Supporting Information

Electrochemically Promoted Tandem Cyclization of Functionalized Methylenecyclopropanes: Synthesis of Tetracyclic Benzazepine Derivatives

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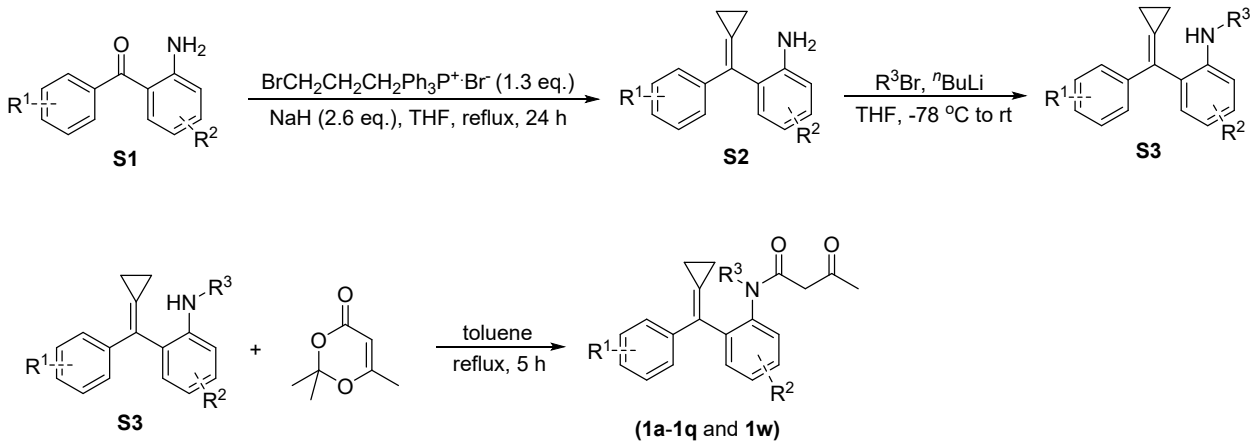
CONTENTS

1. General Remarks

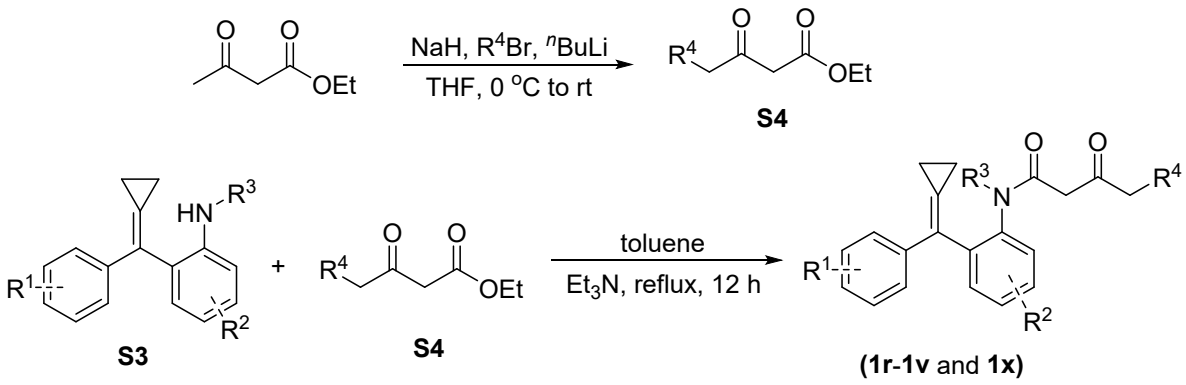
Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with Varian and Agi spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift was reported in ppm down field from internal TMS. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI and HRMS was measured on a HP-5989 instrument.

2. General Procedure for the Synthesis of Substrates



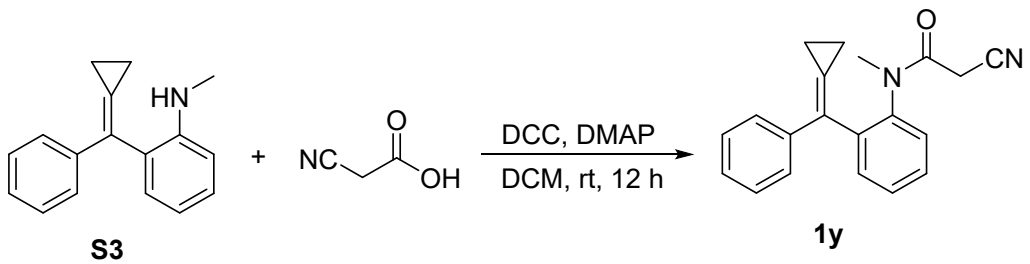
The procedure of preparing substrates **1** was slightly modified by the previous literature.[1] A solution of 3-bromopropyltriphenylphosphonium bromide (5.96 g, 13 mmol) and NaH (624 mg, 26 mmol) in THF (15 mL) was stirred at 65 °C in an oil bath under Ar for 12 h. Afterwards compound **S1** (10 mmol) in THF (10 mL) was added and the reaction solution was stirred at 65 °C in an oil bath for another 12 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 = 80/1) to afford the products **S2** in moderate yields.

A solution of compounds **S2** (4.0 mmol) in THF (15.0 mL) was stirred at -78 °C under Ar. Then ^{n}BuLi (4.0 mmol) was added dropwise, the resulting mixture was stirred at -78 °C for 1.0 h. Then, a solution of R^3Br (4.0 mmol) in THF (5.0 mL) was added dropwise, and warmed to room temperature. Upon completion, this mixture was added a NH_4Cl aqueous solution to quench the reaction and the reaction mixture was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 50/1) to afford the products **S3** in good yields. A solution of compound **S3** (2.0 mmol) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (2.2 mmol) in toluene (20.0 mL) was reflux at 120 °C for 5.0 h. Upon completion, the mixture is cooled to room temperature, and the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the products **1a-1q**, and **1w** in good yields.



Adding NaH (4.4 mmol) to a 50 mL dry Schlenk tube equipped with a magnetic stirrer, and washing the kerosene with ultradry *n*-pentane (5.0 mL x 3). Then ultradry THF (15 mL) is added under Ar at 0 °C. Subsequently, ethyl acetoacetate (4.0 mmol) was added dropwise and the resulting mixture was stirred at 0 °C for about 30 min; ^{n}BuLi (4.0 mmol) was also added dropwise at 0 °C and stirred at 25 °C for about 1.0 h. Finally, R^4Br (6.0 mmol) in THF (5.0 mL) was added dropwise. Upon completion, this reaction mixture was added a NH_4Cl aqueous solution to quench the reaction and the resulting mixture was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 4/1) to afford the products **S4** in good yields.

A solution of compound **S3** (2.0 mmol), Et_3N (3.0 mmol) and **S4** (2.2 mmol) in toluene (20.0 mL) was reflux for 12 h. Upon completion, the mixture is cooled to room temperature, and the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the products **1r**-**1v**, and **1x** in good yields.

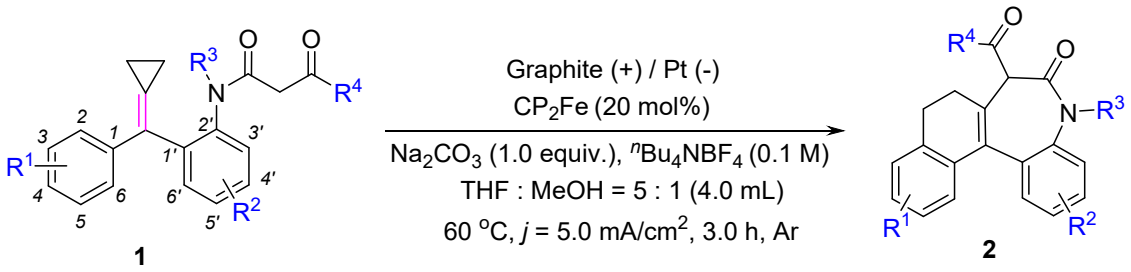


Adding **S3** (2.0 mmol), cyanoacetic acid (2.4 mmol) and DMAP (0.2 mmol) to a 25 mL dry Schlenk tube equipped with a magnetic stirrer, and then dry DCM (10 mL) was added into the

mixture under Ar. DCC (2.2 mmol) was dissolved in DCM (5.0 mL) and was added dropwise. Then, the reaction mixture was stirred at room temperature until the reaction was complete upon monitored by TLC analysis. Then, the reaction mixture was extracted by DCM/H_2O and the organic phase was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **1y** in good yield.

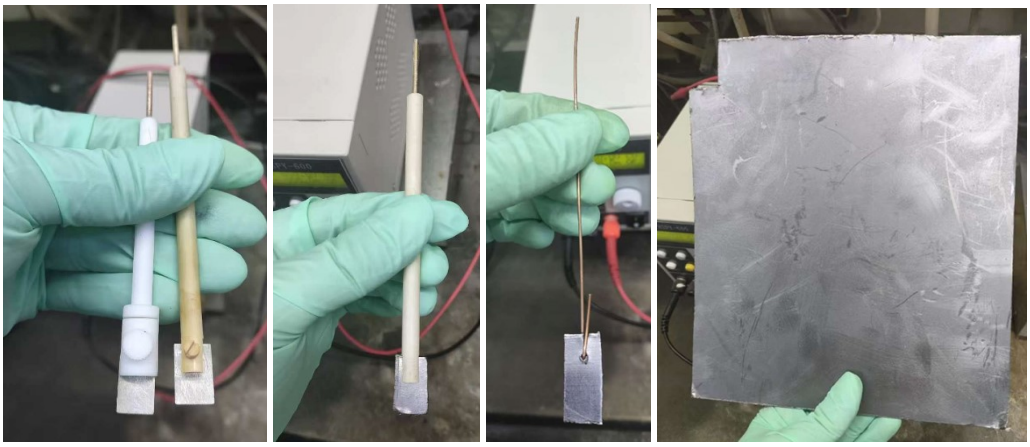
3. General Procedure for the Synthesis of Products

3.1 Method



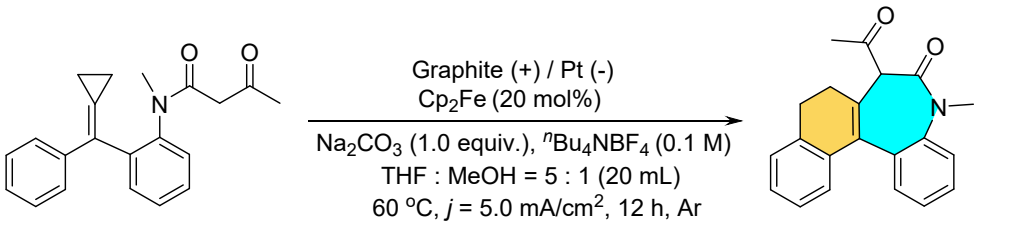
A 10 mL three-necked round-bottomed flask was charged with the substrate (0.2 mmol, 1.0 equiv.), Cp_2Fe (0.04 mmol, 0.2 equiv.), $^nBu_4NBF_4$ (0.4 mmol, 2.0 equiv.), and Na_2CO_3 (0.2 mmol, 1.0 equiv.). The flask was equipped with a condenser, a graphite anode (1.2 cm x 1.0 cm x 1.0 cm) and a platinum plate (1.0 cm x 1.0 cm) cathode. The flask was flushed with argon and then THF (3.3 mL) and MeOH (0.7 mL) were added. The constant current (5.0 mA) electrolysis was carried out at 60 °C until complete consumption of the substrate (monitored by TLC). The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was chromatographed through a silica gel column chromatography eluting with ethyl acetate/hexanes to give the desired product.

3.2 Reaction Setup




500
60

4. Up-scale Reaction

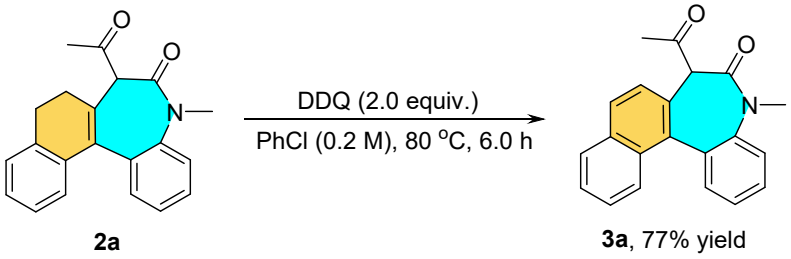


1a, 1 mmol, 320 mg

2a, 136 mg, 43% yield

A 100 mL three-necked round-bottomed flask was charged with the substrate (1.0 mmol, 1.0 equiv.), Cp_2Fe (0.2 mmol, 0.2 equiv.), $^nBu_4NBF_4$ (2.0 mmol, 2.0 equiv.), and Na_2CO_3 (1.0 mmol, 1.0 equiv.). The flask was equipped with a condenser, a graphite anode (1.2 cm x 1.0 cm x 1.0 cm) and a platinum plate (1.0 cm x 1.0 cm) cathode. The flask was flushed with argon and then THF (16.5 mL) and MeOH (3.5 mL) were added. The constant current (5.0 mA) electrolysis was carried out at 60 °C until complete consumption of the substrate (monitored by TLC). The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was chromatographed through a silica gel column chromatography eluting with ethyl acetate/hexanes to give the desired product.

5. Synthetic Transformation



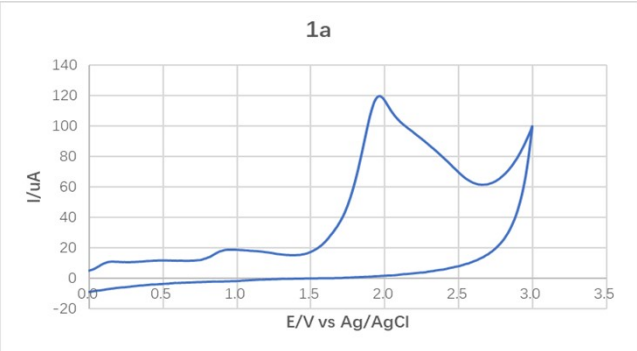
2a **3a**, 77% yield

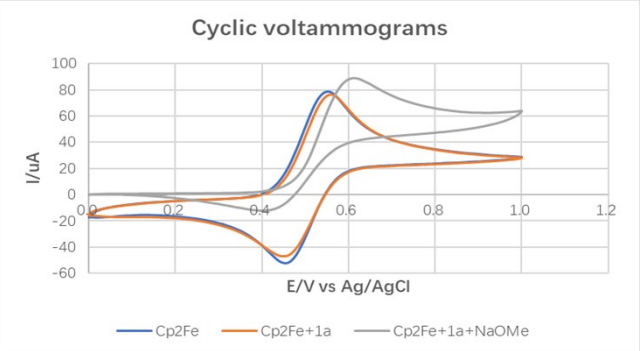
A Schlenk tube (10 mL) equipped with a magnetic stir bar was added **2a** (0.2 mmol) and PhCl (1.0 mL). The reaction mixture was stirred in a preheated oil bath at 80 °C. Then, DDQ (2.0 equiv.) was added in several portions for 1.0 h. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered through a celite. Subsequently, the solvent was removed under reduced pressure and the residue was purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:10) as an eluent to give the desired product **3a**.

6. Mechanistic Investigations

6.1 Cyclic Voltammetry

The cyclic voltammograms were recorded in an electrolyte solution of $^{n}Bu_4NPF_6$ (0.1 M) in MeCN using a glassy carbon disk working electrode (diameter, 1.0 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s. The oxidation potential of **1a** (6.0 mM) was determined as that $\mathbf{E_{p/2}^{ox}}$ = 1.80 V *vs* Ag/AgCl. The oxidation potential of Cp_2Fe (3.0 mM) was determined as that $\mathbf{E_{p/2}^{ox}}$ = 0.49 V *vs* Ag/AgCl.





6.2 Computational Methods, Coordinates and Energies

6.2.1 Computational Details

All DFT calculations were performed with Gaussian 16 program. The geometries of all minima and transition states have been optimized at ωB97X-D/6-31+G(d,p), SMD(MeCN) level of theory. The subsequent frequency calculations on the stationary points were carried out at the same level of theory to ascertain the nature of the stationary points as minima or first-order saddle points on the respective potential energy surfaces. All transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. The intrinsic reaction coordinate (IRC) calculations were carried out at the same level of theory to further authenticate the transition states. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The solvent effect was estimated by the IEFPCM method with radii and nonelectrostatic terms for SMD salvation model in toluene. The Gibbs free energies in acetonitrile (ΔG) obtained at the ωB97X-D/def2-tzvpp, SMD(MeCN)//ωB97X-D/6-31+G(d,p), SMD(MeCN) level were discussed throughout this paper unless otherwise specified.

6.2.2 Computational Coordinates and Energies

Table S1. The total energies, enthalpies and free energies of all species in acetonitrile shown in

	E_{tot} (E_h)	$H_{298,\ acetonitrile}$	$G_{298,\ acetonitrile}$
Elec-radical	-1017.142218	-1016.760899	-1016.838716
TS1-6	-1017.130483	-1016.75017	-1016.822739
TS1-7	-1017.116563	-1016.735931	-1016.808475
INT1-6	-1017.163873	-1016.780793	-1016.853177
INT1-7	-1017.16834	-1016.785048	-1016.856446
INT1-7-open	-1017.21716	-1016.833142	-1016.903019

Calculated at ωB97X-D/def2-tzvpp, SMD(MeCN)//ωB97X-D/6-31+G(d,p), SMD(MeCN)

Coordinates of **Elec-radical**:

C	3.47921600	-0.91602700	-2.19873800
C	4.50385100	-1.64155300	-1.59011800
C	4.49026000	-1.81686500	-0.20682200
C	3.46047700	-1.27473100	0.56015200
C	2.42143200	-0.55125600	-0.04119000
C	2.45091600	-0.37379500	-1.43181300
C	1.30538900	0.01789200	0.76920000
C	0.75342200	1.34087800	0.34695500
C	1.64716500	2.40420900	0.15376500
C	1.20996000	3.67051100	-0.21833400
C	-0.14905700	3.89992000	-0.42676300
C	-1.05185200	2.85562600	-0.26087000
C	-0.61051400	1.58806400	0.12478800
C	0.85321000	-0.61041500	1.85150400
C	-0.06578300	-0.64944100	2.99012600
C	0.94793700	-1.77506100	2.73612300
N	-1.59969400	0.56787800	0.30344600
C	-2.63476000	0.81145400	1.30674100
C	-1.64474900	-0.47837700	-0.54813800
C	-2.71018500	-1.50264300	-0.38027900
O	-0.84437600	-0.65537100	-1.47148700
C	-4.06115600	-1.27172600	-0.84307300
C	-5.04084700	-2.40866400	-0.72059900

O	-4.38073300	-0.17452700	-1.31869700
H	3.47821400	-0.77312400	-3.27555200
H	5.30761500	-2.06145400	-2.18767800
H	5.28840600	-2.36933600	0.28070400
H	3.47159800	-1.40356700	1.63767800
H	1.64924100	0.17597600	-1.91451900
H	2.70803200	2.22820100	0.30847100
H	1.92858700	4.47405500	-0.34712500
H	-0.50427100	4.88094400	-0.72629900
H	-2.11147200	3.01443200	-0.43784500
H	0.11362700	0.02057000	3.82854700
H	-1.11231200	-0.87324100	2.80156700
H	0.56390500	-2.72795500	2.37676500
H	1.79880900	-1.85202900	3.40903200
H	-2.17319800	1.26757700	2.18401500
H	-3.41351900	1.47542300	0.92041600
H	-3.09195200	-0.13220800	1.61048000
H	-2.40271300	-2.48837900	-0.04180300
H	-4.70743500	-3.25204500	-1.33510700
H	-5.08643900	-2.75876500	0.31596300
H	-6.03198100	-2.08905300	-1.04606500

Coordinates of **TS1-6**:

C	-3.14668500	1.97078100	-1.08202600
C	-4.22901000	1.49756200	-0.34085200
C	-3.99582800	0.63151200	0.72503800
C	-2.69658000	0.24611000	1.05132700
C	-1.60140200	0.71488700	0.31565400
C	-1.85047900	1.58035300	-0.75947200
C	-0.20124900	0.25873000	0.62814100
C	0.94509600	1.15317000	0.22588100
C	0.84867900	2.52834800	0.45846600
C	1.88783900	3.40005700	0.15036000
C	3.05544300	2.89373200	-0.41335700
C	3.17877600	1.52778300	-0.64015100
C	2.14251000	0.64526200	-0.30988300
N	2.36563900	-0.74482500	-0.48325700
C	3.71913900	-1.26157300	-0.29653100
C	1.38847700	-1.64070600	-0.83267200
C	0.02654900	-1.09500900	-1.04896700
O	1.64879900	-2.83480000	-0.98925200
C	-1.12694100	-2.00669400	-0.97299000
C	-2.24007200	-1.77659100	-1.96332600
O	-1.19452200	-2.89781600	-0.13071500

H	-3.30977300	2.64093600	-1.92083300
H	-5.24130600	1.79848000	-0.59315400
H	-4.82723800	0.25127100	1.31123000
H	-2.54342000	-0.43066800	1.88320900
H	-1.02710900	1.94398800	-1.36575300
H	-0.06294400	2.92165800	0.89763600
H	1.78162500	4.46217600	0.34680800
H	3.87423600	3.55575000	-0.67753800
H	4.09112200	1.14146900	-1.08079600
H	3.65406000	-2.29895800	0.02834700
H	4.29959800	-1.22288000	-1.22431800
H	4.22510800	-0.67479600	0.47137200
H	-0.03513000	-0.30315400	-1.79351800
H	-3.10683800	-2.38809200	-1.70620100
H	-2.52218900	-0.71969700	-1.99444600
H	-1.88883300	-2.04612200	-2.96673500
C	0.04187500	-0.52705200	1.73184300
C	1.07638800	-1.17199600	2.53317000
C	-0.41434100	-1.48462000	2.73284300
H	1.58038100	-0.58410700	3.29875600
H	1.69906800	-1.93045200	2.06081700
H	-0.78837600	-2.44344200	2.38018400

Coordinates of **TS1-7**:

C	1.40443800	3.48781400	-1.00600700
C	2.70657600	3.49498300	-0.50588400
C	3.09876900	2.50604600	0.39731700
C	2.20066600	1.52544500	0.80096600
C	0.87742500	1.50885300	0.31626200
C	0.50320100	2.50934800	-0.60216800
C	-0.07907900	0.47033500	0.72366100
C	-1.52274800	0.63467500	0.37581900
C	-2.20748200	1.75190900	0.87268900
C	-3.56550500	1.93820400	0.63643800
C	-4.26196300	1.00792500	-0.13314400
C	-3.59627400	-0.09459600	-0.65864600
C	-2.23615800	-0.29771000	-0.40943800
C	0.31845600	-0.69241400	1.34712800
C	-0.23075800	-1.58196600	2.38781400
C	1.22454300	-1.11133300	2.43274800
N	-1.60319800	-1.46633600	-0.91479100
C	-2.12034200	-2.74962500	-0.44093100
C	-0.24952800	-1.32005600	-1.27895400
C	0.70441900	-2.10691000	-0.49142200

O	0.06389000	-0.47599300	-2.10812900
C	2.15572600	-2.10933200	-0.68601700
C	2.90626400	-3.23906800	-0.01300300
O	2.76224200	-1.27747400	-1.35787200
H	1.08993100	4.24303400	-1.72001500
H	3.41027500	4.25970500	-0.82058100
H	4.11172800	2.49660500	0.78850600
H	2.53475800	0.76493400	1.49499600
H	-0.49687700	2.51078400	-1.02048600
H	-1.66171200	2.47473700	1.47275700
H	-4.07324800	2.80479400	1.04798600
H	-5.31940700	1.14533100	-0.33759800
H	-4.12995200	-0.80678800	-1.28067500
H	-0.94302200	-1.14463200	3.08387700
H	-0.39122900	-2.63293900	2.17199000
H	1.99124100	-1.85577600	2.24213900
H	1.49992300	-0.35596100	3.16461000
H	-2.00406700	-2.88283400	0.64087500
H	-3.18218100	-2.81836800	-0.68572400
H	-1.61396200	-3.56169500	-0.96553600
H	0.31058500	-2.94526400	0.06957900
H	2.38316700	-3.63068900	0.86295500
H	3.00394800	-4.06009400	-0.73411400
H	3.90955800	-2.90794700	0.26463900

Coordinates of **INT1-6:**

C	-3.58623800	0.66517100	-1.51519900
C	-4.40532300	1.09632600	-0.47369800
C	-3.87908200	1.17679400	0.81348200
C	-2.55364900	0.81880000	1.05671100
C	-1.72379400	0.37084700	0.02333500
C	-2.26062600	0.31261900	-1.26860600
C	-0.24944000	0.03287700	0.28654700
C	0.65464400	1.24385600	-0.02121400
C	0.18573200	2.55554100	-0.03210000
C	1.04186500	3.62903600	-0.27201800
C	2.39065600	3.38929400	-0.51224400
C	2.87972900	2.08528200	-0.51209000
C	2.02065600	1.01162400	-0.26330600
N	2.52988500	-0.30956000	-0.24087000
C	3.95585100	-0.53263100	-0.03379600
C	1.72641800	-1.38631400	-0.47008600
C	0.25359900	-1.07257500	-0.68614900
O	2.15803600	-2.53579400	-0.53017000

C	-0.53988400	-2.37969900	-0.66773000
C	-0.68464200	-3.08002800	-1.98622300
O	-1.04293600	-2.80062000	0.35683100
H	-3.97531100	0.60319500	-2.52726700
H	-5.43869300	1.37017100	-0.66416900
H	-4.49863300	1.52037800	1.63674100
H	-2.16523500	0.90159200	2.06491500
H	-1.65108400	-0.00099000	-2.10941100
H	-0.86609700	2.74531900	0.15420000
H	0.65231100	4.64208400	-0.27324400
H	3.07043700	4.21276400	-0.70793700
H	3.93013100	1.91044800	-0.71428800
H	4.10023700	-1.56825100	0.26814500
H	4.52547600	-0.34831400	-0.95011400
H	4.31501200	0.12852700	0.75724400
H	0.20811300	-0.66922600	-1.70621000
H	-1.08315600	-4.08618500	-1.84757300
H	-1.37491500	-2.49591500	-2.60780100
H	0.27428300	-3.11543500	-2.51110500
C	0.00797400	-0.30447300	1.72891900
C	0.84821400	-1.24087200	2.48312300
C	-0.61855300	-0.99583000	2.85718900
H	1.61229400	-0.84465900	3.15156900
H	1.10008400	-2.20167100	2.03504100
H	-1.33681300	-1.78518500	2.64417700
H	-0.81310500	-0.43430500	3.77080300

Coordinates of **INT1-7:**

C	2.26438400	3.13427100	-1.08801500
C	3.53115600	2.81585000	-0.59228900
C	3.66750200	1.71812400	0.26102300
C	2.56324000	0.96142700	0.62823500
C	1.26009200	1.28208200	0.16795300
C	1.15452000	2.38644500	-0.72075700
C	0.10000000	0.50788800	0.54195300
C	-1.26014800	1.00204600	0.22659300
C	-1.63659800	2.31099900	0.57791600
C	-2.92030300	2.79234600	0.35305300
C	-3.86918000	1.97009600	-0.25505200
C	-3.52398300	0.67568500	-0.62749300
C	-2.23920400	0.18241900	-0.38742300
C	0.19716900	-0.86998200	1.15527900
C	-0.60696300	-1.11164900	2.41986000
C	0.88990000	-1.07489700	2.48189300

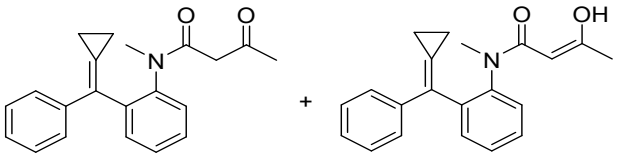
N	-1.95107600	-1.17045300	-0.72410600
C	-2.75428900	-2.19859200	-0.05544000
C	-0.60461600	-1.45786700	-1.01856100
C	0.20965300	-2.03365000	0.13367400
O	-0.09201700	-1.08662400	-2.05646000
C	1.55733800	-2.55469500	-0.35248200
C	1.49577900	-3.79439900	-1.20571700
O	2.61601400	-2.05381900	-0.02537300
H	2.14197100	3.96573600	-1.77623900
H	4.39849800	3.40348300	-0.87757000
H	4.64812500	1.44401900	0.63993400
H	2.70861800	0.09736300	1.25990800
H	0.19201700	2.64139300	-1.14945700
H	-0.90684700	2.94782500	1.06895200
H	-3.18002200	3.80207400	0.65547500
H	-4.87342700	2.33585800	-0.44601400
H	-4.25209500	0.03706700	-1.11809000
H	-1.15478100	-0.26706300	2.82691600
H	-1.09741900	-2.07294600	2.53219200
H	1.42483500	-2.00899500	2.62240100
H	1.35121700	-0.21134500	2.94869500
H	-2.72231400	-2.11759700	1.03628500
H	-3.79122600	-2.10890900	-0.38505500
H	-2.40113700	-3.18525000	-0.36134000
H	-0.30944600	-2.89582700	0.56868400
H	1.36419500	-4.65328500	-0.53575800
H	0.64485500	-3.78131200	-1.89139700
H	2.42725200	-3.91925500	-1.76032300

Coordinates of **INT1-7-open:**

O	2.28441000	-2.24084800	-1.85499000
O	3.22370400	-1.00275600	1.33338000
N	1.87810400	-0.04570200	-1.46589400
C	1.59104500	1.00316100	-0.55000100
C	2.53205800	2.03036600	-0.40239000
C	2.31971200	3.05957400	0.50277300
C	1.16769000	3.06215500	1.29154600
C	0.22988800	2.05148700	1.13615000
C	0.40302000	1.01983000	0.19830300
C	-0.62984100	-0.04595200	0.07721300
C	-2.01837700	0.29993600	-0.17293800
C	-2.47175800	1.60340700	-0.37479400
C	-3.82721600	1.89836000	-0.52274800
C	-4.81026100	0.86489900	-0.39528800

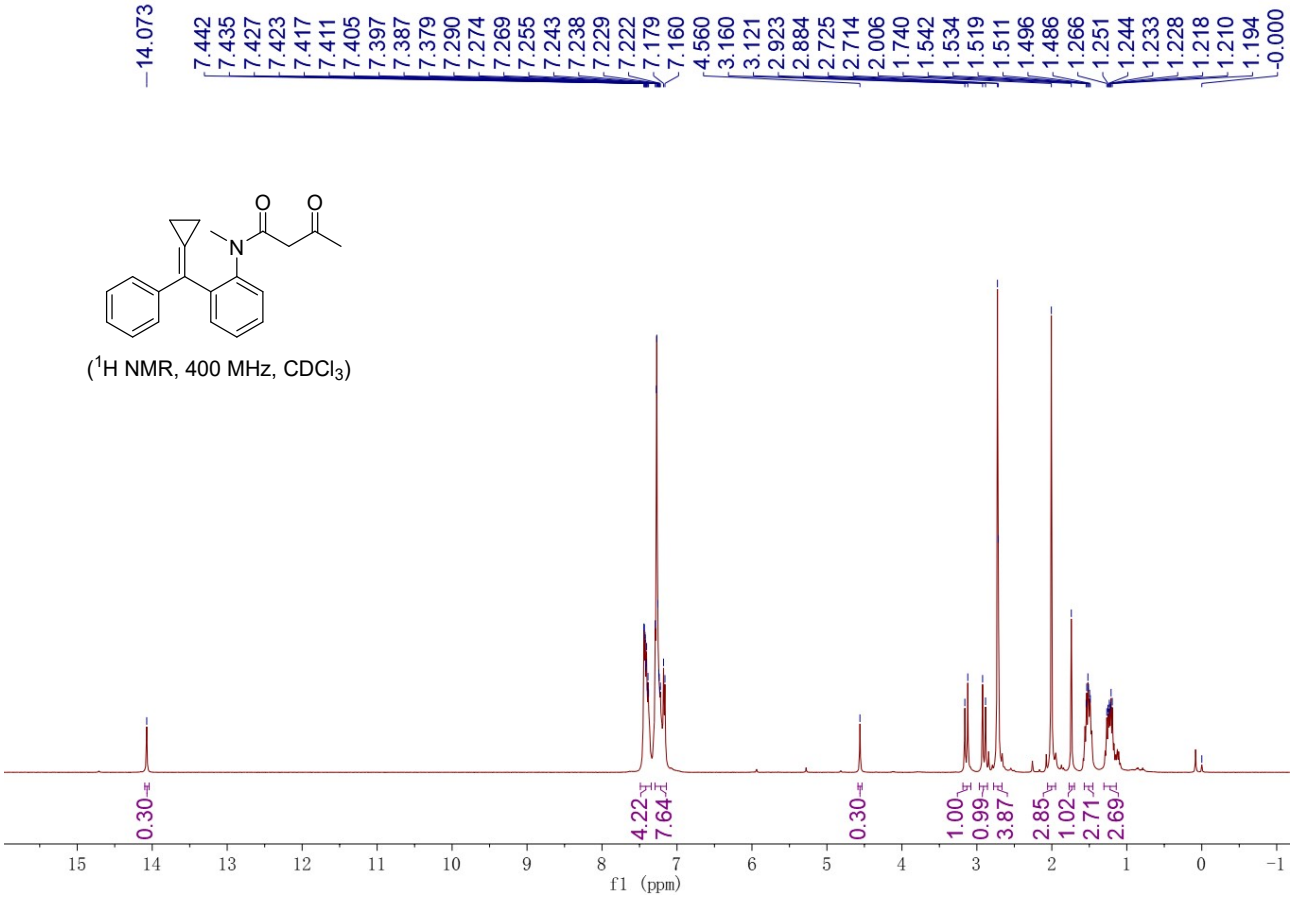
C	-4.43068000	-0.43013300	-0.26813000
C	-2.99152900	-0.84848000	-0.34385200
C	-2.63847200	-2.01027600	0.59234000
C	-1.22283900	-2.48777700	0.29706800
C	-0.24514300	-1.34900700	0.21194700
C	1.22059400	-1.71790100	0.23391800
C	1.86058900	-1.36311800	-1.10610900
C	2.03857900	-1.25709100	1.44780600
C	1.32823100	-1.23834200	2.77041100
C	2.47664600	0.28944900	-2.75639200
H	3.44531600	2.00429500	-0.98778600
H	3.06267200	3.84371700	0.61061200
H	1.00441300	3.84557600	2.02491300
H	-0.66207100	2.04865600	1.75497200
H	-1.76365300	2.42578100	-0.38896900
H	-4.14084900	2.92655600	-0.67285700
H	-5.86385000	1.13125900	-0.39357300
H	-5.17146100	-1.22090000	-0.17316000
H	-3.35234300	-2.82918800	0.45963700
H	-2.71071100	-1.67144800	1.63342000
H	-0.88113300	-3.18050700	1.07574700
H	-1.20015000	-3.05633000	-0.64502300
H	1.29106200	-2.81090800	0.29392500
H	0.70270400	-2.12976500	2.88166300
H	0.66385200	-0.36841000	2.81009800
H	2.05223100	-1.17645700	3.58425200
H	2.16872200	1.29696400	-3.03589700
H	2.11931800	-0.41628200	-3.50707500
H	3.56990800	0.23841700	-2.72077700
H	-2.83723900	-1.23955400	-1.37098200

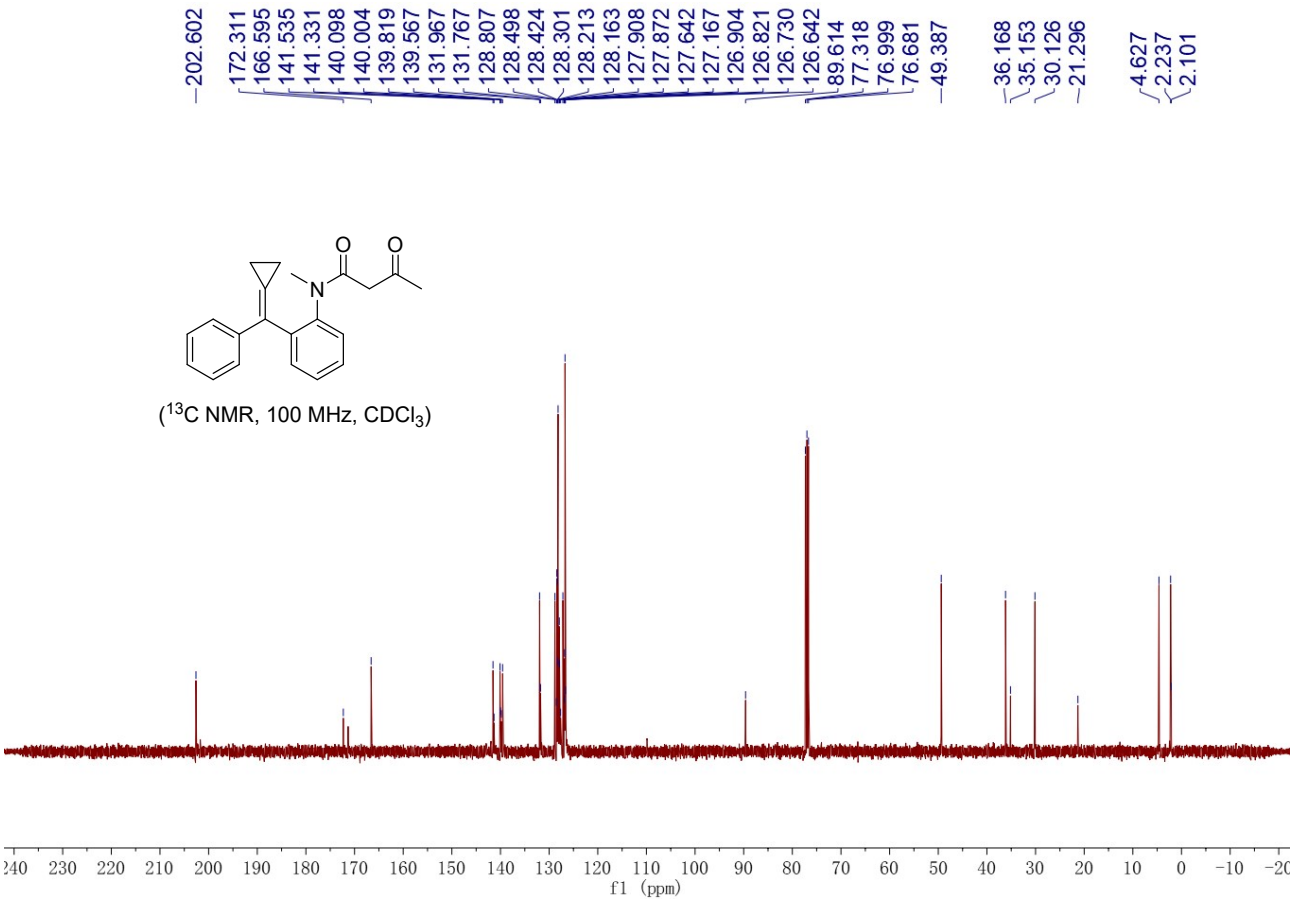
7. Characterization Data of Substrates



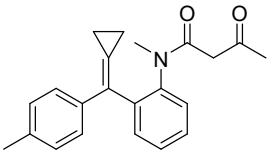
(major) (minor)

N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1a**): Yield: 512 mg, 80%, brown solid, m.p. 120-122 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.07 (s, 0.30H), 7.51 – 7.33 (m, 4.22H), 7.28 – 7.11 (m, 7.64H), 4.55 (s, 0.30H), 3.13 (d, *J* = 15.8 Hz, 1H), 2.90 (d, *J* = 15.8 Hz, 1H), 2.77 – 2.66 (m, 3.87H), 2.00 (s, 2.85H), 1.73 (s, 1H), 1.59 – 1.46 (m, 2.70H), 1.22 (m, 2.70H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.6, 172.3, 171.3, 166.6, 141.5, 141.3, 140.1, 140.0, 139.8, 139.6, 132.0, 131.8, 128.8, 128.5, 128.4, 128.3, 128.2, 128.2, 127.9, 127.9, 127.6, 127.2, 126.9, 126.8, 126.7, 126.6, 89.6, 49.4, 36.2, 35.2, 30.1, 21.3, 4.6, 2.2, 2.1; IR (neat): ν 3058, 2977, 2914, 1732, 1635, 1339, 1184, 918, 769, 699 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$: 342.14645, found: 342.14584.

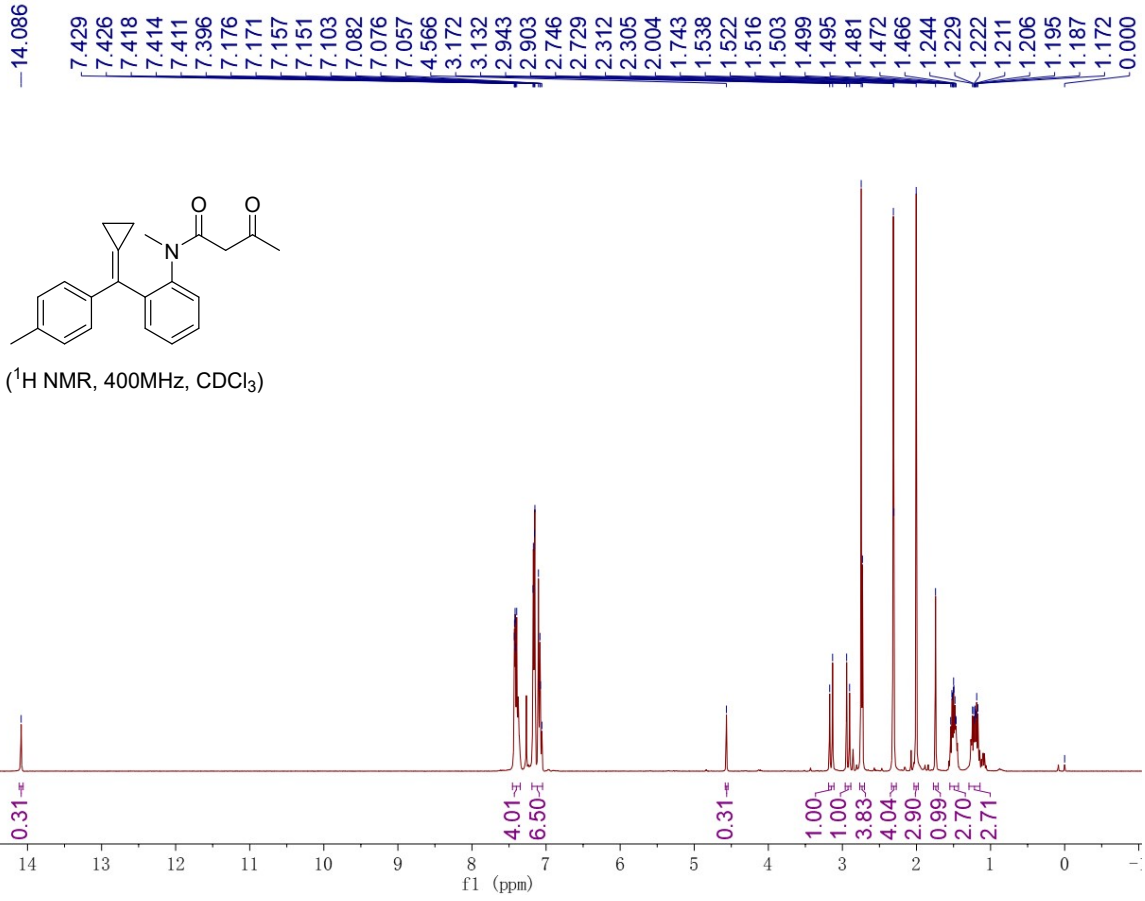


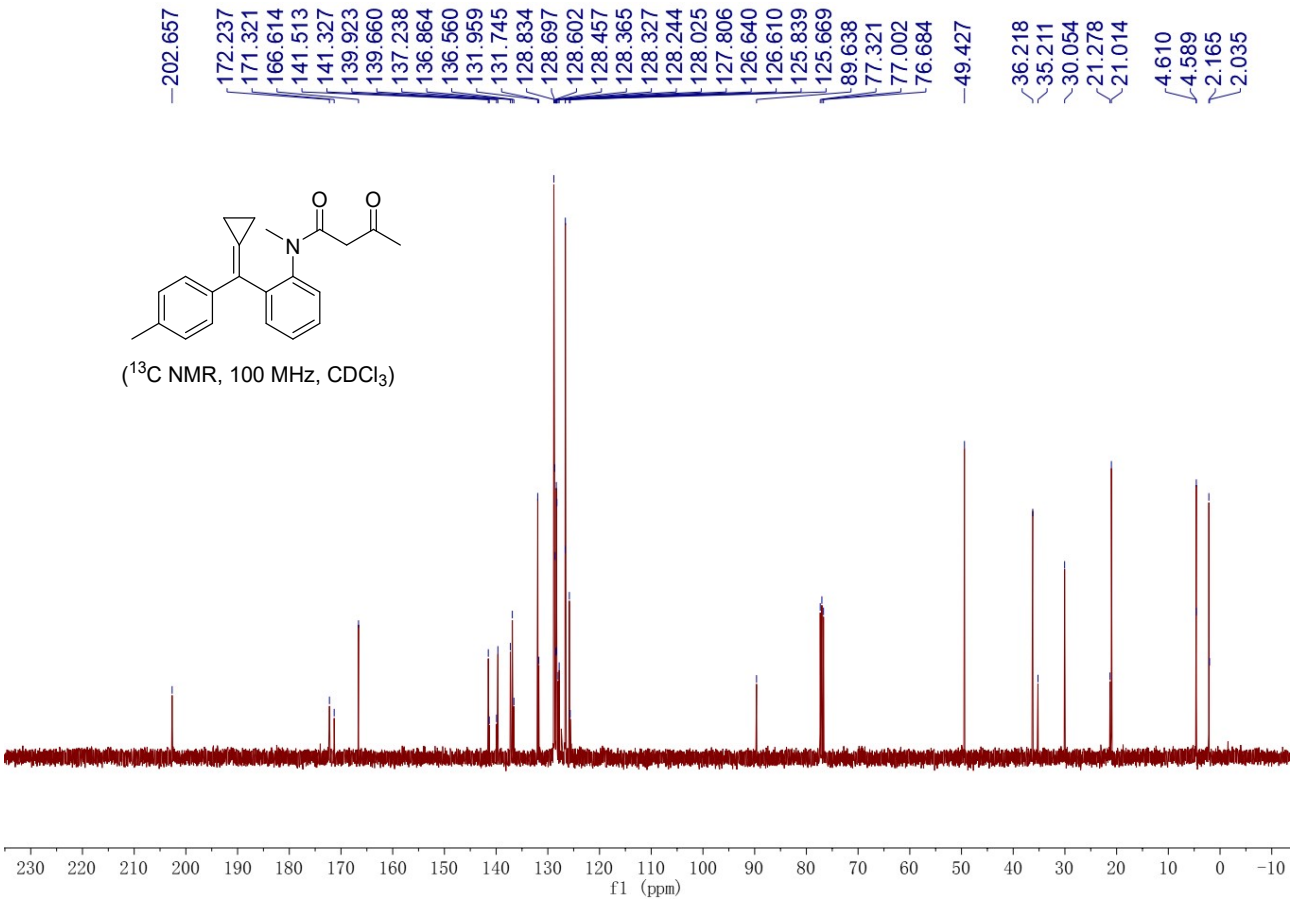


(^{13}C NMR, 100 MHz, $CDCl_3$)

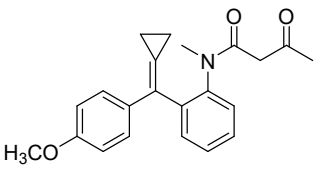


N-(2-(cyclopropylidene(p-tolyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1b**): Yield: 506 mg, 76%, brown solid, m.p. 156-158 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.09 (s, 0.31H), 7.45 – 7.35 (m, 4.0H), 7.19 – 7.05 (m, 6.5H), 4.57 (s, 0.31H), 3.15 (d, *J* = 15.8 Hz, 1H), 2.92 (d, *J* = 15.8 Hz, 1H), 2.77 – 2.70 (m, 3.83H), 2.34 – 2.27 (m, 4H), 2.00 (s, 2.9H), 1.74 (s, 1H), 1.55 – 1.43 (m, 2.7H), 1.29 – 1.14 (m, 2.7H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 172.2, 171.3, 166.6, 141.5, 141.3, 139.9, 139.7, 137.2, 136.9, 136.6, 132.0, 131.7, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 126.6, 126.6, 125.8, 125.7, 89.6, 49.4, 36.2, 35.2, 30.1, 21.3, 21.0, 4.6, 4.6, 2.2, 2.0; IR (neat): ν 3060, 2922, 2820, 1701, 1354, 1229, 1043, 819, 772, 723 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.16210, found: 356.16288.

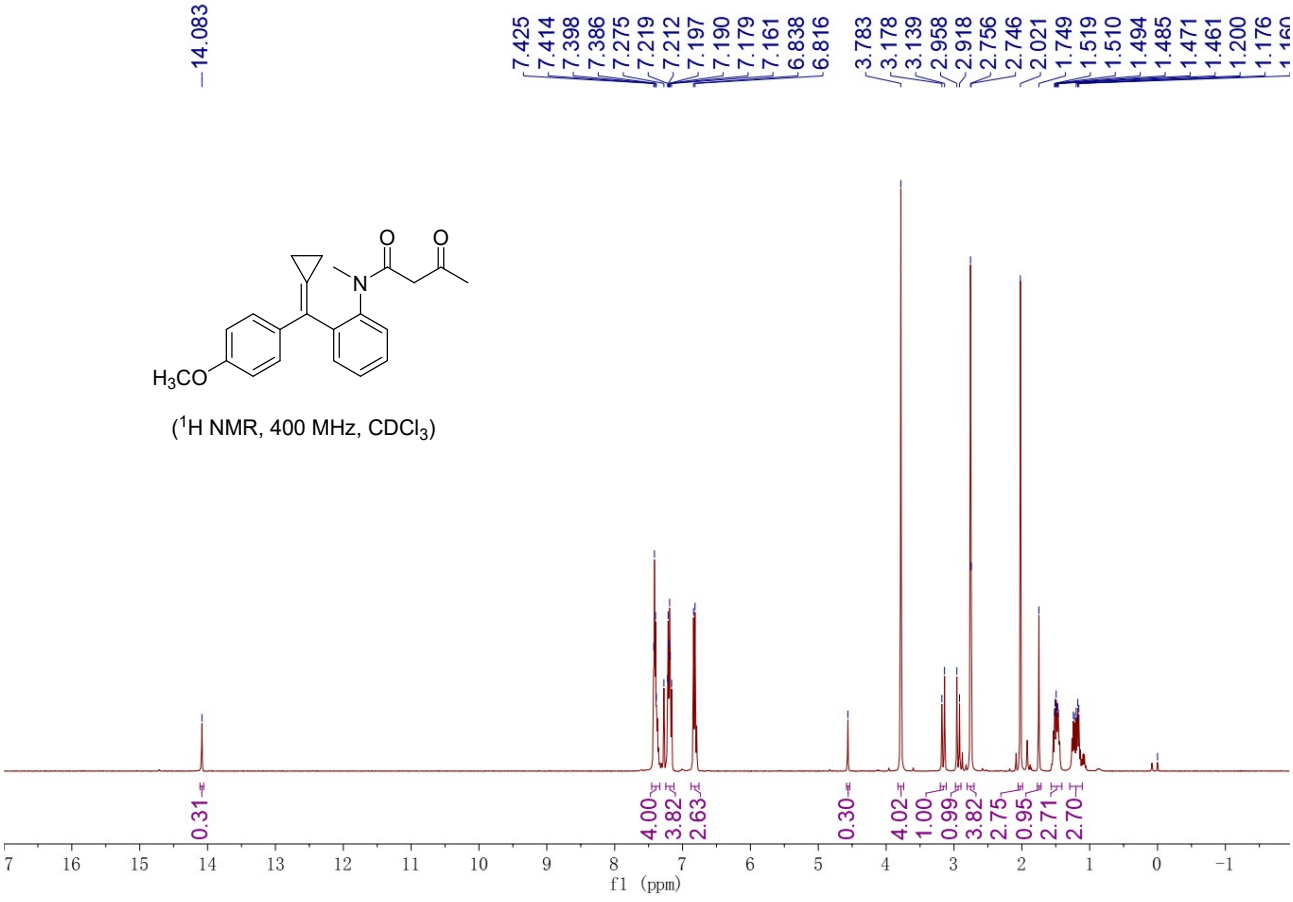


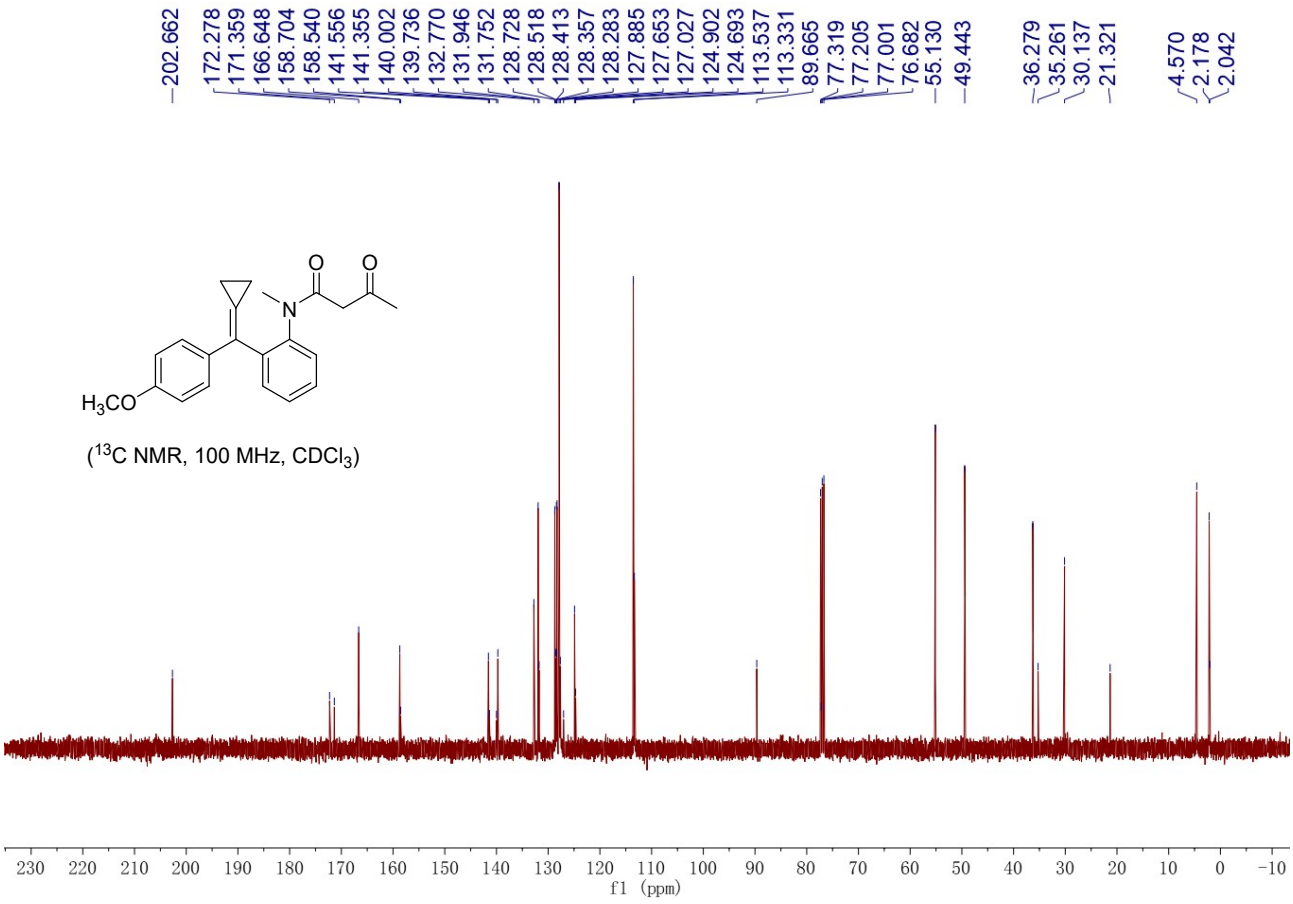


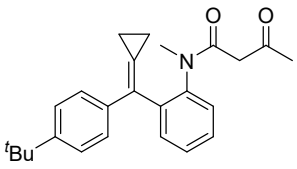
(^{13}C NMR, 100 MHz, $CDCl_3$)



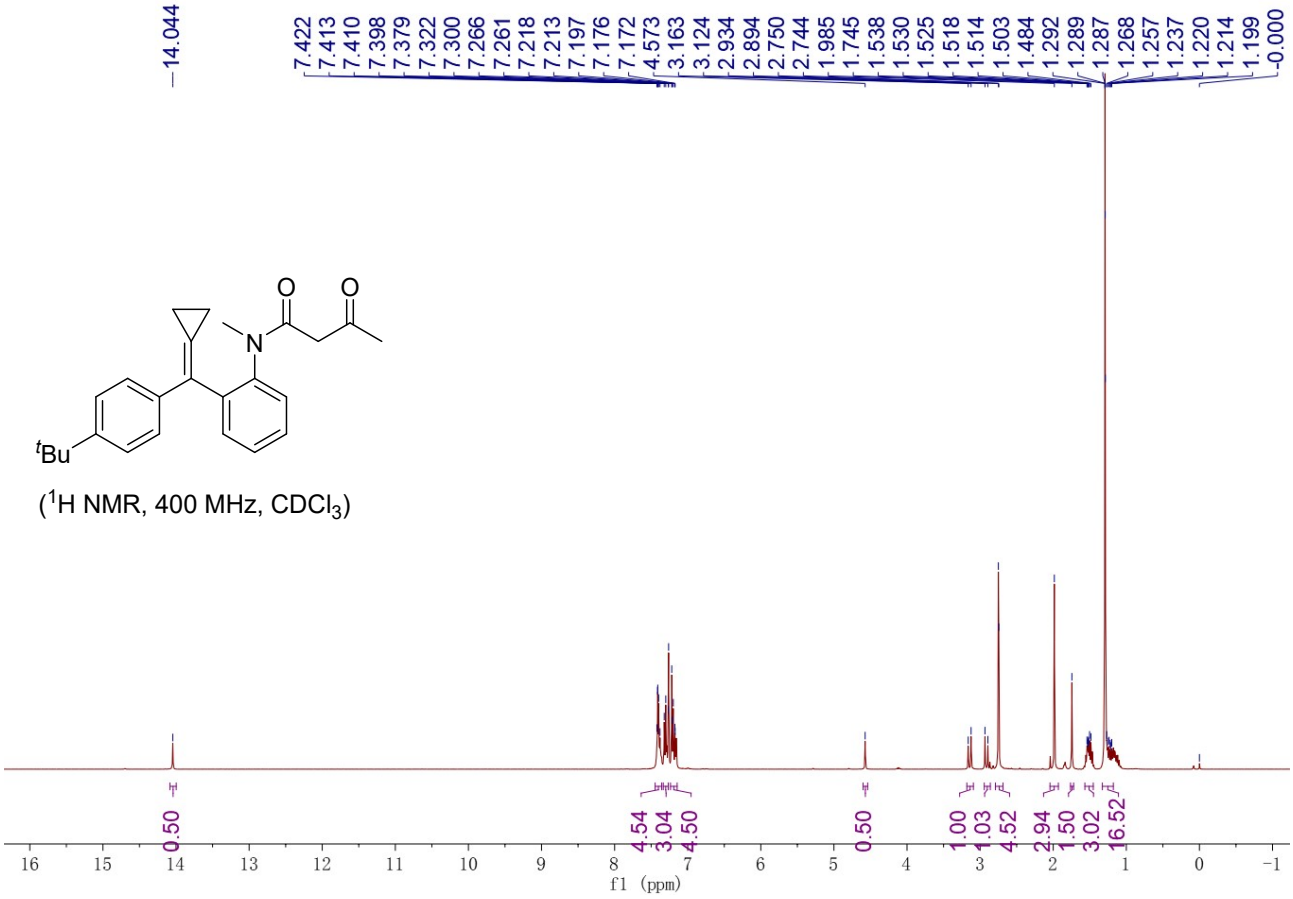
N-(2-(cyclopropylidene(4-methoxyphenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1c**): Yield: 567 mg, 81%, brown solid, m.p. 105-107 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.08 (s, 0.31H), 7.46 – 7.34 (m, 4H), 7.25 – 7.13 (m, 3.82H), 6.88 – 6.76 (m, 2.63H), 4.56 (s, 0.3H), 3.83 – 3.74 (m, 4H), 3.16 (d, *J* = 15.8 Hz, 1H), 2.94 (d, *J* = 15.8 Hz, 1H), 2.79 – 2.72 (m, 3.82H), 2.02 (s, 2.75H), 1.75 (s, 0.95H), 1.57 – 1.41 (m, 2.7H), 1.29 – 1.11 (m, 2.7H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 172.3, 171.4, 166.6, 158.7, 158.5, 141.6, 141.4, 140.0, 139.7, 132.8, 131.9, 131.8, 128.7, 128.5, 128.4, 128.4, 128.3, 127.9, 127.7, 127.0, 124.9, 124.7, 113.5, 113.3, 89.7, 55.1, 49.4, 36.3, 35.3, 30.1, 21.3, 4.6; IR (neat): ν 2925, 2828, 1654, 1489, 1354, 1249, 1035, 767 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_3Na$ $[M+Na]^+$: 372.15701, found: 372.15683.



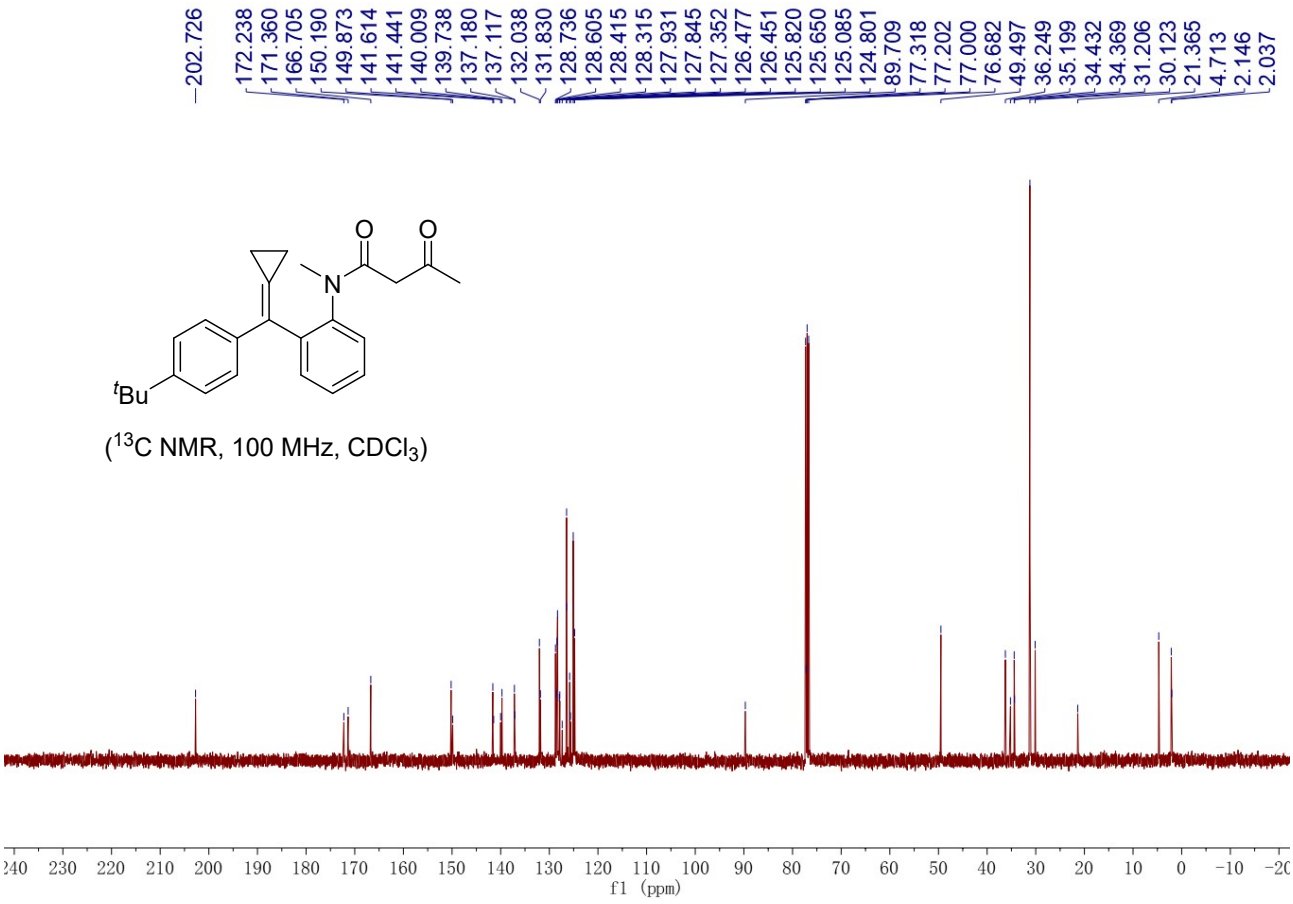

202.662
172.278
171.359
166.648
158.704
158.540
141.556
141.355
140.002
139.736
132.770
131.946
131.752
128.728
128.518
128.413
128.357
128.283
127.885
127.653
127.027
124.902
124.693
113.537
113.331
89.665
77.319
77.205
77.001
76.682
55.130
49.443
36.279
35.261
30.137
21.321
4.570
2.178
2.042
O
O
N
H3CO
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



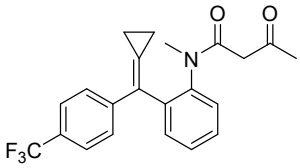
N-(2-((4-(*tert*-butyl)phenyl)(cyclopropylidene)methyl)phenyl)-N-methyl-3-oxobutanamide (**1d**): Yield: 622 mg, 83%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.04 (s, 0.5H), 7.45 – 7.36 (m, 4.54H), 7.33 – 7.27 (m, 3H), 7.24 – 7.14 (m, 4.5H), 4.57 (s, 0.5H), 3.14 (d, *J* = 15.8 Hz, 1H), 2.91 (d, *J* = 15.8 Hz, 1H), 2.79 – 2.69 (m, 4.52H), 1.98 (s, 3H), 1.74 (s, 1.5H), 1.57 – 1.45 (m, 3H), 1.33 – 1.18 (m, 16.5H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 172.2, 171.4, 166.7, 150.2, 149.9, 141.6, 141.4, 140.0, 139.7, 137.2, 137.1, 132.0, 131.8, 128.7, 128.6, 128.4, 128.3, 127.9, 127.8, 127.4, 126.5, 126.5, 125.8, 125.6, 125.1, 124.8, 89.7, 49.5, 36.2, 35.2, 34.4, 34.4, 31.2, 30.1, 21.4, 4.7, 2.1, 2.0; IR (neat): ν 2948, 2904, 2859, 1715, 1597, 1357, 1252, 1173, 767, 656 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{25}H_{29}NO_2Na$ $[M+Na]^+$: 398.20905, found: 398.20904.



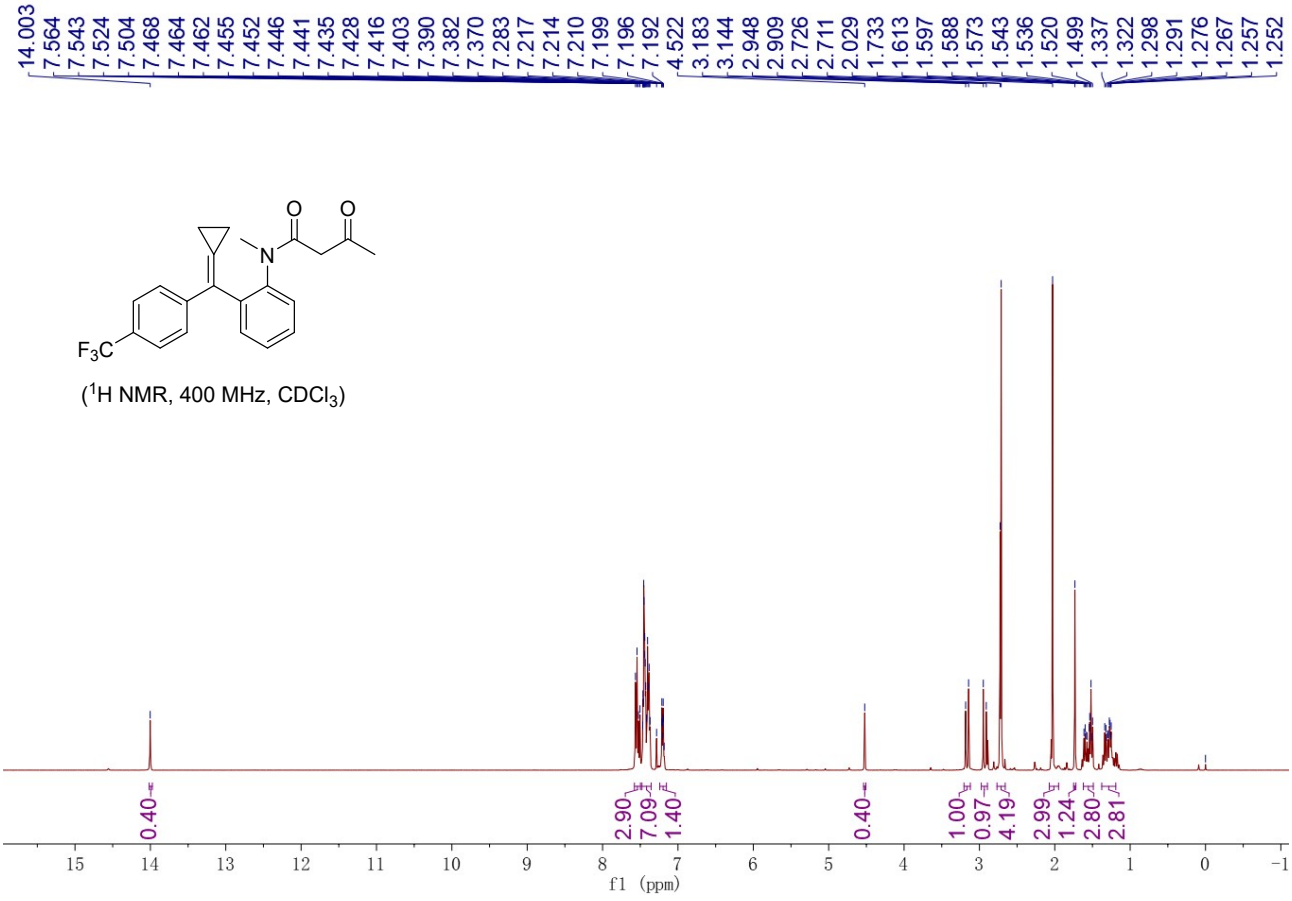
(^{1}H NMR, 400 MHz, $CDCl_3$)



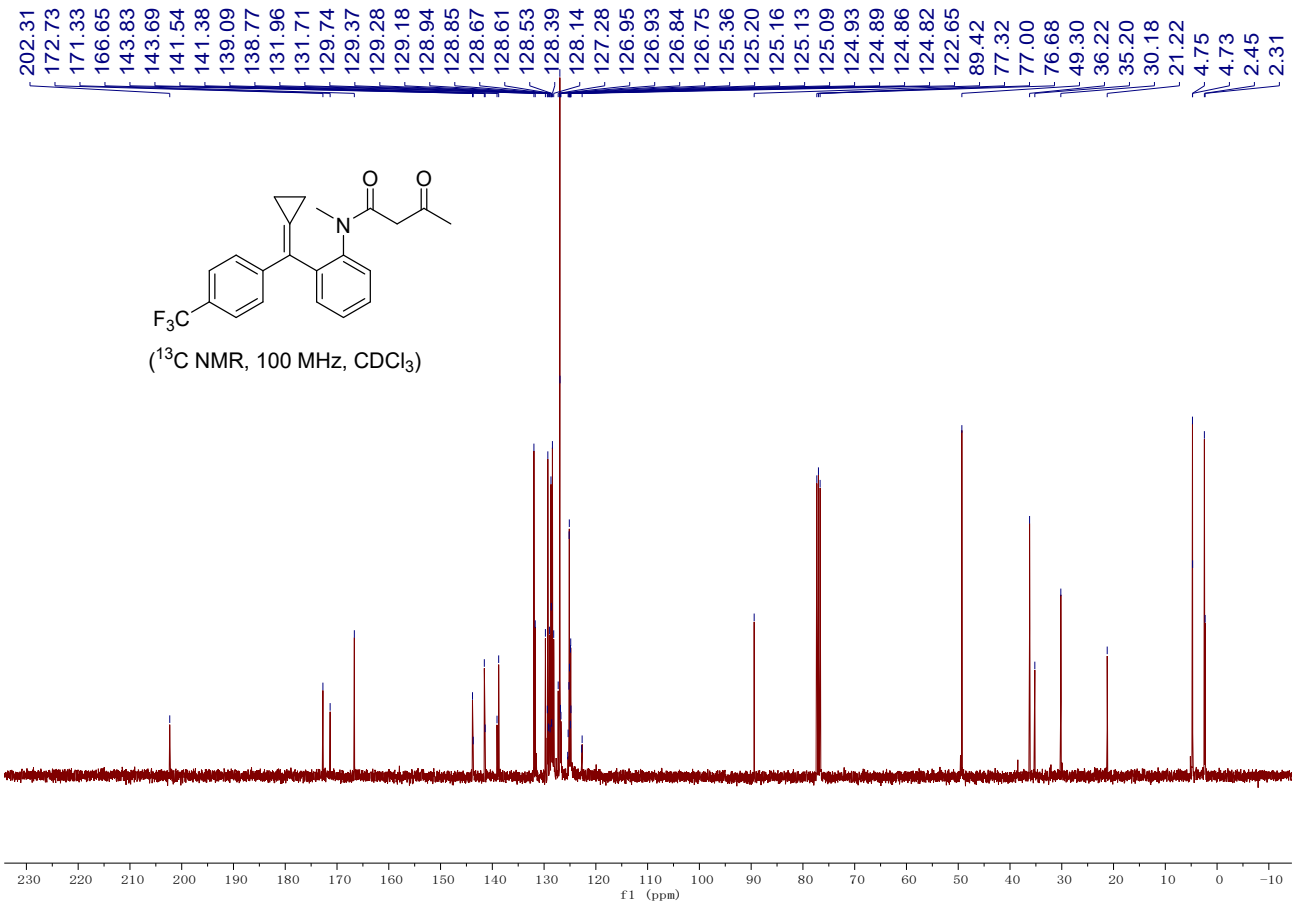
(^{13}C NMR, 100 MHz, $CDCl_3$)



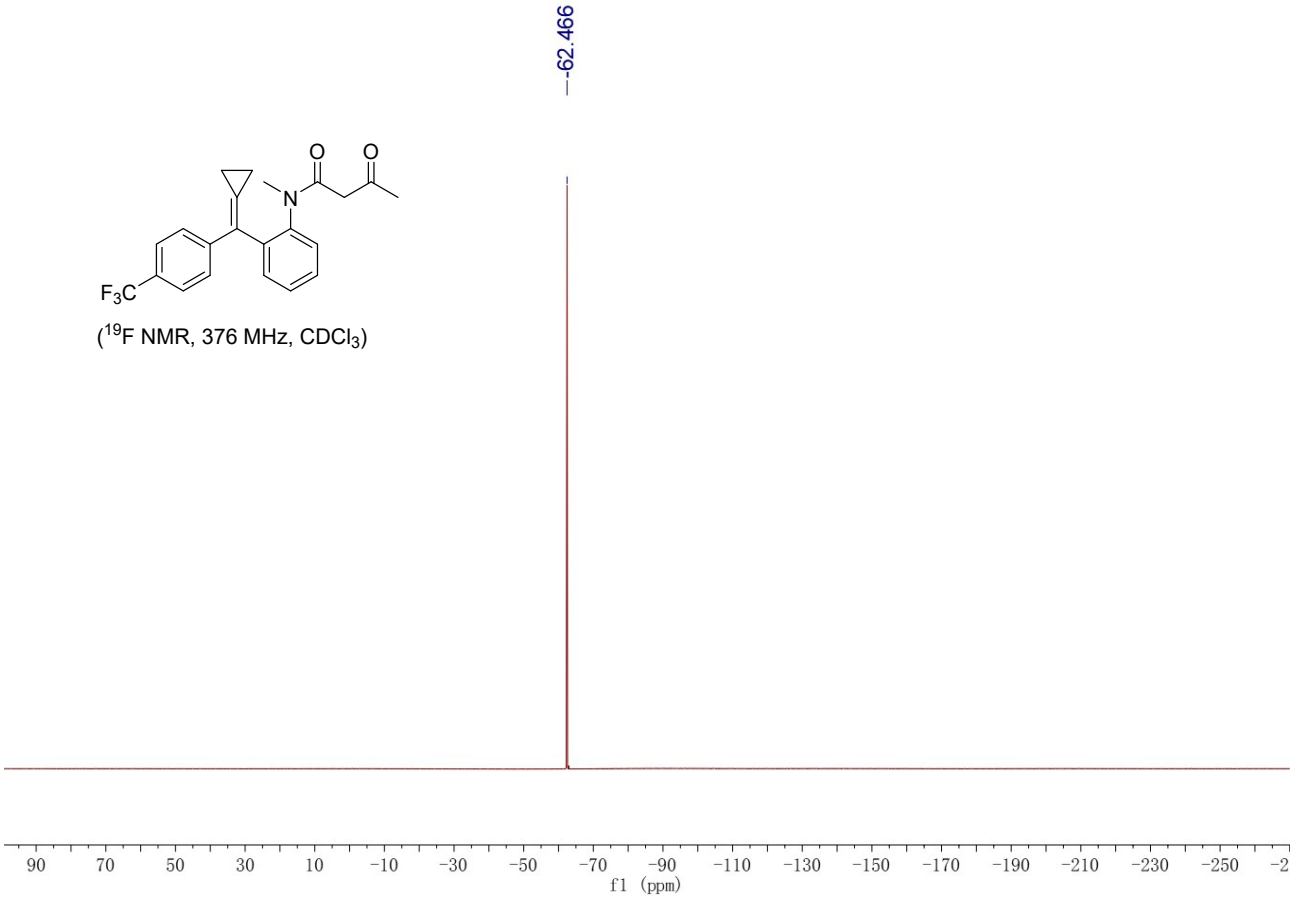
N-(2-(cyclopropylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1e**): Yield: 595 mg, 77%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.00 (s, 0.4H), 7.58 – 7.50 (m, 2.9H), 7.48 – 7.36 (m, 7.1H), 7.24 – 7.15 (m, 1.4H), 4.52 (s, 0.4H), 3.16 (d, *J* = 15.7 Hz, 1H), 2.93 (d, *J* = 15.7 Hz, 1H), 2.77 – 2.66 (m, 4.2H), 2.03 (s, 3H), 1.73 (s, 1.24H), 1.62 – 1.49 (m, 2.8H), 1.38 – 1.19 (m, 2.8H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 172.7, 171.3, 166.7, 143.8, 143.7, 141.5, 141.4, 139.1, 138.8, 132.0, 131.7, 129.7, 129.4, 129.3, 129.2, 128.9, 128.6, 128.5 (q, *J* = 28.0 Hz), 127.3, 127.0, 126.9, 126.8, 126.7, 125.1 (q, *J* = 3.0 Hz), 124.9 (q, *J* = 3.0 Hz), 124.1 (q, *J* = 270.0 Hz), 124.0 (q, *J* = 270.0 Hz), 89.4, 77.3, 77.0, 76.7, 49.3, 36.2, 35.2, 30.2, 21.2, 4.8, 4.7, 2.4, 2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; IR (neat): ν 3060, 2974, 2924, 1716, 1637, 1482, 1162, 1113, 1068, 1015, 848, 770 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{20}F_3NO_2Na$ $[M+Na]^+$: 410.13383, found: 410.13418.



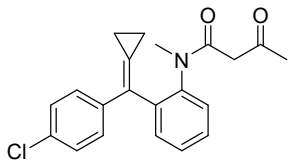
(^{1}H NMR, 400 MHz, $CDCl_3$)



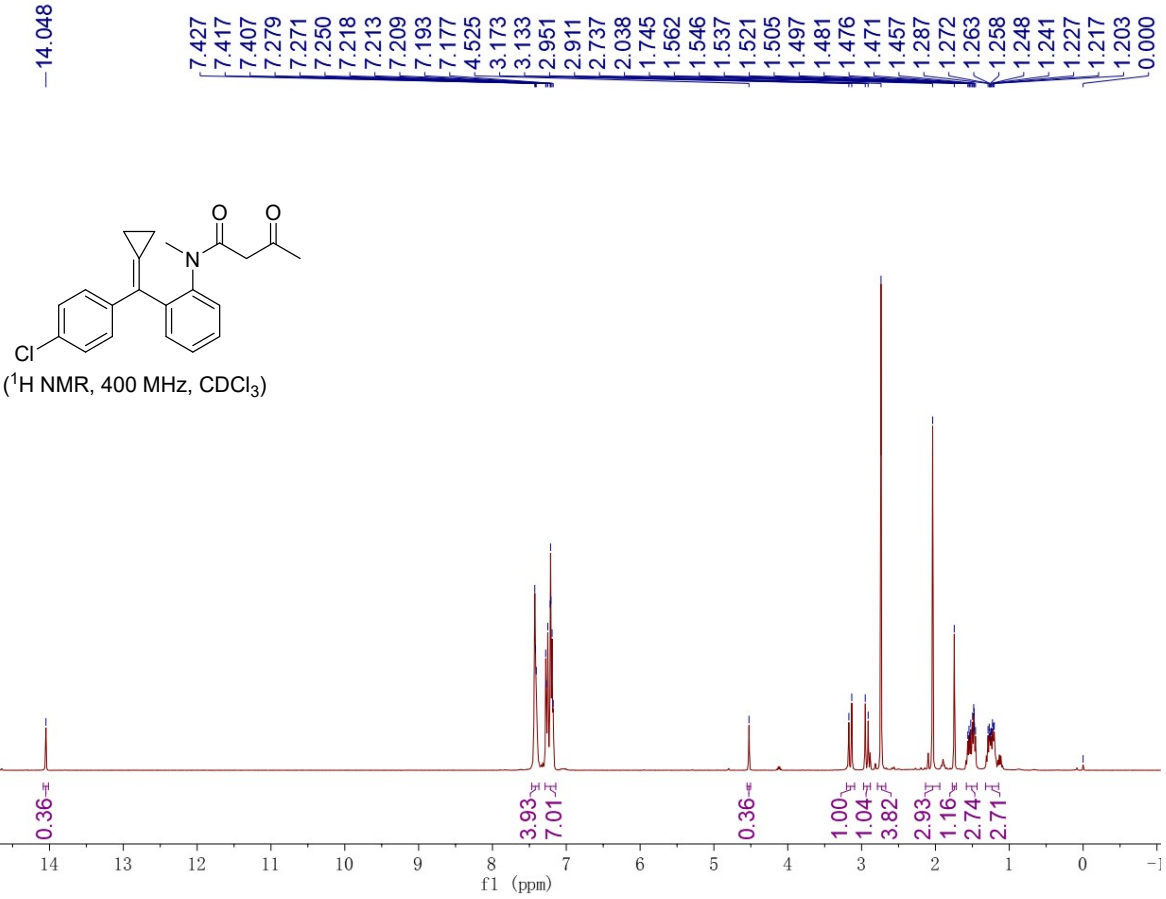
(^{13}C NMR, 100 MHz, $CDCl_3$)

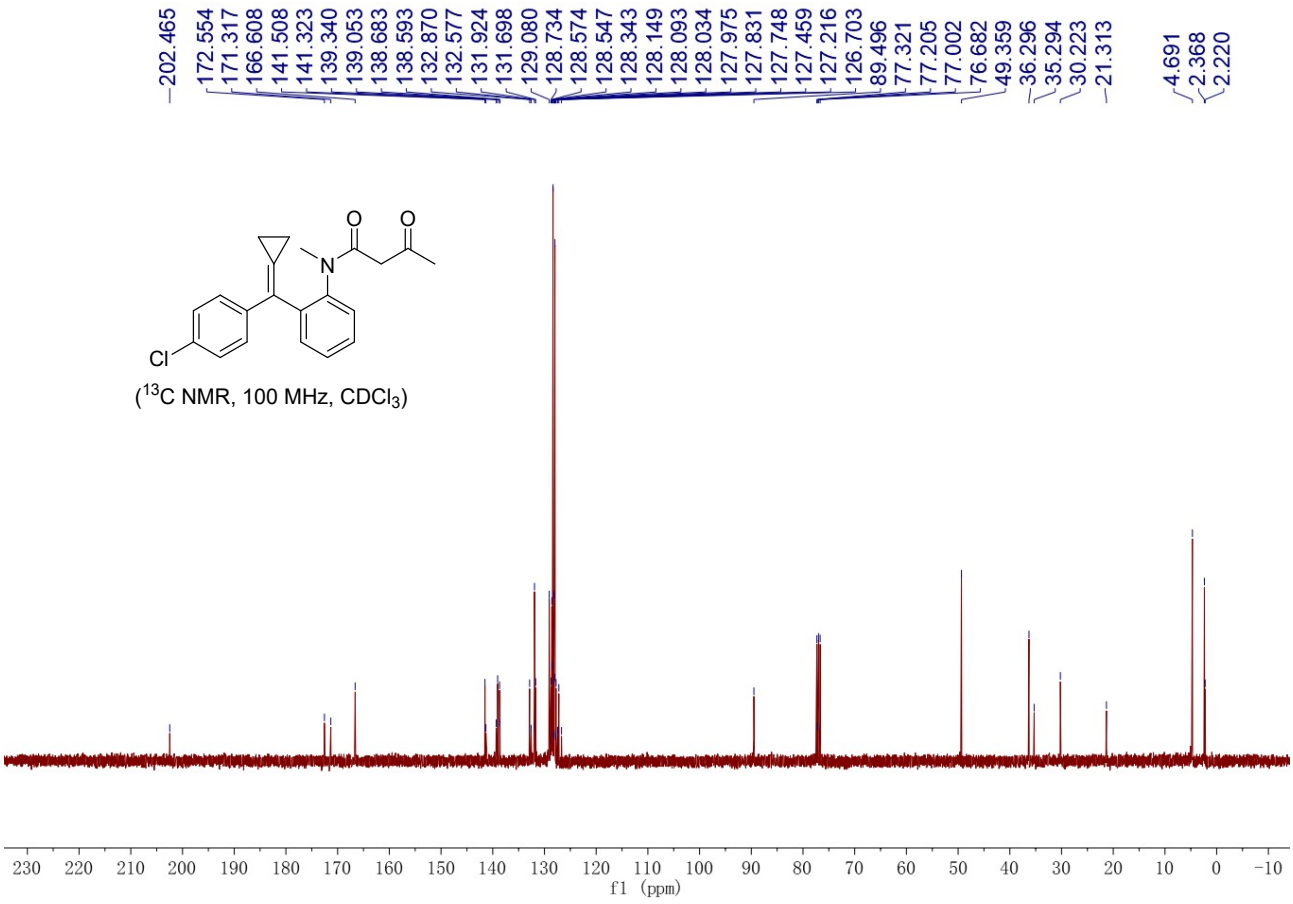


(^{19}F NMR, 376 MHz, $CDCl_3$)

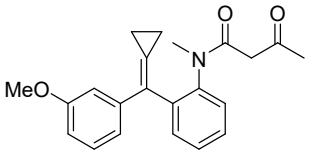


N-(2-((4-chlorophenyl)(cyclopropylidene)methyl)phenyl)-N-methyl-3-oxobutanamide (**1f**): Yield: 482 mg, 73%, brown solid, m.p. 113-115 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.05 (s, 0.36H), 7.47 – 7.37 (m, 3.93H), 7.29 – 7.14 (m, 7H), 4.53 (s, 0.36H), 3.15 (d, *J* = 15.7 Hz, 1H), 2.93 (d, *J* = 15.8 Hz, 1H), 2.79 – 2.67 (m, 3.82H), 2.04 (s, 3H), 1.74 (s, 1.16H), 1.58 – 1.44 (m, 2.74H), 1.32 – 1.14 (m, 2.71H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.5, 172.6, 171.3, 166.6, 141.5, 141.3, 139.3, 139.1, 138.7, 138.6, 132.9, 132.6, 131.9, 131.7, 129.1, 128.7, 128.6, 128.5, 128.3, 128.1, 128.1, 128.0, 128.0, 127.7, 127.5, 127.2, 126.7, 89.5, 49.4, 36.3, 35.3, 30.2, 21.3, 4.7, 2.4, 2.2; IR (neat): ν 2964, 2940, 1730, 1488, 1374, 1092, 833, 780, 756 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_2Na$ $[M+Na]^+$: 376.10748, found: 376.10792.

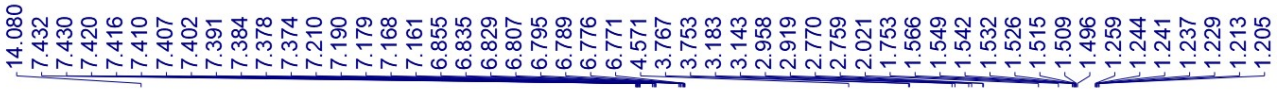


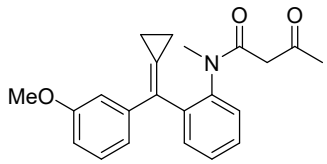


(^{13}C NMR, 100 MHz, $CDCl_3$)

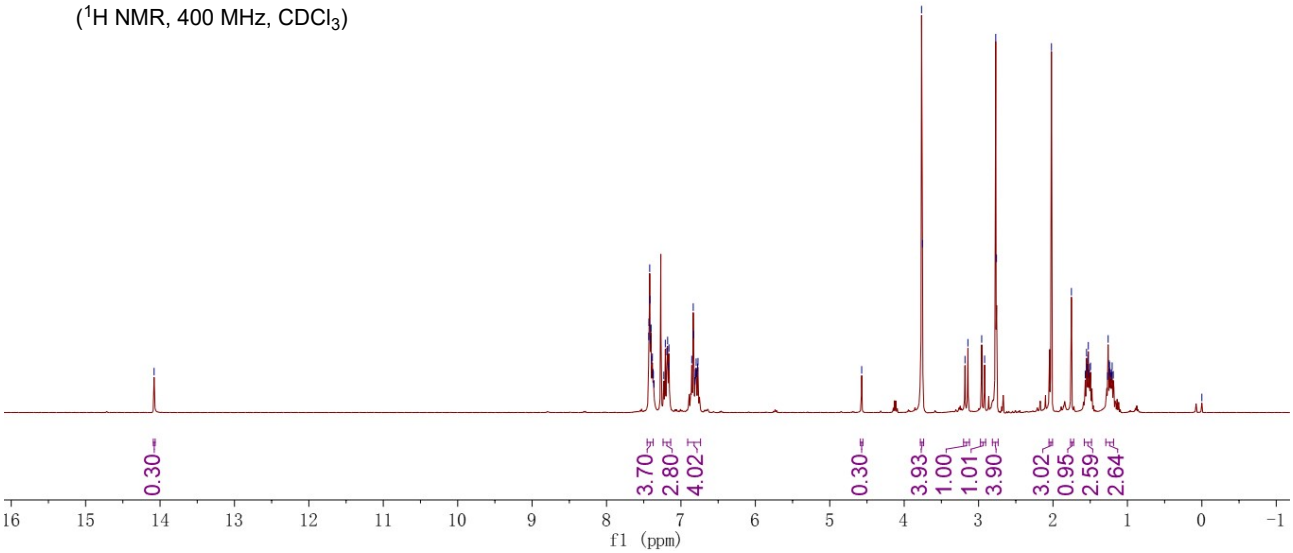


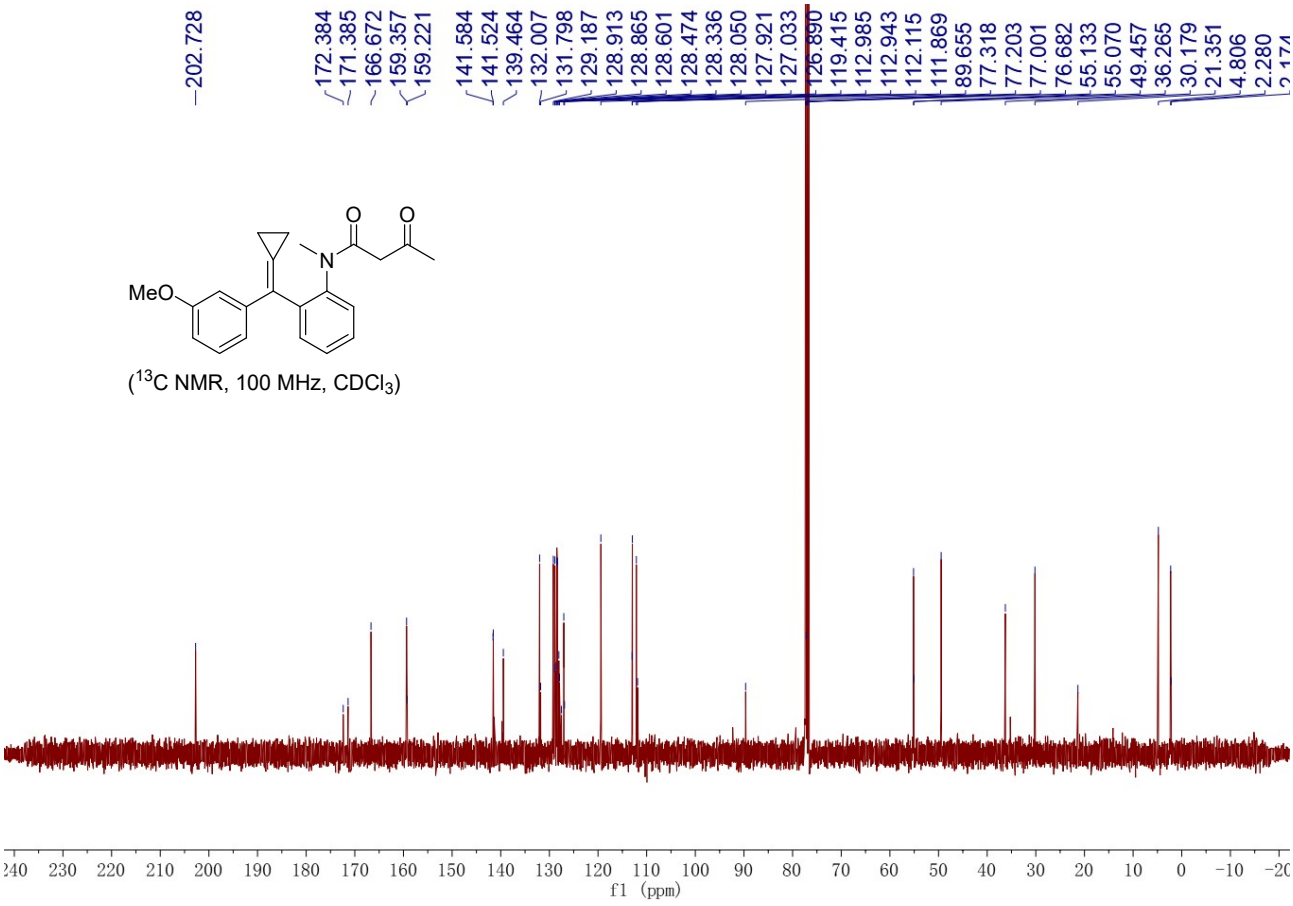
N-(2-(cyclopropylidene(3-methoxyphenyl)methyl)phenyl)-4-methyl-N-(2l5-propa-1,2-dien-1-yl)benzenesulfonamide (**1g**): Yield: 553 mg, 79%, brown solid, m.p. 87-89 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.08 (s, 0.3H), 7.45 – 7.37 (m, 3.7H), 7.24 – 7.14 (m, 2.8H), 6.91 – 6.74 (m, 4H), 4.57 (s, 0.3H), 3.78 – 3.74 (m, 3.9H), 3.16 (d, *J* = 15.7 Hz, 1H), 2.94 (d, *J* = 15.7 Hz, 1H), 2.81 – 2.74 (m, 3.9H), 2.02 (s, 3H), 1.75 (s, 0.9H), 1.58 – 1.48 (m, 2.6H), 1.29 – 1.19 (m, 2.6H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 172.4, 171.4, 166.7, 159.4, 159.2, 141.6, 141.5, 139.5, 132.0, 131.8, 129.2, 128.9, 128.9, 128.6, 128.5, 128.3, 128.0, 127.9, 127.5, 127.0, 126.9, 119.4, 113.0, 112.9, 112.1, 111.9, 89.7, 55.1, 55.1, 49.5, 36.3, 35.2, 30.2, 21.4, 4.8, 2.3, 2.2; IR (neat): ν 3019, 2946, 2836, 1719, 1593, 1486, 1424, 1312, 1161, 773, 702 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_3Na$ $[M+Na]^+$: 372.15701, found: 372.15721.



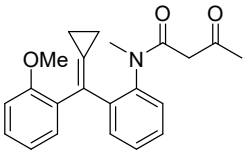


(^{1}H NMR, 400 MHz, $CDCl_3$)

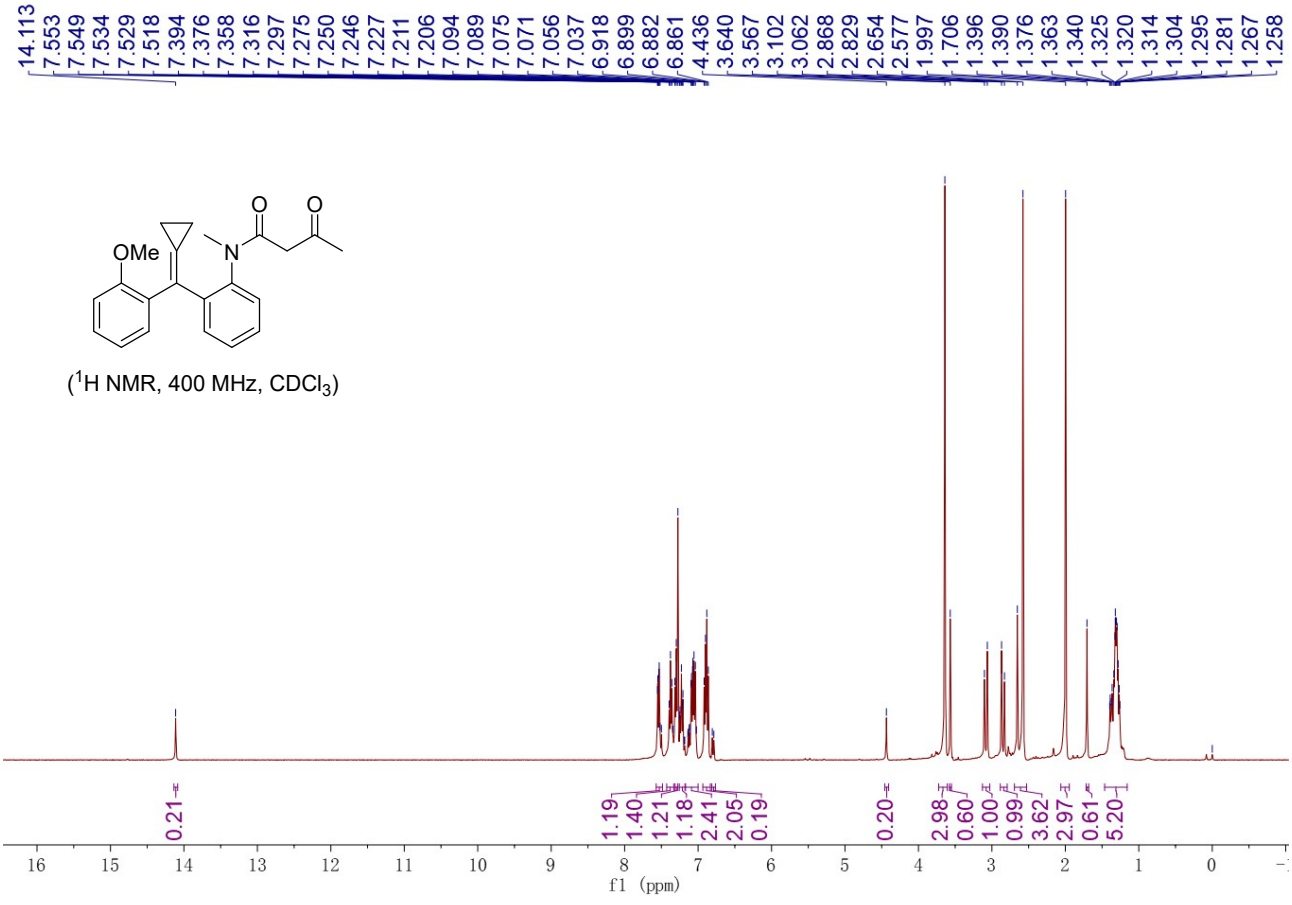


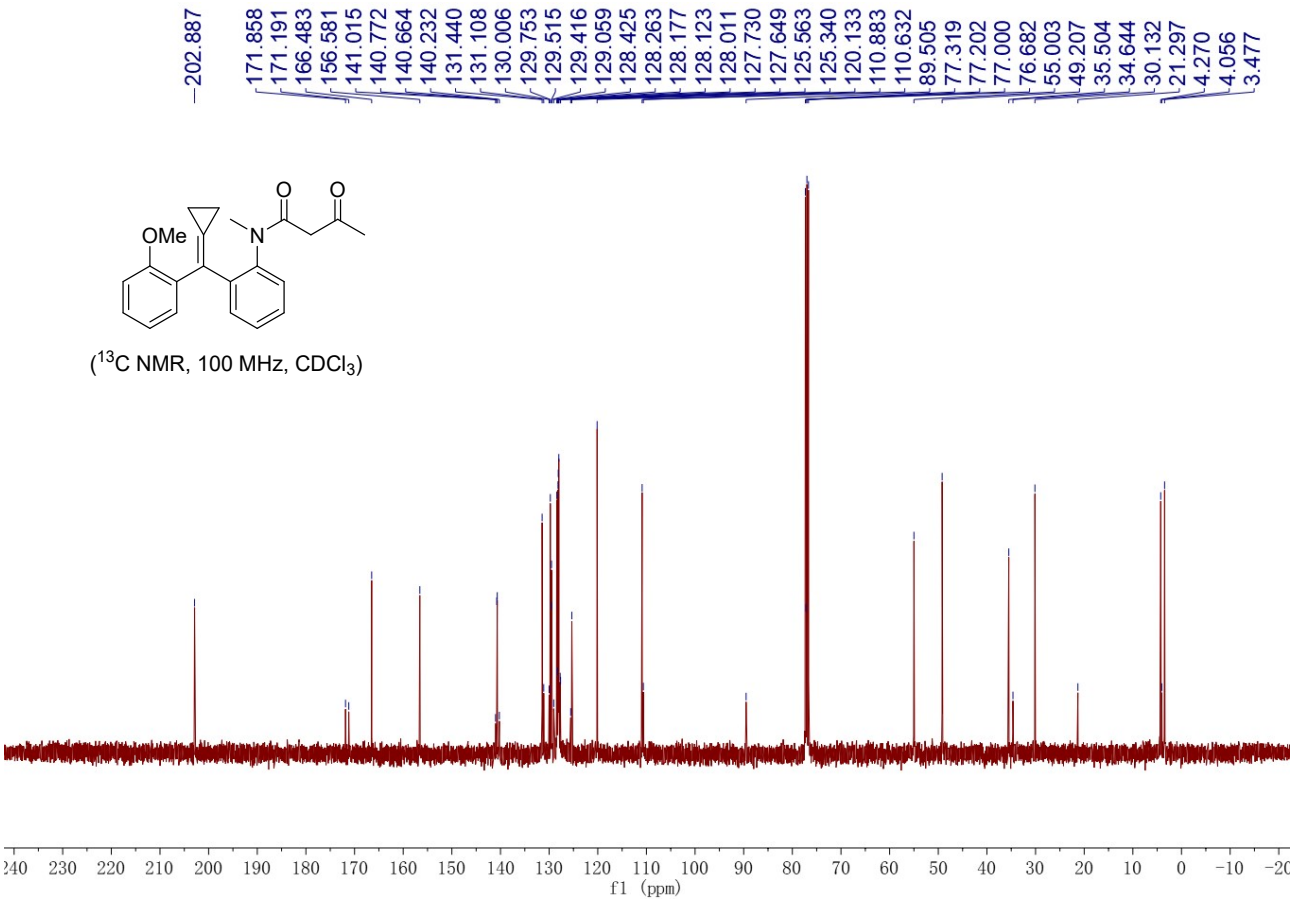


(^{13}C NMR, 100 MHz, $CDCl_3$)

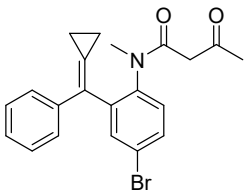


N-(2-(cyclopropylidene(2-methoxyphenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1h**): Yield: 567 mg, 81%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.11 (s, 0.2H), 7.57 – 7.48 (m, 1.2H), 7.43 – 7.33 (m, 1.4H), 7.31 – 7.28 (m, 1.2H), 7.26 – 7.17 (m, 1.2H), 7.18 – 7.00 (m, 2.4H), 6.93 – 6.83 (m, 2H), 6.80 (d, *J* = 8.2 Hz, 0.2H), 4.44 (s, 0.2H), 3.64 (s, 3H), 3.57 (s, 0.6H), 3.08 (d, *J* = 15.8 Hz, 1H), 2.85 (d, *J* = 15.8 Hz, 1H), 2.69 – 2.53 (m, 3.6H), 2.00 (s, 3H), 1.71 (s, 0.6H), 1.46 – 1.16 (m, 5.2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.9, 171.9, 171.2, 166.5, 156.6, 141.0, 140.8, 140.7, 140.2, 131.4, 131.1, 130.0, 129.8, 129.5, 129.4, 129.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 125.6, 125.3, 120.1, 110.9, 110.6, 89.5, 55.0, 49.2, 35.5, 34.6, 30.1, 21.3, 4.3, 4.1, 3.5; IR (neat): ν 3480, 3050, 2964, 2833, 1727, 1640, 1488, 1250, 1116, 902 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_3Na$ [M+Na]$^{+}$: 372.25701, found: 372.15622.

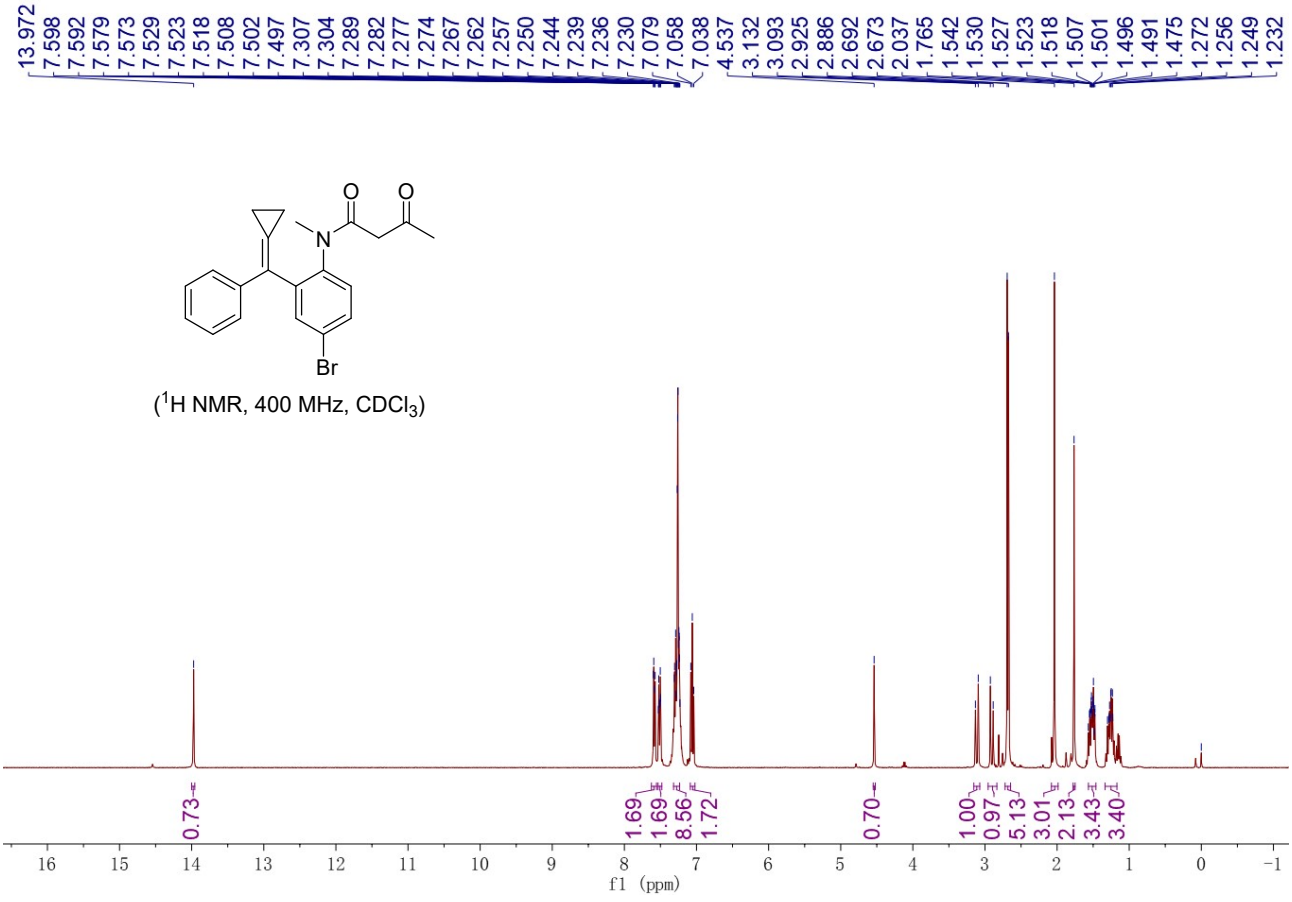


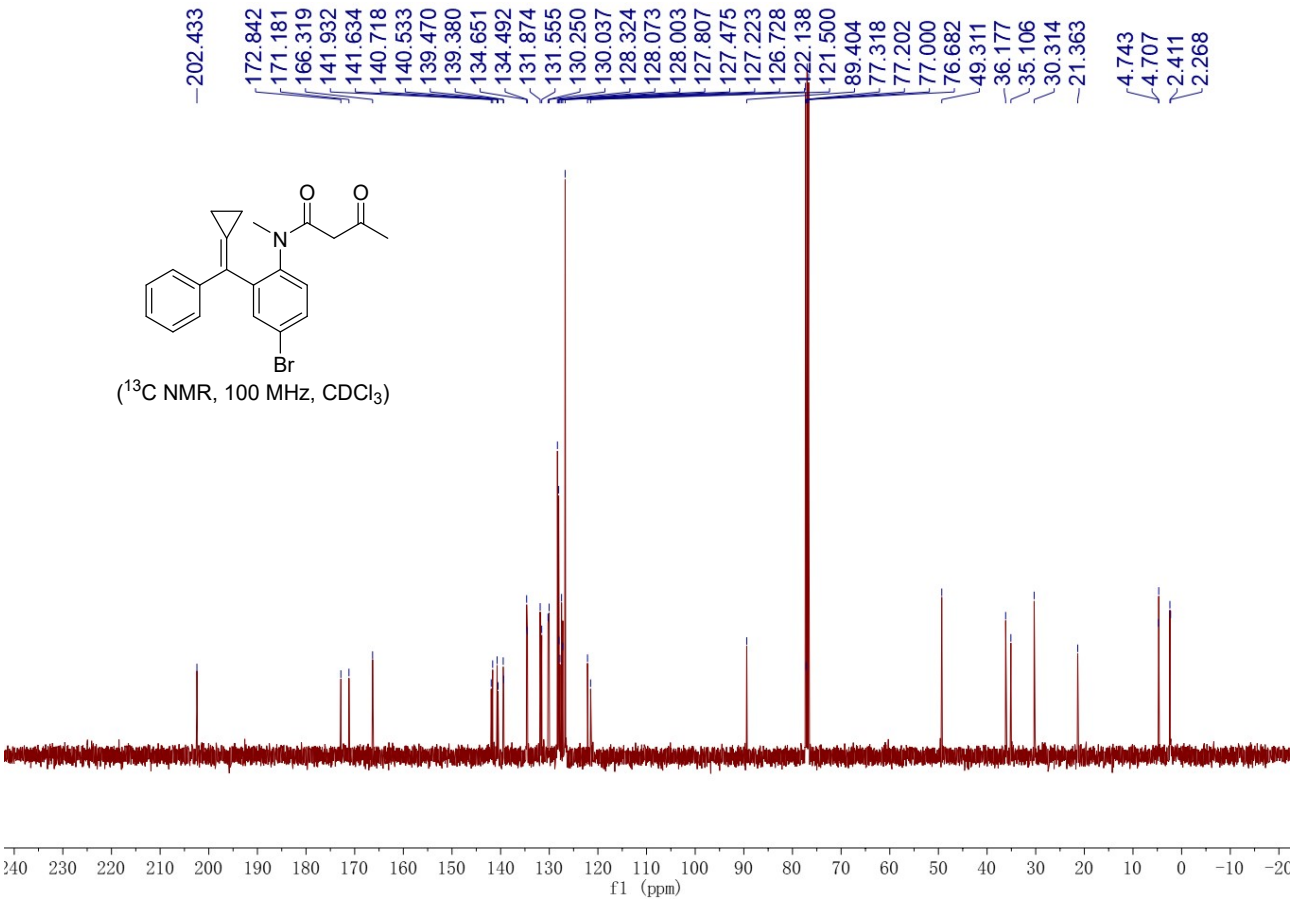


(^{13}C NMR, 100 MHz, $CDCl_3$)

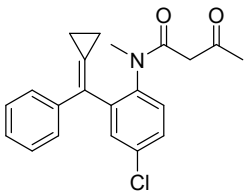


N-(4-bromo-2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (1i): Yield: 603 mg, 76%, brown solid, m.p. 116-118 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 13.97 (s, 0.73H), 7.62 – 7.55 (m, 1.7H), 7.53 – 7.48 (m, 1.7H), 7.32 – 7.23 (m, 8.5H), 7.09 – 7.02 (m, 1.7H), 4.54 (s, 0.7H), 3.11 (d, *J* = 15.7 Hz, 1H), 2.91 (d, *J* = 15.7 Hz, 1H), 2.72 – 2.64 (m, 5.1H), 2.04 (s, 3H), 1.76 (s, 2.1H), 1.57 – 1.46 (m, 3.4H), 1.34 – 1.17 (m, 3.4H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 172.8, 171.2, 166.3, 141.9, 141.6, 140.7, 140.5, 139.5, 139.4, 134.6, 134.5, 131.9, 131.6, 130.2, 130.0, 128.3, 128.1, 128.0, 127.8, 127.5, 127.2, 126.7, 122.1, 121.5, 89.4, 49.3, 36.2, 35.1, 30.3, 21.4, 4.7, 4.7, 2.4, 2.3; IR (neat): ν 2959, 2914, 2849, 1714, 1492, 1450, 1375, 1171, 765, 741 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_2BrNa$ $[M+Na]^+$: 420.05696, found: 420.05704.

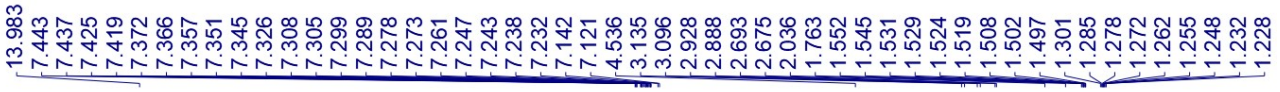


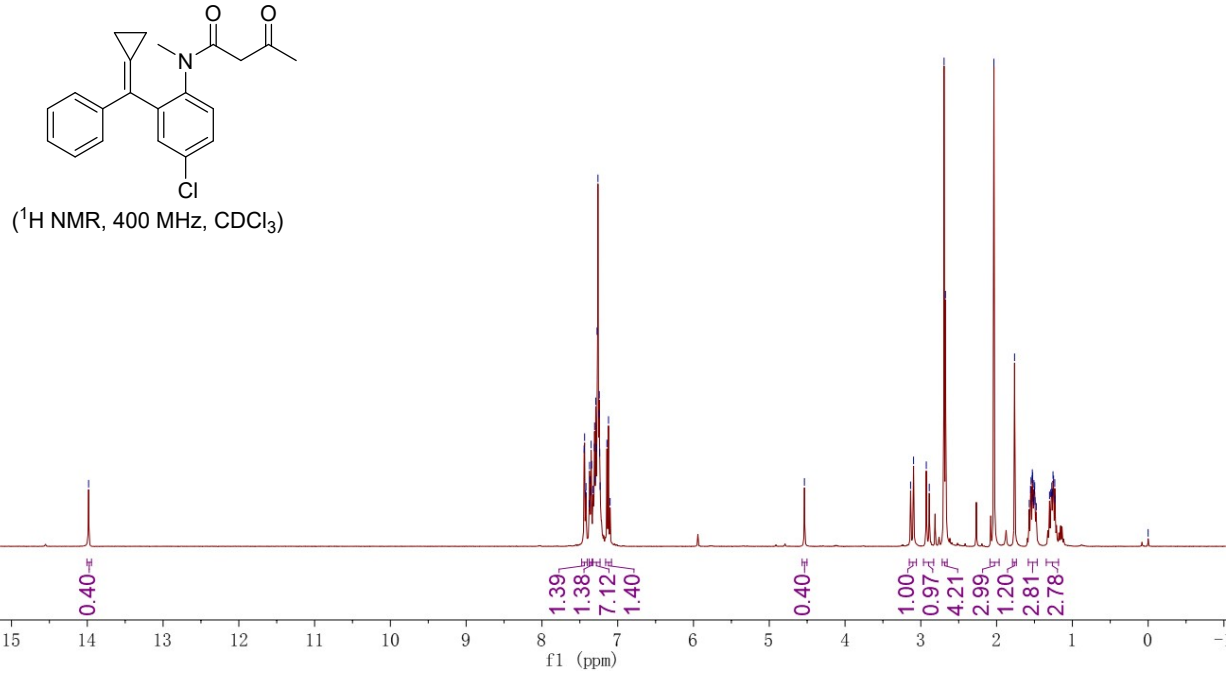


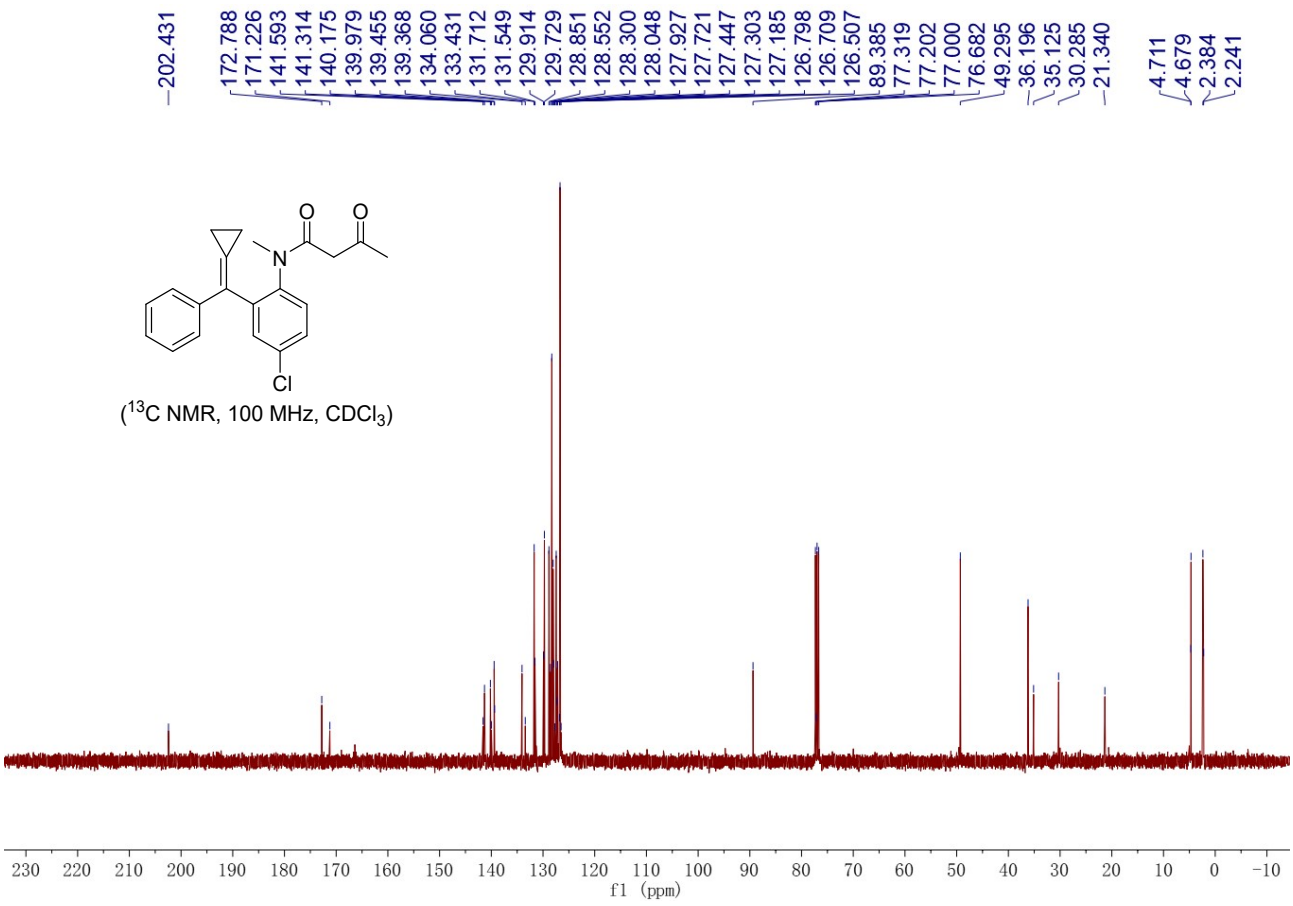
(^{13}C NMR, 100 MHz, $CDCl_3$)



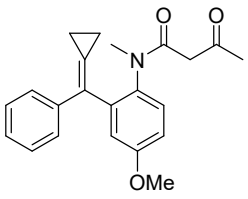
N-(4-chloro-2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1j**): Yield: 508 mg, 72%, brown solid, m.p. 97-99 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 13.98 (s, 0.4H), 7.48 – 7.40 (m, 1.4H), 7.38 – 7.34 (m, 1.4H), 7.33 – 7.23 (m, 7.1H), 7.16 – 7.08 (m, 1.4H), 4.54 (s, 0.4H), 3.12 (d, *J* = 15.7 Hz, 1H), 2.91 (d, *J* = 15.7 Hz, 1H), 2.72 – 2.65 (m, 4.2H), 2.04 (s, 3H), 1.76 (s, 1.2H), 1.58 – 1.46 (m, 2.8H), 1.34 – 1.18 (m, 2.8H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 172.8, 171.2, 141.6, 141.3, 140.2, 140.0, 139.5, 139.4, 134.1, 133.4, 131.7, 131.5, 129.9, 129.7, 128.9, 128.6, 128.3, 128.0, 127.9, 127.7, 127.4, 127.3, 127.2, 126.8, 126.7, 89.4, 49.3, 36.2, 35.1, 30.3, 21.3, 4.7, 4.7, 2.4, 2.2; IR (neat): ν 2940, 2922, 2883, 1714, 1482, 1349, 1235, 823, 775, 741 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_2ClNa$ $[M+Na]^+$: 376.10748, found: 376.10673.



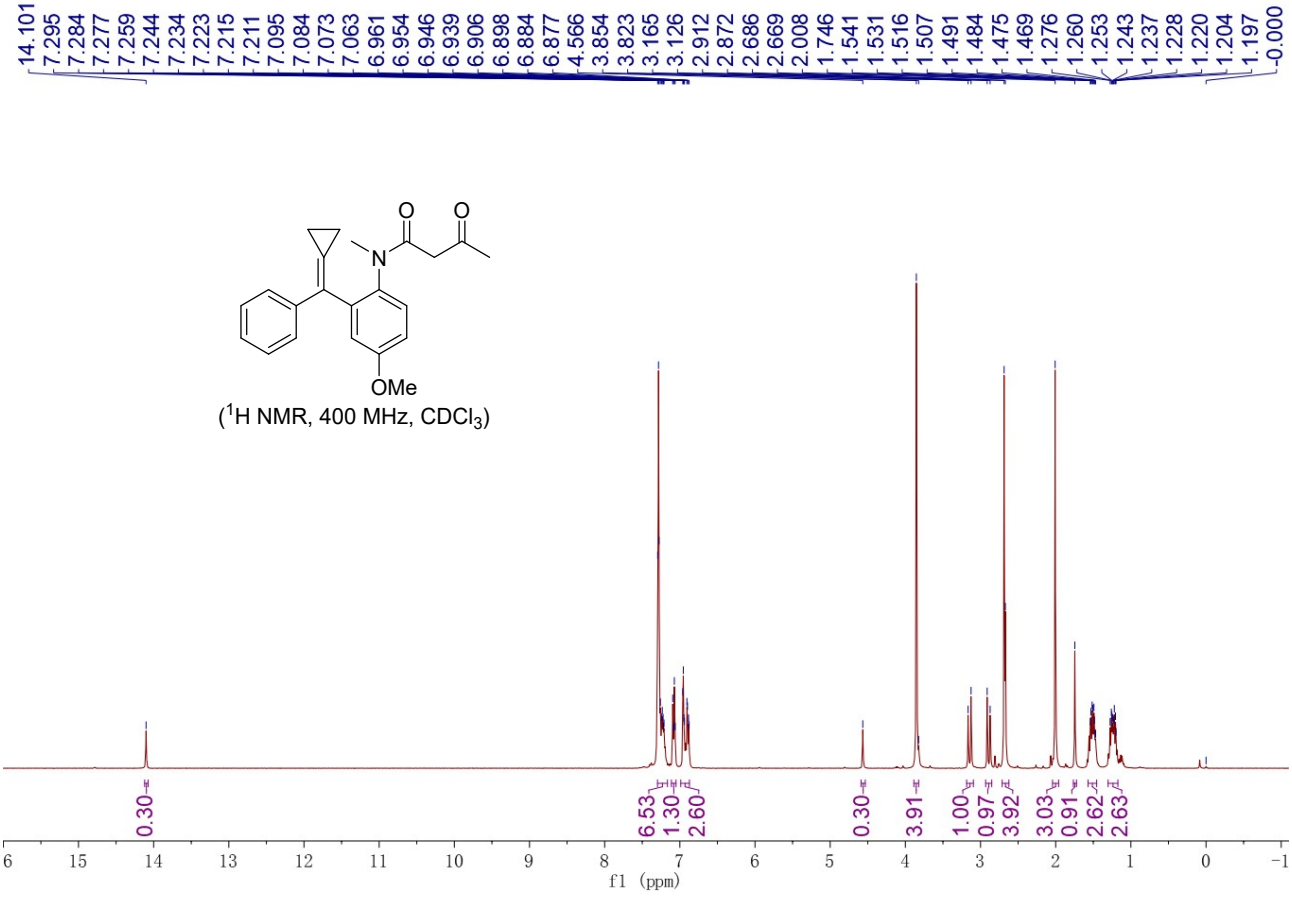


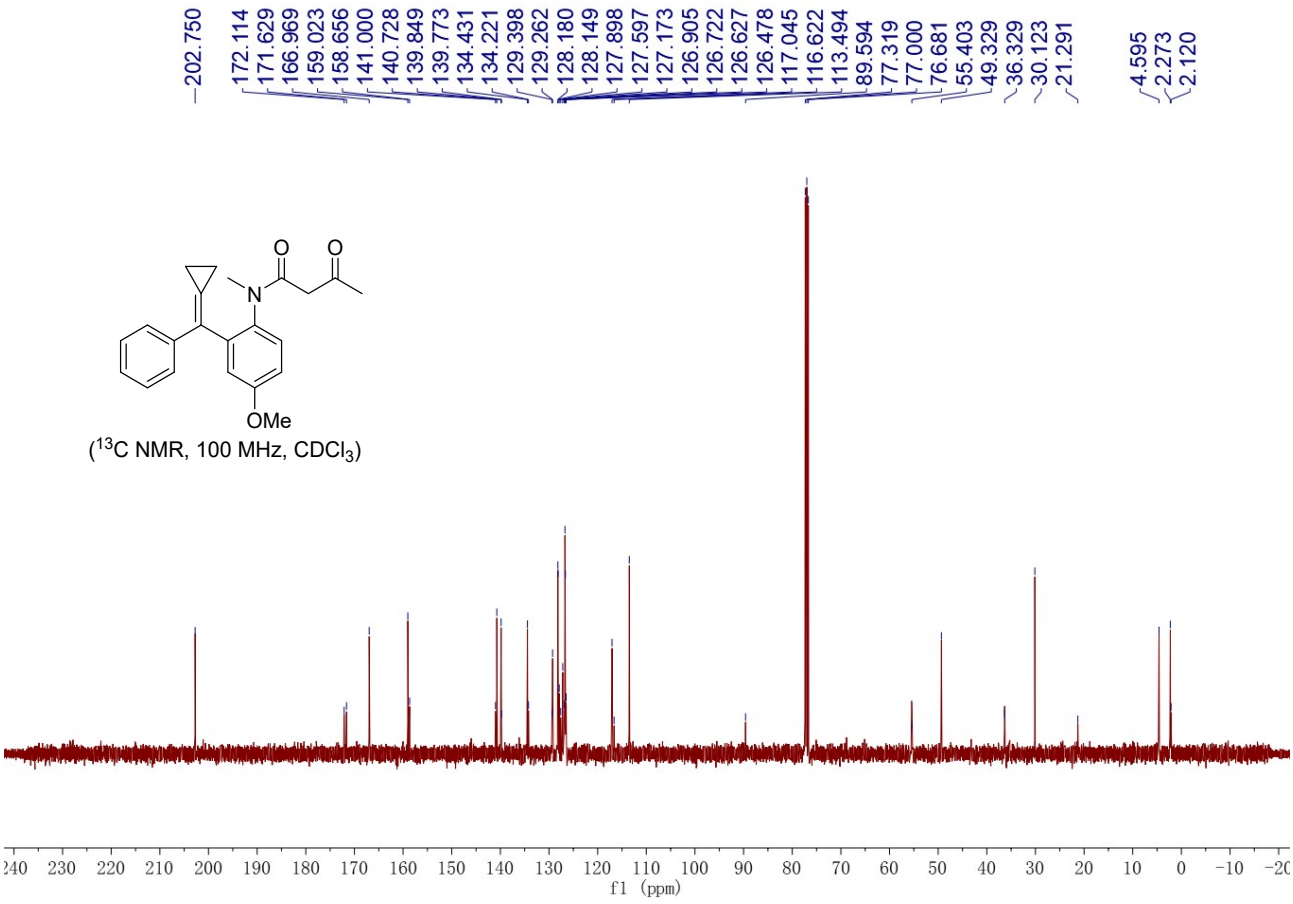


(^{13}C NMR, 100 MHz, $CDCl_3$)

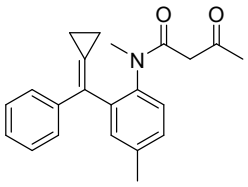


N-(2-(cyclopropylidene(phenyl)methyl)-4-methoxyphenyl)-N-methyl-3-oxobutanamide (**1k**): Yield: 539 mg, 77%, brown solid, m.p. 114-116 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.10 (s, 0.3H), 7.30 – 7.16 (m, 6.53H), 7.11 – 7.05 (m, 1.3H), 6.99 – 6.87 (m, 2.6H), 4.57 (s, 0.3H), 3.89 – 3.82 (m, 3.9H), 3.15 (d, *J* = 15.8 Hz, 1H), 2.89 (d, *J* = 15.7 Hz, 1H), 2.71 – 2.62 (m, 3.9H), 2.01 (s, 3H), 1.75 (s, 0.9H), 1.57 – 1.45 (m, 2.6H), 1.30 – 1.17 (m, 2.6H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.8, 172.1, 171.6, 167.0, 159.0, 158.7, 141.0, 140.7, 139.8, 139.8, 134.4, 134.2, 129.4, 129.3, 128.2, 128.1, 127.9, 127.6, 127.2, 126.9, 126.7, 126.6, 126.5, 117.0, 116.6, 113.5, 89.6, 49.3, 36.3, 30.1, 21.3, 4.6, 2.3, 2.1; IR (neat): ν 3013, 2925, 2825, 1710, 1498, 1356, 1222, 1030, 834, 768 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_3Na$ $[M+Na]^+$: 372.25701, found: 372.25617.

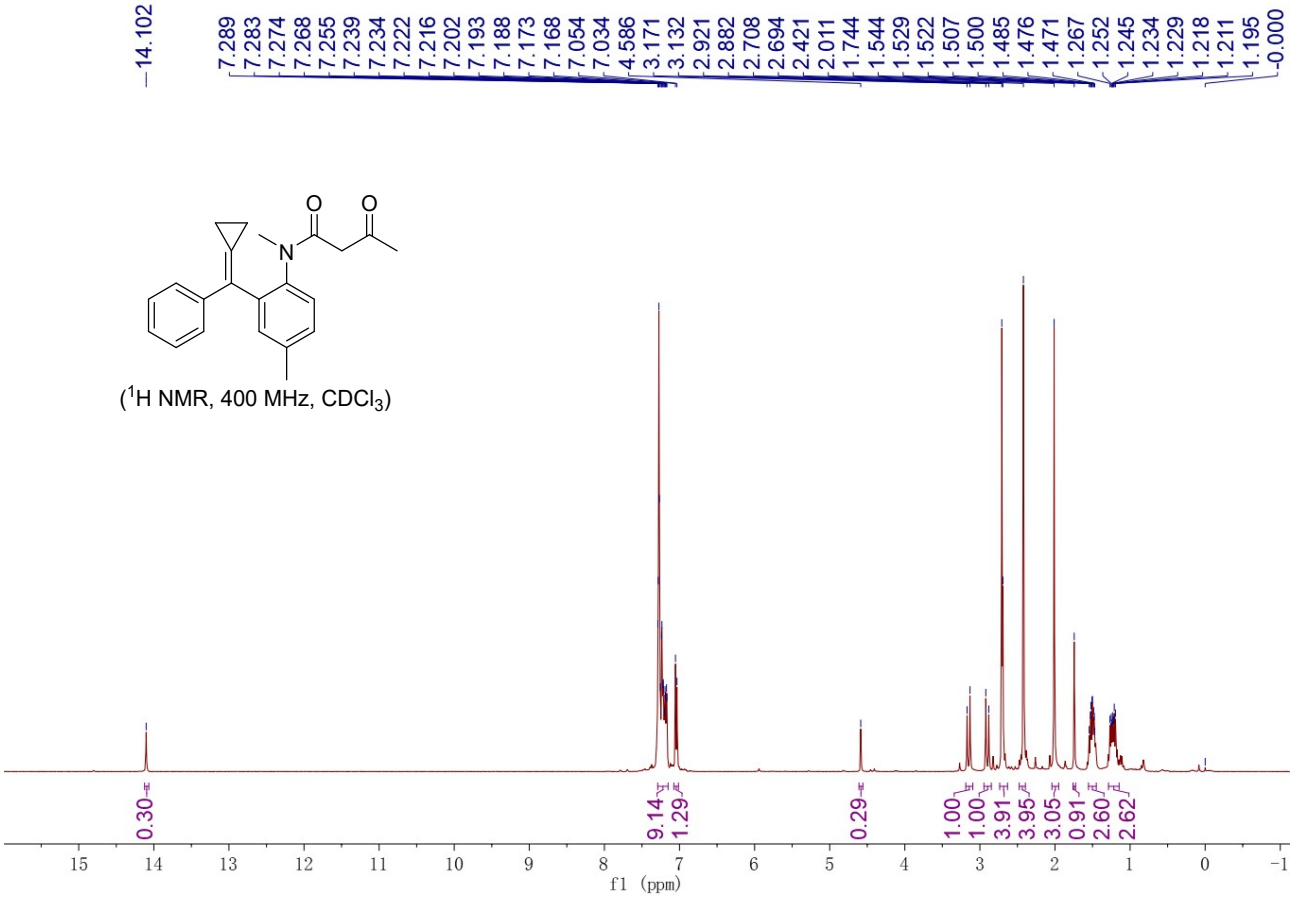


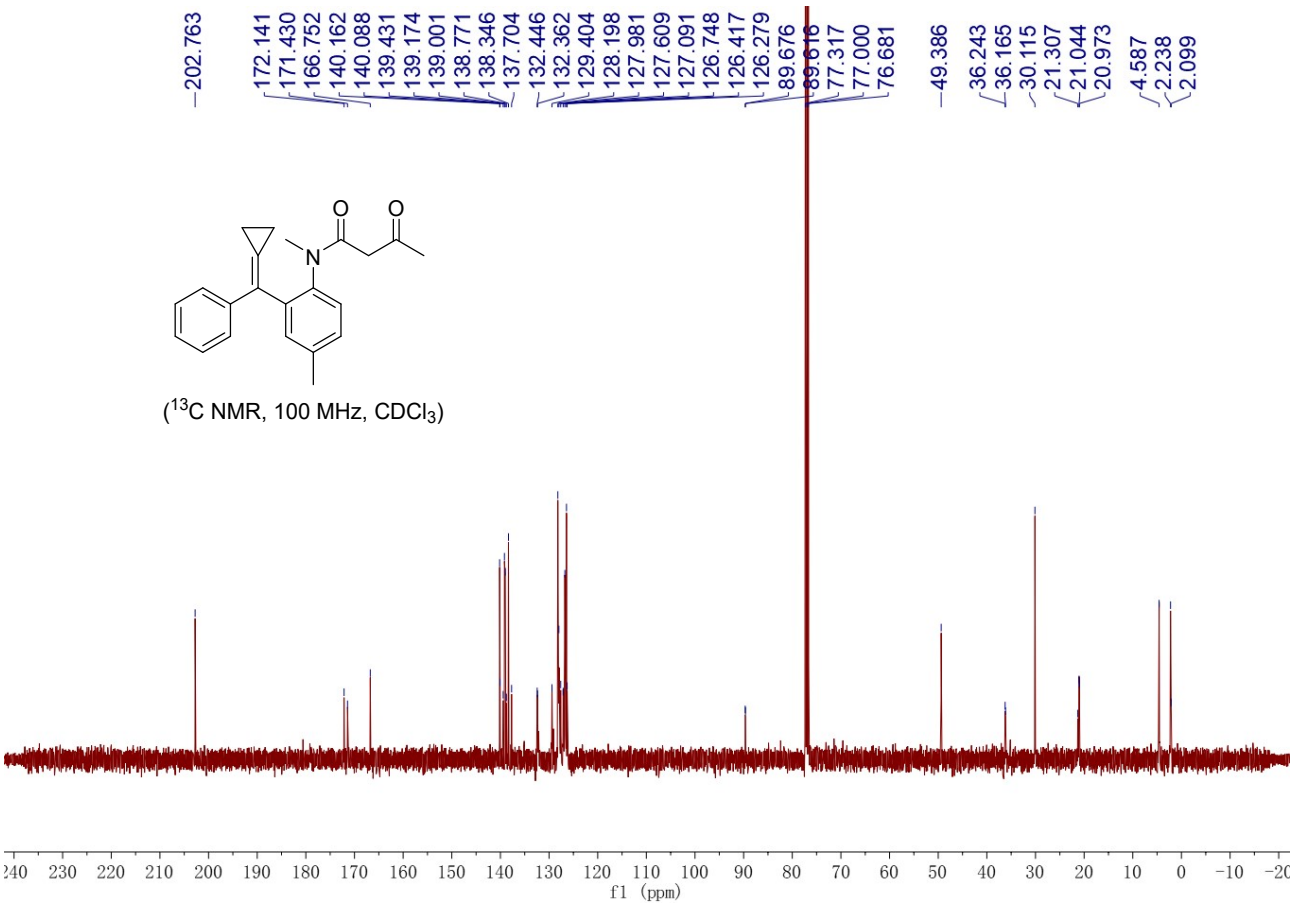


(^{13}C NMR, 100 MHz, $CDCl_3$)

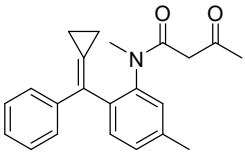


N-(2-(cyclopropylidene(phenyl)methyl)-4-methylphenyl)-N-methyl-3-oxobutanamide (1l): Yield: 553 mg, 83%, brown solid, m.p. 101-103 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.10 (s, 0.3H), 7.29 – 7.15 (m, 9.14H), 7.08 – 7.01 (m, 1.3H), 4.59 (s, 0.3H), 3.15 (d, *J* = 15.8 Hz, 1H), 2.90 (d, *J* = 15.8 Hz, 1H), 2.74 – 2.63 (m, 3.9H), 2.48 – 2.39 (m, 3.9H), 2.01 (s, 3H), 1.74 (s, 0.9H), 1.55 – 1.45 (m, 2.6H), 1.29 – 1.15 (m, 2.6H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.8, 172.1, 171.4, 166.8, 140.2, 140.1, 139.4, 139.2, 139.0, 138.8, 138.3, 137.7, 132.4, 132.4, 129.4, 128.2, 128.0, 127.6, 127.1, 126.7, 126.4, 126.3, 89.7, 89.6, 49.4, 36.2, 36.2, 30.1, 21.3, 21.0, 21.0, 4.6, 2.2, 2.1; IR (neat): ν 2959, 2919, 2849, 1711, 1490, 1374, 1235, 1127, 824, 741, 731 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.16210, found: 356.16248.

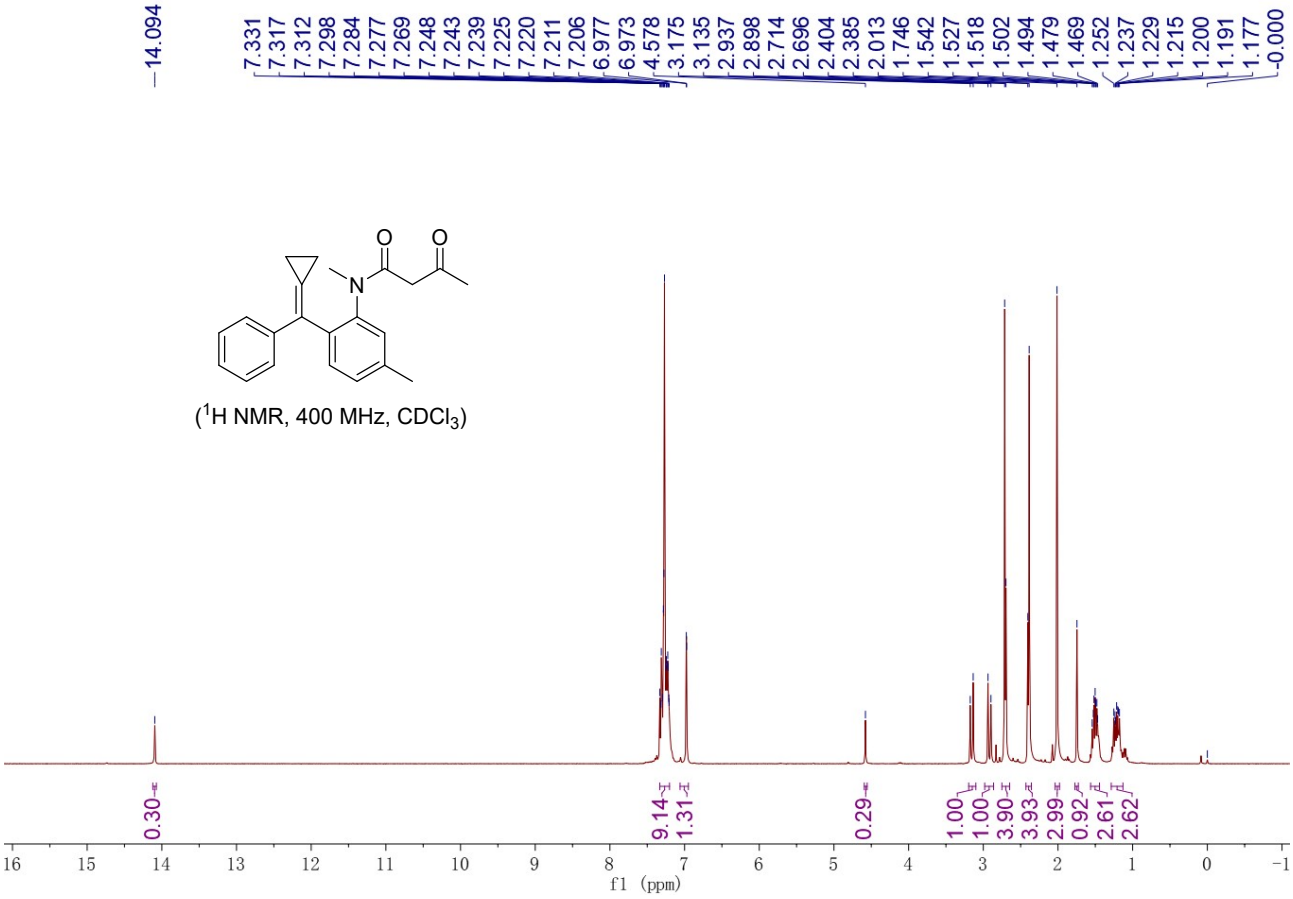


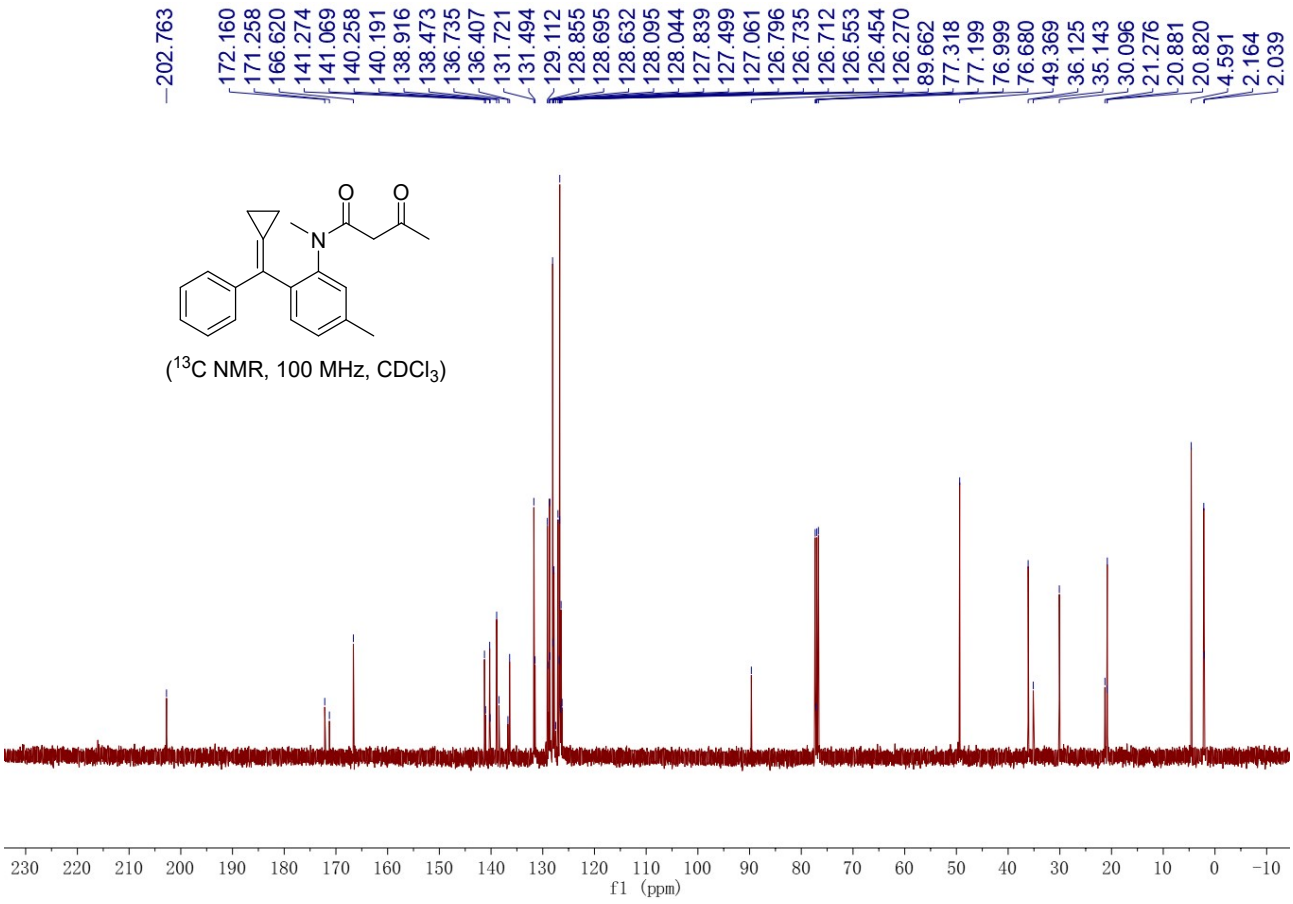


(^{13}C NMR, 100 MHz, $CDCl_3$)

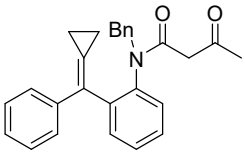


N-(2-(cyclopropylidene(phenyl)methyl)-5-methylphenyl)-N-methyl-3-oxobutanamide (**1m**): Yield: 546 mg, 82%, brown solid, m.p. 133-135 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.09 (s, 0.3H), 7.33 – 7.20 (m, 9.1H), 7.06 – 6.95 (m, 1.3H), 4.58 (s, 0.3H), 3.16 (d, *J* = 15.8 Hz, 1H), 2.98 – 2.86 (m, 1H), 2.71 (d, *J* = 7.0 Hz, 3.9H), 2.43 – 2.36 (m, 3.9H), 2.01 (s, 3H), 1.75 (s, 0.9H), 1.56 – 1.44 (m, 2.6H), 1.29 – 1.13 (m, 2.6H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.8, 172.2, 171.3, 166.6, 141.3, 141.1, 140.3, 140.2, 138.9, 138.5, 136.7, 136.4, 131.7, 131.5, 129.1, 128.9, 128.7, 128.6, 128.1, 128.0, 127.8, 127.1, 126.8, 126.7, 126.7, 126.6, 126.5, 126.3, 89.7, 49.4, 36.1, 35.1, 30.1, 21.3, 20.9, 20.8, 4.6, 2.2, 2.0; IR (neat): ν 3418, 3032, 2969, 2919, 1717, 1607, 1371, 1109, 770, 700 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$: 356.16210, found: 356.16142.

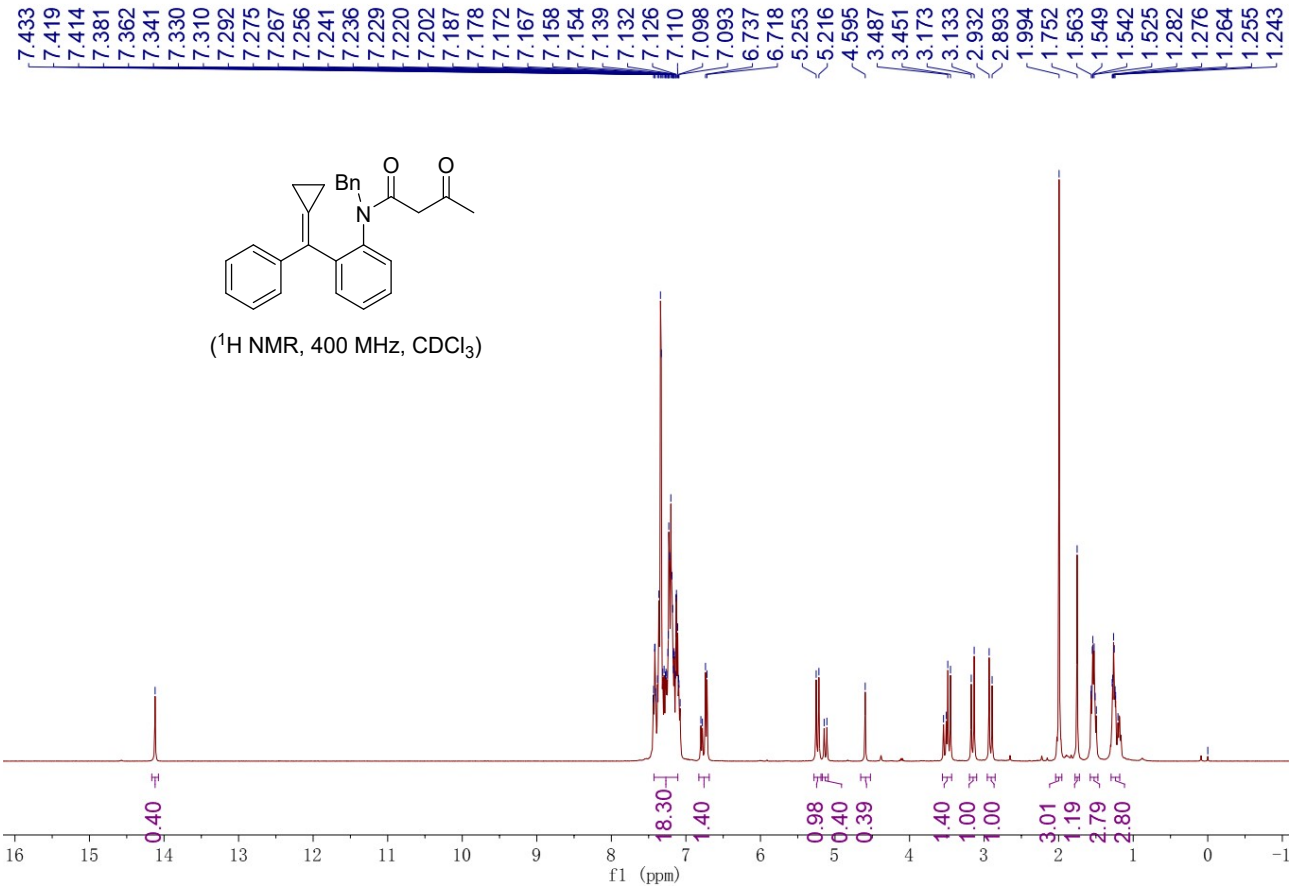


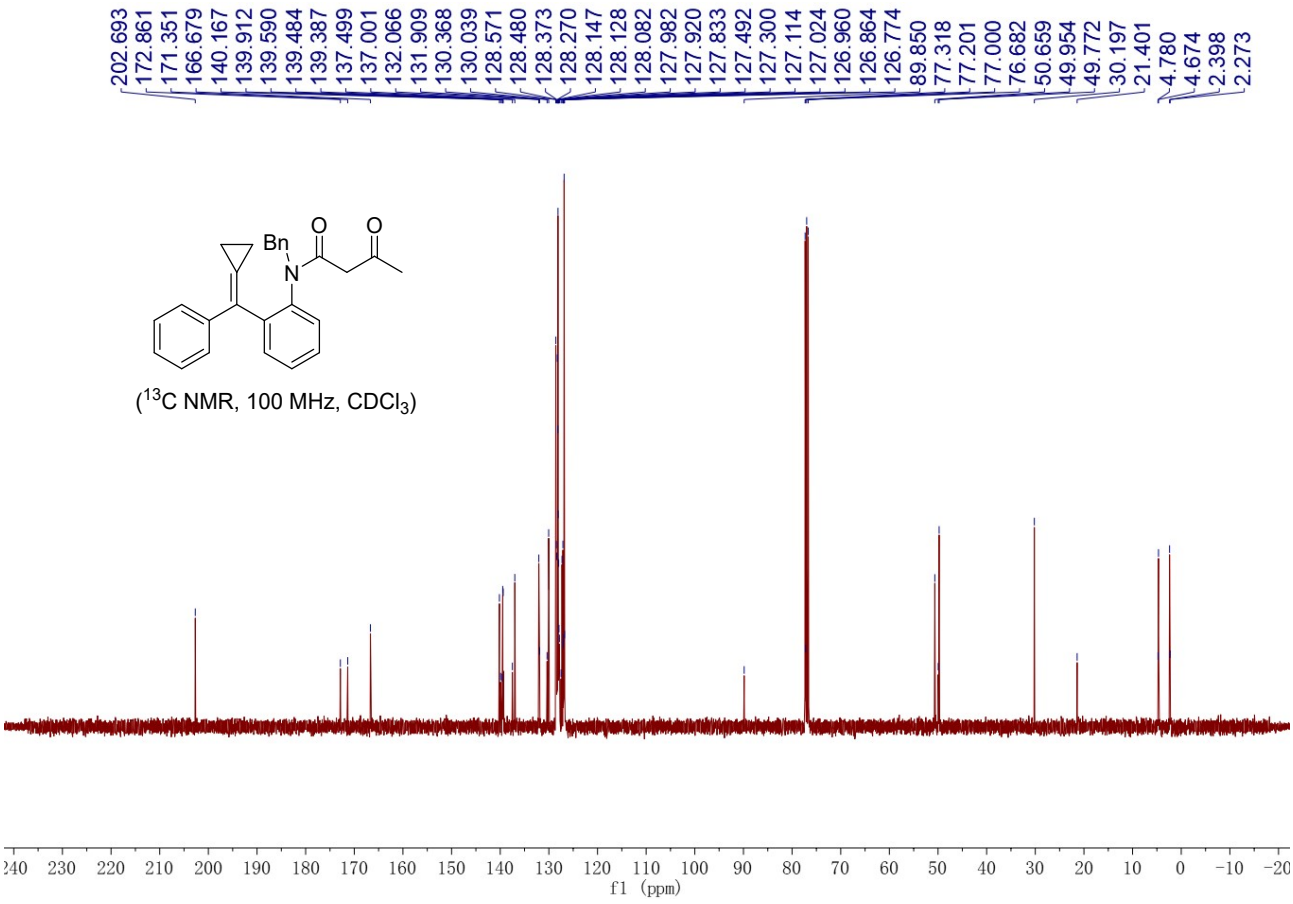


(^{13}C NMR, 100 MHz, $CDCl_3$)

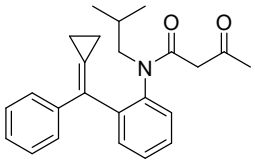


N-benzyl-N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-3-oxobutanamide (**1n**): Yield: 632 mg, 80%, brown solid, m.p. 106-108 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.12 (s, 0.4H), 7.43 – 7.11 (m, 18.3H), 6.83 – 6.69 (m, 1.4H), 5.23 (d, *J* = 14.5 Hz, 1H), 5.13 (d, *J* = 14.8 Hz, 0.4H), 4.59 (s, 0.4H), 3.56 – 3.44 (m, 1.4H), 3.15 (d, *J* = 15.8 Hz, 1H), 2.91 (d, *J* = 15.8 Hz, 1H), 1.99 (s, 3H), 1.75 (s, 1.2H), 1.58 – 1.47 (m, 2.8H), 1.30 – 1.18 (m, 2.8H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 172.9, 171.4, 166.7, 140.2, 139.9, 139.6, 139.5, 139.4, 137.5, 137.0, 132.1, 131.9, 130.4, 130.0, 128.6, 128.5, 128.4, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.5, 127.3, 127.1, 127.0, 127.0, 126.9, 126.8, 89.8, 50.7, 50.0, 49.8, 30.2, 21.4, 4.8, 4.7, 2.4, 2.3; IR (neat): ν 3058, 2935, 2828, 1714, 1652, 1447, 1253, 1169, 777, 732, 699, 637 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{27}H_{25}NO_2Na$ [M+Na]$^{+}$: 418.17775, found: 418.17694.

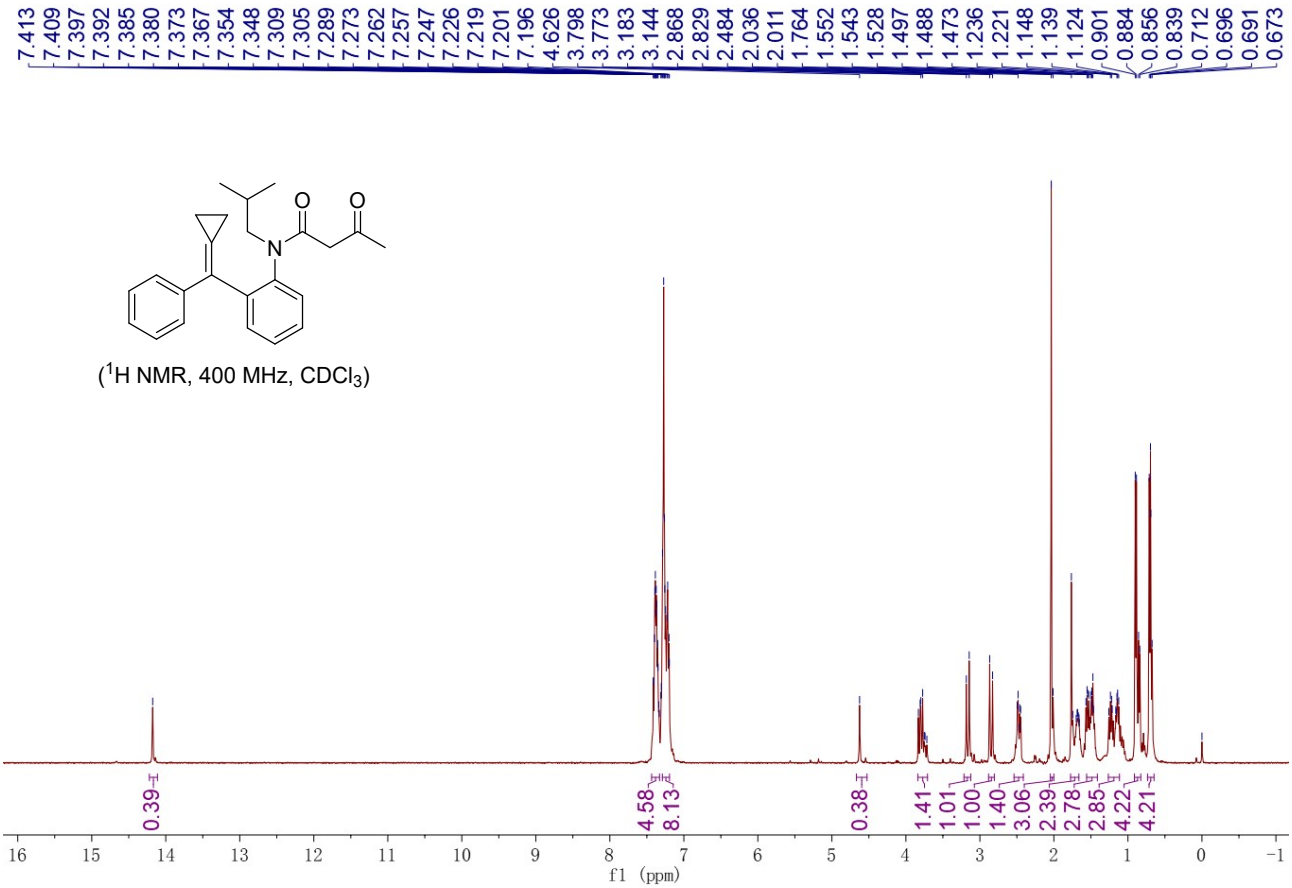


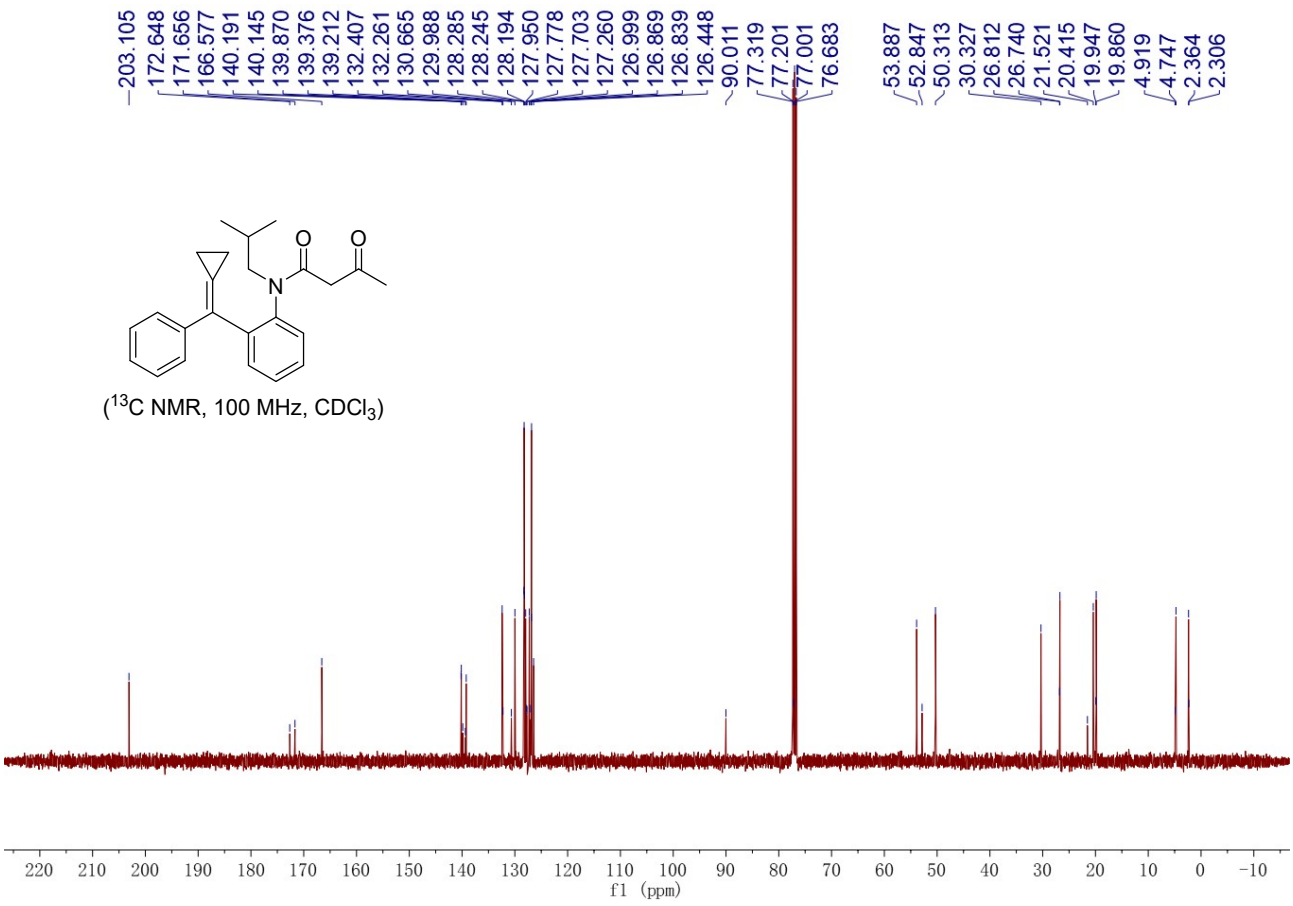


(^{13}C NMR, 100 MHz, $CDCl_3$)

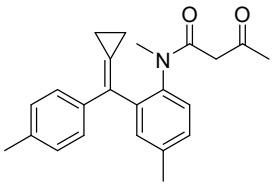


N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-isobutyl-3-oxobutanamide (**1o**): Yield: 534 mg, 74%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.18 (s, 0.4H), 7.44 – 7.33 (m, 4.6H), 7.29 – 7.19 (m, 8.1H), 4.63 (s, 0.4H), 3.84 – 3.71 (m, 1.4H), 3.16 (d, *J* = 15.7 Hz, 1H), 2.85 (d, *J* = 15.6 Hz, 1H), 2.54 – 2.41 (m, 1.4H), 2.05 – 2.00 (m, 3H), 1.77 – 1.66 (m, 2.4H), 1.56 – 1.41 (m, 2.8H), 1.26 – 1.11 (m, 2.8H), 0.91 – 0.83 (m, 4.2H), 0.73 – 0.65 (m, 4.2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 203.1, 172.6, 171.7, 166.6, 140.2, 140.1, 139.9, 139.4, 139.2, 132.4, 132.3, 130.7, 130.0, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.3, 127.0, 126.9, 126.8, 126.4, 90.0, 53.9, 52.8, 50.3, 30.3, 26.8, 26.7, 21.5, 20.4, 19.9, 19.9, 4.9, 4.7, 2.4, 2.3; IR (neat): ν 2966, 2925, 1878, 1708, 1448, 1383, 1245, 1055, 776, 738 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{24}H_{27}NO_2Na$ $[M+Na]^+$: 384.19340, found: 384.19421.

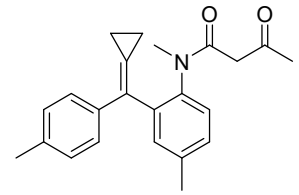




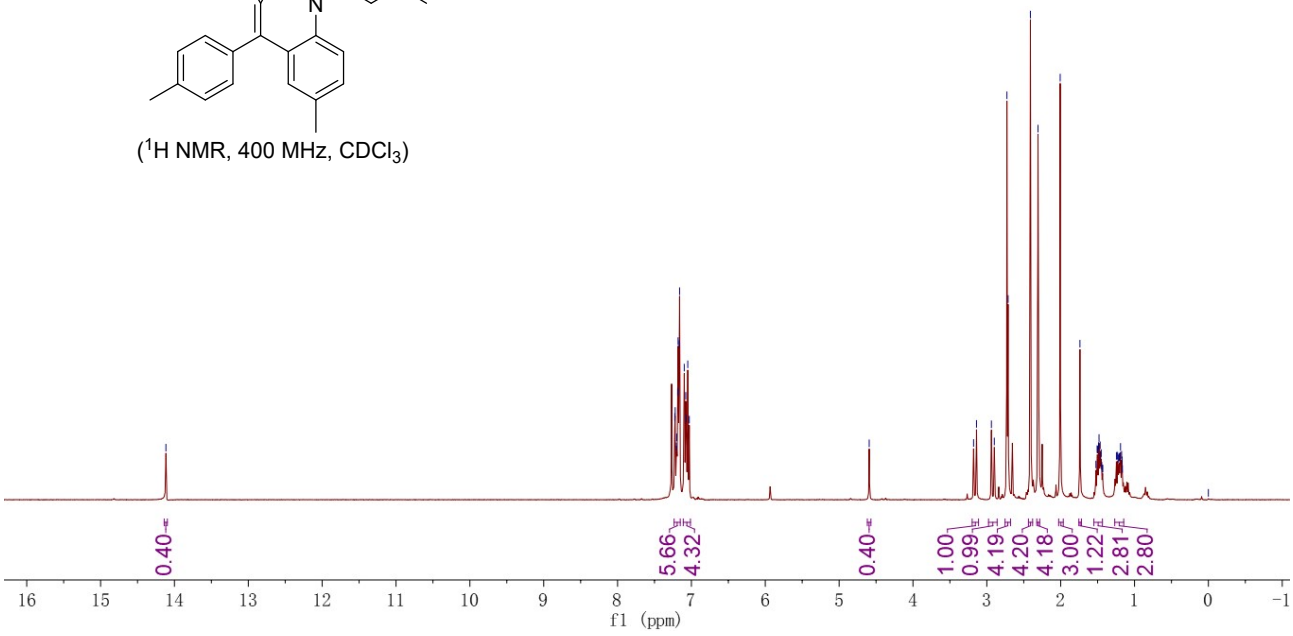
(^{13}C NMR, 100 MHz, $CDCl_3$)

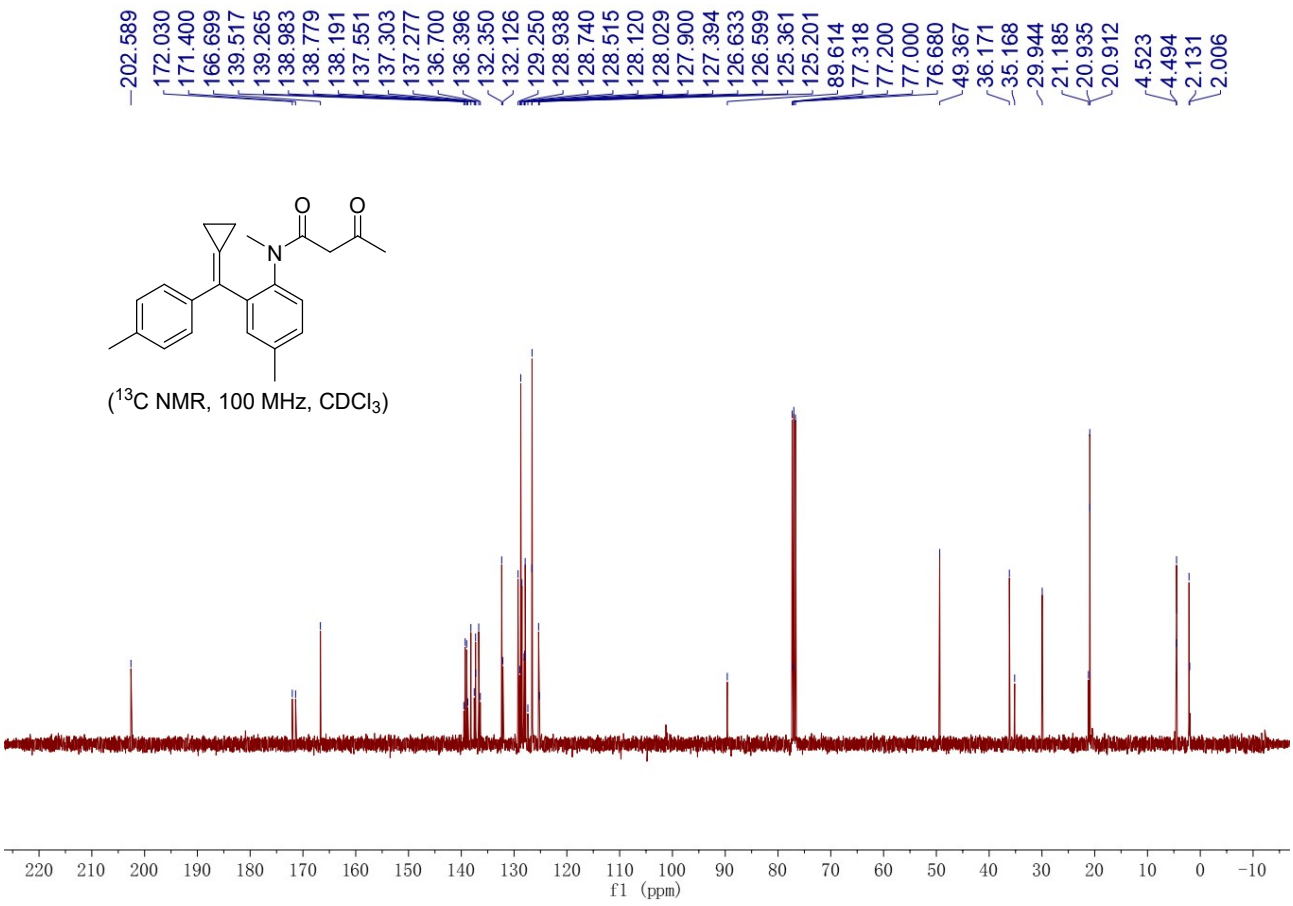


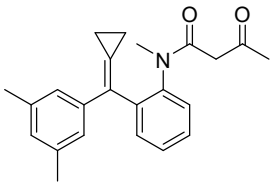
N-(2-(cyclopropylidene(p-tolyl)methyl)-4-methylphenyl)-N-methyl-3-oxobutanamide (**1p**): Yield: 583 mg, 84%, brown solid, m.p. 137-139 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.12 (s, 0.4H), 7.23 – 7.15 (m, 5.6H), 7.11 – 7.01 (m, 4.3H), 4.59 (s, 0.4H), 3.16 (d, *J* = 15.7 Hz, 1H), 2.92 (d, *J* = 15.7 Hz, 1H), 2.75 – 2.68 (m, 4.2H), 2.44 – 2.38 (m, 4.2H), 2.32 – 2.28 (m, 4.2H), 2.01 (s, 3H), 1.74 (s, 1.2H), 1.55 – 1.43 (m, 2.8H), 1.27 – 1.15 (m, 2.8H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.6, 172.0, 171.4, 166.7, 139.5, 139.3, 139.0, 138.8, 138.2, 137.6, 137.3, 137.3, 136.7, 136.4, 132.4, 132.1, 129.3, 128.9, 128.7, 128.5, 128.1, 128.0, 127.9, 126.6, 126.6, 125.4, 125.2, 89.6, 49.4, 36.2, 35.2, 29.9, 21.2, 20.9, 20.9, 4.5, 4.5, 2.1, 2.0; IR (neat): ν 3000, 2974, 2922, 1721, 1503, 1387, 1174, 1114, 824 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{25}NO_2Na$ [M+Na]$^{+}$: 370.17775, found: 370.17779.



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

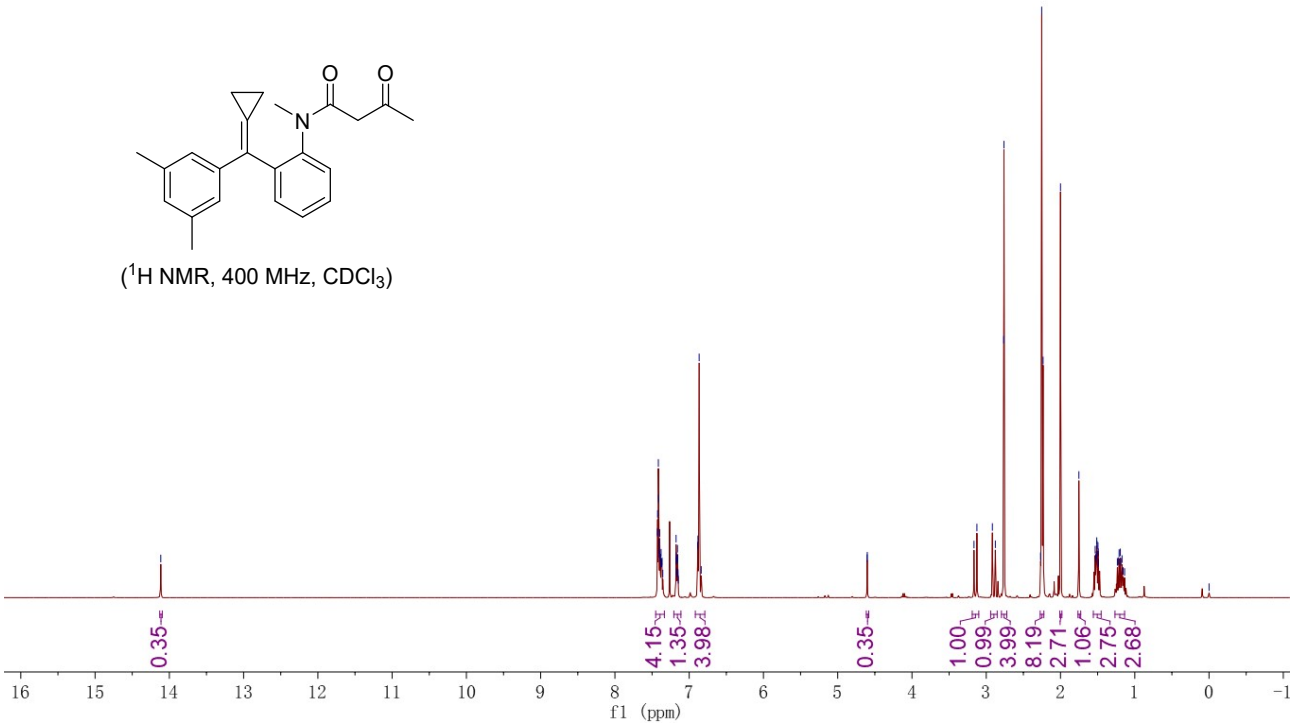


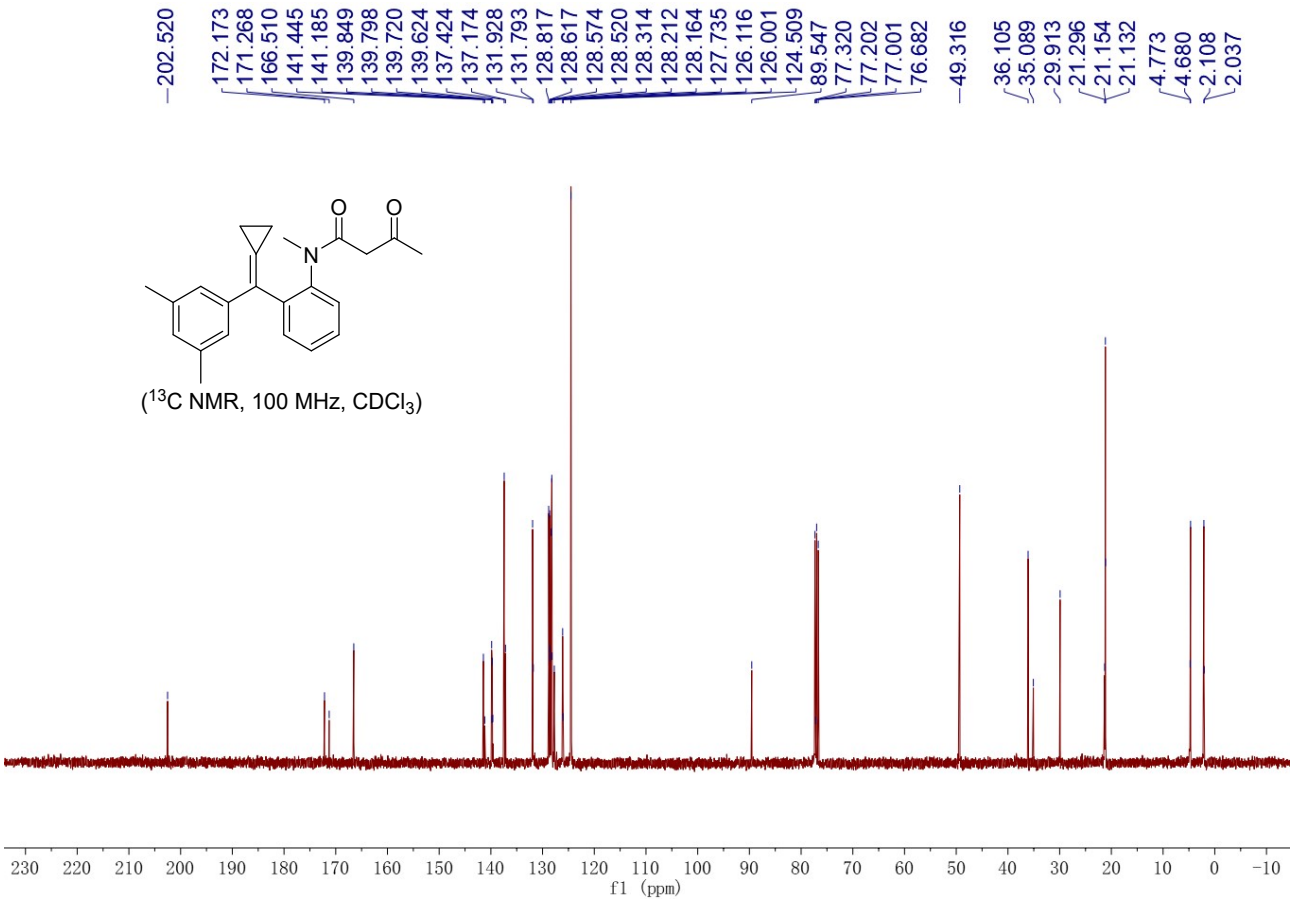

202.589
172.030
171.400
166.699
139.517
139.265
138.983
138.779
138.191
137.551
137.303
137.277
136.700
136.396
132.350
132.126
129.250
128.938
128.740
128.515
128.120
128.029
127.900
127.394
126.633
126.599
125.361
125.201
89.614
77.318
77.200
77.000
76.680
49.367
36.171
35.168
29.944
21.185
20.935
20.912
4.523
4.494
2.131
2.006
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

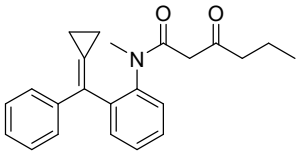


N-(2-(cyclopropylidene(3,5-dimethylphenyl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1q**): Yield: 541 mg, 78%, yellow solid, m.p. 158-160 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.12 (s, 0.35H), 7.45 – 7.33 (m, 4.15H), 7.21 – 7.11 (m, 1.35H), 6.92 – 6.79 (m, 4H), 4.60 (s, 0.35H), 3.15 (d, *J* = 15.8 Hz, 1H), 2.90 (d, *J* = 15.8 Hz, 1H), 2.80 – 2.72 (m, 4H), 2.27 – 2.22 (m, 8.2H), 2.01 – 1.98 (m, 2.7H), 1.75 (s, 1H), 1.56 – 1.45 (m, 2.7H), 1.27 – 1.14 (m, 2.7H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.5, 172.2, 171.3, 166.5, 141.4, 141.2, 139.8, 139.8, 139.7, 139.6, 137.4, 137.2, 131.9, 131.8, 128.8, 128.6, 128.6, 128.5, 128.3, 128.2, 128.2, 127.7, 126.1, 126.0, 124.5, 89.5, 49.3, 36.1, 35.1, 29.9, 21.3, 21.2, 21.1, 4.8, 4.7, 2.1, 2.0; IR (neat): ν 3052, 2976, 2917, 1728, 1586, 1468, 1295, 1187, 920, 839, 778, 699, 683 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{25}NO_2Na$ $[M+Na]^+$: 370.17775, found: 370.17753.

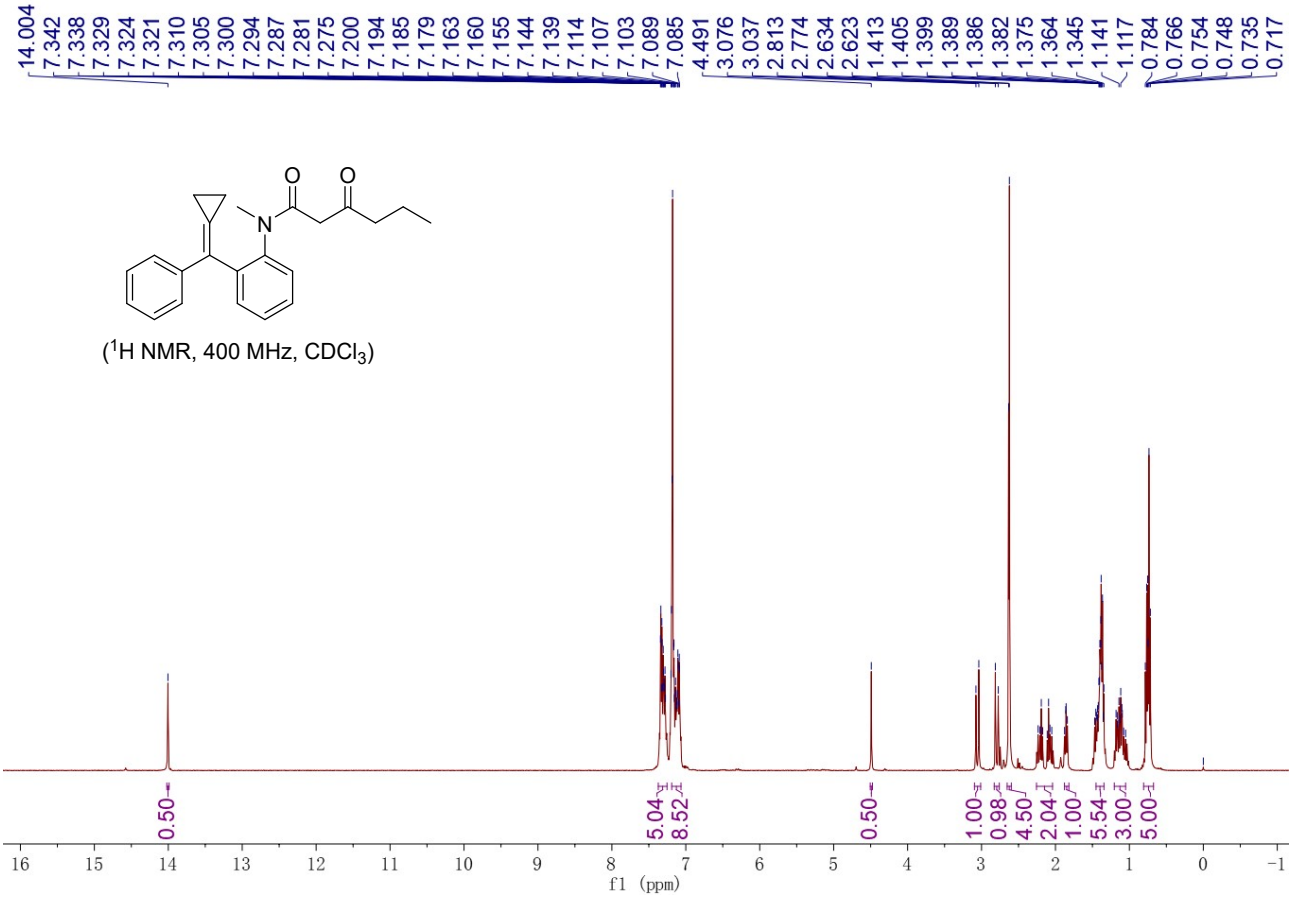
(^{1}H NMR, 400 MHz, $CDCl_3$)

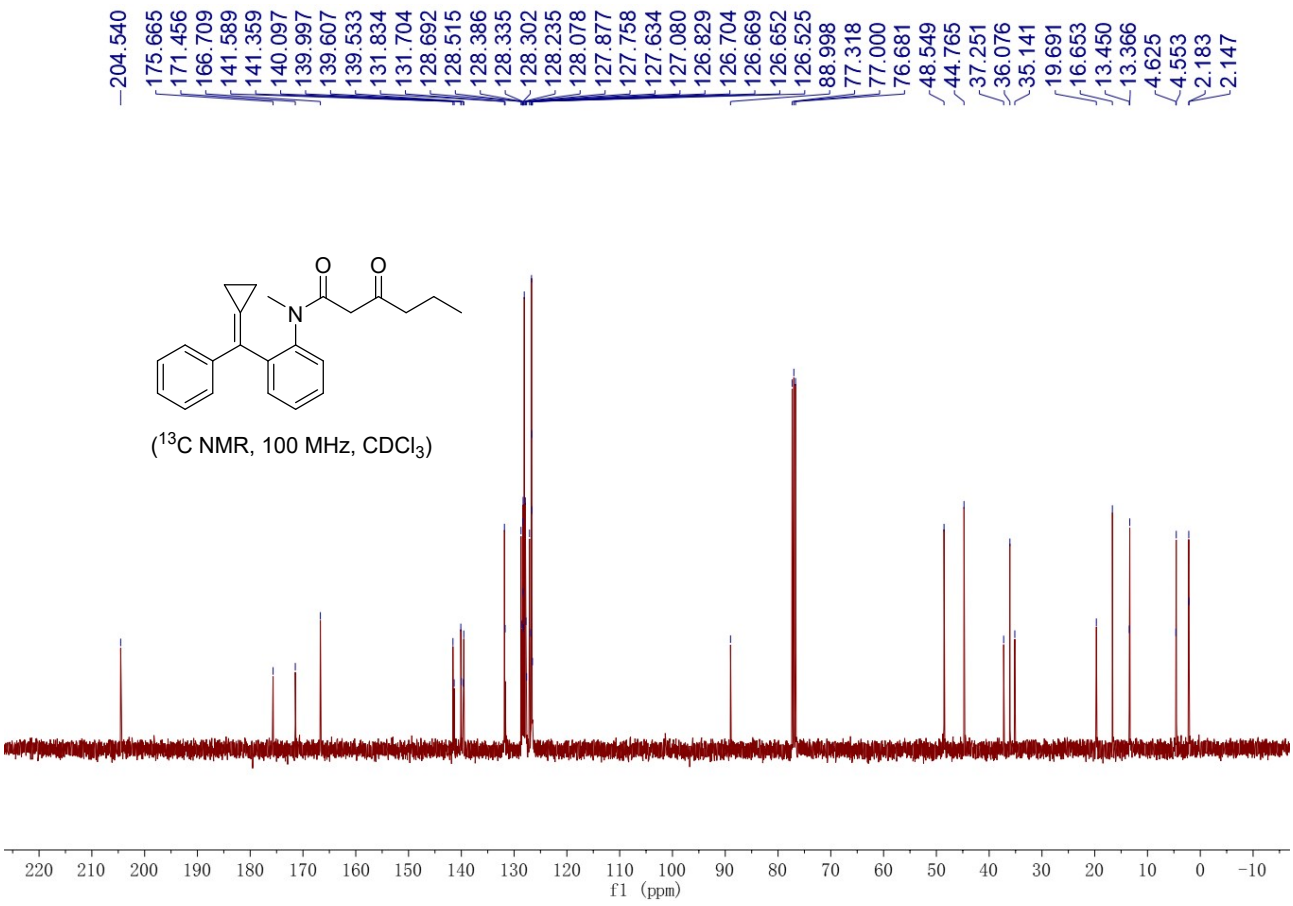


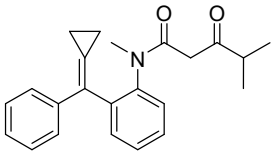

202.520
172.173
171.268
166.510
141.445
141.185
139.849
139.798
139.720
139.624
137.424
137.174
131.928
131.793
128.817
128.617
128.574
128.520
128.314
128.212
128.164
127.735
126.116
126.001
124.509
89.547
77.320
77.202
77.001
76.682
49.316
36.105
35.089
29.913
21.296
21.154
21.132
4.773
4.680
2.108
2.037
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



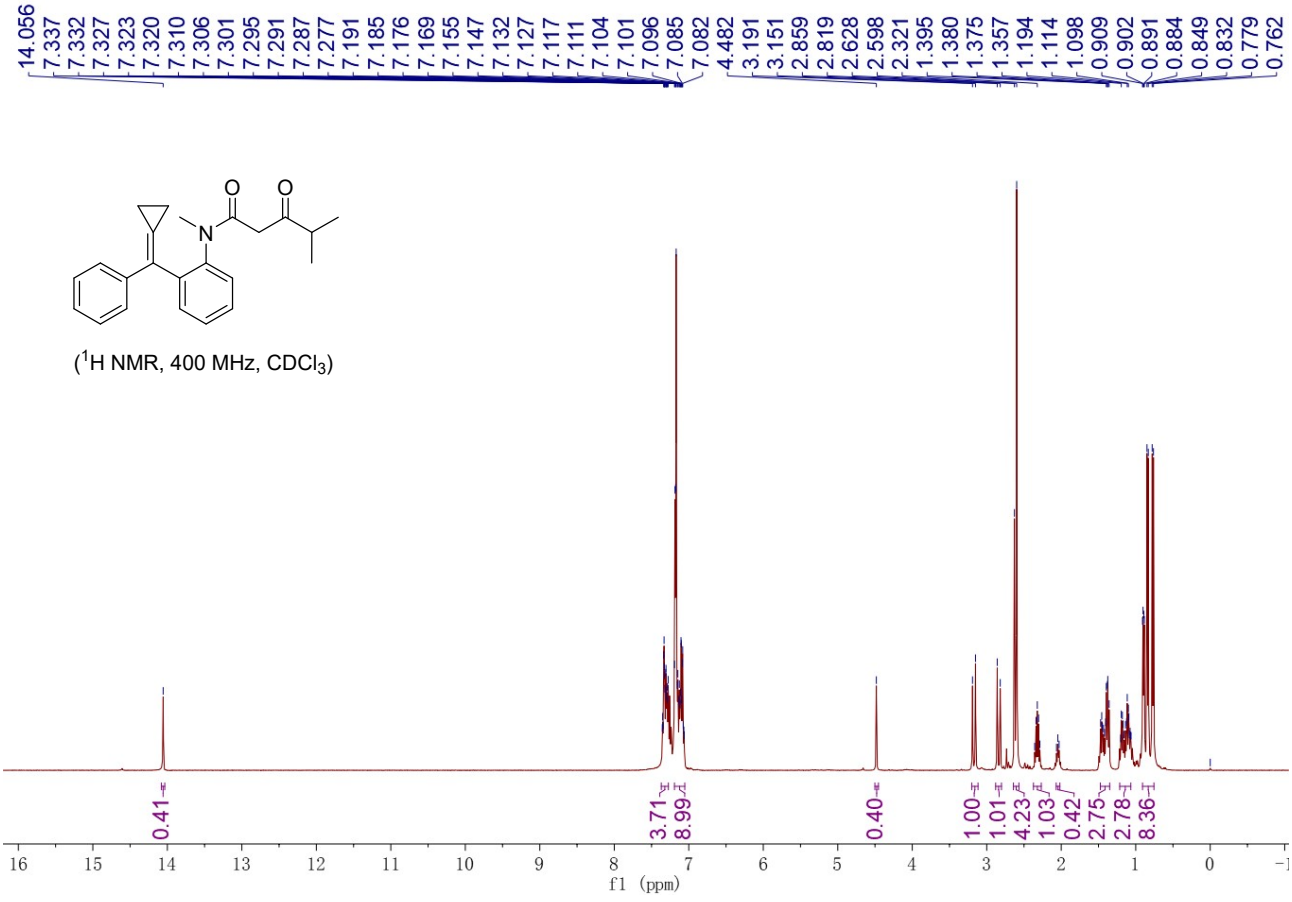
N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methyl-3-oxohexanamide (**1r**): Yield: 500 mg, 72%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.00 (s, 0.5H), 7.37 – 7.25 (m, 5H), 7.19 – 7.06 (m, 8.5H), 4.49 (s, 0.5H), 3.06 (d, *J* = 15.7 Hz, 1H), 2.79 (d, *J* = 15.7 Hz, 1H), 2.65 – 2.60 (m, 4.5H), 2.26 – 2.04 (m, 2H), 1.88 – 1.82 (m, 1H), 1.45 – 1.34 (m, 5.5H), 1.20 – 1.05 (m, 3H), 0.81 – 0.67 (m, 5H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 204.5, 175.7, 171.5, 166.7, 141.6, 141.4, 140.1, 140.0, 139.6, 139.5, 131.8, 131.7, 128.7, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.1, 126.8, 126.7, 126.7, 126.7, 126.5, 89.0, 48.5, 44.8, 37.3, 36.1, 35.1, 19.7, 16.7, 13.5, 13.4, 4.6, 4.6, 2.2, 2.1; IR (neat): ν 3060, 2959, 2867, 1722, 1427, 1384, 10723, 765, 751 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{25}NO_2Na$ $[M+Na]^+$: 370.17775, found: 370.17696.

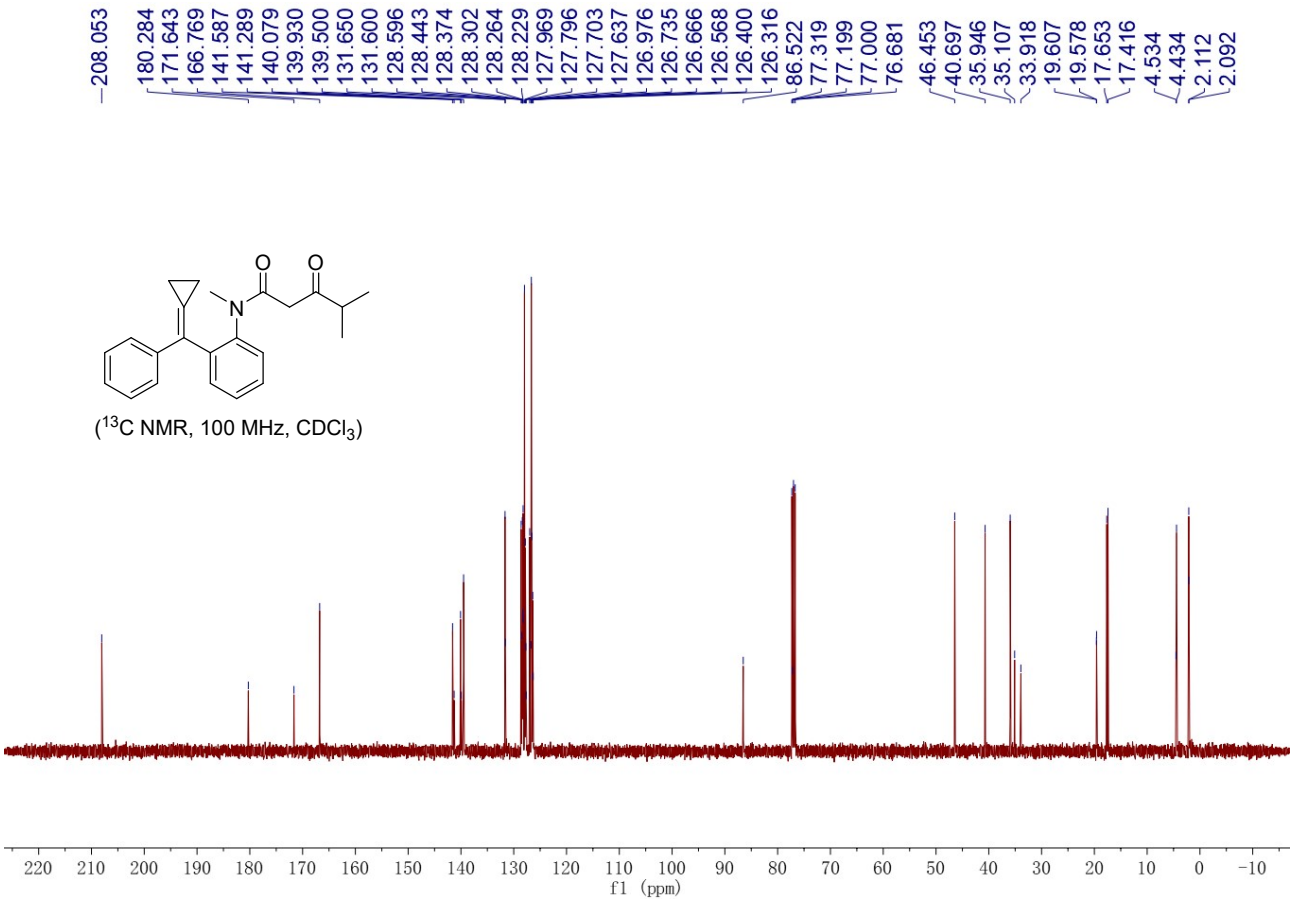



204.540
175.665
171.456
166.709
141.589
141.359
140.097
139.997
139.607
139.533
131.834
131.704
128.692
128.515
128.386
128.335
128.302
128.235
128.078
127.877
127.758
127.634
127.080
126.829
126.704
126.669
126.652
126.525
88.998
77.318
77.000
76.681
48.549
44.765
37.251
36.076
35.141
19.691
16.653
13.450
13.366
4.625
4.553
2.183
2.147
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

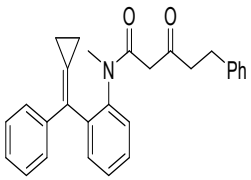


N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N,4-dimethyl-3-oxopentanamide (**1s**): Yield: 548 mg, 79%, brown solid, m.p. 114-116 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.06 (s, 0.4H), 7.37 – 7.27 (m, 3.7H), 7.19 – 7.05 (m, 9H), 4.48 (s, 0.4H), 3.17 (d, *J* = 16.1 Hz, 1H), 2.84 (d, *J* = 16.1 Hz, 1H), 2.64 – 2.57 (m, 4.2H), 2.37 – 2.27 (m, 1H), 2.07 – 2.02 (m, 0.4H), 1.47 – 1.35 (m, 2.8H), 1.21 – 1.07 (m, 2.8H), 0.91 – 0.76 (m, 8.4H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 208.1, 180.3, 171.6, 166.8, 141.6, 141.3, 140.1, 139.9, 139.5, 131.7, 131.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.0, 126.7, 126.7, 126.6, 126.4, 126.3, 86.5, 46.5, 40.7, 35.9, 35.1, 33.9, 19.6, 19.6, 17.7, 17.4, 4.5, 4.4, 2.1, 2.1; IR (neat): ν 3452, 2972, 2925, 2870, 1708, 1655, 1444, 1377, 1044, 766 cm^{-1}; HRMS (ESI-TOF) Calcd for $C20H19NO_2Na$ $[M+Na]^+$: 370.17775, found: 370.17696.

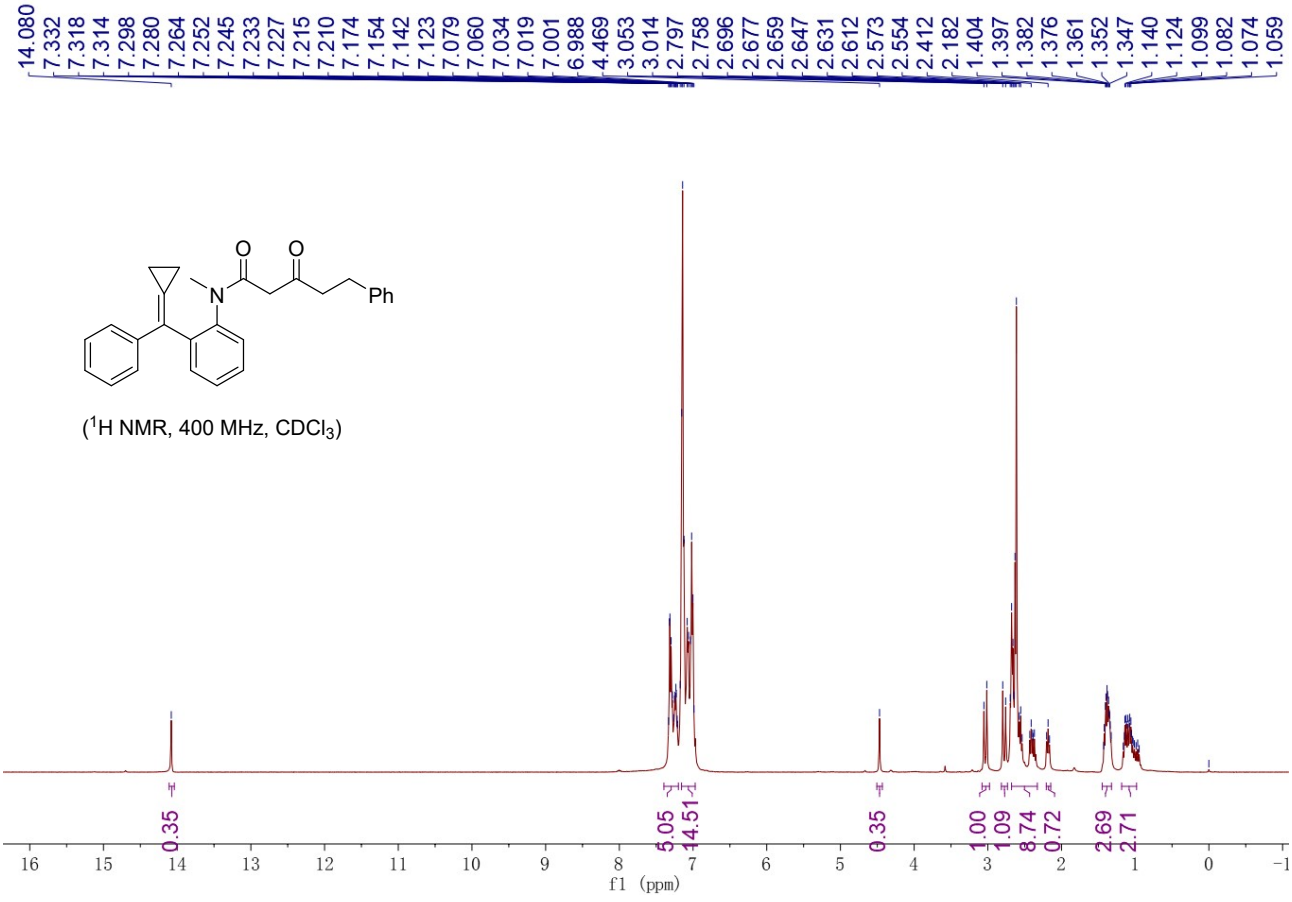


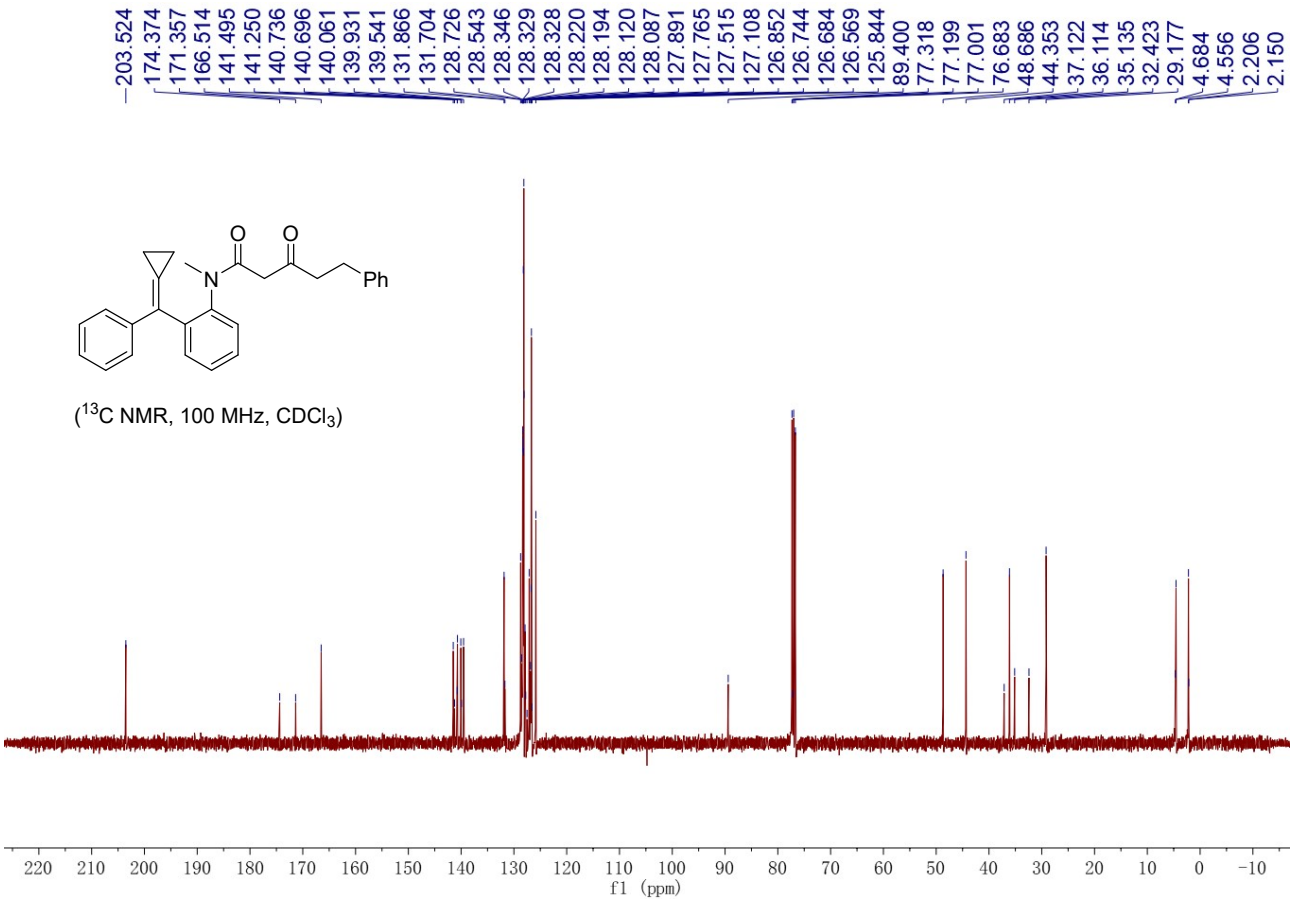


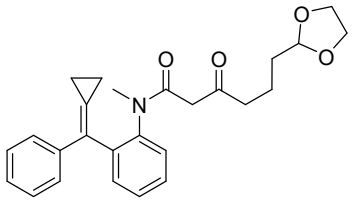
(^{13}C NMR, 100 MHz, $CDCl_3$)



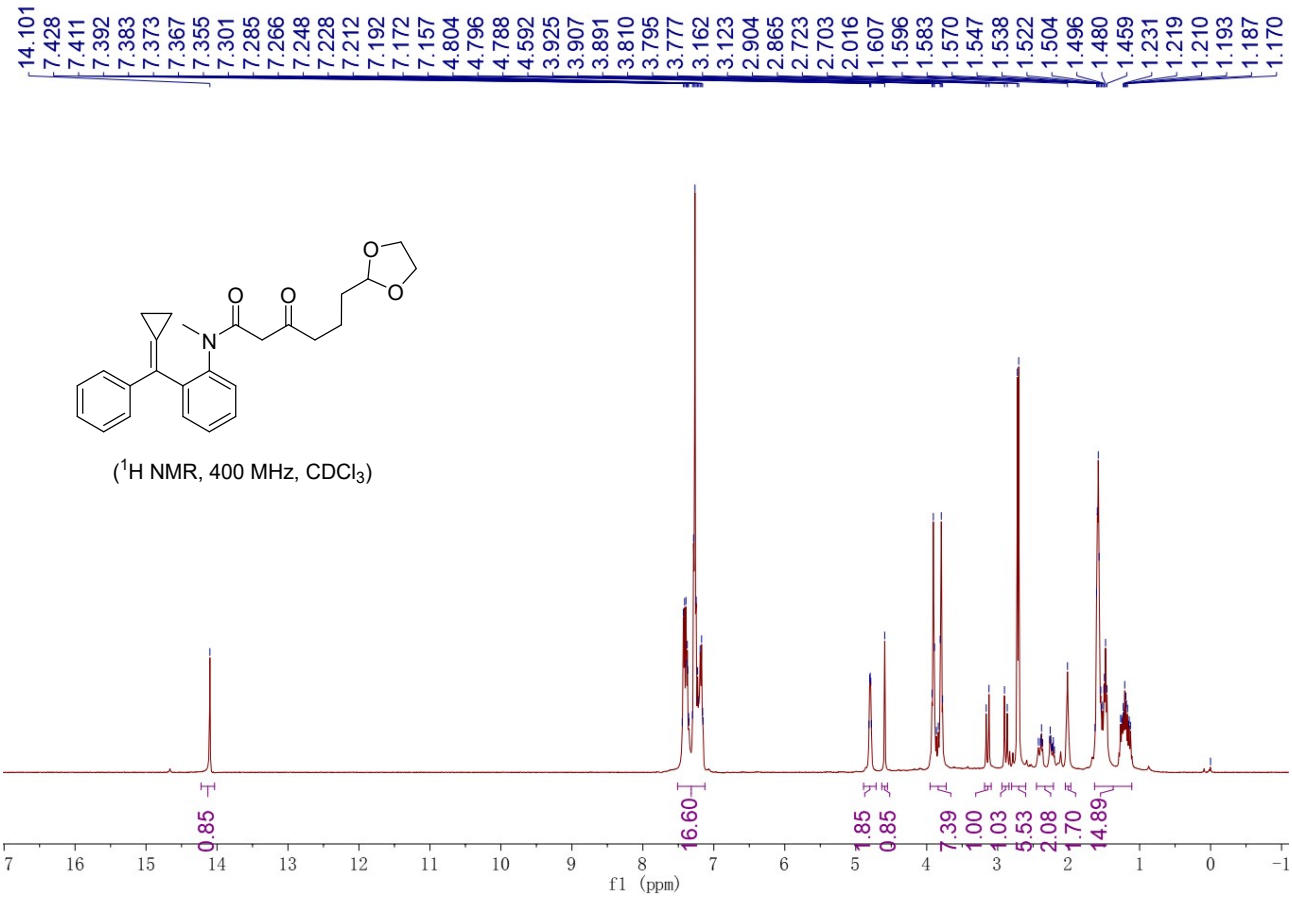
N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methyl-3-oxo-5-phenylpentanamide (**1w**): Yield: 670 mg, 82%, brown solid, m.p. 89-91 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.08 (s, 0.35H), 7.40 – 7.20 (m, 5H), 7.16 – 6.97 (m, 14.5H), 4.47 (s, 0.35H), 3.03 (d, *J* = 15.6 Hz, 1H), 2.78 (d, *J* = 15.6 Hz, 1H), 2.68 – 2.33 (m, 8.74H), 2.18 (t, *J* = 7.9 Hz, 0.72H), 1.45 – 1.32 (m, 2.7H), 1.18 – 0.98 (m, 2.7H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 203.5, 174.4, 171.4, 166.5, 141.5, 141.3, 140.7, 140.7, 140.1, 139.9, 139.5, 131.9, 131.7, 128.7, 128.5, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.8, 127.5, 127.1, 126.9, 126.7, 126.7, 126.6, 125.8, 89.4, 48.7, 44.4, 37.1, 36.1, 35.1, 32.4, 29.2, 4.7, 4.6, 2.2, 2.1; IR (neat): ν 3058, 3026, 2927, 1709, 1651, 1446, 1106, 766, 749 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{28}H_{27}NO_2Na$ $[M+Na]^+$: 432.19340, found: 432.19394.

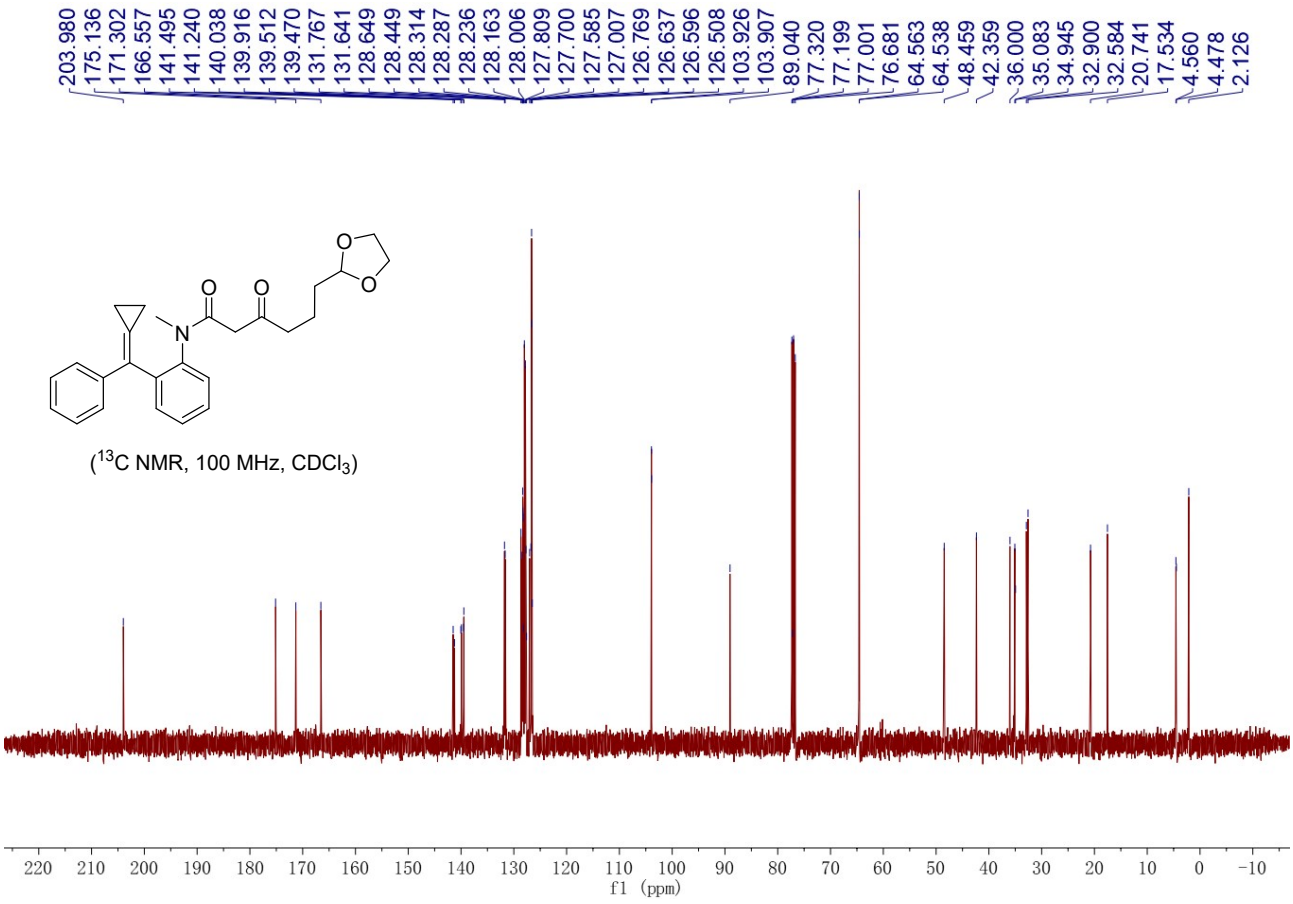



203.524
174.374
171.357
166.514
141.495
141.250
140.736
140.696
140.061
139.931
139.541
131.866
131.704
128.726
128.543
128.346
128.329
128.328
128.220
128.194
128.120
128.087
127.891
127.765
127.515
127.108
126.852
126.744
126.684
126.569
125.844
89.400
77.318
77.199
77.001
76.683
48.686
44.353
37.122
36.114
35.135
32.423
29.177
4.684
4.556
2.206
2.150
O
O
N
Ph
(13C NMR, 100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

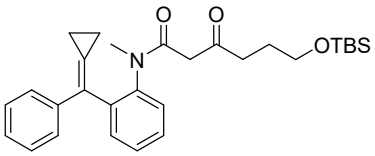


N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-6-(1,3-dioxolan-2-yl)-N-methyl-3-oxohexanamide (**1x**): Yield: 647 mg, 77%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.10 (s, 0.85H), 7.51 – 7.13 (m, 16.6H), 4.89 – 4.71 (m, 1.85H), 4.59 (s, 0.85H), 3.95 – 3.72 (m, 7.4H), 3.14 (d, *J* = 15.6 Hz, 1H), 2.88 (d, *J* = 15.6 Hz, 1H), 2.80 – 2.60 (m, 5.5H), 2.45 – 2.21 (m, 2H), 2.05 – 1.97 (m, 1.7H), 1.63 – 1.11 (m, 14.9H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 204.0, 175.1, 171.3, 166.6, 141.5, 141.2, 140.0, 139.9, 139.5, 139.5, 131.8, 131.6, 128.6, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.8, 127.7, 127.6, 127.0, 126.8, 126.6, 126.6, 126.5, 103.9, 103.9, 89.0, 64.6, 64.5, 48.5, 42.4, 36.0, 35.1, 34.9, 32.9, 32.6, 20.7, 17.5, 4.6, 4.5, 2.1; IR (neat): ν 3050, 3026, 2969, 1599, 1490, 1440, 1355, 1343, 1169, 1091, 1023, 941, 894, 753 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{26}H_{29}NO_2Na$ $[M+Na]^+$: 442.19888, found: 442.19858.

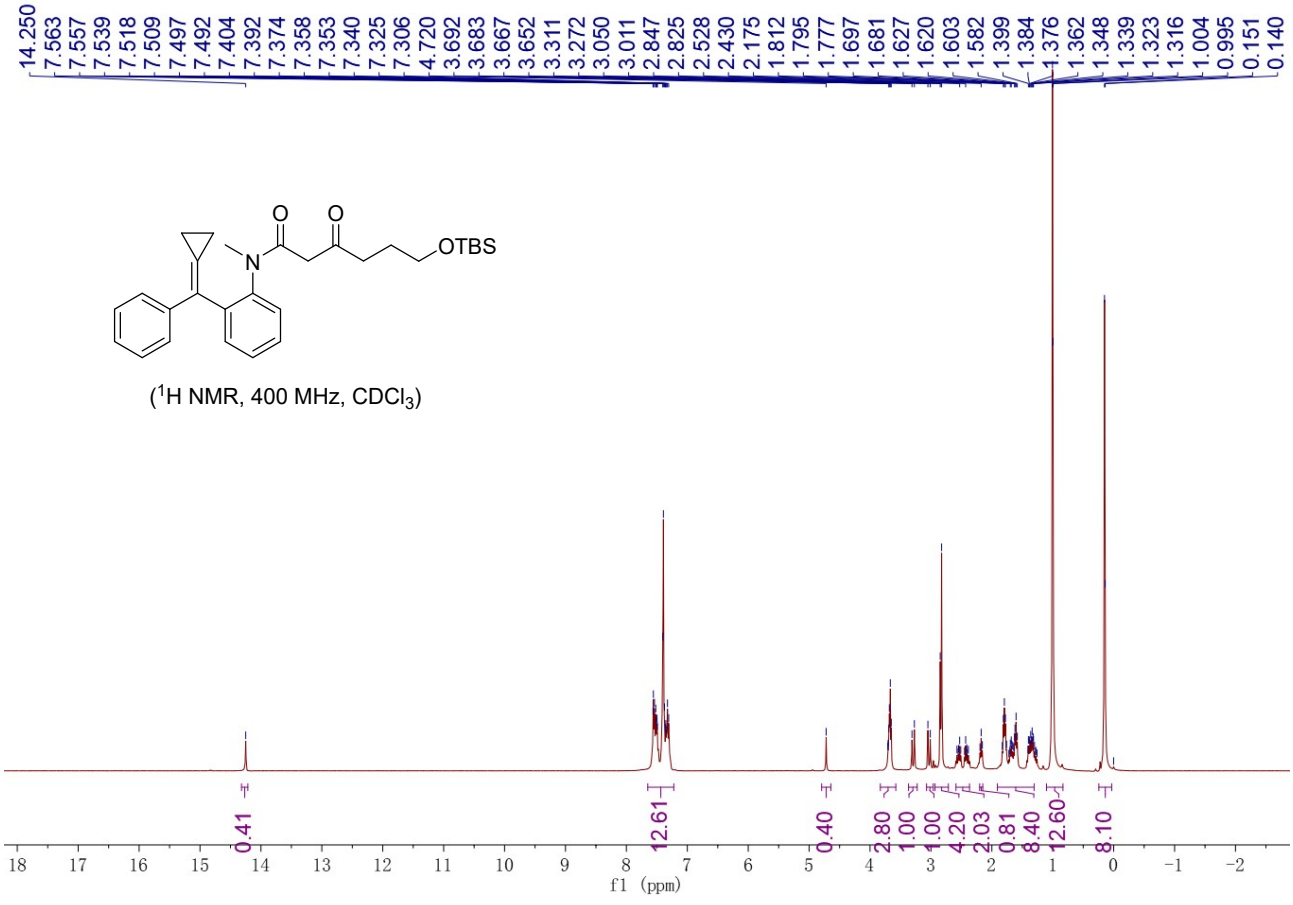


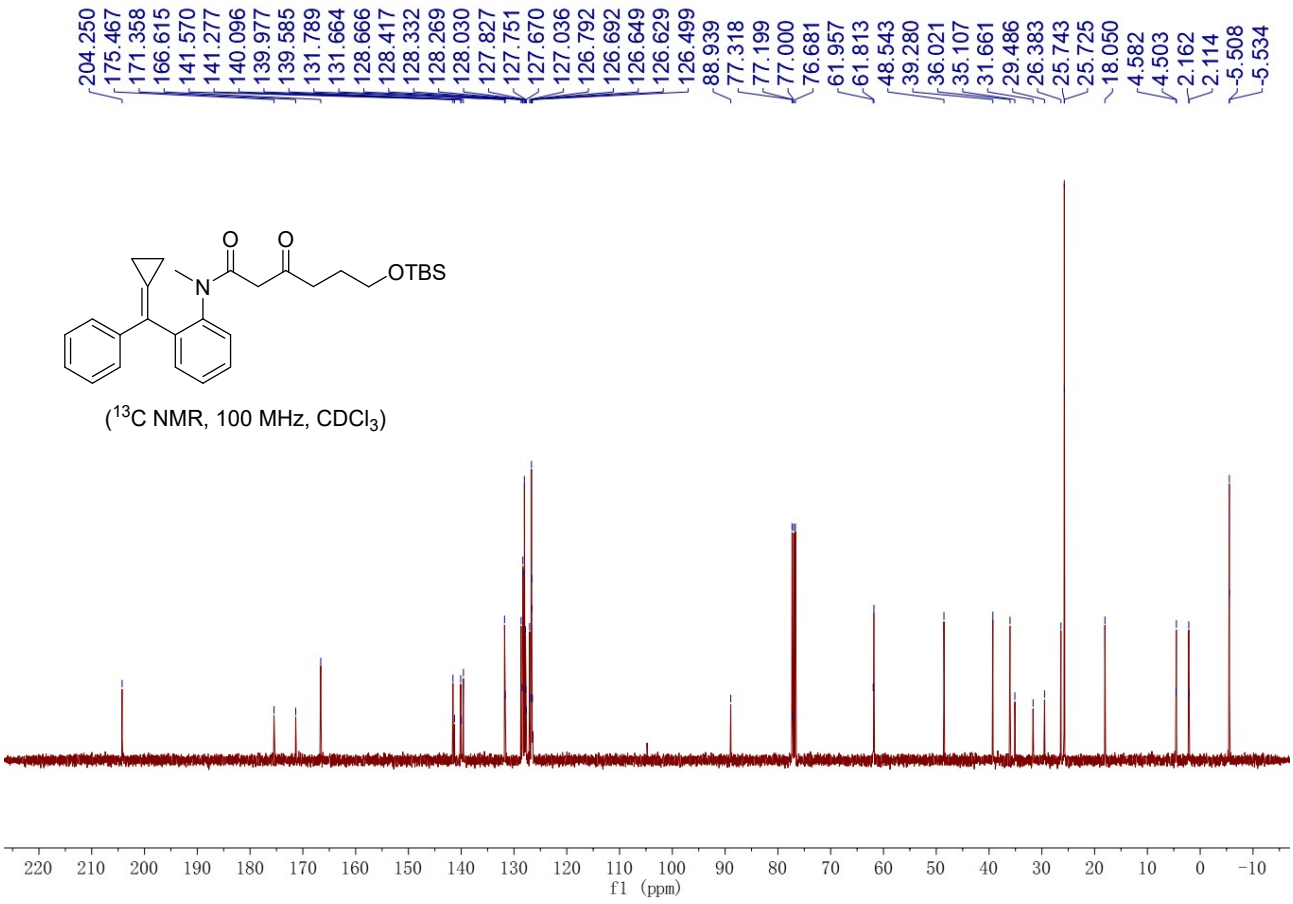


(^{13}C NMR, 100 MHz, $CDCl_3$)

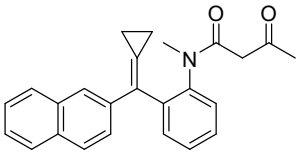


6-((*tert*-butyldimethylsilyl)oxy)-N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methyl-3-oxohexanamide (**1y**): Yield: 792 mg, 83%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.25 (s, 0.4H), 7.65 – 7.22 (m, 12.6H), 4.72 (s, 0.4H), 3.83 – 3.58 (m, 2.8H), 3.29 (d, *J* = 15.7 Hz, 1H), 3.03 (d, *J* = 15.7 Hz, 1H), 2.93 – 2.71 (m, 4.2H), 2.59 – 2.37 (m, 2H), 2.20 – 2.15 (m, 0.8H), 1.91 – 1.31 (m, 8.4H), 1.10 – 0.83 (m, 12.6H), 0.24 – 0.03 (m, 8.1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 204.3, 175.5, 171.4, 166.6, 141.6, 141.3, 140.1, 140.0, 139.6, 131.8, 131.7, 128.7, 128.4, 128.3, 128.3, 128.0, 127.8, 127.8, 127.7, 127.0, 126.8, 126.7, 126.6, 126.6, 126.5, 88.9, 62.0, 61.8, 48.5, 39.3, 36.0, 35.1, 31.7, 29.5, 26.4, 25.7, 25.7, 18.1, 4.6, 4.5, 2.2, 2.1, -5.5, -5.5; IR (neat): ν 2953, 2927, 2852, 1717, 1659, 1366, 1093, 833, 730, 664 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{29}H_{39}NO_3SiNa$ $[M+Na]^+$: 500.25914, found: 500.26002.

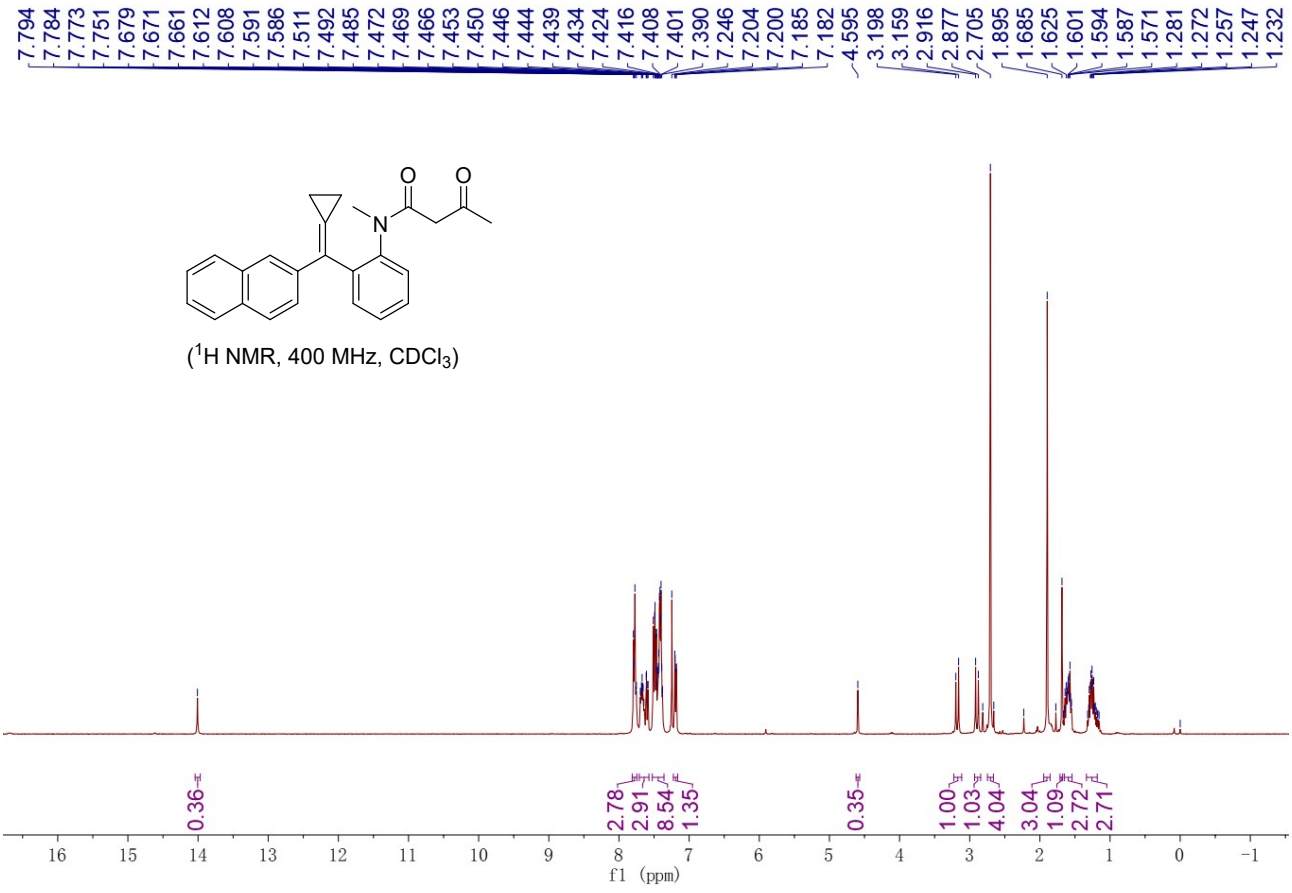


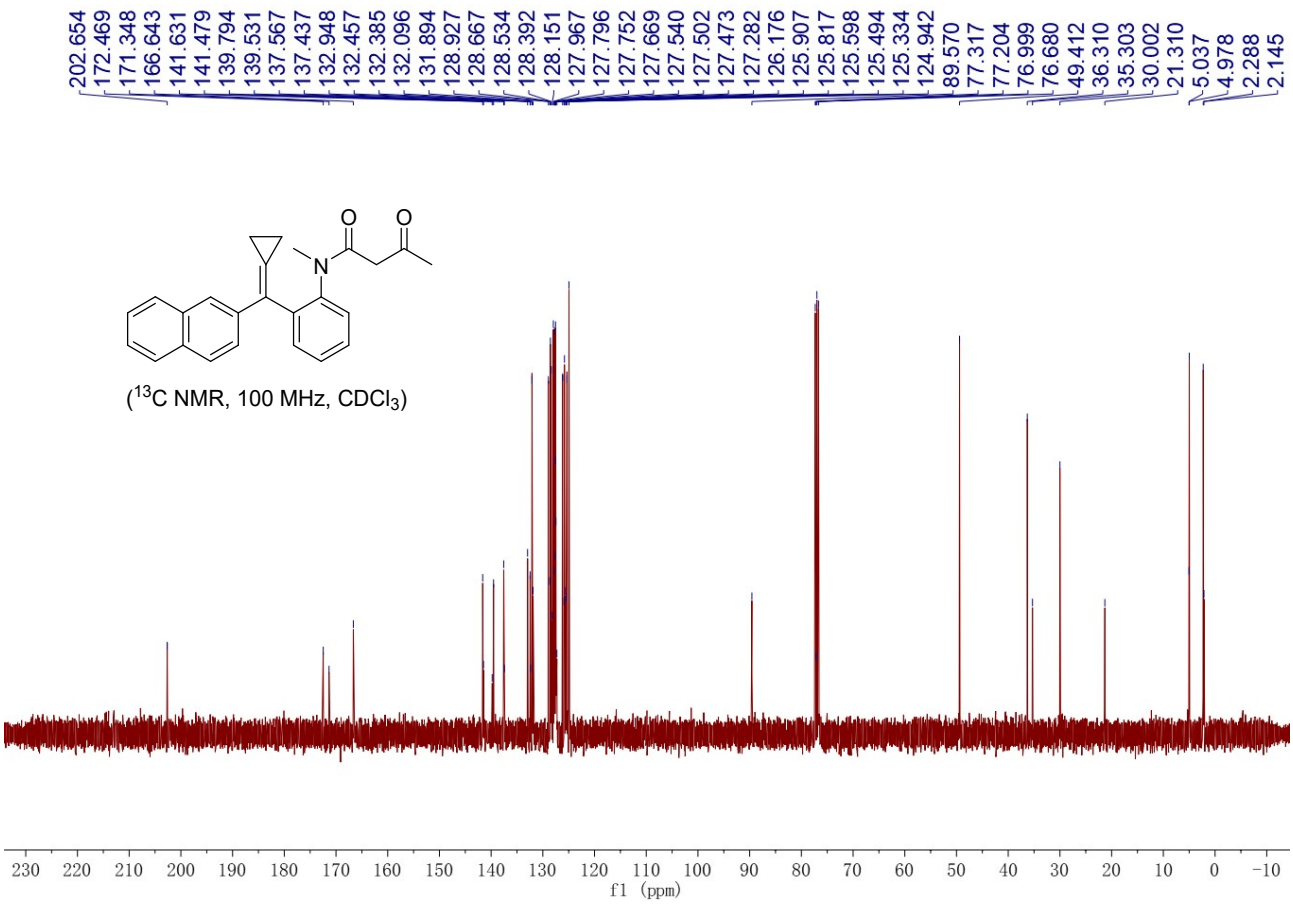


(^{13}C NMR, 100 MHz, $CDCl_3$)



N-(2-(cyclopropylidene(naphthalen-2-yl)methyl)phenyl)-N-methyl-3-oxobutanamide (**1z**): Yield: 512 mg, 70%, brown solid, m.p. 128-130 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 14.01 (s, 0.36H), 7.81 – 7.74 (m, 2.78H), 7.71 – 7.57 (m, 2.9H), 7.53 – 7.36 (m, 8.54H), 7.22 – 7.16 (m, 1.35H), 4.60 (s, 0.35H), 3.18 (d, *J* = 15.7 Hz, 1H), 2.90 (d, *J* = 15.7 Hz, 1H), 2.75 – 2.66 (m, 4H), 1.90 (s, 3H), 1.68 (s, 1H), 1.65 – 1.54 (m, 2.7H), 1.34 – 1.18 (m, 2.7H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 172.5, 171.3, 166.6, 141.6, 141.5, 139.8, 139.5, 137.6, 137.4, 132.9, 132.5, 132.4, 132.1, 131.9, 128.9, 128.7, 128.5, 128.4, 128.2, 128.0, 127.8, 127.8, 127.7, 127.5, 127.5, 127.5, 127.3, 126.2, 125.9, 125.8, 125.6, 125.5, 125.3, 124.9, 89.6, 49.4, 36.3, 35.3, 30.0, 21.3, 5.0, 5.0, 2.3, 2.1; IR (neat): ν 3050, 2966, 2917, 1724, 1632, 1461, 1298, 819, 739 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{25}H_{23}NO_2Na$ $[M+Na]^+$: 392.16210, found: 392.16213.

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171.348
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141.479
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139.531
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137.437
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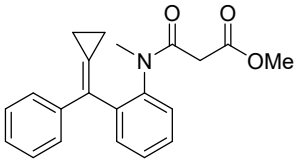
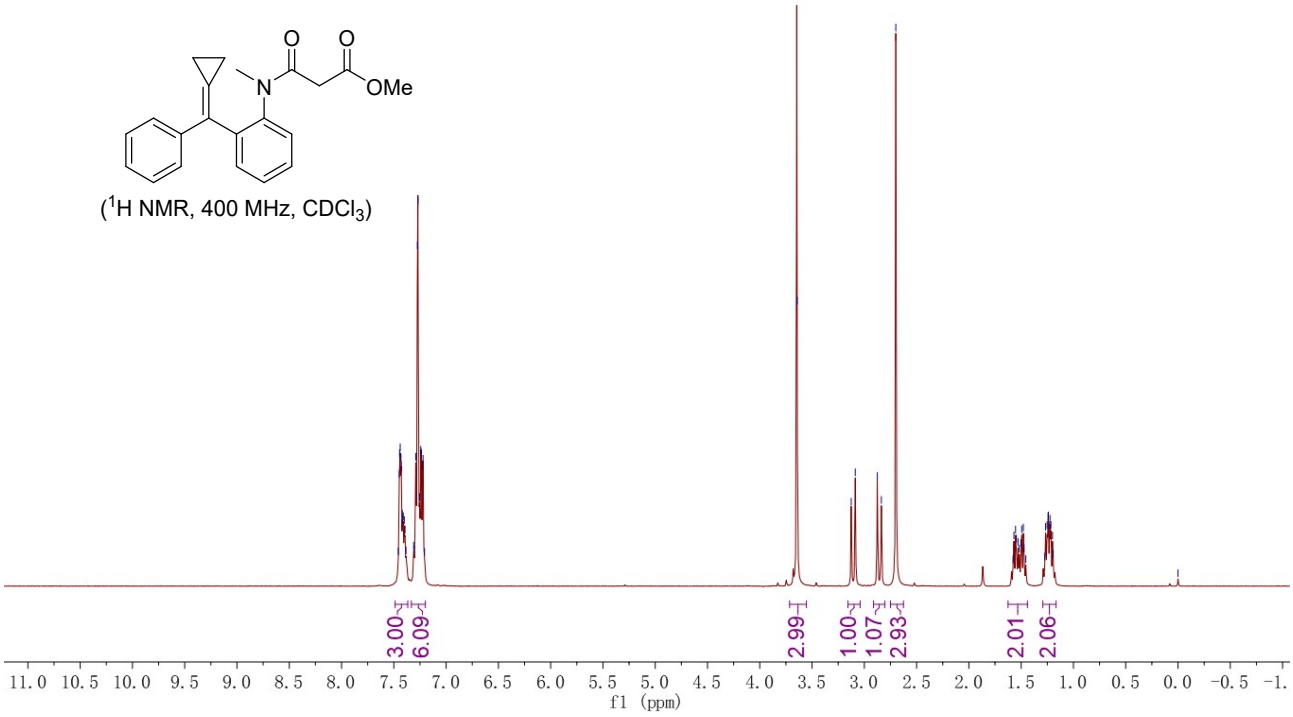
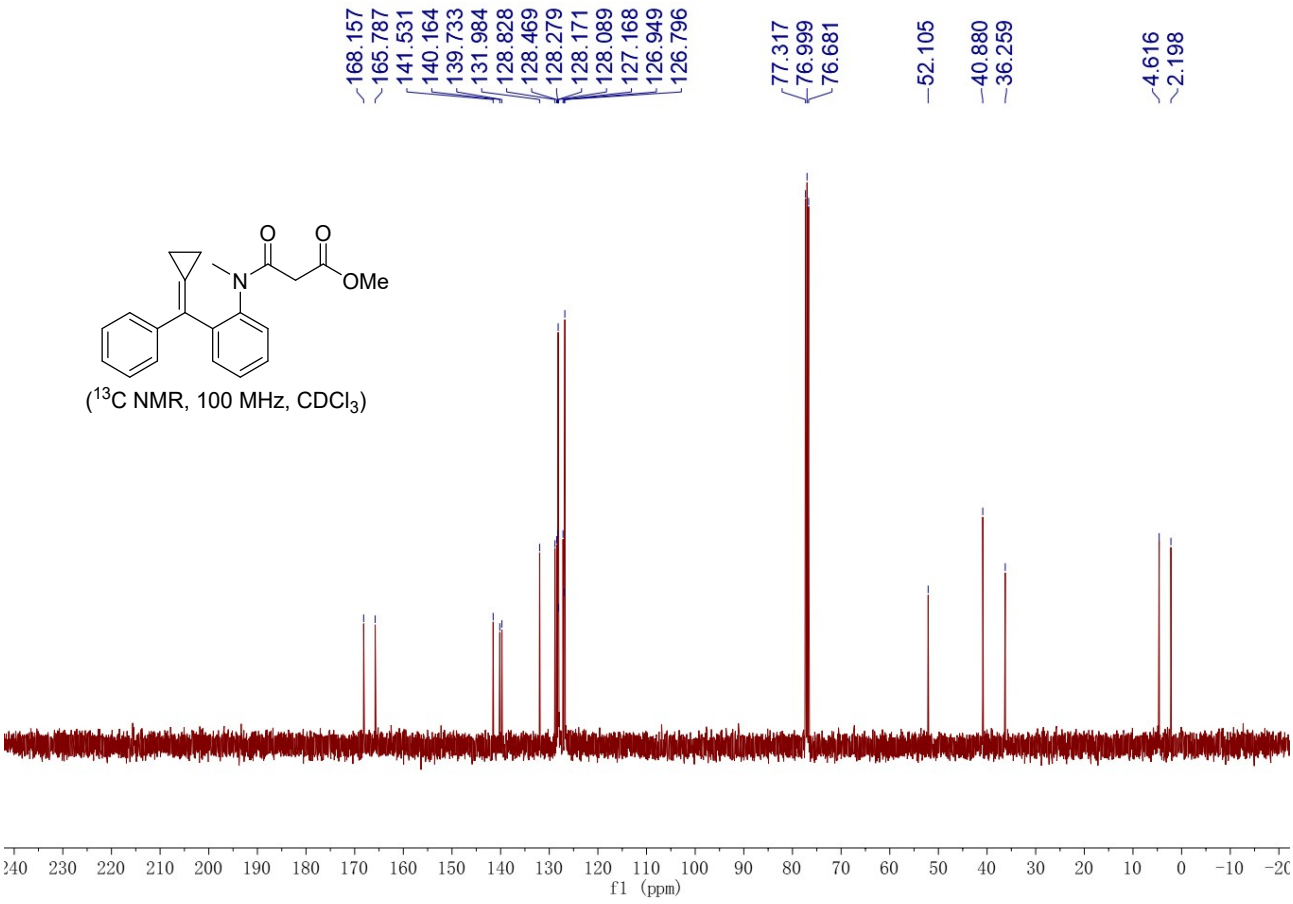
131.894
128.927
128.667
128.534
128.392
128.151
127.967
127.796
127.752
127.669
127.540
127.502
127.473
127.282
126.176
125.907
125.817
125.598
125.494
125.334
124.942
89.570
77.317
77.204
76.999
76.680
49.412
36.310
35.303
30.002
21.310
5.037
4.978
2.288
2.145
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

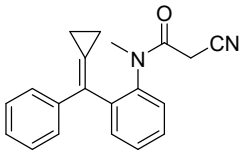


methyl 3-((2-(cyclopropylidene(phenyl)methyl)phenyl)(methyl)amino)-3-oxopropanoate (**1aa**): Yield: 556 mg, 83%, brown solid, m.p. 124-126 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 – 7.37 (m, 3H), 7.33 – 7.20 (m, 6H), 3.64 (s, 3H), 3.11 (d, *J* = 15.6 Hz, 1H), 2.86 (d, *J* = 15.4 Hz, 1H), 2.70 (s, 3H), 1.63 – 1.44 (m, 2H), 1.29 – 1.17 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 168.2, 165.8, 141.5, 140.2, 139.7, 132.0, 128.8, 128.5, 128.3, 128.2, 128.1, 127.2, 126.9, 126.8, 52.1, 40.9, 36.3, 4.6, 2.2; IR (neat): ν 3063, 3024, 2943, 1715, 1655, 1386, 1242, 1020, 785, 700 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{21}NO_3Na$ $[M+Na]^+$: 358.14136, found: 358.14148.

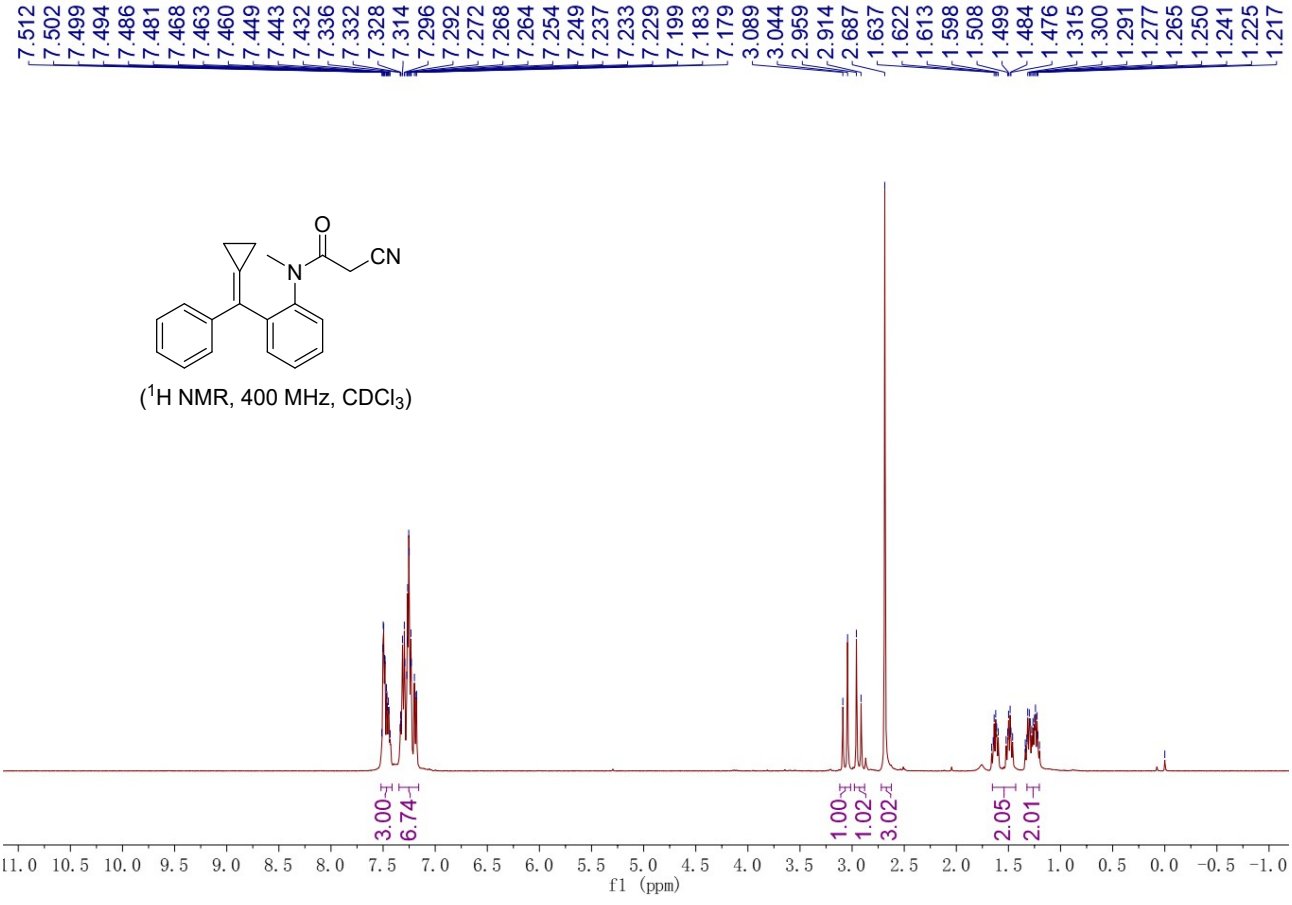


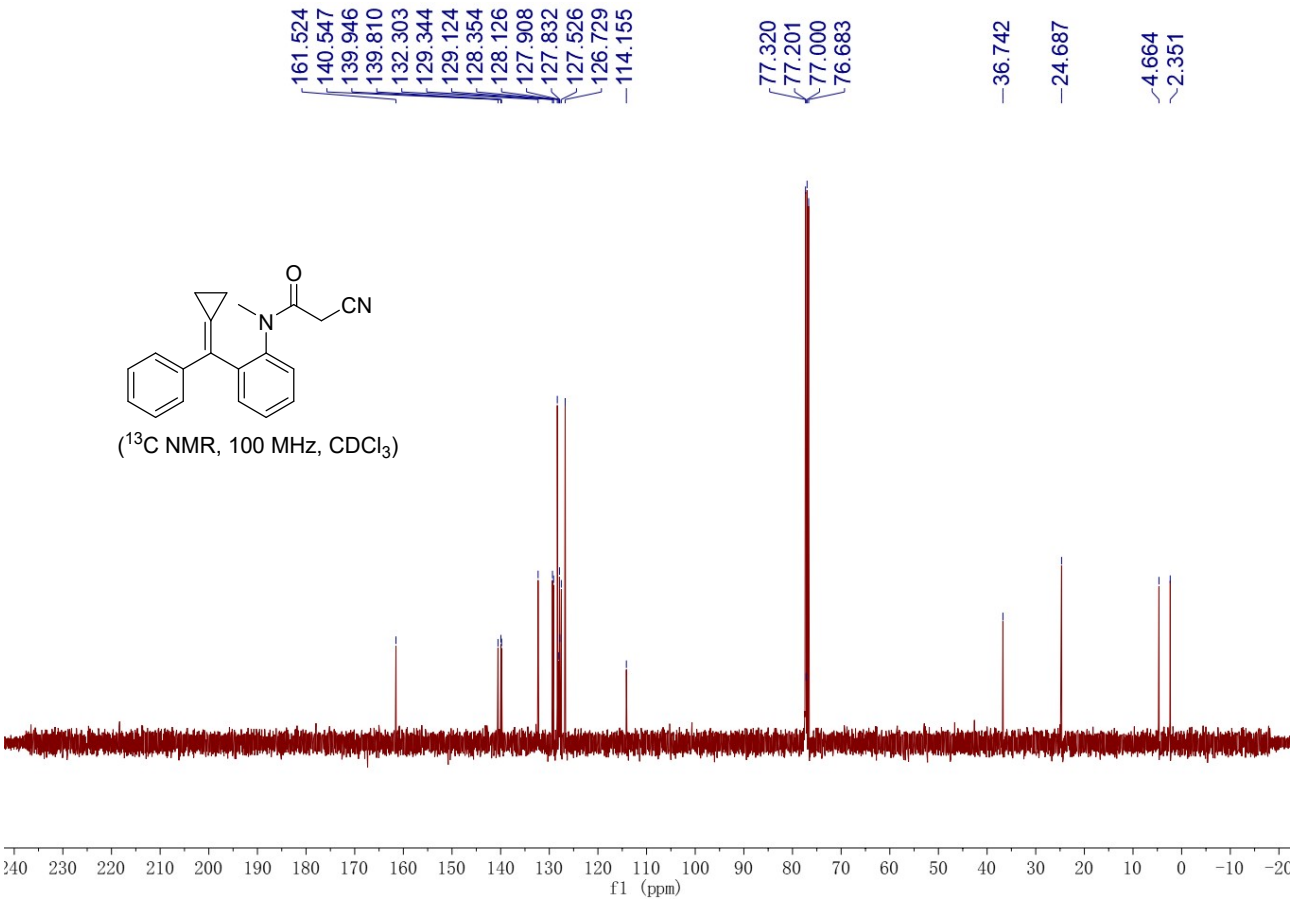


(^{13}C NMR, 100 MHz, $CDCl_3$)



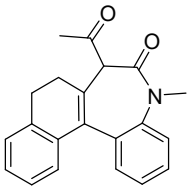
2-cyano-N-(2-(cyclopropylidene(phenyl)methyl)phenyl)-N-methylacetamide (**1ab**): Yield: 507 mg, 84%, brown solid, m.p. 117-119 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 – 7.41 (m, 3H), 7.35 – 7.16 (m, 6H), 3.07 (d, *J* = 18.2 Hz, 1H), 2.94 (d, *J* = 17.9 Hz, 1H), 2.69 (s, 3H), 1.65 – 1.43 (m, 2H), 1.32 – 1.20 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS)δ 161.5, 140.5, 139.9, 139.8, 132.3, 129.3, 129.1, 128.4, 128.1, 127.9, 127.8, 127.5, 126.7, 114.2, 36.7, 24.7, 4.7, 2.4; IR (neat): ν 3063, 3042, 2977, 2265, 1720, 1490, 1392, 1302, 1109, 810, 699 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}N_2ONa$ $[M+Na]^+$: 325.13113, found: 325.13074.



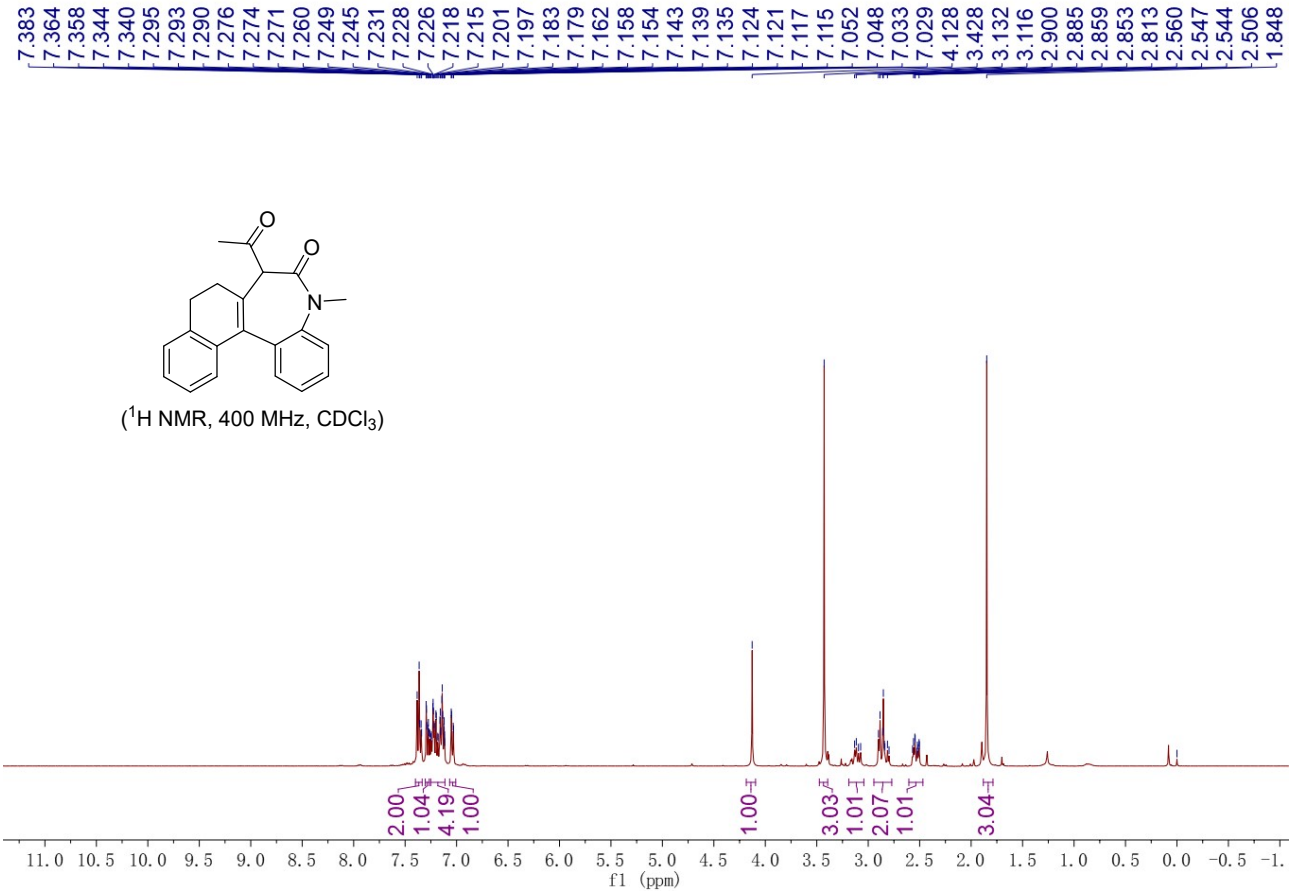


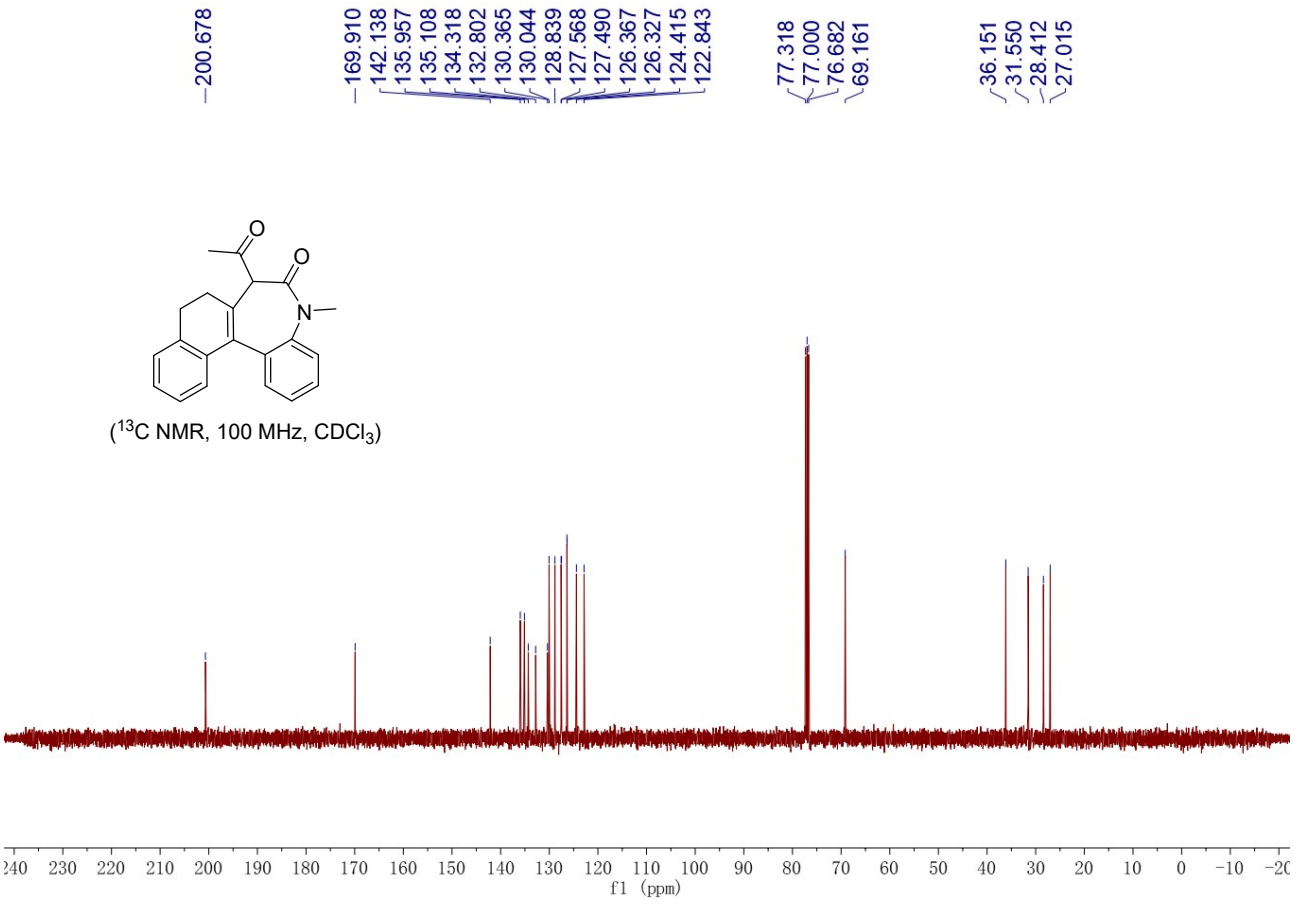
(^{13}C NMR, 100 MHz, $CDCl_3$)

8.Characterization Data of Products.

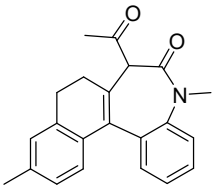


7-acetyl-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2a**): Yield: 34 mg, 53%, white solid, m.p. 193-195 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.11 (m, 4H), 7.07 – 7.01 (m, 1H), 4.13 (s, 1H), 3.43 (s, 3H), 3.19 – 3.04 (m, 1H), 2.94 – 2.77 (m, 2H), 2.61 – 2.47 (m, 1H), 1.85 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.7, 169.9, 142.1, 136.0, 135.1, 134.3, 132.8, 130.4, 130.0, 128.8, 127.6, 127.5, 126.4, 126.3, 124.4, 122.8, 69.2, 36.2, 31.6, 28.4, 27.0; IR (neat): ν 2953, 2919, 2859, 1718, 1645, 1591, 1354, 1179, 741, 667 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}NO_2Na$ [M+Na]$^{+}$: 340.13080, found: 340.13007.

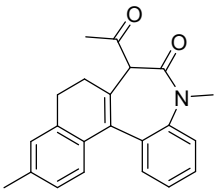




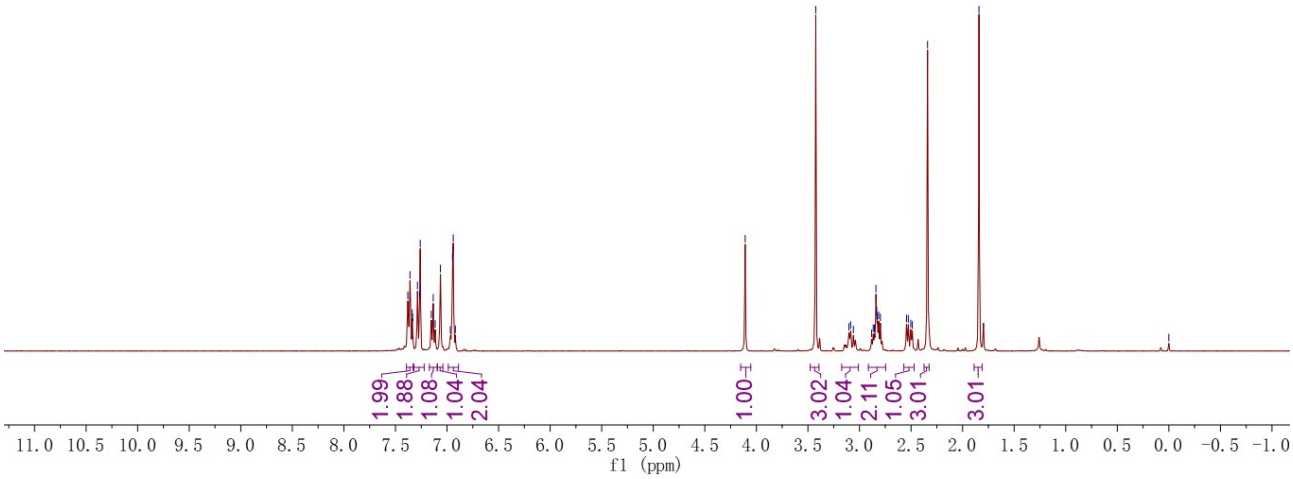
(^{13}C NMR, 100 MHz, $CDCl_3$)

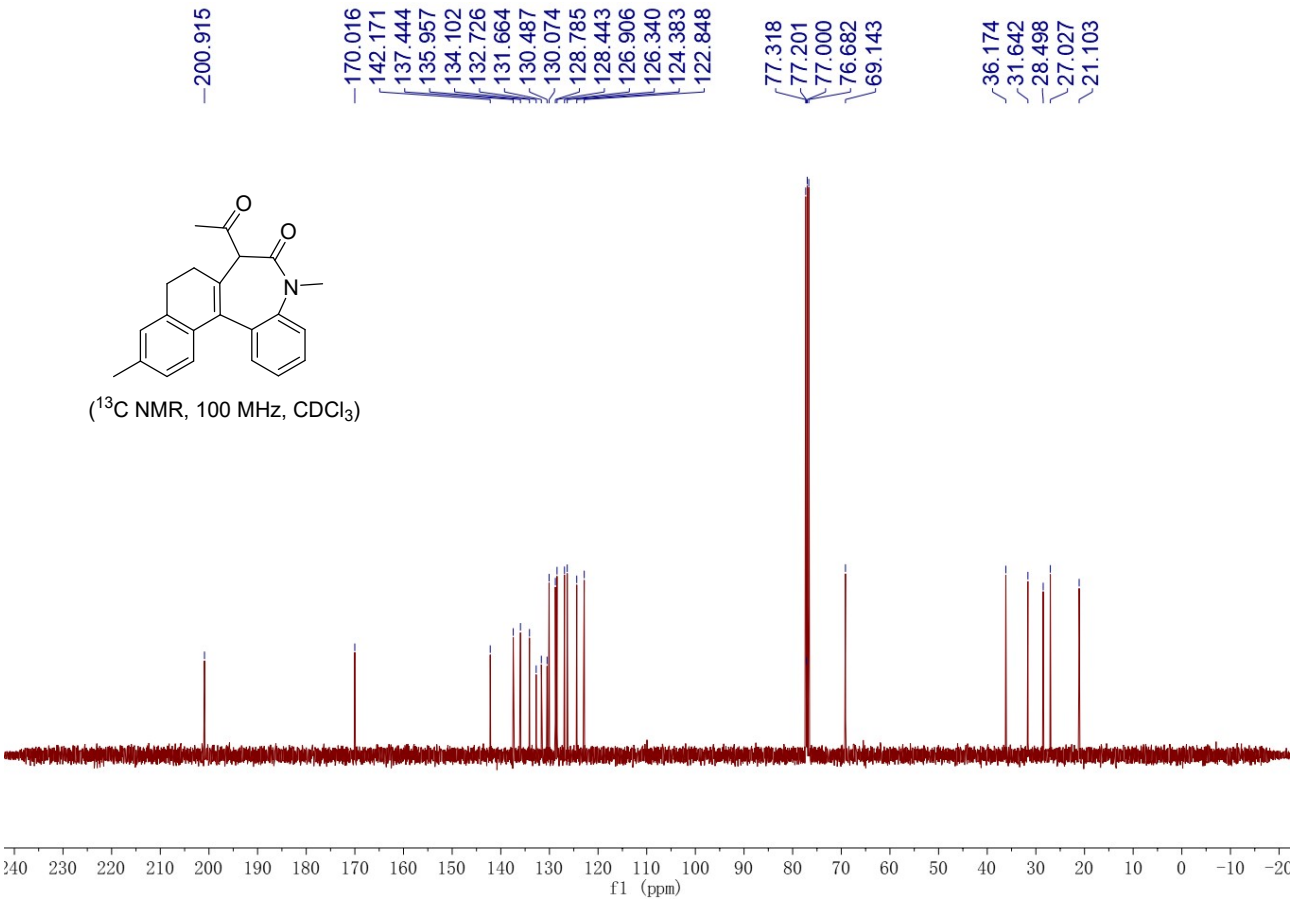


7-acetyl-5,11-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2b**): Yield: 30 mg, 45%, white solid, m.p. 156-158 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.22 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.99 – 6.89 (m, 2H), 4.11 (s, 1H), 3.42 (s, 3H), 3.17 – 3.01 (m, 1H), 2.91 – 2.75 (m, 2H), 2.57 – 2.47 (m, 1H), 2.34 (s, 3H), 1.84 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.9, 170.0, 142.2, 137.4, 136.0, 134.1, 132.7, 131.7, 130.5, 130.1, 128.8, 128.4, 126.9, 126.3, 124.4, 122.8, 69.1, 36.2, 31.6, 28.5, 27.0, 21.1; IR (neat): ν 3060, 2922, 2820, 1701, 1354, 1229, 1174, 1043, 819, 774 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_2Na$ $[M+Na]^+$: 332.16451, found: 332.16484.

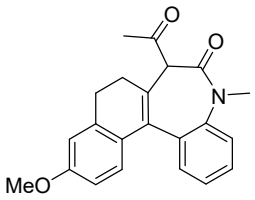


(^{1}H NMR, 400 MHz, $CDCl_3$)

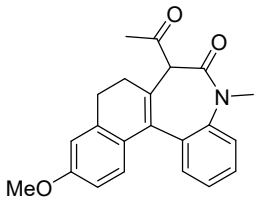




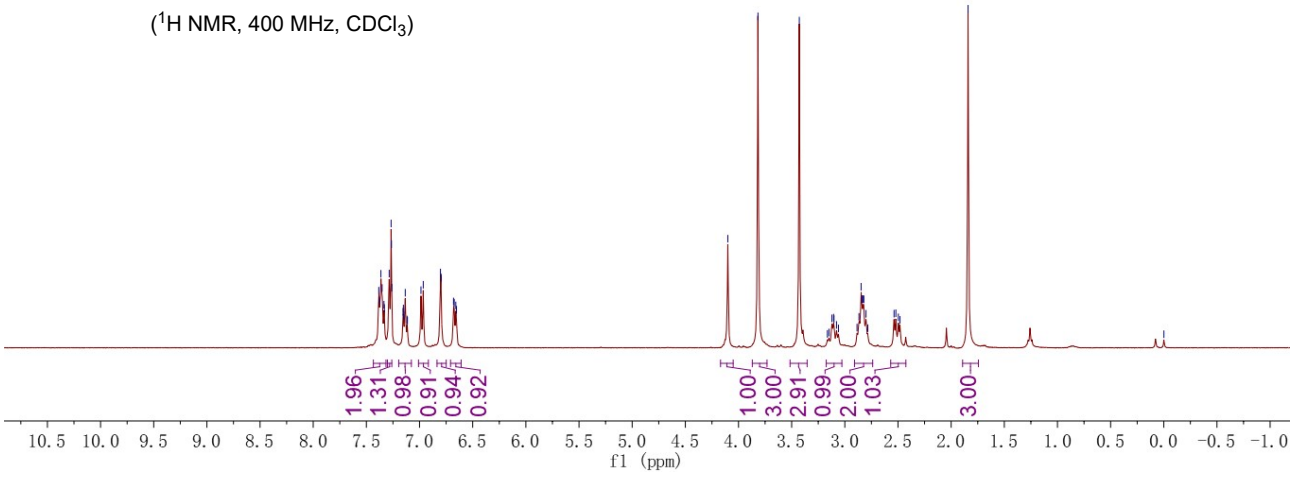
(^{13}C NMR, 100 MHz, $CDCl_3$)

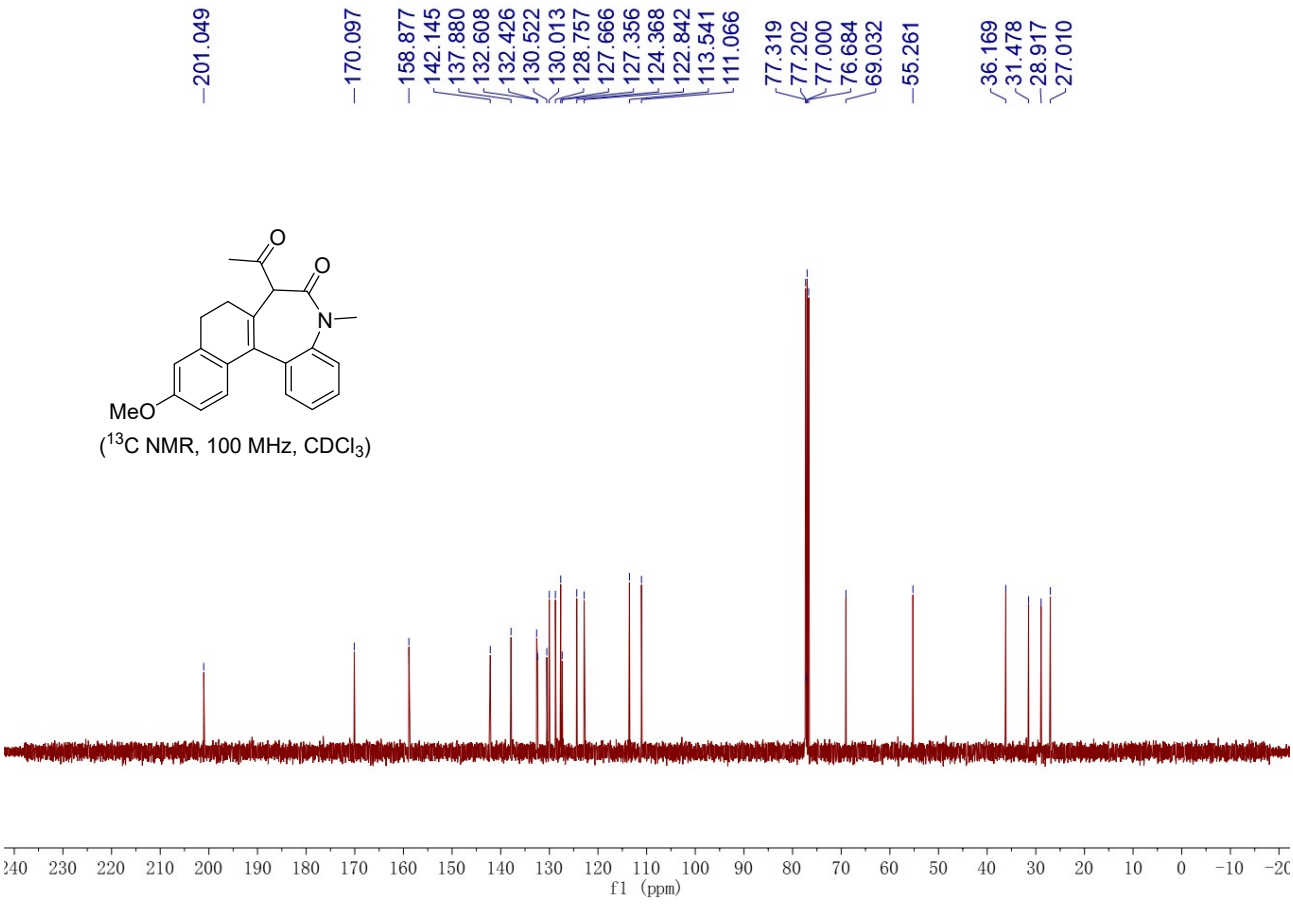


7-acetyl-11-methoxy-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2c**): Yield: 30 mg, 43%, white solid, m.p. >200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.20 – 7.08 (m, 1H), 6.98 (d, J = 8.6 Hz, 1H), 6.80 (d, J = 2.5 Hz, 1H), 6.67 (dd, J_1 = 8.6, J_2 = 2.7 Hz, 1H), 4.10 (s, 1H), 3.82 (s, 3H), 3.43 (s, 3H), 3.17 – 3.03 (m, 1H), 2.91 – 2.74 (m, 2H), 2.57 – 2.43 (m, 1H), 1.84 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.0, 170.1, 158.9, 142.1, 137.9, 132.6, 132.4, 130.5, 130.0, 128.8, 127.7, 127.4, 124.4, 122.8, 113.5, 111.1, 69.0, 55.3, 36.2, 31.5, 28.9, 27.0; IR (neat): ν 2925, 2828, 1654, 1489, 1354, 1249, 1035, 767 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_3Na$ [M+Na]$^{+}$: 348.15942, found: 348.15923.

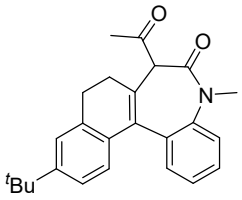


(^{1}H NMR, 400 MHz, $CDCl_3$)

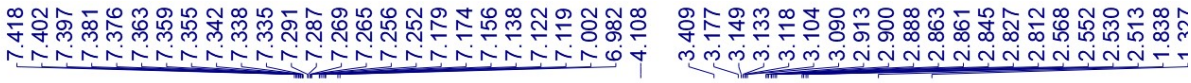




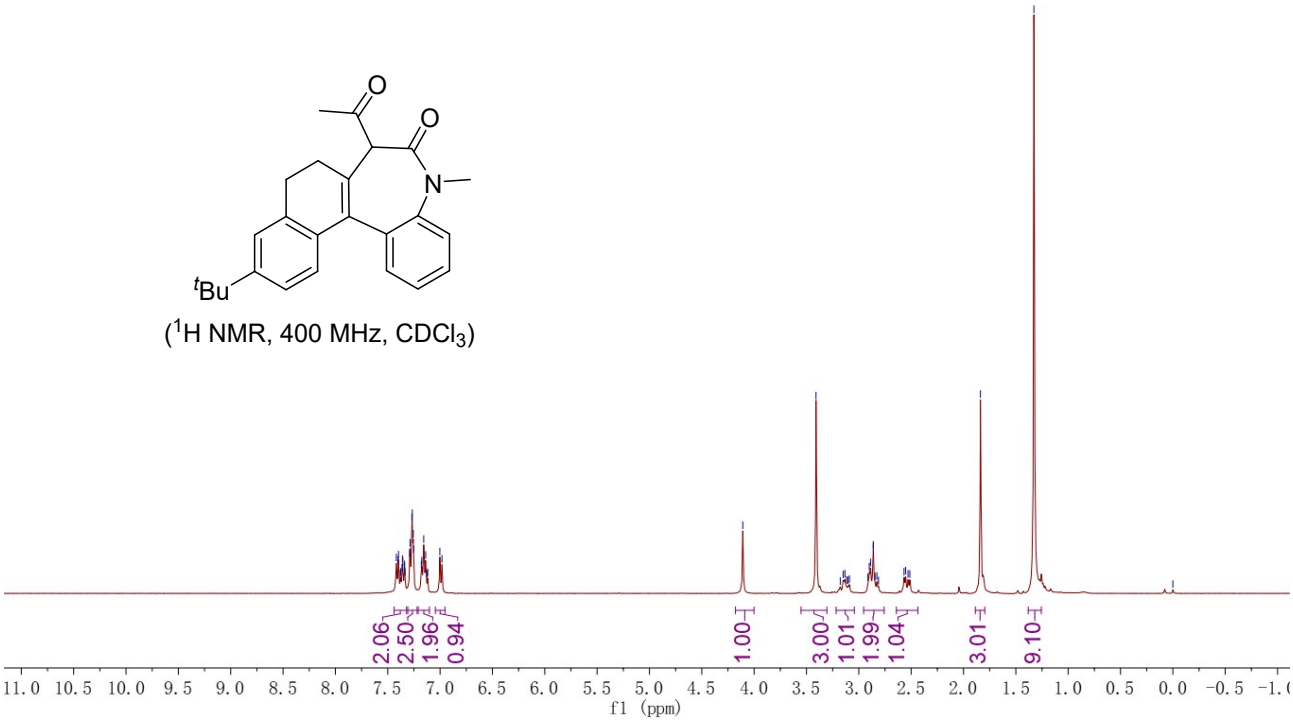
(^{13}C NMR, 100 MHz, $CDCl_3$)

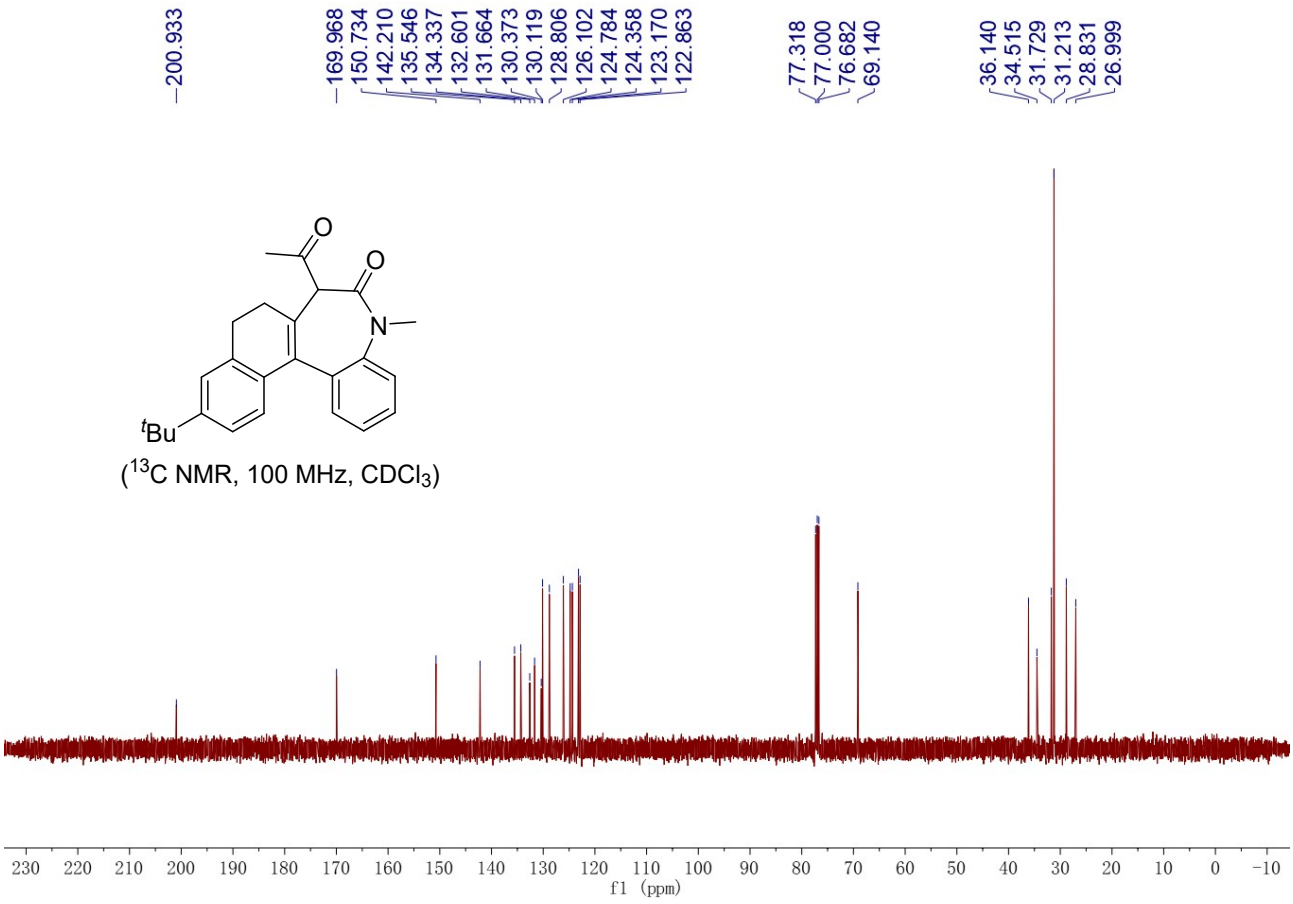


7-acetyl-11-(*tert*-butyl)-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2d**): Yield: 34 mg, 46%, white solid, m.p. > 200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 – 7.32 (m, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.10 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 4.11 (s, 1H), 3.41 (s, 3H), 3.22 – 3.04 (m, 1H), 2.95 – 2.76 (m, 2H), 2.64 – 2.44 (m, 1H), 1.84 (s, 3H), 1.33 (s, 9H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.9, 170.0, 150.7, 142.2, 135.5, 134.3, 132.6, 131.7, 130.4, 130.1, 128.8, 126.1, 124.8, 124.4, 123.2, 122.9, 69.1, 36.1, 34.5, 31.7, 31.2, 28.8, 27.0; IR (neat): ν 2948, 2904, 2859, 1715, 1597, 1357, 1252, 1173, 846, 767 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{25}H_{28}NO_2Na$ $[M+Na]^+$: 374.21146, found: 374.21120.



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

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77.000
76.682
69.140
36.140
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31.729
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28.831
26.999
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N
tBu
(13C NMR, 100 MHz, CDCl3)
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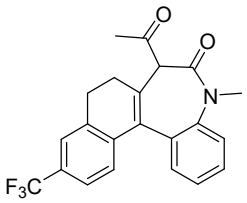
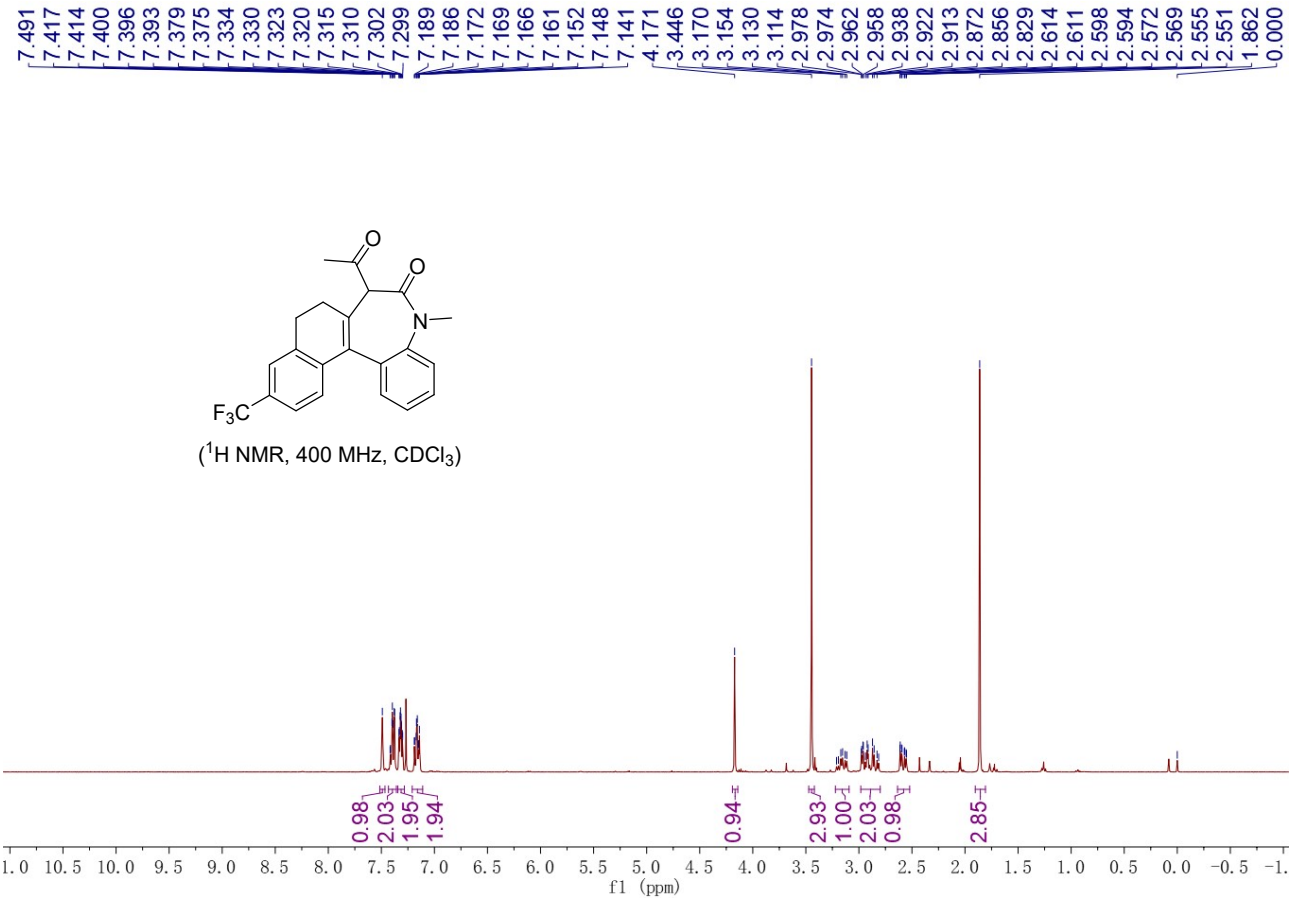
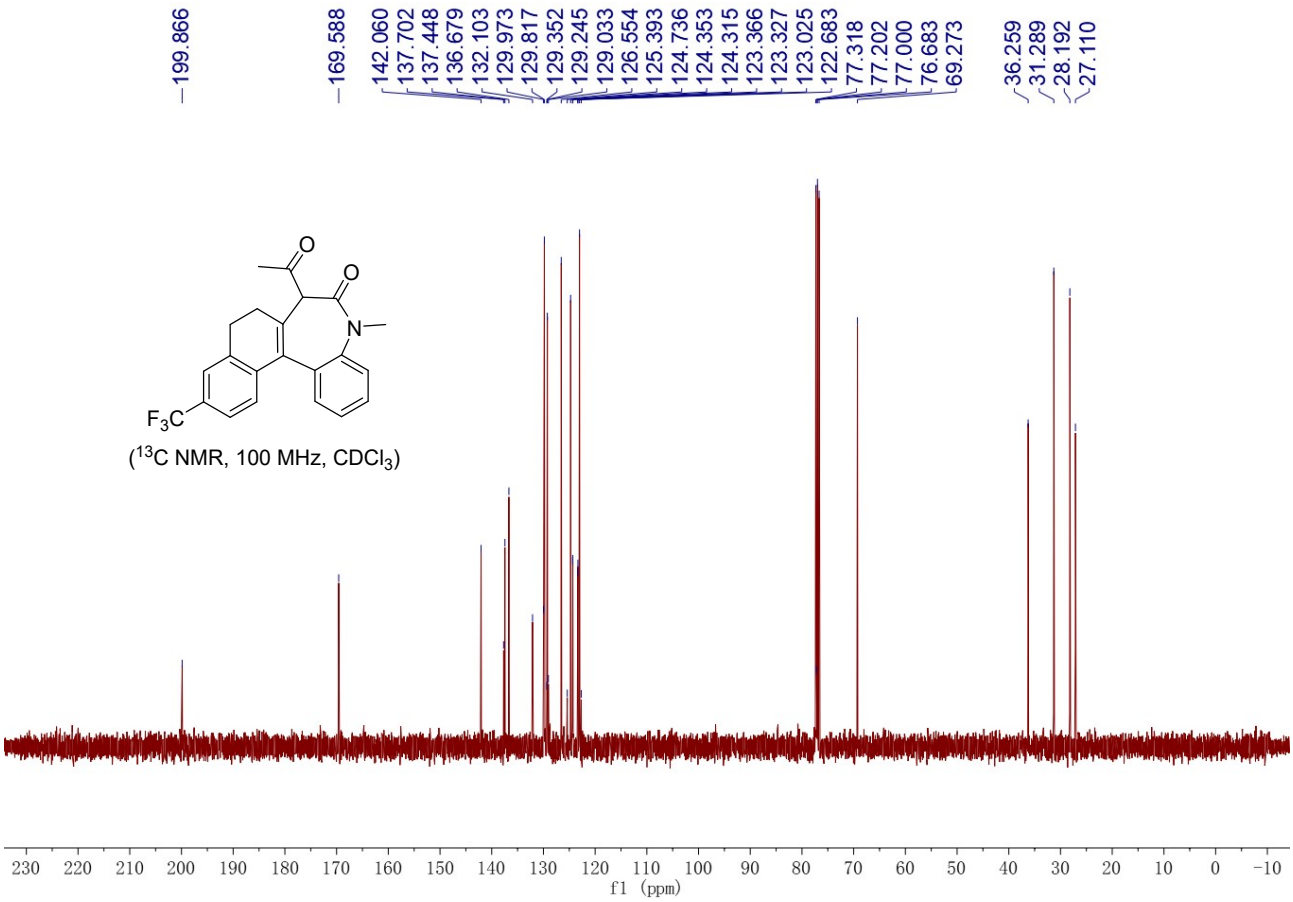
f1 (ppm)

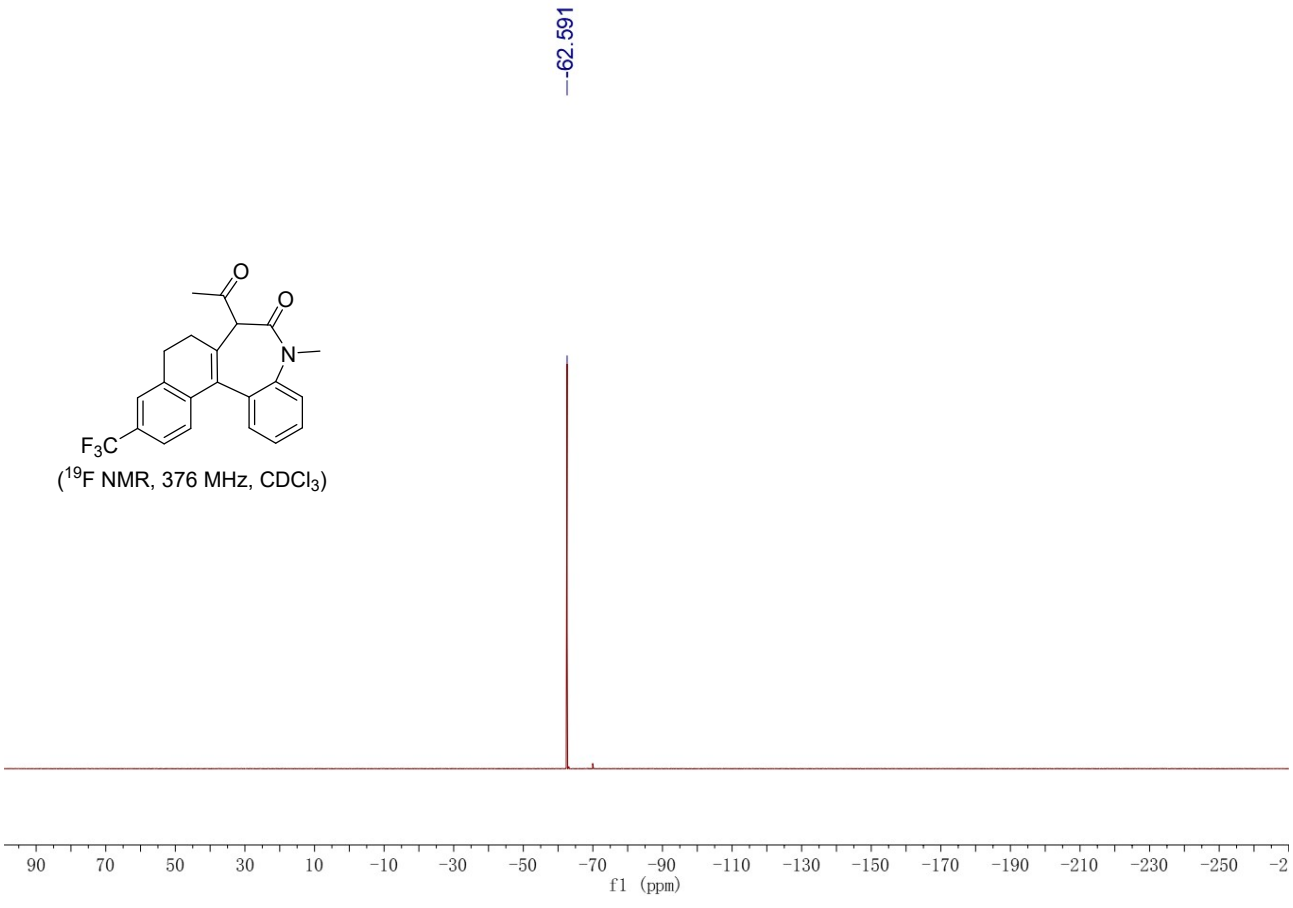


7-acetyl-5-methyl-11-(trifluoromethyl)-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2e**): Yield: 31 mg, 40%, white solid, m.p. 197-199 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51 – 7.47 (m, 1H), 7.43 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.21 – 7.11 (m, 2H), 4.17 (s, 1H), 3.45 (s, 3H), 3.22 – 3.09 (m, 1H), 2.98 – 2.80 (m, 2H), 2.64 – 2.52 (m, 1H), 1.86 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 199.9, 169.6, 142.1, 137.7, 137.4, 136.7, 132.1, 130.0, 129.8, 129.2 (q, J = 32.0 Hz), 127.8 (q, J = 270.0 Hz), 125.4, 124.7, 124.4 (q, J = 3.6 Hz), 123.3 (q, J = 3.6 Hz), 122.7, 69.3, 36.3, 31.3, 28.2, 27.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; IR (neat): ν 2948, 2923, 1895, 1715, 1663, 1335, 1320, 1109, 901, 835, 769, 714 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{19}F_3NO_2$ $[M+H]^+$: 386.13624, found: 386.13669.

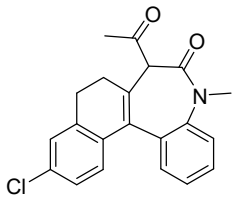




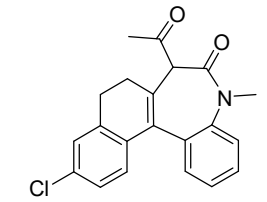
(^{13}C NMR, 100 MHz, $CDCl_3$)



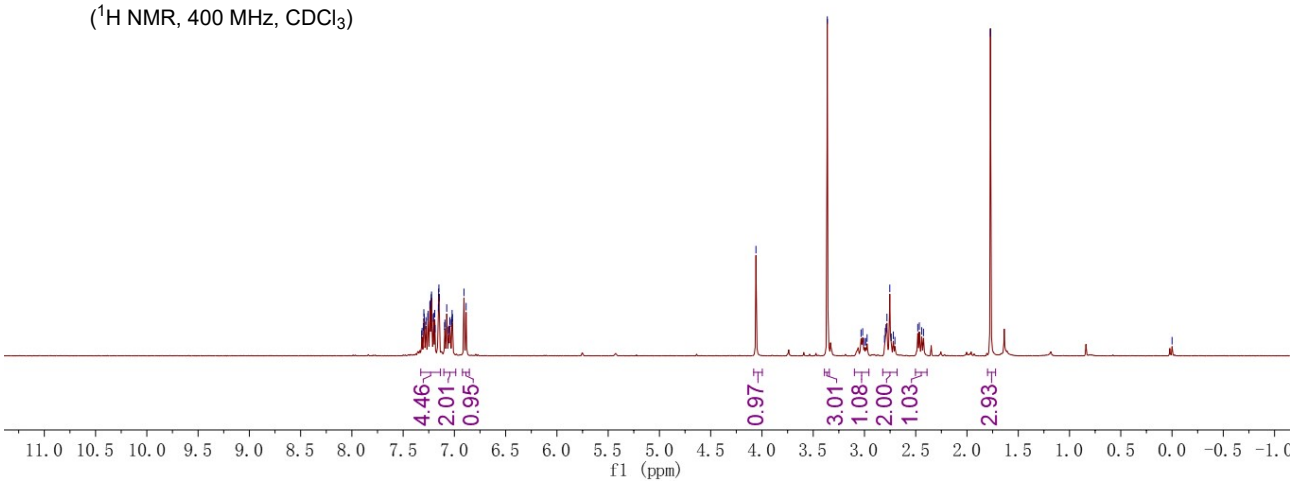
(^{19}F NMR, 376 MHz, $CDCl_3$)

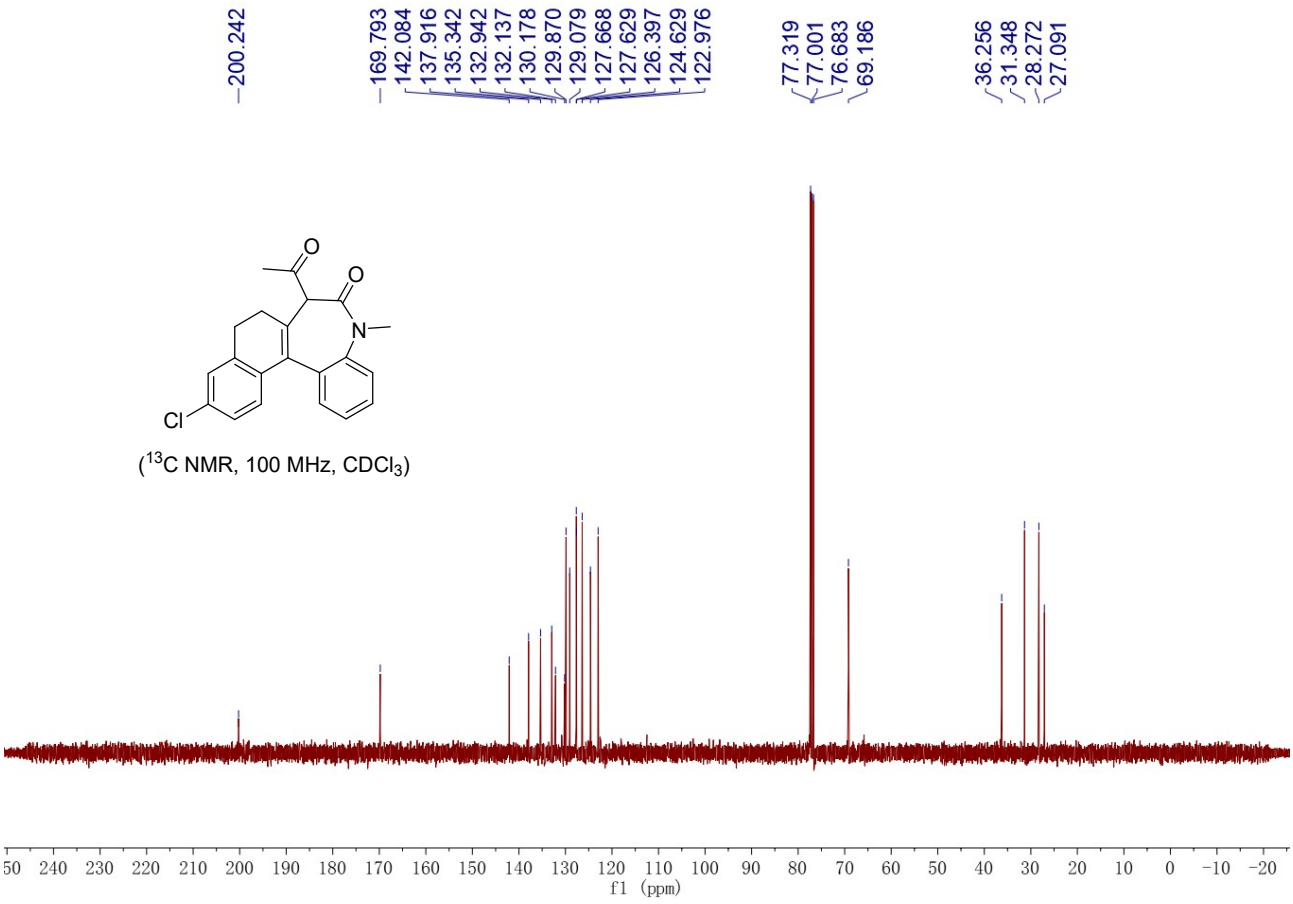


7-acetyl-11-chloro-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2f**): Yield: 34 mg, 48%, white solid, m.p. > 200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33 – 7.14 (m, 4H), 7.10 – 6.99 (m, 2H), 6.92 – 6.85 (m, 1H), 4.06 (s, 1H), 3.36 (s, 3H), 3.10 – 2.96 (m, 1H), 2.82 – 2.68 (m, 2H), 2.50 – 2.39 (m, 1H), 1.77 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.2, 169.8, 142.1, 137.9, 135.3, 132.9, 132.1, 130.2, 129.9, 129.1, 127.7, 127.6, 126.4, 124.6, 123.0, 69.2, 36.3, 31.3, 28.3, 27.1; IR (neat): ν 2925, 2899, 2844, 1716, 1444, 1360, 1242, 1177, 818, 761, 720 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{18}NO_2ClNa$ $[M+Na]^+$: 374.09183, found: 374.09114.



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




200.242
169.793
142.084
137.916
135.342
132.942
132.137
130.178
129.870
129.079
127.668
127.629
126.397
124.629
122.976
77.319
77.001
76.683
69.186
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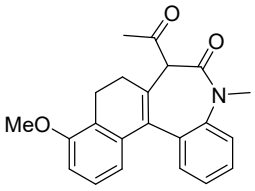
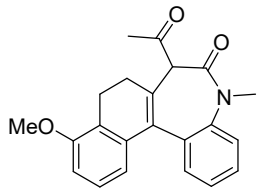
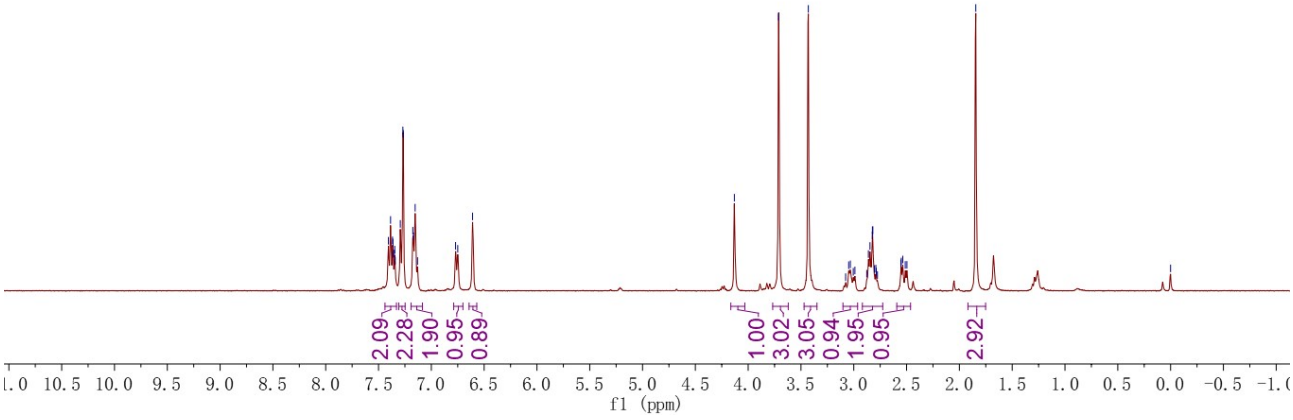
31.348
28.272
27.091
O
O
N
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

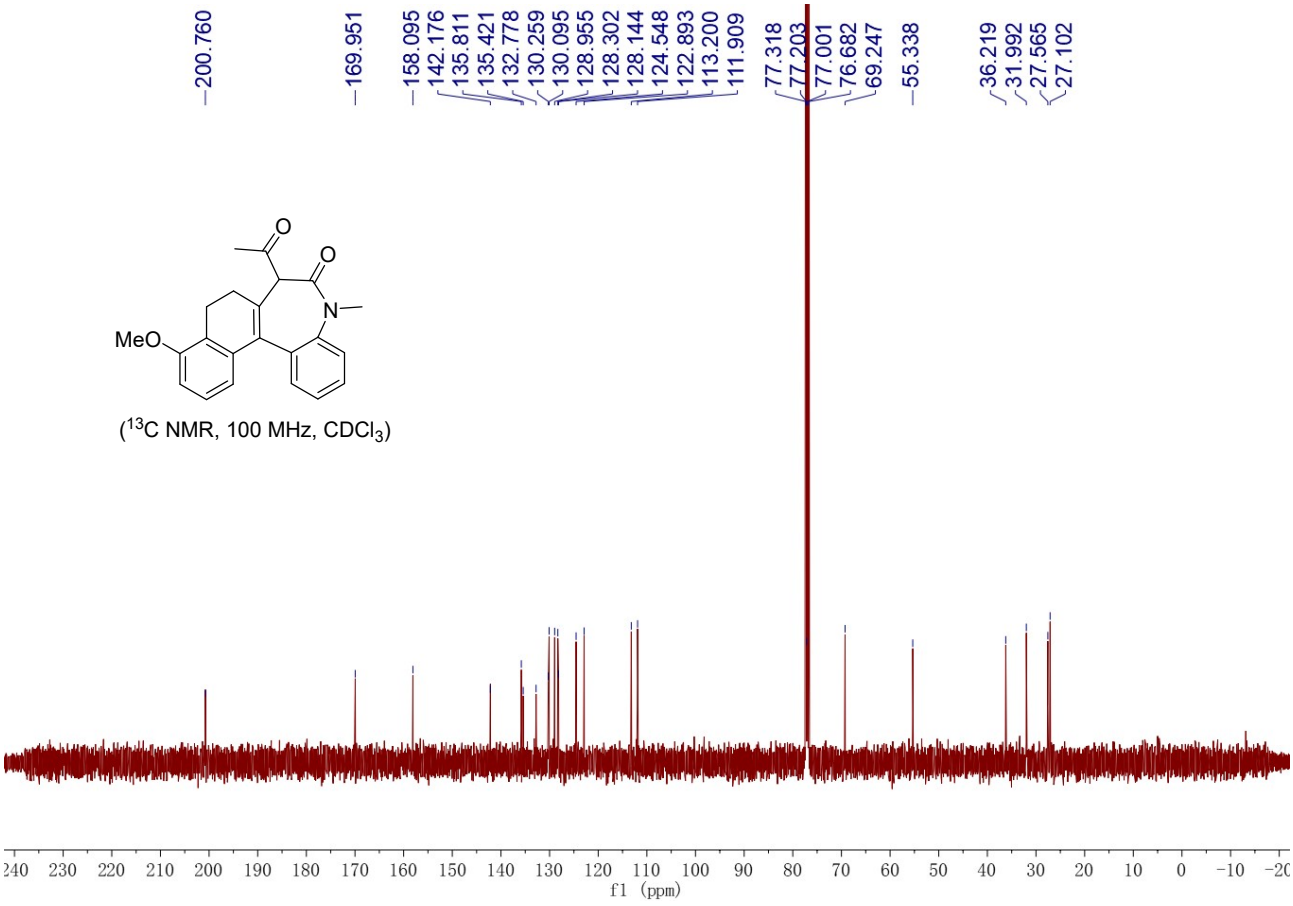


7-acetyl-10-methoxy-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2g**): Yield: 36 mg, 51%, white solid, m.p. 191-193 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 – 7.33 (m, 2H), 7.31 – 7.25 (m, 2H), 7.19 – 7.08 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.64 – 6.57 (m, 1H), 4.13 (s, 1H), 3.71 (s, 3H), 3.43 (s, 3H), 3.10 – 2.96 (m, 1H), 2.92 – 2.73 (m, 2H), 2.59 – 2.46 (m, 1H), 1.84 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.8, 170.0, 158.1, 142.2, 135.8, 135.4, 132.8, 130.3, 130.1, 129.0, 128.3, 128.1, 124.5, 122.9, 113.2, 111.9, 69.2, 55.3, 36.2, 32.0, 27.6, 27.1; IR (neat): ν 2958, 2919, 2833, 1711, 1645, 1599, 1469, 1356, 1266, 1182, 1087, 770, 732 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.15942, found: 348.15921.

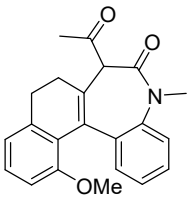


(^{1}H NMR, 400 MHz, $CDCl_3$)

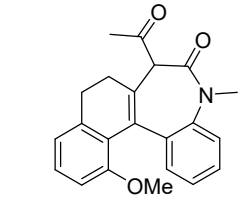




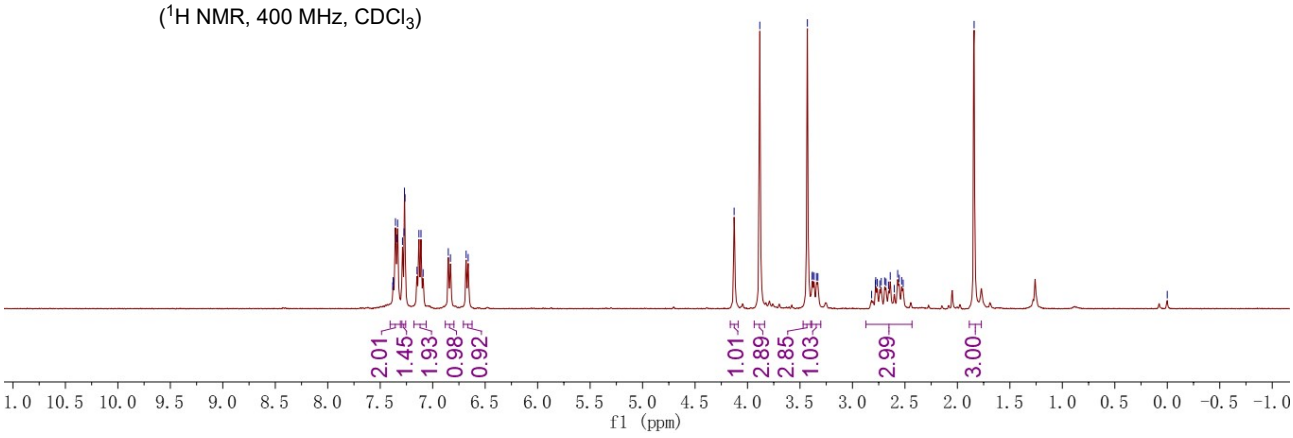
(^{13}C NMR, 100 MHz, $CDCl_3$)

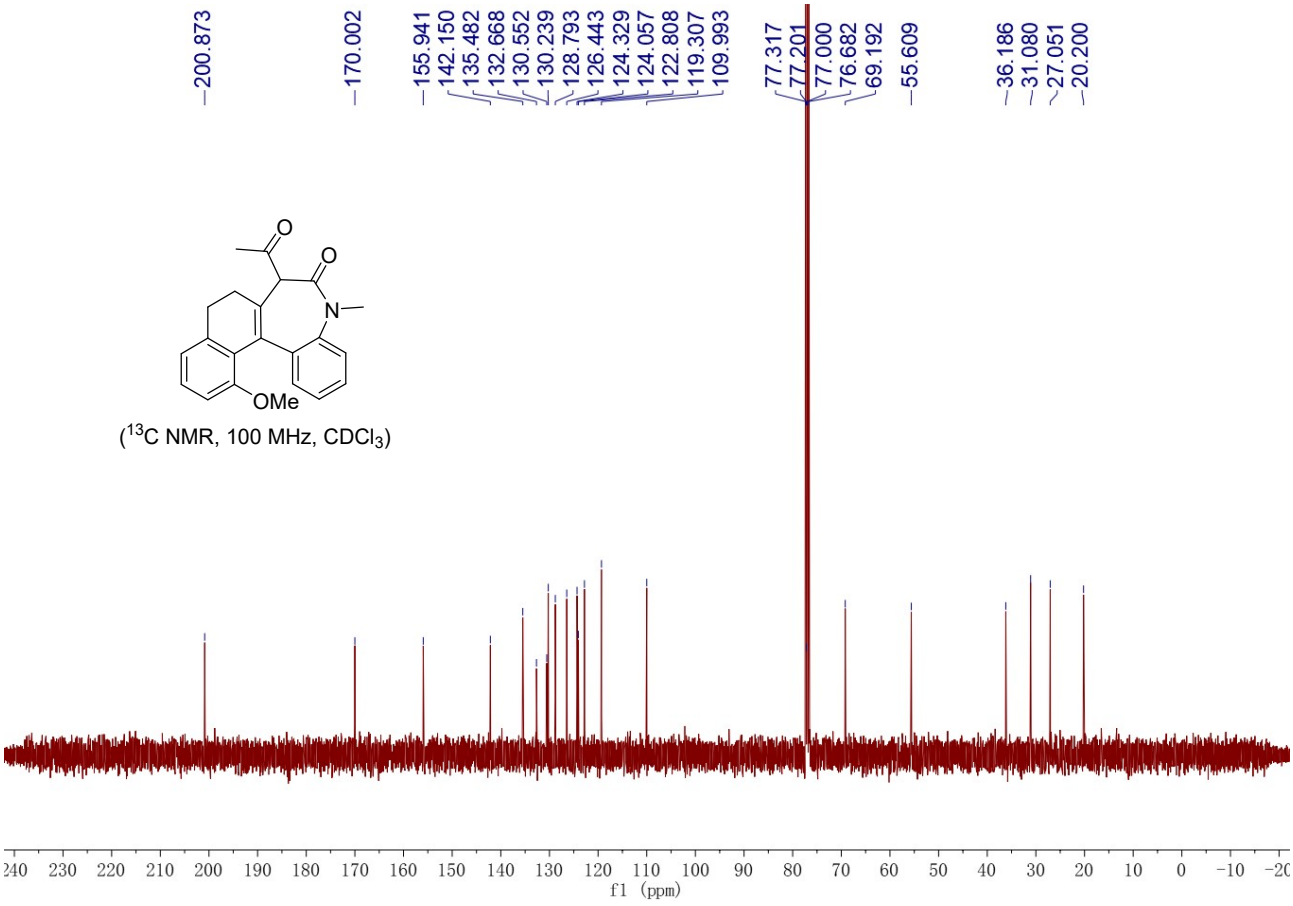


7-acetyl-13-methoxy-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2h**): Yield: 26 mg, 37%, white solid, m.p. 176-178 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.12 (q, *J* = 8.2, 7.7 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.13 (s, 1H), 3.88 (s, 3H), 3.43 (s, 3H), 3.39 – 3.30 (m, 1H), 2.87 – 2.43 (m, 3H), 1.84 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.9, 170.0, 155.9, 142.1, 135.5, 132.7, 130.6, 130.2, 128.8, 126.4, 124.3, 124.1, 122.8, 119.3, 110.0, 69.2, 55.6, 36.2, 31.1, 27.1, 20.2; IR (neat): ν 2997, 2914, 2828, 1709, 1598, 1490, 1446, 1353, 1223, 1210, 1034, 807, 773, 698 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{21}NO_3Na$ $[M+Na]^+$: 370.14136, found: 370.14072.

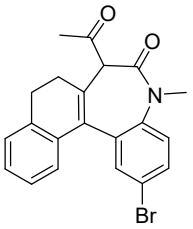


(^{1}H NMR, 400 MHz, $CDCl_3$)

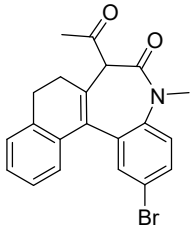




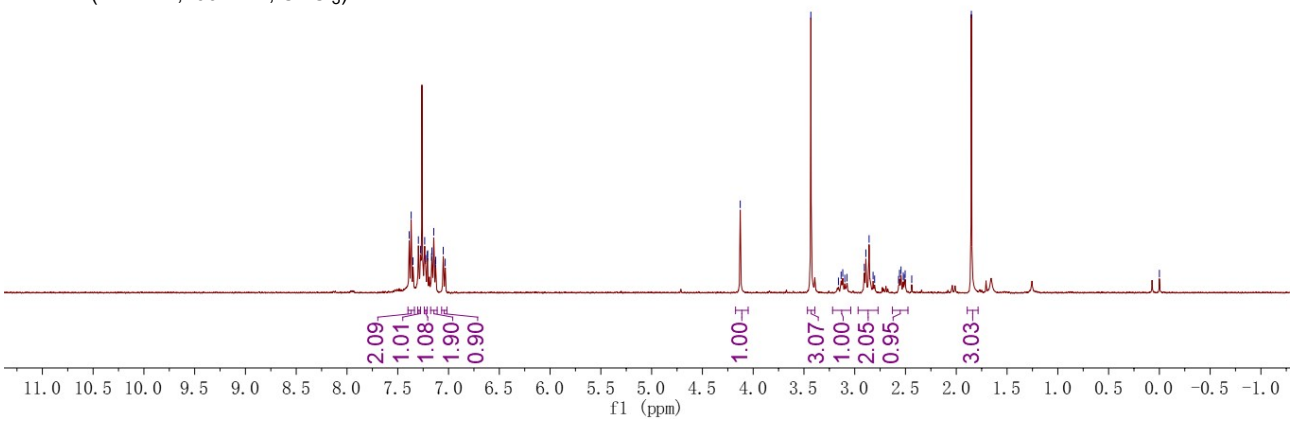
(^{13}C NMR, 100 MHz, $CDCl_3$)

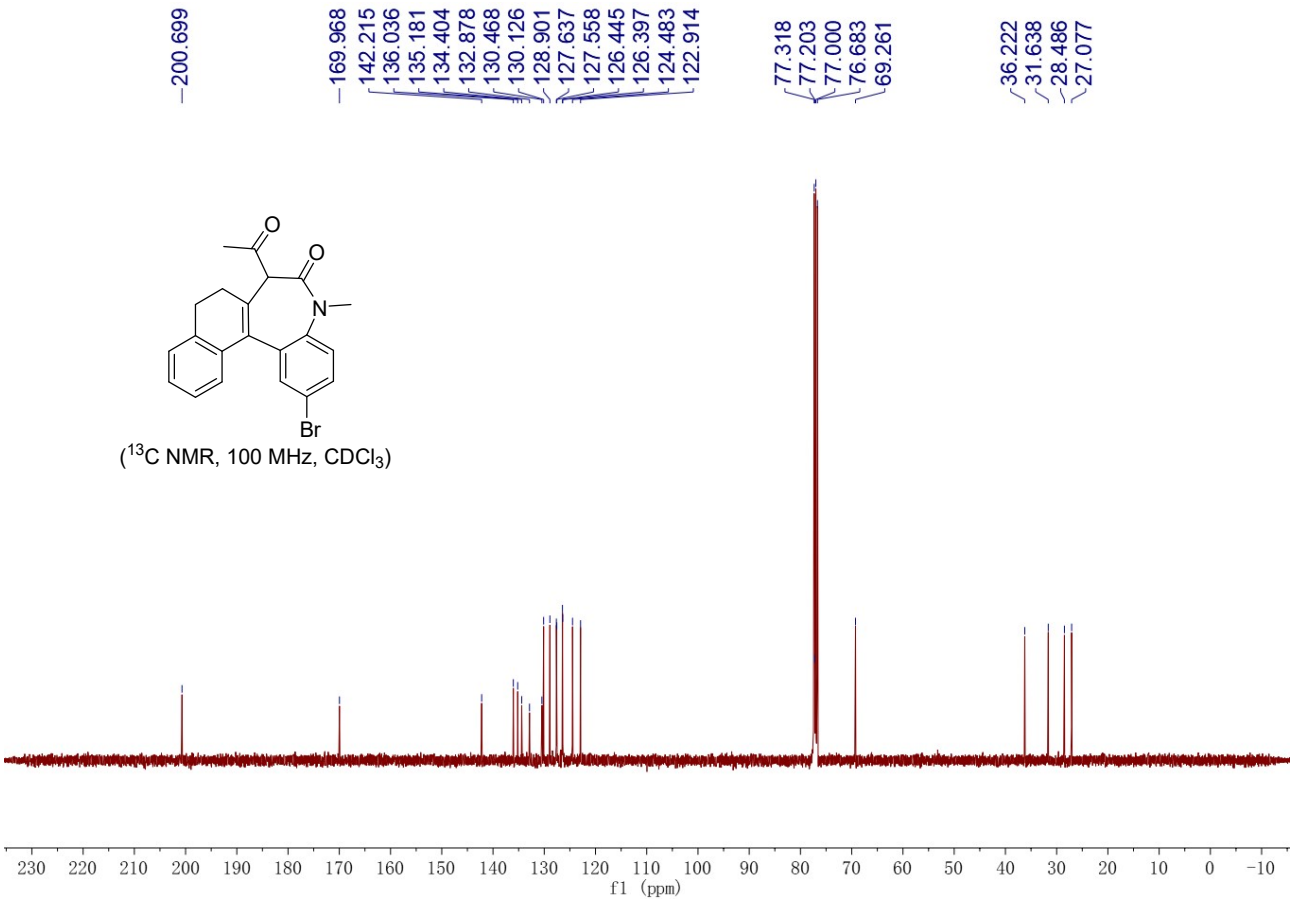


7-acetyl-2-bromo-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2i**): Yield: 33 mg, 42%, white solid, m.p. 195-197 ^{o}C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40 – 7.34 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.11 (m, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 4.13 (s, 1H), 3.43 (s, 3H), 3.22 – 3.04 (m, 1H), 2.97 – 2.77 (m, 2H), 2.63 – 2.48 (m, 1H), 1.85 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.7, 170.0, 142.2, 136.0, 135.2, 134.4, 132.9, 130.5, 130.1, 128.9, 127.6, 127.6, 126.4, 126.4, 124.5, 122.9, 69.3, 36.2, 31.6, 28.5, 27.1; IR (neat): ν 2959, 2914, 1849, 1714, 1492, 1357, 1171, 765, 741 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}BrNO_2$ $[M+H]^+$: 396.05992, found: 396.05978.

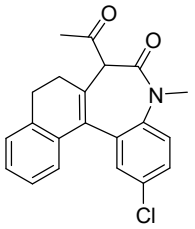


(^{1}H NMR,400 MHz, $CDCl_3$)

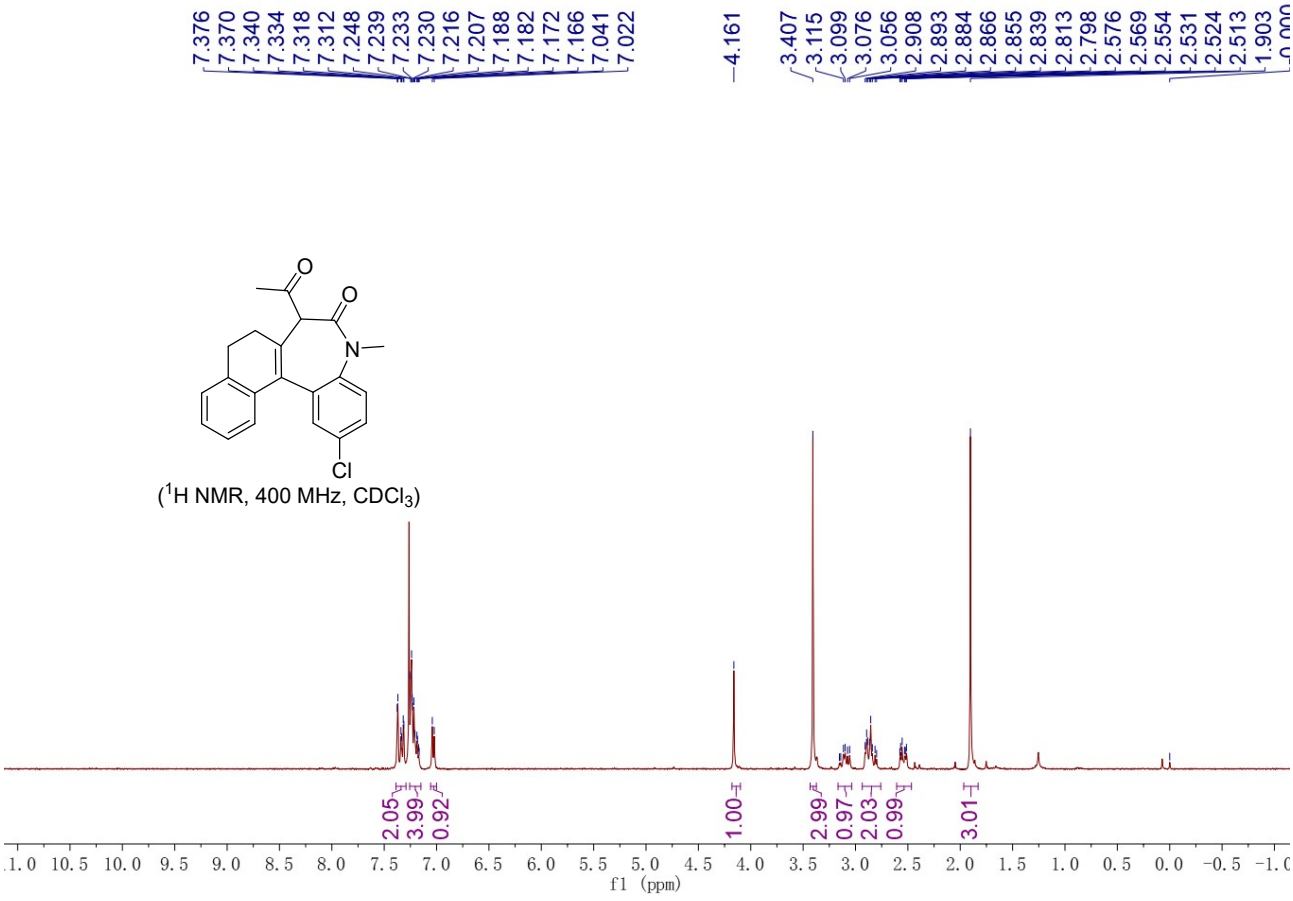


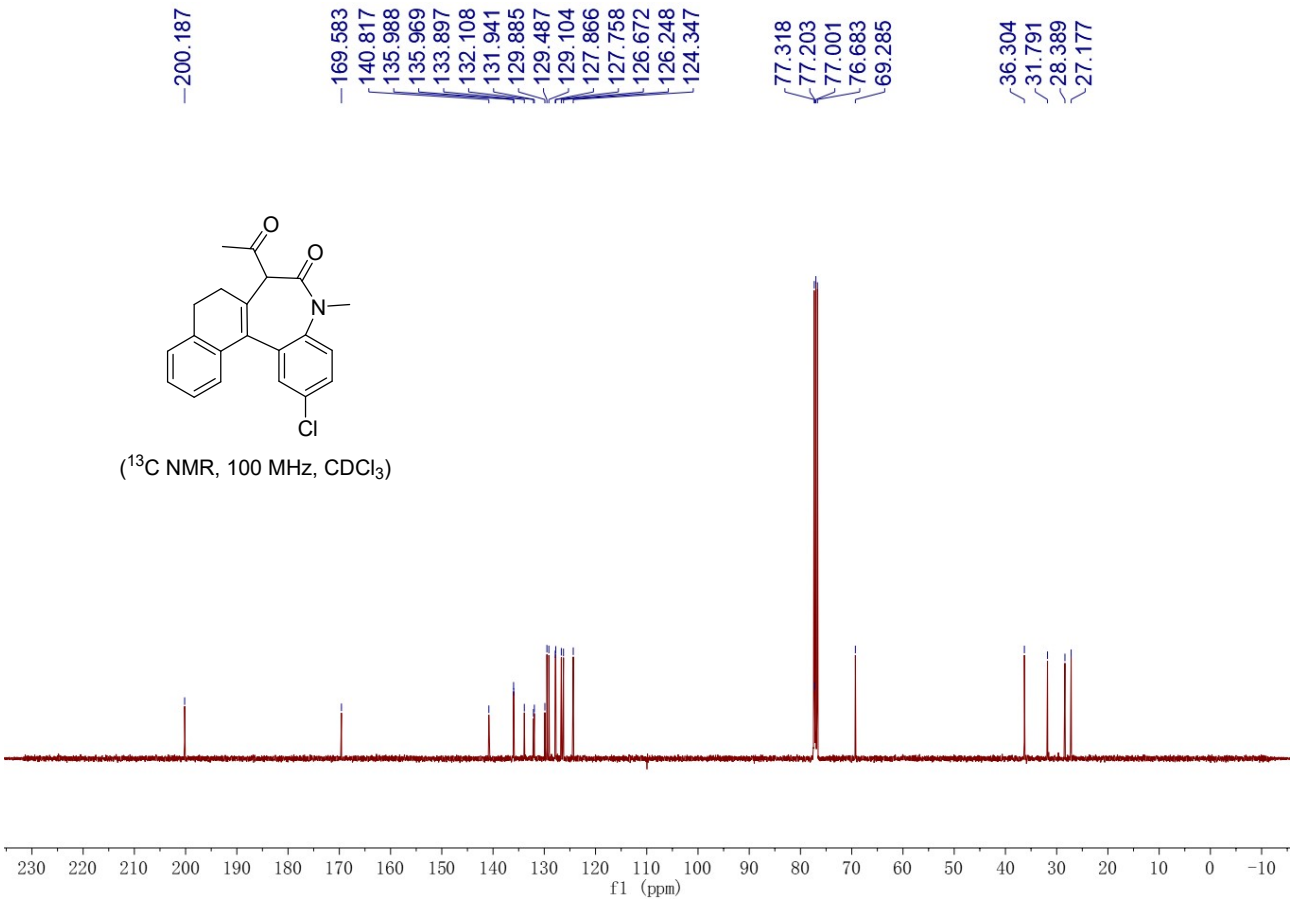


(^{13}C NMR, 100 MHz, $CDCl_3$)

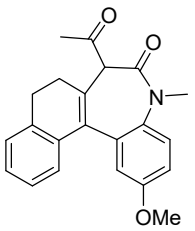


7-acetyl-2-chloro-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2j**): Yield: 29 mg, 42%, white solid, m.p. > 200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39 – 7.29 (m, 2H), 7.26 – 7.15 (m, 4H), 7.03 (d, *J* = 7.5 Hz, 1H), 4.16 (s, 1H), 3.41 (s, 3H), 3.17 – 3.04 (m, 1H), 2.94 – 2.76 (m, 2H), 2.61 – 2.47 (m, 1H), 1.90 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.2, 169.6, 140.8, 136.0, 136.0, 133.9, 132.1, 131.9, 129.9, 129.5, 129.1, 127.9, 127.8, 126.7, 126.2, 124.3, 69.3, 36.3, 31.8, 28.4, 27.2; IR (neat): ν 2940, 2922, 2883, 1714, 1482, 1401, 1235, 1143, 823, 775 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}NO_2Cl$ $[M+H]^+$: 352.10988, found: 352.11002.

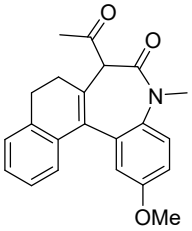




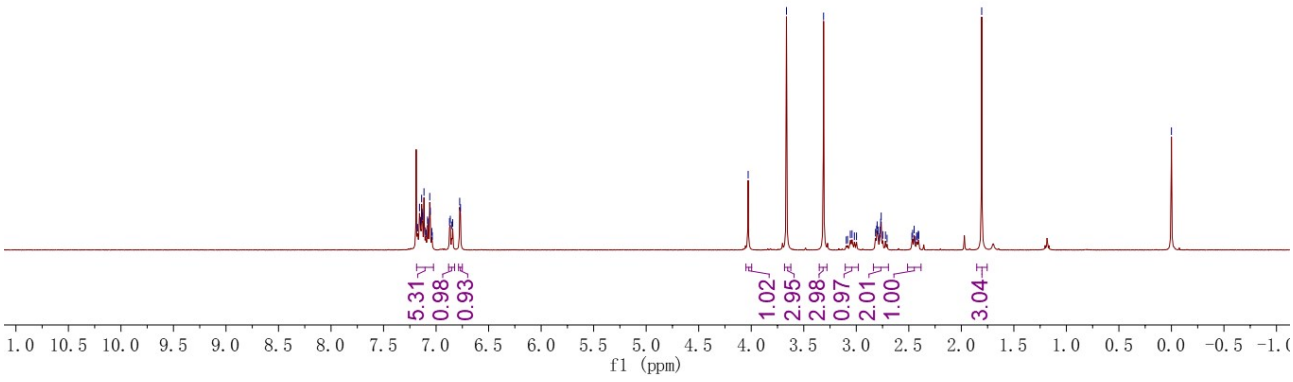
(^{13}C NMR, 100 MHz, $CDCl_3$)

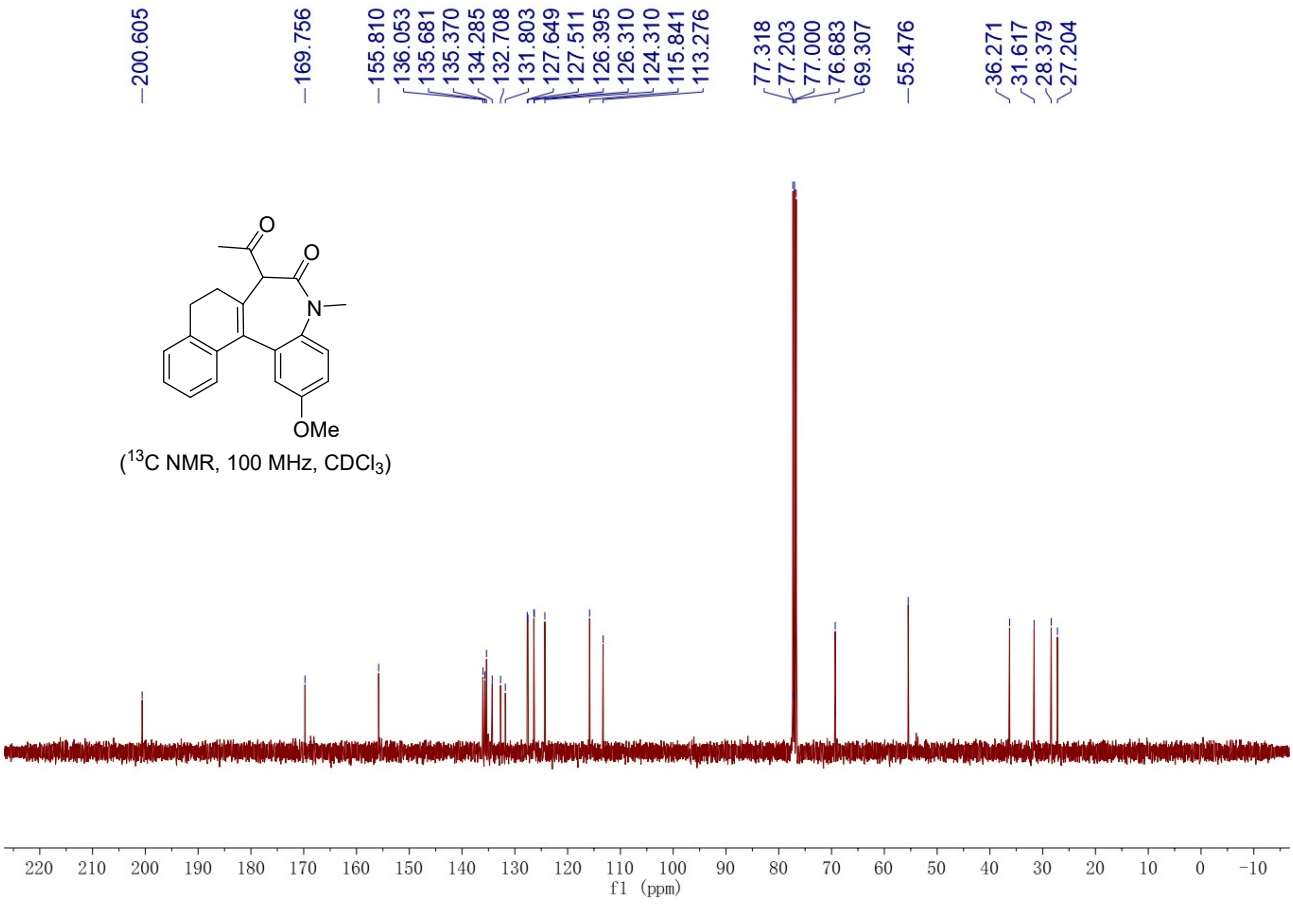


7-acetyl-2-methoxy-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2k**): Yield: 33 mg, 47%, white solid, m.p. 185-187 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.19 – 7.02 (m, 5H), 6.86 (dd, J_1 = 9.0, J_2 = 3.0 Hz, 1H), 6.77 (d, J = 3.0 Hz, 1H), 4.03 (s, 1H), 3.66 (s, 3H), 3.31 (s, 3H), 3.11 – 2.98 (m, 1H), 2.84 – 2.69 (m, 2H), 2.51 – 2.38 (m, 1H), 1.81 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.6, 169.8, 155.8, 136.1, 135.7, 135.4, 134.3, 132.7, 131.8, 127.6, 127.5, 126.4, 126.3, 124.3, 115.8, 113.3, 69.3, 55.5, 36.3, 31.6, 28.4, 27.2; IR (neat): ν 3013, 2925, 2825, 1710, 1498, 1356, 1222, 1170, 1030, 834, 768 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.15942, found: 348.15921.

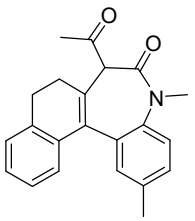


(^{1}H NMR, 400 MHz, $CDCl_3$)

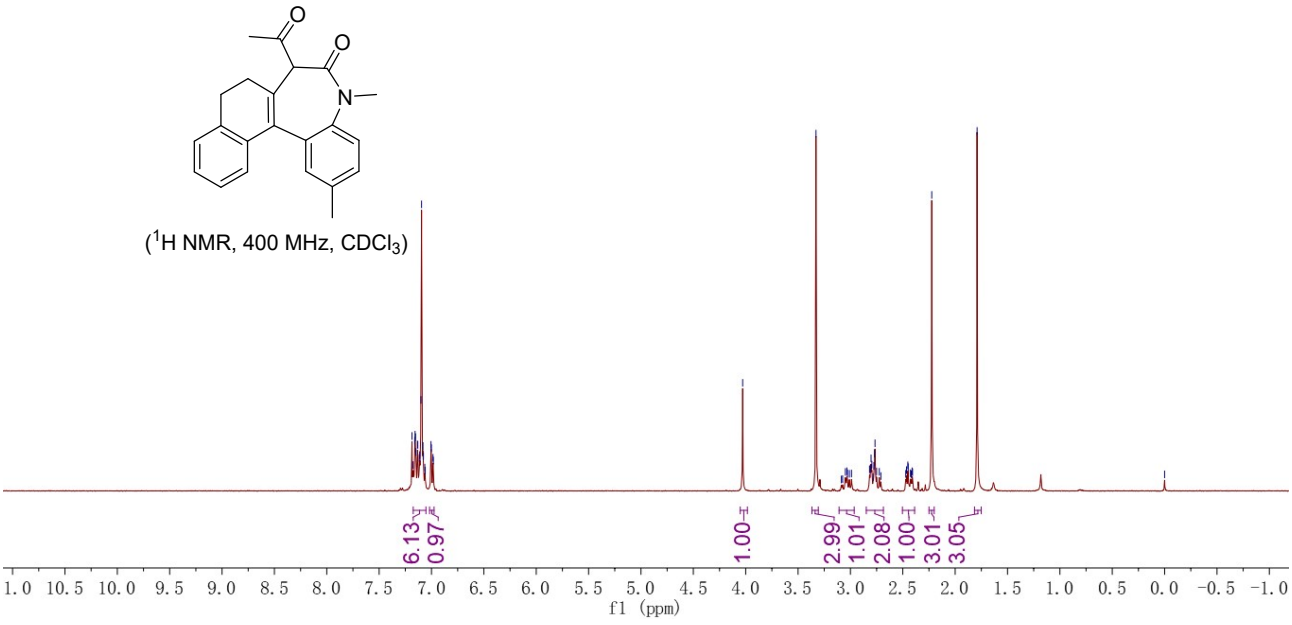


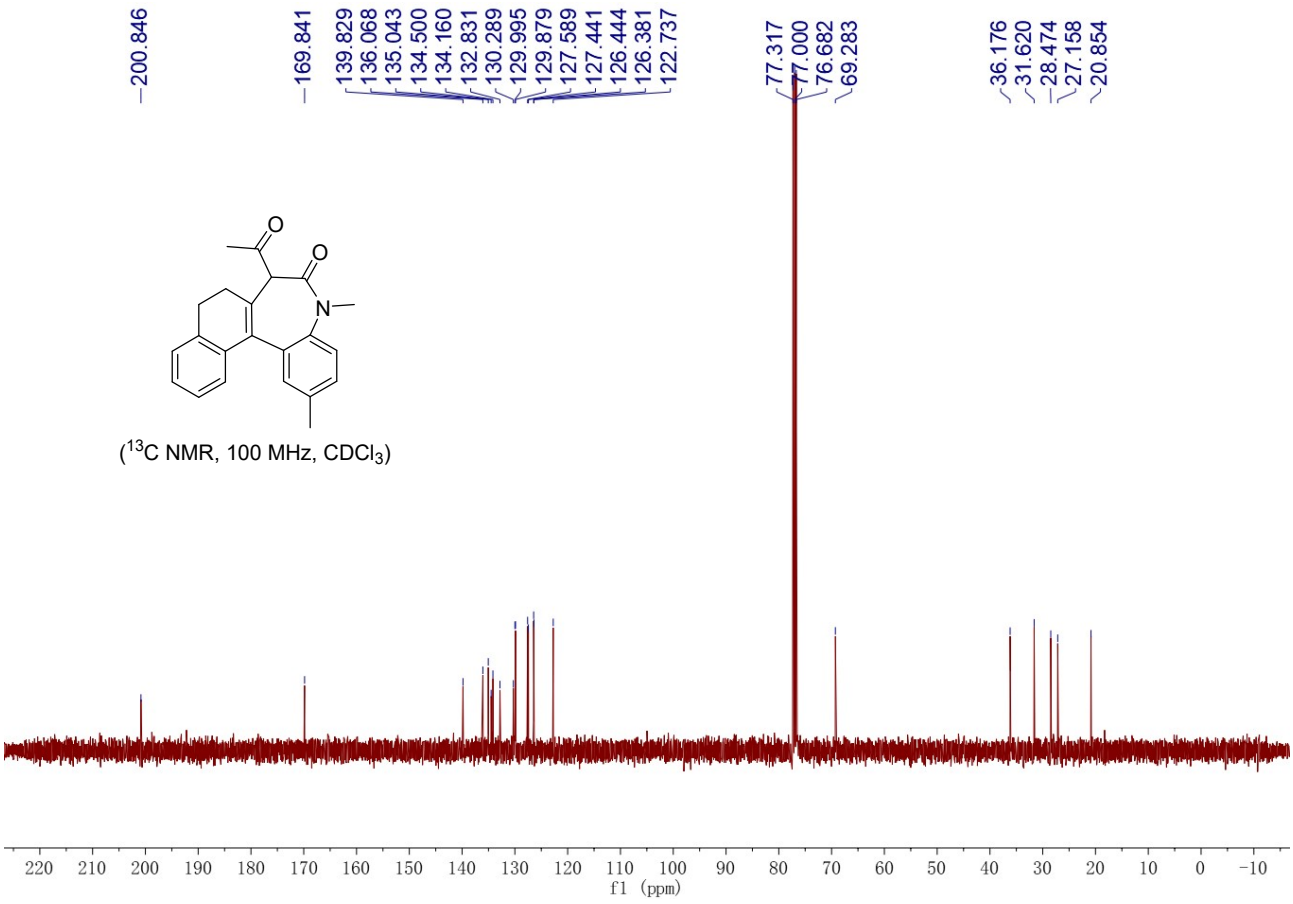


(^{13}C NMR, 100 MHz, $CDCl_3$)

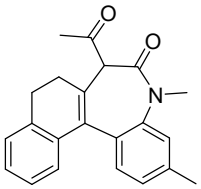


7-acetyl-2,5-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2l**): Yield: 26 mg, 40%, white solid, m.p. > 200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.17 – 7.05 (m, 6H), 6.99 (dd, J_1 = 7.6, J_2 = 1.4 Hz, 1H), 4.03 (s, 1H), 3.33 (s, 3H), 3.11 – 2.96 (m, 1H), 2.85 – 2.69 (m, 2H), 2.50 – 2.39 (m, 1H), 2.22 (s, 3H), 1.79 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, CDCl3, TMS) δ 200.8, 169.8, 139.8, 136.1, 135.0, 134.5, 134.2, 132.8, 130.3, 130.0, 129.9, 127.6, 127.4, 126.4, 126.4, 122.7, 69.3, 36.2, 31.6, 28.5, 27.2, 20.9; IR (neat): ν 2959, 2919, 2849, 1711, 1490, 1347, 1235, 1127, 824, 741 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{21}NO_2Na$ $[M+Na]^+$: 354.14645, found: 354.14705.

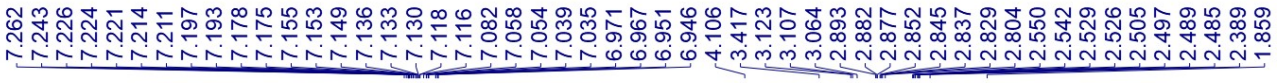


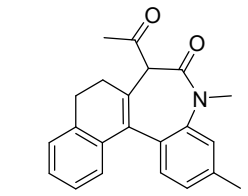


(^{13}C NMR, 100 MHz, $CDCl_3$)

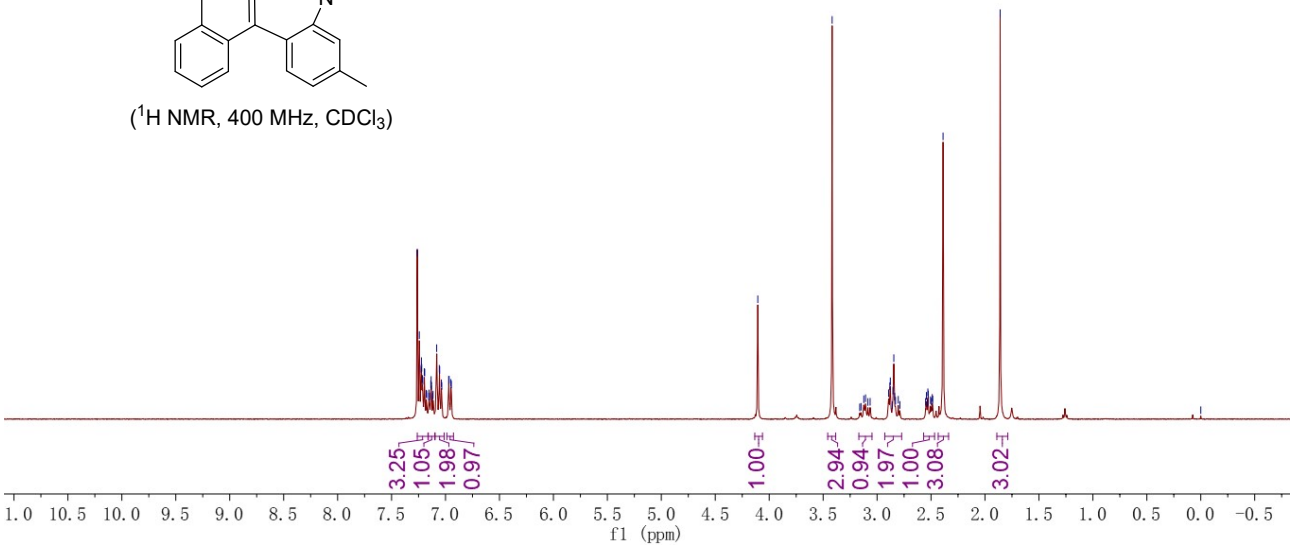


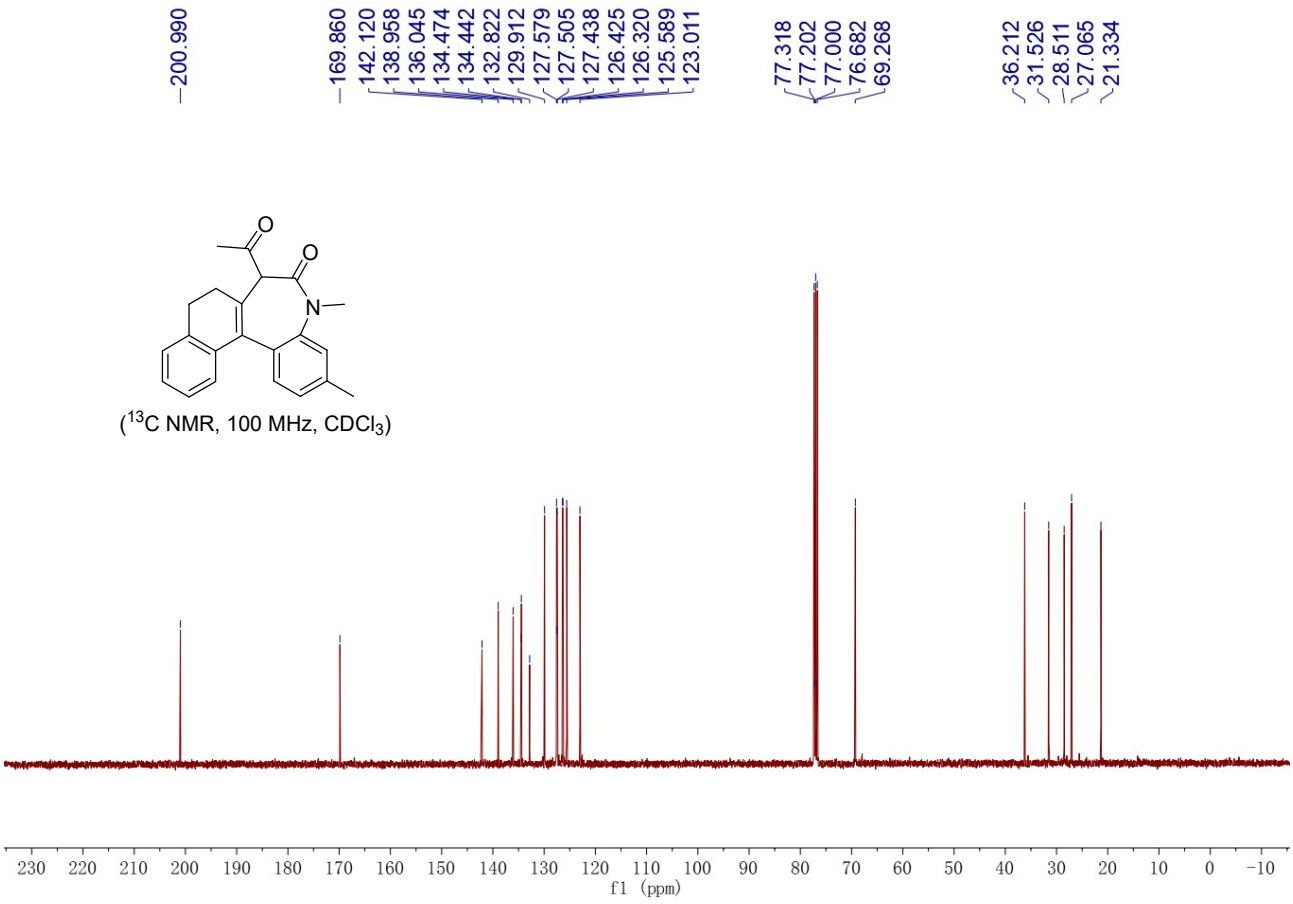
7-acetyl-3,5-dimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2m**): Yield: 25 mg, 37%, white solid, m.p. >200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ δ 7.26 – 7.16 (m, 3H), 7.16 – 7.10 (m, 1H), 7.10 – 7.01 (m, 2H), 6.96 (dd, J_1 = 8.1, J_2 = 1.7 Hz, 1H), 4.11 (s, 1H), 3.42 (s, 3H), 3.17 – 3.05 (m, 1H), 2.93 – 2.77 (m, 2H), 2.57 – 2.47 (m, 1H), 2.39 (s, 3H), 1.86 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.0, 169.9, 142.1, 139.0, 136.0, 134.5, 134.4, 132.8, 129.9, 127.6, 127.5, 127.4, 126.4, 126.3, 125.6, 123.0, 69.3, 36.2, 31.5, 28.5, 27.1, 21.3; IR (neat): ν 3034, 2927, 2825, 1712, 1612, 1414, 1352, 1252, 1179, 822, 741, 661 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_2$ $[M+H]^+$: 332.16451, found: 332.16454.



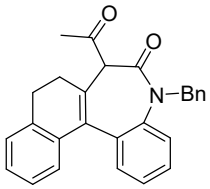


(^{1}H NMR, 400 MHz, $CDCl_3$)

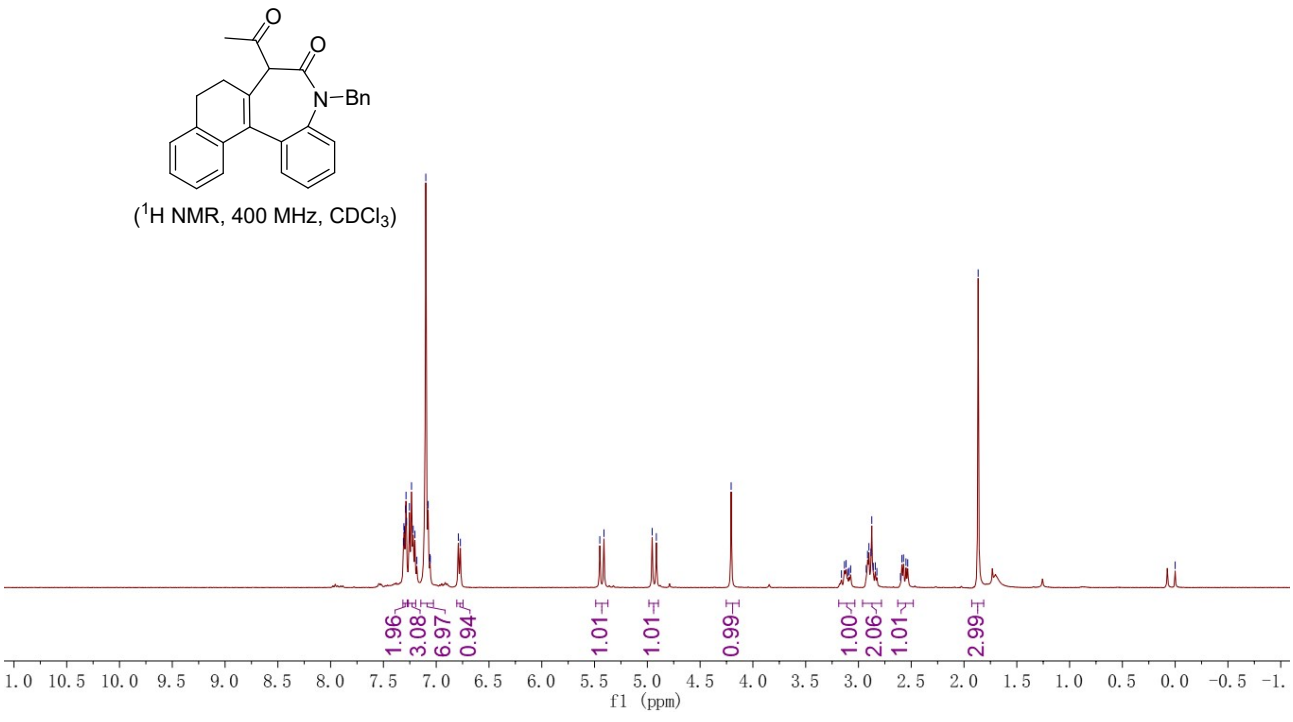


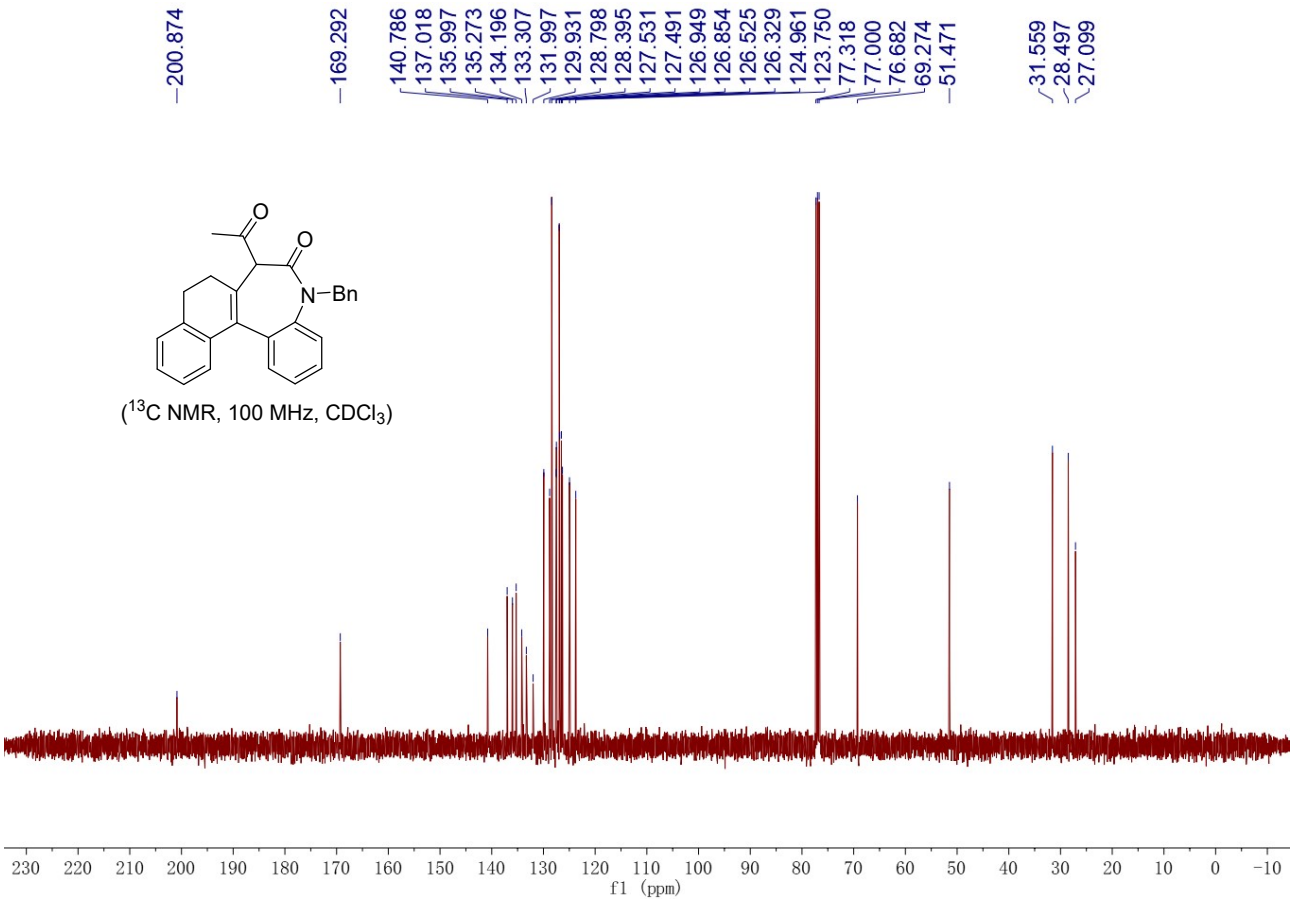


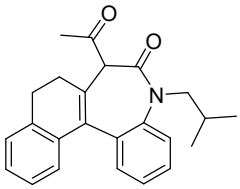
(^{13}C NMR, 100 MHz, $CDCl_3$)



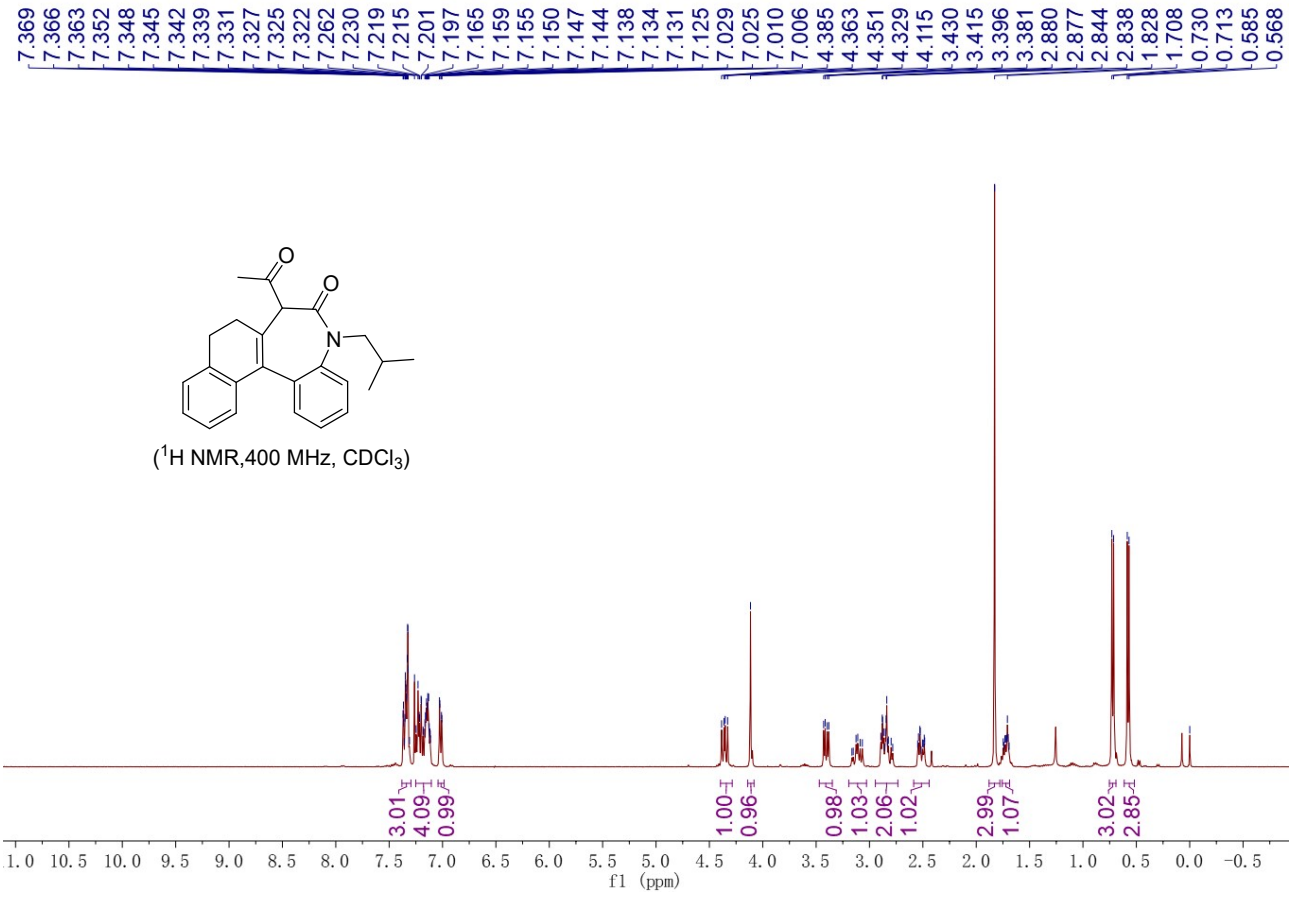
7-acetyl-5-benzyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2n**): Yield: 39 mg, 51%, white solid, m.p. > 200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 7.15 – 7.03 (m, 7H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.43 (d, *J* = 15.7 Hz, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.21 (s, 1H), 3.19 – 3.03 (m, 1H), 2.96 – 2.78 (m, 2H), 2.63 – 2.48 (m, 1H), 1.87 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.9, 169.3, 140.8, 137.0, 136.0, 135.3, 134.2, 133.3, 132.0, 129.9, 128.8, 128.4, 127.5, 127.5, 126.9, 126.9, 126.5, 126.3, 125.0, 123.7, 69.3, 51.5, 31.6, 28.5, 27.1; IR (neat): ν 3058, 2935, 2828, 1714, 1652, 1447, 1253, 1169, 777, 732 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{27}H_{24}NO_2$ $[M+H]^+$: 394.18016, found: 394.17974.

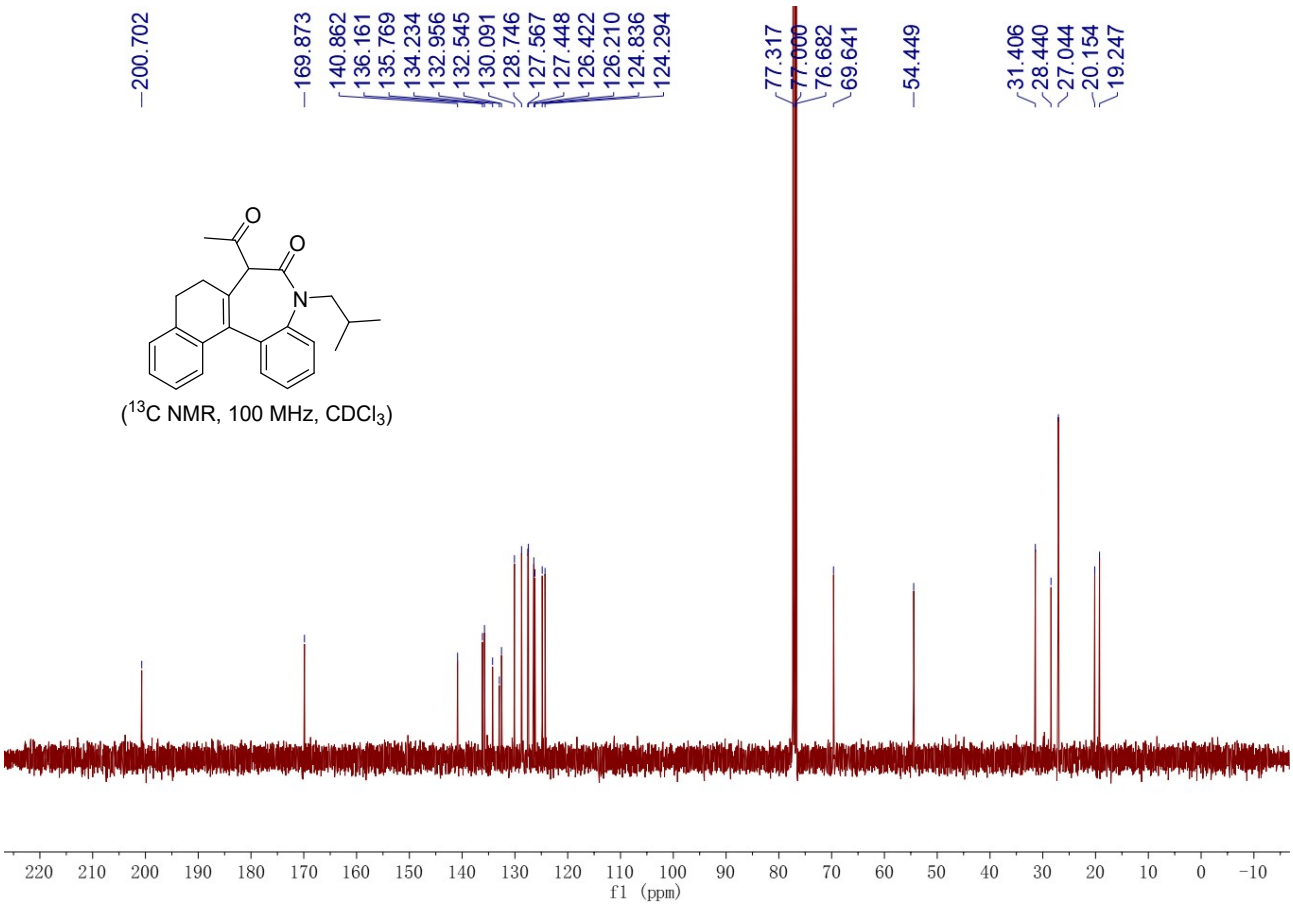


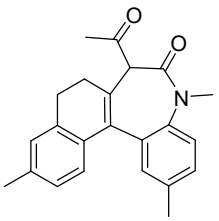

200.874
169.292
140.786
137.018
135.997
135.273
134.196
133.307
131.997
129.931
128.798
128.395
127.531
127.491
126.949
126.854
126.525
126.329
124.961
123.750
77.318
77.000
76.682
69.274
51.471
31.559
28.497
27.099
O
O
N–Bn
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



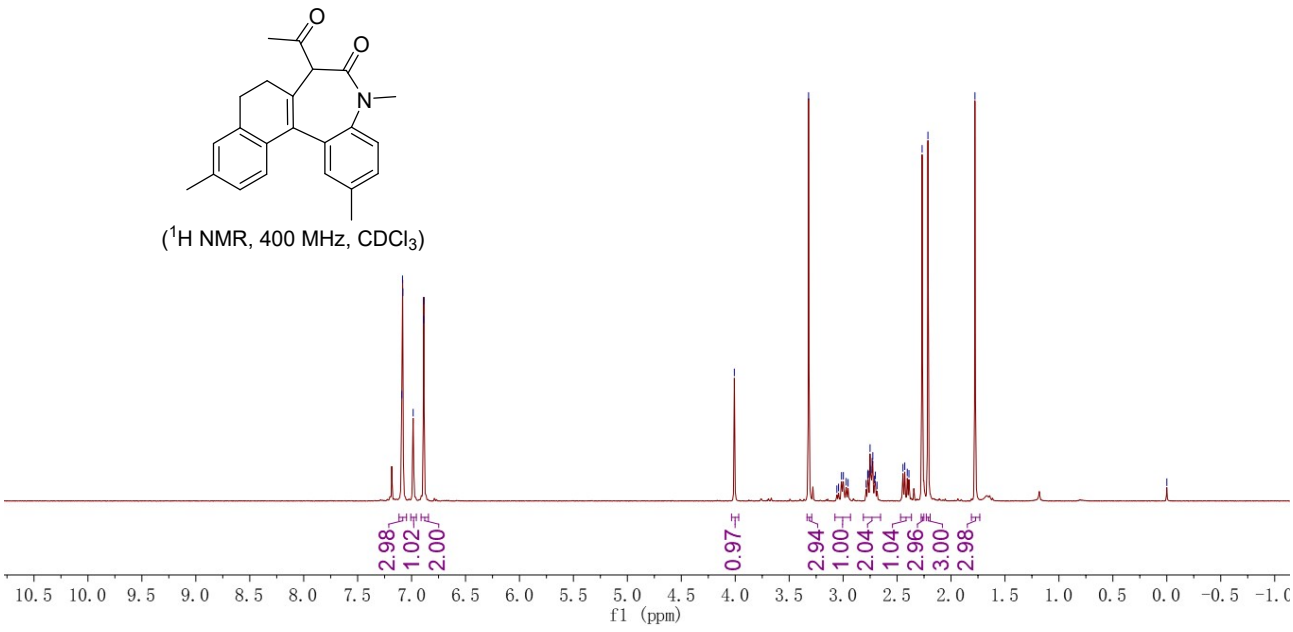
7-acetyl-5-isobutyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2o**): Yield: 30 mg, 43%, white solid, m.p. 192-194 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 – 7.30 (m, 3H), 7.25 – 7.11 (m, 4H), 7.02 (dd, J_1 = 7.6, J_2 = 1.4 Hz, 1H), 4.36 (dd, J_1 = 13.6, J_2 = 9.1 Hz, 1H), 4.12 (s, 1H), 3.41 (dd, J_1 = 13.6, J_2 = 5.9 Hz, 1H), 3.19 – 3.03 (m, 1H), 2.94 – 2.73 (m, 2H), 2.59 – 2.44 (m, 1H), 1.83 (s, 3H), 1.76 – 1.69 (m, 1H), 0.72 (d, J = 6.6 Hz, 3H), 0.58 (d, J = 6.6 Hz, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.7, 169.9, 140.9, 136.2, 135.8, 134.2, 133.0, 132.5, 130.1, 128.7, 127.6, 127.4, 126.4, 126.2, 124.8, 124.3, 69.6, 54.4, 31.4, 28.4, 27.0, 20.2, 19.2; IR (neat): ν 2966, 2925, 2878, 1708, 1448, 1383, 1245, 1056, 776, 738 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{24}H_{26}NO_2Na$ $[M+H]^+$: 360.19581, found: 360.19585.

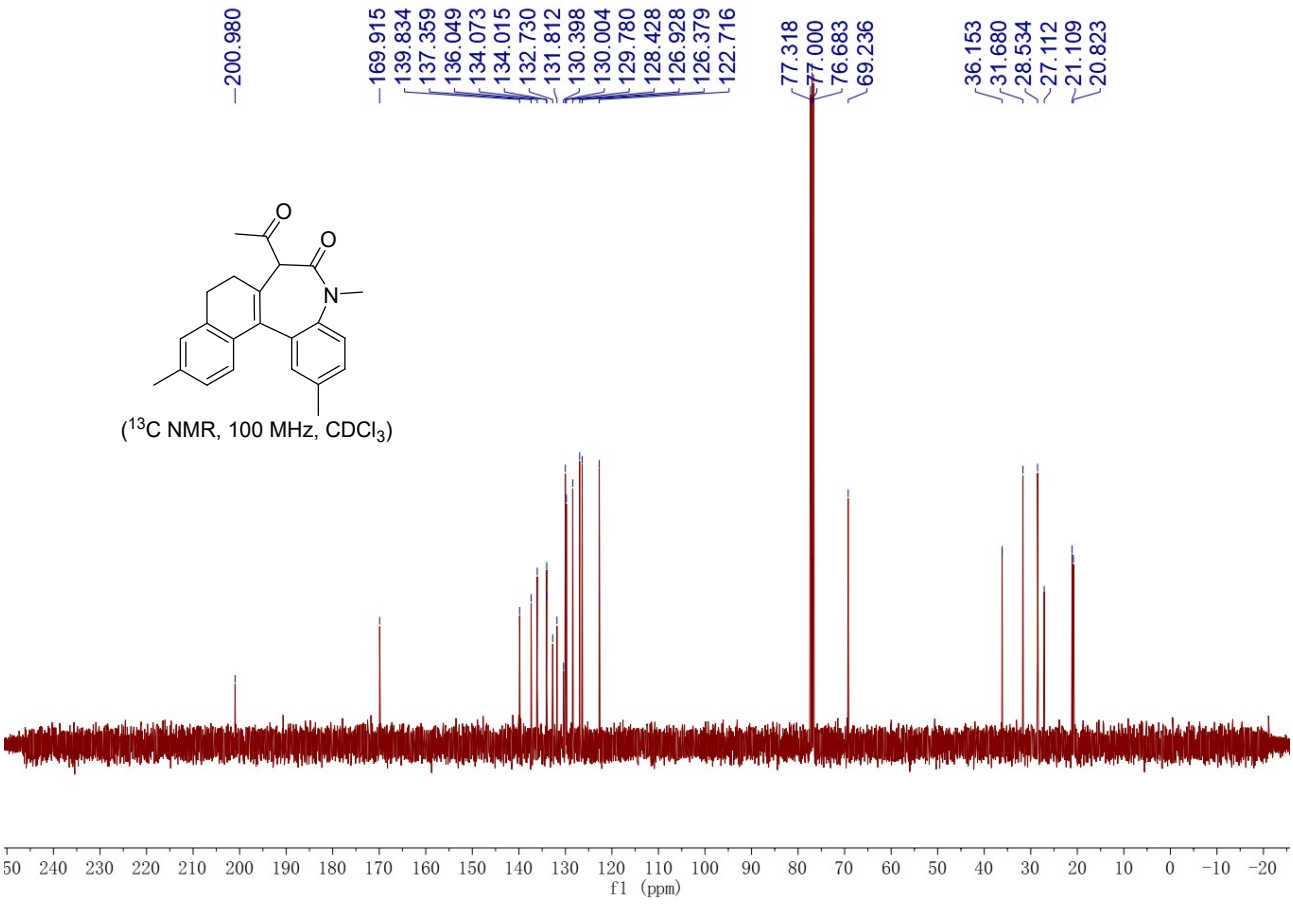


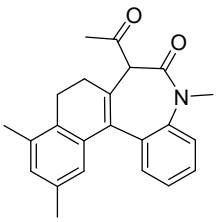

200.702
169.873
140.862
136.161
135.769
134.234
132.956
132.545
130.091
128.746
127.567
127.448
126.422
126.210
124.836
124.294
77.317
77.000
76.682
69.641
54.449
31.406
28.440
27.044
20.154
19.247
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



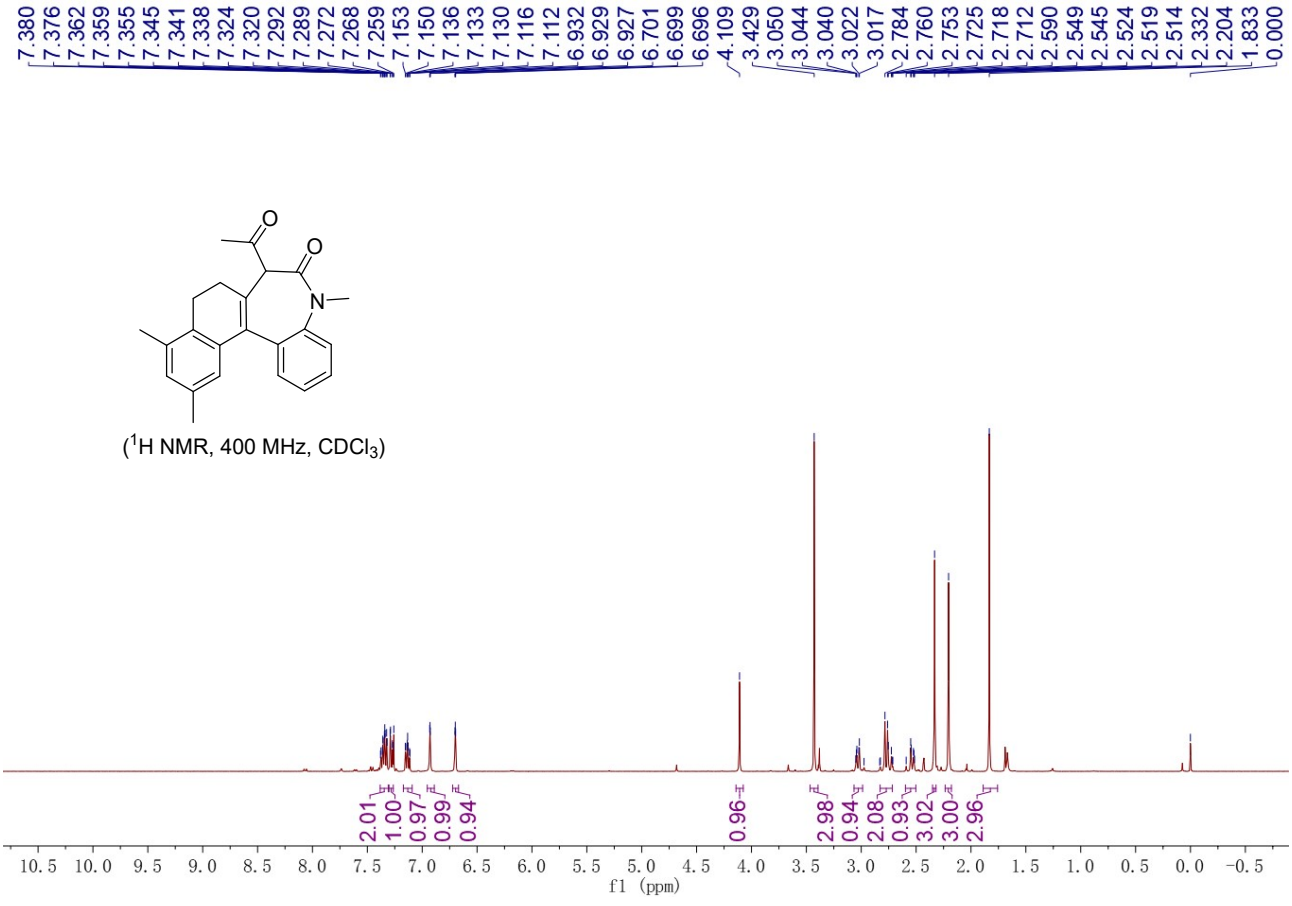
7-acetyl-2,5,11-trimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2p**): Yield: 30 mg, 44%, white solid, m.p. >200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.12 – 7.05 (m, 3H), 7.01 – 6.96 (m, 1H), 6.91 – 6.84 (m, 2H), 4.01 (s, 1H), 3.32 (s, 3H), 3.08 – 2.93 (m, 1H), 2.81 – 2.65 (m, 2H), 2.47 – 2.37 (m, 1H), 2.27 (s, 3H), 2.21 (s, 3H), 1.78 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.0, 169.9, 139.8, 137.4, 136.0, 134.1, 134.0, 132.7, 131.8, 130.4, 130.0, 129.8, 128.4, 126.9, 126.4, 122.7, 69.2, 36.2, 31.7, 28.5, 27.1, 21.1, 20.8; IR (neat): ν 3041, 2983, 2911, 1679, 1599, 1492, 1343, 1161, 1062, 896, 757, 674 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{24}NO_2Na$ $[M+H]^+$: 346.18016, found: 346.17986.

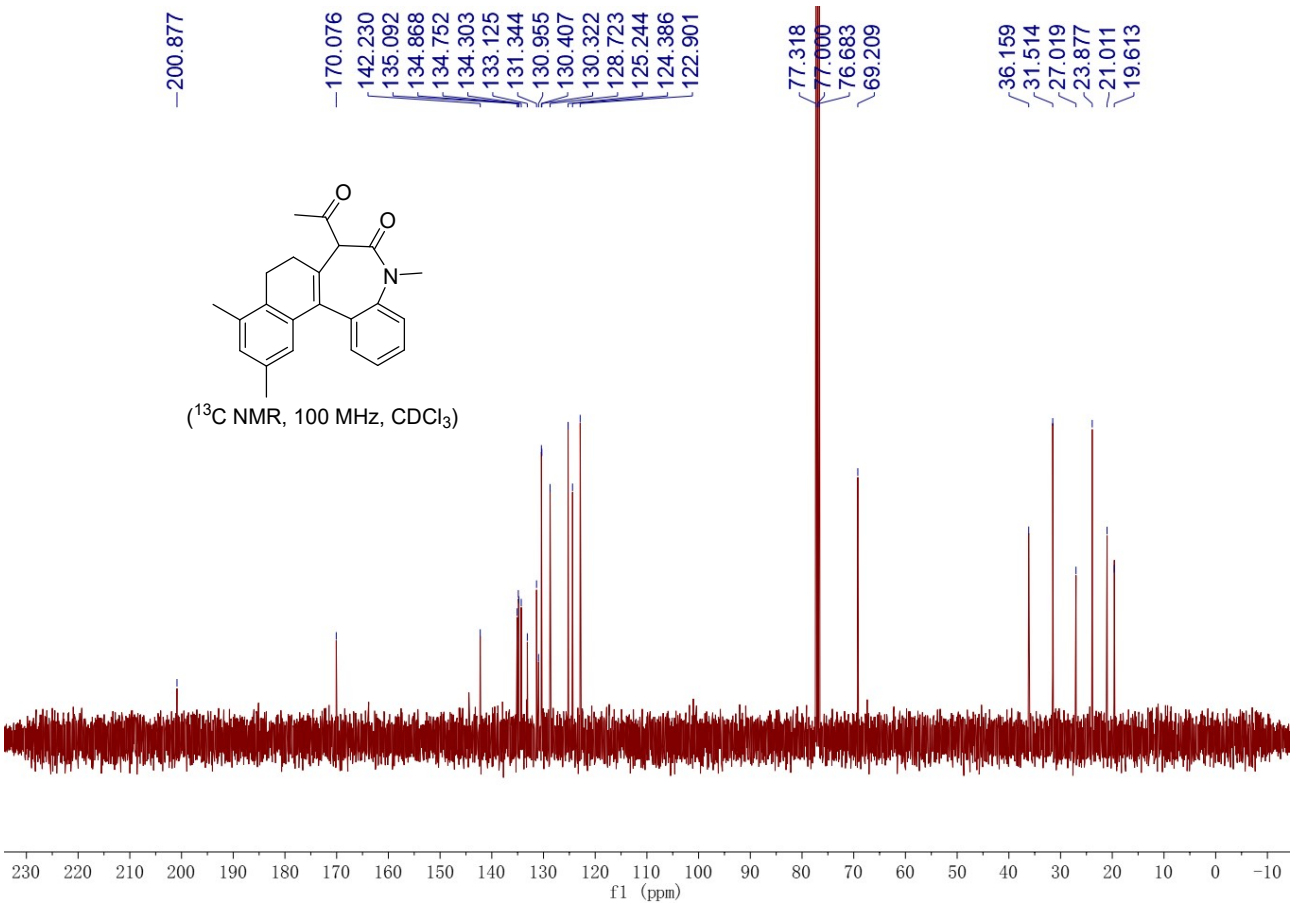


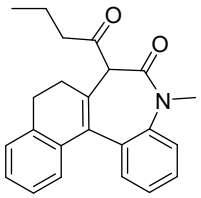

200.980
169.915
139.834
137.359
136.049
134.073
134.015
132.730
131.812
130.398
130.004
129.780
128.428
126.928
126.379
122.716
77.318
77.000
76.683
69.236
36.153
31.680
28.534
27.112
21.109
20.823
O
O
N
(13C NMR, 100 MHz, CDCl3)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



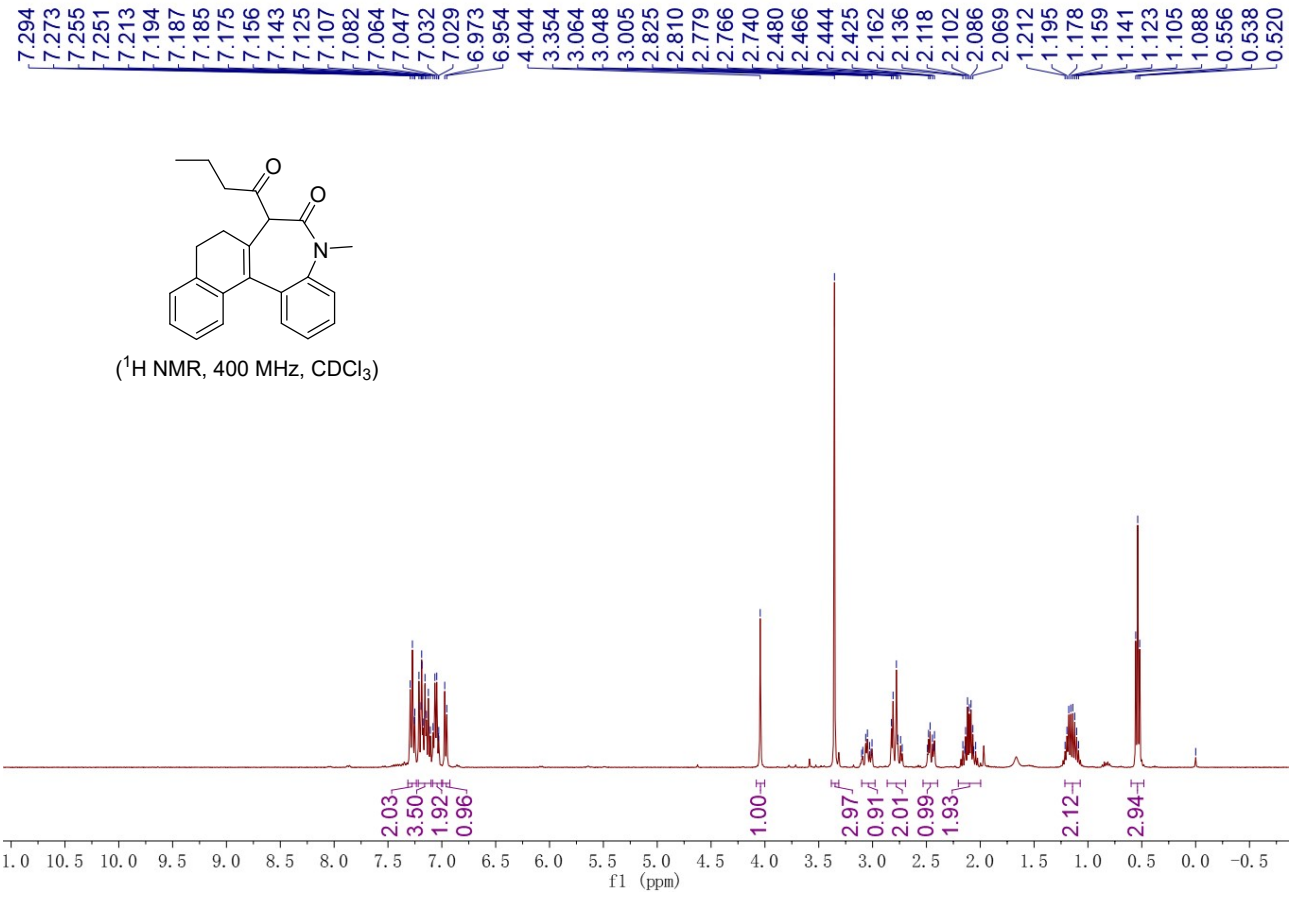
7-acetyl-5,10,12-trimethyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2q**): Yield: 30 mg, 44%, white solid, m.p. >200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.17 – 7.09 (m, 1H), 6.95 – 6.89 (m, 1H), 6.72 – 6.67 (m, 1H), 4.11 (s, 1H), 3.43 (s, 3H), 3.07 – 2.99 (m, 1H), 2.83 – 2.72 (m, 2H), 2.60 – 2.50 (m, 1H), 2.33 (s, 3H), 2.20 (s, 3H), 1.83 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 200.9, 170.1, 142.2, 135.1, 134.9, 134.8, 134.3, 133.1, 131.3, 131.0, 130.4, 130.3, 128.7, 125.2, 124.4, 122.9, 69.2, 36.2, 31.5, 27.0, 23.9, 21.0, 19.6; IR (neat): ν 3051, 2984, 1688, 1581, 1452, 1355, 1165, 1084, 1061, 886, 750 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{24}NO_2$ $[M+H]^+$: 346.18070, found: 346.18059.

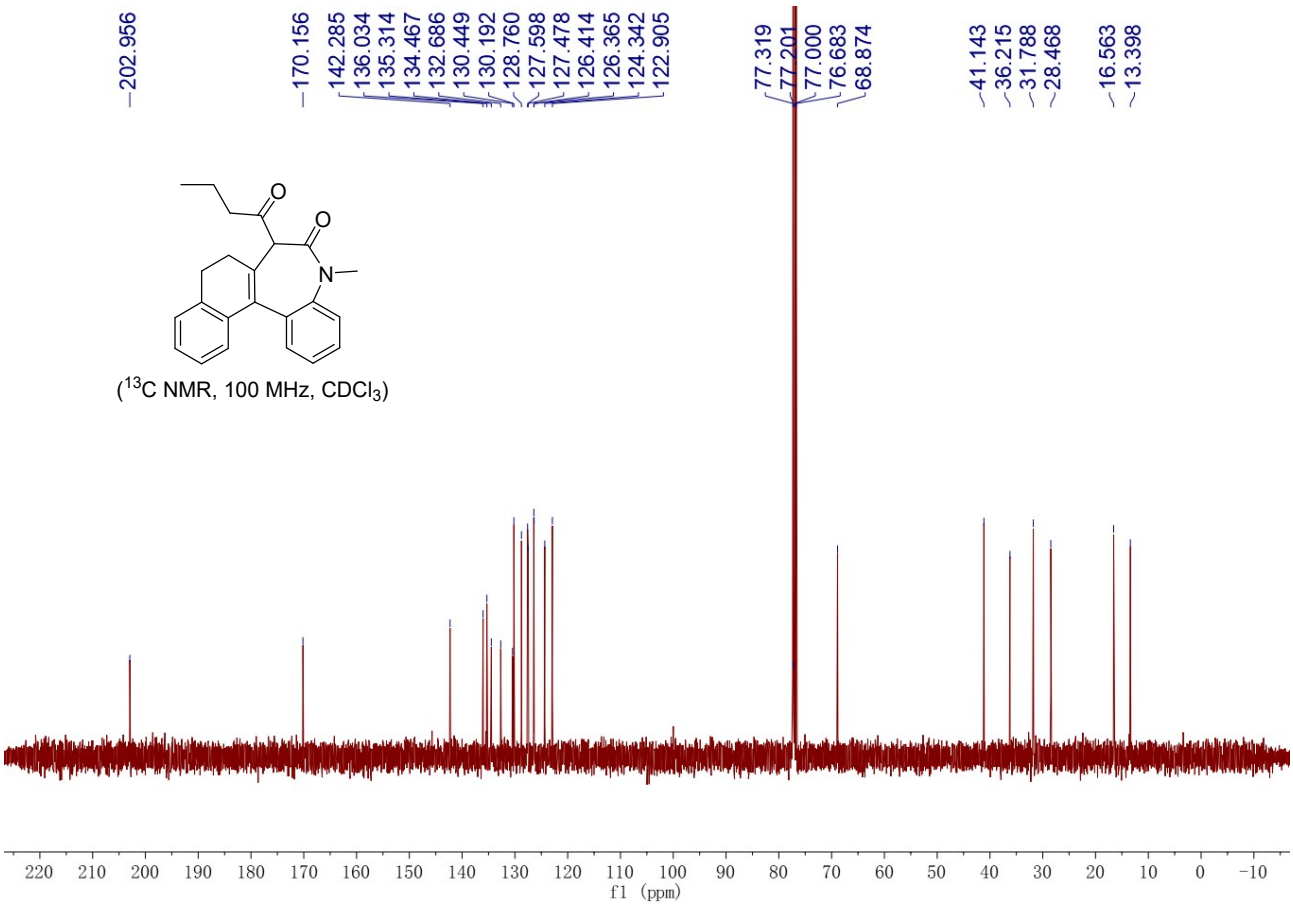



200.877
170.076
142.230
135.092
134.868
134.752
134.303
133.125
131.344
130.955
130.407
130.322
128.723
125.244
124.386
122.901
77.318
77.000
76.683
69.209
36.159
31.514
27.019
23.877
21.011
19.613
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

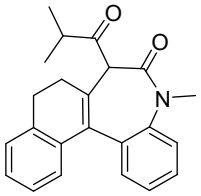


7-butyryl-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2r**): Yield: 31 mg, 45%, white solid, m.p. 155-157 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.10 (m, 3H), 7.09 – 7.00 (m, 2H), 6.99 – 6.93 (m, 1H), 4.04 (s, 1H), 3.35 (s, 3H), 3.10 – 2.98 (m, 1H), 2.86 – 2.70 (m, 2H), 2.53 – 2.40 (m, 1H), 2.20 – 2.00 (m, 2H), 1.21 – 1.07 (m, 2H), 0.54 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 203.0, 170.2, 142.3, 136.0, 135.3, 134.5, 132.7, 130.4, 130.2, 128.8, 127.6, 127.5, 126.4, 126.4, 124.3, 122.9, 68.9, 41.1, 36.2, 31.8, 28.5, 16.6, 13.4; IR (neat): ν 2969, 2983, 2870, 1707, 1652, 1482, 1351, 1243, 1111, 1025, 769,741 cm^{-1}; HRMS (EI-TOF) Calcd for $C_{23}H_{23}NO_2Na$ $[M+Na]^+$: 368.16210, found: 368.16237.

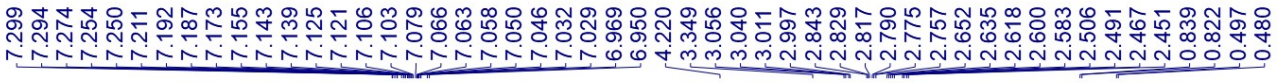


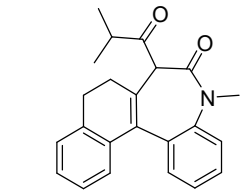


(^{13}C NMR, 100 MHz, $CDCl_3$)

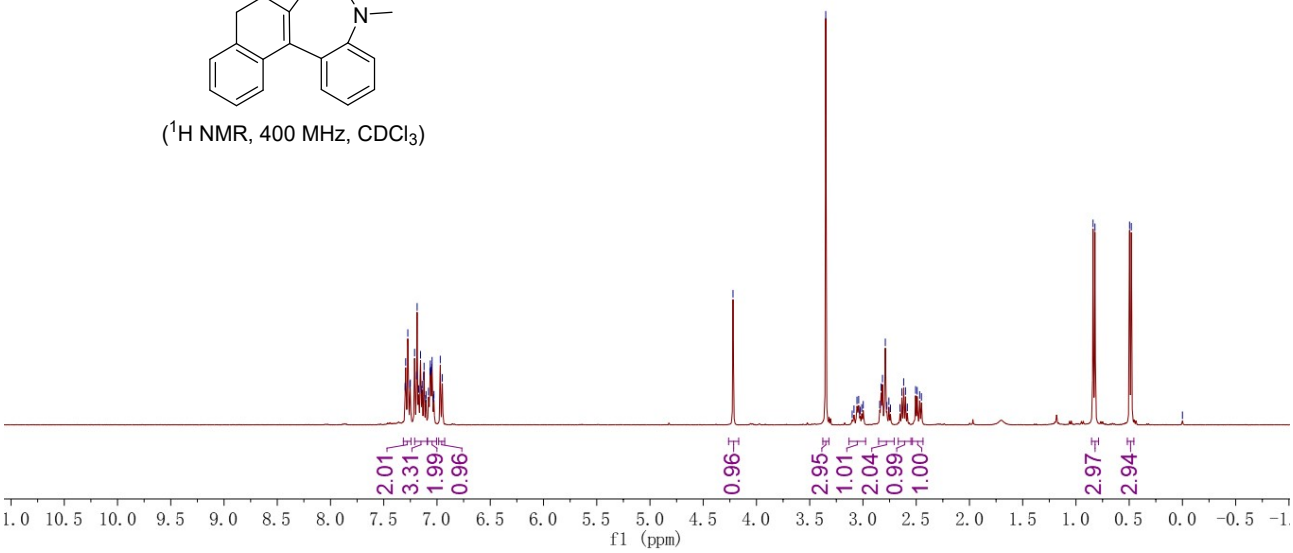


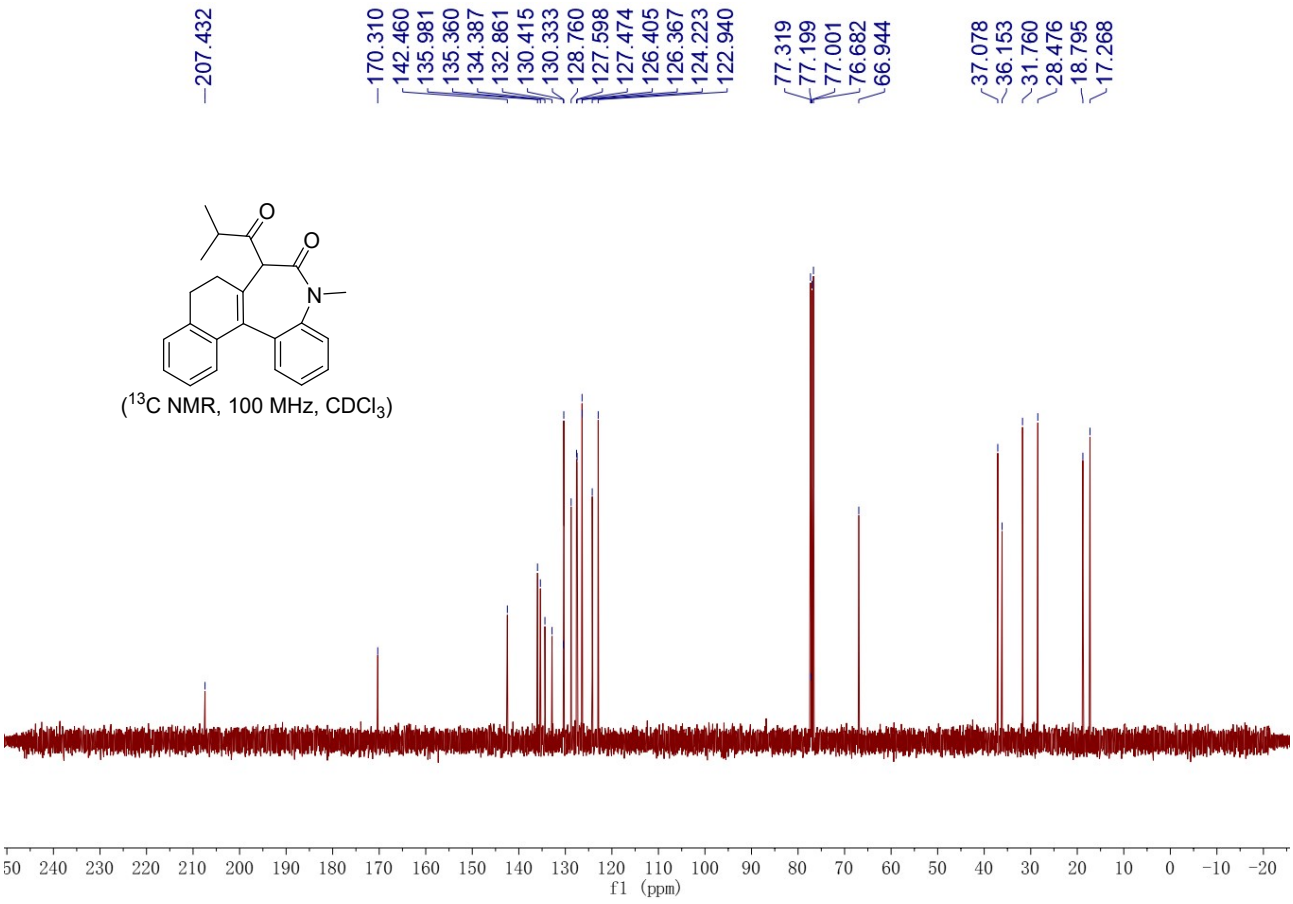
7-isobutyryl-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2s**): Yield: 30 mg, 40%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32 – 7.24 (m, 2H), 7.21 – 7.09 (m, 3H), 7.09 – 7.00 (m, 2H), 6.98 – 6.93 (m, 1H), 4.22 (s, 1H), 3.35 (s, 3H), 3.13 – 2.98 (m, 1H), 2.85 – 2.71 (m, 2H), 2.62 (p, *J* = 6.9 Hz, 1H), 2.54 – 2.44 (m, 1H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.49 (d, *J* = 6.6 Hz, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 207.4, 170.3, 142.5, 136.0, 135.4, 134.4, 132.9, 130.4, 130.3, 128.8, 127.6, 127.5, 126.4, 126.4, 124.2, 122.9, 66.9, 37.1, 36.2, 31.8, 28.5, 18.8, 17.3; IR (neat): ν 2969, 2927, 2875, 1708, 1655, 1445, 1359, 1025, 999, 769 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{24}NO_2$ $[M+H]^+$: 34618016, found: 346.17979.

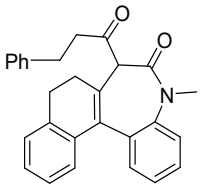




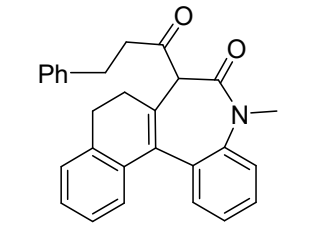
(^{1}H NMR, 400 MHz, $CDCl_3$)



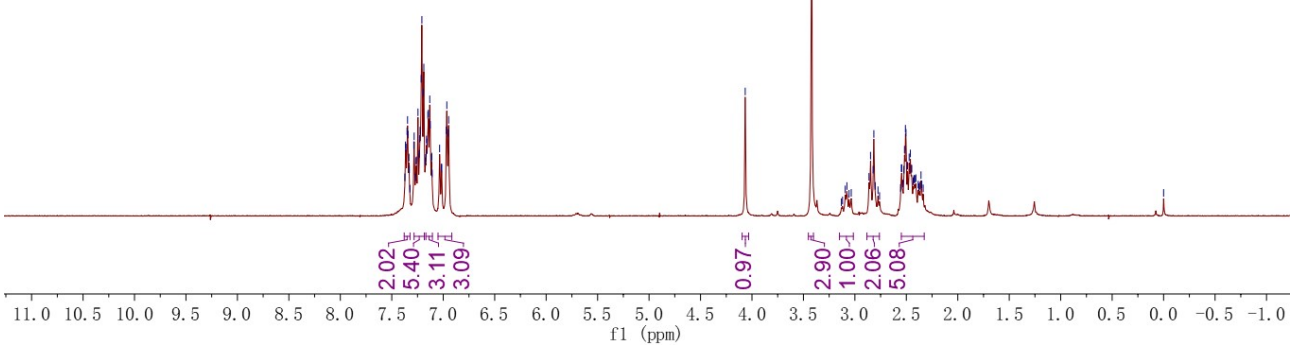

207.432
170.310
142.460
135.981
135.360
134.387
132.861
130.415
130.333
128.760
127.598
127.474
126.405
126.367
124.223
122.940
77.319
77.199
77.001
76.682
66.944
37.078
36.153
31.760
28.476
18.795
17.268
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

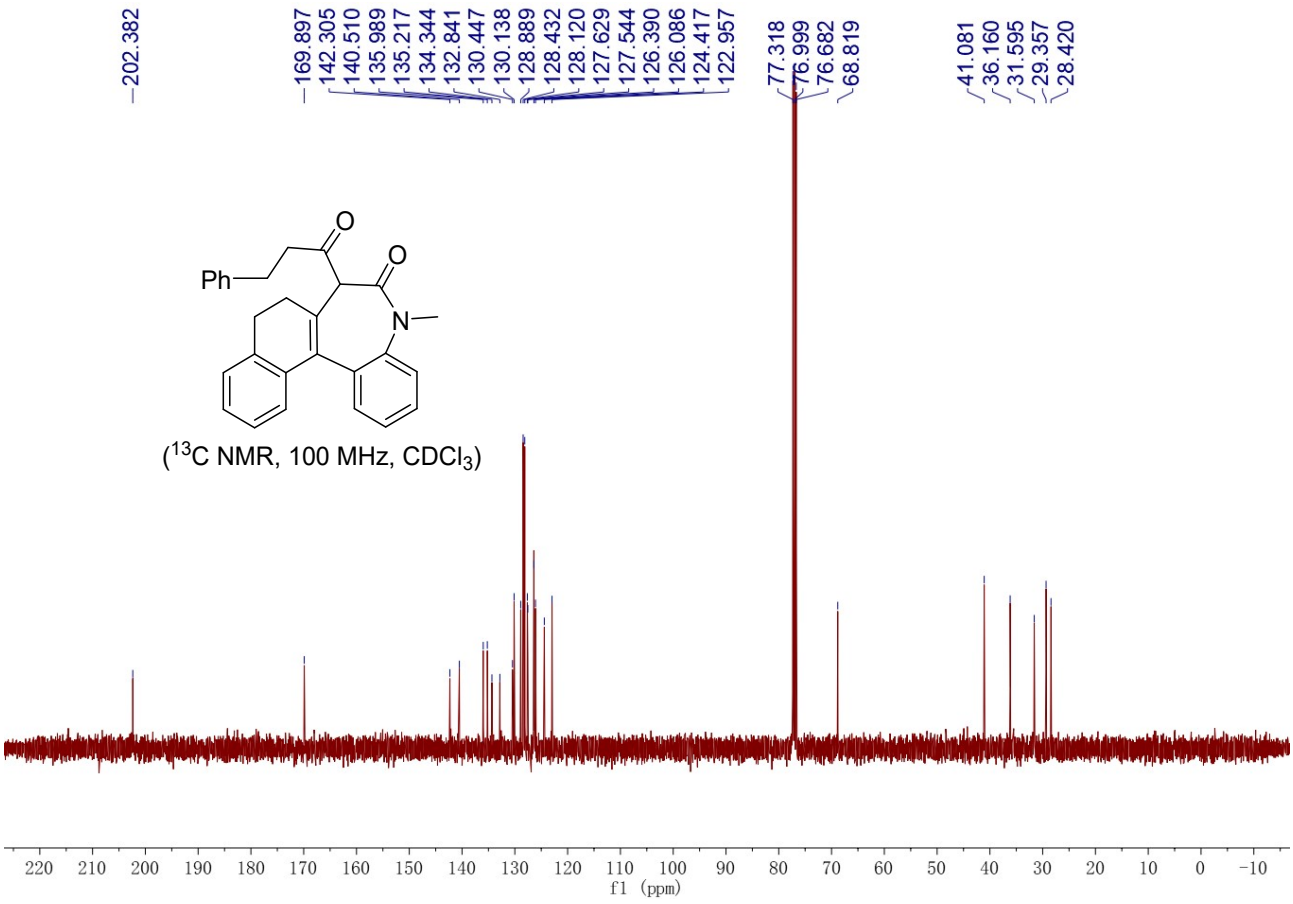


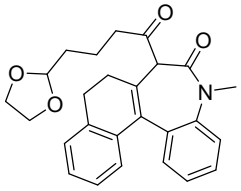
5-methyl-7-(3-phenylpropanoyl)-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2t**): Yield: 29 mg, 36%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 – 7.32 (m, 2H), 7.28 – 7.18 (m, 5H), 7.17 – 7.11 (m, 3H), 7.05 – 6.92 (m, 3H), 4.07 (s, 1H), 3.42 (s, 3H), 3.15 – 3.01 (m, 1H), 2.88 – 2.76 (m, 2H), 2.55 – 2.33 (m, 5H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 169.9, 142.3, 140.5, 136.0, 135.2, 134.3, 132.8, 130.4, 130.1, 128.9, 128.4, 128.1, 127.6, 127.5, 126.4, 126.1, 124.4, 123.0, 68.8, 41.1, 36.2, 31.6, 29.4, 28.4; IR (neat): ν 3058, 2935, 2878, 1711, 1655, 1445, 1357, 908, 769, 667 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{28}H_{26}NO_2$ $[M+H]^+$: 408.19581, found: 408.19586.



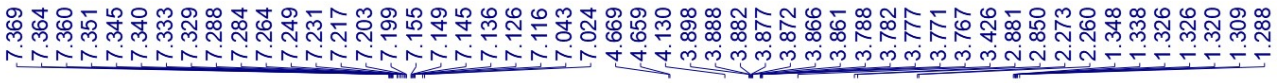
(^{1}H NMR, 400 MHz, $CDCl_3$)

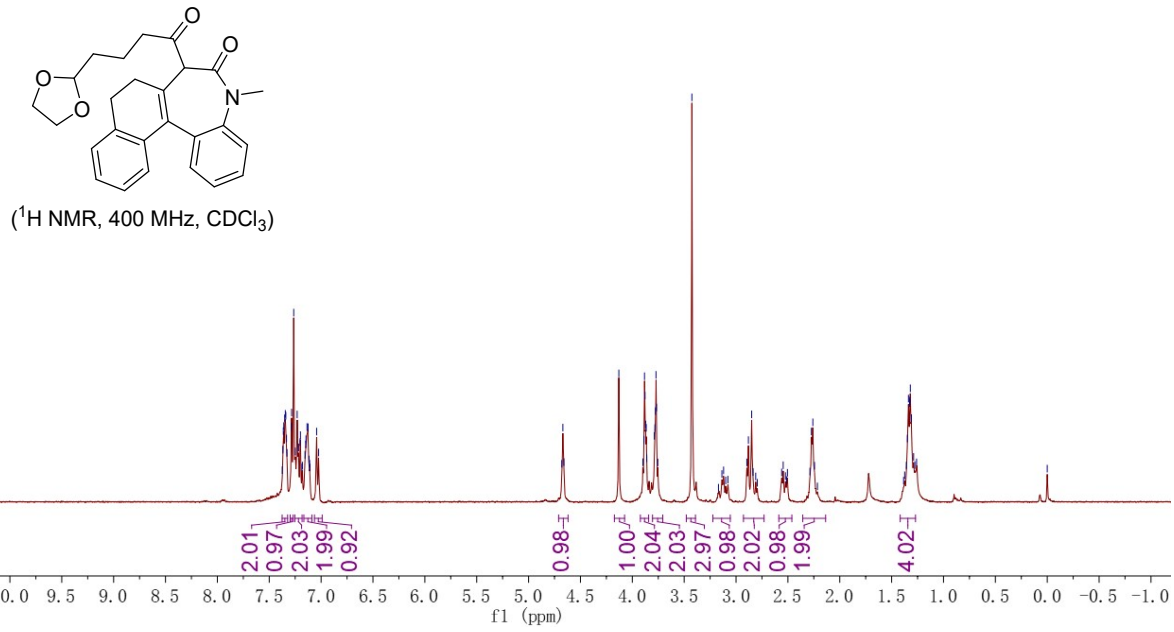


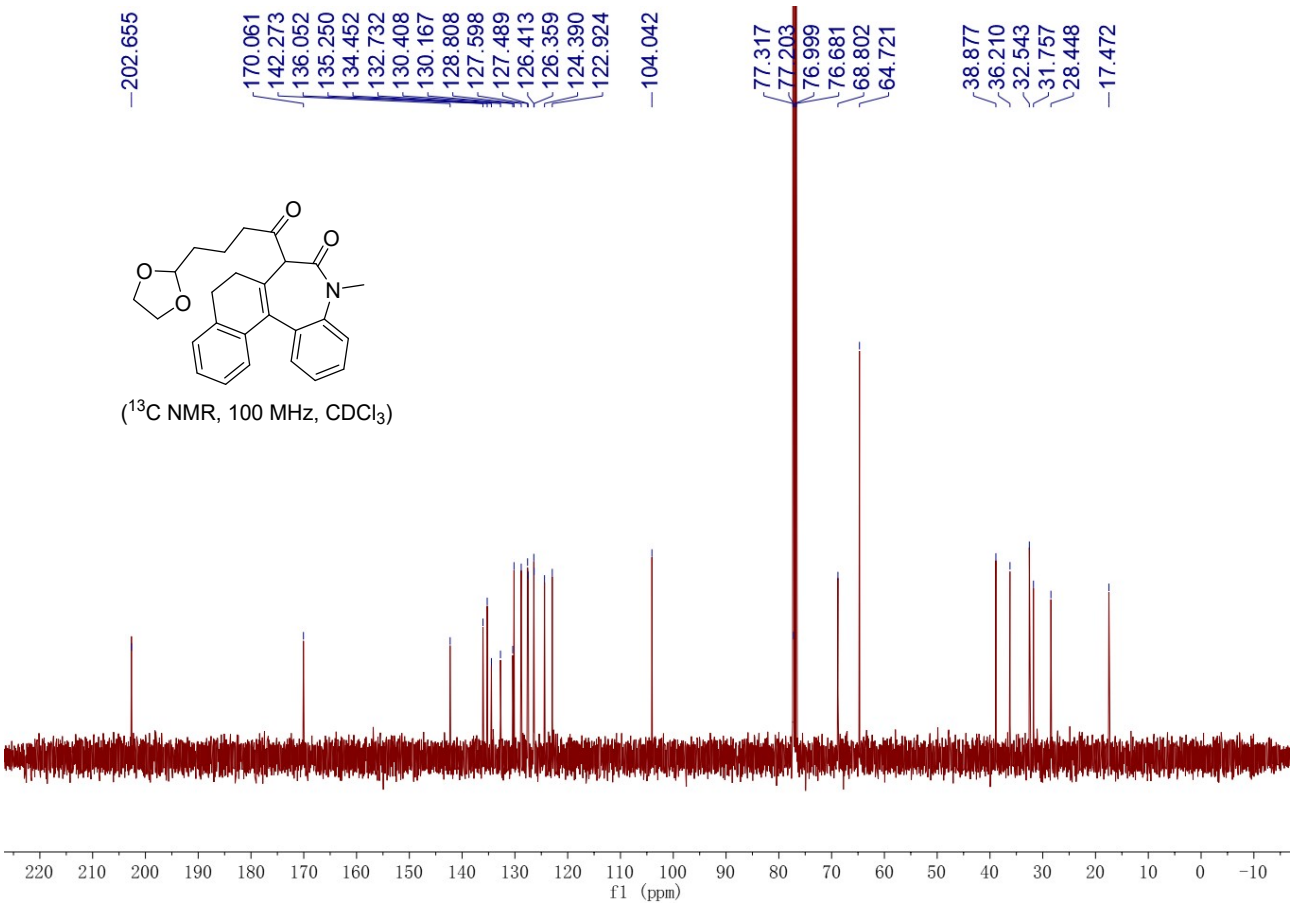

202.382
169.897
142.305
140.510
135.989
135.217
134.344
132.841
130.447
130.138
128.889
128.432
128.120
127.629
127.544
126.390
126.086
124.417
122.957
77.318
76.999
76.682
68.819
41.081
36.160
31.595
29.357
28.420
O
O
Ph
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



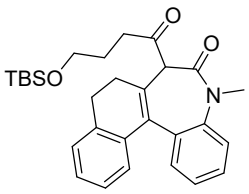
7-(4-(1,3-dioxolan-2-yl)butanoyl)-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2u**): Yield: 27 mg, 33%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.09 (m, 2H), 7.06 – 6.99 (m, 1H), 4.66 (t, *J* = 4.1 Hz, 1H), 4.13 (s, 1H), 3.92 – 3.84 (m, 2H), 3.81 – 3.71 (m, 2H), 3.43 (s, 3H), 3.22 – 3.06 (m, 1H), 2.93 – 2.73 (m, 2H), 2.59 – 2.46 (m, 1H), 2.36 – 2.14 (m, 2H), 1.42 – 1.27 (m, 4H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.7, 170.1, 142.3, 136.1, 135.3, 134.5, 132.7, 130.4, 130.2, 128.8, 127.6, 127.5, 126.4, 126.4, 124.4, 122.9, 104.0, 68.8, 64.7, 38.9, 36.2, 32.5, 31.8, 28.4, 17.5; IR (neat): ν 3021, 2925, 2823, 1710, 1655, 1358, 902, 770, 699 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{26}H_{27}NO_4Na$ [M+Na]$^{+}$: 440.18323, found: 440.18321.



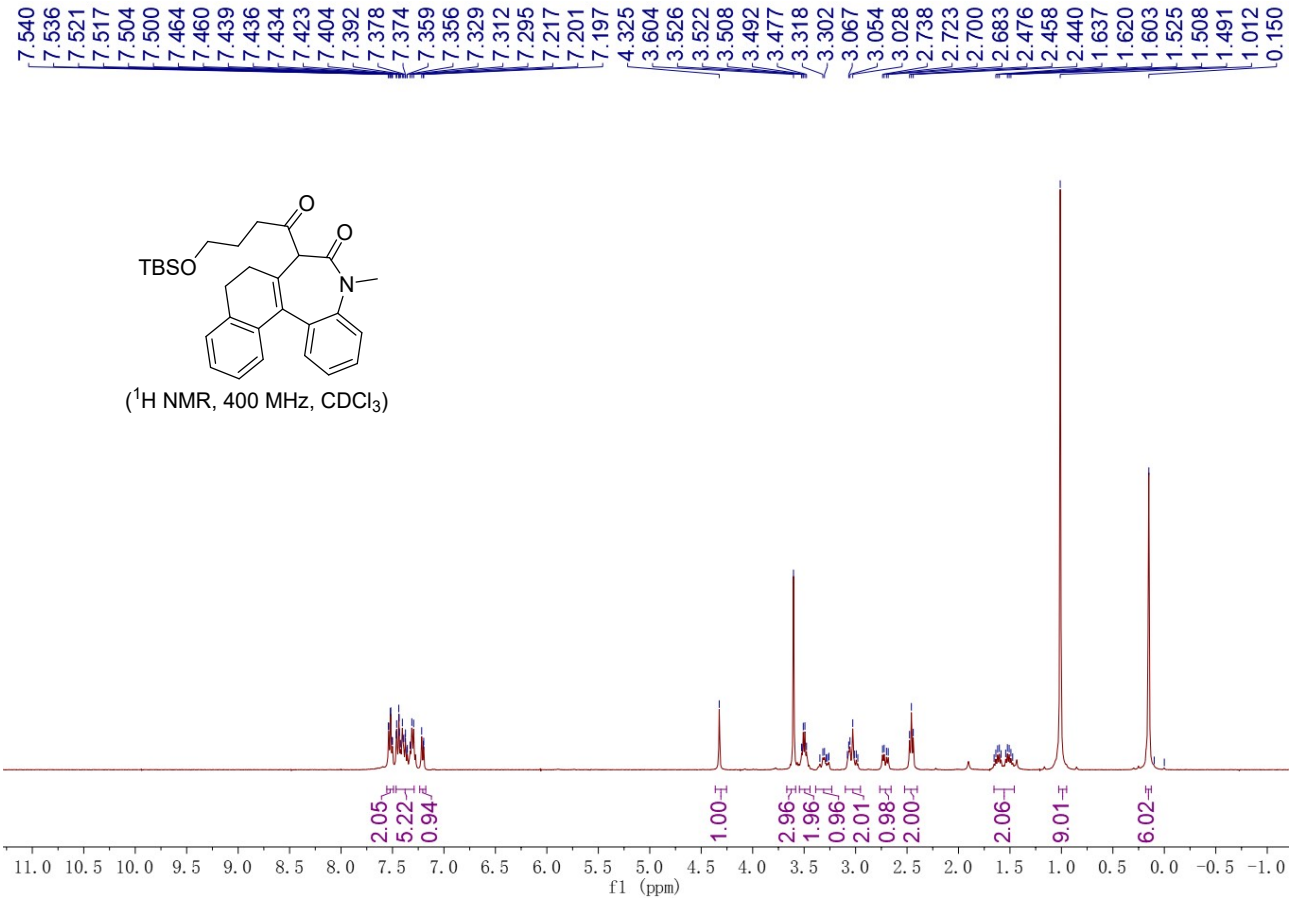


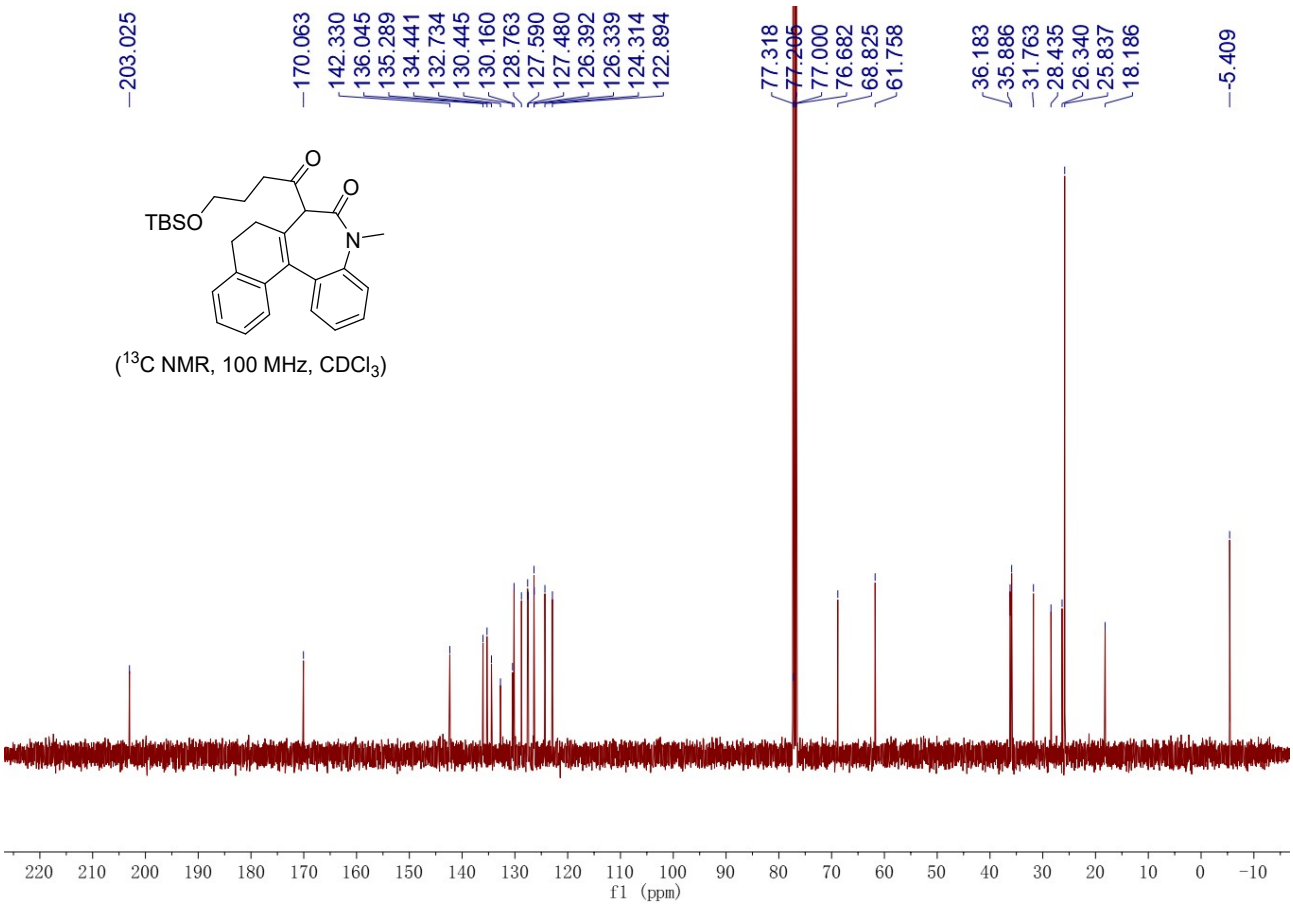


(^{13}C NMR, 100 MHz, $CDCl_3$)

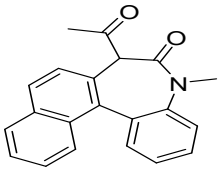


7-(4-((*tert*-butyldimethylsilyl)oxy)butanoyl)-5-methyl-5,7,8,9-tetrahydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**2v**): Yield: 44 mg, 46%, brown oil; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 – 7.49 (m, 2H), 7.47 – 7.29 (m, 5H), 7.24 – 7.18 (m, 1H), 4.32 (s, 1H), 3.60 (s, 3H), 3.55 – 3.44 (m, 2H), 3.39 – 3.23 (m, 1H), 3.10 – 2.95 (m, 2H), 2.76 – 2.66 (m, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.66 – 1.46 (m, 2H), 1.01 (s, 9H), 0.15 (s, 6H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 203.0, 170.1, 142.3, 136.0, 135.3, 134.4, 132.7, 130.4, 130.2, 128.8, 127.6, 127.5, 126.4, 126.3, 124.3, 122.9, 68.8, 61.8, 36.2, 35.9, 31.8, 28.4, 26.3, 25.8, 18.2, -5.4; IR (neat): ν 2963, 2927, 2852, 1717, 1659, 1356, 1093, 833, 730 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{29}H_{38}NO_3Si$ $[M+H]^+$: 476.26155, found: 476.26109.

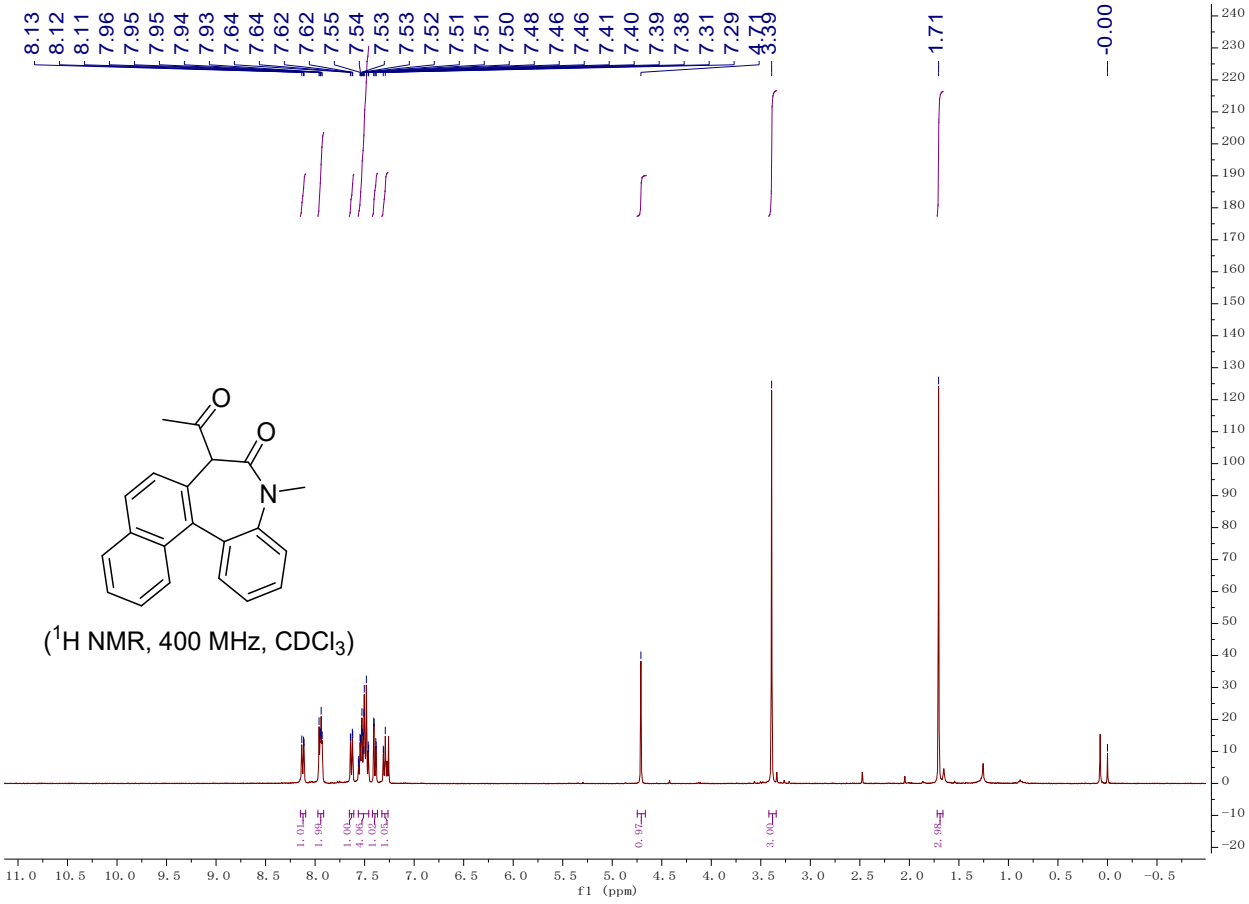




(^{13}C NMR, 100 MHz, $CDCl_3$)



7-acetyl-5-methyl-5,7-dihydro-6H-benzo[b]naphtho[1,2-d]azepin-6-one (**3a**): Yield: 48 mg, 77%, white solid, m.p. > 200 °C; Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.15 – 8.10 (m, 1H), 7.97 – 7.91 (m, 2H), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.42 – 7.37 (m, 1H), 7.33 – 7.26 (m, 1H), 4.71 (s, 1H), 3.39 (s, 3H), 1.71 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.0, 170.9, 141.9, 134.0, 134.0, 133.0, 132.3, 131.1, 130.6, 129.6, 129.4, 128.5, 127.4, 126.9, 126.2, 126.1, 124.7, 123.4, 69.5, 35.9, 27.2; IR (neat): ν 3065, 2961, 2924, 1714, 1595, 1497, 1352, 1262, 1174, 1043, 821, 747, 676 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.13321, found: 316.13341.


8.13
8.12
8.11
7.96
7.95
7.95
7.94
7.93
7.64
7.64
7.62
7.62
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.48
7.46
7.46
7.41
7.40
7.39
7.38
7.31
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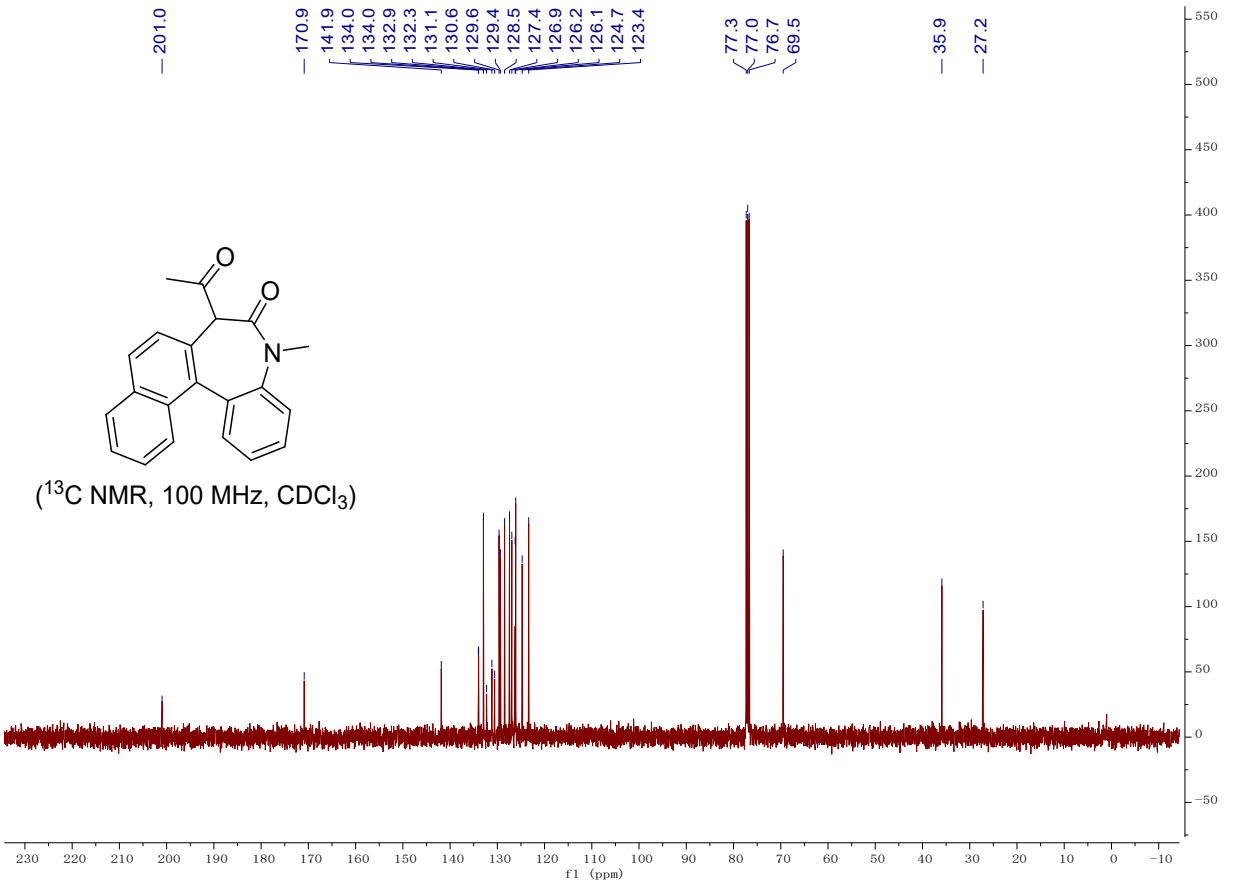
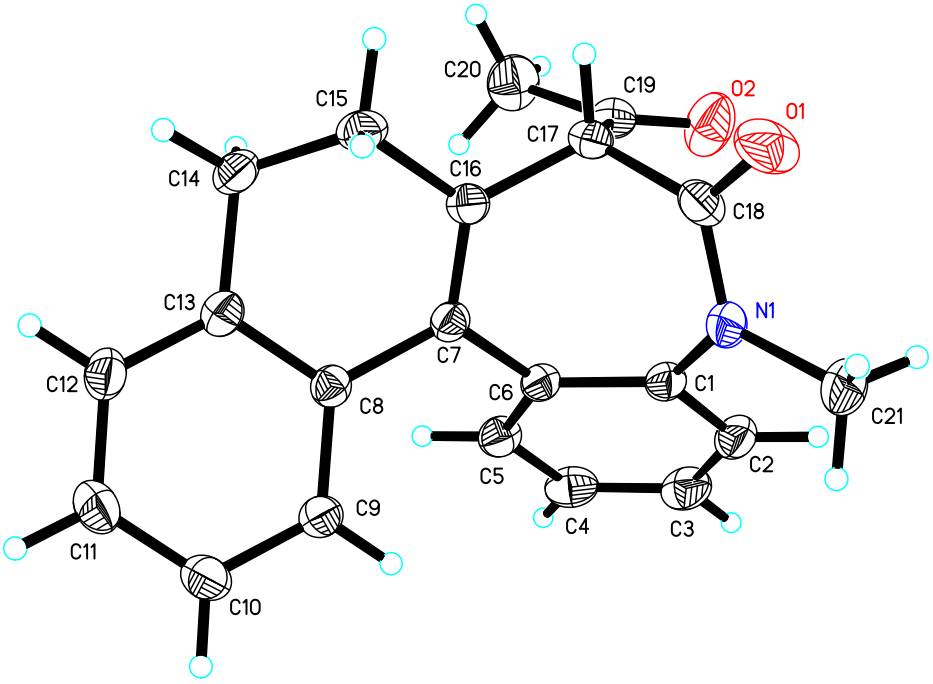
3.39
1.71
-0.00
O
O
N
(^{1}H NMR, 400 MHz, $CDCl_3$)
f1 (ppm)


201.0
170.9
141.9
134.0
134.0
132.9
132.3
131.1
130.6
129.6
129.4
128.5
127.4
126.9
126.2
126.1
124.7
123.4
77.3
77.0
76.7
69.5
35.9
27.2
O
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

9. X-ray Data



Single crystals of **2a** were grown in dichloromethane and hexanes. Dichloromethane (2.0 mL) was added to **2a** (25 mg in a 4.0 mL vial) followed by 2 drops of hexanes. The 4.0 mL vial was capped and placed at room temperature in the experimental cabinet for 5.0 days, whereupon crystals were formed. A colorless crystal of **2a** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **2a** have been deposited in CCDC with number 2240048 and displayed at 30% ellipsoid contour probability level.

Table S2. Crystal data and structure refinement for 2a.

Identification code	**2a**	
Empirical formula	$C_{21}H_{19}NO_2$	
Formula weight	317.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.6372(4) Å	α = 90°
	b = 18.5055(9) Å	β = 107.348(2)°
	c = 12.0312(6) Å	γ = 90°
Volume	1623.02(14) $Å^3$	
Z	4	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	672	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.827 to 25.997°	
Index ranges	-9<=h<=9, -19<=k<=22, -14<=l<=12	
Reflections collected	7981	
Independent reflections	3168 [R(int) = 0.0554]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4526	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3168 / 0 / 220	
Goodness-of-fit on F2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1278	
R indices (all data)	R1 = 0.0665, wR2 = 0.1418	
Extinction coefficient	0.058(9)	
Largest diff. peak and hole	0.204 and -0.196 e.$Å^{-3}$	

10. References

1) (a) K. Chen, R. Sun, Q. Xu, Y. Wei, M. Shi, Thermal induced intramolecular [2 + 2] cycloaddition of allene-ACPs, *Org. Biomol. Chem*., 2013, **11**, 3949-3953. (b) K. Chen, Z.-Z. Zhu, J.-X. Liu, X.-Y. Tang, Y. Wei and M. Shi, Substrate-controlled Rh(II)-catalyzed single-electron-transfer (SET): divergent synthesis of fused indoles, *Chem. Commun.*, 2016, **52**, 350-353; (c) X.-S. Ning, X. Liang, K.-F. Hu, C.-Z. Yao, J.-P. Qu and Y.-B. Kang, Pd-^{t}BuONO Cocatalyzed Aerobic Indole Synthesis, *Adv. Synth. Catal.*, 2018, **360**, 1590-1594.