Support information

Visible-light mediated intramolecular radical cyclizations of α-brominated amide-tethered alkylidenecyclopropanes

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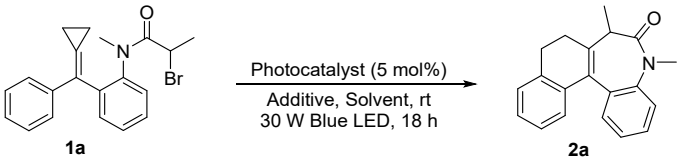
CONTENTS

1. General Remarks.

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR), 600 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 150 MHz (^{13}C NMR) and 564 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift was reported in ppm down field from internal TMS. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, EI and HRMS was measured on a HP-5989 instrument. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. Commercially available reagents were used without further purification. Organic solvents used were dried by standard methods when necessary. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was performed by using GENERAL-REAGENT silica gel (300-400 mesh). All reactions were performed under argon using standard Schlenk techniques. The 15 W and 30 W Blue LED (Manufacturer: Liang yuan-Light Factory, Model: PAR 38, Wavelength: 425 nm) was directly purchased from the supermarket.

2. Optimization of Reaction Conditions

Table S1 Optimization of Reaction Conditions



1a **2a**

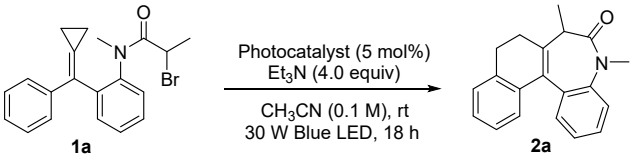
Entry[a]	Photocatalyst	Additive (equiv)	Solvent	Yield (%)[b]
1	$[Ru(bpy)_3](PF_6)_2$	Et_3N (4.0)	CH_3CN	38
2	$[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$	Et_3N (4.0)	CH_3CN	36
3	4CzIPN	Et_3N (4.0)	CH_3CN	65
4	$Ir(ppy)_3$	Et_3N (4.0)	CH_3CN	50
5	4CzIPN	TMEDA (4.0)	CH_3CN	30
6	4CzIPN	DIPEA (4.0)	CH_3CN	40
7	4CzIPN	K_2CO_3 (4.0)	CH_3CN	NR
8	4CzIPN	Et_3N (4.0)	DCE	51
9	4CzIPN	Et_3N (4.0)	Dioxane	58
10	**4CzIPN**	**Et_3N (4.0)**	**DME**	**72 (62)[c]**
11	4CzIPN	Et_3N (4.0)	THF	69
12	4CzIPN	Et_3N (4.0)	DCM	33
13	4CzIPN	Et_3N (4.0)	acetone	55
14	4CzIPN	Et_3N (10.0)	DME	42
15	4CzIPN	Et_3N (2.0)	DME	61
16[d]	—	Et_3N (4.0)	DME	NR
17[e]	4CzIPN	Et_3N (4.0)	DME	NR
18[f]	4CzIPN	—	DME	NR

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), photocatalyst (0.005 mmol, 5.0 mol%) and additive (0.4 mmol, 4.0 equiv) were placed in a reaction tube and Ar was charged. Then 1.0 mL solvent was added and the mixture was stirred exposing to blue LED light (30 W) at room temperature for 18 h. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzen as an internal standard. [c]Isolated yield on 0.2 mmol scale. [d]Reaction was conducted in the absence of photocatalyst. [e]Reaction was conducted in the absence of light source. [f]Reaction was conducted in the absence of additive.

To get **2a** in higher yield, we tried to optimize the reaction conditions and the selected results are shown in Table S1. The photocatalysts with different reduction potentials were employed in the reaction system along with utilizing Et_3N as an additive and CH_3CN as solvent and we found that these photocatalysts could promote the reaction smoothly and the organophotocatalyst 4CzIPN gave the best result, affording **2a** in 65% yield (Table S1, entries 1-4, for more information see Table S2). Next, the other alkyl amines such as TMEDA (*N*,*N*,*N*',*N*'-tetramethylethylenediamine) and DIPEA (*N*,*N*-diisopropylethylamine) were used in this reaction, furnishing **2a** in 30% and 40% yields, respectively (Table S1, entries 5 and 6). The use of inorganic base K_2CO_3 as additive failed to afford **2a**, indicating that aminoalkyl radical generated from alkyl amine played the key role in this XAT promoted intramolecular cyclization reaction (Table S1, entry 7). The evaluation of solvent effects displayed that DME

(1,2-dimethoxyethane) was the solvent of choice, providing the desired product **2a** in 72% yield (Table S1, entries 8-13). Decreasing the amount of Et_3N to 2.0 equivalents (Table S1, entry 15) or increasing to 10.0 equivalents (Table S1, entry 14) were both conducive, however, giving **2a** in lower yield. The control experiments demonstrated that the reaction cannot proceed in the absence of photocatalyst, light source irradiation or Et_3N (Table S1, entries 16-18).

Table S2 Screening of optimal photocatalyst



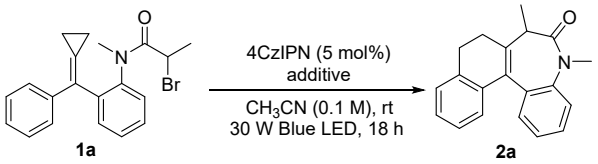
1a **2a**

entry[a]	Photocatalyst	E ($PC^{\bullet+}$/PC*)	E (PC/$PC^{\bullet-}$)	**2a** yield[e] (%)
1	4CzIPN	-1.04 V	-1.21 V	65
2	$[Ir[dF(CF_3)ppy]_2(dtbpy)]PF_6$	-0.89 V	-1.37 V	55
3	$[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$	-0.92 V	-1.44 V	23
4	$[Ru(bpy)_3](PF_6)_2$	-0.81 V	-1.33 V	38
5	$[Ir[dF(CF_3)ppy]_2(bpy)]PF_6$	-1.00 V	-1.37 V	36
6	Fluorescein[d]	-1.55 V	-1.22 V	44
7	$Ir(ppy)_3$	-1.73 V	-2.19 V	50
8	$[Ir(dtbbpy)(ppy)_2]PF_6$	-0.96 V	-1.51 V	42
9	$[Ir(dF(CF_3)ppy)_2(5,5'\text{-}CF_3bpy)]PF_6$	-0.69 V	-0.43 V	29
10[b]	4CzIPN	-1.04 V	-1.21 V	63
11[c]	4CzIPN	-1.04 V	-1.21 V	62

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), photocatalyst (0.005 mmol, 5.0 mol%) and Et_3N (0.4 mmol, 4.0 equiv) were placed in a reaction tube and Ar was charged. Then 0.5 mL solvent was added and the mixture was stirred exposing to blue LED light (30 W) at room temperature for 18 h. [b]15 W Blue LED was used. [c]The reaction time is 24 h. [d]The value of redox potentials here taken that of Fluorescein Na salt due to 4.0 equivalents of Et_3N were used. [e]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzen as an internal standard.

In this intramolecular cyclization reaction, all the photocatalysts used can provide the final product. However, when comparing the reduction potentials of **1a** (E_{red} = -1.57 V *vs* SCE, see Cyclic Voltammetry Experiments below) with the involved photocatalysts except for $Ir(ppy)_3$ (entry 7), the direct SET (single electron transfer) process could not proceed between the photocatalyst and the substrata **1a**. This result indicates that the mechanism of the cascade reaction involves a XAT (halogen atom transfer) process, which is in accordance with the previously reported conclusion.[1] All the data of reduction potentials in the excited and reduced state of photocatalyst are referred to the previous literature.[2-7]

Table S3 Screening of optimal additive

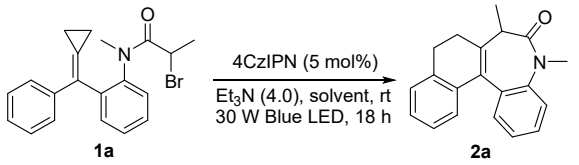


1a **2a**

[a]entry	additive (equiv)	yield[b] (%)
1	K_2CO_3 (2.0)	NR
2	DABCO (2.0)	NR
3	pyridine (4.0)	trace
4	TBAF (4.0)	NR
5	DIPA (4.0)	49
6	DIPEA (4.0)	40
7	TMEDA (4.0)	30
8	Et_3N (2.0)	61
9	Et_3N (4.0)	65
10	Et_3N (6.0)	63
11	Et_3N (10.0)	42

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), 4CzIPN (0.005 mmol, 5.0 mol%) and additive were placed in a reaction tube and Ar was charged. Then 0.5 mL solvent was added and the mixture was stirred exposing to blue LED light (30 W) at room temperature for 18 h. [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

Table S4 Screening of optimal solvent

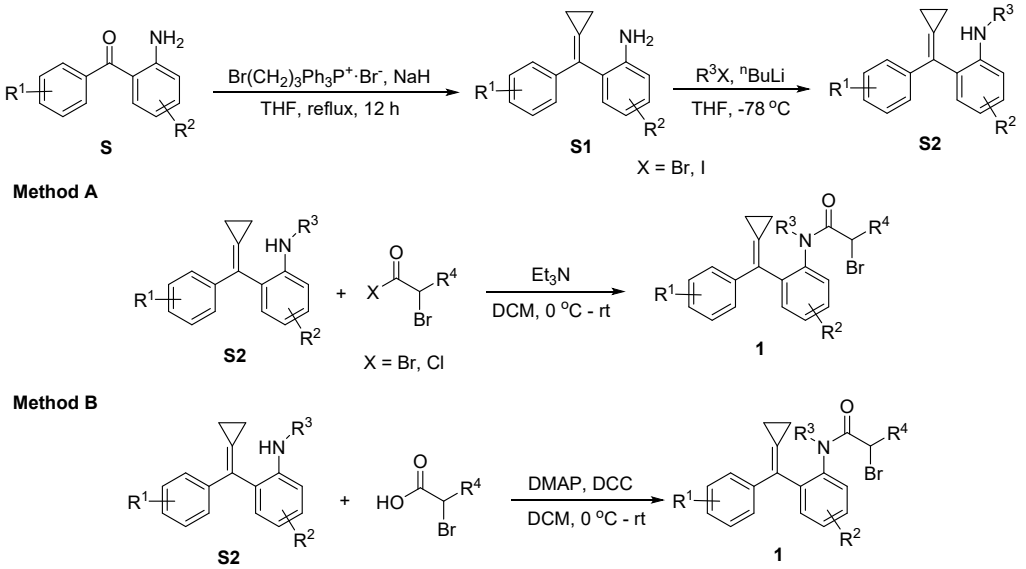


1a **2a**

entry[a]	solvent	**2a** yield[c] (%)
1	DCM	33
2	DMSO	32
3	DCE	51
4	Dioxane	58
5	EtOAc	52
6	THF	69
7	acetone	55
8	Et_2O	40
9	**DME**	**72(62)[d]**
10	EtOH	42
11[b]	DME	71

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), 4CzIPN (0.005 mmol, 5.0 mol%) and Et_3N (0.4 mmol, 4.0 equiv) were placed in a reaction tube and Ar was charged. Then 0.5 mL solvent was added and the mixture was stirred exposing to blue LED light (30 W) at room temperature for 18 h. [b]6.0 equiv Et_3N instead. [c]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard. [d]Isolated yield on 0.2 mmol

3. General Procedure for the Synthesis of Substrates 1.



Compound **S1** and procedure for the synthesis of substrates **1** was modified according to the previous literature.[8]

A solution of 3-bromopropyltriphenylphosphonium bromide (5.57 g, 13 mmol) and NaH (60% in oil, 0.96 g, 24 mmol) in THF (30 mL) was stirred at 65 °C in an oil bath under Ar for 4 h. Afterwards compound **S** (10 mmol) in THF (10 mL) was added and the reaction solution was stirred at 65 °C in an oil bath for another 8 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 40/1) to afford the products **S1** in moderate yields.

A solution of compound **S1** (2.0 mmol) in THF (20 mL) was stirred at -78 °C under Ar, ^{n}BuLi (2.0 mmol) was added dropwise for 20 min by a syringe pump. Upon completion, the reaction system continued to be stirred at -78 °C for another 20 minutes, then R^3X was injected in one portion and the temperature of the reaction system gradually was warmed to room temperature. The reaction was quenched by water after 2 h and extracted with EtOAc for 3 times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the compounds **S2** in high yields.

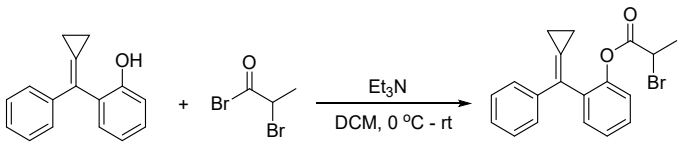
Method A

A solution of compound **S2** (1.0 equiv) in DCM (10 mL) was stirred at 0 °C in an ice bath under Ar. Then Et_3N (1.5 equiv) and the corresponding acyl chloride or acyl bromide (1.2 equiv) were added respectively. The reaction system was warmed to room temperature 1 h later and the mixture was reacted for another 2 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the substrates **1a - 1v**, **1x** and **1y** in high yields.

Method B

A solution of compound **S2** (2.0 mmol), the corresponding carboxylic acid (2.0 mmol) and 4-dimethylaminopyridine (0.1 mmol) in DCM (10 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (2.2 mmol) in DCM (5 mL) was added dropwise for 15 min. The reaction system was warmed to room temperature and stirred overnight. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10/1) to afford the products **1z**, **1aa** and **1ac** - **1af** in moderate to high yields.

Synthesis of substrate 1w



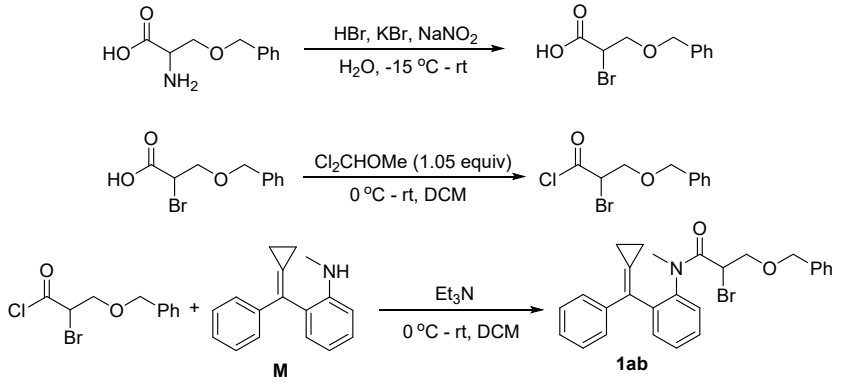
S3 **1w**

Compound **S3** was prepared from (2-hydroxyphenyl)(phenyl)methanone and the procedure was the same as the way mentioned above.

A solution of compound **S3** (1.0 equiv) in DCM (10 mL) was stirred at 0 °C in an ice bath under Ar. Then Et_3N (1.5 equiv) and the corresponding acyl bromide (1.2 equiv) were added respectively. The reaction system was warmed to room temperature after 1 h later and the reaction mixture was stirred for another 2 h. The solvent was removed under reduced pressure

and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the substrate **1w** (580 mg, 81% yield).

Synthesis of substrate 1ab

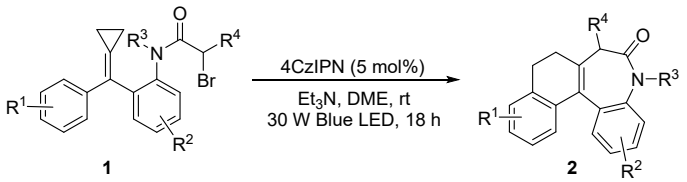


A solution of *O*-benzylserine (1.95 g, 10.0 mmol, 1.0 equiv), HBr (48% solution, 2.5 mL) and KBr (4.04 g, 34 mmol, 3.4 equiv) in water (10 mL) was stirred at -15 °C for 10 min. Then the solution of $NaNO_2$ (0.86 g, 12.5 mmol, 1.25 equiv) in water (5 mL) was added dropwise for 20 min by a syringe pump. After the addition, the reaction system was slowly warmed up to room temperature and the reaction mixture was stirred for another 3 hours. Upon completion, the solution was extracted with Et_2O for three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford 3-(benzyloxy)-2-bromopropanoic acid (2.26 g, 8.7 mmol, 87% yield) as a pale yellow oil, which was used for the next reaction without further purification.[9]

To an oven dried 50 mL round-bottom flask equipped with a magnetic stir bar, 3-(benzyloxy)-2-bromopropanoic acid (518 mg, 2.0 mmol, 1.0 equiv) and DCM (5 mL) were added and the mixture was stirred in an ice bath for 10 min, Cl_2CHOMe (0.19 mL, 2.1 mmol, 1.05 equiv) was injected into the solution slowly and was stirred for another 1 h.[10] Afterwards, the mixture was transferred into the solution of compound **M** (471 mg, 2.0 mmol, 1.0 equiv) and Et_3N (3.0 mmol, 1.5 equiv) in DCM and the resulting mixture was stirred overnight. The reaction was quenched by water and extracted with DCM for 3 times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed

under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the substrate **1ab** (423 mg, 44% yield).

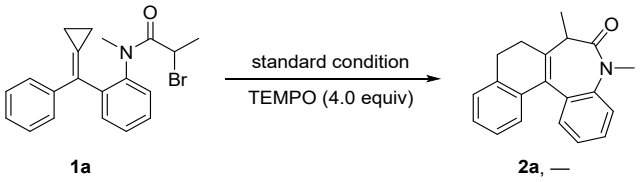
4. General Procedure for the Synthesis of Products 2.



In an flame dried Schlenk tube (20 mL) equipped with a magnetic stir bar, substrate **1** (0.2 mmol) and photocatalyst 4CzIPN (0.01 mmol, 5 mol%) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Et_3N (0.8 mmol, 4.0 equiv) and degassed DME (2.0 mL, 0.1 M) were injected into the tube sequentially. The mixture was placed 5 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, EtOAc (5 mL) was added into the tube to dilute the mixture.

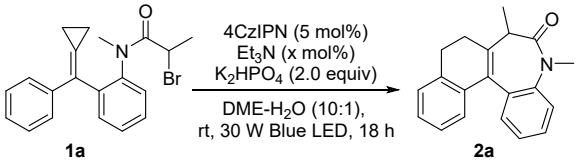
5. Mechanistic Studies

5.1 Radical Trapping Experiment



In an flame dried Schlenk tube (20 mL) equipped with a magnetic stir bar, substrate **1a** (0.2 mmol), photocatalyst 4CzIPN (0.01 mmol, 5 mol%) and TEMPO (0.8 mmol, 4.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Et_3N (0.8 mmol, 4.0 equiv) and degassed DME (2 mL, 0.1 M) were injected into the tube sequentially. The mixture was placed 5 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, 1,3,5-trimethoxybenzene (0.1 mmol, 0.5 equiv) as an internal standard was added into the tube, then EtOAc (5 mL) was added to dilute the mixture. The mixture was concentrated in *vacuo* and the yield of product **2a** was determined by ^1H NMR spectroscopy.

5.2 Sub-stoichiometry amount of Et_3N with additional base used Experiment



Et_3N (mol%)	yield (%)
200	62
20	58
5	57
—	—

In four Schlenk tubes (20 mL) equipped with magnetic stir bars, substrate **1a** (0.1 mmol), photocatalyst 4CzIPN (0.005 mmol, 5 mol%) and K_2HPO_4 (0.4 mmol, 4.0 equiv) were added into each tube. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then different amount of Et_3N (200 mol%), Et_3N (20 mol%), Et_3N (5 mol%), Et_3N (—) were added into tubes, respectively. Degassed DME (2 mL) and H_2O (0.2 mL) were injected into the tube sequentially. The mixture was placed 5 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard was added into the tube, then EtOAc (5

mL) was added to dilute the mixture. The mixture was concentrated in *vacuo* and the yield of product **2a** was determined by ^{1}H NMR spectroscopy.

For the catalytic use of Et_3N (5 mol%) combine with inorganic base, theoretically the final product should be obtained in a maximum yield of 15% if every molecular of Et_3N promoted XAT process up to 3. The final product was obtained in 57% yield under this condition, however, indicating other species responsible for cleavage of the C-halogen bond existed in the reaction. Additionally, the requirement of simultaneous oxidation of 4CzIPN$^{-\cdot}$ and the intermediate **III** (see proposed mechanism in scheme 6) would generate the redox imbalance. Hence, a radical chain process should exist in the reaction, where α-aminoalkyl radicals acting as initiators.[11] Thus, the catalytic amount of Et_3N can initiate the reaction and the inorganic bases probably play as auxiliary bases for deprotonation of intermediate **IV** shown in Scheme 6. Besides, considering radical intermediate **III** was an electron-rich species and in a conjugated system, it probably underwent a XAT or SET event with substrate **1a** to afford **2a** along with the regeneration of intermediate **I**.

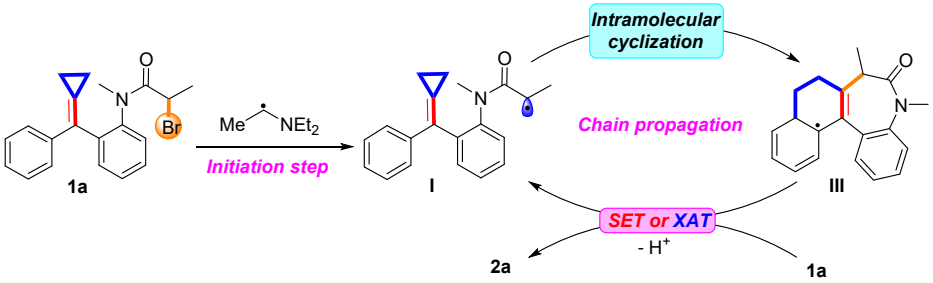


Figure S1. Proposed radical chain process.

5.3 Emission Quenching Studies[12]

All the emission intensities were recorded by Varian Cary Eclipse spectrometer. Solutions of 4CzIPN (2 x 10^{-5} M) in dry DME were excited at 372 nm and the emission intensity was collected at 527 - 528 nm. Solutions of different concentration of Et_3N and substrate **1i** (white solid, highest yield among all the substrates) were prepared respectively and introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum.

For the Et_3N: $y = 364.07x + 0.9983$, $R^2 = 0.9938$;

For the substrate **1i**: $y = 21.74x + 1.0025$, $R^2 = 0.9800$;

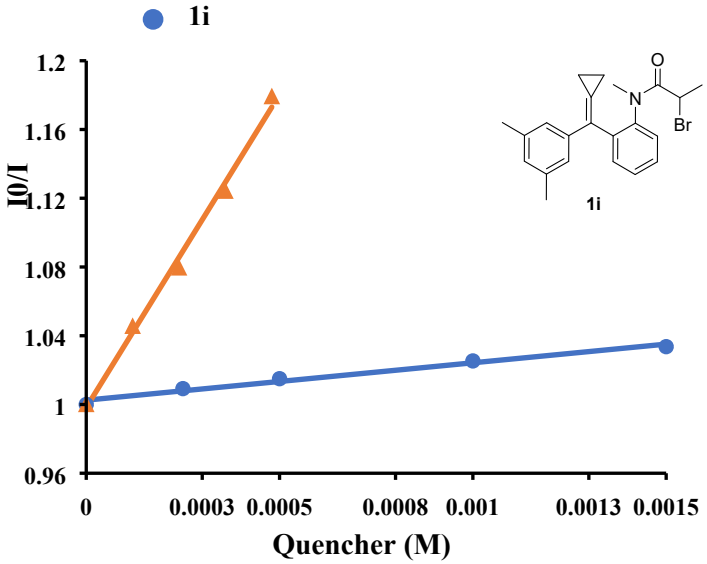


Figure S2.

5.4 Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CS350H. A solution of the substrate **1a** in MeCN (0.001 M) was tested with 0.1 M Bu_4NPF_6 as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and a saturated calomel electrode reference electrode. Ar was bubbled into the system for 20 min to degas the solution. Scan rate = 0.1 V/s, 2 sweep segments, a sample interval of 0.001 V.

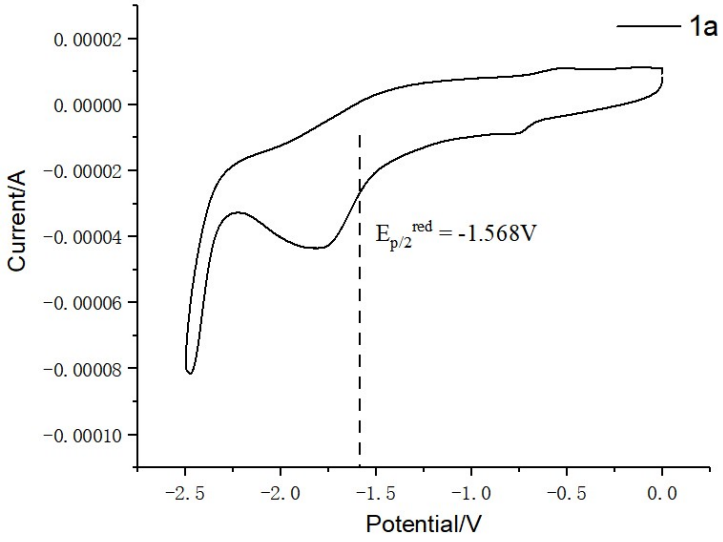
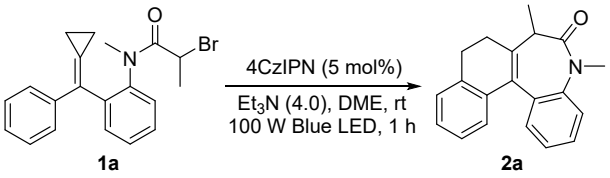


Figure S3.

5.5 Quantum Yield Determination [13]

To further investigate the mechanism of the reactions, we employed the model reaction of **1a** to **2a** to measure the quantum yield.



A cuvette equipped with a magnetic stir bar was added substrate **1a** (0.1 mmol), Et_3N (0.4 mmol) and dry 1,2-dimethoxyethane (2.0 mL). After which, 4CzIPN (0.005 mmol) was added at room temperature. The heterogeneous mixture was degassed by bubbling argon for 20 min and placed at a distance (app. 5 cm) from 100 W Blue LED for 1 h, The reaction mixture was concentrated in *vacuo* and analyzed by ^{1}H NMR spectrum using CH_2Br_2 as an internal standard. The quantum yield is calculated to be 0.26.

$$\phi = \frac{n_x}{n_p} = \frac{n_x}{\frac{\Delta E \times S \times t}{N_A h\upsilon}} = \frac{n_x \times N_A \times h \times c}{\Delta E \times S \times t \times \lambda}$$

$$= \frac{0.045 \times 10^{-3} mol \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} J{\cdot}s \times 2.998 \times 10^{8} m{\cdot}s^{-1}}{(7.0 \times 10^{-3} W{\cdot}cm^{-2} \times 2cm^2) \times 3600s \times 415 \times 10^{-9} m} = 0.26$$

n_x is the amount of photochemical or photophysical events x occurred during irradiation, n_p is the number of photons absorbed by the reactant. E is the radiant power. S is the irradiated area: 2 cm^2; t is the irradiated time: 3600 s; N_A is the Avogadro constant: 6.022×10^{23}/mol; h is the Planck constant: 6.626×10^{-34} J • s; v is the frequency of incident light; c is velocity of light 2.998×10^8 m/s). λ is the wavelength: 415 nm; n_x was analyzed by ^{1}H NMR, ΔE was measured by ILT1400 Portable Radiometer/Photometer.

The quantum yield expected to be > 1 in chain process, however, we still cannot exclude the possible radical chain mechanism of this reaction considering the factors of existence of inefficient initiation step or short-lived chains.[14]

6. Proposed Reaction Mechanisms

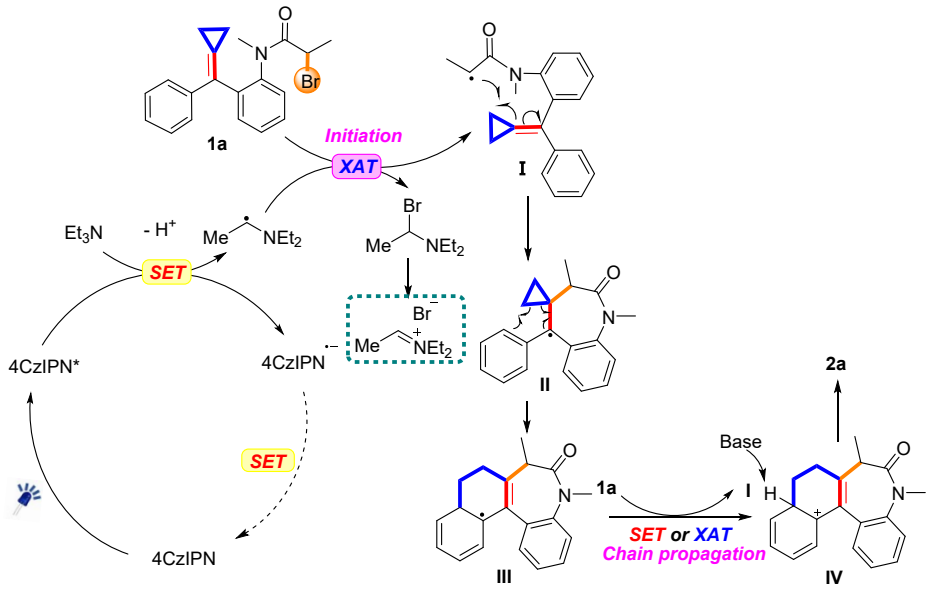


Figure S4. Proposed mechanism for the production of **2a**.

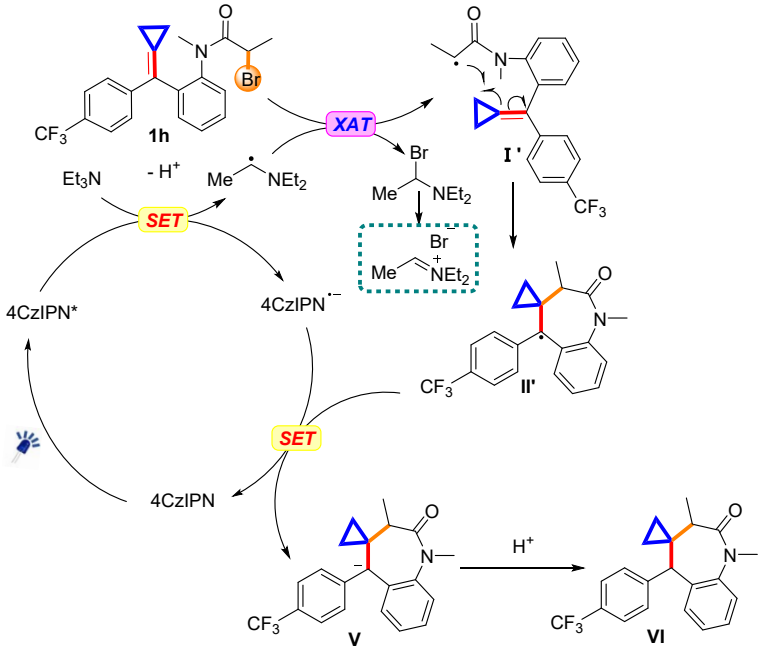
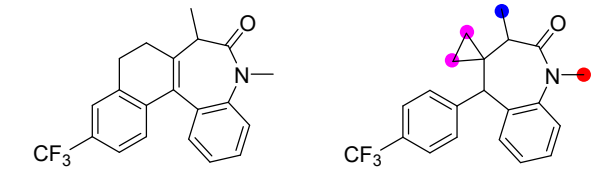


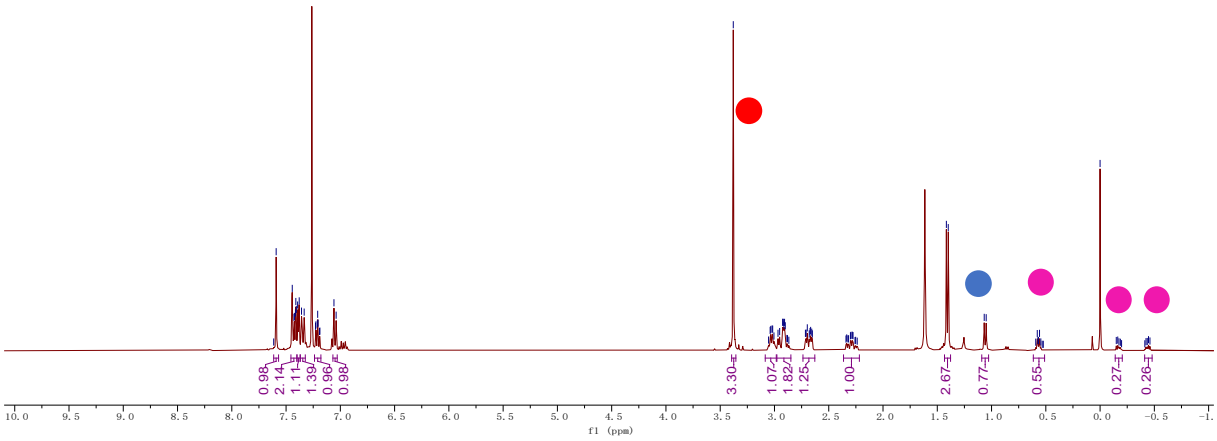
Figure S5. Proposed mechanism for the production of three-membered ring unopened by-product.

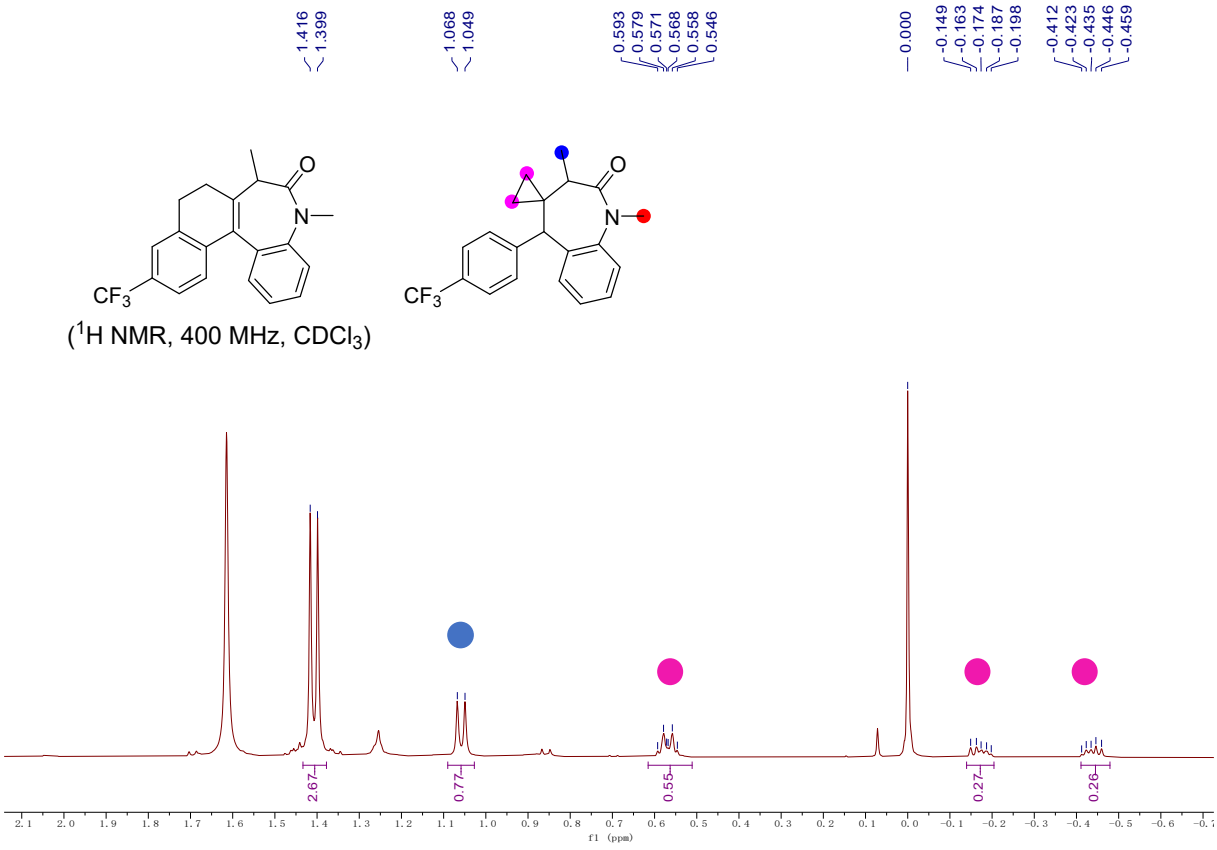
In this intramolecular radical cyclization, impurities with regular chemical shifts were found in the ^{1}H NMR (see spectra of **2h** and **2j** taken as examples shown below). We speculated it could be the three-membered ring unopened by-product and proposed a plausible mechanism for the by-product (Figure S5, substrate 1h was taken as an example). The intermediate **II** possibly underwent a SET event with 4CzIPN$^{\bullet-}$ to provide the anionic intermediate **V**, which

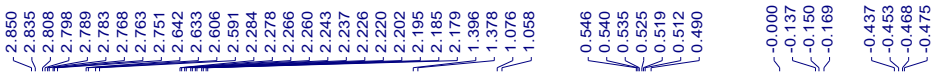
afforded the by-product **VI** via protonation. Notably, presumably due to the similar polarity and molecular weight, it was hard to separate these two kinds of compounds.

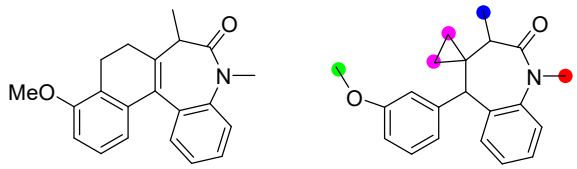


(^{1}H NMR, 400 MHz, $CDCl_3$)

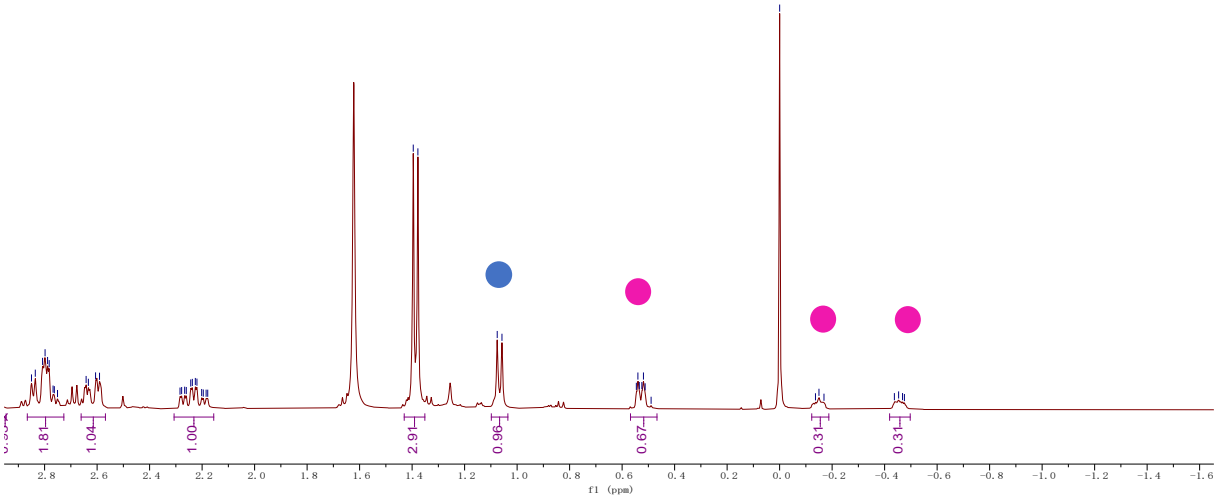



1.416
1.399
1.068
1.049
0.593
0.579
0.571
0.568
0.558
0.546
0.000
-0.149
-0.163
-0.174
-0.187
-0.198
-0.412
-0.423
-0.435
-0.446
-0.459
O
N
CF3
O
N
CF3
(1H NMR, 400 MHz, CDCl3)
2.67
0.77
0.55
0.27
0.26
f1 (ppm)
7.484
7.464
7.370
7.366
7.346
7.330
7.325
7.217
7.203
7.187
7.166
7.129
7.109
7.048
7.028
6.710
6.703
6.689
6.683
6.538
6.531
3.791
3.699
3.370
3.361
3.006
3.000
2.988
2.982
2.970
2.850
2.835
2.808
2.798
2.789
2.783
2.768
2.763
2.642
2.633
2.606
2.591
2.284
2.278
2.266
2.260
2.243
2.237
2.226
2.220
2.202
2.195
2.185
1.396
1.378
1.076
1.058
0.546
0.540
0.535
0.525
0.519
0.512
-0.000
-0.150
O
N
MeO
O
N
O
(1H NMR, 400 MHz, CDCl3)
0.95
1.42
1.11
0.88
0.99
0.85
0.82
0.95
2.61
2.77
0.93
1.81
1.04
1.00
2.91
0.96
0.67
0.31
0.31
f1 (ppm)

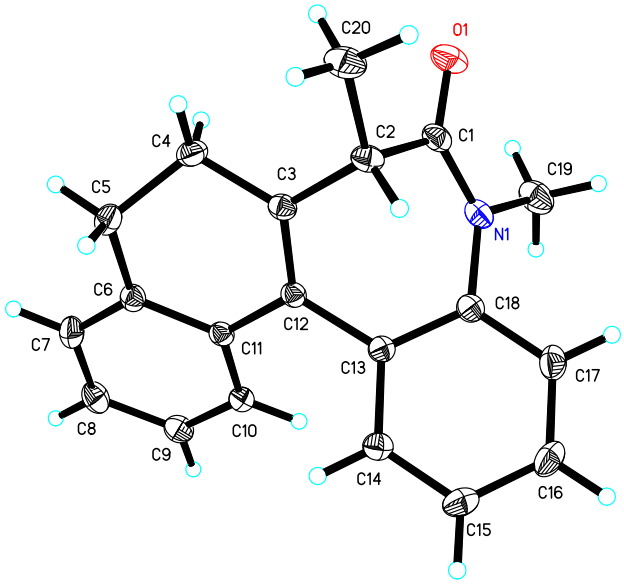




(^{1}H NMR, 400 MHz, $CDCl_3$)



7. X-ray data.



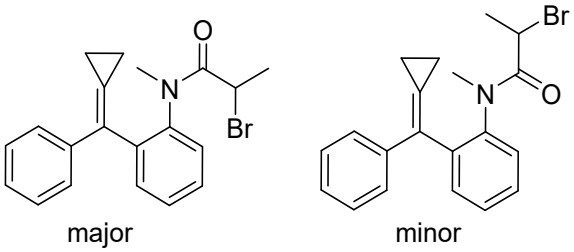
Single crystals of **2a** were grown in EtOH and hexanes. EtOH (2.0 mL) was added to **2a** (29 mg in a 4 mL vial) followed by hexanes (0.5 mL). The 4 mL vial was capped with a needle and placed at room temperature in the experimental cabinet for 2 weeks, whereupon the crystals were formed.

The crystal data of **2a** have been deposited in CCDC with number 2082928. Empirical Formula: $C_{20}H_{19}NO$; Formula Weight: 289.36; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.150 x 0.130mm; Crystal System: Orthorhombic; Lattice Parameters: a = 9.2952(3)Å, b = 15.1908(6)Å, c = 21.6017(8)Å, α = 90°, β = 90°, γ = 90°, V = 3050.19(19)Å^3; Space group: P b c a; Z = 8; D_{calc}= 1.260 g/cm^3; F_{000} = 1232; Final R induces [I>2sigma(I)]: R1 = 0.0370; wR2 = 0.0909.

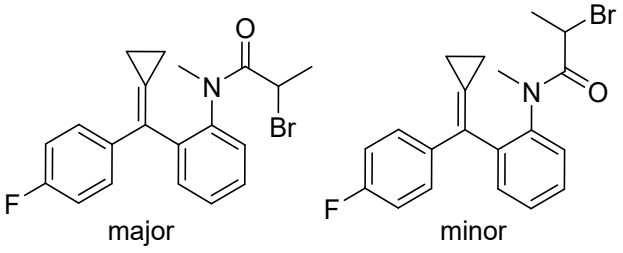
Table S5. Crystal data and structure refinement for 2a.

Empirical formula	$C_{20}H_{19}NO$	
Formula weight	289.36	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 9.2952(3) Å	α= 90°.
	b = 15.1908(6) Å	β= 90°.
	c = 21.6017(8) Å	γ = 90°.
Volume	3050.19(19) $Å^3$	
Z	8	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	1232	
Crystal size	0.200 x 0.150 x 0.130 mm^3	
Theta range for data collection	2.737 to 25.998°.	
Index ranges	-11<=h<=11, -18<=k<=16, -26<=l<=23	
Reflections collected	14282	
Independent reflections	2976 [R(int) = 0.0275]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6646	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2976 / 0 / 202	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0909	
R indices (all data)	R1 = 0.0447, wR2 = 0.0970	
Extinction coefficient	0.019(2)	
Largest diff. peak and hole	0.215 and -0.160 $e.Å^{-3}$	

8. Characterization Data of Substrates

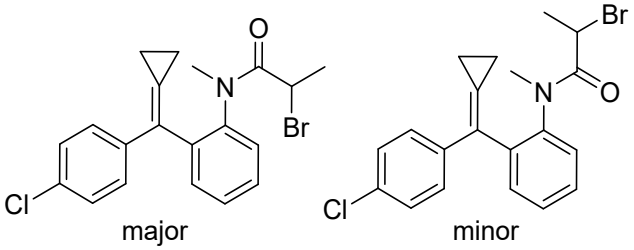


2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-4methylpropanamide (1a): A white solid, 570 mg, 75% yield, major : minor = 6.7 : 1. M.p.: 177-178 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 - 7.43 (m, 4H), 7.31 - 7.27 (m, 2H), 7.23 - 7.19 (m, 3H), 4.31 (q, *J* = 7.0 Hz, 1H, *minor isomer*) & 4.05 (q, *J* = 6.7 Hz, 1H), 2.71 (s, 3H, *minor isomer*) & 2.63 (s, 3H), 1.72 (d, *J* = 7.0 Hz, 3H, *minor isomer*), 1.52 - 1.48 (m, 1H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.33 - 1.24 (m, 2H), 1.13 - 1.05 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 170.7 & 169.2 (*minor isomer*), 141.7 (*minor isomer*) & 141.4, 141.1 (*minor isomer*), 140.7 (*minor isomer*), 140.1, 140.0, 132.3, 131.8, 129.1, 128.7, 128.6, 128.4, 128.2, 127.7, 127.6, 127.3, 127.1, 126.7, 126.6 (there are multiple peaks between 132.3 - 126.6 due to rotamers), 39.3 (*minor isomer*) & 37.5, 25.4 (*minor isomer*)& 23.1, 19.0 (*minor isomer*) & 15.3, 4.8 & 4.5 (*minor isomer*), 2.7 (*minor isomer*) & 2.0; IR(EtOH): ν 3055, 2971, 2935, 1731, 1659, 1488, 1446, 1376, 1074, 766, 753, 698 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{20}NONaBr$ 392.0620; found 392.0619.

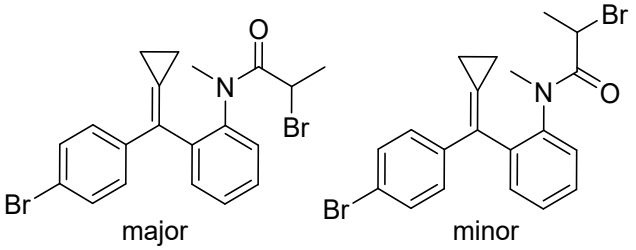


2-bromo-*N*-(2-(cyclopropylidene(4-fluorophenyl)methyl)phenyl)-*N*-methylpropanamide (1b): A white solid, 545 mg, 70% yield, major : minor = 5 : 1. M.p.: 147-149 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50 - 7.40 (m, 4H), 7.20 - 7.14 (m, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 4.29 (q, *J* = 7.0 Hz, 1H, *minor isomer*) & 4.04 (q, *J* = 6.7 Hz, 1H), 2.63 (s, 3H) & 2.50 (s, 3H, *minor isomer*), 1.72 (d, *J* = 7.1 Hz, 3H, *minor isomer*) & 1.51 (d, *J*

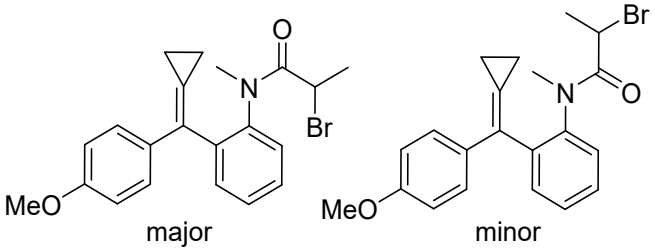
= 6.7 Hz, 3H), 1.48 - 1.45 (m, 2H), 1.32 - 1.28 (m, 1H), 1.13 - 1.05 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.6 (*minor isomer*) &169.2, 161.9 (d, *J* = 246.1 Hz), 141.0, 139.6, 136.1 (d, *J* = 3.5 Hz), 132.1, 131.6, 129.2, 128.8, 128.4, 128.2 (d, *J* = 8.3 Hz), 127.6, 126.7, 115.3 (d, *J* = 21.3 Hz), 115.2, 42.5 (*minor isomer*) & 39.0, 37.28 & 37.25 (*minor isomer*), 23.3 (*minor isomer*) & 20.9, 4.7 & 4.4 (*minor isomer*), 2.5 (minor isomer) & 2.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -114.6 & -115.0 (*minor isomer*); IR (acetone) ν 3039, 2966, 2919, 1654, 1593, 1506, 1484, 1446, 1379, 1221, 1155, 1094, 829, 805, 773, 749 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{20}NOFBr$ 388.0706; found 388.0711.



2-bromo-*N*-(2-((4-chlorophenyl)(cyclopropylidene)methyl)phenyl)-*N*-methylpropanamide (1c): A white solid, 572 mg, 71% yield, major : minor = 3.3 : 1. M.p.: 152-154 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$,TMS) δ 7.51 - 7.45 (m, 2H), 7.45 - 7.40 (m, 2H), 7.25 - 7.19 (m, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 4.23 (q, *J* = 6.8 Hz, 1H, *minor isomer*) & 3.97 (q, *J* = 6.6 Hz, 1H), 2.71 (s, 3H) & 2.55 (s, 3H, *minor isomer*), 1.57 (d, *J* = 6.9 Hz, 3H, *minor isomer*) 1.48 (t, *J* = 7.2 Hz, 2H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.28 (t, *J* = 6.8 Hz, 1H), 1.17 - 1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.7 (*minor isomer*) & 169.2, 141.2 (*minor isomer*) & 141.1, 139.9 (*minor isomer*) & 139.4, 139.1 (*minor isomer*) & 138.5, 133.1, 132.8, 132.1, 131.7, 129.7, 129.3, 128.8, 128.5, 128.45, 128.42, 128.3, 127.9, 127.7, 127.6, 126.9 (there are multiple peaks between 133.1 - 126.9 due to rotamers), 42.4 (*minor isomer*) & 39.0, 37.4, 23.3 (*minor isomer*) & 20.9, 4.8 & 4.5 (*minor isomer*), 2.5 (*minor isomer*) & 2.2; IR (EtOH): ν 2973, 2921, 1666, 1489, 1448, 1381, 1091, 1044, 879, 821, 757 cm^{-1}; HRMS(ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{19}NONaClBr$ 426.0230; found 426.0237.

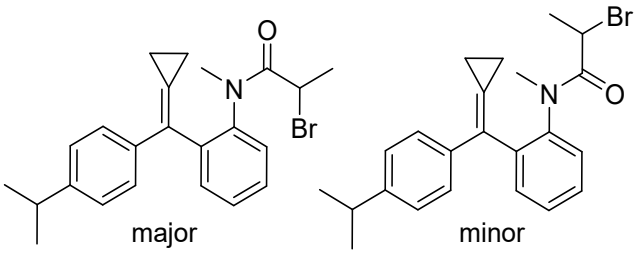


2-bromo-*N*-(2-((4-bromophenyl)(cyclopropylidene)methyl)phenyl)-*N*-methylpropanamide (1d): A yellow solid, 645 mg, 72% yield, major : minor = 3.7 : 1. M.p.: 131-133 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 - 7.45 (m, 2H), 7.44 - 7.39 (m, 4H), 7.08 (d, *J* = 8.5 Hz, 2H), 4.22 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.97 (q, *J* = 6.6 Hz, 1H), 2.71 (s, 3H) & 2.55 (s, 3H, *minor isomer*), 1.56 (d, *J* = 6.8 Hz, 3H, *minor isomer*) 1.51 - 1.44 (m, 2H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.33 - 1.27 (m, 1H), 1.16 - 1.07 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.2, 141.1, 139.3, 139.0, 131.7, 131.5, 131.4, 129.3, 128.8, 128.7, 128.5, 128.3, 127.8, 127.7, 121.2, 42.4 (*minor isomer*) & 39.0, 37.4, 20.3(*minor isomer*) & 20.9, 4.8 & 4.6 (*minor isomer*), 2.6 (*minor isomer*) & 2.2; IR (EtOH): ν 2971, 2924, 1666, 1486, 1447, 1382, 1089, 1045, 879, 771, 756 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{19}NONaBr_2$ 469.9725; found 469.9714.

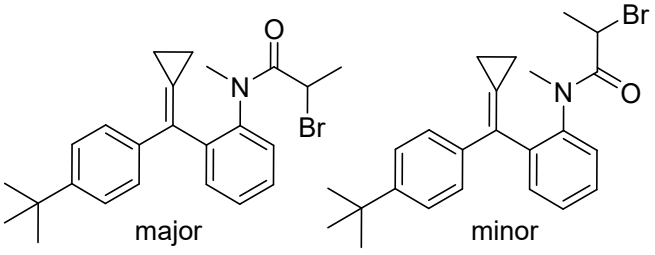


2-bromo-*N*-(2-(cyclopropylidene(4-methoxyphenyl)methyl)phenyl)-*N*-methylpropanamide (1e): A yellow solid, 640 mg, 80% yield, major : minor = 5 : 1. M.p.: 133-135 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 - 7.39 (m, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.83 - 6.77 (m, 2H), 4.25 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 4.00 (q, *J* = 6.6 Hz, 1H), 3.79 (s, 3H, *minor isomer*) & 3.78 (s, 3H), 2.73 (s, 3H) & 2.55 (s, 3H, *minor isomer*), 1.57 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.46 (t, *J* = 8.4 Hz, 2H), 1.32 (d, *J* = 6.6 Hz, 3H), 1.28 - 1.20 (m, 1H), 1.12 - 1.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.6 (*minor isomer*) & 169.2, 158.8 & 158.7 (*minor isomer*), 141.3 (*minor isomer*) & 141.1,

140.6 (*minor isomer*) & 140.1, 133.2 (*minor isomer*) & 132.6, 132.1 (*minor isomer*) & 131.7, 128.9, 128.6, 128.4, 128.2, 128.0, 127.8, 127.6, 124.8, 113.7, 55.2, 42.6 (*minor isomer*) & 39.3, 37.4, 23.3 (*minor isomer*) & 21.0, 4.6 & 4.4 (*minor isomer*), 2.3 (*minor isomer*) & 2.0; IR (EtOH): ν 2971, 2927, 1654, 1509, 1446, 1385, 1300, 1245, 1167, 1029, 825, 790, 777 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{22}NO_2NaBr$ 422.0726; found 422.0719.

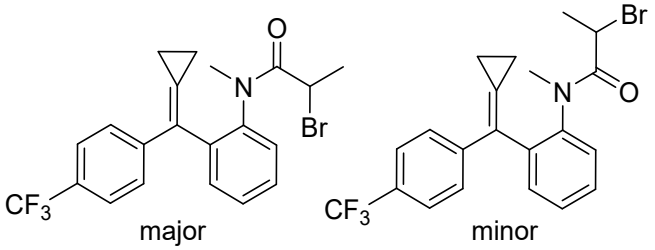


2-bromo-*N*-(2-(cyclopropylidene(4-isopropylphenyl)methyl)phenyl)-*N*-methylpropanamide (1f): A yellow oil, 580 mg, 70% yield, major : minor = 8.3 : 1. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 - 7.44 (m, 3H), 7.43 - 7.39 (m, 1H), 7.13 (s, 4H), 4.31 (q, *J* = 7.0 Hz, 1H, *minor isomer*) & 4.02 (q, *J* = 6.7 Hz, 1H), 2.90 - 2.81 (m, 1H), 2.67 (s, 3H) & 2.47 (s, 3H, *minor isomer*), 1.48 (t, *J* = 7.2 Hz, 2H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.24 - 1.22 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.11 - 1.03 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$,TMS,) δ 170.7, 148.1, 141.4, 140.3, 137.4, 131.8, 129.0, 128.6, 128.5, 127.8, 126.7, 126.4, 125.6, 37.6, 33.8, 24.0, 23.9, 23.2, 15.6, 4.8, 2.0; IR (acetone): ν 2959, 2919, 2861, 1659, 1589, 1485, 1446, 1372, 1099, 1060, 843, 826, 762 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{27}NOBr$ 412.1270; found 412.1279.

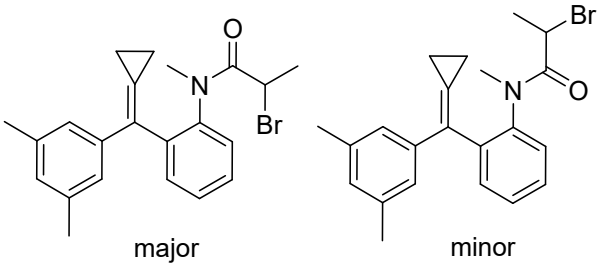


2-bromo-*N*-(2-((4-(tert-butyl)phenyl)(cyclopropylidene)methyl)phenyl)-*N*-methylpropanamide (1g): A white solid, 632 mg, 74% yield, major : minor = 5 : 1. M.p.: 97-99 °C. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.46 (d, *J* = 2.7 Hz, 3H),

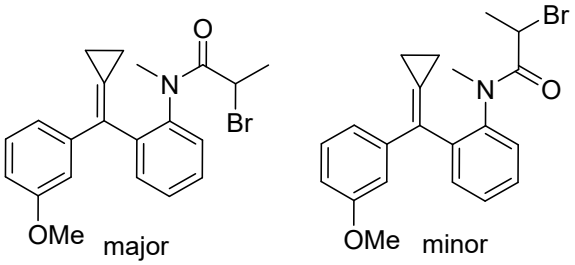
7.43 - 7.40 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 4.01 (q, *J* = 6.7 Hz, 1H) & 3.95 (q, *J* = 6.5 Hz, 1H, *minor isomer*), 2.76 (s, 3H, *minor isomer*) & 2.68 (s, 3H), 1.72 (d, *J* = 7.0 Hz, 3H, *minor isomer*), 1.48 (t, *J* = 7.5 Hz, 2H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.27 (s, 9H), 1.23 - 1.15 (m, 1H), 1.13 - 1.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, *major isomer*) δ 170.6, 150.3, 141.3, 140.2, 136.9, 131.8, 128.9, 128.6, 128.2, 127.7, 126.3, 125.6, 125.2, 37.5, 34.4, 31.2, 23.1, 15.5, 4.7, 1.9; IR (EtOH): ν 2963, 2866, 1640, 1486, 1447, 1384, 1267, 1088, 1045, 837, 758 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{29}NOBr$ 426.1427; found 426.1421.



2-bromo-*N*-(2-(cyclopropylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-*N*-methylpropanamide (1h): A white solid, 530 mg, 61% yield, major : minor = 3.4 : 1. M.p.: 101-103 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, *major isomer*) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.53 - 7.47 (m, 2H), 7.49 - 7.41 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.23 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.96 (q, *J* = 6.6 Hz, 1H), 2.69 (s, 3H) & 2.51 (s, 3H, *minor isomer*), 1.57 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.53 (td, *J* = 7.0, 3.7 Hz, 2H), 1.39 - 1.34 (m, 1H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.22 - 1.11 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.3, 143.6, 141.1, 139.1, 131.8, 129.54, 129.50, 129.3 (q, *J* = 33.2 Hz), 128.9, 128.6, 127.3, 126.9, 125.4 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 271.3 Hz), 42.3 (*minor isomer*) & 38.9, 37.4, 23.3 (*minor isomer*) & 20.9, 4.9 & 4.7 (*minor isomer*), 2.7 (*minor isomer*) & 2.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.4 (*minor isomer*) & -62.5; IR (acetone): ν 3060, 2976, 2919, 1666, 1615, 1487, 1445, 1373, 1311, 1217, 1163, 1119, 1068, 1015, 848, 770, 753 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}NOF_3Br$ 438.0674; found 438.0679.

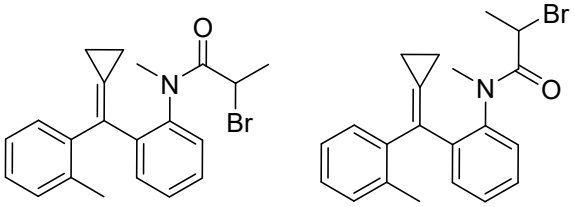


2-bromo-*N*-(2-(cyclopropylidene(3,5-dimethylphenyl)methyl)phenyl)-*N*-methylpropanamide (1i): A white solid, 625 mg, 75% yield, major : minor = 5 : 1. M.p.: 112-114 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.52- 7.38 (m, 4H), 6.89- 6.83 (m, 1H), 6.82 - 6.79 (m, 2H), 4.23 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.96 (q, *J* = 6.5 Hz, 1H), 2.76 (s, 3H) & 2.54 (s, 1H, *minor isomer*), 2.26 (s, 6H, *minor isomer*) & 2.24 (s, 6H), 1.57 (d, *J* = 6.8 Hz, 3H, *minor isomer*), 1.51 - 1.46 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.21 (td, *J* = 9.2, 6.0 Hz, 1H), 1.09 (td, *J* = 9.2, 6.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.2, 141.1, 140.1, 139.7, 137.8, 131.8, 129.0, 128.9, 128.6, 128.3, 126.1, 124.4, 39.4, 37.3, 21.3, 20.8, 4.9, 2.0; IR (EtOH) ν 2971, 2911, 1667, 1598, 1485, 1447, 1373, 1270, 1044, 769, 701, 655 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{24}NONaBr$ 420.0933; found 420.0925.



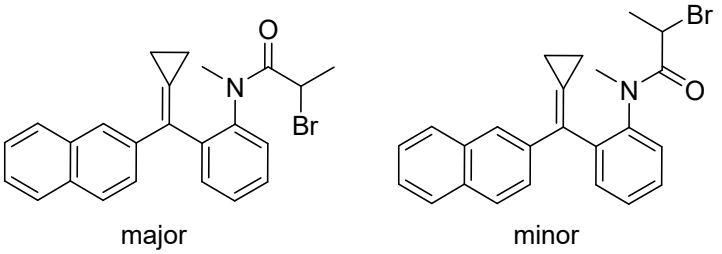
2-bromo-*N*-(2-(cyclopropylidene(3-methoxyphenyl)methyl)phenyl)-*N*-methylpropanamide (1j): A yellow oil, 620 mg, 77% yield, major : minor = 7 : 1. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48 - 7.39 (m, 4H), 7.23 - 7.16 (m, 1H), 6.83 - 6.73 (m, 3H), 4.25 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 4.00 (q, *J* = 6.6 Hz, 1H), 3.77 (s, 3H, *minor isomer*) & 3.75 (s, 3H), 2.76 (s, 3H) & 2.55 (s, 3H, *minor isomer*), 1.57 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.54 - 1.47 (m, 2H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.27 - 1.20 (m, 1H), 1.15 - 1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, *major isomer*) δ 169.6 (*minor isomer*)

& 169.2, 159.44 & 159.37 (*minor isomer*), 141.9 (*minor isomer*) & 141.3, 141.0, 140.3 (*minor isomer*) & 139.7, 132.0 (*minor isomer*) & 131.7, 129.3, 129.0, 128.6, 128.33, 128.30, 126.8, 126.2, 119.7 (*minor isomer*) & 119.3, 112.9 (*minor isomer*) & 112.8, 112.5 (*minor isomer*) & 112.1, 55.1, 42.5 (*minor isomer*) & 39.3, 37.3 & 37.2 (*minor isomer*), 23.2 (*minor isomer*) & 20.9, 4.8 & 4.5 (*minor isomer*), 2.4 (*minor isomer*) & 2.0; IR (acetone) ν 2974, 2924, 2832, 1665, 1596, 1577, 1486, 1447, 1425, 1361, 1259, 1221, 1164, 1045, 977, 773, 746, 689 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}NO_2Br$ 400.0906; found 400.0912.

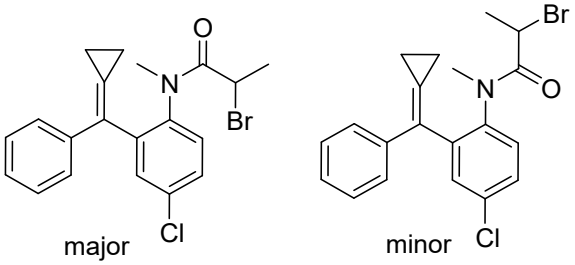


major minor

2-bromo-*N*-(2-(cyclopropylidene(o-tolyl)methyl)phenyl)-*N*-methylpropanamide (1k): A brown oil, 546 mg, 71% yield, major : minor = 3 : 1. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.50 - 7.36 (m, 2H), 7.31 (dt, *J* = 7.7, 2.8 Hz, 1H), 7.17 - 7.09 (m, 3H), 7.00 (dd, *J* = 5.6, 3.5 Hz, 1H), 4.20 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.88 (q, *J* = 6.6 Hz, 1H), 2.52 (s, 3H) & 2.25 (s, 1H, *minor isomer*), 2.06 (s, 3H) & 2.03 (s, 3H, *minor isomer*), 1.26 - 1.17 (m, 1H), 1.55 (d, *J* = 6.9 Hz, 3H, *minor isomer*) 1.45 - 1.33 (m, 5H), 1.32 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.4 (*minor isomer*) & 168.9, 141.6 (*minor isomer*) & 141.2, 140.7 (*minor isomer*) & 140.6, 139.9 (*minor isomer*) & 139.5, 135.8 (*minor isomer*) & 135.7, 132.3 (*minor isomer*) & 132.0, 130.7, 130.2, 129.9, 129.3, 129.1, 128.74, 128.68, 127.4, 126.1(*minor isomer*) & 125.5, 41.7 (*minor isomer*) & 39.3, 36.4 & 36.1 (*minor isomer*), 23.1 (*minor isomer*), 21.1, 20.8, 4.9 & 4.3 (*minor isomer*), 3.5 (*minor isomer*) & 3.3; IR (neat) ν 2974, 2923, 1669, 1483, 1444, 1414, 1372, 1108, 1064, 762, 737, 724 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{22}NONaBr$ 406.0777; found 406.0781.

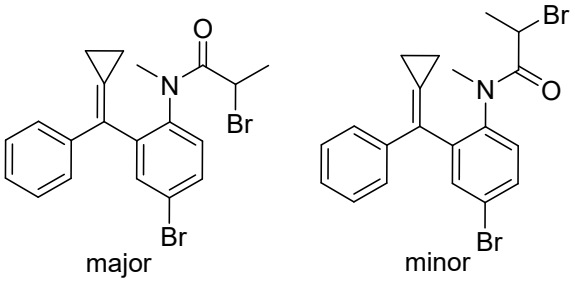


2-bromo-*N*-(2-(cyclopropylidene(naphthalen-2-yl)methyl)phenyl)-*N*-methylpropanamide (1l): A white solid, 630 mg, 75% yield, major : minor = 4 : 1. M.p.: 195-197 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.70 - 7.66 (m, 1H), 7.56 - 7.48 (m, 4H), 7.45 (d, *J* = 10.2 Hz, 2H), 7.41 (dd, *J* = 6.3, 3.3 Hz, 2H), 4.29 (q, *J* = 6.8 Hz, 1H, *minor isomer*) & 4.02 (q, *J* = 6.5 Hz, 1H), 2.67 (s, 3H) & 2.41 (s, 3H, *minor isomer*), 1.60 - 1.54 (m, 2H), 1.46 - 1.25 (m, 2H), 1.16 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.8 (*minor isomer*) & 169.3, 141.3, 140.0, 137.5, 133.2, 132.6, 131.9, 129.2, 128.8, 128.7, 128.6, 128.3, 128.0, 127.7, 127.4, 126.3, 126.0, 125.4, 124.9, 42.6 (*minor isomer*) & 39.3, 37.5, 23.3 (*minor isomer*) & 21.0, 5.1, 2.2; IR (neat) ν 3055, 2971, 2914, 1666, 1596, 1487, 1447, 1422, 1383, 1269 1062, 817, 774, 749 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{22}NONaBr$ 442.0777; found 442.0781.

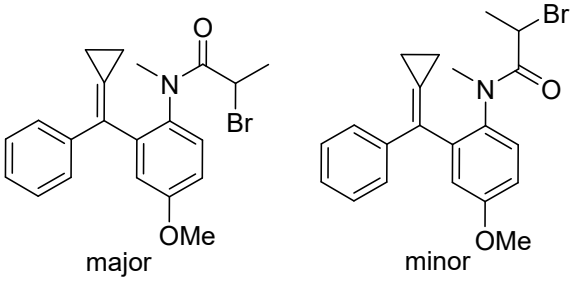


2-bromo-*N*-(4-chloro-2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylpropanamide (1m): A pale yellow oil, 612 mg, 76% yield, major : minor = 5 : 1. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (dq, *J* = 5.5, 2.5 Hz, 2H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.26 - 7.18 (m, 3H), 4.22 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.93 (q, *J* = 6.6 Hz, 1H), 2.67 (s, 3H) & 2.44 (s, 3H, *minor isomer*), 1.56 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.50 (t, *J* = 7.9 Hz, 2H), 1.38 - 1.31 (m, 1H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.21 - 1.10 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.1, 141.8, 139.7, 139.4, 134.4, 131.6, 129.9, 129.2, 128.6, 127.6, 126.7, 39.0, 37.2, 20.9, 4.8, 2.3; IR (EtOH) ν 2972,

2918, 2867, 1655, 1483, 1445, 1400, 1375, 1274, 1090, 1047, 880, 775, 748, 696 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{19}NONaClBr$ 426.0230; found 426.0232.

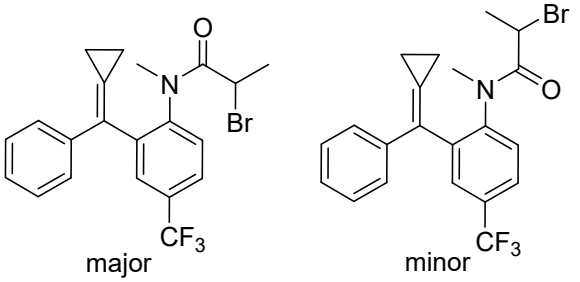


2-bromo-*N*-(4-bromo-2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylpropanamide (1n): A light yellow solid, 580 mg, 64% yield, major : minor = 5 : 1. M.p.: 141-143 °C. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 - 7.56 (m, 2H), 7.34 - 7.27 (m, 3H), 7.25 - 7.17 (m, 3H), 4.21 (q, *J* = 6.8 Hz, 1H, *minor isomer*) & 3.93 (q, *J* = 6.5 Hz, 1H), 2.67 (s, 3H) & 2.44 (s, 3H, *minor isomer*), 1.57 (d, *J* = 6.9 Hz, 1H, *minor isomer*), 1.50 (t, *J* = 7.9 Hz, 2H), 1.39 - 1.31 (m, 1H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.21 - 1.10 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.2, 142.0, 140.2, 139.4, 134.5, 132.2, 130.1, 128.6, 127.9, 127.6, 126.7, 122.5, 39.0, 37.3, 20.9, 4.8, 2.3; IR (neat) ν 3057, 2968, 1666, 1480, 1424, 1397, 1373, 1277, 1114, 1079, 908, 825, 769, 728, 697 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{20}NOBr_2$ 447.9906; found 447.9915.

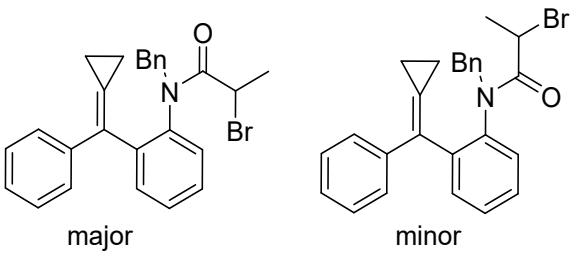


2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)-4-methoxyphenyl)-*N*-methylpropanamide (1o): A light yellow solid, 542 mg, 67% yield, major : minor = 4 : 1. M.p.: 134-135 °C. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35 - 7.32 (m, 1H), 7.31 - 7.27 (m, 2H), 7.25 - 7.20 (m, 3H), 7.00 - 6.94 (m, 2H), 4.28 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 4.00 (q, *J* = 6.6 Hz, 1H), 3.89 (s, 3H), 2.67 (s, 3H) & 2.44 (s, 3H, *minor isomer*), 1.57 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.49 (t, *J* = 7.6 Hz, 2H), 1.30 - 1.27 (m, 1H),

1.26 (d, J = 6.5 Hz, 3H), 1.13 (dt, J = 9.0, 7.5 Hz, 1H) ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.7, 159.3, 141.2, 139.8, 133.9, 129.4, 128.6, 128.4, 128.3, 127.4, 127.2, 126.7, 126.6, 117.2, 113.6, 55.6, 42.4, 39.3, 37.5, 21.0, 4.8, 2.2; IR (neat) ν 2959, 2909, 1664, 1597, 1493, 1462, 1445, 1370, 1297, 1236, 1173, 1034, 822, 803, 766, 700 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}NOBr$ 400.0912; found 400.0913.

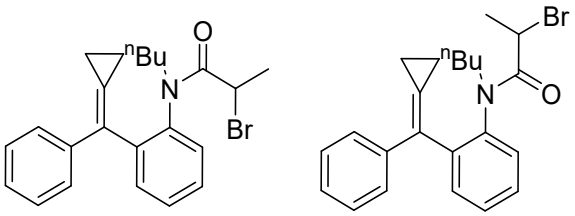


2-bromo-N-(2-(cyclopropylidene(phenyl)methyl)-4-(trifluoromethyl)phenyl)-N-methylpropanamide (1p): A light green solid, 320 mg, 37% yield, major : minor = 5 : 1. M.p.: 107-109 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.33 - 7.23 (m, 3H), 7.18 (d, J = 6.9 Hz, 2H), 4.17 (q, J = 6.9 Hz, 1H, *minor isomer*) & 3.90 (q, J = 6.5 Hz, 1H), 2.71 (s, 3H) & 2.49 (s, 3H, *minor isomer*), 1.57 (d, J = 6.9 Hz, 3H, *minor isomer*), 1.53 (t, J = 8.0 Hz, 2H), 1.40 - 1.32 (m, 1H), 1.30 (d, J = 6.6 Hz, 3H), 1.22 - 1.11 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 168.8, 144.2, 140.9, 139.2, 130.8 (q, J = 32.4 Hz), 129.1, 128.6 (q, J = 4.1 Hz), 128.5, 128.3, 127.6, 127.0, 126.6, 126.0 (q, J = 4.1 Hz), 123.6 (q, J = 270.9 Hz), 38.9, 37.1, 20.8, 4.8, 2.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.37 & -62.43 (*minor isomer*); IR(neat): 2978, 1667, 1612, 1496, 1426, 1376, 1206, 1123, 1080, 975, 793, 762, 670; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{19}NOF_3NaBr$ 460.0494; found 460.0493.



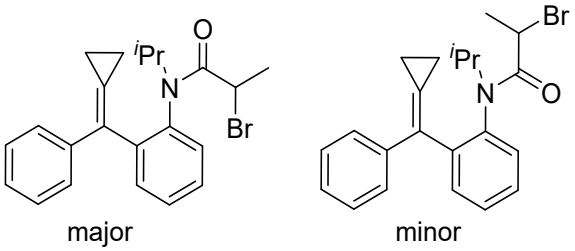
***N*-benzyl-2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)propanamide(1q)**: A

light green solid, 680 mg, 75% yield, major : minor = 6.7 : 1. M.p.: 191-193 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.46 - 7.41 (m, 2H), 7.37 - 7.28 (m, 4H), 7.26 - 7.21 (m, 5H), 7.13 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 14.6 Hz, 1H) & 4.80 (d, *J* = 14.6 Hz, 1H, *minor isomer*), 4.25 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.94 (q, *J* = 6.6 Hz, 1H), 3.34 (d, *J* = 14.7 Hz, 1H) & 2.98 (d, *J* = 14.7 Hz, 1H, *minor isomer*), 1.59 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.56 - 1.46 (m, 2H), 1.33 - 1.27 (m, 1H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.17 (td, *J* = 9.2, 6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.4 (*minor isomer*) & 169.0, 140.3 (*minor isomer*), 140.1 (*minor isomer*), 139.8, 139.6, 139.3 (*minor isomer*) & 138.9, 136.9, 132.0 (*minor isomer*) & 131.5, 129.4, 128.5, 128.21, 128.17, 128.0, 127.1, 126.9, 126.6, 126.5, 51.3, 42.9 (*minor isomer*) & 39.1, 23.1 (*minor isomer*) & 20.6, 4.4 & 4.2 (*minor isomer*), 2.2 (*minor isomer*) & 2.0; IR(EtOH): ν 3057, 3026, 2974, 2929, 1664, 1485, 1447, 1397, 1174, 1042, 765, 749, 697 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}NONaBr$ 468.0933; found 468.0939.

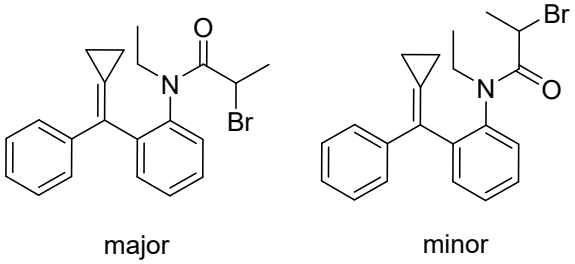


2-bromo-*N*-butyl-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)propenamide (1r): A pale yellow oil, 672 mg, 83% yield, major : minor = 8 : 1. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 - 7.39 (m, 4H), 7.30 - 7.26 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 3H), 4.21 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.85 (q, *J* = 6.5 Hz, 1H), 3.66 - 3.63 (m, 1H) & 3.27 – 3.12 (m, 1H, *minor isomer*), 2.48 - 2.45 (m, 1H) & 2.24 – 2.17 (m, 1H, *minor isomer*), 1.61 (d, *J* = 6.9 Hz, 3H, *minor isomer*) 1.59 - 1.50 (m, 2H), 1.49 - 1.43 (m, 1H), 1.43 - 1.31 (m, 2H), 1.27 - 1.17 (m, 2H), 1.15 (d, *J* = 6.5 Hz, 3H), 1.14 - 1.09 (m, 1H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 168.9, 140.1, 140.0, 139.9, 132.1, 129.5, 128.7, 128.52, 128.46, 127.3, 126.7, 48.9, 40.3, 29.1, 21.0, 20.1, 13.8, 4.8, 2.3; IR (EtOH): ν 2974, 2929, 2866, 1663, 1486, 1446, 1403, 1372, 1267, 1078, 1046, 880, 765, 753 cm^{-1}; HRMS

(ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{26}NONaBr$ 434.1090; found 434.1085.

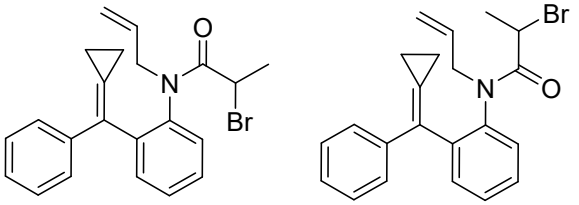


2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-isopropylpropanamide (1s): A yellow oil, 580mg, 73% yield, major : minor = 10 : 1. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50 - 7.38 (m, 4H), 7.31 - 7.27 (m, 1H), 7.26 - 7.18 (m, 4H), 4.15 (q, *J* = 6.8 Hz, 1H, *minor isomer*) & 3.74 (q, *J* = 6.5 Hz, 1H), 3.70 - 3.60 (m, 1H) & 3.37 (m, 1H, *minor isomer*), 1.58 (d, *J* = 6.6 Hz, 3H, *minor isomer*), 1.56 - 1.38 (m, 2H), 1.17 (dd, *J* = 8.9, 6.4 Hz, 2H), 1.11 (t, *J* = 6.7 Hz, 6H), 1.01 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 168.9, 140.22, 140.19, 140.1, 132.3, 129.7, 128.6, 128.5, 128.4, 127.2, 126.9, 54.4, 42.1, 21.1, 20.4, 18.8, 4.8, 2.4; IR (EtOH) ν 3052, 3974, 2922, 1658, 1594, 1485, 1445, 1424, 1373, 1349, 1281, 1059, 981, 907, 764, 727, 696, 679 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{24}NONaBr$ 420.0933; found 420.0936.



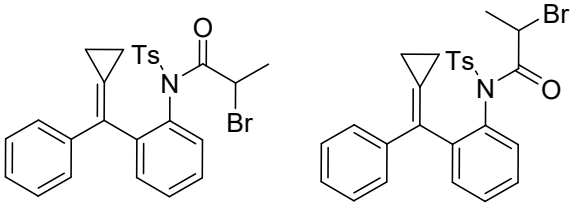
2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-ethylpropanamide (1t): A yellow oil, 465 mg, 55% yield, major : minor = 5 : 1. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51 - 7.41 (m, 4H), 7.26 (t, *J* = 3.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 3H), 4.20 (q, *J* = 6.9 Hz, 1H, *minor isomer*) & 3.85 (q, *J* = 6.5 Hz, 1H), 3.65 (dq, *J* = 14.2, 7.1 Hz, 1H) & 3.26 (dq, *J* = 14.2, 7.1 Hz, 1H, *minor isomer*), 2.52 (dq, *J* = 14.1, 7.1 Hz, 1H) & 2.34 - 2.24 (m, 1H, *minor isomer*), 1.55 - 1.40 (m, 2H), 1.21 (dd, *J* = 9.2, 5.8 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.15 - 1.09 (m, 1H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS,)

δ 168.7, 140.1, 140.0, 139.9, 132.0, 129.4, 128.7, 128.6, 128.5, 127.3, 126.7, 44.2, 40.2, 21.0, 12.2, 4.7, 2.2; IR (neat) ν 3060, 2968, 2931, 1662, 1486, 1446, 1401, 1372, 1260, 764, 733, 696 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}NOBr$ 384.0957; found 384.0959.



major minor

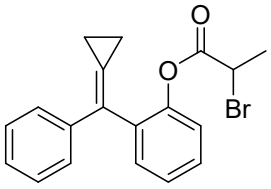
***N*-allyl-2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)propenamide (1u)**: A yellow oil, 380 mg, 48% yield, major : minor = 6 : 1. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, *major isomer*) δ 7.50 - 7.41 (m, 4H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 3H), 5.85 - 5.73 (m, 1H), 5.13 - 5.02 (m, 2H) & 4.98 – 4.90 (m, 2H, *minor isomer*), 4.24 (q, *J* = 6.9 Hz, 1H, *minor isomer*), 4.20 - 4.10 (m, 1H), 3.94 (q, *J* = 6.5 Hz, 1H), 3.88 - 3.81 (m, 1H, *minor isomer*), 2.95 (dd, *J* = 15.1, 7.3 Hz, 1H) & 2.67 (dd, *J* = 15.0, 8.0 Hz, 1H, *minor isomer*), 1.58 (d, *J* = 6.9 Hz, 3H, *minor isomer*), 1.51-1.47 (m, 2H), 1.32 - 1.20 (m, 4H), 1.18 - 1.07 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS, *major isomer*) δ 168.9, 140.1, 140.0, 139.9, 132.5, 131.8, 129.4, 128.8, 128.6, 128.5, 127.4, 126.9, 126.8, 117.5, 51.9, 39.8, 20.8, 4.8, 2.2; IR (neat) ν 3066, 2973, 2917, 1661, 1486, 1447, 1396, 907, 755, 727, 697 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{22}NONaBr$ 418.0777; found 418.0774.



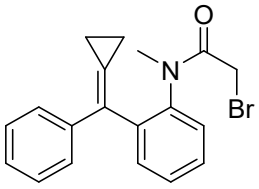
major minor

2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-tosylpropanamide (1v): A white solid, 572 mg, 56% yield, major : minor = 6 : 1. M.p.: 188-190 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.70 - 7.59 (m, 2H), 7.58 - 7.52 (m, 2H), 7.40 - 7.35 (m, 2H), 7.31 (dd, *J* = 7.9, 2.6 Hz, 4H), 7.22 - 7.17 (m, 1H), 3.50

(q, *J* = 6.5 Hz, 1H) & 3.22 (q, *J* = 7.2 Hz, 1H, *minor isomer*), 2.43 (d, *J* = 3.9 Hz, 3H), 1.69 - 1.63 (m, 1H), 1.51 -1.42 (m, 1H), 1.40- 1.33 (m, 1H), 1.23 - 1.14 (m, 1H), 0.72 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.1, 144.9, 144.5, 143.3, 139.8, 135.6, 133.8, 132.8, 132.1, 130.7, 130.5, 129.6, 129.3, 129.2, 128.7, 128.5, 128.1, 127.2, 127.1, 126.8, 126.1, 40.3, 21.7, 19.6, 6.2 (*minor isomer*) & 4.4, 2.9 & 1.3 (*minor isomer*); IR (EtOH) ν 2976, 2927, 1696, 1440, 1358, 1173, 1147, 1086, 1046, 874, 812, 757, 696 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}NO_3NaSBr$ 532.0552; found 532.0544.

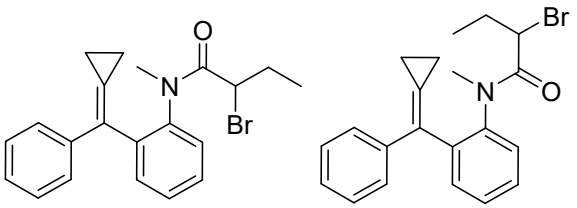


2-(cyclopropylidene(phenyl)methyl)phenyl 2-bromopropanoate (1w): A yellow oil, 580 mg, 81% yield. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 - 7.36 (m, 4H), 7.34 - 7.29 (m, 1H), 7.26 (s, 2H), 7.23 - 7.18 (m, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 4.01 (q, *J* = 6.9 Hz, 1H), 1.61 - 1.56 (m, 1H), 1.54 (d, *J* = 6.3 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.30 - 1.17 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 168.1, 148.1, 139.8, 133.9, 131.6, 128.4, 128.2, 126.9, 126.7, 126.4, 122.2, 39.6, 21.2, 5.4, 2.1; IR (EtOH) ν 2977, 2935, 1747, 1641, 1442, 1336, 1215, 1185, 1140, 1073, 1045, 905, 878, 843, 767, 745 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{17}BrO_2Na$ 379.0306; found 379.0308.



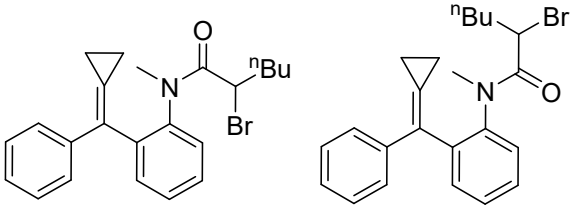
2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylacetamide (1x): A white solid, 563 mg, 79% yield. M.p.: 125-127 °C, Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48 - 7.40 (m, 3H), 7.33 - 7.19 (m, 6H), 3.52 (d, *J* = 11.3 Hz, 1H), 3.32 (d, *J* = 11.2 Hz, 1H), 2.72 (s, 3H), 1.58-1.45 (m, 2H), 1.26-1.19 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 166.2, 141.4, 140.2, 139.7, 132.1, 129.0, 128.8, 128.4, 128.1, 127.4, 126.9,

37.1, 27.6, 4.8, 2.3; IR (EtOH) ν 3052, 2966, 1665, 1593, 1484, 1445, 1433, 1379, 1300, 1099, 1074, 1047, 898, 773, 764, 753, 697 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{18}NONaBr$ 378.0464; found 378.0466.



major minor

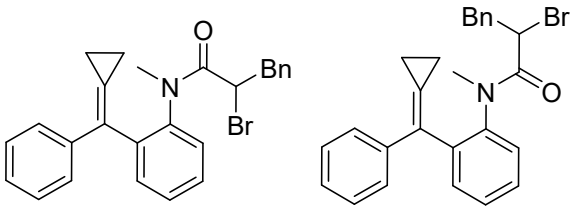
2-bromo-N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methylbutanamide (1y): A white solid, 620 mg, 81% yield, major : minor = 3 : 1. M.p.: 180-182 °C. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 - 7.43 (m, 4H), 7.28 (s, 2H), 7.22 - 7.19 (m, 3H), 4.05 (t, *J* = 7.1 Hz, 1H, *minor isomer*), 3.71 (dd, *J* = 10.0, 4.3 Hz, 1H), 2.72 (s, 3H) & 2.49 (s, 3H, *minor isomer*), 1.90 - 1.76 (m, 2H), 1.49 (t, *J* = 7.8 Hz, 2H), 1.40 - 1.22 (m, 2H), 1.21 - 1.06 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS,) δ 168.9, 141.2 (*minor isomer*) & 141.0, 140.6 (*minor isomer*), 140.5 (*minor isomer*), 140.1, 139.8, 132.0 (*minor isomer*) & 131.8, 128.9, 128.73, 128.70, 128.6, 128.5, 128.3, 128.1, 128.0, 127.2, 127.0, 126.8, 126.8, 126.6 (there are multiple peaks between 128.9 - 126.6 due to rotamers), 49.4 (*minor isomer*) & 48.0, 37.4 & 37.1 (*minor isomer*), 29.8 (*minor isomer*) & 27.1, 12.1 (*minor isomer*) & 11.7, 4.6 & 4.4 (*minor isomer*), 2.4 (*minor isomer*) & 2.2; IR (EtOH) ν 3055, 2972, 2930, 1661, 1596, 1486, 1446, 1424, 1384, 1340, 1302, 1076, 903, 765, 729, 696 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{22}NONaBr$ 406.0777; found 406.0782.



major minor

2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylhexanamide (1z): A

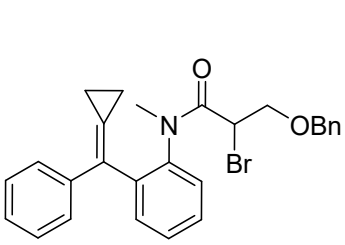
light yellow oil, 480 mg, 58% yield, major : minor = 2 : 1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, *major isomer*) δ 7.45 (t, *J* = 4.2 Hz, 3H), 7.30 - 7.27 (m, 3H), 7.23 - 7.20 (m, 3H), 4.13 (dd, *J* = 8.5, 5.8 Hz, 1H, *minor isomer*) & 3.75 (dd, *J* = 10.0, 4.3 Hz, 1H), 2.72 (s, 3H) & 2.49 (s, 3H, *minor isomer*), 1.90 - 1.70 (m, 2H), 1.48 (t, *J* = 8.1 Hz, 2H), 1.36 - 1.27 (m, 2H), 1.21 - 1.15 (m, 2H), 1.14 - 1.05 (m, 2H), 0.86 (t, *J* = 7.1 Hz, 3H) & 0.74 (t, *J* = 7.1 Hz, 3H, *minor isomer*); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 169.1, 141.0, 140.2, 139.8, 132.1 (*minor isomer*) & 131.9, 129.0, 128.9, 128.8, 128.71, 128.66, 128.4, 128.2, 128.1, 127.3, 127.2, 127.1, 127.0, 126.7 (there are multiple peaks between 129.0 - 126.7 due to rotamers), 48.2 (*minor isomer*) & 46.6, 37.6 & 37.2 (*minor isomer*), 35.8 (*minor isomer*) & 33.9, 29.6 & 29.2 (*minor isomer*), 22.4 & 21.5 (*minor isomer*), 14.0 & 13.7 (*minor isomer*), 4.7 & 4.5 (*minor isomer*), 2.45 & 2.37 (*minor isomer*); IR (neat) ν 2956, 2929 2870, 1660, 1596, 1486, 1446, 1385, 1103, 908, 765, 751, 696 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{26}NONaBr$ 434.1090; found 434.1088.



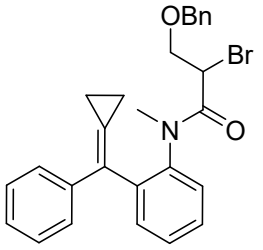
major minor

2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methyl-3-phenylpropanamide (1aa): A white solid, 565 mg, 63% yield, major : minor = 5 : 3. M.p.: 213-215 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48 - 7.41 (m, 3H), 7.25 - 7.20 (m, 6H), 7.08 - 7.02 (m, 2H), 6.87 (d, *J* = 6.5 Hz, 2H), 5.87 (d, *J* = 7.9 Hz, 1H), 4.20 (dd, *J* = 8.9, 6.6 Hz, 1H) & 4.06 (dd, *J* = 9.4, 5.1 Hz, 1H, *minor isomer*), 3.29 (dd, *J* = 13.3, 9.0 Hz, 1H) & 3.09 (dd, *J* = 15.1, 9.5 Hz, 1H, *minor isomer*), 2.96 (dd, *J* = 13.3, 6.5 Hz, 1H), 2.75 (s, 3H, *minor isomer*) & 2.35 (s, 3H), 1.33 - 1.28 (m, 2H), 1.27 - 1.18 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS, *major isomer*) δ 168.5 (*minor isomer*) & 168.3, 140.87 (*minor isomer*) & 140.85, 140.76 & 140.6 (*minor isomer*), 140.3 & 139.7 (*minor isomer*), 137.6 (*minor isomer*) & 137.2, 131.9 (*minor isomer*) & 131.6, 129.5, 129.4, 129.1, 129.0,

128.9, 128.73, 128.69, 128.5, 128.4, 128.28, 128.25, 128.19, 128.04, 128.01, 127.21, 127.15, 127.0, 126.9, 126.8 (there are multiple peaks between 129.5 - 126.8 due to rotamers), 46.7 & 45.4 (*minor isomer*), 43.1 & 39.9 (*minor isomer*), 37.8 (*minor isomer*) & 37.1, 4.5 (*minor isomer*) & 4.4, 2.7 (*minor isomer*) & 2.6; IR (neat) ν 3029, 2928, 2958, 1664, 1493, 1445, 1373, 1229, 902, 774, 752, 700, 665 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}NONaBr$ 468.0933; found 468.0925.

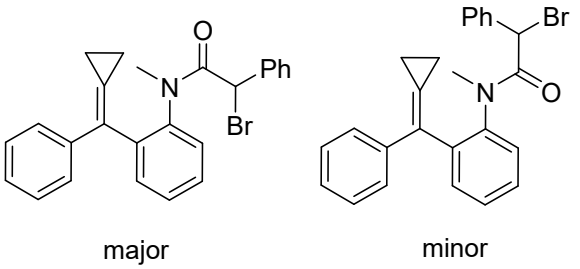


major



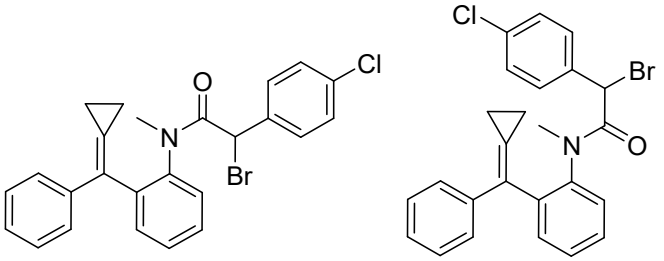
minor

3-(benzyloxy)-2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylpropanamide (1ab): A brown oil, 423 mg, 44% yield, major : minor = 3 : 1. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS, *major isomer*) δ 7.45 - 7.41 (m, 3H), 7.39 - 7.34 (m, 3H), 7.34 - 7.31 (m, 3H), 7.25 - 7.24 (m, 2H), 7.20 - 7.15 (m, 3H), 4.48 (s, 2H), 4.26 (dd, *J* = 8.4, 6.1 Hz, 1H, *minor isomer*), 4.01 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.80 (dd, *J* = 9.8, 8.5 Hz, 1H, *minor isomer*), 3.63 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.56 (dd, *J* = 9.8, 6.1 Hz, 1H, *minor isomer*), 3.29 (dd, *J* = 10.8, 4.9 Hz, 1H), 2.62 (s, 3H), 2.49 (s, 3H, *minor isomer*), 1.34 - 1.29 (m, 2H), 1.25 - 1.17 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS δ 167.4, 140.7, 140.4, 140.3, 137.5, 131.9, 129.0, 128.8, 128.6, 128.5, 128.4, 128.33, 128.26, 128.2, 128.1, 127.9, 127.8, 127.7, 127.2, 127.1, 126.9, 74.0 & 73.2 (*minor isomer*), 72.6 (*minor isomer*) & 71.3, 43.0 (*minor isomer*) & 42.8, 37.4 (*minor isomer*) & 37.0, 4.6 & 4.5 (*minor isomer*), 2.6 (*minor isomer*) & 2.1; IR (neat) ν 3074, 3024, 2920, 2867, 1769, 1659, 1452, 1112, 1075, 1027, 908, 729, 696 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{26}NO_2NaBr$ 498.1039; found 498.1037.



major minor

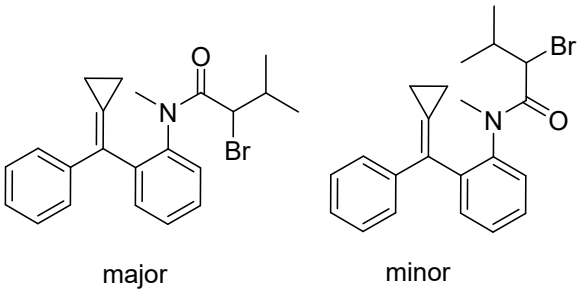
2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methyl-2-phenylacetamide (1ac): A white solid, 445 mg, 51% yield, major : minor = 5 : 3. M.p.: 213-215 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (d, *J* = 8.6 Hz, 1H), 7.50 - 7.41 (m, 2H), 7.32 (d, *J* = 4.3 Hz, 4H), 7.25 - 7.16 (m, 5H), 7.06 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 1H) & 5.22 (s, 1H, *minor isomer*), 2.70 (s, 3H, *minor isomer*) & 2.50 (s, 3H), 1.71 (td, *J* = 9.0, 5.5 Hz, 1H), 1.50 - 1.37 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 166.6, 141.0, 140.5, 140.3, 137.0, 131.9, 128.8, 128.75, 128.73, 128.6, 128.34, 128.30, 128.26, 128.1, 127.3, 127.1, 49.5, 37.3, 4.9, 2.3; IR (neat) ν 3065, 3026, 2974, 1663, 1596, 1485, 1446, 1373, 1103, 908, 765, 751, 726, 694 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{22}NONaBr$ 454.0777; found 454.0770.



major minor

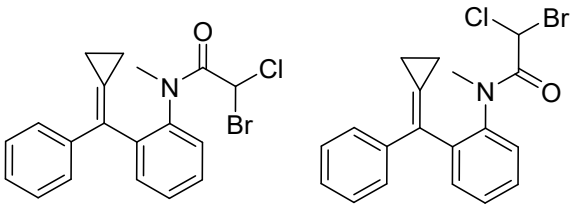
2-bromo-2-(4-chlorophenyl)-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylacetamide (1ad): A white solid, 380 mg, 40% yield, major : minor = 4 : 1. M.p.: 210-212 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, *major isomer*) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.50 - 7.42 (m, 2H), 7.31 (d, *J* = 6.1 Hz, 4H), 7.25 (s, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.25 (s, 1H) & 5.15 (s, 1H, *minor isomer*), 2.72 (s, 3H, *minor isomer*) & 2.49 (s, 3H), 1.75 - 1.66 (m, 1H), 1.52 - 1.40 (m, 2H), 1.32 - 1.23 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 166.3, 140.9, 140.41, 140.37, 135.6, 134.7, 132.0, 130.6, 129.6, 128.9, 128.83, 128.81, 128.7, 128.6, 128.4, 127.3, 127.1,

48.3, 37.3, 4.8, 2.3; IR (neat) ν 3066, 2973, 2931, 1664, 1488, 1373, 1091, 1015, 907, 832, 766, 750, 726, 696 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{21}NONaClBr$ 488.0387; found 488.0383.



major minor

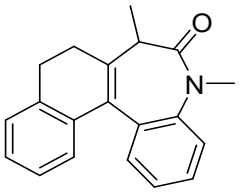
2-bromo-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*,3-dimethylbutanamide (1ae): A yellow oil, 326 mg, 41% yield, major : minor = 100 : 94. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.47 - 7.36 (m, 6H), 7.29 (d, *J* = 5.6 Hz, 5H), 7.24 - 7.17 (m, 4H), 7.09 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.94 (d, *J* = 7.3 Hz, 1H, *minor isomer*), 3.55 (d, *J* = 9.3 Hz, 1H), 2.60 (s, 3H), 2.48 (s, 3H, *minor isomer*), 2.18 - 2.04 (m, 1H, *minor isomer*), 1.96 (dq, *J* = 13.6, 6.7 Hz, 1H), 1.52 (td, *J* = 8.4, 7.8, 4.6 Hz, 1H), 1.46 - 1.38 (m, 2H), 1.35 (td, *J* = 8.2, 4.0 Hz, 2H), 1.25 - 1.20 (m, 1H), 1.19 - 1.11 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.69 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 168.9, 168.6 (*minor isomer*), 141.3 (*minor isomer*), 141.0, 140.7, 140.4, 139.9 (*minor isomer*), 132.1 (*minor isomer*), 132.0, 129.6, 129.2, 129.0, 128.9, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 127.3, 127.3, 127.1, 127.0, 126.9, 55.7 (*minor isomer*), 52.9, 37.8, 37.3 (*minor isomer*), 33.5 (*minor isomer*), 31.9, 20.7, 20.6 (*minor isomer*), 19.8 (*minor isomer*), 19.5, 4.6, 4.5 (*minor isomer*), 2.4 (*minor isomer*), 2.3; IR (neat) ν 2971, 2934, 2875, 1659, 1486, 1445, 1378, 909, 765, 751, 728, 696 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{24}NONaBr$ 420.0933; found 420.0934.



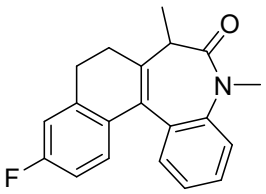
major minor

2-bromo-2-chloro-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-methylacetamide (1af): A white solid, 473 mg, 60% yield, major : minor = 2 : 1. M.p.: 163-165 ^{o}C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51 - 7.48 (m, 3H), 7.30 - 7.28 (m, 3H), 7.24 - 7.21 (m, 3H), 5.75 (s, 1H, *minor isomer*) & 5.69 (s, 1H), 2.58 (s, 3H), 1.47 - 1.36 (m, 2H), 1.31 - 1.23 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 164.1, 140.2, 140.0, 132.0, 129.4, 129.3, 128.45, 128.41, 128.0, 127.5, 127.0, 52.0 (*minor isomer*) & 50.4, 37.8 (*minor isomer*) & 37.7, 4.7, 2.4 (*minor isomer*) & 2.1; IR (neat) ν 3049, 2971, 1674, 1594, 1483, 1445, 1381, 1299, 1106, 794, 776, 766, 754, 698 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{17}NONaClBr$ 412.0074; found 412.0072.

9. Characterization Data of Products.

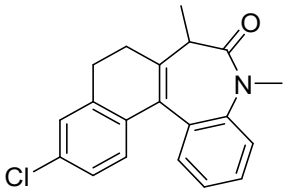


5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2a): A white solid, 36 mg, 62% yield. m.p.: 176-178 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.46 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 - 7.37 (m, 1H), 7.35 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.22 - 7.17 (m, 2H), 7.14 (td, *J* = 7.3, 1.4 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 6.2 Hz, 1H), 3.37 (s, 3H), 3.00 (qd, *J* = 7.1, 2.4 Hz, 1H), 2.92 (td, *J* = 16.1, 6.3 Hz, 1H), 2.82 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.63 (dd, *J* = 16.7, 4.4 Hz, 1H), 2.27 (tdd, *J* = 16.8, 6.1, 2.5 Hz, 1H), 1.39 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.7, 142.8, 140.0, 136.0, 135.0, 131.7, 130.8, 130.2, 128.0, 127.4, 126.7, 126.4, 126.2, 123.9, 122.1, 40.1, 35.6, 28.2, 23.4, 12.6; IR (EtOH) ν 2971, 2879, 2830, 1651, 1601, 1445, 1366, 1090, 1046, 766, 735, 724, 651 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{20}NO$ 290.1539; found 290.1537.

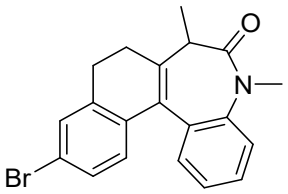


11-fluoro-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2b): A white solid, 30 mg, 48% yield. m.p. 135-137 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.44 - 7.38 (m, 2H), 7.35 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.19 (ddd, *J* = 7.8, 7.1, 1.4 Hz, 1H), 6.94 - 6.89 (m, 2H), 6.78 (tdd, *J* = 8.5, 2.8, 1.0 Hz, 1H), 3.38 (s, 3H), 2.97 (qd, *J* = 7.0, 2.3 Hz, 1H), 2.89 (dd, *J* = 16.7, 5.9 Hz, 1H), 2.80 (dd, *J* = 16.3, 5.1 Hz, 1H), 2.62 (dd, *J* = 16.7, 6.4 Hz, 1H), 2.25 (tdd, *J* = 16.9, 6.0, 2.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.7, 161.4 (d, *J* = 245.5 Hz), 142.7, 139.0, 138.5 (d, *J* = 7.7 Hz), 131.5, 131.1 (d, *J* = 3.5 Hz), 130.0, 129.9, 128.1, 127.8 (d, *J* = 8.3 Hz), 123.9, 122.1, 114.4 (d, *J* = 21.3 Hz), 112.6 (d, *J* = 20.7 Hz), 39.9, 35.6, 28.3, 23.1, 12.6; ^{19}F NMR (564 MHz, $CDCl_3$)

δ -115.6; IR (acetone) ν 2937, 1666, 1598, 1488, 1446, 1363, 1268, 1244, 1225, 1089, 922, 864, 765 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}NOF$ 308.1445; found 308.1441.

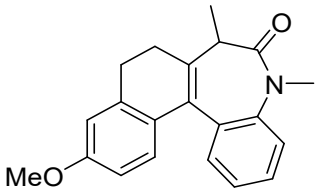


11-chloro-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2c): A colorless oil, 38 mg, 58% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 - 7.37 (m, 2H), 7.35 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.22 - 7.16 (m, 2H), 7.08 - 7.03 (m, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 3.37 (s, 3H), 3.01 - 2.94 (m, 1H), 2.88 (dd, *J* = 15.5, 6.2 Hz, 1H), 2.79 (dd, *J* = 14.3, 5.2 Hz, 1H), 2.63 (dd, *J* = 17.1, 6.7 Hz, 1H), 2.25 (tdd, *J* = 16.8, 6.3, 2.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.6, 142.7, 140.2, 137.9, 133.5, 132.1, 131.3, 131.1, 129.9, 128.3, 127.6, 127.4, 126.2, 124.0, 122.2, 40.1, 35.7, 28.0, 23.2, 12.6; IR (neat) ν2970, 2935, 2885, 1666, 1597, 1479, 1445, 1362, 1260, 1218, 1084, 1046, 879, 832, 758 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}NOCl$ 324.1149; found 324.1153.

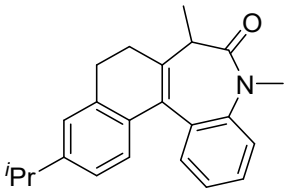


11-bromo-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2d): A colorless oil, 40 mg, 54% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41 - 7.31 (m, 4H), 7.24 - 7.15 (m, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.37 (s, 3H), 2.96 (td, *J* = 9.8, 8.4 Hz, 1H), 2.88 (dd, *J* = 16.3, 5.6 Hz, 1H), 2.79 (dd, *J* = 15.4, 4.3 Hz, 1H), 2.62 (dd, *J* = 17.9, 5.6 Hz, 1H), 2.24 (tdd, *J* = 16.9, 6.2, 2.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.6, 142.8, 140.4, 138.2, 133.9, 131.3, 130.6, 130.3, 129.9, 129.2, 128.3, 127.9, 124.0, 122.2, 120.3, 40.2, 35.7, 27.9, 23.2, 12.6; IR (EtOH) ν 3050, 2940, 2870, 2820,

1663, 1597, 1478, 1446, 1361, 1265, 1228, 1121, 1095, 1002, 904, 822, 763, 730, 701 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}NOBr$ 368.0644; found 368.0638.

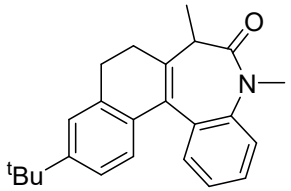


11-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2e): A white solid, 41 mg, 64% yield, m.p.: 180-182 °C. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (d, *J* = 6.2 Hz, 1H), 7.40 - 7.32 (m, 2H), 7.21 - 7.15 (m, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.79 - 6.75 (m, 1H), 6.63 (dd, *J* = 8.5, 2.7 Hz, 1H), 3.80 (s, 3H), 3.36 (s, 3H), 3.00 - 2.85 (m, 2H), 2.78 (dd, *J* = 16.2, 5.1 Hz, 1H), 2.60 (dd, *J* = 16.6, 6.3 Hz, 1H), 2.25 (tdd, *J* = 16.8, 6.1, 2.5 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.9, 158.4, 142.7, 137.9, 137.4, 131.9, 130.7, 130.4, 130.1, 127.9, 127.5, 123.8, 122.1, 113.4, 111.0, 55.3, 39.9, 35.7, 30.3, 28.7, 23.3, 12.7; IR (EtOH) ν 3057, 2935, 2831, 1662, 1597, 1488, 1451, 1364, 1251, 1227, 1092, 1035, 763, 732, 654 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}NO_2$ 320.1645; found 320.1646.

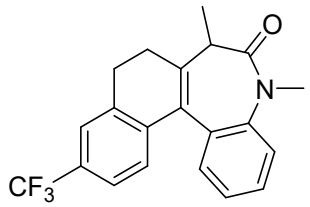


11-isopropyl-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2f): A colorless oil, 42 mg, 63% yield. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.42 - 7.30 (m, 2H), 7.22 - 7.14 (m, 1H), 7.07 (s, 1H), 6.97 (d, *J* = 6.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.34 (s, 3H), 3.02 - 2.94 (m, 1H), 2.87 (t, *J* = 6.9 Hz, 1H), 2.81 (dd, *J* = 15.1, 4.2 Hz, 1H), 2.62 (dd, *J* = 16.0, 5.4 Hz, 1H), 2.26 (tdd, *J* = 16.9, 6.3, 2.4 Hz, 1H), 1.38 (d, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 5.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 172.8, 147.6, 142.7, 139.0, 136.0, 132.7, 131.8, 130.7, 130.2, 127.9, 126.3,

125.7, 124.1, 123.8, 122.1, 40.0, 35.6, 33.8, 28.9, 28.4, 24.0, 23.5, 12.6; IR (acetone) ν 2957, 2924, 2866, 1666, 1597, 1488, 1445, 1361, 1300, 1220, 1118, 1091, 832, 762, 742 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{26}NO$ 332.2008; found 332.2006.

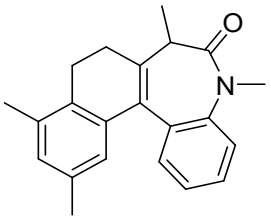


11-(tert-butyl)-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2g): A colorless oil, 50 mg, 72% yield. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 - 7.36 (m, 1H), 7.34 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.23 (s, 1H), 7.21 - 7.15 (m, 1H), 7.13 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.34 (s, 3H), 2.99 (td, *J* = 7.0, 2.3 Hz, 1H), 2.92 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.82 (dd, *J* = 16.1, 5.2 Hz, 1H), 2.62 (dd, *J* = 16.8, 4.3 Hz, 1H), 2.27 (tdd, *J* = 16.8, 6.2, 2.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.7, 149.8, 142.7, 139.1, 135.6, 132.3, 131.8, 130.6, 130.2, 128.0, 126.0, 124.6, 123.8, 123.0, 122.1, 40.1, 35.6, 34.5, 31.3, 28.6, 23.6, 12.6; IR (EtOH) ν 2965, 1648, 1589, 1440, 1364, 1267, 1085, 1047, 880, 762, 742 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{28}NO$ 346.2165; found 346.2169.

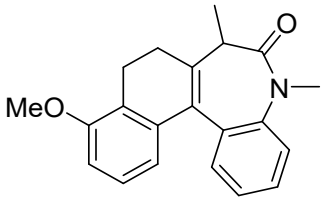


5,7-dimethyl-11-(trifluoromethyl)-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2h): A pale green oil, 37 mg, 52% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (s, 1H), 7.46 - 7.40 (m, 2H), 7.39 (d, *J* = 5.8 Hz, 1H), 7.35 (d, *J* = 9.8 Hz, 1H), 7.21 (ddd, *J* = 8.2, 6.9, 1.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 3.38 (s, 3H), 3.09 - 2.98 (m, 1H), 2.98 - 2.85 (m, 2H), 2.74 - 2.63 (m, 1H), 2.36 - 2.22 (m, 1H), 1.41 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.4, 142.8, 142.5, 136.5, 131.1, 130.2, 130.0, 129.9, 128.5,

128.4 (q, J = 32.4 Hz), 126.4, 124.23 (q, J = 272.3 Hz), 124.15 (q, J = 4.2 Hz), 124.14, 123.2 (q, J = 4.2 Hz), 122.3, 40.4, 35.7, 27.9, 23.2, 12.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.4; IR (neat) ν 3063, 2940, 1667, 1598, 1448, 1360, 1323, 1277, 1160, 1100, 1096, 1071, 901, 837, 763, 735 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{19}NOF_3$ 358.1413; found 358.1407.

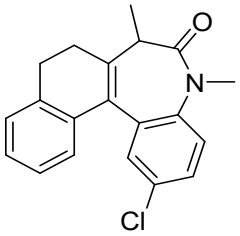


5,7,10,12-tetramethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2i): A white solid, 46 mg, 74% yield, m.p.: 183-185 °C. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 - 7.32 (m, 3H), 7.18 (t, J = 6.6 Hz, 1H), 6.87 (s, 1H), 6.62 (s, 1H), 3.36 (s, 3H), 3.04 - 2.93 (m, 2H), 2.68 - 2.51 (m, 2H), 2.31 (s, 3H), 2.31 - 2.14(m, 1H),2.19 (s, 3H), 1.39 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 172.8, 142.7, 139.6, 134.84, 134.82, 134.5, 132.2, 131.2, 131.0, 130.3, 129.6, 127.8, 125.2, 123.8, 122.0, 40.0, 35.6, 23.5, 23.2, 21.0, 19.5, 12.5; IR (neat) ν 2946, 2828, 1659, 1598, 1445, 1365, 1221, 1107, 1047, 907, 857, 764, 750 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{24}NO$ 318.1852; found 318.1852.

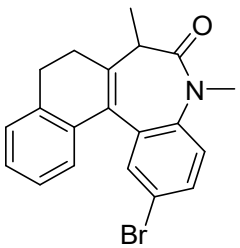


12-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2j): A yellow oil, 30 mg, 47% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (d, J = 7.9 Hz, 1H), 7.37 - 7.32 (m, 1H), 7.22 - 7.15 (m, 1H), 7.12 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.70 (dd, J = 8.2, 2.7 Hz, 1H), 6.53 (d, J = 2.6 Hz, 1H), 3.70 (s, 3H), 3.36 (s, 3H), 3.05 - 2.95 (m, 1H), 2.87 - 2.73 (m, 2H), 2.62 (dd, J = 15.7, 4.7 Hz, 1H), 2.23 (tdd, J = 16.4, 6.9, 2.5 Hz, 1H), 1.39 (d, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.7, 158.1,

142.7, 140.7, 136.0, 131.6, 130.8, 130.1, 128.3, 128.1, 128.0, 124.0, 122.1, 113.3, 111.0, 76.8, 55.3, 40.2, 35.6, 27.3, 23.7, 12.6; IR (EtOH) ν 2936, 2836, 1663, 1597, 1489, 1453, 1361, 1302, 1213, 1117, 1043, 908, 807, 785, 763 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}NO_2$ 320.1645; found 320.1640.

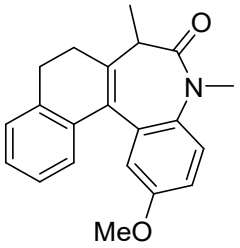


2-chloro-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2m): A pale yellow oil, 41 mg, 63% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (d, *J* = 2.5 Hz, 1H), 7.36 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.23 - 7.12 (m, 3H), 6.99 - 6.92 (m, 1H), 3.34 (s, 3H), 2.97 (td, *J* = 8.4, 5.4 Hz, 1H), 2.92 - 2.78 (m, 2H), 2.63 (dd, *J* = 16.9, 4.1 Hz, 1H), 2.25 (tdd, *J* = 16.8, 6.5, 2.5 Hz, 1H),1.40 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.4, 141.3, 140.9, 136.0, 134.4, 133.3, 130.1, 129.7, 129.4, 128.2, 127.5, 127.1, 126.5, 126.1, 123.5, 40.2, 35.7, 28.1, 23.5, 12.6; IR (EtOH) ν 3073, 2935, 2880, 1667, 1479, 1450, 1401, 1354, 1296, 1221, 1104, 907, 818, 767, 728, 704 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}NOCl$ 324.1149; found 324.1143.

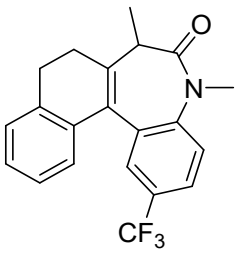


2-bromo-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2n): A yellow oil, 45 mg, 61% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.24 - 7.14 (m, 4H), 6.97 - 6.92 (m, 1H), 3.34 (s, 3H), 3.01 - 2.93 (m, 1H), 2.92 - 2.77 (m, 2H), 2.63 (dd, *J* = 16.9, 6.2 Hz, 1H), 2.25 (tdd, *J* = 16.8,

6.5, 2.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.4, 141.7, 141.0, 136.0, 134.4, 133.7, 132.7, 131.1, 130.0, 127.5, 127.1, 126.5, 126.1, 123.8, 117.1, 40.2, 35.6, 28.1, 23.5, 12.6; IR (neat) ν 2971, 2945, 2878, 2819, 1662, 1478, 1398, 1352, 1297, 1114, 1095, 906, 817, 788, 656 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}NOBr$ 368.0644; found 368.0638.

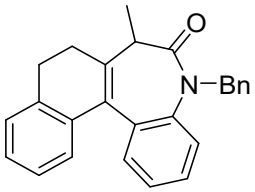


2-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2o): A light green oil, 38 mg, 60% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.28 - 7.24 (m, 1H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.17 - 7.08 (m, 2H), 7.04 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.99 - 6.92 (m, 2H), 3.77 (s, 3H), 3.32 (s, 3H), 3.04 (qd, *J* = 7.1, 2.3 Hz, 1H), 2.92 (td, *J* = 16.0, 6.2 Hz, 1H), 2.82 (ddd, *J* = 15.2, 6.3, 2.1 Hz, 1H), 2.62 (ddd, *J* = 17.0, 6.5, 2.2 Hz, 1H), 2.25 (tdd, *J* = 16.8, 6.3, 2.5 Hz, 1H), 1.38 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 155.5, 140.2, 136.5, 136.0, 134.9, 132.8, 130.7, 127.5, 126.7, 126.3, 126.2, 123.4, 115.3, 113.3, 55.6, 40.1, 35.7, 28.2, 23.4, 12.7; IR (neat) ν 2928, 2830, 1659, 1496, 1461, 1415, 1284, 1222, 1114, 1041, 907, 767, 728 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}NO_2$ 320.1645; found 320.1652.

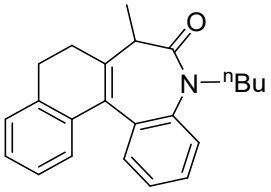


5,7-dimethyl-2-(trifluoromethyl)-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one(2p): A light green oil, 42 mg, 59% yield. Eluent: PE/EA = 10/1. Containing trace

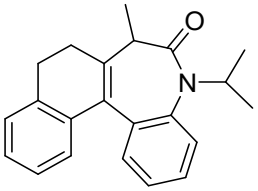
amount of three-membered ring unopened by-product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.76 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.24 - 7.09 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 3.39 (s, 3H), 3.00 - 2.89 (m, 2H), 2.85 (ddd, *J* = 15.3, 6.5, 2.1 Hz, 1H), 2.66 (ddd, *J* = 16.8, 6.2, 2.1 Hz, 1H), 2.28 (tdd, *J* = 16.8, 6.4, 2.5 Hz, 1H), 1.41 (d, *J* = 7.1 Hz, 3H); ^{3}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.5, 145.2, 141.2, 136.0, 134.4, 132.0, 130.3, 127.7, 127.6 (q, *J* = 4.1 Hz), 127.2, 126.6, 126.008 (q, *J* = 33.8 Hz), 126.005, 124.8 (q, *J* = 4.1 Hz), 123.9 (q, *J* = 270.9 Hz), 122.6, 40.3, 35.7, 28.0, 23.5, 12.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.2; IR (EtOH) ν 2972, 2881, 1697, 1381, 1310, 1137, 1087, 1045, 879, 803; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{19}NOF_3$ 358.1413; found 358.1412.



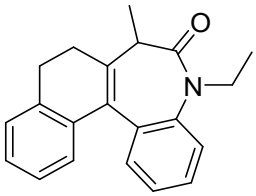
5-benzyl-7-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2q): A green oil, 38 mg, 52% yield. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.15 - 7.08 (m, 2H), 7.05 - 6.93 (m, 4H), 6.89 (d, *J* = 7.1 Hz, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 5.57 (d, *J* = 15.4 Hz, 1H), 4.74 (d, *J* = 15.5 Hz, 1H), 3.12 (qd, *J* = 6.9, 2.3 Hz, 1H), 2.92 (td, *J* = 15.9, 6.2 Hz, 1H), 2.82 (ddd, *J* = 15.2, 6.3, 2.0 Hz, 1H), 2.64 (ddd, *J* = 16.7, 6.2, 2.0 Hz, 1H), 2.27 (tdd, *J* = 16.8, 6.3, 2.5 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.2, 141.0, 139.8, 137.4, 135.942, 135.935, 134.6, 133.4, 131.3, 130.0, 128.3, 127.9, 127.2, 127.1, 126.8, 126.7, 126.6, 126.1, 124.4, 123.0, 50.6, 40.2, 28.2, 23.4, 12.6; IR (EtOH) ν 3026, 2937, 2869, 1663, 1597, 1483, 1447, 1375, 1295, 1192, 767, 749, 725, 697 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{23}NONa$ 388.1671; found 388.1680.



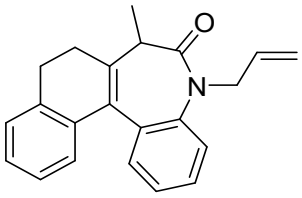
5-butyl-7-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2r): A pale yellow oil, 35 mg, 53% yield. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 - 7.33 (m, 3H), 7.23 - 7.06 (m, 4H), 6.93 (d, *J* = 7.5 Hz, 1H), 4.37 (dt, *J* = 13.6, 7.7 Hz, 1H), 3.57 - 3.48 (m, 1H), 2.98 (qt, *J* = 7.0, 3.7 Hz, 1H), 2.89 (dd, *J* = 16.3, 6.2 Hz, 1H), 2.82 (dd, *J* = 15.2, 4.3 Hz, 1H), 2.61 (dd, *J* = 16.8, 4.2 Hz, 1H), 2.24 (tdd, *J* = 16.8, 6.4, 2.5 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.34 - 1.27 (m, 2H), 1.10 - 0.94 (m, 2H), 0.64 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.0, 141.3, 140.2, 136.0, 134.9, 133.3, 130.9, 130.0, 128.0, 127.3, 126.6, 126.2, 124.2, 123.1, 47.1, 40.3, 30.0, 28.2, 23.3, 19.6, 13.6, 12.5; IR (acetone) ν 2956 2932, 2872, 1663, 1597, 1483, 1447, 1483, 1447, 1375, 1222, 1205, 1092, 1092, 766, 751, 730 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{26}NO$ 332.2008; found 332.2011.



5-isopropyl-7-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2s): A colorless oil, 32 mg, 51% yield. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 - 7.37 (m, 2H), 7.34 (td, *J* = 8.2, 7.6, 1.6 Hz, 1H), 7.25 - 7.18 (m, 2H), 7.17 - 7.08 (m, 2H), 6.97 (d, *J* = 7.3 Hz, 1H), 4.59 - 4.54 (m, 1H), 2.98 (qd, *J* = 7.1, 2.4 Hz, 1H), 2.94 - 2.77 (m, 2H), 2.59 (dd, *J* = 15.8, 5.3 Hz, 1H), 2.26 (tdd, *J* = 16.8, 6.5, 2.5 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.37 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 172.3, 140.4, 140.2, 136.0, 135.0, 134.2, 130.8, 129.8, 127.4, 127.2, 126.7, 126.3, 126.1, 125.0, 124.8, 50.2, 41.0, 28.1, 23.4, 22.5, 20.7, 12.4; IR (EtOH) ν 2972, 2928, 2867, 1647, 1591, 1483, 1448, 1378, 1295, 1087, 1046, 879, 766, 731 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{24}NO$ 318.1852; found 318.1845.

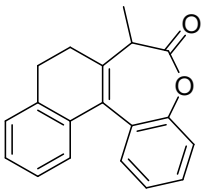


5-ethyl-7-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2t): A brown oil, 32 mg, 52% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.42 - 7.35 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.17 - 7.07 (m, 2H), 6.95 (d, *J* = 5.9 Hz, 1H), 4.31 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.60 (dq, *J* = 13.9, 7.0 Hz, 1H), 2.98 (qd, *J* = 7.2, 2.5 Hz, 1H), 2.89 (dd, *J* = 16.3, 6.1 Hz, 1H), 2.82 (dd, *J* = 15.2, 4.4 Hz, 1H), 2.61 (dd, *J* = 14.9, 6.3 Hz, 1H), 2.25 (tdd, *J* = 16.8, 6.4, 2.4 Hz, 1H), 1.39 (d, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 171.4, 141.1, 140.1, 136.1, 135.1, 133.3, 130.8, 130.0, 128.0, 127.4, 126.7, 126.3, 126.2, 124.3, 123.1, 43.0, 40.3, 28.1, 23.3, 13.1, 12.5; IR (neat) ν 2956, 2931, 2872, 2830, 1659, 1596, 1482, 1446, 1376, 1277, 1295, 1221, 909, 788, 750, 726 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}NO$ 304.1695; found 304.1691.

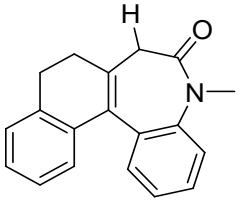


5-allyl-7-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2u): A light green oil, 34 mg, 54% yield. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (ddd, *J* = 8.2, 4.9, 1.5 Hz, 2H), 7.36 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H), 7.22 - 7.07 (m, 4H), 6.93 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.78 - 5.64 (m, 1H), 5.01 (dd, *J* = 7.1, 1.5 Hz, 1H), 4.98 (t, *J* = 1.6 Hz, 1H), 4.62 (ddt, *J* = 16.0, 5.0, 1.7 Hz, 1H), 4.35 (ddt, *J* = 15.9, 5.6, 1.6 Hz, 1H), 3.04 (qd, *J* = 7.1, 2.4 Hz, 1H), 2.92 (td, *J* = 15.9, 6.2 Hz, 1H), 2.82 (ddd, *J* = 15.2, 6.3, 2.1 Hz, 1H), 2.62 (ddd, *J* = 16.4, 6.1, 1.7 Hz, 1H), 2.26 (tdd, *J* = 16.8, 6.3, 2.5 Hz, 1H), 1.41 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 171.8, 141.6, 140.1, 136.1, 135.0, 133.7, 132.7, 131.1, 130.1, 129.7, 128.0, 127.45, 127.37, 126.7, 126.4, 126.2, 124.2, 122.7, 116.3, 50.6, 40.2, 28.2, 23.4, 12.6; IR (neat) ν 3055, 2968, 2940, 2884, 1652, 1597, 1490, 1455, 1369, 1226, 1205,

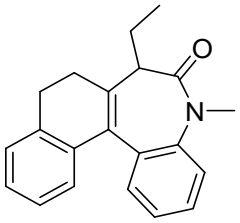
932, 919, 727, 704 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{22}NO$ 316.1695; found 316.1699.



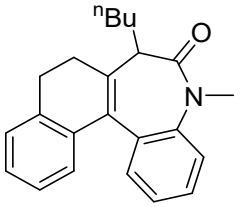
7-methyl-8,9-dihydrobenzo[b]naphtho[1,2-d]oxepin-6(7H)-one (2w): A colorless oil, 28 mg, 50% yield. Eluent: PE/EA = 10/1. ^1H NMR (600 MHz, $CDCl_3$, TMS) δ 7.48 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.44 - 7.39 (m, 1H), 7.29 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.26 - 7.17 (m, 3H), 7.17 - 7.11 (m, 1H), 7.04 (dd, *J* = 7.7, 1.3 Hz, 1H), 3.23 (qd, *J* = 7.0, 2.5 Hz, 1H), 2.93 (td, *J* = 16.9, 16.3, 6.3 Hz, 1H), 2.86 (ddd, *J* = 15.2, 6.2, 2.0 Hz, 1H), 2.62 (ddd, *J* = 16.3, 6.0, 1.8 Hz, 1H), 2.32 (tdd, *J* = 16.7, 6.2, 2.6 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 170.9, 150.8, 136.1, 135.1, 133.9, 131.7, 130.4, 129.2, 127.8, 127.5, 127.4, 126.5, 126.4, 124.3, 120.5, 39.6, 28.0, 23.1, 12.9; IR (EtOH) ν 3055, 2935, 2836, 1761, 1602, 1481, 1441, 1247, 1211, 1135, 1085, 1030, 906, 769, 729, 703 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{17}O_2$ 277.1223; found 277.1226.



5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2x): A white solid, 35 mg, 63% yield, m.p.:145-147 °C. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 - 7.31 (m, 2H), 7.22 - 7.09 (m, 4H), 7.03 (d, *J* = 7.4 Hz, 1H), 3.36 (s, 3H), 3.06 (s, 2H), 2.99 (dd, *J* = 15.6, 6.9 Hz, 1H), 2.86 - 2.69 (m, 2H), 2.50 - 2.42 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 171.2, 143.0, 136.2, 136.0, 134.6, 131.7, 130.9, 130.1, 128.0, 127.7, 126.8, 126.3, 126.0, 124.0, 122.4, 42.6, 35.8, 30.7, 28.3; IR (EtOH) ν 3055, 2922, 2825, 1662, 1598, 1481, 1445, 1356, 1263, 1117, 1090, 908, 765, 747, 727, 661 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{18}NO$ 276.1382; found 276.1384.

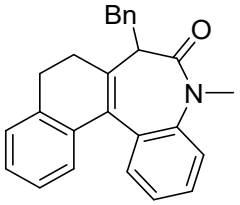


7-ethyl-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2y): A white solid, 35 mg, 57% yield, m.p.:180-182 °C. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 - 7.35 (m, 2H), 7.22 - 7.17 (m, 2H), 7.17 - 7.07 (m, 2H), 6.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.36 (s, 3H), 2.92 (td, *J* = 16.5, 16.0 Hz, 1H), 2.82 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.71 (td, *J* = 8.7, 6.6 Hz, 1H), 2.56 (dd, *J* = 16.5, 6.1 Hz, 1H), 2.25 (tdd, *J* = 16.8, 6.1, 2.4 Hz, 1H), 2.13 - 2.02 (m, 1H), 1.88 - 1.78 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 171.5, 142.9, 139.5, 136.1, 134.9, 131.7, 131.3, 130.2, 128.0, 127.4, 126.7, 126.4, 126.2, 123.9, 122.2, 47.9, 35.5, 28.2, 23.6, 20.3, 12.5; IR (EtOH) ν 2970, 2878, 1647, 1597, 1482, 1446, 1378, 1342, 1086, 1048, 879, 765, 664 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}NO$ 304.1695; found 304.1699.

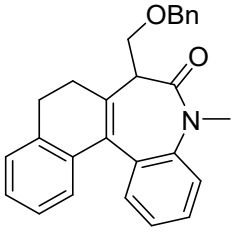


7-butyl-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2z): A yellow oil, 37 mg, 55% yield. Eluent: PE/EA = 10/1. Containing trace amount of three-membered ring unopened by-product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50 - 7.33 (m, 3H), 7.23 - 7.05 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 1H), 3.36 (d, *J* = 1.9 Hz, 3H), 2.99 - 2.73 (m, 3H), 2.57 (dd, *J* = 15.6, 5.2 Hz, 1H), 2.26 (tdd, *J* = 16.7, 6.2, 2.3 Hz, 1H), 2.13 - 1.99 (m, 1H), 1.85 - 1.72 (m, 1H), 1.34 (dd, *J* = 7.4, 3.3 Hz, 2H), 1.24 - 1.10 (m, 2H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 171.6, 142.9, 139.6, 136.1, 134.9, 131.6, 131.2, 130.2, 128.0, 127.4, 126.7, 126.4, 126.2, 123.9, 122.2, 46.3, 35.5, 30.3, 28.2, 27.0, 23.7, 23.0,

14.1; IR (neat) ν 2957, 2920, 2870, 2850, 1663, 1597, 1482, 1445, 1364, 908, 765, 727, 664 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{26}NO$ 332.2008; found 332.2014.



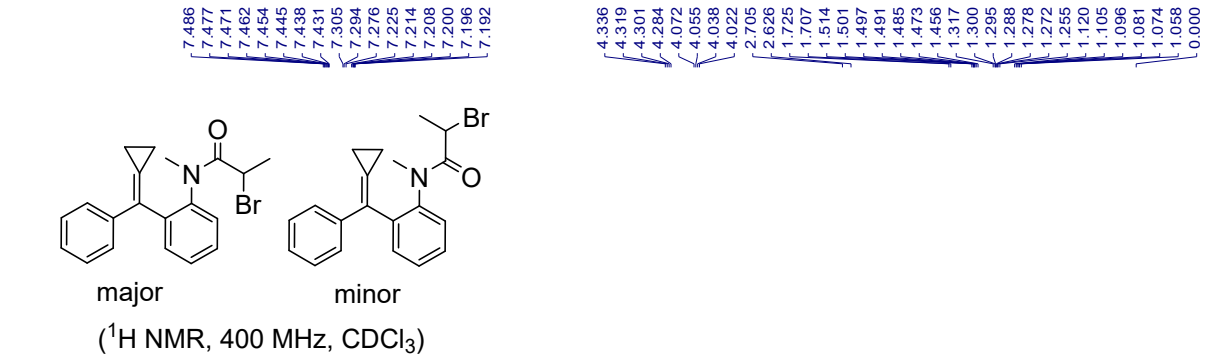
7-benzyl-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2aa): A light green oil, 30 mg, 41% yield. Eluent: PE/EA = 10/1. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.42 - 7.31 (m, 2H), 7.24 - 7.07 (m, 9H), 6.96 (d, *J* = 7.4 Hz, 1H), 3.42 (dd, *J* = 12.4, 5.4 Hz, 1H), 3.35 (s, 3H), 3.31 - 3.19 (m, 2H), 2.87 - 2.69 (m, 2H), 2.58 (ddd, *J* = 16.4, 5.8, 2.4 Hz, 1H), 2.33 (tdd, *J* = 14.2, 7.4, 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 170.9, 142.8, 139.8, 139.0, 136.1, 134.8, 131.5, 130.2, 128.7, 128.3, 128.2, 127.5, 126.9, 126.4, 126.2, 126.0, 124.0, 122.4, 46.4, 35.7, 32.6, 28.1, 23.9; IR (neat) ν 3015, 2954, 2934, 1659, 1596, 1492, 1452, 1369, 1344, 1088, 917, 768, 747, 722, 700, 665 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{24}NO$ 366.1852; found 366.1854.



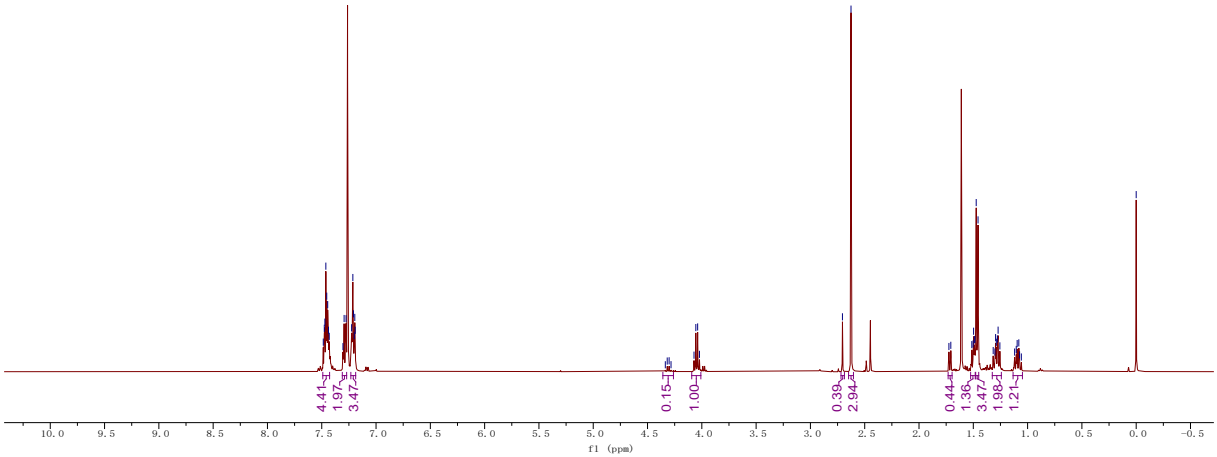
7-((benzyloxy)methyl)-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (2ab): A light green oil, 24 mg, 30% yield. Eluent: PE/EA = 10/1. ^1H NMR (600 MHz, $CDCl_3$, TMS) δ 7.44 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 - 7.36 (m, 1H), 7.35 - 7.30 (m, 5H), 7.29 - 7.27 (m, 1H), 7.22 - 7.16 (m, 2H), 7.16 - 7.12 (m, 1H), 7.12 - 7.07 (m, 1H), 6.94 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.06 - 3.99 (m, 2H), 3.20 (ddd, *J* = 8.7, 6.4, 2.3 Hz, 1H), 2.98 (td, *J* = 16.2, 15.8, 6.3 Hz, 1H), 2.79 (ddd, *J* = 15.1, 5.9, 1.9 Hz, 1H), 2.52 (ddd, *J* = 16.2, 6.3, 1.9 Hz, 1H), 2.31 (tdd, *J* = 16.7, 5.9, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 170.3, 142.5, 138.0, 137.6, 136.1, 134.8, 131.8, 131.5,

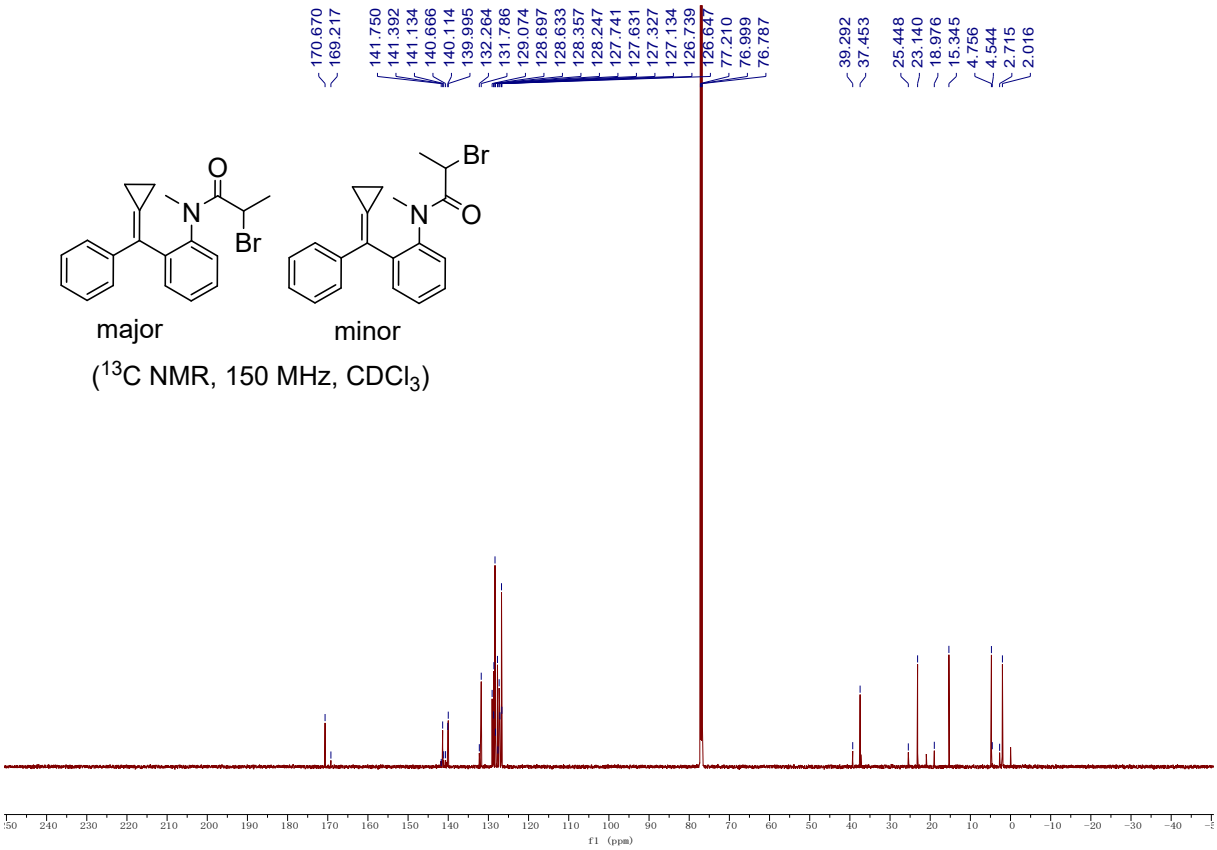
130.4, 128.4, 128.1, 128.0, 127.8, 127.5, 126.9, 126.4, 126.2, 124.1, 122.3, 73.7, 67.2, 46.3, 35.4, 28.1, 23.8; IR (neat) ν 2914, 2870, 1659, 1482, 1446, 1367, 1086, 908, 769, 729, 697, 663 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{26}NO_2$ 396.1964; found 396.1965.

10. Spectroscopic Data of Substrates (NMR Spectrum)

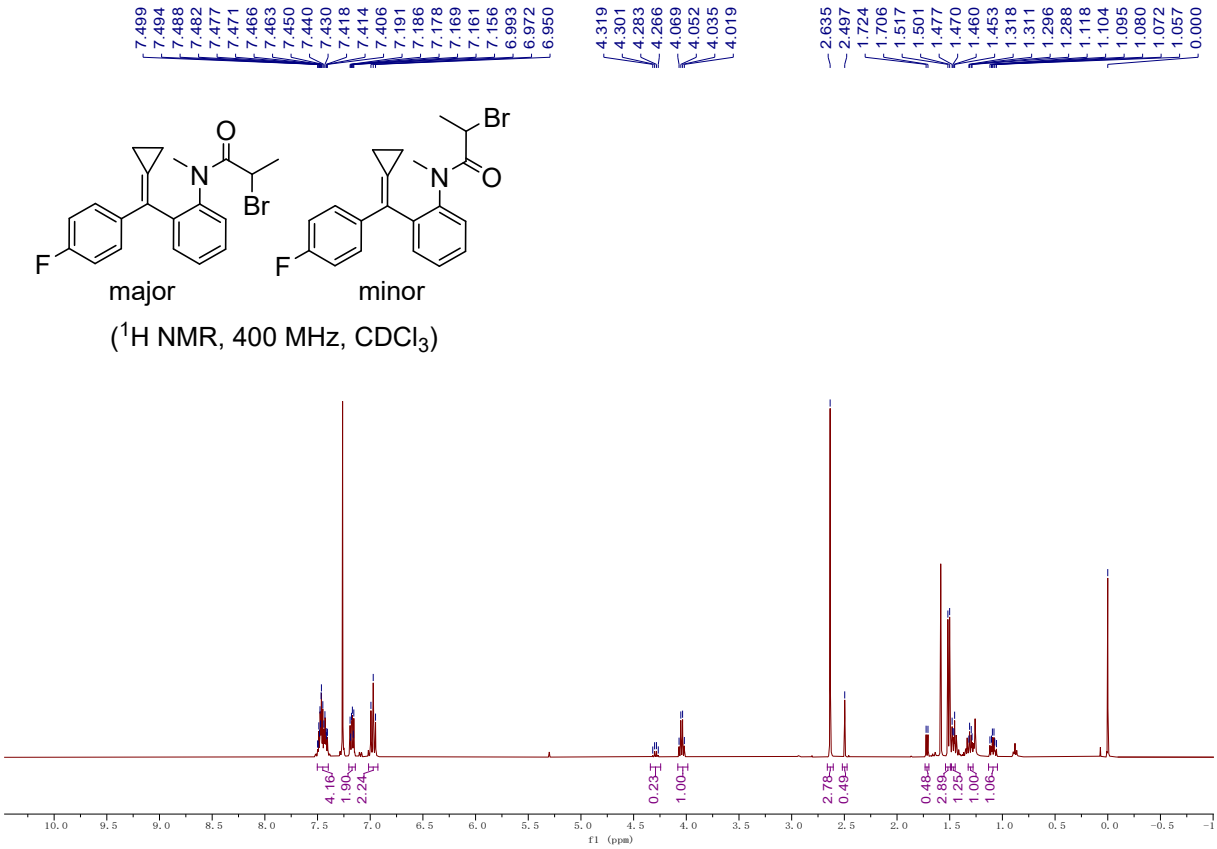


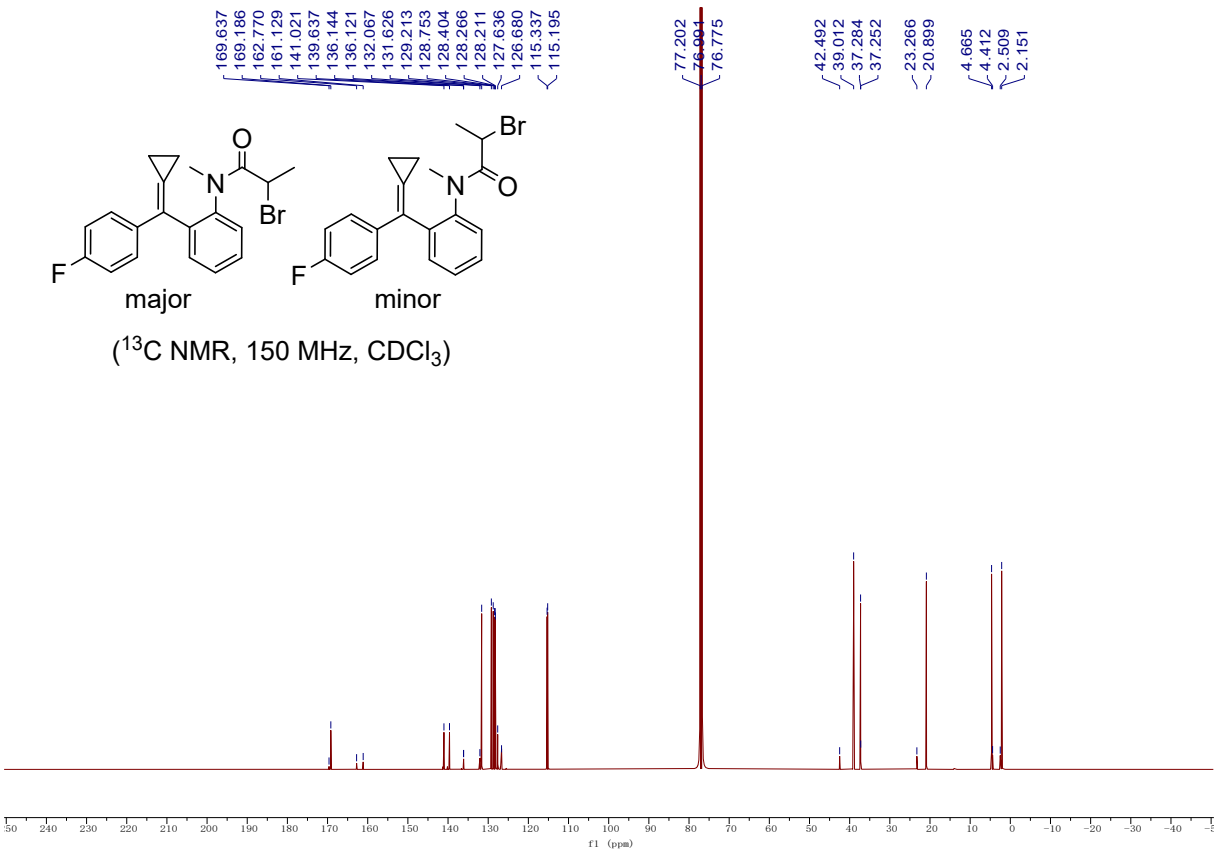
(^{1}H NMR, 400 MHz, $CDCl_3$)

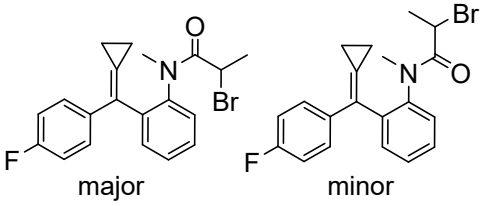




(^{13}C NMR, 150 MHz, $CDCl_3$)

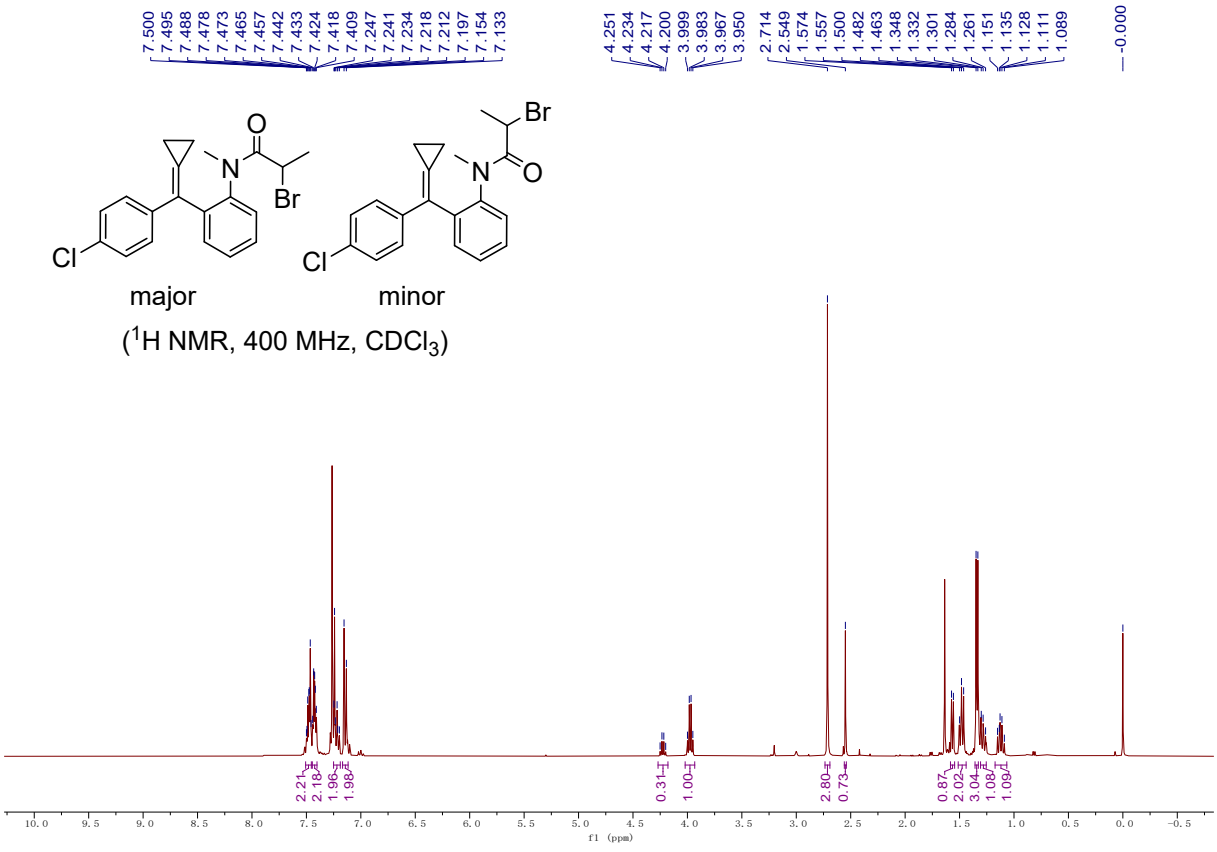

major
minor
(1H NMR, 400 MHz, CDCl3)

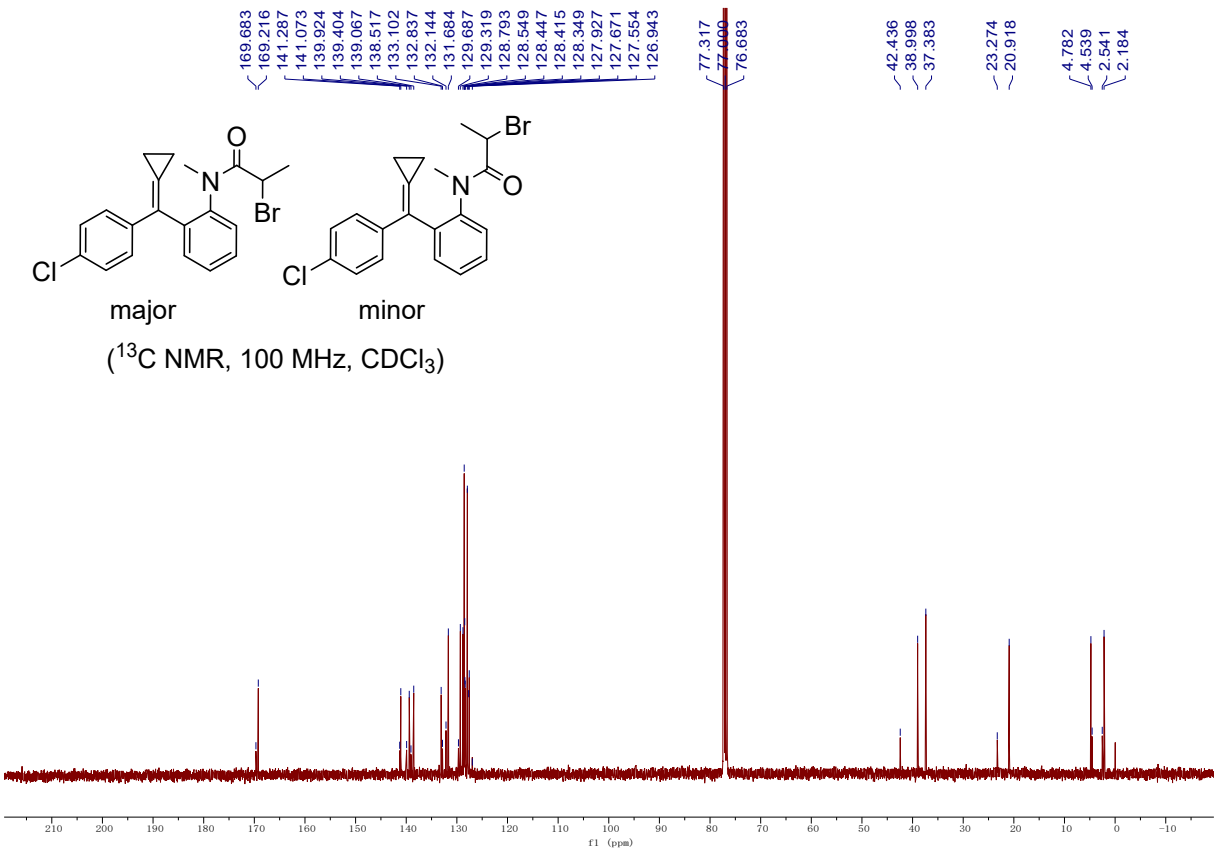

major
minor
(13C NMR, 150 MHz, CDCl3)

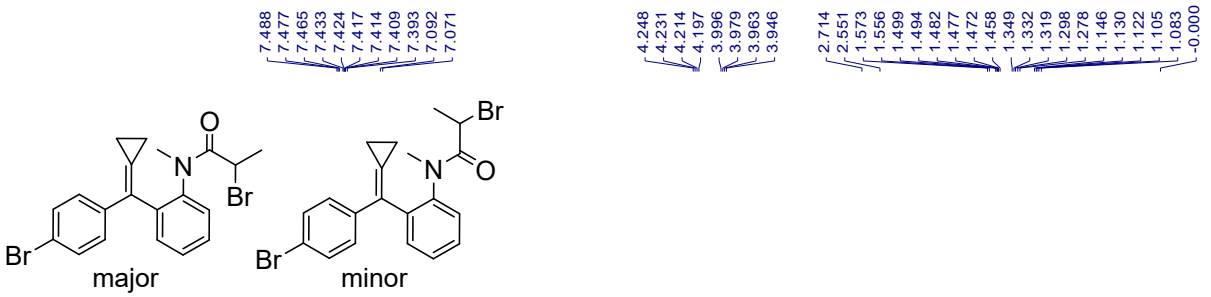


major minor

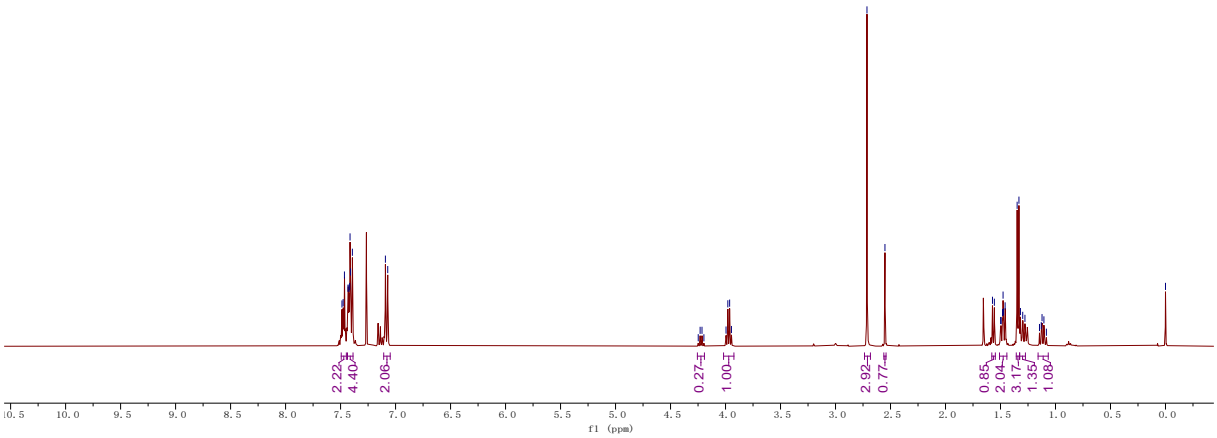
(^{19}F NMR, 564 MHz, $CDCl_3$)

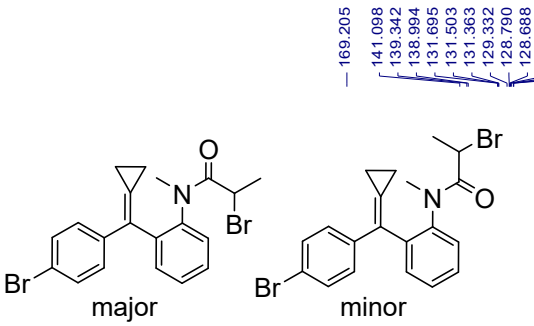

major
minor
(1H NMR, 400 MHz, CDCl3)


major
minor
(13C NMR, 100 MHz, CDCl3)

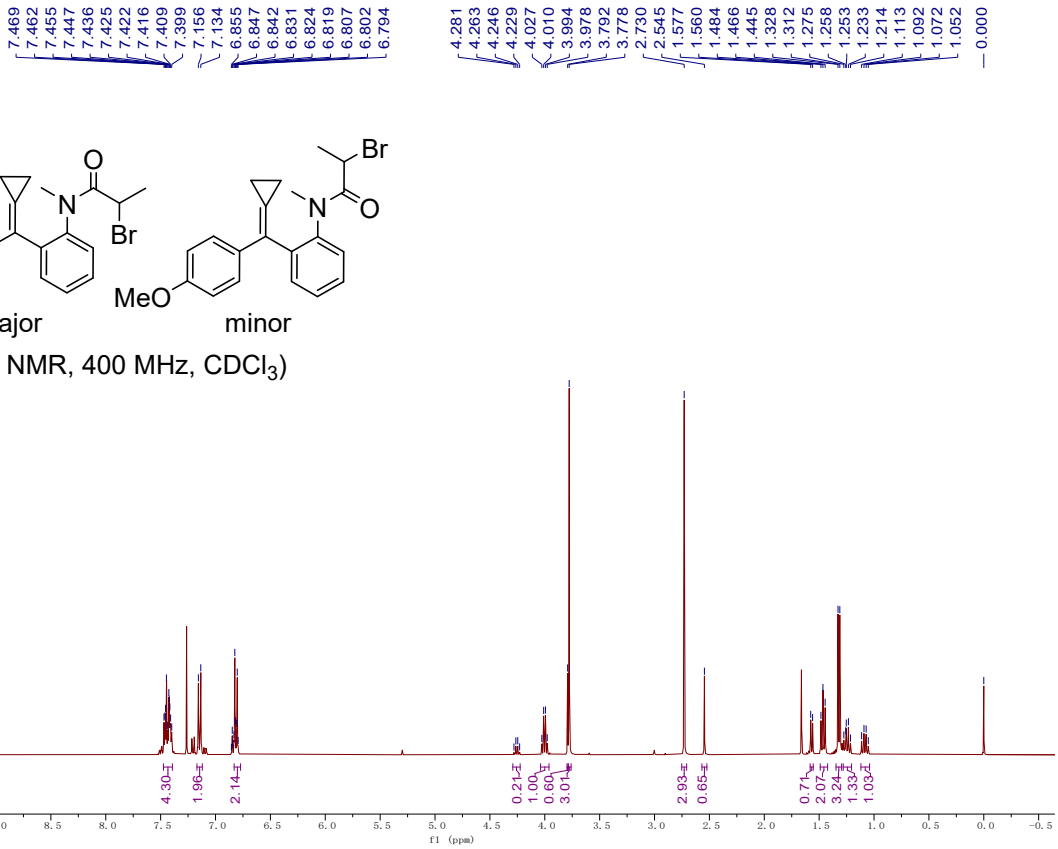


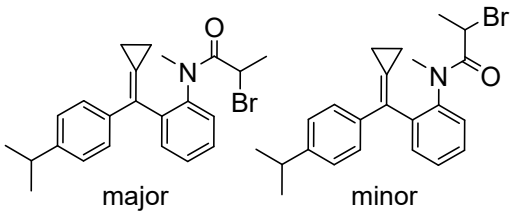
(^{1}H NMR, 400 MHz, $CDCl_3$)



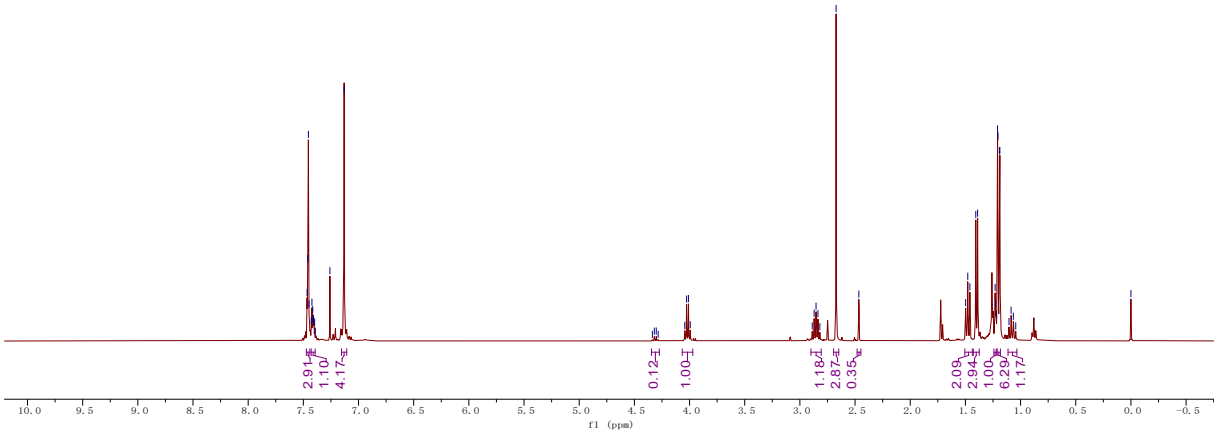


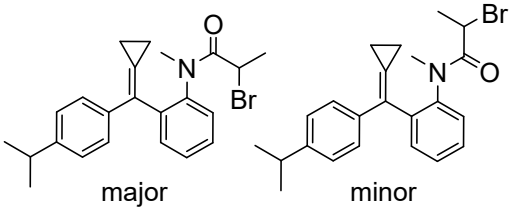
(^{13}C NMR, 150 MHz, $CDCl_3$)


7.469
7.462
7.455
7.447
7.436
7.425
7.422
7.416
7.409
7.399
7.156
7.134
6.855
6.847
6.842
6.831
6.824
6.819
6.807
6.802
6.794
4.281
4.263
4.246
4.229
4.027
4.010
3.994
3.978
3.792
3.778
2.730
2.545
1.577
1.560
1.484
1.466
1.445
1.328
1.312
1.275
1.258
1.253
1.233
1.214
1.113
1.092
1.072
1.052
0.000
Br
O
N
Br
MeO
major
Br
N
O
MeO
minor
(^{1}H NMR, 400 MHz, $CDCl_3$)
4.30
1.96
2.14
0.21
1.00
0.60
3.01
2.93
0.65
0.71
2.07
3.24
1.33
1.03
f1 (ppm)
169.640
169.216
158.845
158.664
141.290
141.089
140.586
140.076
133.195
132.635
132.119
131.685
128.945
128.634
128.350
128.244
128.038
127.837
127.599
124.808
113.734
77.318
77.000
76.682
55.248
42.649
39.255
37.373
23.315
20.975
4.648
4.413
2.345
1.991
Br
O
N
Br
MeO
major
Br
N
O
MeO
minor
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

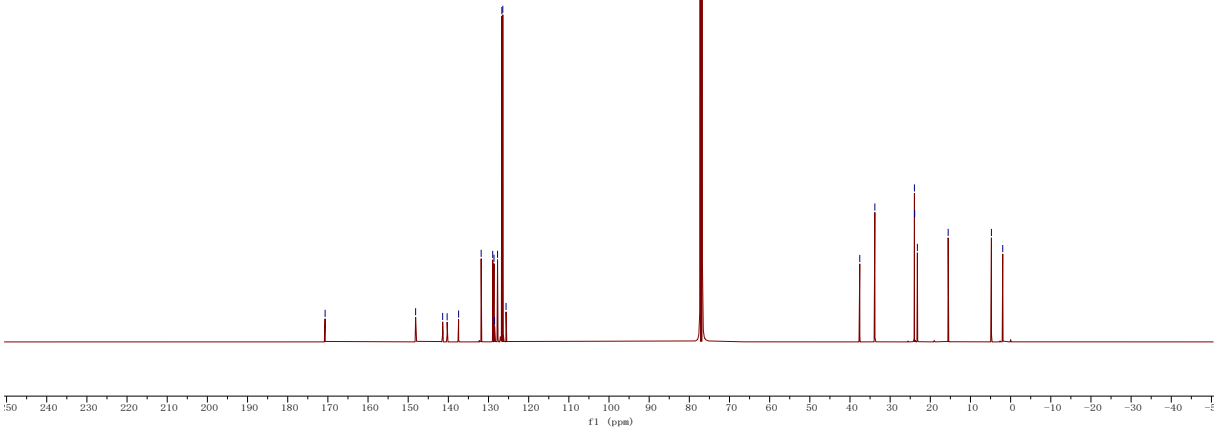


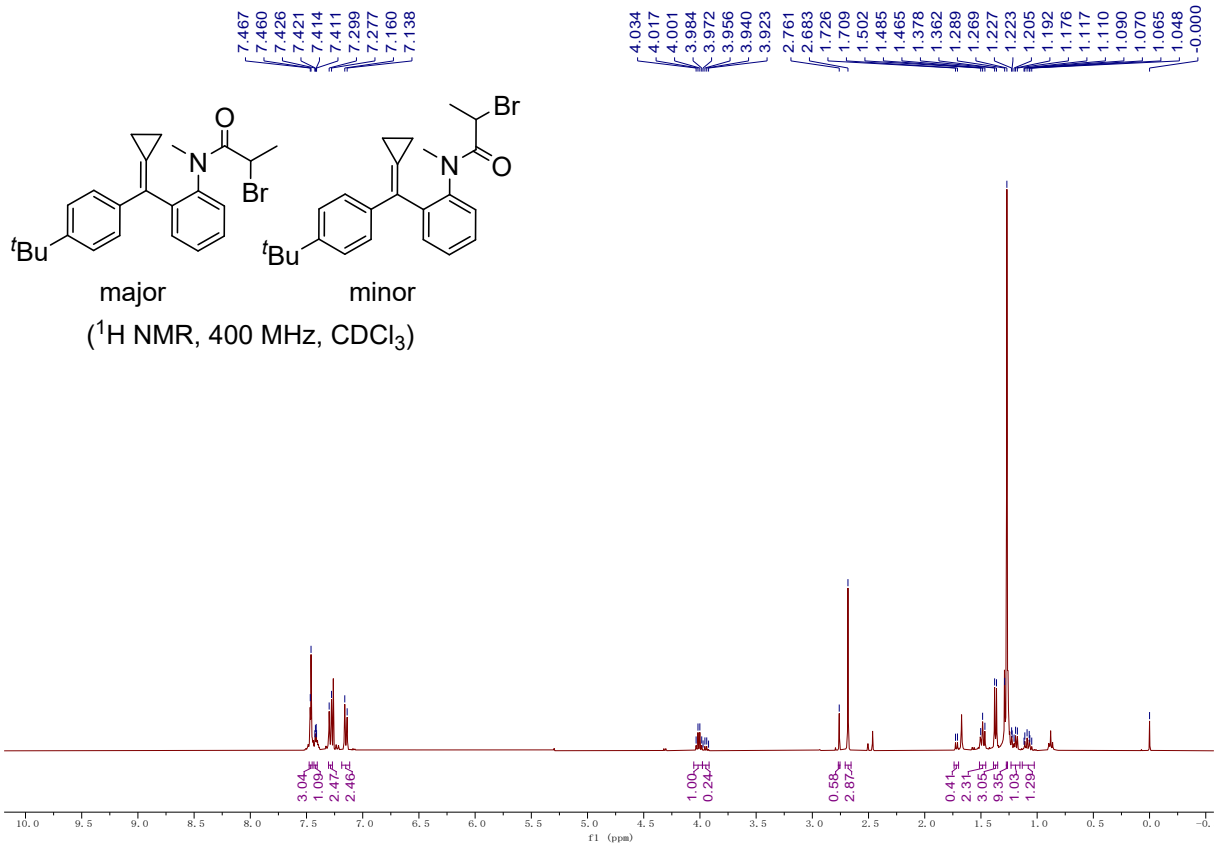
(^{1}H NMR, 400 MHz, $CDCl_3$)

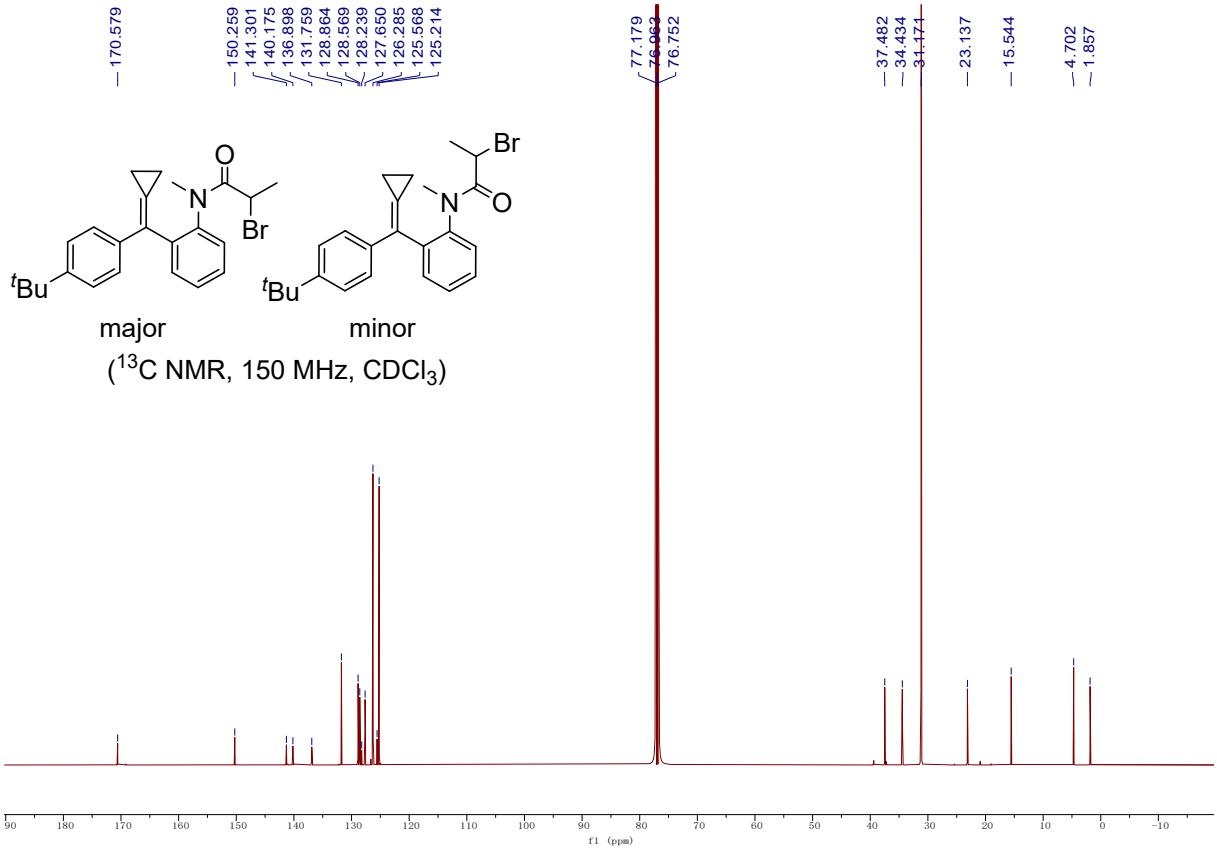


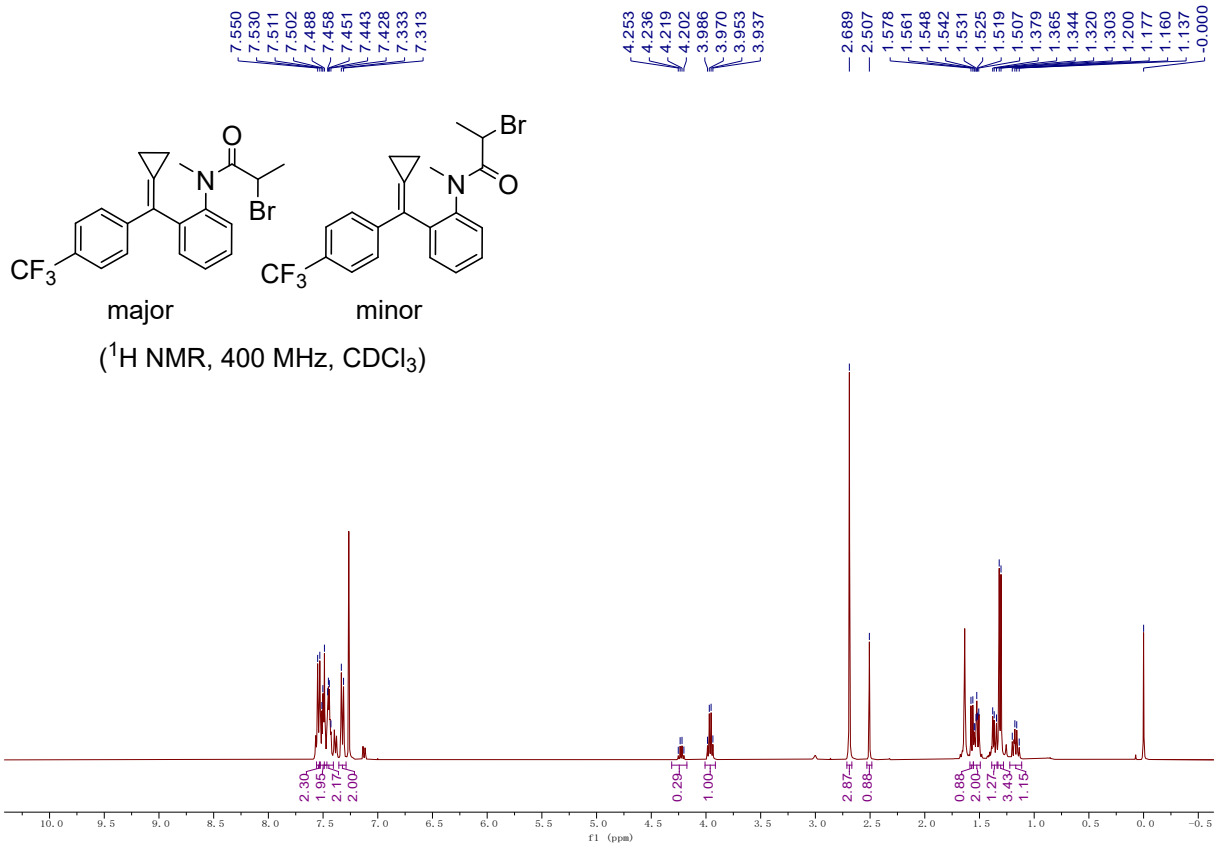


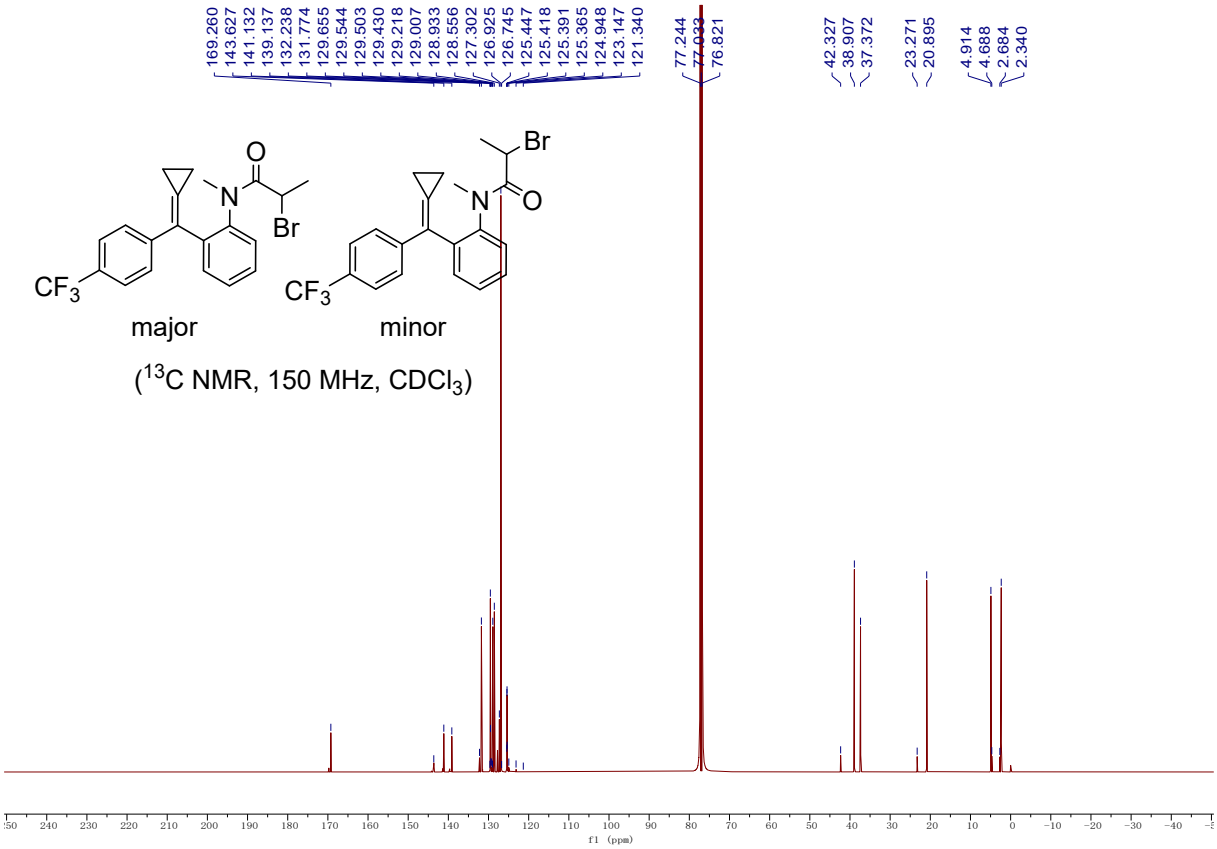
(^{13}C NMR, 150 MHz, $CDCl_3$)

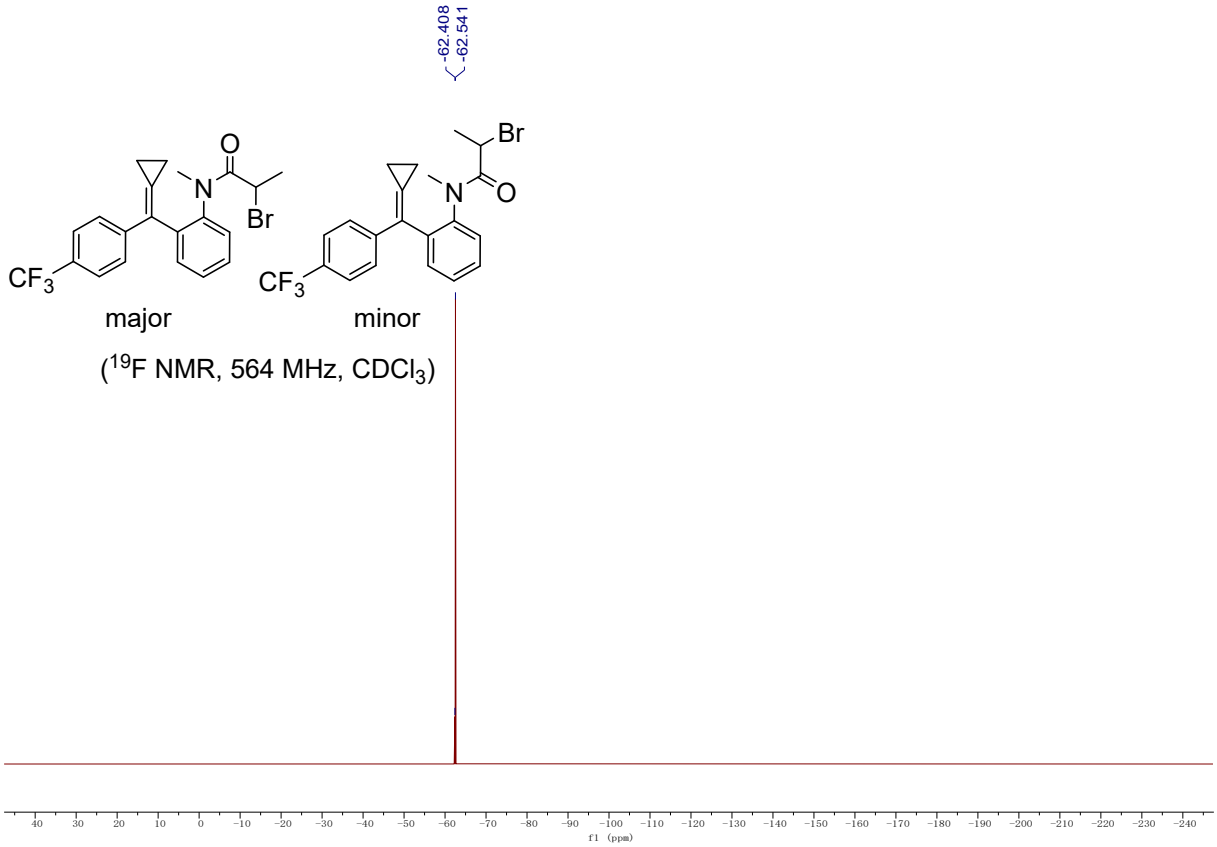


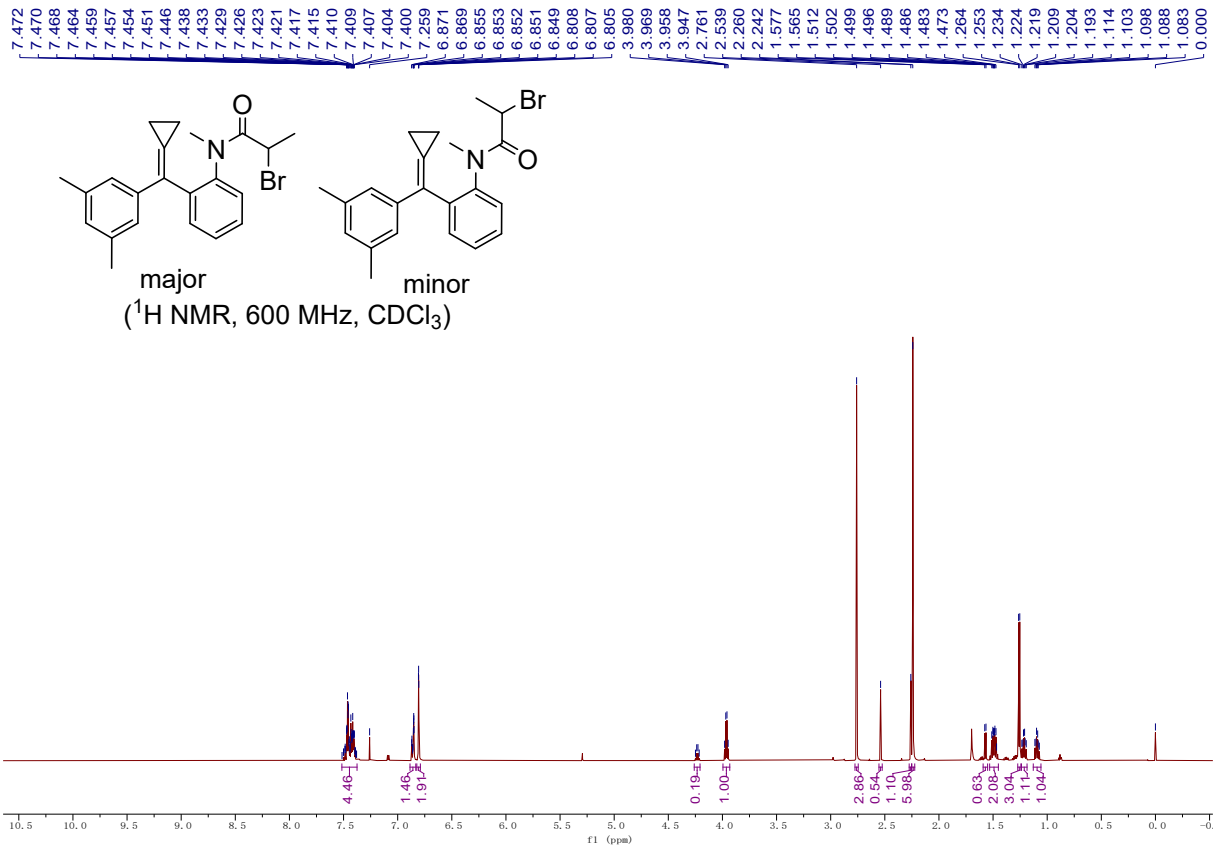

major
minor
(^{1}H NMR, 400 MHz, $CDCl_3$)

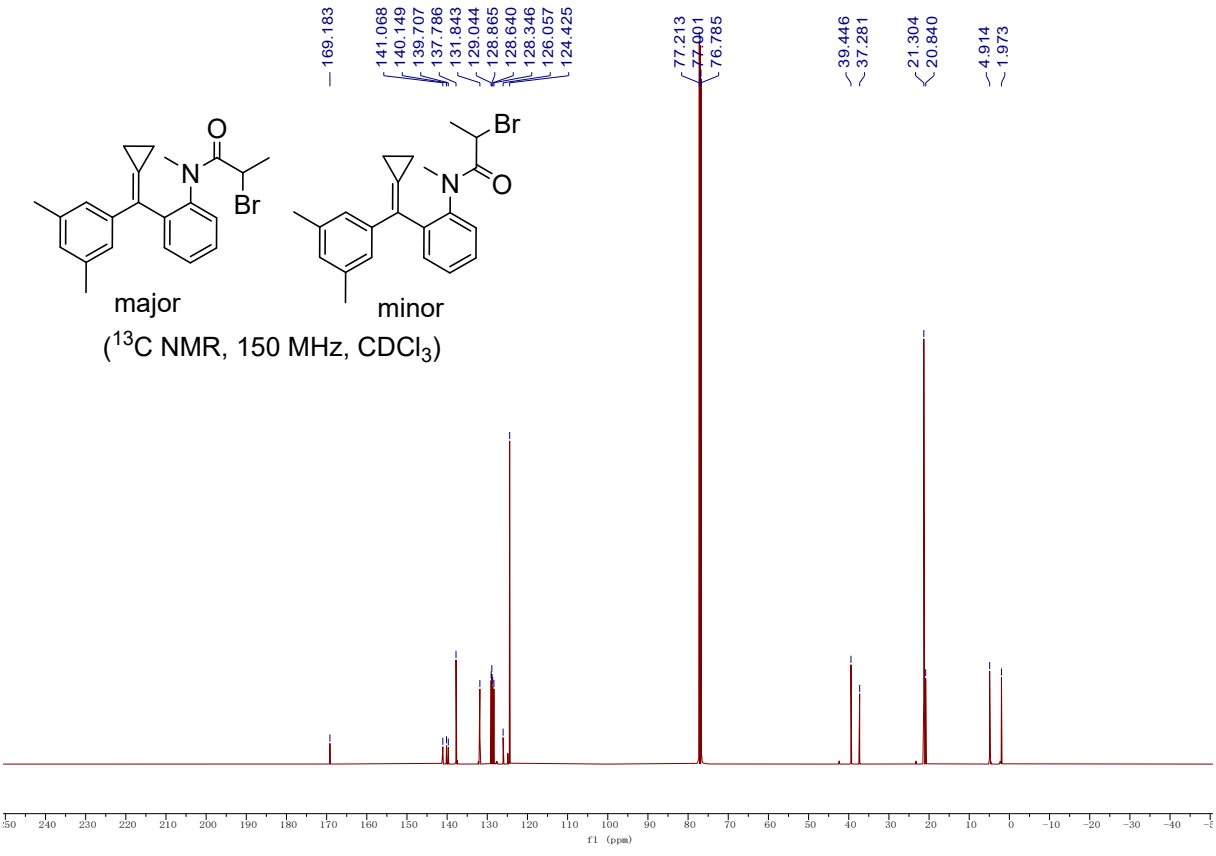

major
minor
(^{13}C NMR, 150 MHz, $CDCl_3$)

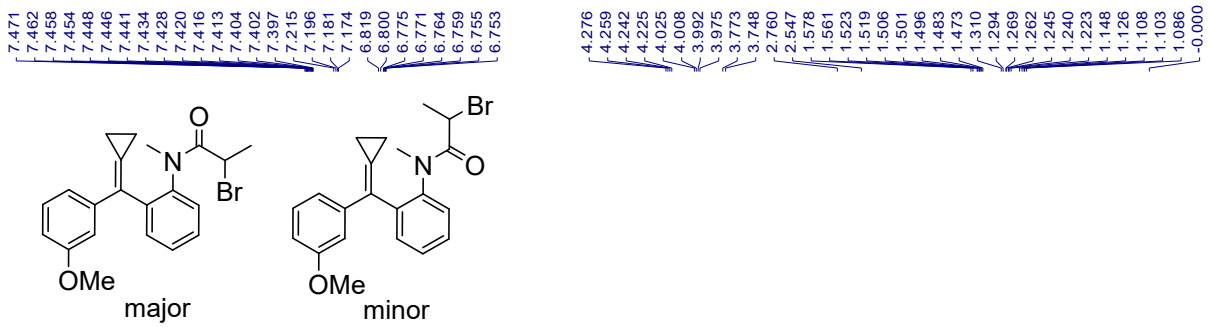

major
minor
(1H NMR, 400 MHz, CDCl3)


major
minor
(13C NMR, 150 MHz, CDCl3)

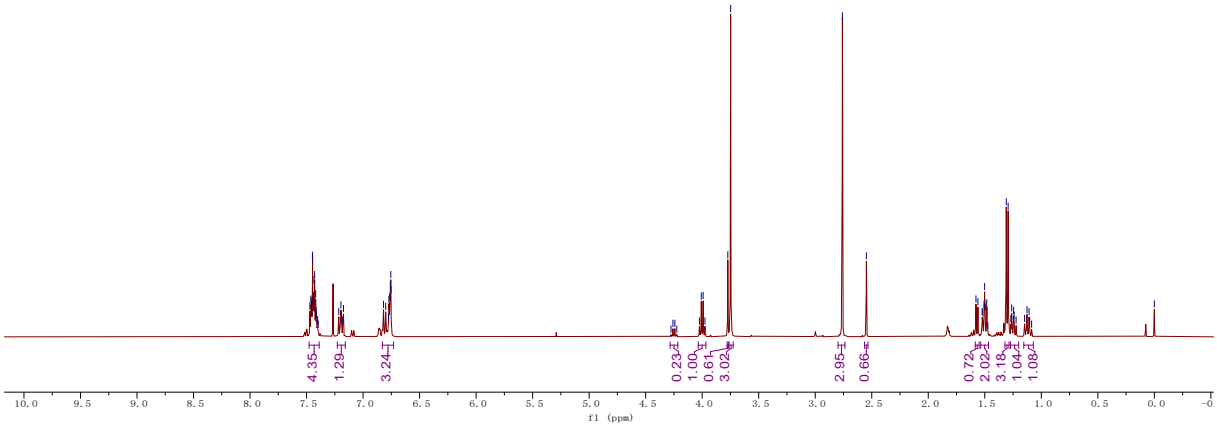

-62.408
-62.541
O
N
Br
CF3
major
Br
N
O
CF3
minor
(19F NMR, 564 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


major
minor
(1H NMR, 600 MHz, CDCl3)

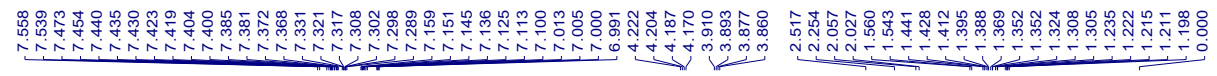

major
minor
(13C NMR, 150 MHz, CDCl3)

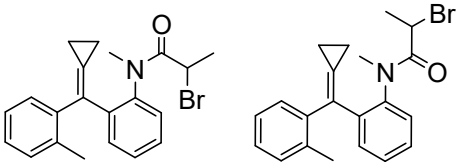


(^{1}H NMR, 400 MHz, $CDCl_3$)



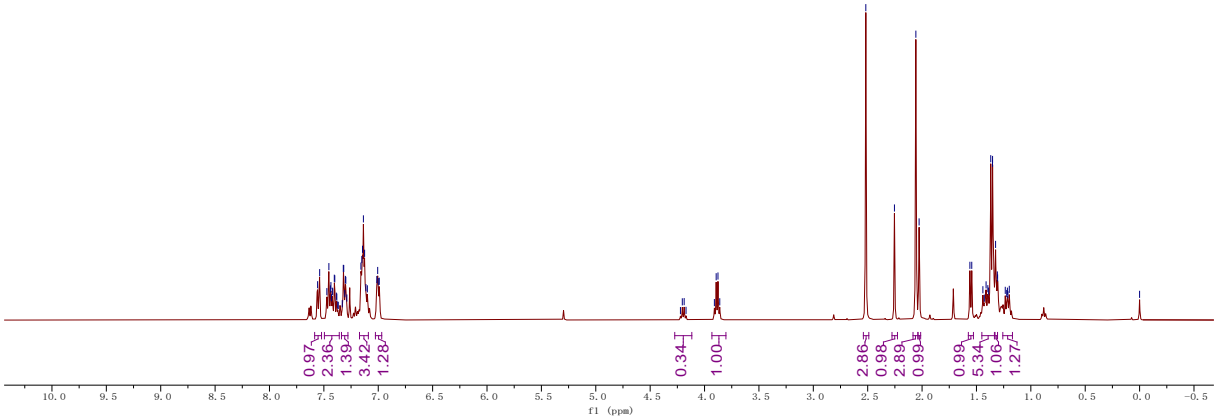
(^{13}C NMR, 100 MHz, $CDCl_3$)

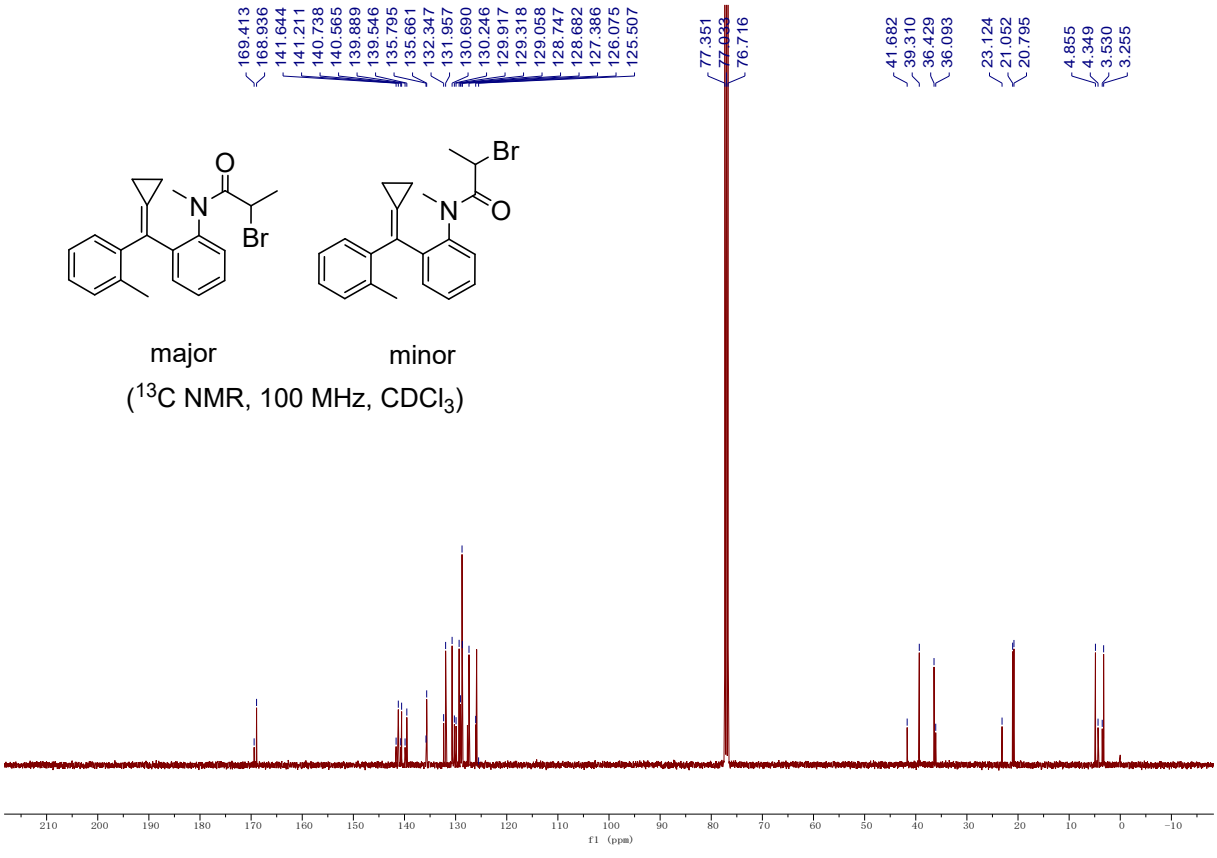




major minor

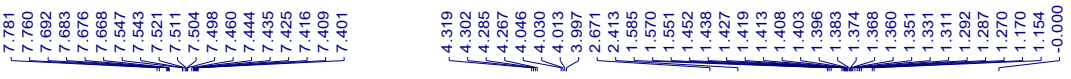
(^{1}H NMR, 400 MHz, $CDCl_3$)

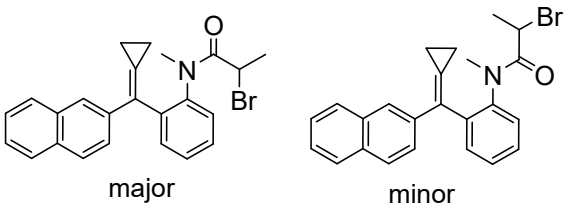




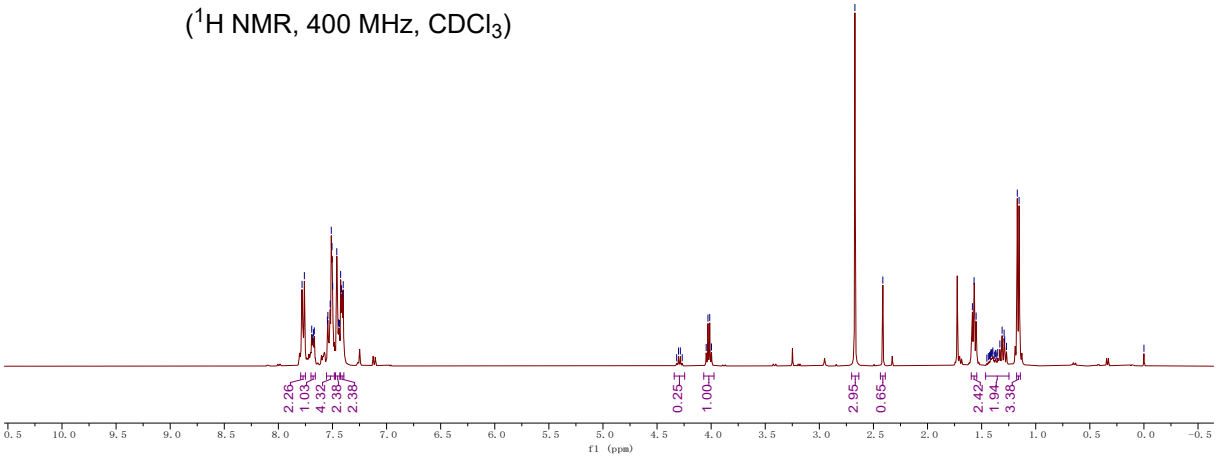
major minor

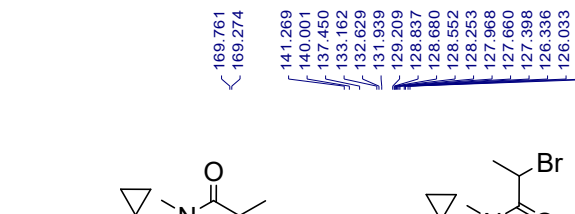
(^{13}C NMR, 100 MHz, $CDCl_3$)



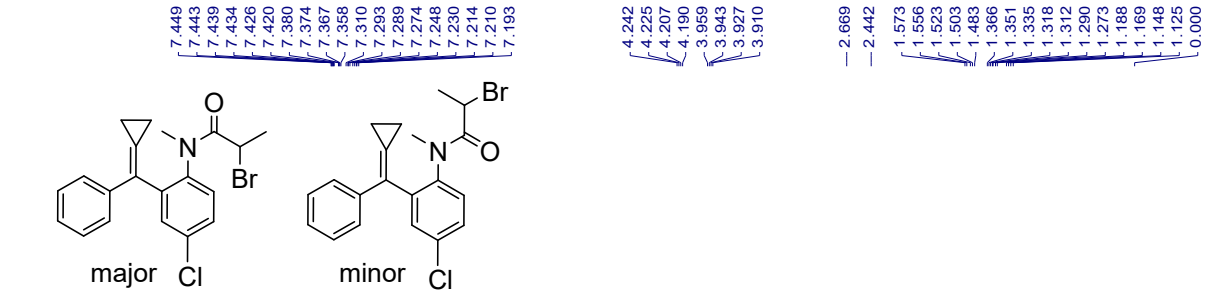


(^{1}H NMR, 400 MHz, $CDCl_3$)

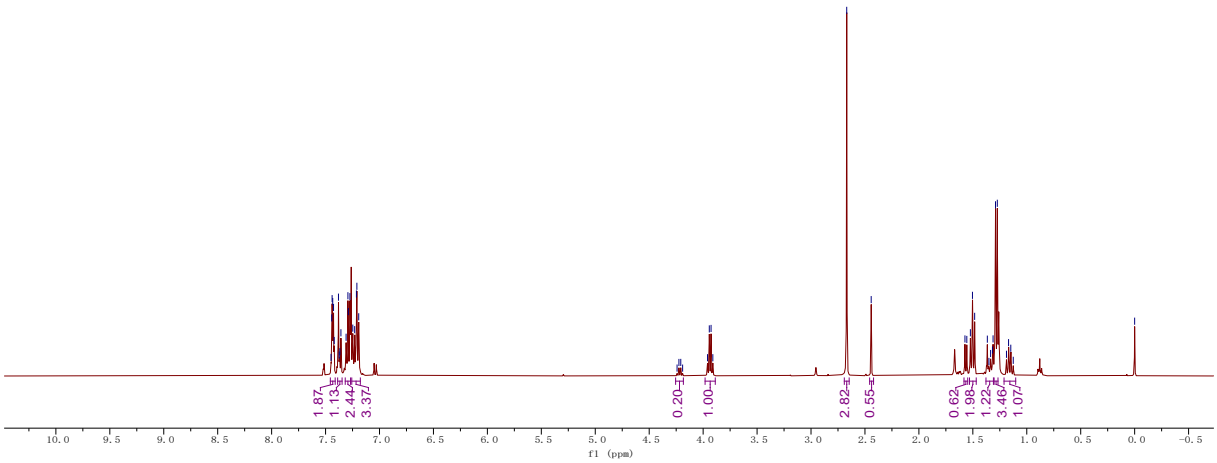


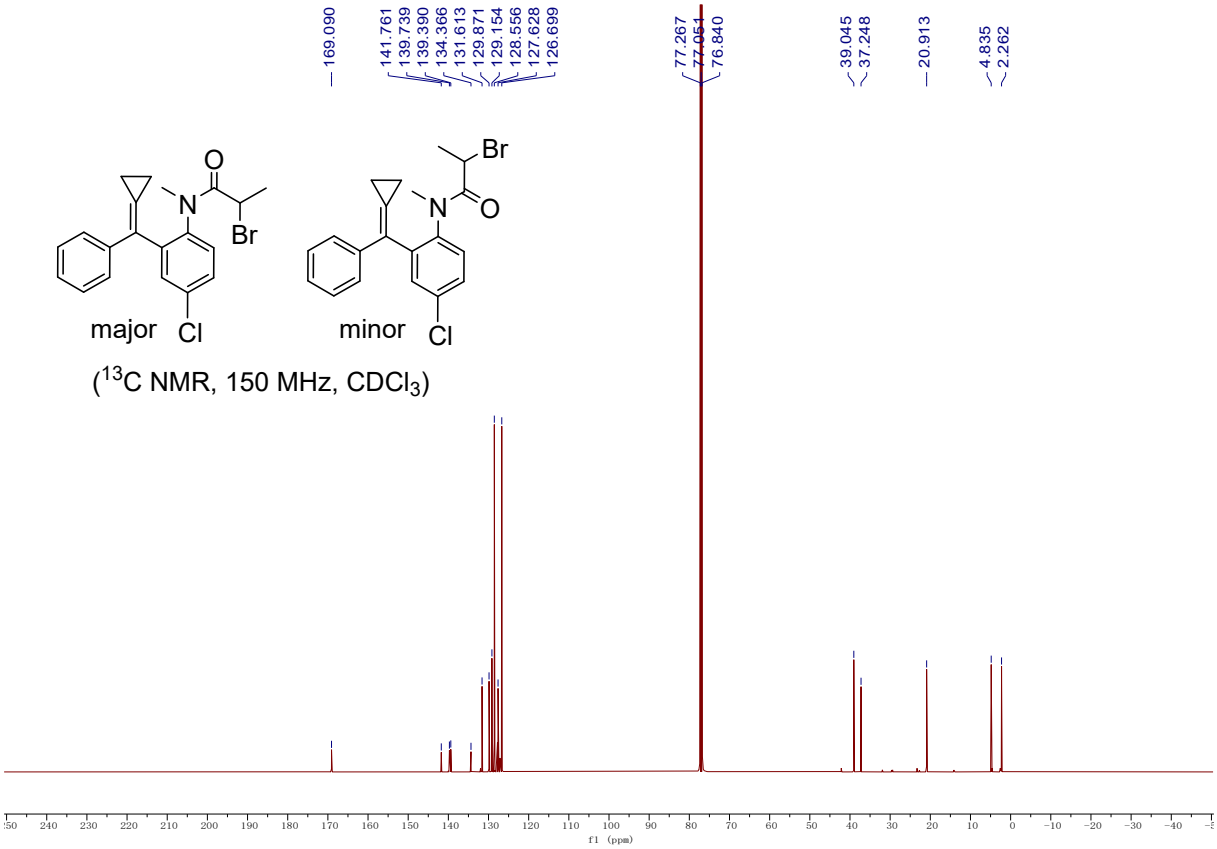


(^{13}C NMR, 150 MHz, $CDCl_3$)

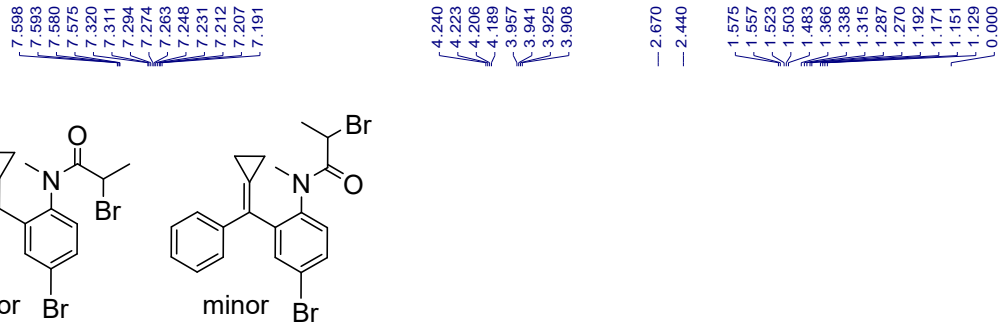


(^{1}H NMR, 400 MHz, $CDCl_3$)

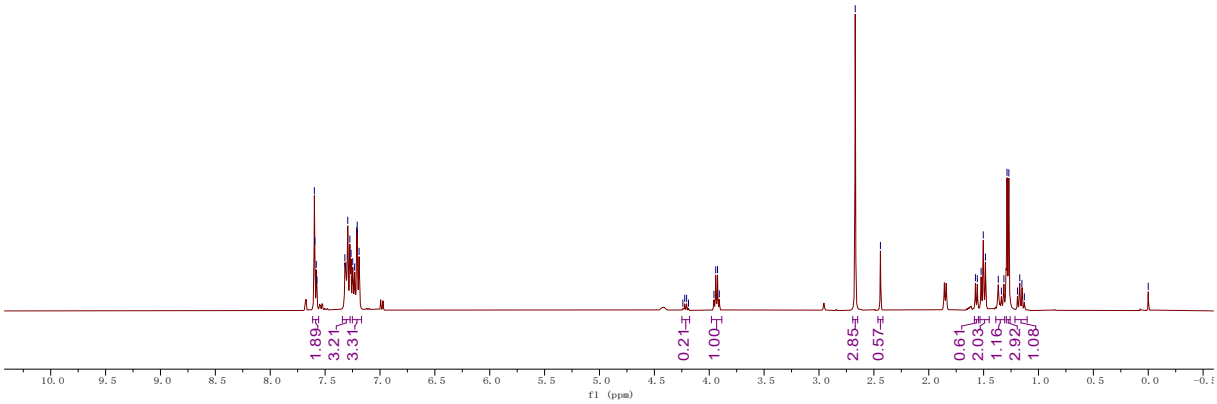


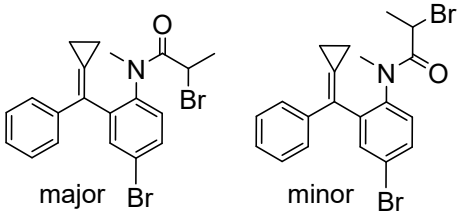


(^{13}C NMR, 150 MHz, $CDCl_3$)

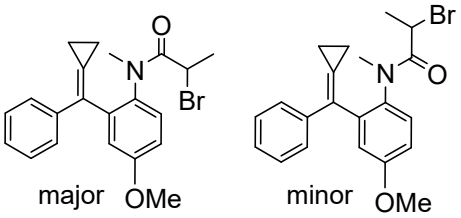


(^{1}H NMR, 400 MHz, $CDCl_3$)

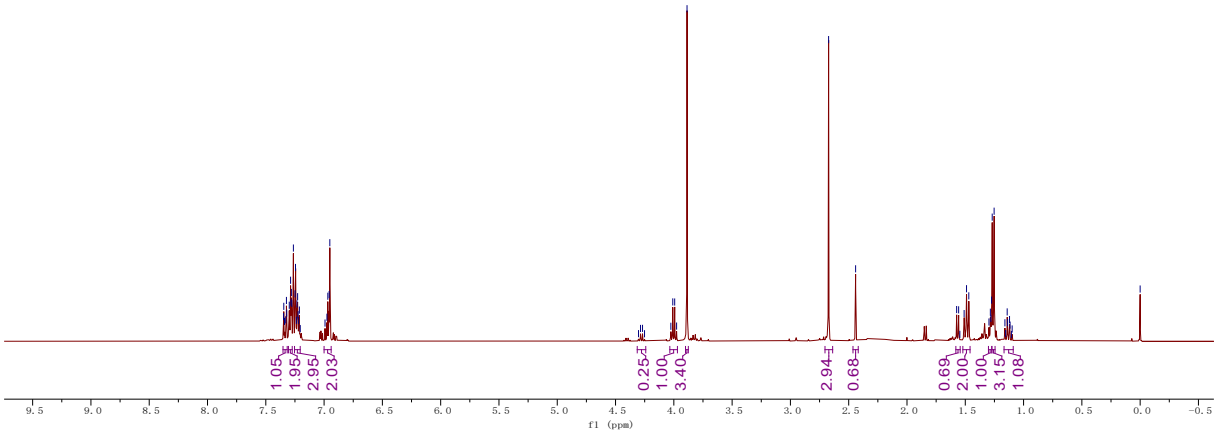


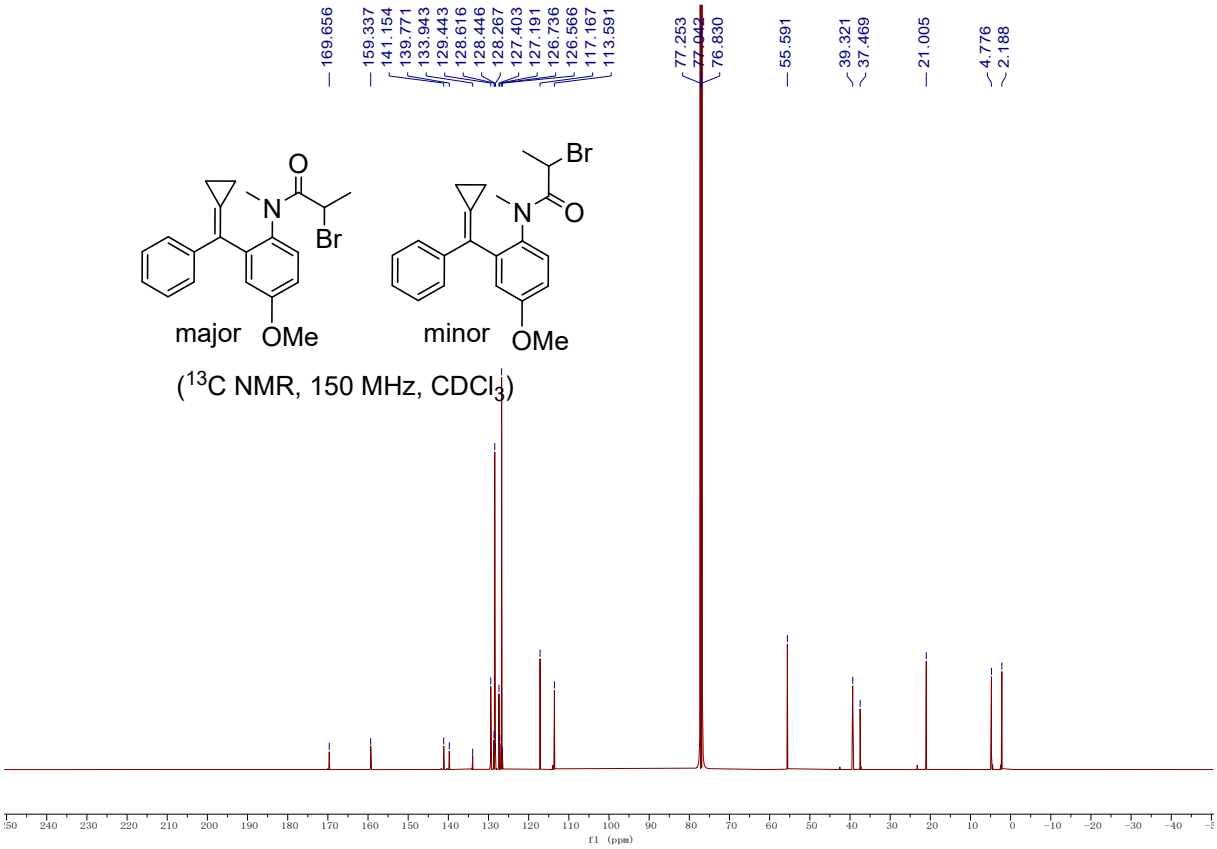


(^{13}C NMR, 150 MHz, $CDCl_3$)

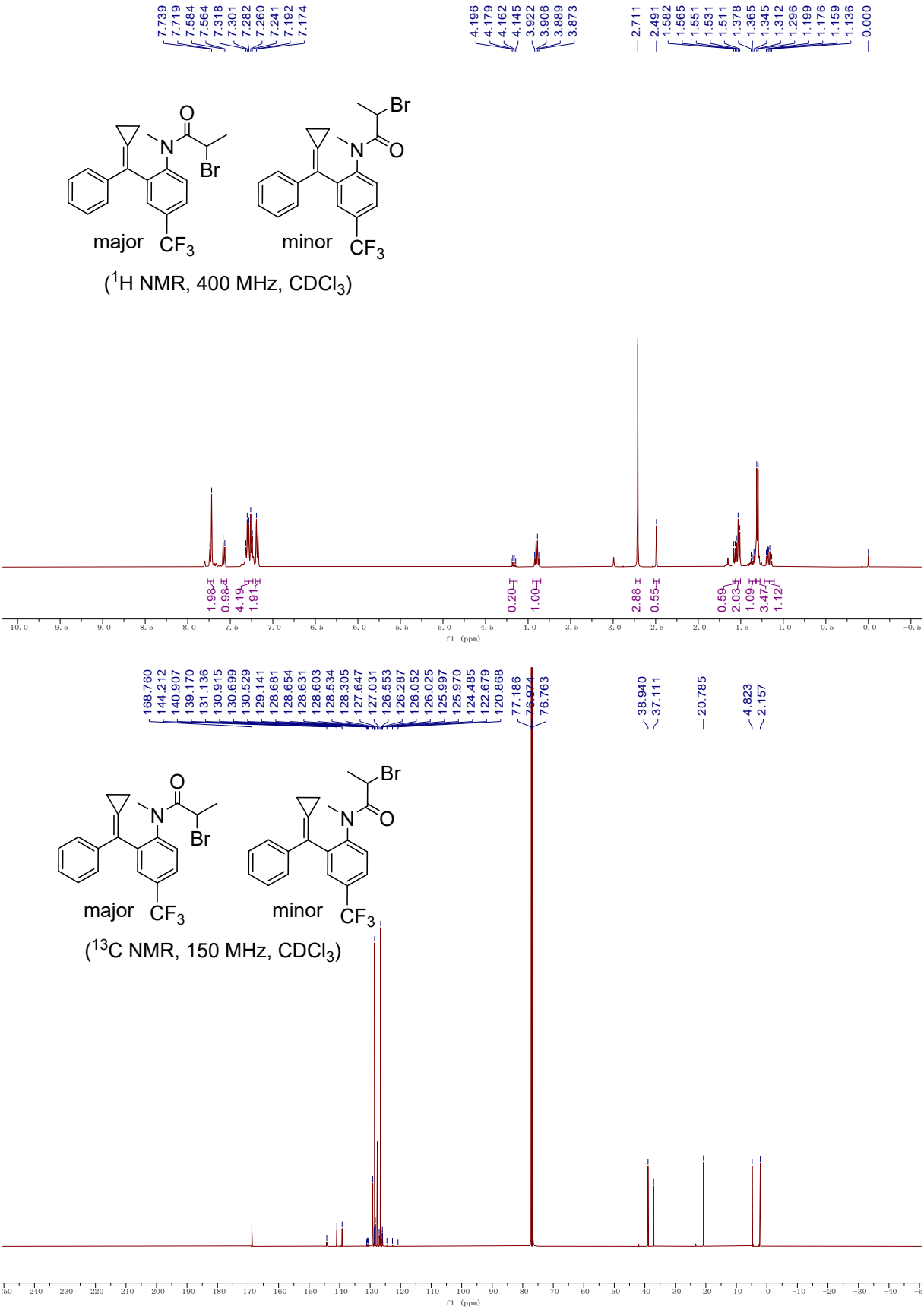


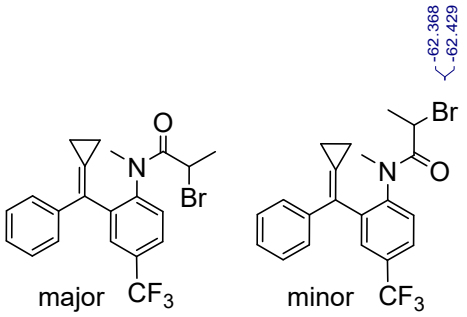
(^{1}H NMR, 400 MHz, $CDCl_3$)



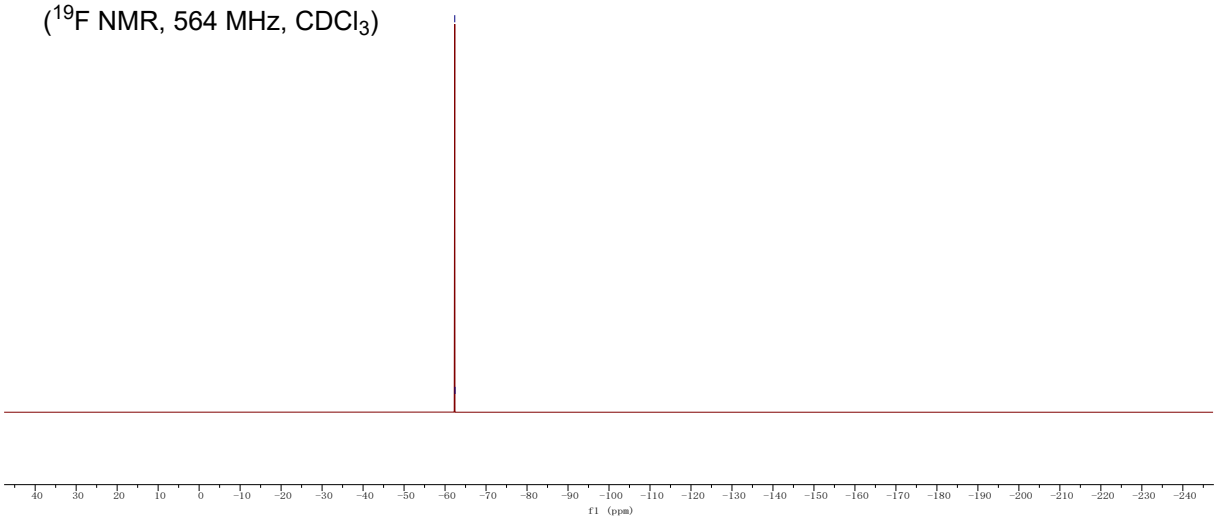


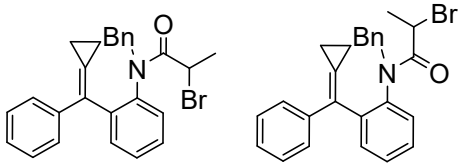
(^{13}C NMR, 150 MHz, $CDCl_3$)


major
minor
(^{1}H NMR, 400 MHz, $CDCl_3$)
major
minor
(^{13}C NMR, 150 MHz, $CDCl_3$)



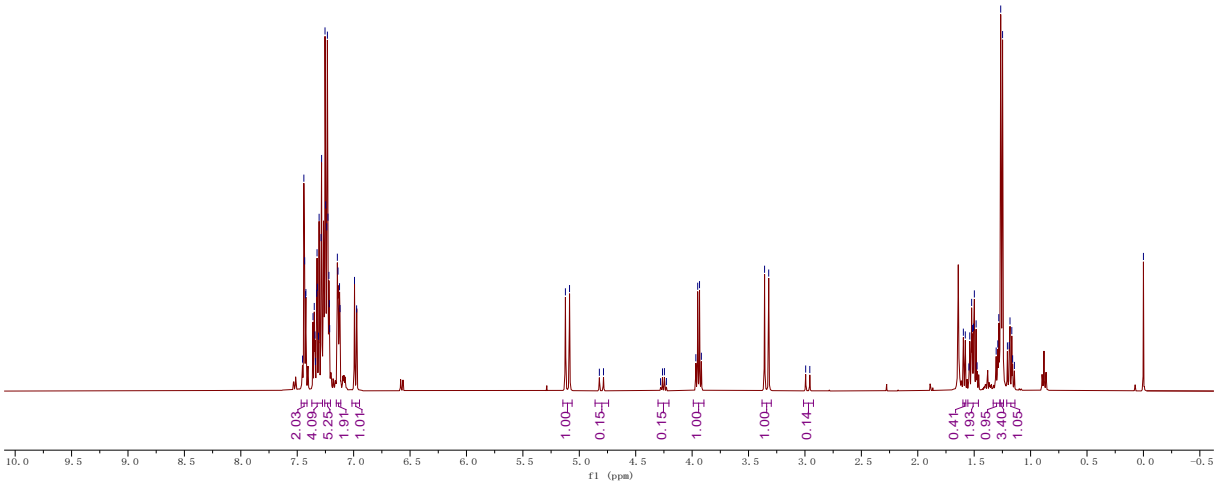
(^{19}F NMR, 564 MHz, $CDCl_3$)

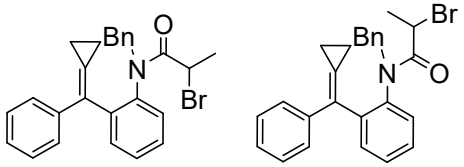




major minor

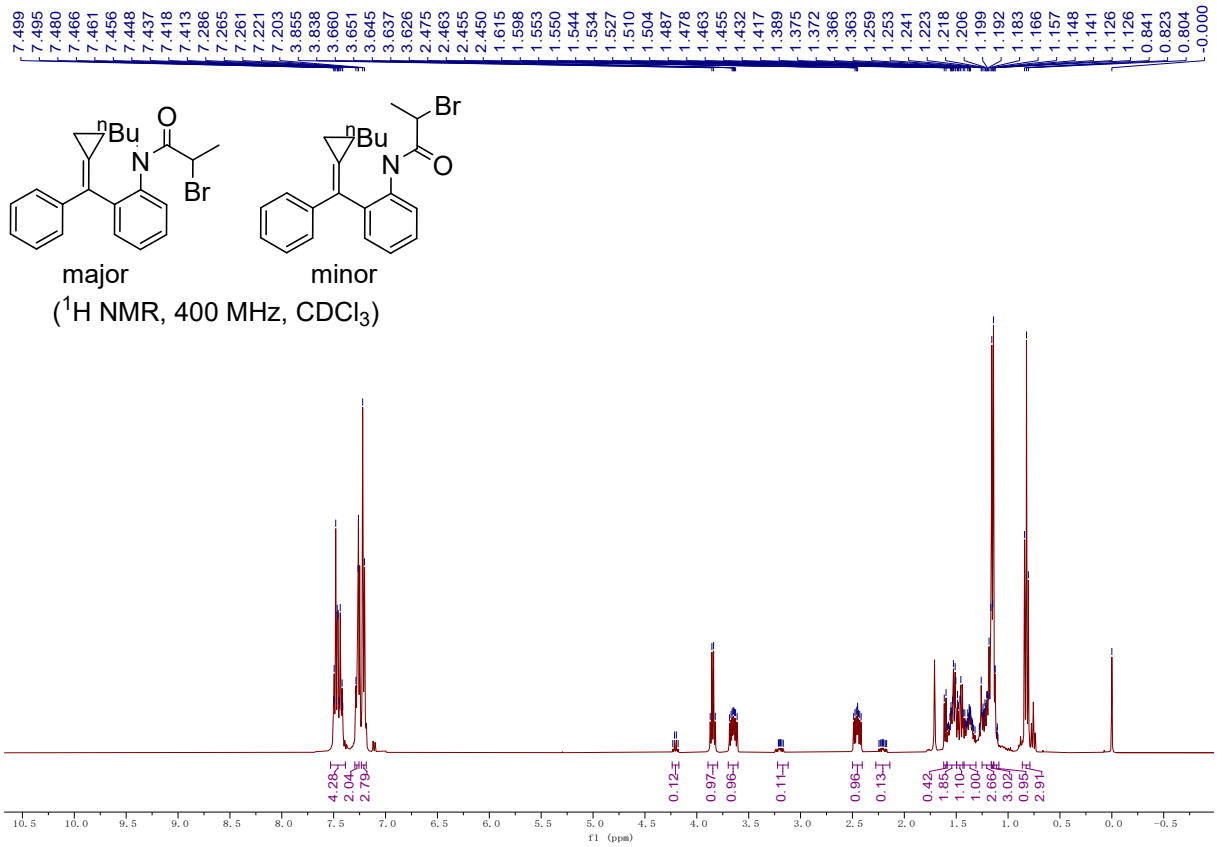
(^{1}H NMR, 400 MHz, $CDCl_3$)

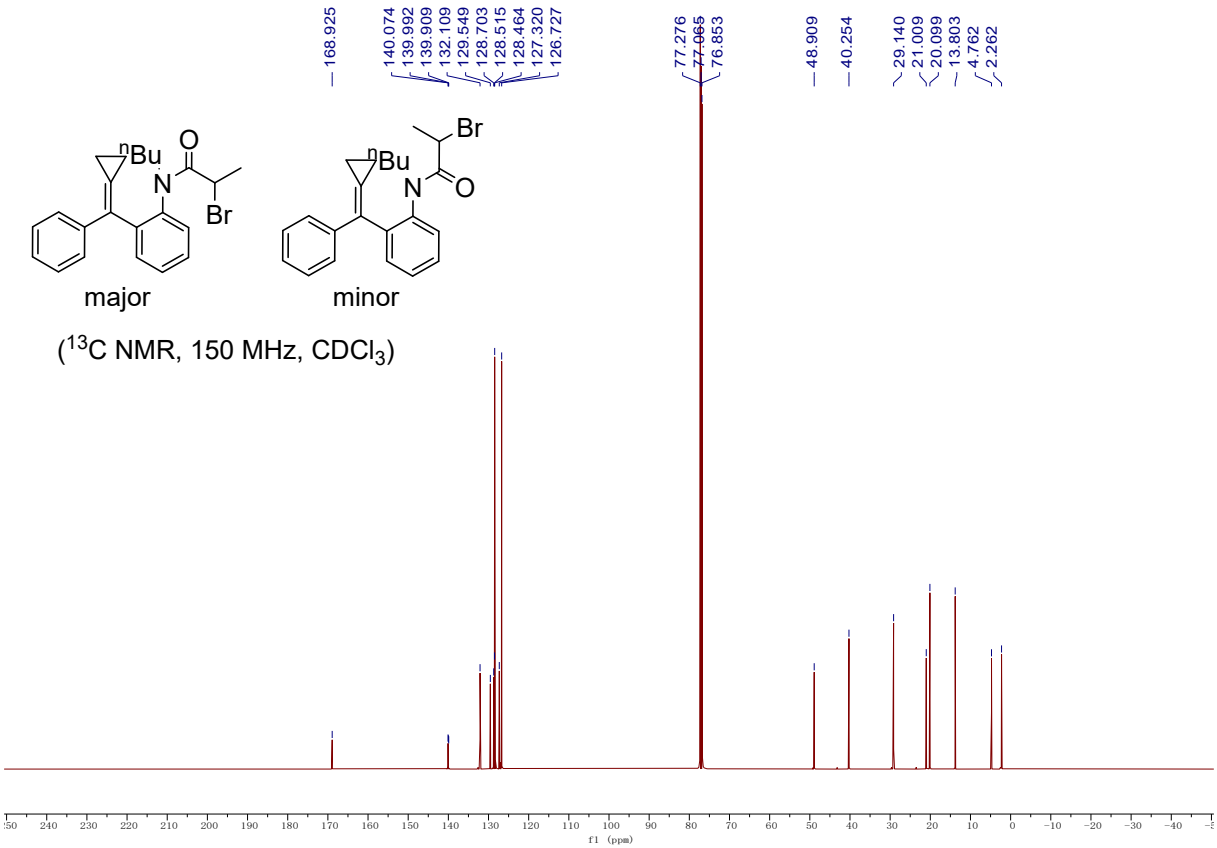


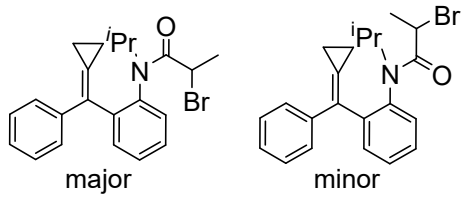


major minor

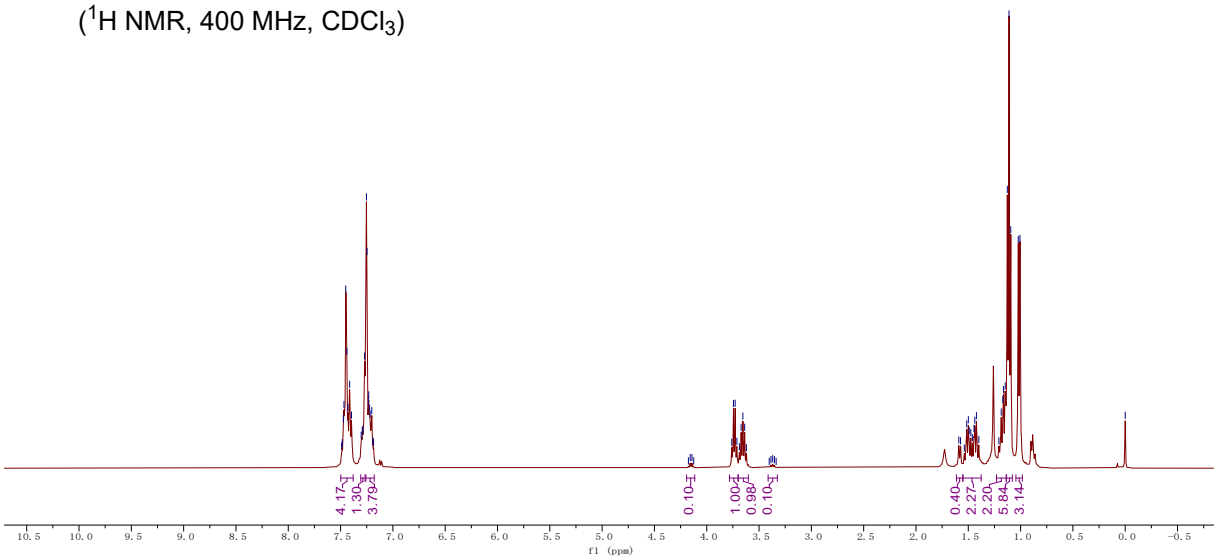
(^{13}C NMR, 100 MHz, $CDCl_3$)

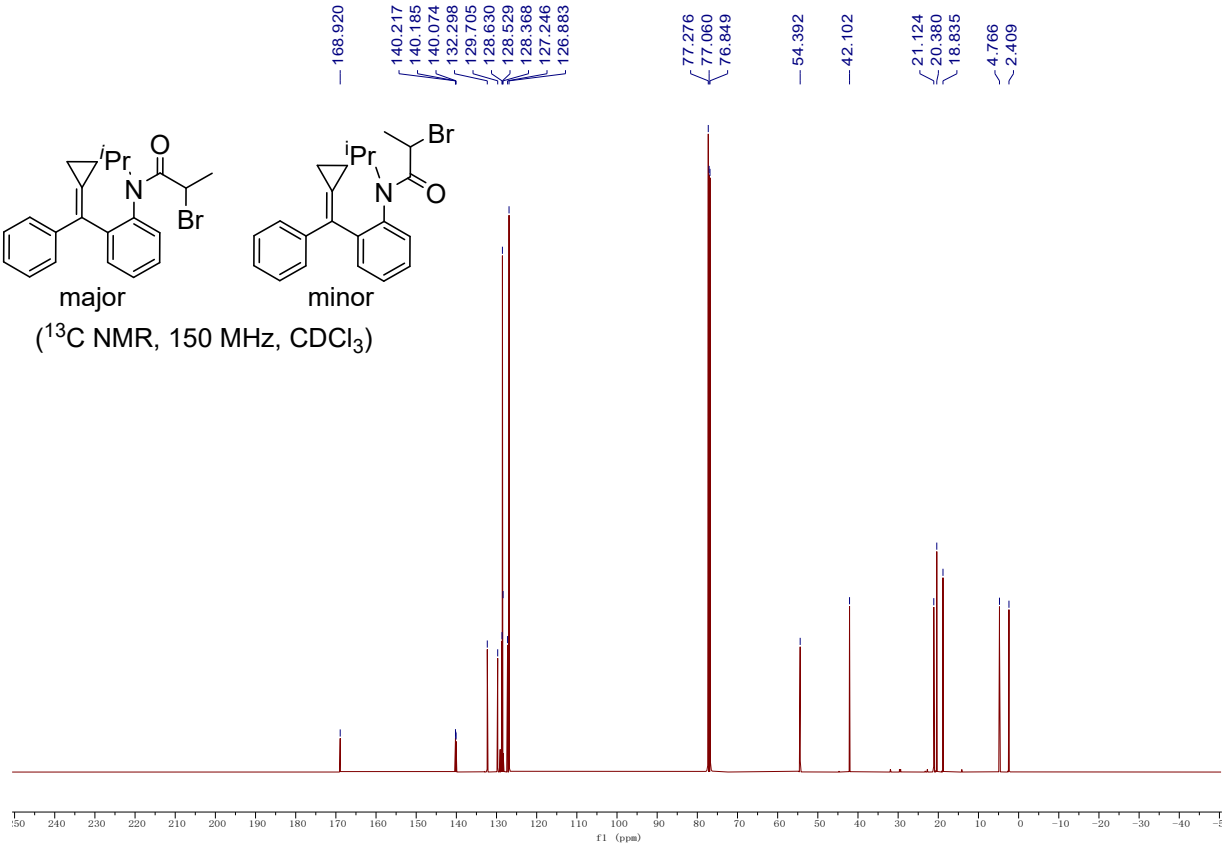

major
minor
(1H NMR, 400 MHz, CDCl3)


major
minor
(13C NMR, 150 MHz, CDCl3)

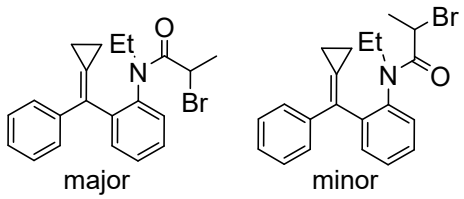


(^{1}H NMR, 400 MHz, $CDCl_3$)

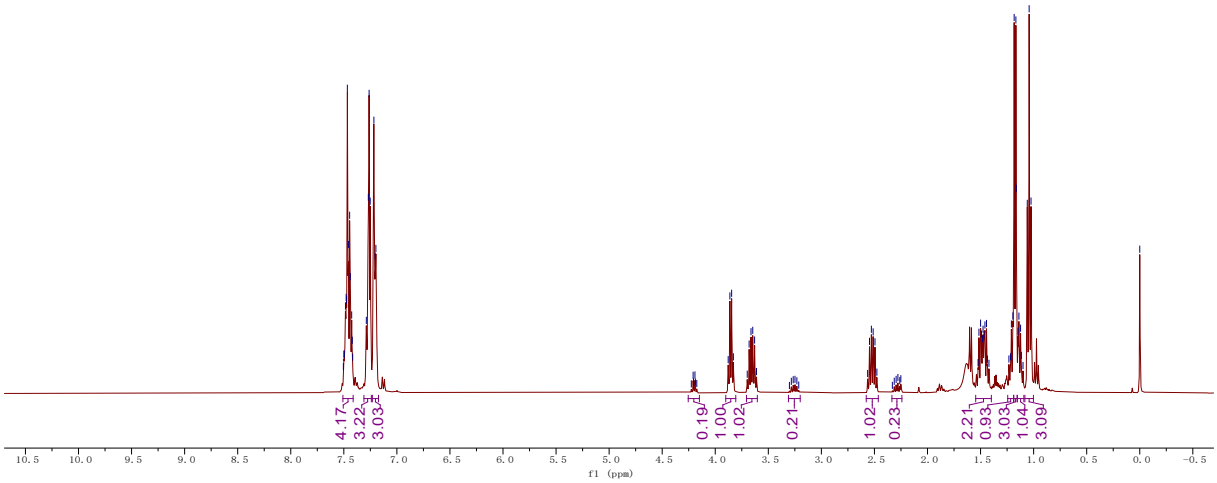


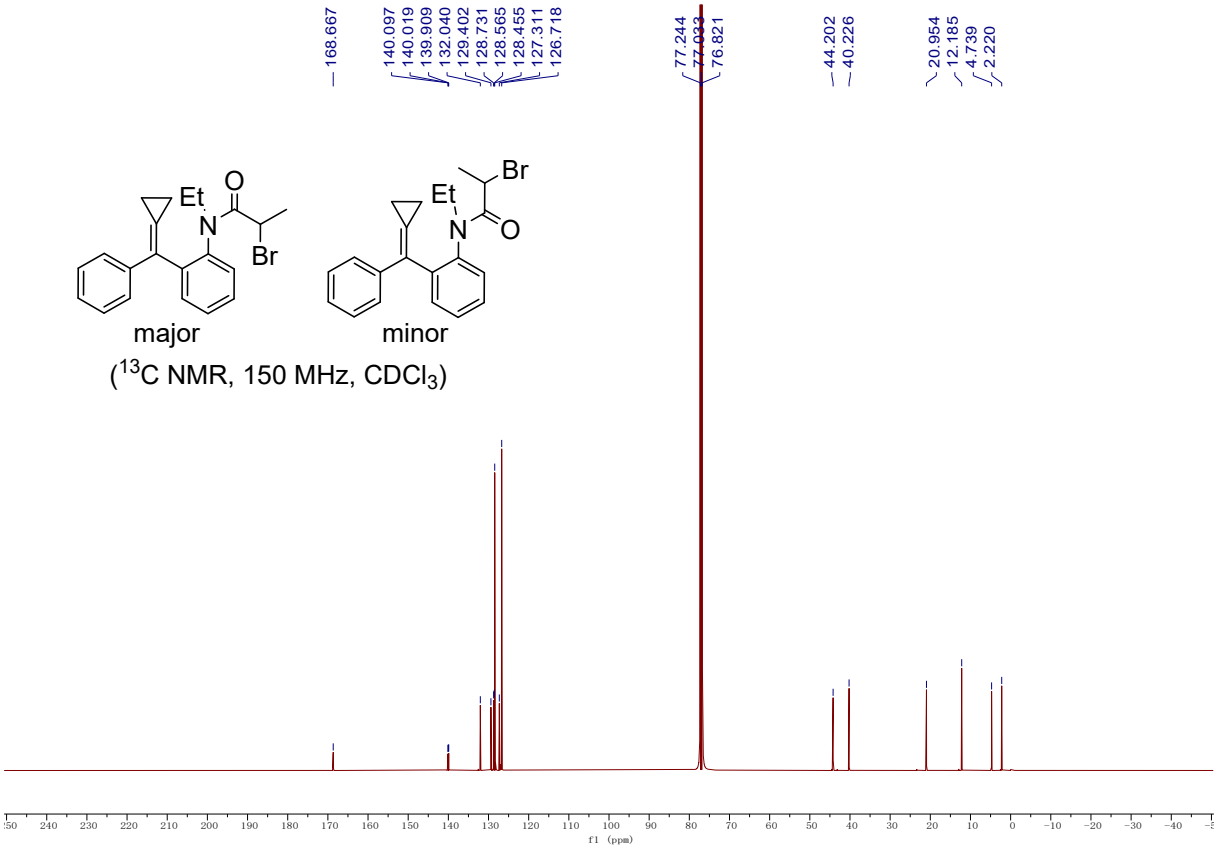


(^{13}C NMR, 150 MHz, $CDCl_3$)

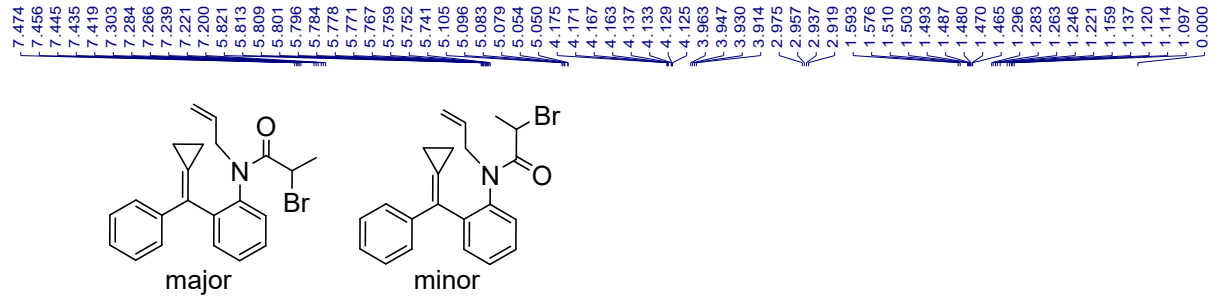


(^{1}H NMR, 400 MHz, $CDCl_3$)



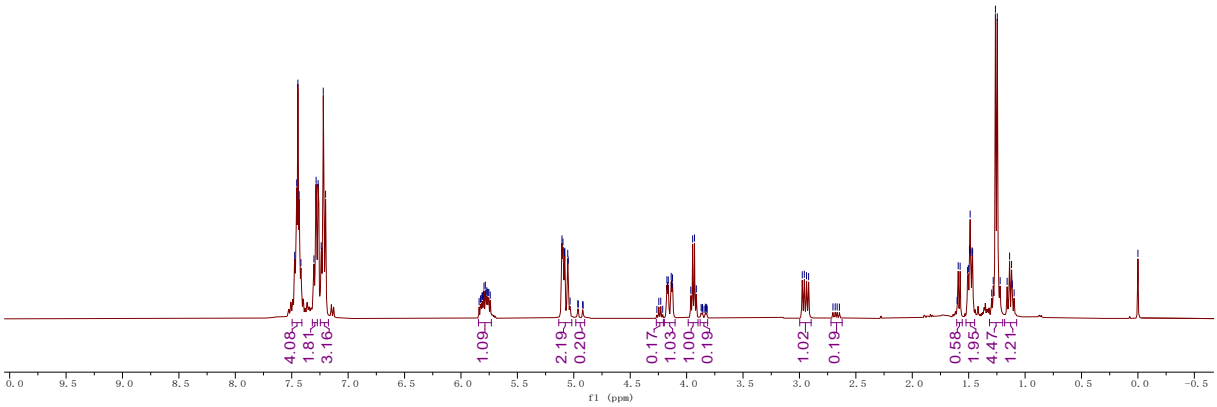


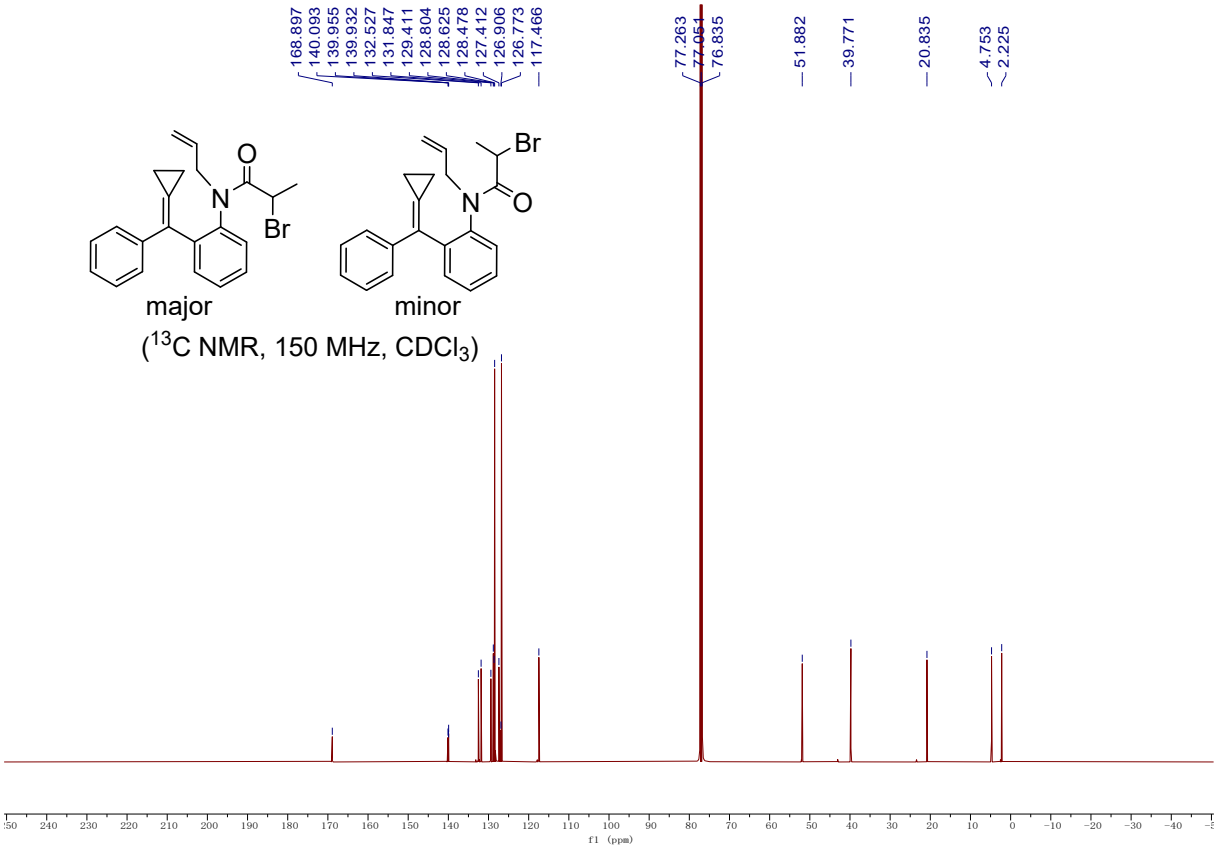
(^{13}C NMR, 150 MHz, $CDCl_3$)



major minor

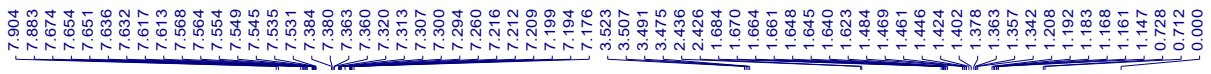
(^{1}H NMR, 400 MHz, $CDCl_3$)

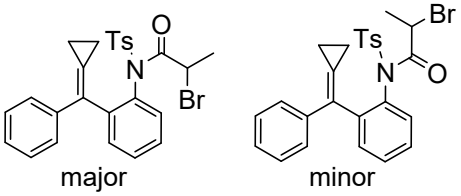




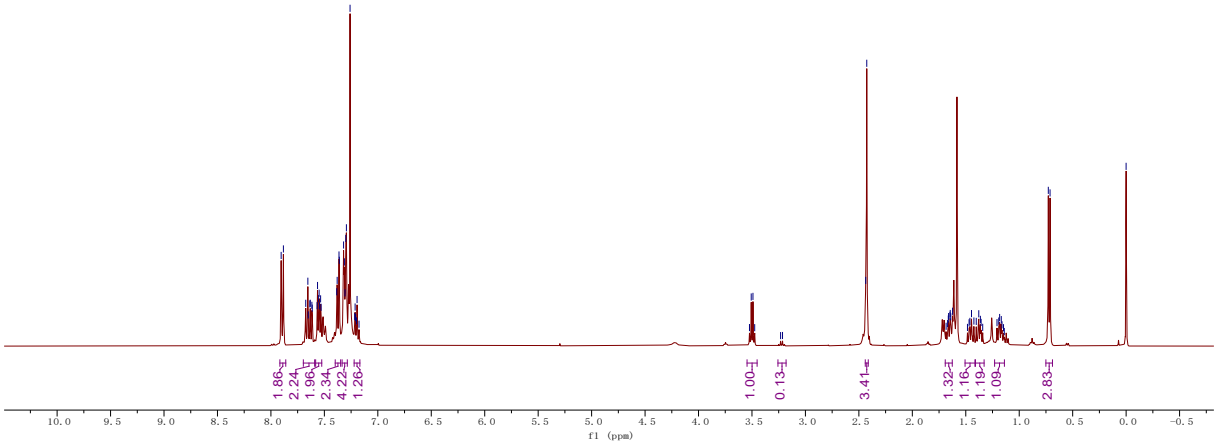
major minor

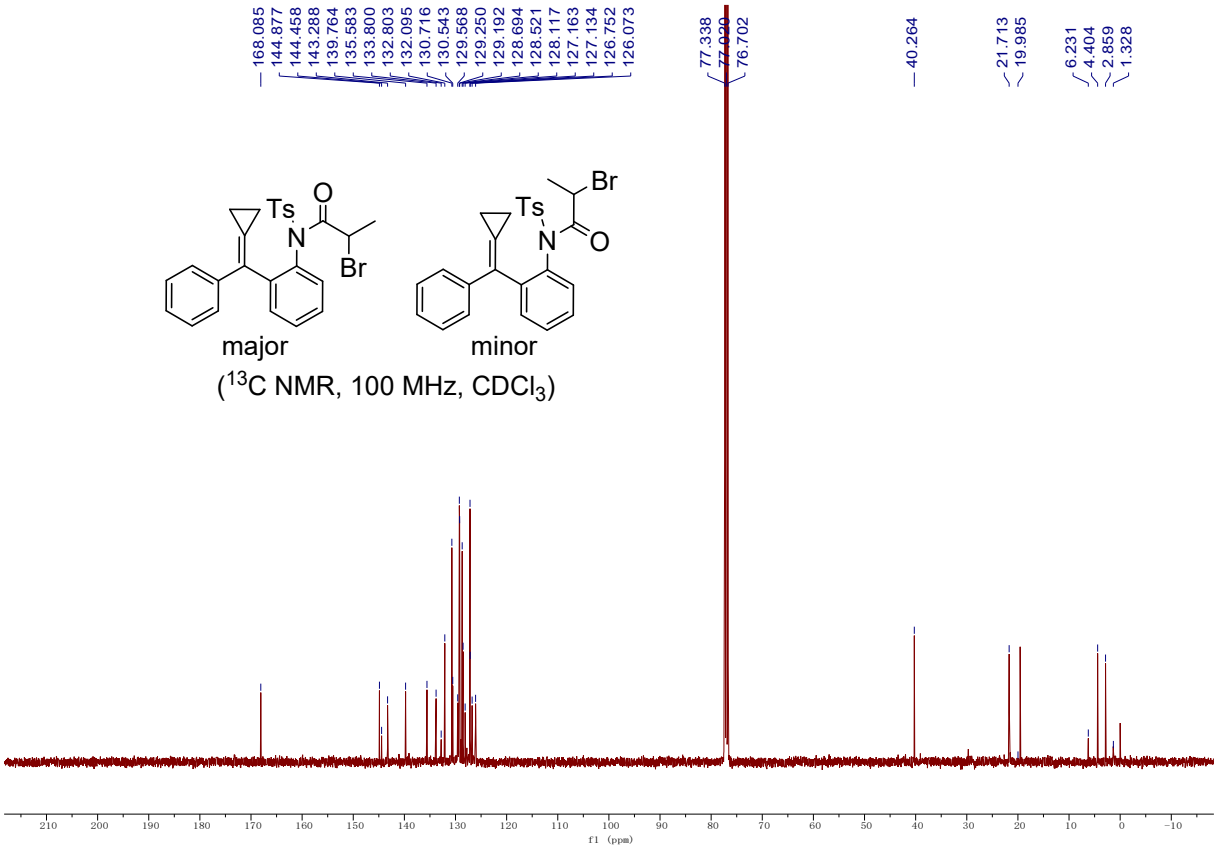
(^{13}C NMR, 150 MHz, $CDCl_3$)



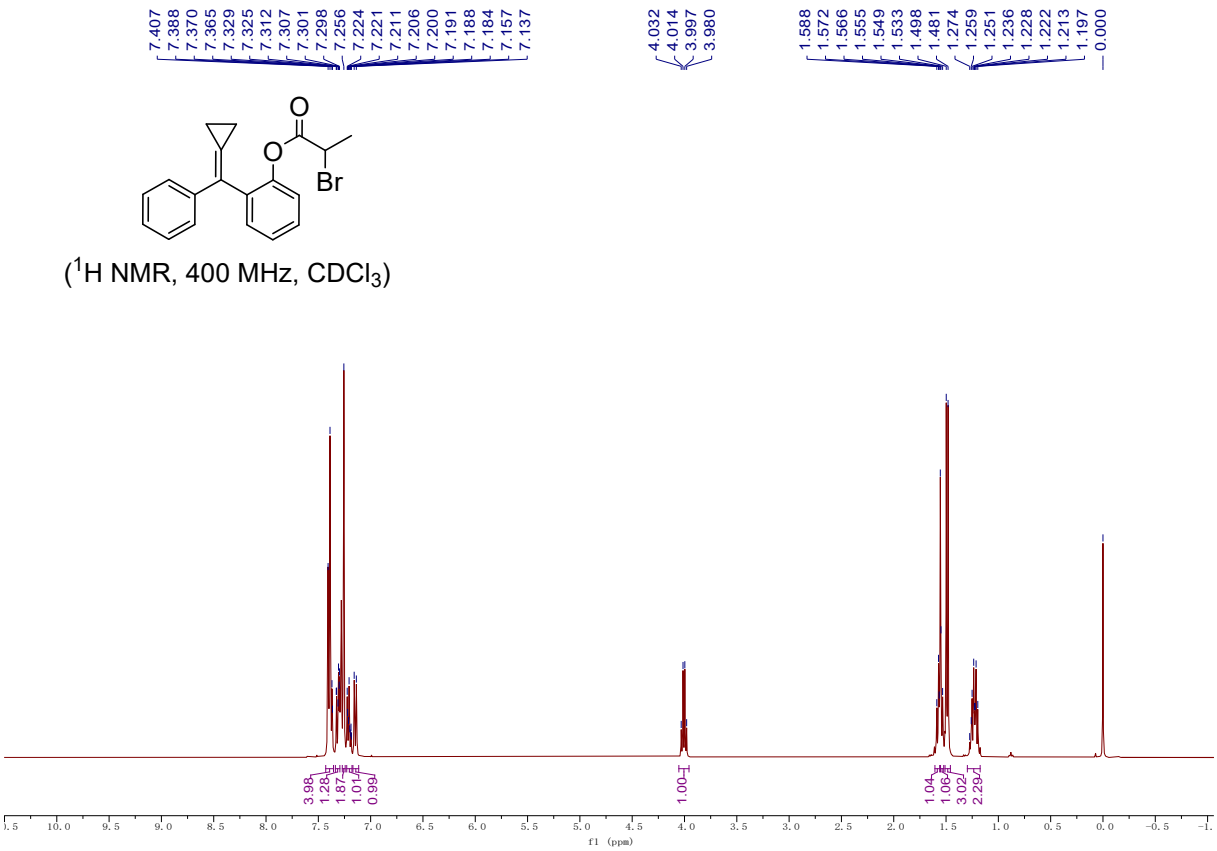


(^{1}H NMR, 400 MHz, $CDCl_3$)

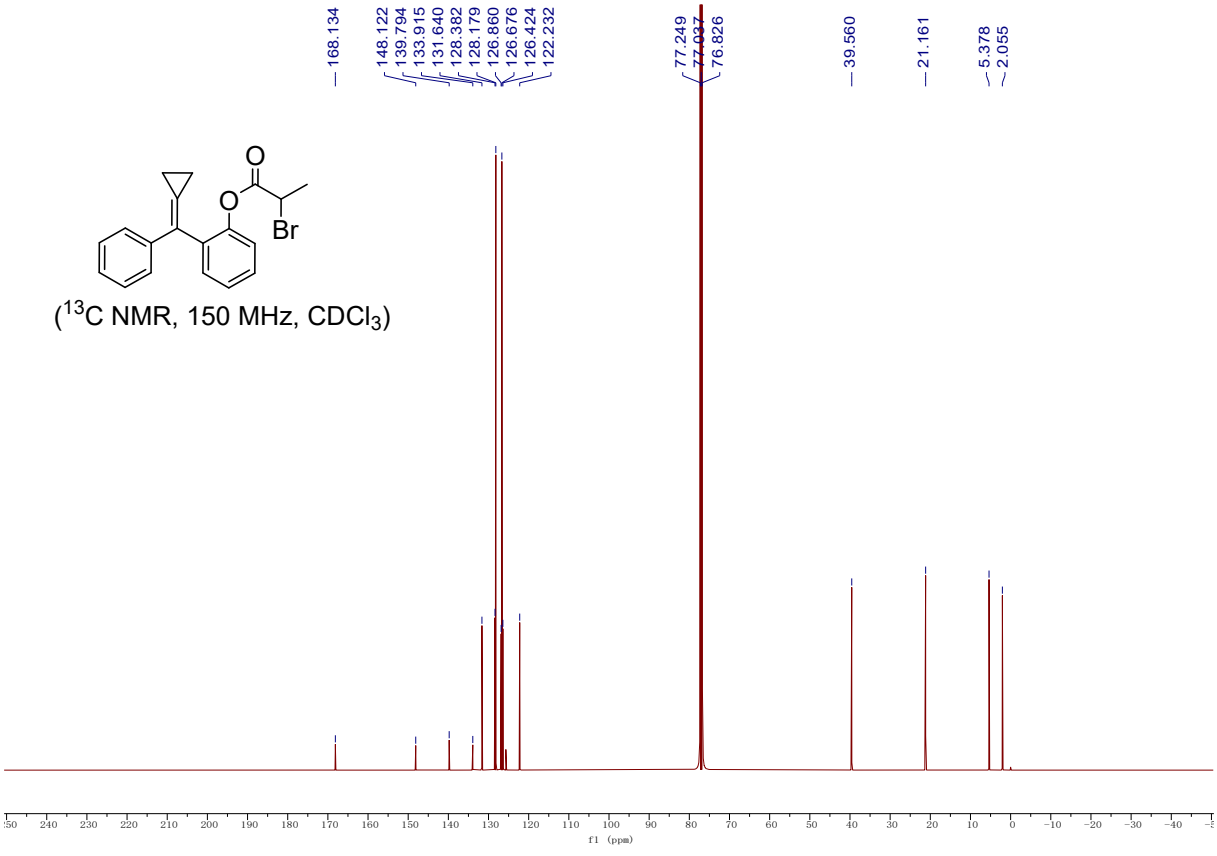




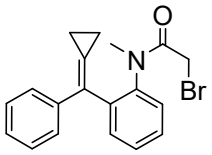
(^{13}C NMR, 100 MHz, $CDCl_3$)



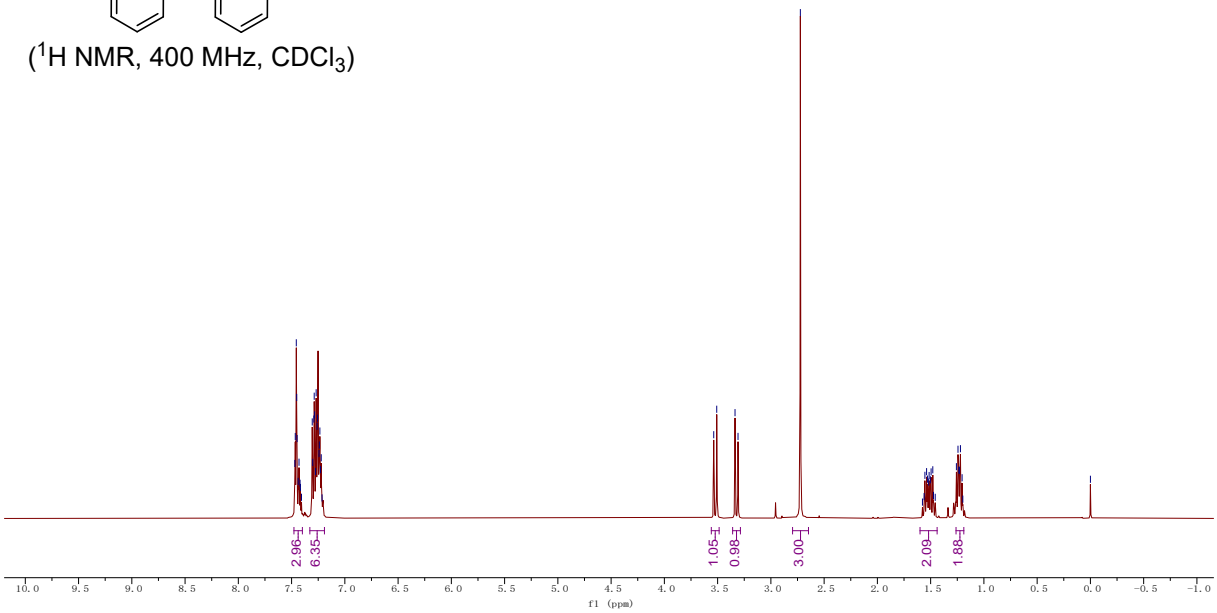
(^{1}H NMR, 400 MHz, $CDCl_3$)

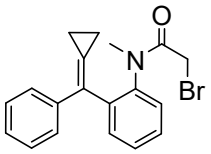


(^{13}C NMR, 150 MHz, $CDCl_3$)

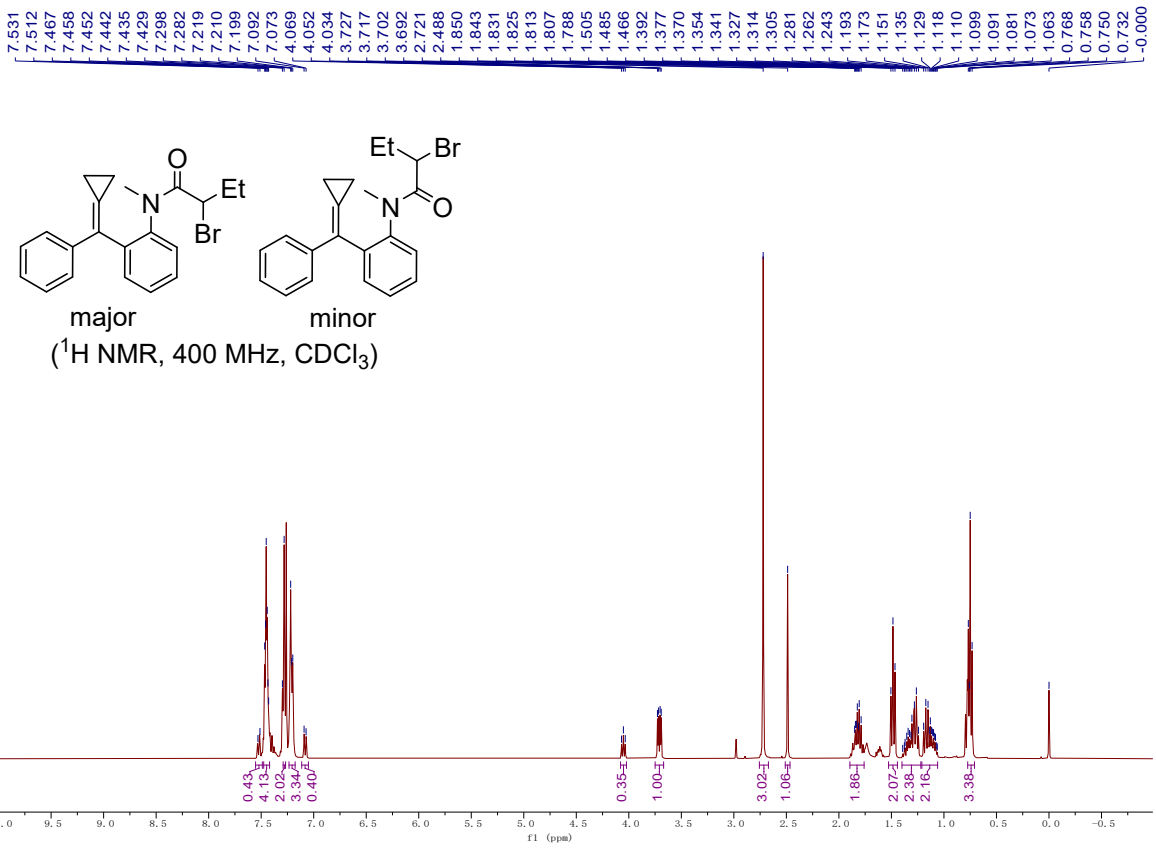


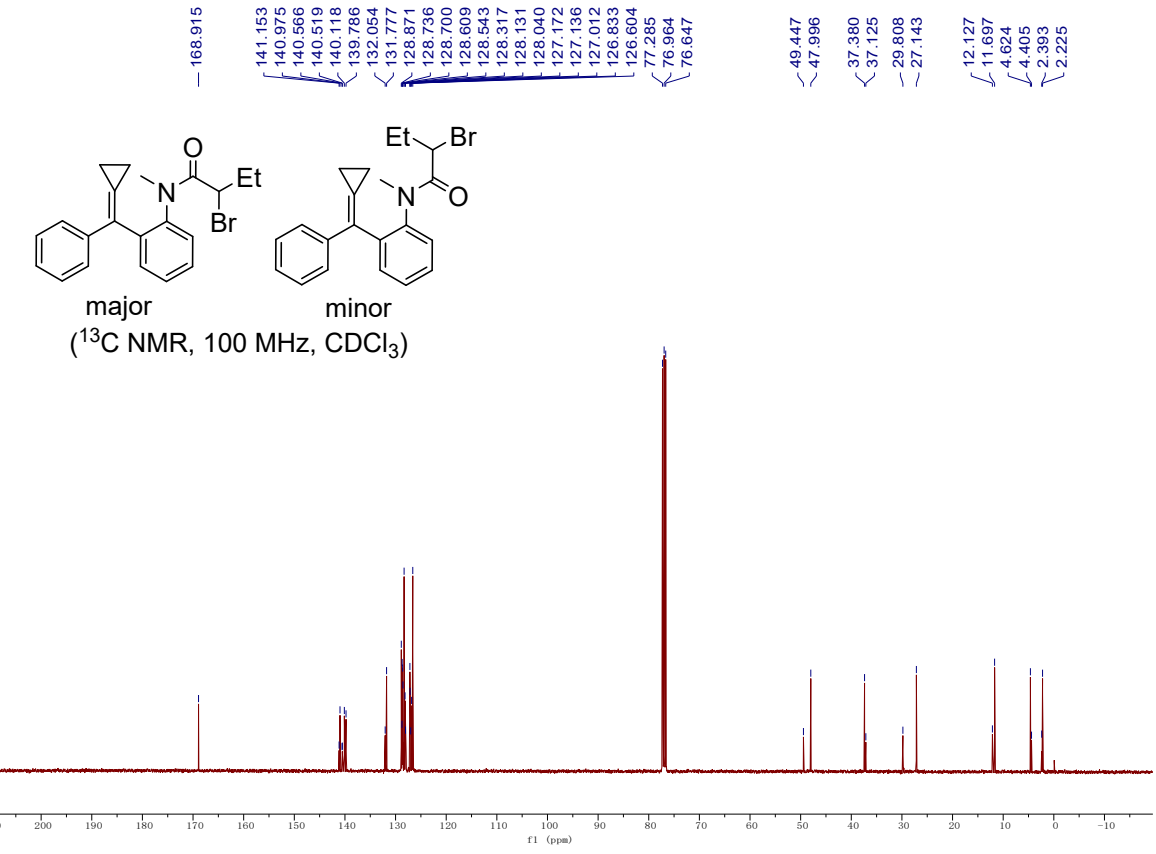
(^{1}H NMR, 400 MHz, $CDCl_3$)

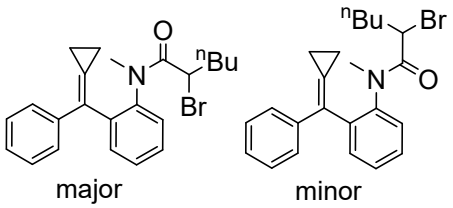




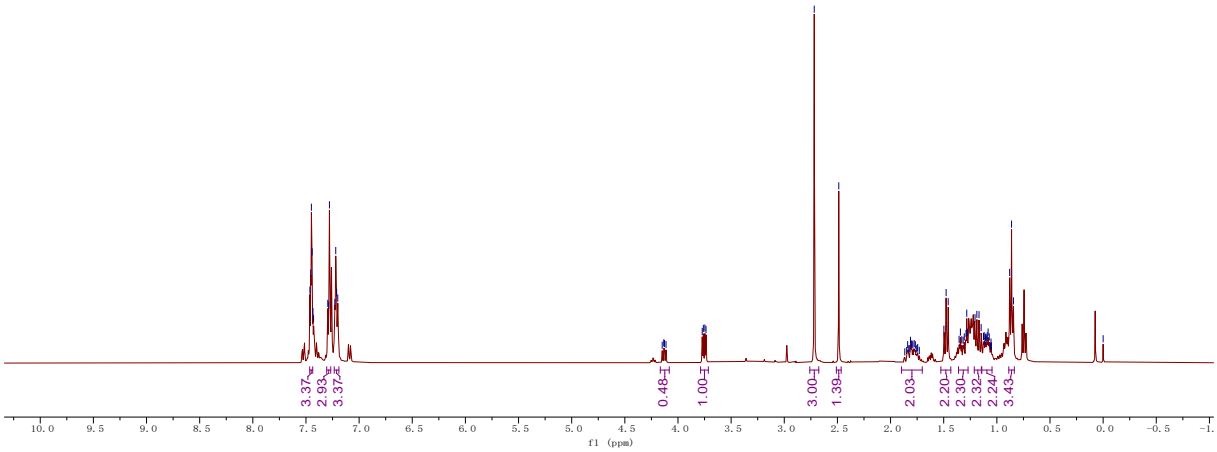
(^{13}C NMR, 150 MHz, $CDCl_3$)

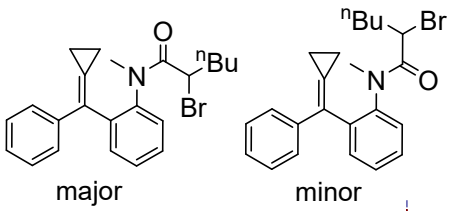

major
minor
(1H NMR, 400 MHz, CDCl3)


major
minor
(13C NMR, 100 MHz, CDCl3)

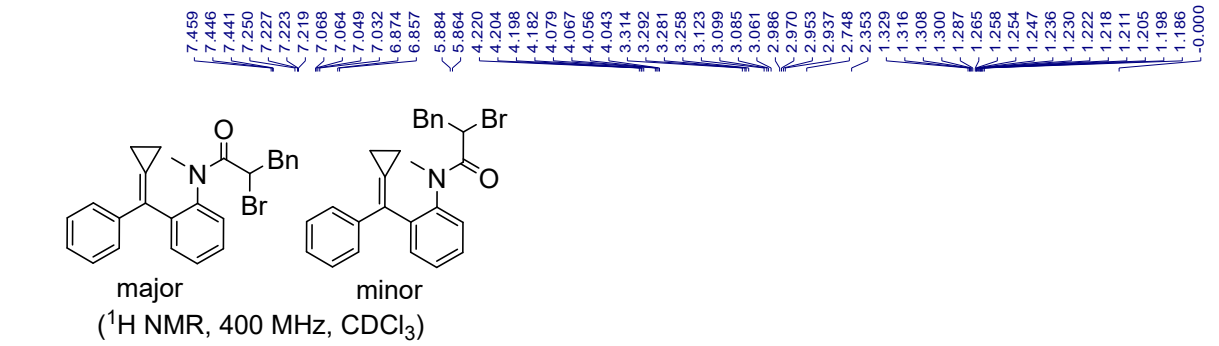


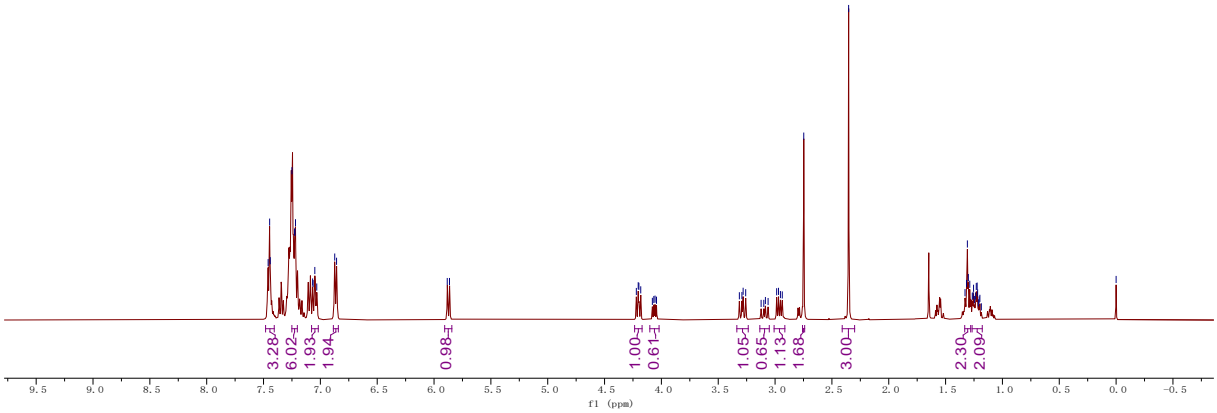
(^{1}H NMR, 400 MHz, $CDCl_3$)

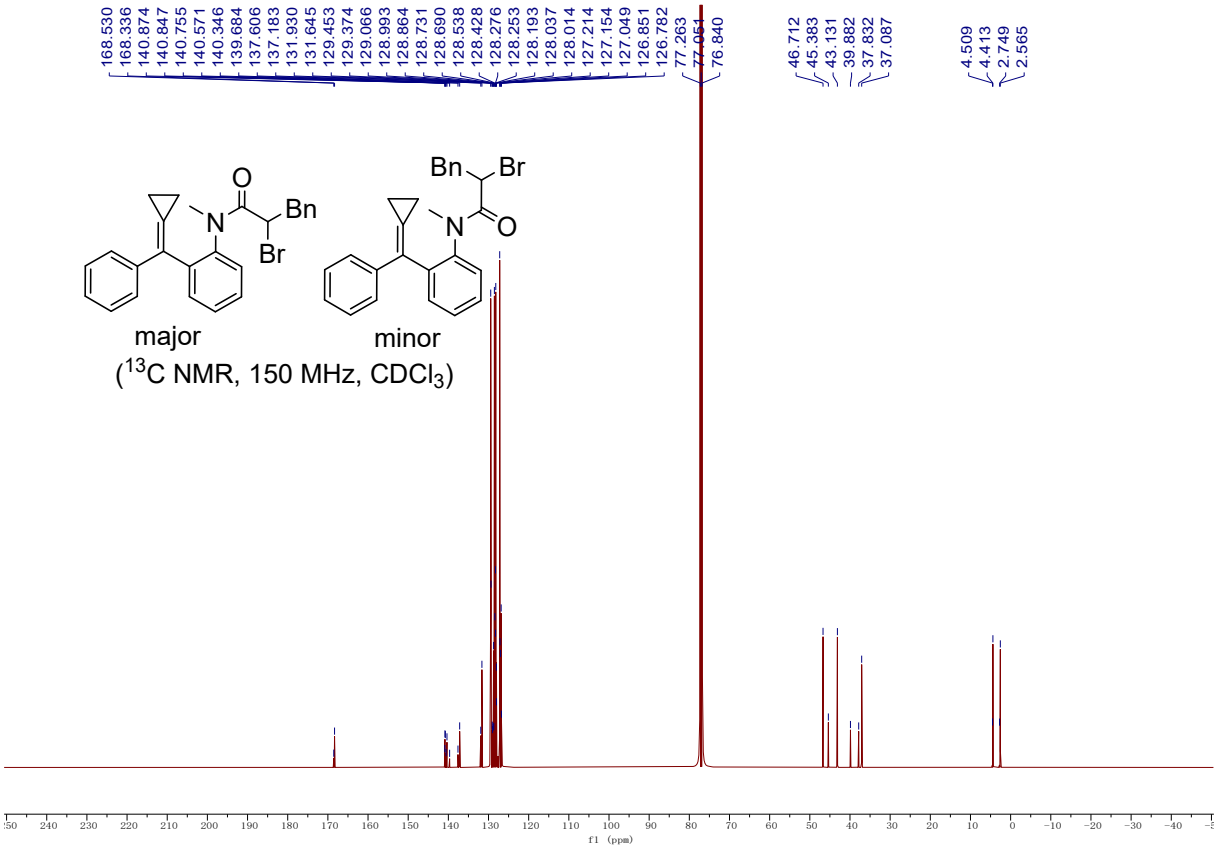


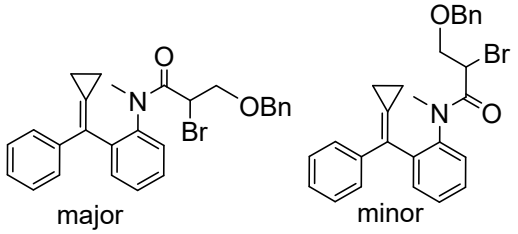


(^{13}C NMR, 150 MHz, $CDCl_3$)

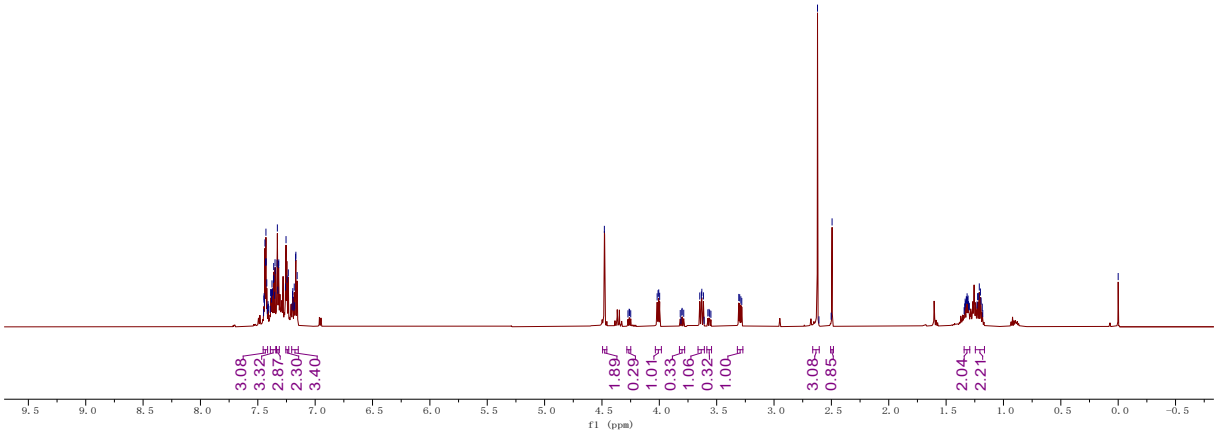

major
minor
(1H NMR, 400 MHz, CDCl3)

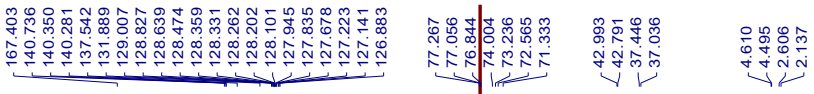


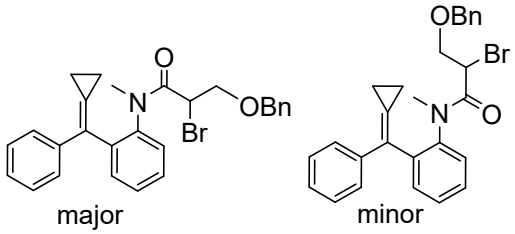

major
minor
(13C NMR, 150 MHz, CDCl3)



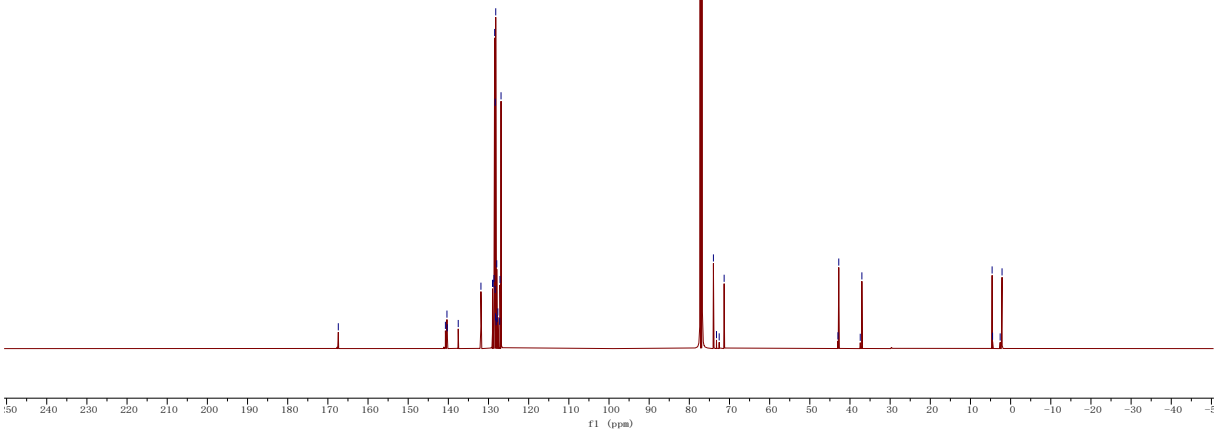
(^{1}H NMR, 400 MHz, $CDCl_3$)

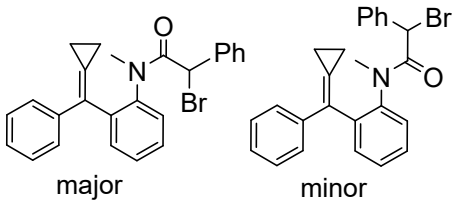






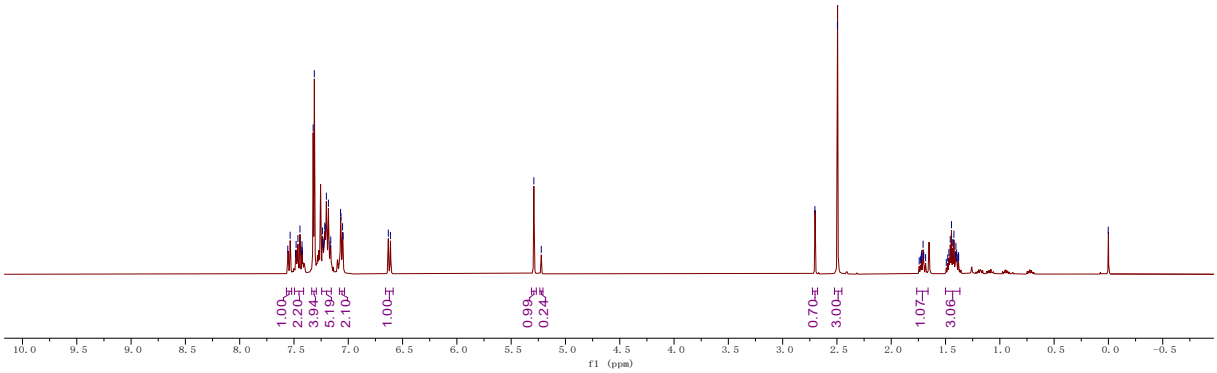
(^{13}C NMR, 150 MHz, $CDCl_3$)

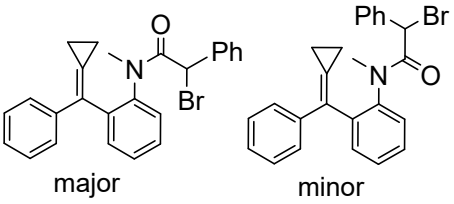




major minor

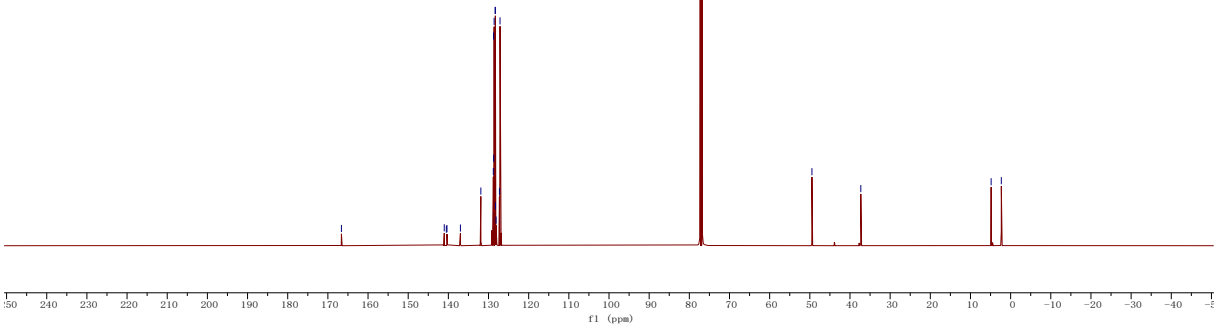
(^{1}H NMR, 400 MHz, $CDCl_3$)

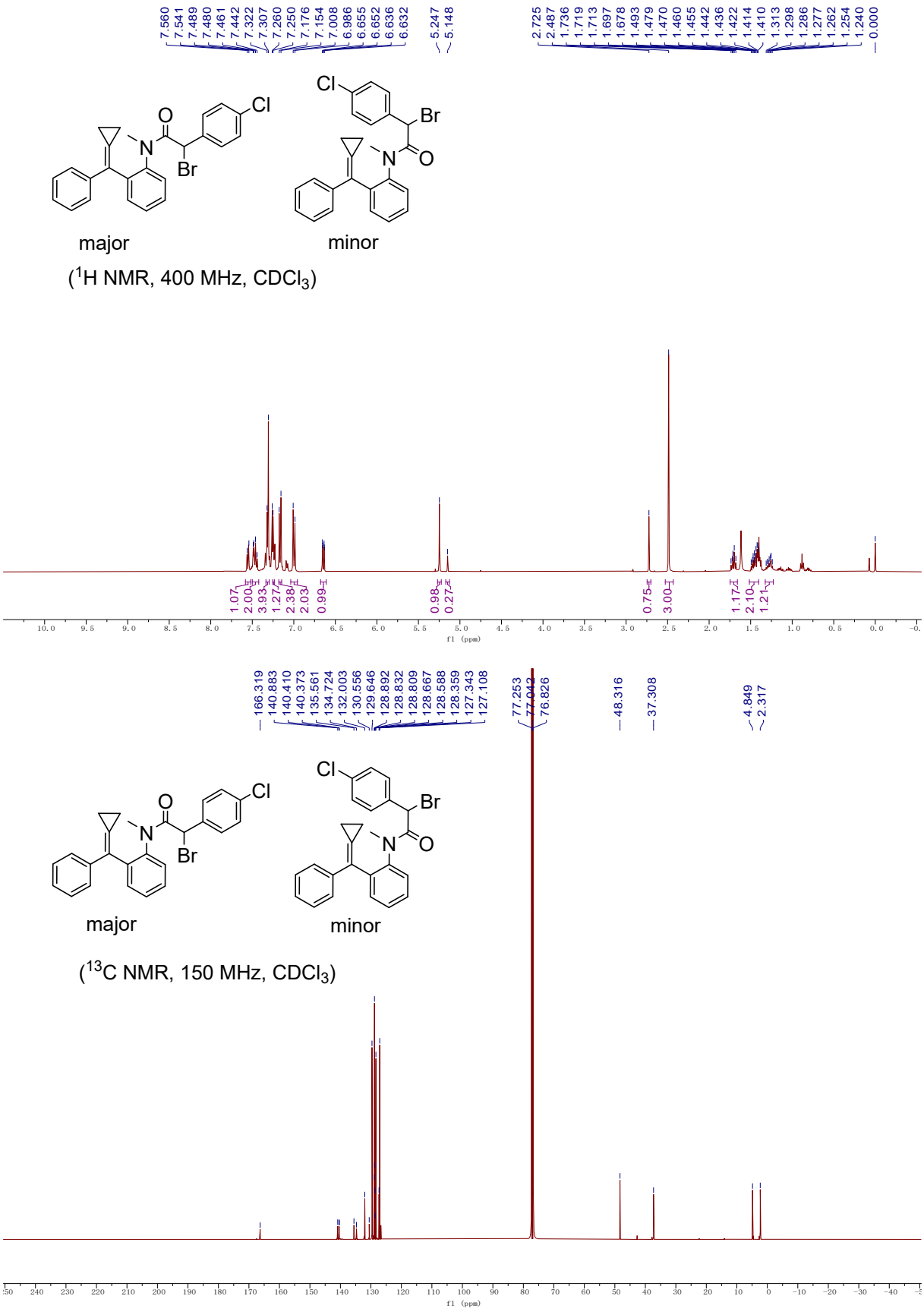


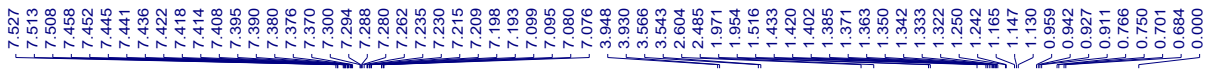


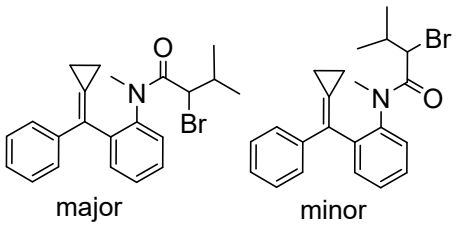
major minor

(^{13}C NMR, 150 MHz, $CDCl_3$)



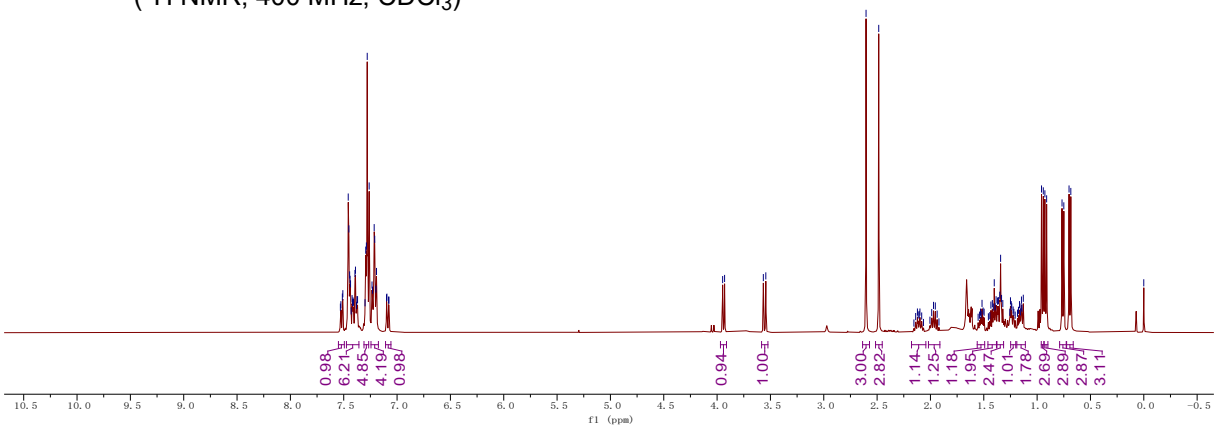

major
minor
(1H NMR, 400 MHz, CDCl3)
major
minor
(13C NMR, 150 MHz, CDCl3)

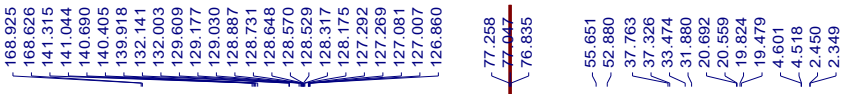


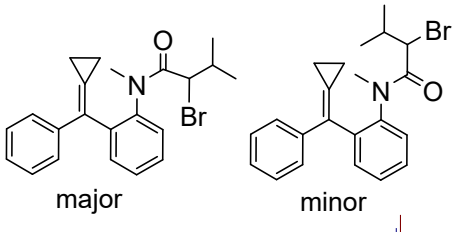


major minor

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

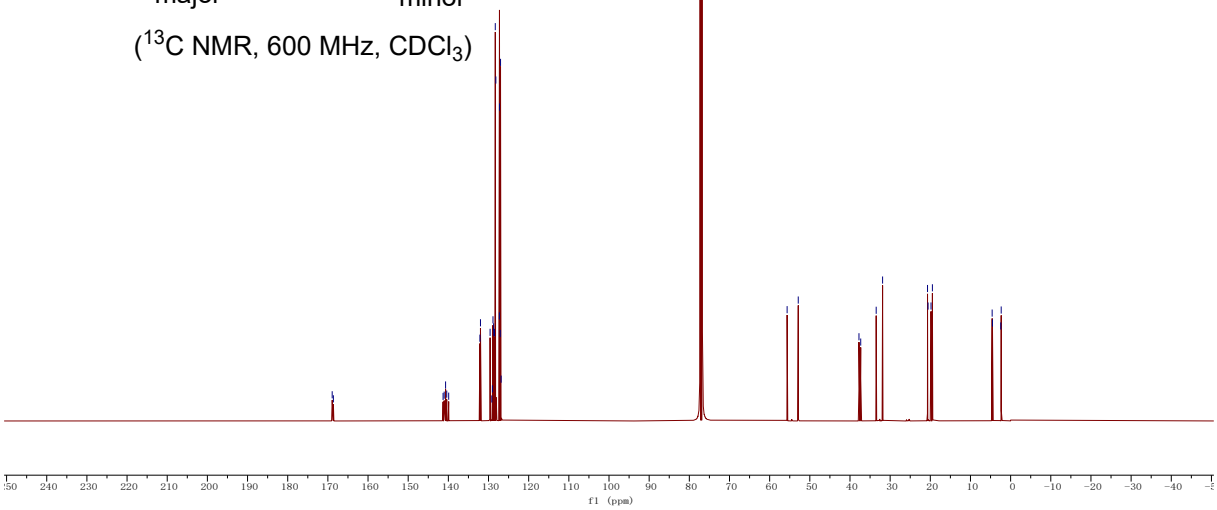


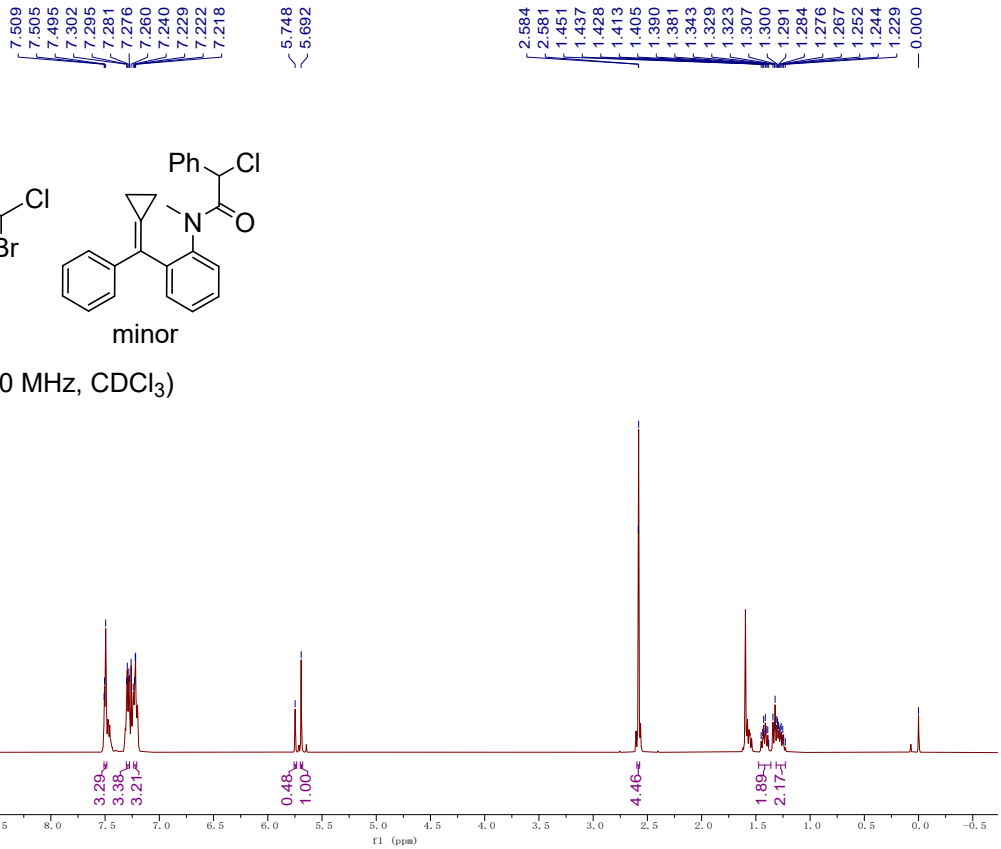




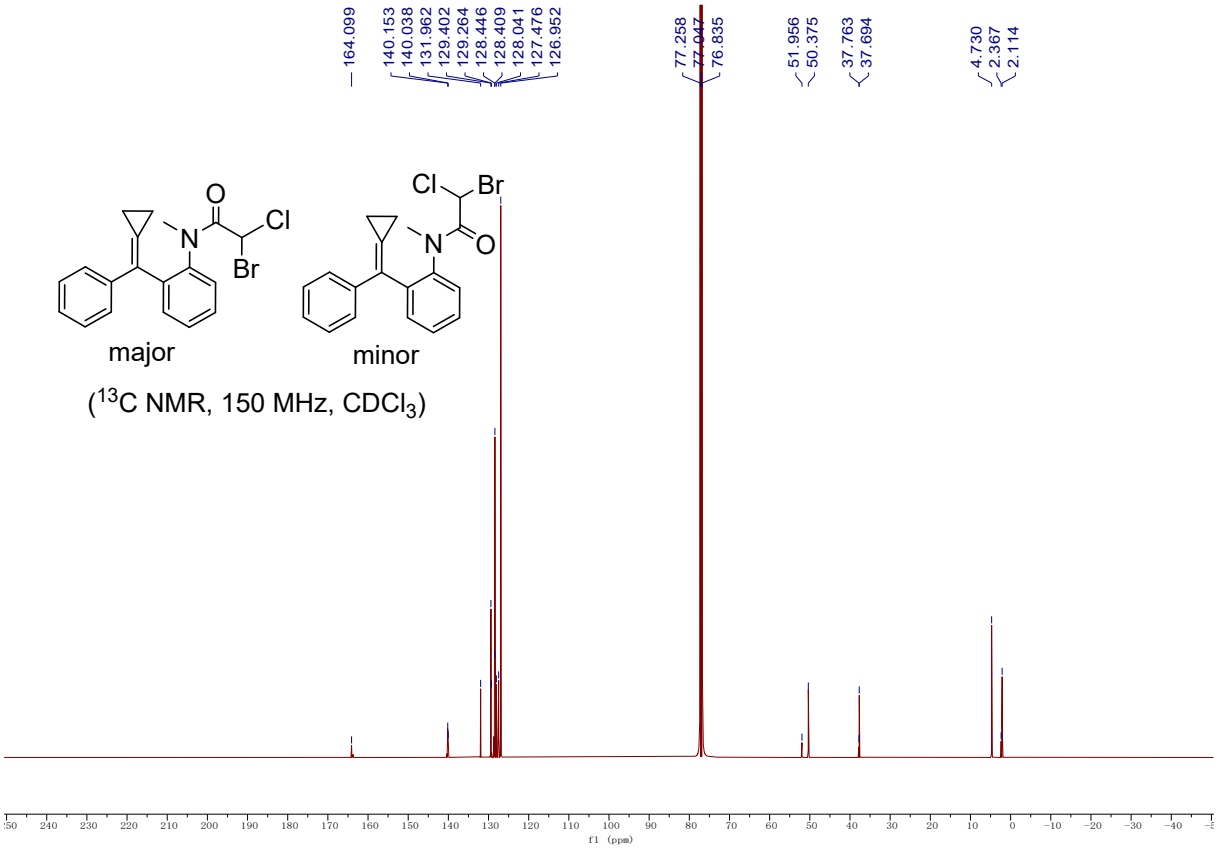
major minor

(^{13}C NMR, 600 MHz, $CDCl_3$)



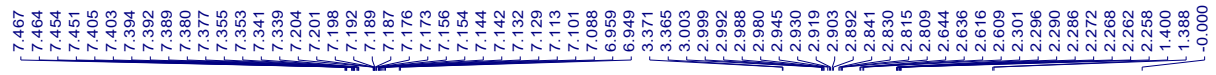


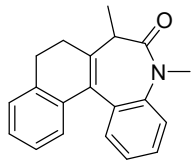
(^{1}H NMR, 400 MHz, $CDCl_3$)



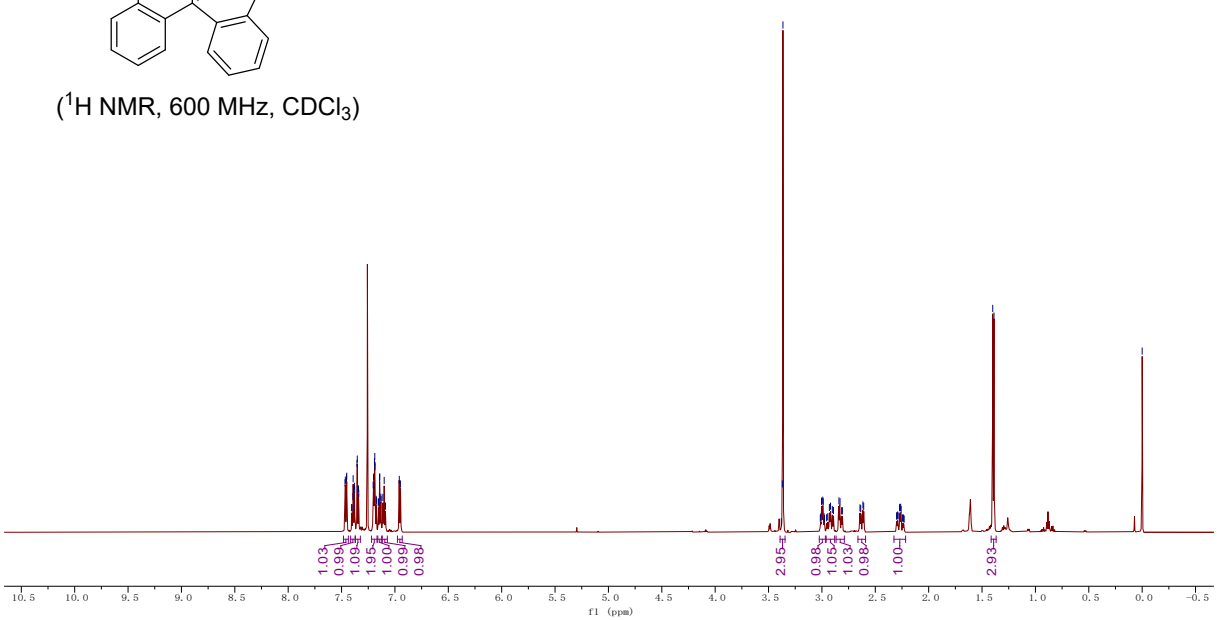
(^{13}C NMR, 150 MHz, $CDCl_3$)

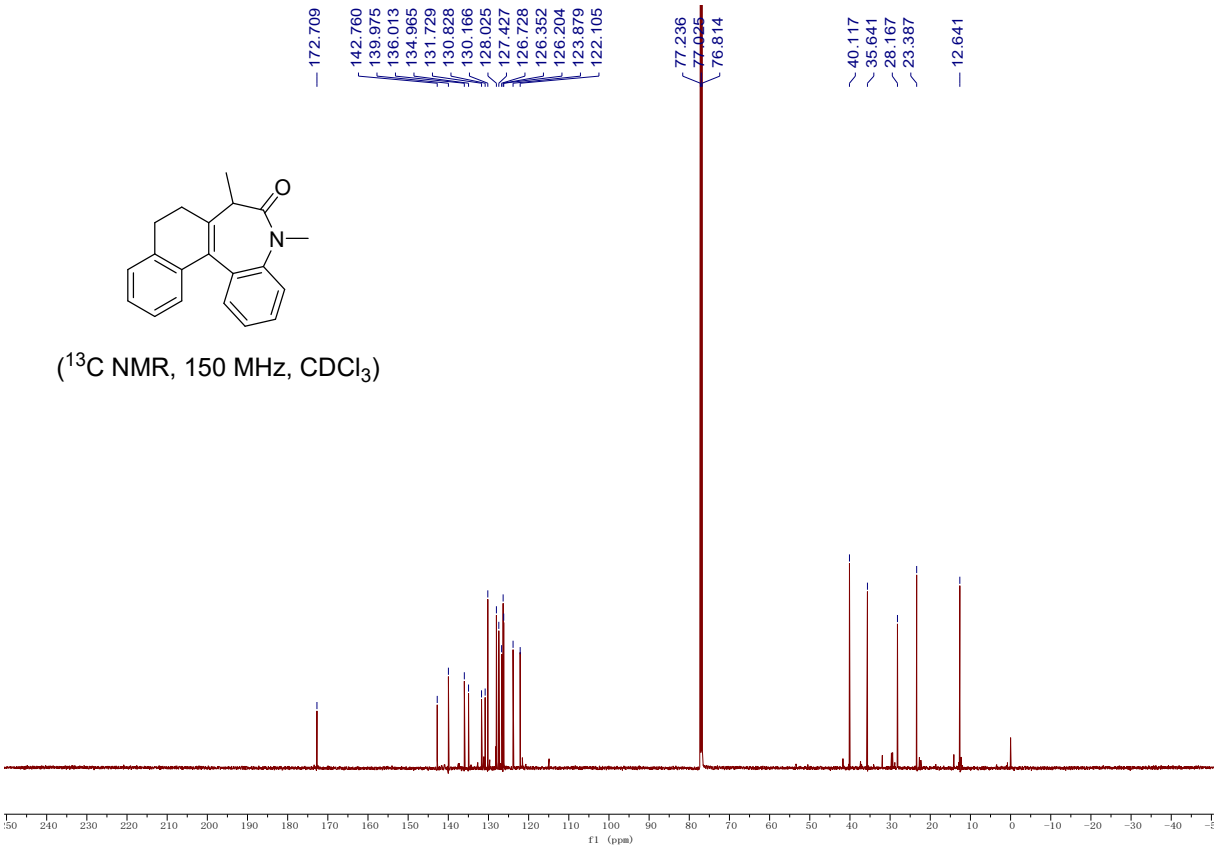
11. Spectroscopic Data of Products (NMR Spectrum)



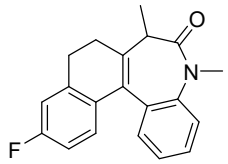


(^{1}H NMR, 600 MHz, $CDCl_3$)

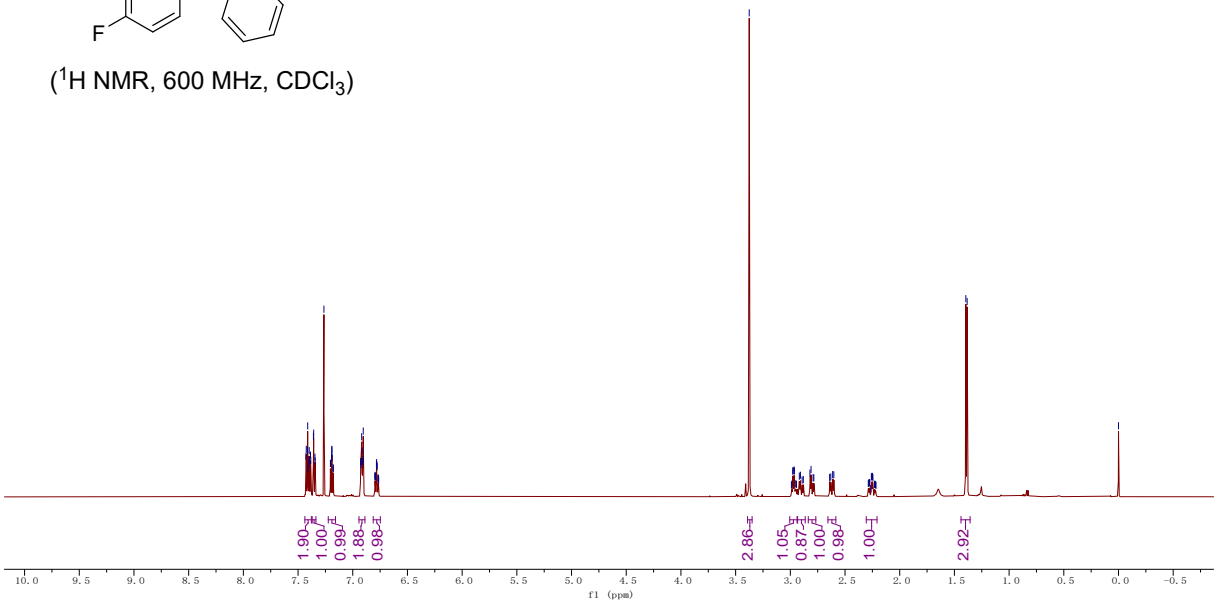


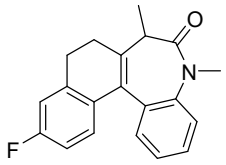


(^{13}C NMR, 150 MHz, $CDCl_3$)

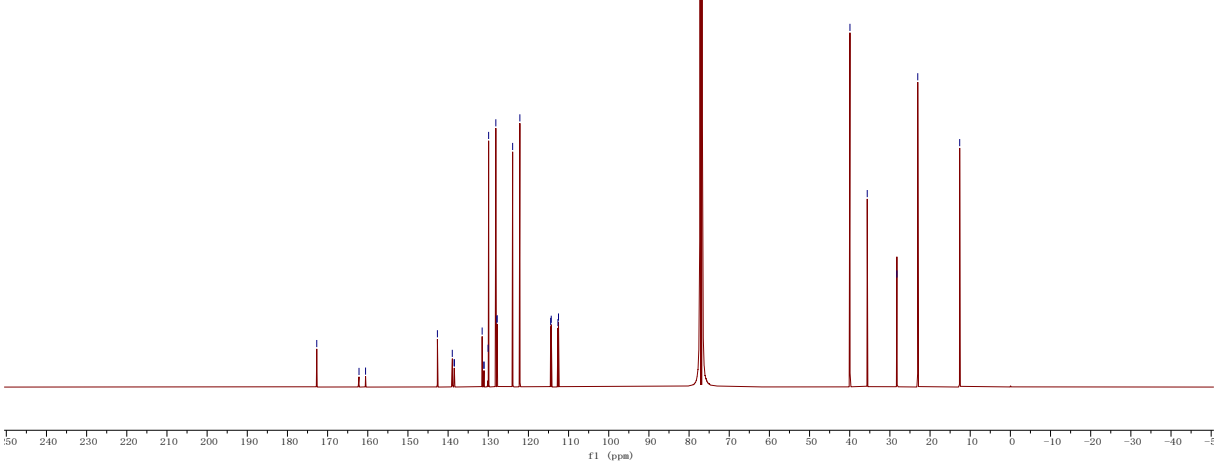


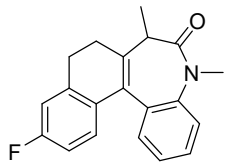
(^{1}H NMR, 600 MHz, $CDCl_3$)



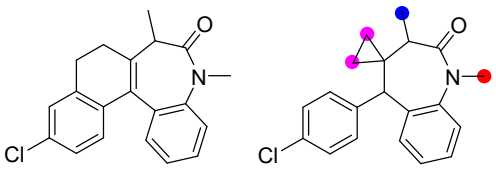


(^{13}C NMR, 150 MHz, $CDCl_3$)



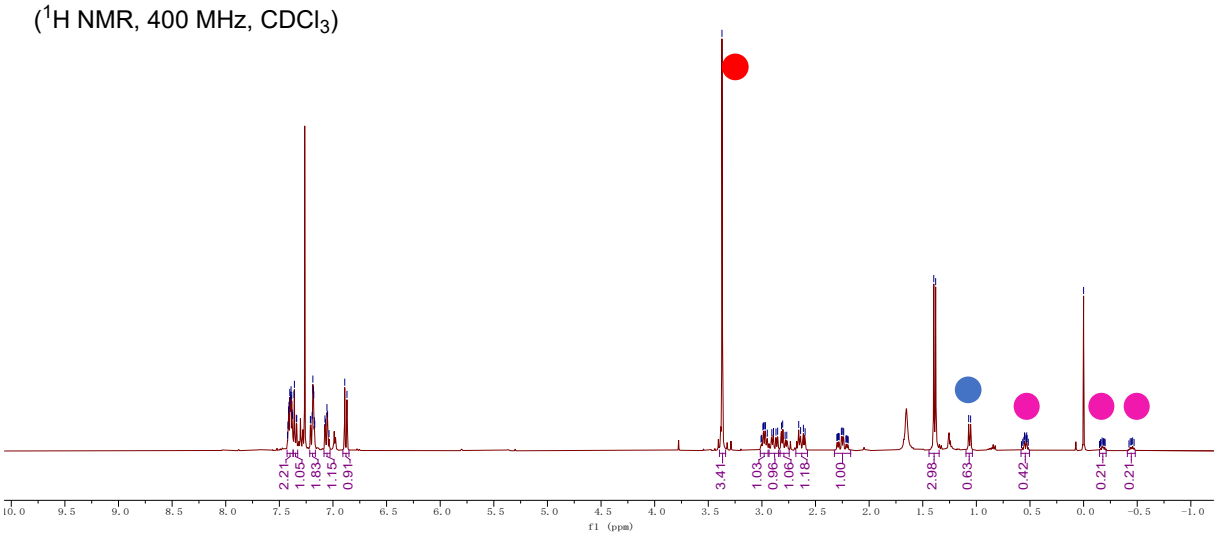


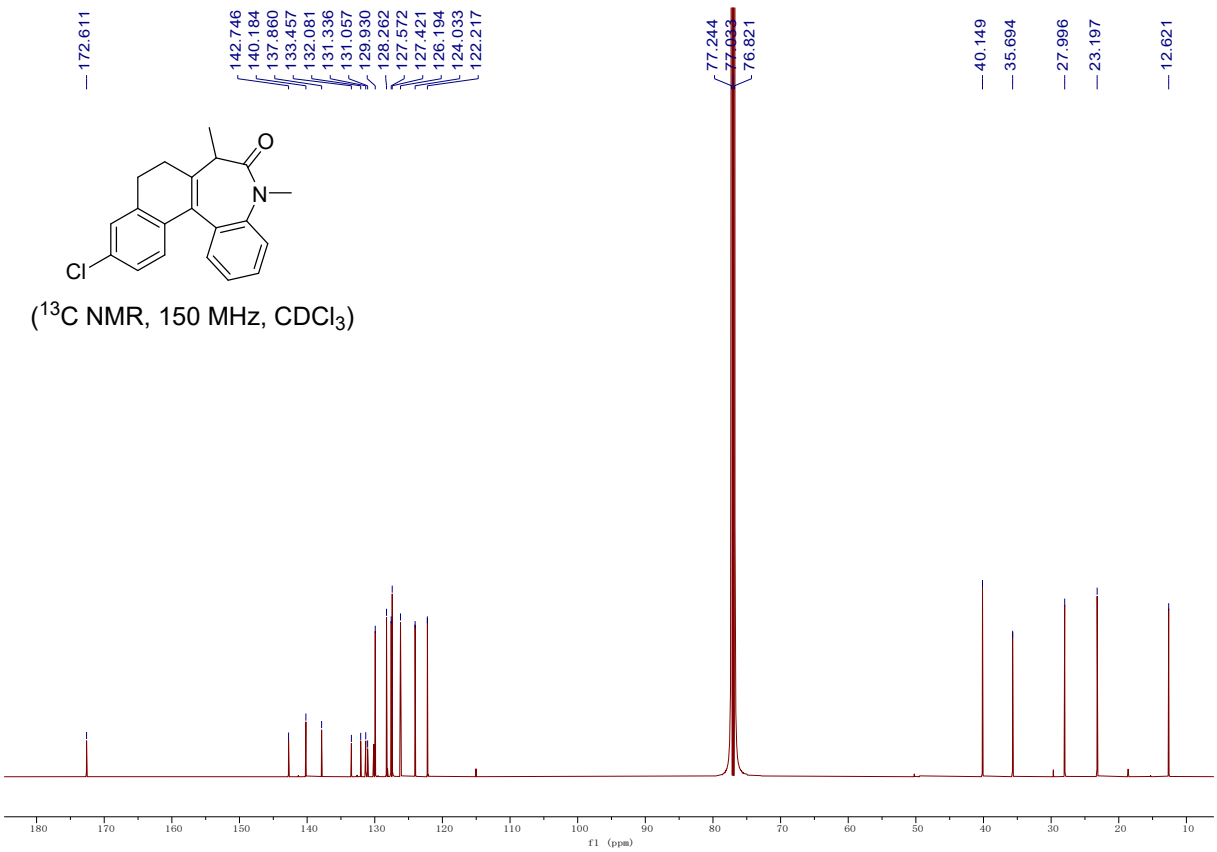
(^{19}F NMR, 564 MHz, $CDCl_3$)



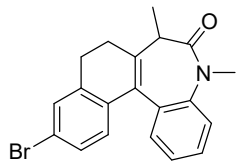
Speculated by-product

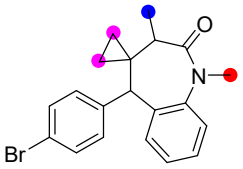
(^{1}H NMR, 400 MHz, $CDCl_3$)





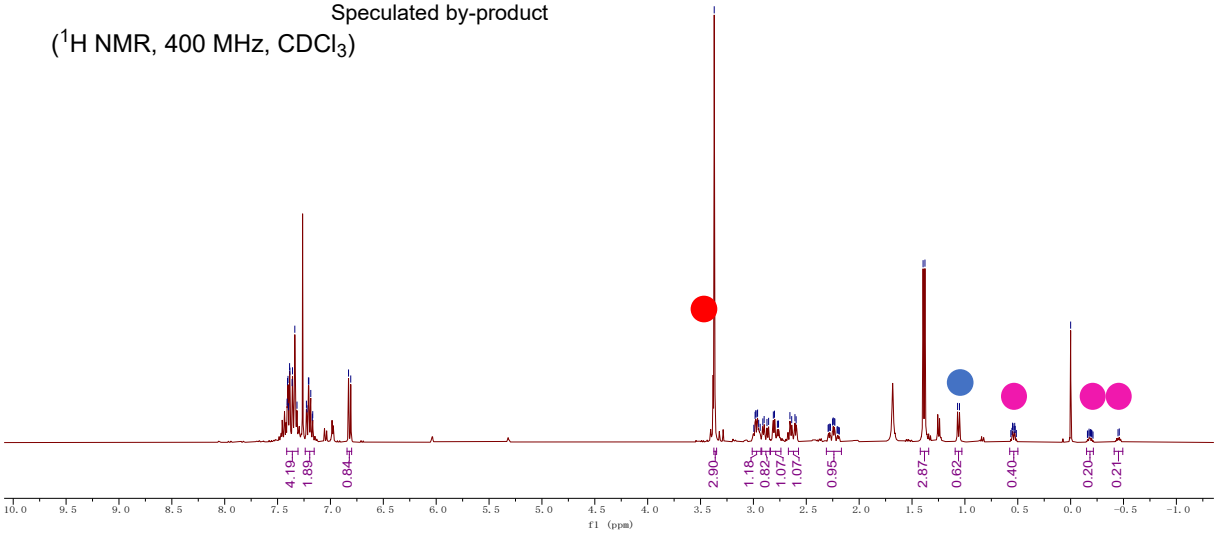
(^{13}C NMR, 150 MHz, $CDCl_3$)

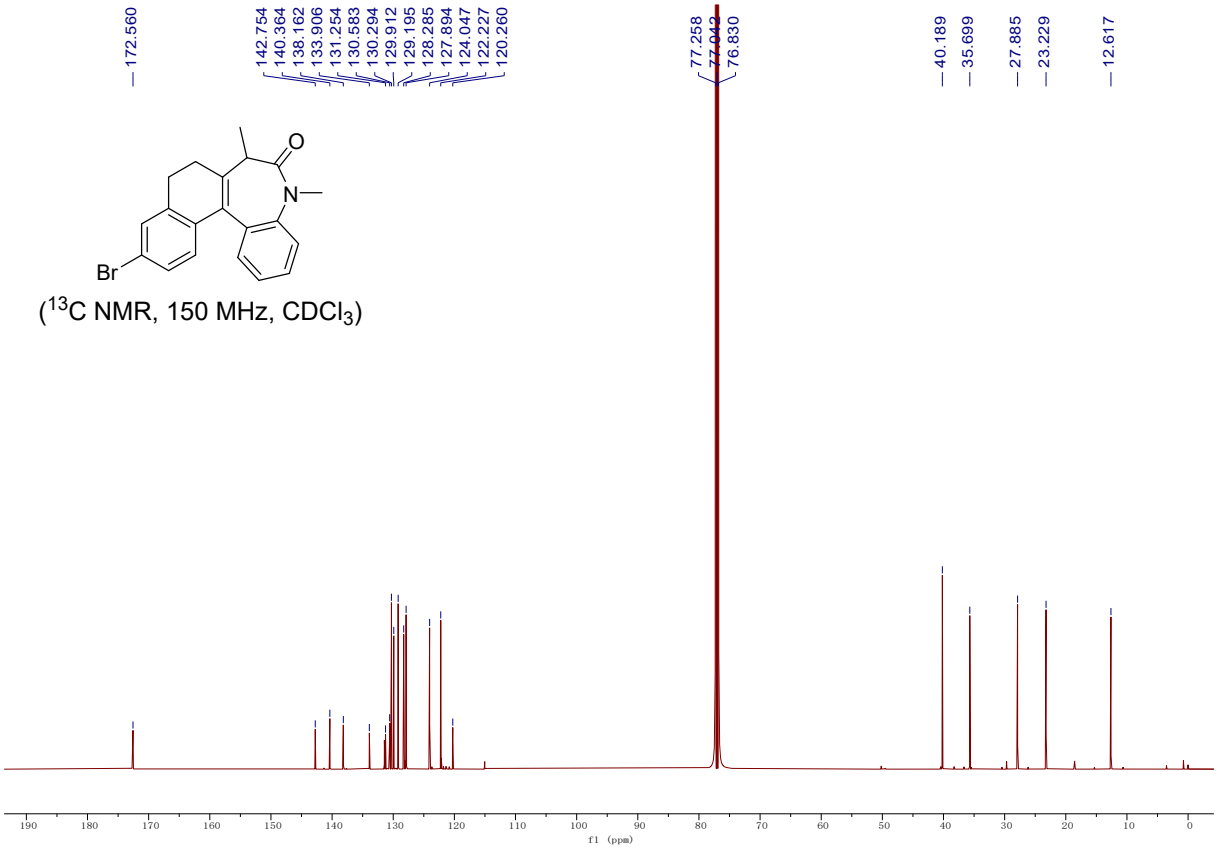




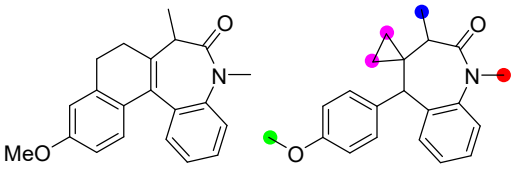
Speculated by-product

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



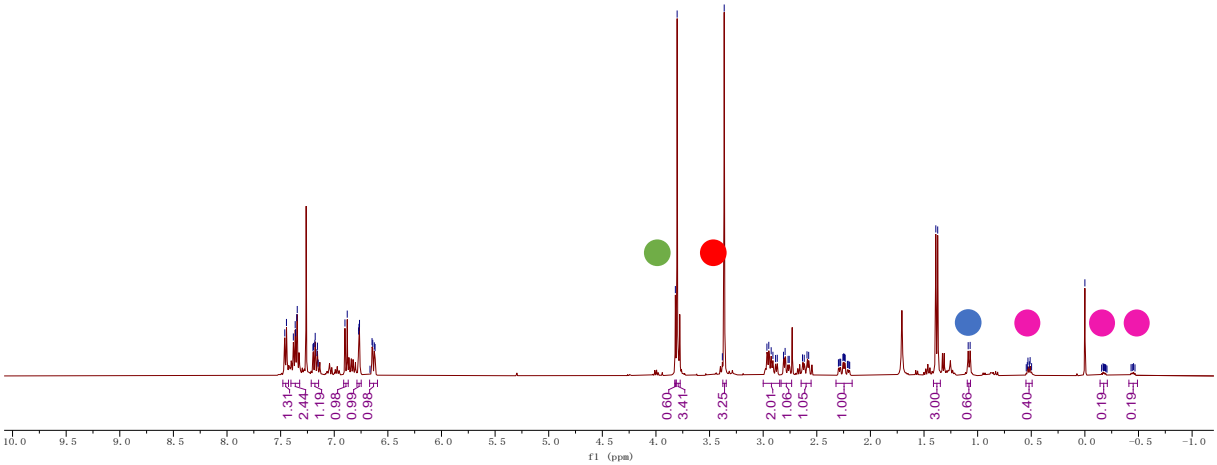


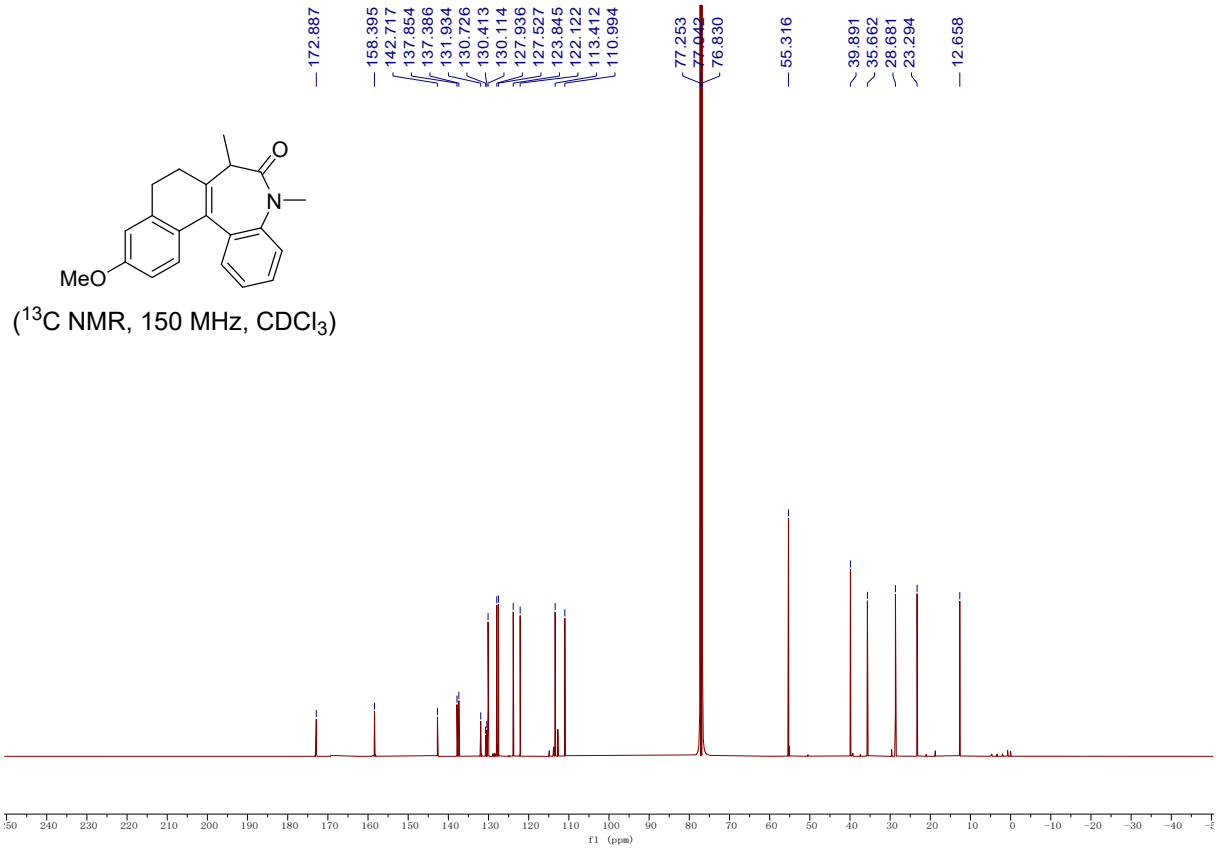
(^{13}C NMR, 150 MHz, $CDCl_3$)



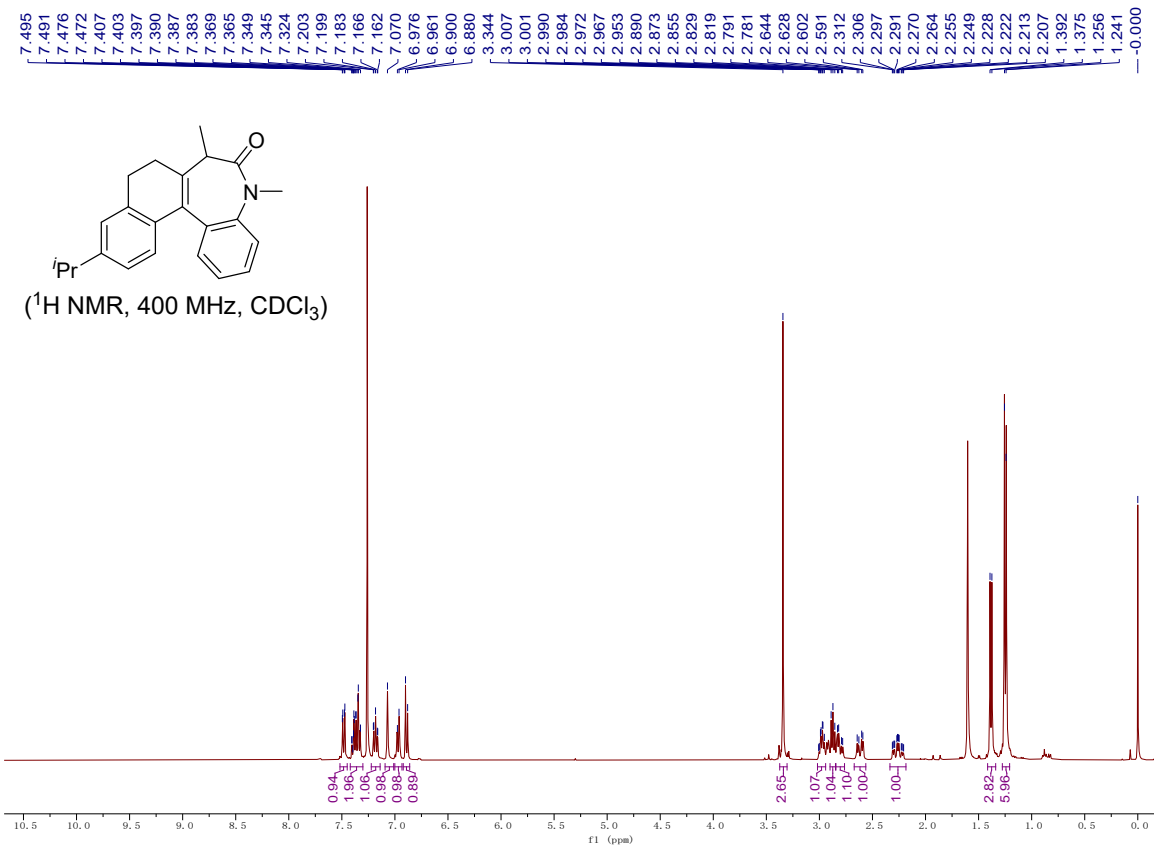
Speculated by-product

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

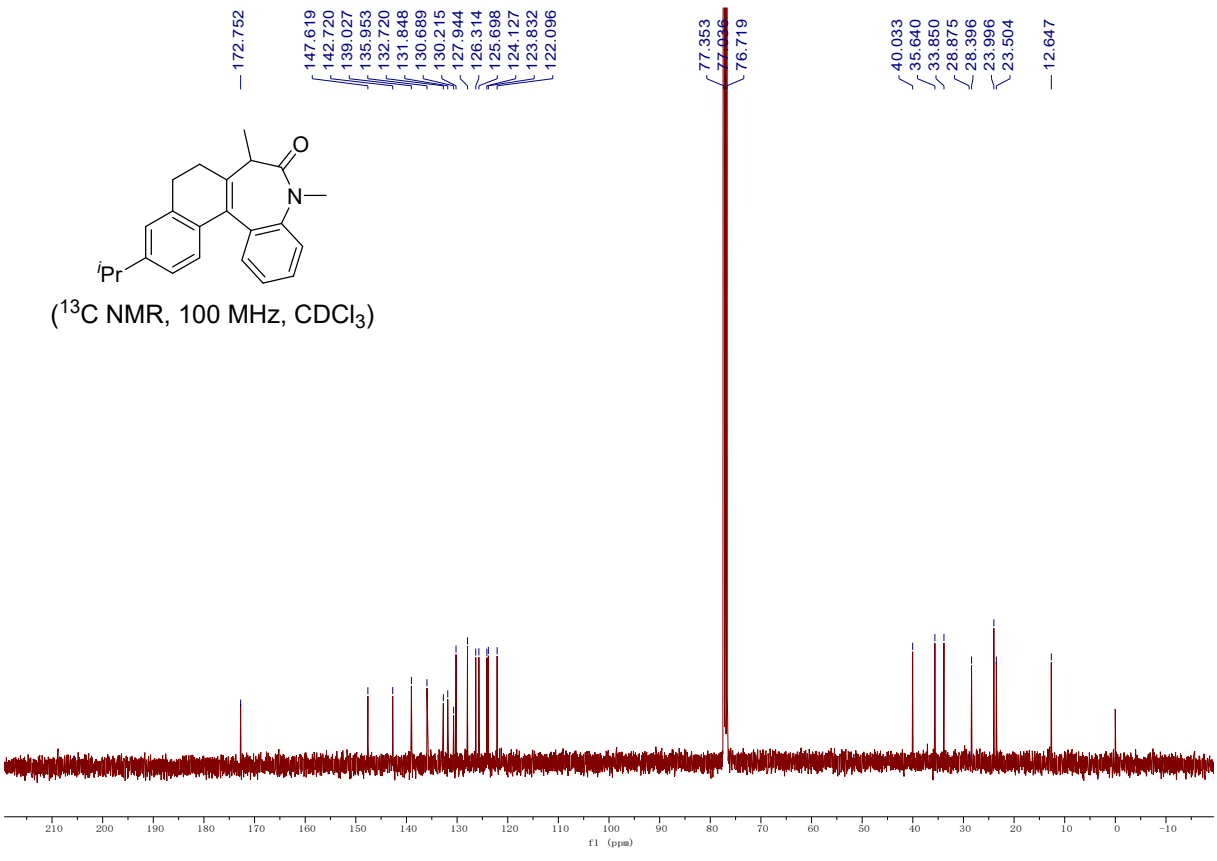




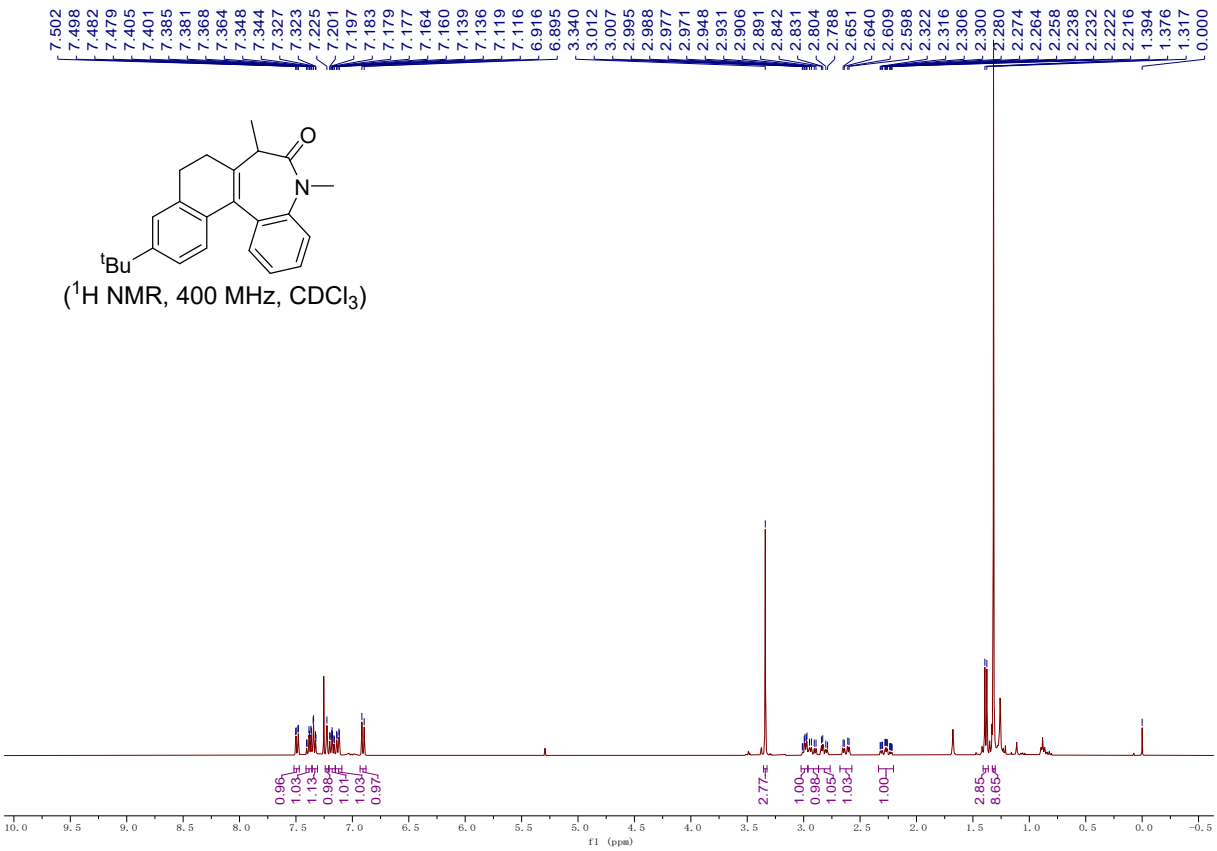
(^{13}C NMR, 150 MHz, $CDCl_3$)



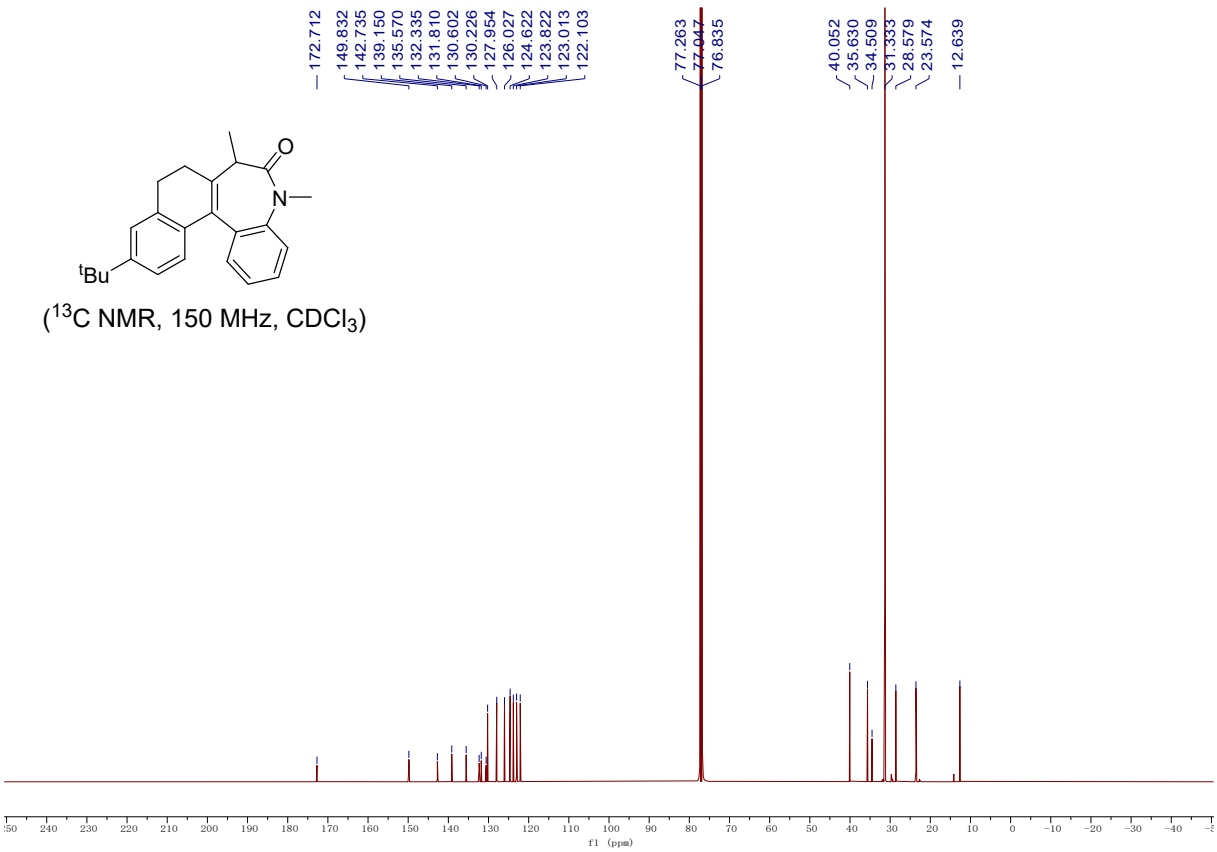
(^{1}H NMR, 400 MHz, $CDCl_3$)



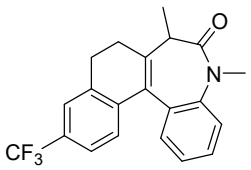
(^{13}C NMR, 100 MHz, $CDCl_3$)

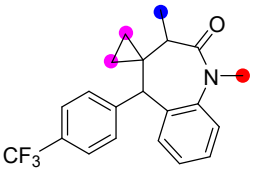


(^{1}H NMR, 400 MHz, $CDCl_3$)



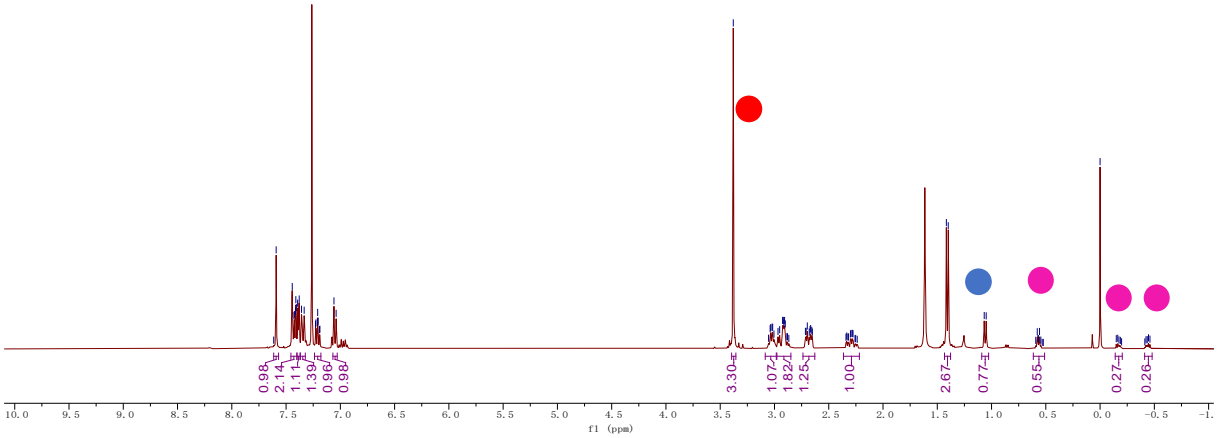
(^{13}C NMR, 150 MHz, $CDCl_3$)

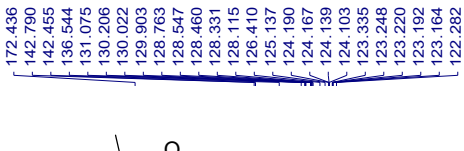


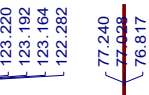


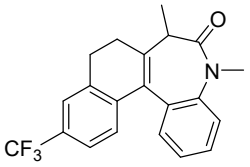
Speculated by-product

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

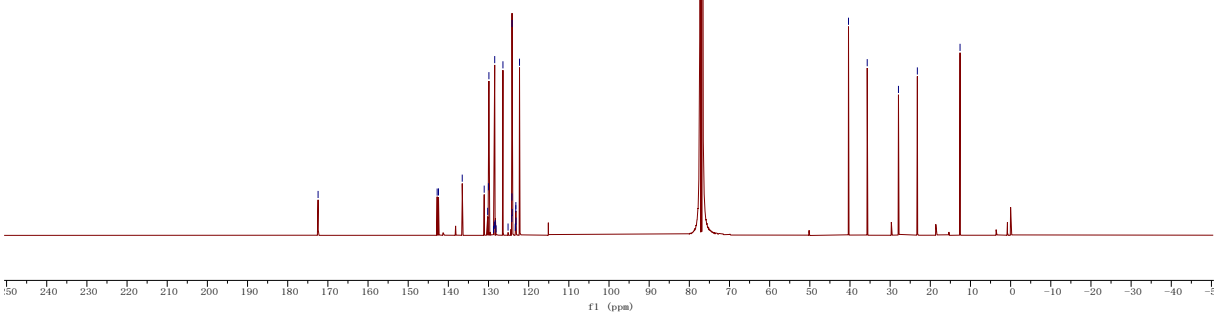


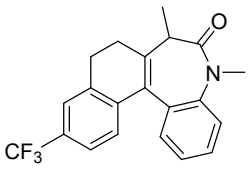




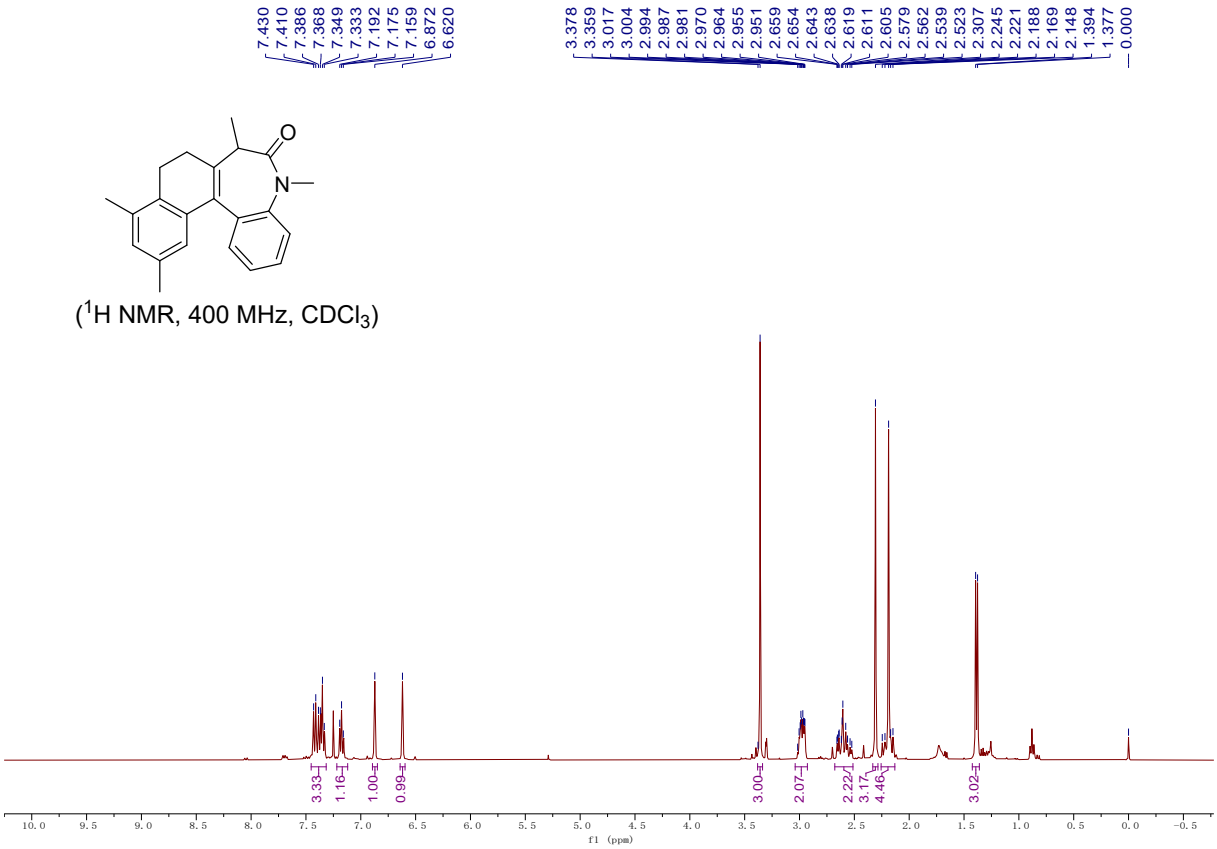


(^{13}C NMR, 150 MHz, $CDCl_3$)

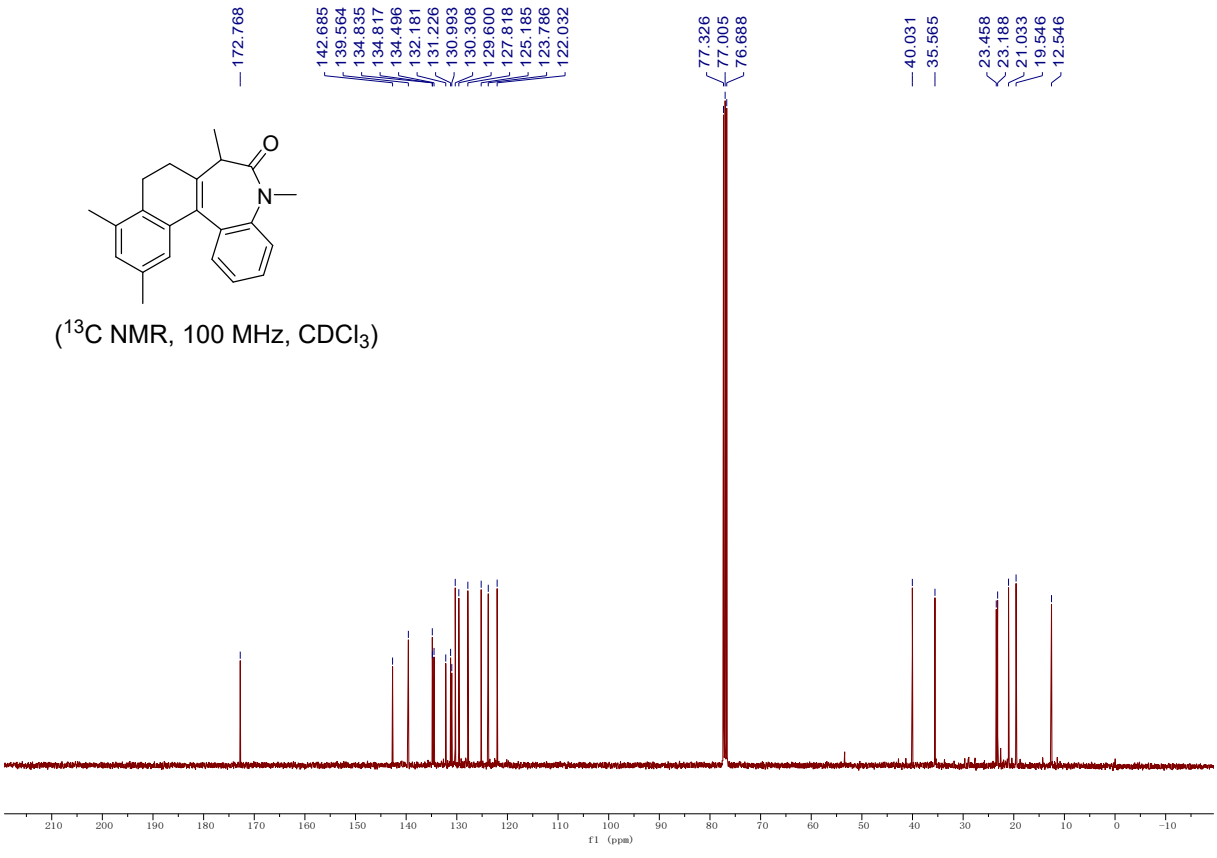




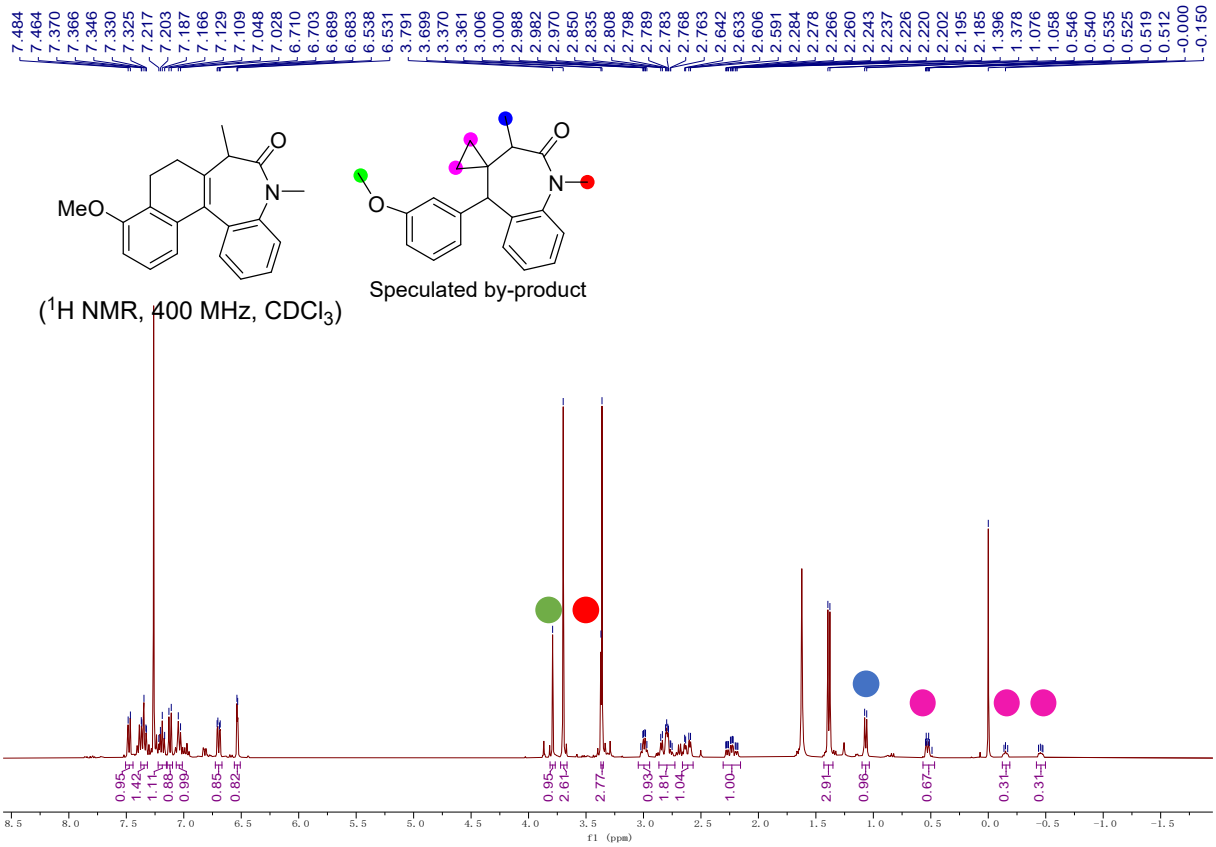
(^{19}F NMR, 564 MHz, $CDCl_3$)

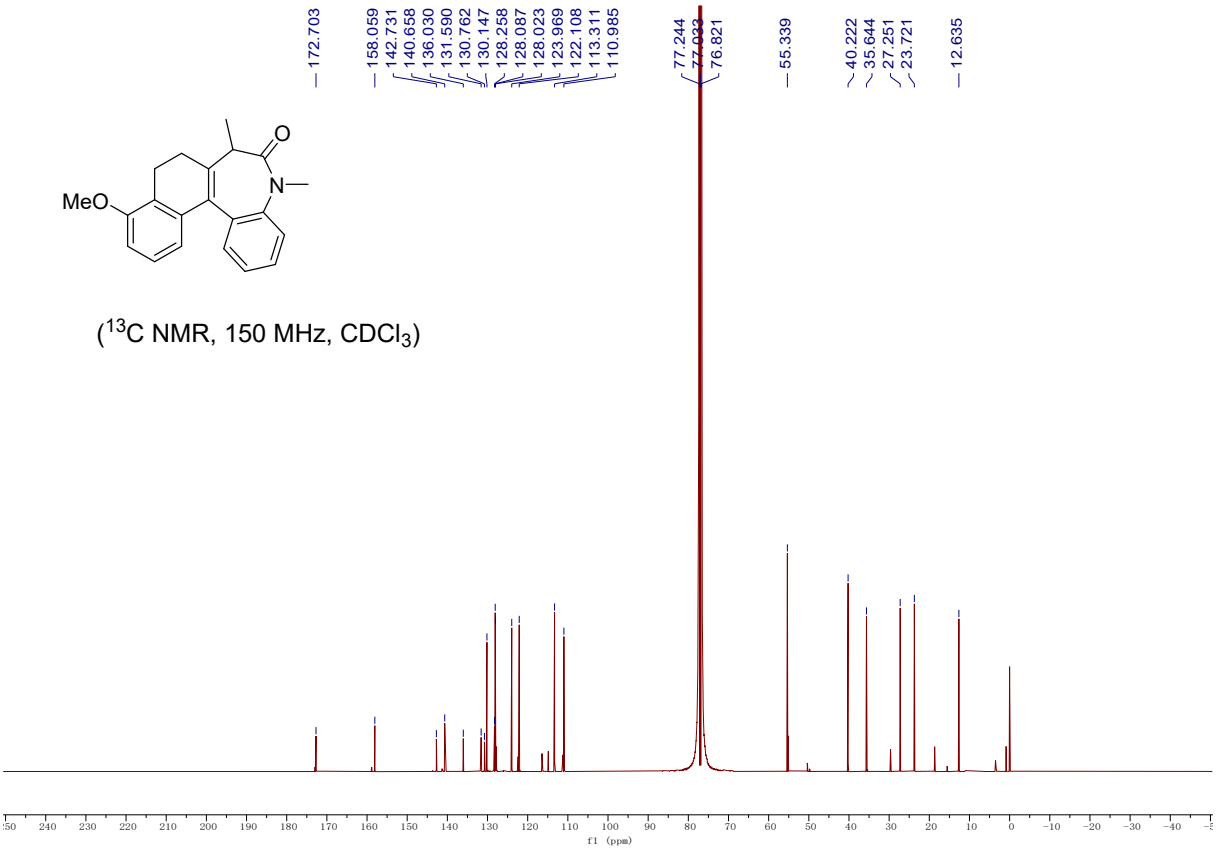


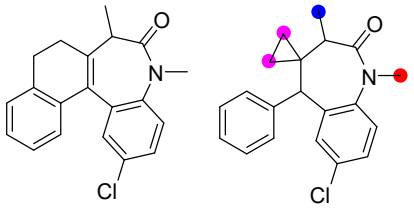
(^{1}H NMR, 400 MHz, $CDCl_3$)



(^{13}C NMR, 100 MHz, $CDCl_3$)

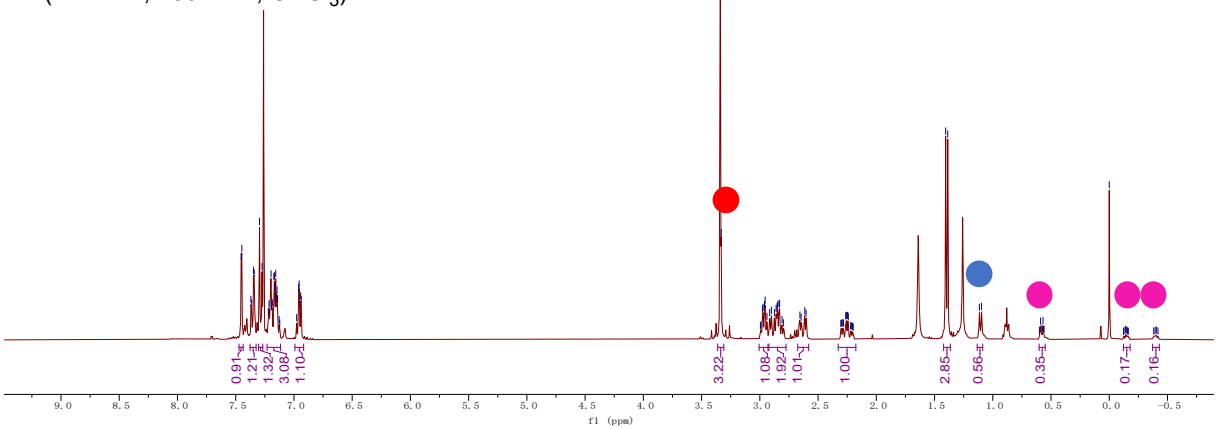

7.484
7.464
7.370
7.366
7.346
7.330
7.325
7.217
7.203
7.187
7.166
7.129
7.109
7.048
7.028
6.710
6.703
6.689
6.683
6.538
6.531
3.791
3.699
3.370
3.361
3.006
3.000
2.988
2.982
2.970
2.850
2.835
2.808
2.798
2.789
2.783
2.768
2.763
2.642
2.633
2.606
2.591
2.284
2.278
2.266
2.260
2.243
2.237
2.226
2.220
2.202
2.195
2.185
1.396
1.378
1.076
1.058
0.546
0.540
0.535
0.525
0.519
0.512
-0.000
-0.150
MeO
O
N
O
N
O
Speculated by-product
(^{1}H NMR, 400 MHz, CDCl$_3$)
0.95
1.42
1.11
0.88
0.99
0.85
0.82
0.95
2.61
2.77
0.93
1.81
1.04
1.00
2.91
0.96
0.67
0.31
0.31
f1 (ppm)

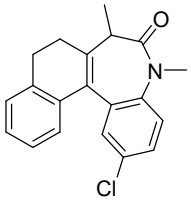

172.703
158.059
142.731
140.658
136.030
131.590
130.762
130.147
128.258
128.087
128.023
123.969
122.108
113.311
110.985
77.244
77.033
76.821
55.339
40.222
35.644
27.251
23.721
12.635
MeO
O
N
(^{13}C NMR, 150 MHz, CDCl$_3$)
f1 (ppm)



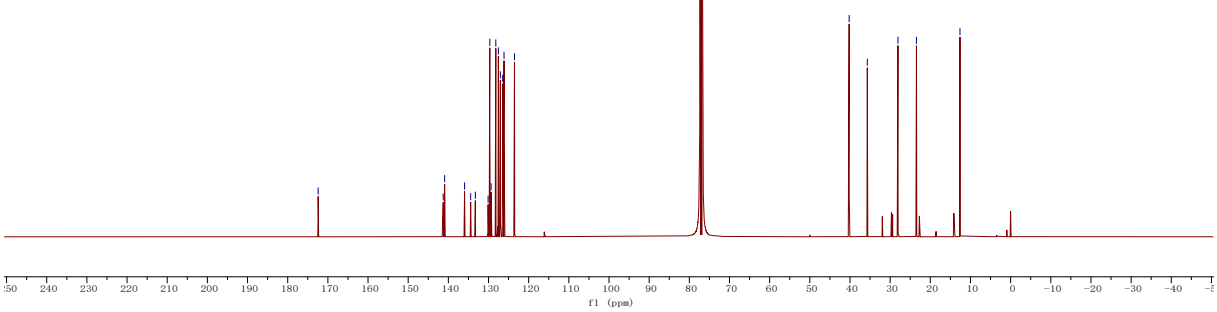
Speculated by-product

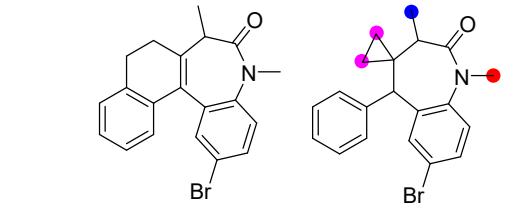
(^{1}H NMR, 400 MHz, $CDCl_3$)





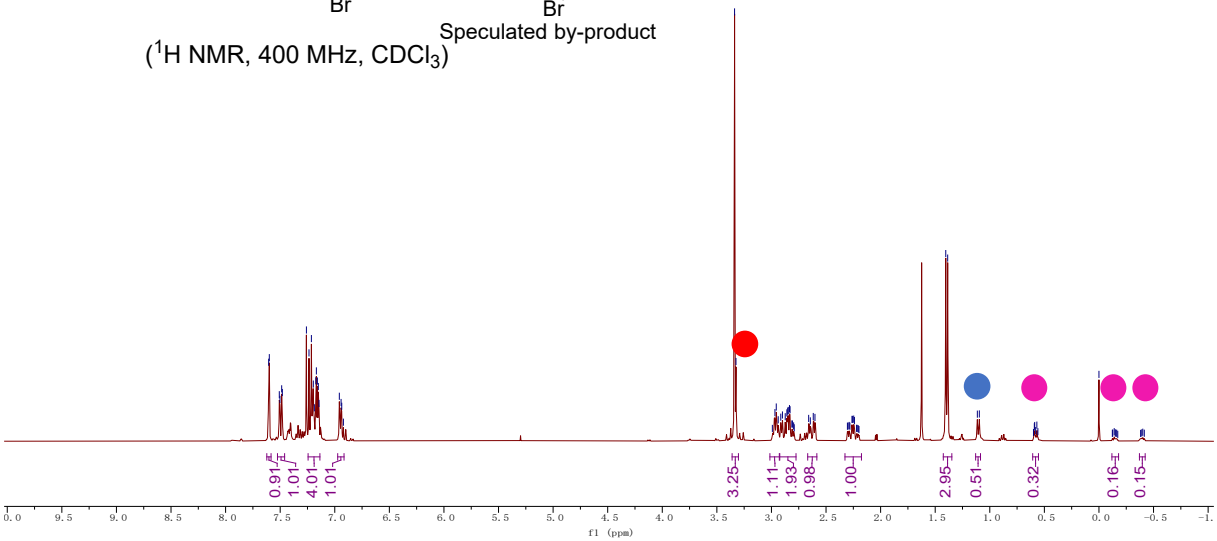
(^{13}C NMR, 150 MHz, $CDCl_3$)

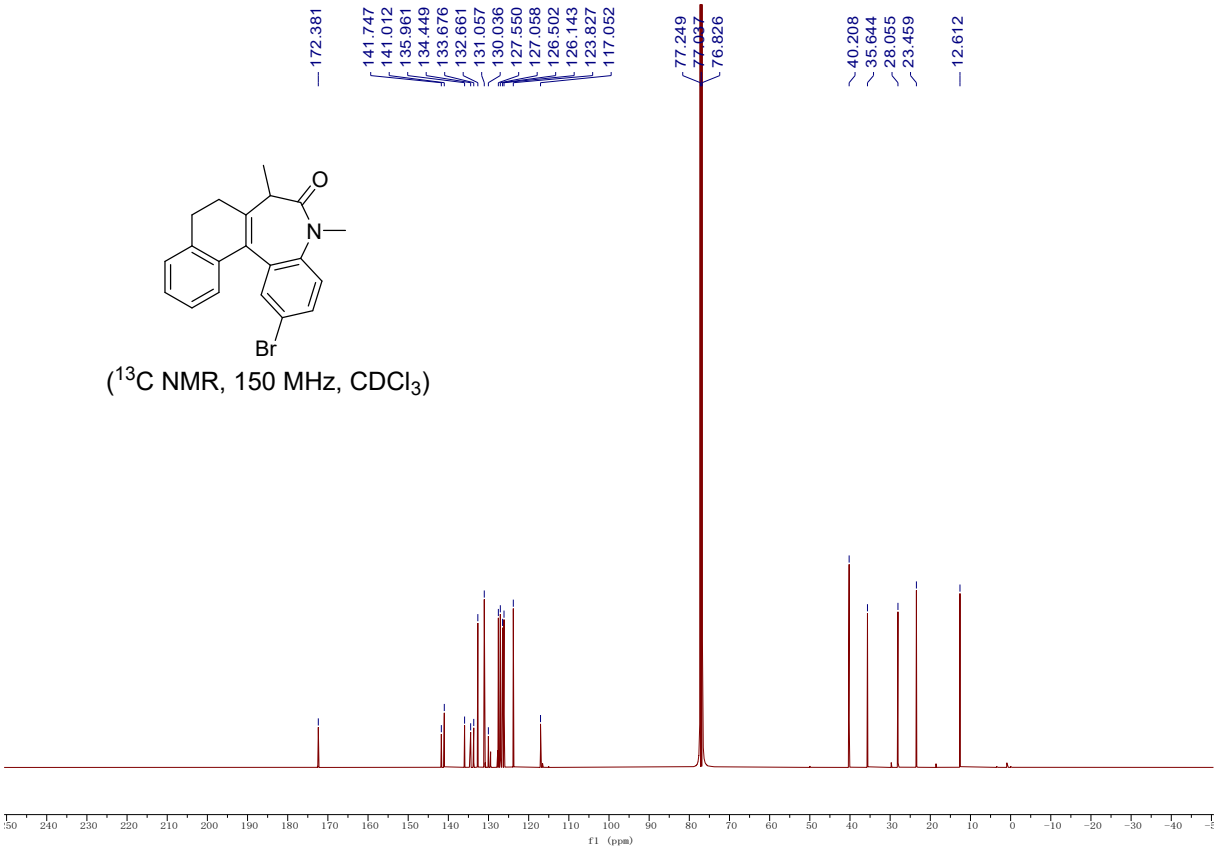




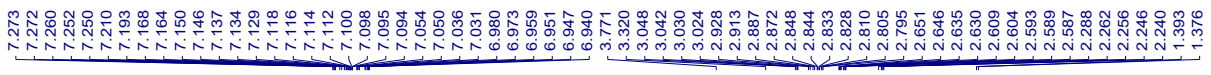
Speculated by-product

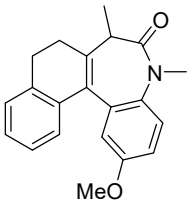
(^{1}H NMR, 400 MHz, $CDCl_3$)



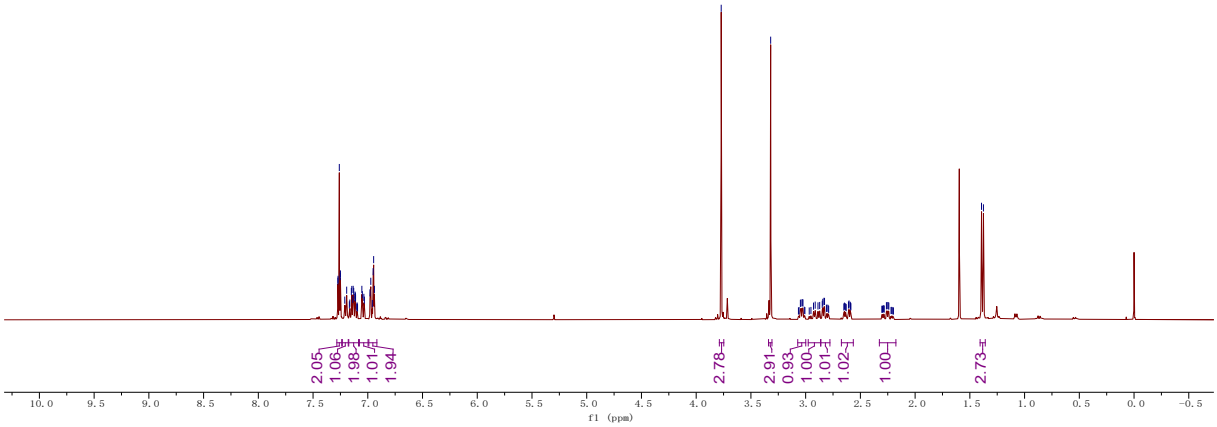


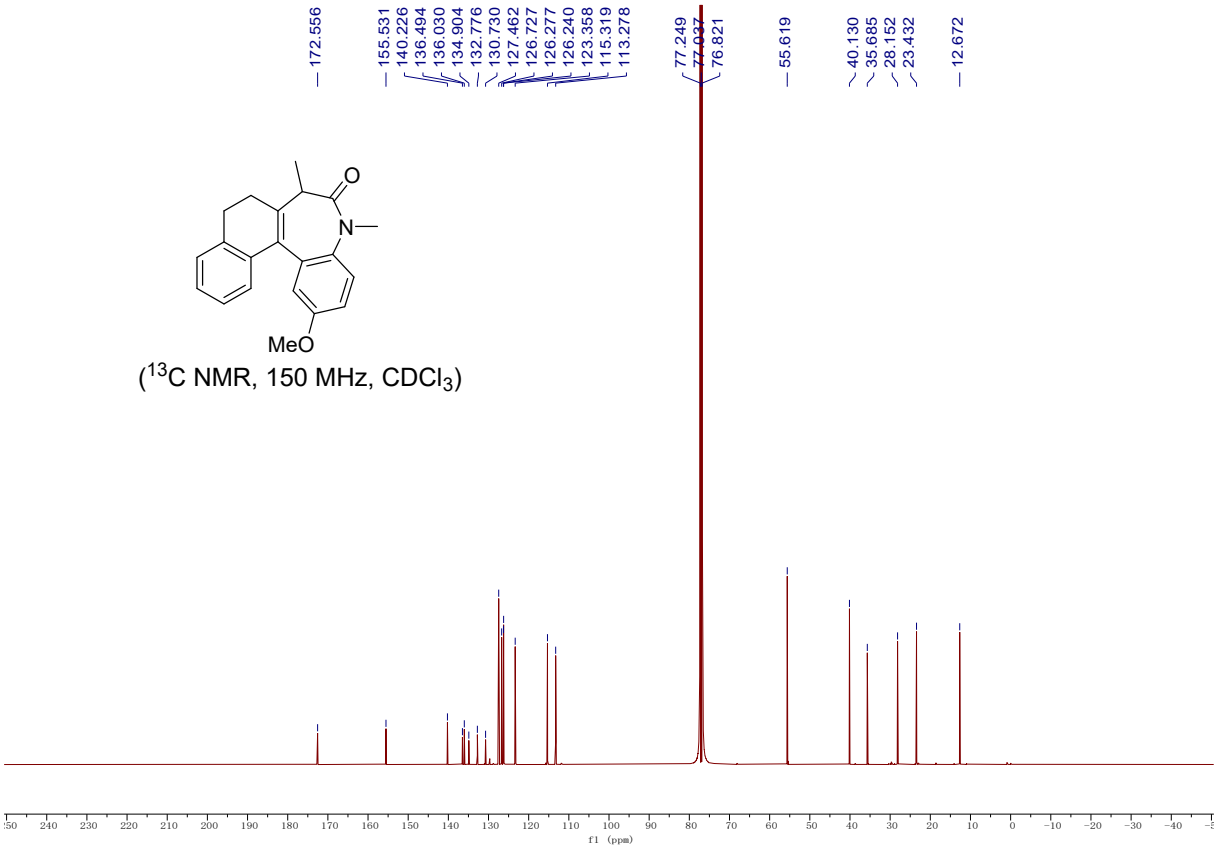
(^{13}C NMR, 150 MHz, $CDCl_3$)



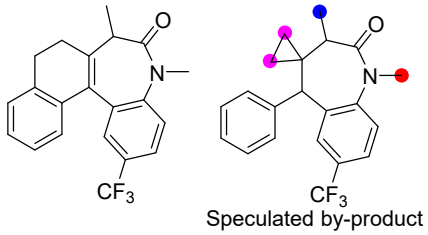


(^{1}H NMR, 400 MHz, $CDCl_3$)



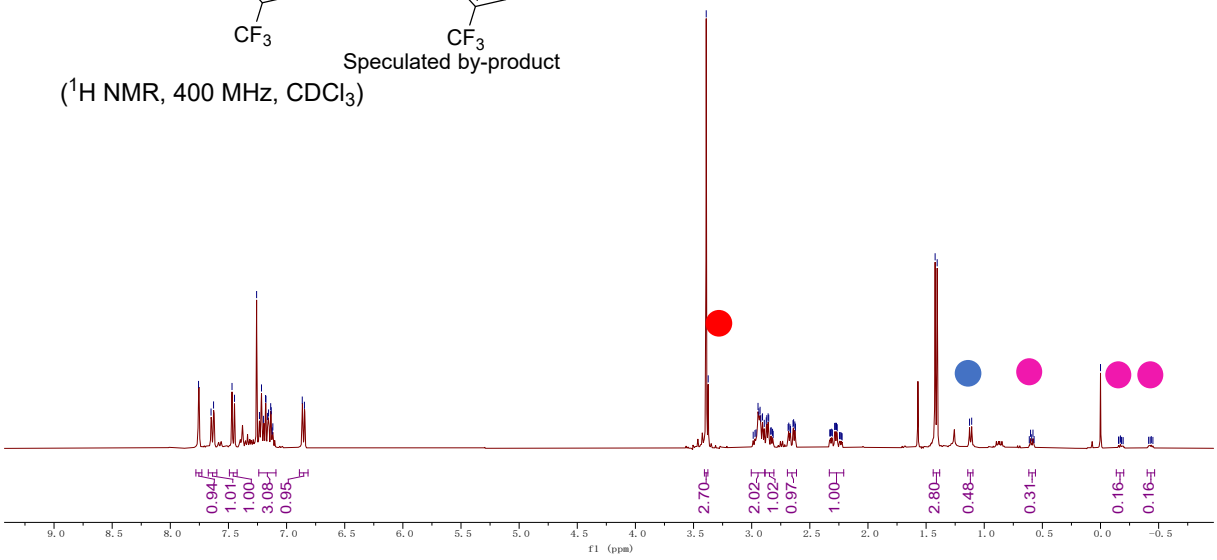


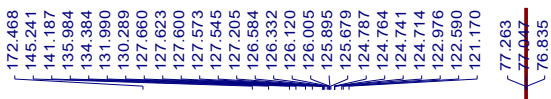
(^{13}C NMR, 150 MHz, $CDCl_3$)

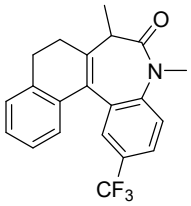


Speculated by-product

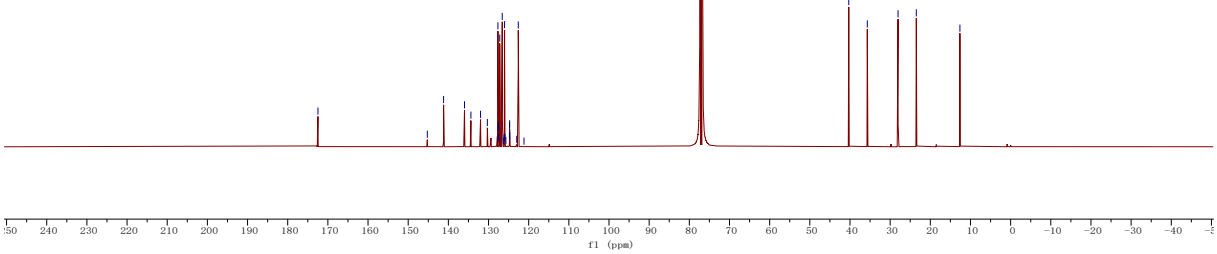
(^{1}H NMR, 400 MHz, $CDCl_3$)

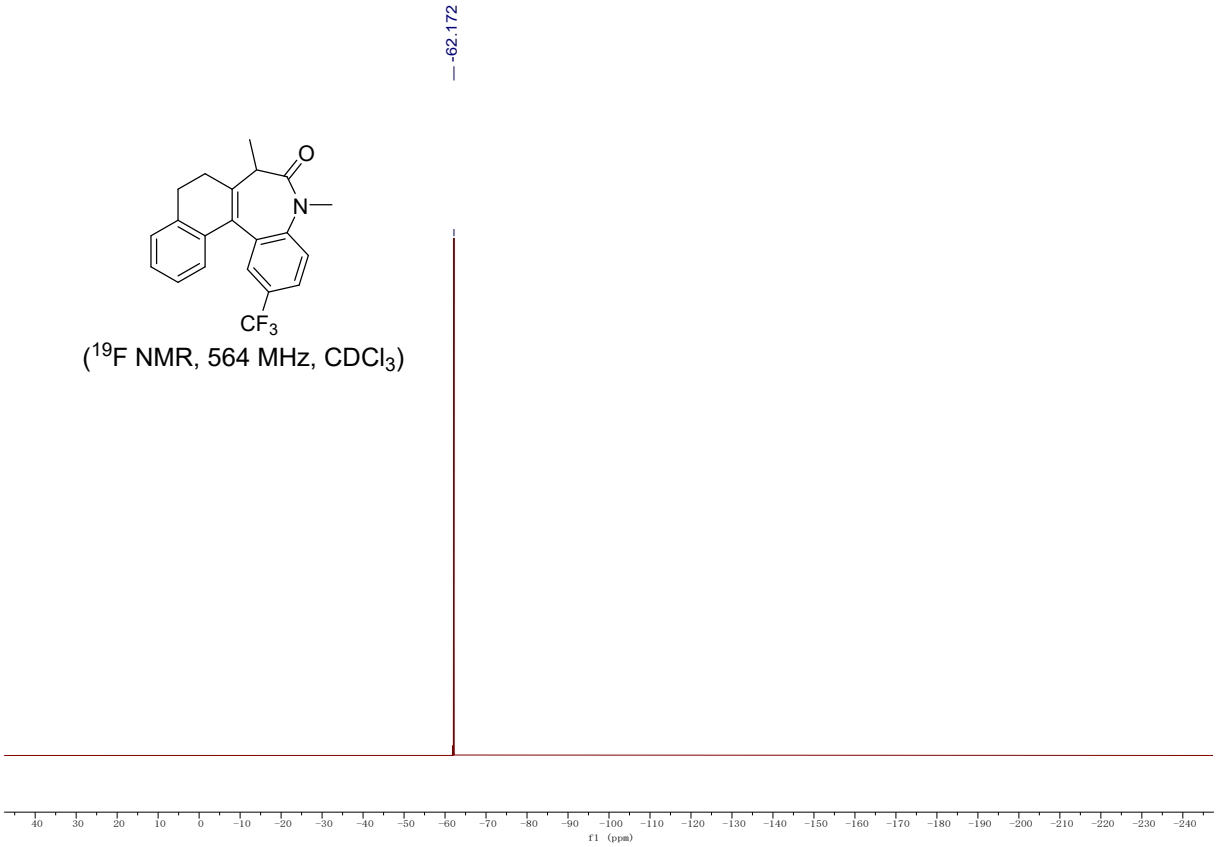




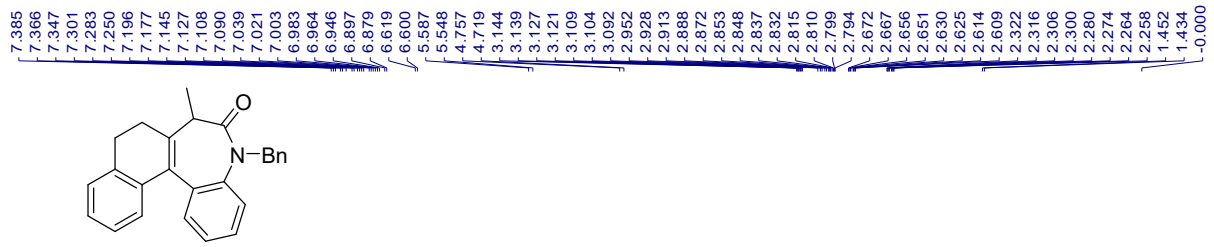


(^{13}C NMR, 150 MHz, $CDCl_3$)

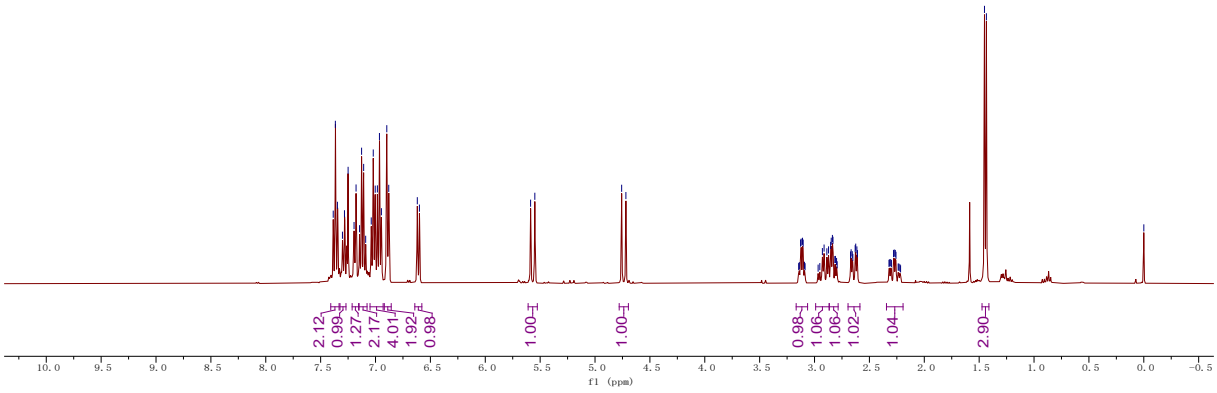


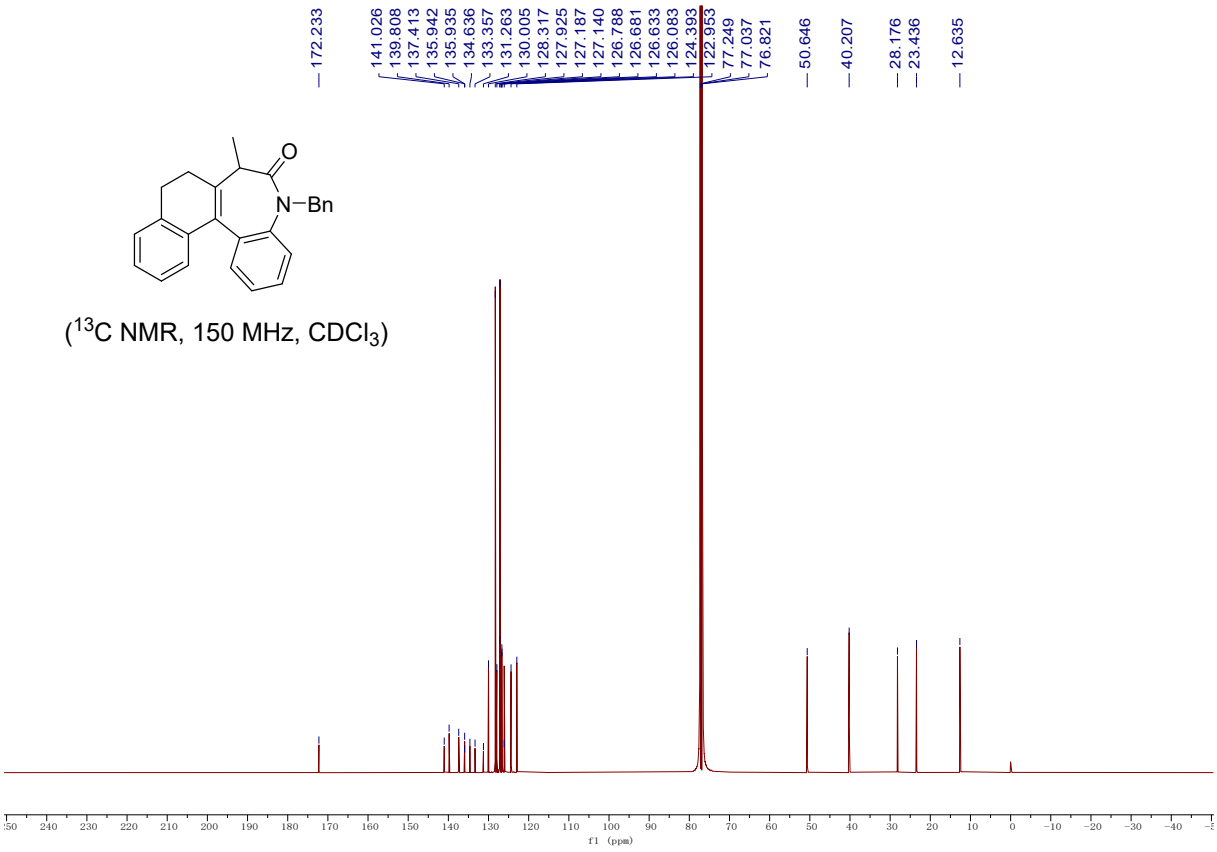


(^{19}F NMR, 564 MHz, $CDCl_3$)

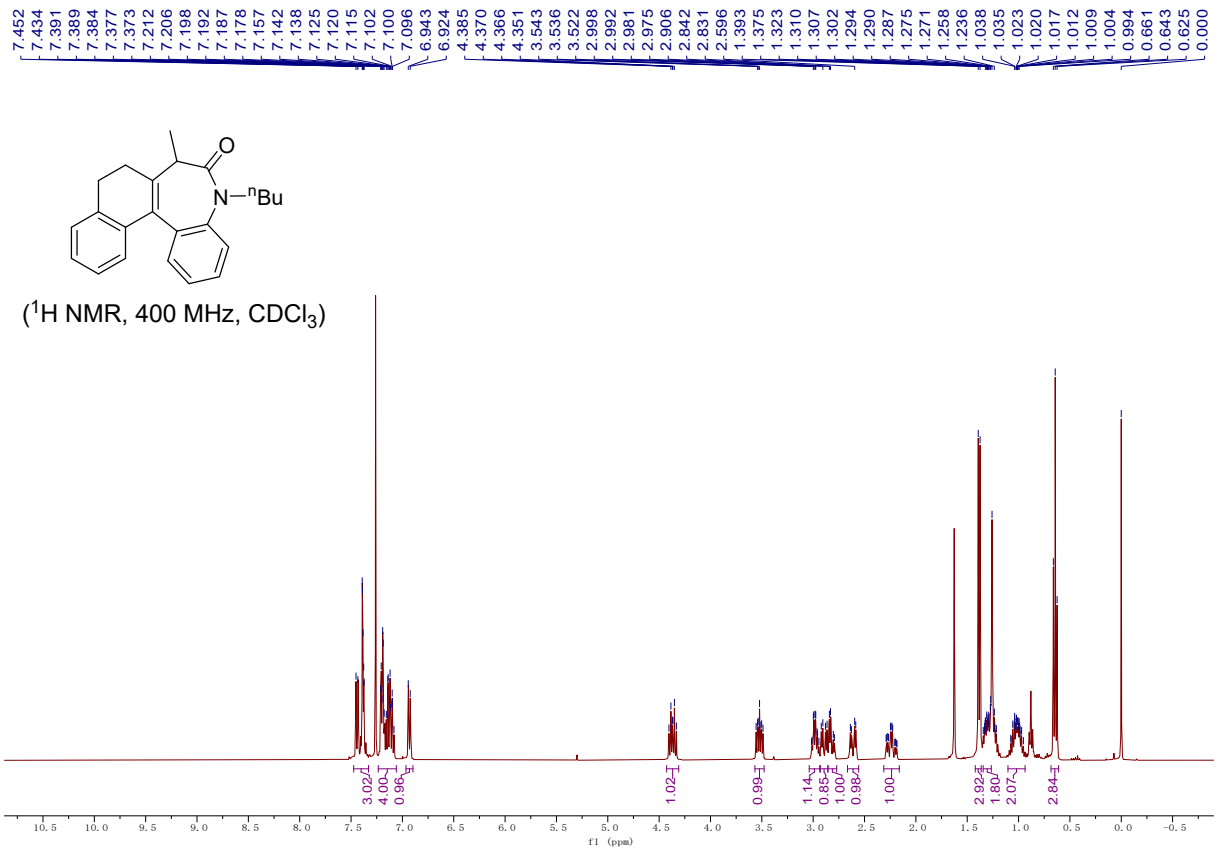


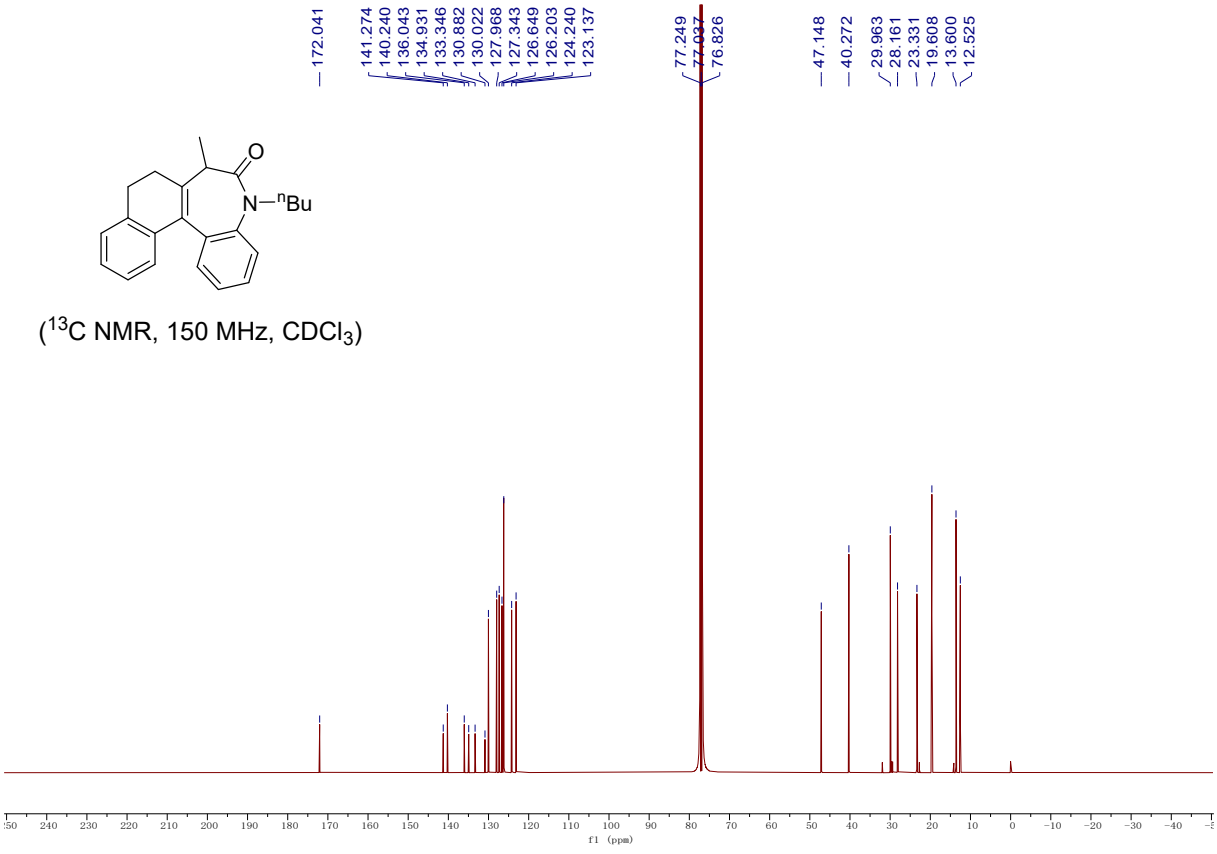
(^{1}H NMR, 400 MHz, $CDCl_3$)

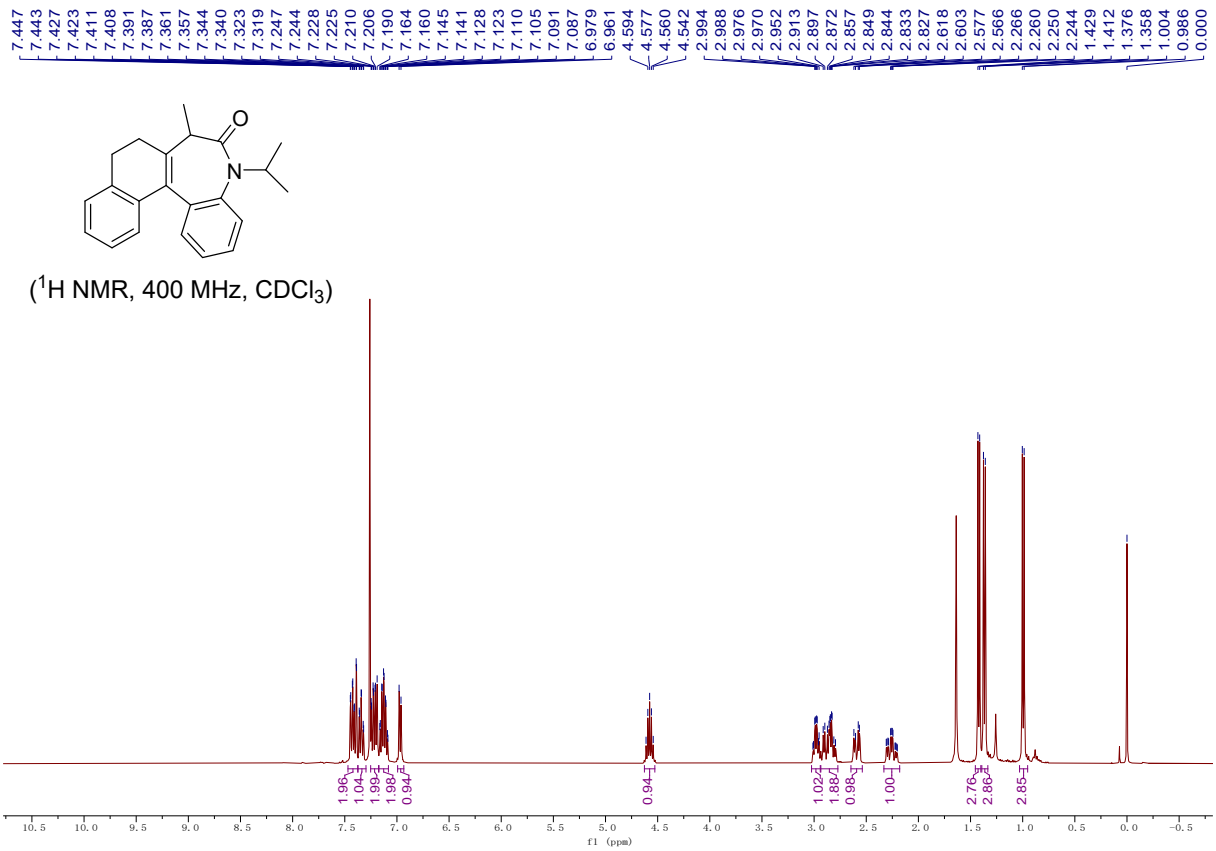


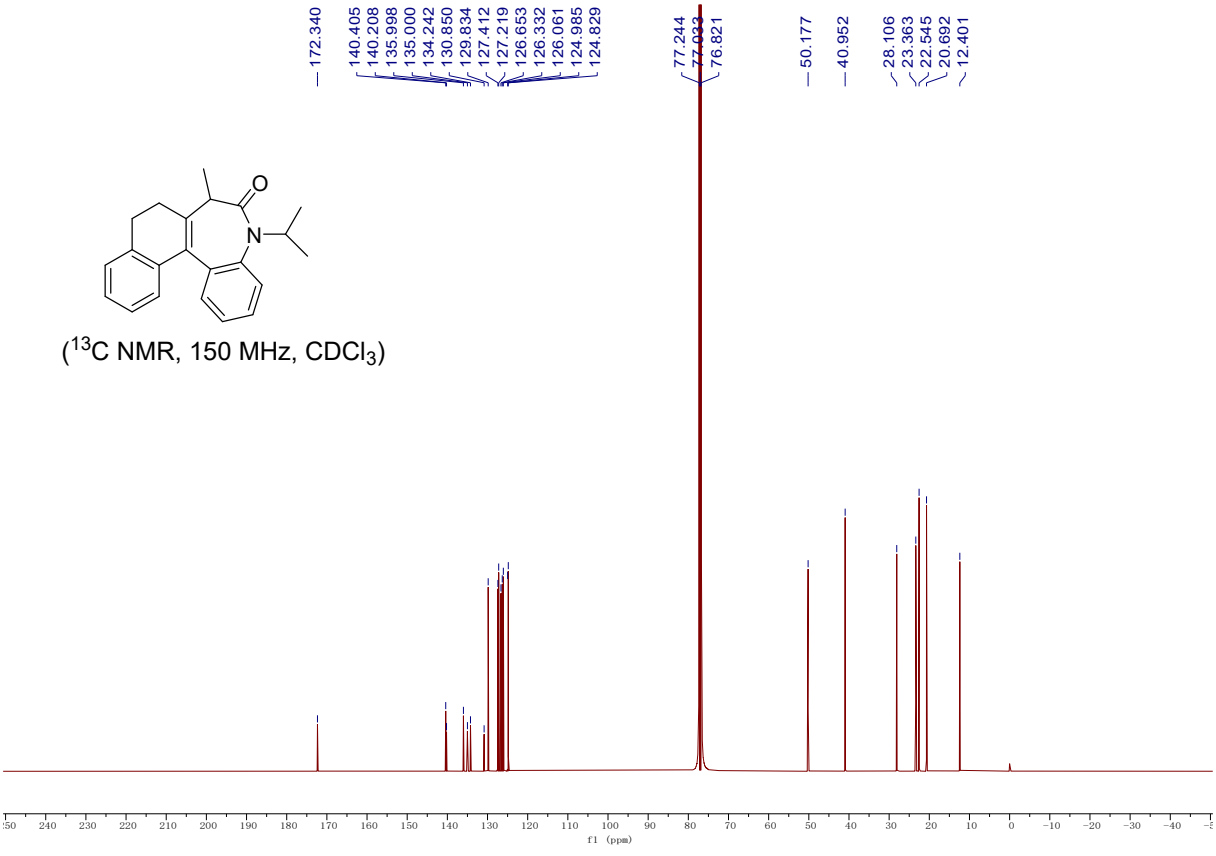


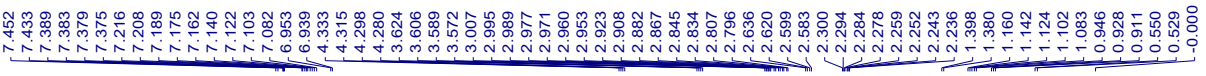
(^{13}C NMR, 150 MHz, $CDCl_3$)

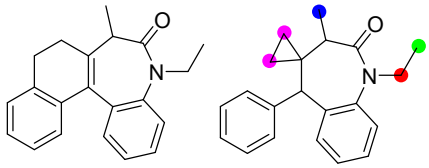

7.452
7.434
7.391
7.389
7.384
7.377
7.373
7.212
7.206
7.198
7.192
7.187
7.178
7.157
7.142
7.138
7.125
7.120
7.115
7.102
7.100
7.096
6.943
6.924
4.385
4.370
4.366
4.351
3.543
3.536
3.522
2.998
2.992
2.981
2.975
2.906
2.842
2.831
2.596
1.393
1.375
1.323
1.310
1.307
1.302
1.294
1.290
1.287
1.275
1.271
1.258
1.236
1.038
1.035
1.023
1.020
1.017
1.012
1.009
1.004
0.994
0.661
0.643
0.625
0.000
O
N—nBu
(1H NMR, 400 MHz, CDCl3)
3.02
4.00
0.96
1.02
0.99
1.14
0.85
1.00
0.98
1.00
2.92
1.80
2.07
2.84
f1 (ppm)


172.041
141.274
140.240
136.043
134.931
133.346
130.882
130.022
127.968
127.343
126.649
126.203
124.240
123.137
77.249
77.037
76.826
47.148
40.272
29.963
28.161
23.331
19.608
13.600
12.525
O
N—nBu
(13C NMR, 150 MHz, CDCl3)
f1 (ppm)


7.447
7.443
7.427
7.423
7.411
7.408
7.391
7.387
7.361
7.357
7.344
7.340
7.323
7.319
7.247
7.244
7.228
7.225
7.210
7.206
7.190
7.164
7.160
7.145
7.141
7.128
7.123
7.110
7.105
7.091
7.087
6.979
6.961
4.594
4.577
4.560
4.542
2.994
2.988
2.976
2.970
2.952
2.913
2.897
2.872
2.857
2.849
2.844
2.833
2.827
2.618
2.603
2.577
2.566
2.266
2.260
2.250
2.244
1.429
1.412
1.376
1.358
1.004
0.986
0.000
O
N
(1H NMR, 400 MHz, CDCl3)
1.96
1.04
1.99
1.98
0.94
0.94
1.02
1.88
0.98
1.00
2.76
2.86
2.85
f1 (ppm)

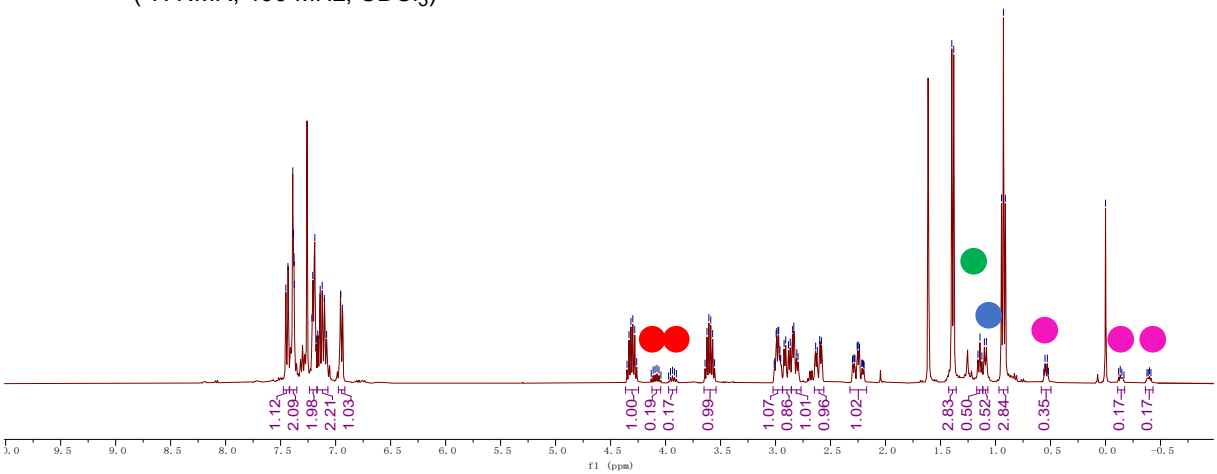

172.340
140.405
140.208
135.998
135.000
134.242
130.850
129.834
127.412
127.219
126.653
126.332
126.061
124.985
124.829
77.244
77.033
76.821
50.177
40.952
28.106
23.363
22.545
20.692
12.401
O
N
(13C NMR, 150 MHz, CDCl3)
f1 (ppm)

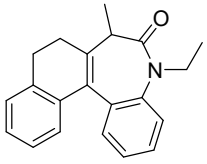




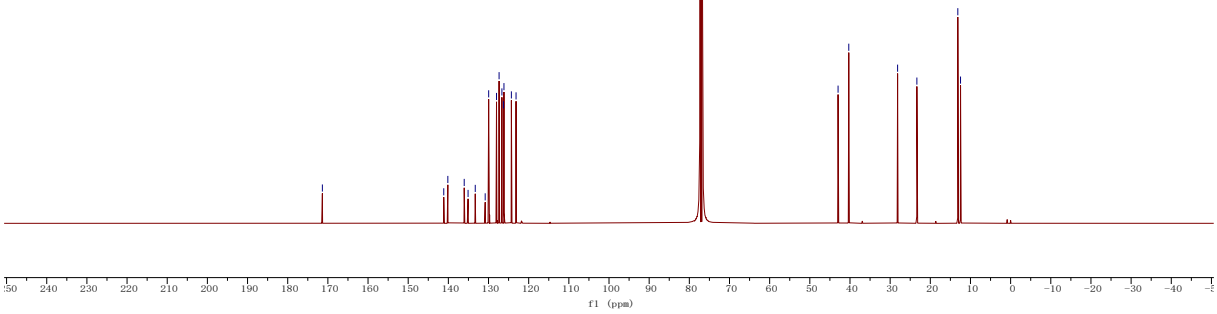
Speculated by-product

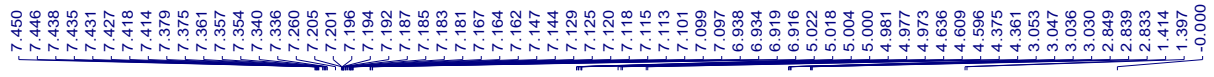
(^{1}H NMR, 400 MHz, $CDCl_3$)

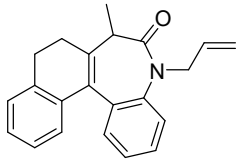




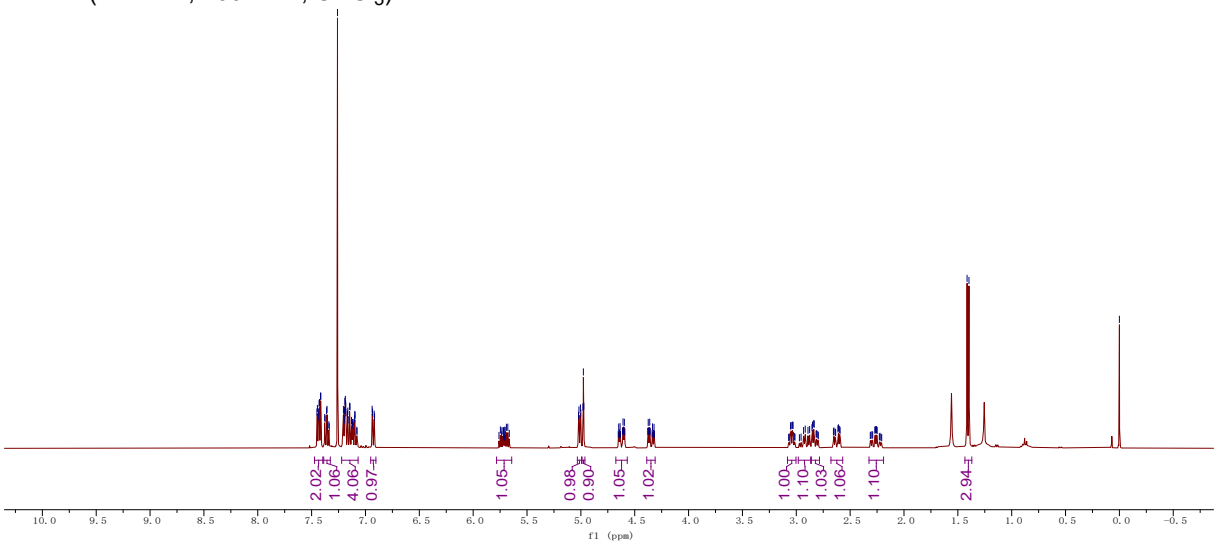
(^{13}C NMR, 150 MHz, $CDCl_3$)

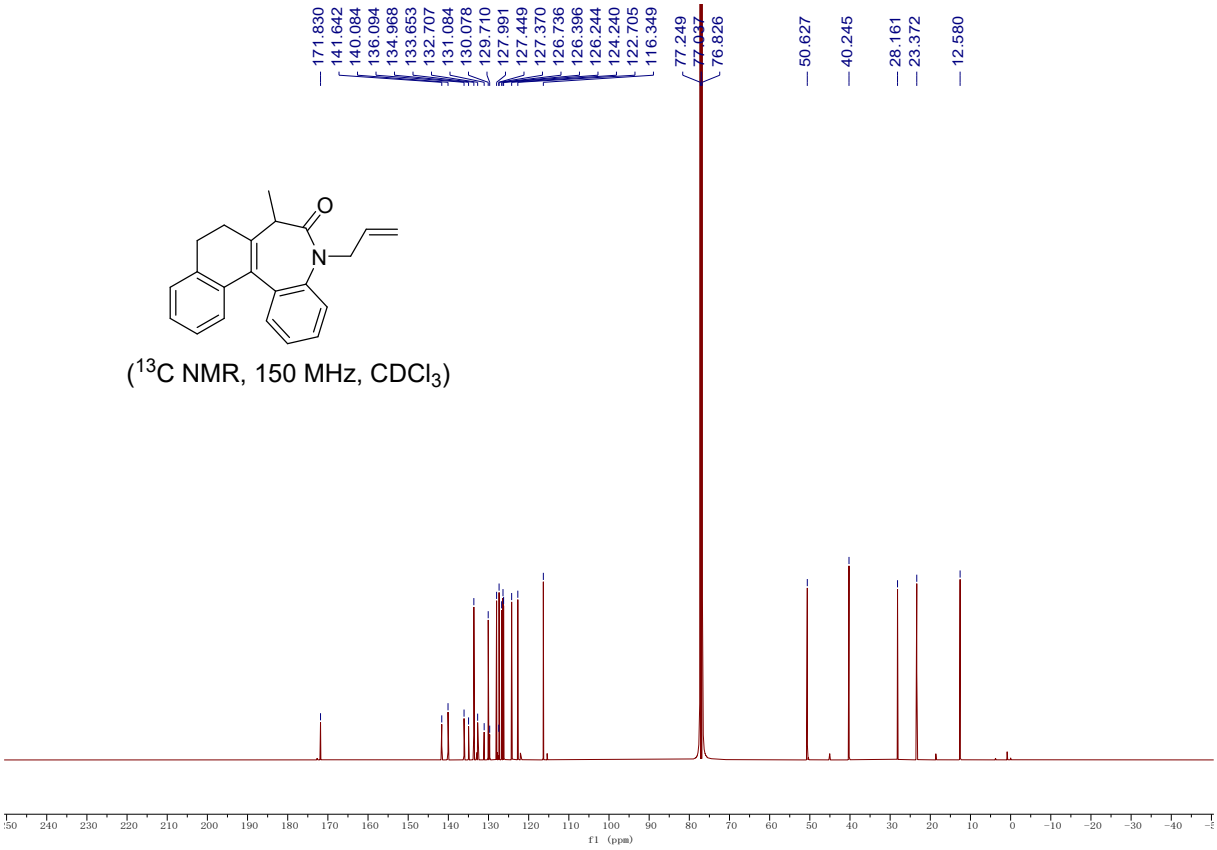




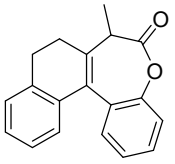


(^{1}H NMR, 400 MHz, $CDCl_3$)

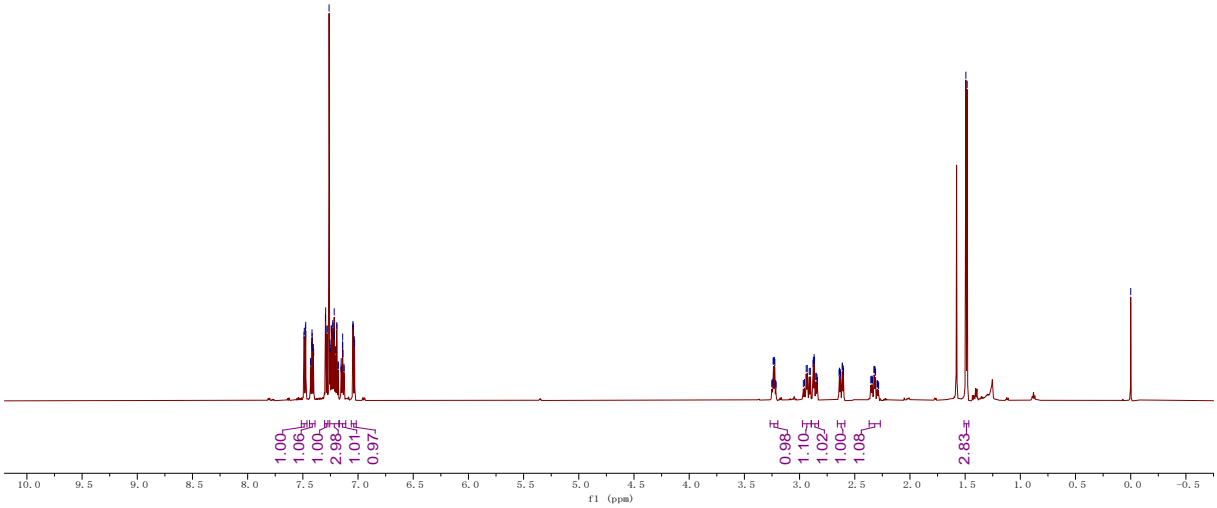


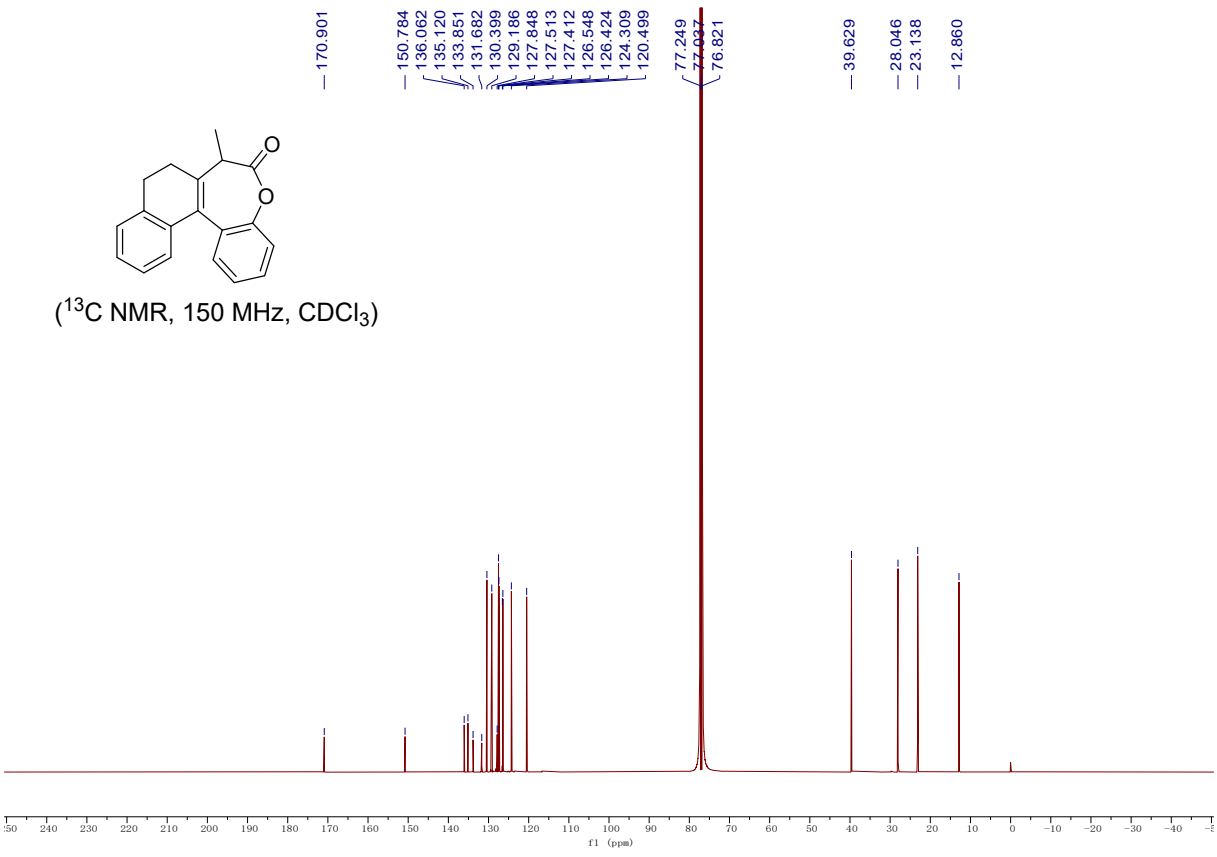


(^{13}C NMR, 150 MHz, $CDCl_3$)

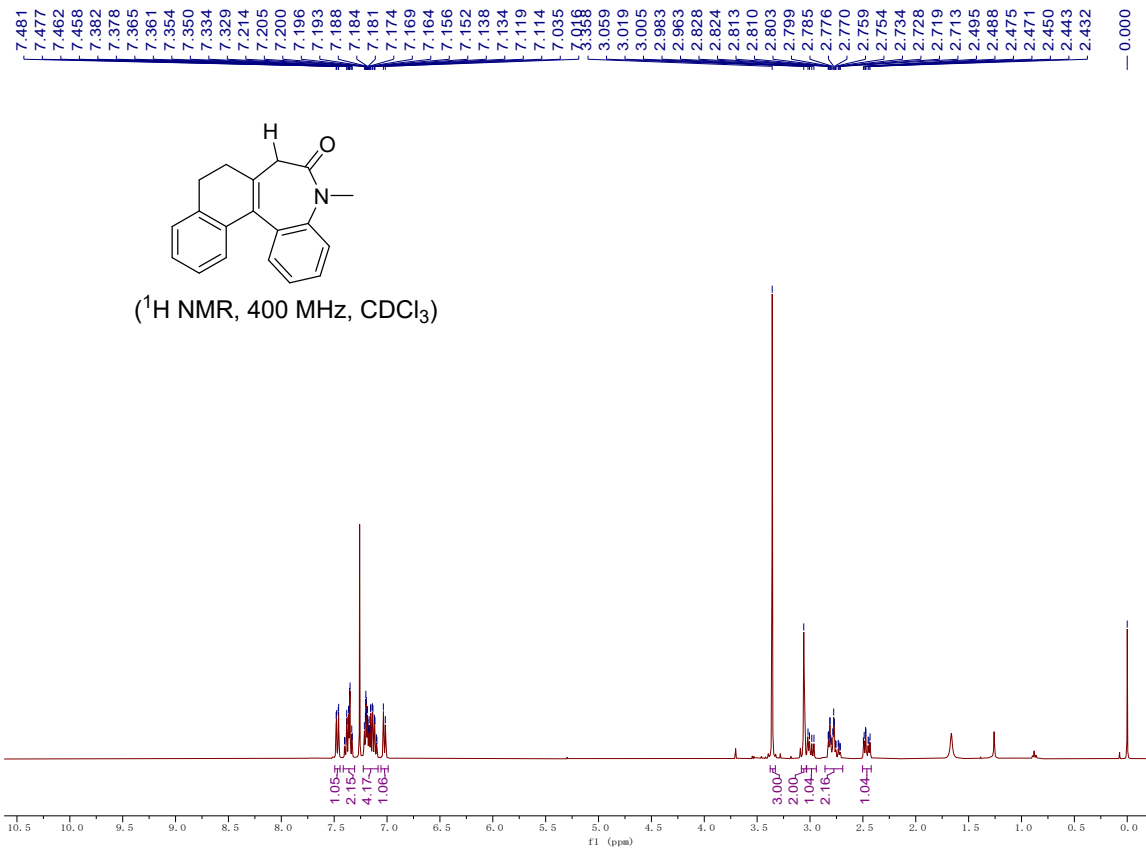


(^{1}H NMR, 600 MHz, $CDCl_3$)

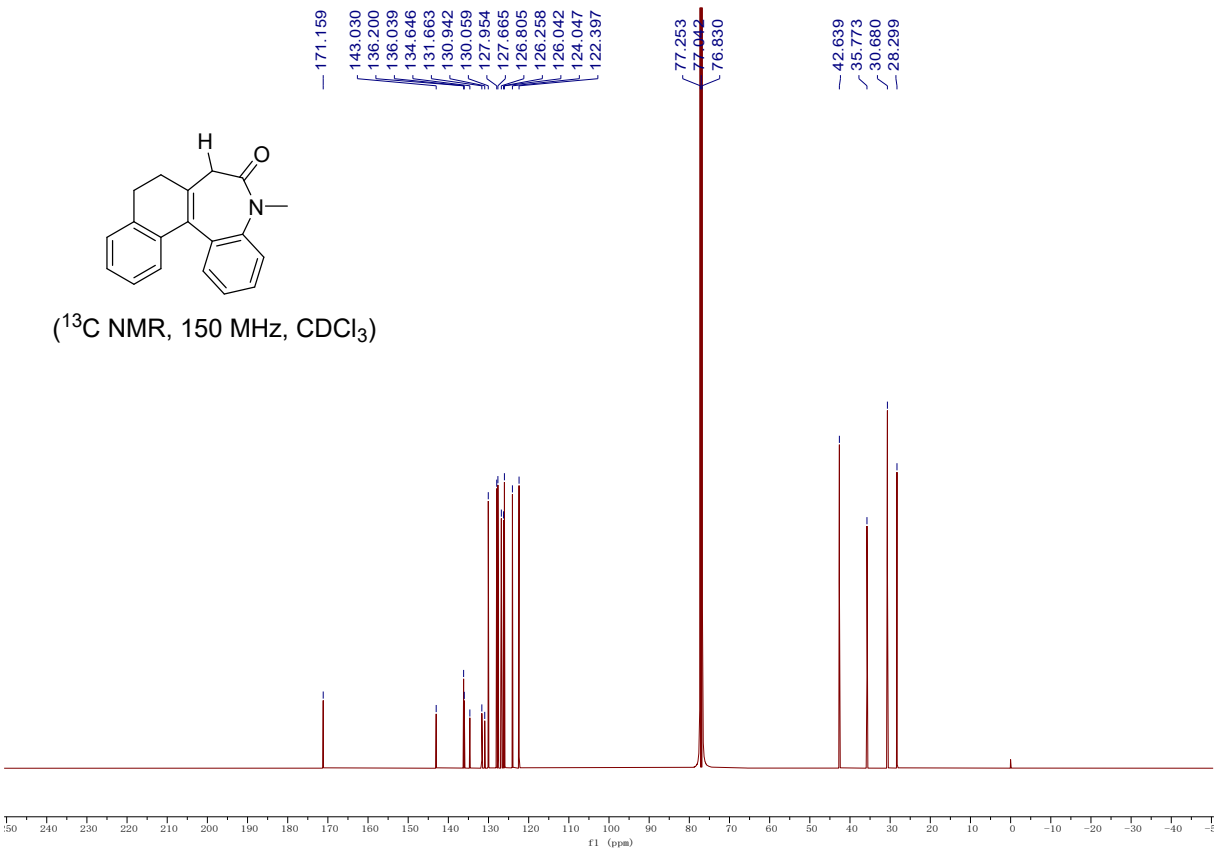




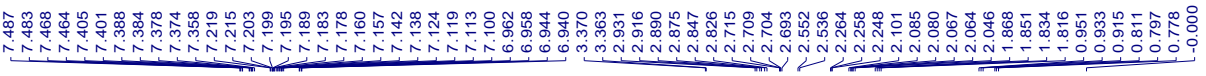
(^{13}C NMR, 150 MHz, $CDCl_3$)

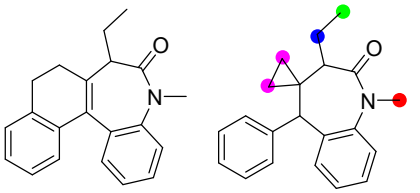


(^{1}H NMR, 400 MHz, $CDCl_3$)



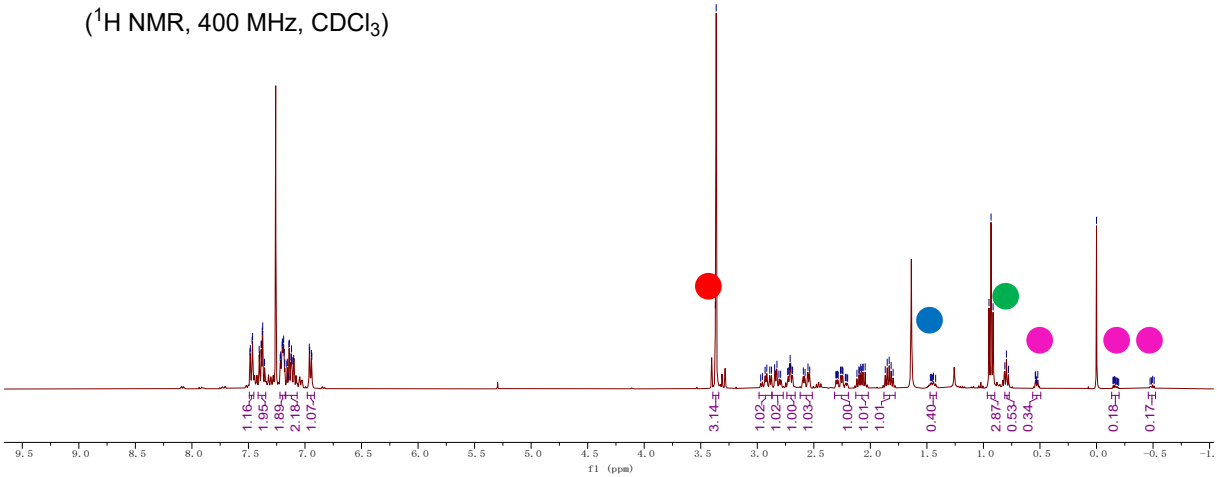
(^{13}C NMR, 150 MHz, $CDCl_3$)

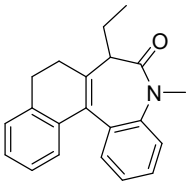




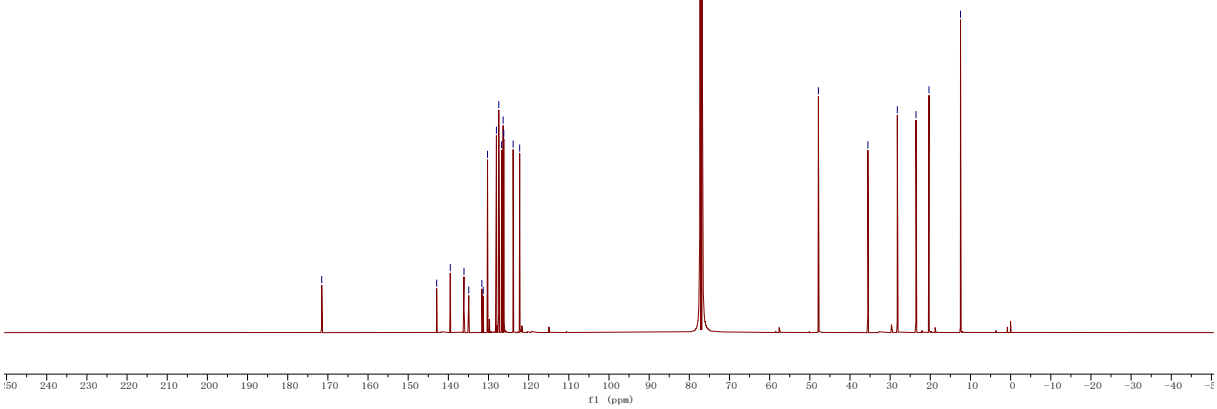
Speculated by-product

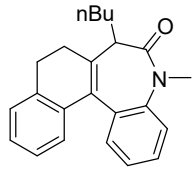
(^{1}H NMR, 400 MHz, $CDCl_3$)



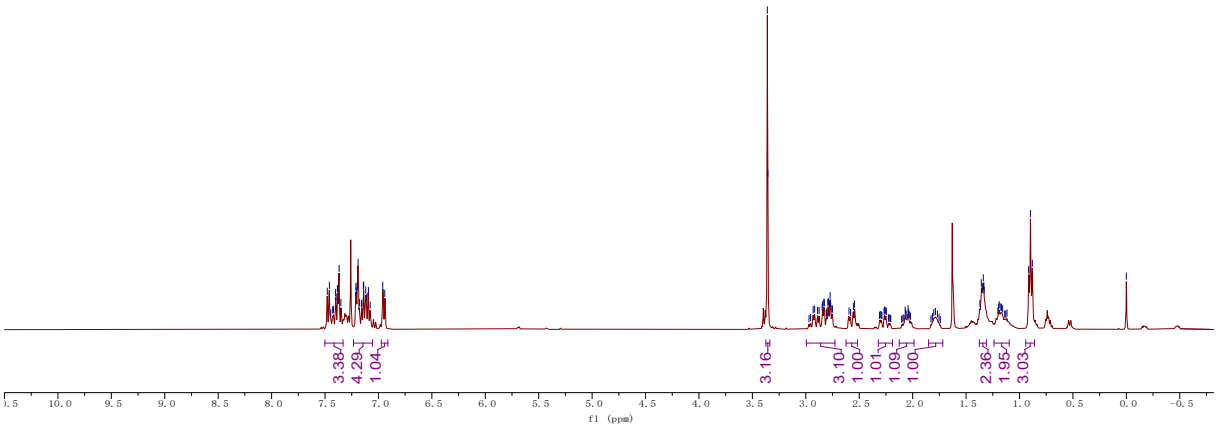


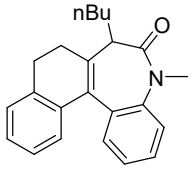
(^{13}C NMR, 150 MHz, $CDCl_3$)



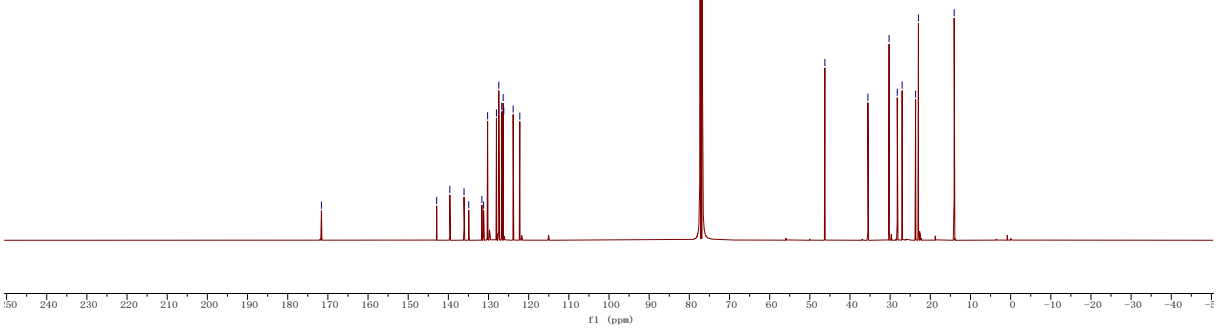


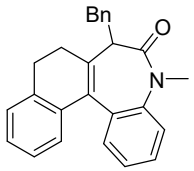
(^{1}H NMR, 400 MHz, $CDCl_3$)



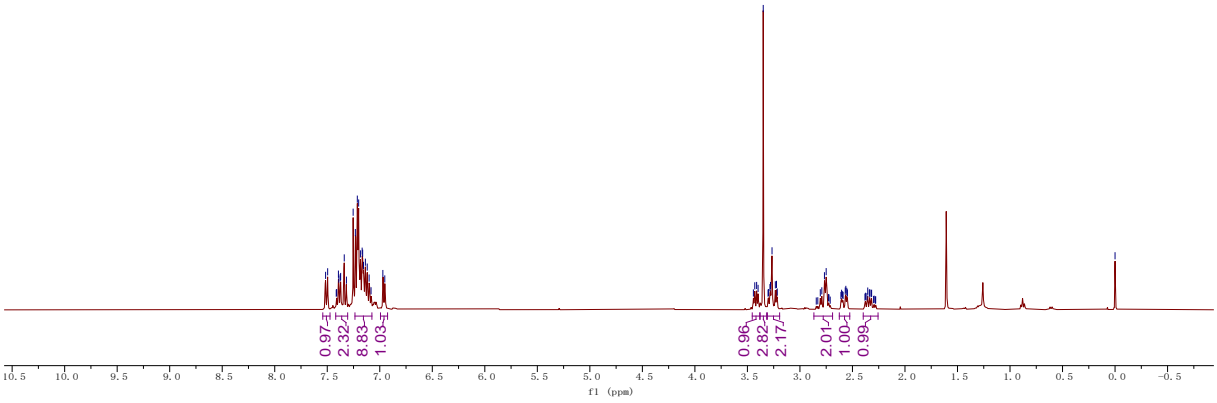


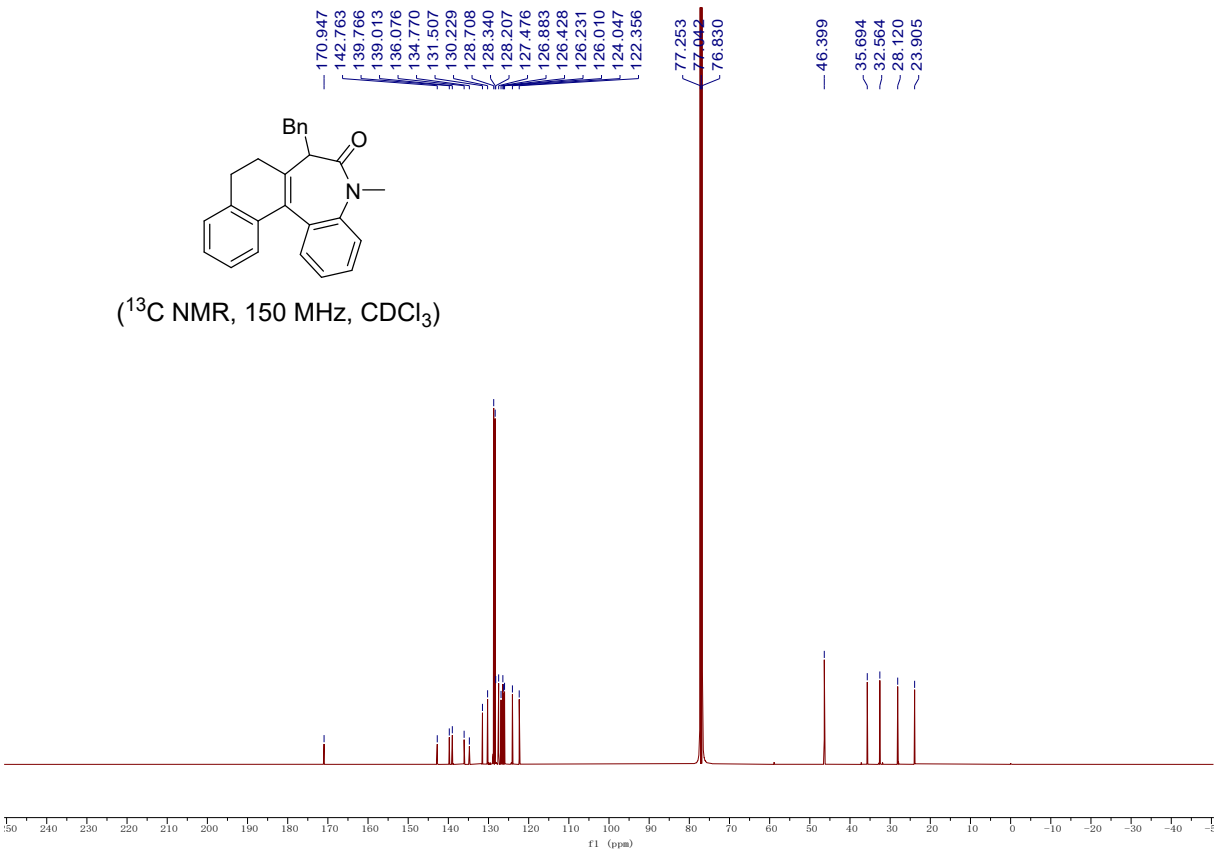
(^{13}C NMR, 150 MHz, $CDCl_3$)



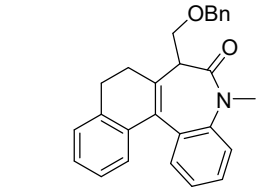


(^{1}H NMR, 400 MHz, $CDCl_3$)

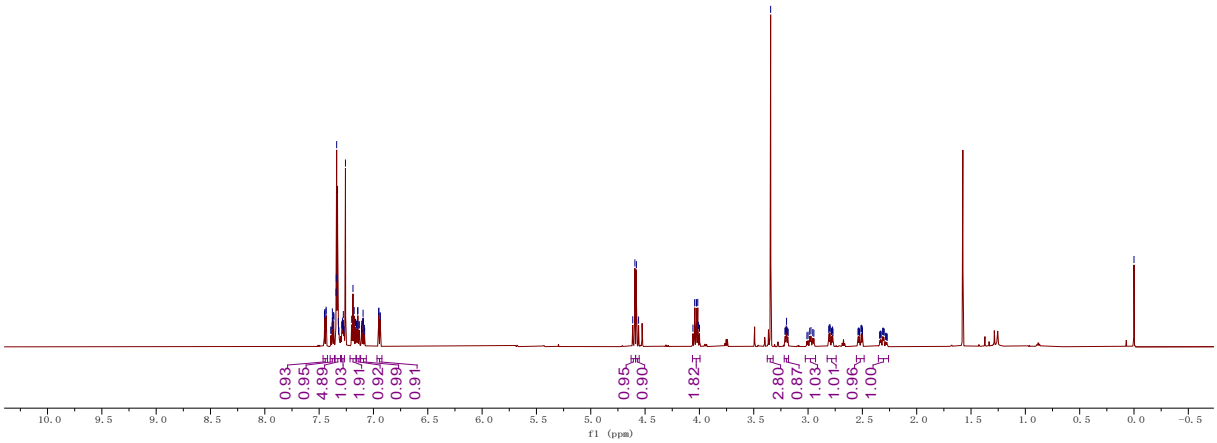


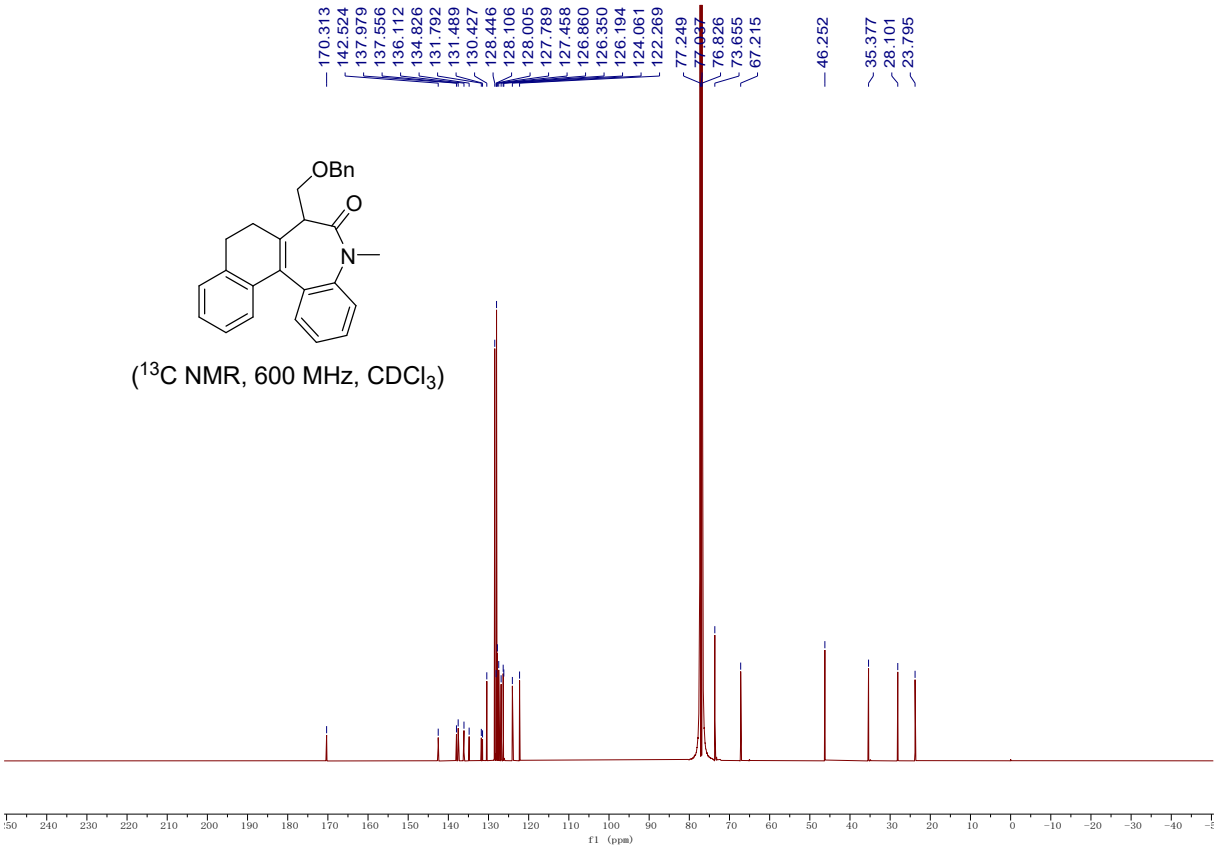


(^{13}C NMR, 150 MHz, $CDCl_3$)



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





(^{13}C NMR, 600 MHz, $CDCl_3$)

12. References

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