

Supporting Information

Difunctionalization of *gem*-Difluoroalkenes for Amination and Heteroarylation via Metal-Free Photocatalysis

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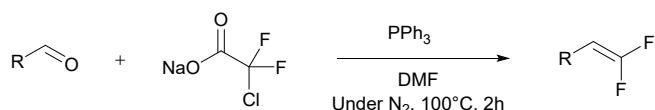
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1. General methods

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. The 30W LED was purchased from Taobao (<https://gpiled.taobao.com/>, manufacture: Shenzhen Star Sources Lighting Technology Co., Ltd). A clip fan was placed over the reaction vials to cool down the reaction system during the whole process of the reaction. The progress of all the reactions was monitored by Agilent HPLC-MS (1200-6110). All the compounds were purified by column chromatography. Chromatography was performed on silica gel (100–200 mesh). Nuclear magnetic resonance spectra were recorded on Brucker Avance III 400/500/600 NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Low-resolution mass spectra (LRMS) were recorded using Agilent HPLC-MS (1200-6110). High-resolution mass spectra (HRMS) were recorded on an Agilent 1290-6545 UHPLC-QTOF (ESI) mass spectrometer.

2. Experimental procedures

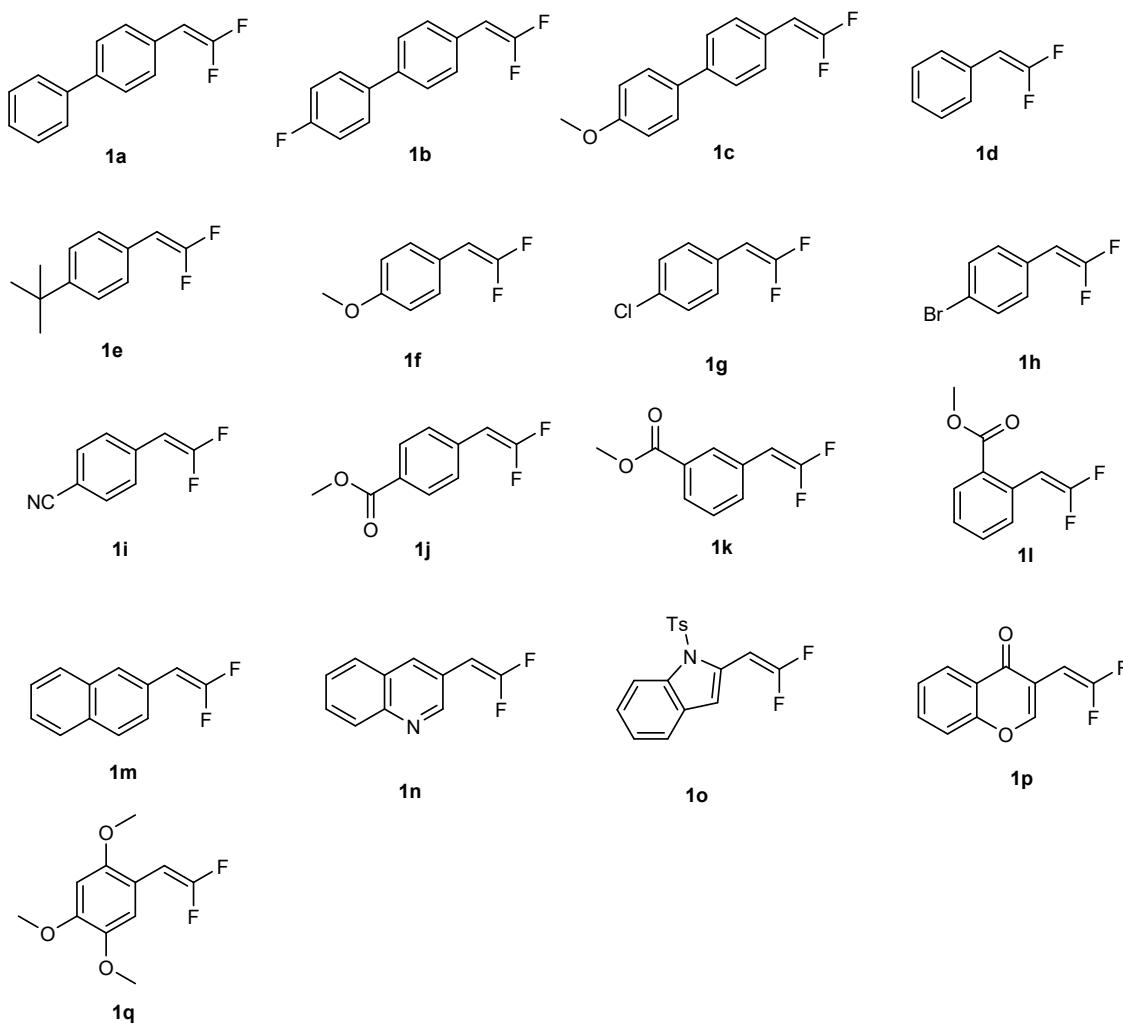
2.1. General procedure A for the preparation of *gem*-difluoroalkenes



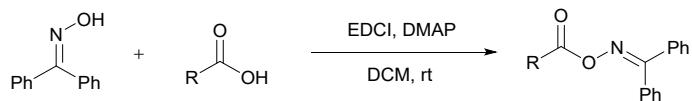
gem-Difluoroalkenes were prepared as reported procedure. Aldehyde (1.0 mmol, 1.0 eq.) and triphenylphosphine (1.2 mmol, 1.2 eq.) were added to a 25 mL two-neck flask equipped with a magnetic stirrer. Then 3 mL anhydrous DMF was added under nitrogen and the mixture was heated to 100 °C in an oil bath. Sodium difluorochloroacetate (1.5 mmol, 1.5 eq.) was dissolved in anhydrous 1mL DMF and added to the reaction solution, stirring was continued for 2 h at 100 °C. The reaction solution was then cooled to room temperature, 20 mL water and 10 × 3 mL ethyl acetate were added and the layers were separated. The organic phase was concentrated in vacuo and purified by column chromatography on silica gel to give the desired product.

gem-Difluoroalkenes **1a-1o** are reported compounds and the NMR data are in accordance with the literature.^{1, 2}

List of all *Gem*-difluoroalkenes:



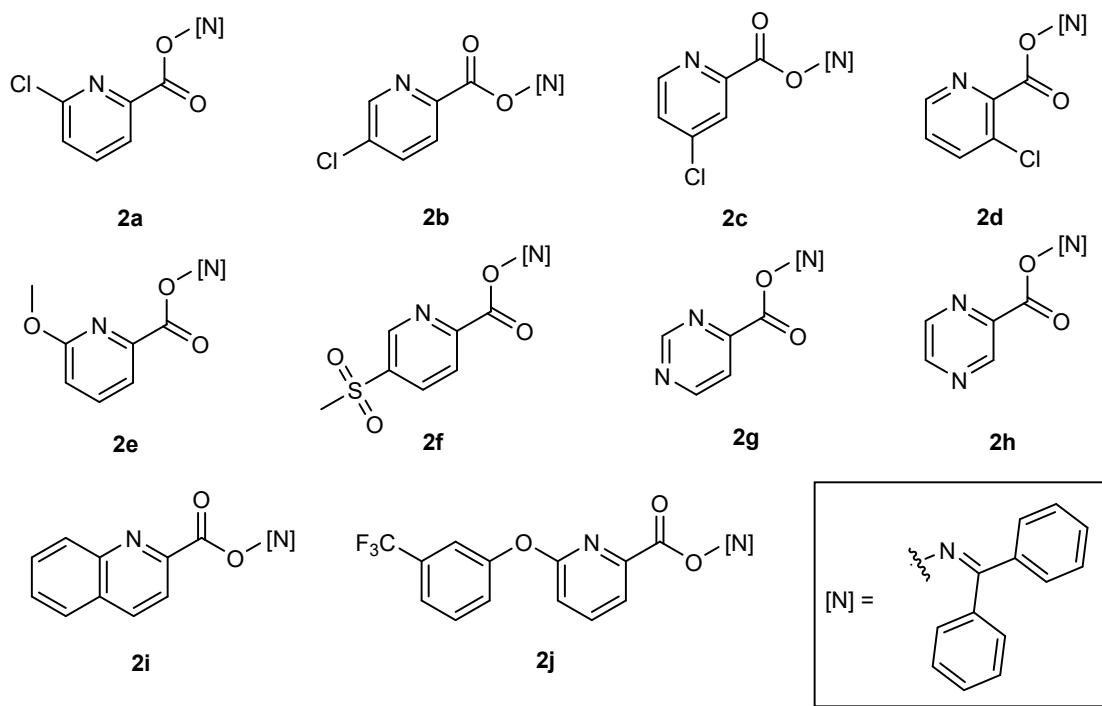
2.2. General procedure B for the preparation of oxime esters



Oxime esters were prepared as reported procedure. To a solution of ketoxime (2.0 mmol, 1.0 eq.) and carboxylic acid (2.0 mmol, 2.0 eq.) in 10 mL CH₂Cl₂, DMAP (0.2 mmol, 0.2 eq.) and EDCI (5.0 mmol, 2.5 eq.) were added. The mixture was stirred at room temperature under inert atmosphere until the reaction was complete as observed from HPLC-MS monitoring. Then 20 mL water was added and the CH₂Cl₂ layer was separated, dried over anhydrous Na₂SO₄ and concentrated. The crude was purified by silica gel column chromatography (petroleum ether / ethylacetate as eluent) to give the corresponding compound.

Oxime esters **2a**, **2c**, **2h** and **2i** are reported compounds and the NMR data are in accordance with the literature.³

List of all oxime esters:



2.3. Optimization of the reaction conditions

Table S1 Screening of photocatalysts and solvent

Entry	Photocatalyst	Solvent	Yield (%) ^a
1	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆)	EtOAc	26
2	<i>fac</i> -Ir(dFppy) ₃	EtOAc	20
3	4CzIPN	EtOAc	30
4	Thioxanthone	EtOAc	46
5	[Ru(bpy) ₃](PF ₆) ₂	EtOAc	n.d.
6	Mes-Acr+BF4-	EtOAc	n.d.
7	[Ir(dF(CF ₃) ₂ ppy) ₂ (bpy)]PF ₆	EtOAc	24
8	Thioxanthone	DMSO	62
9	Thioxanthone	DMF	13
10	Thioxanthone	MeCN	40
11	Thioxanthone	THF	Trace
12	Thioxanthone	DCE	23

^aIsolated yields

Table S2 Screening of wavelength

Entry	Wavelength	Yield (%) ^a
1	405	62
2	440	trace
3	365	65

^aIsolated yields**Table S3** Screening of substrate ratio and concentration

Entry	1a / 2a (mmol)	Concentration	Yield (%) ^a
1	0.15 / 0.15	0.2 M	65
2	0.15 / 0.15	0.1 M	59
3	0.15 / 0.15	0.4 M	52
4	0.15 / 0.15	0.05 M	40
5	0.15 / 0.30	0.2 M	69
6	0.15 / 0.45	0.2 M	71
7	0.30 / 0.15	0.2 M	56

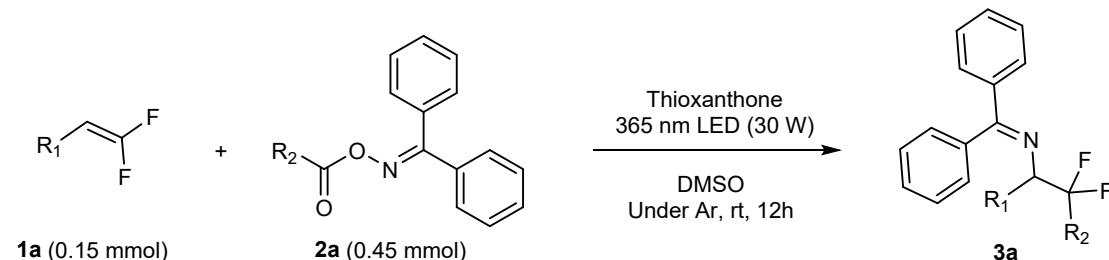
^aIsolated yields**Table S4** Control experiment

Entry	Variation from standard conditions	Yield (%) ^a
1	none	71
2	4h	45
3	8h	67
4	16h	68

5	In the dark	n.d.
6	In the air	trace
7	no catalyst	trace

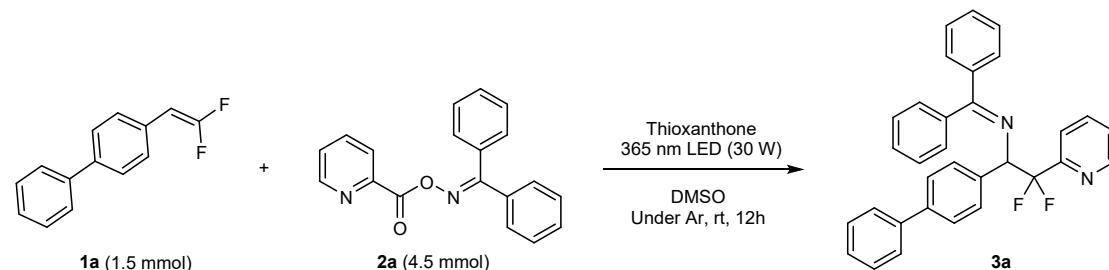
^aIsolated yields

2.4. General procedure C for the difunctionalization of *gem*-difluoroalkenes



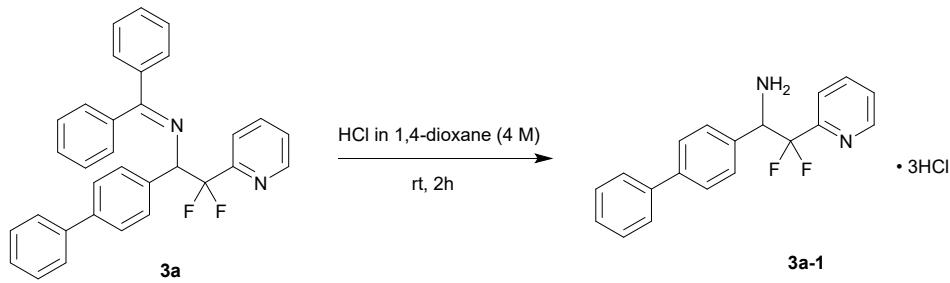
To an oven dried 4 mL vial with a magnetic stir bar was added thioxanthone (0.008 mmol, 5 mol%), oxime esters (0.45 mmol, 3.0 eq.), *gem*-difluoroalkenes (0.15 mmol, 1.0 eq.), and dry DMSO (0.75 mL, 0.2 M). The vial was purged by argon for a short time (about 2 min). Then the vial was capped and stirred under irradiation with a 365 nm LED (30 W, distance app. 3 cm) for 12 hours. The reaction was kept under room temperature with a fan. After irradiation, the reaction mixture was transferred to a 25 mL round bottom flask with the aid of 3 × 3 mL DCM and 0.5 mL Et₃N. The solvent was removed under reduced pressure, and then the residue was purified by column chromatography on silica gel ethyl with acetate/petroleum ether (pre-basified with 0.3 % Et₃N in petroleum ether) to afford the desired products.

2.5. Scale-up reaction



To an oven dried 20 mL vial with a magnetic stir bar was added thioxanthone (0.08 mmol, 5 mol%), oxime ester **2a** (4.5 mmol, 3.0 eq.), *gem*-difluoroalkene **1a** (1.5 mmol, 1.0 eq.), and dry DMSO (7.5 mL, 0.2 M). The vial was purged by argon for a short time (about 2 min). Then the vial was capped and stirred under irradiation with a 365 nm LED (30 W, distance app. 3 cm) for 12 hours. The reaction was kept under room temperature with a fan. After irradiation, the reaction mixture was transferred to a 100 mL round bottom flask with the aid of 15 × 3 mL DCM and 3 mL Et₃N. The solvent was removed under reduced pressure, and then the residue was purified by column chromatography on silica gel ethyl with 5% acetate/petroleum ether (pre-basified with 0.3 % Et₃N in petroleum ether) to afford **3a** (468 mg, 60% yield).

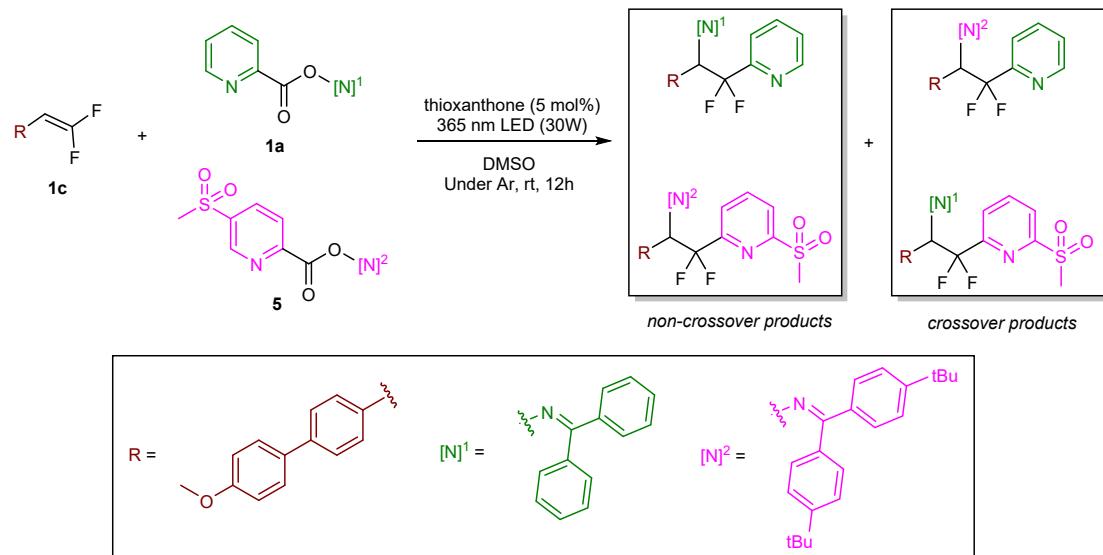
2.6. Benzophenone removal reaction



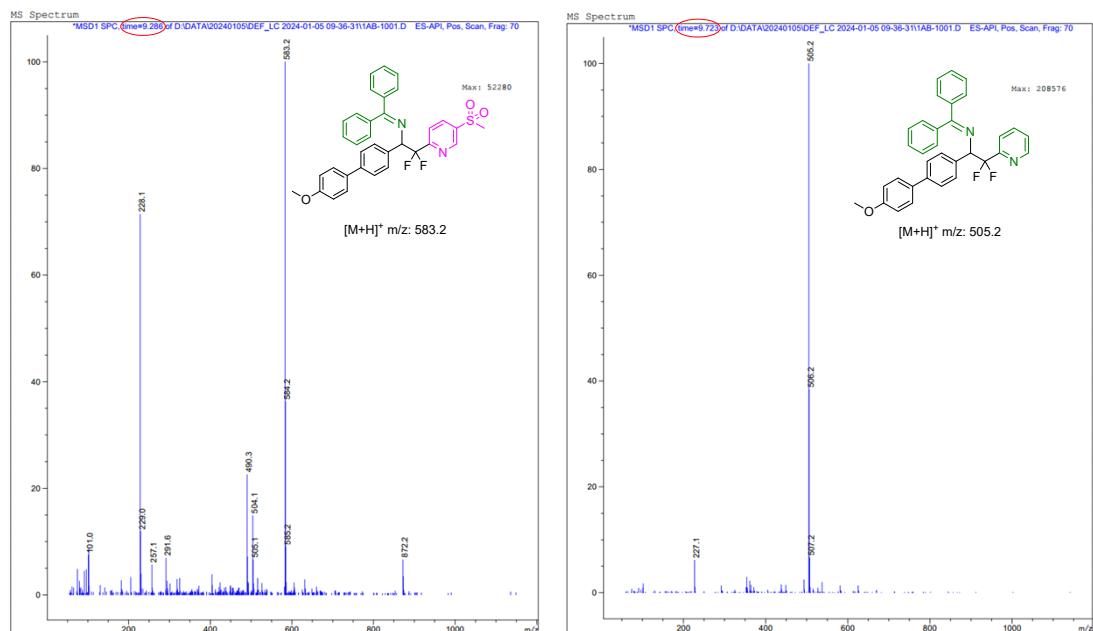
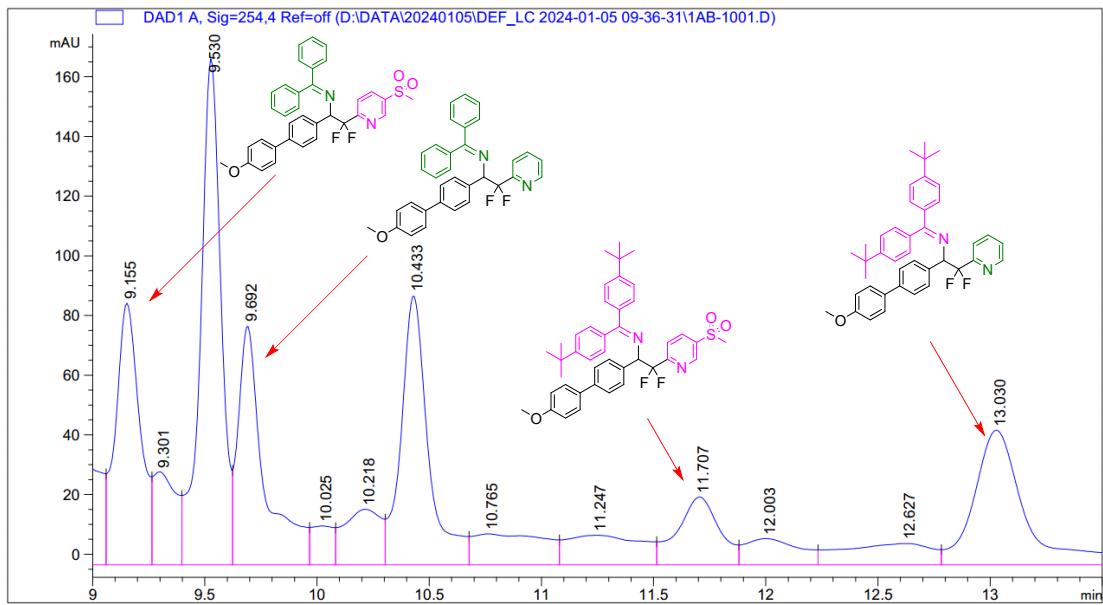
To a 25 mL pear-shaped flask equipped with a magnetic stirrer was added **3a** (0.5 mmol), 4 mL hydrogen chloride in 1,4-dioxane (4 M). The reaction mixture was stirred at room temperature for 2 h and filtered. The residue was washed with 20 mL DCM and dried to give product as an orange solid (192 mg, yield 91%).

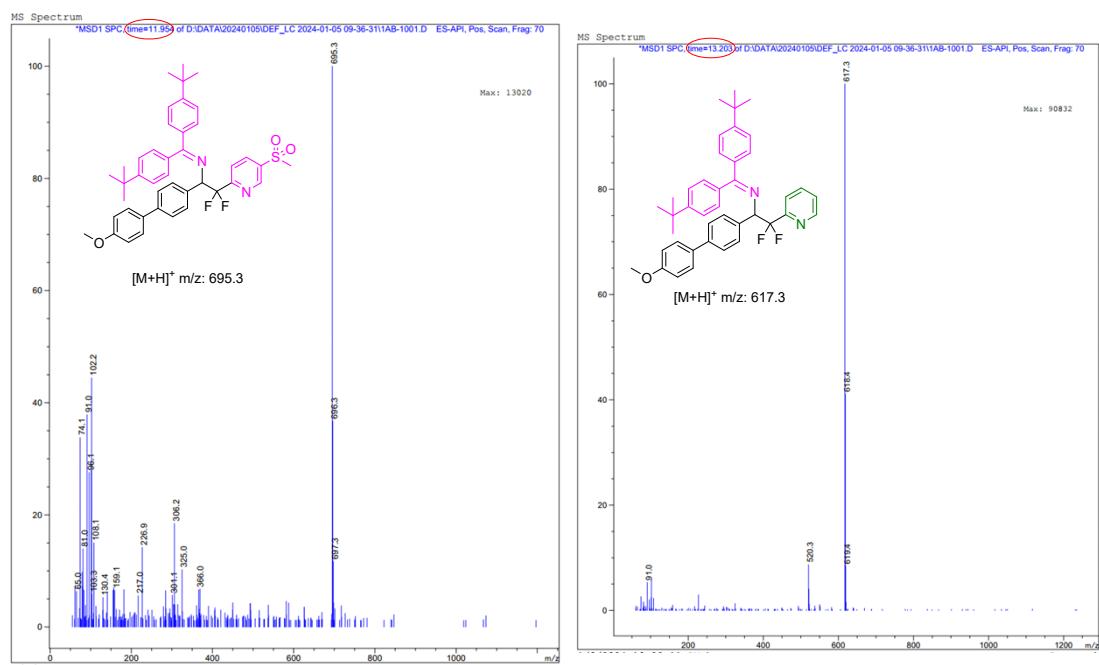
3. Mechanistic studies

3.1. Radical crossover experiment



To an oven dried 4 mL vial with a magnetic stir bar was added thioxanthone (0.016 mmol, 5 mol%), oxime esters **1a** (0.45 mmol, 1.5 eq.), oxime esters **5** (0.45 mmol, 1.5 eq.), *gem*-difluoroalkenes (0.30 mmol, 1.0 eq.), and dry DMSO (1.50 mL, 0.2 M). The vial was purged by argon for a short time (about 1 min). Then the vial was capped and stirred under irradiation with a 365 nm LED (30 W, distance app. 3 cm) for 12 hours. The reaction was kept under room temperature with a fan. Then the crude reaction mixture was analyzed by HPLC-MS.



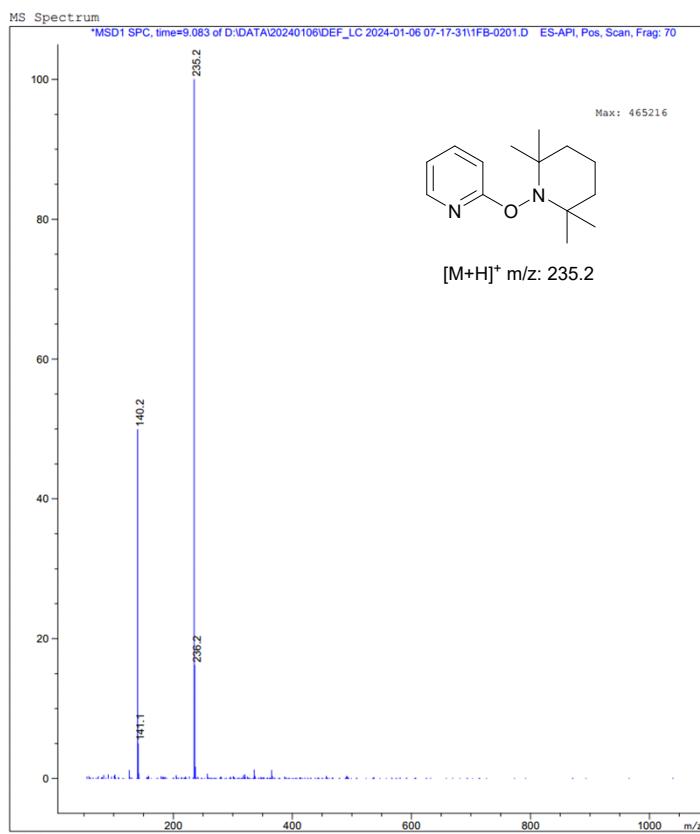


3.2. Radical trapping experiments

TEMPO/AIBN trapping experiments were conducted under standard condition following General procedure A using 3.0 equiv. TEMPO/AIBN as an additive. No trace of products was observed as determined from ESI-MS.

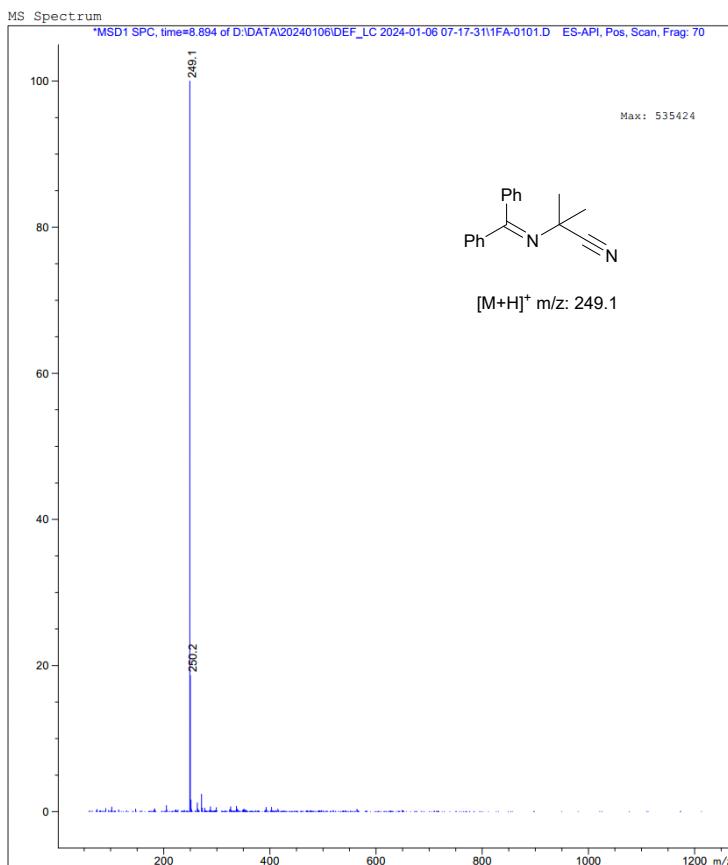
For TEMPO trapping experiment, the mass spectrum showed a peak corresponding to the coupled product between TEMPO radical and pyridyl radical.





For AIBN trapping experiment, the mass spectrum showed a peak corresponding to the coupled product between AIBN radical and imine radical.

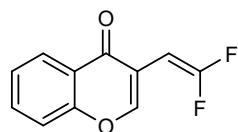




1. S.-S. Yan, D.-S. Wu, J.-H. Ye, L. Gong, X. Zeng, C.-K. Ran, Y.-Y. Gui, J. Li and D.-G. Yu, ACS Catalysis, 2019, 9, 6987-6992.
2. H. J. Tang, L. Z. Lin, C. Feng and T. P. Loh, Angew Chem Int Ed Engl, 2017, 56, 9872-9876.
3. X. K. Qi, M. J. Zheng, C. Yang, Y. Zhao, L. Guo and W. Xia, J Am Chem Soc, 2023, 145, 16630-16641.

Characterization data of products

3-(2,2-difluorovinyl)-4H-chromen-4-one (**1p**)



General procedure A was followed to obtain **1p** (112 mg, 54%) as a white solid.

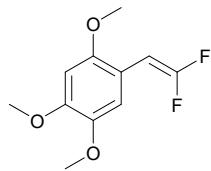
¹H NMR (600 MHz, CDCl₃) δ 8.25 – 8.21 (m, 1H), 8.14 (s, 1H), 7.70 – 7.67 (m, 1H), 7.47 – 7.40 (m, 2H), 5.60 (dd, *J* = 28.2, 2.2 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 175.43 (d, *J* = 2.4 Hz), 156.47 (dd, *J* = 294.4, 290.3 Hz), 156.14, 153.20 (dd, *J* = 12.3, 2.6 Hz), 134.04, 131.68 (d, *J* = 3.0 Hz), 126.28, 125.55, 123.28, 118.29, 71.86 (dd, *J* = 33.9, 14.6 Hz);

¹⁹F NMR (471 MHz, CDCl₃) δ -80.15, -81.46.

HPLC-MS (ESI) m/z: 209.2 [M+H]⁺.

1-(2,2-difluorovinyl)-2,4,5-trimethoxybenzene (1q**)**



General procedure A was followed to obtain **1q** (96 mg, 42%) as a white solid.

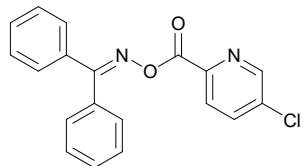
¹H NMR (400 MHz, CDCl₃) δ 7.01 (s, 1H), 6.51 (s, 1H), 5.59 (dd, *J* = 21.7, 9.9 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 155.91 (dd, *J* = 293.9, 287.7 Hz), 151.00 (dd, *J* = 4.3, 2.6 Hz), 148.98, 143.25, 111.77 (dd, *J* = 8.4, 2.8 Hz), 110.75 (t, *J* = 3.8 Hz), 97.58, 76.13 (dd, *J* = 27.9, 16.2 Hz), 56.76, 56.62, 56.17;

¹⁹F NMR (471 MHz, CDCl₃) δ -85.34, -85.39.

HPLC-MS (ESI) m/z: 231.2 [M+H]⁺.

diphenylmethanone O-(5-chloropicolinoyl) oxime (2b**)**



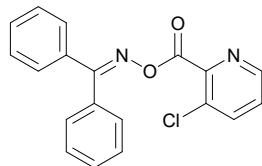
General procedure B was followed to obtain **2b** (471 mg, 70%) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 8.66 (d, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.67 – 7.64 (m, 3H), 7.50 – 7.46 (m, 4H), 7.43 – 7.37 (m, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 166.85, 161.62, 149.43, 145.02, 136.70, 136.01, 134.45, 132.54, 131.34, 130.03, 129.39, 129.08, 128.57, 128.40, 125.93.

HPLC-MS (ESI) m/z: 337.2 [M+H]⁺.

diphenylmethanone O-(3-chloropicolinoyl) oxime (2d**)**



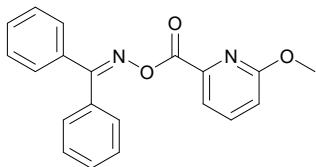
General procedure B was followed to obtain **2d** (416 mg, 62%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.52 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.48 – 7.31 (m, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 166.68, 162.74, 147.52, 138.36, 134.65, 132.37, 131.27, 130.83, 129.93, 129.42, 129.29, 128.55, 128.27, 126.37.

HPLC-MS (ESI) m/z: 337.2 [M+H]⁺.

diphenylmethanone O-(6-methoxypicolinoyl) oxime (2e**)**



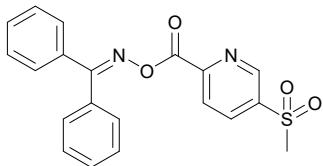
General procedure B was followed to obtain **2e** (452 mg, 68%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.51 – 7.44 (m, 6H), 7.39 (t, *J* = 7.5 Hz, 2H), 6.87 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.80 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 165.79, 163.66, 162.66, 144.53, 139.01, 134.88, 132.85, 131.08, 129.67, 129.41, 129.35, 128.52, 128.18, 118.98, 115.63, 53.62

HPLC-MS (ESI) m/z: 333.2 [M+H]⁺.

diphenylmethanone O-(5-(methylsulfonyl)picolinoyl) oxime (**2f**)



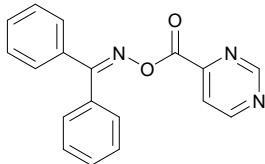
General procedure B was followed to obtain **2e** (456 mg, 60%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 9.21 (d, *J* = 1.9 Hz, 1H), 8.29 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.52 – 7.47 (m, 4H), 7.45 – 7.39 (m, 4H), 3.11 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 167.45, 161.02, 151.19, 148.92, 139.47, 136.78, 134.24, 132.35, 131.57, 130.22, 129.45, 129.09, 128.67, 128.49, 125.25, 44.84.

HPLC-MS (ESI) m/z: 381.2 [M+H]⁺.

diphenylmethanone O-pyrimidine-4-carbonyl oxime (**2g**)



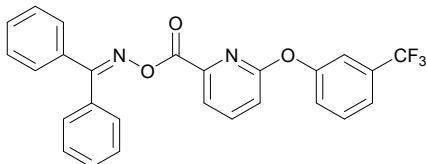
General procedure B was followed to obtain **2g** (316 mg, 52%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 1H), 8.89 (d, *J* = 5.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 4.8 Hz, 1H), 7.54 – 7.46 (m, 6H), 7.44 – 7.37 (m, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 166.95, 160.75, 159.07, 158.64, 153.49, 133.70, 131.77, 131.05, 129.71, 128.93, 128.54, 128.14, 127.97, 120.44.

HPLC-MS (ESI) m/z: 304.2 [M+H]⁺.

diphenylmethanone O-(6-(3-(trifluoromethyl)phenoxy)picolinoyl) oxime (**2j**)



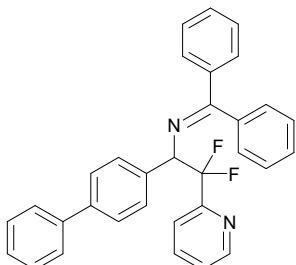
General procedure B was followed to obtain **2j** (509 mg, 55%) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.77 (m, 1H), 7.69 (d, *J* = 6.9 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.40 – 7.35 (m, 4H), 7.34 (d, *J* = 6.9 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 166.30, 162.18, 153.96, 145.36, 140.59, 134.87, 132.28, 132.03 (q, *J* = 32.7 Hz), 131.14, 130.02, 129.96, 129.45, 129.43, 128.53, 128.09, 124.29, 123.82 (q, *J* = 272.4 Hz), 121.32 (q, *J* = 3.6 Hz), 121.16, 117.82 (q, *J* = 3.6 Hz), 116.37.

HPLC-MS (ESI) m/z: 463.2 [M+H]⁺.

N-(1-([1,1'-biphenyl]-4-yl)-2,2-difluoro-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3a**)



General procedure C was followed to obtain **3a** (51 mg, 71%) as a yellow solid. m.p. 140–142 °C.
IR (KBr, *v*, cm⁻¹) 1630 (C=N), 1280 (C-F).

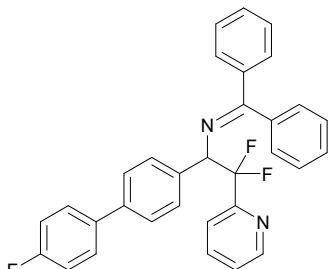
¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 4.5 Hz, 1H), 7.75 (td, *J* = 7.7, 1.4 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.57 – 7.49 (m, 4H), 7.47 – 7.27 (m, 12H), 5.28 (dd, *J* = 18.0, 7.6 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 170.98, 154.44 (dd, *J* = 31.0, 25.3 Hz), 149.24, 141.02, 140.76, 139.53, 136.69, 136.53, 136.01, 130.52, 129.82, 128.86, 128.39, 128.11, 127.73, 127.36, 127.22, 126.87, 124.47, 121.74, 119.64 (dd, *J* = 251.6, 245.8 Hz), 69.85 (dd, *J* = 29.8, 22.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -102.08 (d, *J* = 249.2 Hz), -115.03 (d, *J* = 245.4 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₃₂H₂₄F₂N₂, 475.1980; found 475.1981.

N-(2,2-difluoro-1-(4'-fluoro-[1,1'-biphenyl]-4-yl)-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3b**)



General procedure C was followed to obtain **3b** (52 mg, 70%) as a yellow solid. m.p. 145–147 °C.
¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 4.6 Hz, 1H), 7.75 (td, *J* = 7.8, 1.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.52 (m, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.27 (m, 9H), 7.11 (t, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 6.8 Hz, 2H), 5.27 (dd, *J* = 18.0, 7.5 Hz, 1H).

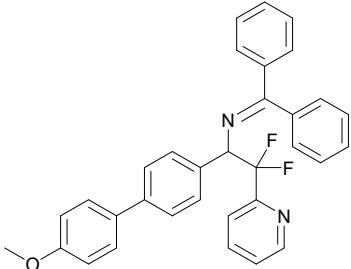
¹³C NMR (126 MHz, CDCl₃) δ 171.03, 162.59 (d, *J* = 246.2 Hz), 154.41 (dd, *J* = 31.2, 24.8 Hz), 149.26, 139.80, 139.50, 137.15 (d, *J* = 3.0 Hz), 136.72, 136.55, 135.99, 130.56, 129.89, 128.87, 128.76 (d, *J* = 8.0 Hz), 128.41, 128.12, 127.71, 126.74, 124.50, 121.74, 119.60 (dd, *J* = 251.7, 245.4 Hz), 115.72 (d, *J*

= 21.4 Hz), 69.80 (dd, J = 30.0, 22.4 Hz).

$^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -101.84 (d, J = 245.6 Hz), -115.29 (d, J = 245.4 Hz).

ESI-HRMS (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{23}\text{F}_3\text{N}_2$, 493.1886; found 493.1887.

N-(2,2-difluoro-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3c**)



General procedure C was followed to obtain **3c** (57 mg, 76%) as a white solid. m.p. 156-158 °C.

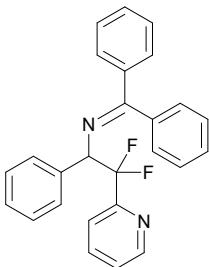
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.60 (d, J = 4.6 Hz, 1H), 7.74 (td, J = 7.7, 1.6 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.57 – 7.52 (m, 4H), 7.49 – 7.46 (m, 2H), 7.42 – 7.33 (m, 6H), 7.32 – 7.26 (m, 3H), 6.99 – 6.95 (m, 2H), 6.75 – 6.71 (m, 2H), 5.26 (dd, J = 18.0, 7.6 Hz, 1H), 3.85 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.88, 159.25, 154.48 (dd, J = 31.0, 25.2 Hz), 149.24, 140.35, 139.56, 136.51, 136.02, 133.58, 130.49, 129.78, 128.86, 128.82, 128.38, 128.22, 128.10, 127.74, 126.41, 124.45, 121.74, 119.64 (dd, J = 251.7, 245.8 Hz), 114.30, 69.85 (dd, J = 29.9, 22.5 Hz), 55.48.

$^{19}\text{F NMR}$ (753 MHz, CDCl_3) δ -102.11 (d, J = 245.2 Hz), -115.07 (d, J = 245.5 Hz).

ESI-HRMS (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{26}\text{F}_2\text{N}_2\text{O}$, 505.2086; found 505.2088.

N-(2,2-difluoro-1-phenyl-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3d**)



General procedure C was followed to obtain **3d** (57 mg, 60%) as a yellow oil.

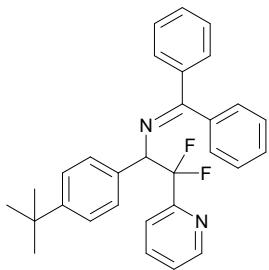
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.59 (d, J = 4.5 Hz, 1H), 7.72 (td, J = 7.7, 1.5 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.42 – 7.32 (m, 6H), 7.30 – 7.27 (m, 6H), 6.73 – 6.69 (m, 2H), 5.24 (dd, J = 17.8, 7.9 Hz, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.85, 154.47 (dd, J = 31.1, 25.4 Hz), 149.21, 139.53, 137.64, 137.63, 136.48, 136.02, 130.48, 129.46, 128.84, 128.79, 128.35, 128.12, 128.08, 128.00, 127.69, 124.42, 121.69, 119.60 (dd, J = 251.4, 246.2 Hz), 70.06 (dd, J = 29.6, 22.5 Hz).

$^{19}\text{F NMR}$ (753 MHz, CDCl_3) δ -102.49 (d, J = 245.6 Hz), -114.98 (d, J = 245.5 Hz).

ESI-HRMS (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{F}_2\text{N}_2$, 399.1667; found 399.1668.

N-(1-(4-(tert-butyl)phenyl)-2,2-difluoro-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3e**)



General procedure C was followed to obtain **3e** (49 mg, 72%) as a white solid. m.p. 123-125 °C.

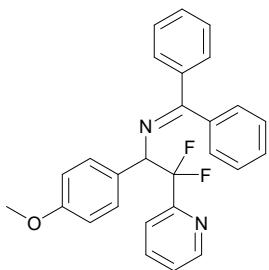
¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 4.5 Hz, 1H), 7.68 (td, *J* = 7.7, 1.5 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.38 – 7.28 (m, 4H), 7.26 – 7.20 (m, 7H), 6.64 (dd, *J* = 8.0, 1.2 Hz, 2H), 5.16 (dd, *J* = 18.6, 7.3 Hz, 1H), 1.27 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 170.49, 154.59 (dd, *J* = 31.5, 25.0 Hz), 150.75, 149.18, 139.63, 136.43, 135.99, 134.45, 130.38, 129.03, 128.82, 128.74, 128.28, 128.04, 127.77, 125.05, 124.37, 121.71, 119.62 (dd, *J* = 251.6, 245.7 Hz), 69.85 (dd, *J* = 30.3, 22.2 Hz), 34.63, 31.50.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.83 (d, *J* = 244.8 Hz), -115.66 (d, *J* = 263.0 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₃₀H₂₈F₂N₂, 455.2293; found 455.2292.

N-(2,2-difluoro-1-(4-methoxyphenyl)ethyl)-1,1-diphenylmethanimine (**3f**)



General procedure C was followed to obtain **3f** (42 mg, 65%) as a white solid. m.p. 98-100 °C.

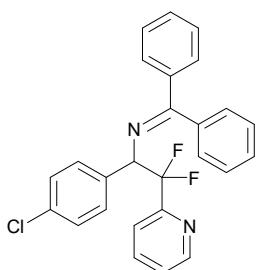
¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.5 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.43 – 7.24 (m, 9H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.74 – 6.68 (m, 2H), 5.17 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.79 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.59, 159.34, 154.56 (dd, *J* = 30.9, 25.6 Hz), 149.19, 139.58, 136.45, 136.06, 130.44, 129.77, 128.81, 128.75, 128.34, 128.07, 127.70, 124.37, 121.70, 119.63 (dd, *J* = 251.2, 245.6 Hz), 113.58, 69.47 (dd, *J* = 29.8, 22.7 Hz), 55.30.

¹⁹F NMR (471 MHz, CDCl₃) δ -102.67 (d, *J* = 244.8 Hz), -115.14 (d, *J* = 261.8 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₇H₂₂F₂N₂O, 429.1773; found 429.1773.

N-(1-(4-chlorophenyl)-2,2-difluoro-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3g**)



General procedure C was followed to obtain **3g** (41 mg, 63%) as a white solid. m.p. 140-142 °C.

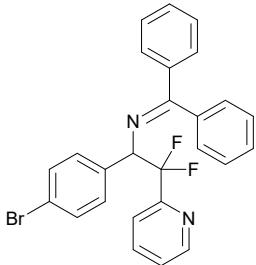
¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.2 Hz, 1H), 7.74 (td, *J* = 7.7, 1.5 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.31 – 7.25 (m, 7H), 6.69 (dd, *J* = 8.1, 1.3 Hz, 2H), 5.21 (dd, *J* = 17.7, 7.6 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 171.33, 154.13 (dd, *J* = 31.1, 25.1 Hz), 149.26, 139.27, 136.60, 136.12, 135.84, 133.88, 130.72, 130.66, 128.92, 128.83, 128.45, 128.38, 128.13, 127.54, 124.57, 121.65, 119.38 (dd, *J* = 251.7, 245.8 Hz), 69.30 (dd, *J* = 29.9, 22.5 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -102.23 (d, *J* = 246.2 Hz), -115.17 (d, *J* = 263.3 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₆H₁₉ClF₂N₂, 433.1278; found 433.1280.

N-(1-(4-bromophenyl)-2,2-difluoro-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3h**)



General procedure C was followed to obtain **3h** (44 mg, 62%) as a white solid. m.p. 145–147 °C.

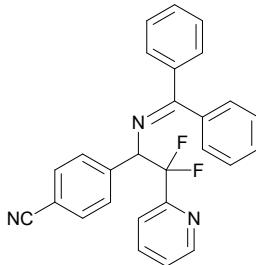
¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.6 Hz, 1H), 7.75 (td, *J* = 7.7, 1.5 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.44 – 7.38 (m, 3H), 7.38 – 7.32 (m, 3H), 7.31 – 7.26 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.70 (dd, *J* = 8.1, 1.3 Hz, 2H), 5.21 (dd, *J* = 17.7, 7.6 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 171.37, 154.10 (dd, *J* = 31.1, 25.1 Hz), 149.26, 139.25, 136.63, 136.61, 135.83, 131.32, 131.07, 130.67, 128.93, 128.83, 128.45, 128.13, 127.54, 124.57, 122.17, 121.64, 119.31 (dd, *J* = 251.9, 245.8 Hz), 69.36 (dd, *J* = 29.9, 22.5 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -102.17 (d, *J* = 246.5 Hz), -115.16 (d, *J* = 263.4 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₆H₁₉BrF₂N₂, 477.0772; found 477.0772.

4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyridin-2-yl)ethyl)benzonitrile (**3i**)



General procedure C was followed to obtain **3i** (36 mg, 56%) as a white solid. m.p. 122–124 °C.

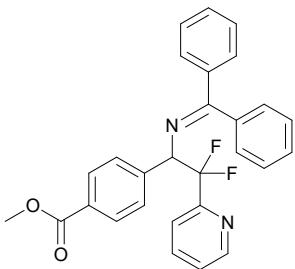
¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.5 Hz, 1H), 7.77 (td, *J* = 7.7, 1.5 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.46 (m, 4H), 7.44 – 7.26 (m, 7H), 6.69 – 6.63 (m, 2H), 5.31 (dd, *J* = 17.9, 7.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 172.14, 153.78 (dd, *J* = 31.0, 24.9 Hz), 149.34, 143.00, 139.00, 136.74, 135.71, 131.95, 130.91, 130.24, 129.09, 128.87, 128.56, 128.21, 127.41, 124.76, 121.63, 119.26 (dd, *J* = 252.4, 246.1 Hz), 118.96, 111.93, 69.50 (dd, *J* = 30.0, 22.3 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -101.17 (d, *J* = 251.6 Hz), -115.32 (d, *J* = 264.9 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₇H₁₉F₂N₃, 424.1620; found 424.1622.

methyl 4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyridin-2-yl)ethyl)benzoate (**3j**)



General procedure C was followed to obtain **3j** (49 mg, 71%) as a white solid. m.p. 114–116 °C.

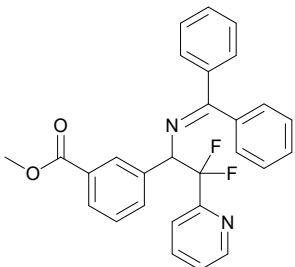
¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.74 (td, *J* = 7.7, 1.5 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 6.71 – 6.66 (m, 2H), 5.30 (dd, *J* = 17.6, 7.7 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.61, 167.16, 154.06 (dd, *J* = 30.9, 25.1 Hz), 149.29, 142.77, 139.23, 136.62, 135.83, 130.71, 129.76, 129.48, 129.40, 128.94, 128.86, 128.47, 128.15, 127.53, 124.60, 121.64, 119.42 (dd, *J* = 251.9, 246.3 Hz), 69.75 (dd, *J* = 29.7, 22.5 Hz), 52.24.

¹⁹F NMR (471 MHz, CDCl₃) δ -102.10 (d, *J* = 246.4 Hz), -114.73 (d, *J* = 263.4 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₂F₂N₂O₂, 457.1722; found 457.1724.

methyl 3-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyridin-2-yl)ethyl)benzoate (**3k**)



General procedure C was followed to obtain **3k** (51 mg, 75%) as a yellow oil.

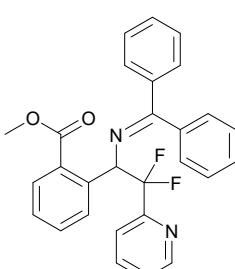
¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.5 Hz, 1H), 8.03 (s, 1H), 7.97 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.74 (td, *J* = 7.7, 1.5 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.42 – 7.26 (m, 8H), 6.70 – 6.66 (m, 2H), 5.31 (dd, *J* = 18.0, 7.4 Hz, 1H), 3.89 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.48, 154.17 (dd, *J* = 31.2, 25.0 Hz), 167.13, 149.29, 139.30, 138.04, 136.59, 135.90, 134.07, 130.65, 130.16, 129.35, 128.93, 128.91, 128.46, 128.24, 128.12, 127.55, 124.56, 121.65, 119.43 (dd, *J* = 251.8, 245.8 Hz), 69.70 (dd, *J* = 30.0, 22.3 Hz), 52.20.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.77 (d, *J* = 249.4 Hz), -115.42 (d, *J* = 264.1 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₂F₂N₂O₂, 457.1722; found 457.1723.

methyl 2-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyridin-2-yl)ethyl)benzoate (**3l**)



General procedure C was followed to obtain **3l** (36 mg, 52%) as a yellow oil.

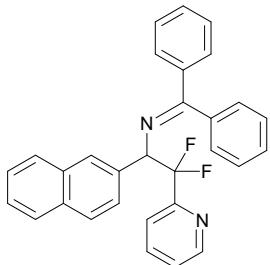
¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 4.4 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.72 – 7.66 (m, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.34 (m, 8H), 6.73 (d, *J* = 6.9 Hz, 2H), 6.47 (dd, *J* = 17.3, 7.3 Hz, 1H), 3.55 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.43, 167.55, 154.44 (dd, *J* = 30.2, 26.3 Hz), 149.24, 139.52, 138.20, 136.84, 136.34, 131.66, 131.44, 130.66, 130.53, 130.27, 128.89, 128.45, 128.37, 128.10, 127.62, 127.57, 124.35, 121.61, 119.80 (dd, *J* = 252.0, 247.2 Hz), 64.32 (dd, *J* = 29.1, 22.1 Hz), 51.89.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.22 (d, *J* = 253.0 Hz), -114.13 (d, *J* = 263.8 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₂F₂N₂O₂, 457.1722; found 457.1721.

N-(2,2-difluoro-1-(naphthalen-1-yl)-2-(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**3m**)



General procedure C was followed to obtain **3m** (54 mg, 80%) as a white solid. m.p. 96-98 °C.

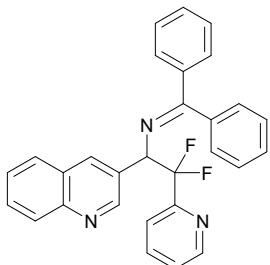
¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 4.6 Hz, 1H), 7.84 – 7.75 (m, 4H), 7.73 (td, *J* = 7.8, 1.6 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 5H), 6.70 (dd, *J* = 8.1, 1.2 Hz, 2H), 5.40 (dd, *J* = 17.8, 7.8 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 171.19, 154.43 (dd, *J* = 31.1, 25.1 Hz), 149.28, 139.52, 136.55, 135.99, 135.22, 133.25, 130.54, 128.89, 128.86, 128.67, 128.38, 128.32, 128.12, 127.73, 127.71, 127.66, 127.22, 126.06, 125.92, 124.49, 121.67, 119.73 (dd, *J* = 251.7, 245.9 Hz), 70.17 (dd, *J* = 29.6, 22.4 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -102.10 (d, *J* = 245.7 Hz), -114.67 (d, *J* = 262.9 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₃₀H₂₂F₂N₂, 449.1824; found 449.1825.

N-(2,2-difluoro-2-(pyridin-2-yl)-1-(quinolin-3-yl)ethyl)-1,1-diphenylmethanimine (**3n**)



General procedure C was followed to obtain **3n** (39 mg, 58%) as a brown oil.

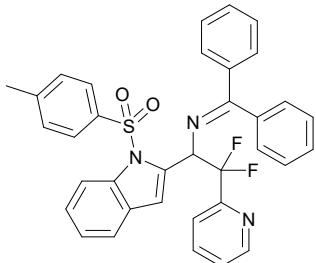
¹H NMR (400 MHz, CDCl₃) δ 8.78 (d, *J* = 1.8 Hz, 1H), 8.62 (d, *J* = 4.5 Hz, 1H), 8.23 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.68 (m, 3H), 7.58 – 7.51 (m, 3H), 7.43 – 7.27 (m, 7H), 6.73 – 6.67 (m, 2H), 5.51 (dd, *J* = 17.7, 7.6 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 172.09, 153.91 (dd, *J* = 31.1, 25.1 Hz), 151.46, 149.39, 147.93, 139.12, 136.81, 136.77, 135.82, 130.83, 130.81, 129.68, 129.32, 129.11, 128.91, 128.64, 128.22, 128.18, 127.97, 127.43, 126.75, 124.76, 121.63, 119.45 (dd, *J* = 251.8, 245.8 Hz), 68.02 (dd, *J* = 30.2, 22.5 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -101.53 (d, *J* = 247.9 Hz), -114.65 (d, *J* = 265.0 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₉H₂₁F₂N₃, 450.1776; found 450.1776.

N-(2,2-difluoro-2-(pyridin-2-yl)-1-(1-tosyl-1H-indol-2-yl)ethyl)-1,1-diphenylmethanimine (**3o**)



General procedure C was followed to obtain **3o** (55 mg, 62%) as a yellow oil.

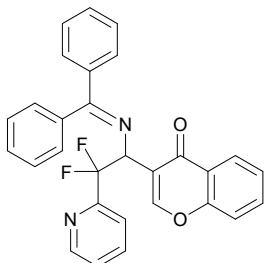
¹H NMR (500 MHz, CDCl₃) δ 8.57 (d, *J* = 4.5 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.44 (s, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.26 (m, 6H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 2H), 5.51 (dd, *J* = 16.7, 8.8 Hz, 1H), 2.32 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.34, 154.11 (dd, *J* = 30.2, 25.9 Hz), 149.27, 144.97, 139.23, 136.53, 135.61, 135.35, 135.11, 130.65, 130.02, 129.90, 128.88, 128.43, 128.13, 127.56, 126.94, 126.22, 124.69, 124.54, 123.28, 121.89, 119.67 (dd, *J* = 251.2, 246.1 Hz), 119.43, 119.41, 113.50, 63.77 (dd, *J* = 30.2, 23.9 Hz), 21.69.

¹⁹F NMR (753 MHz, CDCl₃) δ -103.01 (d, *J* = 246.3 Hz), -112.76 (d, *J* = 245.0 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₃₅H₂₇F₂N₃OS, 592.1865; found 592.1864.

3-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyridin-2-yl)ethyl)-4H-chromen-4-one (**3p**)



General procedure C was followed to obtain **3p** (55 mg, 30%) as a yellow solid. m.p. 93–95 °C.

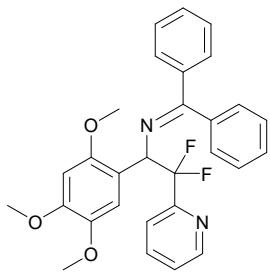
¹H NMR (500 MHz, CDCl₃) δ 8.55 (d, *J* = 4.5 Hz, 1H), 8.37 (s, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71 (td, *J* = 7.7, 1.4 Hz, 1H), 7.64 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.46 – 7.40 (m, 2H), 7.39 – 7.35 (m, 4H), 7.32 – 7.27 (m, 3H), 6.87 – 6.81 (m, 2H), 5.83 (dd, *J* = 15.6, 8.4 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 174.92, 171.83, 157.55, 156.10, 153.80 (dd, *J* = 30.0, 25.5 Hz), 149.20, 139.49, 136.54, 135.62, 133.58, 130.70, 129.14, 129.04, 128.59, 128.16, 127.60, 126.42, 125.21, 124.56, 124.15, 121.49, 121.29 (dd, *J* = 251.8, 247.4 Hz), 121.19, 118.22, 60.08 (dd, *J* = 29.8, 23.3 Hz).

¹⁹F NMR (753 MHz, CDCl₃) δ -103.82 (d, *J* = 246.0 Hz), -113.67 (d, *J* = 261.6 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₉H₂₀F₂N₂O₂, 467.1566; found 467.1566.

N-(2,2-difluoro-2-(pyridin-2-yl)-1-(2,4,5-trimethoxyphenyl)ethyl)-1,1-diphenylmethanimine (**3q**)



General procedure C was followed to obtain **3q** (44 mg, 60%) as a yellow oil.

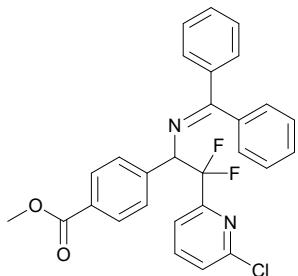
¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 4.6 Hz, 1H), 7.72 (td, *J* = 7.7, 1.5 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.26 (m, 7H), 7.18 (s, 1H), 6.74 (d, *J* = 6.7 Hz, 2H), 6.35 (s, 1H), 5.72 (dd, *J* = 17.5, 7.9 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.43 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.69, 154.75 (dd, *J* = 30.3, 26.0 Hz), 151.68, 149.27, 149.06, 142.93, 139.75, 136.64, 136.18, 130.29, 128.76, 128.33, 128.11, 128.03, 127.69, 124.19, 121.87, 120.22 (dd, *J* = 251.1, 245.9 Hz), 117.42, 114.42, 96.80, 61.79 (dd, *J* = 30.6, 23.0 Hz), 56.69, 56.32, 56.07.

¹⁹F NMR (753 MHz, CDCl₃) δ -102.78 (d, *J* = 244.0 Hz), -114.67 (d, *J* = 259.9 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₉H₂₆F₂N₂O₃, 489.1984; found 489.1985.

methyl 4-(2-(6-chloropyridin-2-yl)-1-((diphenylmethylene)amino)-2,2-difluoroethyl)benzoate (**4a**)



General procedure C was followed to obtain **4a** (46 mg, 63%) as a white solid. m.p. 139–141 °C.

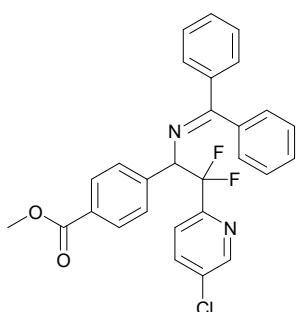
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.29 (d, *J* = 7.7 Hz, 2H), 6.72 (d, *J* = 6.9 Hz, 2H), 5.31 (dd, *J* = 19.5, 6.3 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.93, 167.14, 154.82 (dd, *J* = 33.9, 25.3 Hz), 151.24, 142.45, 139.36, 139.12, 135.75, 130.80, 129.92, 129.56, 129.44, 129.05, 128.85, 128.57, 128.18, 125.57, 120.01, 118.70 (dd, *J* = 252.9, 246.3 Hz), 69.20 (dd, *J* = 30.5, 21.2 Hz), 52.25.

¹⁹F NMR (471 MHz, CDCl₃) δ -99.12 (d, *J* = 249.3 Hz), -117.13 (d, *J* = 268.0 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₁ClF₂N₂O₂, 491.1332; found 491.1334.

methyl 4-(2-(5-chloropyridin-2-yl)-1-((diphenylmethylene)amino)-2,2-difluoroethyl)benzoate (**4b**)



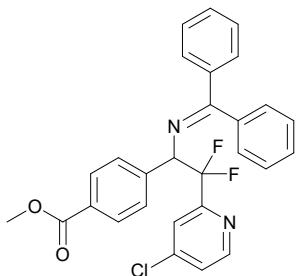
General procedure C was followed to obtain **4b** (38 mg, 52%) as a white solid. m.p. 103-105 °C.
¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, *J* = 2.2 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.72 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.42 – 7.28 (m, 8H), 6.74 – 6.70 (m, 2H), 5.28 (dd, *J* = 17.1, 7.9 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.85, 167.09, 152.23 (dd, *J* = 31.5, 26.2 Hz), 148.22, 142.50, 139.11, 136.36, 135.78, 133.23, 130.87, 129.92, 129.44, 129.01, 128.87, 128.54, 128.23, 127.50, 122.64, 119.25 (dd, *J* = 251.6, 246.4 Hz), 69.59 (dd, *J* = 29.4, 22.9 Hz), 52.25.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.34 (d, *J* = 248.5 Hz), -113.56 (d, *J* = 264.3 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₁ClF₂N₂O₂, 491.1332; found 491.1335.

methyl 4-(2-(4-chloropyridin-2-yl)-1-((diphenylmethylene)amino)-2,2-difluoroethyl)benzoate (**4c**)



General procedure C was followed to obtain **4c** (31 mg, 42%) as a white solid. m.p. 135-137 °C.

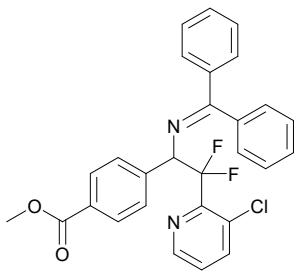
¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, *J* = 5.2 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.28 (m, 1H), 6.71 (d, *J* = 7.0 Hz, 2H), 5.28 (dd, *J* = 17.6, 7.7 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.96, 167.10, 155.67 (dd, *J* = 31.3, 26.0 Hz), 150.17, 144.97, 142.41, 139.11, 135.81, 130.87, 129.95, 129.46, 129.03, 128.88, 128.52, 128.24, 127.53, 124.98, 122.49, 119.02 (dd, *J* = 252.5, 247.4 Hz), 69.53 (dd, *J* = 29.5, 22.4 Hz), 52.26.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.65 (d, *J* = 247.7 Hz), -114.61 (d, *J* = 264.9 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₁ClF₂N₂O₂, 491.1332; found 491.1332.

methyl 4-(2-(3-chloropyridin-2-yl)-1-((diphenylmethylene)amino)-2,2-difluoroethyl)benzoate (**4d**)



General procedure C was followed to obtain **4d** (37 mg, 50%) as a white solid. m.p. 115-117 °C.

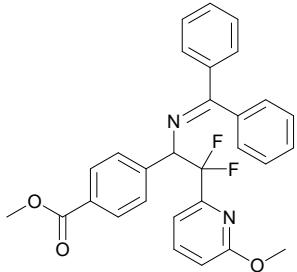
¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, *J* = 4.5 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.33 – 7.24 (m, 3H), 6.75 (d, *J* = 7.0 Hz, 2H), 5.44 (dd, *J* = 16.7, 8.5 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.69, 167.14, 149.91 (t, *J* = 26.6 Hz), 146.58, 142.45, 139.49, 139.16, 135.98, 130.76, 129.89, 129.62, 129.45, 129.09, 128.95, 128.43, 128.15, 127.62, 125.47, 119.34 (dd, *J* = 256.1, 247.8 Hz), 69.45 (dd, *J* = 28.0, 22.0 Hz), 52.23.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.09 (d, *J* = 261.0 Hz), -109.03 (d, *J* = 253.9 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₈H₂₁ClF₂N₂O₂, 491.1332; found 491.1334.

methyl 4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(6-methoxypyridin-2-yl)ethyl)benzoate (**4e**)



General procedure C was followed to obtain **4e** (38 mg, 52%) as a white solid. m.p. 106-108 °C.

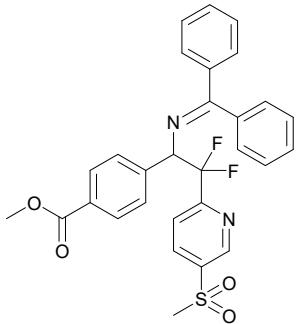
¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.47 – 7.34 (m, 6H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 6.8 Hz, 2H), 6.71 (d, *J* = 8.3 Hz, 1H), 5.34 (dd, *J* = 15.2, 9.8 Hz, 1H), 3.91 (s, 3H), 3.68 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.34, 167.16, 163.58, 151.14 (dd, *J* = 30.1, 26.4 Hz), 142.94, 139.40, 138.94, 136.05, 130.67, 129.73, 129.49, 129.38, 128.96, 128.85, 128.36, 128.15, 127.81, 119.14 (dd, *J* = 251.3, 247.2 Hz), 114.11, 112.23, 69.55 (dd, *J* = 28.1, 22.8 Hz), 53.44, 52.22.

¹⁹F NMR (471 MHz, CDCl₃) δ -105.22 (d, *J* = 243.7 Hz), -112.22 (d, *J* = 243.9 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₉H₂₄F₂N₂O₃, 487.1827; found 487.1828.

Methyl 4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(5-(methylsulfonyl)pyridin-2-yl)ethyl)benzoate (**4f**)



General procedure C was followed to obtain **4f** (38 mg, 48%) as a white solid. m.p. 177-179 °C.

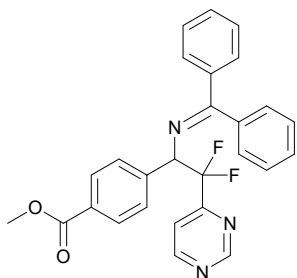
¹H NMR (400 MHz, CDCl₃) δ 9.10 (d, *J* = 2.0 Hz, 1H), 8.30 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.43 – 7.28 (m, 8H), 6.71 (d, *J* = 6.9 Hz, 2H), 5.33 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.91 (s, 3H), 3.10 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 172.37, 167.00, 159.07 (dd, *J* = 31.5, 26.0 Hz), 148.07, 142.03, 138.83, 137.68, 136.19, 135.60, 131.07, 130.11, 129.52, 129.41, 129.12, 128.83, 128.61, 128.30, 127.39, 122.25, 119.00 (dd, *J* = 252.2, 246.7 Hz), 69.39 (dd, *J* = 29.0, 22.6 Hz), 52.30, 44.98.

¹⁹F NMR (471 MHz, CDCl₃) δ -101.23 (d, *J* = 250.1 Hz), -113.90 (d, *J* = 265.8 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₉H₂₄F₂N₂O₄S, 535.1498; found 535.1499.

methyl 4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyrimidin-4-yl)ethyl)benzoate (**4g**)



General procedure C was followed to obtain **4g** (37mg, 54%) as a white solid. m.p. 123-125 °C.

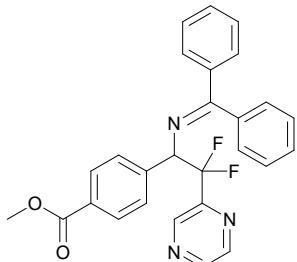
¹H NMR (400 MHz, CDCl₃) δ 9.23 (s, 1H), 8.85 (d, *J* = 5.1 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 5.0 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.28 (m, 8H), 6.71 (d, *J* = 6.9 Hz, 2H), 5.27 (dd, *J* = 17.4, 7.7 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 172.38, 167.02, 162.00 (dd, *J* = 32.8, 26.3 Hz), 158.68, 158.07, 141.90, 138.87, 135.60, 131.03, 130.14, 130.10, 129.53, 129.41, 129.14, 128.86, 128.60, 128.27, 127.42, 118.78, 118.47 (dd, *J* = 252.0, 246.7 Hz), 69.22 (dd, *J* = 28.7, 22.3 Hz), 52.29.

¹⁹F NMR (471 MHz, CDCl₃) δ -103.83 (d, *J* = 255.2 Hz), -116.49 (d, *J* = 250.3 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₇H₂₁F₂N₃O₂, 458.1675; found 458.1677.

methyl 4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(pyrazin-2-yl)ethyl)benzoate (**4h**)



General procedure C was followed to obtain **4h** (31 mg, 45%) as a white solid. m.p. 120-123 °C.

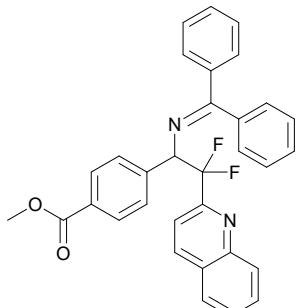
¹H NMR (400 MHz, CDCl₃) δ 8.94 (s, 1H), 8.62 (d, *J* = 2.3 Hz, 1H), 8.55 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.28 (m, 8H), 6.73 (d, *J* = 7.0 Hz, 2H), 5.24 (dd, *J* = 16.4, 7.9 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (201 MHz, CDCl₃) δ 172.28, 167.02, 149.60 (dd, *J* = 30.3, 26.7 Hz), 145.71, 143.68, 143.60, 142.07, 138.87, 135.73, 131.03, 130.10, 129.53, 129.36, 129.09, 128.88, 128.59, 128.31, 127.45, 119.09 (dd, *J* = 251.4, 247.1 Hz), 69.70 (dd, *J* = 29.0, 23.6 Hz), 52.27.

¹⁹F NMR (753 MHz, CDCl₃) δ -102.00 (d, *J* = 253.1 Hz), -114.28 (d, *J* = 266.7 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₂₇H₂₁F₂N₃O₂, 458.1675; found 458.1675.

methyl 4-(1-((diphenylmethylene)amino)-2,2-difluoro-2-(quinolin-2-yl)ethyl)benzoate (**4i**)



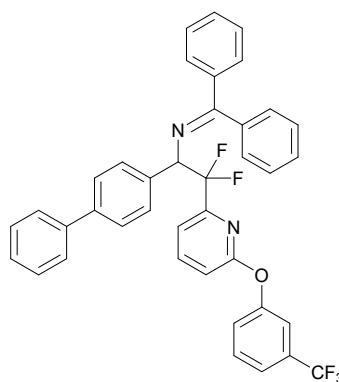
General procedure C was followed to obtain **4i** (43 mg, 56%) as a yellow solid. m.p. 133-135 °C.
¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.21 (m, 5H), 6.58 (d, *J* = 7.0 Hz, 2H), 5.50 (dd, *J* = 18.5, 6.9 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.62, 167.21, 154.47 (dd, *J* = 31.9, 24.3 Hz), 147.43, 142.85, 139.18, 136.85, 135.89, 130.67, 130.11, 129.83, 129.65, 129.42, 128.91, 128.86, 128.38, 128.22, 128.11, 127.86, 127.62, 119.49 (dd, *J* = 252.3, 246.8 Hz), 118.49, 70.02 (dd, *J* = 30.3, 21.9 Hz), 52.24.

¹⁹F NMR (471 MHz, CDCl₃) δ -99.45 (d, *J* = 248.0 Hz), -115.30 (d, *J* = 265.8 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₃₂H₂₄F₂N₂O₂, 507.1879; found 507.1881.

N-(1-([1,1'-biphenyl]-4-yl)-2,2-difluoro-2-(6-(3-(trifluoromethyl)phenoxy)pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (**4j**)



General procedure C was followed to obtain **4j** (51 mg, 54%) as a yellow oil.

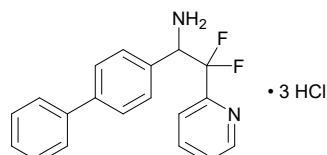
¹H NMR (400 MHz, CDCl₃) δ 7.77 (t, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 4H), 7.45 (dt, *J* = 14.9, 7.9 Hz, 7H), 7.39 – 7.27 (m, 9H), 7.25 – 7.18 (m, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 7.1 Hz, 2H), 5.14 (dd, *J* = 16.1, 9.4 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 170.95, 161.92, 154.08, 152.54 (dd, *J* = 31.1, 27.0 Hz), 140.92, 140.68, 140.31, 139.58, 136.54, 135.87, 131.91 (q, *J* = 32.7 Hz), 130.55, 129.93, 129.79, 128.89, 128.87, 128.73, 128.29, 128.13, 127.56, 127.39, 127.17, 126.78, 124.32, 123.89 (q, *J* = 272.4 Hz), 121.21 (q, *J* = 3.6 Hz), 119.12 (dd, *J* = 250.8, 246.5 Hz), 118.11 (q, *J* = 3.6 Hz), 116.93, 112.90, 110.94, 106.34, 69.29 (dd, *J* = 28.1, 22.8 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -62.52, -103.77 (d, *J* = 248.6 Hz), -111.77 (d, *J* = 260.3 Hz).

ESI-HRMS (m/z) [M+H]⁺ calcd for C₃₉H₂₇F₅N₂O, 635.2116; found 635.2114.

1-([1,1'-biphenyl]-4-yl)-2,2-difluoro-2-(pyridin-2-yl)ethan-1-amine trihydrochloride (**3a-1**)



Benzophenone removal reaction was followed to obtain **3a-1** (192 mg, 91%) as an orange solid.

¹H NMR (500 MHz, DMSO) δ 9.42 (br, 2H), 8.74 (d, *J* = 4.6 Hz, 1H), 7.91 (td, *J* = 7.8, 1.6 Hz, 1H), 7.68 – 7.62 (m, 4H), 7.59 – 7.54 (m, 2H), 7.51 – 7.42 (m, 4H), 7.40 – 7.35 (m, 1H), 5.77 (br, 3H), 5.56 – 5.49 (m, 1H).

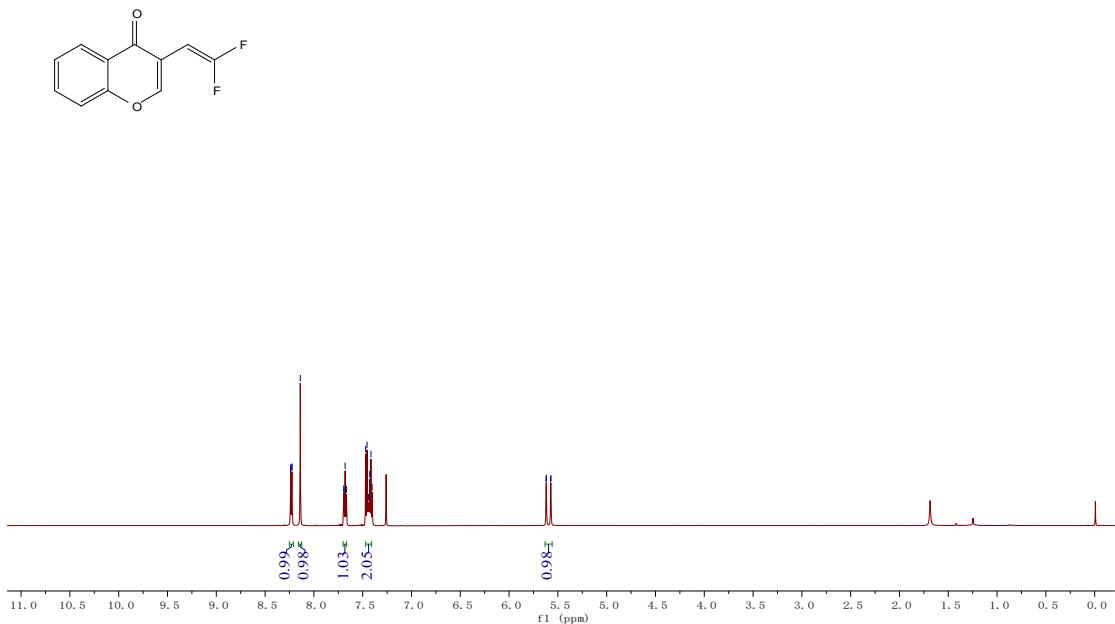
¹³C NMR (126 MHz, DMSO) δ 150.24 (t, $J = 28.6$ Hz), 149.67, 141.04, 138.89, 138.09, 129.69, 129.52, 129.01, 127.96, 126.70, 126.62, 126.24, 120.96, 118.39 (t, $J = 249.5$ Hz), 56.52 (t, $J = 25.5$ Hz).

¹⁹F NMR (471 MHz, DMSO) δ -97.16 (d, $J = 257.3$ Hz), -112.83 (d, $J = 268.7$ Hz).

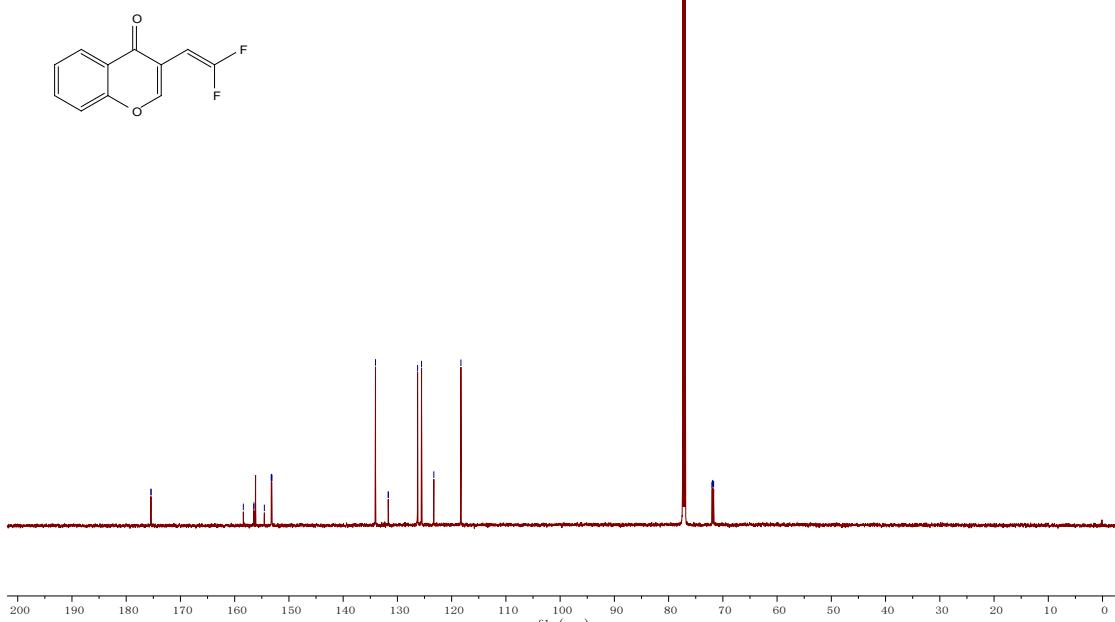
ESI-HRMS (m/z) [M+H]⁺ calcd for C₁₉H₁₆F₂N₂, 311.1354; found 311.1356.

NMR Data

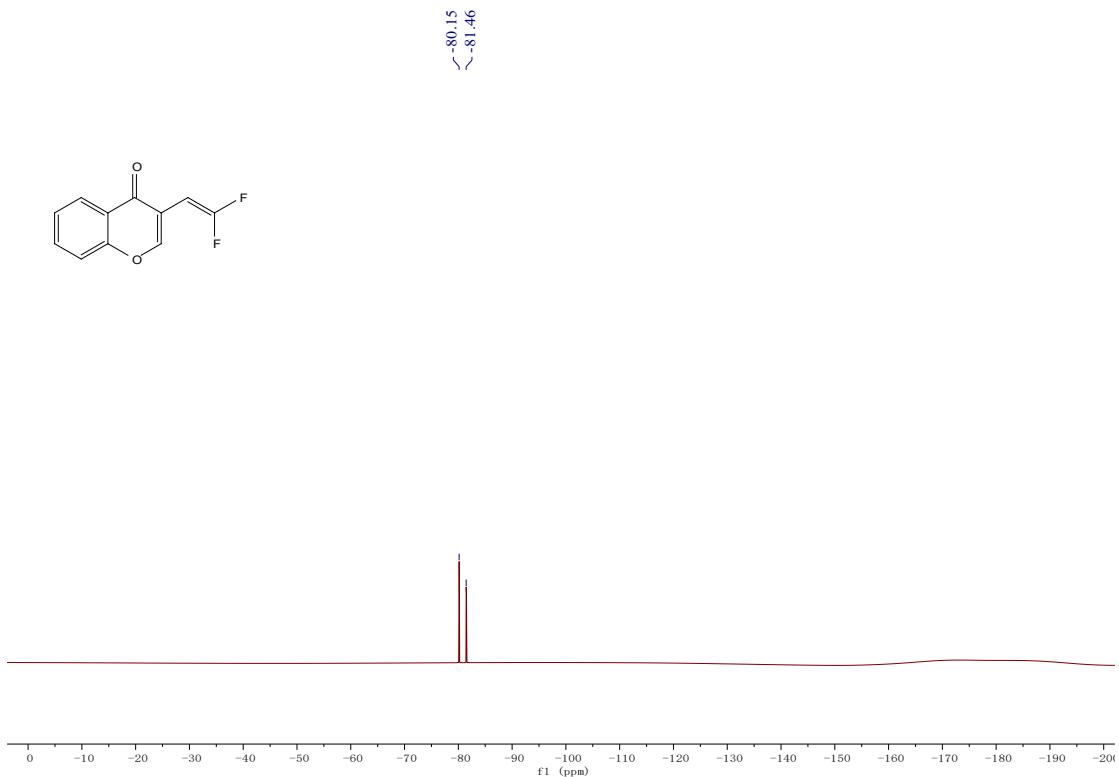
¹H NMR (400 MHz, CDCl₃) spectrum of **1p**



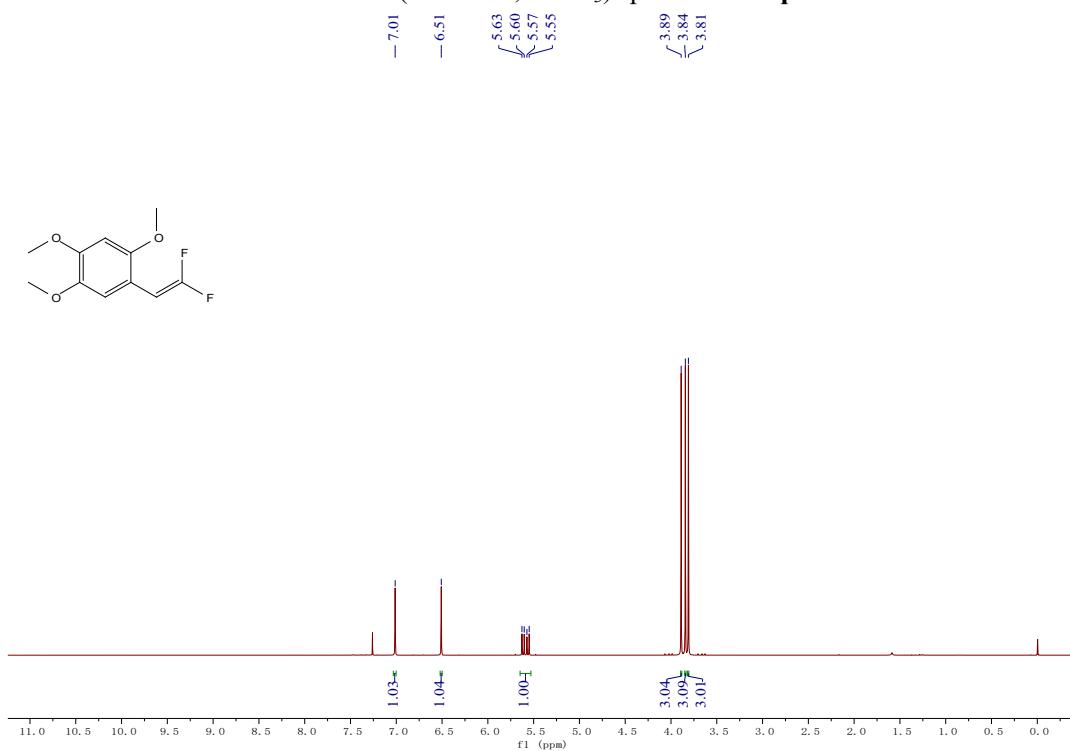
¹³C NMR (151 MHz, CDCl₃) spectrum of **1p**



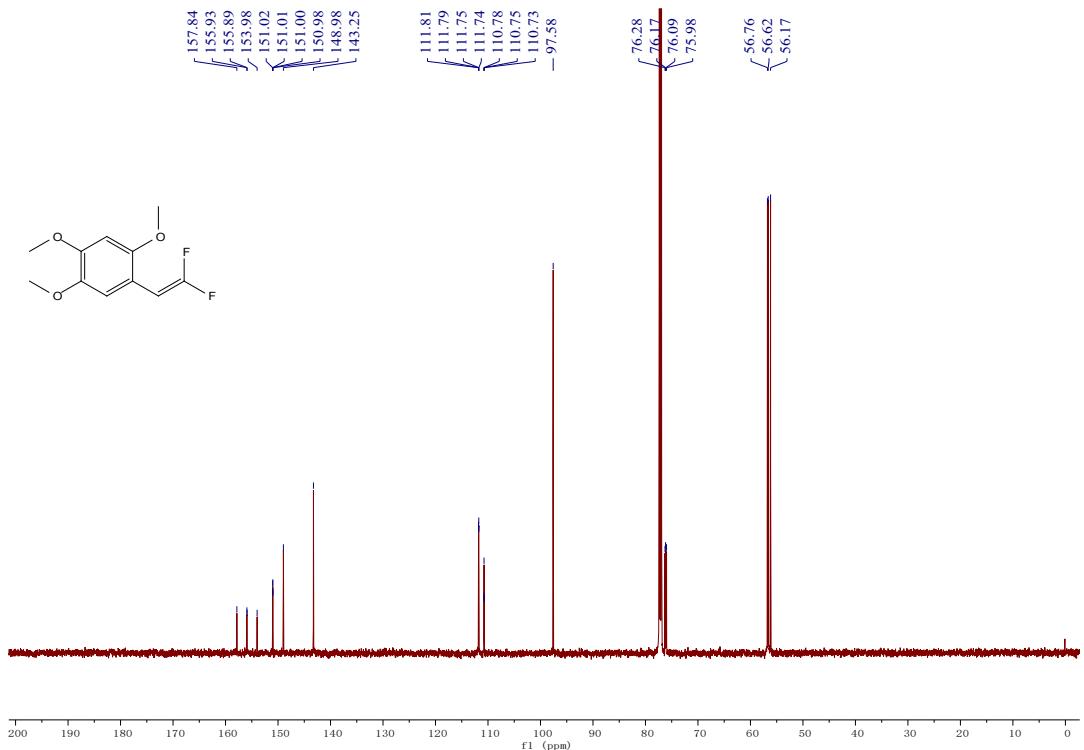
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **1p**



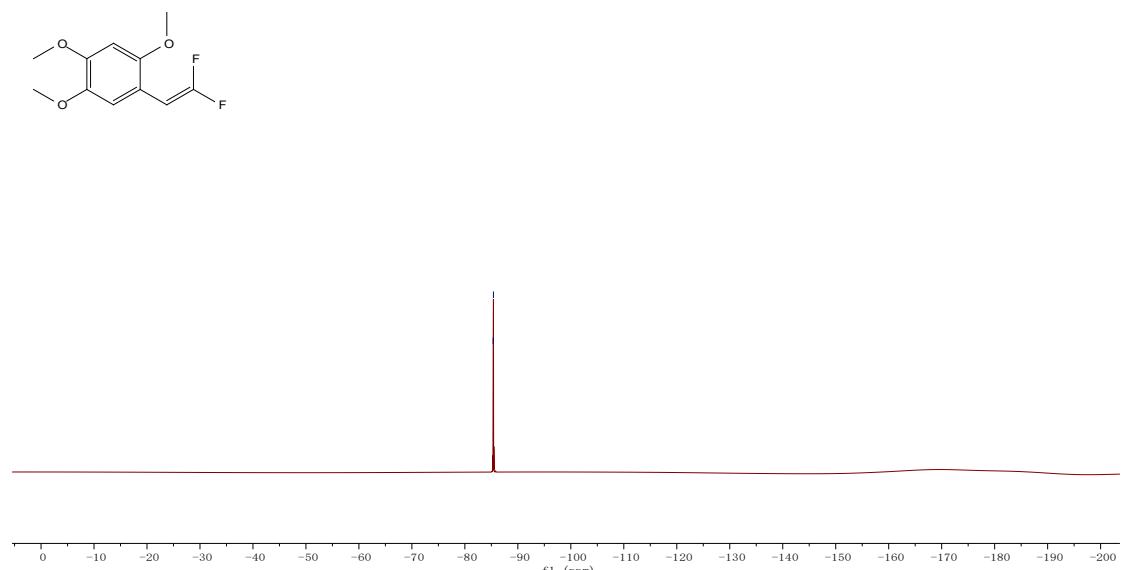
¹H NMR (400 MHz, CDCl₃) spectrum of **1q**



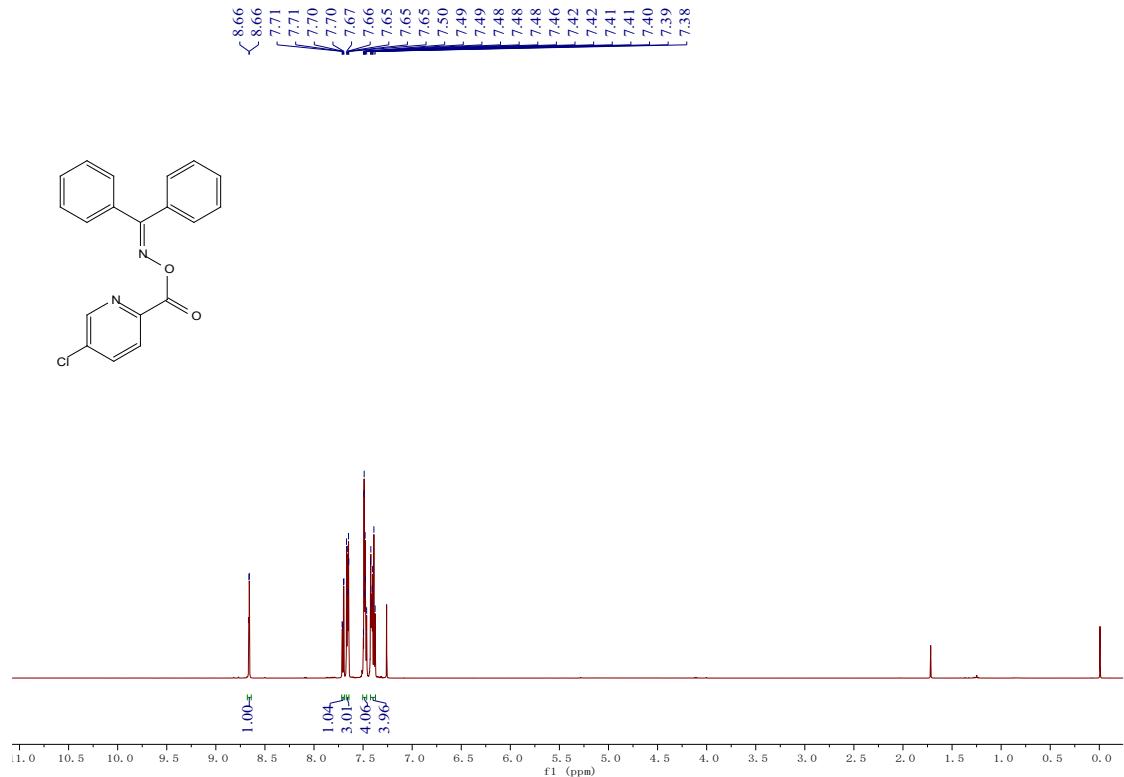
¹³C NMR (151 MHz, CDCl₃) spectrum of **1q**



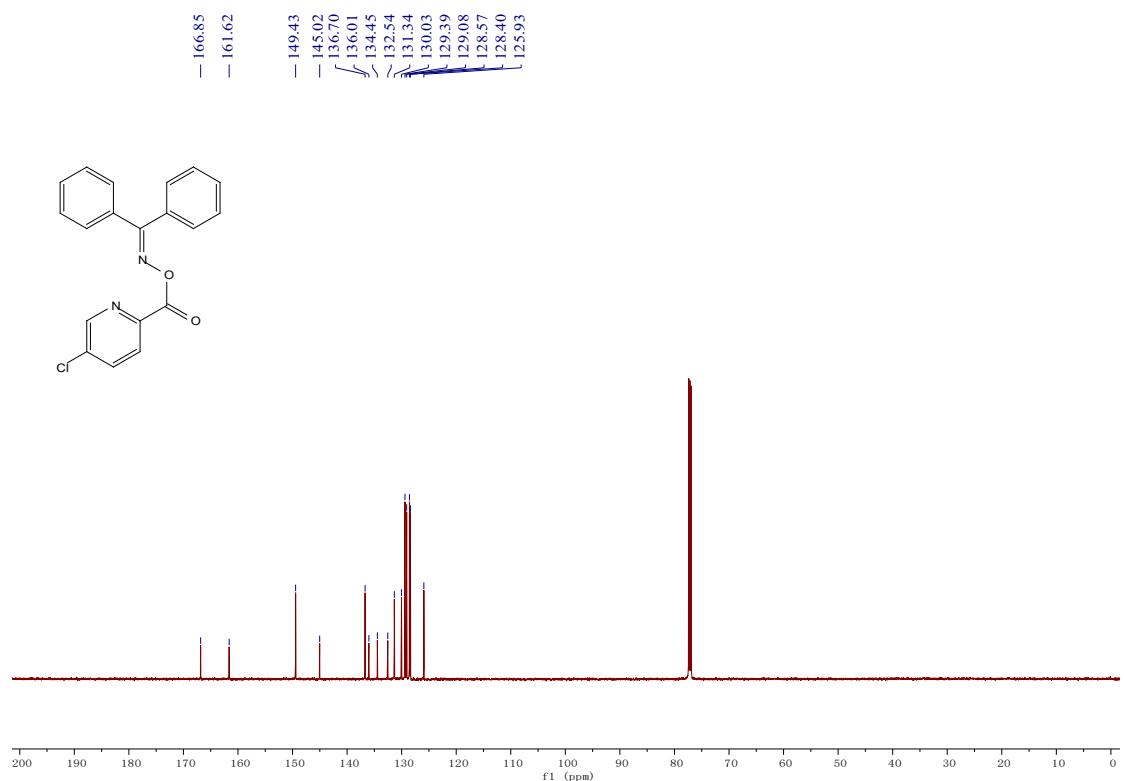
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **1q**



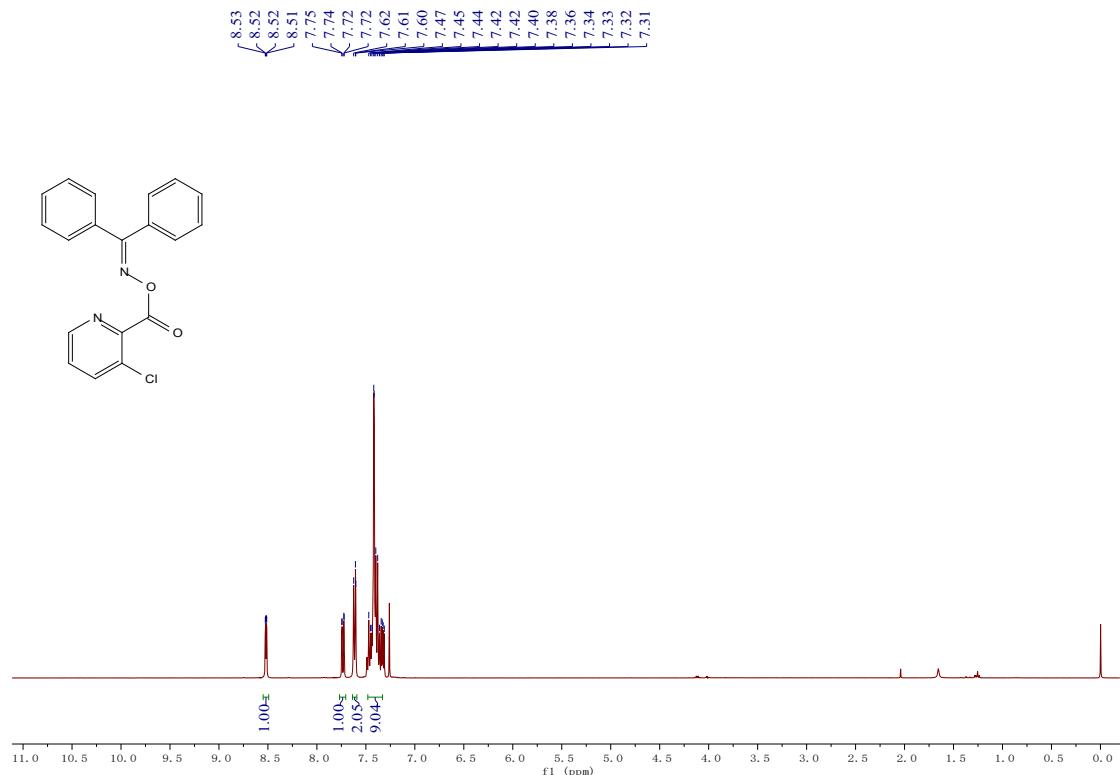
¹H NMR (600 MHz, CDCl₃) spectrum of **2b**



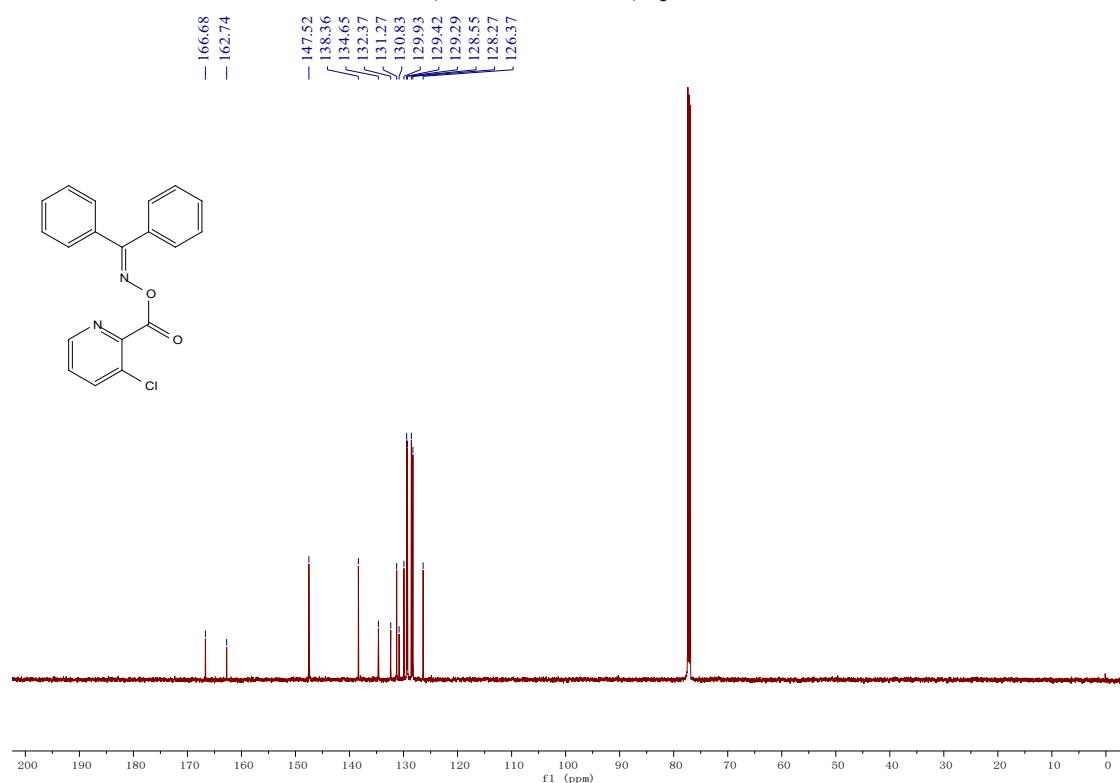
¹C NMR (151 MHz, CDCl₃) spectrum of **2b**



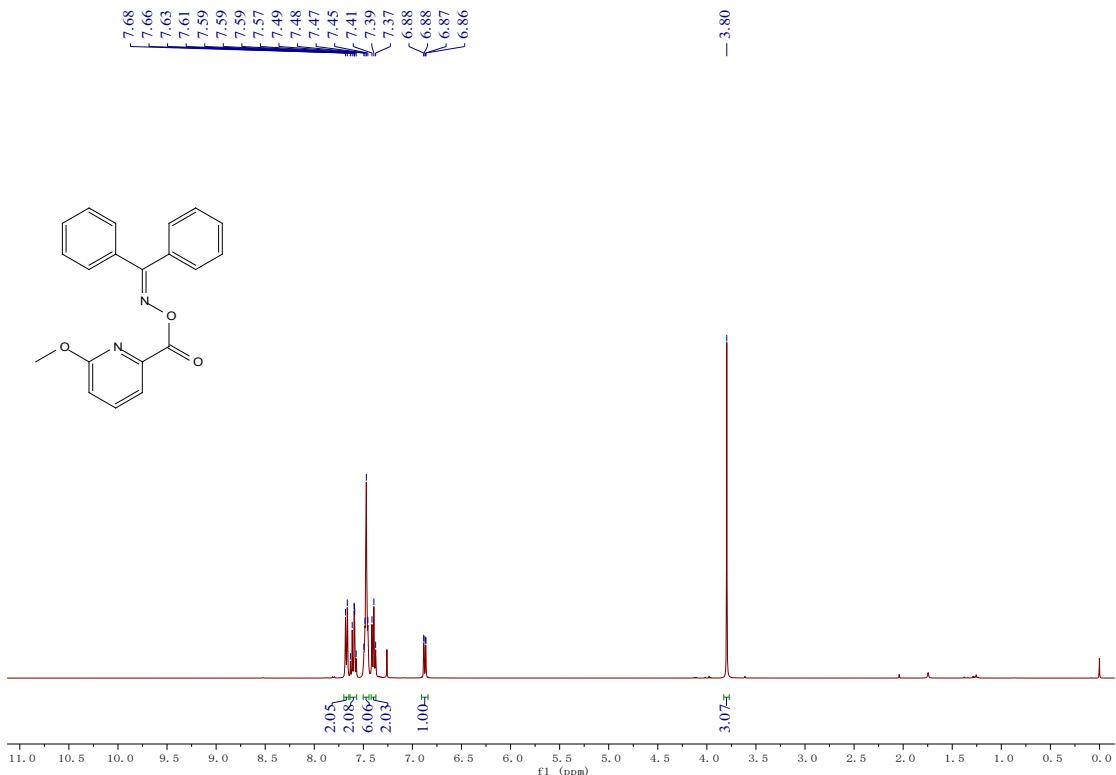
¹H NMR (400 MHz, CDCl₃) spectrum of **2d**



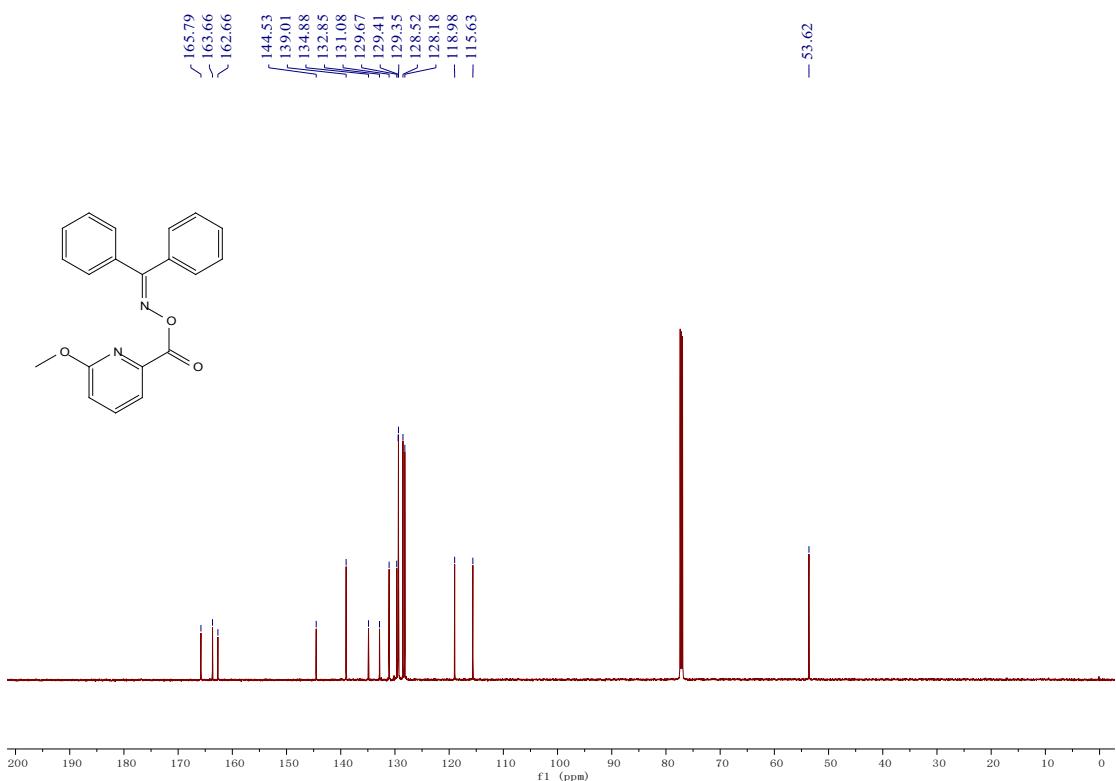
¹³C NMR (151 MHz, CDCl₃) spectrum of **2d**



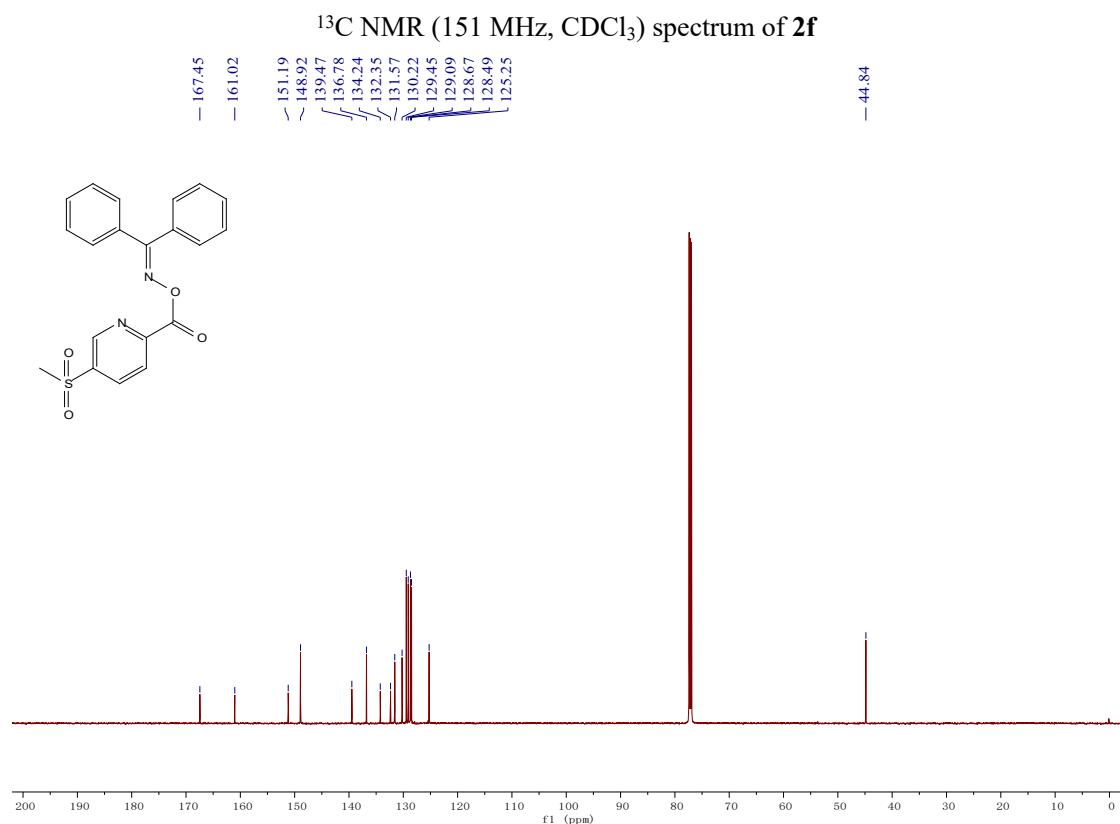
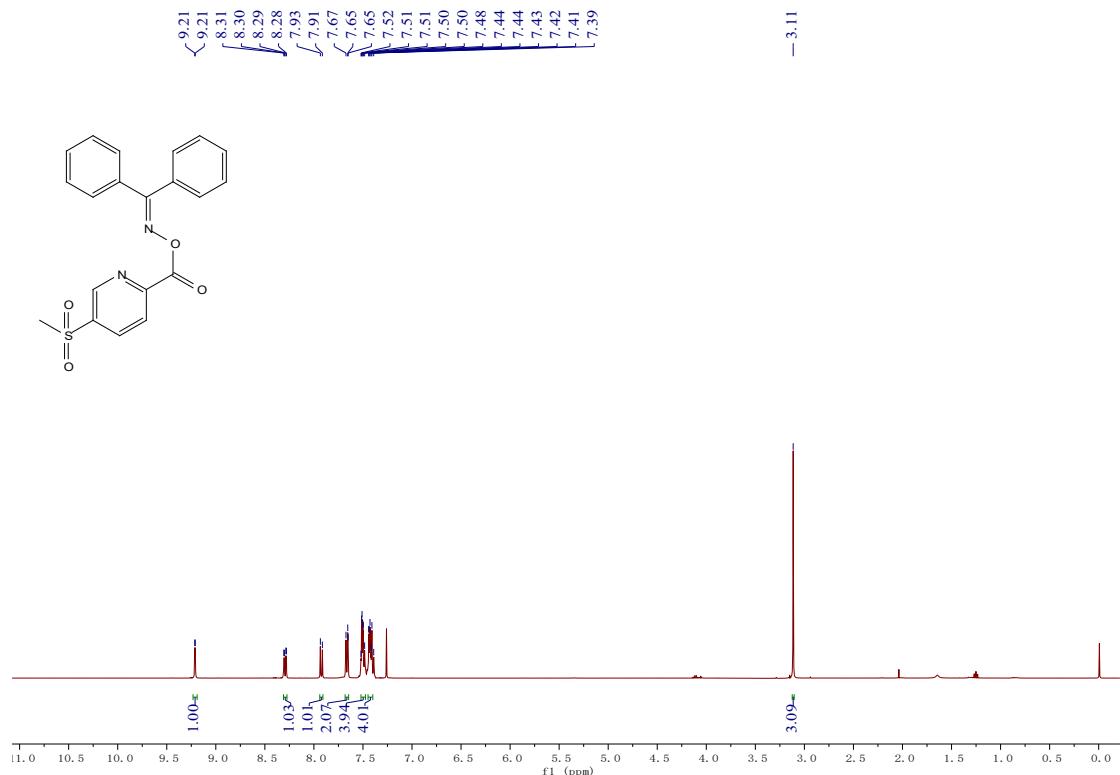
¹H NMR (400 MHz, CDCl₃) spectrum of **2e**



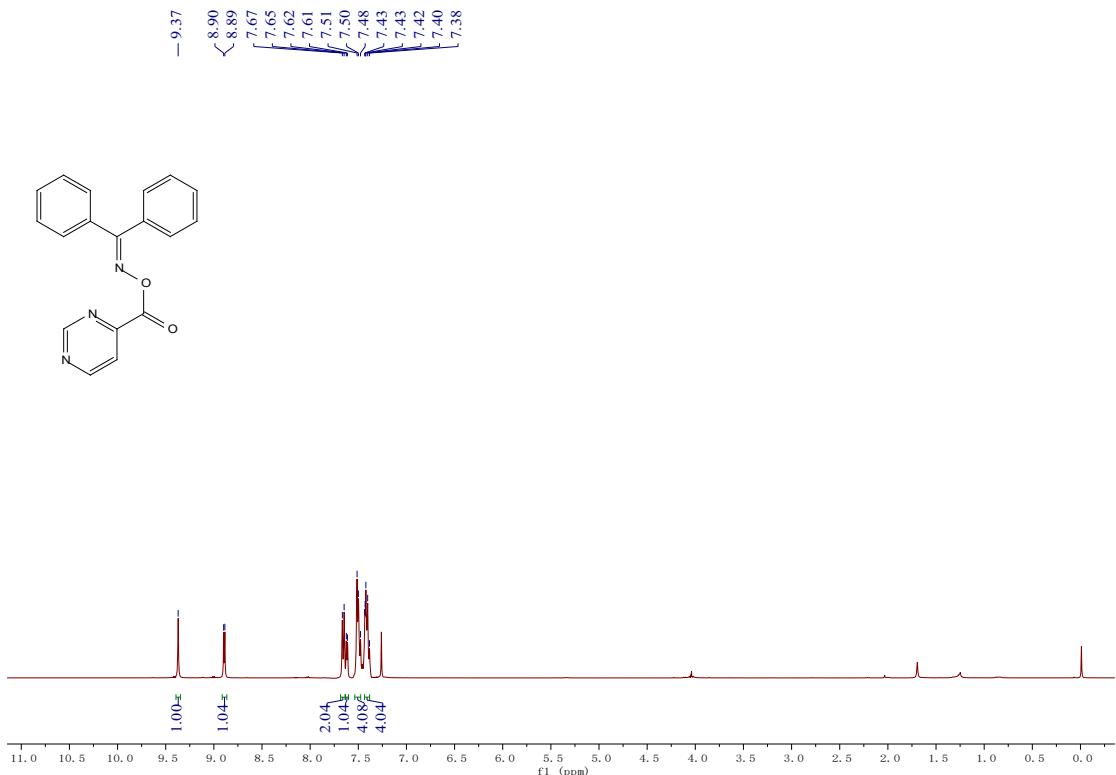
¹C NMR (151 MHz, CDCl₃) spectrum of **2e**



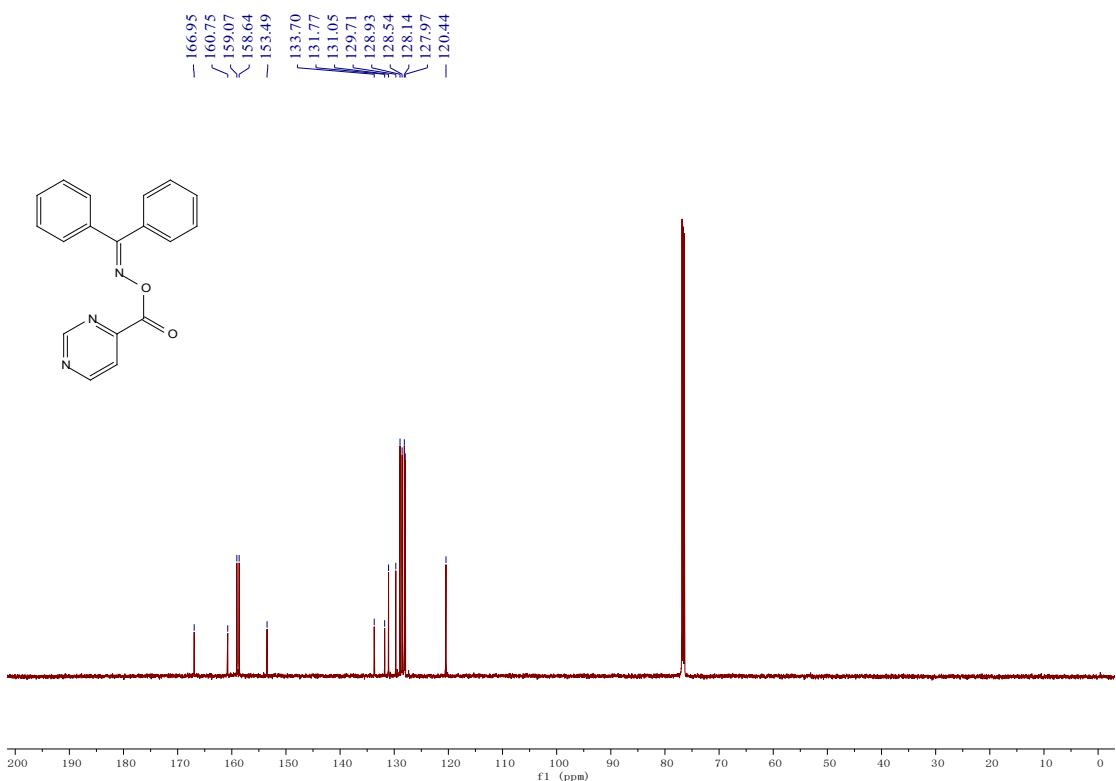
¹H NMR (400 MHz, CDCl₃) spectrum of **2f**



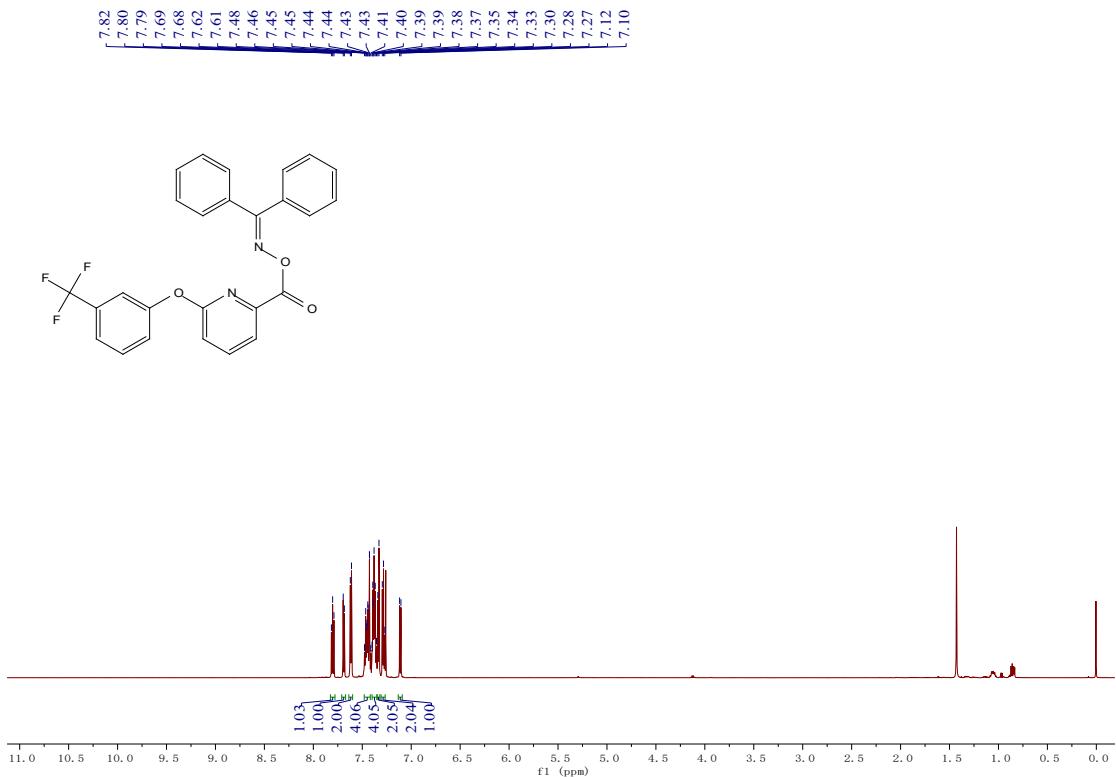
¹H NMR (400 MHz, CDCl₃) spectrum of **2g**



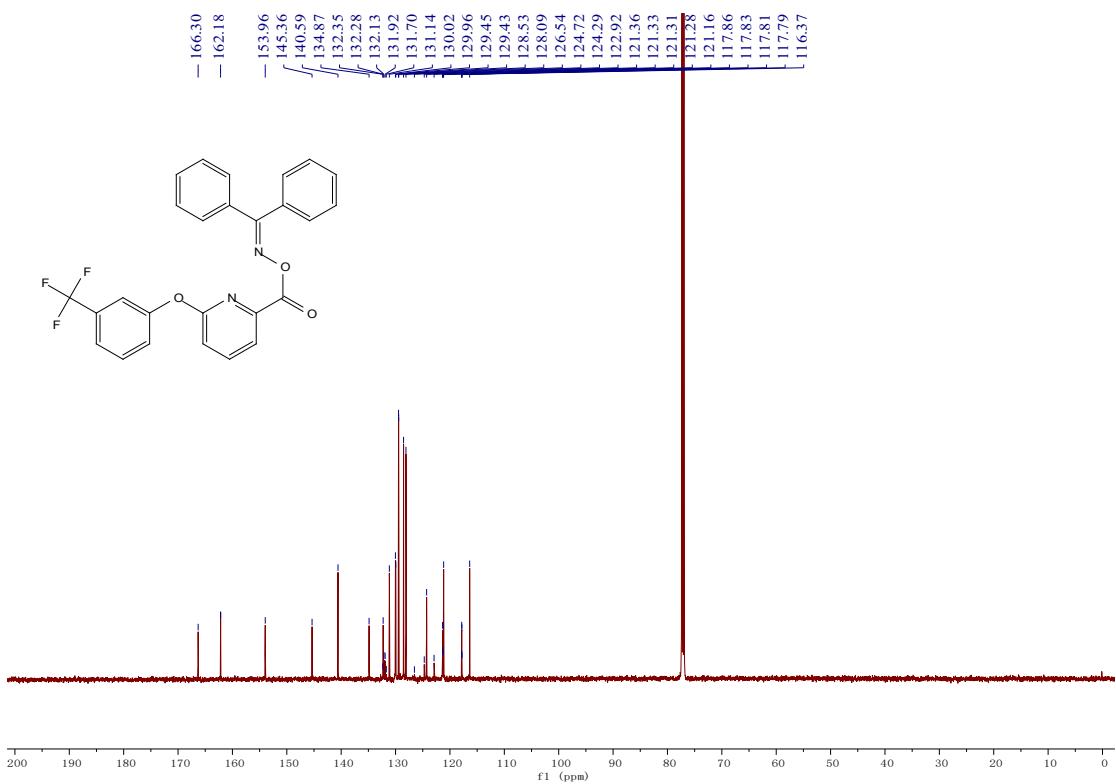
¹³C NMR (151 MHz, CDCl₃) spectrum of **2g**



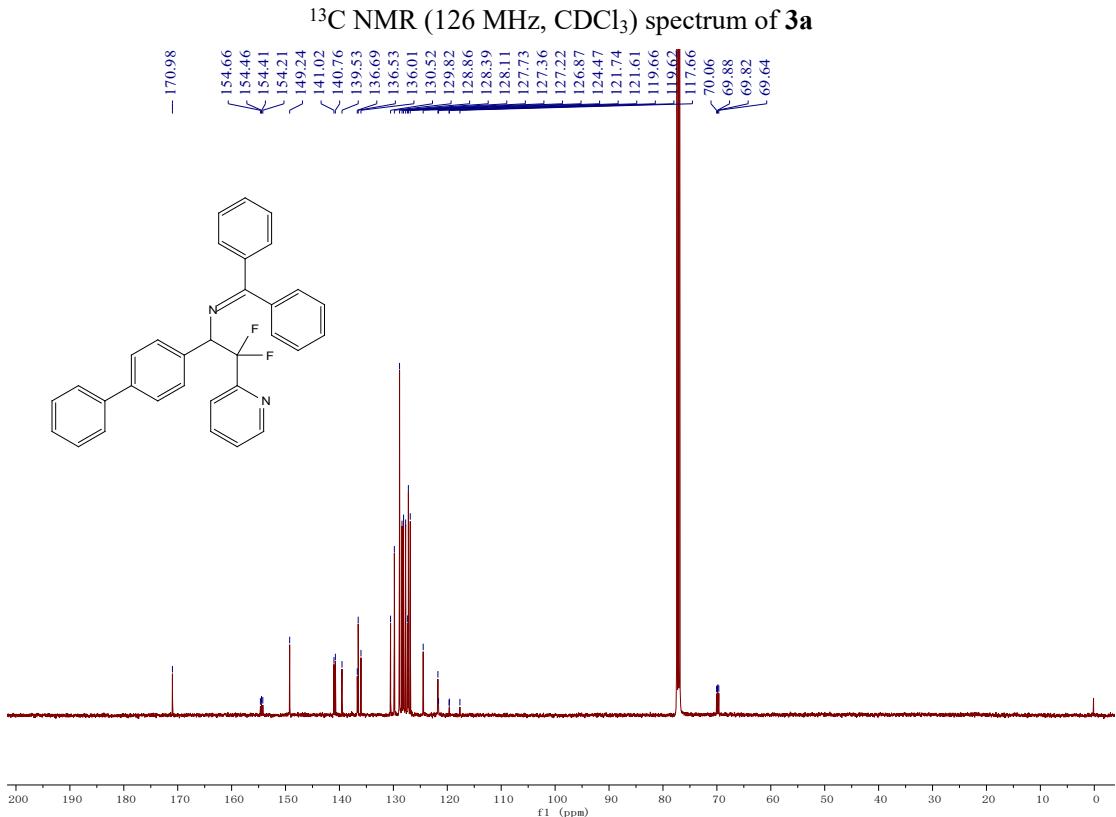
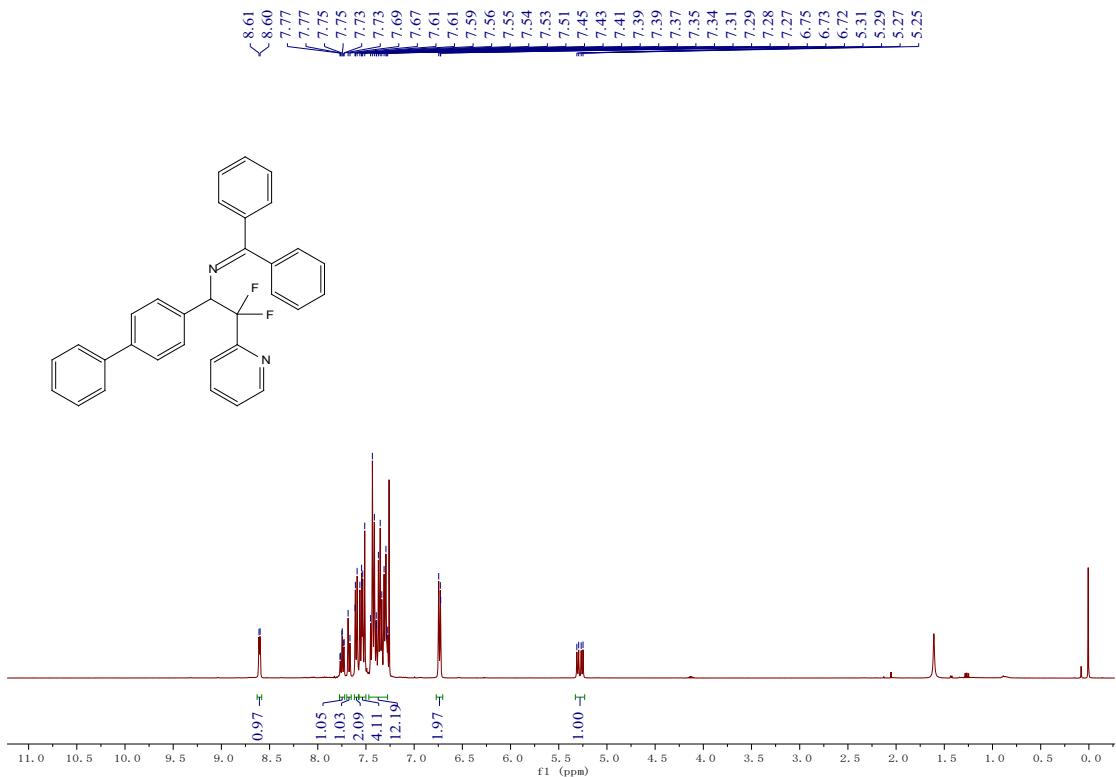
¹H NMR (600 MHz, CDCl₃) spectrum of **2j**



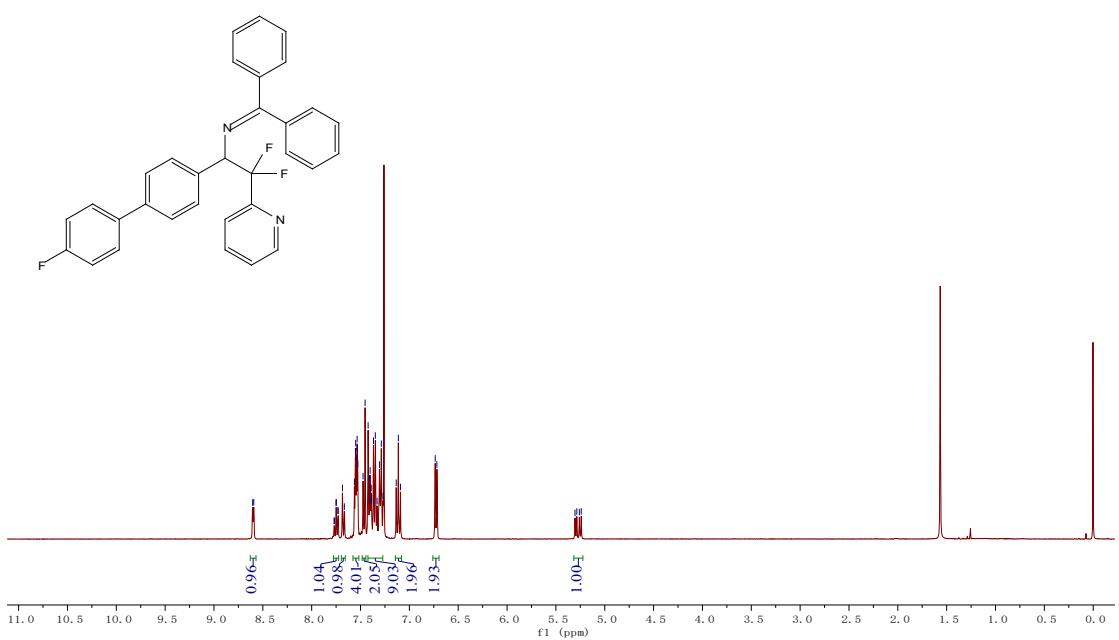
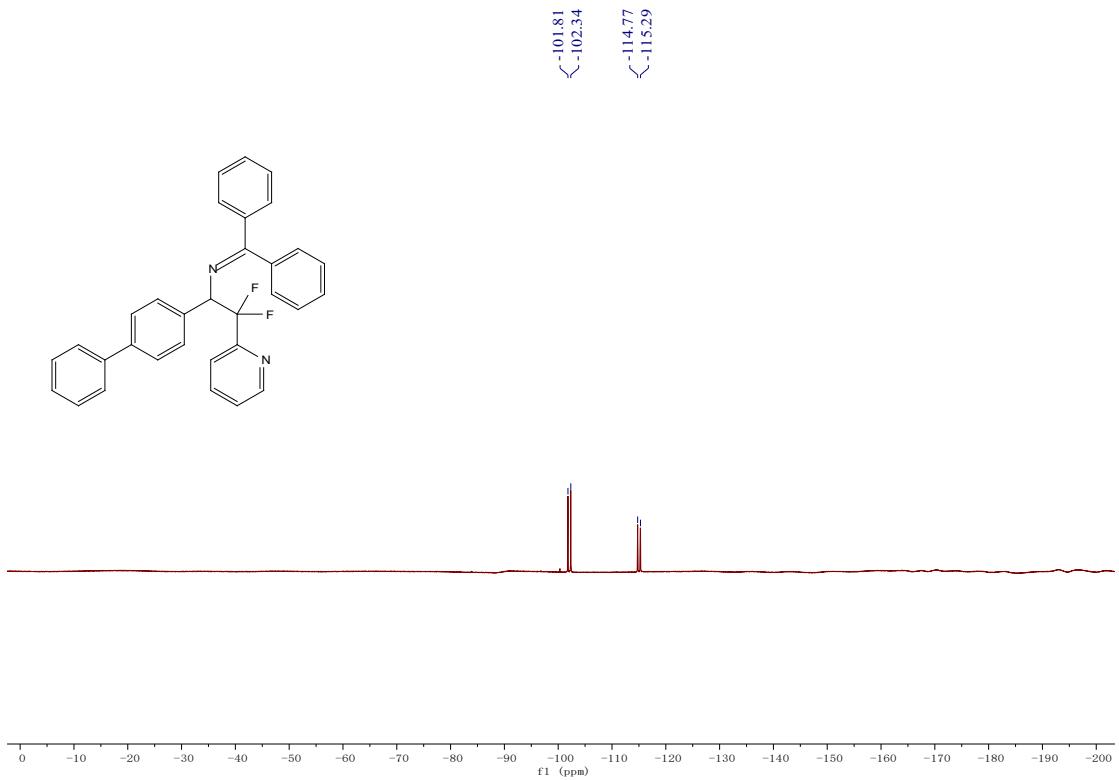
¹³C NMR (151 MHz, CDCl₃) spectrum of **2j**



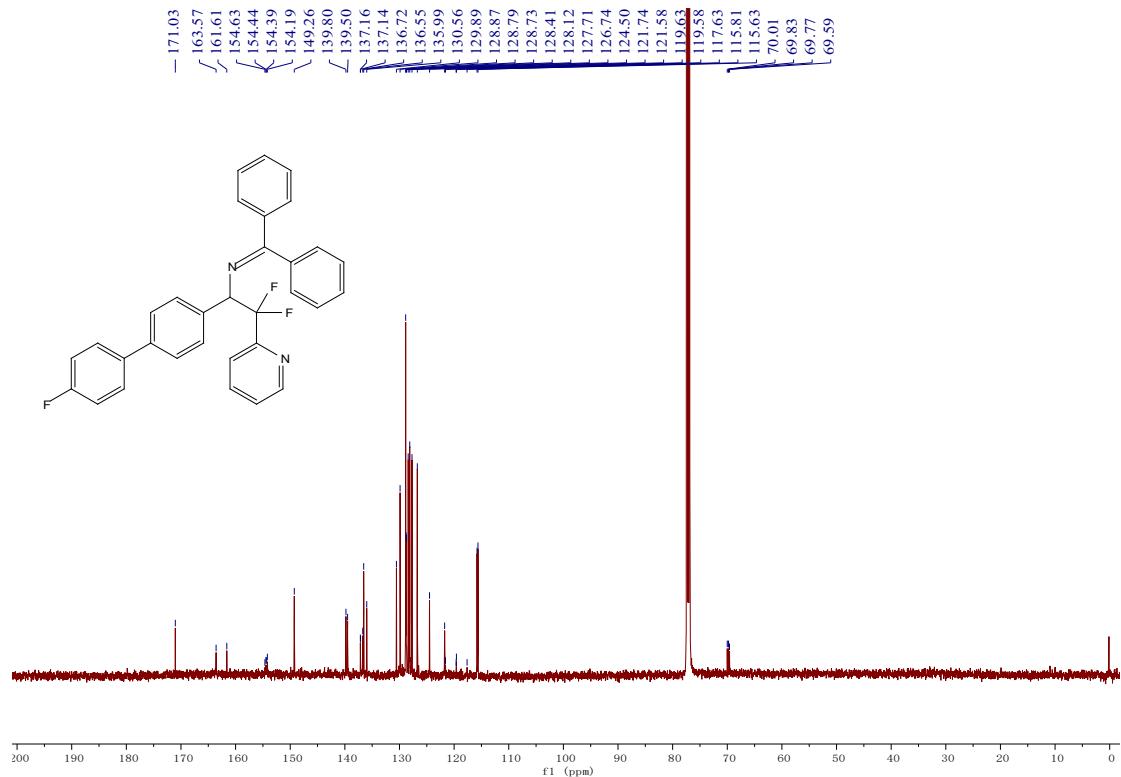
¹H NMR (400 MHz, CDCl₃) spectrum of **3a**



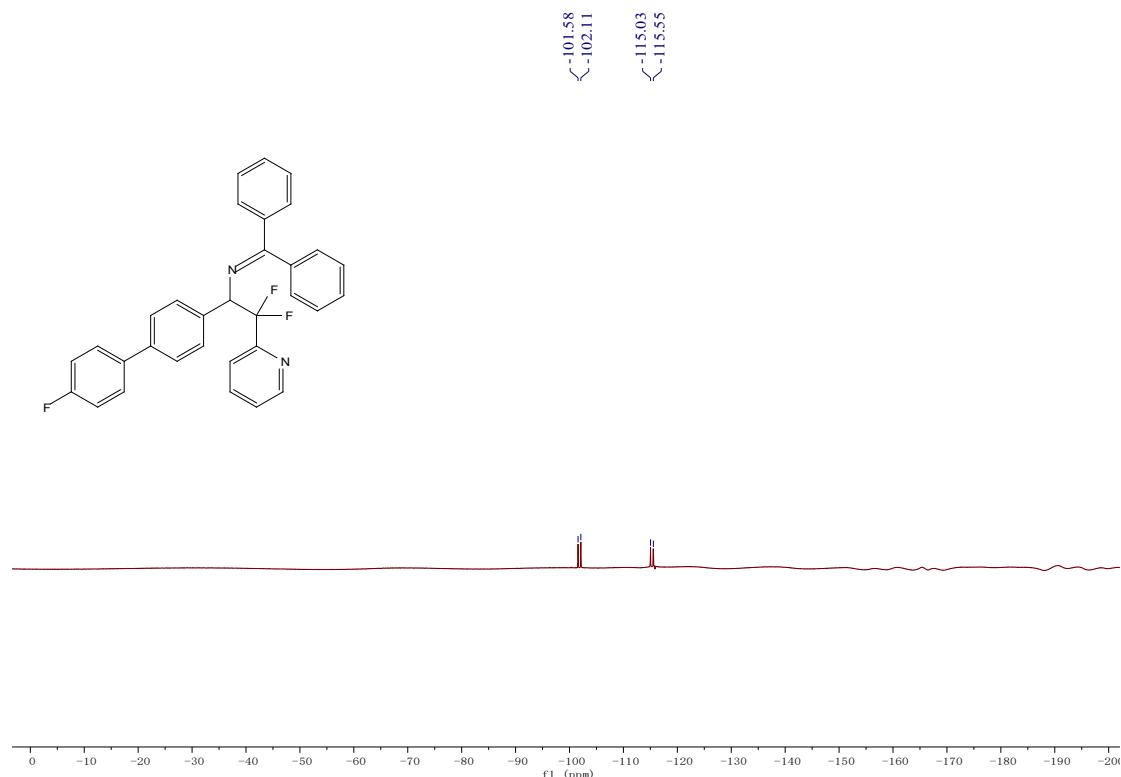
1⁹F NMR (471 MHz, CDCl₃) spectrum of 3a



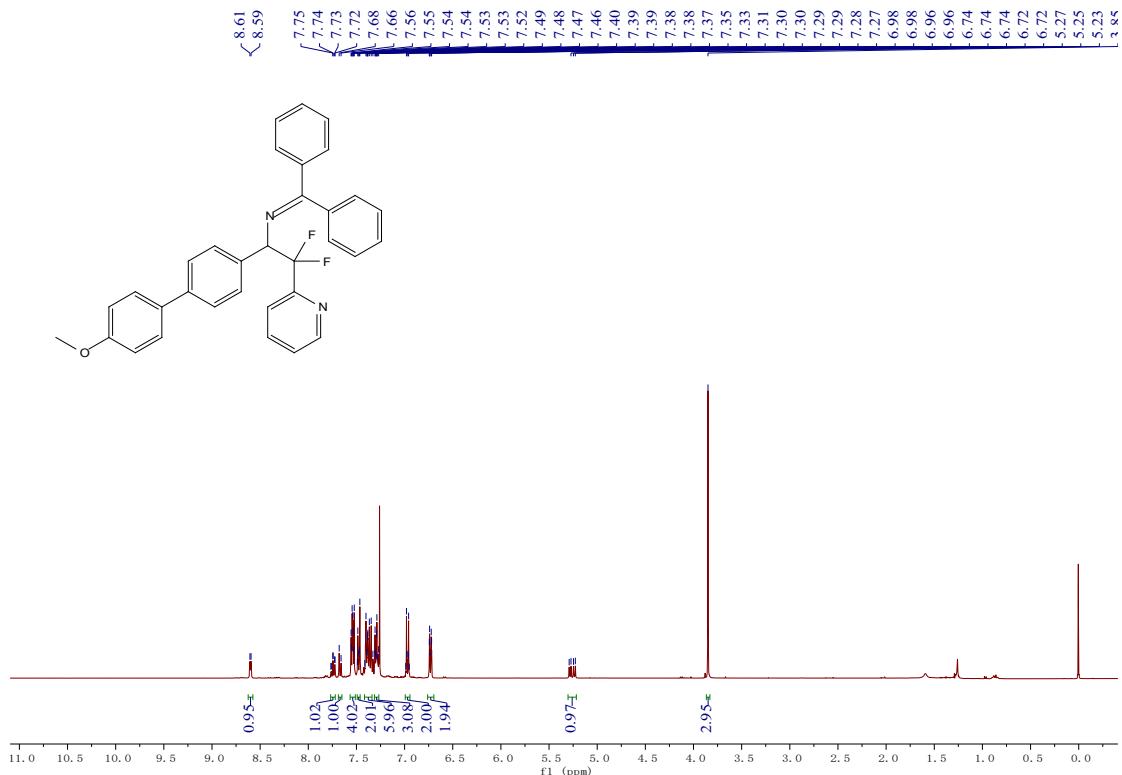
¹³C NMR (126 MHz, CDCl₃) spectrum of **3b**



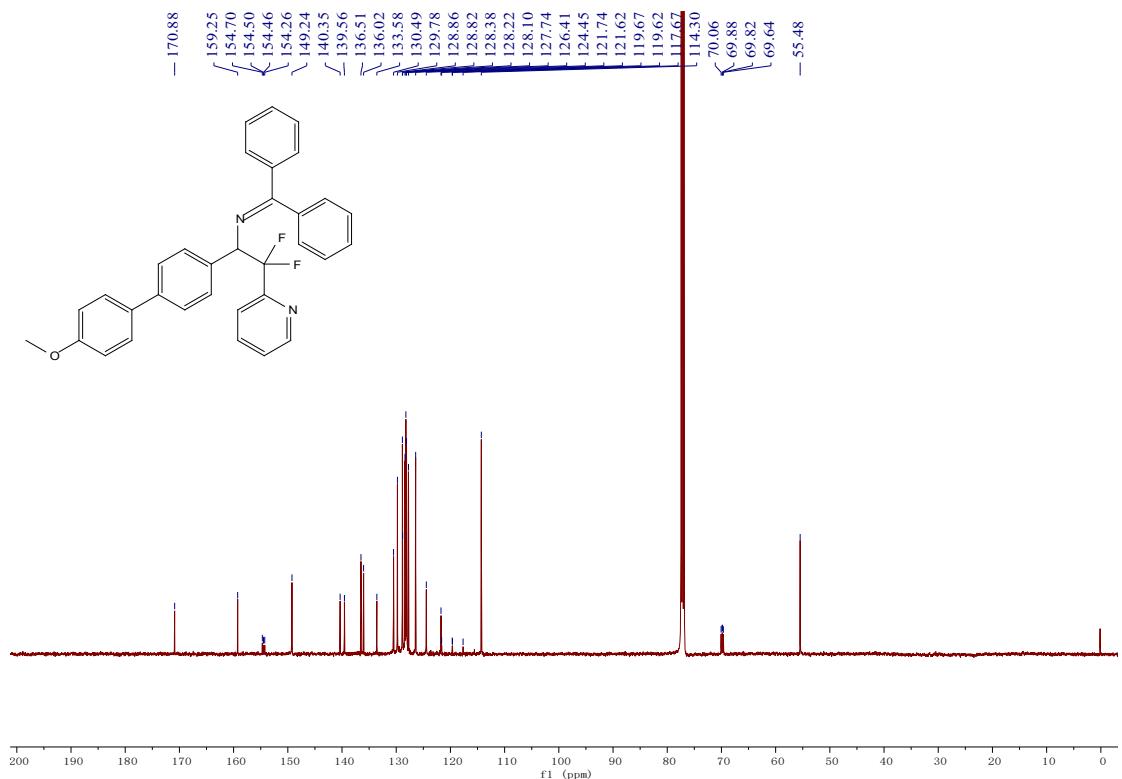
¹⁹F NMR (471 MHz, CDCl_3) spectrum of **3b**



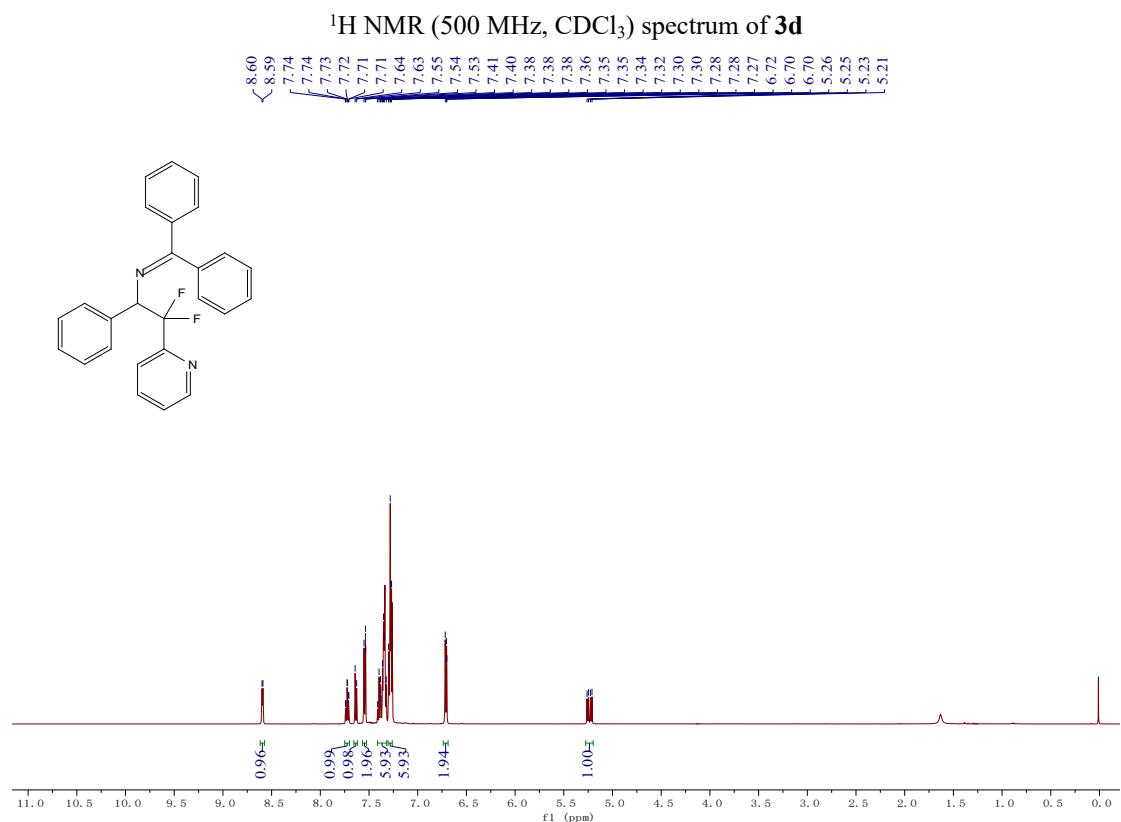
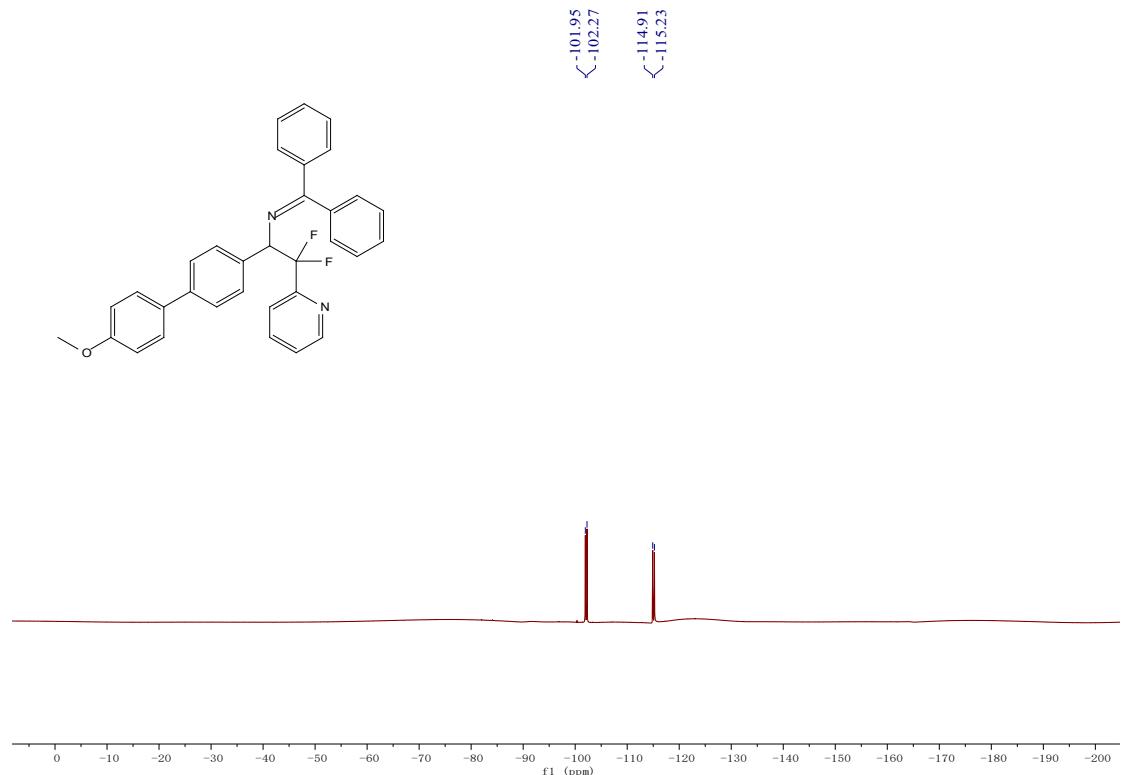
¹H NMR (400 MHz, CDCl_3) spectrum of **3c**



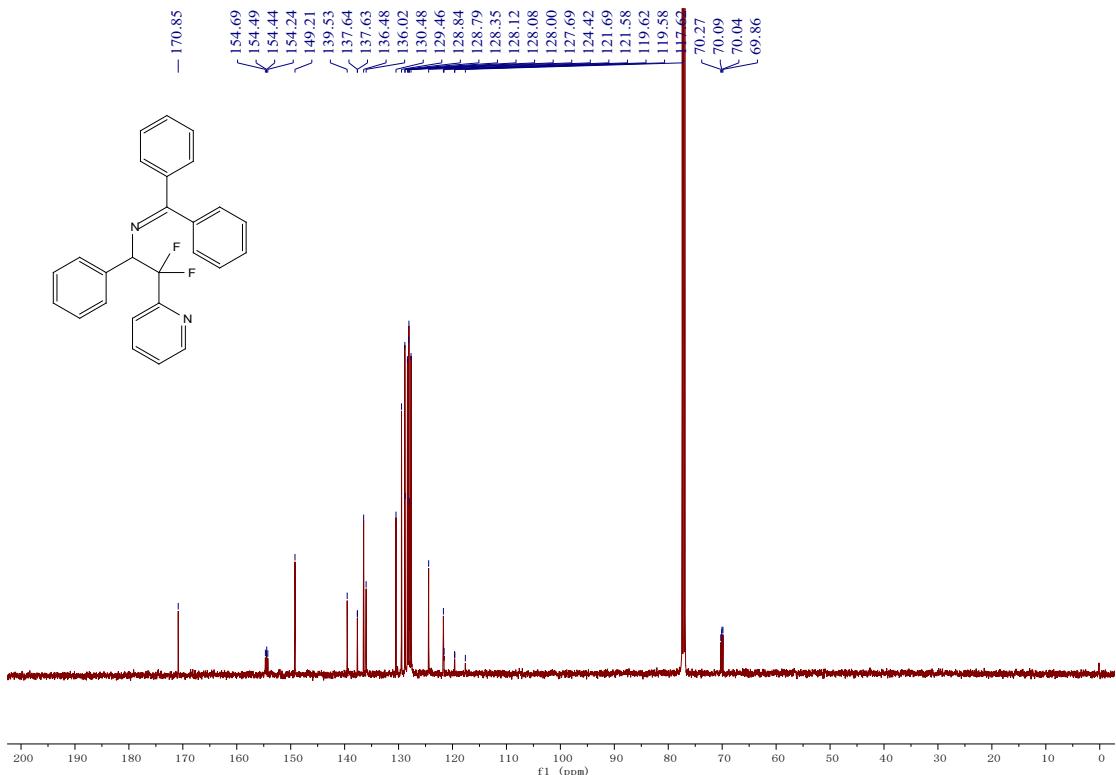
¹³C NMR (126 MHz, CDCl₃) spectrum of **3c**



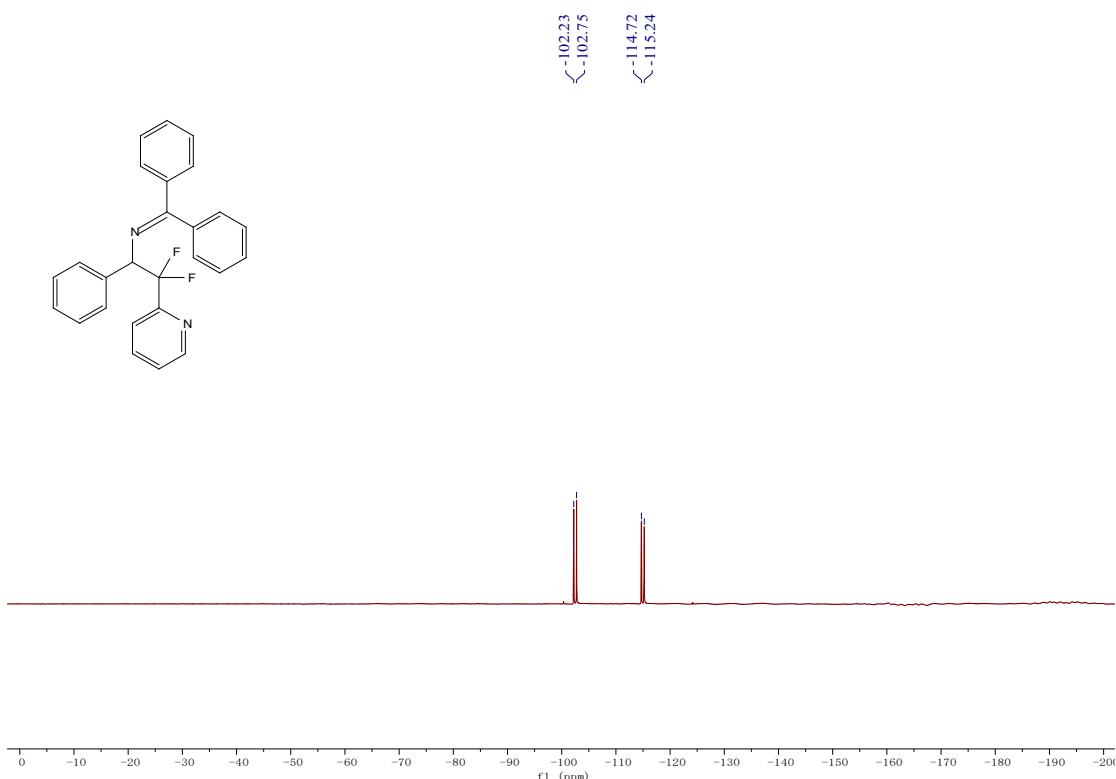
¹⁹F NMR (753 MHz, CDCl₃) spectrum of **3c**



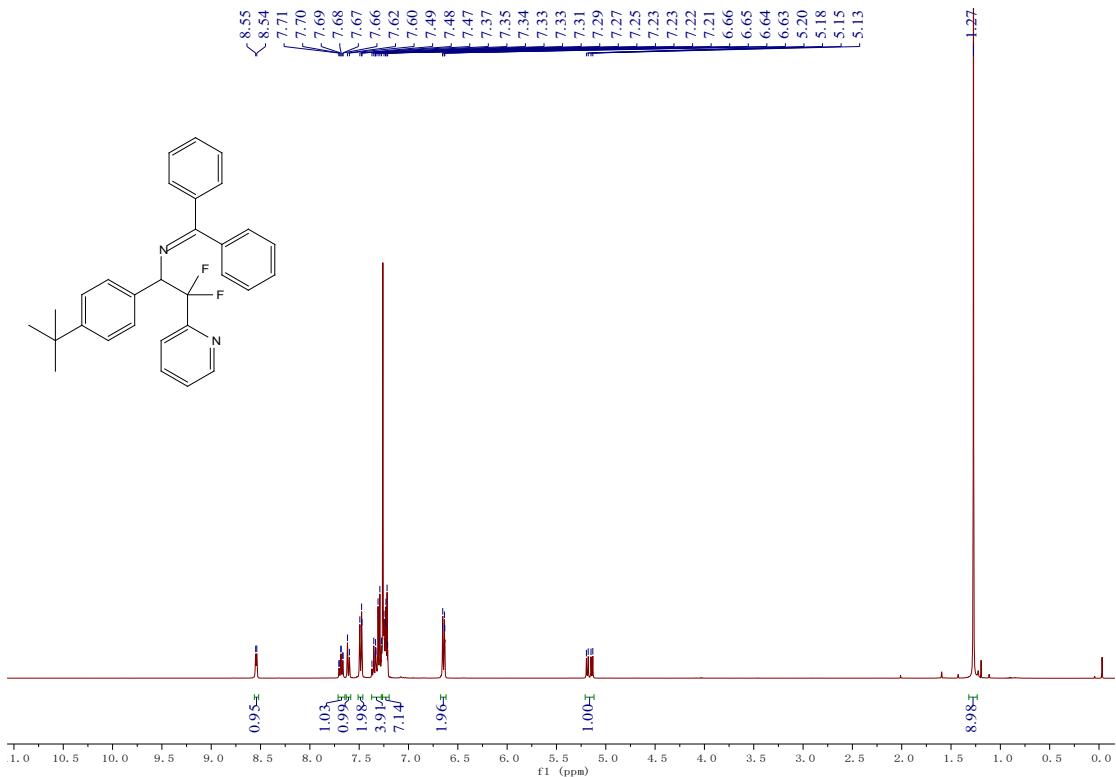
^{13}C NMR (126 MHz, CDCl_3) spectrum of **3d**



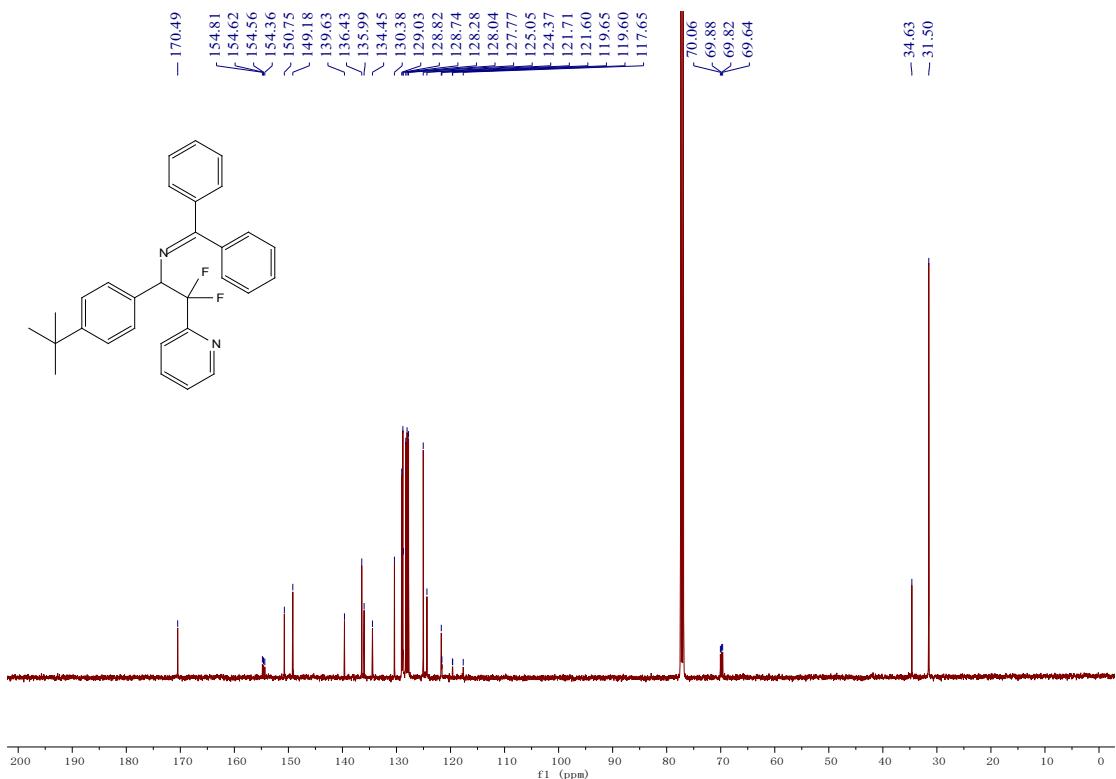
¹⁹F NMR (471 MHz, CDCl₃) spectrum of 3d



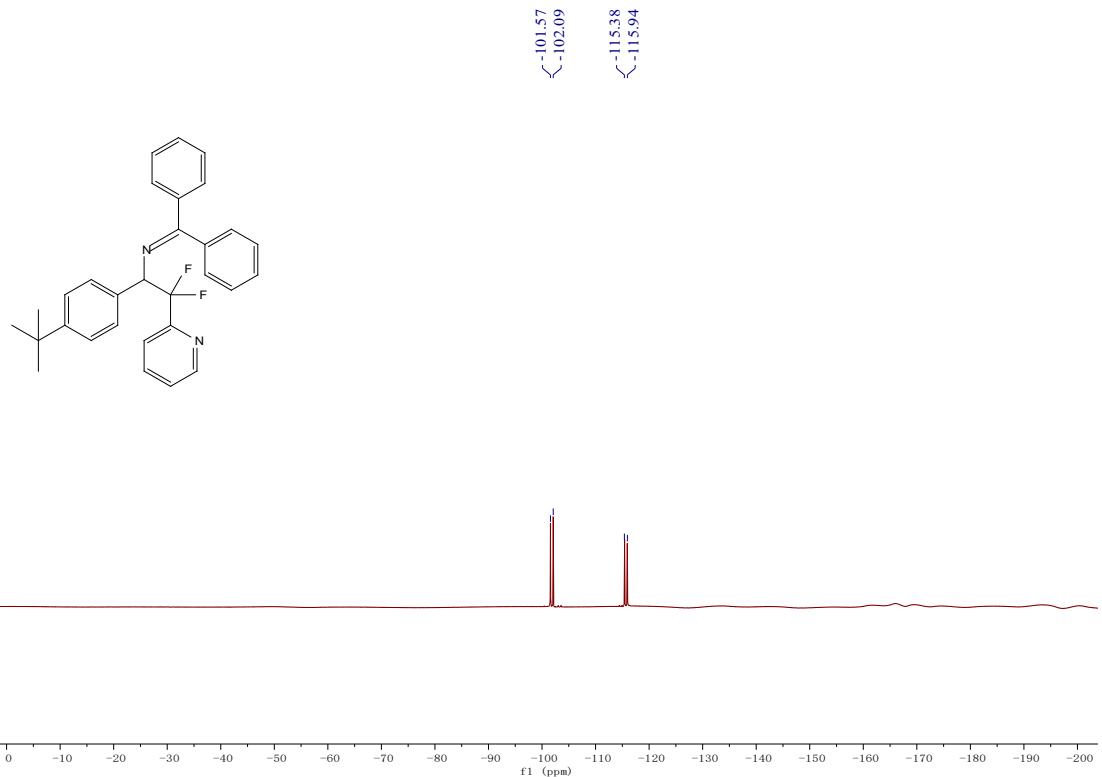
¹H NMR (400 MHz, CDCl₃) spectrum of 3e



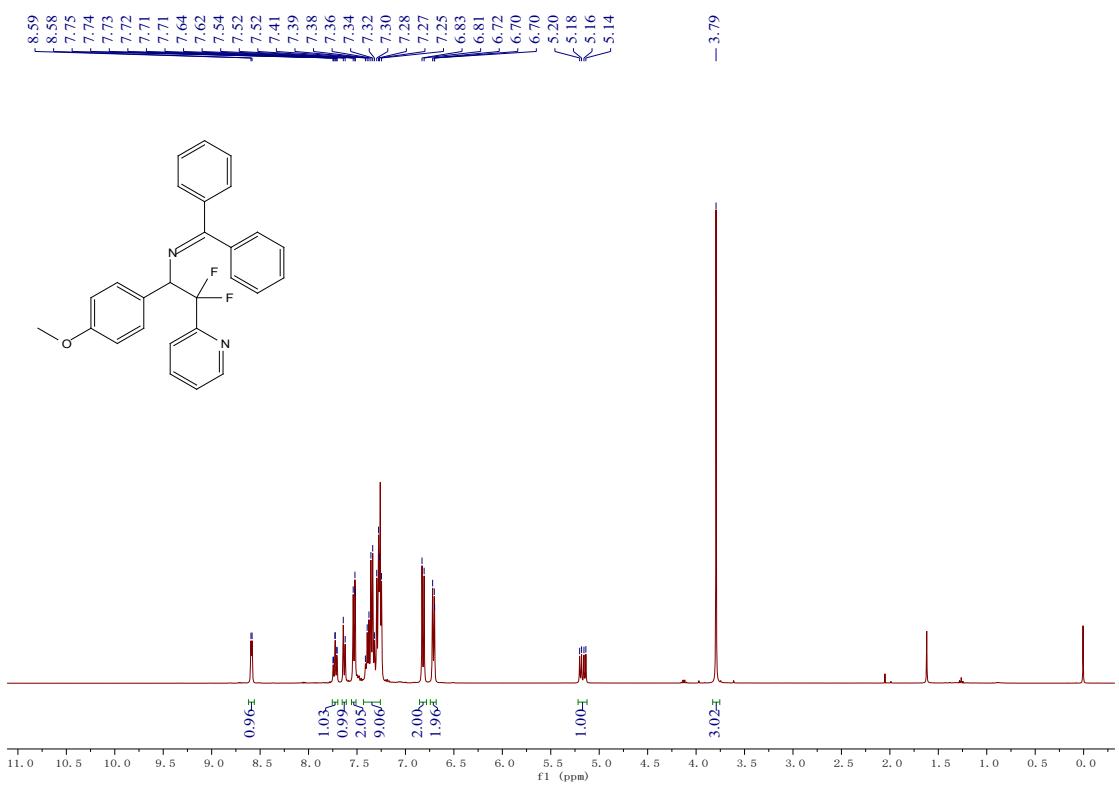
¹³C NMR (126 MHz, CDCl₃) spectrum of **3e**



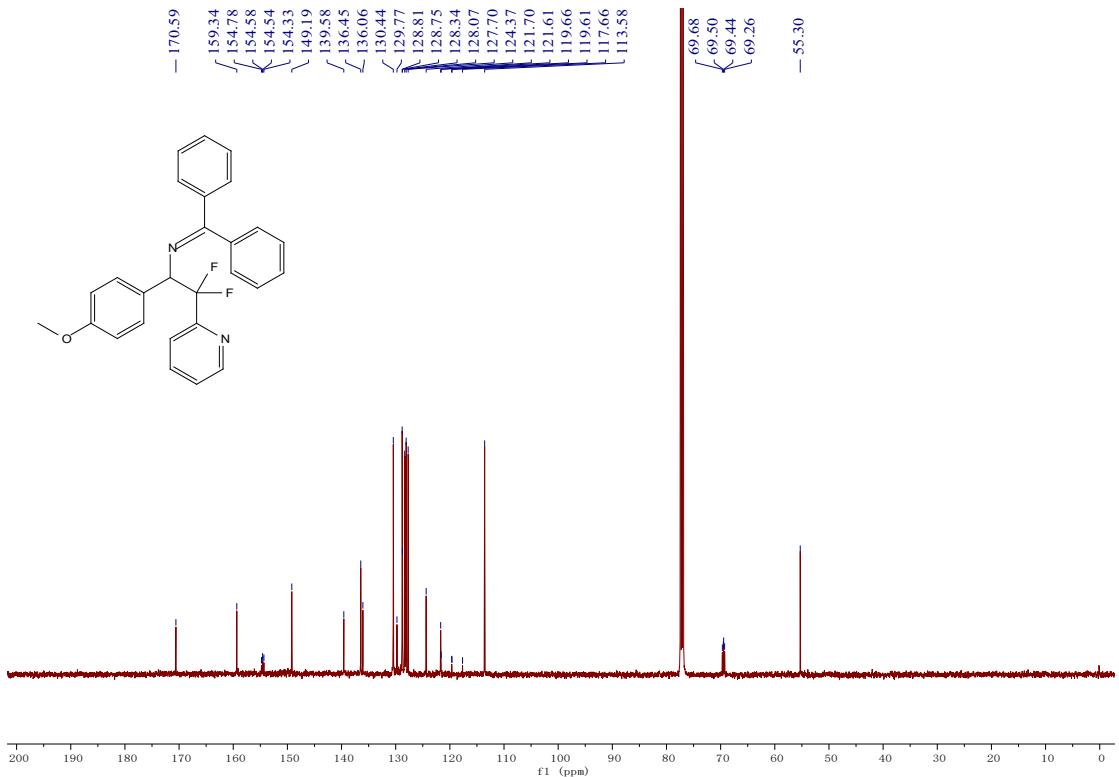
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **3e**



¹H NMR (400 MHz, CDCl₃) spectrum of **3f**

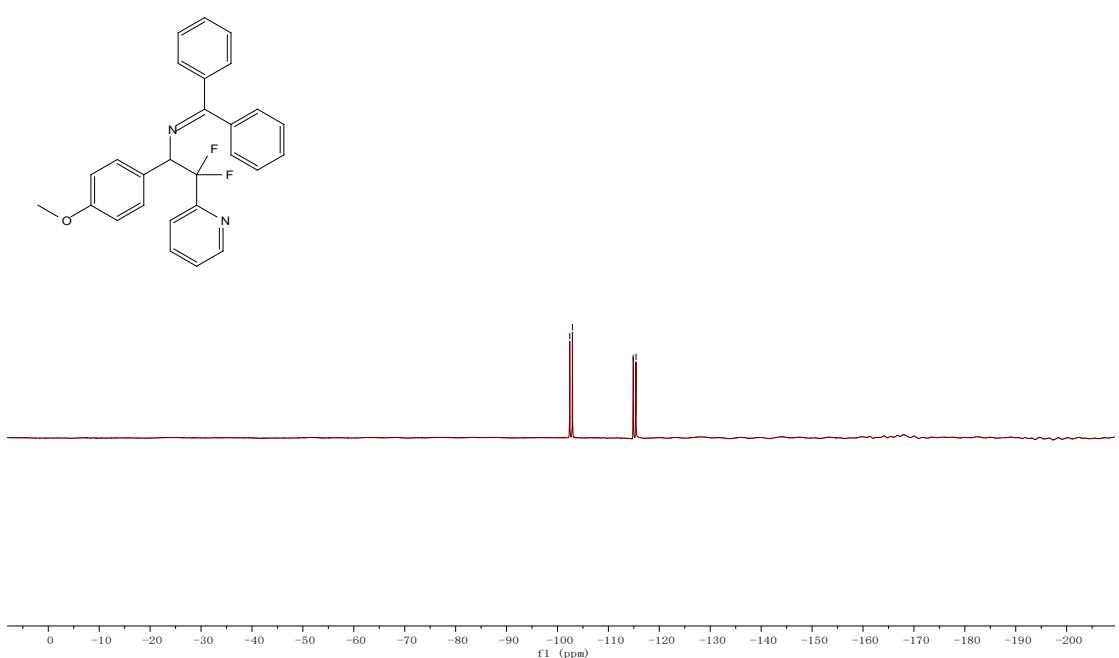


¹³C NMR (126 MHz, CDCl₃) spectrum of **3f**

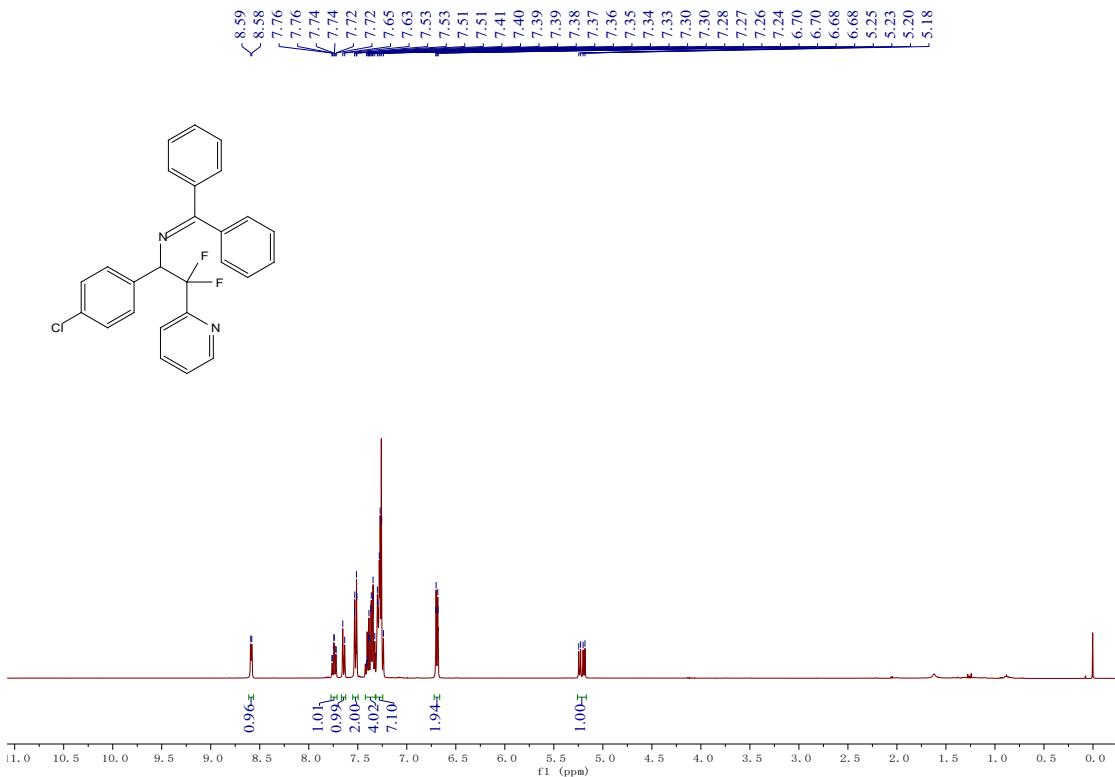


¹⁹F NMR (471 MHz, CDCl₃) spectrum of 3f

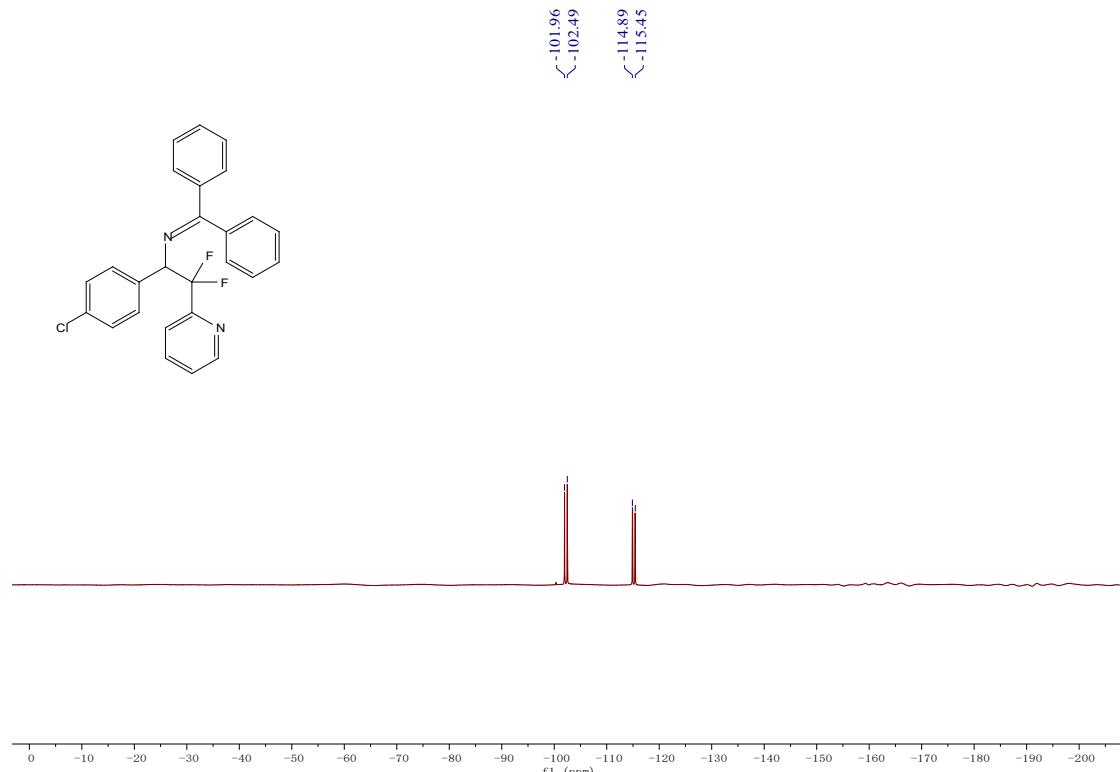
102.41
102.93
114.86
115.42



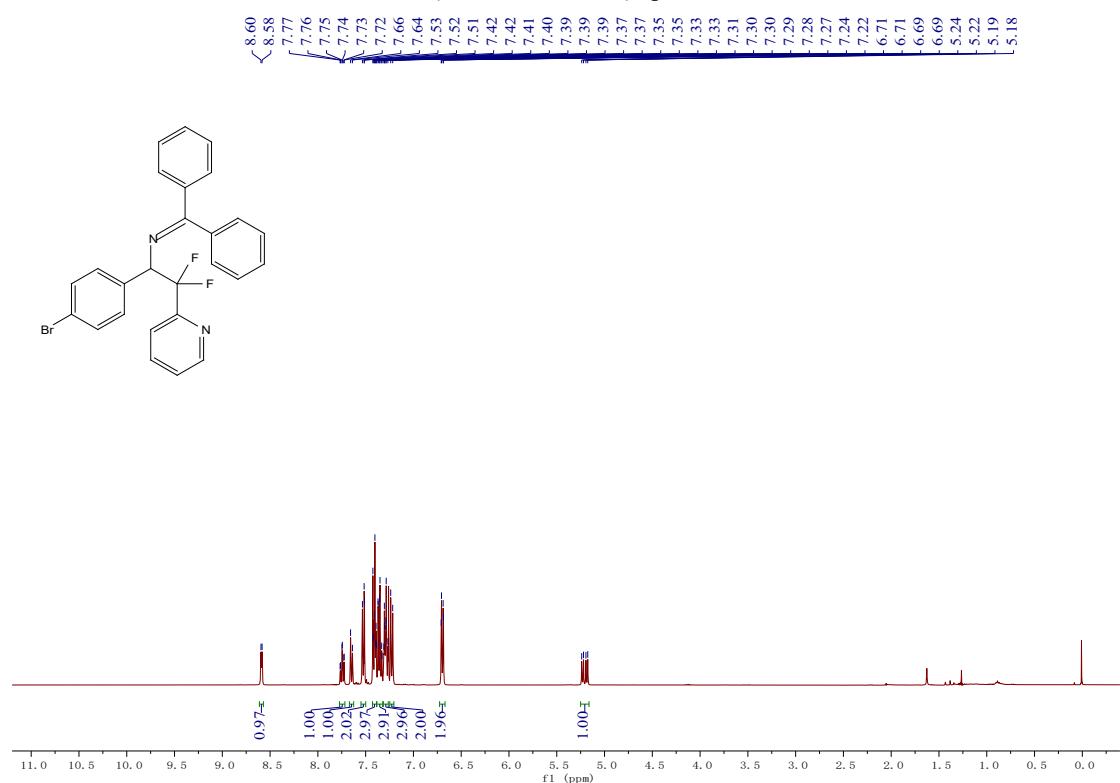
¹H NMR (400 MHz, CDCl₃) spectrum of 3g



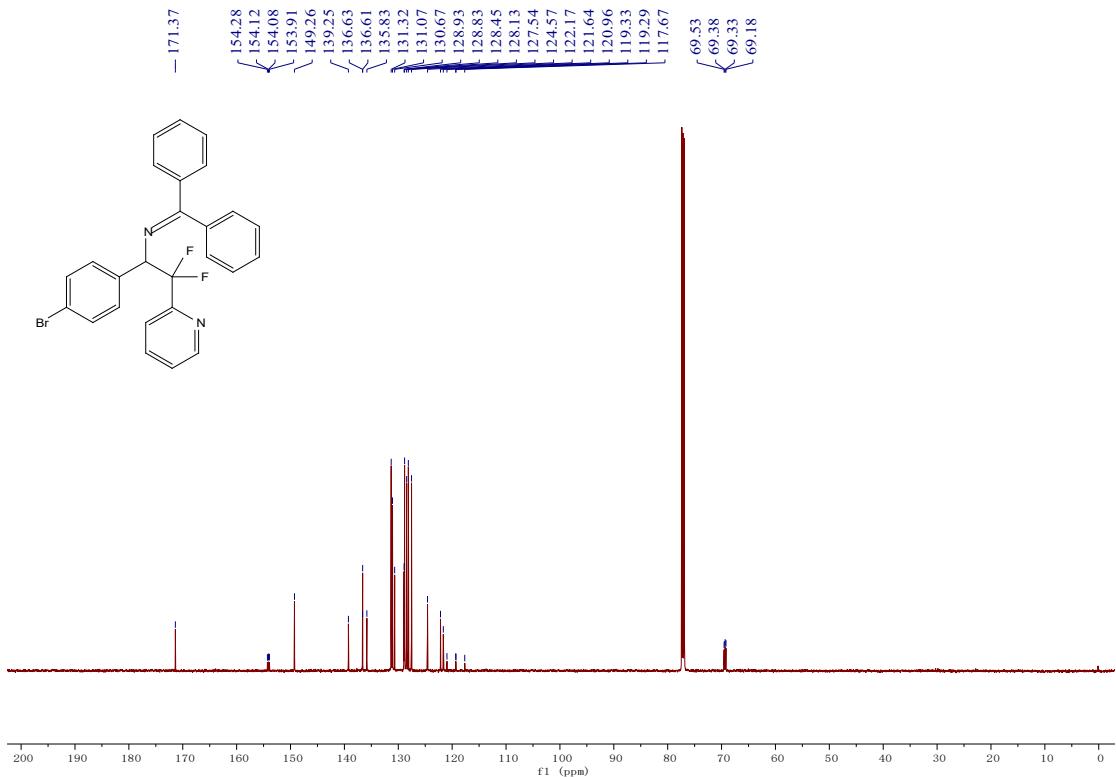
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **3g**



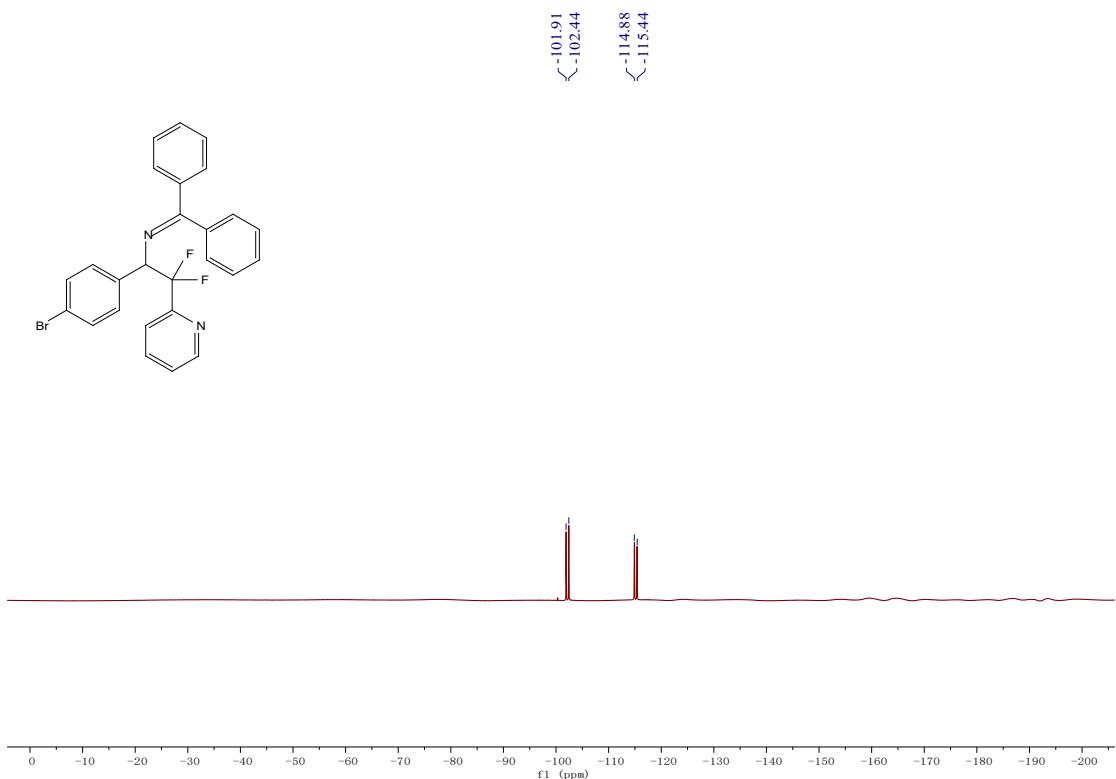
¹H NMR (400 MHz, CDCl₃) spectrum of **3h**



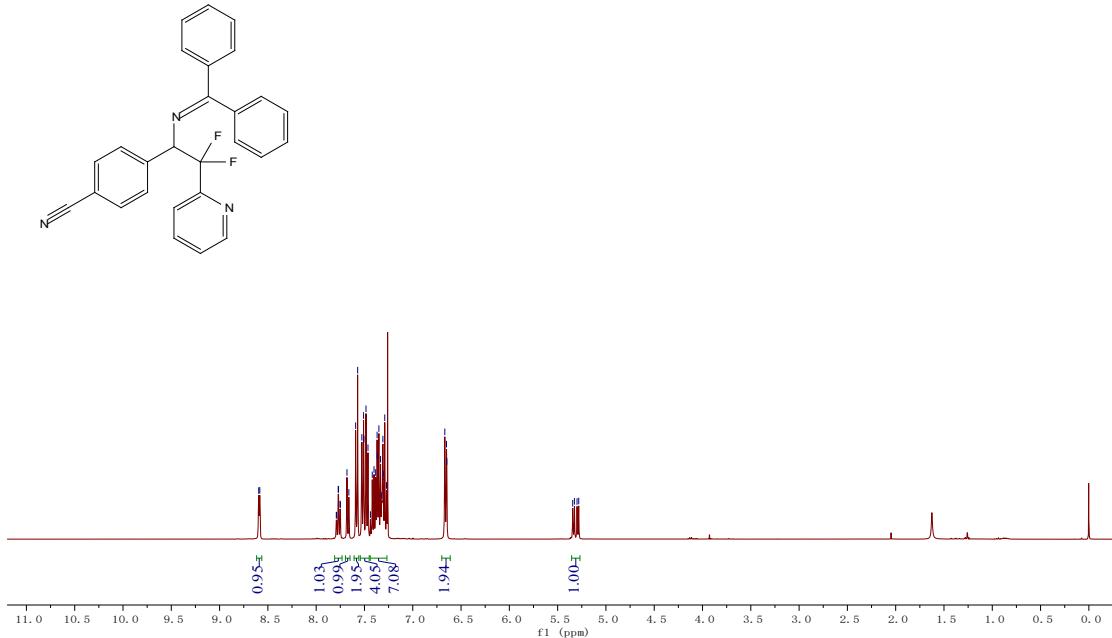
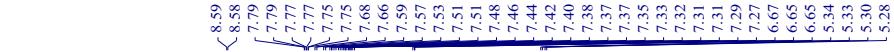
¹³C NMR (151 MHz, CDCl₃) spectrum of **3h**



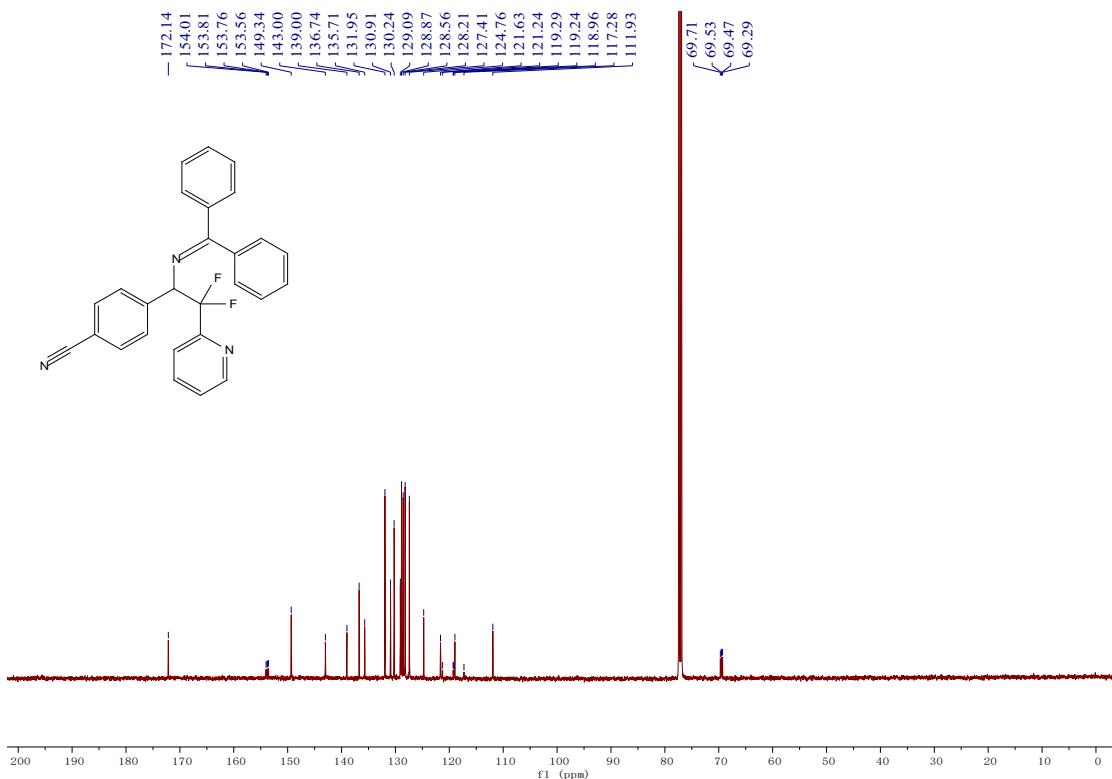
^{13}C NMR (400 MHz, CDCl_3) spectrum of **3h**



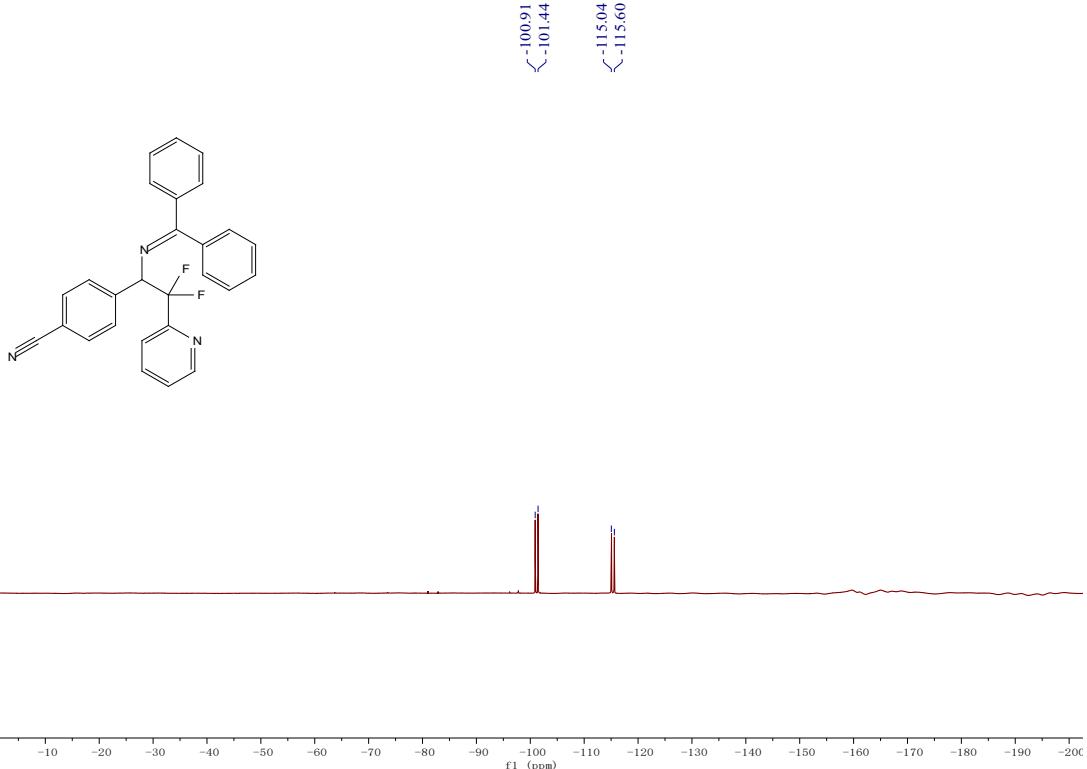
^1H NMR (400 MHz, CDCl_3) spectrum of **3i**

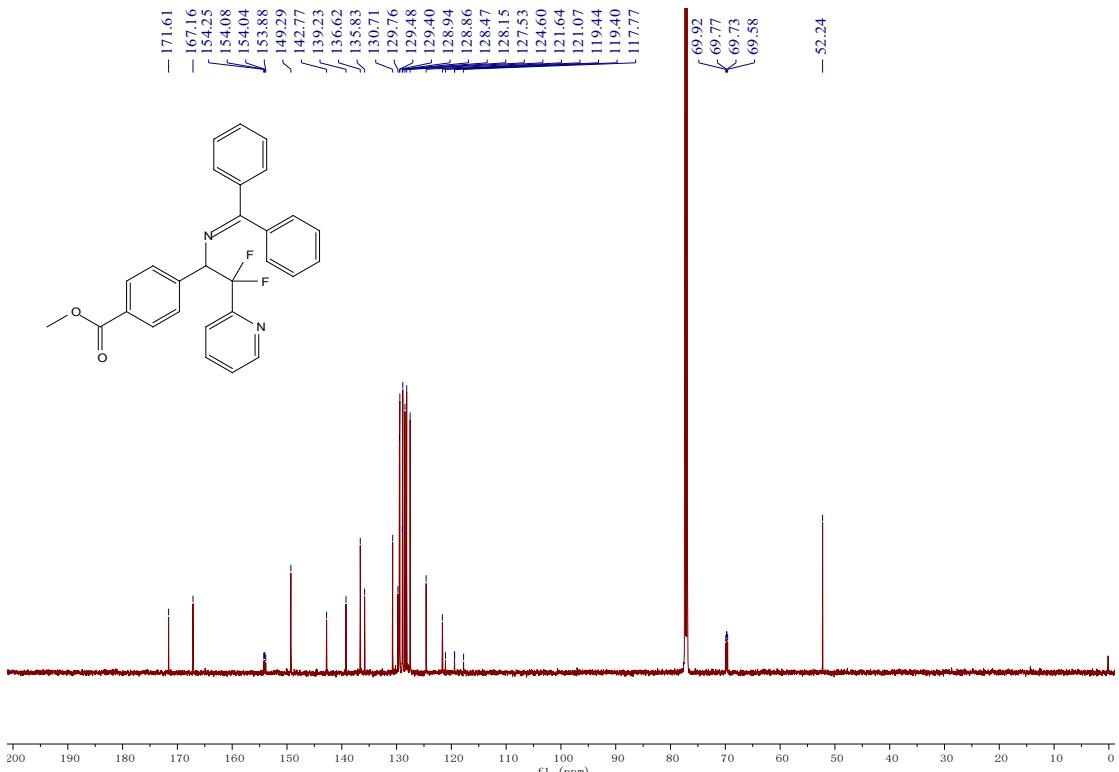


¹H NMR (126 MHz, CDCl₃) spectrum of 3i

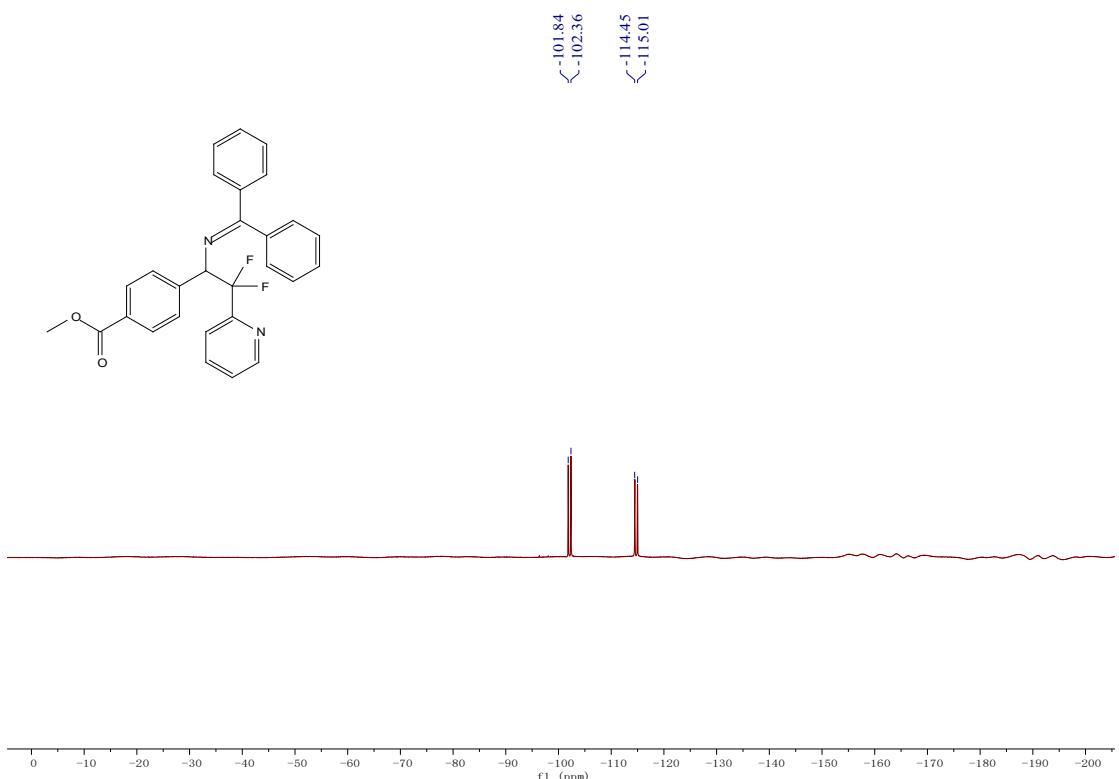


¹⁹F NMR (471 MHz, CDCl₃) spectrum of 3i

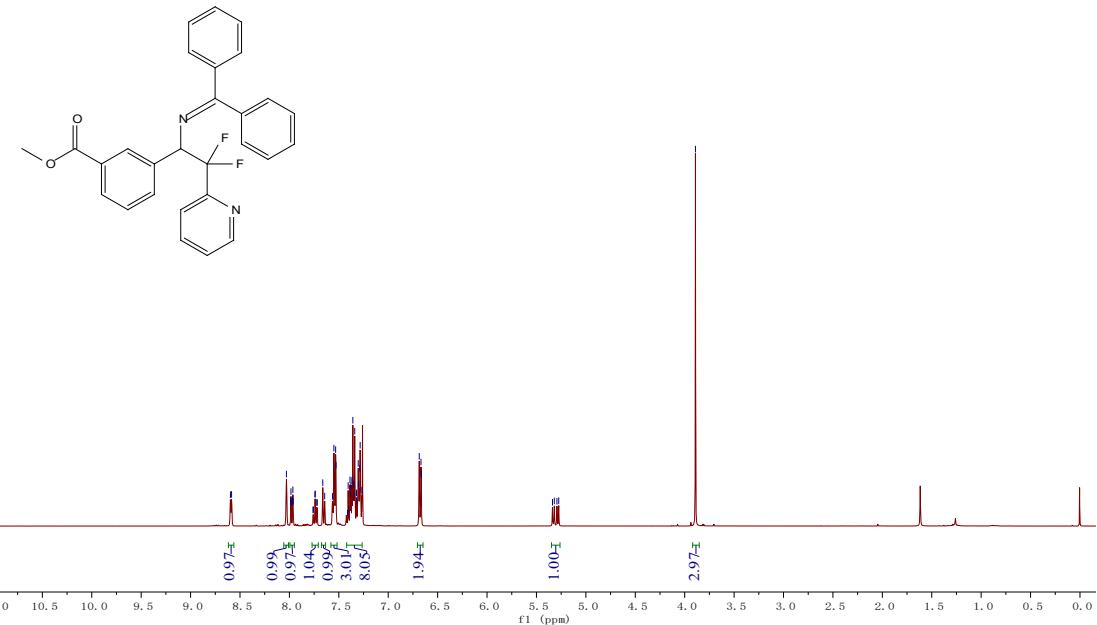




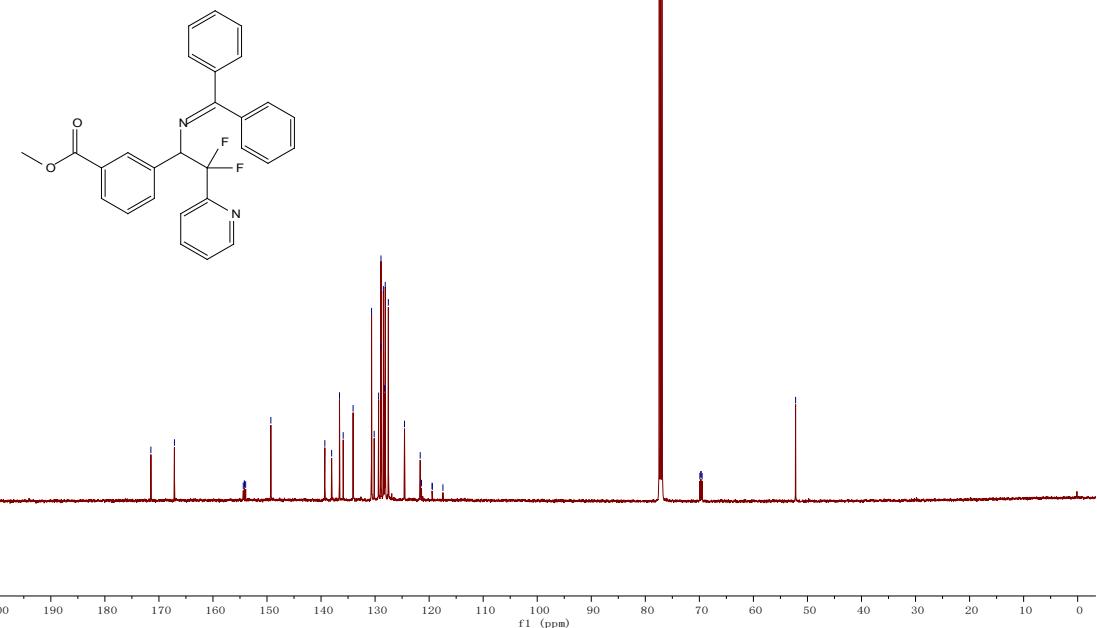
¹⁹F NMR (471 MHz, CDCl₃) spectrum of 3j



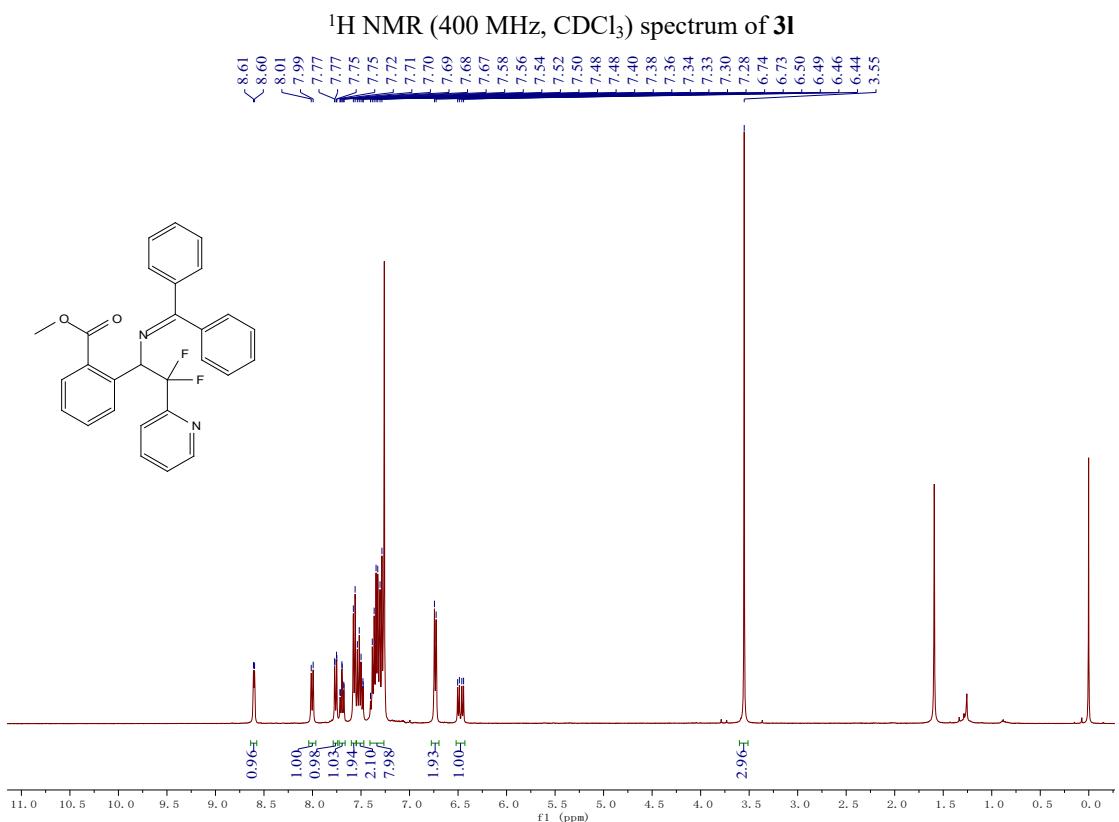
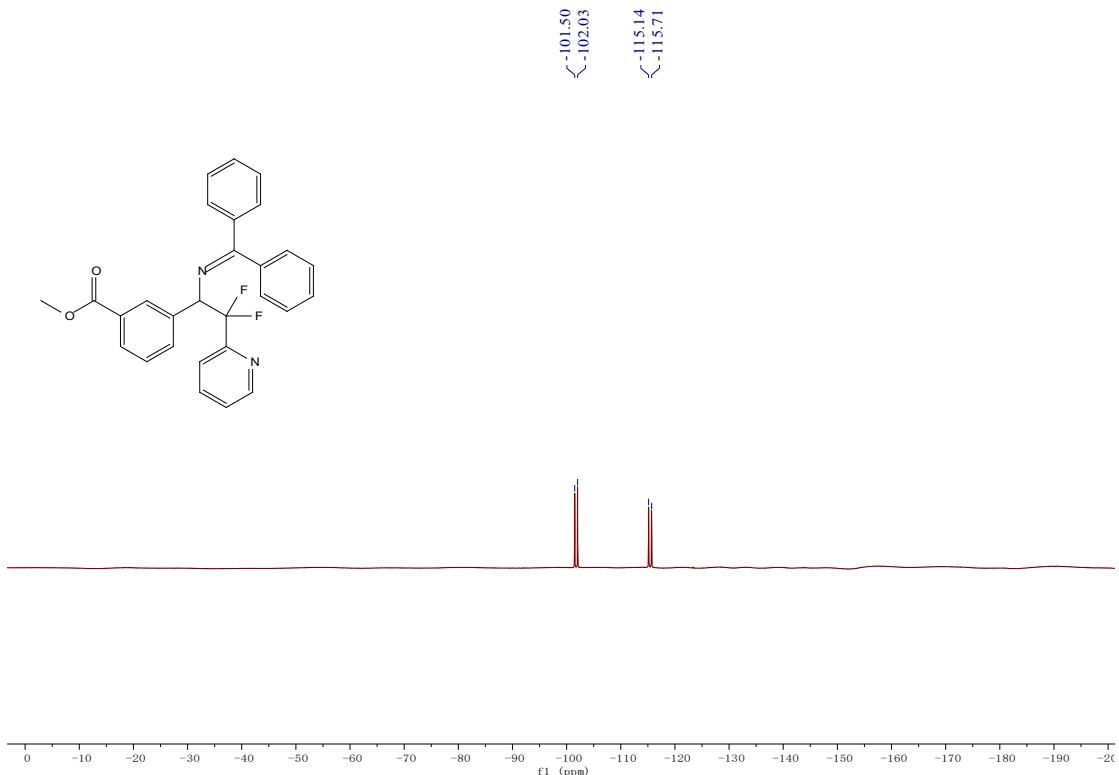
¹H NMR (400 MHz, CDCl₃) spectrum of 3k



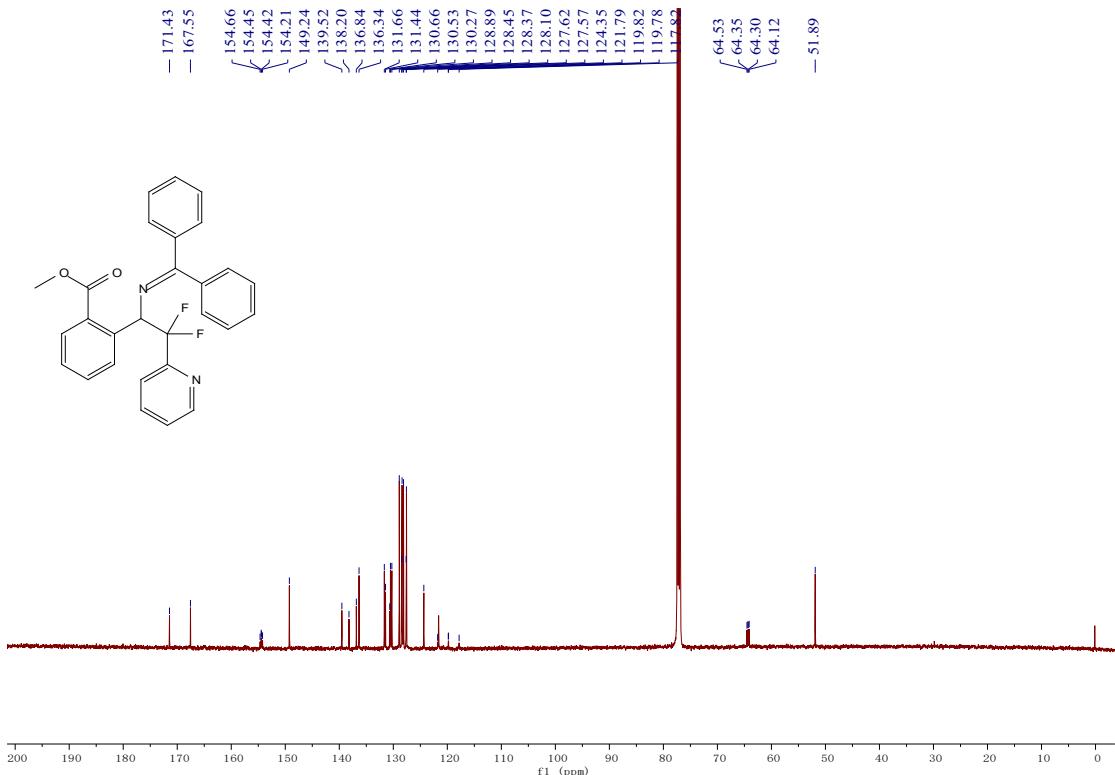
¹³C NMR (126 MHz, CDCl₃) spectrum of **3k**



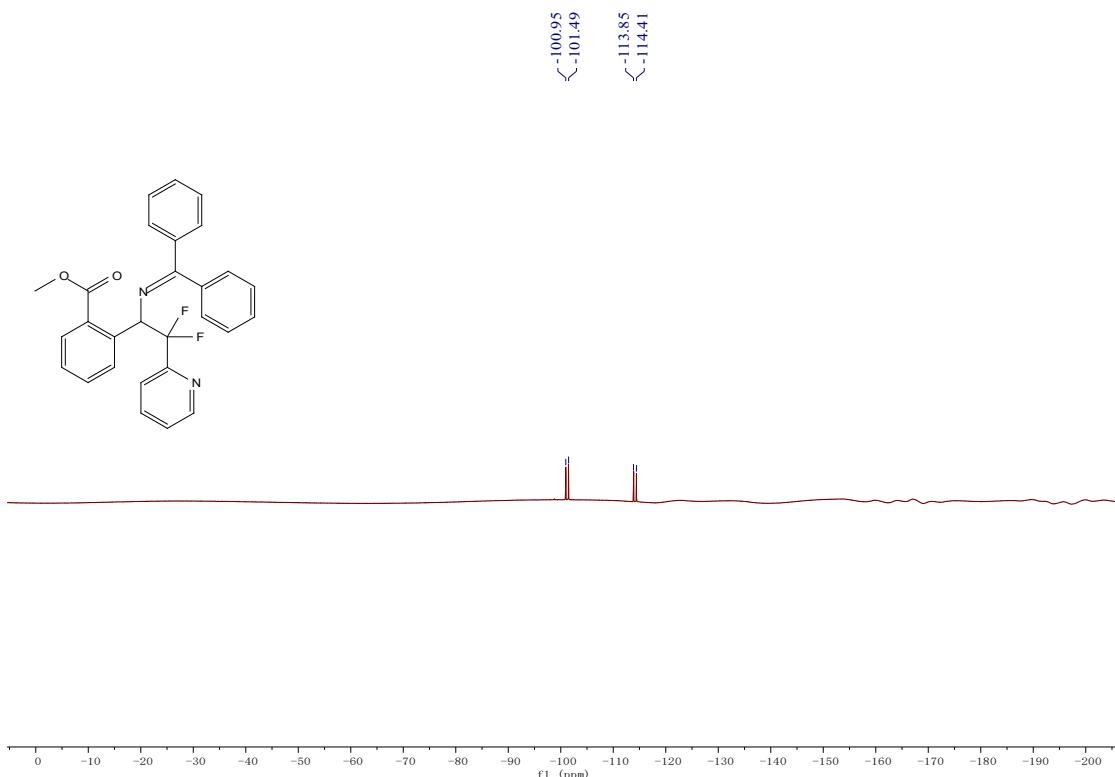
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **3k**



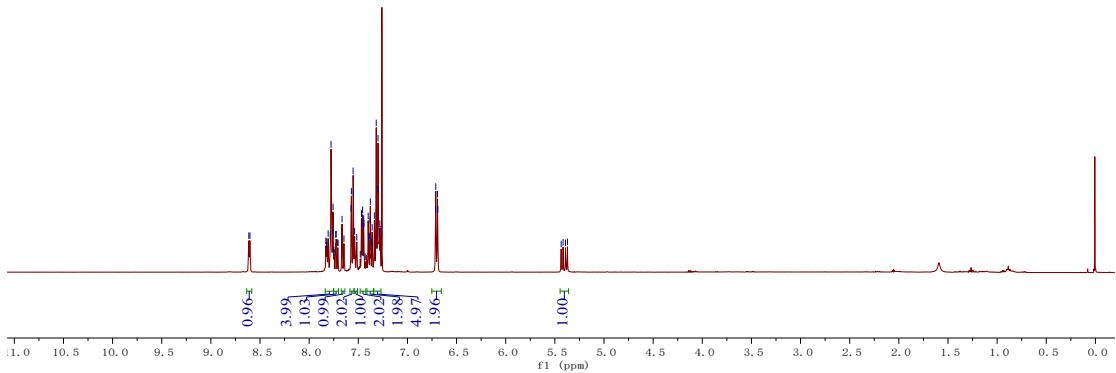
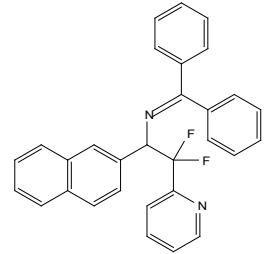
¹³C NMR (126 MHz, CDCl₃) spectrum of 3l



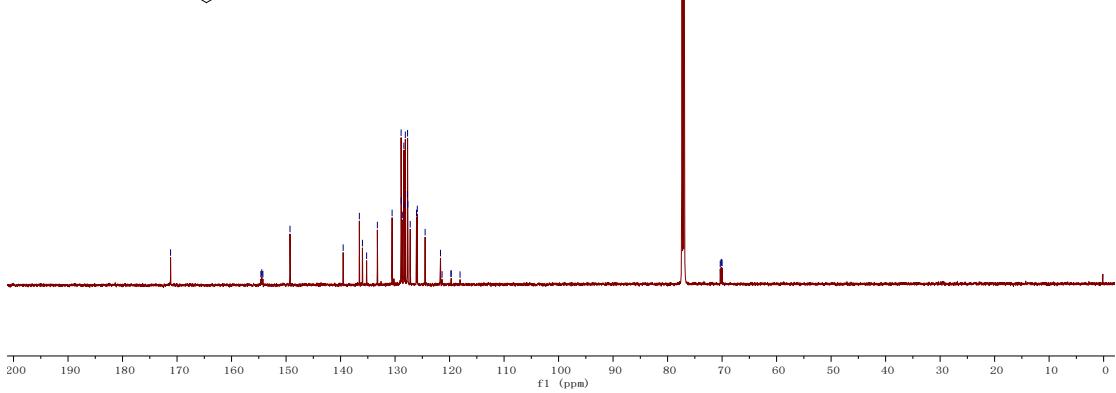
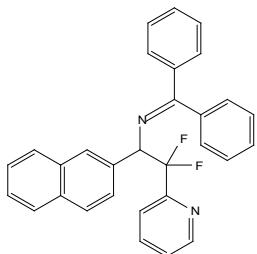
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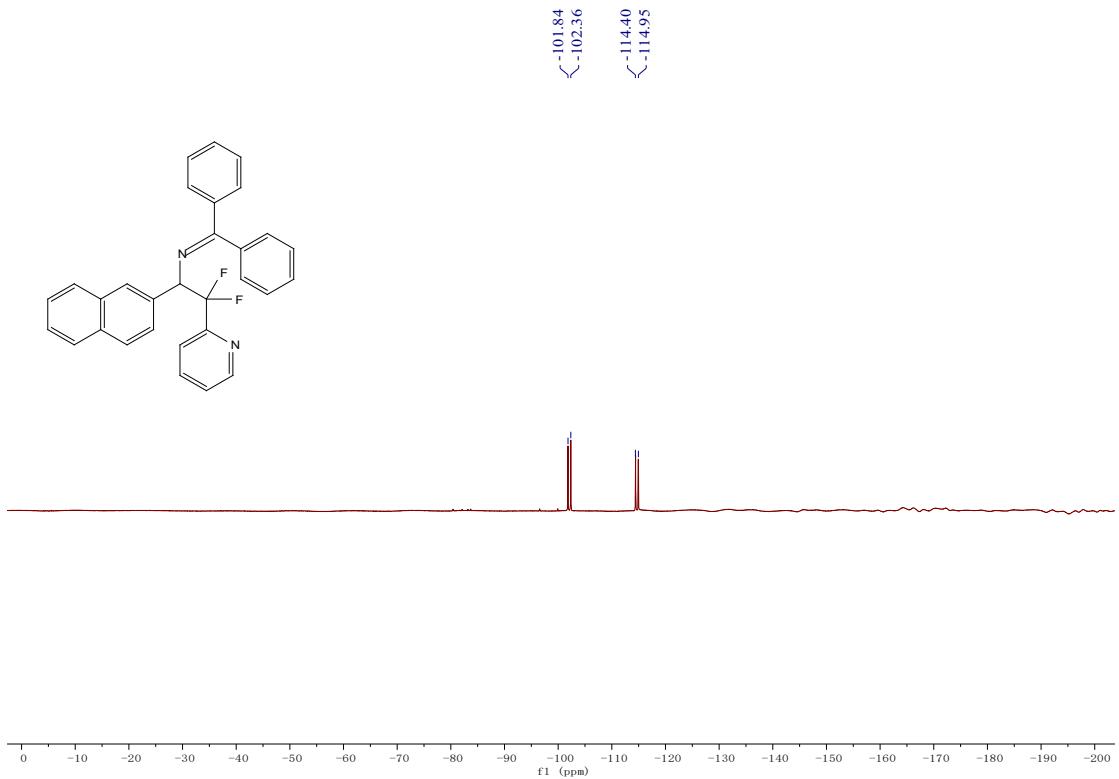
¹H NMR (400 MHz, CDCl₃) spectrum of **3m**



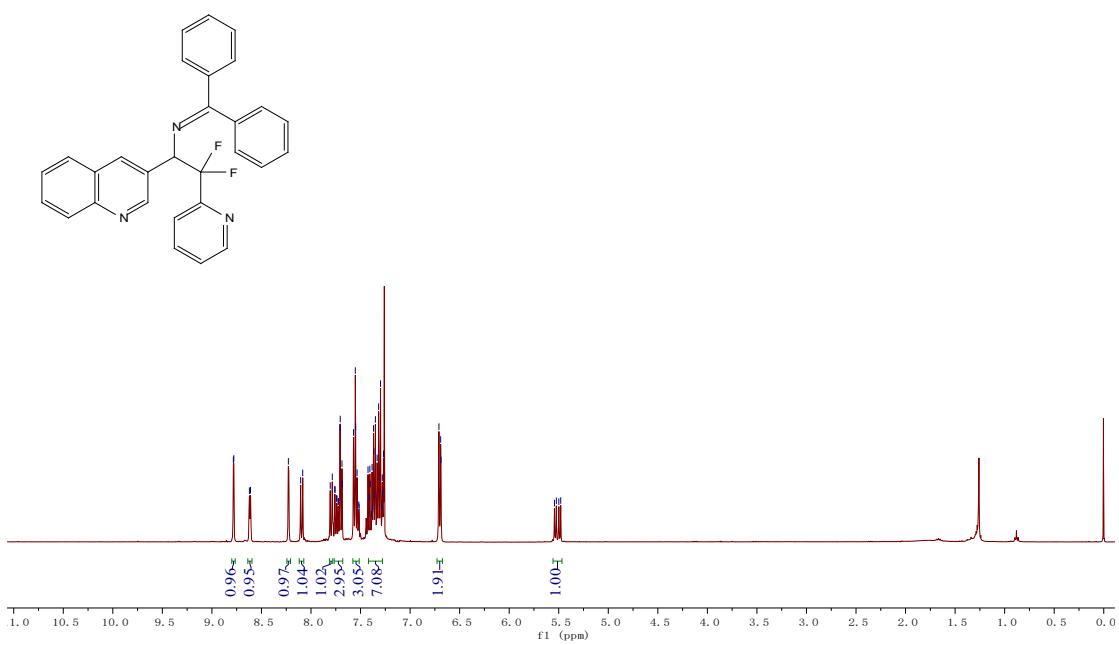
¹³C NMR (151 MHz, CDCl₃) spectrum of **3m**



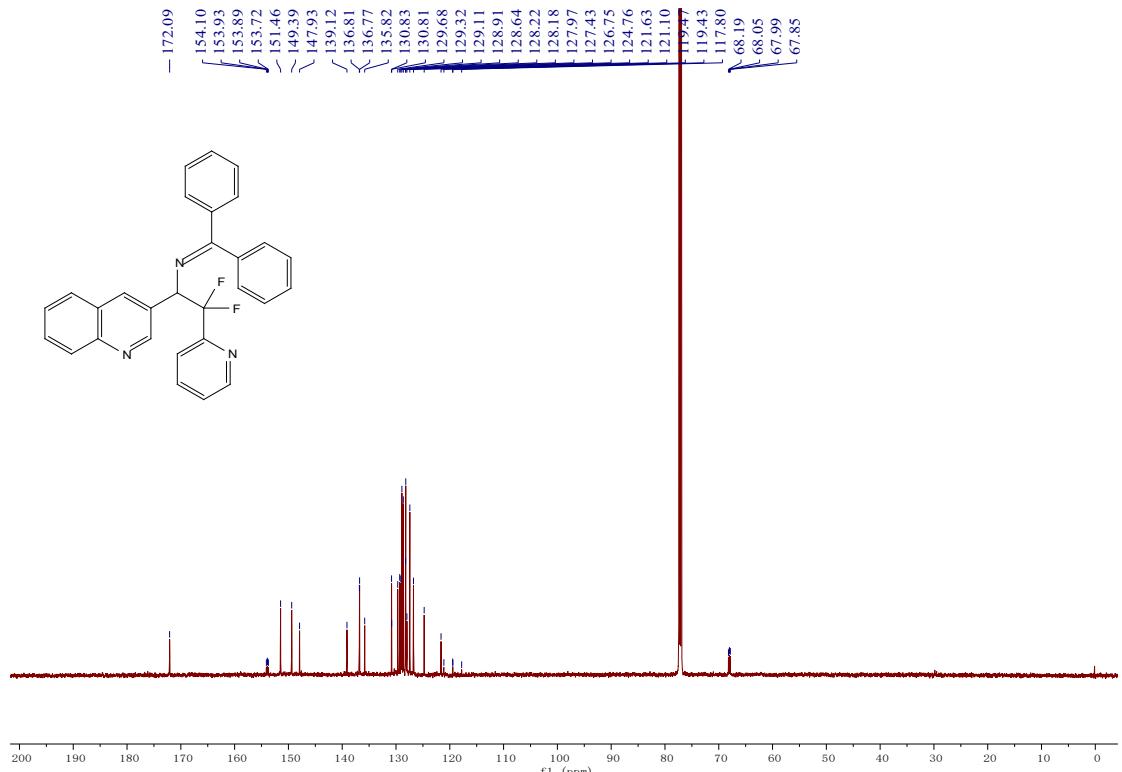
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **3m**



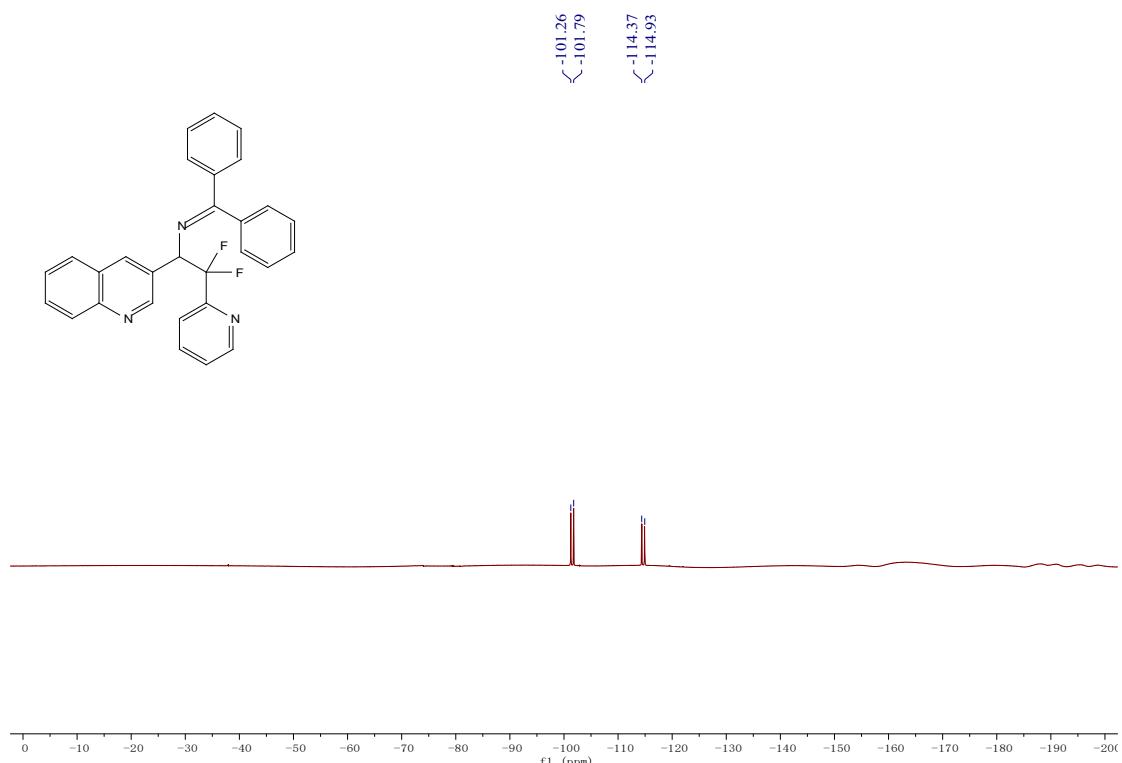
¹H NMR (400 MHz, CDCl₃) spectrum of **3n**



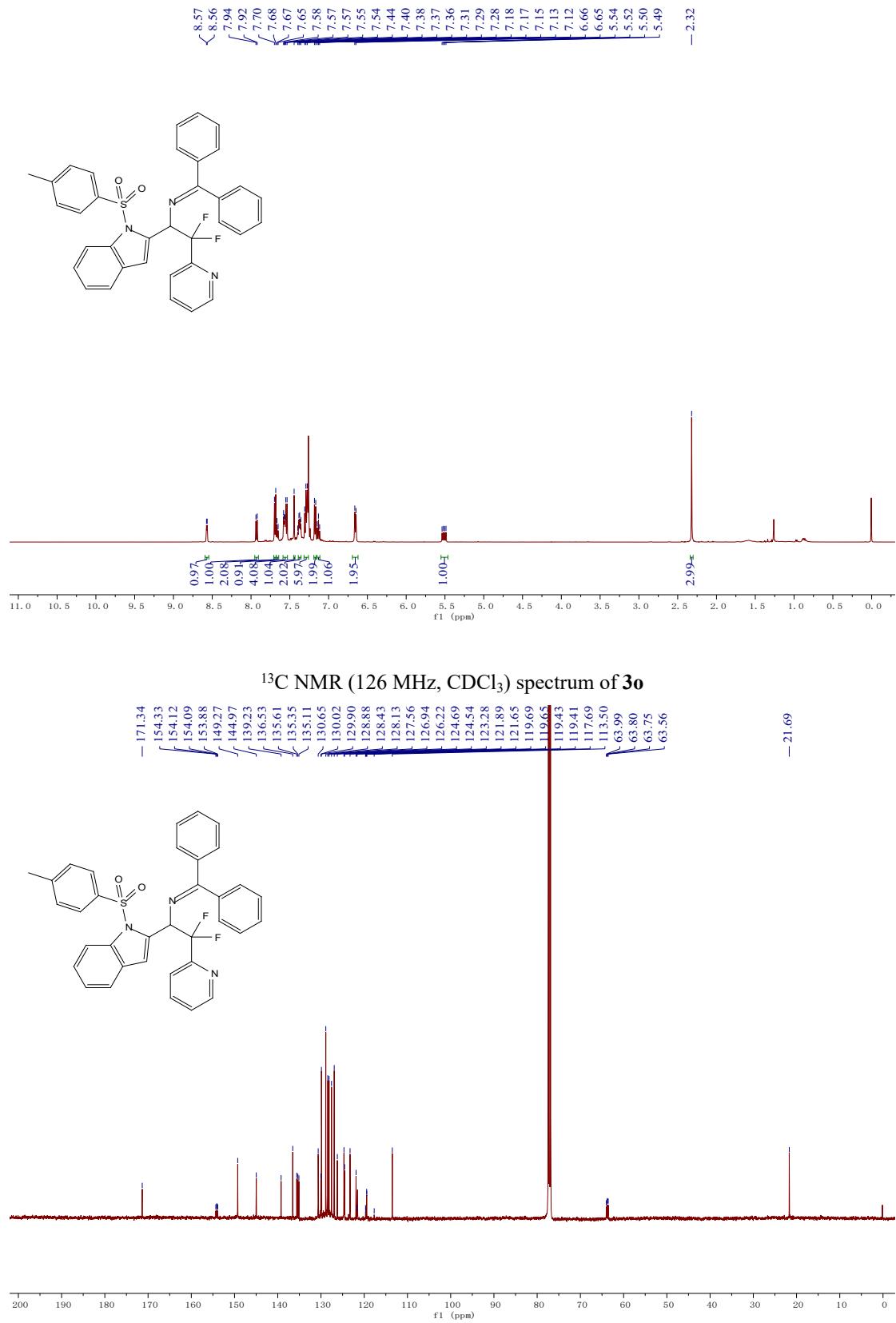
¹³C NMR (151 MHz, CDCl₃) spectrum of **3n**



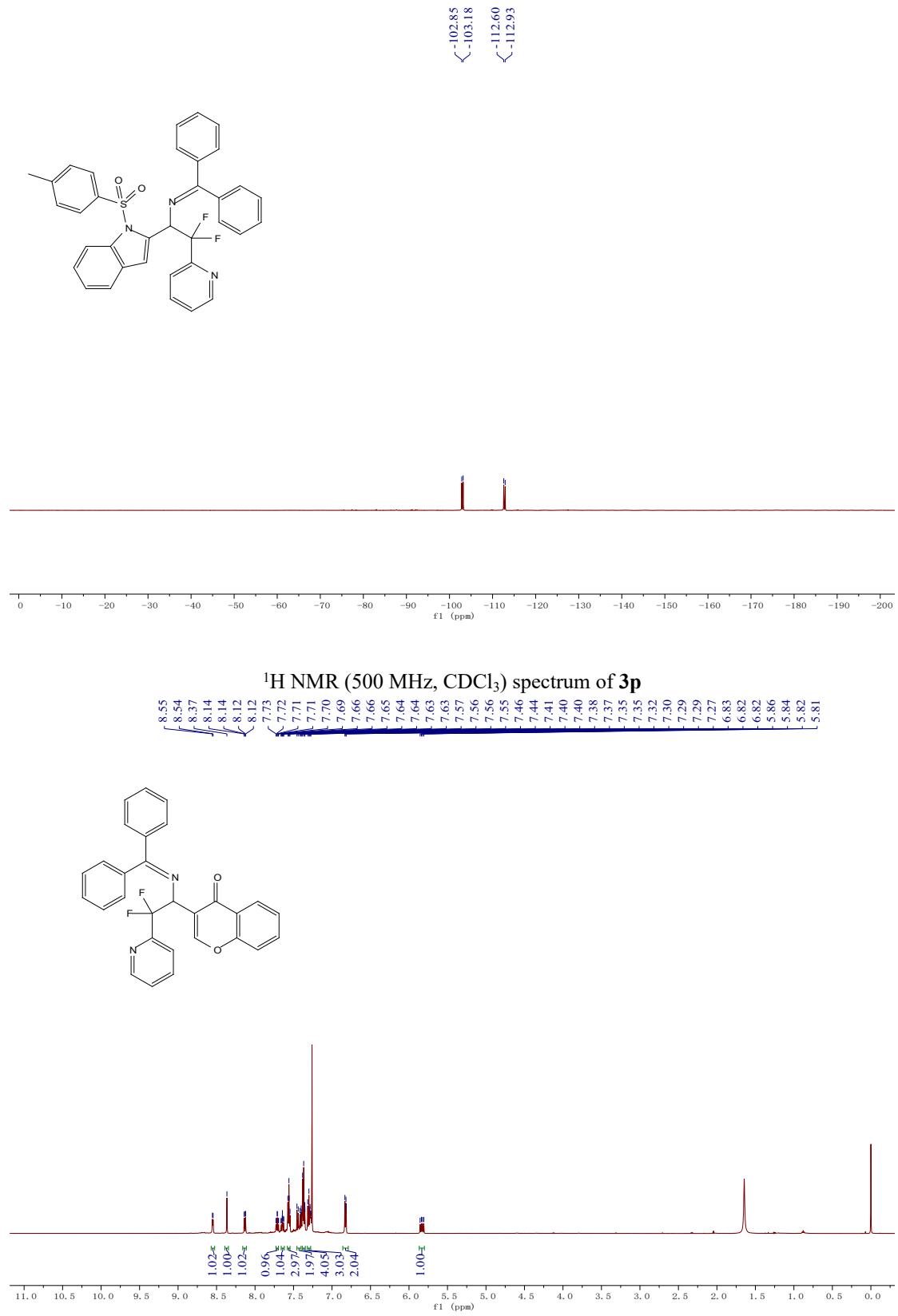
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **3n**



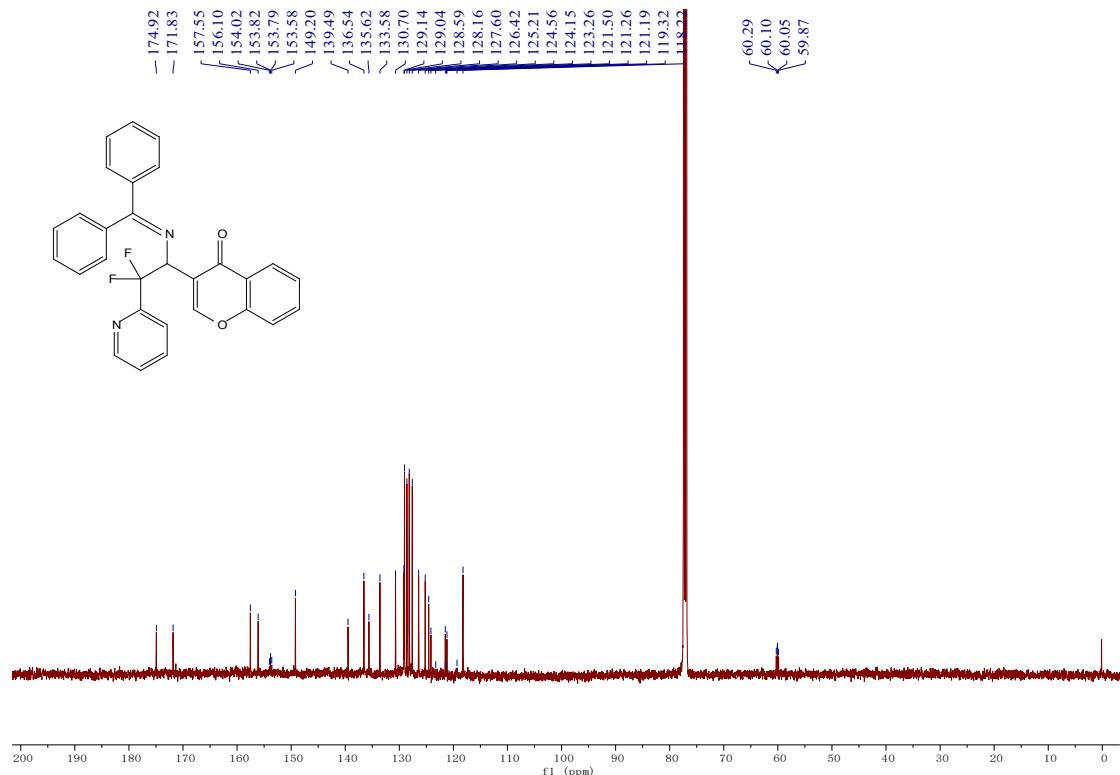
¹H NMR (500 MHz, CDCl₃) spectrum of **3o**



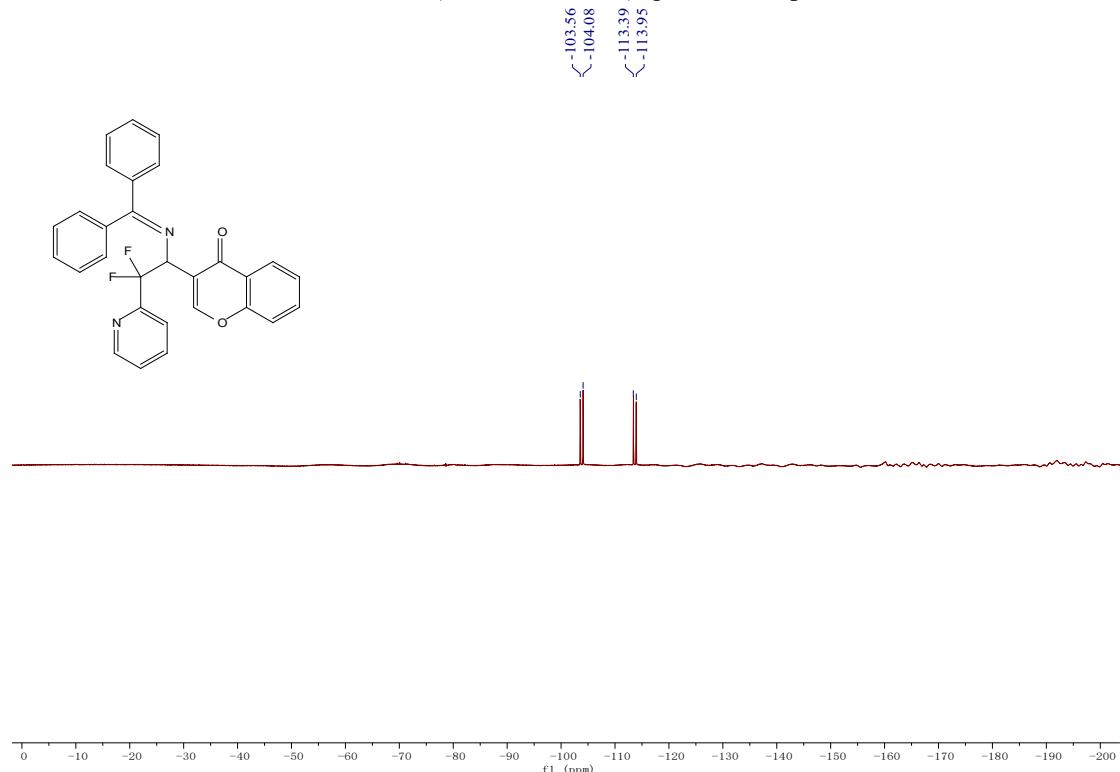
¹⁹F NMR (753 MHz, CDCl₃) spectrum of **3o**



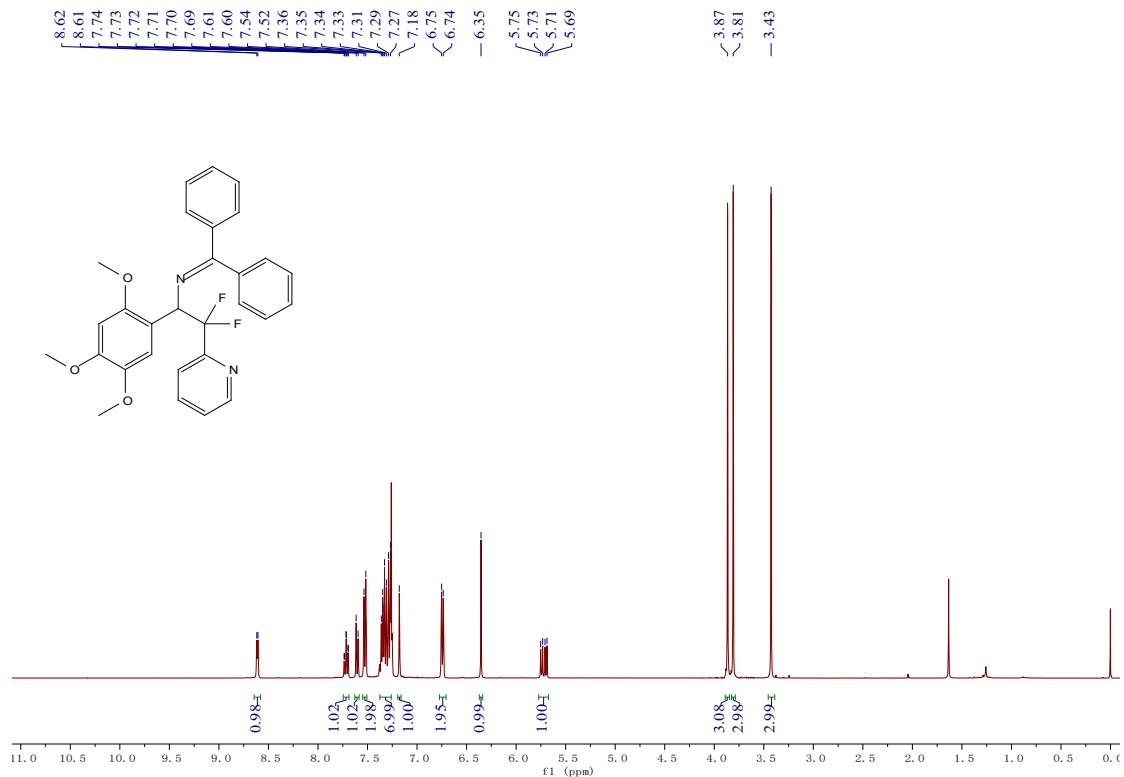
¹³C NMR (126 MHz, CDCl₃) spectrum of **3p**



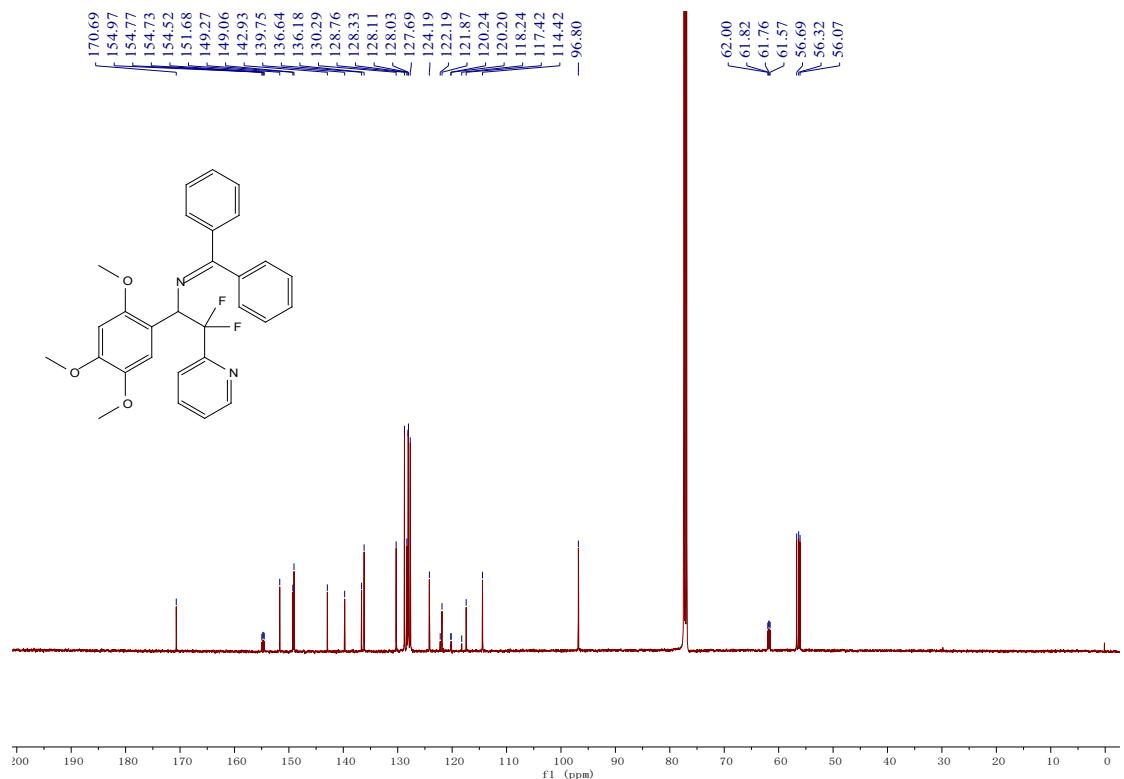
¹⁹F NMR (753 MHz, CDCl₃) spectrum of 3p



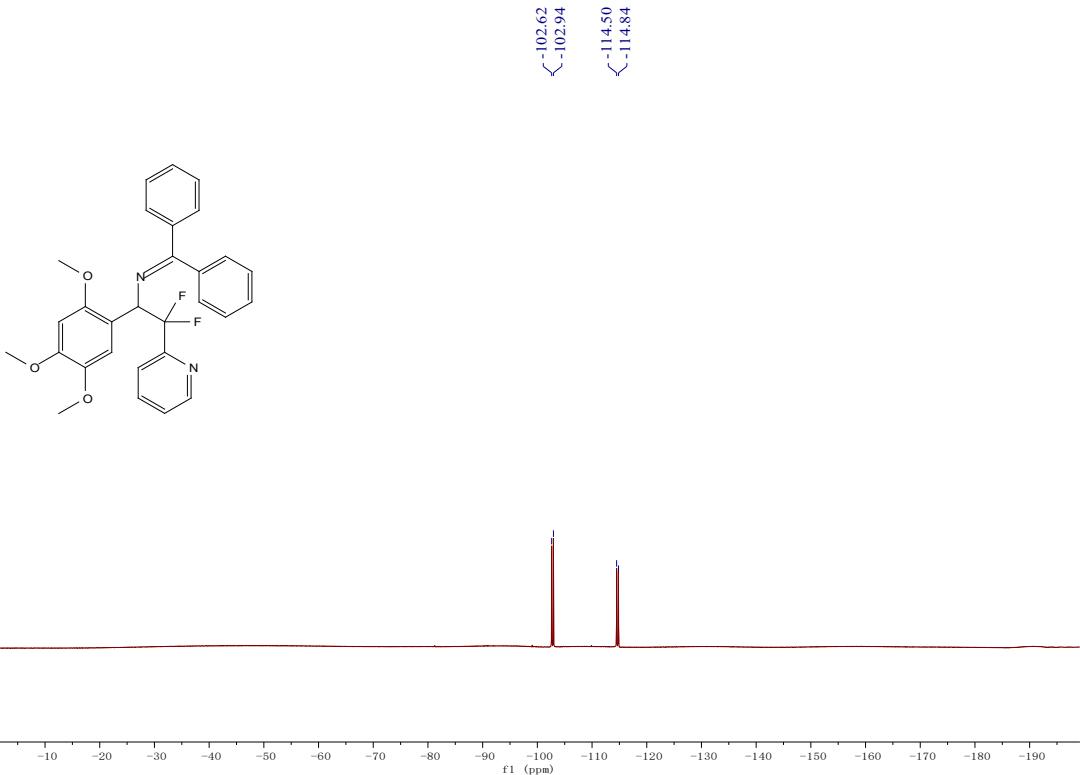
¹H NMR (400 MHz, CDCl₃) spectrum of 3q



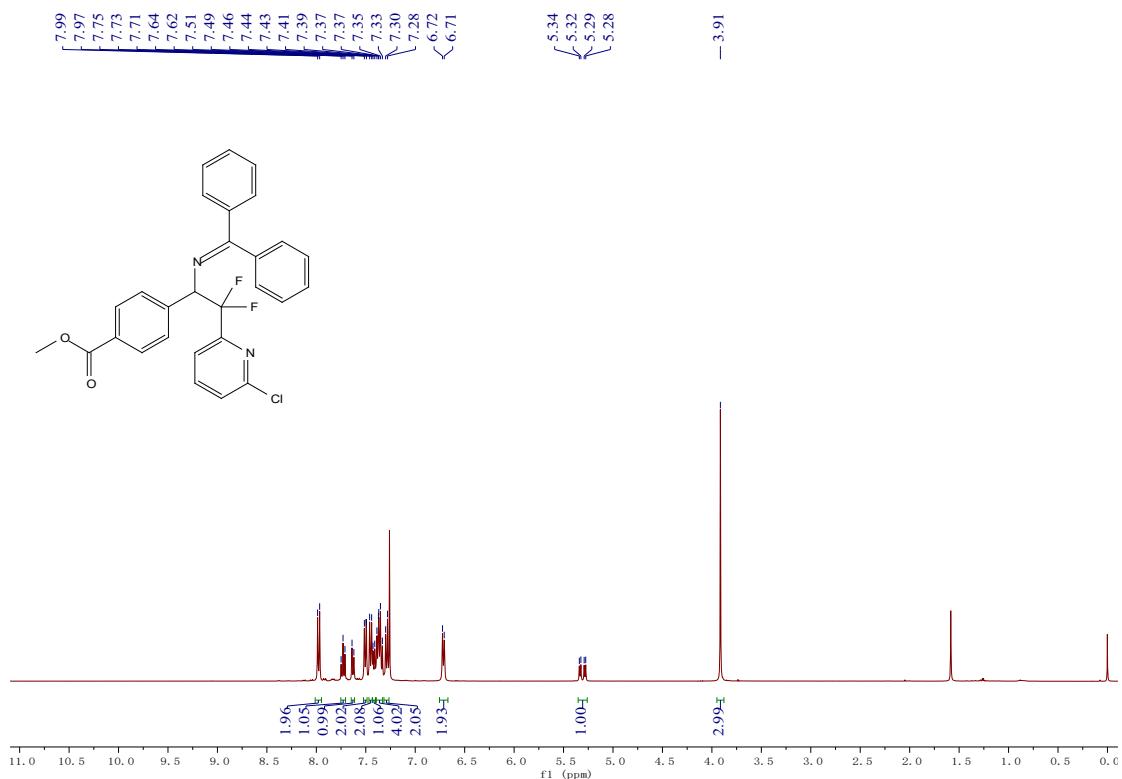
^{13}C NMR (126 MHz, CDCl_3) spectrum of **3q**



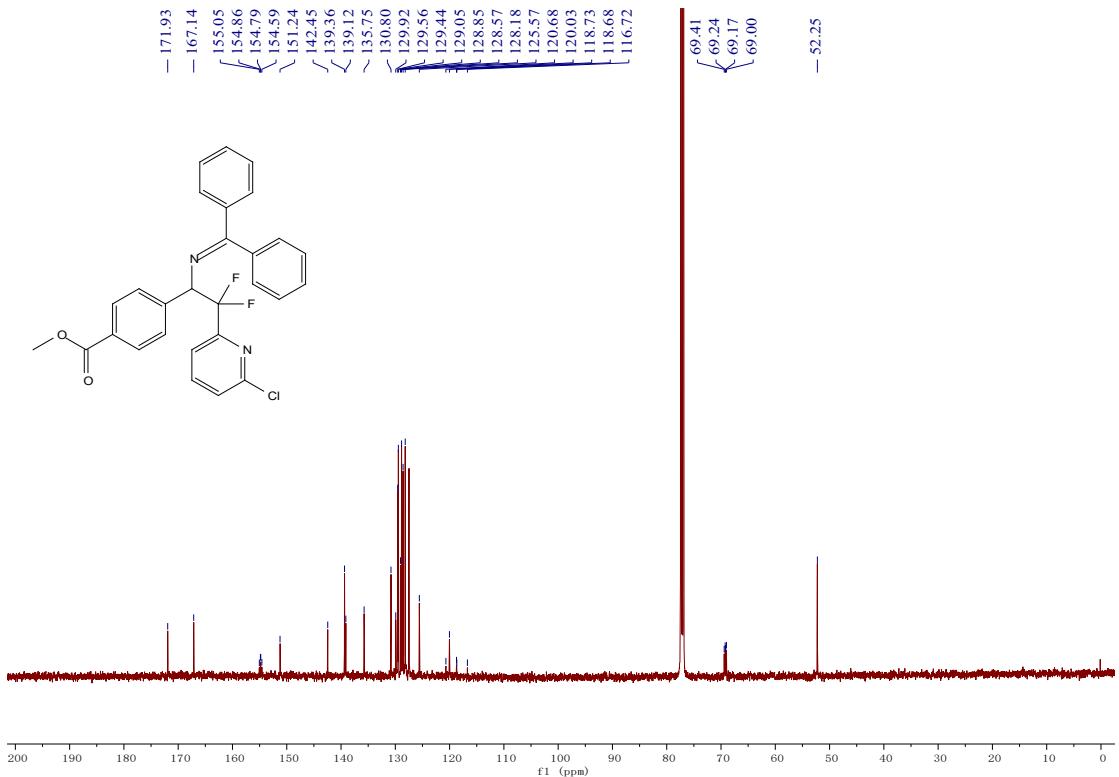
^{19}F NMR (753 MHz, CDCl_3) spectrum of **3q**



^1H NMR (400 MHz, CDCl_3) spectrum of 4a

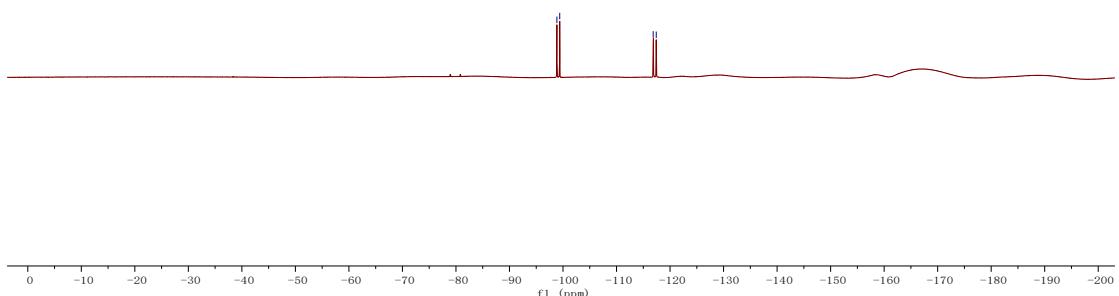


^{13}C NMR (126 MHz, CDCl_3) spectrum of 4a

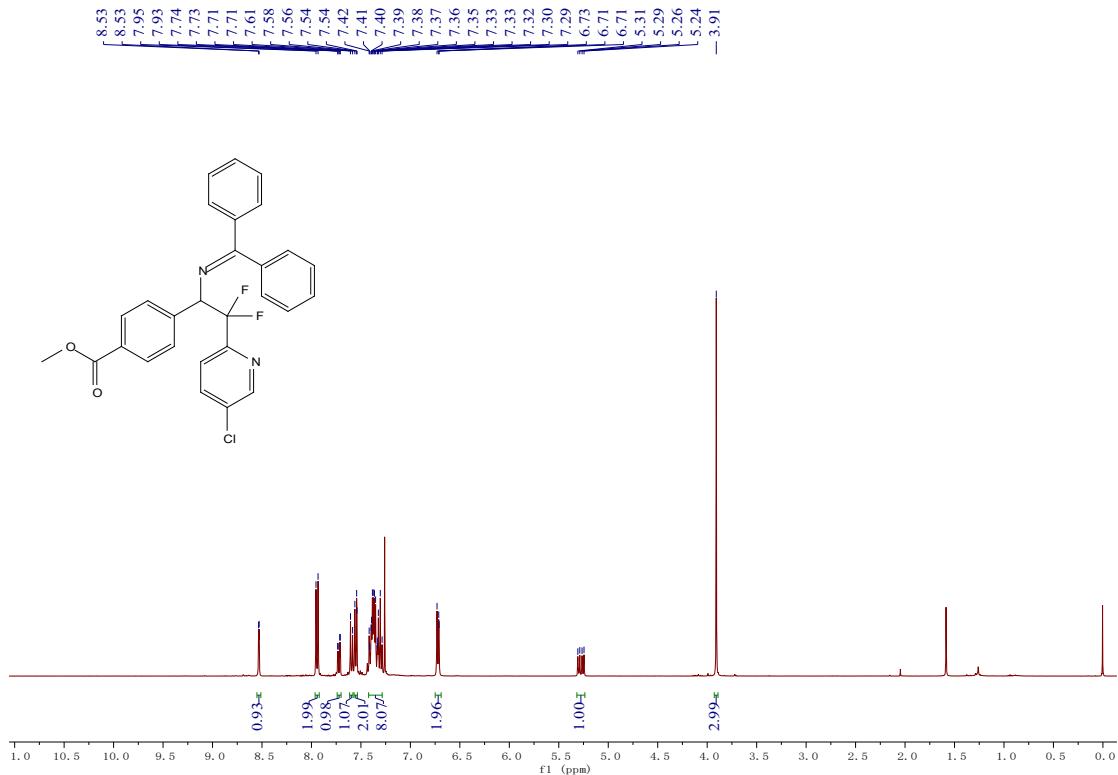


¹⁹F NMR (471 MHz, CDCl₃) spectrum of 4a

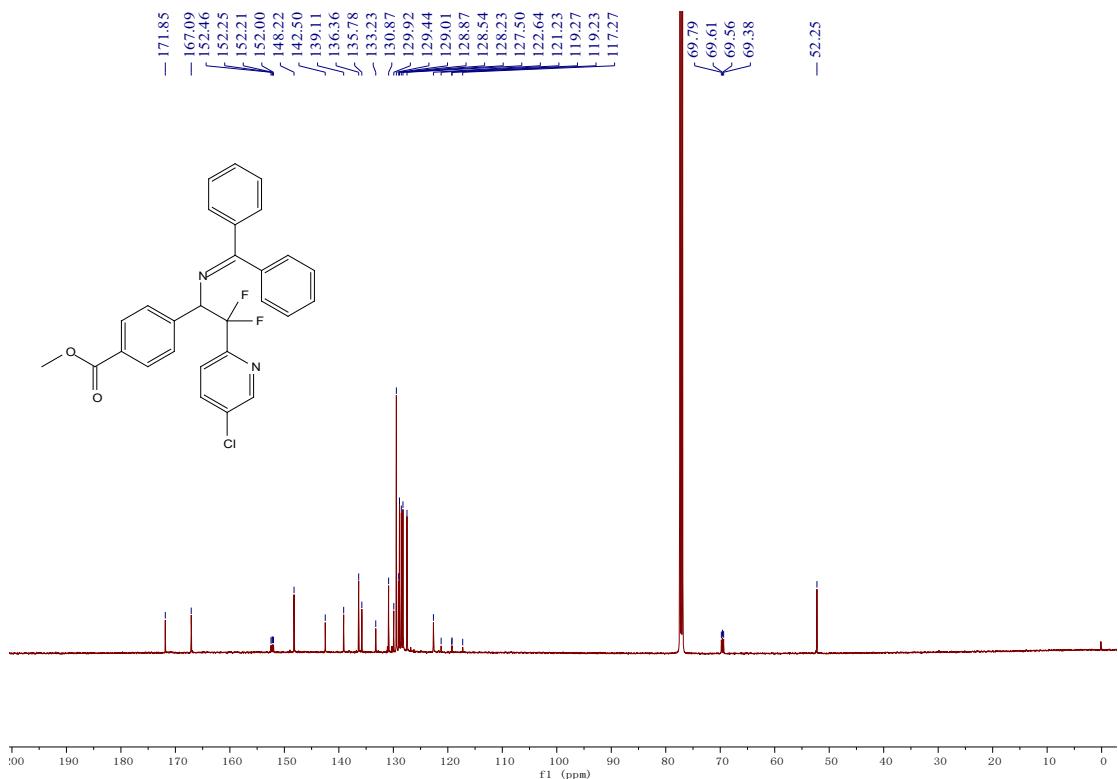
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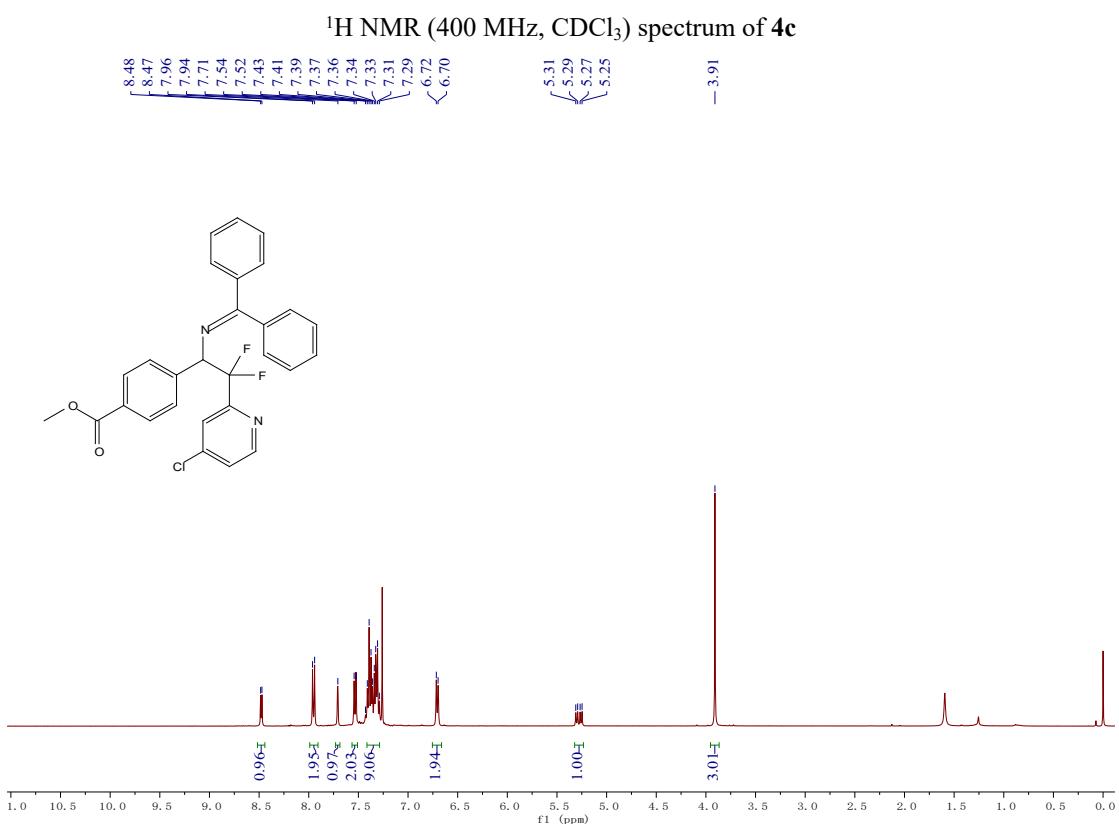
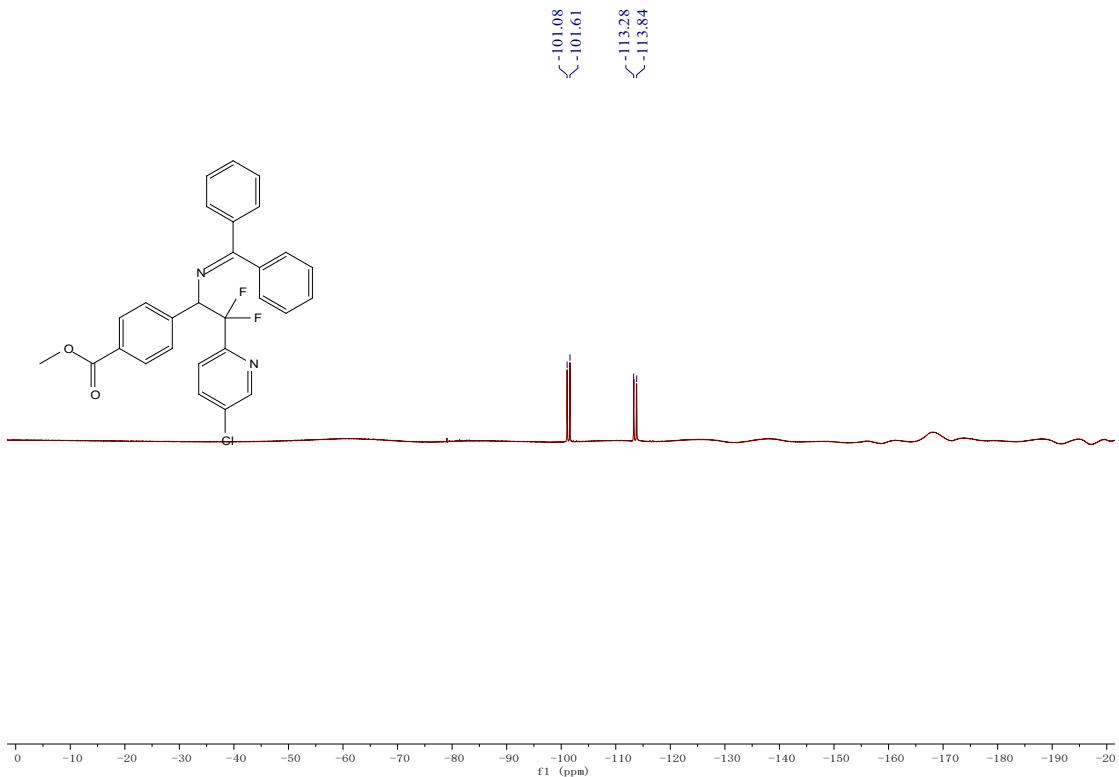
¹H NMR (400 MHz, CDCl₃) spectrum of 4b



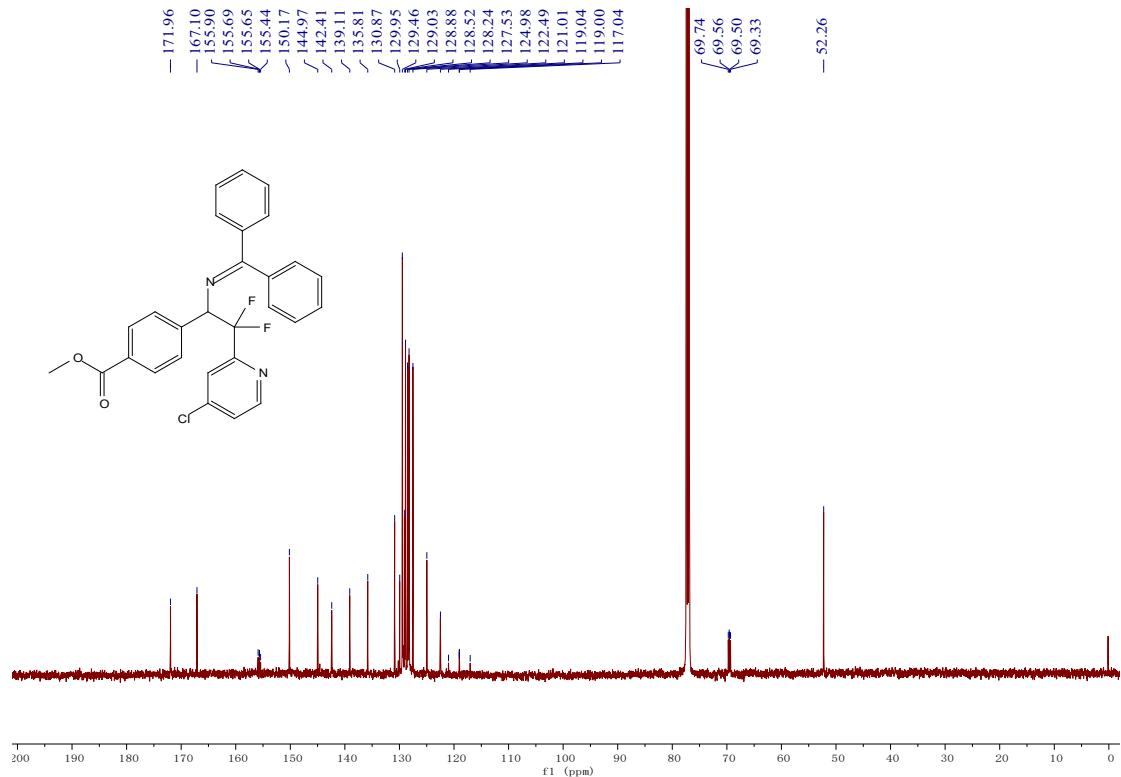
¹³C NMR (126 MHz, CDCl₃) spectrum of **4b**



¹⁹F NMR (471 MHz, CDCl₃) spectrum of **4b**

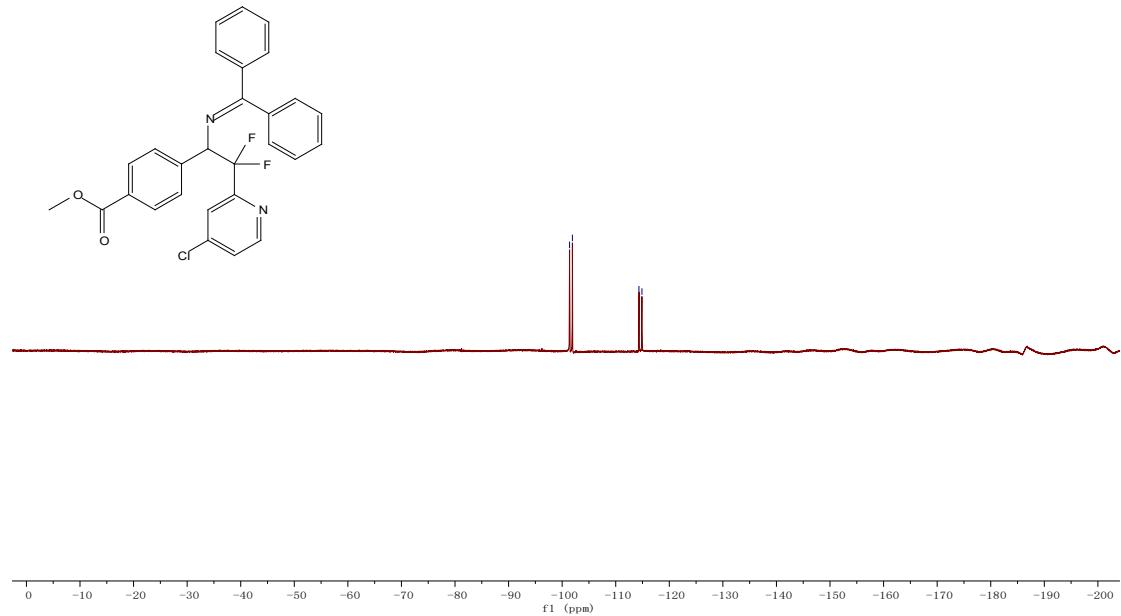


${}^{13}\text{C}$ NMR (126 MHz, CDCl_3) spectrum of **4c**

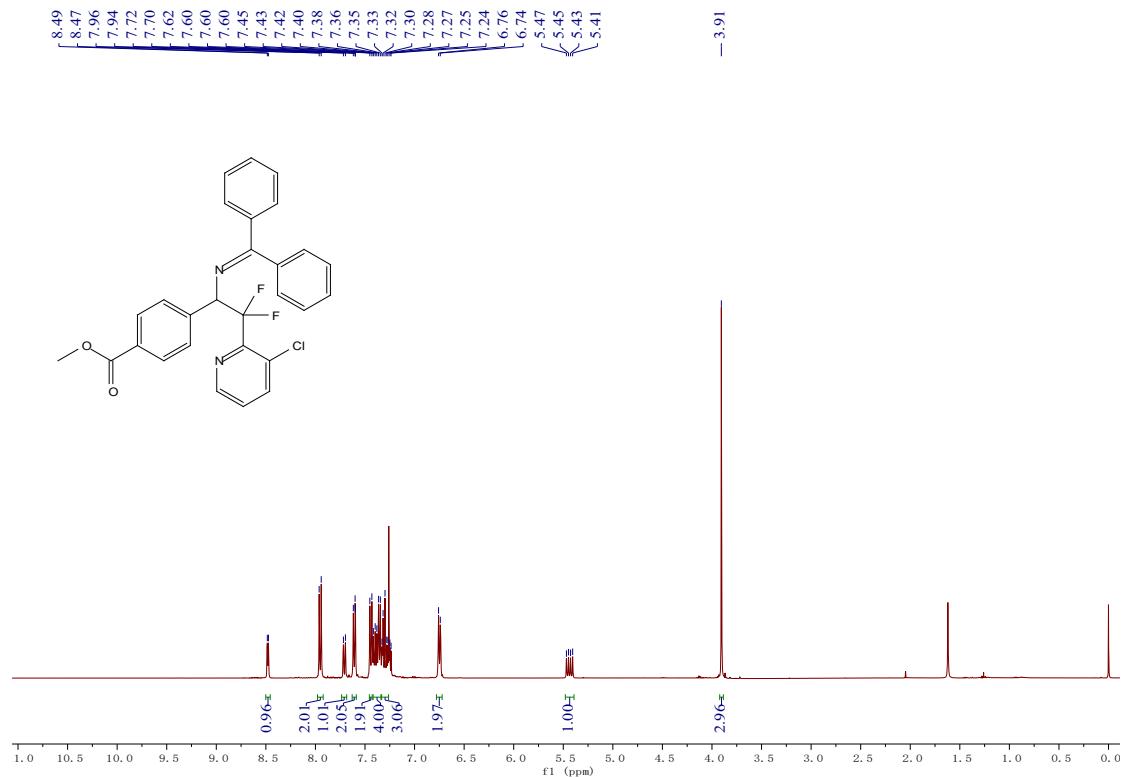


¹⁹F NMR (471 MHz, CDCl₃) spectrum of **4c**

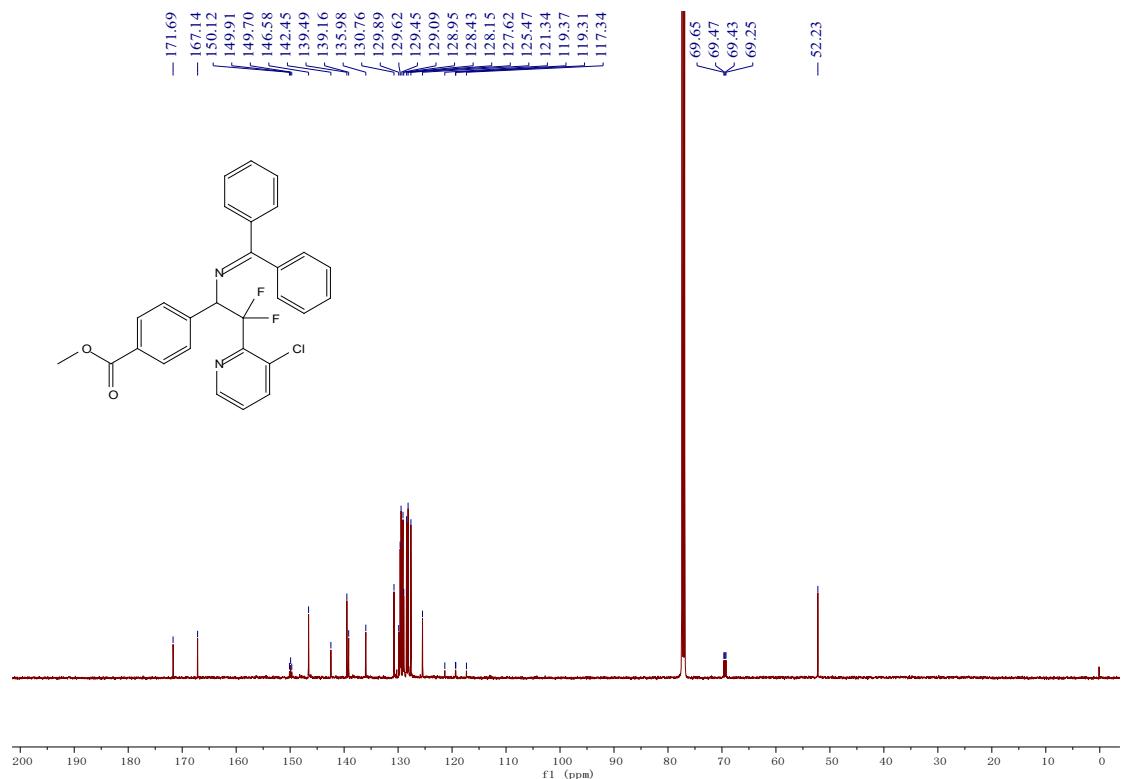
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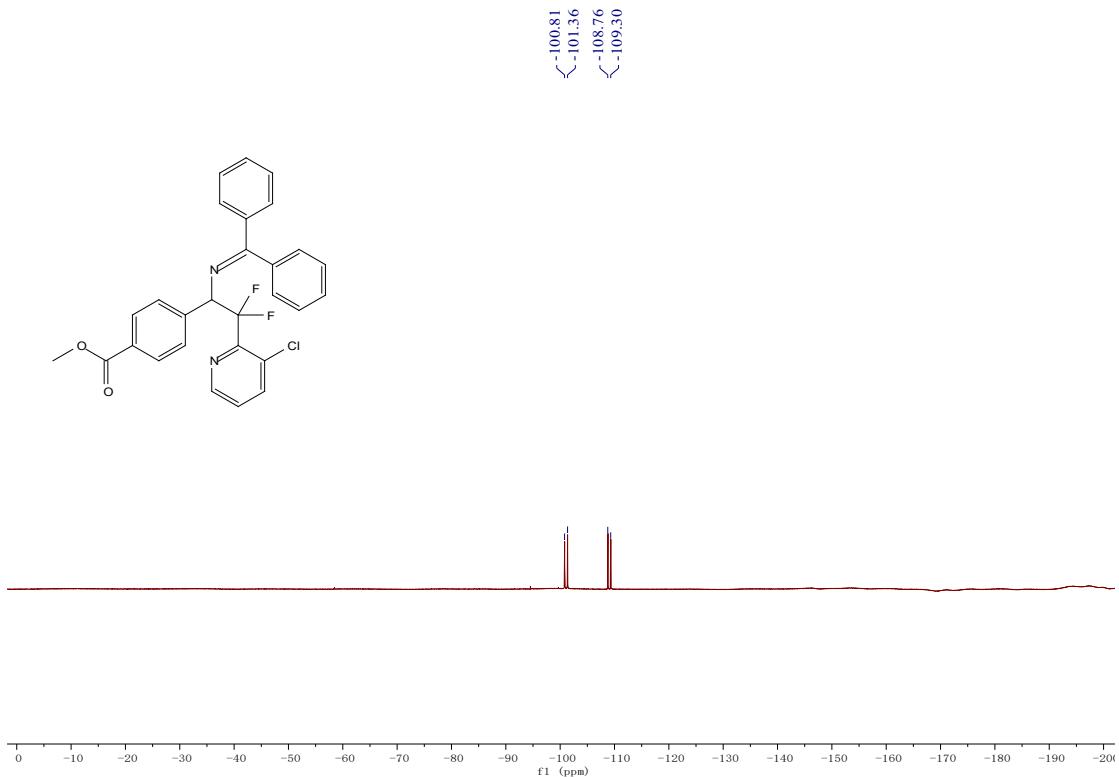
¹H NMR (400 MHz, CDCl₃) spectrum of **4d**



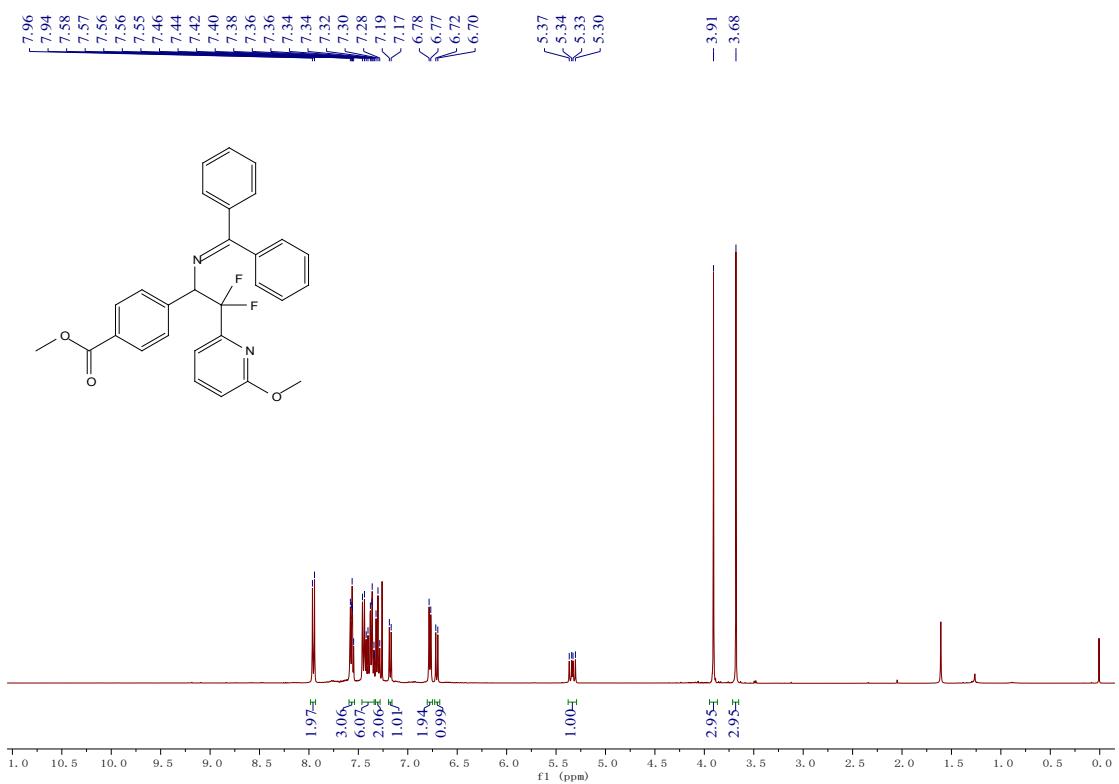
^{13}C NMR (126 MHz, CDCl_3) spectrum of **4d**



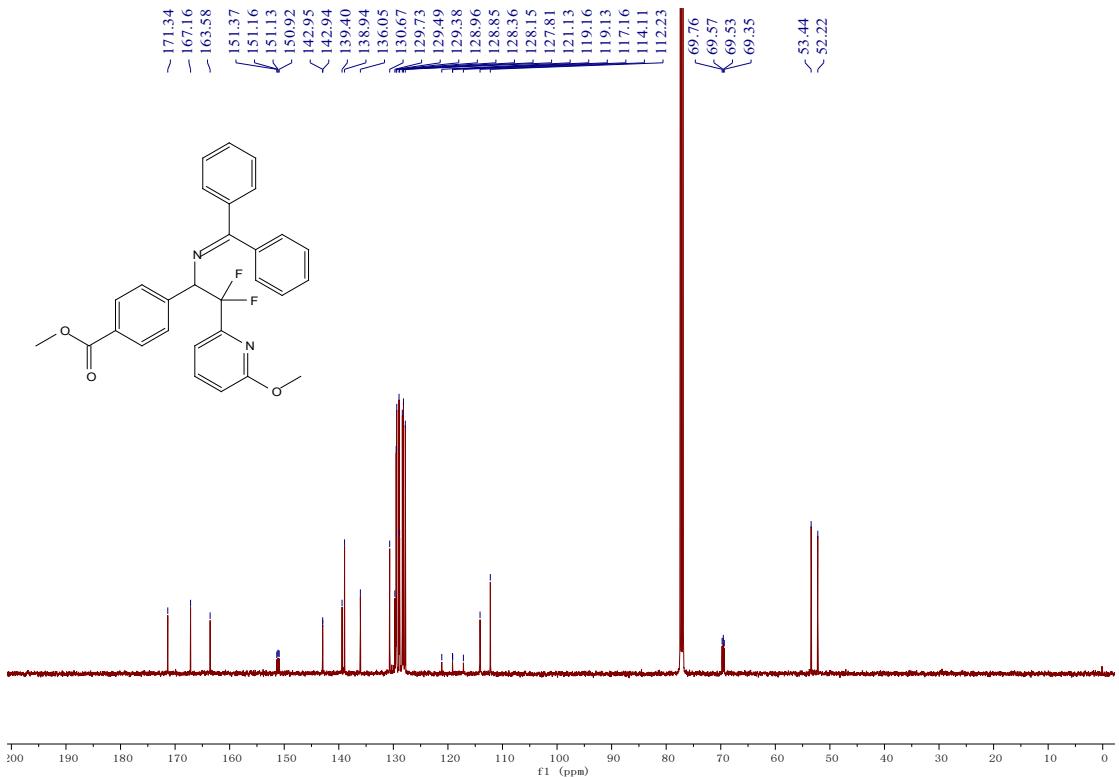
^{19}F NMR (471 MHz, CDCl_3) spectrum of **4d**



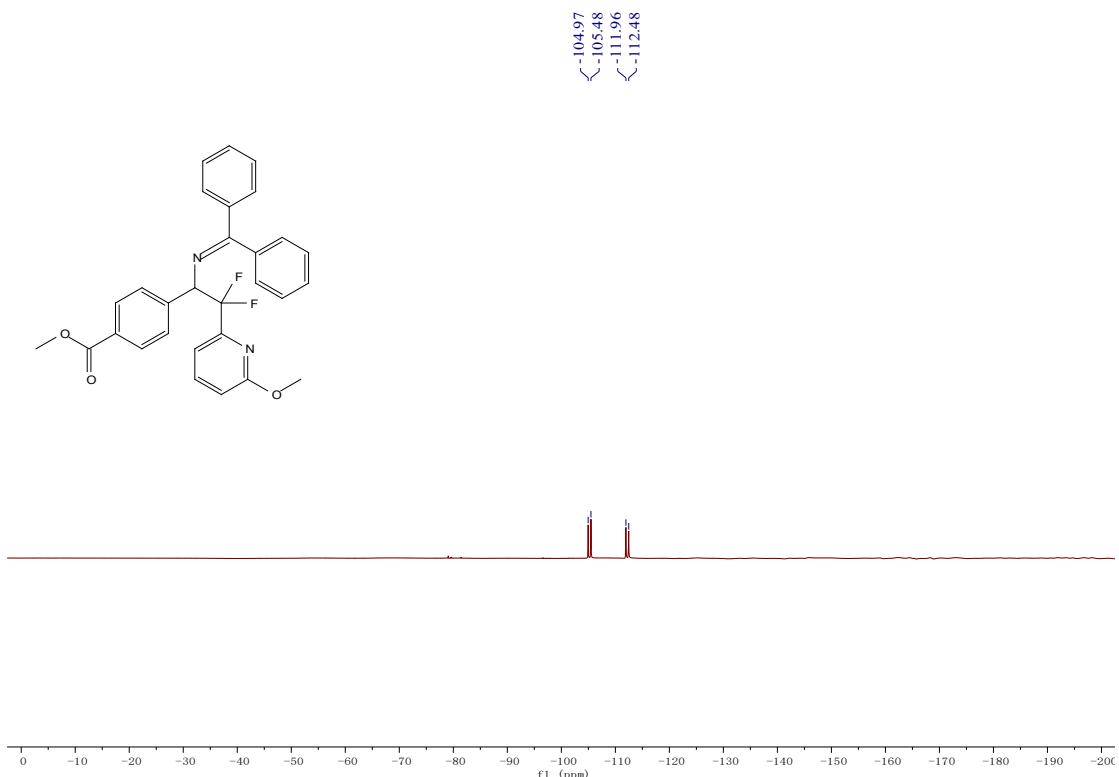
^1H NMR (400 MHz, CDCl_3) spectrum of **4e**



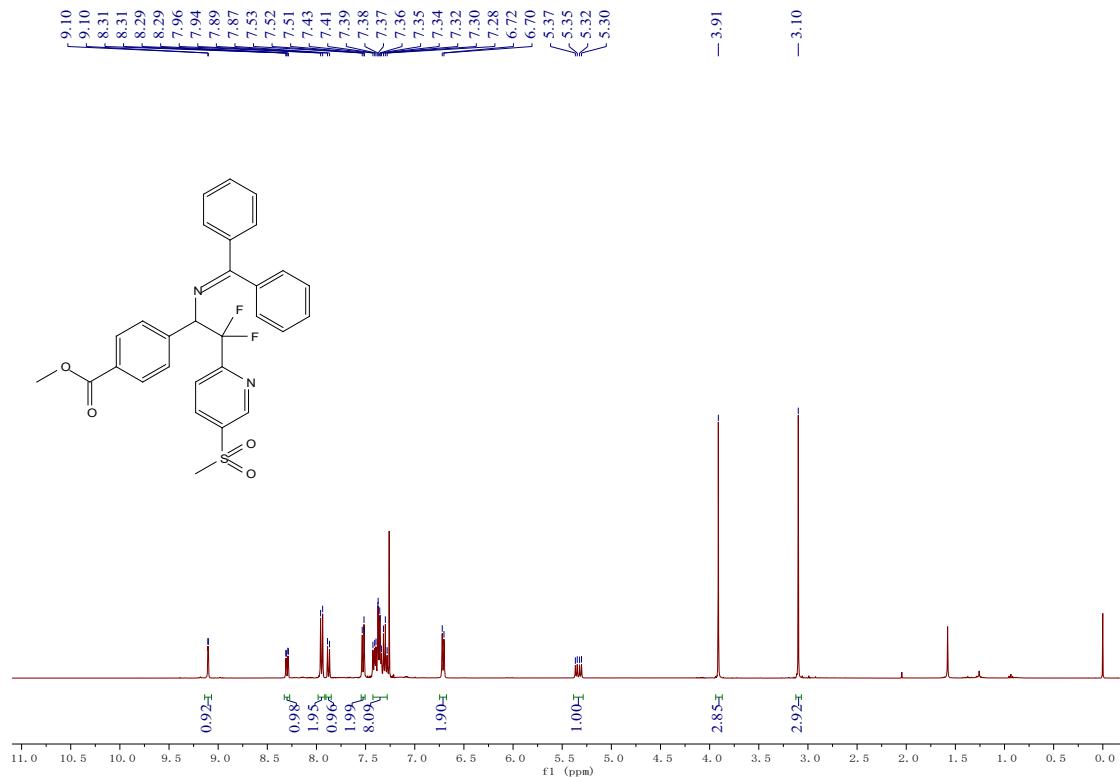
^{13}C NMR (126 MHz, CDCl_3) spectrum of **4e**



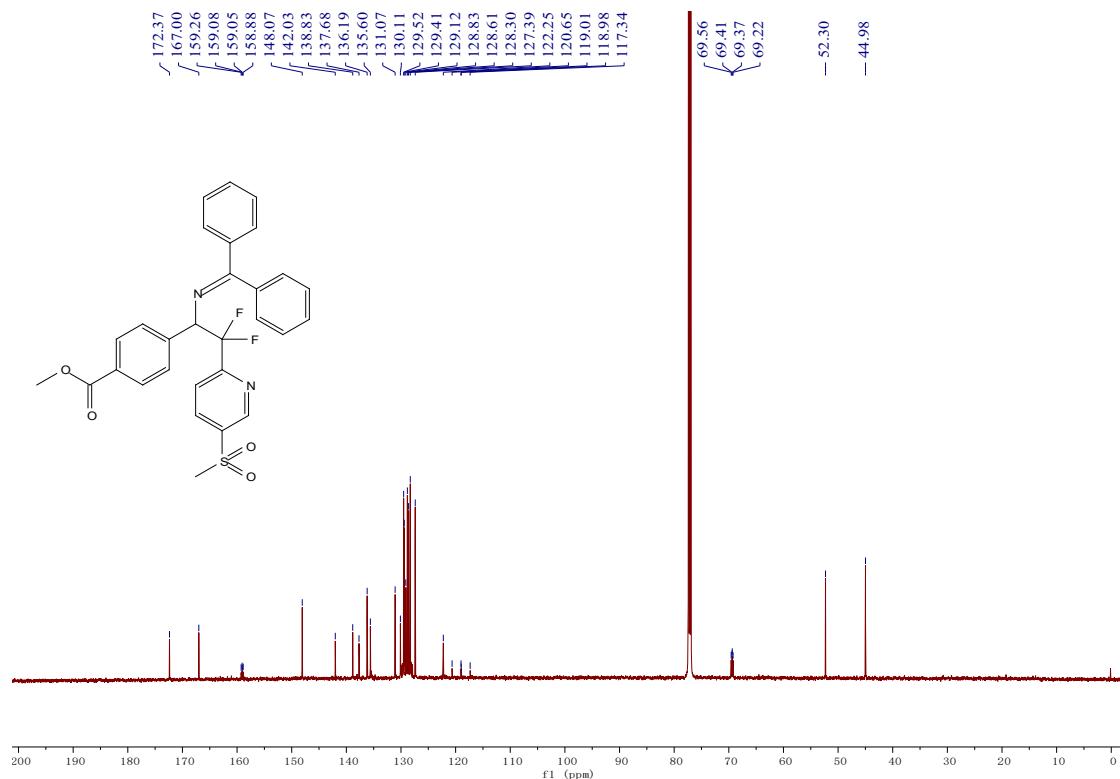
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **4e**



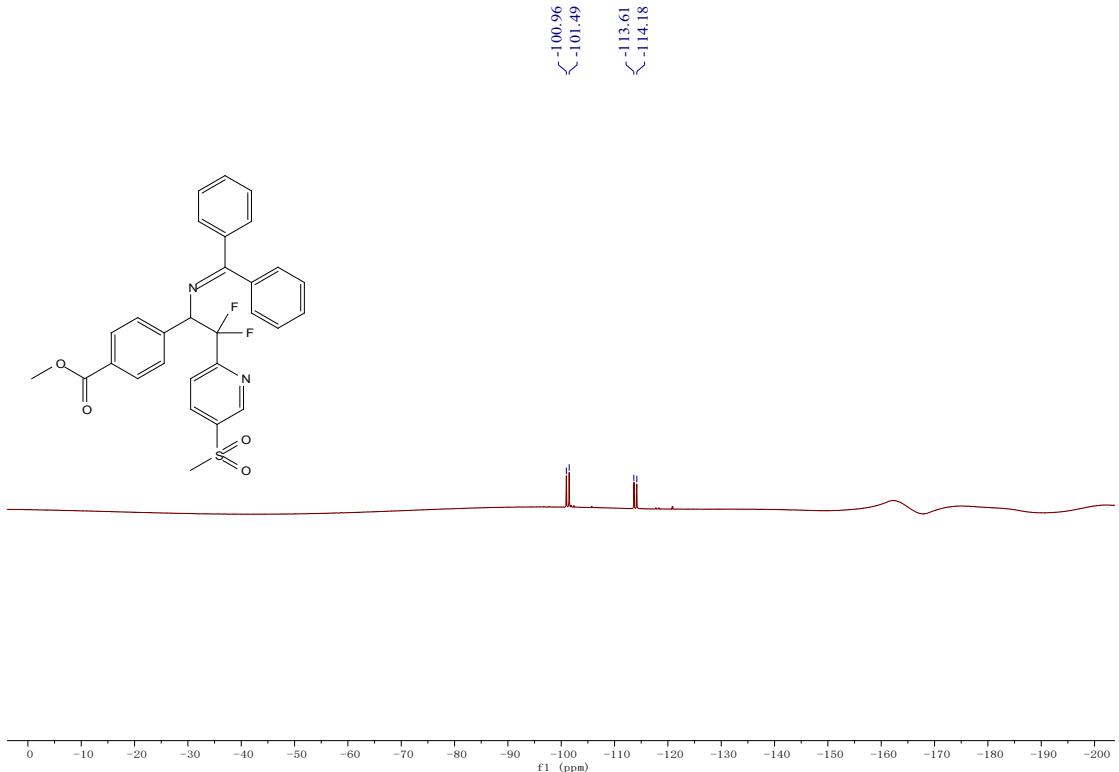
¹H NMR (400 MHz, CDCl₃) spectrum of **4f**



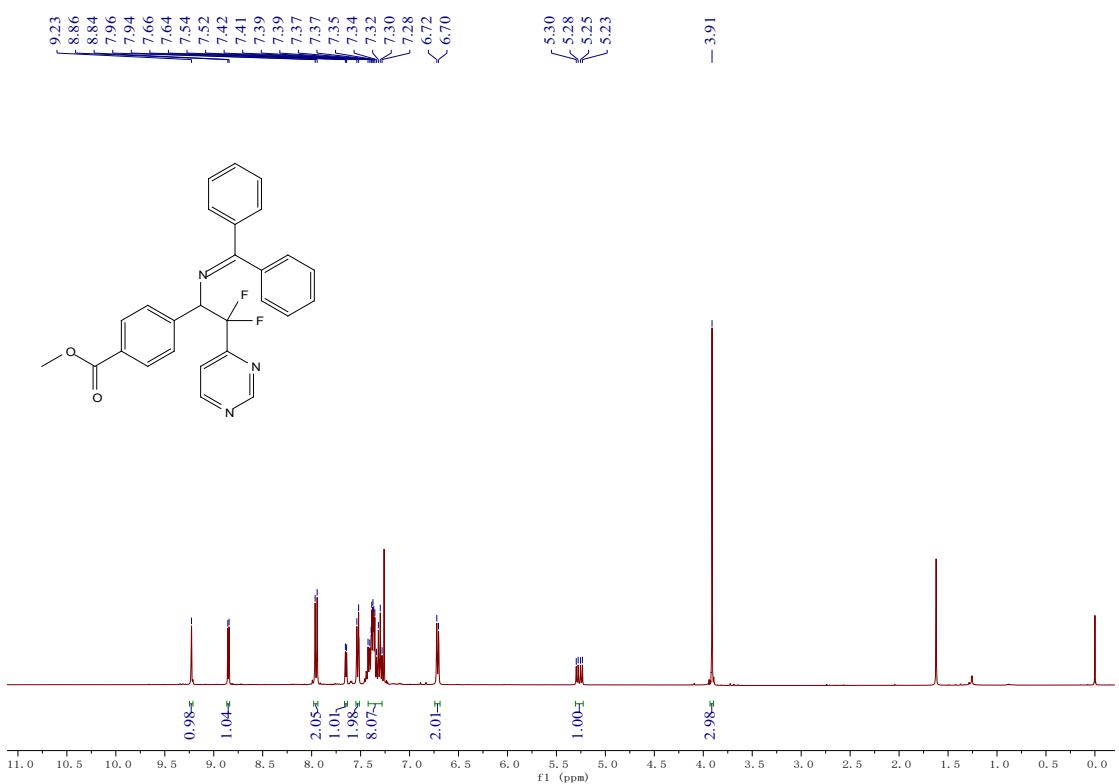
¹³C NMR (151 MHz, CDCl₃) spectrum of **4f**



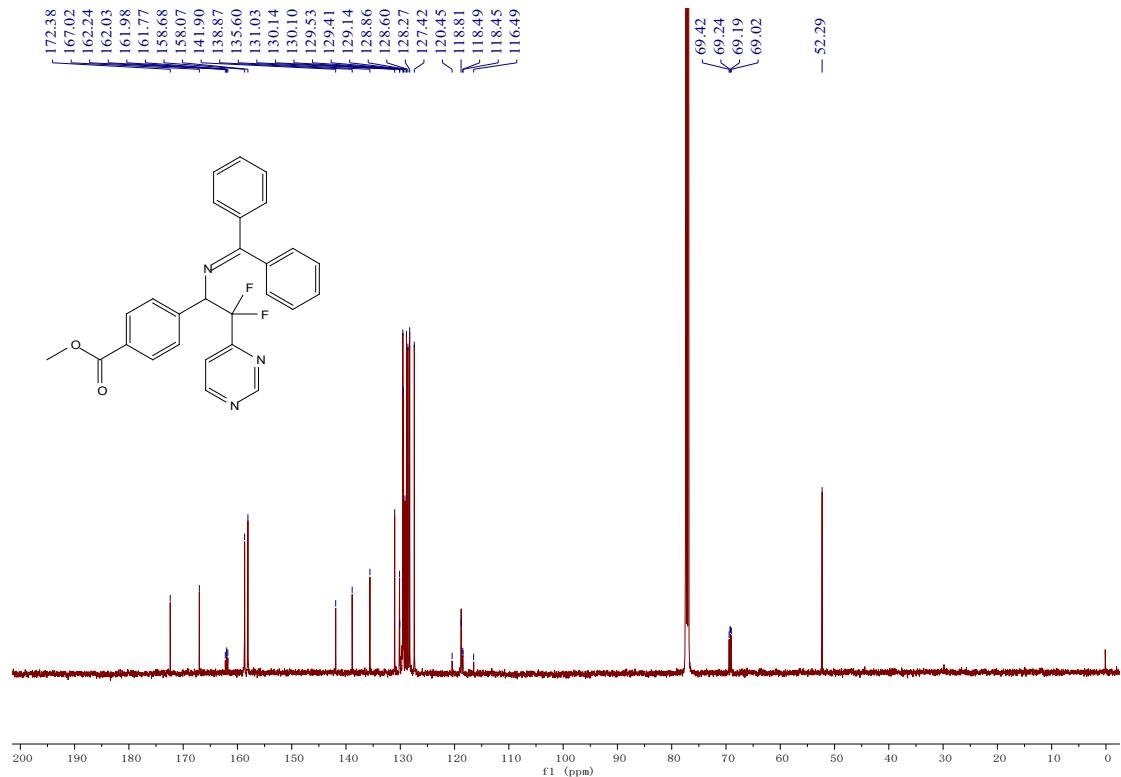
¹⁹F NMR (471 MHz, CDCl₃) spectrum of **4f**



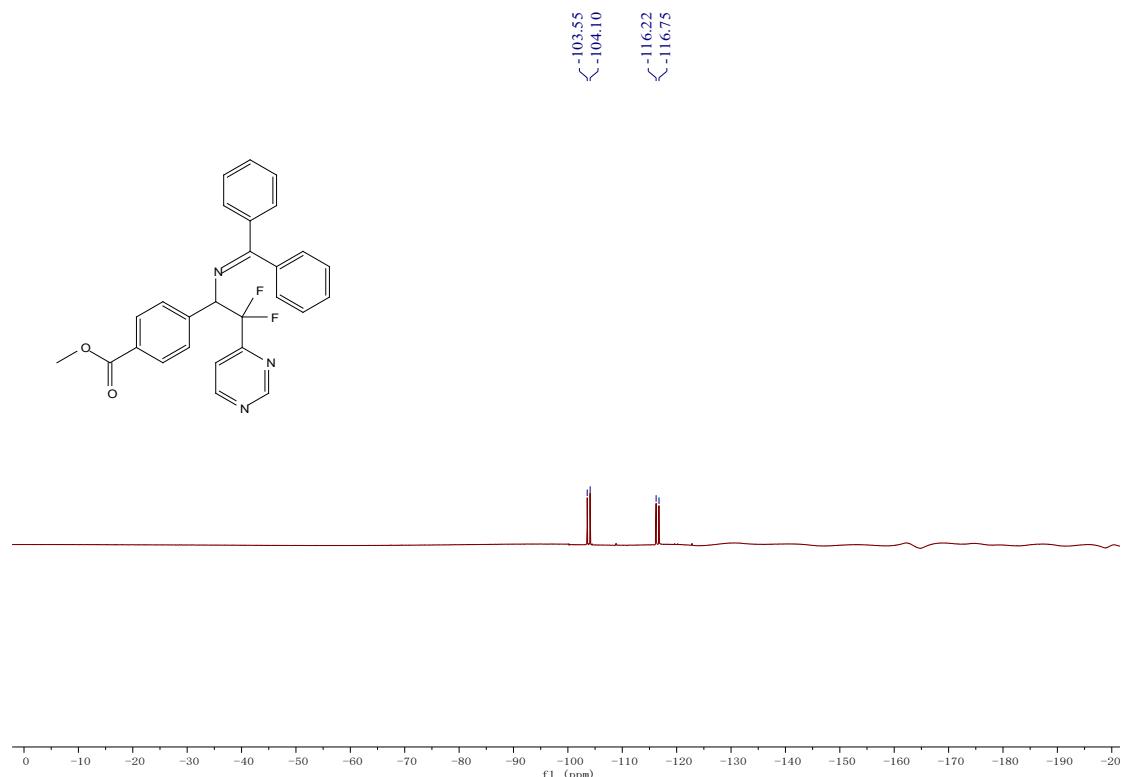
¹H NMR (400 MHz, CDCl₃) spectrum of **4g**



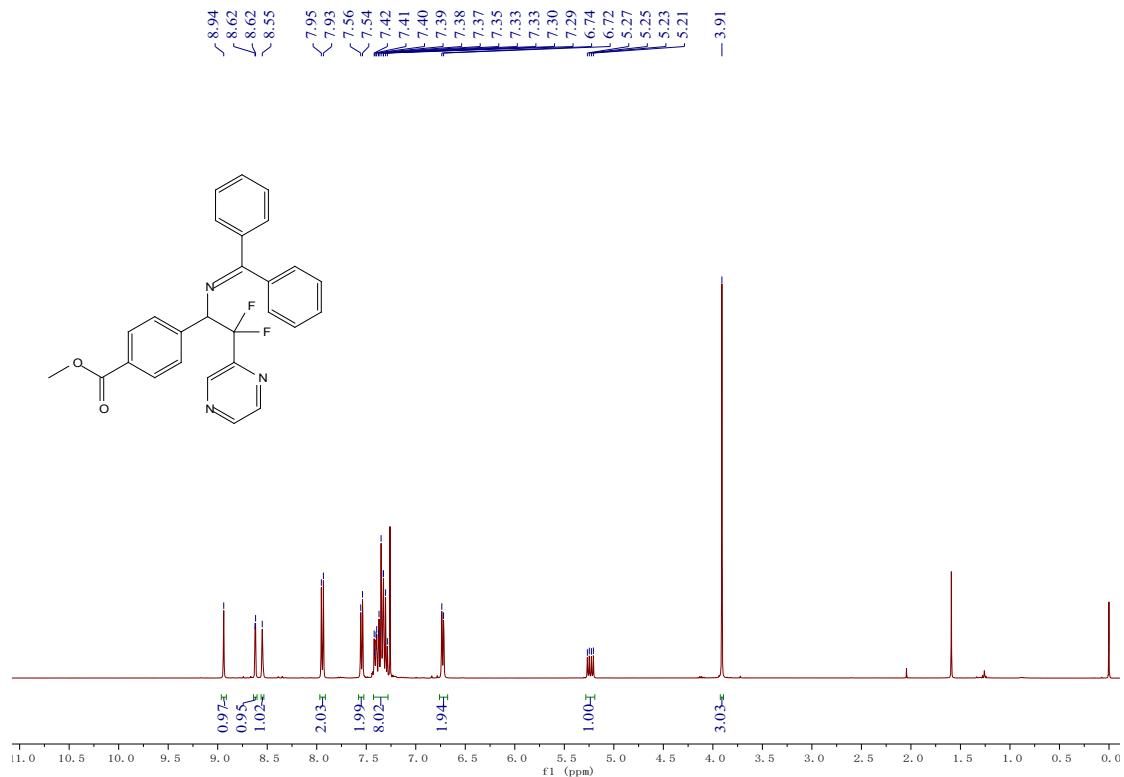
¹³C NMR (126 MHz, CDCl₃) spectrum of **4g**



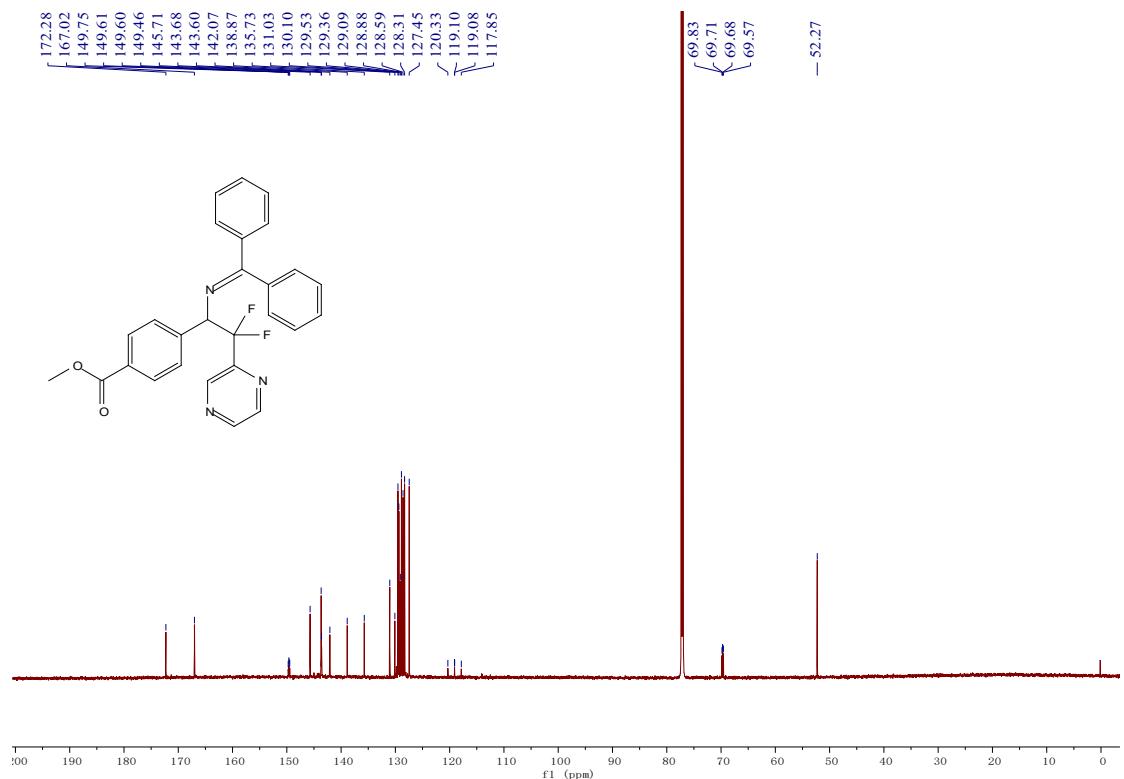
¹⁹F NMR (471 MHz, CDCl₃) spectrum of 4g



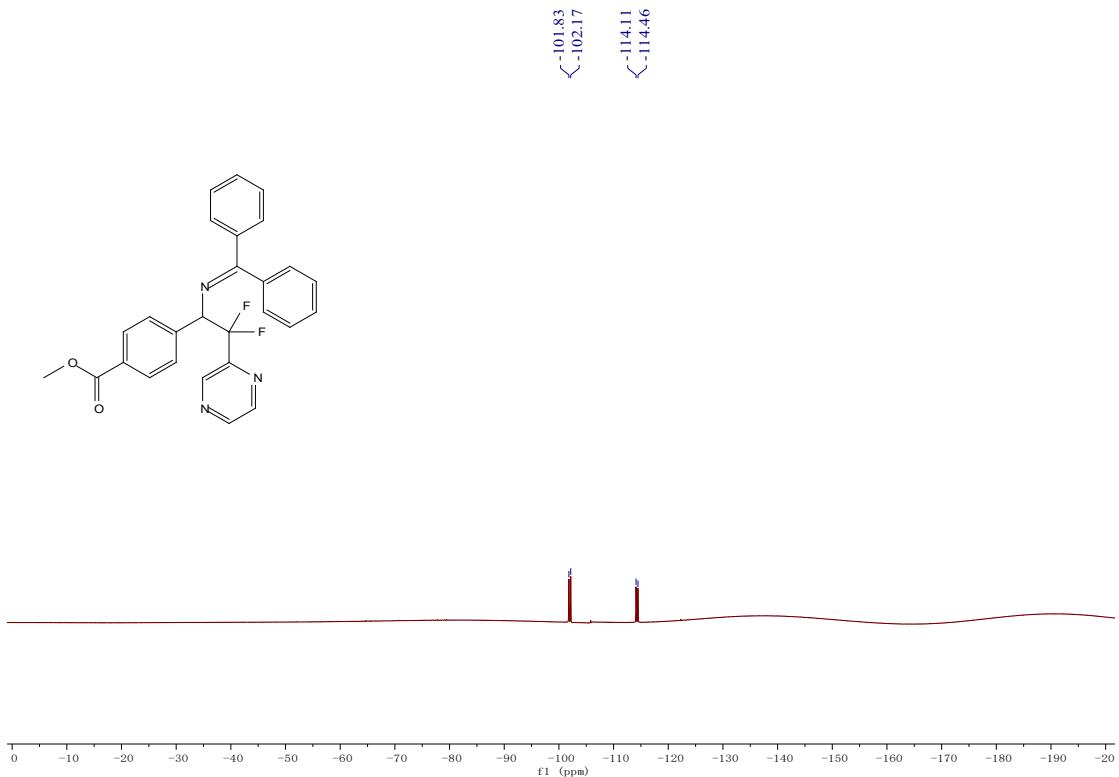
¹H NMR (400 MHz, CDCl₃) spectrum of 4h



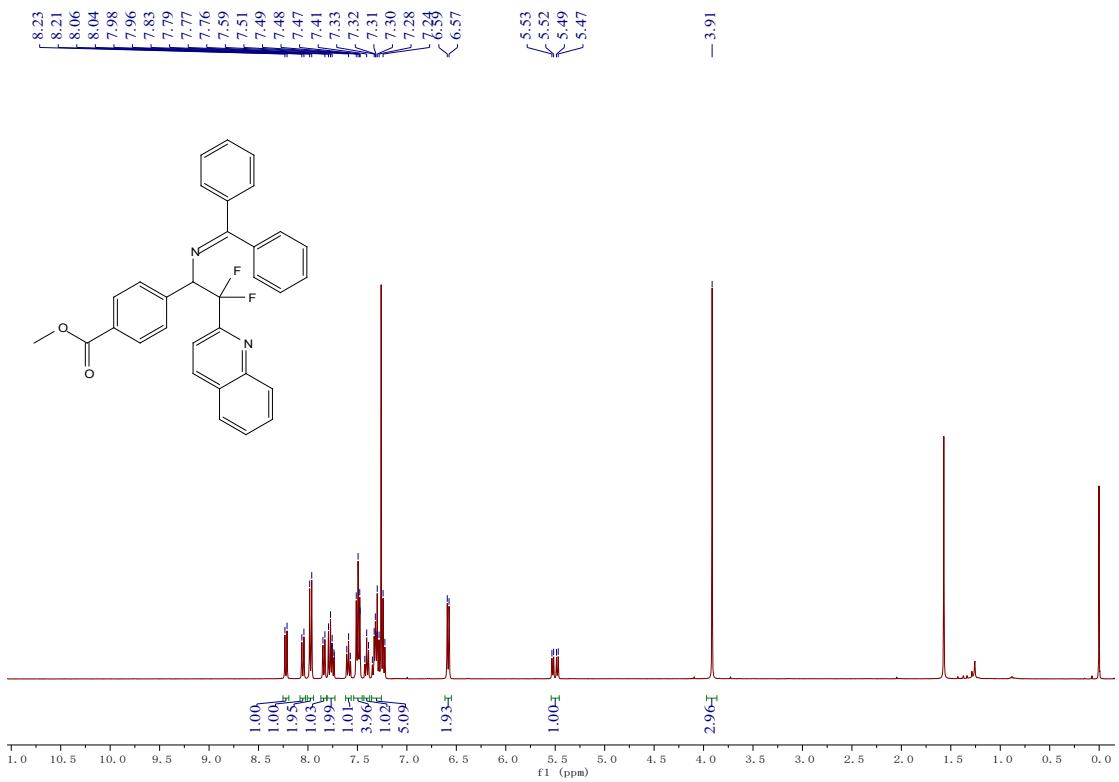
¹³C NMR (201 MHz, CDCl₃) spectrum of **4h**



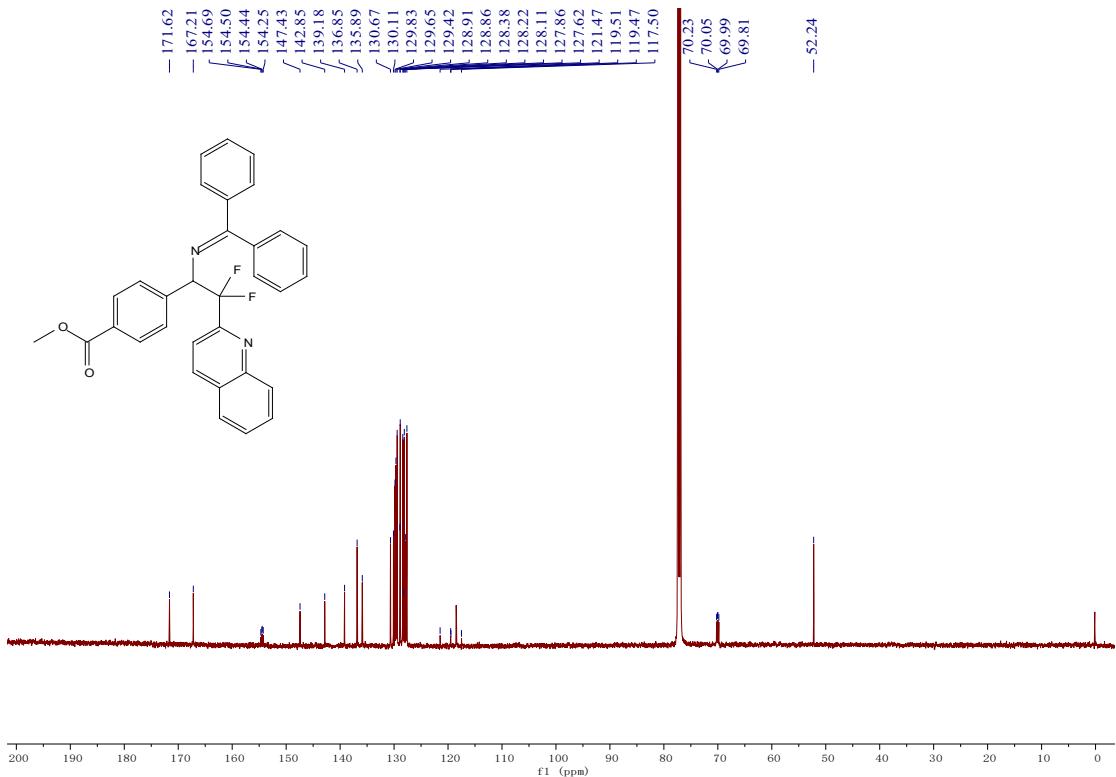
¹⁹F NMR (753 MHz, CDCl₃) spectrum of **4h**



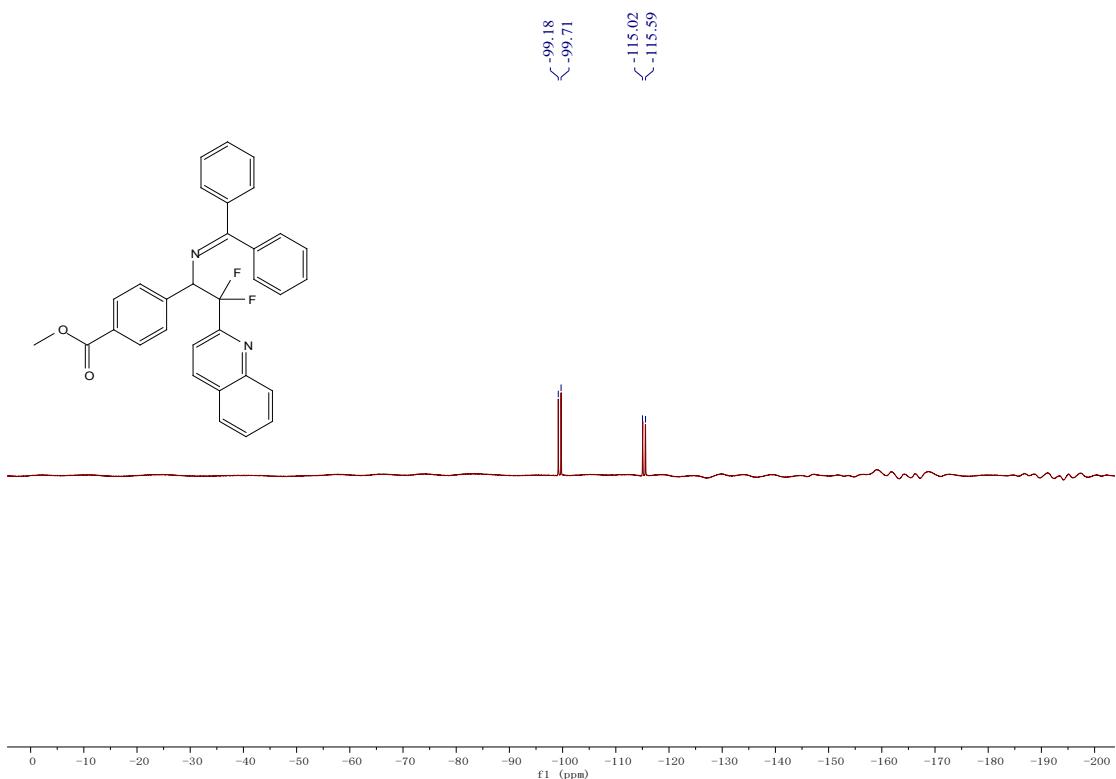
¹H NMR (400 MHz, CDCl₃) spectrum of 4i



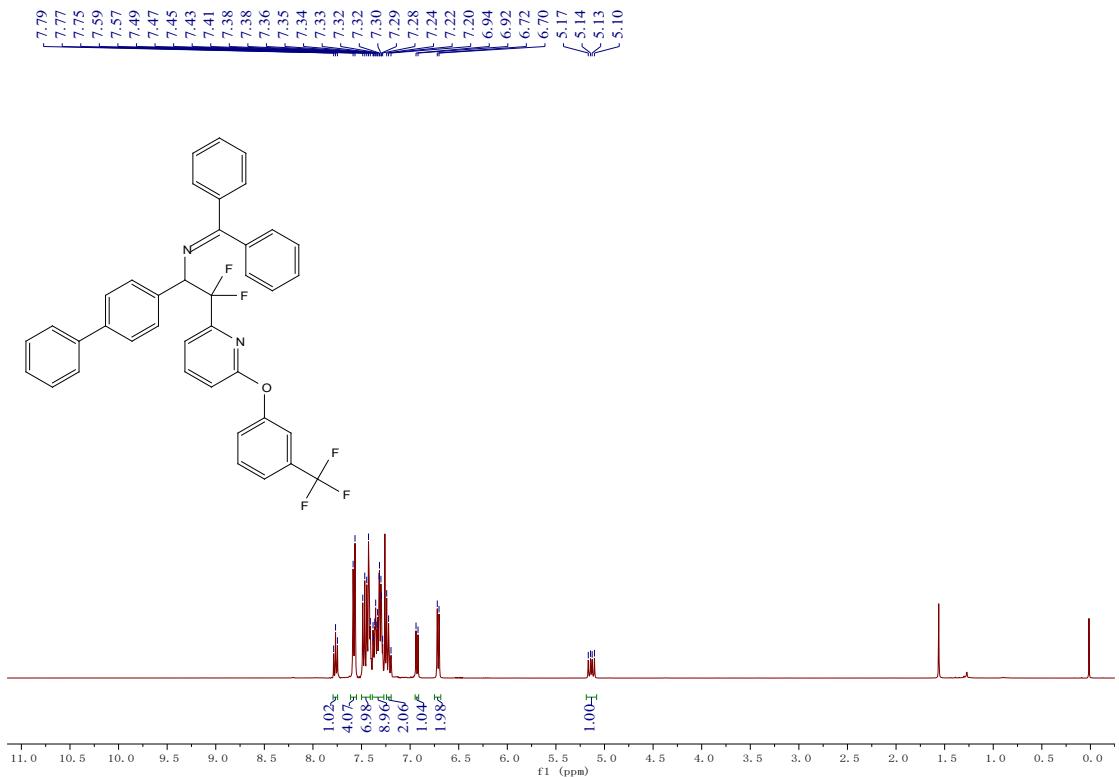
¹³C NMR (126 MHz, CDCl₃) spectrum of 4i



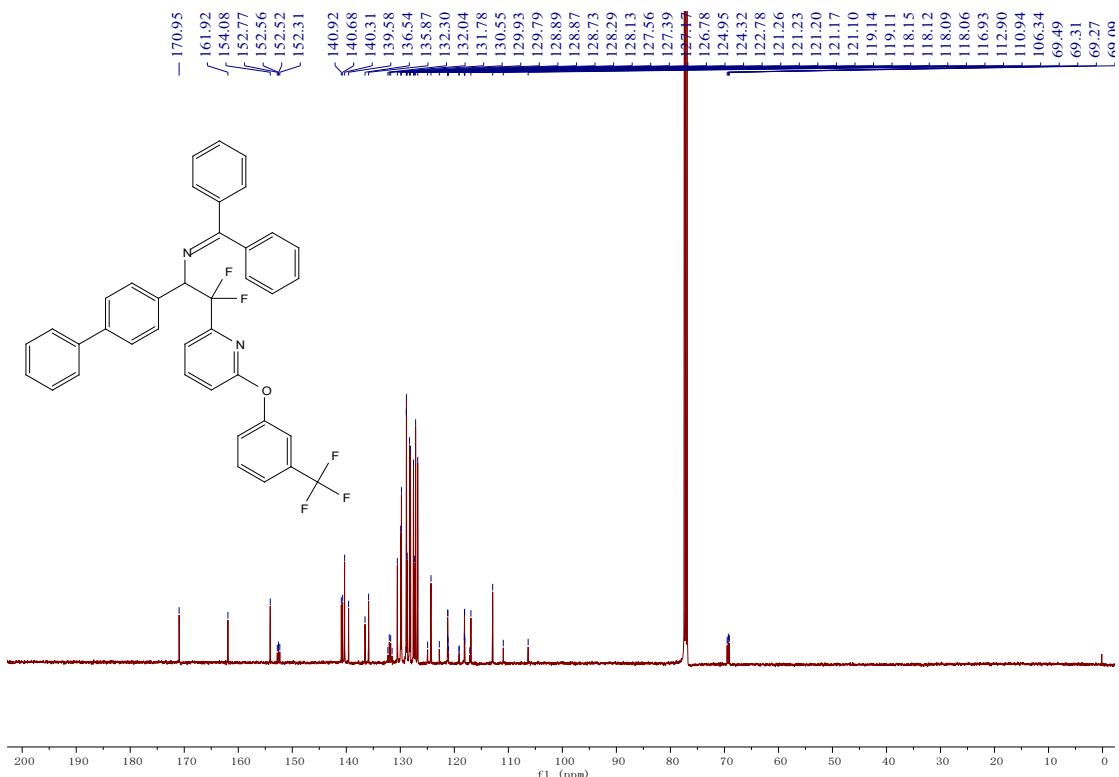
¹³C NMR (400 MHz, CDCl₃) spectrum of 4i



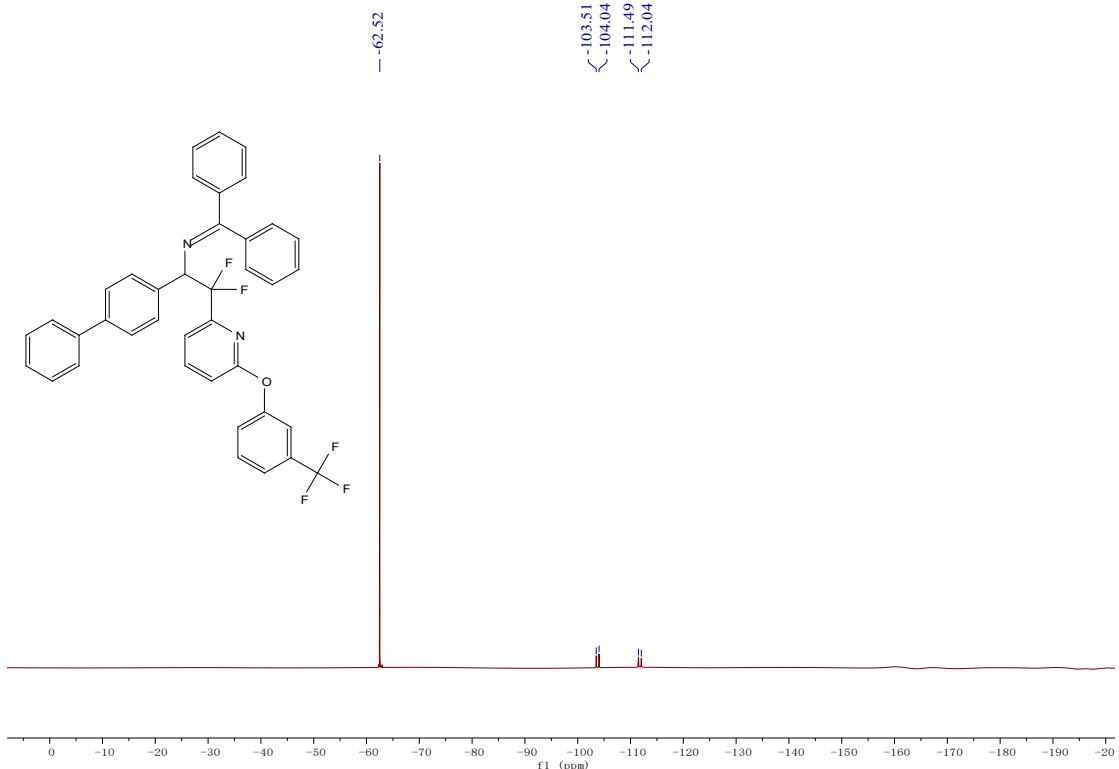
¹H NMR (400 MHz, CDCl₃) spectrum of 4j



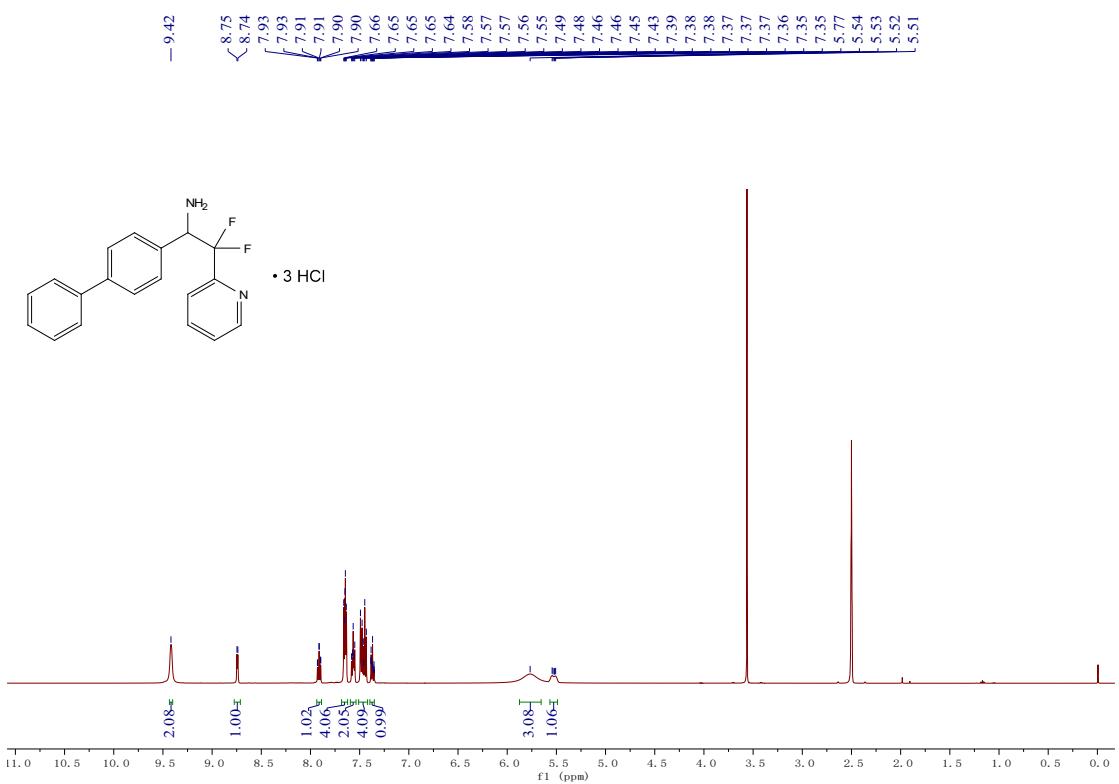
^{13}C NMR (126 MHz, CDCl_3) spectrum of 4j



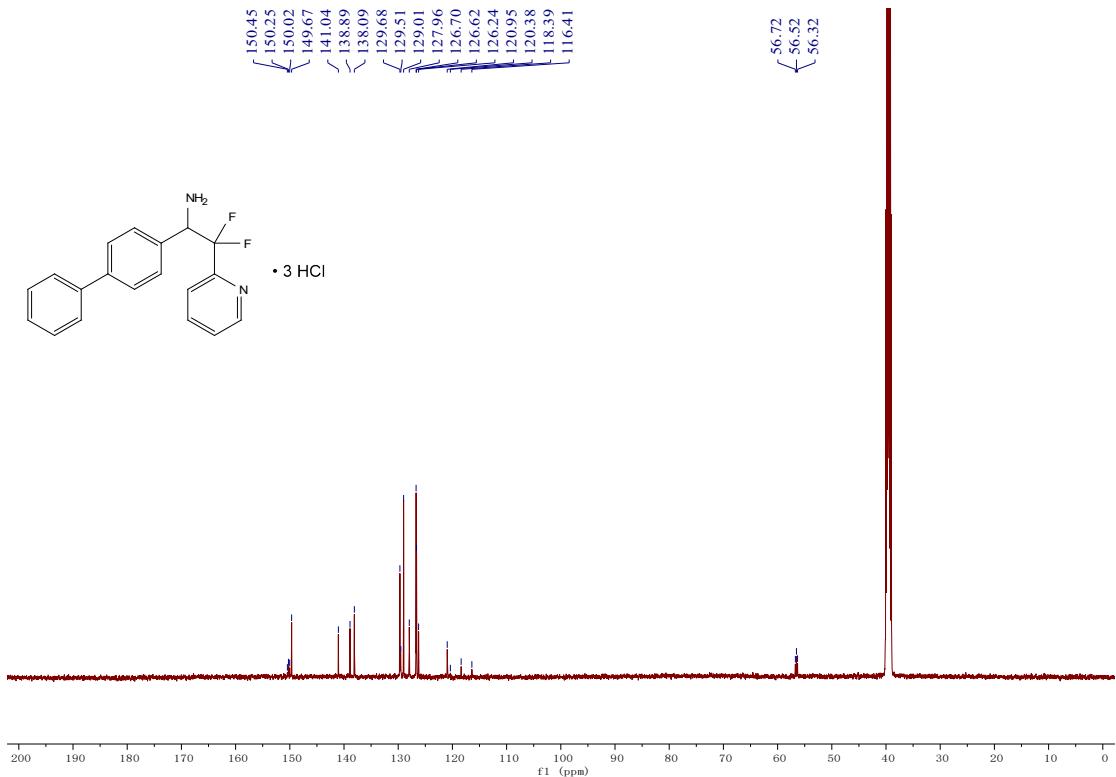
^{19}F NMR (471 MHz, CDCl_3) spectrum of 4j



^1H NMR (500 MHz, DMSO) spectrum of 3a-1

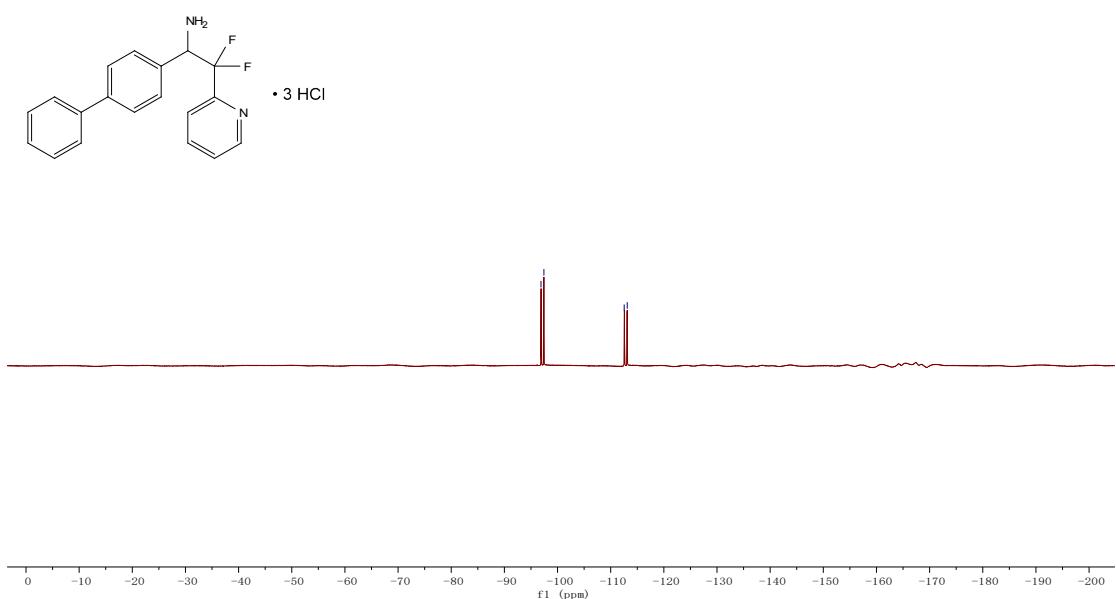


^1H NMR (500 MHz, DMSO) spectrum of 3a-1 · 3 HCl



^{19}F NMR (471 MHz, DMSO) spectrum of **3a-1**

$\begin{cases} -96.89 \\ -97.44 \\ -112.54 \\ -113.11 \end{cases}$



IR Data of **3a**

