
Supporting Information

Ruthenium-Catalyzed Hydroxyl-Directed *peri*-Selective C-H Activation and Annulation of 1-Naphthols with CF₃-Imidoyl Sulfoxonium Ylides for the Synthesis of 2-(Trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amines

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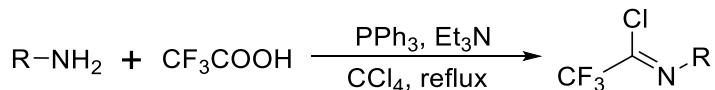
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1. General Information

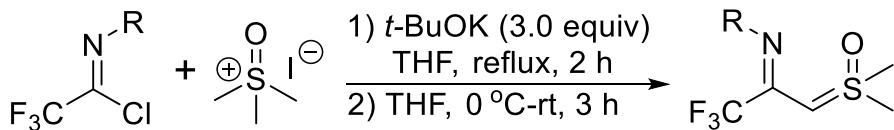
Unless otherwise noted, all reactions were carried out under N₂ atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ¹NMR spectra were recorded on a Bruker Avance operating at for ¹H NMR at 400 MHz, ¹³C NMR at 100 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl₃ (¹H NMR δ 7.26, ¹³C NMR δ 77.16) or DMSO-D₆ (¹H NMR δ 2.50, ¹³C NMR δ 39.52) as solvent. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected.

1.1 Preparation of Fluorinated Imidoyl Chlorides¹



A 100 mL two-necked flask equipped with a septum cap, a condenser, and a Teflon-coated magnetic stir bar was charged with PPh₃ (9.84 g, 37.5 mmol), Et₃N (2.1 mL, 15 mmol), CCl₄ (20.0 mL), and TFA (1.2 mL, 15 mmol). After the solution was stirred for about 10 min (ice bath), amine (15 mmol) dissolved in CCl₄ (20.0 mL) was added. The mixture was then refluxed under stirring (3 h). After the reaction was completed, residual solid Ph₃PO, PPh₃ and Et₃N-HCl were washed with petroleum ether several times. Then the petroleum ether was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel or neutral alumina to afford the corresponding product.

1.2 Preparation of CF₃-Imidoyl Sulfoxonium Ylides²



Trimethylsulfoxonium iodide (30 mmol, 3.0 equiv) was suspended in THF (150 mL) in a 250 mL round bottom flask, *t*-BuOK (30 mmol, 3.0 equiv) was added and the mixture was stirred at room temperature for 2 hours. Then, fluorinated imidoyl chloride (10 mmol, 1.0 equiv) was added. The mixture was stirred at room temperature for 3 hours and then filtered through a plug of celite before all volatiles were removed under vacuum. Purification by flash chromatography (petroleum ether/EtOAc = 2 : 1) afforded products. For the CF₃-imidoyl sulfoxonium ylide **2f**, a yellow solid was obtained in 85% yield and the H¹-NMR spectrum of **2f** was consistent with the reported data.

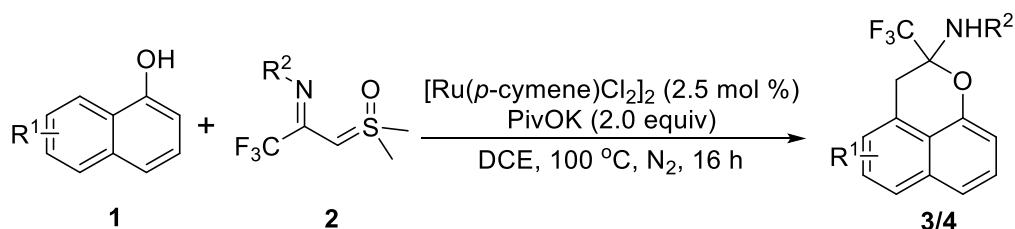
3-(dimethyl(oxo)-λ⁶-sulfanylidene)-1,1,1-trifluoro-N-(4-methoxyphenyl)propan-2-imine (2f)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 2:1, R_f = 0.3) to give the titled product **2f** as a yellow solid (2.5g, 85%).

¹H NMR (400 MHz, CDCl₃) δ 6.86 – 6.71 (m, 4H), 4.12 (s, 1H), 3.77 (s, 3H), 3.47 (s, 4H, rotamer), 3.19 (s, 2H, rotamer).

2. Experimental Procedures

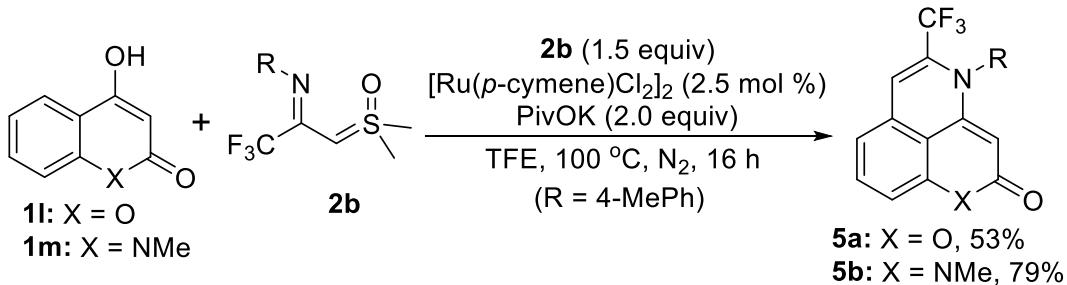
2.1 General Procedure for the Synthesis of Products 3/4



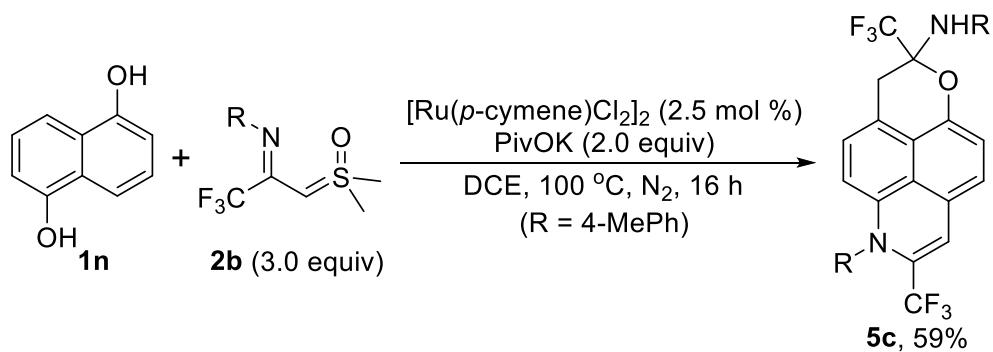
Under Nitrogen atmosphere, naphthalen-1-ol **1** (0.2 mmol, 1.0 equiv), CF₃-imidoyl sulfoxonium ylides (TFISYs) **2** (0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2.0 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then

the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the products **3/4**.

2.2 General Procedure for the Synthesis of Compounds **5a-c**.



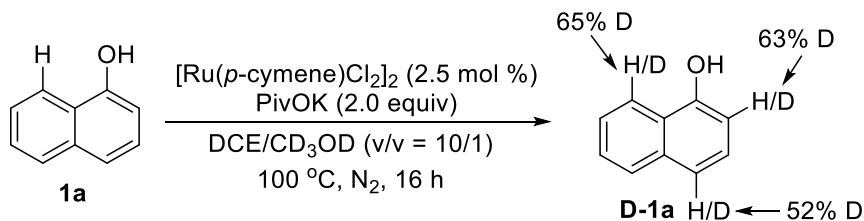
Under Nitrogen atmosphere, substrates **1l** & **1m** (0.2 mmol, 1.0 equiv), TFISY **2b** (83.1 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), TFE (2.0 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **5a** as a yellow solid (36.6 mg, 53%) and **5b** as a yellow solid (56.2 mg, 79%).



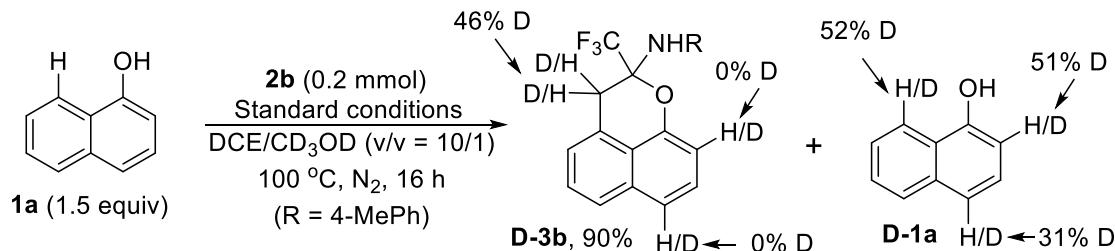
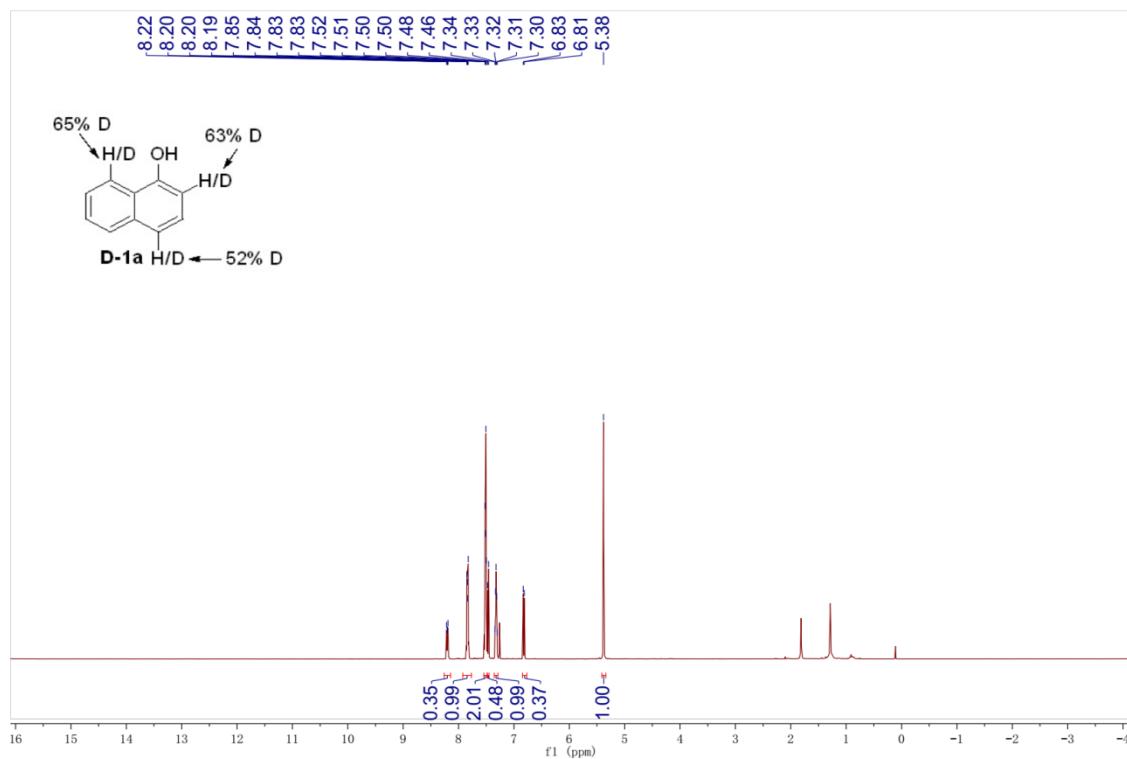
Under Nitrogen atmosphere, naphthalene-1,5-diol **1n** (32.0 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (166.2 mg, 0.6 mmol, 3.0 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2.0 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed

and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **5c** as a yellow oil (63.4 mg, 59%).

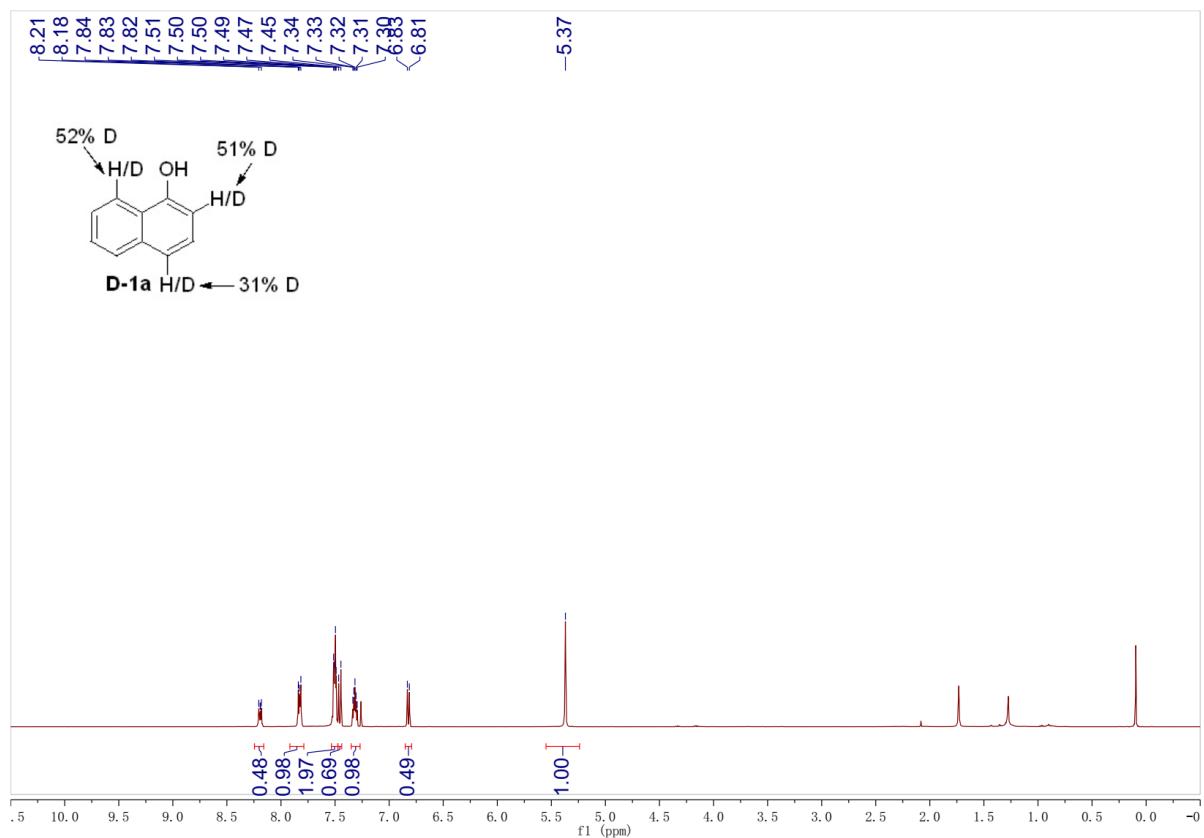
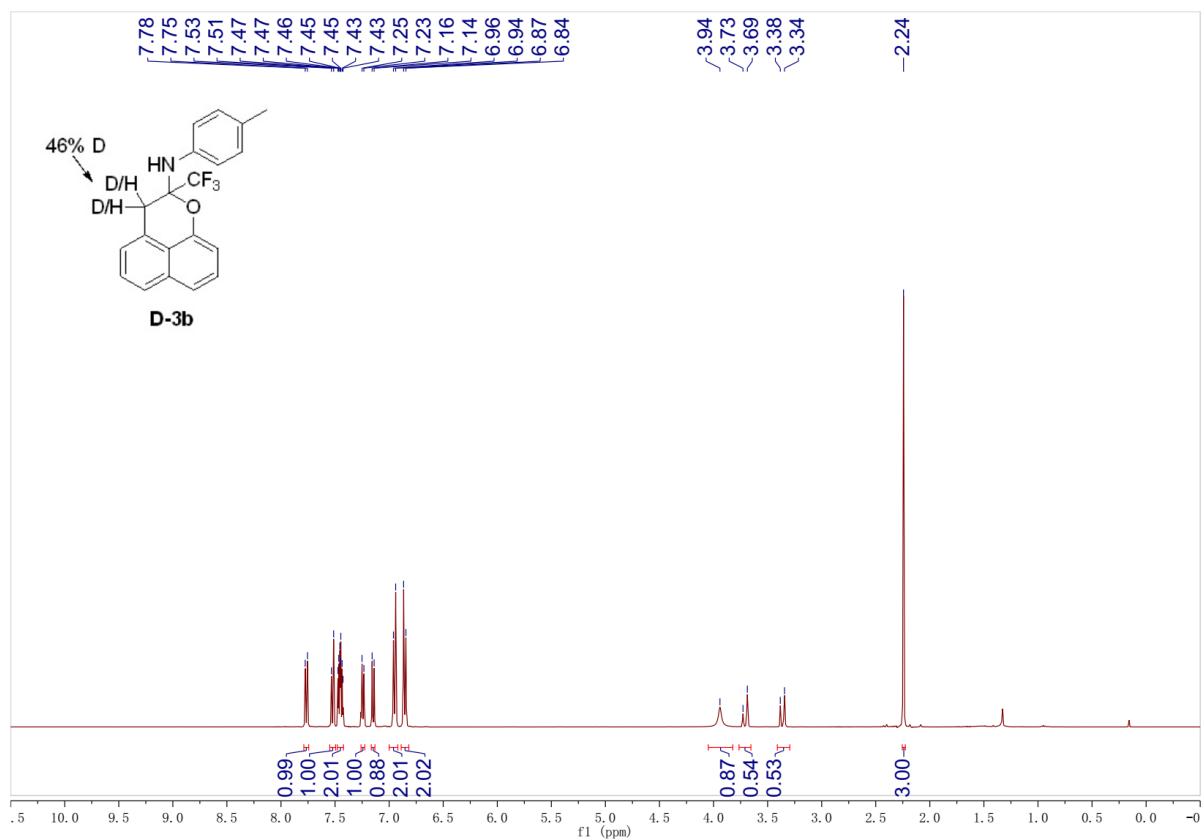
2.3 H/D Exchange Experiments



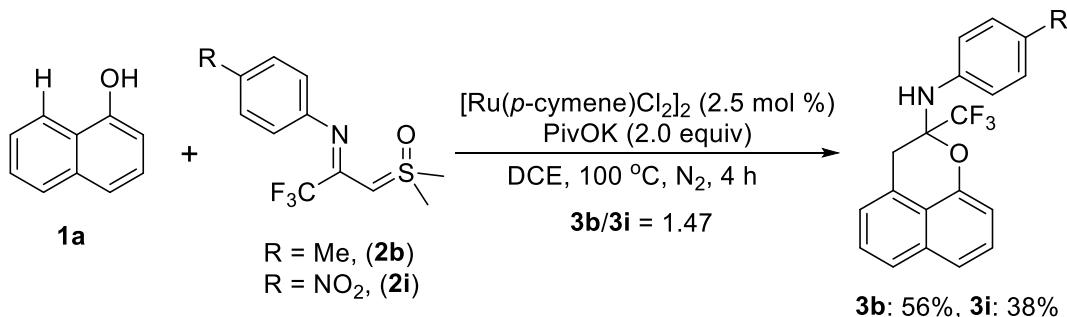
Under Nitrogen atmosphere, naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE/CD₃OD (2.0/0.2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **D-1a**. The D-incorporation in **D-1a** was determined by ¹H-NMR spectroscopy.



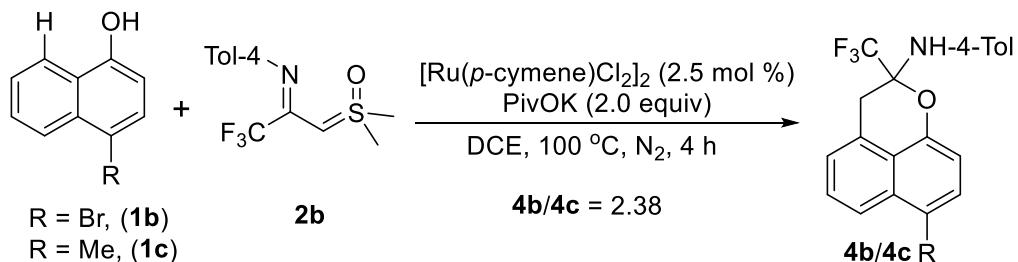
Under Nitrogen atmosphere, naphthalen-1-ol **1a** (43.2 mg, 0.3 mmol, 1.5 equiv), TFISY **2b** (55.4 mg, 0.2 mmol, 1.0 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE/CD₃OD (2.0/0.2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **D-3b** (49.9 mg, 90%) and **D-1a**. The D-incorporation in **D-3b** and **D-1a** was determined by ¹H-NMR spectroscopy.



2.4 Competition Experiments

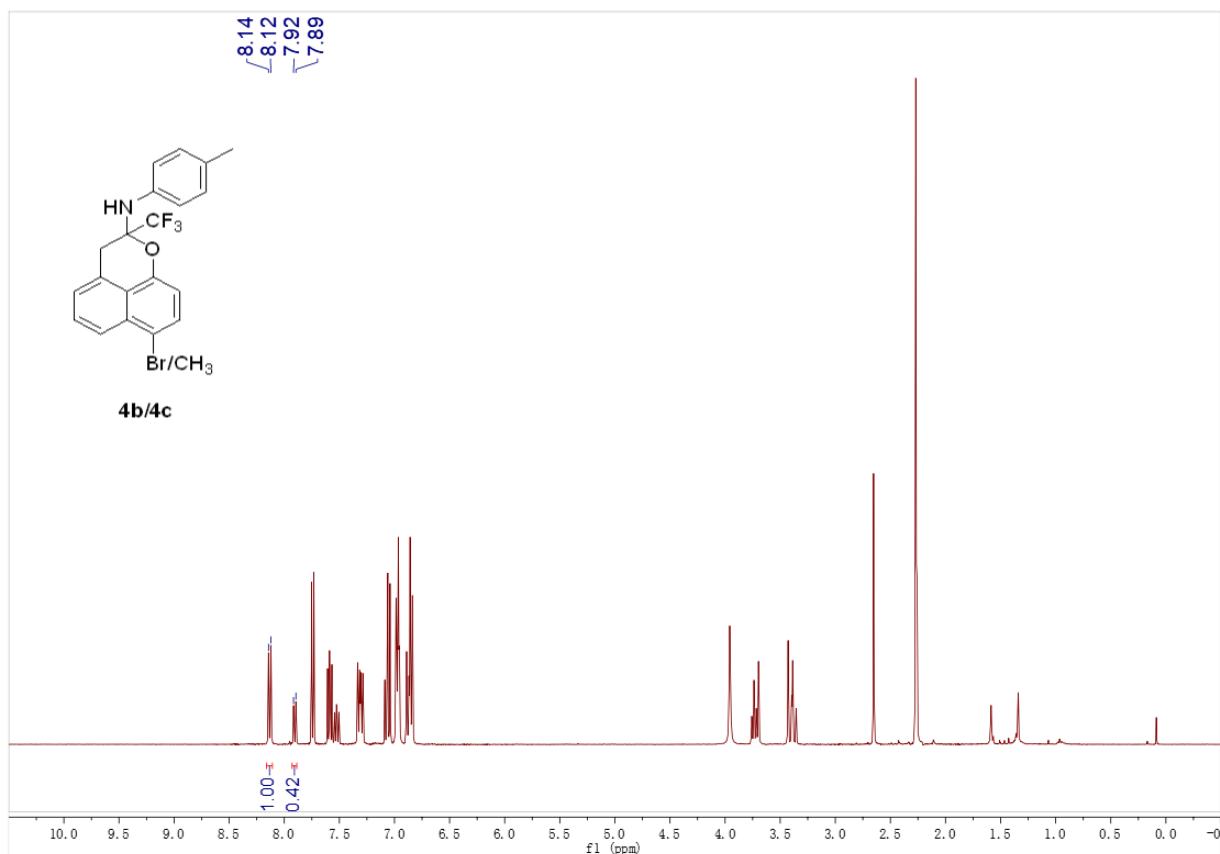


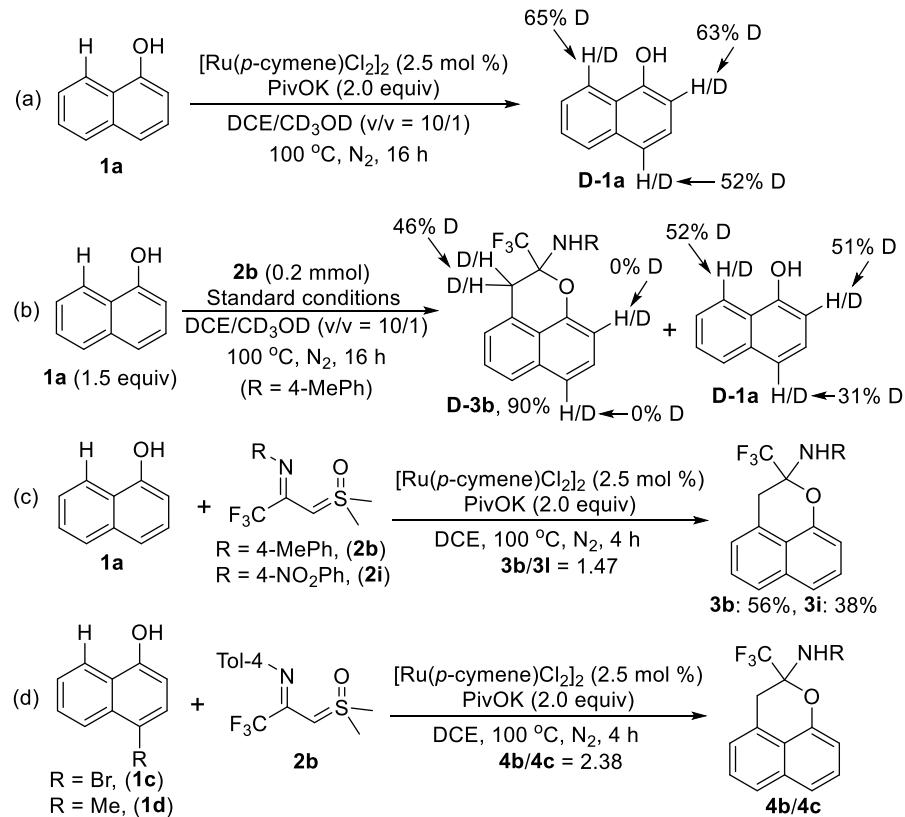
Under Nitrogen atmosphere, naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (41.6 mg, 0.15 mmol), TFISY **2i** (46.2 mg, 0.15 mmol), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2.0 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **3b** as a white solid (38.4 mg, 56%) and product **3i** as a white solid (28.4 mg, 38%).



Under Nitrogen atmosphere, 4-bromonaphthalen-1-ol **1b** (44.4 mg, 0.2 mmol, 1.0 equiv), 4-methylnaphthalen-1-ol **1c** (31.6 mg, 0.2 mmol, 1.0 equiv), TFISY (**2b**) (83.1 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2.0 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel

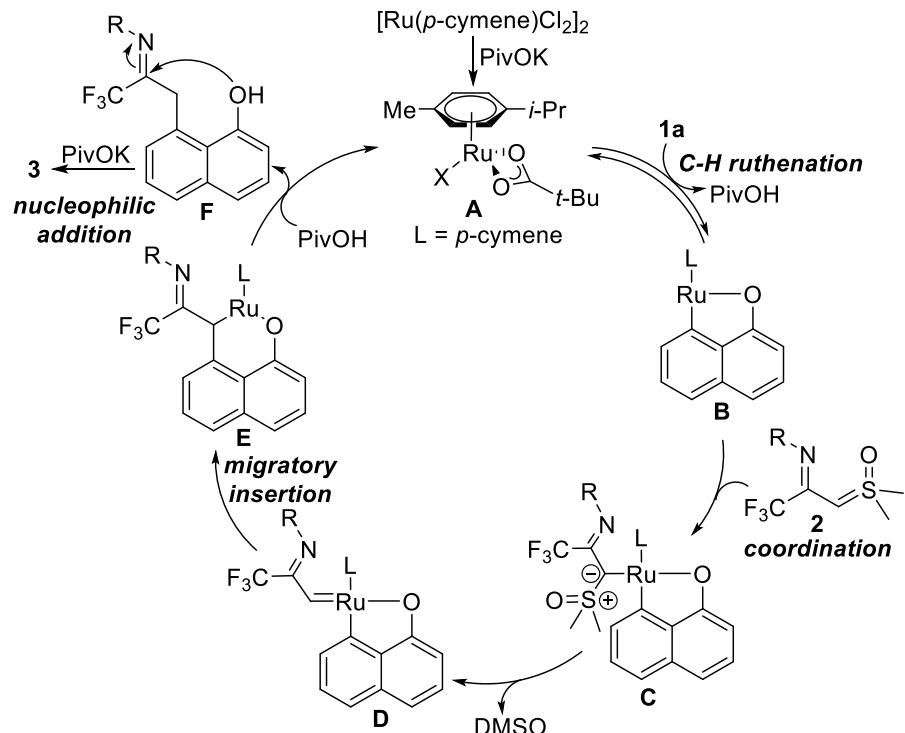
(petroleum ether/EtOAc = 10/1) to yield the product **4b** and **4c** as a yellow solid. The ratio of **4b** and **4f** was determined by ^1H -NMR analysis.



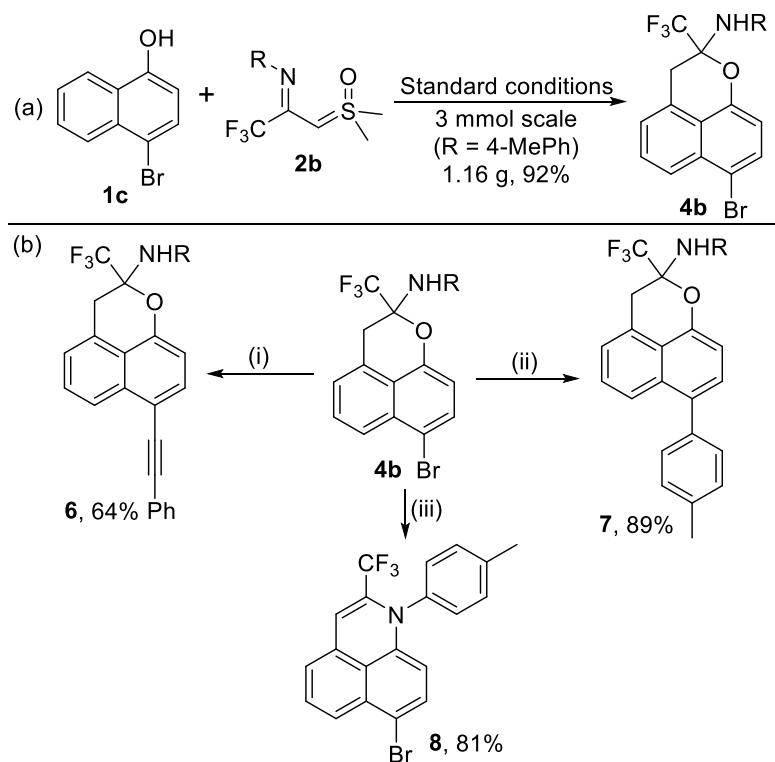


Scheme S1. Control experiments

2.5 Plausible Reaction Mechanism (Scheme S2)



2.6 Scale-up Reaction and Synthetic Transformation



(a) Scale-up Reaction: Under Nitrogen atmosphere, 4-bromonaphthalen-1-ol **1c** (665.9 mg, 3.0 mmol, 1.0 equiv), TFISY **2b** (1246.8 mg, 4.5 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (45.9 mg, 2.5 mol %), PivOK (841.5 mg, 6.0 mmol, 2.0 equiv), DCE (30.0 mL) (extra dry) were added to an oven-dried 100 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 50 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **4b** as a yellow solid (1.16 g, 92%).

(b) Synthetic Transformation:

(i) Under Nitrogen atmosphere, product **4b** (84.5 mg, 0.20 mmol, 1.0 equiv), phenylacetylene (30.6 mg, 0.3 mmol, 1.5 equiv), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]_2$ (7.0 mg, 5.0 mol %), CuI (1.9 mg, 5.0 mol %), Et₃N (0.4 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 90 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 10 mL). The extract was combined

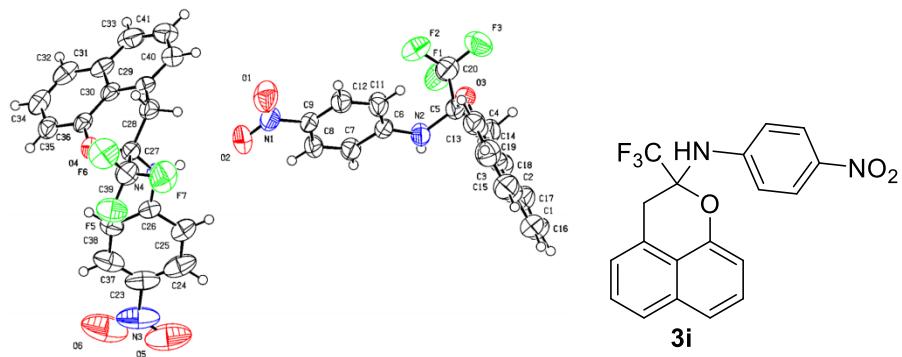
and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **6** as a yellow solid (56.7 mg, 64%).

(ii) Under Nitrogen atmosphere, product **4b** (84.5 mg, 0.2 mmol, 1.0 equiv), *p*-tolylboronic acid (40.8 mg, 0.3 mmol, 1.5 equiv), Pd(PPh₃)₄ (11.6 mg, 5.0 mol %), K₂CO₃ (55.3 mg, 0.4 mmol, 2.0 equiv), toluene/H₂O (1.5 mL/0.5 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 4 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **7** as a white solid (77.2 mg, 89%).

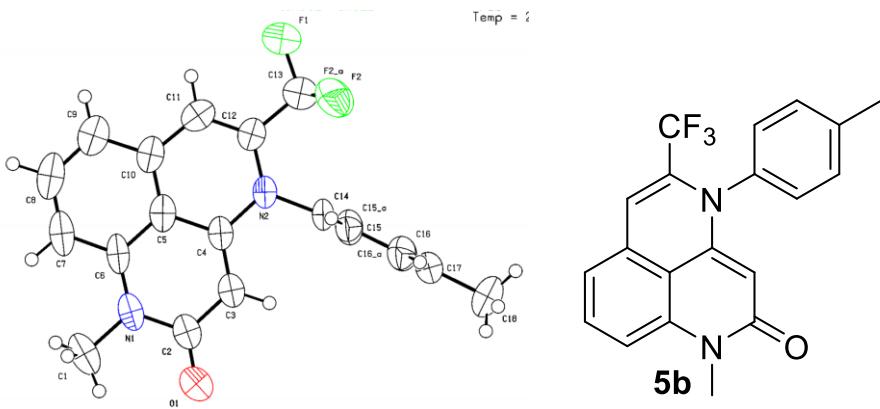
(iii) Product **4b** (84.5 mg, 0.2 mmol, 1.0 equiv), DMF (1.5 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then slowly adding NaH (4.8 mg, 0.4 mmol, 2.0 equiv) into the mixed solution under stirring at 0 °C (ice bath) for 10 min. TsCl (46.4 mg, 0.3 mmol, 1.5 equiv) was dissolved in DMF (0.5 mL) and was added dropwise to the mixed solution. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 8 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **8** as a yellow solid (65.4 mg, 81%).

3 The Crystal Structure of Product **3i** and **5b**

Figure S1. ORTEP drawing of **3i/5b** with ellipsoid contour at 30% probability level



CCDC: 2191211



CCDC: 2207921

(a) Method for crystal growth of **3i/5b:**

0.05 mmol of **3i** or **5b** was dissolved in 2.0 mL of solvent (Petroleum ether/EtOAc/DCM = 3/1/1) in 3.0 mL sample bottle. After about 12 hours of natural volatilization at room temperature, single crystal could be obtained.

(b) Crystallographic structure analysis of **3i/5b:**

A suitable single crystal was mounted on a Xcalibur, Atlas, Gemini ultra at 296(2), 100.01(10), 296(2) and 296 K, using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The intensity data were collected with CrysAlisPro program and reduced by CrysAlisPro program. The structure was solved by direct methods, expended by difference Fourier syntheses and refined by Full-matrix squares on F2 using SHELXL program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. Details of the X-Ray experiments and crystal data are summarized in **Table S1** and **Table S2**.

Table S1. Crystal data and structure refinement for **3i**

Empirical formula	C ₁₉ H ₁₃ F ₃ N ₂ O ₃
Formula weight	374.31
Temperature/K	296(2)
Crystal system	monoclinic
Space group	C2/c
a/ \AA	41.244(8)
b/ \AA	8.6774(18)
c/ \AA	20.550(4)

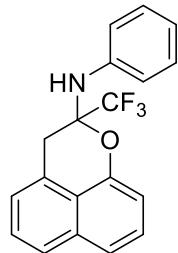
$\alpha/^\circ$	90
$\beta/^\circ$	112.864(3)
$\gamma/^\circ$	90
Volume/ \AA^3	6777(2)
Z	16
$\rho_{\text{calc}}/\text{cm}^3$	1.468
μ/mm^{-1}	0.122
F(000)	3072.0
Crystal size/mm ³	0.22 × 0.19 × 0.18
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/°	2.144 to 54.936
Index ranges	-53 ≤ h ≤ 47, -11 ≤ k ≤ 11, -20 ≤ l ≤ 26
Reflections collected	20268
Independent reflections	7676 [R _{int} = 0.0300, R _{sigma} = 0.0393]
Data/restraints/parameters	7676/14/495
Goodness-of-fit on F ²	1.064
Final R indexes [I>=2σ (I)]	R ₁ = 0.0515, wR ₂ = 0.1531
Final R indexes [all data]	R ₁ = 0.0880, wR ₂ = 0.1780
Largest diff. peak/hole / e \AA^{-3}	0.44/-0.36

Table S2. Crystal data and structure refinement for **5b**

Empirical formula	C ₂₀ H ₁₅ F ₃ N ₂ O
Formula weight	356.34
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	Ama2
a/ \AA	7.222(5)
b/ \AA	15.626(11)
c/ \AA	14.524(10)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	1639.0(19)

Z	4
ρ_{calc} g/cm ³	1.444
μ/mm^{-1}	0.114
F(000)	736.0
Crystal size/mm ³	0.18 × 0.15 × 0.05
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/°	3.828 to 55.094
Index ranges	-9 ≤ h ≤ 8, -20 ≤ k ≤ 20, -18 ≤ l ≤ 14
Reflections collected	4945
Independent reflections	1671 [$R_{\text{int}} = 0.0555$, $R_{\text{sigma}} = 0.0601$]
Data/restraints/parameters	1671/1/150
Goodness-of-fit on F^2	1.007
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0400$, $wR_2 = 0.0759$
Final R indexes [all data]	$R_1 = 0.0861$, $wR_2 = 0.0896$
Largest diff. peak/hole / e Å ⁻³	0.14/-0.12
Flack parameter	0.7(10)

4 Characterization Data of the Corresponding Products



N-phenyl-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3a**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2a** (79.0 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, $R_f = 0.5$) to give the titled product **3a** as a white solid (62.5 mg, 95%).

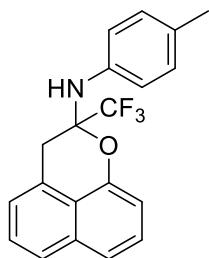
¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, $J = 8.4$ Hz, 1H), 7.50 – 7.44 (m, 1H), 7.42 – 7.33 (m, 2H), 7.19 (d, $J = 6.5$ Hz, 1H), 7.11 – 7.02 (m, 3H), 6.89 (d, $J = 8.1$ Hz, 2H), 6.84 – 6.77 (m, 1H), 3.96 (s, 1H), 3.69 – 3.64 (m, 1H), 3.30 (d, $J = 16.4$ Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.4, 142.2, 133.7, 128.8, 127.2, 126.9, 126.3, 125.3, 124.2, 124.0 (C-F, q, ¹J_(C-F) = 288.1 Hz), 121.7, 121.7, 120.7, 119.5, 112.1, 86.5 (C-F, q, ²J_(C-F) = 31.8 Hz), 33.9.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 104.3-106.1 °C

HRMS (ESI): [M+H]⁺ calcd. for C₁₉H₁₅F₃NO⁺ 330.1100, found 330.1101.



N-(*p*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (3b**)**

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **3b** as a white solid (65.3 mg, 95%).

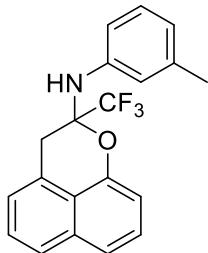
¹H NMR (400 M Hz, CDCl₃) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 3.80 – 3.70 (br, 1H), 3.69 (d, *J* = 16.4 Hz, 1H), 3.35 (d, *J* = 16.4 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.7, 139.4, 133.7, 131.6, 129.3, 127.2, 126.8, 126.3, 125.5, 124.2, 124.0 (C-F, q, ¹J_(C-F) = 288.2 Hz), 121.6, 120.7, 120.6, 112.0, 86.7 (C-F, q, ²J_(C-F) = 31.4 Hz), 33.6, 20.7.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 99.7-102.4 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₁₇F₃NO⁺ 344.1257, found 344.1255.



N-(*m*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3c**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2c** (83.2 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **3c** as a yellow solid (60.3 mg, 88%).

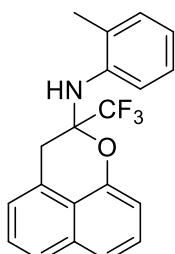
$^1\text{H NMR}$ (400 M Hz, CDCl_3) δ 7.70 (d, J = 8.4 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.43 – 7.33 (m, 2H), 7.19 (d, J = 6.9 Hz, 1H), 7.12 – 7.03 (m, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.82 – 6.71 (m, 1H), 6.66 (s, 1H), 6.63 (d, J = 7.6 Hz, 1H), 3.92 (s, 1H), 3.73 – 3.54 (m, 1H), 3.29 (d, J = 16.4 Hz, 1H), 2.17 (s, 3H).

$^{13}\text{C NMR}$ (101 M Hz, CDCl_3) δ 148.5, 142.1, 138.4, 133.7, 128.6, 127.2, 126.8, 126.3, 125.4, 124.2, 124.0 (C-F, q, $^1J_{(C-F)}$ = 288.1 Hz), 122.5, 121.7, 120.7, 120.4, 116.6, 112.0, 86.5 (C-F, q, $^2J_{(C-F)}$ = 31.8 Hz), 33.8, 21.5.

$^{19}\text{F NMR}$ (377 M Hz, CDCl_3) δ -79.5.

M.p. 70.1-71.6 °C

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{NO}^+$ 344.1257, found 344.1258.



N-(*o*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3d**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2d** (83.2 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1

mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **3d** as a yellow solid (64.3 mg, 94%).

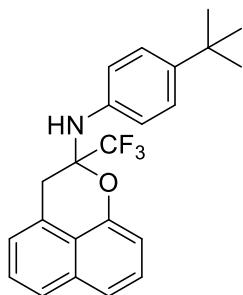
^1H NMR (400 M Hz, CDCl_3) δ 7.74 (d, J = 8.4 Hz, 1H), 7.55 – 7.46 (m, 1H), 7.47 – 7.39 (m, 3H), 7.23 (d, J = 6.1 Hz, 1H), 7.16 – 7.09 (m, 1H), 7.11 – 7.05 (m, 1H), 6.94 – 6.88 (m, 1H), 6.83 – 6.69 (m, 1H), 3.82 (s, 1H), 3.79 – 3.56 (m, 1H), 3.47 (d, J = 16.4 Hz, 1H), 1.88 (s, 3H).

^{13}C NMR (101 M Hz, CDCl_3) δ 148.6, 140.3, 133.7, 130.2, 127.2, 126.9, 126.8, 126.7, 126.3, 125.4, 124.1, 124.0 (C-F, q, $^1J_{(C-F)}$ = 287.6 Hz), 121.7, 121.6, 120.6, 119.8, 112.0, 86.7 (C-F, q, $^2J_{(C-F)}$ = 31.8 Hz), 33.7, 17.6.

^{19}F NMR (377 M Hz, CDCl_3) δ -80.0.

M.p. 106.4–108.7 °C

HRMS (ESI): [M+H]⁺ calcd. for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{NO}^+$ 344.1257, found 344.1259.



N-(4-(tert-butyl)phenyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (3e)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2e** (95.8 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **3e** as a white solid (68.5 mg, 89%).

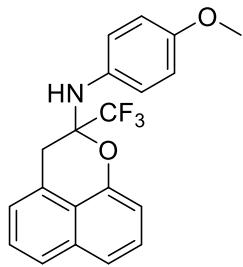
^1H NMR (400 M Hz, CDCl_3) δ 7.75 (d, J = 8.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 7.23 (d, J = 7.1 Hz, 1H), 7.19 – 7.05 (m, 3H), 7.11 – 6.75 (m, 2H), 3.80 – 3.65 (br, 1H), 3.71 (d, J = 16.4 Hz, 1H), 3.38 (d, J = 16.4 Hz, 1H), 1.27 (s, 9H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.7, 144.8, 139.5, 133.7, 127.2, 126.8, 126.3, 125.6, 125.5, 124.1, 124.0 (C-F, q, ¹J_(C-F) = 288.1 Hz), 121.6, 120.7, 119.9, 112.0, 86.6 (C-F, q, ²J_(C-F) = 31.5 Hz), 34.2, 33.6, 31.5.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.6.

M.p. 127.8-129.4 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₃H₂₃F₃NO⁺ 386.1726, found 386.1728.



N-(4-methoxyphenyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[de]chromen-2-amine (3f**)**

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2f** (83.8 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.3) to give the titled product **3f** as a yellow solid (66.3 mg, 92%).

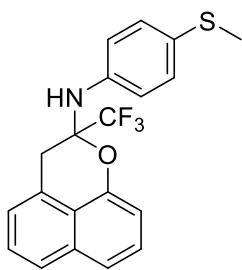
¹H NMR (400 M Hz, CDCl₃) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.12 – 7.07 (m, 1H), 6.88 – 6.78 (m, 2H), 6.70 – 6.64 (m, 2H), 3.84 – 3.75 (br, 1H), 3.71 (s, 3H), 3.69 – 3.61 (m, 1H), 3.35 (d, *J* = 16.3 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 155.9, 148.9, 134.6, 133.7, 127.2, 126.7, 126.4, 125.7, 124.4, 124.1, 123.9 (C-F, q, ¹J_(C-F) = 287.6 Hz), 121.5, 120.7, 113.9, 111.8, 87.0 (C-F, q, ²J_(C-F) = 31.0 Hz), 55.5, 33.0.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.9.

M.p. 90.4-92.5 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₁₇F₃NO₂⁺ 360.1206, found 360.1205.



N-(4-(methylthio)phenyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (3g**)**

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2g** (88.0 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3g** as a white solid (69.2 mg, 94%).

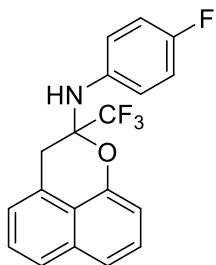
¹H NMR (400 M Hz, CDCl₃) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.48 – 7.37 (m, 2H), 7.24 (d, *J* = 7.0 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.09 – 7.03 (m, 2H), 6.92 – 6.81 (m, 2H), 3.98 (s, 1H), 3.78 – 3.61 (m, 1H), 3.32 (d, *J* = 16.4 Hz, 1H), 2.38 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.3, 140.3, 133.7, 130.2, 128.8, 127.2, 126.9, 126.3, 125.1, 124.3, 121.8, 123.8 (C-F, q, ¹*J*_(C-F) = 288.0 Hz), 120.6, 120.3, 112.1, 86.3 (C-F, q, *J*_(C-F) = 31.9 Hz), 33.8, 17.5.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 127.5–128.9 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₁₇F₃NOSNa⁺ 398.0797, found 398.0789.



N-(4-fluorophenyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (3h**)**

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2h** (84.4 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified

via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3h** as a yellow solid (65.1 mg, 94%).

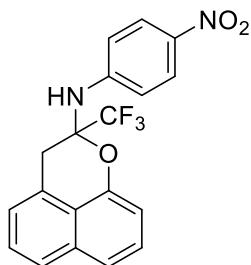
¹H NMR (400 M Hz, CDCl₃) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.89 – 6.74 (m, 4H), 3.92 (s, 1H), 3.80 – 3.59 (m, 1H), 3.33 (d, *J* = 16.3 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 158.7 (C-F, d, ²*J*_(C-F) = 240.9 Hz), 148.4, 137.9 (C-F, d, ⁵*J*_(C-F) = 2.7 Hz), 133.7, 127.2, 126.9, 126.4, 125.2, 124.3, 123.9 (C-F, q, ¹*J*_(C-F) = 287.7 Hz), 122.6 (C-F, d, ⁴*J*_(C-F) = 7.9 Hz), 121.7, 120.7, 115.3 (C-F, d, ³*J*_(C-F) = 22.3 Hz), 112.0, 86.6 (C-F, q, ²*J*_(C-F) = 31.4 Hz), 33.5.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.7, -121.4.

M.p. 95.7-97.3 °C

HRMS (ESI): [M+H]⁺ calcd. for C₁₉H₁₄F₄NO₂⁺ 348.1006, found 348.1005.



N-(4-nitrophenyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[de]chromen-2-amine (**3i**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2i** (92.5 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.3) to give the titled product **3i** as a yellow solid (68.9 mg, 92%).

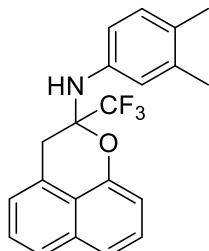
¹H NMR (400 M Hz, CDCl₃) δ 8.07 – 7.88 (m, 2H), 7.85 – 7.67 (m, 1H), 7.52 – 7.46 (m, 1H), 7.49 – 7.41 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.12 – 7.06 (m, 1H), 7.06 – 6.88 (m, 2H), 4.69 (s, 1H), 4.05 – 3.62 (m, 1H), 3.35 (d, *J* = 16.5 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.9, 147.3, 140.7, 133.7, 127.3, 127.2, 126.5, 125.3, 124.7, 124.0, 123.8 (C-F, q, ¹*J*_(C-F) = 287.7 Hz), 122.4, 120.4, 115.9, 112.3, 85.8 (C-F, q, ²*J*_(C-F) = 32.9 Hz), 34.3.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 162.9–164.7 °C

HRMS (ESI): [M+H]⁺ calcd. for C₁₉H₁₄F₃N₂O₃⁺ 375.0951, found 375.0950.



N-(3,4-dimethylphenyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3j**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2j** (87.4 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **3j** as a yellow solid (66.3 mg, 93%).

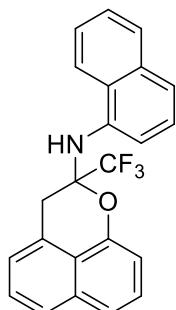
¹H NMR (400 M Hz, CDCl₃) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.82 – 6.72 (m, 1H), 6.67 (s, 1H), 3.80 – 3.65 (m, 1H), 3.69 (d, *J* = 16.4 Hz, 1H), 3.35 (d, *J* = 16.4 Hz, 1H), 2.26 – 2.07 (m, 6H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.7, 139.7, 136.8, 133.7, 130.3, 129.8, 127.2, 126.8, 126.3, 125.6, 124.1, 124.0 (C-F, q, ¹J_(C-F) = 288.2 Hz), 122.1, 121.5, 120.8, 117.9, 111.9, 86.7 (C-F, q, ²J_(C-F) = 31.5 Hz), 33.6, 19.9, 19.0.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 95.4–97.2 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₁H₁₉F₃NO⁺ 358.1413, found 358.1414.



N-(naphthalen-1-yl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3k**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2k** (94.0 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3k** as a yellow solid (64.7 mg, 85%).

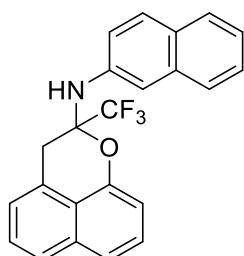
¹H NMR (400 M Hz, CDCl₃) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 3H), 7.48 – 7.34 (m, 3H), 7.32 (t, *J* = 8.2 Hz, 1H), 7.27 – 7.18 (m, 1H), 7.16 (d, *J* = 6.9 Hz, 1H), 4.49 (s, 1H), 3.77 (d, *J* = 16.5 Hz, 1H), 3.61 (d, *J* = 16.5 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 149.3, 136.9, 134.2, 133.7, 128.5, 128.5, 127.2, 126.7, 126.3, 125.7, 125.7, 125.5, 124.1 (C-F, q, ¹J_(C-F) = 287.6 Hz), 124.0, 123.8, 121.5, 121.3, 120.5, 119.2, 111.6, 87.3 (C-F, q, ²J_(C-F) = 31.3 Hz), 32.9.

¹⁹F NMR (377 M Hz, CDCl₃) δ -80.1.

M.p. 138.5–140.2 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₃H₁₇F₃NO⁺ 380.1257, found 380.1259.



N-(naphthalen-2-yl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3l**)

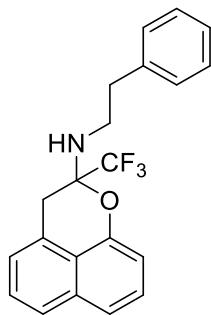
General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2l** (94.0 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3l** as a yellow oil (58.6 mg, 77%).

¹H NMR (400 M Hz, CDCl₃) δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 4.5 Hz, 1H), 7.53 (d, *J* = 4.6 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.21 – 7.12 (m, 2H), 7.08 – 7.02 (m, 1H), 6.98 – 6.83 (m, 1H), 3.70 – 3.60 (m, 1H), 3.28 (d, *J* = 16.4 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.3, 139.8, 134.2, 133.7, 129.3, 128.4, 127.5, 127.3, 127.0, 126.3, 126.3, 125.2, 124.3, 124.1 (C-F, q, ¹J_(C-F) = 287.9 Hz), 123.9, 121.8, 120.7, 120.6, 114.4, 112.1, 86.5 (C-F, q, ²J_(C-F) = 31.9 Hz), 34.0.

¹⁹F NMR (377 M Hz, CDCl₃) δ -73.1.

HRMS (ESI): [M+H]⁺ calcd. for C₂₃H₁₇F₃NO⁺ 380.1257, found 380.1258.



N-phenethyl-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**3m**)

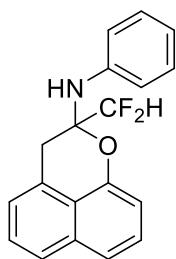
General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2m** (87.4 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **3m** as a yellow oil (51.6 mg, 72%).

¹H NMR (400 M Hz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.49 – 7.41 (m, 1H), 7.43 – 7.35 (m, 1H), 7.15 (d, *J* = 6.9 Hz, 1H), 7.12 – 7.05 (m, 1H), 7.03 – 6.95 (m, 3H), 6.87 – 6.66 (m, 2H), 3.70 – 3.47 (m, 1H), 3.20 – 3.11 (m, 2H), 3.05 – 2.89 (m, 1H), 2.55 – 2.44 (m, 1H), 2.44 – 2.30 (m, 1H), 1.83 (s, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.9, 138.6, 133.9, 128.3, 128.2, 127.3, 126.8, 126.3, 126.2, 124.6, 125.5, 124.1 (C-F, q, ¹J_(C-F) = 285.5 Hz), 121.2, 120.7, 111.8, 87.0 (C-F, q, ²J_(C-F) = 31.0 Hz), 42.3, 36.3, 33.3.

¹⁹F NMR (377 M Hz, CDCl₃) δ -80.4.

HRMS (ESI): [M+H]⁺ calcd. for C₂₁H₁₉F₃NO⁺ 358.1413, found 358.1416.



2-(difluoromethyl)-N-phenyl-2,3-dihydrobenzo[de]chromen-2-amine (3n)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2n** (73.6 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3q** as a white solid (57.3 mg, 92%).

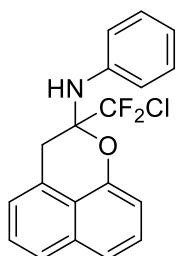
¹H NMR (400 M Hz, CDCl₃) δ 7.79 – 7.62 (m, 1H), 7.51 – 7.48 (m, 1H), 7.47 – 7.43 (m, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.11 – 7.06 (m, 1H), 7.01 – 6.95 (m, 2H), 6.90 – 6.83 (m, 1H), 6.64 – 6.13 (m, 1H), 4.09 (s, 1H), 3.94 – 3.64 (m, 1H), 3.56 – 3.08 (m, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.9, 142.5, 133.8, 129.3, 127.2, 126.7, 126.3, 126.1, 124.5, 121.3, 121.4, 118.4, 111.9, 112.0 (dd, ¹J_(C-F) = 242.1, 239.6 Hz), 86.6 (dd, ²J_(C-F) = 28.1, 24.4 Hz), 31.8 (t, ³J_(C-F) = 2.6 Hz).

¹⁹F NMR (377 M Hz, CDCl₃) -133.2 (dd, 1F, *J*_(F-F) = 282.7, *J*_(H-F) = 54.8 Hz), -135.6 (dd, 1F, *J*_(F-F) = 282.7, *J*_(H-F) = 56.4 Hz).

M.p. 113.6–115.1 °C

HRMS (ESI): [M+H]⁺ calcd. for C₁₉H₁₆F₂NO⁺ 312.1194, found 312.1193.



2-(chlorodifluoromethyl)-N-phenyl-2,3-dihydrobenzo[de]chromen-2-amine (3o)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2o** (83.9 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3o** as a white solid (66.6 mg, 96%).

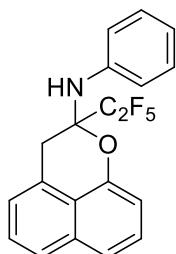
¹H NMR (400 M Hz, CDCl₃) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.15 – 7.08 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.91 – 6.83 (m, 1H), 4.07 (s, 1H), 3.87 – 3.73 (m, 1H), 3.45 (d, *J* = 16.5 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.9, 142.3, 133.7, 129.8 (dd, ¹*J*_(C-F) = 306.7, 303.7 Hz), 128.7, 127.1, 126.7, 126.3, 125.8, 124.0, 121.9, 121.7, 120.7, 120.1, 111.9, 89.7 (t, ²*J*_(C-F) = 25.6 Hz), 34.1.

¹⁹F NMR (377 M Hz, CDCl₃) δ -63.3 (d, *J* = 165.1 Hz), -64.8 (d, *J* = 165.0 Hz).

M.p. 94.3-96.6 °C

HRMS (ESI): [M+H]⁺ calcd. for C₁₉H₁₅ClF₂NO⁺ 346.0805, found 349.0806.



2-(perfluoroethyl)-N-phenyl-2,3-dihydrobenzo[de]chromen-2-amine (**3p**)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2p** (94.0 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **3p** as a white solid (67.9 mg, 89%).

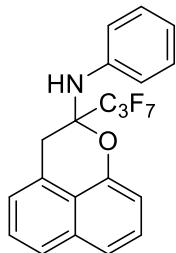
¹H NMR (400 M Hz, CDCl₃) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.46 – 7.36 (m, 2H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.16 – 7.07 (m, 1H), 7.11 – 7.05 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.79 (m, 1H), 4.03 (s, 1H), 3.90 – 3.65 (m, 1H), 3.43 (d, *J* = 16.5 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.1, 142.4, 133.6, 128.7, 127.2, 126.8, 126.3, 125.4, 124.2, 121.7, 121.6, 120.7, 119.6, 119.3 (C-F, qt, *J*_(C-F) = 287.9 Hz, 35.6 Hz), 114.0 (C-F, tq, *J*_(C-F) = 266.7 Hz, 35.3 Hz), 112.2, 87.6 (C-F, t, *J*_(C-F) = 24.4 Hz), 34.0.

¹⁹F NMR (377 M Hz, CDCl₃) δ -78.7, -116.5 – -126.5 (m).

M.p. 72.9-74.3 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₁₅F₅NO⁺ 380.1068, found 380.1069.



2-(3,3,3,3,3,3,3-heptafluoro-3λ⁸-prop-1-yn-1-yl)-N-phenyl-2,3-dihydrobenzo[de]chromen-2-amine
(3q)

General procedure was followed with naphthalen-1-ol **1a** (28.8 mg, 0.2 mmol, 1.0 equiv), TFISY **2q** (109.0 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate =10:1, R_f = 0.3) to give the titled product **3q** as a white solid (64.3 mg, 75%).

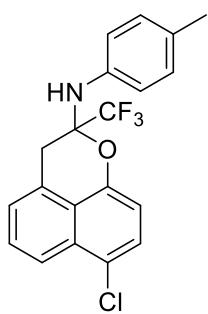
¹H NMR (400 M Hz, CDCl₃) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.47 – 7.38 (m, 2H), 7.19 (d, *J* = 6.9 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.12 – 7.05 (m, 2H), 6.91 – 6.83 (m, 3H), 4.06 (s, 1H), 3.78 (d, *J* = 16.5 Hz, 1H), 3.45 (d, *J* = 16.5 Hz, 1H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.1, 142.4, 133.6, 128.7, 127.2, 126.8, 126.3, 125.4, 124.1, 121.8, 121.8, 120.7, 119.8, 112.1, 118.1 (C-F, qt, *J*_(C-F) = 288.5 Hz, 34.1 Hz), 115.4 (C-F, tt, *J*_(C-F) = 266.8 Hz, 29.5 Hz), 110.3 (C-F, tq, *J*_(C-F) = 268.8 Hz, 37.5 Hz), 88.6 (C-F, t, *J*_(C-F) = 24.8 Hz), 33.8 (C-F, t, *J*_(C-F) = 3.3 Hz).

¹⁹F NMR (377 M Hz, CDCl₃) δ -80.5 (t, *J* = 10.8 Hz), -117.0 – -120.1 (m), -123.3 (t, *J* = 3.8 Hz).

M.p. 103.7-105.6 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₁H₁₅F₇NO⁺ 430.1036, found 430.1038.



7-chloro-*N*-(*p*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (4a**)**

General procedure was followed with naphthalen-1-ol **1b** (35.7 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **4a** as a white solid (68.8 mg, 91%).

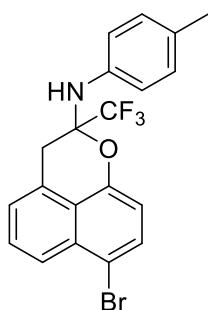
$^1\text{H NMR}$ (400 M Hz, CDCl_3) δ 8.12 (d, J = 8.6 Hz, 1H), 7.55 (dd, J = 8.6, 7.0 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 6.9 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 3.84 – 3.57 (m, 2H), 3.36 (d, J = 16.4 Hz, 1H), 2.23 (s, 3H).

$^{13}\text{C NMR}$ (101 M Hz, CDCl_3) δ 147.7, 139.1, 131.8, 130.8, 129.4, 127.4, 127.2, 126.0, 125.1, 124.7, 123.9 (C-F, q, $^1J_{(C-F)}$ = 288.1 Hz), 123.8, 121.6, 120.6, 112.3, 86.9 (C-F, q, $^2J_{(C-F)}$ = 31.5 Hz), 33.4, 20.7.

$^{19}\text{F NMR}$ (377 M Hz, CDCl_3) δ -79.6.

M.p. 138.4–140.2 °C

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{16}\text{ClF}_3\text{NO}^+$ 385.1731, found 385.1735.



7-bromo-*N*-(*p*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (4b**)**

General procedure was followed with naphthalen-1-ol **1c** (44.6 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.5) to give the titled product **4b** as a yellow solid (78.3 mg, 93%).

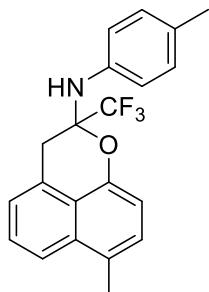
¹H NMR (400 M Hz, CDCl₃) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 1H), 3.83 – 3.54 (m, 1H), 3.37 (d, *J* = 16.4 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.4, 139.1, 132.0, 131.9, 130.9, 129.4, 127.6, 126.5, 126.0, 125.2, 123.9 (C-F, q, ¹J_(C-F) = 288.0 Hz), 121.8, 120.6, 114.7, 112.9, 86.9 (C-F, q, ²J_(C-F) = 31.6 Hz), 33.3, 20.7.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 145.8-147.2 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₁₆BrF₃NO⁺ 422.0362, found 422.0361.



7-methyl-N-(*p*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (**4c**)

General procedure was followed with naphthalen-1-ol **1d** (31.6 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **4c** as a brown solid (57.9 mg, 81%).

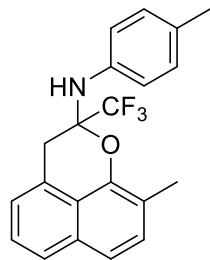
¹H NMR (400 M Hz, CDCl₃) δ 7.76 – 7.69 (m, 1H), 7.42 – 7.30 (m, 1H), 7.17 – 7.07 (m, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 3.90 – 3.30 (br, 1H), 3.56 (d, *J* = 16.3 Hz, 1H), 3.19 (d, *J* = 16.3 Hz, 1H), 2.47 (s, 3H), 2.09 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 146.9, 139.6, 132.6, 131.4, 129.3, 128.1, 127.6, 126.0, 125.9, 124.1, 124.1 (C-F, q, ¹J_(C-F) = 288.3 Hz), 123.6, 120.8, 120.3, 111.7, 86.6 (C-F, q, ²J_(C-F) = 31.4 Hz), 33.9, 20.7, 18.9.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.3.

M.p. 70.2-71.5 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₁H₁₉F₃NO⁺ 358.1413, found 358.1418.



9-methyl-N-(*p*-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-2-amine (4d**)**

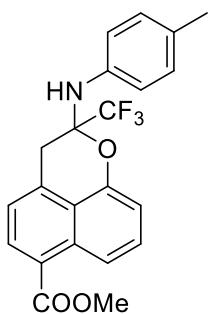
General procedure was followed with naphthalen-1-ol **1e** (31.6 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **4d** as a colorless oil (65.0 mg, 91%).

¹H NMR (400 M Hz, CDCl₃) δ 7.77 – 7.64 (m, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 3.85 – 3.50 (br, 1H), 3.79 – 3.61 (m, 1H), 3.36 (d, *J* = 16.2 Hz, 1H), 2.46 (s, 3H), 2.24 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 145.4, 139.3, 132.2, 131.7, 130.4, 129.1, 126.8, 125.2, 124.8, 124.2, 124.1 (C-F, q, ¹J_(C-F) = 287.5 Hz), 121.0, 120.9, 120.5, 86.4 (C-F, q, ²J_(C-F) = 31.4 Hz), 33.7, 20.7, 15.6.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.4.

HRMS (ESI): [M+H]⁺ calcd. for C₂₁H₁₉F₃NO⁺ 358.1413, found 358.1414.



Methyl-2-(*p*-tolylamino)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromene-6-carboxylate (4e)

General procedure was followed with naphthalen-1-ol **1f** (40.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **4e** as a yellow solid (80.1 mg, 99%).

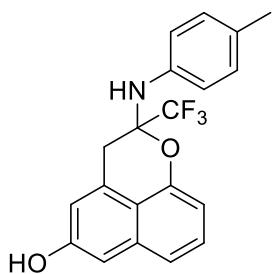
¹H NMR (400 M Hz, CDCl₃) δ 8.58 (d, *J* = 8.7 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.27 – 7.05 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.99 (s, 3H), 3.98 (s, 1H), 3.69 (d, *J* = 16.6 Hz, 1H), 3.39 (d, *J* = 16.7 Hz, 1H), 2.21 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 167.7, 148.8, 139.1, 131.9, 131.6, 131.3, 130.6, 129.3, 129.1, 126.1, 123.9 (C-F, q, ¹*J*_(C-F) = 288.3 Hz), 123.1, 121.2, 120.8, 120.1, 112.7, 86.5 (C-F, q, ²*J*_(C-F) = 31.5 Hz), 77.5, 52.3, 33.8, 20.7.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 141.8–143.3 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₂H₁₉F₃NO₃⁺ 402.1312, found 402.1313.



2-(*p*-tolylamino)-2-(trifluoromethyl)-2,3-dihydrobenzo[*de*]chromen-5-ol (4f)

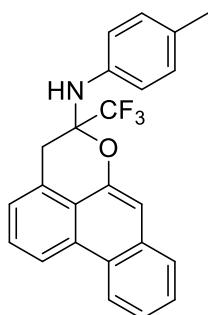
General procedure was followed with naphthalen-1-ol **1g** (32.0 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, R_f = 0.3) to give the titled product **4f** as a yellow oil (38.3 mg, 53%).

¹H NMR (400 M Hz, DMSO) δ 9.86 (s, 1H), 7.42 – 7.21 (m, 2H), 7.05 – 6.93 (m, 2H), 6.93 – 6.80 (m, 5H), 6.40 (s, 1H), 3.51 (d, *J* = 16.2 Hz, 1H), 3.41 (d, *J* = 16.3 Hz, 1H), 2.11 (s, 3H).

¹³C NMR (101 M Hz, DMSO) δ 155.8, 148.0, 141.3, 135.0, 128.9, 128.0, 127.7, 127.2, 124.3 (q, ¹*J*_(C-F) = 290.9 Hz), 119.7, 117.0, 116.9, 114.8, 108.1, 106.8, 86.2 (q, ²*J*_(C-F) = 30.8 Hz), 32.9, 20.0.

¹⁹F NMR (377 M Hz, DMSO) δ -73.2.

HRMS (ESI): [M+H]⁺ calcd. for C₂₀H₁₇F₃NO₂⁺ 360.1206, found 360.1208.



N-(*p*-tolyl)-5-(trifluoromethyl)-4,5-dihydrodibenzo[*de,g*]chromen-5-amine (**4g**)

General procedure was followed with naphthalen-1-ol **1h** (38.9 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **4g** as a yellow solid (55.4 mg, 70%).

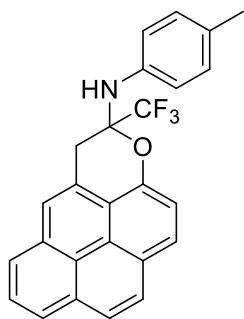
¹H NMR (400 M Hz, CDCl₃) δ 8.58 (d, *J* = 8.5 Hz, 2H), 7.86 – 7.68 (m, 1H), 7.68 – 7.60 (m, 1H), 7.60 – 7.51 (m, 2H), 7.38 (d, *J* = 8.9 Hz, 2H), 4.00 – 3.60 (br, 1H), 3.77 (d, *J* = 16.3 Hz, 1H), 3.40 (d, *J* = 16.4 Hz, 1H), 2.21 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 146.5, 139.4, 133.1, 131.7, 131.0, 129.3, 127.9, 127.3, 127.1, 126.2, 125.8, 125.1, 124.1 (C-F, q, ¹J_(C-F) = 288.4 Hz), 122.9, 122.1, 121.3, 120.6, 110.7, 86.8 (C-F, q, ²J_(C-F) = 31.4 Hz), 33.6, 20.7.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.4.

M.p. 122.1-124.3 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₄H₁₉F₃NO⁺ 394.1413, found 394.1412.



N-(*p*-tolyl)-4-(trifluoromethyl)-4,5-dihydrophenaleno[2,1,9-*def*]chromen-4-amine (**4h**)

General procedure was followed with naphthalen-1-ol **1i** (46.5 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **4h** as a yellow solid (80.9 mg, 97%).

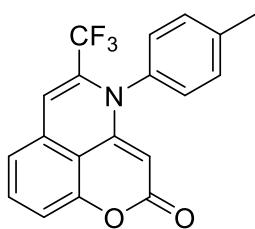
¹H NMR (400 M Hz, CDCl₃) δ 8.14 – 8.05 (m, 2H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.01 – 7.86 (m, 3H), 7.71 (s, 1H), 7.71 – 7.64 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 4.04 (s, 1H), 3.87 – 3.72 (m, 1H), 3.62 – 3.37 (m, 1H), 2.20 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 146.8, 139.3, 131.5, 131.5, 131.2, 129.3, 127.1, 126.7, 126.5, 126.3, 125.6, 124.8, 124.8, 124.7, 124.4, 124.2, 124.1, 124.1 (C-F, q, ¹J_(C-F) = 288.0 Hz), 120.3, 115.7, 115.1, 87.1 (C-F, q, ²J_(C-F) = 31.7 Hz), 34.1, 20.6.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.0.

M.p. 195.1-196.9 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₆H₁₉F₃NO⁺ 418.1413, found 418.1410.



4-(p-tolyl)-5-(trifluoromethyl)pyrano[2,3,4-ij]isoquinolin-2(4H)-one (5a**)**

General procedure was followed with **1l** (32.4 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), TFE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, R_f = 0.6) to give the titled product **5a** as a yellow solid (36.6 mg, 53%).

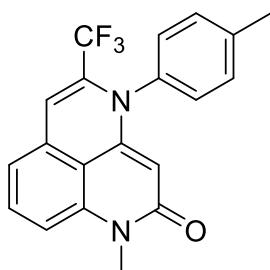
¹H NMR (400 M Hz, CDCl₃) δ 7.57 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.18 – 7.04 (m, 3H), 6.83 (s, 1H), 4.52 (s, 1H), 2.44 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 162.6, 153.9, 153.6, 140.7, 134.1, 133.3, 131.6 (C-F, q, ²*J*_(C-F) = 32.6 Hz), 131.2, 129.5, 129.1, 120.1, 120.1 (C-F, q, ¹*J*_(C-F) = 273.3 Hz), 116.4, 113.9, 113.9, 109.2 (C-F, q, ³*J*_(C-F) = 6.1 Hz), 85.4, 21.4.

¹⁹F NMR (377 M Hz, CDCl₃) δ -61.4.

M.p. 256.1–258.0 °C

HRMS (ESI): [M+H]⁺ calcd. for C₁₉H₁₂F₃NO₂Na⁺ 366.0712, found 366.0715.



1-methyl-4-(p-tolyl)-5-(trifluoromethyl)-1H-benzo[de][1,6]naphthyridin-2(4H)-one (5b**)**

General procedure was followed with **1m** (35.0 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column

chromatography (petroleum ether / ethyl acetate = 3:1, R_f = 0.3) to give the titled product **5b** as a yellow solid (56.2 mg, 79%).

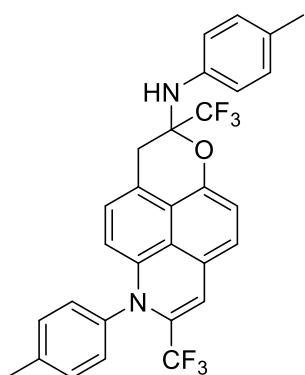
$^1\text{H NMR}$ (400 M Hz, CDCl_3) δ 7.52 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.65 (s, 1H), 4.93 (s, 1H), 3.48 (s, 3H), 2.42 (s, 3H).

$^{13}\text{C NMR}$ (101 M Hz, CDCl_3) δ 163.2, 150.7, 140.7, 140.2, 134.8, 132.2, 131.7 (C-F, q, $^2J_{(C-F)}$ = 32.2 Hz), 131.1, 130.5, 129.6, 120.3 (C-F, q, $^1J_{(C-F)}$ = 273.4 Hz), 117.2, 115.1, 112.4, 108.1 (C-F, q, $^3J_{(C-F)}$ = 6.3 Hz), 93.8, 29.1, 21.4.

$^{19}\text{F NMR}$ (377 M Hz, CDCl_3) δ -61.7.

M.p. 262.3-264.4 °C

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{N}_2\text{O}\text{Na}^+$ 379.1029, found 379.1030.



N,6-di-p-tolyl-2,7-bis(trifluoromethyl)-3,6-dihydro-2H-chromeno[6,5,4-def]quinolin-2-amine (**5c**)

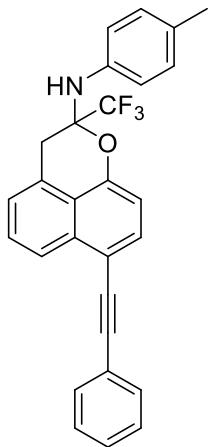
General procedure was followed with naphthalen-1-ol **1n** (32.0 mg, 0.2 mmol, 1.0 equiv), TFISY **2b** (83.2 mg, 0.3 mmol, 1.5 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), PivOK (56.1 mg, 0.4 mmol, 2.0 equiv), DCE (2 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **5c** as a yellow oil (63.4 mg, 59%).

$^1\text{H NMR}$ (400 M Hz, CDCl_3) δ 7.42 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.8 Hz, 1H), 6.91 – 6.82 (m, 6H), 6.58 (s, 1H), 6.22 (s, 1H), 5.47 (d, J = 8.0 Hz, 1H), 3.23 (d, J = 16.0 Hz, 1H), 3.14 (d, J = 15.7 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 144.7, 142.9, 141.3, 139.0, 135.9, 131.2, 130.4, 129.9 (C-F, q, ²J_(C-F) = 30.6 Hz), 128.9, 127.7, 126.6, 126.3, 125.3 (C-F, q, ¹J_(C-F) = 290.3 Hz), 125.0, 120.5 (C-F, q, ¹J_(C-F) = 272.7 Hz), 121.7, 116.9, 116.7, 114.8, 113.5, 108.3 (C-F, q, ³J_(C-F) = 5.6 Hz), 104.8, 84.5 (C-F, q, ²J_(C-F) = 31.6 Hz), 32.1, 20.8, 20.0.

¹⁹F NMR (377 M Hz, CDCl₃) δ -56.8, -73.4.

HRMS (ESI): [M+H]⁺ calcd. for C₃₀H₂₂F₆N₂ONa⁺ 563.1529, found 563.1539.



7-(phenylethynyl)-N-(p-tolyl)-2-(trifluoromethyl)-2,3-dihydrobenzo[de]chromen-2-amine (6**)**

General procedure was followed with product **4b** (84.5 mg, 0.2 mmol, 1.0 equiv), phenylacetylene (30.6 mg, 0.3 mmol, 1.5 equiv), [Pd(PPh₃)₂Cl₂]₂ (7.0 mg, 5.0 mol %), CuI (1.9 mg, 5.0 mol %), Et₃N (0.4 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **6** as a yellow solid (56.7 mg, 64%).

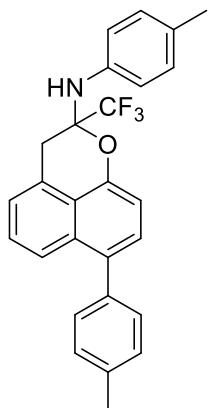
¹H NMR (400 M Hz, CDCl₃) δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.58 – 7.52 (m, 1H), 7.43 – 7.36 (m, 3H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 1H), 3.80 – 3.65 (m, 1H), 3.38 (d, *J* = 16.4 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 148.4, 139.1, 132.0, 131.9, 130.9, 129.4, 127.6, 126.5, 126.1, 125.2, 123.9 (q, ¹J_(C-F) = 287.8 Hz), 121.8, 120.7, 114.7, 112.9, 86.9 (C-F, q, ²J_(C-F) = 31.9 Hz), 33.3, 20.7.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.3.

M.p. 147.9-149.4 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₈H₂₁F₃NO⁺ 444.1570, found 444.1571.



N,7-di-p-tolyl-2-(trifluoromethyl)-2,3-dihydrobenzo[de]chromen-2-amine (7)

General procedure was followed with product **4b** (84.5 mg, 0.2 mmol, 1.0 equiv), *p*-tolylboronic acid (40.8 mg, 0.3 mmol, 1.5 equiv), Pd(PPh₃)₄ (11.6 mg, 5.0 mol %), K₂CO₃ (55.3 mg, 0.4 mmol, 2.0 equiv), toluene/H₂O (1.5 mL/0.5 mL). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.6) to give the titled product **7** as a white solid (77.2 mg, 89%).

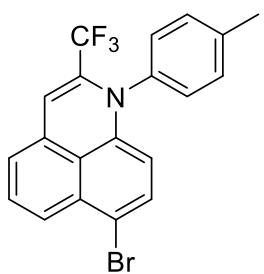
¹H NMR (400 M Hz, CDCl₃) δ 7.90 – 7.73 (m, 1H), 7.37 – 7.27 (m, 4H), 7.28 – 7.21 (m, 2H), 7.18 (d, *J* = 7.0 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.94 – 6.87 (m, 2H), 6.88 – 6.81 (m, 2H), 3.92 (s, 1H), 3.67 (d, *J* = 16.3 Hz, 1H), 3.31 (d, *J* = 16.1 Hz, 1H), 2.41 (s, 3H), 2.18 (s, 3H).

¹³C NMR (101 M Hz, CDCl₃) δ 147.9, 139.6, 137.6, 136.9, 134.4, 131.9, 131.5, 130.2, 129.4, 129.1, 128.1, 126.2, 125.6, 125.4, 124.2, 123.9 (C-F, q, ¹J_(C-F) = 288.3 Hz), 120.8, 120.4, 111.8, 86.6 (q, ²J_(C-F) = 31.5 Hz), 33.9, 21.3, 20.7.

¹⁹F NMR (377 M Hz, CDCl₃) δ -79.5.

M.p. 115.3–117.1 °C

HRMS (ESI): [M+H]⁺ calcd. for C₂₇H₂₃F₃NO⁺ 434.1726, found 434.1726.



7-bromo-1-(p-tolyl)-2-(trifluoromethyl)-1H-benzo[de]quinoline (8**)**

General procedure was followed with product **4b** (84.5 mg, 0.2 mmol, 1.0 equiv), TsCl (46.4 mg, 0.30 mmol, 1.5 equiv), NaH (4.8 mg, 0.40 mmol, 2.0 equiv), DMF (2.0 ml). Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.4) to give the titled product **8** as a yellow solid (65.4 mg, 81%).

$^1\text{H NMR}$ (400 M Hz, CDCl₃) δ 7.56 (d, J = 8.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.36 – 7.27 (m, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.17 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 7.1 Hz, 1H), 5.47 (d, J = 8.5 Hz, 1H), 2.45 (s, 3H).

$^{13}\text{C NMR}$ (101 M Hz, CDCl₃) δ 144.3, 139.6, 136.2, 133.7, 132.4 (C-F, q, $^2J_{(C-F)}$ = 31.5 Hz), 131.8, 131.4, 131.3, 130.4, 129.2, 128.3, 122.9, 120.5 (C-F, q, $^1J_{(C-F)}$ = 273.2 Hz), 117.3, 110.3, 108.5 (C-F, q, $^3J_{(C-F)}$ = 6.4 Hz), 105.9, 21.5.

$^{19}\text{F NMR}$ (377 M Hz, CDCl₃) δ -62.3.

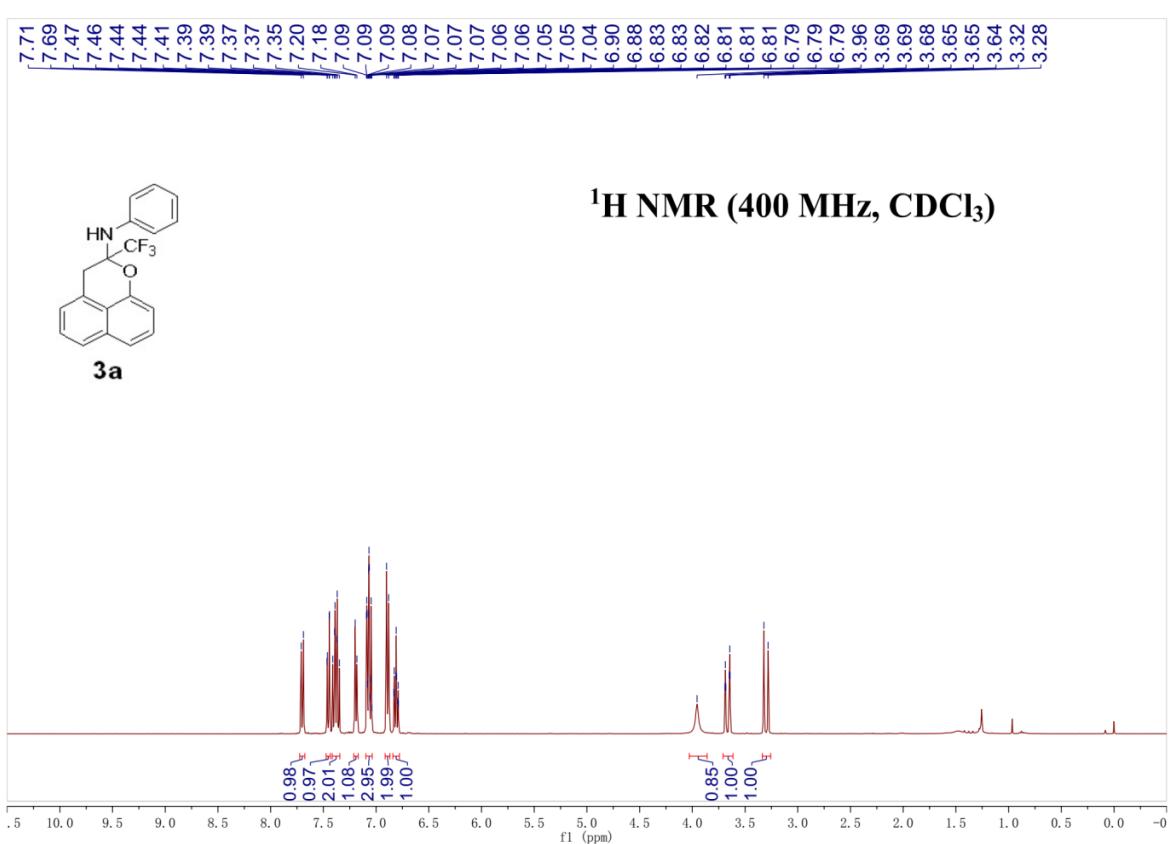
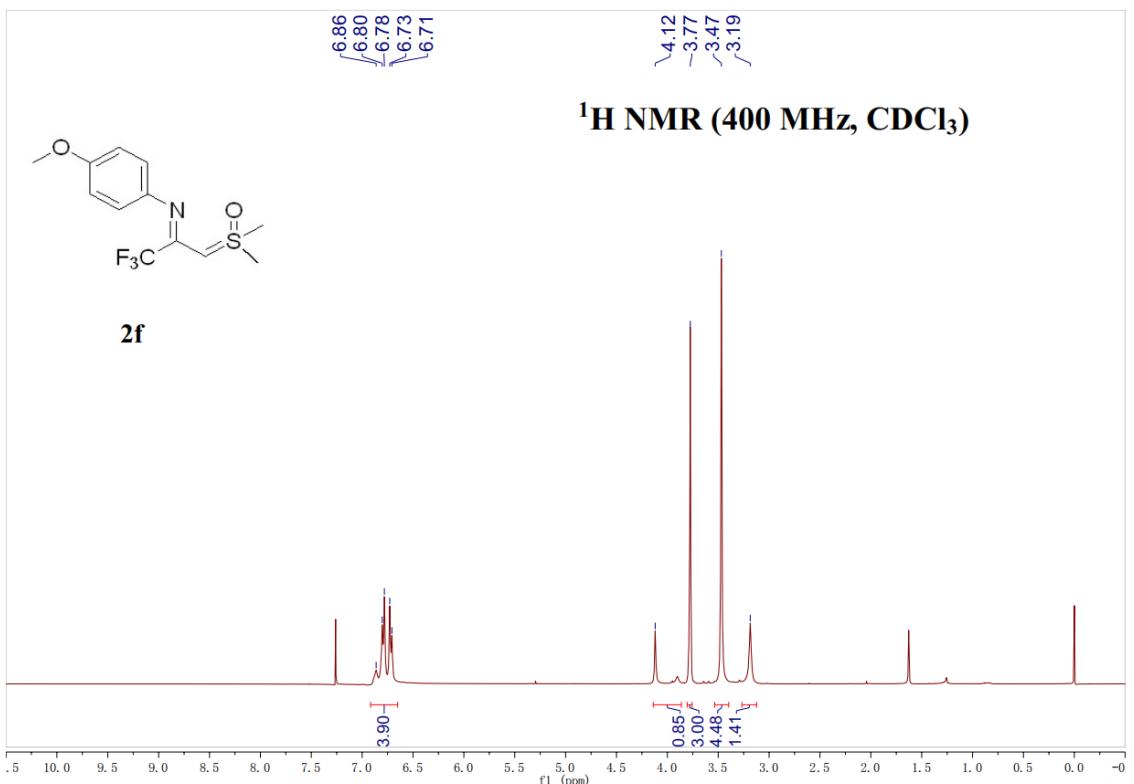
M.p. 119.8-121.4 °C

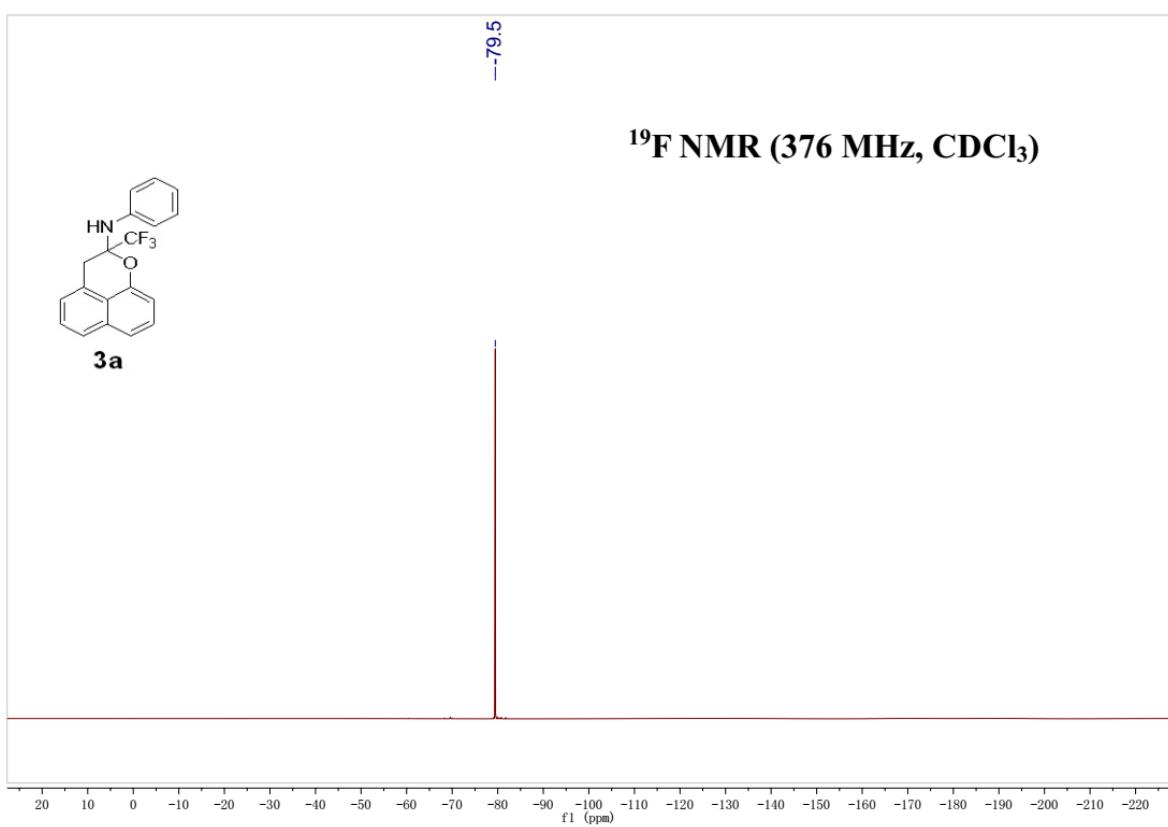
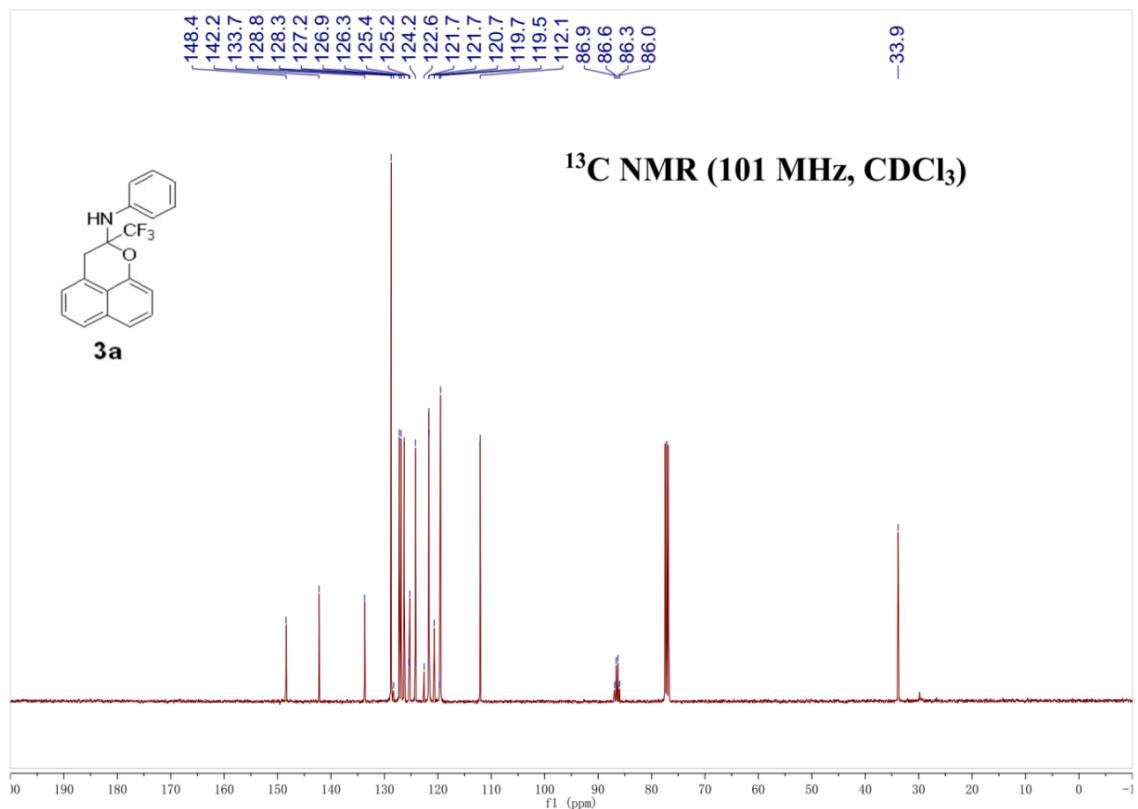
HRMS (ESI): [M] calcd. for C₂₀H₁₃BrF₃N 403.0183, found 403.0180.

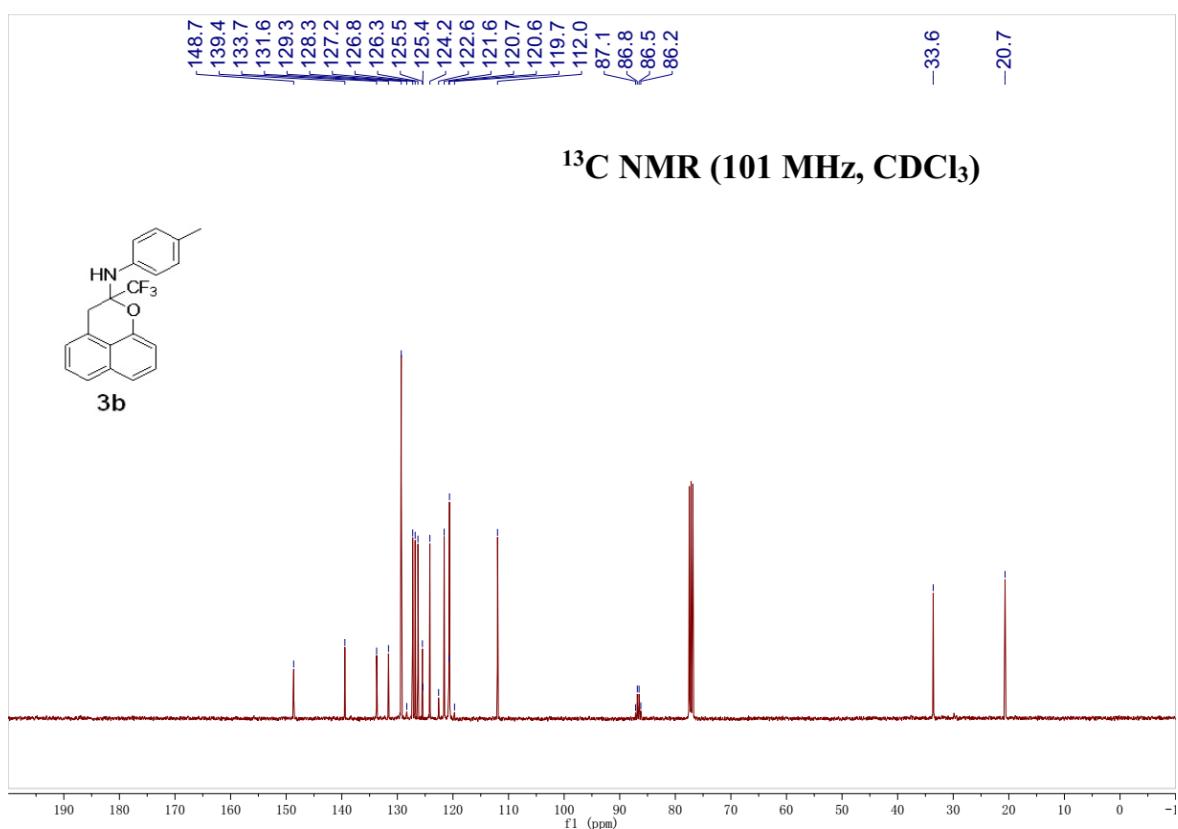
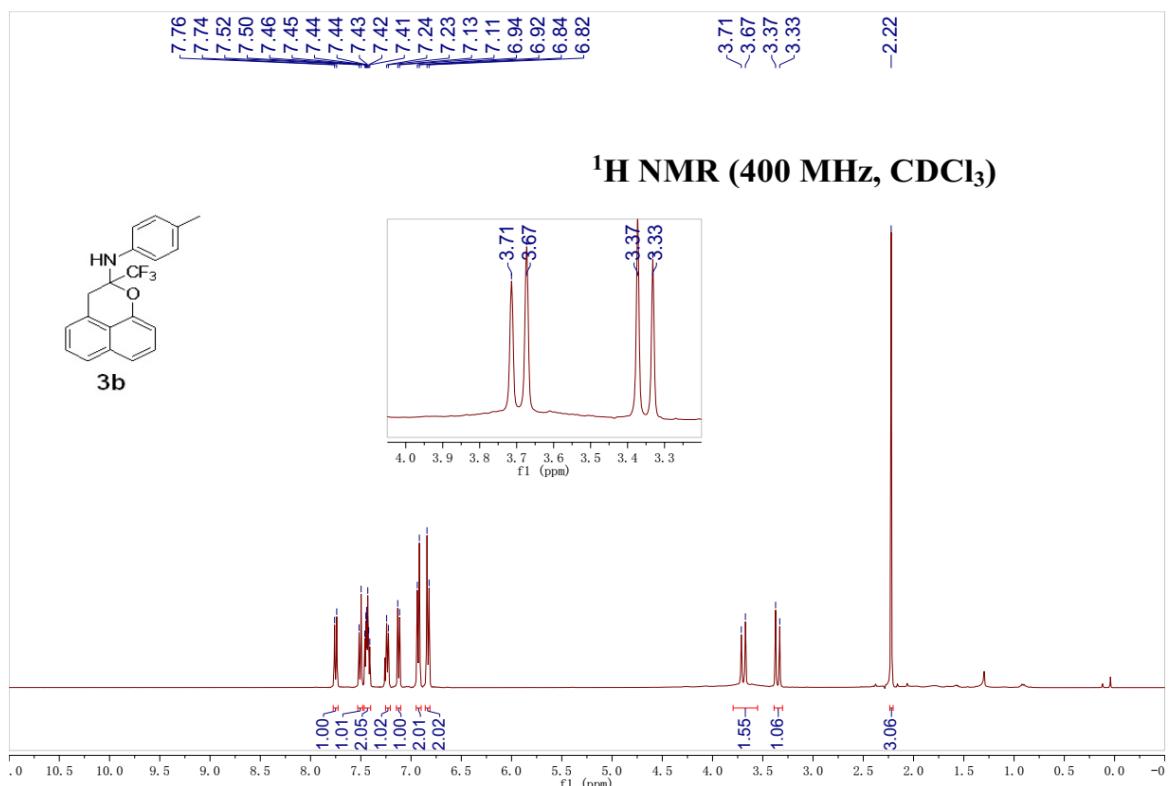
5 References

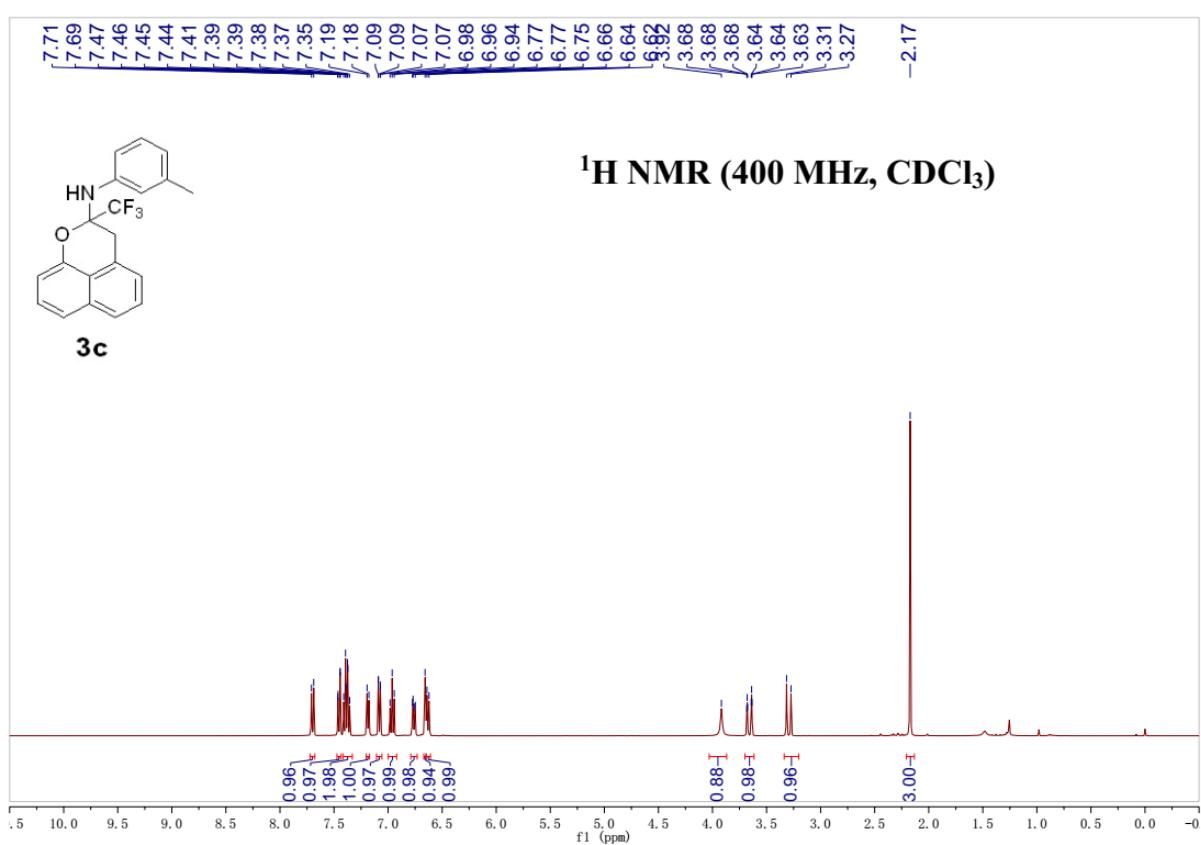
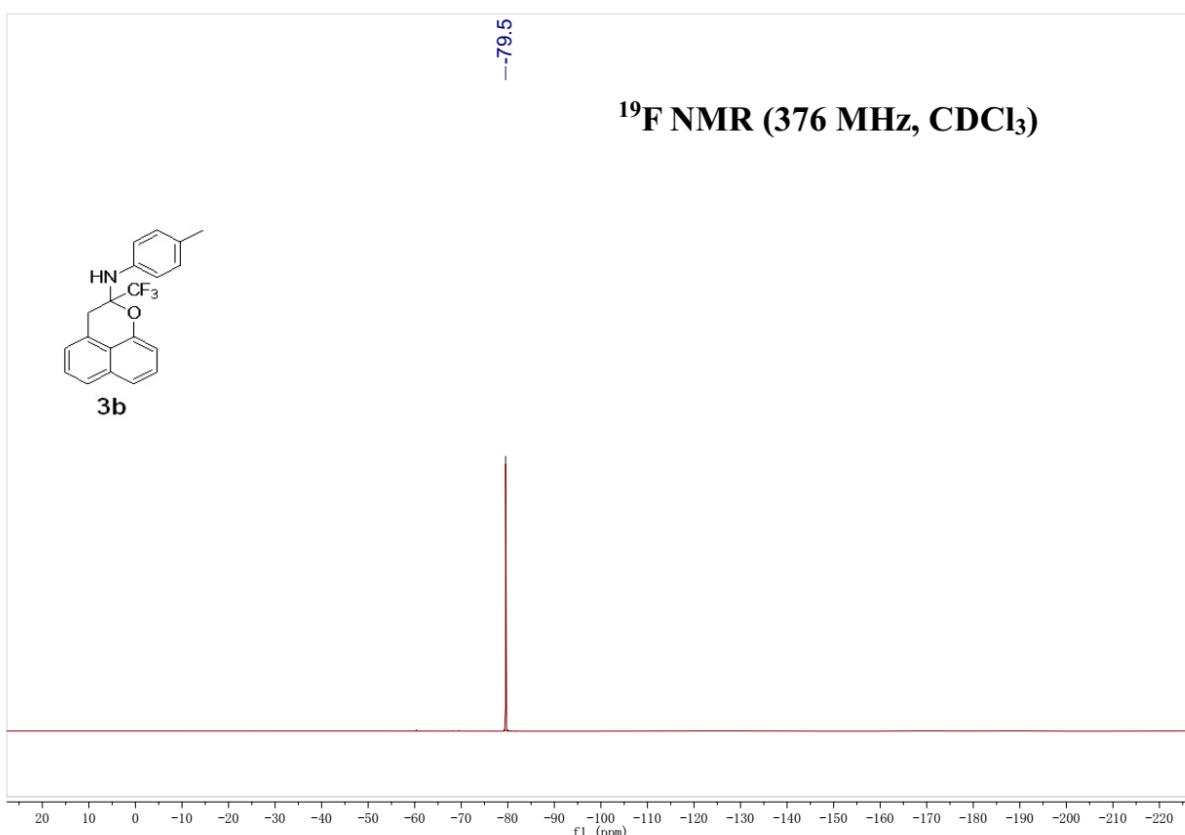
- (1) Tamura, K.; Mizukami,H.; Maeda, K.; Watanabe,H.; Uneyama, K. One-pot synthesis of trifluoroacetimidoyl Halides. *J. Org. Chem.* **1993**, *58*, 32-35.
- (2) Wen, S.; Tian, Q.; Chen, Y.; Zhang, Y.; Cheng, G. Annulation of CF₃-imidoyl sulfoxonium ylides with 1,3-dicarbonyl compounds: Access to 1,2,3-trisubstituted 5-trifluoromethylpyrroles. *Org. Lett.* **2021**, *23*, 7407-7411.

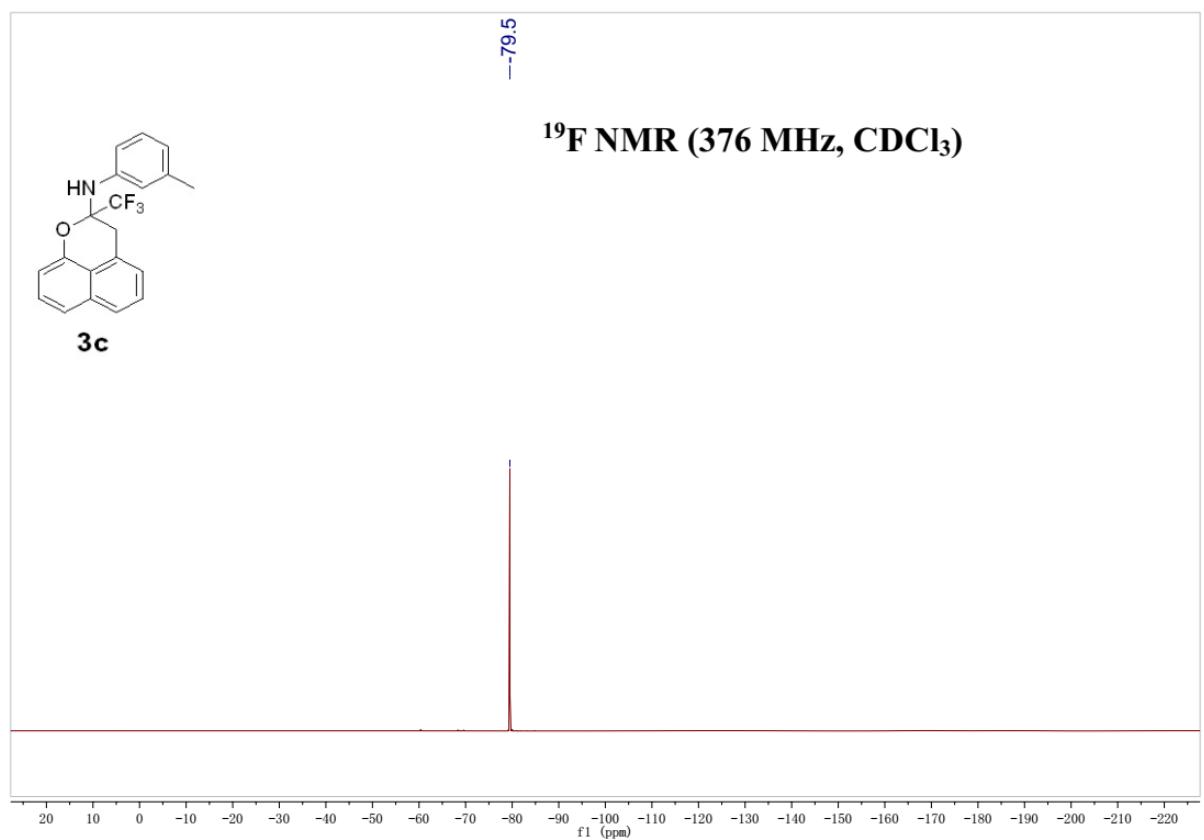
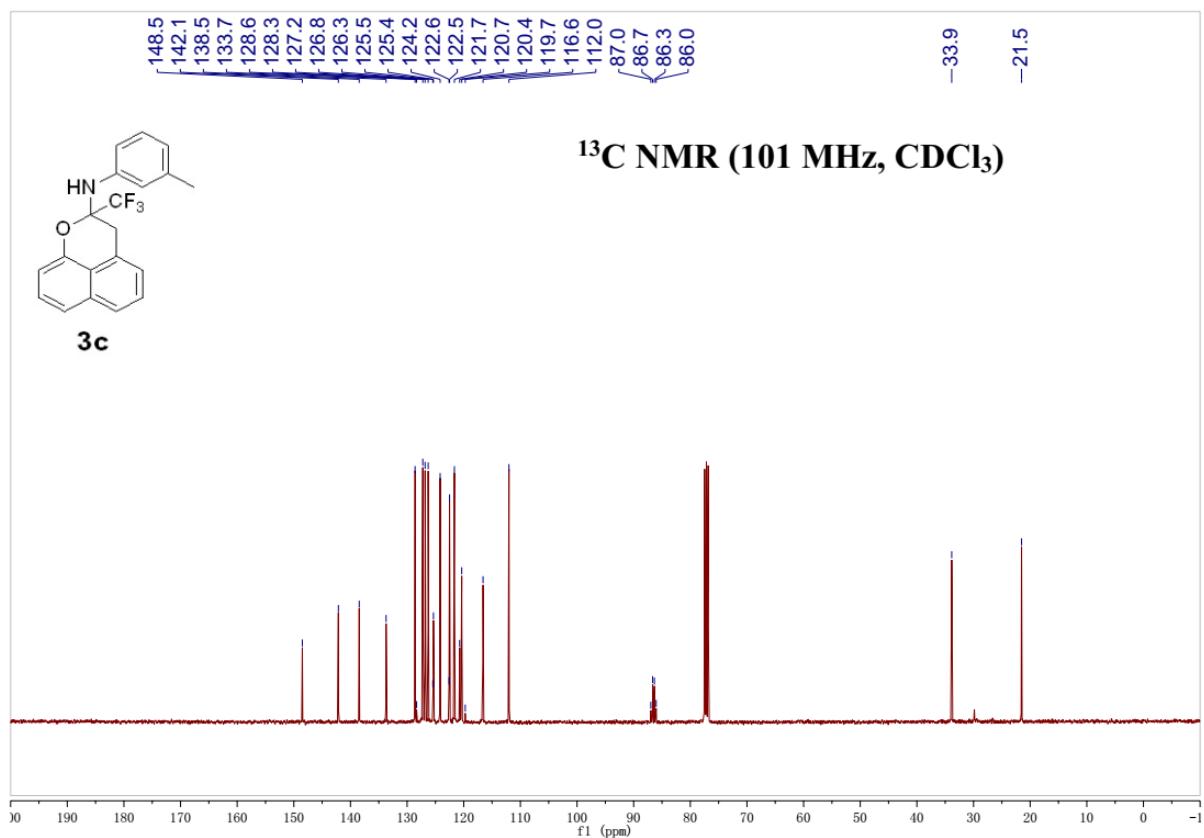
6 Copy of ^1H , ^{13}C and ^{19}F NMR Spectra of Products





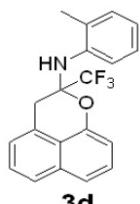
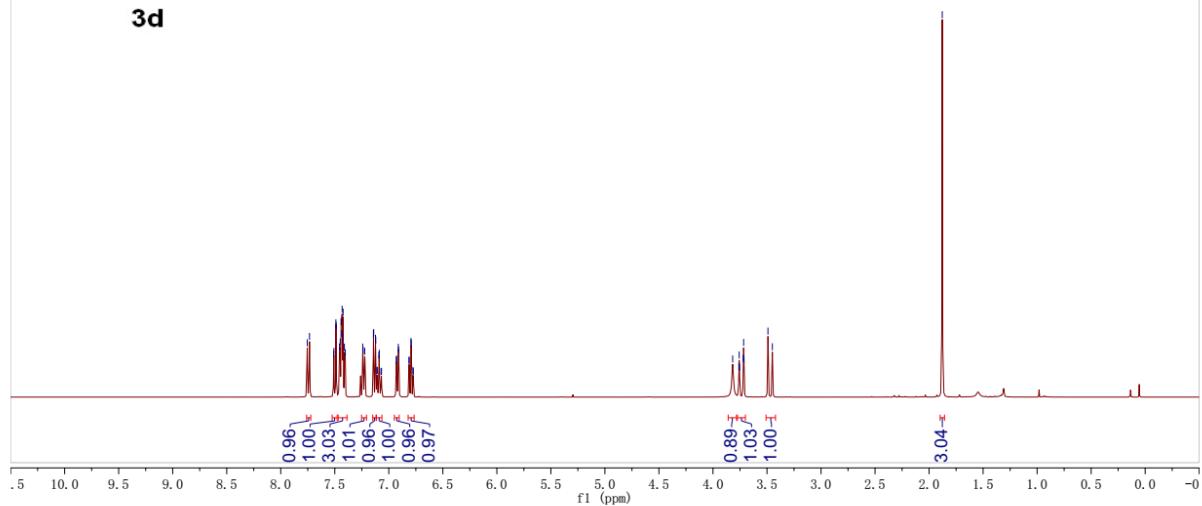
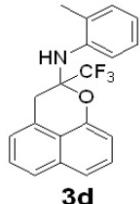




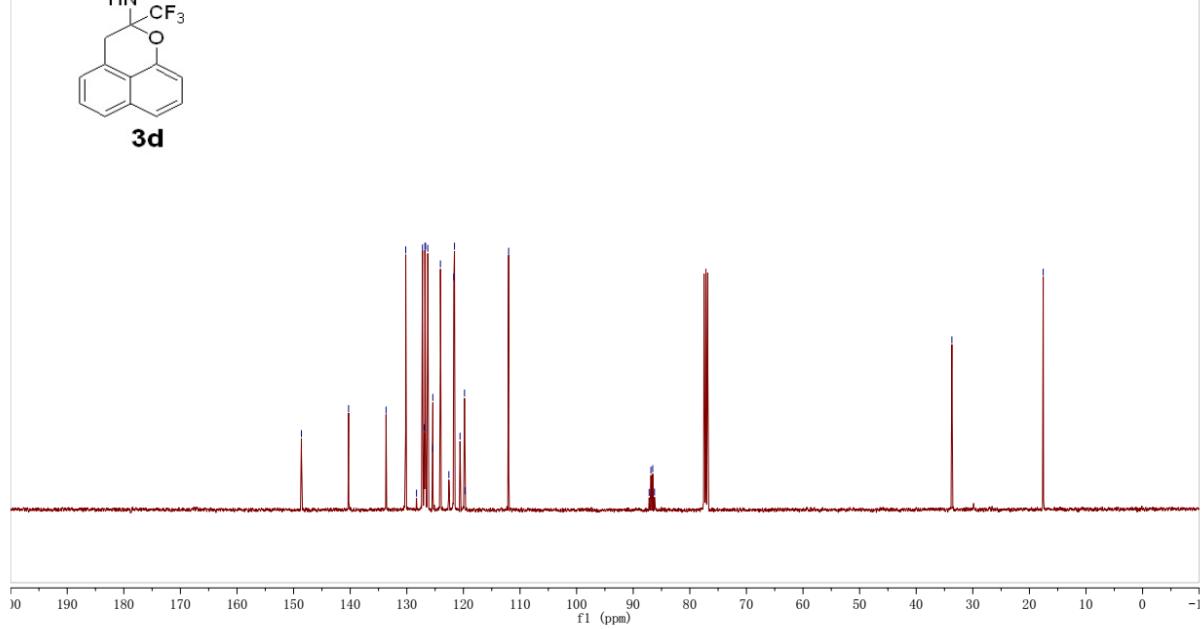


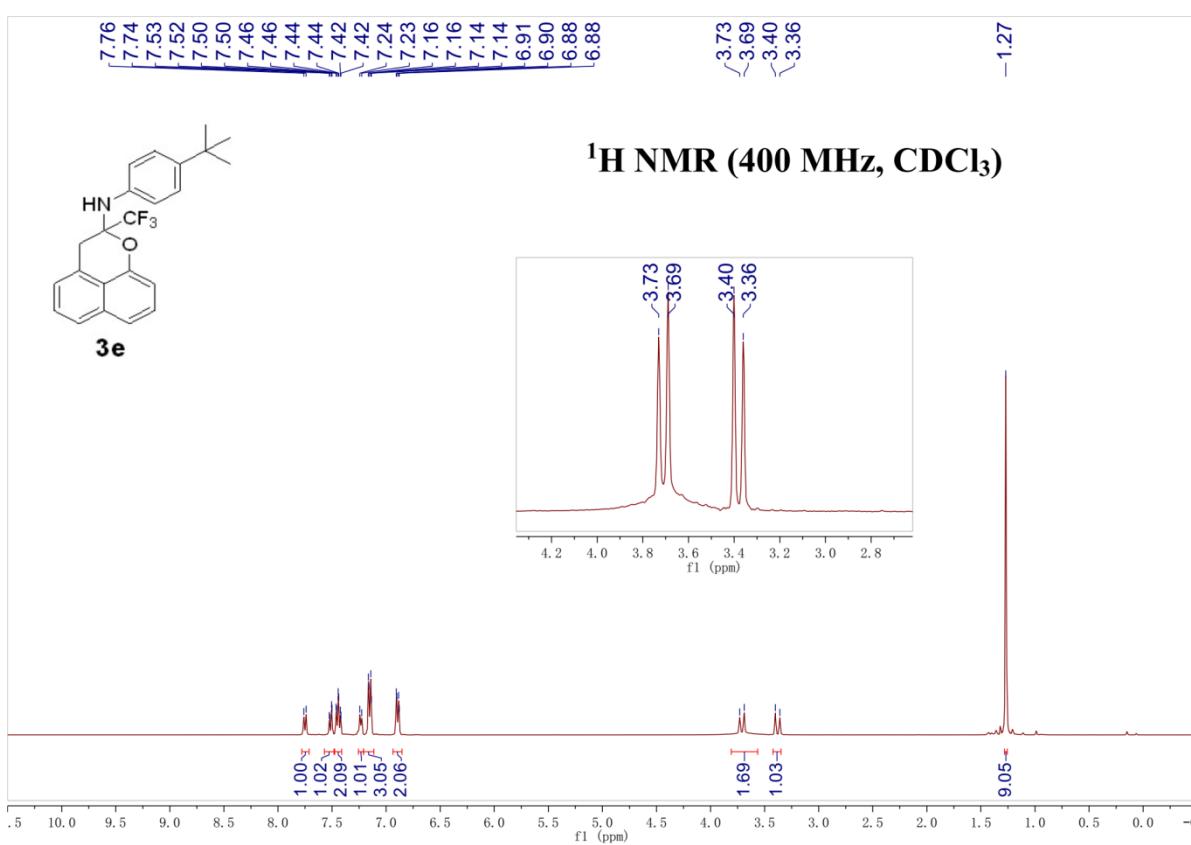
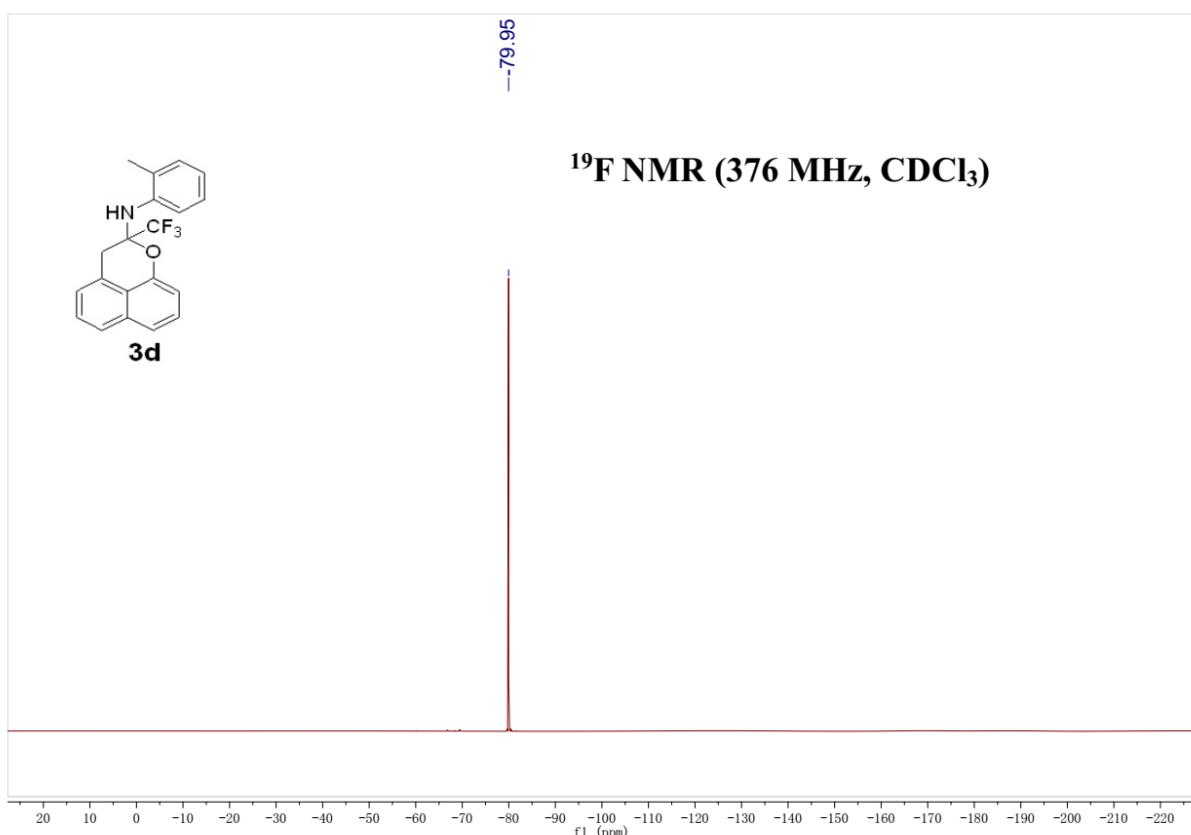


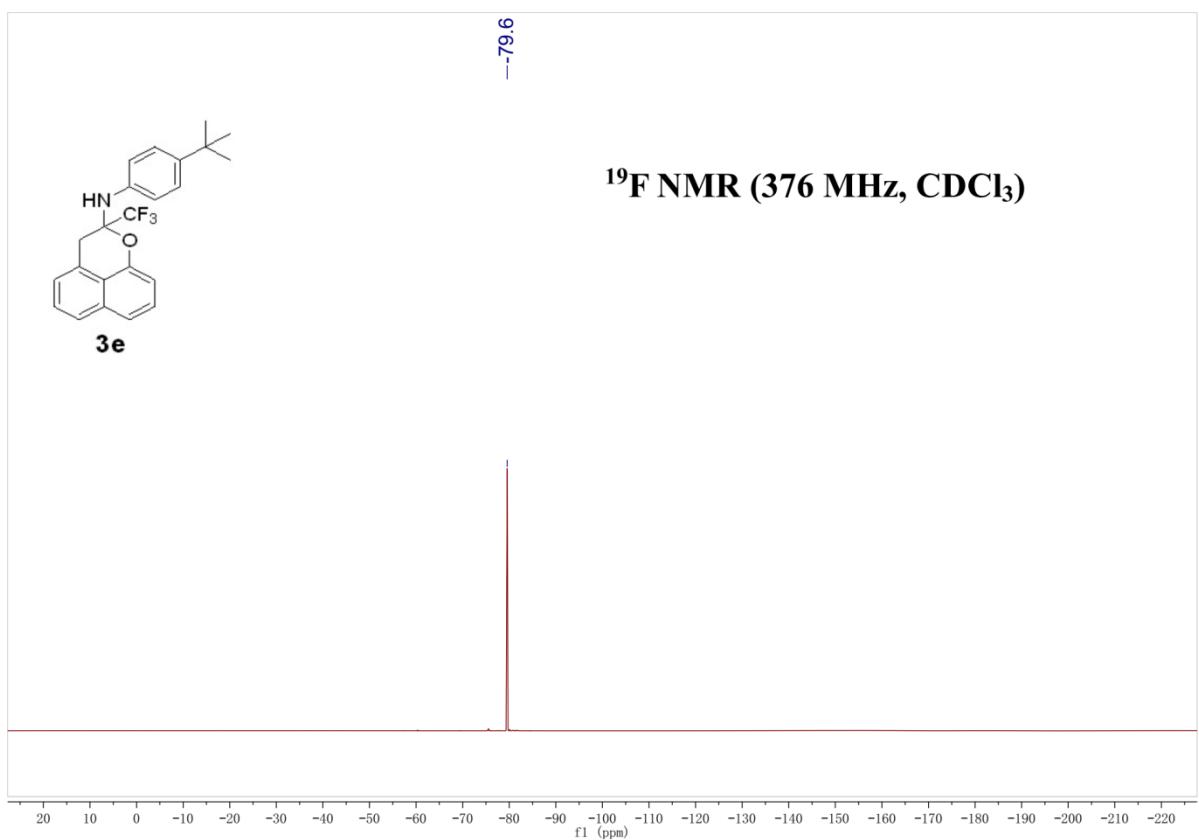
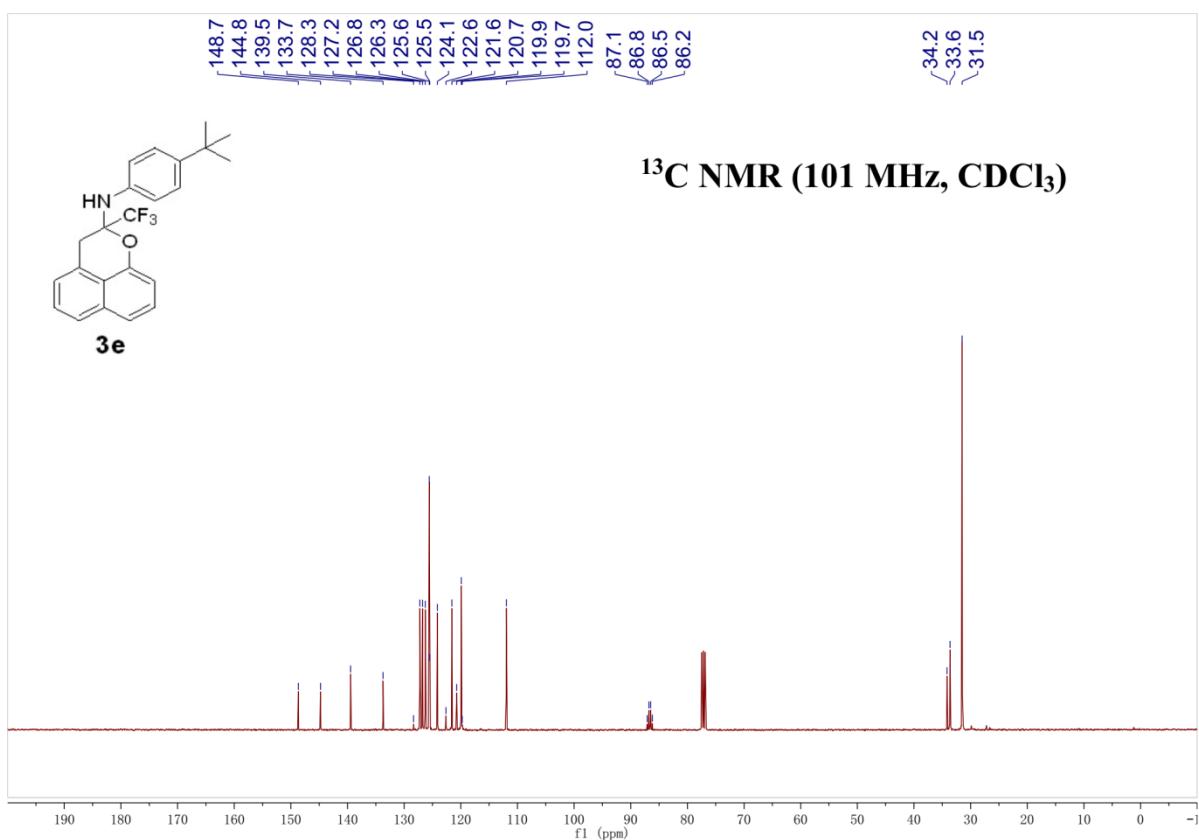
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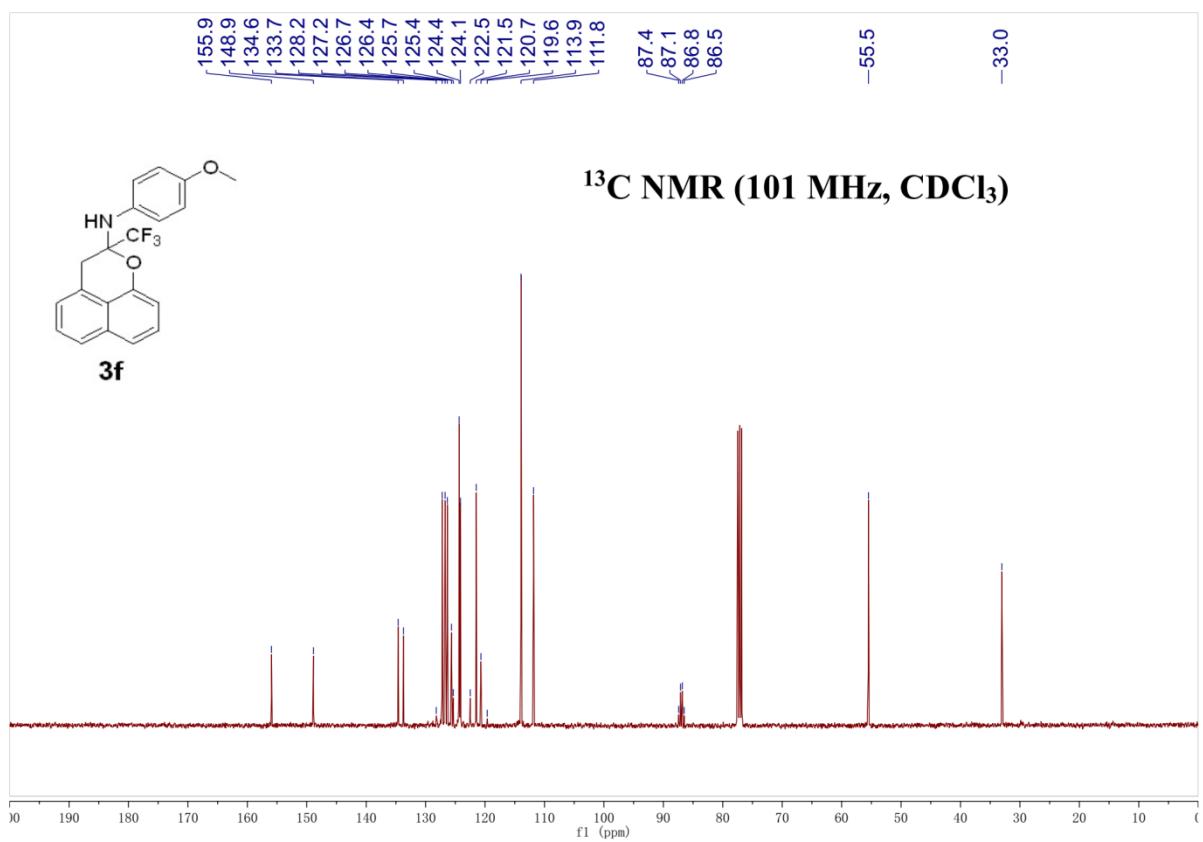
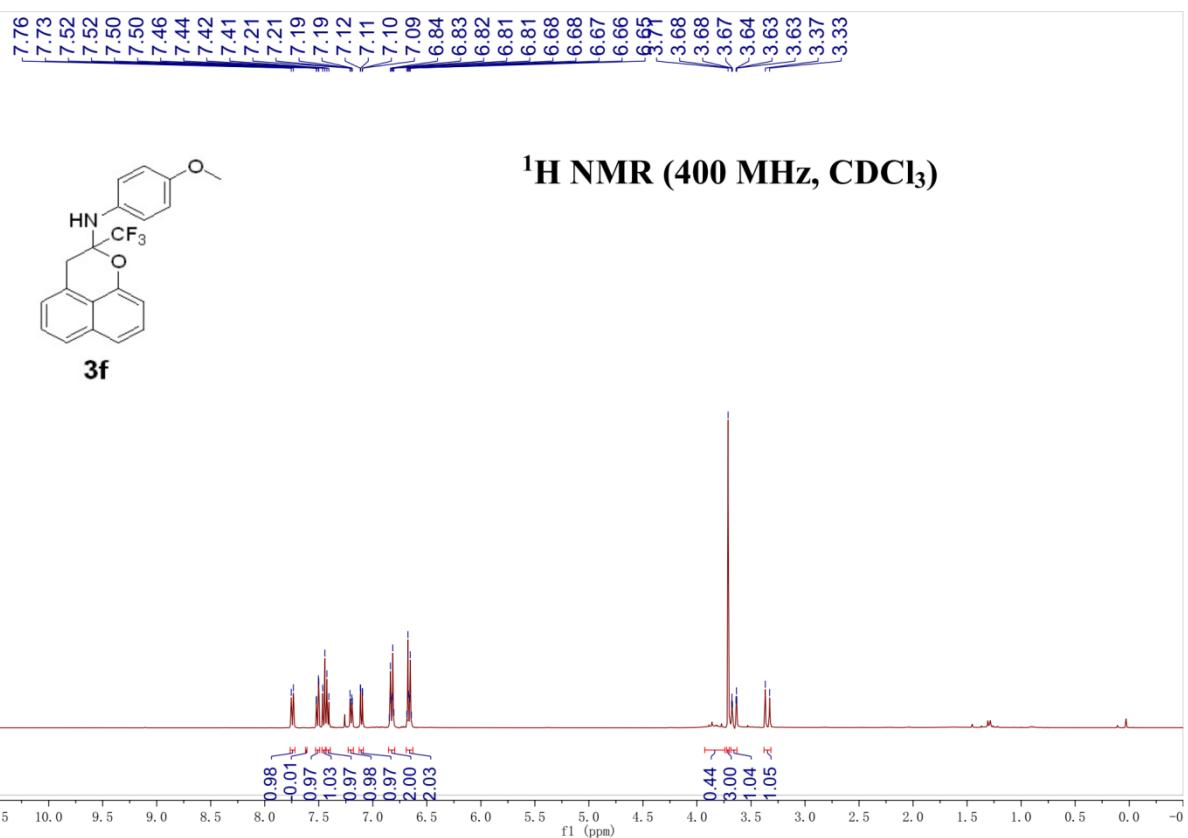


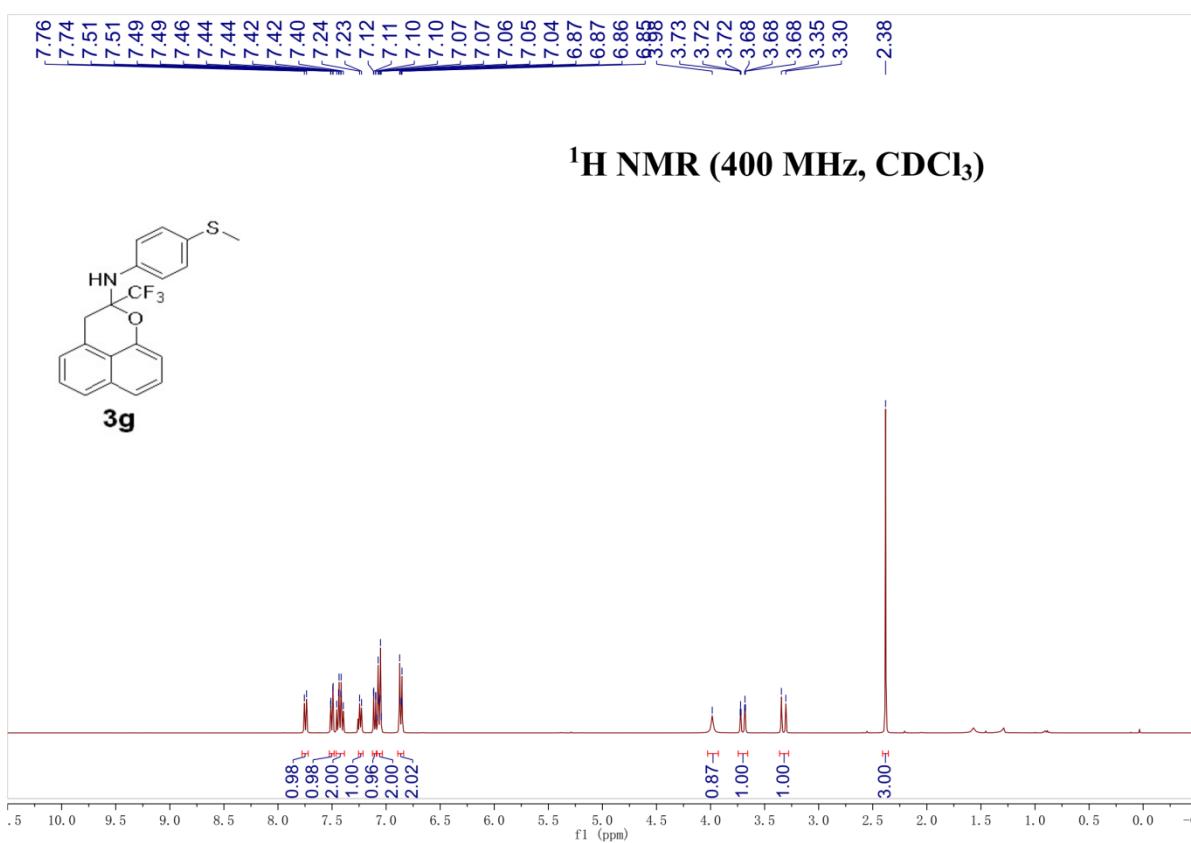
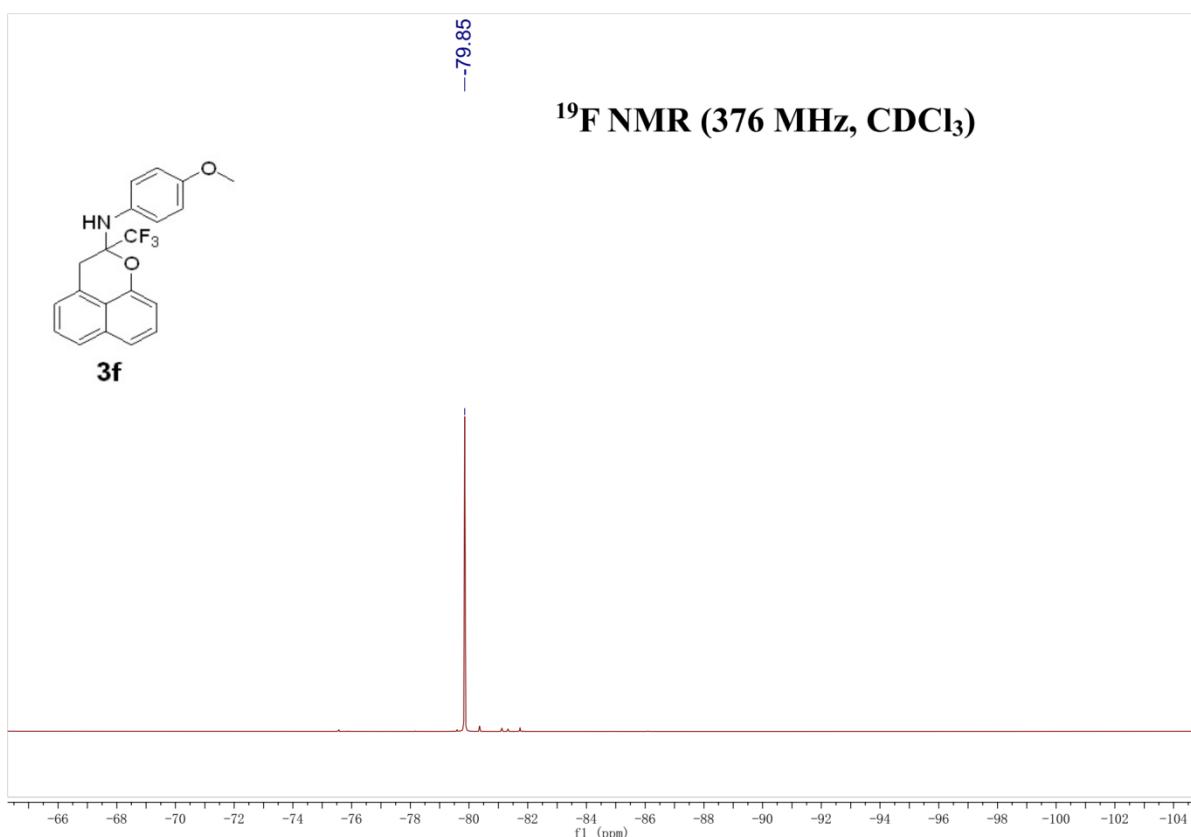
¹³C NMR (101 MHz, CDCl₃)

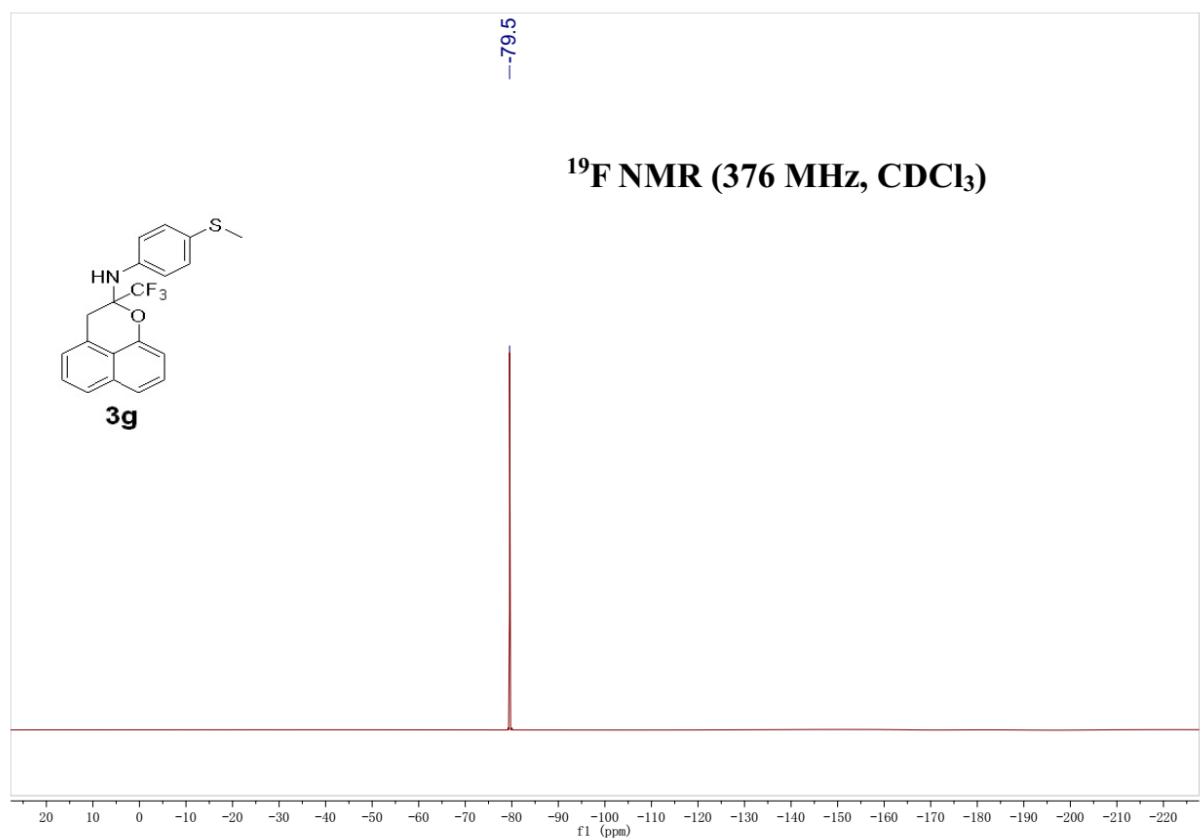
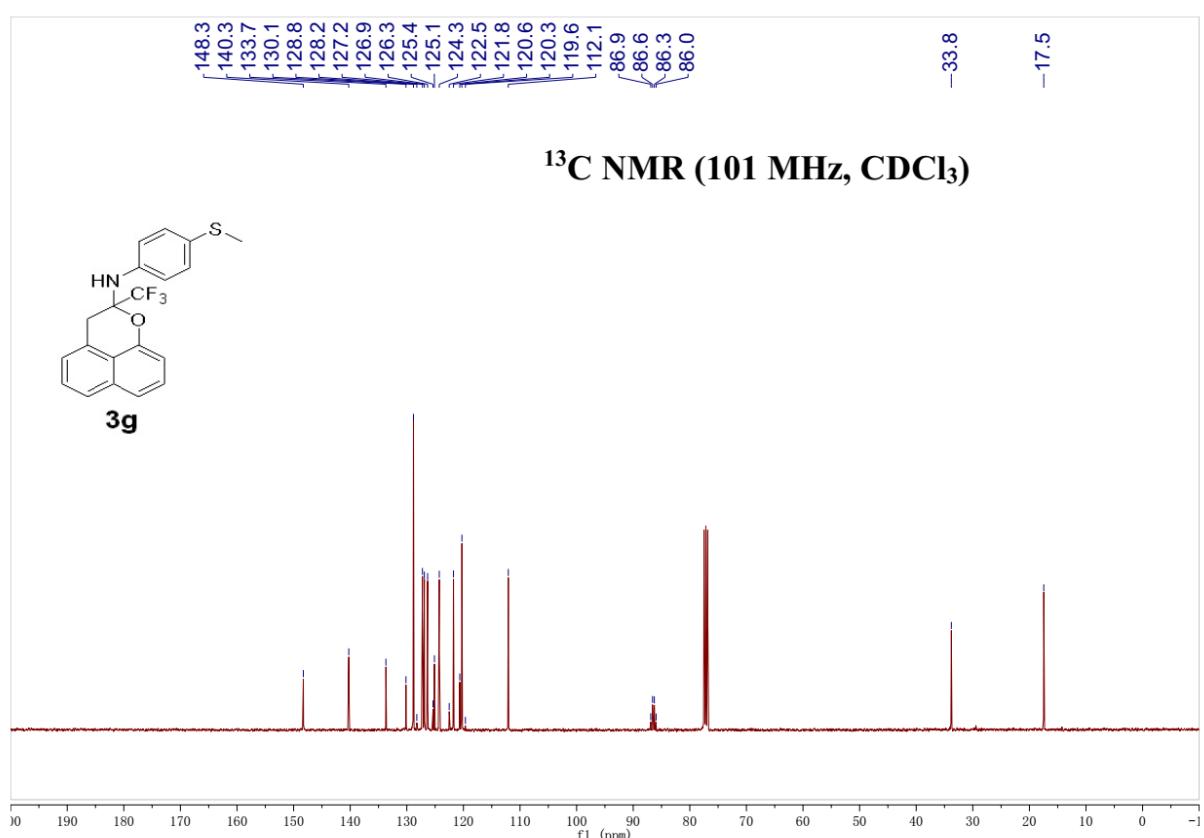


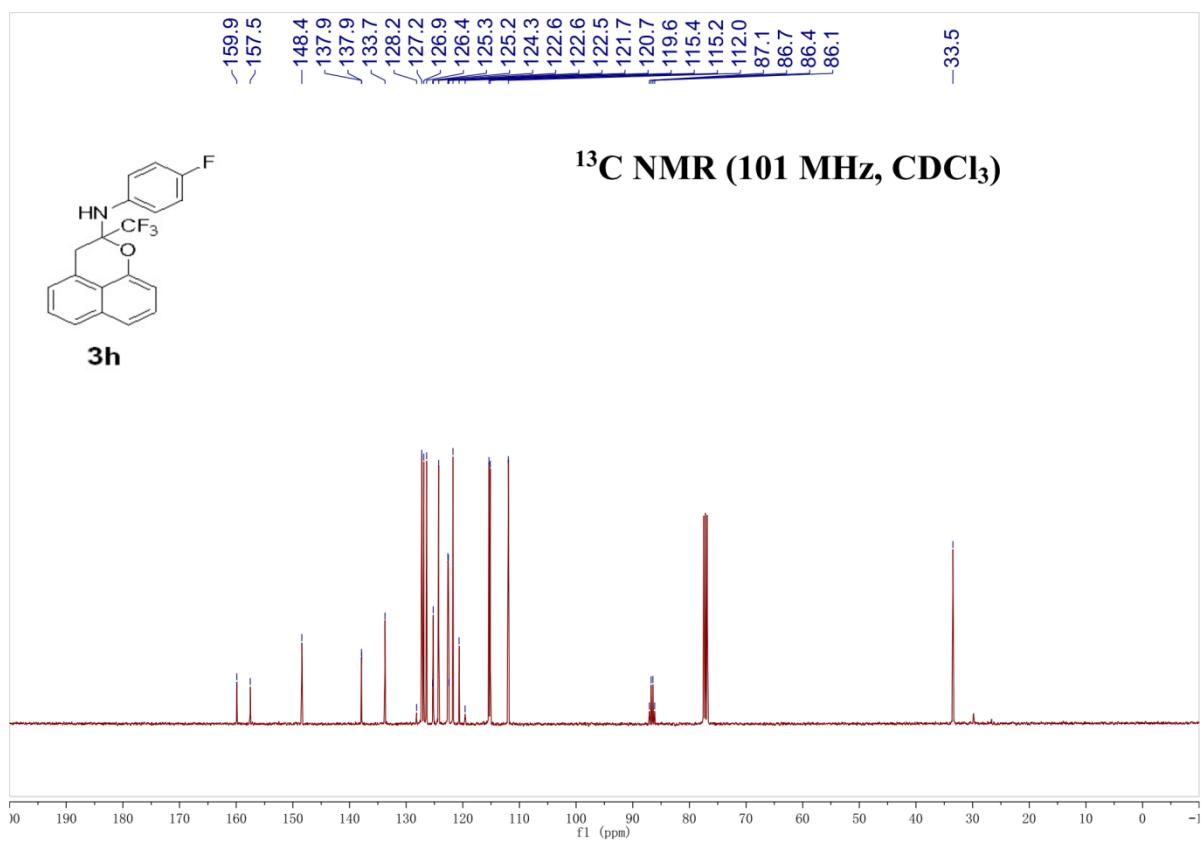
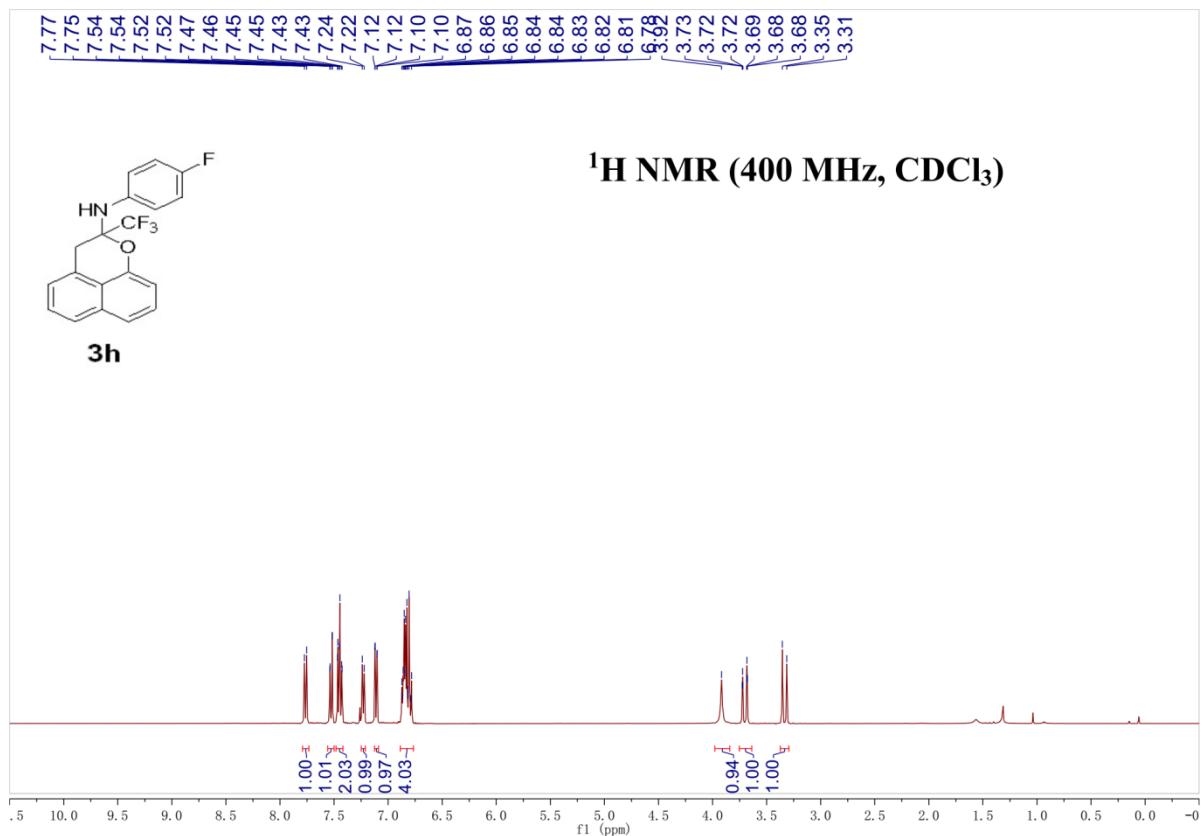


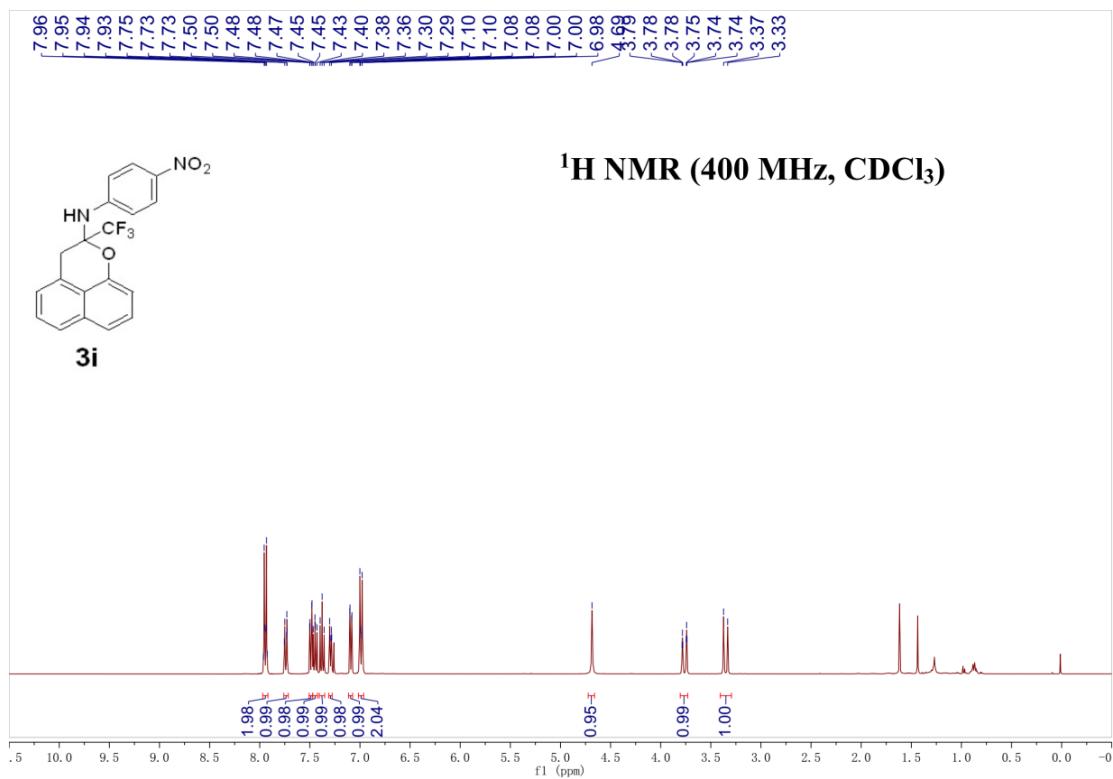
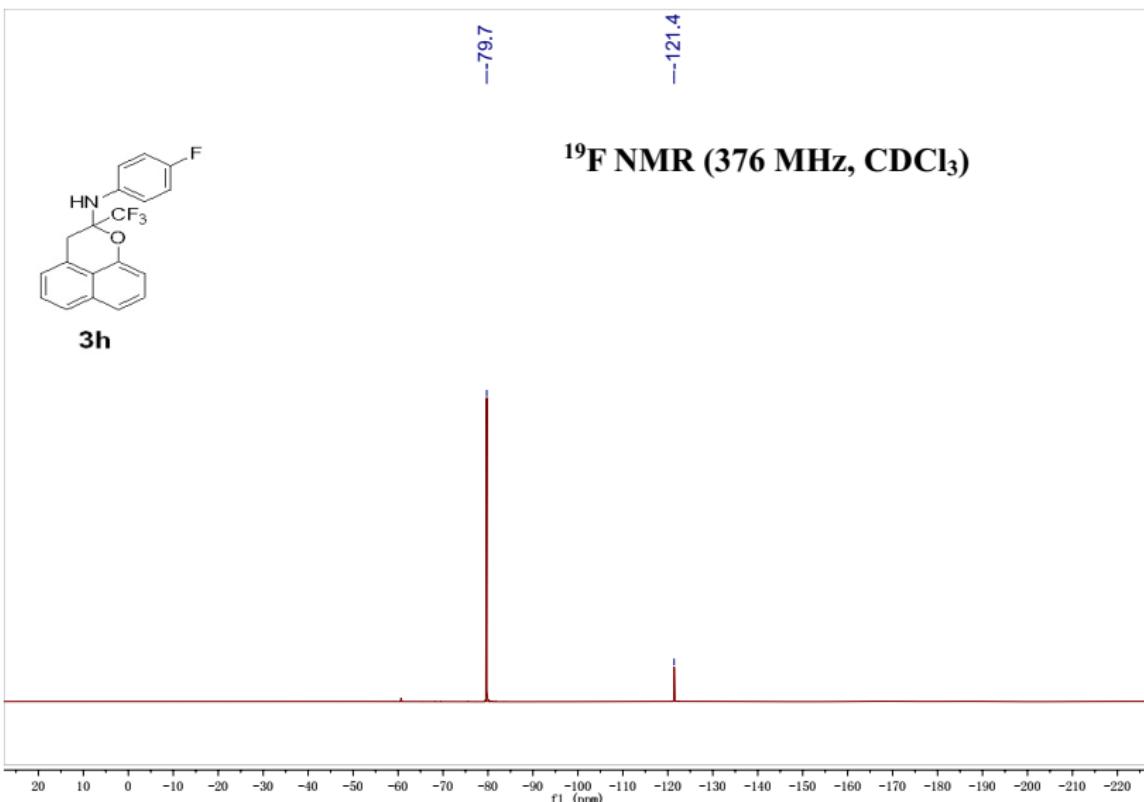


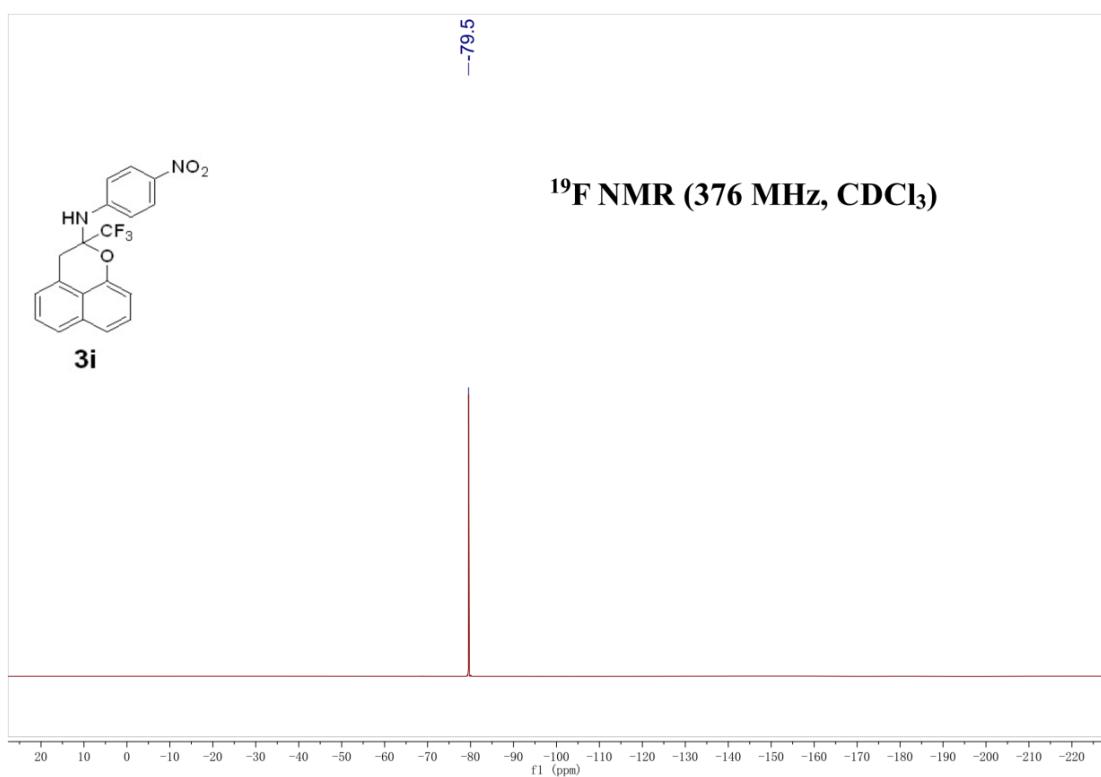
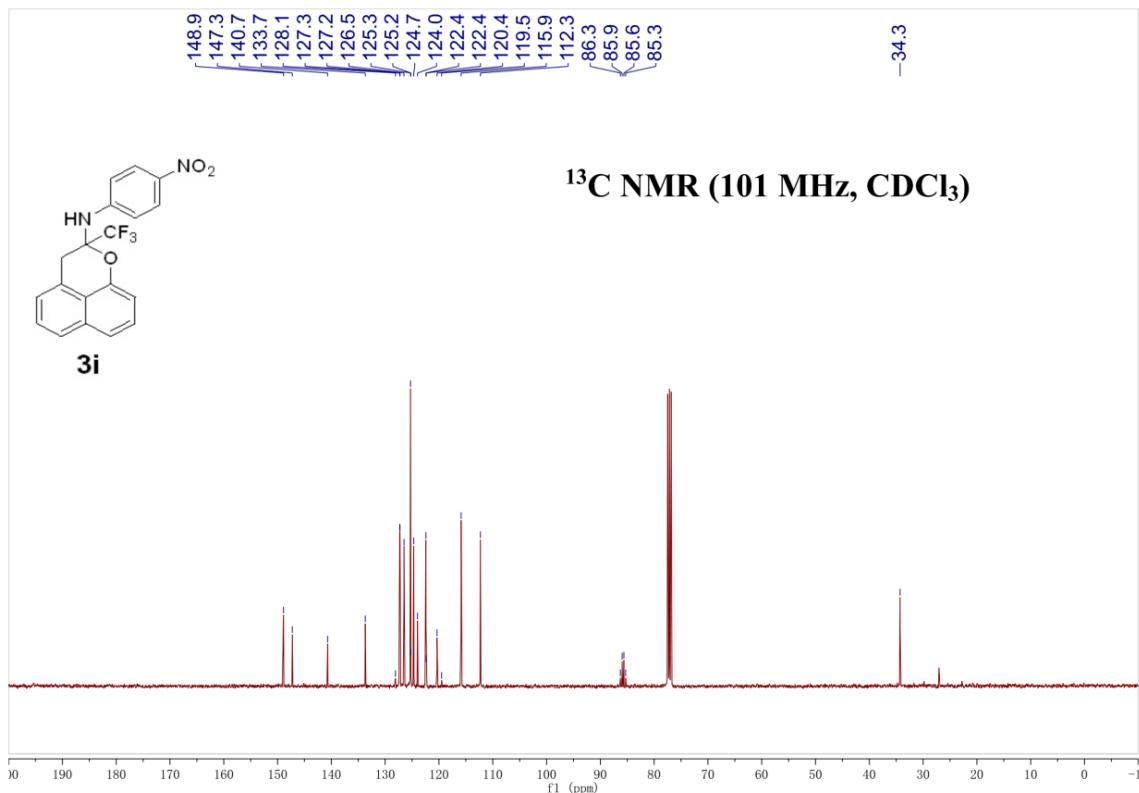


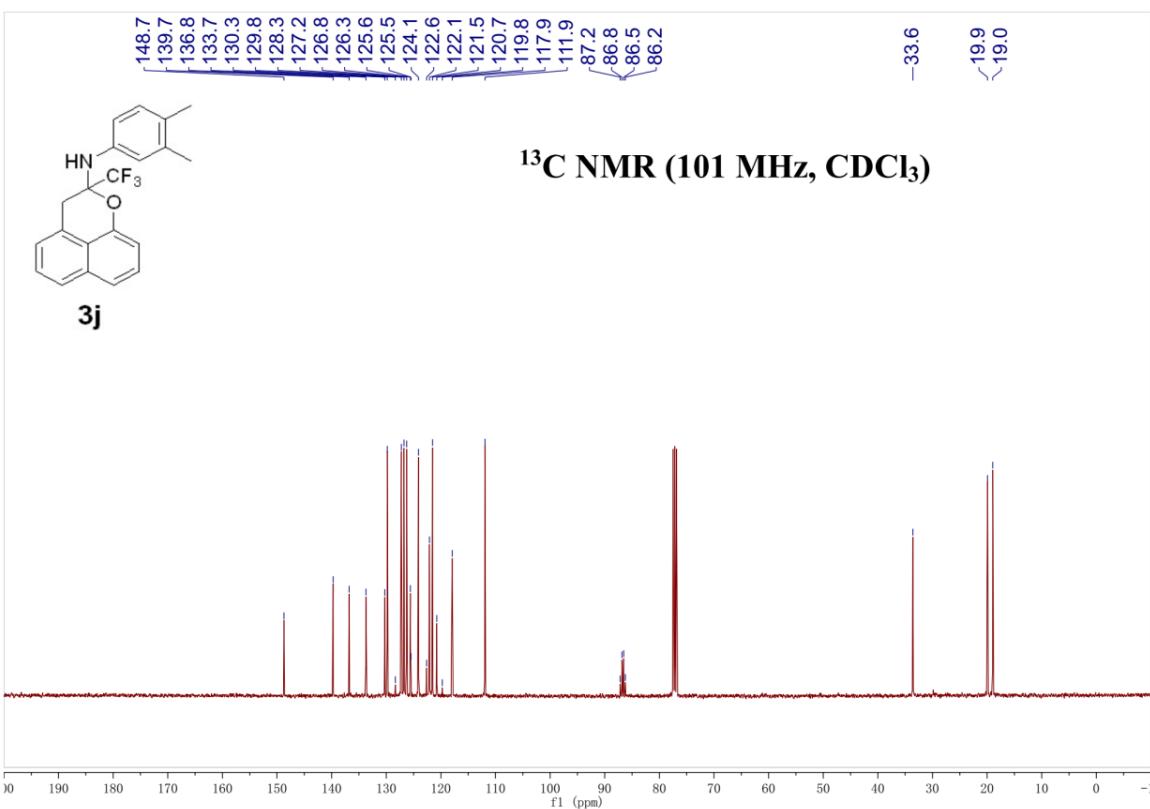
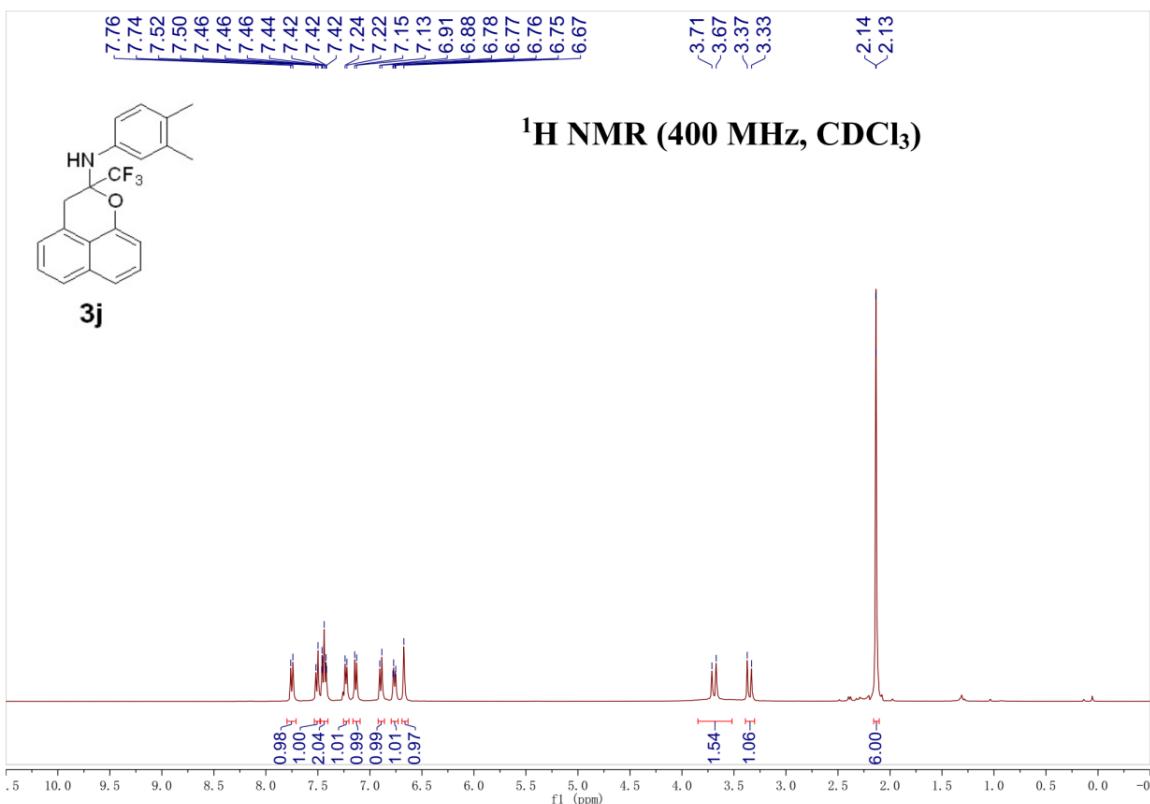


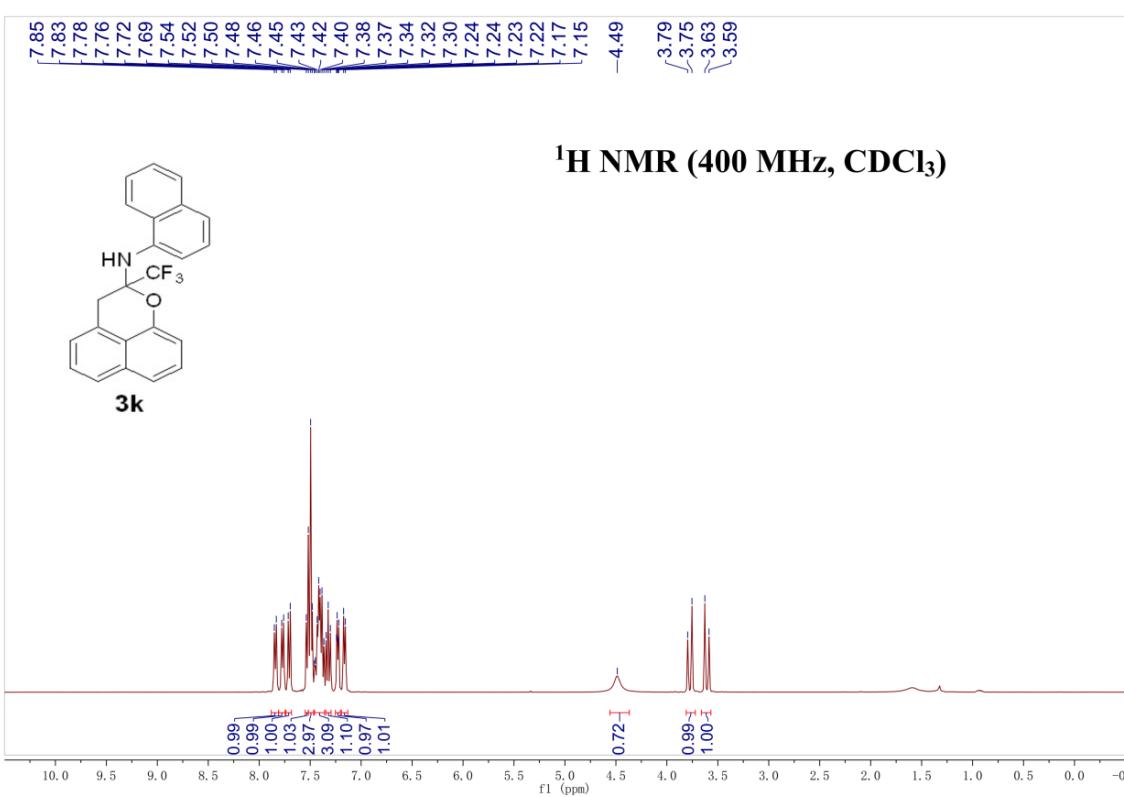
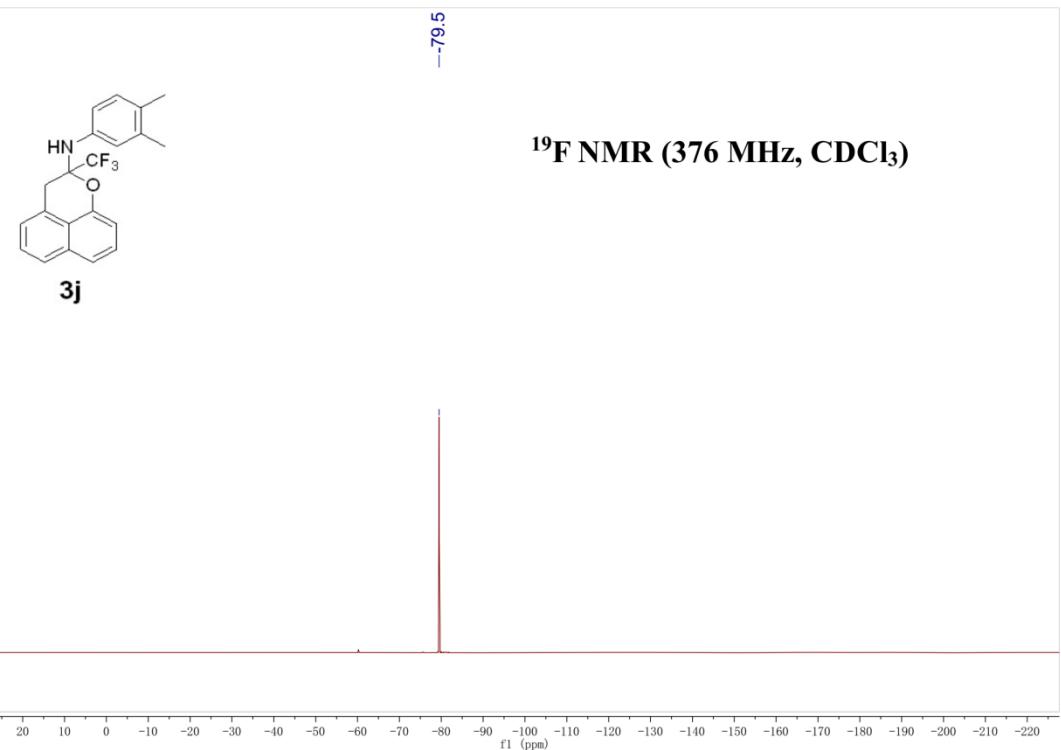


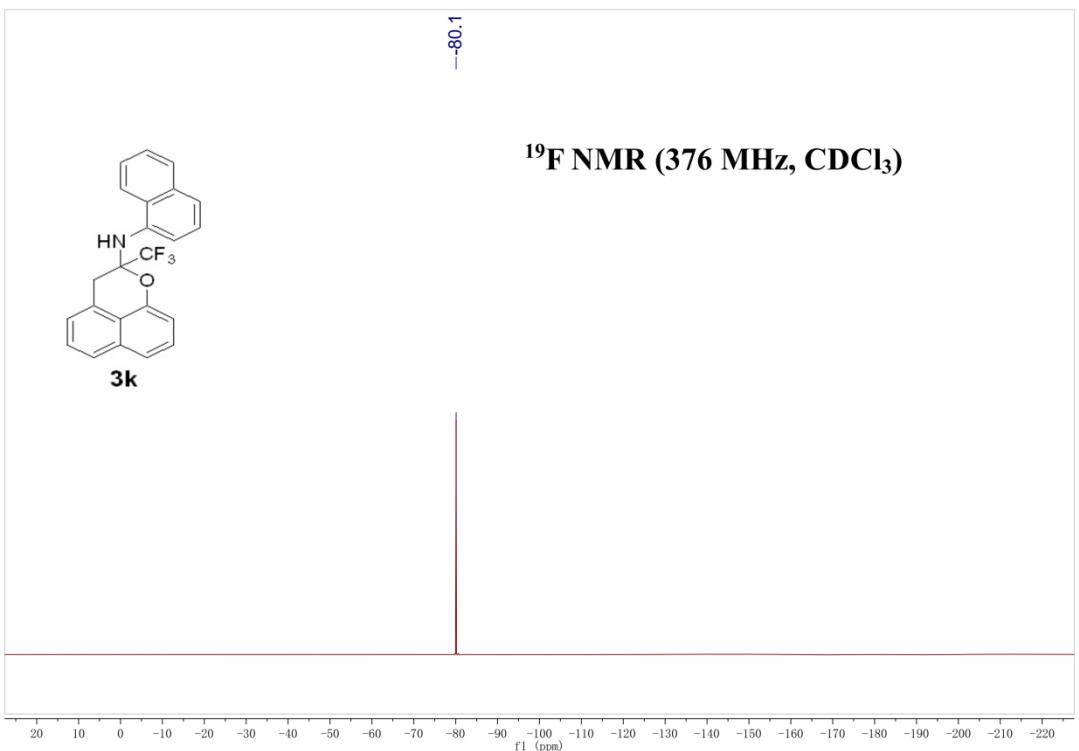
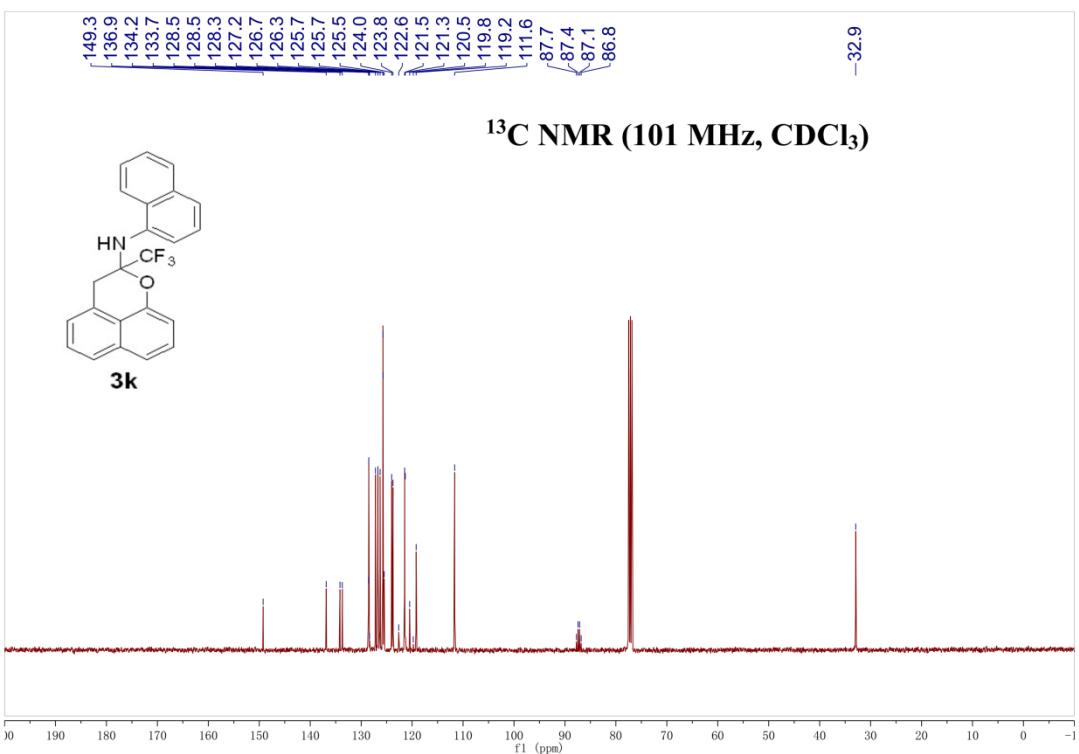


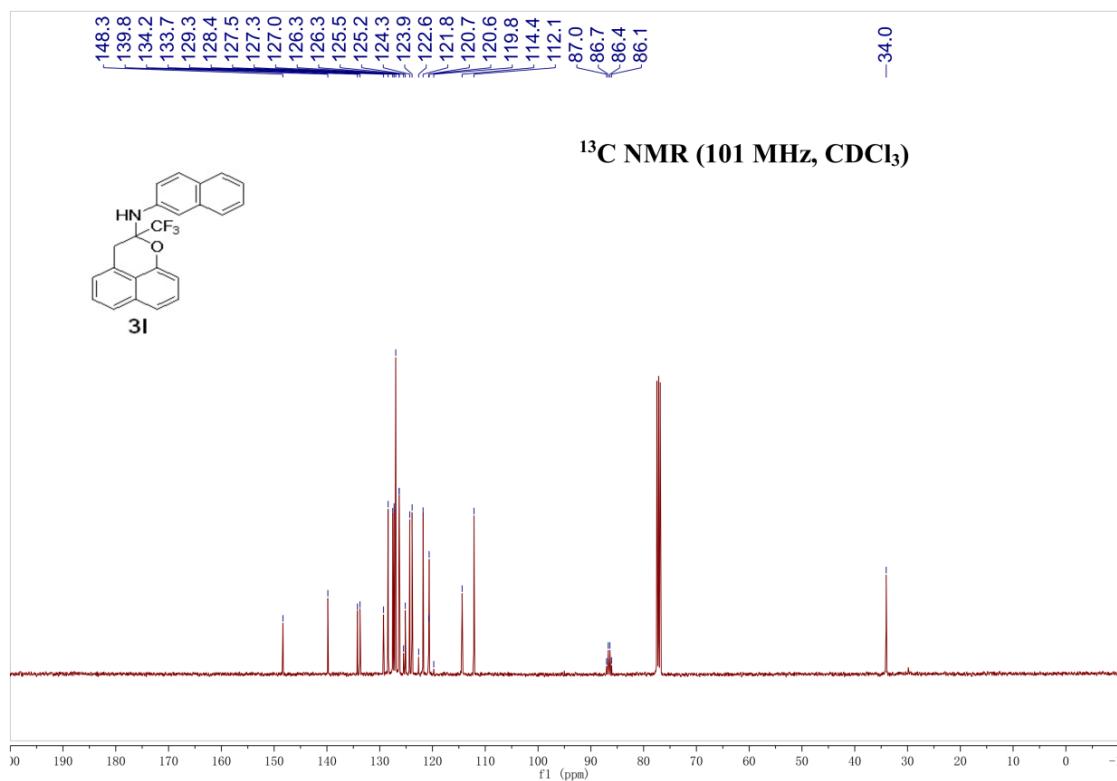
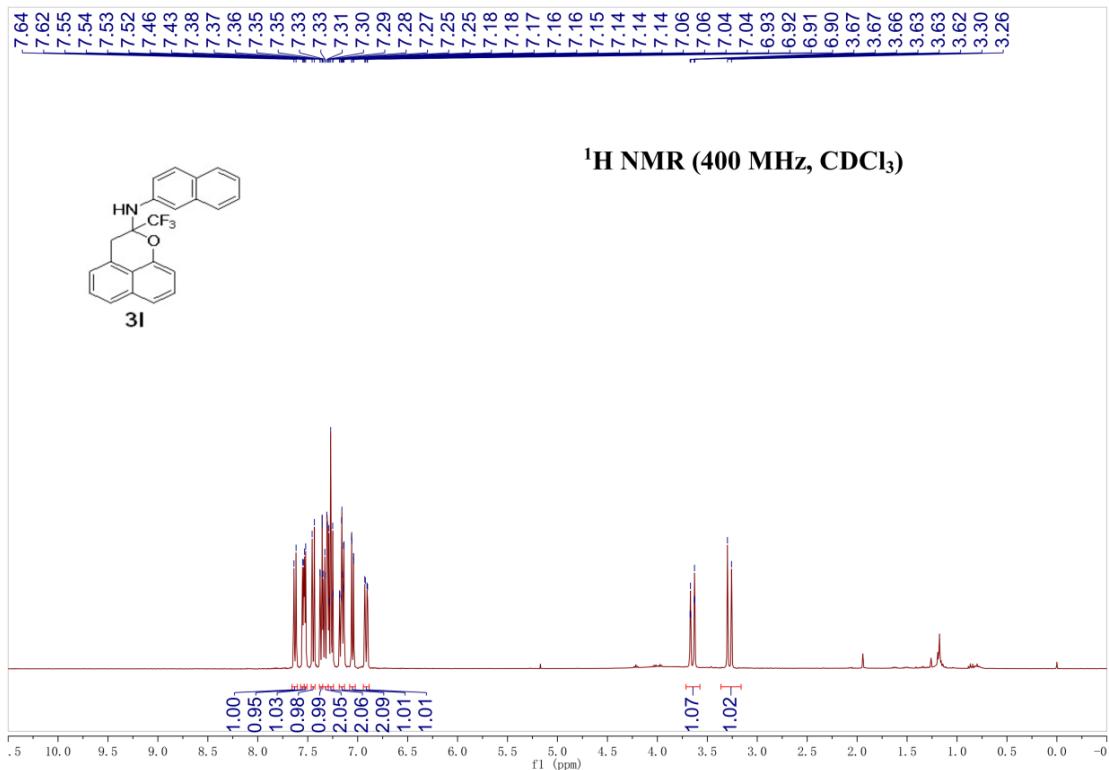


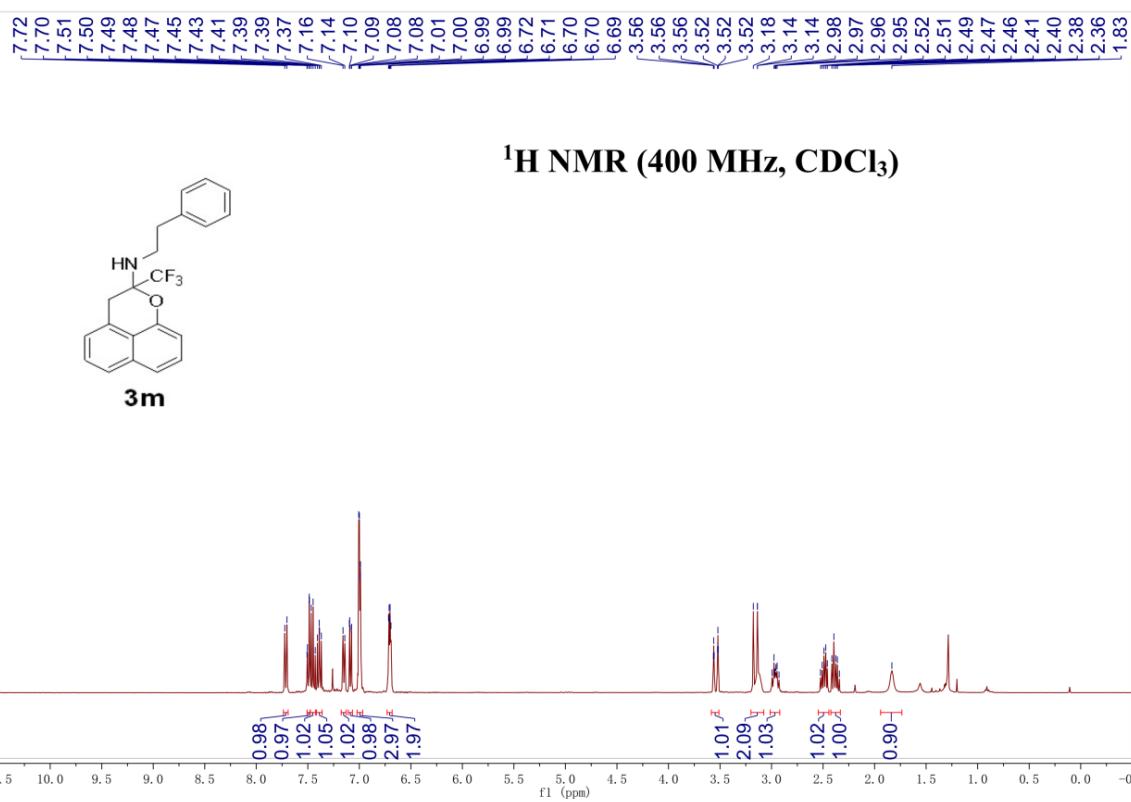
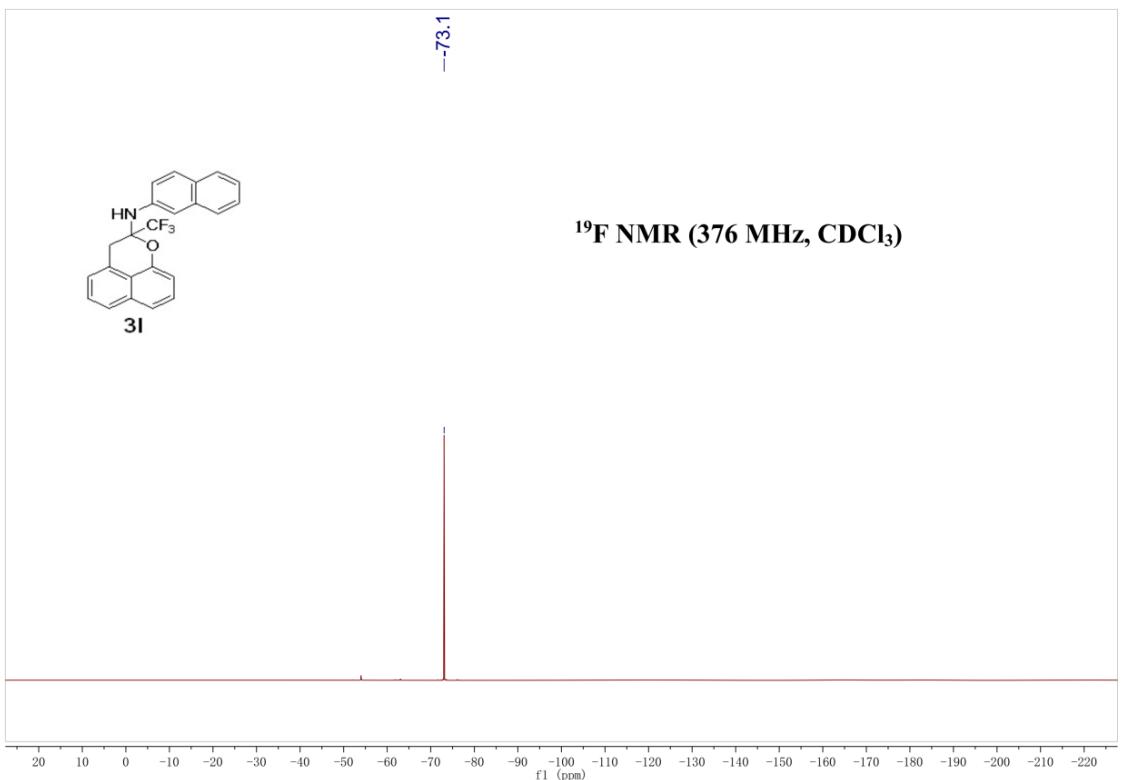


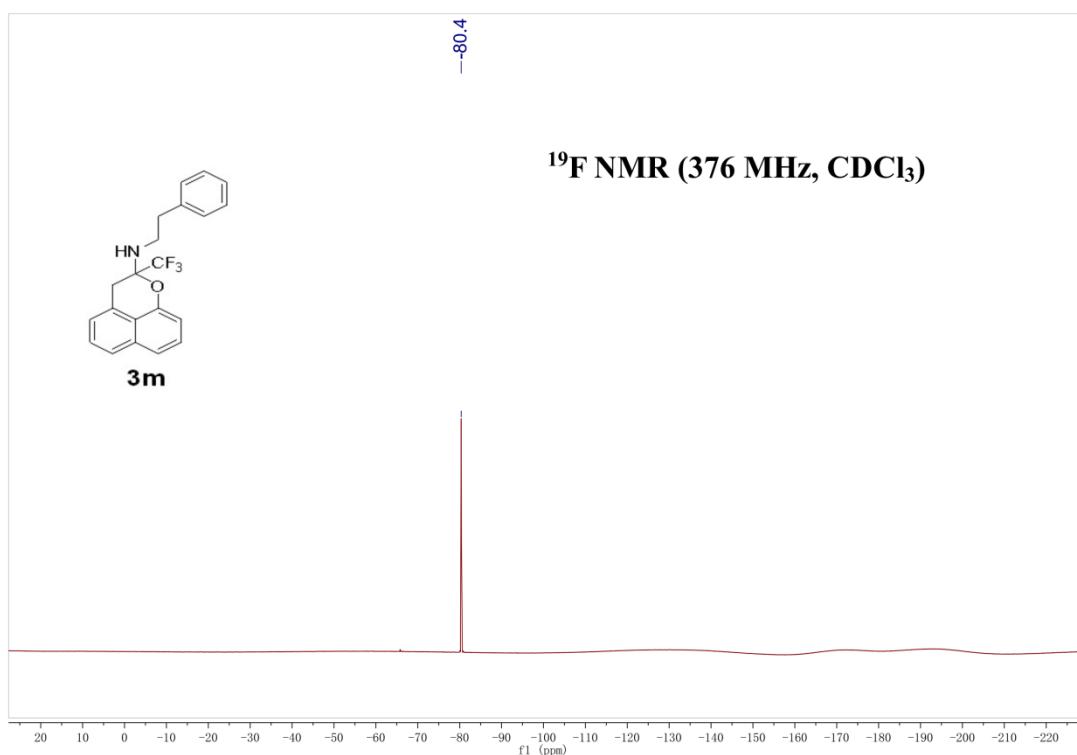
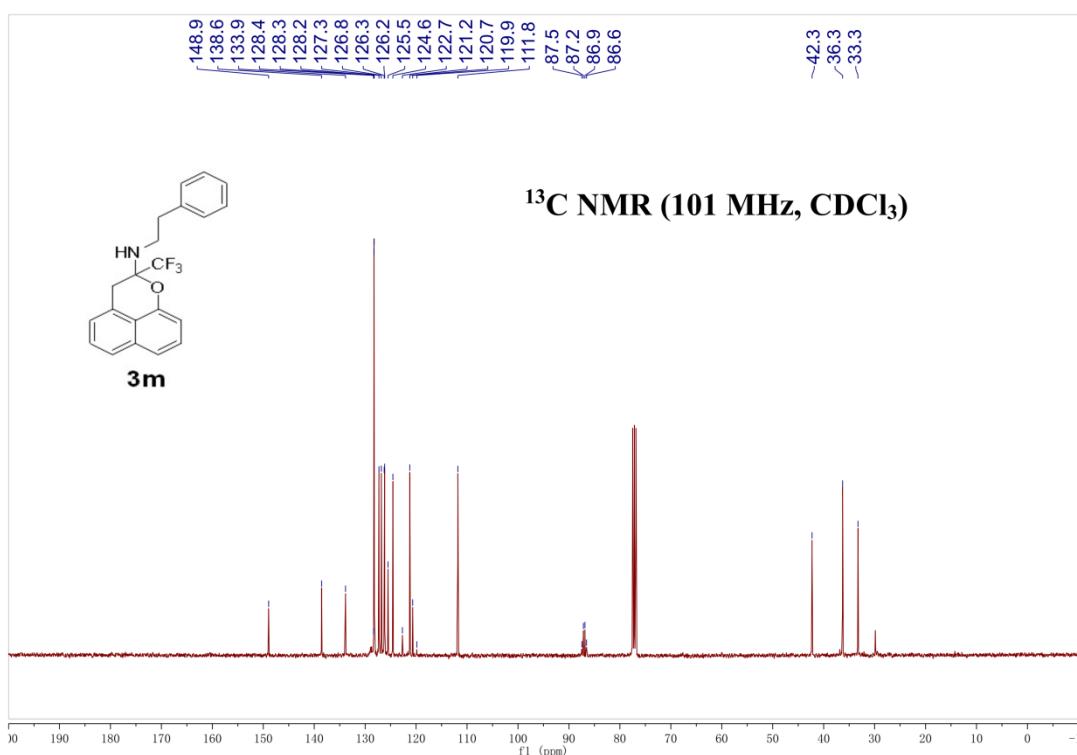


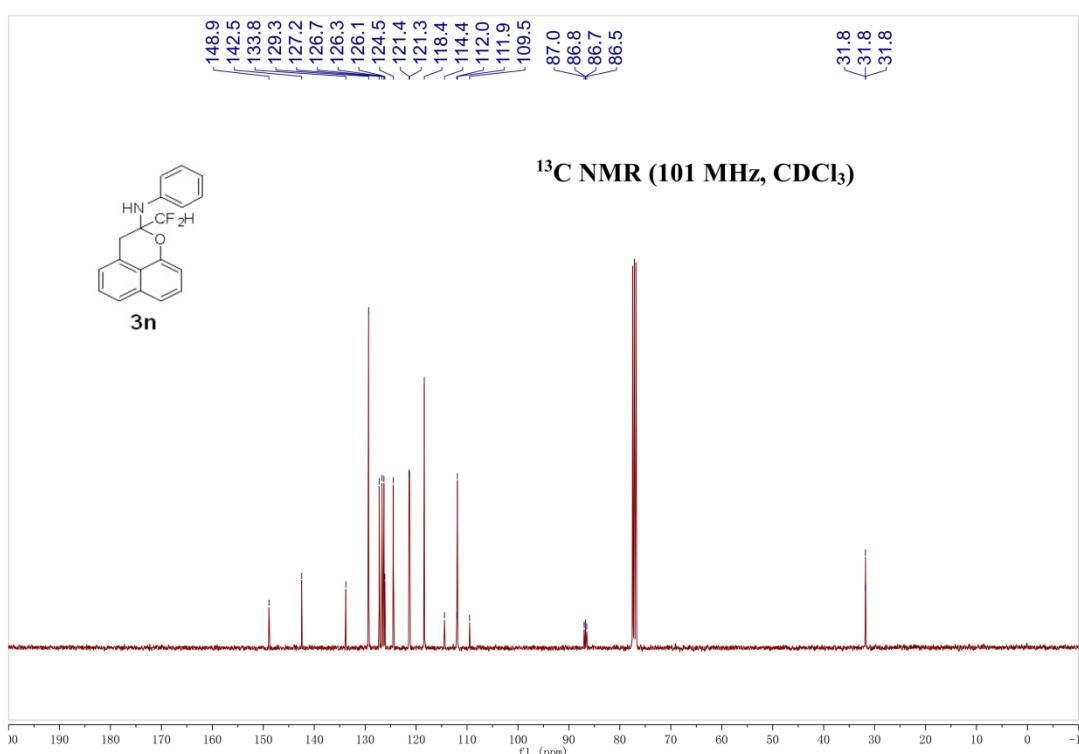
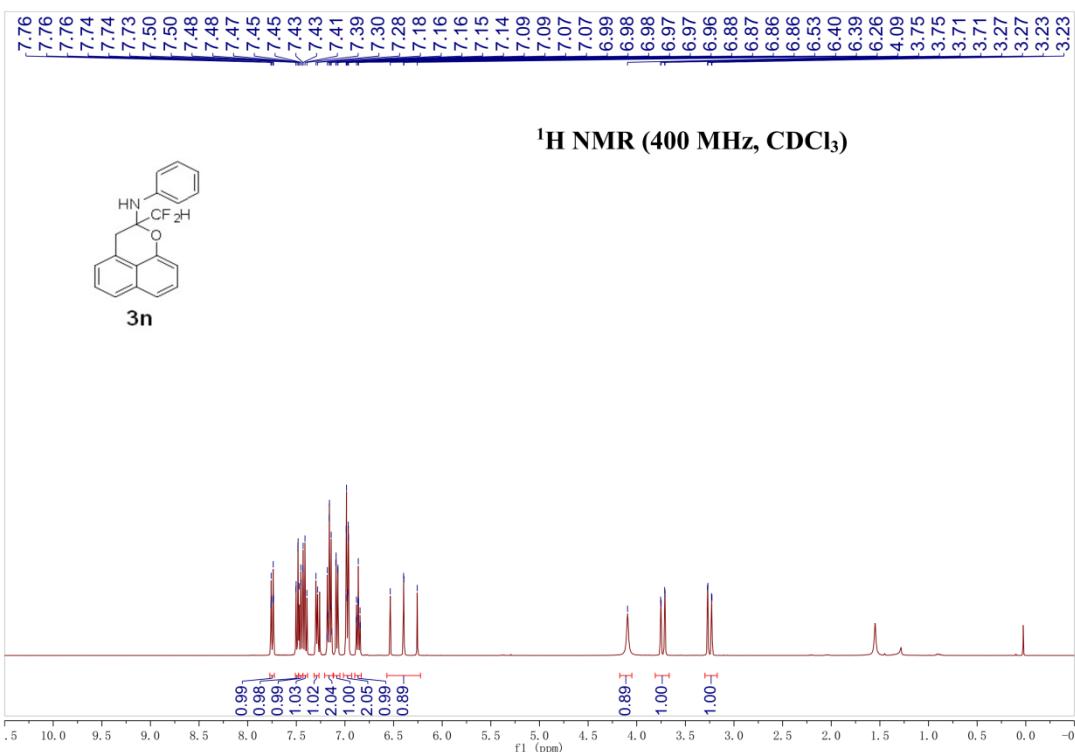


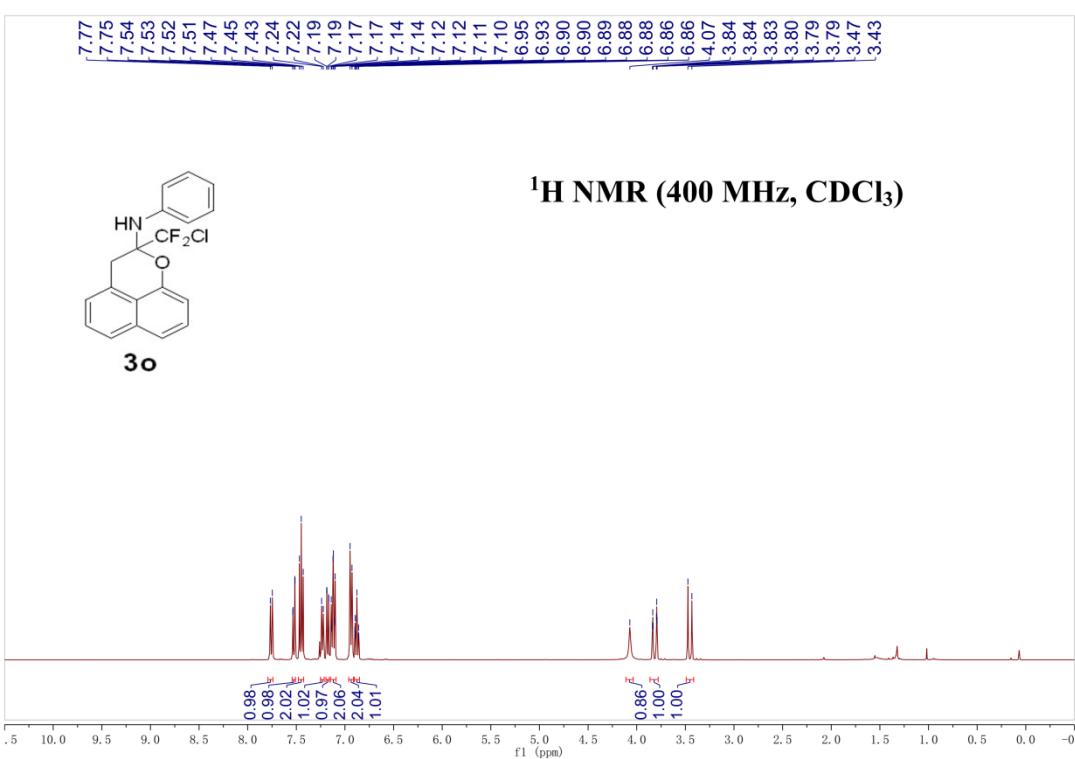
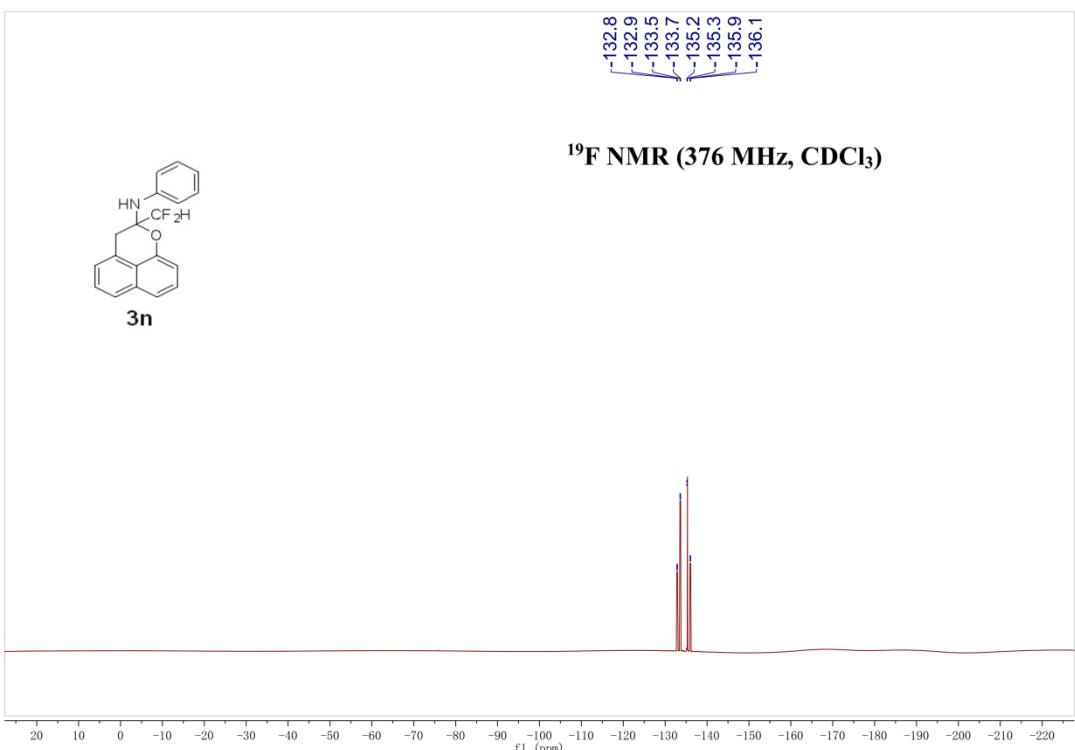


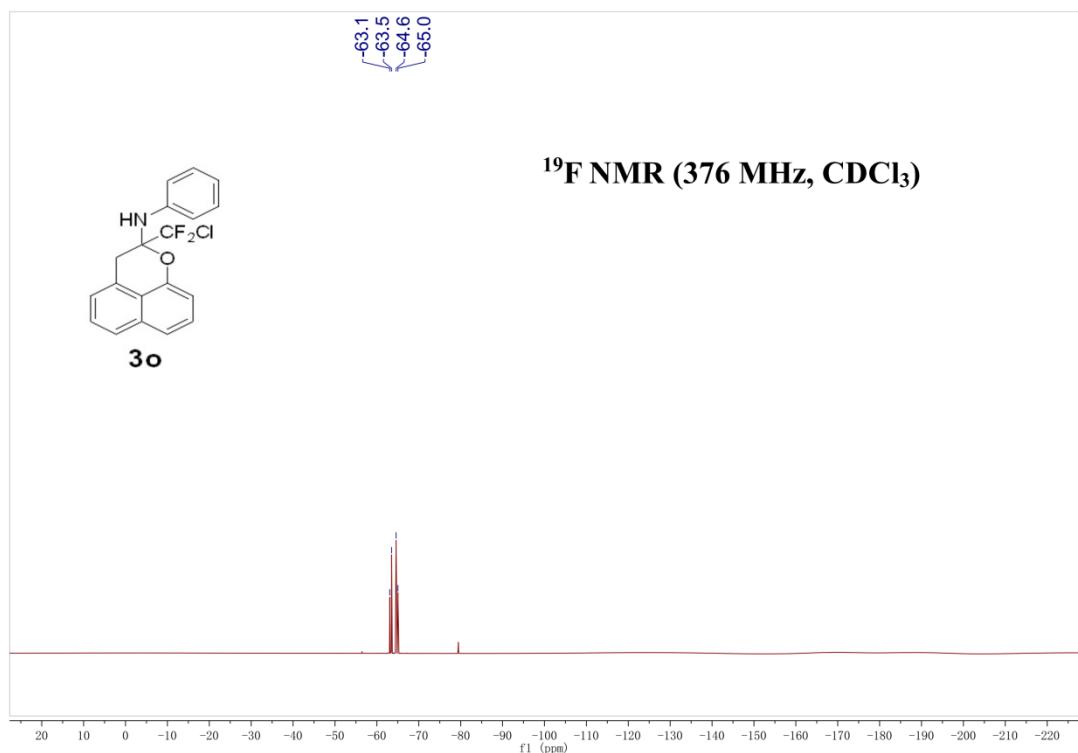
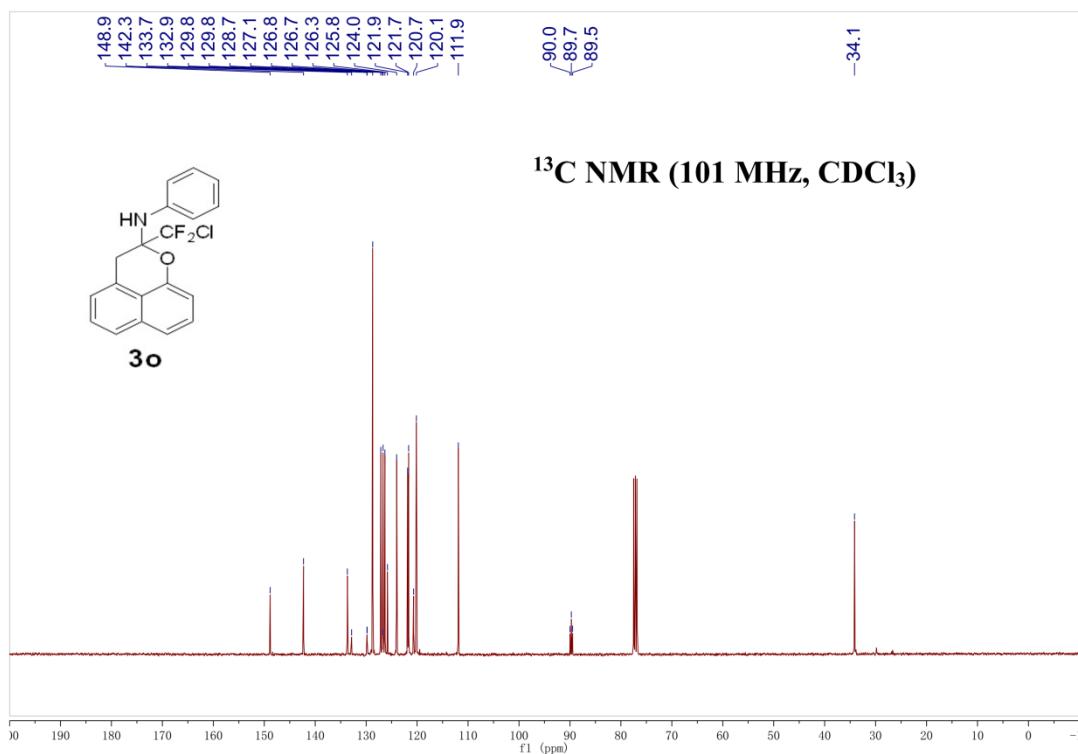


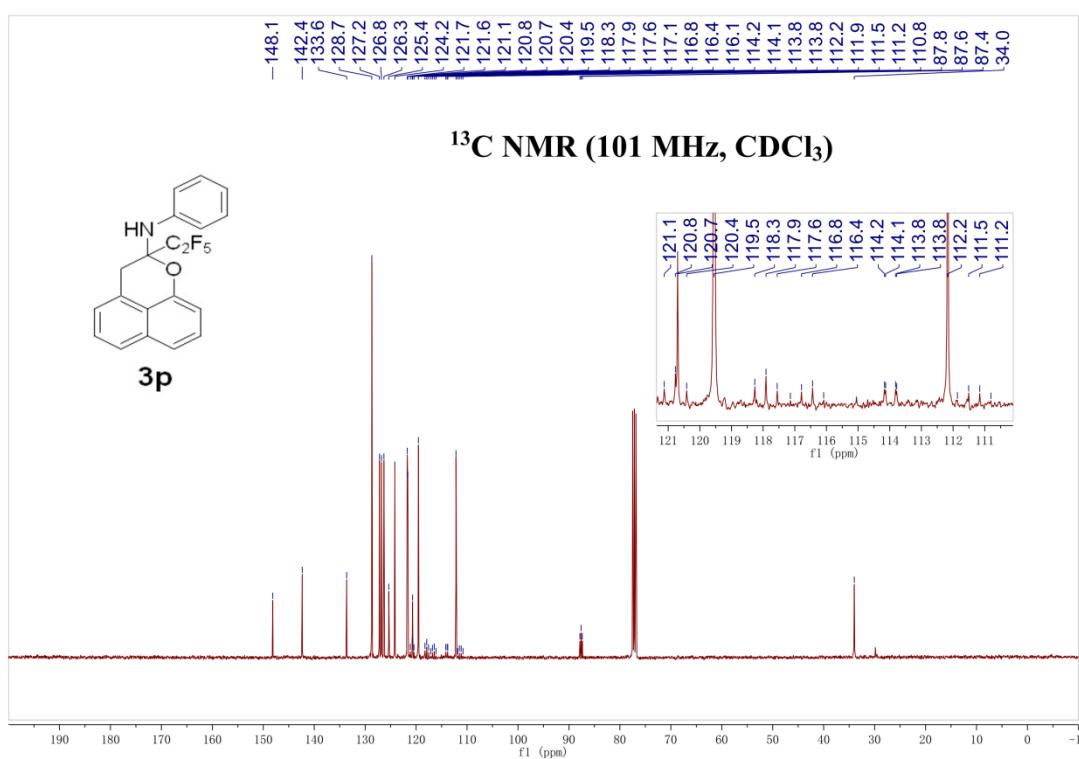
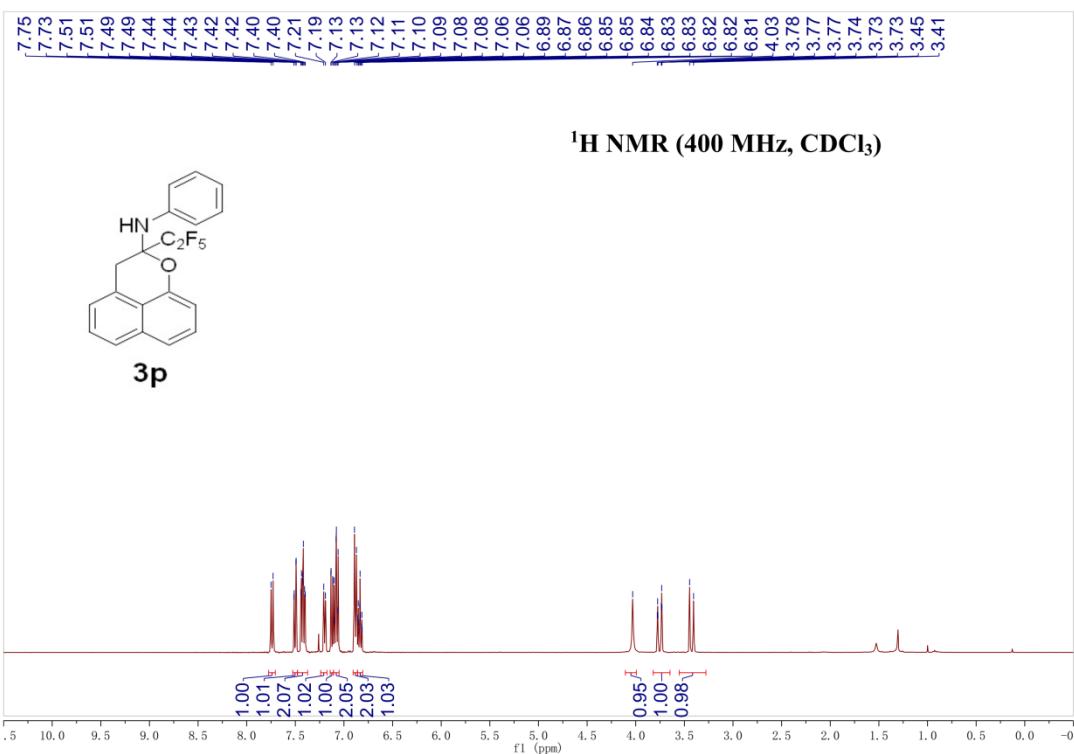


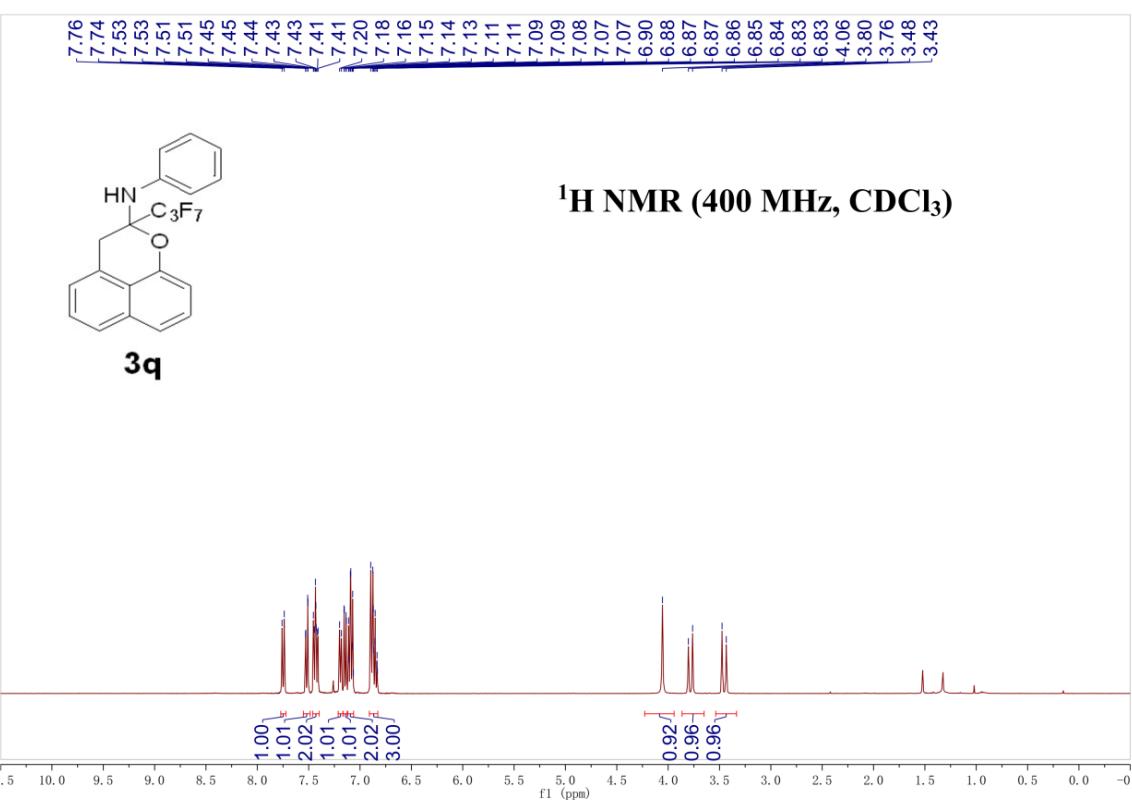
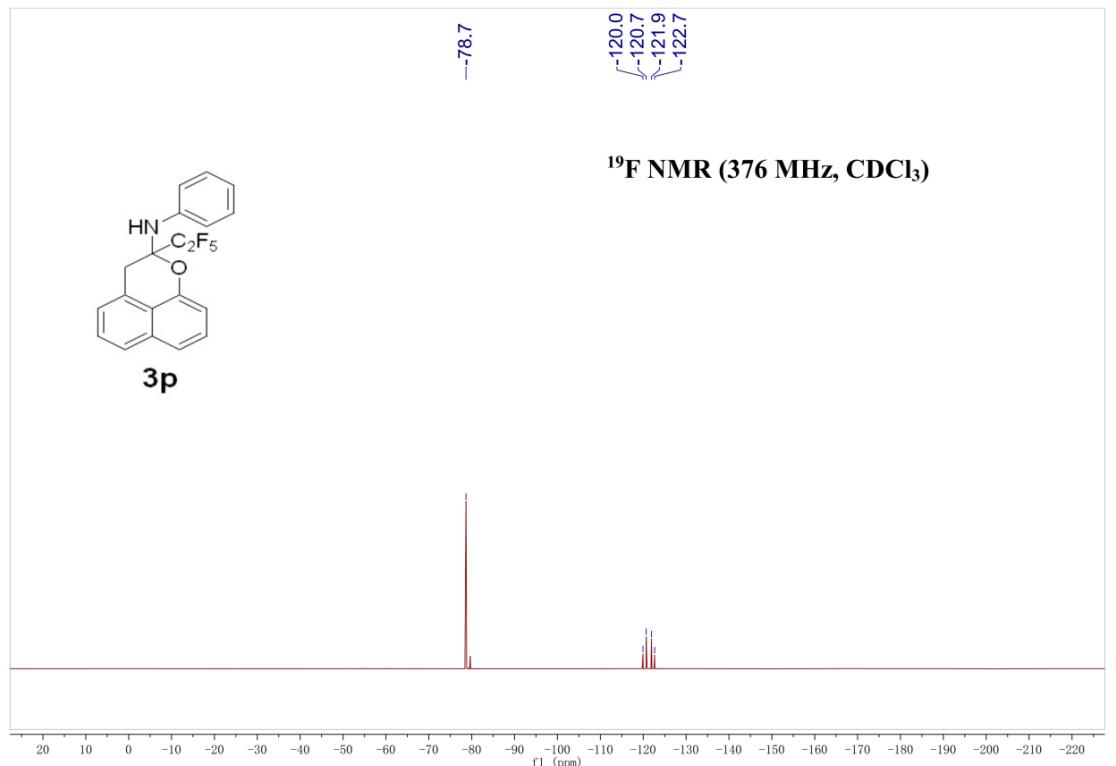


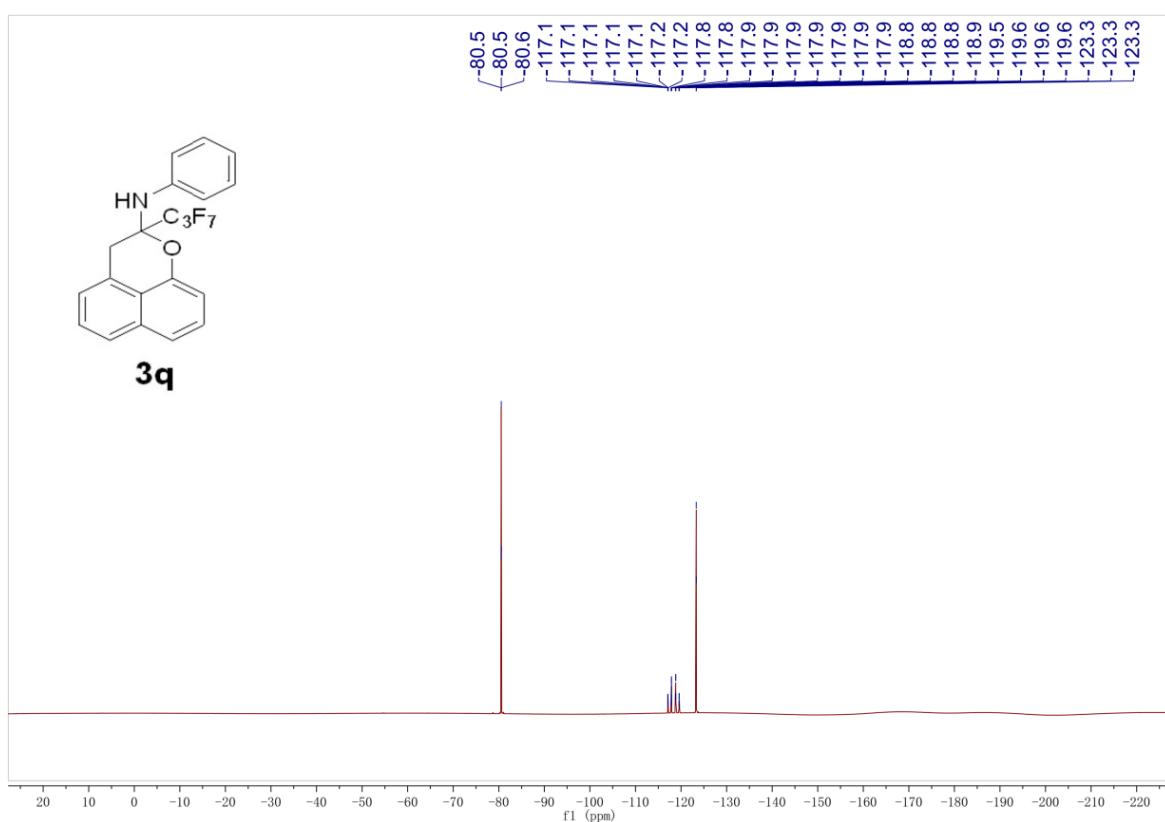
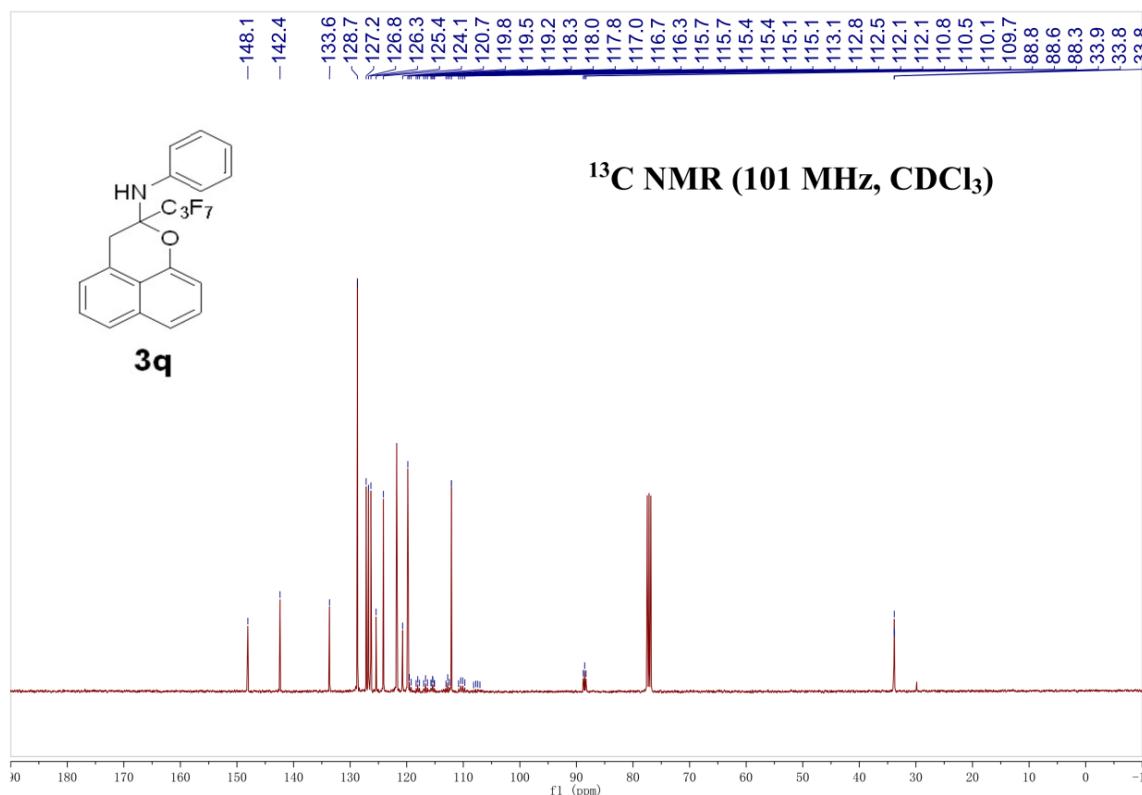


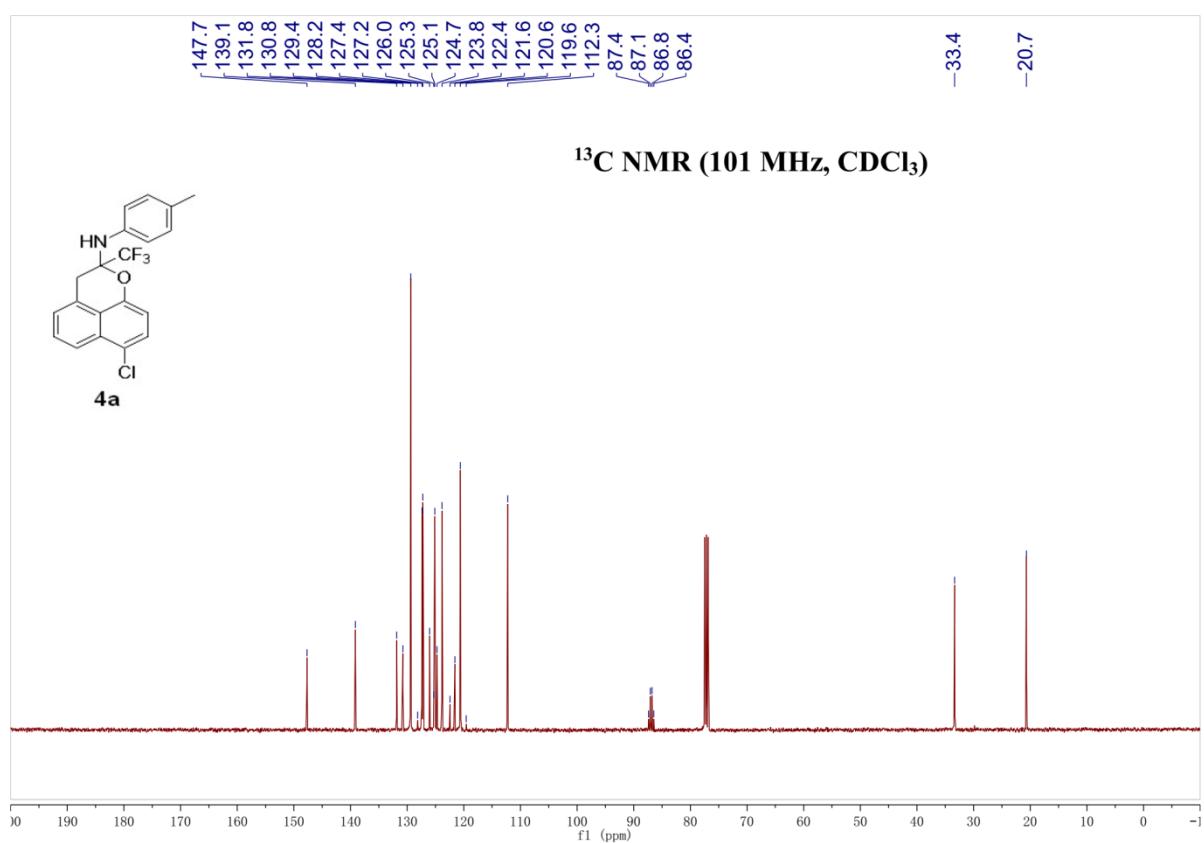
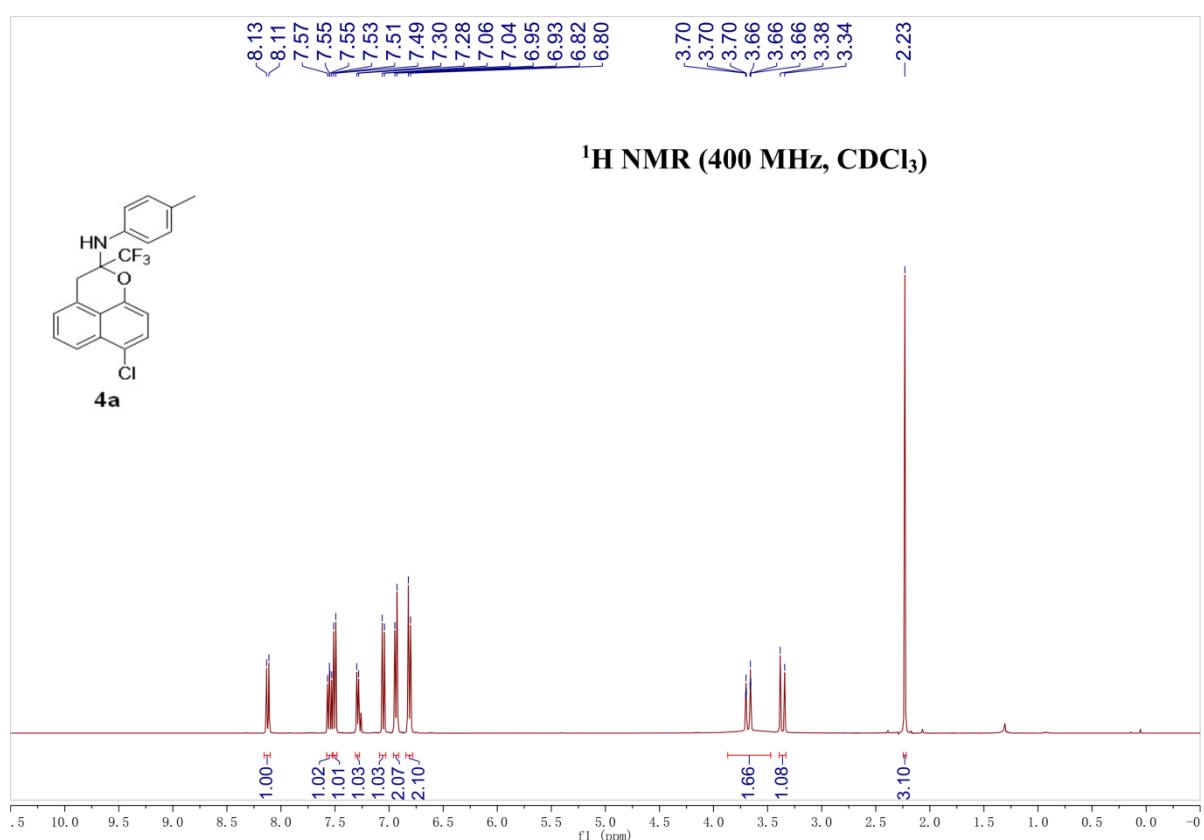


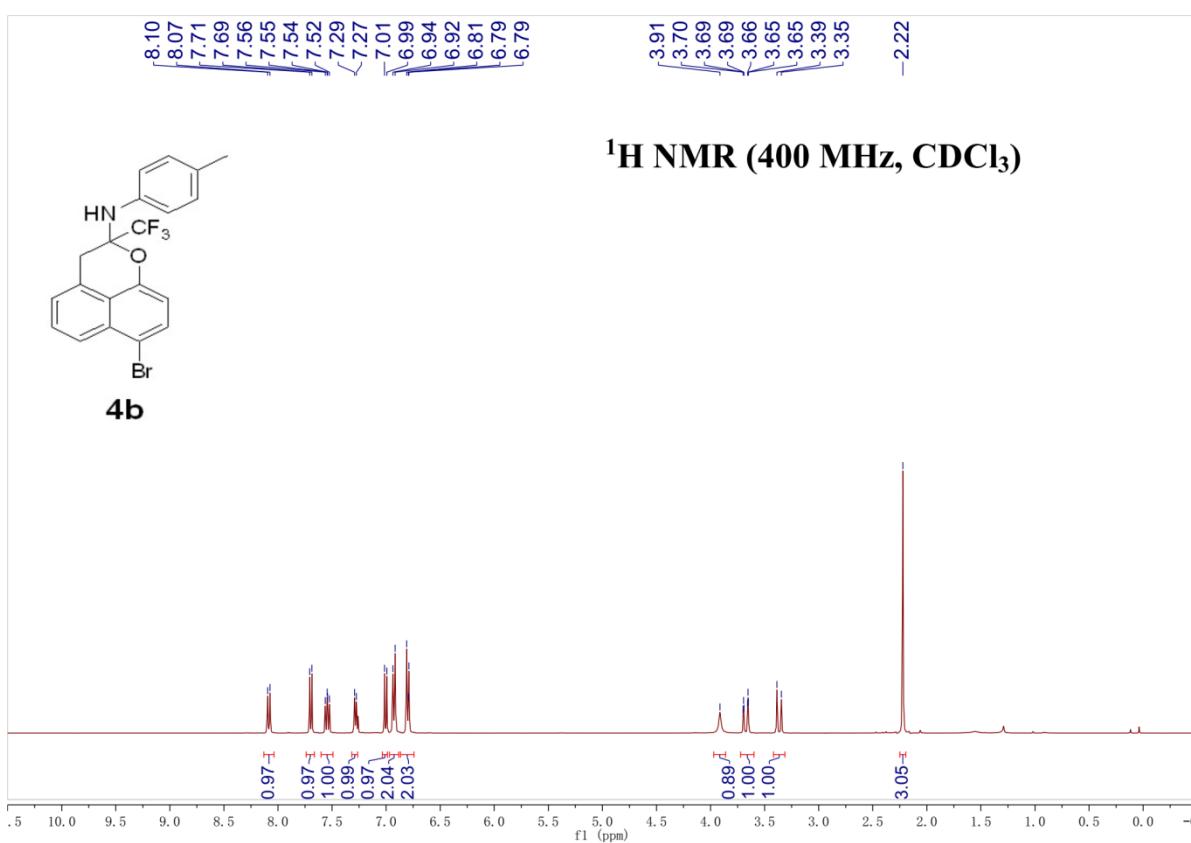
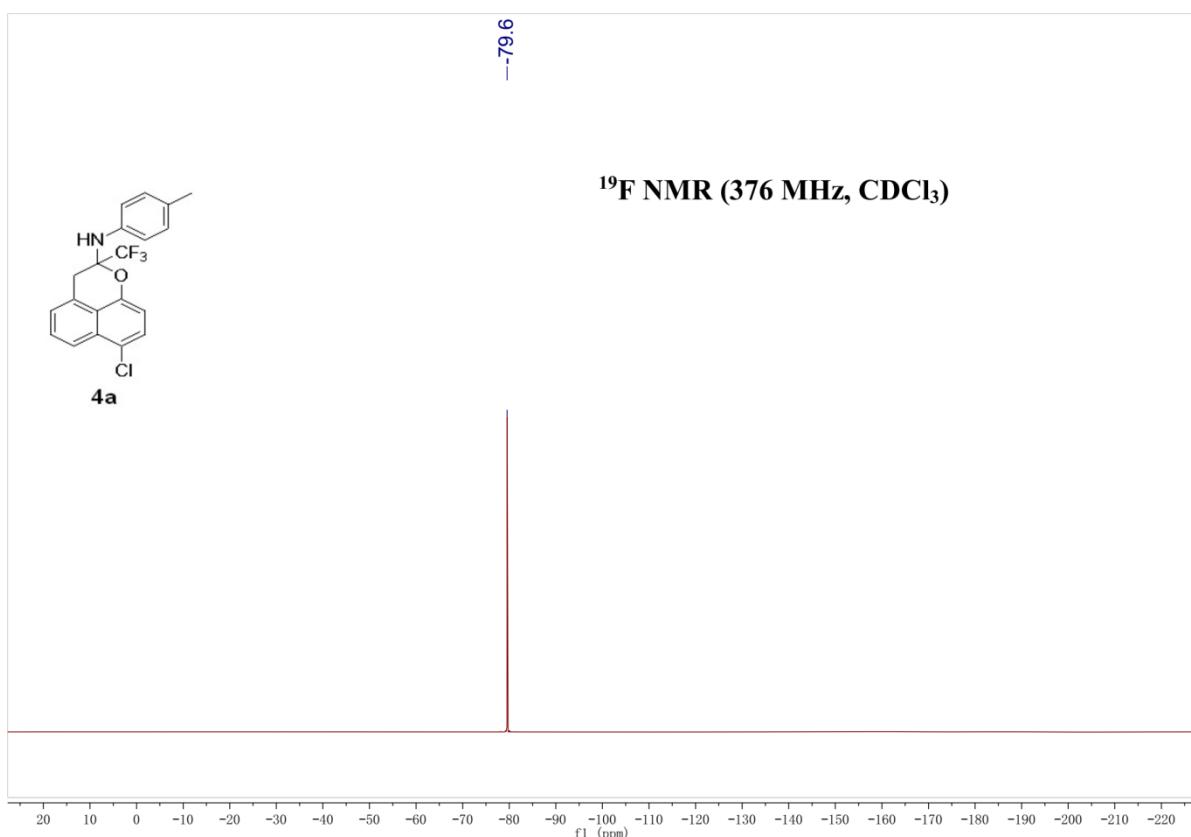


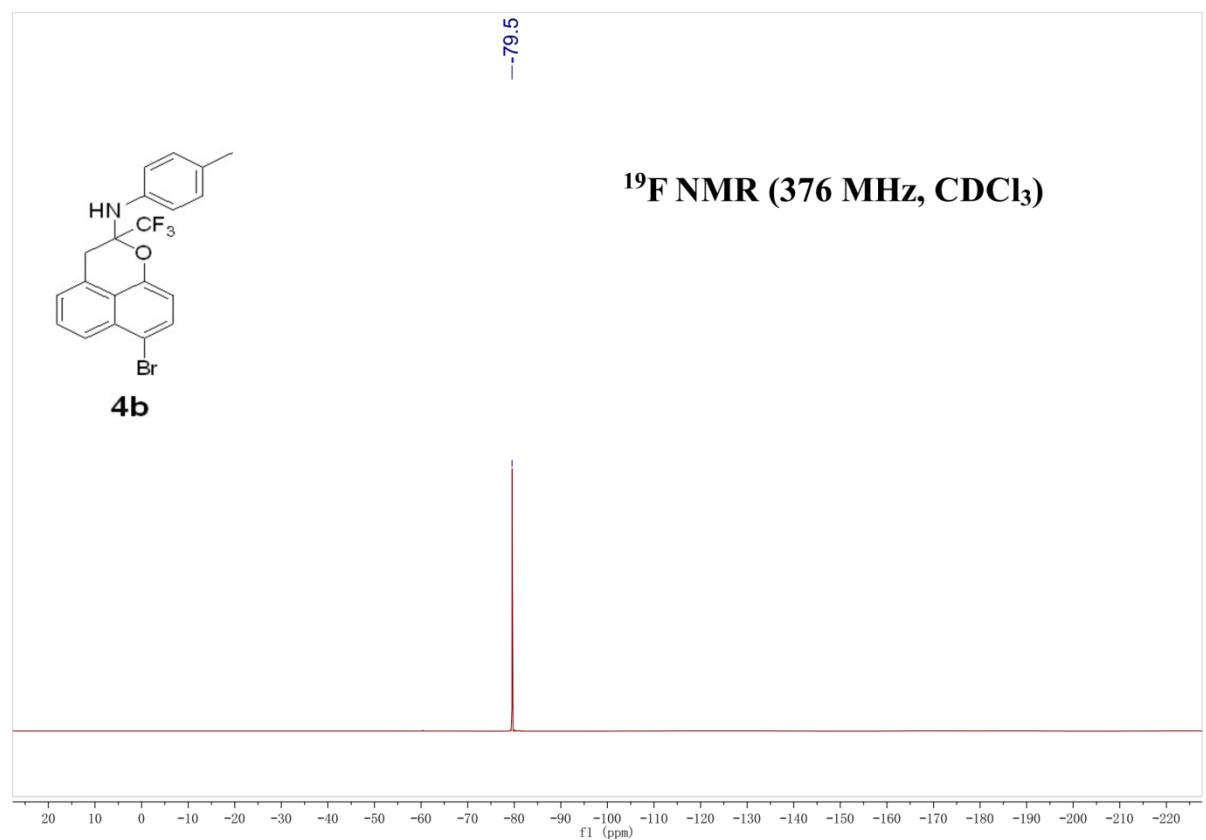
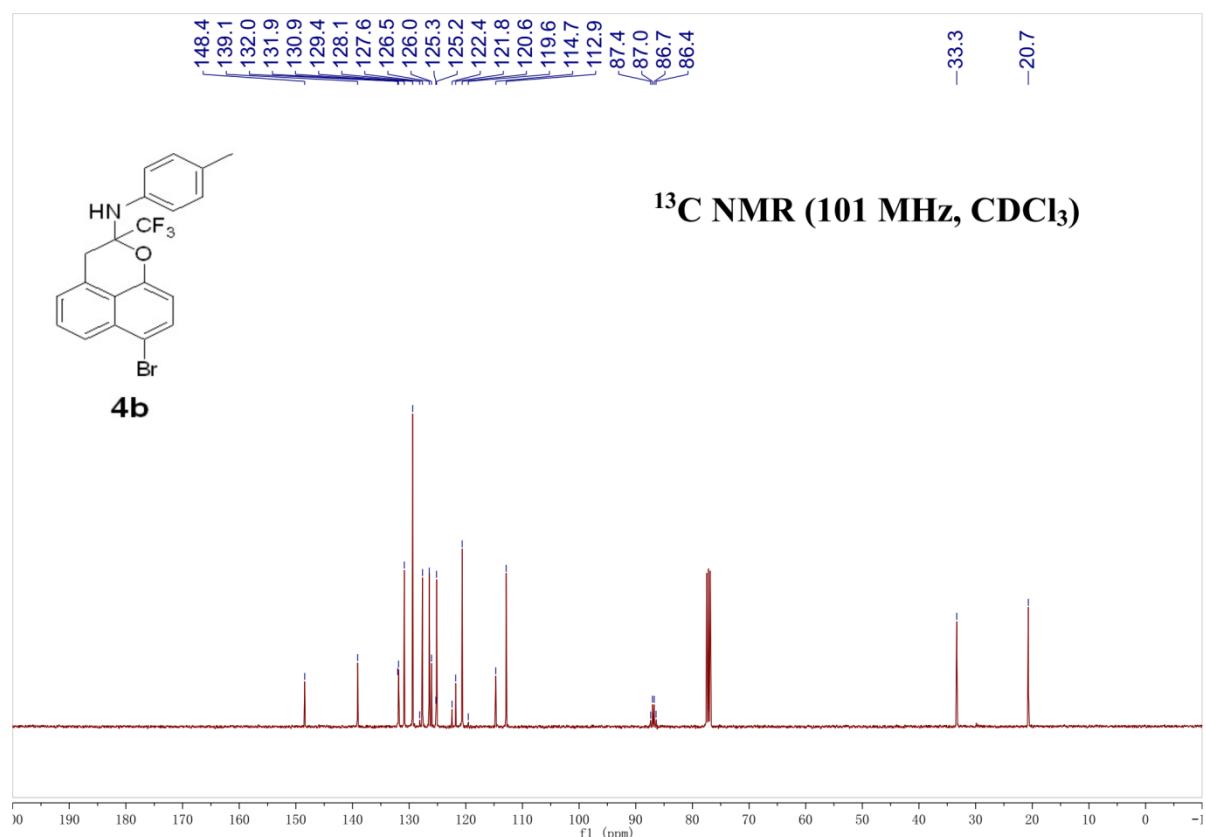


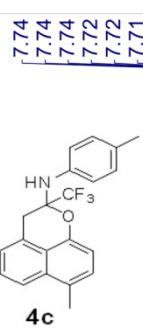




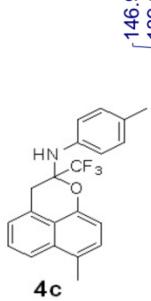
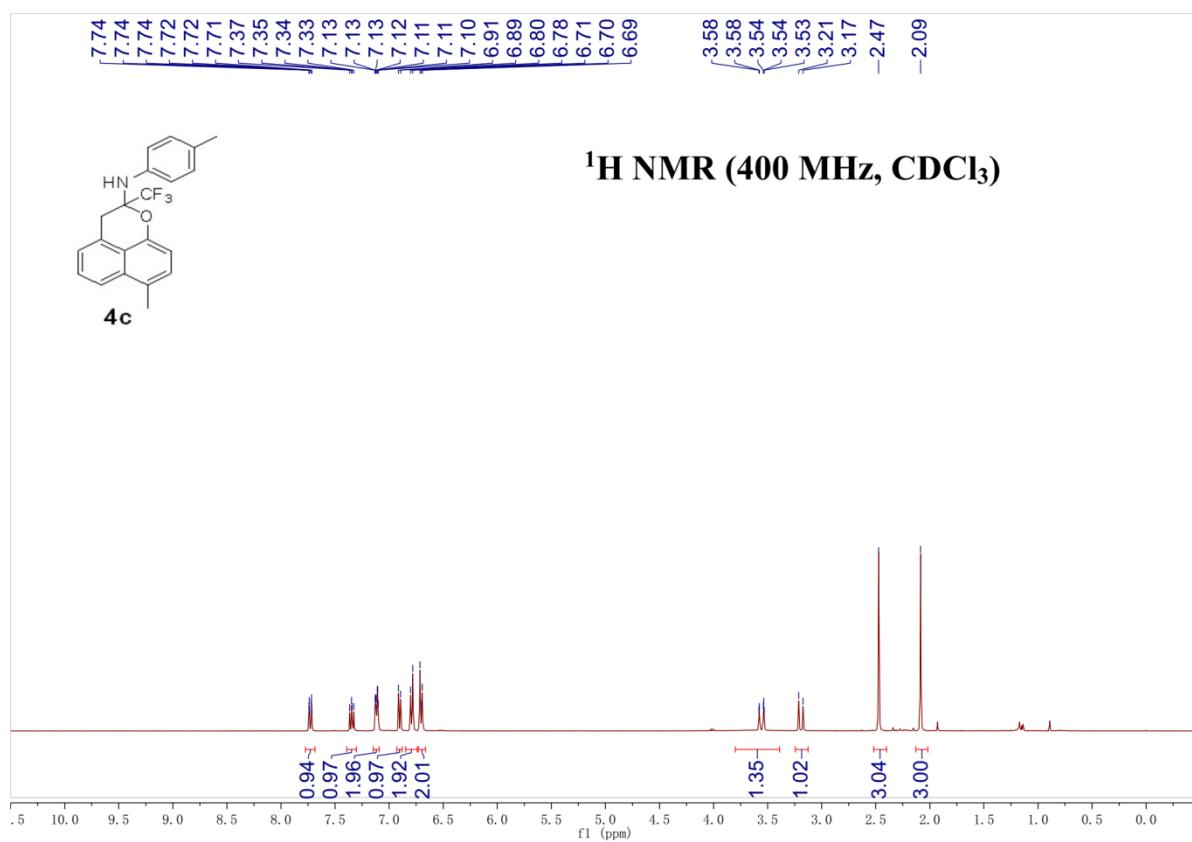




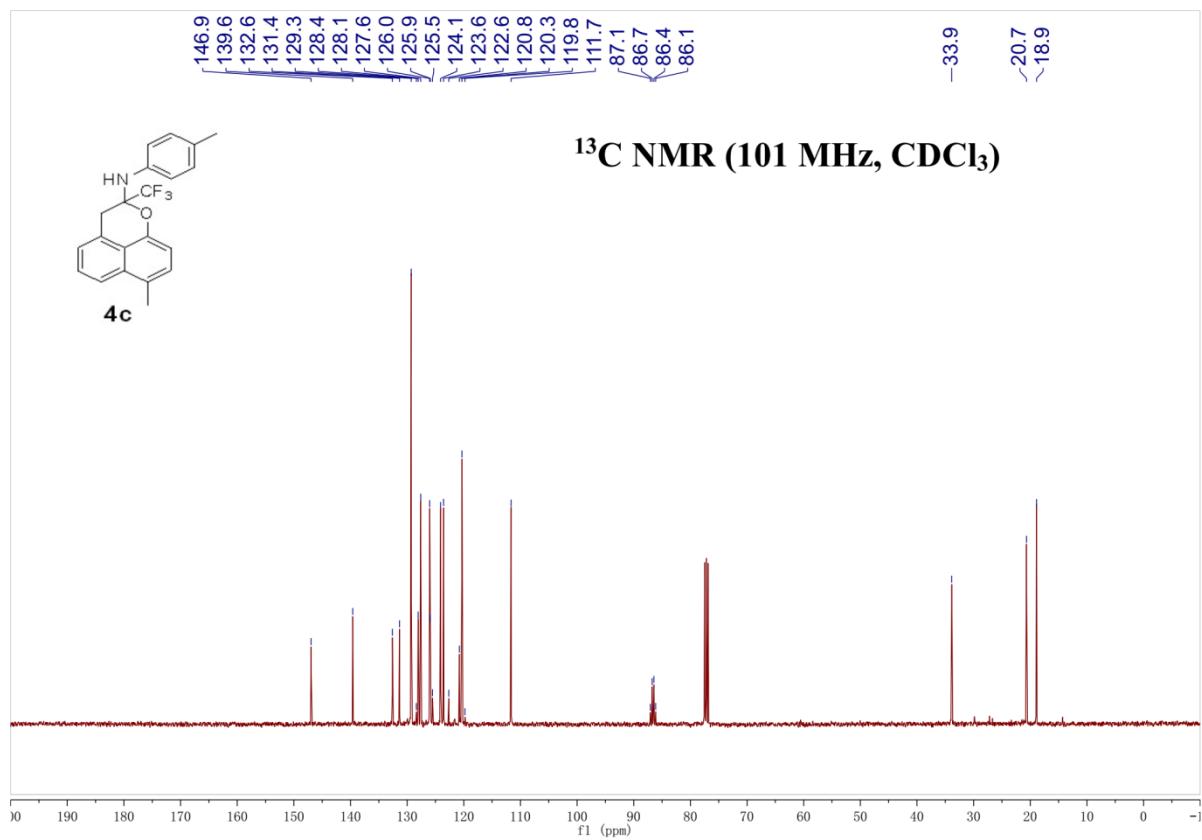


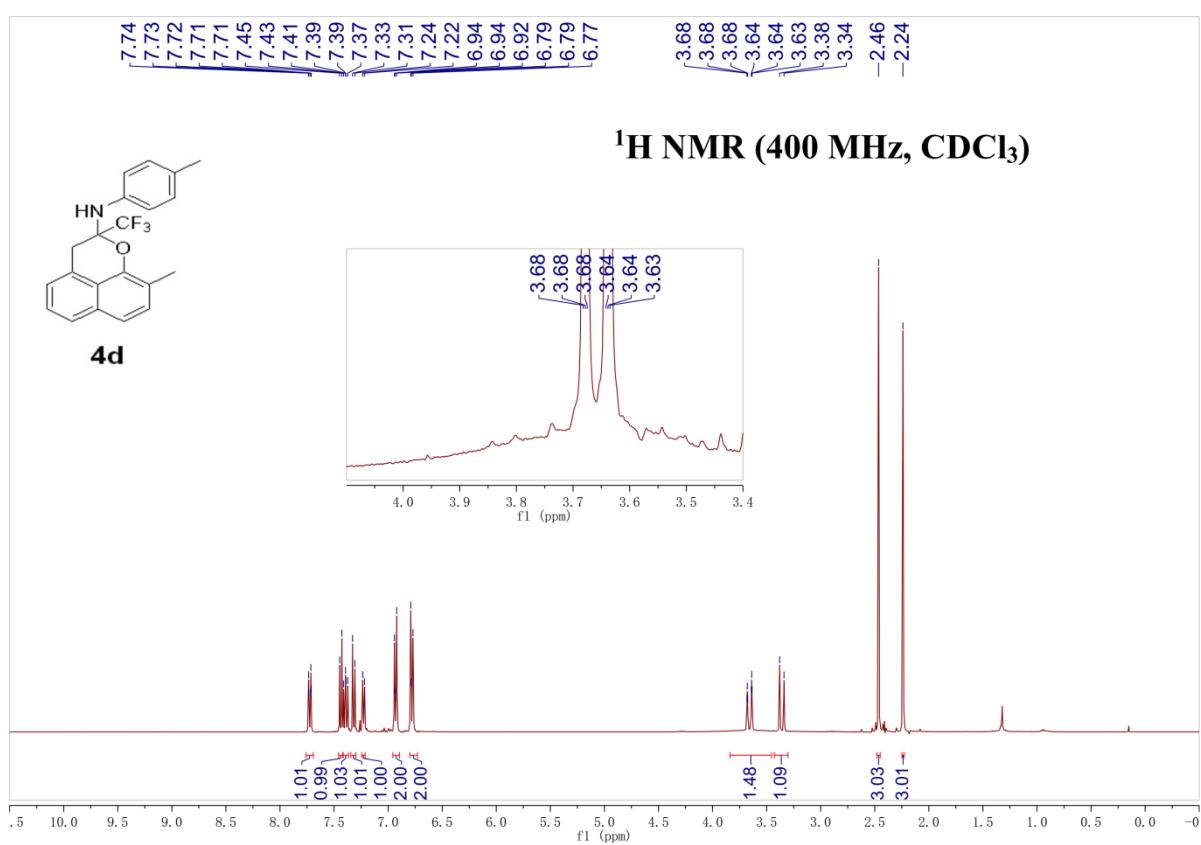
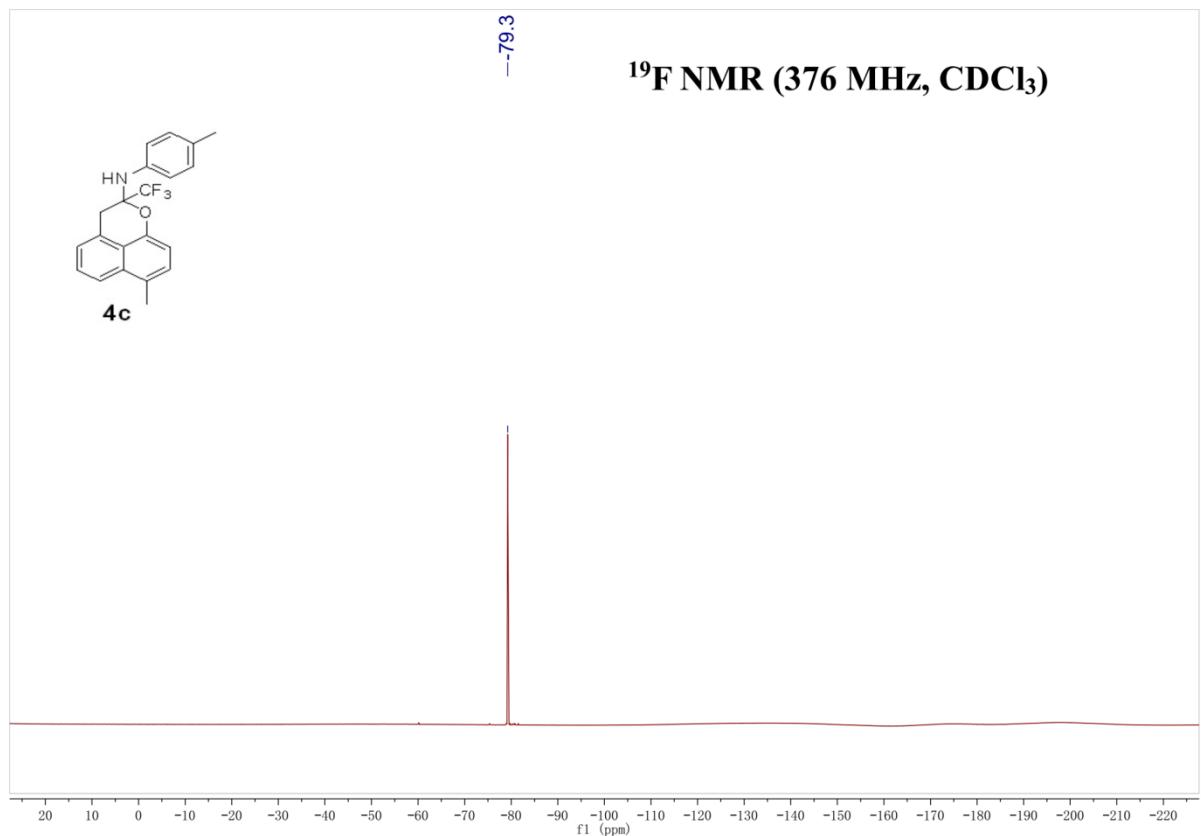


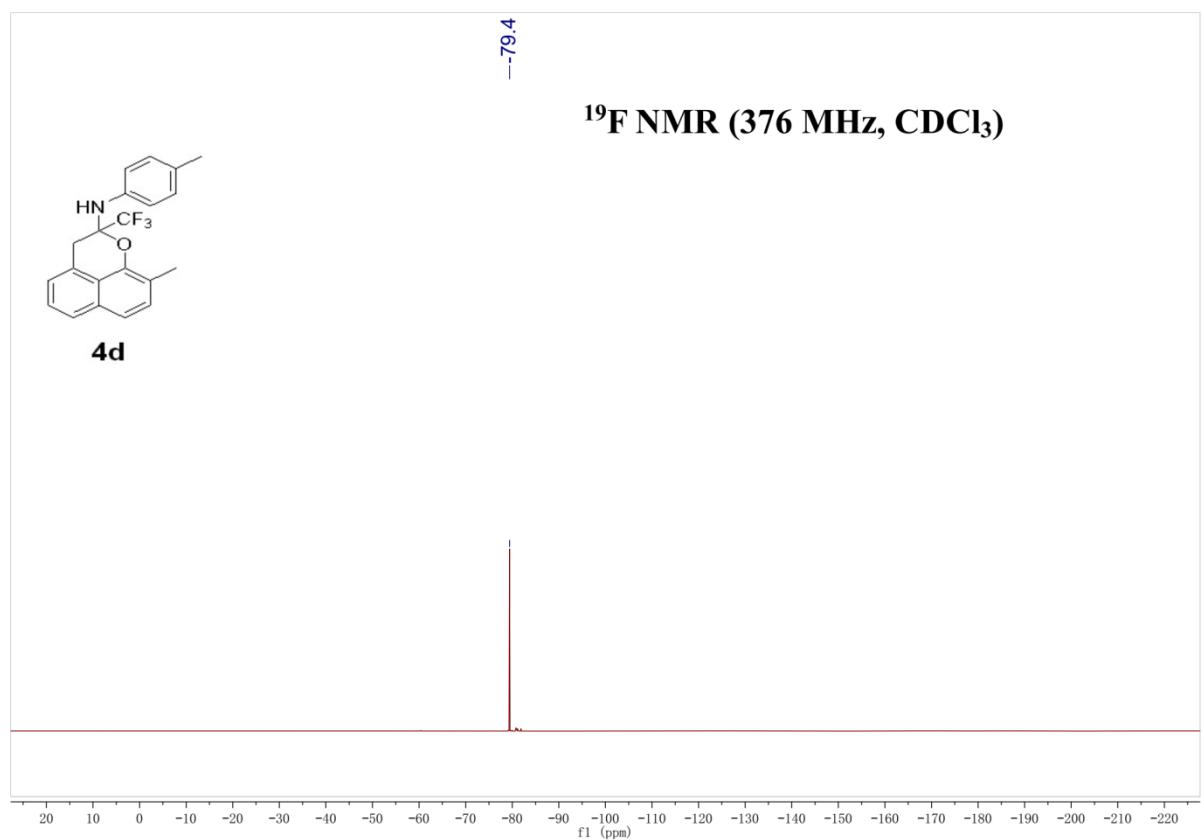
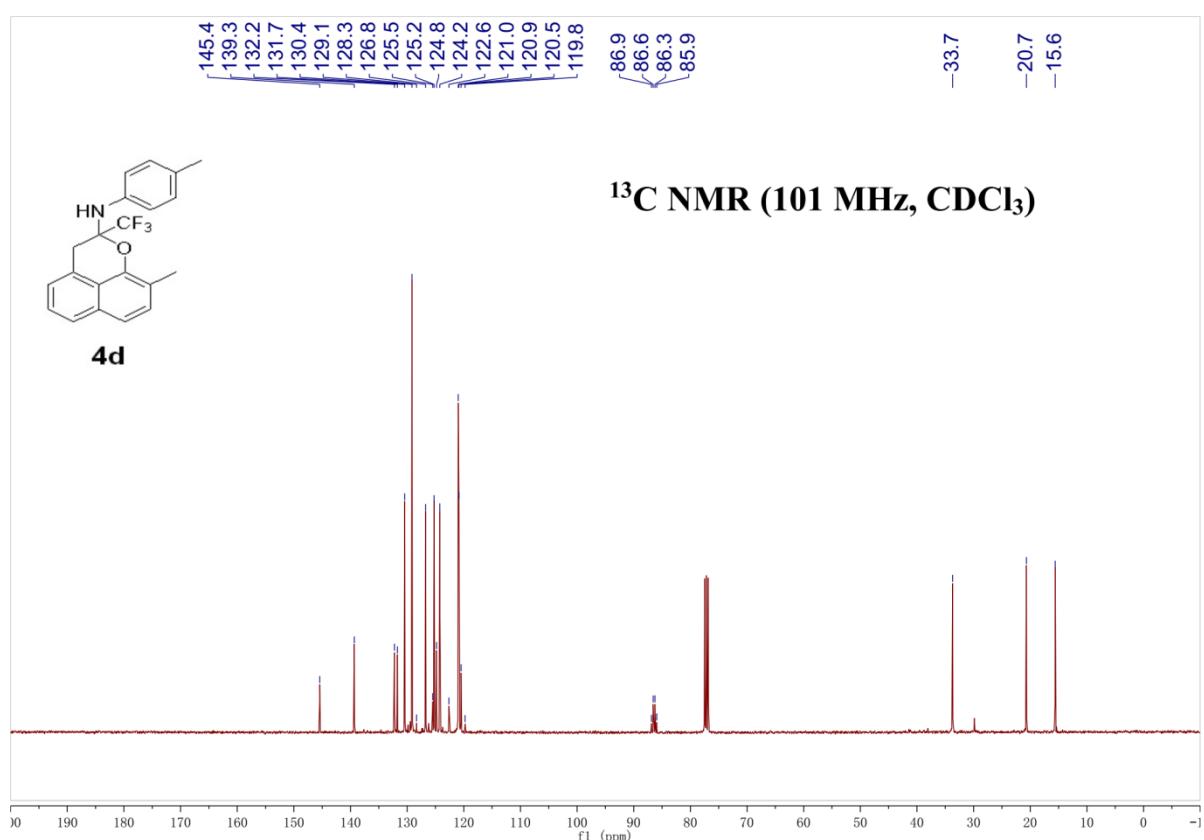
¹H NMR (400 MHz, CDCl₃)

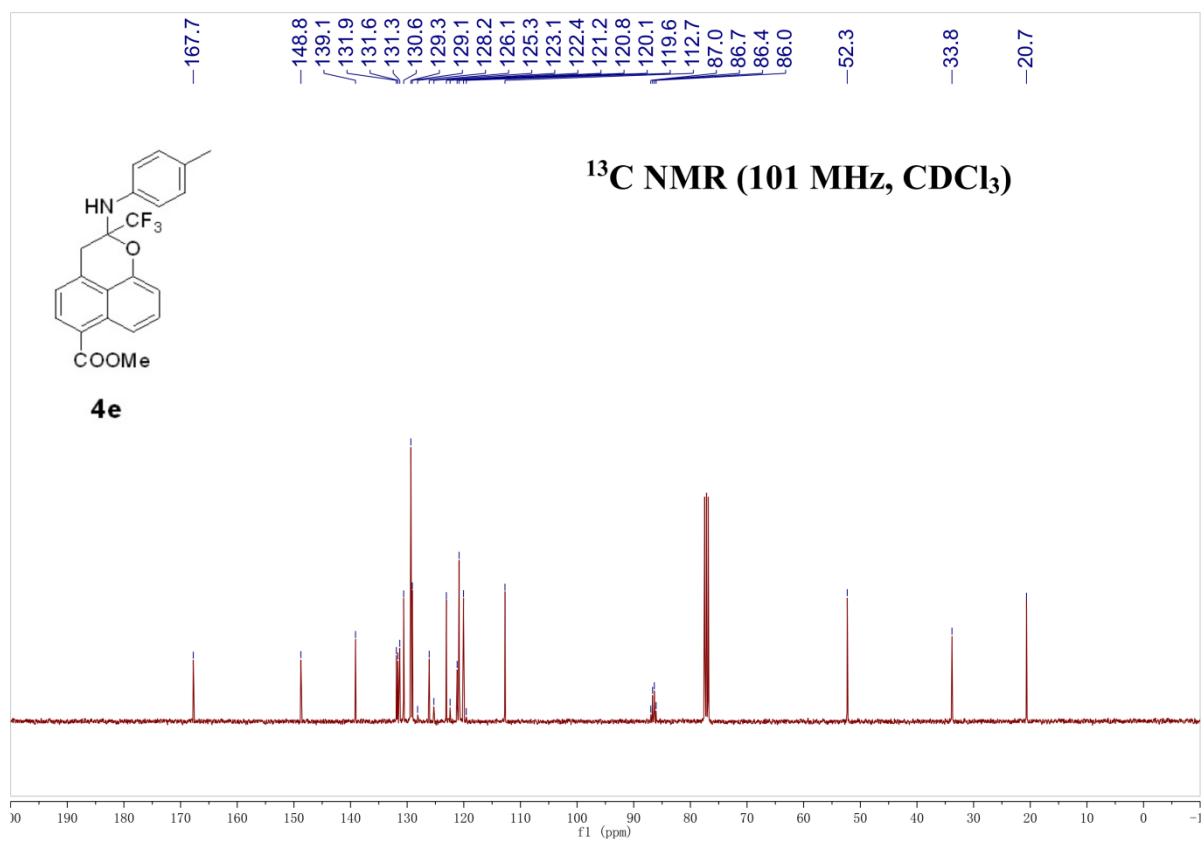
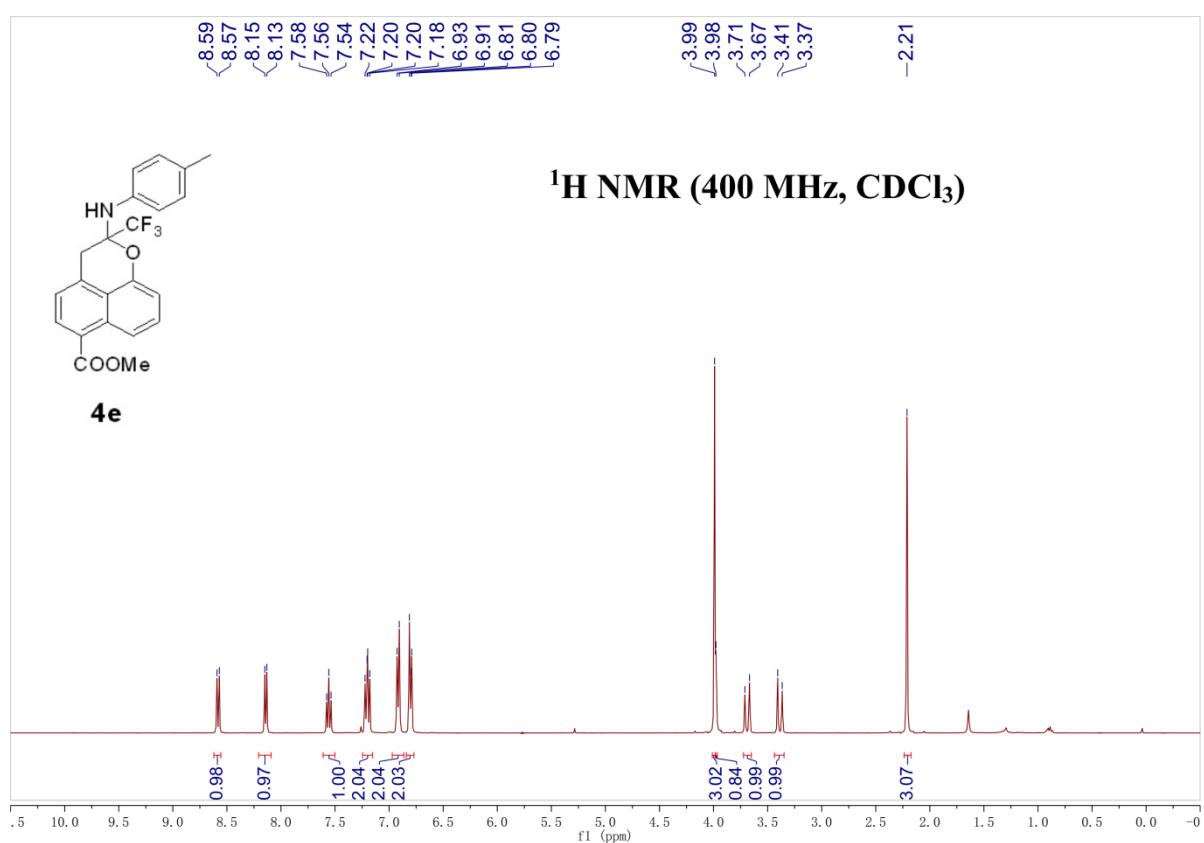


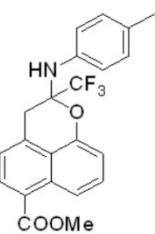
¹³C NMR (101 MHz, CDCl₃)





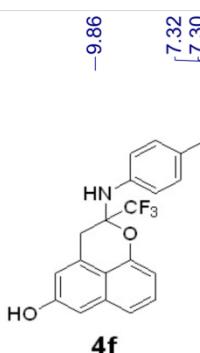
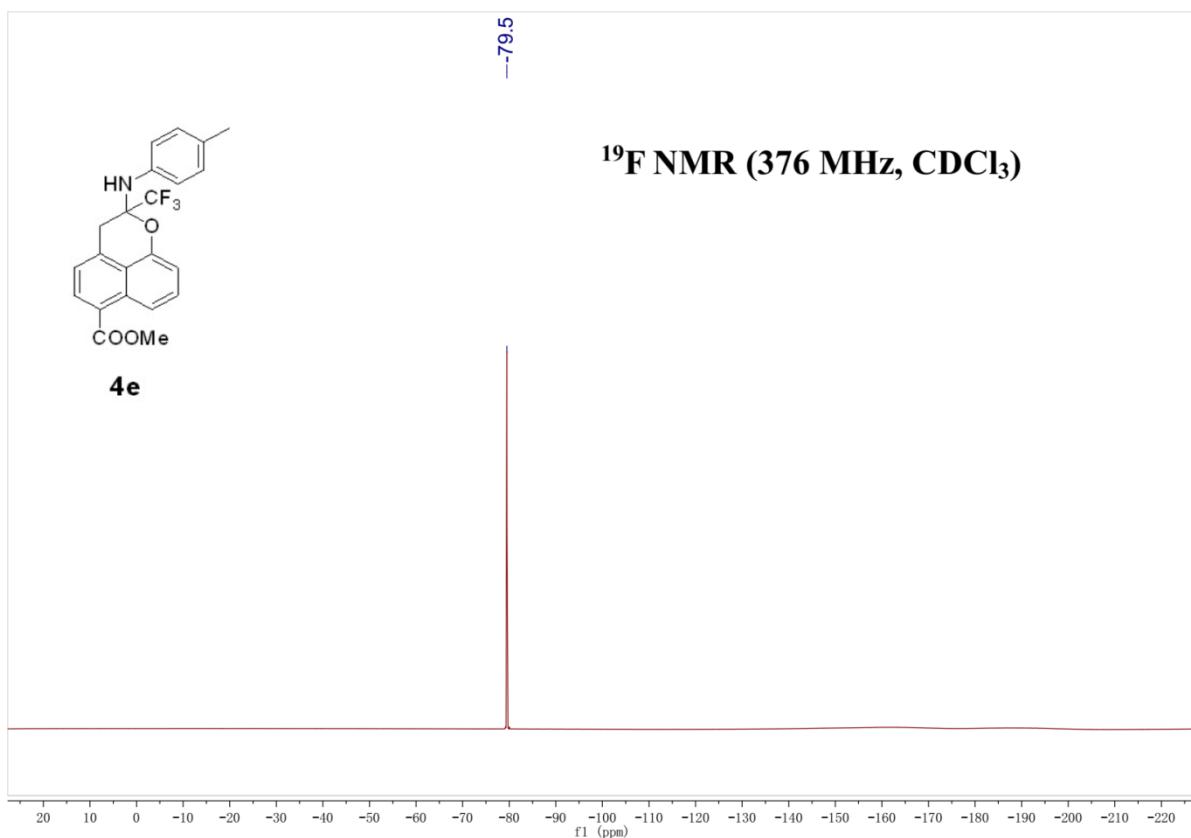






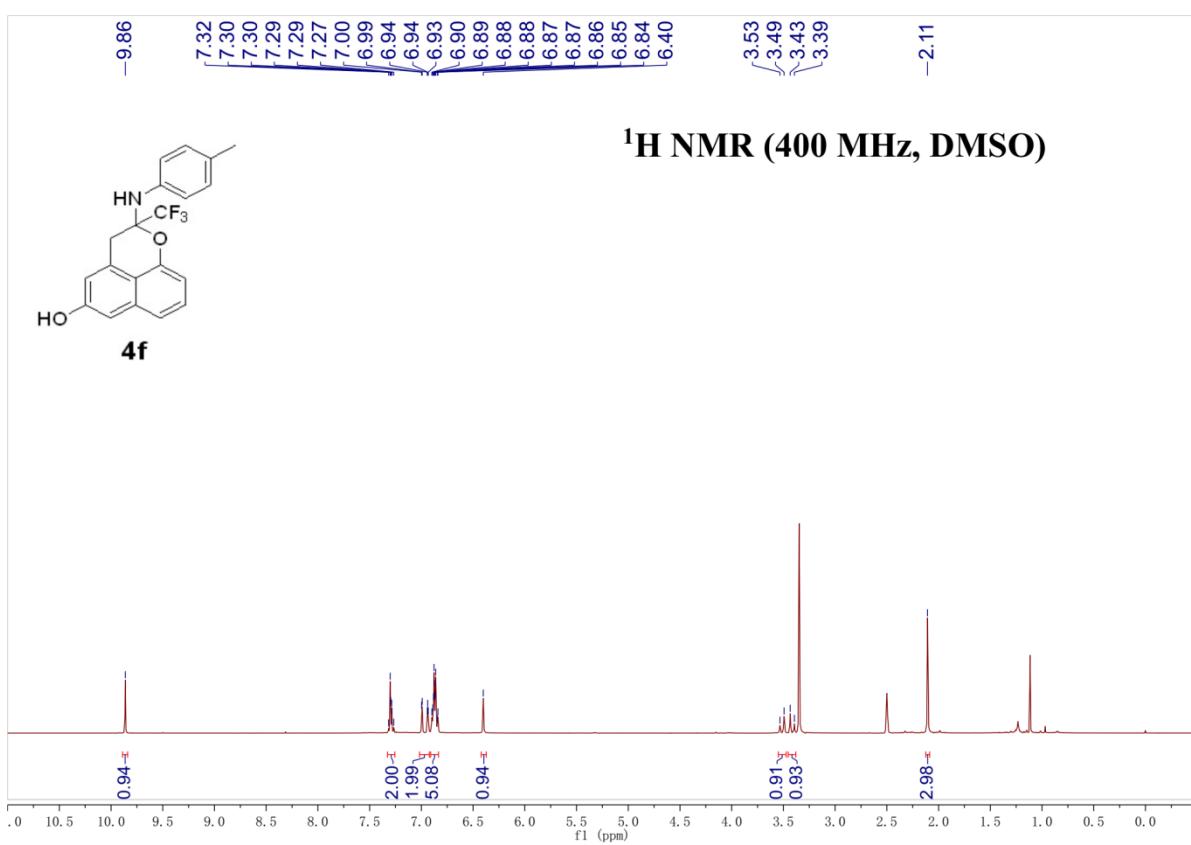
4e

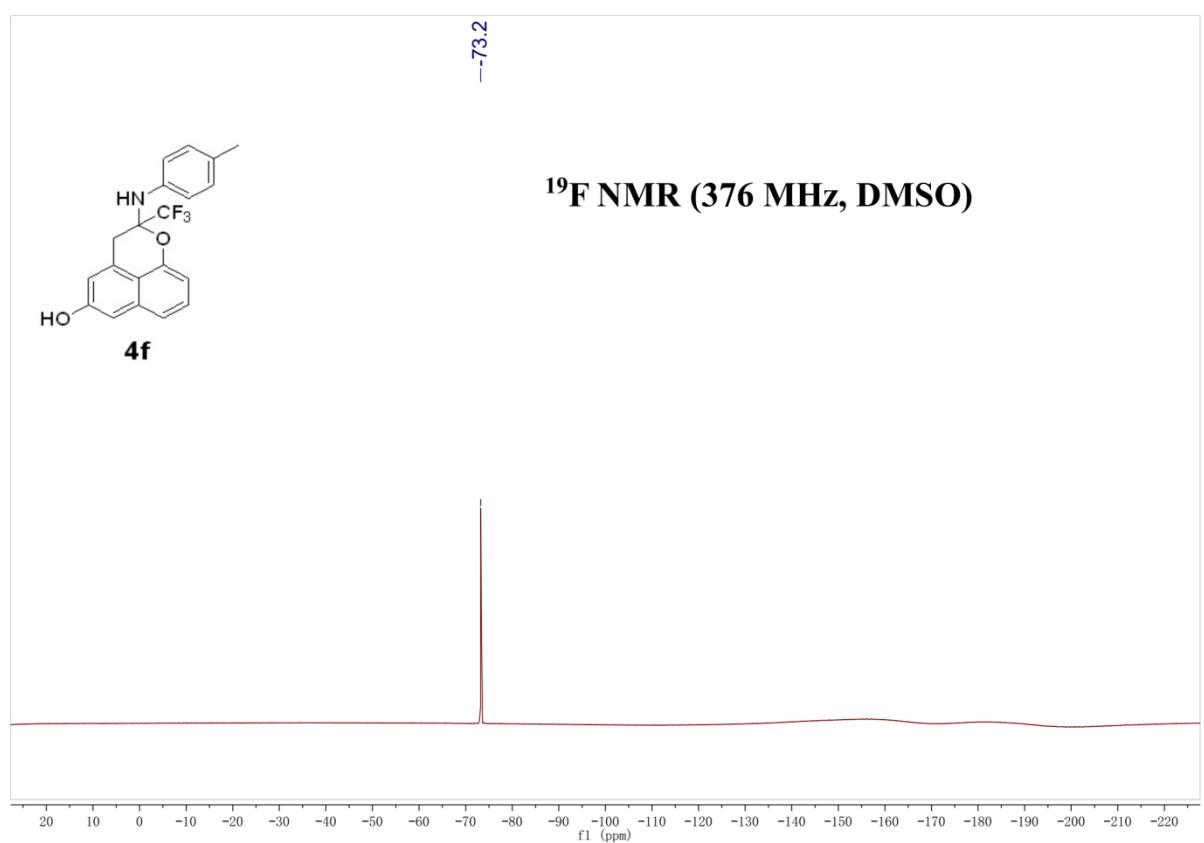
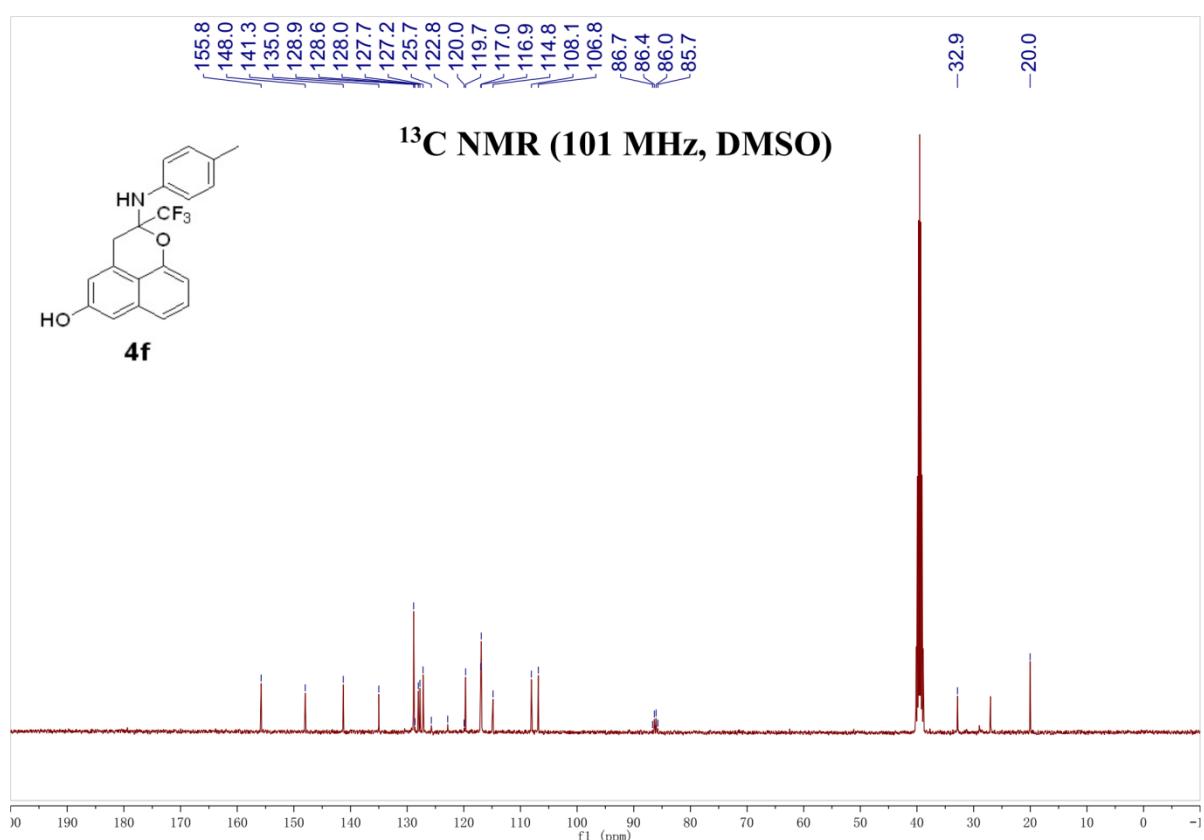
¹⁹F NMR (376 MHz, CDCl₃)

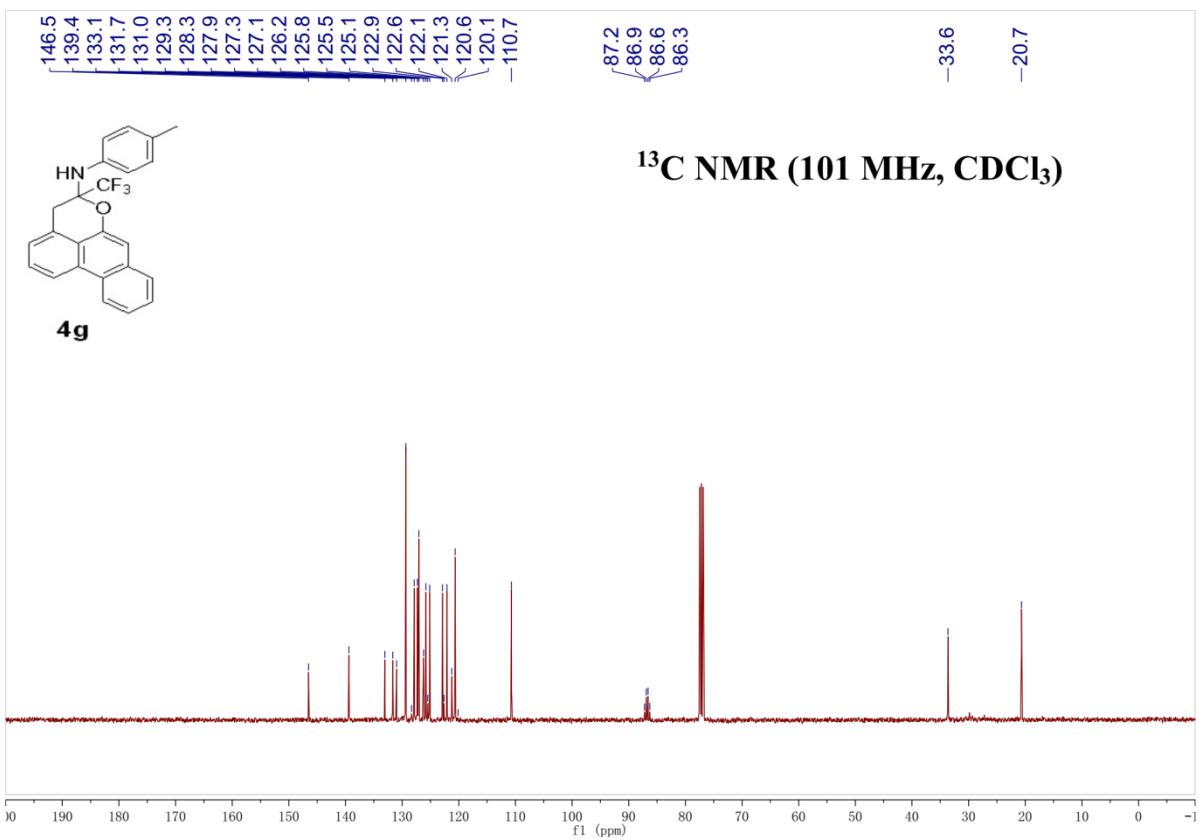
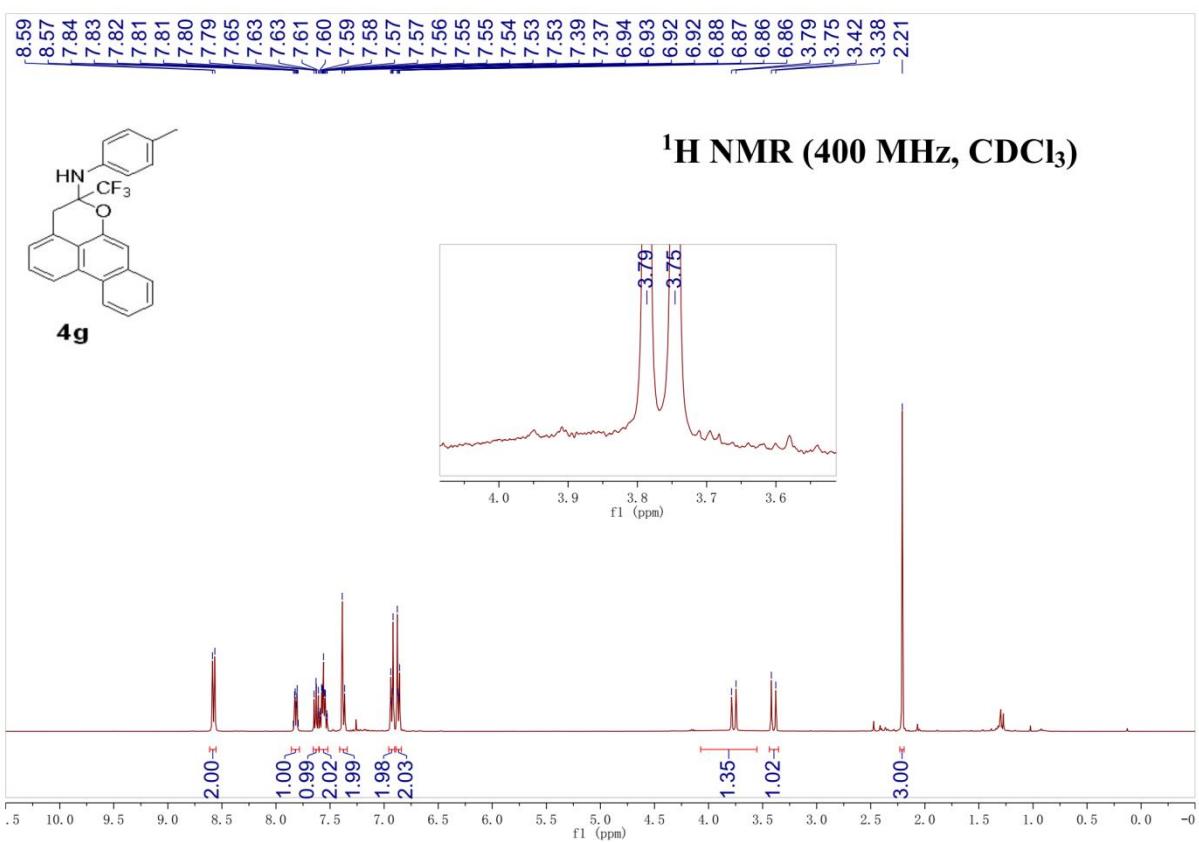


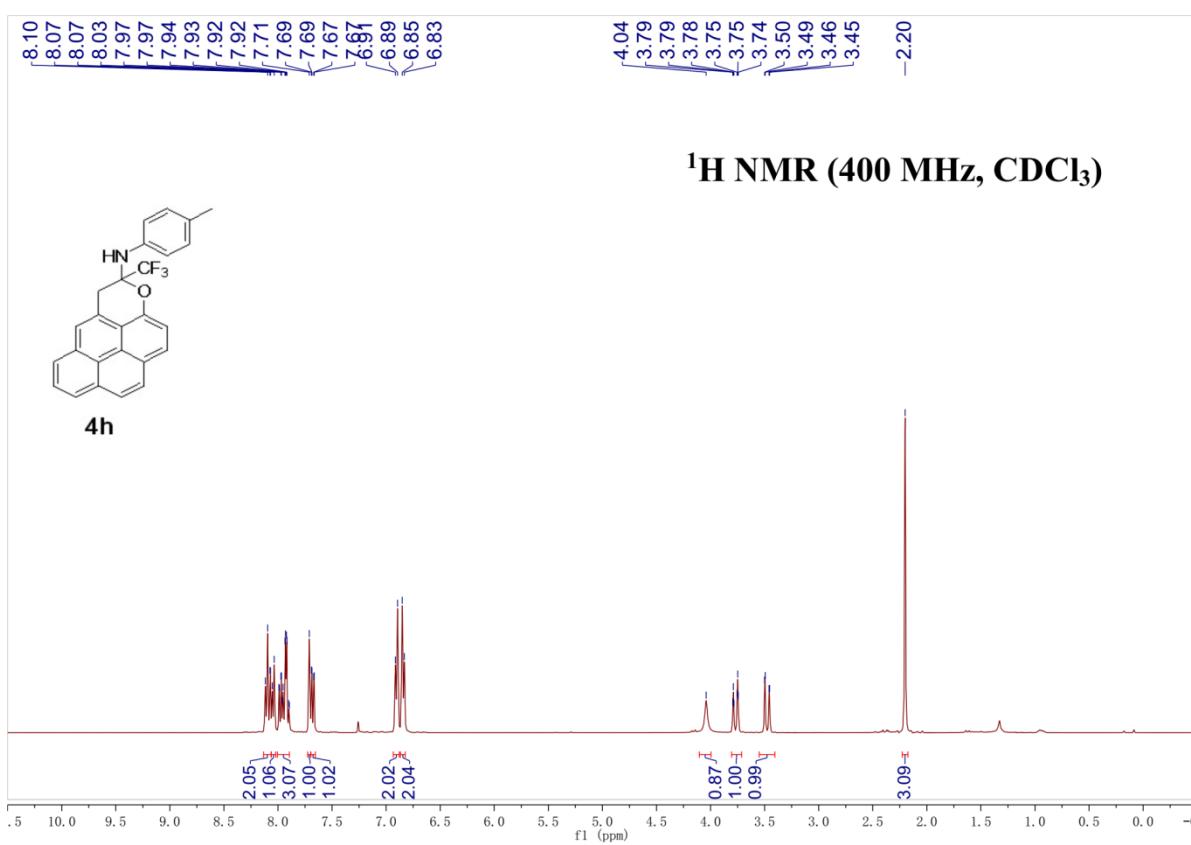
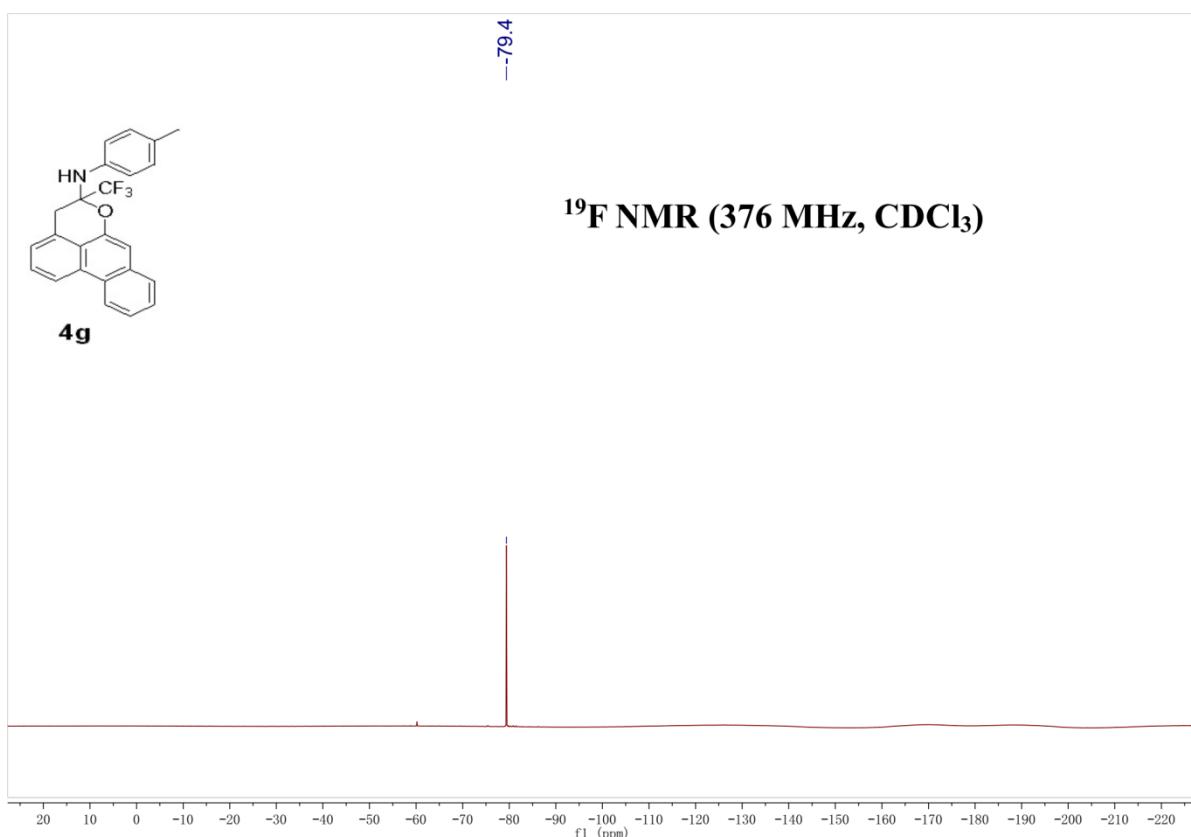
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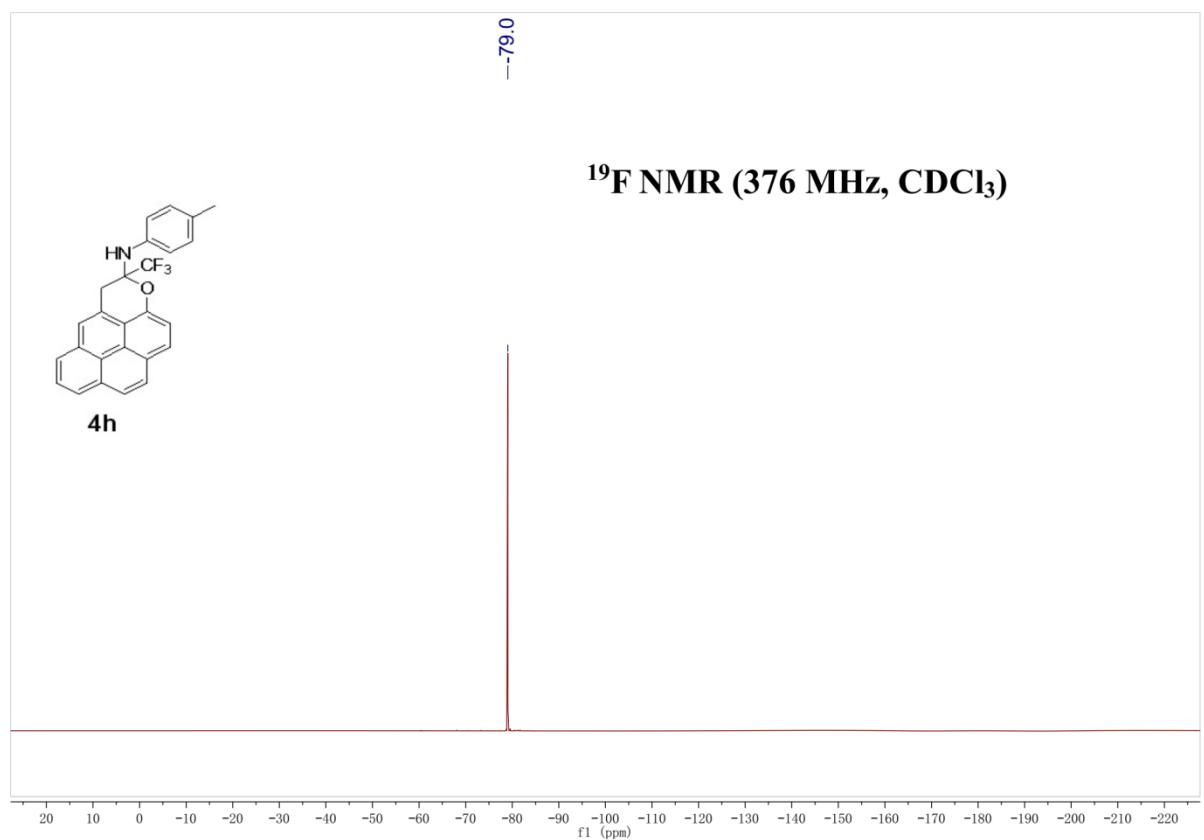
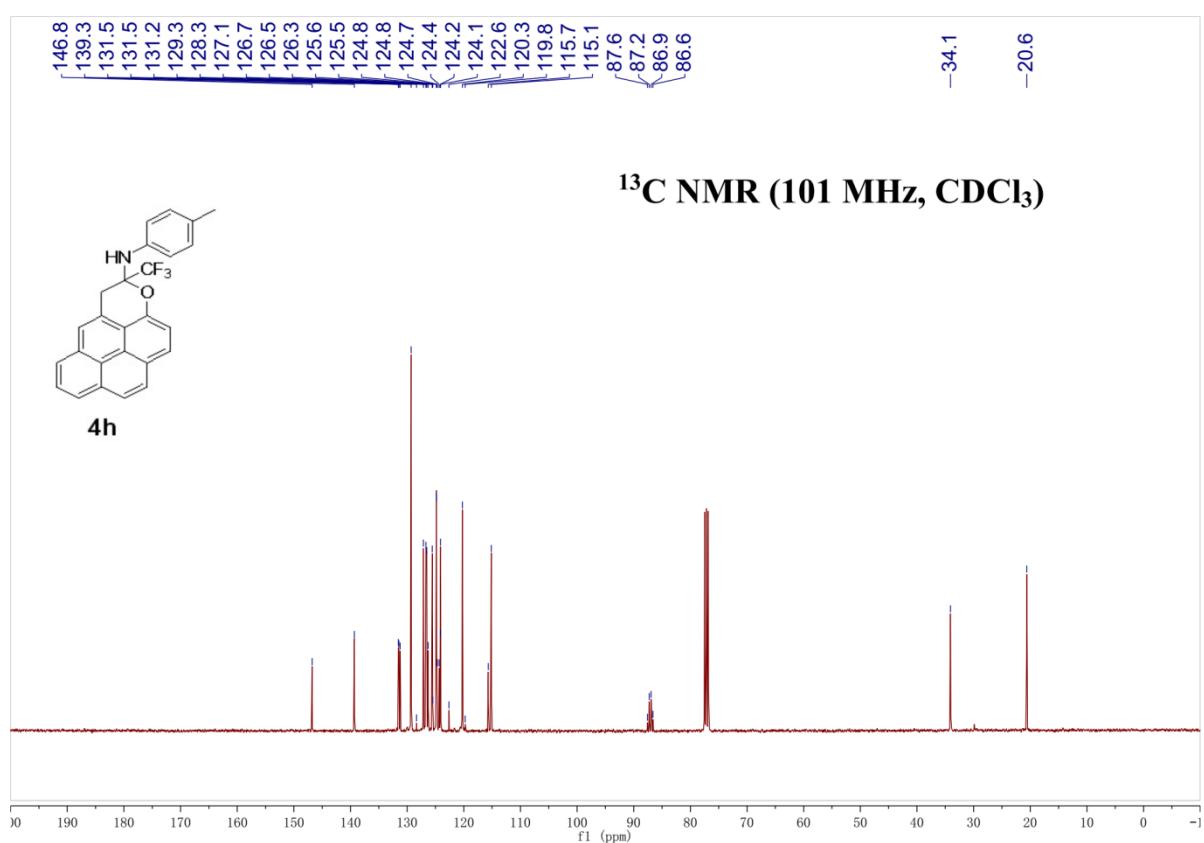
¹H NMR (400 MHz, DMSO)

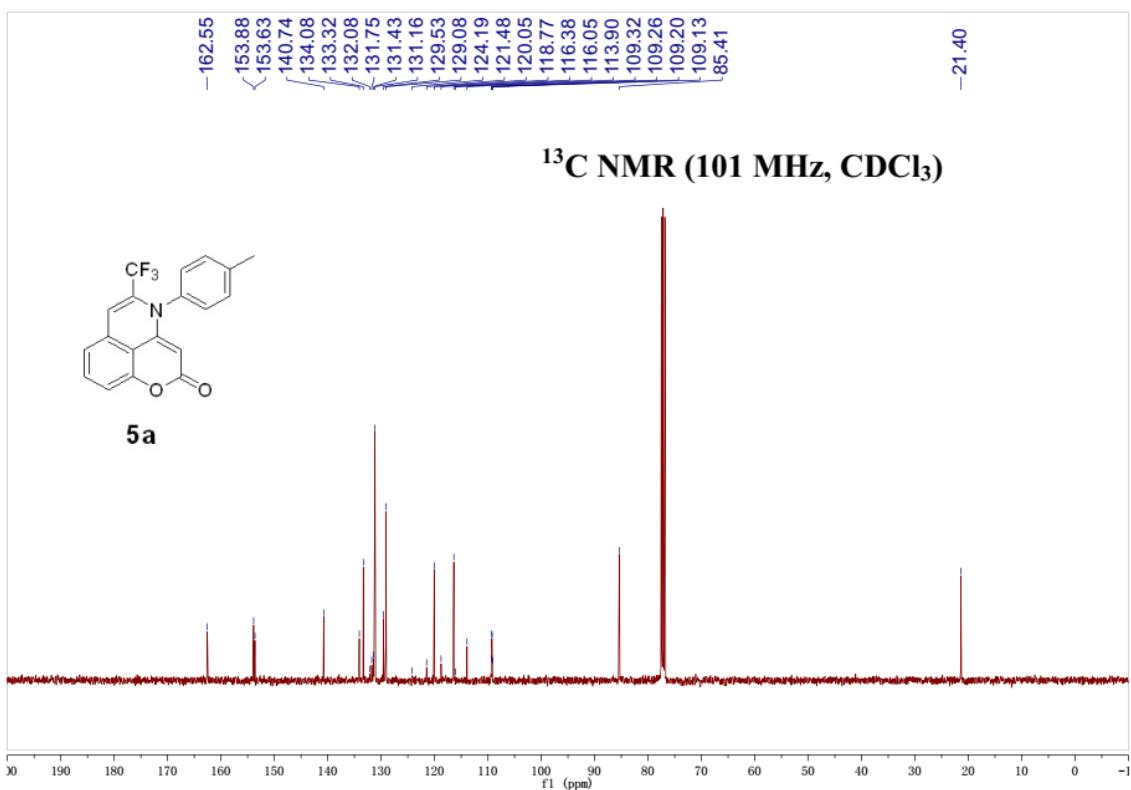
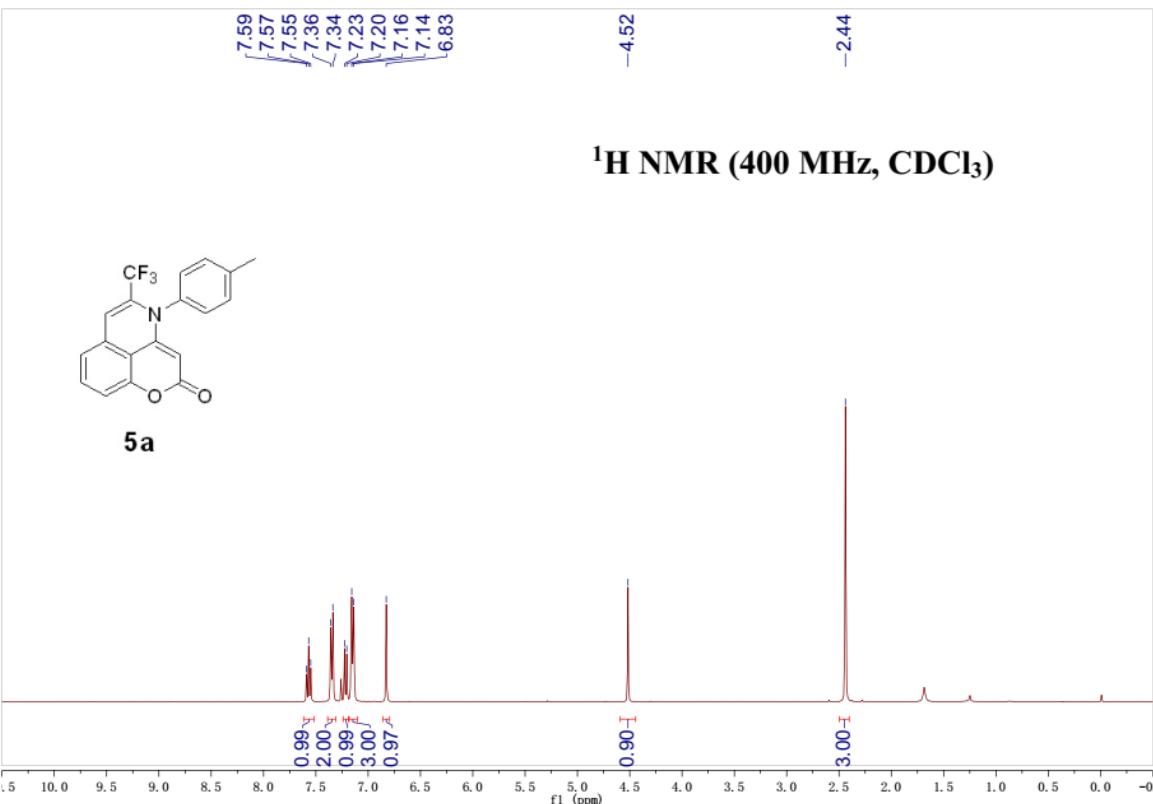






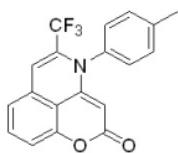




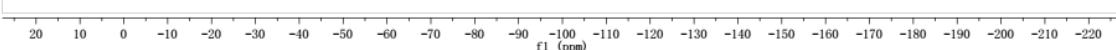


-61.4

¹⁹F NMR (376 MHz, CDCl₃)



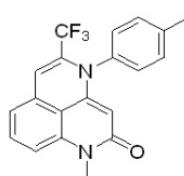
5a



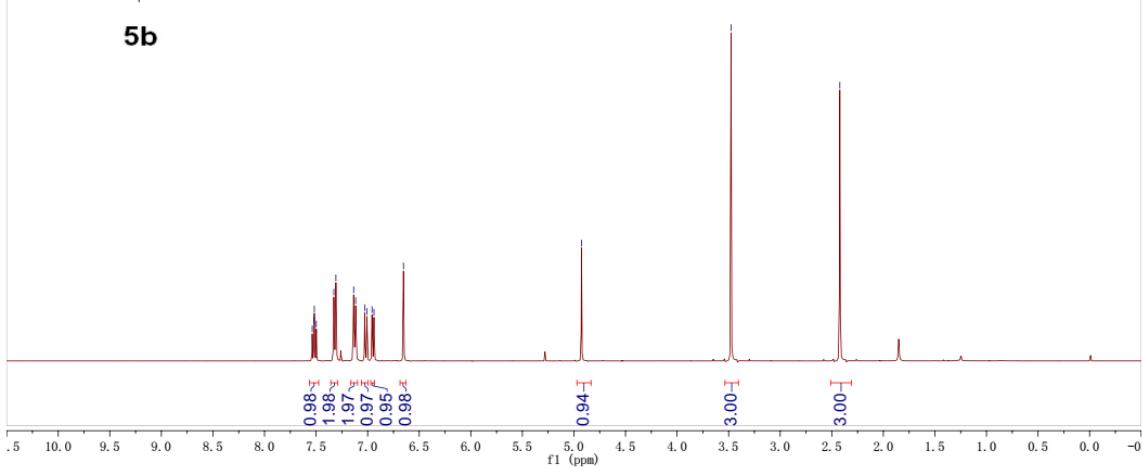
7.54
7.52
7.52
7.50
7.50
7.33
7.31
7.14
7.12
7.03
7.01
6.96
6.94
6.65

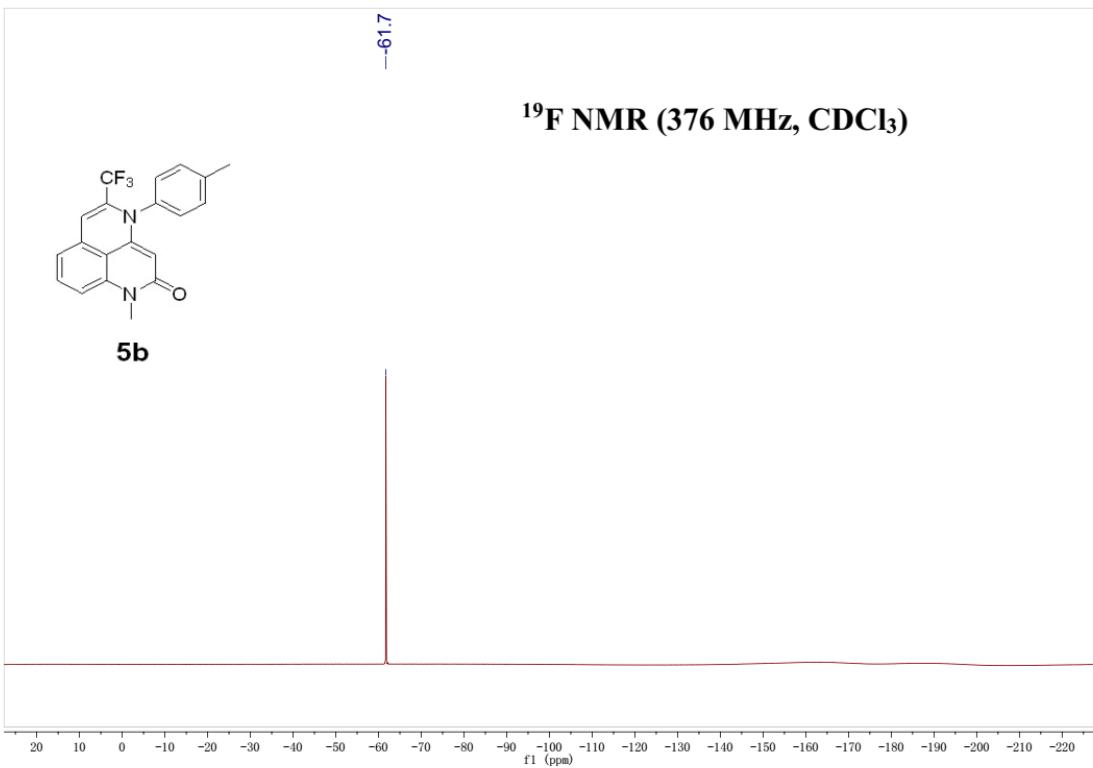
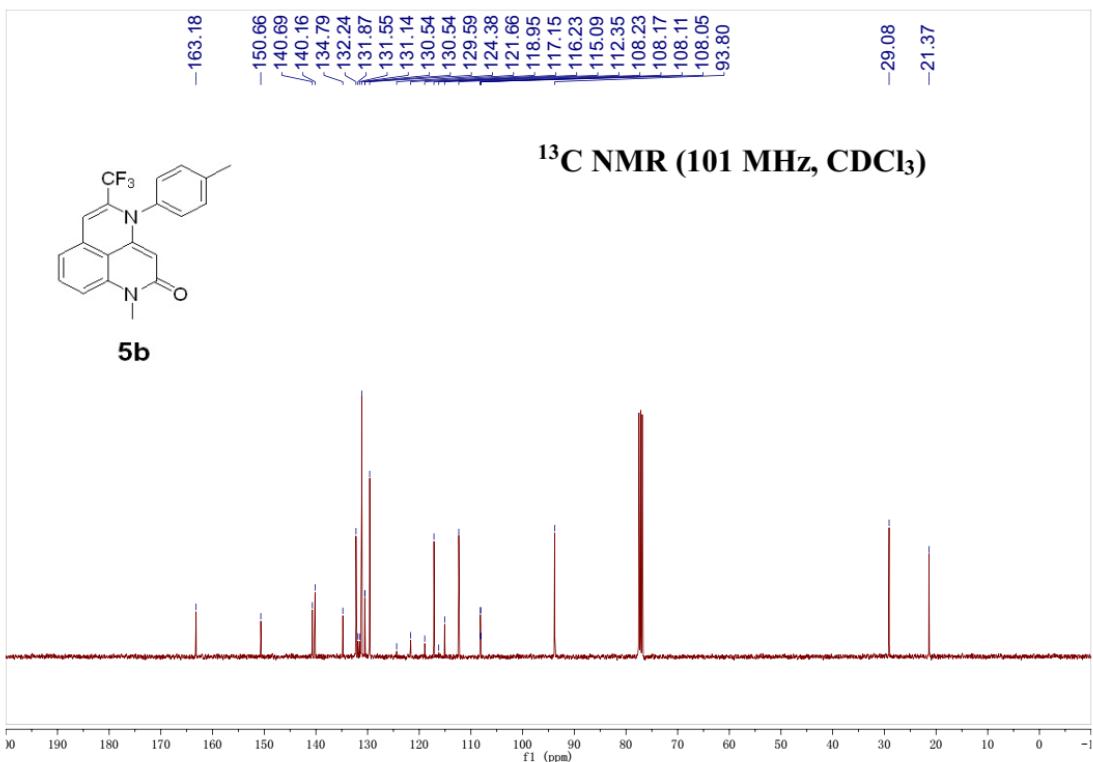
-4.93
-3.48
-2.42

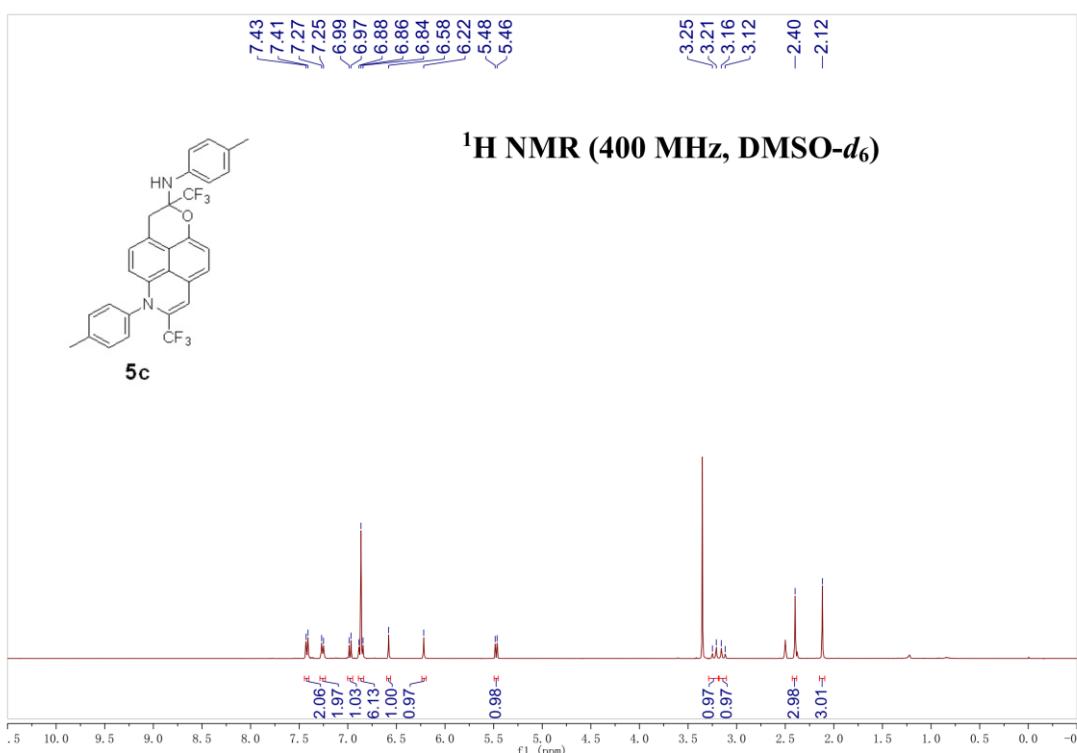
¹H NMR (400 MHz, CDCl₃)

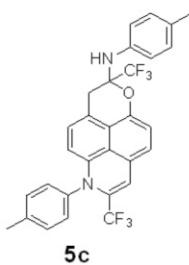


5b

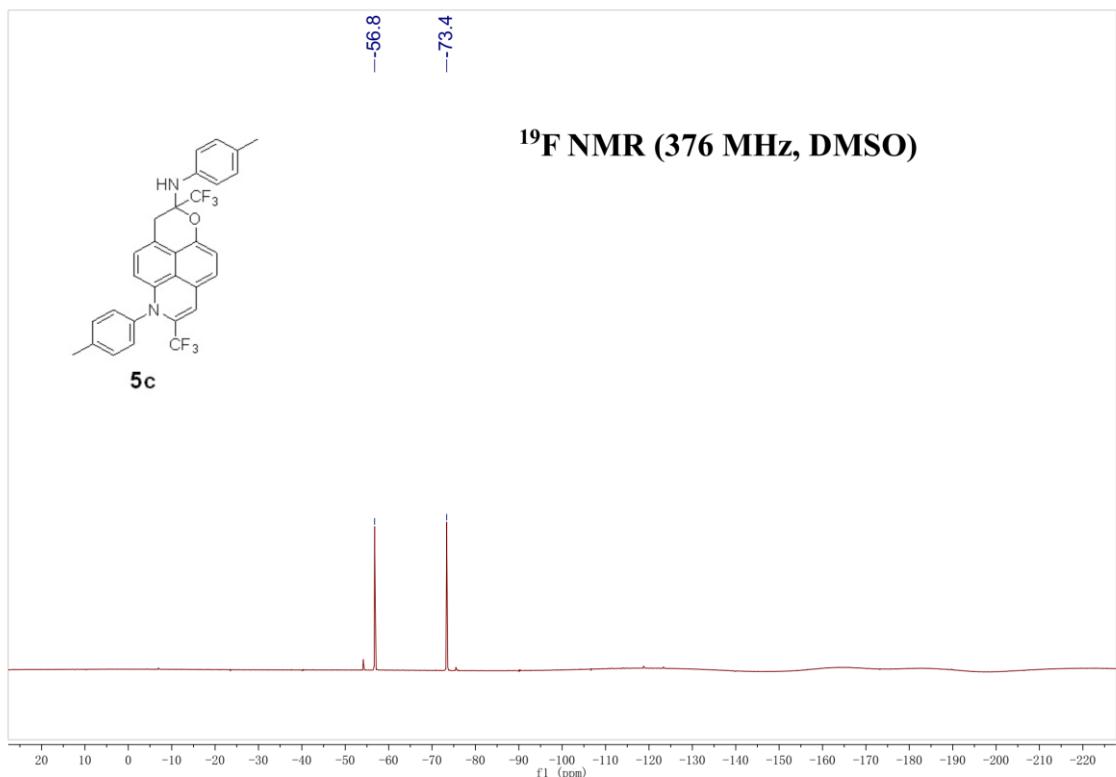








¹⁹F NMR (376 MHz, DMSO)



¹H NMR (400 MHz, CDCl₃)

