

Supporting Information for
Neighboring Phenolic Group-Enabled *gem*-Difluoroallylboration of
Imines for the Catalyst-Free Synthesis of *gem*-Difluorohomoallyl
Amines

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Contents

General methods	S1
Additional experiments	S2
General procedure for the synthesis of <i>gem</i>-difluoroallylboronates	S2
General procedure for the <i>gem</i>-difluoroallylboration of imines	S3
Characterization data of the reaction products	S4
Deprotection of compound 3cb	S25
X-ray structure of 3na	S27
¹H, ¹³C, and ¹⁹F NMR spectra	S29

General methods

All reactions and manipulations involving air-sensitive compounds were carried out using standard Schlenk techniques. Anhydrous Et₂O, toluene and THF were distilled from sodium benzophenone ketyl. Anhydrous CH₂Cl₂ and CHCl₃ were distilled from CaH₂ under an atmosphere of nitrogen. All reactions were monitored by TLC. TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. ¹H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard (CDCl₃, δ = 7.26 ppm). ¹³C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard (CDCl₃, δ = 77.2 ppm). ¹⁹F NMR (471 MHz) spectra were recorded on a Bruker Avance 500 instrument. Infrared spectra were recorded on a NICOLET FT/IR-200 spectrometer. High resolution MS (P-ESI HRMS) were obtained on Thermo Fisher Q Exactive Mass Spectrometer.

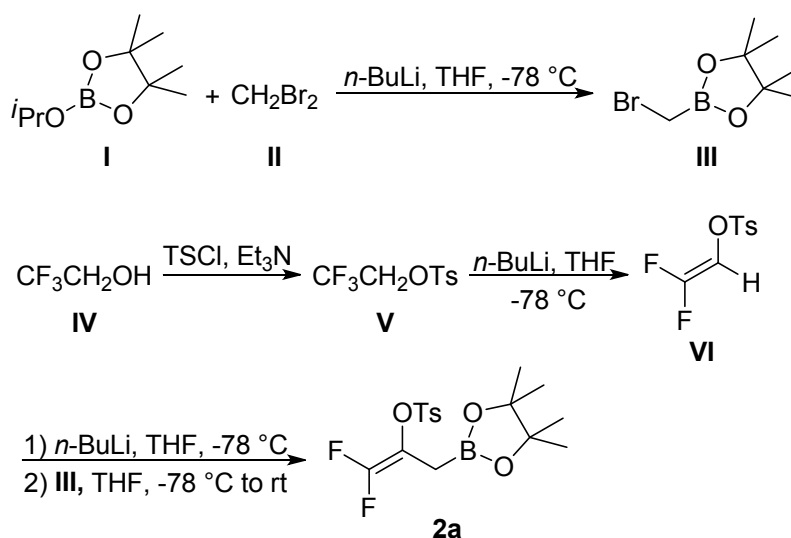
Additional experiments

Table S-1: Optimization of the *gem*-difluoroallylboration of imines^[a]

entry	additive	solvent	t/h	yield/% ^b
1	none	CHCl ₃	48	75
2	none	Et ₂ O	48	70
3	none	EtOAc	48	71
4	none	CH ₃ CN	48	73
5 ^c	H ₂ O	THF	24	96
6 ^c	EtOH	THF	24	94
7 ^d	MeOH	THF	24	99
8 ^{d,e}	MeOH	THF	22	98
9 ^{d,f}	MeOH	THF	18	99 (96)

^a Reaction conditions: **1c** (0.1 mmol), **2a** (0.12 mmol), solvent (0.5 mL). ^b NMR yield was determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard, and data in parenthesis is isolated yield. ^c Additive (2.0 equiv). ^d Additive (5.0 equiv). ^e Solvent (0.25 mL). ^f Solvent (0.1 mL).

General procedure for the synthesis of *gem*-difluoroallylboronates



(1) Synthesis of compound **III**: To a solution of compound **I** (18.6 g, 100 mmol) and dibromomethane **II** (19.2 g, 110 mmol) in anhydrous THF (300 mL) was added dropwise *n*-BuLi (2.5 M in hexane, 44 mL) over 30 min at -78 °C. The mixture was stirred at -78 °C for 1 h, then the cooling bath was removed and the reaction mixture was stirred at rt for 3 h. The mixture was cooled again to 0 °C, and a solution of

concentrated sulfuric acid (2.5 mL) in methanol (6.5 mL) was added dropwise over 5 min. The volatiles were removed under vacuum, and the residue was distilled (110 °C/20 torr) to give compound **III** (18.2 g, 83% yield) as a colorless liquid.^[1]

(2) Synthesis of compound **V**: To a solution of compound **IV** (5.0 g, 50 mmol) and triethylamine (18.2 g, 180 mmol) in anhydrous THF (50 mL) was added tosyl chloride (12.0 g, 62.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, then stirred at rt overnight. The mixture was then washed with brine (50 mL) and dried over Na₂SO₄. After concentration under vacuum, the residue was purified by chromatography (PE:EA = 5:1) to give compound **V** (11.7 g, 92% yield) as a colorless solid.^[2]

(3) Synthesis of compound **VI**: To a solution of compound **V** (7.6 g, 30 mmol) in anhydrous THF (150 mL) was added dropwise *n*-BuLi (2.5 M in hexane, 27.6 mL) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 45 min. The reaction was then quenched with a mixture of H₂O/THF (1:1, 100 mL). The mixture was concentrated under vacuum and extracted with ethyl acetate (3×60 mL). The combined organic phase was dried over Na₂SO₄. After concentration under vacuum, the residue was purified by chromatography (PE:EA = 10:1) to give compound **VI** (6.2 g, 88% yield) as a colorless liquid.^[2]

(4) Synthesis of compound **2a**: To a solution of compound **VI** (3.5 g, 15 mmol) in anhydrous THF (100 mL) was added dropwise *n*-BuLi (2.5 M in hexane, 6.0 mL) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h, then compound **III** (3.3 g, 15 mmol) was added. After stirring at -78 °C for 2 h, the reaction mixture was warmed up to 60 °C and stirred at that temperature for 4 h. The mixture was cooled to rt, then H₂O (50 mL) was added to quench the reaction. The mixture was concentrated under vacuum and extracted with ethyl acetate (3×50 mL). The combined organic phase was dried over Na₂SO₄. After concentration under vacuum, the residue was purified by chromatography (PE:EA = 15:1) to give compound **2a** (3.8 g, 68% yield) as a sticky yellow oil.^[1]

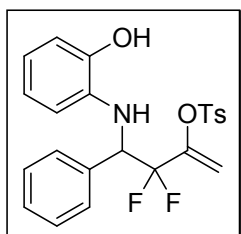
Compounds **2b-2r** were synthesized according to the literature procedure.^[3]

General procedure for *gem*-difluoroallylboration of imines

To a 2 mL test tube with a stir bar was added imine (0.2 mmol) and *gem*-difluoroallylborationate (0.24 mmol), anhydrous THF (0.2 mL) and MeOH (5.0 equiv),

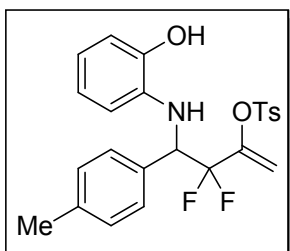
and the reaction mixture was stirred at rt for the time indicated in the table. Then the reaction mixture was directly subjected to preparative thin layer chromatography to give desired products.

Characterization data of the reaction products



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-phenylbut-1-en-2-yl 4-methylbenzenesulfonate (3ca):

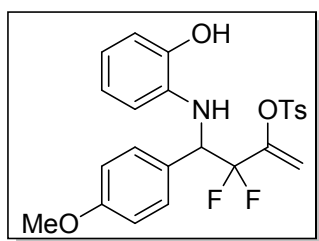
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 97% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, 8.2 Hz, 2H), 7.33 (d, 6.2 Hz, 2H), 7.28 - 7.24 (m, 5H), 6.70 - 6.65 (m, 2H), 6.61 (t, 7.3 Hz, 1H), 6.39 (d, 7.7 Hz, 1H), 5.50 (d, 1.4 Hz, 1H), 5.32 (d, 3.1 Hz, 1H), 4.75 (dd, 15.4 Hz, 10.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.1 (dd, 33.3 Hz, 29.9 Hz), 145.9, 144.3, 134.8, 134.4, 132.2, 130.0, 129.9, 129.8, 128.5, 128.4, 121.3, 119.2, 116.8 (t, 250.5 Hz), 114.8, 114.7, 105.9 (t, 4.6 Hz), 60.4 (dd, 27.6 Hz, 23.8 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -107.4 (dd, 255.9 Hz, 9.0 Hz, 1F), -113.9 (dd, 255.9 Hz, 15.6 Hz, 1F); IR (KBr): 3419, 2922, 1597, 1513, 1452, 1366, 1174, 1086, 950, 715 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{F}_2\text{NO}_4\text{SNa}$ 468.1057, found 468.1048.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(p-tolyl)but-1-en-2-yl 4-methylbenzenesulfonate (3da):

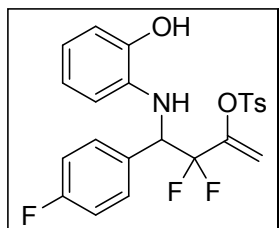
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained

in 98% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, 8.2 Hz, 2H), 7.25 (d, 8.0 Hz, 2H), 7.21 (d, 7.7 Hz, 2H), 7.08 (d, 7.8 Hz, 2H), 6.69 - 6.65 (m, 2H), 6.59 (t, 7.4 Hz, 1H), 6.40 (d, 7.7 Hz, 1H), 5.49 (d, 1.4 Hz, 1H), 5.32 (d, 3.1 Hz, 1H), 4.72 (dd, 15.5 Hz, 10.4 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.2 (dd, 33.4 Hz, 30.1 Hz), 145.9, 144.3, 138.3, 134.5, 132.2, 131.7, 129.9, 129.2, 128.5, 128.3, 121.3, 119.2, 116.9 (t, 250.4 Hz), 114.6, 114.1, 105.8 (t, 4.6 Hz), 60.1 (dd, 27.7 Hz, 23.8 Hz), 21.7, 21.1; ^{19}F NMR (471 MHz, CDCl_3) δ -107.4 (dd, 255.8 Hz, 9.1 Hz, 1F), -113.9 (dd, 255.7 Hz, 15.7 Hz, 1F); IR (KBr): 3493, 1597, 1513, 1449, 1366, 1268, 1174, 1086, 1040, 726 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{F}_2\text{NO}_4\text{SNa}$ 482.1214, found 482.1208.



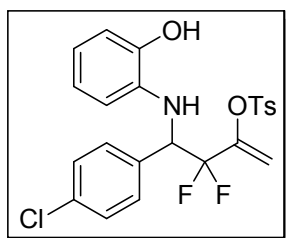
3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(4-methoxyphenyl)but-1-en-2-yl 4-methylbenzenesulfonate (3ea):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 97% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, 8.2 Hz, 2H), 7.25 (t, 7.4 Hz, 4H), 6.80 (d, 8.6 Hz, 2H), 6.70 - 6.65 (m, 2H), 6.60 (t, 7.4 Hz, 1H), 6.40 (d, 7.7 Hz, 1H), 5.49 (s, 1H), 5.31 (d, 3.2 Hz, 1H), 4.71 (dd, 14.8 Hz, 10.9 Hz, 1H), 3.74 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 146.2 (dd, 33.3 Hz, 30.4 Hz), 145.9, 144.4, 134.5, 132.2, 129.9, 129.5, 128.5, 126.8, 121.3, 119.1, 116.9 (t, 250.2 Hz), 114.6, 114.1, 113.9, 105.8 (t, 4.5 Hz), 59.8 (dd, 27.7 Hz, 23.8 Hz), 55.2, 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -107.8 (dd, 255.3 Hz, 9.8 Hz, 1F), -113.8 (dd, 255.3 Hz, 15.2 Hz, 1F); IR (KBr): 3416, 1610, 1511, 1449, 1366, 1247, 1173, 1035, 950, 728 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{F}_2\text{NO}_5\text{SNa}$ 498.1163, found 498.1157.



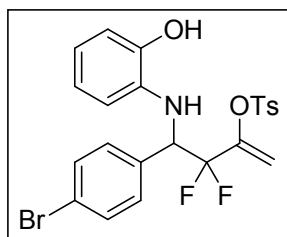
3,3-difluoro-4-(4-fluorophenyl)-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3fa):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 96% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, 8.2 Hz, 2H), 7.33 - 7.28 (m, 2H), 7.26 (d, 8.0 Hz, 2H), 6.95 (t, 8.6 Hz, 2H), 6.71 - 6.66 (m, 2H), 6.61 (t, 7.4 Hz, 1H), 6.35 (d, 7.7 Hz, 1H), 5.50 (s, 1H), 5.33 (d, 3.2 Hz, 1H), 4.76 (dd, 15.5 Hz, 9.9 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.8 (d, 247.5 Hz), 146.0, 145.9 (dd, 33.4 Hz, 29.9 Hz), 144.1, 134.3, 132.1, 130.1 (d, 8.2 Hz), 129.9, 128.5, 121.3, 119.2, 116.7 (t, 250.6 Hz), 115.5, 115.3, 114.7, 113.7, 105.9 (t, 4.6 Hz), 59.7 (dd, 28.2 Hz, 24.2 Hz), 21.7; ¹⁹F NMR (471 MHz, CDCl₃) δ -107.2 (dd, 256.2 Hz, 9.4 Hz, 1F), -113.2 - -113.6 (m, 1F), -114.3 (dd, 256.2 Hz, 15.6 Hz, 1F); IR (KBr): 3421, 1599, 1509, 1366, 1226, 1174, 1096, 1051, 950, 726 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₃H₂₁F₃NO₄S 464.1143, found 464.1138.



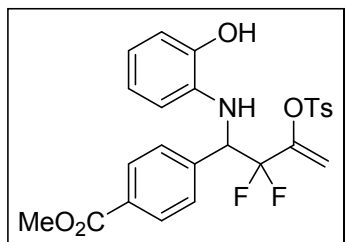
4-(4-chlorophenyl)-3,3-difluoro-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3ga):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 96% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, 8.2 Hz, 2H), 7.27 - 7.23 (m, 6H), 6.71 - 6.66 (m, 2H), 6.61 (t, 7.4 Hz, 1H), 6.34 (d, 7.7 Hz, 1H), 5.52 (s, 1H), 5.35 (d, 3.3 Hz, 1H), 4.75 (dd, 15.6 Hz, 9.7 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 146.0, 145.8 (dd, 33.4 Hz, 29.7 Hz), 144.1, 134.4, 134.2, 133.4, 132.1, 129.9, 129.8, 128.6, 128.5, 121.4, 119.2, 116.6 (t, 250.9 Hz), 114.7, 113.7, 106.0 (t, 4.6 Hz), 59.8 (dd, 28.2 Hz, 24.1 Hz), 21.7; ¹⁹F NMR (471 MHz, CDCl₃) δ -107.0 (dd, 256.5 Hz, 9.1 Hz, 1F), -114.2 (dd, 256.5 Hz, 15.6 Hz, 1F); IR (KBr): 3420, 1660, 1597, 1514, 1365, 1173, 1088, 1014, 950, 727 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₃H₂₁ClF₂NO₄S 480.0848, found 480.0842.



4-(4-bromophenyl)-3,3-difluoro-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3ha):

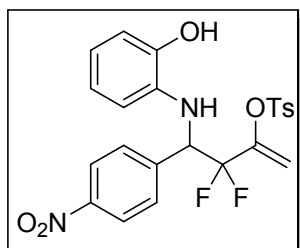
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 97% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, 8.2 Hz, 2H), 7.39 (d, 8.3 Hz, 2H), 7.26 (d, 8.0 Hz, 2H), 7.20 (d, 8.1 Hz, 2H), 6.71 - 6.66 (m, 2H), 6.61 (t, 7.4 Hz, 1H), 6.34 (d, 7.7 Hz, 1H), 5.52 (s, 1H), 5.35 (d, 3.2 Hz, 1H), 4.74 (dd, 15.6 Hz, 9.7 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.0, 145.8 (dd, 33.4 Hz, 29.9 Hz), 144.1, 134.1, 133.9, 132.0, 131.6, 130.1, 129.9, 128.5, 122.7, 121.4, 119.2, 116.5 (t, 250.5 Hz), 114.7, 113.6, 106.0 (t, 4.6 Hz), 59.8 (dd, 28.2 Hz, 24.2 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -106.9 (dd, 256.5 Hz, 9.1 Hz, 1F), -114.2 (dd, 256.6 Hz, 15.6 Hz, 1F); IR (KBr): 3420, 1660, 1596, 1514, 1365, 1173, 1076, 1051, 950, 726 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{BrF}_2\text{NO}_4\text{S}$ 524.0343, found 524.0337.



methyl 4-(2,2-difluoro-1-((2-hydroxyphenyl)amino)-3-(tosyloxy)but-3-en-1-yl)benzoate (3ia):

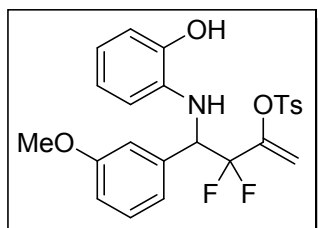
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 92% yield as a brown solid. ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, 8.2 Hz, 2H), 7.75 (d, 8.2 Hz, 2H), 7.42 (d, 8.0 Hz, 2H), 7.25 (d, 8.0 Hz, 2H), 6.72 (d, 7.5 Hz, 1H), 6.64 (t, 7.4 Hz, 1H), 6.59 (t, 7.4 Hz, 1H), 6.33 (d, 7.7 Hz, 1H), 5.52 (s, 1H), 5.35 (d, 3.1 Hz, 1H), 4.86 (dd, 15.9 Hz, 9.2 Hz, 1H), 3.88 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.0, 146.0, 145.8 (dd, 33.5 Hz, 29.5 Hz), 144.1, 140.3, 134.2, 132.0,

130.2, 129.9, 129.7, 128.6, 128.5, 121.2, 119.1, 116.6 (t, 251.2 Hz), 114.6, 113.2, 106.0 (t, 4.6 Hz), 60.0 (dd, 28.2 Hz, 24.2 Hz), 52.3, 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -106.4 (dd, 257.0 Hz, 8.1 Hz, 1F), -114.4 (dd, 257.0 Hz, 16.0 Hz, 1F); IR (KBr): 3390, 1703, 1600, 1517, 1436, 1371, 1294, 1192, 956, 745 cm^{-1} ; mp = 95.1-96.3 $^{\circ}\text{C}$; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{24}\text{F}_2\text{NO}_6\text{S}$ 504.1292, found 504.1287.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(4-nitrophenyl)but-1-en-2-yl 4-methylbenzenesulfonate (3ja):

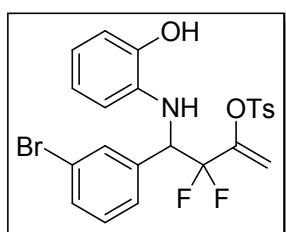
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 95% yield as a brown solid. ^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, 8.6 Hz, 2H), 7.75 (d, 8.2 Hz, 2H), 7.53 (d, 8.4 Hz, 2H), 7.28 (d, 8.0 Hz, 2H), 6.73 (d, 7.5 Hz, 1H), 6.67 (t, 7.3 Hz, 1H), 6.63 (t, 7.3 Hz, 1H), 6.29 (d, 7.6 Hz, 1H), 5.56 (s, 1H), 5.41 (d, 3.1 Hz, 1H), 4.92 (dd, 16.1 Hz, 8.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.1, 146.2, 145.4 (dd, 33.5 Hz, 29.2 Hz), 143.9, 142.4, 133.8, 132.0, 129.9, 129.5, 128.5, 123.6, 121.5, 119.5, 116.3 (t, 251.4 Hz), 114.8, 113.3, 106.3 (t, 4.6 Hz), 59.9 (dd, 28.9 Hz, 24.1 Hz), 21.8; ^{19}F NMR (471 MHz, CDCl_3) δ -105.8 (dd, 257.8 Hz, 8.2 Hz, 1F), -114.5 (dd, 257.8 Hz, 16.1 Hz, 1F); IR (KBr): 3359, 1664, 1610, 1523, 1365, 1180, 1098, 1057, 946, 745 cm^{-1} ; mp = 164.3-165.6 $^{\circ}\text{C}$; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{F}_2\text{N}_2\text{O}_6\text{S}$ 491.1088, found 491.1083.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(3-methoxyphenyl)but-1-en-2-yl 4-methylbenzenesulfonate (3ka):

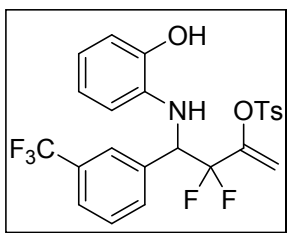
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained

in 94% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, 8.2 Hz, 2H), 7.25 (d, 8.0 Hz, 2H), 7.19 (t, 7.9 Hz, 1H), 6.93 (d, 7.6 Hz, 1H), 6.89 (s, 1H), 6.80 (dd, 8.2 Hz, 1.0 Hz, 1H), 6.69 - 6.65 (m, 2H), 6.59 (t, 7.4 Hz, 1H), 6.41 (d, 7.7 Hz, 1H), 5.49 (s, 1H), 5.34 (d, 3.1 Hz, 1H), 4.73 (dd, 15.6 Hz, 10.1 Hz, 1H), 3.74 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.5, 146.1 (dd, 35.9 Hz, 29.9 Hz), 145.9, 144.3, 136.5, 134.5, 132.1, 130.0, 129.9, 129.4, 128.4, 121.3, 120.9, 119.1, 116.8 (t, 250.7 Hz), 114.6, 114.2, 113.9, 105.8 (t, 4.6 Hz), 60.3 (dd, 28.0 Hz, 23.9 Hz), 55.2, 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -107.1 (dd, 256.0 Hz, 8.5 Hz, 1F), -113.8 (dd, 255.9 Hz, 15.7 Hz, 1F); IR (KBr): 3418, 1660, 1597, 1513, 1451, 1262, 1174, 1039, 950, 722 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{F}_2\text{NO}_5\text{SNa}$ 498.1163, found 498.1157.



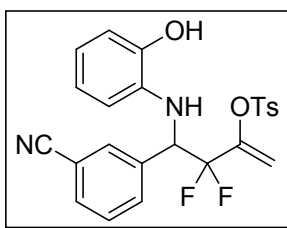
4-(3-bromophenyl)-3,3-difluoro-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3la):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 95% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, 8.2 Hz, 2H), 7.46 (s, 1H), 7.39 (d, 8.0 Hz, 1H), 7.27 (d, 7.9 Hz, 3H), 7.14 (t, 7.8 Hz, 1H), 6.71 - 6.67 (m, 2H), 6.61 (t, 7.4 Hz, 1H), 6.35 (d, 7.7 Hz, 1H), 5.53 (s, 1H), 5.38 (d, 2.9 Hz, 1H), 4.73 (dd, 16.5 Hz, 8.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.1, 145.7 (dd, 34.1 Hz, 31.2 Hz), 144.0, 137.3, 134.1, 132.0, 131.7, 131.5, 130.0, 129.9, 128.5, 127.1, 122.5, 121.4, 119.1, 116.5 (t, 251.0 Hz), 114.7, 113.3, 106.2 (t, 4.5 Hz), 59.7 (dd, 28.7 Hz, 23.9 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -105.8 (dd, 257.3 Hz, 8.0 Hz, 1F), -114.8 (dd, 257.3 Hz, 16.5 Hz, 1F); IR (KBr): 3418, 1659, 1513, 1450, 1366, 1191, 1174, 1051, 950, 724 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{BrF}_2\text{NO}_4\text{S}$ 524.0343, found 524.0337.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(3-(trifluoromethyl)phenyl)but-1-en-2-yl 4-methylbenzenesulfonate (3ma):

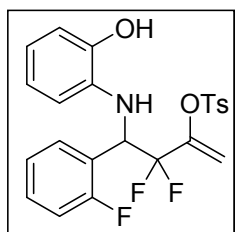
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 97% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, 8.2 Hz, 2H), 7.58 (s, 1H), 7.54 (t, 7.1 Hz, 2H), 7.40 (t, 7.7 Hz, 1H), 7.27 (d, 8.0 Hz, 2H), 6.72 - 6.67 (m, 2H), 6.62 (t, 7.4 Hz, 1H), 6.34 (d, 7.7 Hz, 1H), 5.54 (s, 1H), 5.40 (d, 2.6 Hz, 1H), 4.84 (dd, 16.8 Hz, 8.3 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 146.2, 145.7 (dd, 34.0 Hz, 31.4 Hz), 144.0, 136.1, 134.1, 132.0, 131.8, 130.8 (q, 35.1 Hz), 130.0, 129.0, 128.5, 125.4 (q, 3.7 Hz), 125.3 (q, 3.6 Hz), 124.0 (q, 272.9 Hz), 121.4, 119.3, 116.5 (t, 251.0 Hz), 114.8, 113.4, 106.32 (t, 4.6 Hz), 59.9 (dd, 29.0 Hz, 23.9 Hz), 21.7; ¹⁹F NMR (471 MHz, CDCl₃) δ -62.5 (s, 3F), -105.3 (dd, 257.9 Hz, 7.7 Hz, 1F), -115.3 (dd, 257.9 Hz, 16.8 Hz, 1F); IR (KBr): 3500, 1660, 1597, 1514, 1368, 1326, 1170, 1122, 952, 730 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₄H₂₁F₅NO₄S 514.1111, found 514.1106.



4-(3-cyanophenyl)-3,3-difluoro-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3na):

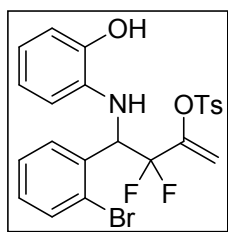
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 98% yield as a brown solid. ¹H NMR (500 MHz, (CD₃)₂SO) δ 9.65 (s, 1H), 7.88 - 7.83 (m, 3H), 7.74 (dd, 14.0 Hz, 7.8 Hz, 2H), 7.55 - 7.51 (m, 1H), 7.41 (d, 8.0 Hz, 2H), 6.70 (d, 7.5 Hz, 1H), 6.57 - 6.50 (m, 3H), 5.61 (d, 3.3 Hz, 1H), 5.54 (s, 1H), 5.36 - 5.13 (m, 1H), 5.05 (d, 10.4 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (126 MHz, DMSO-d₆) δ 146.7, 145.7 (dd, 33.6 Hz, 28.4 Hz), 145.2, 137.4, 134.2, 133.8, 132.8, 132.6, 131.7,

130.6, 130.0, 128.8, 120.0, 119.0, 118.8, 117.1 (t, 251.2 Hz), 114.6, 112.7, 111.7, 107.3, 58.2 (dd, 30.2 Hz, 23.2 Hz), 21.7; ^{19}F NMR (471 MHz, DMSO) δ -101.7 (d, 257.4 Hz, 1F), -114.7 (dd, 257.4 Hz, 19.6 Hz, 1F); IR (KBr): 3341, 2360, 2238, 1595, 1516, 1376, 1192, 1087, 958, 779 cm^{-1} ; mp = 176.9-178.0 $^{\circ}\text{C}$; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{21}\text{F}_2\text{N}_2\text{O}_4\text{S}$ 471.1190, found 471.1185.



3,3-difluoro-4-(2-fluorophenyl)-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (30a):

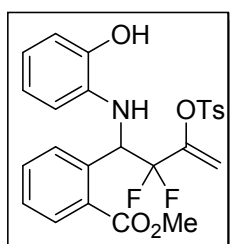
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 90% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, 8.2 Hz, 2H), 7.35 (t, 7.6 Hz, 1H), 7.26 - 7.22 (m, 3H), 7.11 - 6.96 (m, 2H), 6.75 - 6.65 (m, 2H), 6.60 (t, 7.3 Hz, 1H), 6.45 (d, 7.8 Hz, 1H), 5.57 (s, 1H), 5.43 (s, 1H), 5.23 (dd, 18.3 Hz, 7.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.4 (d, 248.0 Hz), 146.0 (dd, 34.3 Hz, 28.9 Hz), 145.9, 144.2, 134.0, 132.1, 130.2 (d, 8.4 Hz), 130.1, 129.8, 129.2 (d, 2.9 Hz), 128.4, 124.3 (d, 3.4 Hz), 122.1 (d, 13.5 Hz), 121.4, 119.3, 116.6 (t, 250.9 Hz), 115.3 (d, 22.4 Hz), 114.7, 106.1 (t, 4.6 Hz), 53.3 (dd, 28.1 Hz, 23.9 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -105.8 (dd, 257.8 Hz, 7.5 Hz, 1F), -115.8 (dd, 257.8 Hz, 18.0 Hz, 1F), -117.6 (d, 5.8 Hz, 1F); IR (KBr): 3501, 1662, 1596, 1488, 1452, 1174, 1091, 1052, 950, 756 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{NO}_4\text{SNa}$ 486.0963, found 486.0957.



4-(2-bromophenyl)-3,3-difluoro-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3pa):

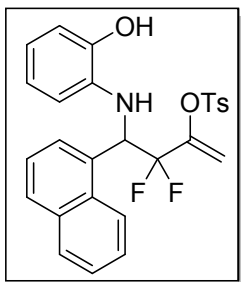
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained

in 95% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.80 - 7.73 (m, 4H), 7.46 - 7.42 (m, 2H), 7.21 (d, 8.1 Hz, 2H), 6.70 (d, 7.6 Hz, 1H), 6.62 (t, 7.5 Hz, 1H), 6.57 (t, 7.4 Hz, 1H), 6.43 (d, 7.7 Hz, 1H), 5.49 (s, 1H), 5.34 (d, 3.3 Hz, 1H), 4.94 (dd, 15.3 Hz, 10.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.0 (dd, 33.4 Hz, 28.2 Hz), 145.9, 144.3, 134.5, 133.3, 133.0, 132.0, 129.8, 128.4, 128.2, 127.6, 126.2, 125.6, 121.2, 119.1, 116.9 (t, 250.4 Hz), 114.6, 113.8, 105.9 (t, 4.5 Hz), 60.6 (dd, 30.4 Hz, 23.2 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -107.0 (dd, 255.9 Hz, 9.3 Hz, 1F), -113.3 (dd, 255.8 Hz, 15.4 Hz, 1F); IR (KBr): 3418, 1659, 1597, 1512, 1366, 1174, 1085, 1040, 950, 726 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{BrF}_2\text{NO}_4\text{SNa}$ 546.0162, found 546.0157.



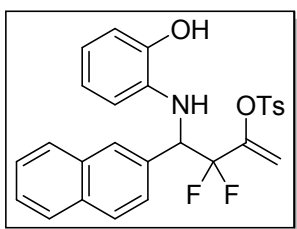
methyl 2-(2,2-difluoro-1-((2-hydroxyphenyl)amino)-3-(tosyloxy)but-3-en-1-yl)benzoate (3qa):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 84% yield as a brown solid. ^1H NMR (500 MHz, CDCl_3) δ 7.92 - 7.84 (m, 1H), 7.77 (d, 8.3 Hz, 2H), 7.54 (d, 7.8 Hz, 1H), 7.39 (dd, 11.1 Hz, 4.1 Hz, 1H), 7.30 (t, 7.6 Hz, 1H), 7.21 (d, 8.1 Hz, 2H), 6.68 (t, 6.8 Hz, 2H), 6.63 - 6.43 (m, 3H), 5.56 - 5.48 (m, 1H), 5.39 (s, 1H), 3.95 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.3, 146.3 (dd, 34.1 Hz, 28.7 Hz), 145.7, 143.6, 135.9, 134.4, 132.1, 132.0, 131.5, 130.5, 129.7, 128.6, 128.2, 128.1, 121.5, 118.4, 116.7 (t, 250.6 Hz), 114.5, 113.2, 105.5 (t, 4.6 Hz), 53.8 (dd, 30.2 Hz, 22.4 Hz), 52.4, 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -104.0 (d, 259.7 Hz, 1F), -116.8 (dd, 259.7 Hz, 20.2 Hz, 1F); IR (KBr): 3580, 1713, 1673, 1597, 1360, 1178, 1089, 1070, 950, 743 cm^{-1} ; mp = 84.7-86.0 $^{\circ}\text{C}$; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{F}_2\text{NO}_6\text{SNa}$ 526.1112, found 526.1106.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(naphthalen-1-yl)but-1-en-2-yl 4-methylbenzenesulfonate (3ra):

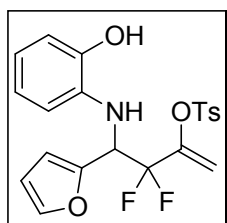
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 83% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, 8.2 Hz, 2H), 7.51 (d, 7.6 Hz, 1H), 7.40 (d, 7.8 Hz, 1H), 7.25 (d, 8.0 Hz, 2H), 7.20 (t, 7.4 Hz, 1H), 7.10 (t, 7.3 Hz, 1H), 6.71 - 6.66 (m, 2H), 6.58 (t, 7.5 Hz, 1H), 6.39 (d, 7.8 Hz, 1H), 5.62 (s, 1H), 5.55 - 5.40 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.4, 146.0 (dd, 35.4 Hz, 28.9 Hz), 145.9, 143.7, 134.4, 134.0, 132.8, 132.1, 130.1, 130.0, 129.8, 129.3, 128.6, 128.5, 128.4, 127.7, 125.9, 121.5, 118.9, 116.6 (t, 250.9 Hz), 114.6, 113.2, 106.2 (t, 4.6 Hz), 57.8 (dd, 31.1 Hz, 22.2 Hz), 21.8; ^{19}F NMR (471 MHz, CDCl_3) δ -103.8 (d, 260.2 Hz, 1F), -117.9 (dd, 260.1 Hz, 20.4 Hz, 1F); IR (KBr): 3418, 1661, 1514, 1449, 1366, 1174, 1087, 1042, 950, 727 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{F}_2\text{NO}_4\text{SNa}$ 518.1214, found 518.1208.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-(naphthalen-2-yl)but-1-en-2-yl 4-methylbenzenesulfonate (3sa):

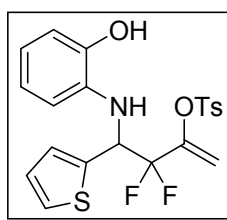
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 86% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, 8.0 Hz, 1H), 7.89 - 7.82 (m, 1H), 7.77 (d, 8.2 Hz, 3H), 7.63 (d, 7.2 Hz, 1H), 7.56 - 7.44 (m, 2H), 7.43 - 7.35 (m, 1H), 7.23 (t, 6.3 Hz, 2H), 6.76 - 6.61 (m, 1H), 6.60 - 6.45 (m, 2H), 6.32 - 6.18 (m, 1H), 5.76 (dd, 18.7 Hz, 4.7 Hz, 1H), 5.55 (s, 1H), 5.46 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.3 (dd, 35.3 Hz, 28.5 Hz), 145.9, 143.9, 134.4,

133.7, 132.5, 132.2, 130.7, 129.9, 129.1, 129.0, 128.5, 126.5, 125.8, 125.6, 125.3, 122.7, 121.4, 118.7, 117.0 (t, 250.9 Hz), 114.6, 113.1, 106.0 (d, 4.5 Hz), 50.5 (dd, 30.2 Hz, 24.1 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -103.5 (d, 259.3 Hz, 1F), -116.1 (d, 259.7 Hz, 1F); IR (KBr): 3418, 1661, 1597, 1512, 1367, 1174, 1083, 1041, 950, 718 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{F}_2\text{NO}_4\text{SNa}$ 518.1214, found 518.1208.



3,3-difluoro-4-((furan-2-yl)methyl)-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3ta):

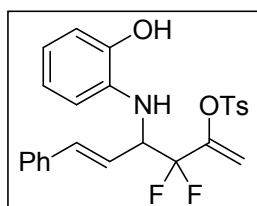
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 96% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, 8.2 Hz, 2H), 7.34 (s, 1H), 7.28 (d, 8.0 Hz, 2H), 6.79 - 6.64 (m, 3H), 6.56 (d, 7.3 Hz, 1H), 6.35 - 6.22 (m, 2H), 5.51 (d, 2.0 Hz, 1H), 5.39 (d, 3.4 Hz, 1H), 4.84 (dd, 14.4 Hz, 10.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.1, 146.0, 145.9 (dd, 33.8 Hz, 28.9 Hz), 145.4, 142.9, 133.8, 132.0, 129.9, 128.5, 121.1, 120.6, 116.2 (t, 251.4 Hz), 115.5, 114.9, 110.5, 109.9, 106.0 (t, 4.6 Hz), 55.5 (dd, 28.9 Hz, 25.1 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -108.1 (dd, 254.8 Hz, 10.2 Hz, 1F), -112.6 (dd, 254.8 Hz, 14.6 Hz, 1F); IR (KBr): 3501, 1597, 1514, 1450, 1366, 1174, 1083, 1040, 950, 734 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{F}_2\text{NO}_5\text{SNa}$ 458.0850, found 458.0844.



3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-((thiophen-2-yl)methyl)but-1-en-2-yl 4-methylbenzenesulfonate (3ua):

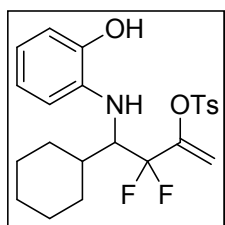
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 92% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, 8.2 Hz, 2H), 7.27

(d, 8.0 Hz, 2H), 7.24 - 7.20 (m, 1H), 7.03 (d, 2.8 Hz, 1H), 6.92 (dd, 4.8 Hz, 3.8 Hz, 1H), 6.73 - 6.67 (m, 3H), 6.54 (d, 7.6 Hz, 1H), 5.52 (d, 1.7 Hz, 1H), 5.40 (d, 3.3 Hz, 1H), 5.04 (dd, 15.0 Hz, 10.1 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.0, 145.9 (dd, 33.0 Hz, 30.0 Hz), 144.8, 138.1, 134.1, 132.1, 129.9, 128.5, 127.4, 126.9, 126.1, 121.3, 120.0, 116.4 (t, 251.1 Hz), 114.8, 114.6, 106.2 (t, 4.5 Hz), 56.9 (dd, 29.0 Hz, 25.3 Hz), 21.8; ^{19}F NMR (471 MHz, CDCl_3) δ -107.3 (dd, 254.8 Hz, 9.7 Hz, 1F), -113.8 (dd, 254.7 Hz, 15.1 Hz, 1F); IR (KBr): 3501, 1661, 1597, 1512, 1450, 1365, 1174, 1083, 950, 707 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{F}_2\text{NO}_4\text{S}_2\text{Na}$ 474.0621, found 474.0616.



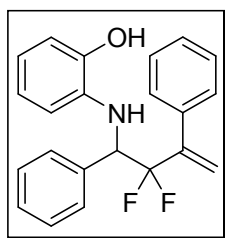
(*E*)-3,3-difluoro-4-((2-hydroxyphenyl)amino)-6-phenylhexa-1,5-dien-2-yl 4-methylbenzenesulfonate (3va):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 94% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, 8.2 Hz, 2H), 7.30 - 7.22 (m, 7H), 6.80 - 6.71 (m, 2H), 6.70 - 6.57 (m, 3H), 6.08 (dd, 15.9 Hz, 6.6 Hz, 1H), 5.55 (s, 1H), 5.46 (d, 3.5 Hz, 1H), 4.51 - 4.33 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.2 (t, 31.4 Hz), 145.9, 144.6, 136.0, 134.8, 134.5, 132.2, 129.9, 128.5, 128.4, 128.1, 126.7, 122.2, 121.3, 119.5, 117.1 (t, 250.4 Hz), 114.8, 114.5, 106.0 (t, 4.6 Hz), 58.9 (dd, 27.6 Hz, 25.3 Hz), 21.7; ^{19}F NMR (471 MHz, CDCl_3) δ -108.7 (dd, 254.8 Hz, 10.3 Hz, 1F), -112.5 (dd, 254.8 Hz, 13.6 Hz, 1F); IR (KBr): 3419, 1660, 1596, 1514, 1449, 1366, 1175, 1082, 950, 734 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{F}_2\text{NO}_4\text{SNa}$ 494.1214, found 494.1208.



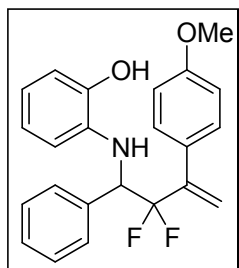
4-cyclohexyl-3,3-difluoro-4-((2-hydroxyphenyl)amino)but-1-en-2-yl 4-methylbenzenesulfonate (3wa):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 92% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, 8.2 Hz, 2H), 7.30 (d, 8.0 Hz, 2H), 6.76 (s, 1H), 6.66 (s, 1H), 6.55 (s, 2H), 5.44 (s, 1H), 5.39 (d, 3.3 Hz, 1H), 5.06 (s, 1H), 4.21 (s, 1H), 3.69 (s, 1H), 2.42 (s, 3H), 1.83 - 1.49 (m, 7H), 1.30 - 0.96 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 147.1 (t, 32.1 Hz), 145.8, 142.6, 136.9, 132.4, 129.9, 128.5, 121.6, 118.4 (t, 251.4 Hz), 114.7, 111.9, 105.3 (d, 4.6 Hz), 59.5 (t, 24.4 Hz), 38.4, 31.2, 26.8, 26.3, 26.0, 25.9, 21.7; ¹⁹F NMR (471 MHz, CDCl₃) δ -108.3 (s, 2F); IR (KBr): 3502, 2926, 2853, 1609, 1521, 1365, 1174, 1088, 947, 729 cm⁻¹; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₂₃H₂₇F₂NO₄Na 474.1527, found 474.1521.



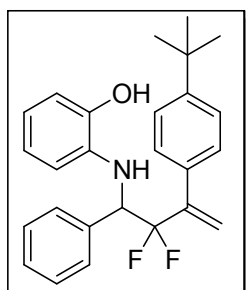
2-((2,2-difluoro-1,3-diphenylbut-3-en-1-yl)amino)phenol (3cb):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 97% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.36 - 7.26 (m, 10H), 6.65 (d, 3.1 Hz, 1H), 6.57 (d, 3.8 Hz, 2H), 6.23 - 6.14 (m, 1H), 5.74 (s, 1H), 5.47 (s, 1H), 4.59 (dd, 14.4 Hz, 11.3 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 144.4, 143.3 (t, 22.2 Hz), 136.7, 135.9, 134.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 121.2, 121.0 (t, 250.9 Hz), 120.3 (t, 8.8 Hz), 119.1, 114.5, 114.3, 61.9 (dd, 27.6 Hz, 25.1 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -101.8 (d, 250.7 Hz, 1F), -107.6 (dd, 250.3 Hz, 12.5 Hz, 1F); IR (KBr): 3418, 2923, 1610, 1511, 1450, 1265, 1170, 1025, 848, 695 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₂H₂₀F₂NO 352.1513, found 352.1508.



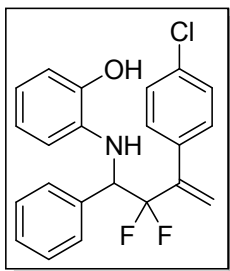
2-((2,2-difluoro-3-(4-methoxyphenyl)-1-phenylbut-3-en-1-yl)amino)phenol (3cc):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 96% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.30 - 7.25 (m, 7H), 6.85 (d, 8.6 Hz, 2H), 6.65 (d, 6.8 Hz, 1H), 6.56 (t, 6.2 Hz, 2H), 6.21 (d, 7.2 Hz, 1H), 5.66 (s, 1H), 5.41 (s, 1H), 4.65 - 4.55 (m, 1H), 3.80 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 159.6, 144.3, 142.6 (t, 22.2 Hz), 136.0, 134.8, 129.7, 129.0, 128.6, 128.1 (2C), 121.2, 121.1 (t, 250.2 Hz), 119.3 (t, 8.8 Hz), 118.8, 114.4, 113.9, 113.8, 61.8 (dd, 27.6 Hz, 25.1 Hz), 55.3; ¹⁹F NMR (471 MHz, CDCl₃) δ -102.5 (dd, 249.5 Hz, 8.6 Hz, 1F), -107.3 (dd, 249.5 Hz, 13.6 Hz, 1F); IR (KBr): 3417, 2960, 1607, 1510, 1451, 1246, 1173, 1026, 835, 727 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₃H₂₂F₂NO₂ 382.1619, found 382.1613.



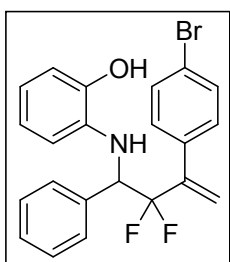
2-((3-(4-(tert-butyl)phenyl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3cd):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 89% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.41 - 7.19 (m, 9H), 6.65 (d, 3.8 Hz, 1H), 6.61 - 6.44 (m, 2H), 6.27 - 6.04 (m, 1H), 5.68 (s, 1H), 5.46 (s, 1H), 4.64 (dd, 13.7 Hz, 11.8 Hz, 1H), 1.33 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 151.4, 144.5, 143.0 (t, 22.3 Hz), 136.0, 134.7, 133.6, 128.6, 128.1, 128.0, 125.7, 125.3, 121.1, 121.0 (t, 249.5 Hz), 119.8 (t, 8.9 Hz), 118.9, 114.4, 114.2, 61.9 (dd, 30.3 Hz, 24.7 Hz), 34.6, 31.3; ¹⁹F NMR (471 MHz, CDCl₃) δ -101.8 (dd, 249.5 Hz, 9.1 Hz, 1F), -107.2 (dd, 249.5 Hz, 14.0 Hz, 1F); IR (KBr): 3419, 2962, 1610, 1510, 1452, 1267, 1173, 1030, 907, 732 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₆H₂₈F₂NO 408.2139, found 408.2134.



2-((3-(4-chlorophenyl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3ce):

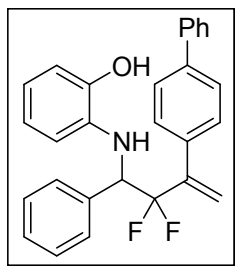
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 96% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.27 (s, 9H), 6.65 (d, 6.6 Hz, 1H), 6.58 (t, 6.2 Hz, 2H), 6.22 (d, 7.0 Hz, 1H), 5.75 (s, 1H), 5.45 (s, 1H), 4.56 (dd, 14.2 Hz, 11.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.3, 142.4 (t, 22.7 Hz), 135.7, 135.1, 134.5, 129.9, 128.9, 128.6, 128.5, 128.3, 128.2, 121.3, 120.8 (t, 250.2 Hz), 120.7 (t, 8.7 Hz), 118.8, 114.4, 114.1, 61.9 (dd, 28.1 Hz, 24.8 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -101.9 (dd, 250.9 Hz, 8.8 Hz, 1F), -107.8 (dd, 250.9 Hz, 14.6 Hz, 1F); IR (KBr): 3418, 2921, 1610, 1512, 1451, 1265, 1172, 1087, 834, 731 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{ClF}_2\text{NO}$ 386.1123, found 386.1118.



2-((3-(4-bromophenyl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3cf):

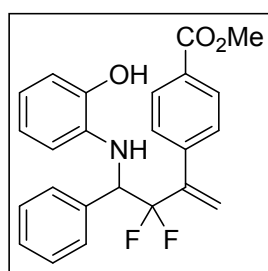
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 92% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, 8.4 Hz, 2H), 7.27 (s, 5H), 7.20 (d, 8.3 Hz, 2H), 6.66 (d, 7.1 Hz, 1H), 6.61 - 6.55 (m, 2H), 6.22 (d, 7.7 Hz, 1H), 5.76 (s, 1H), 5.46 (s, 1H), 4.56 (dd, 14.8 Hz, 11.0 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.2, 142.4 (t, 22.6 Hz), 135.7, 135.6, 134.5, 131.6, 130.2, 128.6, 128.3, 128.2, 122.8, 121.3, 120.8 (t, 8.6 Hz), 120.6 (t, 251.7 Hz), 119.1, 114.4, 114.1, 61.8 (dd, 28.1 Hz, 24.7 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -101.9 (dd, 251.0 Hz, 8.8 Hz, 1F), -107.8 (dd, 250.9 Hz, 14.7 Hz, 1F); IR (KBr): 3419, 1610, 1511, 1451, 1266,

1172, 1070, 1030, 906, 729 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{BrF}_2\text{NO}$ 430.0618, found 430.0613.



2-((3-([1,1'-biphenyl]-4-yl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3cg):

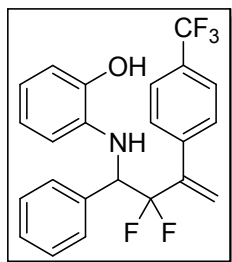
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 95% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.63 - 7.58 (m, 2H), 7.55 (d, 8.4 Hz, 2H), 7.44 (dd, 12.4 Hz, 7.8 Hz, 4H), 7.35 (dd, 10.5 Hz, 4.2 Hz, 1H), 7.33 - 7.23 (m, 5H), 6.73 - 6.62 (m, 1H), 6.57 (d, 3.9 Hz, 2H), 6.30 - 6.17 (m, 1H), 5.75 (s, 1H), 5.52 (s, 1H), 4.69 - 4.61 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.5, 142.9 (t, 22.4 Hz), 141.2, 140.4, 135.9, 135.6, 134.6, 128.9, 128.8, 128.6, 128.2, 127.6, 127.4, 127.1, 127.0, 121.3, 121.1 (t, 249.6 Hz), 120.3 (t, 8.7 Hz), 119.1, 114.5, 114.4, 62.0 (dd, 28.0 Hz, 24.8 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -102.0 (d, 250.2 Hz, 1F), -107.1 (dd, 250.1 Hz, 13.1 Hz, 1F); IR (KBr): 3418, 3031, 1610, 1512, 1450, 1265, 1172, 1031, 906, 721 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{28}\text{H}_{24}\text{F}_2\text{NO}$ 428.1826, found 428.1821.



methyl 4-(3,3-difluoro-4-((2-hydroxyphenyl)amino)-4-phenylbut-1-en-2-yl)benzoate (3ch):

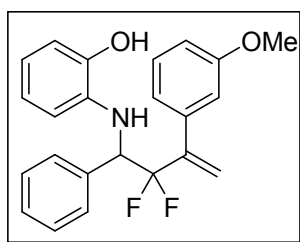
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 96% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, 8.3 Hz, 2H), 7.42 (d, 8.2 Hz, 2H), 7.27 - 7.25 (m, 5H), 6.68 (d, 6.5 Hz, 1H), 6.55 (t, 6.1 Hz, 2H), 6.18 (d,

6.9 Hz, 1H), 5.83 (s, 1H), 5.53 (s, 1H), 4.59 (dd, 14.8 Hz, 10.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.1, 144.2, 142.8 (t, 22.7 Hz), 141.4, 135.7, 134.7, 129.9, 129.7, 128.6, 128.5, 128.3, 128.2, 121.4 (t, 8.6 Hz), 121.1, 120.8 (t, 249.1 Hz), 118.7, 114.4, 113.4, 61.8 (t, 28.1 Hz), 52.3; ^{19}F NMR (471 MHz, CDCl_3) δ -101.1 (d, 251.5 Hz, 1F), -107.7 (dd, 251.5 Hz, 14.4 Hz, 1F); IR (KBr): 3417, 1699, 1609, 1513, 1437, 1276, 1180, 1034, 907, 727 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{22}\text{F}_2\text{NO}_3$ 410.1568, found 410.1562.



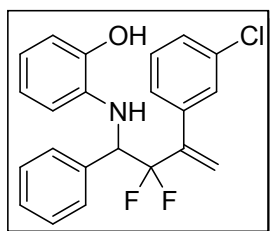
2-((2,2-difluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)amino)phenol (3ci):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 87% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, 8.1 Hz, 2H), 7.43 (d, 8.1 Hz, 2H), 7.27 (s, 5H), 6.66 (s, 1H), 6.61 - 6.50 (m, 2H), 6.21 (dd, 7.0 Hz, 2.0 Hz, 1H), 5.84 (s, 1H), 5.52 (s, 1H), 4.56 (dd, 15.2 Hz, 10.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.2, 142.6 (t, 22.8 Hz), 140.3, 135.6, 134.4, 130.5 (q, 32.6 Hz), 128.9, 128.6, 128.4, 128.3, 125.3 (q, 3.6 Hz), 124.0 (q, 294.3 Hz), 123.0, 121.7 (t, 8.6 Hz), 120.7 (t, 251.7 Hz), 119.2, 114.5, 114.1, 62.0 (dd, 28.2 Hz, 24.8 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -62.7 (s, 3F), -101.3 (dd, 251.7 Hz, 7.5 Hz, 1F), -107.7 (dd, 251.6 Hz, 14.9 Hz, 1F); IR (KBr): 3419, 1612, 1512, 1452, 1323, 1166, 1121, 1064, 848, 730 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{19}\text{F}_5\text{NO}$ 420.1387, found 420.1381.



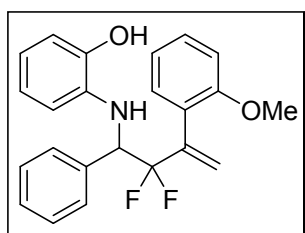
2-((2,2-difluoro-3-(3-methoxyphenyl)-1-phenylbut-3-en-1-yl)amino)phenol (3cj):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 95% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.33 - 7.19 (m, 6H), 6.95 (d, 7.6 Hz, 1H), 6.88 (dd, 11.6 Hz, 3.1 Hz, 2H), 6.64 (d, 6.3 Hz, 1H), 6.56 (s, 2H), 6.21 (d, 7.0 Hz, 1H), 5.75 (s, 1H), 5.48 (s, 1H), 4.66 - 4.53 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.4, 144.3, 143.2 (t, 22.2 Hz), 138.0, 135.9, 134.7, 129.4, 128.7, 128.3, 128.2, 121.3, 121.0, 120.9 (t, 245.3 Hz), 120.32 (t, 8.8 Hz), 119.0, 114.4, 114.3, 114.2, 113.9, 61.8 (dd, 28.0 Hz, 24.9 Hz), 55.2; ^{19}F NMR (471 MHz, CDCl_3) δ -101.3 (d, 250.1 Hz, 1F), -108.1 (dd, 250.2 Hz, 14.6 Hz, 1F); IR (KBr): 3417, 3033, 1598, 1512, 1451, 1234, 1170, 1031, 906, 721 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{F}_2\text{NO}_2$ 382.1619, found 382.1613.



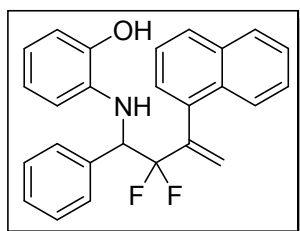
2-((3-(3-chlorophenyl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3ck):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 94% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.34 - 7.17 (m, 9H), 6.65 (d, 6.6 Hz, 1H), 6.58 (t, 6.6 Hz, 2H), 6.23 (d, 7.1 Hz, 1H), 5.77 (s, 1H), 5.47 (s, 1H), 4.58 (dd, 14.2 Hz, 11.4 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.2, 142.3 (t, 22.8 Hz), 138.4, 135.6, 134.5, 134.3, 129.6, 128.7, 128.6, 128.5, 128.4, 128.3, 126.6, 121.3, 121.2 (t, 8.7 Hz), 120.7 (t, 250.7 Hz), 119.1, 114.5, 114.1, 62.0 (t, 27.1 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -101.4 (dd, 251.3 Hz, 7.2 Hz, 1F), -107.5 (dd, 251.2 Hz, 14.5 Hz, 1F); IR (KBr): 3419, 3063, 1610, 1511, 1451, 1265, 1174, 1031, 906, 728 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{ClF}_2\text{NO}$ 386.1123, found 386.1118.



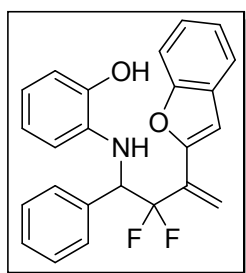
2-((2,2-difluoro-3-(2-methoxyphenyl)-1-phenylbut-3-en-1-yl)amino)phenol (3cl):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 95% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, 6.8 Hz, 2H), 7.32 - 7.22 (m, 4H), 7.18 (d, 7.5 Hz, 1H), 6.90 (td, 7.5, 0.7 Hz, 1H), 6.84 (d, 8.2 Hz, 1H), 6.68 (s, 1H), 6.58 (s, 2H), 6.27 (s, 1H), 5.92 (d, 1.9 Hz, 1H), 5.48 (s, 1H), 4.69 - 4.58 (m, 1H), 3.57 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 157.0, 144.9, 140.0 (t, 24.6 Hz), 136.0, 134.8, 131.1, 129.6, 128.9, 128.1 (2C), 125.7, 122.4 (t, 7.9 Hz), 121.2, 121.0 (t, 249.8 Hz), 120.3, 119.2, 114.6, 114.5, 110.9, 61.9 (dd, 29.6 Hz, 26.7 Hz), 55.3; ¹⁹F NMR (471 MHz, CDCl₃) δ -97.3 (d, 249.4 Hz, 1F), -110.6 (dd, 249.3 Hz, 18.2 Hz, 1F); IR (KBr): 3397, 3032, 1597, 1514, 1492, 1242, 1170, 1024, 907, 727 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₃H₂₂F₂NO₂ 382.1619, found 382.1613.



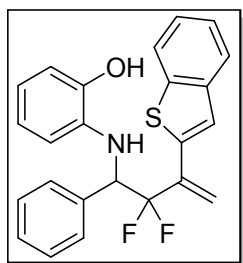
2-((2,2-difluoro-3-(naphthalen-1-yl)-1-phenylbut-3-en-1-yl)amino)phenol (3cm):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 95% yield as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, 8.4 Hz, 1H), 7.84 - 7.75 (m, 2H), 7.48 - 7.12 (m, 9H), 6.64 (s, 1H), 6.54 (s, 2H), 6.19 (d, 2.1 Hz, 1H), 6.14 (s, 1H), 5.54 (s, 1H), 4.60 (d, 19.2 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 143.8, 141.8 (t, 24.2 Hz), 135.6, 134.4, 134.2, 134.1, 133.6, 132.4, 128.8, 128.7, 128.2 (2C), 128.0, 127.1, 126.2, 125.9, 124.9, 122.8 (t, 8.1 Hz), 121.4, 120.6 (t, 250.8 Hz), 118.5, 114.4, 113.5, 61.0 (dd, 31.2 Hz, 24.3 Hz); IR (KBr): 3419, 3059, 1610, 1511, 1451, 1264, 1167, 1037, 906, 726 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₆H₂₂F₂NO 402.1669, found 402.1664.



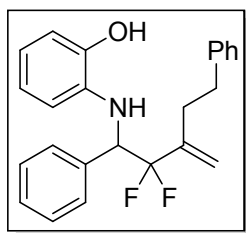
2-((3-(benzofuran-2-yl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3cn):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 93% yield as a brown solid. ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, 7.7 Hz, 1H), 7.44 (d, 8.2 Hz, 1H), 7.36 (d, 6.7 Hz, 2H), 7.31 - 7.25 (m, 4H), 7.21 (t, 7.5 Hz, 1H), 6.85 (s, 1H), 6.67 (d, 6.8 Hz, 1H), 6.61 (dd, 17.6 Hz, 7.5 Hz, 2H), 6.40 (d, 7.3 Hz, 1H), 6.11 (s, 1H), 5.58 (s, 1H), 4.99 (t, 12.4 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 154.5, 150.7, 144.6, 135.9, 134.8, 132.9 (t, 25.8 Hz), 128.6, 128.5 (2C), 128.4, 125.3, 123.1, 121.6, 121.3, 120.5 (t, 250.9 Hz), 119.3, 119.0 (t, 8.2 Hz), 114.6, 114.3, 111.1, 106.0 (t, 3.2 Hz), 63.1 (t, 26.0 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -104.8 (dd, 251.2 Hz, 11.4 Hz, 1F), -105.5 (dd, 251.2 Hz, 11.8 Hz, 1F); IR (KBr): 3272, 1614, 1593, 1515, 1450, 1254, 1164, 1032, 941, 742 cm⁻¹; mp = 140.6-141.5 °C; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₄H₂₀F₂NO₂ 392.1462, found 392.1457.



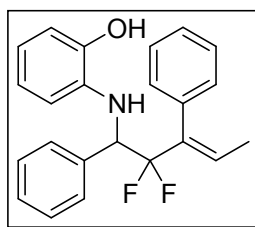
2-((3-(benzo[b]thiophen-2-yl)-2,2-difluoro-1-phenylbut-3-en-1-yl)amino)phenol (3co):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 92% yield as a brown solid. ¹H NMR (500 MHz, CDCl₃) δ 7.82 - 7.67 (m, 2H), 7.41 (s, 1H), 7.34 - 7.32 (m, 4H), 7.28 - 7.25 (m, 3H), 6.66 (dd, 6.8 Hz, 2.0 Hz, 1H), 6.60 - 6.55 (m, 8.1 Hz, 2H), 6.33 (dd, 7.1 Hz, 1.9 Hz, 1H), 5.72 (s, 1H), 5.59 (s, 1H), 4.92 (t, 12.6 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 144.5, 140.1, 139.3, 138.1, 136.6 (t, 24.6 Hz), 135.9, 134.7, 128.5, 128.4, 128.3, 125.2, 124.6, 124.1, 123.8, 122.0, 121.2, 120.9 (t, 8.5 Hz), 120.8 (t, 251.2 Hz), 119.2, 114.5, 114.4, 62.5 (t, 25.5 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -105.2 (d, 11.5 Hz, 2F); IR (KBr): 3305, 3061, 1614, 1515, 1452, 1249, 1165, 1104, 922, 788 cm⁻¹; mp = 108.2-108.9 °C; HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₄H₂₀F₂NOS 408.1234, found 408.1228.



2-((2,2-difluoro-3-methylene-1,5-diphenylpentyl)amino)phenol (3cp):

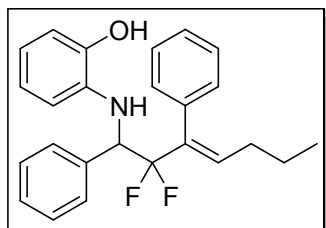
According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 90% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, 6.9 Hz, 2H), 7.35 - 7.28 (m, 3H), 7.28 - 7.21 (m, 2H), 7.17 (t, 7.3 Hz, 1H), 7.10 (d, 7.0 Hz, 2H), 6.73 - 6.64 (m, 2H), 6.61 (td, 7.5 Hz, 1.3 Hz, 1H), 6.43 (dd, 7.7 Hz, 1.2 Hz, 1H), 5.49 (s, 1H), 5.24 (s, 1H), 4.70 - 4.63 (m, 1H), 2.81 - 2.66 (m, 2H), 2.39 - 2.24 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.5, 142.7 (t, 22.9 Hz), 141.1, 136.1, 134.8, 128.6, 128.4 (3C), 128.3, 126.1, 121.6 (t, 248.0 Hz), 121.4, 119.2, 116.6 (t, 8.5 Hz), 114.5, 114.4, 62.6 (dd, 28.7 Hz, 26.0 Hz), 34.0, 32.4; ^{19}F NMR (471 MHz, CDCl_3) δ -104.6 (dd, 245.7 Hz, 9.8 Hz, 1F), -108.5 (dd, 245.7 Hz, 14.3 Hz, 1F); IR (KBr): 3541, 2932, 1610, 1515, 1450, 1267, 1144, 1107, 926, 743 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{F}_2\text{NO}$ 380.1826, found 380.1821.



(*E*)-2-((2,2-difluoro-1,3-diphenylpent-3-en-1-yl)amino)phenol (3cq):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 92% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.31 - 7.30 (m, 5H), 7.29 - 7.22 (m, 3H), 7.17 (s, 2H), 6.65 (d, 6.7 Hz, 1H), 6.56 (t, 7.6 Hz, 2H), 6.41 - 6.28 (m, 1H), 6.18 (d, 7.2 Hz, 1H), 4.44 (dd, 18.1 Hz, 7.5 Hz, 1H), 1.63 - 1.31 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.1, 136.1, 136.0 (t, 21.7 Hz), 134.8, 134.6, 130.2, 129.5 (t, 9.6 Hz), 128.8, 128.4, 128.2, 128.1, 127.9, 121.4, 121.0 (t, 249.5 Hz), 118.8, 114.5, 114.0, 61.5 (dd, 31.7 Hz, 25.1 Hz), 14.5; ^{19}F NMR (471 MHz, CDCl_3) δ -98.1 (d, 246.4 Hz, 1F), -112.0 (dd, 246.3 Hz, 17.8 Hz, 1F); IR (KBr): 3421, 2928, 1610,

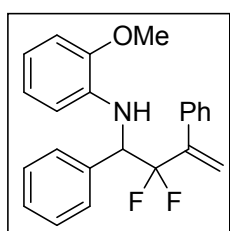
1512, 1453, 1268, 1167, 1035, 849, 697 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{F}_2\text{NO}$ 366.1669, found 366.1664.



(*E*)-2-((2,2-difluoro-1,3-diphenylhept-3-en-1-yl)amino)phenol (**3cr**):

According to the general procedure of the *gem*-difluoroallylboration of imines for the synthesis of racemic *gem*-difluorohomoallyl amines, the title compound was obtained in 90% yield as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.36 - 7.24 (m, 8H), 7.16 (d, 3.4 Hz, 2H), 6.66 (d, 6.3 Hz, 1H), 6.57 (t, 6.5 Hz, 2H), 6.24 (td, 7.5 Hz, 2.8 Hz, 1H), 6.19 (d, 6.9 Hz, 1H), 4.98 (s, 1H), 4.64 (s, 1H), 4.42 (dd, 17.6 Hz, 7.6 Hz, 1H), 1.90 - 1.84 (m, 2H), 1.41 - 1.28 (m, 2H), 0.79 (t, 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.1, 136.1, 135.2 - 134.7 (4C), 130.1, 128.8, 128.3, 128.2, 128.1, 127.8, 121.4, 120.9 (t, 246.8 Hz), 118.7, 114.4, 113.9, 61.4 (dd, 30.6 Hz, 24.9 Hz), 30.6, 22.3, 13.6; ^{19}F NMR (471 MHz, CDCl_3) δ -98.7 (d, 245.5 Hz, 1F), -111.6 (dd, 245.4 Hz, 17.3 Hz, 1F); IR (KBr): 3418, 1610, 1523, 1453, 1268, 1172, 1086, 1027, 848, 708 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{26}\text{F}_2\text{NO}$ 394.1982, found 394.1977.

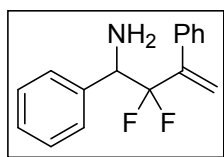
Deprotection of compound **3cb**



N-(2,2-difluoro-1,3-diphenylbut-3-en-1-yl)-2-methoxyaniline (**4**):

To a solution of compound **3cb** (175.7 mg, 0.5 mmol) in acetone (5 mL) was added K_2CO_3 (0.42 mg, 3.0 mmol) and CH_3I (0.14 mg, 1.0 mmol). The reaction mixture was stirred at rt until the complete consumption of compound **3cb** as indicated by TLC analysis (about 5 h), then the mixture was filtered through a short pad of celite and washed with CH_2Cl_2 . The filtrate was dried and concentrated under vacuum. The residue was purified by column chromatography (PE:EA = 5:1) to afford title

compound **4** (168.1 mg, 92% yield) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.41 - 7.17 (m, 10H), 6.72 - 6.70 (m, 1H), 6.63 - 6.48 (m, 2H), 6.11 (dd, 5.6 Hz, 3.7 Hz, 1H), 5.72 (s, 1H), 5.46 (s, 1H), 5.07 (d, 7.3 Hz, 1H), 4.74 - 4.59 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.9, 143.2 (t, 22.3 Hz), 136.7, 136.0, 135.9, 135.8, 128.6, 128.5, 128.4, 128.3, 128.1, 121.0, 120.9 (t, 250.2 Hz), 120.2 (t, 8.8 Hz), 117.2, 110.8, 109.5, 61.0 (dd, 28.5 Hz, 24.6 Hz), 55.5; ^{19}F NMR (471 MHz, CDCl_3) δ -101.3 (dd, 249.7 Hz, 9.5 Hz), -108.1 (dd, 249.7 Hz, 14.9 Hz); IR (KBr): 3419, 3061, 2939, 1601, 1511, 1456, 1247, 1221, 1025, 1731, 696 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{F}_2\text{NO}$ 366.1669, found 366.1664.



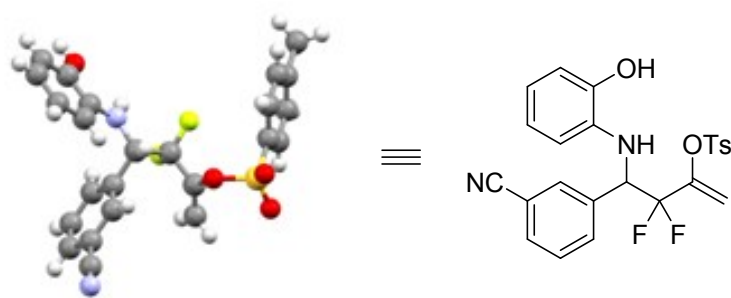
2,2-difluoro-1,3-diphenylbut-3-en-1-amine (**5**):

To a solution of **4** (73.1 mg, 0.2 mmol) in MeCN/ H_2O (4 mL, 1:1) was added trichloroisocyanuric acid (TCCA) (47.3 mg, 0.1 mmol) and 1 M aqueous H_2SO_4 (0.2 mL). The mixture was stirred at rt for 16 h, then washed with CH_2Cl_2 (3×8 mL). The resulting aqueous phase was subsequently brought to basic (pH = 10.5) through the addition of 5.0 M of aqueous KOH, and extracted with EtOAc (3×10 mL). Then the organic layer was concentrated under vacuum to afford title compound **5** (21.7 mg, 42% yield) as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.70 - 6.85 (m, 10H), 5.63 (s, 1H), 5.42 (s, 1H), 4.15 (t, 13.0 Hz, 1H), 1.78 (br, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.2 (t, 22.6 Hz), 137.5, 137.4, 136.8, 128.4, 128.3 (2C), 128.2, 128.1, 121.4 (t, 248.7 Hz), 120.2 (t, 8.9 Hz), 59.3 (t, 26.2 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -105.0 (dd, 245.2 Hz, 11.4 Hz), -107.9 (dd, 245.3 Hz, 13.7 Hz); IR (KBr): 3390, 3032, 1493, 1160, 1022, 718, 695 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{N}$ 260.1251, found 260.1245.

References

- [1] B. Zhang and X. Zhang, *Chin. J. Chem.*, 2016, **34**, 477–480.
- [2] T. M. Gøgsig, L. S. Søbjerg, A. T. Lindhardt, K. L. Jensen and T. Skrydstrup, *J. Org. Chem.*, 2008, **73**, 3404–3410.
- [3] Y. Liu, Y.-H. Zhou, Y.-L. Zhao and J.-P. Qu, *Org. Lett.*, 2017, **19**, 946–949.

X-ray structure of 3na



CCDC 1831916

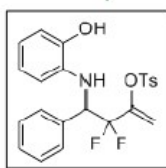
Crystal data for compound 8

Identification code	T
Empirical formula	C ₂₄ H ₂₀ F ₂ N ₂ O ₄ S
Formula weight	470.48
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	$a = 10.457(6)$ Å $b = 18.104(11)$ Å $c = 11.424(7)$ Å
	$a = 90^\circ$ $b = 98.239(11)^\circ$ $g = 90^\circ$
Volume	$2140(2)$ Å ³
Z	4
Density (calculated)	1.460 Mg/m ³
Absorption coefficient	0.204 mm ⁻¹
F(000)	976
Crystal size	$0.130 \times 0.120 \times 0.100$ mm ³
Theta range for data collection	1.968 to 24.998°
Index ranges	$-12 \leq h \leq 12$, $-21 \leq k \leq 21$, $-13 \leq l \leq 13$
Reflections collected	14986
Independent reflections	3768 [R(int) = 0.1128]
Completeness to theta = 24.998°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²

Data / restraints / parameters	3768 / 0 / 299
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0596$, $wR_2 = 0.1309$
R indices (all data)	$R_1 = 0.0969$, $wR_2 = 0.1482$
Extinction coefficient	n/a
Largest diff. peak and hole	0.372 and -0.373 e.Å ⁻³

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

table2
YX-1-50-H



^1H NMR (CDCl_3 , 500 MHz)

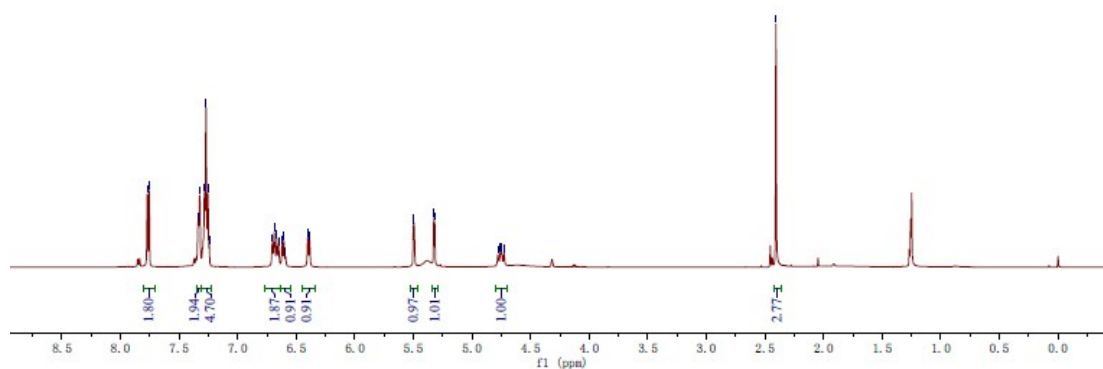
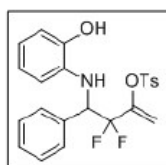


table2
YX-1-50-H



^{13}C NMR (CDCl_3 , 126 MHz)

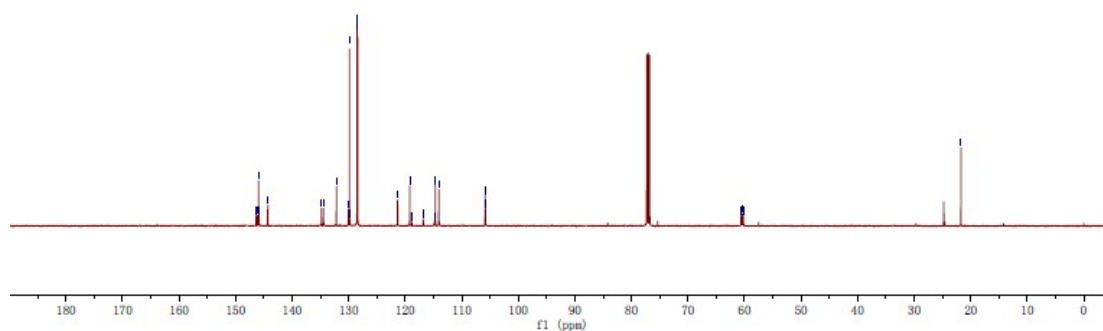
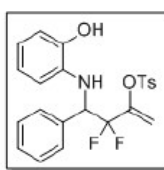


table2
YX-1-50-H



^{19}F NMR (CDCl_3 , 471 MHz)

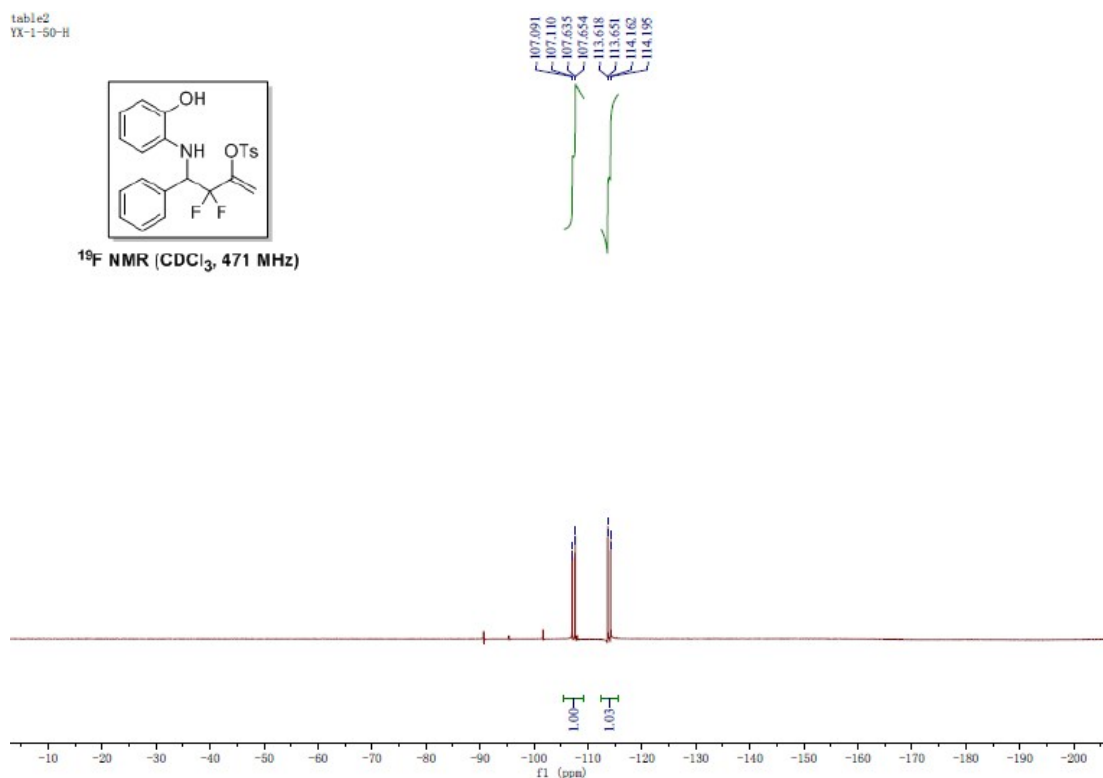
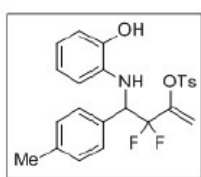


table2
YX-2-1-H



^1H NMR (CDCl_3 , 500 MHz)

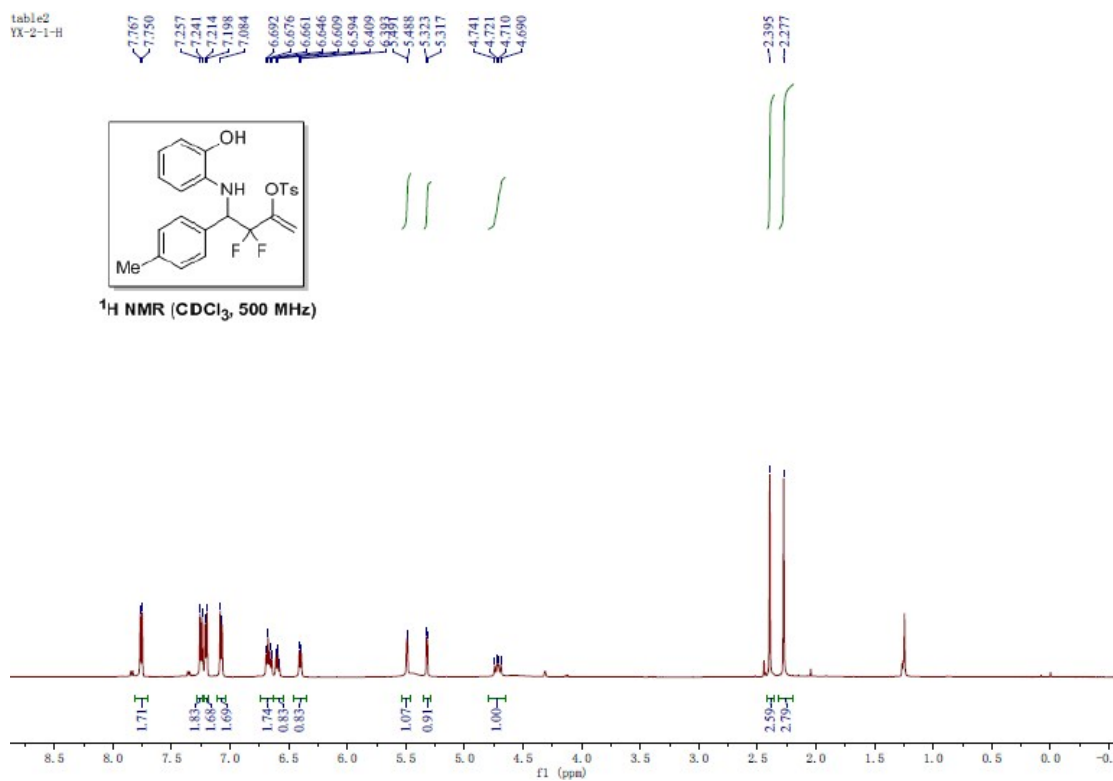
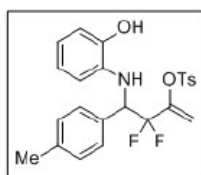


table2
YX-2-1-C

146.447
146.208
146.182
145.943
145.892
144.354
138.259
129.851
129.149
128.491
128.284
121.303
119.151
116.860
114.641
108.493
108.399
105.762

60.328
60.137
60.106
59.917

21.711
21.116



¹³C NMR (CDCl₃, 126 MHz)

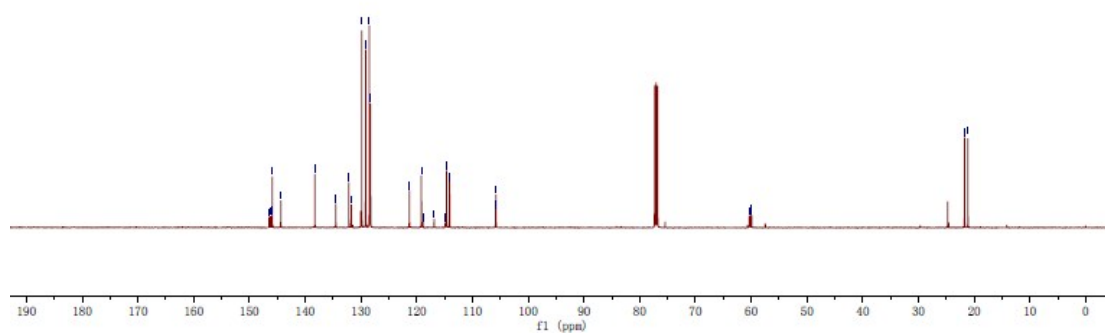
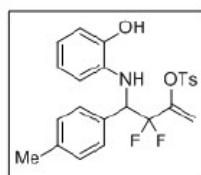


table2
YX-2-1-F



¹⁹F NMR (CDCl₃, 471 MHz)

107.078
107.097
107.621
107.641
113.644
113.677
114.187
114.220

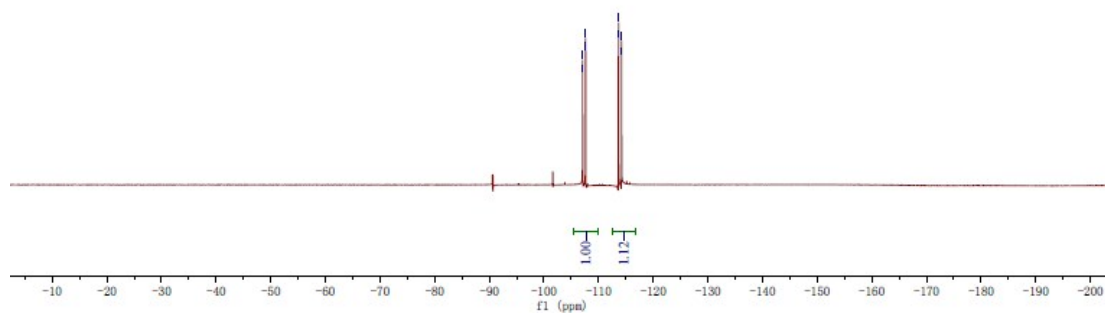


table2
YX-2-2-H

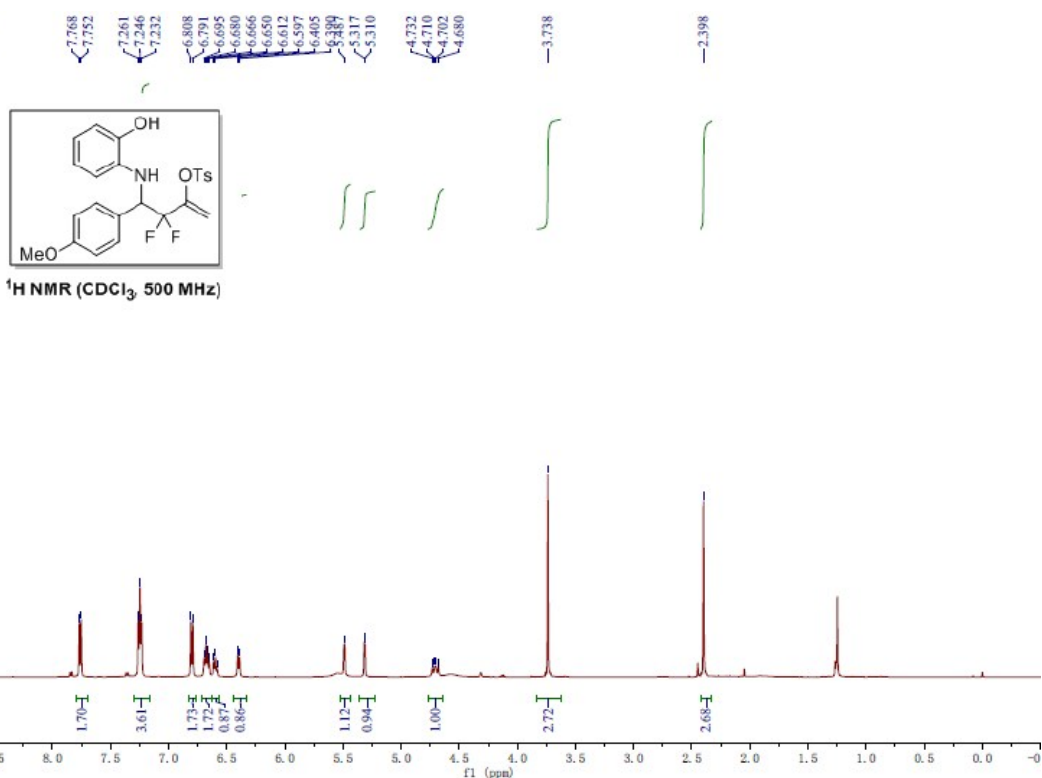


table2
YX-2-2-C

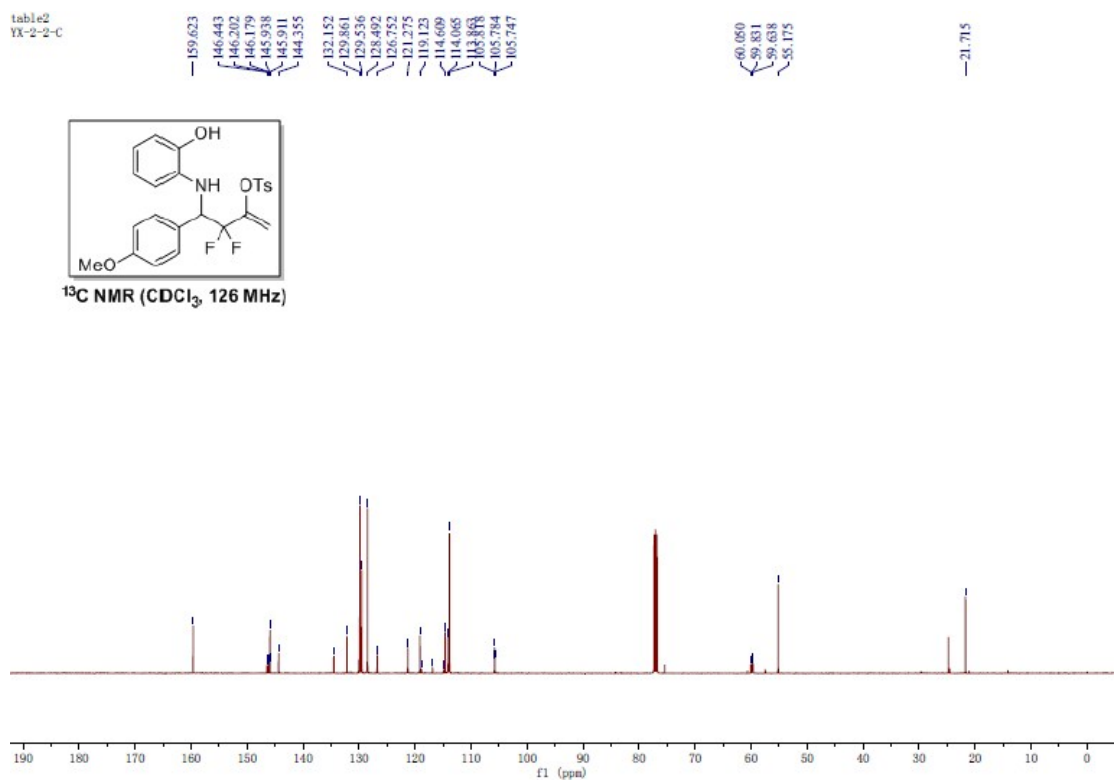
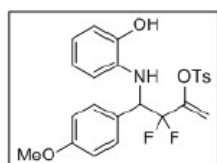


table2
YX-2-2-F



^{19}F NMR (CDCl_3 , 471 MHz)

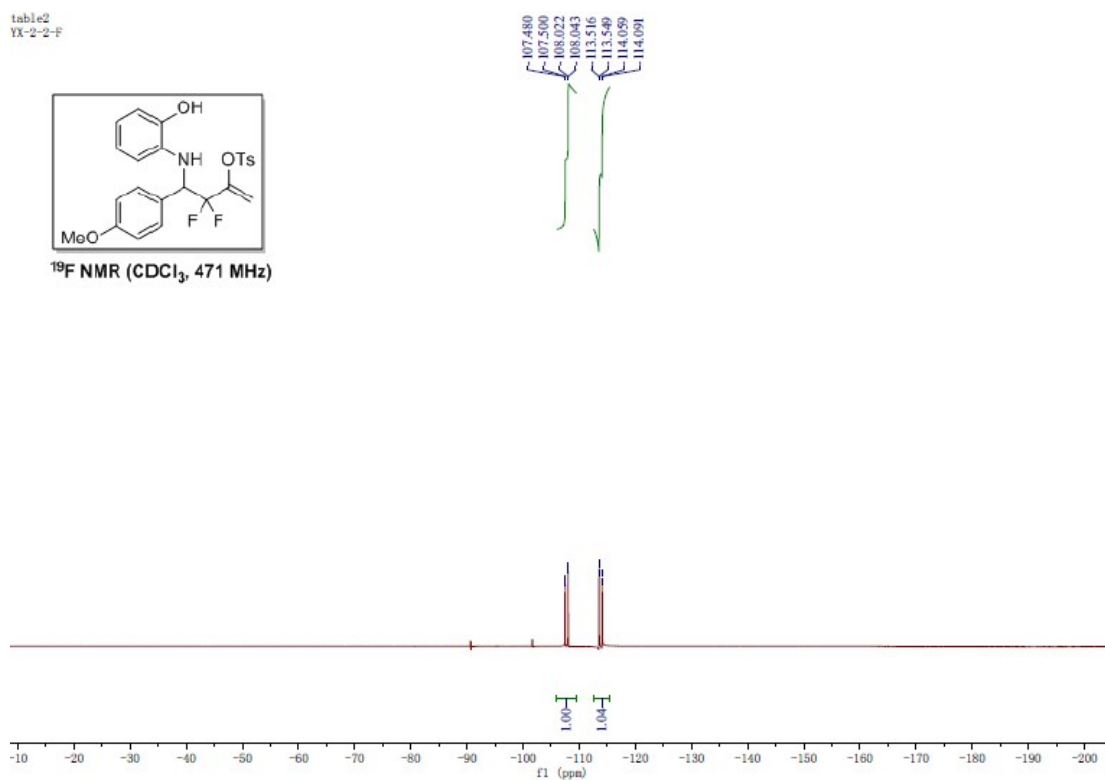
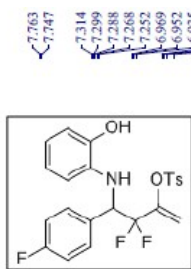


table2
YX-2-3-H



^1H NMR (CDCl_3 , 500 MHz)

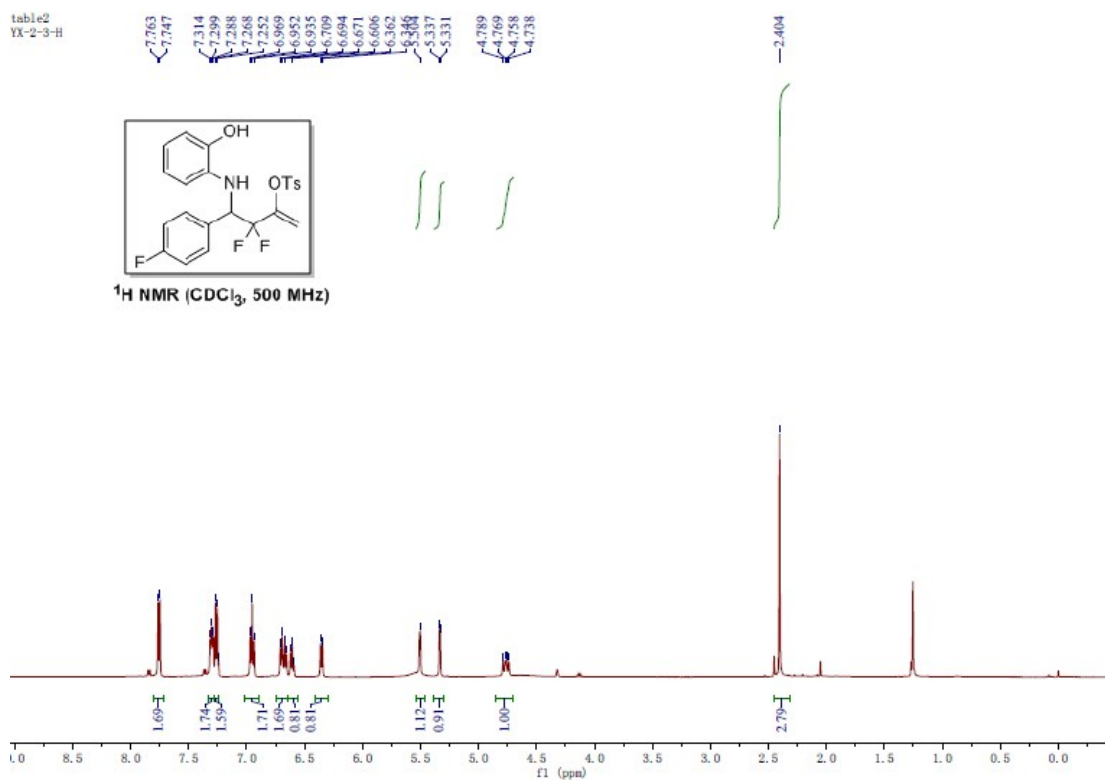
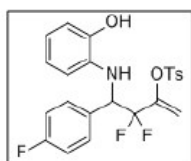


table2
YX-2-3-C

163.761
161.797
146.187
146.032
145.950
145.922
145.685
144.142
132.062
130.151
130.085
129.992
128.485
119.175
115.491
115.319
114.689
113.993
113.929
113.892

59.893
59.702
59.670
59.478

21.719



¹³C NMR (CDCl₃, 126 MHz)

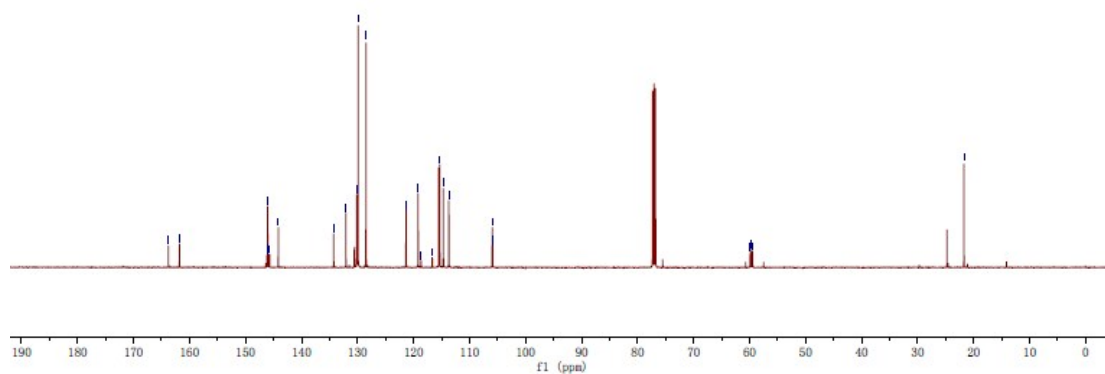
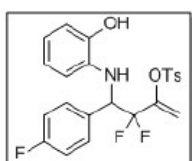


table2
YX-2-3-F

106.943
106.963
107.488
107.508
113.406
113.418
113.425
113.435
113.445
113.452
113.464
113.997
114.030
114.541
114.574



¹⁹F NMR (CDCl₃, 471 MHz)

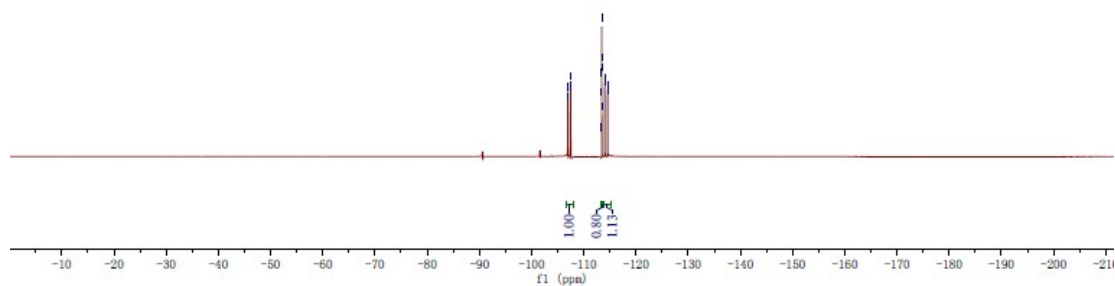
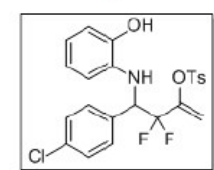


table2
YX-2-4-H



¹H NMR (CDCl₃, 500 MHz)

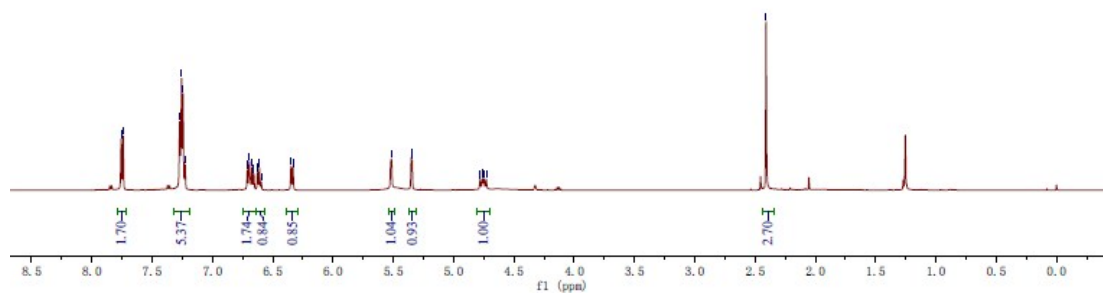
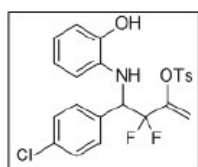


table2
YX-2-4-C



¹³C NMR (CDCl₃, 126 MHz)

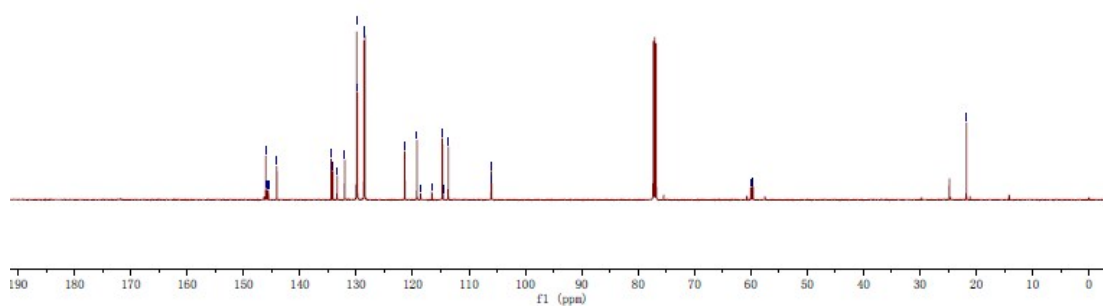
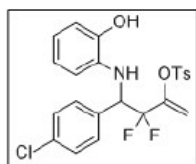


table2
YX-2-4-F



^{19}F NMR (CDCl_3 , 471 MHz)

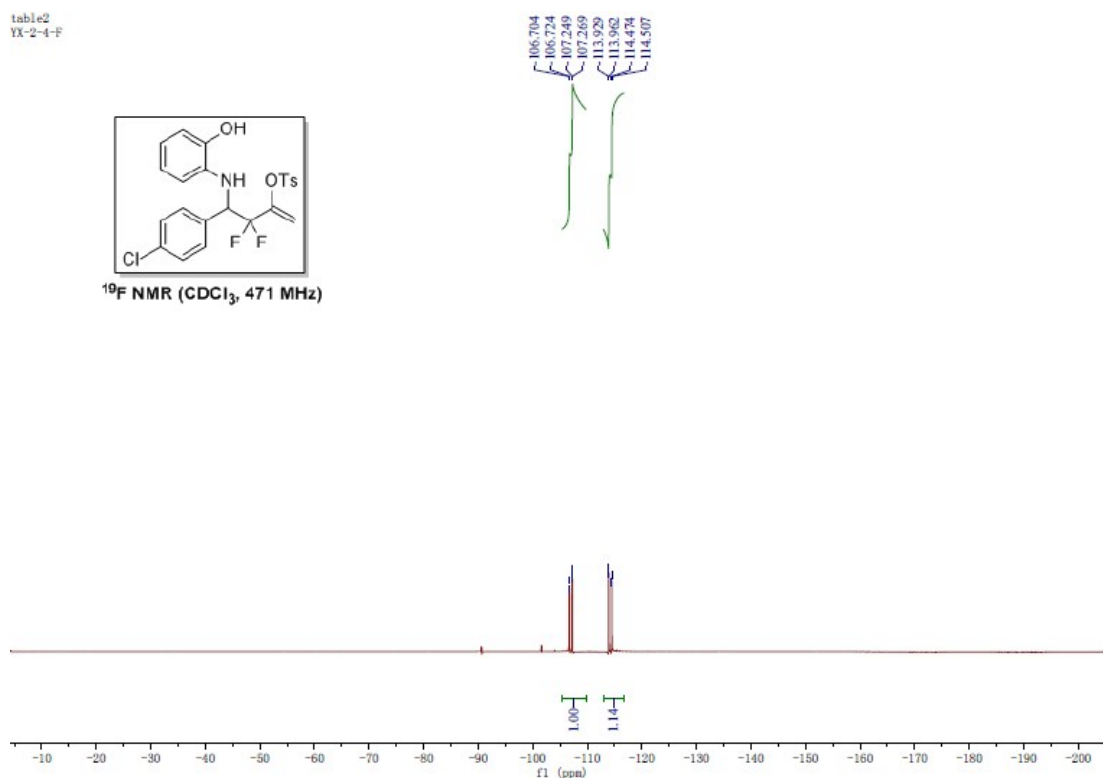
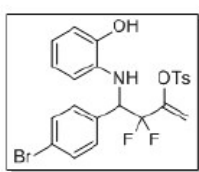


table2
YX-2-5-H



^1H NMR (CDCl_3 , 500 MHz)

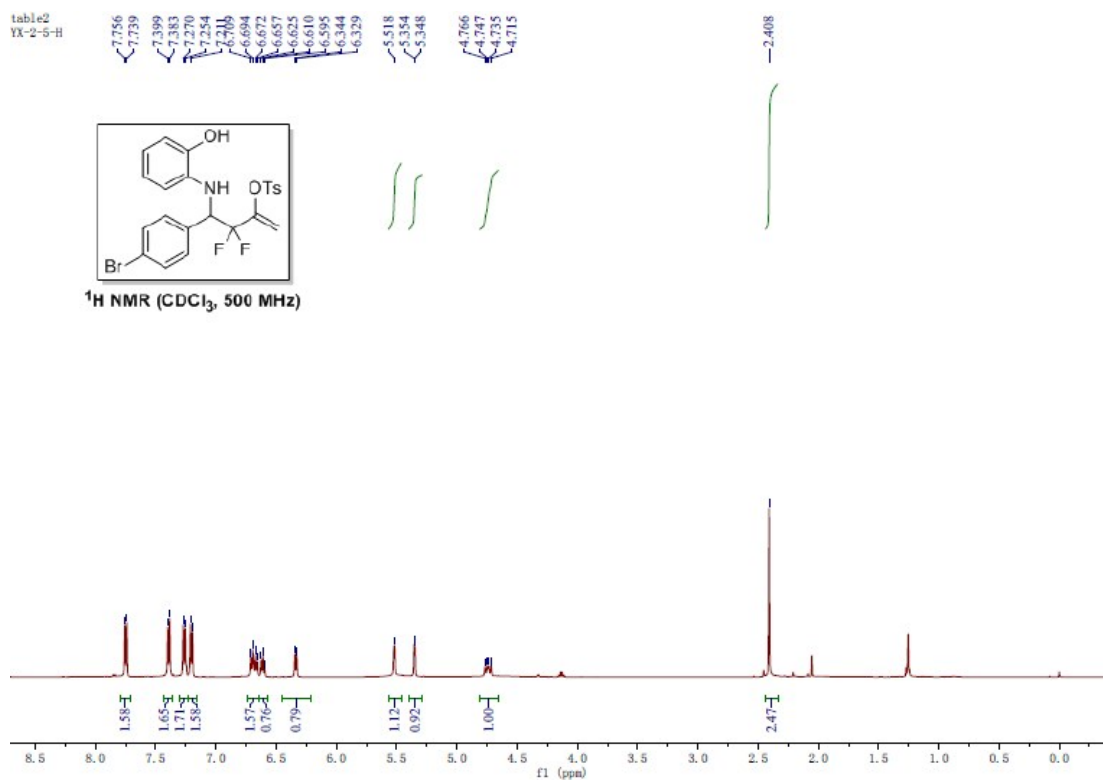
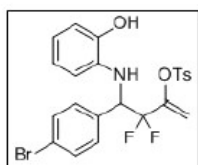


table2
YX-2-S-C

146.033
145.804
145.776
145.539
144.068
131.582
130.119
129.903
128.463
122.651
121.379
119.229
114.709
113.631
106.040
106.003

60.053
59.861
59.829
59.637

21.740



¹³C NMR (CDCl₃, 126 MHz)

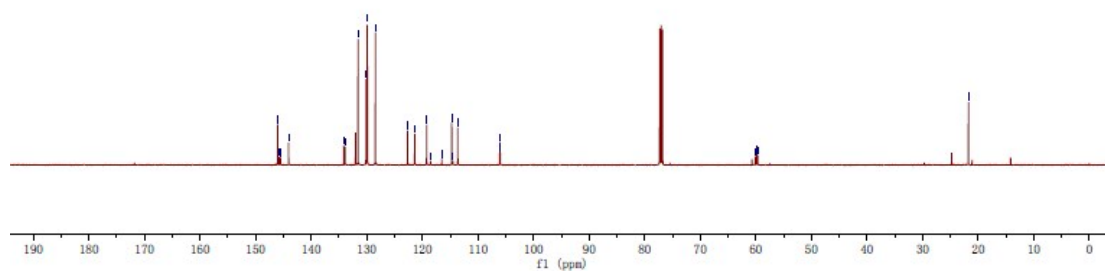
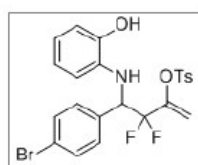


table2
YX-2-S-F

106.623
106.643
107.168
107.188
113.942
113.976
114.487
114.521



¹⁹F NMR (CDCl₃, 471 MHz)

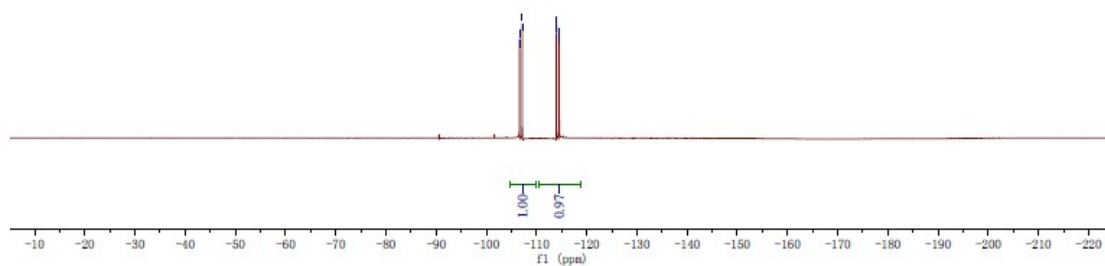
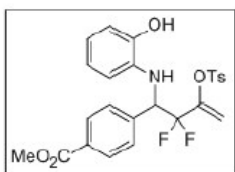


table2
YX-2-6-H



¹H NMR (CDCl₃, 500 MHz)

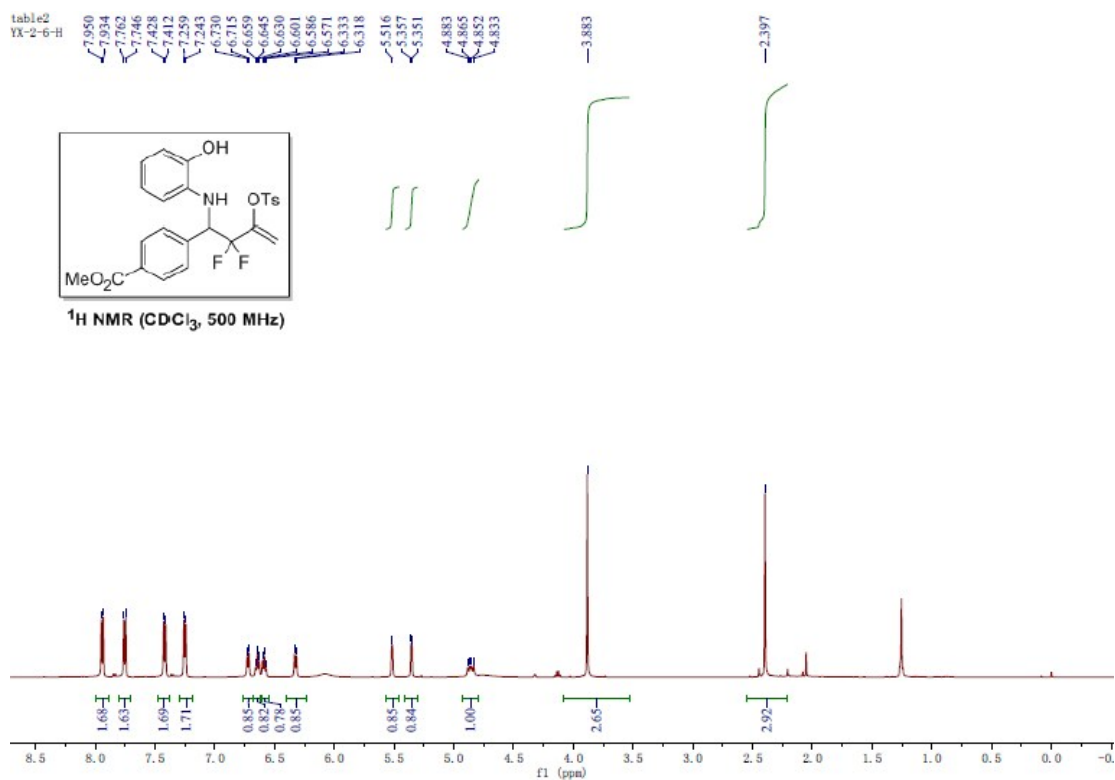
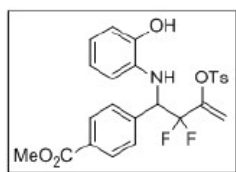


table2
YX-2-6-C



¹³C NMR (CDCl₃, 126 MHz)

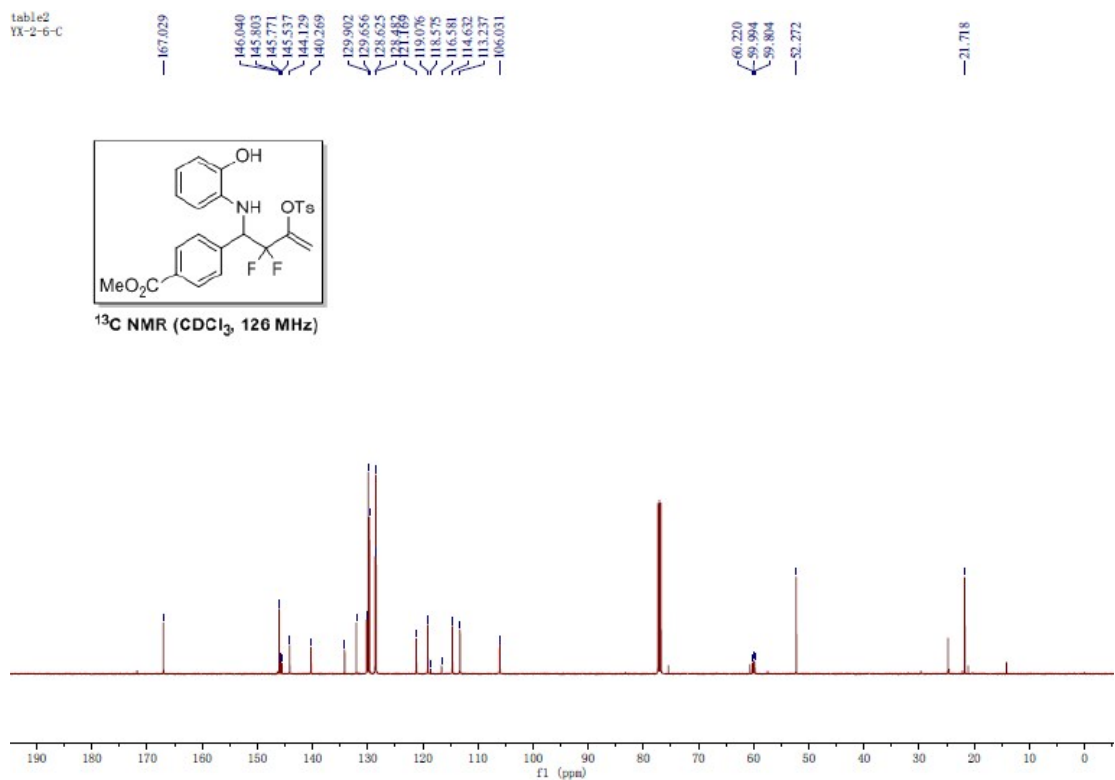
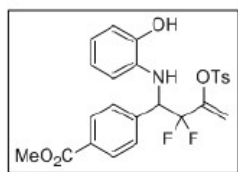


table2
YX-2-6-F



^{19}F NMR (CDCl_3 , 471 MHz)

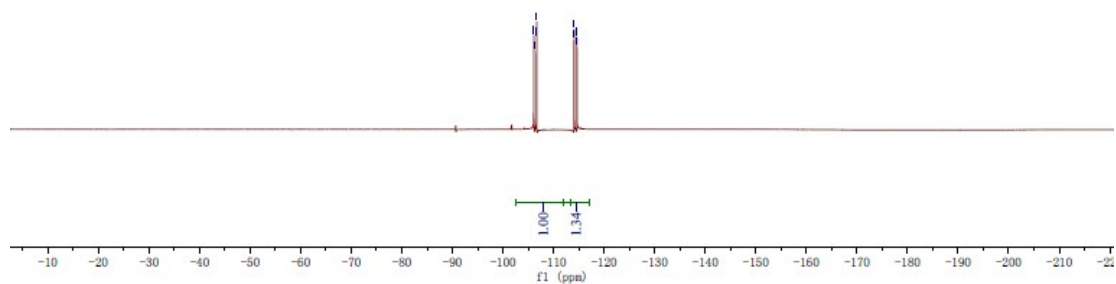
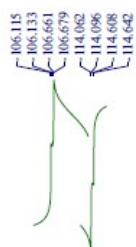
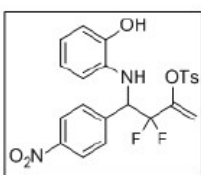


table2
YX-2-7-H



^1H NMR (CDCl_3 , 500 MHz)

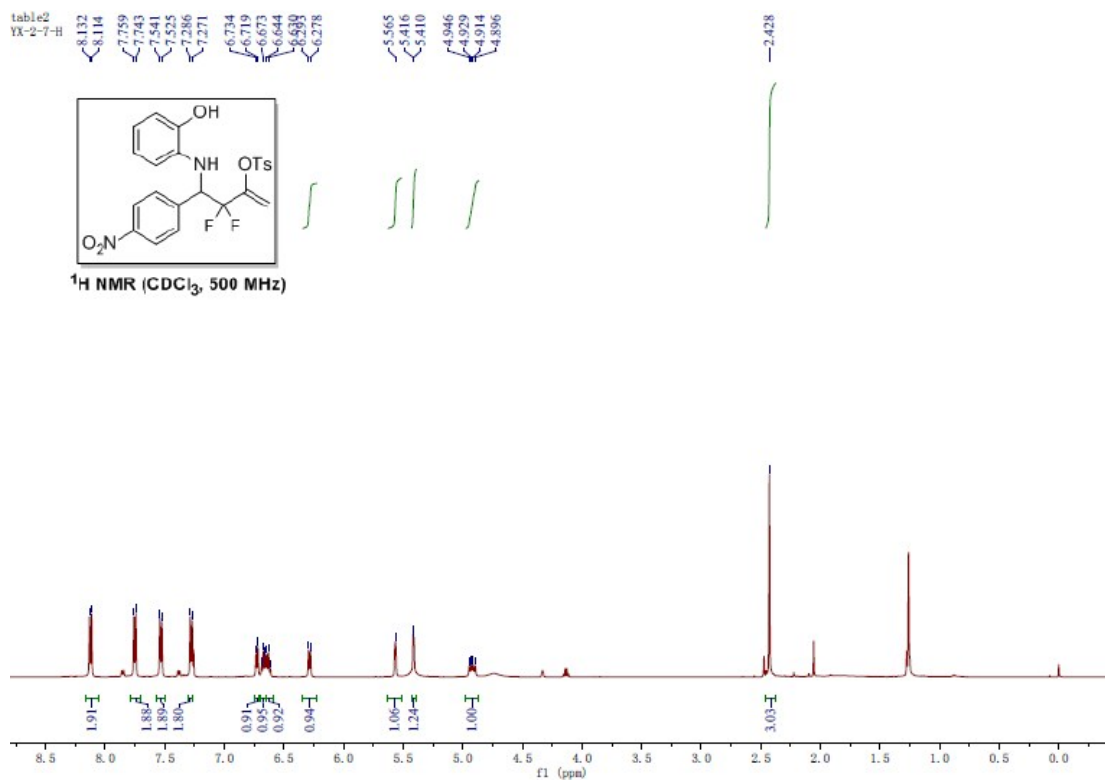
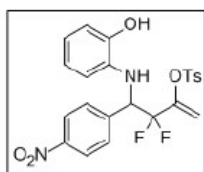


table2
YX-2-7-C

148.068
146.189
145.673
145.441
145.407
145.175
143.875
142.407
133.766
131.995
129.944
129.527
128.473
123.546
121.491
119.446
114.844
106.269

61.082
59.890
59.852
59.661

21.756



¹³C NMR (CDCl₃, 126 MHz)

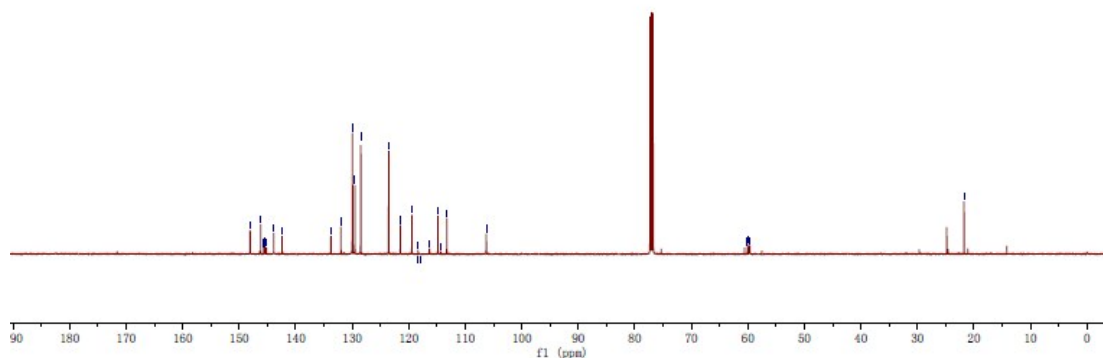
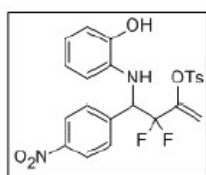
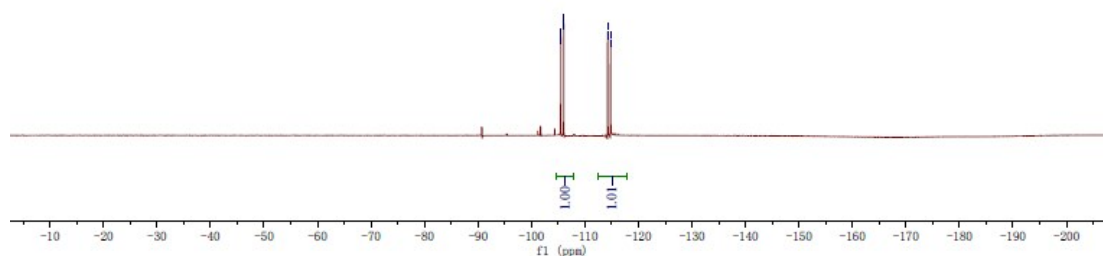


table2
YX-2-7-F



¹⁹F NMR (CDCl₃, 471 MHz)

105.489
105.506
106.037
106.054
114.235
114.269
114.733
114.817



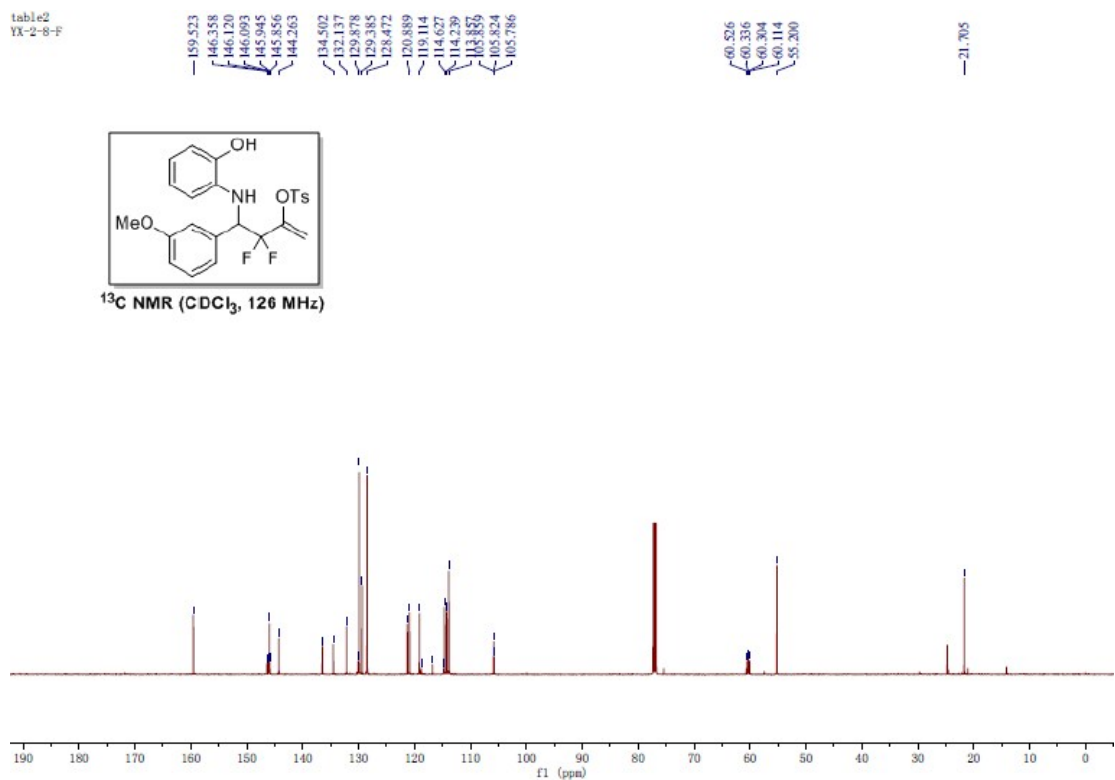
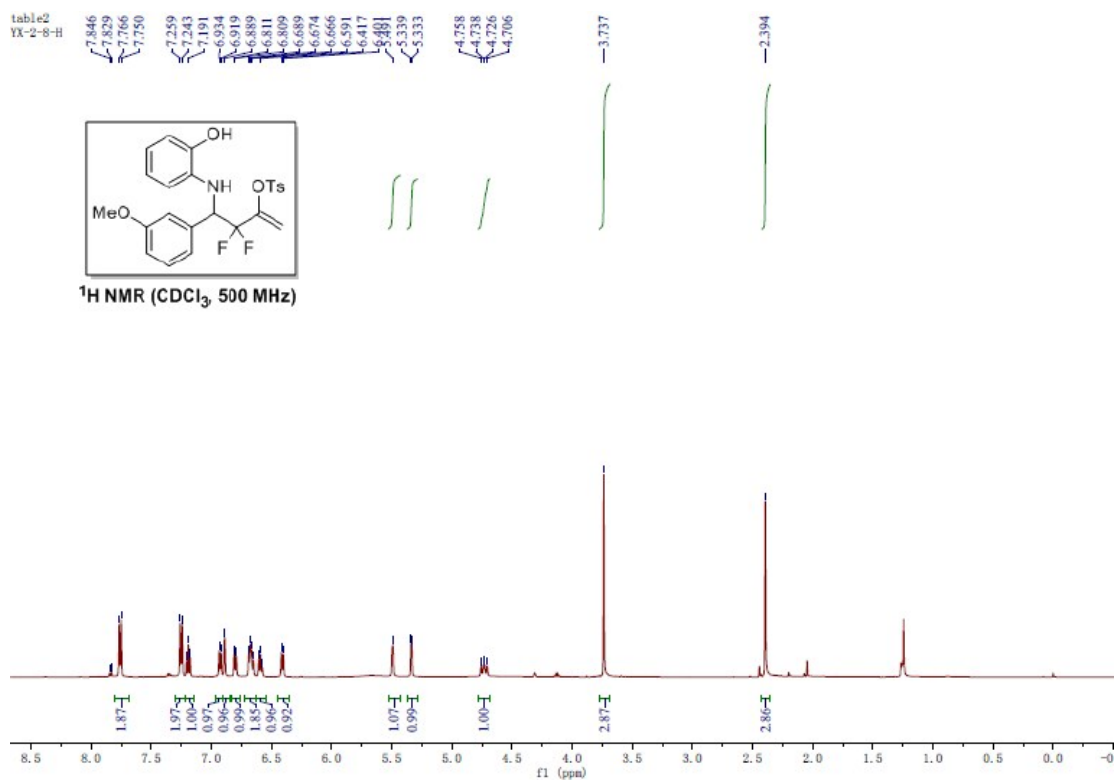
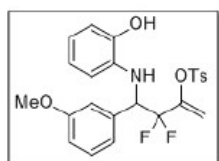


table2
YX-2-8-F



^{19}F NMR (CDCl_3 , 471 MHz)

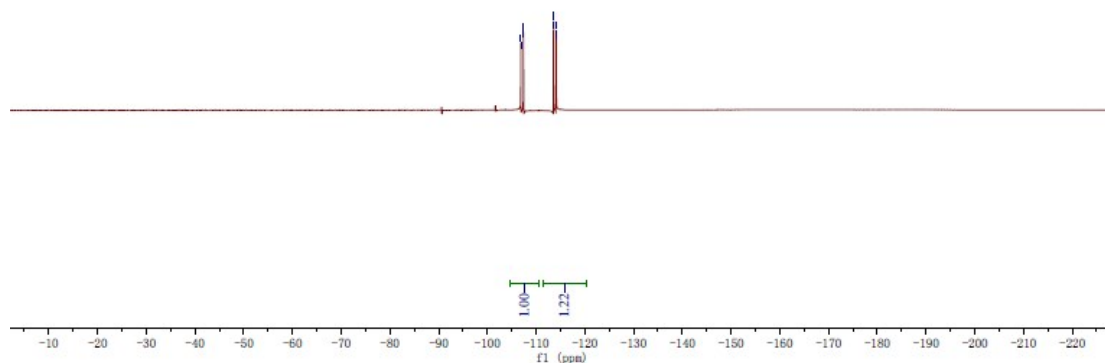
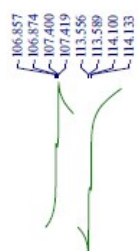
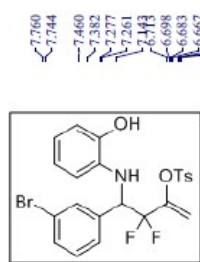


table2
YX-2-10-H



^1H NMR (CDCl_3 , 500 MHz)

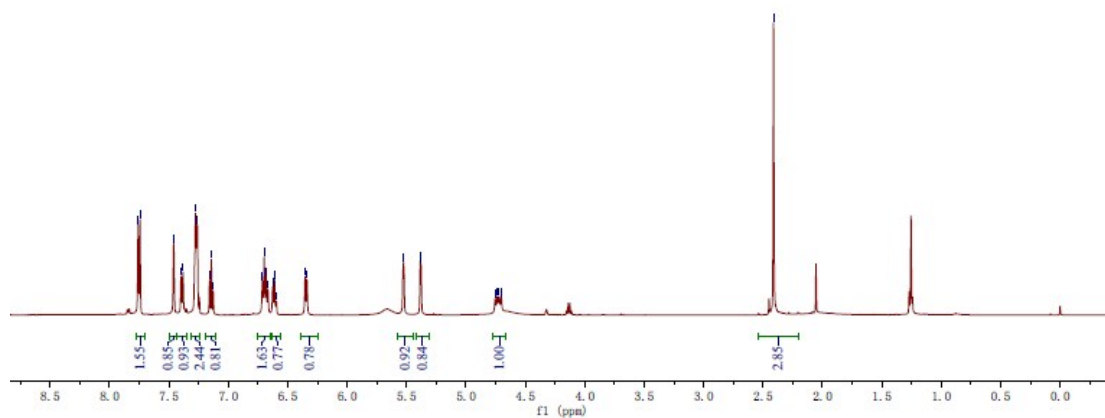
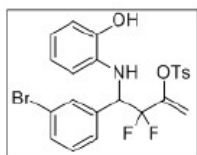


table2
YX-2-10-C

146.054
146.016
145.783
145.747
145.514
143.975
131.692
131.467
129.956
129.928
128.446
127.117
122.516
119.130
114.708
113.323
113.228
106.189
106.162

59.901
59.711
59.673
59.483

21.752



¹³C NMR (CDCl₃, 125 MHz)

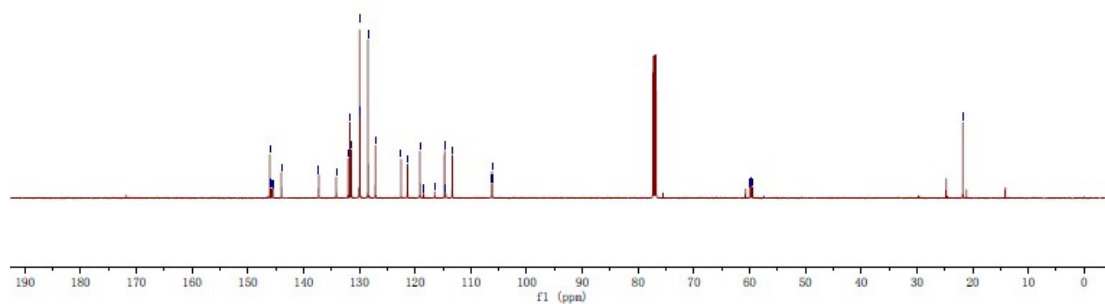
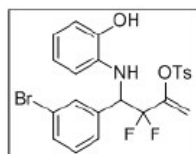
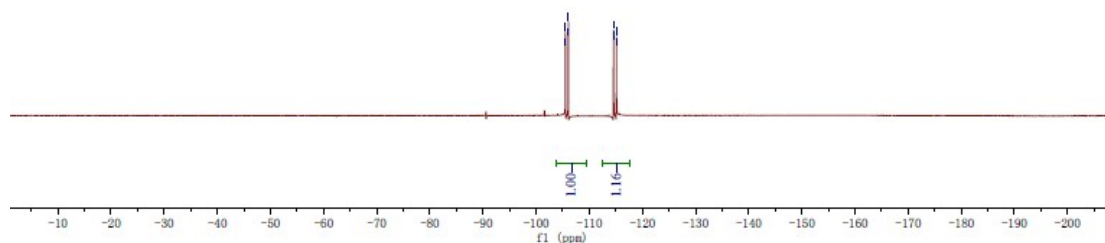


table2
YX-2-10-F



¹⁹F NMR (CDCl₃, 471 MHz)

105.513
105.530
106.060
106.077
114.549
114.583
115.095
115.130



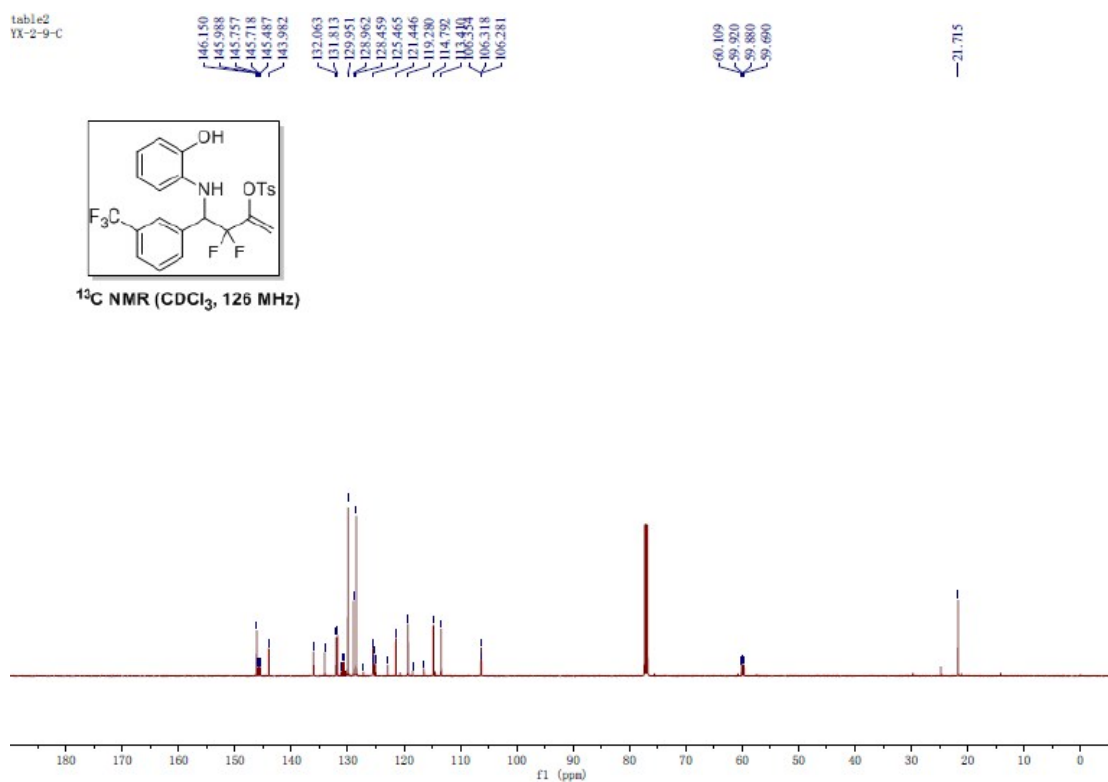
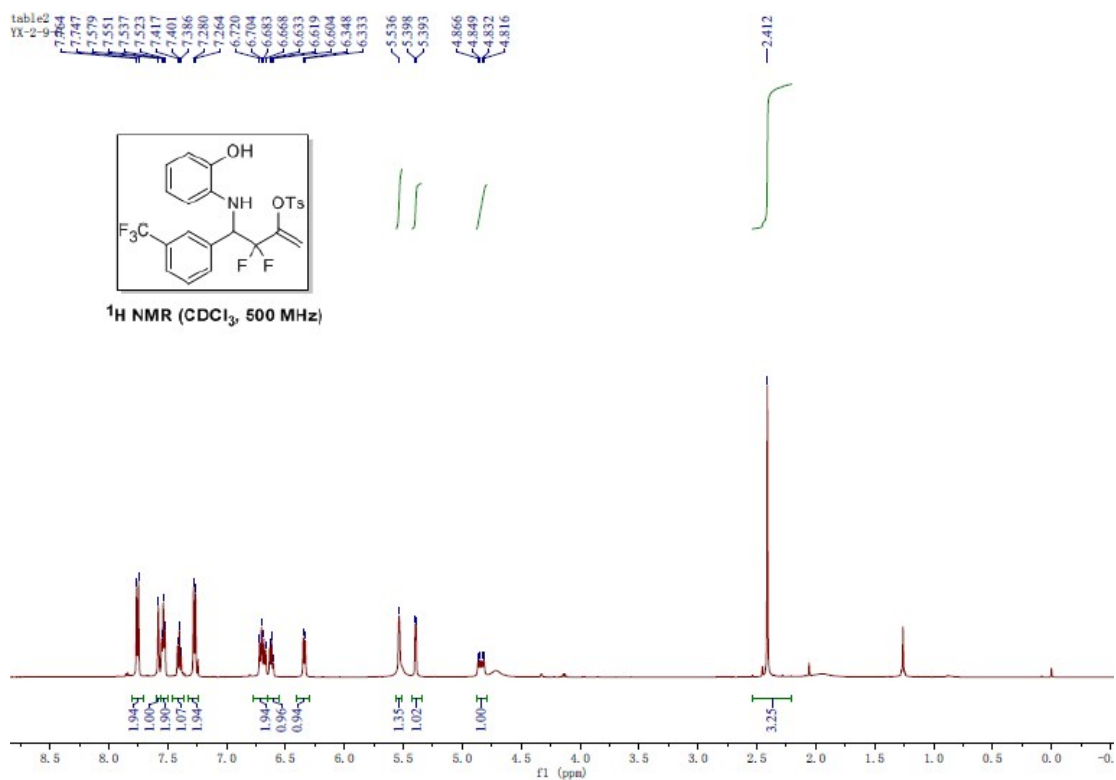
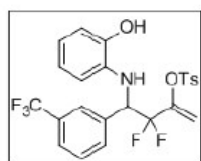


table2
YX-2-9-F



¹⁹F NMR (CDCl₃, 471 MHz)

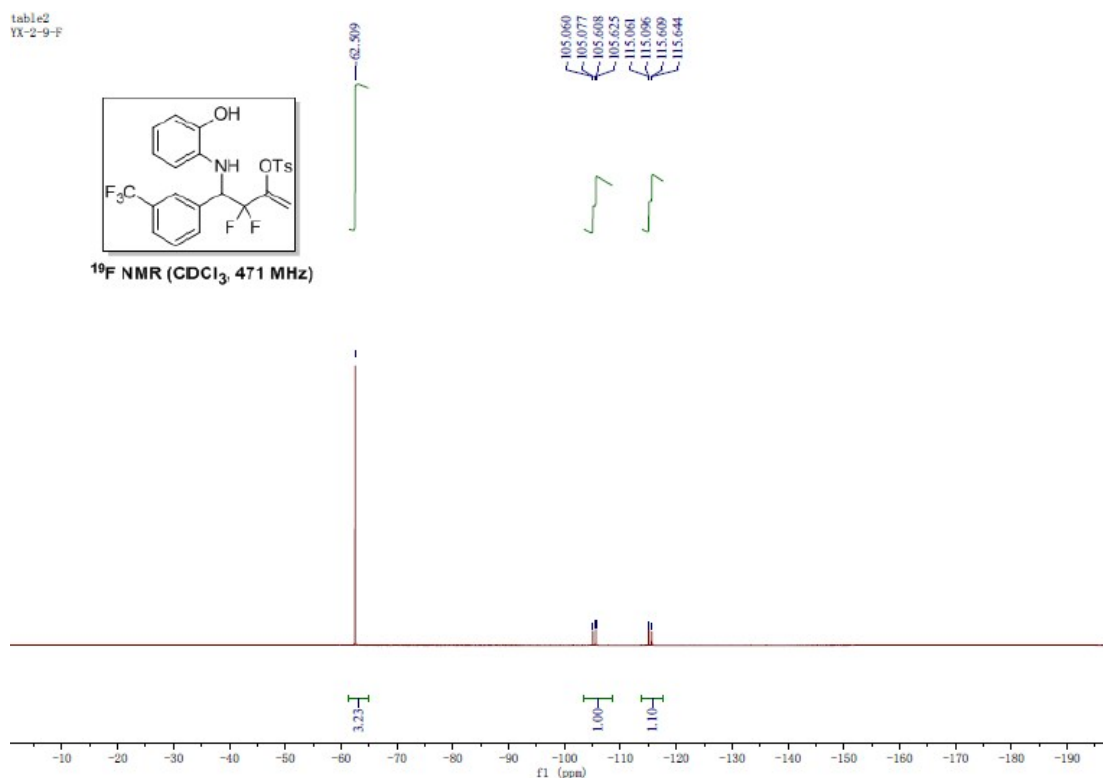
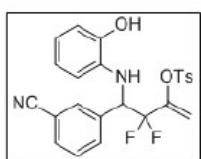


table2
YX-2-11-H



¹H NMR (DMSO-d₆, 500 MHz)

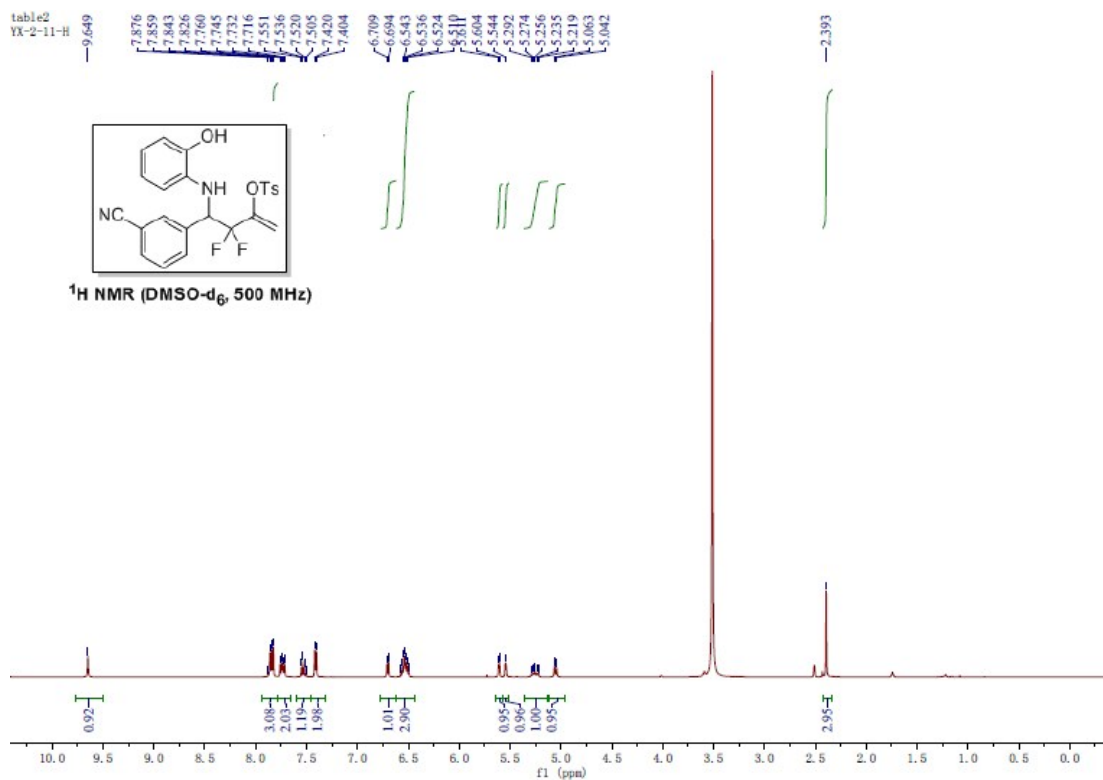
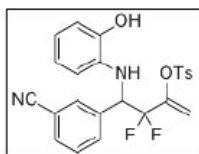


table2
YX-2-11-C

146.713
145.974
145.749
145.482
145.212
134.164
132.649
131.664
130.646
130.032
128.989
119.086
119.007
118.832
117.119
115.125
114.601
112.741
111.730
107.306

58.457
58.274
58.218
58.034

21.658



¹³C NMR (DMSO-d₆, 126 MHz)

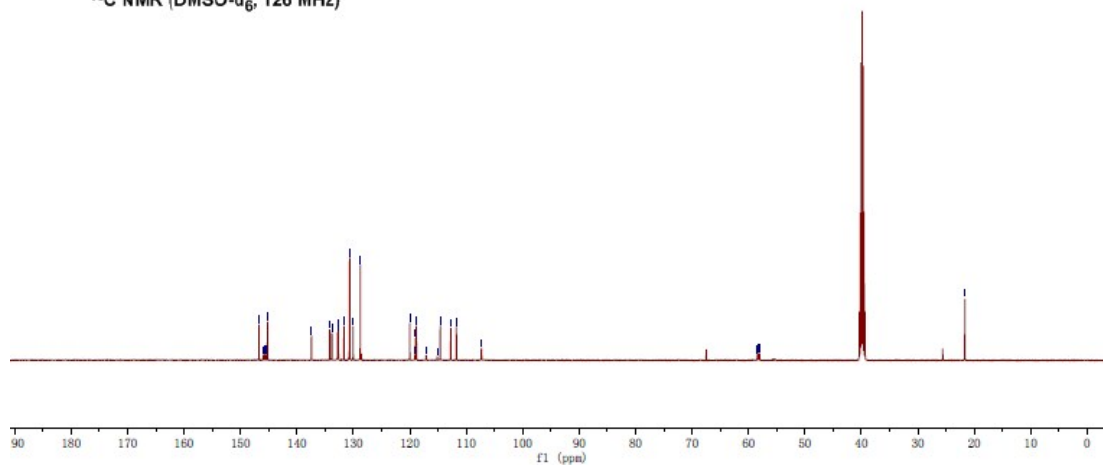
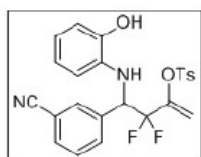


table2
YX-2-11-F



¹⁹F NMR (DMSO-d₆, 471 MHz)

101.453
102.000
114.463
114.504
115.009
115.051

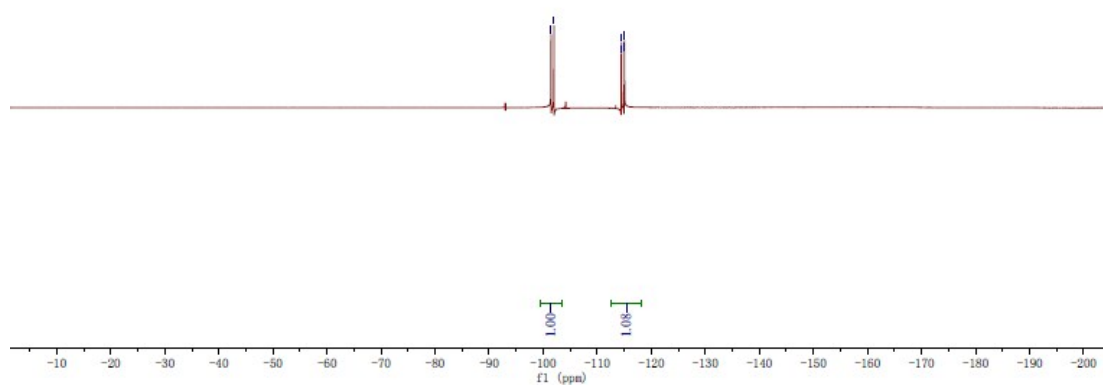
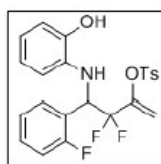


table2
YX-2-13-H

7.783
7.767
7.351
7.267
7.251
7.049
7.033
6.695
6.688
6.682
6.617
6.602
6.460
6.445
5.866
5.433
5.251
5.236
5.214
5.200



¹H NMR (CDCl₃, 500 MHz)

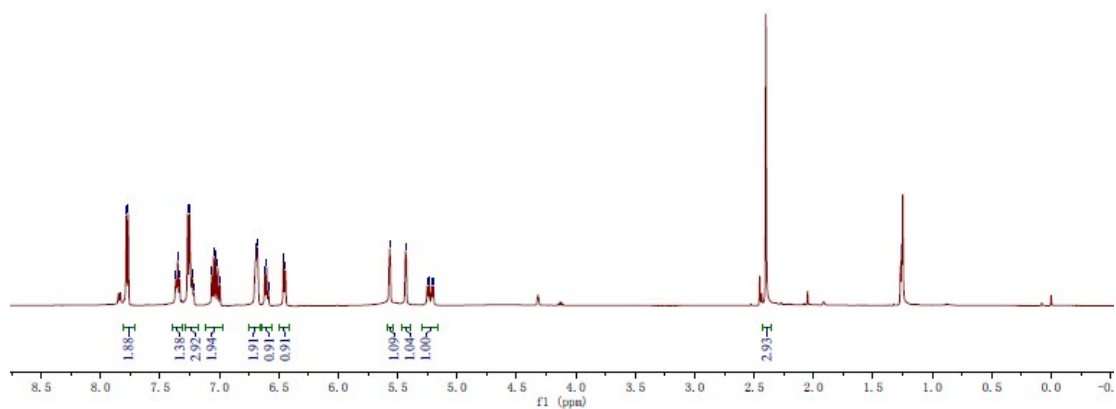
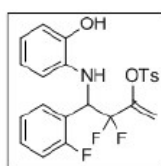


table2
YX-2-13-C

162.402
160.434
146.268
145.880
144.166
132.143
130.207
130.140
129.842
128.470
124.336
124.309
121.407
119.256
105.170
105.135
106.098



¹³C NMR (CDCl₃, 126 MHz)

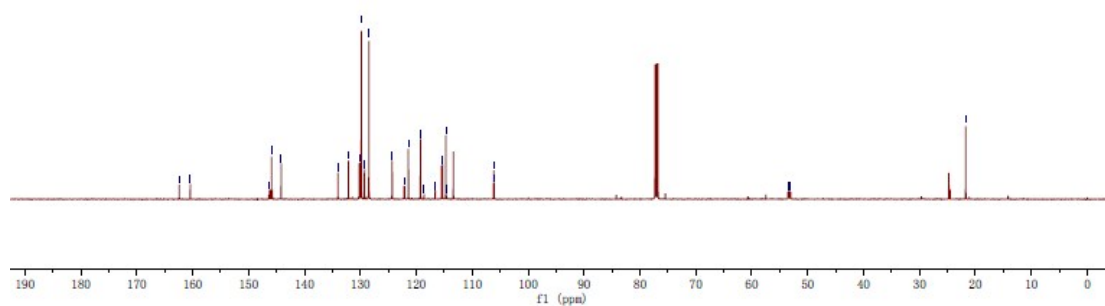
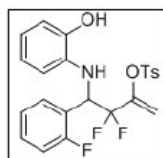


table2
YX-2-13-F



¹⁹F NMR (CDCl₃, 471 MHz)

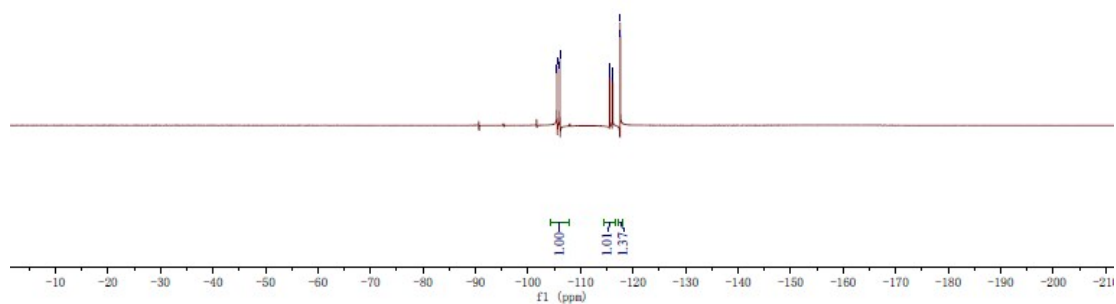
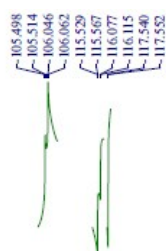
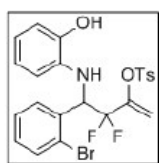


table2
YX-2-13-F
7.806
7.771
7.764
7.751
7.734
7.443
7.437
7.220
7.204
6.687
6.638
6.623
6.608
6.587
6.572
6.558
6.434
6.418
5.493
5.344
5.337
4.961
4.941
4.931
4.910



¹H NMR (CDCl₃, 500 MHz)

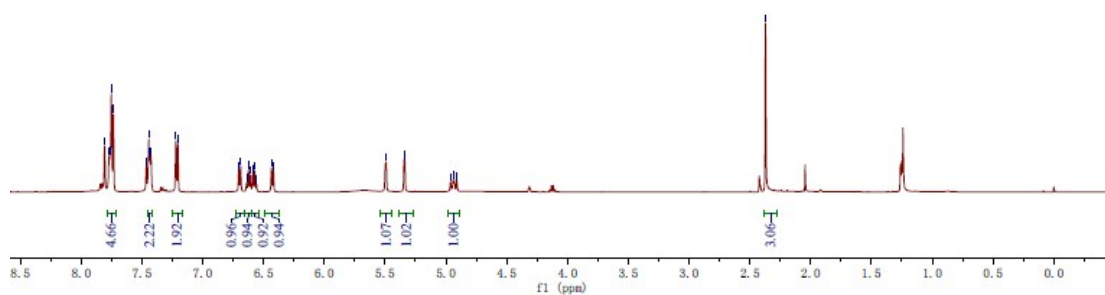
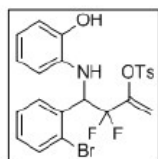


table2
YX-2-12-C

146.294
146.056
146.031
145.907
145.792
144.258
129.842
128.443
128.404
128.090
127.602
126.295
126.167
119.113
114.636
113.884
113.854
105.948

60.789
60.599
60.568
60.376

21.703



¹³C NMR (CDCl₃, 126 MHz)

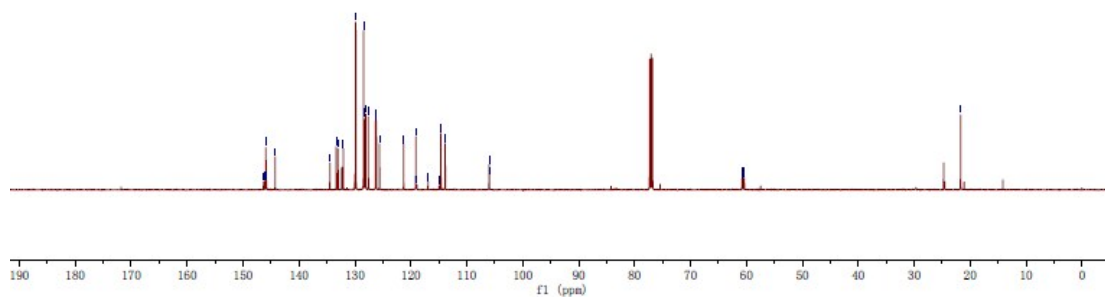
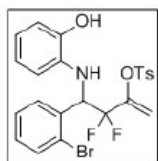
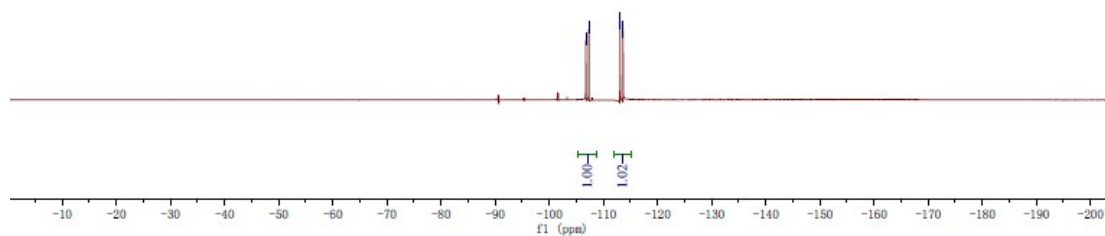


table2
YX-2-12-F



¹⁹F NMR (CDCl₃, 471 MHz)

106.754
106.774
107.298
107.318
113.065
113.098
113.609
113.641



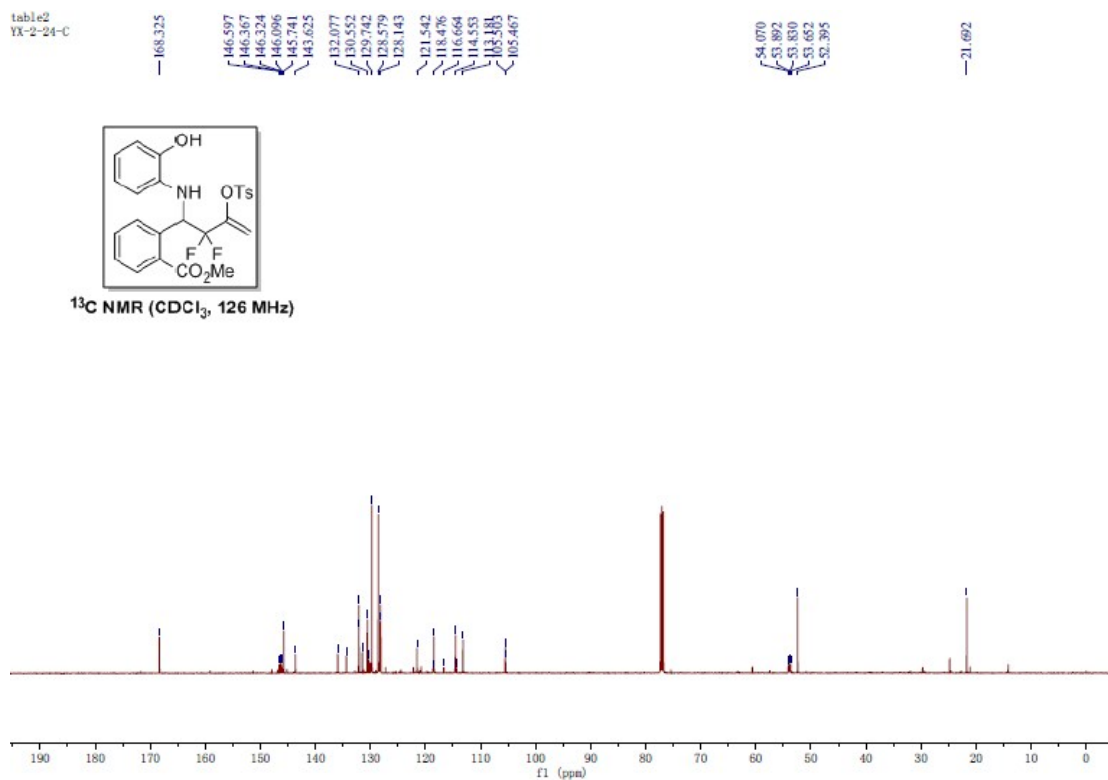
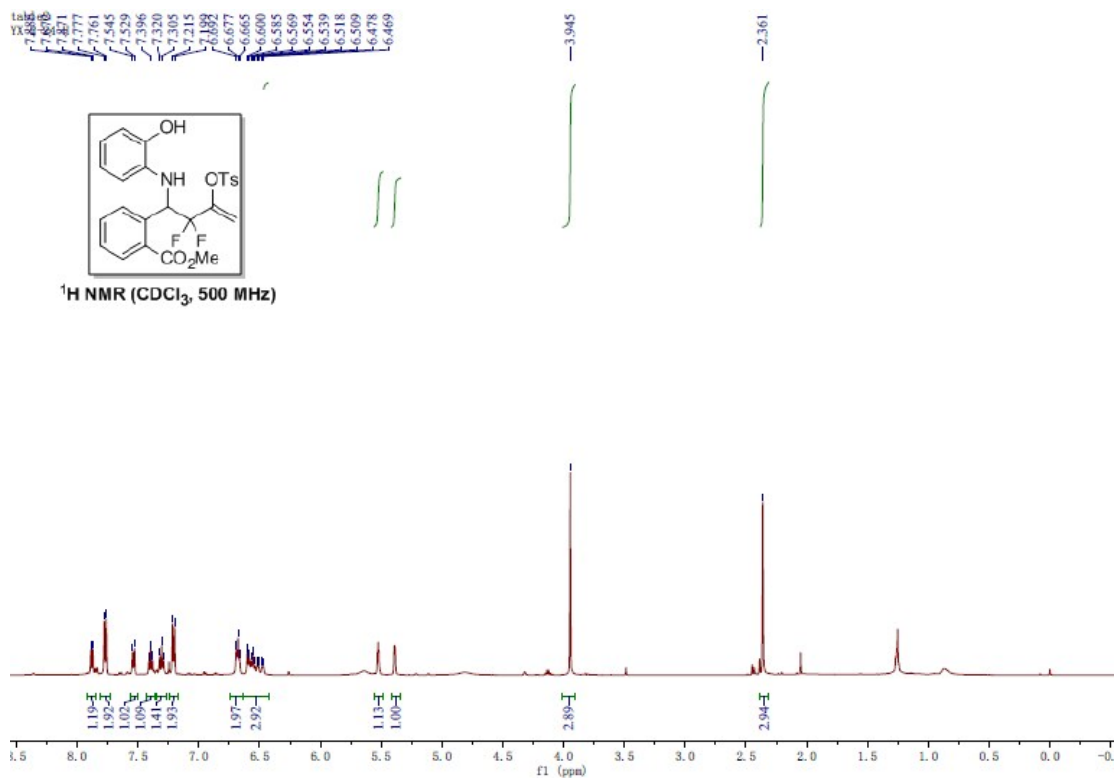
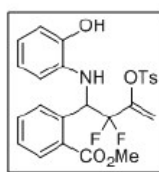


table2
YX-2-24-F



¹⁹F NMR (CDCl₃, 471 MHz)

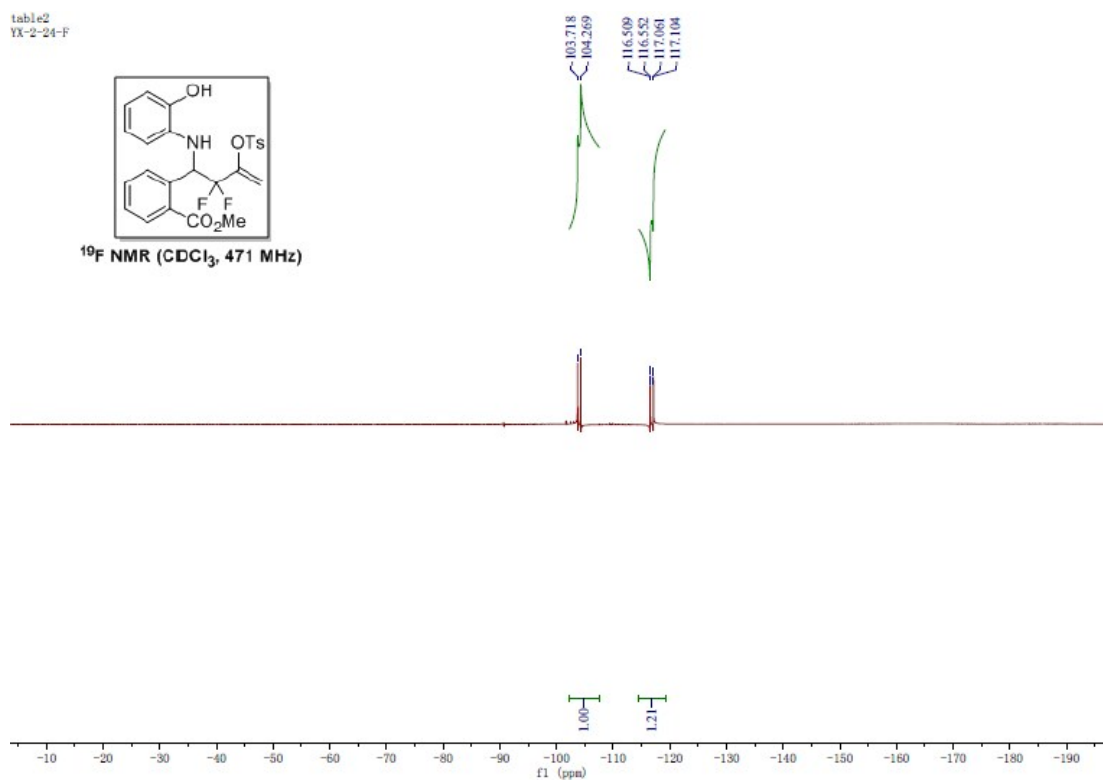
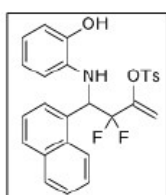


table2
YX-2-24-F



¹H NMR (CDCl₃, 500 MHz)

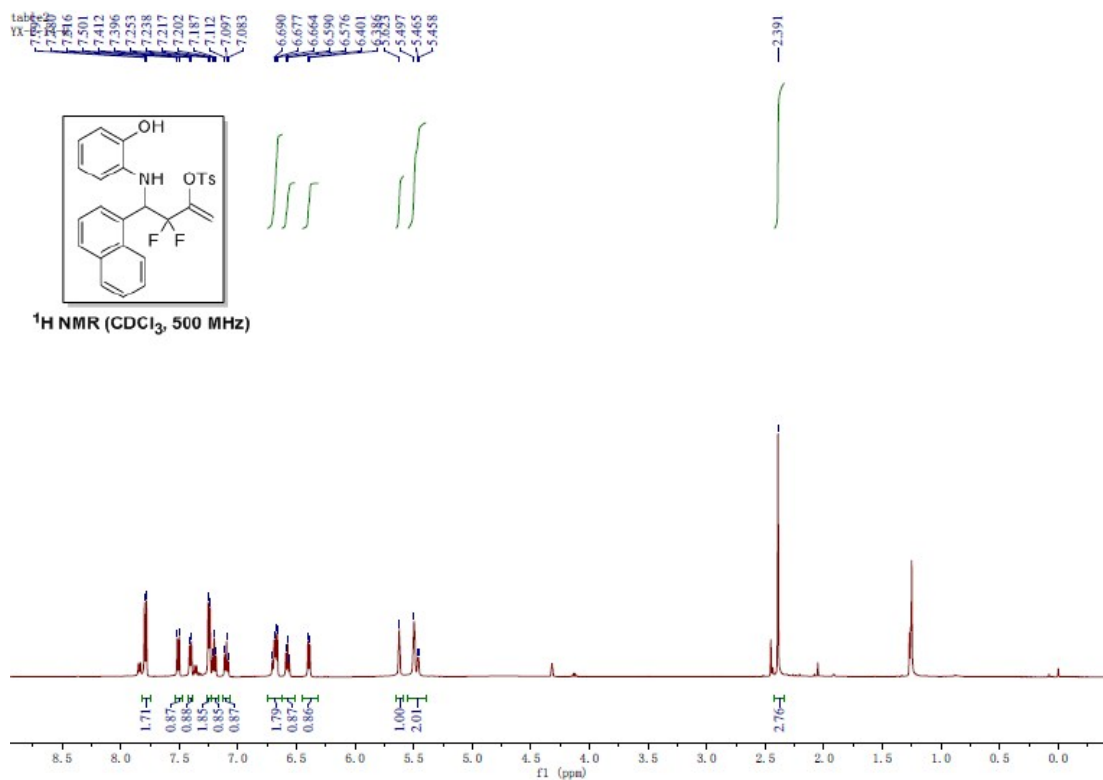
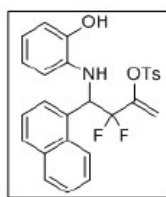


table2
YX-2-14-C

146.424
146.314
146.094
146.032
145.911
145.813
143.745
132.809
129.983
129.840
129.300
128.614
127.733
121.549
118.908
114.629
108.185
106.163
106.126

58.073
57.898
57.827
57.651

21.766



¹³C NMR (CDCl₃, 126 MHz)

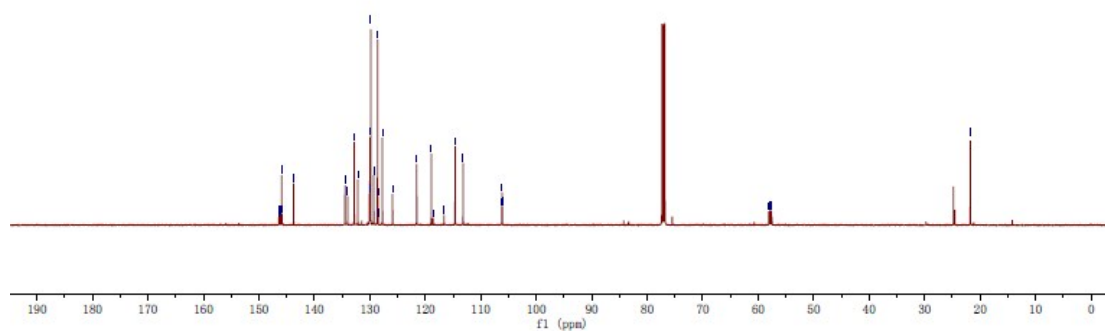
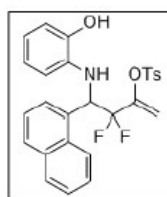
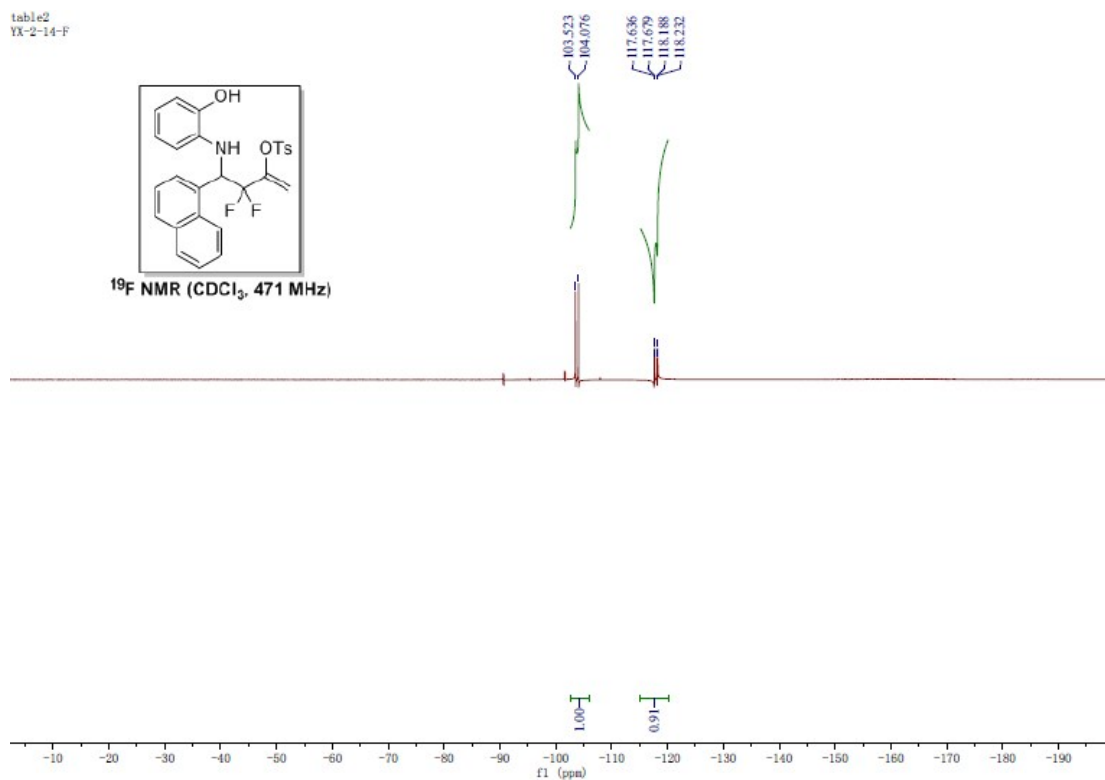


table2
YX-2-14-F



¹⁹F NMR (CDCl₃, 471 MHz)



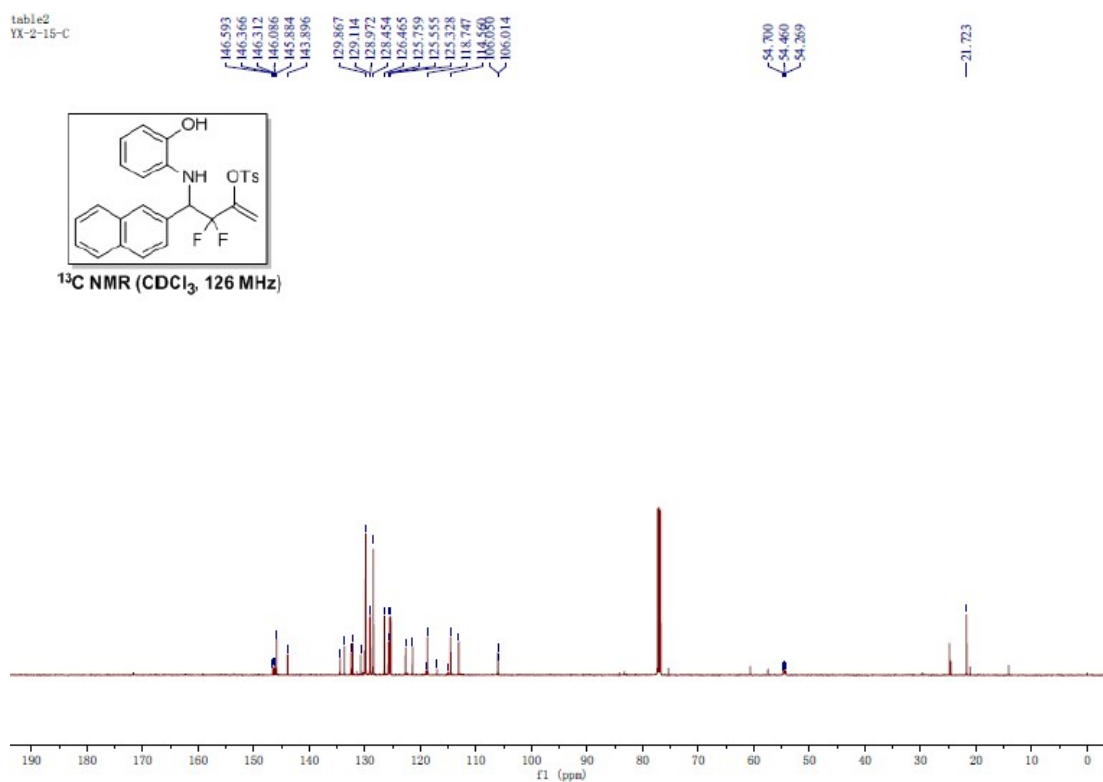
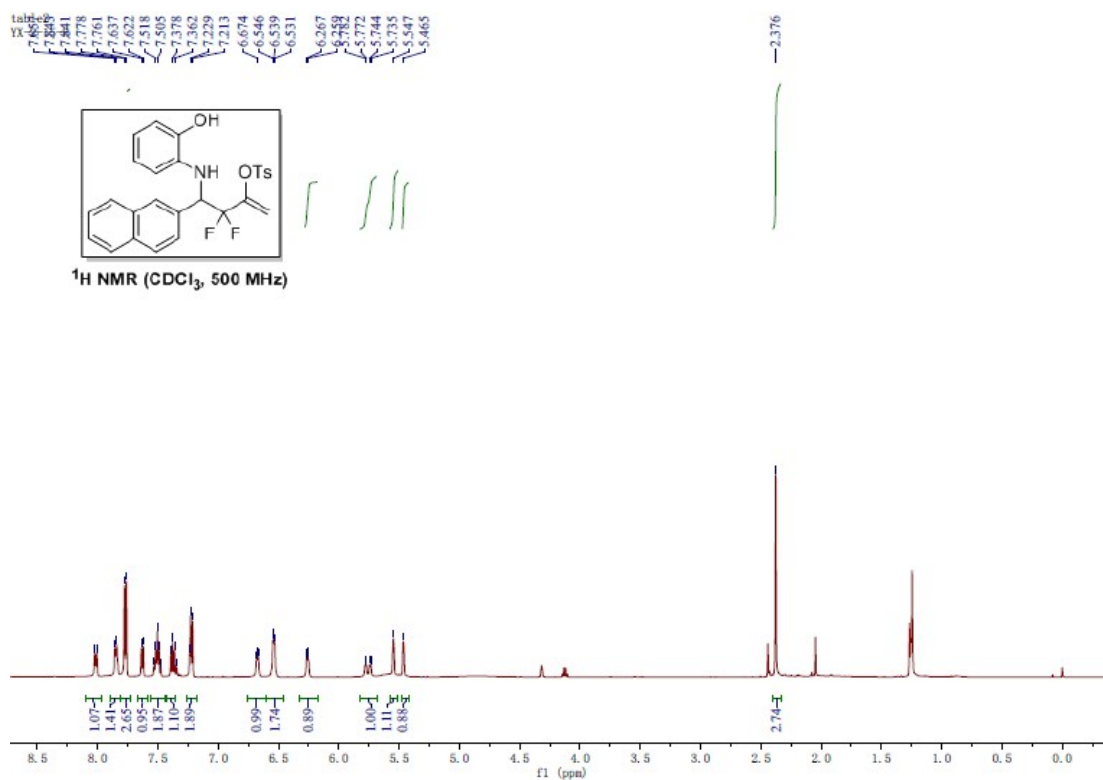
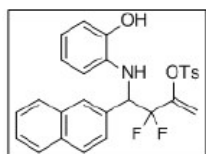


table2
YX-2-15-F



^{19}F NMR (CDCl_3 , 471 MHz)

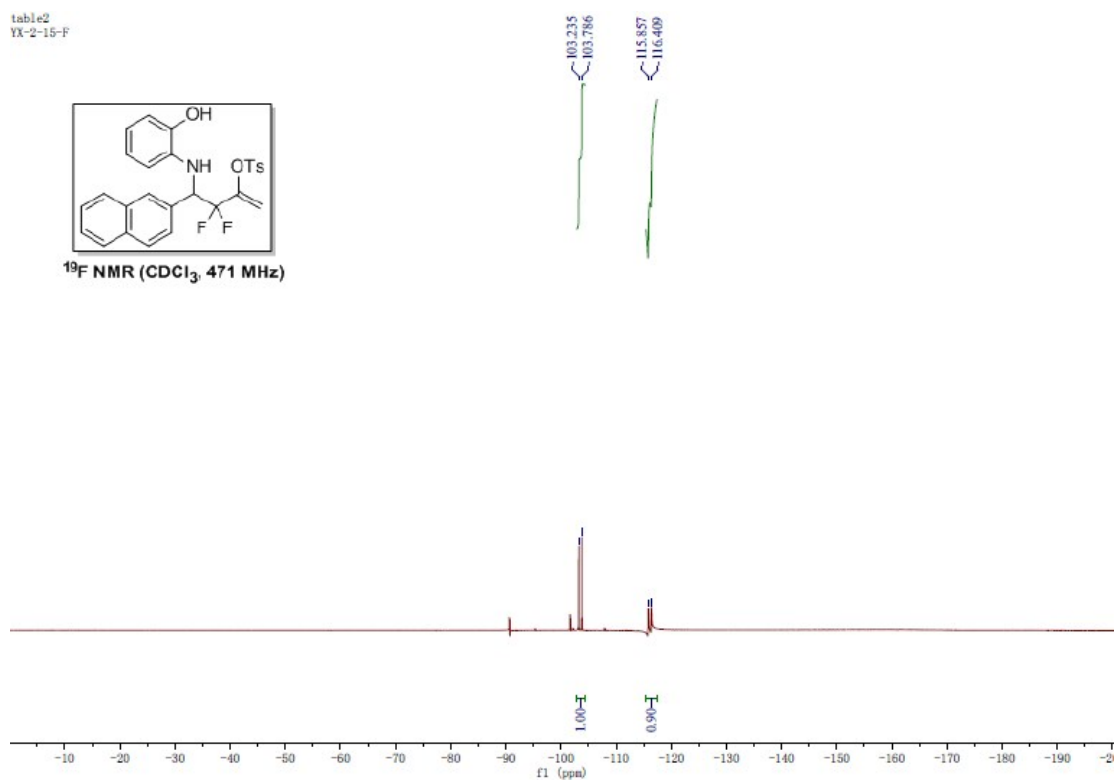
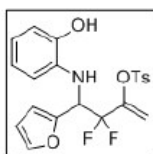


table2
YX-2-17-H



^1H NMR (CDCl_3 , 500 MHz)

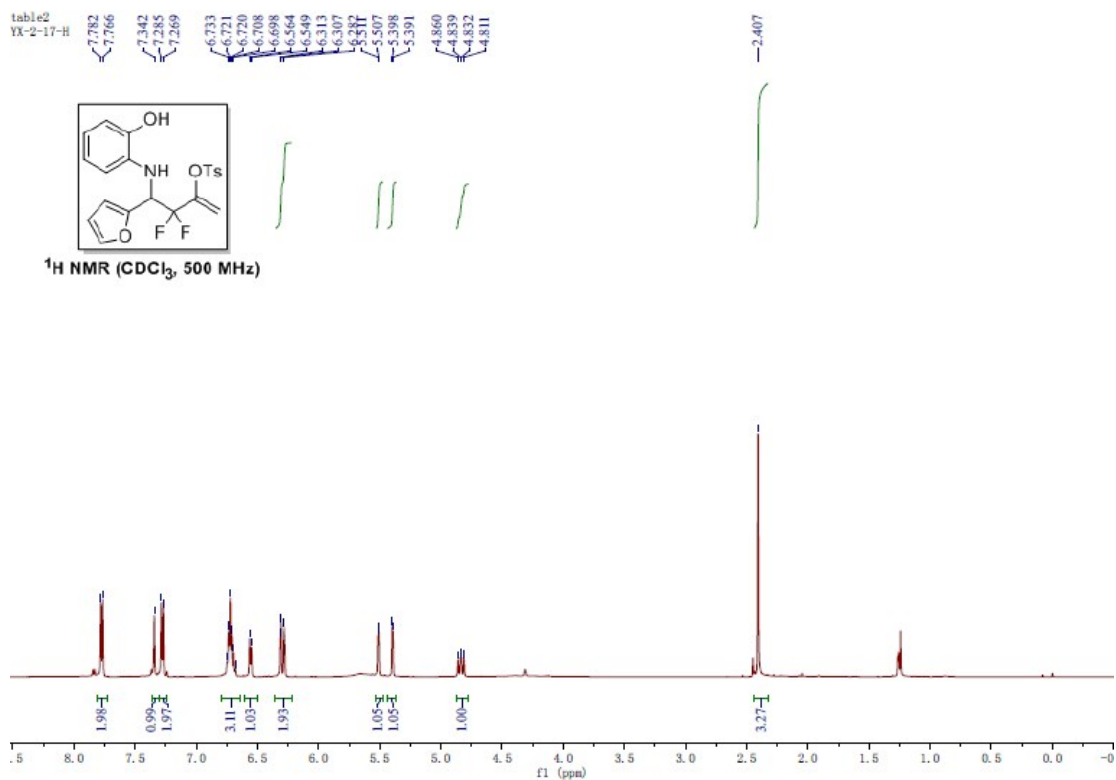
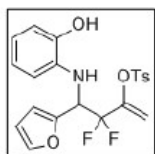


table2
YX-2-17-C

148.157
148.135
146.222
145.993
145.725
145.413
133.855
132.073
129.866
128.501
121.137
120.617
118.211
115.476
114.886
110.497
109.884
106.000
105.964
105.928

55.745
55.541
55.516
55.312

21.714



¹³C NMR (CDCl₃, 126 MHz)

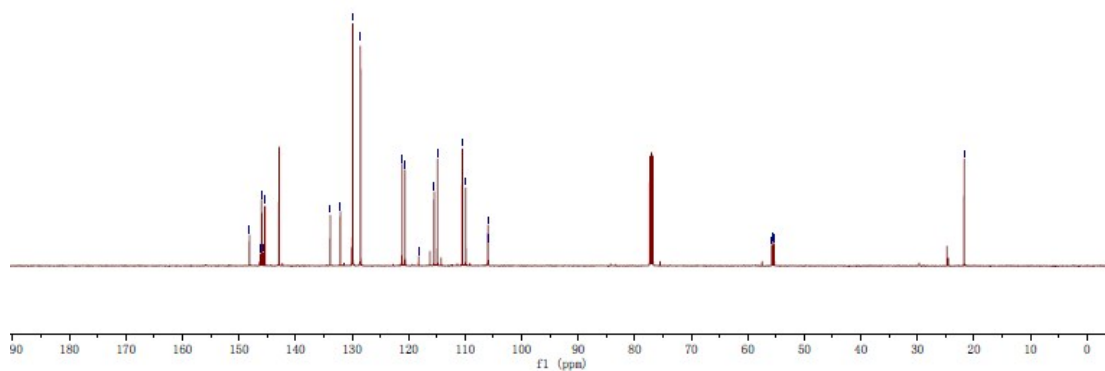
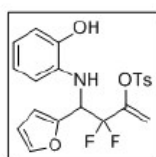


table2
YX-2-17-F



¹⁹F NMR (CDCl₃, 471 MHz)

107.822
107.843
108.363
108.385
112.336
112.367
112.878
112.909

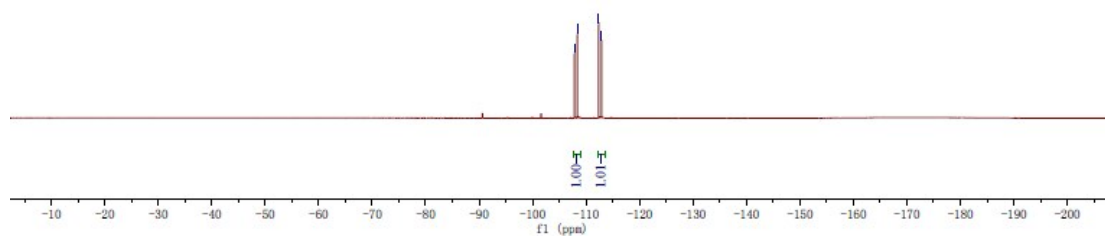


table2
YX-2-18-H

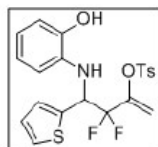
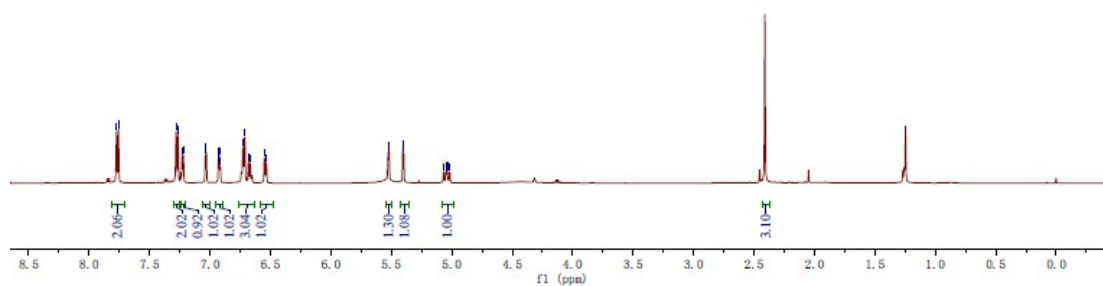
¹H NMR (CDCl₃, 500 MHz)

table2
YX-2-18-C

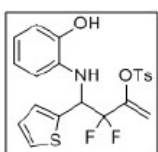
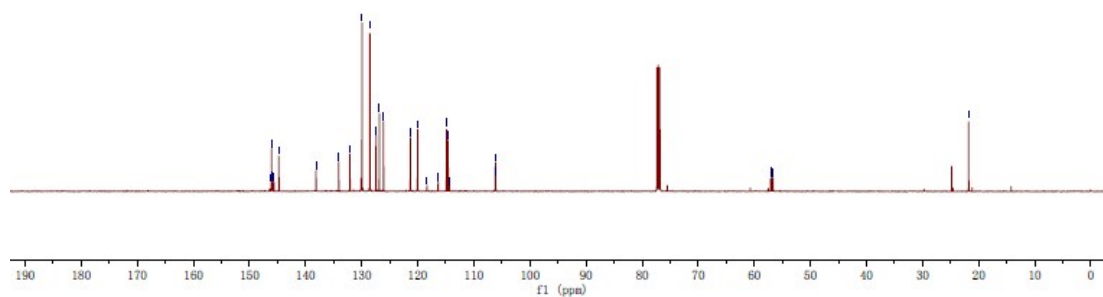
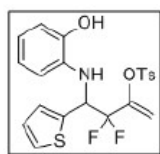
¹³C NMR (CDCl₃, 126 MHz)

table2
YX-2-18-F



¹⁹F NMR (CDCl₃, 471 MHz)

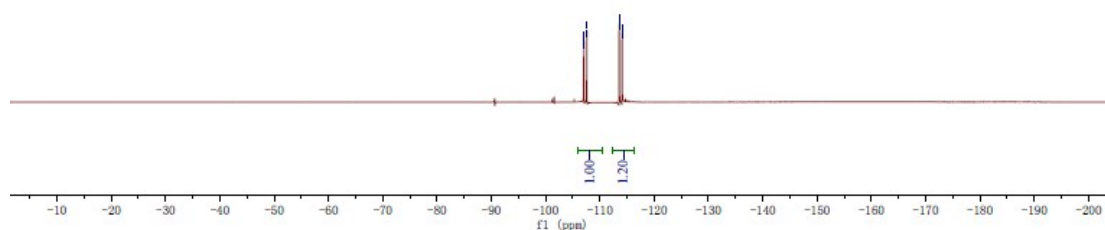
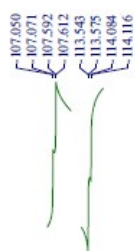
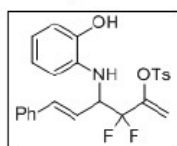


table2
YX-2-19-H



¹H NMR (CDCl₃, 500 MHz)

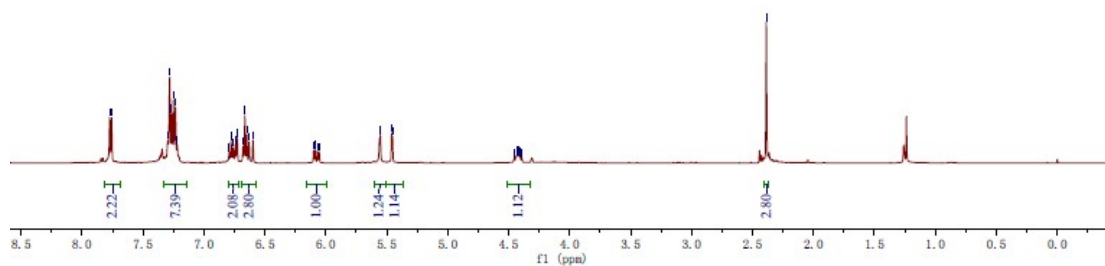
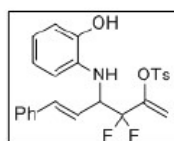


table2
YX-2-19-C

146.404
146.155
145.937
144.593
134.842
129.876
128.530
128.465
128.075
126.697
121.316
119.482
114.796
106.001
105.964

59.185
58.984
58.765

21.710



¹³C NMR (CDCl₃, 126 MHz)

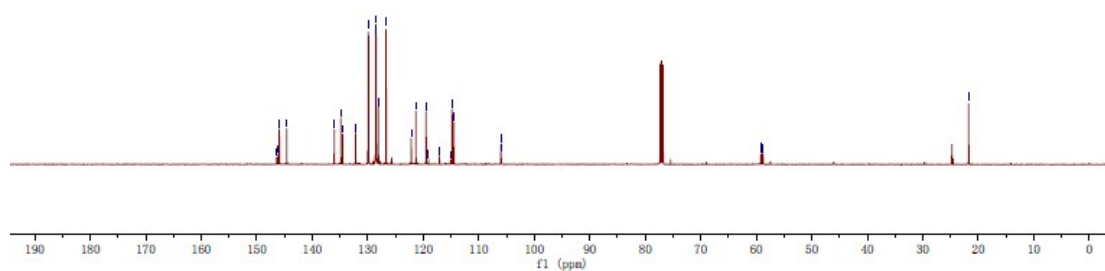
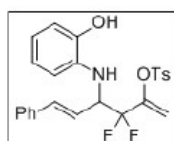


table2
YX-2-19-F



¹⁹F NMR (CDCl₃, 471 MHz)

108.424
108.446
108.965
108.987
112.265
112.294
112.806
112.835

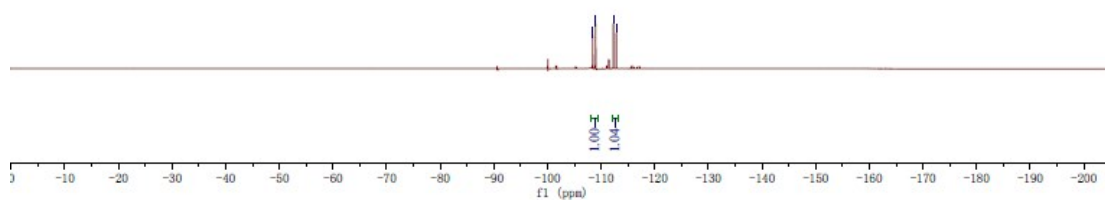
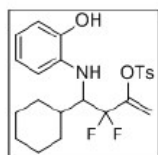


table2
YX-2-20-H

7.782
7.766
7.310
7.294
6.763
6.656
6.550
5.436
5.395
5.389
5.059
4.208
3.685
2.424
1.788
1.772
1.715
1.691
1.658
1.608
1.577
1.256
1.250
1.220
1.199
1.173
1.158
1.142
1.115
1.090
1.067
1.043



¹H NMR (CDCl₃, 500 MHz)

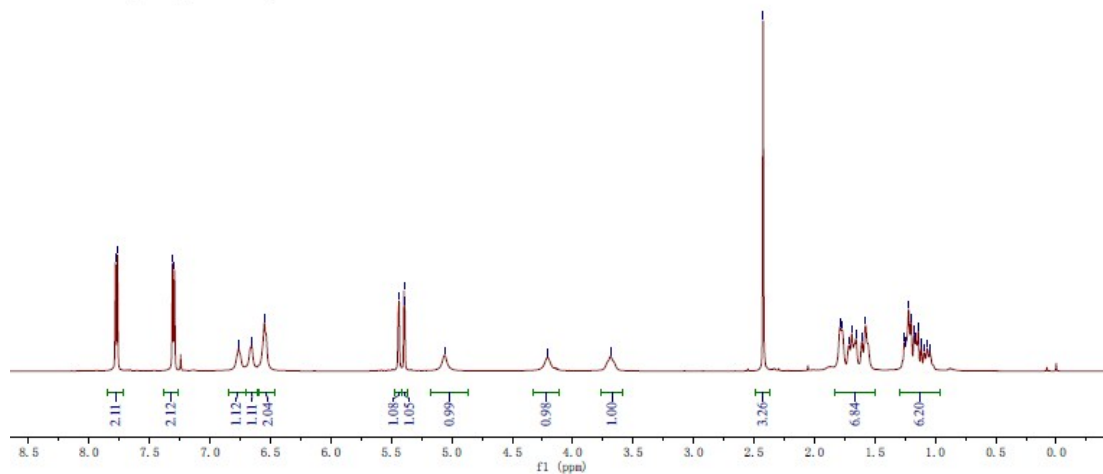
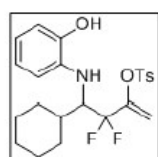


table2
YX-2-20-C

147.356
147.102
146.847
145.849
142.640
136.862
132.348
129.859
128.474
121.598
120.393
118.407
117.247
114.654
105.342
105.336
59.661
59.455
59.261
38.447
31.208
26.763
26.327
26.058
25.941
21.730



¹³C NMR (CDCl₃, 126 MHz)

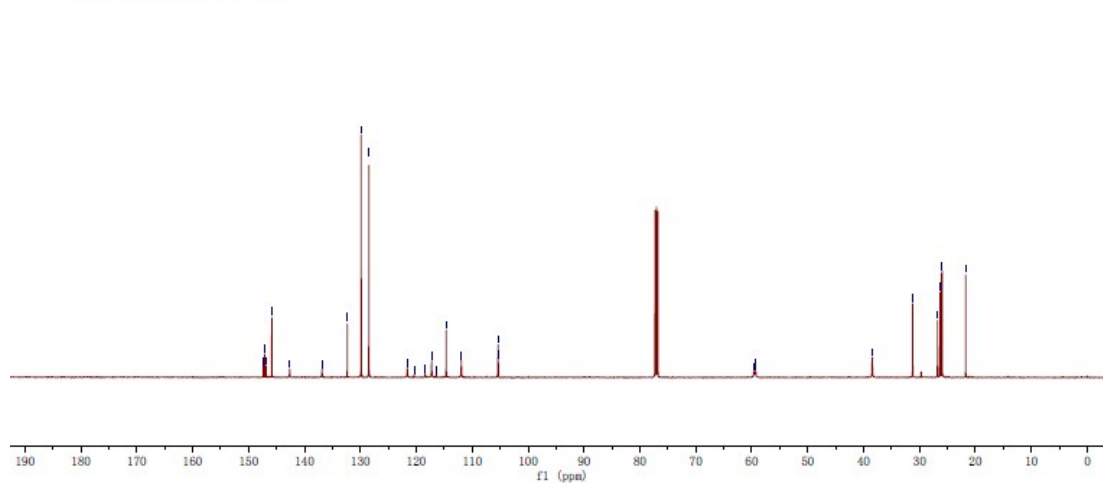
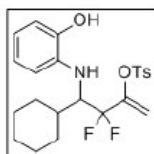


table2
YX-2-20-F



¹⁹F NMR (CDCl₃, 471 MHz)

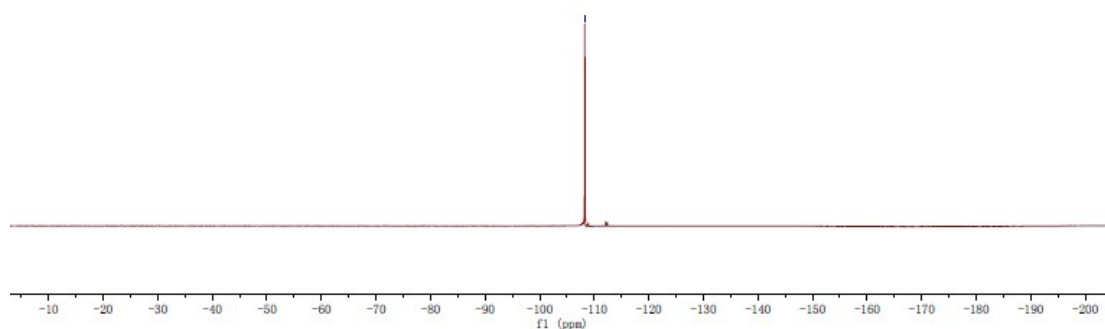
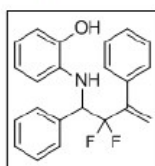


table3
YX-2-1-H

7.363
7.348
7.338
7.328
7.314
7.273
7.269
7.259
-6.650
-6.643
-6.569
-6.562
-6.208
-6.191
-5.736
-5.469
4.620
4.597
4.591
4.568



¹H NMR (CDCl₃, 500 MHz)

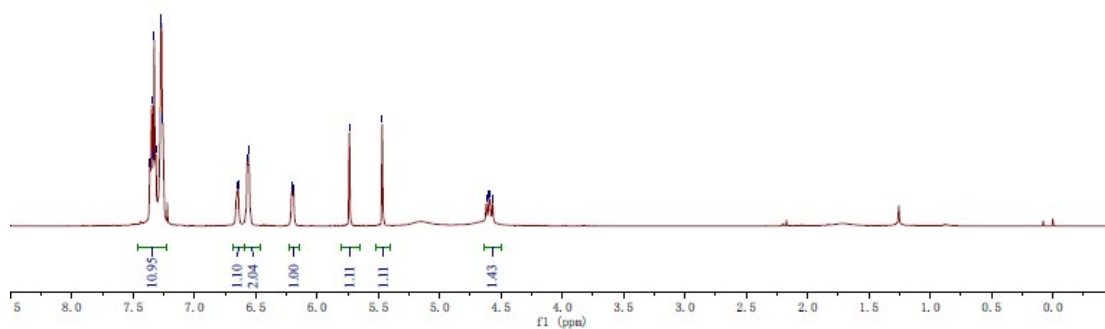
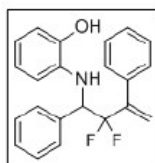


table3
YX-2-1-C

144.407
143.443
143.267
143.091
136.680
135.694
135.694
128.468
128.426
128.385
128.229
128.208
122.961
121.253
120.970
120.364
120.294
120.224
119.076
114.458
114.312
62.110
61.891
61.692



¹³C NMR (CDCl₃, 126 MHz)

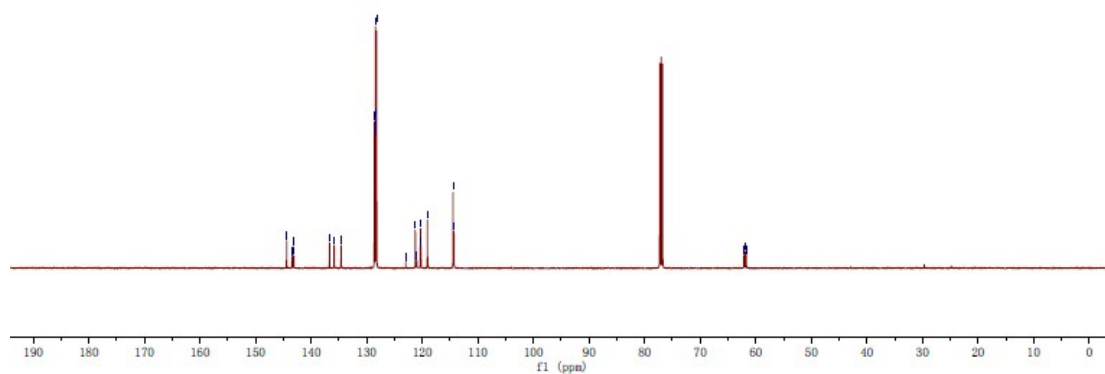
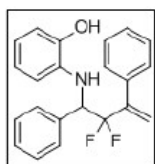


table3
YX-2-1-F

101.526
102.058
107.295
107.321
107.827
107.853



¹⁹F NMR (CDCl₃, 471 MHz)

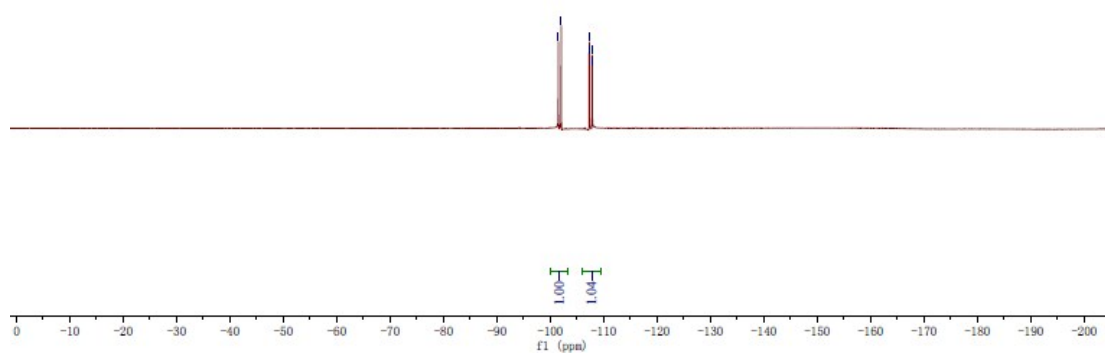
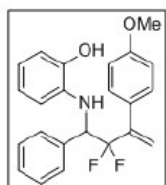


table3
YX-3-3-H



¹H NMR (CDCl₃, 500 MHz)

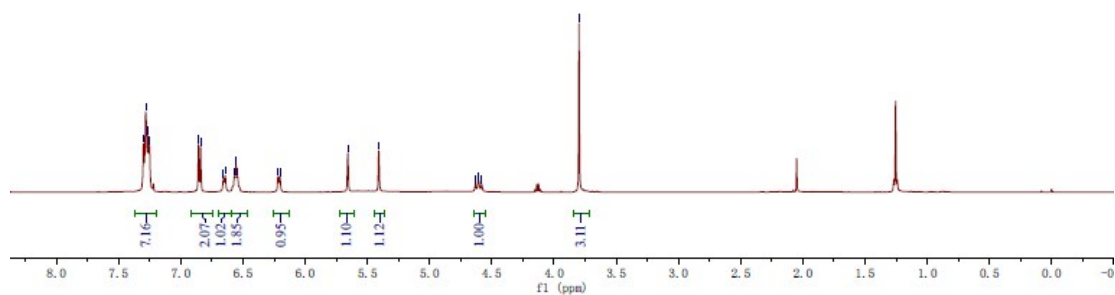
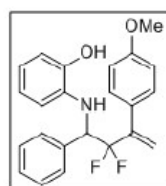


table3
YX-3-3-C



¹³C NMR (CDCl₃, 126 MHz)

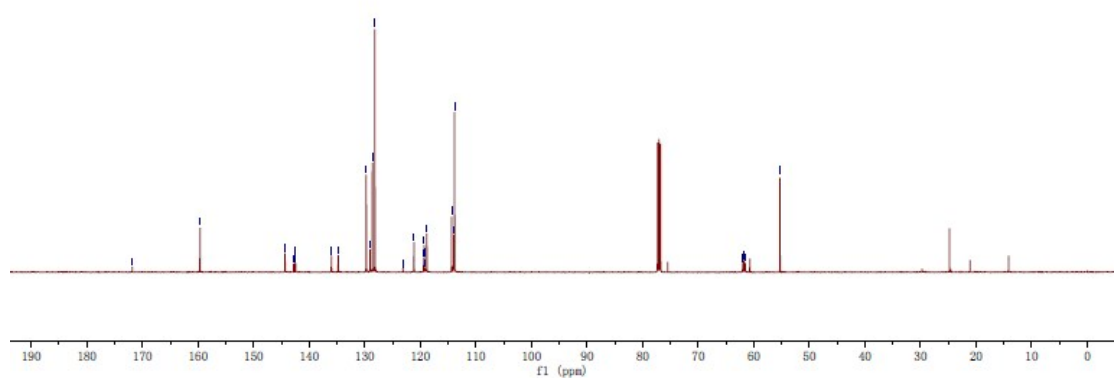
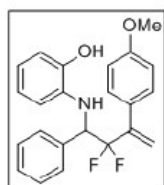


table3
YX-3-3-F



^{19}F NMR (CDCl_3 , 471 MHz)

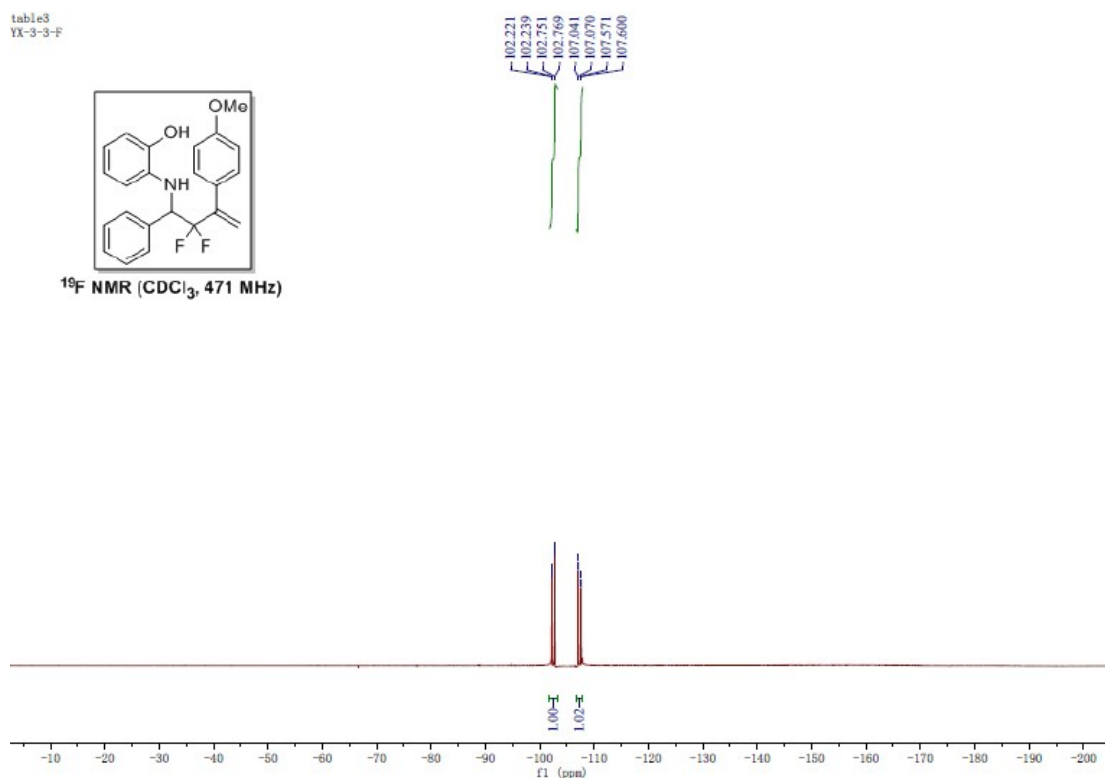
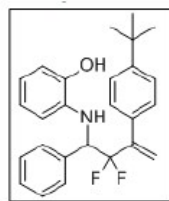


table3
YX-3-4-H



^1H NMR (CDCl_3 , 500 MHz)

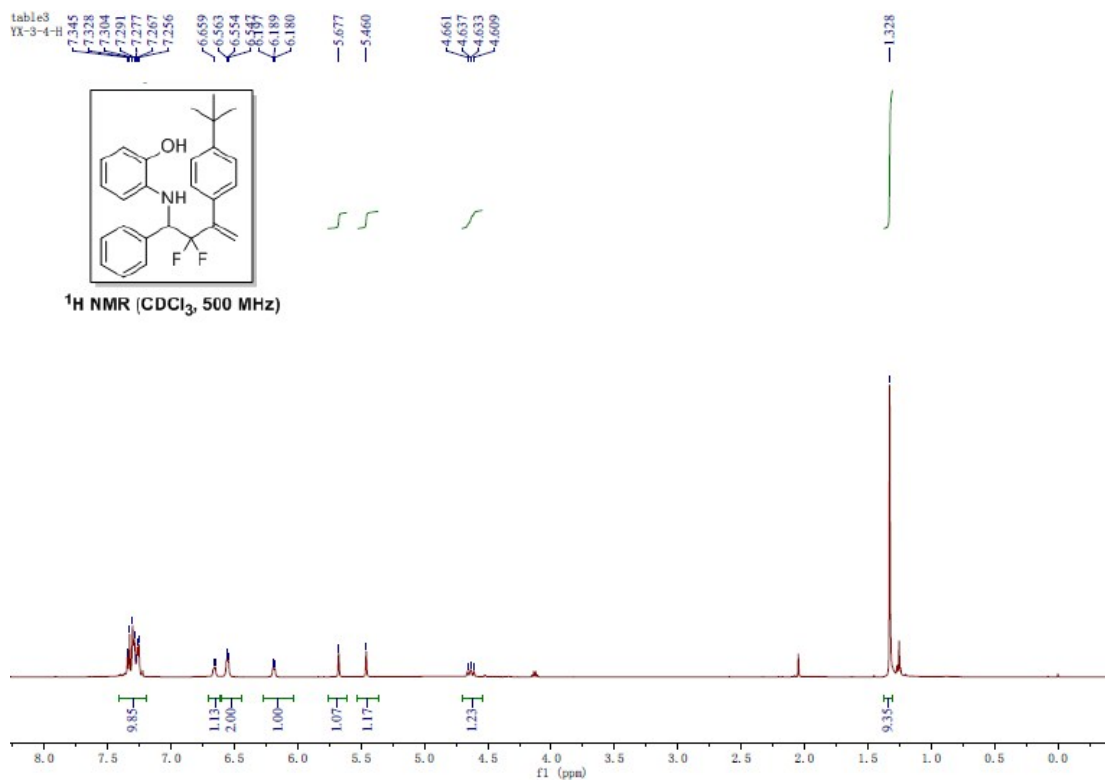
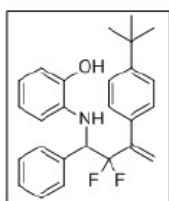


table3
YX-3-4-C

151.392
144.456
142.988
135.844
134.734
133.627
128.637
128.157
128.092
127.550
125.669
125.339
123.087
121.107
119.865
119.795
119.724
119.118
118.927
114.422
114.197

62.097
61.901
61.678

34.572
31.267



¹³C NMR (CDCl₃, 126 MHz)

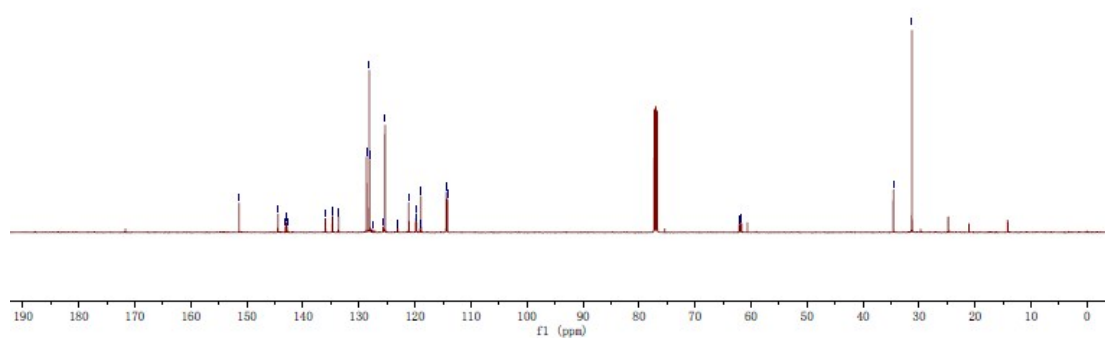
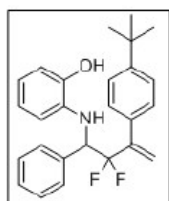


table3
YX-3-4-F



¹⁹F NMR (CDCl₃, 471 MHz)

101.523
101.543
102.053
102.073
106.899
106.929
107.439
107.459

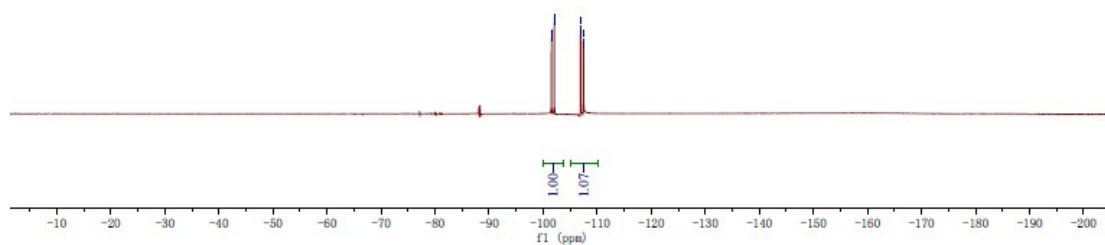
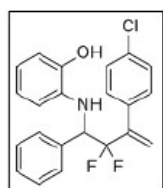


table3
YX-3-8-H



¹H NMR (CDCl₃, 500 MHz)

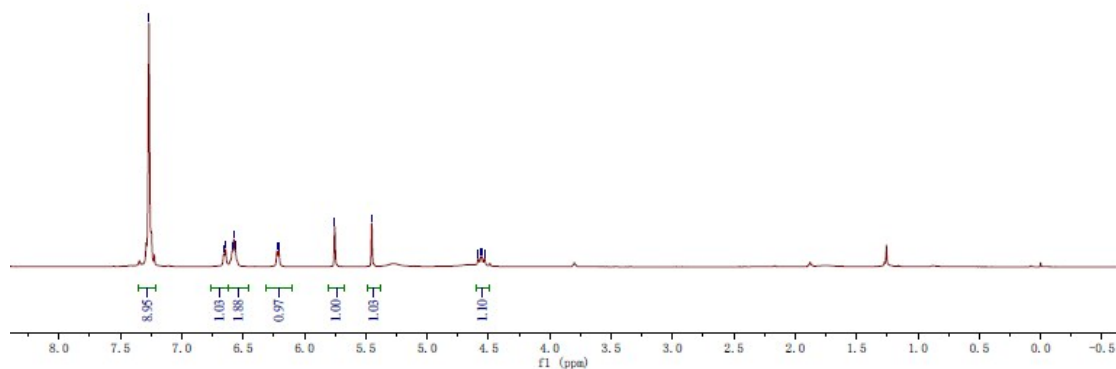
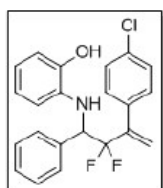


table3
YX-3-8-C



¹³C NMR (CDCl₃, 126 MHz)

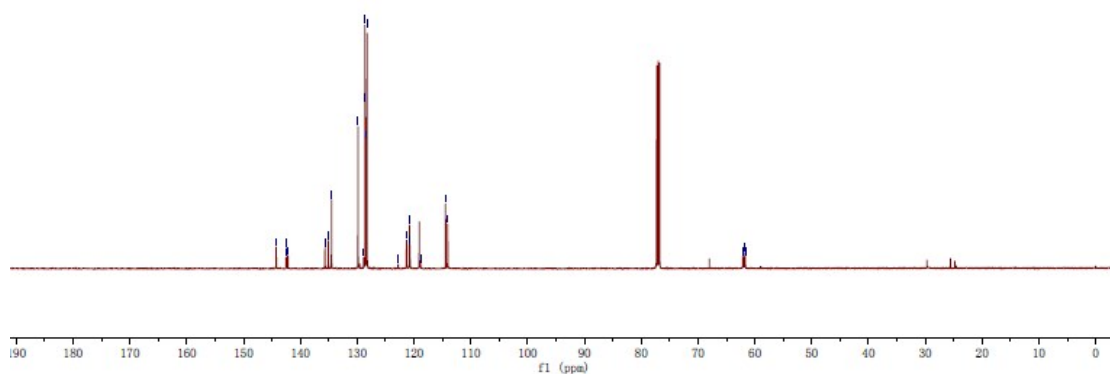
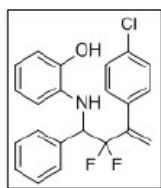


table3
YX-3-8-F



^{19}F NMR (CDCl_3 , 471 MHz)

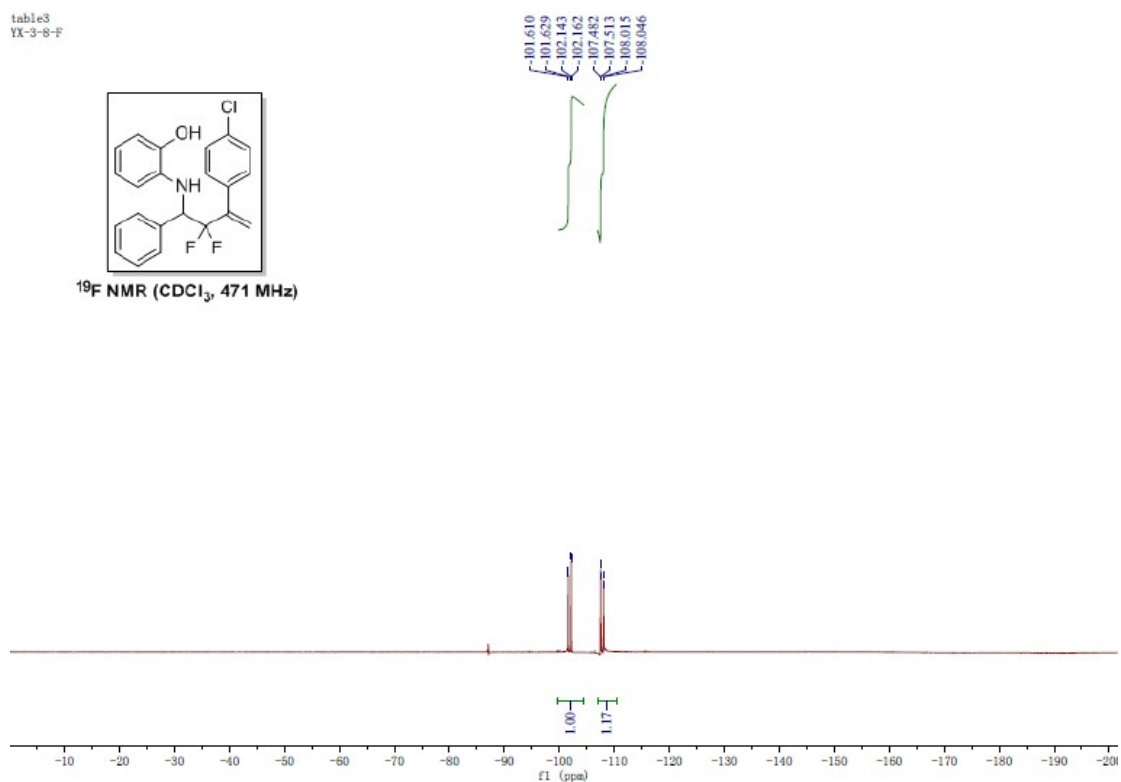
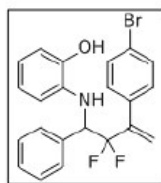


table3
YX-3-6-H



^1H NMR (CDCl_3 , 500 MHz)

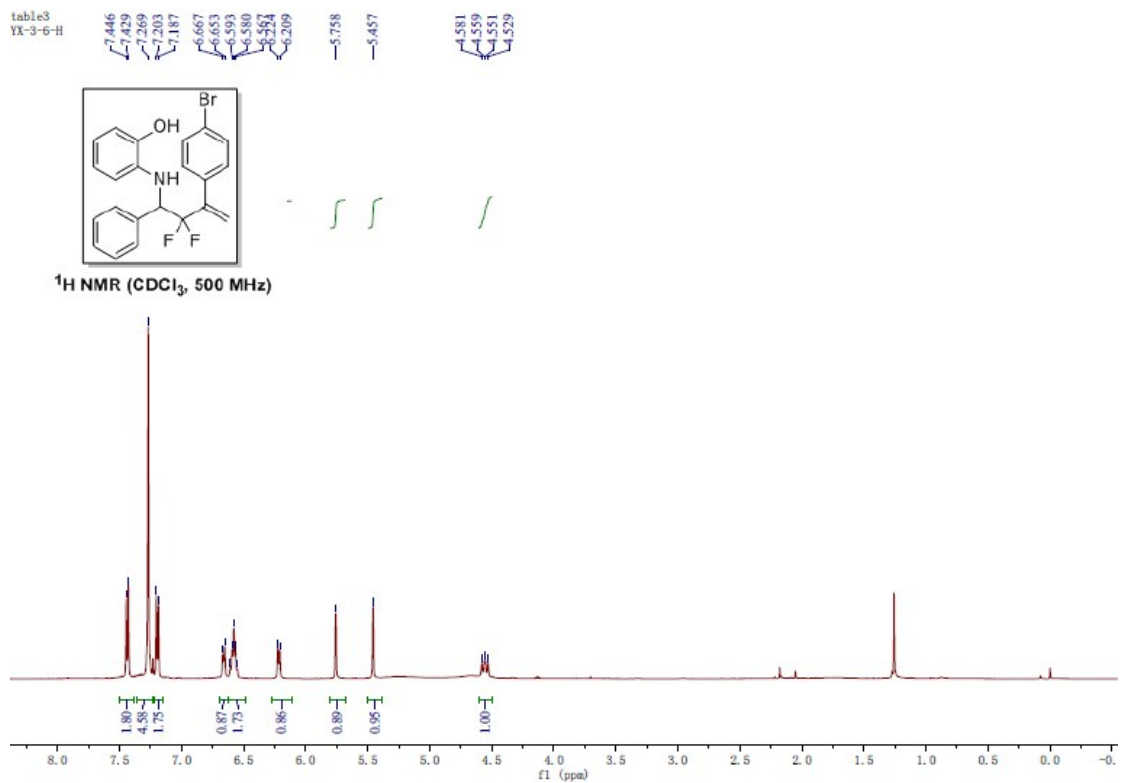
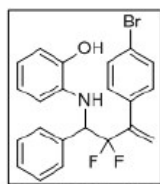


table3
YX-3-6-C

144.244
142.584
142.404
142.225
135.653
135.552
134.503
131.572
130.148
128.566
128.324
128.279
122.749
121.315
120.858
120.789
120.721
119.063
118.753
114.436
114.059

62.078
61.855
61.659



¹³C NMR (CDCl₃, 126 MHz)

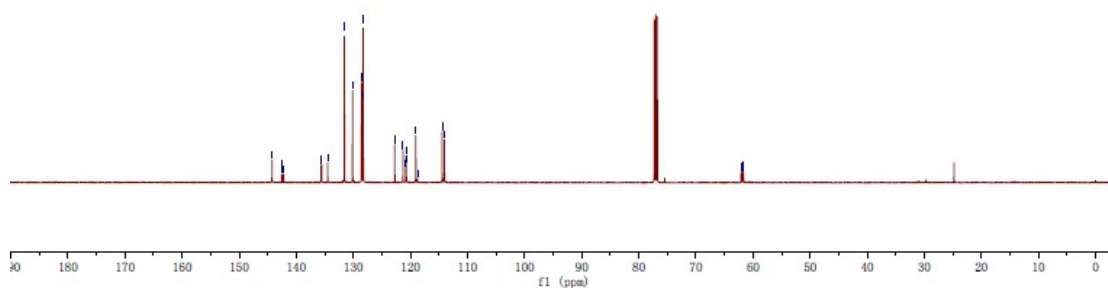
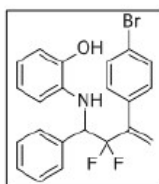
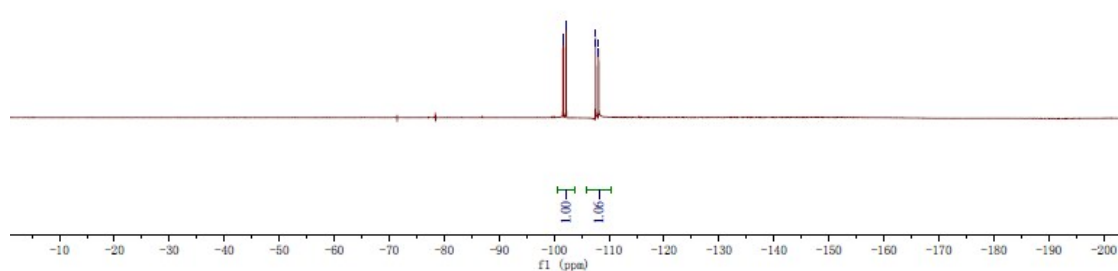


table3
YX-3-6-F

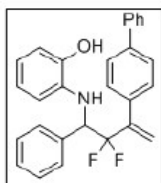


¹⁹F NMR (CDCl₃, 471 MHz)

101.638
101.657
102.172
102.190
107.531
107.562
108.063
108.095



7.688
7.686
7.544
7.442
7.433
7.417
7.300
7.271
7.266
7.262
6.689
6.681
5.575
5.526
5.237
5.228
-5.753
-5.523
4.677
4.653
4.627



¹H NMR (CDCl₃, 500 MHz)

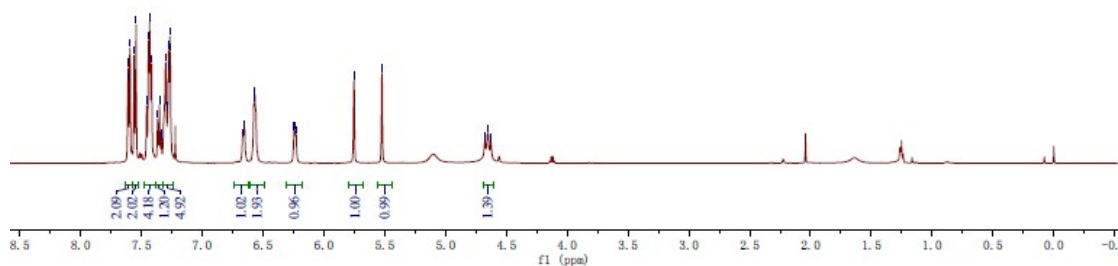
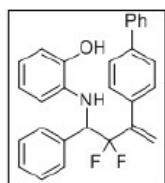


table3
YX-3-9-C

144.450
143.112
142.936
142.758
141.155
140.394
135.915
135.573
134.632
128.879
128.846
128.645
128.236
127.566
127.388
127.081
127.052
123.035
121.295
121.054
120.324
120.256
120.185
119.122
114.465
114.395
62.258
62.036
61.839



¹³C NMR (CDCl₃, 125 MHz)

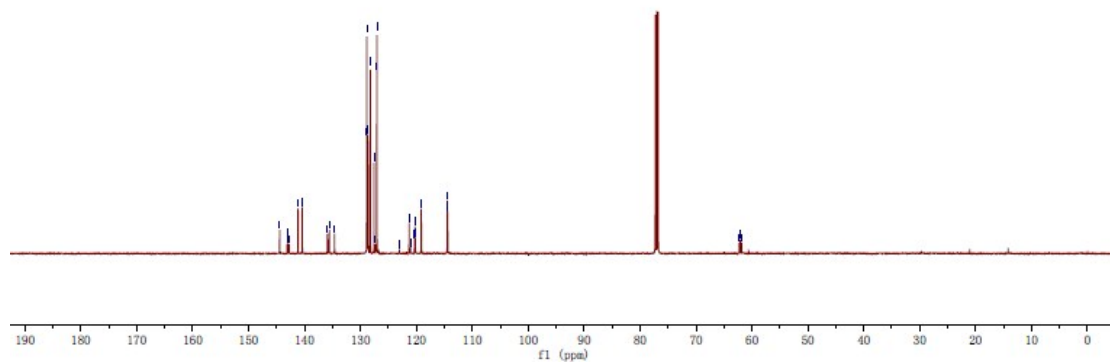
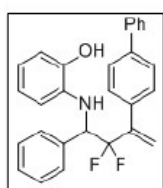


table3
YX-3-9-F



¹⁹F NMR (CDCl₃, 471 MHz)

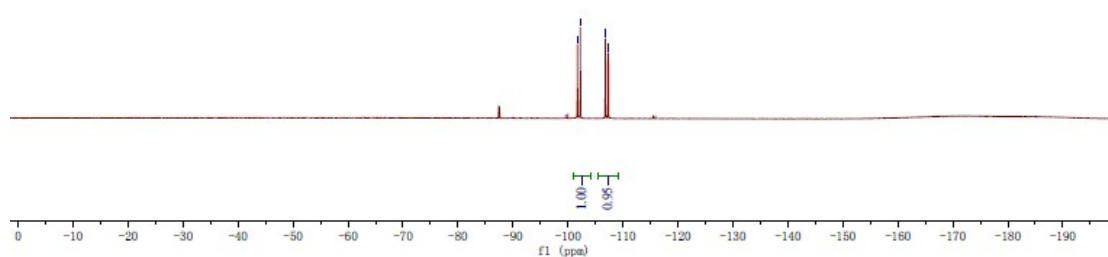
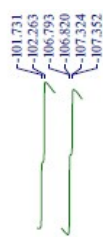
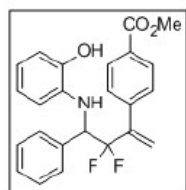


table3
YX-3-9-F



¹H NMR (CDCl₃, 500 MHz)

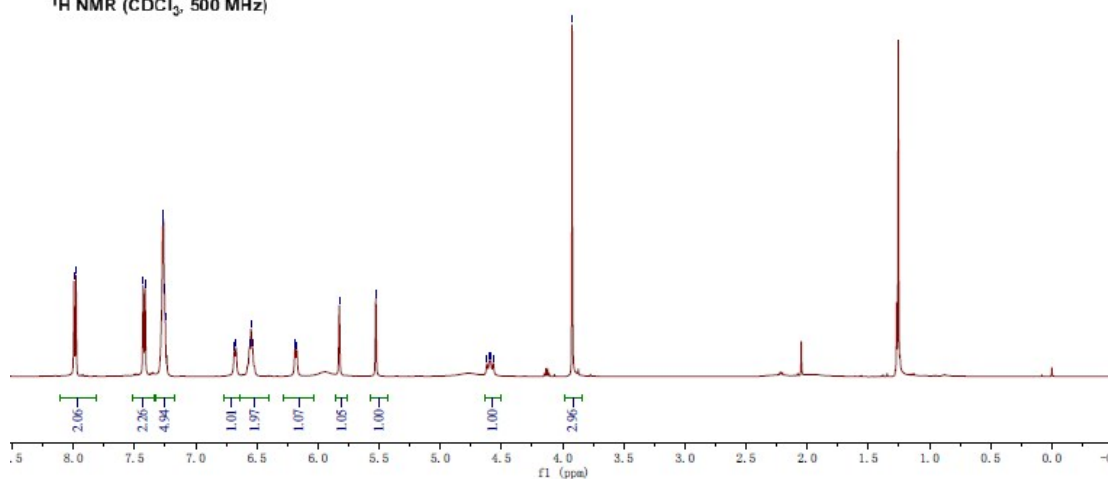
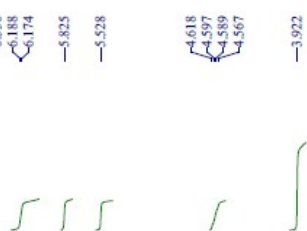
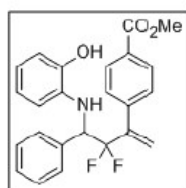


table3
YX-3-5-C



¹³C NMR (CDCl₃, 126 MHz)

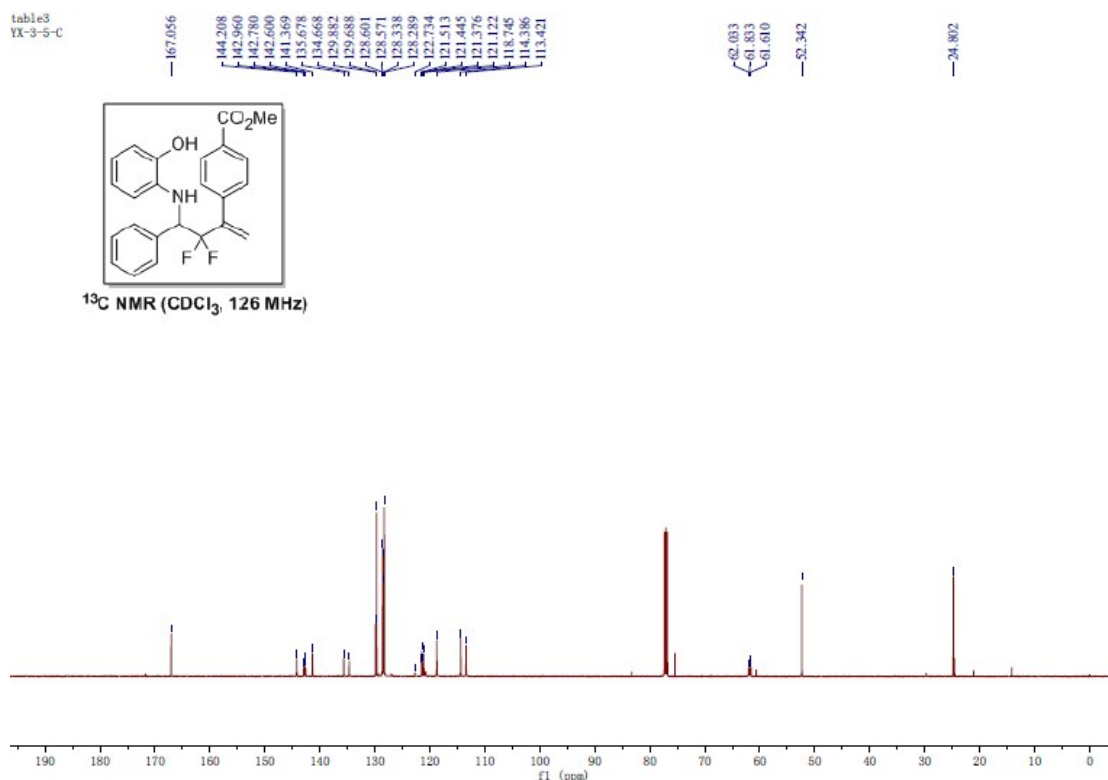
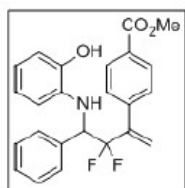


table3
YX-3-5-F



¹⁹F NMR (CDCl₃, 471 MHz)

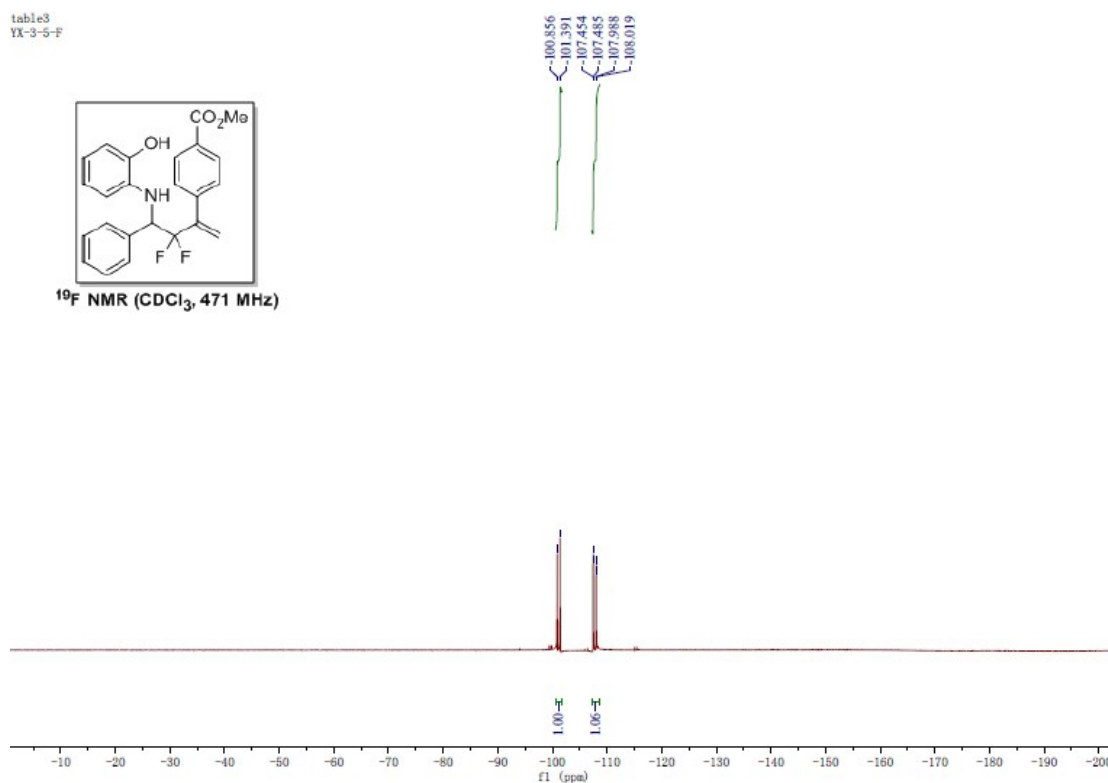
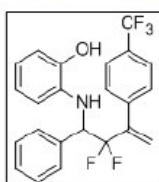


table3
YX-3-7-H



¹H NMR (CDCl₃, 500 MHz)

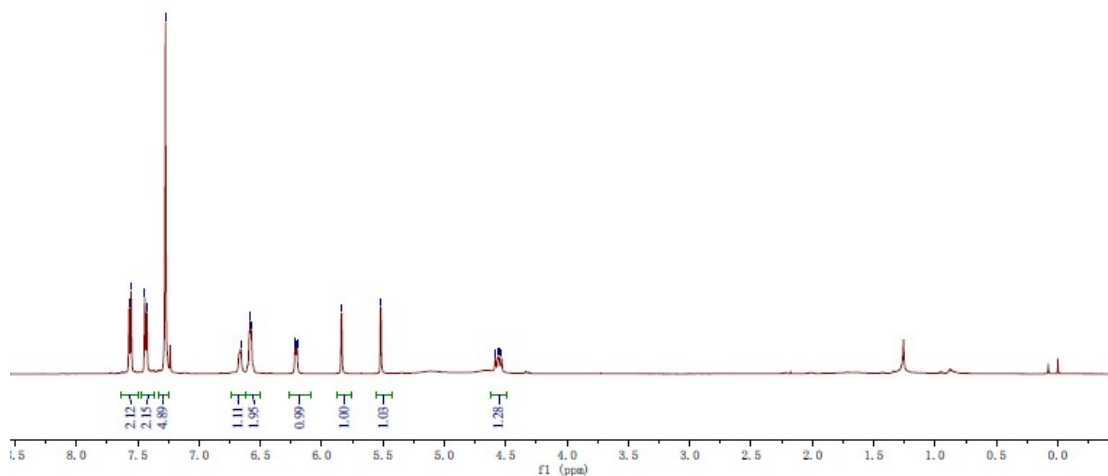
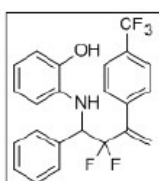


table3
YX-3-7-C



¹³C NMR (CDCl₃, 126 MHz)

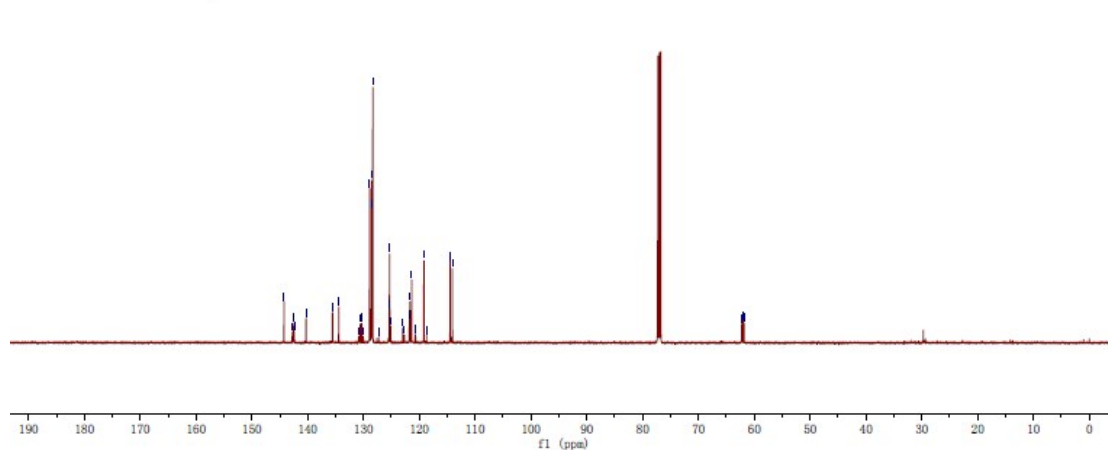


table3
YX-3-7-F

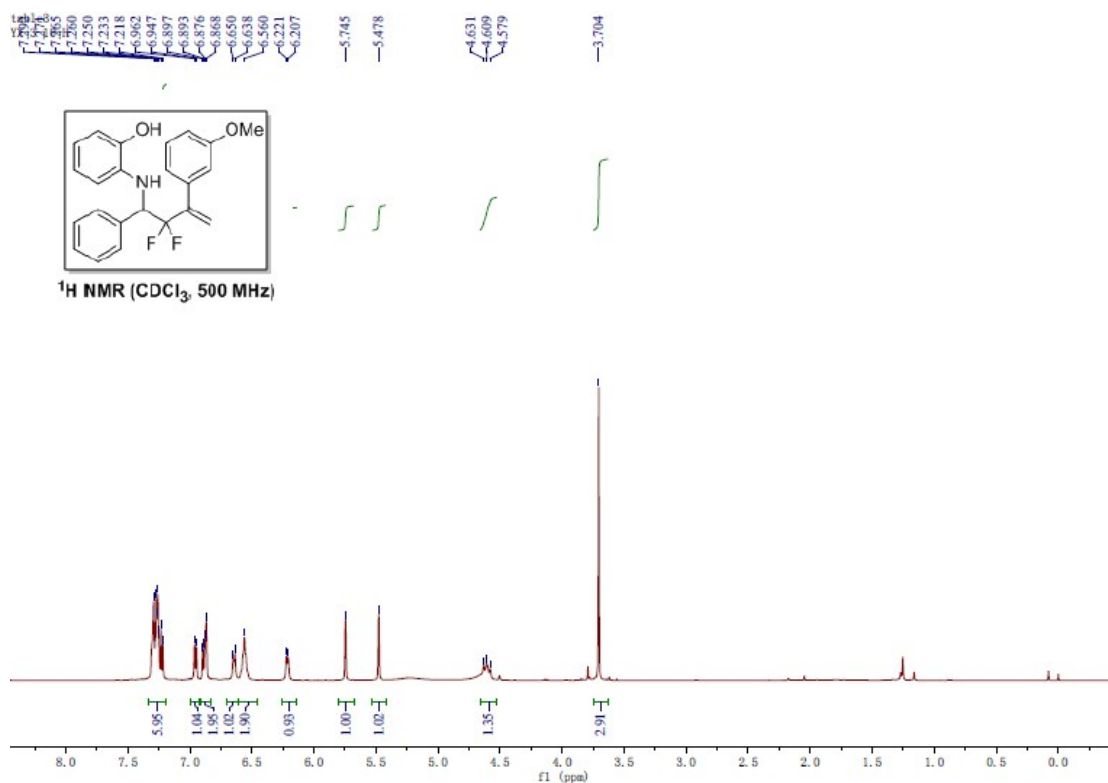
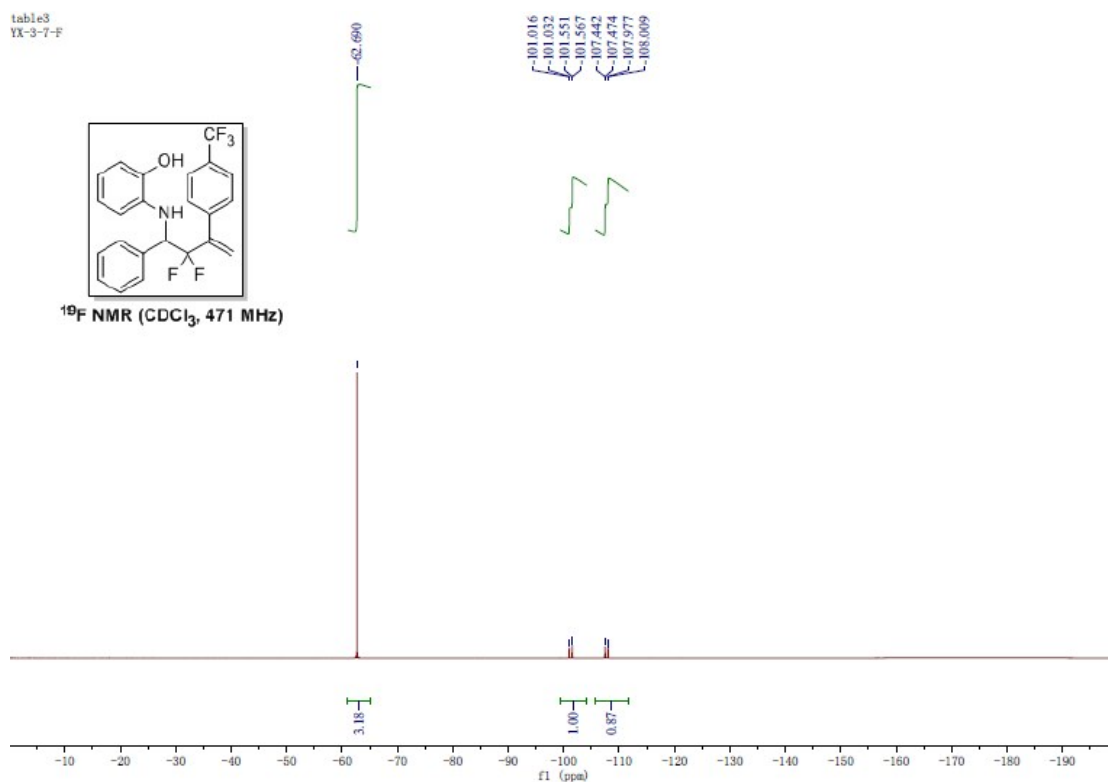


table3
YX-3-10-C

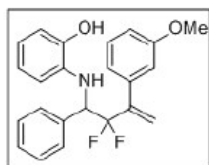
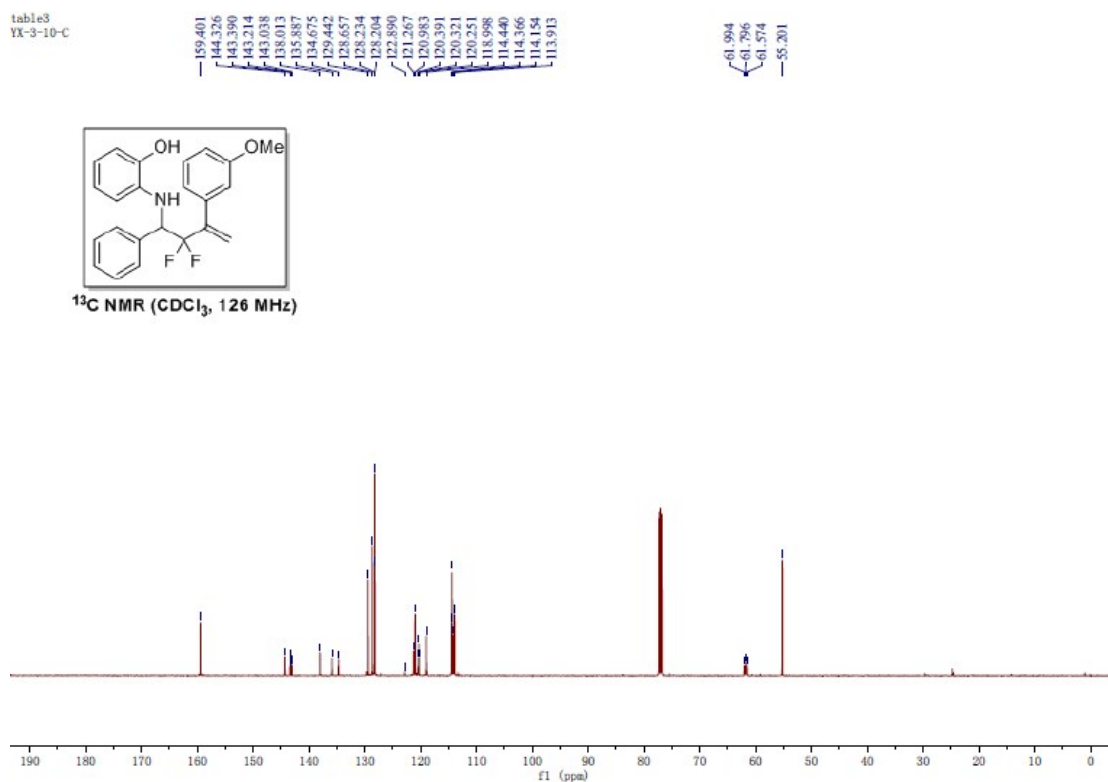
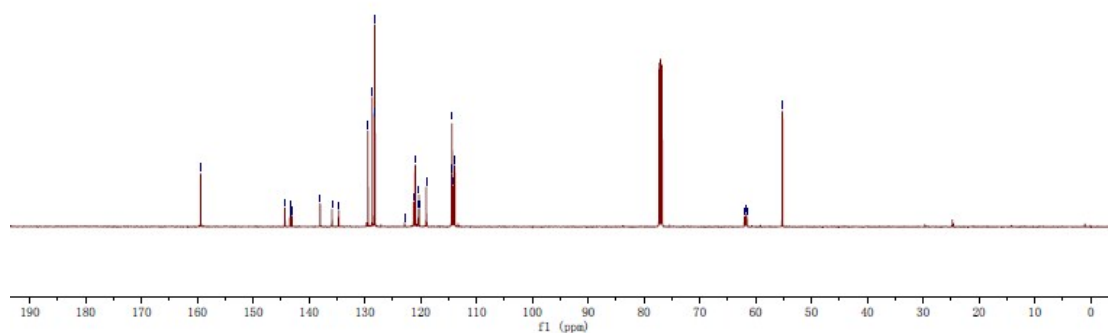
¹³C NMR (CDCl₃, 126 MHz)

table3
YX-3-10-F

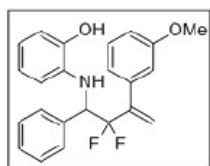
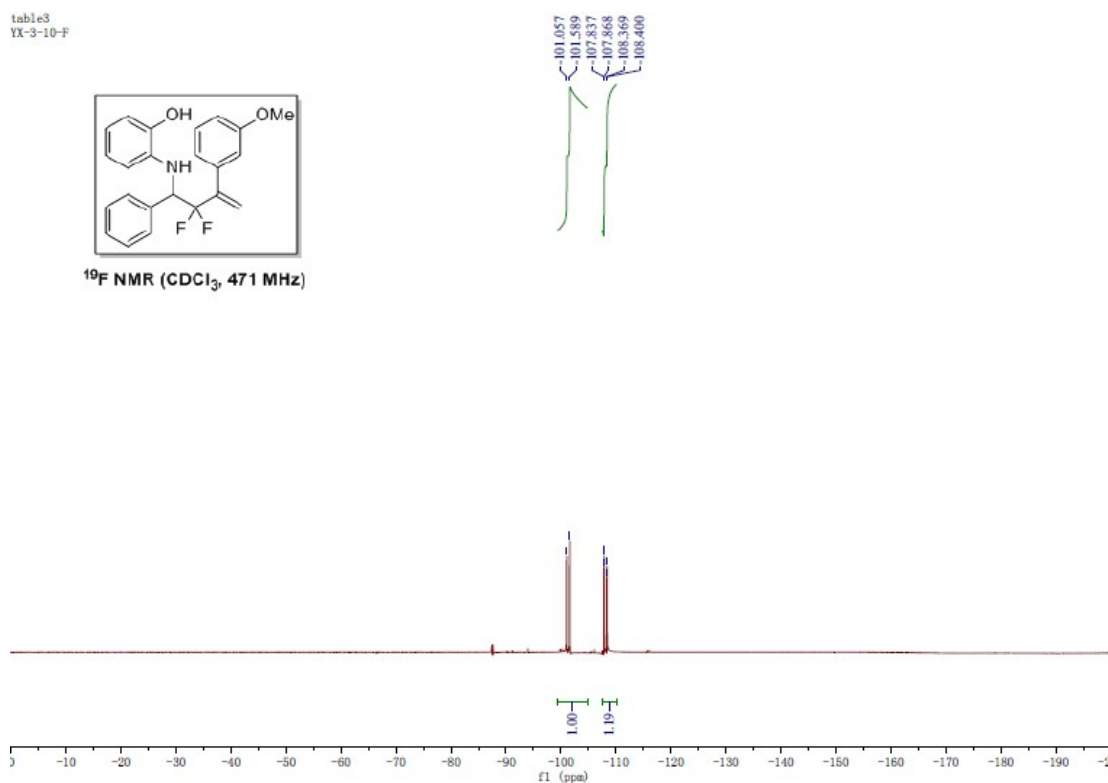
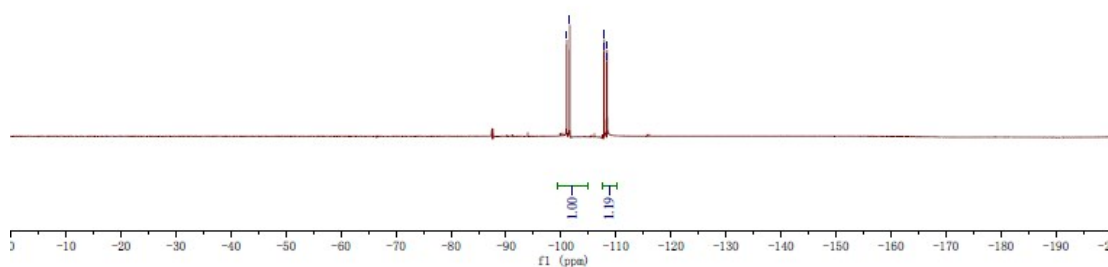
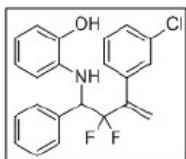
¹⁹F NMR (CDCl₃, 471 MHz)

table3
YX-3-11
7.293
7.281
7.275
7.264
7.229
7.224
7.219
7.216
6.648
6.594
6.581
6.568
6.551
6.527
5.772
5.473
4.604
4.581
4.576
4.552



¹H NMR (CDCl₃, 500 MHz)

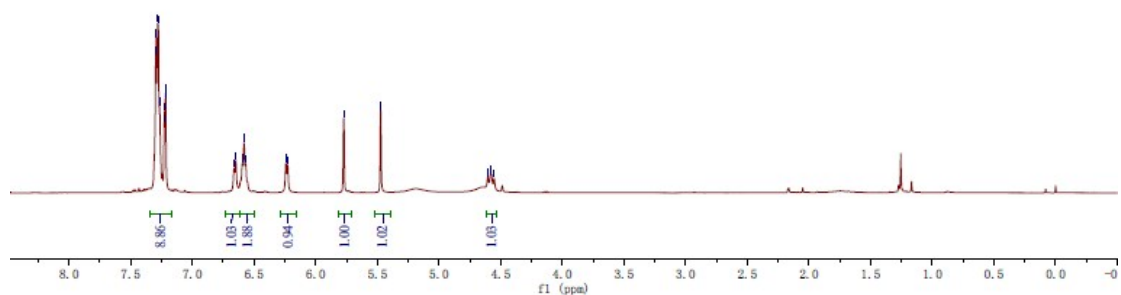
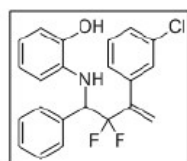


table3
YX-3-11-C

144.234
142.513
142.331
142.150
138.379
135.634
134.513
134.249
129.627
128.676
128.591
128.495
128.365
128.284
126.645
122.710
121.336
121.307
121.237
121.168
120.721
119.111
118.737
114.482
114.081
62.206
62.001
61.786



¹³C NMR (CDCl₃, 126 MHz)

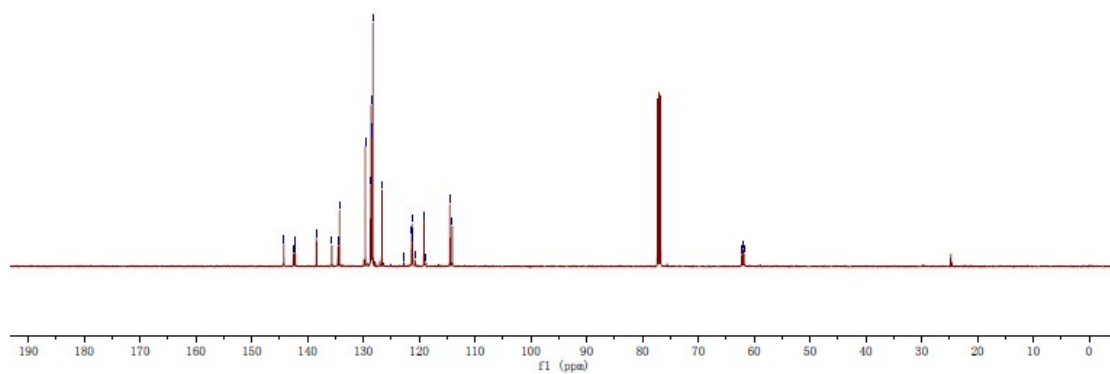
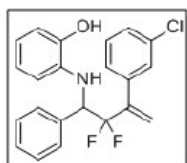


table3
YX-3-11-F



^{19}F NMR (CDCl_3 , 471 MHz)

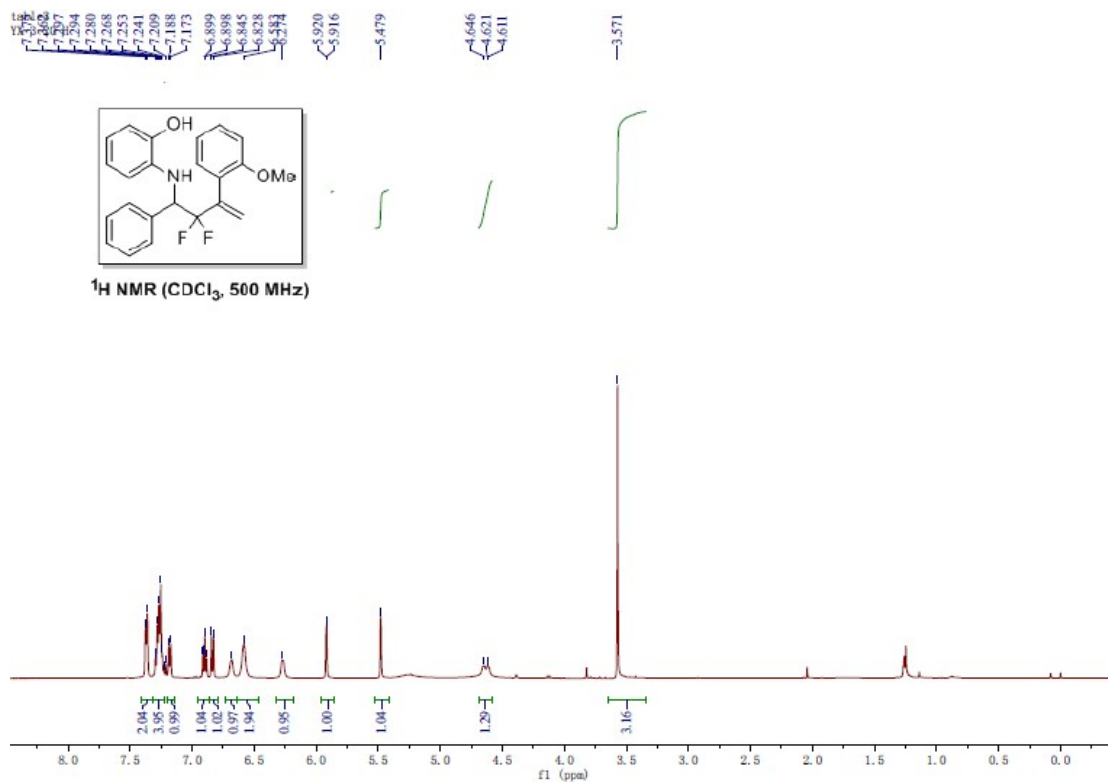
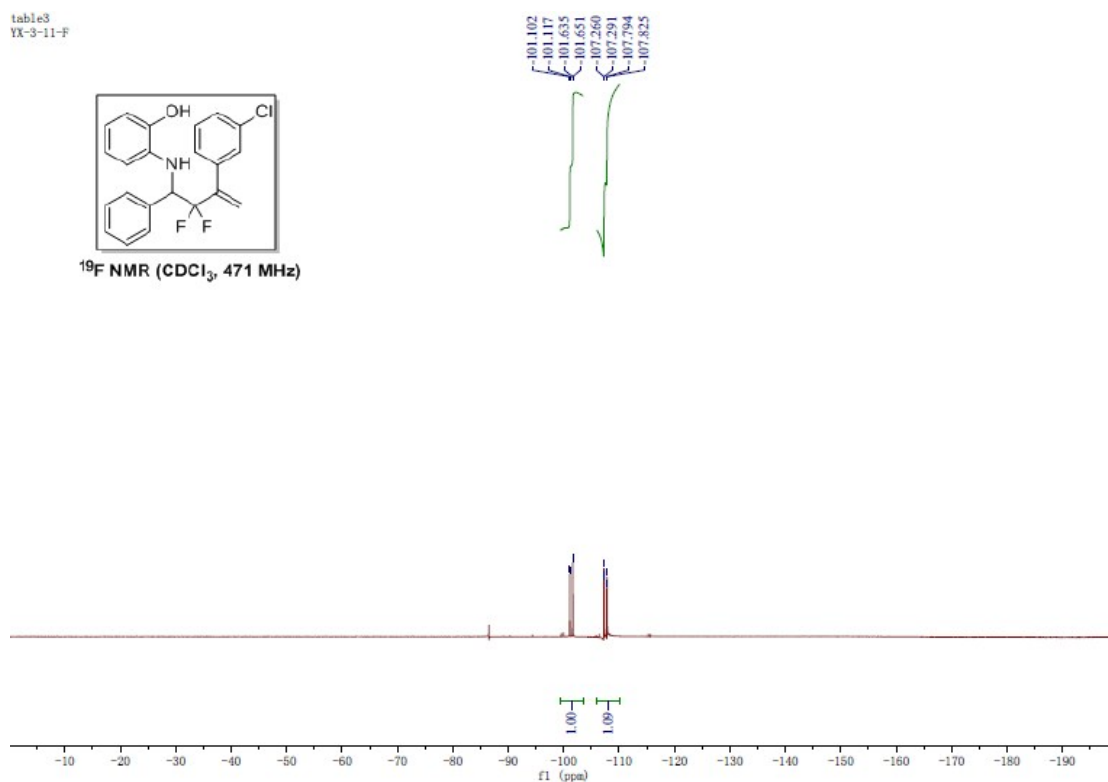
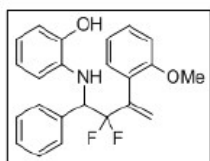


table3
YX-3-20-C



^{13}C NMR (CDCl_3 , 126 MHz)

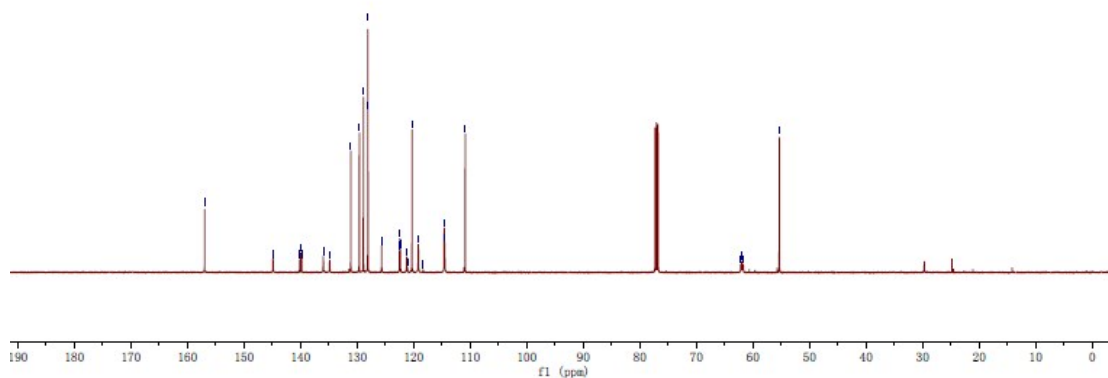
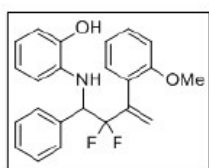


table3
YX-3-20-F



^{19}F NMR (CDCl_3 , 471 MHz)

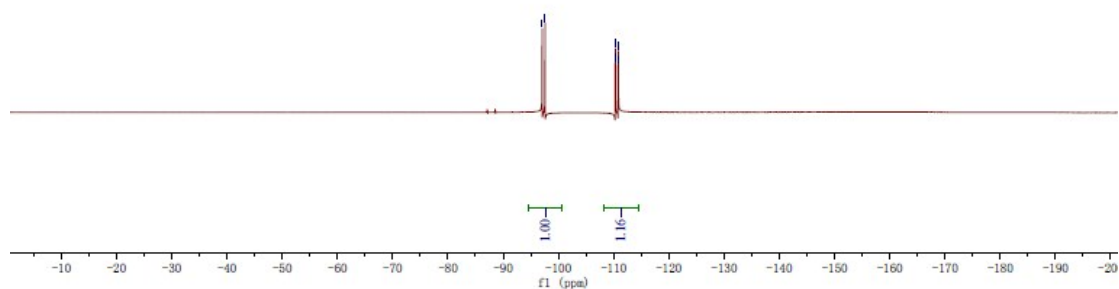
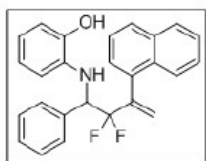


table3
YX-3-15-H



¹H NMR (CDCl₃, 500 MHz)

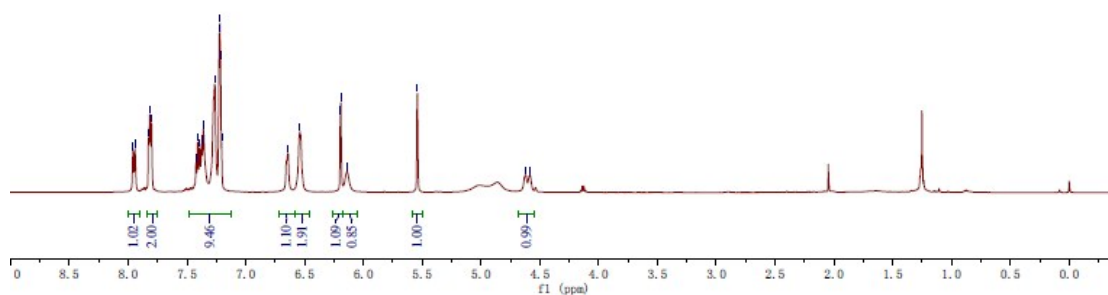
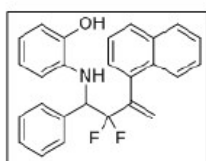
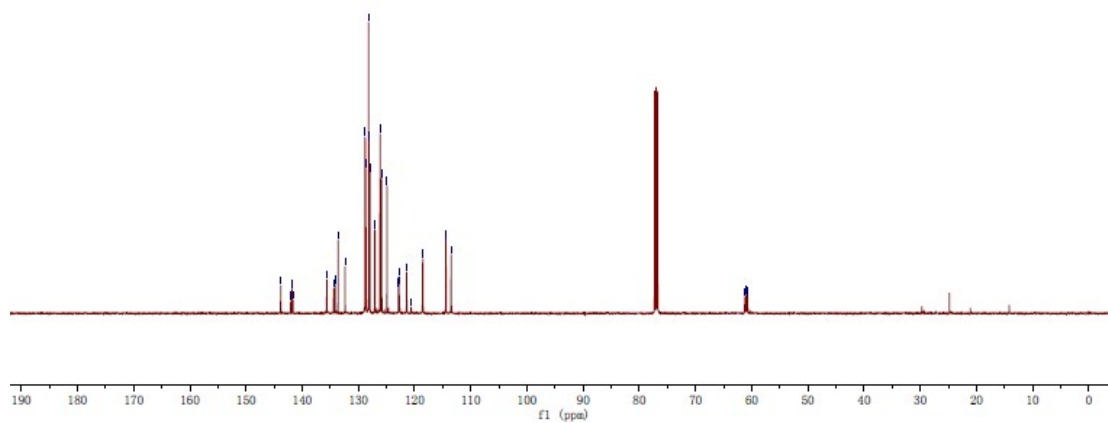


table3
YX-3-15-C



¹³C NMR (CDCl₃, 126 MHz)



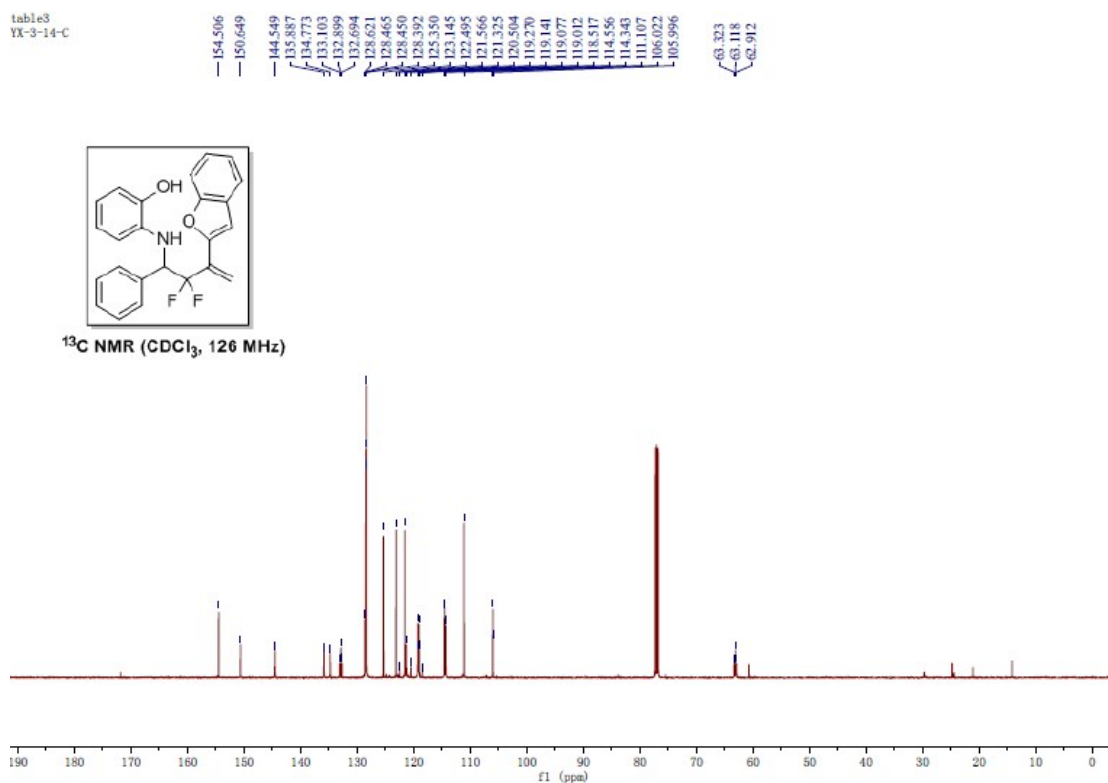
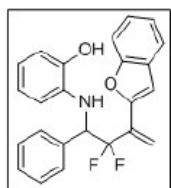
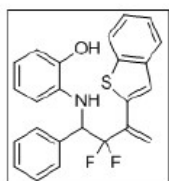
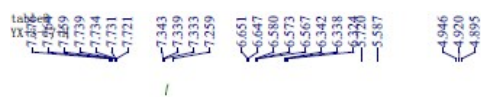
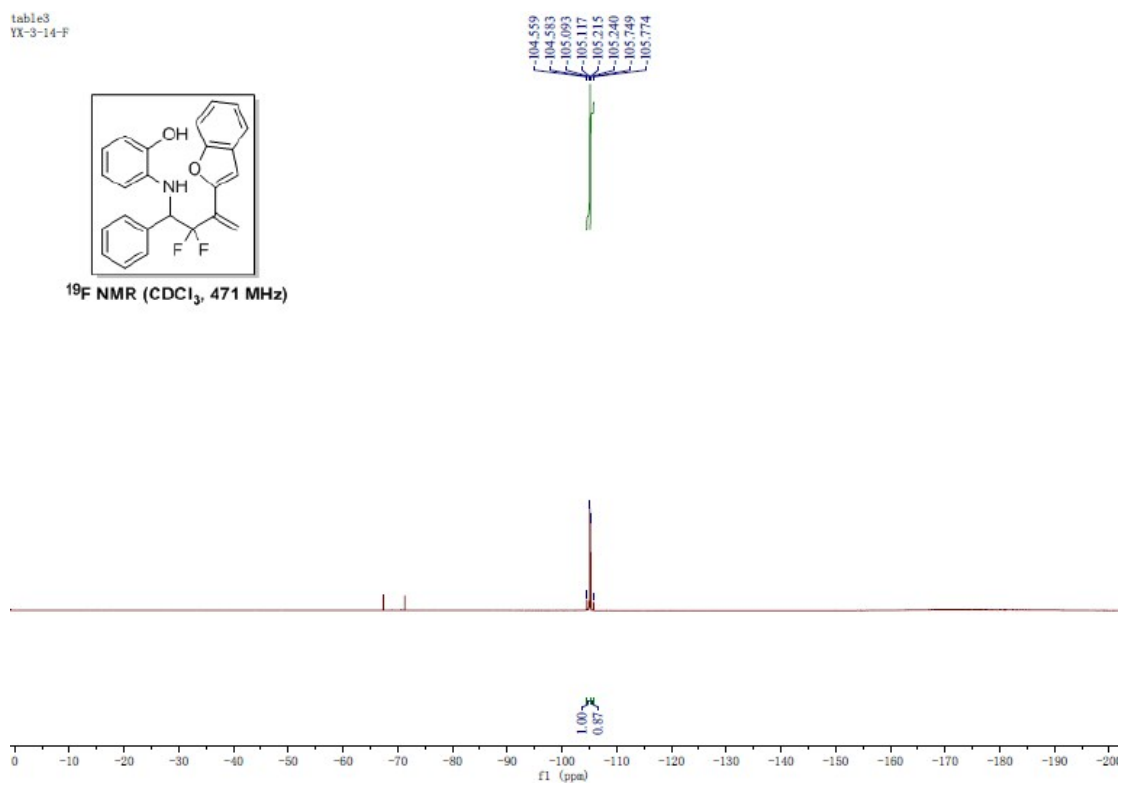


table3
YX-3-14-F



¹⁹F NMR (CDCl₃, 471 MHz)



¹H NMR (CDCl₃, 500 MHz)

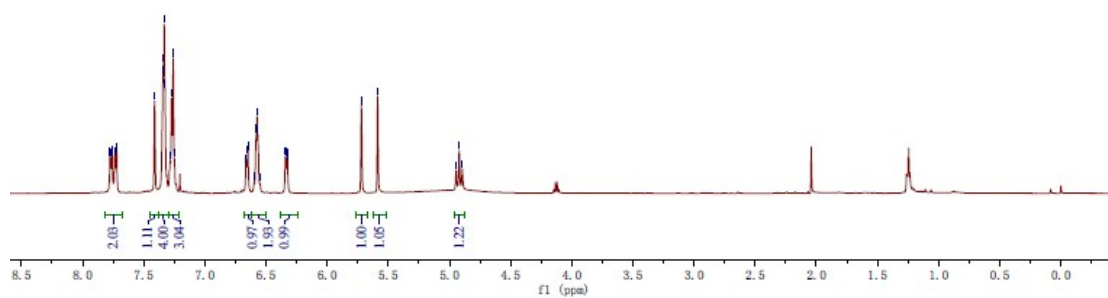
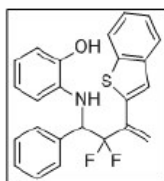


table3
YX-3-17-C

144.528
140.089
139.327
138.148
136.810
136.613
136.420
135.918
134.721
128.457
128.382
128.316
125.196
124.625
124.145
123.766
122.891
121.958
121.268
120.916
120.850
120.782
119.217
118.904
114.510
114.395

62.653
62.450
62.248



¹³C NMR (CDCl₃, 126 MHz)

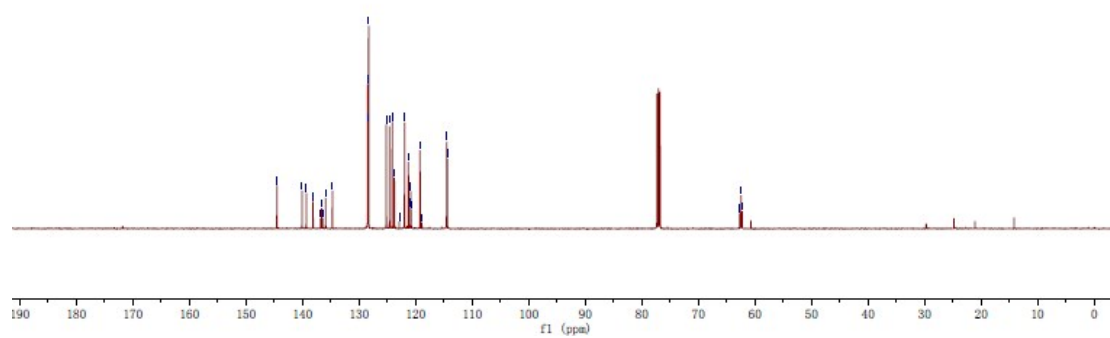
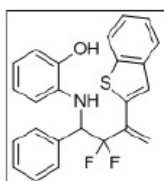


table3
YX-3-17-F

105.223
105.248



¹⁹F NMR (CDCl₃, 471 MHz)

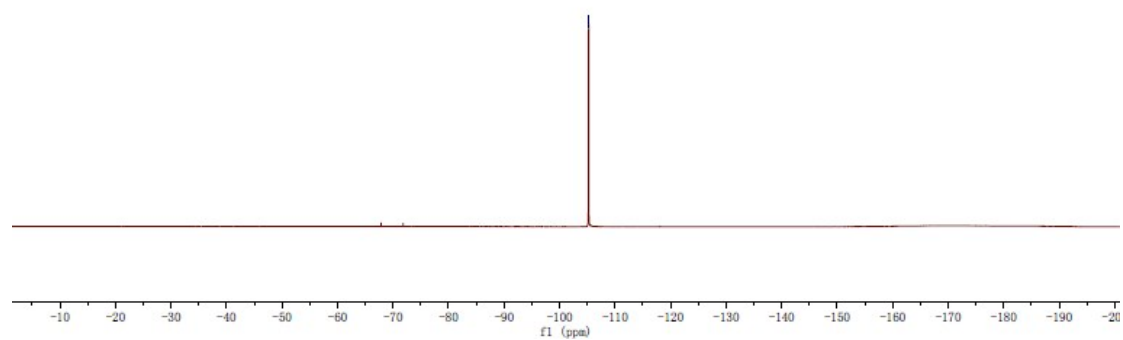
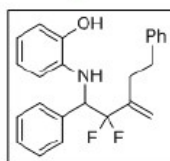


table3
YX-3-13-C

7.486
7.480
7.469
7.303
7.300
7.263
7.248
7.233
7.230
7.171
7.110
7.096
5.707
5.705
5.689
5.670
5.667
5.616
5.613
5.442
5.440
5.427
5.488
5.236
4.700
4.673
4.649
2.788
2.775
2.760
2.754
2.747
2.741
2.728
2.723
2.708
2.695
2.387
2.371
2.354
2.338
2.322
2.307
2.292
2.275
2.259
2.242



¹H NMR (CDCl₃, 500 MHz)

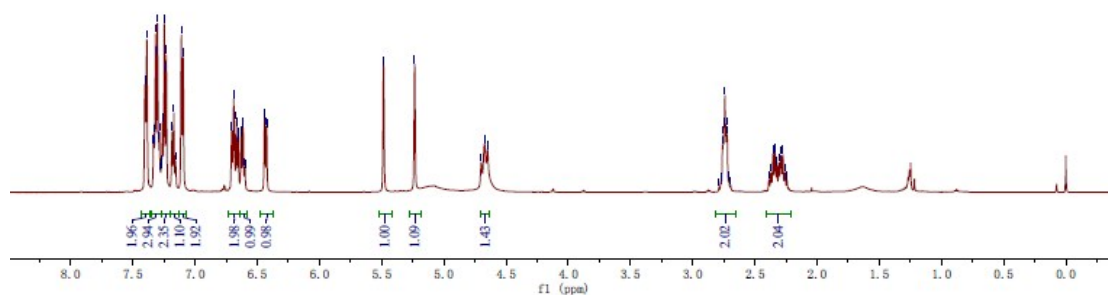
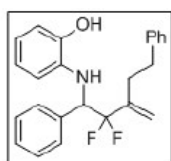


table3
YX-3-13-C

144.545
142.859
142.675
142.493
141.150
136.079
134.753
128.583
128.395
128.373
128.305
126.057
123.520
121.552
121.395
119.588
119.204
116.722
116.655
116.586
114.544
114.445

62.860
62.632
62.426

34.018
32.363



¹³C NMR (CDCl₃, 126 MHz)

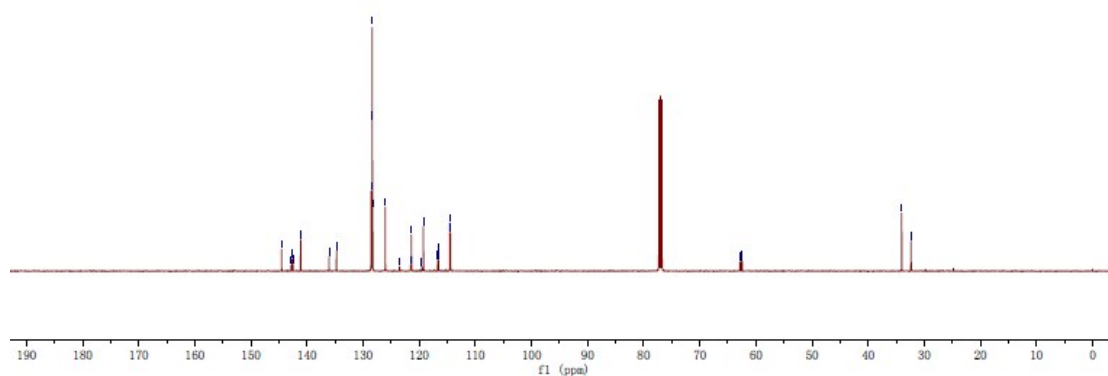
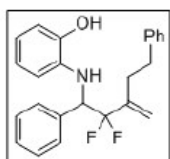
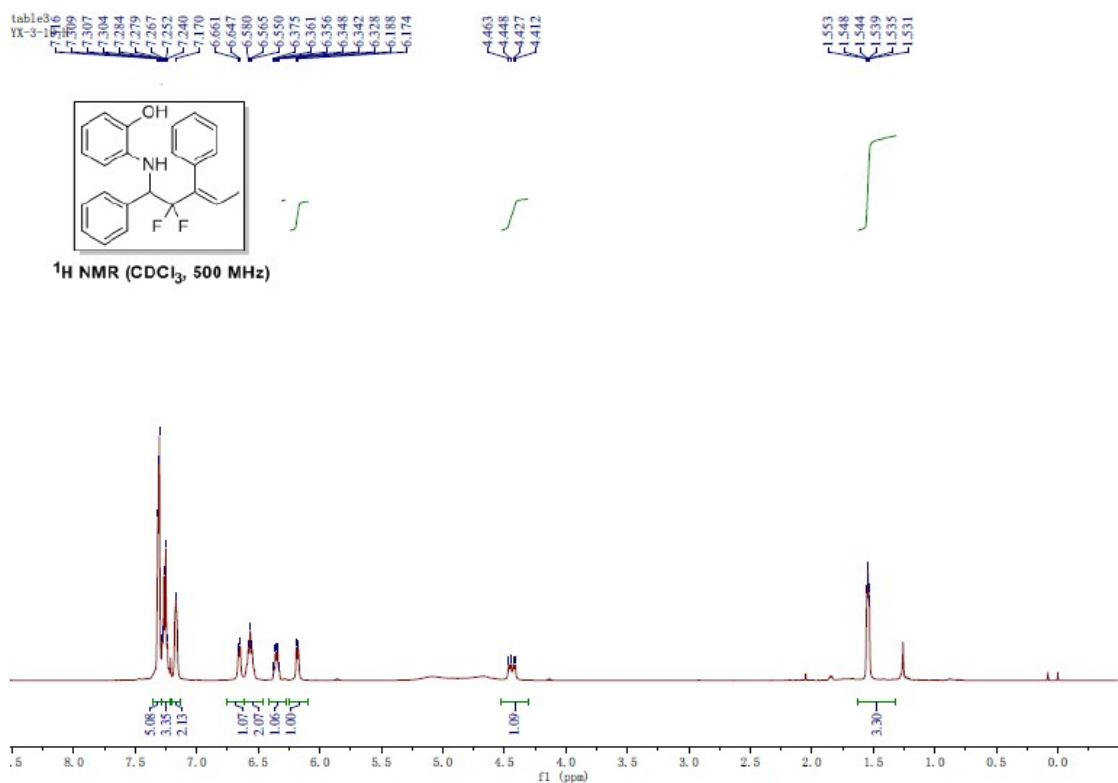
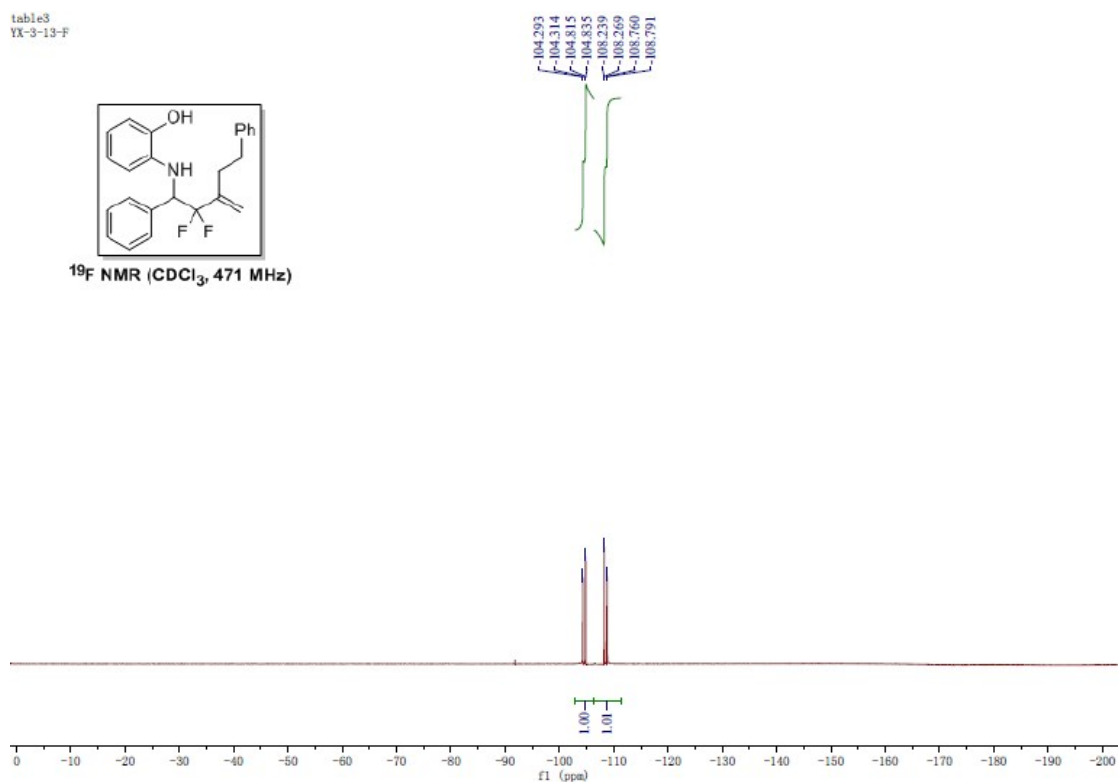


table3
YX-3-13-F



^{19}F NMR (CDCl_3 , 471 MHz)



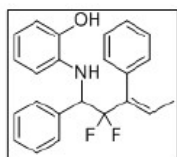
^1H NMR (CDCl_3 , 500 MHz)

table3
YX-3-19-C

144.114
136.192
136.112
136.022
135.850
134.781
134.599
130.166
129.605
129.540
129.464
128.826
128.360
128.184
128.115
127.910
122.928
121.426
120.971
118.967
118.761
114.464
113.998

61.729
61.485
61.286

14.465



¹³C NMR (CDCl₃, 126 MHz)

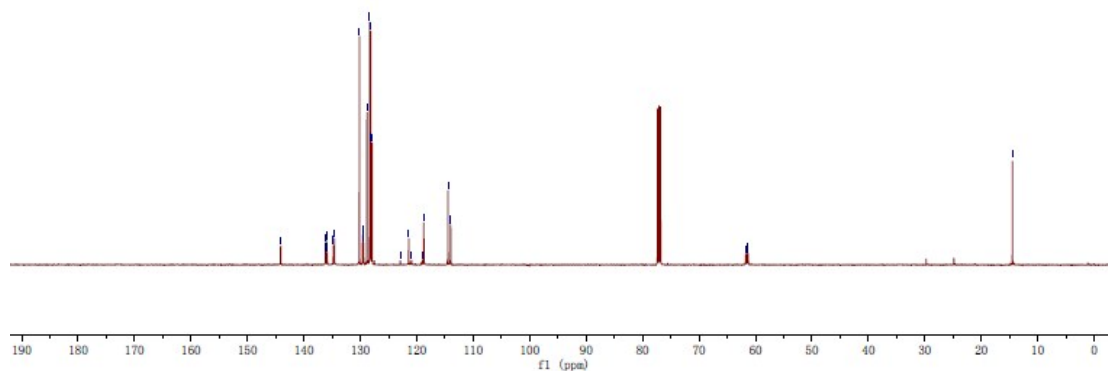
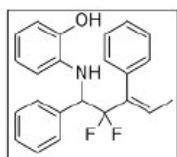
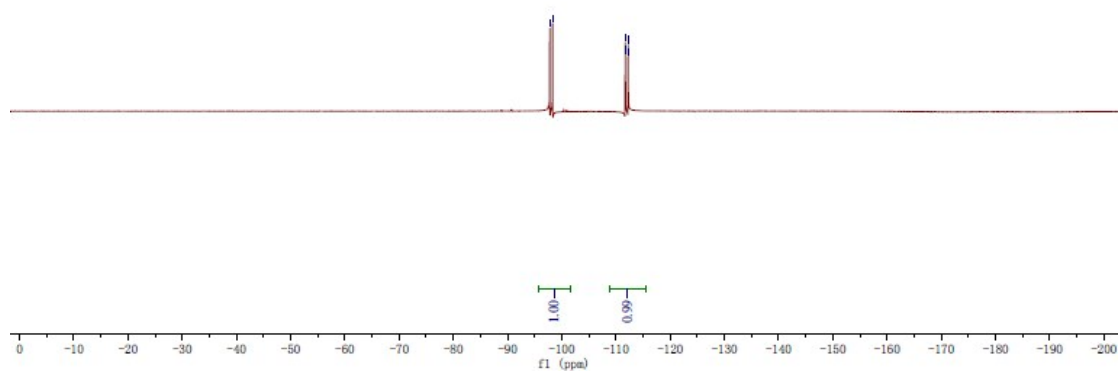


table3
YX-3-19-F



¹⁹F NMR (CDCl₃, 471 MHz)

97.787
98.310
111.693
111.731
112.216
112.254



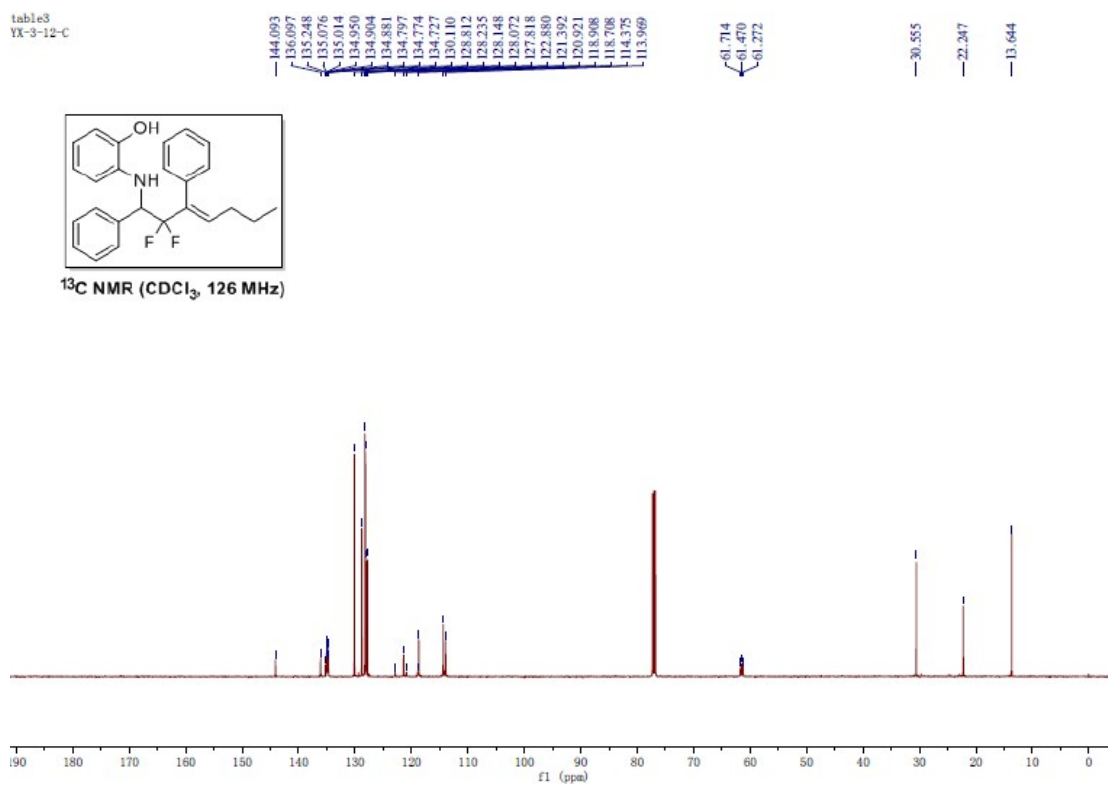
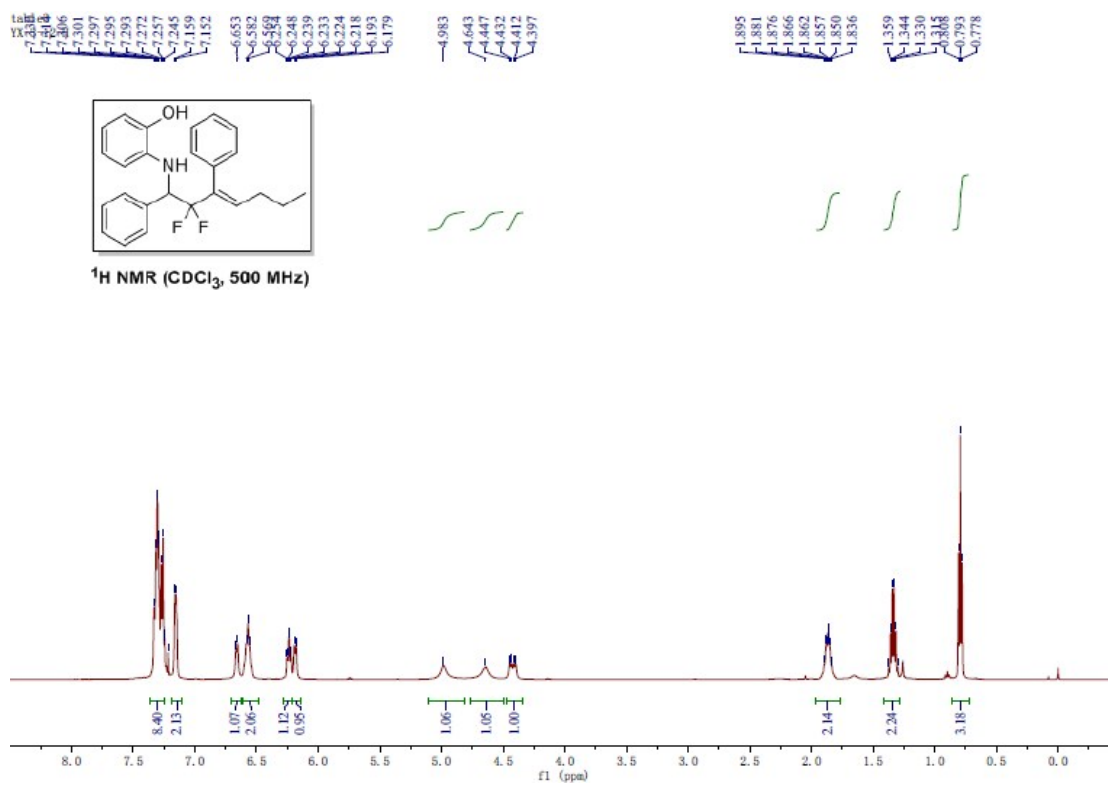
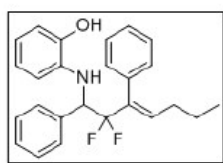
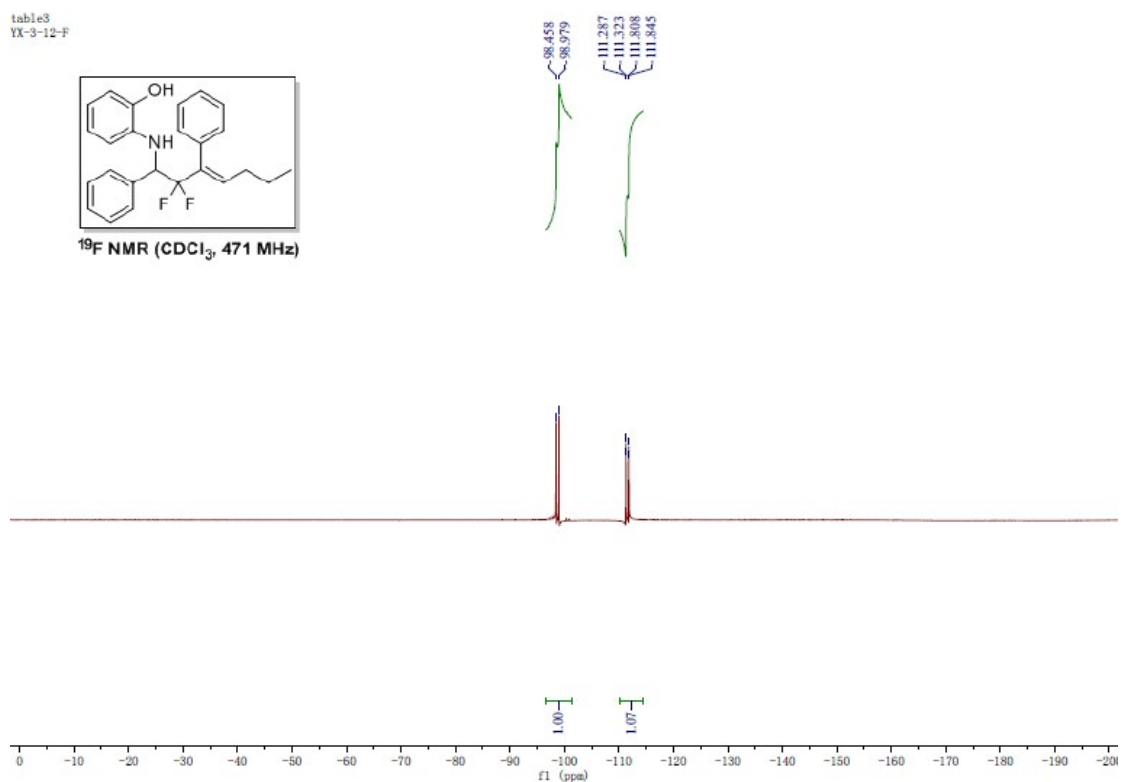


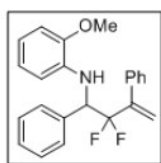
table3
YX-3-12-F



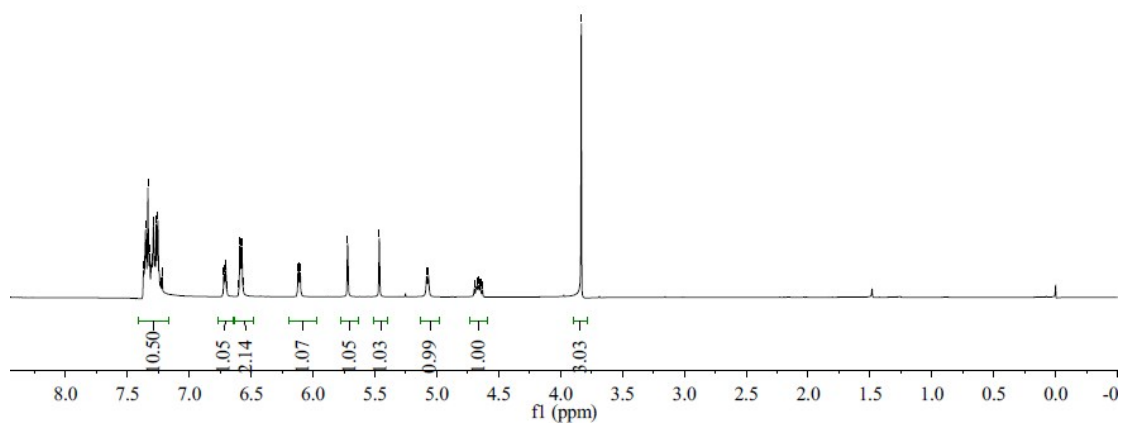
¹⁹F NMR (CDCl₃, 471 MHz)



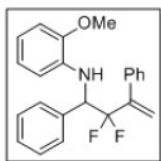
核磁
YX-3-12-F
7.365
7.346
7.334
7.320
7.302
7.289
7.267
7.253
6.592
6.580
6.573
6.121
6.114
6.106
5.464
5.082
5.067
4.697
4.677
4.666
4.650
4.646
3.832



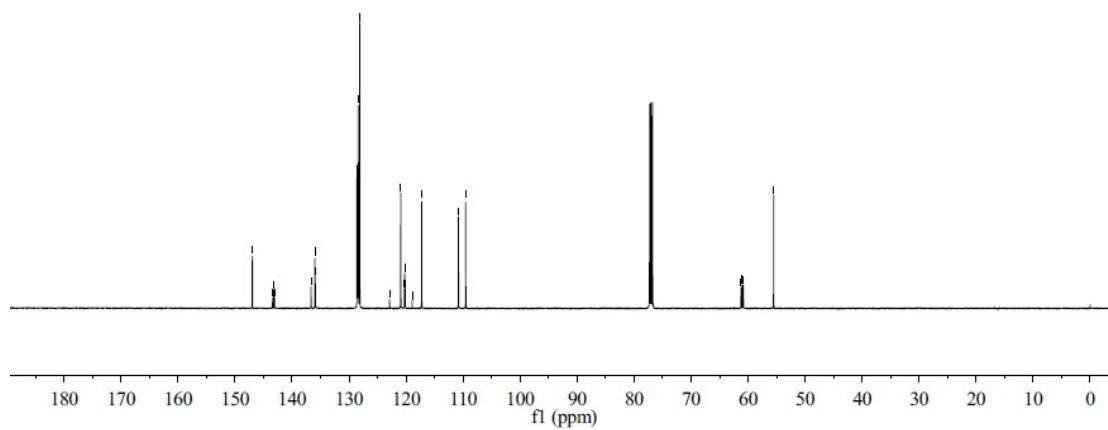
¹H NMR (CDCl₃, 500 MHz)



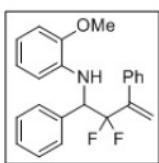
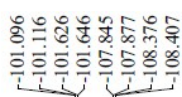
A-HYY
YX-48-2-II



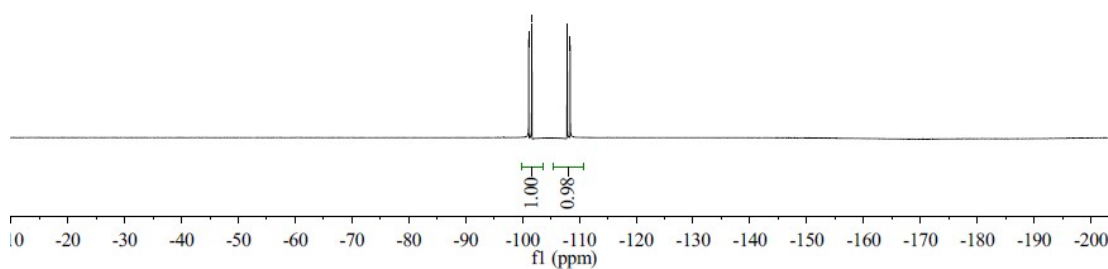
¹³C NMR (CDCl₃, 126 MHz)



核磁
YX-48-2-II



¹⁹F NMR (CDCl₃, 471 MHz)



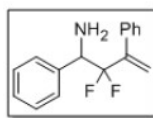
核磁
YX-53-H

7.345
7.288
7.281
7.276
7.253
7.222
7.217

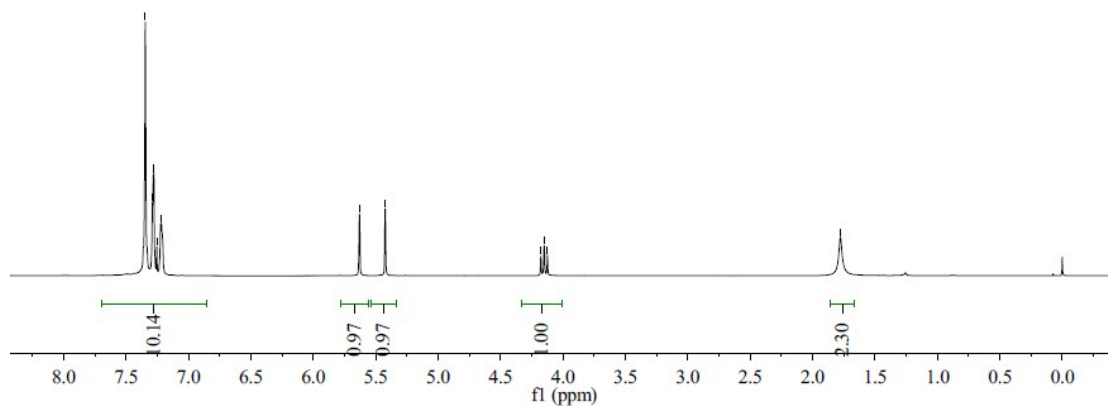
-5.629
-5.424

4.176
4.150
4.124

-1.777



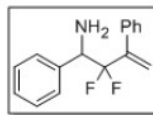
¹H NMR (CDCl₃, 500 MHz)



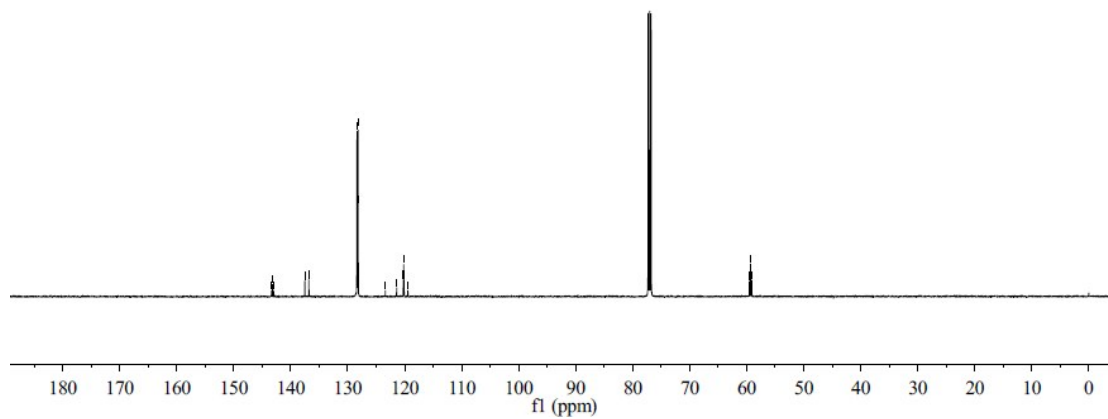
A-HYY
YX-53-F

143.362
143.184
143.005
137.528
137.499
136.809
128.389
128.338
128.296
128.182
128.145
123.385
121.411
120.249
120.178
120.107
119.433

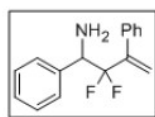
59.529
59.322
59.114



¹³C NMR (CDCl₃, 126 MHz)



核磁
YX-53-C



^{19}F NMR (CDCl_3 , 471 MHz)

104.805
104.830
105.326
105.351
107.667
107.696
108.189
108.218

