

Supporting Information

Enantioselective Synthesis of Fluoroalkyl-substituted *syn*-Diamines by the Asymmetric *gem*-Difunctionalization of 2,2,2-Trifluorodiazoethane

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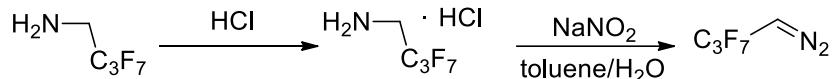
1. General information.

Nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR and ¹⁹F NMR) were recorded with Bruker Avance III 400 (400 MHz, ¹H at 400 MHz, ¹³C at 100 MHz, ¹⁹F NMR at 376MHz) or Bruker Ascend TM 500 (500 MHz, ¹H at 500 MHz, ¹³C at 125 MHz, ¹⁹F NMR at 470MHz) respectively, using CDCl₃ as reference standard (δ 7.26 ppm) for ¹H NMR and (δ 77.0 ppm) for ¹³C NMR. HRMS (ion trap) were recorded using ESI (SHIMADZU LCMS-IT-TOF or Waters-Synapt-HDMS). Melting points were uncorrected (METTLER TOLEDO MP50). Enantioselectivities were determined with HPLC using Chiralpak IC, AD-H columns. The racemic standards used in HPLC studies were prepared according to the general procedure using racemic BINOL-derived phosphoric acid catalyst **rac-PPA**.

Unless otherwise noted, apart from distilled toluene, all solvents and reagents were obtained commercially and used directly without further purification. Chiral BINOL-derived phosphoric acids **6** were prepared according to the literature procedures.¹ 4 Å molecular sieve was dried in a Muffle furnace at 250 °C over 5 h. 2,2,2-Trifluorodiazethane **1a** and perfluorodiazopropane **1b** were synthesized by following literature procedure.² 2,2-Difluorodiazethane **1d** was synthesized by following literature procedure.³ Pre-coated silica gel plates GF-254 were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (300-400 mesh).

2. General experimental procedure

General procedure for the synthesis of perfluorodiazobutane **1c**:



Polyfluoroamine (5 mmol) and H₂O (5 mL) were added to a 50 mL round-bottom flask and stirred at room temperature. Then 1 mL HCl (aq, 6N) was added to the above mixture and stirred for 2h at room temperature and then the mixture was placed at -20 °C until it was completely frozen. Then the white solid, polyfluoride ammonium salts, was obtained in equivalent yield after the frozen

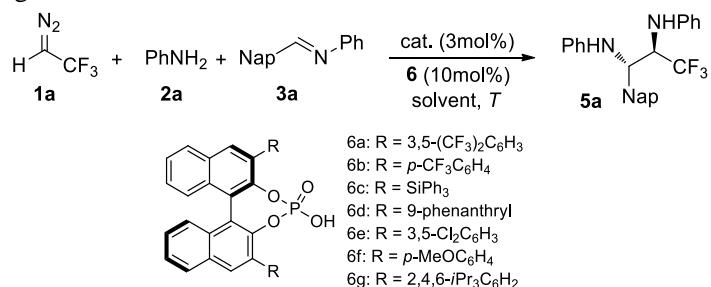
product was treated by freeze dryer. Polyfluoride ammonium salts (5 mmol), sodium nitrite (6.25 mmol) and toluene (10 mL) were added to a 50 mL round-bottom flask and then stirred for 0.5 h at 0 °C. Then 1.5 mL of H₂O was added to the above mixture and stirred for 2 h at 0 °C. After the aqueous phase was removed, the organic phase (diazo solution in toluene) was stored in the freezer (-20 °C) and was used directly in key reactions. The concentration of the above diazo was determined by following literature² procedure as about 0.5 M.

General procedure for the catalytic asymmetric *gem*-difunctionalization of fluoroalkyl-substituted diazo compound with aromatic amine and imine (in situ generation).

Under Ar atmosphere, a mixture of porphyrin iron complex (3 mol%, 0.006 mmol), **6a** (10 mol%, 0.02 mmol), aromatic amines **2** (0.42 mmol, 2.1 equiv.), aromatic aldehydes **4** (0.2 mmol, 1.0 equiv.) and 4 Å M.S. (300mg) was stirred in distilled toluene (2 mL) at -10 °C for 20 min., then a solution of **1** (0.3 mmol, 1.5 equiv.) in distilled toluene (1 mL) was added slowly to the above mixture. The progress of the reaction was monitored by TLC. After the reaction was complete, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 20/1-10/1) to give the pure product **5**. Without addition of the 4 Å M.S., and toluene instead of distilled toluene, the reaction was completed in 10 min.. In contrast, under the addition of the 4 Å M.S., distilled toluene as the solvent, the reaction needed 30 min. to be completed by TLC.

3. Reaction conditions optimization

Table S1: Screening of reaction conditions^[a]

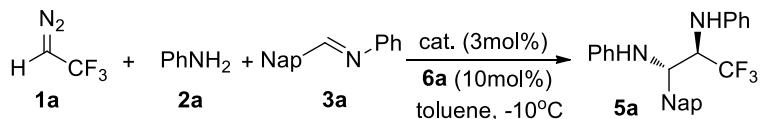


Entry	Cat.	6	Solvent	T[°C]	Yield[%] ^[b]	d.r. ^[c]	e.r. ^[d]
1	Rh ₂ (OAc) ₄	-	DCM	25	-	-	-

2	Rh ₂ (esp) ₂	-	DCM	25	-	-	-
3	FeTPP ^{Cl}	-	DCM	25	75	>95:5	50:50
4	FeTPP ^{Cl}	6a	DCM	25	87	>95:5	85:15
5	FeTPP ^{Cl}	6b	DCM	25	82	>95:5	70:30
6	FeTPP ^{Cl}	6c	DCM	25	79	>95:5	55:45
7	FeTPP ^{Cl}	6d	DCM	25	76	>95:5	55:45
8	FeTPP ^{Cl}	6e	DCM	25	81	>95:5	70:30
9	FeTPP ^{Cl}	6f	DCM	25	87	>95:5	75:25
10	FeTPP ^{Cl}	6g	DCM	25	83	>95:5	65:35
11	FeTPP ^{Cl}	6a	DCM	0	85	>95:5	90:10
12	FeTPP ^{Cl}	6a	DCM	-10	83	>95:5	92:8
13	FeTPP ^{Cl}	6a	DCM	-20	76	>95:5	88:12
14	FeTPP ^{Cl}	6a	DCE	-10	86	>95:5	89:11
15	FeTPP ^{Cl}	6a	CHCl ₃	-10	83	>95:5	80:20
16	FeTPP ^{Cl}	6a	toluene	-10	84	>95:5	95:5

[a] A mixture of catalyst (3mol%, 0.006 mmol), chiral PPA (10mol%, 0.02 mmol), aniline **2a** (0.22 mmol, 1.1 equiv.), imine **3a** (0.2 mmol, 1.0 equiv.) was stirred in the corresponding solvent (2 mL) at the corresponding temperature, then a solution of **1a** (0.3 mmol, 1.5 equiv.) in the corresponding solvent (1 mL) was added slowly to the above mixture. [b] Isolated yields. [c] Determined by ¹H NMR analysis of crude reaction mixture. [d] Determined by chiral HPLC analysis of the major diastereomer.

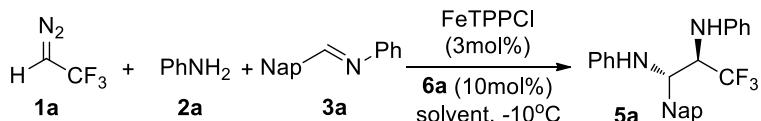
Table S2: Porphyrin iron complexes screening^[a]



Entry	Cat.	Yield[%] ^[b]	d.r. ^[c]	e.r. ^[d]
1	FeTPP ^{Cl}	84	>95:5	95:5
2	Fe(<i>p</i> -MeTPP) ^{Cl}	83	>95:5	94:6
3	Fe(<i>p</i> -OMeTPP) ^{Cl}	81	>95:5	91:9
4	Fe(<i>p</i> -CITPP) ^{Cl}	85	>95:5	90:10
5	Fe(TPPF ₂₀) ^{Cl}	83	>95:5	88:12

[a] A mixture of porphyrin iron complex (3mol%, 0.006 mmol), **6a** (10mol%, 0.02 mmol), aniline **2a** (0.22 mmol, 1.1 equiv.), imine **3a** (0.2 mmol, 1.0 equiv.) was stirred in toluene (2 mL) at -10 °C, then a solution of diazo **1a** (0.3 mmol, 1.5 equiv.) in toluene (1 mL) was added slowly to the above mixture. [b] Isolated yields. [c] Determined by ¹H NMR analysis of crude reaction mixture. [d] Determined by chiral HPLC analysis of the major diastereomer.

Table S3: Aromatic hydrocarbon solvent screening^[a]



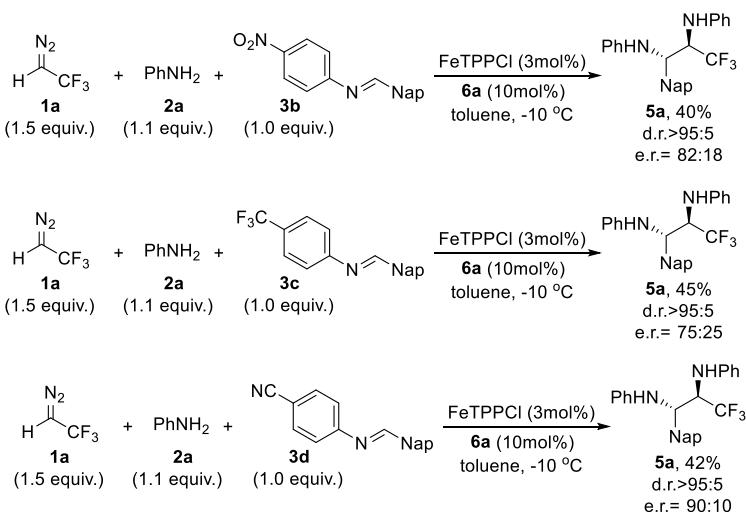
Entry	Solvent	Yield[%] ^[b]	d.r. ^[c]	e.r. ^[d]
1	toluene	84	>95:5	95:5

2	xylene	60	>95:5	80:20
3	<i>p</i> -xylene	50	>95:5	80:20
4	chlorobenzene	20	>95:5	55:45
5	anisole	<5	-	-
6	fluorobenzene	80	>95:5	93:7
7	(trifluoromethyl)benzene	78	>95:5	86:14

[a] A mixture of FeTPP^{Cl} (3mol%, 0.006 mmol), **6a** (10mol%, 0.02 mmol), aniline **2a** (0.22 mmol, 1.1 equiv.), imine **3a** (0.2 mmol, 1.0 equiv.) was stirred in the corresponding solvent (2 mL) at -10 °C for 20min., then a solution of diazo **1a** (0.3 mmol, 1.5 equiv.) in the corresponding solvent (1 mL) was added slowly to the above mixture. [b] Isolated yields. [c] Determined by ¹H NMR analysis of crude reaction mixture. [d] Determined by chiral HPLC analysis of the major diastereomer.

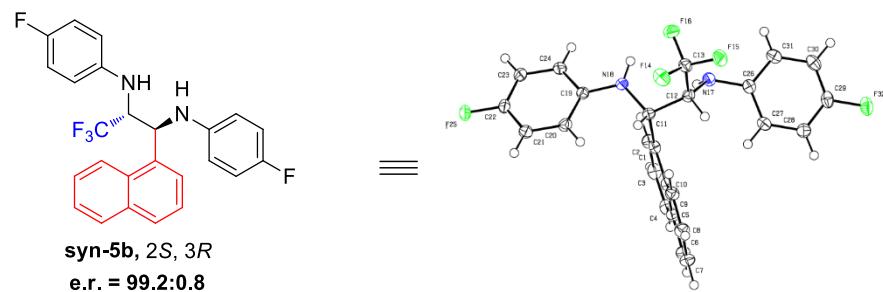
4. Amine exchange reaction of imines:

With the optimum reaction conditions in hand, we explored the scope of the multi-component reaction by investigating imines **3**. We found the amine exchange reaction would undergo rapidly between aniline **2a** and different imines under standard conditions. Therefore, we used in situ preparation of imine to avoid side reactions.



5. X-Ray structure of product **5b** (CCDC 1918088):

The product **5b** (e.r. = 98:2) was recrystallized from n-hexane to give the colorless flaky crystal, of which e.r. value increased to 99.2:0.8.



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Bond precision: C-C = 0.0031 Å          Wavelength=1.54184

Cell:           a=8.4300(1)      b=11.6177(1)      c=10.9180(1)
               alpha=90          beta=108.357(1)     gamma=90
Temperature:   100 K

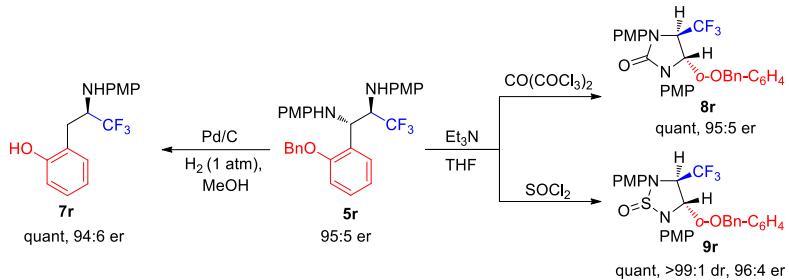
Calculated                               Reported
Volume          1014.866(18)        1014.865(18)
Space group     P 21                  P 1 21 1
Hall group      P 2yb                P 2yb
Moietiy formula C25 H19 F5 N2       C25 H19 F5 N2
Sum formula     C25 H19 F5 N2       C25 H19 F5 N2
Mr              442.42              442.42
Dx,g cm-3      1.448               1.448
Z               2                   2
Mu (mm-1)       1.004               1.004
F000            456.0               456.0
F000'           457.69              457.69
h,k,lmax        10,14,13          10,14,13
Nref            4291 [ 2255]        4176
Tmin,Tmax      0.786,0.904       0.617,1.000
Tmin'           0.740

Correction method= # Reported T Limits: Tmin=0.617 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.85/0.97          Theta(max)= 76.735
R(reflections)= 0.0317( 4143)       wR2(reflections)= 0.0857( 4176)
S = 1.037                           Npar= 289

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6. Product derivatizations.



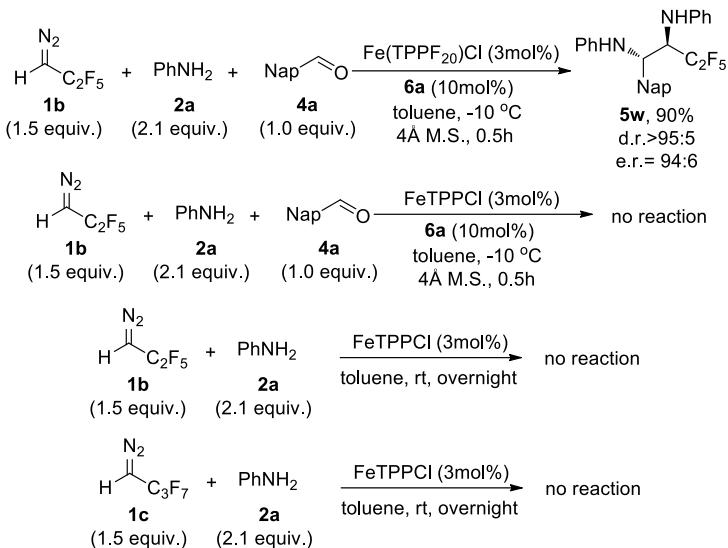
General procedure for compound **7r:** To a solution of 1.0 mmol **5r** in 5mL of MeOH was added 10% Pd/C under hydrogen atmosphere. Then, the mixture was stirred at room temperature overnight. After the reaction was completed, the residue was purified by silica gel chromatography to give the product **7r** in quantity yield.

General procedure for compound **8r:** To a solution of 1.0 mmol **5r** in 5mL of THF was added 0.5 mL Et_3N . Then the 1.2 mmol triphosgene gave was added to the above mixture at 0 °C. After 0.5h, the reaction was completed by TLC. The residue was purified by silica gel chromatography to give the product **8r** in quantity yield.

General procedure for compound **9r:** To a solution of 1.0 mmol **5r** in 5mL of THF was added 0.5 mL Et_3N . Then the 1.2 mmol thionyl chloride was added to the above mixture at 0 °C. After 0.5h, the reaction was completed by TLC. The residue was purified by silica gel chromatography to give the product **9r** in quantity yield.

7. The properties of polyfluoro-substituted diazo compounds.

Under the standard conditions the perfluorodiazopropane and perfluorodiazobutane remained without any conversion, since the electron withdrawing effect by multiple fluorine atoms. Moreover, the reaction of N-H insertion of the perfluorodiazopropane or perfluorodiazobutane didn't work at room temperature under FeTPP_{Cl} catalysis and the diazo compound remained. Once Fe(TPPF₂₀)Cl was substituted for FeTPP_{Cl} as the catalyst, the corresponding desired product **5w** was obtained in excellent yield at the same conditions.



8. DFT calculations of N-H insertion of fluoroalkyl-substituted diazo compounds under FeTPPCl.

From previous work on iron porphyrin carbenes employed functionals, we will find UB3LYP suitable to calculate these reactions. All the calculations were carried out with the Gaussian 09 package. Geometry optimization and frequency analyses were performed with the combination of 6-31G(d) and LANL2TZ(f). The LANL2TZ(f) basis set with ECP was used for Fe, and the 6-31G(d) was used for other atoms. Frequency analysis was conducted to verify the stationary points to obtain the thermodynamic energy corrections. Furthermore, intrinsic reaction coordinate calculations have been employed to confirm the transition structures connecting reactants and products. Single point energies were performed at the UB3LYP/Def2-TZVP basis set for all atoms using SMD solvation model (solvent = dichloroethane and chloroform) with the Grimme's D3 dispersion corrections. The porphyrin ligand was modeled as porphine in order to simplified calculation model and the carbene used was CHCF₃.

We use the aniline to achieve the N-H insertion reaction and discuss the details of how to execute the process of hydrogen atom transfer from the aniline to the carbene. The ammonium ylide can be obtained easily through the nucleophilic attack as previous studies and this reaction is exergonic by 15.5 kcal/mol. Differ from the system calculated before, the ammonium ylide cannot transfer to the enamine intermediate owing to the -CF₃ substituent. A study of the 1,2-proton shift has been done to give the fact that the energy barrier of 35.8kcal/mol so that we use the water molecule to facilitate the transformation. Formation of TS-2 is favored (endergonic by 18.0 kcal/mol) and we

can assume that the iron-associated ylide *via* the water-assisted [1,2]-H shift may occur to some extent. For comparison, we calculated the free ylide way which has a moderate value of 7.9 kcal/mol dissociated from the iron porphyrin catalyst. As shown in Figure 2, the overall activation barrier of 24 kcal/mol can be calculated of the [1,2] proton shift. This well illustrates water molecular can reduce the transition state energy. In the same way, we calculated the energy required the H₂O associated ylide way. Therefore, the H₂O plays an important role in the whole process. At the same computer level, the metal-assisted proton shift's relative free energy is 4.5 kcal/mol higher than the free ylide way. Given the energy barrier of 13.5kcal/mol, the free ylide way became much easier at room temperature.

To confirm our conjecture about the rationality of existence of free ylide, the DFT calculation of trifluoromethyl metal carbene's N-H insertion were conducted in detail. As shown in Figure S1, the free ylide's generation was a suitable path to give the N-H insertion's product and the H₂O played an important role by hydrogen bonding to assist free ylide to produce the N-H insertion product. Inspired by the results of the above DFT calculations, and in combination with the experimental results, the pivotal process of the multi-component reactions might similar to the above reaction process, and the H₂O competed with chiral PPA to speed up the reaction rate and reduce enantioselectivity of the reaction in such the asymmetric transformation.

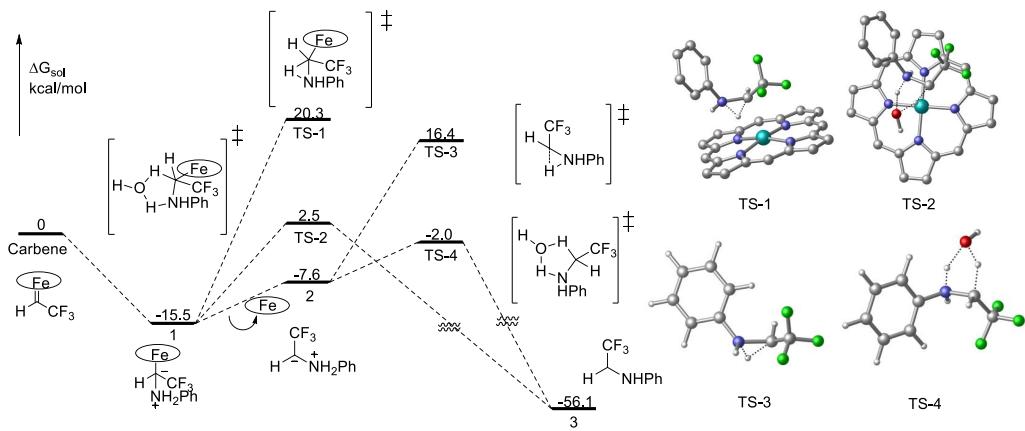
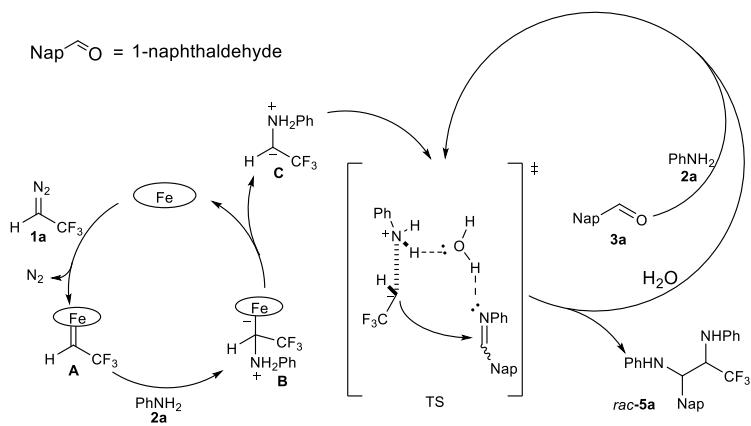


Figure S1. Computed free energy profiles for possible pathways of the [1,2]-proton shift in DCE for the iron porphyrin carbonid insertion into the N-H bond of aniline at room temperature. Nucleophilic attack and hydrogen atom transfer was studied on the triplet surface.

The H₂O generated from formation of imine, competed with chiral PPA to speed up the reaction rate and reduce enantioselectivity of the reaction in such the asymmetric transformation.



To probe the role of the unique physicochemical properties of the fluorine atoms in stabilizing the active intermediates, N-H insertion reactions of 2,2,2-trifluorodiazooethane (**1a**) and 2,2-difluorodiazooethane (**1d**) were conducted. The corresponding computed transition state energies of the different fluoroalkyl-substituted intermediates were determined by DFT calculations as shown in Figure S2. Although this is not the rate-determining step of the N-H insertion reaction, the transition state energies of the trifluoro-substituted active intermediates are clearly lower than that of the difluoro-substituted ones. As shown in Figure S2, trifluoromethyl-substituted metal carbene's relative free energy is 1.5 kcal/mol lower than difluoromethyl substituted metal carbene. Besides, trifluoromethyl substituted ammonium ylide's relative free energy is 1.0 kcal/mol lower than difluoromethyl substituted ammonium ylide. The results of the DFT calculations provide reasonable support that the fluorine atoms stabilize the active intermediates specifically by the precise figures.

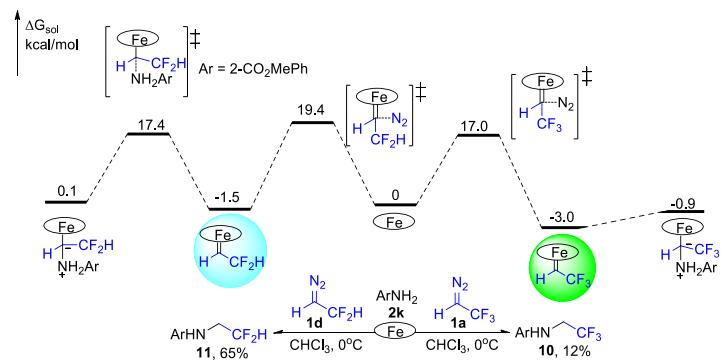


Figure S2. Computed transition state energies for the N-H insertion of different fluoroalkyl-substituted carbenes in CHCl_3 at 0°C .

The 2,2-difluorodiazooethane was very unstable in alkaline environments, which was discovered by Mykhailiuk's group. Due to its suitable nucleophilic and alkaline properties, methyl 2-

aminobenzoate (**2k**) was selected as the best nucleophile for N-H insertion reaction of different fluoroalkyl-substituted carbenes by screening conditions as shown in Table S5.

The 2,2-difluorodiazooethane was very unstable under FeTPPCl catalysis in alkaline environments to release nitrogen rapidly. On the other hand, the difluoro-substituted diazo compound had been catalytically decomposed before the nucleophilic attack of aromatic amines with weak nucleophilic ability to the metal carbene.

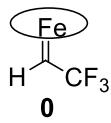
Table S5: Screening of aromatic amines for N-H insertion of fluoroalkyl-substituted diazo compounds.

Entry	Ar	T[°C]	Solvent	N-H insertion of 1a	N-H insertion of 1d
1	Ph	0	CHCl ₃	88%	-
2	4-ClC ₆ H ₄	0	CHCl ₃	81%	-
3	4-CNC ₆ H ₄	0	CHCl ₃	<5%	-
4	4-NO ₂ C ₆ H ₄	0	CHCl ₃	0	-
5	2,4-(COOMe) ₂ C ₆ H ₃	0	CHCl ₃	0	-
6	3,4-(COOMe) ₂ C ₆ H ₃	0	CHCl ₃	<5%	-
7	2-COOMeC ₆ H ₃	0	CHCl ₃	12%	65%

Reaction conditions: a mixture of 1 mmol aromatic amines and FeTPPCl 0.03mmol was stirred in CHCl₃ (4mL) at 0 °C, then a solution of 1.5 mmol **1a** and **1d** in CHCl₃ (20 mL) was added slowly to the above mixture and the mixture was stirred for overnight. Yield of the isolated product is reported.

Computational Details:

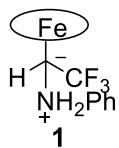
All the calculations were carried out with the Gaussian 09 package.⁴ Geometry optimization and transition states involved were performed at the UB3LYP functional,⁵ with the LANL2TZ(f) basis set⁶ with ECP for iron and the 6-31G(d) basis set⁷ for all other atoms. Frequency analysis was conducted at the same level to verify the stationary points to be an energy minimum or saddle points. Single point energies were calculated using the Def2-TZVP basis set⁸ for all atoms. Solvent effects were computed by the SMD⁹ solvation model in dichloroethane and chloroform. Dispersion corrections were computed with the Grimme's D3 method.¹⁰



carbene
triplet

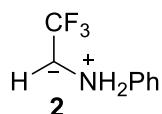
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N	0.01213800	1.98186500	-0.55459100
H	0.97240500	5.19092100	-0.45447900
C	-1.16290800	2.67604400	-0.73669000
C	-0.92406700	4.09718500	-0.71875600
H	-1.69064800	4.85078200	-0.84693500
C	0.41059700	4.26799700	-0.52098600
C	-2.40592400	2.09896900	-0.93275300
H	-3.25477600	2.76119400	-1.07065800
N	-1.68903300	-0.24993800	-0.80880200
C	-2.38093900	-1.44232500	-0.92319400
C	-3.77701900	-1.19785400	-1.16049000
H	-4.52246800	-1.97177200	-1.29079400
C	-3.93967500	0.15316300	-1.18940400
H	-4.84782200	0.72087000	-1.34707300
C	-2.64355300	0.73536900	-0.96704200
C	2.33580300	2.70543300	-0.24279900
H	2.99688700	3.56156000	-0.15073800
H	5.39527600	-0.71342500	0.13829000
C	4.47964400	-0.14753900	0.02207400
C	3.17329700	-0.73009300	-0.14049900
H	5.06320200	1.97891300	0.08457000
N	2.21657100	0.25267400	-0.27984100
C	2.90603400	1.44407200	-0.18406600
C	4.31326100	1.20340100	-0.00504600
C	-1.81878900	-2.70421600	-0.84351800
H	-2.47979200	-3.55888800	-0.94668800
H	2.21898900	-4.84452900	-0.28488300
C	1.44671100	-4.09193300	-0.38110500
C	0.11176300	-4.26505000	-0.57877000
H	-0.44344400	-5.18901000	-0.67757300
C	-0.47076500	-2.95042200	-0.64676300
N	0.49808400	-1.97978700	-0.49841700
C	1.67945000	-2.67105700	-0.32974200
C	2.92657100	-2.09401700	-0.15408700
H	3.77542500	-2.75960900	-0.03171600

C	0.09707100	-0.15112300	1.54494500
C	-1.13920900	0.00403000	2.34493800
Fe	0.22269300	0.00172900	-0.32609000
F	-1.88124000	1.08390300	2.00069100
F	-0.83473500	0.14425900	3.66347300
F	-1.97902900	-1.07237400	2.26338800
H	0.79907700	-0.85442100	1.99316800



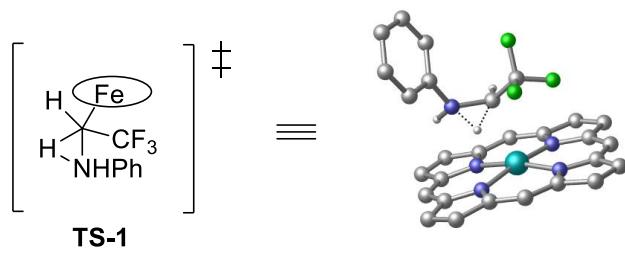
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N	0.45530200	-1.22746800	-1.83736800
H	-1.27458600	-2.81513800	-4.22644200
C	0.99470900	-2.49342900	-1.82893500
C	0.33372700	-3.32563800	-2.80449200
H	0.57448400	-4.36434900	-2.99451300
C	-0.59699300	-2.54657800	-3.42548100
C	2.06804400	-2.90242200	-1.04266100
H	2.38392700	-3.93745200	-1.13652000
N	2.56765500	-0.75565800	0.03780300
C	3.56038900	-0.33924700	0.89118400
C	4.45234200	-1.43411500	1.20112100
H	5.31725100	-1.36201400	1.84844700
C	3.98314300	-2.51977100	0.53010600
H	4.38478400	-3.52530500	0.51031000
C	2.81038400	-2.08633600	-0.19724100
C	-1.30273400	-0.15009600	-3.18176000
H	-2.02821000	-0.30102800	-3.97588800
H	-2.08179800	4.29293300	-2.17246200
C	-1.69502700	3.28112400	-2.17653200
C	-0.63752100	2.80143300	-1.32099100
H	-2.80998600	2.22606500	-3.76282000
N	-0.37793300	1.47437600	-1.58379000
C	-1.23281700	1.11958900	-2.61116700
C	-2.06097300	2.24092500	-2.98085100
C	3.69104200	0.94721700	1.39920300
H	4.52330000	1.13729800	2.07054100
H	1.70069900	5.11087400	1.37171300
C	1.93493300	4.06962400	1.18741200
C	2.96855100	3.33495600	1.68074400
H	3.75623500	3.64613000	2.35537200

C	2.83416900	2.00714700	1.12552700
N	1.73669600	1.94037900	0.30272500
C	1.17455200	3.19357700	0.32350700
C	0.05837300	3.58856900	-0.40655800
H	-0.26443500	4.62012600	-0.29704500
C	-0.53762400	-0.10526100	1.03079100
C	-0.25917400	-1.09440800	2.10280900
Fe	0.99770700	0.30918800	-0.62102500
F	-0.26184600	-2.37471300	1.59783200
F	-1.16013200	-1.14512500	3.14661300
F	0.93487400	-0.87501700	2.68159400
H	-0.78002900	0.86325200	1.47191500
N	-1.77553700	-0.55859200	0.25841000
C	-3.12398000	-0.49363800	0.85360600
C	-3.86205400	0.67736600	0.69485500
C	-3.62910600	-1.58642400	1.55432100
C	-5.13668100	0.75459700	1.25830800
H	-3.44970300	1.51432700	0.13610900
C	-4.90546100	-1.49825900	2.10984800
H	-3.02712200	-2.48058700	1.68060400
C	-5.65922300	-0.33110500	1.96409000
H	-5.72133600	1.66200200	1.13881200
H	-5.30885700	-2.34415900	2.65858000
H	-6.65232500	-0.26870600	2.39937700
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H	-1.56995000	-1.51111100	-0.05946400



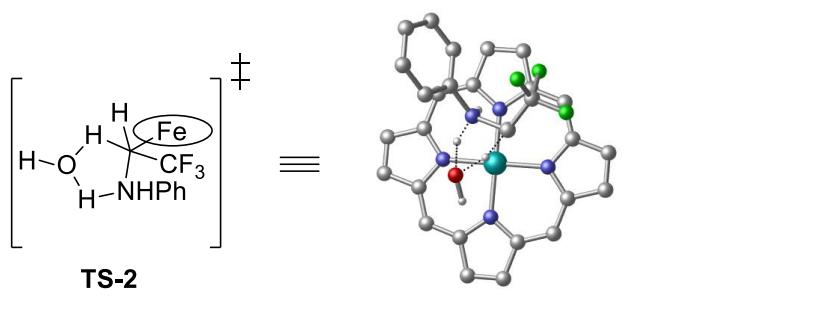
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F	-2.51722600	0.36519800	1.20161200
F	-1.92948600	-1.41690800	0.10380800
F	-3.47732600	-0.15970100	-0.73300400
H	-1.01750100	0.49620400	-1.74008100
N	-0.23278300	1.22011600	0.11519600
C	1.08187100	0.50860900	0.06498000
C	2.24232500	1.27270700	-0.01669700
C	1.12056800	-0.88250500	0.07831600
C	3.47991700	0.62876900	-0.07794200
H	2.18856000	2.36001400	-0.03539500
C	2.36329300	-1.51378800	0.02733200

H	0.19514300	-1.44584900	0.11500800
C	3.54063500	-0.76458100	-0.05195200
H	4.39008600	1.21725100	-0.14823900
H	2.40924500	-2.59886900	0.04339400
H	4.50245800	-1.26687100	-0.10066800
H	-0.02695900	2.21325900	-0.02841000
H	-0.62156900	1.16464100	1.06580200



C	0.98654400	0.97040700	2.67601200
N	0.21469600	-0.00356700	2.07756800
H	2.54565700	0.93911500	4.29049700
C	0.56148000	-1.18539400	2.69646100
C	1.58903500	-0.95281000	3.68359100
H	2.02622800	-1.71991800	4.31041400
C	1.84946700	0.38394000	3.67417000
C	-0.02214500	-2.41960100	2.44202100
H	0.35803400	-3.27393700	2.99416200
N	-1.69678800	-1.68601500	0.79826400
C	-2.69507100	-2.33837700	0.11639500
C	-2.71588900	-3.73474900	0.47189400
H	-3.41190100	-4.46283500	0.07466100
C	-1.71284000	-3.92587000	1.37432000
H	-1.41806300	-4.84215000	1.87013100
C	-1.08274300	-2.64501000	1.57178000
C	0.94917200	2.32415400	2.36343100
H	1.62274600	2.98000500	2.90740900
H	-1.17607900	5.41762400	-0.32800800
C	-0.86710400	4.49679700	0.15076800
C	-1.42091400	3.19771200	-0.13074100
H	0.69884000	5.07034100	1.59626100
N	-0.81640600	2.24094700	0.65070700
C	0.10486600	2.91462900	1.42506600
C	0.07707600	4.32217000	1.12045100
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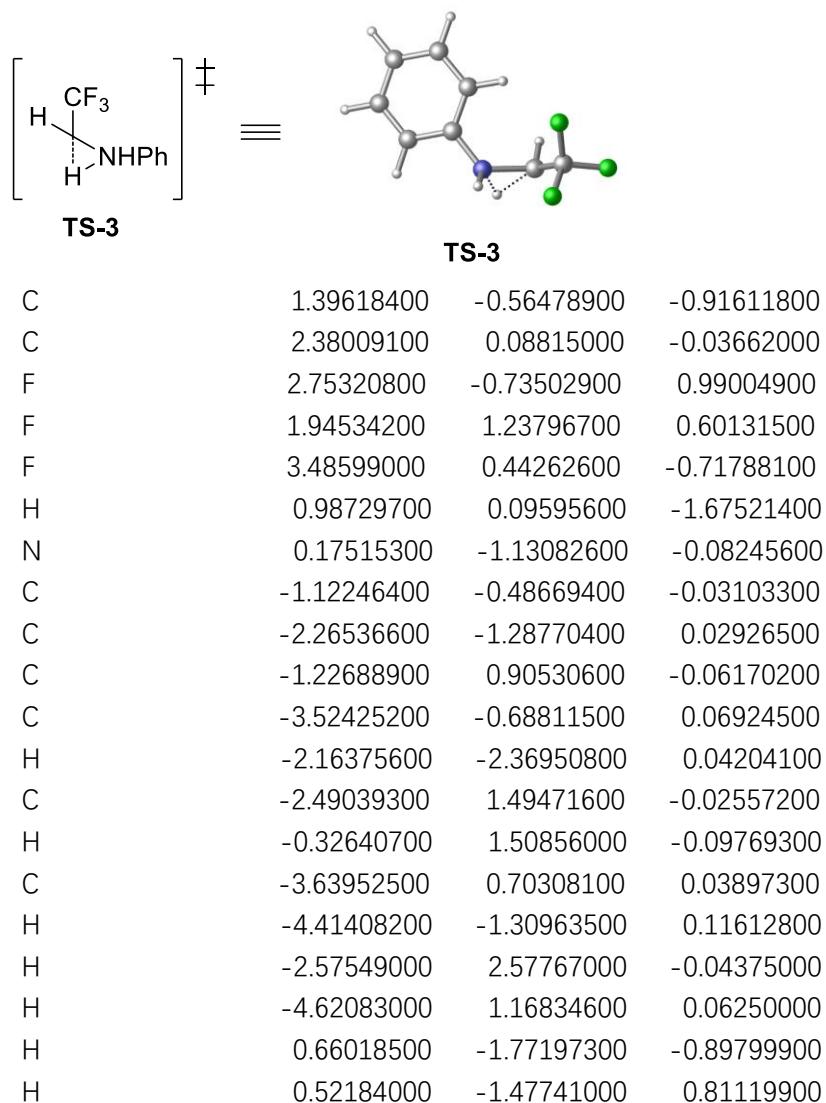
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C	-4.14025000	1.50817100	-2.18672600
C	-4.46362800	0.19099100	-2.10624200
H	-5.25132800	-0.34344800	-2.62229100
C	-3.54306600	-0.40890900	-1.16552100
N	-2.66550000	0.53525100	-0.68493900
C	-3.02524300	1.71920100	-1.28930000
C	-2.43684900	2.95330000	-1.05180200
H	-2.82490100	3.80539200	-1.60206000
C	0.60482600	0.05684500	-1.16547600
C	0.69539900	-1.27283800	-1.82757700
Fe	-1.15678000	0.23947500	0.58298200
F	1.26438900	-2.20410200	-1.02103000
F	1.41695500	-1.29737800	-2.99175200
F	-0.53969300	-1.70388700	-2.16577800
H	0.20279400	0.81800800	-1.83275500
N	1.93075300	0.47603000	-0.49036400
C	3.27364800	0.19041800	-0.95299100
C	3.65080300	0.41820100	-2.27874800
C	4.20274000	-0.27468200	-0.01974200
C	4.96821800	0.17660300	-2.66768600
H	2.91675200	0.76360300	-2.99855300
C	5.52010800	-0.51004000	-0.41585200
H	3.88396400	-0.44617700	1.00444200
C	5.90448000	-0.28588200	-1.73933400
H	5.26332400	0.35061700	-3.69878100
H	6.24299700	-0.87388200	0.30905900
H	6.92868000	-0.47503100	-2.04864100
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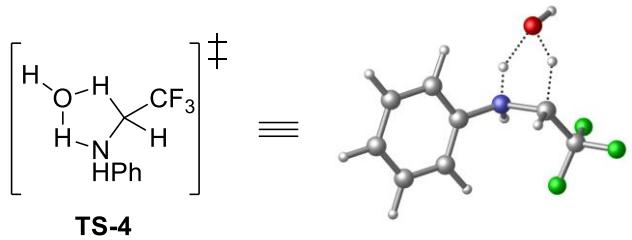


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N	1.57111400	2.16751500	0.57405300
H	0.47058600	5.21893400	1.40546600

C	2.35193100	3.00936700	-0.18956400
C	1.99836000	4.38400600	0.05170900
H	2.46638600	5.23363300	-0.42889500
C	0.99588400	4.37672100	0.97339900
C	3.34824100	2.60308500	-1.06565100
H	3.88558500	3.37494700	-1.60771200
N	3.13697700	0.18403700	-0.69755800
C	3.80261600	-0.90536600	-1.21789500
C	4.81163900	-0.48075400	-2.15401900
H	5.46877000	-1.14864200	-2.69632100
C	4.75393900	0.87870000	-2.20438600
H	5.35415300	1.55792100	-2.79631400
C	3.71144500	1.28451400	-1.29706200
C	-0.22507400	2.57648000	2.20200700
H	-0.80584100	3.34055200	2.70920300
H	-2.05025000	-1.21973400	4.08069600
C	-1.45348600	-0.54058600	3.48542000
C	-0.44456900	-0.94880500	2.54716000
H	-2.11027100	1.49071000	4.04632100
N	0.12946300	0.15626700	1.94421300
C	-0.49814200	1.25138800	2.51237300
C	-1.48463700	0.82374000	3.46670800
C	3.54159400	-2.23007800	-0.89961000
H	4.14224500	-2.99189200	-1.38666600
H	0.78142600	-4.89657200	1.65049600
C	1.26687000	-4.04559700	1.19030600
C	2.29319600	-4.03503000	0.29565000
H	2.82586300	-4.87615500	-0.12934300
C	2.56267700	-2.65456200	-0.01256400
N	1.71111900	-1.82676100	0.68837600
C	0.91135300	-2.67142100	1.43168000
C	-0.09460500	-2.26791900	2.29672800
H	-0.64748400	-3.04102800	2.82012100
C	-1.57008800	-1.31617600	-1.45076800
C	-2.63931700	-2.21358900	-0.94229600
Fe	1.64920100	0.17072400	0.63342000
F	-3.85953500	-1.98904200	-1.48089800
F	-2.83404200	-2.14129800	0.42575400
F	-2.30984500	-3.49883700	-1.20614500
H	-0.61794000	-1.67407000	-1.05052100
N	-1.69221000	0.12298600	-0.92971700
C	-3.01504800	0.76264800	-0.95960900
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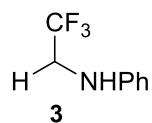
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C	-4.74236600	1.87401800	-2.19887300
H	-2.88560900	1.13856000	-3.06888300
C	-5.49349700	2.00274900	-1.02805100
H	-5.57842500	1.59917200	1.09008600
H	-5.12699500	2.26087800	-3.13830200
H	-6.46461700	2.48938300	-1.05513300
H	-1.25992000	0.23974500	-0.00577200
H	-1.09411200	0.57433200	-1.69309700
O	-0.88154000	0.17777300	-3.34069400
H	-0.00231700	-0.04055400	-3.68573100
H	-1.28058200	-0.81996900	-2.73349200





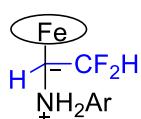
TS-4

C	-1.19915400	0.44199800	-0.56569700
C	-2.24992500	-0.52547000	-0.17530600
F	-2.86302400	-0.15084800	0.98868500
F	-1.79111700	-1.80413600	0.08784500
F	-3.18863300	-0.64843600	-1.12710000
H	-0.67303700	0.09032200	-1.45275200
N	-0.18078400	0.55355600	0.58433200
C	1.19201600	0.14366600	0.30190200
C	2.10985300	1.12384900	-0.07001000
C	1.54749000	-1.20213200	0.38127400
C	3.42226600	0.74223200	-0.35537600
H	1.78974200	2.15980000	-0.13948800
C	2.86358700	-1.56821000	0.10137100
H	0.79935200	-1.94627200	0.63882500
C	3.80070400	-0.59830000	-0.26514400
H	4.14773100	1.49641400	-0.64597200
H	3.15496400	-2.61258800	0.16497200
H	4.82406300	-0.88931000	-0.48404300
H	-0.26550000	1.63539100	0.73141000
H	-0.53640200	0.07484800	1.41591800
O	-0.91368800	2.88012000	0.00104400
H	-1.36975400	1.86718700	-0.49527400
H	-1.63222300	3.29334500	0.50476700



C	1.30555600	0.50749000	0.87363000
C	2.35025400	-0.10656700	-0.05197600
F	2.84356600	0.80255100	-0.91509100
F	1.85356200	-1.13052600	-0.77655300
F	3.38450800	-0.58640600	0.67725800
H	0.98089400	-0.27232700	1.57222900
N	0.18801000	1.08510300	0.16936800
C	-1.07143500	0.48082400	0.09547300

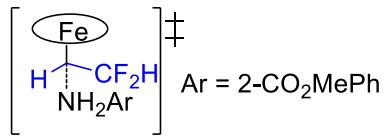
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C	-3.47659600	0.71799000	-0.16771700
H	-2.09677200	2.36969300	-0.12511000
C	-2.51317900	-1.47041800	0.07829800
H	-0.37109600	-1.56188300	0.23084300
C	-3.64154900	-0.66681600	-0.08444800
H	-4.34115400	1.36414600	-0.29704800
H	-2.61830700	-2.55118000	0.12972400
H	-4.63061300	-1.10984500	-0.15245600
H	0.16916700	2.09417300	0.15942400
H	1.82521900	1.27512000	1.45726200



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C	-0.34457100	-2.83477000	1.18242200
N	-1.30906800	-2.02444300	0.62571500
H	0.01358600	-5.04949100	1.17109800
C	-2.17543700	-2.86895600	-0.02919200
C	-1.73514400	-4.23864900	0.10224600
H	-2.24716600	-5.09213200	-0.32391400
C	-0.60221400	-4.21790700	0.85289500
C	-3.33523200	-2.48172500	-0.68830700
H	-3.92285000	-3.26434600	-1.15886600
N	-3.21054600	-0.07713800	-0.22981800
C	-4.03250900	0.98715800	-0.51581400
C	-5.19344000	0.53872000	-1.25167000
H	-5.99455300	1.18338000	-1.59100200
C	-5.06436300	-0.80655200	-1.40675400
H	-5.73696800	-1.49658600	-1.90060500
C	-3.82570300	-1.18407200	-0.76364700
C	0.71658500	-2.40661400	1.97148300
H	1.39320100	-3.16666000	2.34856800
H	2.55819800	1.37876700	3.88108200
C	1.94647700	0.70357400	3.29515700
C	0.82018400	1.10802500	2.49231100
H	2.74871500	-1.31906600	3.67608900
N	0.24796400	0.00321800	1.88893400
C	0.97383400	-1.08873500	2.33053100
C	2.03955300	-0.65547700	3.19724900
C	-3.78432400	2.30530200	-0.15446900

H	-4.51644300	3.04996700	-0.45281200
H	-0.80362500	5.00656400	2.10586900
C	-1.29513200	4.15627100	1.64962200
C	-2.46162500	4.12584600	0.95082200
H	-3.12630200	4.94630900	0.71089700
C	-2.68576700	2.74962500	0.57199000
N	-1.66490900	1.95410200	1.03884700
C	-0.80499900	2.79759400	1.70397900
C	0.35420300	2.41173000	2.36821000
H	0.91714000	3.19056300	2.87462900
C	-0.19200500	0.43535400	-1.22283600
C	-0.64998900	-0.14438600	-2.50157900
Fe	-1.41764200	-0.01819700	0.69351400
F	-0.39512000	-1.50753600	-2.51916300
F	0.00099200	0.33181100	-3.66202100
H	-0.19812600	1.52546600	-1.24789800
N	1.21687800	-0.03763500	-0.93135300
C	2.44142200	0.58821300	-1.50197000
C	2.34064800	1.64892100	-2.39007800
C	3.69914800	0.10088500	-1.09774900
C	3.50197200	2.23291600	-2.90330900
H	1.36328500	1.97965300	-2.71398000
C	4.85151500	0.69286200	-1.63164800
C	4.75654300	1.75510500	-2.52978800
H	3.41722800	3.05510800	-3.60762600
H	5.82601200	0.29545000	-1.36687100
H	5.65848300	2.19711800	-2.94243800
H	1.27776400	-0.01047200	0.09964700
H	1.24673400	-1.04292500	-1.15438900
C	3.79798400	-1.14447300	-0.26350000
O	3.06206600	-2.09128900	-0.45589900
O	4.76418700	-1.24312200	0.67418000
C	5.32149500	-0.08934500	1.32437800
H	6.28450100	0.17468700	0.87815300
H	4.64317900	0.76558800	1.28236400
H	5.47317800	-0.38043300	2.36538300
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C	-0.08693200	-0.05219200	-3.09113000
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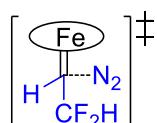
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C	1.35315400	-1.65506900	-2.69971600
C	0.64087000	-2.02099200	-3.90254200
H	0.81699000	-2.92430000	-4.47298200
C	-0.25273400	-1.02477200	-4.14600600
C	2.35310600	-2.41608000	-2.10861200
H	2.61641400	-3.35516400	-2.58588800
N	2.89489000	-0.90415300	-0.24234600
C	3.87214700	-0.92666300	0.72665500
C	4.67353800	-2.11976700	0.60406200
H	5.50994200	-2.36627200	1.24576500
C	4.17672500	-2.81969700	-0.45060100
H	4.52180100	-3.76093100	-0.85940000
C	3.07419800	-2.05466900	-0.97999300
C	-0.83955200	1.10522700	-2.95946000
H	-1.61433700	1.28476600	-3.69683500
H	-1.35133400	4.89258700	-0.38253000
C	-1.02721800	3.93209700	-0.76346300
C	0.02425700	3.13406800	-0.18143300
H	-2.24443500	3.54140400	-2.56290000
N	0.20995700	1.98293000	-0.91182300
C	-0.69528300	2.04581400	-1.94881000
C	-1.47255700	3.25736100	-1.85918500
C	4.07538800	0.05733000	1.68664300
H	4.88967200	-0.09078200	2.38922100
H	2.49458100	4.15048700	3.11620300
C	2.63272800	3.22001200	2.58022800
C	3.56799800	2.25350600	2.78770200
H	4.35638400	2.22551900	3.52915900
C	3.33337400	1.22513400	1.80361300
N	2.26536100	1.56791400	1.00421000
C	1.82340500	2.78934700	1.46692300
C	0.76553000	3.50860500	0.93357900
H	0.51658200	4.45518700	1.40341700
C	0.16794500	-0.31882800	0.82900800
C	0.63502800	-1.22326800	1.92396900
Fe	1.44531600	0.46416800	-0.47031500
F	0.82586200	-2.52284500	1.46120500
F	-0.26204300	-1.34443100	2.97008500
H	-0.49690300	0.43947900	1.25998700
N	-1.61231700	-1.66025100	0.30479700
C	-2.83272900	-1.64710200	0.98354700
C	-2.98792100	-2.40511800	2.15838100

C	-3.90784100	-0.82806300	0.55255600
C	-4.18659500	-2.39347700	2.85891300
H	-2.14647400	-2.98860500	2.51684300
C	-5.11114200	-0.83713700	1.27771900
C	-5.26481300	-1.61680300	2.41786500
H	-4.28335700	-2.99946300	3.75574800
H	-5.94469800	-0.24301800	0.91492800
H	-6.20761500	-1.62154900	2.95600700
H	-1.67606600	-1.39995100	-0.67503800
H	-1.03664000	-2.48038900	0.45730400
C	-3.81299800	-0.08329100	-0.73681200
O	-3.25356200	-0.53918600	-1.71749500
O	-4.42872600	1.12036800	-0.85338600
C	-4.57623900	2.01895900	0.25547800
H	-5.64025800	2.16844600	0.46241800
H	-4.07772700	1.64690400	1.15276400
H	-4.12285000	2.96647500	-0.04659800
H	1.58867900	-0.89631200	2.35168800



C	-0.09550600	3.07289300	-0.39578500
N	-0.70299500	1.83873400	-0.47915100
H	-0.84184400	5.18661800	-0.43761500
C	-2.04592400	2.10660800	-0.60859700
C	-2.28568500	3.52923300	-0.60738500
H	-3.26154200	3.98830300	-0.70207900
C	-1.07355000	4.12981200	-0.47420000
C	-3.03762600	1.15101300	-0.74770700
H	-4.06174800	1.49639400	-0.84805600
N	-1.58877900	-0.83525600	-0.65702000
C	-1.85583000	-2.19002200	-0.75082300
C	-3.26255300	-2.41635700	-0.93811600
H	-3.71918100	-3.39182900	-1.04696200
C	-3.85864100	-1.19176000	-0.95455100
H	-4.90742400	-0.95374300	-1.07825100
C	-2.81756700	-0.21657400	-0.77626900
C	1.26725700	3.28249100	-0.27251100
H	1.61704300	4.30860500	-0.21540400
H	5.28466800	1.05399800	0.03170300
C	4.23139200	1.28781400	-0.05805900
C	3.18207700	0.30811200	-0.16539900

H	4.09179300	3.48923900	-0.04124300
N	1.95333300	0.92329600	-0.27936200
C	2.21902400	2.27612600	-0.22339200
C	3.63288700	2.51024800	-0.09488000
C	-0.90929900	-3.19924300	-0.67779400
H	-1.25789500	-4.22407200	-0.75909300
H	3.62160300	-3.89713100	-0.23430400
C	2.64316400	-3.43974200	-0.30891600
C	1.43325900	-4.04275000	-0.46111500
H	1.20857900	-5.09898000	-0.53708200
C	0.45088300	-2.99069000	-0.51915900
N	1.05333000	-1.75513800	-0.40635300
C	2.39974400	-2.01932300	-0.27590300
C	3.39417100	-1.06201600	-0.15363300
H	4.41775200	-1.41055000	-0.05661300
C	0.10638500	-0.11918300	1.62653900
C	-1.08713600	-0.54922100	2.40029300
Fe	0.15408000	0.03716800	-0.24925200
F	-2.15984700	0.29199700	2.20278500
F	-0.79446200	-0.51007000	3.74785700
H	1.04161600	-0.49054300	2.05093000
H	-1.44048200	-1.56630900	2.17623300



C	-2.61502300	-1.20473900	-0.93921200
N	-1.25101600	-1.32236100	-0.78589500
H	-4.27614000	-2.67839400	-1.23894300
C	-0.98806700	-2.67298300	-0.83734400
C	-2.20977800	-3.41544500	-1.02360200
H	-2.26603200	-4.49359500	-1.10163500
C	-3.21732400	-2.50549400	-1.09470100
C	0.27190700	-3.24818700	-0.78559300
H	0.33078500	-4.33036800	-0.84570300
N	1.57158200	-1.17422000	-0.63782800
C	2.92379000	-0.90932700	-0.65065100
C	3.67627000	-2.13465600	-0.76286600
H	4.75668200	-2.19009300	-0.79904800
C	2.77216000	-3.14886600	-0.79785900
H	2.95252400	-4.21332500	-0.87631700
C	1.46461200	-2.54416300	-0.72402800

C	-3.32180900	-0.01109000	-0.92900100
H	-4.39778400	-0.06385200	-1.06219900
H	-2.78899200	4.53932500	-0.40356700
C	-2.60758200	3.47559500	-0.48946400
C	-1.30853900	2.85961900	-0.39870600
H	-4.57625800	2.54980500	-0.84918000
N	-1.41589600	1.49313200	-0.55898400
C	-2.75905400	1.24487200	-0.75106500
C	-3.50448700	2.47728100	-0.71539200
C	3.49166000	0.35049300	-0.54756400
H	4.57512200	0.41507700	-0.55974800
H	2.43095800	4.80759600	-0.04419700
C	2.37304200	3.73255900	-0.15743500
C	3.38797900	2.83490600	-0.27655200
H	4.45507000	3.01696900	-0.27590300
C	2.78120300	1.53397300	-0.41285900
N	1.40834100	1.64006900	-0.38650500
C	1.14348800	2.98329100	-0.23565300
C	-0.12173500	3.55293200	-0.21718400
H	-0.18454900	4.63012200	-0.09879100
Fe	0.06482900	0.14328800	-0.42642600
C	-0.13847200	0.15781900	1.55353900
C	-1.38053100	-0.39698100	2.20168900
N	2.06963800	-1.24372300	2.37501600
N	1.14739300	-0.63864500	2.60558200
H	0.01191300	1.17726700	1.92755600
F	-1.38893300	-1.76892900	2.17546000
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H	-2.28428400	-0.04485300	1.69182500

(Fe)

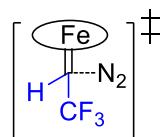
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C	0.65264800	-2.97046600	0.00005900
C	0.02972100	-4.27087000	0.00019000
H	0.56877800	-5.20971000	0.00027400
C	-1.31431400	-4.06377900	0.00012300
C	2.02291500	-2.76007200	0.00006700
H	2.66472900	-3.63555700	0.00012600
N	1.97856000	-0.30497000	-0.00001200
C	2.97052400	0.65258300	0.00004600
C	4.27092400	0.02967800	0.00013400

H	5.20979200	0.56869500	0.00016600
C	4.06382300	-1.31428200	0.00018400
H	4.79689600	-2.11090300	0.00026300
C	2.63618700	-1.51677900	0.00006700
C	-2.76019000	-2.02282100	-0.00000400
H	-3.63583900	-2.66441100	-0.00001100
H	-4.79689600	2.11090300	-0.00025000
C	-4.06382300	1.31428200	-0.00017800
C	-2.63618700	1.51677900	-0.00007000
H	-5.20979300	-0.56869500	-0.00020400
N	-1.97856000	0.30497000	0.00001700
C	-2.97052400	-0.65258300	-0.00004900
C	-4.27092400	-0.02967800	-0.00015600
C	2.76019000	2.02282100	-0.00000100
H	3.63583900	2.66441100	-0.00000600
H	-0.56877800	5.20971000	-0.00025300
C	-0.02972100	4.27087000	-0.00017900
C	1.31431400	4.06377900	-0.00014500
H	2.11094300	4.79683700	-0.00019200
C	1.51687800	2.63614200	-0.00004600
N	0.30503700	1.97872500	0.00001600
C	-0.65264800	2.97046600	-0.00006100
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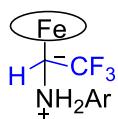
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C	-1.16290800	2.67604400	-0.73669000
C	-0.92406800	4.09718500	-0.71875600
H	-1.69064900	4.85078200	-0.84693500
C	0.41059600	4.26799700	-0.52098600
C	-2.40592400	2.09896900	-0.93275300
H	-3.25477600	2.76119400	-1.07065800
N	-1.68903300	-0.24993800	-0.80880200
C	-2.38093900	-1.44232500	-0.92319400
C	-3.77701900	-1.19785500	-1.16049000
H	-4.52246800	-1.97177300	-1.29079400
C	-3.93967500	0.15316200	-1.18940400

H	-4.84782200	0.72086900	-1.34707300
C	-2.64355300	0.73536900	-0.96704200
C	2.33580300	2.70543300	-0.24279900
H	2.99688600	3.56156000	-0.15073800
H	5.39527600	-0.71342400	0.13829000
C	4.47964400	-0.14753800	0.02207400
C	3.17329700	-0.73009300	-0.14049900
H	5.06320200	1.97891400	0.08457000
N	2.21657100	0.25267400	-0.27984100
C	2.90603400	1.44407200	-0.18406600
C	4.31326100	1.20340200	-0.00504600
C	-1.81878900	-2.70421600	-0.84351800
H	-2.47979100	-3.55888800	-0.94668800
H	2.21899000	-4.84452900	-0.28488300
C	1.44671200	-4.09193300	-0.38110500
C	0.11176400	-4.26505000	-0.57877000
H	-0.443444300	-5.18901000	-0.67757300
C	-0.47076500	-2.95042200	-0.64676300
N	0.49808400	-1.97978700	-0.49841700
C	1.67945000	-2.67105700	-0.32974200
C	2.92657100	-2.09401700	-0.15408700
H	3.77542500	-2.75960800	-0.03171600
C	0.09707100	-0.15112300	1.54494500
C	-1.13920900	0.00403000	2.34493800
Fe	0.22269300	0.00172900	-0.32609000
F	-1.88124000	1.08390300	2.00069100
F	-0.83473500	0.14425900	3.66347300
F	-1.97902900	-1.07237400	2.26338800
H	0.79907700	-0.85442100	1.99316800



C	-2.72432300	-0.71555800	-1.12892800
N	-1.40470900	-1.06029400	-0.91152900
H	-4.58961500	-1.88627000	-1.52886100
C	-1.37284700	-2.43783000	-0.96567000
C	-2.68958200	-2.96196700	-1.21559000
H	-2.92539900	-4.01484300	-1.30442200
C	-3.52539600	-1.89276400	-1.33078500
C	-0.23115800	-3.21907700	-0.86576100
H	-0.35385800	-4.29593000	-0.92818000

N	1.39037200	-1.38934700	-0.69427000
C	2.76925300	-1.35194400	-0.73983100
C	3.30910400	-2.68325800	-0.85316800
H	4.36470100	-2.91597000	-0.91102800
C	2.24966000	-3.53609700	-0.86121000
H	2.25269100	-4.61613700	-0.93592100
C	1.06095500	-2.72360900	-0.77812100
C	-3.22366200	0.57733200	-1.12475700
H	-4.28546200	0.70826900	-1.30854000
H	-1.97366500	4.94309900	-0.34413300
C	-1.96688800	3.86860400	-0.47677500
C	-0.79142000	3.03935800	-0.38244200
H	-4.04412200	3.30195000	-0.95281700
N	-1.11507400	1.71832600	-0.60771400
C	-2.47120300	1.70986200	-0.85760000
C	-3.00577600	3.04540600	-0.78583600
C	3.53908600	-0.20220600	-0.66358900
H	4.61810100	-0.31533000	-0.70082600
H	3.21526600	4.34708100	-0.00510300
C	2.98258300	3.30098900	-0.15935000
C	3.84061700	2.25838200	-0.33870900
H	4.92298100	2.27025000	-0.35588300
C	3.03173600	1.07875700	-0.50245800
N	1.69182400	1.39949200	-0.44468800
C	1.64952400	2.76061400	-0.23651600
C	0.49111800	3.52347800	-0.16933400
H	0.60281000	4.59060100	-0.00323400
Fe	0.11457000	0.14202300	-0.44708700
C	-0.05535900	0.16538100	1.53170400
C	-1.20741500	-0.49095600	2.26801500
N	2.15069300	-1.19544600	2.28633300
N	1.33719900	-0.44394800	2.51382000
H	-0.01431300	1.21037900	1.85041500
F	-1.24519000	-1.82870000	2.08961200
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F	-1.15014400	-0.28248200	3.60630300



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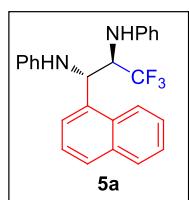
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C	-1.90546000	-2.97096500	0.18735000
C	-1.35958100	-4.29487800	0.36908500
H	-1.79696200	-5.20275500	-0.02733800
C	-0.23397300	-4.15705100	1.12263800
C	-3.09163800	-2.69614400	-0.48603600
H	-3.61474800	-3.53701900	-0.93209200
N	-3.16855200	-0.27565900	-0.10095600
C	-4.08936500	0.69846800	-0.40262100
C	-5.21478800	0.12808600	-1.11048100
H	-6.07534500	0.68755800	-1.45521600
C	-4.96197000	-1.20163100	-1.23505400
H	-5.57238000	-1.96315400	-1.70432500
C	-3.68562700	-1.44527200	-0.59860800
C	0.93862500	-2.19951300	2.15780500
H	1.66839800	-2.88650100	2.57500500
H	2.51412600	1.81459300	3.82206600
C	1.94902500	1.06516600	3.28099800
C	0.79218500	1.33987900	2.46831100
H	2.88832400	-0.86913600	3.78817700
N	0.29918300	0.16448800	1.93060700
C	1.10181200	-0.84713700	2.43597900
C	2.13786300	-0.28866200	3.26577000
C	-3.96679400	2.04374000	-0.07936400
H	-4.77274800	2.70568800	-0.38252300
H	-1.16900100	5.07520200	1.99083900
C	-1.59905700	4.16849600	1.58312000
C	-2.78335900	4.01401700	0.92854800
H	-3.52308800	4.76667800	0.68584600
C	-2.89636300	2.61153200	0.60387200
N	-1.79635800	1.92411600	1.05746800
C	-0.99162300	2.85982400	1.66263700
C	0.21873400	2.59662200	2.29848000
H	0.72899000	3.43890400	2.75752800
C	-0.14820200	0.44806100	-1.16280800
C	-0.51487100	-0.12566400	-2.47828900
Fe	-1.37161900	-0.03429900	0.75214700
F	-0.36503100	-1.48373400	-2.48942400
F	0.24308000	0.29954100	-3.56058400
F	-1.78893400	0.16379300	-2.80264800
H	-0.20022700	1.53571100	-1.18710000
N	1.26180200	0.03456200	-0.82034300
C	2.47762300	0.68895600	-1.37570600
C	2.37525700	1.84803000	-2.13088900
C	3.73515400	0.12897700	-1.07926600

C	3.53133800	2.45308800	-2.63012000
H	1.39931100	2.25522000	-2.35980600
C	4.88189400	0.74062300	-1.60404300
C	4.78365500	1.89626300	-2.37719900
H	3.44369600	3.35346800	-3.23071600
H	5.85248900	0.28730700	-1.43185400
H	5.68049500	2.35272600	-2.78493900
H	1.27722200	0.10833100	0.21506600
H	1.35576000	-0.97775600	-0.99439000
C	3.83270400	-1.18609100	-0.36104000
O	3.04797800	-2.08784500	-0.58168000
O	4.84779400	-1.39703800	0.50226500
C	5.44269800	-0.32289900	1.25219200
H	6.32341400	0.07463200	0.74101000
H	4.72432700	0.47830400	1.44171100
H	5.74780500	-0.76777100	2.20102100

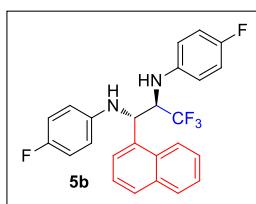
9. Characterization data of new compounds

(1*S*, 2*R*)-3,3,3-Trifluoro-1-(naphthalen-1-yl)-N¹,N²-diphenylpropane-1,2-diamine **5a**: Yield: 81%,



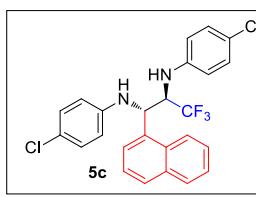
66mg. White solid, m.p. 83-85 °C. $R_f = 0.3$ (PE:EtOAc=20:1). **¹H NMR** (500 MHz, CDCl₃): δ 8.24 (d, $J = 8.5$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.2$ Hz, 1H), 7.73-7.65 (m, 2H), 7.63 (dd, $J = 11.1, 3.9$ Hz, 1H), 7.43-7.35 (m, 1H), 7.17 (dd, $J = 8.4, 7.5$ Hz, 2H), 7.04 (dd, $J = 8.4, 7.5$ Hz, 2H), 6.79 (t, $J = 7.3$ Hz, 1H), 6.76 (t, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 2H), 6.29 (d, $J = 7.9$ Hz, 2H), 5.87 (d, $J = 5.1$ Hz, 1H), 4.71 (d, $J = 6.2$ Hz, 1H), 4.51-4.38 (m, 1H), 4.28 (d, $J = 8.8$ Hz, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 146.5, 146.3, 134.8, 134.3, 130.3, 129.7, 129.4, 129.3, 128.8, 127.1, 126.0 (q, $J_{CF} = 283.8$ Hz), 125.9, 125.7, 124.8, 121.6, 119.8, 118.9, 114.6, 114.3, 61.0 (q, $J_{CF} = 27.5$ Hz), 52.2 ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ -72.7 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₂F₃N₂ 407.1730 [M+H⁺]; found 407.1723. **HPLC**: (Chiral AD-H, $\lambda = 224$ nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), t_{minor} = 13.41 min, t_{major} = 16.68 min.

(1*S*,2*R*)-3,3,3-Trifluoro-N¹,N²-bis(4-fluorophenyl)-1-(naphthalen-1-yl)propane-1,2-diamine **5b**:



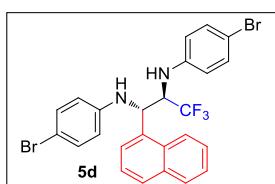
Yield: 78%, 69mg. Colorless solid, m.p. 122-124 °C. R_f = 0.3 (PE:EtOAc=20:1). **¹H NMR** (500 MHz, CDCl₃) δ 8.15 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 6.7 Hz, 2H), 7.36 (t, J = 7.7 Hz, 1H), 6.82 (t, J = 8.6 Hz, 2H), 6.67 (t, J = 8.6 Hz, 2H), 6.58 (dd, J = 8.8, 4.3 Hz, 2H), 6.13 (dd, J = 8.7, 4.2 Hz, 2H), 5.72 (d, J = 3.5 Hz, 1H), 4.57 (d, J = 4.4 Hz, 1H), 4.23 (dd, J = 14.4, 7.2 Hz, 1H), 4.15 (d, J = 8.5 Hz, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 157.7 (d, J_{CF} = 47.5 Hz), 155.8 (d, J_{CF} = 46.3 Hz), 142.7 (d, J_{CF} = 1.25 Hz), 142.4 (d, J_{CF} = 1.25 Hz), 134.3, 134.2, 130.2, 129.8, 128.9, 127.2, 126.0, 125.8 (q, J_{CF} = 283.8 Hz), 125.6, 124.6, 121.4, 115.8 (d, J_{CF} = 21.3 Hz), 115.7 (d, J_{CF} = 22.5 Hz), 115.6 (d, J_{CF} = 8.8 Hz), 115.5 (d, J_{CF} = 8.8 Hz), 61.9 (q, J_{CF} = 27.5 Hz), 52.7 ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ -72.8, -124.9, -126.0 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₀F₅N₂ 443.1541 [M+H⁺]; found 443.1543. **HPLC:** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 5.57 min, t_{minor} = 6.73 min.

(1*S*,2*R*)-N¹,N²-Bis(4-chlorophenyl)-3,3,3-trifluoro-1-(naphthalen-1-yl)propane-1,2-diamine **5c**:



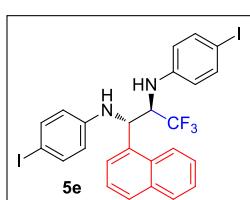
Yield: 82%, 78mg. White solid, m.p. 94-96 °C. R_f = 0.3 (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 8.14 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.72-7.65 (m, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.38-7.30 (m, 1H), 7.07 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.9 Hz, 2H), 6.09 (d, J = 8.8 Hz, 2H), 5.76 (d, J = 6.3 Hz, 1H), 4.65 (d, J = 7.0 Hz, 1H), 4.36-4.27 (m, 1H), 4.23 (d, J = 8.7 Hz, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 144.9, 144.7, 134.3, 133.9, 130.1, 129.9, 129.2, 129.1, 129.0, 127.4, 126.1, 125.7, 125.6 (q, J_{CF} = 283.8 Hz), 124.5, 123.7, 121.3, 115.7, 115.3, 61.0 (q, J_{CF} = 27.5 Hz), 52.2 ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ -72.8 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₀Cl₂F₃N₂ 475.0950 [M+H⁺]; found 475.0956. **HPLC:** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 7.83 min, t_{minor} = 10.26 min.

(1*S*,2*R*)-N¹,N²-Bis(4-bromophenyl)-3,3,3-trifluoro-1-(naphthalen-1-yl)propane-1,2-diamine **5d**:



Yield: 80%, 90mg. White solid, m.p. 156-158 °C. $R_f = 0.3$ (PE:EtOAc=10:1). **1H NMR** (500 MHz, CDCl₃): δ 8.12 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.68 (ddd, $J = 8.4, 6.9, 1.3$ Hz, 1H), 7.63-7.57 (m, 1H), 7.52 (d, $J = 7.2$ Hz, 1H), 7.36-7.27 (m, 1H), 7.19 (d, $J = 8.9$ Hz, 2H), 7.04 (d, $J = 8.9$ Hz, 2H), 6.51 (d, $J = 8.9$ Hz, 2H), 6.03 (d, $J = 8.9$ Hz, 2H), 5.74 (d, $J = 6.2$ Hz, 1H), 4.64 (d, $J = 7.1$ Hz, 1H), 4.35-4.26 (m, 1H), 4.21 (d, $J = 8.7$ Hz, 1H) ppm; **13C NMR** (125 MHz, CDCl₃): δ 145.3, 145.1, 134.2, 133.8, 132.1, 132.0, 130.1, 129.9, 129.0, 127.4, 126.1, 125.7, 125.5 ($J_{CF} = 283.8$ Hz), 124.5, 121.2, 116.1, 115.7, 111.7, 110.8, 60.8 ($J_{CF} = 27.5$ Hz), 52.0 ppm; **19F NMR** (470 MHz, CDCl₃): δ -72.8 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₀Br₂F₃N₂ 562.9940, 564.9921 [M+H⁺]; found 562.9939, 565.0250. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 8.16 min, t_{minor} = 10.93 min.

(1*S*,2*R*)-3,3,3-Trifluoro-N¹,N²-bis(4-iodophenyl)-1-(naphthalen-1-yl)propane-1,2-diamine **5e**:

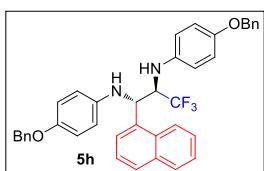


Yield: 79%, 104mg. Light yellow solid, m.p. 76-78 °C. $R_f = 0.3$ (PE:EtOAc=10:1) **1H NMR** (400 MHz, CDCl₃): δ 8.11 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.71 – 7.64 (m, 1H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.51 (d, $J = 7.1$ Hz, 1H), 7.34 (dd, $J = 17.1, 8.3$ Hz, 3H), 7.21 (d, $J = 8.7$ Hz, 2H), 6.41 (d, $J = 8.8$ Hz, 2H), 5.92 (d, $J = 8.7$ Hz, 2H), 5.73 (d, $J = 6.4$ Hz, 1H), 4.65 (d, $J = 7.0$ Hz, 1H), 4.36 – 4.26 (m, 1H), 4.22 (d, $J = 8.8$ Hz, 1H) ppm; **13C NMR** (100 MHz, CDCl₃): δ 146.0, 145.7, 138.0, 137.9, 134.2, 133.7, 130.0, 129.9, 129.1, 127.4, 126.1, 125.7, 125.5 ($J_{CF} = 280.0$ Hz), 124.5, 121.2, 116.6, 116.2, 81.2, 80.1, 60.6 ($J_{CF} = 28.0$ Hz), 51.8 ppm; **19F NMR** (376 MHz, CDCl₃): δ -72.8 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₀I₂F₃N₂ 658.9663 [M+H⁺]; found 658.9667. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 12.04 min, t_{minor} = 16.30 min.

(1*S*,2*R*)-3,3,3-Trifluoro-1-(naphthalen-1-yl)-N¹,N²-di-p-tolylpropane-1,2-diamine **5f**: Yield: 82%, 71mg. Light yellow oil. $R_f = 0.4$ (PE:EtOAc=20:1). **1H NMR** (500 MHz, CDCl₃): δ 8.25 (d, $J = 8.5$ Hz, 1H), 8.00 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.70 (dd, $J = 9.6, 7.3$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 2H), 6.86 (d, $J = 8.3$ Hz, 2H), 6.63 (d, $J = 8.4$ Hz, 2H), 6.21 (d, $J = 8.3$ Hz, 2H), 5.83 (s, 1H), 4.65 (s, 1H), 4.43 – 4.31 (m, 1H), 4.20 (d, $J = 8.6$ Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H) ppm; **13C NMR** (125 MHz, CDCl₃): δ 143.1, 142.9, 133.9, 133.1, 129.2, 128.7, 128.6, 128.5, 127.9, 127.5, 126.9, 125.9, 124.9 (q, $J_{CF} = 283.8$ Hz), 124.7, 124.6, 123.6, 120.6, 113.5, 113.3, 60.3 (q, $J_{CF} = 27.5$ Hz), 51.2, 19.3, 19.2 ppm; **19F NMR** (376 MHz, CDCl₃): δ -72.7 ppm; **HRMS (m/z)** (ESI): calc. for C₂₇H₂₆F₃N₂ 435.2043 [M+H⁺]; found 435.2042. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), t_{major} = 7.80 min, t_{minor} = 9.75 min.

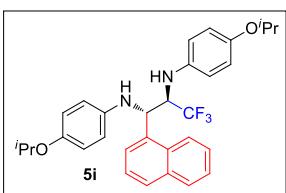
(1*S*,2*R*)-3,3,3-Trifluoro-N¹,N²-bis(4-methoxyphenyl)-1-(naphthalen-1-yl)propane-1,2-diamine **5g**: Yield: 85%, 79mg. Light yellow oil. $R_f = 0.3$ (PE:EtOAc=5:1). **1H NMR** (500 MHz, CDCl₃): δ 8.21 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.70 – 7.65 (m, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.7$ Hz, 1H), 6.73 (d, $J = 9.0$ Hz, 2H), 6.63 (d, $J = 9.0$ Hz, 2H), 6.60 (d, $J = 8.9$ Hz, 2H), 6.23 (d, $J = 8.9$ Hz, 2H), 5.74 (s, 1H), 4.52 (s, 1H), 4.27 – 4.21 (m, 1H), 4.11 (s, 1H), 3.71 (s, 3H), 3.69 (s, 3H) ppm; **13C NMR** (125 MHz, CDCl₃): δ 153.5, 152.9, 140.6, 140.3, 135.0, 134.3, 130.4, 129.7, 128.6, 127.0, 126.1 (q, $J_{CF} = 283.8$ Hz), 125.8, 125.7, 124.7, 121.6, 116.1, 116.0, 114.9, 114.7, 60.4 (q, $J_{CF} = 27.5$ Hz); 55.7, 55.6, 52.9 ppm; **19F NMR** (470 MHz, CDCl₃) δ -72.7 ppm; **HRMS (m/z)** (ESI): calc. for C₂₇H₂₆F₃N₂O₂ 467.1941 [M+H⁺]; found 467.1944. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 11.21 min, t_{minor} = 12.95 min.

(1*S*,2*R*)-N¹,N²-Bis(4-(benzyloxy)phenyl)-3,3,3-trifluoro-1-(naphthalen-1-yl)propane-1,2-diamine



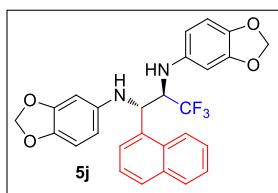
5h: Yield: 80%, 99mg. White solid, m.p. 138-140 °C. $R_f = 0.2$ (PE:EtOAc=5:1). **¹H NMR** (500 MHz, CDCl₃): δ 8.21 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.68 (t, $J = 7.0$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.44 – 7.37 (m, 9H), 7.34 (dt, $J = 6.8$, 3.7 Hz, 2H), 6.80 (d, $J = 8.9$ Hz, 2H), 6.68 (d, $J = 8.9$ Hz, 2H), 6.63 (d, $J = 8.9$ Hz, 2H), 6.23 (d, $J = 8.8$ Hz, 2H), 5.74 (s, 1H), 4.96 (s, 2H), 4.93 (s, 2H), 4.52 (s, 1H), 4.30 – 4.17 (m, 1H), 4.10 (d, $J = 8.5$ Hz, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 152.7, 152.2, 140.8, 140.5, 137.5, 137.4, 135.0, 134.3, 130.4, 129.7, 128.7, 128.6, 127.9, 127.8, 127.6, 127.5, 127.1, 126.1 (q, $J_{CF} = 283.8$ Hz), 125.9, 125.7, 124.7, 121.7, 116.1, 116.0, 115.9, 115.8, 70.7, 70.6, 62.3 (q, $J_{CF} = 27.5$ Hz), 52.9 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.6 ppm; **HRMS (m/z)** (ESI): calc. for C₃₉H₃₄F₃N₂O₂ 619.2567 [M+H⁺]; found 619.2569. **HPLC:** (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 33.51 min, t_{minor} = 38.29 min.

(1*S*,2*R*)-3,3,3-Trifluoro-N¹,N²-bis(4-isopropoxyphenyl)-1-(naphthalen-1-yl)propane-1,2-diamine



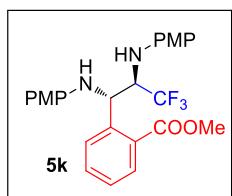
5i: Yield: 81%, 85mg. White solid, m.p. 113-115 °C. $R_f = 0.2$ (PE:EtOAc=5:1). **¹H NMR** (500 MHz, CDCl₃): δ 8.17 (d, $J = 8.5$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.63 (t, $J = 5.8$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 6.69 (d, $J = 8.8$ Hz, 2H), 6.61 – 6.52 (m, 4H), 6.18 (d, $J = 8.7$ Hz, 2H), 5.69 (s, 1H), 4.46 (s, 1H), 4.31 (tp, $J = 12.0, 6.0$ Hz, 2H), 4.24 – 4.16 (m, 1H), 4.05 (d, $J = 8.3$ Hz, 1H), 1.31 – 1.19 (m, 12H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 151.6, 151.0, 140.6, 140.4, 135.0, 134.2, 130.3, 129.6, 128.5, 127.0, 126.1 (q, $J_{CF} = 283.8$ Hz), 125.8, 125.7, 124.8, 121.7, 117.6, 117.4, 116.0, 115.9, 70.8, 70.7, 62.3 (q, $J_{CF} = 27.5$ Hz), 53.0, 22.2, 22.2, 22.1, 22.1 ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ -72.7 ppm; **HRMS (m/z)** (ESI): calc. for C₃₁H₃₄F₃N₂O₂ 523.2567 [M+H⁺]; found 523.2566. **HPLC:** (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 7.31 min, t_{minor} = 10.89 min.

(*1S,2R*)-N¹,N²-Bis(benzo[*d*][1,3]dioxol-5-yl)-3,3,3-trifluoro-1-(naphthalen-1-yl)propane-1,2-



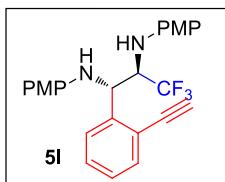
diamine **5j**: Yield: 79%, 78mg. Colorless oil. $R_f = 0.2$ (PE:EtOAc=5:1)
¹H NMR (500 MHz, CDCl₃): δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.07 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.80 (dd, *J* = 5.4, 1.2 Hz, 2H), 5.78-5.77 (m, 3H), 5.71 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.67 (s, 1H), 4.49 (s, 1H), 4.20 – 4.12 (m, 1H), 4.06 (d, *J* = 8.6 Hz, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 148.3, 148.2, 142.0, 141.7, 141.3, 140.6, 134.7, 134.3, 130.2, 129.7, 128.8, 127.1, 125.9, 125.9 (q, *J*_{CF} = 283.8 Hz), 125.6, 124.6, 121.5, 108.6, 108.4, 107.0, 106.6, 100.9, 100.7, 97.7, 97.6, 62.4 (q, *J*_{CF} = 27.5 Hz), 53.0 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.7 ppm; **HRMS (m/z)** (ESI): calc. for C₂₇H₂₂F₃N₂O₄ 495.1526 [M+H⁺]; found 495.1528. **HPLC**: (Chiral IC, λ = 254 nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), tminor = 12.10 min, tmajor = 13.31 min.

Methyl 2-((*1S,2R*)-3,3,3-trifluoro-1,2-bis((4-methoxyphenyl)amino)propyl)benzoate **5k**: Yield:



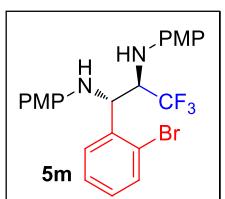
78%, 74mg. Light yellow oil. $R_f = 0.3$ (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 6.1 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 6.31 (d, *J* = 8.9 Hz, 2H), 5.74 (s, 1H), 4.47 (s, 1H), 4.35 (ddd, *J* = 10.4, 7.9, 2.9 Hz, 1H), 3.99 (d, *J* = 8.8 Hz, 1H), 3.95 (s, 3H), 3.69 (s, 6H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 168.2, 153.3, 152.8, 141.6, 140.8, 140.1, 132.6, 131.2, 129.0, 128.6, 127.7, 125.8 (q, *J*_{CF} = 283.8 Hz), 115.7, 115.7, 114.8, 114.7, 62.4 (q, *J*_{CF} = 27.5 Hz), 55.6, 55.6, 54.2, 52.5 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.1 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₆F₃N₂O₄ 475.1839 [M+H⁺]; found 475.1837. **HPLC**: (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 83/17, Flow rate = 1.0 mL/min), tminor = 11.95 min, tmajor = 17.80 min.

(1*S*,2*R*)-1-(2-Ethynylphenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5l**:



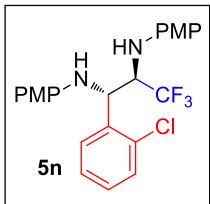
Yield: 81%, 71mg. Light yellow oil. $R_f = 0.3$ (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.62 (dd, $J = 7.0, 1.4$ Hz, 1H), 7.47 (d, $J = 7.1$ Hz, 1H), 7.33 – 7.25 (m, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 6.65 (d, $J = 8.8$ Hz, 2H), 6.41 (d, $J = 8.8$ Hz, 2H), 5.43 (s, 1H), 4.48 (s, 1H), 4.33 (dd, $J = 10.3, 4.9$ Hz, 1H), 4.06 (d, $J = 8.6$ Hz, 1H), 3.76 (s, 6H), 3.55 (s, 1H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 153.4, 152.9, 142.4, 140.7, 140.0, 133.5, 129.5, 127.7, 127.3, 125.8 (q, $J_{CF} = 283.8$ Hz), 120.4, 115.9, 114.8, 114.7, 84.2, 80.9, 62.4, 62.1, 61.9, 61.7, 55.7, 55.6, 55.3 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.6 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₄F₃N₂O₂ 441.1784 [M+H⁺]; found 441.1781. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 8.70 min, t_{minor} = 10.48 min.

(1*S*,2*R*)-1-(2-Bromophenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5m**:



Yield: 75%, 74mg. Light yellow oil. $R_f = 0.3$ (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.61 (dd, $J = 7.9, 0.9$ Hz, 1H), 7.42 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.18 (dd, $J = 10.9, 4.0$ Hz, 1H), 7.12 (td, $J = 7.7, 1.6$ Hz, 1H), 6.74 (d, $J = 8.9$ Hz, 2H), 6.65 (d, $J = 8.9$ Hz, 2H), 6.56 (d, $J = 8.9$ Hz, 2H), 6.29 (d, $J = 8.9$ Hz, 2H), 5.31 (s, 1H), 4.38 (s, 1H), 4.22 – 4.12 (m, 1H), 3.92 (d, $J = 8.8$ Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 153.6, 153.0, 140.5, 139.7, 138.4, 133.3, 129.5, 129.1, 128.0, 125.7 (q, $J_{CF} = 283.8$ Hz), 122.9, 115.9, 115.9, 114.9, 114.7, 61.5 (q, $J_{CF} = 27.5$ Hz), 56.2, 55.7, 55.6 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.6 ppm; **HRMS (m/z)** (ESI): calc. for C₂₃H₂₃BrF₃N₂O₂ 495.0890, 497.0872 [M+H⁺]; found 495.0891, 497.0854. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 7.24 min, t_{minor} = 8.53 min.

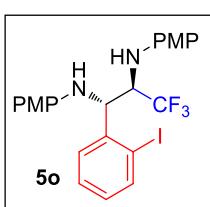
(1*S*,2*R*)-1-(2-Chlorophenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5n**:

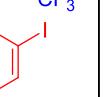


5n

Yield: 77%, 70mg. Light yellow oil. $R_f = 0.3$ (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.43 (d, $J = 7.7$ Hz, 2H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 7.5$ Hz, 1H), 6.77 – 6.71 (m, 2H), 6.70 – 6.64 (m, 2H), 6.60 – 6.54 (m, 2H), 6.36 – 6.29 (m, 2H), 5.35 (s, 1H), 4.37 (s, 1H), 4.17 (s, 1H), 3.95 (d, $J = 7.4$ Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 153.6, 153.0, 140.6, 139.7, 137.1, 132.6, 130.0, 129.2, 128.8, 127.4, 125.7 (q, $J_{CF} = 283.8$ Hz), 116.0, 115.9, 114.9, 114.7, 61.6 (q, $J_{CF} = 27.5$ Hz), 55.7, 55.6, 53.9 ppm; **¹⁹F NMR** (376 MHz, CDCl₃): δ -72.7 ppm; **HRMS (m/z)** (ESI): calc. for C₂₃H₂₃ClF₃N₂O₂ 451.1395 [M+H⁺]; found 451.1394. **HPLC:** (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 7.32 min, t_{minor} = 8.62 min.

(1S,2R)-3,3,3-Trifluoro-1-(2-iodophenyl)-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5o:**

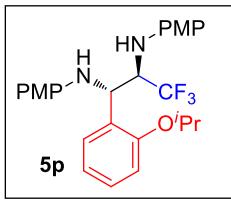




5o

 Yield: 79%, 86mg. Light yellow oil. $R_f = 0.3$ (PE:EtOAc=10:1). **^1H NMR** (500 MHz, CDCl_3): δ 7.89 (d, $J = 7.8$ Hz, 1H), 7.38 (dd, $J = 7.7, 0.9$ Hz, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 6.99 – 6.92 (m, 1H), 6.73 (d, $J = 8.9$ Hz, 2H), 6.64 (d, $J = 8.9$ Hz, 2H), 6.53 (d, $J = 8.9$ Hz, 2H), 6.26 (d, $J = 8.8$ Hz, 2H), 5.15 (s, 1H), 4.40 (s, 1H), 4.16 – 4.07 (m, 1H), 3.92 (d, $J = 8.7$ Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H) ppm; **^{13}C NMR** (125 MHz, CDCl_3): δ 153.5, 153.0, 140.8, 140.5, 140.1, 139.6, 129.9, 129.0, 128.8, 125.6 (q, $J_{CF} = 283.8$ Hz), 116.0, 115.9, 114.8, 114.7, 98.6, 61.5 (q, $J_{CF} = 27.5$ Hz), 60.6, 55.7, 55.6 ppm; **^{19}F NMR** (470 MHz, CDCl_3): δ -72.2 ppm; **HRMS (m/z)** (ESI): calc. for $\text{C}_{23}\text{H}_{23}\text{IF}_3\text{N}_2\text{O}_2$ 543.0751 [$\text{M}+\text{H}^+$]; found 543.0754. **HPLC:** (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 13.12 min, t_{minor} = 15.52 min.

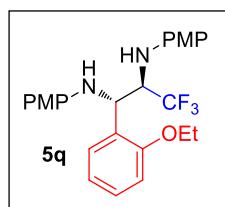
(1S,2R)-3,3,3-Trifluoro-1-(2-isopropoxypyhenyl)-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine



5p: Yield: 81%, 77mg. Brown oil. $R_f = 0.2$ (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.24 (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 6.82 (t, $J = 7.5$ Hz, 1H), 6.73 (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 8.8$ Hz, 2H), 6.59 (d, $J = 8.6$ Hz, 2H), 6.43 (d, $J = 8.8$ Hz, 2H), 5.08 (s, 1H), 4.68 (dt, $J = 12.1, 6.1$ Hz, 1H), 4.24 – 4.18 (m, 1H), 4.03 (s, 1H), 3.84 – 3.75 (m, 1H), 3.72 (s, 3H).

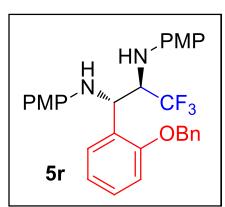
(s, 3H), 3.71 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 154.6, 153.3, 152.7, 141.4, 140.7, 128.7, 128.6, 128.4, 126.2 (q, *J*_{CF} = 283.8 Hz), 120.4, 116.0, 115.8, 114.8, 114.7, 112.2, 69.6, 61.5 (q, *J*_{CF} = 27.5 Hz), 55.7, 55.6, 53.4, 22.1, 21.9 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -73.0 ppm; **HRMS (m/z)** (ESI): calc. for C₂₆H₃₀F₃N₂O₃ 475.2203 [M+H⁺]; found 475.2201. **HPLC:** (Chiral AD-H, λ= 254 nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 5.94 min, t_{minor} = 10.00 min.

(1*S*,2*R*)-1-(2-Ethoxyphenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5q**:



Yield: 85%, 78mg. Brown oil. R_f = 0.3 (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.23 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 8.8 Hz, 2H), 5.10 (d, *J* = 3.4 Hz, 1H), 4.22 – 4.17 (m, 2H), 4.10 – 4.04 (m, 2H), 4.03 (s, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 155.9, 153.4, 152.8, 141.4, 140.7, 128.8, 128.3, 127.8, 126.2 (q, *J*_{CF} = 283.8 Hz), 120.8, 116.0, 115.8, 114.8, 114.7, 111.4, 63.6, 61.6 (q, *J*_{CF} = 27.5 Hz), 55.7, 55.6, 53.3, 14.7 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -73.0 ppm; **HRMS (m/z)** (ESI): calc. for C₂₅H₂₈F₃N₂O₃ 461.2047 [M+H⁺]; found 461.2044. **HPLC:** (Chiral AD-H, λ= 254 nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 7.53 min, t_{minor} = 11.71 min.

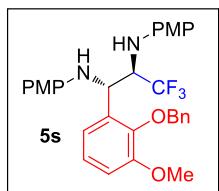
(1*S*,2*R*)-1-(2-(Benzylxy)phenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-



diamine **5r**: Yield: 80%, 84mg. Light yellow oil. R_f = 0.3 (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.42 – 7.31 (m, 5H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.17 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 8.5 Hz, 2H), 5.12 (s, 3H), 4.29 (s, 1H), 4.23 (d, *J* = 3.9 Hz, 1H), 3.96 (d, *J* = 7.5 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 155.7, 153.3, 152.8, 141.2, 140.6, 136.6, 128.9, 128.8, 128.6, 128.2, 128.0, 127.5, 126.0 (q, *J*_{CF} = 283.8 Hz), 121.3, 115.9, 115.8, 114.8, 114.7, 112.1, 70.4, 61.5 (q, *J*_{CF} = 27.5 Hz), 55.7, 55.6, 53.5 ppm; **¹⁹F NMR** (376 MHz, CDCl₃): δ -72.6 ppm; **HRMS (m/z)** (ESI): calc. for C₃₀H₃₀F₃N₂O₃ 523.2203 [M+H⁺]; found

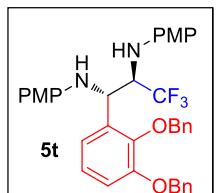
523.2206. **HPLC:** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 10.86 min, t_{minor} = 13.49 min.

(1*S*,2*R*)-1-(2-(Benzylxy)-3-methoxyphenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)



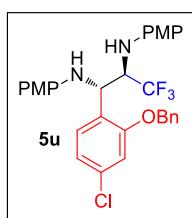
propane-1,2-diamine **5s**: Yield: 85%, 94mg. White solid, m.p. 136-138 °C. R_f = 0.2 (PE:EtOAc=10:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.46 (d, J = 5.6 Hz, 2H), 7.39 (d, J = 6.1 Hz, 3H), 6.97 (t, J = 7.8 Hz, 1H), 6.91 (dd, J = 16.0, 7.6 Hz, 2H), 6.68 (dd, J = 8.1, 5.1 Hz, 4H), 6.38 (d, J = 6.8 Hz, 4H), 5.24 – 5.15 (m, 2H), 5.09 (s, 1H), 4.25 – 4.20 (m, 1H), 3.95 (s, 1H), 3.93 (s, 3H), 3.85 – 3.77 (m, 1H), 3.72 (s, 3H), 3.72 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 153.3, 152.6, 144.8, 140.9, 140.5, 137.4, 133.7, 128.7, 128.6, 128.3, 125.9 (q, J_{CF} = 283.8 Hz), 124.2, 119.9, 116.0, 115.7, 114.8, 114.7, 112.2, 74.7, 61.9 (q, J_{CF} = 27.5 Hz), 55.9, 55.7, 55.6, 52.8 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.5 ppm; **HRMS (m/z)** (ESI): calc. for C₃₁H₃₂F₃N₂O₄ 553.2309 [M+H⁺]; found 553.2305. **HPLC:** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 8.22 min, t_{minor} = 10.96 min.

(1*S*,2*R*)-1-(2,3-Bis(benzylxy)phenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-



diamine **5t**: Yield: 82%, 103mg. White solid, m.p. 99-101 °C. R_f = 0.2 (PE:EtOAc=5:1). **¹H NMR** (500 MHz, CDCl₃): δ 7.49 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.37 (dd, J = 14.0, 7.8 Hz, 6H), 6.94 (s, 3H), 6.68 (d, J = 8.5 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 6.37 – 6.35 (m, 4H), 5.25 – 5.13 (m, 4H), 5.09 (s, 1H), 4.23 (d, J = 5.1 Hz, 1H), 3.92 (s, 1H), 3.89 – 3.76 (m, 1H), 3.71 (s, 6H) ppm; **¹³C NMR** (125 MHz, CDCl₃): δ 153.3, 152.7, 151.8, 145.3, 140.9, 140.4, 137.2, 136.7, 133.9, 129.3 (q, J_{CF} = 283.8 Hz), 128.8, 128.7, 128.6, 128.3, 128.2, 127.7, 124.2, 120.4, 116.0, 115.8, 114.8, 114.6, 114.0, 74.8, 71.1, 61.9 (q, J_{CF} = 27.5 Hz), 55.7, 55.6, 52.9 ppm; **¹⁹F NMR** (470 MHz, CDCl₃): δ -72.5 ppm; **HRMS (m/z)** (ESI): calc. for C₃₇H₃₆F₃N₂O₄ 629.2622 [M+H⁺]; found 629.2623. **HPLC:** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 11.37 min, t_{minor} = 13.41 min.

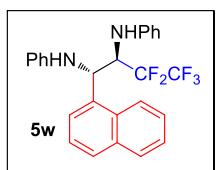
(1*S*,2*R*)-1-(2-(Benzylxy)-4-chlorophenyl)-3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5u**: Yield: 83%, 92mg. Light yellow oil. $R_f = 0.2$ (PE:EtOAc=5:1).



1H NMR (500 MHz, CDCl₃): δ 7.40 (s, 5H), 7.24 (d, $J = 8.2$ Hz, 1H), 7.01 (s, 1H), 6.88 (d, $J = 8.1$ Hz, 1H), 6.71 (d, $J = 8.7$ Hz, 2H), 6.68 (d, $J = 8.7$ Hz, 2H), 6.51 (d, $J = 8.7$ Hz, 2H), 6.38 (d, $J = 8.7$ Hz, 2H), 5.13 (s, 2H), 5.10 (s, 1H), 4.25 (s, 1H), 4.22 – 4.18 (m, 1H), 3.94 (d, $J = 8.2$ Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H) ppm; **13C NMR** (125 MHz, CDCl₃): δ 156.2, 153.4, 152.9, 140.9, 140.1, 135.8, 134.3, 129.5, 128.9, 128.5, 127.6, 126.7, 125.9 (q, $J_{CF} = 283.8$ Hz), 121.4, 115.9, 115.9, 114.8, 114.7, 112.8, 70.8, 61.3 (q, $J_{CF} = 27.5$ Hz), 55.7, 53.0 ppm; **19F NMR** (470 MHz, CDCl₃): δ -72.5 ppm; **HRMS (m/z)** (ESI): calc. for C₃₀H₂₉ClF₃N₂O₃ 557.1813 [M+H⁺]; found 557.1814. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 11.25 min, t_{minor} = 13.80 min.

(1*S*,2*R*)-1-(2-(benzyloxy)-5-chlorophenyl)-3,3,3-Trifluoro-N¹,N²-bis(4-methoxyphenyl)propane-1,2-diamine **5v**: Yield: 81%, 90mg. Brown oil. $R_f = 0.2$ (PE:EtOAc=10:1). **1H NMR** (500 MHz, CDCl₃): δ 7.42 – 7.32 (m, 5H), 7.20 (d, $J = 8.2$ Hz, 1H), 6.98 (d, $J = 1.4$ Hz, 1H), 6.84 (dd, $J = 8.2, 1.5$ Hz, 1H), 6.68 (d, $J = 8.9$ Hz, 2H), 6.65 (d, $J = 8.8$ Hz, 2H), 6.48 (d, $J = 8.5$ Hz, 2H), 6.35 (d, $J = 8.8$ Hz, 2H), 5.09 (s, 2H), 5.07 (d, $J = 2.8$ Hz, 1H), 4.23 – 4.14 (m, 1H), 3.84 – 3.79 (m, 1H), 3.78 – 3.71 (m, 1H), 3.70 (s, 3H), 3.68 (s, 3H) ppm; **13C NMR** (125 MHz, CDCl₃): δ 156.2, 153.4, 152.9, 140.9, 140.2, 135.8, 134.3, 129.5, 128.9, 128.5, 127.6, 126.7, 125.9 (q, $J_{CF} = 283.8$ Hz), 121.4, 115.9, 115.8, 114.8, 114.7, 112.9, 70.8, 61.3 (q, $J_{CF} = 27.5$ Hz), 55.7, 53.0 ppm; **19F NMR** (470 MHz, CDCl₃): δ -72.5 ppm; **HRMS (m/z)** (ESI): calc. for C₃₀H₂₉ClF₃N₂O₃ 557.1813 [M+H⁺]; found 557.1819. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 90/10, Flow rate = 1.0 mL/min), t_{major} = 11.58 min, t_{minor} = 14.25 min.

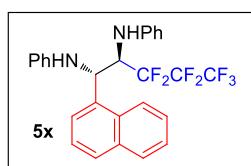
(1*S*,2*R*)-3,3,4,4,4-Pentafluoro-1-(naphthalen-1-yl)-N¹,N²-diphenylbutane-1,2-diamine **5w**: Yield: 90%, 82mg. Colorless solid, m.p. 115–117 °C. $R_f = 0.3$ (PE:EtOAc=20:1). **1H NMR** (400 MHz, CDCl₃): δ 8.18 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.74 – 7.68 (m, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.54 (d, $J = 7.2$ Hz, 1H), 7.28 (dd, $J = 9.9, 4.7$ Hz, 1H), 7.12 (t, $J = 7.9$ Hz, 2H), 6.88 (t, $J = 7.9$ Hz, 2H),



S40

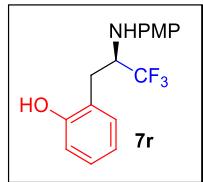
6.73 (t, $J = 7.3$ Hz, 1H), 6.65 (dd, $J = 16.0, 7.7$ Hz, 3H), 5.98 (s, 1H), 5.93 (d, $J = 8.0$ Hz, 2H), 4.75 (s, 1H), 4.50 (dd, $J = 21.9, 6.6$ Hz, 1H), 4.14 (d, $J = 9.3$ Hz, 1H) ppm; **^{13}C NMR** (125 MHz, CDCl_3): δ 146.0, 145.9, 134.4, 134.2, 130.3, 129.8, 129.3, 129.1, 128.6, 127.2, 125.9, 125.7, 125.0, 121.1, 119.5, 118.6, 114.3, 113.6, 58.4 (dd, $J_{CF} = 24.6, 19.3$ Hz), 51.0 ppm (Carbon with directly attached fluorine appear as broad multiplets and are not reported); **^{19}F NMR** (470 MHz, CDCl_3): δ -82.2 (s), -117.2 (d, $J = 275.6$ Hz), -127.0 (d, $J = 275.6$ Hz) ppm; **HRMS** (m/z) (ESI): calc. for $\text{C}_{26}\text{H}_{22}\text{F}_5\text{N}_2$ 457.1698 [$\text{M}+\text{H}^+$]; found 457.1695. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 5.71 min, t_{minor} = 6.35 min.

(1*S*,2*R*)-3,3,4,4,5,5,5-Heptafluoro-1-(naphthalen-1-yl)-N¹,N²-diphenylpentane-1,2-diamine **5x**:



Yield: 86%, 87mg. Colorless solid, m.p. 121-123 °C. $R_f = 0.3$ (PE:EtOAc=20:1). **^1H NMR** (500 MHz, CDCl_3): δ 8.21 (d, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.57 (d, $J = 7.2$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 1H), 7.15 (t, $J = 7.7$ Hz, 2H), 6.90 (t, $J = 7.7$ Hz, 2H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 2H), 6.66 (t, $J = 7.3$ Hz, 1H), 6.05 (s, 1H), 5.93 (d, $J = 8.0$ Hz, 2H), 4.80 (d, $J = 5.2$ Hz, 1H), 4.64 (dd, $J = 22.0, 8.8$ Hz, 1H), 4.21 (d, $J = 9.3$ Hz, 1H) ppm; **^{13}C NMR** (125 MHz, CDCl_3): δ 146.0, 145.8, 134.4, 134.2, 130.3, 129.8, 129.4, 129.1, 128.6, 127.2, 125.9, 125.8, 125.2, 121.1, 119.5, 118.6, 114.3, 113.6, 58.4 (dd, $J_{CF} = 24.7, 19.2$ Hz), 51.1 (d, $J_{CF} = 3.2$ Hz) ppm (Carbon with directly attached fluorine appear as broad multiplets and are not reported); **^{19}F NMR** (470 MHz, CDCl_3): δ -80.4 (dd, $J = 11.6, 9.7$ Hz, 3F), -113.9 – -115.5 (m, 1F), -122.7 – -123.7 (m, 1F), -124.6 – -126.4 (m, 2F) ppm; **HRMS** (m/z) (ESI): calc. for $\text{C}_{27}\text{H}_{22}\text{F}_7\text{N}_2$ 507.1666 [$\text{M}+\text{H}^+$]; found 507.1665. **HPLC**: (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 98/2, Flow rate = 1.0 mL/min), t_{major} = 8.87 min, t_{minor} = 10.14 min.

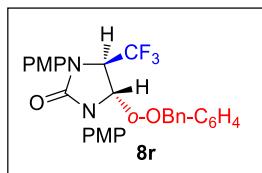
(*R*)-2-(3,3,3-Trifluoro-2-((4-methoxyphenyl)amino)propyl)phenol **7r**: quantitative yield, 50mg.



Light yellow solid, m.p. 89-91 °C. $R_f = 0.3$ (PE:EtOAc=5:1). **^1H NMR** (500 MHz, CDCl_3): δ 7.56 (s, 1H), 7.15 (t, $J = 7.3$ Hz, 2H), 6.88 (t, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 7.9$ Hz, 1H), 6.72 (d, $J = 8.9$ Hz, 2H), 6.60 (d, $J = 8.9$ Hz, 2H), 3.97 (dd, $J = 12.7, 6.5$ Hz, 1H), 3.87 (s, 1H), 3.73 (s, 3H), 3.11 – 3.03 (m, 2H) ppm; **^{13}C NMR**

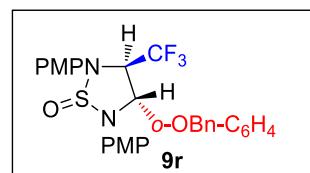
(125 MHz, CDCl₃): δ 154.8, 154.3, 139.7, 131.4, 128.9, 126.1 (q, *J*_{CF} = 282.8 Hz), 123.3, 120.9, 117.6, 116.6, 114.8, 60.7 (q, *J*_{CF} = 27.8 Hz), 55.6, 32.1 (q, *J*_{CF} = 1.9 Hz) ppm; ¹⁹F NMR (470 MHz, CDCl₃) δ -75.6 ppm; HRMS (*m/z*) (ESI): calc. for C₁₆H₁₇F₃NO₂ 312.1206 [M+H⁺]; found 312.1201. HPLC: (Chiral IC, λ= 244 nm, hexane/2-propanol = 97/3, Flow rate = 1.0 mL/min), t_{major} = 19.96 min, t_{minor} = 24.03 min.

(4*S,5R*)-4-(2-(Benzylxy)phenyl)-1,3-bis(4-methoxyphenyl)-5-(trifluoromethyl)imidazolidin-2-



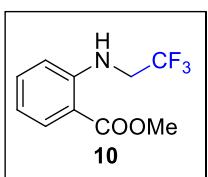
one **8r**: quantitative yield, 88mg. Light yellow oil. R_f = 0.2 (PE:EtOAc=5:1). ¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.28 (m, 9H), 7.23 – 7.17 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.82 – 6.76 (m, 2H), 5.62 (d, *J* = 2.3 Hz, 1H), 5.24 – 5.12 (m, 2H), 4.45 – 4.37 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 157.9, 156.1, 155.8, 155.7, 136.1, 131.5, 130.8, 130.2, 128.7, 128.4, 127.7, 127.6, 126.5, 126.4, 124.4 (q, *J*_{CF} = 283.3 Hz), 122.0, 121.5, 114.3, 114.2, 112.7, 70.6, 63.7 (q, *J*_{CF} = 30.5 Hz), 55.5, 55.4, 54.2 ppm; ¹⁹F NMR: (376 MHz, CDCl₃): δ -75.92 ppm; HRMS (*m/z*) (ESI): calc. for C₃₁H₂₈F₃N₂O₄ 549.1996 [M+H⁺]; found 549.1993. HPLC: (Chiral AD-H, λ= 254 nm, hexane/2-propanol = 70/30, Flow rate = 1.0 mL/min), t_{major} = 17.66 min, t_{minor} = 56.54 min.

(3*S,4R*)-3-(2-(Benzylxy)phenyl)-2,5-bis(4-methoxyphenyl)-4-(trifluoromethyl)-1,2,5-



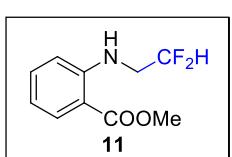
thiadiazolidine 1-oxide **9r**: quantitative yield, 91mg. Light yellow oil. R_f = 0.2 (PE:EtOAc=5:1). ¹H NMR (400 MHz, CDCl₃): δ 8.10 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 – 7.27 (m, 6H), 7.21 – 7.16 (m, 2H), 7.15 – 7.11 (m, 2H), 7.08 (td, *J* = 7.7, 0.7 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.81 – 6.74 (m, 2H), 5.91 (d, *J* = 3.8 Hz, 1H), 5.20 – 5.07 (m, 2H), 4.76 – 4.62 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 159.0, 156.6, 155.9, 136.5, 133.0, 130.7, 130.1, 130.0, 129.7, 128.6, 128.2, 127.6, 126.1, 124.6 (q, *J*_{CF} = 282.3 Hz), 122.2, 121.7, 114.7, 114.7, 111.8, 73.1 (q, *J*_{CF} = 29.4 Hz), 70.4, 60.5, 55.5, 55.4 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -75.0 ppm; HRMS (*m/z*) (ESI): calc. for C₃₀H₂₇F₃N₂O₄Na 591.1536 [M+Na⁺]; found 591.1531. HPLC: (Chiral AD-H, λ= 254 nm, hexane/2-propanol = 70/30, Flow rate = 1.0 mL/min), t_{major} = 11.97 min, t_{minor} = 31.36 min.

Methyl 2-((2,2,2-trifluoroethyl)amino)benzoate **10**: **¹H NMR** (400 MHz, CDCl₃): δ 8.18 (s, 1H),



7.95 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 3.92 – 3.83 (m, 5H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 169.0, 149.9, 134.7, 131.8, 124.9 (q, *J_{CF}* = 280.4 Hz), 116.6, 111.4, 111.2, 51.8, 44.8 (q, *J_{CF}* = 33.9 Hz) ppm; **¹⁹F NMR** (376 MHz, CDCl₃): δ -72.0 ppm; **HRMS (m/z)** (ESI): calc. for C₁₀H₁₁F₃NO₂ 234.0742 [M+H⁺]; found 234.0749.

Methyl 2-((2,2-difluoroethyl)amino)benzoate **11**: **¹H NMR** (400 MHz, CDCl₃): δ 7.98 (d, *J* = 7.9



Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.15 (tt, *J* = 55.5, 4.4 Hz, 1H), 4.10 (td, *J* = 15.2, 4.4 Hz, 2H), 3.90 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃): δ 167.7, 143.8, 134.5, 131.1, 121.1, 114.5 (t, *J_{CF}* = 239.6 Hz), 114.2, 111.6, 63.1 (t, *J_{CF}* = 24.1 Hz), 52.2 ppm; **¹⁹F NMR** (376 MHz, CDCl₃): δ -121.3 ppm; **HRMS (m/z)** (ESI): calc. for C₁₀H₁₂F₂NO₂ 216.0836 [M+H⁺]; found 216.0830.

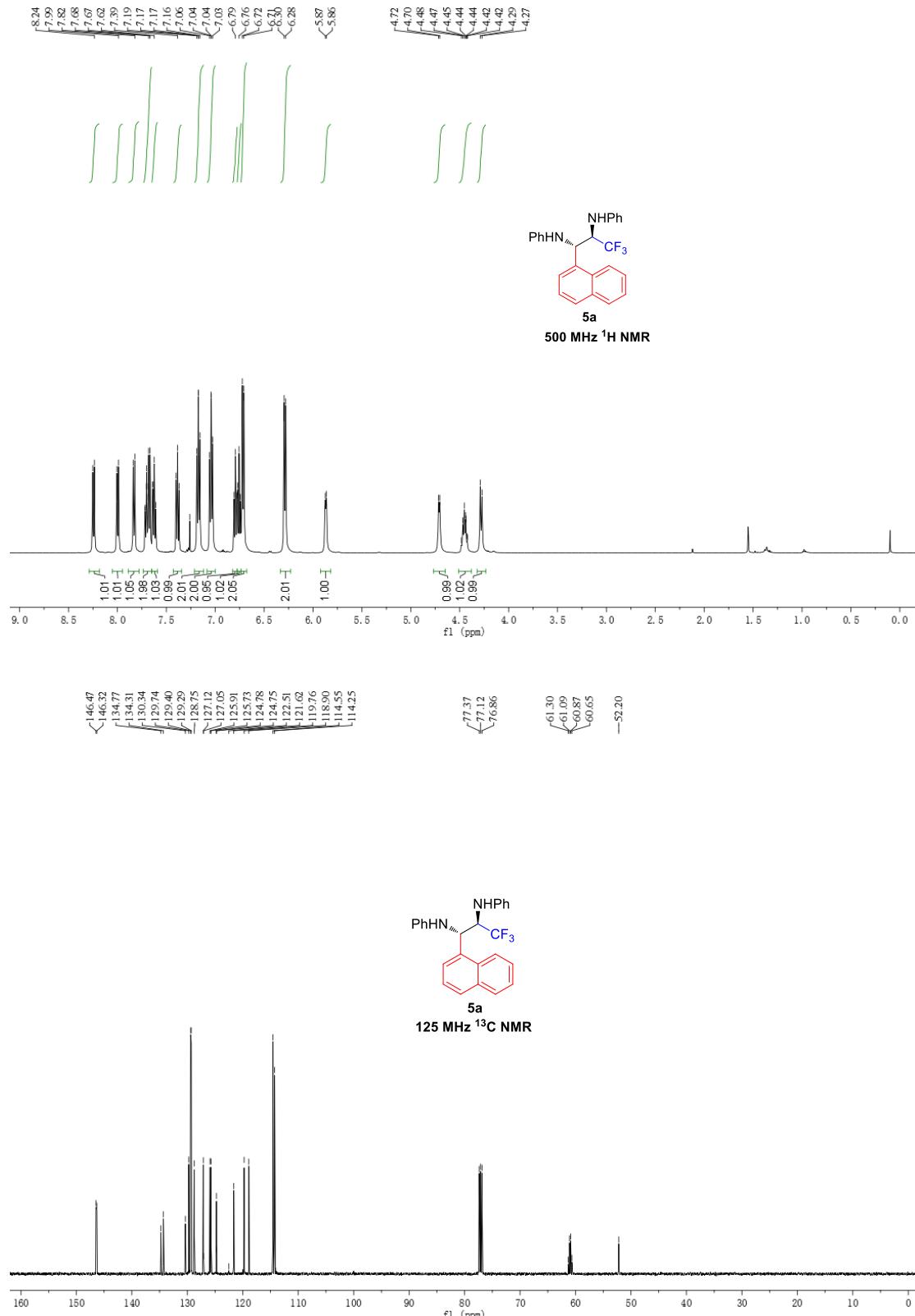
10. References

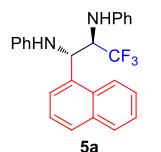
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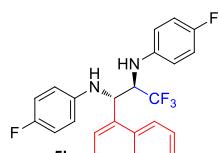
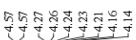
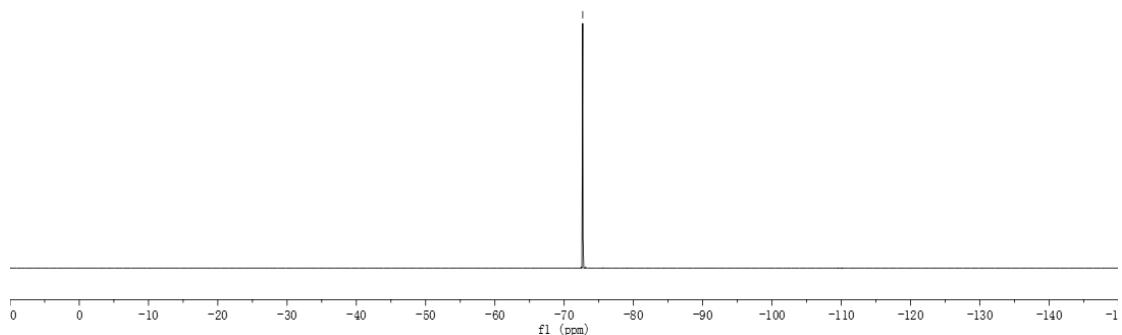
11. NMR and HPLC Spectra

NMR Spectra of all products

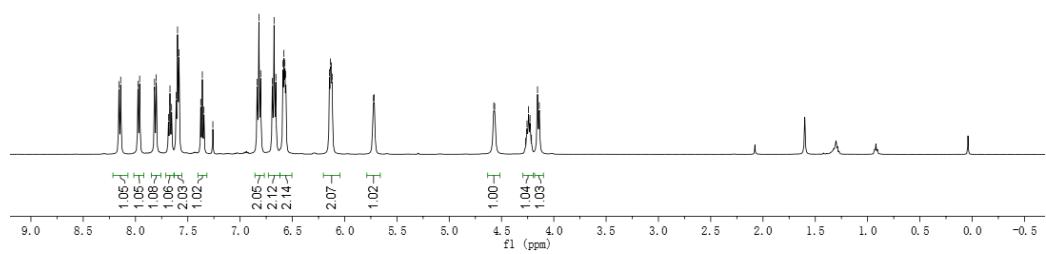


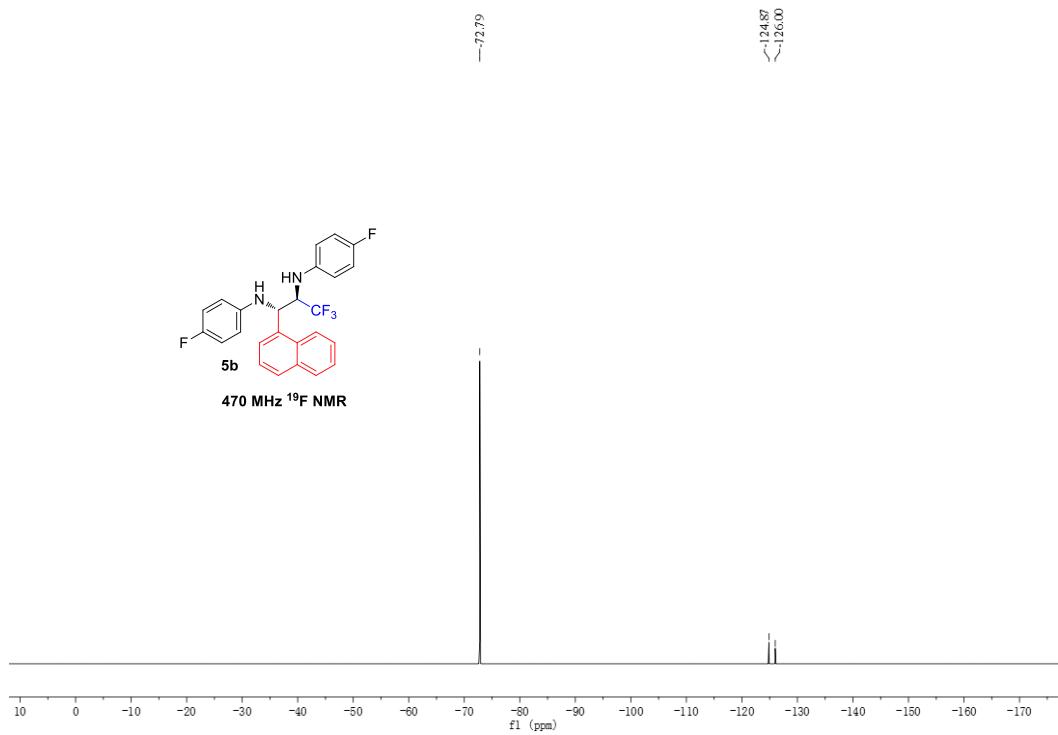
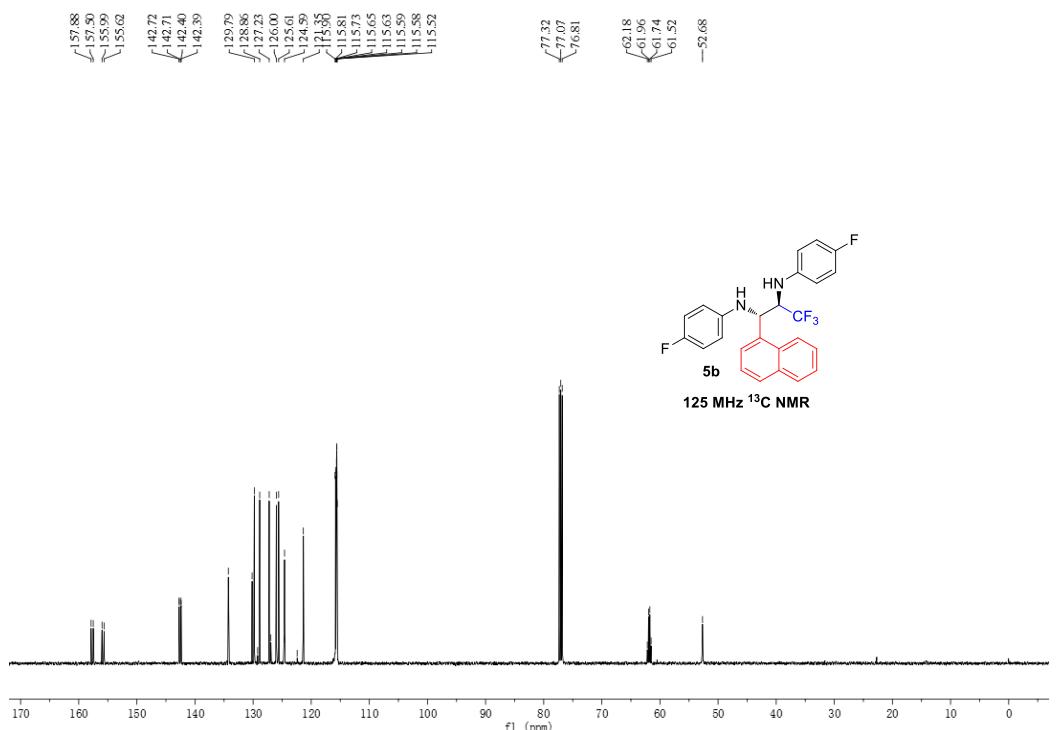


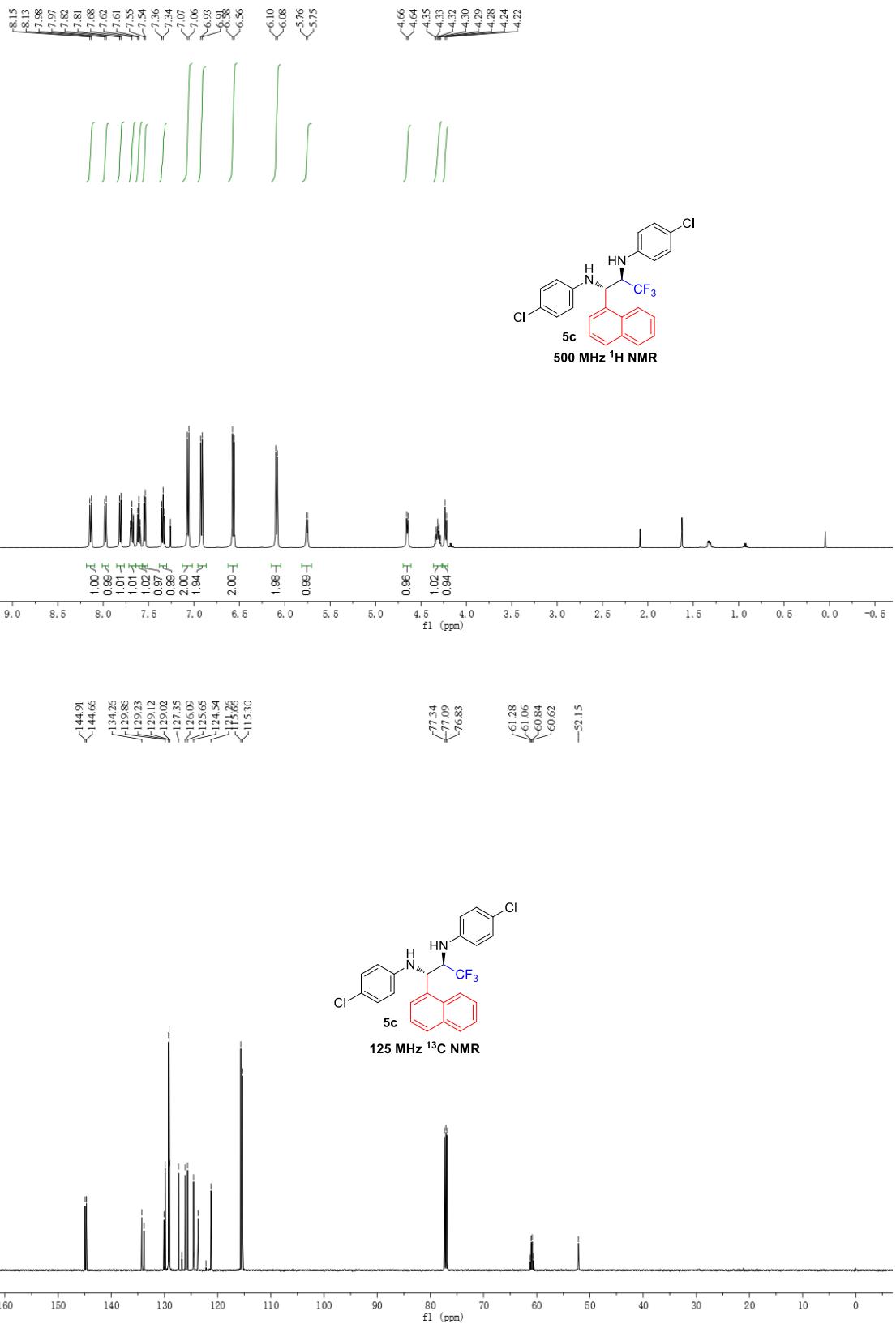
5a
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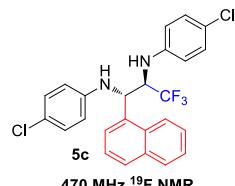


500 MHz ^1H NMR

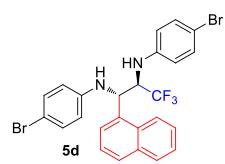
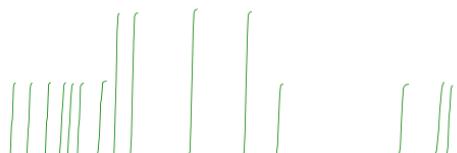
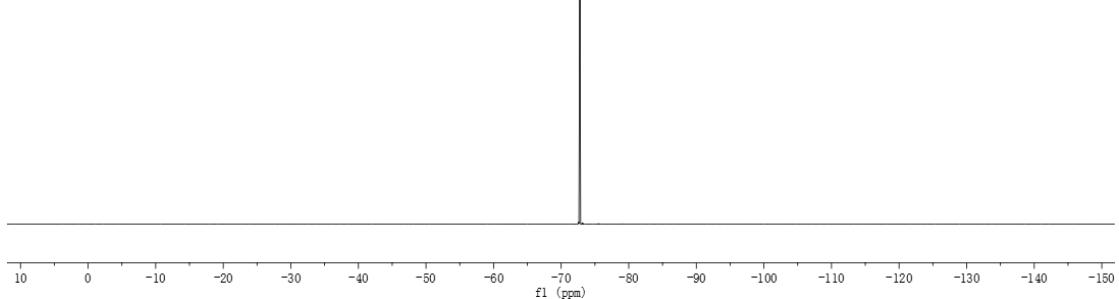




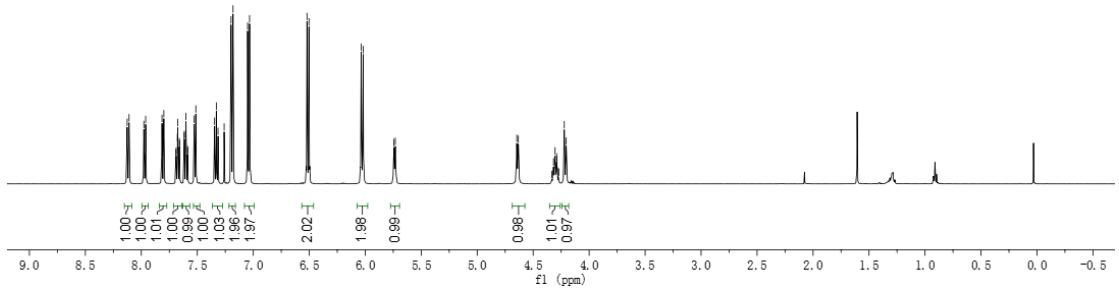


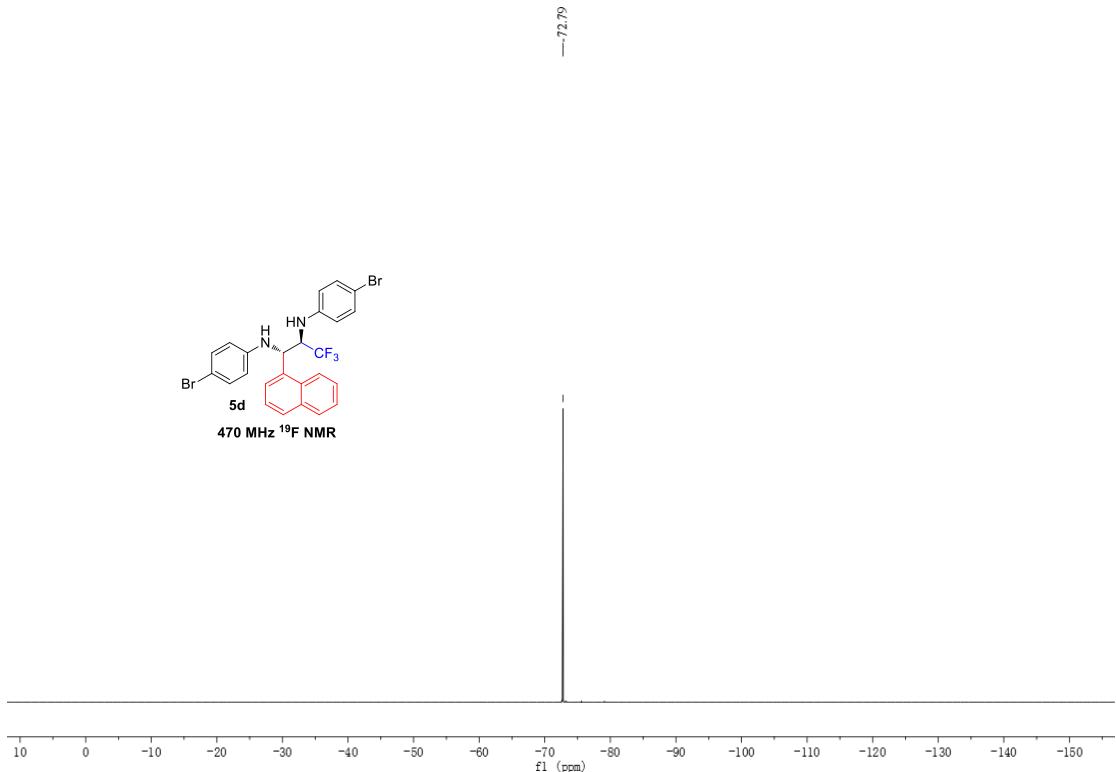
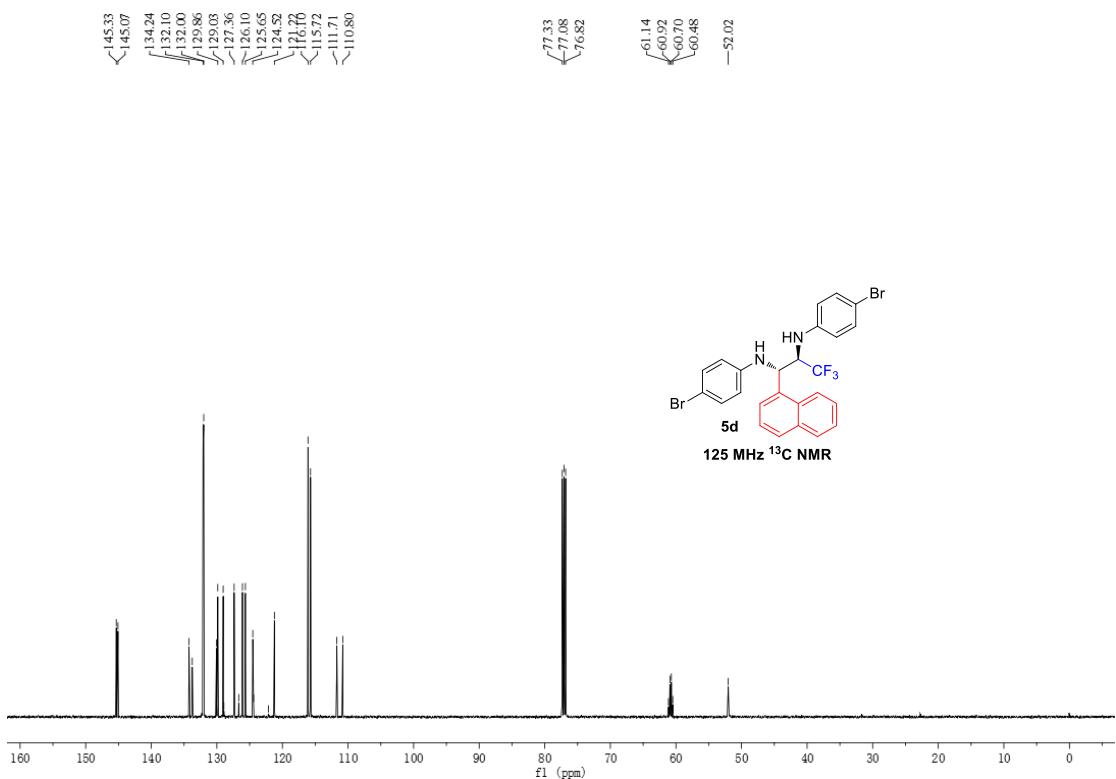


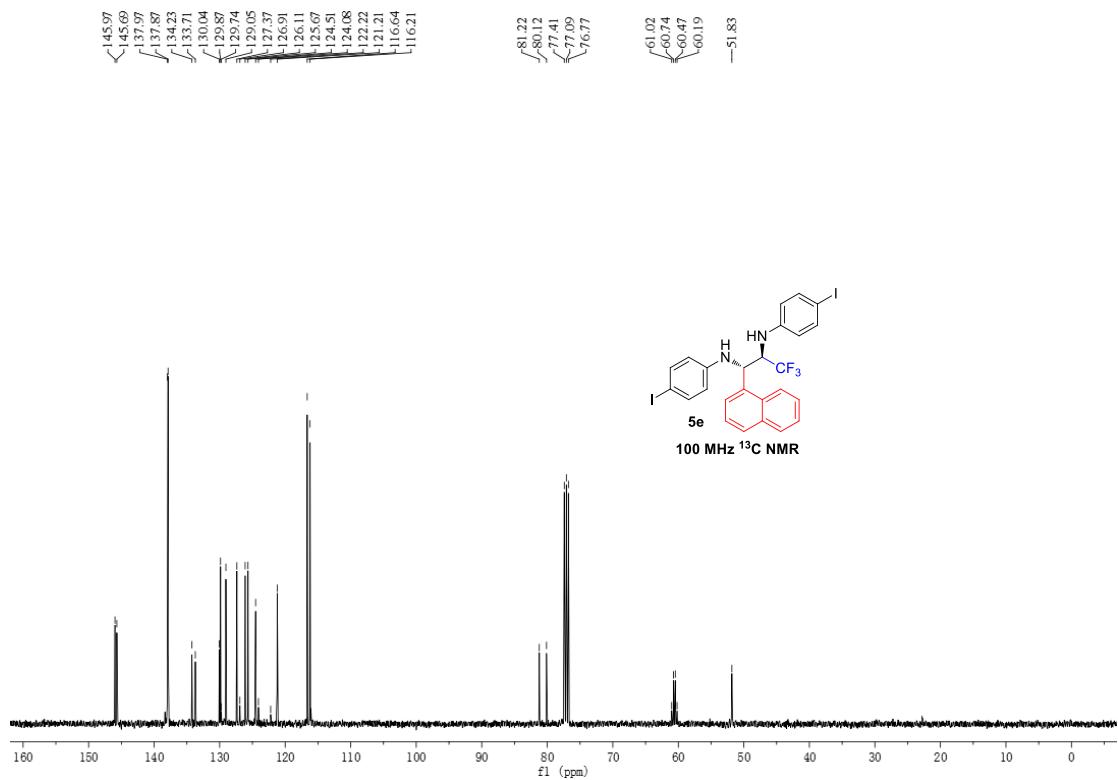
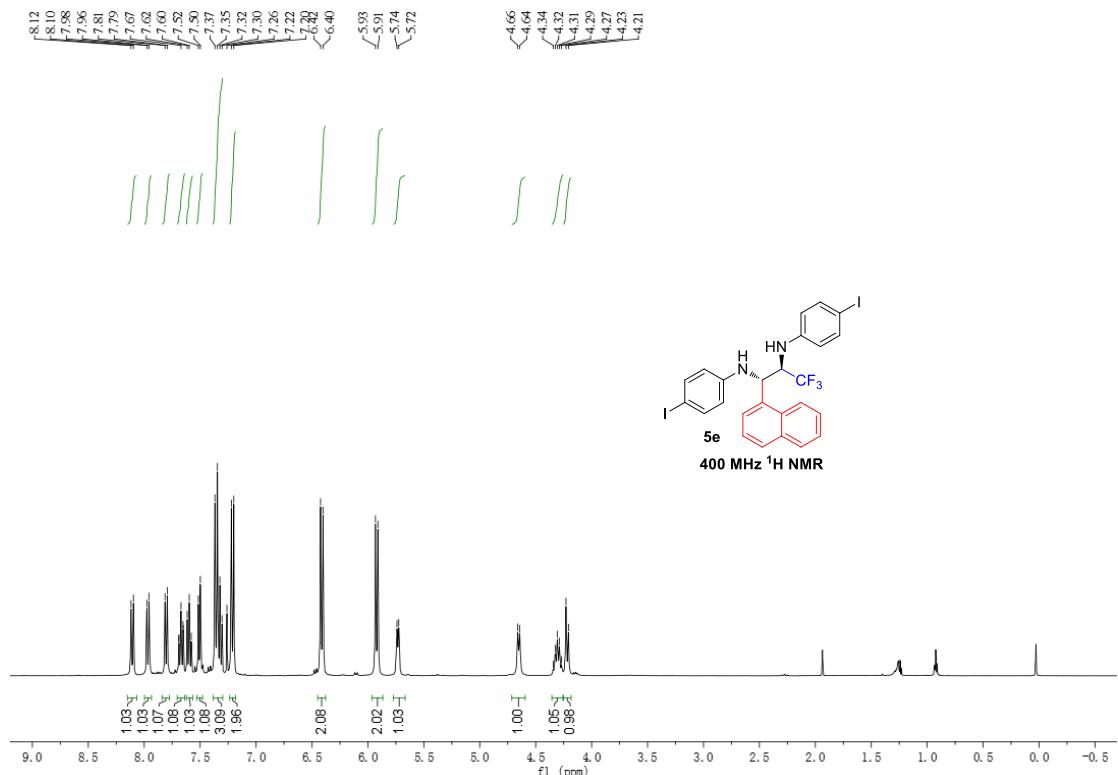
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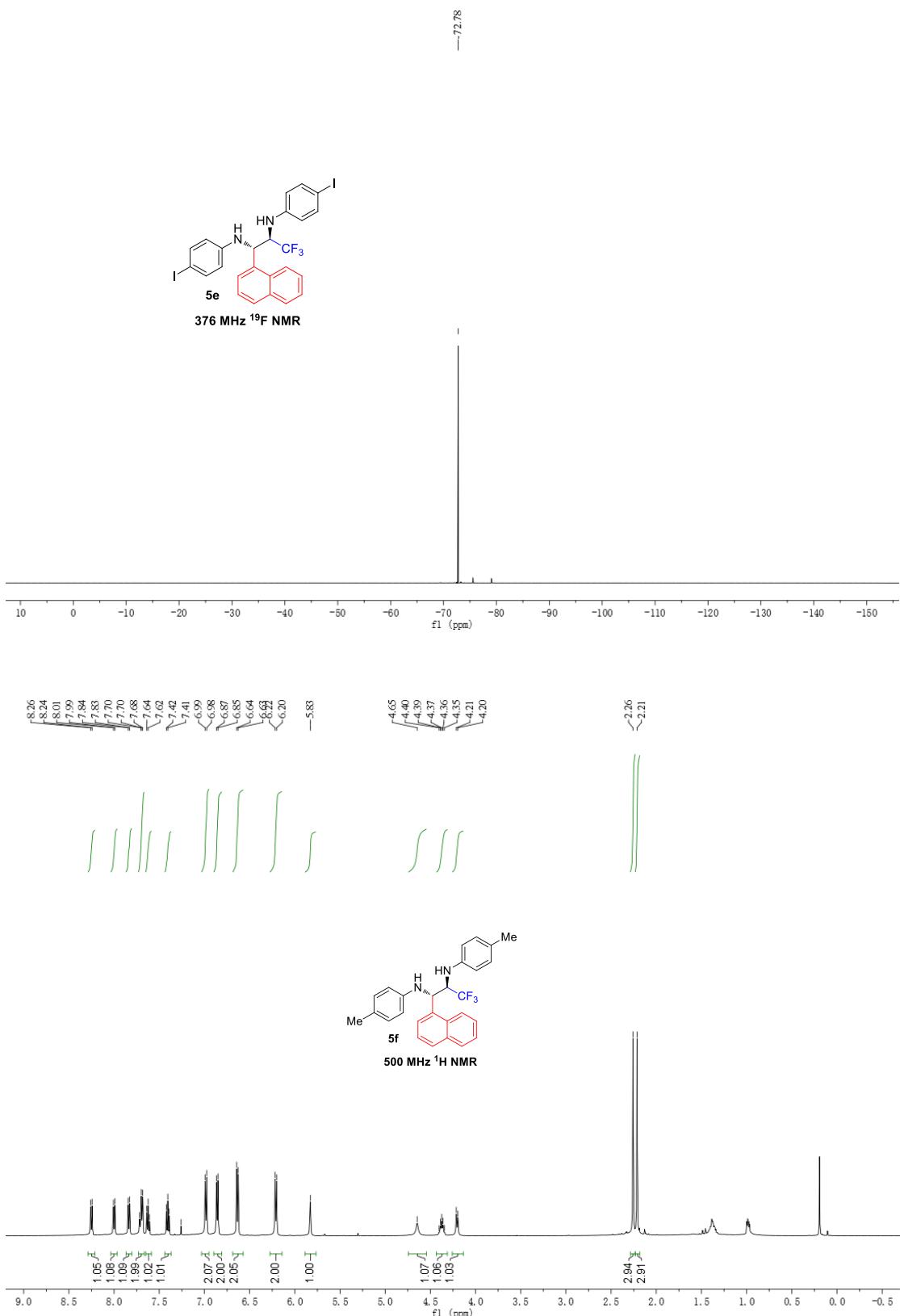


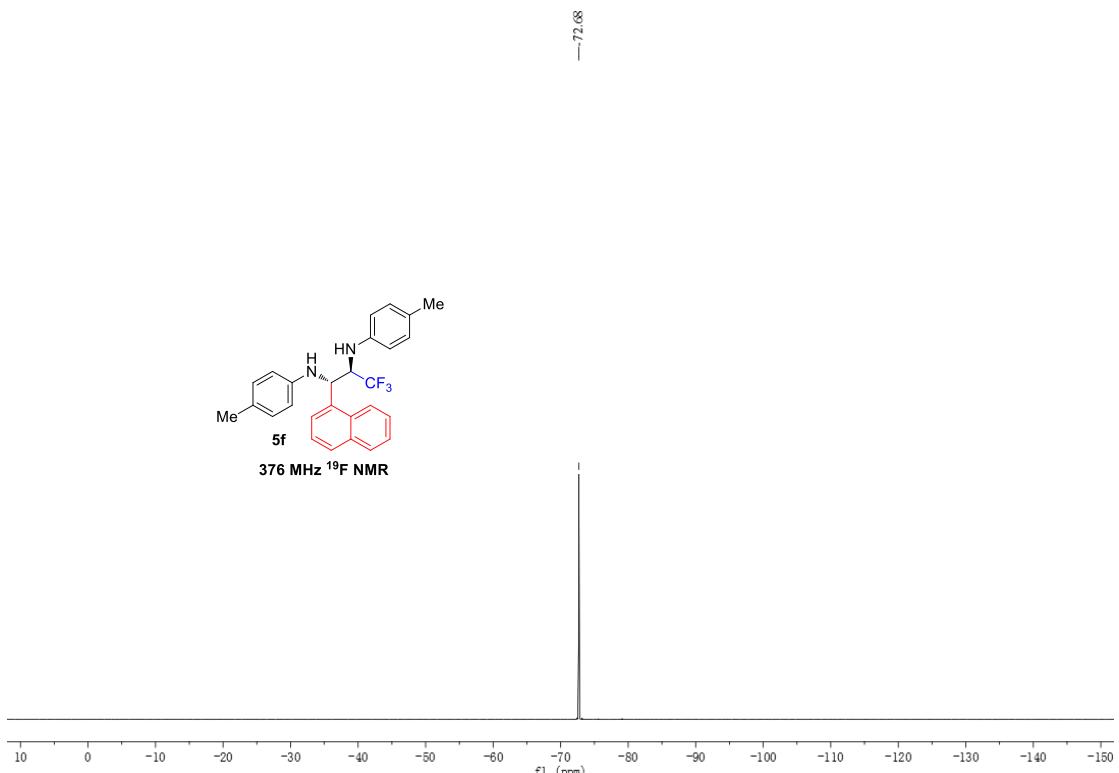
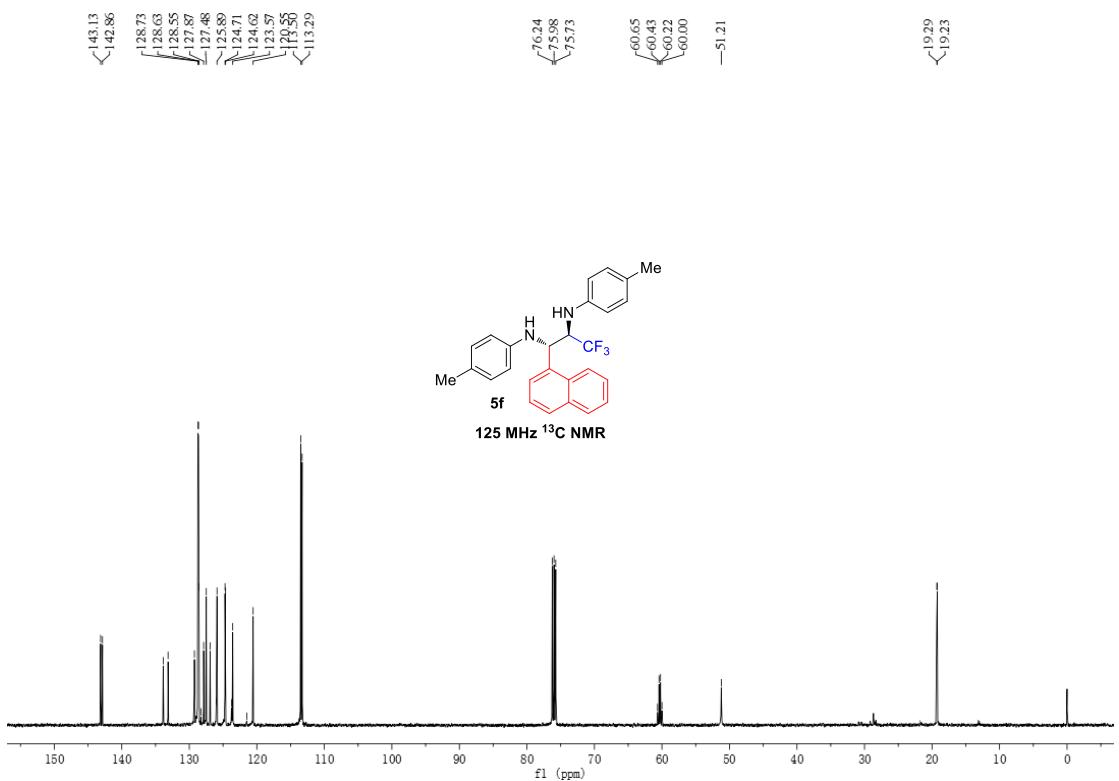
500 MHz ^1H NMR

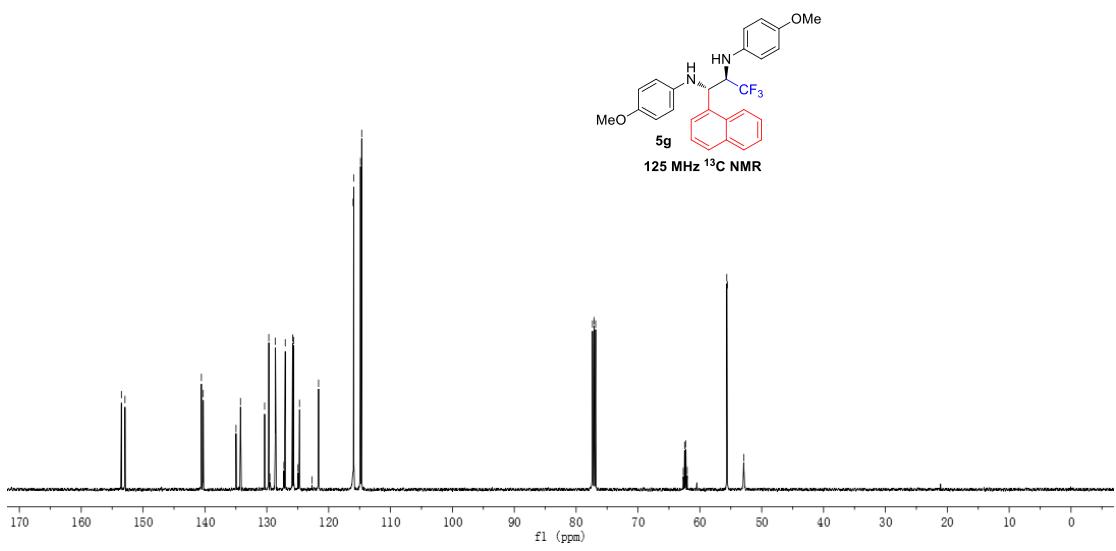
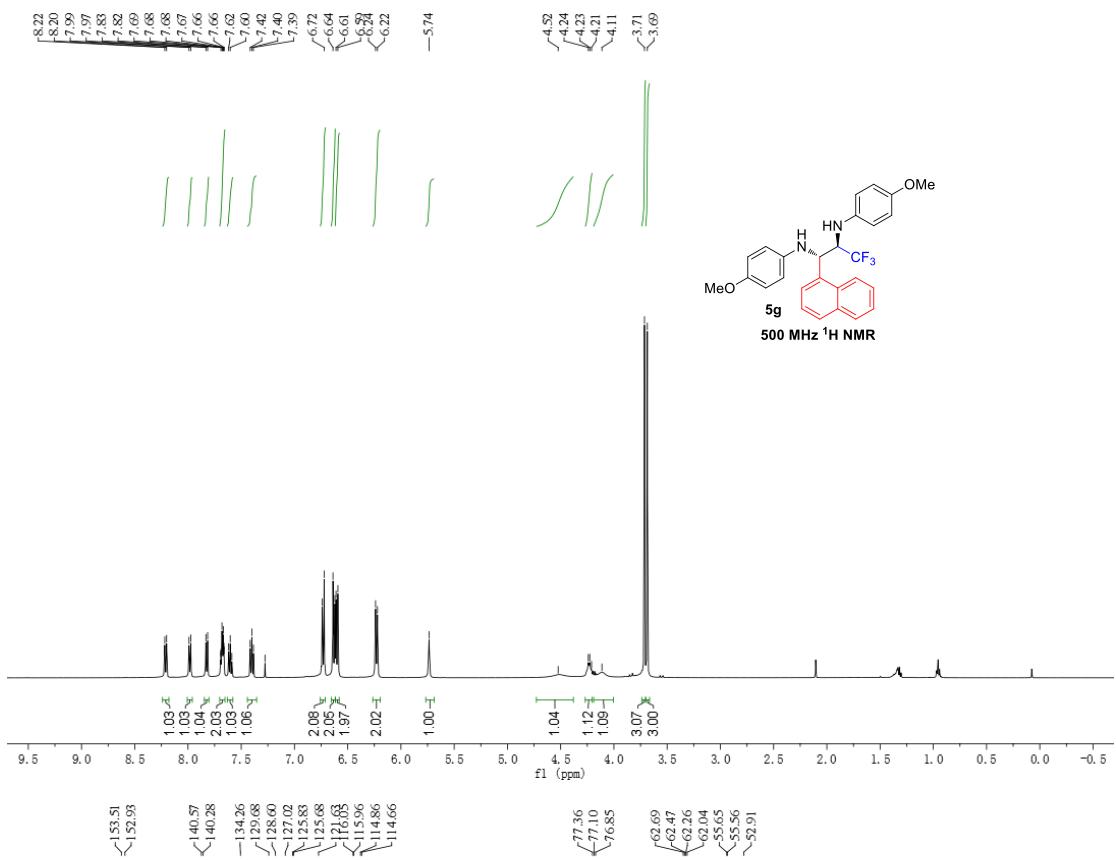


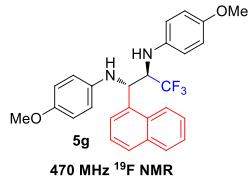




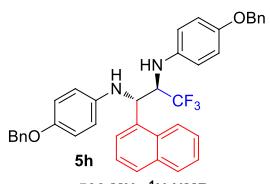
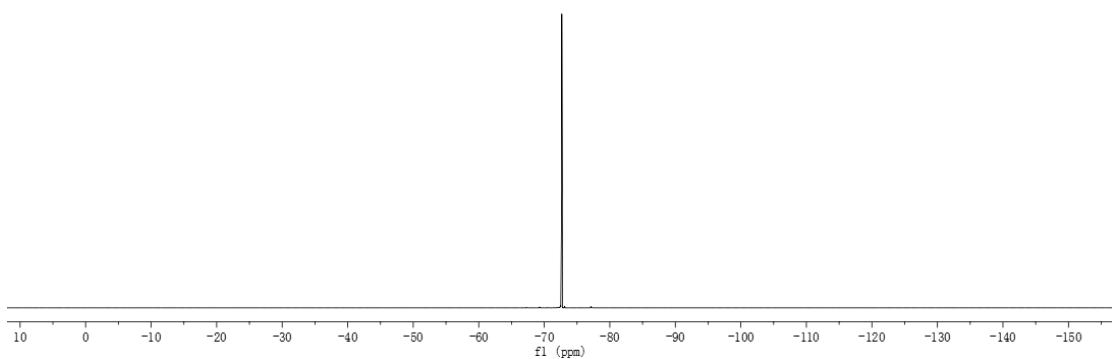




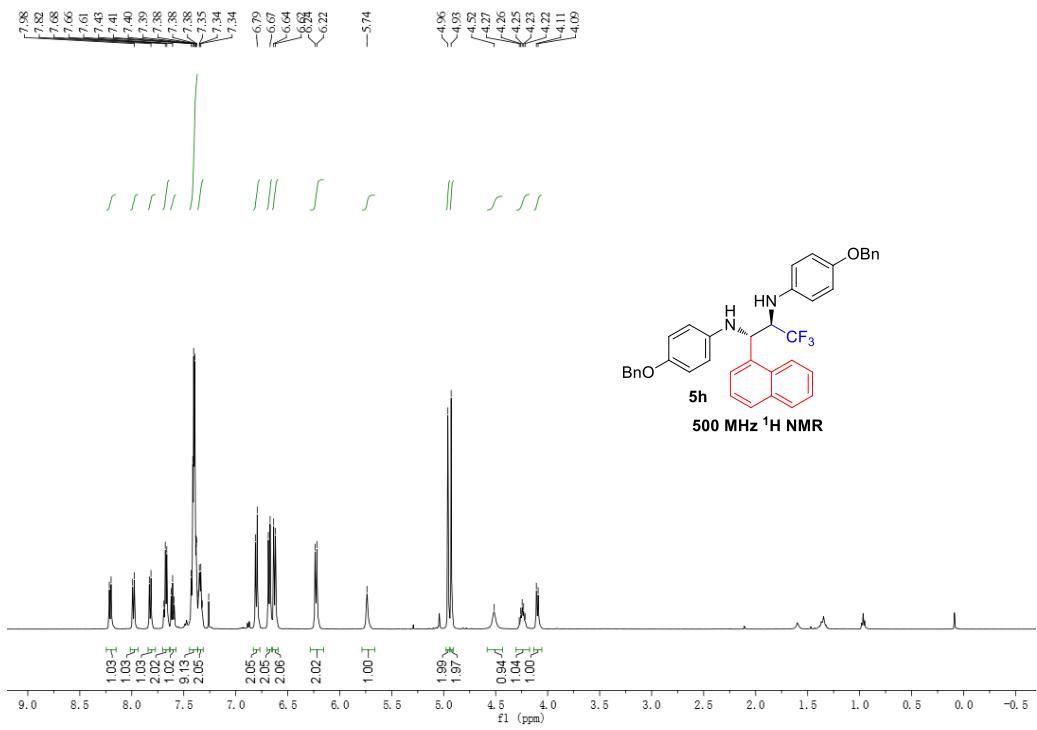


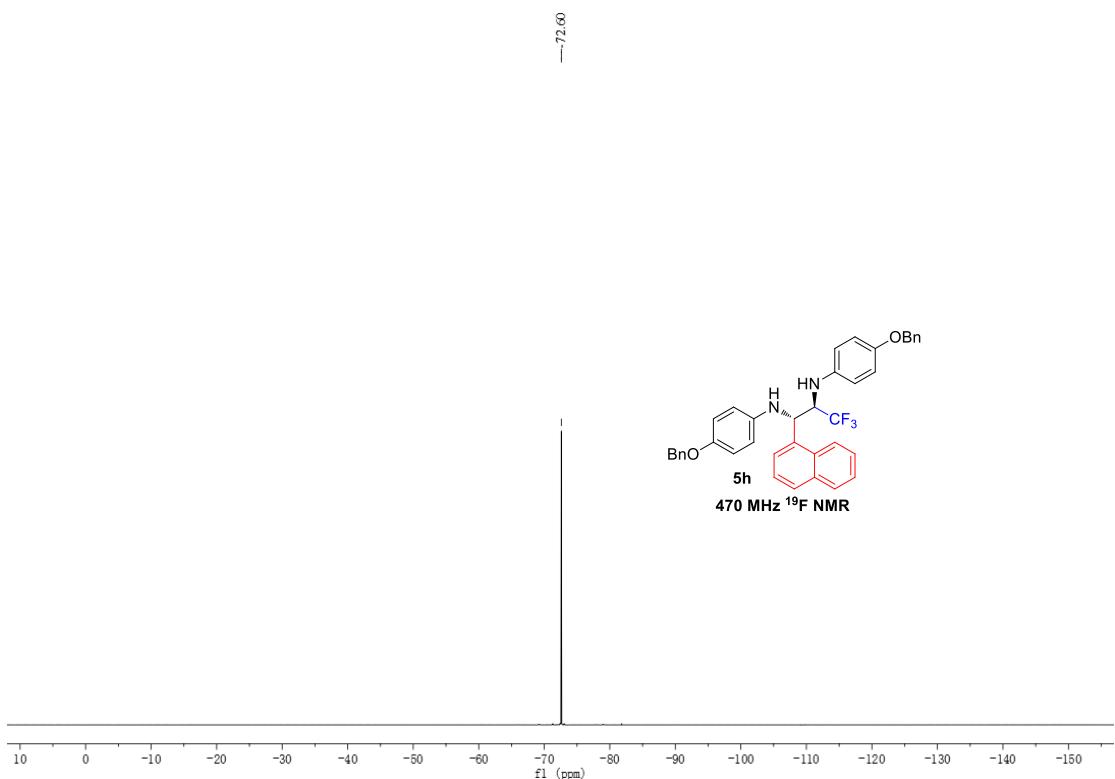
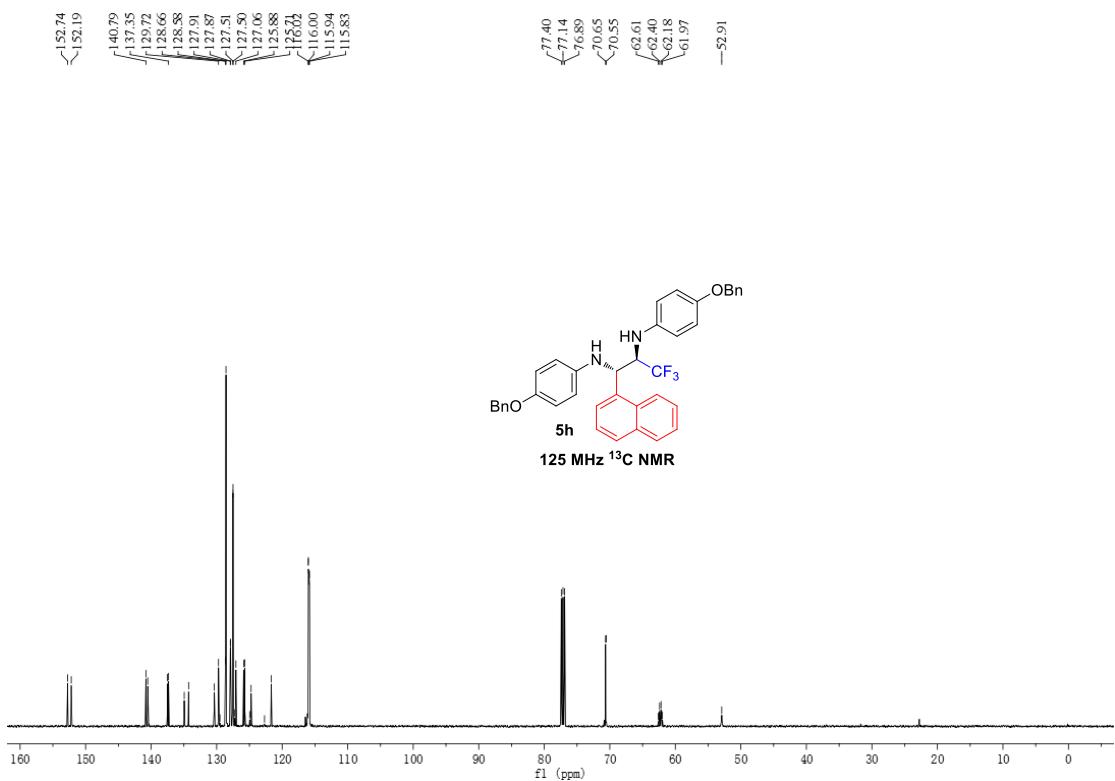


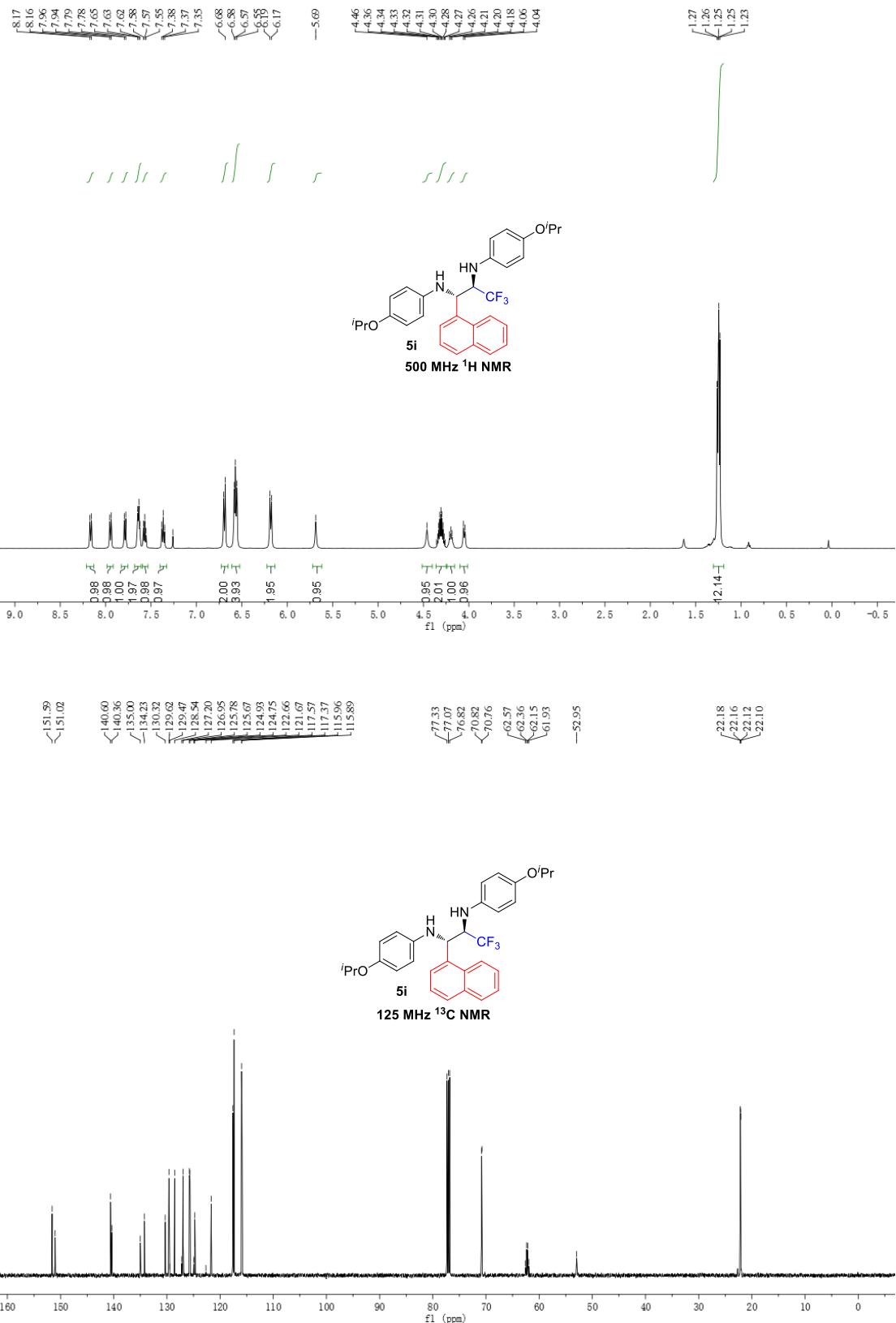
470 MHz ^{19}F NMR

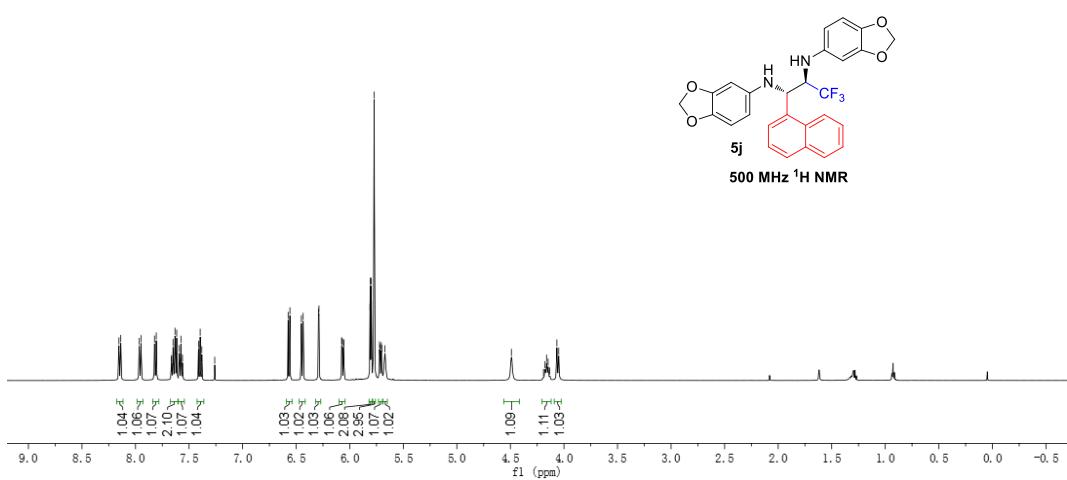
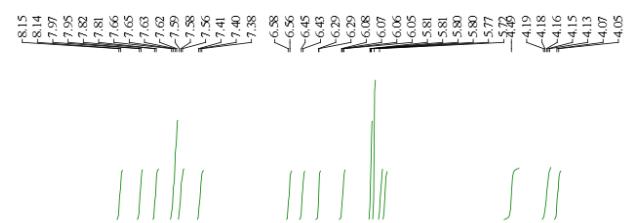
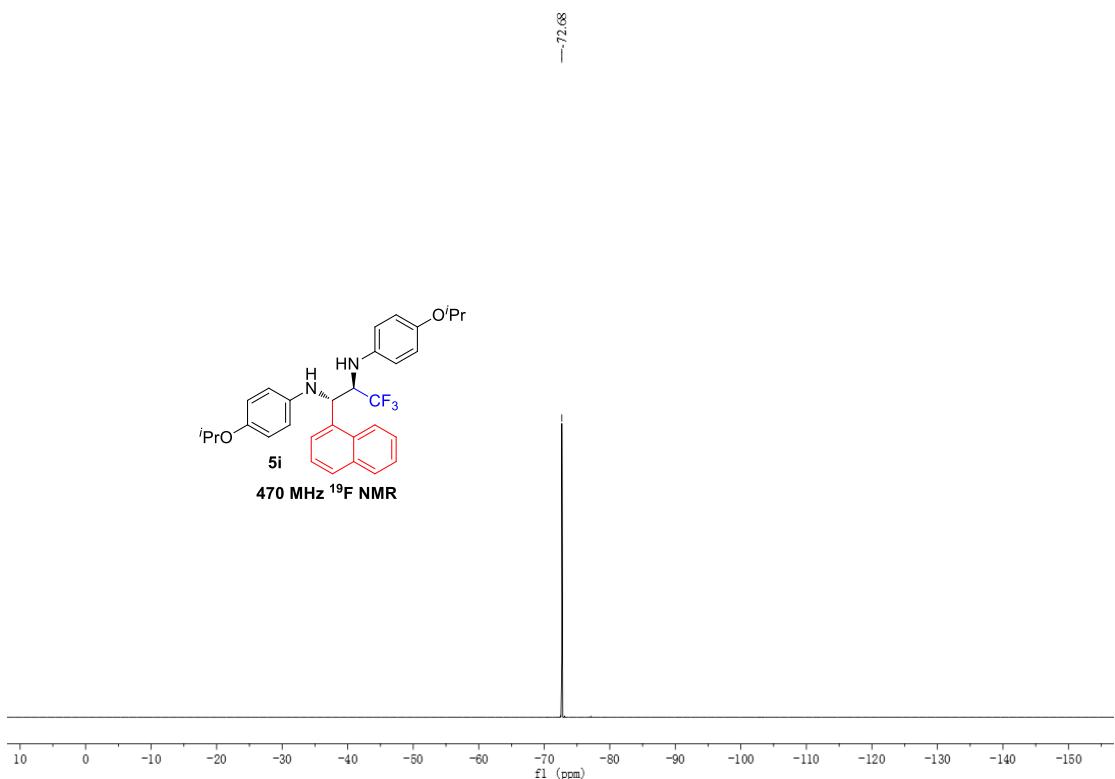


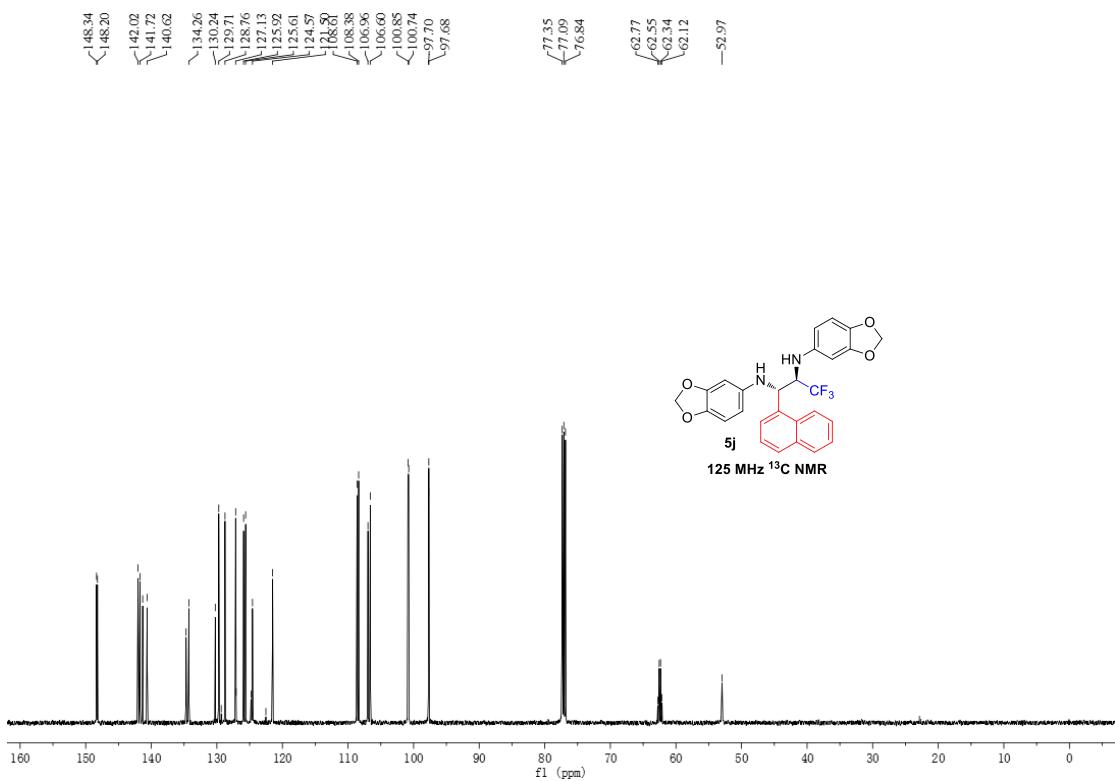
500 MHz ^1H NMR



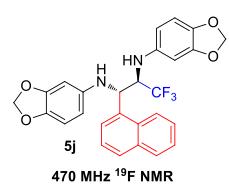


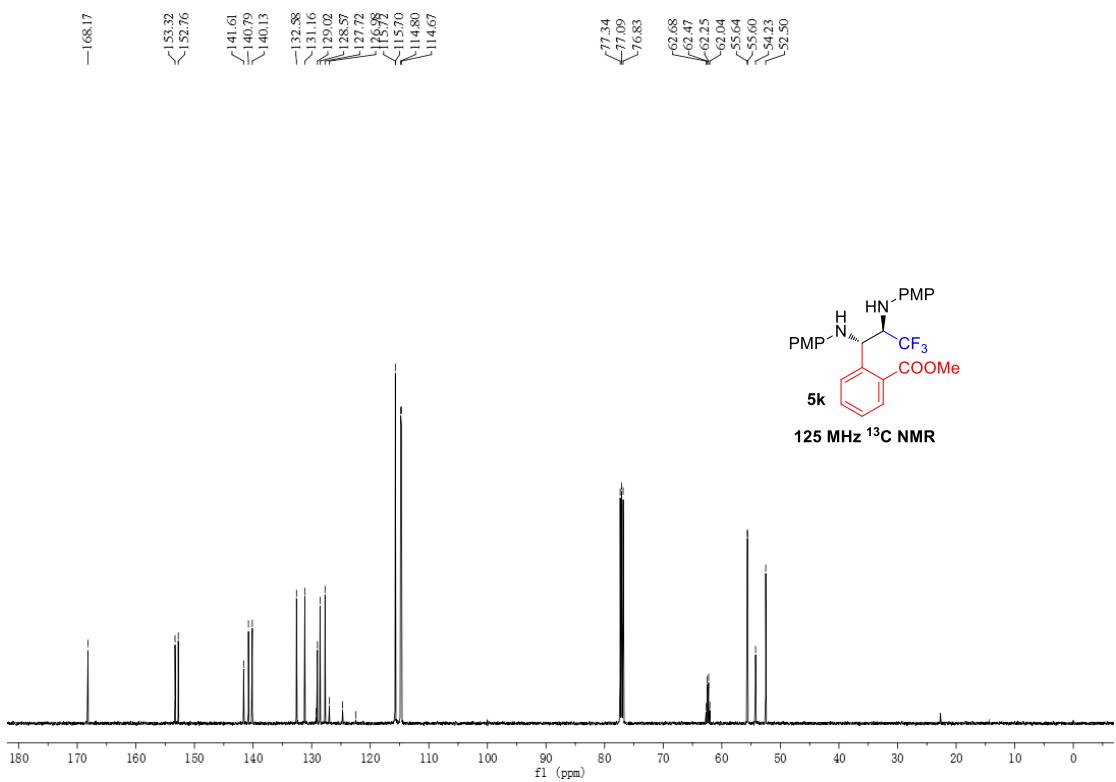
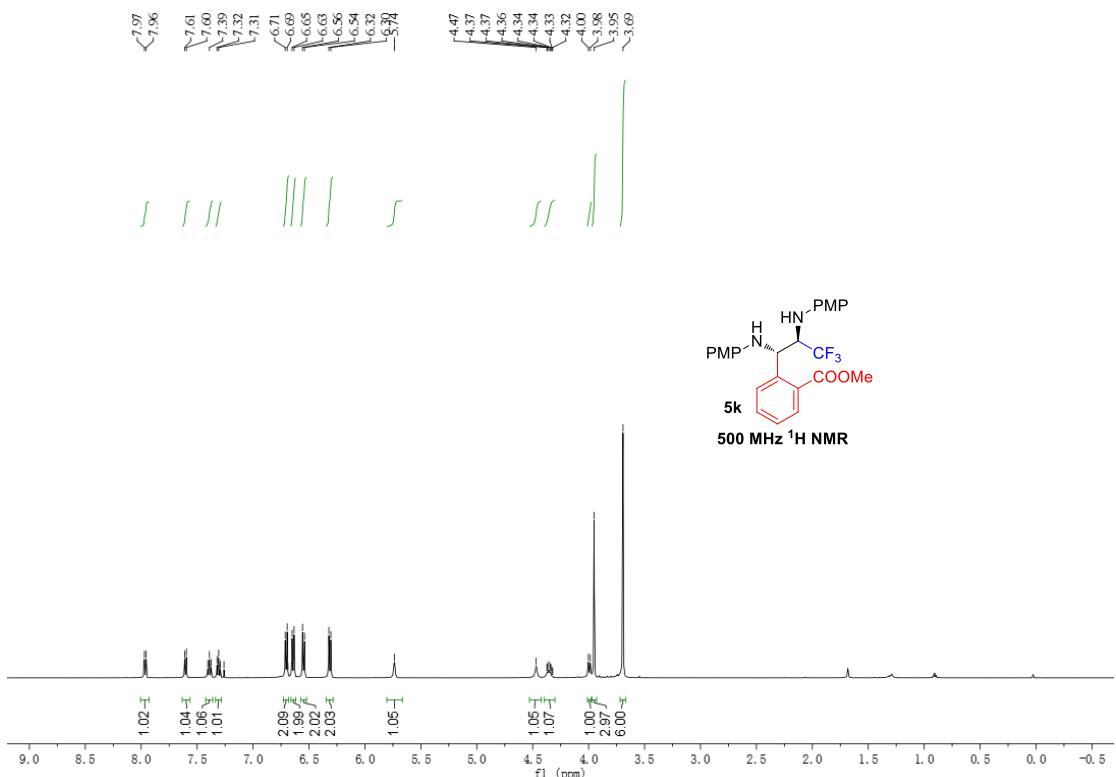


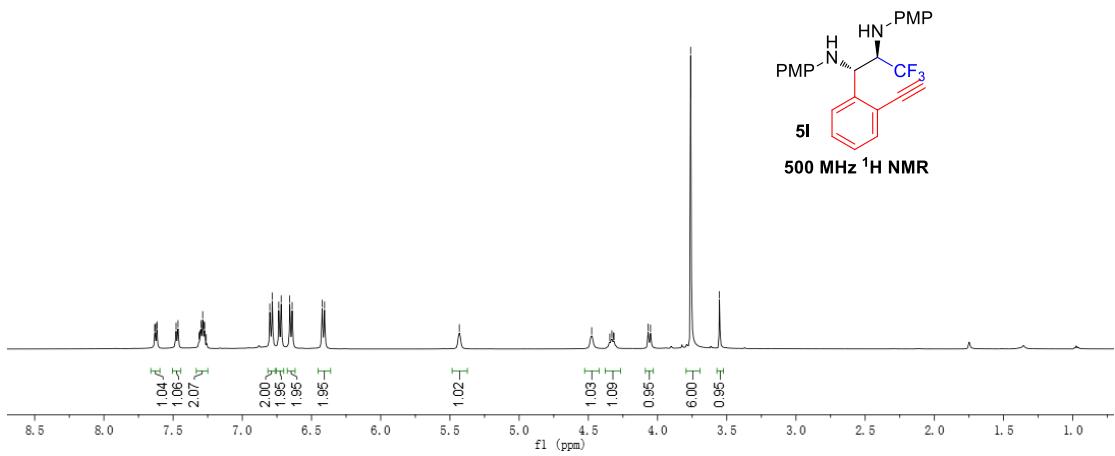
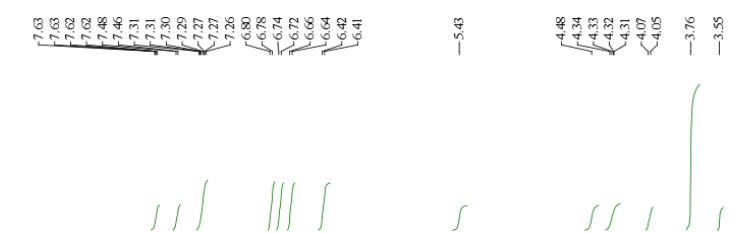
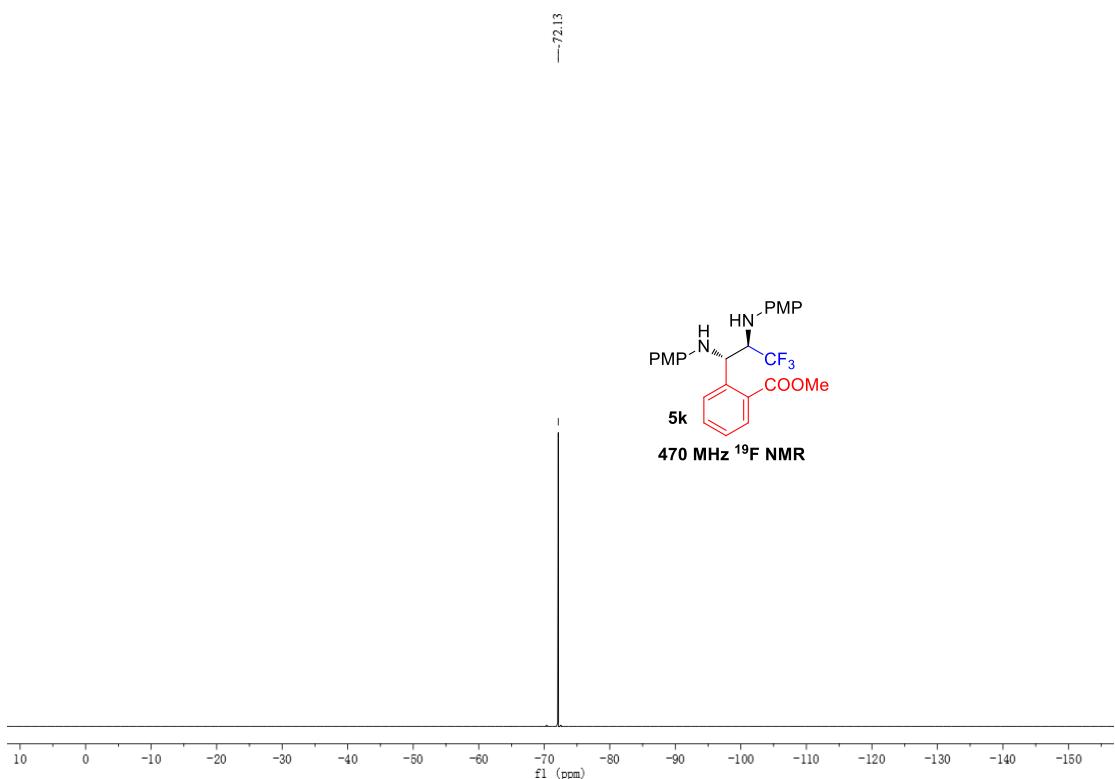


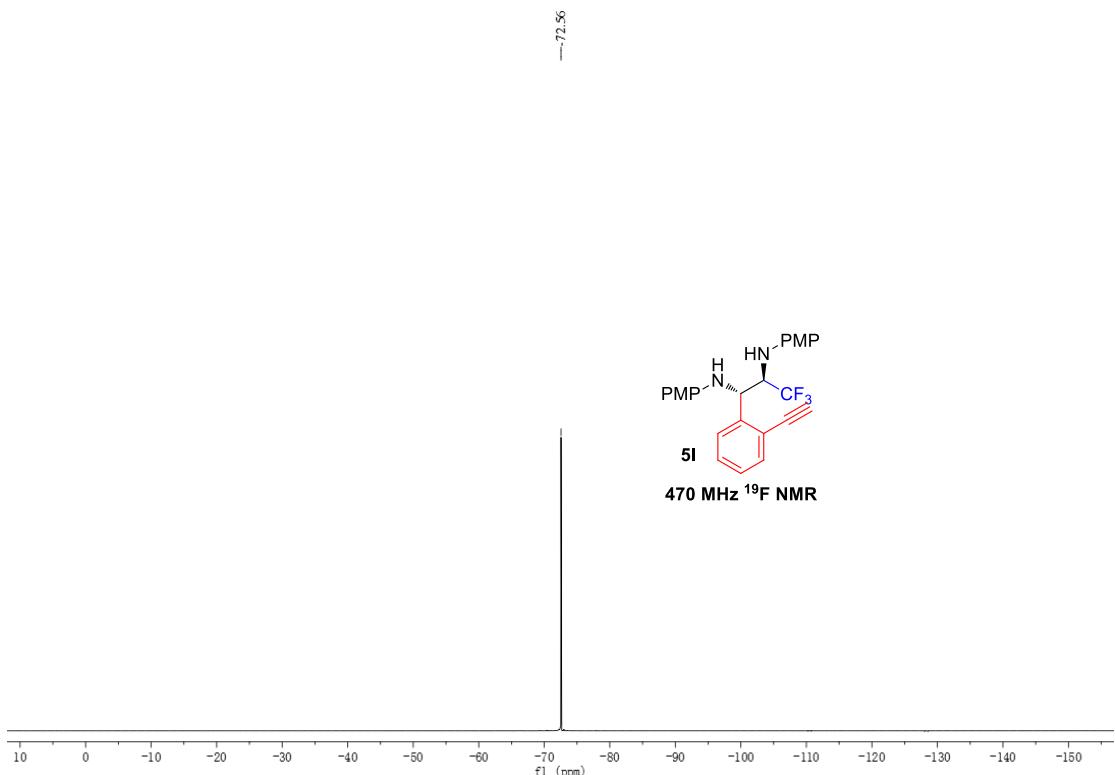
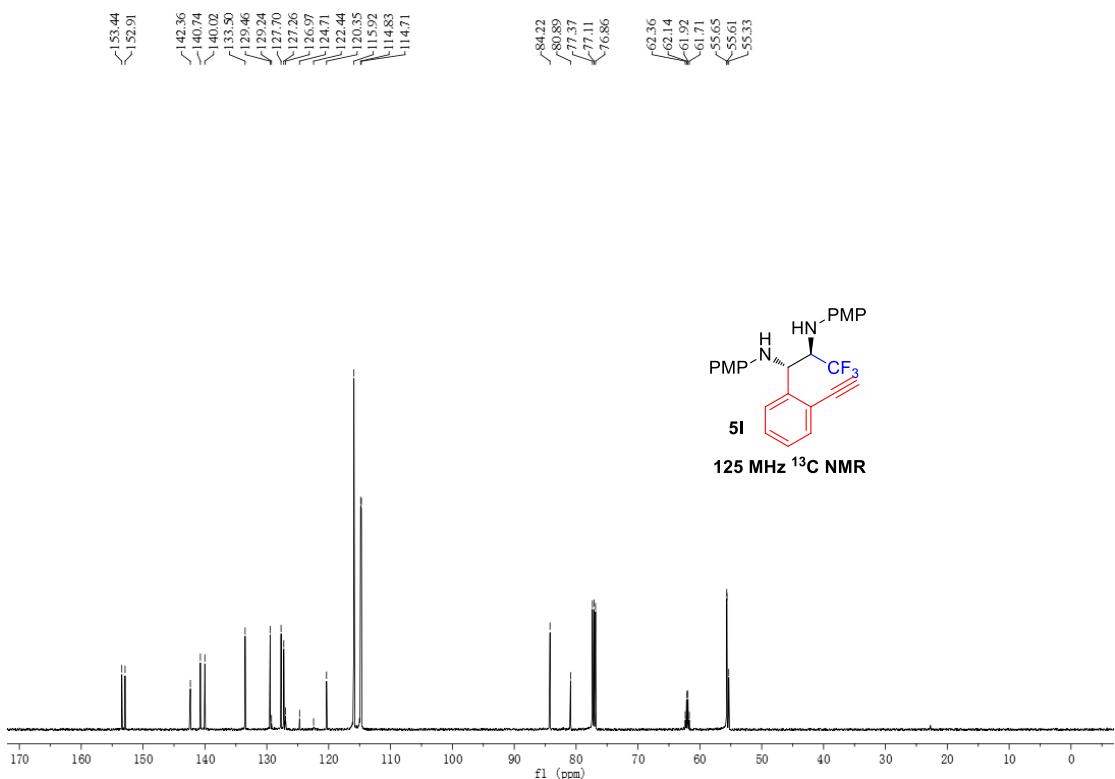


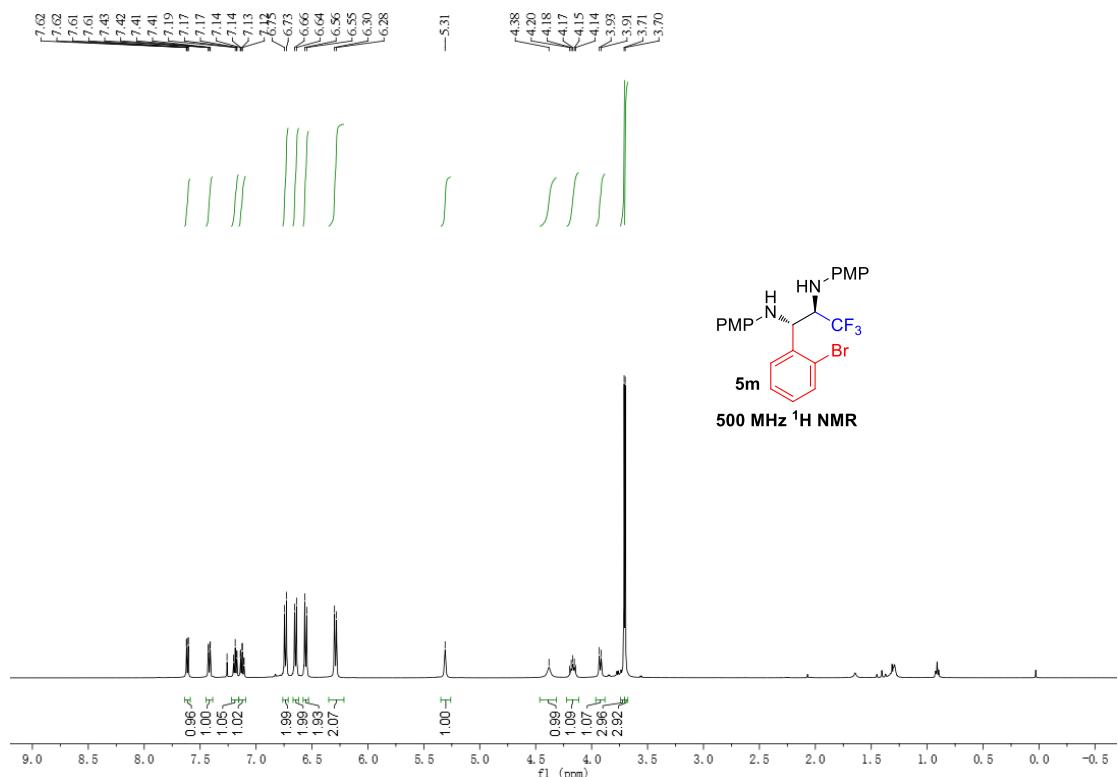
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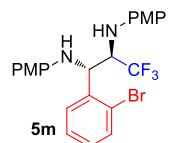
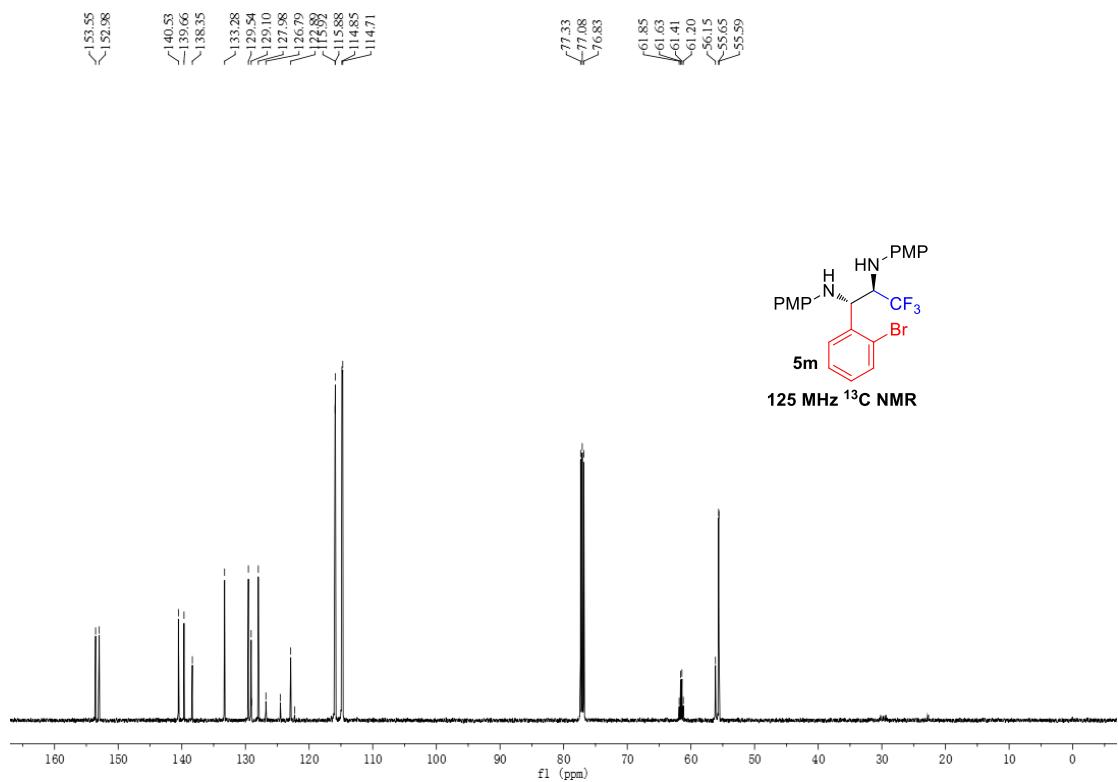




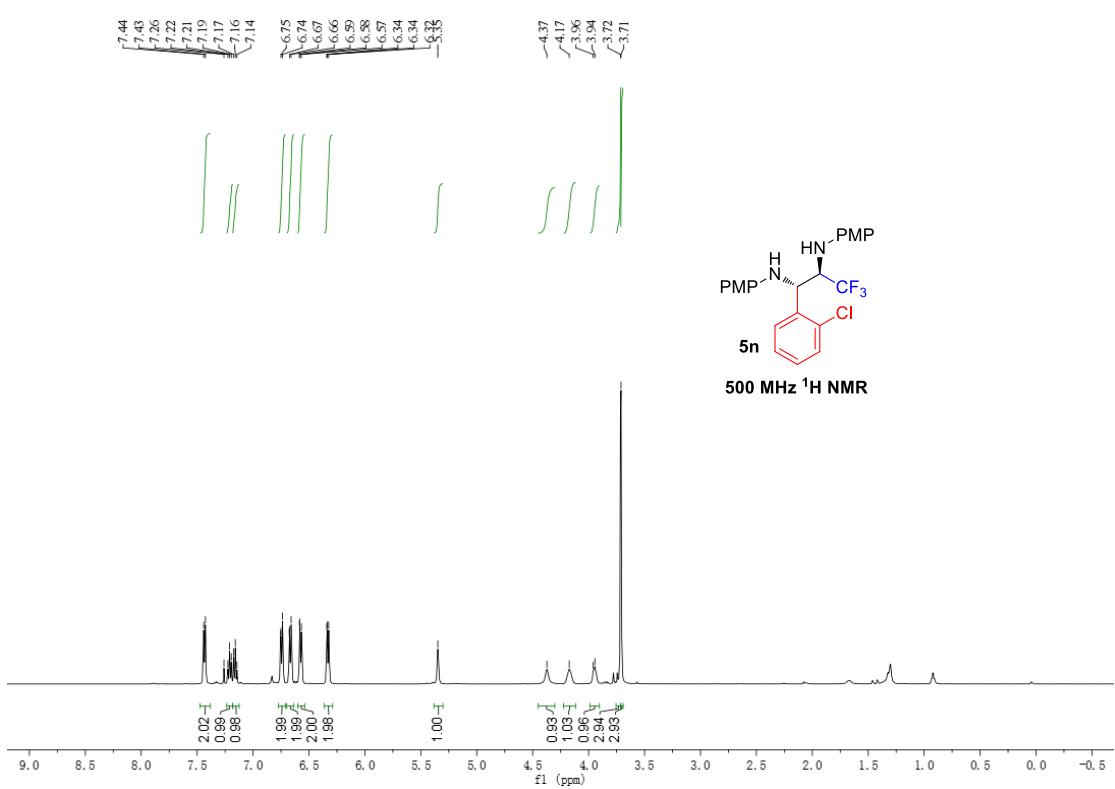
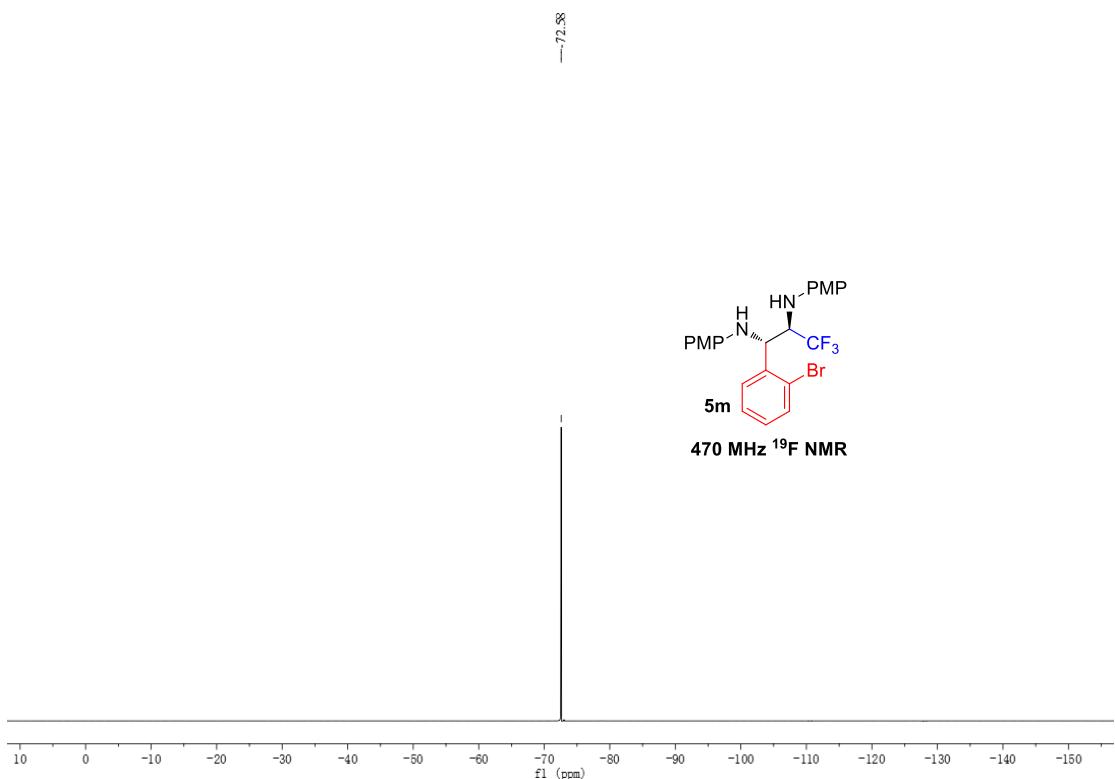


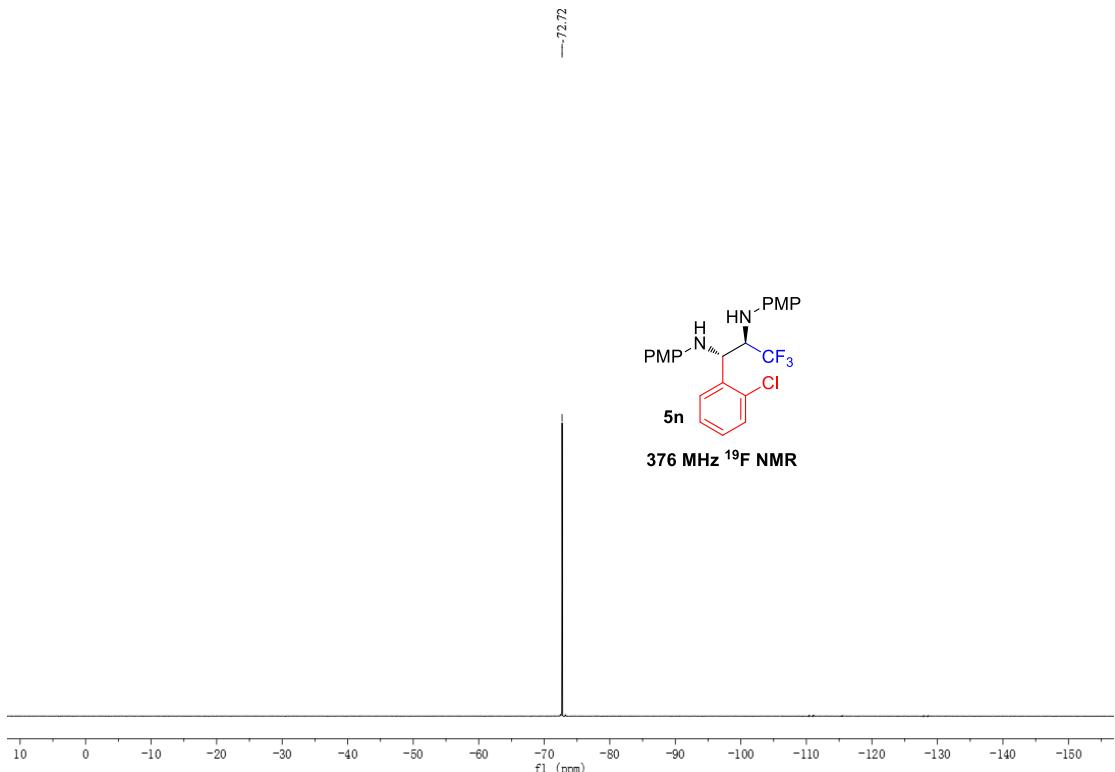
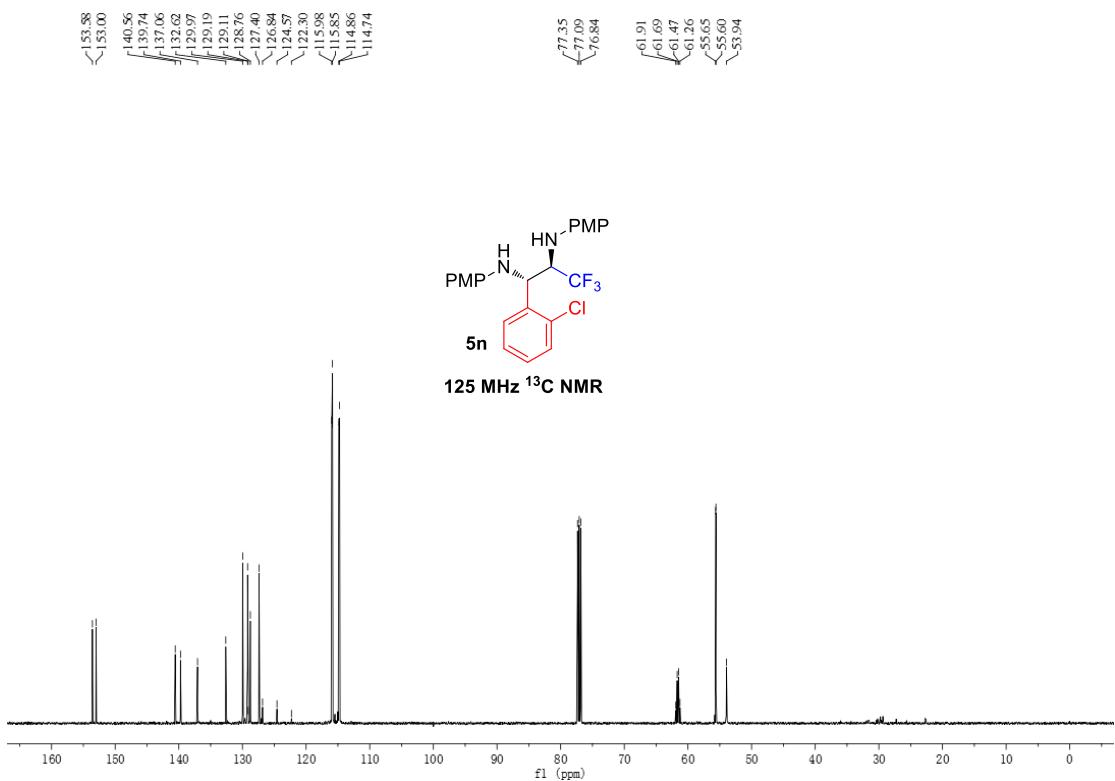


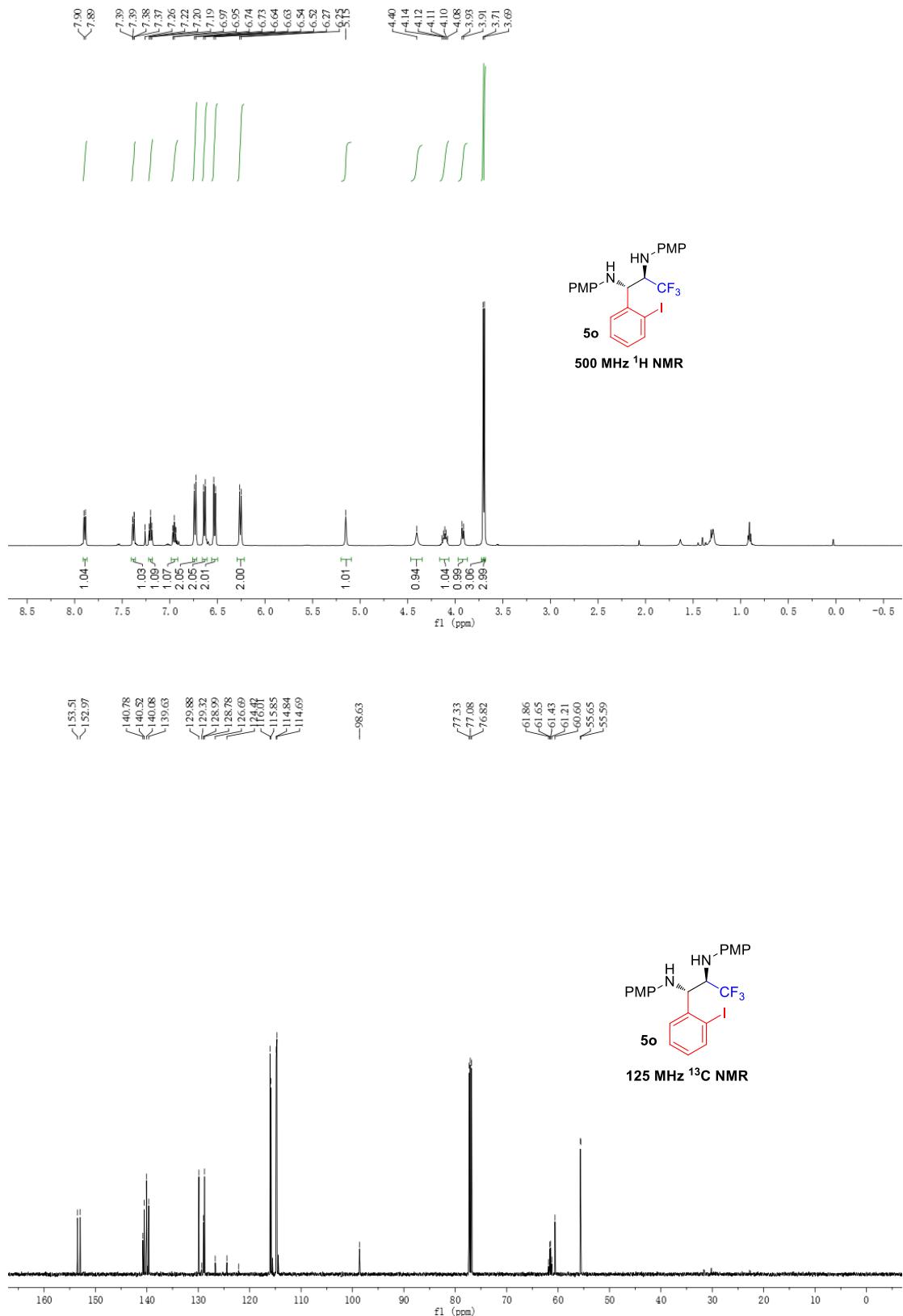
500 MHz ^1H NMR

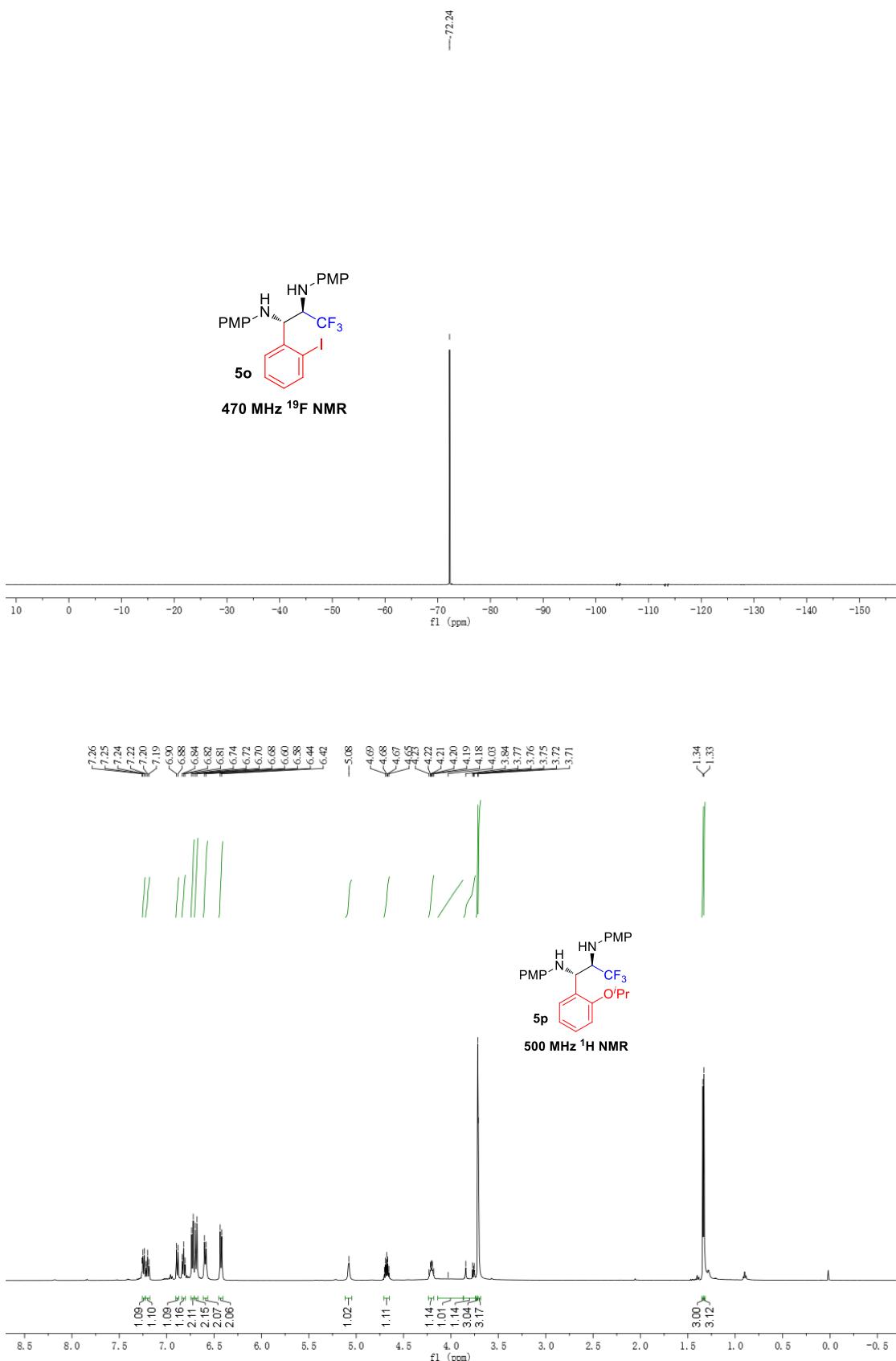


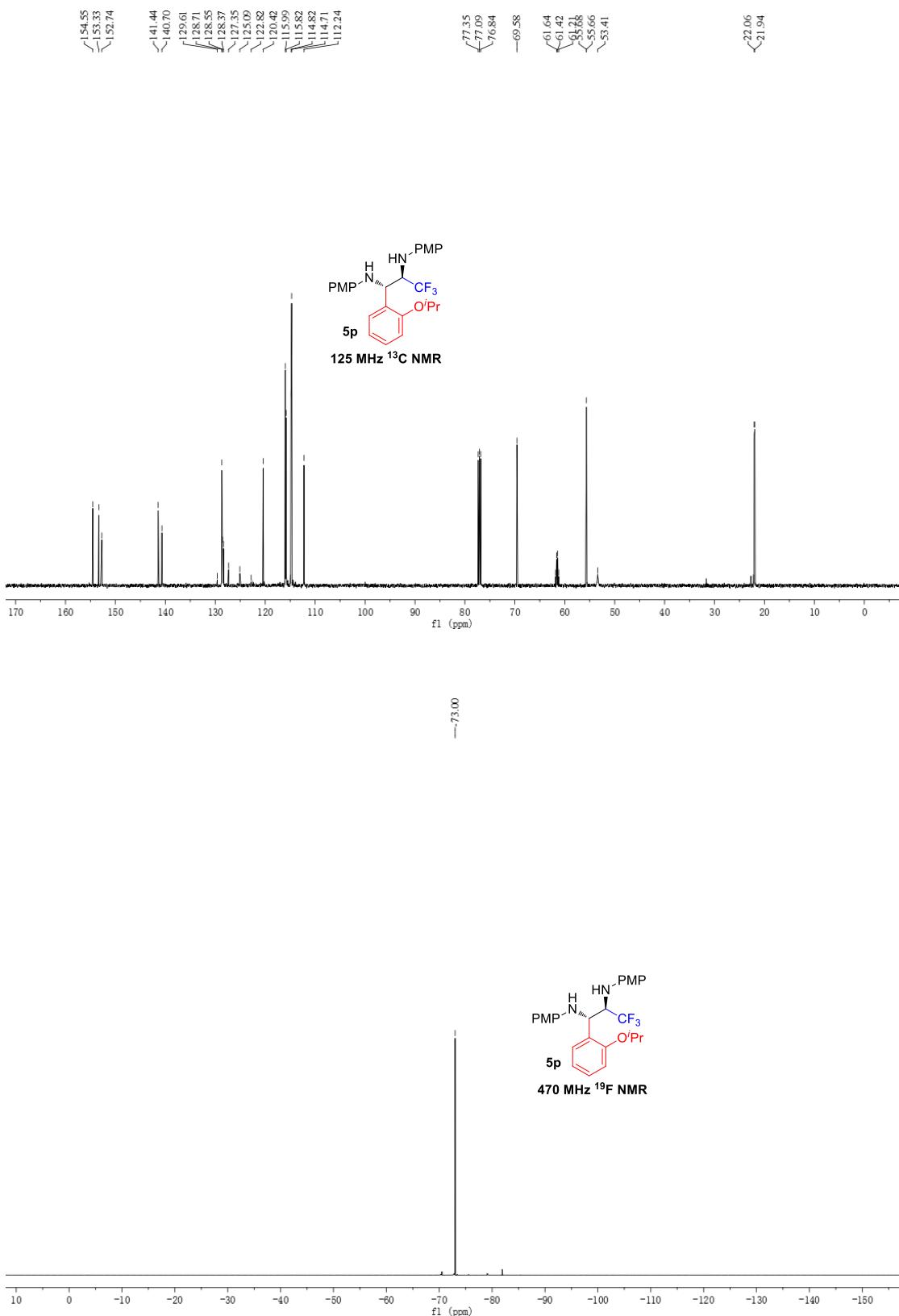
125 MHz ^{13}C NMR

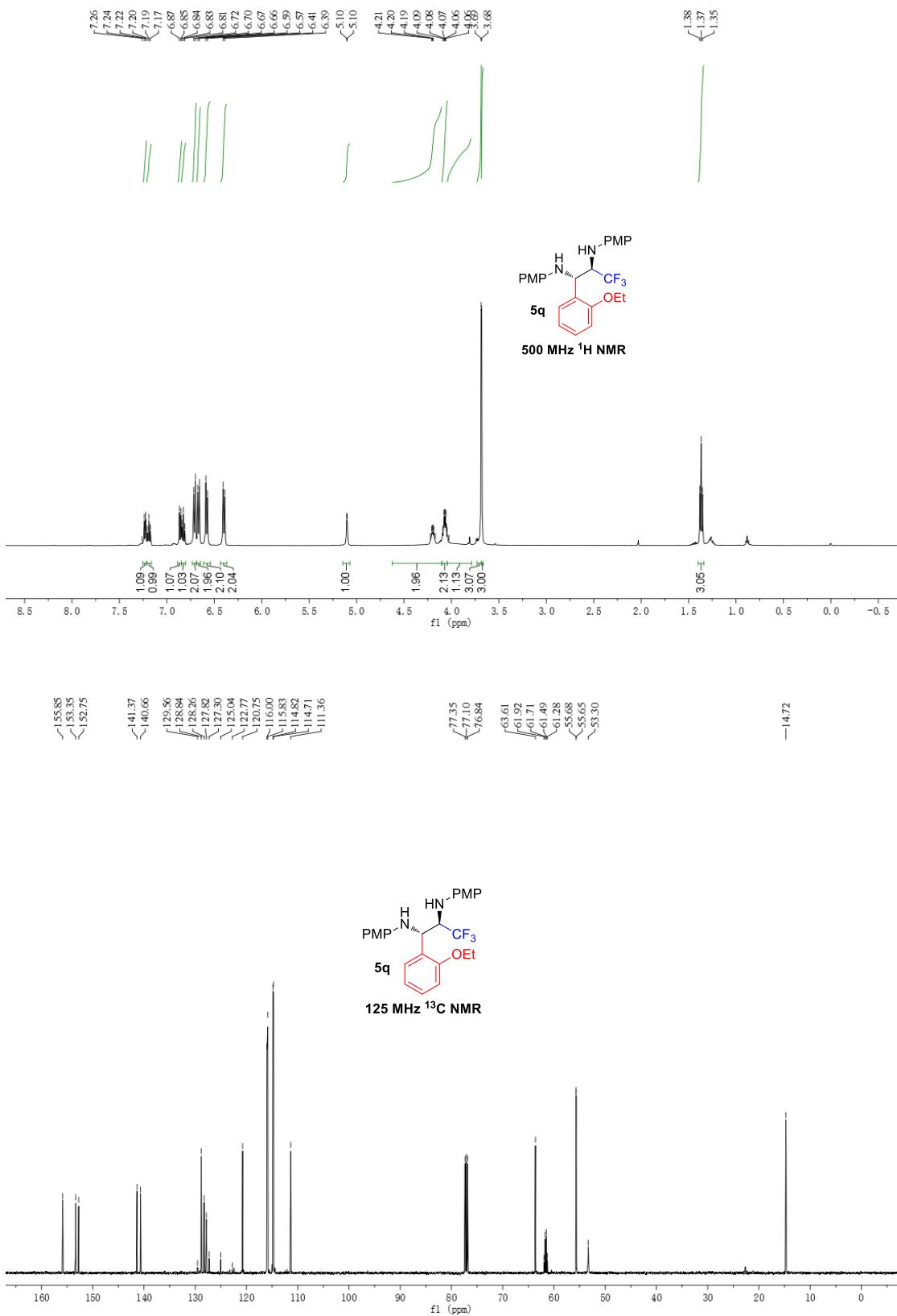


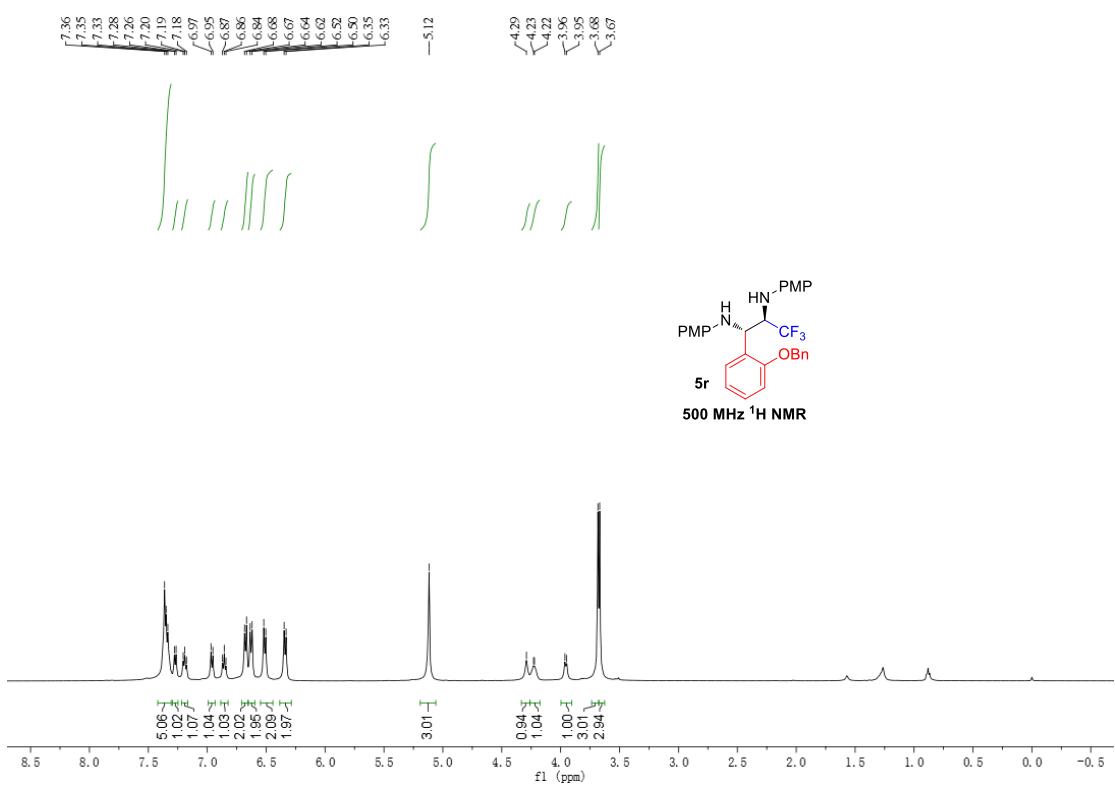
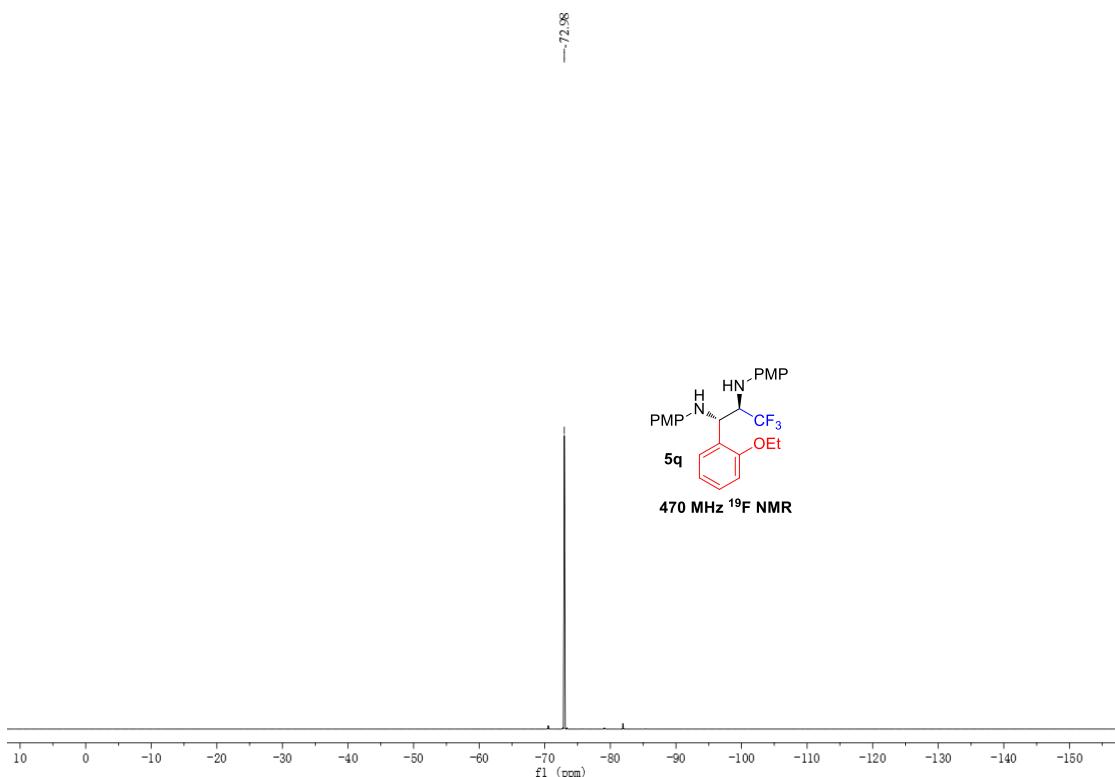


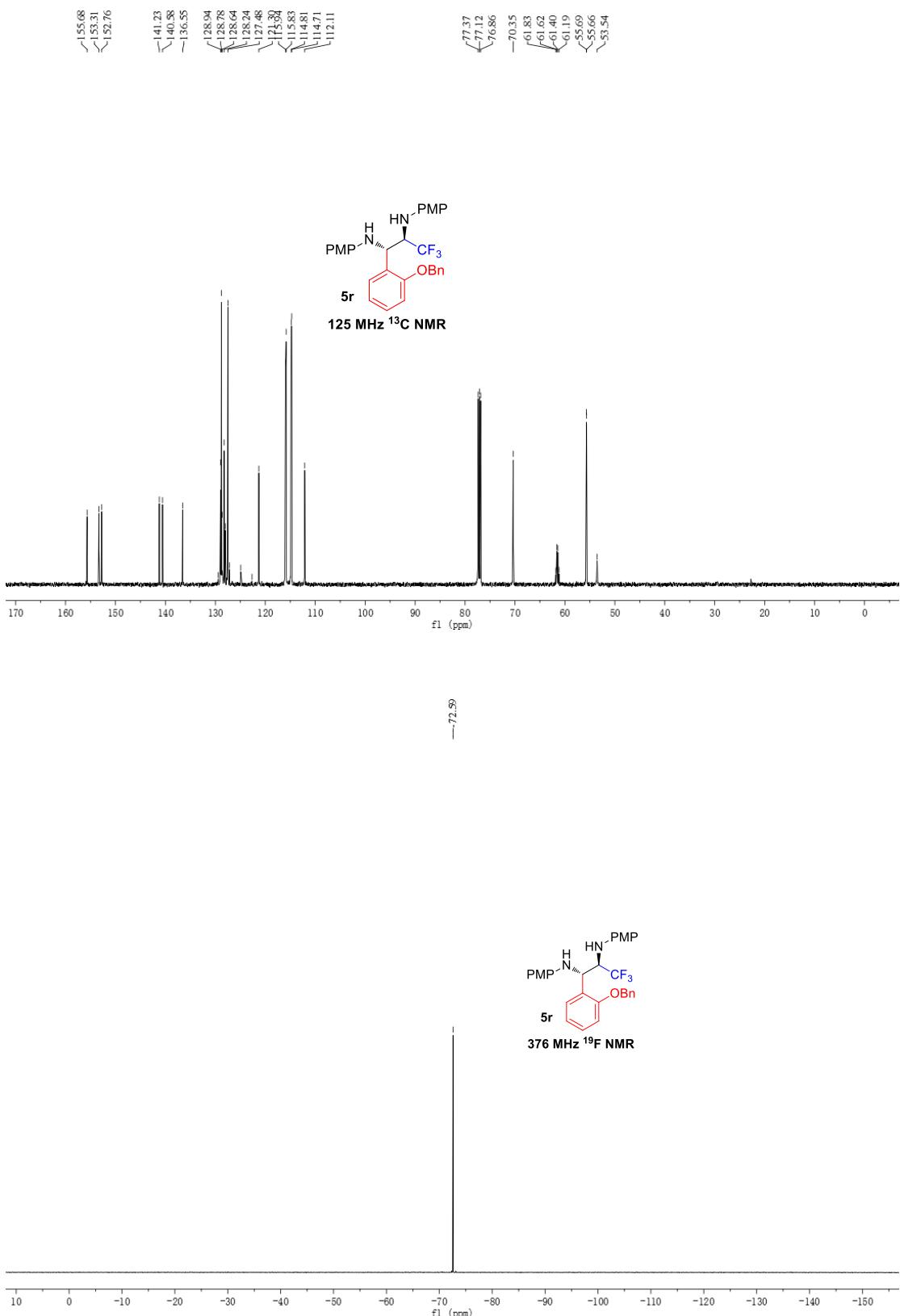


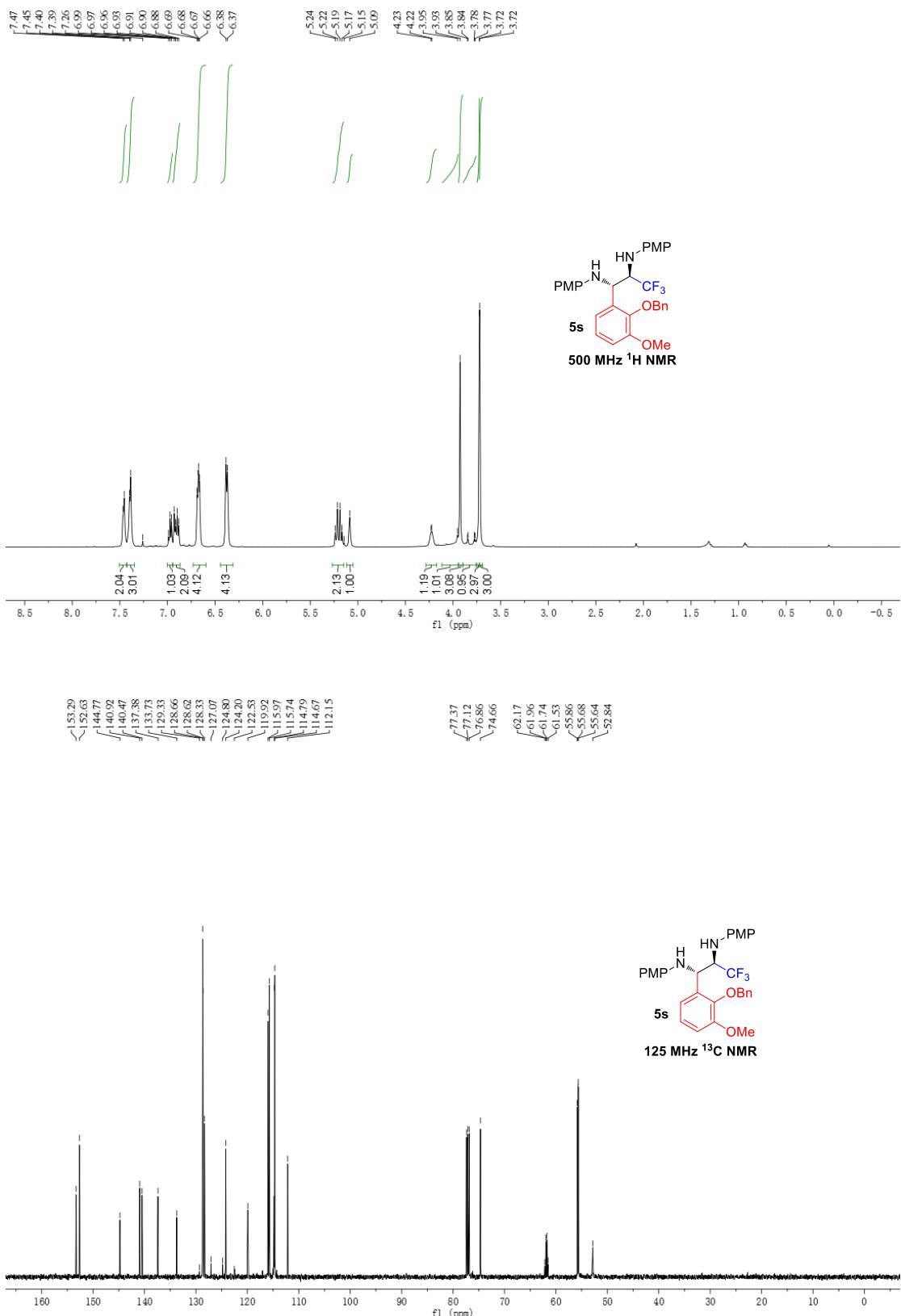


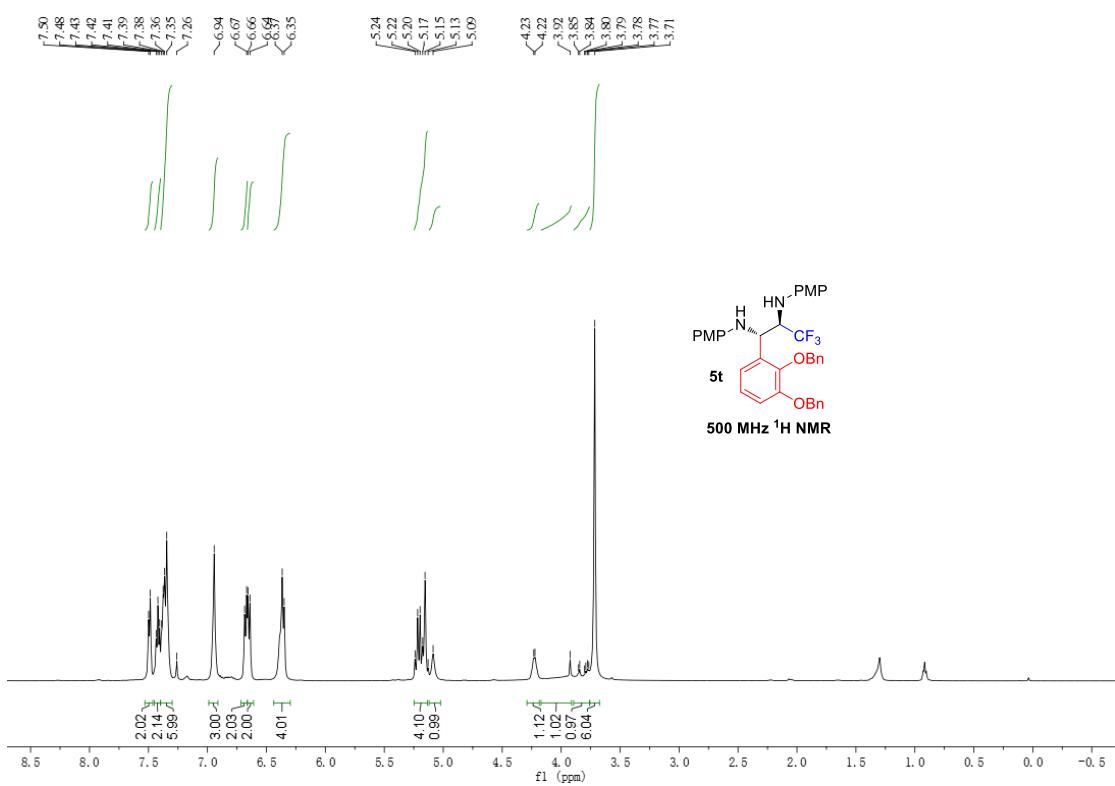
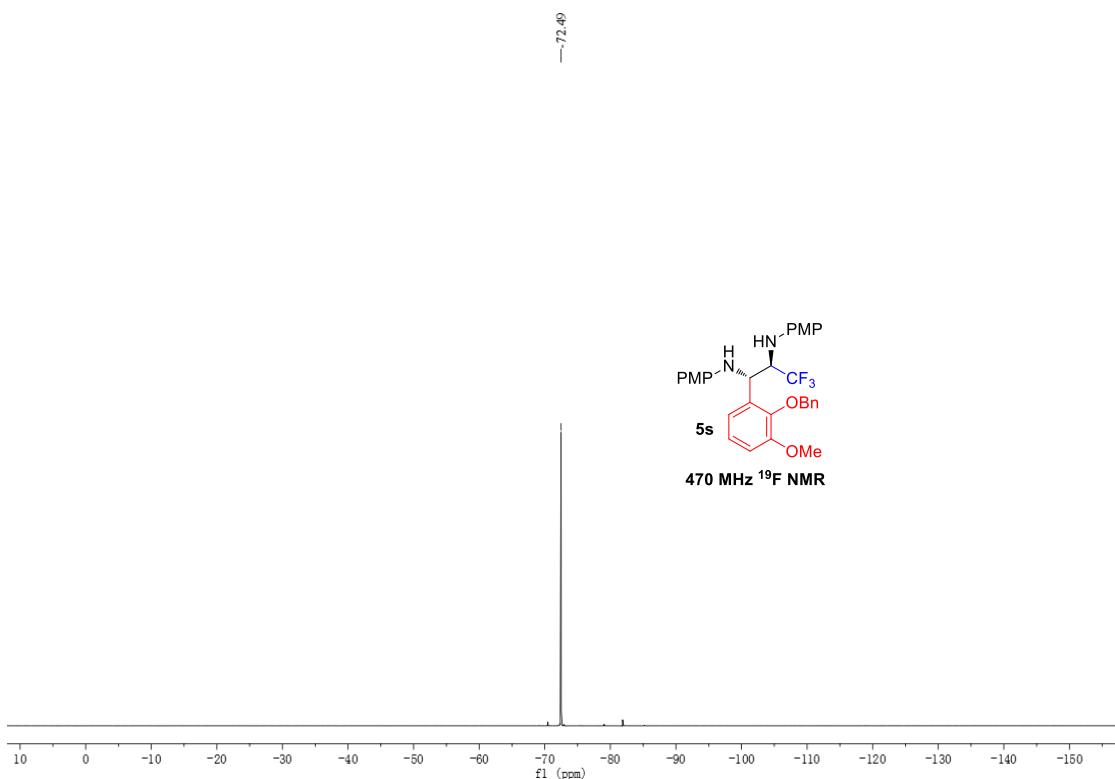


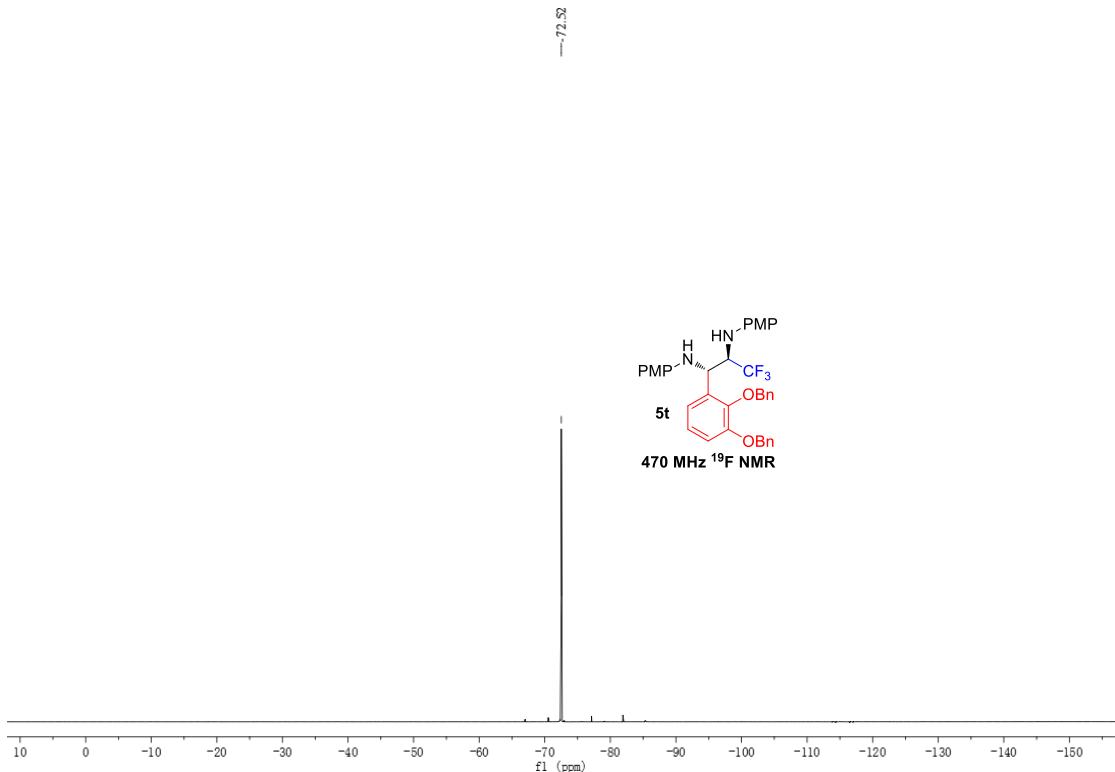
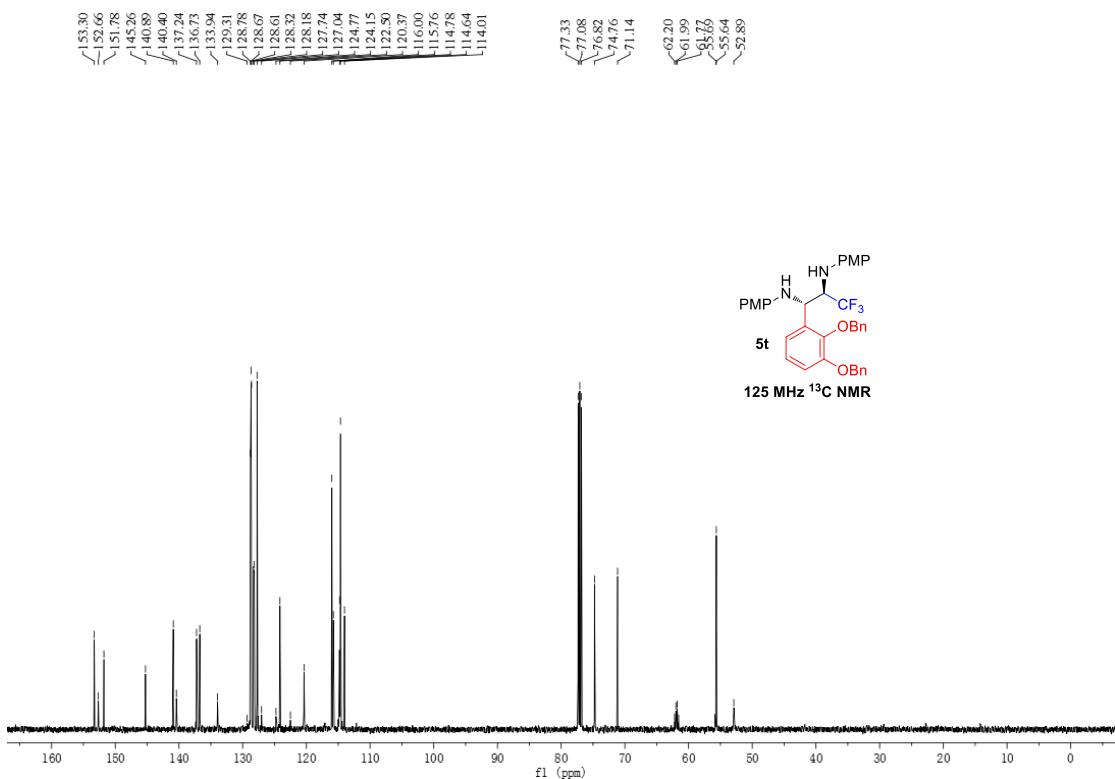


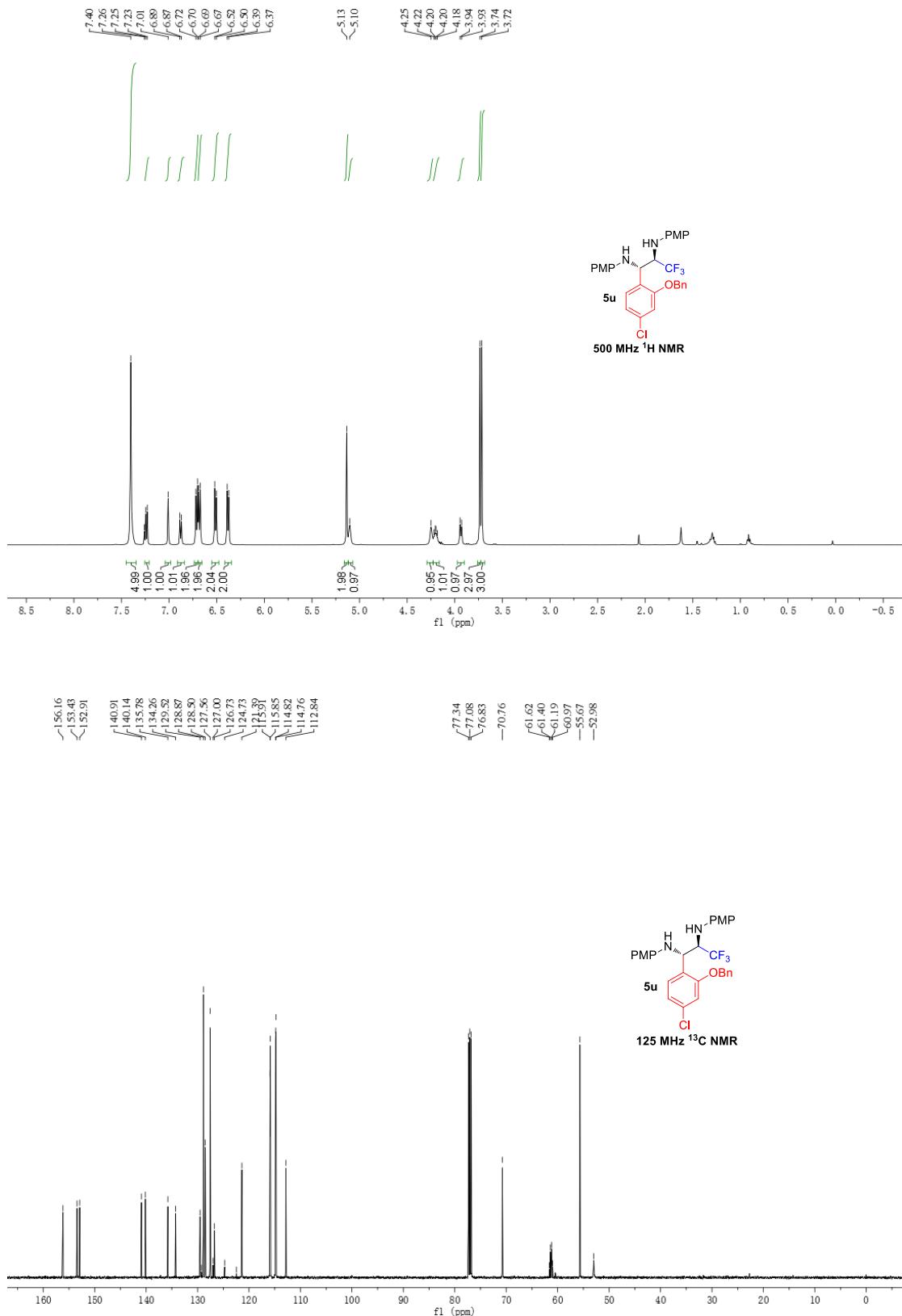


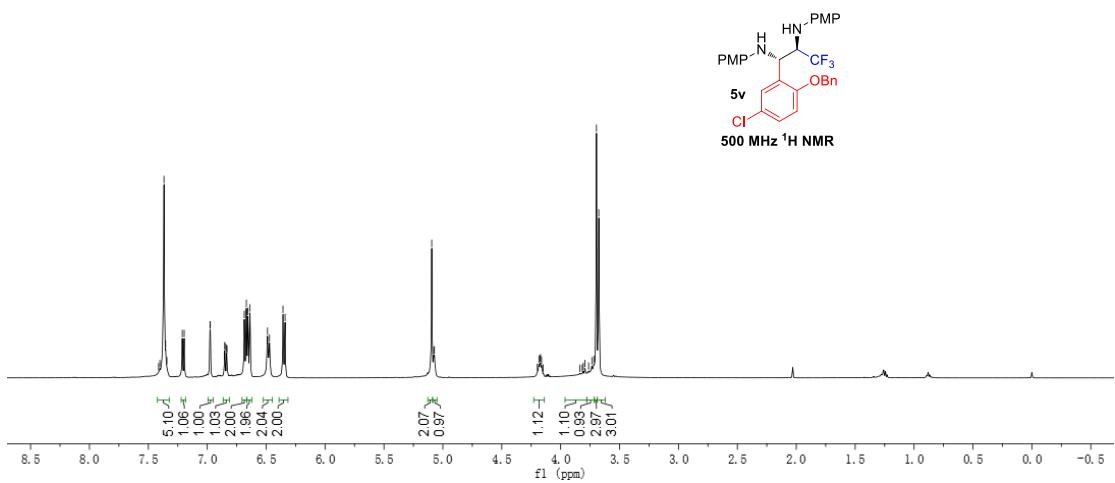
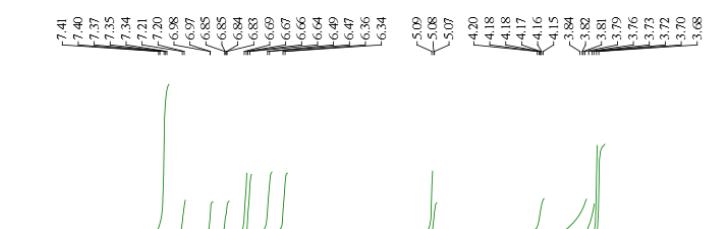
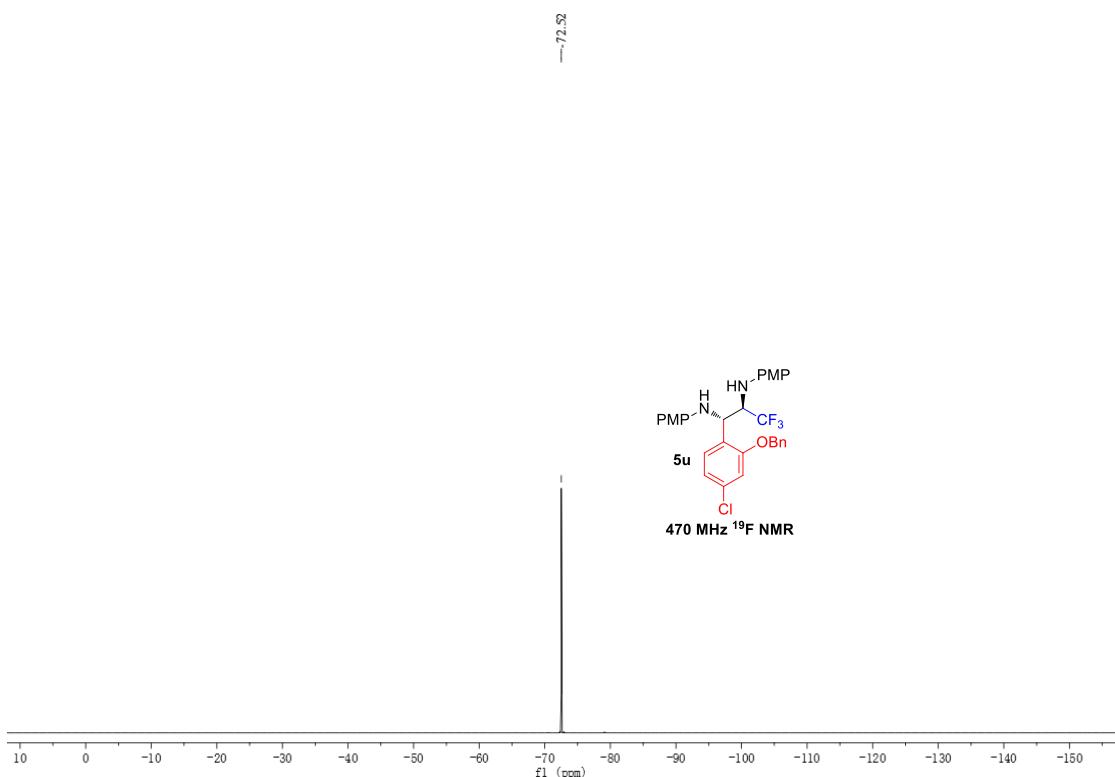


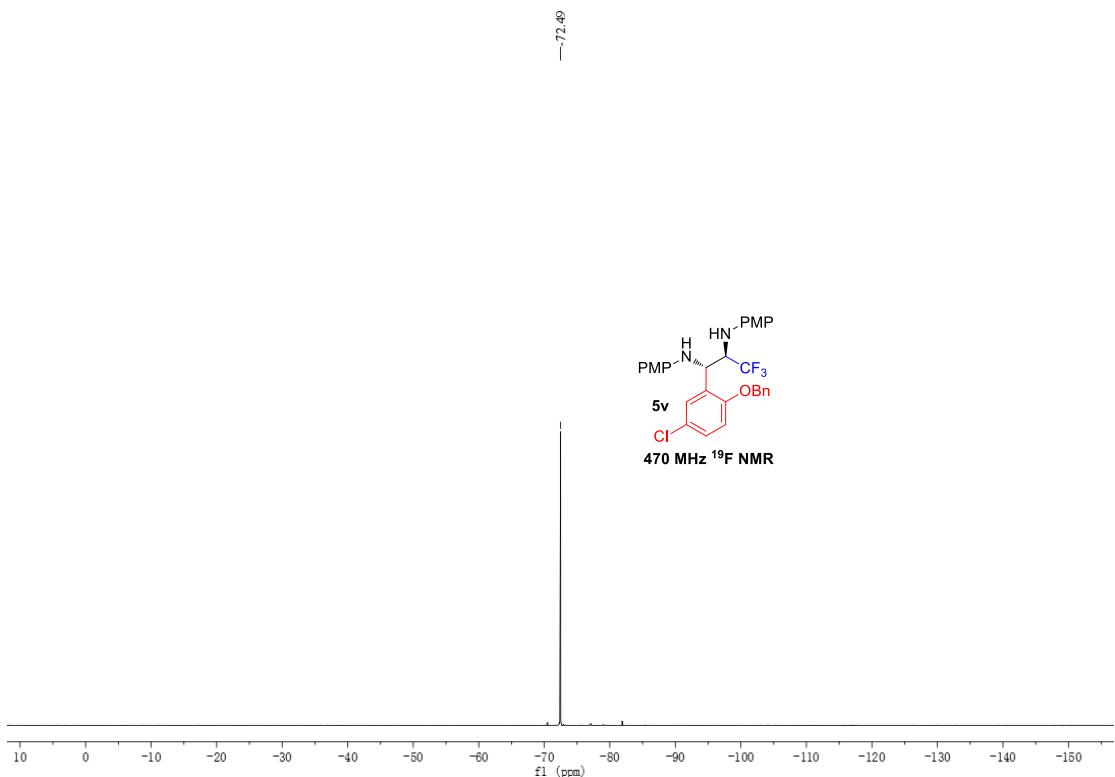
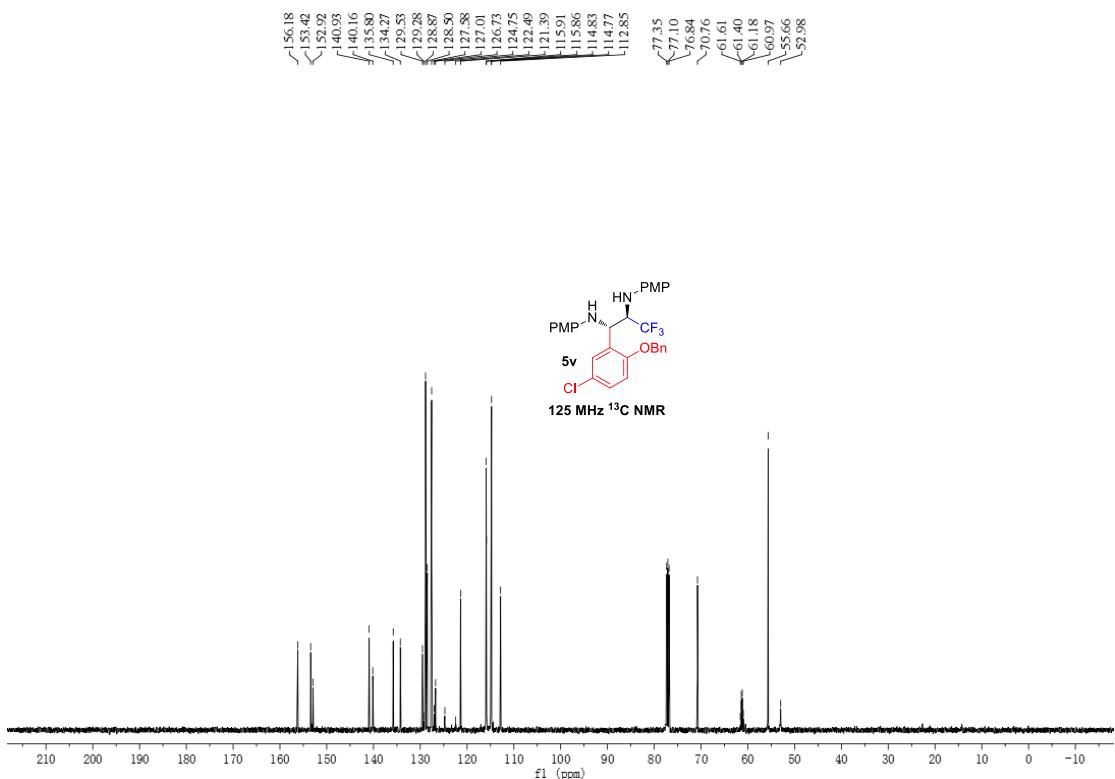


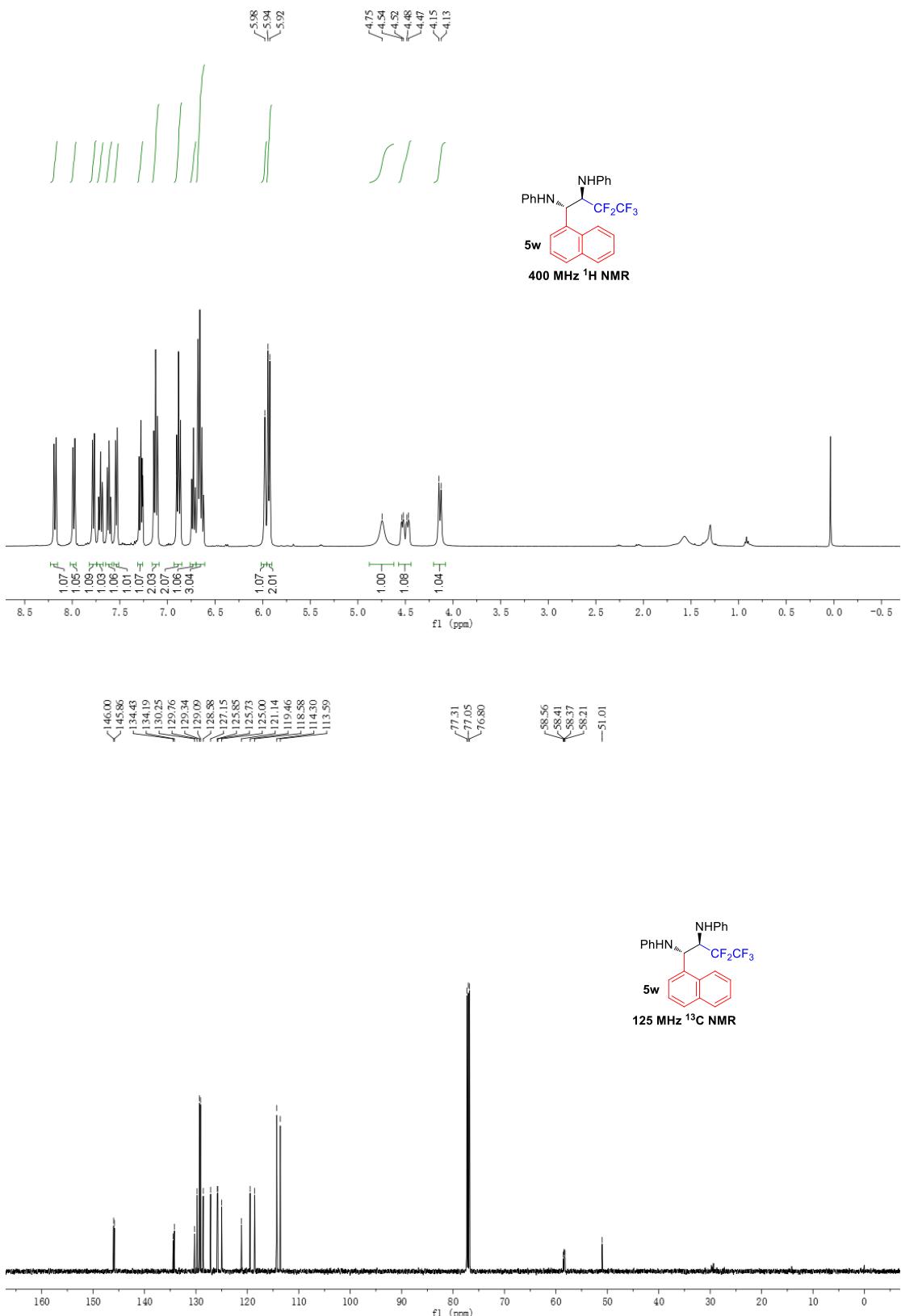


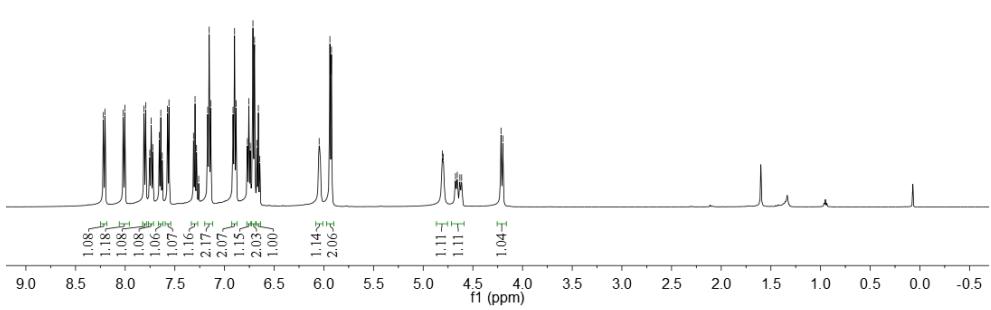
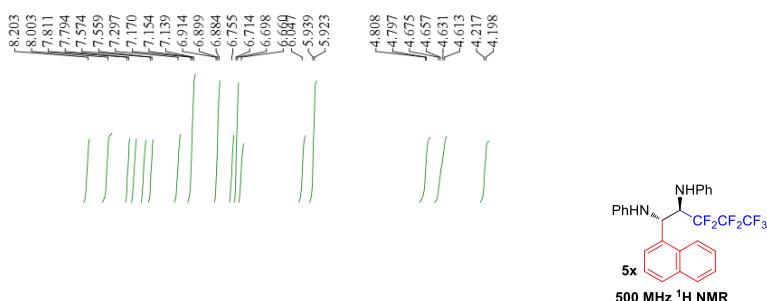
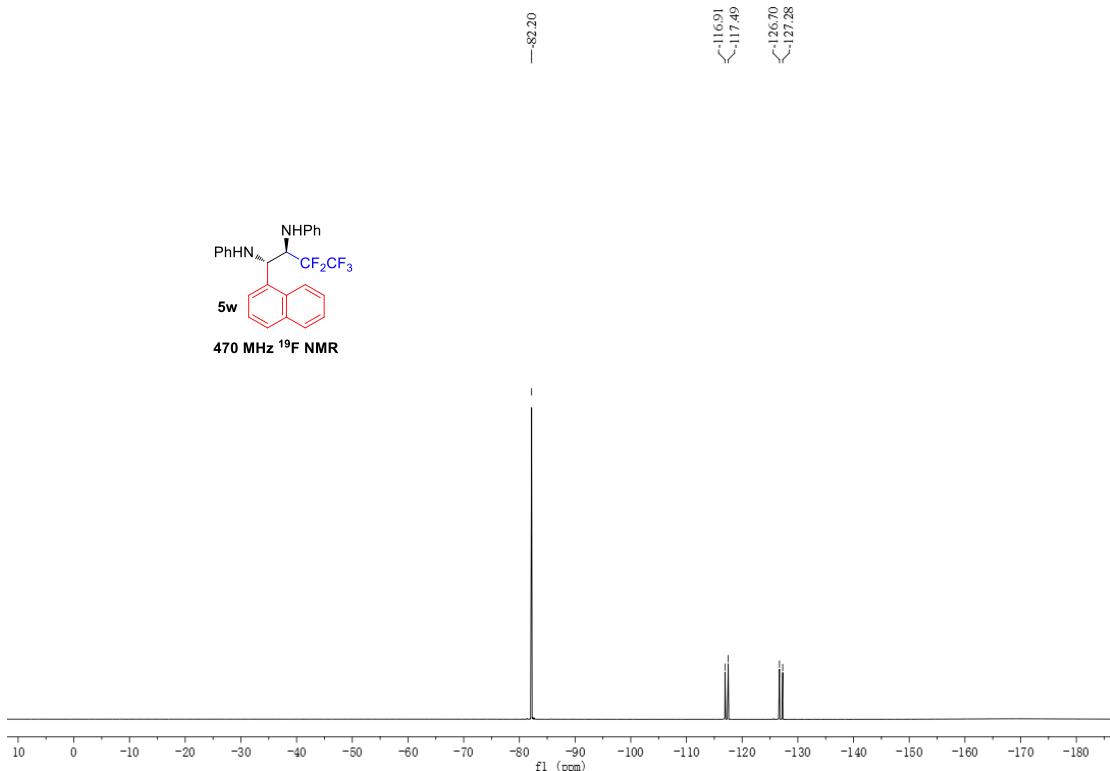


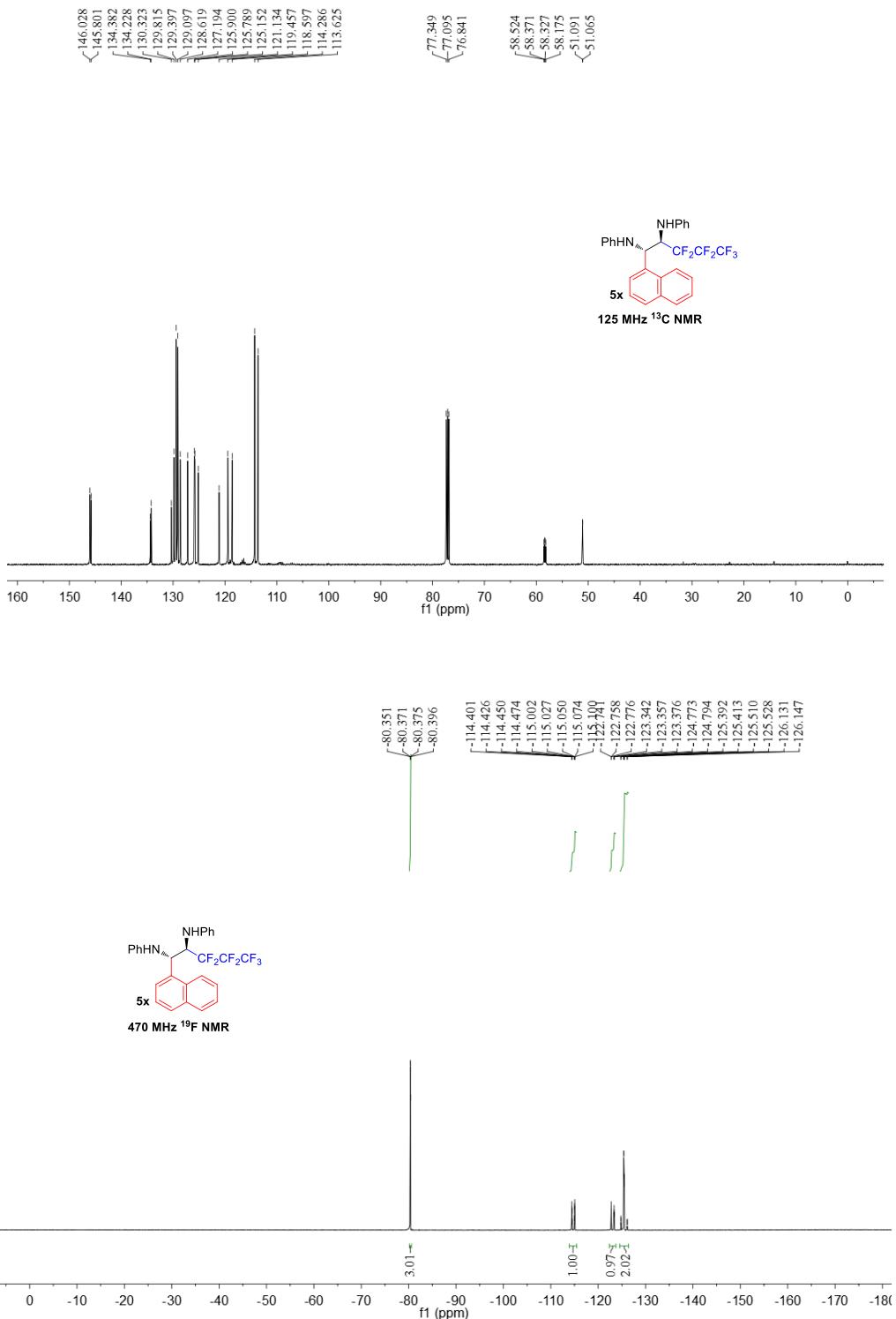


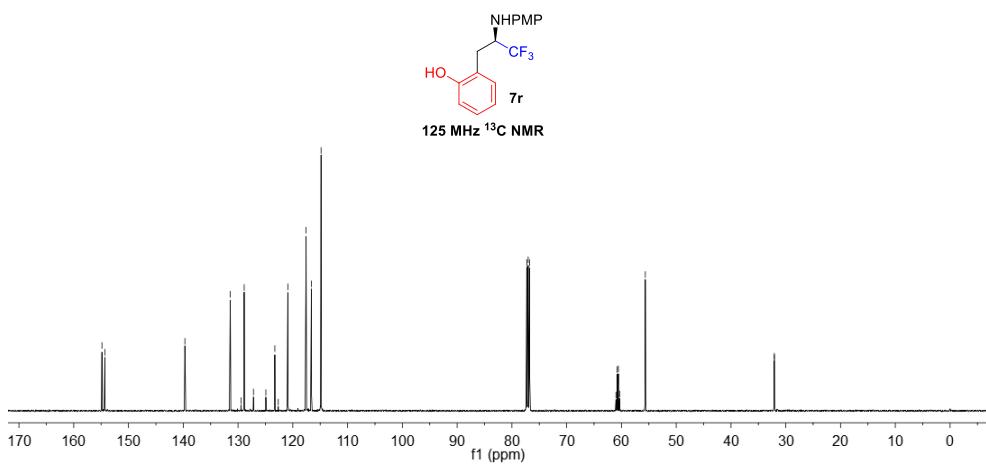
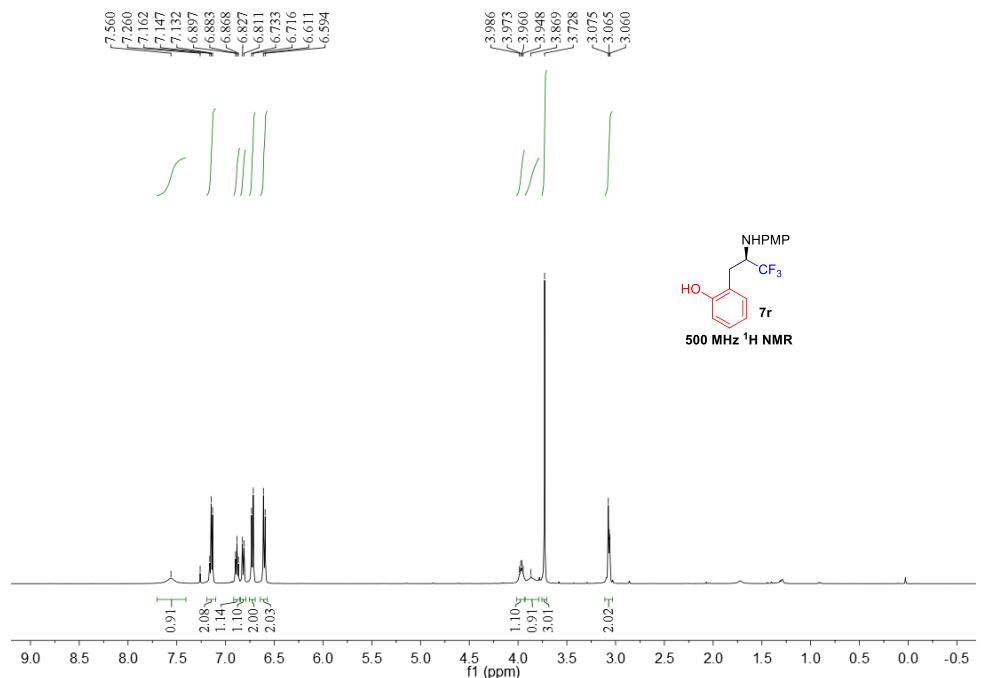


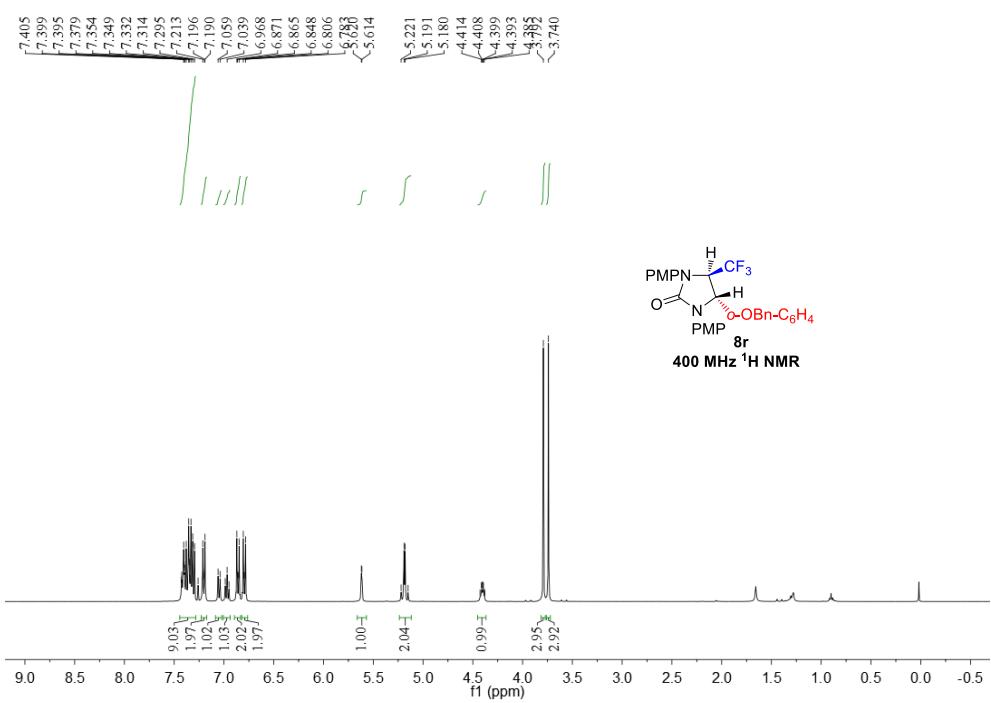
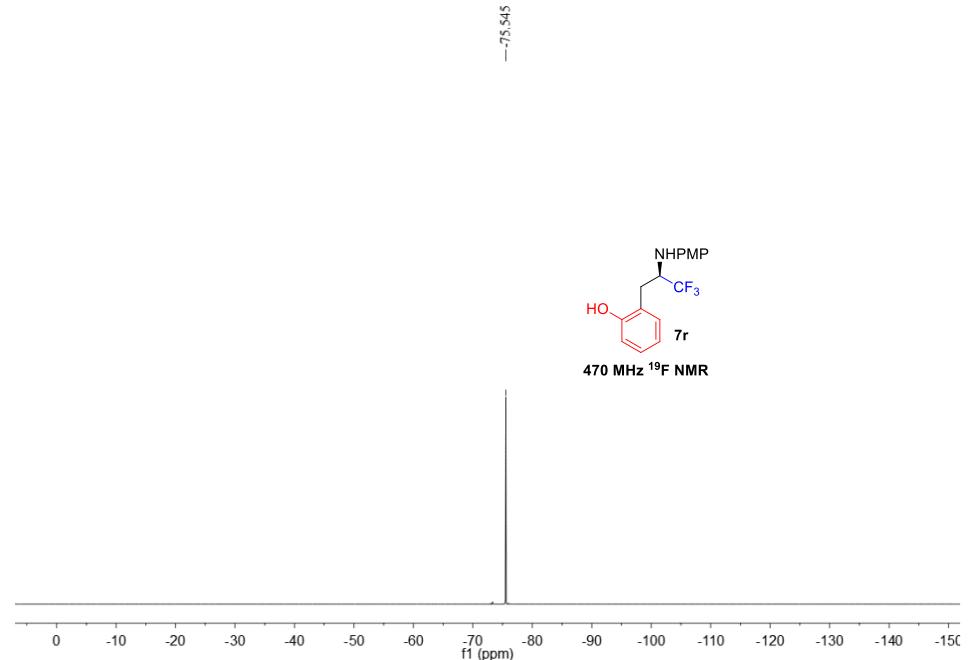


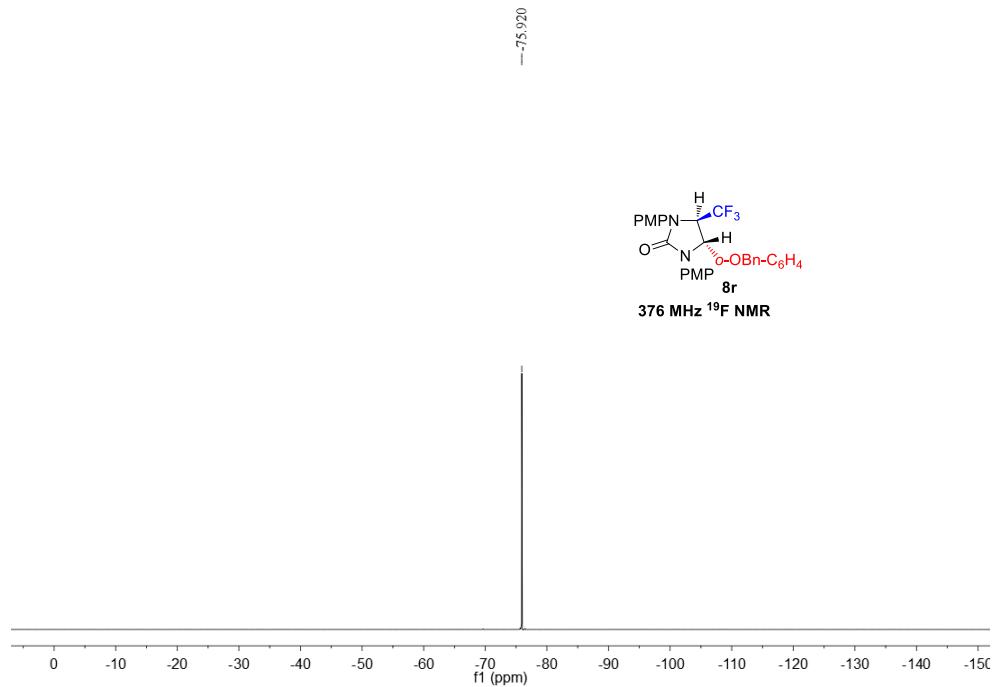
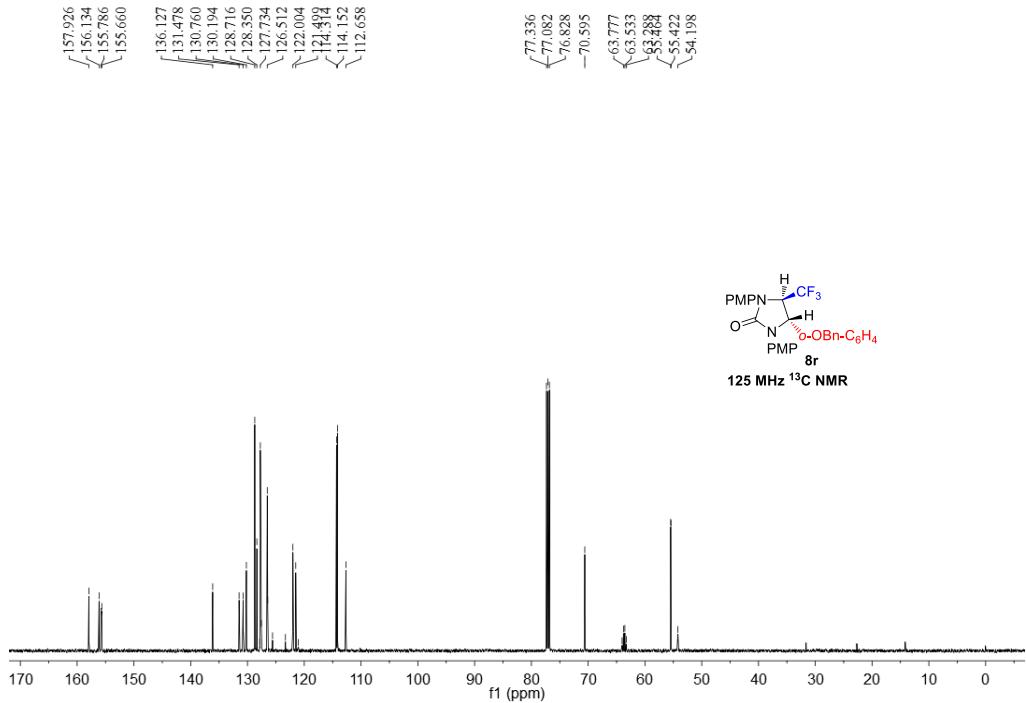


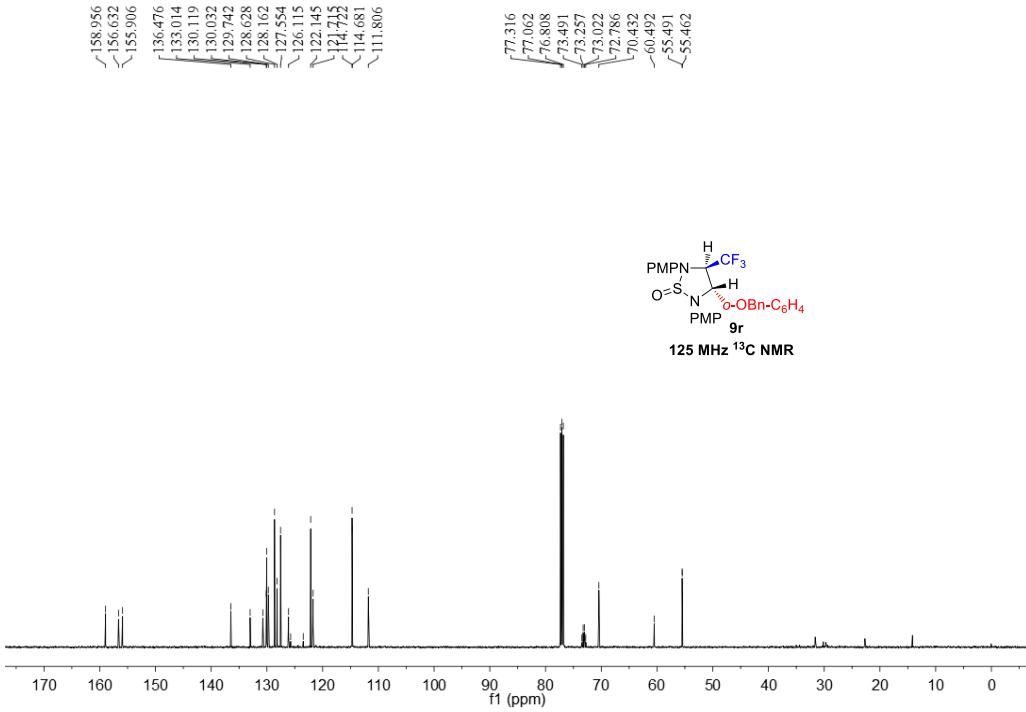
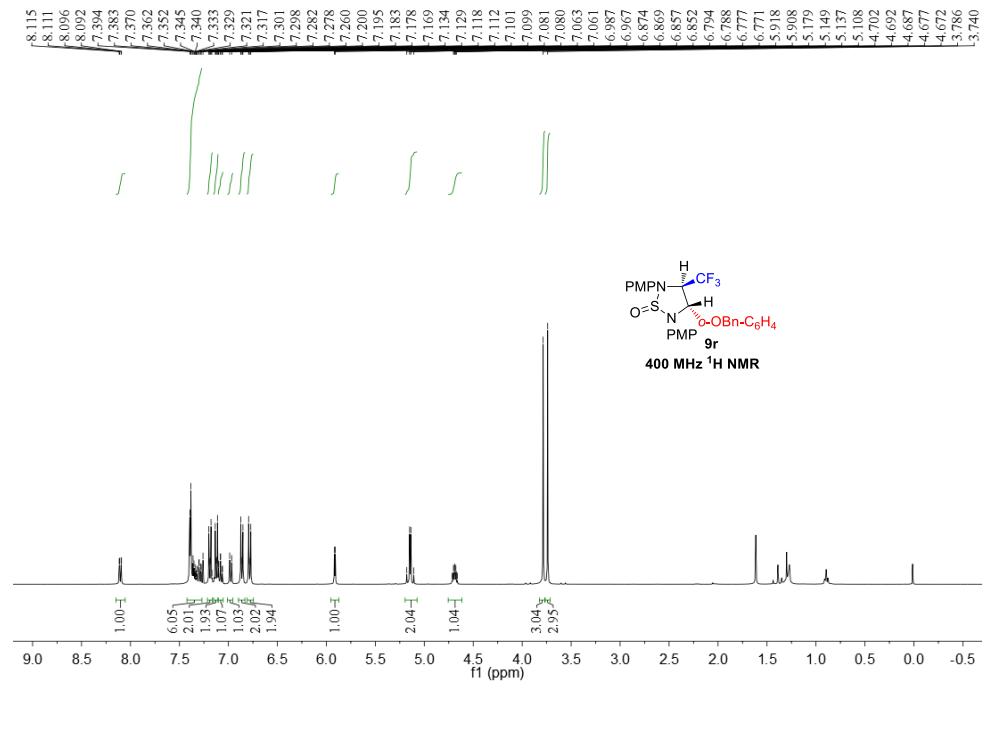


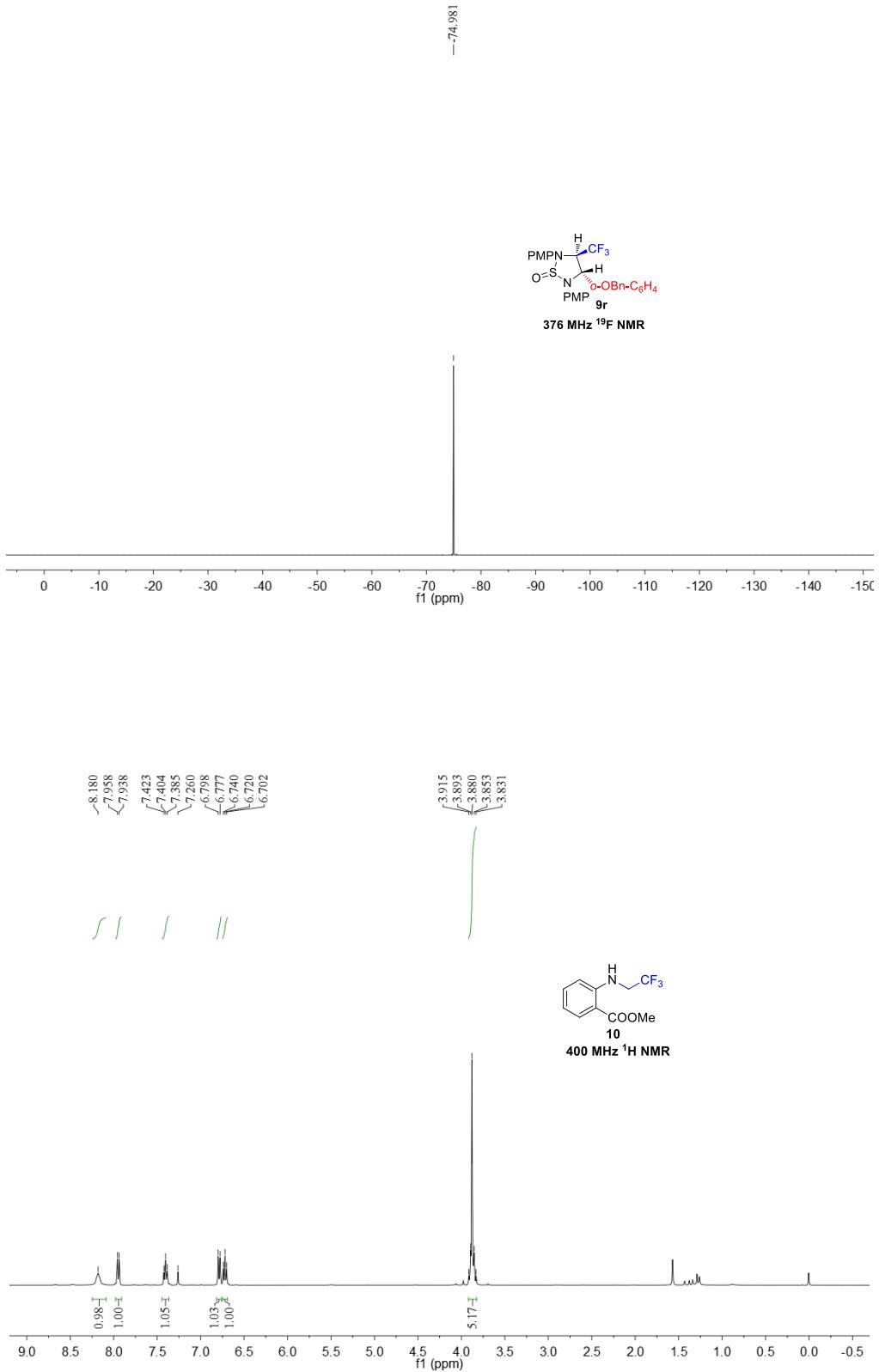


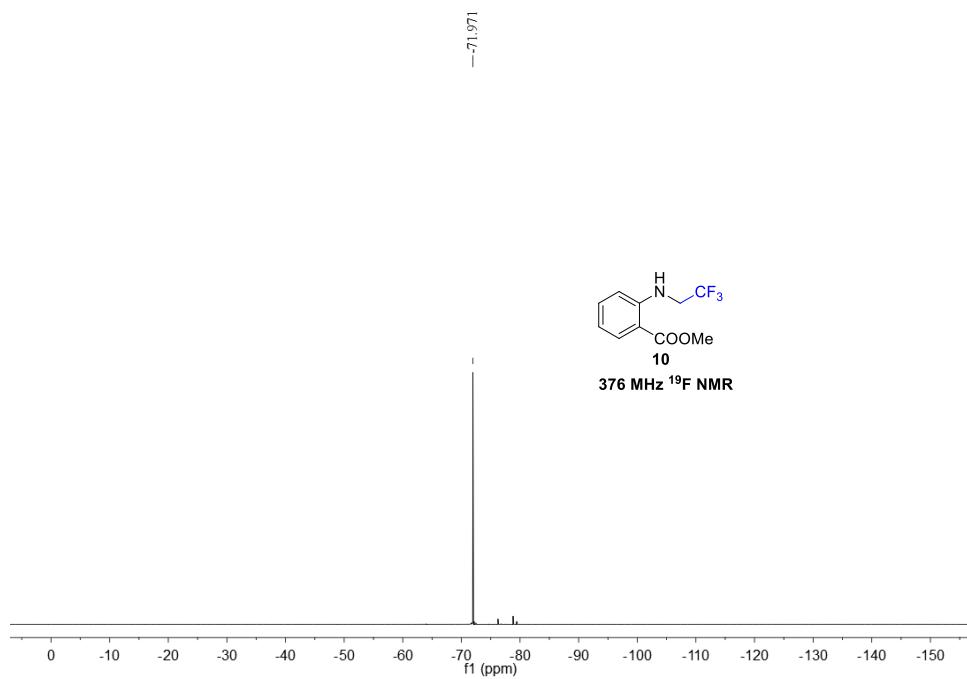
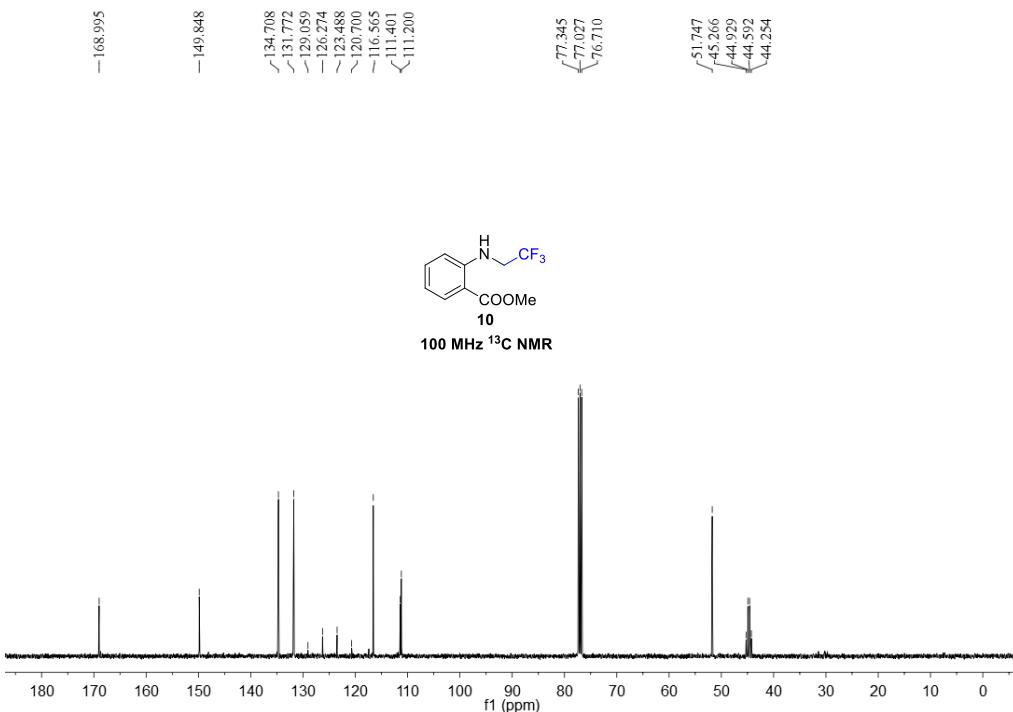


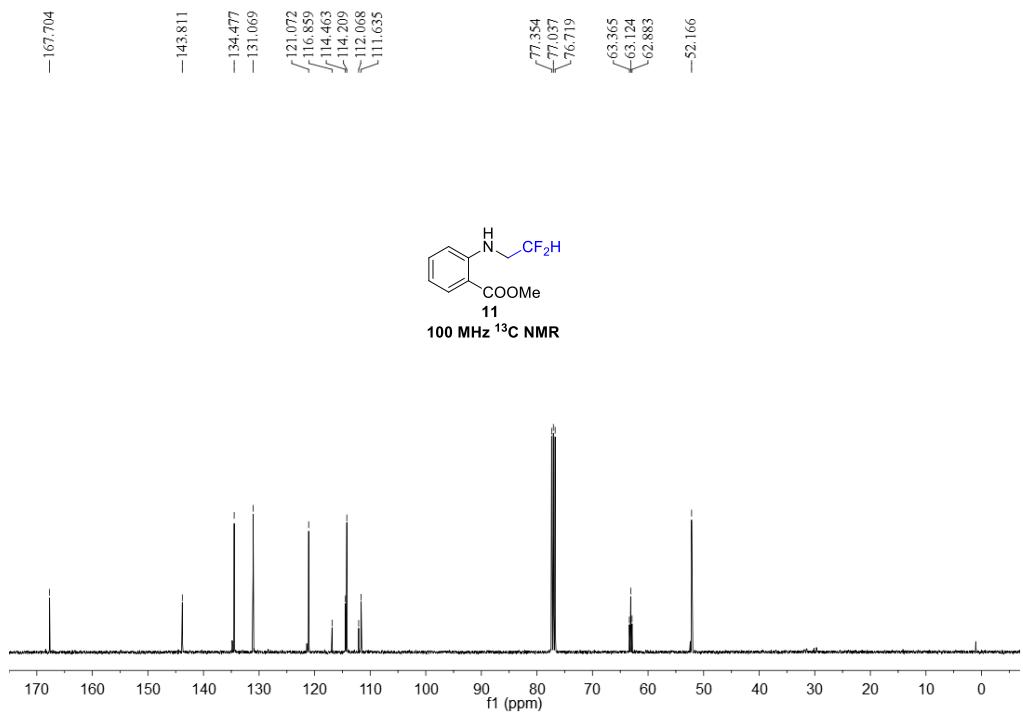
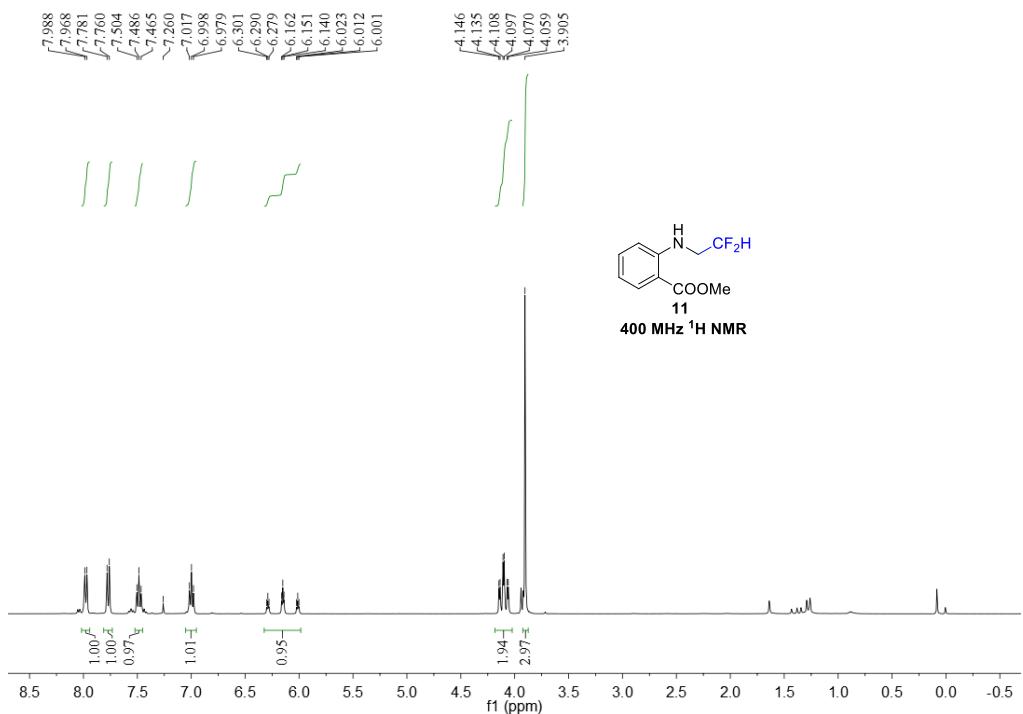


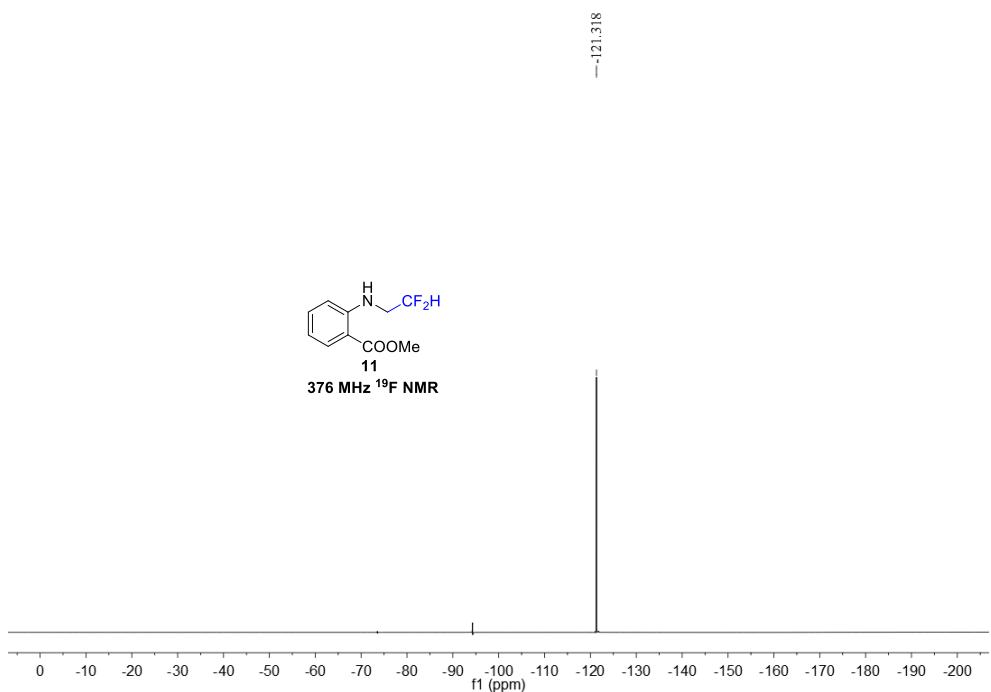




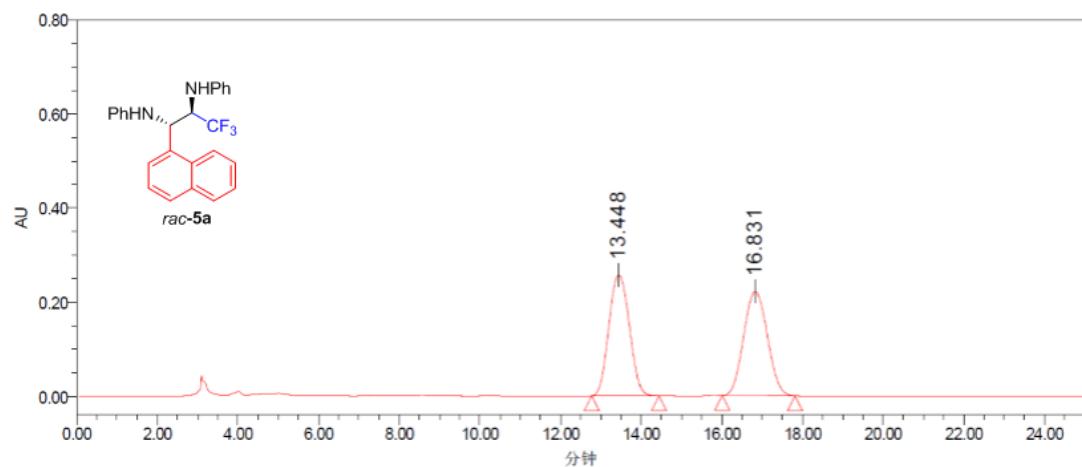




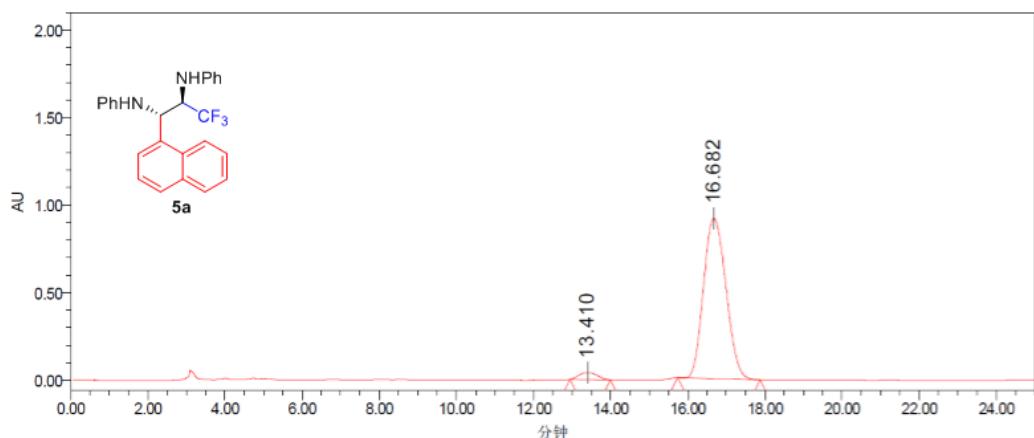




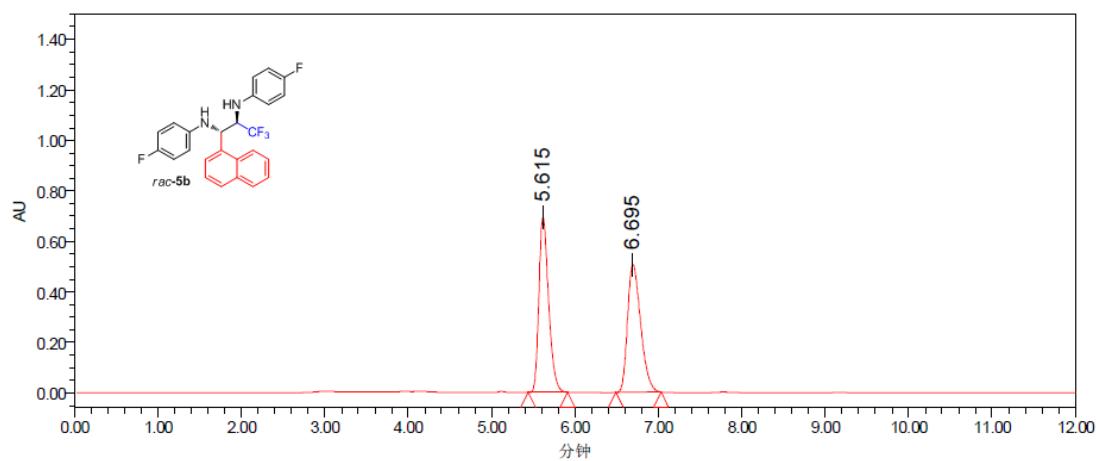
HPLC chromatograms of all products



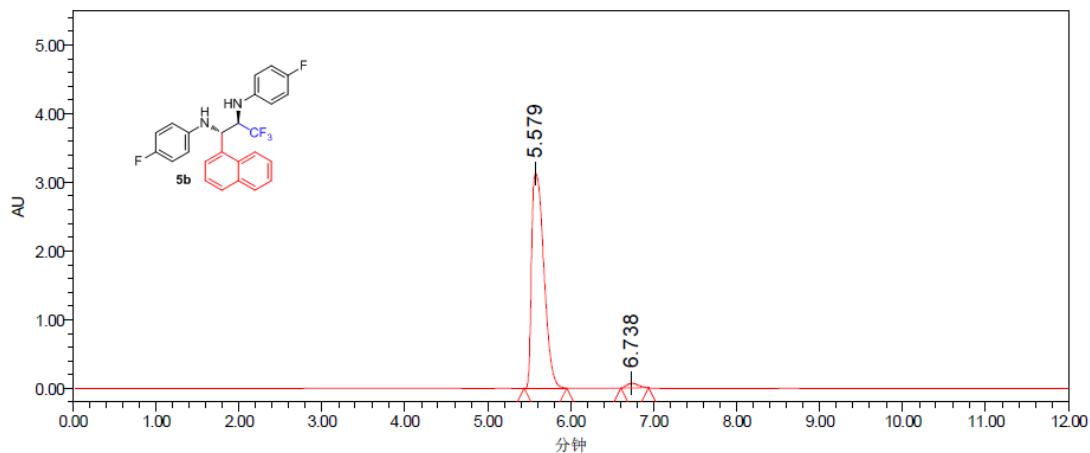
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	13.448	9052899	50.23
2	16.831	8968737	49.77



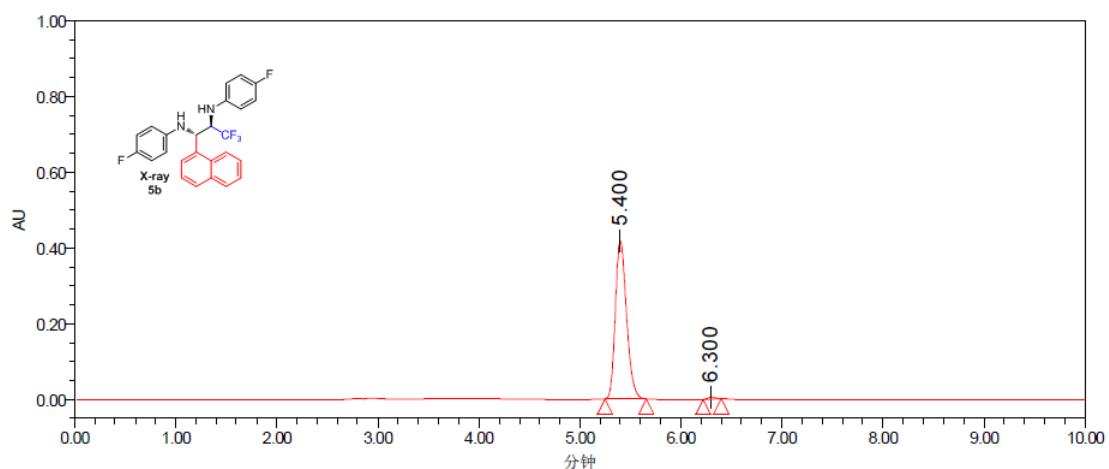
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	13.410	1340321	3.52
2	16.682	36696949	96.48



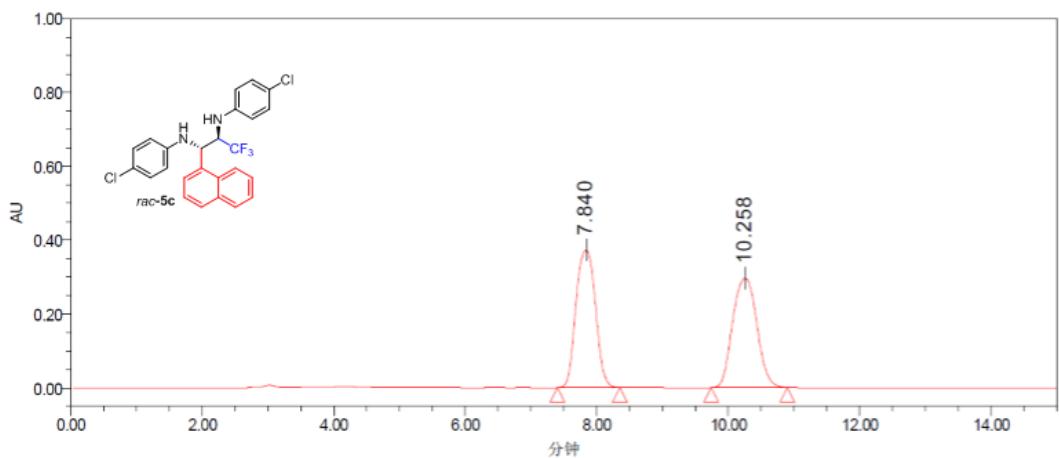
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	5.615	5628260	50.51
2	6.695	5514839	49.49



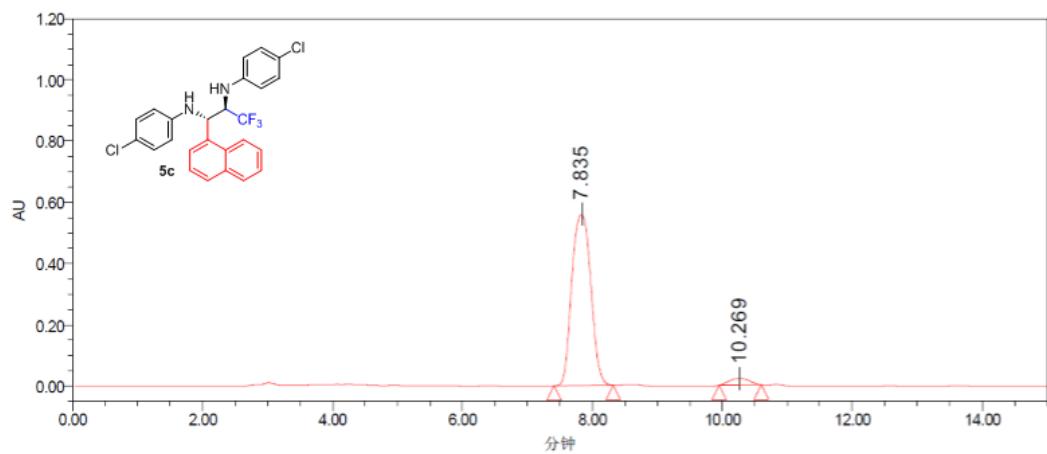
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	5.579	32073324	98.01
2	6.738	650325	1.99



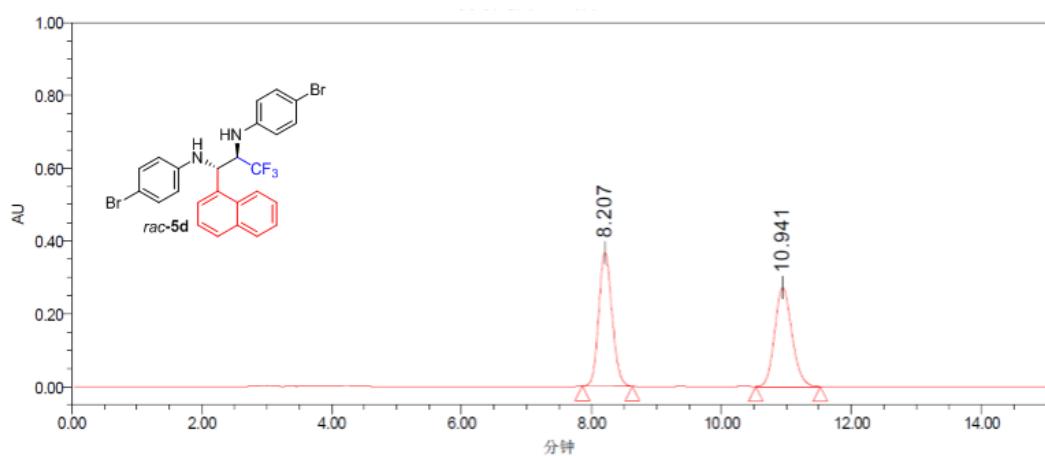
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	5.400	3212070	99.22
2	6.700	25142	0.78



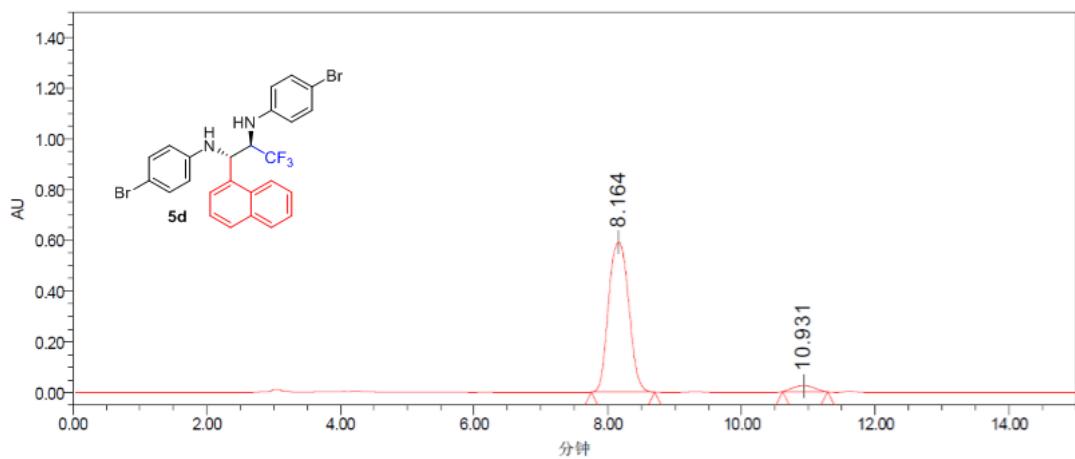
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	7.840	7682072	50.36
2	10.258	7573628	49.64



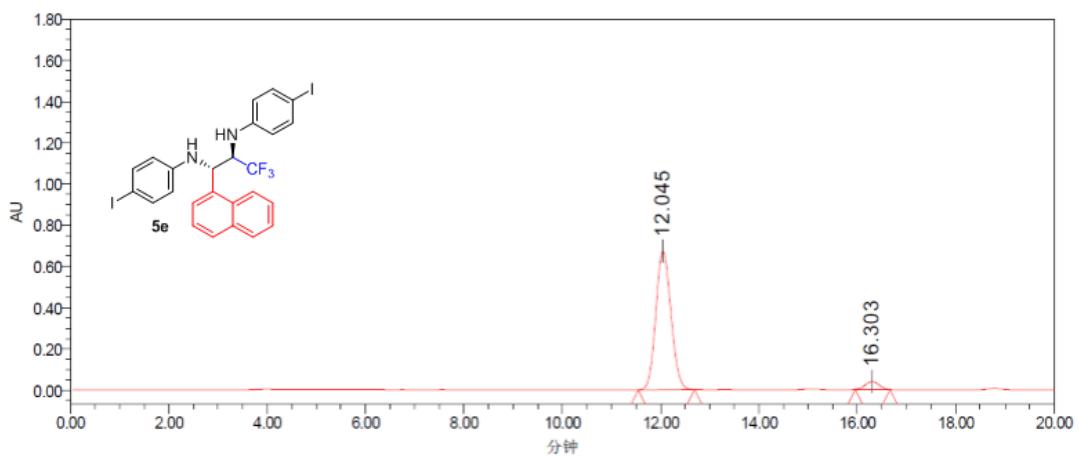
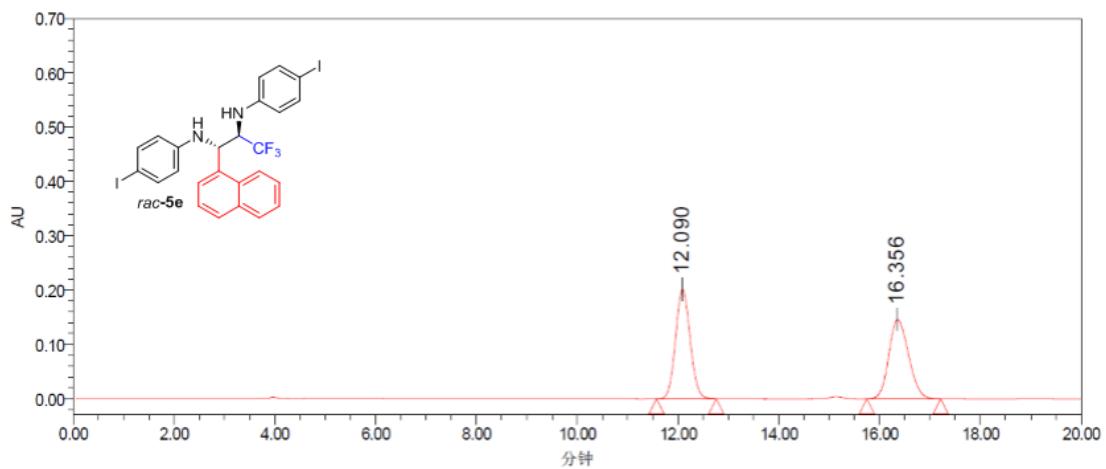
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	7.835	11412563	95.96
2	10.269	481048	4.04

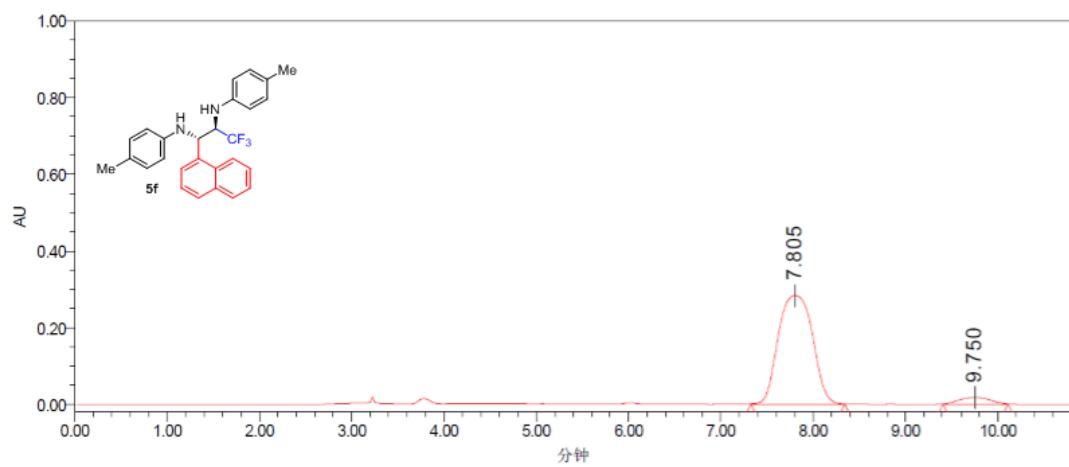
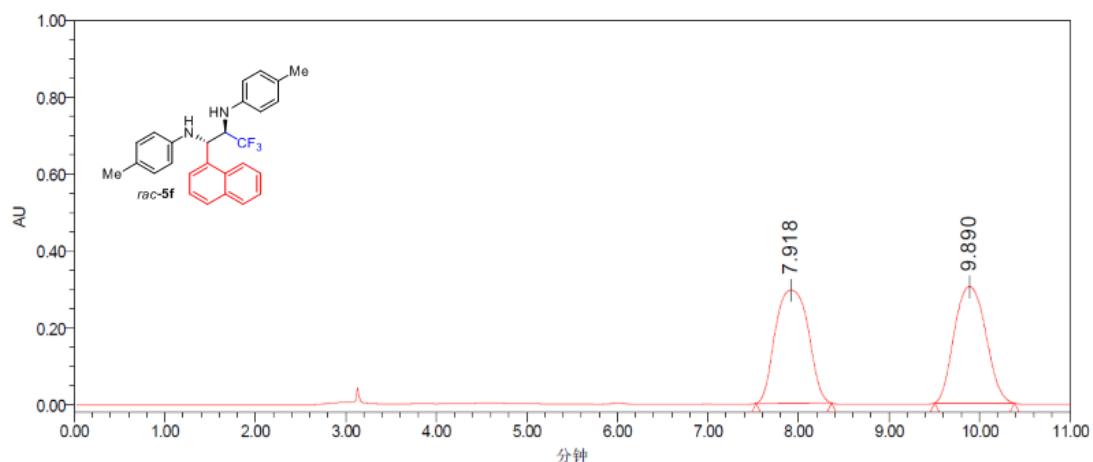


Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	8.207	5182348	50.67
2	10.941	5045905	49.33

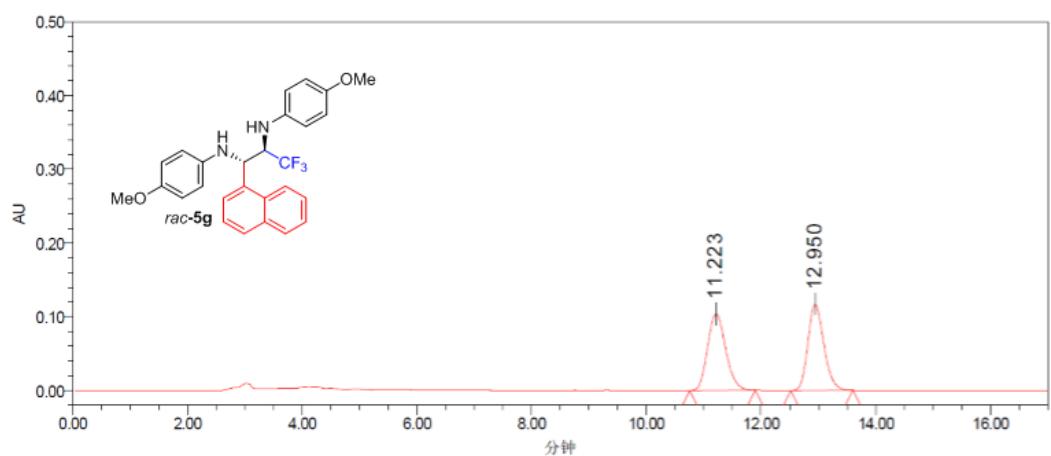


Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	8.164	12389147	95.95
2	10.931	526461	4.05

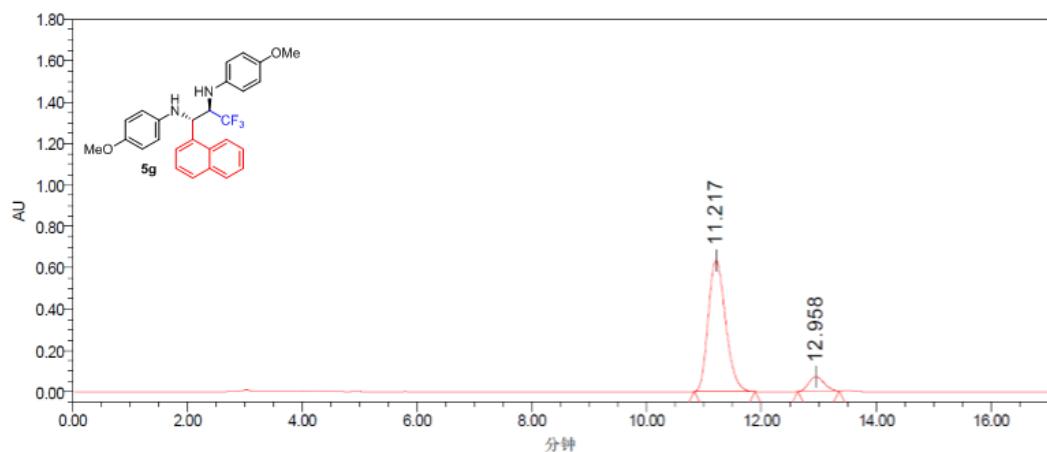




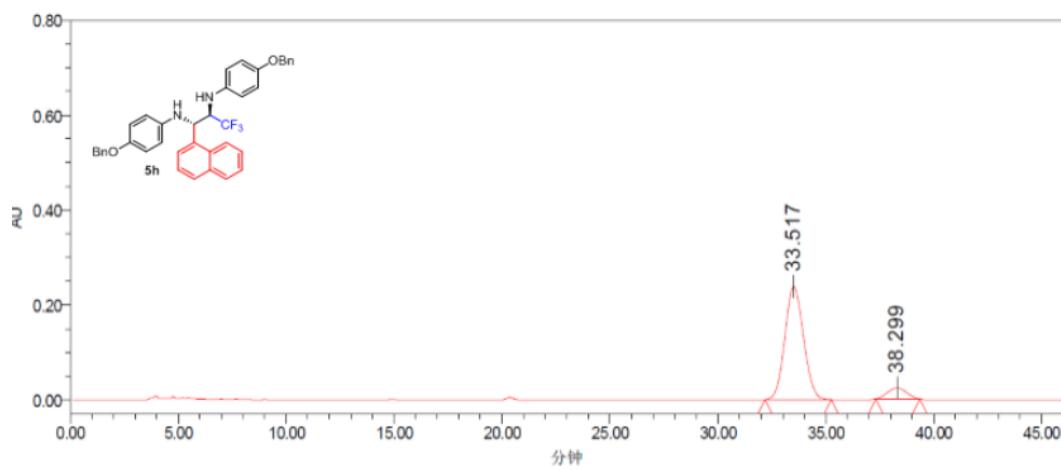
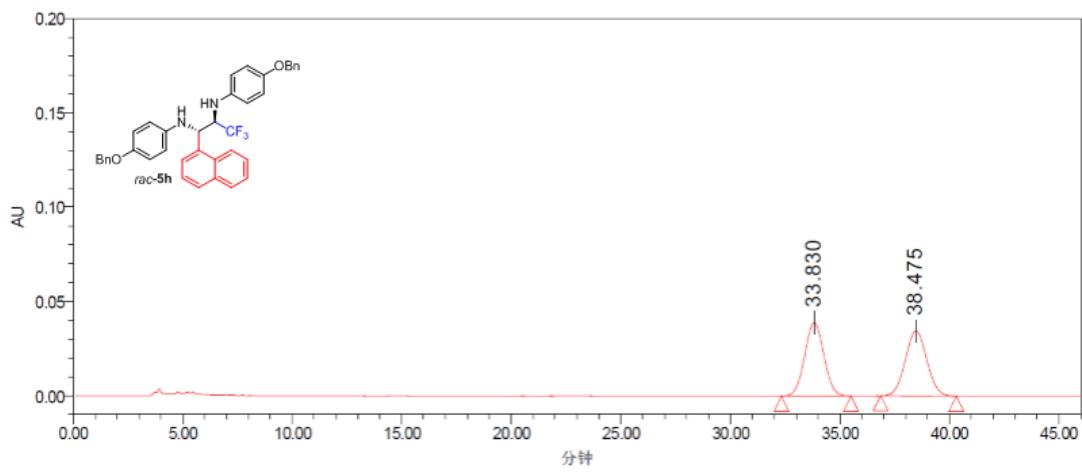
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	7.805	7285130	94.94
2	9.750	389390	5.06

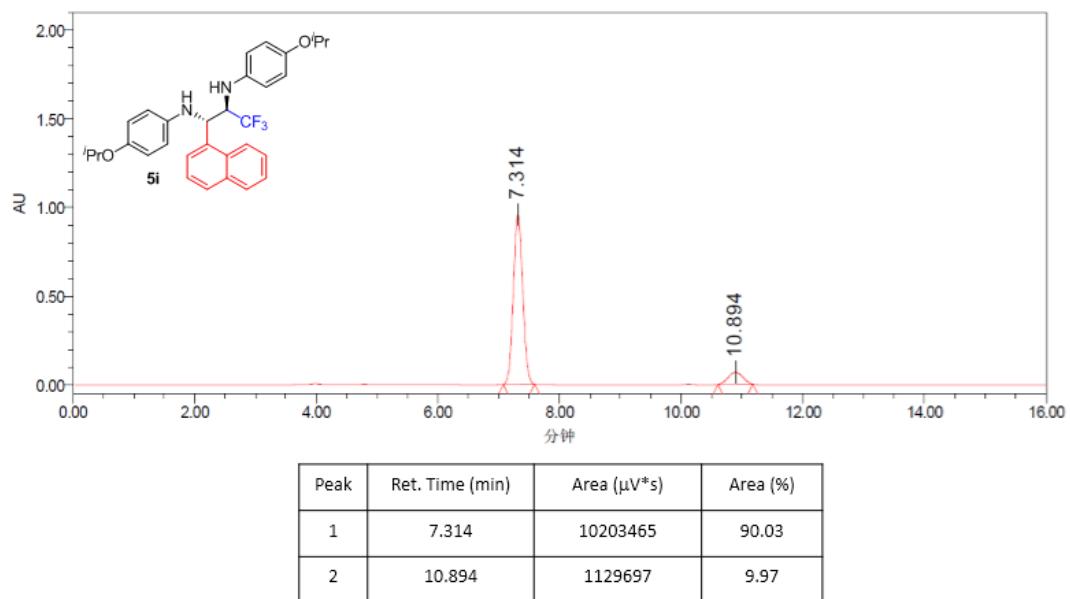
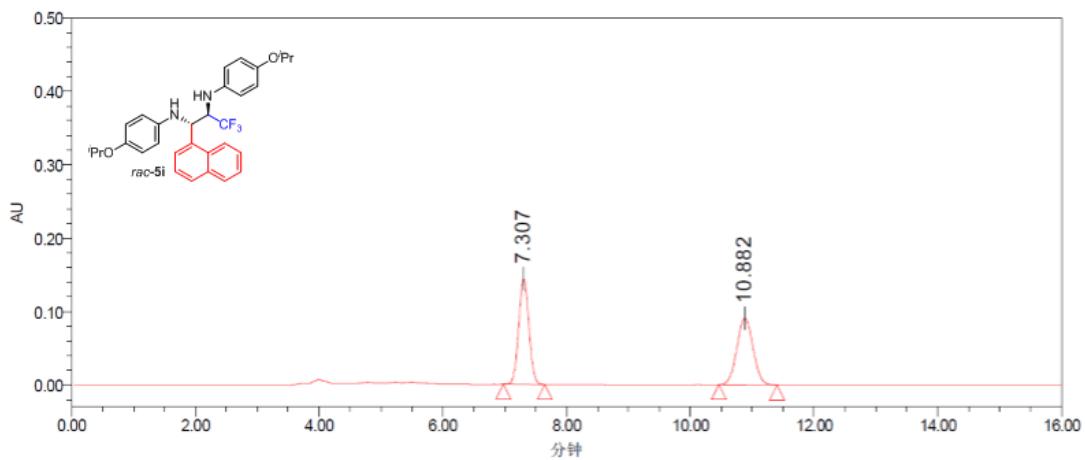


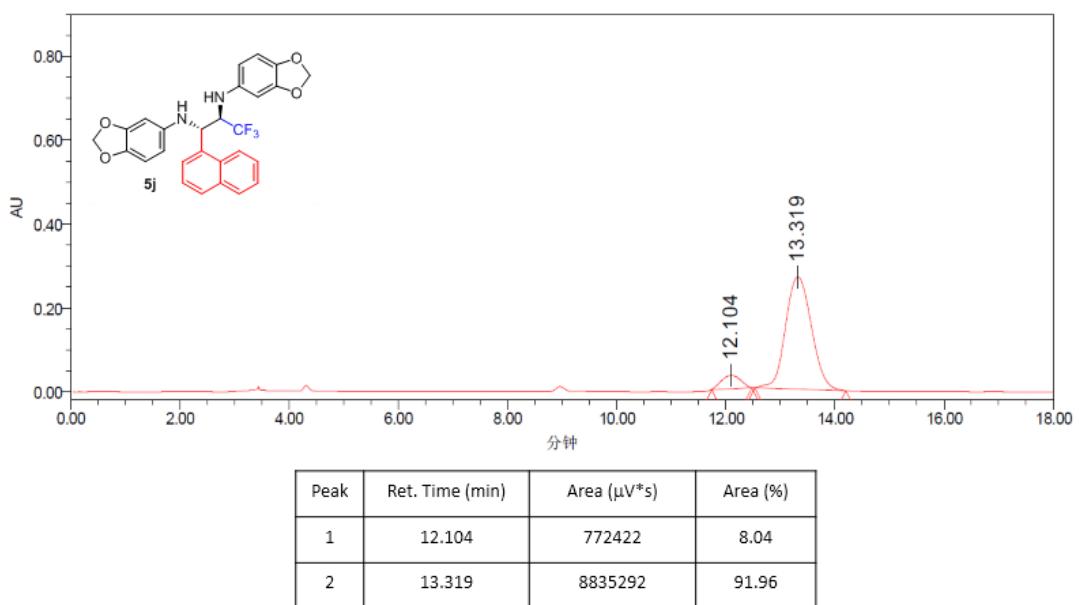
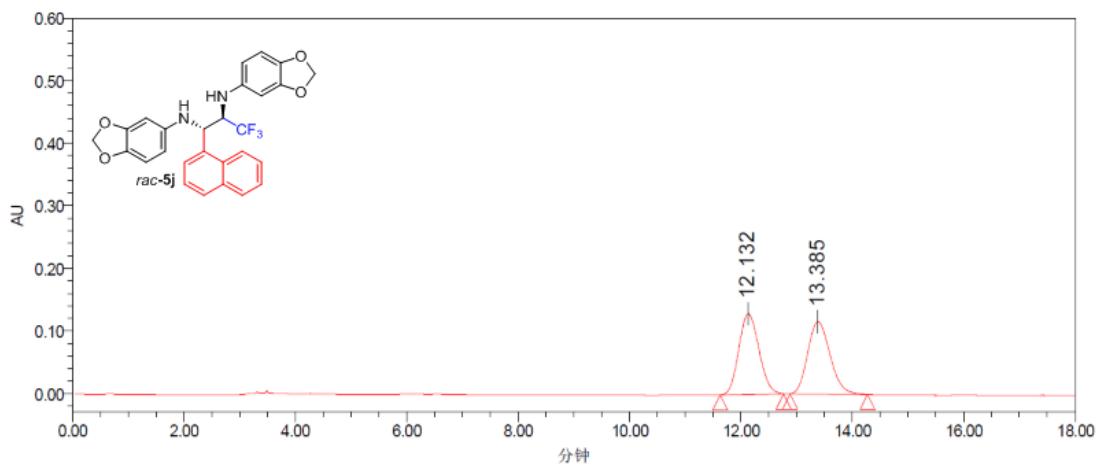
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.223	2274461	50.09
2	12.950	2265880	49.91

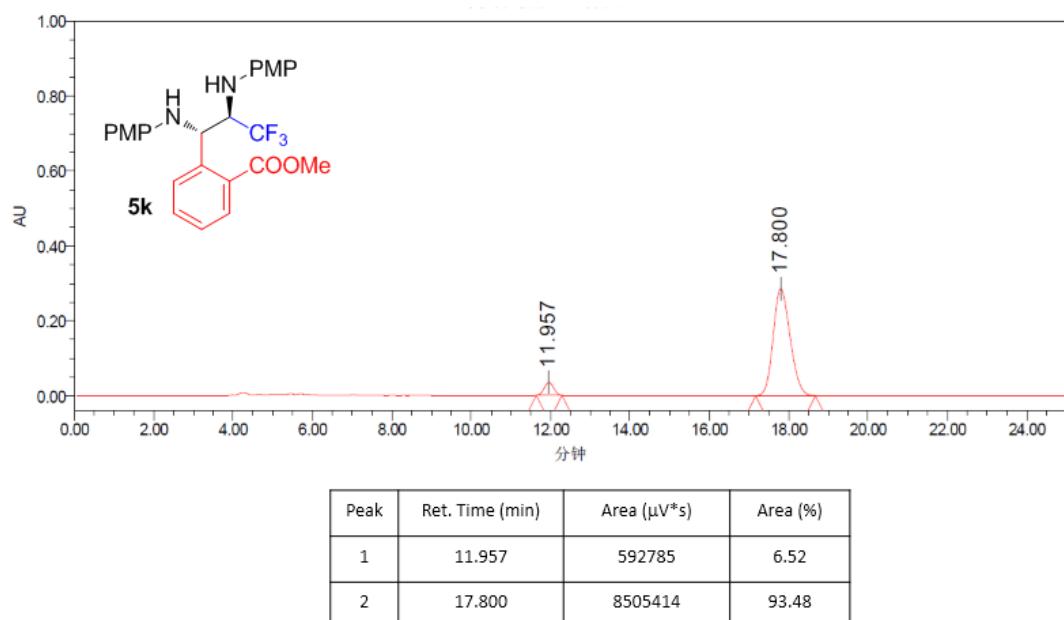
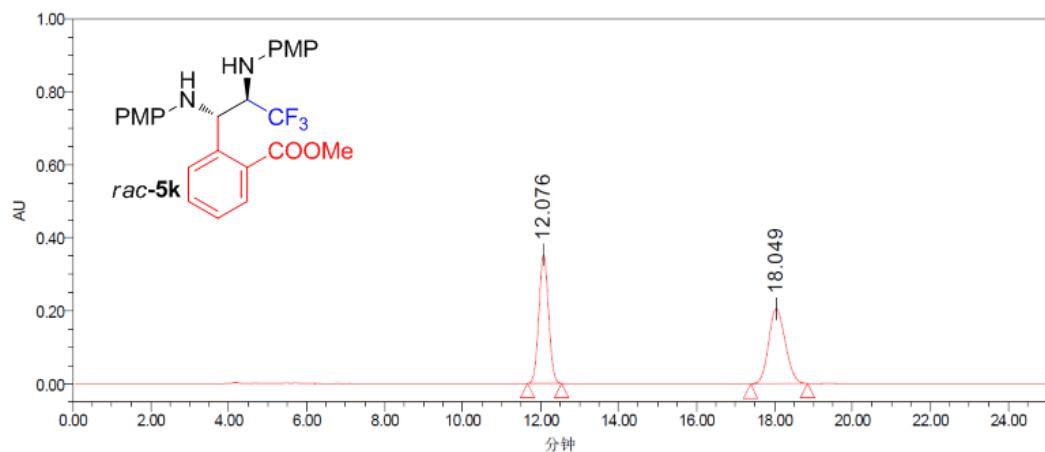


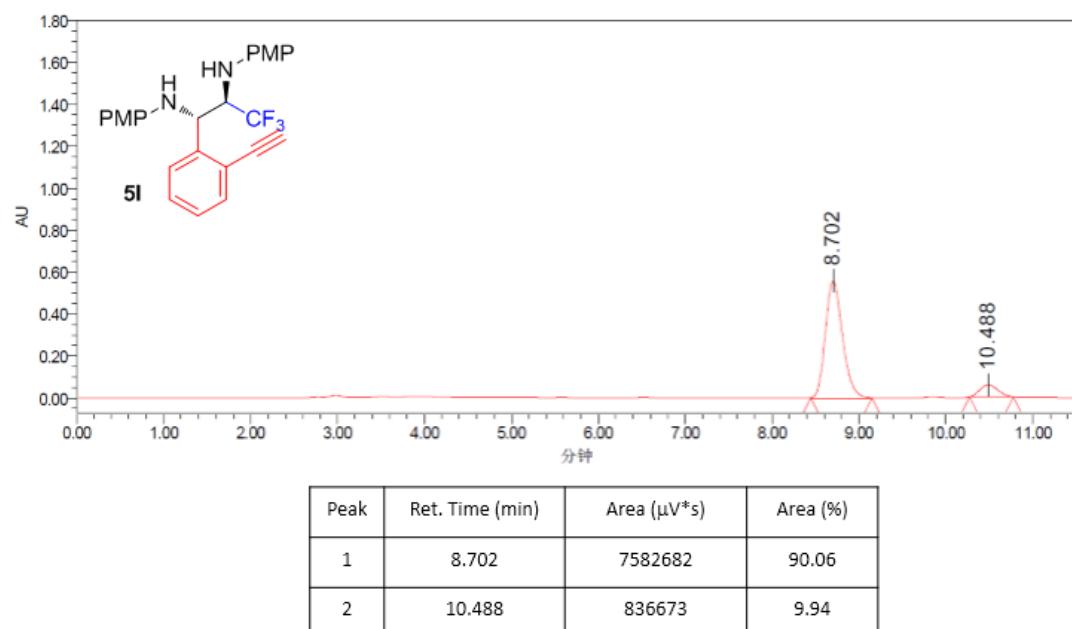
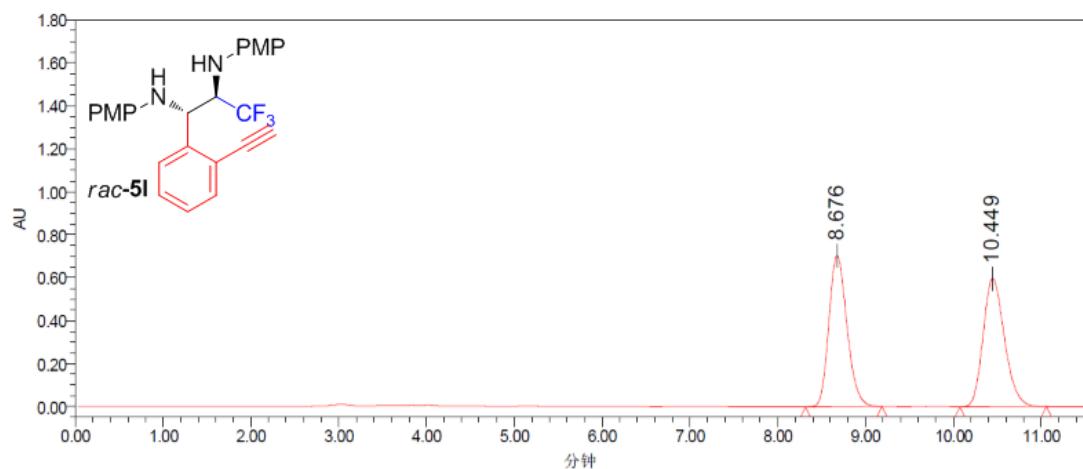
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.217	13301011	90.97
2	12.958	1321001	9.03

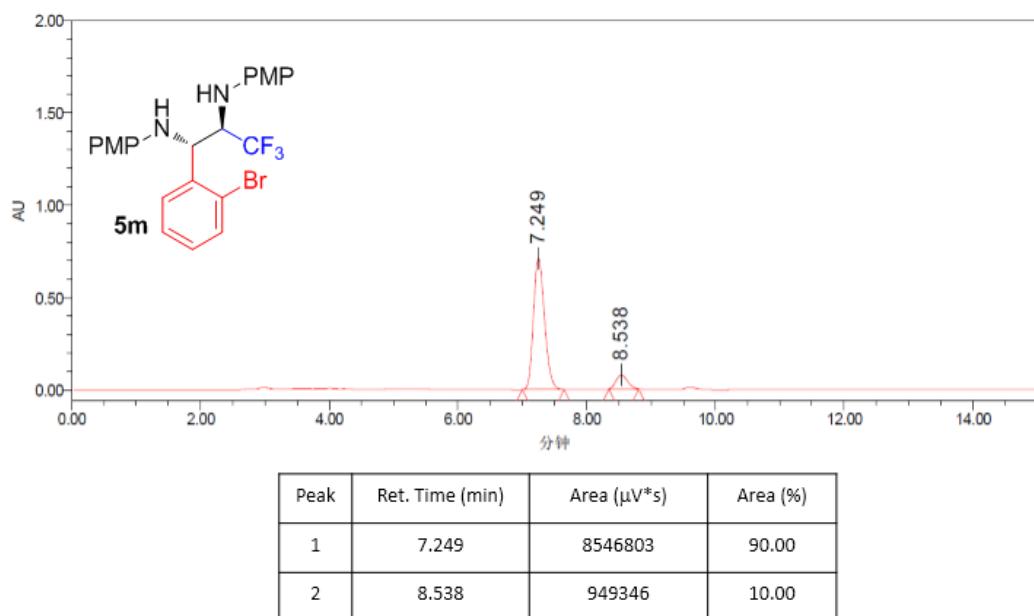
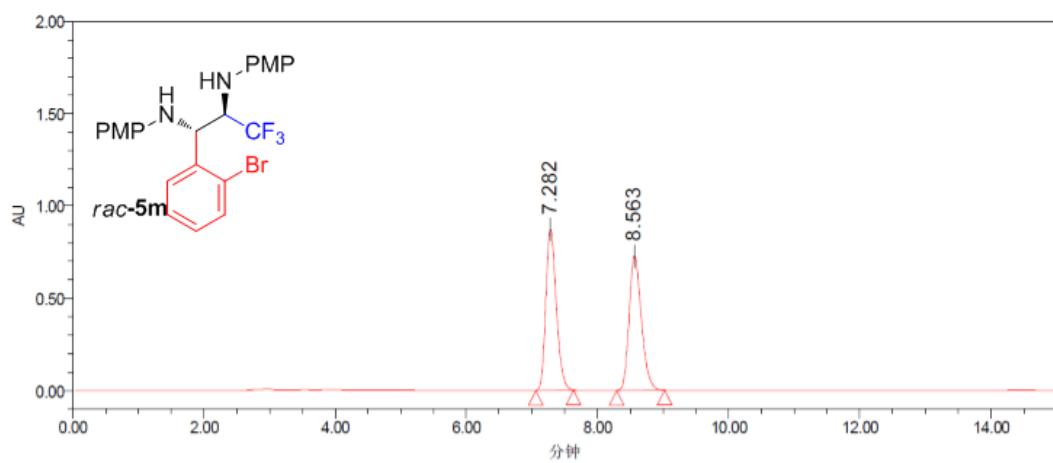


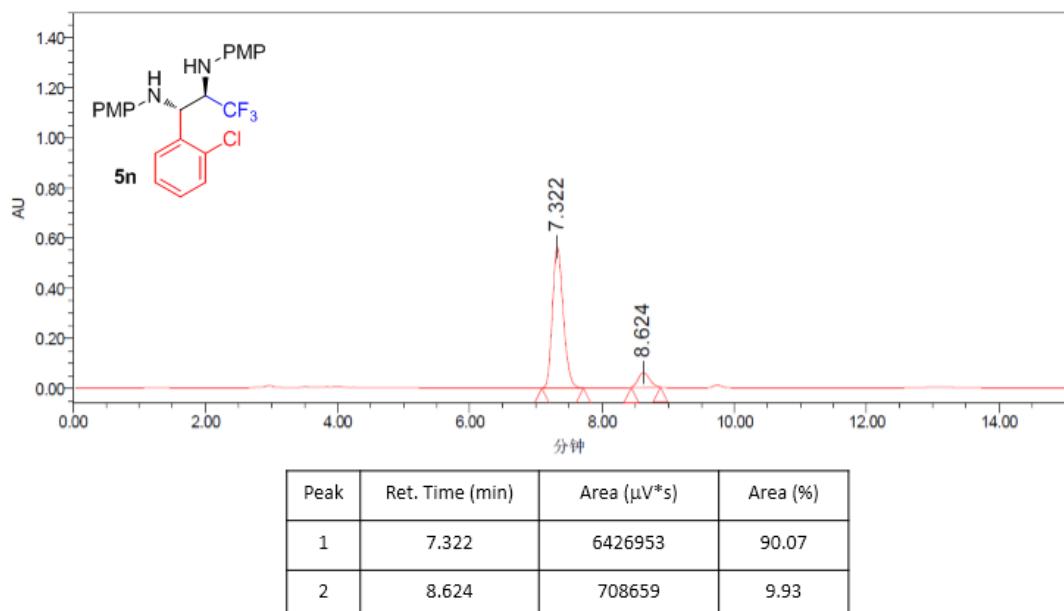
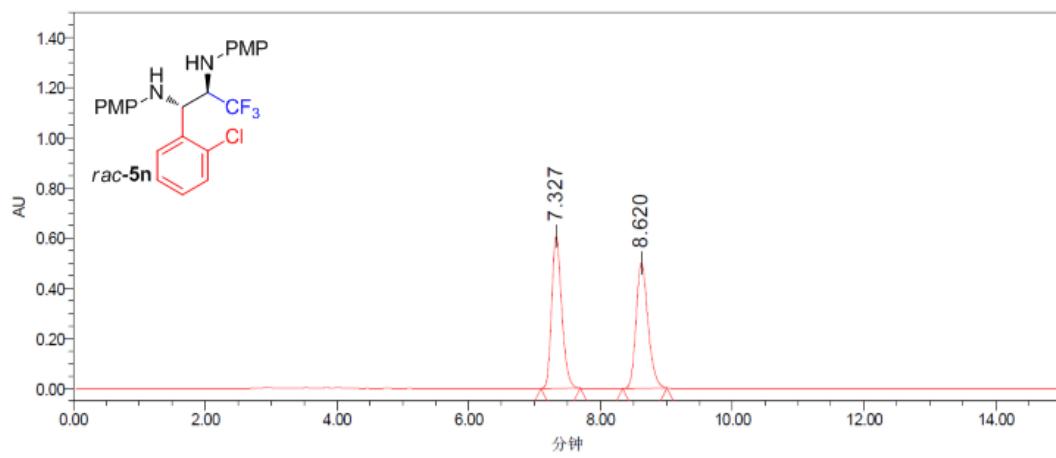


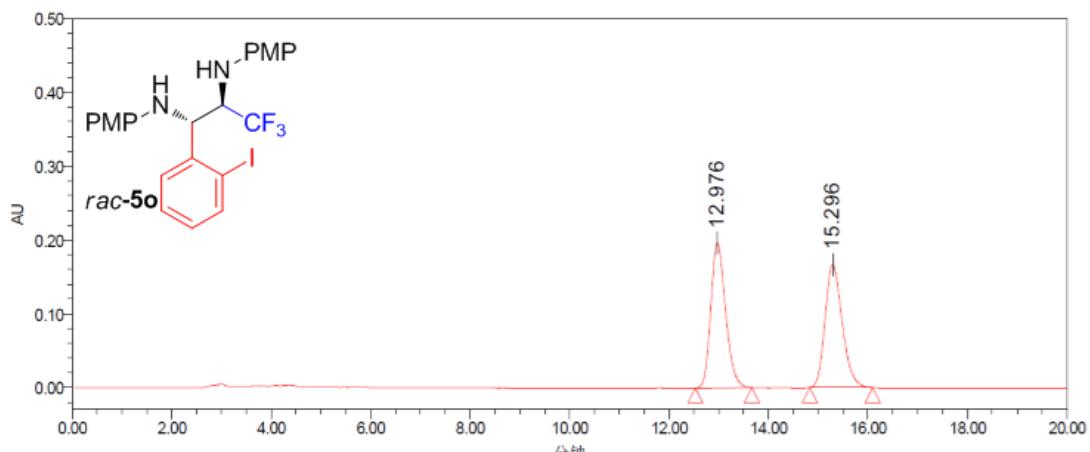




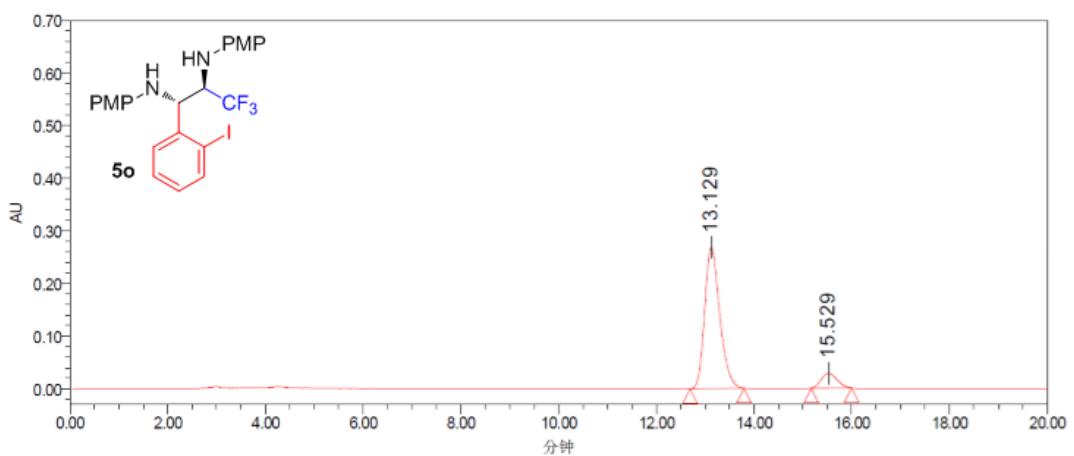




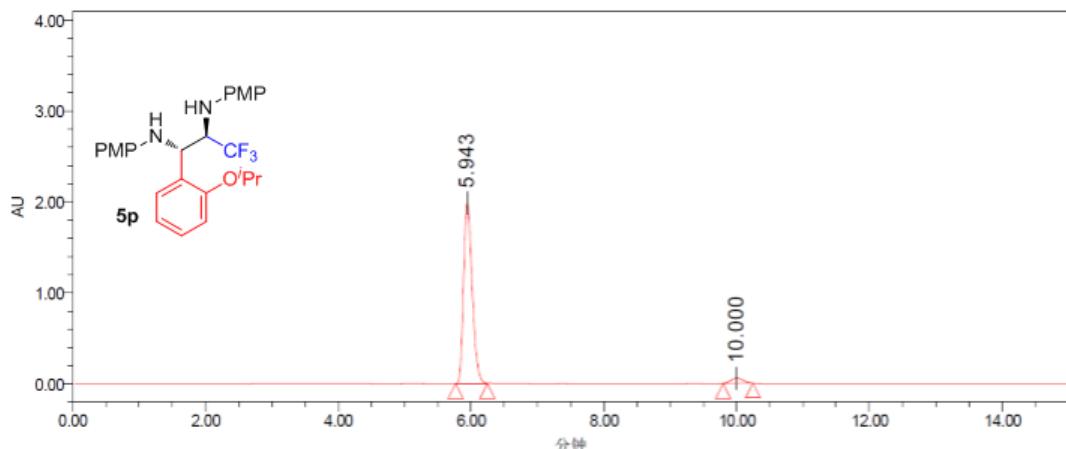
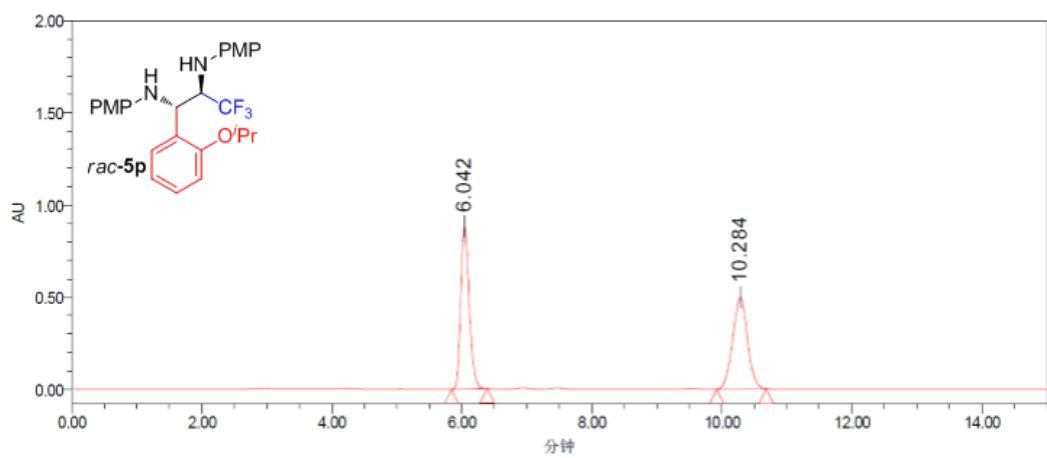


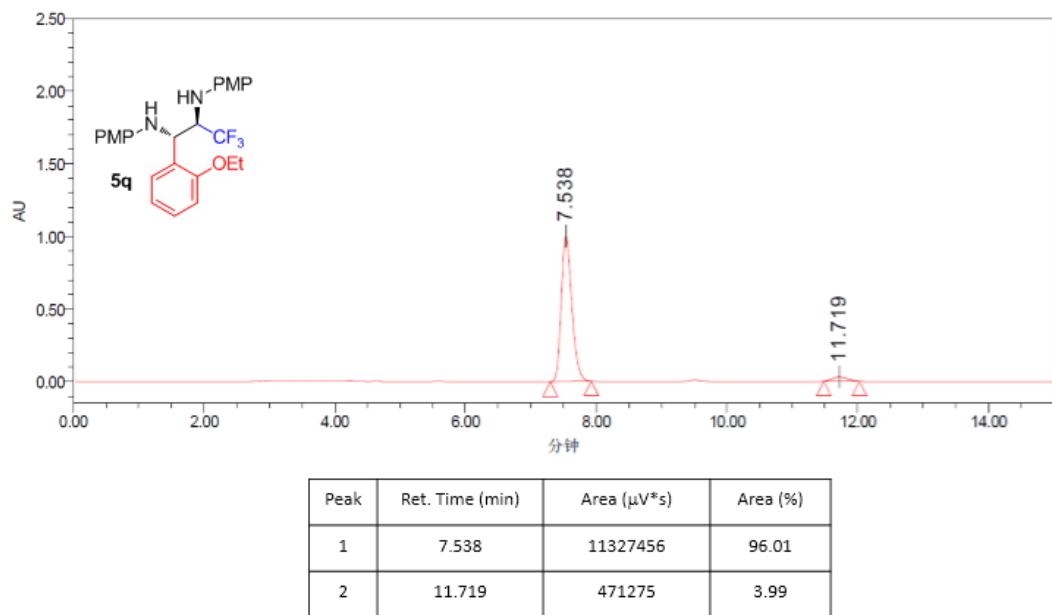
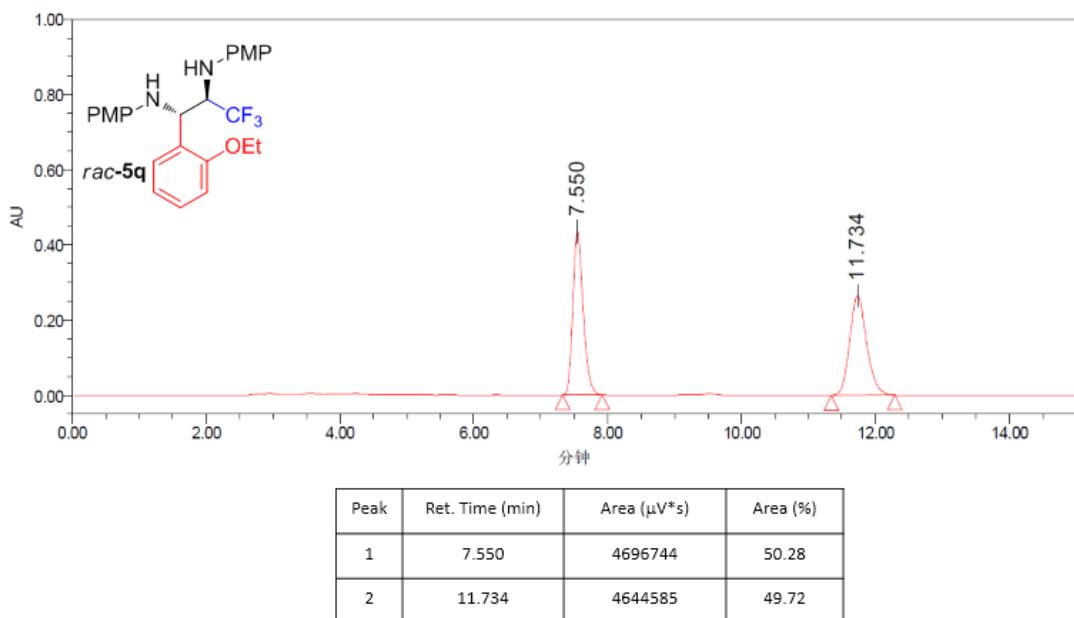


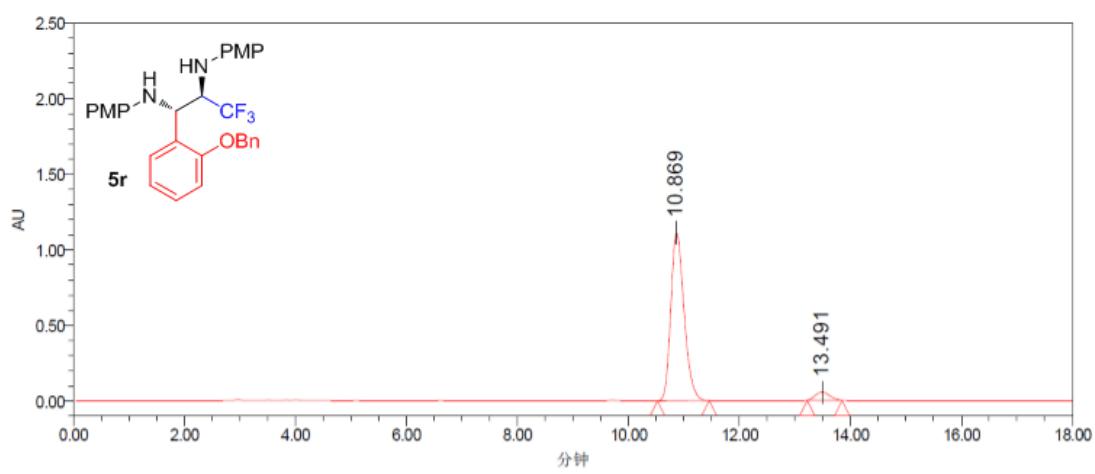
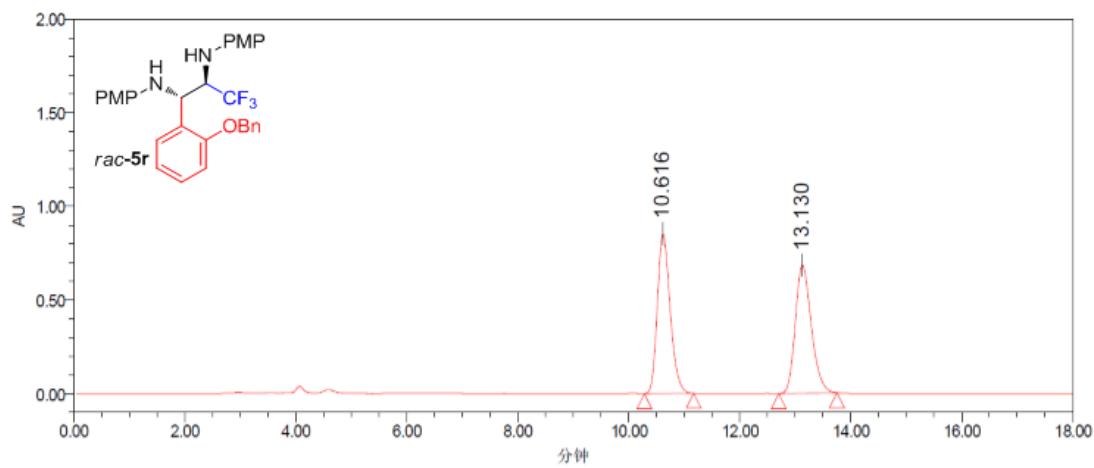
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	12.976	4048025	50.43
2	15.296	3978503	49.57

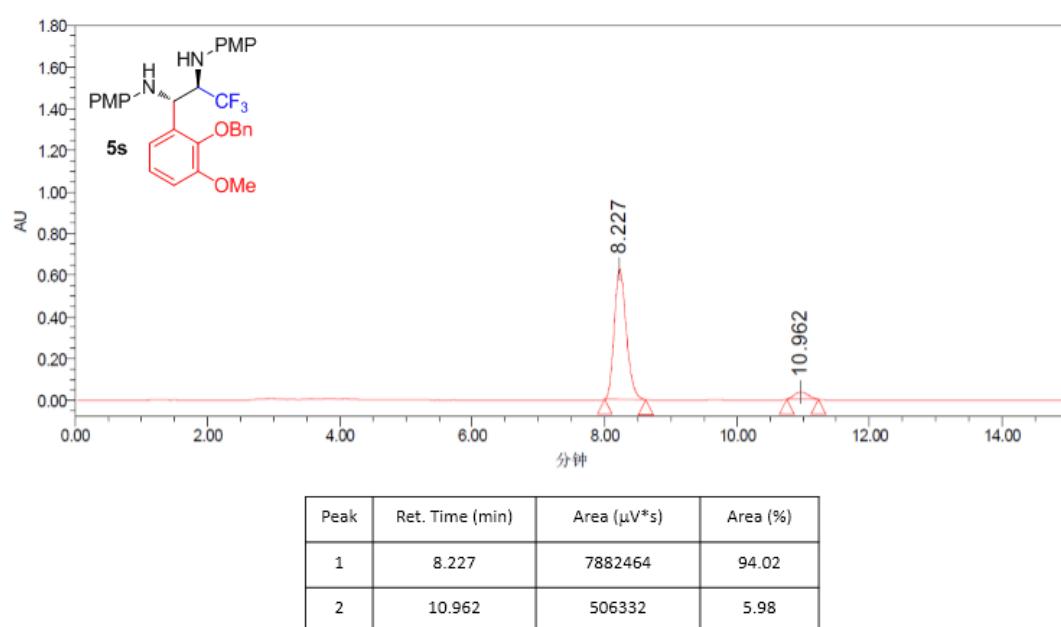
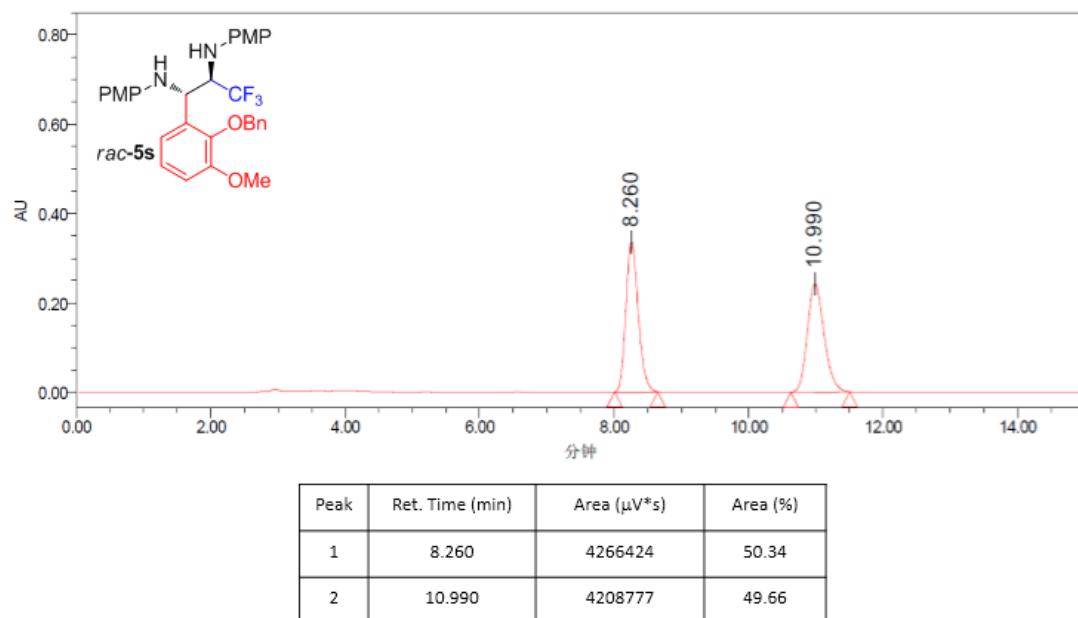


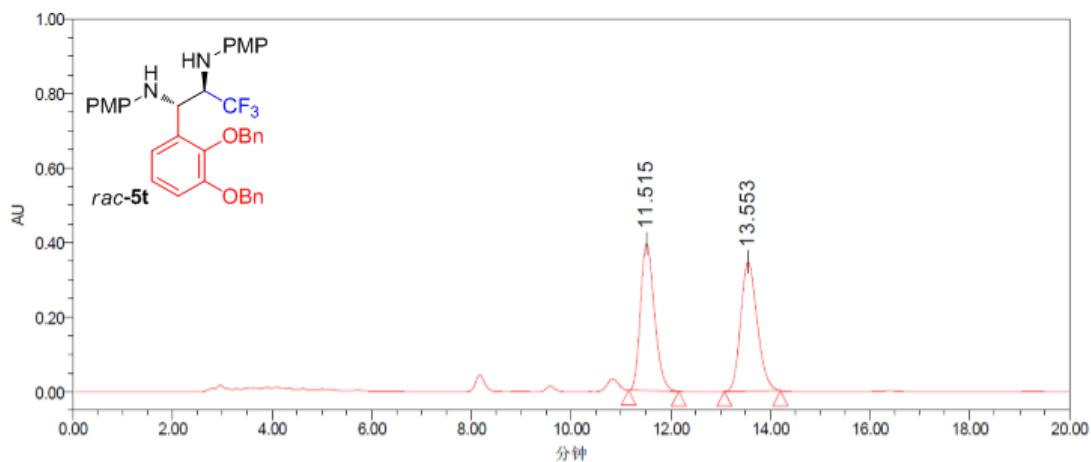
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	13.129	5738325	90.00
2	15.529	637427	10.00



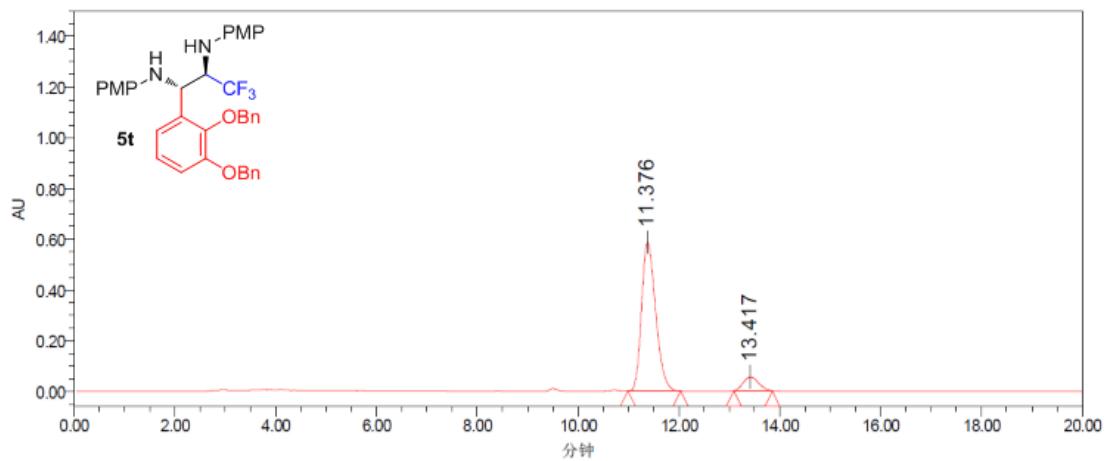




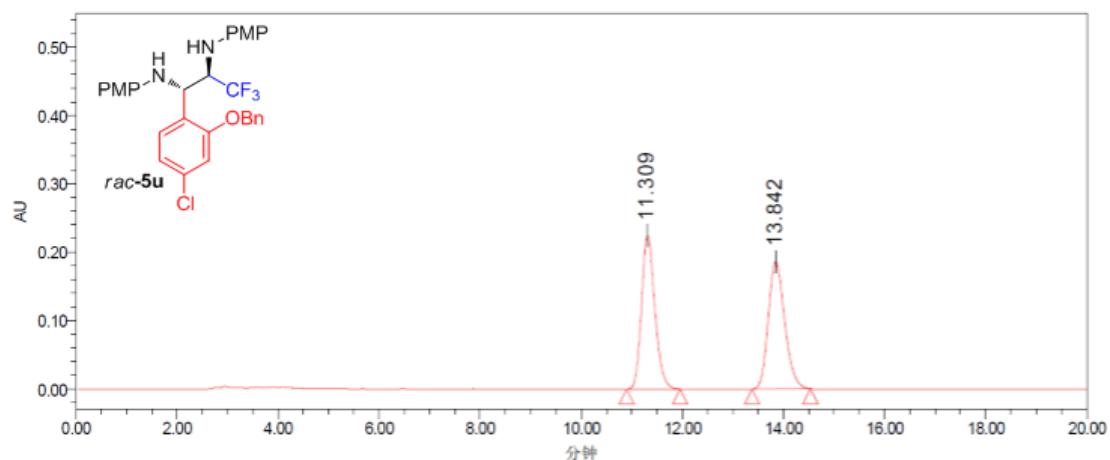




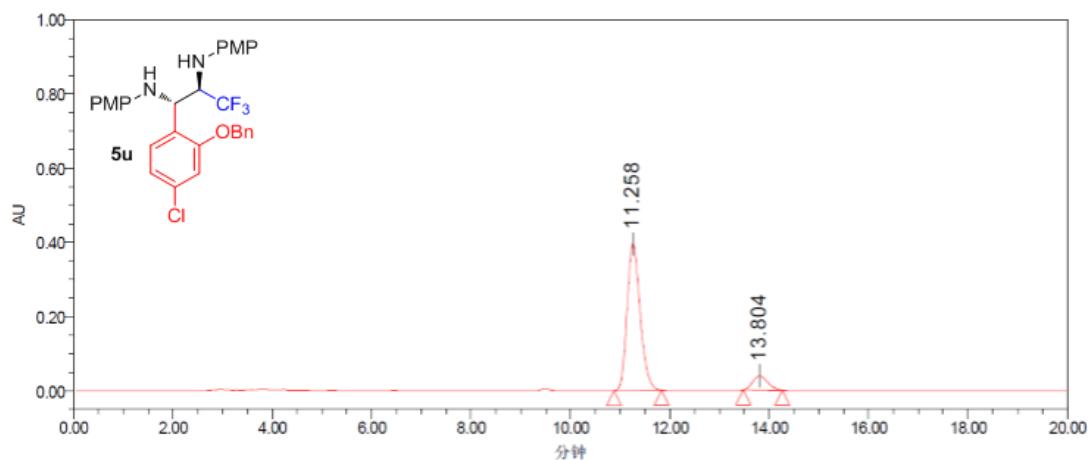
Peak	Ret. Time (min)	Area ($\mu\text{V*s}$)	Area (%)
1	11.515	7679388	49.16
2	13.553	7942626	50.84



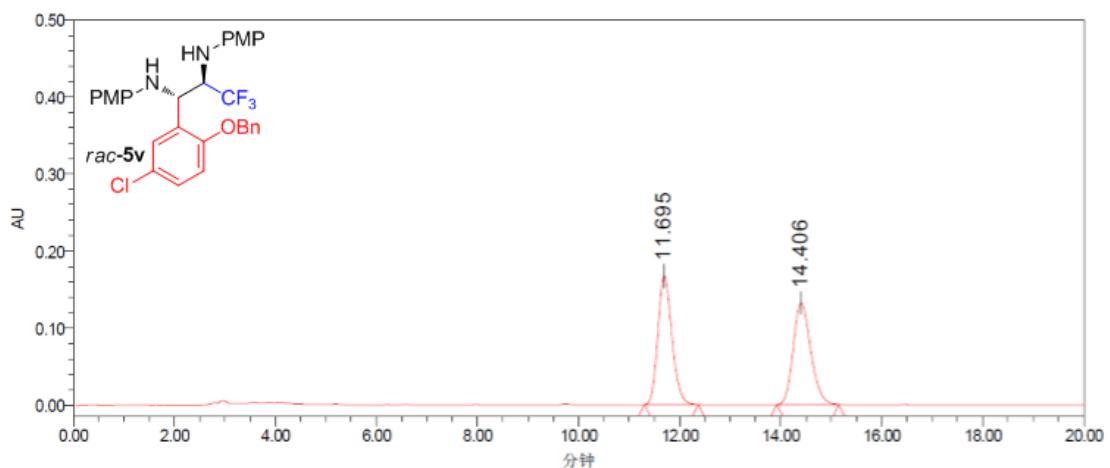
Peak	Ret. Time (min)	Area ($\mu\text{V*s}$)	Area (%)
1	11.376	11391199	91.01
2	13.417	1133354	8.99



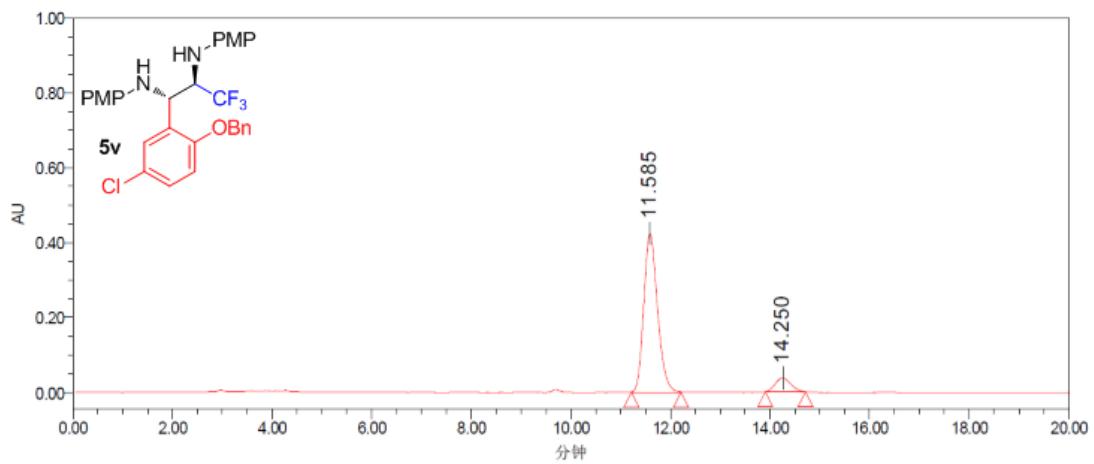
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.309	4073307	49.16
2	13.842	4213048	50.84



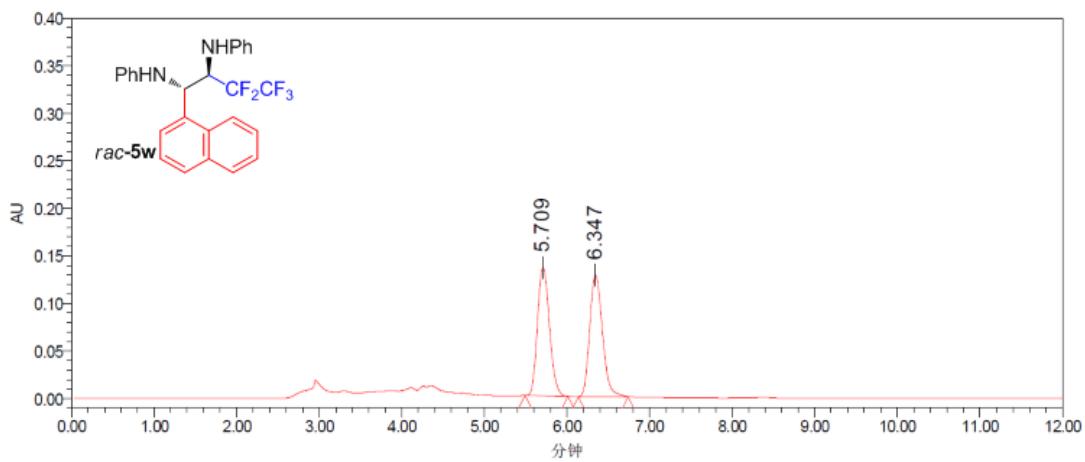
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.258	7140759	90.00
2	13.804	793634	10.00



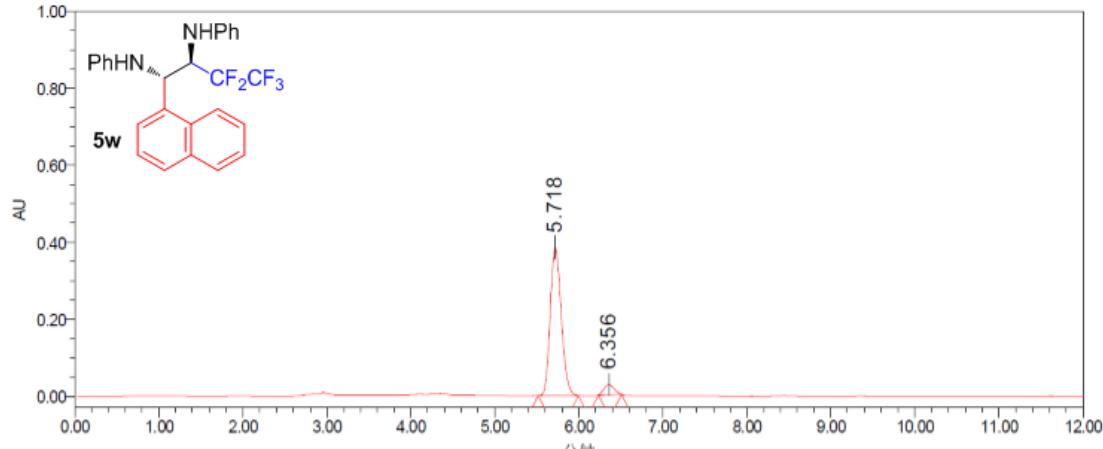
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.695	3241771	50.32
2	14.406	3200352	49.68



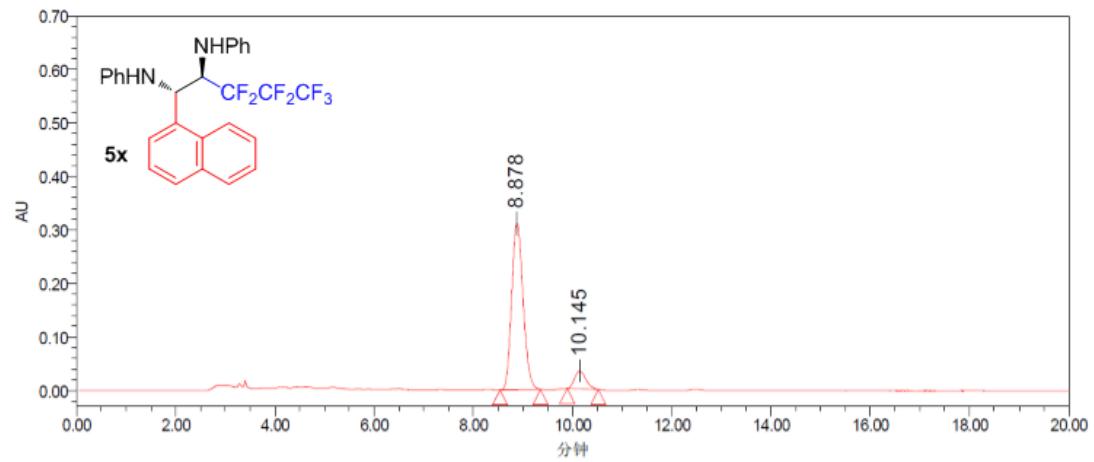
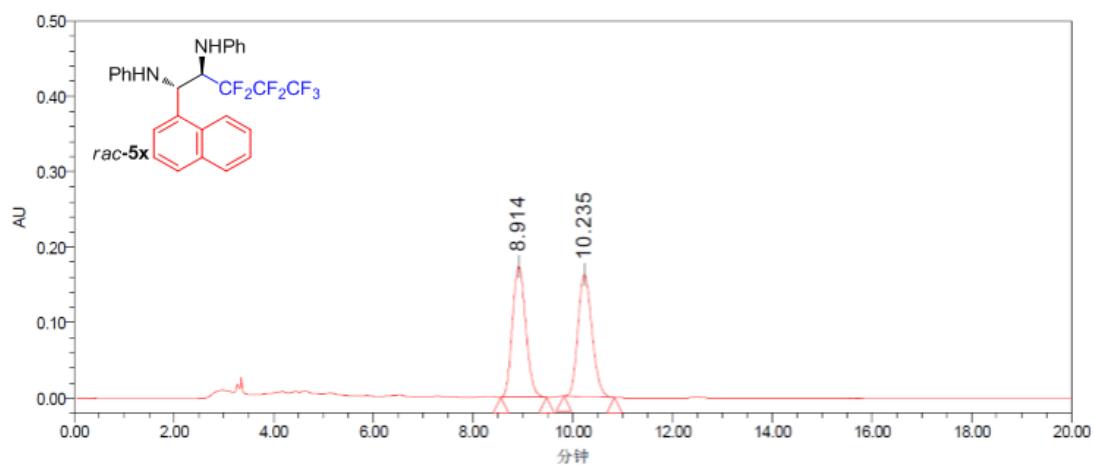
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.585	8082441	91.01
2	14.250	798805	8.99

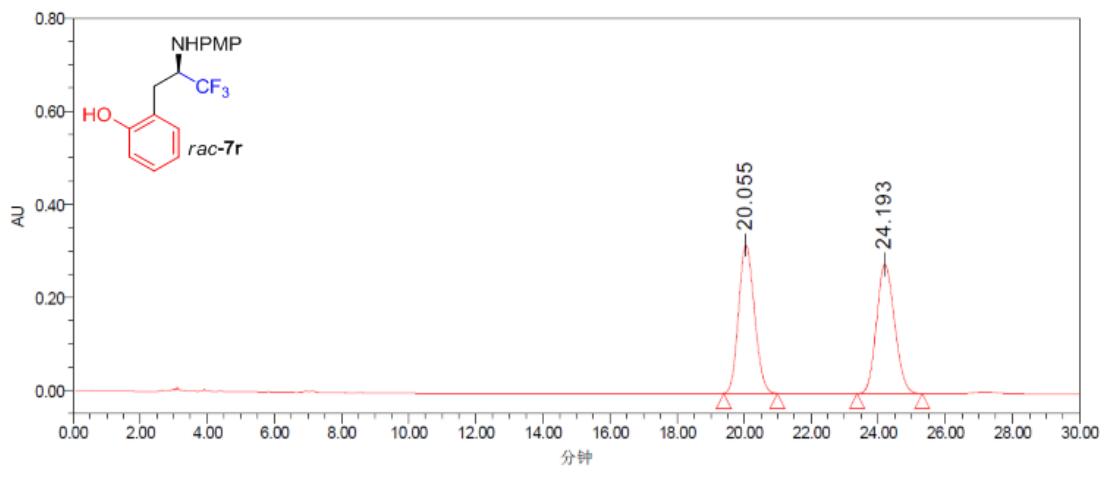


Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	5.709	1365746	49.81
2	6.347	1376042	50.19

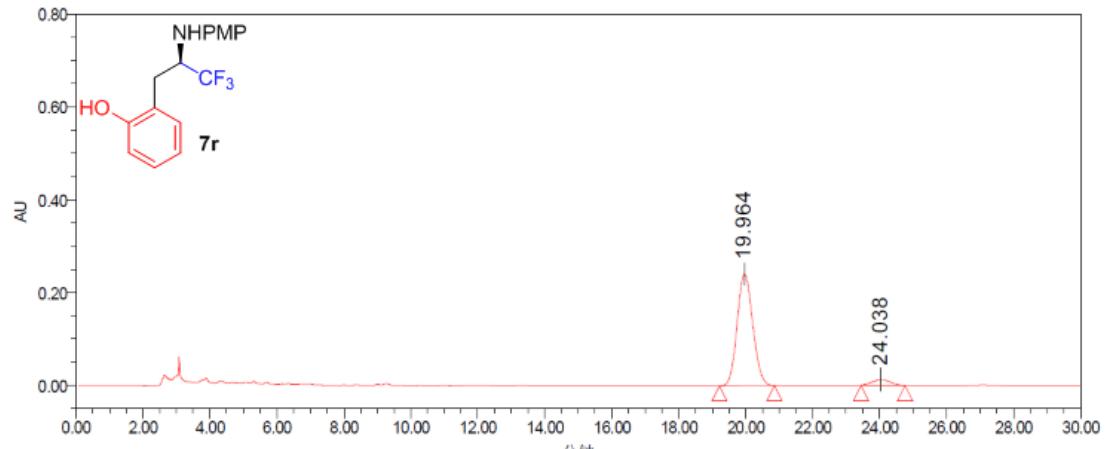


Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	5.718	3509353	93.97
2	6.356	225176	6.03

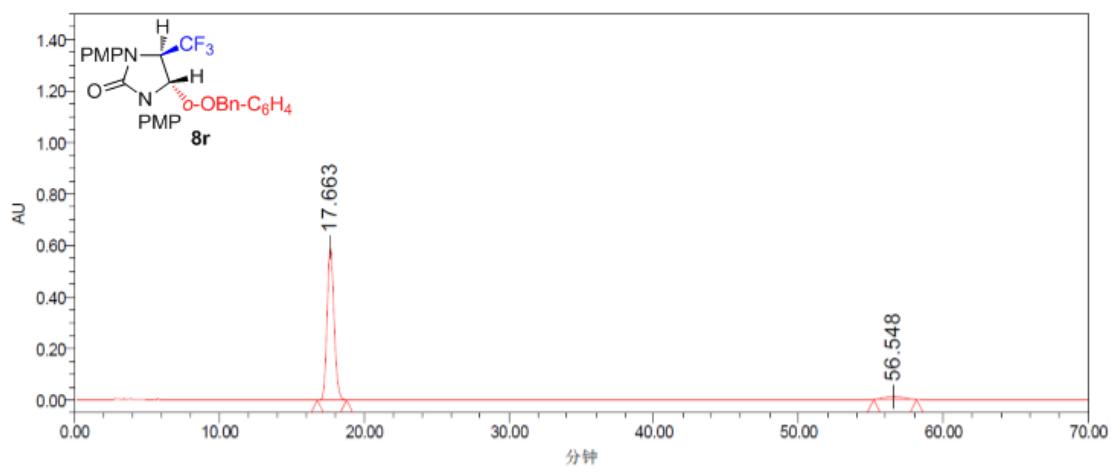
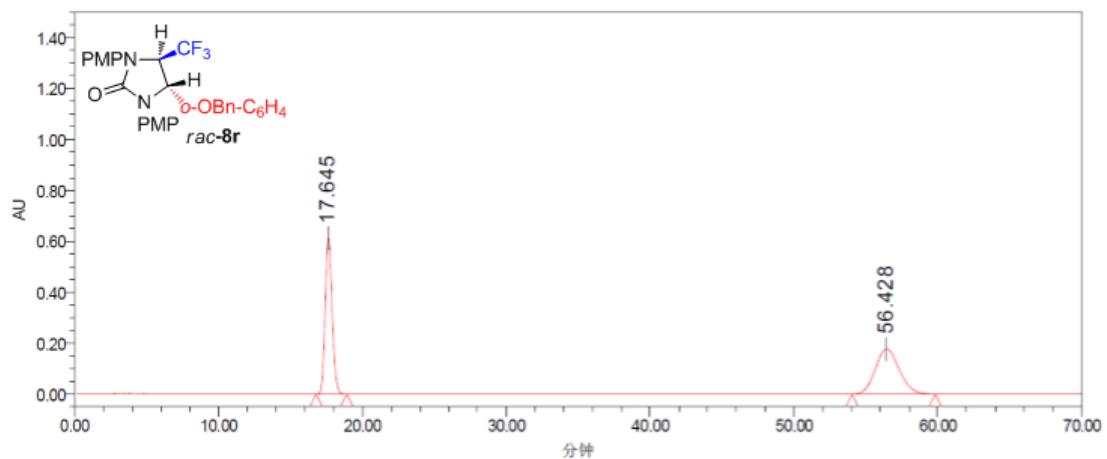




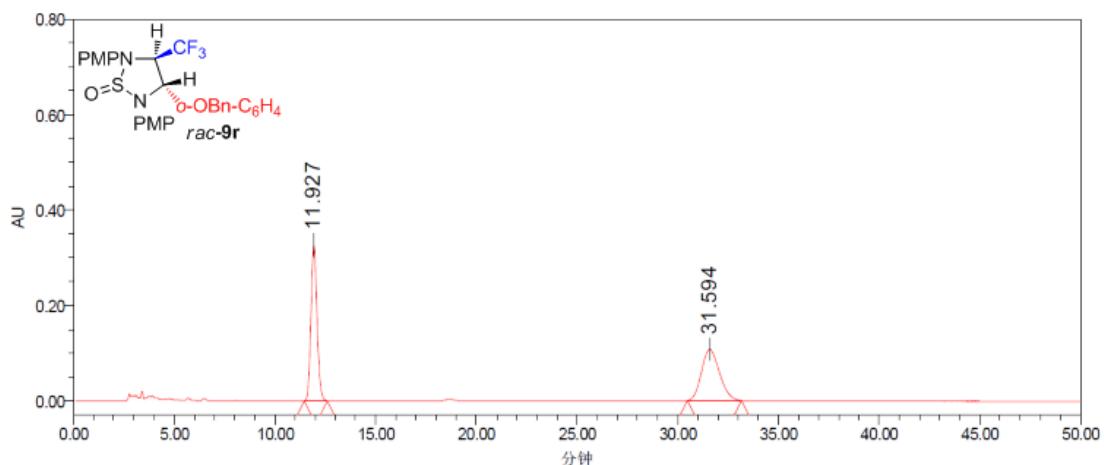
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	20.055	10336826	49.82
2	24.193	10412644	50.18



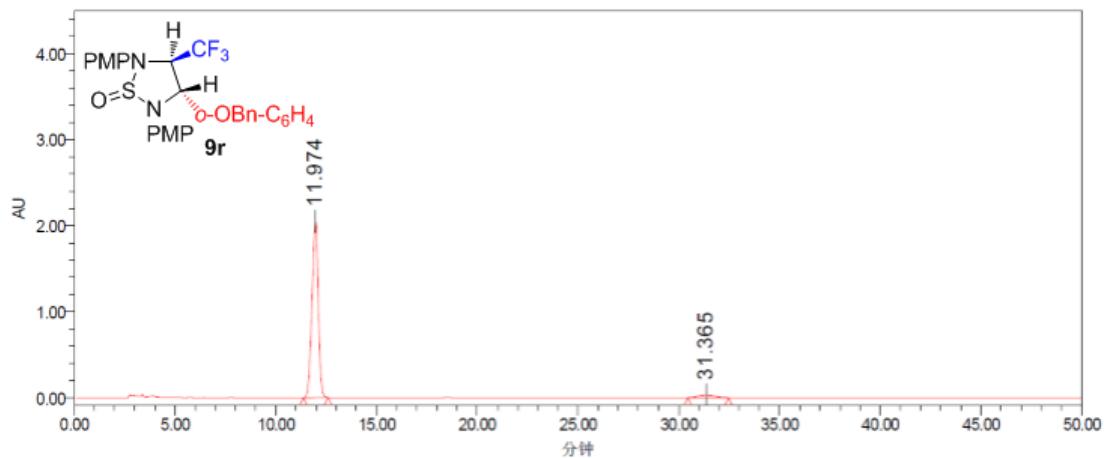
Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	19.964	7739323	94.10
2	24.038	485412	5.90



Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	17.663	19881378	94.99
2	56.548	1048752	5.01



Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.927	6854594	50.54
2	31.594	6709070	49.46



Peak	Ret. Time (min)	Area ($\mu\text{V}^*\text{s}$)	Area (%)
1	11.974	44816462	96.07
2	31.365	1834041	3.93