Supporting Information

Preparation and Application of *α*-Imino Ketones through One-pot Tandem Reactions Based on Heyns Rearrangement

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Content

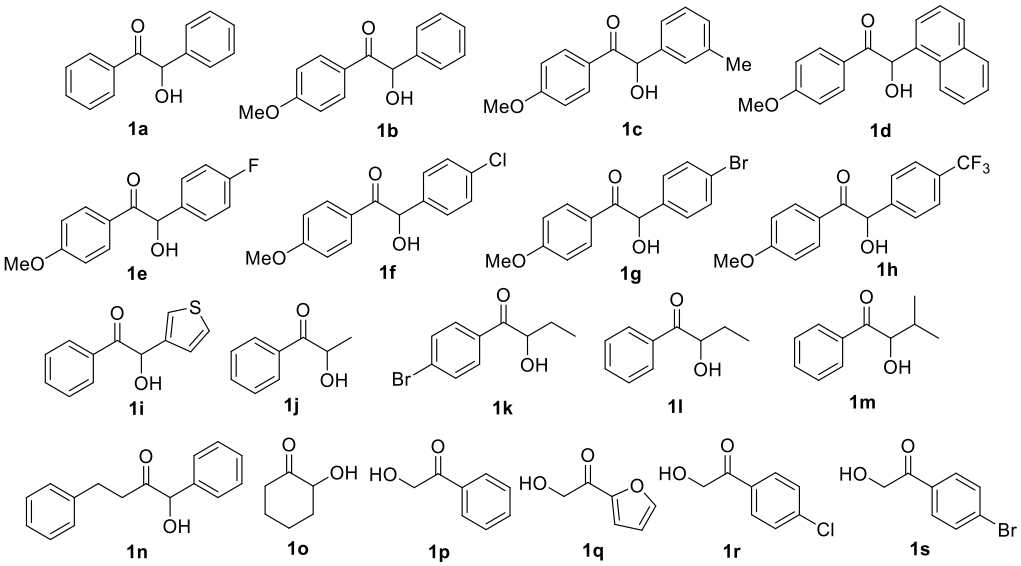
1.General experimental procedures

All reactions that required anhydrous or airless conditions were carried by standard procedures under an argon atmosphere. Commercially available reagents from Tansoole and Adamas-beta were used as received. The solvents were dried by distillation over the appropriate drying reagents.

^{1}H NMR spectra were recorded on commercial instruments (400 MHz and 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.28). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (101 MHz and 151 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). Mass spectra were recorded on a ThermoQuest Finnigan LCQDECA system equipped with an ESI source. The single crystal *X*-ray diffraction measurement was performed on a Xcalibur, Eos diffractometer. The crystal was kept at 293.15 K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

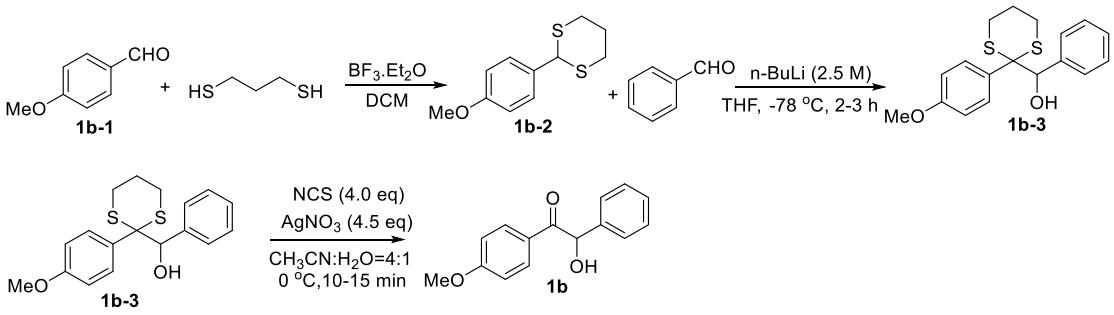
2. Preparation of starting materials

(1). Synthesis of hydroxy ketones



Scheme S1 Hydroxy ketones used in this experiment

1b-1l, **1n** were prepared from commercially available aldehyde derivatives according to the reported procedure.[4] **1j-1m** were obtained according to known literature.[5] **1q-1s** were synthesized according to known literature.[6] Preparations **1b** and **1j** are representative examples. Except for these, all are purchased through commercials.



Scheme S2 Method for preparation of the hydroxy ketone 1b

Synthesis of **1b-2**

To a solution of 4-methoxy benzaldehyde **1b-1** (1.36 g, 10 mmol, 1 equiv) and 1,3-propanedithiol (1.19 g, 11 mmol, 1.1 equiv.) in dichloromethane (40 mL), $BF_3.Et_2O$ (425.8 mg, 3 mmol, 30 mol%) was added at room temperature. The reaction was monitored by TLC. Aqueous $NaHCO_3$ was added after the completion of the reaction (3 h). The organic layer was washed with saturated brine solution, concentrated to get **1b-2**. The crude **1b-2** was washed with hexane and sufficiently pure to be used

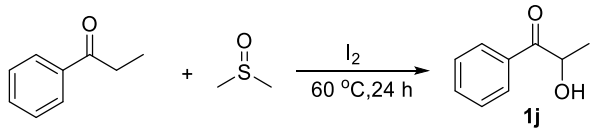
for the next step without column purification.

Synthesis of **1b-3**

To the solution of **1b-2** (2.26 g, 10 mmol, 1 equiv.) in dry THF, n-BuLi (2.5 M) (4.4 mL, 1.1 equiv.) was added at -78 ˚C. After stirring at the same temperature for 2 h, benzaldehyde (1.17 g, 11 mmol, 1.1 equiv.) was added slowly and the reaction was continued for 1 h. After completion of the reaction, aqueous NH_4Cl was added to the reaction mixture. Solvent THF was evaporated and the residue was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using mixtures of ethyl acetate and petroleum ether, **1b-3** is a yellow solid, yield: 83%.

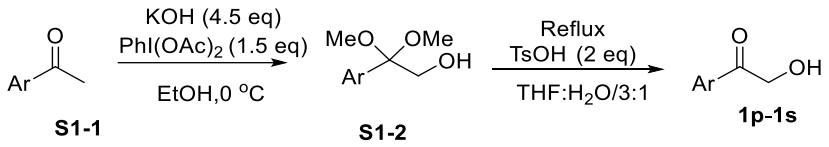
Synthesis of **1b**

To the solution of **1b-3** (1.66 g, 5 mmol, 1 equiv.) in acetonitrile/water (4:1), Nchlorosuccinimide (2.67 g, 20 mmol, 4 equiv.) and $AgNO_3$ (3.82 g, 22.5 mmol, 4.5 equiv.) were added at room temperature. The mixture was stirred at room temperature. After completion of the reaction, aqueous $Na_2S_2O_3$ solution was added. The compound was extracted with EtOAc, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using mixtures of ethyl acetate and petroleum ether, **1b** is a colorless solid, yield: 87%.



Scheme S3 Method for preparation of the hydroxy ketone 1j

The reaction of propiophenone (680 mg, 5 mmol), I_2 (260 mg, 2 mol%), DMSO (10 mL), at 60 ℃ (oil bath) under air for 24 h, afforded 540 mg of **1j** purified by column chromatography (petroleum ether /EtOAc) on silica gel, **1j** is a yellow liquid, yield: 72%.

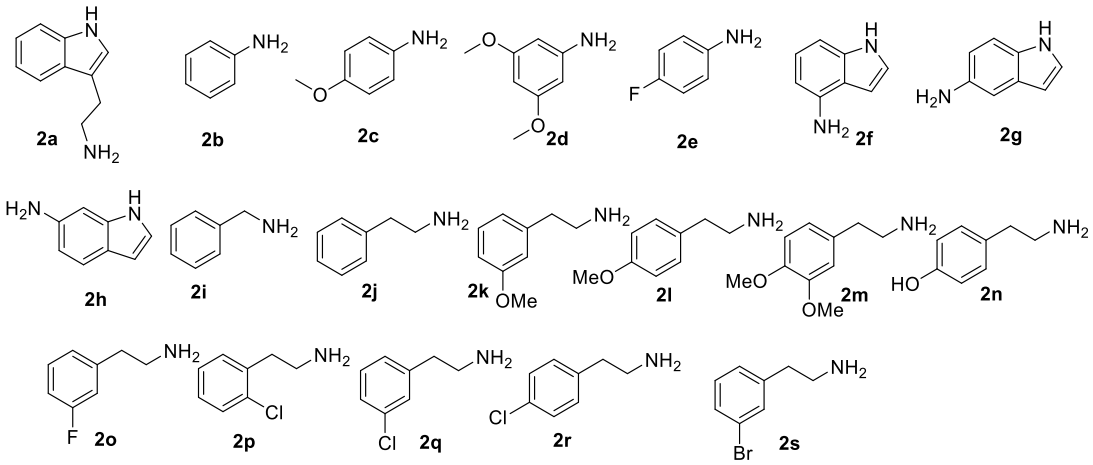


Scheme S4 Method for preparation of the hydroxy ketones (**1p-1s**)

To a solution of KOH (112.5 mmol) in MeOH (150 mL) was added a suspension of ketone **S1-1** (25.0 mmol) in EtOH (50 mL) at 0 ℃. Then $PhI(OAc)_2$ (37.5 mmol) was added portion-wise. After stirring for 3 h at 0 °C, the reaction was quenched by the addition of water. Remove the MeOH under the vacuum. The product was extracted with EtOAc (50 mL × 3), and the combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, crude **S1-2** was obtained as a white solid without further purification. **S1-2** was dissolved

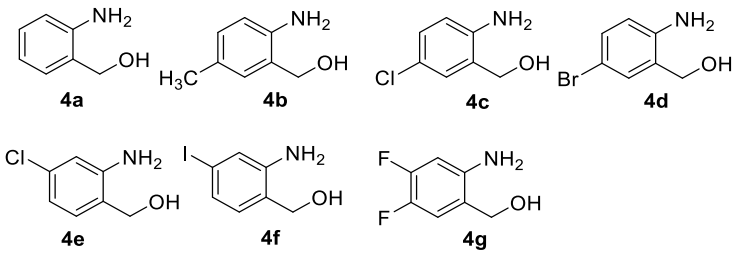
in THF: H_2O (37.5 mL: 12.5 mL) with the addition of *p*-TsOH (46.5 mmol). The mixture was heated to reflux for 4.5 h, monitored the reaction with TLC. Quenched the reaction with sat. $NaHCO_3$ and extracted the product with EtOAc (50 mL × 3). The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography (petroleum ether /EtOAc = 5/1 to 3/1) afforded substrates **1p-1s**.

(2) All amines used in the experiment were commercially purchased

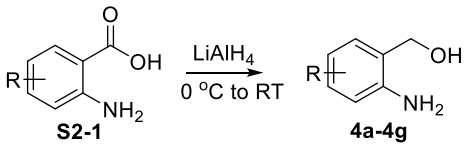


Scheme S5 Amines used in this experiment

(3) Synthesis of *o*-amino benzyl alcohol derivatives



Scheme S6 *o*-Amino benzyl alcohols used in this experiment



Scheme S7 Method for preparation of the *o*-amino benzyl alcohols 4a-4g

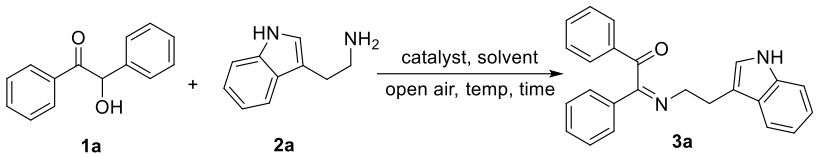
Added a solution of $LiAlH_4$ in THF (1 M, 10 mL) dropwise to a solution of 2-amino-benzoic

acid (3 mmol) in dry THF (10 mL) and maintain the temperature at 0 °C. Allow the resulting mixture to warm to room temperature and stir for 2 h. Hydrolyzed the mixture by addition of water (2.5 mL) and 5% NaOH (7.5 mL). Filtered the resulting suspension and washed the precipitate with ethyl acetate. Evaporated the combined organic layer. Recrystallize the residue from ethyl acetate and petroleum ether to obtain the products **4a**-**4g**.

3. Screening the reaction conditions

(1) Screening the reaction conditions for the synthesis of α-imino ketones **3a**-**3z1**.

Table S1 Optimization of the reaction conditions[a]



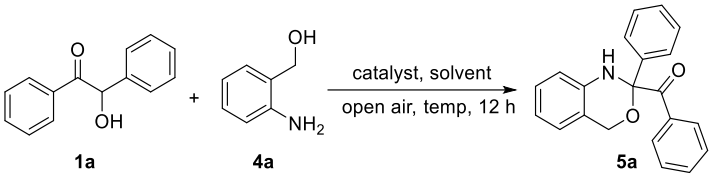
1a **2a** **3a**

Entry	Catalyst	Solvent	Temp (^{o}C)	Yield[b]
1	Diphenyl phosphate	DCM	25	25
2	TFA	DCM	25	30
3	TsOH	DCM	25	33
4	$BF_3.Et_2O$	DCM	25	46
5	$Al(OTf)_3$	DCM	25	32
7	$Cu(OTf)_2$	DCM	25	29
8	$BF_3.Et_2O$	$CHCl_3$	25	52
9	$BF_3.Et_2O$	CCl_4	25	43
10	$BF_3.Et_2O$	DCE	25	32
11	$BF_3.Et_2O$	CH_3CN	25	61
12	$BF_3.Et_2O$	PhMe	25	54
13	$BF_3.Et_2O$	CH_3CN	10	58
14	$BF_3.Et_2O$	CH_3CN	35	63
15	$BF_3.Et_2O$	CH_3CN	45	65
16	$BF_3.Et_2O$	CH_3CN	55	80
17	$BF_3.Et_2O$	CH_3CN	65	68
18[c]	$BF_3.Et_2O$	CH_3CN	55	80
19[d]	$BF_3.Et_2O$	CH_3CN	55	73
20[e]	$BF_3.Et_2O$	CH_3CN	55	78

[a] Reactions were conducted using 0.2 mmol of **1a** and 0.2 mmol of **2a** with 10 mol% of catalyst in solvent (2 mL) for 8 h. [b] Isolated yield. [c] Oxygen atmosphere. [d] Reaction time: 6 h. [e] Reaction time: 10 h.

(2) Screening the reaction conditions for the synthesis of N, O-ketals **5a-5t**.

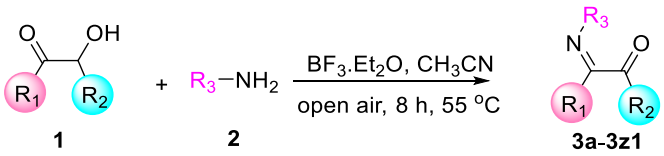
Table S2 Optimize the reaction conditions of α-imino ketones 5a-5t [a]



Entry	Catalyst	Solvent	Temp (^{o}C)	Yield[b]
1	TFA	$CHCl_3$	25	45
2	TsOH	$CHCl_3$	25	40
3	HCl	$CHCl_3$	25	42
4	$Al(OTf)_3$	$CHCl_3$	25	30
5	$BF_3.Et_2O$	$CHCl_3$	25	38
6	TFA	DCM	25	40
7	TFA	DCE	25	52
8	TFA	PhMe	25	44
9	TFA	THF	25	22
10	TFA	CH_3CN	25	47
11	TFA	DCE	30	68
12	TFA	DCE	40	55
13	TFA	DCE	50	54
14[c]	TFA	DCE	30	82
15[d]	TFA	DCE	30	63
16[e]	TFA	DCE	30	43
17[f]	TFA	DCE	30	75
18[g]	TFA	DCE	30	43

[a] Reactions were conducted using 0.2 mmol of **1a** and 0.2 mmol of **4a** with 10 mol% of catalyst in solvent (2 mL) for 12 h. [b] Isolated yield. [c] 3 Å molecular sieve (100 mg) were added. [d] 4 Å molecular sieve (100 mg) were added. [e] 5 Å molecular sieve (100 mg) were added. [f] Oxygen atmosphere. [g] DDQ (1 equiv) were added.

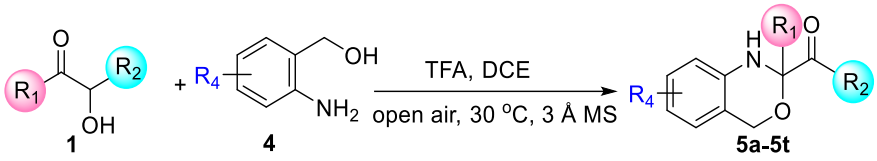
4. General procedure for the preparation of products



Scheme S8 General procedure for products 3a-3z1

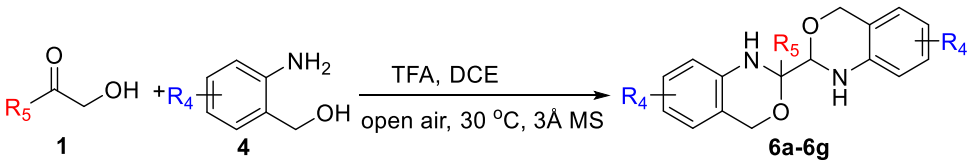
General procedure (1) for products **3a-3z1**: To a stirred solution of α-hydroxyl ketones **1** (0.2 mmol) and amines **2** (0.2 mmol) in CH_3CN (2 mL) was added $BF_3{\cdot}Et_2O$ (0.02 mmol) at room temperature, then the reaction mixture was stirred for 8 h at 55 °C (oil bath) under air. After the

completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), washed with brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude products were purified by column chromatography (eluting with petroleum ether / EtOAc) to give *α*-imino ketones **3a-3z1**.



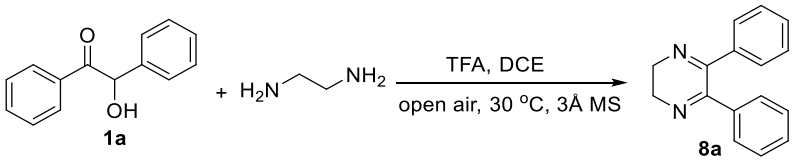
Scheme S9 General procedure for products 5a-5t

General procedure (2) for products **5a-5t**: To a stirred solution of *α*-hydroxyl ketones **1** (0.2 mmol) and *o*-amino benzyl alcohols **4** (0.2 mmol) in DCE (2 mL) was added TFA (0.02 mmol) and 3Å molecular sieve (100 mg) at room temperature, then the reaction mixture was stirred for 12 h at 30 °C (oil bath) under air. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), washed with brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude products were purified by column chromatography (eluting with petroleum ether / EtOAc) to give N,O-ketals **5a-5t**.



Scheme S10 General procedure for products 6a-6g

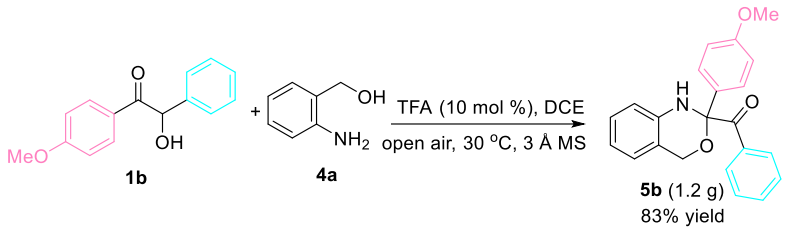
General procedure (3) for products **6a-6g**: To a stirred solution of *α*-hydroxyl ketones **1** (0.2 mmol) and *o*-amino benzyl alcohols **4** (0.4 mmol) in DCE (2 mL) was added TFA (0.02 mmol) and 3Å molecular sieve (100 mg) at room temperature, then the reaction mixture was stirred for 12 h at 30 °C (oil bath) under air. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), washed with brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude products were purified by column chromatography (eluting with petroleum ether / EtOAc) to give bicyclic ketal lactone derivatives **6a-6g**.



Scheme S11 General procedure for products 6h

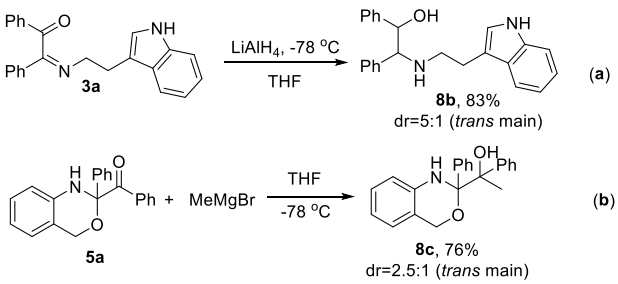
General procedure (4) for products **8a**: To a stirred solution of *α*-hydroxyl ketone **1a** (0.2 mmol) and ethylenediamine (0.2 mmol) in DCE (2 mL) was added TFA (0.02 mmol) and 3Å molecular sieve (100 mg) at room temperature, then the reaction mixture was stirred for 12 h at 30 °C (oil bath) under air. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), washed with brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude product was purified by column chromatography (eluting with petroleum ether / EtOAc). **8a** is a yellow solid, 38.4 mg, yield: 82%.

5. Gram-scale synthesis of 5b



To a stirred solution of *α*-hydroxyl ketones **1b** (4.2 mmol, 1.02 g) and *o*-amino benzyl alcohols **4** (4.2 mmol, 0.52 g) in DCE (30 mL) was added TFA (0.42 mmol) and 3Å molecular sieve (500 mg) at room temperature, then the reaction mixture was stirred for 12 h at 30 °C (oil bath) under air. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (50 mL), washed with brine (3 × 50 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude product was purified by column chromatography (eluting with petroleum ether / EtOAc), **5b** is a yellow solid, 1.2 g, yield: 83%.

6. General procedures for the preparation of 8b and 8c



Scheme S12 General procedures for the preparation of 8b and 8c

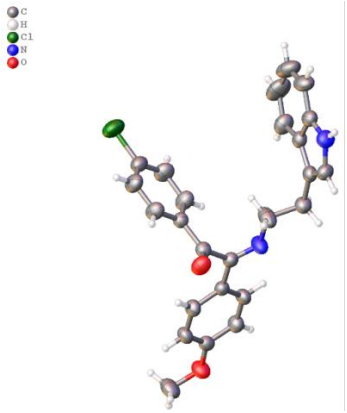
Procedure (5): anhydrous THF (2 mL) was added to the test tube containing $LiAlH_4$ (1 mmol, 2.5 equiv.), and put the mixture at -78 °C under argon. After 5 minutes, the THF solution of **3a** (0.4

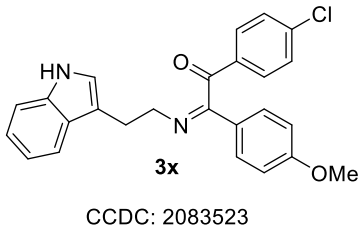
mmol,1 equiv.) was added slowly into the test tube. Continue to react at this temperature for 6 hours. After completion of the reaction, aqueous NH_4Cl (5 mL) was added to the reaction mixture. The solvent was evaporated and the residue was extracted with ethyl acetate (5 mL×3). The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using mixtures of ethyl acetate and petroleum ether, **8b** is a colorless oil, 118.3 mg, yield: 83%.

Procedure (6): anhydrous THF (2 mL) was added to the test tube containing **5a** (0.4 mmol,1 equiv.), and put the mixture at -78 °C under argon. After 5 minutes, MeMgBr (1 mmol, 2 equiv.) was added slowly to the reaction, Continue to react at this temperature for 4 hours. After completion of the reaction, aqueous NH_4Cl was added to the reaction mixture. The solvent was evaporated and the residue was extracted with ethyl acetate(5 mL×3). The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using mixtures of ethyl acetate and petroleum ether, **8c** is a colorless oil, 100.7 mg, yield: 76%.

7. *X*-ray single crystal data for 3x, 5f and 6g

(1). *X*-ray single crystal data for **3x** (50 % Prob)





3x

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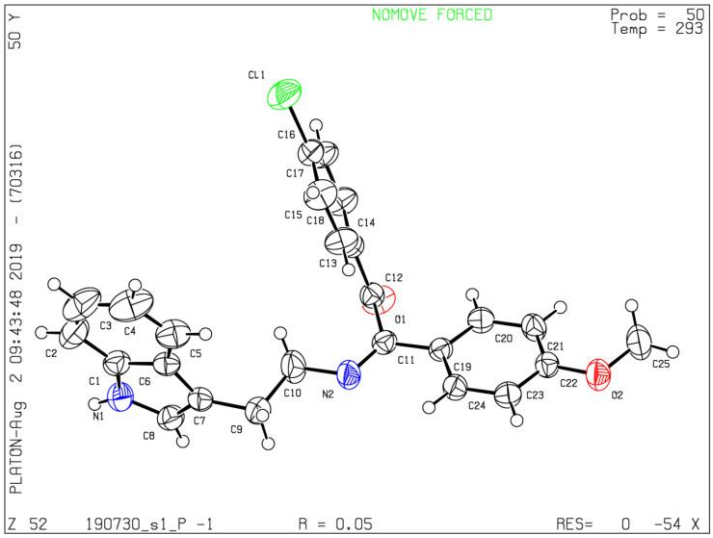
Table S3 *X*-ray single crystal data for 3x

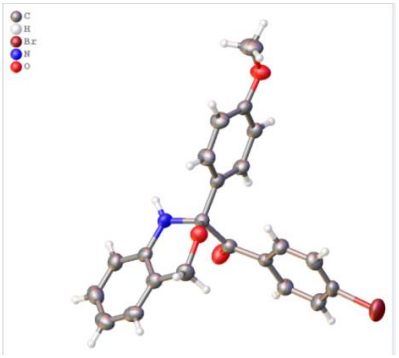
Empirical formula	$C_{25}H_{21}ClN_2O_2$
Formula weight	416.89
Z	2
Space group	P-1
a/Å	8.7434(5)
b/Å	10.9162(6)
c/Å	11.5616(7)
α/°	103.762(5)
β/°	92.287(5)
γ/°	98.322(5)
Volume/Å3	1057.35(11)
ρ_{calc}g/cm3	1.309

μ/mm^{-1}	0.205
F(000)	436.0
Temperature/K	293.15



Crystallization: Crystals of compound **3x** suitable for X-ray analysis were grown from the solvent of isopropanol /dichloromethane /petroleum ether by slow evaporation method.

(2). *X*-ray single crystal data for **5f** (50 % Prob)



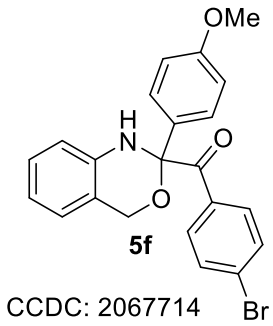
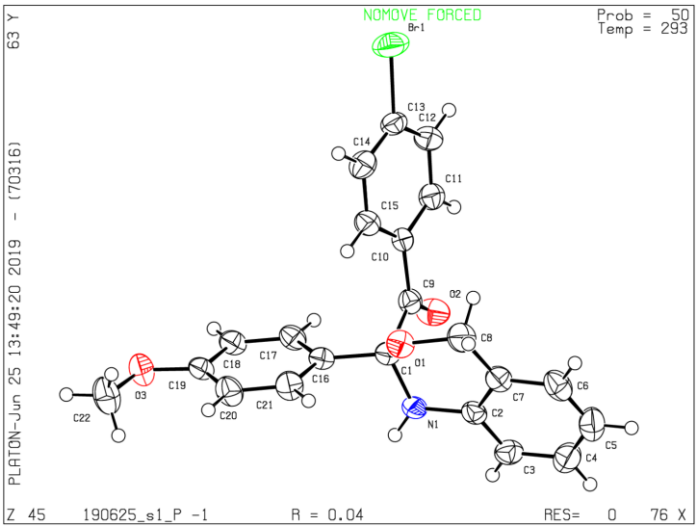


Table S4 *X*-ray single crystal data for 5f

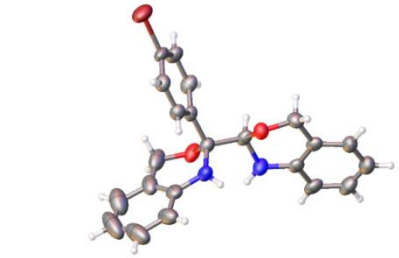
Empirical formula	$C_{22}H_{18}BrNO_3$
Formula weight	424.28
Z	2
Space group	P-1
a/Å	7.1972(7)
b/Å	10.0781(10)
c/Å	13.8883(13)
α/°	70.266(9)
β/°	85.325(8)
γ/°	77.108(8)
Volume/Å3	924.28(17)
ρ_{calc}g/cm3	1.525

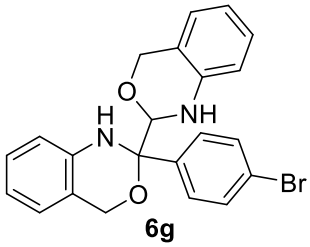
μ/mm^{-1}	2.246
F(000)	432.0
Temperature/K	293.15



Crystallization: Crystals of compound **5f** suitable for X-ray analysis were grown from the solvent of isopropanol /dichloromethane / hexane by slow evaporation method.

(3). *X*-ray single crystal data for **6g** (50 % Prob)





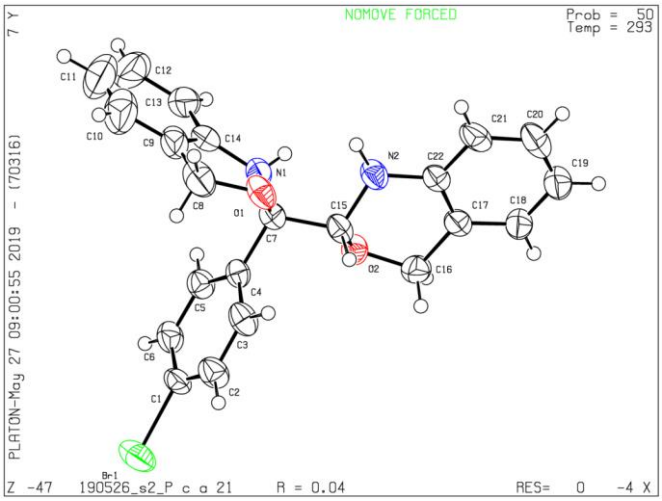
6g

CCDC: 2067715

Table S5 *X*-ray single crystal data for 6g

Empirical formula	$C_{22}H_{19}BrN_2O_2$
Formula weight	423.30
Z	4
Space group	Pca21
a/Å	14.7033(9)
b/Å	15.1233(12)
c/Å	8.5642(6)
α/°	90
β/°	90
γ/°	90
Volume/Å3	1904.4(2)
ρ_{calc}g/cm3	1.476

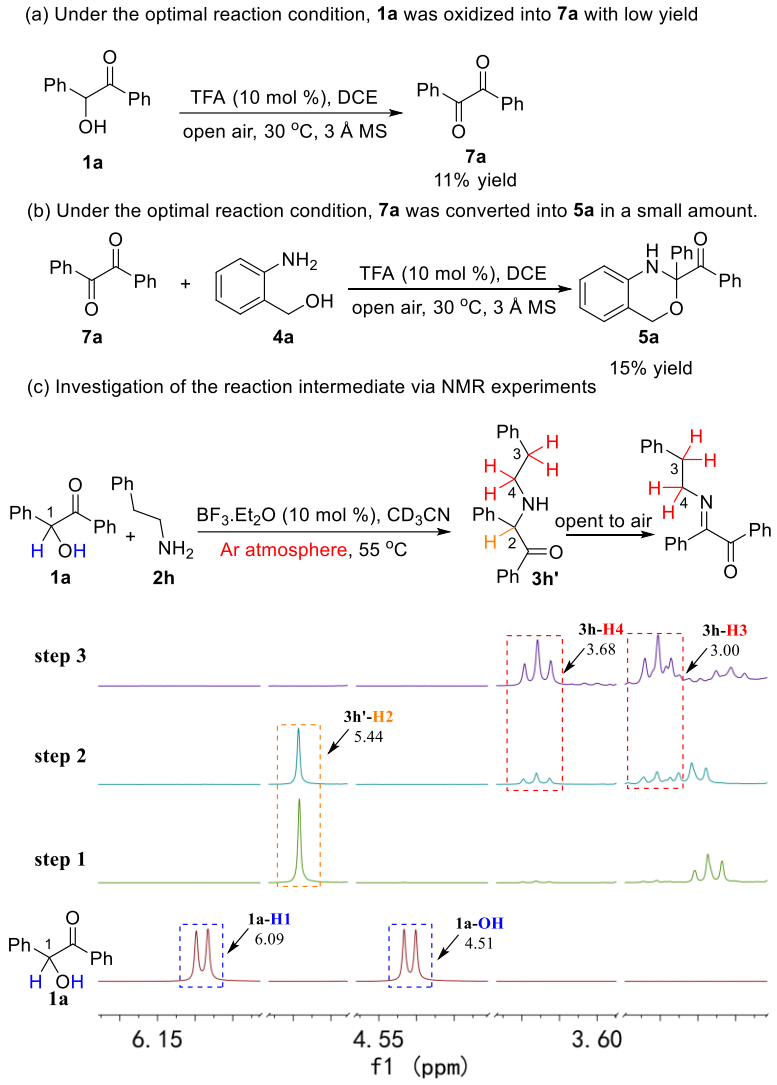
μ/mm^{-1}	2.178
F(000)	864.0
Temperature/K	293.15



Crystallization: Crystals of compound **6g** suitable for X-ray analysis were grown from the solvent of isopropanol /dichloromethane / hexane by slow evaporation method.

8. In-situ NMR monitoring experiment

According to the results of the reaction, the possibility of the reaction with diketone as an intermediate was ruled out (Scheme S12a and S12b). The in-situ NMR experiments were conducted to study the reaction mechanism (Scheme S12c). Under argon atmosphere, add **1e** (0.025 mmol), **2h** (0.025 mmol), $BF_3{\cdot}Et_2O$ (0.0025 mmol) and CD_3CN (0.5 mL) to the NMR tube, and then put the NMR tube at 55 ºC (oil bath) for 12 hours, the signals of **1e** at 4.51 and 6.09 ppm disappeared, replaced by the appearance of new signals at 5.44 ppm, which was assigned to the group of Heyns rearrangement intermediate (**3h'**) (step 1, Scheme S12). After putting the NMR tube in the air for 3 hours, we found that with the weakening of the signal at 5.44 ppm, the product signal peaks began to appear at 3.00 and 3.68 ppm (step 2, Scheme S12). Continue to place it in the air for 5 hours, the signal peak at 5.44 almost disappears, and the peak of the product (**3h**) increases (step 3, Scheme S12).

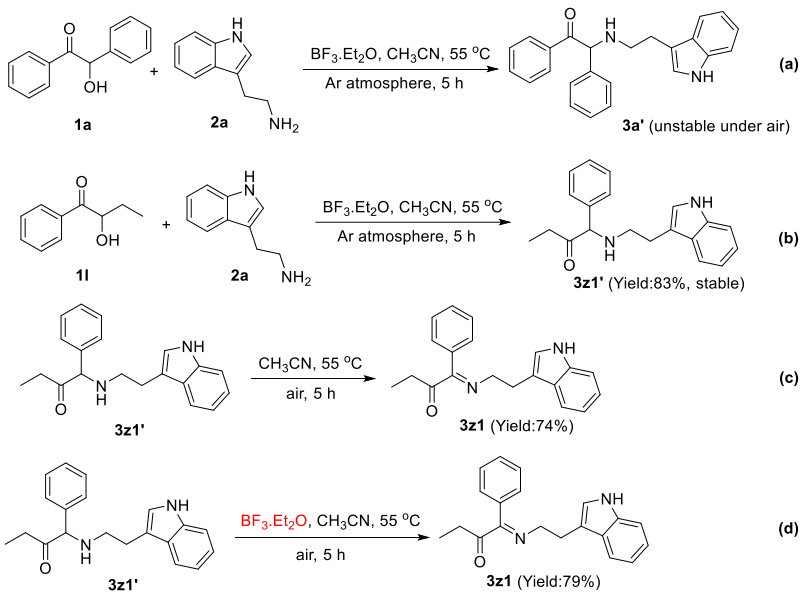


Scheme S12 Partial typical peaks of the in-situ NMR spectra in product formation process

Step 1: equal equiv. of **2h**, **1a** and catalytic $BF_3.Et_2O$ were reacted in CD_3CN (0.5 mL) at 55 °C for 12 h under argon atmosphere; **Step 2**: the mixture obtained from **step 1** was exposed to air oxidation for 3 h at 55 °C; **Step 3**: Air oxidation for an additional 5 h at 55 °C.

9. Control experiments

To explore whether catalyst is involved in the oxidation process of *α*-aminoketone, we conducted the control experiments (Scheme S15). Initially, we found that the stability of *α*-amino ketone **3a'** and **3z1'** was different. **3a'** is very unstable and oxidized into the corresponding ketone imine very quickly during the purification process. However, **3z1'** is stable and could be obtained by purification via silica column. Then the role of the catalyst was investigated based on scheme S15c and scheme S15d. According to the result, **3a'** could be oxidized without catalyst under the similar reaction condition.



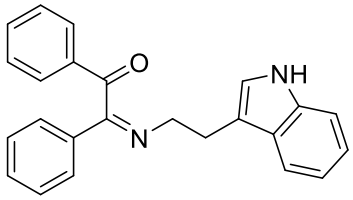
Scheme S15 control experiments for figure out the role of the catalyst in the oxidation step

General procedure (7) for product **3z1'**: To a stirred solution of *α*-hydroxyl ketones **1l** (2 mmol, 328.2 mg) and tryptamine **2a** (2 mmol, 320.4 mg) in CH_3CN (20 mL) was added $BF_3{\cdot}Et_2O$ (2 mmol, 28.4 mg) at room temperature, then the reaction mixture was stirred for 5 h at 55 °C (oil bath) under argon atmosphere. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude products were purified by column chromatography (eluting with petroleum ether / EtOAc) to give **3z1'** (508 mg, yield: 83%).

General procedure for scheme S15c: *α*-Aminoketone **3z1'** (0.1 mmol, 30.6 mg) was added to CH_3CN (1 mL) at room temperature, then the reaction mixture was stirred for 5 h at 55 °C (oil bath) under air. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (5 mL), washed with brine (2× 5 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude products were purified by column chromatography (eluting with petroleum ether / EtOAc) to give **3z1** (22.5 mg, yield: 74%).

General procedure for scheme S15d: To a stirred solution of *α*-aminoketone **3z1'** (0.1 mmol, 30.6 mg) in CH_3CN (1 mL) was added $BF_3{\cdot}Et_2O$ (0.01 mmol, 1.4 mg) at room temperature, then the reaction mixture was stirred for 5 h at 55 °C (oil bath) under air. After the completion of the reaction (TLC), the mixture was cooled to room temperature, diluted with ethyl acetate (5 mL), washed with brine (2× 5 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporator. The crude products were purified by column chromatography (eluting with petroleum ether / EtOAc) to give **3z1** (24.0 mg, yield: 79%).

10. Characterization of products



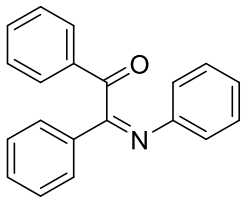
(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-1,2-diphenylethan-1-one (**3a**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow solid (56.3 mg , yield: 80%), M.p. 67-70 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.88-7.80 (m, 2H), 7.80-7.73 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49-7.36 (m, 6H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 3.82 (t, *J* = 7.5 Hz, 2H), 3.23 (dt, *J* = 14.9, 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 166.8, 136.1, 135.3, 134.6, 130.9, 129.2, 129.2, 128.7, 127.4, 121.9, 119.2, 118.9, 114.0, 111.0, 54.9, 26.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}N_2ONa$ 375.1473, found: 375.1471



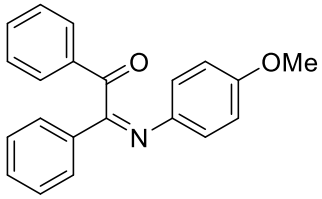
(Z)-1,2-diphenyl-2-(phenylimino)ethan-1-one (**3b**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a yellow solid (30.2 mg, yield: 53%), M.p. 92-95 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.56-7.42 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.00-6.82 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 166.3, 149.2, 135.1, 134.7, 134.3, 131.7, 129.3, 128.8, 128.6, 128.1, 124.7, 120.5, 77.3, 77.0, 76.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO$ 286.1232, found: 286.1222



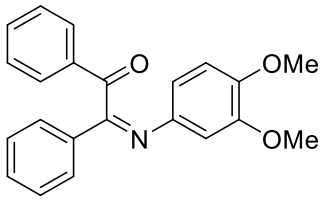
(Z)-2-((3-methoxyphenyl)imino)-1,2-diphenylethan-1-one (**3c**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a yellow solid (39.1 mg, yield: 62%), M.p. 116-118 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.85 (m, 2H), 7.80 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.56-7.41 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.01-6.87 (m, 2H), 6.78-6.64 (m, 2H), 3.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 165.4, 157.1, 142.3, 135.4, 134.6, 134.3, 131.4, 129.3, 128.9, 128.8, 128.0, 122.3, 113.9, 55.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{18}NO_2$ 316.1338, found: 316.1332



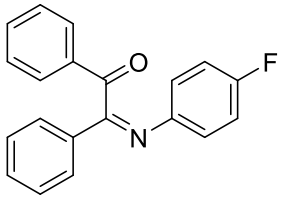
(Z)-2-((3,4-dimethoxyphenyl)imino)-1,2-diphenylethan-1-one (**3d**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow solid (49.0 mg, yield: 71%), M.p. 75-77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.1 Hz, 2H), 7.85 (d, J = 7.4 Hz, 2H), 7.57-7.40 (m, 4H), 7.35 (t, J = 7.7 Hz, 2H), 6.70 (d, J = 9.1 Hz, 1H), 6.36-6.21 (m, 2H), 3.71 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 166.4, 158.2, 151.4, 135.4, 134.5, 134.2, 132.3, 131.4, 129.1, 128.7, 128.6, 128.2, 121.4, 103.4, 99.2, 55.3, 55.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}NO_3$ 346.1443, found: 346.1438



(Z)-2-((4-fluorophenyl)imino)-1,2-diphenylethan-1-one (**3e**)

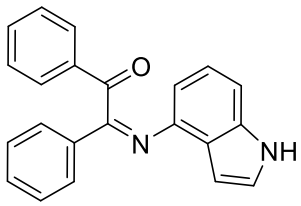
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a yellow solid (28.5 mg, yield: 47%), M.p. 101-103 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 6.92-6.79 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 166.8, 160.9, 160.0 (d, *J* = 244.0 Hz), 159.2, 145.3, 135.0, 134.8 (d, *J* = 64.8 Hz), 134.5 (d, *J* = 13.6 Hz), 134.5, 131.8, 129.2, 128.9, 128.9 (d, *J* = 12.0 Hz), 128.8, 128.1, 122.1 (d, *J* = 8.2 Hz), 115.5, 115.4 (d, *J* = 22.6 Hz), 77.2, 77.0, 76.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.51.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}FNO$ 304.1138, found: 304.1128



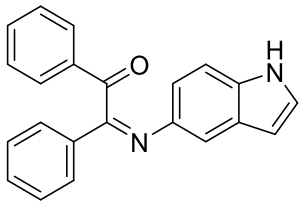
(Z)-2-((1H-indol-4-yl)imino)-1,2-diphenylethan-1-one (**3f**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow solid (36.3 mg, yield: 56%), M.p. 145-148 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.51 (dt, J = 14.6, 7.0 Hz, 3H), 7.36 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.12 (t, J = 2.7 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 6.91 (t, J = 7.7 Hz, 1H), 6.68 (s, 1H), 6.52 (d, J = 7.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 165.4, 142.0, 136.3, 135.4, 134.5, 133.9, 131.5, 129.0, 128.8, 128.5, 128.3, 123.6, 122.0, 121.4, 110.0, 108.2, 101.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1341, found: 325.1335



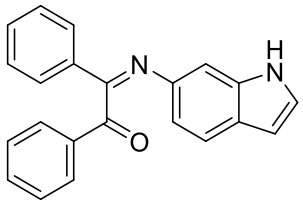
(Z)-2-((1H-indol-5-yl)imino)-1,2-diphenylethan-1-one (**3g**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow solid (42.1 mg, yield: 65%), M.p. 163-166 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.59-7.36 (m, 4H), 7.29 (dd, J = 9.5, 5.7 Hz, 2H), 7.24 (s, 1H), 7.14 (d, J = 8.6 Hz, 1H), 7.07 (t, J = 2.4 Hz, 1H), 6.93 (dd, J = 8.5, 1.5 Hz, 1H), 6.42 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 164.8, 142.1, 135.7, 134.5, 134.1, 133.7, 131.2, 129.3, 128.8, 128.0, 127.9, 124.9, 117.0, 112.4, 111.2, 103.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1341, found: 325.1339



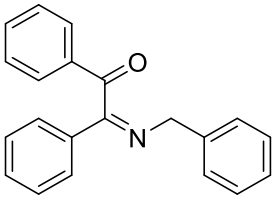
(Z)-2-((1H-indol-6-yl)imino)-1,2-diphenylethan-1-one (**3h**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow solid (39.5 mg, yield: 61%), M.p. 125-127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.00-7.89 (m, 2H), 7.87-7.77 (m, 2H), 7.56-7.39 (m, 5H), 7.30 (dd, *J* = 12.8, 5.2 Hz, 2H), 7.10-7.02 (m, 1H), 7.00 (s, 1H), 6.87 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.40 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 165.0, 144.2, 135.8, 135.5, 134.4, 134.3, 131.4, 129.3, 128.8, 128.8, 128.1, 125.5, 124.4, 120.8, 115.0, 103.0, 102.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1341, found: 325.1335



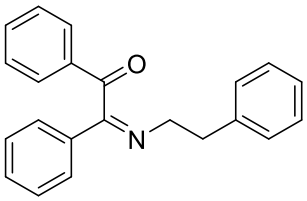
(Z)-2-(benzylimino)-1,2-diphenylethan-1-one (**3i**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a yellow solid (40.1 mg, yield: 67%), M.p. 71-73 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 10.5, 3.4 Hz, 2H), 7.87-7.78 (m, 2H), 7.67 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.59-7.48 (m, 2H), 7.49-7.38 (m, 3H), 7.38-7.32 (m, 4H), 7.31-7.24 (m, 1H), 4.70 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 167.1, 139.1, 135.2, 134.8, 134.7, 131.1, 129.4, 129.3, 129.1, 128.70, 128.5, 128.0, 127.5, 127.0, 57.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{18}NO$ 300.1388, found: 300.1386



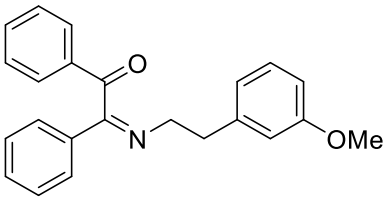
(Z)-2-(phenethylimino)-1,2-diphenylethan-1-one (**3j**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a white solid (39.5 mg, yield: 63%), M.p. 83-86 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.75-7.67 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48-7.34 (m, 5H), 7.30-7.21 (m, 2H), 7.21-7.10 (m, 3H), 3.72 (t, *J* = 7.4 Hz, 2H), 3.04 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 166.9, 139.8, 135.2, 134.6, 130.9, 129.2, 129.2, 129.0, 128.7, 128.4, 127.3, 126.2, 55.6, 37.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}NO$ 314.1545, found: 314.1543



(Z)-2-((3-methoxyphenethyl)imino)-1,2-diphenylethan-1-one (**3k**)

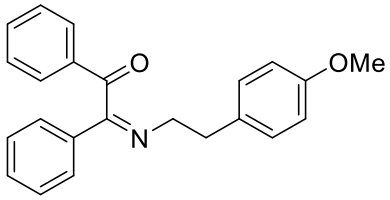
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a white solid (50.8 mg, yield: 74%), M.p. 52-55 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.76 (m, 2H), 7.75-7.69 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49-7.35 (m, 5H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.75 (dd, *J* = 10.3, 4.8 Hz, 2H), 6.69 (s, 1H), 3.84-3.64 (m,

5H), 3.04 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 166.9, 159.5, 141.4, 135.2, 134.6, 130.9, 129.3, 129.2, 129.2, 128.7, 127.3, 121.4, 114.4, 111.8, 55.5, 55.1, 37.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}NO_2$ 344.1651, found: 344.1648



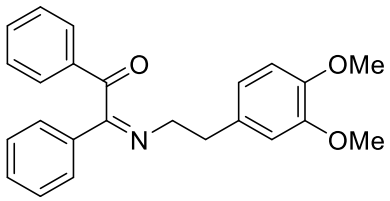
(Z)-2-((4-methoxyphenethyl)imino)-1,2-diphenylethan-1-one (**3l**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a white solid (48.7 mg, yield: 71%), M.p. 104-105 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 2H), 7.76-7.70 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49-7.35 (m, 5H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.70 (t, *J* = 7.3 Hz, 2H), 3.00 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 166.8, 158.0, 135.2, 134.6, 134.5, 131.9, 130.9, 129.9, 129.2, 128.7, 127.3, 113.7, 55.9, 55.2, 36.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}NO_2$ 344.1651, found: 344.1644



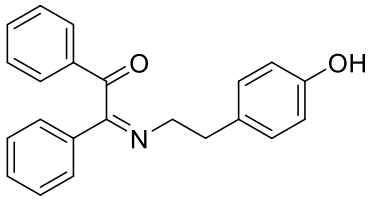
(Z)-2-((3,4-dimethoxyphenethyl)imino)-1,2-diphenylethan-1-one (**3m**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (11:1) to afford a white oil (56.7 mg, yield: 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48-7.34 (m, 5H), 6.72 (dt, *J* = 8.2, 4.9 Hz, 2H), 6.63 (d, *J* = 1.5 Hz, 1H), 3.86 (s, 3H), 3.80-3.66 (m, 5H), 3.00 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 166.9, 148.7, 147.4, 135.2, 134.5, 132.4, 130.9, 129.2, 129.1, 128.8, 127.2, 120.9, 112.2, 111.0, 55.9, 55.8, 55.7, 37.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{24}NO_3$ 374.1756, found: 374.1750



(Z)-2-((4-hydroxyphenethyl)imino)-1,2-diphenylethan-1-one (**3n**)

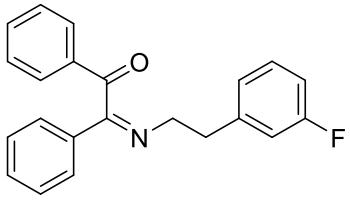
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a white solid (50.7 mg, yield: 77%),

M.p. 135-138 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.75-7.68 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.39 (ddd, *J* = 9.3, 8.4, 4.8 Hz, 5H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.54 (s, 1H), 3.70 (t, *J* = 7.3 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 167.3, 154.2, 135.0, 134.7, 134.4, 131.5, 131.0, 130.1, 129.2, 128.8, 127.3, 115.3, 55.9, 36.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}NO_2Na$ 352.1313, found: 352.1306



(Z)-2-((3-fluorophenethyl)imino)-1,2-diphenylethan-1-one (**3o**)

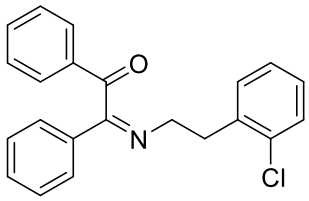
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a white solid (46.3 mg, yield: 70%), M.p. 79-81 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.76-7.68 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51-7.35 (m, 5H), 7.21 (dd, *J* = 14.0, 7.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.92-6.81 (m, 2H), 3.72 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, δ 160.9 (d, *J* = 245.3 Hz), 159.7, 140.5 (d, *J* = 7.3 Hz), 133.2, 132.8, 132.6, 129.1, 127.8 (d, *J* = 8.3 Hz), 127.3 (d, *J* = 8.7 Hz), 126.8, 125.4, 122.8 (d, *J* = 2.7 Hz), 113.9 (d, *J* = 20.8 Hz), 111.1 (d, *J* = 21.0 Hz), 53.1, 35.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.74.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}FNO$ 332.1451, found: 332.1447



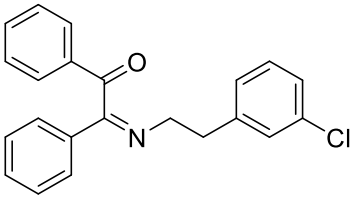
(Z)-2-((2-chlorophenethyl)imino)-1,2-diphenylethan-1-one (**3p**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a white solid (47.2 mg, yield: 68%), M.p. 69-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.78 (m, 2H), 7.78-7.70 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50-7.35 (m, 5H), 7.32-7.23 (m, 2H), 7.17 (ddd, *J* = 13.8, 7.1, 1.8 Hz, 2H), 3.76 (t, *J* = 7.3 Hz, 2H), 3.18 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 167.1, 137.3, 135.2, 134.6, 134.2, 131.3, 130.9, 129.4, 129.2, 129.2, 128.7, 127.7, 127.3, 126.7, 53.4, 35.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}ClNO$ 348.1155, found: 348.1152



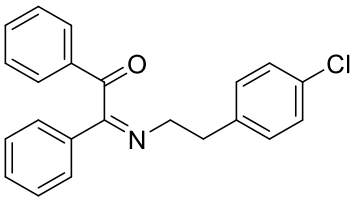
(Z)-2-((3-chlorophenethyl)imino)-1,2-diphenylethan-1-one (**3q**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a white solid (50.0 mg, yield: 72%), M.p. 106-109 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.75-7.69 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49-7.35 (m, 5H), 7.19 (dd, *J* = 7.7, 5.7 Hz, 2H), 7.13 (s, 1H), 7.07 (dd, *J* = 7.5, 4.3 Hz, 1H), 3.71 (t, *J* = 7.2 Hz, 2H), 3.09-2.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 167.2, 141.9, 135.1, 134.7, 134.5, 134.0, 131.0, 129.6, 129.3, 129.2, 129.1, 128.7, 127.3, 126.4, 55.0, 37.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}ClNO$ 348.1155, found: 348.1150



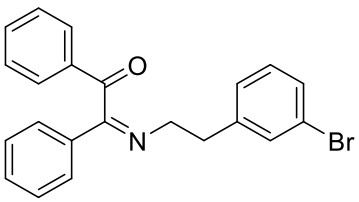
(Z)-2-((4-chlorophenethyl)imino)-1,2-diphenylethan-1-one (**3r**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a white solid (50.7 mg, yield: 73%), M.p. 62-65 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 10.9, 4.2 Hz, 4H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.42 (tt, *J* = 14.4, 7.3 Hz, 5H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.70 (t, *J* = 7.0 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 167.1, 138.3, 135.1, 134.6, 134.5, 131.9, 131.0, 130.4, 129.2, 129.1, 128.7, 128.4, 127.2, 55.2, 36.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}ClNO$ 348.1155, found: 348.1154



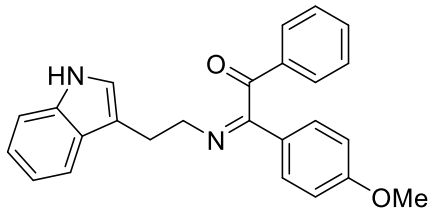
(Z)-2-((3-bromophenethyl)imino)-1,2-diphenylethan-1-one (**3s**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a white oil (60.2 mg, yield: 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50-7.36 (m, 5H), 7.36-7.28 (m, 2H), 7.12 (d, *J* = 6.5 Hz, 2H), 3.71 (t, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 167.2, 142.2, 135.1, 134.7, 134.5, 132.0, 131.0, 129.9, 129.3, 129.1, 128.7, 127.7, 127.3, 122.4, 55.0, 37.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}BrNO$ 392.0650, found: 392.0645



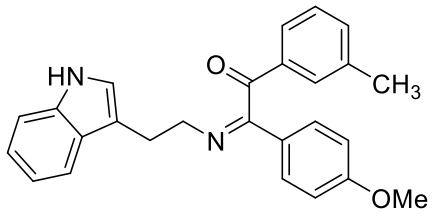
(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-2-(4-methoxyphenyl)-1-phenylethan-1-one (**3t**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow oil (65.7 mg, yield: 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.83 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47-7.37 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.90 (t, *J* = 9.7 Hz, 2H), 3.83 (s, 3H), 3.79 (t, *J* = 7.5 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 166.1, 161.8, 136.2, 134.7, 134.6, 129.2, 129.2, 129.0, 128.1, 127.6, 122.0, 121.8, 119.2, 118.9, 114.1, 114.0, 111.0, 55.4, 54.7, 27.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}N_2O_2$ 383.1760, found: 383.1756



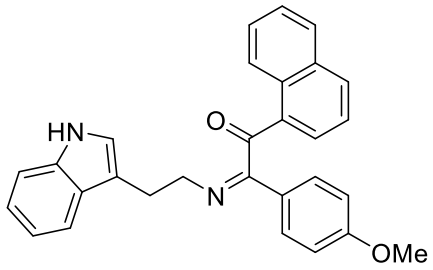
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a yellow oil (68.1 mg, yield: 86%).

(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-2-(4-methoxyphenyl)-1-(m-tolyl)ethan-1-one(**3u**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.77-7.65 (m, 3H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.48-7.36 (m, 2H), 7.35-7.25 (m, 2H), 7.21-7.11 (m, 1H), 7.06 (dd, *J* = 11.0, 3.9 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.83 (d, *J* = 8.6 Hz, 3H), 3.80 – 3.66 (m, 2H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 166.1, 161.7, 139.1, 136.1, 135.4, 134.8, 129.3, 129.0, 129.0, 128.2, 127.6, 126.8, 121.9, 121.8, 119.2, 118.9, 114.2, 114.1, 111.0, 55.4, 54.7, 27.0, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}N_2O_2$ 397.1916, found: 397.1915



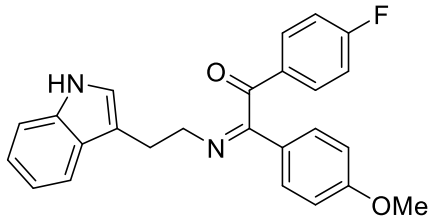
(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-2-(4-methoxyphenyl)-1-(naphthalen-1-yl)ethan-1-one(**3v**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a yellow oil (64.8 mg, yield: 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.86-7.72 (m, 4H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33-7.22 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 18.7, 8.0 Hz, 4H), 3.89 (dd, *J* = 9.6, 5.1 Hz, 2H), 3.83 (s, 3H), 3.21 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 166.5, 161.7, 136.1, 135.6, 134.7, 134.1, 130.1, 129.5, 129.2, 128.8, 128.7, 127.6, 127.0, 126.0, 124.7, 122.0, 121.8, 119.1, 118.9, 114.1, 114.1, 111.0, 55.4, 54.5, 27.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{25}N_2O_2$ 433.1916, found: 433.1917



(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)ethan-1-one(**3w**)

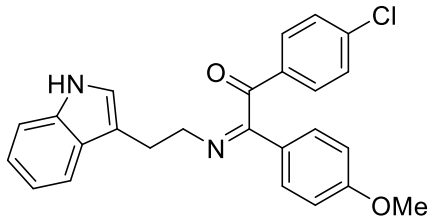
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (13:1) to afford a hite solid (66.4 mg, yield: 83%), M.p. 152-155 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.74 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.00 (ddd, *J* = 10.0, 8.4, 5.4 Hz, 4H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.84 (d, *J* = 6.2 Hz, 3H), 3.78 (t, *J* = 7.0 Hz, 2H), 3.20 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (d, *J* = 257.5 Hz), 165.8, 161.8, 136.2, 131.9 (d, *J* = 9.7 Hz), 129.0, 127.7 (d, *J* = 34.8 Hz), 122.0 (d, *J* = 11.4 Hz), 119.2, 118.9, 116.3 (d, *J* = 22.2 Hz), 114.1 (d, *J* = 9.7 Hz), 111.0, 55.4, 54.7, 27.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.09.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}FN_2O_2$ 401.1665, found: 401.1658



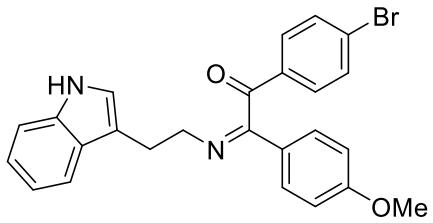
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (13:1) to afford a white oil (69.1 mg, yield: 83%).

(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-1-(4-chlorophenyl)-2-(4-methoxyphenyl)ethan-1-one (**3x**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.77-7.55 (m, 4H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.40-7.30 (m, 2H), 7.26 (s, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.02 (dd, *J* = 18.8, 6.8 Hz, 2H), 6.86 (dd, *J* = 31.2, 8.5 Hz, 2H), 3.84 (d, *J* = 6.5 Hz, 3H), 3.77 (dd, *J* = 14.9, 7.5 Hz, 2H), 3.19 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 165.5, 161.8, 141.0, 136.1, 133.0,131.6, 130.4, 129.4, 128.9, 128.6, 127.8, 127.5, 122.0, 119.2, 118.9, 114.4, 114.1, 111.0, 55.4, 54.6, 27.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}ClN_2O_2$ 417.1370, found: 417.1363



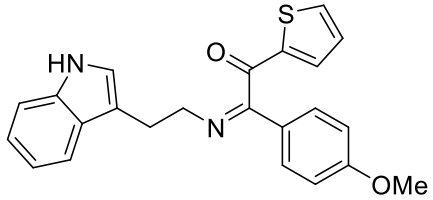
(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-1-(4-bromophenyl)-2-(4-methoxyphenyl)ethan-1-one(**3y**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (13:1) to afford a yellow solid (64.4 mg, yield: 70%), M.p. 141-144 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 8.01 (s, 1H), 7.72-7.63 (m, 3H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.77 (t, *J* = 7.3 Hz, 2H), 3.20 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 165.3, 161.9, 137.3, 136.4, 136.1, 131.4, 130.7, 129.0, 128.1, 127.7, 127.5, 123.5, 122.0, 121.9, 119.3, 118.8, 114.2, 114.0, 111.1, 55.4, 54.7, 27.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}BrN_2O_2$ 461.0865, found: 461.0863



(Z)-2-((2-(1H-indol-3-yl)ethyl)imino)-2-(4-methoxyphenyl)-1-(thiophen-2-yl)ethan-1-one(**3z**)

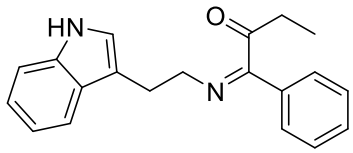
Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (13:1) to afford a yellow oil (47.3 mg, yield: 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.77-7.64 (m, 3H), 7.49 (dd, J = 8.0, 4.2 Hz, 2H), 7.32

(d, J = 8.1 Hz, 1H), 7.27 (dd, J = 5.4, 3.2 Hz, 1H), 7.18 (dd, J = 11.1, 4.0 Hz, 1H), 7.07 (dd, J = 11.0, 3.9 Hz, 1H), 6.99 (d, J = 2.1 Hz, 1H), 6.95-6.87 (m, 2H), 3.84 (d, J = 3.1 Hz, 3H), 3.80 (dd, J = 13.3, 5.8 Hz, 2H), 3.20 (t, J = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 166.0, 161.8, 140.5, 136.1, 136.0, 129.1, 127.9, 127.6, 127.3, 126.2, 122.0, 121.9, 119.2, 119.0, 114.2, 114.1, 111.1, 55.4, 54.7, 27.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_2S$ 389.1324, found: 389.1320



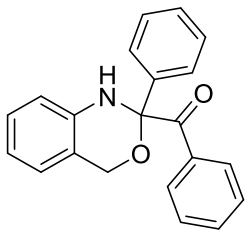
(Z)-1-((2-(1H-indol-3-yl)ethyl)imino)-1-phenylbutan-2-one(**3z1**)

Prepared according to general procedure (1) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a yellow solid (45.6 mg, yield: 75%), M.p. 115-118 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.37 (dd, *J* = 16.2, 8.4 Hz, 4H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 4.08 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.51 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.13 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 174.6, 136.2, 135.8, 132.0, 128.7, 128.1, 127.4, 122.6, 122.0, 119.5, 118.7, 112.4, 111.1, 47.4, 31.7, 25.0, 9.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_2O$ 305.1654, found: 305.1642



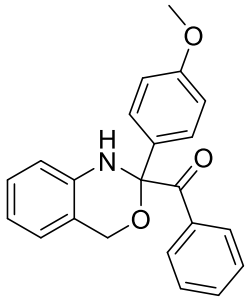
phenyl(2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)methanone (**5a**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a light yellow solid (51.7 mg, yield: 82%), M.p. 99-101 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.72-7.61 (m, 2H), 7.53 (dd, *J* = 13.2, 5.8 Hz, 1H), 7.46-7.32 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.90-6.73 (m, 3H), 5.12 (s, 1H), 4.92 (d, *J* = 15.0 Hz, 1H), 4.83 (d, *J* = 15.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 140.4, 139.5, 133.7, 133.2, 130.5, 129.0, 128.9, 128.3, 127.9, 125.8, 124.5, 119.3, 119.1, 115.7, 91.0, 64.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{17}NO_2Na$ 338.1157, found: 338.1157



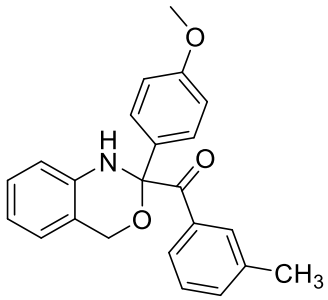
(2-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone (**5b**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a light yellow solid (58.7 mg, yield: 85%), M.p. 115-118 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.06 (m, 2H), 7.53 (ddd, *J* = 12.7, 8.1, 4.7 Hz, 3H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.95-6.88 (m, 2H), 6.88-6.72 (m, 3H), 5.09 (s, 1H), 4.84 (dd, *J* = 35.2, 15.0 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 160.0, 140.4, 133.9, 133.1, 131.5, 130.4, 128.3, 127.9, 127.3, 124.5, 119.4, 119.0, 115.7, 114.3, 90.8, 64.1, 55.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}NO_3Na$ 368.1263, found: 368.1253



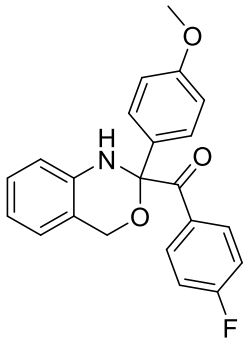
(2-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(m-tolyl)methanone (**5c**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a light yellow solid (57.5 mg, yield: 80%), M.p. 89-91 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.85 (m, 2H), 7.59-7.50 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.95-6.87 (m, 2H), 6.87-6.72 (m, 3H), 5.09 (s, 1H), 4.84 (q, *J* = 15.0 Hz, 2H), 3.81 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 160.0, 140.4, 138.0, 133.9, 131.6, 130.8, 128.1, 127.8, 127.7, 127.4, 124.5, 119.4, 118.9, 115.7, 114.3, 90.8, 64.0, 55.3, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}NO_3Na$ 382.1419, found: 382.1416



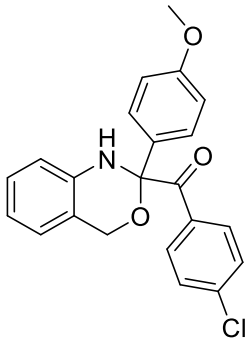
(4-fluorophenyl)(2-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)methanone (**5d**)
Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a light yellow solid (55.2 mg, yield: 76%), M.p. 133-136 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.14 (m, 2H), 7.57-7.47 (m, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 7.10-7.01 (m, 2H), 6.95-6.88 (m, 2H), 6.88-6.74 (m, 3H), 5.08 (s, 1H), 4.97-4.71 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 165.6 (d, *J* = 255.7 Hz), 160.1, 140.3, 133.3 (d, *J* = 9.2 Hz), 131.4, 130.1 (d, *J* = 3.0 Hz), 127.9, 127.2, 124.5, 119.1 (d, *J* = 18.4 Hz), 115.7, 115.5, 115.3, 90.8, 64.1, 55.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -104.48.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}FNO_3Na$ 386.1168, found: 386.1160

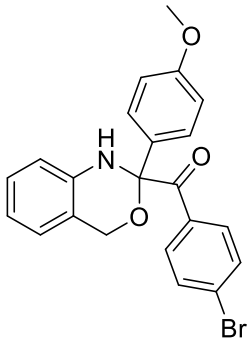


(4-chlorophenyl)(2-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)methanone (**5e**)
Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a light yellow solid (59.1 mg, yield: 78%), M.p. 140-143 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.04 (m, 2H), 7.55-7.47 (m, 2H), 7.39-7.31 (m, 2H), 7.14 (t, *J* = 7.0 Hz, 1H), 6.96-6.88 (m, 2H), 6.81 (dq, *J* = 14.8, 7.2 Hz, 3H), 5.06 (s, 1H), 4.83 (dt, *J* = 52.2, 16.8 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 160.1, 140.3, 139.6, 132.1, 132.0, 131.2, 128.6, 128.0, 127.3, 124.5, 119.3, 119.1, 115.7, 114.4, 90.8, 64.1, 55.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}ClNO_3Na$ 402.0873, found: 402.0869



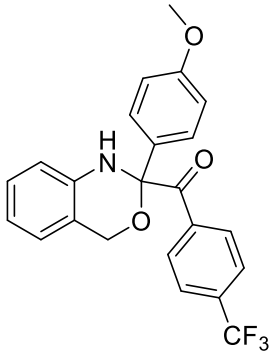
(4-bromophenyl)(2-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)methanone (**5f**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a light yellow solid (68.5 mg, yield: 81%), M.p. 145-147 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.51 (dd, *J* = 8.8, 2.2 Hz, 4H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.79 (dd, *J* = 14.9, 7.6 Hz, 2H), 5.07 (s, 1H), 4.85 (dd, *J* = 46.4, 15.0 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.8, 160.1, 140.2, 132.5, 132.0, 131.6, 131.2, 128.5, 128.0, 127.3, 124.5, 119.2, 119.1, 115.7, 114.4, 90.8, 64.1, 55.3.

HRMS (ESI) m/z: [M+Na]$^{+}$ calcd for $C_{22}H_{18}BrNO_3Na$ 446.0368, found: 446.0367



(2-(4-methoxyphenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(4-(trifluoromethyl)phenyl)methanone(**5g**)

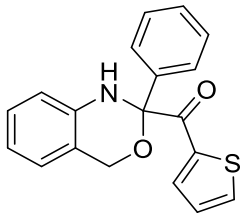
Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a white solid (66.9 mg, yield: 81%), M.p. 123-126 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.82 (dt, *J* = 15.9, 7.6 Hz, 3H), 5.08 (s, 1H), 4.85 (dd, *J* = 55.8, 15.0 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.0, 160.2, 140.0, 130.7 (d, *J* = 5.2 Hz), 128.0, 127.3, 125.2 (q, *J* = 3.6 Hz), 124.5, 119.2 (d, *J* = 2.3 Hz), 115.8, 114.5, 90.8, 64.1, 55.3.

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.24.

HRMS (ESI) m/z: [M+Na]$^{+}$ calcd for $C_{23}H_{18}F_3NO_3Na$ 436.1136, found: 436.1129



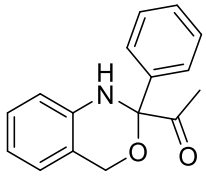
(2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(thiophen-3-yl)methanone (**5h**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a yellow oil (45.0 mg, yield: 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.67 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.61-7.51 (m, 2H), 7.24 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.13 (td, *J* = 8.0, 1.3 Hz, 1H), 6.93-6.88 (m, 2H), 6.85 (dd, *J* = 18.2, 7.9 Hz, 2H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 5.22 (s, 1H), 4.89 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 160.0, 140.1, 137.2, 135.8, 131.3, 129.2, 127.9, 127.7, 125.2, 124.5, 119.5, 118.9, 115.7, 114.3, 90.6, 63.9, 55.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}NO_2S$ 322.0902, found: 322.0896



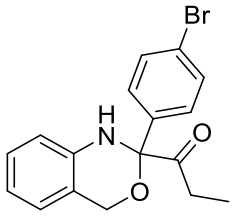
1-(2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)ethan-1-one (**5i**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a white oil (42.5 mg, yield: 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.56 (m, 2H), 7.45-7.32 (m, 3H), 7.13 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H), 6.75 (td, J = 7.4, 0.8 Hz, 1H), 5.52 (s, 1H), 4.99-4.75 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 139.1, 138.5, 129.0, 129.0, 127.8, 127.4, 124.6, 119.9, 118.7, 116.1, 89.5, 63.2, 23.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}NO_2Na$ 276.1000, found: 276.0995



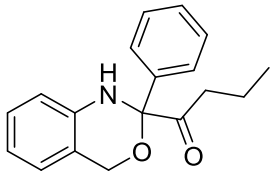
1-(2-(4-bromophenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)propan-1-one (**5j**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (12:1) to afford a light yellow solid (55.2 mg, yield: 80%), M.p. 65-67 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.90-6.66 (m, 3H), 4.96-4.64 (m, 3H), 2.20 (dt, *J* = 15.0, 7.5 Hz, 1H), 2.06-1.85 (m, 1H), 1.00 (dd, *J* = 9.7, 5.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 140.6, 132.3, 131.9, 131.8, 131.7, 128.9, 128.4, 127.9, 124.4, 119.1, 119.0, 115.9, 91.4, 64.0, 31.6, 7.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}BrNO_2Na$ 368.0262, found: 368.0260



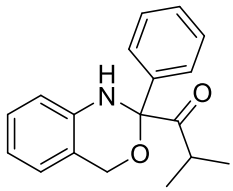
Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a white soild (46.1 mg, yield: 82%), M.p. 47-49 °C.

1-(2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)butan-1-one (**5k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.62 (m, 2H), 7.46-7.37 (m, 2H), 7.35 (ddd, *J* = 7.2, 3.5, 1.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.74 (td, *J* = 7.5, 0.8 Hz, 1H), 5.56 (s, 1H), 4.85 (q, *J* = 14.5 Hz, 2H), 2.95 (ddd, *J* = 18.2, 8.2, 6.2 Hz, 1H), 2.78-2.58 (m, 1H), 1.71-1.40 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 139.3, 138.7, 129.0, 128.9, 127.8, 127.4, 124.6, 119.9, 118.6, 116.0, 89.5, 63.1, 37.0, 16.9, 13.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_2Na$ 304.1313, found: 304.1310



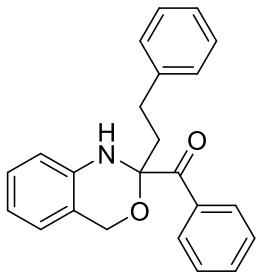
2-methyl-1-(2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)propan-1-one (**5l**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a colorless oil (45.5 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.45-7.37 (m, 2H), 7.37-7.30 (m, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 0.7 Hz, 1H), 5.60 (s, 1H), 4.86 (q, *J* = 14.4 Hz, 2H), 3.60 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.18 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 139.3, 138.6, 128.9, 128.9, 127.8, 127.5, 124.6, 120.0, 118.5, 115.8, 89.5, 63.1, 33.7, 20.0, 19.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_2Na$ 304.1313, found: 304.1310



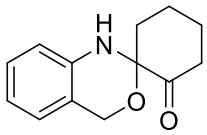
(2-phenethyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone(**5m**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a yellow soild (61.1 mg, yield: 89%), M.p. 92-95 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 8.0, 6.6 Hz, 3H), 7.17 (td, *J* = 16.0, 7.3 Hz, 5H), 6.90-6.74 (m, 3H), 5.00 (s, 1H), 4.88 (dd, *J* = 48.4, 14.9 Hz, 2H), 2.89 (dtd, *J* = 25.6, 13.6, 4.9 Hz, 2H), 2.57 (ddd, *J* = 13.7, 12.0, 5.3 Hz, 1H), 2.19 (ddd, *J* = 13.8, 12.2, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 141.2, 140.8, 133.6, 130.1, 128.7,128.5,128.4, 127.9, 126.1, 124.4, 119.2, 118.9, 116.0, 90.9, 77.4, 77.1, 76.8, 64.1, 40.4, 29.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}NO_2Na$ 366.1470, found: 366.1460



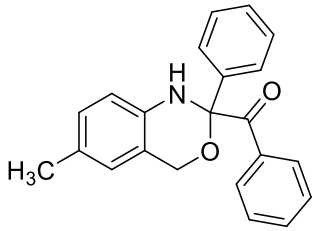
1,4-dihydrospiro[benzo[d][1,3]oxazine-2,1'-cyclohexan]-2'-one(**5n**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8:1) to afford a colorless oil (37.8 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 12.2, 7.7 Hz, 2H), 4.92 (d, *J* = 14.8 Hz, 1H), 4.71 (d, *J* = 14.9 Hz, 1H), 4.67 (s, 1H), 2.92 (td, *J* = 13.0, 6.1 Hz, 1H), 2.51-2.36 (m, 2H), 2.22-1.95 (m, 2H), 1.79-1.64 (m, 2H), 1.63-1.50 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 139.8, 127.8, 124.6, 119.7, 119.0, 116.6, 86.3, 77.4, 77.1, 76.8, 62.7, 38.5, 38.2, 28.0, 20.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NO_2Na$ 240.1000, found: 240.0989



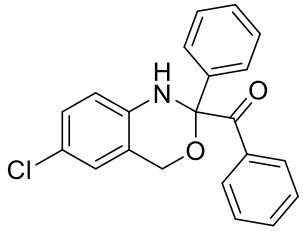
(6-methyl-2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone (**5o**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a yellow soild (54.6 mg, yield: 83%), M.p. 97-99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.05 (m, 2H), 7.69-7.61 (m, 2H), 7.56-7.47 (m, 1H), 7.38 (qt, *J* = 7.3, 2.7 Hz, 5H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.74 (t, *J* = 9.4 Hz, 1H), 6.66 (d, *J* = 10.8 Hz, 1H), 4.95 (s, 1H), 4.84 (dd, *J* = 36.0, 15.0 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 139.6, 138.0, 133.8, 133.1, 130.4, 129.0, 128.9, 128.6, 128.6, 128.3, 125.8, 124.9, 119.5, 116.1, 91.1, 64.1, 63.1, 20.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}NO_2Na$ 352.1313, found: 352.1312



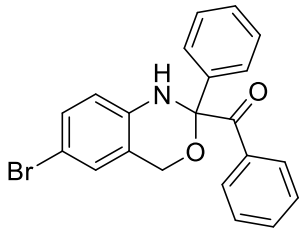
(6-chloro-2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone (**5p**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a white soild (52.4 mg, yield: 75%), M.p. 85-87 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.68-7.57 (m, 2H), 7.57-7.48 (m, 1H), 7.46-7.33 (m, 5H), 7.09 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 5.12 (s, 1H), 4.82 (dd, *J* = 42.8, 15.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 139.1, 139.0, 133.5, 133.4, 130.4, 129.1, 129.1, 128.3, 127.9, 125.7, 124.4, 123.8, 120.7, 116.9, 91.0, 63.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}ClNO_2Na$ 372.0767, found: 372.0765



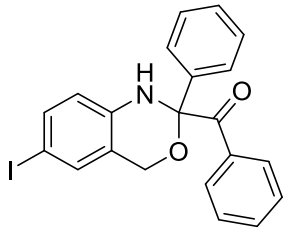
(6-bromo-2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone (**5q**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a yellow soild (61.3 mg, yield: 78%), M.p. 130-133 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.03 (m, 2H), 7.61 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46-7.33 (m, 5H), 7.23 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 5.14 (s, 1H), 4.82 (dd, *J* = 41.9, 15.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 139.5, 139.0, 133.4, 133.4, 130.7, 130.4, 129.1, 129.1, 128.7, 128.3, 127.3, 126.5, 125.7, 121.1, 117.2, 110.8, 90.9, 63.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}BrNO_2Na$ 416.0262, found: 416.0263



(6-iodo-2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone(**5r**)\

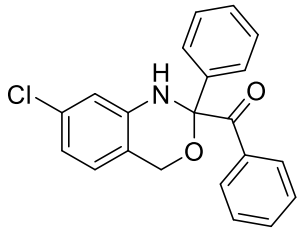
Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a yellow soild (68.8 mg, yield: 78%),

M.p. 127-129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.03 (m, 2H), 7.60 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45-7.32 (m, 6H), 7.15 (s, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.14 (s, 1H), 4.80 (dd, *J* = 42.2, 15.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 140.1, 139.0, 136.6, 133.4, 133.4, 133.1, 130.5, 129.2, 129.1, 128.4, 125.7, 121.6, 117.6, 90.9, 80.2, 77.4, 77.1, 76.7, 63.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}INO_2Na$ 464.0123, found: 464.0115



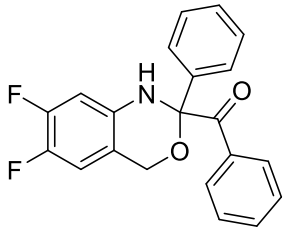
(7-chloro-2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone (**5s**)

Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a white soild (51.7 mg, yield: 74%), M.p. 115-117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.06 (m, 2H), 7.65-7.57 (m, 2H), 7.56-7.47 (m, 1H), 7.44-7.33 (m, 5H), 6.85-6.69 (m, 3H), 5.19 (s, 1H), 4.81 (dd, *J* = 42.6, 15.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 141.5, 139.0, 133.4, 133.4, 133.3, 130.5, 129.1, 129.1, 128.3, 125.7, 125.6, 118.9, 117.4, 115.2, 90.8, 63.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}ClNO_2Na$ 372.0767, found: 372.0763



(6,7-difluoro-2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)(phenyl)methanone (**5t**)

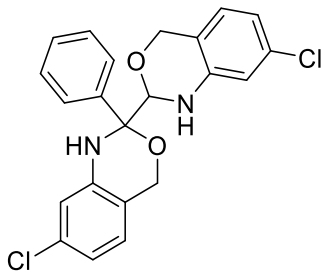
Prepared according to general procedure (2) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1) to afford a yellow soild (51.3 mg, yield: 73%), M.p. 73-76 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.60 (dt, *J* = 13.4, 4.6 Hz, 2H), 7.55-7.49 (m, 1H), 7.45-7.32 (m, 5H), 6.74-6.57 (m, 2H), 5.05 (s, 1H), 4.78 (dd, *J* = 44.9, 15.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 138.8, 133.4 (d, *J* = 8.5 Hz), 130.4, 129.2 (d, *J* = 8.9 Hz), 128.4, 125.6, 113.0 (d, *J* = 18.6 Hz), 104.6 (d, *J* = 20.4 Hz), 90.8, 63.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -138.74 (d, *J* = 21.8 Hz), -149.74 (d, *J* = 21.8 Hz).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}F_2NO_2Na$ 374.0969, found: 374.0963



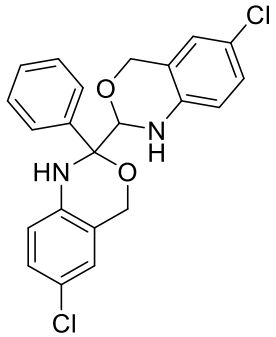
(2'R)-7,7'-dichloro-2-phenyl-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d][1,3]oxazine (**6a**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil (66.8 mg, yield: 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.45-7.34 (m, 3H), 6.84 (d, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.75-6.69 (m, 3H), 6.68 (t, *J* = 2.4 Hz, 1H), 5.24 (s, 1H), 4.97 (t, *J* = 4.2 Hz, 2H), 4.73 (s, 2H), 4.65 (d, *J* = 14.6 Hz, 1H), 4.44 (d, *J* = 14.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 141.2, 139.5, 133.2, 133.2, 128.8, 128.7, 127.9, 125.8, 125.7, 118.6, 118.6, 118.5, 115.7, 115.2, 87.0, 86.9, 67.8, 62.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}Cl_2N_2O_2$ 413.0824, found: 413.0813



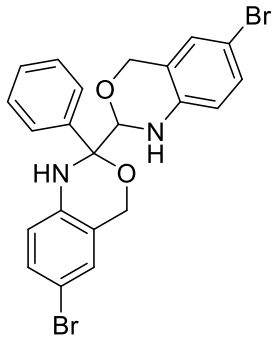
6,6'-dichloro-2-phenyl-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d][1,3]oxazine (**6b**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil colorless oil (64.3 mg, yield: 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.36 (m, 5H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.16 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.90 (dd, *J* = 5.5, 3.2 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.98 (dd, *J* = 32.0, 12.5 Hz, 2H), 4.65 (dd, *J* = 56.3, 14.9 Hz, 2H), 4.29 (dd, *J* = 25.9, 12.5 Hz, 2H), 3.70 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 142.3, 139.5, 129.2, 129.1, 128.7, 128.5, 127.9, 127.9, 127.7, 125.6, 125.4, 124.9, 124.4, 120.3, 119.1, 91.4, 77.4, 77.0, 76.7, 64.9, 63.2, 52.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}Cl_2N_2O_2$ 413.0824, found: 413.0823



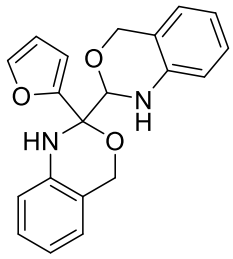
(2'R)-6,6'-dibromo-2-phenyl-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d][1,3]oxazine (**6c**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil yellow oil (78 mg, yield: 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.40 (tt, *J* = 8.8, 4.5 Hz, 3H), 7.25-7.15 (m, 2H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.93 (d, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 5.18 (s, 1H), 4.95 (s, 1H), 4.89 (s, 1H), 4.73 (s, 2H), 4.65 (d, *J* = 14.8 Hz, 1H), 4.45 (d, *J* = 14.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 139.3, 139.1, 130.6, 130.6, 128.8, 128.8, 127.9, 127.4, 127.4, 122.4, 122.4, 118.0, 117.4, 110.7, 110.6, 87.2, 87.1, 67.5, 61.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}Br_2N_2O_2$ 500.9813, found: 500.9808



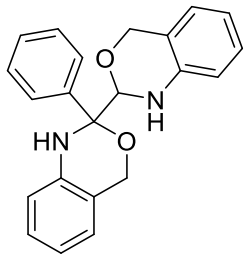
2-(thiophen-2-yl)-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d][1,3]oxazine (**6d**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil yellow oil (44.8 mg, yield: 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.12 (dt, *J* = 15.5, 7.6 Hz, 2H), 6.89 (dt, *J* = 15.0, 7.5 Hz, 2H), 6.85 - 6.74 (m, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 3.2 Hz, 1H), 6.36 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.28 (s, 1H), 5.05 (s, 1H), 4.92 (dd, *J* = 46.2, 14.4 Hz, 2H), 4.78 – 4.69 (m, 2H), 4.49 (d, *J* = 14.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 143.5, 141.6, 140.0, 127.9, 127.7, 124.6, 120.6, 120.4, 118.9, 118.8, 116.2, 116.1, 112.5, 110.4, 84.6, 83.9, 77.4, 77.0, 76.7, 68.1, 63.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_3$ 335.1396, found: 335.1393



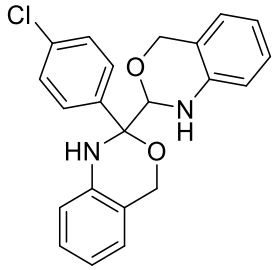
2-phenyl-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d] [1,3] oxazine (**6e**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil colorless oil (52.3 mg, yield: 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.39 (dt, *J* = 14.0, 7.3 Hz, 3H), 7.20-7.06 (m, 2H), 6.89 (d, *J* = 5.7 Hz, 2H), 6.77 (ddd, *J* = 32.0, 13.2, 7.7 Hz, 4H), 5.21 (s, 1H), 5.02 (s, 1H), 4.90 (s, 1H), 4.78 (d, *J* = 15.4 Hz, 2H), 4.71 (d, *J* = 14.6 Hz, 1H), 4.51 (d, *J* = 14.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 140.1, 140.0, 128.6,128.5, 128.1, 127.7, 124.7, 124.6, 120.7, 120.7, 118.9, 118.6, 116.6, 116.0, 87.6, 87.2, 68.1, 62.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_2$ 345.1603, found: 345.1598



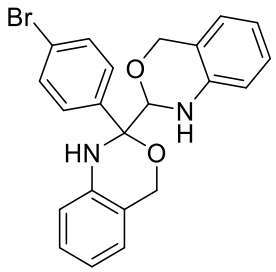
(2'R)-2-(4-chlorophenyl)-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d][1,3]oxazine (**6f**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil colorless oil (55.2 mg, yield: 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.21-7.05 (m, 2H), 6.89 (t, *J* = 6.3 Hz, 2H), 6.79 (ddd, *J* = 11.8, 11.0, 5.8 Hz, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.17 (s, 1H), 4.95 (s, 1H), 4.85 (s, 1H), 4.80 (s, 2H), 4.71 (d, *J* = 14.6 Hz, 1H), 4.50 (d, *J* = 14.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 139.8, 138.6, 134.5, 129.7, 128.8, 127.8, 127.8, 124.7, 124.7, 124.6, 119.0, 119.0, 116.9, 115.9, 87.4, 87.0, 68.1, 62.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}ClN_2O_2$ 379.1213, found: 379.1207



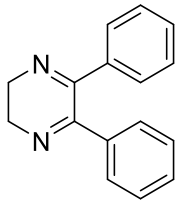
(2'R)-2-(4-bromophenyl)-1,1',4,4'-tetrahydro-2H,2'H-2,2'-bibenzo[d][1,3]oxazine (**6g**)

Prepared according to general procedure (3) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil yellow oil (66.7 mg, yield: 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.45 (m, 4H), 7.19-7.06 (m, 2H), 6.89 (t, *J* = 6.7 Hz, 2H), 6.86-6.73 (m, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.16 (s, 1H), 4.95 (s, 1H), 4.84 (s, 1H), 4.78 (d, *J* = 15.0 Hz, 2H), 4.71 (d, *J* = 14.6 Hz, 1H), 4.50 (d, *J* = 14.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 139.7, 139.1, 131.8, 130.1, 127.8, 127.8, 124.7, 124.6, 122.8, 120.7, 120.6, 119.1, 119.0, 117.0, 115.9, 87.4, 87.0, 68.1, 62.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}BrN_2O_2$ 423.0708, found: 423.0700



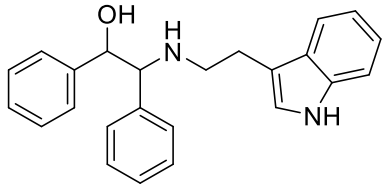
5,6-diphenyl-2,3-dihydropyrazine (**8a**)

Prepared according to general procedure (4) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1) to afford a colorless oil yellow solid (38.4 mg, yield: 82%), M.p. 140-145 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 4H), 7.33 (ddd, *J* = 6.3, 3.7, 1.3 Hz, 2H), 7.30-7.22 (m, 4H), 3.72 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 137.8, 129.6, 128.1, 127.9, 45.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}N_2$ 235.1235, found: 235.1230



2-((2-(1H-indol-3-yl)ethyl)amino)-1,2-diphenylethan-1-ol(**8b**), dr=5:1

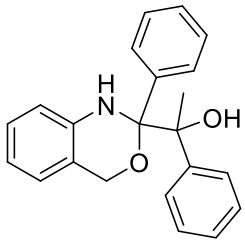
Prepared according to general procedure (5) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:1) to afford a colorless oil yellow oil (118.3 mg, yield: 83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.04 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27-7.16 (m, 9H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.09 (dd, *J* = 6.5, 4.0 Hz, 3H), 7.00-6.93 (m, 2H), 6.92 (d, *J* = 1.3 Hz, 1H), 6.84 (s, 1H), 4.87 (d, *J* = 5.5 Hz, 1H), 4.56 (d, *J* = 8.6 Hz, 1H), 3.95 (d, *J* = 5.6 Hz, 1H), 3.67 (d, *J* = 8.6 Hz, 1H), 3.20 (s, 2H), 3.06-2.86 (m, 4H), 2.85-2.79 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3 (Main product), 140.6, 134.0 (Main product), 139.3, 136.4, 128.3, 128.2 (Main product), 128.1, 127.9 (Main product), 127.7 (Main product), 127.4, 127.4, 127.4, 126.9 (Main product), 126.8, 122.0 (Main product), 121.9 (Main product), 121.8, 119.3 (Main product), 118.8 (Main product), 113.7 (Main product), 111.2 (Main product), 77.6 (Main

product), 76.5, 70.4 (Main product), 68.7, 47.4 (Main product), 47.3, 25.9 (Main product), 25.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O$ 357.1967, found: 357.1958



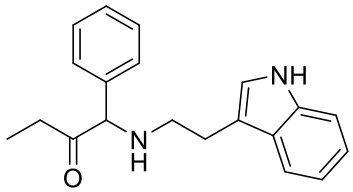
1-phenyl-1-(2-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-yl)ethan-1-ol(**8c**), dr=2.5:1

Prepared according to general procedure (6) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4:1) to afford a colorless oil yellow oil (100.7 mg, yield: 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 12.0, 7.4 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 17.5, 7.6 Hz, 2H), 7.29-7.16 (m, 13H), 7.11-6.99 (m, 4H), 6.75 (t, *J* = 7.8 Hz, 2H), 6.69 (td, *J* = 14.2, 7.3 Hz, 3H), 4.86 (s, 1H), 4.69 (ddd, *J* = 60.8, 42.7, 14.7 Hz, 4H), 3.26 (s, 1H), 2.91 (s, 1H), 1.73 (s, 3H), 1.69 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 142.4, 141.8 (Main product), 140.5 (Main product), 140.3, 138.5 (Main product), 138.2, 133.5, 133.0 (Main product), 130.2 (Main product), 129.9 (Main product), 129.8 (Main product), 129.0 (Main product), 128.3 (Main product), 128.2, 128.2 (Main product), 128.1, 127.5 (Main product), 127.4 (Main product), 127.2, 127.2, 127.2, 126.9 (Main product), 126.0 (Main product), 124.4 (Main product), 124.4, 121.7, 120.6 (Main product), 119.2, 118.6 (Main product), 117.5, 116.5 (Main product), 90.8, 90.6 (Main product), 79.1 (Main product), 78.7, 63.0 (Main product), 62.8, 26.1, 24.8 (Main product), 24.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}NO_2Na$ 354.1470, found: 354.1462



1-((2-(1H-indol-3-yl)ethyl)amino)-1-phenylbutan-2-one (**3z1'**)

Prepared according to general procedure (7) and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:1) to afford a colorless oil colorless oil (508 mg, yield: 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.41-7.30 (m, 4H), 7.27 (s, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 4.44 (s, 1H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.89-2.74 (m, 2H), 2.44 (s, 1H), 2.35 (q, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

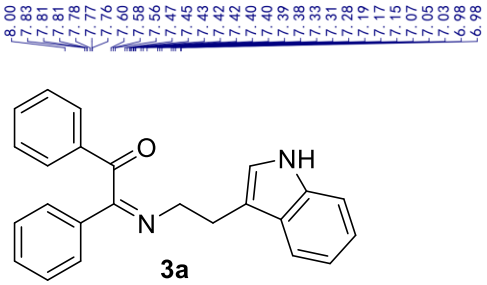
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 138.3, 136.4, 128.9, 128.1, 128.1, 127.4, 122.0, 121.9, 119.2, 118.9, 113.8, 111.1, 72.3, 47.2, 33.0, 25.9, 7.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}NO_2$ 309.1729, found: 309.1725

References

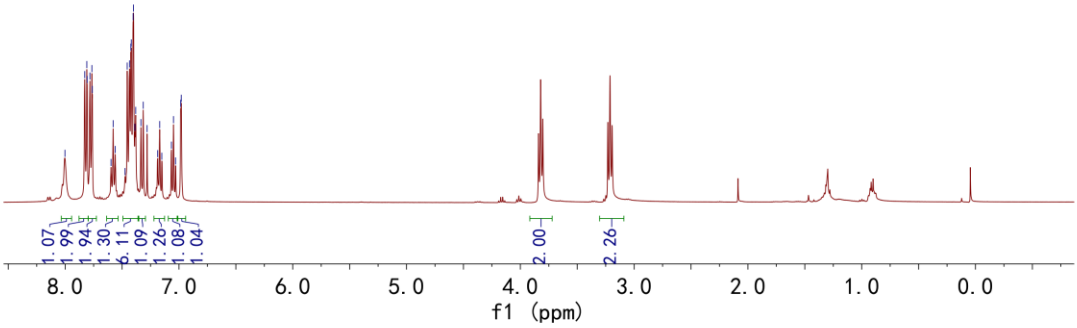
(1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J Appl Crystallogr* **2009,** *42*, 339-341.
(2) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr A* **2008,** *64*, 112-122.
(3) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr C* **2015,** *71*, 3-8.
(4) Kothapalli, R. B.; Niddana, R.; Balamurugan, R. Synthesis of Chiral alpha-Diarylacetic Esters by Stereospecific 1,2-Aryl Migration Promoted by in Situ Generated Acetals from Benzoins. *Org. Lett.* **2014,** *16*, 1278-1281.
(5) Liang, Y. F.; Wu, K.; Song, S.; Li, X. Y.; Huang, X. Q.; Jiao, N. I-2- or NBS-Catalyzed Highly Efficient alpha-Hydroxylation of Ketones with Dimethyl Sulfoxide. *Org. Lett.* **2015,** *17*, 876-879.
(6) Wang, H. Y.; Yang, K.; Bennett, S. R.; Guo, S. R.; Tang, W. P. Iridium-Catalyzed Dynamic Kinetic Isomerization: Expedient Synthesis of Carbohydrates from Achmatowicz Rearrangement Products. *Angew. Chem., Int. Ed.* **2015,** *54*, 8756-8759.

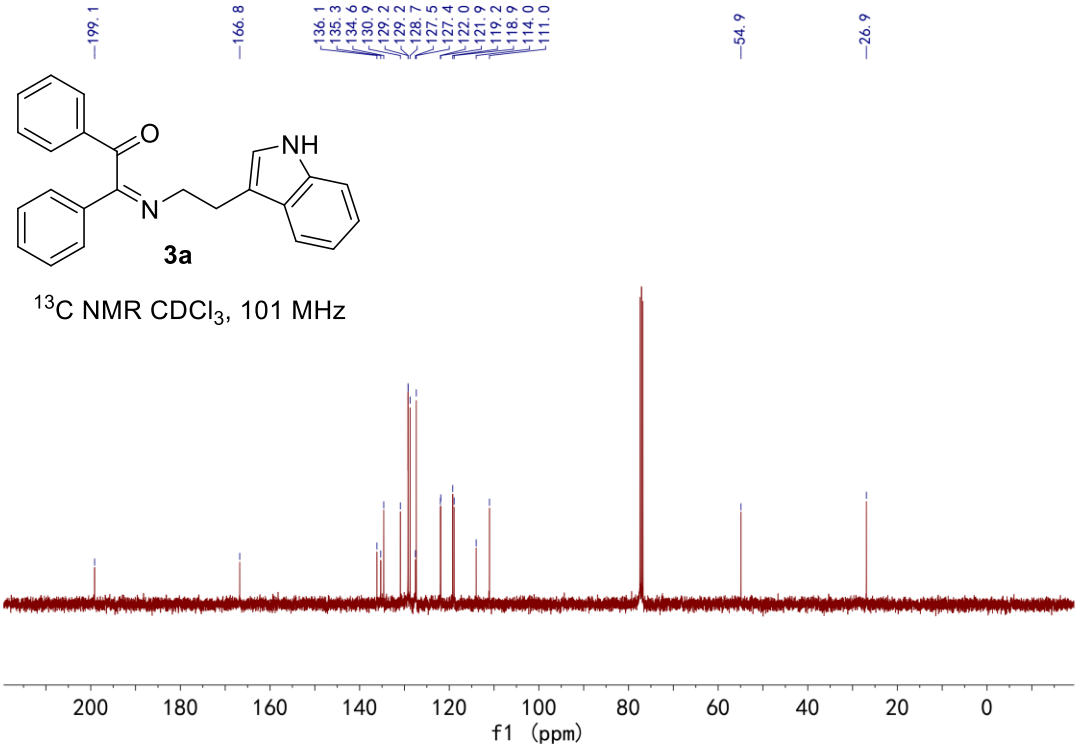
^{1}H and ^{13}C NMR spectra



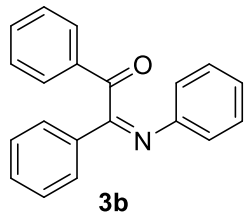
3a

^{1}H NMR $CDCl_3$, 400 MHz



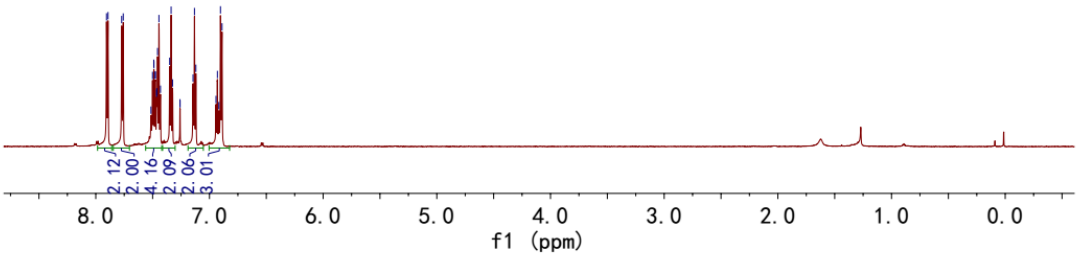


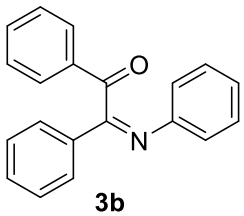
^{13}C NMR $CDCl_3$, 101 MHz



3b

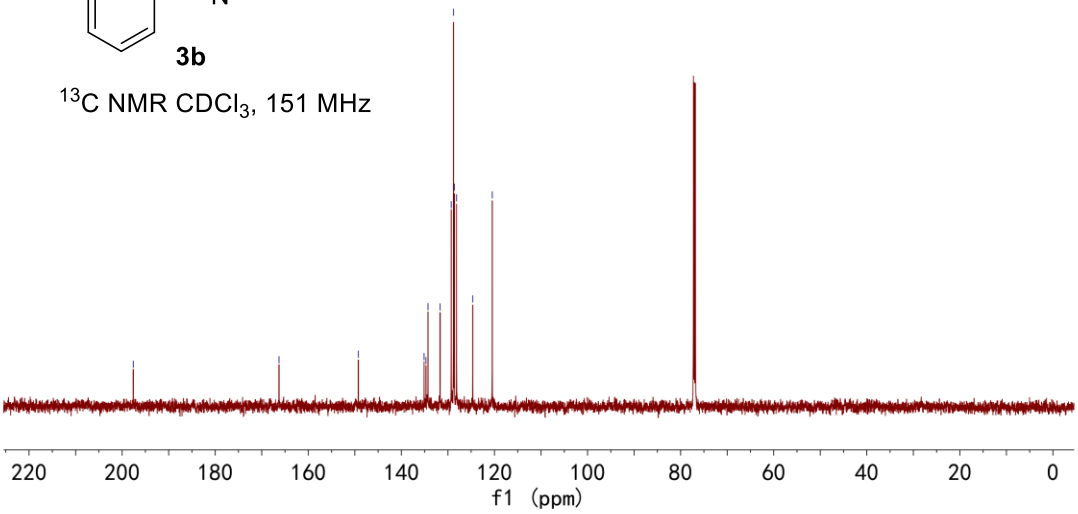
^{1}H NMR $CDCl_3$, 600 MHz

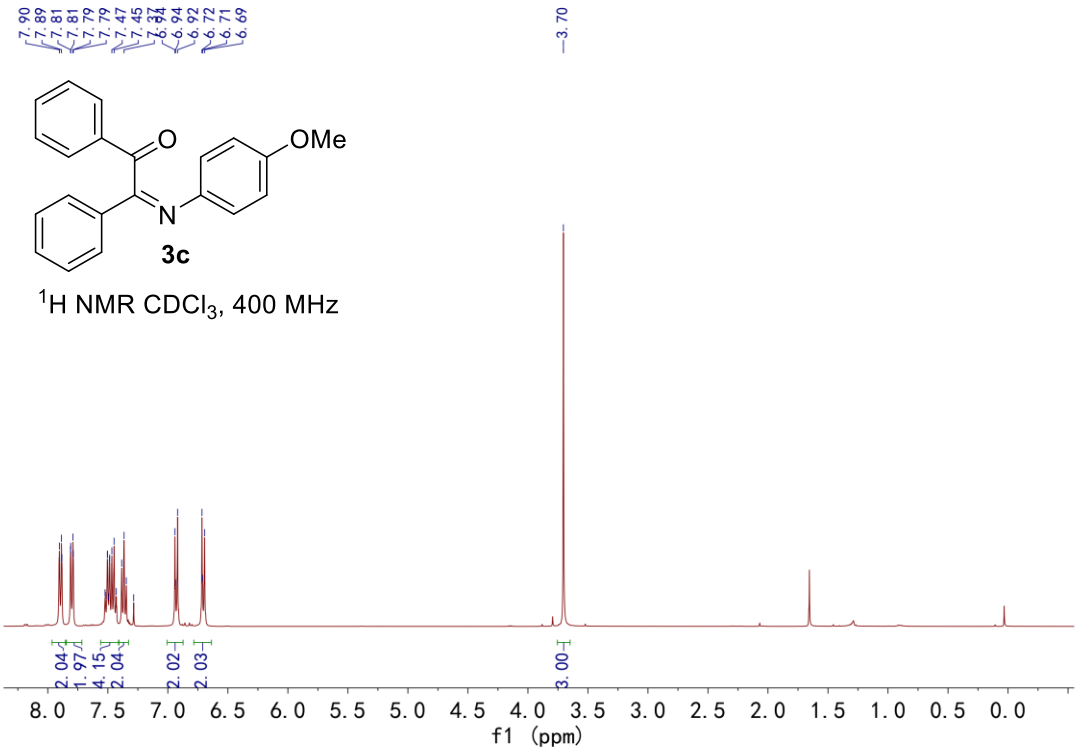




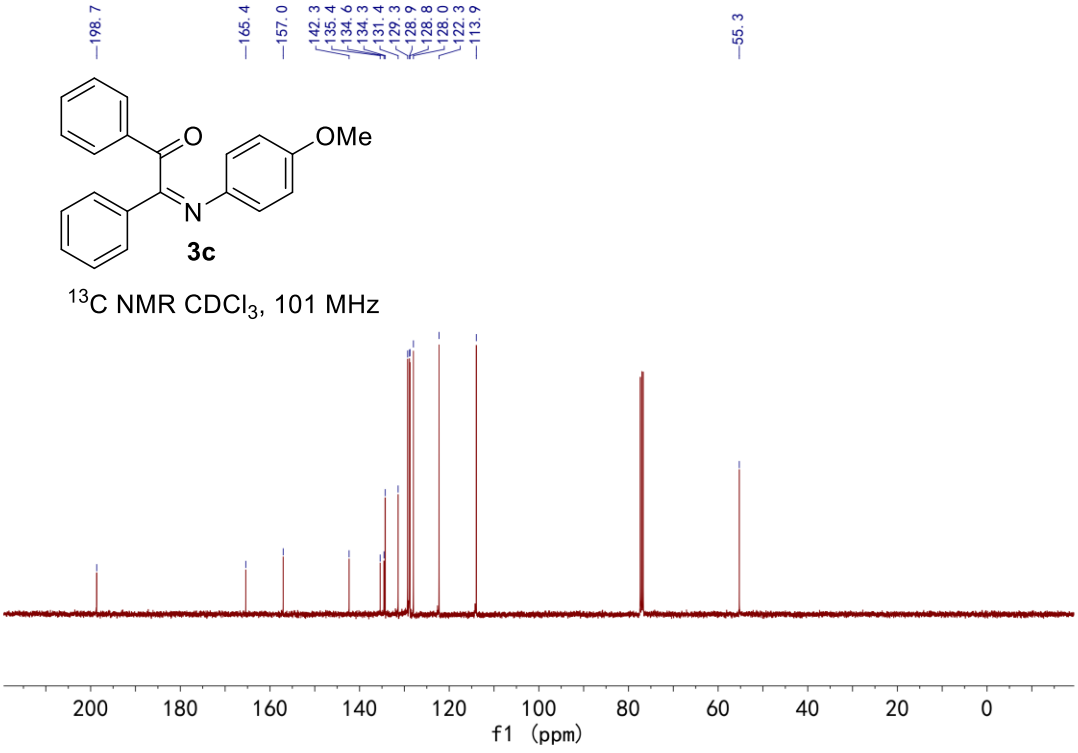
3b

^{13}C NMR $CDCl_3$, 151 MHz

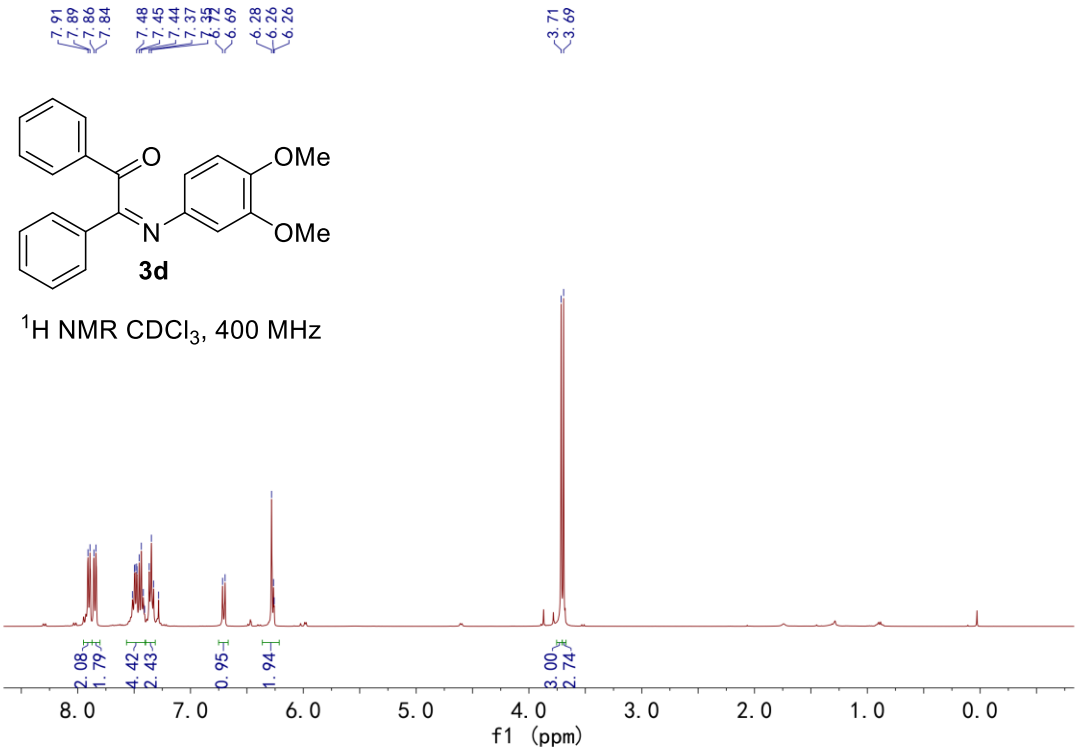




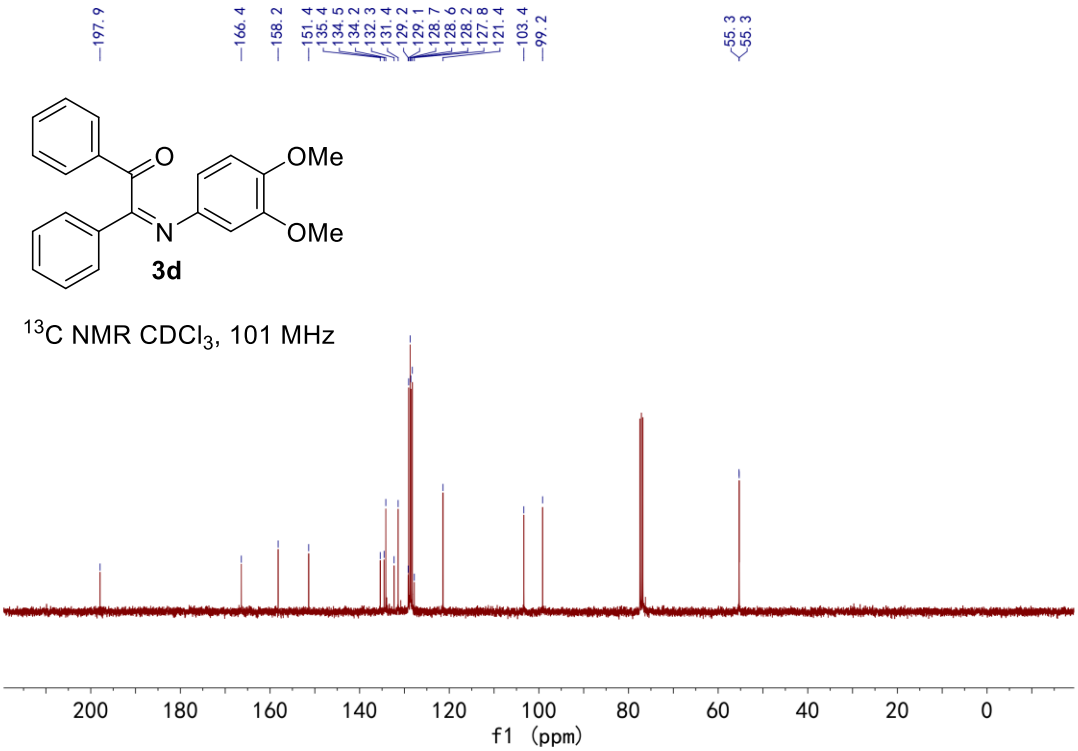
^{1}H NMR $CDCl_3$, 400 MHz



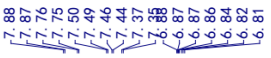
^{13}C NMR $CDCl_3$, 101 MHz

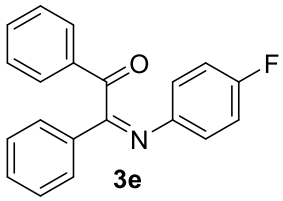


^{1}H NMR $CDCl_3$, 400 MHz



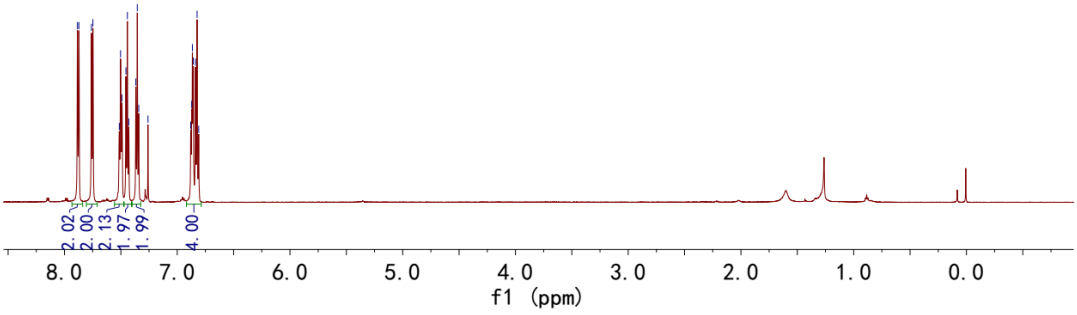
^{13}C NMR $CDCl_3$, 101 MHz

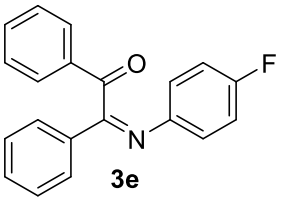




3e

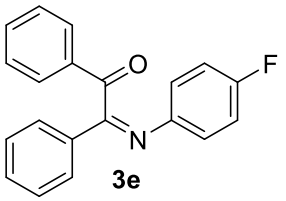
^{1}H NMR $CDCl_3$, 600 MHz





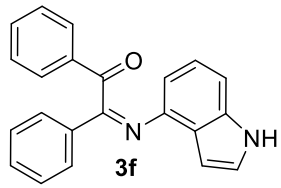
3e

^{13}C NMR $CDCl_3$, 151 MHz



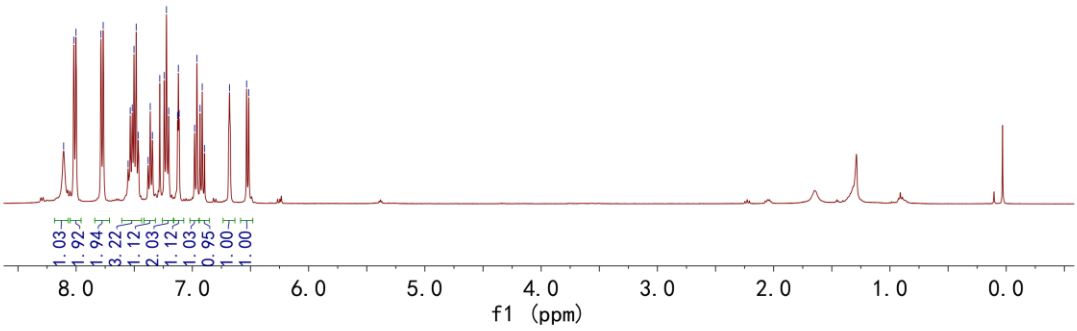
3e

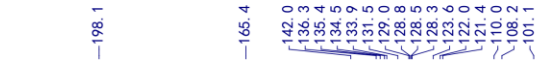
^{19}F NMR $CDCl_3$, 376 MHz

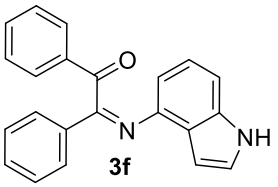


3f

^{1}H NMR $CDCl_3$, 400 MHz

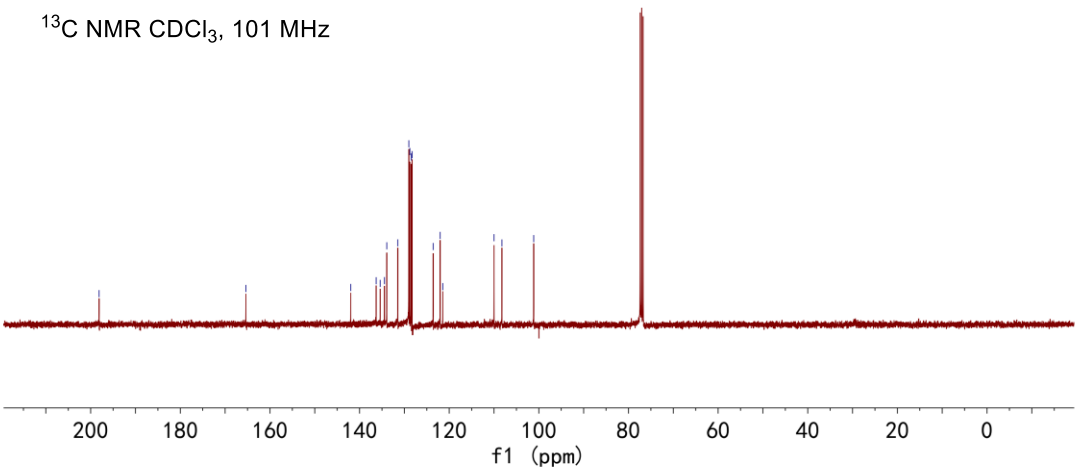


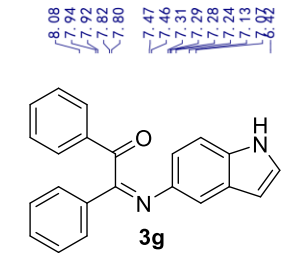




3f

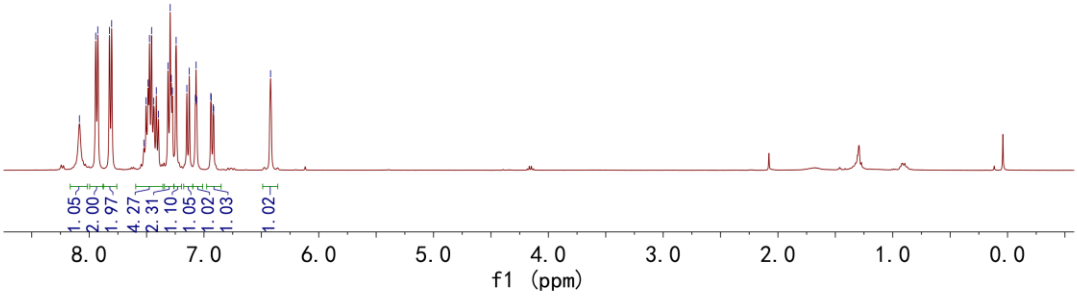
^{13}C NMR $CDCl_3$, 101 MHz

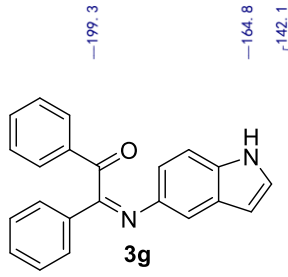




3g

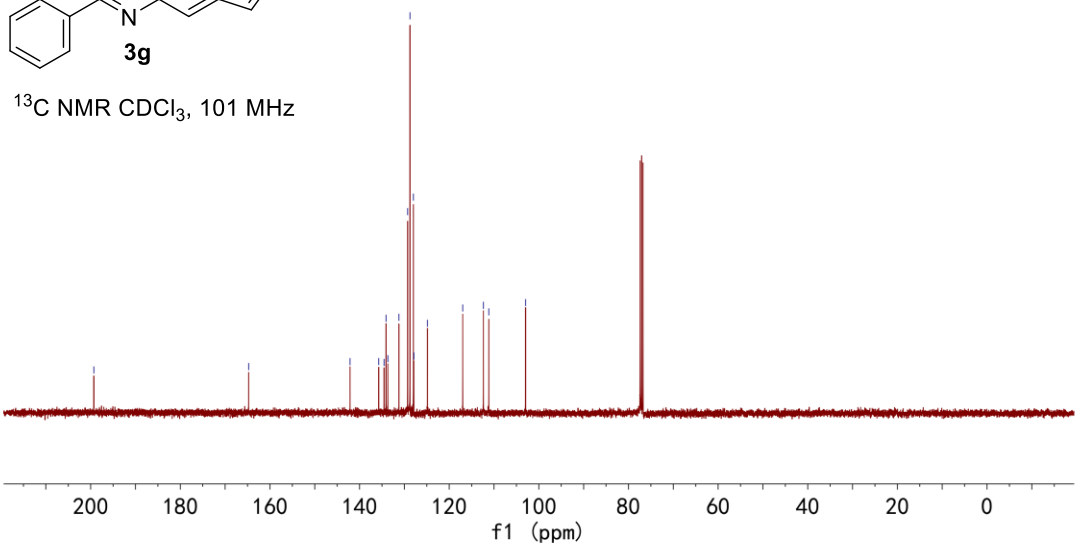
^{1}H NMR $CDCl_3$, 400 MHz

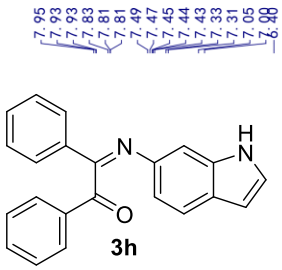




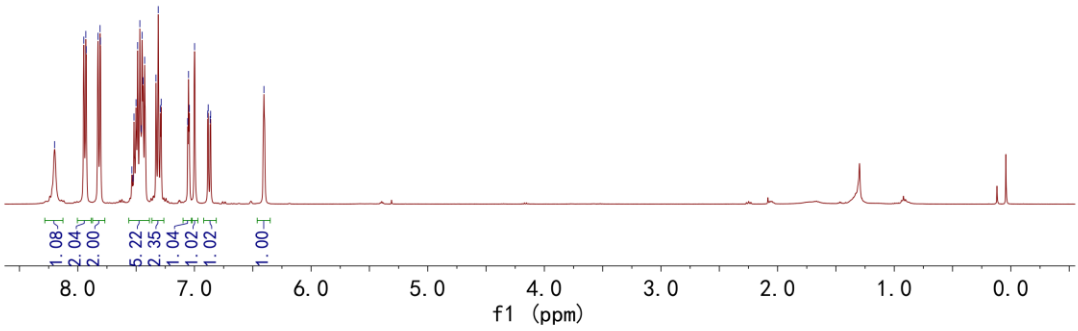
3g

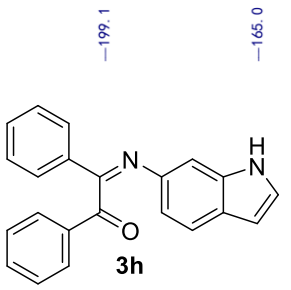
^{13}C NMR $CDCl_3$, 101 MHz



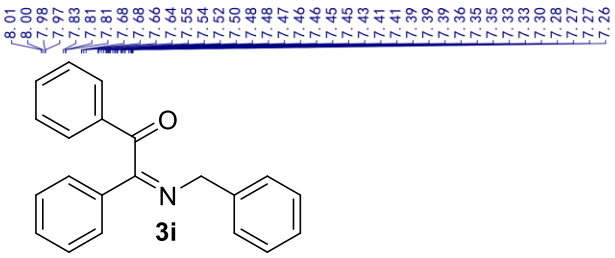


^{1}H NMR $CDCl_3$, 400 MHz





^{13}C NMR $CDCl_3$, 101 MHz



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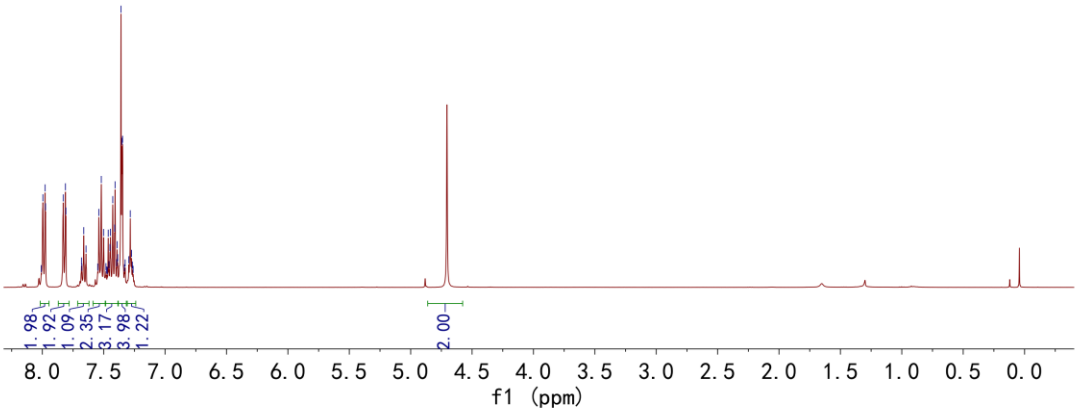
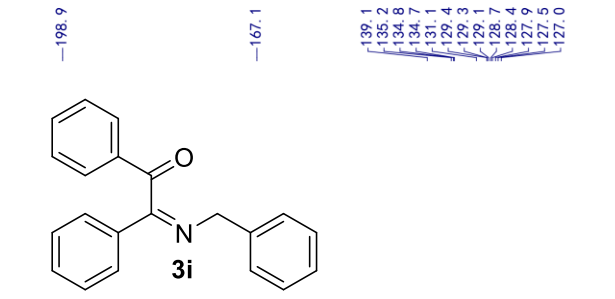
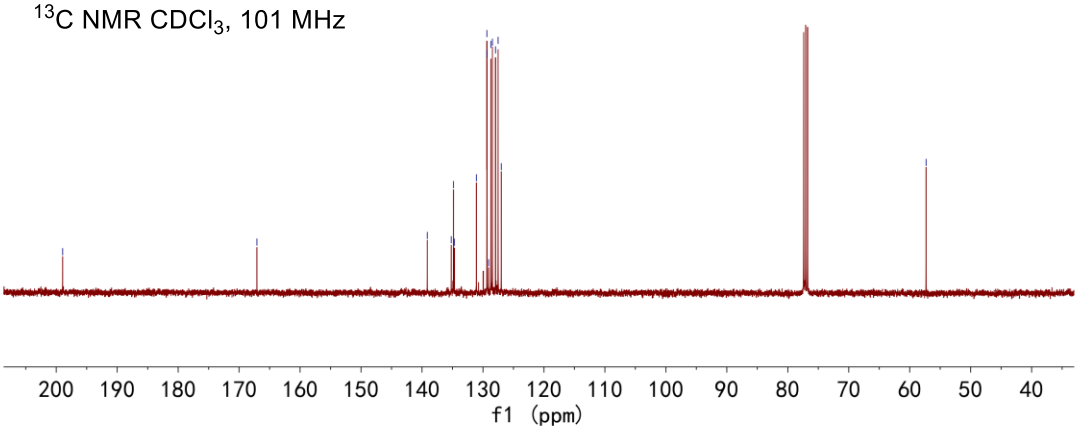
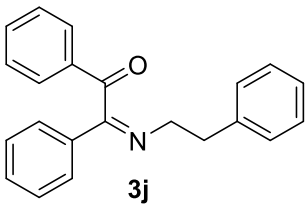




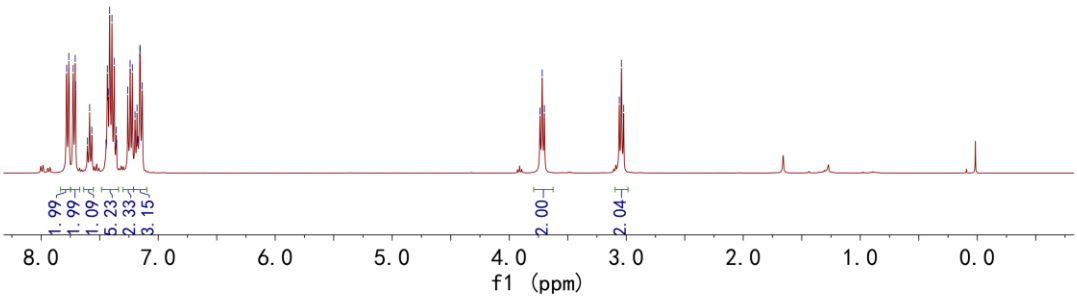
^{13}C NMR $CDCl_3$, 101 MHz

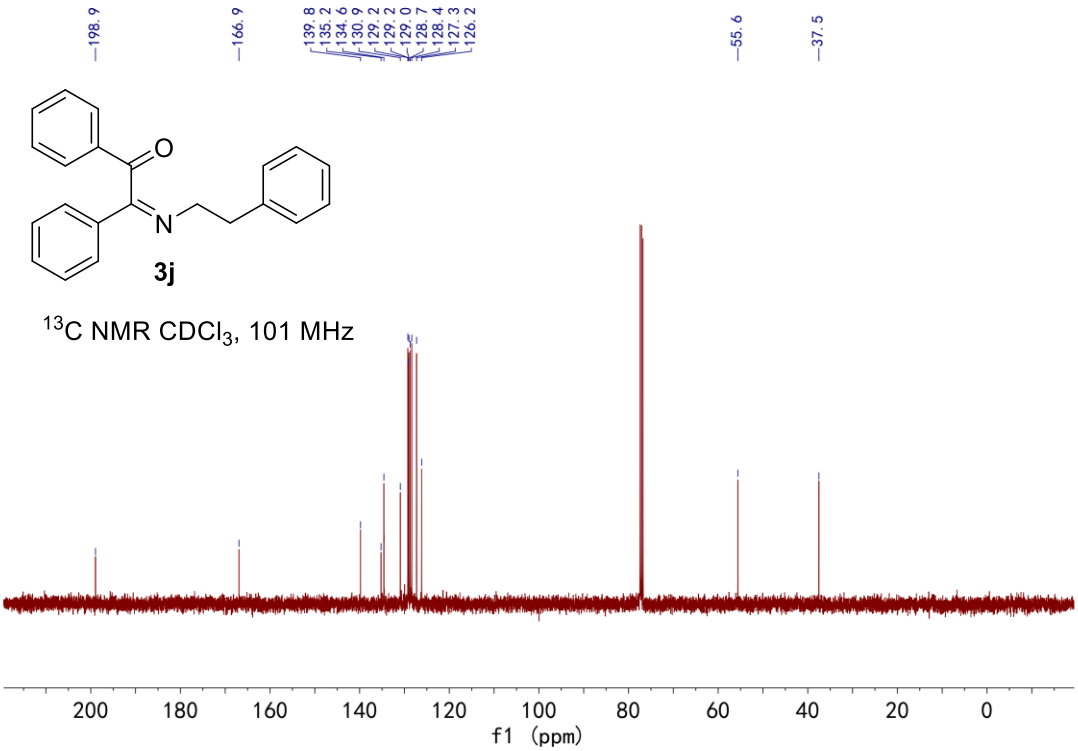




3j

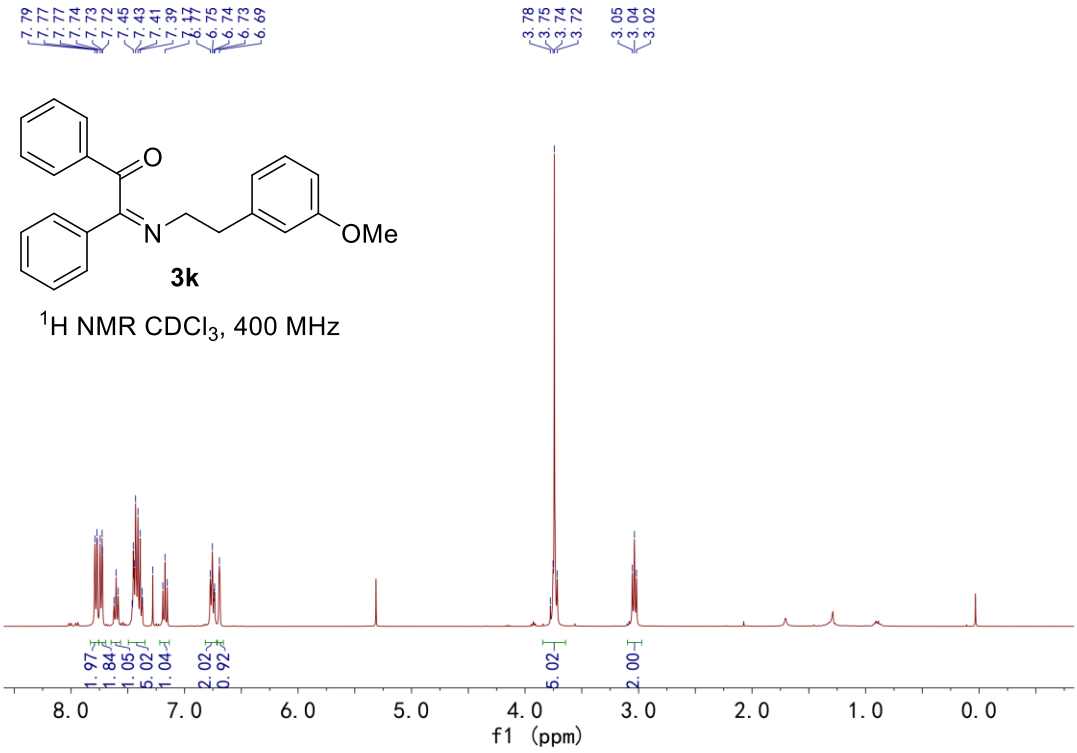
^{1}H NMR $CDCl_3$, 400 MHz





3j

^{13}C NMR $CDCl_3$, 101 MHz


7.79
7.77
7.77
7.74
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7.72
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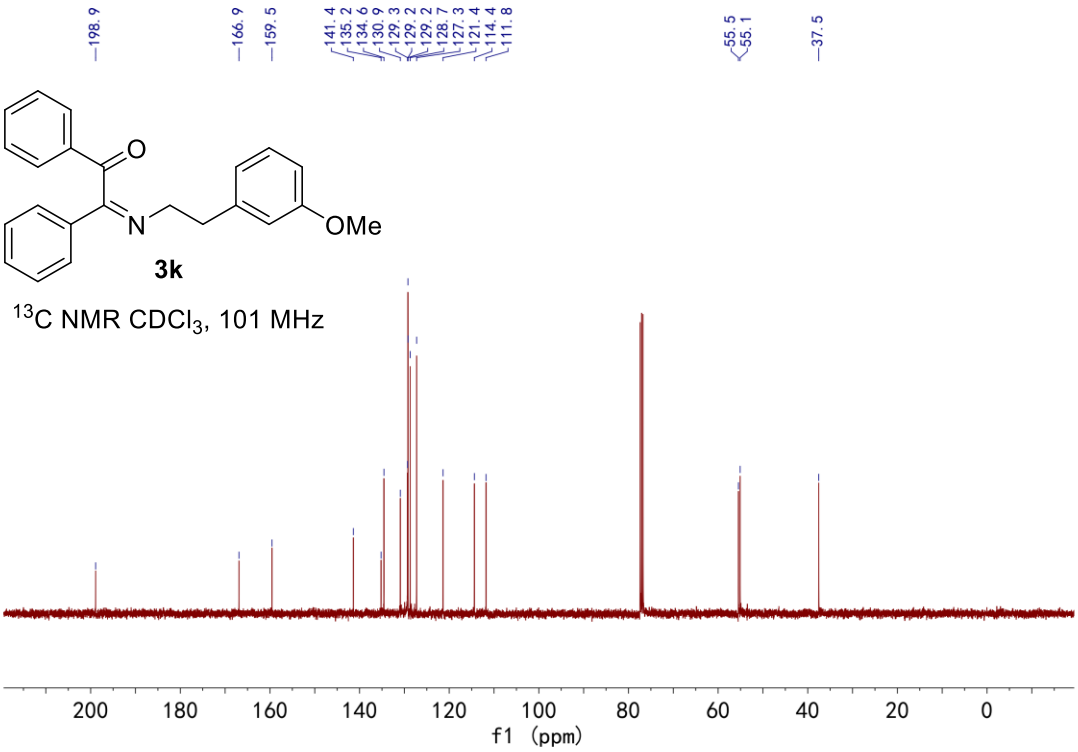
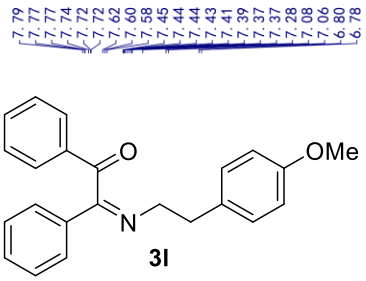
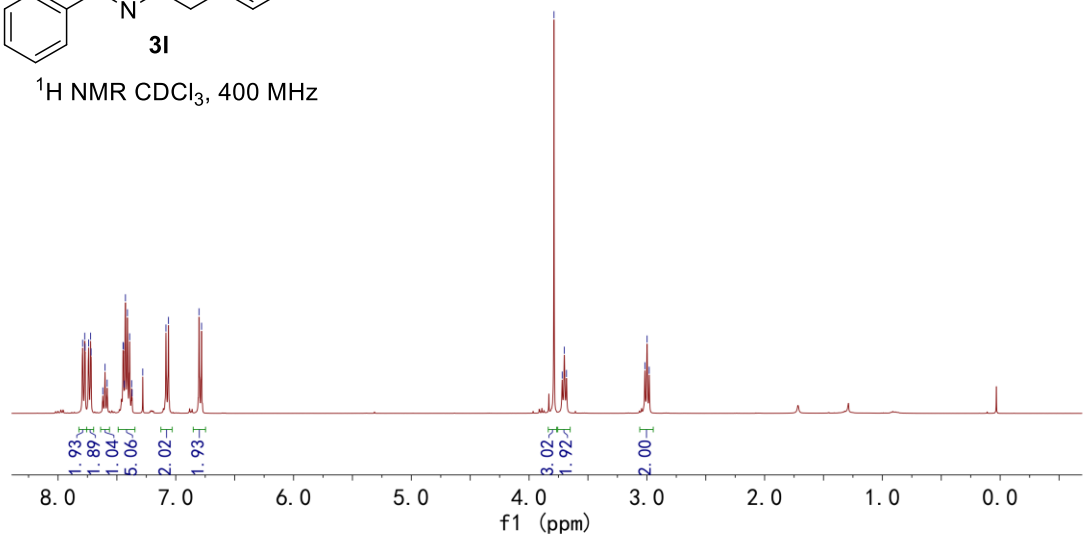
6.73
6.69
3.78
3.75
3.74
3.72
3.05
3.04
3.02
O
N
OMe
3k
1H NMR CDCl3, 400 MHz
1.97
1.84
1.05
5.02
1.04
2.02
0.92
5.02
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

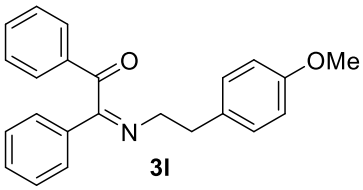

198.9
166.9
159.5
141.4
135.2
134.6
130.9
129.3
129.2
129.2
128.7
127.3
121.4
114.4
111.8
55.5
55.1
37.5
O
N
OMe
3k
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



3l

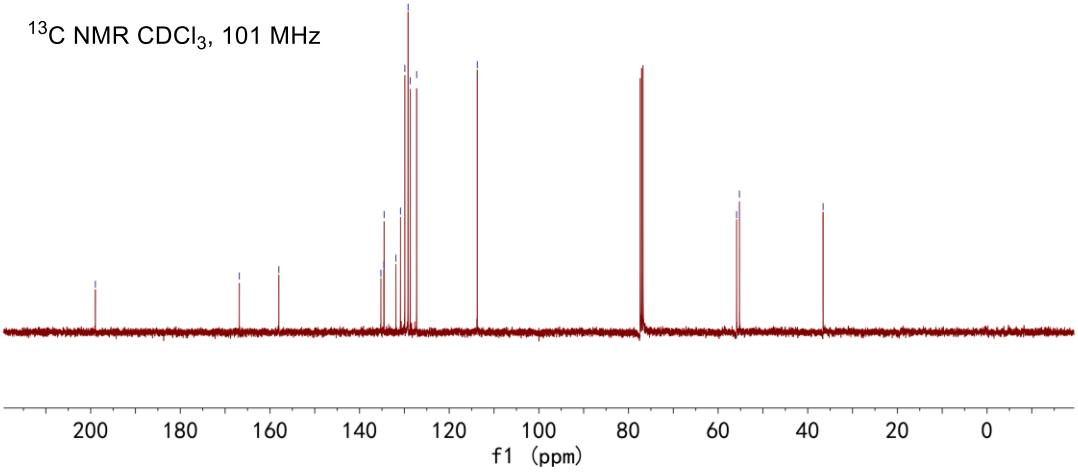
^{1}H NMR $CDCl_3$, 400 MHz

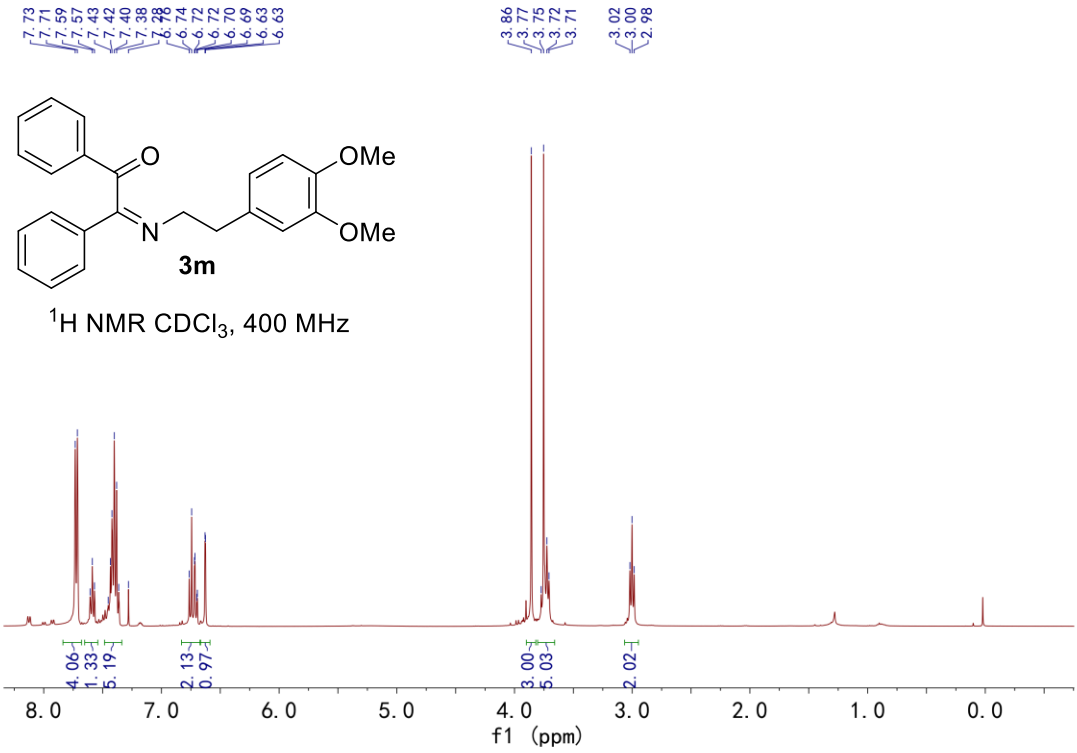




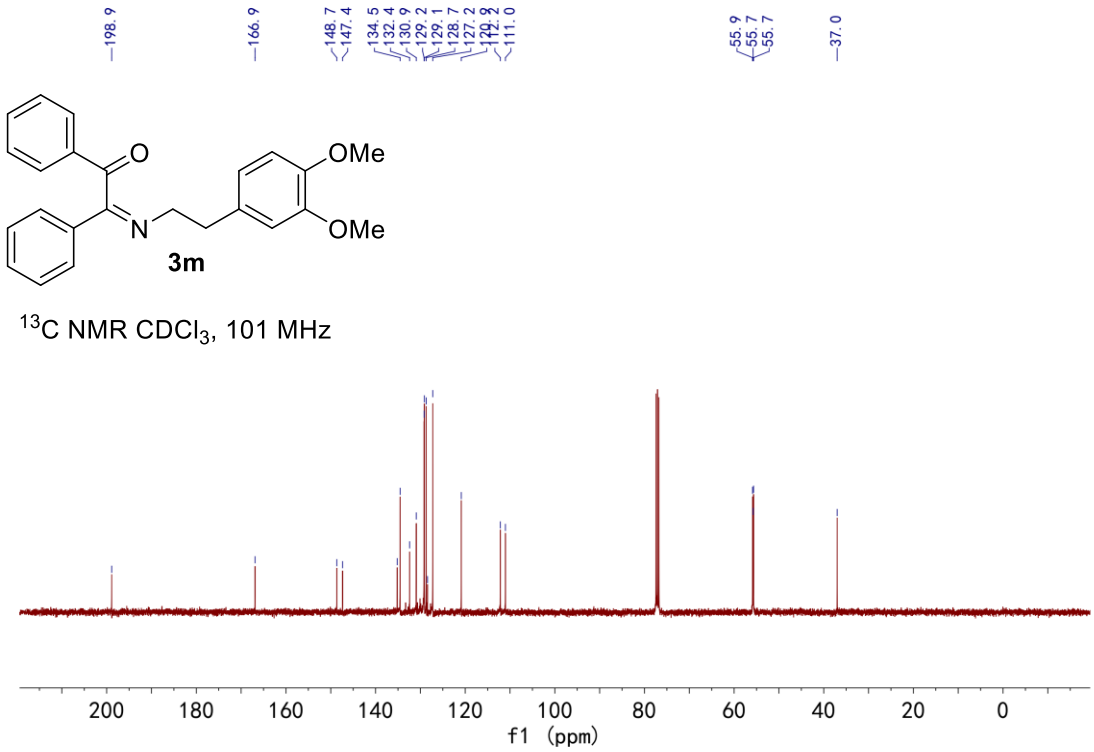
3l

^{13}C NMR $CDCl_3$, 101 MHz

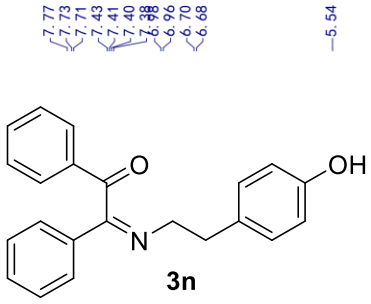




^{1}H NMR $CDCl_3$, 400 MHz

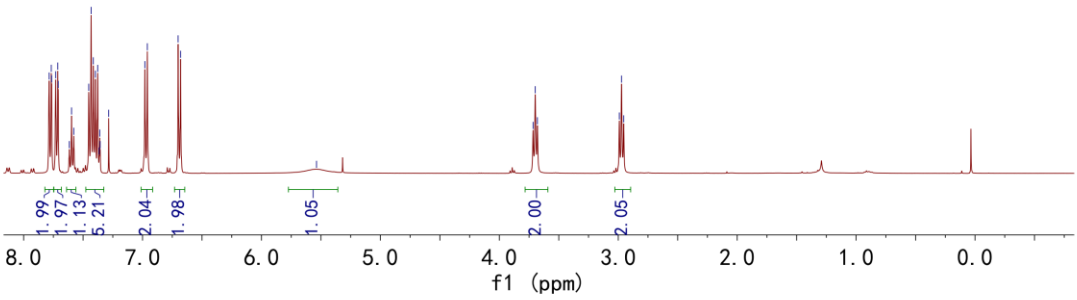


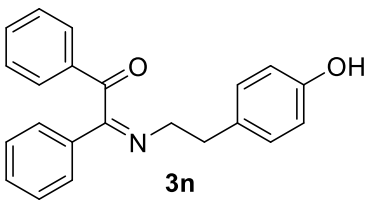
^{13}C NMR $CDCl_3$, 101 MHz



3n

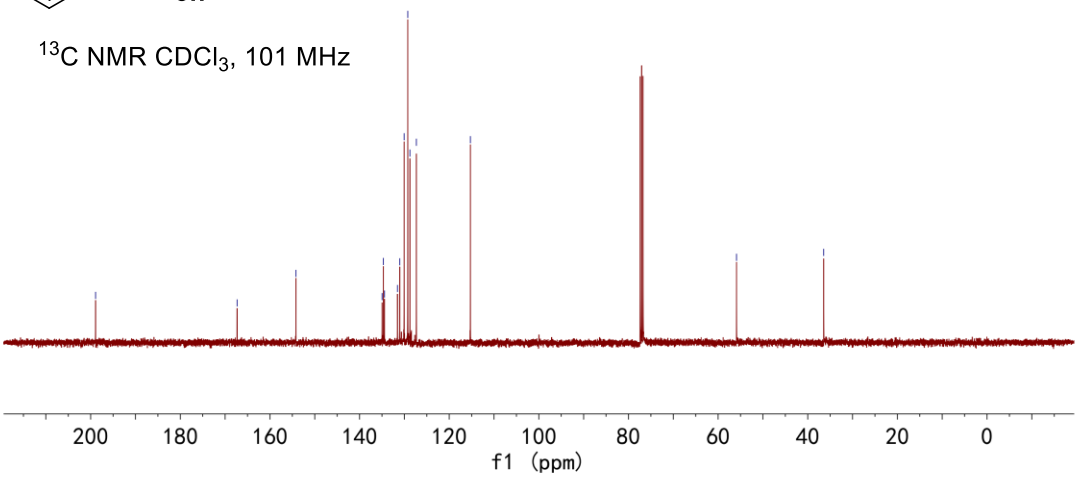
^{1}H NMR $CDCl_3$, 400 MHz

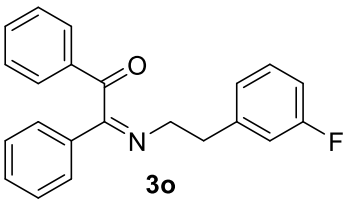




3n

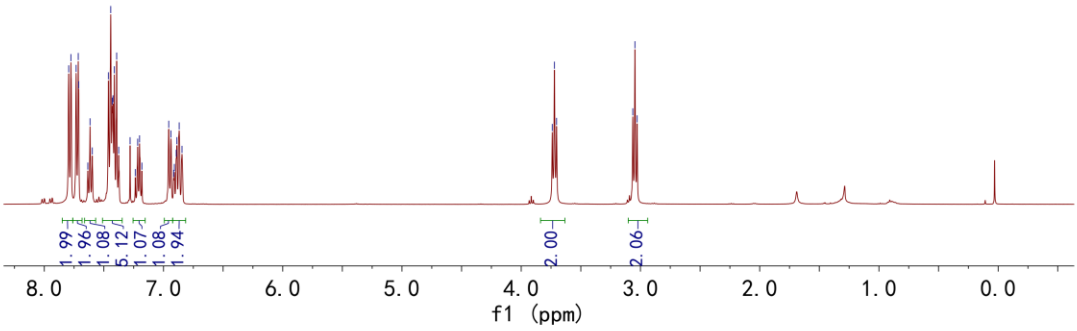
^{13}C NMR $CDCl_3$, 101 MHz

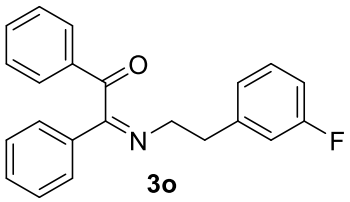




3o

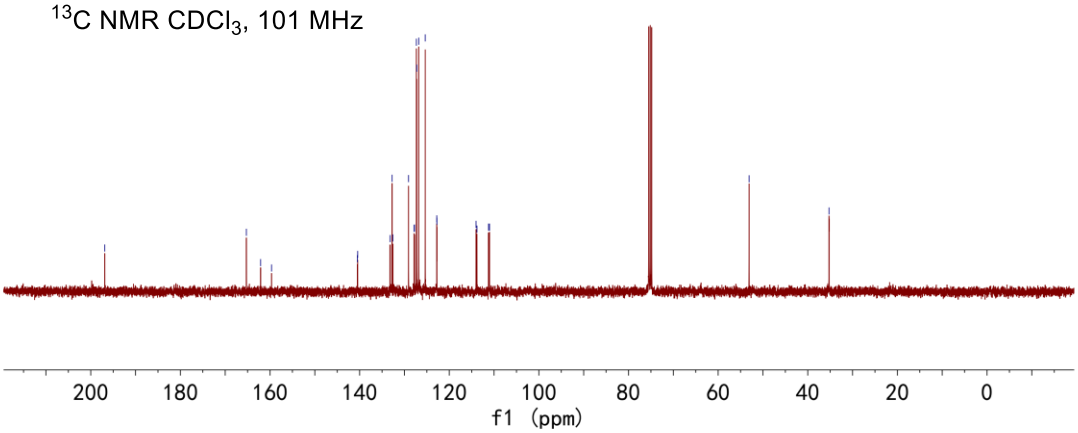
^{1}H NMR $CDCl_3$, 400 MHz

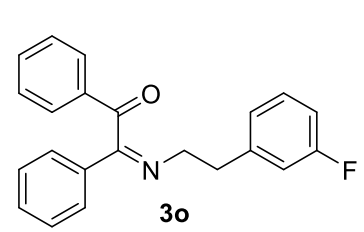




3o

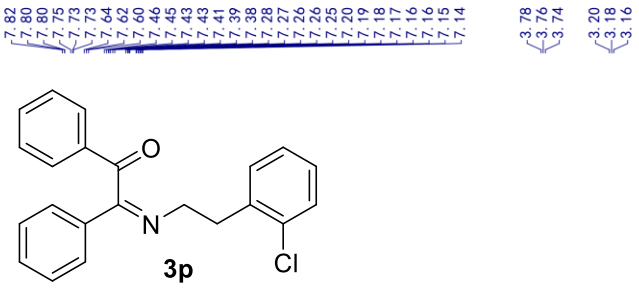
^{13}C NMR $CDCl_3$, 101 MHz



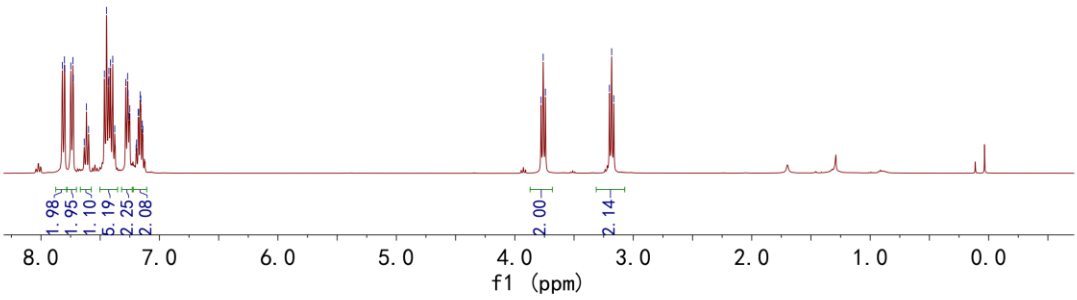


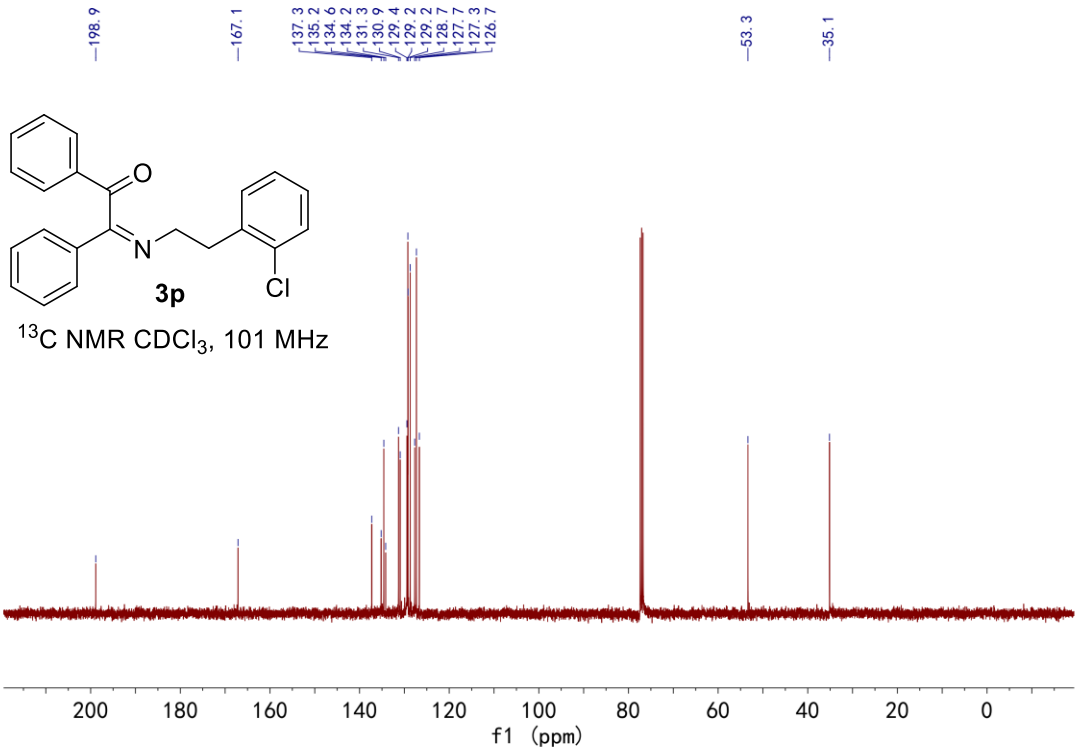
3o

^{19}F NMR $CDCl_3$, 376 MHz

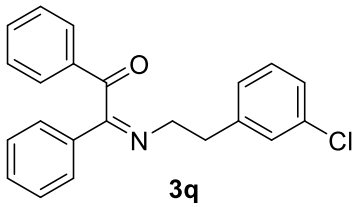


^{1}H NMR $CDCl_3$, 400 MHz



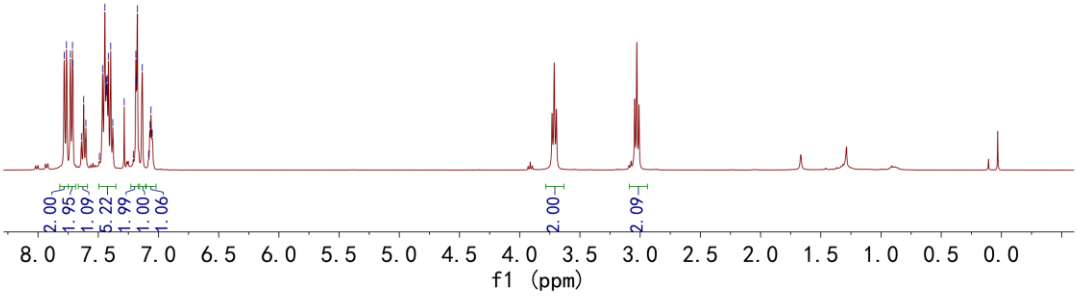


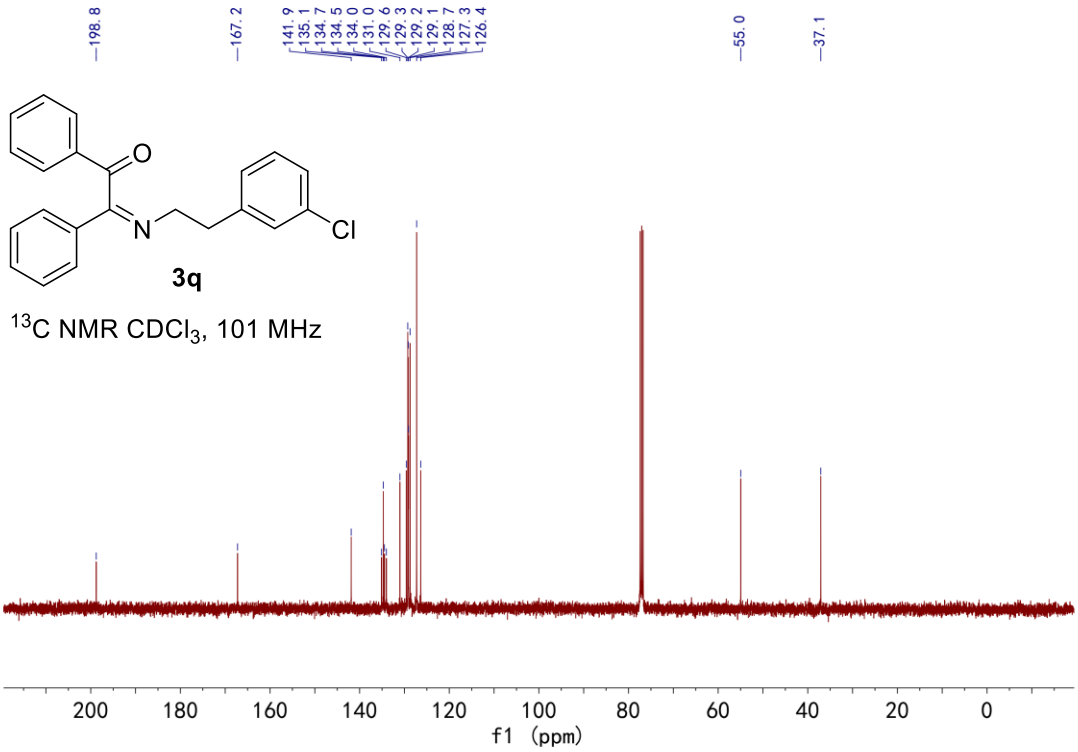
^{13}C NMR $CDCl_3$, 101 MHz



3q

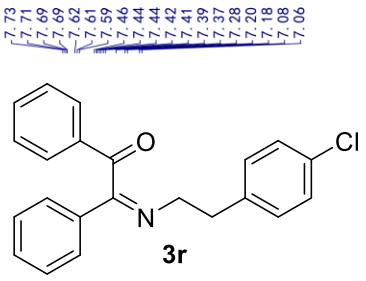
^{1}H NMR $CDCl_3$, 400 MHz





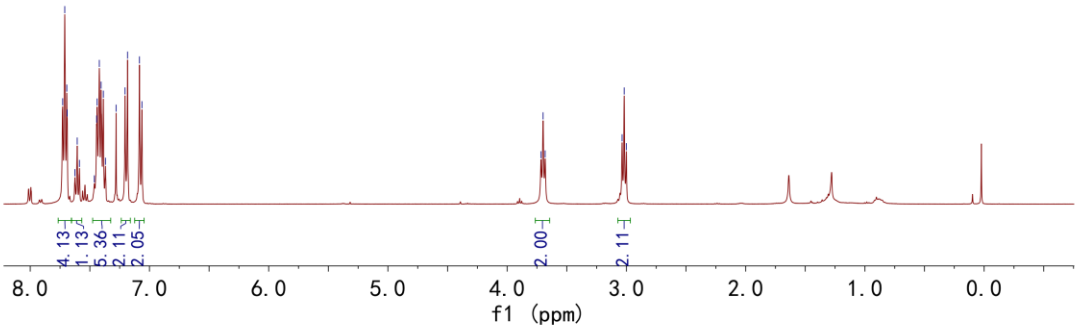
3q

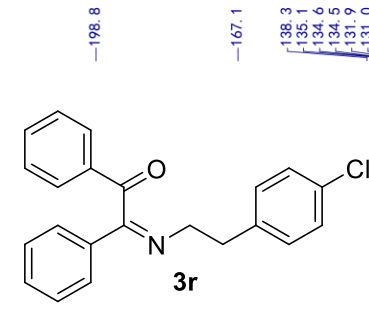
^{13}C NMR $CDCl_3$, 101 MHz



3r

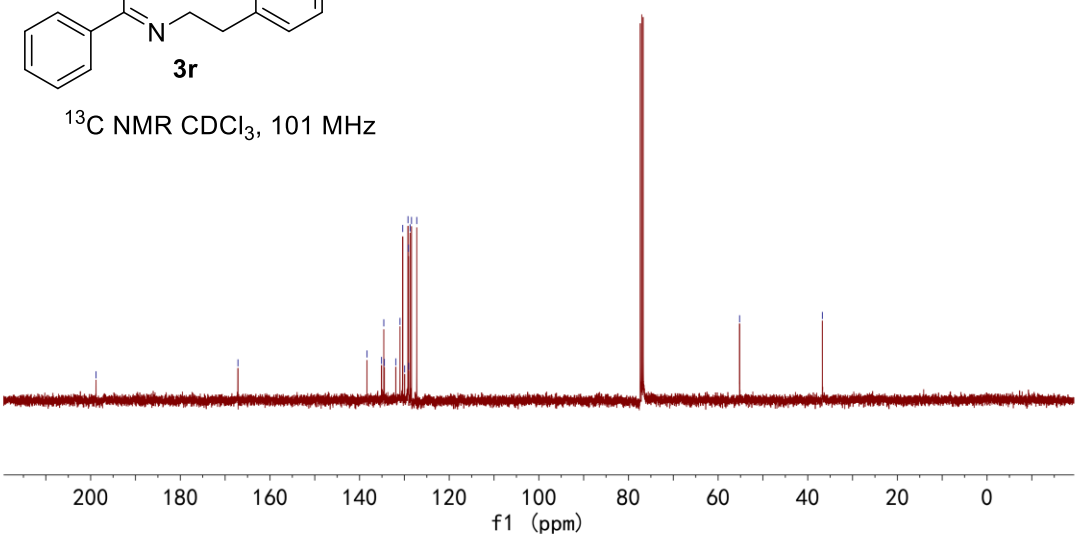
^{1}H NMR $CDCl_3$, 400 MHz

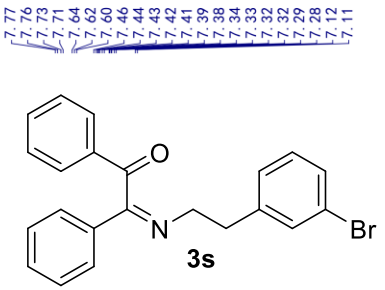




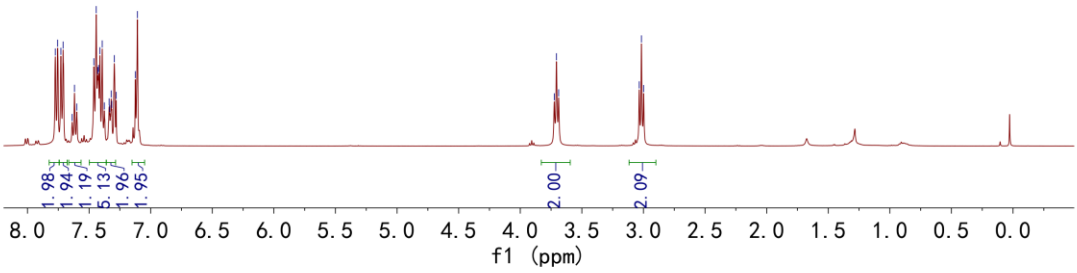
3r

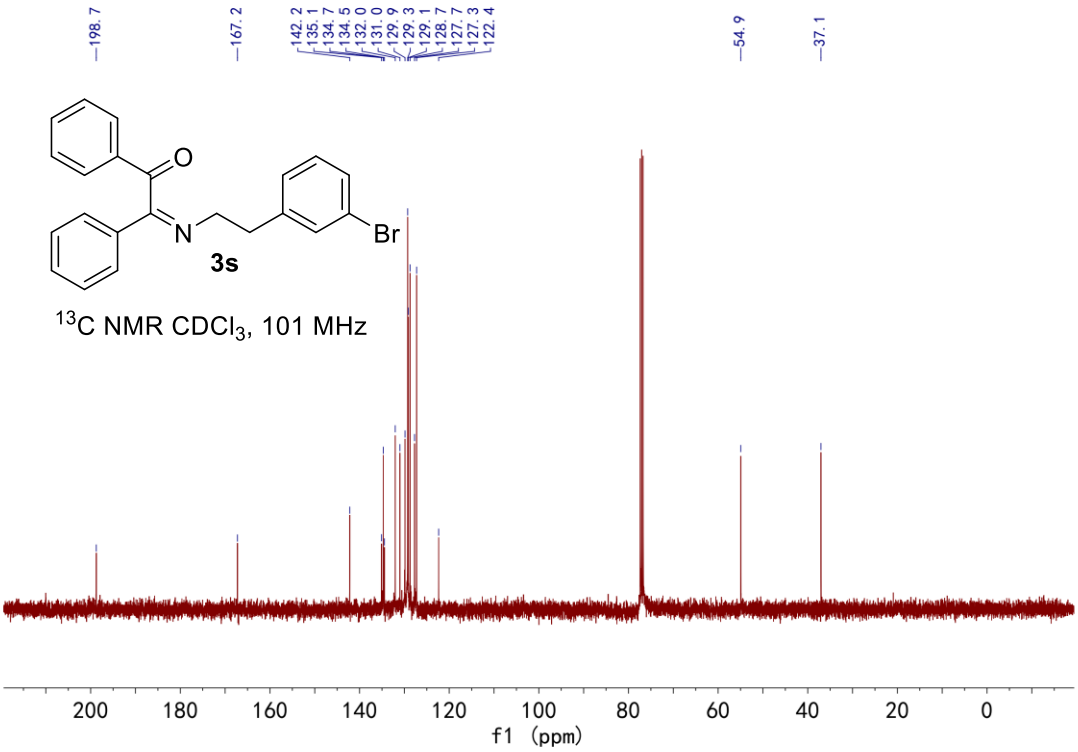
^{13}C NMR $CDCl_3$, 101 MHz



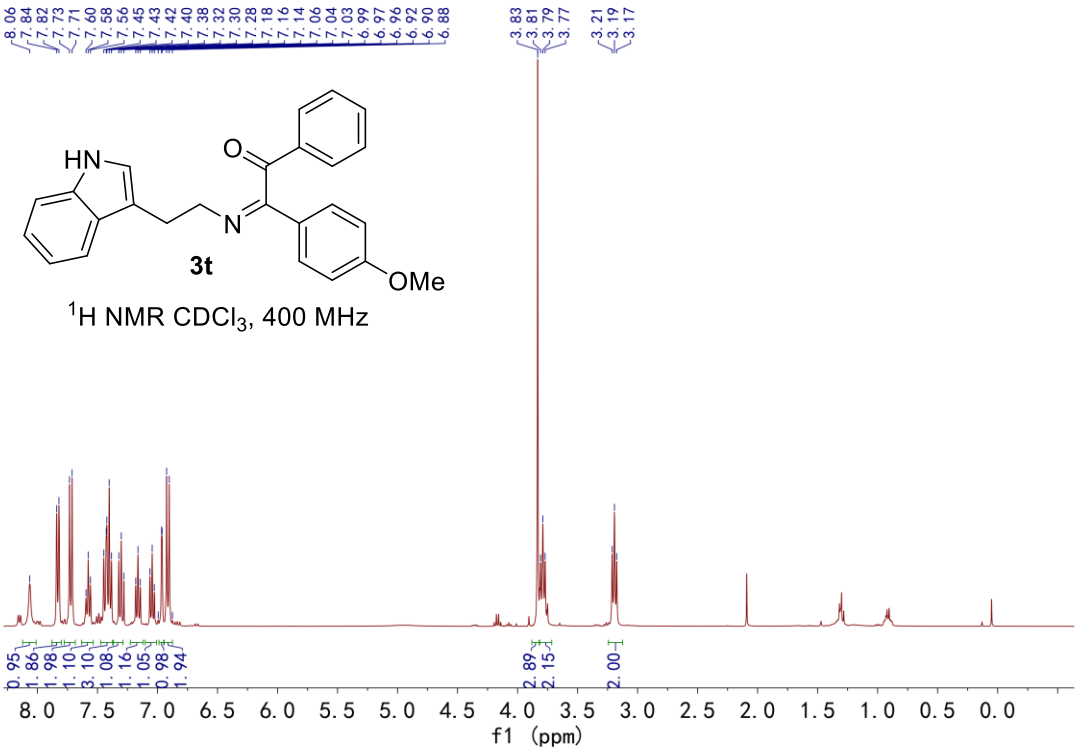


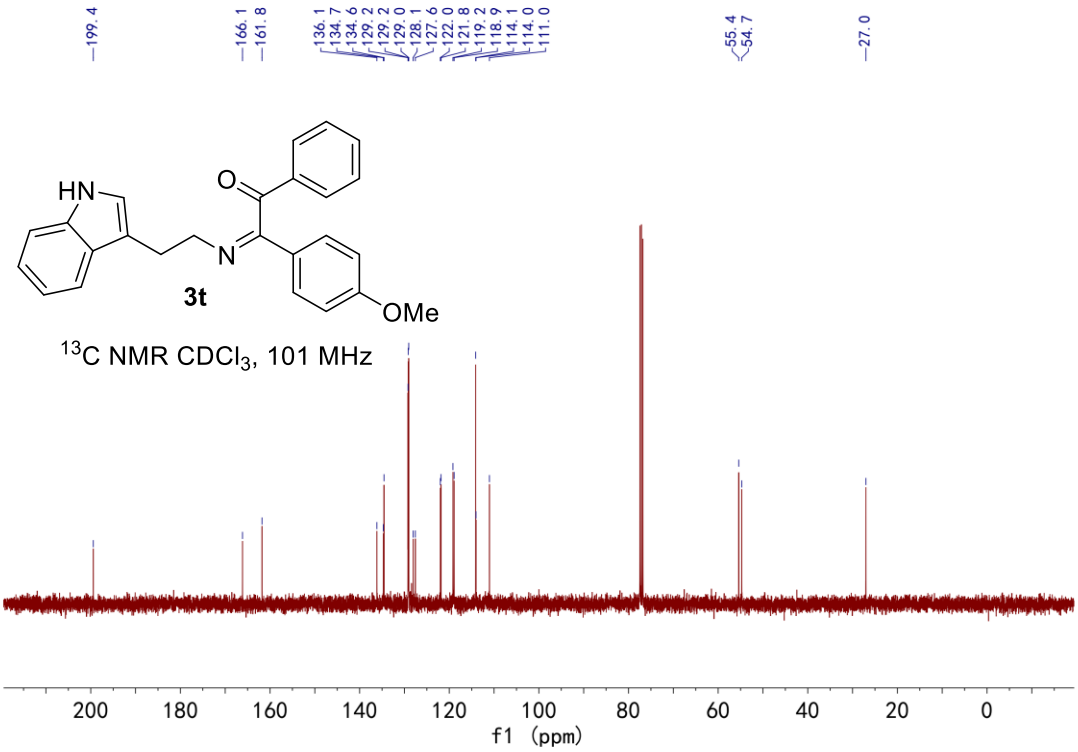
^{1}H NMR $CDCl_3$, 400 MHz

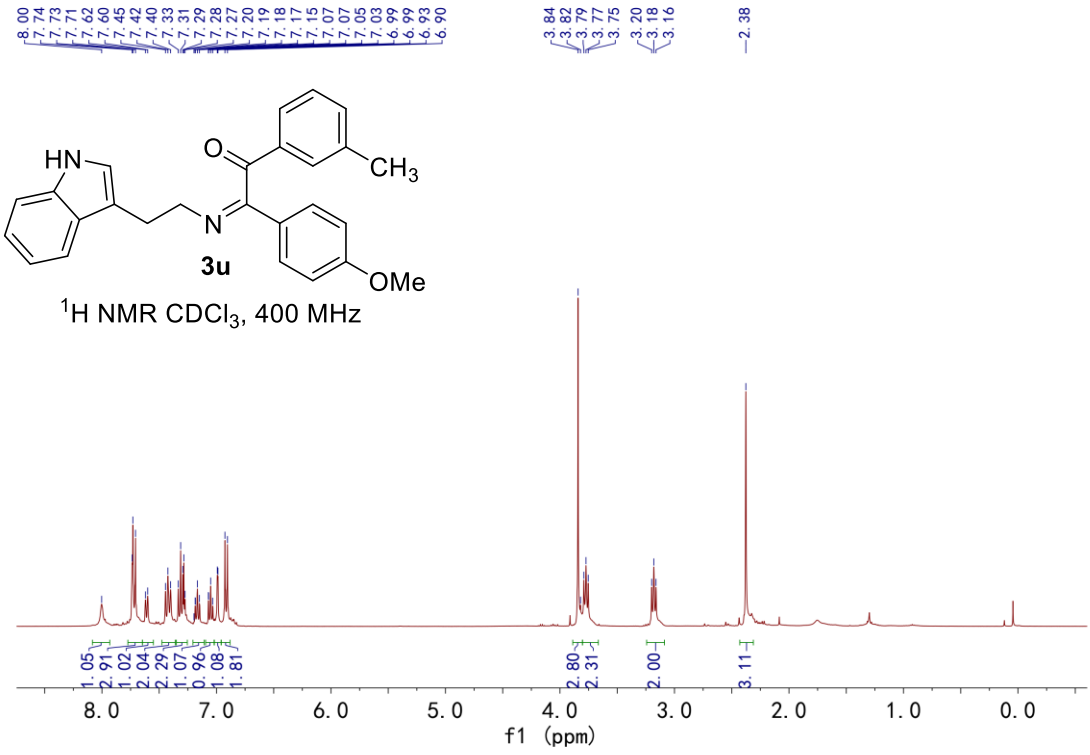


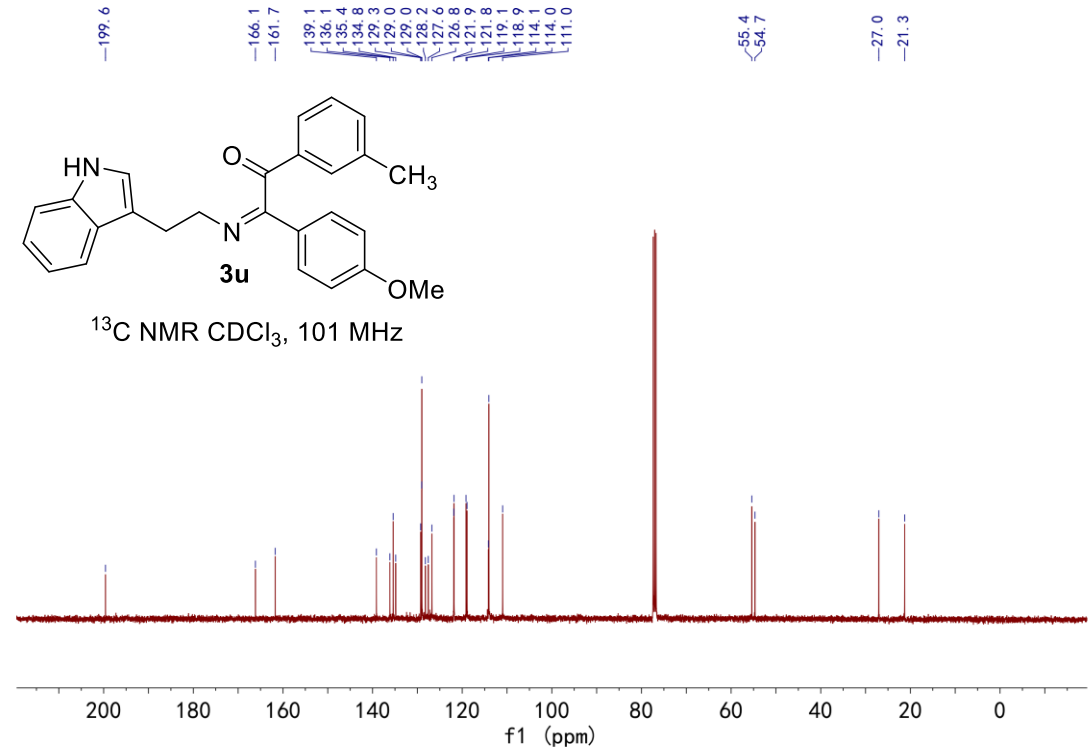


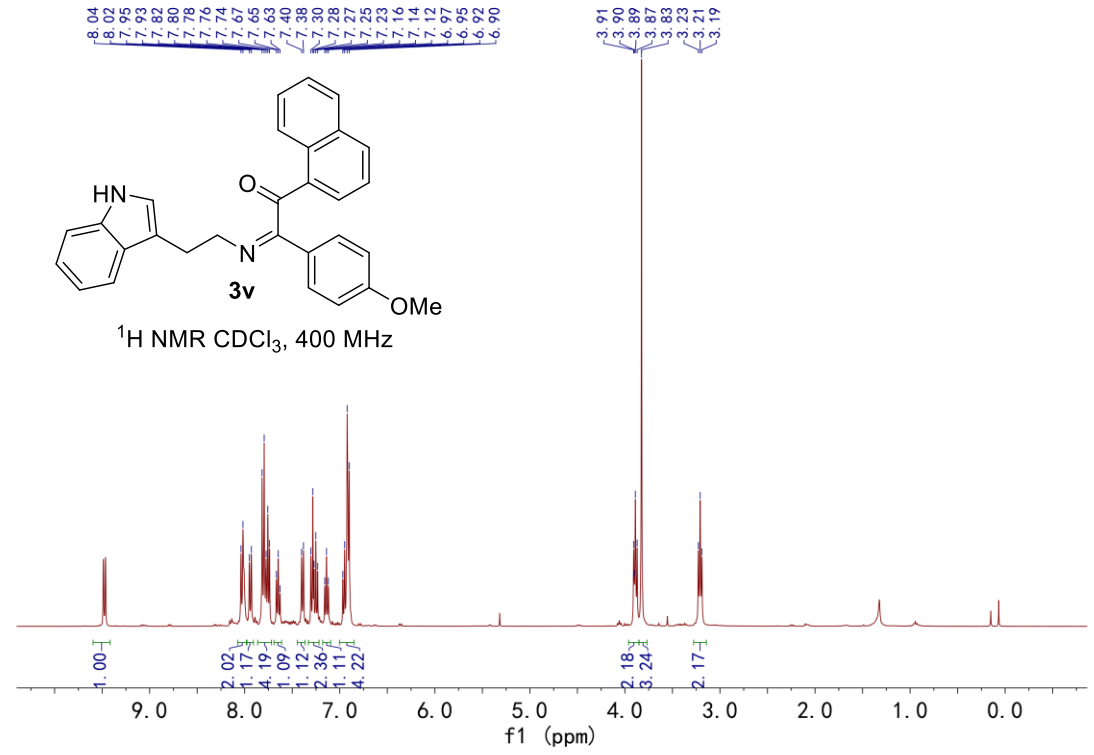
^{13}C NMR $CDCl_3$, 101 MHz

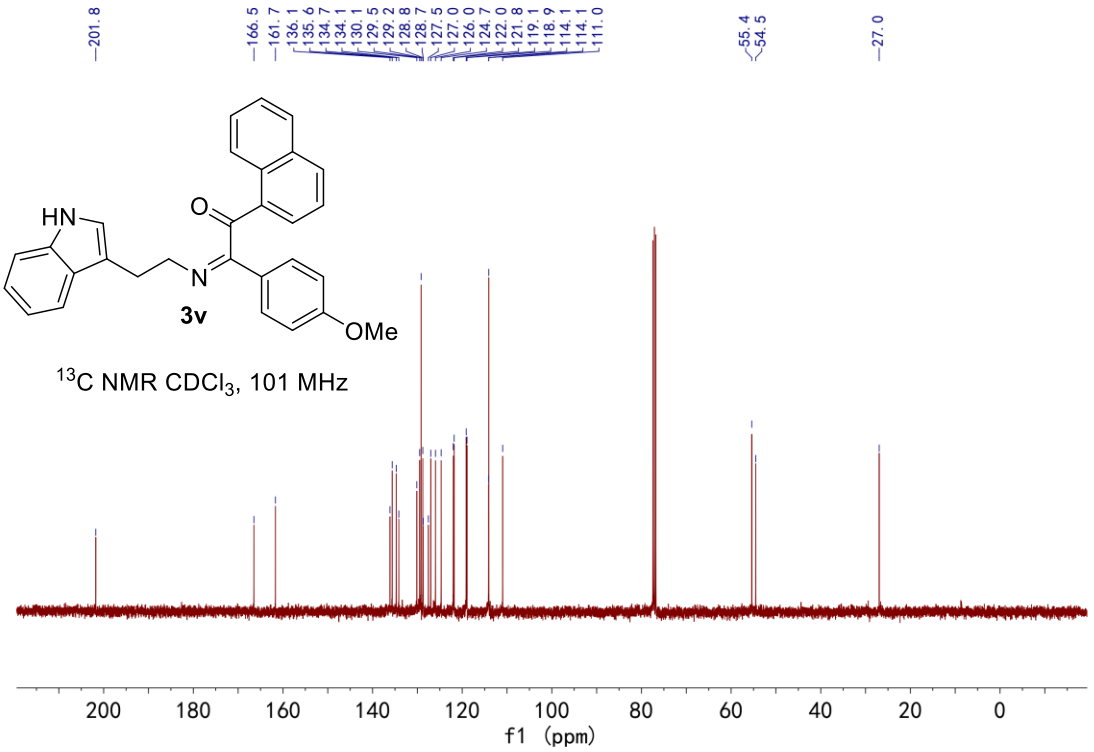

HN
O
N
OMe
3t
1H NMR CDCl3, 400 MHz
f1 (ppm)

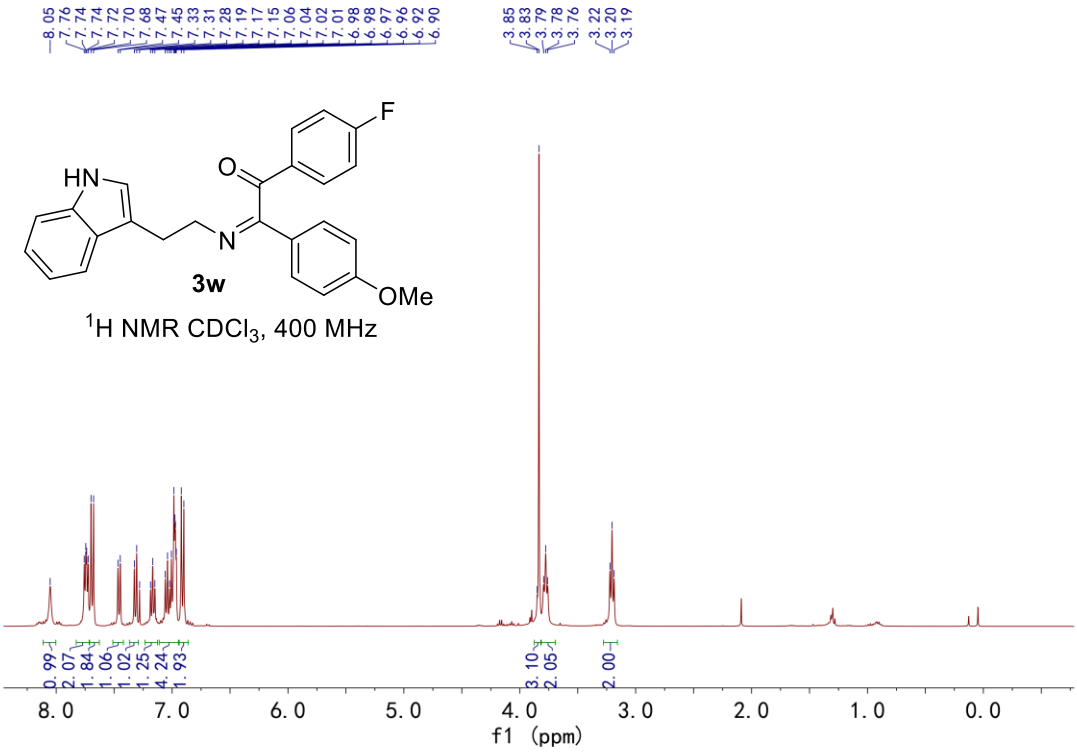

HN
O
N
OMe
3t
13C NMR CDCl3, 101 MHz
f1 (ppm)

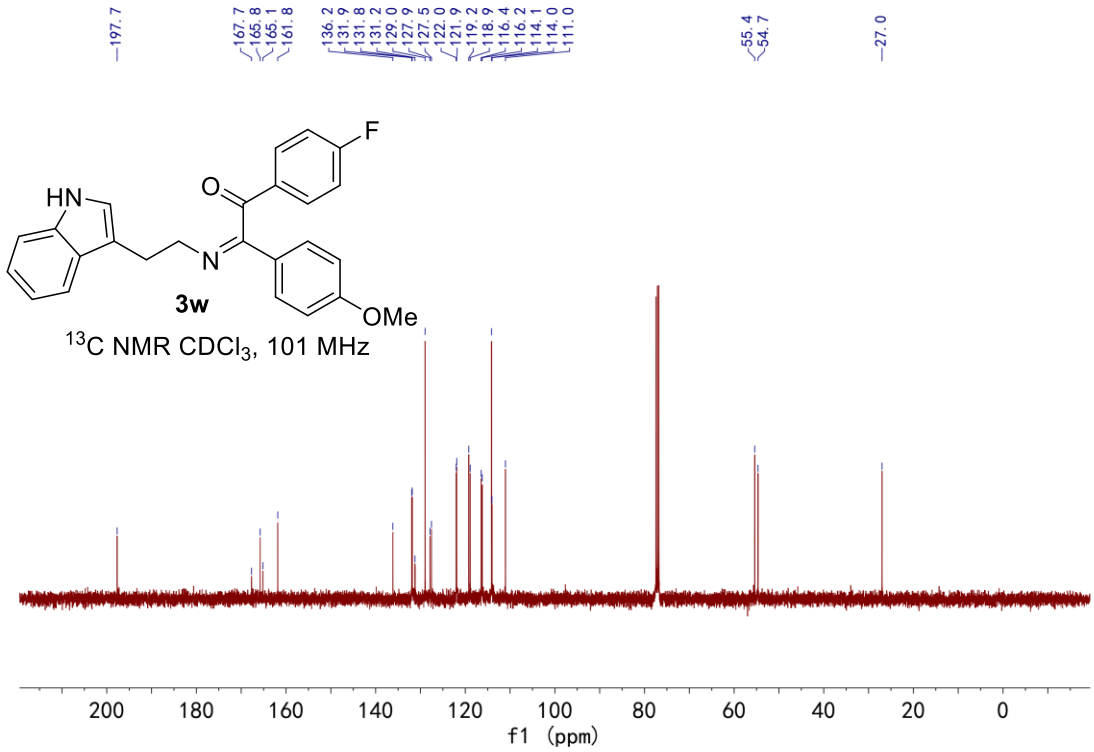

HN
O
CH3
N
3u
OMe
1H NMR CDCl3, 400 MHz
f1 (ppm)

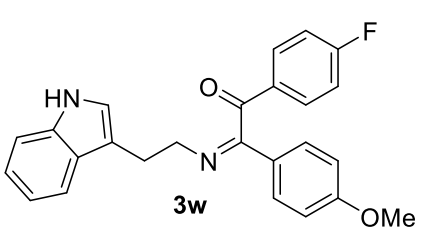

HN
O
CH3
N
3u
OMe
13C NMR CDCl3, 101 MHz
f1 (ppm)


HN
O
N
OMe
3v
1H NMR CDCl3, 400 MHz
f1 (ppm)


HN
O
N
OMe
3v
13C NMR CDCl3, 101 MHz
f1 (ppm)

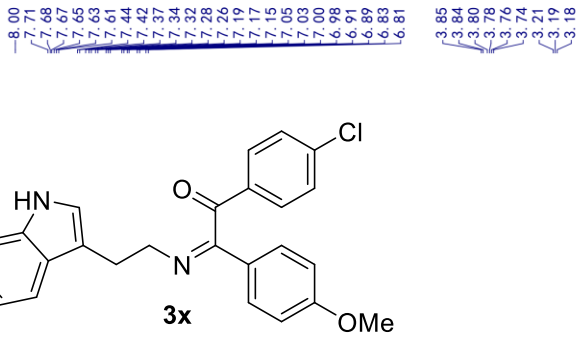

F
O
HN
N
OMe
3w
^{1}H NMR CDCl$_3$, 400 MHz
f1 (ppm)


F
O
HN
N
OMe
3w
^{13}C NMR CDCl$_3$, 101 MHz
f1 (ppm)



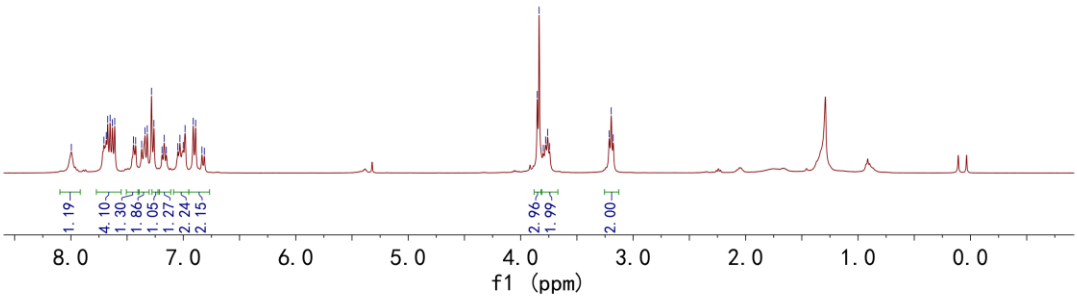
3w

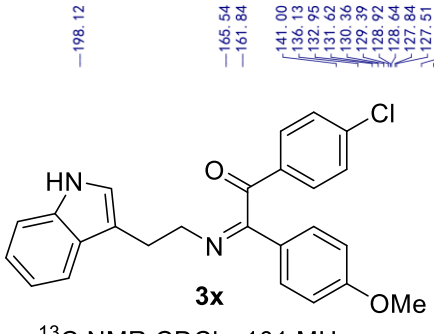
^{19}F NMR $CDCl_3$, 376 MHz



3x

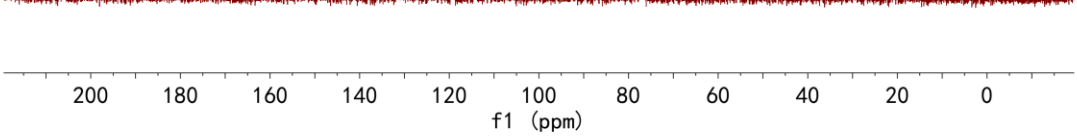
^{1}H NMR $CDCl_3$, 400 MHz

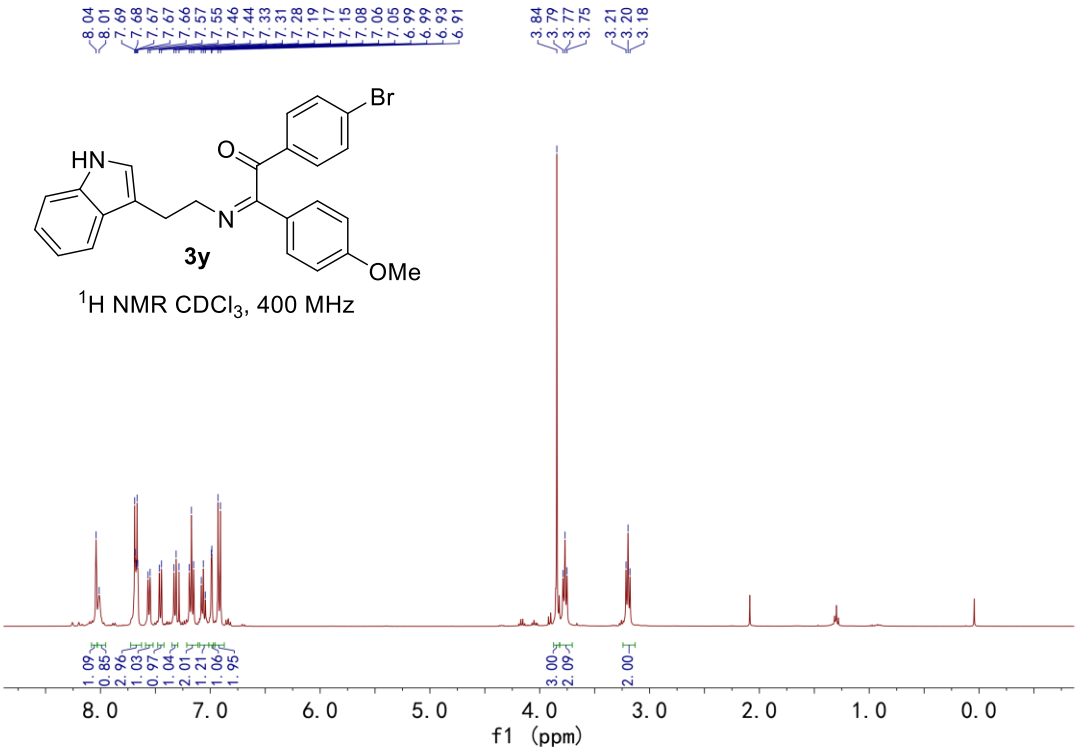


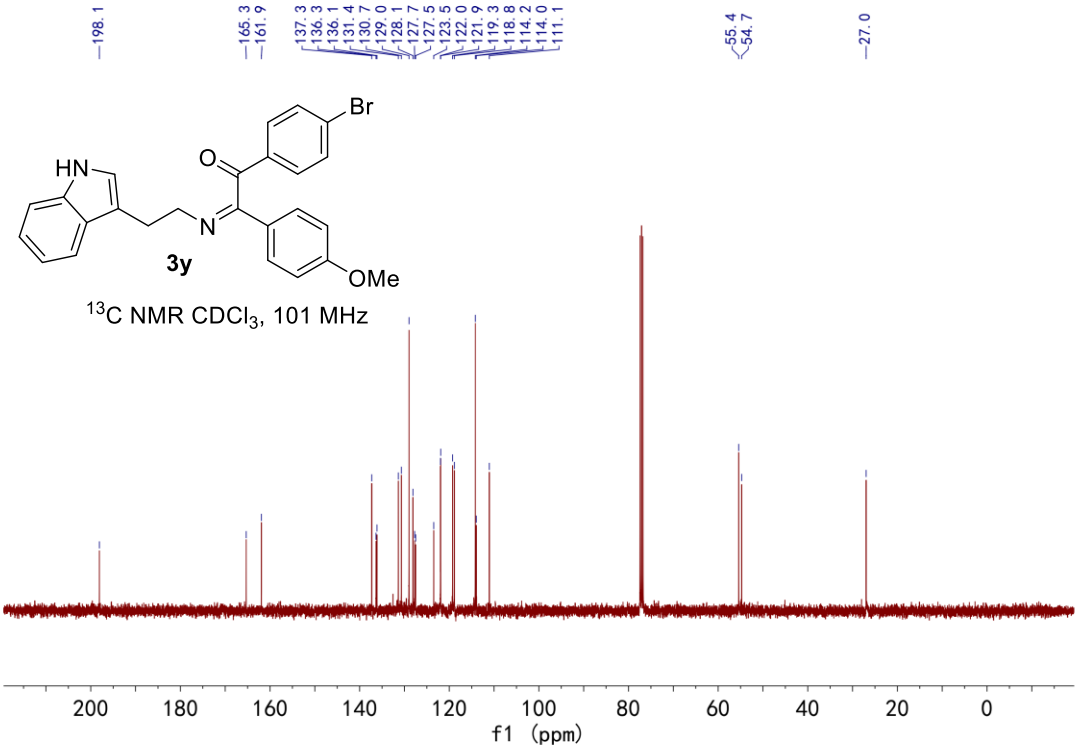


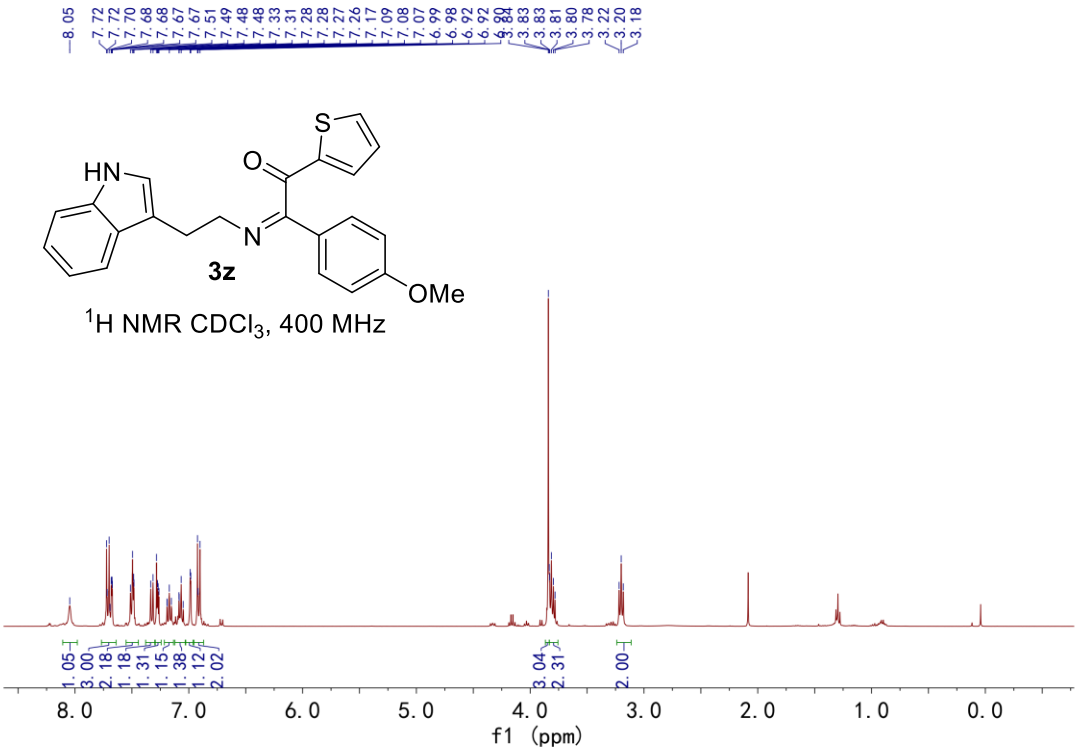
3x

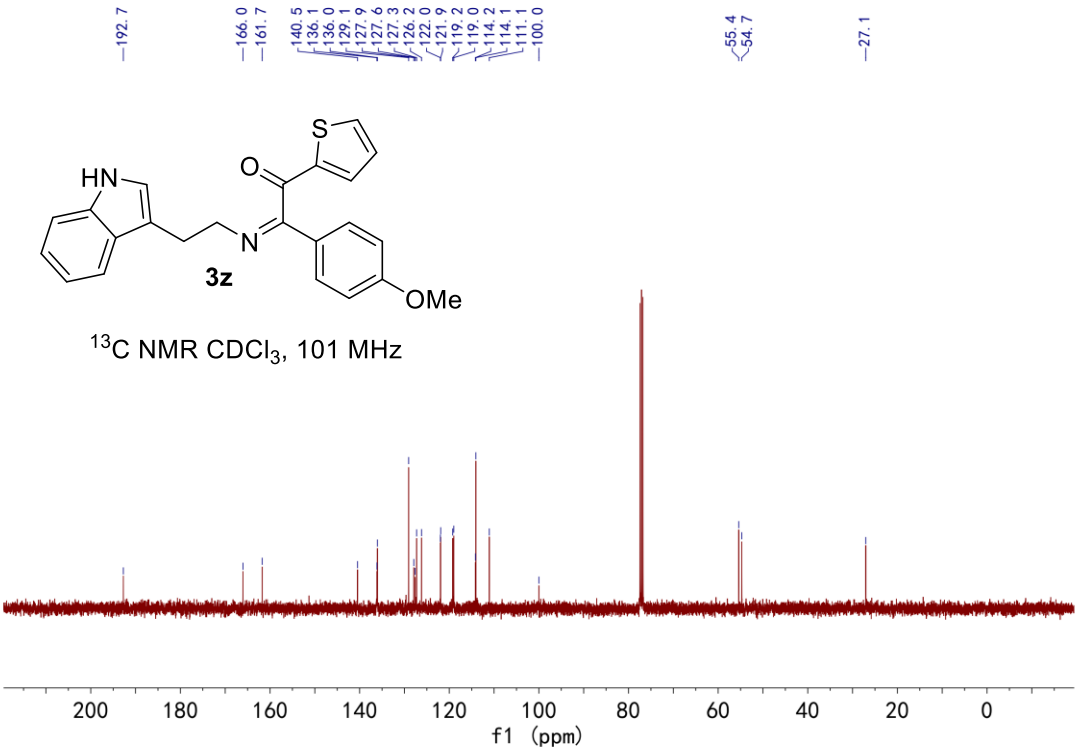
^{13}C NMR $CDCl_3$, 101 MHz

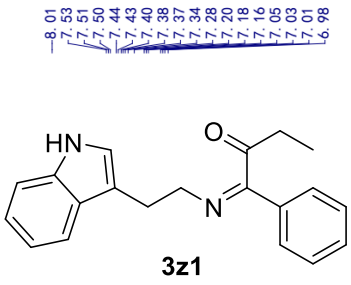



Br
O
HN
N
OMe
3y
^{1}H NMR CDCl$_3$, 400 MHz
f1 (ppm)


Br
O
HN
N
OMe
3y
^{13}C NMR CDCl$_3$, 101 MHz
f1 (ppm)

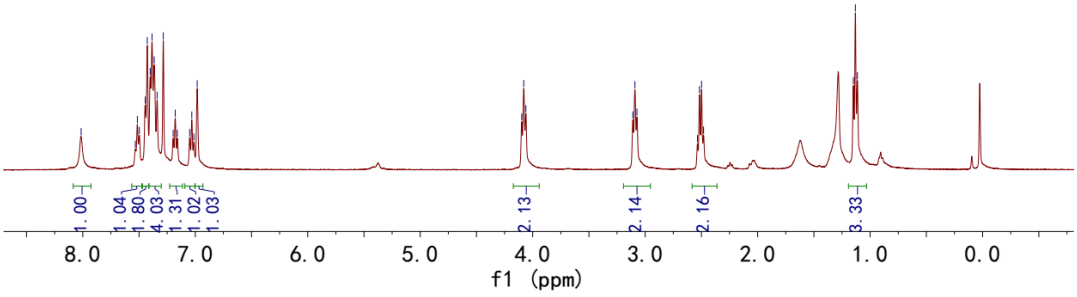

8.05
7.72
7.70
7.68
7.67
7.51
7.49
7.48
7.33
7.31
7.28
7.27
7.26
7.17
7.09
7.08
7.07
6.99
6.98
6.92
6.90
3.84
3.83
3.81
3.80
3.78
3.22
3.20
3.18
S
O
HN
N
3z
OMe
1H NMR CDCl3, 400 MHz
1.05
3.00
2.18
1.18
1.31
1.15
1.38
1.12
2.02
3.04
2.31
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

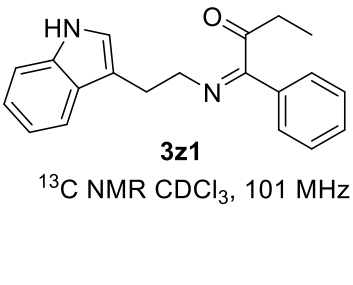

192.7
166.0
161.7
140.5
136.1
136.0
129.1
127.9
127.6
127.3
126.2
122.0
121.9
119.2
119.0
114.2
114.1
111.1
100.0
55.4
54.7
27.1
S
O
HN
N
3z
OMe
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



3z1

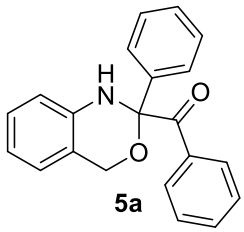
^{1}H NMR $CDCl_3$, 400 MHz





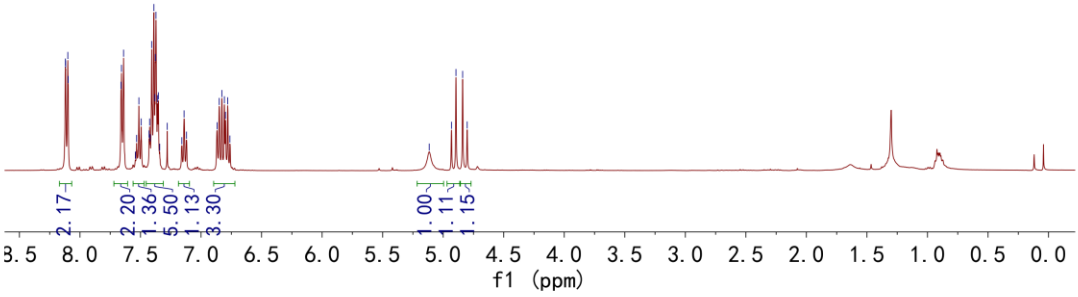
3z1

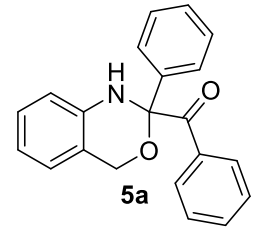
^{13}C NMR $CDCl_3$, 101 MHz



5a

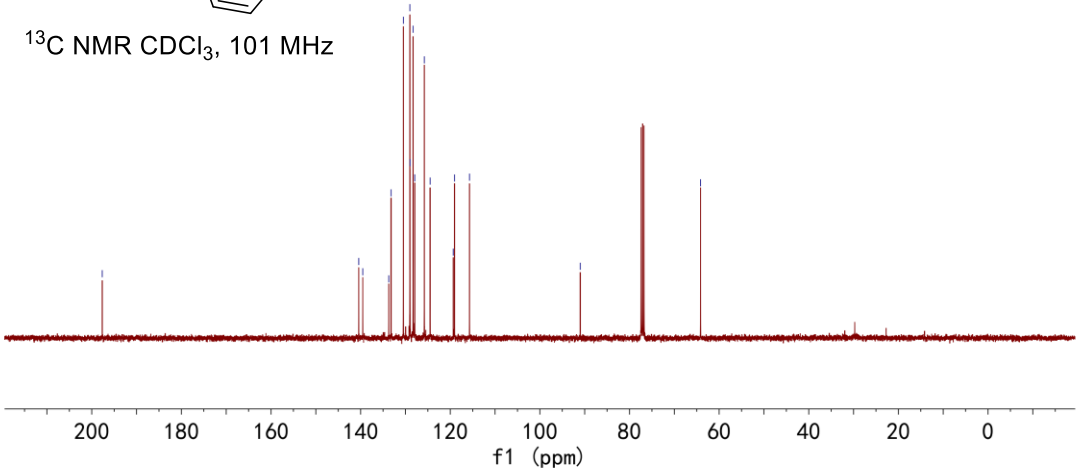
^{1}H NMR $CDCl_3$, 400 MHz

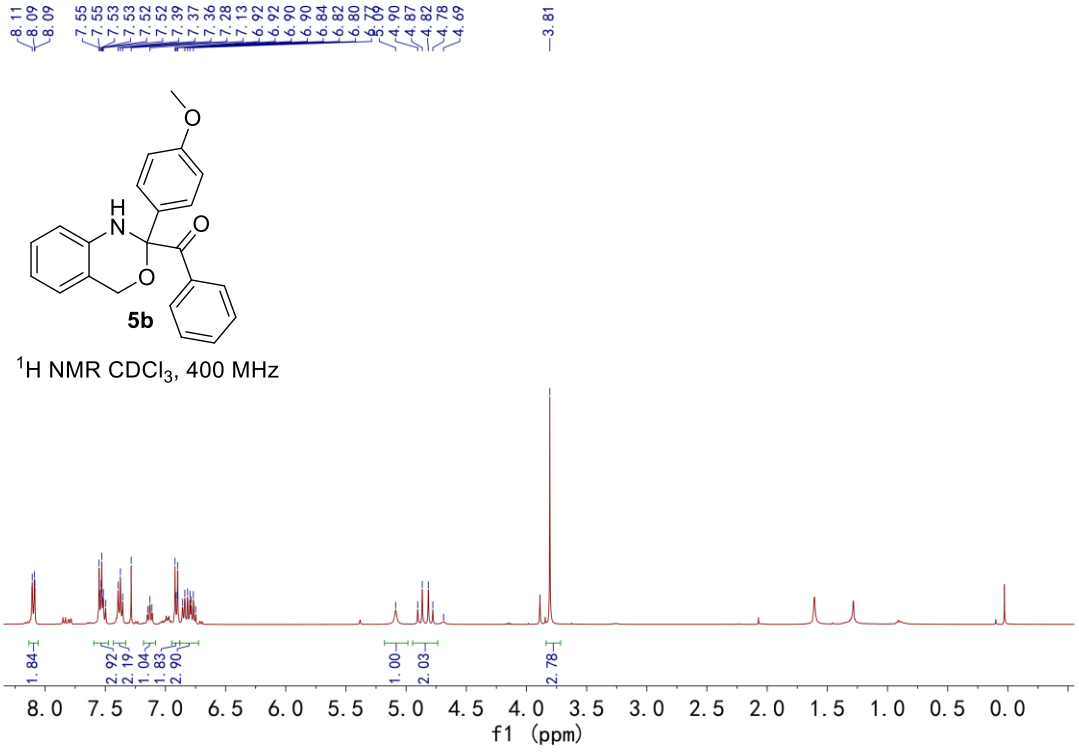




5a

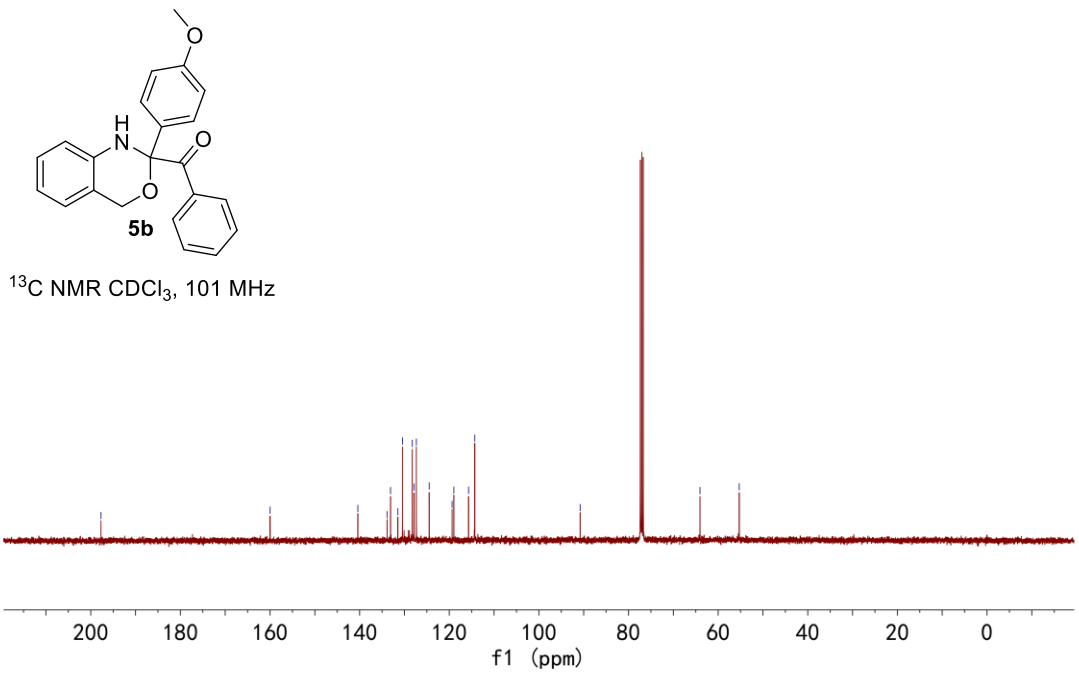
^{13}C NMR $CDCl_3$, 101 MHz





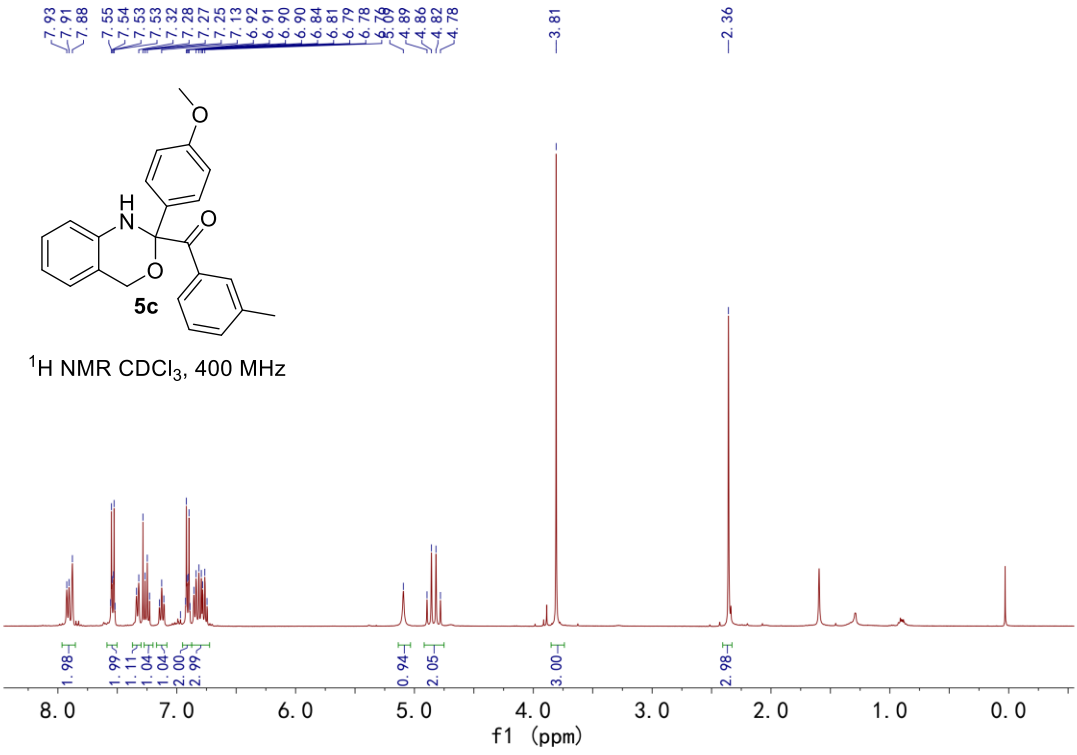
5b

^{1}H NMR $CDCl_3$, 400 MHz

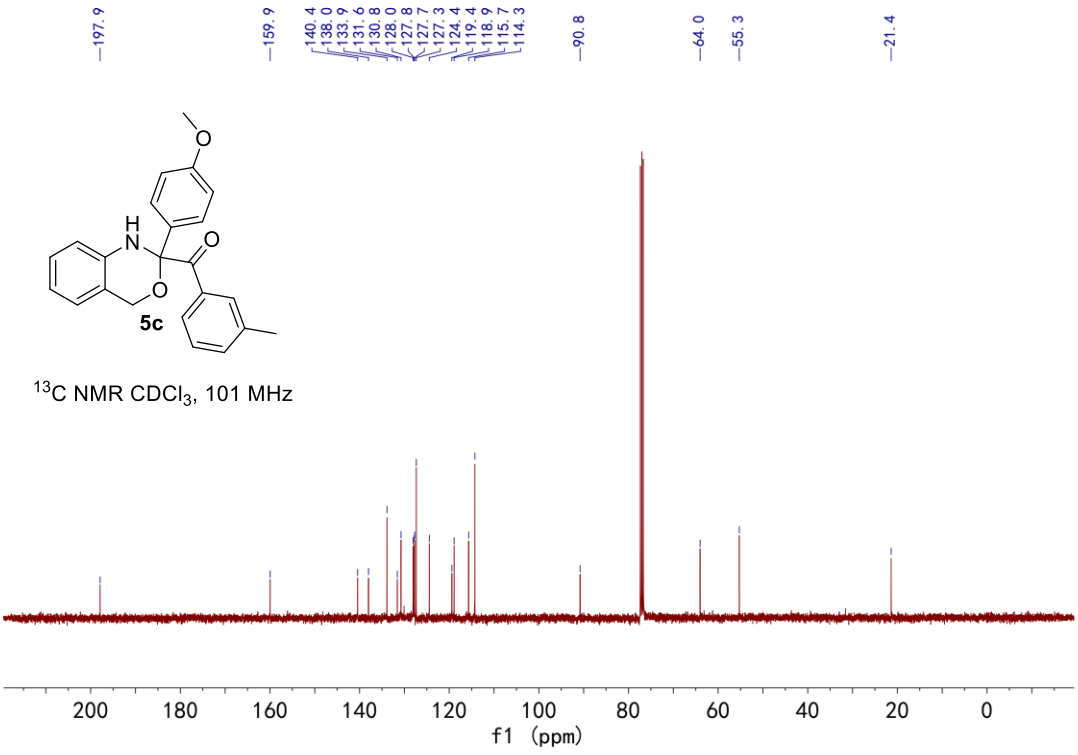


5b

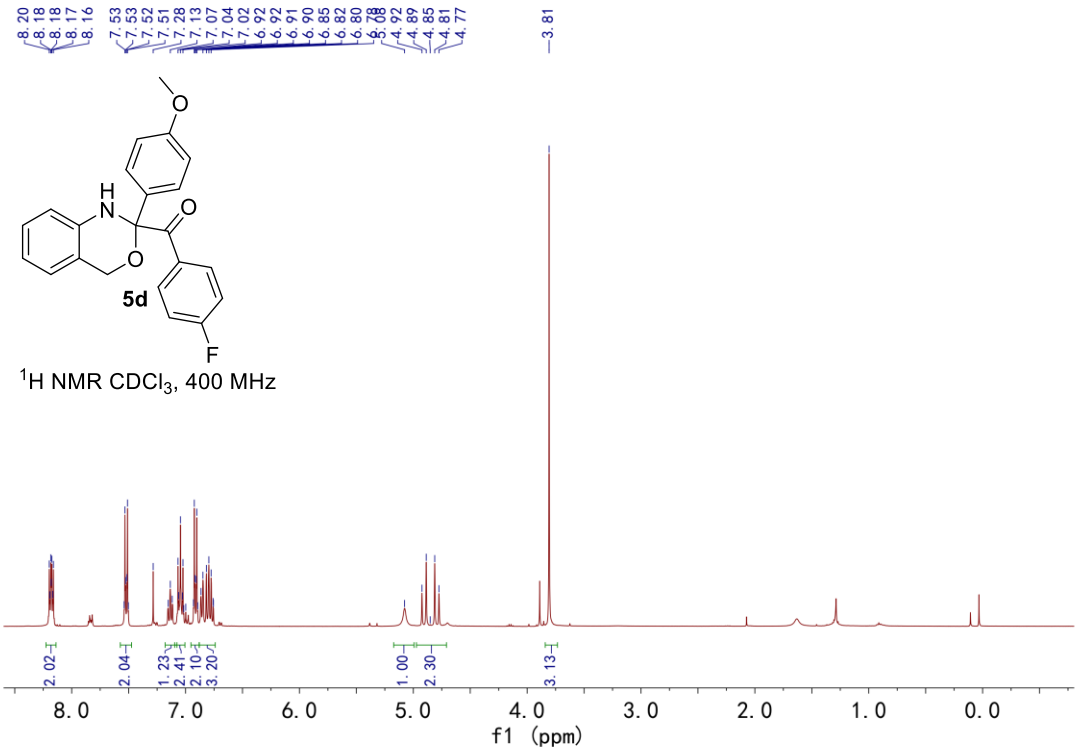
^{13}C NMR $CDCl_3$, 101 MHz



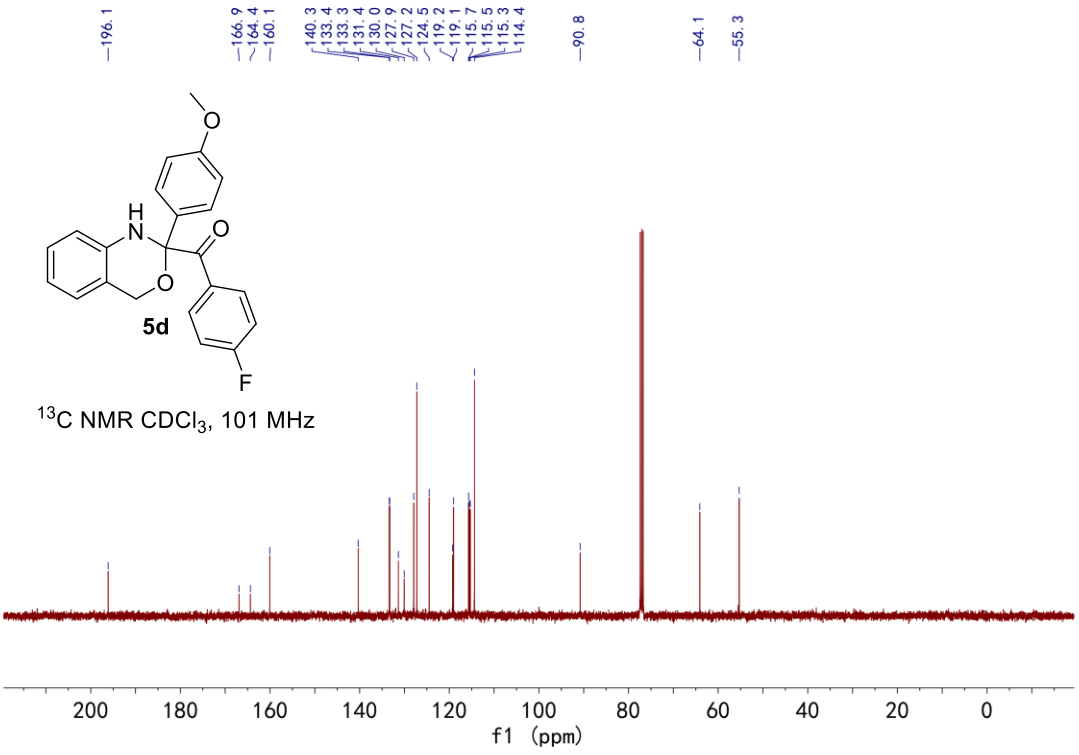
^{1}H NMR $CDCl_3$, 400 MHz



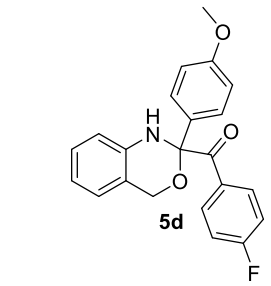
^{13}C NMR $CDCl_3$, 101 MHz



^{1}H NMR $CDCl_3$, 400 MHz

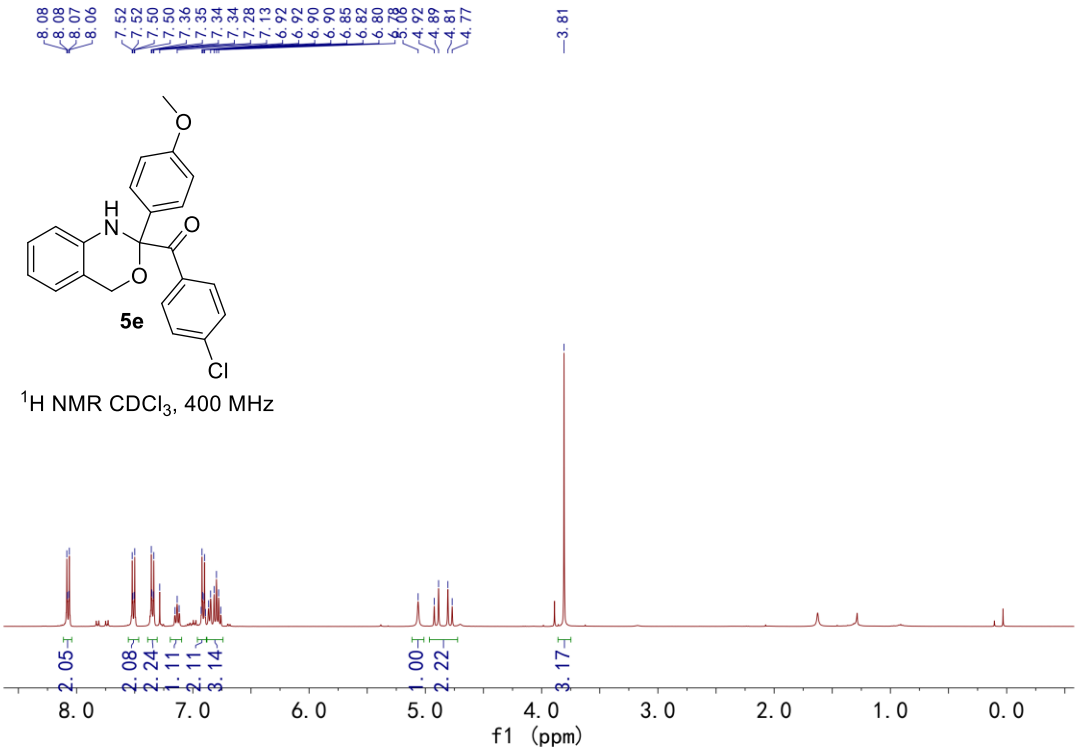


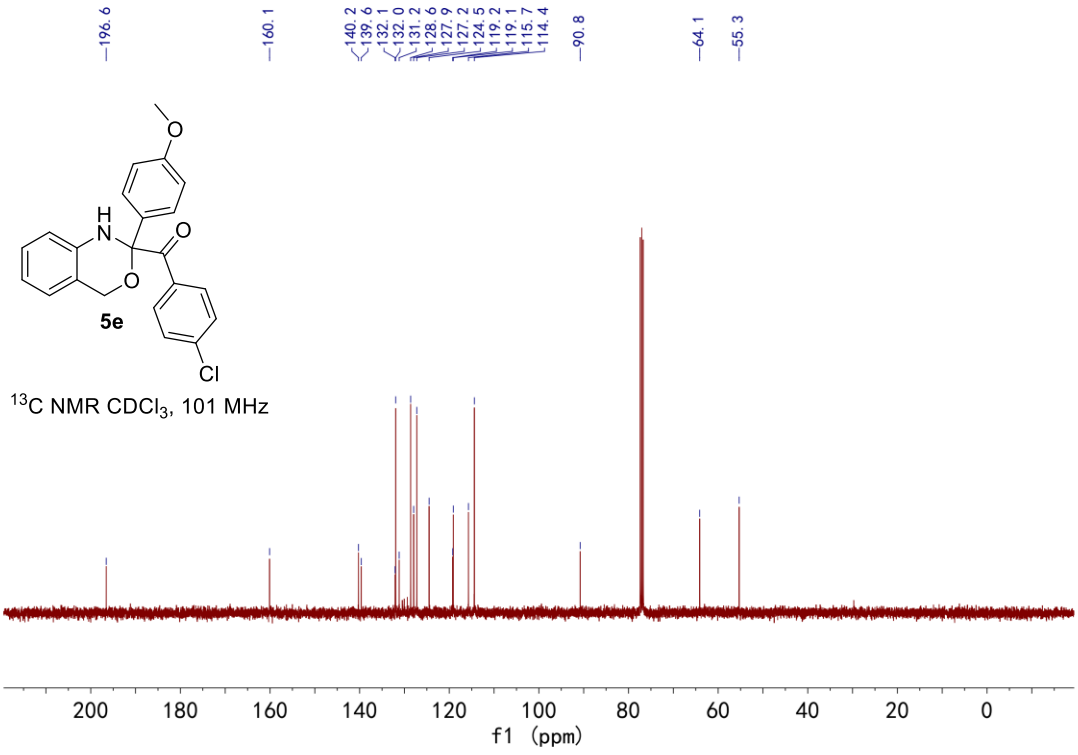
^{13}C NMR $CDCl_3$, 101 MHz

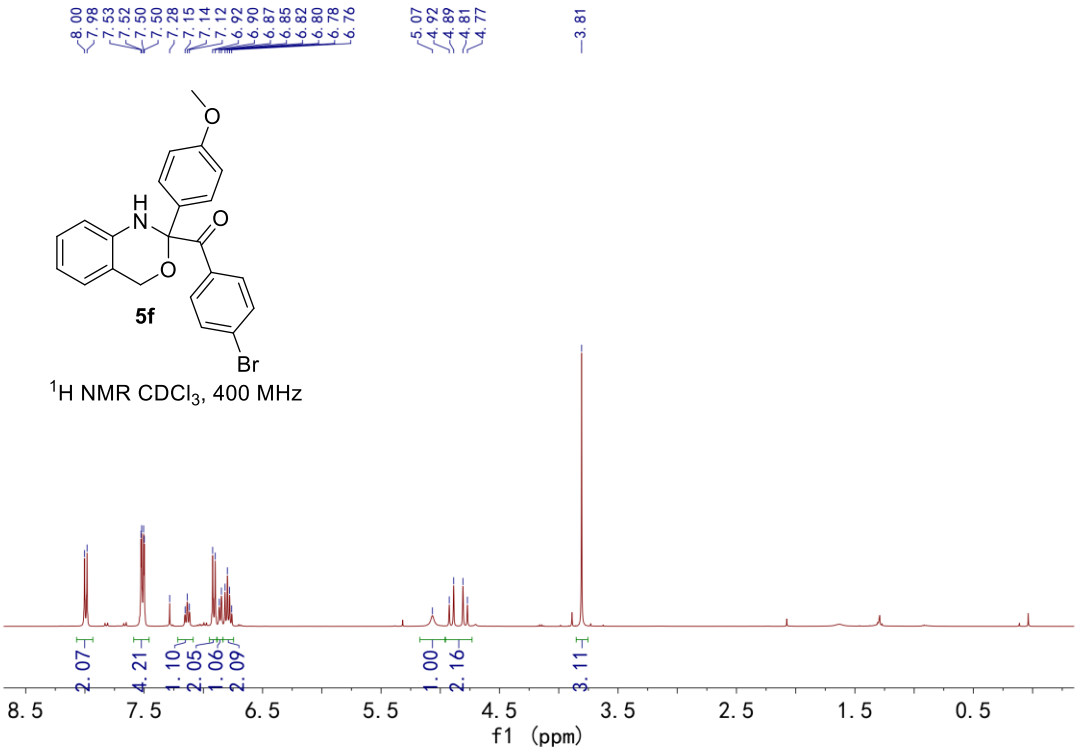


5d

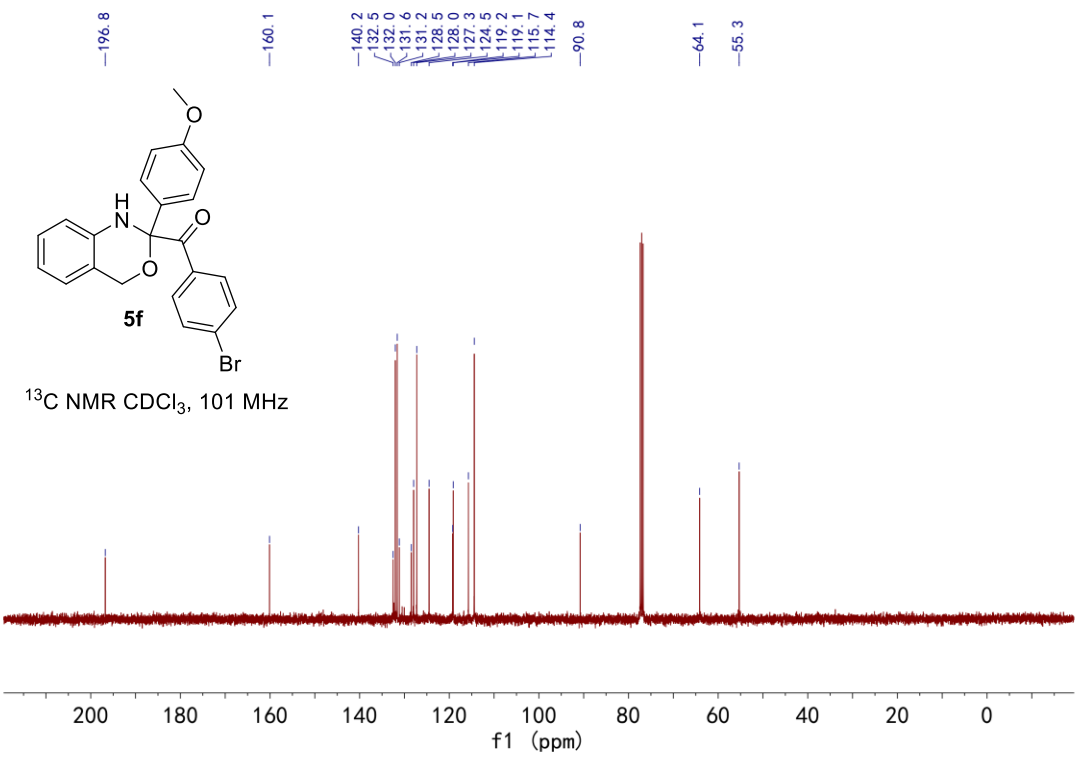
^{19}F NMR $CDCl_3$, 376 MHz


8.08
8.08
8.07
8.06
7.52
7.52
7.50
7.50
7.36
7.35
7.34
7.34
7.28
7.13
6.92
6.92
6.90
6.90
6.85
6.82
6.80
4.92
4.89
4.81
4.77
3.81
O
H
N
O
O
Cl
5e
1H NMR CDCl3, 400 MHz
2.05
2.08
2.24
1.11
2.11
3.14
1.00
2.22
3.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

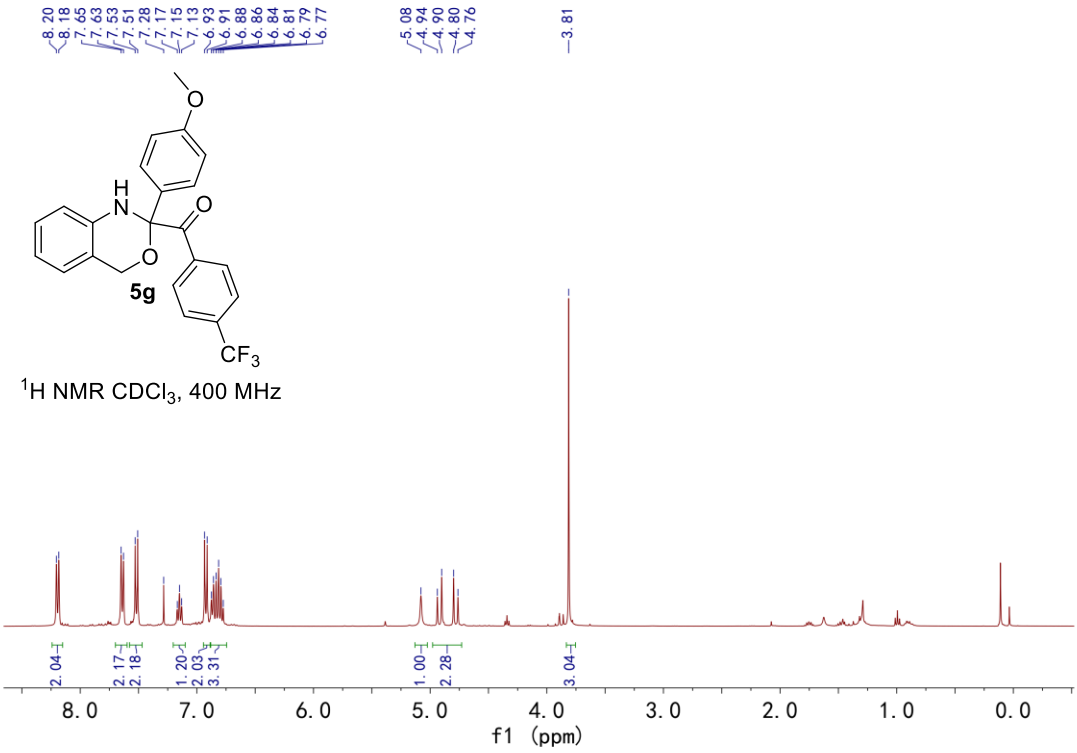

196.6
160.1
140.2
139.6
132.1
132.0
131.2
128.6
127.9
127.2
124.5
119.2
119.1
115.7
114.4
90.8
64.1
55.3
O
H
N
O
O
Cl
5e
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



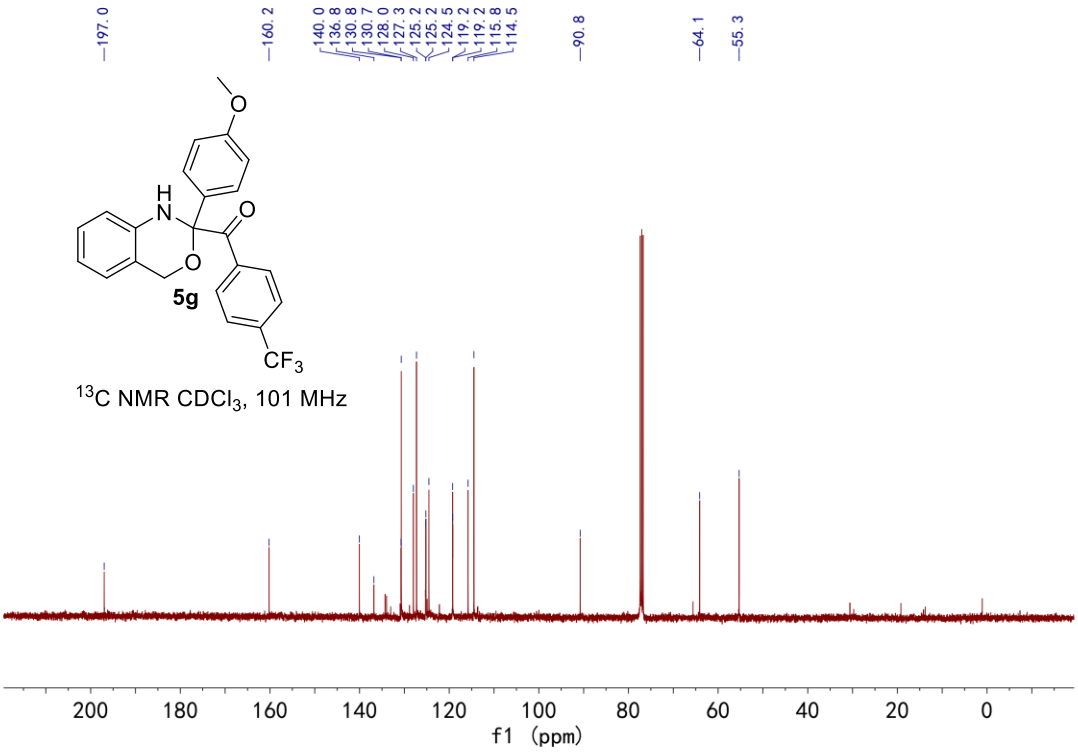
^{1}H NMR $CDCl_3$, 400 MHz



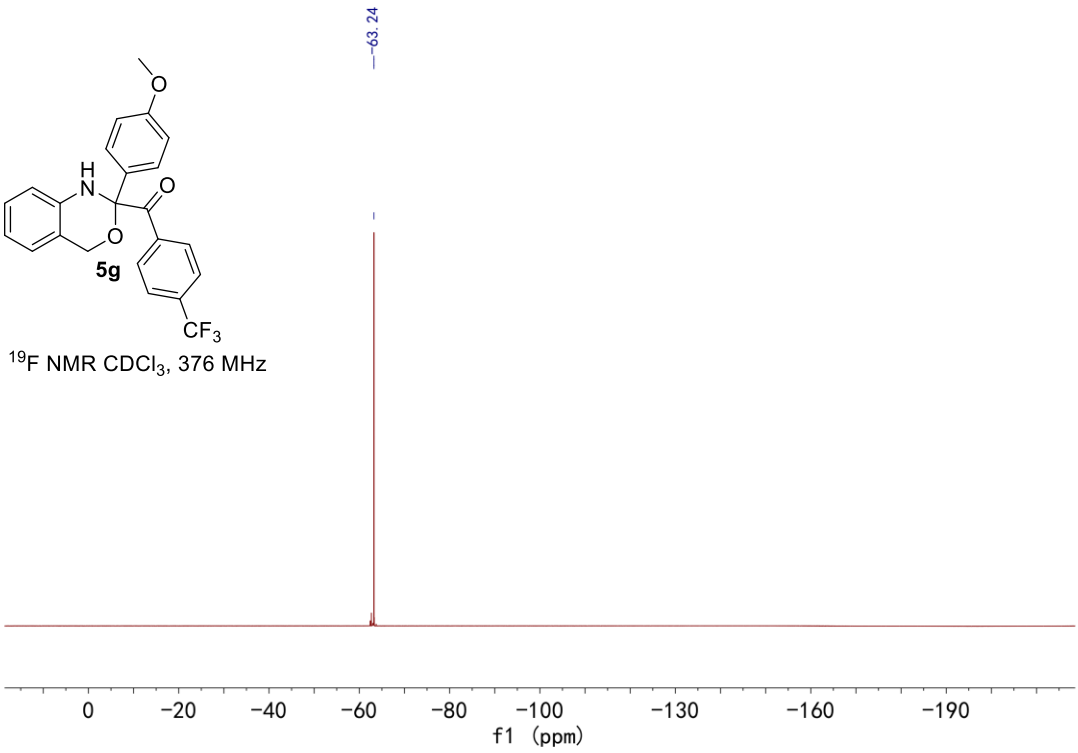
^{13}C NMR $CDCl_3$, 101 MHz



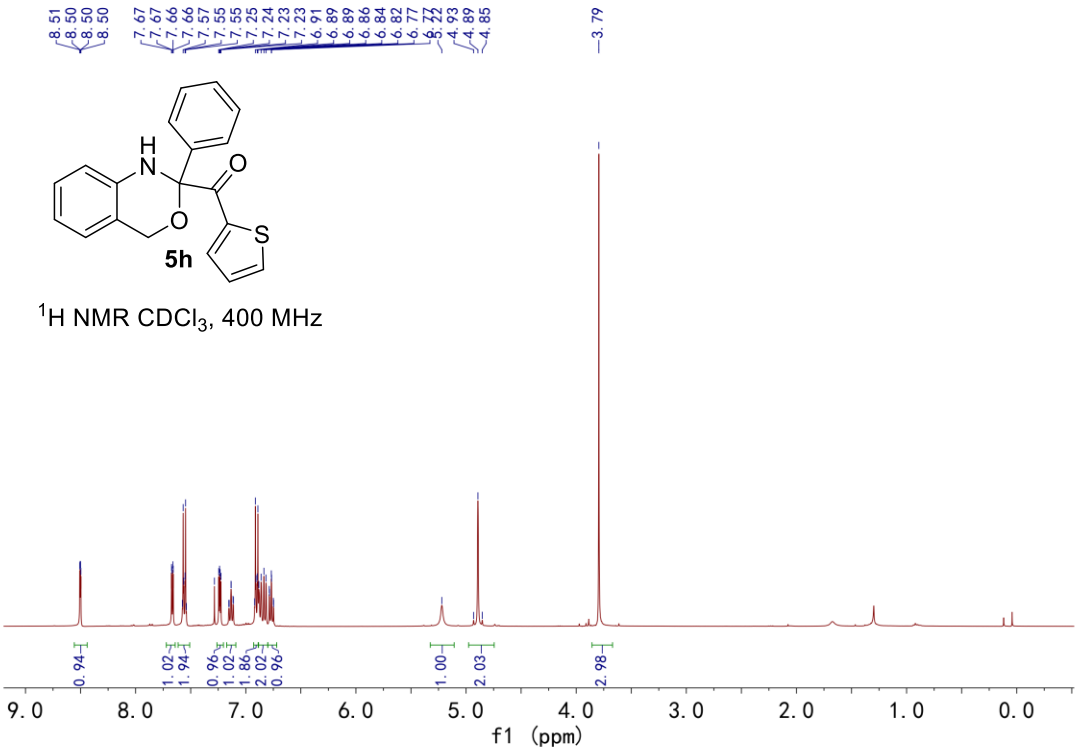
^{1}H NMR $CDCl_3$, 400 MHz



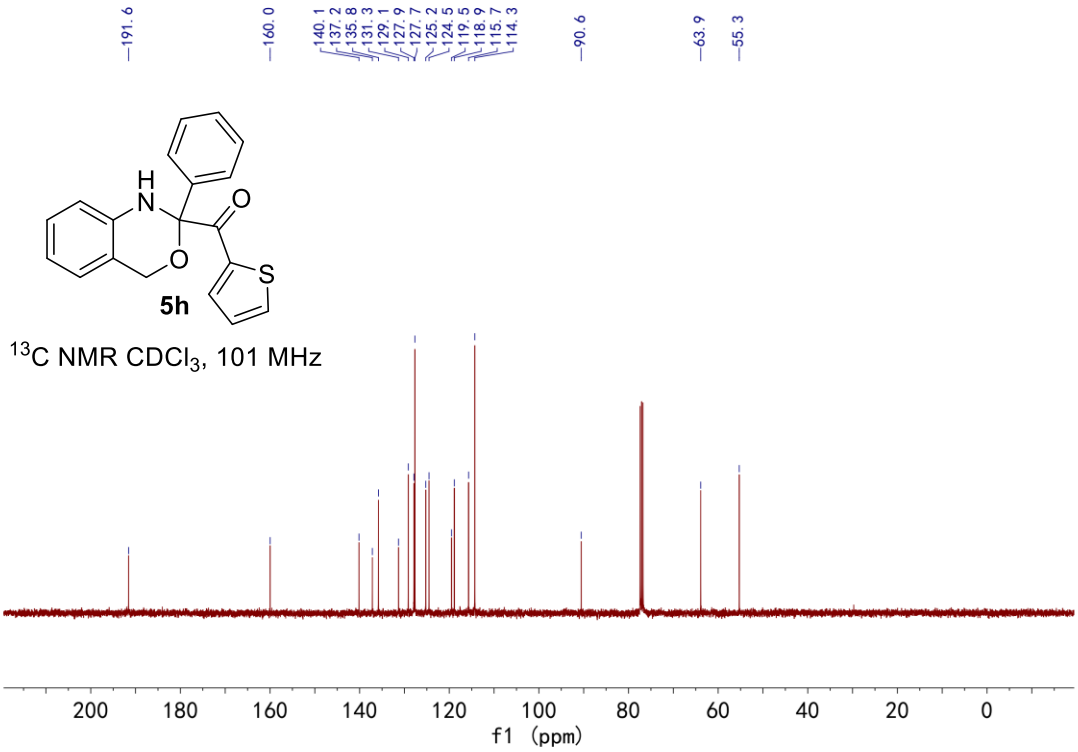
^{13}C NMR $CDCl_3$, 101 MHz



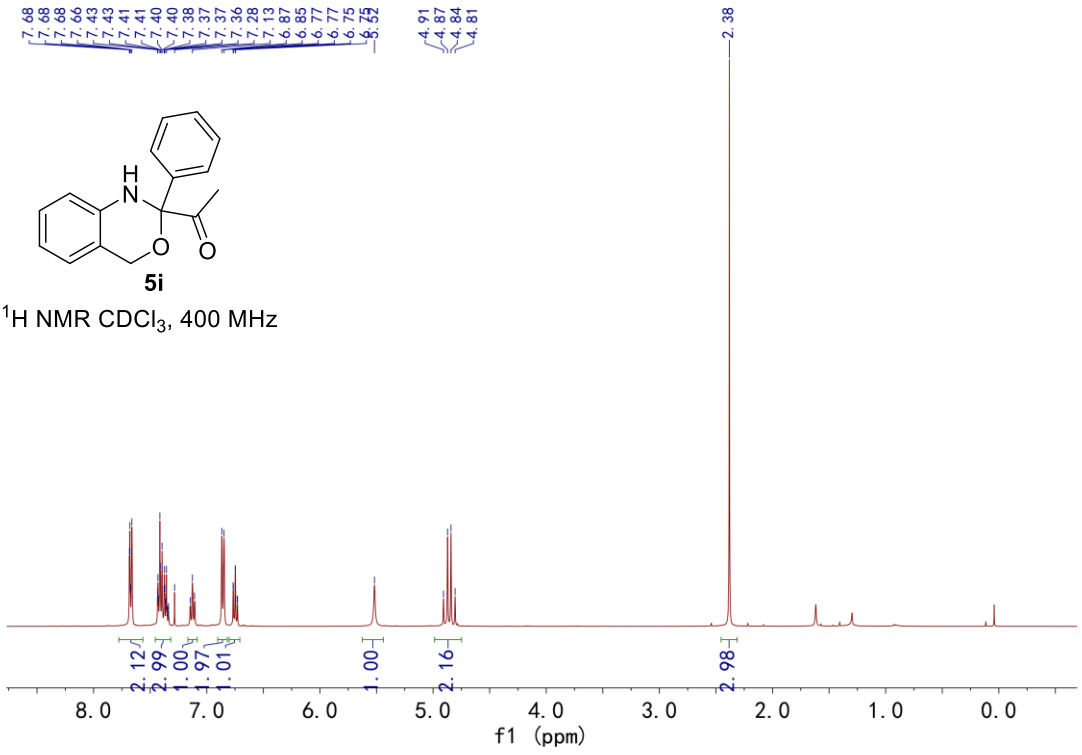
^{19}F NMR $CDCl_3$, 376 MHz



^{1}H NMR $CDCl_3$, 400 MHz

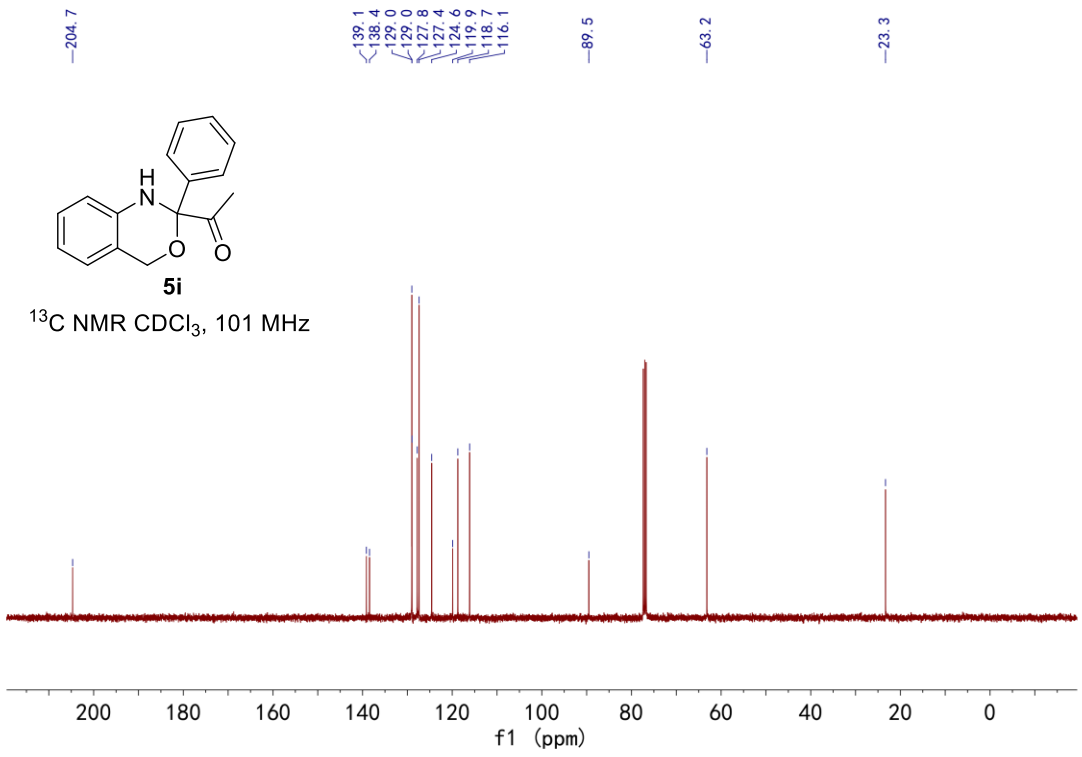


^{13}C NMR $CDCl_3$, 101 MHz



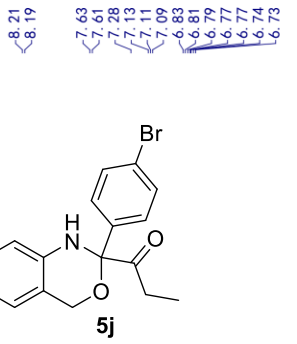
5i

^{1}H NMR $CDCl_3$, 400 MHz



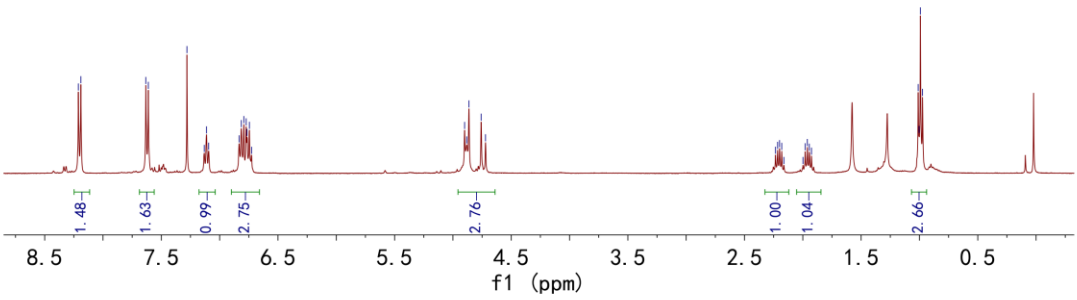
5i

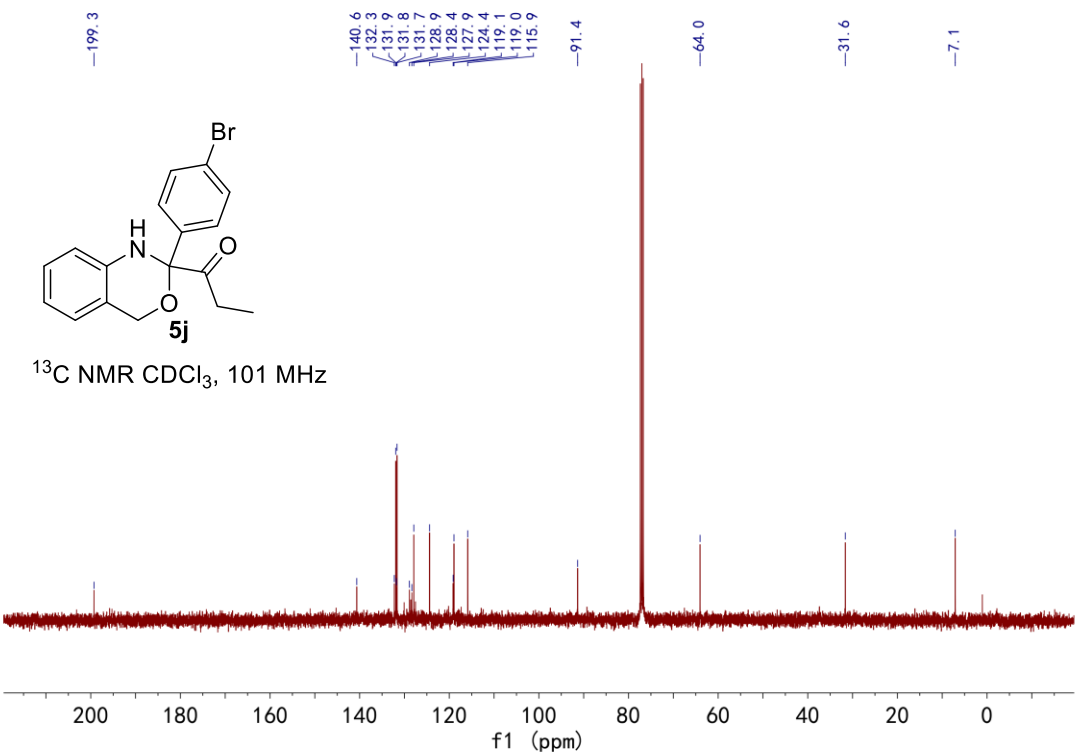
^{13}C NMR $CDCl_3$, 101 MHz



5j

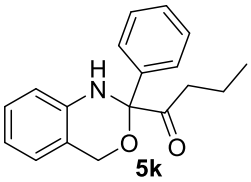
^{1}H NMR $CDCl_3$, 400 MHz





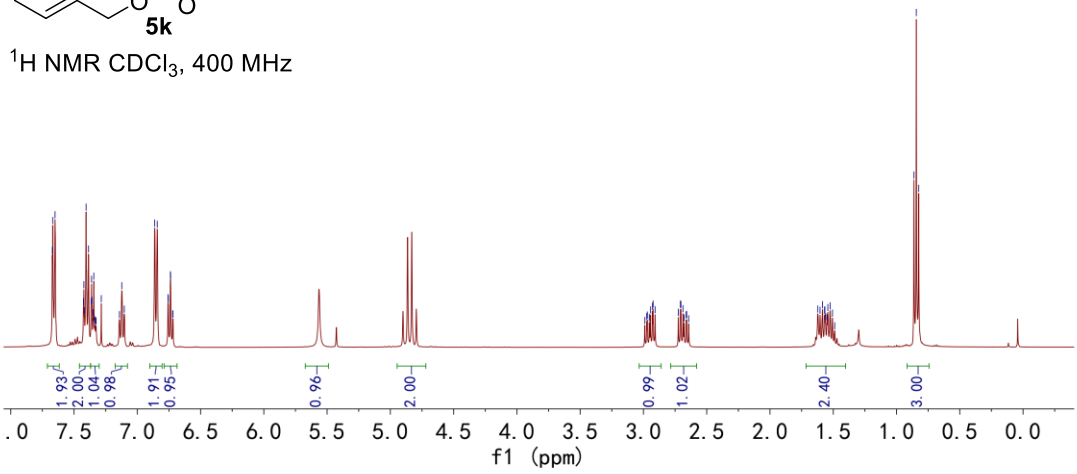
5j

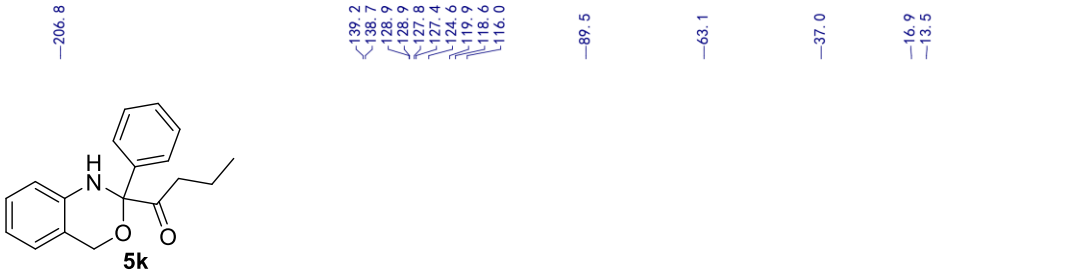
^{13}C NMR $CDCl_3$, 101 MHz



5k

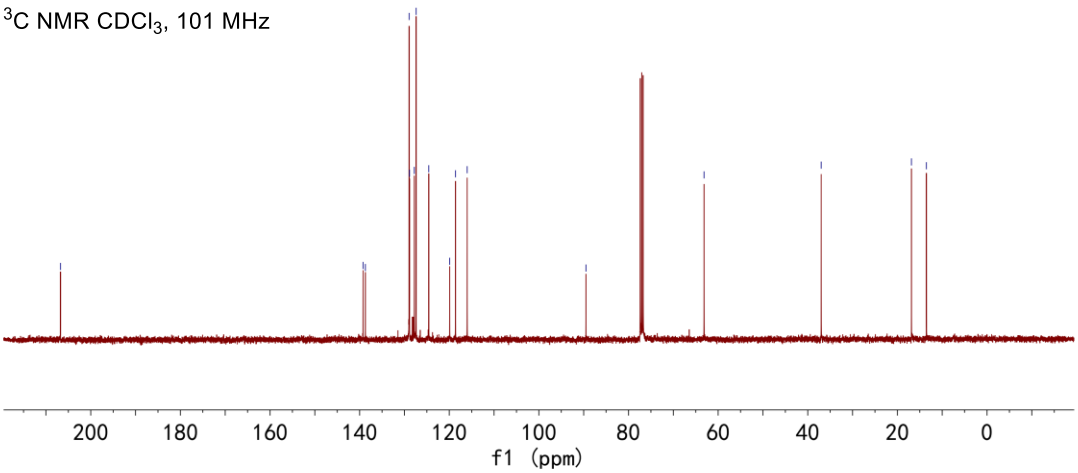
^{1}H NMR $CDCl_3$, 400 MHz

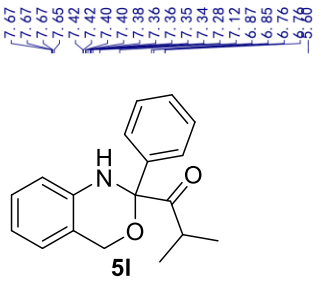




5k

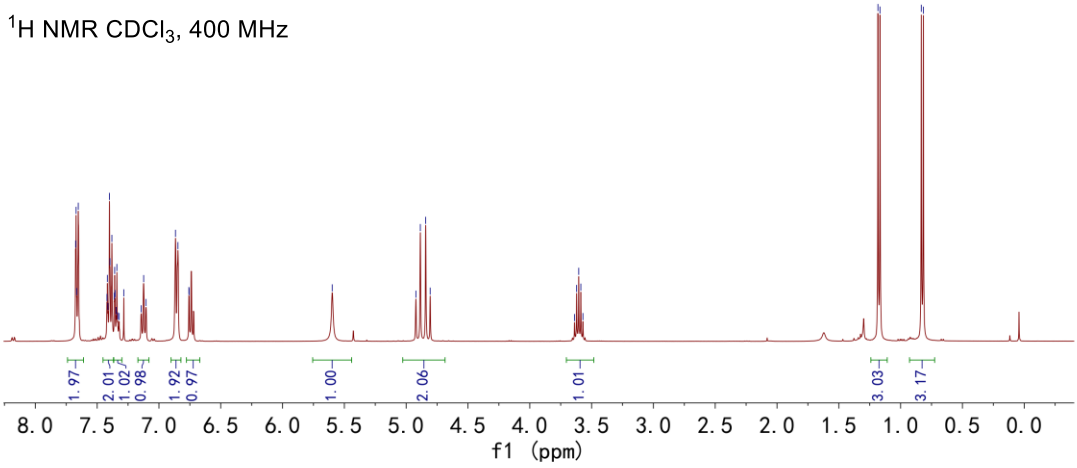
^{13}C NMR $CDCl_3$, 101 MHz

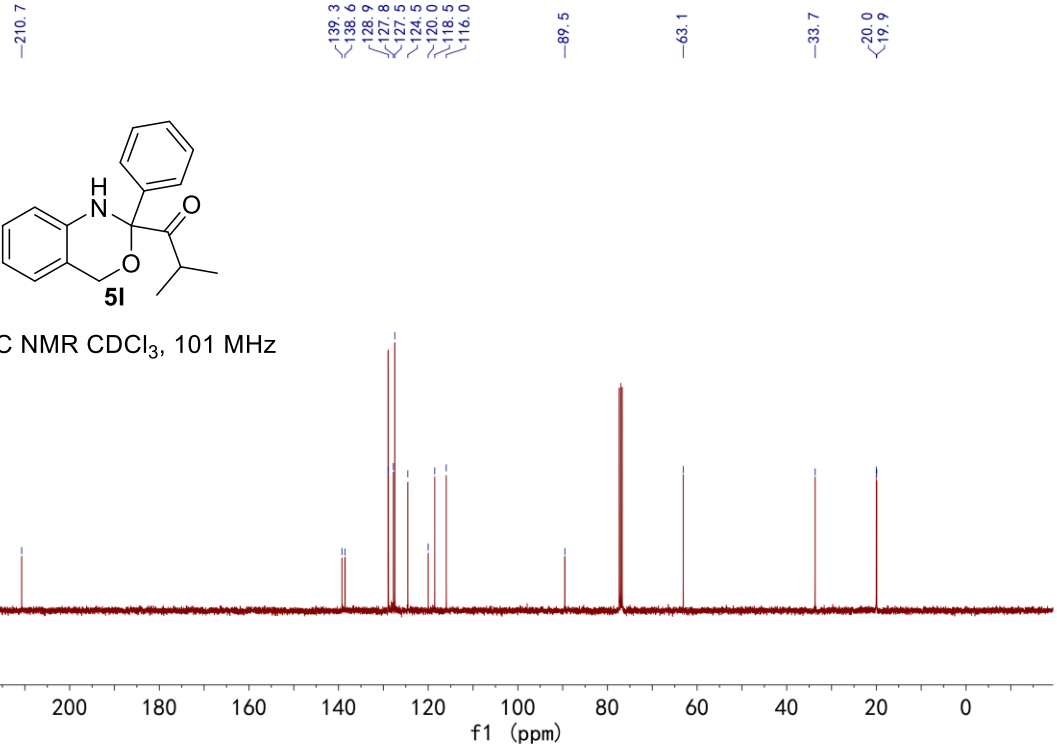




5l

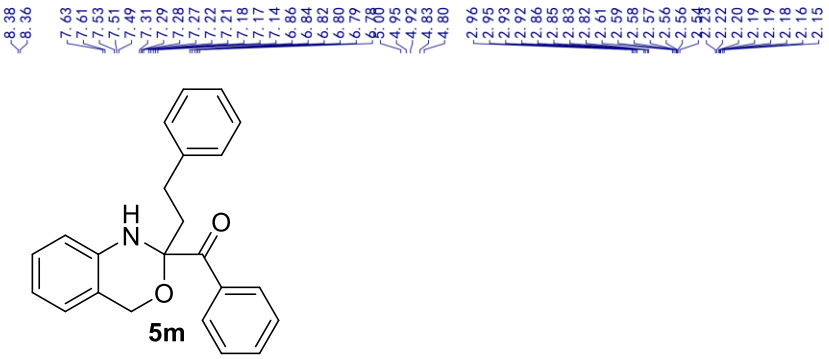
^{1}H NMR $CDCl_3$, 400 MHz





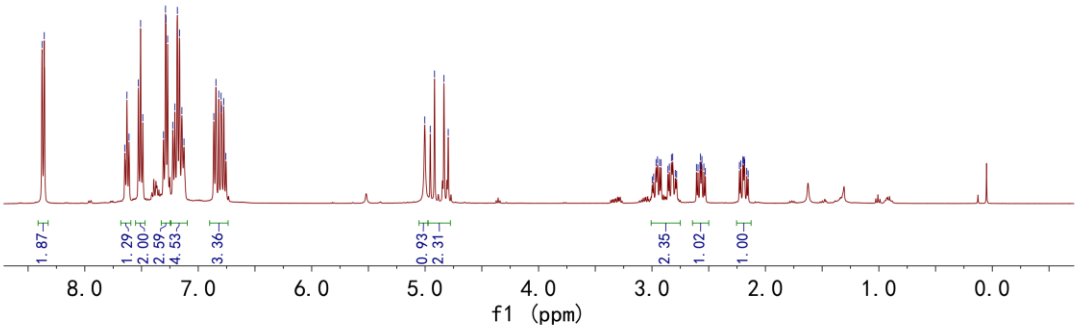
5l

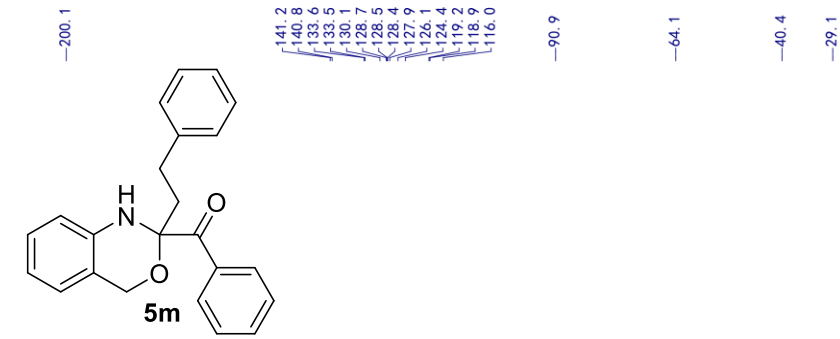
^{13}C NMR $CDCl_3$, 101 MHz



5m

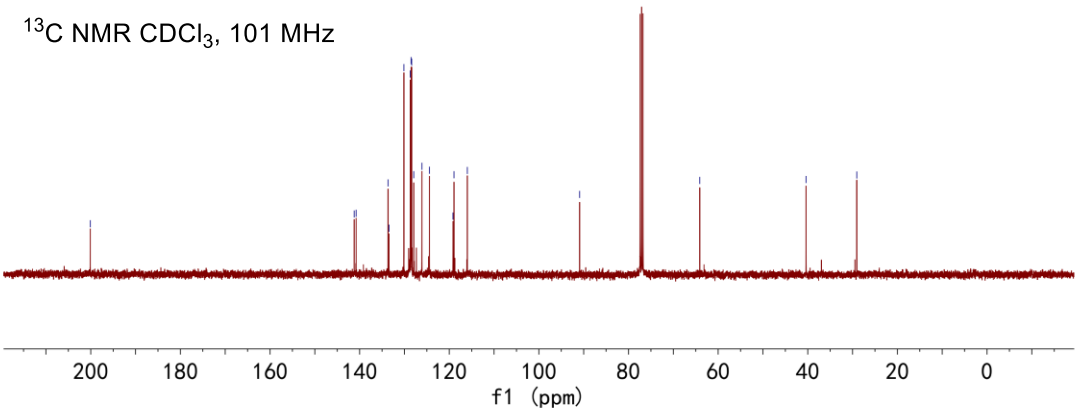
^{1}H NMR $CDCl_3$, 400 MHz

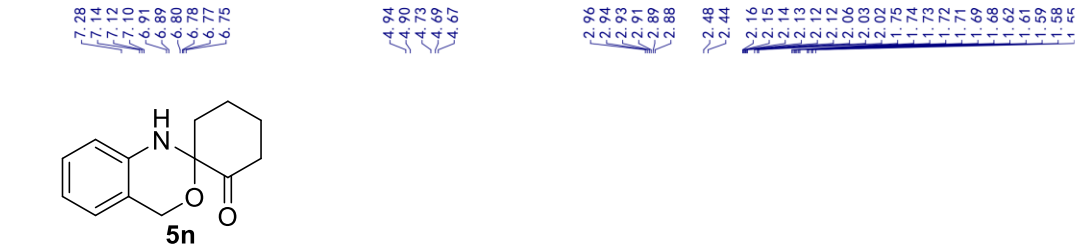




5m

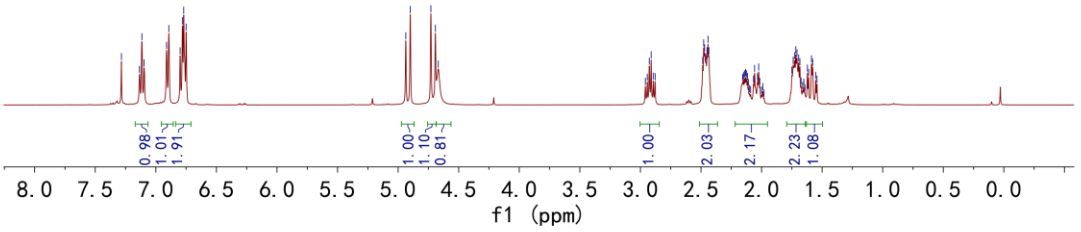
^{13}C NMR $CDCl_3$, 101 MHz

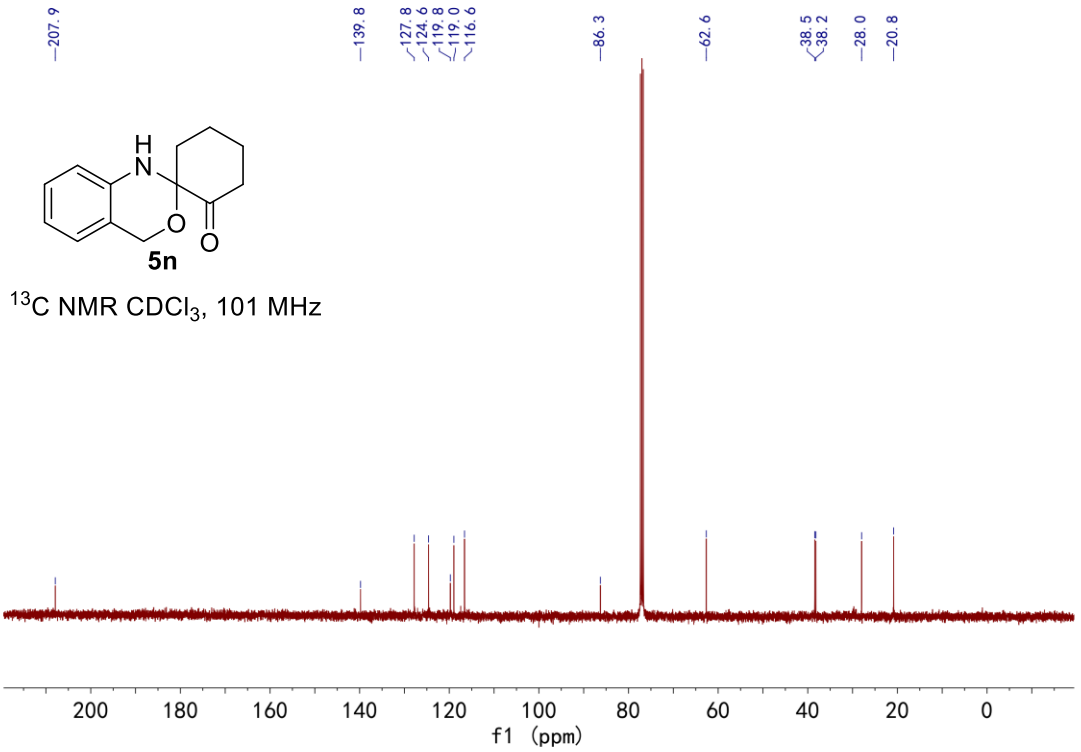




5n

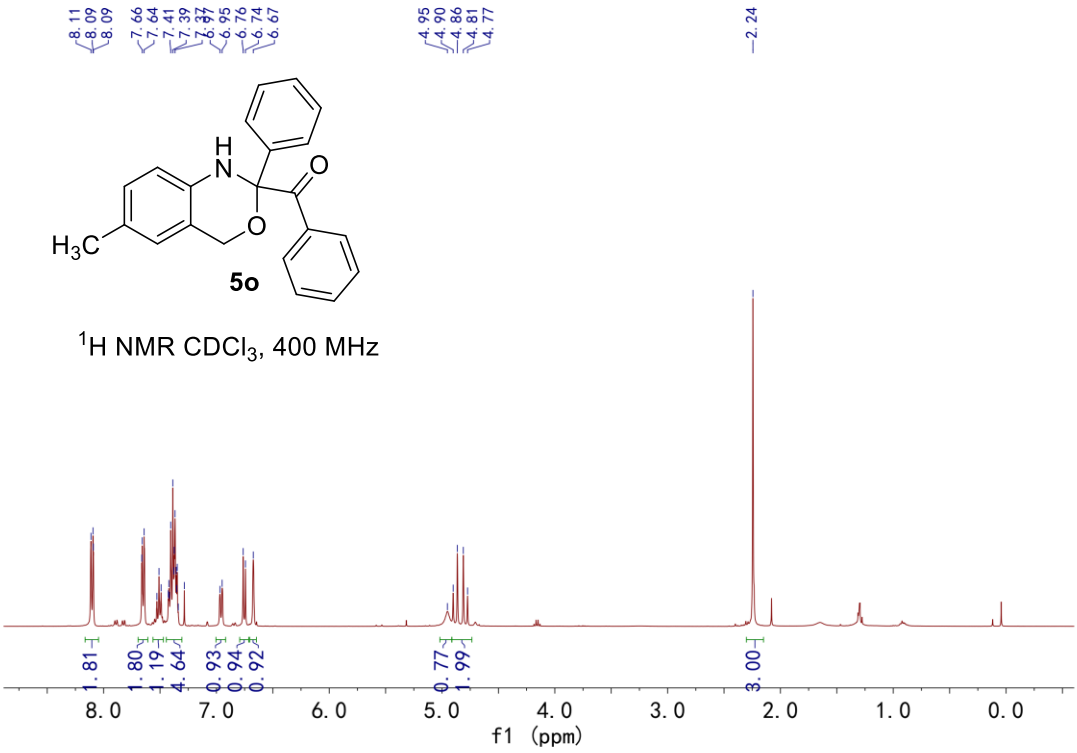
^{1}H NMR $CDCl_3$, 400 MHz

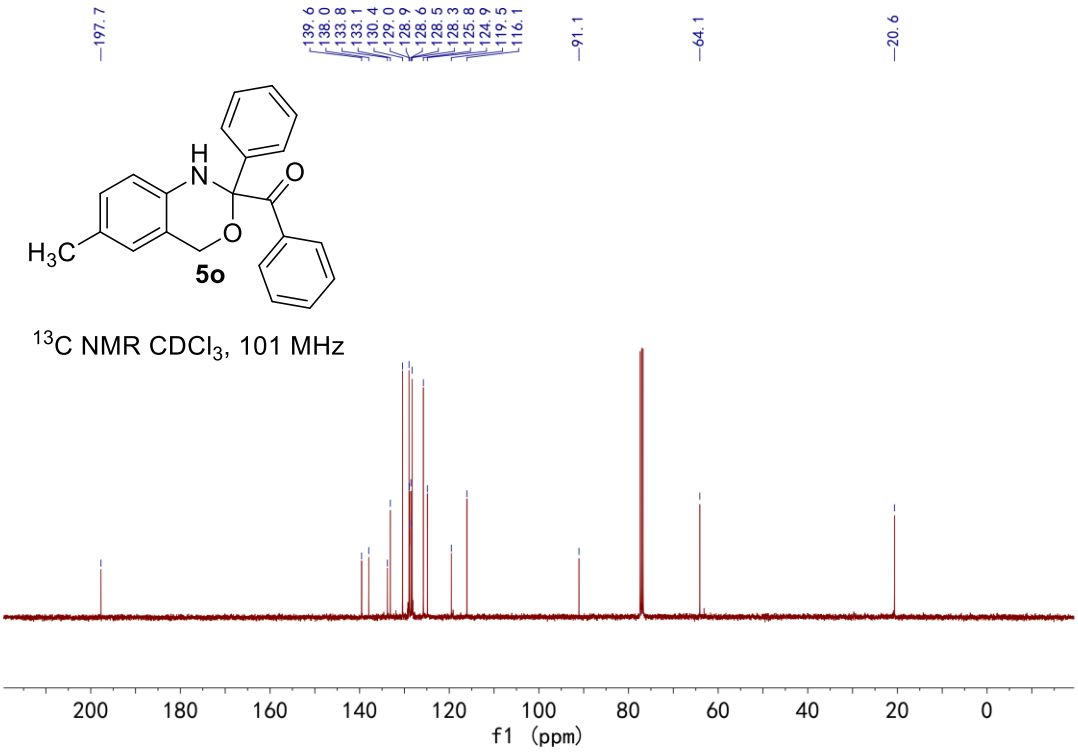


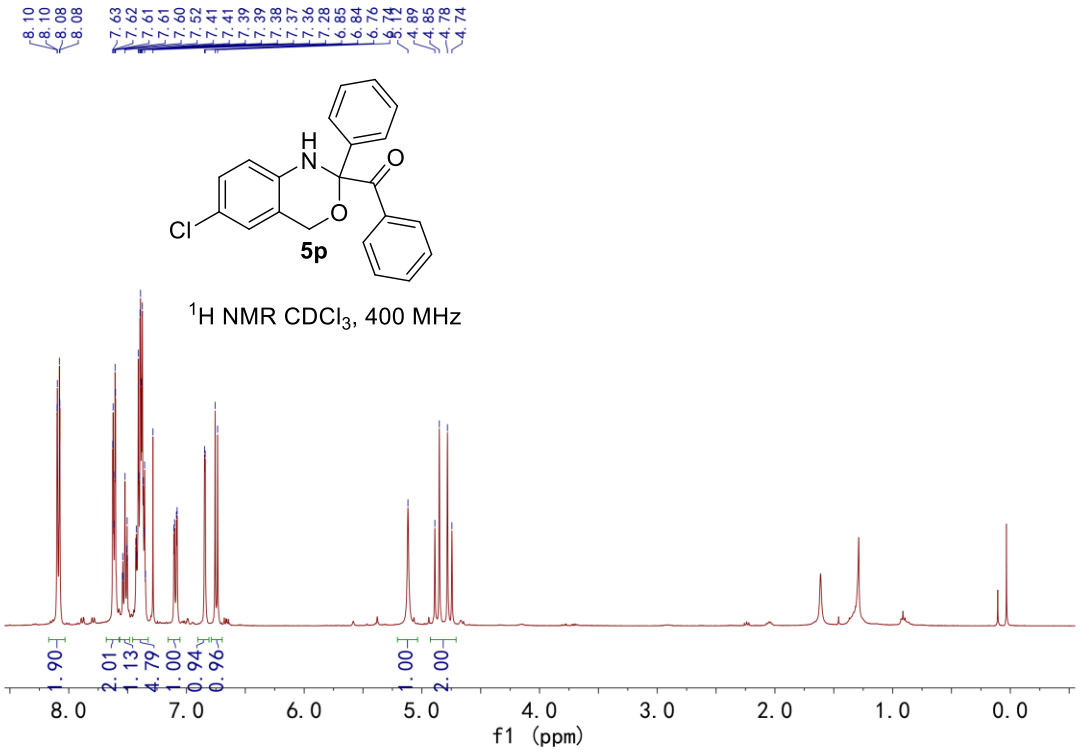


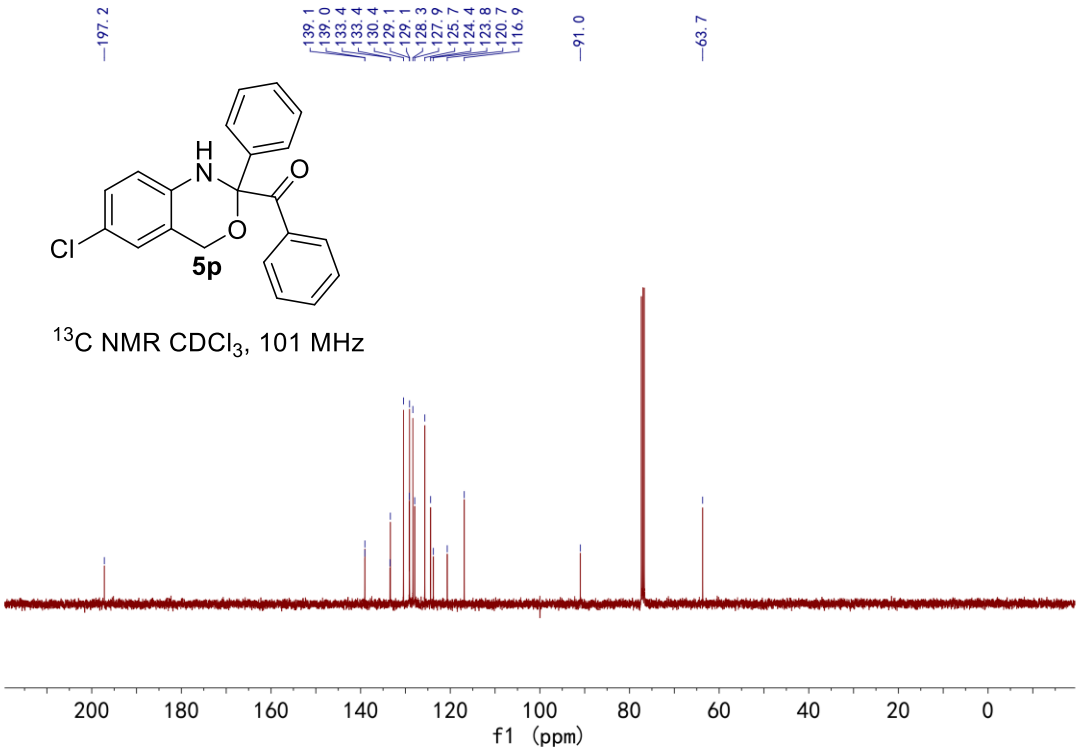
5n

^{13}C NMR $CDCl_3$, 101 MHz


8.11
8.09
8.09
7.66
7.64
7.41
7.39
6.95
6.76
6.74
6.67
4.95
4.90
4.86
4.81
4.77
2.24
H
N
O
O
H3C
5o
1H NMR CDCl3, 400 MHz
1.81
1.80
1.19
4.64
0.93
0.94
0.92
0.77
1.99
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


197.7
139.6
138.0
133.8
133.1
130.4
129.0
128.9
128.6
128.5
128.3
125.8
124.9
119.5
116.1
91.1
64.1
20.6
H
N
O
O
H3C
5o
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.10
8.10
8.08
8.08
7.63
7.62
7.61
7.61
7.60
7.52
7.41
7.41
7.39
7.39
7.38
7.37
7.36
7.28
6.85
6.84
6.76
6.74
4.89
4.85
4.78
4.74
H
N
O
O
Cl
5p
1H NMR CDCl3, 400 MHz
1.90
2.01
1.13
4.79
1.00
0.94
0.96
1.00
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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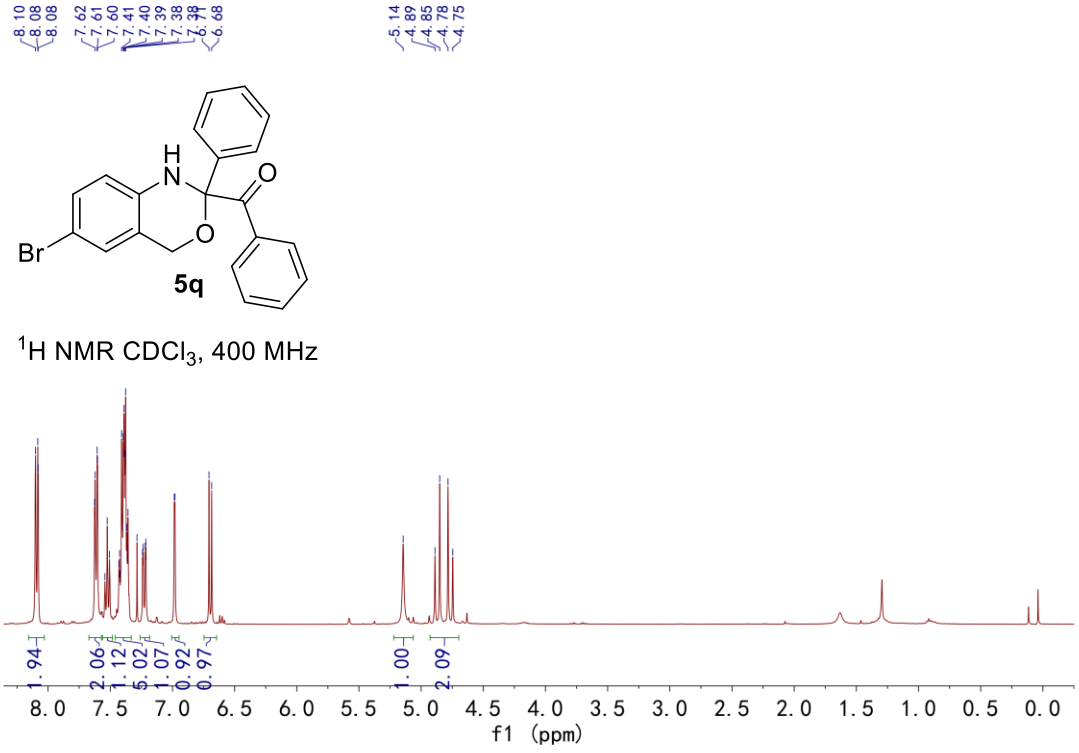
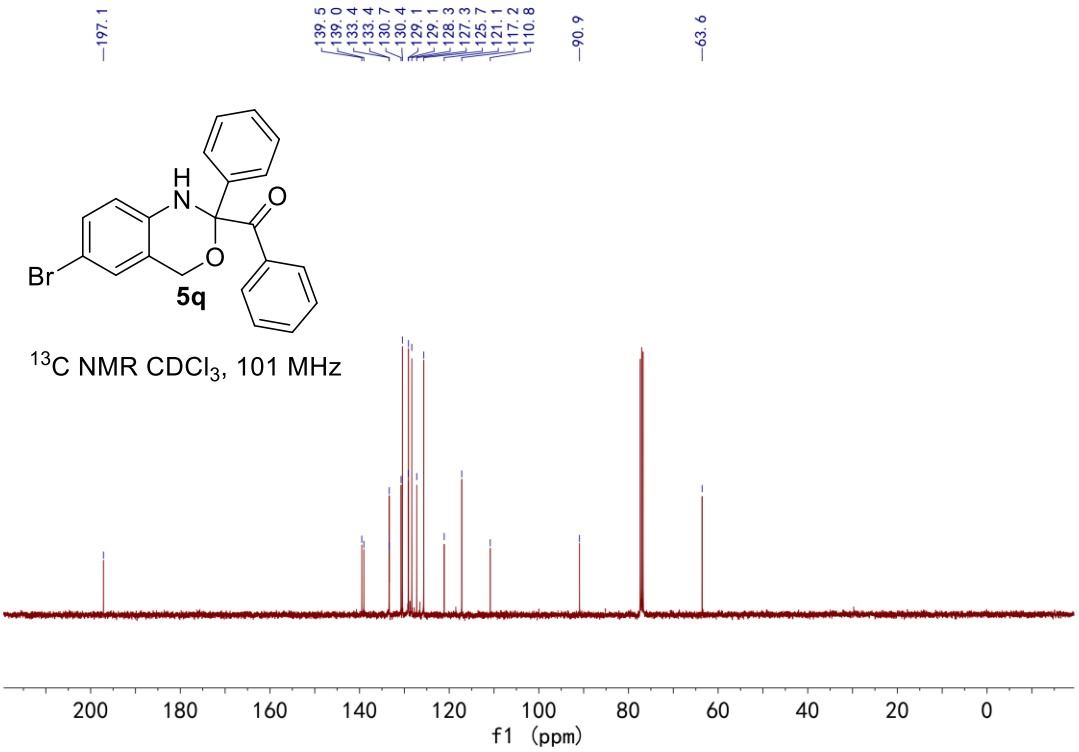
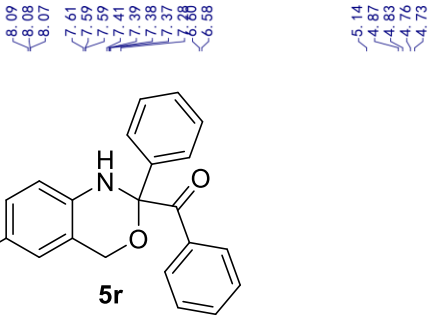
139.1
139.0
133.4
133.4
130.4
129.1
129.1
128.3
127.9
125.7
124.4
123.8
120.7
116.9
91.0
63.7
H
N
O
O
Cl
5p
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

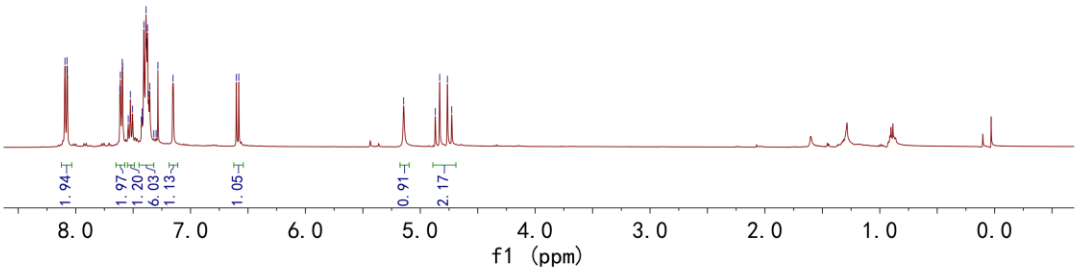

8.10
8.08
8.08
7.62
7.61
7.60
7.41
7.40
7.39
7.38
6.68
5.14
4.89
4.85
4.78
4.75
H
N
O
O
Br
5q
1H NMR CDCl3, 400 MHz
1.94
2.06
1.12
5.02
1.07
0.92
0.97
1.00
2.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

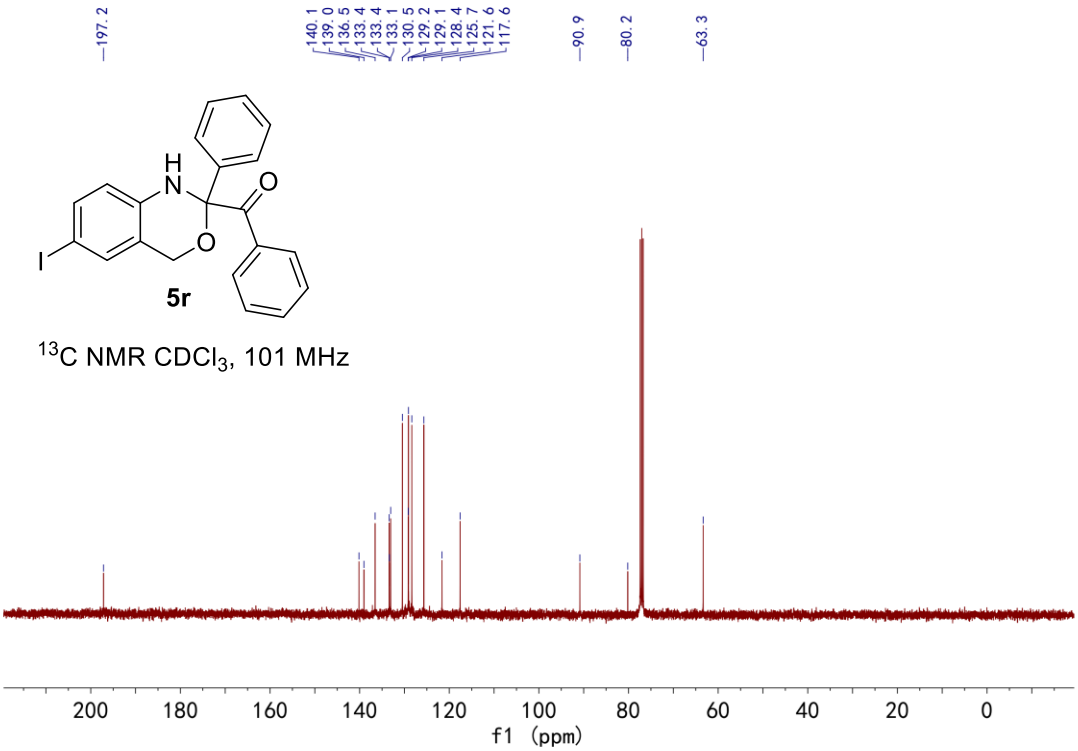

197.1
139.5
139.0
133.4
133.4
130.7
130.4
129.1
129.1
128.3
127.3
125.7
121.1
117.2
110.8
90.9
63.6
H
N
O
O
Br
5q
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



5r

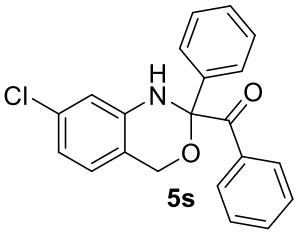
^{1}H NMR $CDCl_3$, 400 MHz





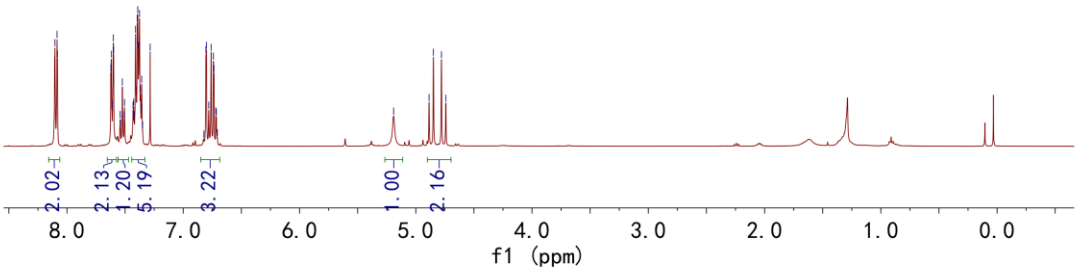
5r

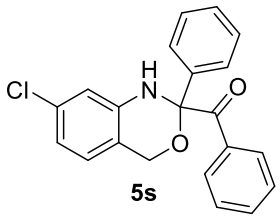
^{13}C NMR $CDCl_3$, 101 MHz



5s

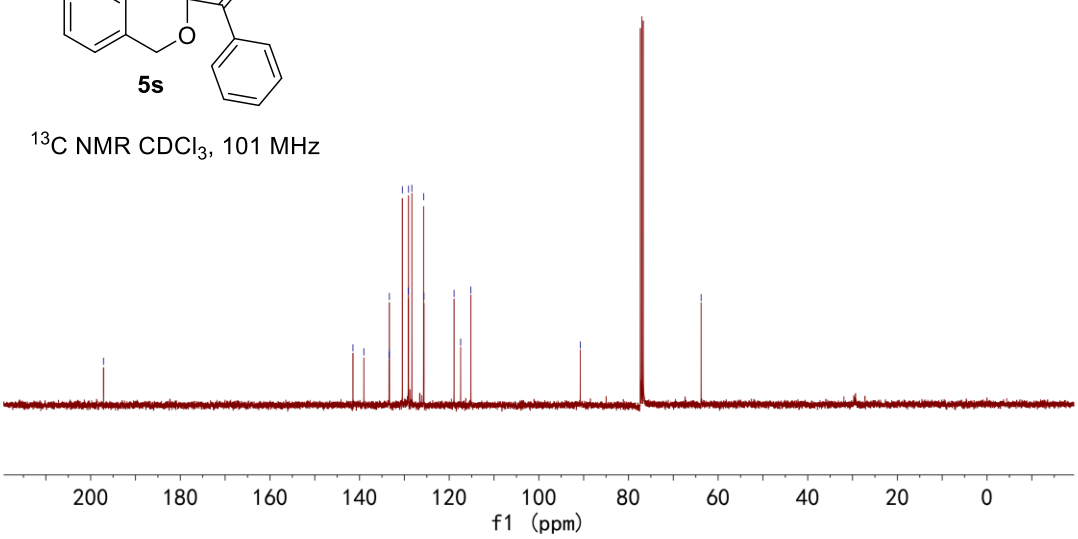
^{1}H NMR $CDCl_3$, 400 MHz

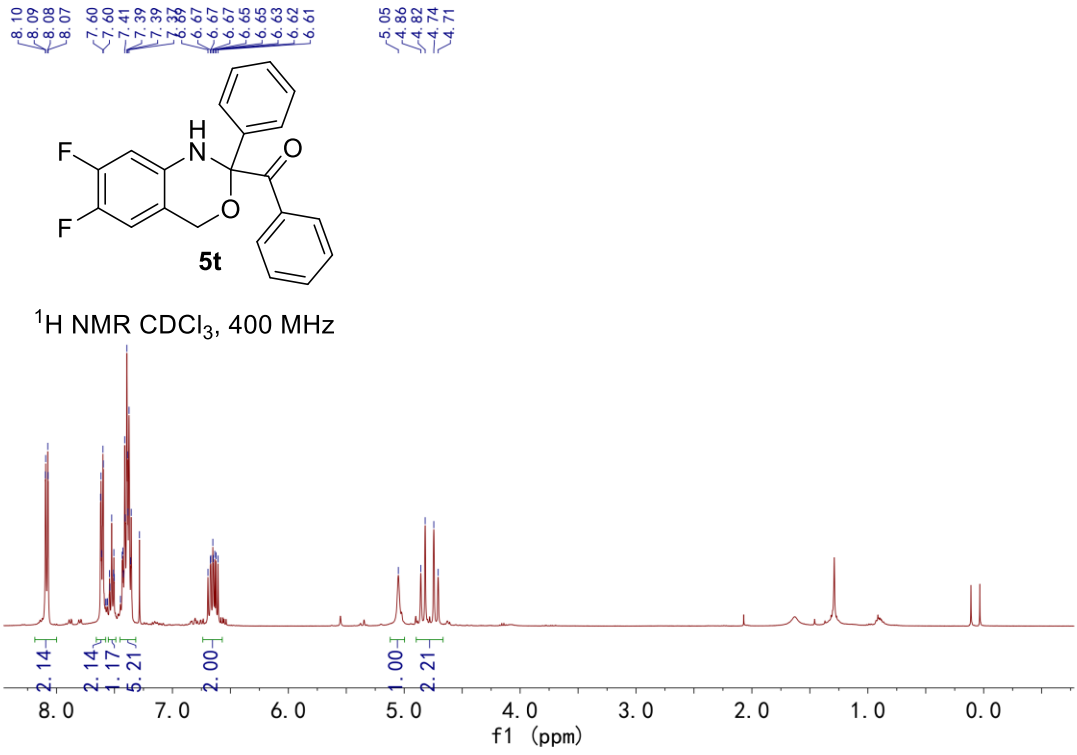


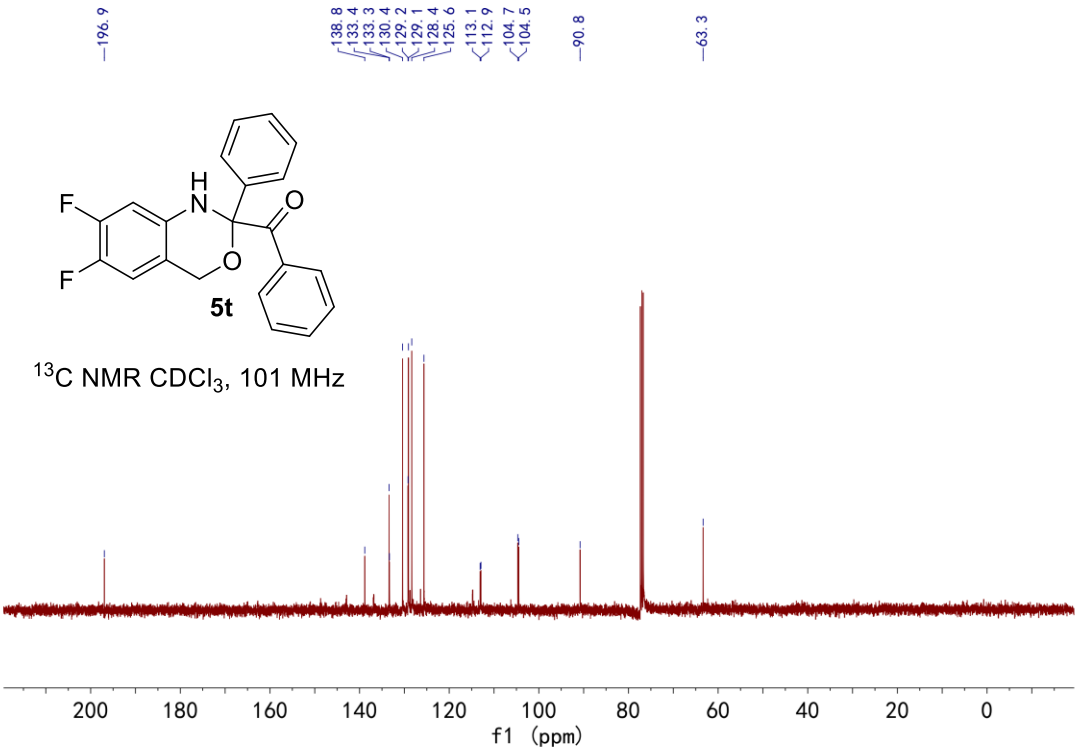


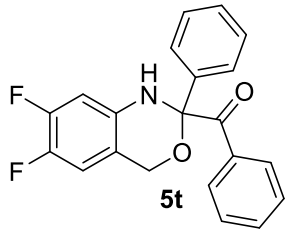
5s

^{13}C NMR $CDCl_3$, 101 MHz



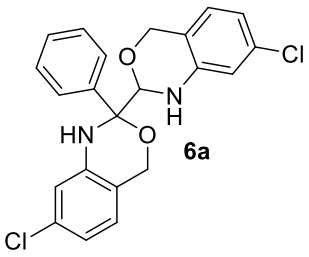

8.10
8.09
8.08
8.07
7.60
7.60
7.41
7.39
7.39
6.67
6.67
6.65
6.63
6.62
6.61
5.05
4.86
4.82
4.74
4.71
F
F
H
N
O
O
5t
1H NMR CDCl3, 400 MHz
2.14
2.14
1.17
5.21
2.00
1.00
2.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


196.9
138.8
133.4
133.3
130.4
129.2
129.1
128.4
125.6
113.1
112.9
104.7
104.5
90.8
63.3
F
F
H
N
O
O
5t
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



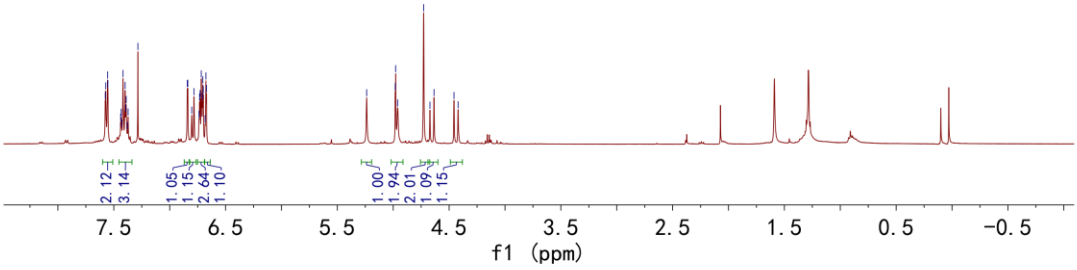
5t

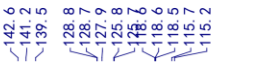
^{19}F NMR $CDCl_3$, 376 MHz

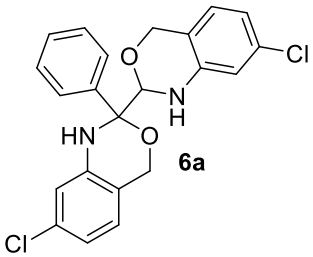


6a

^{1}H NMR $CDCl_3$, 400 MHz

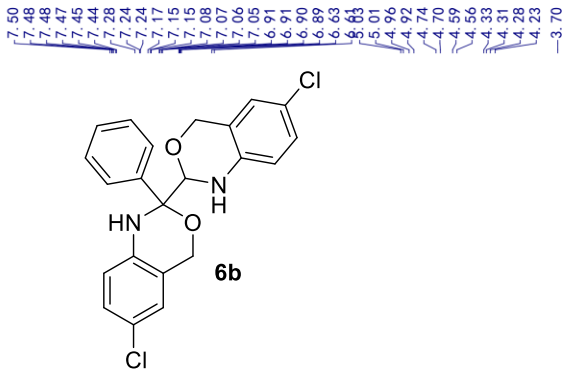






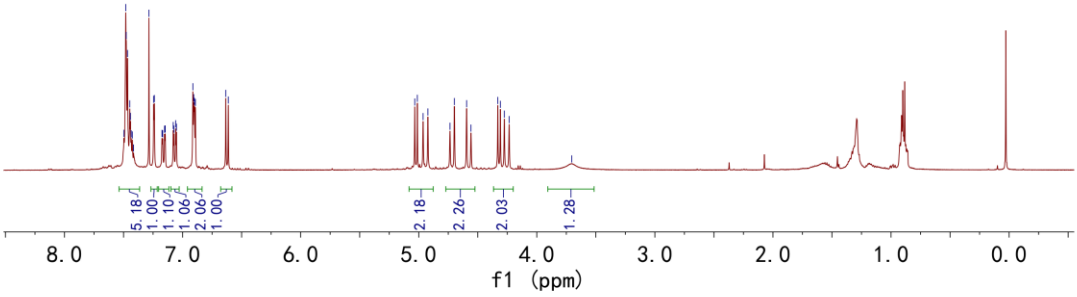
6a

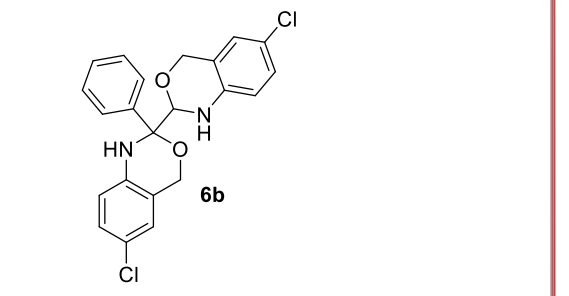
^{13}C NMR $CDCl_3$, 101 MHz



6b

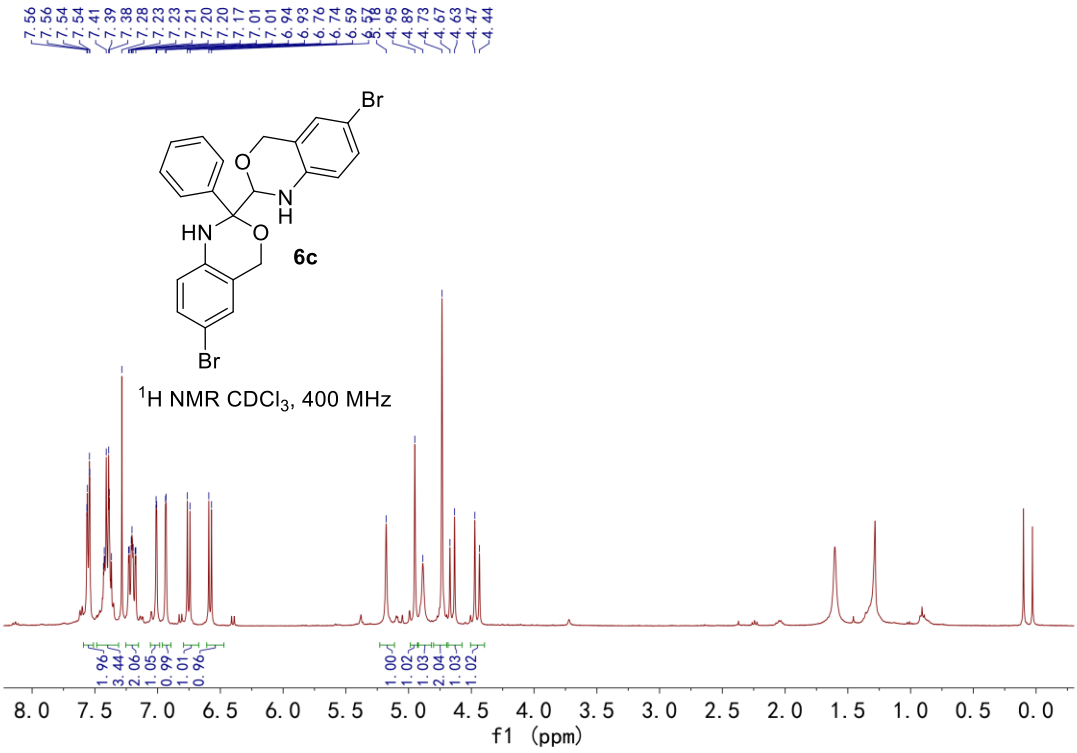
^{1}H NMR $CDCl_3$, 400 MHz

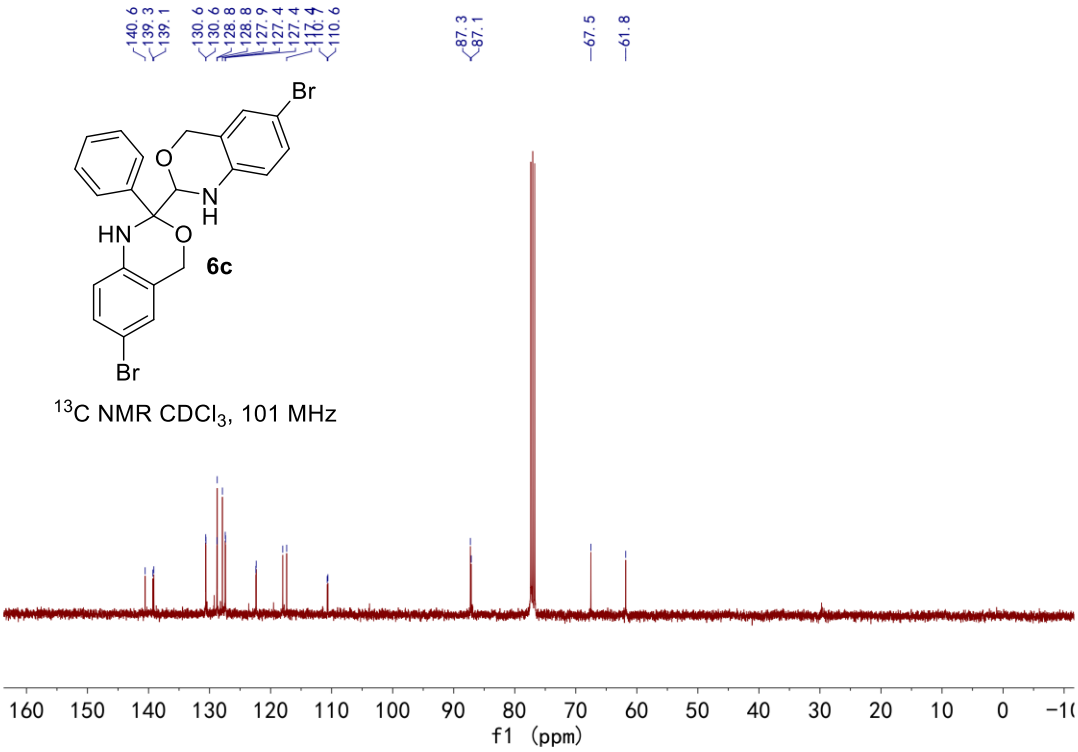


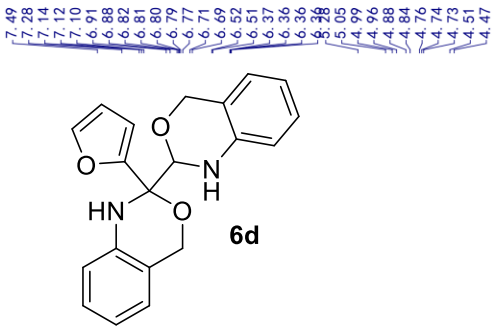


6b

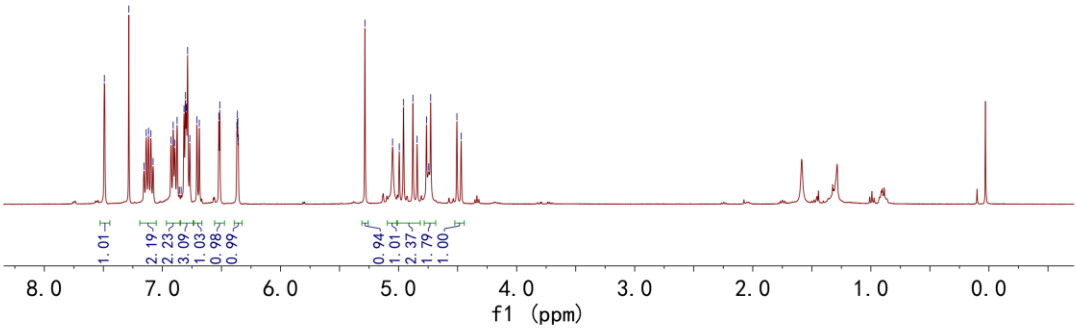
^{13}C NMR $CDCl_3$, 101 MHz

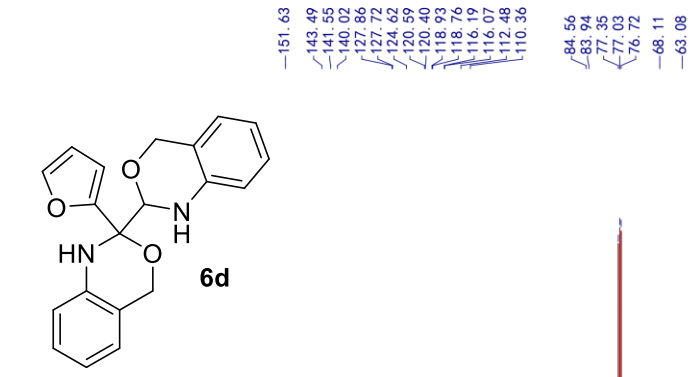

7.56
7.56
7.54
7.54
7.41
7.39
7.38
7.28
7.23
7.21
7.20
7.17
7.01
6.94
6.93
6.76
6.74
6.59
6.57
5.18
4.95
4.89
4.73
4.67
4.63
4.47
4.44
Br
O
N
H
HN
O
6c
Br
1H NMR CDCl3, 400 MHz
1.96
3.44
2.06
1.05
0.99
1.01
0.96
1.00
1.02
1.03
2.04
1.03
1.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.6
139.3
139.1
130.6
130.6
128.8
128.8
127.9
127.4
127.4
87.3
87.1
67.5
61.8
Br
O
N
H
HN
O
6c
Br
13C NMR CDCl3, 101 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

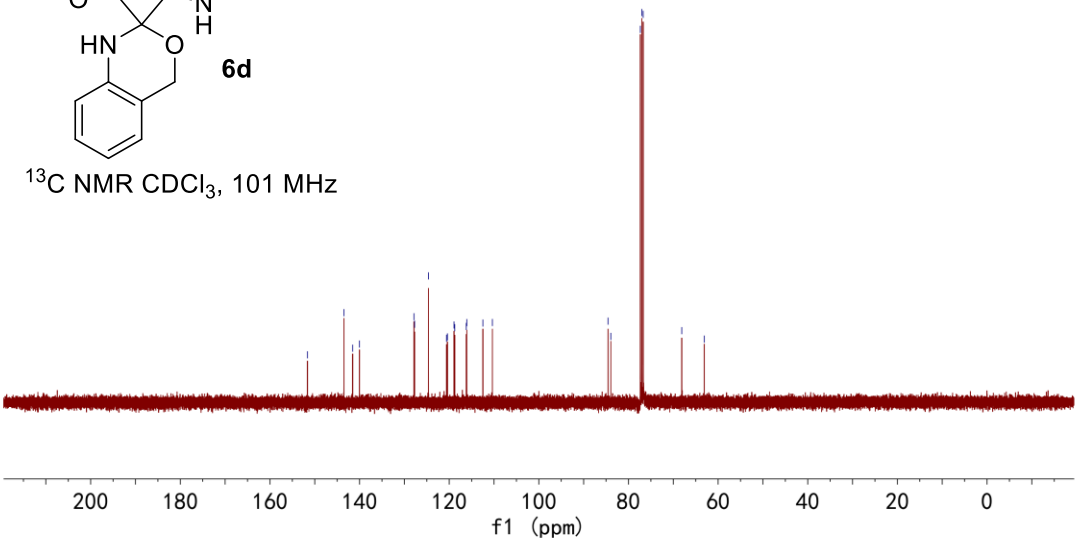


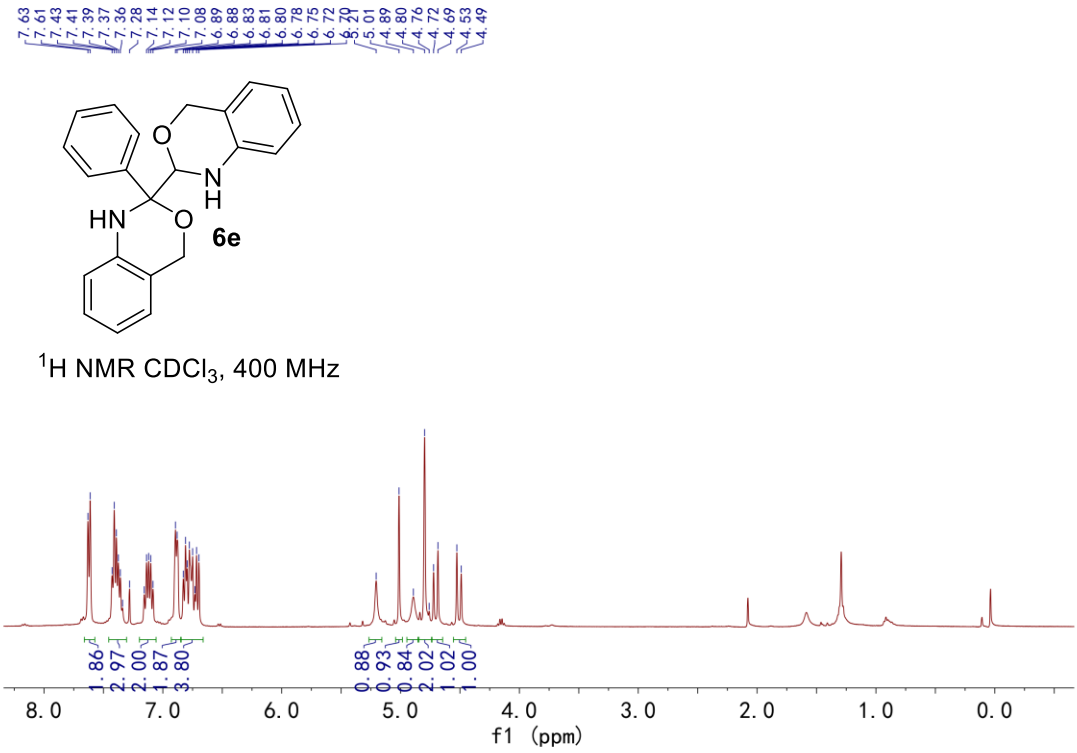
^{1}H NMR $CDCl_3$, 400 MHz



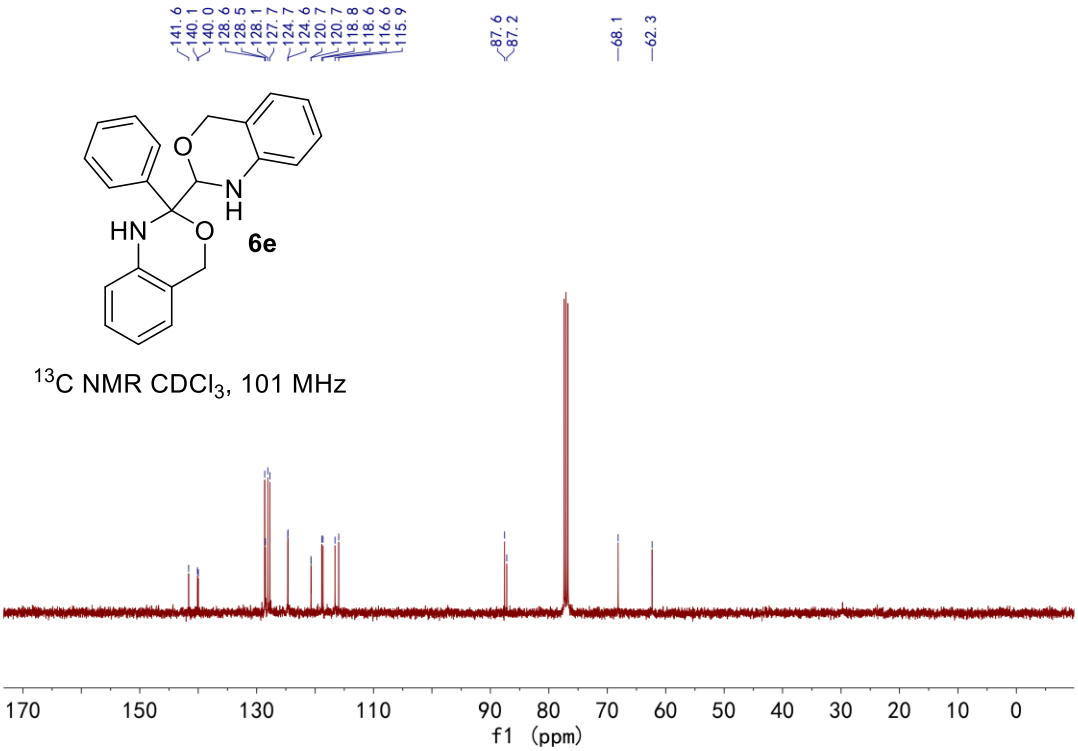


^{13}C NMR $CDCl_3$, 101 MHz

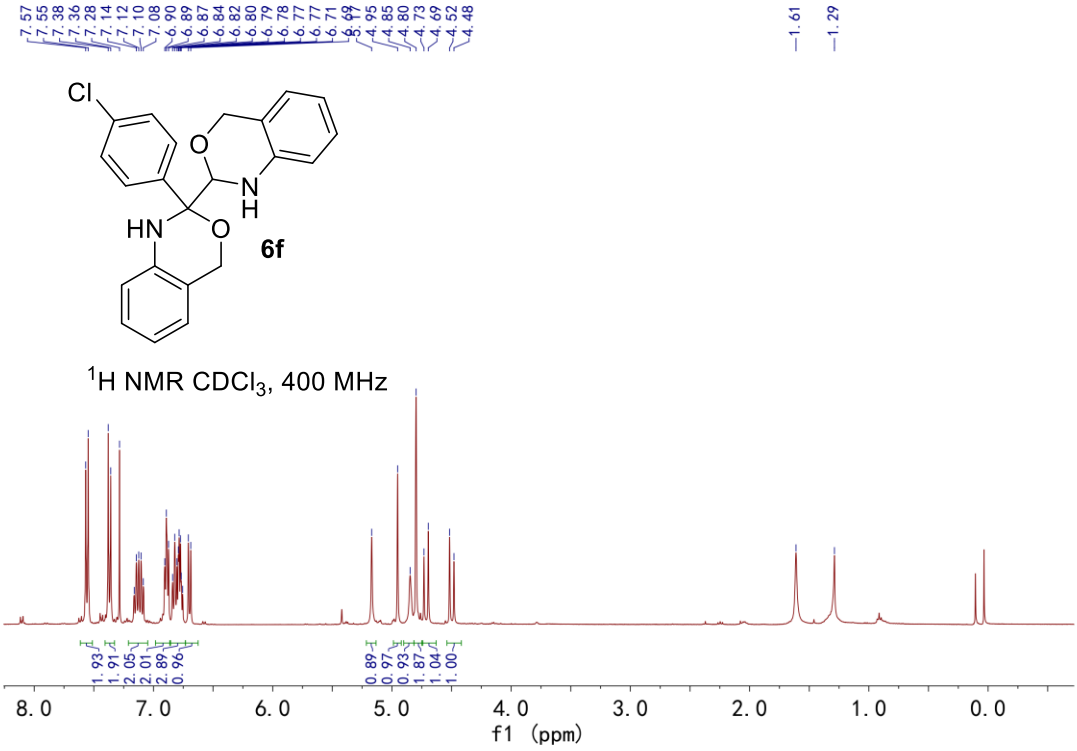


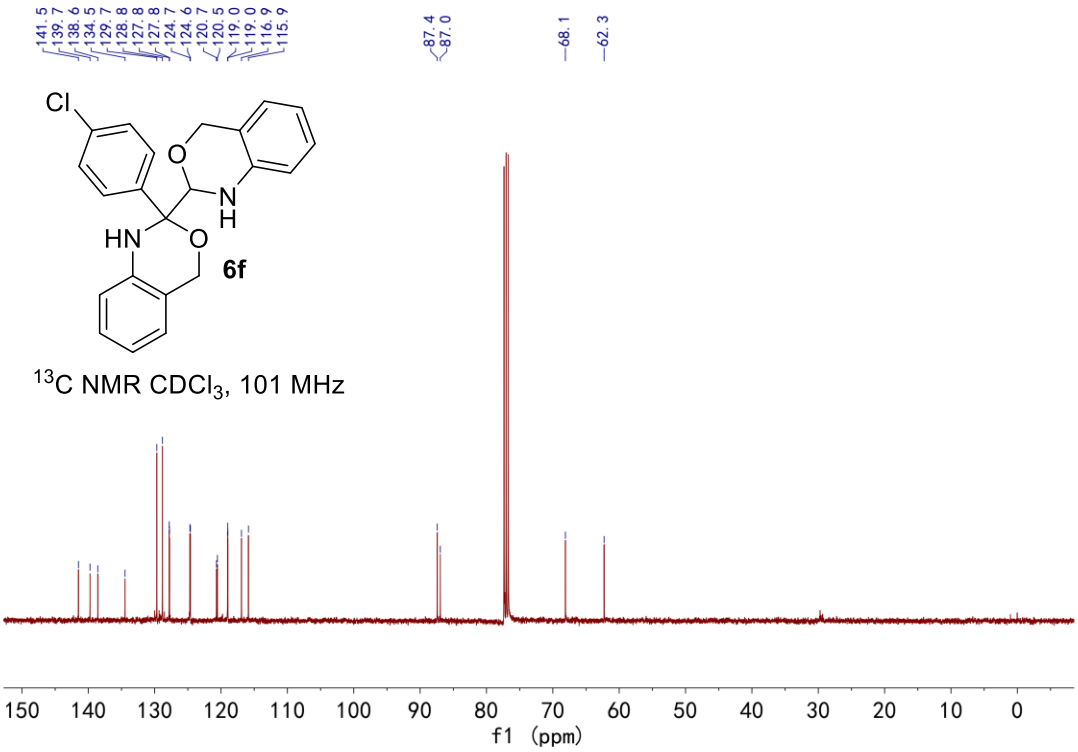


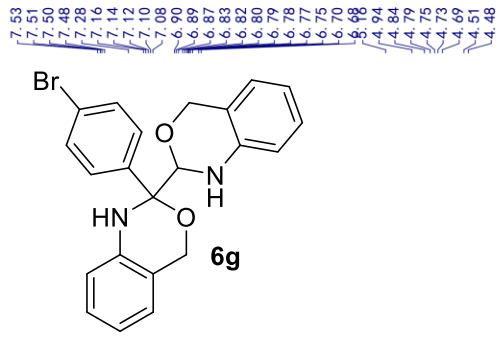
^{1}H NMR $CDCl_3$, 400 MHz



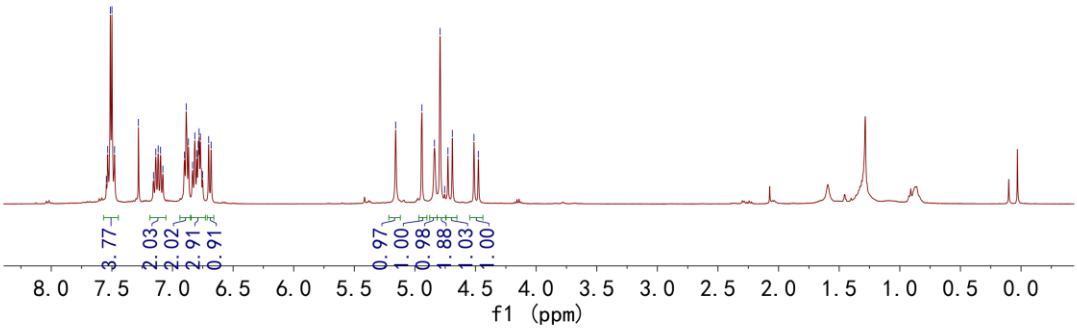
^{13}C NMR $CDCl_3$, 101 MHz

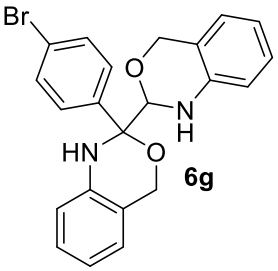

7.57
7.55
7.38
7.36
7.28
7.14
7.12
7.10
7.08
6.90
6.89
6.87
6.84
6.82
6.80
6.79
6.78
6.77
6.71
4.95
4.85
4.80
4.73
4.69
4.52
4.48
1.61
1.29
Cl
O
N
H
HN
O
6f
1H NMR CDCl3, 400 MHz
1.93
1.91
2.05
2.01
2.89
0.96
0.89
0.97
0.93
1.87
1.04
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


141.5
139.7
138.6
134.5
129.7
128.8
127.8
127.8
124.7
124.6
120.7
120.5
119.0
119.0
116.9
115.9
87.4
87.0
68.1
62.3
Cl
O
N
H
HN
O
6f
13C NMR CDCl3, 101 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

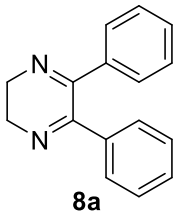


^{1}H NMR $CDCl_3$, 400 MHz



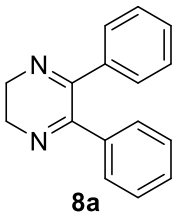


^{13}C NMR $CDCl_3$, 101 MHz



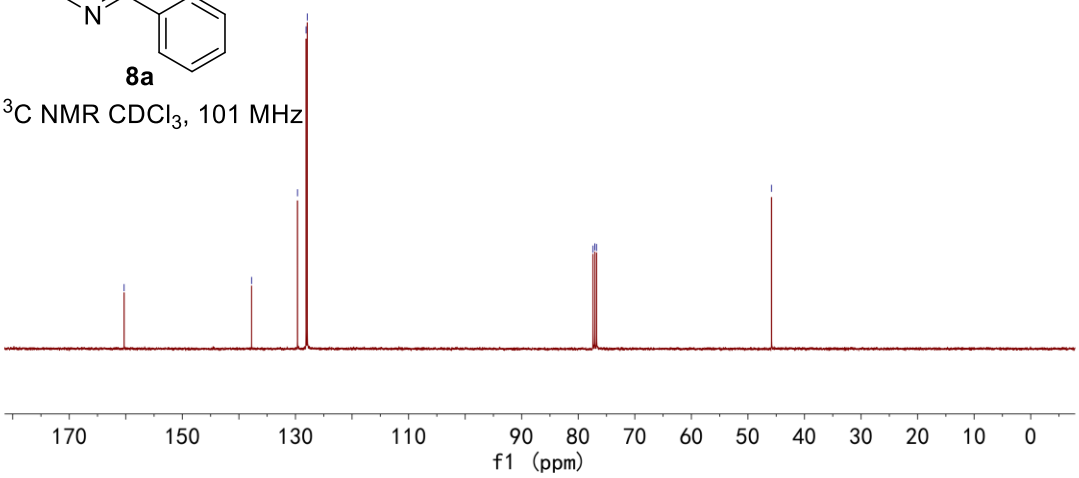
8a

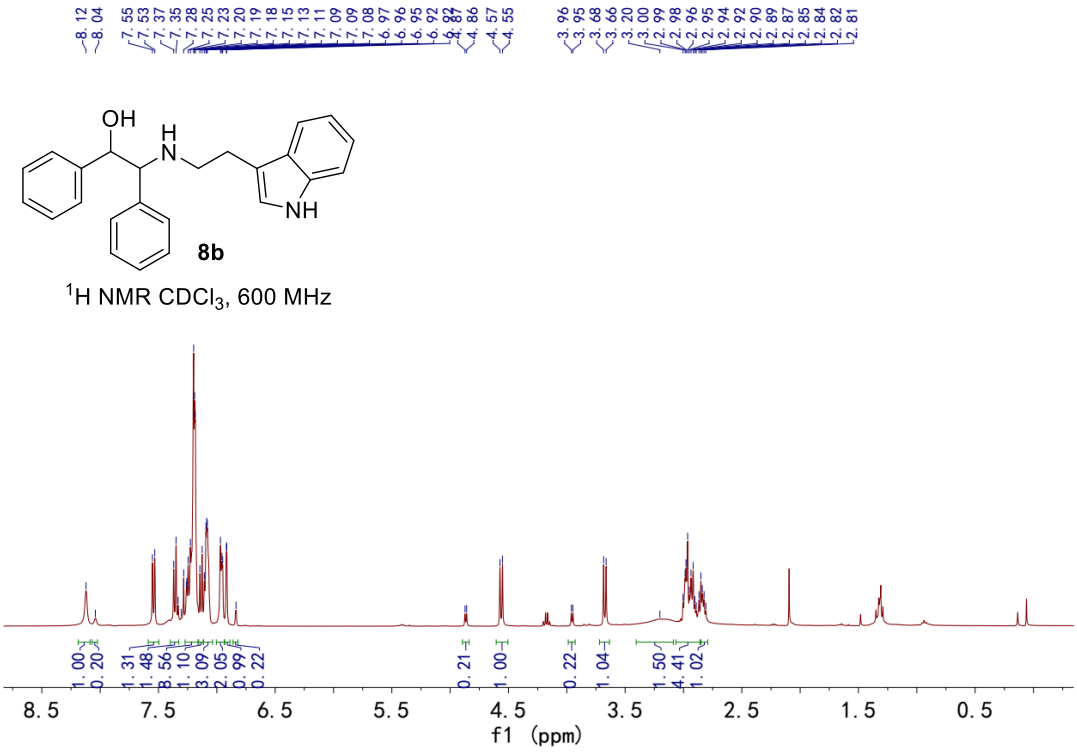
^{1}H NMR $CDCl_3$, 400 MHz

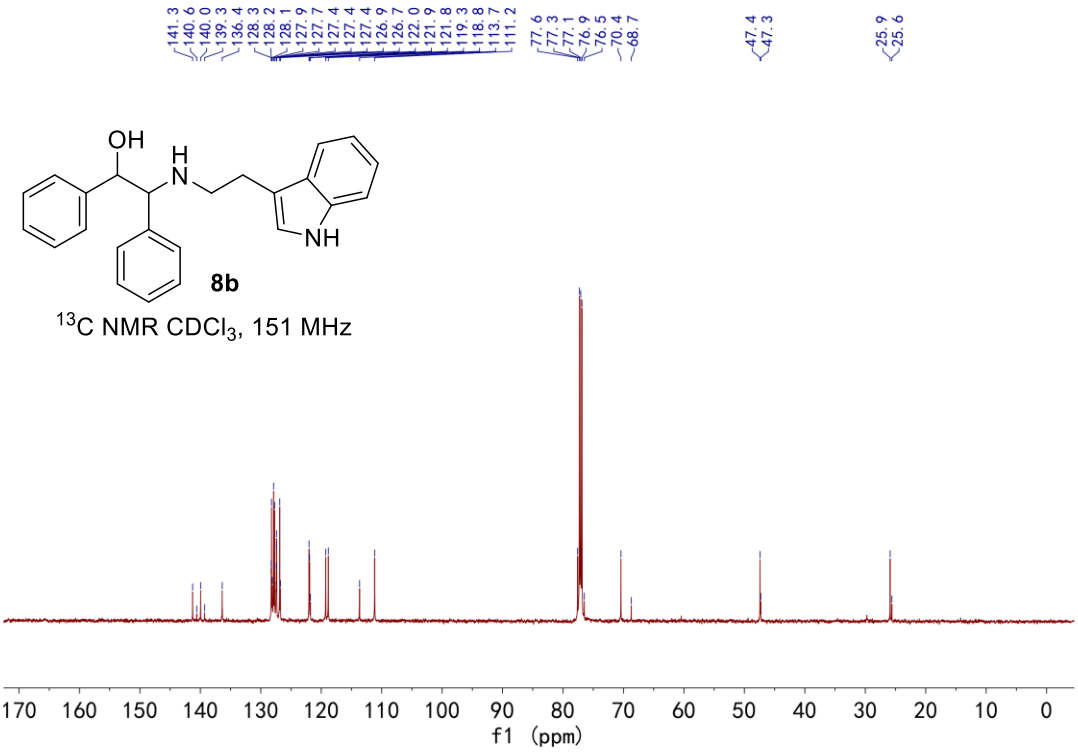


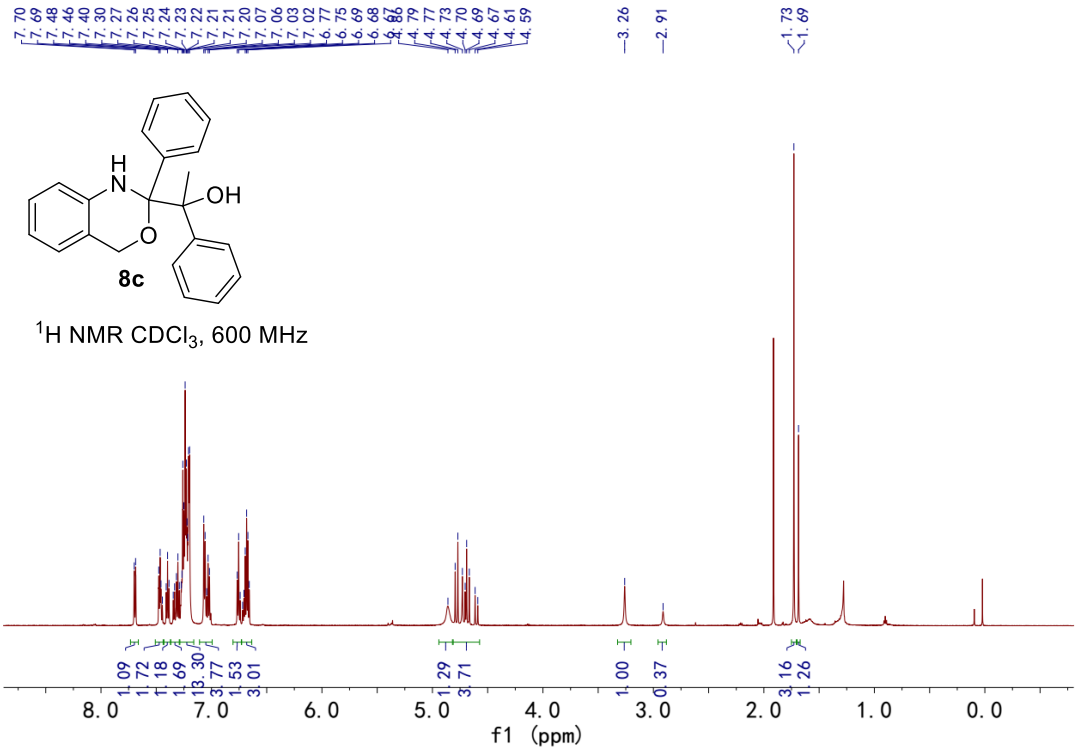
8a

^{13}C NMR $CDCl_3$, 101 MHz

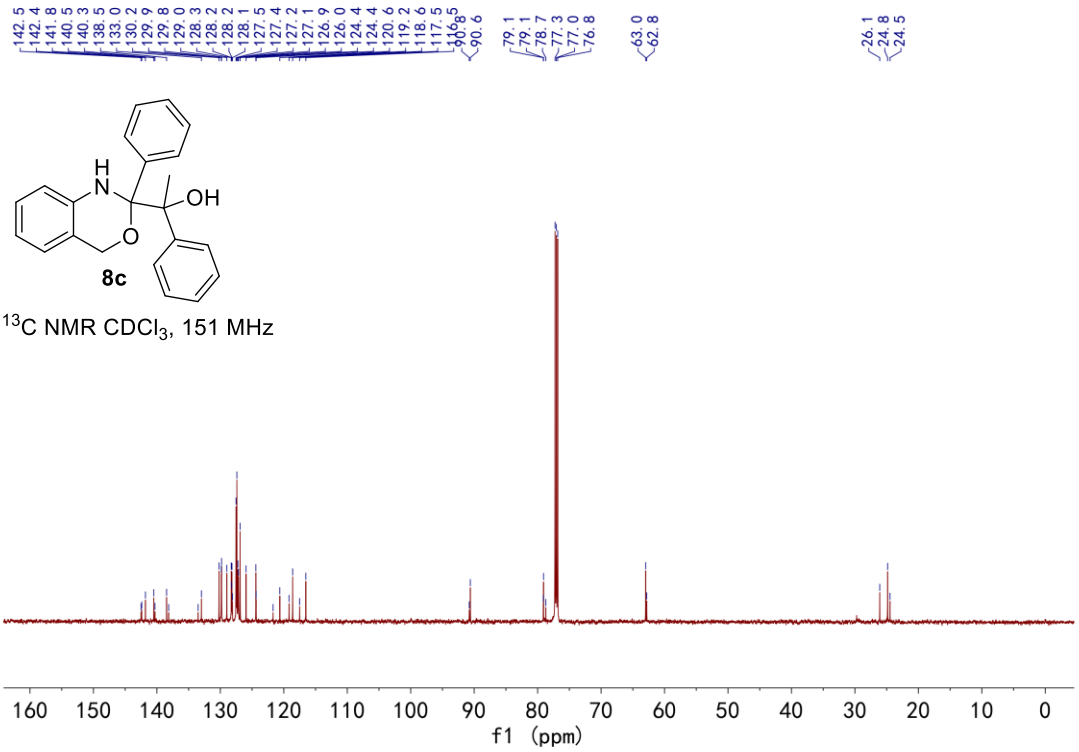



8.12
8.04
7.55
7.53
7.37
7.35
7.28
7.25
7.23
7.20
7.19
7.18
7.15
7.13
7.11
7.09
7.09
7.08
6.97
6.96
6.95
6.92
4.86
4.57
4.55
3.96
3.95
3.68
3.66
3.20
3.00
2.99
2.98
2.96
2.95
2.94
2.92
2.90
2.89
2.87
2.85
2.84
2.82
2.81
OH
H
N
NH
8b
1H NMR CDCl3, 600 MHz
1.00
0.20
1.31
1.48
3.56
1.10
3.09
2.05
0.99
0.22
0.21
1.00
0.22
1.04
1.50
4.41
1.02
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

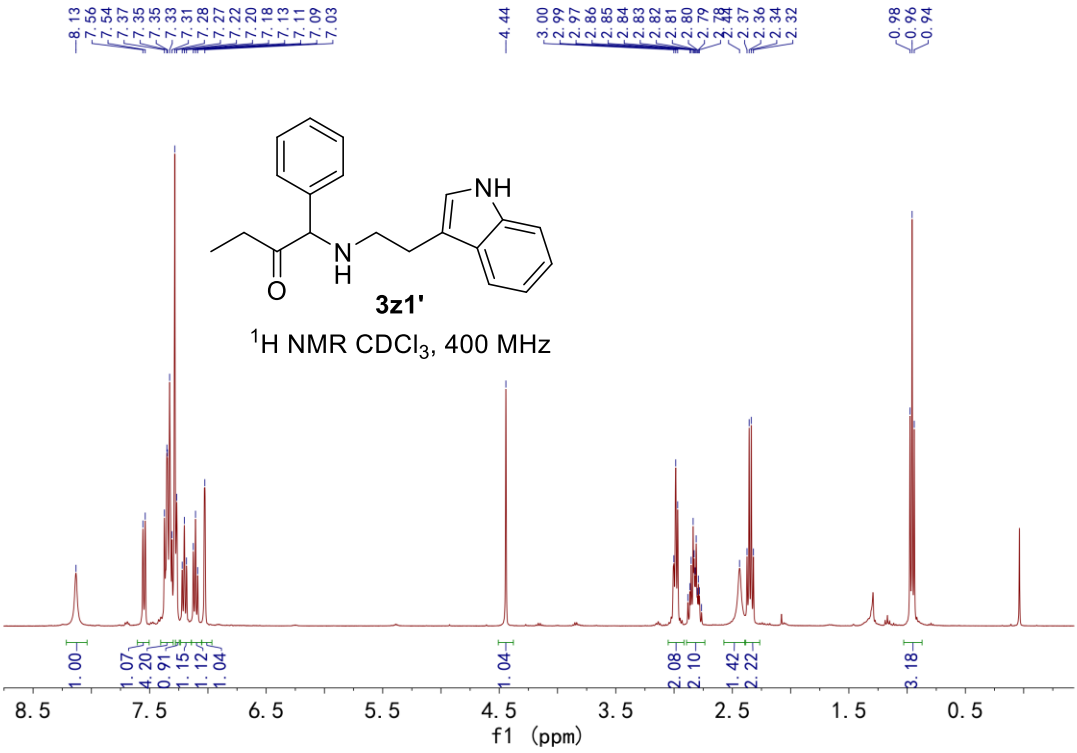

141.3
140.6
140.0
139.3
136.4
128.3
128.2
128.1
127.9
127.7
127.4
127.4
127.4
126.9
126.7
122.0
121.9
121.8
119.3
118.8
113.7
111.2
77.6
77.3
77.1
76.9
76.5
70.4
68.7
47.4
47.3
25.9
25.6
OH
H
N
NH
8b
13C NMR CDCl3, 151 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

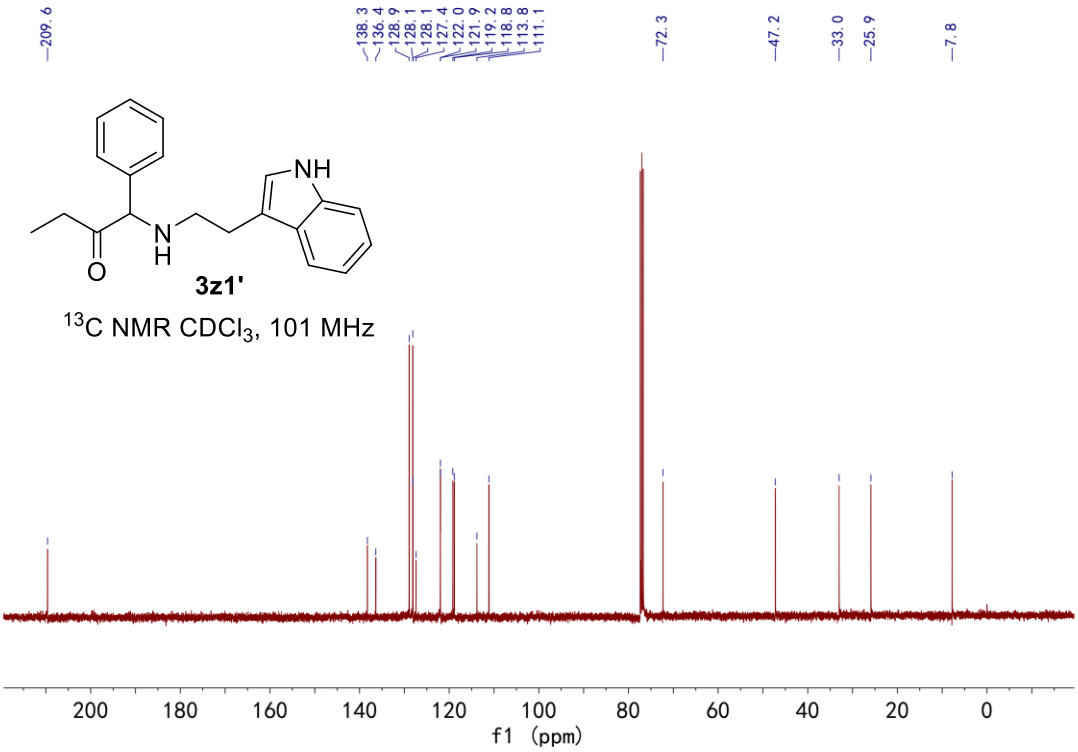


^{1}H NMR $CDCl_3$, 600 MHz



^{13}C NMR $CDCl_3$, 151 MHz


8.13
7.56
7.54
7.37
7.35
7.33
7.31
7.28
7.27
7.22
7.20
7.18
7.13
7.11
7.09
7.03
4.44
3.00
2.99
2.97
2.86
2.85
2.84
2.83
2.82
2.81
2.80
2.79
2.37
2.36
2.34
2.32
0.98
0.96
0.94
NH
N
H
O
3z1'
1H NMR CDCl3, 400 MHz
1.00
1.07
4.20
0.91
1.15
1.12
1.04
1.04
2.08
2.10
1.42
2.22
3.18
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


209.6
138.3
136.4
128.9
128.1
128.1
127.4
122.0
121.9
119.2
118.8
113.8
111.1
72.3
47.2
33.0
25.9
7.8
NH
N
H
O
3z1'
13C NMR CDCl3, 101 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)