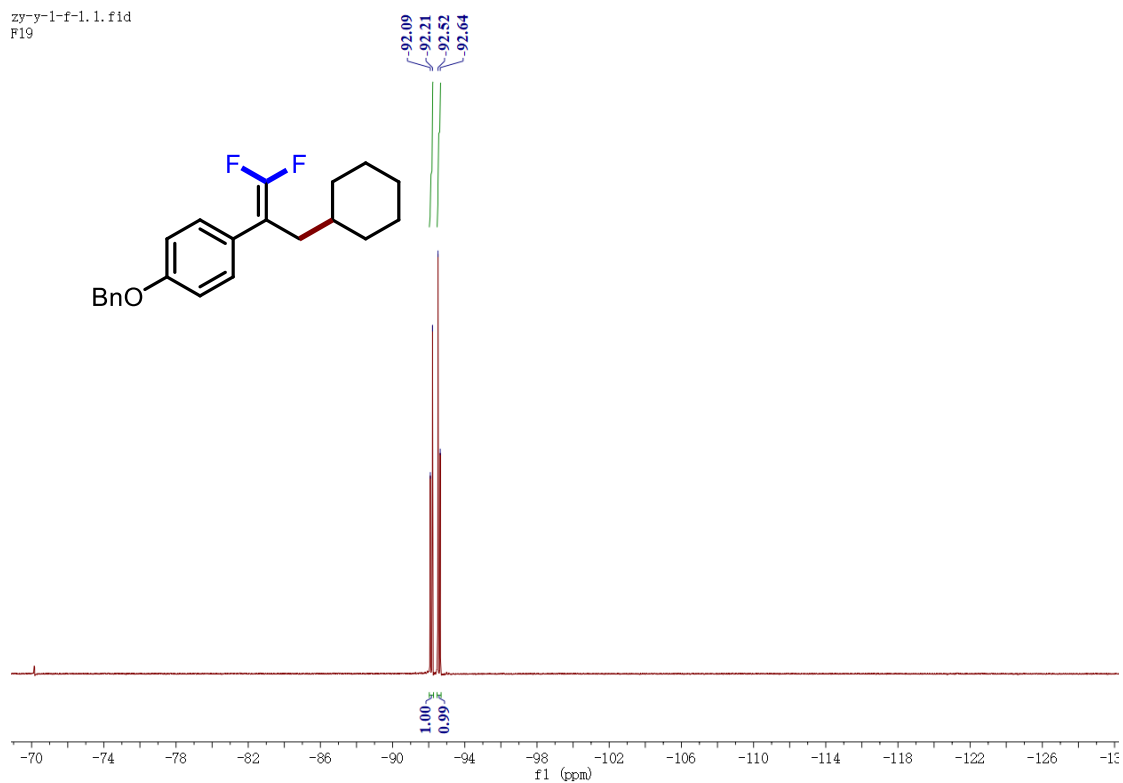


$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) spectrum of compound **3a**.



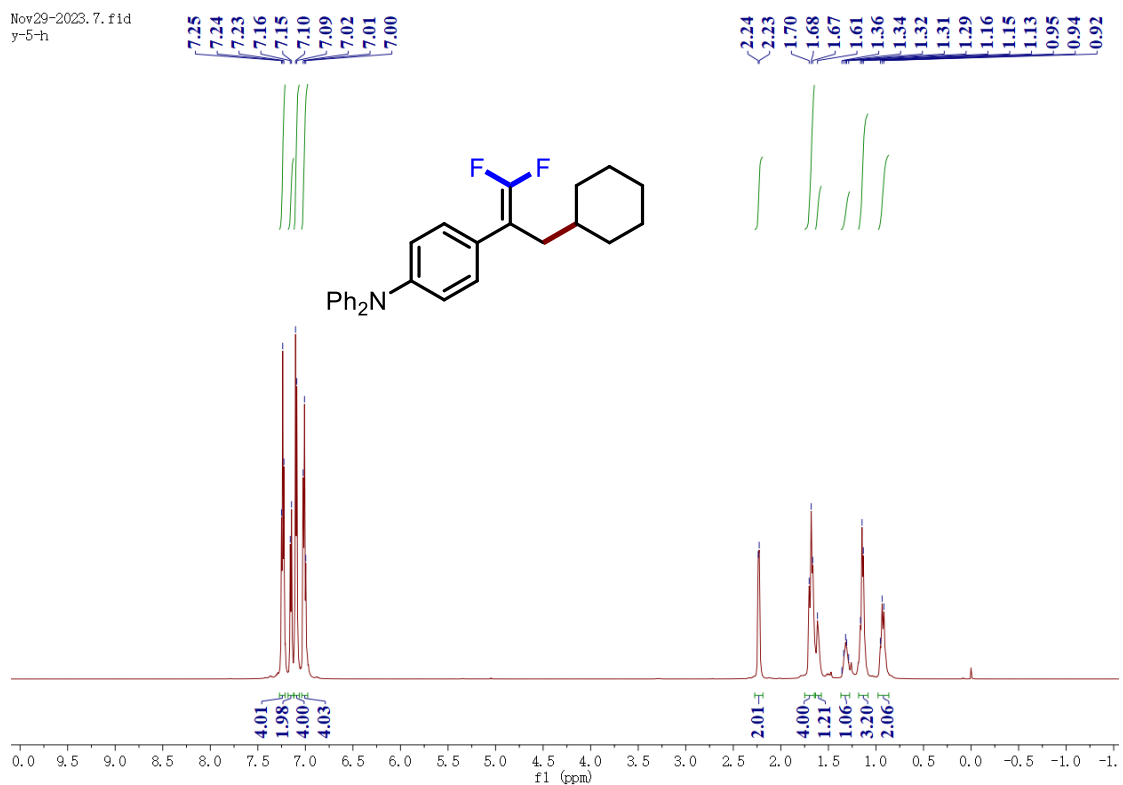
$^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) spectrum of compound **3a**.

zy-y-1-f-1.1.fid
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3a**.

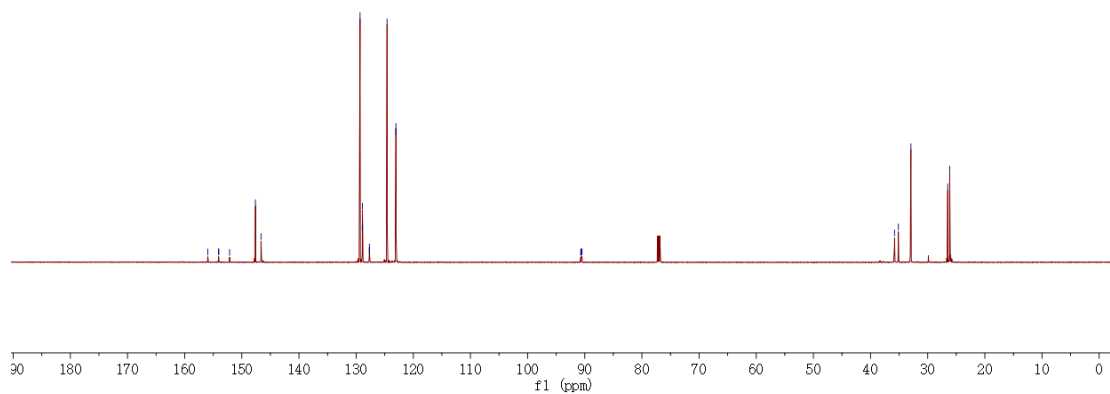
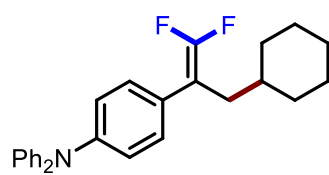
Nov29-2023. 7.fid
y-5-h



¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3b**.

Nov29-2023. 8. f1d
y-5-c

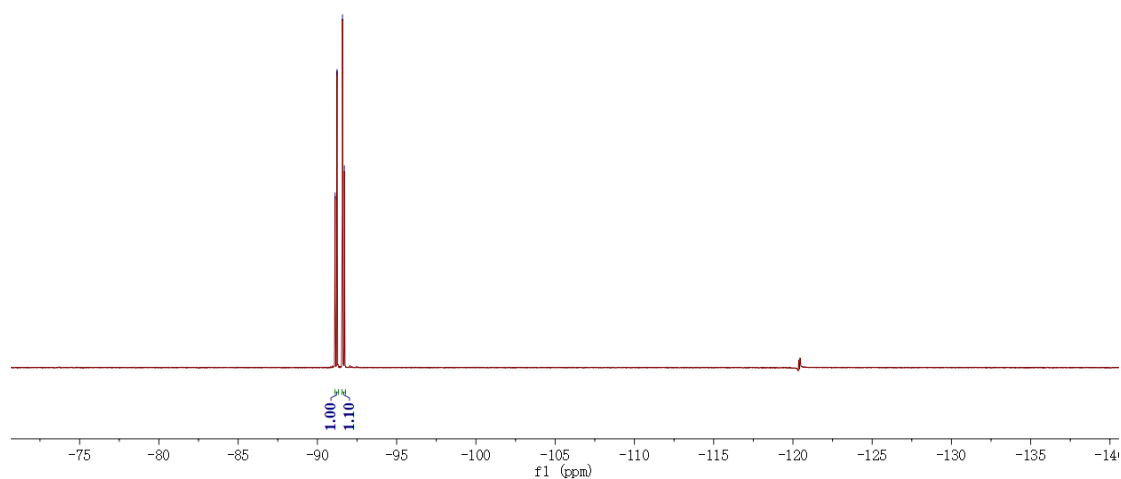
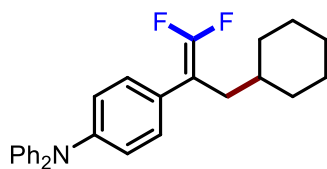
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26.15



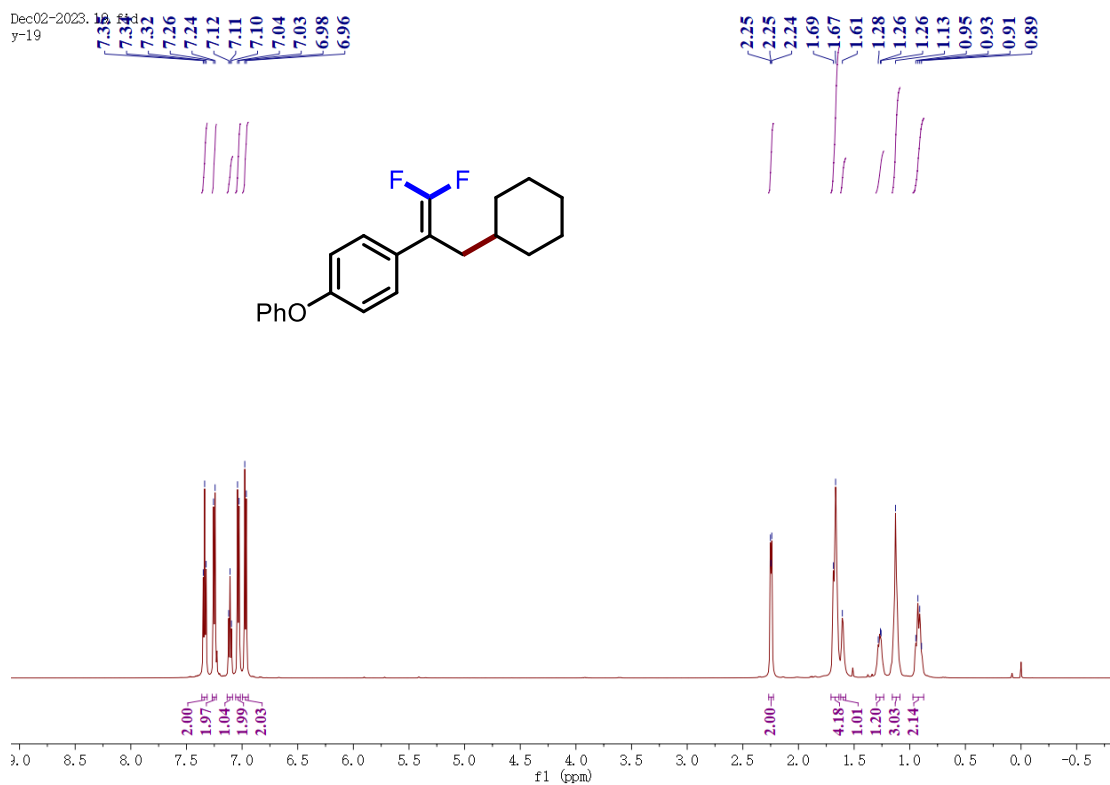
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zy-y-5-f-1.1. f1d
F19

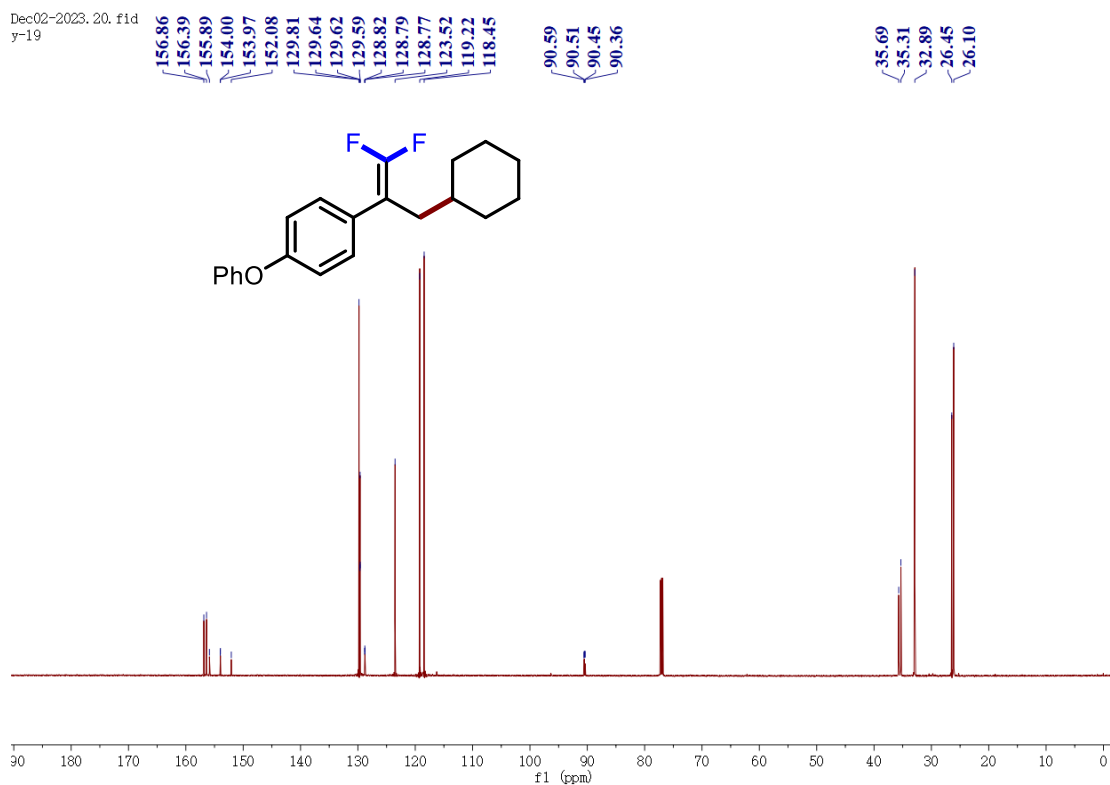
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¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3b**.

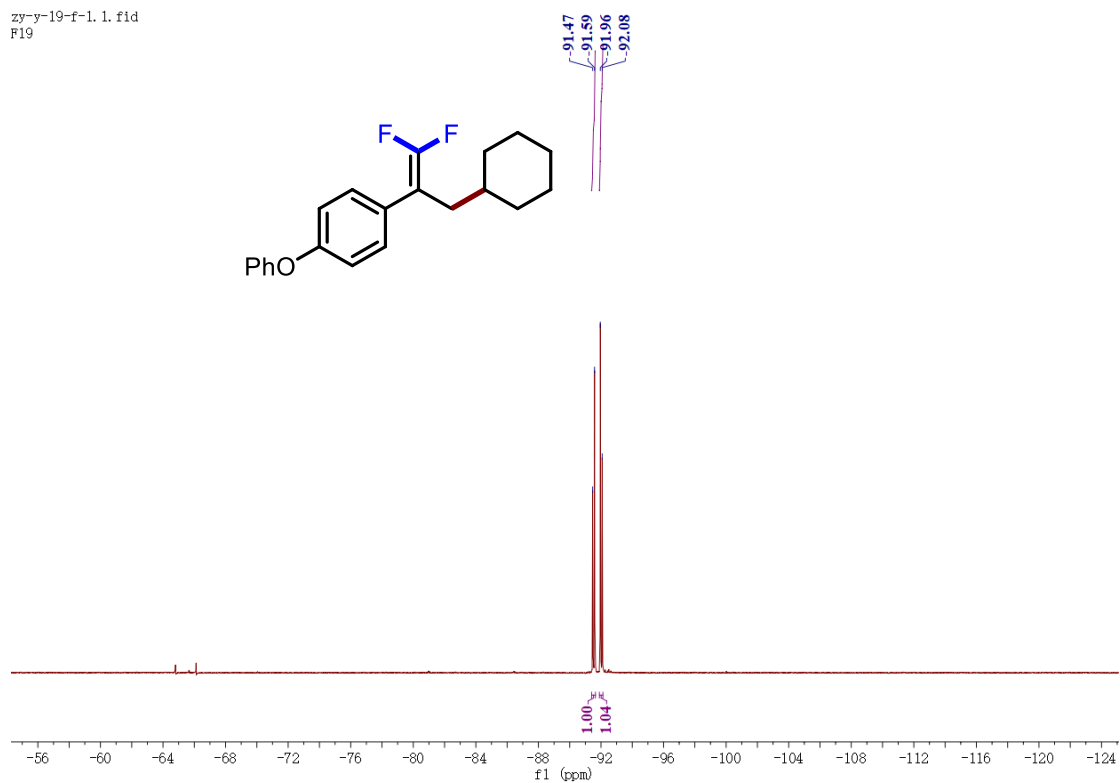


$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) spectrum of compound **3c**.

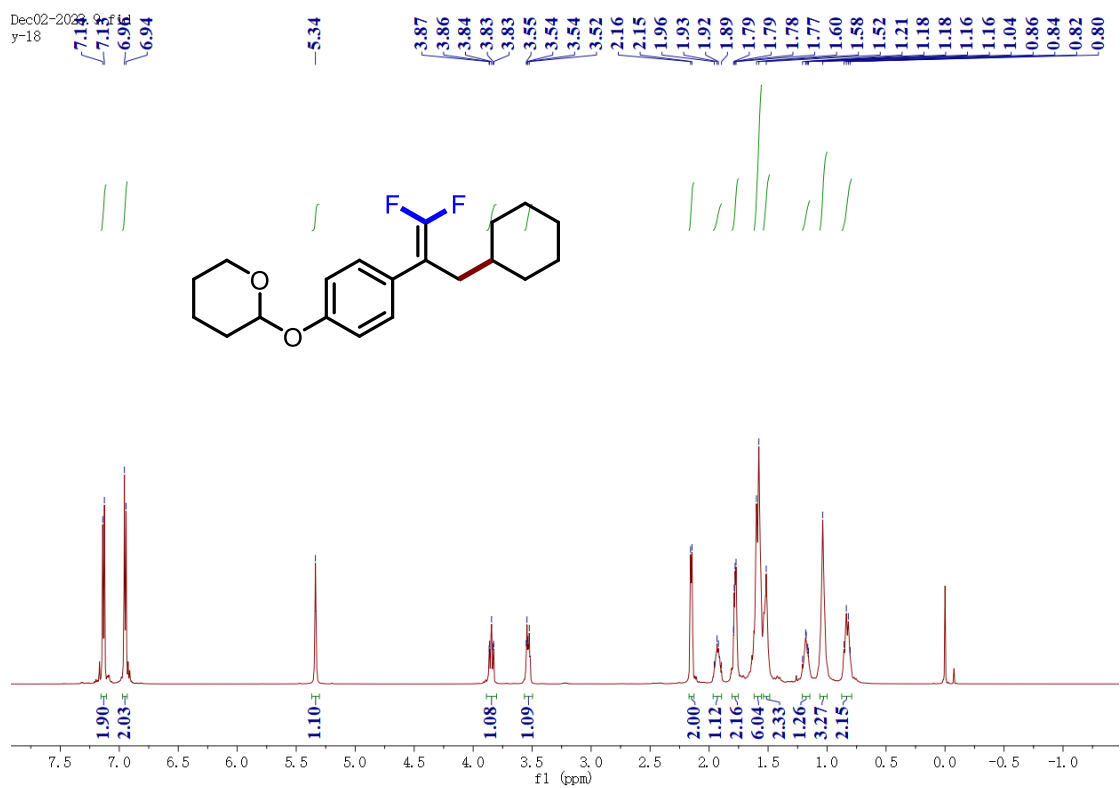


$^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) spectrum of compound **3c**.

zy-y-19-f-1.1.fid
F19

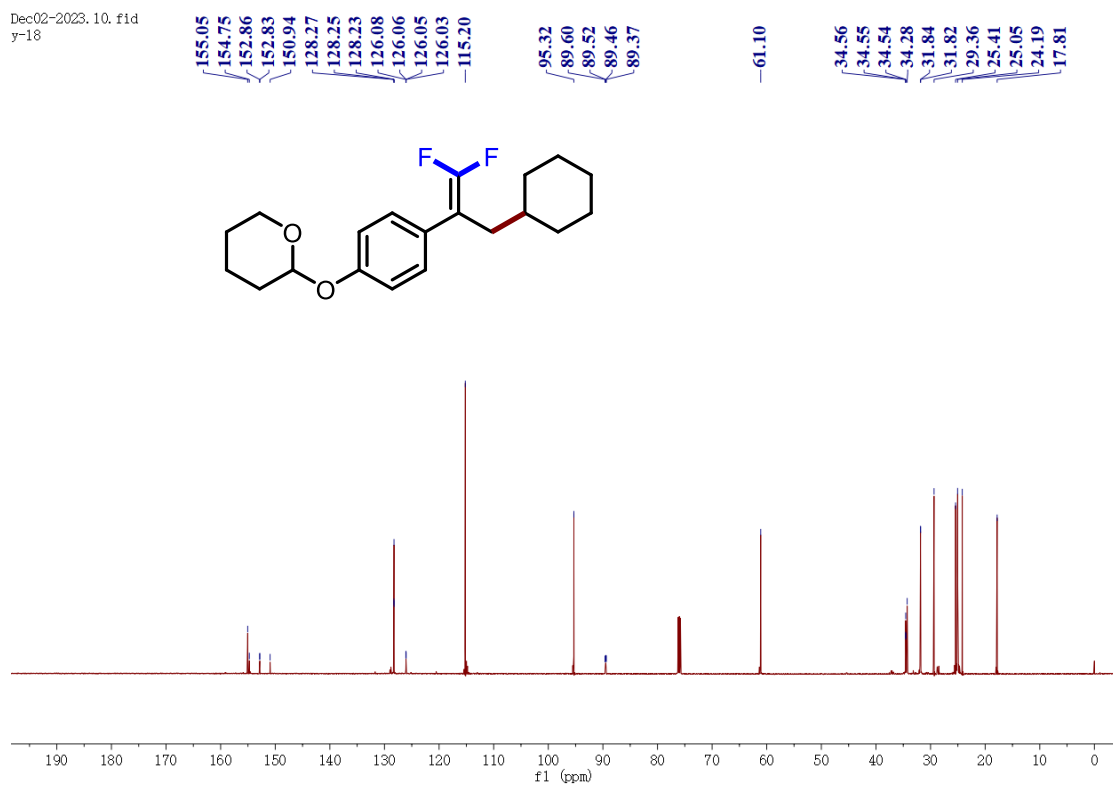


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3c.



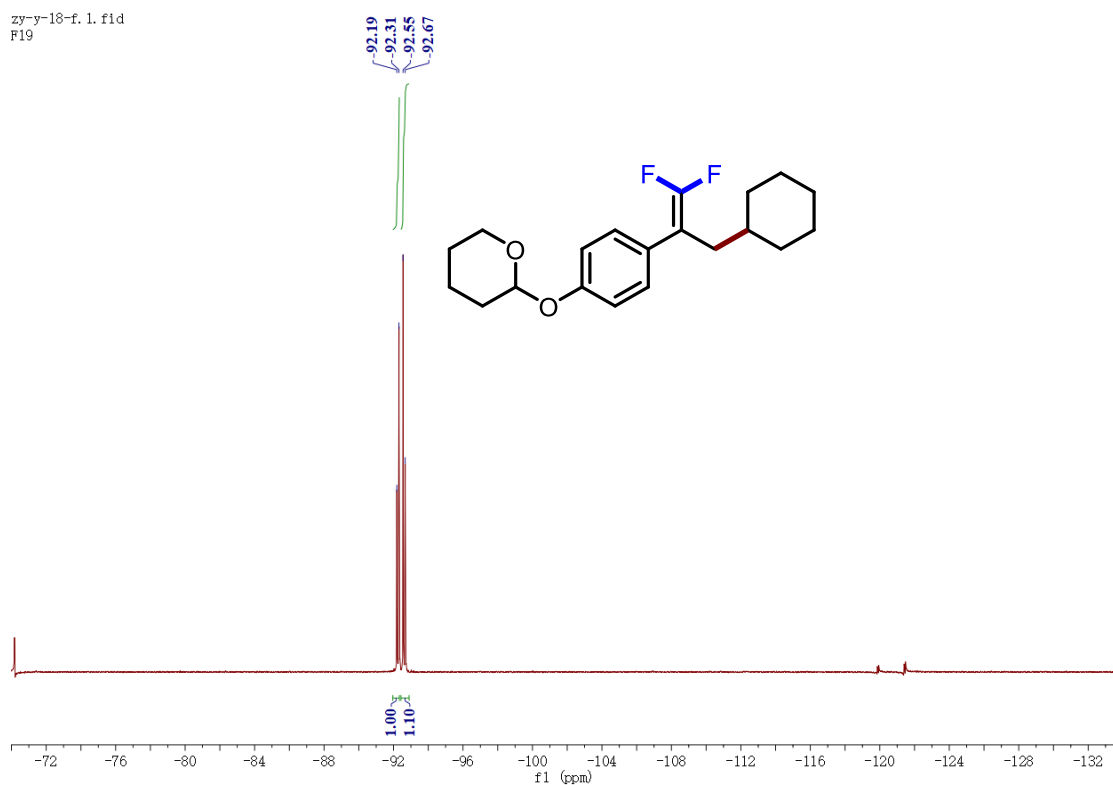
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3d.

Dec02-2023. 10. f1d
y-18

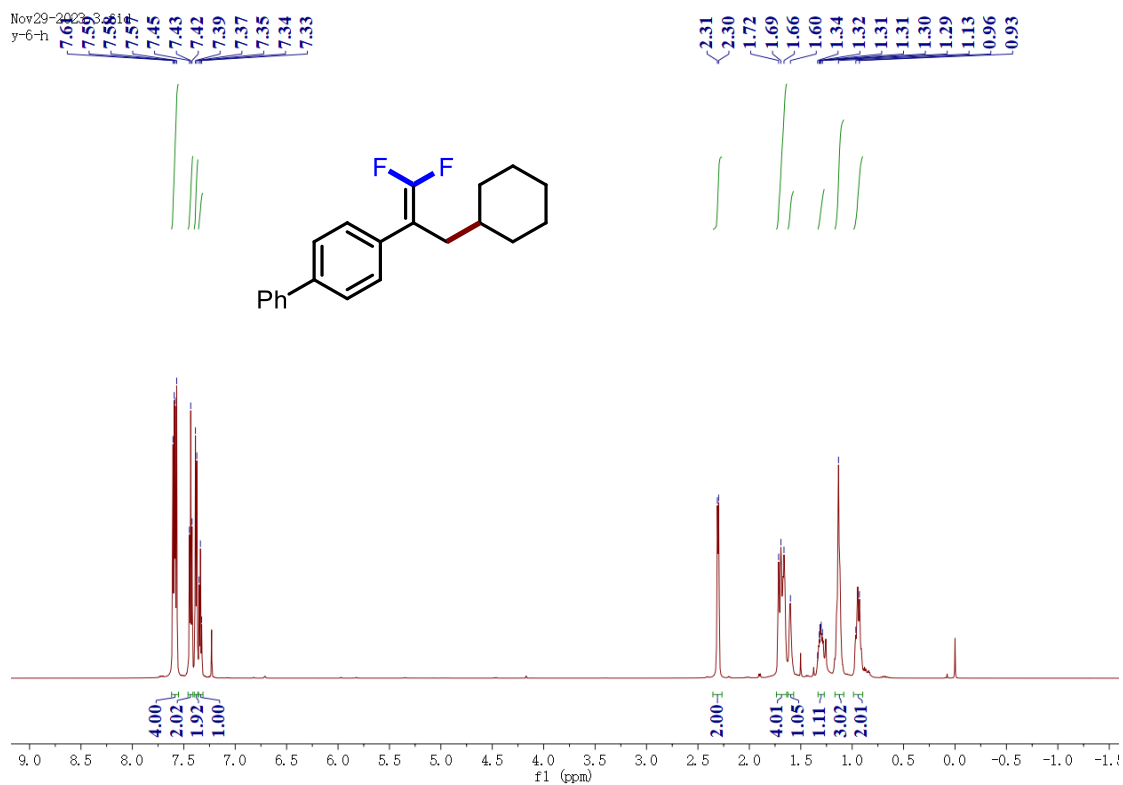


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3d**.

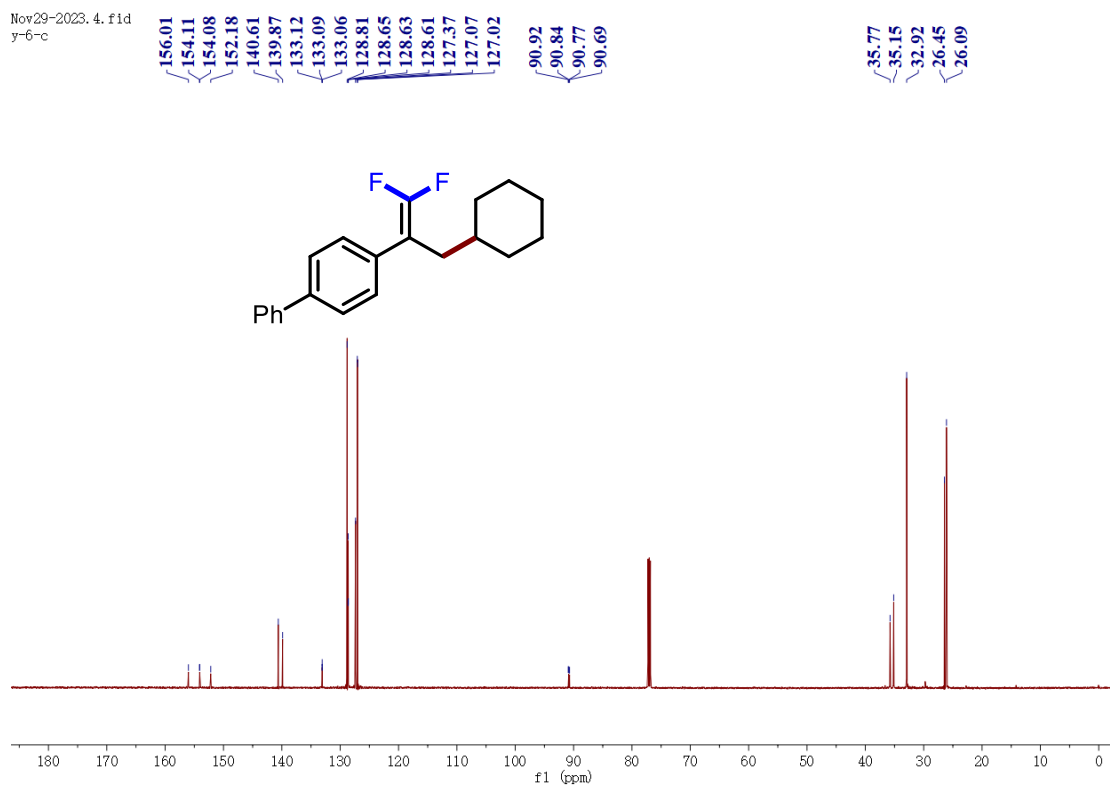
zy-y-18-f. 1. f1d
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3d**.

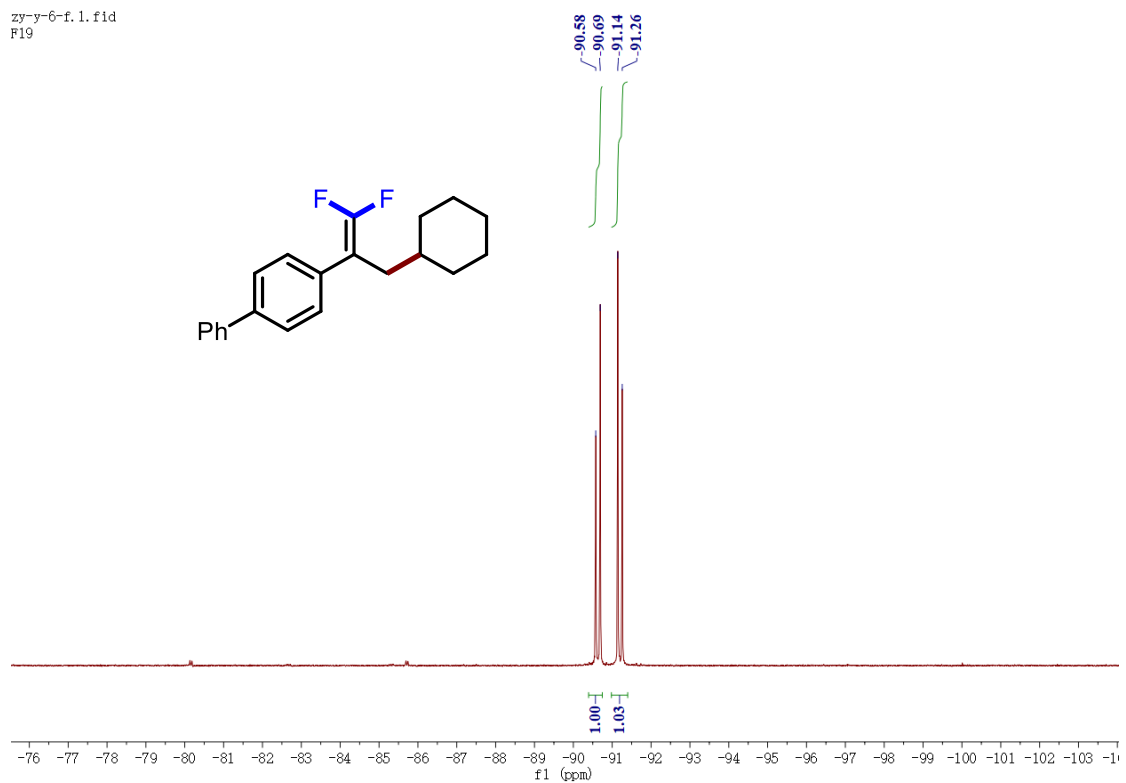


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3e.



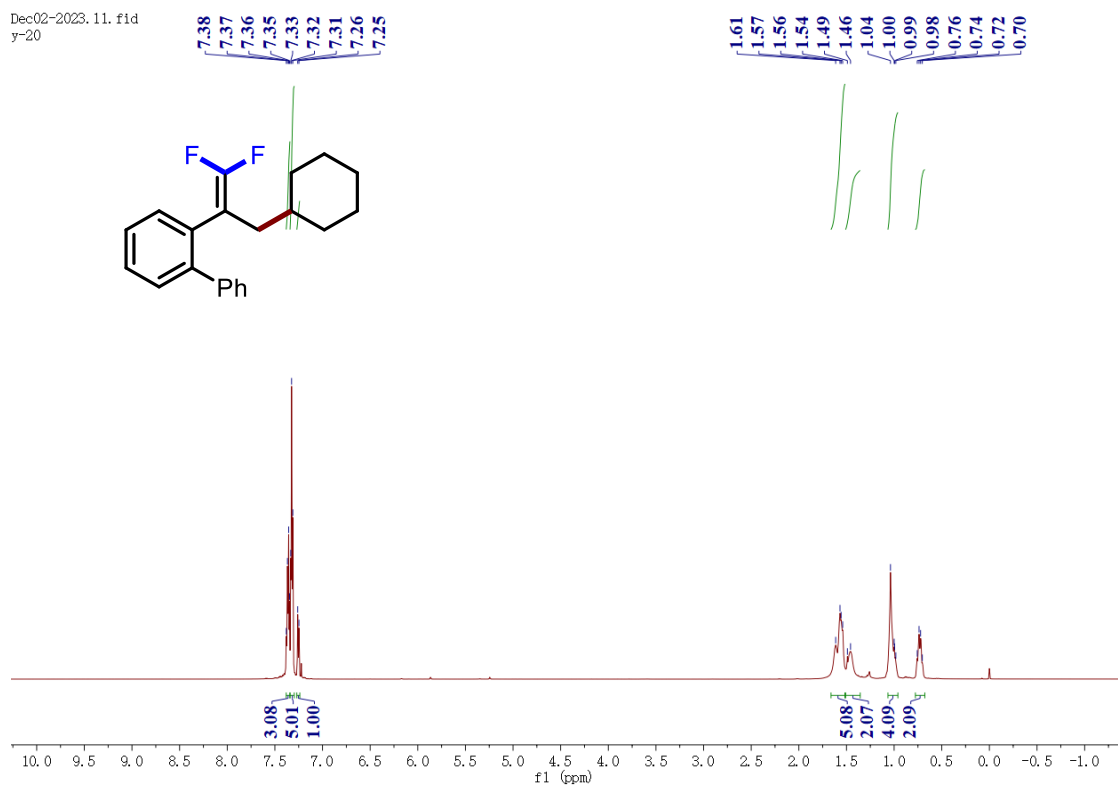
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 3e.

zy-y-6-f.1.fid
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3e**.

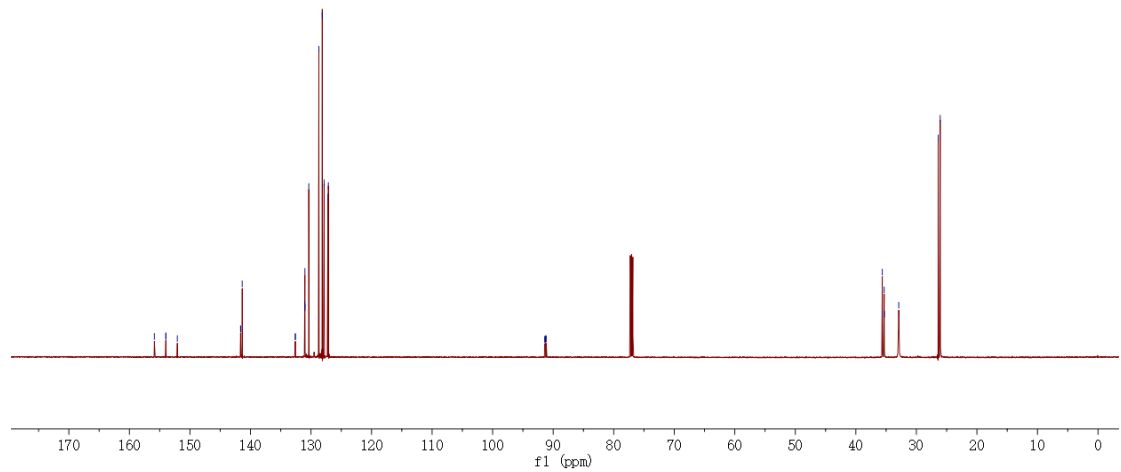
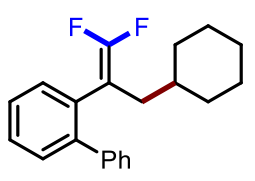
Dec02-2023.11.fid
y-20



¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3f**.

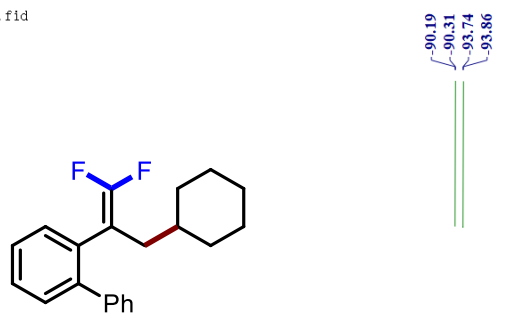
Dec02-2023. 12. 88
y-20

155.88
153.99
153.98
152.09
141.64
141.62
141.37
132.61
132.58
131.02
131.01
130.99
130.37
128.70
128.14
127.84
127.21
127.13
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35.63
35.33
35.32
35.30
32.91
26.40
26.06

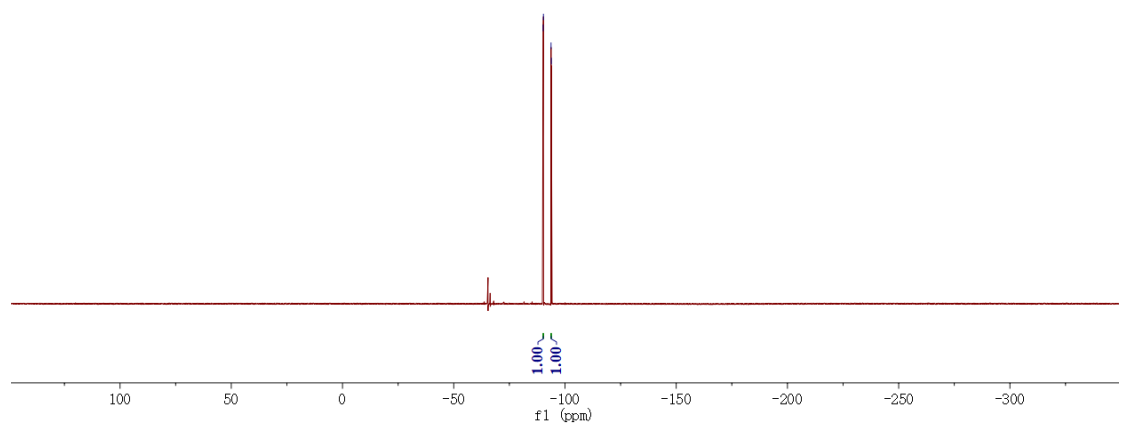


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3f**.

zy-y-20f. 1. fid
F19

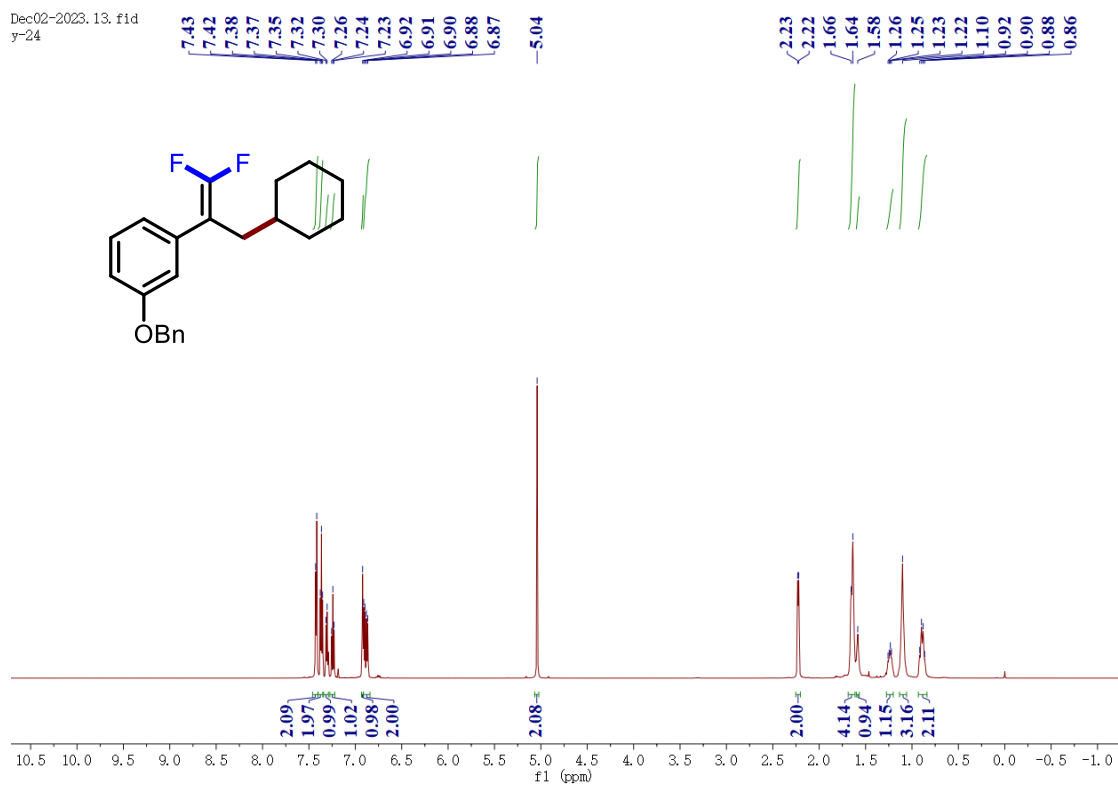


90.19
90.31
93.74
93.86



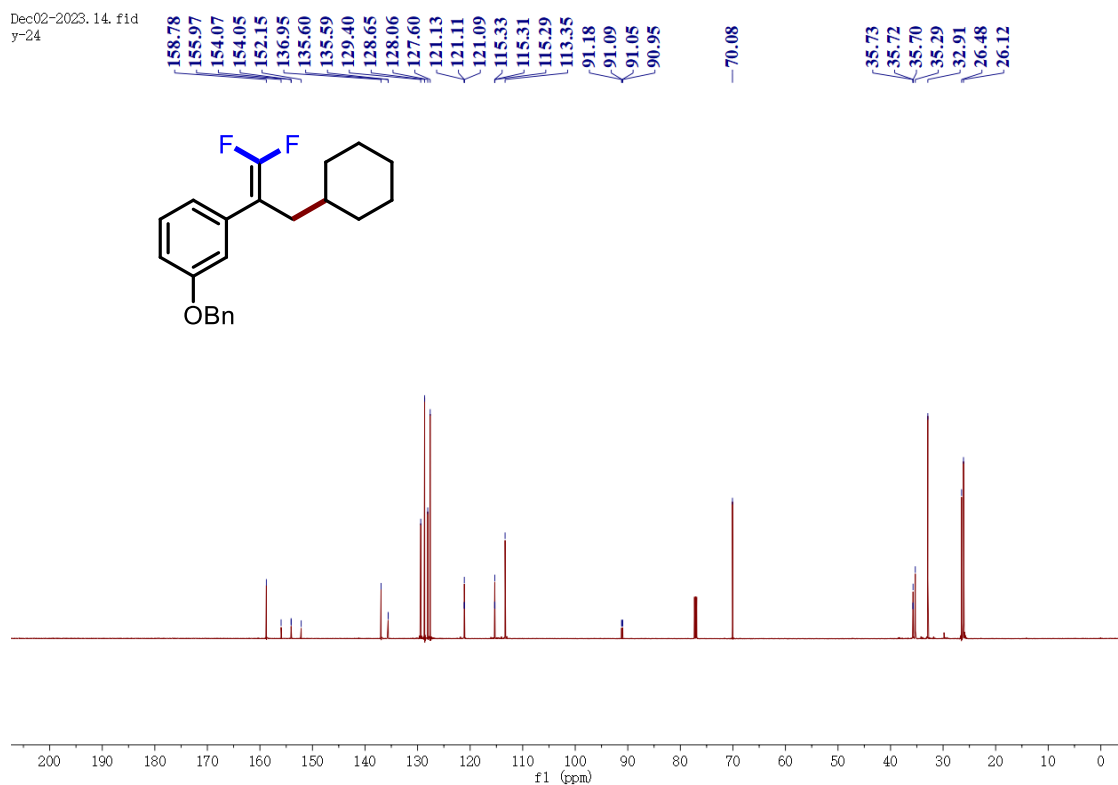
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3f**.

Dec02-2023. 13. f1d
y-24



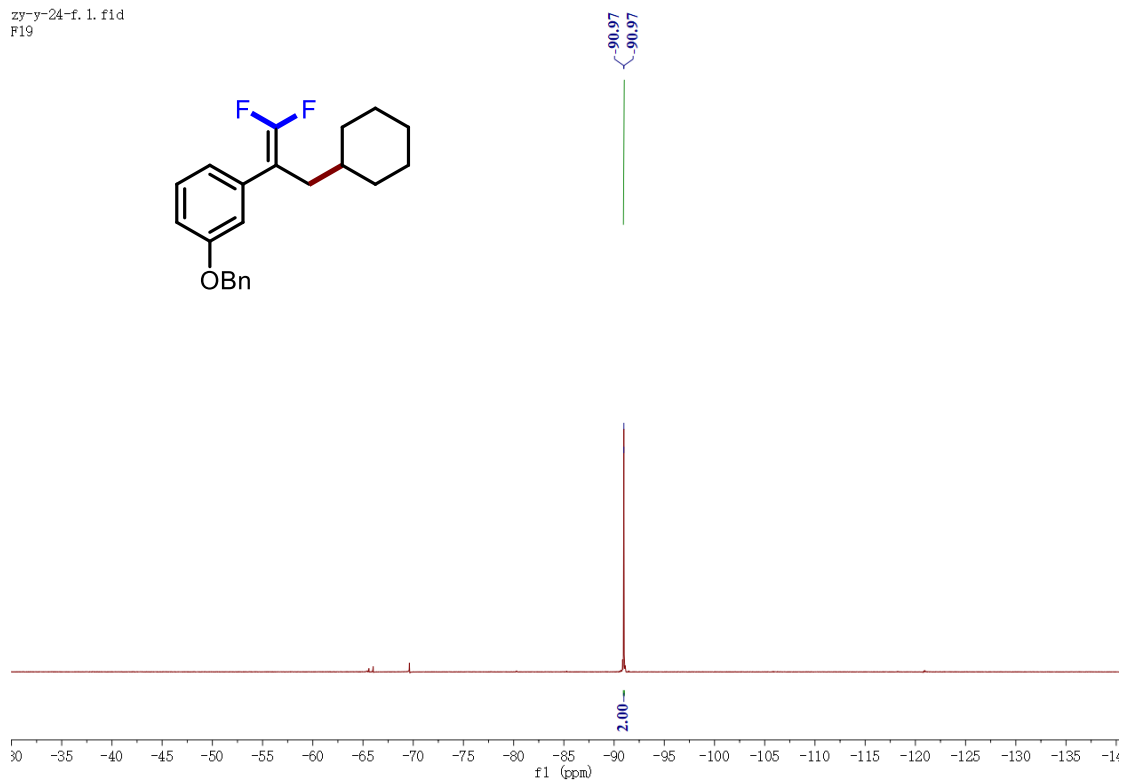
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3g**.

Dec02-2023. 14. f1d
y-24

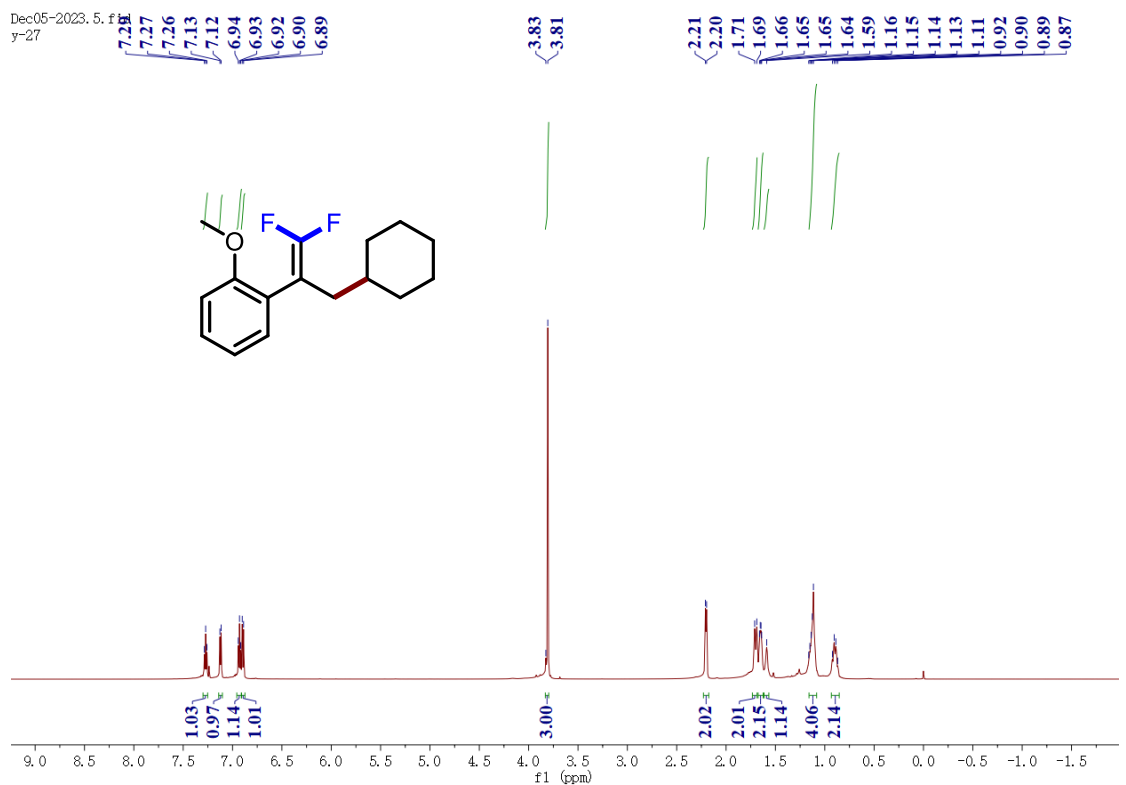


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3g**.

zy-y-24-f. 1. fid
F19

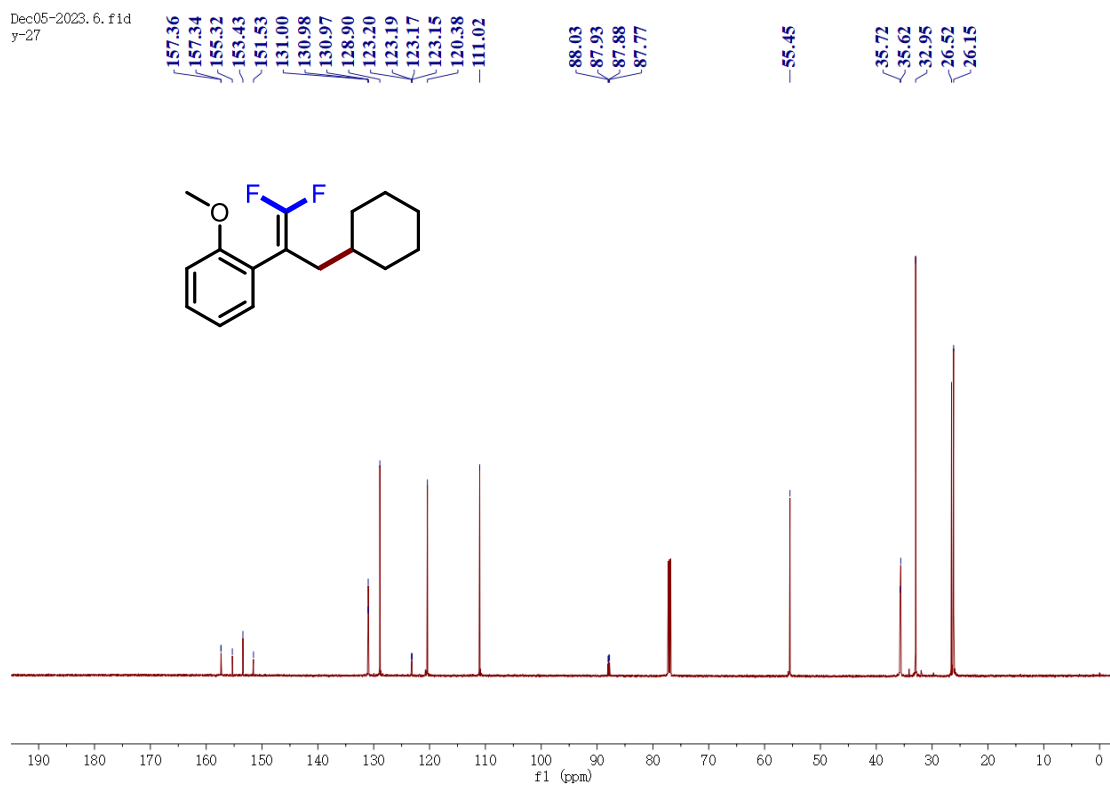


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3g**.



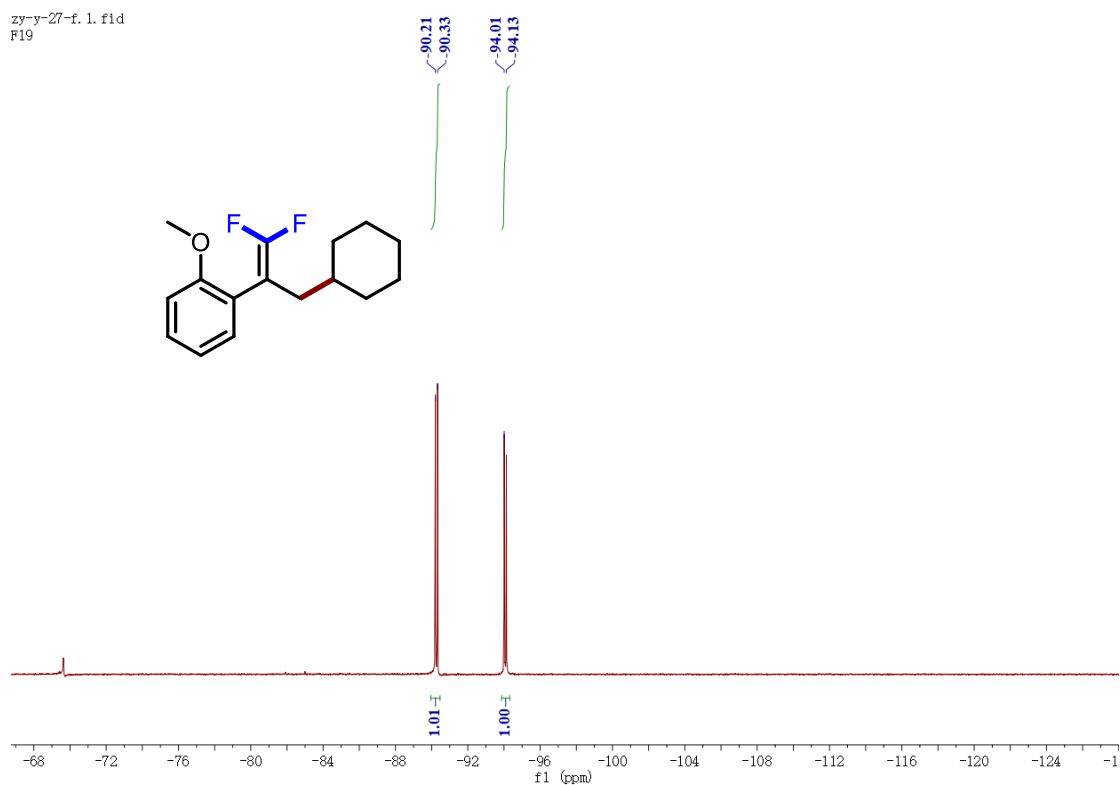
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3h**.

Dec05-2023. 6. f1d
y-27



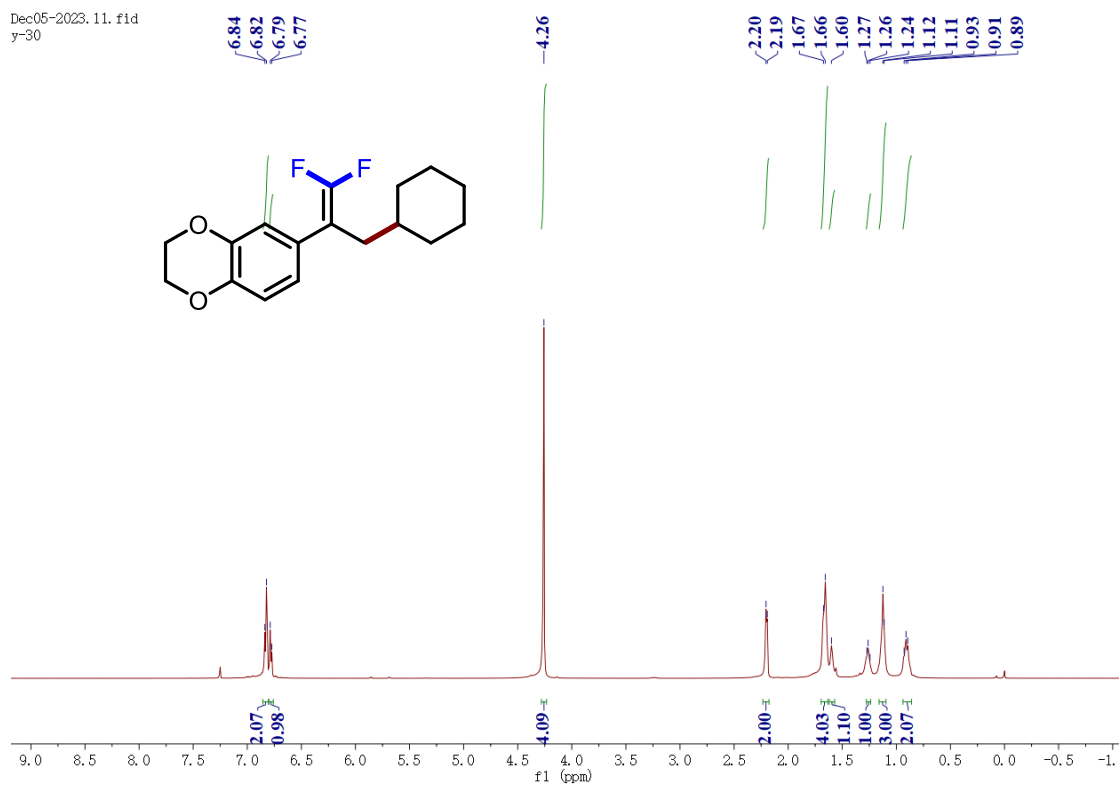
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 3h.

zy-y-27-f. 1. f1d
F19



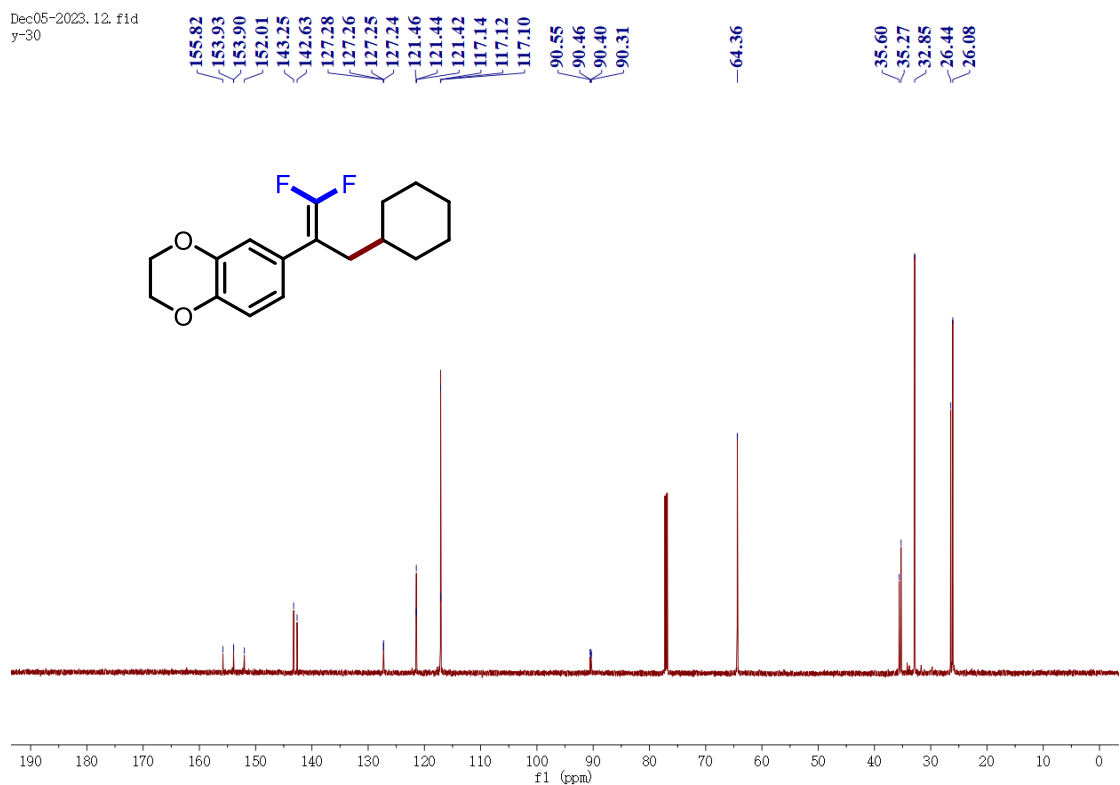
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3h.

Dec05-2023. 11. fid
y-30



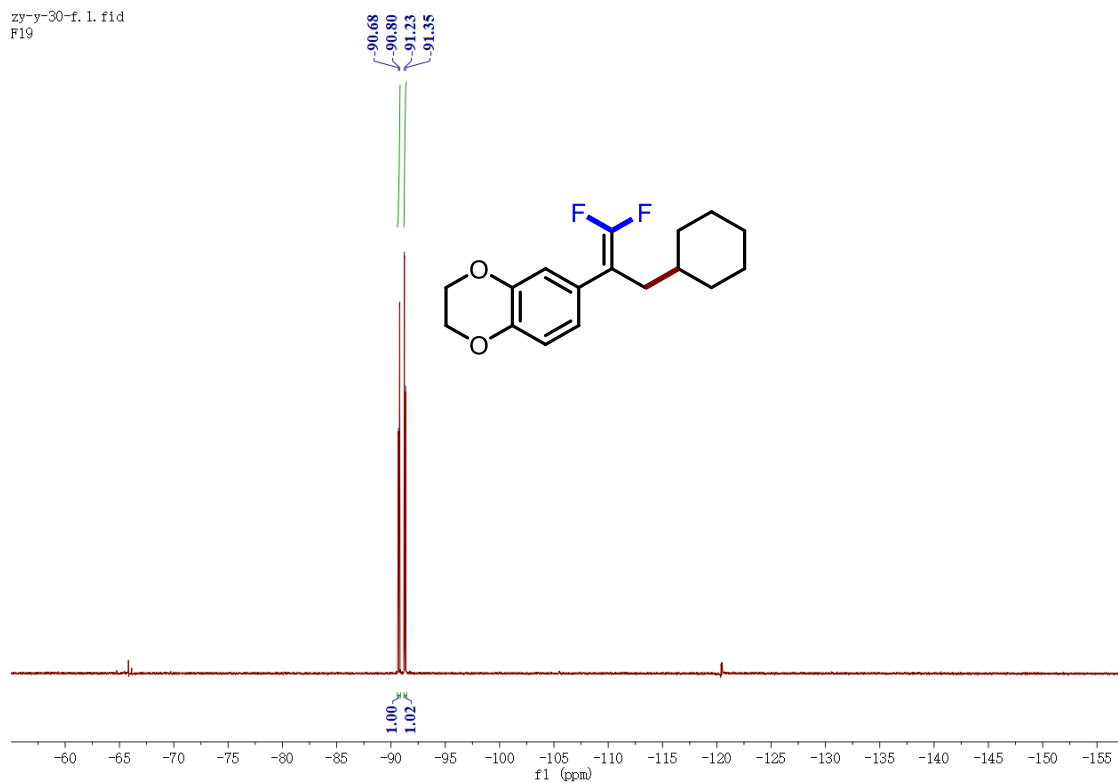
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3i**.

Dec05-2023. 12. fid
y-30



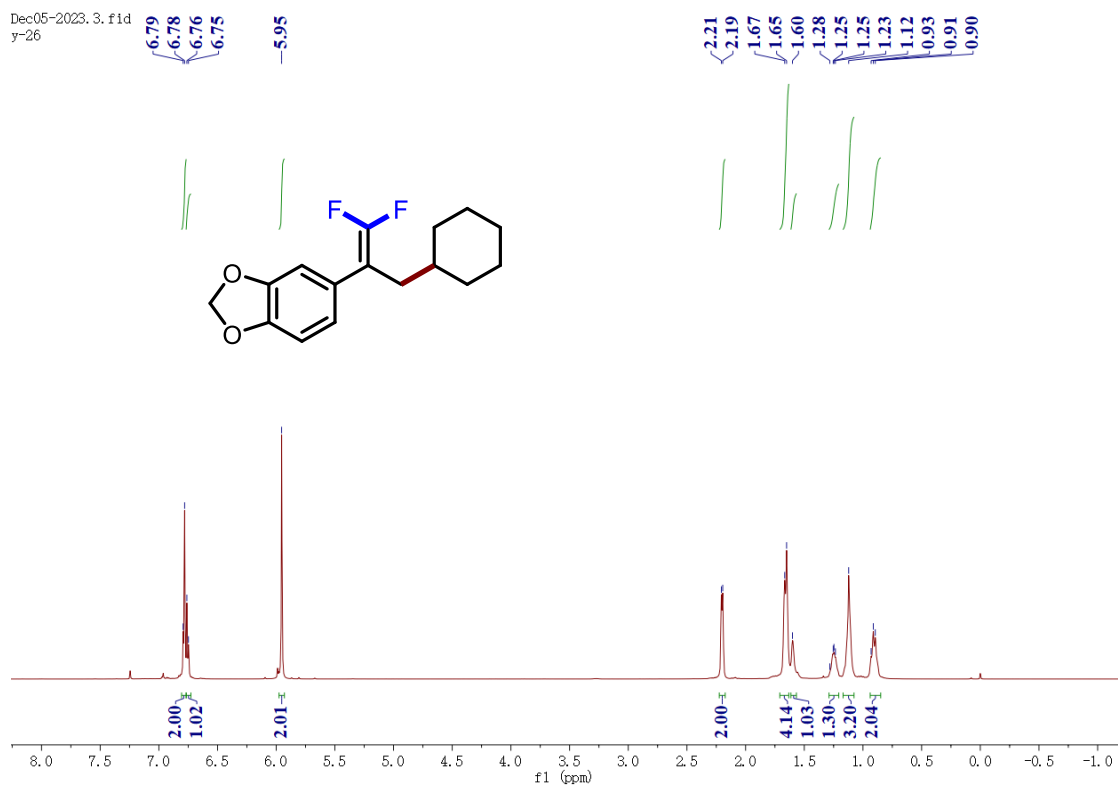
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3i**.

zy-y-30-f. 1. fid
F19



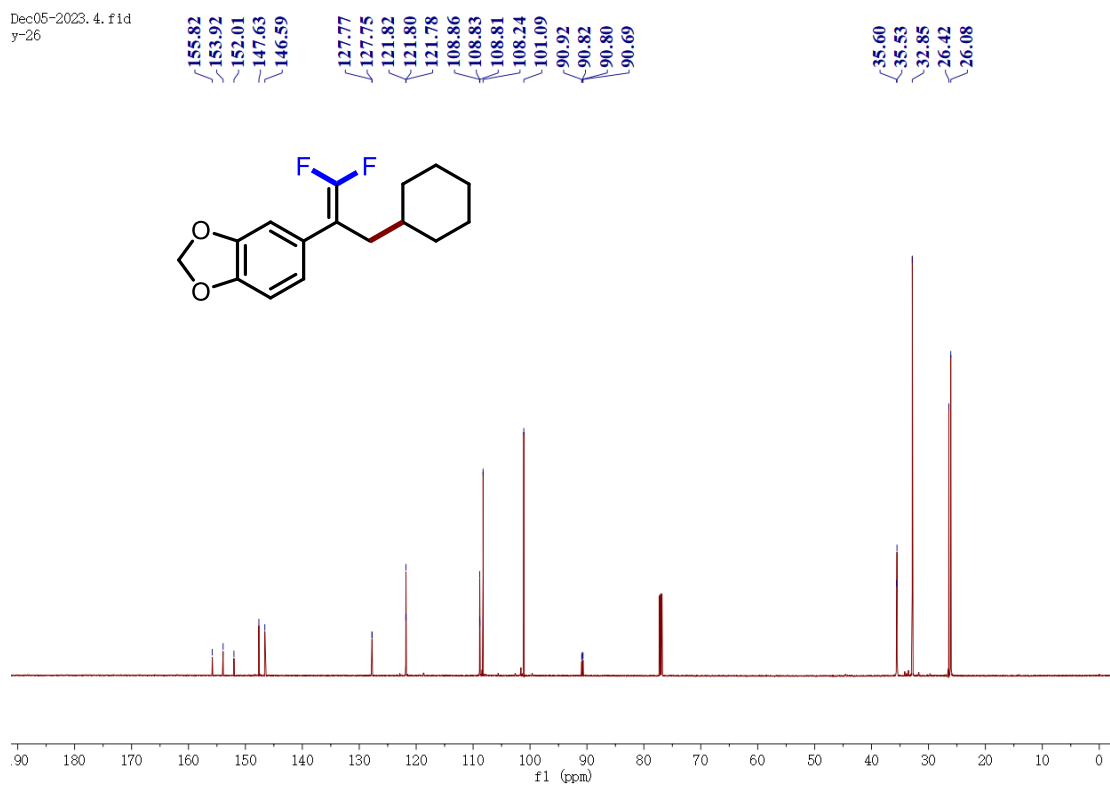
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3i**.

Dec05-2023. 3. fid
y-26



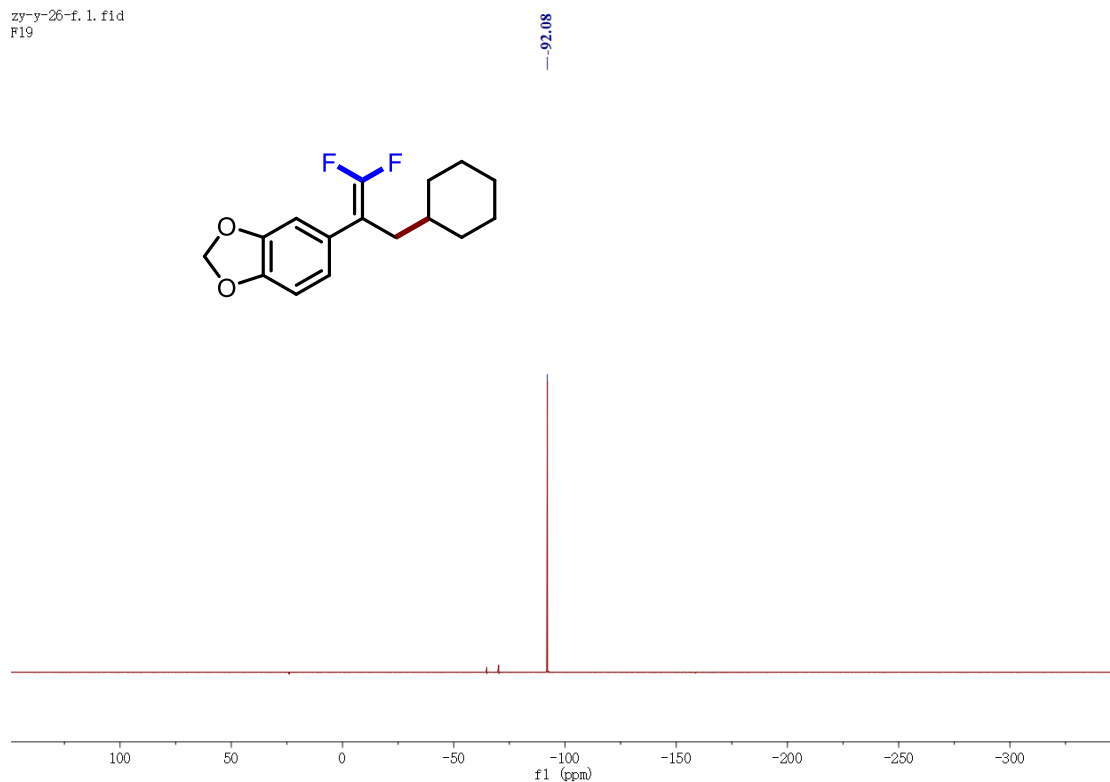
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3j**.

Dec05-2023. 4. f1d
y-26



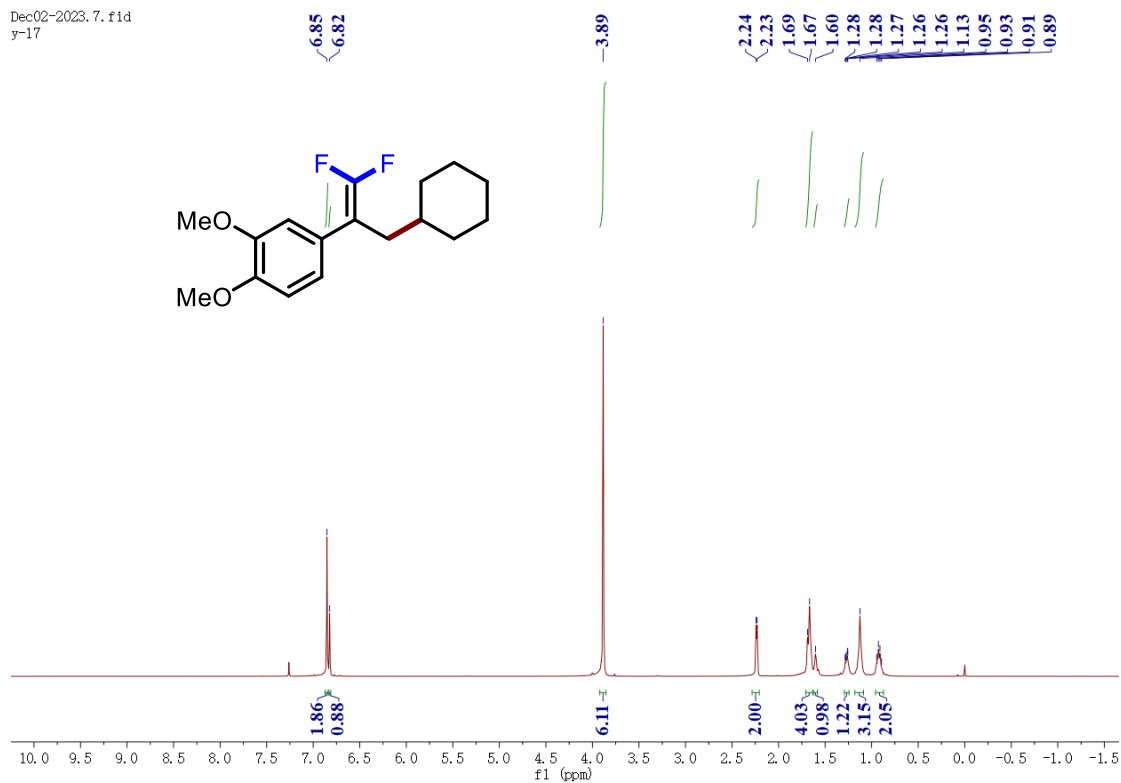
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 3j.

zy-y-26-f. 1. f1d
F19



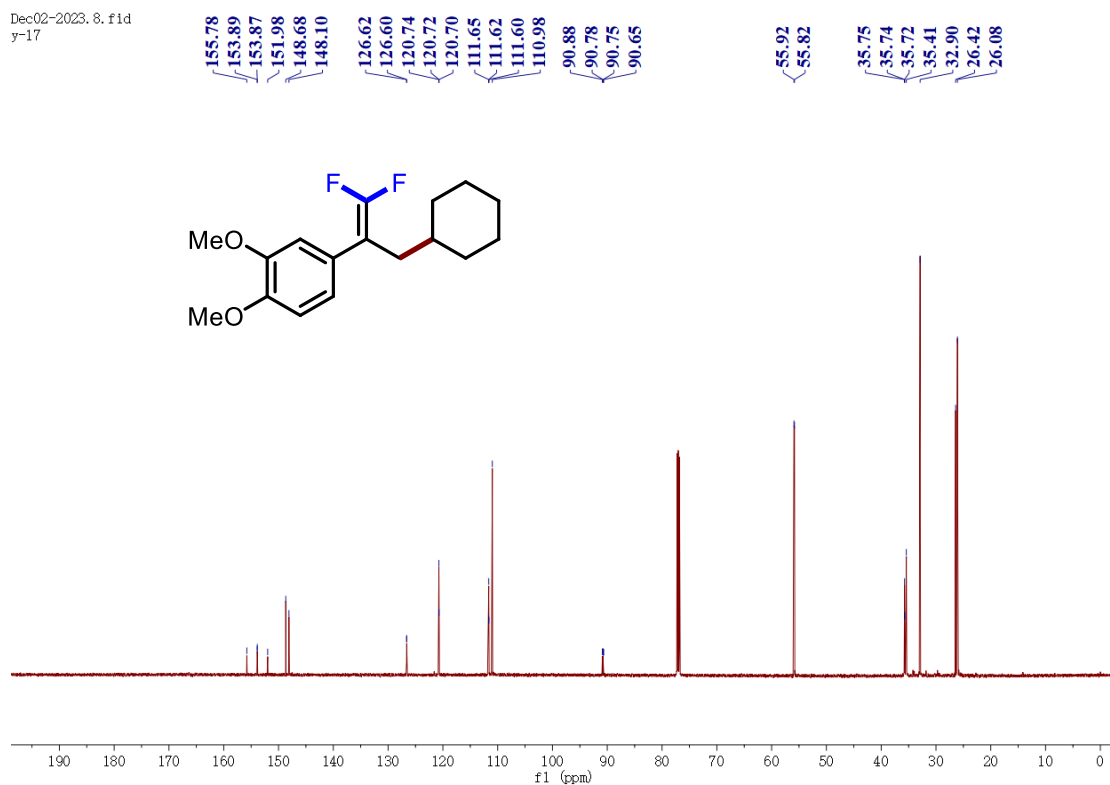
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3j.

Dec02-2023. 7. f1d
y-17



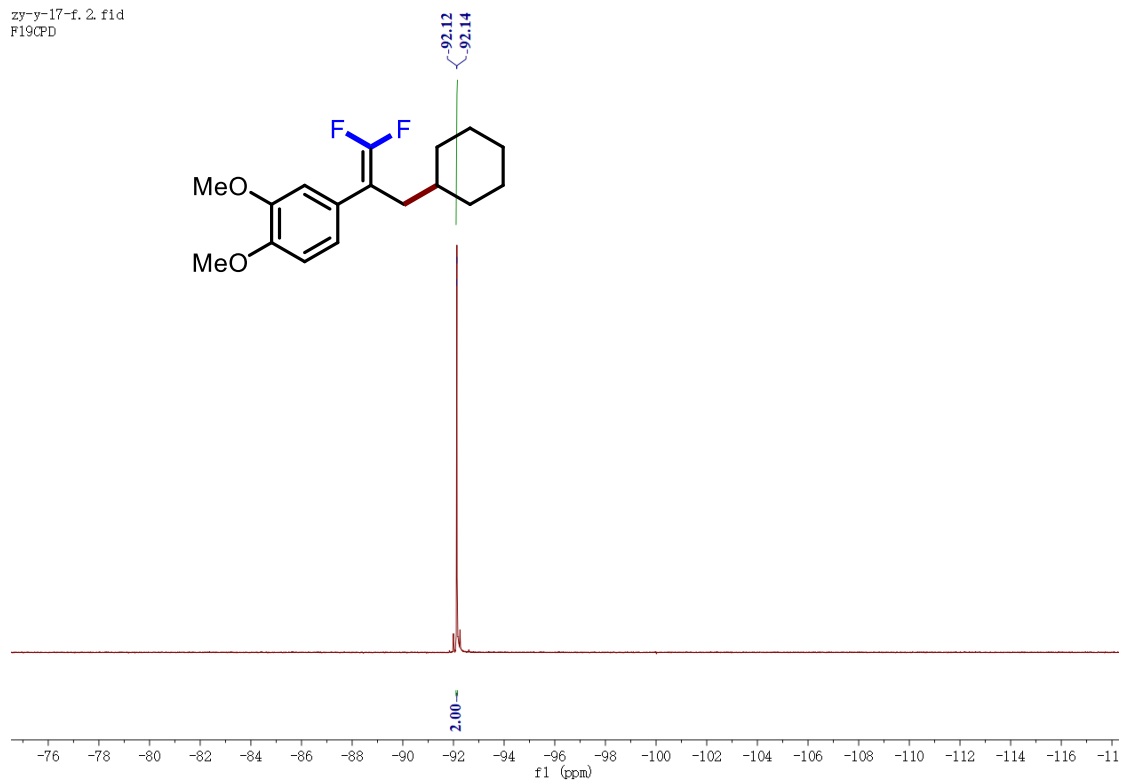
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3k**.

Dec02-2023. 8. f1d
y-17



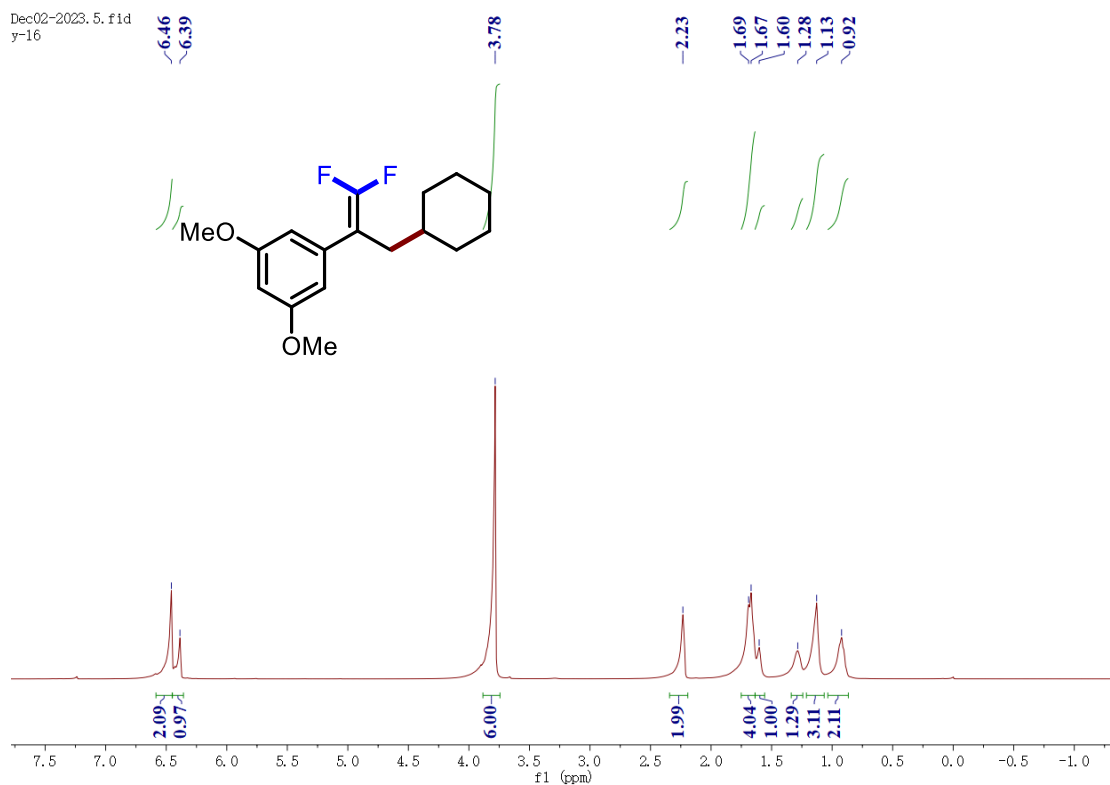
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3k**.

zy-y-17-f. 2. fid
F19CPD



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3k.

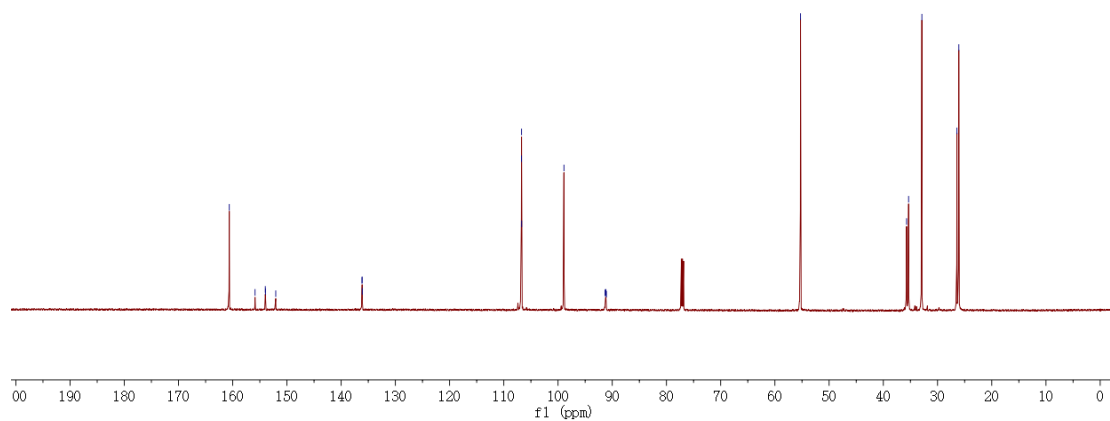
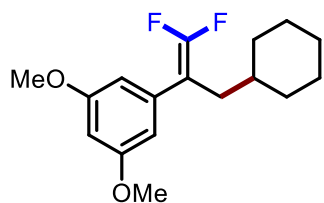
Dec02-2023. 5. fid
y-16



¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3l.

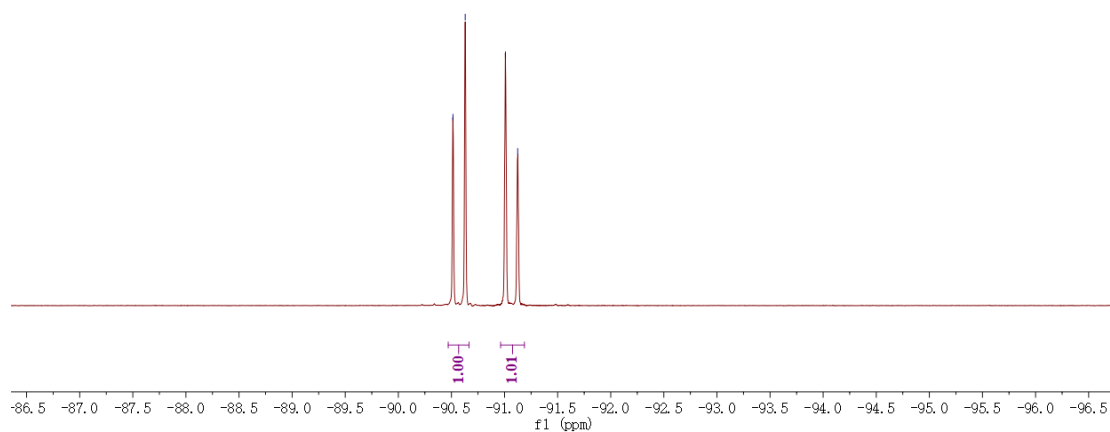
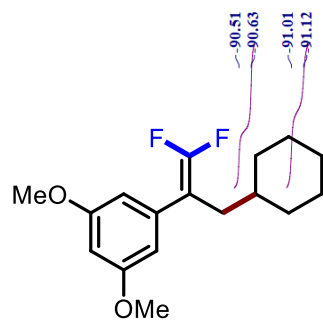
Dec02-2023. 6. f1d
y-16

160.63 155.88 153.99 153.96 152.06 136.15 136.13 136.10 106.75 106.73 106.71 98.91 91.31 91.23 91.16 91.08 -55.27 35.71 35.34 32.89 26.42 26.07



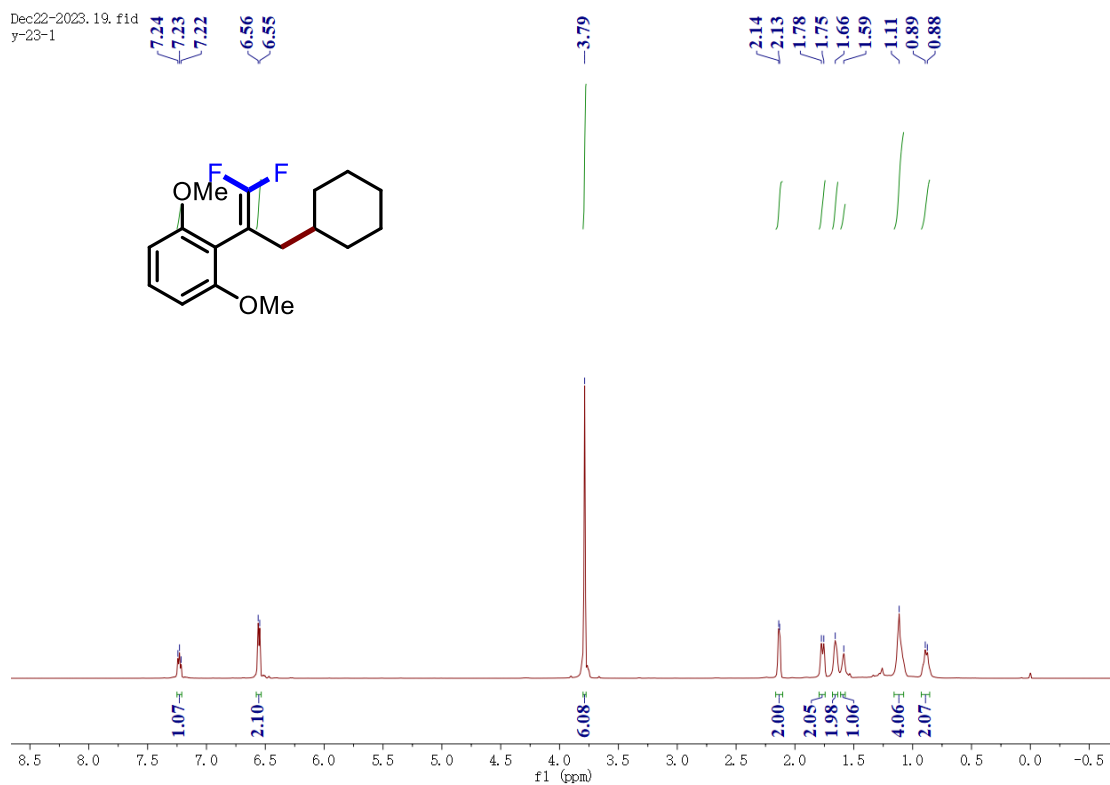
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 31.

zy-y-16-f. 1. f1d
F19



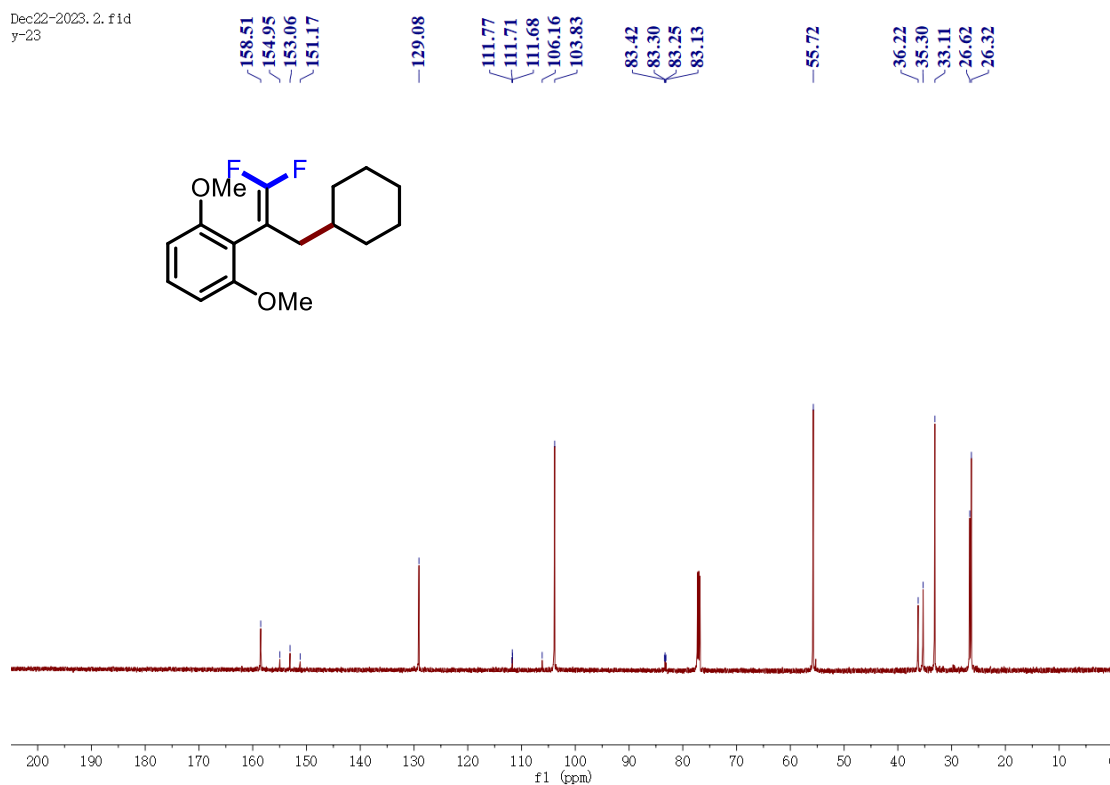
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 31.

Dec22-2023. 19. f1d
y-23-1



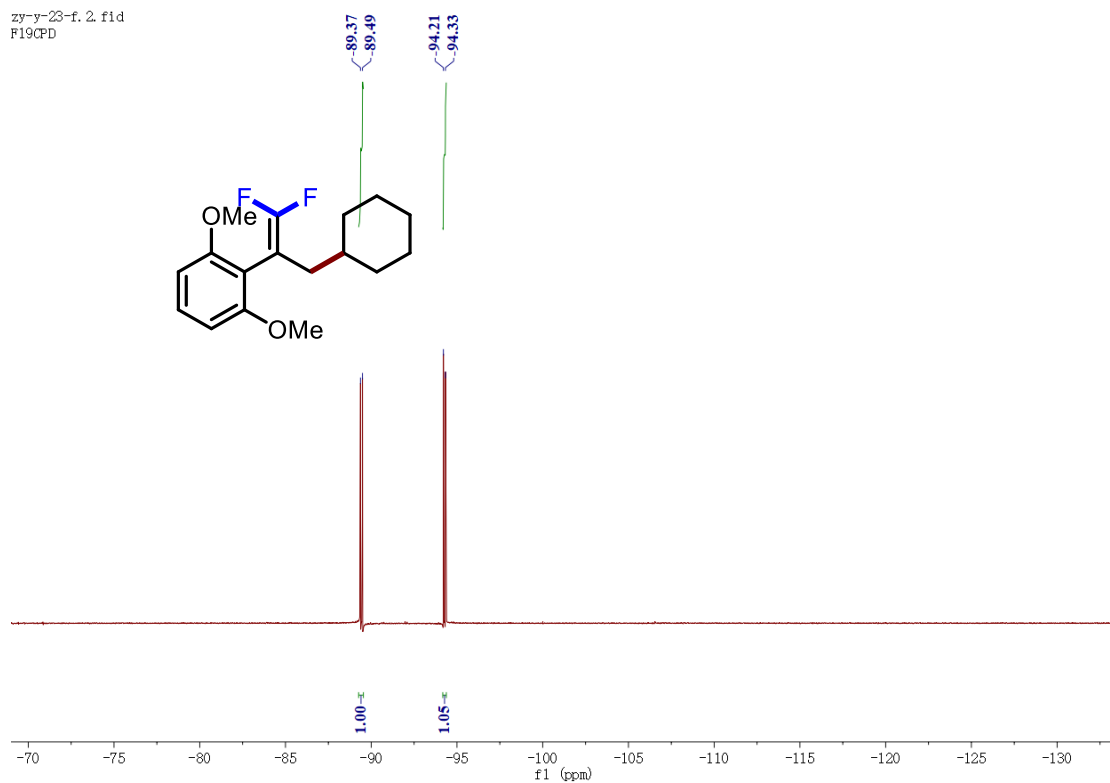
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3m**.

Dec22-2023. 2. f1d
y-23



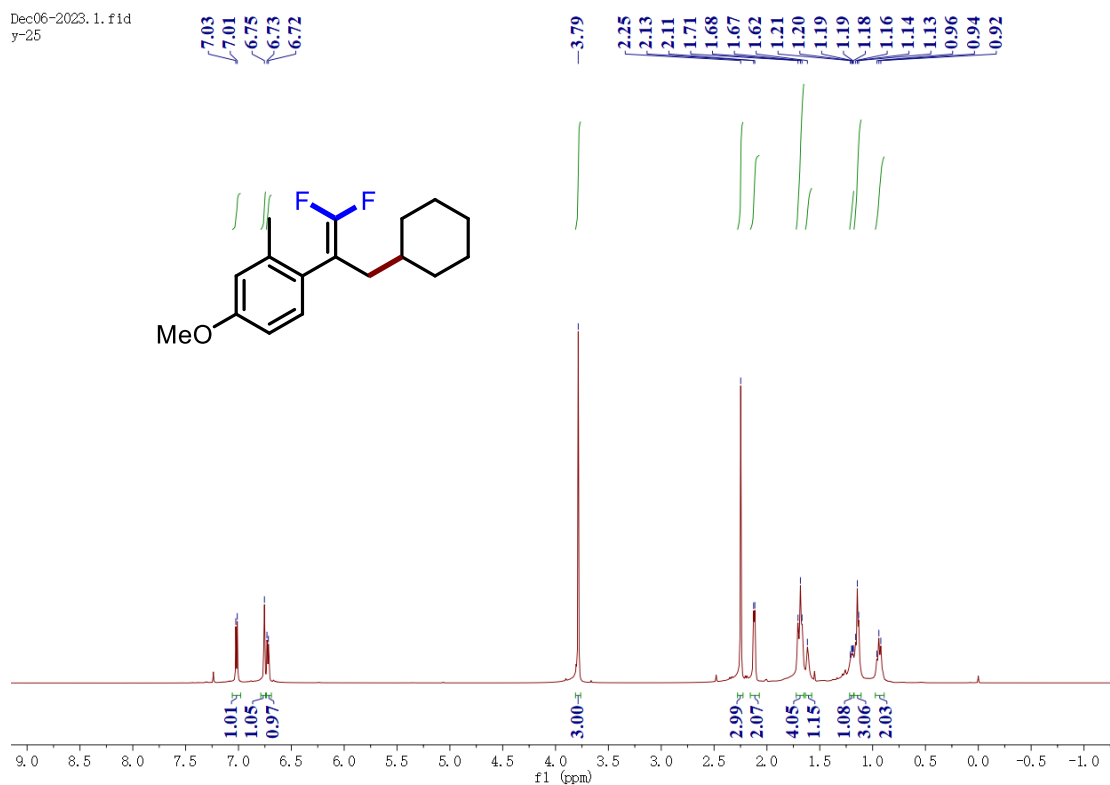
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3m**.

zy-y-23-f. 2. fid
F19CPD



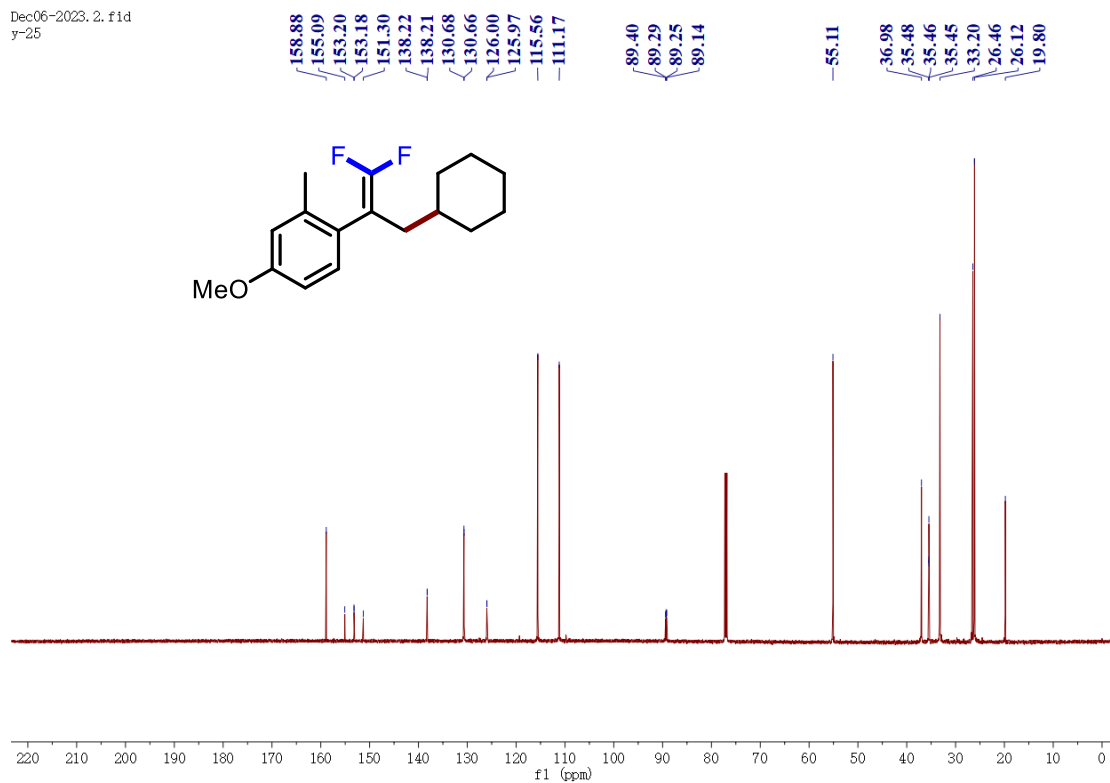
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3m.

Dec06-2023. 1. fid
y-25



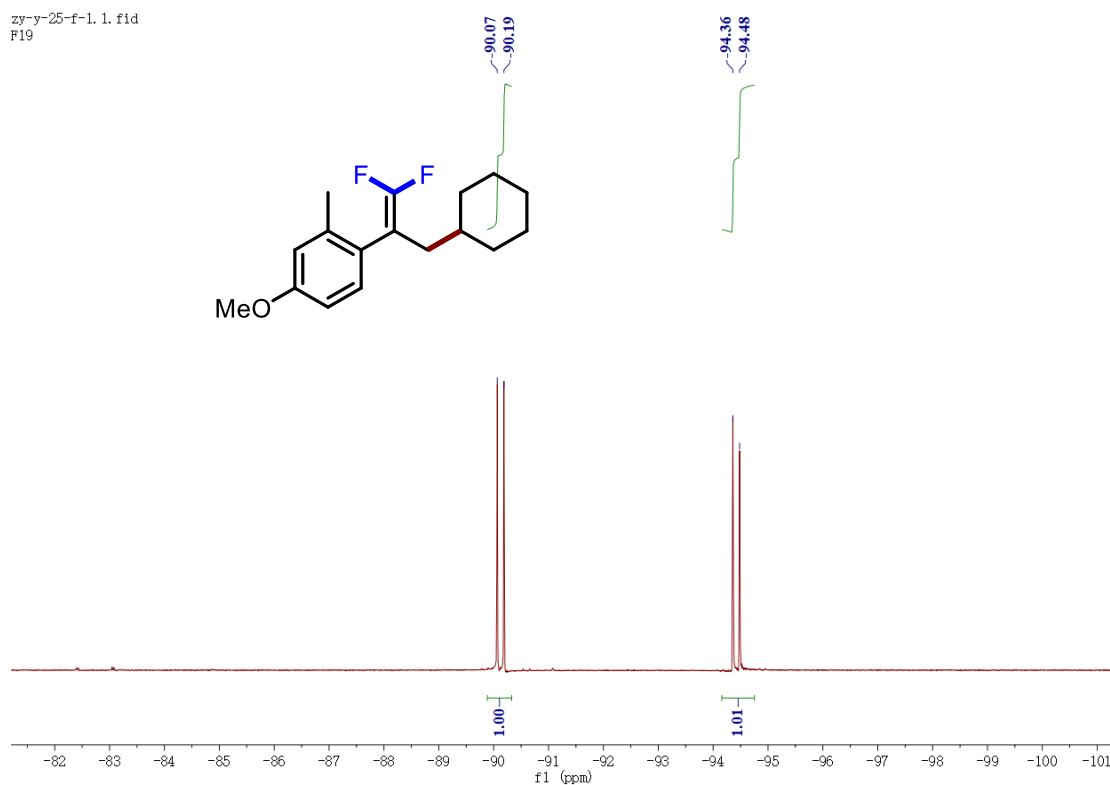
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3n.

Dec06-2023. 2. f1d
y-25



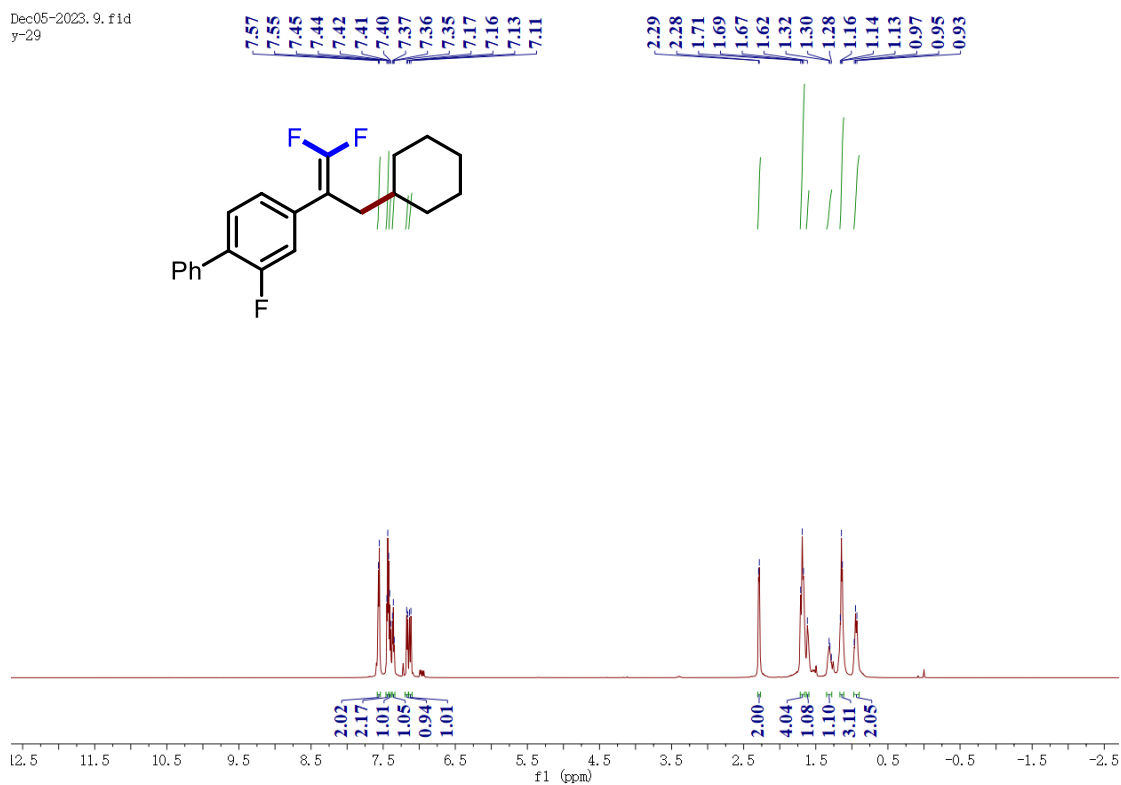
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3n**.

zy-y-25-f-1. 1. f1d
F19



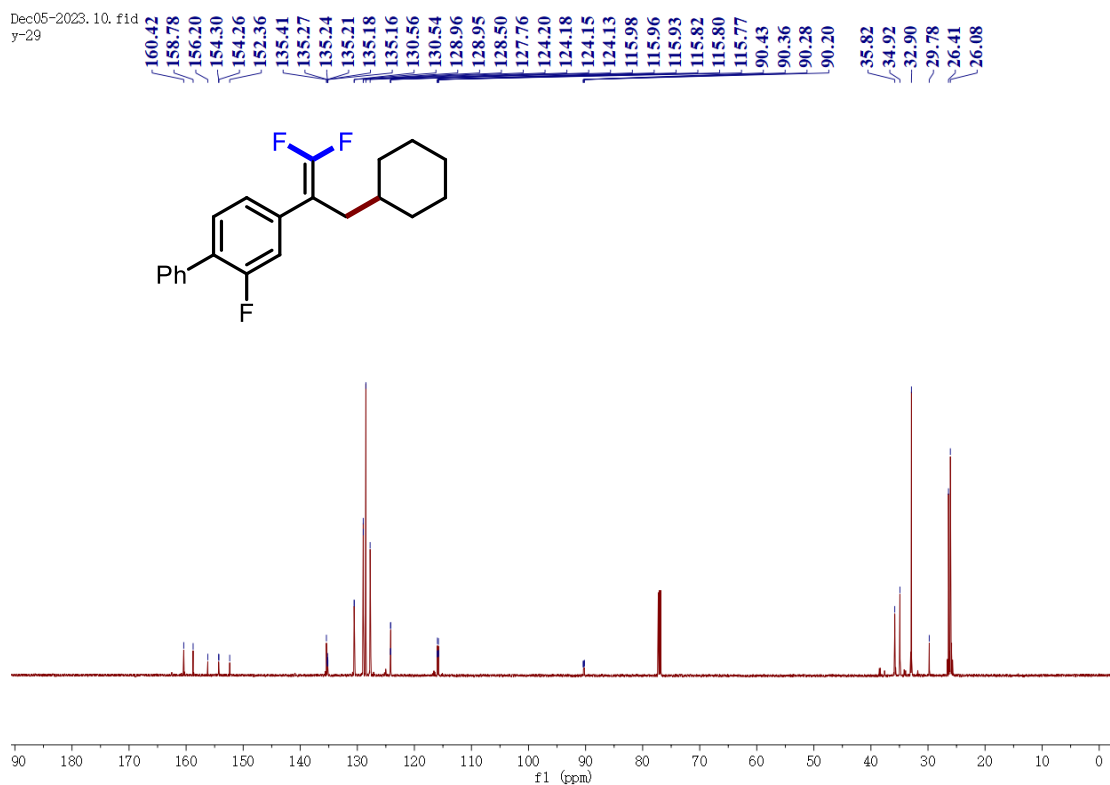
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3n**.

Dec05-2023. 9. f1d
y-29

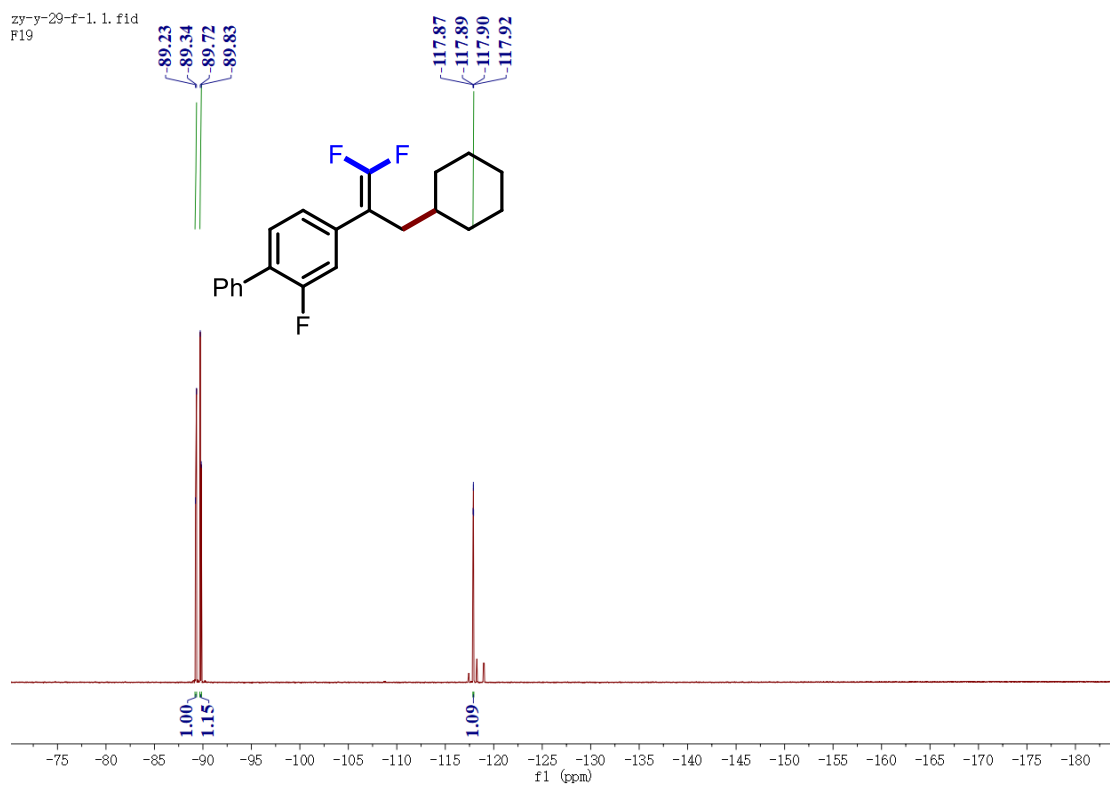


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3o**.

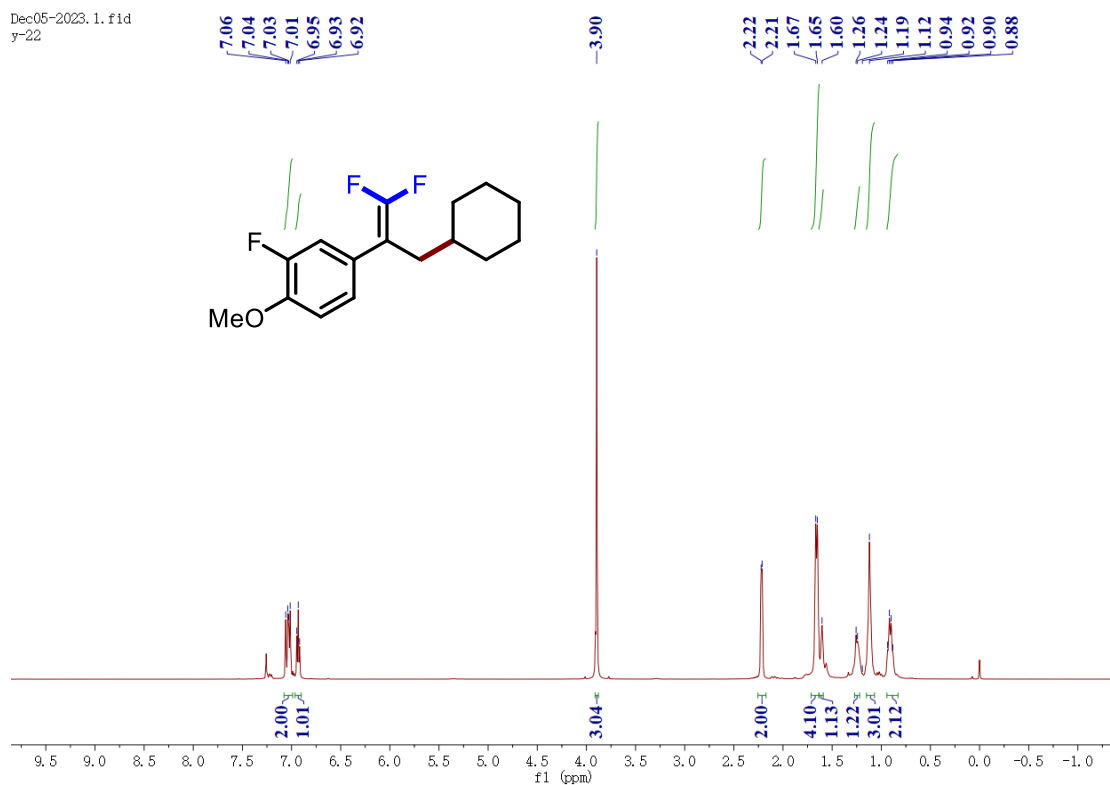
Dec05-2023. 10. f1d
y-29



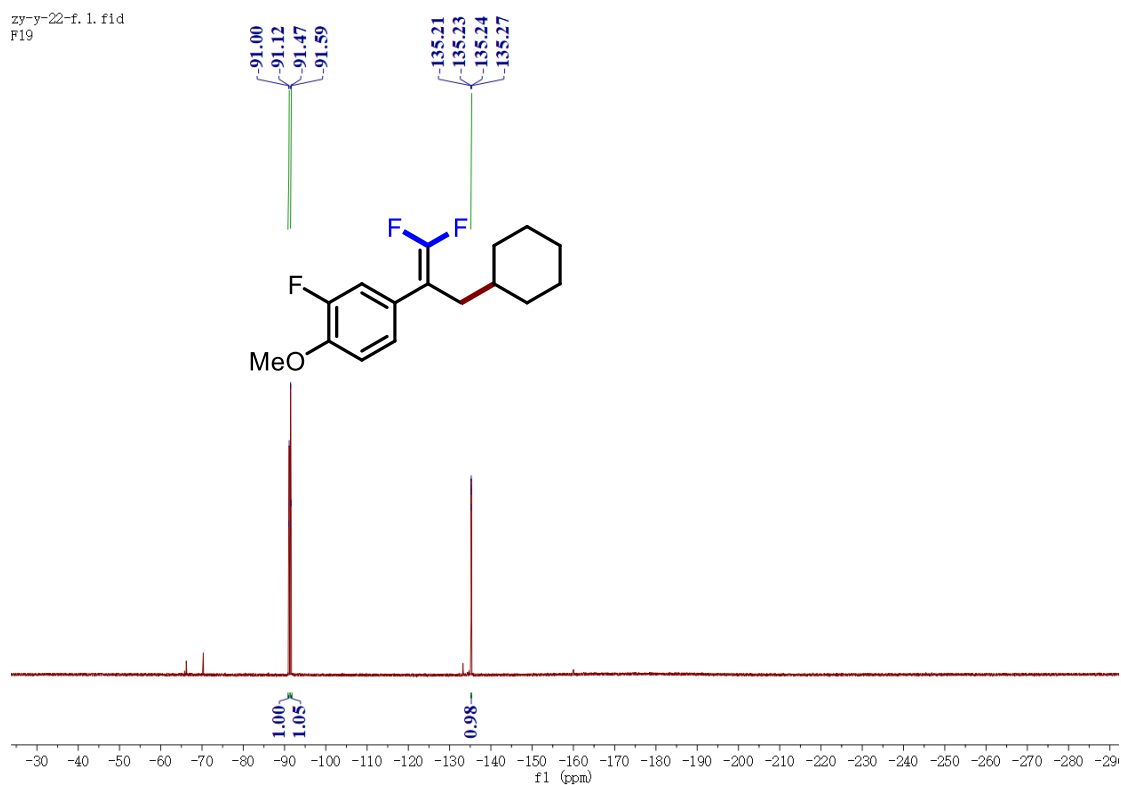
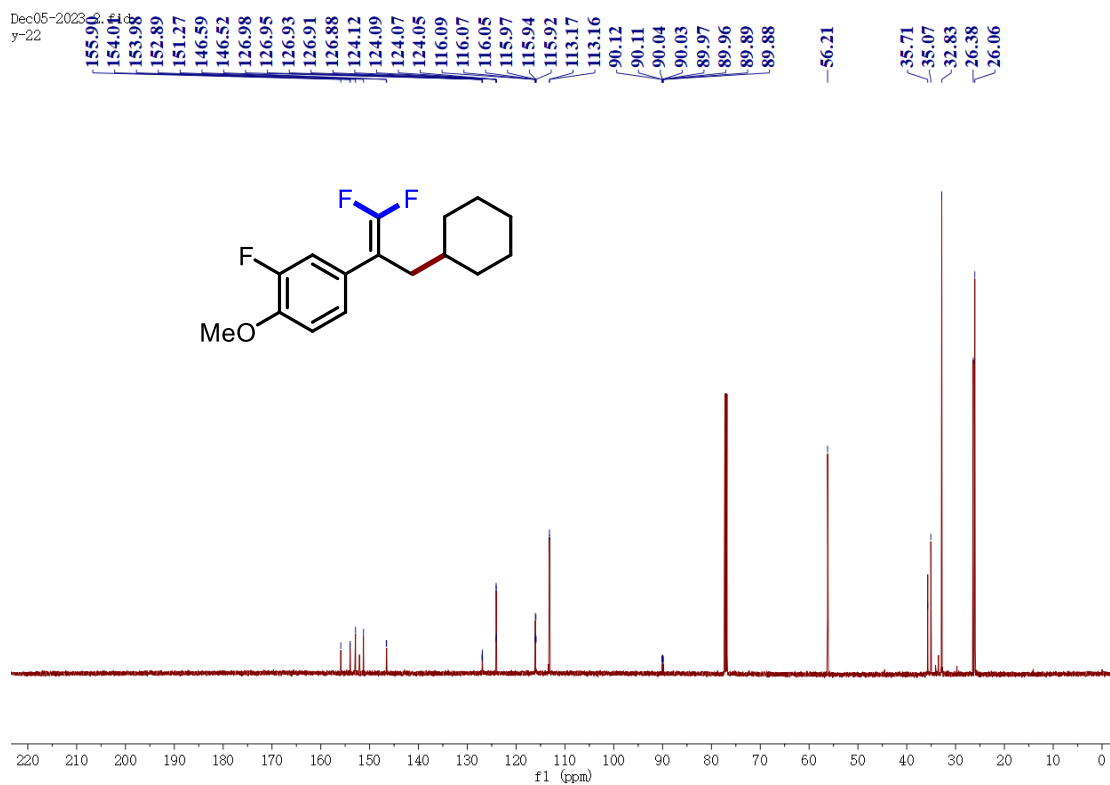
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3o**.



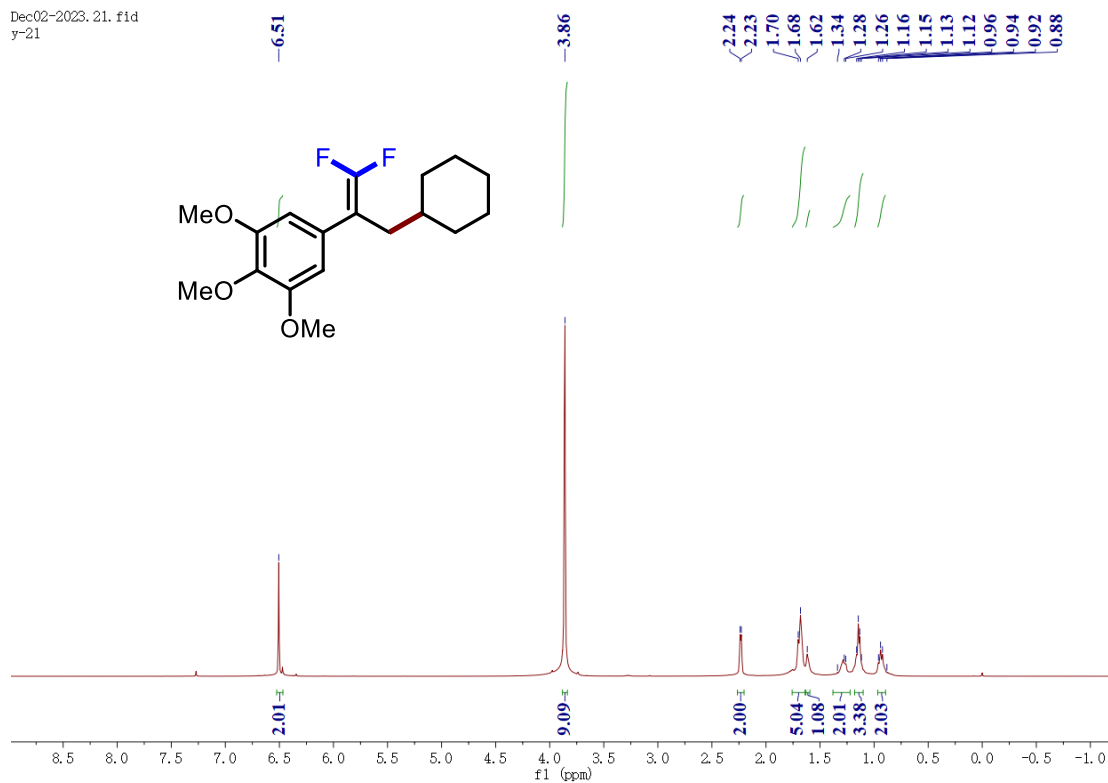
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3o**.



^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3p**.

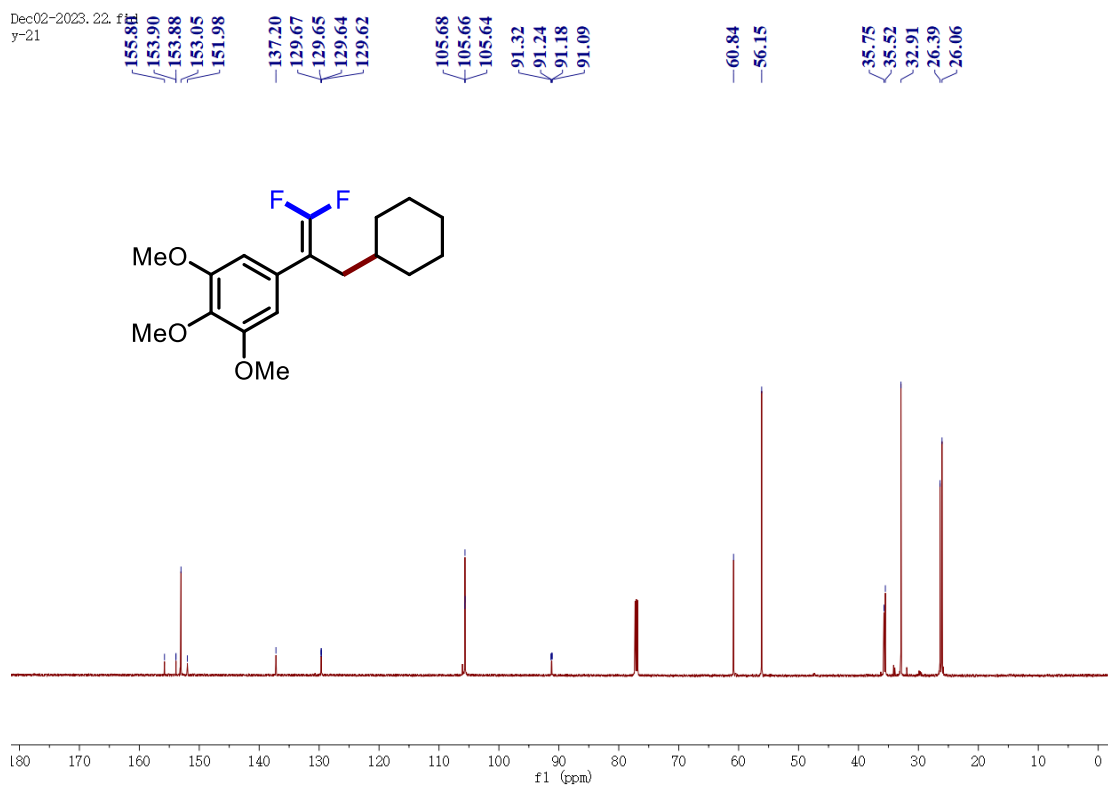


Dec02-2023. 21. fid
y-21



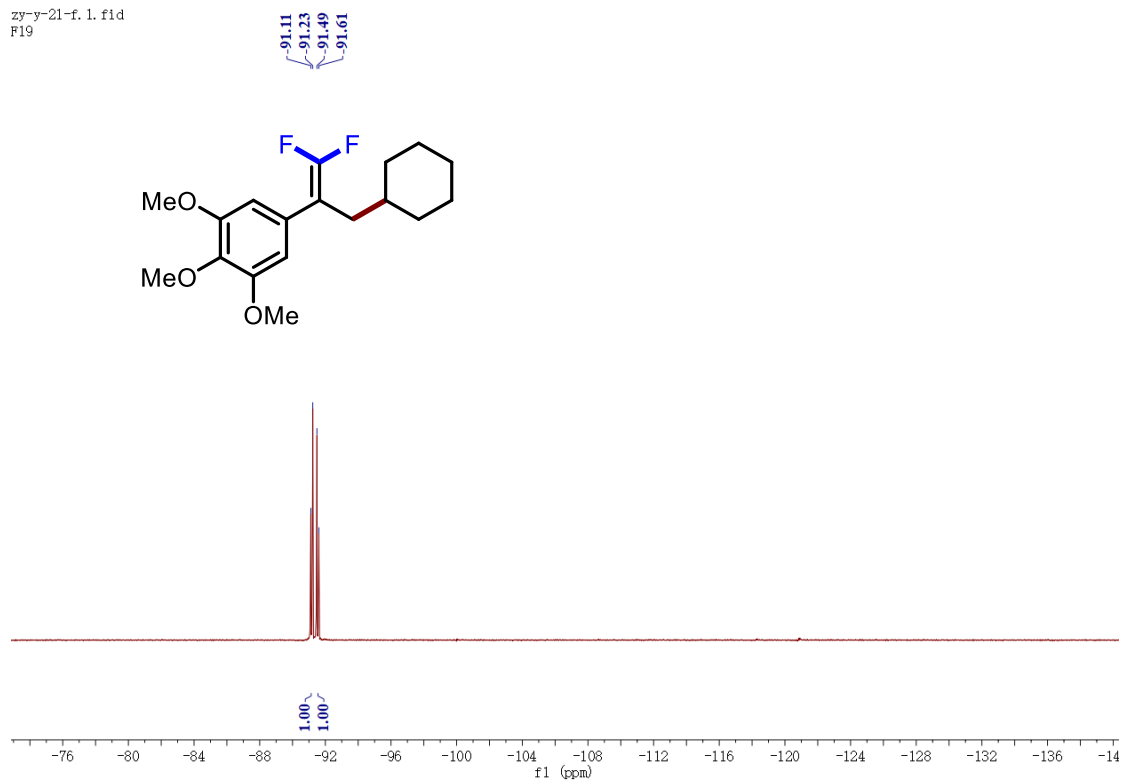
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3q**.

Dec02-2023. 22. fid
y-21

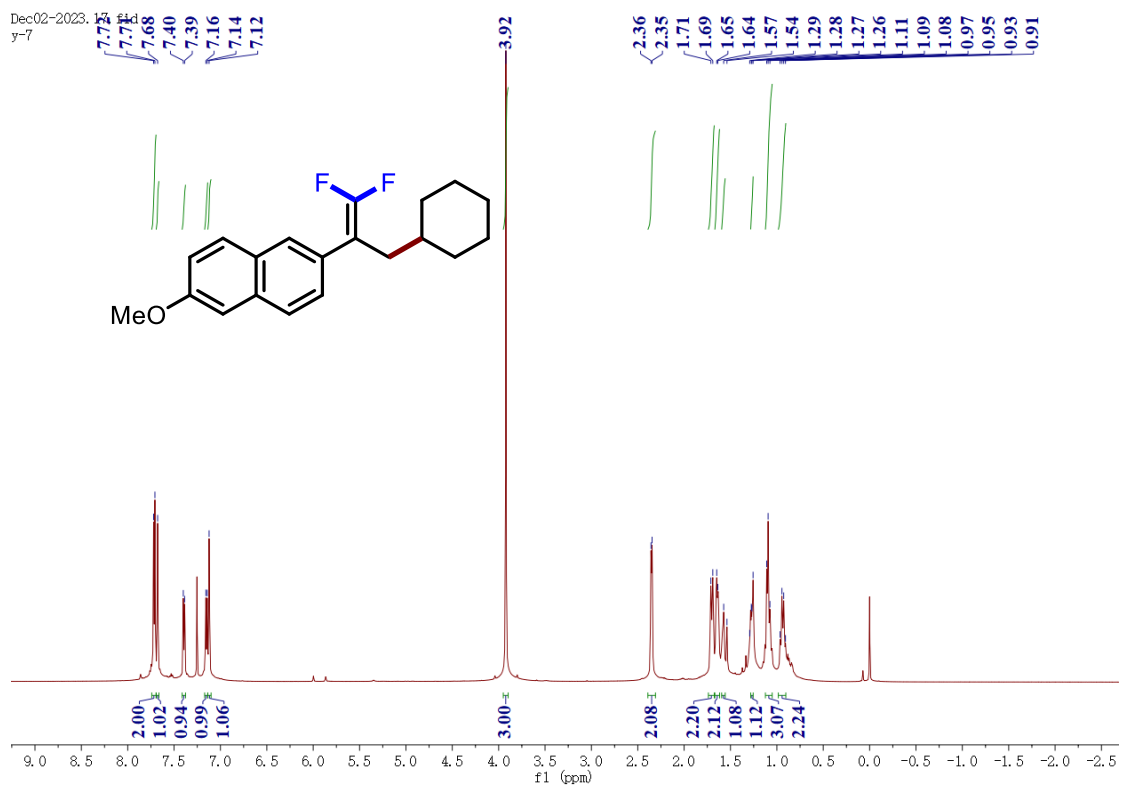


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3q**.

zy-y-21-f. 1. fid
F19

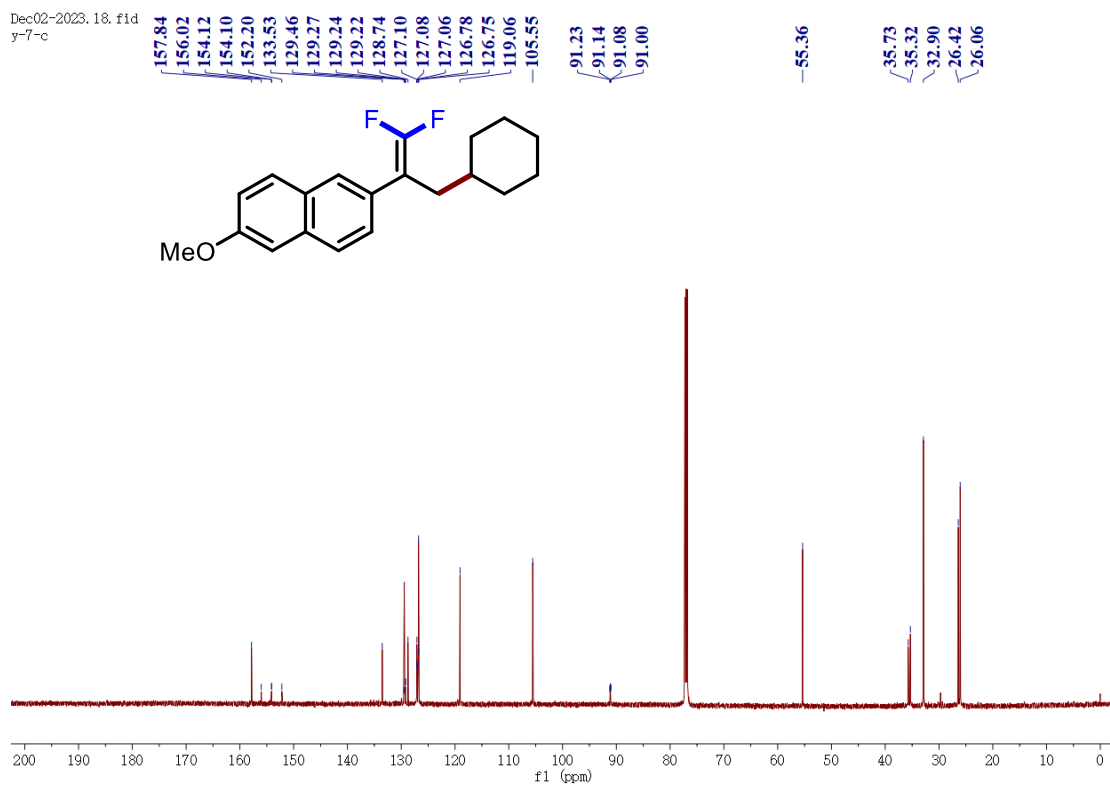


^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3q**.



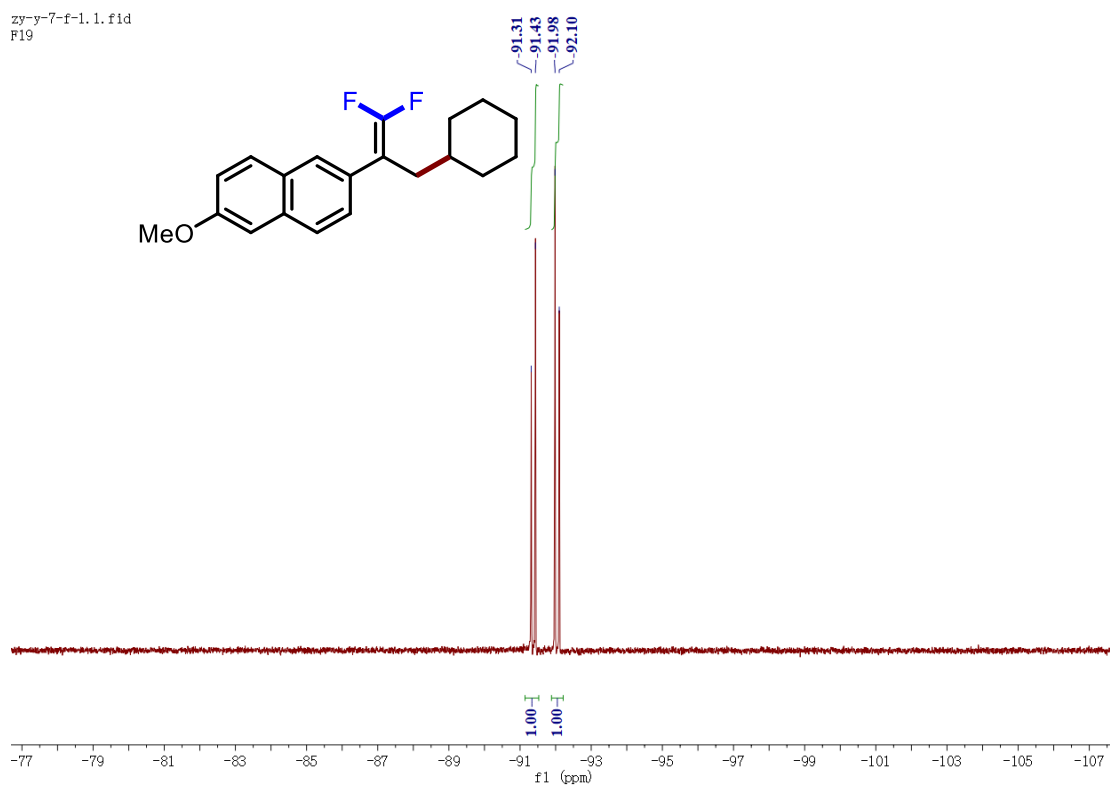
^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3r**.

Dec02-2023. 18. fid
y-7-c

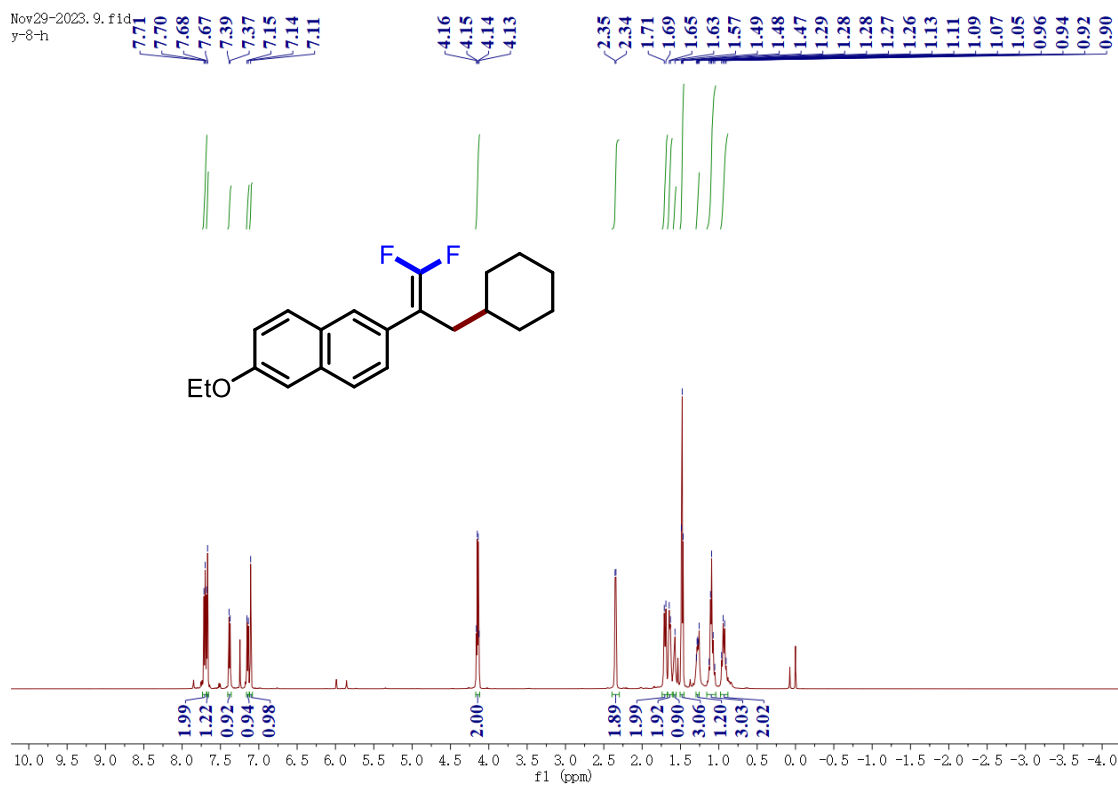


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3r**.

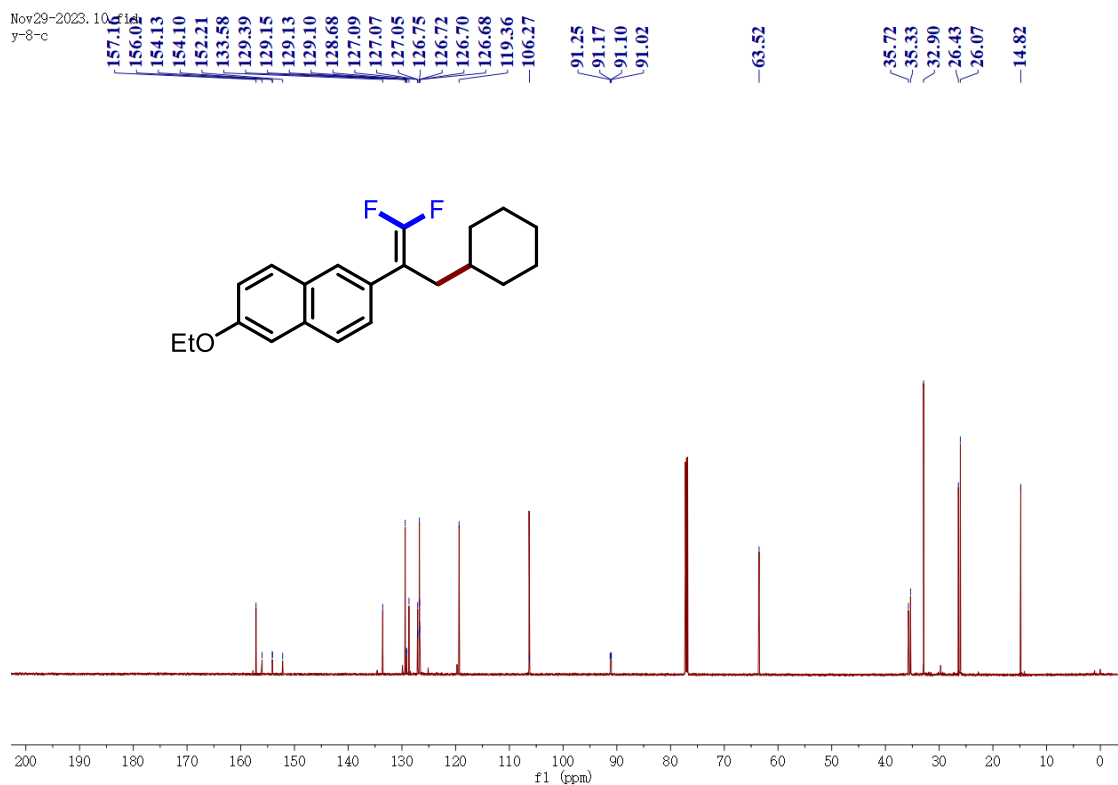
zy-y-7-f-1.1. fid
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3r**.

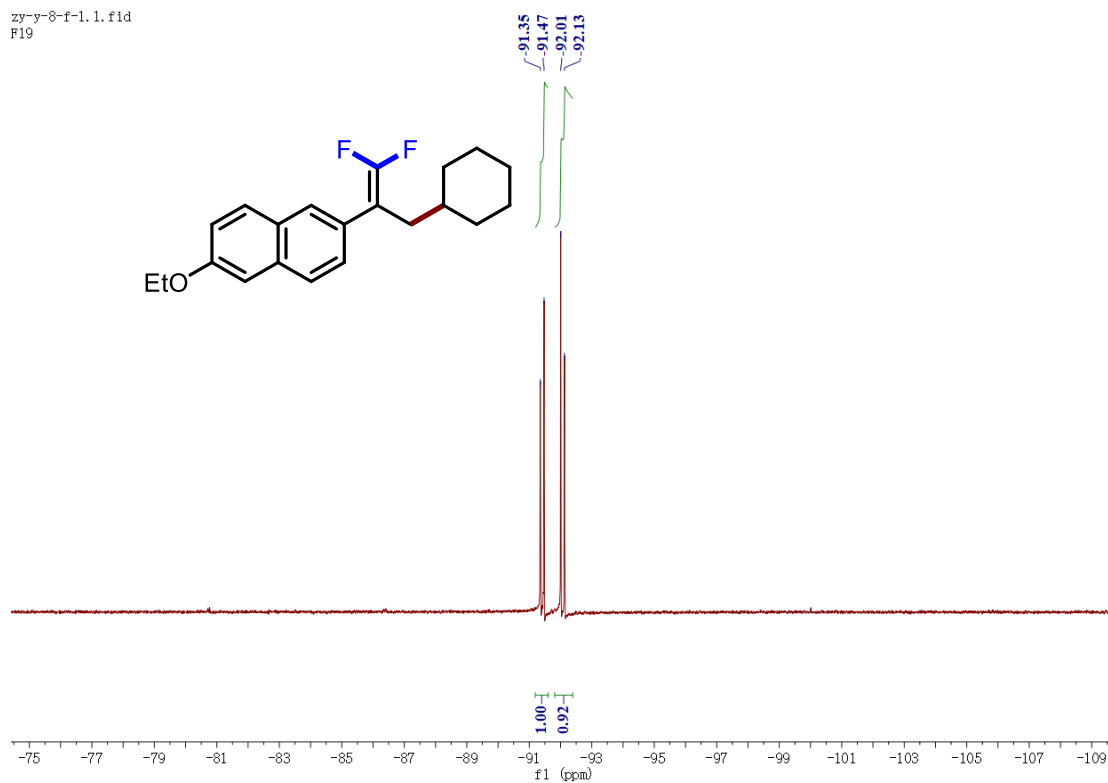


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3s**.

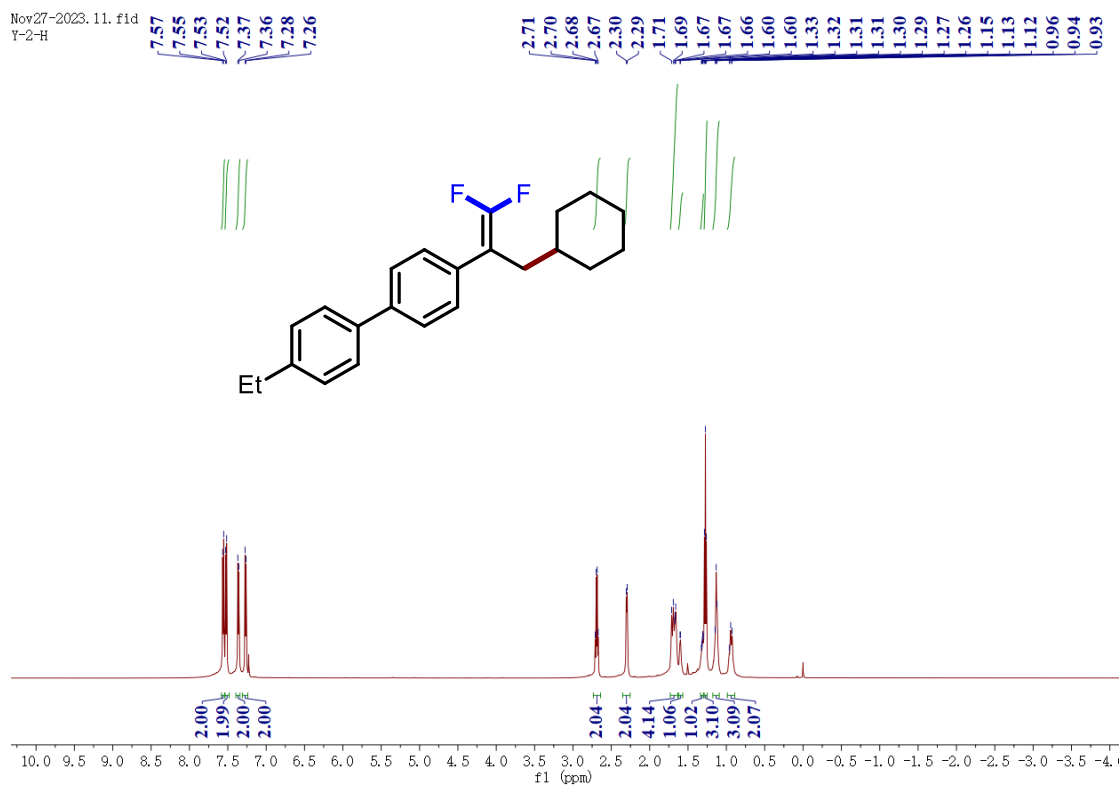


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3s**.

zy-y-8-f-1.1.fid
F19

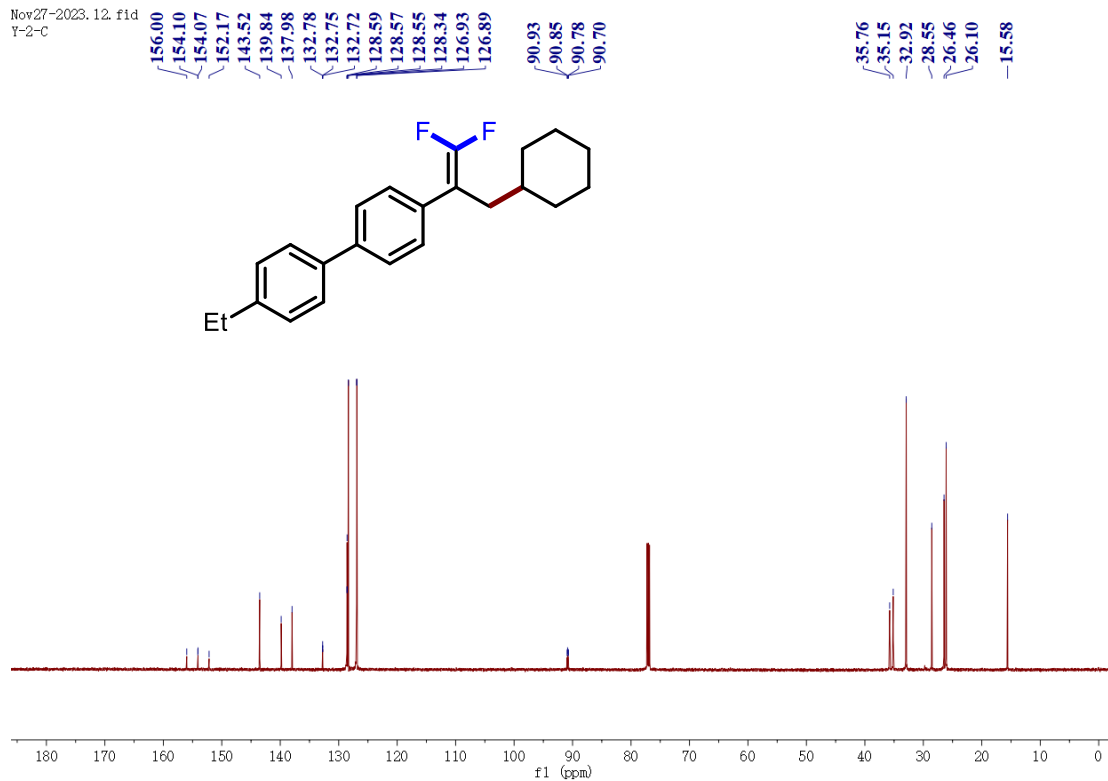


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3s.



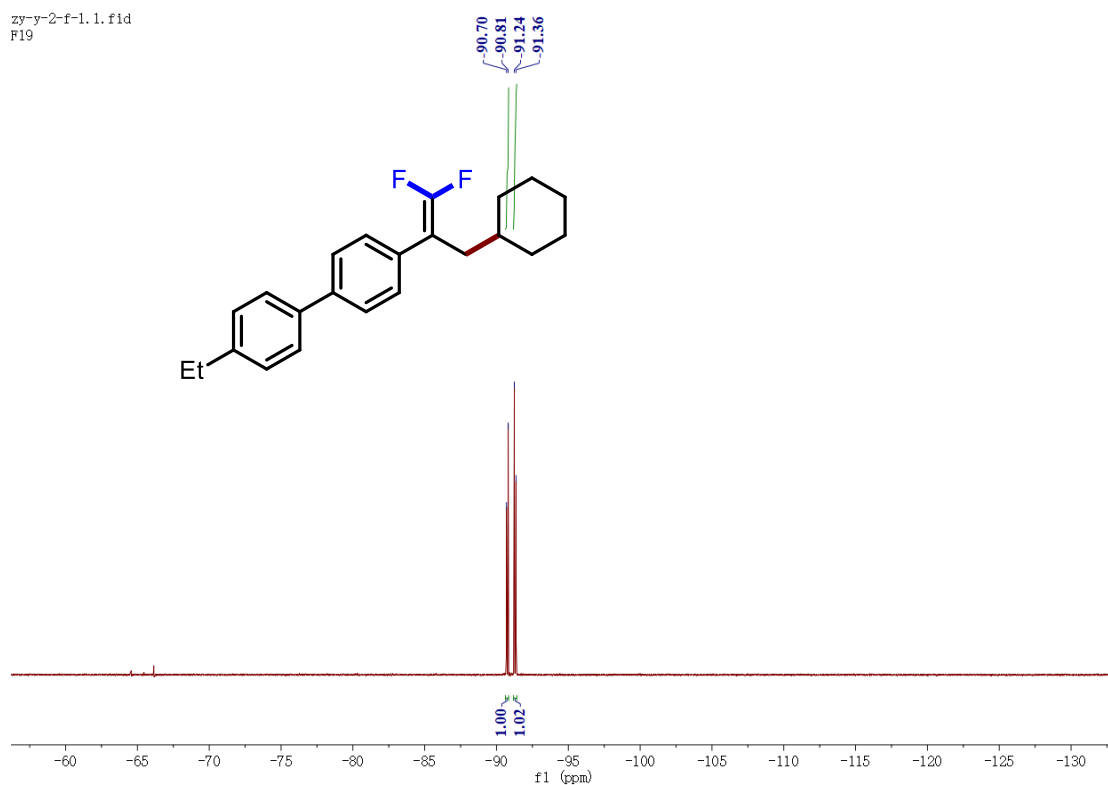
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3t.

Nov27-2023. 12. fid
T-2-C

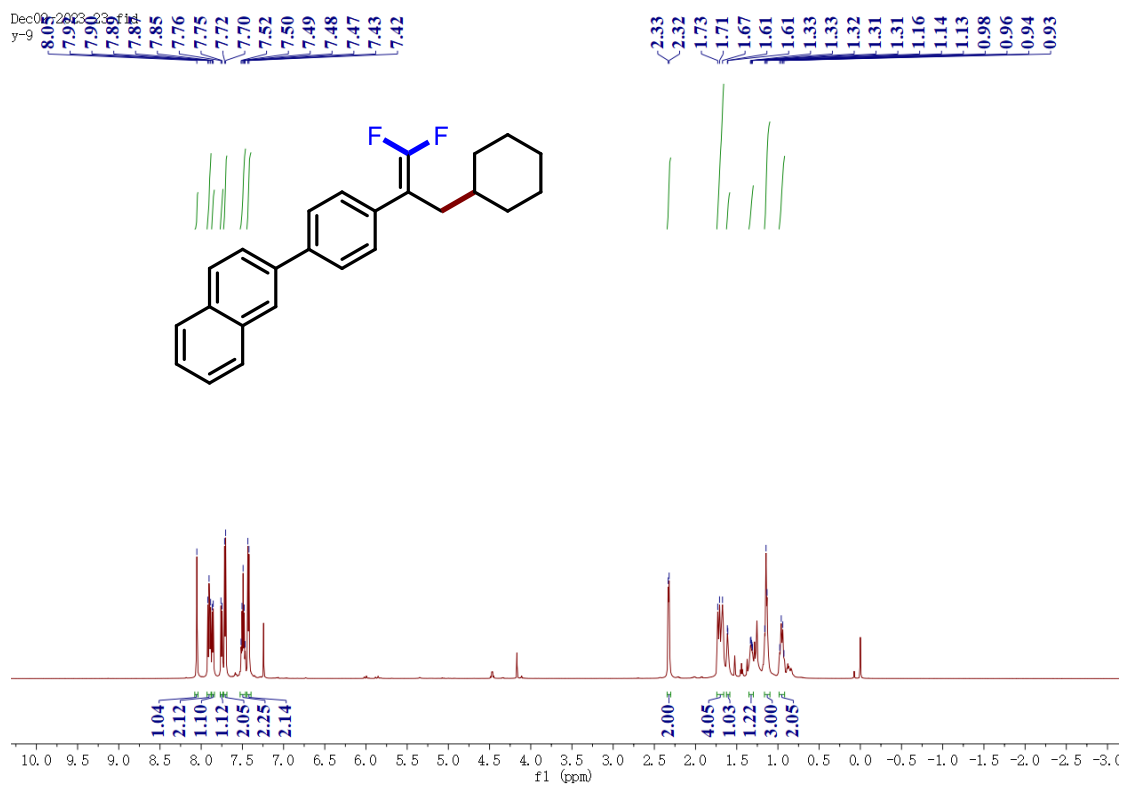


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3t**.

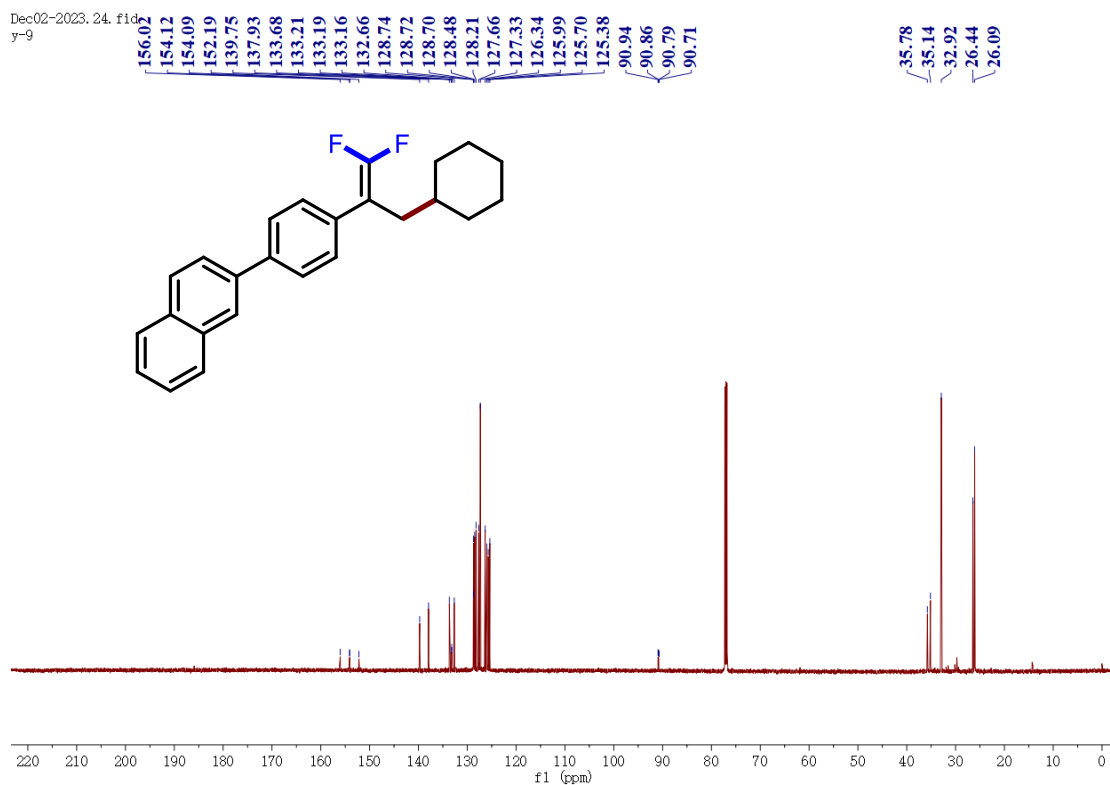
zy-y-2-f-1.1. fid
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3t**.

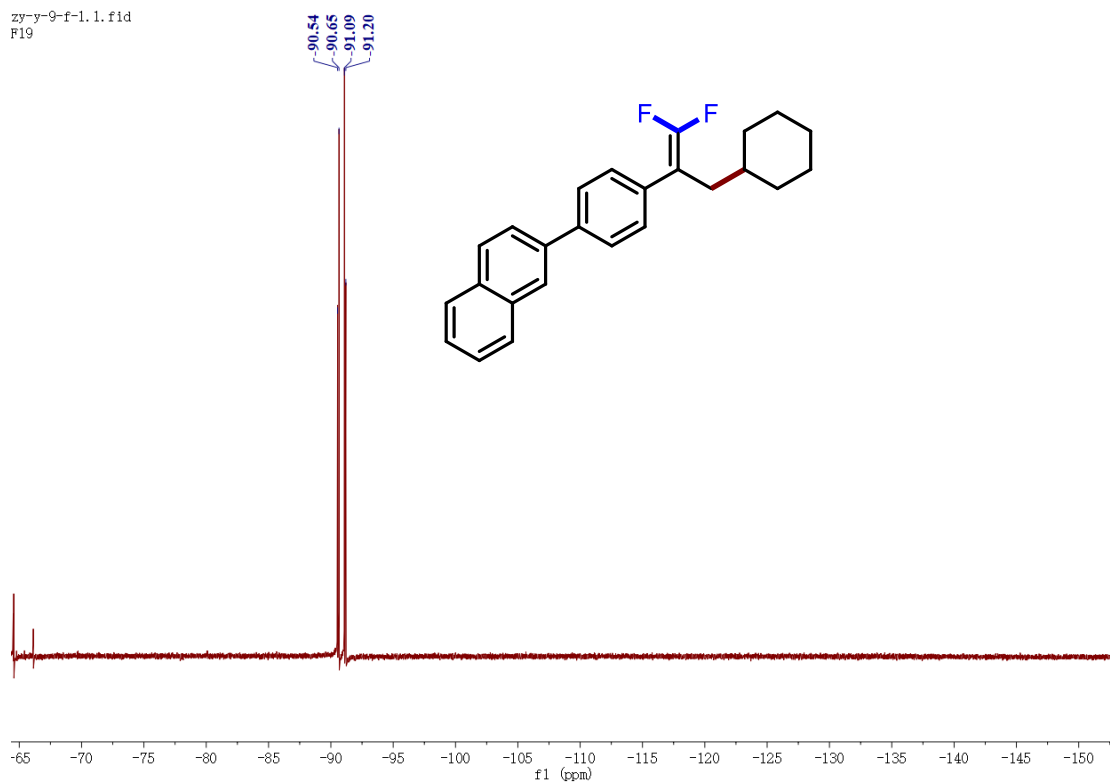


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3u**.

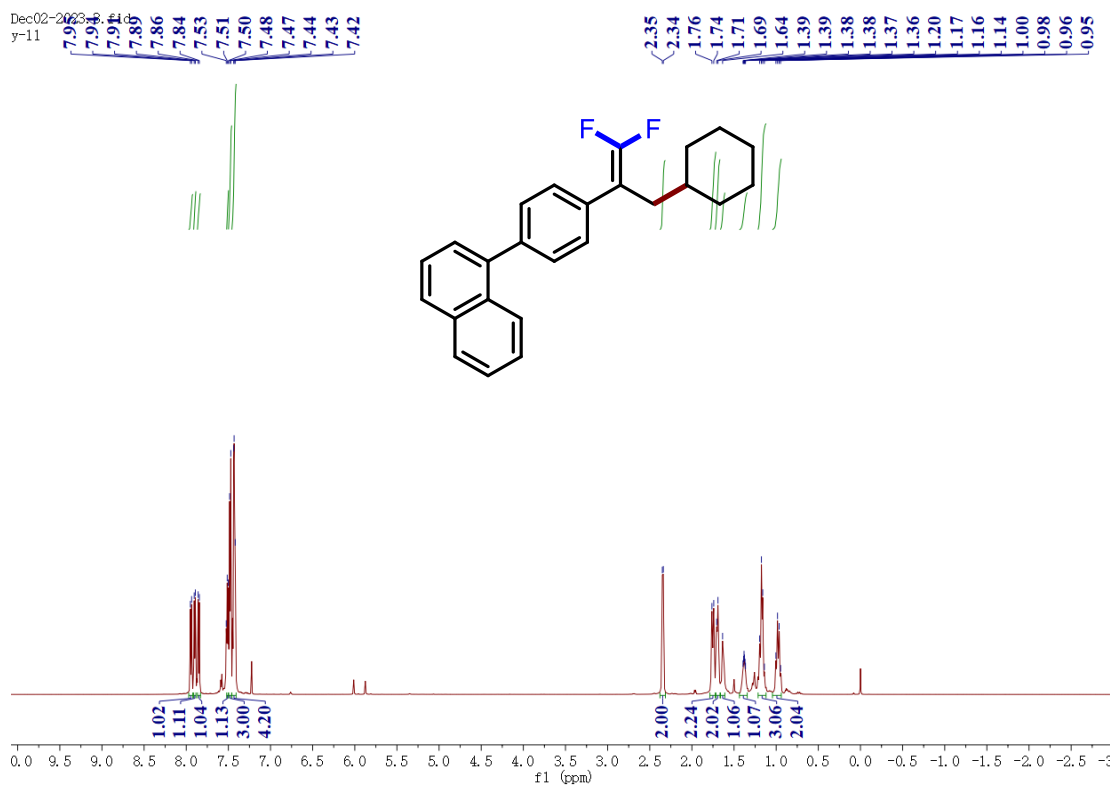


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3u**.

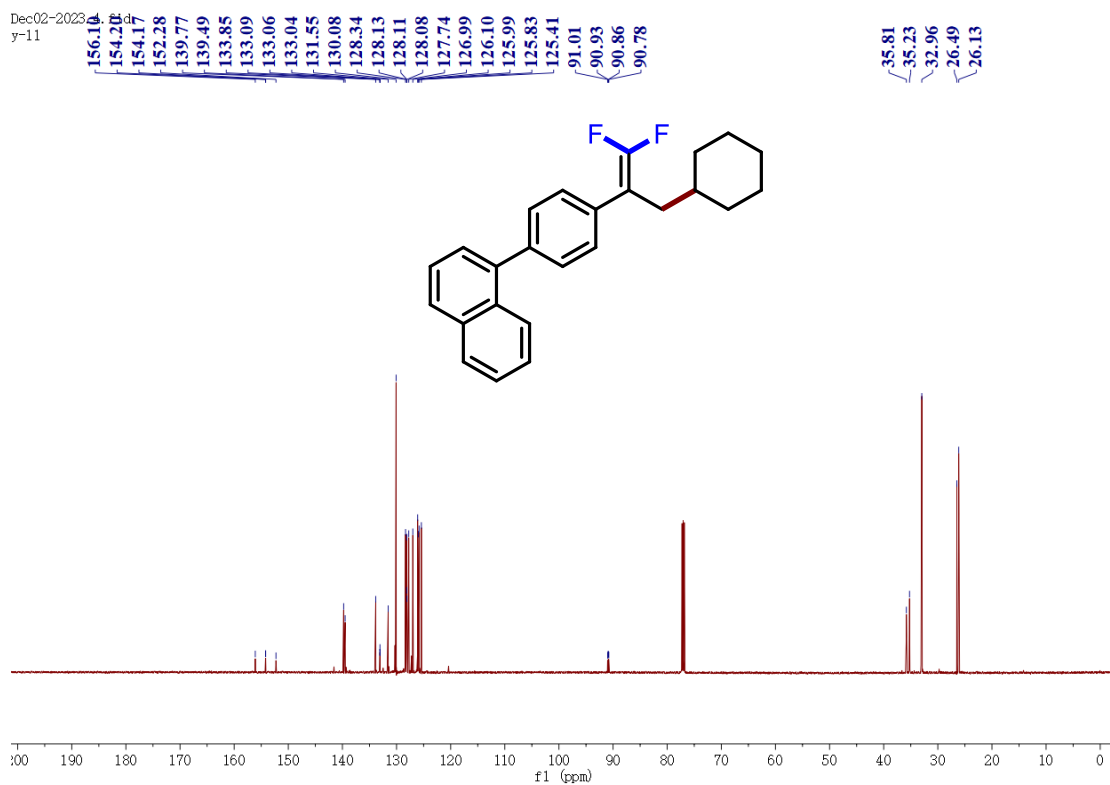
zy-y-9-f-1.1.fid
F19



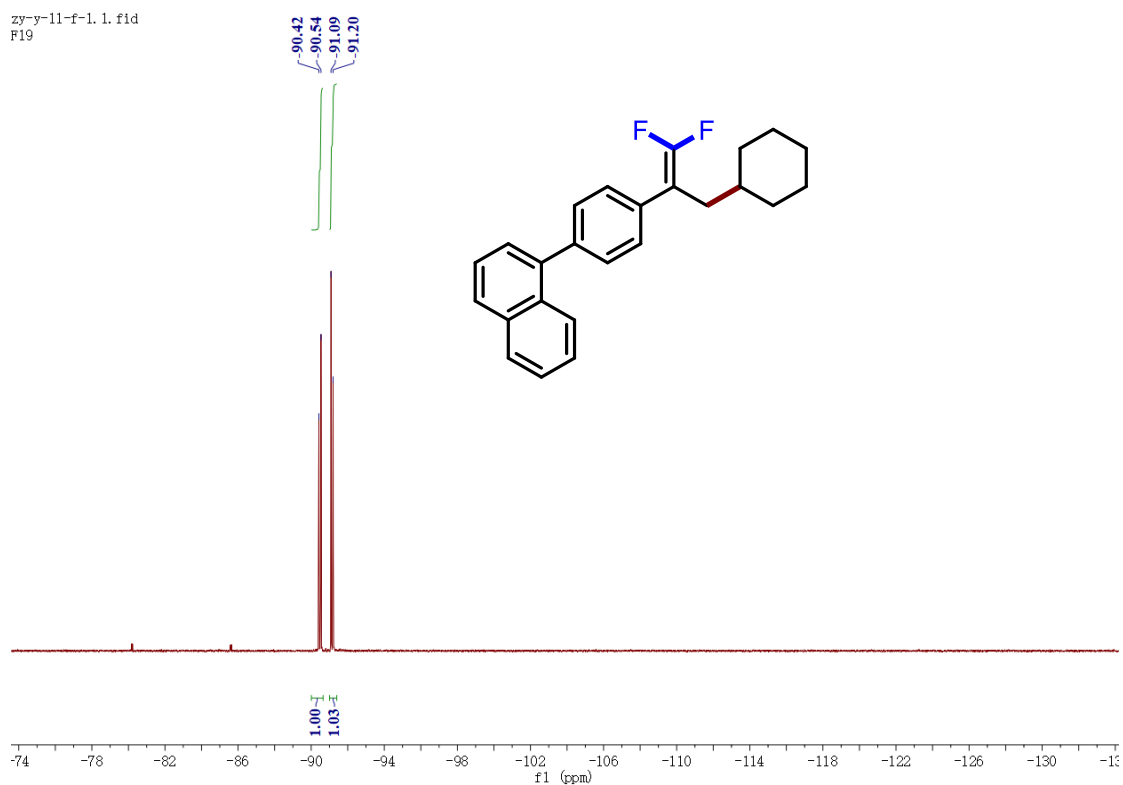
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3u**.



^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3v**.

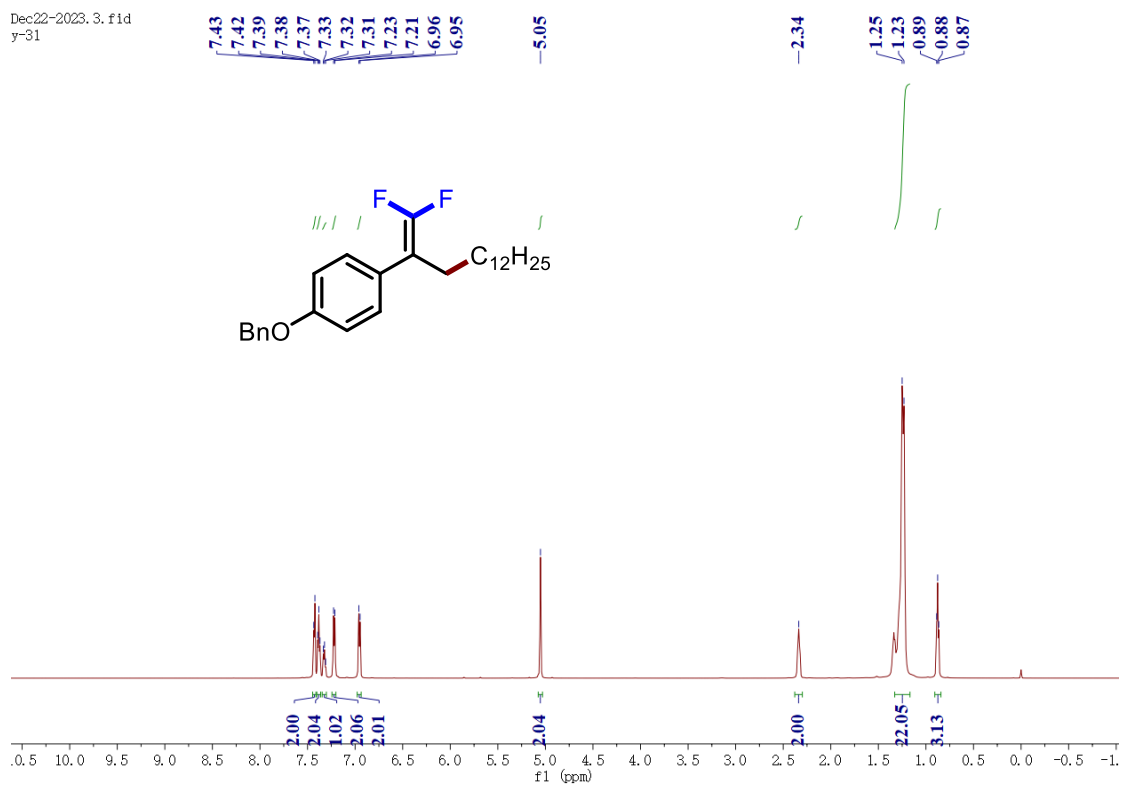


^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3v**.



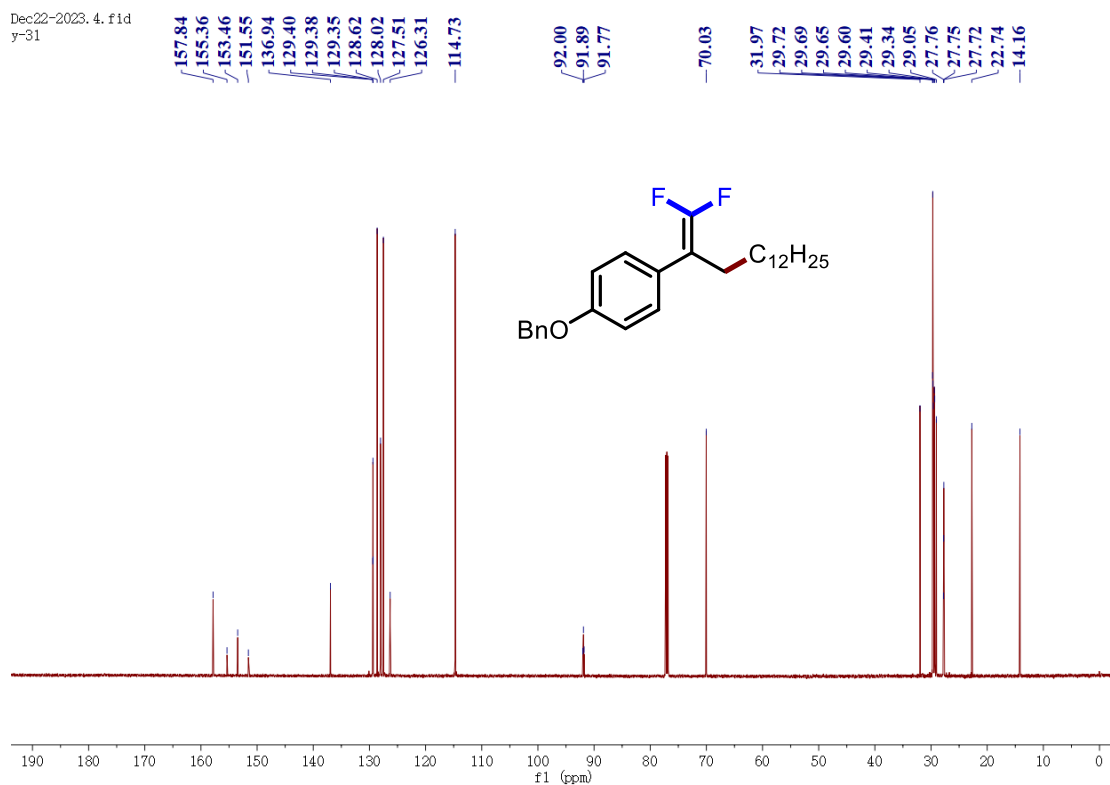
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3v**.

Dec22-2023. 3. f1d
y-31



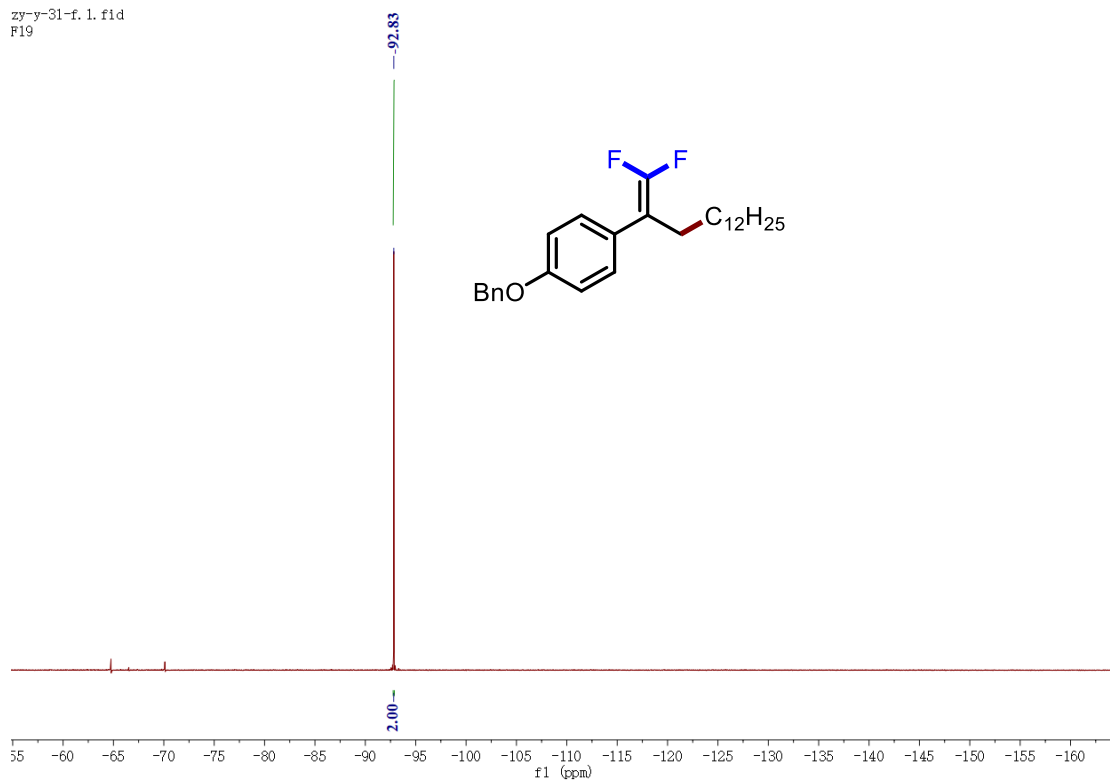
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3aa**.

Dec22-2023. 4. f1d
y-31

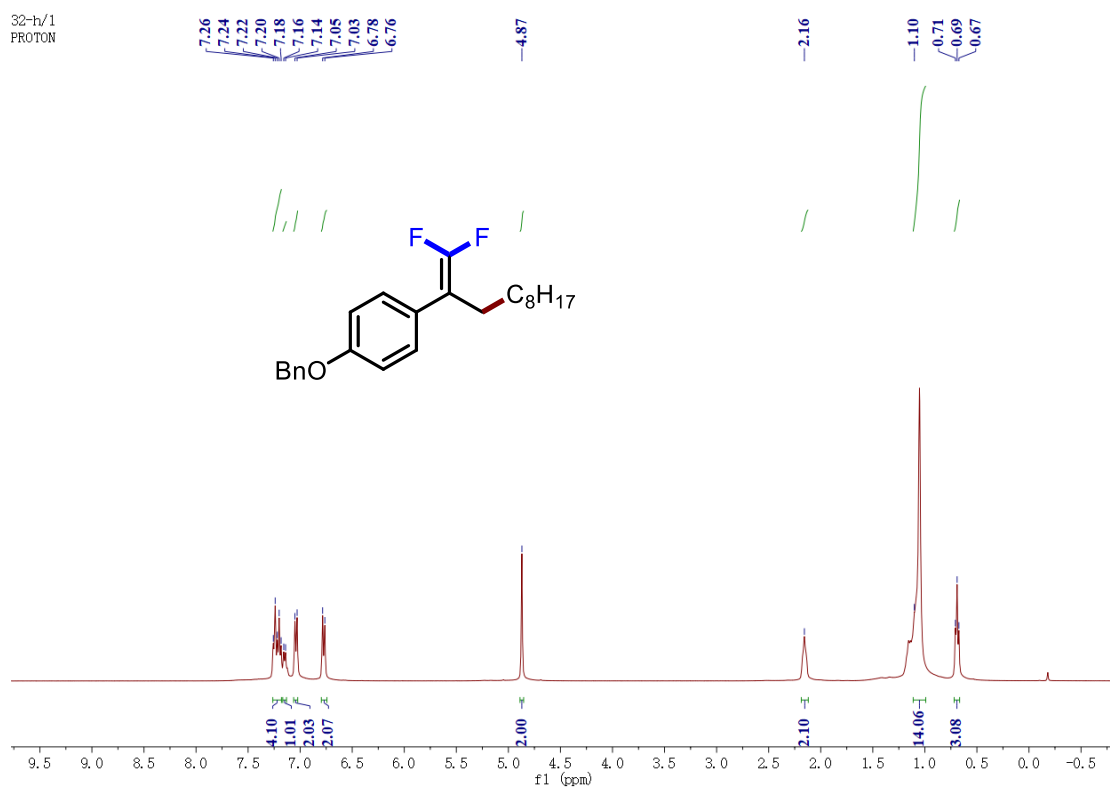


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3aa**.

zy-y-31-f. 1. fid
F19



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3aa**.



^1H NMR (400 MHz, Chloroform-*d*) spectrum of compound **3ab**.

Dec22-2023. 6. f1d
y-32

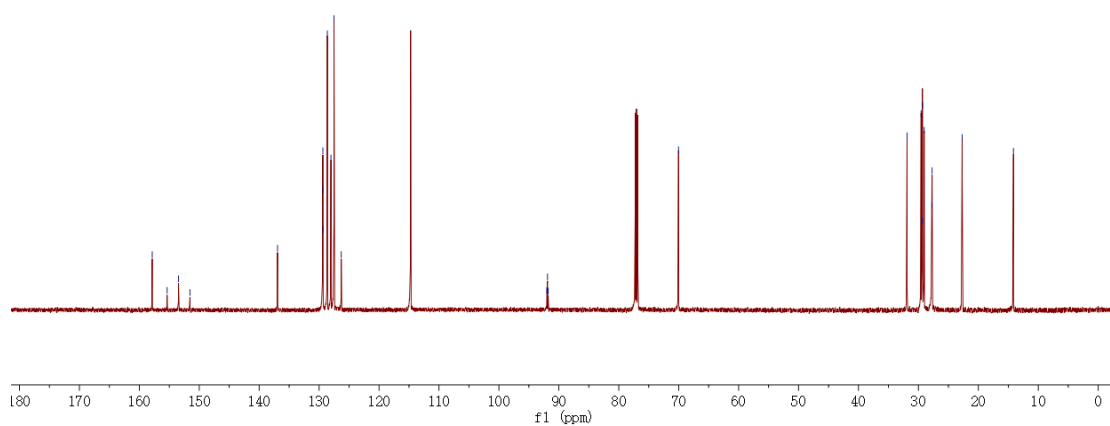
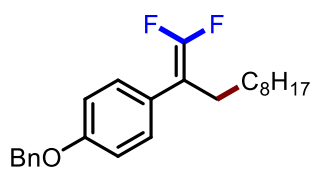
157.84
155.36
153.46
151.55

136.94
129.40
129.38
129.36
128.63
128.03
127.52
126.31

92.01
91.89
91.78

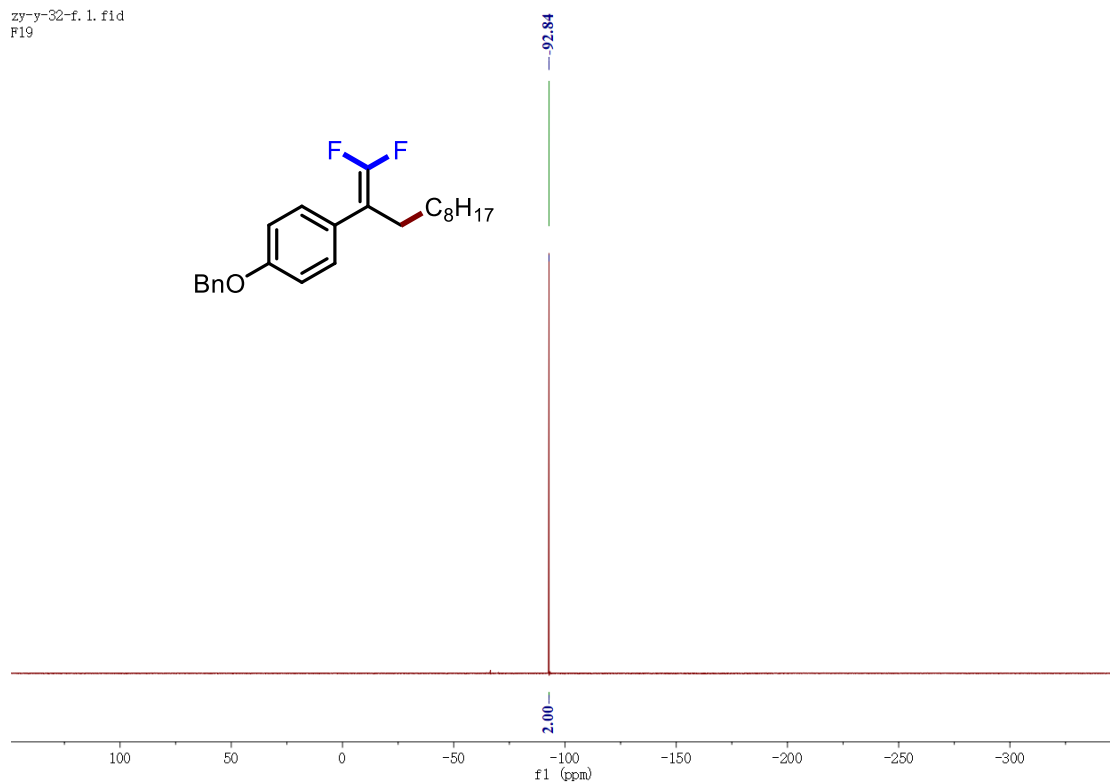
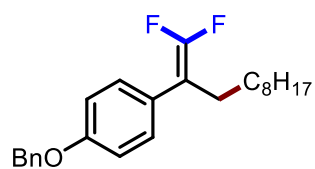
70.03

31.90
29.55
29.35
29.30
29.04
27.76
22.70
14.15



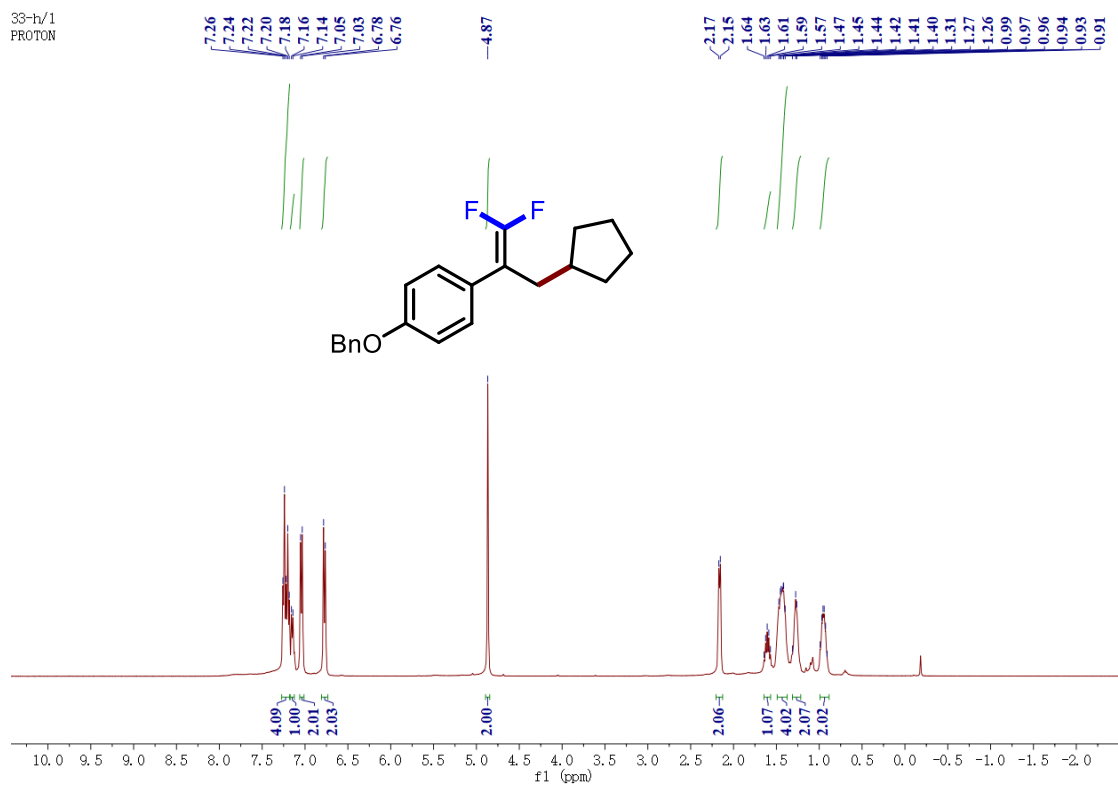
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ab**.

zy-y-32-f. 1. f1d
F19



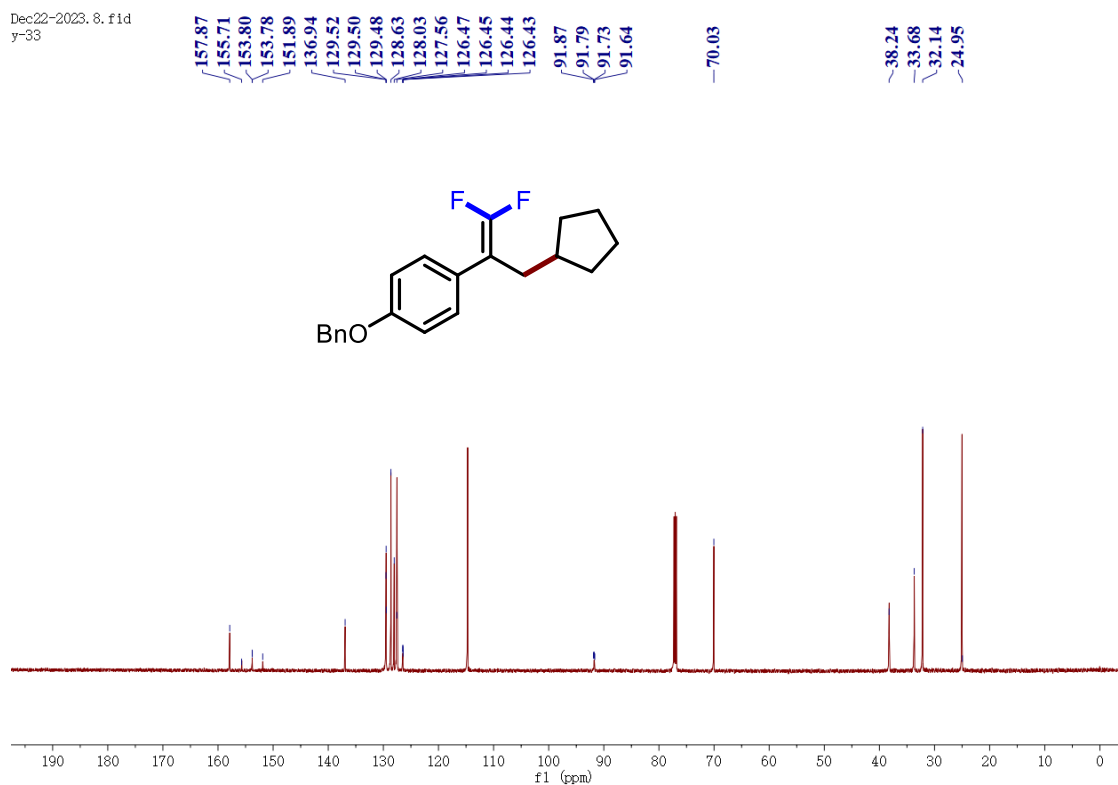
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ab**.

33-h/1
PROTON



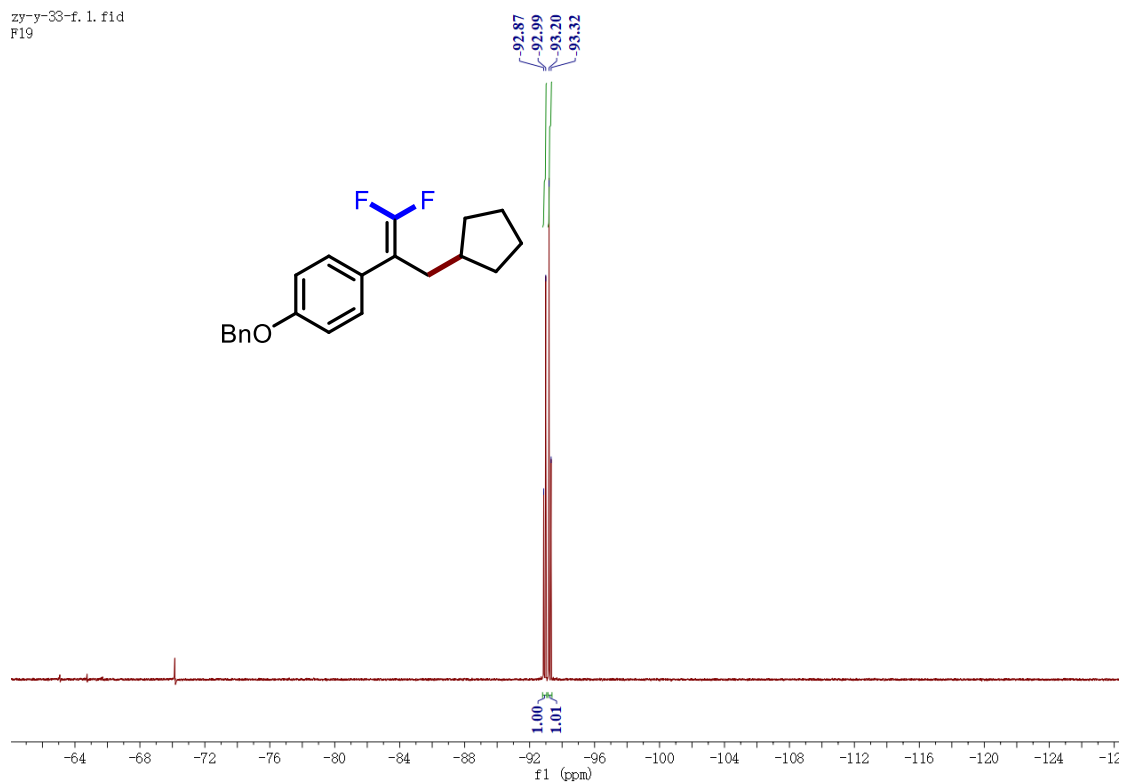
¹H NMR (400 MHz, Chloroform-*d*) spectrum of compound **3ac**.

Dec22-2023. 8. f1d
y-33



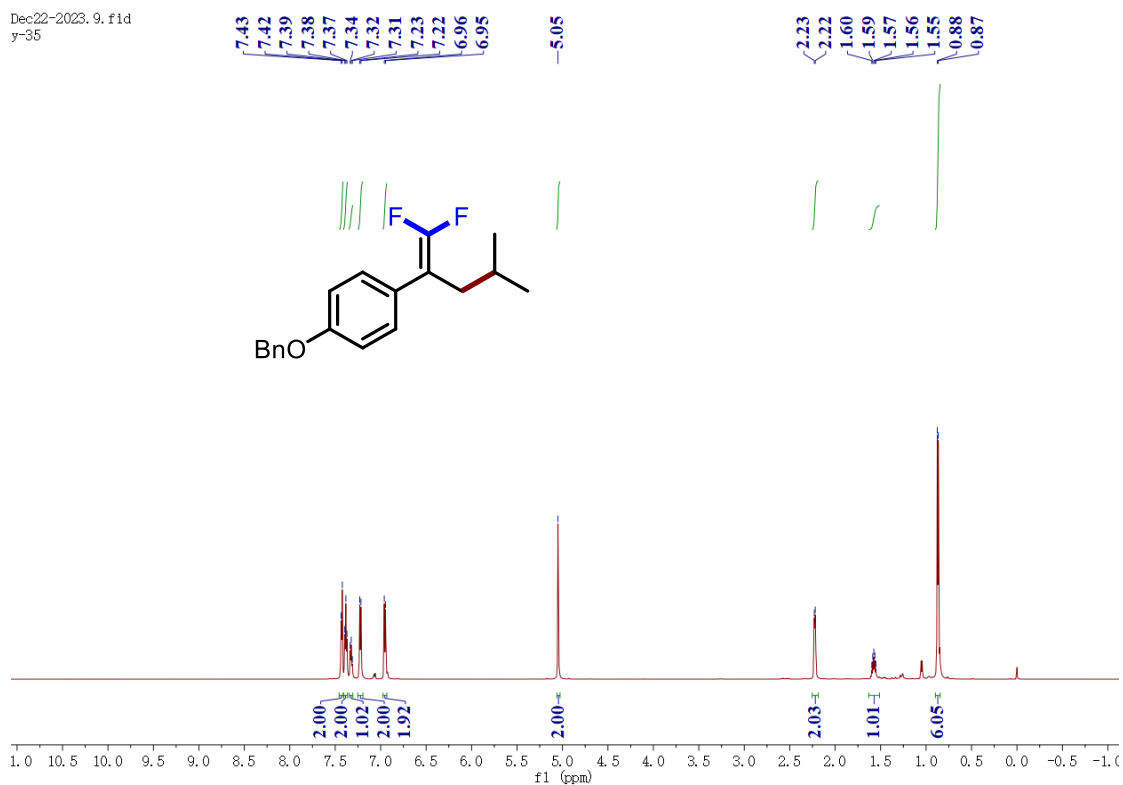
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ac**.

zy-y-33-f. 1. fid
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ac**.

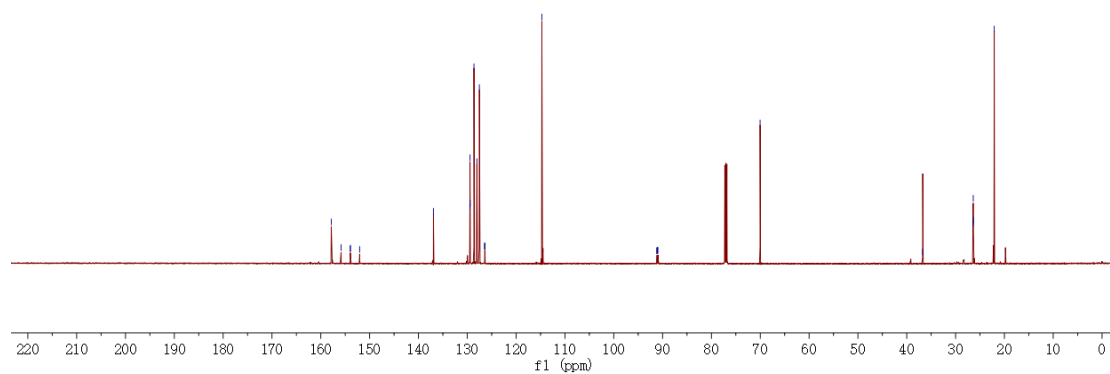
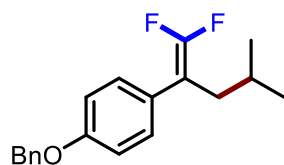
Dec22-2023. 9. fid
y-35



¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ad**.

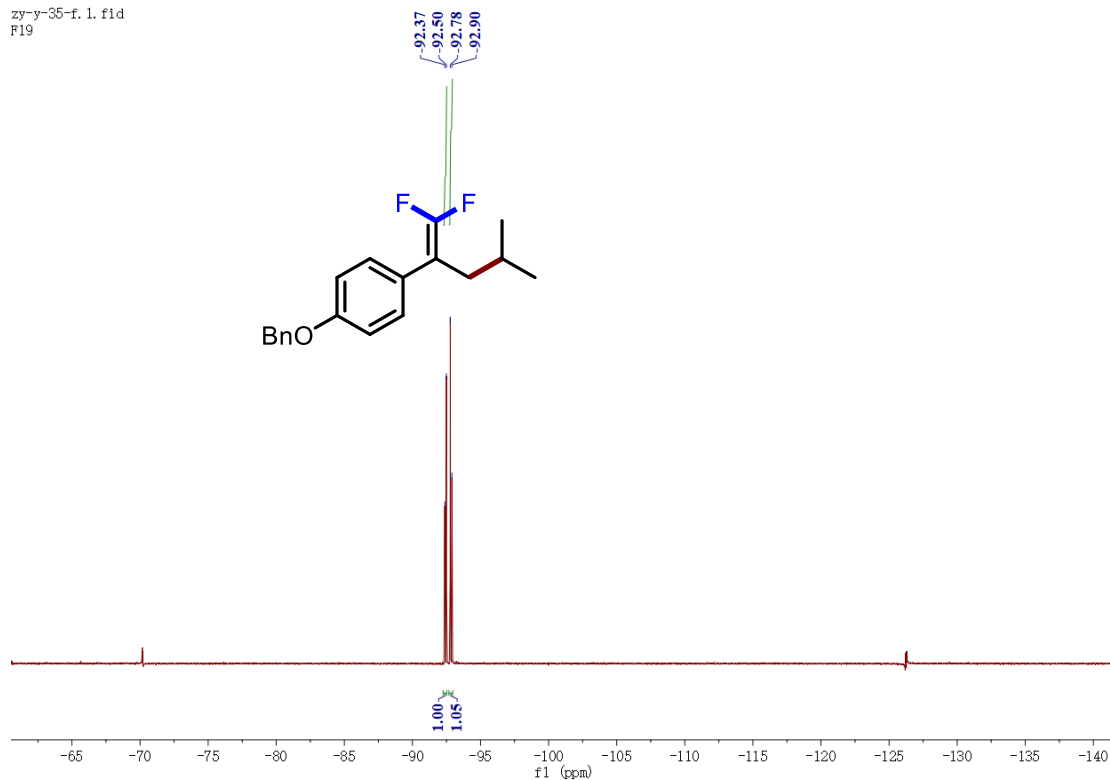
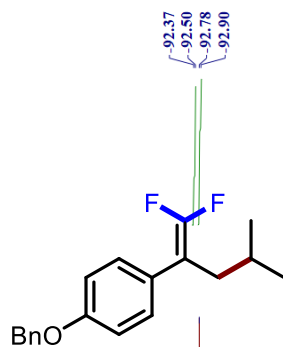
Dec22-2023. 10. f1d
y-35

157.86
155.85
153.96
153.93
152.04
136.93
129.46
129.44
129.41
128.63
128.04
127.52
126.43
126.42
126.41
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90.97
70.03
36.75
26.40
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26.36
22.08

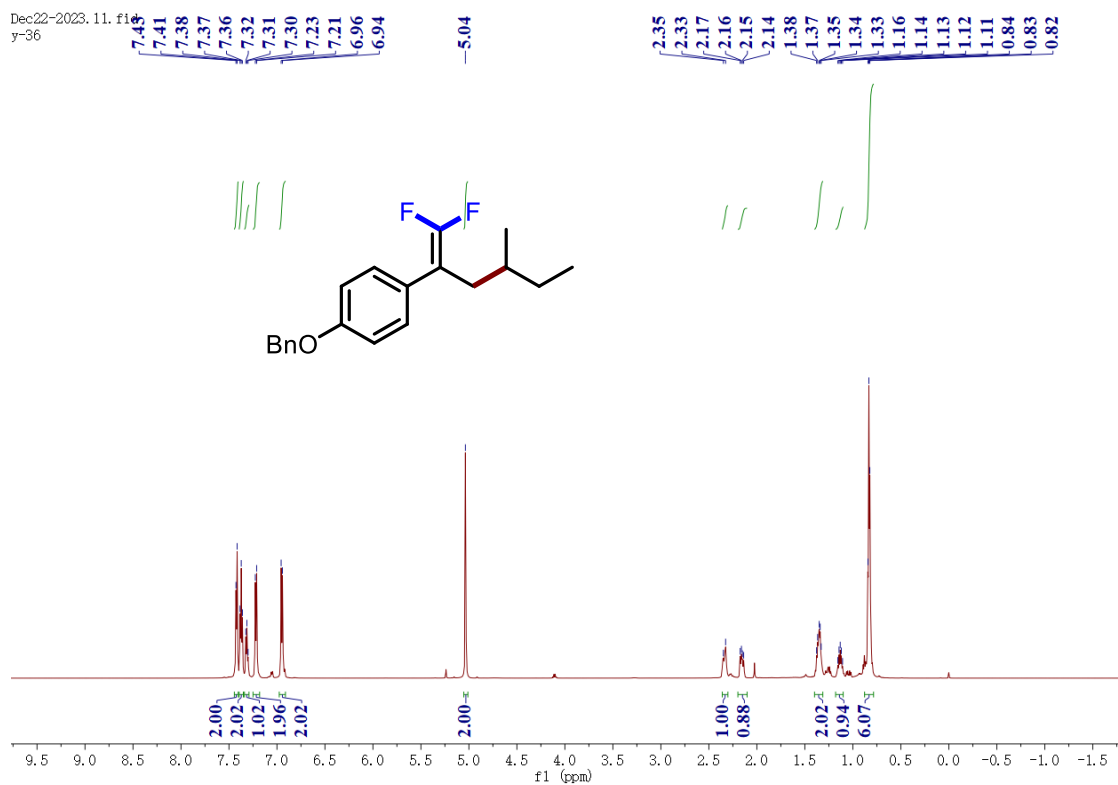


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ad**.

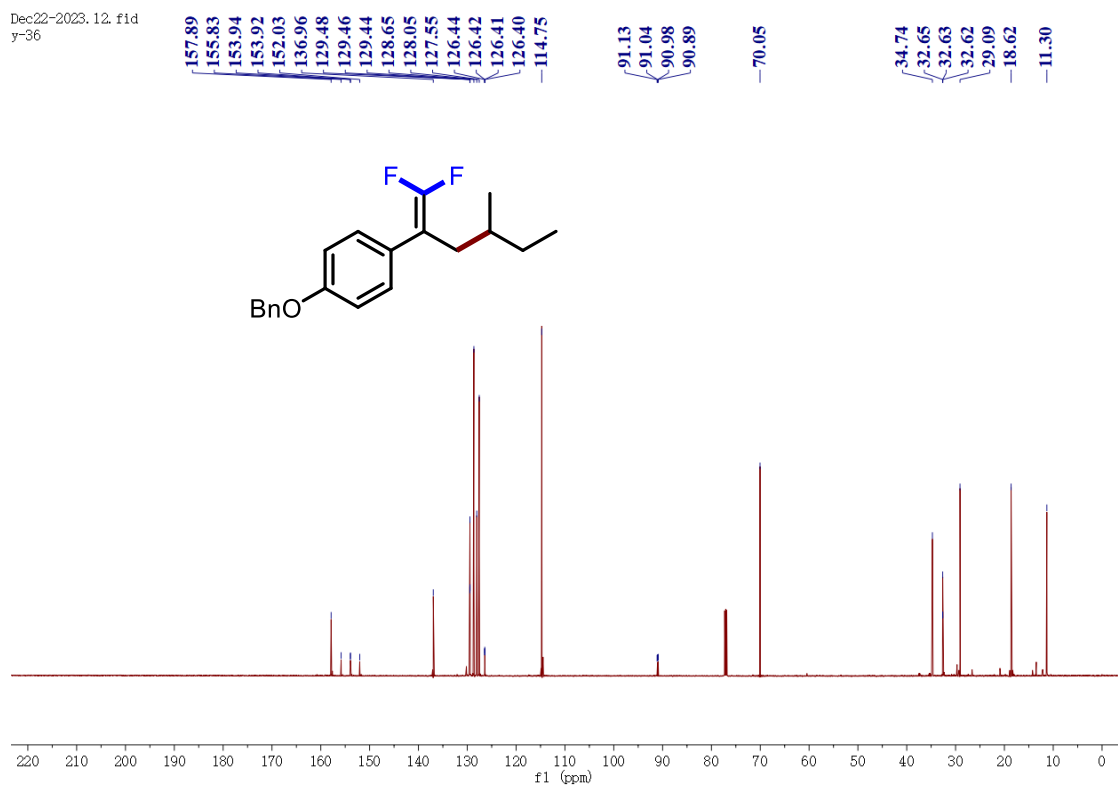
zy-y-35-f. 1. f1d
F19



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ad**.

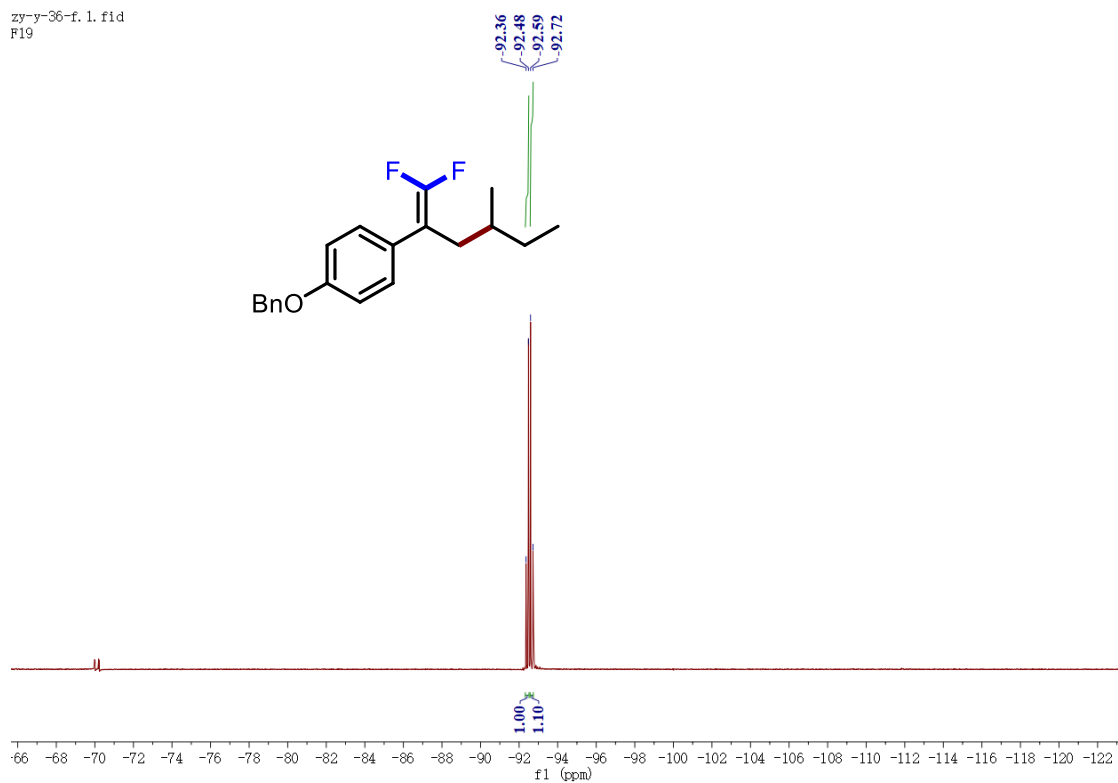


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ae**.

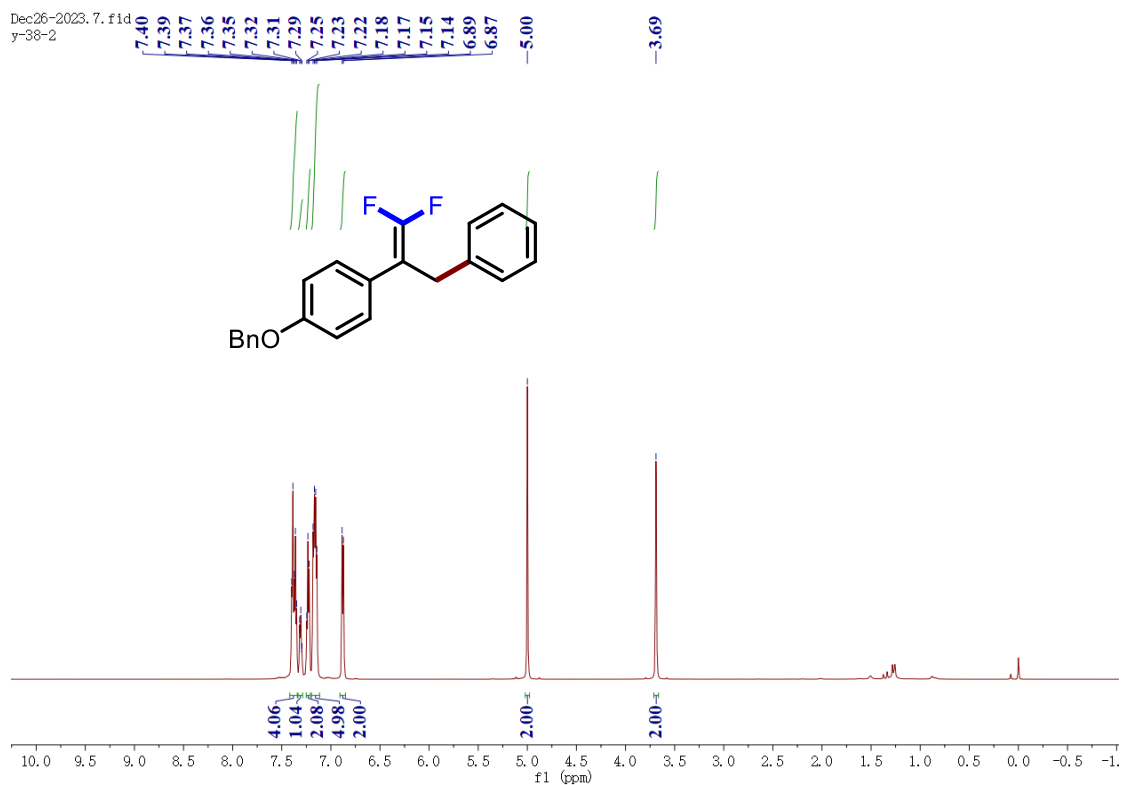


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ae**.

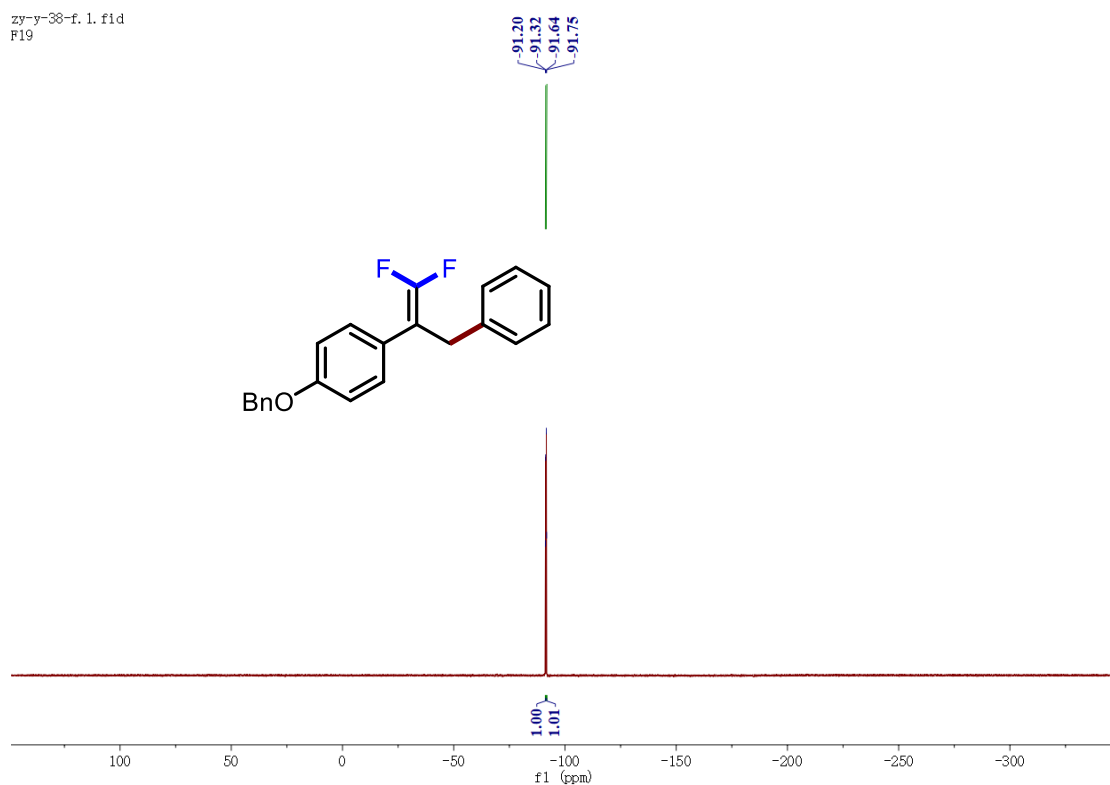
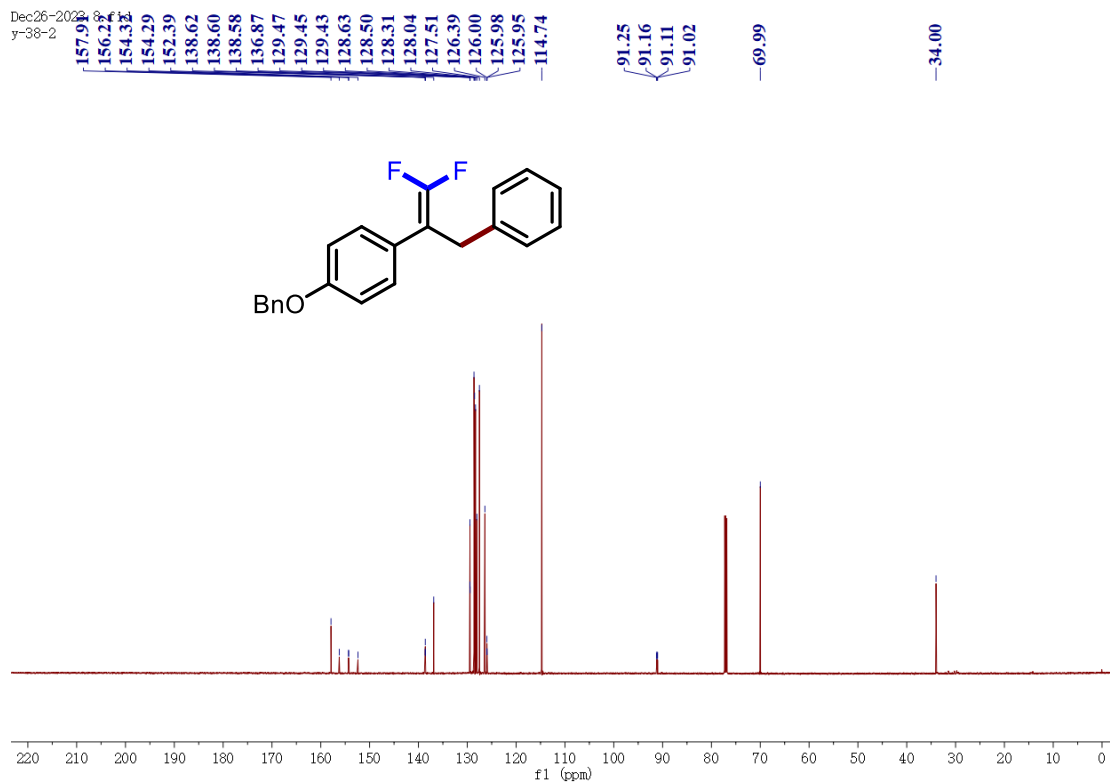
zy-y-36-f.1.fid
F19



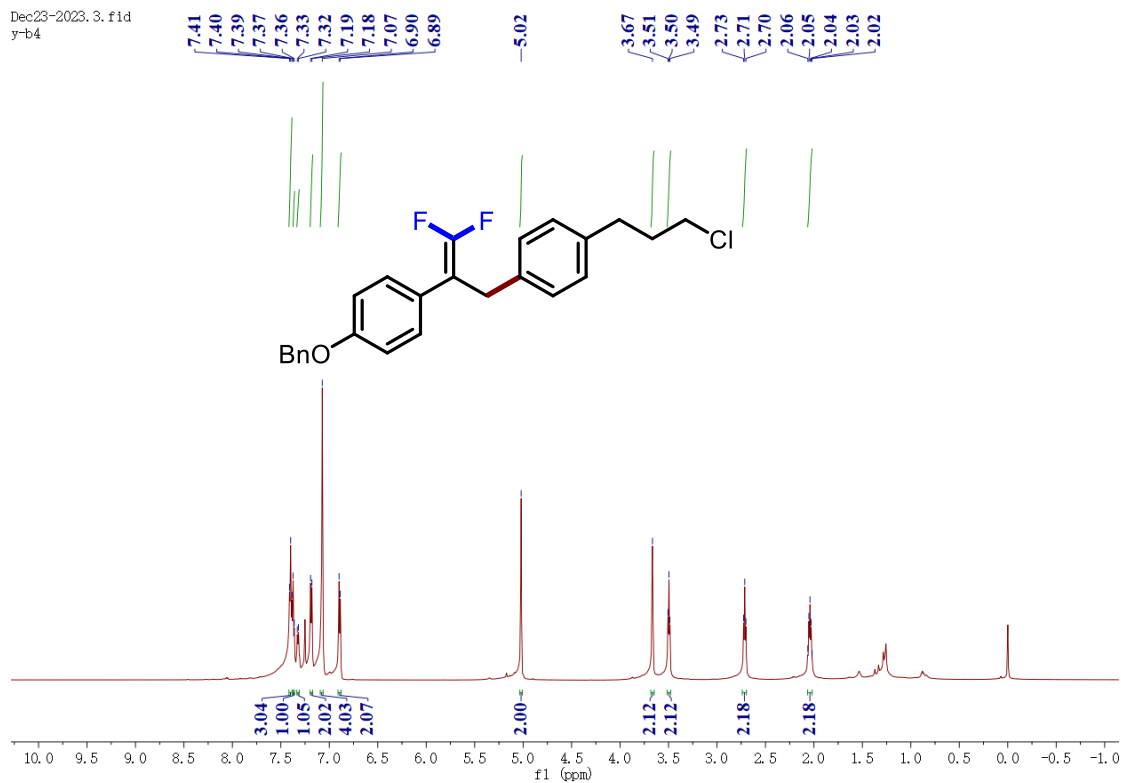
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ae**.



¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3af**.

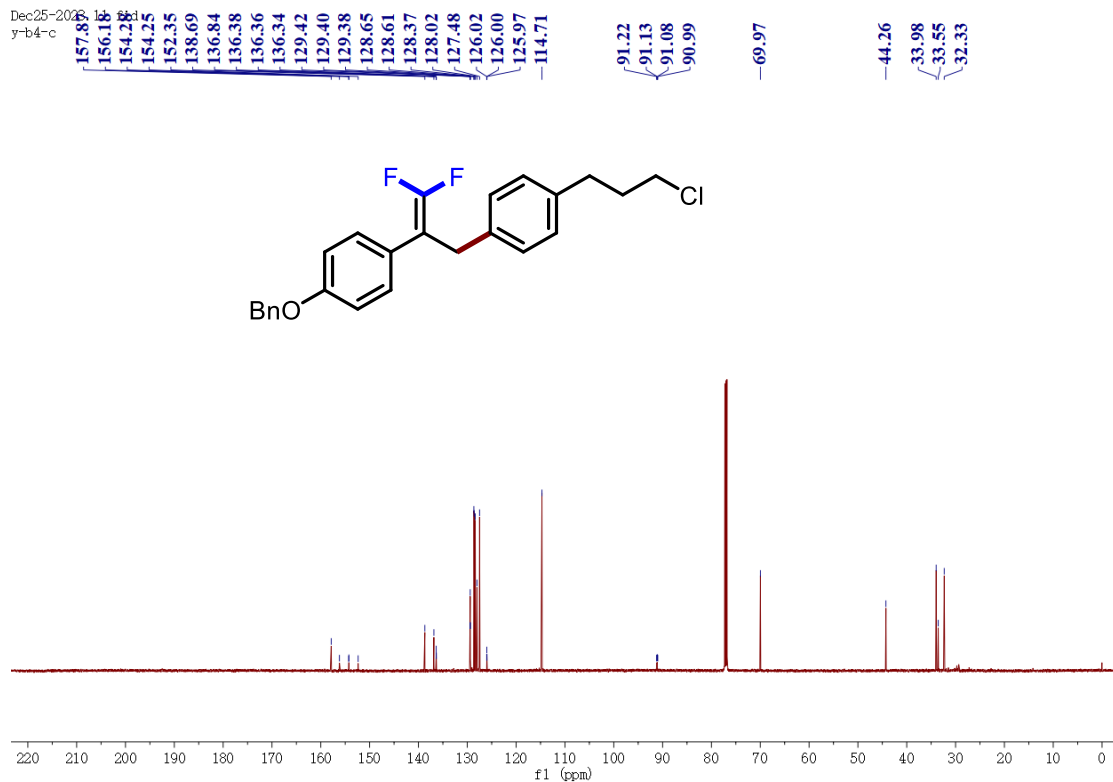


Dec23-2023. 3. f1d
y-b4



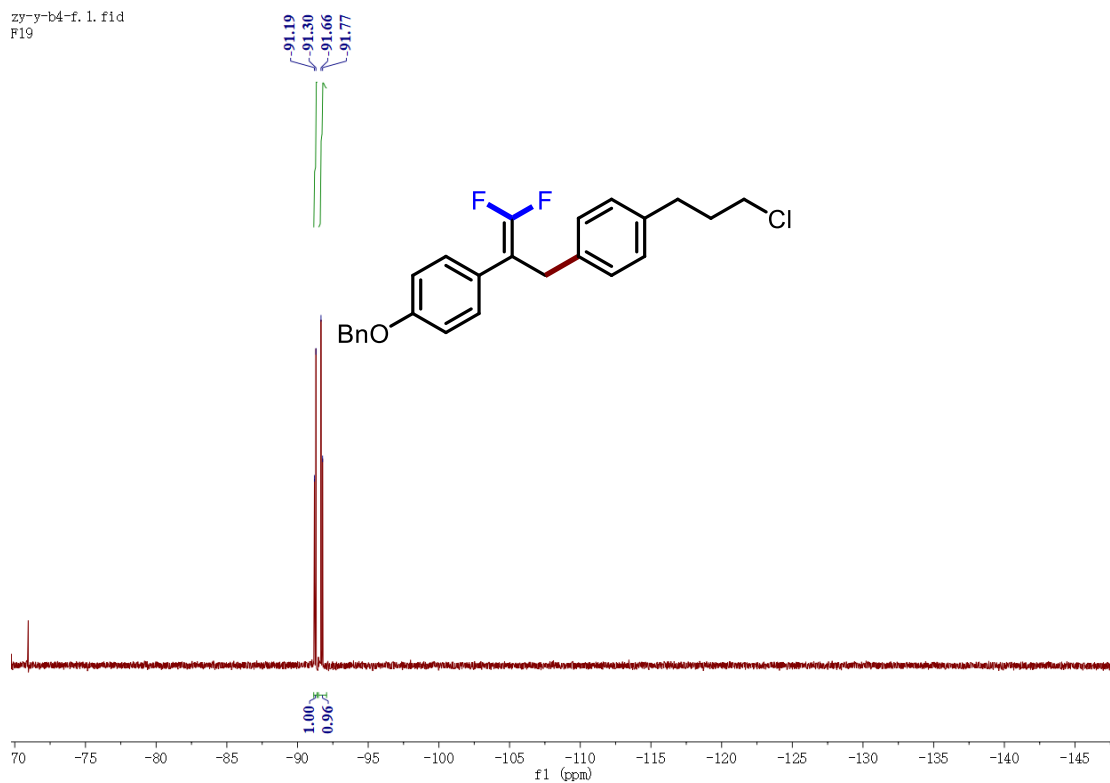
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ag**.

Dec25-2023
y-b4-c



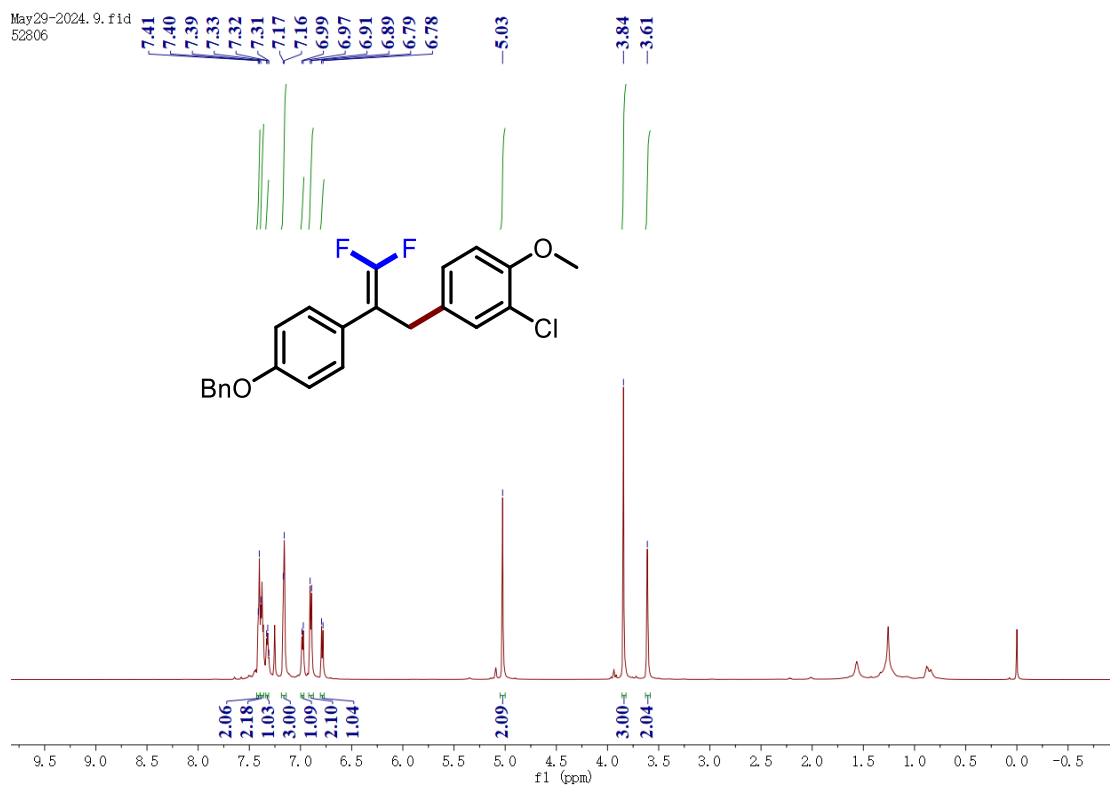
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ag**.

zy-y-b4-f.1.fid
F19

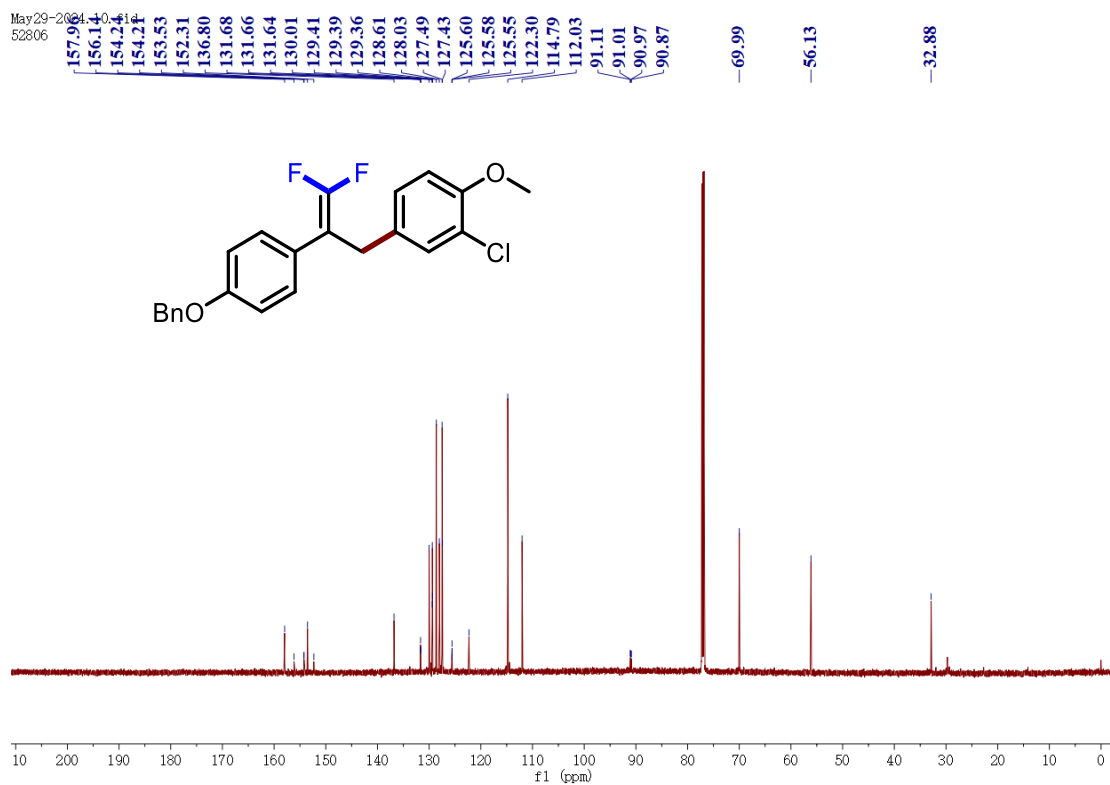


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ag**.

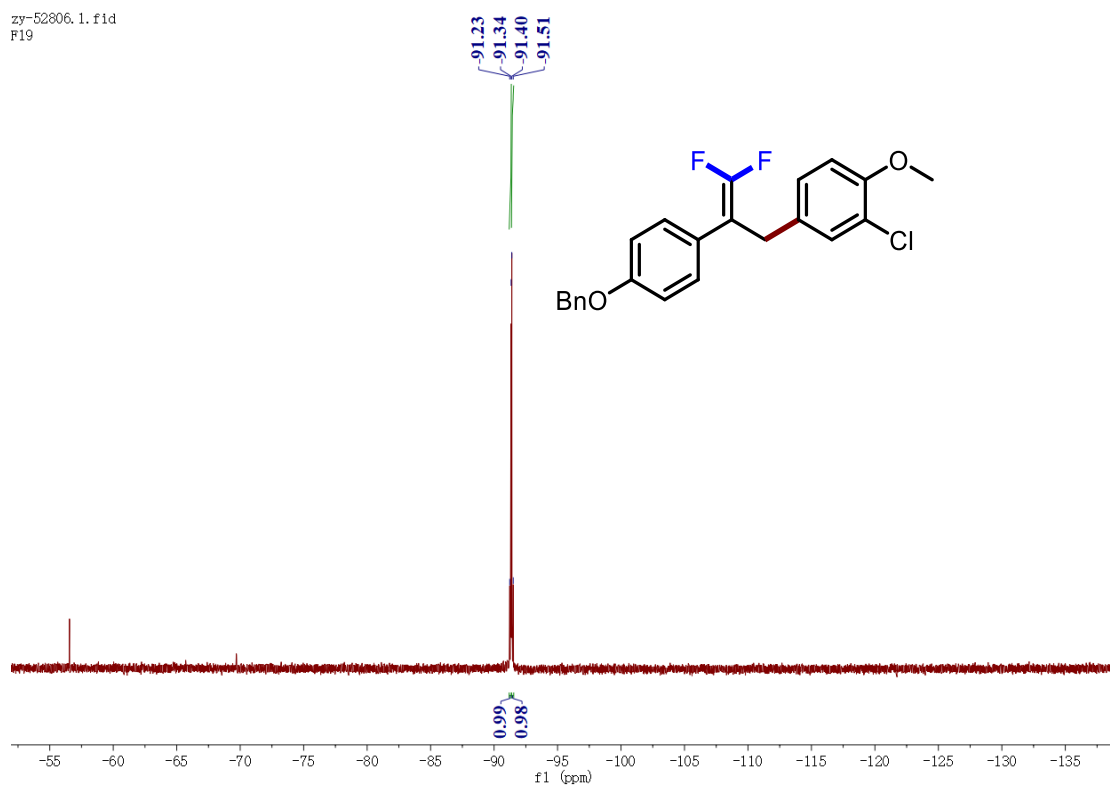
May29-2024. 9.fid
52806



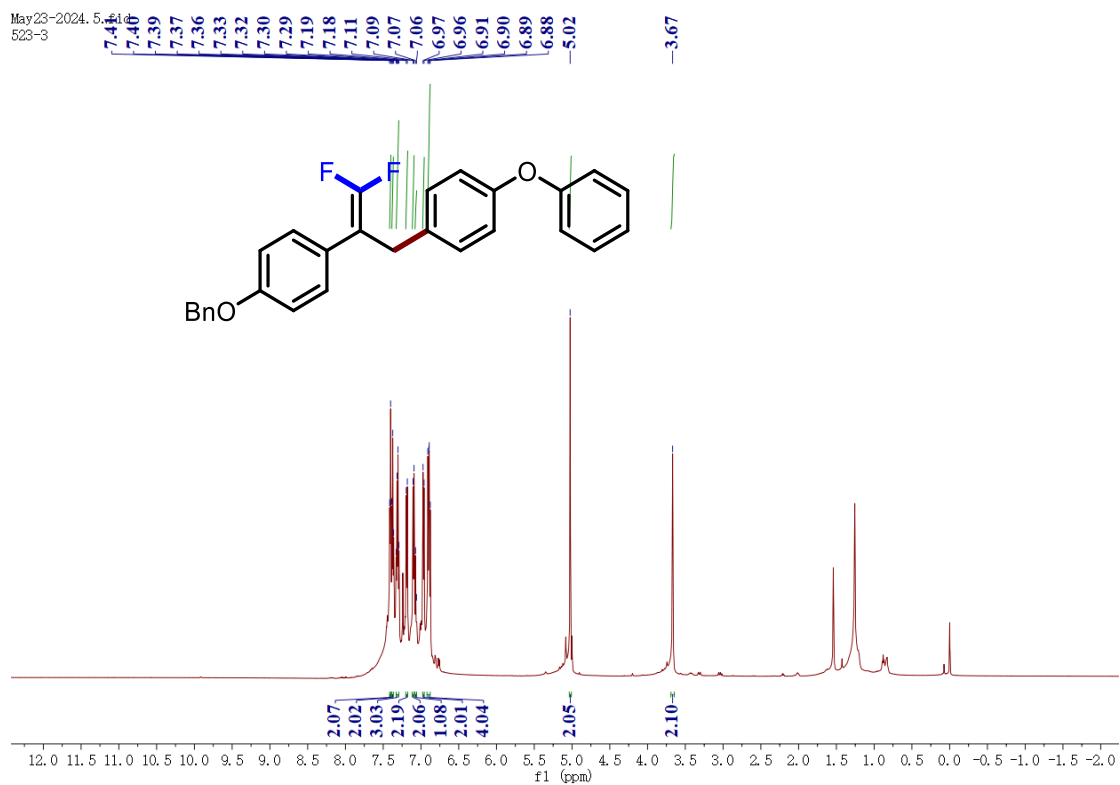
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ah**.



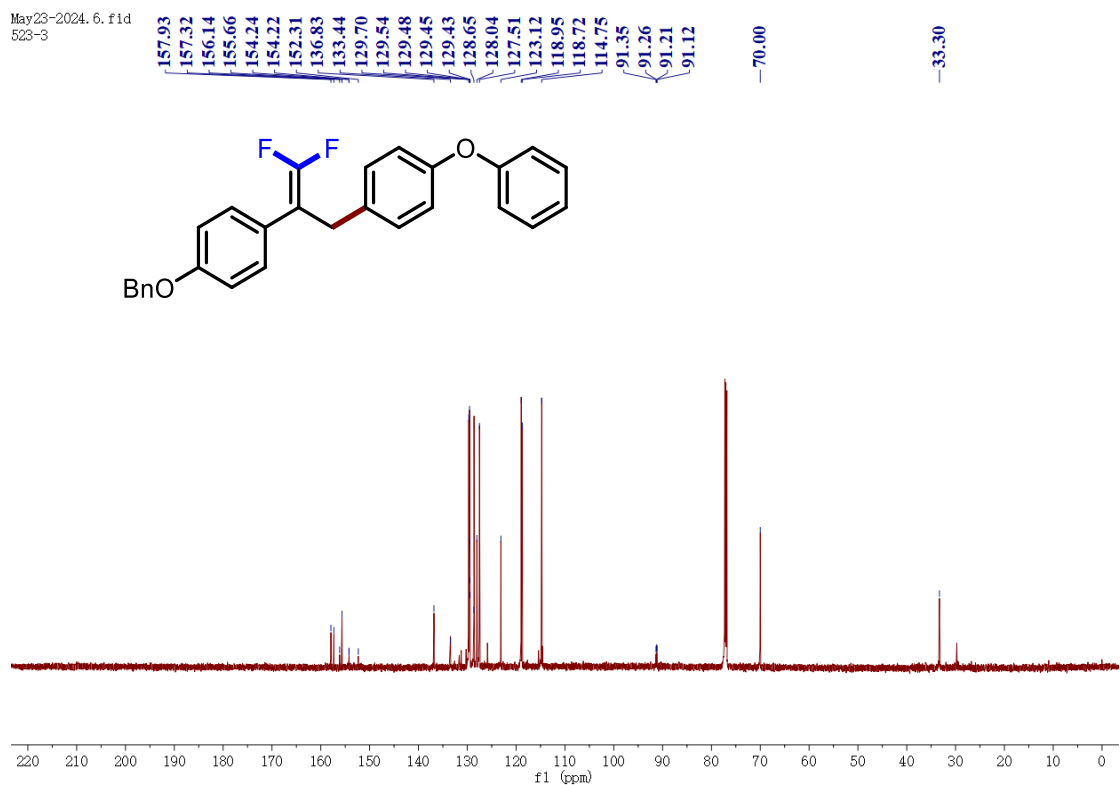
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ah**.



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ah**.

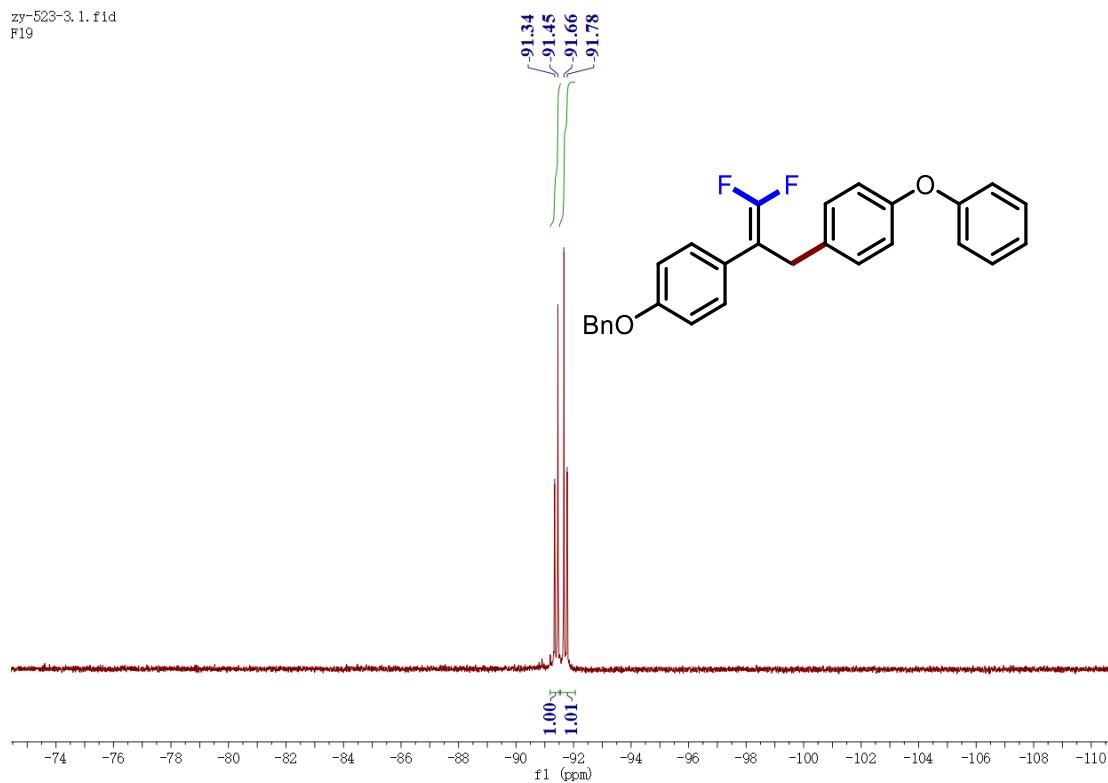


^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ai**.



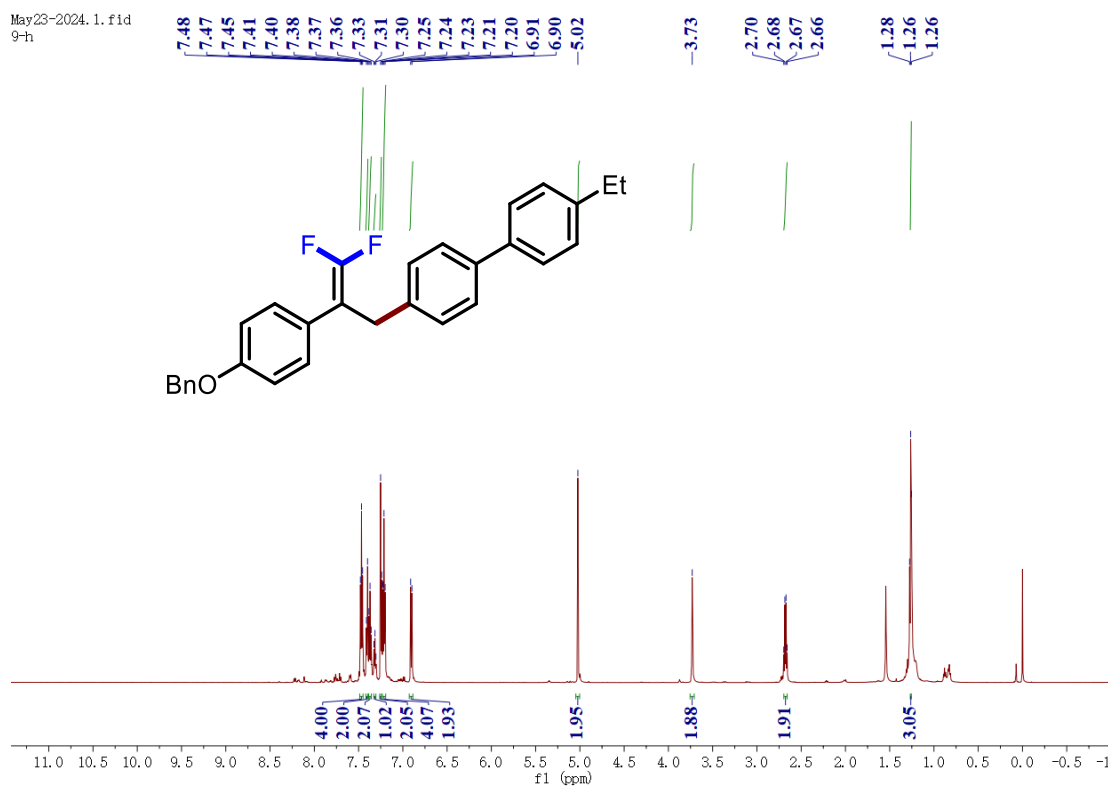
^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ai**.

zy-523-3.1.fid
F19

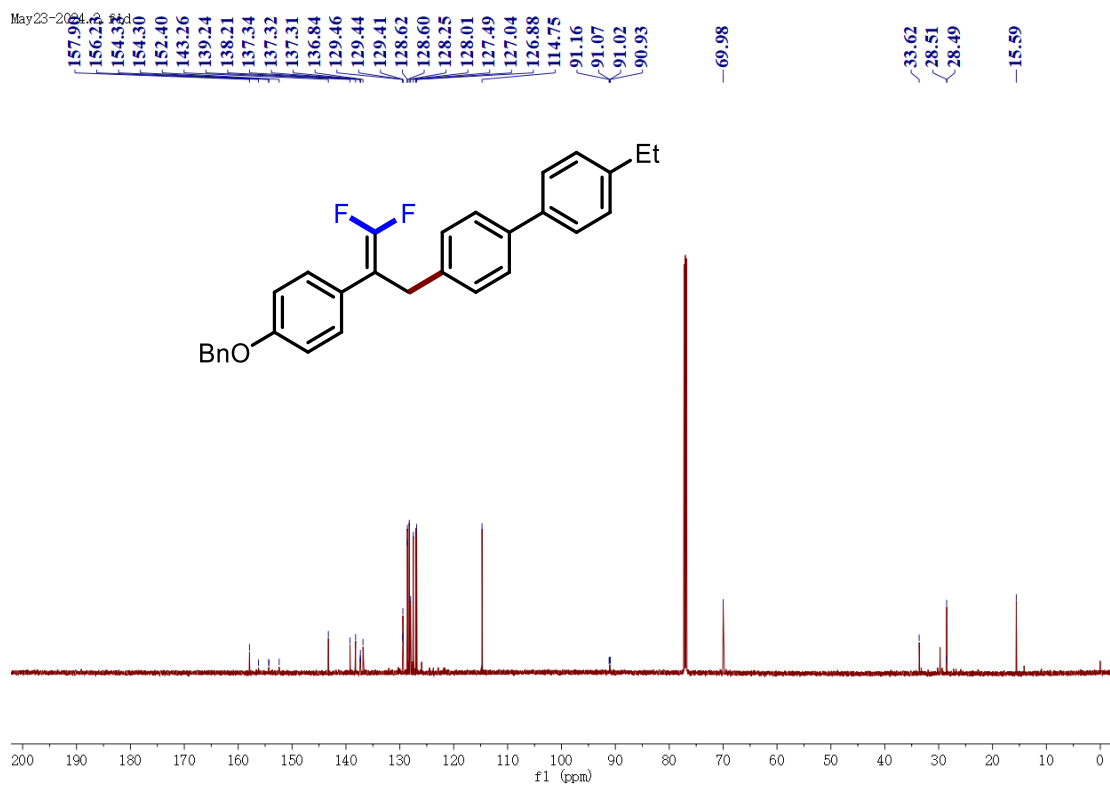


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ai**.

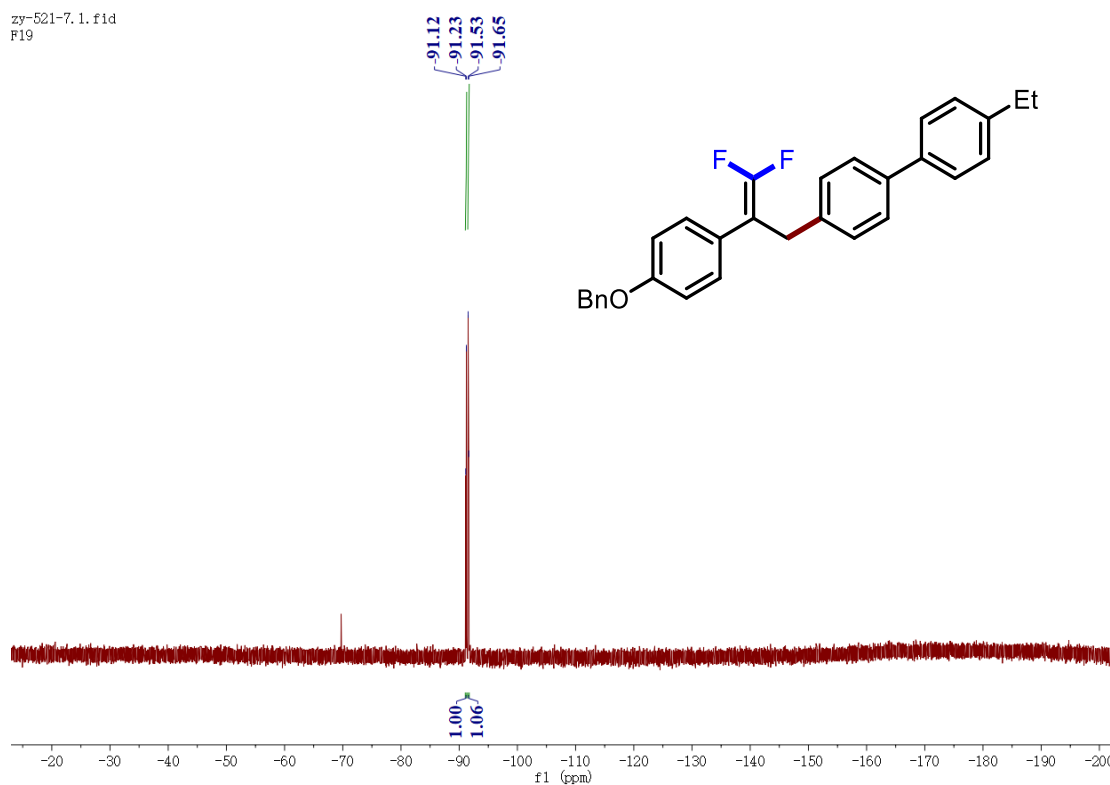
May23-2024.1.fid
9-h



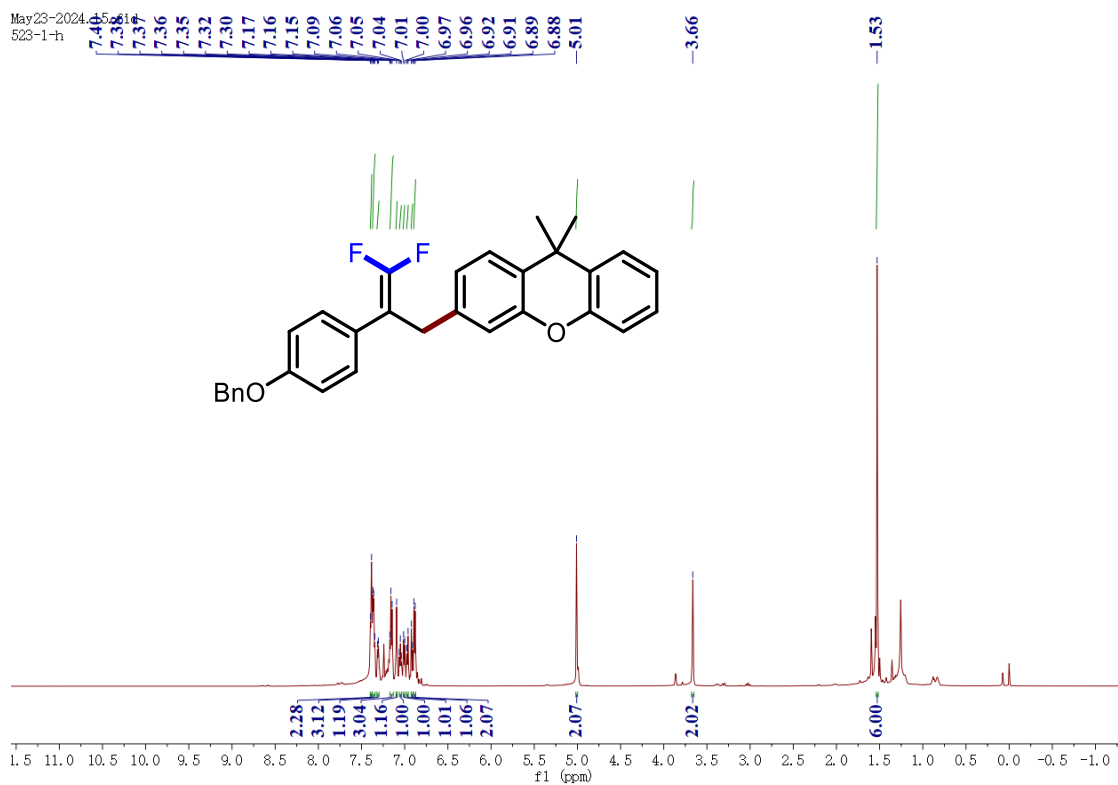
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3aj**.



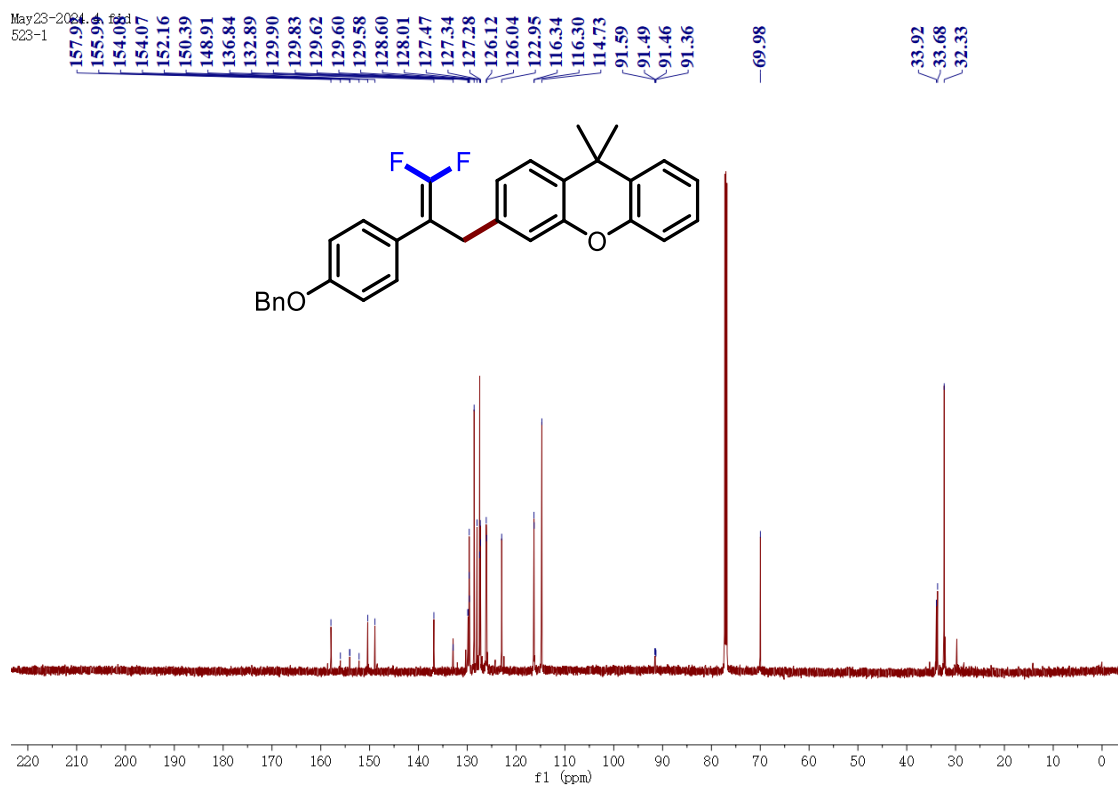
^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3aj**.



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3aj**.



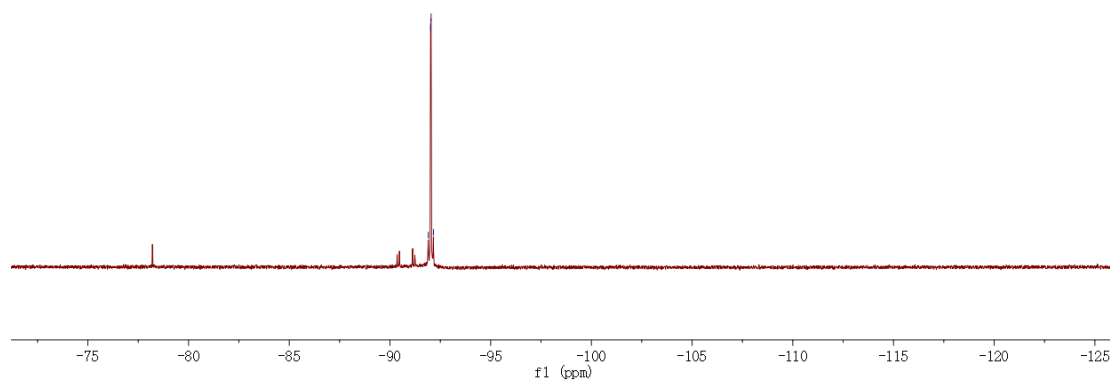
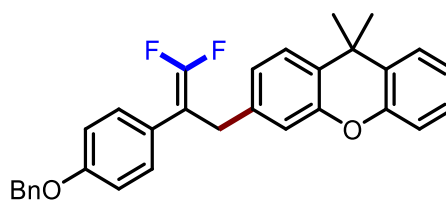
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ak**.



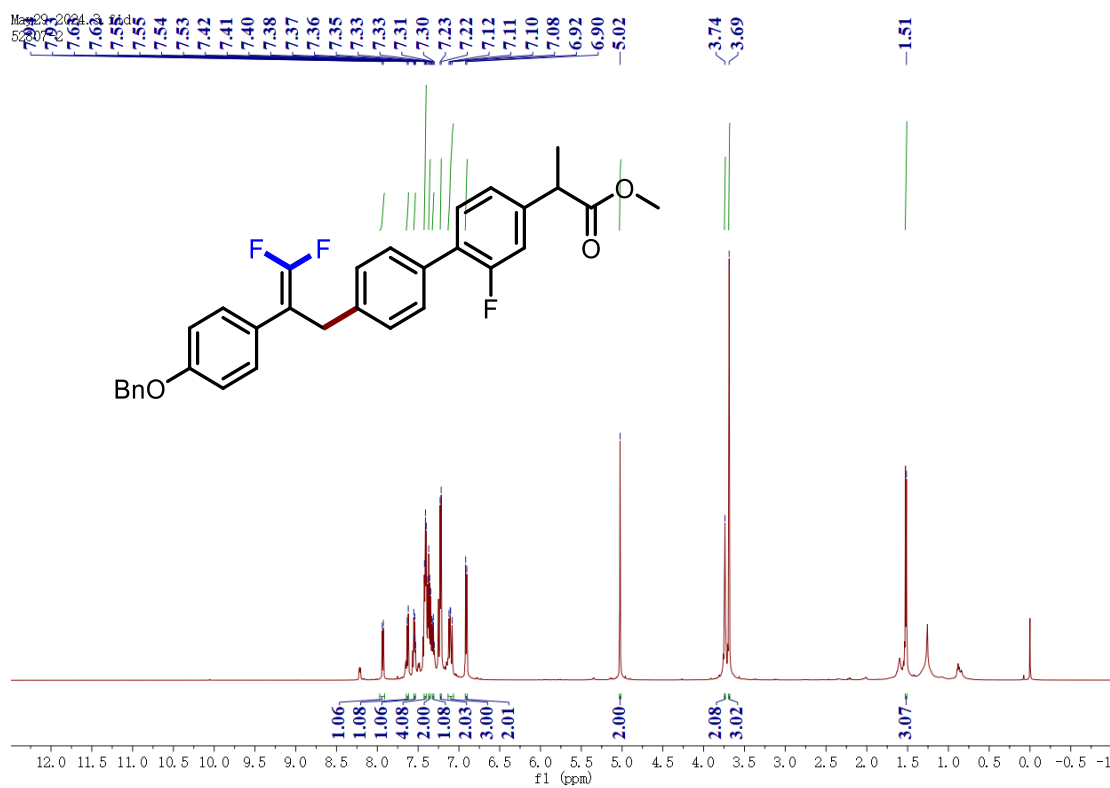
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ak**.

zy-523-1.1.f1d
F19

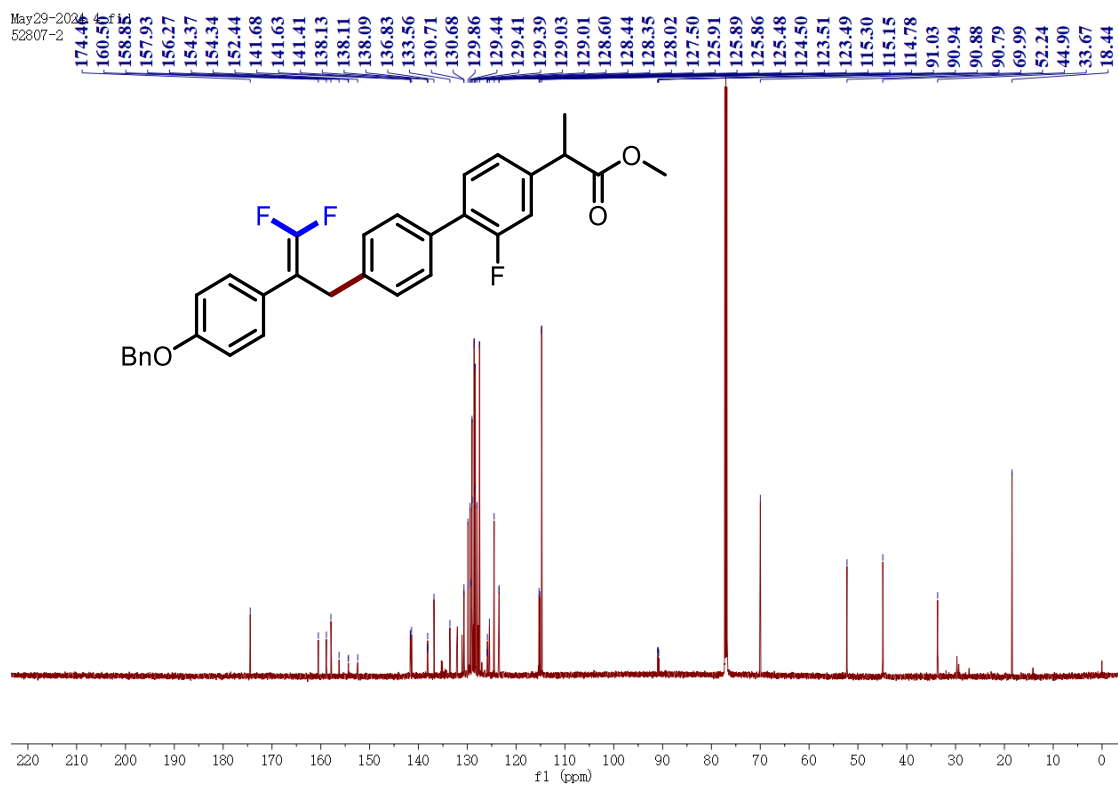
91.90
92.02
92.04
92.16



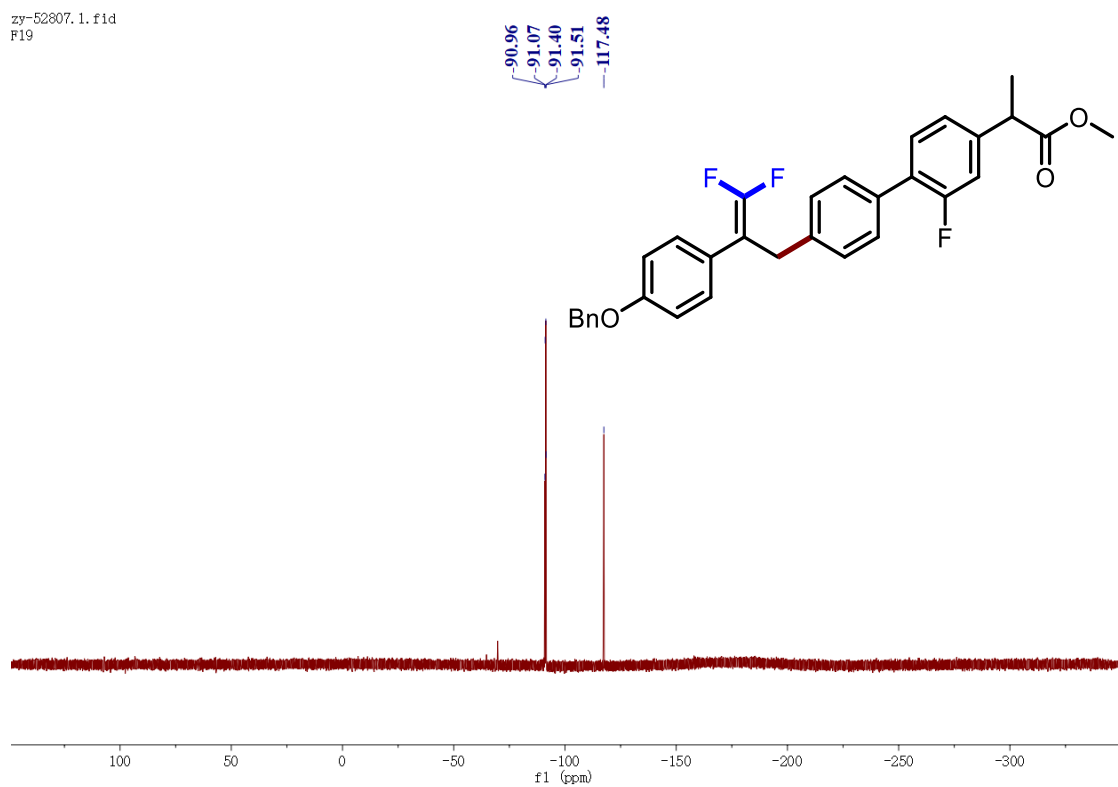
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3ak.



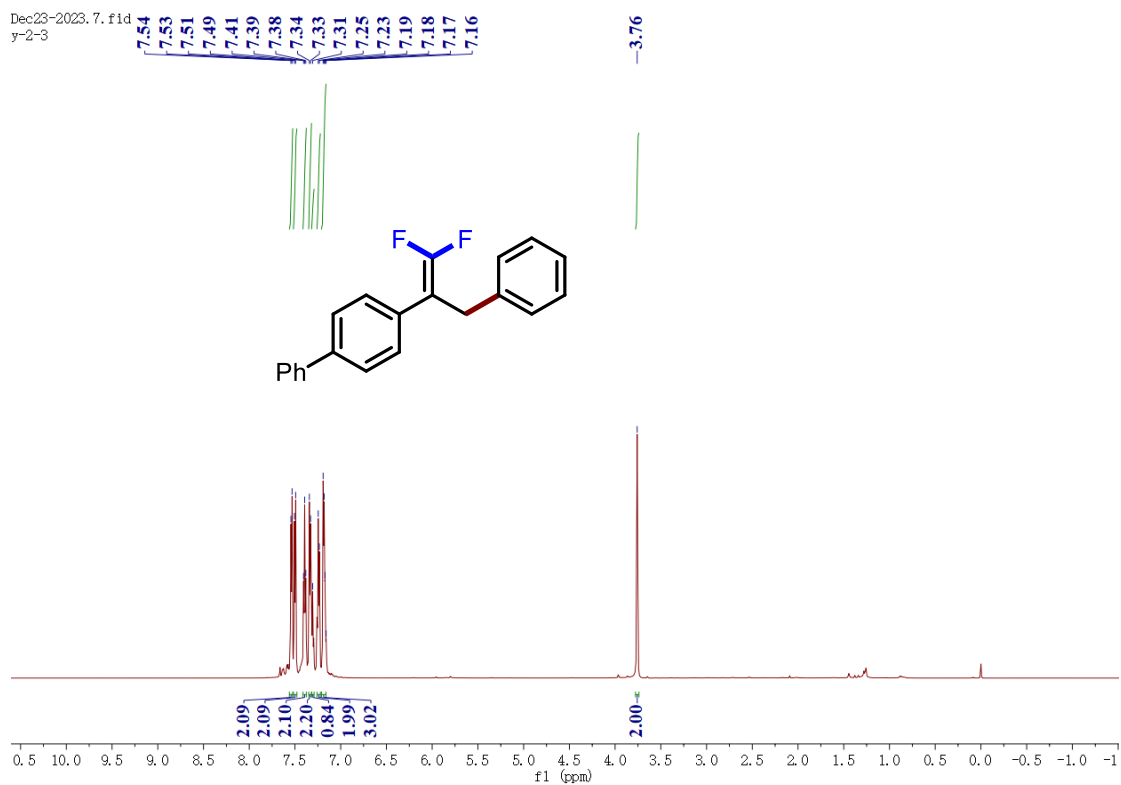
^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3al.



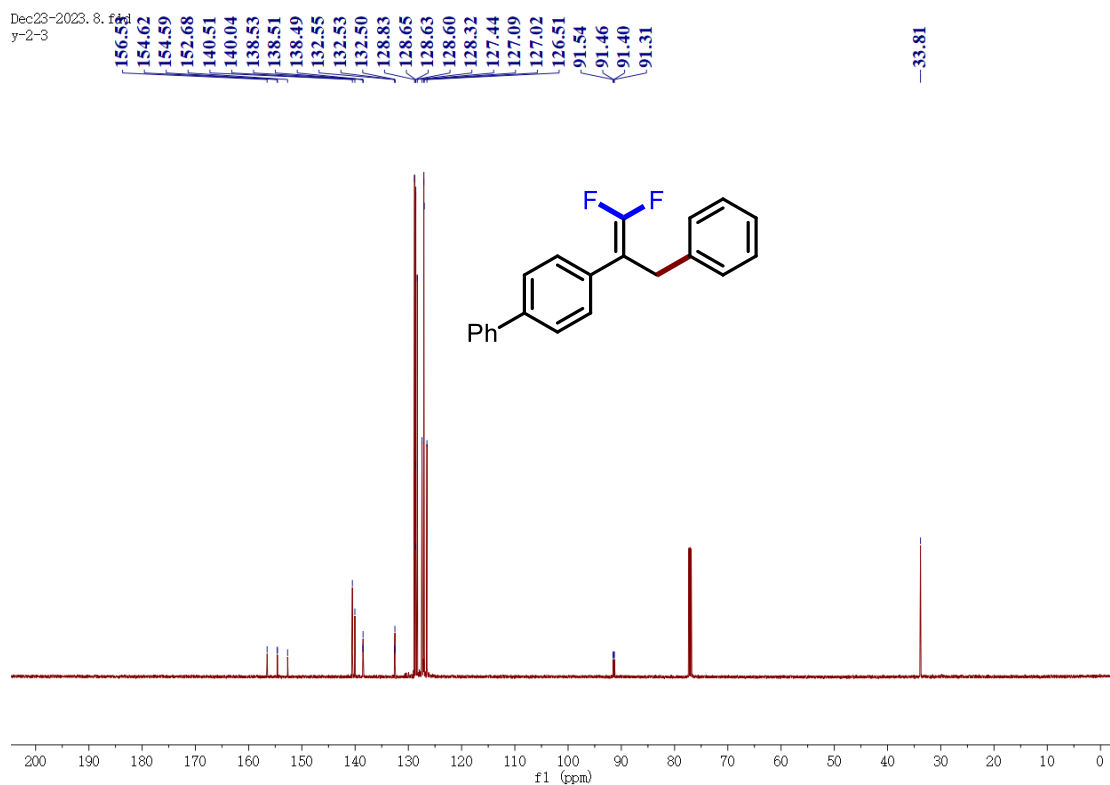
^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound 3al.



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3al.

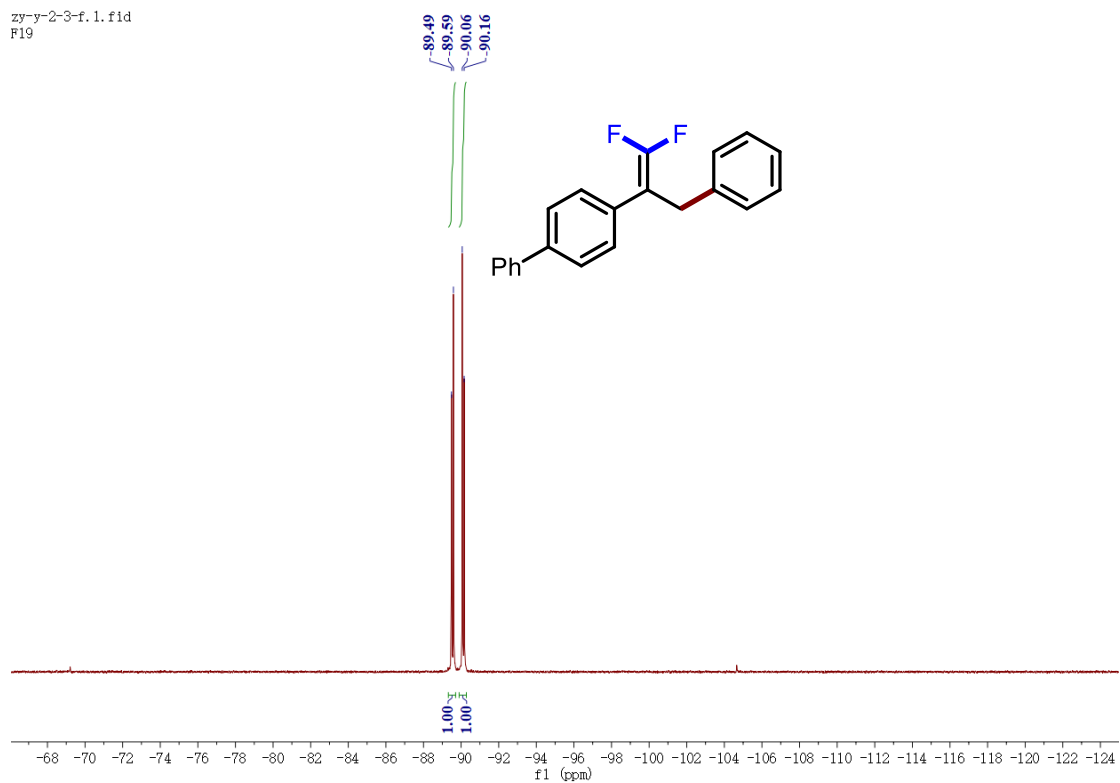


^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3am**.

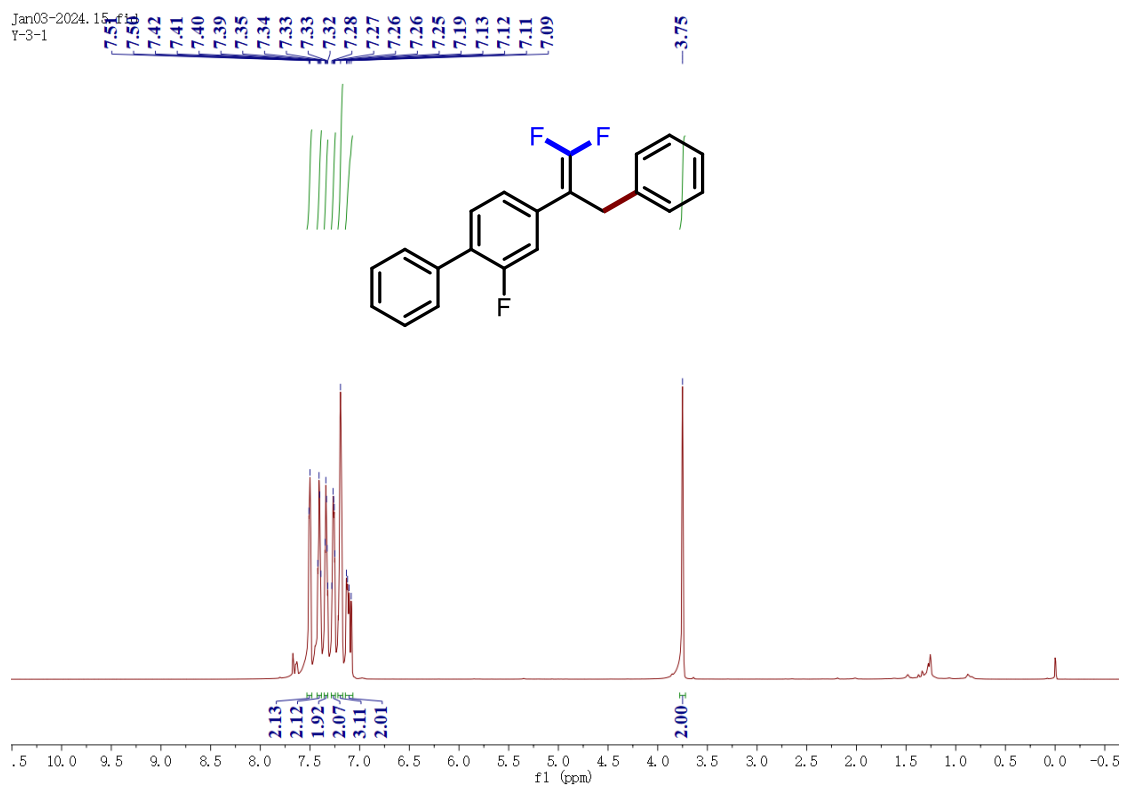


^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3am**.

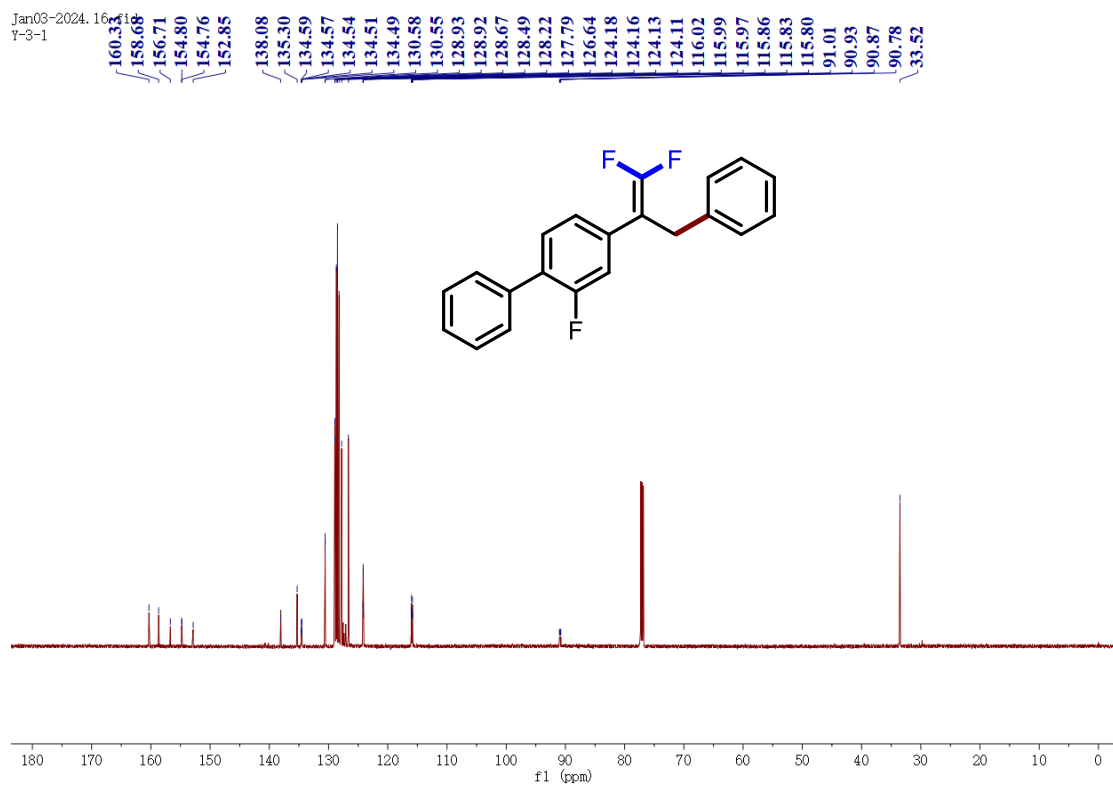
zy-y-2-3-f.1.fid
F19



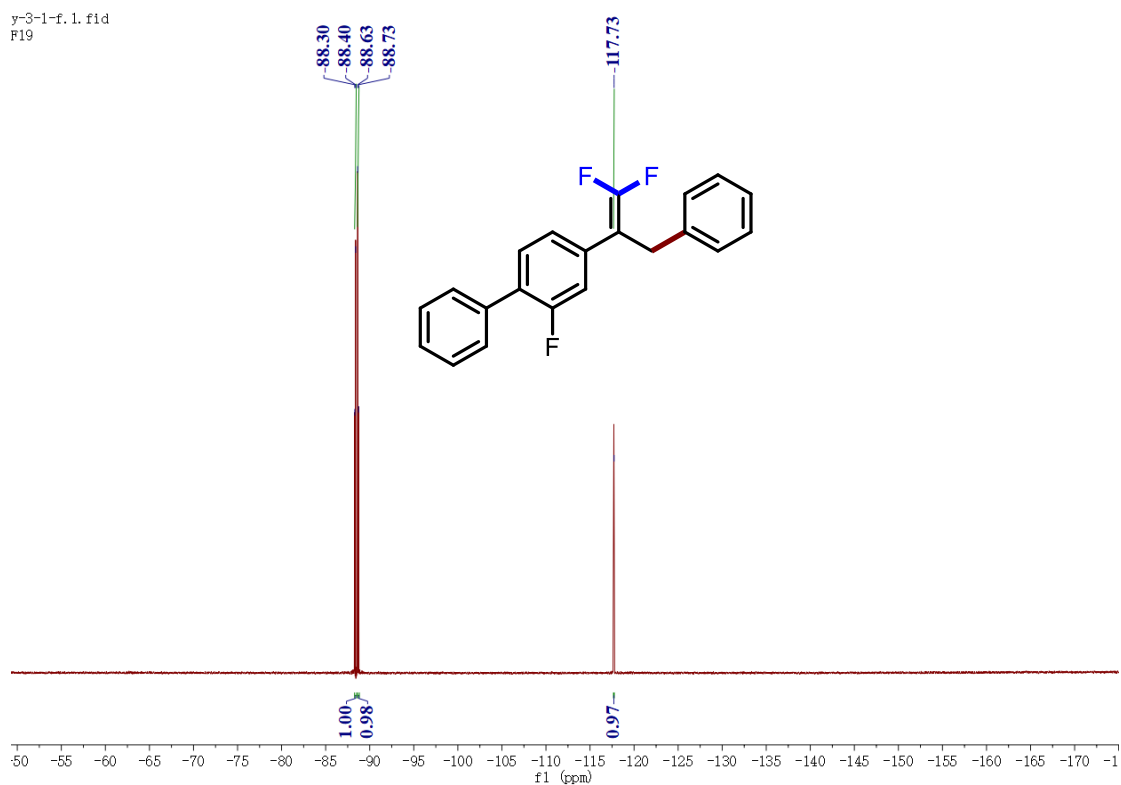
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3am**.



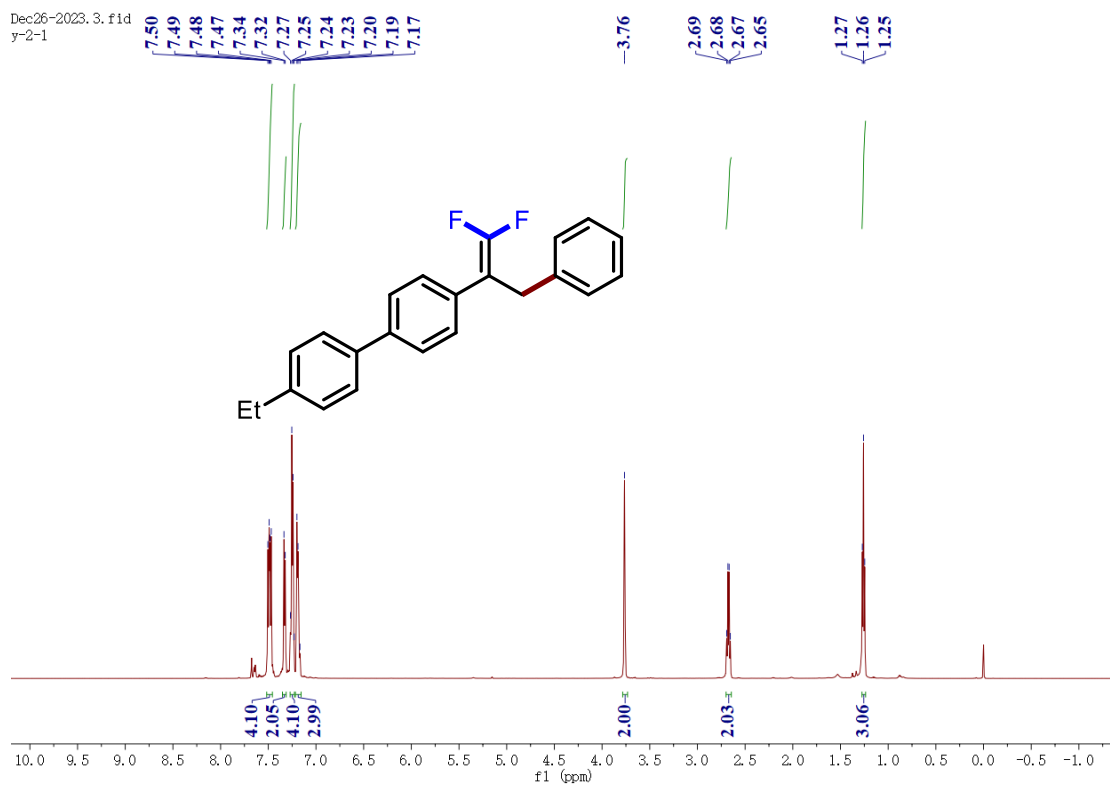
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3am**.



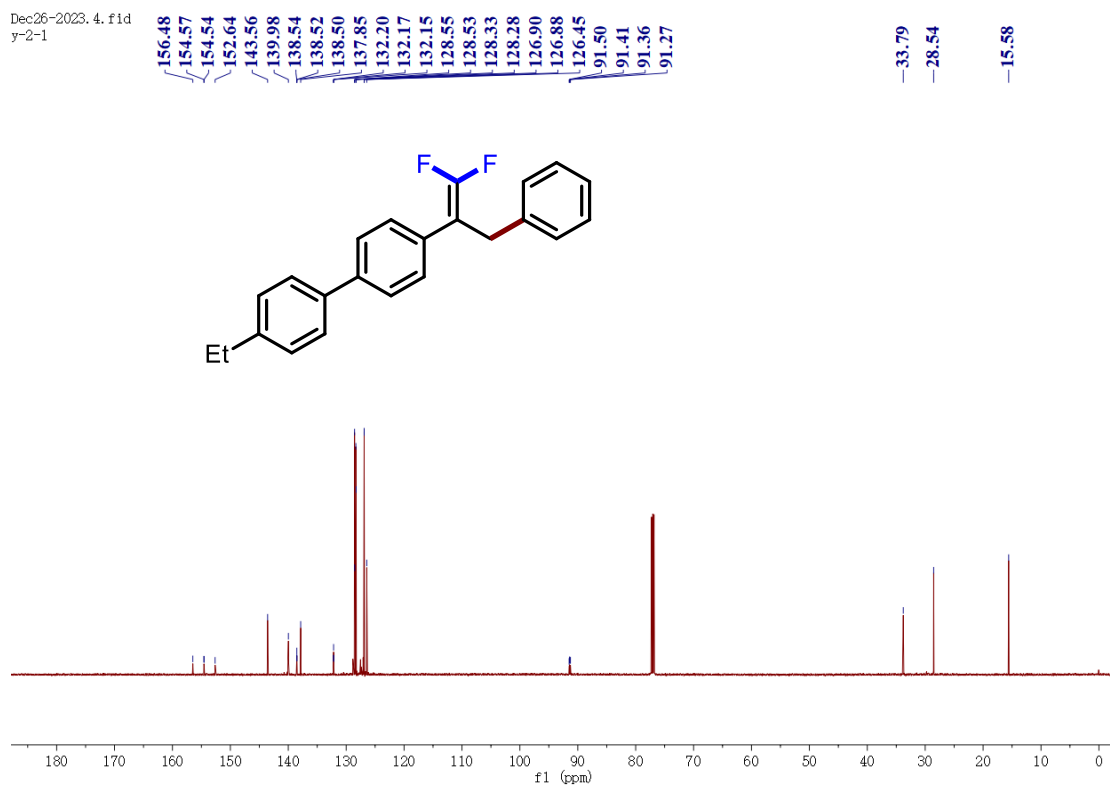
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 3an.



¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3an.

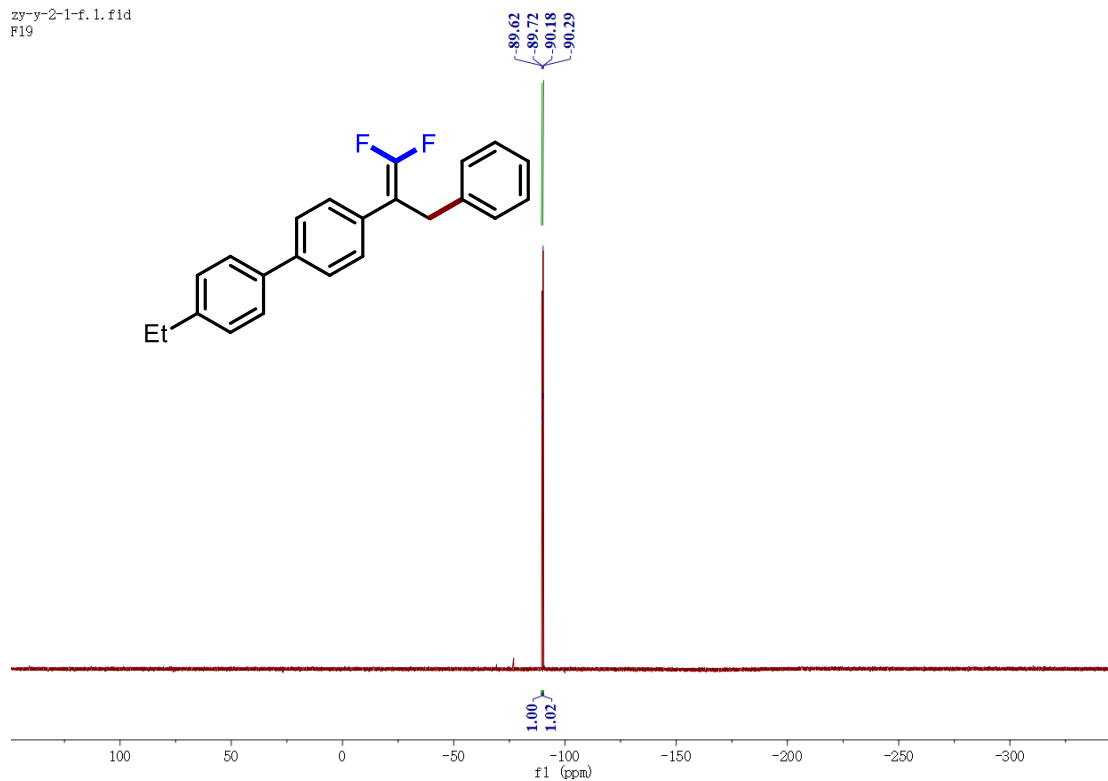


^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ao**.



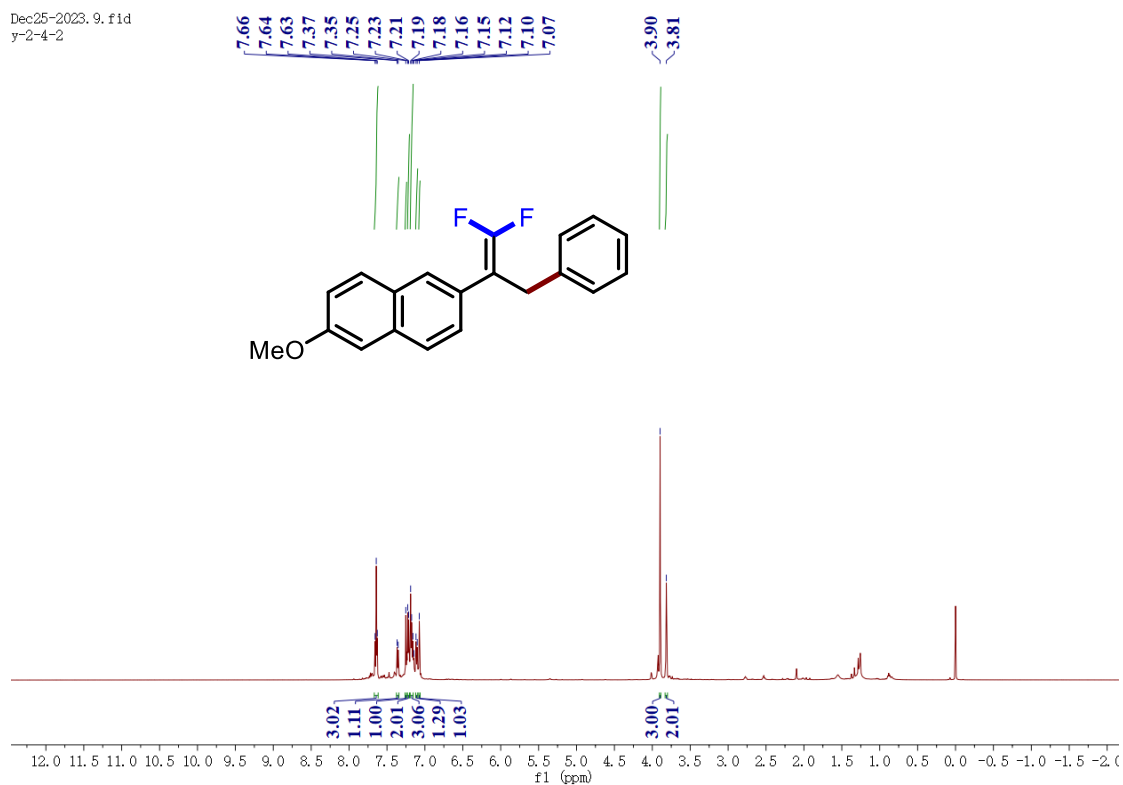
^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ao**.

zy-y-2-1-f.1.fid
F19

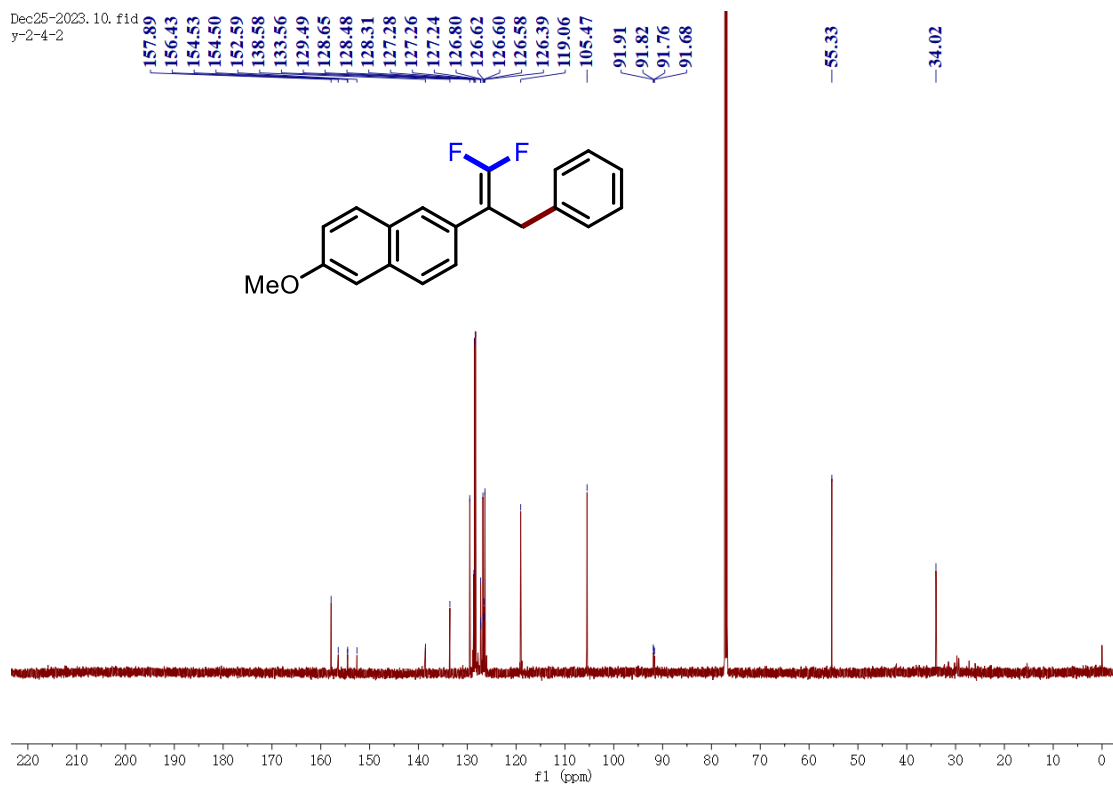


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ao**.

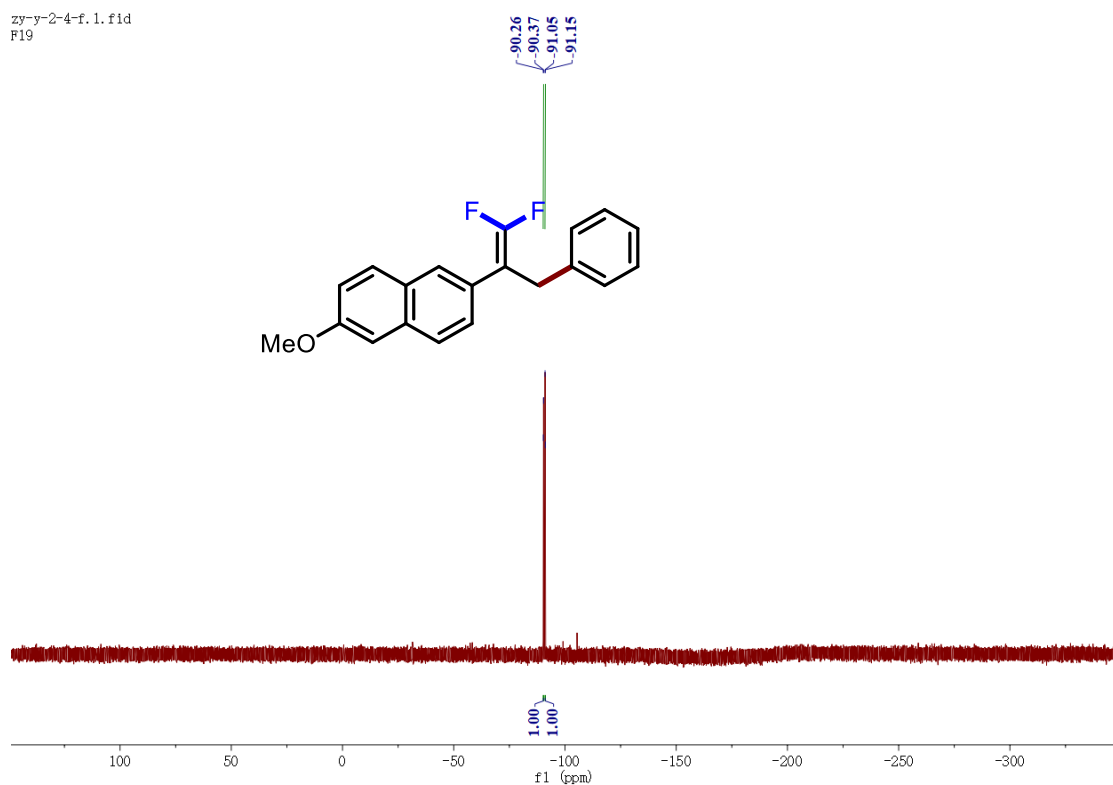
Dec25-2023.9.fid
y-2-4-2



¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ap**.

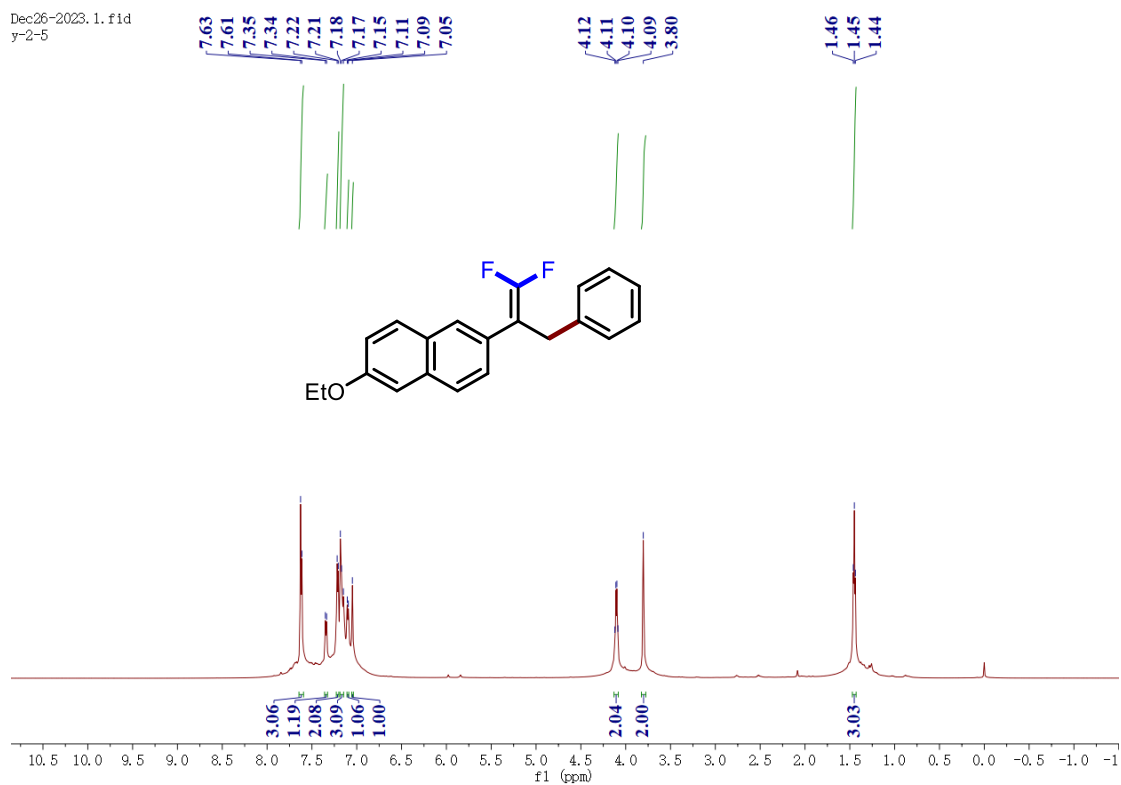


^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ap**.

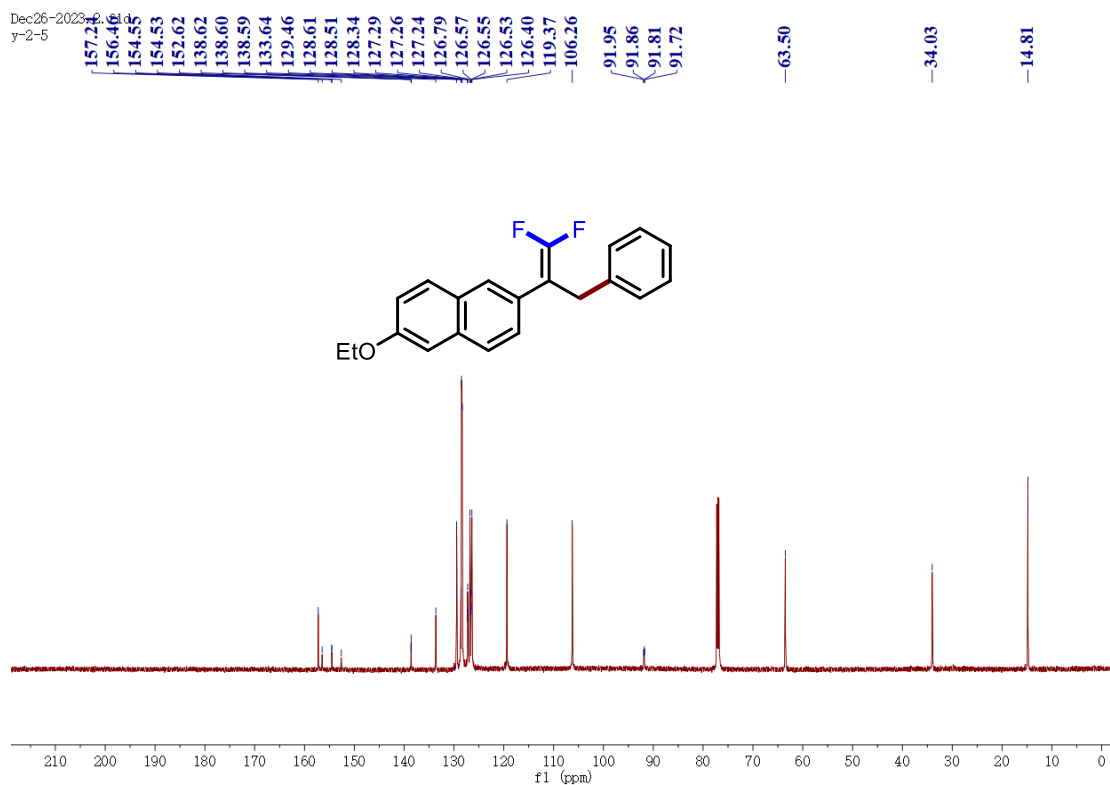


^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ap**.

Dec26-2023. 1. f1d
y-2-5

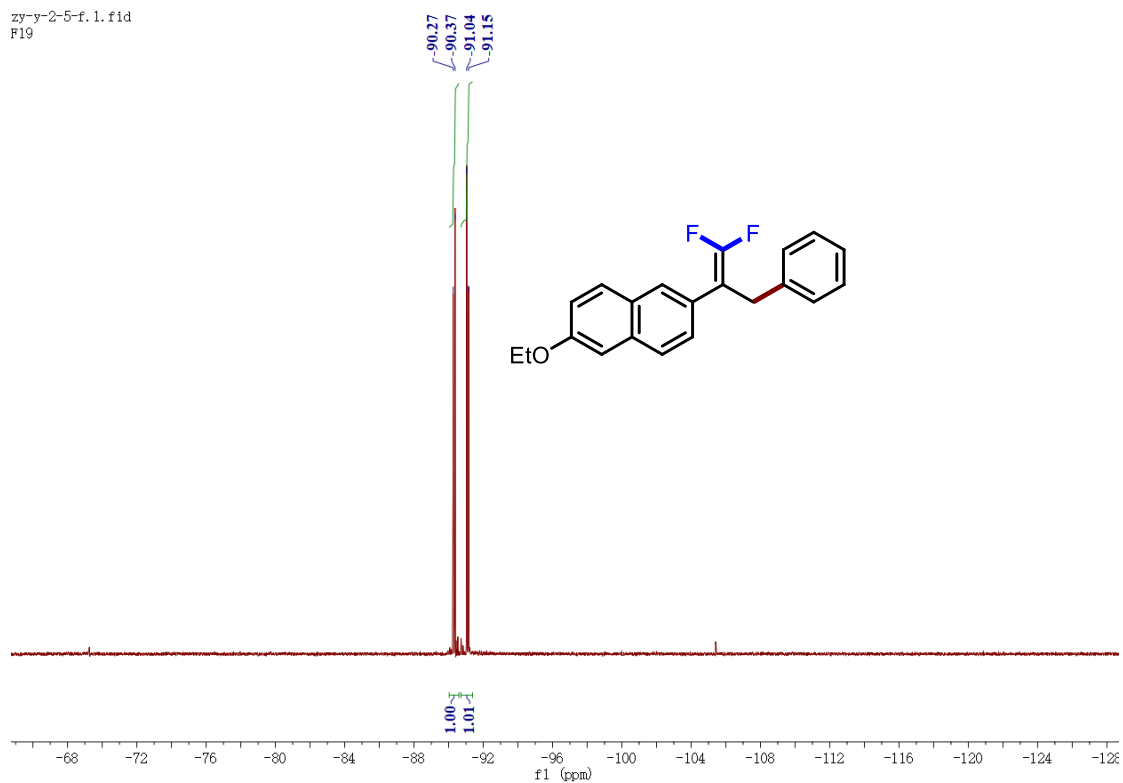


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3aq**.



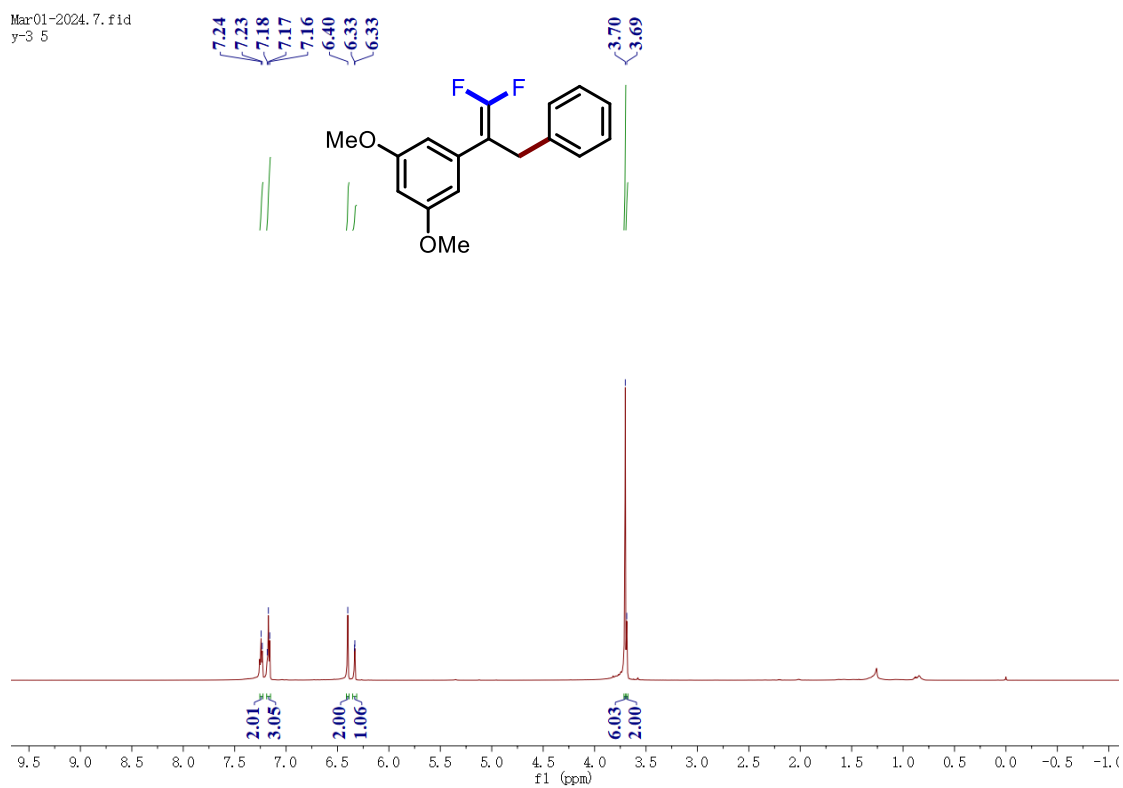
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3aq**.

zy-y-2-5-f.1.fid
F19



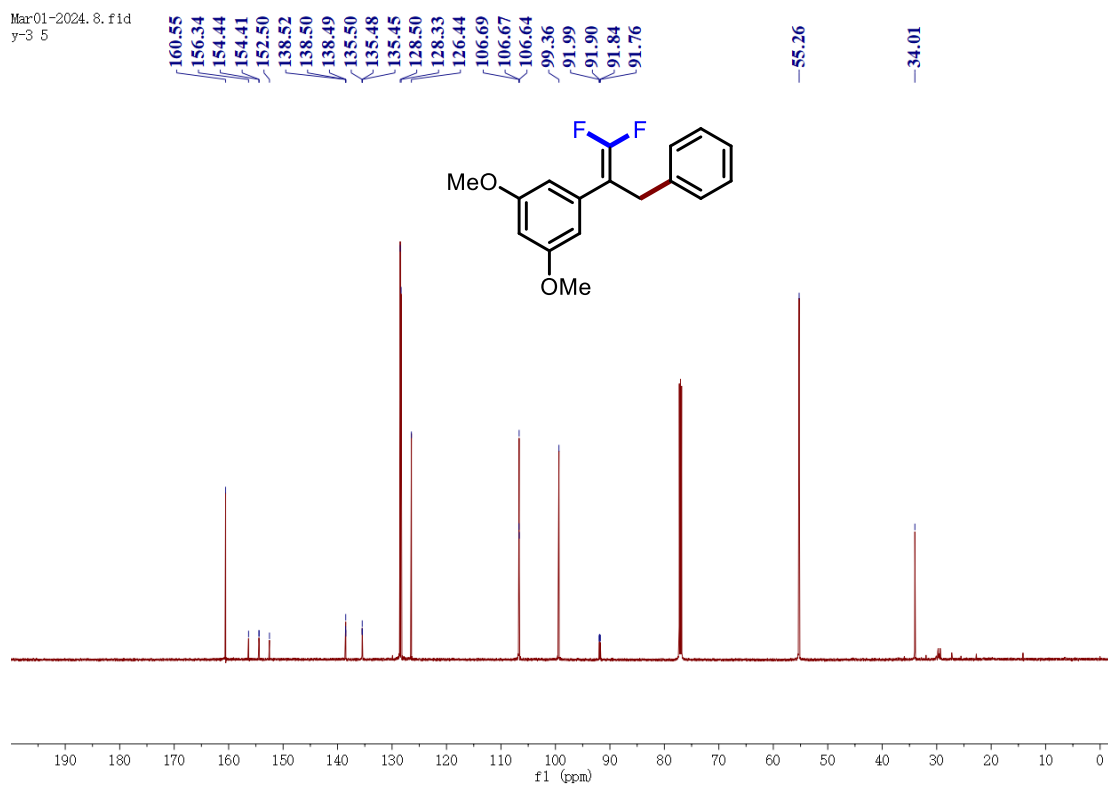
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3aq**.

Mar01-2024.7.fid
y-3 5



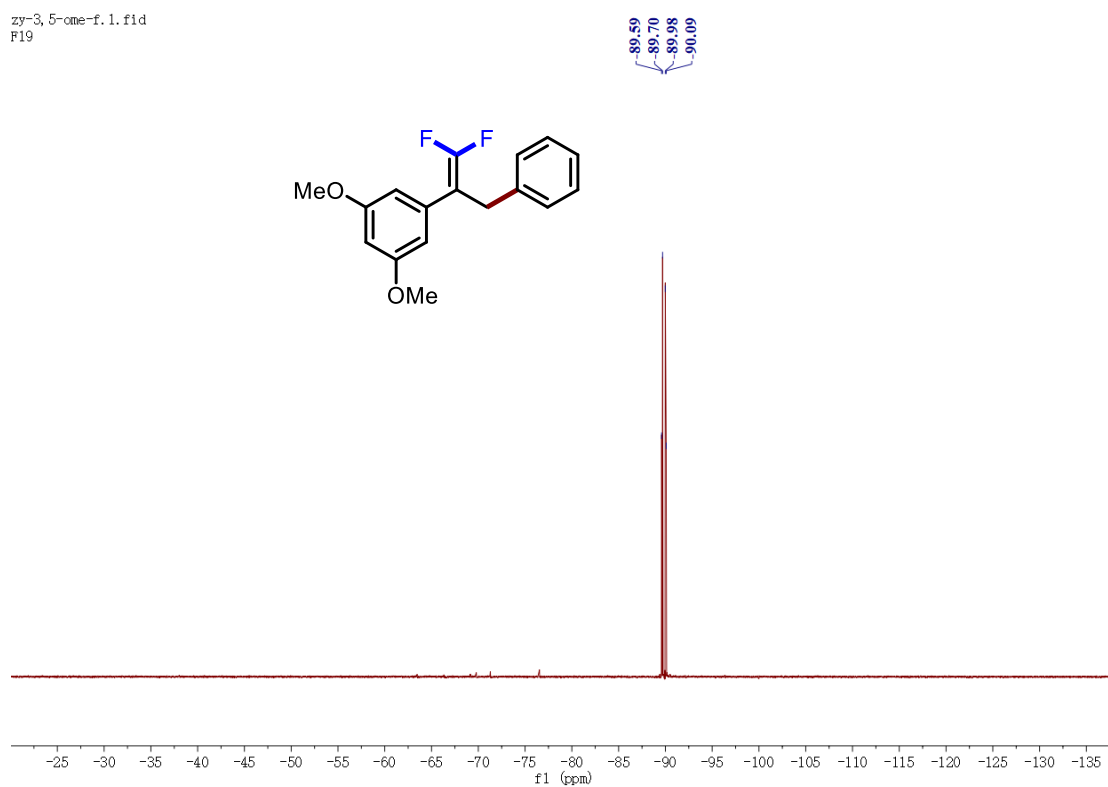
^1H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3ar**.

Mar01-2024_8.fid
y-3 5



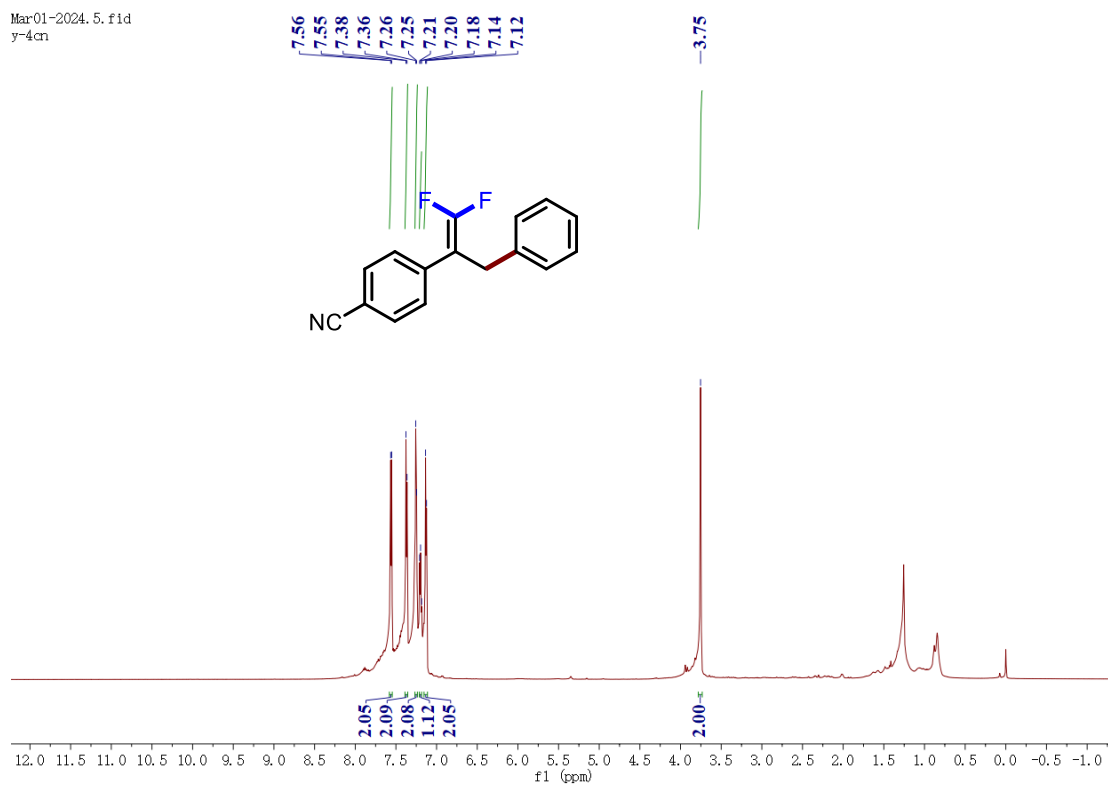
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3ar**.

zy-3_5-ome-f.1.fid
F19



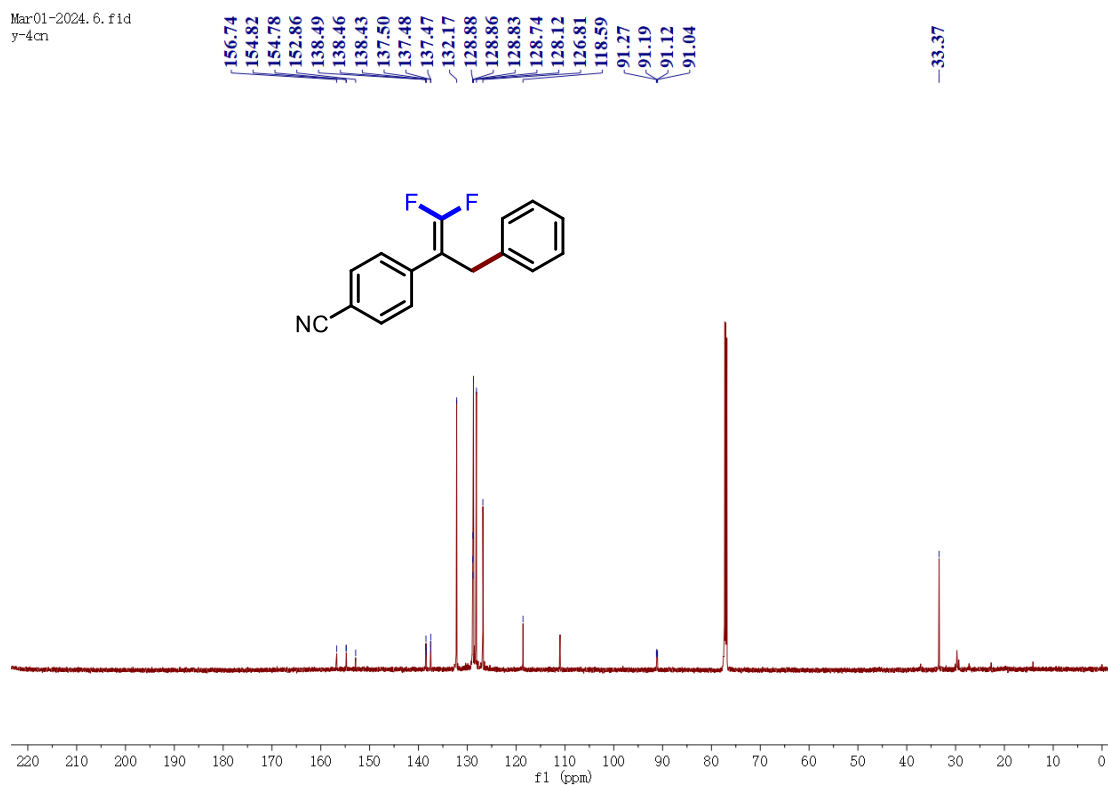
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **3ar**.

Mar01-2024. 5. fid
y-4cn



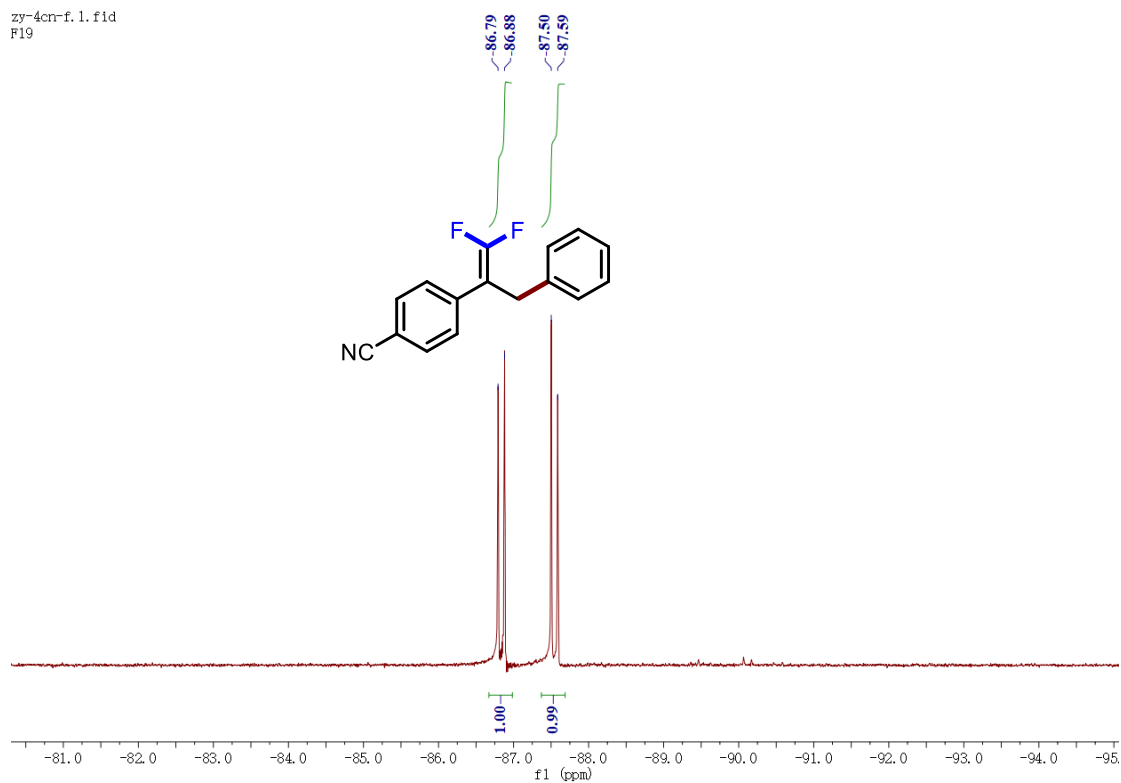
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **3as**.

Mar01-2024. 6. fid
y-4cn

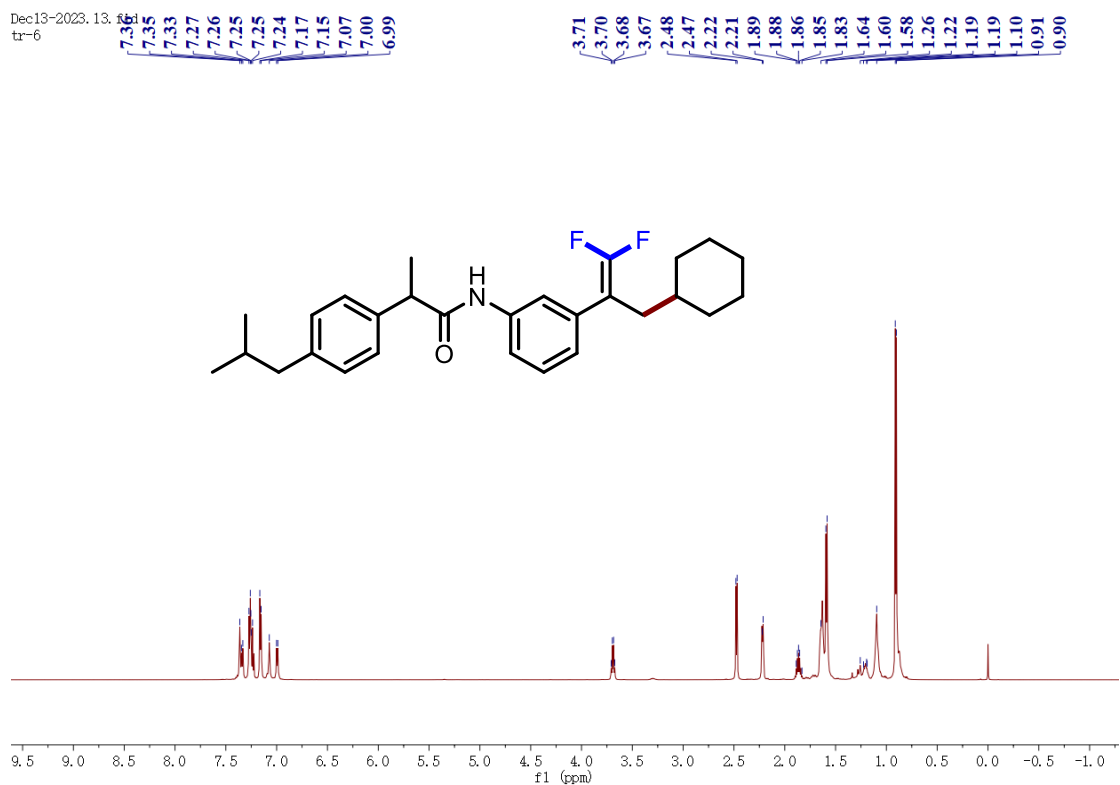


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **3as**.

zy-4cn-f.1.fid
F19

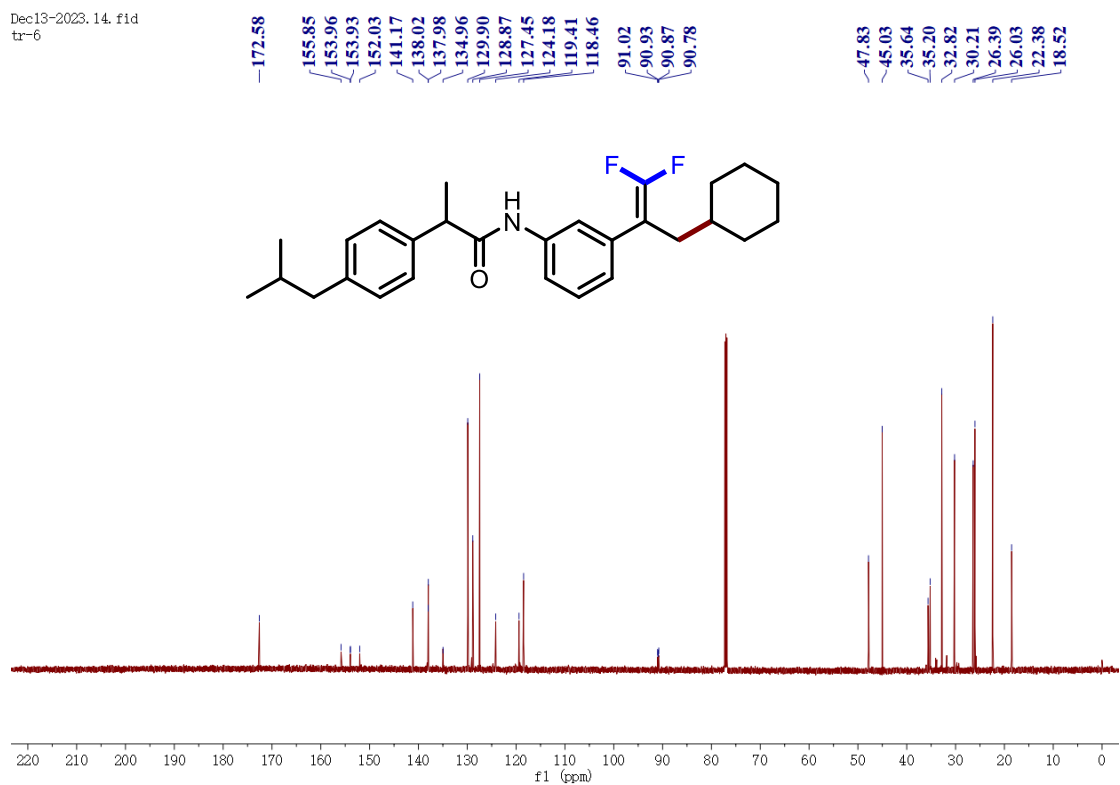


¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound 3as.



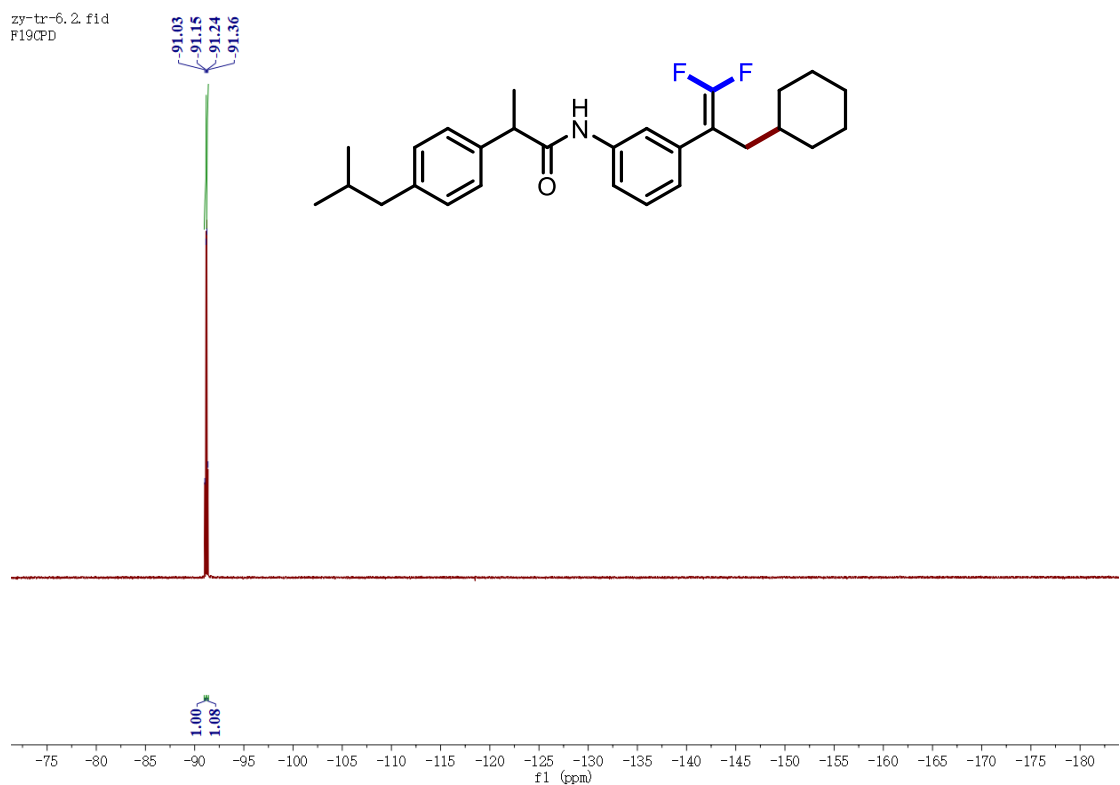
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 4a.

Dec13-2023. 14. fid
tr-6

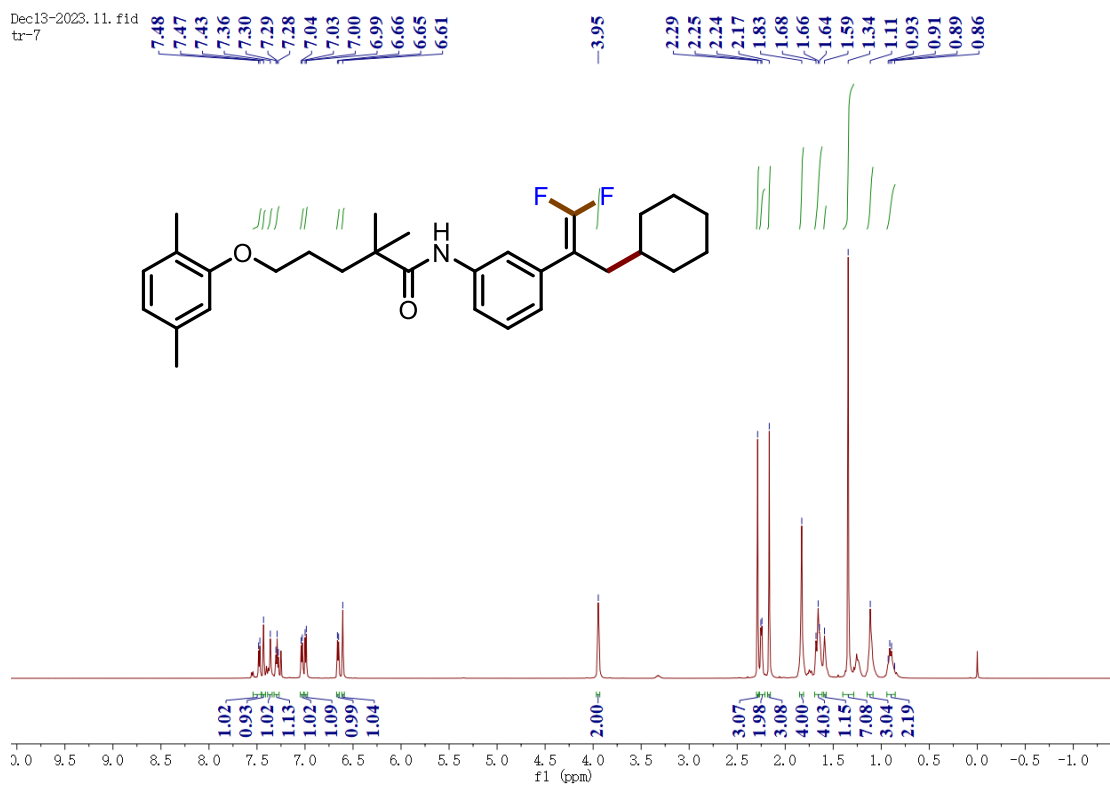


^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **4a**.

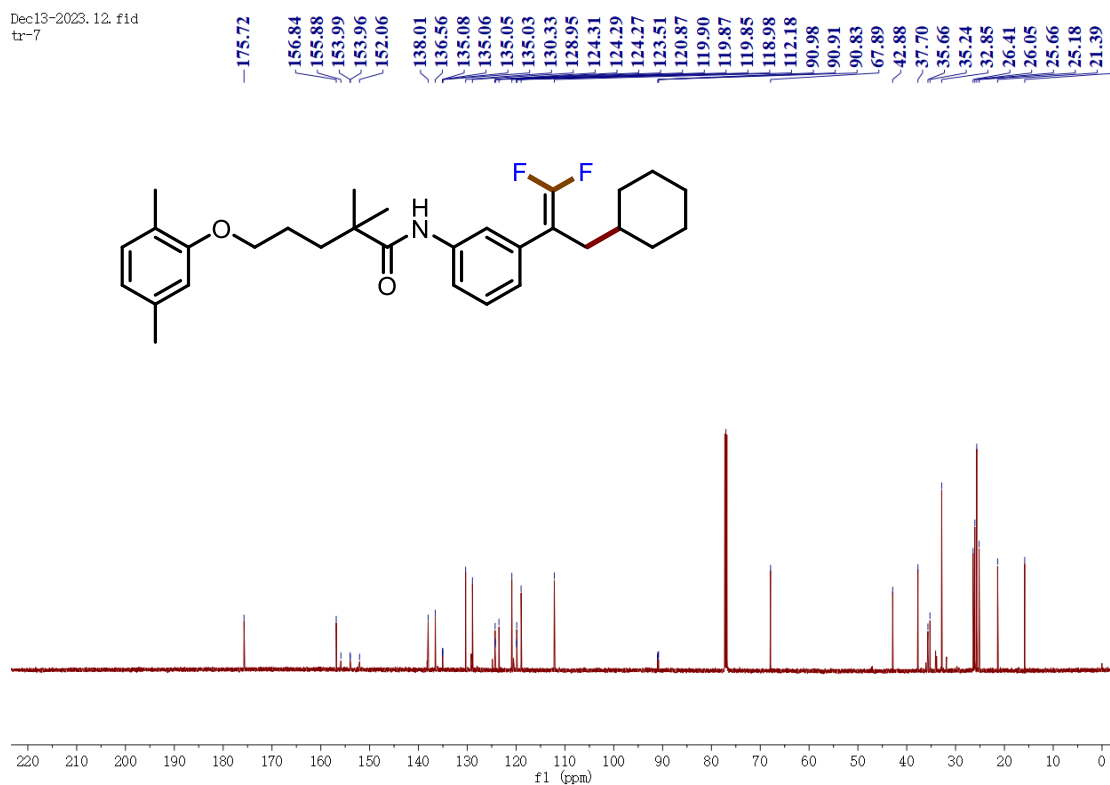
zy-tr-6.2.fid
F19CPD



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **4a**.

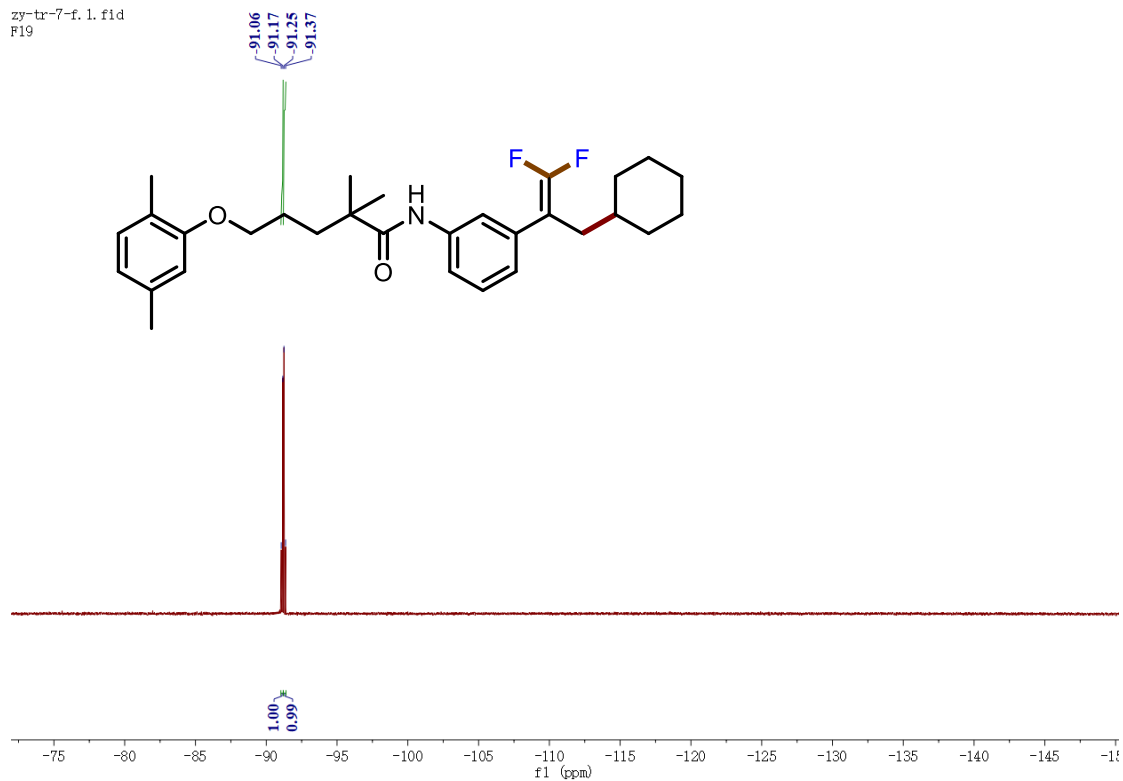


¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **4b.**



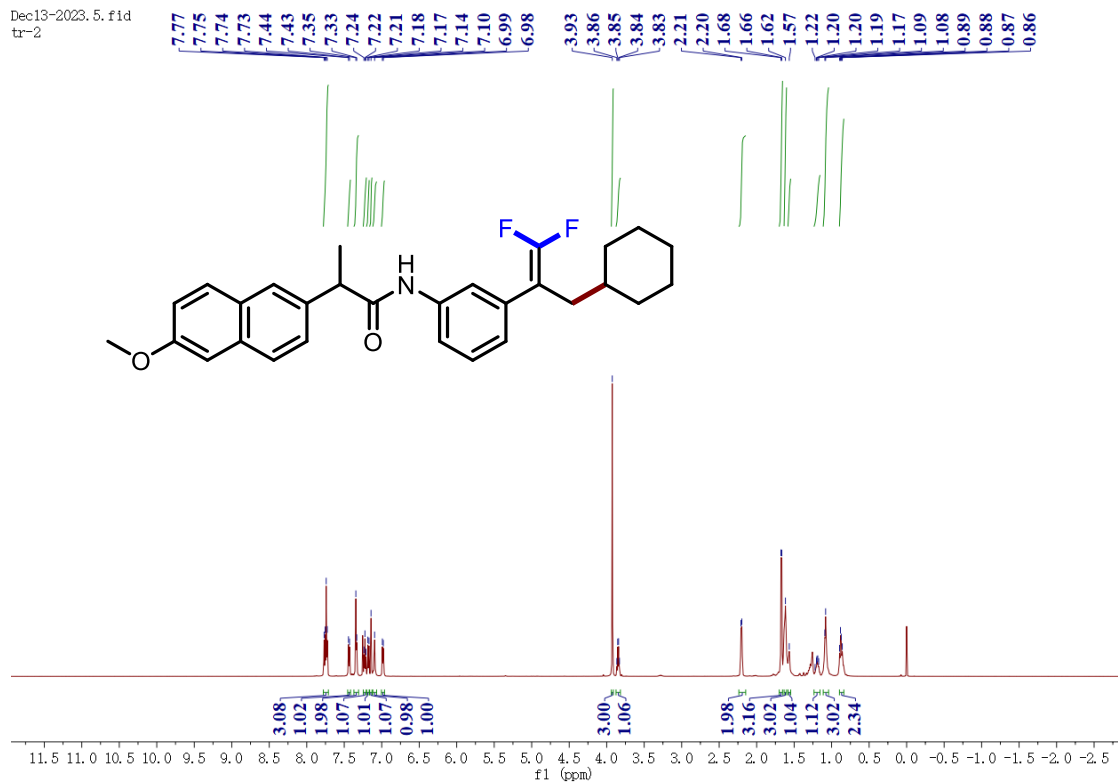
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **4b.**

zy-tr-7-f. 1. fid
F19



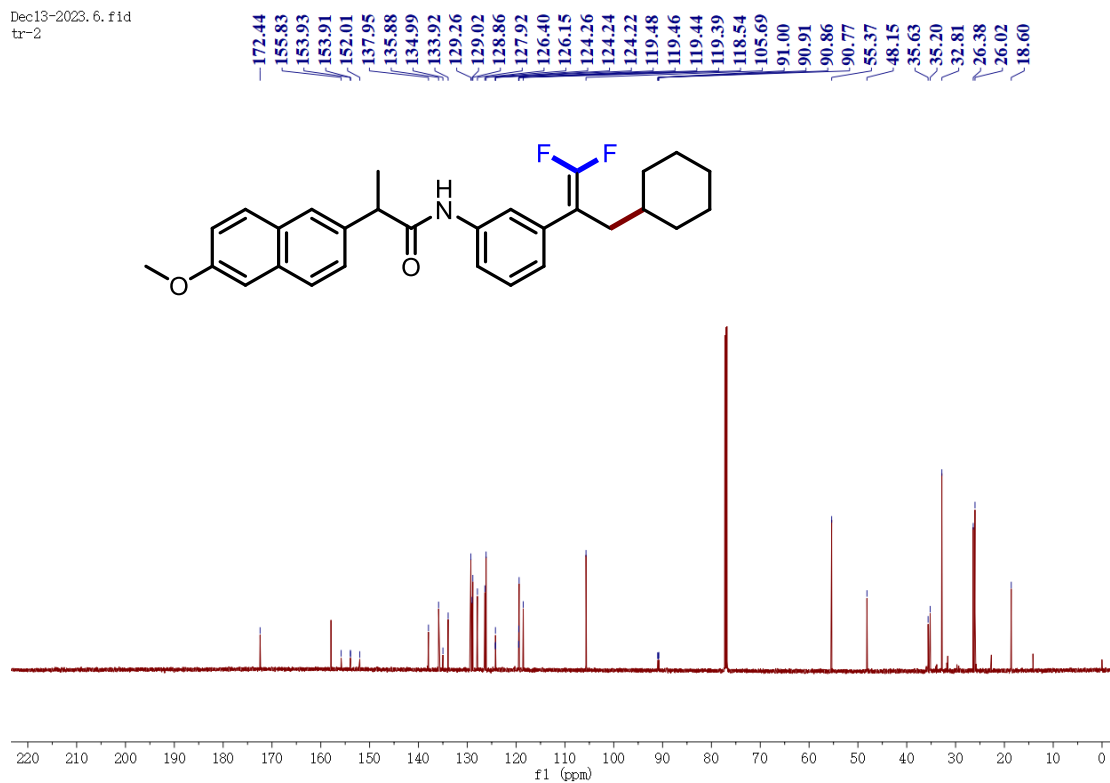
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **4b**.

Dec13-2023. 5. fid
tr-2



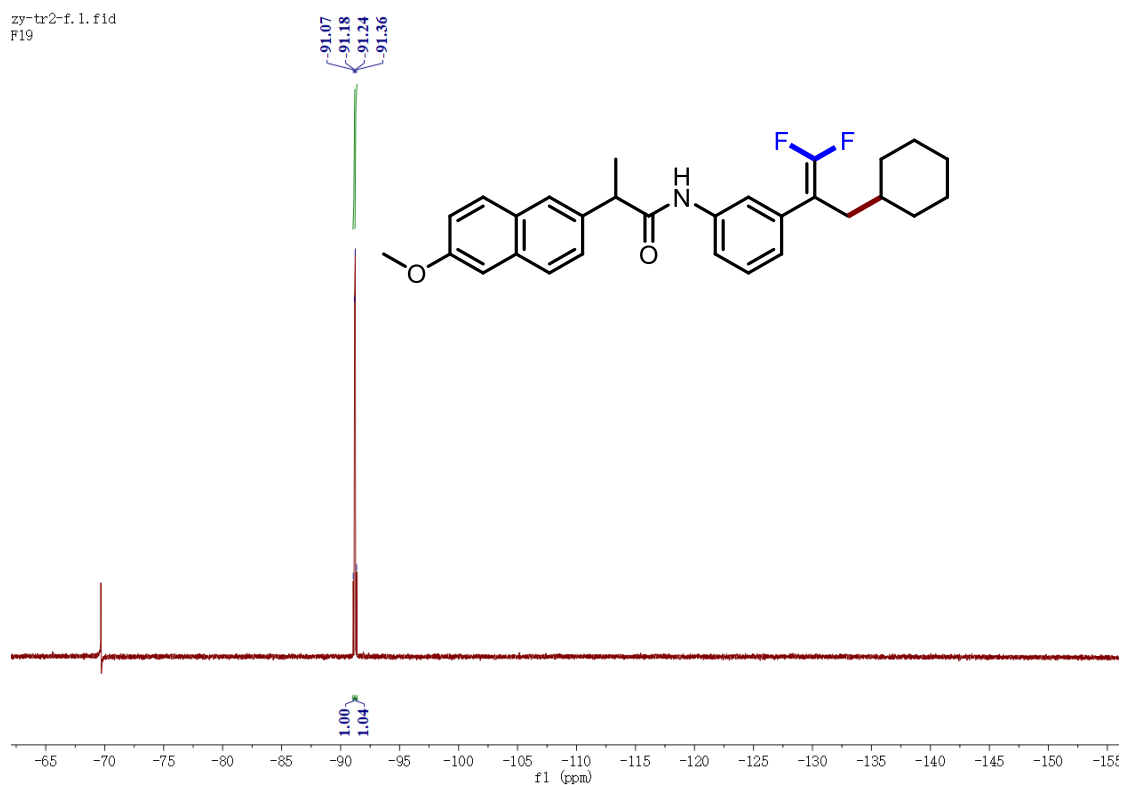
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound **4c**.

Dec13-2023. 6. f1d
tr-2



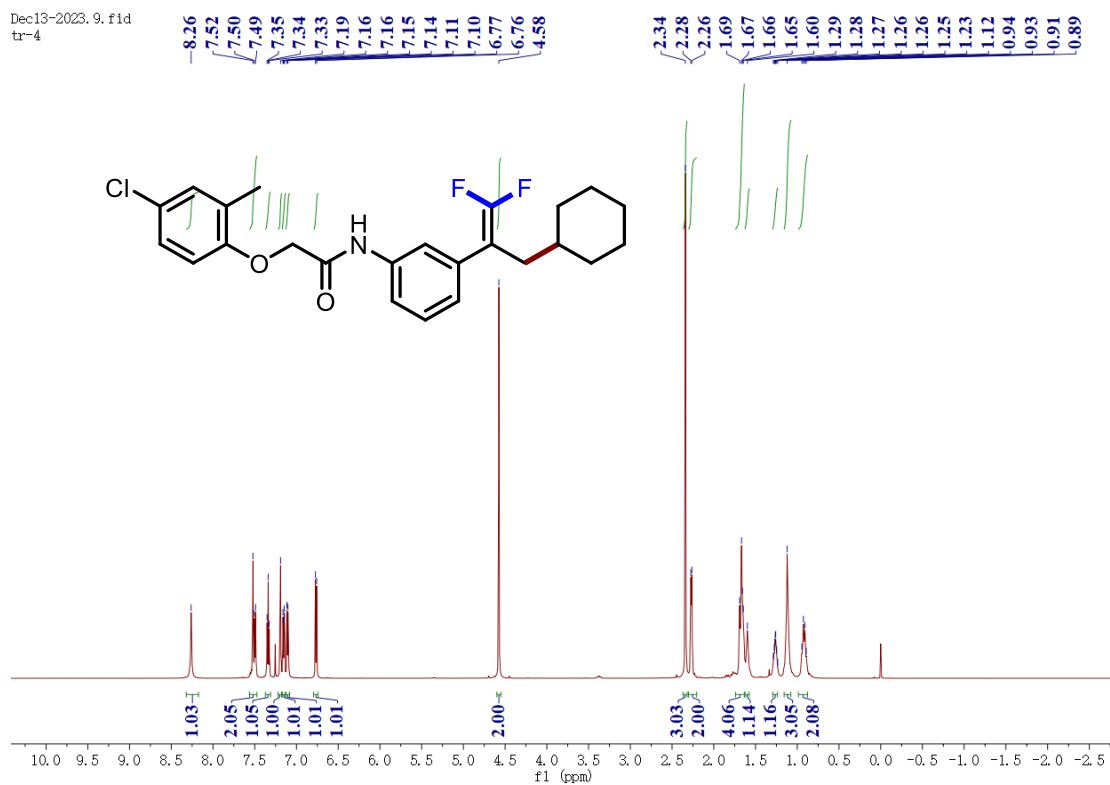
¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound **4c**.

zy-tr2-f. 1. f1d
F19



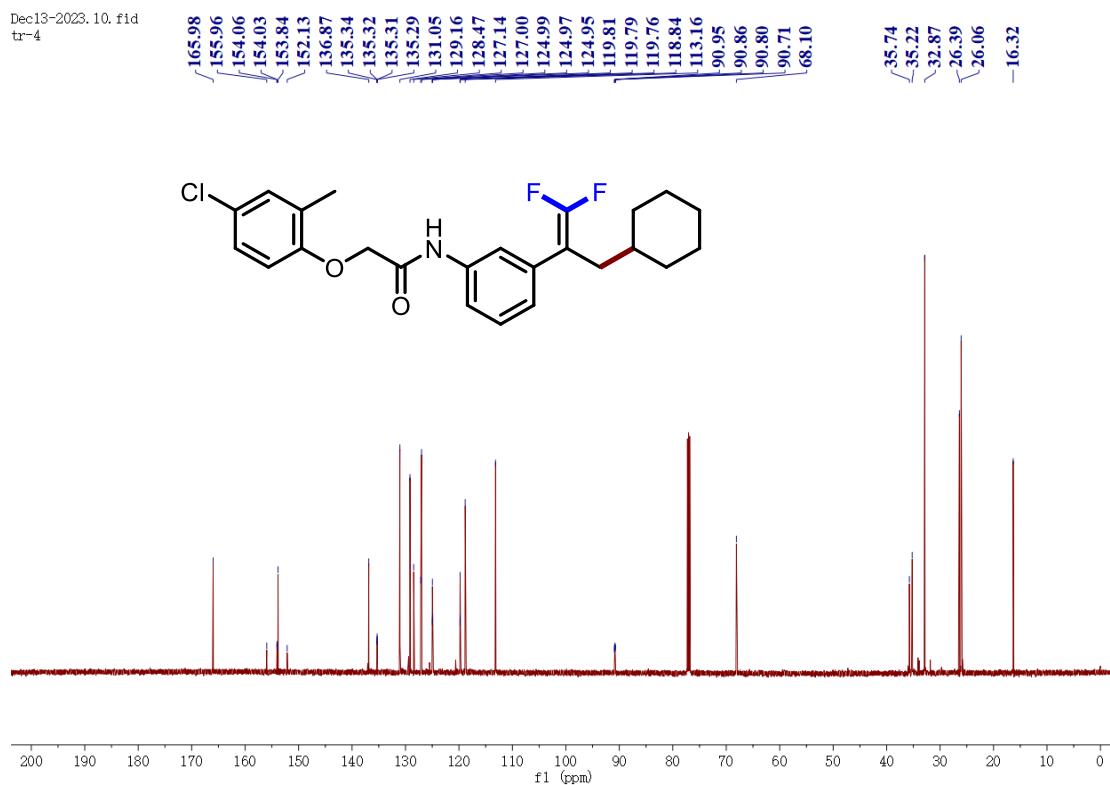
¹⁹F NMR (376 MHz, Chloroform-*d*) spectrum of compound **4c**.

Dec13-2023. 9. fid
tr-4



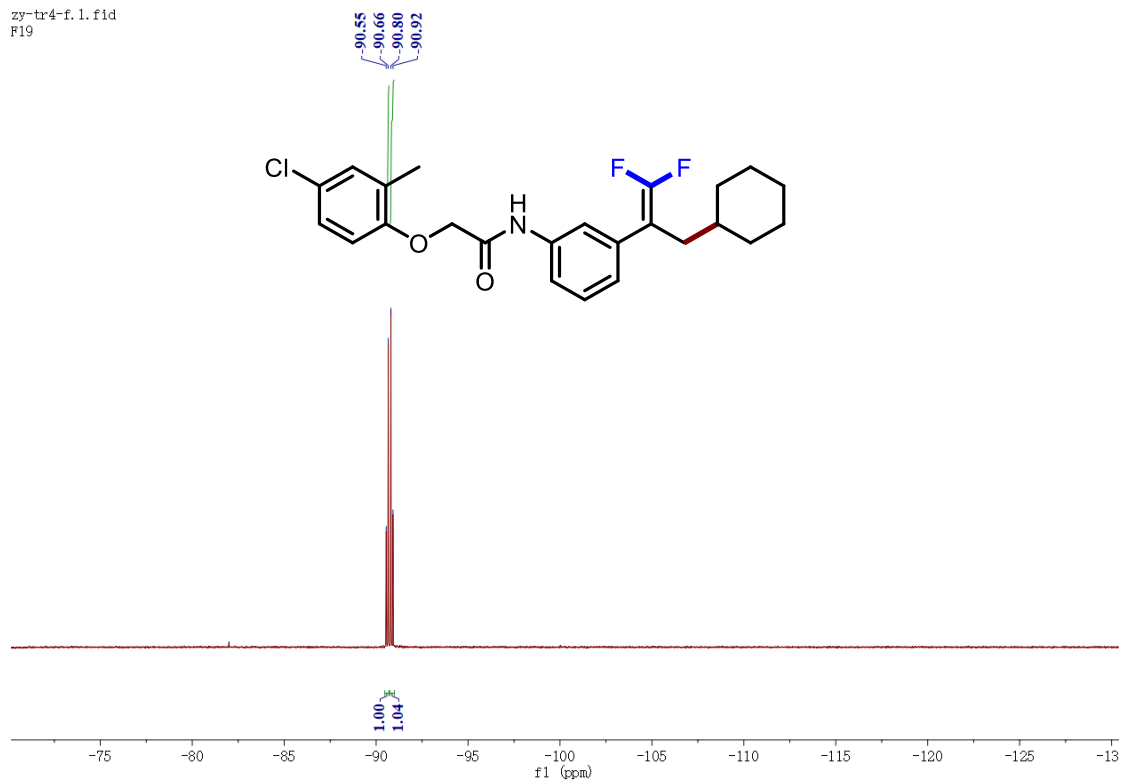
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 4d.

Dec13-2023. 10. fid
tr-4

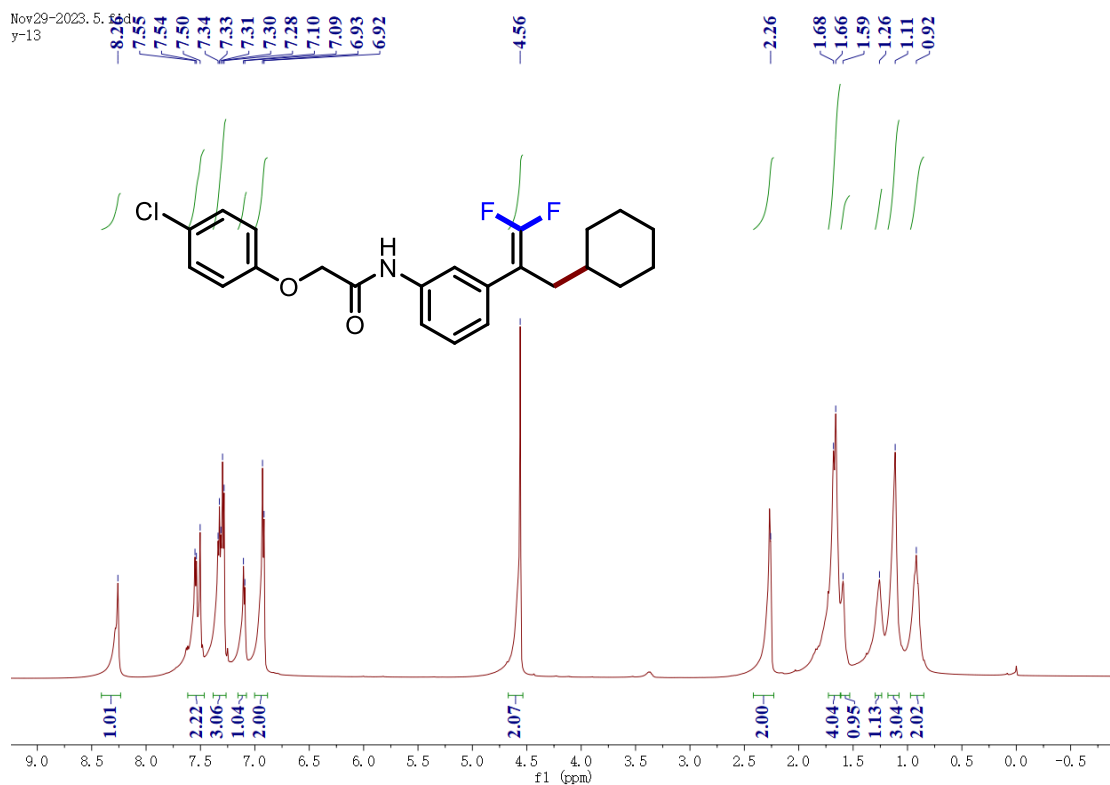


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 4d.

zy-tr4-f.1.fid
F19



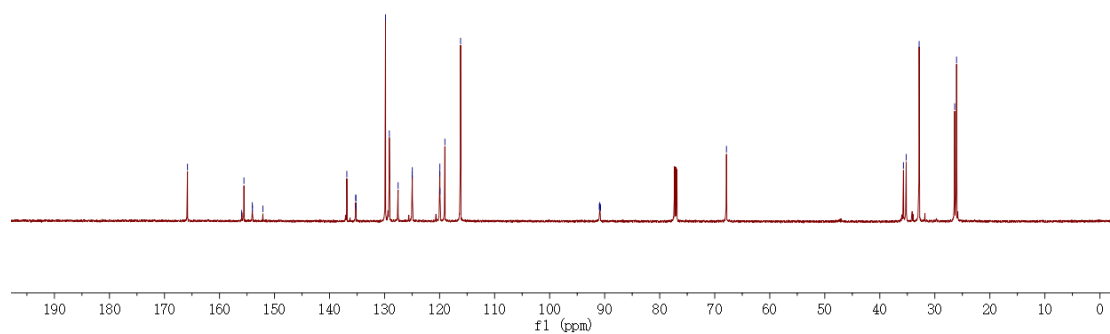
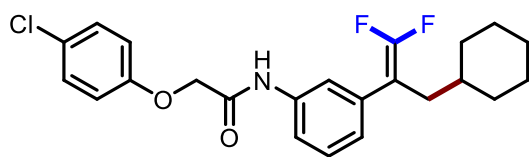
¹⁹F NMR (376 MHz, Chloroform-d) spectrum of compound 4d.



¹H NMR (600 MHz, Chloroform-d) spectrum of compound 4e.

Nov29-2023. 6. f1d
y-13-c

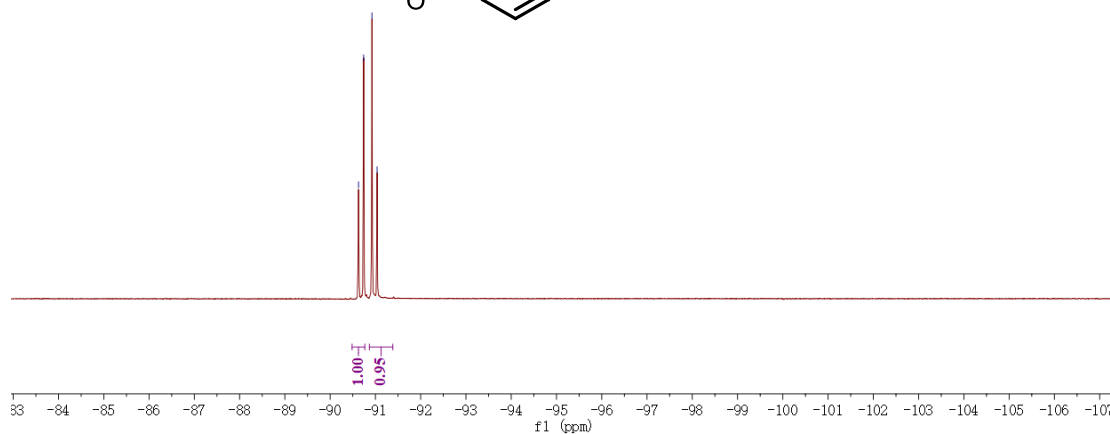
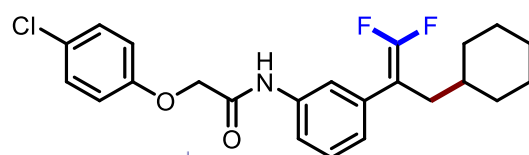
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129.82
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124.98
124.96
119.97
119.95
119.93
119.04
116.19
90.98
90.90
90.83
90.75
-67.87
35.71
35.20
32.85
26.39
26.05



^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **4e**.

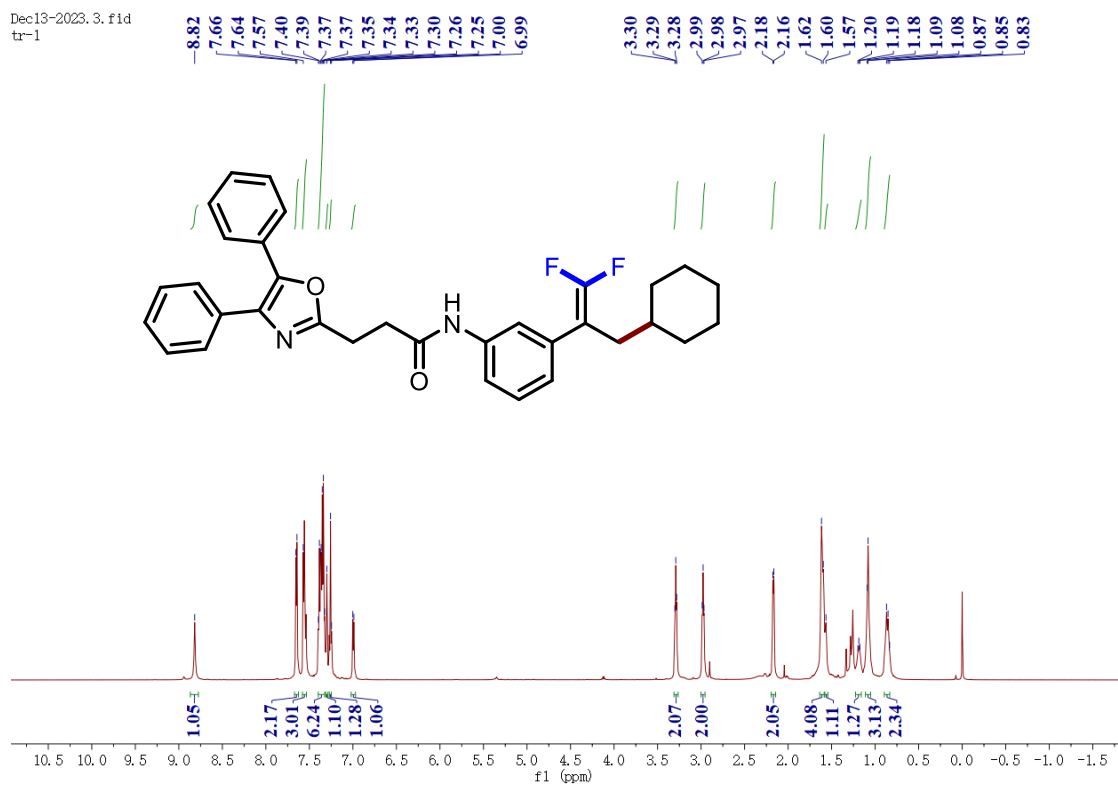
zy-y-13-f-1. 1. f1d
F19

90.63
90.74
90.92
91.04



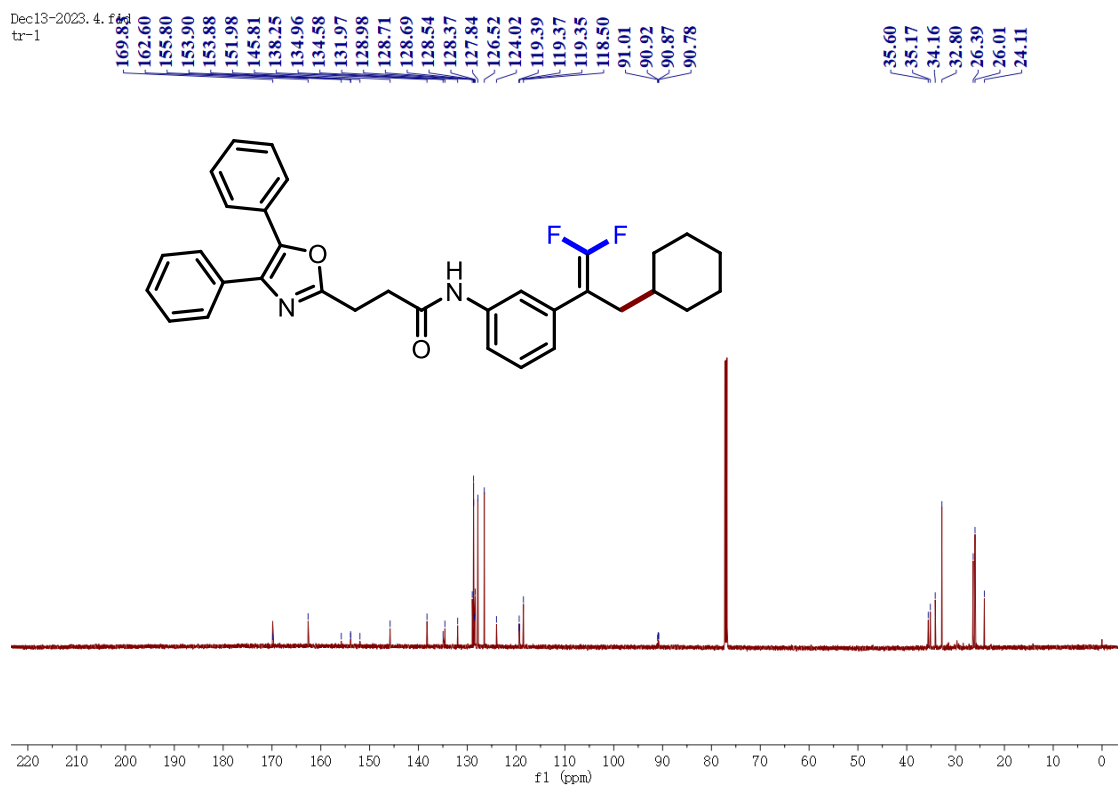
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **4e**.

Dec13-2023. 3. f1d
tr-1



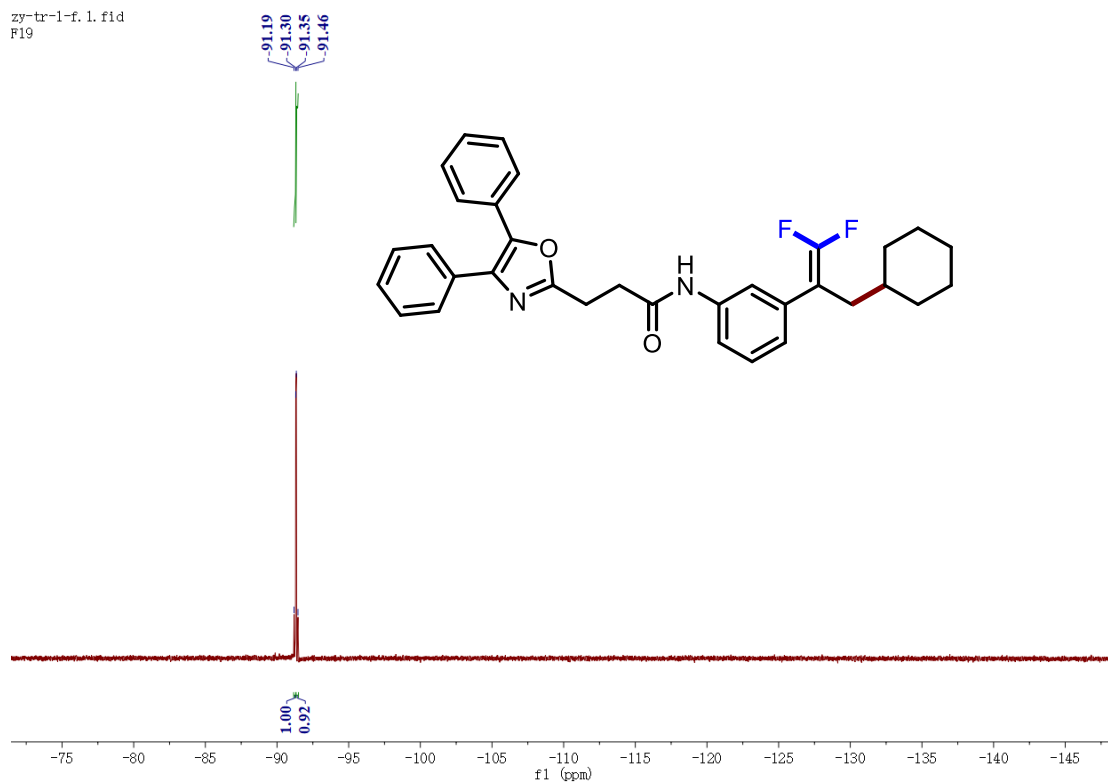
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 4f.

Dec13-2023. 4. f1d
tr-1

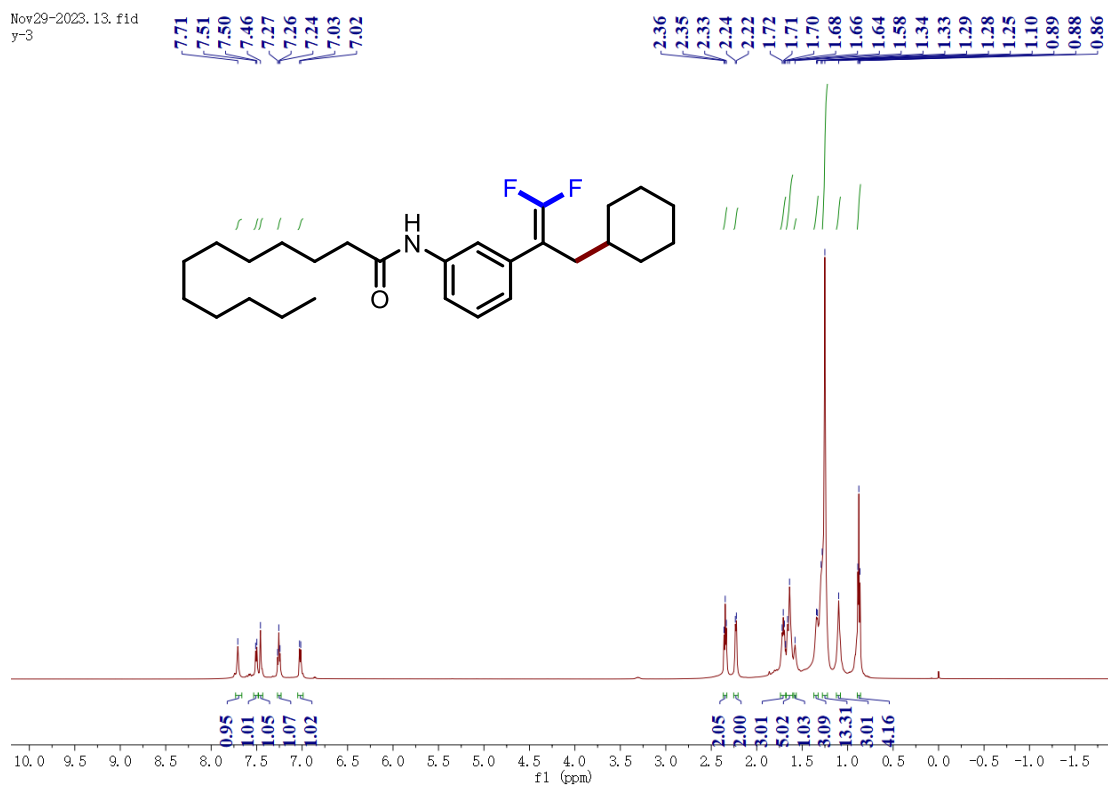


¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 4f.

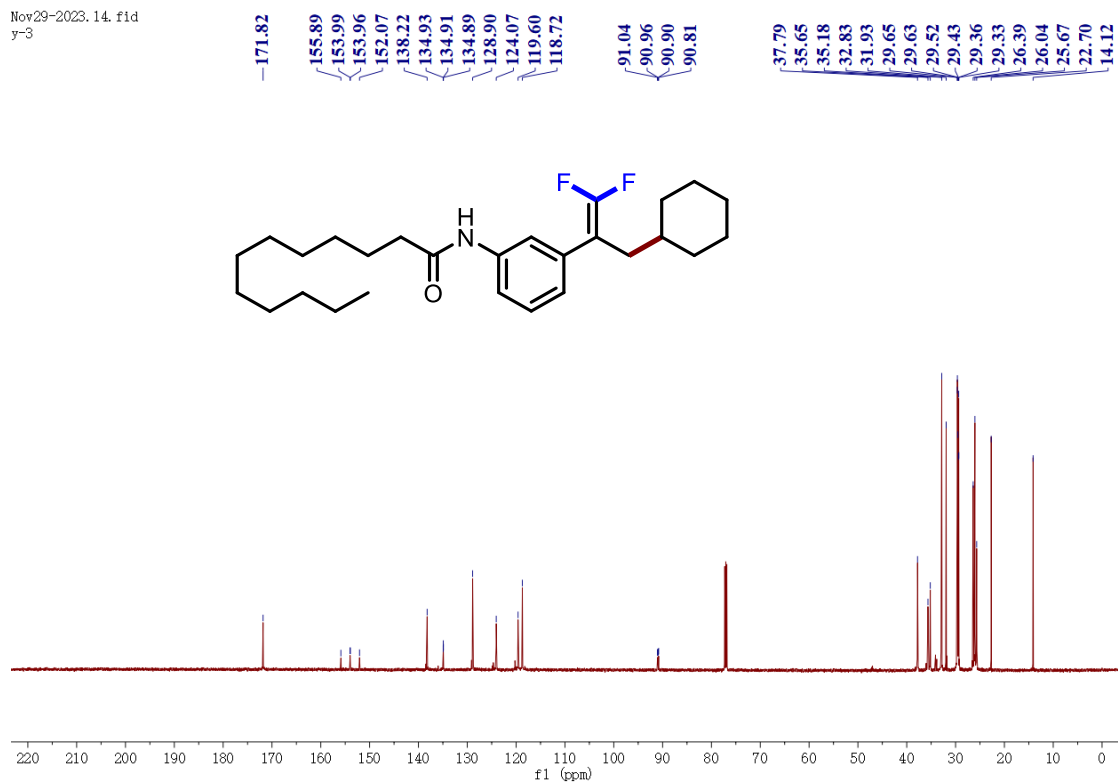
zy-tr-1-f. 1. fid
F19



Nov29-2023. 13. fid
y-3

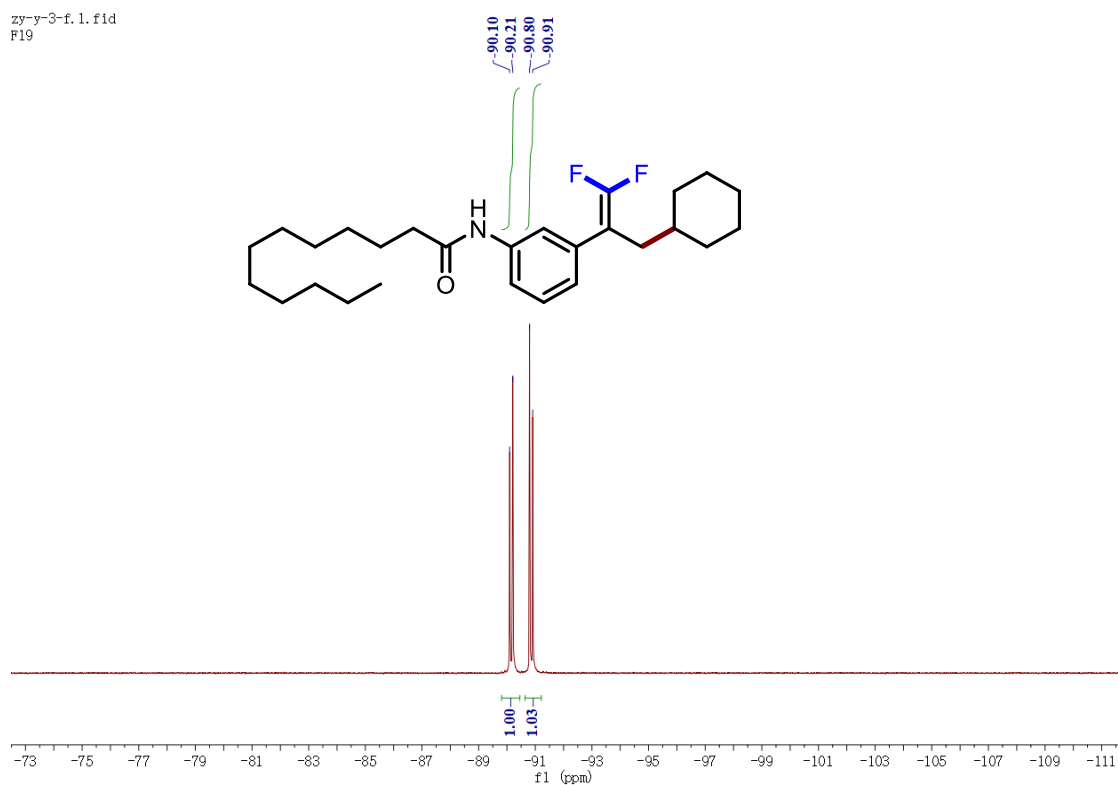


Nov29-2023. 14. fid
y-3



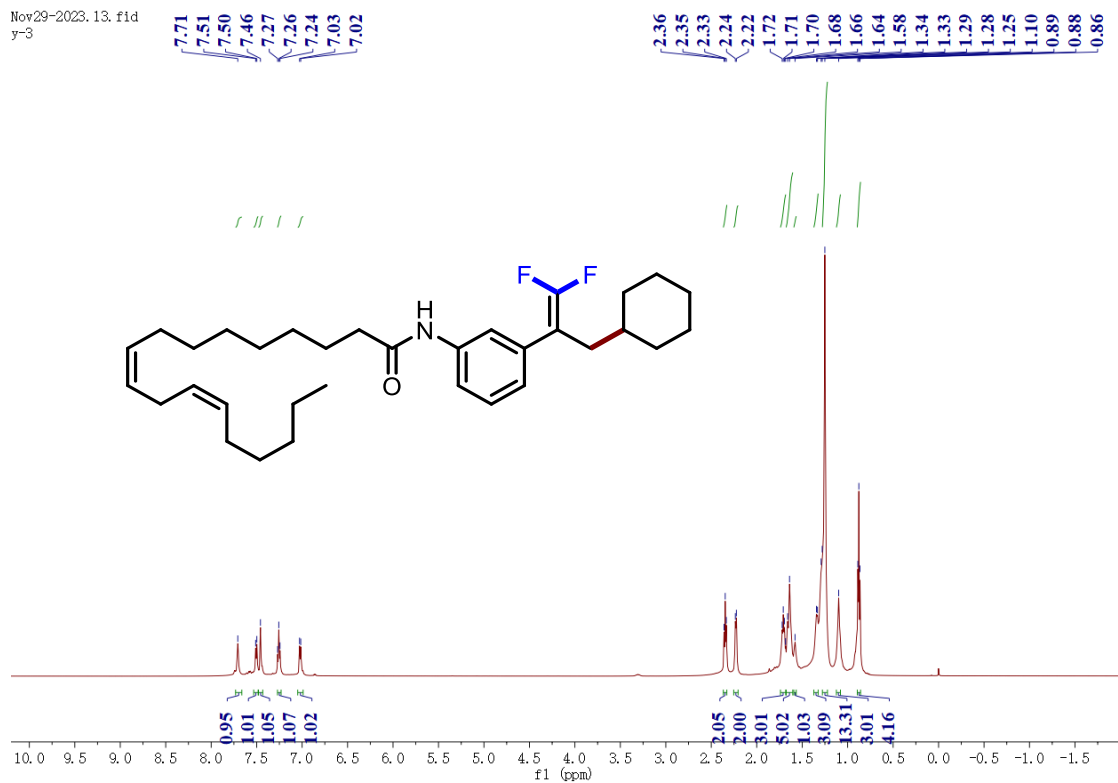
^{13}C NMR (150 MHz, Chloroform-*d*) spectrum of compound **4g**.

zy-y-3-f. 1. fid
F19



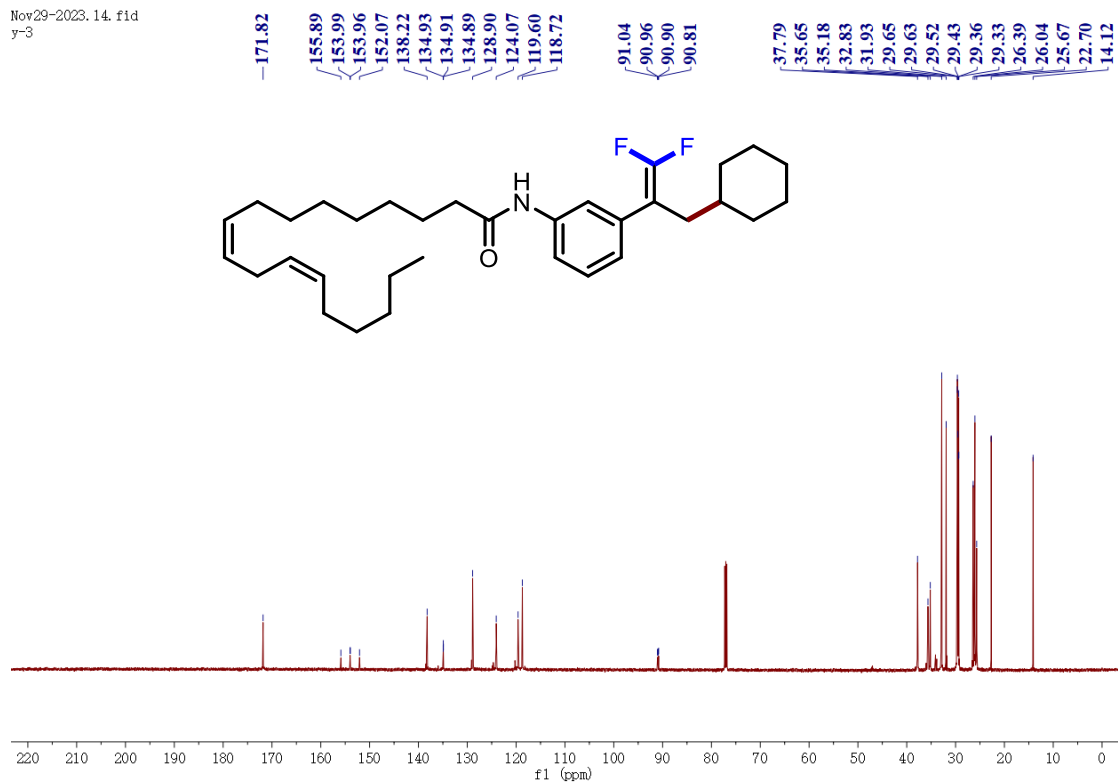
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **4g**.

Nov29-2023. 13. f1d
y-3



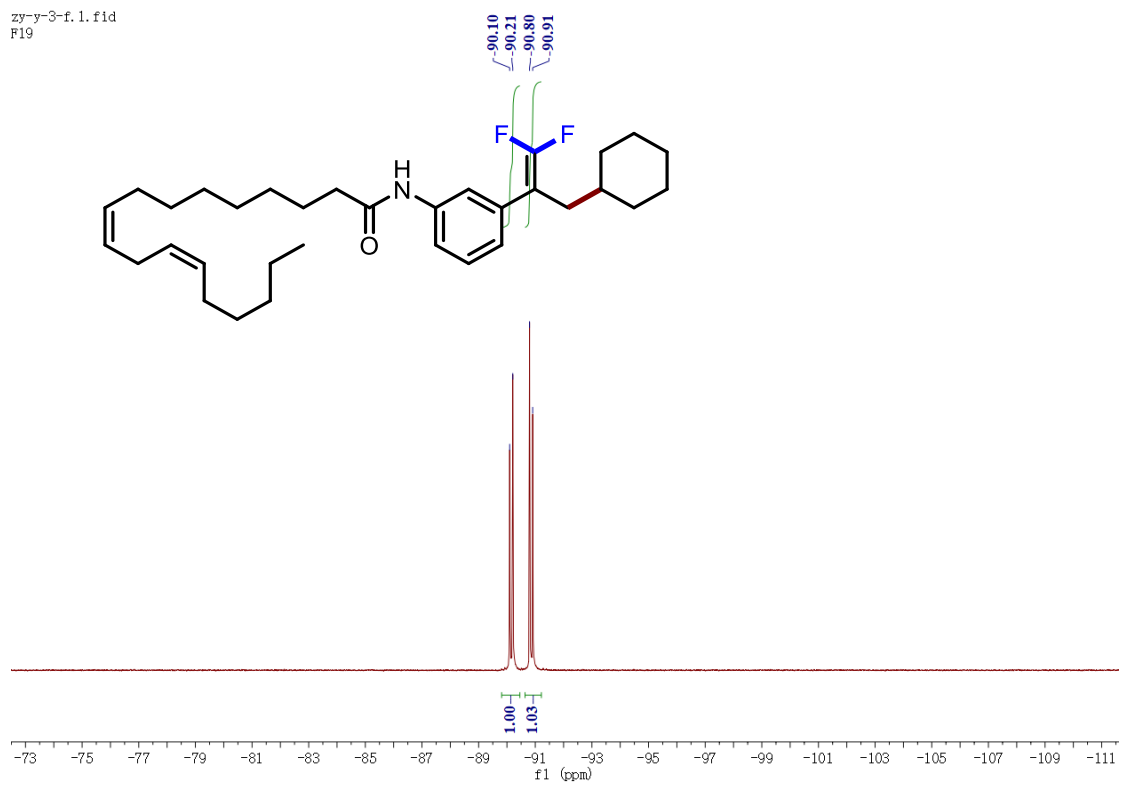
¹H NMR (600 MHz, Chloroform-*d*) spectrum of compound 4h.

Nov29-2023. 14. f1d
y-3



¹³C NMR (150 MHz, Chloroform-*d*) spectrum of compound 4h.

zy-y-3-f.1.fid
F19



^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of compound **4h**.