Site-Selective Allylic C-H Amination with Aliphatic Amines

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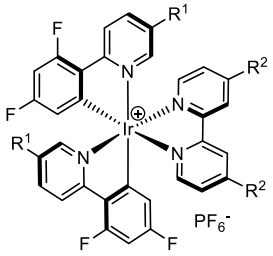
Contents

General Information

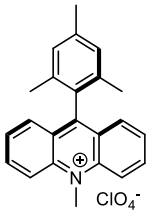
All manipulations were carried out by standard schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 ºC). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million related to internal tetramethyl silane (TMS, 0 ppm for ^{1}H NMR), $CDCl_3$ (77.00 ppm for ^{13}C NMR). All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet), dd (doublet and doublet), dt (doublet and triplet), td (triplet and doublet). Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). High resolution mass spectra (HRMS) were measured with a Bruker UltiMate 3000 & Compact and accurate masses were reported for the molecular ion + Hydrogen (M+H). Enantiomeric excesses were determined with a SHIMADZU LC-20ADXR system using chiral stationary phase columns (DAICEL) by comparing the samples with the corresponding racemic samples. Column and elution details were specified in each entry. All kinds of Iridium photocatalysts were purchased from China Bidepharm company. All cobaloxime catalyst was prepared following literature procedures [32,33].

The catalysts and structures involved in this paper are as follows：

Photocatalyst:

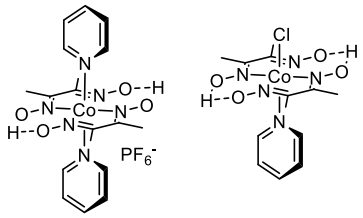


Ir-A : $R^1 = CF_3$, R^2 = dtbpy [Ir(dFCF_3ppy)$_2$(dtbpy)]PF_6
Ir-B : $R^1 = CH_3$, R^2 = dtbpy [Ir(dFMeppy)$_2$(dtbpy)]PF_6
Ir-C : $R^1 = CH_3$, $R^2 = CF_3$ [Ir(dFMeppy)$_2$(dCF_3bpy)]PF_6



Acr$^+$-Mes ClO_4^-

Cobaloxime catalyst:



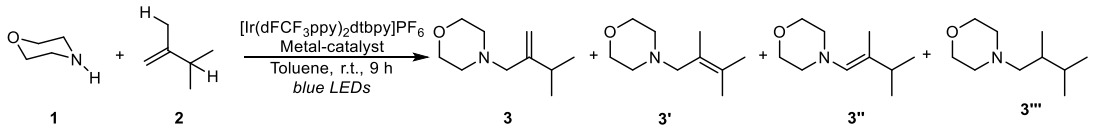
[Co(dmgH)$_2$Py$_2$]PF_6 **Co(dmgH)$_2$ClPy** **Co(dmg) (dmgH)Cl$_2$**

Co(dmgBF$_2$)$_2$(H$_2$O)$_2$: Sol = H_2O
Co(dmgBF$_2$)$_2$(MeOH)$_2$: Sol = MeOH
Co(dmgBF$_2$)$_2$(MeCN)$_2$: Sol = MeCN
Co(dmgBF$_2$)$_2$(Py)$_2$: Sol = Py

Experimental Procedures

Note: All the isolated yield is the average of three individual experiments.

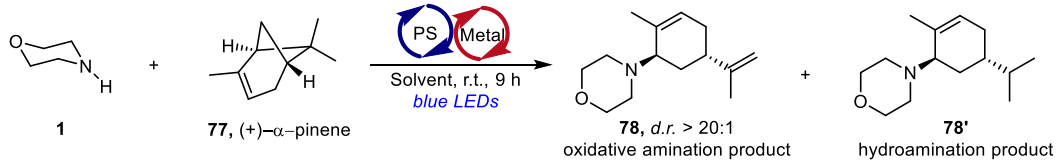
Conditions screening



Entry	Metal-catalyst	Overall yields	Ratio of **3 : 3' : 3'' : 3'''**
1	$[Co(dmgH)_2Py_2]PF_6$	55%	100:0:0:0
2	$Co(dmgH)_2ClPy$	42%	83:17:0:0
3	$Co(dmg)(dmgH)Cl_2$	59%	66:33:0:0
4	$Co(dmgBF_2)_2(H_2O)_2$	23%	100:0:0:0
5	$Pd(MeCN)_4(BF_4)_2$	trace	-
6	$Ni(NTf)_2$	trace	-
7	-	n.d.	-
8[a]	$[Co(dmgH)_2Py_2]PF_6$	n.d.	-
9[b]	$[Co(dmgH)_2Py_2]PF_6$	n.d.	-

Table S1. A solution of morpholine **1** (0.2 mmol, 17.4 mg), 2,3-dimethylbut-1-ene **2** (0.5 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%) and Co-complex (2.5 mol%) in degased toluene (5 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. Then, the pure product was obtained using the purification procedure A. [a]Without Ir-catalyst. [b]Without illumination.

Conditions screening of the synthesis of aminated limonene



Entry	Photocatalyst	Metal-catalyst	Solvent	Overall yields	Ratio of **78:78'**
1	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	Toluene	99%	>20:1
2	Ir-B	$[Co(dmgH)_2Py_2]PF_6$	Toluene	42%	>20:1
3	Ir-C	$[Co(dmgH)_2Py_2]PF_6$	Toluene	35%	>20:1
4	Acr^+-Mes ClO_4^-	$[Co(dmgH)_2Py_2]PF_6$	Toluene	n.d.	-
5	Ir-A	$Co(dmgH)_2ClPy$	Toluene	73%	>20:1
6	Ir-A	$Co(dmg)(dmgH)Cl_2$	Toluene	39%	>20:1
7	Ir-A	$Co(dmgBF_2)_2(H_2O)_2$	Toluene	88%	>20:1
8	Ir-A	$Pd(MeCN)_4(BF_4)_2$	Toluene	18%	1 : 3
9	Ir-A	$Ni(NTf)_2$	Toluene	17%	1 : 5.6
10	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	THF	trace	-
11	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	DCE	trace	-

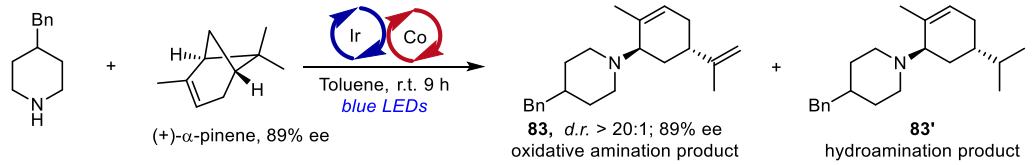
12	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	MeCN	trace	-
13	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	1,4-Dioxane	42%	>20:1
14	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	MeOH	n.d.	-
15	-	$Co(dmgBF_2)_2(H_2O)_2$	Toluene	n.d.	-
16	Ir-A	-	Toluene	n.d.	-
17[a]	Ir-A	$Co(dmgBF_2)_2(H_2O)_2$	Toluene	n.d.	-

Table S2. A solution of morpholine **1** (0.2 mmol, 17.4 mg), (+)-α-pinene **77** (1 mL), photocatalyst (1 mol%) and metal catalyst (5 mol%) in degased solvent (5 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. Then, the pure product was obtained using the purification procedure B. The diastereoselectivity of the product is confirmed by 2D NMR. [a]Without illumination.

When piperidine derivatives or other aliphatic amine were used, the selectivity of oxidative amination (**OA**) and hydroamination (**HA**) decreased significantly under the combination of $[Ir((dFCF_3)ppy)_2(dtbpy)]PF_6$ and $[Co(dmgH)_2Py_2]PF_6$.

Further conditions screening as follow:

When $Co(dmgH)_2ClPy$ or $Co(dmg)(dmgH)Cl_2$ was used, the main product was the aminated product after carbocation ring opening and trace aminated limonene was detected.



Entry	Photocatalyst	Metal-catalyst	Overall yields	Ratio of **83** : **83'**
1	Ir-A	$[Co(dmgH)_2Py_2]PF_6$	42%	2.1 : 1
2	Ir-A	$Co(dmgH)_2ClPy$	trace	-
3	Ir-A	$Co(dmg)\ (dmgH)Cl_2$	trace	-
4	Ir-A	$Co(dmgBF_2)_2(H_2O)_2$	66%	>20:1
5	Ir-A	$Co(dmgBF_2)_2(MeCN)_2$	65%	>20:1
6	Ir-A	$Co(dmgBF_2)_2(Py)_2$	53%	8:1
7	Ir-A	$Co(dmgBF_2)_2(MeOH)_2$	50%	>20:1
8	Ir-B	$Co(dmgBF_2)_2(H_2O)_2$	38%	>20:1

Table S3. A solution of 4-benzylpiperidine (0.2 mmol, 35.2 mg), (+)-α-pinene **77** (1 mL), photocatalyst (1 mol%) and metal catalyst (5 mol%) in degased toluene (5 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. Then, the pure product was obtained using the purification procedure B. HPLC (OJ-H-2%iPropanol-0.5mL-15min, detection at 214 nm): retention time = 7.3 min (major) and 7.9 min (minor).

Procedure A for Photocatalytic Allylic Amination of Unactivated Olefins

A solution of amine (0.2 mmol), olefins (0.5 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) and $[Co(dmgH)_2py_2]PF_6$ (2.5 mol%, 3.0 mg) in degased toluene (6 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. After completion of the reaction, the

solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the specified procedure.

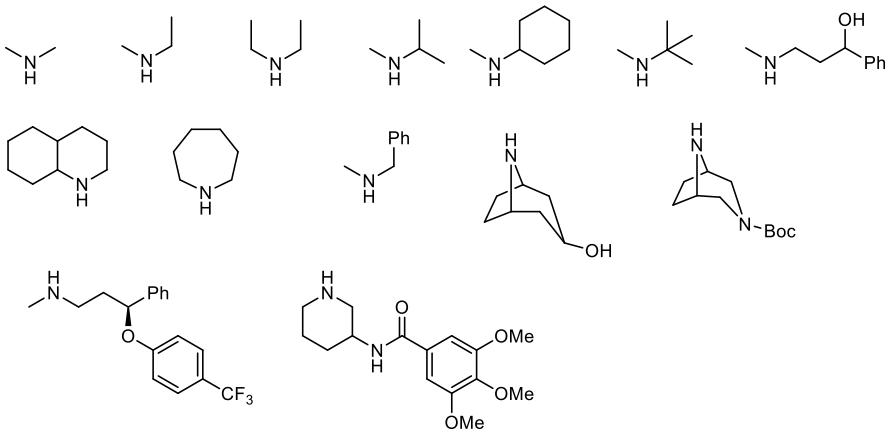
Procedure B for Photocatalytic Allylic Amination of Aryl Olefin

A solution of morpholine (0.2 mmol, 17.4 mg), olefins (0.8 mmol), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) and $[Co(dmgH)_2py_2]PF_6$ (2.5 mol%, 3.0 mg) in degased toluene (6 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the specified procedure.

Procedure C for Photocatalytic Allylic Amination of Unactivated Olefins

A solution of amine (0.2 mmol), olefins (0.5 mL), $[Ir(dFMeppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) and $[Co(dmgH)_2py_2]PF_6$ (2.5 mol%, 3.0 mg) in degased toluene (6 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the specified procedure.

Note: the following amines were used via Procedure C:



Procedure D for Photocatalytic Allylic Amination of Pinene

A solution of amine (0.2 mmol), pinene (1 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) and $Co(dmgBF_2)_2(H_2O)_2$ (5 mol%, 4.6 mg) in degased toluene (5 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 9 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the specified procedure.

Purification Procedure A

After completion the solvent was extracted twice with 0.5 M HCl (20 mL). Then the water phase was collected and excess sodium carbonate were added to slightly basic conditions. The resulting solution was extracted three times with CH_2Cl_2 (20 mL x 3). Then the organic phase was dried over sodium sulfate and concentrated to obtain the named product.

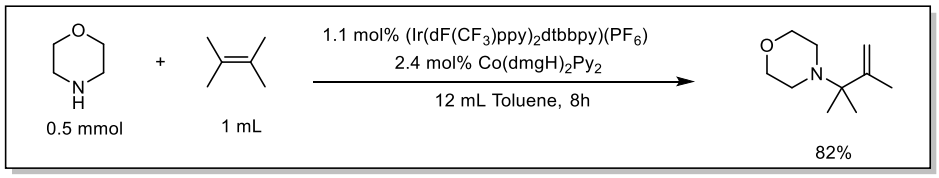
Purification Procedure B

After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on neutral alumina.

Purification Procedure C

After completion the solvent was extracted twice with 0.5 M HCl (20 mL). Then the water phase was collected and excess sodium carbonate were added to slightly basic conditions. The resulting solution was extracted three times with CH_2Cl_2 (20 mL x 3). Then the organic phase was dried over sodium sulfate and added 1 mL 2.0 mol/L HCl (in ethyl acetate). Subsequently the mixture was concentrated to obtain the named product.

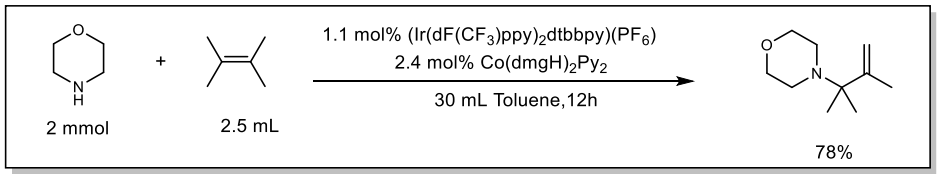
Procedure for Reaction under Sunshine



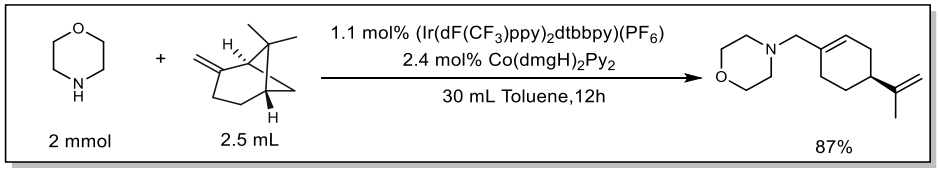
A solution of morpholine (0.5 mmol, 44 uL), 2-methyl-2-butene (1 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 6.25 mg) and $[Co(dmgH)_2py_2]PF_6$ (2.5 mol%, 7.5 mg) in degased toluene (12 mL) were stirred under nitrogen atmosphere and irradiated by sunshine for 8 h (from 9:00 to 17:00). After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the Purification Procedure A. 69.3mg colorless liquid was obtained in 82% yield.

Before the reaction:  After the reaction: 

Procedure for Scale-up Reaction



A solution of morpholine (2 mmol, 174 uL), 2-methyl-2-butene (2.5 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 25 mg) and $[Co(dmgH)_2py_2]PF_6$ (2.5 mol%, 30 mg) in degased toluene (30 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 ºC for 12 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the Purification Procedure A. 263 mg colorless liquid was obtained in 78% yield.



A solution of morpholine (2 mmol, 174 uL), (-)-β-pinene (2.5 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 25 mg) and $Co(dmgBF_2)_2(H_2O)_2$ (5 mol%, 46 mg) in degased toluene (30 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 ºC for 12 h. After completion of

the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained using the Purification Procedure A. 385 mg colorless liquid was obtained in 87% yield.

Mechanistic Study

X-ray fine absorption spectrum (XAFS) for Co

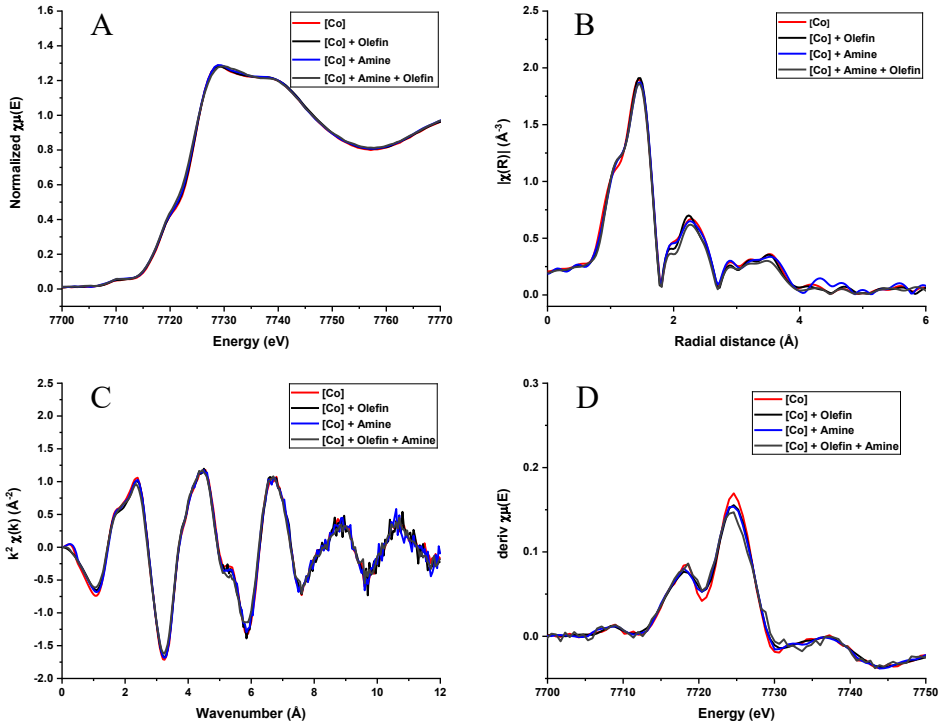


Fig. S1 X-ray absorption fine structure (XAFS) spectrum for $[Co(dmgH)_2py_2]PF_6$. (A) The normalized X-ray absorption near edge structure (XANES). (B) Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectrum. (C) k-space EXAFS spectrum. (D) First derivative XANES spectrum.

[Co]: $[Co(dmgH)_2py_2]PF_6$ (60.8mg, 0.1 mmol) was added to the XAFS solution cell in a glovebox beforehand. Then, 2.0 mL of MeCN was injected into the cell. XAFS spectrum was measured at room temperature.

[Co] + Olefin: $[Co(dmgH)_2py_2]PF_6$ (60.8mg, 0.1 mmol) was added to the XAFS solution cell in a glovebox beforehand. Then, 2.0 mL of MeCN was injected into the cell. Then, tetramethylethylene (98uL, 1mmol) was added into the solution and stirred under N_2 at room temperature for 20 minutes. XAFS spectrum was measured at room temperature.

[Co] + Amine: $[Co(dmgH)_2py_2]PF_6$ (60.8mg, 0.1 mmol) was added to the XAFS solution cell in a glovebox beforehand. Then, 2.0 mL of MeCN was injected into the cell. Then, morpholine (90 uL, 1 mmol) was added into the solution and stirred under N_2 at room temperature for 20 minutes. XAFS spectrum was measured at room temperature.

[Co] + Olefin + Amine: $[Co(dmgH)_2py_2]PF_6$ (60.8mg, 0.1 mmol) was added to the XAFS solution cell in a glovebox beforehand. Then, 2.0 mL of MeCN was injected into the cell. Then, morpholine (90 uL, 1 mmol) and tetramethylethylene (98uL, 1mmol) were added into the solution and stirred under N_2 at room temperature for 20 minutes. XAFS spectrum was measured at room temperature.

The EPR experiments

In-situ illumination experiments:

A solution of morpholine (0.2 mmol, 17.4 mg) and $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) in degassed toluene were placed in resonant cavity and irradiated by 3W blue LEDs at 25 °C for 5 minutes (Fig. S2A). EPR spectra was recorded at room temperature on Bruker A-200 spectrometer operated at 9.823 GHz. Control experiments (Fig. S2B): a solution of $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) in degassed toluene were placed in resonant cavity and irradiated by 3W blue LEDs at 25 °C for 5 minutes. EPR spectra was recorded at room temperature on Bruker A-200 spectrometer operated at 9.823 GHz. There was no radical sign in other control experiments, such as without illumination or without $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$.

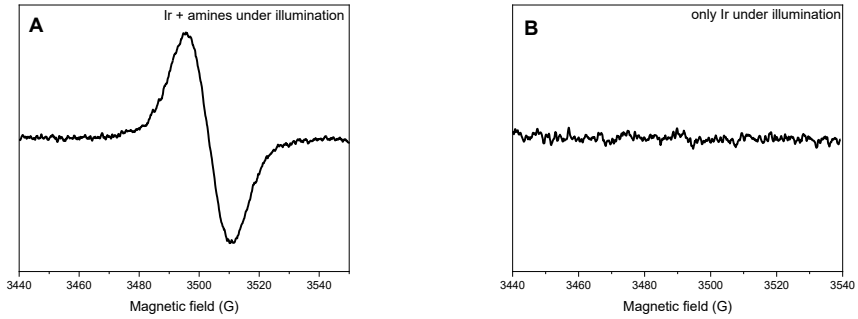


Fig. S2 (A) In-situ illumination experiments. (B) The control experiments

Spin-trapping experiments:

A solution of morpholine (0.2 mmol, 17.4 mg), 2-methyl-2-butene (0.5 mL), $[Ir(dFCF_3ppy)_2dtbpy)]PF_6$ (1 mol%, 2.5 mg) and $[Co(dmgH)_2py_2]PF_6$ (2.5 mol%, 3.0 mg) in degased toluene (6 mL) were stirred under nitrogen atmosphere and irradiated by 3W blue LEDs at 25 °C for 15 minutes. Then 40 uL spin-trapping reagent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was added under nitrogen atmosphere and reacted for two minutes. The mixture was put into a simple melting point tube for EPR test. EPR spectra was recorded at room temperature on Bruker A-200 spectrometer operated at 9.823 GHz. Typical spectrometer parameters were shown as follows, sweep width: 100 G; center field set: 3505G; time constant: 163.84 ms; sweep time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 9.823 GHz; receiver gain: 1.00×10^4; microwave power: 22.10 mW.

A C-centered radical trapped by DMPO was detected (Fig. S3A, g = 2.00648, A_H = 15 G, A_N = 21.46 G) while same radical sign was not detected without irradiation.

The control experiments showed the reaction between morpholine and DMPO which can generate a N-centered radical sign (Fig. S3B, g = 2.00651, A_H = 13.6 G, A_{N1} = 15.6 G, A_{N2} = 2.11 G). The same radical signs were detected in other control experiments.

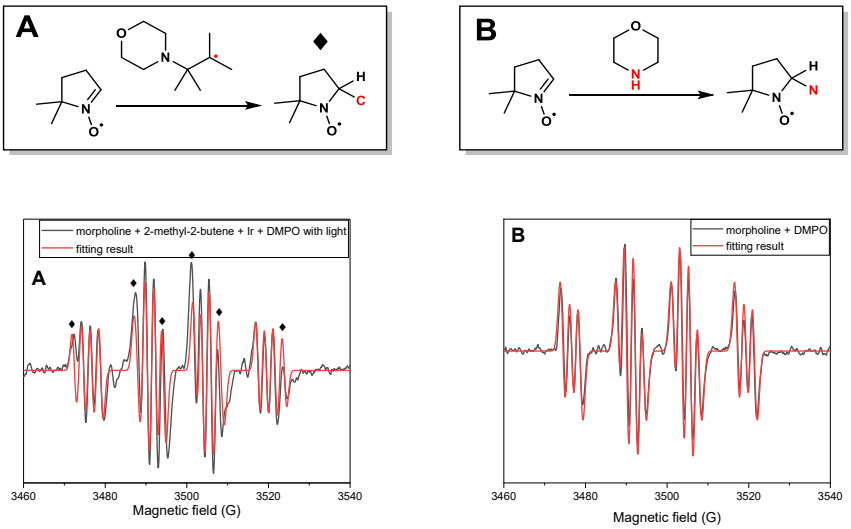


Fig. S3 The EPR experiments with spin-trapping reagents. (A) Spin-trapping experiments for the C-centered radicals. (B) The control experiments.

DFT calculation

Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package[34]. Geometries were optimized using the B3LYP[35,36] functional and Grimme's D3(BJ) dispersion correction[37,38] with a mixed basis set of LANL2DZ for Co and 6-31G(d) for other atoms. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure. Solvation energy corrections were calculated in toluene solvent with the SMD continuum solvation model[39] based on the gas phase optimized geometries. The M06[40] functional with a mixed basis set of SDD for Co and 6-311+G(d,p) for other atoms were used for single-point energy calculations.

3D structures of key transition states

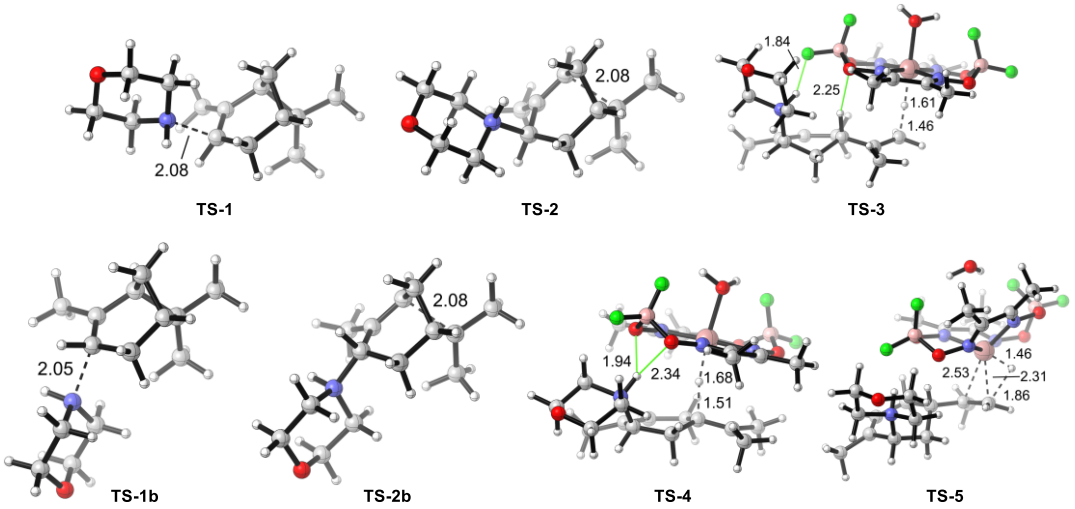


Fig. S4 The optimized 3D structures of key transition states.

Additional computational results

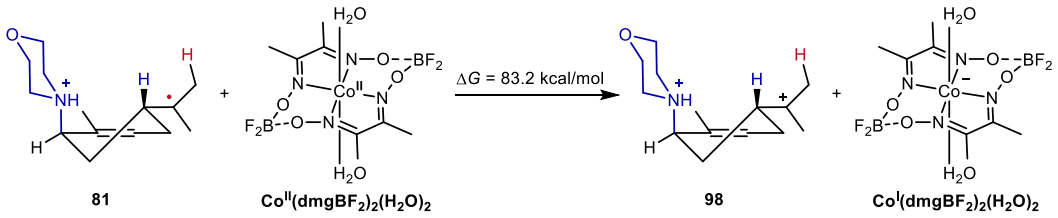


Fig. S5 The oxidation of carbon-centered radical **81** to carbocation **98** using cobaloxime catalyst.

The oxidative dehydrogenation pathway for the C–H cleavage is also considered in DFT calculation. Computational results suggested that the oxidation of carbon-centered radical **81** to carbocation **98** using cobaloxime catalyst is endergonic by 83.2 kcal/mol (Fig. S4). Thus, this possibility is less likely for site-selective C–H cleavage. Another reaction pathway of remote C–H cleavage of α-pinene (**77**) starts from the radical addition of N-centered radical **100** to the C=C double bond of α-pinene (Fig. S5). The radical addition transition state **TS-6** has an activation free energy of 20.5 kcal/mol, which is much higher than that of following ring-opening transition state **TS-7** and HAT transition state **TS-8**. Comparison between **TS-8** and **TS-9** shows that the primary C–H cleavage is also favored in this pathway. However, because the overall activation free energy (20.5 kcal/mol) in this reaction pathway is 10.1 kcal/mol higher than that in Fig. 4B, this possibility could also be ruled out.

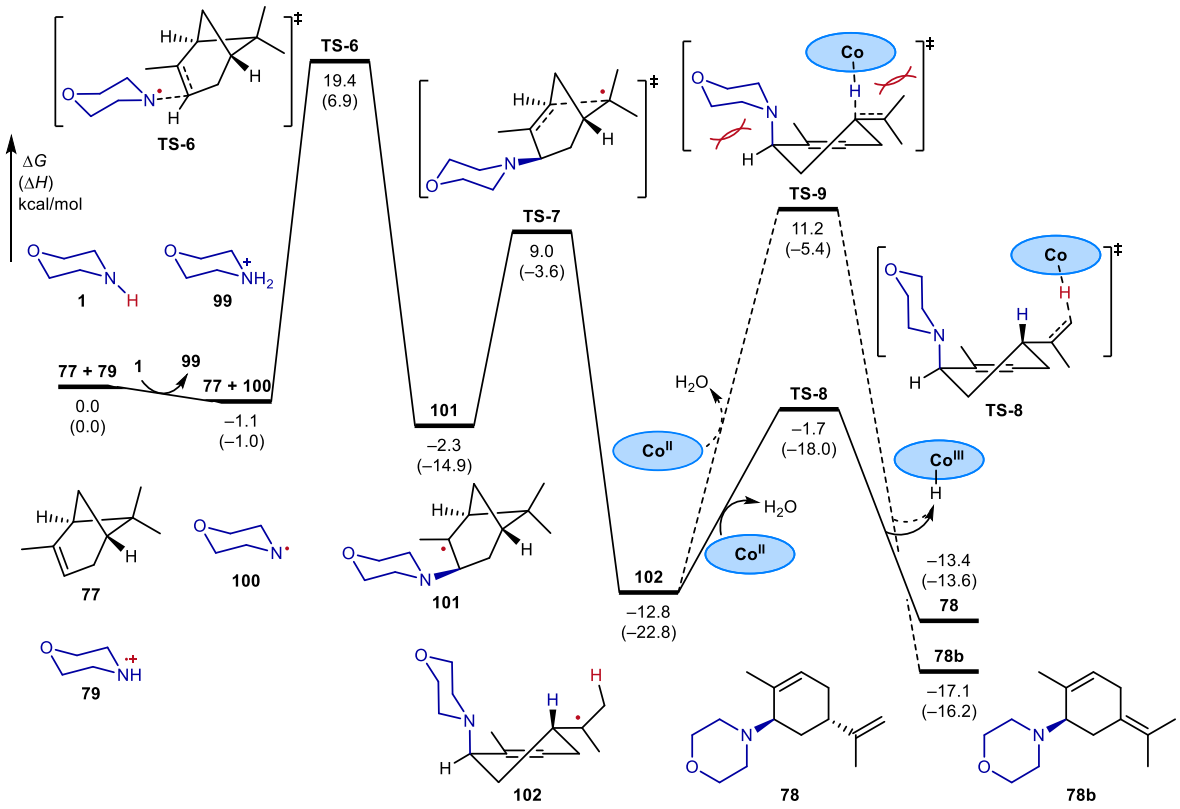


Fig. S6 Free energy profile of another reaction pathway of remote C–H cleavage of α-pinene (**77**).

In the computational study, the site-selectivity of C–H cleavage during the formation of product **8** and **9** has also been calculated. As shown in Fig. S6, the HAT transition states **TS-11** and **TS-10** for primary and secondary C–H cleavage have the same activation free energy. This result is consistent with the experimentally observed ratio between terminal and internal olefins (2.5:1). In another case, only terminal olefin **9** is observed in the experiment. The calculated energy difference between HAT transition states **TS-13** and **TS-12** is 2.9 kcal/mol, which corresponds to a ratio greater than 99:1. Therefore, the computational results are in good accordance with the experimental results. The increased site-selectivity of primary C–H cleavage could be attributed to the greater steric hindrance of isopropyl group. These results also prove that the HAT mechanism is reliable for the cobaloxime promoted site-selective C–H cleavage.

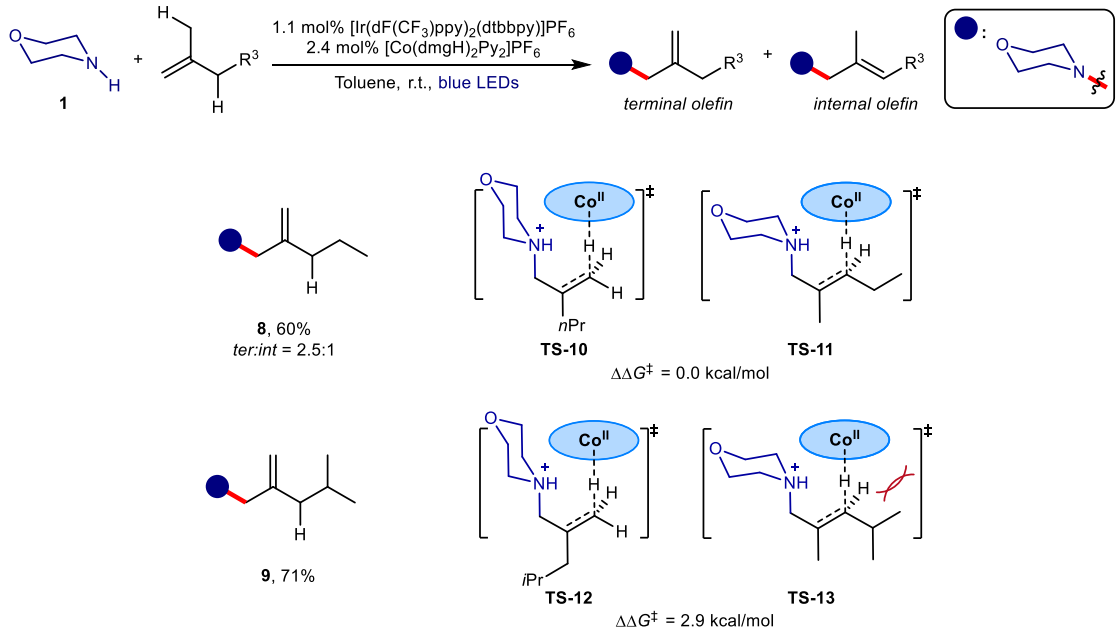


Fig. S7 Calculated site-selectivity of C–H cleavage during the formation of product **8** and **9**.

Cartesian coordinates (Å) and energies of optimized structures

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B3LYP-D3(BJ) SCF energy: -390.70120750 a.u.
B3LYP-D3(BJ) enthalpy: -390.453071 a.u.
B3LYP-D3(BJ) free energy: -390.497457 a.u.
M06 SCF energy in solution: -390.45170252 a.u.
M06 enthalpy in solution: -390.203566 a.u.
M06 free energy in solution: -390.247952 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.081414	-0.329349	0.206698
C	0.870511	1.161372	-0.240697
C	-0.123606	-0.636883	-0.762737
C	0.319501	0.609854	-1.584314
C	-0.288866	1.812930	0.534891
C	-1.440375	-0.282746	-0.090740
C	0.954292	-0.682911	1.687061
C	2.404360	-0.906812	-0.313250
C	-1.506493	0.913569	0.509509
C	-2.567770	-1.270496	-0.143980
H	1.755544	1.807764	-0.264393
H	-0.146553	-1.615942	-1.253149
H	1.104304	0.396265	-2.312150
H	-0.479059	1.179257	-2.068813
H	-0.525881	2.792093	0.092615

H	0.010922	2.016993	1.573917
H	1.775456	-0.230592	2.257669
H	1.019670	-1.769666	1.826153
H	0.010714	-0.347717	2.121197
H	2.583021	-0.697856	-1.371385
H	3.247886	-0.491921	0.252761
H	2.422493	-1.995948	-0.182526
H	-2.416830	1.250390	1.002463
H	-2.281659	-2.218289	0.333481
H	-2.834403	-1.513902	-1.182015
H	-3.463424	-0.892098	0.359527

79

B3LYP-D3(BJ) SCF energy: -287.52827818 a.u.
B3LYP-D3(BJ) enthalpy: -287.386189 a.u.
B3LYP-D3(BJ) free energy: -287.421649 a.u.
M06 SCF energy in solution: -287.44482031 a.u.
M06 enthalpy in solution: -287.302731 a.u.
M06 free energy in solution: -287.338191 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.219880	0.755148	0.228196
C	1.219832	0.755221	0.228191
C	-1.171173	-0.784004	-0.218906
H	-1.278643	0.765983	1.319664
H	-2.084562	1.249551	-0.216982
C	1.171214	-0.783955	-0.218898
H	2.084501	1.249646	-0.216992
H	1.278600	0.766043	1.319660
H	-2.021697	-1.300757	0.228197
H	-1.205254	-0.837682	-1.313312
H	2.021769	-1.300650	0.228213
H	1.205309	-0.837613	-1.313305
N	-0.000033	1.345982	-0.208690
O	0.000037	-1.332157	0.302641
H	-0.000050	1.826394	-1.106951

95

B3LYP-D3(BJ) SCF energy: -678.26752982 a.u.
B3LYP-D3(BJ) enthalpy: -677.874161 a.u.
B3LYP-D3(BJ) free energy: -677.937165 a.u.
M06 SCF energy in solution: -677.91992765 a.u.
M06 enthalpy in solution: -677.526559 a.u.

M06 free energy in solution: -677.589563 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.038075	-0.158132	-0.012023
C	-2.078342	-1.261522	0.553295
C	-1.841750	0.139682	-1.046242
C	-1.447893	-1.355636	-0.856353
C	-1.037658	-0.652609	1.510330
C	-0.853494	1.008565	-0.352028
C	-3.513702	0.967125	0.904258
C	-4.254048	-0.745442	-0.734521
C	-0.489957	2.331102	-0.929910
H	-2.538185	-2.154354	0.985589
H	-2.112099	0.504386	-2.039749
H	-2.002324	-2.003394	-1.533930
H	-0.388287	-1.603434	-0.926603
H	-0.283483	-1.408436	1.770016
H	-1.498440	-0.357605	2.462117
H	-4.224486	0.573009	1.639163
H	-4.036851	1.736346	0.324993
H	-2.708286	1.461128	1.455385
H	-4.007945	-1.557868	-1.421992
H	-4.961567	-1.140639	0.003600
H	-4.771153	0.033099	-1.305519
H	-1.402015	2.914405	-1.119604
H	-0.009425	2.206587	-1.910707
H	0.167006	2.915986	-0.281923
C	-0.395666	0.571204	0.895290
C	2.600422	1.155610	0.233229
C	2.099837	-1.190782	-0.221318
C	4.095835	0.788633	0.215683
H	2.292898	1.464604	-0.769315
H	2.401554	1.970489	0.935313
C	3.617406	-1.458854	-0.218344
H	1.548045	-2.054497	0.159021
H	1.772254	-0.974880	-1.241923
H	4.682642	1.625782	-0.169748
H	4.438608	0.558412	1.237516
H	3.855552	-2.262075	-0.919756
H	3.942994	-1.762483	0.789879
H	0.063255	1.301241	1.555449
N	1.794366	-0.016279	0.606797
O	4.316076	-0.308679	-0.646195
H	1.913067	-0.236083	1.596634

95b

B3LYP-D3(BJ) SCF energy: -678.26408731 a.u.
B3LYP-D3(BJ) enthalpy: -677.871220 a.u.
B3LYP-D3(BJ) free energy: -677.934060 a.u.
M06 SCF energy in solution: -677.91634210 a.u.
M06 enthalpy in solution: -677.523475 a.u.
M06 free energy in solution: -677.586315 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.219263	0.872366	0.571037
C	2.539775	0.815947	-0.959763
C	2.420460	-0.704935	0.540045
C	3.393206	-0.445144	-0.672792
C	1.304183	0.383477	-1.772563
C	1.236722	-1.406183	-0.040811
C	0.875381	1.426391	1.029094
C	3.327479	1.553538	1.382471
C	0.742718	-2.666378	0.578159
H	3.025322	1.686743	-1.408509
H	2.806388	-1.190321	1.439366
H	4.403232	-0.221114	-0.333056
H	3.437342	-1.218794	-1.444019
H	1.579298	0.206929	-2.822107
H	0.545623	1.180580	-1.801115
H	0.834055	2.507902	0.855225
H	0.739477	1.263161	2.104668
H	0.038721	0.965059	0.507460
H	4.333642	1.216622	1.124285
H	3.289769	2.636166	1.215686
H	3.179413	1.376451	2.453391
H	1.560583	-3.394684	0.661435
H	-0.075417	-3.124298	0.015468
H	0.408540	-2.475619	1.607956
C	-2.236560	0.706108	-1.075832
C	-2.205979	-0.621307	0.977522
C	-3.763856	0.881391	-0.877021
H	-1.722853	1.554620	-0.614902
H	-1.983263	0.667207	-2.138836
C	-3.734868	-0.396453	1.081900
H	-1.927718	-1.602437	1.370739
H	-1.694291	0.154415	1.551956
H	-4.079317	1.856747	-1.254628
H	-4.303264	0.091952	-1.423387

H	-4.034582	-0.354117	2.131671
H	-4.270358	-1.222282	0.588000
N	-1.785869	-0.516447	-0.418164
O	-4.072203	0.842519	0.498168
C	0.714599	-0.877479	-1.208234
H	0.037309	-1.466963	-1.816020
H	-2.044089	-1.346974	-0.948195

TS-1

B3LYP-D3(BJ) SCF energy: -678.26746590 a.u.
B3LYP-D3(BJ) enthalpy: -677.874513 a.u.
B3LYP-D3(BJ) free energy: -677.934270 a.u.
M06 SCF energy in solution: -677.92124624 a.u.
M06 enthalpy in solution: -677.528293 a.u.
M06 free energy in solution: -677.588050 a.u.
Imaginary frequency: -47.8404 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.990939	-0.127895	0.021666
C	-2.050361	-1.252796	0.574866
C	-1.822572	0.102467	-1.061545
C	-1.478903	-1.400510	-0.854862
C	-0.953843	-0.665565	1.482928
C	-0.790863	0.962974	-0.421651
C	-3.389811	1.032746	0.930574
C	-4.255318	-0.685120	-0.639477
C	-0.466927	2.293646	-1.008845
H	-2.524489	-2.118484	1.045592
H	-2.118389	0.456030	-2.052013
H	-2.085276	-2.040824	-1.494068
H	-0.434939	-1.695416	-0.963289
H	-0.226162	-1.449632	1.730691
H	-1.373527	-0.335845	2.441072
H	-4.084045	0.680645	1.701794
H	-3.908124	1.808140	0.355279
H	-2.546865	1.510111	1.438996
H	-4.065796	-1.520109	-1.317737
H	-4.947615	-1.038206	0.133558
H	-4.765490	0.099902	-1.207845
H	-1.394208	2.851651	-1.199683
H	0.017962	2.181644	-1.989491
H	0.175255	2.901401	-0.366521
C	-0.277996	0.530476	0.826226

C	2.552067	1.154554	0.302474
C	2.017818	-1.162287	-0.269378
C	4.036379	0.764898	0.278442
H	2.251240	1.508515	-0.686458
H	2.357250	1.939742	1.038724
C	3.527508	-1.447703	-0.274312
H	1.455444	-2.036595	0.067278
H	1.688592	-0.886682	-1.274780
H	4.639528	1.611835	-0.056908
H	4.368891	0.477591	1.289627
H	3.757152	-2.217786	-1.014556
H	3.844626	-1.810702	0.717353
H	0.090179	1.310485	1.489179
N	1.717393	-0.024083	0.622401
O	4.250496	-0.289770	-0.637601
H	1.865652	-0.299989	1.595568

TS-1b

B3LYP-D3(BJ) SCF energy: -678.25853687 a.u.
B3LYP-D3(BJ) enthalpy: -677.865473 a.u.
B3LYP-D3(BJ) free energy: -677.925766 a.u.
M06 SCF energy in solution: -677.91289102 a.u.
M06 enthalpy in solution: -677.519827 a.u.
M06 free energy in solution: -677.580120 a.u.
Imaginary frequency: -125.3119 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	2.471836	0.879721	0.039349
C	2.250481	0.190746	-1.348014
C	2.446896	-0.585774	0.629740
C	2.990953	-1.046402	-0.779571
C	0.765175	-0.173913	-1.573610
C	1.072061	-1.168515	0.714718
C	1.449446	1.882312	0.554837
C	3.865689	1.510768	0.160916
C	0.693712	-2.026237	1.874374
H	2.660676	0.686350	-2.232282
H	3.041790	-0.791467	1.522883
H	4.075296	-0.967121	-0.837335
H	2.687535	-2.036351	-1.131807
H	0.650954	-0.710325	-2.521787
H	0.165875	0.740339	-1.661819
H	1.469399	2.796748	-0.049318

H	1.677907	2.166555	1.588340
H	0.436320	1.489514	0.536316
H	4.675657	0.868360	-0.190902
H	3.900402	2.435539	-0.426041
H	4.074525	1.770735	1.204379
H	1.488738	-2.750222	2.096296
H	-0.236481	-2.581682	1.713778
H	0.580854	-1.417163	2.783366
C	-2.480617	-0.548829	-1.153429
C	-1.905102	0.813936	0.792592
C	-3.958948	-0.338777	-0.800041
H	-2.147184	0.231174	-1.842969
H	-2.319988	-1.526341	-1.617793
C	-3.409497	0.949202	1.071346
H	-1.323163	0.820171	1.717316
H	-1.580983	1.638680	0.154603
H	-4.559397	-0.306208	-1.712076
H	-4.317666	-1.174454	-0.176071
H	-3.615594	1.918839	1.530655
H	-3.738252	0.157310	1.765264
N	-1.642178	-0.449318	0.065784
O	-4.142153	0.894489	-0.135013
C	0.249391	-1.050468	-0.440829
H	-0.264817	-1.964764	-0.734471
H	-1.858792	-1.231529	0.686827

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B3LYP-D3(BJ) SCF energy: -678.27457074 a.u.
B3LYP-D3(BJ) enthalpy: -677.878935 a.u.
B3LYP-D3(BJ) free energy: -677.938651 a.u.
M06 SCF energy in solution: -677.93548200 a.u.
M06 enthalpy in solution: -677.539846 a.u.
M06 free energy in solution: -677.599562 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.876833	-0.018250	0.096952
C	-2.034389	-1.234711	0.610427
C	-1.796318	0.032231	-1.083857
C	-1.618392	-1.494260	-0.855504
C	-0.802505	-0.774385	1.407064
C	-0.602225	0.792755	-0.615401
C	-3.048559	1.207738	0.991779
C	-4.259469	-0.437767	-0.415599

C	-0.309487	2.147108	-1.186512
H	-2.563700	-2.022103	1.155531
H	-2.145872	0.381116	-2.059173
H	-2.354773	-2.078338	-1.406374
H	-0.634652	-1.927516	-1.047967
H	-0.152437	-1.644015	1.573899
H	-1.100905	-0.421804	2.399181
H	-3.703224	0.968908	1.837708
H	-3.522588	2.022727	0.433461
H	-2.113231	1.598813	1.402198
H	-4.236093	-1.308613	-1.074811
H	-4.912635	-0.680948	0.430468
H	-4.724729	0.385958	-0.967878
H	-1.227812	2.608479	-1.568717
H	0.383564	2.105539	-2.042019
H	0.123804	2.832648	-0.448538
C	-0.019605	0.368501	0.696377
C	2.421196	1.160083	0.435646
C	1.840050	-1.079496	-0.418777
C	3.877835	0.704524	0.456569
H	2.174746	1.606375	-0.527105
H	2.201220	1.870456	1.236362
C	3.332636	-1.402409	-0.373741
H	1.239183	-1.963785	-0.206027
H	1.545596	-0.664531	-1.384176
H	4.527914	1.560750	0.264235
H	4.137780	0.290917	1.445907
H	3.574481	-2.093651	-1.183992
H	3.586076	-1.892538	0.581723
H	0.049356	1.235682	1.364492
N	1.509360	-0.030991	0.611950
O	4.116953	-0.243725	-0.562100
H	1.724170	-0.433749	1.532221

80b

B3LYP-D3(BJ) SCF energy: -678.27377372 a.u.
B3LYP-D3(BJ) enthalpy: -677.877983 a.u.
B3LYP-D3(BJ) free energy: -677.937211 a.u.
M06 SCF energy in solution: -677.93490132 a.u.
M06 enthalpy in solution: -677.539111 a.u.
M06 free energy in solution: -677.598339 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	2.583016	0.708024	0.013910
C	2.105084	0.117749	-1.355379
C	2.281388	-0.736433	0.590146
C	2.591088	-1.268341	-0.854270
C	0.566582	0.110552	-1.462113
C	0.820987	-0.917132	0.863566
C	1.852539	1.902315	0.619903
C	4.085340	1.021886	0.011168
C	0.344032	-1.713348	2.037706
H	2.547605	0.533427	-2.265236
H	2.899387	-1.086571	1.421211
H	3.656441	-1.425986	-1.013738
H	2.058592	-2.161849	-1.194445
H	0.264309	-0.256351	-2.448019
H	0.188858	1.133913	-1.370951
H	1.999197	2.796855	0.003248
H	2.249750	2.122987	1.616939
H	0.779585	1.741448	0.730411
H	4.699433	0.228730	-0.421088
H	4.273359	1.935084	-0.565021
H	4.437780	1.195821	1.033770
H	1.037732	-1.616752	2.877507
H	0.276789	-2.790906	1.803099
H	-0.645123	-1.411202	2.414357
C	-2.418952	-0.551031	-1.221225
C	-1.712715	0.847896	0.693699
C	-3.859527	-0.334330	-0.763123
H	-2.111175	0.228430	-1.919288
H	-2.275393	-1.532296	-1.680793
C	-3.192080	0.980900	1.047495
H	-1.070931	0.849588	1.575506
H	-1.405719	1.643896	0.015820
H	-4.519578	-0.321226	-1.632948
H	-4.177643	-1.159278	-0.102891
H	-3.368270	1.955776	1.506695
H	-3.482874	0.202208	1.773459
N	-1.495464	-0.461166	-0.028429
O	-3.998627	0.910634	-0.110632
C	-0.031776	-0.810513	-0.371228
H	-0.154552	-1.817714	-0.802485
H	-1.790338	-1.194106	0.627410

TS-2

B3LYP-D3(BJ) SCF energy: -678.26060773 a.u.

B3LYP-D3(BJ) enthalpy: -677.867435 a.u.
B3LYP-D3(BJ) free energy: -677.927500 a.u.
M06 SCF energy in solution: -677.91597979 a.u.
M06 enthalpy in solution: -677.522807 a.u.
M06 free energy in solution: -677.582872 a.u.
Imaginary frequency: -525.3032 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	3.014974	-0.333903	-0.025219
C	1.897278	-1.329040	0.344160
C	1.591257	0.812700	0.960744
C	1.427414	-0.569710	1.596325
C	0.739809	-1.329105	-0.672220
C	0.709338	1.158969	-0.067231
C	3.261986	0.043384	-1.459370
C	4.270363	-0.394171	0.807939
C	0.727834	2.506666	-0.733046
H	2.244355	-2.359235	0.498993
H	2.100598	1.607339	1.501275
H	2.099068	-0.706578	2.443474
H	0.416372	-0.812185	1.960325
H	0.055910	-2.143139	-0.401593
H	1.102042	-1.567750	-1.675363
H	3.712210	-0.801125	-2.004466
H	3.965543	0.879419	-1.525817
H	2.353587	0.327896	-1.997727
H	4.089651	-0.611716	1.863380
H	4.929758	-1.189281	0.424652
H	4.832574	0.543367	0.742074
H	1.363174	3.204169	-0.180174
H	-0.269612	2.960862	-0.805772
H	1.117469	2.450079	-1.759940
C	-0.026177	0.030088	-0.725747
C	-2.370577	-1.011565	-0.943462
C	-2.147668	1.078616	0.336142
C	-3.699589	-1.239190	-0.225899
H	-2.518254	-0.432891	-1.858381
H	-1.875440	-1.952798	-1.187034
C	-3.483971	0.740331	0.990606
H	-1.478579	1.615900	1.009661
H	-2.295368	1.661690	-0.575218
H	-4.386882	-1.763548	-0.893352
H	-3.545010	-1.865764	0.669110
H	-4.018758	1.664081	1.221246
H	-3.316827	0.195792	1.935695

H	-0.290200	0.289923	-1.754691
N	-1.449356	-0.194348	-0.071433
O	-4.304903	-0.011707	0.119678
H	-1.276287	-0.724836	0.789913

TS-2b

B3LYP-D3(BJ) SCF energy: -678.25177903 a.u.
B3LYP-D3(BJ) enthalpy: -677.858382 a.u.
B3LYP-D3(BJ) free energy: -677.918036 a.u.
M06 SCF energy in solution: -677.90874437 a.u.
M06 enthalpy in solution: -677.515347 a.u.
M06 free energy in solution: -677.575001 a.u.
Imaginary frequency: -550.4695 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	2.686448	0.685424	-0.404019
C	2.141060	-0.507406	-1.213902
C	2.175718	-0.734359	1.028228
C	2.564267	-1.577511	-0.192414
C	0.598424	-0.523879	-1.313191
C	0.806855	-0.542213	1.242391
C	1.930669	1.982485	-0.329965
C	4.184419	0.869187	-0.427616
C	0.217637	-0.165212	2.570844
H	2.564634	-0.598756	-2.222632
H	2.842135	-0.671826	1.885652
H	3.635066	-1.774746	-0.220218
H	2.050241	-2.544871	-0.268882
H	0.296864	-1.256517	-2.068167
H	0.243311	0.451616	-1.653987
H	1.848424	2.449704	-1.324092
H	2.445000	2.696785	0.320483
H	0.917654	1.853638	0.058705
H	4.745030	-0.068295	-0.430691
H	4.475275	1.418979	-1.337292
H	4.521450	1.466492	0.426227
H	1.014059	-0.049607	3.310478
H	-0.455740	-0.944801	2.968378
H	-0.348272	0.778666	2.577005
C	-2.447880	-1.130694	-0.736259
C	-1.711510	1.083941	0.062159
C	-3.879079	-0.693455	-0.432467
H	-2.163102	-0.865975	-1.755877

H	-2.309548	-2.203887	-0.584845
C	-3.180010	1.393489	0.342845
H	-1.043878	1.584457	0.761225
H	-1.453431	1.366445	-0.957406
H	-4.559981	-1.156474	-1.149761
H	-4.169219	-1.024717	0.579325
H	-3.356789	2.461716	0.201264
H	-3.433190	1.139008	1.386344
N	-1.490726	-0.407685	0.185795
O	-4.021606	0.705859	-0.559549
C	-0.043477	-0.913817	0.050631
H	-0.197152	-2.003716	0.045040
H	-1.762159	-0.652273	1.145968

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B3LYP-D3(BJ) SCF energy: -678.28986821 a.u.
B3LYP-D3(BJ) enthalpy: -677.894898 a.u.
B3LYP-D3(BJ) free energy: -677.959022 a.u.
M06 SCF energy in solution: -677.94519434 a.u.
M06 enthalpy in solution: -677.550224 a.u.
M06 free energy in solution: -677.614348 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.979724	-1.156216	-0.067418
C	-1.783466	-0.253007	-0.209953
C	-1.085280	2.156519	-0.713911
C	-2.133095	1.095664	-0.886051
C	-1.055851	0.028626	1.118106
C	-0.008893	2.081255	0.085297
C	-3.947853	-0.947994	1.056323
C	-3.444116	-1.894789	-1.283450
C	0.883779	3.271486	0.344438
H	-1.085675	-0.772066	-0.895179
H	-1.269010	3.093744	-1.237338
H	-3.068357	1.484210	-0.455763
H	-2.346985	0.939114	-1.950283
H	-0.867884	-0.905865	1.657784
H	-1.690645	0.636150	1.770558
H	-4.623058	-1.804556	1.151452
H	-4.589168	-0.062878	0.893963
H	-3.456787	-0.803268	2.025726
H	-2.610490	-2.183691	-1.935812
H	-3.995366	-2.802846	-1.012445

H	-4.134192	-1.289612	-1.898258
H	0.578812	4.126340	-0.264508
H	1.942609	3.080747	0.138275
H	0.819424	3.573978	1.398050
C	0.233694	0.826150	0.895855
C	1.903931	-1.084651	1.199452
C	2.346823	0.521452	-0.611990
C	2.784870	-2.081926	0.450347
H	2.499526	-0.473166	1.881101
H	1.111584	-1.585958	1.756465
C	3.193781	-0.563255	-1.272677
H	1.857922	1.164206	-1.344924
H	2.951825	1.123311	0.067544
H	3.301943	-2.720096	1.170075
H	2.163445	-2.725742	-0.195188
H	4.011831	-0.096238	-1.825130
H	2.582291	-1.139896	-1.987984
H	0.710071	1.081624	1.847203
N	1.266292	-0.129669	0.216824
O	3.773045	-1.416923	-0.307704
H	0.706339	-0.690362	-0.437742

H_2O

B3LYP-D3(BJ) SCF energy: -76.40759806 a.u.
B3LYP-D3(BJ) enthalpy: -76.382681 a.u.
B3LYP-D3(BJ) free energy: -76.404126 a.u.
M06 SCF energy in solution: -76.42222122 a.u.
M06 enthalpy in solution: -76.397304 a.u.
M06 free energy in solution: -76.418749 a.u.

Cartesian coordinates

ATOM	X	Y	Z
O	0.000000	0.000000	0.119426
H	0.000000	0.762602	-0.477706
H	0.000000	-0.762602	-0.477706

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B3LYP-D3(BJ) SCF energy: -677.71625942 a.u.
B3LYP-D3(BJ) enthalpy: -677.331301 a.u.
B3LYP-D3(BJ) free energy: -677.391844 a.u.
M06 SCF energy in solution: -677.37374625 a.u.
M06 enthalpy in solution: -676.988788 a.u.

M06 free energy in solution: -677.049331 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.068650	-1.107532	0.040688
C	1.841160	-0.220766	0.165775
C	1.130715	2.193022	0.602448
C	2.186766	1.144928	0.796467
C	1.082089	0.003278	-1.149708
C	0.038718	2.083974	-0.170525
C	3.585951	-1.472094	-1.136043
C	3.683563	-1.539998	1.348729
C	-0.866577	3.258774	-0.454237
H	1.170805	-0.738221	0.880158
H	1.321992	3.149051	1.087089
H	3.116713	1.520667	0.344030
H	2.407910	1.031494	1.864115
H	0.886862	-0.951482	-1.648167
H	1.699331	0.588743	-1.838853
H	4.473262	-2.095962	-1.184731
H	3.170207	-1.166388	-2.090734
H	2.946100	-2.044297	1.988140
H	4.516841	-2.227708	1.185963
H	4.065818	-0.684709	1.920158
H	-0.551154	4.138404	0.112614
H	-1.918809	3.071672	-0.213750
H	-0.830181	3.519495	-1.520233
C	-0.208754	0.798835	-0.929611
C	-1.870861	-1.132062	-1.136812
C	-2.291922	0.533580	0.625812
C	-2.731977	-2.107878	-0.337990
H	-2.482371	-0.547644	-1.828009
H	-1.085460	-1.647795	-1.690518
C	-3.120101	-0.532467	1.338576
H	-1.794175	1.204364	1.326969
H	-2.912350	1.107847	-0.063605
H	-3.257680	-2.773445	-1.025936
H	-2.095076	-2.725487	0.317980
H	-3.931320	-0.051252	1.888912
H	-2.492494	-1.080209	2.062619
H	-0.703284	1.015999	-1.881118
N	-1.221847	-0.139852	-0.199061
O	-3.710631	-1.422601	0.414294
H	-0.648040	-0.674928	0.464562

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B3LYP-D3(BJ) SCF energy: -677.73116700 a.u.
B3LYP-D3(BJ) enthalpy: -677.346400 a.u.
B3LYP-D3(BJ) free energy: -677.406943 a.u.
M06 SCF energy in solution: -677.38379751 a.u.
M06 enthalpy in solution: -676.999031 a.u.
M06 free energy in solution: -677.059574 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.039124	-1.525216	0.082124
C	1.915735	-0.209662	-0.209996
C	1.531088	2.141515	0.644056
C	2.405122	0.914845	0.684287
C	1.235135	0.329796	-1.450043
C	0.423856	2.282886	-0.099366
C	1.590805	-2.649337	-0.825510
C	2.718424	-2.042975	1.328060
C	-0.365948	3.564080	-0.173807
H	1.863454	2.979176	1.254067
H	3.418870	1.217149	0.373211
H	2.514852	0.594271	1.724939
H	0.964656	-0.445132	-2.166736
H	1.893626	1.027704	-1.979798
H	0.849271	-3.282030	-0.318967
H	1.173787	-2.328830	-1.781455
H	2.110325	-2.823451	1.801311
H	3.671821	-2.515801	1.058771
H	2.931796	-1.278512	2.075567
H	0.041984	4.318003	0.504334
H	-1.424302	3.424901	0.078618
H	-0.338308	3.977281	-1.190574
C	0.003593	1.139947	-0.998490
C	-1.702416	-0.741958	-1.205201
C	-1.864152	0.729210	0.760086
C	-2.465224	-1.795671	-0.406077
H	-2.389896	-0.090665	-1.749880
H	-1.002622	-1.200682	-1.903590
C	-2.611272	-0.403013	1.459958
H	-1.267068	1.316222	1.458472
H	-2.557088	1.381109	0.224687
H	-3.084165	-2.388191	-1.083151
H	-1.753851	-2.474787	0.094237
H	-3.338242	0.018576	2.157214
H	-1.902769	-1.023558	2.034860

H	-0.584003	1.503504	-1.845739
N	-0.924649	0.142478	-0.261851
O	-3.329118	-1.193370	0.533991
H	2.441290	-3.304770	-1.049282
H	-0.251156	-0.458547	0.249433

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B3LYP-D3(BJ) SCF energy: -677.94169573 a.u.
B3LYP-D3(BJ) enthalpy: -677.546767 a.u.
B3LYP-D3(BJ) free energy: -677.610585 a.u.
M06 SCF energy in solution: -677.71079780 a.u.
M06 enthalpy in solution: -677.315869 a.u.
M06 free energy in solution: -677.379687 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.154757	-0.995441	0.108828
C	1.813901	-0.402989	0.221571
C	1.162183	2.042906	0.668935
C	2.161893	0.963861	0.972612
C	1.033521	-0.158681	-1.079964
C	0.086720	1.973336	-0.127464
C	3.955339	-0.868655	-1.117558
C	3.730696	-1.698203	1.260487
C	-0.714654	3.203353	-0.477156
H	1.230583	-0.999067	0.933822
H	1.421238	3.000308	1.118211
H	3.151745	1.344527	0.682294
H	2.223253	0.758450	2.046006
H	0.805762	-1.115838	-1.559523
H	1.638660	0.407690	-1.792808
H	5.011834	-1.100509	-0.971571
H	3.831988	0.104251	-1.606804
H	3.542823	-1.603437	-1.836525
H	3.083401	-1.746800	2.136833
H	3.982563	-2.724421	0.933562
H	4.710375	-1.266190	1.518605
H	-0.372083	4.070308	0.092321
H	-1.787675	3.091351	-0.299331
H	-0.593794	3.435865	-1.543378
C	-0.234151	0.681844	-0.855559
C	-1.967660	-1.180827	-1.087572
C	-2.434395	0.633944	0.527382
C	-2.972702	-2.035455	-0.314532

H	-2.466861	-0.602659	-1.868281
H	-1.179348	-1.791354	-1.530388
C	-3.401550	-0.329991	1.212462
H	-1.963779	1.313213	1.238815
H	-2.940635	1.197438	-0.257682
H	-3.475013	-2.709746	-1.011760
H	-2.451268	-2.649481	0.440108
H	-4.222644	0.243255	1.648406
H	-2.891161	-0.869698	2.028997
H	-0.679628	0.917705	-1.825750
N	-1.328557	-0.163263	-0.151837
O	-3.960095	-1.230867	0.283888
H	-0.873055	-0.689394	0.602736

TS-3

B3LYP-D3(BJ) SCF energy: -2181.25631206 a.u.
B3LYP-D3(BJ) enthalpy: -2180.571242 a.u.
B3LYP-D3(BJ) free energy: -2180.687592 a.u.
M06 SCF energy in solution: -2181.31237317 a.u.
M06 enthalpy in solution: -2180.627303 a.u.
M06 free energy in solution: -2180.743653 a.u.
Imaginary frequency: -1597.1984 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	-1.865474	-0.049454	-0.343098
N	-0.482160	-1.338772	-0.333223
O	0.773515	-1.130146	-0.810964
C	-0.785416	-2.484430	0.192126
C	0.149894	-3.647368	0.264176
H	0.952082	-3.526568	-0.464805
H	-0.380416	-4.581693	0.061773
H	0.590528	-3.735785	1.266131
N	-2.818823	-1.429460	0.529738
O	-4.069623	-1.307919	0.984887
C	-2.163736	-2.536494	0.721679
C	-2.731680	-3.741691	1.397841
H	-3.750187	-3.534477	1.725472
H	-2.126450	-4.026366	2.266539
H	-2.749994	-4.597604	0.713110
N	-3.175319	1.300921	-0.151398
O	-4.376144	1.114256	0.406676
C	-2.812958	2.506039	-0.489026
C	-3.692886	3.703576	-0.336720

H	-4.739177	3.393132	-0.347809
H	-3.516158	4.428858	-1.135049
H	-3.505522	4.205663	0.621379
N	-0.849445	1.397764	-1.006599
O	0.465064	1.310991	-1.336048
C	-1.427336	2.562439	-0.992082
C	-0.764441	3.836780	-1.403272
H	-0.701728	4.532278	-0.557704
H	-1.345233	4.334682	-2.187418
H	0.238550	3.635325	-1.778725
O	-2.512601	-0.859017	-2.207803
H	-2.104331	-0.433828	-2.978384
H	-3.480018	-0.708489	-2.207458
B	0.871981	-0.028884	-1.838737
F	2.261332	0.090492	-2.021532
F	0.174387	-0.362062	-2.973146
B	-4.920504	-0.289263	0.250873
F	-6.135858	-0.309119	0.831381
F	-4.913088	-0.604339	-1.119513
C	0.396972	0.300427	2.566463
C	1.624375	0.731758	1.788310
C	3.063901	2.742852	1.149408
C	1.699162	2.248537	1.532902
C	2.960148	0.240096	2.369010
C	4.191551	2.018297	1.099886
C	-0.817324	0.933376	2.358539
C	0.437414	-1.008097	3.301070
C	5.547263	2.666756	0.947904
H	1.498294	0.245582	0.810763
H	3.136520	3.814904	0.973348
H	1.400240	2.789823	2.443154
H	0.981920	2.532677	0.757638
H	2.926243	-0.818806	2.628793
H	3.190174	0.774142	3.298241
H	-1.668310	0.649628	2.975331
H	-1.327872	0.393317	1.107123
H	-0.840079	1.964394	2.012689
H	1.105608	-0.966578	4.171447
H	-0.556131	-1.292259	3.657716
H	0.811975	-1.820950	2.660833
H	5.444604	3.743264	0.788177
H	6.147914	2.265459	0.125800
H	6.137792	2.522674	1.862866
C	4.118548	0.534619	1.408348
C	3.822843	-1.778762	0.385383
C	5.193396	-0.083072	-0.805028

C	3.880158	-2.595141	-0.903113
H	4.623874	-2.071804	1.069023
H	2.854033	-1.905398	0.864645
C	5.168278	-1.023738	-2.007310
H	5.153281	0.955223	-1.130232
H	6.088118	-0.251403	-0.200972
H	3.840393	-3.656466	-0.645286
H	3.017833	-2.350281	-1.536830
H	6.103865	-0.905255	-2.558837
H	4.330893	-0.772587	-2.669265
H	5.060774	0.190282	1.847139
N	4.006113	-0.305245	0.108200
O	5.093611	-2.374219	-1.590989
H	3.183662	0.007971	-0.434140

TS-4

B3LYP-D3(BJ) SCF energy: -2181.24555955 a.u.
B3LYP-D3(BJ) enthalpy: -2180.561309 a.u.
B3LYP-D3(BJ) free energy: -2180.678503 a.u.
M06 SCF energy in solution: -2181.29947356 a.u.
M06 enthalpy in solution: -2180.615223 a.u.
M06 free energy in solution: -2180.732417 a.u.
Imaginary frequency: -1303.0134 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	-1.165244	-0.146521	-0.682148
N	-0.327275	-1.831913	-0.619009
O	0.912561	-2.076260	-1.117677
C	-0.991037	-2.777653	-0.031458
C	-0.513842	-4.185906	0.105099
H	0.404676	-4.328462	-0.464059
H	-1.274934	-4.882734	-0.261106
H	-0.327951	-4.435235	1.157456
N	-2.520565	-1.062276	0.274920
O	-3.664949	-0.507865	0.695689
C	-2.299131	-2.324094	0.491534
C	-3.262744	-3.246122	1.163427
H	-4.132141	-2.688191	1.510362
H	-2.794013	-3.755103	2.012970
H	-3.600879	-4.019958	0.464012
N	-1.929692	1.579036	-0.601631
O	-3.070673	1.854459	0.048886
C	-1.227785	2.550966	-1.110115

C	-1.636691	3.986695	-1.078336
H	-2.664492	4.069168	-0.724406
H	-1.561192	4.436942	-2.073503
H	-0.986456	4.563246	-0.407885
N	0.204559	0.796318	-1.557132
O	1.373115	0.228641	-1.957900
C	0.049283	2.080336	-1.680030
C	1.066245	2.992321	-2.282163
H	1.627813	3.505046	-1.490348
H	0.589858	3.760583	-2.897028
H	1.766350	2.421528	-2.893662
O	-2.202635	-0.831241	-2.437161
H	-1.663440	-0.741435	-3.239564
H	-3.023786	-0.306112	-2.502536
B	1.257879	-1.247067	-2.332340
F	2.544140	-1.611878	-2.645435
F	0.320633	-1.395366	-3.326992
B	-4.105141	0.744035	-0.035952
F	-5.202852	1.191116	0.607990
F	-4.286440	0.438664	-1.390628
C	-1.000519	-0.160110	2.944181
C	0.009284	0.473888	2.203226
C	1.240466	2.636102	1.671709
C	-0.033733	1.995145	2.114815
C	1.417165	-0.119245	2.353193
C	2.436487	2.060556	1.469709
C	-0.835064	-1.562930	3.457792
C	-2.290466	0.531425	3.263063
C	3.666033	2.943730	1.369563
H	-0.415290	0.148418	0.790190
H	1.200052	3.723994	1.633747
H	-0.252192	2.411331	3.110598
H	-0.865881	2.327893	1.490278
H	1.386714	-1.180318	2.105142
H	1.662461	-0.081585	3.421944
H	-1.799755	-2.001111	3.725243
H	-0.209485	-1.582570	4.363842
H	-0.348417	-2.224047	2.731092
H	-2.512898	1.360615	2.590548
H	-3.133928	-0.162277	3.220538
H	-2.254105	0.931306	4.289690
H	3.390253	3.988992	1.530184
H	4.198945	2.896514	0.416519
H	4.389662	2.676695	2.150673
C	2.608023	0.561763	1.639241
C	3.939781	0.462331	-0.609884

C	3.446461	-1.615655	0.554082
C	5.358305	0.380366	-0.061540
H	3.865015	-0.107445	-1.535818
H	3.597773	1.474119	-0.803913
C	4.892335	-1.622597	1.037292
H	2.785127	-2.122416	1.253989
H	3.362172	-2.102244	-0.417364
H	6.044340	0.811924	-0.794175
H	5.468469	0.940116	0.878198
H	5.229499	-2.659747	1.104471
H	4.984171	-1.175326	2.040504
H	3.495121	0.399527	2.256469
N	2.948499	-0.196041	0.332216
O	5.745809	-0.968902	0.121264
H	2.083674	-0.257622	-0.224995

TS-5

B3LYP-D3(BJ) SCF energy: -2181.21291553 a.u.
B3LYP-D3(BJ) enthalpy: -2180.525318 a.u.
B3LYP-D3(BJ) free energy: -2180.638764 a.u.
M06 SCF energy in solution: -2181.27485047 a.u.
M06 enthalpy in solution: -2180.587253 a.u.
M06 free energy in solution: -2180.700699 a.u.
Imaginary frequency: -84.5606 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	-1.434119	-0.079047	-0.687729
N	-0.357481	1.474243	-0.426953
O	0.919489	1.357461	0.078854
C	-0.980542	2.606934	-0.294541
C	-0.391086	3.866550	0.237178
H	0.688167	3.782565	0.347587
H	-0.831903	4.062147	1.220836
H	-0.637065	4.708629	-0.416638
N	-2.802915	1.280730	-0.748753
O	-4.066974	1.071327	-1.105464
C	-2.399894	2.512303	-0.637285
C	-3.304234	3.694378	-0.722975
H	-3.515707	4.043988	0.295172
H	-4.244261	3.417661	-1.198485
H	-2.838205	4.512451	-1.279952
N	-2.745411	-1.398115	-0.357026
O	-3.928113	-1.385516	-1.017321

C	-2.679219	-2.060418	0.760519
C	-3.764245	-2.959181	1.251489
H	-4.404872	-3.255035	0.420648
H	-4.386544	-2.417900	1.973367
H	-3.349605	-3.843548	1.743001
N	-0.817625	-0.740081	1.093072
O	0.342618	-0.437270	1.720039
C	-1.482317	-1.758969	1.556914
C	-1.123046	-2.516761	2.794090
H	-0.311048	-2.018891	3.322601
H	-0.813907	-3.540212	2.547970
H	-1.991071	-2.593138	3.456947
O	-2.702757	2.038307	2.167588
H	-1.872500	1.649889	2.482559
H	-3.273093	1.293169	1.913498
B	0.917021	0.924316	1.511576
F	2.282520	0.782315	1.804000
F	0.259098	1.836323	2.305664
B	-4.717029	-0.178755	-0.550835
F	-5.957802	-0.254038	-1.067585
F	-4.641525	-0.096457	0.847064
C	0.192211	-1.808746	-1.549616
C	1.531237	-1.629409	-0.826829
C	3.302533	-2.845566	0.558252
C	1.845410	-2.715174	0.217825
C	2.710356	-1.502346	-1.816912
C	4.319031	-2.190392	-0.019045
C	-0.230697	-0.884736	-2.483878
C	-0.489156	-3.150885	-1.506889
C	5.759000	-2.581220	0.212310
H	1.464896	-0.677626	-0.308612
H	3.537172	-3.616423	1.290273
H	1.532066	-3.703515	-0.142084
H	1.272220	-2.526843	1.129856
H	2.488108	-0.776669	-2.601422
H	2.895026	-2.456132	-2.324085
H	-1.727846	0.142452	-2.100315
H	-0.934430	-1.189841	-3.252560
H	0.365852	-0.007130	-2.713523
H	-0.701438	-3.479731	-0.485226
H	-1.428803	-3.138114	-2.062137
H	0.166144	-3.909759	-1.955072
H	5.831354	-3.358352	0.977698
H	6.402536	-1.750714	0.518580
H	6.191887	-2.985829	-0.712578
C	4.006203	-1.147466	-1.073847

C	3.680294	1.340784	-1.485253
C	5.151307	0.605770	0.371112
C	3.734850	2.733225	-0.860580
H	4.456890	1.221985	-2.245244
H	2.698060	1.166051	-1.919376
C	5.092441	2.042700	0.879696
H	5.180416	-0.098573	1.201387
H	6.017230	0.459840	-0.278564
H	3.657077	3.476996	-1.657414
H	2.887782	2.859277	-0.173606
H	6.030909	2.273452	1.388825
H	4.264684	2.155859	1.592375
H	4.834341	-1.064748	-1.785137
N	3.925052	0.269441	-0.449096
O	4.961331	2.951909	-0.196470
H	3.141412	0.293980	0.224579

$Co^{II}(dmgBF_2)_2(H_2O)_2$

B3LYP-D3(BJ) SCF energy: -1579.36719541 a.u.
B3LYP-D3(BJ) enthalpy: -1579.047643 a.u.
B3LYP-D3(BJ) free energy: -1579.132180 a.u.
M06 SCF energy in solution: -1579.79422009 a.u.
M06 enthalpy in solution: -1579.474668 a.u.
M06 free energy in solution: -1579.559205 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Co	0.000021	-0.000042	-0.000575
N	1.282139	1.378294	-0.256123
O	2.578920	1.162282	-0.554419
C	0.822902	2.591334	-0.179852
C	1.665465	3.813525	-0.352161
H	2.719829	3.535588	-0.337543
H	1.465064	4.536188	0.445488
H	1.448425	4.308587	-1.307301
N	-1.187991	1.476548	0.149163
O	-2.488324	1.364689	0.471899
C	-0.631198	2.648389	0.098532
C	-1.365785	3.927494	0.337005
H	-2.438495	3.758545	0.232890
H	-1.043672	4.703753	-0.363695
H	-1.175558	4.295624	1.353426
N	-1.282132	-1.378393	0.255527
O	-2.578792	-1.162287	0.554302

C	-0.822681	-2.591423	0.180256
C	-1.664853	-3.813684	0.353956
H	-2.719264	-3.535853	0.341469
H	-1.445791	-4.309051	1.308469
H	-1.465986	-4.536105	-0.444323
N	1.187965	-1.476557	-0.149848
O	2.488365	-1.364686	-0.472314
C	0.631409	-2.648470	-0.098244
C	1.366235	-3.927652	-0.335522
H	2.438917	-3.758360	-0.231681
H	1.175969	-4.296864	-1.351540
H	1.044364	-4.703272	0.365998
O	-0.419512	-0.208851	-2.236682
H	-1.393169	-0.105868	-2.154359
H	-0.105590	0.587007	-2.692511
O	0.418919	0.209815	2.235728
H	1.392372	0.103528	2.155188
H	0.101391	-0.584101	2.692452
B	3.147284	-0.106656	0.034308
F	4.445288	-0.164039	-0.347049
F	2.968387	-0.056031	1.438228
B	-3.147411	0.106621	-0.034515
F	-4.445249	0.164001	0.347322
F	-2.968891	0.055841	-1.438370

$CoH(dmgBF_2)_2H_2O$

B3LYP-D3(BJ) SCF energy: -1503.50109091 a.u.
B3LYP-D3(BJ) enthalpy: -1503.199740 a.u.
B3LYP-D3(BJ) free energy: -1503.282027 a.u.
M06 SCF energy in solution: -1503.92409711 a.u.
M06 enthalpy in solution: -1503.622746 a.u.
M06 free energy in solution: -1503.705033 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Co	-0.000333	-0.002626	-0.196776
N	-1.256494	-1.404592	-0.320321
O	-2.585791	-1.235223	-0.318111
C	-0.746666	-2.590668	-0.452076
C	-1.562633	-3.835445	-0.583193
H	-2.611584	-3.610261	-0.390426
H	-1.218871	-4.600422	0.120731
H	-1.471872	-4.251910	-1.594061
N	1.246777	-1.413050	-0.320069

O	2.577140	-1.252053	-0.315946
C	0.728971	-2.595647	-0.452214
C	1.534844	-3.847358	-0.580602
H	2.593984	-3.617730	-0.465727
H	1.375066	-4.310801	-1.561639
H	1.238801	-4.577476	0.180578
N	1.251226	1.417104	-0.272243
O	2.579108	1.249995	-0.338231
C	0.745031	2.607358	-0.402342
C	1.572384	3.838806	-0.579155
H	2.600376	3.637851	-0.275506
H	1.169919	4.669890	0.007360
H	1.580193	4.148342	-1.632119
N	-1.242547	1.426341	-0.273004
O	-2.571512	1.266661	-0.337092
C	-0.727502	2.612982	-0.402695
C	-1.541406	3.854173	-0.574927
H	-2.592130	3.634673	-0.385125
H	-1.443540	4.239814	-1.597404
H	-1.203289	4.640755	0.107432
O	-0.001023	-0.262150	1.827833
H	-0.816287	0.129143	2.193493
H	0.815948	0.125240	2.193777
B	-3.071560	0.024811	0.358134
F	-4.420727	0.026443	0.249168
F	-2.600126	0.052306	1.684012
B	3.071357	0.005398	0.358530
F	4.420464	-0.002082	0.249301
F	2.600285	0.038076	1.684356
H	-0.000031	0.046379	-1.658218

$Co^{I}(dmgBF_2)_2(H_2O)_2$

B3LYP-D3(BJ) SCF energy: -1579.41532245 a.u.
B3LYP-D3(BJ) enthalpy: -1579.097575 a.u.
B3LYP-D3(BJ) free energy: -1579.185971 a.u.
M06 SCF energy in solution: -1579.89069713 a.u.
M06 enthalpy in solution: -1579.572950 a.u.
M06 free energy in solution: -1579.661346 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Co	-0.066393	0.037301	0.294754
N	1.217118	-1.312744	0.304772
O	2.522398	-1.146809	0.657170

C	0.782518	-2.537144	0.095357
C	1.670263	-3.742749	0.108608
H	2.711153	-3.416218	0.114041
H	1.491439	-4.368065	-0.773506
H	1.500342	-4.367688	0.996385
N	-1.188803	-1.383074	-0.168921
O	-2.515221	-1.296814	-0.471565
C	-0.637438	-2.578079	-0.195794
C	-1.392226	-3.816826	-0.563244
H	-2.436688	-3.715290	-0.258637
H	-0.956206	-4.702119	-0.090155
H	-1.381579	-3.975934	-1.650403
N	-1.266255	1.374168	-0.221392
O	-2.589677	1.205220	-0.499282
C	-0.778156	2.590818	-0.292448
C	-1.604519	3.784291	-0.657999
H	-2.645894	3.603581	-0.382561
H	-1.576702	3.973760	-1.740157
H	-1.242685	4.684909	-0.151974
N	1.153538	1.445300	0.213972
O	2.466195	1.365991	0.557574
C	0.649065	2.633929	-0.022565
C	1.464779	3.889245	-0.023458
H	2.519850	3.628375	-0.122177
H	1.341549	4.451428	0.912757
H	1.172798	4.549225	-0.847626
O	-0.588261	0.037322	2.470213
H	-1.546209	0.011698	2.240715
H	-0.349142	-0.885422	2.648476
O	0.806690	-0.512362	-2.827781
H	1.658627	-0.350891	-2.384661
H	0.185072	-0.329483	-2.099989
B	3.148092	0.106209	0.123065
F	4.414828	0.154490	0.654119
F	3.160335	0.048924	-1.283240
B	-3.167170	-0.057957	0.032355
F	-4.475437	-0.100758	-0.370380
F	-3.067460	-0.043447	1.463239

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B3LYP-D3(BJ) SCF energy: -287.80841826 a.u.
B3LYP-D3(BJ) enthalpy: -287.666031 a.u.
B3LYP-D3(BJ) free energy: -287.700644 a.u.
M06 SCF energy in solution: -287.68645786 a.u.

M06 enthalpy in solution: -287.544071 a.u.
M06 free energy in solution: -287.578684 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.207462	0.710125	0.201016
C	1.198117	0.725599	0.200773
C	-1.167235	-0.762909	-0.198996
H	-1.279481	0.770520	1.303578
H	-2.097191	1.187721	-0.225817
C	1.177175	-0.747972	-0.198761
H	2.081470	1.214752	-0.226214
H	1.269567	0.786971	1.303315
H	-2.012498	-1.309583	0.229083
H	-1.207845	-0.842004	-1.297531
H	2.029421	-1.283637	0.229477
H	1.218822	-0.826756	-1.297259
N	-0.008961	1.363484	-0.327668
O	0.009025	-1.392912	0.292319
H	-0.015312	2.351865	-0.087700

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B3LYP-D3(BJ) SCF energy: -288.18108608 a.u.
B3LYP-D3(BJ) enthalpy: -288.023575 a.u.
B3LYP-D3(BJ) free energy: -288.058498 a.u.
M06 SCF energy in solution: -288.10652043 a.u.
M06 enthalpy in solution: -287.949009 a.u.
M06 free energy in solution: -287.983932 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.258891	-0.664912	-0.233120
C	1.262909	-0.657311	-0.233129
C	-1.174238	0.794307	0.208253
H	-1.278109	-0.746698	-1.321762
H	-2.114742	-1.190332	0.196714
C	1.169388	0.801352	0.208265
H	2.121915	-1.177539	0.196726
H	1.282634	-0.738983	-1.321769
H	-2.028331	1.341661	-0.195676
H	-1.208875	0.865758	1.308027
H	2.020166	1.353850	-0.195651
H	1.203590	0.872978	1.308040
N	0.004177	-1.379213	0.226646

O	-0.004242	1.401670	-0.300443
H	0.007105	-2.347766	-0.112549
H	0.004337	-1.432411	1.253303

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B3LYP-D3(BJ) SCF energy: -287.15375386 a.u.
B3LYP-D3(BJ) enthalpy: -287.025622 a.u.
B3LYP-D3(BJ) free energy: -287.061013 a.u.
M06 SCF energy in solution: -287.02750684 a.u.
M06 enthalpy in solution: -286.899375 a.u.
M06 free energy in solution: -286.934766 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.178838	0.780372	-0.190558
C	-1.178838	0.780371	-0.190558
C	1.168998	-0.719129	0.195089
H	1.202765	0.837640	-1.292183
H	2.079832	1.263285	0.205221
C	-1.168998	-0.719129	0.195089
H	-2.079832	1.263285	0.205221
H	-1.202765	0.837640	-1.292183
H	2.021770	-1.237471	-0.251972
H	1.228590	-0.813922	1.290525
H	-2.021770	-1.237471	-0.251972
H	-1.228590	-0.813922	1.290525
N	0.000000	1.421791	0.342878
O	0.000000	-1.348314	-0.294712

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B3LYP-D3(BJ) SCF energy: -677.84841029 a.u.
B3LYP-D3(BJ) enthalpy: -677.470666 a.u.
B3LYP-D3(BJ) free energy: -677.530285 a.u.
M06 SCF energy in solution: -677.46805596 a.u.
M06 enthalpy in solution: -677.090312 a.u.
M06 free energy in solution: -677.149931 a.u.
Imaginary frequency: -379.4609 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.962625	-0.126093	0.023195
C	-2.007309	-1.234551	0.592822

C	-1.804725	0.105068	-1.040154
C	-1.446745	-1.393865	-0.844124
C	-0.914487	-0.627447	1.493255
C	-0.748126	0.973614	-0.404331
C	-3.378230	1.031973	0.928535
C	-4.228361	-0.713349	-0.613270
C	-0.397279	2.278528	-1.046128
H	-2.478936	-2.101776	1.069507
H	-2.094898	0.452055	-2.037666
H	-2.052752	-2.054827	-1.466195
H	-0.400055	-1.670655	-0.954460
H	-0.170784	-1.388051	1.757271
H	-1.356567	-0.290814	2.440820
H	-4.037592	0.670926	1.727970
H	-3.938161	1.782645	0.356485
H	-2.528871	1.536494	1.393620
H	-4.028850	-1.555500	-1.280952
H	-4.915541	-1.065730	0.166333
H	-4.754232	0.054083	-1.194591
H	-1.304788	2.836677	-1.318243
H	0.166275	2.133673	-1.981283
H	0.207733	2.910114	-0.388474
C	-0.229297	0.556892	0.818430
C	2.511751	1.113459	0.292806
C	1.977551	-1.103832	-0.295114
C	4.002727	0.738595	0.338257
H	2.290451	1.472220	-0.727583
H	2.317507	1.934950	0.994827
C	3.476314	-1.457907	-0.254092
H	1.399632	-1.995774	-0.027330
H	1.723951	-0.816037	-1.330695
H	4.626086	1.580802	0.022147
H	4.276954	0.455574	1.367114
H	3.713524	-2.219650	-1.003345
H	3.727174	-1.848097	0.745324
H	0.173162	1.319641	1.479200
N	1.731780	-0.051280	0.671354
O	4.276270	-0.327564	-0.556225

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B3LYP-D3(BJ) SCF energy: -677.87981235 a.u.
B3LYP-D3(BJ) enthalpy: -677.499459 a.u.
B3LYP-D3(BJ) free energy: -677.558948 a.u.
M06 SCF energy in solution: -677.50546912 a.u.

M06 enthalpy in solution: -677.125116 a.u.
M06 free energy in solution: -677.184605 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.878654	0.019367	0.192369
C	-2.026221	-1.221209	0.623123
C	-1.903302	0.067604	-1.061288
C	-1.739149	-1.472948	-0.876877
C	-0.716967	-0.811406	1.313710
C	-0.623634	0.750950	-0.707630
C	-2.951305	1.237775	1.110904
C	-4.309314	-0.364813	-0.205612
C	-0.161633	1.969240	-1.440212
H	-2.539805	-2.005547	1.192426
H	-2.326615	0.437099	-2.001917
H	-2.522956	-2.044553	-1.377717
H	-0.769753	-1.901241	-1.142370
H	-0.060804	-1.685925	1.379356
H	-0.914976	-0.503215	2.346768
H	-3.545709	1.008341	2.004483
H	-3.443399	2.072376	0.595923
H	-1.974015	1.590406	1.444886
H	-4.354749	-1.227704	-0.875351
H	-4.899379	-0.608125	0.687213
H	-4.804020	0.473978	-0.710730
H	-0.923673	2.322290	-2.144400
H	0.757533	1.793121	-2.022183
H	0.071246	2.797735	-0.752950
C	0.057764	0.334235	0.582016
C	2.414808	1.130812	0.517159
C	1.865298	-0.932767	-0.569725
C	3.840929	0.619816	0.704493
H	2.383377	1.730852	-0.409718
H	2.144933	1.788988	1.351916
C	3.312720	-1.379992	-0.375907
H	1.215096	-1.812163	-0.524288
H	1.753667	-0.485866	-1.574781
H	4.558666	1.444965	0.668904
H	3.922186	0.113986	1.680563
H	3.637986	-2.011356	-1.208264
H	3.389935	-1.955888	0.561150
H	0.052858	1.211944	1.247358
N	1.498949	-0.005499	0.494484
O	4.201461	-0.273249	-0.339600

TS-7

B3LYP-D3(BJ) SCF energy: -677.86316525 a.u.
B3LYP-D3(BJ) enthalpy: -677.485039 a.u.
B3LYP-D3(BJ) free energy: -677.544386 a.u.
M06 SCF energy in solution: -677.48528466 a.u.
M06 enthalpy in solution: -677.107158 a.u.
M06 free energy in solution: -677.166505 a.u.
Imaginary frequency: -609.9538 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	2.962710	-0.350712	0.016886
C	1.811998	-1.335684	0.295974
C	1.525358	0.782952	0.967922
C	1.284692	-0.613644	1.550871
C	0.703538	-1.279261	-0.771764
C	0.685029	1.168289	-0.076416
C	3.290292	0.062990	-1.392630
C	4.180320	-0.483328	0.898914
C	0.737022	2.532601	-0.696226
H	2.137388	-2.378110	0.435089
H	2.027076	1.552179	1.554106
H	1.903086	-0.797453	2.431888
H	0.240165	-0.824384	1.801037
H	0.006509	-2.096752	-0.567081
H	1.122394	-1.461664	-1.767123
H	3.746079	-0.768648	-1.955976
H	4.012979	0.887698	-1.397289
H	2.409474	0.387694	-1.953361
H	3.934272	-0.694462	1.943604
H	4.822755	-1.309698	0.548337
H	4.791389	0.427132	0.872090
H	1.363598	3.212126	-0.108270
H	-0.261139	2.985070	-0.780288
H	1.146646	2.504486	-1.718099
C	-0.101234	0.067798	-0.764583
C	-2.331226	-0.899621	-1.002563
C	-2.097066	1.041187	0.348547
C	-3.618609	-1.241596	-0.258452
H	-2.578745	-0.302952	-1.903301
H	-1.856533	-1.825705	-1.342262
C	-3.381943	0.656603	1.074746
H	-1.433768	1.574670	1.035116
H	-2.350009	1.725214	-0.485672

H	-4.332938	-1.732050	-0.926543
H	-3.383276	-1.924716	0.574497
H	-3.929050	1.549691	1.390960
H	-3.127661	0.059621	1.966180
H	-0.275458	0.381173	-1.811777
N	-1.422492	-0.168298	-0.120212
O	-4.260385	-0.075440	0.232284

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B3LYP-D3(BJ) SCF energy: -677.89639292 a.u.
B3LYP-D3(BJ) enthalpy: -677.516524 a.u.
B3LYP-D3(BJ) free energy: -677.580122 a.u.
M06 SCF energy in solution: -677.51755179 a.u.
M06 enthalpy in solution: -677.137683 a.u.
M06 free energy in solution: -677.201281 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.875448	-1.163680	-0.046800
C	-1.702992	-0.229694	-0.162693
C	-1.048001	2.167401	-0.734681
C	-2.086081	1.089360	-0.881476
C	-1.018509	0.112984	1.168084
C	0.029923	2.098696	0.058032
C	-3.898301	-0.968063	1.029766
C	-3.273876	-1.946062	-1.259679
C	0.959288	3.273084	0.233733
H	-0.934457	-0.718632	-0.775911
H	-1.231900	3.089766	-1.287144
H	-3.037261	1.468629	-0.474521
H	-2.280467	0.892330	-1.944704
H	-0.827417	-0.804873	1.735045
H	-1.662839	0.747870	1.789587
H	-4.517755	-1.864391	1.156740
H	-4.594483	-0.139369	0.799349
H	-3.444963	-0.730719	1.998877
H	-2.401706	-2.234541	-1.859173
H	-3.823392	-2.858095	-0.991631
H	-3.941605	-1.370657	-1.928581
H	0.667553	4.111254	-0.407388
H	2.000956	3.019052	0.006618
H	0.945214	3.622293	1.275453
C	0.300077	0.860823	0.900020
C	1.956562	-0.901187	1.273697

C	2.220019	0.430085	-0.686816
C	2.688526	-2.043358	0.573941
H	2.685344	-0.301614	1.854568
H	1.231636	-1.318081	1.980436
C	2.924945	-0.747313	-1.354940
H	1.689744	1.017316	-1.441339
H	2.990850	1.075246	-0.222168
H	3.280710	-2.622209	1.289071
H	1.947189	-2.709184	0.102209
H	3.688762	-0.395220	-2.054747
H	2.182615	-1.347833	-1.906138
H	0.712274	1.213235	1.863805
N	1.262216	-0.083919	0.284157
O	3.597887	-1.556574	-0.401067

TS-8

B3LYP-D3(BJ) SCF energy: -2180.84341573 a.u.
B3LYP-D3(BJ) enthalpy: -2180.174026 a.u.
B3LYP-D3(BJ) free energy: -2180.290669 a.u.
M06 SCF energy in solution: -2180.87683203 a.u.
M06 enthalpy in solution: -2180.207442 a.u.
M06 free energy in solution: -2180.324085 a.u.
Imaginary frequency: -1562.2270 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	1.896332	-0.037788	0.418833
N	0.311818	-0.975003	0.807011
O	-0.777076	-0.453608	1.402265
C	0.262405	-2.198355	0.376519
C	-0.960211	-3.043805	0.529434
H	-1.174749	-3.211091	1.591068
H	-0.849993	-4.009062	0.032891
H	-1.827362	-2.517919	0.115621
N	2.418975	-1.702673	-0.305421
O	3.599417	-1.934153	-0.902314
C	1.512734	-2.635026	-0.272713
C	1.710306	-4.005375	-0.835612
H	2.749078	-4.127966	-1.142725
H	1.063431	-4.166695	-1.707035
H	1.461197	-4.770443	-0.092451
N	3.348794	0.969963	-0.251967
O	4.396960	0.441652	-0.905854
C	3.219844	2.265598	-0.188448

C	4.211660	3.228834	-0.757553
H	5.097391	2.687968	-1.091084
H	4.504017	3.975575	-0.011278
H	3.786337	3.768483	-1.612927
N	1.240093	1.679208	0.856857
O	0.020012	1.924048	1.377715
C	1.969918	2.684044	0.464795
C	1.548661	4.110825	0.612170
H	1.078269	4.473376	-0.311361
H	2.405831	4.755961	0.823120
H	0.815764	4.196040	1.416111
O	2.658648	-0.646302	2.314365
H	2.269949	-0.045201	2.973239
H	3.623809	-0.535777	2.244456
B	-0.521148	0.792944	2.213780
F	-1.745393	1.195785	2.663862
F	0.402410	0.510452	3.225729
B	4.705245	-0.981406	-0.506901
F	5.800702	-1.355754	-1.213553
F	4.876019	-1.017250	0.886078
C	-0.487237	-0.165930	-2.432458
C	-1.704313	0.456934	-1.798476
C	-2.907447	2.619045	-1.242077
C	-1.601474	1.979930	-1.618883
C	-3.039979	0.102239	-2.472961
C	-4.088796	1.992978	-1.193910
C	0.754236	0.444115	-2.371011
C	-0.595185	-1.578552	-2.933493
C	-5.365335	2.721935	-0.864335
H	-1.773156	0.013954	-0.789927
H	-2.866007	3.683646	-1.012962
H	-1.242229	2.440379	-2.553552
H	-0.859792	2.215292	-0.848326
H	-3.113545	-0.974243	-2.655460
H	-3.127584	0.609908	-3.443175
H	1.590247	-0.009583	-2.901393
H	1.235749	0.199984	-1.032762
H	0.819551	1.524648	-2.266596
H	-1.151976	-1.615839	-3.880194
H	0.392194	-2.015141	-3.110207
H	-1.143977	-2.219176	-2.231563
H	-5.175252	3.775668	-0.636817
H	-5.882261	2.279070	-0.005578
H	-6.066406	2.676154	-1.709282
C	-4.198851	0.522488	-1.551207
C	-5.184141	-1.484581	-0.559406

C	-4.353998	0.173936	0.957760
C	-4.986236	-2.539707	0.527851
H	-6.228181	-1.116143	-0.518996
H	-5.033617	-1.946496	-1.543141
C	-4.130200	-0.924276	1.988766
H	-3.607033	0.954718	1.100833
H	-5.356494	0.604720	1.134356
H	-5.764246	-3.307007	0.461826
H	-4.005684	-3.024455	0.384699
H	-4.274419	-0.533440	2.998880
H	-3.104306	-1.304950	1.903246
H	-5.143330	0.401783	-2.107386
N	-4.227902	-0.396766	-0.384040
O	-5.073826	-1.982898	1.824862

TS-9

B3LYP-D3(BJ) SCF energy: -2180.82424724 a.u.
B3LYP-D3(BJ) enthalpy: -2180.155065 a.u.
B3LYP-D3(BJ) free energy: -2180.271290 a.u.
M06 SCF energy in solution: -2180.85647258 a.u.
M06 enthalpy in solution: -2180.187290 a.u.
M06 free energy in solution: -2180.303515 a.u.
Imaginary frequency: -1370.7756 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	-1.077078	-0.315534	-0.654848
N	-0.420613	-2.005033	-0.156380
O	0.750018	-2.510930	-0.576701
C	-1.168193	-2.677306	0.664709
C	-0.819142	-4.031007	1.193013
H	0.047386	-4.419842	0.657459
H	-1.659822	-4.722787	1.076224
H	-0.578960	-3.983387	2.263026
N	-2.536627	-0.817701	0.440397
O	-3.654579	-0.094733	0.620504
C	-2.427845	-1.983518	1.000843
C	-3.490332	-2.607722	1.846853
H	-3.068755	-3.007827	2.774722
H	-3.963168	-3.441259	1.312488
H	-4.258744	-1.871155	2.081689
N	-1.648278	1.441965	-1.015197
O	-2.759840	1.988416	-0.474914
C	-0.810544	2.189656	-1.668825

C	-1.012153	3.648286	-1.918211
H	-2.031455	3.930159	-1.652994
H	-0.825300	3.896600	-2.967908
H	-0.313058	4.237337	-1.311420
N	0.379685	0.207726	-1.734534
O	1.385154	-0.590142	-2.104261
C	0.379077	1.450749	-2.121059
C	1.457551	2.078199	-2.942695
H	1.993581	2.830800	-2.351498
H	1.040631	2.583067	-3.821103
H	2.164838	1.316271	-3.269394
O	-2.175250	-1.347304	-2.222928
H	-1.522638	-1.586926	-2.905479
H	-2.829410	-0.705393	-2.550995
B	1.162779	-2.069787	-1.958140
F	2.379703	-2.645693	-2.180471
F	0.168711	-2.448625	-2.874753
B	-3.903514	1.006348	-0.385989
F	-4.974653	1.699065	0.081072
F	-4.087773	0.439849	-1.655705
C	-1.084560	0.526381	2.885906
C	-0.036309	1.004938	2.094704
C	1.196392	2.997715	1.111631
C	-0.092961	2.463542	1.655733
C	1.368350	0.530690	2.466162
C	2.387880	2.383476	1.078956
C	-0.939556	-0.732543	3.696715
C	-2.381227	1.267829	3.019618
C	3.619806	3.208207	0.766239
H	-0.355976	0.308010	0.729547
H	1.158955	4.049778	0.826232
H	-0.343035	3.083334	2.532885
H	-0.916092	2.634327	0.959241
H	1.373009	-0.550748	2.587382
H	1.564022	0.943182	3.467477
H	-1.915016	-1.116756	4.008656
H	-0.353639	-0.551242	4.611540
H	-0.416804	-1.523240	3.147318
H	-2.585016	1.927684	2.176239
H	-3.228961	0.583966	3.114664
H	-2.361724	1.887063	3.932540
H	3.354648	4.263612	0.647563
H	4.153524	2.899054	-0.136236
H	4.340245	3.138496	1.591986
C	2.560187	0.951394	1.577798
C	3.704582	0.310590	-0.569727

C	3.262742	-1.362358	1.026437
C	5.178309	0.320855	-0.149957
H	3.585954	-0.446525	-1.347723
H	3.397974	1.262105	-1.003616
C	4.739276	-1.351992	1.430442
H	2.648610	-1.701200	1.864569
H	3.123802	-2.084310	0.217379
H	5.823177	0.525306	-1.011158
H	5.377763	1.088239	0.615401
H	5.065388	-2.357397	1.715486
H	4.909104	-0.684028	2.293354
H	3.431578	0.990681	2.258535
N	2.788774	-0.059157	0.519085
O	5.566462	-0.955402	0.344659

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B3LYP-D3(BJ) SCF energy: -677.32450219 a.u.
B3LYP-D3(BJ) enthalpy: -676.954611 a.u.
B3LYP-D3(BJ) free energy: -677.014694 a.u.
M06 SCF energy in solution: -676.94753054 a.u.
M06 enthalpy in solution: -676.577639 a.u.
M06 free energy in solution: -676.637722 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.962699	-1.107915	0.020027
C	1.756593	-0.195534	0.120888
C	1.080256	2.203459	0.641979
C	2.125338	1.136156	0.812552
C	1.047522	0.101163	-1.202691
C	-0.006345	2.105812	-0.134766
C	3.537212	-1.445727	-1.138906
C	3.498395	-1.621284	1.334919
C	-0.945824	3.267813	-0.334784
H	1.010257	-0.696388	0.753770
H	1.267512	3.141749	1.164991
H	3.075542	1.508339	0.397568
H	2.315330	0.972744	1.881704
H	0.855847	-0.833141	-1.740054
H	1.676445	0.724056	-1.851688
H	4.404926	-2.099970	-1.167436
H	3.173263	-1.088321	-2.096771
H	2.712425	-2.137750	1.902424
H	4.328997	-2.317878	1.186942

H	3.856568	-0.801956	1.971677
H	-0.652083	4.127435	0.276272
H	-1.982635	3.013571	-0.086447
H	-0.947407	3.584495	-1.386888
C	-0.275642	0.839760	-0.932708
C	-1.905841	-0.963364	-1.215986
C	-2.167590	0.441439	0.692635
C	-2.614329	-2.086352	-0.463203
H	-2.649039	-0.396855	-1.811373
H	-1.183353	-1.398518	-1.913997
C	-2.849806	-0.717437	1.414430
H	-1.638103	1.064997	1.417973
H	-2.951077	1.057646	0.210344
H	-3.205173	-2.701582	-1.148362
H	-1.858974	-2.722454	0.026941
H	-3.611298	-0.347531	2.107506
H	-2.093932	-1.285297	1.981696
H	-0.710201	1.154965	-1.899390
N	-1.211948	-0.097674	-0.267374
O	-3.520752	-1.573323	0.500987

78b

B3LYP-D3(BJ) SCF energy: -677.32794869 a.u.
B3LYP-D3(BJ) enthalpy: -676.958458 a.u.
B3LYP-D3(BJ) free energy: -677.020095 a.u.
M06 SCF energy in solution: -676.95136223 a.u.
M06 enthalpy in solution: -676.581872 a.u.
M06 free energy in solution: -676.643509 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.650670	-0.783119	0.062375
C	1.846282	0.287511	-0.067911
C	0.616711	2.350203	0.813880
C	1.637997	1.274992	1.081546
C	1.076874	0.628646	-1.321466
C	-0.335331	2.255392	-0.119670
C	2.922574	-1.798848	-1.022129
C	3.400783	-1.092947	1.337244
C	-1.306937	3.359926	-0.430514
H	0.681819	3.246315	1.430095
H	2.591336	1.759497	1.338240
H	1.338379	0.725999	1.985664
H	1.111666	-0.173206	-2.058779

H	1.511007	1.512178	-1.809623
H	2.672733	-2.810607	-0.672341
H	2.374180	-1.620505	-1.948640
H	3.113867	-2.081843	1.722296
H	4.482680	-1.138244	1.148069
H	3.233693	-0.365169	2.132724
H	-1.182780	4.207707	0.251264
H	-2.348127	3.018163	-0.367674
H	-1.164187	3.727271	-1.456501
C	-0.380243	0.987918	-0.958378
C	-1.108395	-1.350728	-0.987982
C	-2.313376	0.224600	0.344649
C	-1.677375	-2.468881	-0.120143
H	-1.750897	-1.216978	-1.881302
H	-0.115549	-1.654364	-1.328224
C	-2.847670	-0.935823	1.177661
H	-2.206790	1.102196	0.988266
H	-3.047660	0.466856	-0.450019
H	-1.820902	-3.378472	-0.710843
H	-0.968468	-2.682306	0.696923
H	-3.854578	-0.714819	1.543953
H	-2.181338	-1.096017	2.041468
H	-0.944190	1.189872	-1.890591
N	-1.005779	-0.117737	-0.209894
O	-2.946662	-2.126956	0.412952
H	3.992471	-1.816769	-1.273765

TS-10

B3LYP-D3(BJ) SCF energy: -2026.40299559 a.u.
B3LYP-D3(BJ) enthalpy: -2025.791309 a.u.
B3LYP-D3(BJ) free energy: -2025.902630 a.u.
M06 SCF energy in solution: -2026.55846096 a.u.
M06 enthalpy in solution: -2025.946774 a.u.
M06 free energy in solution: -2026.058095 a.u.
Imaginary frequency: -1873.8179 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	1.392709	-0.265105	-0.309627
N	-0.207405	0.120315	-1.242612
O	-1.255783	-0.746530	-1.358425
C	-0.292134	1.308825	-1.752661
C	-1.452646	1.805352	-2.551237
H	-2.151950	0.992988	-2.749509

H	-1.106630	2.212394	-3.506913
H	-1.971074	2.618597	-2.027834
N	1.797565	1.525348	-0.776542
O	2.904251	2.166551	-0.399271
C	0.890275	2.149302	-1.469426
C	1.011533	3.566433	-1.925213
H	2.019298	3.931422	-1.726565
H	0.295977	4.209651	-1.397473
H	0.803793	3.650871	-2.996903
N	2.881965	-0.555752	0.820964
O	3.849633	0.341525	1.037647
C	2.878714	-1.664636	1.504133
C	3.944085	-2.030185	2.484702
H	4.870744	-1.512673	2.230673
H	4.115908	-3.109426	2.495950
H	3.659610	-1.724785	3.500018
N	0.884031	-1.957364	0.369998
O	-0.322138	-2.527694	0.123468
C	1.683907	-2.492200	1.243249
C	1.420478	-3.782236	1.947896
H	1.333004	-3.623639	3.029395
H	2.251080	-4.478924	1.790211
H	0.501963	-4.234584	1.575017
O	2.267751	-0.864206	-2.109896
H	2.077712	-1.791633	-2.326027
H	3.229113	-0.703659	-2.026490
B	-0.838807	-2.227965	-1.247957
F	-2.019404	-2.911904	-1.359036
F	0.111291	-2.504798	-2.203409
B	4.108237	1.276101	-0.123360
F	5.112927	2.093855	0.240253
F	4.354722	0.495243	-1.262383
C	-1.348283	1.077701	1.836571
C	-2.434068	0.045922	1.955280
C	-0.049682	0.693787	2.140182
C	-1.636500	2.501310	1.434646
H	0.677007	1.470477	2.376222
H	0.622588	0.303511	0.947768
H	0.118396	-0.251072	2.656472
H	-0.694171	3.060592	1.457458
H	-1.977470	2.558909	0.389191
C	-4.176680	0.687150	0.225812
C	-3.855371	-1.688069	0.863790
C	-4.995013	0.173112	-0.954726
H	-4.830957	0.878916	1.079598
H	-3.636837	1.597586	-0.028036

C	-4.727493	-2.041974	-0.338686
H	-3.065618	-2.427909	1.004311
H	-4.458016	-1.598868	1.771562
H	-5.751376	0.918179	-1.213238
H	-4.345466	0.015982	-1.831151
H	-5.292598	-2.947543	-0.107325
H	-4.098518	-2.235160	-1.213897
N	-3.173544	-0.346508	0.670873
O	-5.667511	-1.015260	-0.608579
H	-2.463256	-0.468698	-0.085670
H	-2.011774	-0.888281	2.328547
H	-3.225192	0.363855	2.643557
C	-2.664547	3.225202	2.327033
H	-3.619929	2.684441	2.319530
H	-2.307072	3.203501	3.363405
C	-2.893873	4.669491	1.877572
H	-3.277007	4.709913	0.850305
H	-3.619328	5.172269	2.523978
H	-1.962197	5.245317	1.909733

TS-11

B3LYP-D3(BJ) SCF energy: -2026.40509900 a.u.
B3LYP-D3(BJ) enthalpy: -2025.793601 a.u.
B3LYP-D3(BJ) free energy: -2025.903516 a.u.
M06 SCF energy in solution: -2026.55969634 a.u.
M06 enthalpy in solution: -2025.948198 a.u.
M06 free energy in solution: -2026.058113 a.u.
Imaginary frequency: -1760.0029 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	-1.117810	0.123750	-0.477071
N	0.049255	-1.220559	-1.101815
O	1.296373	-0.980544	-1.582695
C	-0.404807	-2.432985	-1.038903
C	0.332289	-3.637313	-1.524012
H	1.290400	-3.346522	-1.954081
H	-0.255360	-4.156002	-2.289659
H	0.497893	-4.349929	-0.707230
N	-2.232747	-1.350773	-0.111135
O	-3.428782	-1.253679	0.482650
C	-1.757382	-2.514393	-0.440455
C	-2.484580	-3.802430	-0.238304
H	-3.524438	-3.601504	0.020602

H	-2.029820	-4.383906	0.573847
H	-2.447912	-4.416173	-1.143726
N	-2.230164	1.459971	0.268856
O	-3.447543	1.248328	0.775676
C	-1.720769	2.655872	0.350556
C	-2.456873	3.803882	0.959604
H	-3.500503	3.786322	0.633023
H	-2.006268	4.761029	0.692725
H	-2.465787	3.715601	2.053183
N	0.058109	1.588782	-0.669095
O	1.328486	1.471362	-1.148222
C	-0.354208	2.730120	-0.205264
C	0.452925	3.986673	-0.221638
H	0.639242	4.342846	0.798588
H	-0.089661	4.780967	-0.745893
H	1.403155	3.818090	-0.727959
O	-1.963922	0.150555	-2.406930
H	-1.485394	0.715375	-3.035114
H	-2.899533	0.421128	-2.316763
B	1.476295	0.384007	-2.210692
F	2.807289	0.436806	-2.547420
F	0.579116	0.600430	-3.226673
B	-4.177526	0.036632	0.212154
F	-5.347922	-0.047117	0.870946
F	-4.282354	0.217477	-1.174302
C	-0.886916	-1.017458	2.992557
C	0.232009	-0.255146	2.275082
C	1.496915	-0.824840	2.093669
C	-1.999294	-0.102005	3.504478
H	-0.386590	-0.091666	0.969642
H	-2.509681	0.414056	2.690327
H	-2.751586	-0.685478	4.043193
H	-1.598283	0.646390	4.198565
C	2.689784	0.069928	1.937974
C	4.127000	1.393912	0.312432
C	3.962793	-1.040071	-0.006524
C	5.501454	1.163309	0.928774
H	4.198146	1.522066	-0.769095
H	3.615834	2.257524	0.742930
C	5.346288	-1.151598	0.621852
H	3.342305	-1.910944	0.189218
H	4.033761	-0.895022	-1.084473
H	6.146511	2.012096	0.690834
H	5.436747	1.084318	2.025889
H	5.878095	-1.985341	0.157889
H	5.282477	-1.353967	1.703344

H	3.518206	-0.266916	2.566275
N	3.240412	0.183793	0.514219
O	6.113133	0.012570	0.379229
H	2.419581	0.347285	-0.087768
H	2.440019	1.094289	2.222594
H	0.236855	0.819439	2.481173
C	1.691279	-2.315286	2.077767
H	1.510698	-2.742533	1.080493
H	2.707759	-2.596675	2.373151
H	0.996103	-2.814710	2.759202
H	-1.307742	-1.787636	2.339325
H	-0.436814	-1.544973	3.843647

TS-12

B3LYP-D3(BJ) SCF energy: -2065.72410265 a.u.
B3LYP-D3(BJ) enthalpy: -2065.082932 a.u.
B3LYP-D3(BJ) free energy: -2065.197054 a.u.
M06 SCF energy in solution: -2065.85351856 a.u.
M06 enthalpy in solution: -2065.212348 a.u.
M06 free energy in solution: -2065.326470 a.u.
Imaginary frequency: -1879.6595 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	1.479040	-0.328337	-0.299434
N	-0.102490	-0.190172	-1.328916
O	-1.098045	-1.124512	-1.335325
C	-0.230581	0.895396	-2.025314
C	-1.382878	1.189462	-2.929044
H	-2.036078	0.320229	-3.005890
H	-1.020818	1.446120	-3.930041
H	-1.956783	2.051779	-2.567187
N	1.804355	1.387120	-1.033448
O	2.858307	2.145227	-0.728668
C	0.892331	1.839187	-1.843573
C	0.952726	3.173108	-2.512645
H	1.931779	3.623113	-2.347570
H	0.185621	3.846970	-2.110344
H	0.777766	3.078463	-3.589280
N	2.937455	-0.349087	0.906127
O	3.846248	0.627009	1.005677
C	2.967128	-1.334820	1.756885
C	4.011370	-1.478560	2.814751
H	4.914476	-0.944294	2.515016

H	4.248023	-2.530412	2.994171
H	3.666751	-1.045813	3.762921
N	1.035803	-1.919369	0.625833
O	-0.127155	-2.592308	0.437611
C	1.829426	-2.262232	1.595890
C	1.609414	-3.439290	2.488227
H	1.468837	-3.118544	3.527385
H	2.483239	-4.099739	2.469976
H	0.733494	-4.000069	2.163204
O	2.452823	-1.150011	-1.955985
H	2.320870	-2.109393	-2.027625
H	3.400327	-0.922387	-1.870832
B	-0.606808	-2.542832	-0.978454
F	-1.743778	-3.304221	-1.013476
F	0.392378	-2.909961	-1.849868
B	4.097525	1.382160	-0.280654
F	5.041862	2.305152	-0.022017
F	4.428954	0.449058	-1.274214
C	-1.404724	1.186527	1.509811
C	-2.445040	0.134536	1.769354
C	-0.103041	0.930329	1.916727
C	-1.746058	2.498722	0.854488
H	0.574154	1.774514	2.041218
H	0.634362	0.385468	0.828693
H	0.089009	0.095679	2.590697
H	-0.834352	3.106703	0.809020
H	-2.044941	2.347995	-0.193871
C	-4.148038	0.366331	-0.097549
C	-3.722706	-1.842728	0.948417
C	-4.889802	-0.389733	-1.195404
H	-4.844909	0.661389	0.690527
H	-3.648493	1.251176	-0.487577
C	-4.528032	-2.447498	-0.199449
H	-2.899058	-2.498666	1.235518
H	-4.363145	-1.638168	1.810495
H	-5.674284	0.253646	-1.601218
H	-4.198630	-0.655480	-2.011692
H	-5.052285	-3.332172	0.168638
H	-3.856809	-2.749425	-1.010007
N	-3.108712	-0.514143	0.548864
O	-5.510731	-1.539462	-0.668870
H	-2.363173	-0.718740	-0.153971
H	-1.997174	-0.696375	2.316546
H	-3.279107	0.526222	2.362533
C	-2.847577	3.321992	1.565761
H	-3.763671	2.714318	1.608153

C	-3.159705	4.582351	0.752036
H	-3.484832	4.335669	-0.266261
H	-3.955053	5.166728	1.225192
H	-2.274741	5.225684	0.676079
C	-2.436642	3.667338	3.001065
H	-1.526824	4.279955	3.005426
H	-3.223868	4.236241	3.505491
H	-2.233960	2.769320	3.595564

TS-13

B3LYP-D3(BJ) SCF energy: -2065.72351311 a.u.
B3LYP-D3(BJ) enthalpy: -2065.082376 a.u.
B3LYP-D3(BJ) free energy: -2065.194965 a.u.
M06 SCF energy in solution: -2065.85042444 a.u.
M06 enthalpy in solution: -2065.209287 a.u.
M06 free energy in solution: -2065.321876 a.u.
Imaginary frequency: -1704.1268 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Co	1.131781	-0.343521	-0.455856
N	0.008809	0.779767	-1.470884
O	-1.257056	0.448091	-1.846069
C	0.513455	1.924937	-1.805869
C	-0.172014	2.935050	-2.664807
H	-1.138638	2.556675	-2.996564
H	0.441423	3.156881	-3.545050
H	-0.313746	3.877481	-2.123138
N	2.307895	1.125206	-0.573265
O	3.515491	1.166352	0.001913
C	1.876007	2.138076	-1.263534
C	2.660928	3.385552	-1.502205
H	2.209263	4.237699	-0.979027
H	2.685718	3.630239	-2.569134
H	3.680601	3.254236	-1.139902
N	2.212714	-1.432408	0.649371
O	3.444204	-1.120377	1.064334
C	1.670453	-2.534748	1.080192
C	2.381995	-3.474367	1.997627
H	3.412470	-3.611938	1.657230
H	1.883276	-4.443019	2.052989
H	2.437369	-3.051001	3.008102
N	-0.087196	-1.765091	-0.210772
O	-1.348515	-1.770521	-0.721343

C	0.299408	-2.731928	0.566354
C	-0.536254	-3.922337	0.906431
H	-0.746640	-3.955807	1.982204
H	-0.005559	-4.846487	0.653050
H	-1.474764	-3.893832	0.353108
O	1.958576	-0.990659	-2.289730
H	1.450865	-1.698845	-2.717738
H	2.883740	-1.259385	-2.119973
B	-1.472979	-1.039474	-2.049189
F	-2.809419	-1.147013	-2.359521
F	-0.592632	-1.560939	-2.963682
B	4.209646	-0.175147	0.150943
F	5.391978	0.065402	0.747243
F	4.290963	-0.782596	-1.110953
C	0.800175	1.947833	2.460587
C	-0.308184	1.003257	1.964825
C	-1.523617	1.477309	1.461900
C	1.982105	1.162816	3.036169
H	0.406209	0.346775	0.849962
H	2.441228	0.503360	2.303710
H	2.756232	1.850911	3.388498
H	1.658664	0.560786	3.895232
C	-2.764339	0.656692	1.656079
C	-4.045035	-1.280666	0.608754
C	-4.219639	0.938224	-0.446322
C	-5.420414	-1.035881	1.213964
H	-4.126134	-1.746980	-0.374020
H	-3.407490	-1.897879	1.243682
C	-5.600299	1.056231	0.189578
H	-3.731061	1.906250	-0.536079
H	-4.274527	0.472585	-1.430878
H	-5.946798	-1.988598	1.305212
H	-5.339748	-0.594029	2.220456
H	-6.248342	1.625354	-0.480807
H	-5.551939	1.596478	1.149040
H	-3.569987	1.257433	2.088112
N	-3.327204	0.031263	0.375010
O	-6.198411	-0.212541	0.366501
H	-2.506702	-0.196023	-0.200353
H	-2.567349	-0.179668	2.328479
H	-0.391135	0.098567	2.575199
C	-1.642406	2.788665	0.739272
H	-1.804058	2.641783	-0.336321
H	-2.489601	3.378393	1.114231
H	-0.740388	3.392607	0.847508
H	1.161833	2.551311	1.619659

C	0.230205	2.888247	3.539910
H	-0.585226	3.514018	3.165287
H	-0.152615	2.309572	4.388745
H	1.019507	3.546896	3.916325

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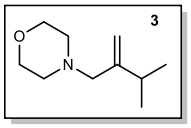
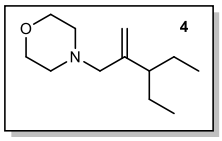
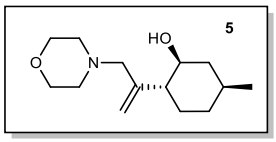
Characterization of Products



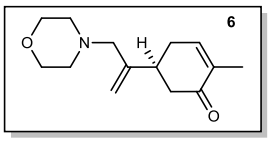
4-(3-methyl-2-methylenebutyl)morpholine (3):
The reaction was carried out following the procedure B using morpholine and 2,3-dimethylbut-1-ene. Then 18.6 mg colorless oily liquid was obtained in 55% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 – 4.90 (m, 1H), 4.89 – 4.87 (m, 1H), 3.72 – 3.68 (m, 4H), 2.94 – 2.88 (m, 2H), 2.42 – 2.31 (m, 5H), 1.05 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.88, 109.99, 67.09, 63.68, 53.73, 31.40, 21.75.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{20}NO$) requires *m/z* 170.1539, found *m/z* 170.1538.



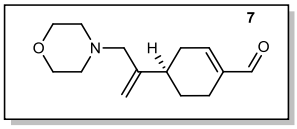
4-(3-ethyl-2-methylenepentyl)morpholine (4):
The reaction was carried out following the procedure B using morpholine and 3-ethyl-2-methylpent-1-ene. Then 19.7 mg colorless oily liquid was obtained in 50% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (q, *J* = 1.6 Hz, 1H), 4.85 (dd, *J* = 2.1, 1.0 Hz, 1H), 3.70 (t, *J* = 4.6 Hz, 4H), 2.81 (s, 1H), 2.42 (s, 2H), 1.92 (d, *J* = 7.0 Hz, 1H), 1.46 – 1.37 (m, 3H), 0.82 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.39, 111.95, 67.09, 62.85, 53.96, 47.17, 25.97, 11.72.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{24}NO$) requires *m/z* 198.1852, found *m/z* 198.1849.



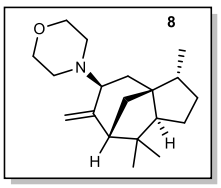
(1*S*,2*R*,5*S*)-5-methyl-2-(3-morpholinoprop-1-en-2-yl)cyclohexan-1-ol (5):
The reaction was carried out following the procedure B using morpholine and (-)-isopulegol. Then 43.1 mg faint yellow oily liquid was obtained in 90% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 – 5.12 (m, 1H), 4.95 (d, *J* = 1.4 Hz, 1H), 3.72 (t, *J* = 4.7 Hz, 4H), 3.39 – 3.25 (m, 1H), 3.02 – 2.82 (m, 2H), 2.56 (d, *J* = 20.5 Hz, 4H), 2.08 – 1.97 (m, 1H), 1.94 – 1.84 (m, 1H), 1.71 – 1.60 (m, 2H), 1.53 – 1.33 (m, 2H), 1.05 – 0.79 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.66, 117.66, 73.17, 66.61, 64.82, 53.12, 52.33, 43.60, 34.51, 31.80, 31.35, 22.13.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{26}NO_2$) requires *m/z* 240.1958, found *m/z* 240.1957.



(*S*)-2-methyl-5-(3-morpholinoprop-1-en-2-yl)cyclohex-2-en-1-one (6):
The reaction was carried out following the procedure B using morpholine and (*S*)-(+)-carvone. Then 18.8 mg faint yellow oily liquid was obtained in 40% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.74 (m, 1H), 5.03 (d, *J* = 1.7 Hz, 1H), 4.95 (d, *J* = 1.7 Hz, 1H), 3.68 (t, *J* = 4.6 Hz, 4H), 3.00 – 2.79 (m, 3H), 2.67 – 2.57 (m, 1H), 2.55 – 2.30 (m, 7H), 1.80 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.94, 147.17, 144.82, 135.32, 113.24, 66.94, 63.54, 53.56, 43.31, 38.71, 31.57, 15.71.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{22}NO_2$) requires *m/z* 236.1645, found *m/z* 236.1637.

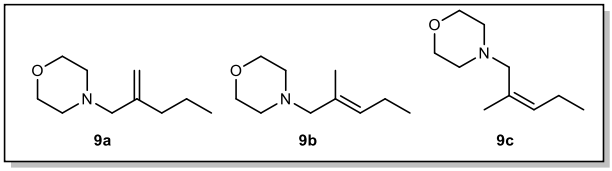


(*R*)-4-(3-morpholinoprop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (7):
The reaction was carried out following the procedure B using morpholine and (*S*)-(-)-perilla aldehyde. Then 17.9 mg faint yellow oily liquid was obtained in 38% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 6.84 (qd, *J* = 2.9, 1.0 Hz, 1H), 5.02 (d, *J* = 1.5 Hz, 1H), 4.92 (s, 1H), 3.69 (t, *J* = 4.6 Hz, 4H), 2.95 (s, 2H), 2.63 – 2.51 (m, 1H), 2.49 – 2.08 (m, 8H), 1.97 – 1.89 (m, 1H), 1.57 – 1.41 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.96, 150.86, 148.78, 141.14, 112.15, 67.00, 63.92, 53.66, 36.93, 32.33, 26.48, 21.56.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{22}NO_2$) requires *m/z* 236.1645, found *m/z* 236.1641.

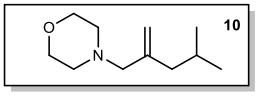


4-((3*R*,3a*R*,5*S*,7*R*,8a*S*)-3,8,8-trimethyl-6-methyleneoctahydro-1*H*-3a,7-methanoazulen-5-yl)morpholine (8):
The reaction was carried out following the procedure B using morpholine and (-)-α-cedrene. Then 29.0 mg faint yellow oily liquid was obtained in 50% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (t, *J* = 2.8 Hz, 1H), 4.75 (t, *J* = 2.9 Hz, 1H), 3.84 – 3.64 (m, 4H), 3.43 – 3.29 (m, 1H), 2.86 – 2.73 (m, 2H), 2.56 – 2.44 (m, 2H), 2.28 (d, *J* = 4.3 Hz, 1H), 1.94 – 1.80 (m, 1H), 1.79 – 1.68 (m, 3H), 1.60 – 1.51 (m, 1H), 1.50 – 1.37 (m, 2H), 1.39 – 1.26 (m, 2H), 1.13 (d, *J* = 11.5 Hz, 1H), 0.95 (d, *J* = 8.2 Hz, 6H), 0.86 (d, *J* = 7.1 Hz, 3H).

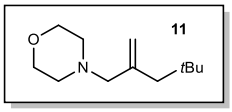
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.27, 109.36, 67.65, 62.89, 60.53, 56.42, 54.23, 43.68, 42.51, 42.06, 36.52, 31.23, 26.53, 26.24, 25.66, 15.40.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{32}NO$) requires *m/z* 290.2478, found *m/z* 290.2473.



4-(2-methylenepentyl)morpholine (9a), (*E*)-4-(2-methylpent-2-en-1-yl)morpholine (9b) and (*Z*)-4-(2-methylpent-2-en-1-yl)morpholine (9c):
The reaction was carried out following the procedure B using morpholine and 2-methylpent-1-ene. Then 20.3 mg faint yellow oily liquid was obtained in 60% isolated yield following purification procedure A. The ratio of different products is determined by ^{1}**H NMR** spectrum and the result of (**9a** : the mixture of **9b** and **9c** = 2.5 : 1) can be concluded by the integral of the double bond.
^{1}H NMR of 9a (400 MHz, $CDCl_3$) δ 4.94 – 4.90 (m, 1H), 4.88 – 4.84 (m, 1H), 3.75 – 3.66 (m, 4H), 2.87 (s, 2H), 2.45 – 2.30 (m, 4H), 2.04 (t, *J* = 7.6 Hz, 2H), 1.48 (h, *J* = 7.4 Hz, 2H), 1.00 – 0.83 (m, 3H).
^{13}C NMR of 9a (101 MHz, $CDCl_3$) δ 145.82, 112.16, 67.02, 64.44, 53.66, 36.22, 20.67, 13.83.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{20}NO$) requires *m/z* 170.1539, found *m/z* 170.1533

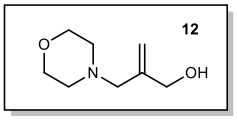


4-(4-methyl-2-methylenepentyl)morpholine (10):
The reaction was carried out following the procedure B using morpholine and 2,4-dimethylpent-1-ene. Then 26.0 mg colorless oily liquid was obtained in 71% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 1H), 4.84 (s, 1H), 3.70 (t, *J* = 4.7 Hz, 4H), 2.83 (s, 2H), 2.38 (t, *J* = 4.6 Hz, 4H), 1.97 – 1.88 (m, 2H), 1.87 – 1.70 (m, 1H), 0.88 (d, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.75, 113.30, 67.07, 64.16, 53.71, 43.88, 25.88, 22.52.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{22}NO$) requires *m/z* 184.1696, found *m/z* 184.1687.

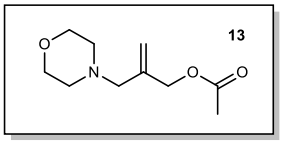


4-(4,4-dimethyl-2-methylenepentyl)morpholine (11):
The reaction was carried out following the procedure B using morpholine and 2,4,4-trimethylpent-1-ene. Then 26.0 mg colorless oily liquid was obtained in 66% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 – 5.04 (m, 1H), 4.87 – 4.83 (m, 1H), 3.78 – 3.61 (m, 4H), 2.88 (t, *J* = 1.1 Hz, 2H), 2.39 (s, 4H), 1.98 (s, 2H), 0.92 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.63, 115.70, 67.07, 65.79, 53.63, 47.06, 31.39, 29.93.

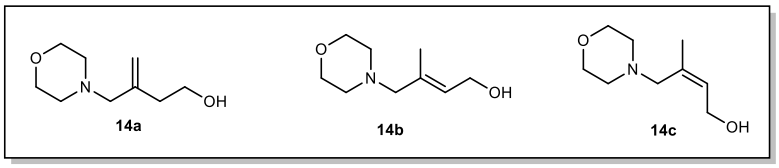
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{24}NO$) requires *m/z* 198.1852, found *m/z* 198.1852.



2-(morpholinomethyl)prop-2-en-1-ol (12):
The reaction was carried out following the procedure B using morpholine and 2-methylprop-2-en-1-ol. Then 18.9 mg colorless oily liquid was obtained in 60% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (d, *J* = 1.5 Hz, 1H), 4.97 (d, *J* = 1.5 Hz, 1H), 4.22 (s, 2H), 3.70 (t, *J* = 4.7 Hz, 4H), 3.12 (s, 2H), 2.58 – 2.42 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.45, 115.87, 67.47, 66.75, 64.23, 53.31.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_8H_{16}NO_2$) requires *m/z* 158.1176, found *m/z* 158.1171.

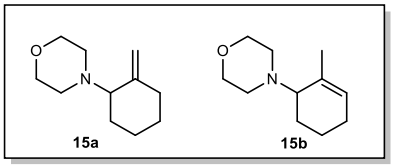


2-(morpholinomethyl)allyl acetate (13):
The reaction was carried out following the procedure B using morpholine and 2-methylallyl acetate. Then 27.5 mg faint yellow oily liquid was obtained in 69% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 – 5.06 (m, 2H), 4.61 (s, 2H), 3.69 (t, *J* = 4.6 Hz, 4H), 2.96 (d, *J* = 1.1 Hz, 2H), 2.43 – 2.32 (m, 4H), 2.10 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.73, 140.36, 115.07, 66.99, 65.29, 62.09, 53.49, 20.97.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{18}NO_3$) requires *m/z* 200.1281, found *m/z* 200.1277.



3-(morpholinomethyl)but-3-en-1-ol (14a), (*E*)-3-methyl-4-morpholinobut-2-en-1-ol (14b) and (*Z*)-3-methyl-4-morpholinobut-2-en-1-ol (14c):
The reaction was carried out following the procedure B using morpholine and 3-methylbut-3-en-1-ol. Then 23.6 mg faint yellow oily liquid was obtained in 69% isolated yield following purification procedure B. The ratio of different products is determined by **^{1}H NMR** spectrum and the result of (**14a** : the mixture of **14b** and **14c** = 6.25 : 1) can be concluded by the integral of the double bond.
^{1}H NMR of 14a (400 MHz, $CDCl_3$) δ 5.05 (d, *J* = 2.0 Hz, 1H), 4.94 (d, *J* = 2.0 Hz, 1H), 3.73 (t, *J* = 4.7 Hz, 4H), 3.65 – 3.57 (m, 2H), 2.94 (s, 2H), 2.60 – 2.46 (m, 4H), 2.43 – 2.34 (m, 2H).
^{13}C NMR of 14a (101 MHz, $CDCl_3$) δ 143.59, 118.66, 66.46, 65.19, 62.49, 53.12, 40.92.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_{18}NO_2$) requires *m/z* 172.1332, found *m/z* 172.1326.



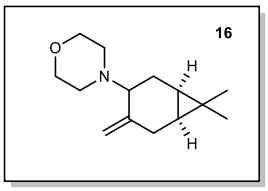
4-(2-methylenecyclohexyl)morpholine (15a) and 4-(2-methylcyclohex-2-en-1-yl)morpholine (15b):

The reaction was carried out following the procedure B using morpholine and 1-methylcyclohex-1-ene. Then 27.2 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure A. The ratio of different products is determined by ^{1}**H NMR** spectrum and the result of (**15a** : **15b =** 2.5 : 1) can be concluded by the integral of the double bond.

^{1}H NMR of 15a (400 MHz, $CDCl_3$) δ 4.75 (dd, *J* = 7.4, 2.2 Hz, 2H), 3.76 – 3.56 (m, 4H), 2.59 (t, *J* = 3.8 Hz, 1H), 2.48 – 2.39 (m, 2H), 2.38 – 2.25 (m, 2H), 2.06 – 1.86 (m, 2H), 1.80 – 1.61 (m, 4H), 1.53 – 1.33 (m, 2H).

^{13}C NMR of 15a (101 MHz, $CDCl_3$) δ 150.11, 109.09, 67.98, 67.38, 50.92, 32.02, 29.64, 28.54, 21.61.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{20}NO$) requires *m/z* 182.1539, found *m/z* 182.1536.



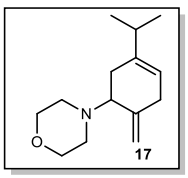
4-((1*R*,6*S*)-7,7-dimethyl-4-methylenebicyclo[4.1.0]heptan-3-yl)morpholine (16):

The reaction was carried out following the procedure B using morpholine and (+)-3-carene. Then 23.9 mg colorless oily liquid was obtained in 54% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 – 4.71 (m, 2H), 3.74 (t, *J* = 4.7 Hz, 4H), 2.58 – 2.47 (m, 3H), 2.44 – 2.41 (m, 1H), 2.40 – 2.32 (m, 3H), 2.22 (d, *J* = 15.7 Hz, 1H), 1.33 – 1.23 (m, 1H), 1.00 (s, 3H), 0.93 (s, 3H), 0.78 (t, *J* = 8.7 Hz, 1H), 0.64 – 0.51 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.58, 110.23, 67.29, 66.75, 51.23, 28.65, 26.46, 23.57, 21.68, 18.45, 16.34, 14.38.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1848.



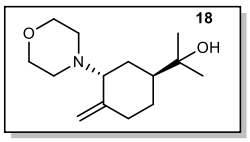
4-((5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)morpholine (17):

The reaction was carried out following the procedure B using morpholine and γ-terpinene. Then 27.0 mg faint yellow oily liquid was obtained in 61% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 4.97 – 4.82 (m, 2H), 3.71 (td, *J* = 4.5, 1.7 Hz, 4H), 2.90 – 2.79 (m, 2H), 2.72 – 2.60 (m, 1H), 2.47 (t, *J* = 4.6 Hz, 4H), 2.34 – 2.26 (m, 1H), 2.24 – 2.16 (m, 2H), 0.99 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.52, 140.75, 117.97, 109.69, 67.53, 66.39, 51.72, 35.11, 32.84, 30.86, 21.58, 21.46.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1848.



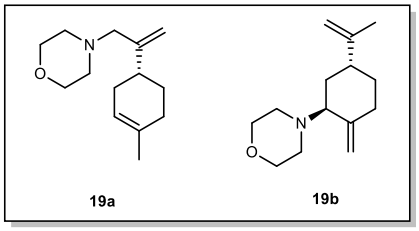
2-((1*S*,3*R*)-4-methylene-3-morpholinocyclohexyl)propan-2-ol (18):

The reaction was carried out following the procedure B using morpholine and (-)-α-terpineol. Then 25.3 mg colorless oily liquid was obtained in 53% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (dt, *J* = 5.6, 2.2 Hz, 2H), 3.70 (t, *J* = 4.7 Hz, 4H), 2.64 (t, *J* = 3.0 Hz, 1H), 2.46 – 2.19 (m, 6H), 2.18 – 2.07 (m, 1H), 1.98 – 1.85 (m, 2H), 1.21 – 1.10 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.59, 110.09, 72.54, 67.94, 67.23, 50.80, 41.42, 30.74, 30.68, 29.26, 27.30, 26.43.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{26}NO_2$) requires *m/z* 240.1958, found *m/z* 240.1953.



(*R*)-4-(2-(4-methylcyclohex-3-en-1-yl)allyl)morpholine (19a) and 4-((1*S*,5*R*)-2-methylene-5-(prop-1-en-2-yl)cyclohexyl)morpholine (19b):

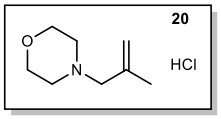
The reaction was carried out following the procedure B using morpholine and (+)-limonene. Then 21.2 mg colorless oily liquid (**18a**) was obtained in 48% isolated yield following purification procedure B and 20.3 mg colorless oily liquid (**18b**) was obtained in 46% isolated yield following purification procedure B.

^{1}H NMR of 19a (400 MHz, $CDCl_3$) δ 5.41 (dt, *J* = 3.7, 1.7 Hz, 1H), 4.95 (d, *J* = 1.6 Hz, 1H), 4.89 (d, *J* = 1.4 Hz, 1H), 3.69 (t, *J* = 4.6 Hz, 4H), 2.92 (d, *J* = 2.6 Hz, 2H), 2.39 (d, *J* = 4.8 Hz, 4H), 2.28 – 1.76 (m, 6H), 1.69 – 1.62 (m, 3H), 1.56 – 1.43 (m, 1H).

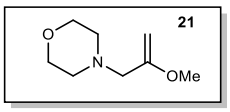
^{13}C NMR of 19a (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.28, 133.76, 120.70, 110.92, 67.04, 63.91, 53.71, 37.29, 31.37, 30.60, 28.10, 23.47.

^{1}H NMR of 19b (400 MHz, $CDCl_3$) δ 4.76 (t, *J* = 1.9 Hz, 2H), 4.71 – 4.55 (m, 2H), 3.70 (t, *J* = 4.8 Hz, 4H), 2.64 (t, *J* = 3.1 Hz, 1H), 2.57 – 2.44 (m, 1H), 2.42 – 2.28 (m, 4H), 2.18 – 2.07 (m, 2H), 1.92 – 1.80 (m, 1H), 1.70 (s, 3H), 1.35 – 1.22 (m, 3H).

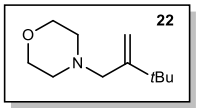
^{13}C NMR of 19b (101 MHz, $CDCl_3$) δ 150.01, 149.50, 110.26, 108.48, 68.05, 67.30, 50.90, 37.91, 34.62, 33.45, 30.89, 20.87.
HRMS of 19a (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1852.
HRMS of 19b (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1856.



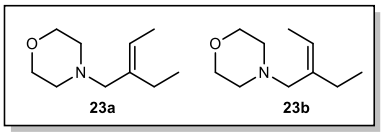
4-(2-methylallyl)morpholine hydrochloride (20):
The reaction was carried out following the procedure B using morpholine and 2-methylprop-1-ene (2.4 mol/L in THF). Then 25.5 mg white powder was obtained in 72% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.60 (s, 1H), 5.29 (d, *J* = 12.2 Hz, 2H), 4.39 (t, *J* = 11.9 Hz, 2H), 3.95 (d, *J* = 12.6 Hz, 2H), 3.58 (d, *J* = 4.3 Hz, 2H), 3.42 (d, *J* = 11.1 Hz, 2H), 2.89 (d, *J* = 10.6 Hz, 2H), 2.08 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.82, 123.18, 63.54, 63.26, 51.82, 22.18.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_8H_{16}NO$) requires *m/z* 142.1226, found *m/z* 142.1222.



4-(2-methoxyallyl)morpholine (21):
The reaction was carried out following the procedure B using morpholine and 2-methoxyprop-1-ene. Then 25.5 mg colorless oily liquid was obtained in 81% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 – 4.01 (m, 2H), 3.79 – 3.70 (m, 4H), 3.58 (s, 3H), 2.99 (s, 2H), 2.46 (t, *J* = 4.7 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99, 84.54, 66.60, 62.42, 54.86, 53.34.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_8H_{16}NO_2$) requires *m/z* 158.1176, found *m/z* 158.1175.



4-(3,3-dimethyl-2-methylenebutyl)morpholine (22):
The reaction was carried out following the procedure B using morpholine and 2,3,3-trimethylbut-1-ene. Then 22.4 mg colorless oily liquid was obtained in 61% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 – 4.95 (m, 2H), 3.70 (t, *J* = 4.6 Hz, 4H), 2.93 (dd, *J* = 1.4, 0.8 Hz, 2H), 2.42 (s, 4H), 1.09 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.81, 109.52, 67.16, 61.26, 53.74, 35.24, 29.38.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{22}NO$) requires *m/z* 184.1696, found *m/z* 184.1697.



(*E*)-4-(2-ethylbut-2-en-1-yl)morpholine (23a) and (*Z*)-4-(2-ethylbut-2-en-1-yl)morpholine (23b):

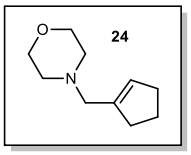
The reaction was carried out following the procedure B using morpholine and 3-methylenepentane. Then 25.4 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure A. The ratio of different products is determined by ^{1}**H NMR** spectrum and the result of (**22a** : **22b =** 1.15 : 1) can be concluded by the integral of the double bond.

^{1}H NMR of 23a (400 MHz, $CDCl_3$) δ 5.36 (q, *J* = 6.8 Hz, 1H), 3.75 – 3.62 (m, 4H), 2.95 (s, 1H), 2.84 (t, *J* = 1.2 Hz, 1H), 2.38 (dt, *J* = 13.8, 4.3 Hz, 4H), 2.16 – 2.03 (m, 2H), 1.75 – 1.54 (m, 3H), 1.00 (dt, *J* = 9.7, 7.5 Hz, 3H).

^{1}H NMR of 23b (400 MHz, $CDCl_3$) δ 5.44 (d, *J* = 6.9 Hz, 1H), 3.75 – 3.62 (m, 4H), 2.95 (s, 1H), 2.84 (t, *J* = 1.2 Hz, 1H), 2.38 (dt, *J* = 13.8, 4.3 Hz, 4H), 2.16 – 2.03 (m, 2H), 1.75 – 1.54 (m, 3H), 1.00 (dt, *J* = 9.7, 7.5 Hz, 3H).

^{13}C NMR of mixture (101 MHz, $CDCl_3$) δ 138.23, 137.84, 121.91, 121.50, 67.11, 67.07, 65.32, 57.00, 53.65, 53.58, 28.68, 21.60, 13.23, 12.85, 12.83, 12.72.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{20}NO$) requires *m/z* 170.1539, found *m/z* 170.1535.



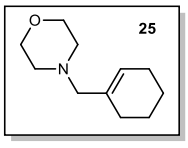
4-(cyclopent-1-en-1-ylmethyl)morpholine (24):

The reaction was carried out following the procedure B using morpholine and methylenecyclopentane. Then 27.7 mg colorless oily liquid was obtained in 83% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 – 5.52 (m, 1H), 3.82 – 3.63 (m, 4H), 3.05 – 2.91 (m, 2H), 2.47 – 2.24 (m, 8H), 1.96 – 1.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.93, 128.01, 66.97, 59.50, 53.79, 33.92, 32.20, 23.34.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{18}NO$) requires *m/z* 168.1383, found *m/z* 168.1381.

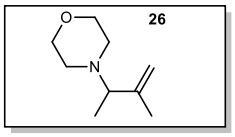


4-(cyclohex-1-en-1-ylmethyl)morpholine (25):

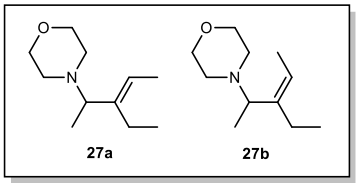
The reaction was carried out following the procedure B using morpholine and methylenecyclohexane. Then 27.2 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.56 (m, 1H), 3.70 (t, *J* = 4.7 Hz, 4H), 2.81 (s, 2H), 2.35 (t, *J* = 4.7 Hz, 4H), 2.07 – 1.90 (m, 4H), 1.70 – 1.50 (m, 4H).

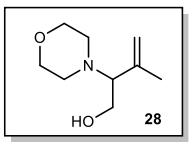
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.30, 125.17, 67.04, 66.38, 53.60, 27.14, 25.16, 22.76, 22.53.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{20}NO$) requires *m/z* 182.1539, found *m/z* 182.1536.



4-(3-methylbut-3-en-2-yl)morpholine (26):
The reaction was carried out following the procedure B using morpholine and 2-methylbut-2-ene. Then 26.4 mg colorless oily liquid was obtained in 85% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 – 4.82 (m, 1H), 4.80 – 4.73 (m, 1H), 3.69 (t, *J* = 4.7 Hz, 4H), 2.76 – 2.66 (m, 1H), 2.49 – 2.29 (m, 4H), 1.69 (t, *J* = 1.2 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.54, 112.16, 67.27, 66.62, 51.04, 17.91, 16.36.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_{18}NO$) requires m/z 156.1383, found m/z 156.1382.

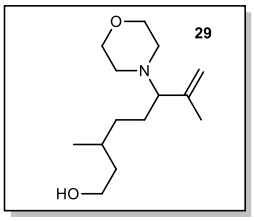


(*E*)-4-(3-ethylpent-3-en-2-yl)morpholine (27a) and (*Z*)-4-(3-ethylpent-3-en-2-yl)morpholine (27b):
The reaction was carried out following the procedure B using morpholine and 3-ethylpent-2-ene. Then 25.6 mg faint yellow oily liquid was obtained in 70% isolated yield following purification procedure A.
^{1}H NMR of mixture (400 MHz, $CDCl_3$) δ 5.39 – 5.25 (m, 1H), 3.77 – 3.60 (m, 4H), 2.89 (dq, *J* = 178.9, 6.6 Hz, 1H), 2.52 – 2.28 (m, 4H), 2.15 – 1.93 (m, 2H), 1.71 – 1.55 (m, 3H), 1.10 (dd, *J* = 6.6, 2.0 Hz, 3H), 1.00 (td, *J* = 7.5, 3.9 Hz, 3H).
^{13}C NMR of mixture (101 MHz, $CDCl_3$) δ 143.36, 142.90, 120.69, 119.06, 67.32, 67.23, 67.01, 59.70, 51.65, 51.00, 23.13, 20.63, 17.15, 16.38, 13.69, 13.00, 12.97, 12.71.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{22}NO$) requires *m/z* 184.1696, found *m/z* 184.1693.

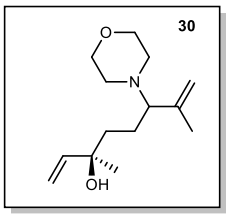


3-methyl-2-morpholinobut-3-en-1-ol (28):
The reaction was carried out following the procedure B using morpholine and 3-methylbut-2-en-1-ol. Then 19.9 mg colorless oily liquid was obtained in 58% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 – 5.01 (m, 1H), 4.89 (d, *J* = 1.7 Hz, 1H), 3.81 – 3.49 (m, 7H), 2.89 (t, *J* = 6.3 Hz, 1H), 2.63 – 2.54 (m, 2H), 2.52 – 2.43 (m, 2H), 1.76 (s, 3H).

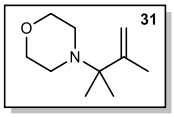
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.01, 115.48, 71.40, 67.32, 59.88, 50.63, 21.17.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_9H_{18}NO_2$) requires *m/z* 172.1332, found *m/z* 172.1326.



2,6-dimethyl-5-morpholinohept-6-en-1-ol (29):
The reaction was carried out following the procedure B using morpholine and citronellol. Then 36.2 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (t, *J* = 1.9 Hz, 1H), 4.83 (d, *J* = 2.7 Hz, 1H), 3.70 (dt, *J* = 10.6, 5.6 Hz, 6H), 2.59 – 2.31 (m, 5H), 1.80 – 1.51 (m, 6H), 1.45 – 1.14 (m, 4H), 1.09 – 0.97 (m, 1H), 0.96 – 0.86 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.19, 114.78, 114.70, 72.58, 67.27, 60.98, 51.51, 51.42, 40.13, 39.41, 33.84, 33.61, 29.62, 29.40, 25.95, 25.88, 19.84, 19.40, 17.99, 17.74.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{28}NO_2$) requires *m/z* 242.2115, found *m/z* 242.2111.



(3*R*)-3,7-dimethyl-6-morpholinoocta-1,7-dien-3-ol (30):
The reaction was carried out following the procedure B using morpholine and linalool. Then 41.2 mg colorless oily liquid was obtained in 86% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 – 5.80 (m, 1H), 5.33 – 5.18 (m, 1H), 5.12 – 5.02 (m, 1H), 4.98 – 4.90 (m, 1H), 4.84 – 4.75 (m, 1H), 3.80 – 3.61 (m, 4H), δ 2.82 – 2.31 (m, 5H), 1.86 – 1.74 (m, 1H), 1.67 (d, *J* = 3.1 Hz, 3H), 1.62 – 1.31 (m, 3H), 1.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.39, 145.28, 143.58, 142.93, 115.44, 114.99, 111.90, 111.60, 72.66, 72.51, 72.35, 71.98, 67.16, 66.93, 51.14, 50.58, 40.68, 39.06, 29.08, 27.72, 24.17, 23.25, 19.66, 18.68.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{26}NO_2$) requires *m/z* 240.1958, found *m/z* 240.1949.



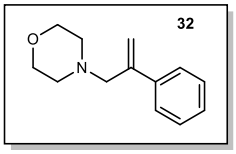
4-(2,3-dimethylbut-3-en-2-yl)morpholine (31):

The reaction was carried out following the procedure B using morpholine and 2,3-dimethylbut-2-ene. Then 28.8 mg colorless oily liquid was obtained in 85% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.79 (m, 2H), 3.77 – 3.63 (m, 4H), 2.55 – 2.42 (m, 4H), 1.77 (d, *J* = 0.7 Hz, 3H), 1.13 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.90, 110.76, 67.93, 60.01, 46.28, 21.30, 18.65.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{20}NO$) requires *m/z* 170.1539, found *m/z* 170.1537.



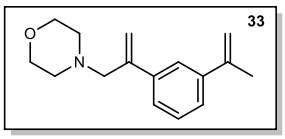
4-(2-phenylallyl)morpholine (32):

The reaction was carried out following the procedure D using morpholine and prop-1-en-2-ylbenzene. Then 22.7 mg colorless oily liquid was obtained in 56% isolated yield following purification procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.48 (m, 2H), 7.37 – 7.23 (m, 3H), 5.49 (d, *J* = 1.6 Hz, 1H), 5.24 (d, *J* = 1.4 Hz, 1H), 3.78 – 3.53 (m, 4H), 3.33 (d, *J* = 1.1 Hz, 2H), 2.47 (dd, *J* = 5.7, 3.5 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.56, 140.18, 128.11, 127.50, 126.24, 115.58, 67.03, 63.48, 53.52.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{18}NO$) requires *m/z* 204.1383, found *m/z* 204.1381.



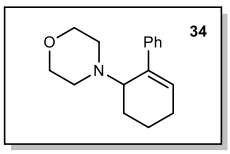
4-(2-(3-(prop-1-en-2-yl)phenyl)allyl)morpholine (33):

The reaction was carried out following the procedure D using morpholine and 1,3-di(prop-1-en-2-yl)benzene. Then 23.3 mg colorless oily liquid was obtained in 48% isolated yield following purification procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 1.8 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.32 – 7.23 (m, 1H), 5.51 (d, *J* = 1.7 Hz, 1H), 5.38 (t, *J* = 1.1 Hz, 1H), 5.25 (d, *J* = 1.5 Hz, 1H), 5.09 (t, *J* = 1.5 Hz, 1H), 3.75 – 3.61 (m, 4H), 3.34 (d, *J* = 1.1 Hz, 2H), 2.48 (dd, *J* = 5.9, 3.5 Hz, 4H), 2.17 (s, 3H).

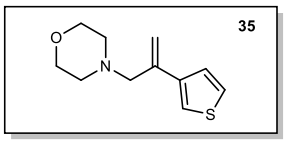
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.57, 143.30, 141.00, 140.16, 127.96, 125.35, 124.69, 123.57, 115.72, 112.44, 67.07, 63.61, 53.48, 21.85.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{22}NO$) requires *m/z* 244.1696, found *m/z* 244.1689.

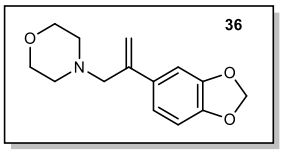


4-(2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)morpholine (34):

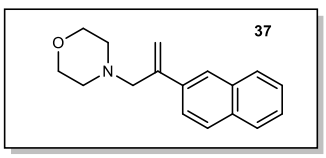
The reaction was carried out following the procedure D using morpholine and 2,3,4,5-tetrahydro-1,1'-biphenyl. Then 25.3 mg colorless oily liquid was obtained in 52% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 6.14 – 6.09 (m, 1H), 3.79 – 3.70 (m, 1H), 3.53 – 3.43 (m, 2H), 3.39 – 3.30 (m, 2H), 2.59 – 2.36 (m, 4H), 2.21 – 2.11 (m, 2H), 1.94 – 1.84 (m, 1H), 1.82 – 1.70 (m, 2H), 1.69 – 1.56 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.04, 139.14, 130.26, 127.49, 126.54, 126.13, 67.47, 59.76, 48.99, 25.95, 22.55, 20.40.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{22}NO$) requires *m/z* 244.1696, found *m/z* 244.1694.



4-(2-(thiophen-3-yl)allyl)morpholine (35):
The reaction was carried out following the procedure D using morpholine and 3-(prop-1-en-2-yl)thiophene. Then 20.9 mg colorless oily liquid was obtained in 50% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.34 – 7.16 (m, 2H), 5.50 (d, *J* = 1.5 Hz, 1H), 5.18 (d, *J* = 1.4 Hz, 1H), 4.01 – 3.43 (m, 4H), 3.27 (d, *J* = 1.2 Hz, 2H), 2.72 – 2.13 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.25, 138.51, 126.00, 124.95, 121.54, 114.38, 67.16, 64.12, 53.57.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{16}NOS$) requires *m/z* 210.0947, found *m/z* 210.0940.

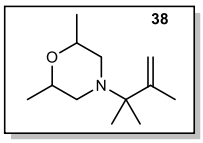


4-(2-(benzo[*d*][1,3]dioxol-5-yl)allyl)morpholine (36):
The reaction was carried out following the procedure D using morpholine and 5-(prop-1-en-2-yl)benzo[*d*][1,3]dioxole. Then 23.2 mg colorless oily liquid was obtained in 47% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 6.93 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 2H), 5.39 (d, *J* = 1.6 Hz, 1H), 5.15 (d, *J* = 1.4 Hz, 1H), 3.75 – 3.58 (m, 4H), 3.27 (d, *J* = 1.1 Hz, 2H), 2.53 – 2.31 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.43, 146.98, 142.92, 134.46, 119.83, 114.79, 107.89, 106.88, 100.94, 67.01, 63.85, 53.48.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}NO_3$) requires *m/z* 248.1281, found *m/z* 248.1275

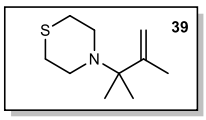


4-(2-(naphthalen-2-yl)allyl)morpholine (37):

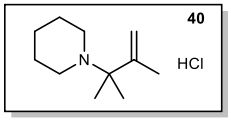
The reaction was carried out following the procedure D using morpholine and 2-(prop-1-en-2-yl)naphthalene. Then 24.3 mg colorless oily liquid was obtained in 48% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.7 Hz, 1H), 7.86 – 7.75 (m, 3H), 7.66 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.51 – 7.39 (m, 2H), 5.63 (d, *J* = 1.5 Hz, 1H), 5.35 (d, *J* = 1.4 Hz, 1H), 3.84 – 3.56 (m, 4H), 3.45 (d, *J* = 1.1 Hz, 2H), 2.65 – 2.42 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.53, 137.44, 133.27, 132.84, 128.23, 127.56, 127.49, 126.01, 125.82, 125.08, 124.66, 116.11, 67.05, 63.50, 53.56.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{20}NO$) requires *m/z* 254.1539, found *m/z* 255.1532.



4-(2,3-dimethylbut-3-en-2-yl)-2,6-dimethylmorpholine (38):
The reaction was carried out following the procedure B using 2,6-dimethylmorpholine and 2,3-dimethylbut-2-ene. Then 31.9 mg colorless oily liquid was obtained in 81% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (dd, *J* = 9.5, 1.7 Hz, 2H), 3.66 – 3.48 (m, 2H), 2.57 (d, *J* = 10.6 Hz, 1H), 1.87 – 1.80 (m, 2H), 1.73 (s, 3H), 1.14 (d, *J* = 6.2 Hz, 6H), 1.09 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.13, 110.59, 72.45, 59.71, 52.13, 21.32, 19.26, 18.68.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{24}NO$) requires *m/z* 198.1852, found *m/z* 198.1852.

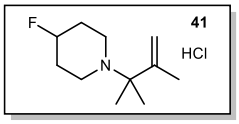


4-(2,3-dimethylbut-3-en-2-yl)thiomorpholine (39):
The reaction was carried out following the procedure B using thiomorpholine and 2,3-dimethylbut-2-ene. Then 20.0 mg colorless oily liquid was obtained in 54% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 – 4.82 (m, 1H), 4.81 – 4.79 (m, 1H), 2.77 – 2.68 (m, 4H), 2.65 – 2.57 (m, 4H), 1.75 – 1.67 (m, 3H), 1.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.58, 110.52, 61.14, 48.49, 29.05, 21.88, 18.62.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{20}NS$) requires *m/z* 186.1311, found *m/z* 186.1309.

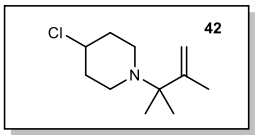


1-(2,3-dimethylbut-3-en-2-yl)piperidine hydrochloride (40):
The reaction was carried out following the procedure B using piperidine and 2,3-dimethylbut-2-ene. Then 30.5 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure C.

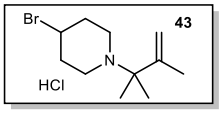
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (s, 1H), 5.36 – 5.20 (m, 2H), 3.56 – 3.47 (m, 2H), 2.80 – 2.58 (m, 4H), 2.14 (q, J = 2.1, 1.5 Hz, 3H), 1.97 – 1.78 (m, 4H), 1.68 – 1.61 (m, 6H), 1.41 – 1.29 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.09, 118.65, 68.23, 48.47, 22.62, 22.38, 21.94, 20.87.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{22}N$) requires *m/z* 168.1747, found *m/z* 168.1741.



1-(2,3-dimethylbut-3-en-2-yl)-4-fluoropiperidine hydrochloride (41):
The reaction was carried out following the procedure B using 4-fluoropiperidine hydrochloride and 2,3-dimethylbut-2-ene (1 equivalent K_2CO_3 was added). Then 29.2 mg colorless oily liquid was obtained in 66% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 5.38 – 5.28 (m, 2H), 4.98 (d, *J* = 48.2 Hz, 1H), 3.44 – 3.33 (m, 2H), 3.18 – 2.85 (m, 4H), 2.20 – 2.08 (m, 5H), 1.66 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.48, 118.85, 83.72 (d, *J* = 170.7 Hz), 68.45, 42.19 (d, *J* = 1.6 Hz), 27.53 (d, *J* = 19.7 Hz), 21.61, 20.43.
^{19}F NMR (377 MHz, $CDCl_3$) δ -188.27.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{21}NF$) requires *m/z* 186.1653, found *m/z* 186.1645.

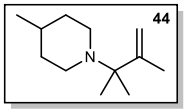


4-chloro-1-(2,3-dimethylbut-3-en-2-yl)piperidine (42):
The reaction was carried out following the procedure B using 4-chloropiperidine and 2,3-dimethylbut-2-ene. Then 27.3 mg colorless oily liquid was obtained in 68% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 – 4.74 (m, 2H), 3.96 (s, 1H), 2.85 – 2.64 (m, 2H), 2.21 (t, *J* = 10.4 Hz, 2H), 2.16 – 1.97 (m, 2H), 1.88 – 1.68 (m, 5H), 1.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.72, 110.08, 60.19, 58.67, 44.30, 36.80, 21.79, 18.66.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{21}NCl$) requires *m/z* 202.1357, found *m/z* 202.1350.

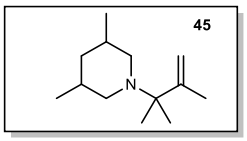


4-bromo-1-(2,3-dimethylbut-3-en-2-yl)piperidine (43):
The reaction was carried out following the procedure B using 4-bromopiperidine hydrobromide and 2,3-dimethylbut-2-ene (1 equivalent K_2CO_3 was added). Then 22.1 mg colorless oily liquid was obtained in 45% isolated yield following purification procedure C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 5.56 – 5.14 (m, 2H), 4.73 (p, *J* = 3.0 Hz, 1H), 3.43 – 3.19 (m, 6H), 2.21 – 2.06 (m, 5H), 1.68 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.84, 119.11, 68.74, 47.97, 42.85, 31.41, 21.89, 20.74.

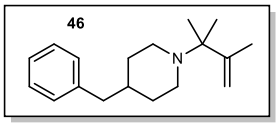
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{21}NBr$) requires *m/z* 246.0852, found *m/z* 246.0859.



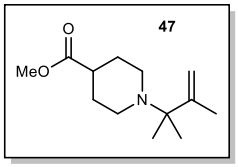
1-(2,3-dimethylbut-3-en-2-yl)-4-methylpiperidine (44):
The reaction was carried out following the procedure B using 4-methylpiperidine and 2,3-dimethylbut-2-ene. Then 25.4 mg colorless oily liquid was obtained in 70% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 – 4.74 (m, 2H), 2.82 – 2.72 (m, 2H), 2.08 – 1.97 (m, 2H), 1.75 (s, 3H), 1.62 – 1.54 (m, 2H), 1.36 – 1.23 (m, 1H), 1.24 – 1.01 (m, 8H), 0.89 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.20, 109.91, 60.57, 46.36, 35.28, 31.37, 21.99, 21.74, 18.83.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{24}N$) requires *m/z* 182.1903, found *m/z* 182.1911



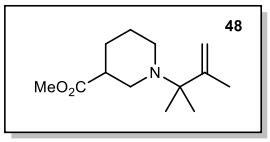
1-(2,3-dimethylbut-3-en-2-yl)-3,5-dimethylpiperidine (45):
The reaction was carried out following the procedure B using 3,5-dimethylpiperidine and 2,3-dimethylbut-2-ene. Then 32.4 mg colorless oily liquid was obtained in 83% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 – 4.73 (m, 2H), 2.70 (d, *J* = 10.3 Hz, 2H), 1.78 – 1.44 (m, 9H), 1.09 (s, 6H), 0.81 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.71, 109.51, 60.01, 54.12, 42.98, 31.97, 21.72, 19.85, 18.84.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{26}N$) requires *m/z* 196.2060, found *m/z* 196.2056.



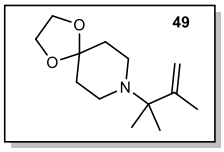
4-benzyl-1-(2,3-dimethylbut-3-en-2-yl)piperidine (46):
The reaction was carried out following the procedure B using 4-benzylpiperidine and 2,3-dimethylbut-2-ene. Then 38.6 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.22 – 7.09 (m, 3H), 4.80 – 4.73 (m, 2H), 2.81 – 2.70 (m, 2H), 2.50 (d, *J* = 7.1 Hz, 2H), 2.02 – 1.87 (m, 2H), 1.74 (s, 3H), 1.64 – 1.54 (m, 2H), 1.51 – 1.39 (m, 1H), 1.25 – 1.13 (m, 2H), 1.07 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.49, 141.10, 129.08, 128.04, 125.58, 109.59, 60.16, 46.17, 43.43, 38.63, 33.35, 21.72, 18.82.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{28}N$) requires *m/z* 258.2216, found *m/z* 258.2211.



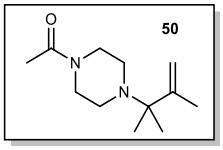
Methyl 1-(2,3-dimethylbut-3-en-2-yl)piperidine-4-carboxylate (47):
The reaction was carried out following the procedure B using methyl piperidine-4-carboxylate and 2,3-dimethylbut-2-ene. Then 32.4 mg colorless oily liquid was obtained in 72% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 – 4.75 (m, 2H), 3.67 (s, 3H), 2.81 (d, *J* = 11.4 Hz, 2H), 2.32 – 2.16 (m, 1H), 2.13 – 1.99 (m, 2H), 1.92 – 1.81 (m, 2H), 1.78 – 1.58 (m, 5H), 1.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.05, 153.04, 109.85, 60.19, 51.46, 45.46, 41.78, 29.27, 21.65, 18.64.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{24}NO_2$) requires *m/z* 226.1802, found *m/z* 226.1798.



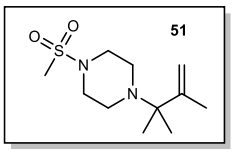
Methyl 1-(2,3-dimethylbut-3-en-2-yl)piperidine-3-carboxylate (48):
The reaction was carried out following the procedure B using methyl piperidine-3-carboxylate and 2,3-dimethylbut-2-ene. Then 24.8 mg colorless oily liquid was obtained in 55% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 – 4.75 (m, 2H), 3.67 (s, 3H), 2.89 (d, *J* = 11.0 Hz, 1H), 2.64 (d, *J* = 10.5 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.32 (t, *J* = 10.5 Hz, 1H), 2.12 (t, *J* = 10.2 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.76 – 1.65 (m, 4H), 1.53 – 1.41 (m, 2H), 1.11 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.23, 152.83, 109.99, 60.39, 51.40, 48.64, 46.27, 42.71, 27.47, 25.30, 22.01, 21.46, 18.60.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{24}NO_2$) requires *m/z* 226.1802, found *m/z* 226.1799.



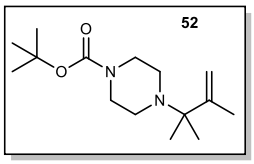
8-(2,3-dimethylbut-3-en-2-yl)-1,4-dioxa-8-azaspiro[4.5]decane (49):
The reaction was carried out following the procedure B using 1,4-dioxa-8-azaspiro[4.5]decane and 2,3-dimethylbut-2-ene. Then 28.4 mg colorless oily liquid was obtained in 63% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 – 4.75 (m, 2H), 3.94 (s, 4H), 2.50 (t, *J* = 5.5 Hz, 4H), 1.75 (d, *J* = 1.4 Hz, 3H), 1.68 (t, *J* = 5.6 Hz, 4H), 1.12 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.97, 109.80, 107.69, 64.02, 60.09, 43.69, 35.74, 21.89, 18.68.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{24}NO_2$) requires *m/z* 226.1802, found *m/z* 226.1793.



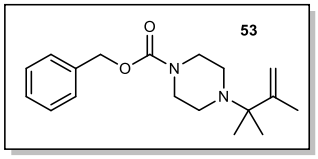
1-(4-(2,3-dimethylbut-3-en-2-yl)piperazin-1-yl)ethan-1-one (50):
The reaction was carried out following the procedure B using 1-(piperazin-1-yl)ethan-1-one and 2,3-dimethylbut-2-ene. Then 28.1 mg colorless oily liquid was obtained in 67% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 – 4.79 (m, 2H), 3.55 (t, *J* = 5.0 Hz, 2H), 3.46 – 3.30 (m, 2H), 2.48 – 2.35 (m, 4H), 2.07 (s, 3H), 1.76 (s, 3H), 1.11 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 151.75, 110.85, 60.12, 47.19, 46.13, 45.44, 42.28, 21.56, 21.33, 18.67.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{23}N_2O$) requires *m/z* 211.1805, found *m/z* 211.1803.



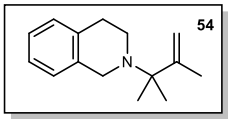
1-(2,3-dimethylbut-3-en-2-yl)-4-(methylsulfonyl)piperazine (51):
The reaction was carried out following the procedure B using 1-(methylsulfonyl)piperazine and 2,3-dimethylbut-2-ene. Then 39.4 mg colorless oily liquid was obtained in 80% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.81 (m, 2H), 3.18 (t, *J* = 4.8 Hz, 4H), 2.77 (s, 3H), 2.59 – 2.52 (m, 4H), 1.73 (s, 3H), 1.13 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.38, 111.16, 60.16, 46.78, 45.24, 33.81, 21.67, 18.62.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{23}N_2O_2S$) requires *m/z* 247.1475, found *m/z* 247.1470.



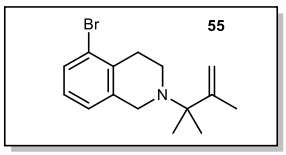
***tert*-butyl 4-(2,3-dimethylbut-3-en-2-yl)piperazine-1-carboxylate (52):**
The reaction was carried out following the procedure B using *tert*-butyl piperazine-1-carboxylate and 2,3-dimethylbut-2-ene. Then 43.5 mg colorless oily liquid was obtained in 81% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 – 4.69 (m, 2H), 3.42 – 3.28 (m, 4H), 2.46 – 2.28 (m, 4H), 1.74 (s, 3H), 1.45 (s, 9H), 1.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.77, 152.06, 110.56, 79.22, 60.04, 45.62, 28.38, 21.54, 18.64.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{29}N_2O_2$) requires *m/z* 269.2224, found *m/z* 269.2222



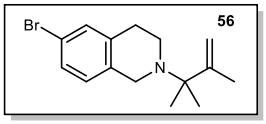
benzyl 4-(2,3-dimethylbut-3-en-2-yl)piperazine-1-carboxylate (53):
The reaction was carried out following the procedure B using benzyl piperazine-1-carboxylate and 2,3-dimethylbut-2-ene. Then 50.2 mg colorless oily liquid was obtained in 83% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 5.12 (s, 2H), 4.87 – 4.71 (m, 2H), 3.45 (t, *J* = 5.1 Hz, 4H), 2.40 (s, 4H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.92, 128.40, 127.86, 127.75, 110.71, 66.86, 60.11, 45.57, 44.66, 21.56, 18.64.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{27}N_2O_2$) requires *m/z* 303.2067, found *m/z* 303.2061.



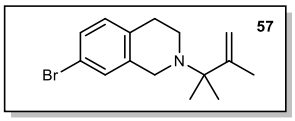
2-(2,3-dimethylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (54):
The reaction was carried out following the procedure B using 1,2,3,4-tetrahydroisoquinoline and 2,3-dimethylbut-2-ene. Then 24.1 mg colorless oily liquid was obtained in 56% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.04 (m, 4H), 5.00 – 4.94 (m, 1H), 4.91 (t, *J* = 1.5 Hz, 1H), 3.76 (s, 2H), 2.86 (t, *J* = 5.7 Hz, 2H), 2.70 (t, *J* = 5.7 Hz, 2H), 1.87 – 1.78 (m, 3H), 1.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.85, 136.36, 135.20, 128.62, 126.79, 125.62, 125.28, 110.30, 60.39, 48.34, 44.23, 30.49, 21.40, 18.96.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{22}N$) requires *m/z* 216.1747, found *m/z* 216.1744.



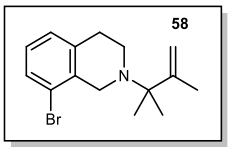
5-bromo-2-(2,3-dimethylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (55):
The reaction was carried out following the procedure B using 5-bromo-1,2,3,4-tetrahydroisoquinoline and 2,3-dimethylbut-2-ene. Then 28.7 mg colorless oily liquid was obtained in 49% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H), 7.07 – 6.97 (m, 2H), 4.96 (s, 1H), 4.91 (t, *J* = 1.5 Hz, 1H), 3.72 (s, 2H), 2.81 (t, *J* = 5.8 Hz, 2H), 2.70 (t, *J* = 5.8 Hz, 2H), 1.81 (s, 3H), 1.25 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.41, 138.99, 135.02, 129.64, 126.63, 125.89, 125.22, 110.57, 60.26, 48.62, 44.25, 31.65, 21.43, 18.91.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NBr$) requires *m/z* 294.0852, found *m/z* 294.0850.



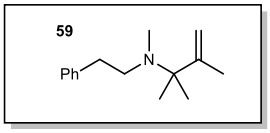
6-bromo-2-(2,3-dimethylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (56):
The reaction was carried out following the procedure B using 6-bromo-1,2,3,4-tetrahydroisoquinoline and 2,3-dimethylbut-2-ene. Then 33.4 mg colorless oily liquid was obtained in 57% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 1H), 4.95 (s, 1H), 4.90 (t, *J* = 1.5 Hz, 1H), 3.67 (s, 2H), 2.82 (t, *J* = 5.6 Hz, 2H), 2.66 (t, *J* = 5.7 Hz, 2H), 1.80 (s, 3H), 1.24 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.49, 137.56, 135.37, 131.32, 128.41, 128.29, 119.10, 110.51, 60.39, 48.00, 43.81, 30.31, 21.41, 18.90.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NBr$) requires *m/z* 294.0852, found *m/z* 294.0855.



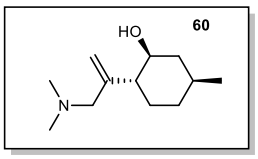
7-bromo-2-(2,3-dimethylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (57):
The reaction was carried out following the procedure B using 7-bromo-1,2,3,4-tetrahydroisoquinoline and 2,3-dimethylbut-2-ene. Then 26.4 mg colorless oily liquid was obtained in 45% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 1H), 4.92 – 4.87 (m, 1H), 3.69 (s, 2H), 2.78 (t, *J* = 5.7 Hz, 2H), 2.67 (t, *J* = 5.7 Hz, 2H), 1.81 (dd, *J* = 1.4, 0.7 Hz, 3H), 1.24 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.45, 138.65, 134.18, 130.26, 129.55, 128.63, 118.79, 110.53, 60.38, 48.09, 43.96, 30.00, 21.40, 18.88.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NBr$) requires *m/z* 294.0852, found *m/z* 294.0846.



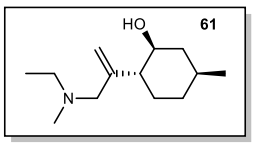
8-bromo-2-(2,3-dimethylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (58):
The reaction was carried out following the procedure B using 8-bromo-1,2,3,4-tetrahydroisoquinoline and 2,3-dimethylbut-2-ene. Then 28.2 mg colorless oily liquid was obtained in 48% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.09 – 6.93 (m, 2H), 4.94 (s, 1H), 4.89 – 4.86 (m, 1H), 3.68 (s, 2H), 2.81 (t, *J* = 5.7 Hz, 2H), 2.60 (t, *J* = 5.6 Hz, 2H), 1.78 (s, 3H), 1.25 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.50, 138.11, 135.58, 129.47, 127.76, 126.85, 123.31, 110.60, 60.63, 49.35, 43.64, 30.86, 21.41, 18.95.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NBr$) requires *m/z* 294.0852, found *m/z* 294.0861.



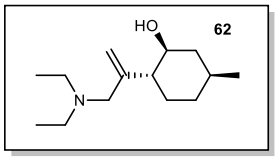
***N*,2,3-trimethyl-*N*-phenethylbut-3-en-2-amine (59):**
The reaction was carried out following the procedure B using *N*-methyl-2-phenylethan-1-amine and 2-methoxyprop-1-ene. Then 20.0 mg faint yellow liquid was obtained in 46% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 4.85 – 4.81 (m, 1H), 4.79 (p, *J* = 1.4 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.55 – 2.46 (m, 2H), 2.27 (s, 3H), 1.79 – 1.66 (m, 3H), 1.09 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.76, 140.93, 128.89, 128.24, 125.86, 110.39, 61.32, 53.47, 35.92, 34.65, 21.63, 18.93.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{24}N$) requires *m/z* 218.1903, found *m/z* 218.1901.



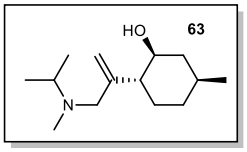
(1*S*,2*R*,5*S*)-2-(3-(dimethylamino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (60):
The reaction was carried out following the procedure C using dimethylamine hydrochloride and (-)-isopulegol (1 equivalent K_2CO_3 was added). Then 22.1 mg faint yellow liquid was obtained in 56% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 1H), 4.96 – 4.89 (m, 1H), 3.35 – 3.19 (m, 1H), 2.90 – 2.69 (m, 2H), 2.26 (s, 6H), 2.05 – 1.95 (m, 1H), 1.94 – 1.81 (m, 1H), 1.73 – 1.58 (m, 1H), 1.52 – 1.35 (m, 2H), 1.05 – 0.85 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.38, 116.79, 72.96, 65.54, 52.17, 44.50, 43.77, 34.60, 31.68, 31.38, 22.19.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{24}NO$) requires *m/z* 198.1852, found *m/z* 198.1855.



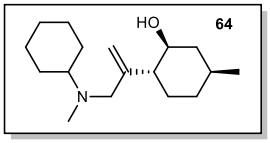
(1*S*,2*R*,5*S*)-2-(3-(ethyl(methyl)amino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (61):
The reaction was carried out following the procedure B using *N*-methylethanamine and (-)-isopulegol. Then 32.5 mg faint yellow liquid was obtained in 77% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (s, 1H), 4.94 (s, 1H), 3.35 – 3.21 (m, 1H), 2.94 – 2.82 (m, 2H), 2.60 – 2.45 (m, 2H), 2.23 (s, 3H), 2.09 – 1.95 (m, 1H), 1.94 – 1.80 (m, 1H), 1.74 – 1.61 (m, 2H), 1.58 – 1.33 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.01 – 0.87 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.38, 116.78, 72.95, 63.74, 52.12, 50.80, 43.88, 40.24, 34.60, 31.82, 31.35, 22.17, 11.85.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{26}NO$) requires *m/z* 212.2009, found *m/z* 212.2006.



(1*S*,2*R*,5*S*)-2-(3-(diethylamino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (62):
The reaction was carried out following the procedure B using diethylamine and (-)-isopulegol. Then 29.7 mg faint yellow liquid was obtained in 66% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 1H), 4.93 (s, 1H), 3.37 – 3.18 (m, 1H), 2.92 (q, *J* = 12.3 Hz, 2H), 2.72 – 2.43 (m, 4H), 2.14 – 1.95 (m, 1H), 1.89 – 1.78 (m, 1H), 1.70 – 1.59 (m, 2H), 1.55 – 1.33 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 6H), 0.93 (d, *J* = 6.5 Hz, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.68, 116.47, 73.01, 59.90, 52.08, 45.23, 44.06, 34.67, 32.01, 31.34, 22.18, 10.67.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{28}NO$) requires *m/z* 226.2165, found *m/z* 226.2163.

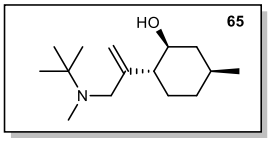


(1*S*,2*R*,5*S*)-2-(3-(isopropyl(methyl)amino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (63):
The reaction was carried out following the procedure B using diethylamine and (-)-isopulegol. Then 32.9 mg faint yellow liquid was obtained in 73% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 1H), 4.92 (s, 1H), 3.33 – 3.19 (m, 1H), 3.07 – 2.82 (m, 3H), 2.16 (s, 3H), 2.08 – 1.97 (m, 1H), 1.90 – 1.75 (m, 1H), 1.72 – 1.61 (m, 2H), 1.58 – 1.37 (m, 2H), 1.15 – 1.03 (m, 6H), 1.00 – 0.87 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.66, 116.17, 73.22, 60.53, 53.49, 51.92, 44.15, 34.67, 34.28, 31.83, 31.32, 22.18, 17.44, 17.11.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{28}NO$) requires *m/z* 226.2165, found *m/z* 226.2166.

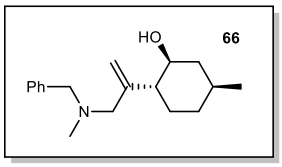


(1*S*,2*R*,5*S*)-2-(3-(cyclohexyl(methyl)amino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (64):
The reaction was carried out following the procedure B using *N*-methylcyclohexanamine and (-)-isopulegol. Then 34.5 mg faint yellow liquid was obtained in 65% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (s, 1H), 4.90 (s, 1H), 3.34 – 3.14 (m, 1H), 3.07 – 2.82 (m, 2H), 2.50 (s, 1H), 2.19 (s, 3H), 2.13 – 1.93 (m, 1H), 1.92 – 1.70 (m, 5H), 1.71 – 1.57 (m, 3H), 1.58 – 1.36 (m, 2H), 1.31 – 1.16 (m, 5H), 1.02 – 0.78 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.77, 116.07, 73.22, 62.87, 60.66, 51.87, 44.18, 35.38, 34.66, 31.85, 31.30, 28.02, 27.76, 26.14, 25.87, 25.84, 22.16.

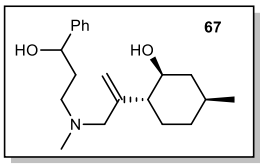
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{32}NO$) requires *m/z* 266.2478, found *m/z* 266.2474.



(1*S*,2*R*,5*S*)-2-(3-(tert-butyl(methyl)amino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (65):
The reaction was carried out following the procedure B using *N*,2-dimethylpropan-2-amine and (-)-isopulegol. Then 35.9 mg faint yellow liquid was obtained in 75% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (s, 1H), 4.94 (s, 1H), 3.28 – 3.14 (m, 2H), 2.61 (d, *J* = 12.1 Hz, 1H), 2.18 (s, 3H), 2.11 – 2.01 (m, 1H), 1.79 – 1.62 (m, 3H), 1.57 – 1.40 (m, 2H), 1.14 (s, 9H), 1.02 – 0.84 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.39, 115.56, 73.85, 58.44, 54.44, 50.88, 44.87, 34.72, 33.10, 31.88, 31.19, 25.75, 22.15.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{30}NO$) requires *m/z* 240.2322, found *m/z* 240.2321.

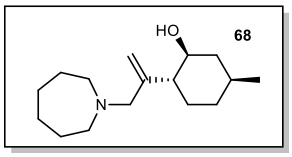


(1*S*,2*R*,5*S*)-2-(3-(benzyl(methyl)amino)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (66):
The reaction was carried out following the procedure B using *N*-methyl-1-phenylmethanamine and (-)-isopulegol. Then 25.7 mg faint yellow liquid was obtained in 47% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (s, 1H), 4.90 (s, 1H), 3.34 – 3.14 (m, 1H), 3.07 – 2.82 (m, 2H), 2.50 (s, 1H), 2.19 (s, 3H), 2.13 – 1.93 (m, 1H), 1.92 – 1.70 (m, 5H), 1.71 – 1.57 (m, 3H), 1.58 – 1.36 (m, 2H), 1.31 – 1.16 (m, 5H), 1.02 – 0.78 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.77, 116.07, 73.22, 62.87, 60.66, 51.87, 44.18, 35.38, 34.66, 31.85, 31.30, 28.02, 27.76, 26.14, 25.87, 25.84, 22.16.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{28}NO$) requires *m/z* 274.2165, found *m/z* 274.2161.

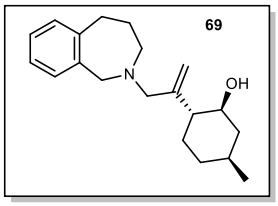


3-(methyl(2-methylallyl)amino)-1-phenylpropan-1-ol (67):
The reaction was carried out following the procedure B using 3-(methylamino)-1-phenylpropan-1-ol and (-)-isopulegol. Then 43.1 mg faint yellow liquid was obtained in 68% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.30 – 7.21 (m, 1H), 5.14 (s, 1H), 5.05 (s, 1H), 4.83 (t, *J* = 3.7 Hz, 1H), 3.49 – 3.30 (m, 1H), 3.07 (d, *J* = 12.5 Hz, 1H), 3.03 – 2.90 (m, 1H), 2.85

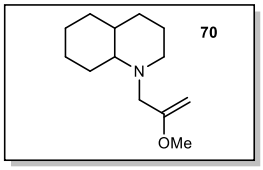
– 2.72 (m, 1H), 2.69 – 2.54 (m, 1H), 2.31 (s, 3H), 2.06 – 1.98 (m, 1H), 1.97 – 1.86 (m, 3H), 1.76 – 1.61 (m, 2H), 1.56 – 1.43 (m, 1H), δ 1.44 – 1.27 (m, 1H)., δ 1.09 – 0.86 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.62, 147.49, 144.70, 144.65, 128.39, 128.37, 127.27, 125.66, 116.45, 116.09, 73.72, 73.41, 73.19, 72.73, 64.72, 64.57, 55.11, 54.69, 50.92, 50.82, 44.00, 41.26, 35.45, 35.28, 34.55, 31.94, 31.68, 31.53, 31.48, 22.16.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{32}NO_2$) requires *m/z* 318.2428, found *m/z* 318.2429.



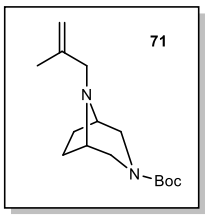
(1*S*,2*R*,5*S*)-2-(3-(azepan-1-yl)prop-1-en-2-yl)-5-methylcyclohexan-1-ol (68):
The reaction was carried out following the procedure B using azepane and (-)-isopulegol. Then 27.6 mg faint yellow liquid was obtained in 55% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (s, 1H), 4.91 (s, 1H), 3.37 – 3.25 (m, 1H), 3.07 – 2.85 (m, 2H), 2.74 – 2.59 (m, 4H), 2.11 – 1.98 (m, 1H), 1.94 – 1.83 (m, 1H), 1.71 – 1.55 (m, 10H), 1.53 – 1.35 (m, 2H), 1.05 – 0.82 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.90, 116.90, 72.85, 64.61, 55.44, 52.48, 43.86, 34.70, 31.92, 31.46, 27.16, 26.70, 22.26.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{30}NO$) requires *m/z* 252.2322, found *m/z* 252.2319.



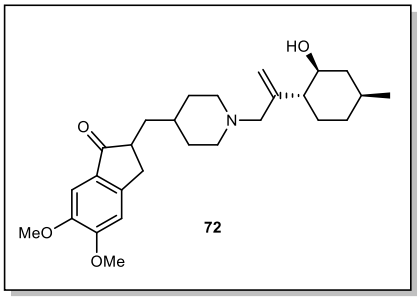
(1*S*,2*R*,5*S*)-5-methyl-2-(3-(1,3,4,5-tetrahydro-2H-benzo[*c*]azepin-2-yl)prop-1-en-2-yl)cyclohexan-1-ol (69):
The reaction was carried out following the procedure B using 2,3,4,5-tetrahydro-1H-benzo[*c*]azepine hydrochloride and (-)-isopulegol (1 equivalent K_2CO_3 was added). Then 34.1 mg faint yellow liquid was obtained in 57% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 4H), 5.09 (d, *J* = 1.5 Hz, 1H), 4.88 (d, *J* = 1.5 Hz, 1H), 3.95 (q, *J* = 14.5 Hz, 2H), 3.39 – 3.23 (m, 1H), 3.15 (q, *J* = 5.4 Hz, 2H), 3.01 – 2.86 (m, 3H), 2.78 (d, *J* = 12.6 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.94 – 1.81 (m, 1H), 1.81 – 1.70 (m, 2H), 1.70 – 1.56 (m, 2H), 1.53 – 1.31 (m, 2H), 1.04 – 0.85 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.25, 142.88, 137.51, 130.35, 128.90, 127.52, 125.96, 116.50, 72.98, 58.31, 57.93, 57.59, 52.34, 43.66, 35.92, 34.59, 31.83, 31.36, 24.31, 22.16.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{30}NO$) requires *m/z* 300.2322, found *m/z* 300.2322.



1-(2-methoxyallyl)decahydroquinoline (70):
The reaction was carried out following the procedure B using decahydroquinoline and 2-methoxyprop-1-ene. Then 27.6 mg colorless oily liquid was obtained in 48% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (s, 2H), 3.55 (s, 3H), 3.48 (d, *J* = 13.8 Hz, 1H), 2.98 (ddt, *J* = 11.7, 4.1, 2.5 Hz, 1H), 2.89 (d, *J* = 13.7 Hz, 1H), 2.21 – 2.08 (m, 2H), 1.77 (ddd, *J* = 14.3, 8.9, 3.6 Hz, 2H), 1.60 (tdd, *J* = 12.0, 5.5, 2.8 Hz, 5H), 1.35 – 1.20 (m, 4H), 1.05 – 0.91 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.02, 84.45, 67.07, 56.62, 55.03, 53.92, 41.93, 33.53, 32.82, 30.33, 26.21, 26.07, 25.67.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{24}NO$) requires *m/z* 210.1852, found *m/z* 210.1850.



***tert*-butyl (1*R*,5*S*)-8-(2-methylallyl)-3,8-diazabicyclo[3.2.1]octane-3-carboxylate (71):**
The reaction was carried out following the procedure C using *tert*-butyl 3,8-diazabicyclo[3.2.1]octane-3-carboxylate and 2-methylpropene (2.4mol/L in THF). Then 41.0 mg faint yellow liquid was obtained in 77% isolated yield following purification procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.82 (m, 2H), 3.81 – 3.66 (m, 1H), 3.65 – 3.51 (m, 1H), 3.20 – 2.93 (m, 4H), 2.86 (s, 2H), 1.93 – 1.82 (m, 2H), 1.78 (s, 3H), 1.68 – 1.53 (m, 2H), 1.45 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.06, 143.33, 112.20, 79.25, 59.51, 58.44, 58.34, 50.97, 49.80, 28.40, 25.06, 24.90, 20.82.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{27}N_2O_2$) requires *m/z* 267.2067, found *m/z* 267.2069.



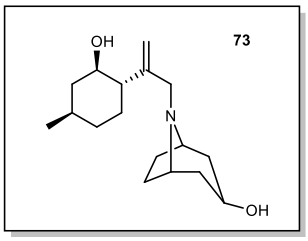
2-((1-(2-((1*R*,2*S*,4*S*)-2-hydroxy-4-methylcyclohexyl)allyl)piperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (72):

The reaction was carried out following the procedure B using 5,6-dimethoxy-2-(piperidin-4-ylmethyl)-2,3-dihydro-1H-inden-1-one and (-)-isopulegol. Then 54.7 mg faint yellow liquid was obtained in 62% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.85 (d, *J* = 1.6 Hz, 1H), 5.11 (t, *J* = 1.0 Hz, 1H), 4.92 (d, *J* = 1.4 Hz, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 3.36 – 3.19 (m, 2H), 3.05 (t, *J* = 14.4 Hz, 2H), 2.96 – 2.81 (m, 2H), 2.74 – 2.61 (m, 2H), 2.16 – 1.83 (m, 5H), 1.81 – 1.69 (m, 2H), 1.71 – 1.52 (m, 3H), 1.53 – 1.26 (m, 5H), 0.94 (d, *J* = 6.5 Hz, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.59, 207.57, 155.41, 149.37, 148.74, 147.81, 129.21, 117.04, 116.99, 107.31, 104.30, 73.14, 73.09, 64.81, 64.76, 56.22, 56.08, 52.82, 52.43, 52.38, 45.42, 43.85, 43.83, 38.45, 34.65, 33.68, 32.45, 32.31, 31.91, 31.43, 22.23.

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{27}H_{40}NO_4$) requires *m/z* 442.2952, found *m/z* 442.2942.



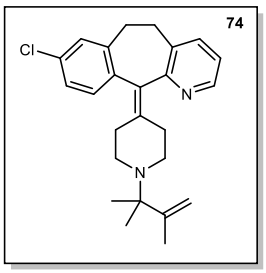
(1*R*,3*R*,5*S*)-8-(2-((1*S*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)allyl)-8-azabicyclo[3.2.1]octan-3-ol (73):

The reaction was carried out following the procedure B using nortropine and (-)-isopulegol. Then 36.3 mg faint yellow liquid was obtained in 65% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 1H), 5.01 (s, 1H), 4.13 (t, *J* = 5.0 Hz, 1H), 3.55 (s, 1H), 3.45 (s, 1H), 3.35 (td, *J* = 10.4, 4.2 Hz, 1H), 3.22 – 2.96 (m, 2H), 2.35 (dd, *J* = 29.6, 11.4 Hz, 4H), 2.19 – 1.94 (m, 4H), 1.83 (d, *J* = 14.9 Hz, 2H), 1.73 – 1.62 (m, 2H), 1.59 – 1.26 (m, 3H), 0.97 (d, *J* = 6.5 Hz, 4H).

. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.59, 117.50, 73.63, 63.55, 57.87, 51.26, 43.80, 34.37, 31.73, 31.42, 25.54, 25.14, 22.05.

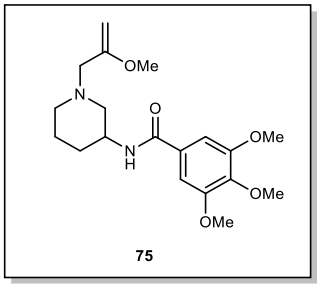
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{30}NO_2$) requires *m/z* 280.2271, found *m/z* 280.2270.



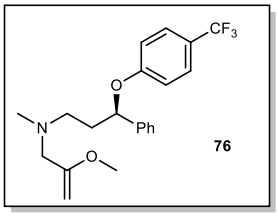
8-chloro-11-(1-(2,3-dimethylbut-3-en-2-yl)piperidin-4-ylidene)-6,11-dihydro-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine (74):

The reaction was carried out following the procedure B using desloratadine and (-)-isopulegol. Then 47.8 mg faint yellow liquid was obtained in 61% isolated yield following purification procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, 1H), 7.43 – 7.38 (m, 1H), 7.16 – 7.01 (m, 4H), 4.76 (d, *J* = 13.7 Hz, 2H), 3.54 – 3.29 (m, 2H), 2.89 – 2.62 (m, 4H), 2.49 – 2.23 (m, 4H), 2.20 – 2.08 (m, 2H), 1.76 (s, 3H), 1.08 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.81, 152.91, 146.42, 140.28, 139.36, 137.84, 136.95, 133.26, 132.29, 131.58, 130.91, 128.75, 125.72, 121.80, 109.73, 60.05, 47.38, 47.33, 31.98, 31.77, 31.30, 21.89, 21.52, 18.69.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{25}H_{30}N_2Cl$) requires *m/z* 393.30920, found *m/z* 393.30930.

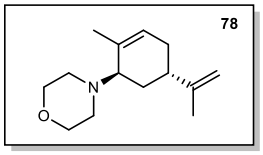


3,4,5-trimethoxy-*N*-(1-(2-methoxyallyl)piperidin-3-yl)benzamide (75):
The reaction was carried out following the procedure B using troxipide and (-)-isopulegol. Then 28.4 mg faint yellow liquid was obtained in 39% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 4.35 – 4.18 (m, 1H), 4.08 (dd, *J* = 15.1, 2.0 Hz, 2H), 3.92 (s, 6H), 3.88 (s, 3H), 3.55 (s, 3H), 3.10 – 2.91 (m, 2H), 2.66 (d, *J* = 19.0 Hz, 2H), 2.56 – 2.44 (m, 1H), 2.36 – 2.21 (m, 1H), 1.85 – 1.70 (m, 2H), 1.68 – 1.54 (m, 2H), 1.45 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.00, 152.99, 140.59, 130.22, 104.37, 61.68, 60.83, 57.51, 56.23, 54.87, 53.78, 45.35, 30.06, 28.63, 21.73.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{29}N_2O_5$) requires *m/z* 365.2071, found *m/z* 365.2065.

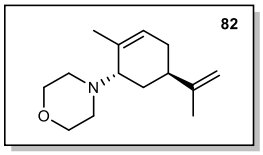


2-methoxy-*N*-methyl-*N*-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)prop-2-en-1-amine (76):
The reaction was carried out following the procedure B using fluoxetine and 2-methoxyprop-1-ene. Then 59.9 mg faint yellow liquid was obtained in 78% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.31 – 7.20 (m, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.30 (dd, *J* = 8.4, 4.6 Hz, 1H), 4.00 (dd, *J* = 20.3, 1.9 Hz, 2H), 3.44 (s, 3H), 3.07 – 2.86 (m, 2H), 2.70 – 2.56 (m, 1H), 2.52 – 2.37 (m, 1H), 2.26 (s, 3H), 2.23 – 2.12 (m, 1H), 2.07 – 1.93 (m, 1H).
^{19}F NMR (377 MHz, $CDCl_3$) δ -61.47.
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.69, 160.40, 141.26, 128.66, 127.67, 126.63 (q, *J* = 3.8 Hz), 125.80, 123.13 – 122.27 (m), 115.72, 83.92, 78.32, 61.19, 54.81, 52.99, 42.45, 36.43.

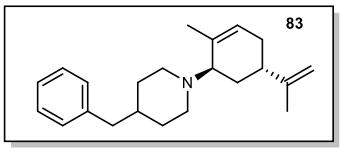
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{21}H_{25}NO_2F_3$) requires *m/z* 380.1832, found *m/z* 380.1830.



4-((1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)morpholine (78):
The reaction was carried out following the procedure A using morpholine and (+)-α-pinene. Then 38.9 mg colorless oily liquid was obtained in 88% isolated yield following purification procedure A. The stereoselectivity of the product is confirmed by 2D NMR.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.62 (m, 1H), 4.75 – 4.65 (m, 2H), 3.77 – 3.56 (m, 4H), 3.01 (d, J = 6.3 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.50 – 2.39 (m, 2H), 2.28 – 2.16 (m, 1H), 2.14 – 2.04 (m, 2H), 1.91 – 1.78 (m, 1H), 1.77 – 1.68 (m, 6H), 1.38 – 1.26 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.38, 133.49, 125.83, 108.70, 67.77, 61.87, 49.57, 38.37, 30.38, 27.20, 21.50, 20.96.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1849.
Optical Rotation: $[\alpha]_D^{18.1}$ = + 27.27 (*c* 0.73, $CHCl_3$)

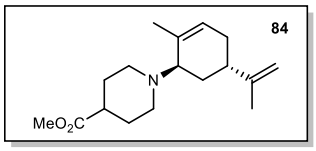


4-((1*S*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)morpholine (82):
The reaction was carried out following the procedure A using morpholine and (-)-α-pinene. Then 37.6 mg colorless oily liquid was obtained in 85% isolated yield following purification procedure A. The stereoselectivity of the product is confirmed by 2D NMR.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 – 5.62 (m, 1H), 4.70 (d, *J* = 12.5 Hz, 2H), 3.77 – 3.54 (m, 4H), 3.11 – 2.86 (m, 1H), 2.76 – 2.57 (m, 2H), 2.53 – 2.38 (m, 2H), 2.27 – 2.16 (m, 1H), 2.13 – 2.04 (m, 2H), 1.95 – 1.78 (m, 1H), 1.74 (s, 6H), 1.37 – 1.29 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.36, 133.51, 125.79, 108.69, 67.78, 61.88, 49.58, 38.38, 30.38, 27.24, 21.48, 20.95.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1851
Optical Rotation: $[\alpha]_D^{18.1}$ = -23.8 (*c* 0.29, $CHCl_3$)

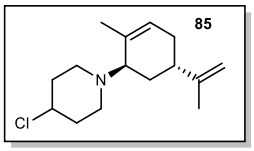


4-benzyl-1-((1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)piperidine (83):
The reaction was carried out following the procedure A using 4-benzylpiperidine and (+)-α-pinene. Then 40.8 mg faint yellow oily liquid was obtained in 66% isolated yield following purification

procedure A. The stereoselectivity of the product is confirmed by 2D NMR. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 2.1 Hz, 2H), 7.22 – 7.10 (m, 3H), 5.68 – 5.55 (m, 1H), 4.68 (d, *J* = 13.1 Hz, 2H), 3.04 (d, *J* = 6.3 Hz, 1H), δ 2.75 – 2.68 (m, 1H), 2.64 (d, *J* = 11.4 Hz, 1H).
, 2.54 – 2.44 (m, 3H), 2.24 – 2.12 (m, 1H), 2.13 – 1.99 (m, 3H), 1.84 – 1.71 (m, 8H), 1.67 – 1.52 (m, 2H), 1.53 – 1.40 (m, 1H), 1.33 – 1.22 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.68, 141.02, 129.07, 128.06, 125.61, 108.49, 61.82, 51.78, 47.49, 43.42, δ 38.55 (d, *J* = 8.9 Hz), 33.16 (d, *J* = 9.2 Hz), 30.47, 26.93, 21.49, 20.99.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{32}N$) requires *m/z* 310.2529, found *m/z* 310.2517.
Optical Rotation: $[\alpha]_D^{17.7}$ = + 43.18 (*c* 0.22, $CHCl_3$)

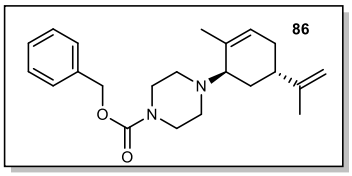


methyl 1-((1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)piperidine-4-carboxylate (84):
The reaction was carried out following the procedure A using methyl piperidine-4-carboxylate and (+)-α-pinene. Then 37.7 mg faint yellow oily liquid was obtained in 68% isolated yield following purification procedure A. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 – 5.60 (m, 1H), 4.80 – 4.61 (m, 2H), 3.67 (s, 3H), 3.12 – 2.93 (m, 1H), 2.88 – 2.75 (m, 1H), 2.75 – 2.64 (m, 1H), 2.61 – 2.47 (m, 1H), 2.33 – 1.95 (m, 6H), 1.92 – 1.79 (m, 3H), 1.74 – 1.67 (m, 7H), 1.38 – 1.26 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.01, 149.50, 134.29, 125.10, 108.59, 61.88, 51.53, 50.82, 46.92, 41.68, 38.53, 30.45, 29.24, 29.15, 26.95, 21.35, 20.97.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{28}NO_2$) requires *m/z* 278.2115, found *m/z* 278.2107.
Optical Rotation: $[\alpha]_D^{15.2}$ = + 66.39 (*c* 0.66, $CHCl_3$)

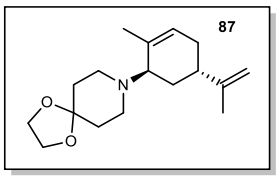


4-chloro-1-((1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)piperidine hydrochloride (85):
The reaction was carried out following the procedure A using 4-chloropiperidine and (+)-α-pinene. Then 31.2 mg white power was obtained in 54% isolated yield following purification procedure A. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 – 5.59 (m, 1H), 4.79 – 4.64 (m, 2H), 4.10 – 3.90 (m, 1H), 3.13 – 3.00 (m, 1H), 2.94 – 2.83 (m, 1H), 2.77 – 2.66 (m, 1H), 2.66 – 2.55 (m, 1H), 2.33 – 2.16 (m, 2H), 2.17 – 1.99 (m, 4H), 1.99 – 1.77 (m, 3H), 1.76 (s, 3H), 1.76 – 1.70 (m, 3H), 1.42 – 1.32 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.41, 134.08, 125.32, 108.68, 61.64, 58.49, 46.58, 38.44, 36.69, 30.44, 27.11, 21.37, 21.00.

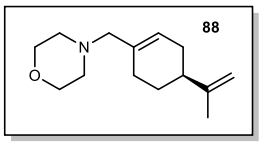
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{25}NCl$) requires *m/z* 254.1670, found *m/z* 254.1663.
Optical Rotation: $[\alpha]_D^{15.1} = +66.67$ (*c* 0.18, $CHCl_3$)



benzyl 4-((1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)piperazine-1-carboxylate (86):
The reaction was carried out following the procedure A using benzyl piperazine-1-carboxylate and (+)-α-pinene. Then 54.5 mg yellow oily liquid was obtained in 77% isolated yield following purification procedure A. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 5.74 – 5.67 (m, 1H), 5.16 (s, 2H), 4.78 – 4.68 (m, 2H), 3.64 – 3.39 (m, 4H), 3.16 – 3.05 (m, 1H), 2.76 – 2.60 (m, 2H), 2.50 – 2.36 (m, 2H), 2.26 – 2.07 (m, 2H), 2.08 – 2.00 (m, 1H), 1.91 – 1.79 (m, 1H), 1.75 (s, 6H), 1.40 – 1.29 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.24, 149.22, 136.76, 133.39, 128.42, 127.91, 127.81, 125.91, 108.77, 66.97, 61.82, 48.85, 44.60, 38.30, 30.38, 27.08, 21.41, 20.94.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{31}N_2O_2$) requires *m/z* 355.2380, found *m/z* 355.2375.
Optical Rotation: $[\alpha]_D^{15.1} = +33.45$ (*c* 0.56, $CHCl_3$)

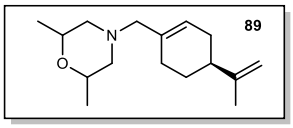


8-((1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)-1,4-dioxa-8-azaspiro[4.5]decane (87):
The reaction was carried out following the procedure A using 1,4-dioxa-8-azaspiro[4.5]decane and (+)-α-pinene. Then 41.0 mg colorless oily liquid was obtained in 74% isolated yield following purification procedure B. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 – 5.58 (m, 1H), 4.74 – 4.64 (m, 2H), 3.95 (d, *J* = 1.7 Hz, 4H), 3.09 (d, *J* = 6.3 Hz, 1H), 2.79 – 2.68 (m, 2H), 2.54 – 2.42 (m, 2H), 2.24 – 2.15 (m, 1H), 2.10 – 2.01 (m, 2H), 1.80 – 1.57 (m, 11H), 1.38 – 1.29 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.52, 134.43, 125.07, 108.60, 107.76, 64.09, 61.51, 46.98, 38.33, 35.80, 30.62, 27.05, 21.44, 21.06.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{28}NO_2$) requires *m/z* 278.2115, found *m/z* 278.2112.
Optical Rotation: $[\alpha]_D^{17.4} = +98.101$ (*c* 0.158, $CHCl_3$)

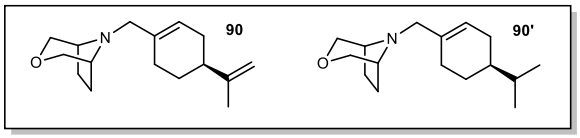


(*S*)-4-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)morpholine (88):

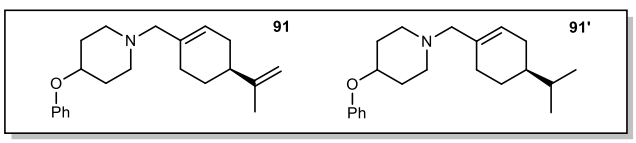
The reaction was carried out following the procedure A using morpholine and (-)-β-pinene. Then 42.4 mg colorless oily liquid was obtained in 96% isolated yield following purification procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (s, 1H), 4.71 (d, *J* = 5.1 Hz, 2H), 3.70 (t, *J* = 4.7 Hz, 4H), 2.95 – 2.69 (m, 2H), 2.35 (s, 4H), 2.19 – 2.02 (m, 4H), 1.87 – 1.71 (m, 5H), 1.52 – 1.37 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.93, 134.14, 124.57, 108.50, 67.06, 65.92, 53.62, 41.20, 30.63, 27.67, 27.58, 20.78.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{24}NO$) requires *m/z* 222.1852, found *m/z* 222.1848.



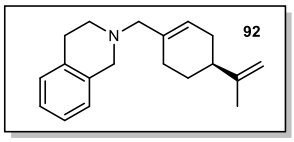
2,6-dimethyl-4-(((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)morpholine (89):
The reaction was carried out following the procedure A using 2,6-dimethylmorpholine and (-)-β-pinene. Then 47.3 mg colorless oily liquid was obtained in 95% isolated yield following purification procedure A. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 4.81 – 4.63 (m, 2H), 3.72 – 3.62 (m, 2H), 2.79 (d, *J* = 6.9 Hz, 2H), 2.65 (tt, *J* = 12.9, 1.9 Hz, 2H), 2.19 – 1.92 (m, 5H), 1.86 – 1.78 (m, 1H), 1.74 (s, 3H), 1.60 (dt, *J* = 11.3, 1.2 Hz, 2H), 1.52 – 1.40 (m, 1H), 1.15 (dd, *J* = 6.3, 2.6 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.90, 134.25, 124.34, 108.48, 71.69, 65.51, 59.55, 59.45, 41.17, 30.59, 27.64, 27.56, 20.78, 19.17.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{28}NO$) requires *m/z* 250.2165, found *m/z* 250.2164.



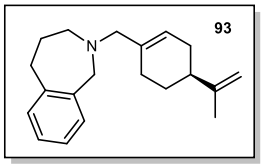
8-(((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)-3-oxa-8-azabicyclo[3.2.1]octane (90):
The reaction was carried out following the procedure A using 3-Oxa-8-azabicyclo[3.2.1]octane hydrochloride and (-)-β-pinene (1 equivalent K_2CO_3 was added). Then 37.1 mg colorless oily liquid was obtained in 75% isolated yield following purification procedure A. This contains 10 % amount of hydroamination product **90'**.
^{1}H NMR of **90** (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 4.71 (d, *J* = 1.5 Hz, 2H), 3.69 (dd, *J* = 10.1, 3.9 Hz, 2H), 3.51 (dt, *J* = 10.1, 2.4 Hz, 2H), 2.98 (ddd, *J* = 9.0, 4.6, 2.3 Hz, 2H), 2.78 (s, 2H), 2.27 – 2.03 (m, 4H), 2.02 – 1.78 (m, 6H), 1.74 (s, 3H), 1.54 – 1.40 (m, 1H).
^{13}C NMR of **90** (101 MHz, $CDCl_3$) δ 150.06, 135.27, 123.33, 108.45, 73.61, 60.24, 60.18, 60.03, 41.31, 30.65, 27.71, 27.56, 24.83, 24.73, 20.79.
HRMS (ESI) of **90** exact mass calculated for $[M+H]^+$ ($C_{16}H_{26}NO$) requires *m/z* 248.2009, found *m/z* 248.2008.



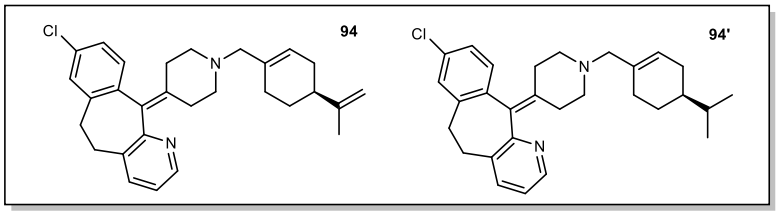
(*S*)-4-phenoxy-1-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)piperidine (91):
The reaction was carried out following the procedure A using 4-phenoxypiperidine hydrochloride and (-)-β-pinene (1 equivalent K_2CO_3 was added). Then 36.1 mg colorless oily liquid was obtained in 58% isolated yield following purification procedure A. This contains 10 % amount of hydroamination product **91'**.
^{1}H NMR of **91** (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 6.92 (dd, *J* = 10.4, 7.6 Hz, 3H), 5.59 (s, 1H), 4.71 (s, 2H), 4.36 – 4.23 (m, 1H), 2.84 (d, *J* = 4.6 Hz, 2H), 2.71 – 2.62 (m, 2H), 2.24 – 2.07 (m, 5H), 2.04 – 1.90 (m, 4H), 1.87 – 1.76 (m, 3H), 1.74 (s, 3H), 1.55 – 1.38 (m, 1H).
^{13}C NMR of **91** (101 MHz, $CDCl_3$) δ 157.46, 150.02, 134.93, 129.41, 123.91, 120.62, 116.06, 108.46, 65.45, 50.71, 41.23, 30.92, 30.65, 27.71, 27.63, 20.80.
HRMS (ESI) of **91** exact mass calculated for $[M+H]^+$ ($C_{21}H_{30}N_1O_1$) requires *m/z* 312.2322, found *m/z* 312.2317.



(*S*)-2-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (92):
The reaction was carried out following the procedure A using 1,2,3,4-tetrahydroisoquinoline and (-)-β-pinene. Then 41.1 mg yellow oily liquid was obtained in 77% isolated yield following purification procedure A. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 3H), 7.10 – 7.03 (m, 1H), 5.71 (s, 1H), 4.78 (s, 2H), 3.66 – 3.49 (m, 2H), 3.11 – 3.00 (m, 2H), 2.98 – 2.88 (m, 2H), 2.76 – 2.62 (m, 2H), 2.28 – 2.06 (m, 5H), 1.92 – 1.83 (m, 1H), 1.80 (s, 3H), 1.60 – 1.49 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.98, 135.13, 134.79, 134.53, 128.62, 126.57, 125.95, 125.44, 124.19, 108.49, 65.27, 56.25, 50.37, 41.22, 30.67, 29.17, 27.69, 27.56, 20.83, 19.98.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{26}N$) requires *m/z* 268.2060, found *m/z* 268.2053.



(*S*)-2-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepine (93):
The reaction was carried out following the procedure A using 2,3,4,5-tetrahydro-1H-benzo[*c*]azepine hydrochloride and (-)-β-pinene (1 equivalent K_2CO_3 was added). Then 45.5 mg yellow oily liquid was obtained in 81% isolated yield following purification procedure A. Trace hydroamination products were mixed.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.03 (m, 4H), 5.51 (s, 1H), 4.73 (s, 2H), 3.79 (s, 2H), 3.02 (t, *J* = 5.2 Hz, 2H), 2.93 – 2.82 (m, 4H), 2.21 – 2.06 (m, 3H), 2.06 – 1.94 (m, 2H), 1.89 – 1.78 (m, 1H), 1.78 – 1.65 (m, 5H), 1.55 – 1.41 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.08, 143.06, 139.64, 135.19, 129.86, 128.65, 126.97, 125.70, 123.98, 108.45, 60.67, 59.14, 58.86, 41.29, 36.06, 30.69, 27.74, 27.45, 25.37, 20.85.
HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{28}N$) requires *m/z* 282.2216, found *m/z* 282.2210.



(*S*)-8-chloro-11-(1-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)piperidin-4-ylidene)-6,11-dihydro-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine (94):

The reaction was carried out following the procedure A using desloratadine and (-)-β-pinene. Then 53.3 mg yellow oily liquid was obtained in 60% isolated yield following purification procedure A. 10% amount of hydroamination product were mixed **94'**.

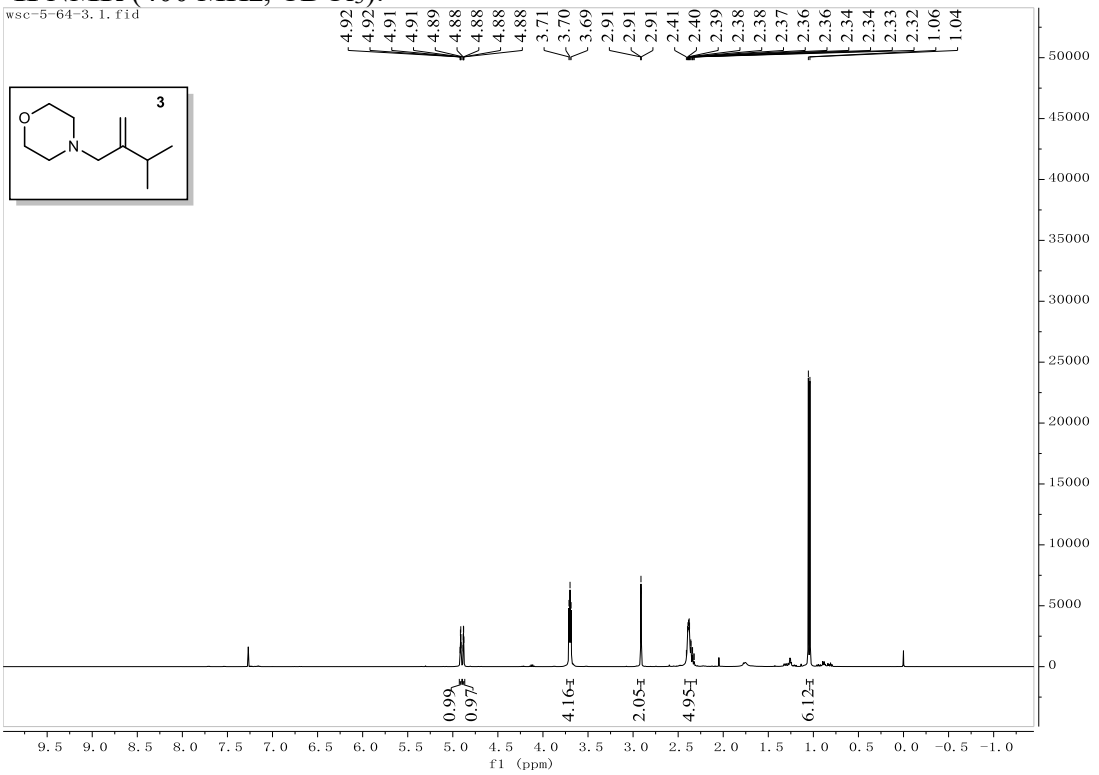
^{1}H NMR of **94** (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.17 – 7.04 (m, 4H), 5.55 (s, 1H), 4.69 (d, *J* = 5.0 Hz, 2H), 3.50 – 3.29 (m, 2H), 2.88 – 2.74 (m, 4H), 2.74 – 2.63 (m, 2H), 2.54 – 2.45 (m, 1H), 2.43 – 2.27 (m, 3H), 2.14 – 1.89 (m, 7H), 1.85 – 1.70 (m, 4H), 1.49 – 1.37 (m, 1H).

^{13}C NMR of **94** (101 MHz, $CDCl_3$) δ 157.69, 149.92, 146.53, 139.52, 139.42, 137.82, 137.09, 134.86, 133.32, 132.44, 132.15, 130.84, 128.84, 125.87, 123.88, 121.93, 108.41, 65.26 (d, *J* = 3.8 Hz), 54.81 (dd, *J* = 9.2, 7.1 Hz), 41.15, 31.78, 31.35, 30.96, 30.74 (d, *J* = 1.5 Hz), 30.58, 27.78 – 27.35 (m), 20.75 .

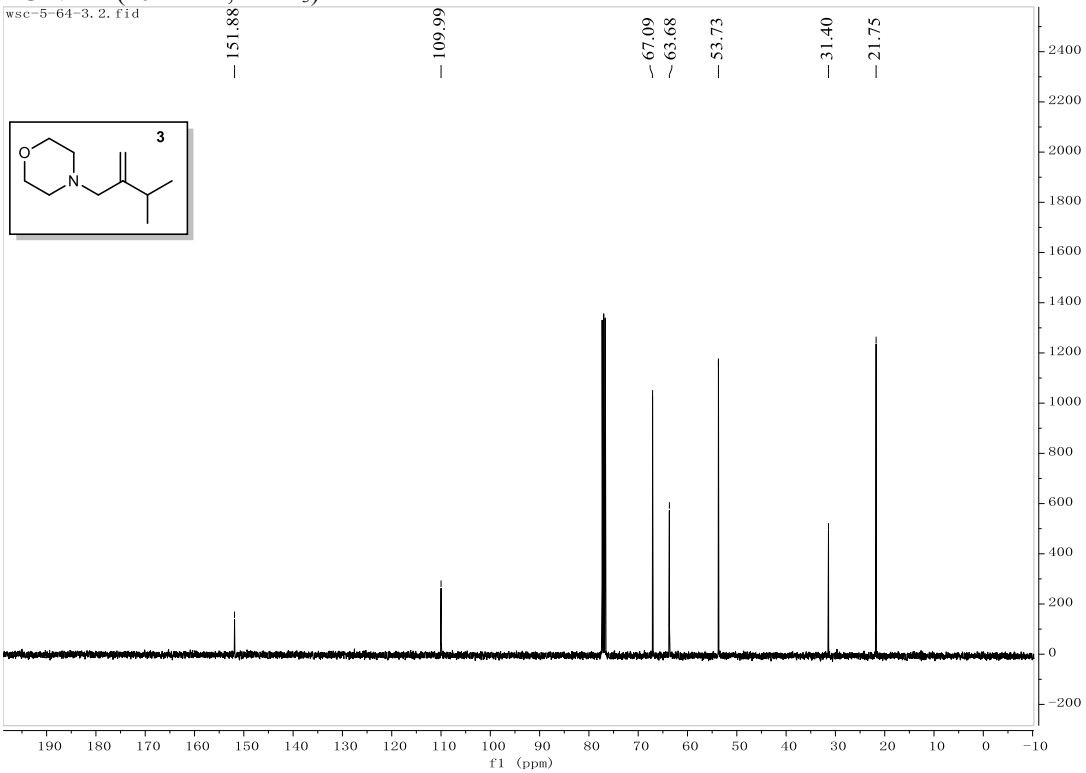
HRMS (ESI) of **94** exact mass calculated for $[M+H]^+$ ($C_{29}H_{34}N_2Cl$) requires *m/z* 445.2405, found *m/z*

NMR Spectrum

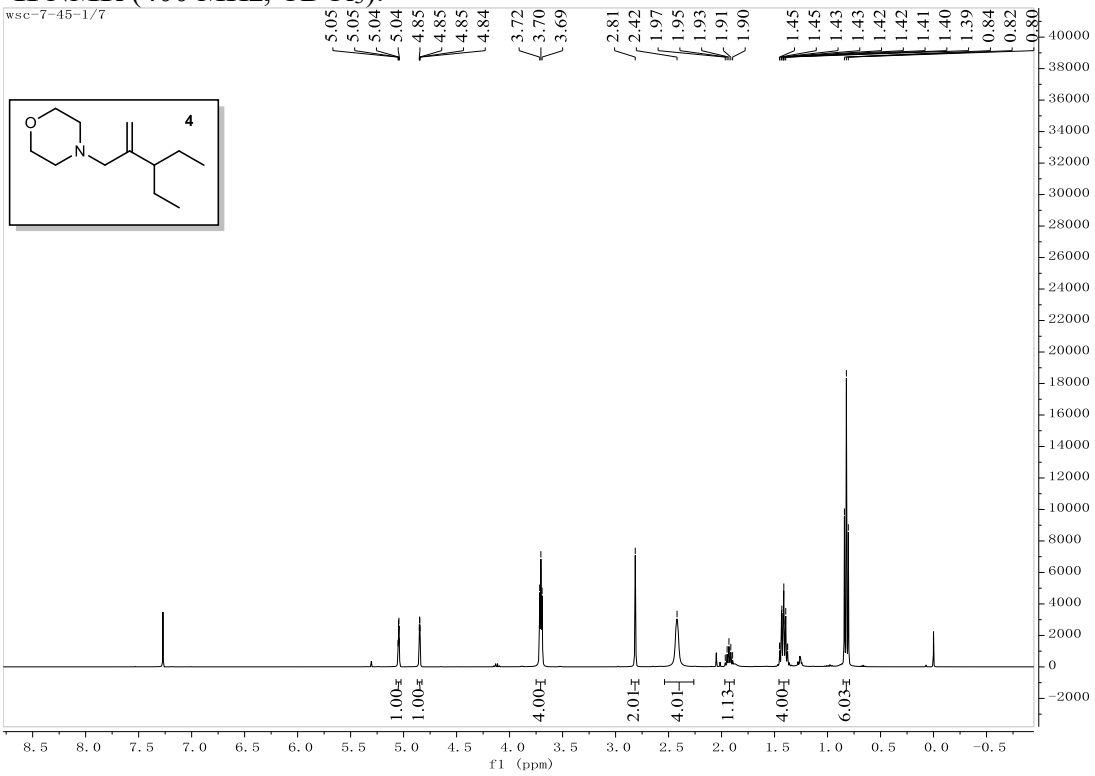
^{1}H NMR (400 MHz, $CDCl_3$):



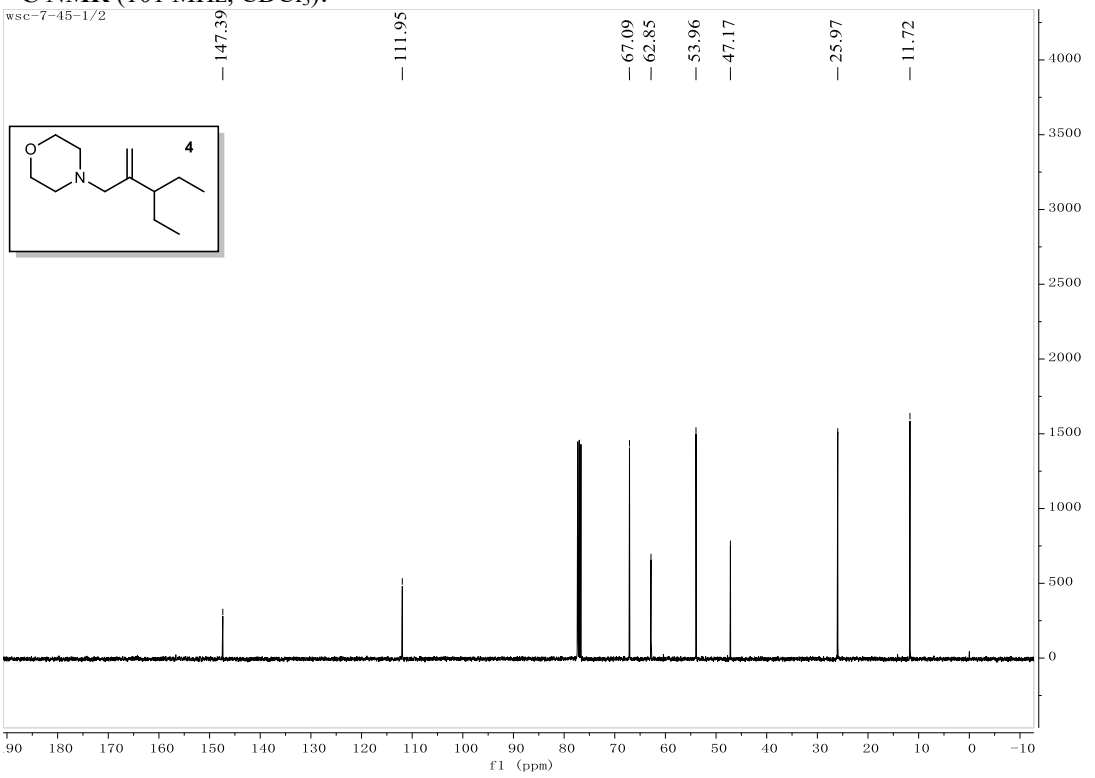
^{13}C NMR (101 MHz, $CDCl_3$):



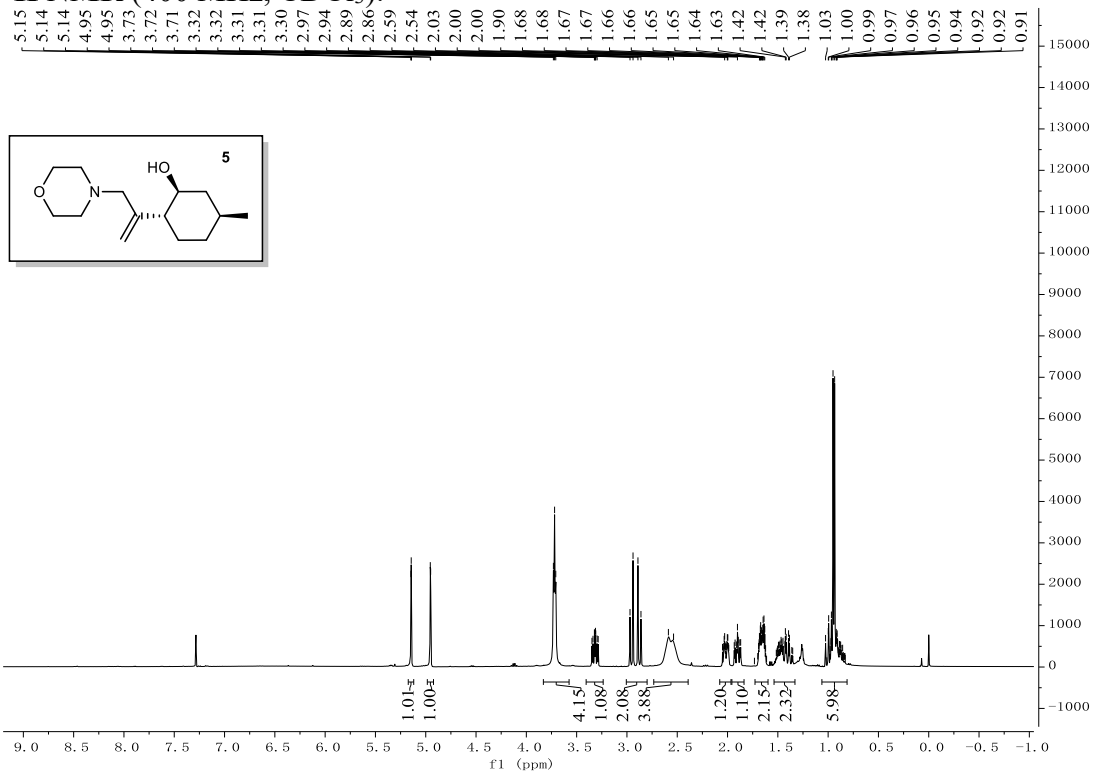
^{1}H NMR (400 MHz, $CDCl_3$):



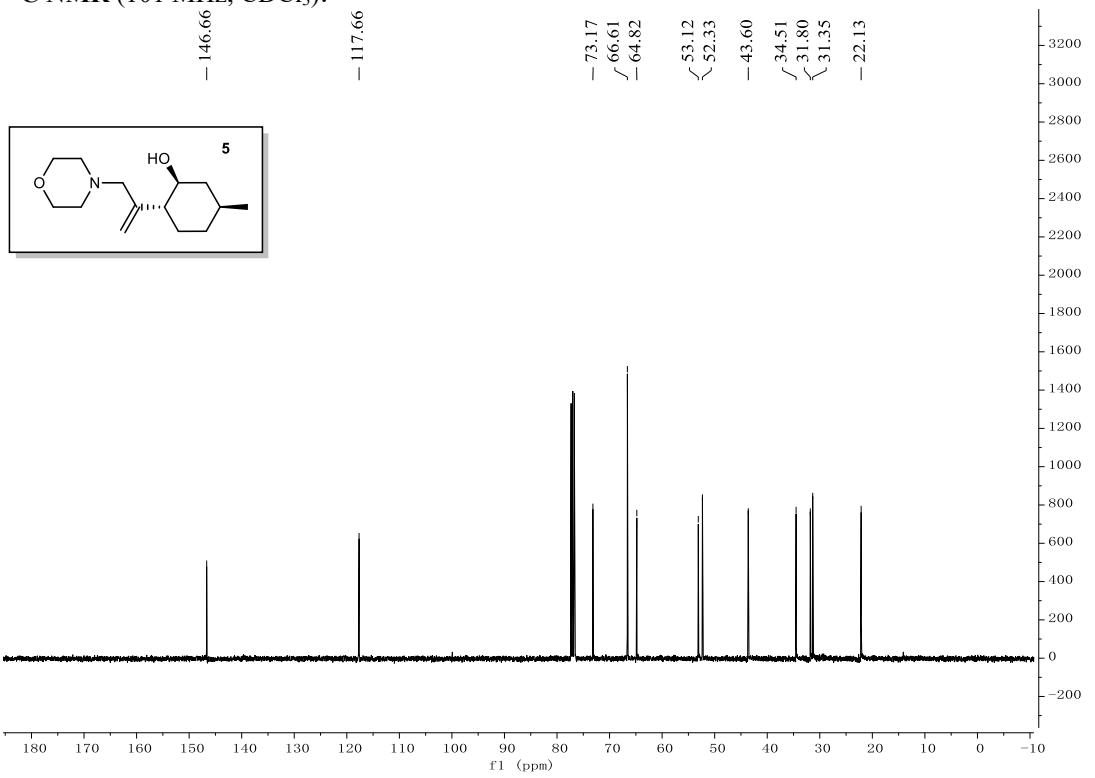
^{13}C NMR (101 MHz, $CDCl_3$):



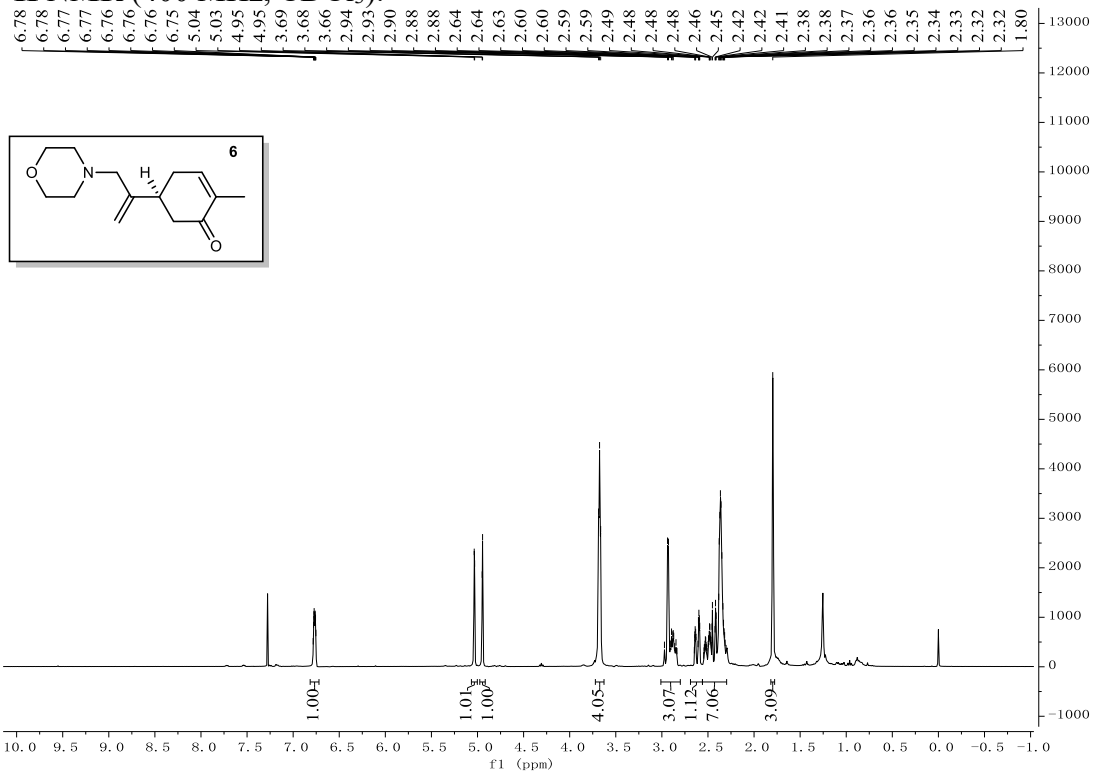
^{1}H NMR (400 MHz, $CDCl_3$):



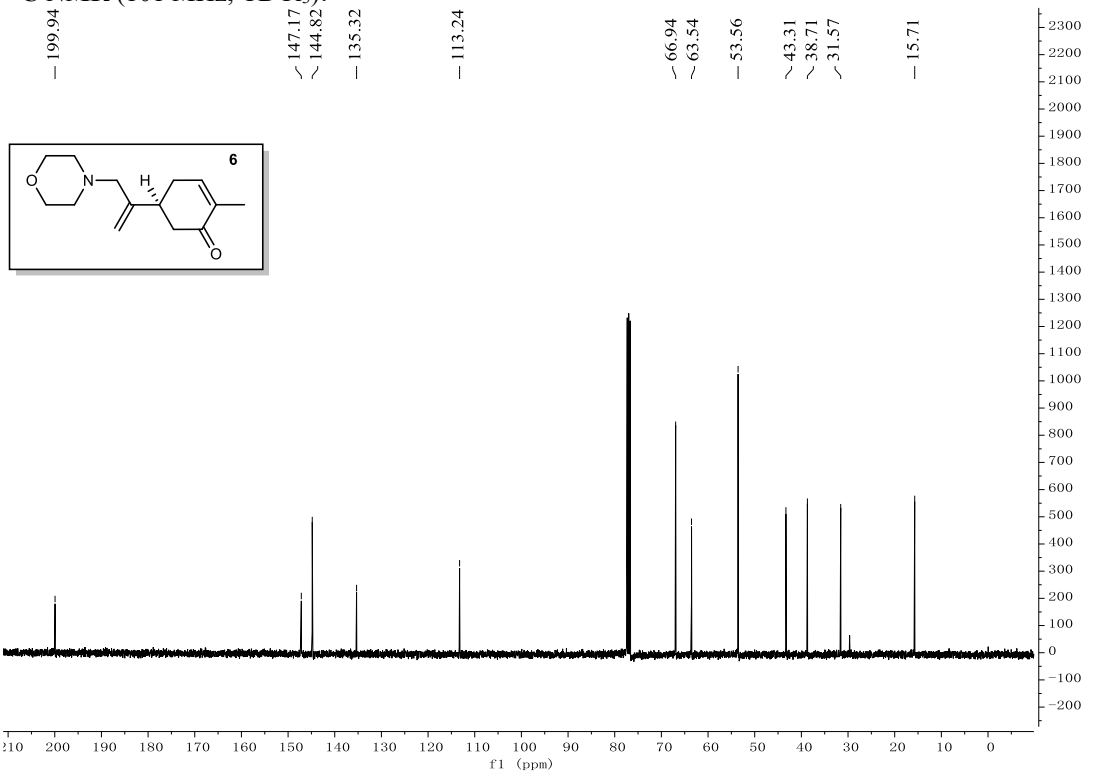
^{13}C NMR (101 MHz, $CDCl_3$):



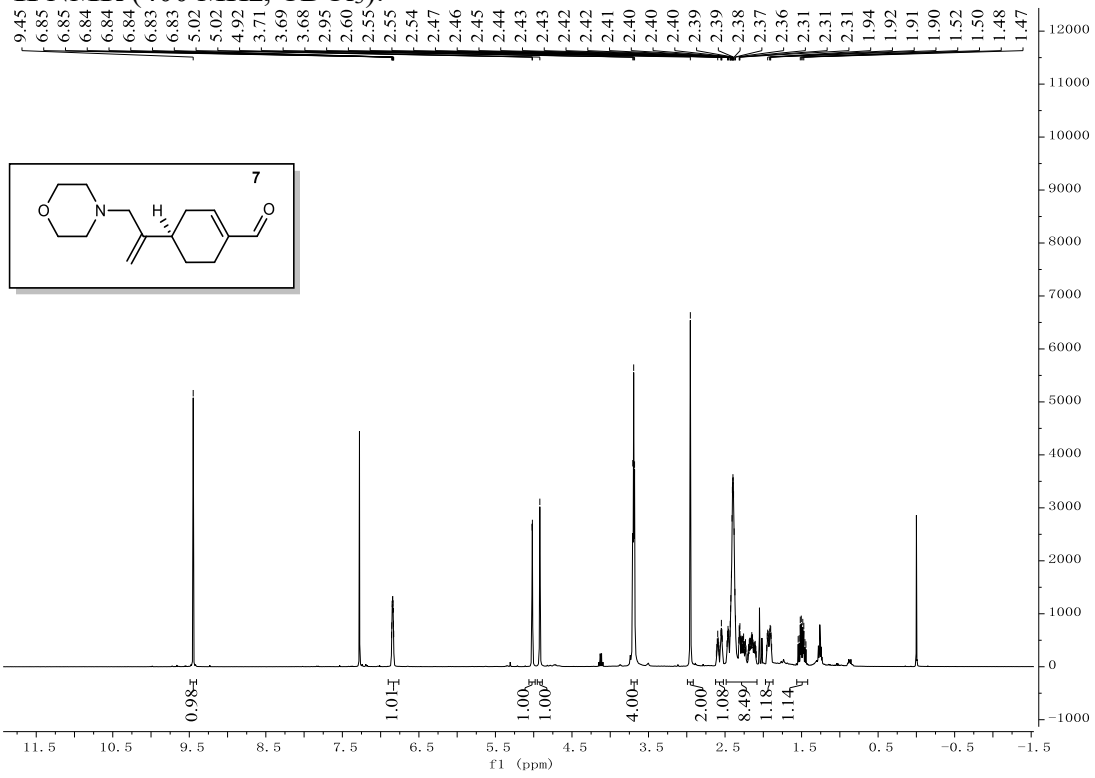
^{1}H NMR (400 MHz, $CDCl_3$):



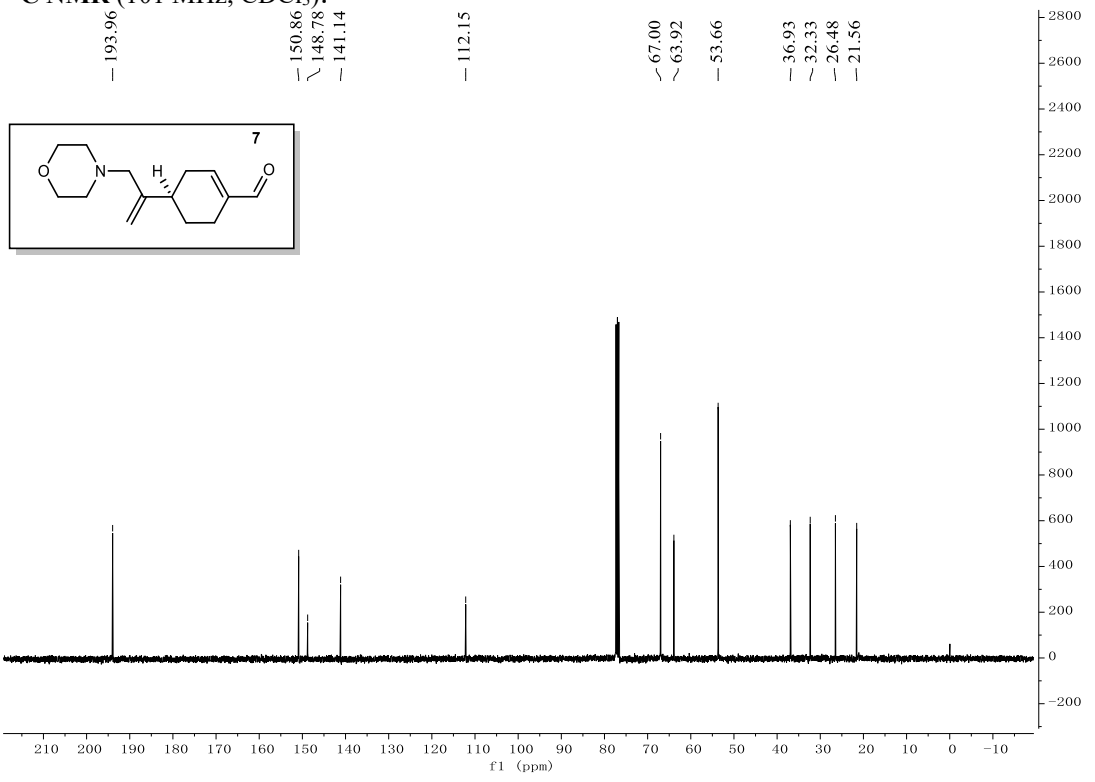
^{13}C NMR (101 MHz, $CDCl_3$):



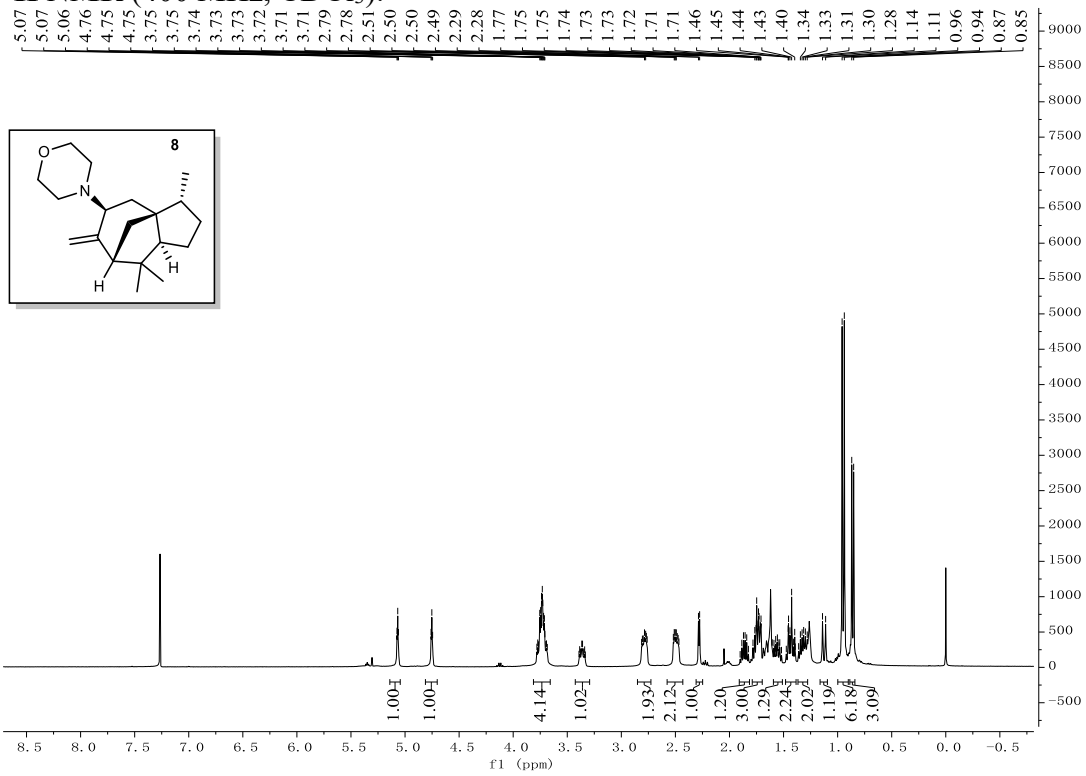
^{1}H NMR (400 MHz, $CDCl_3$):



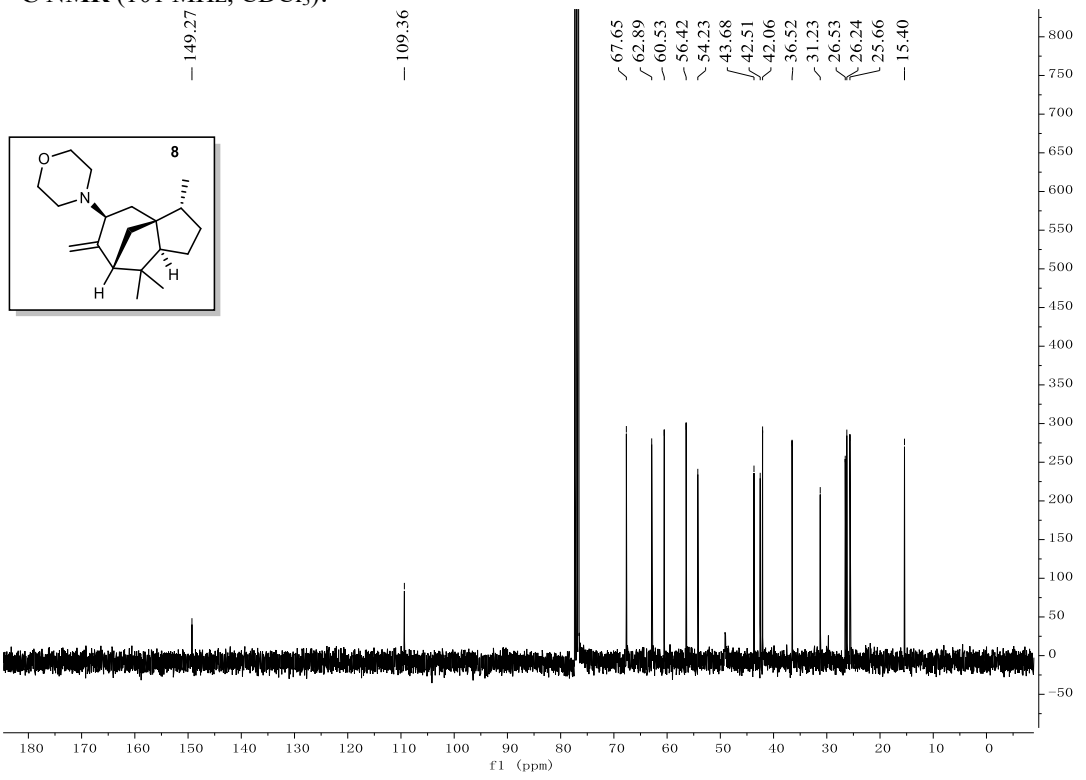
^{13}C NMR (101 MHz, $CDCl_3$):



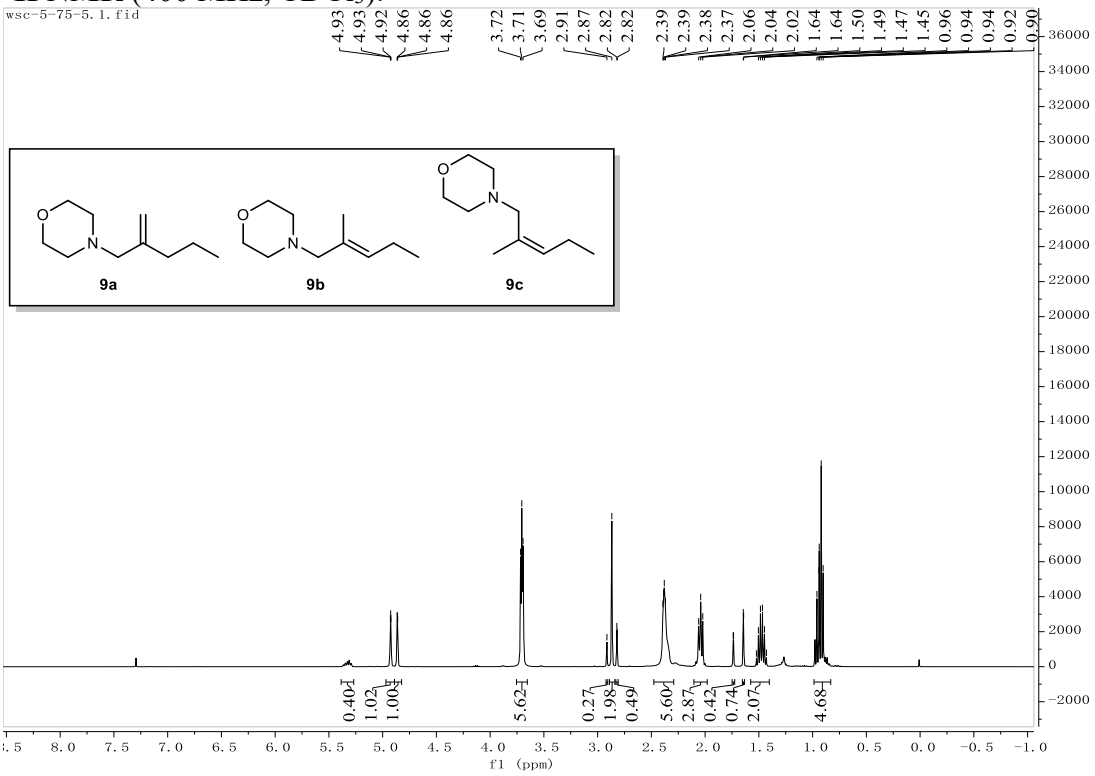
^{1}H NMR (400 MHz, $CDCl_3$):



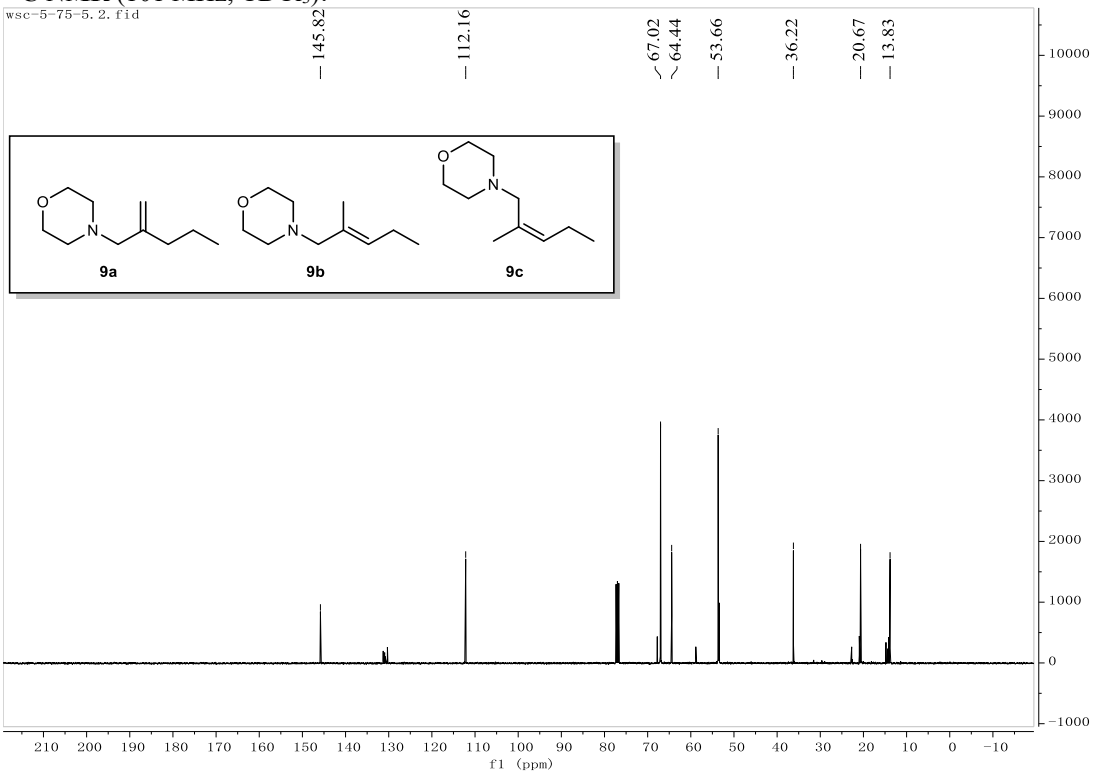
^{13}C NMR (101 MHz, $CDCl_3$):



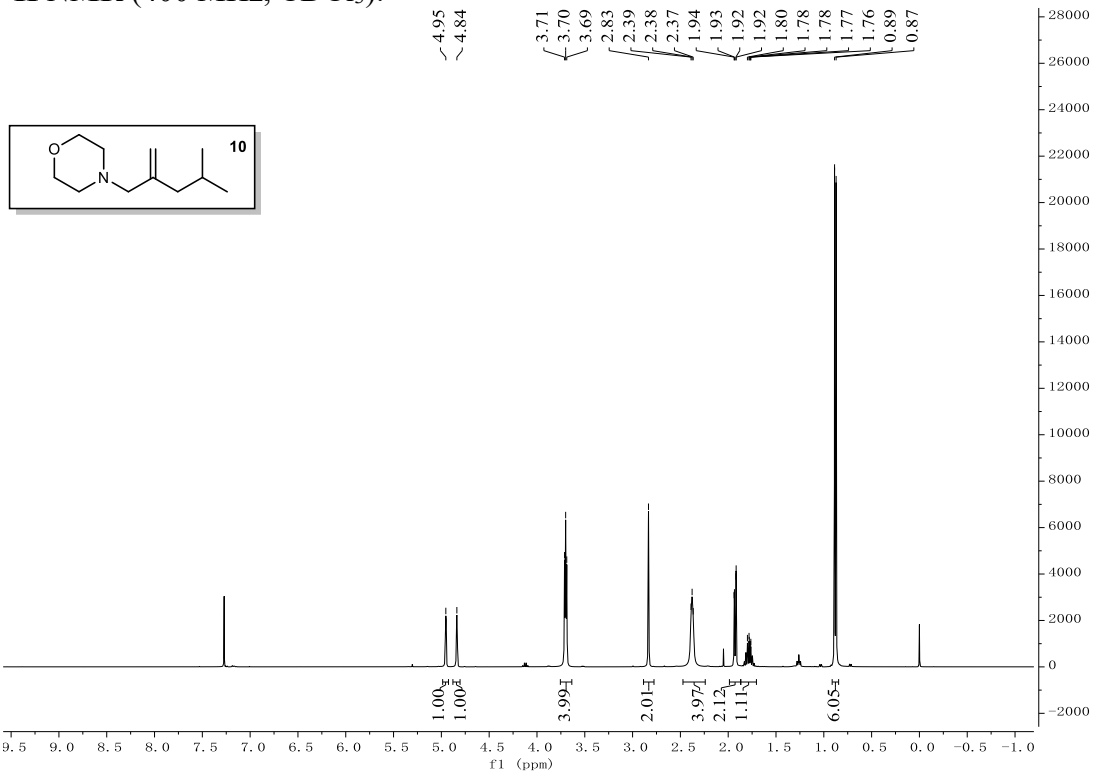
^{1}H NMR (400 MHz, $CDCl_3$):



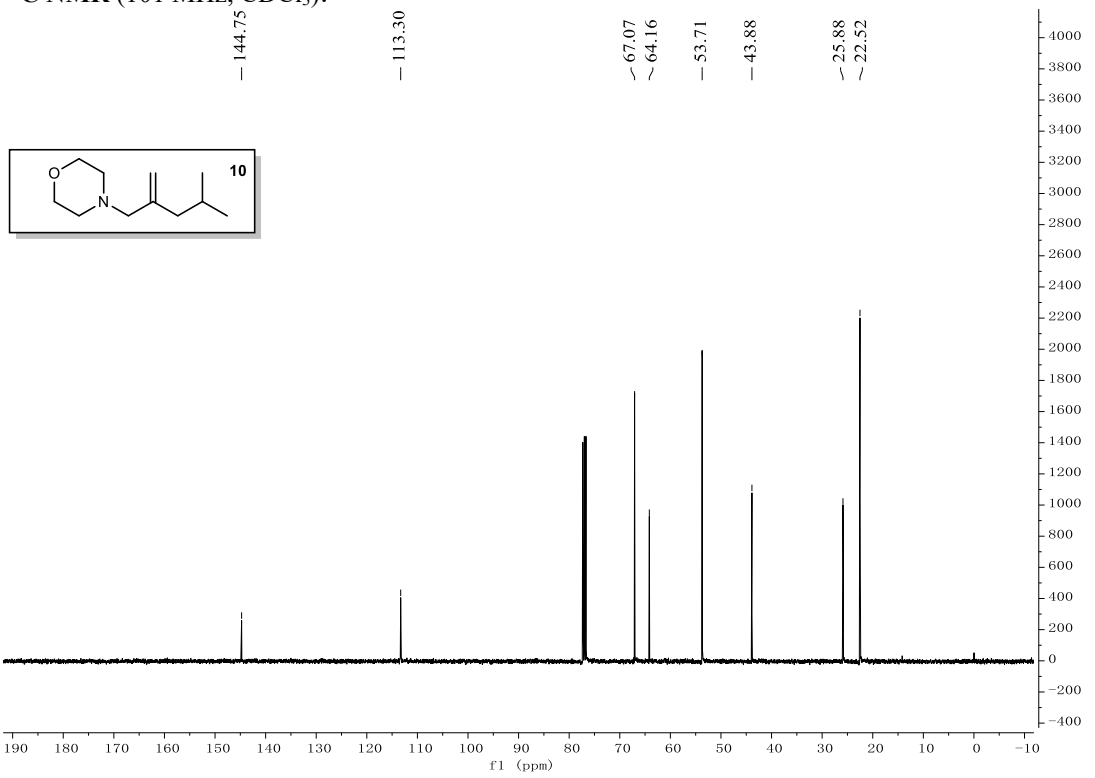
^{13}C NMR (101 MHz, $CDCl_3$):



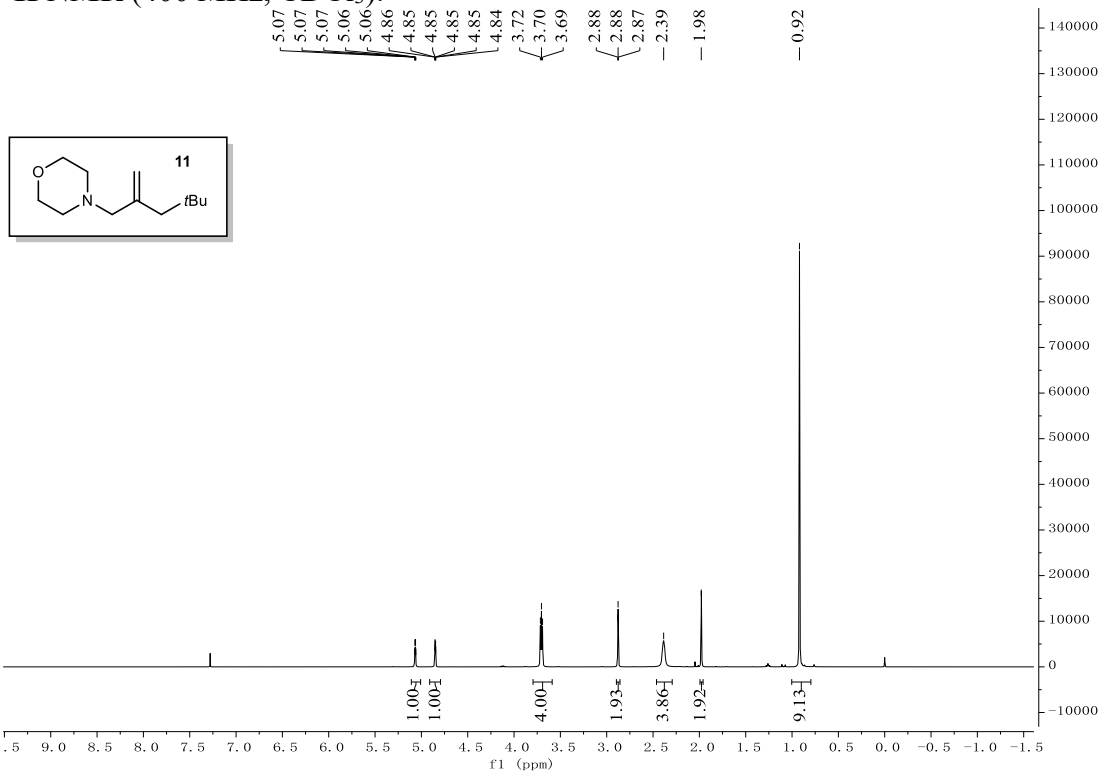
^{1}H NMR (400 MHz, $CDCl_3$):



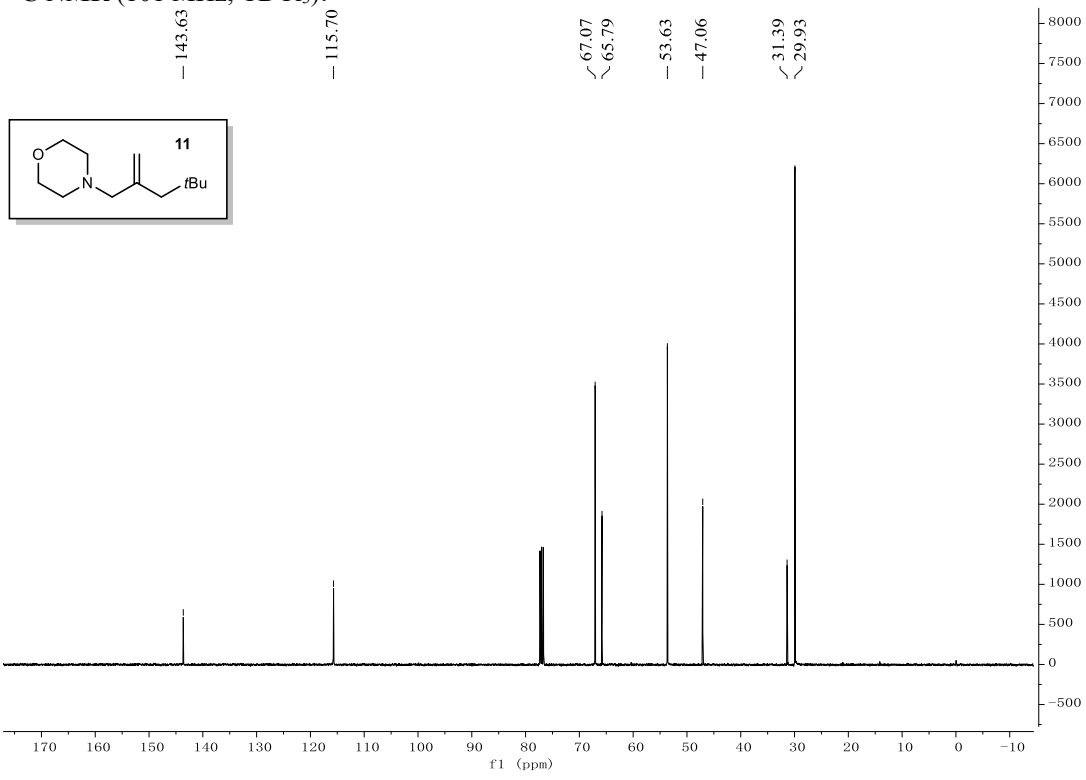
^{13}C NMR (101 MHz, $CDCl_3$):



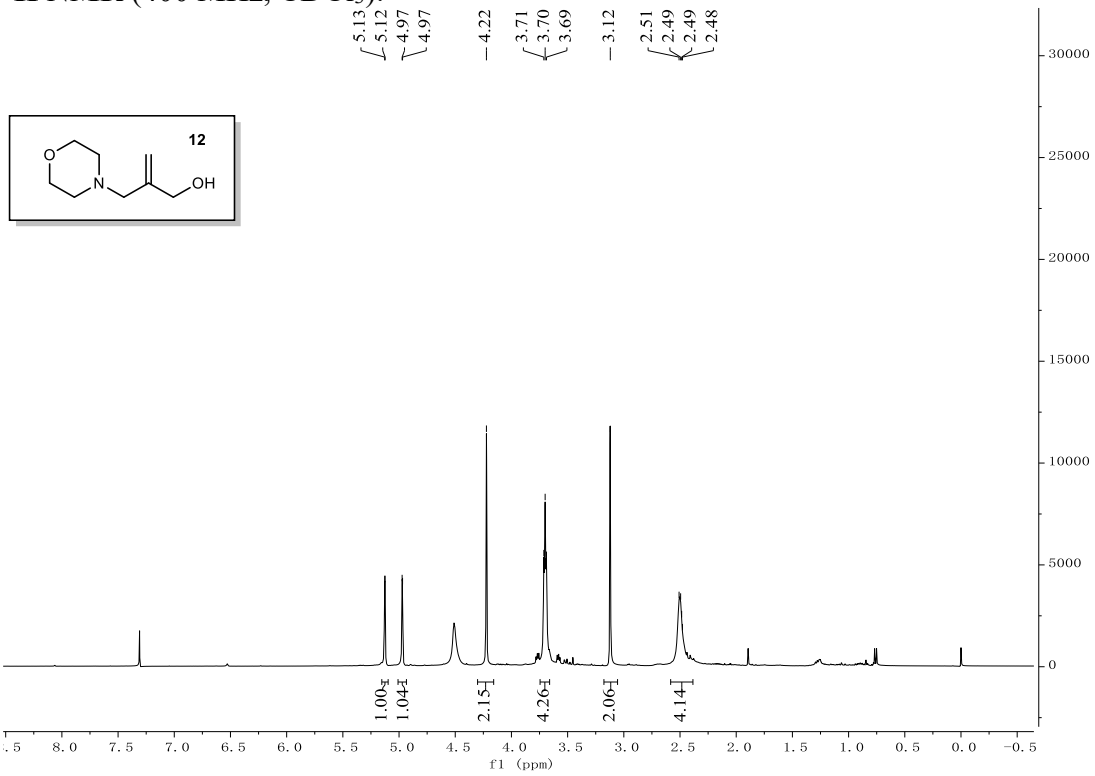
^{1}H NMR (400 MHz, $CDCl_3$):



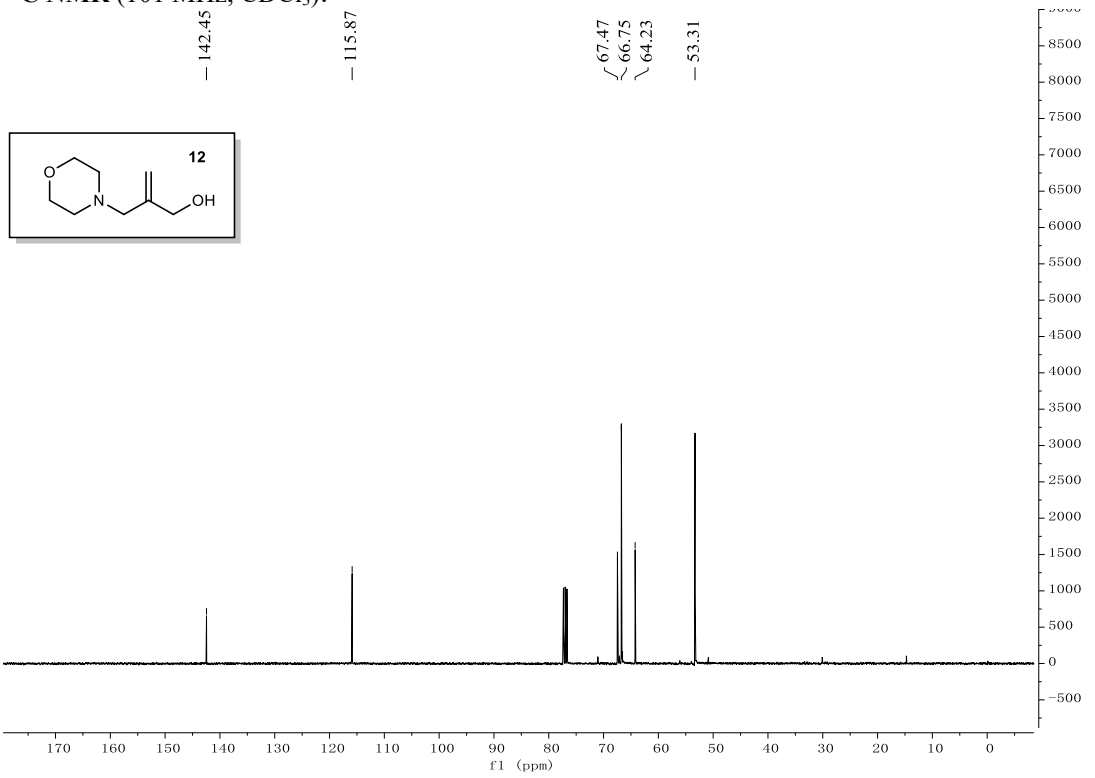
^{13}C NMR (101 MHz, $CDCl_3$):



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



^{13}C NMR (101 MHz, $CDCl_3$):



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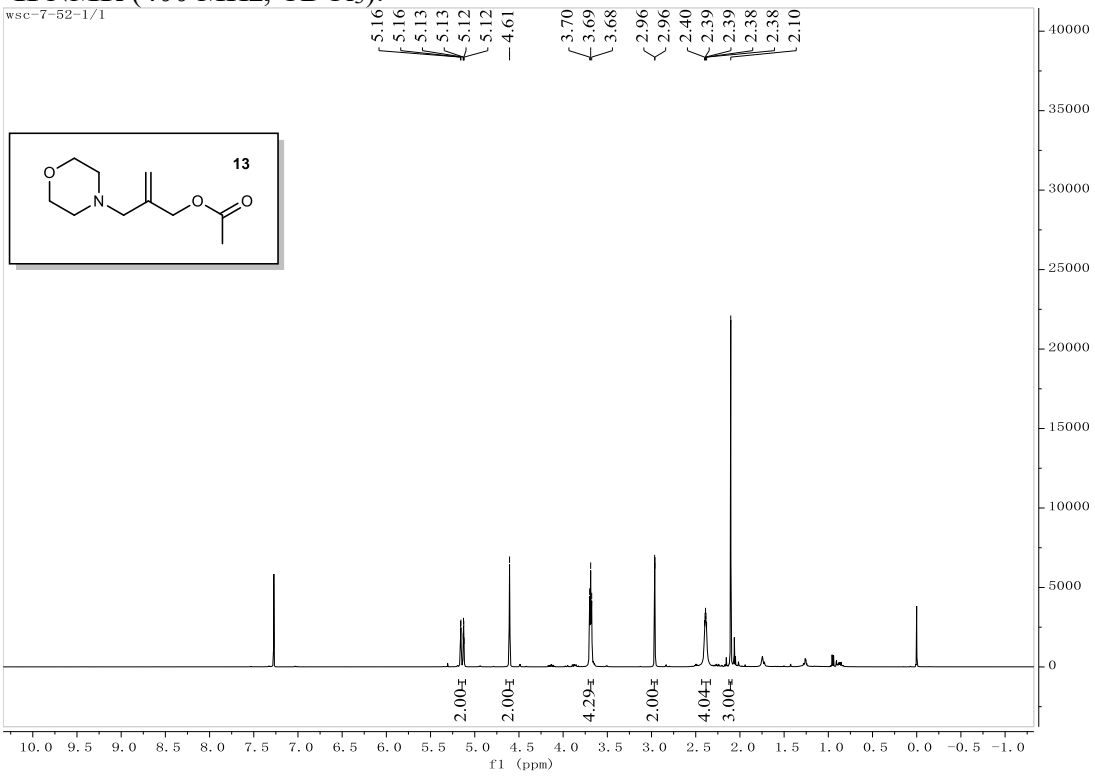

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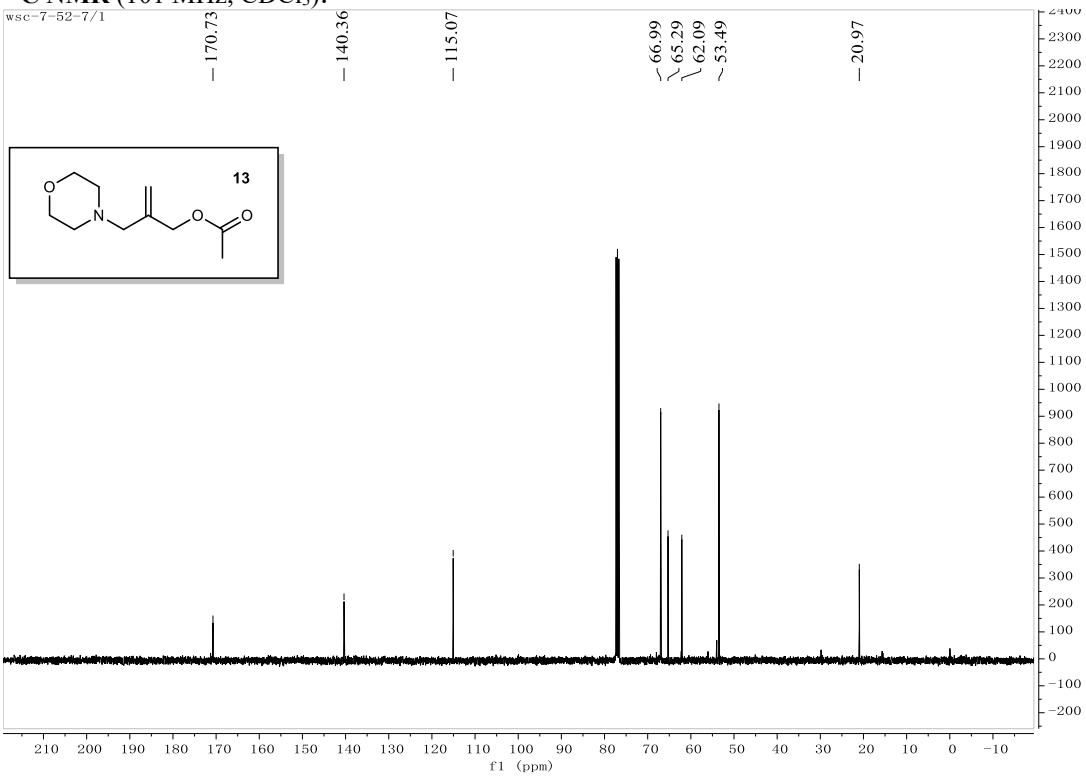

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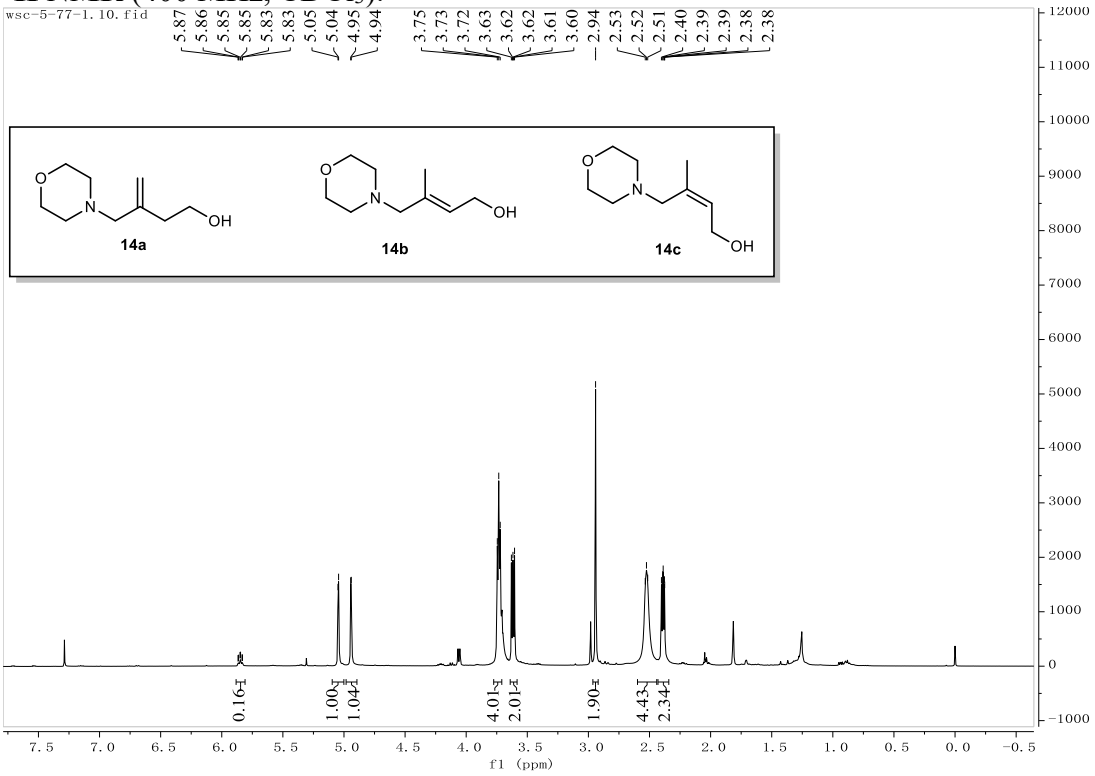

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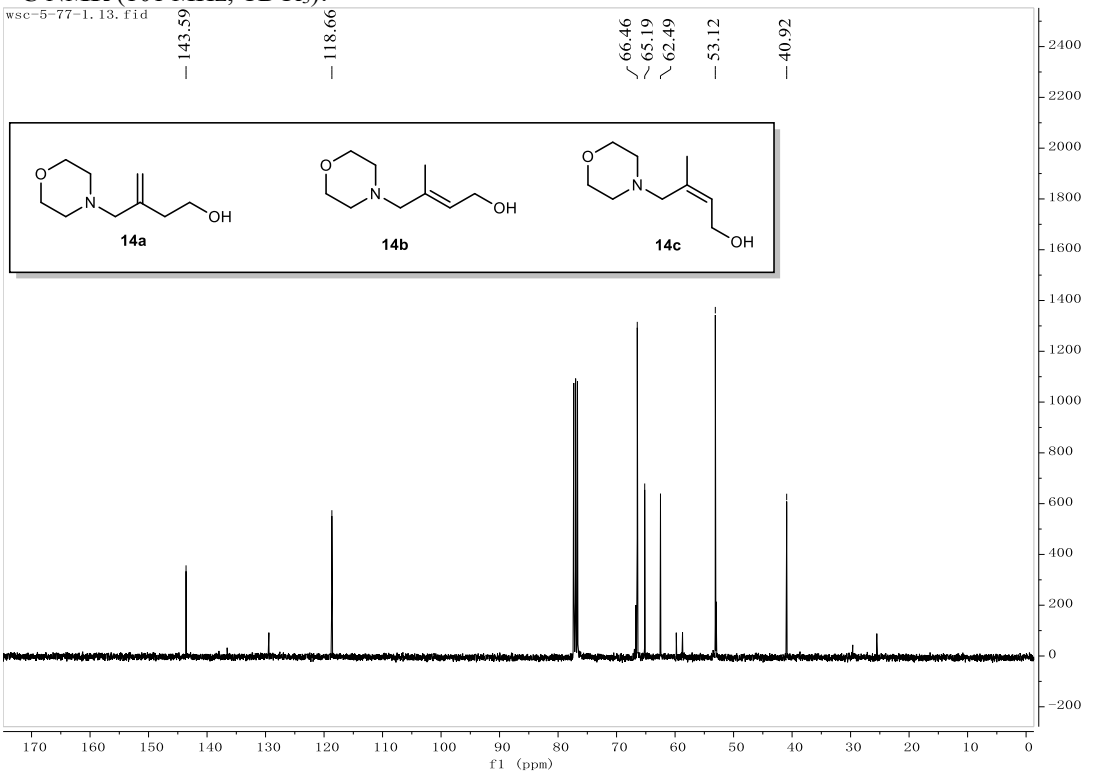

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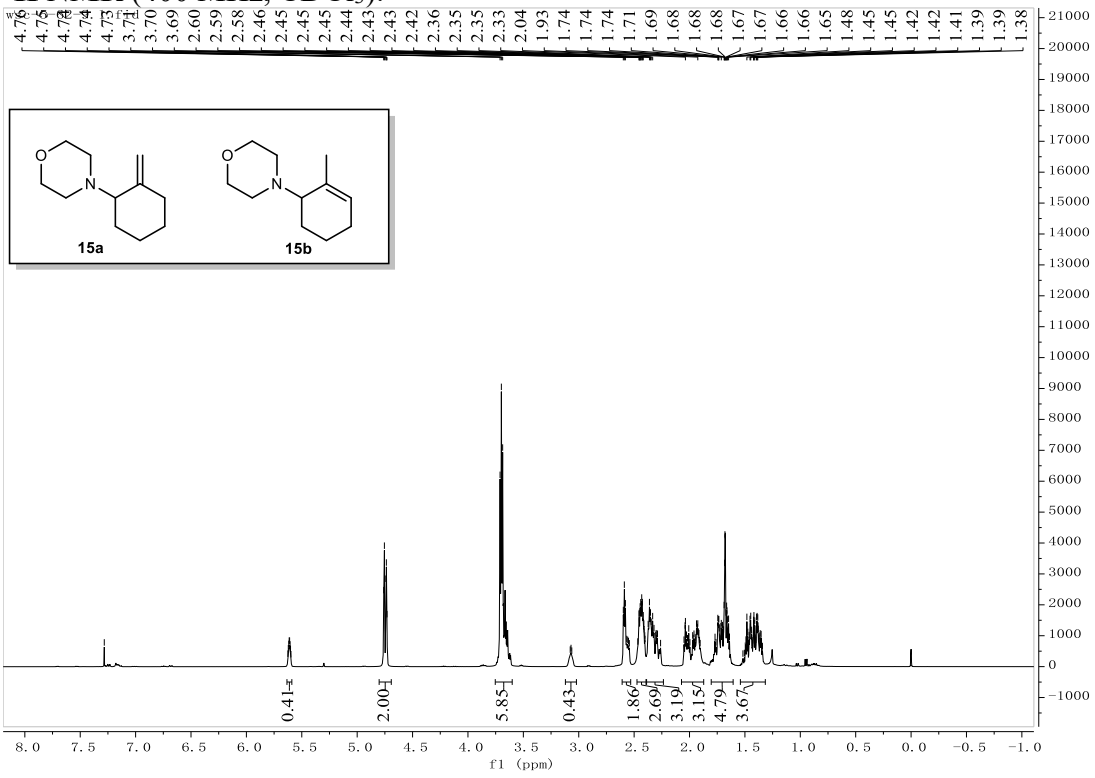

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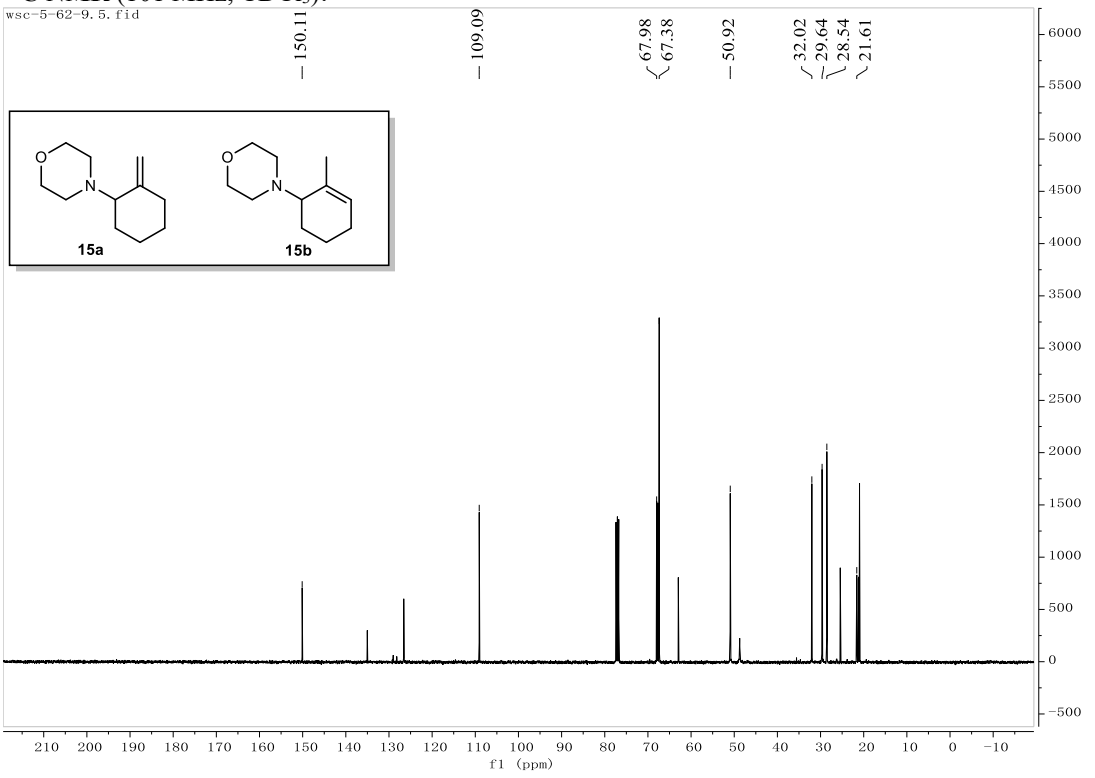

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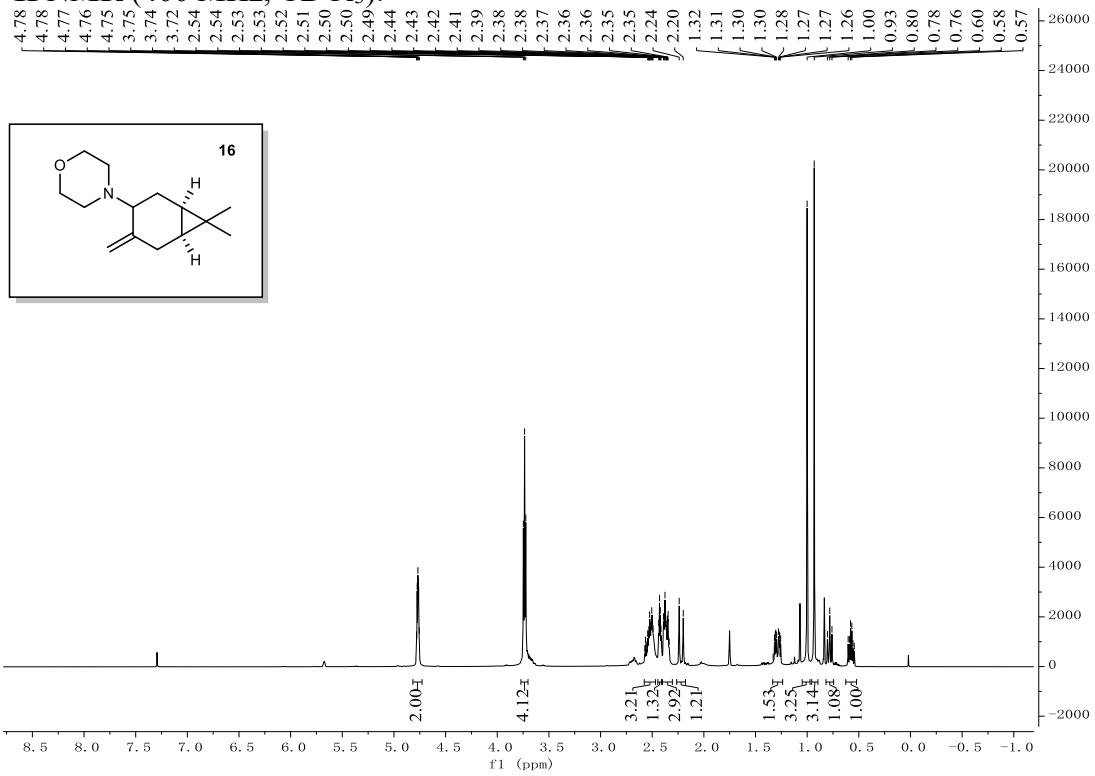

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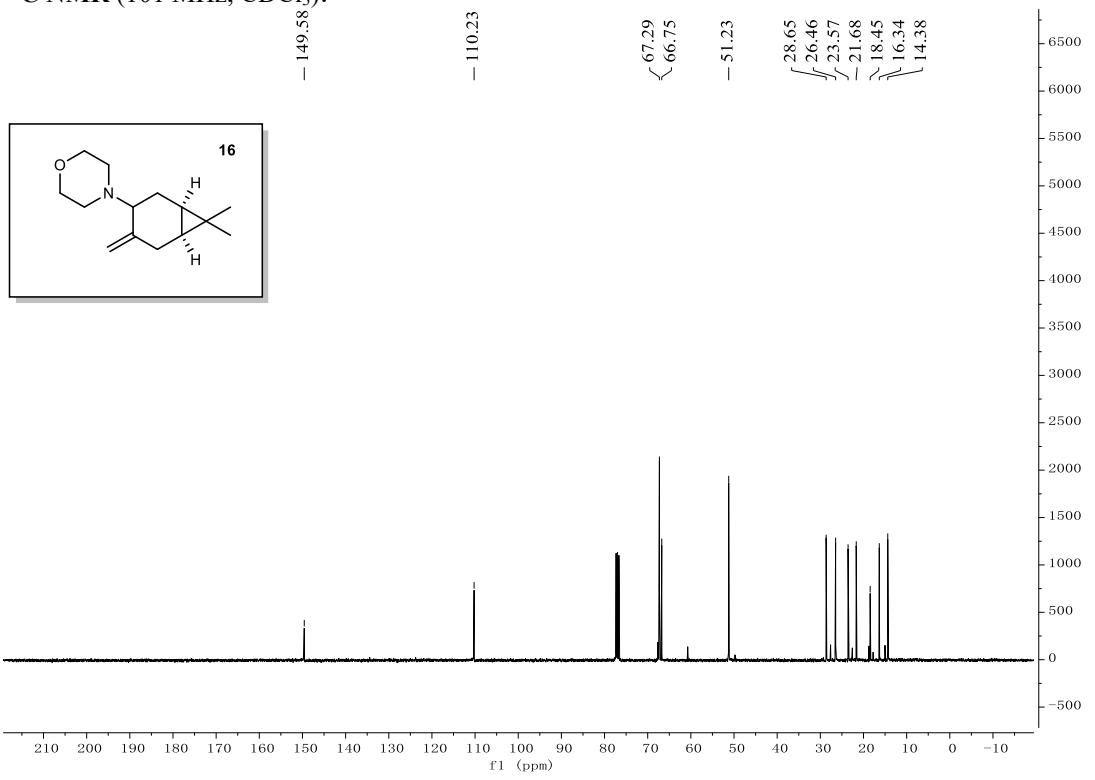

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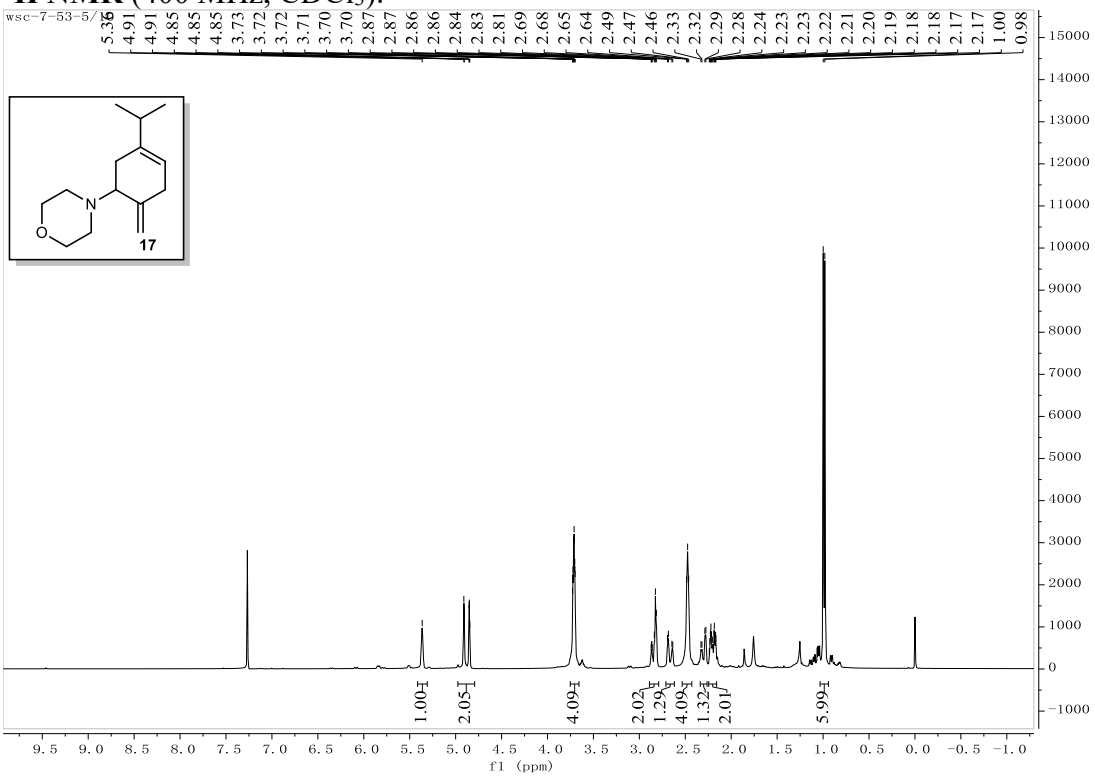

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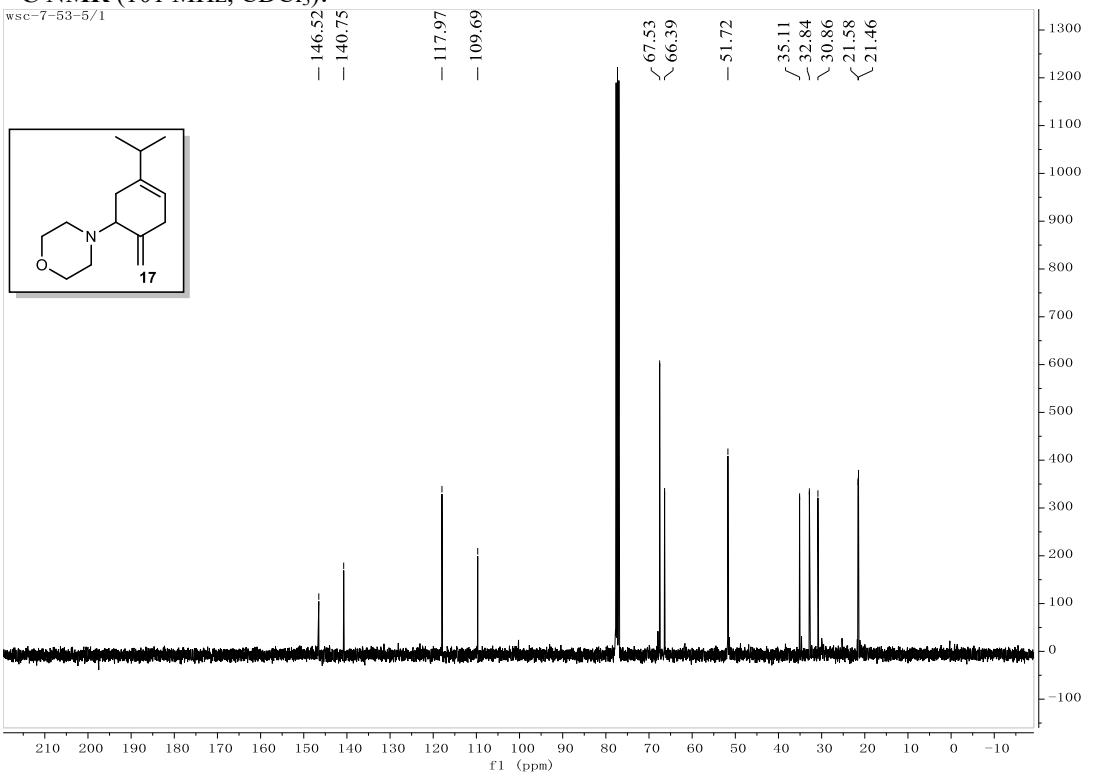

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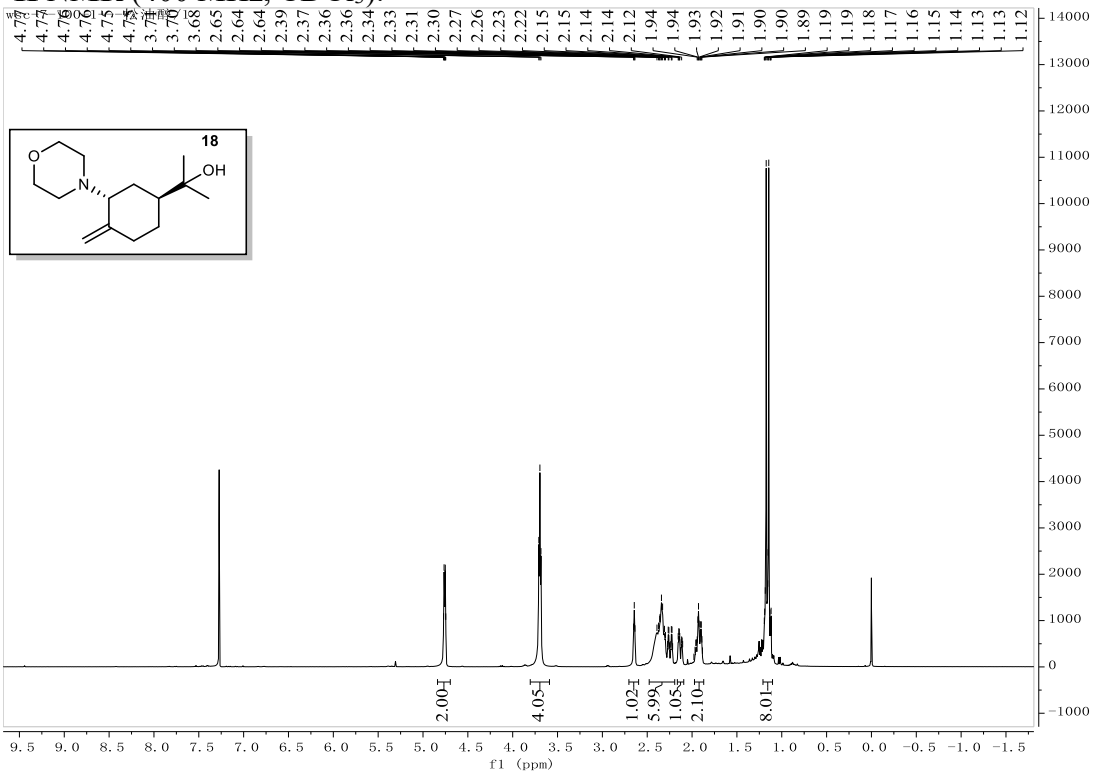

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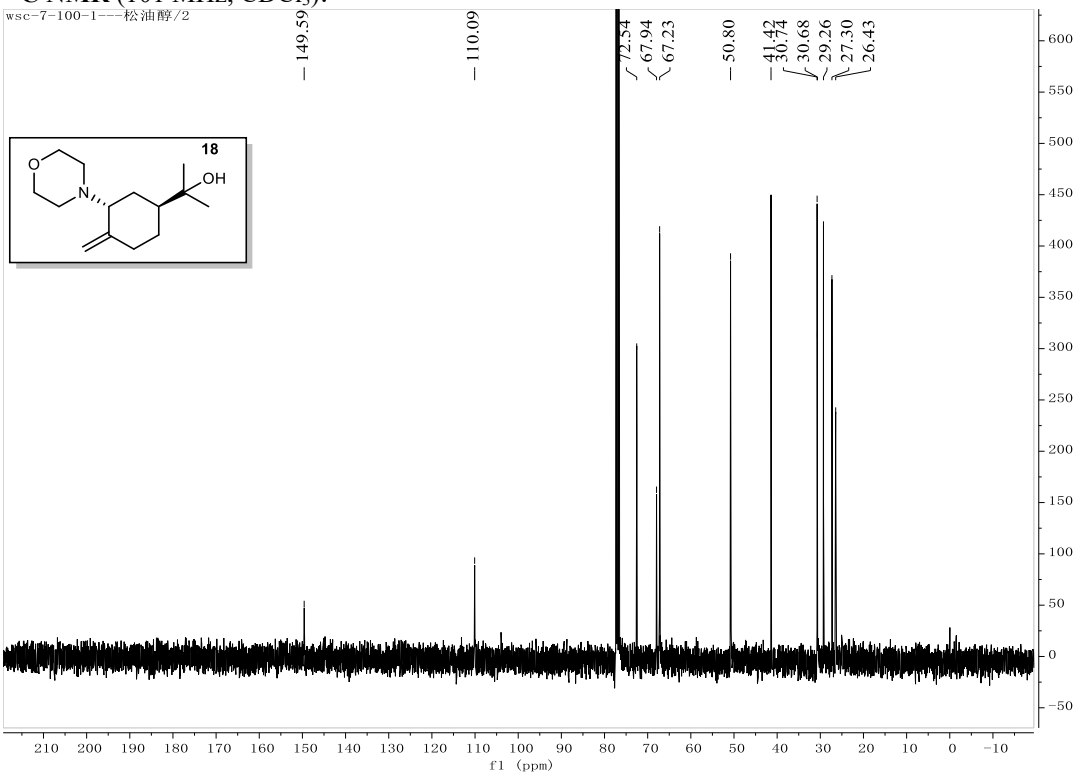

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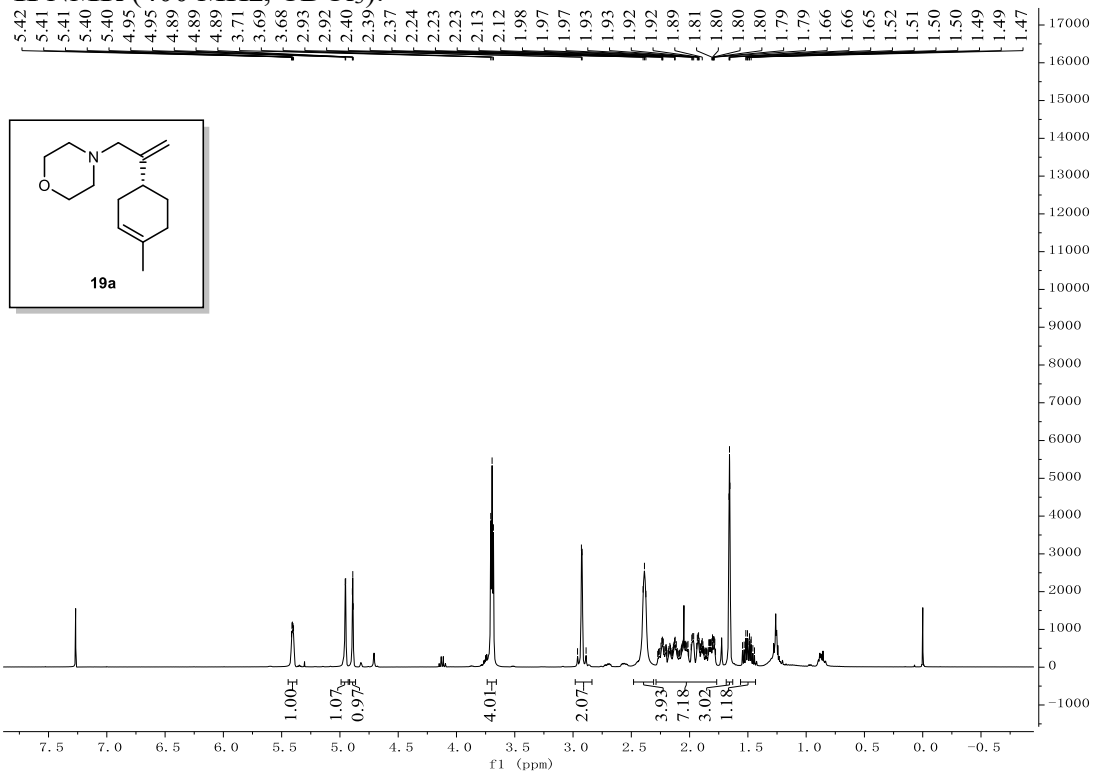

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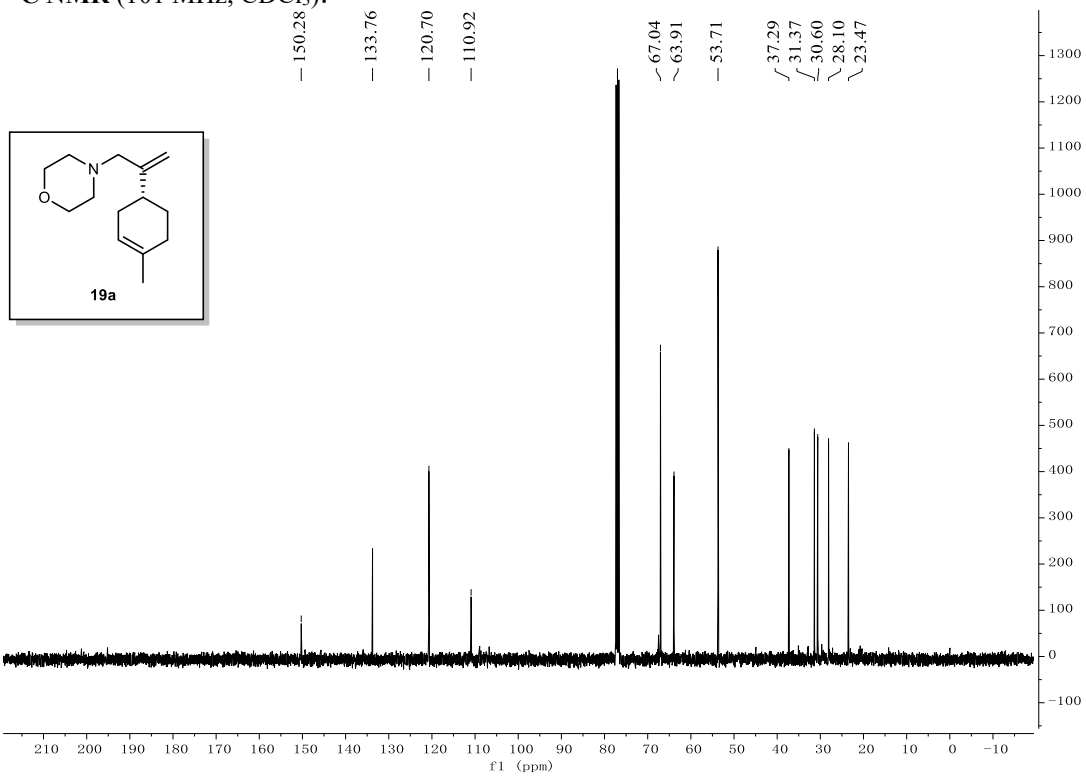

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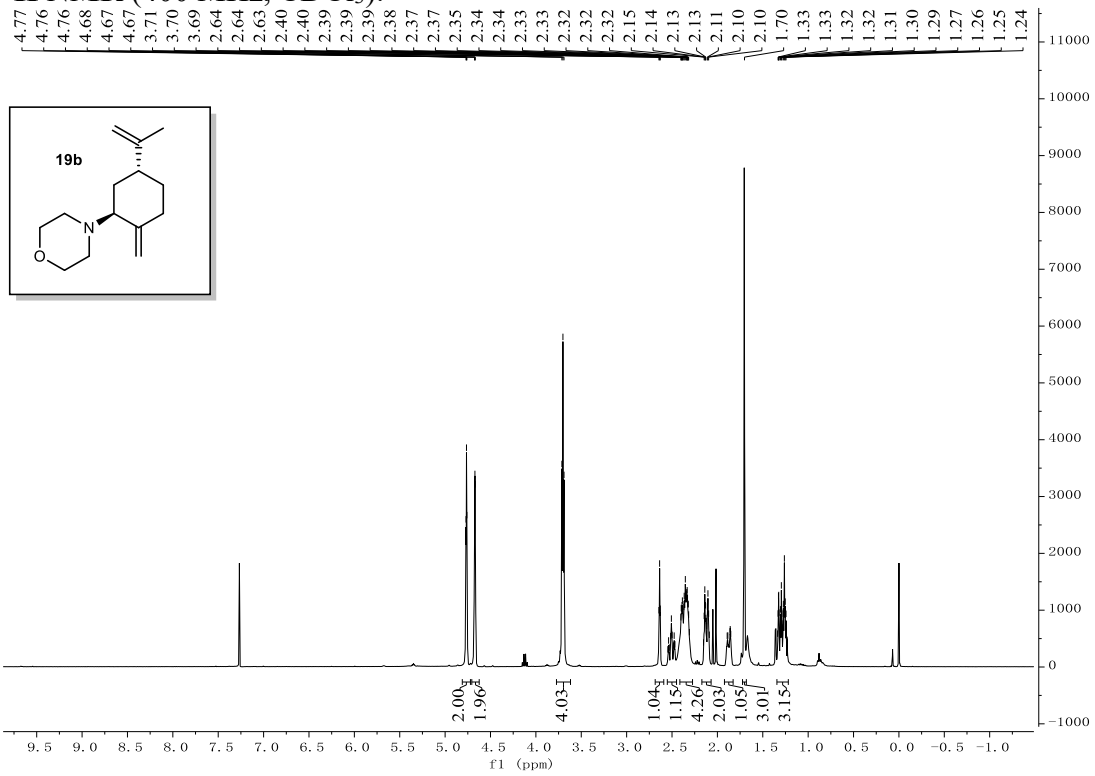

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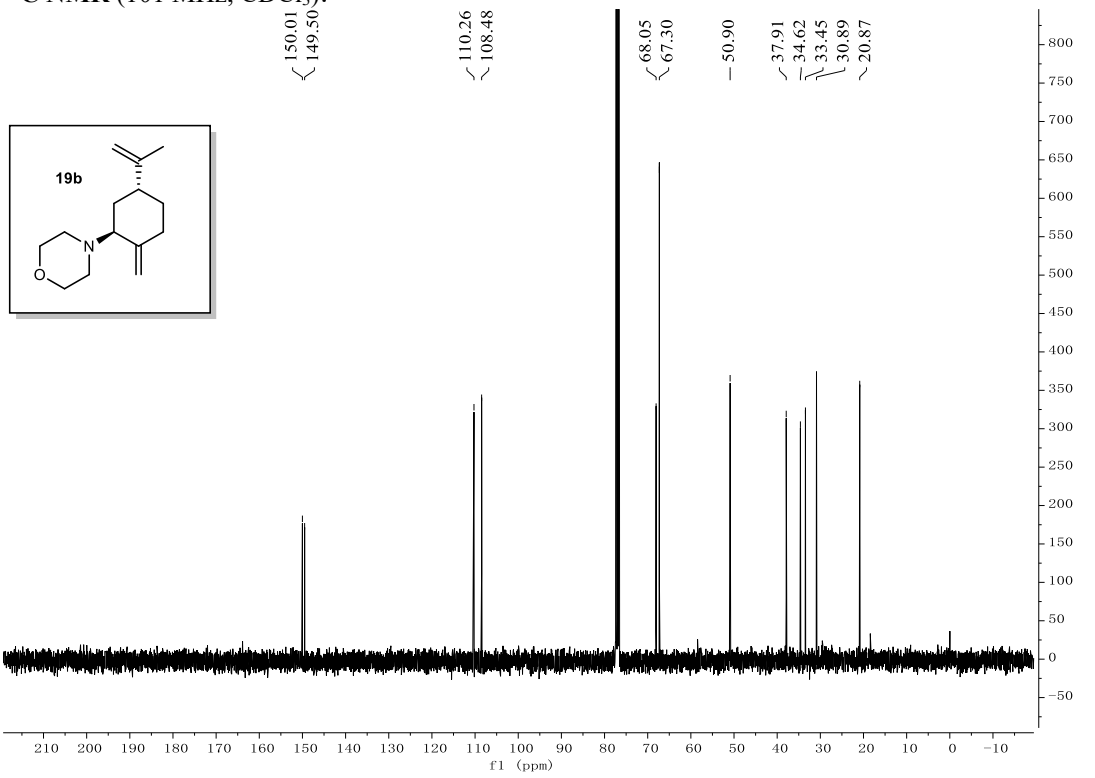

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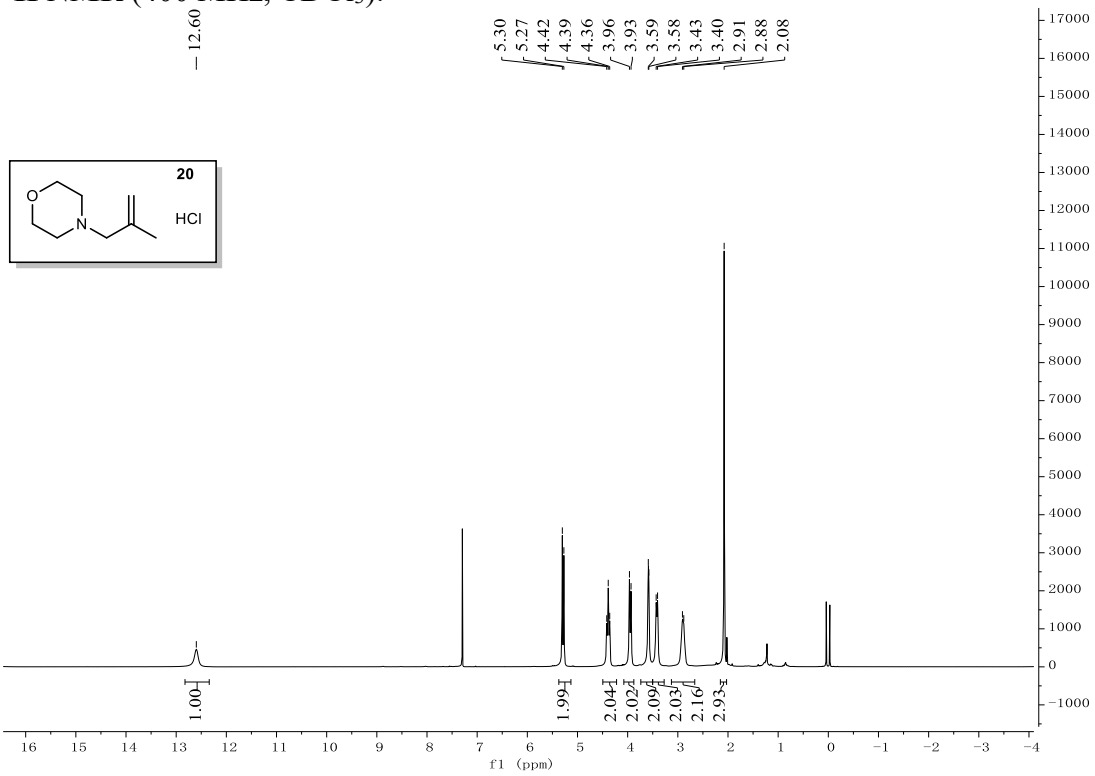

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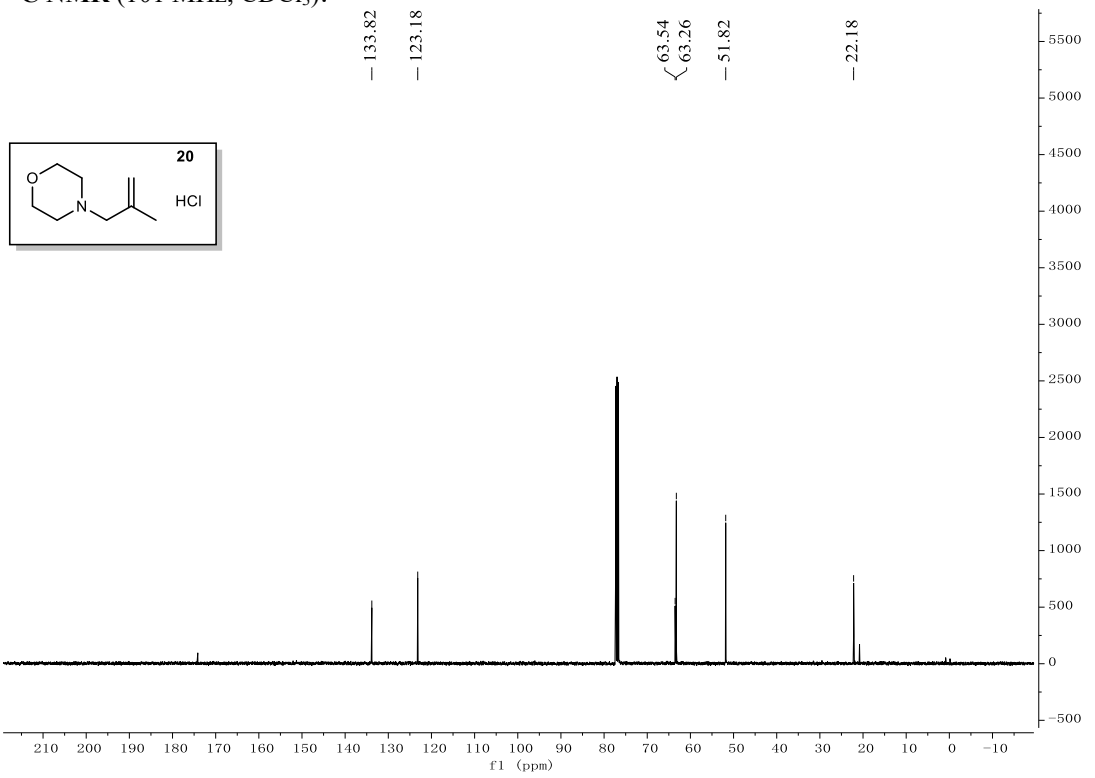

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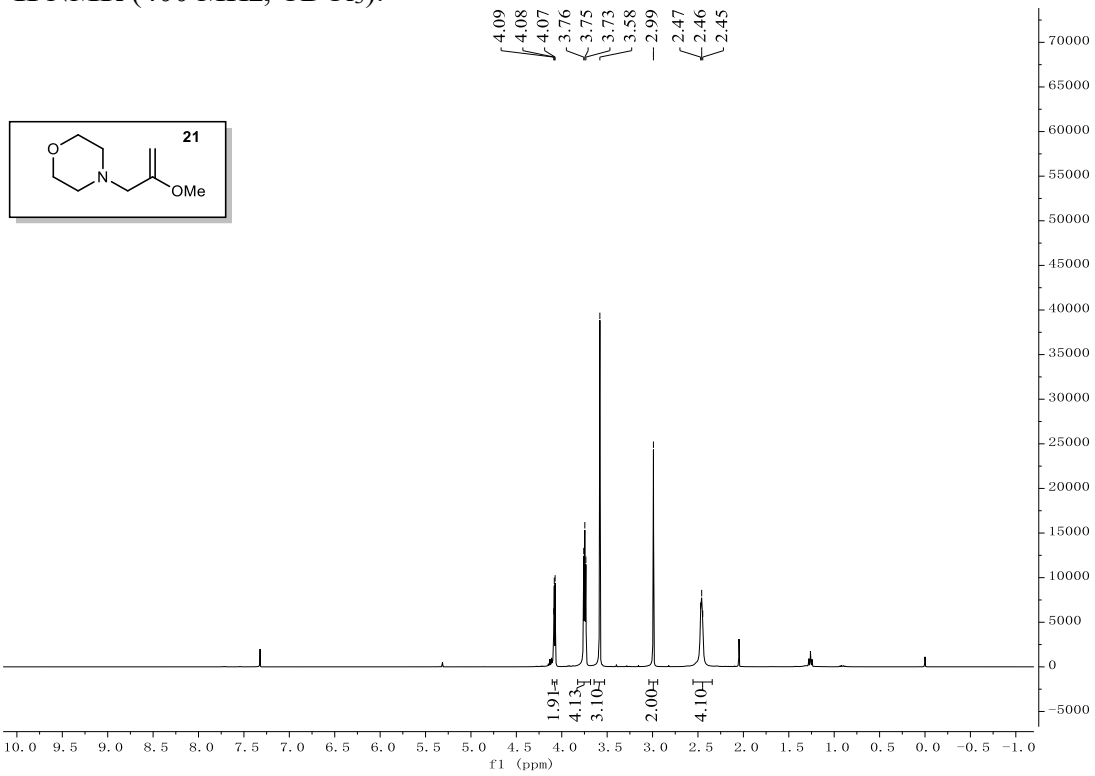

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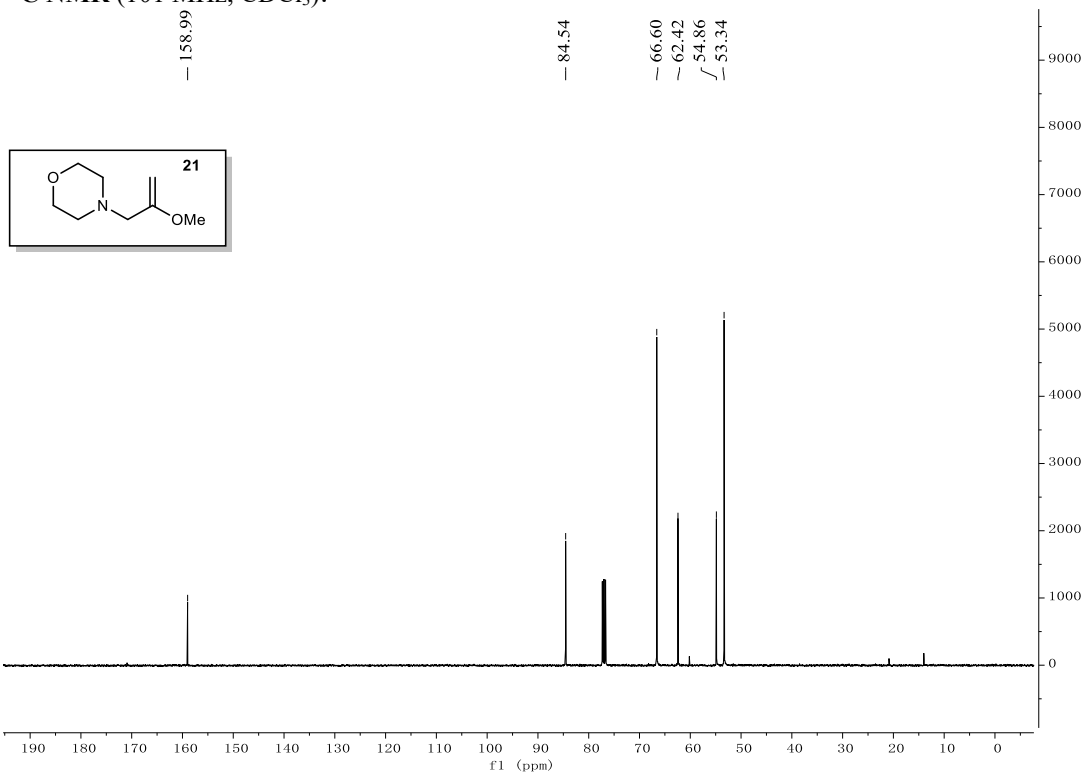

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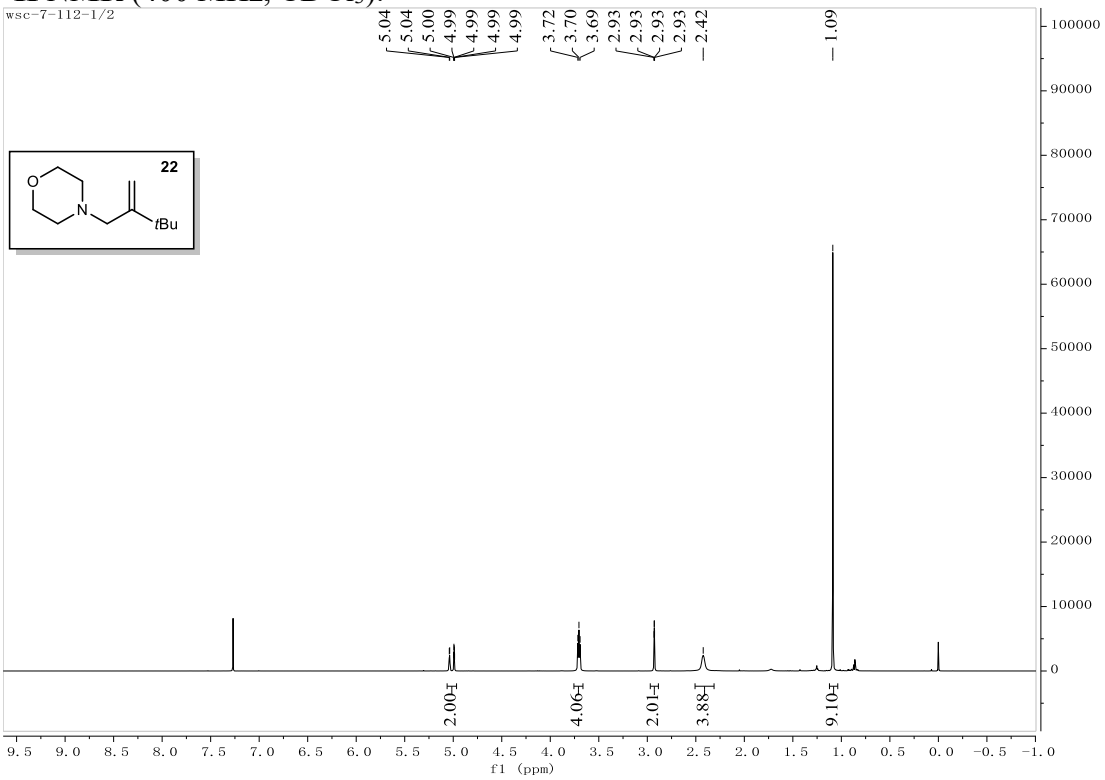

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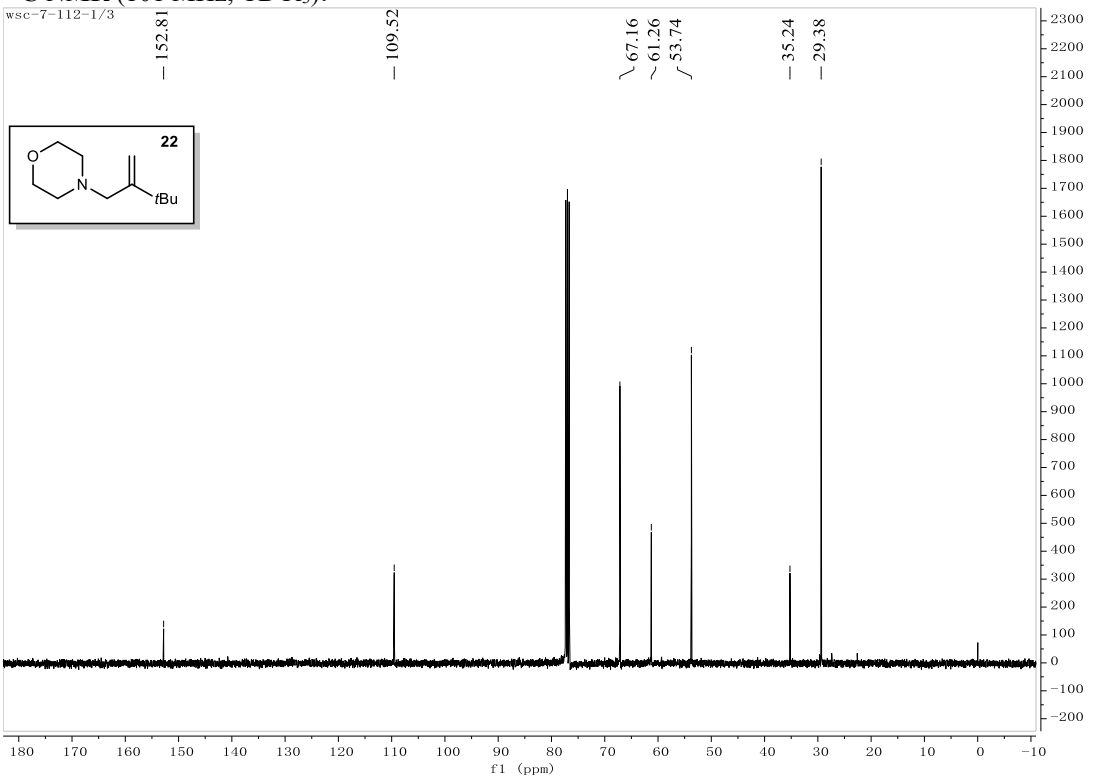

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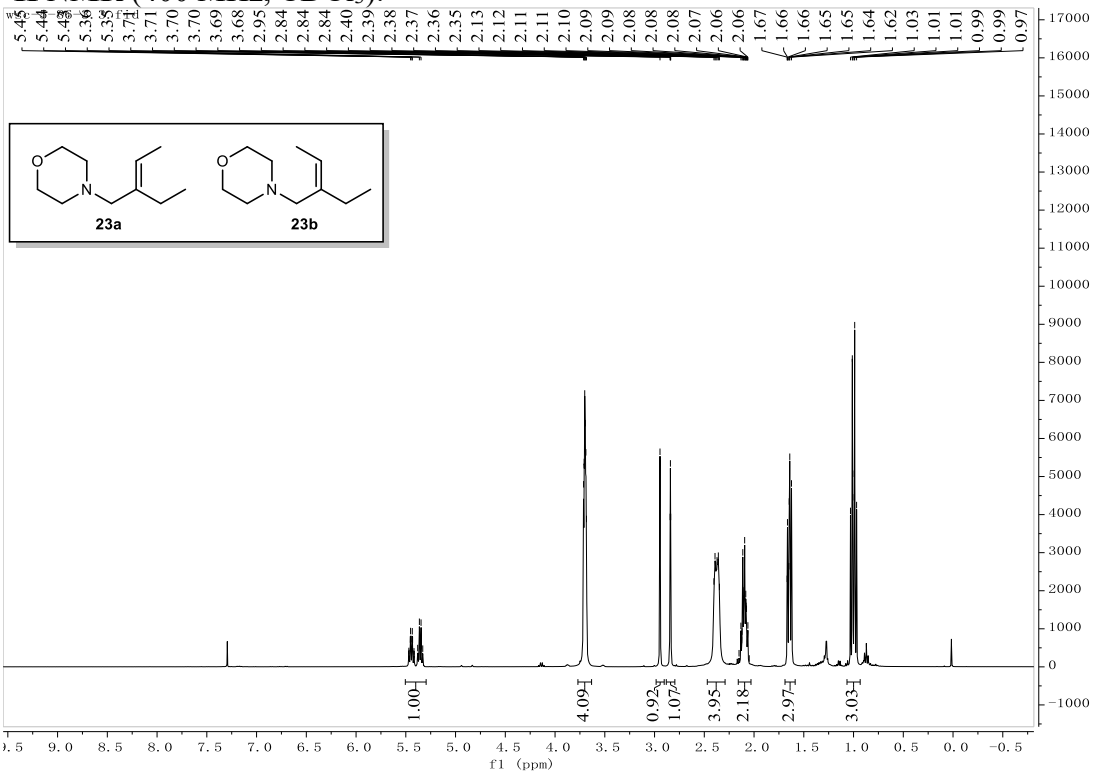

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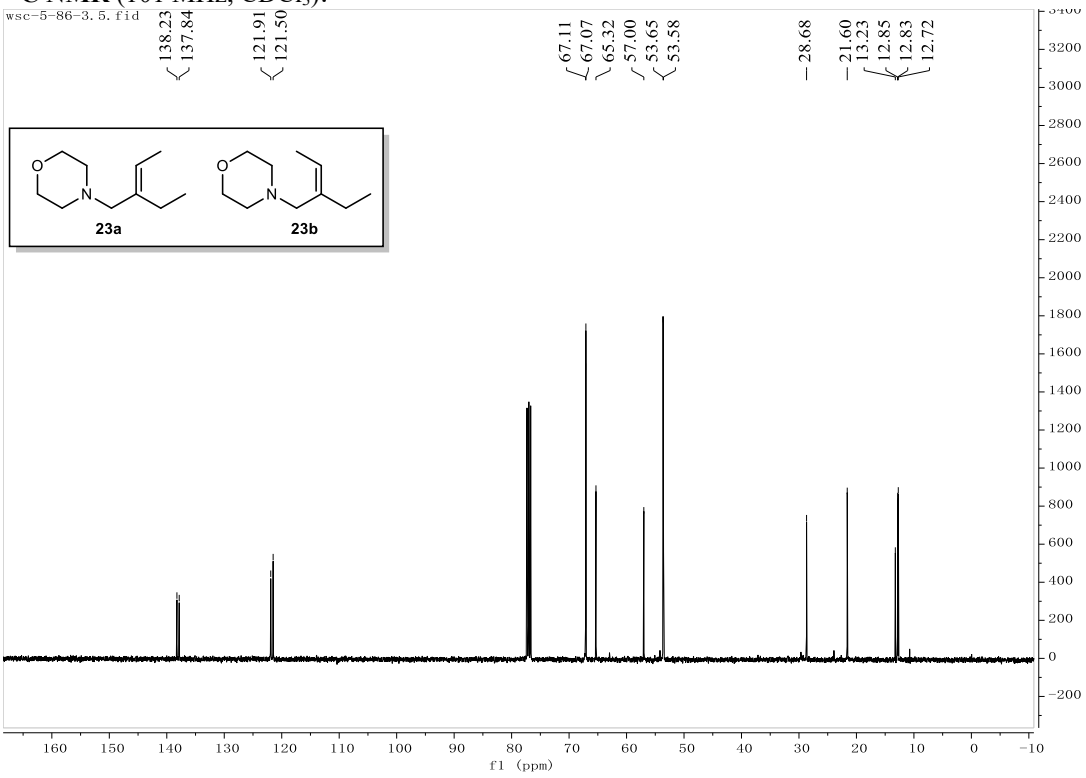

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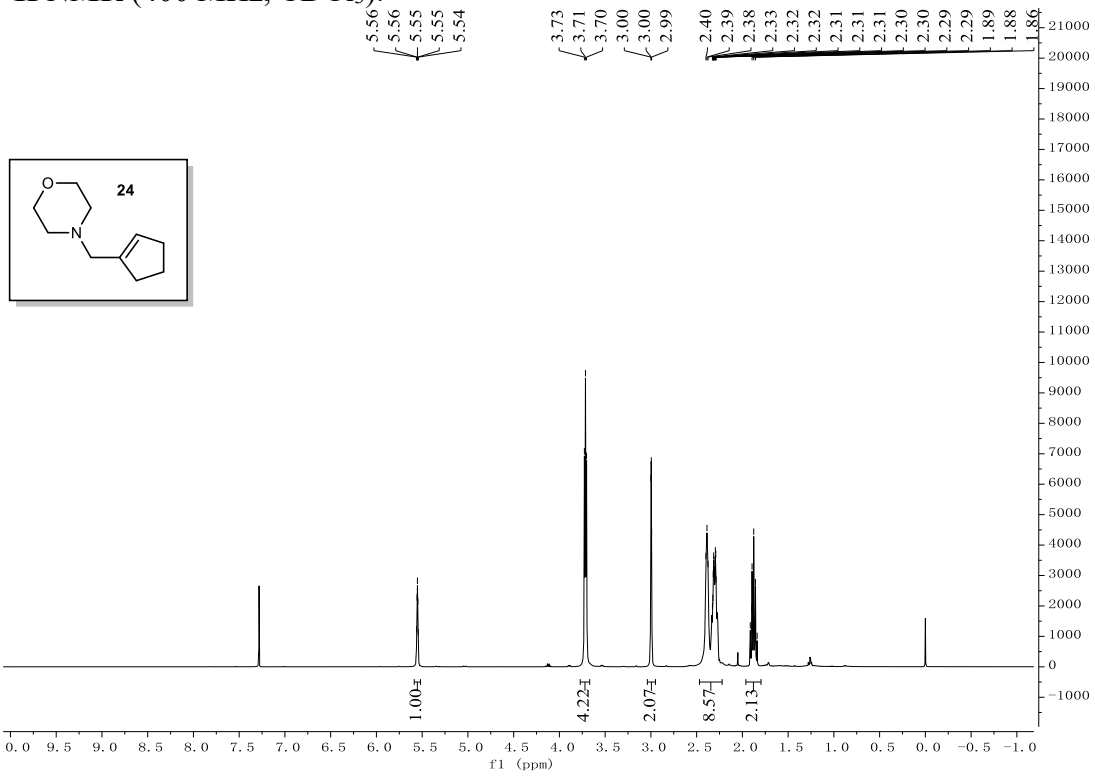

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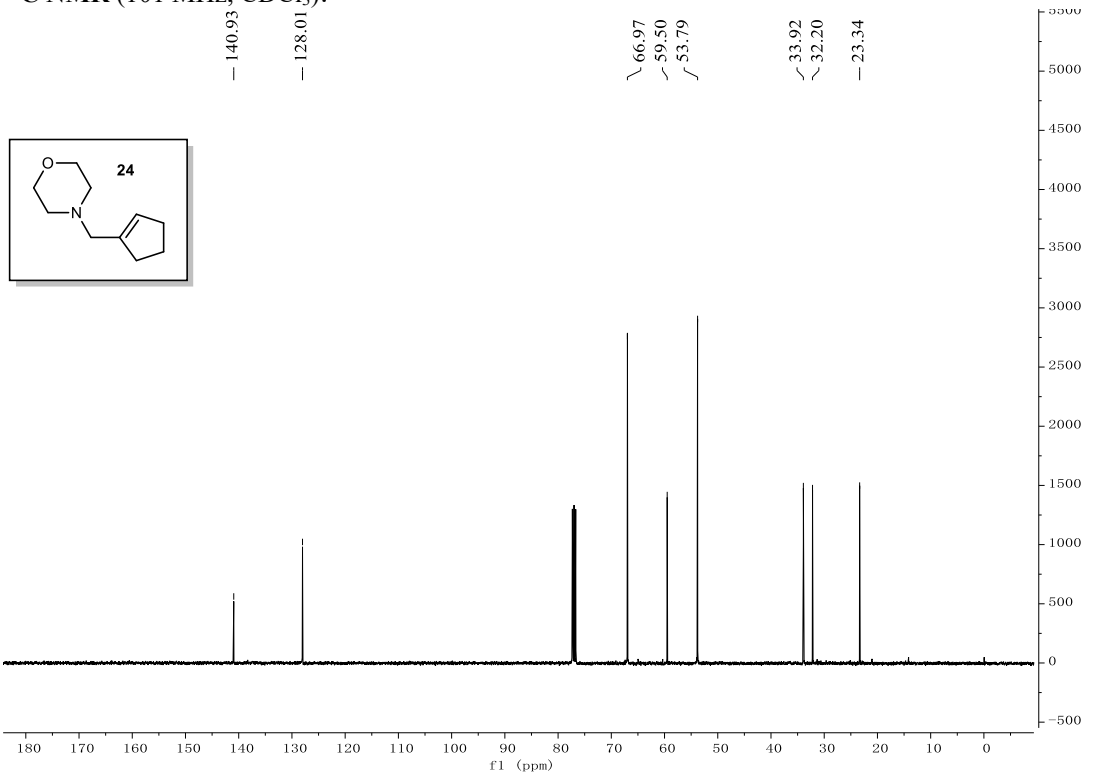

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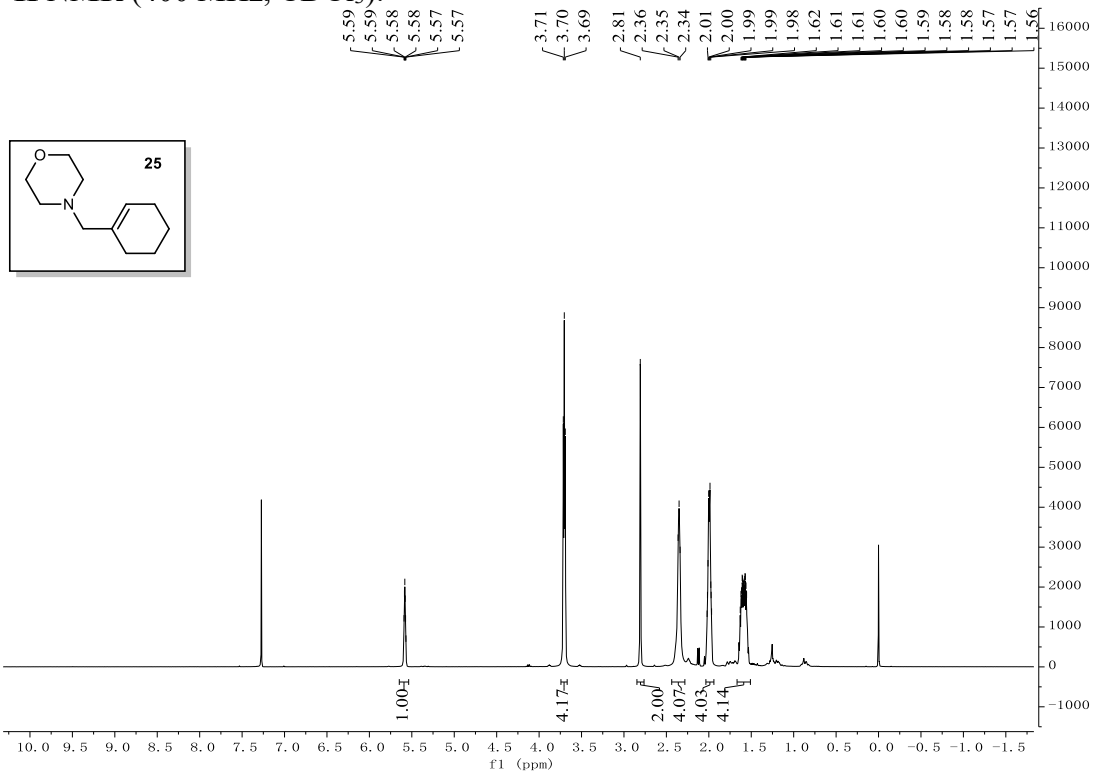

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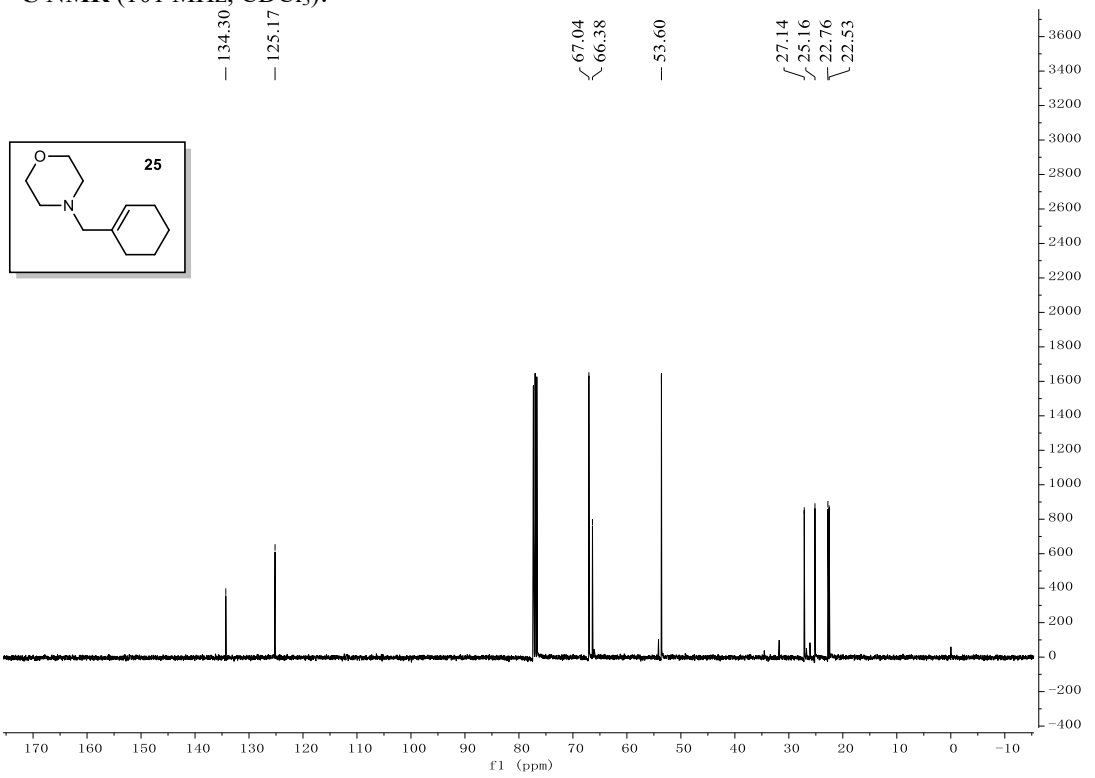

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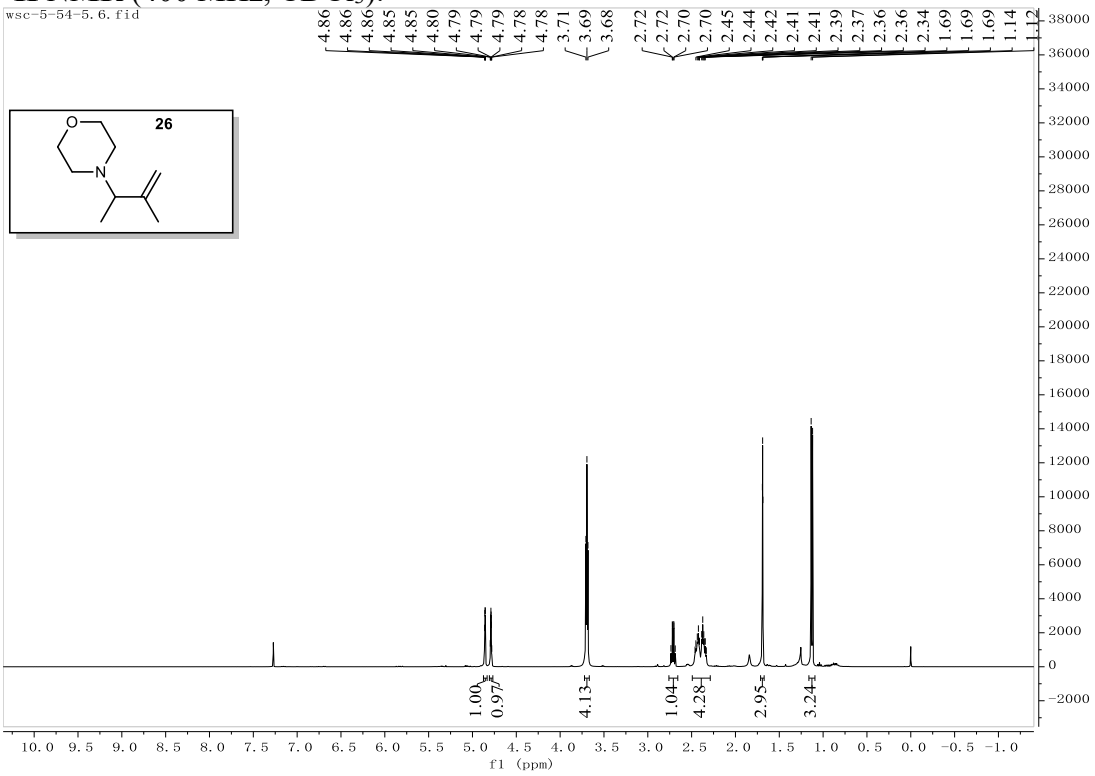

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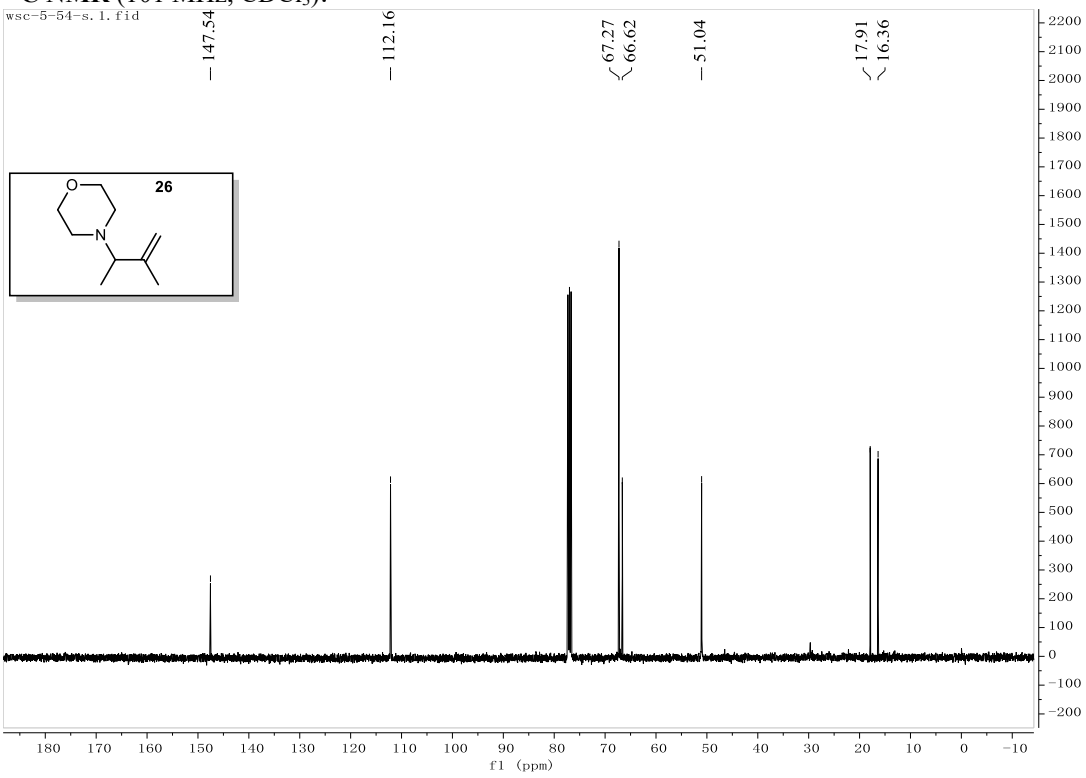

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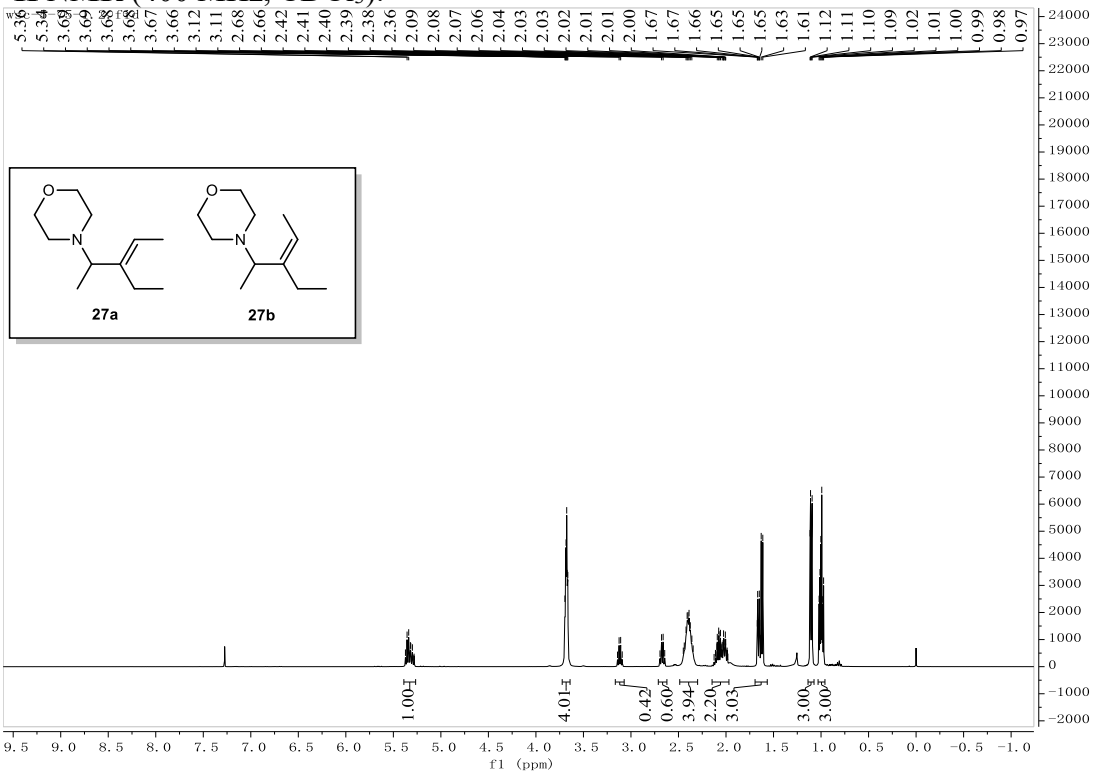

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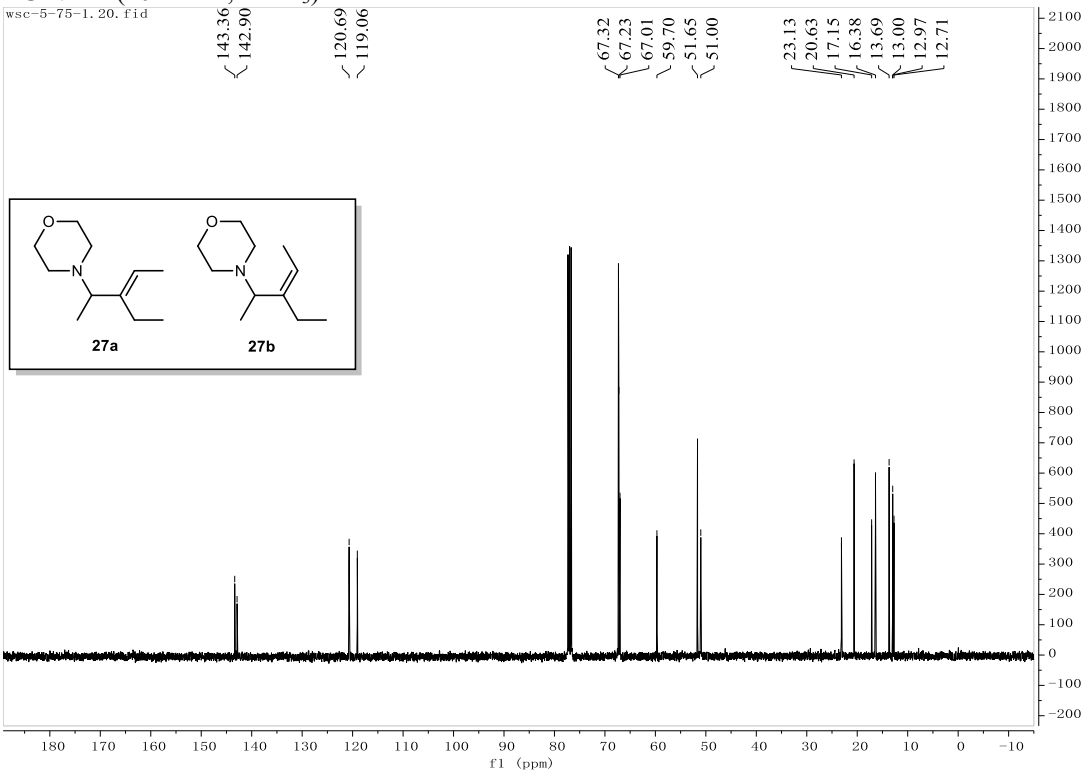

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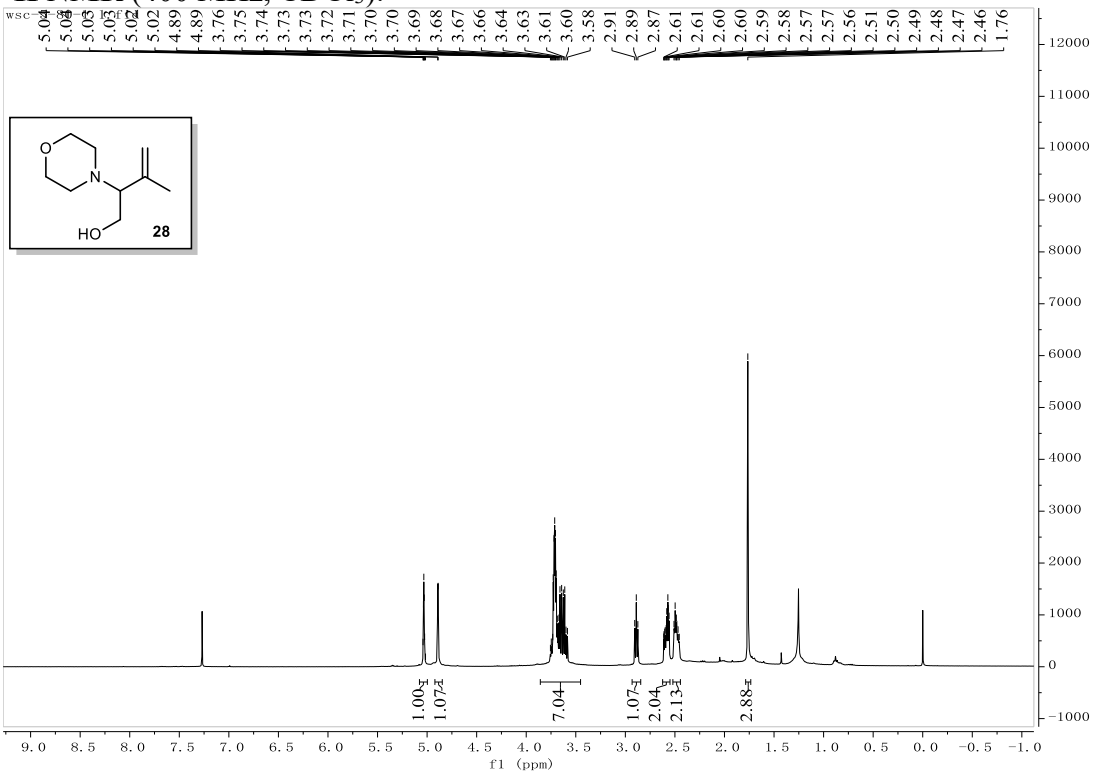

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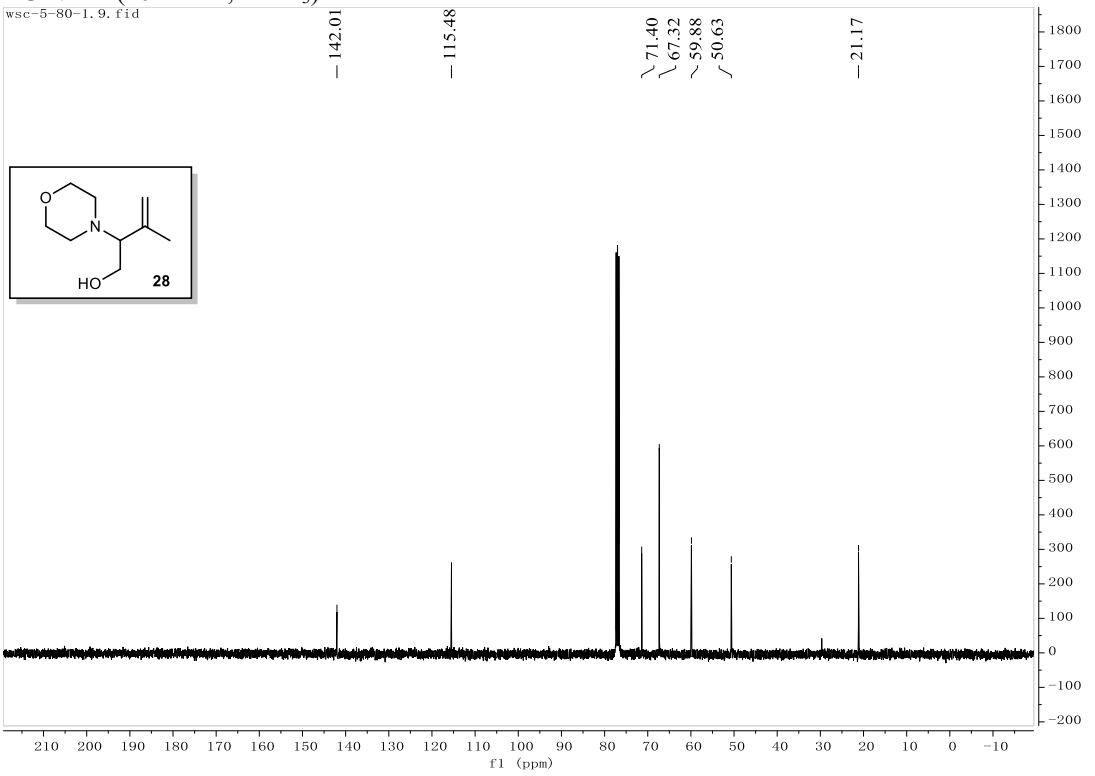

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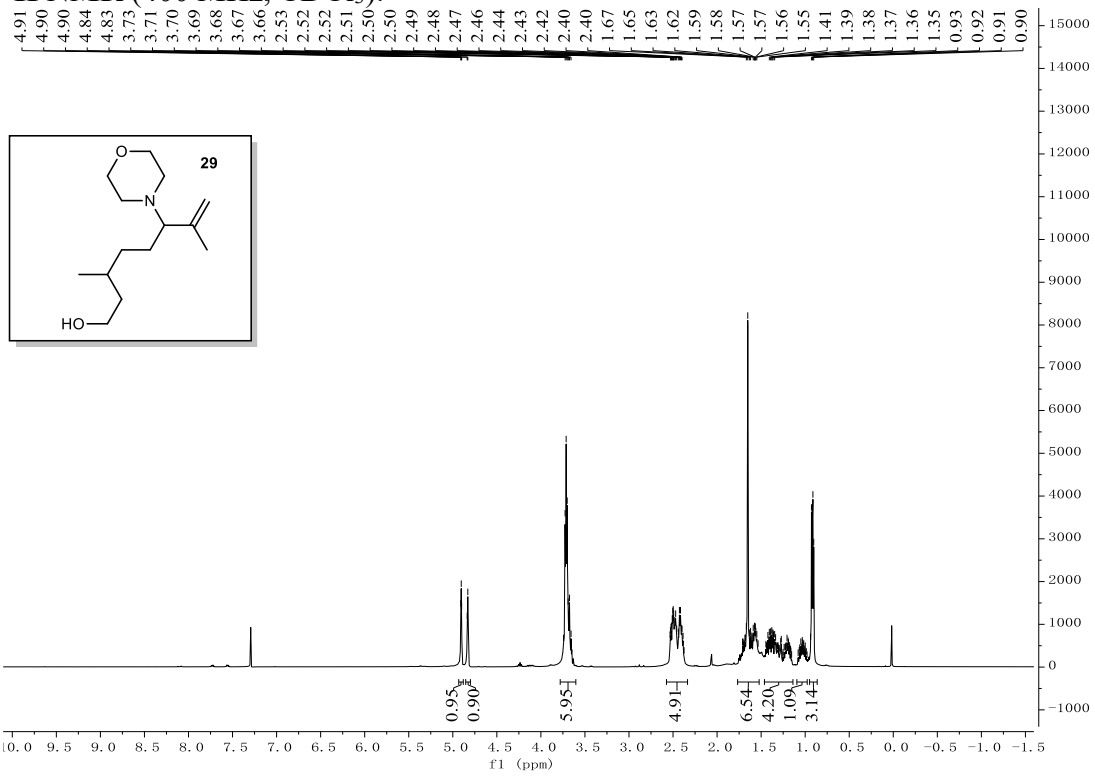

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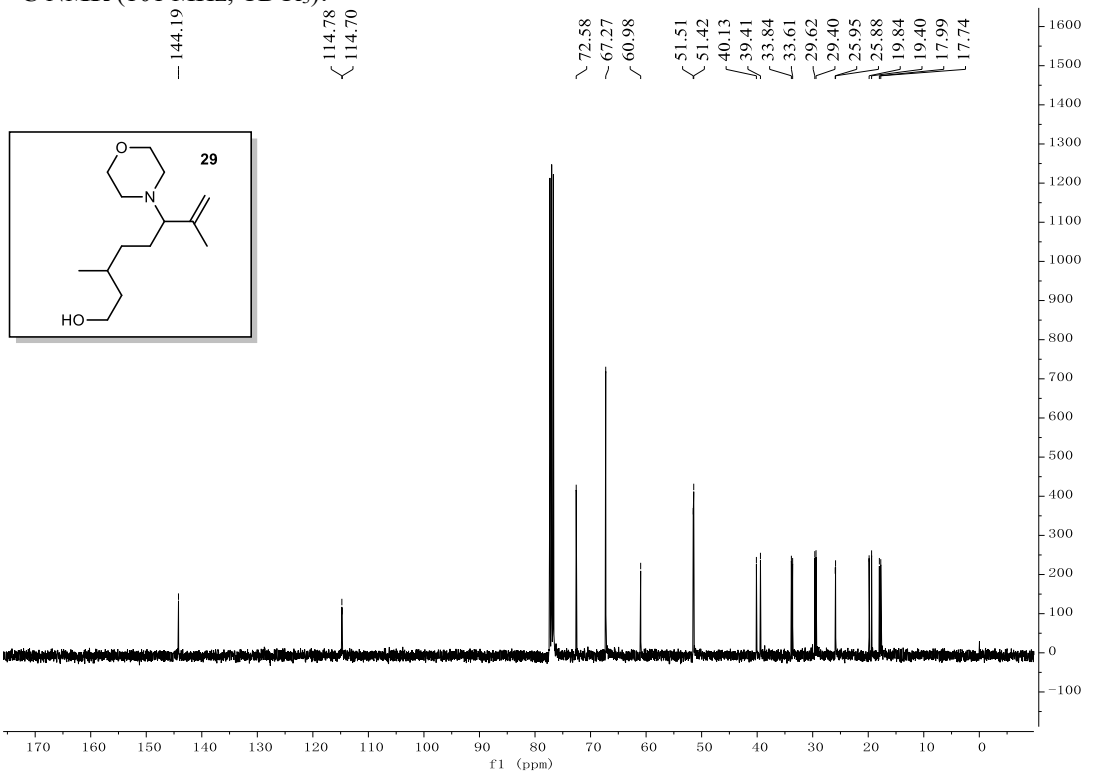

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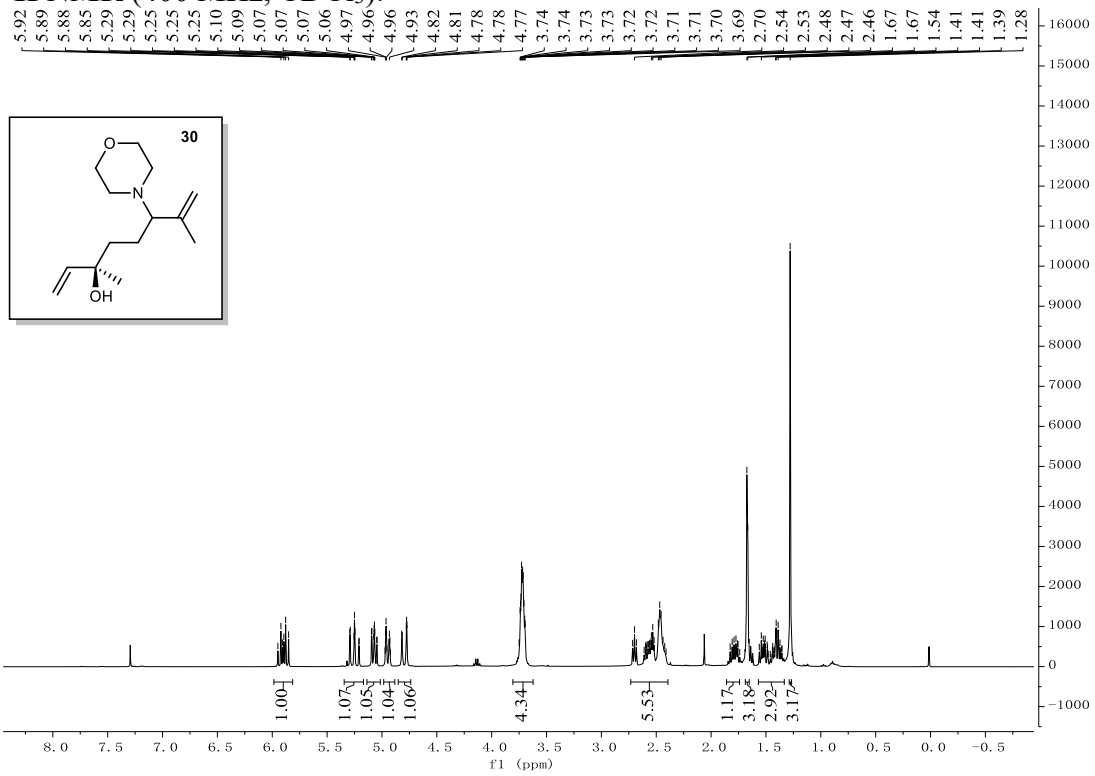

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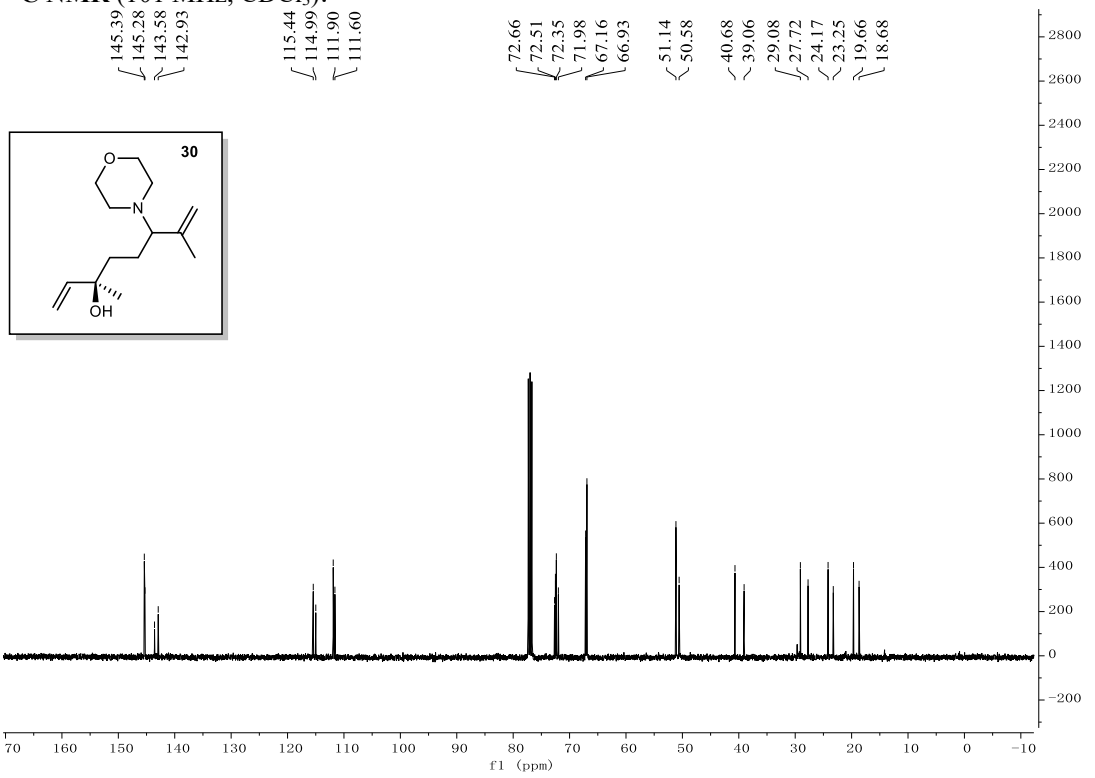

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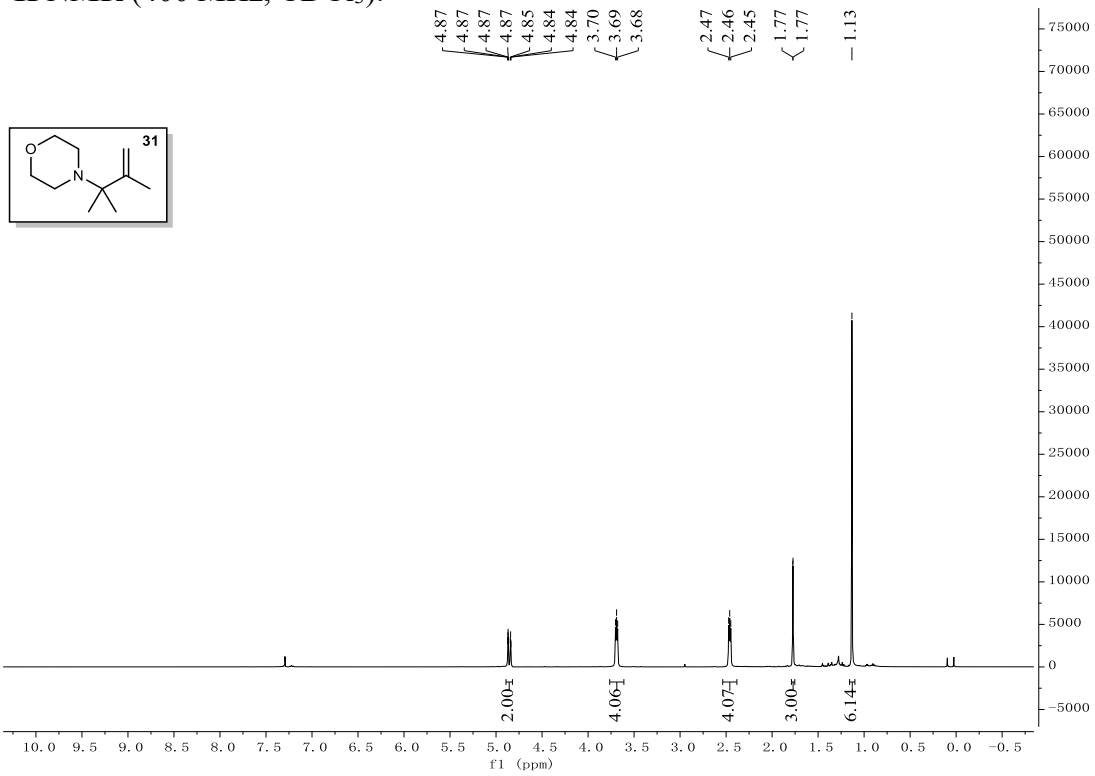

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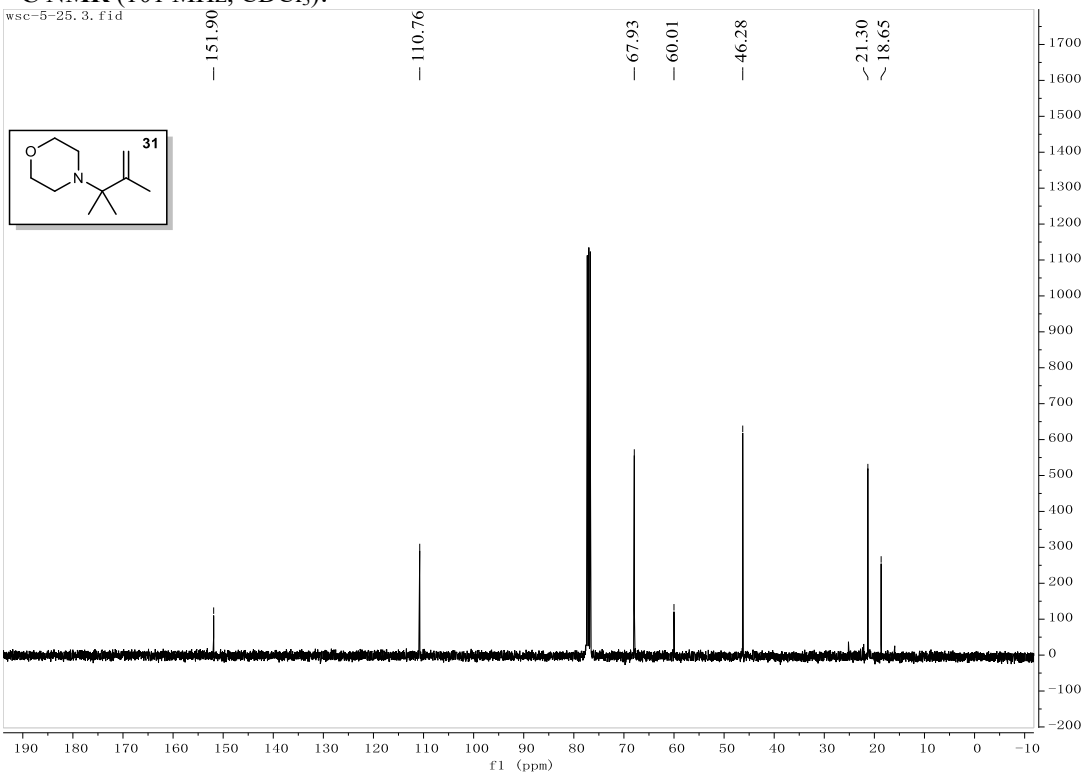

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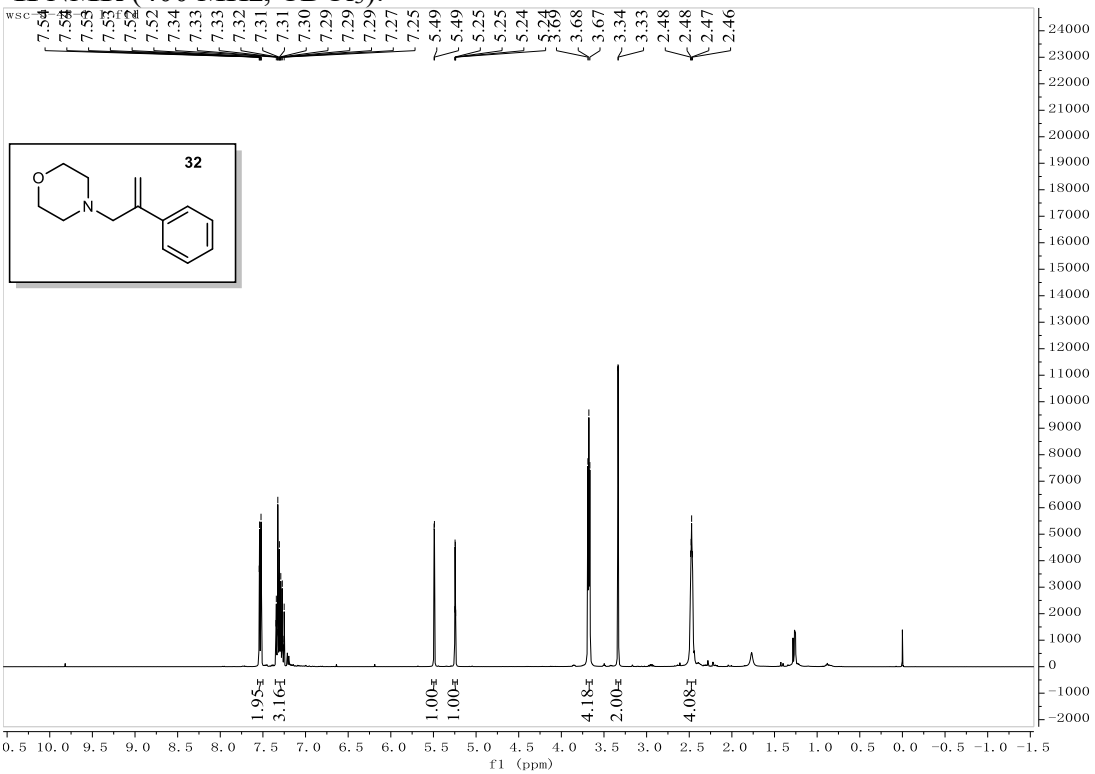

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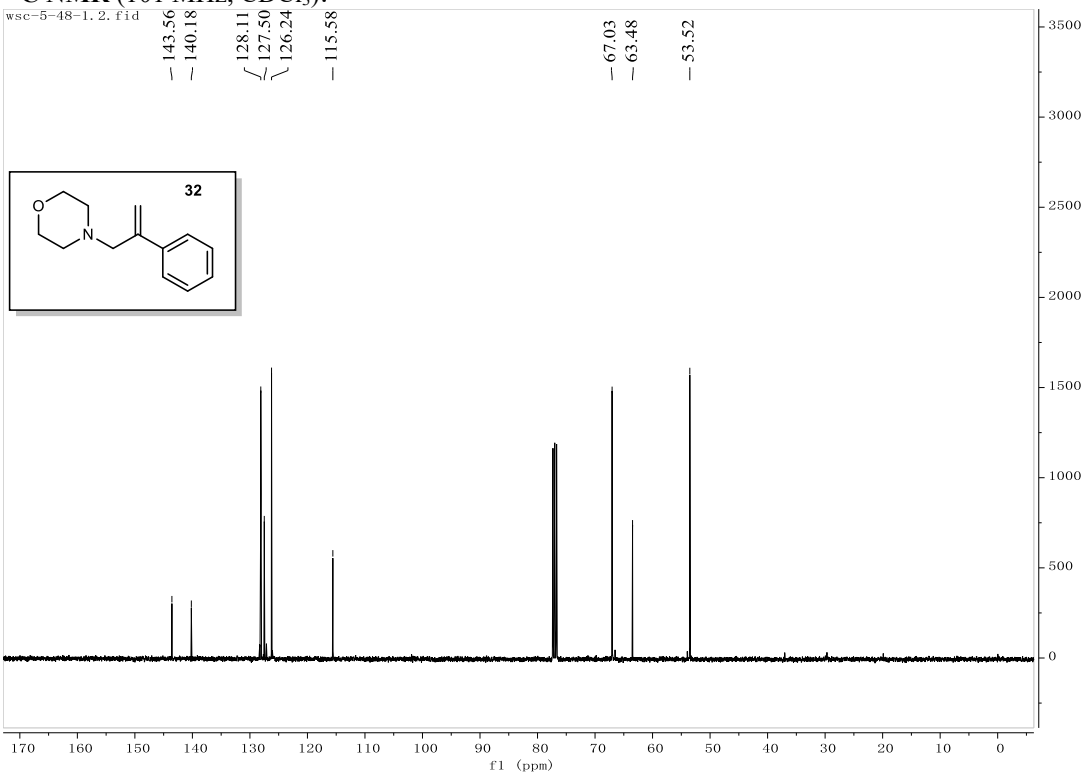

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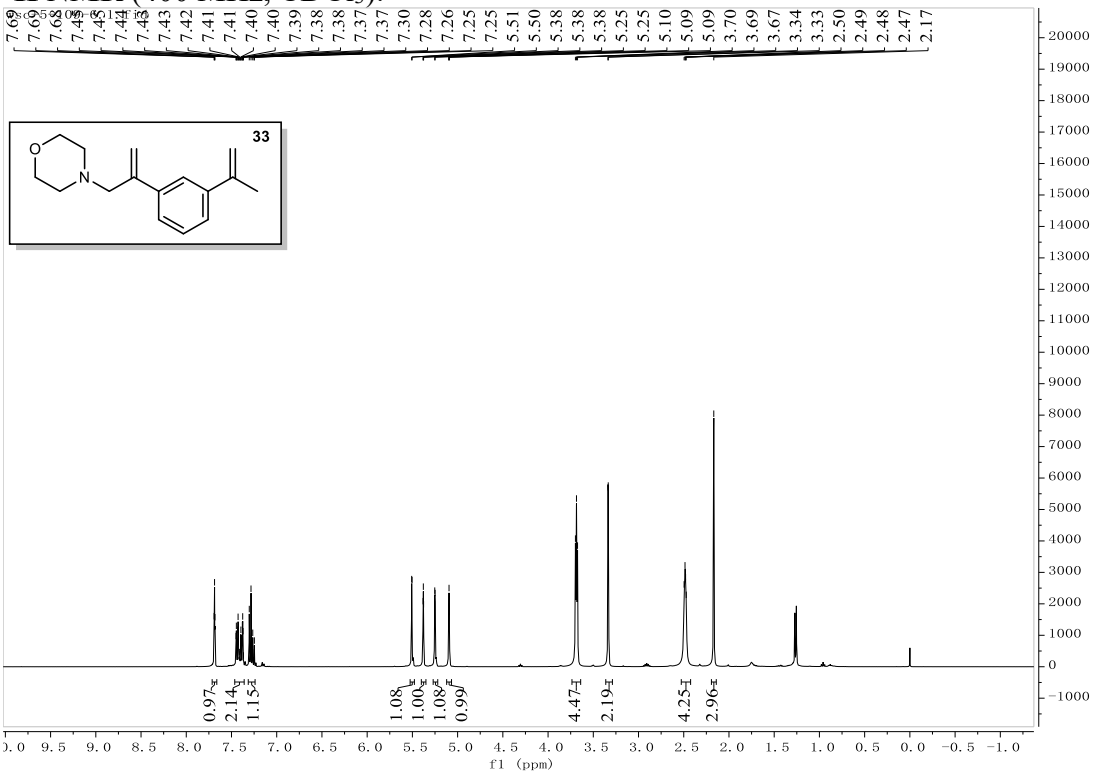

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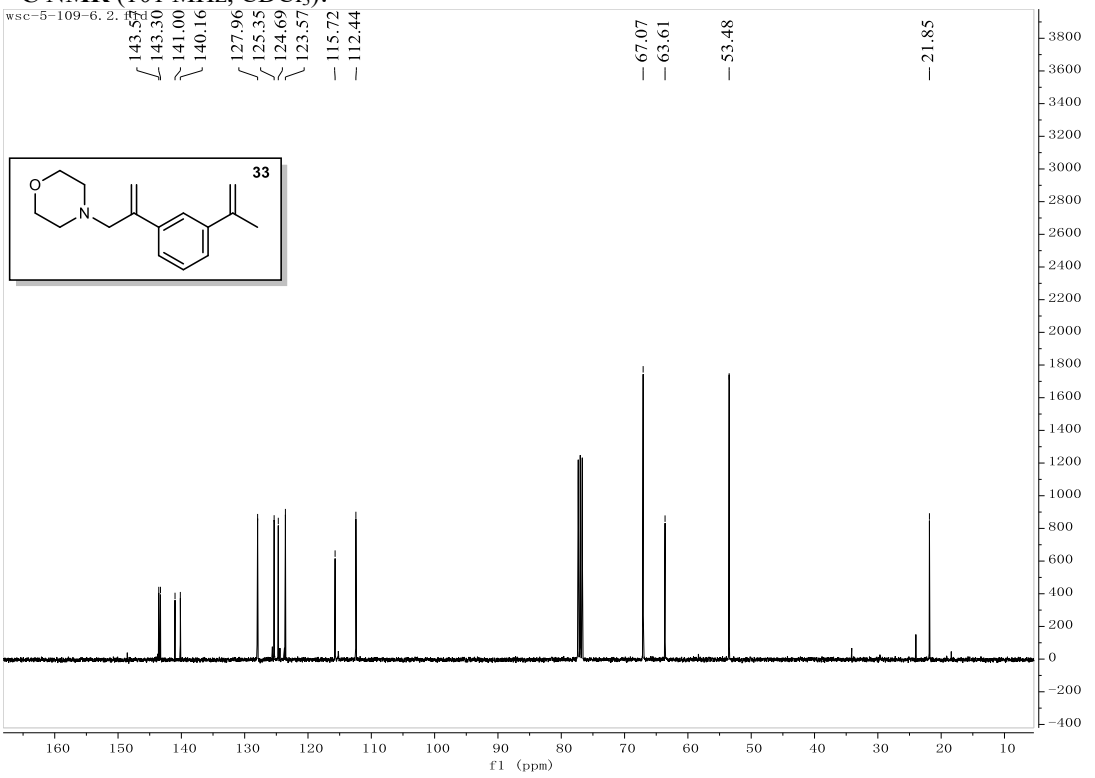

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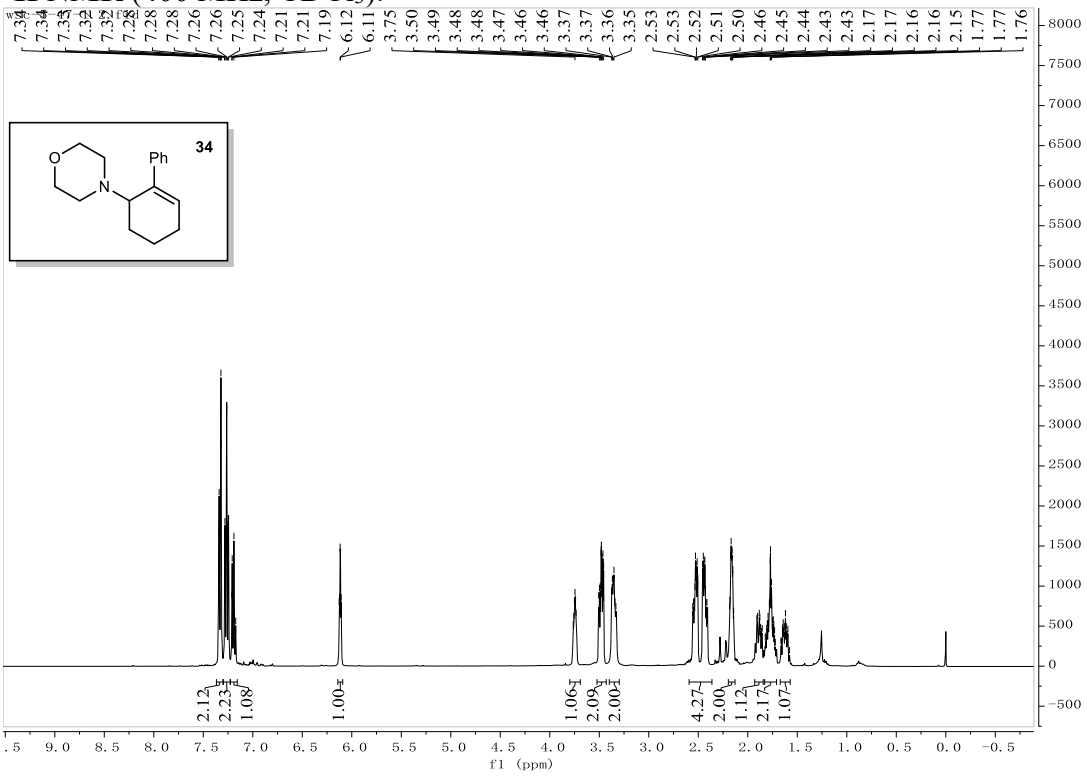

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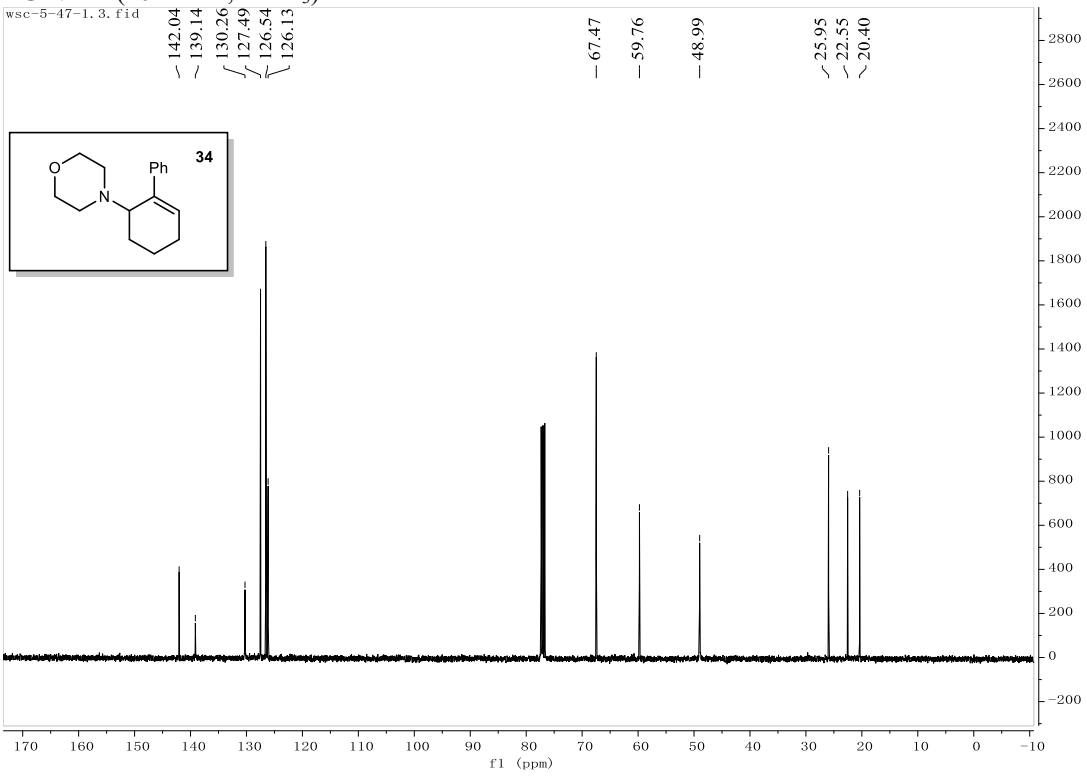

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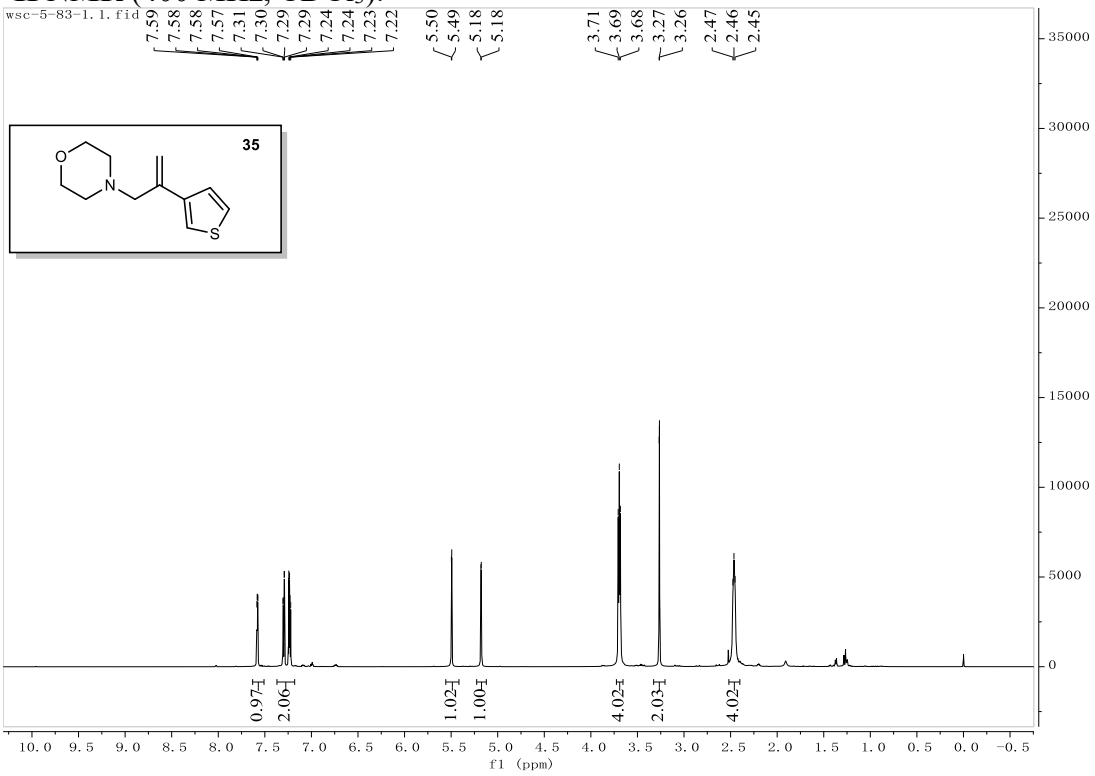

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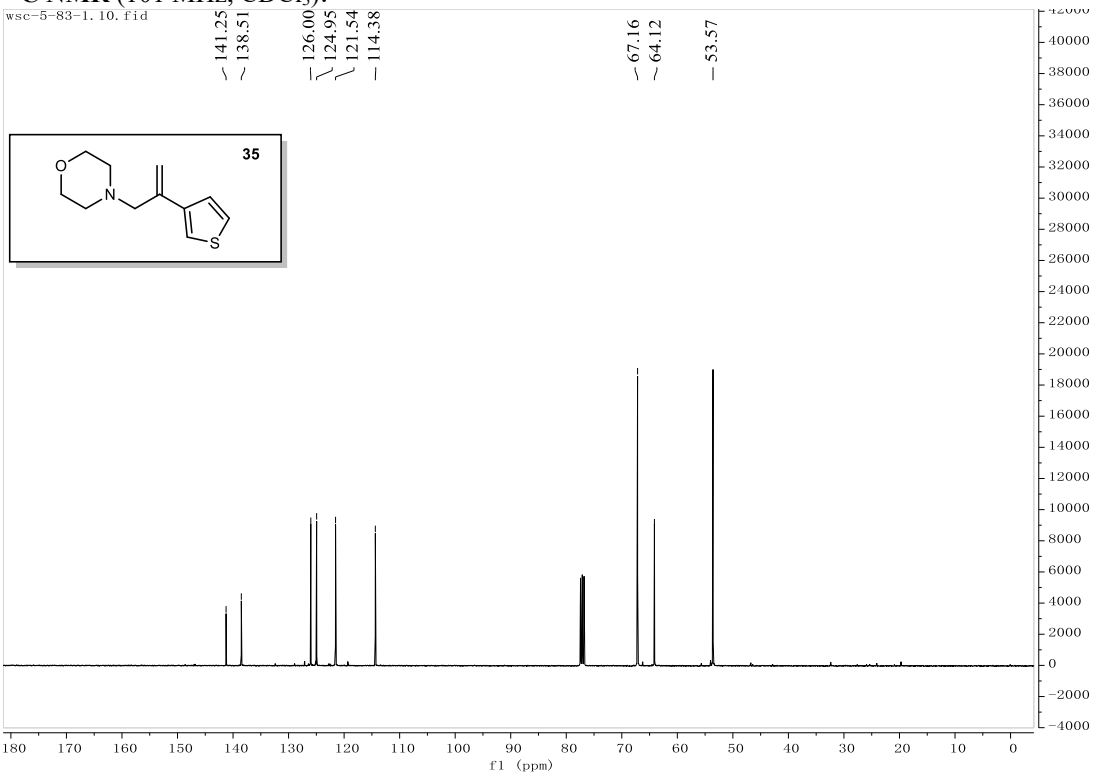

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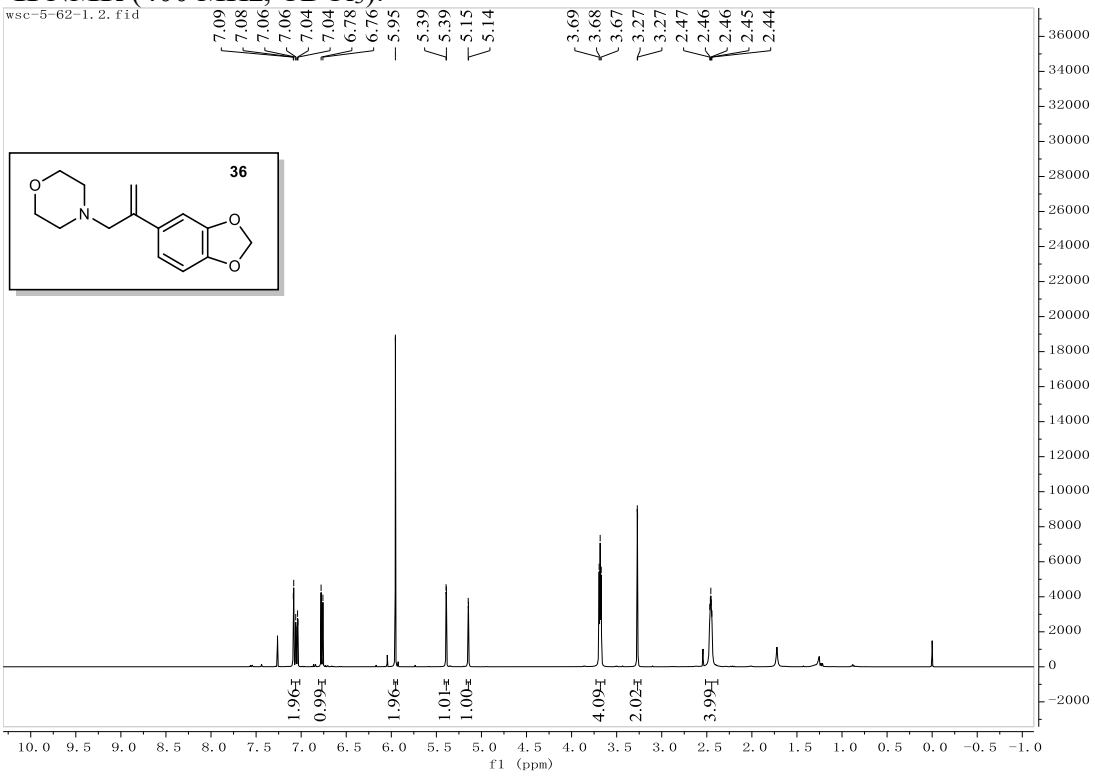

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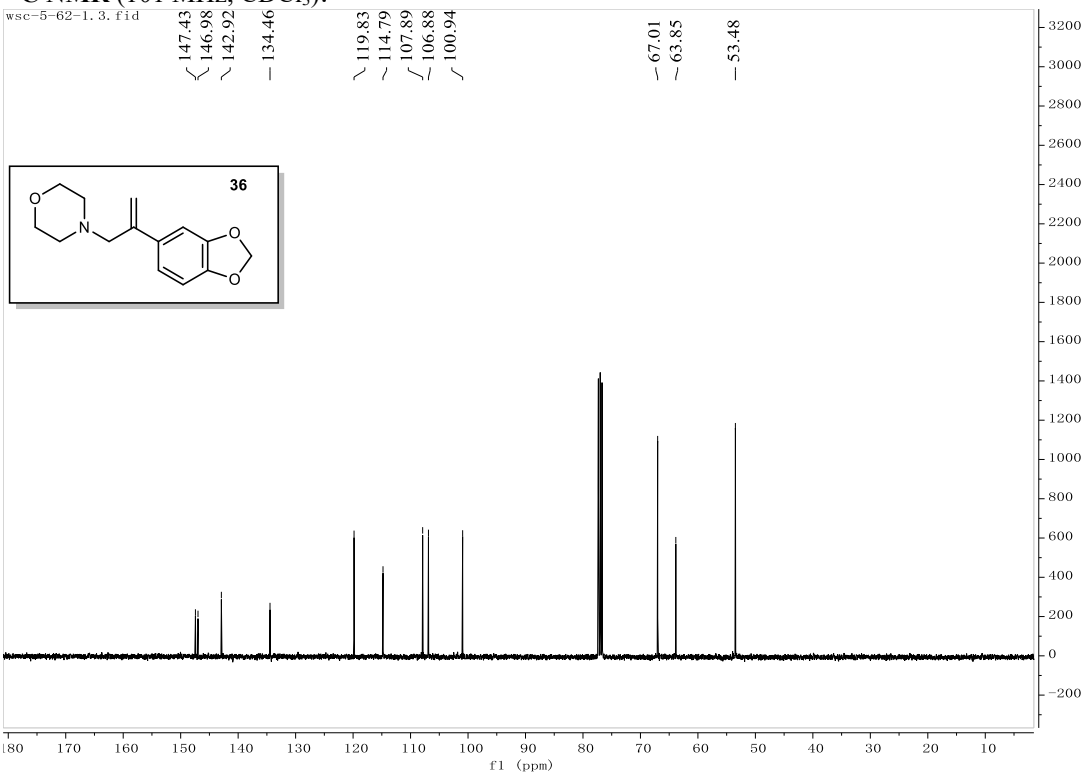

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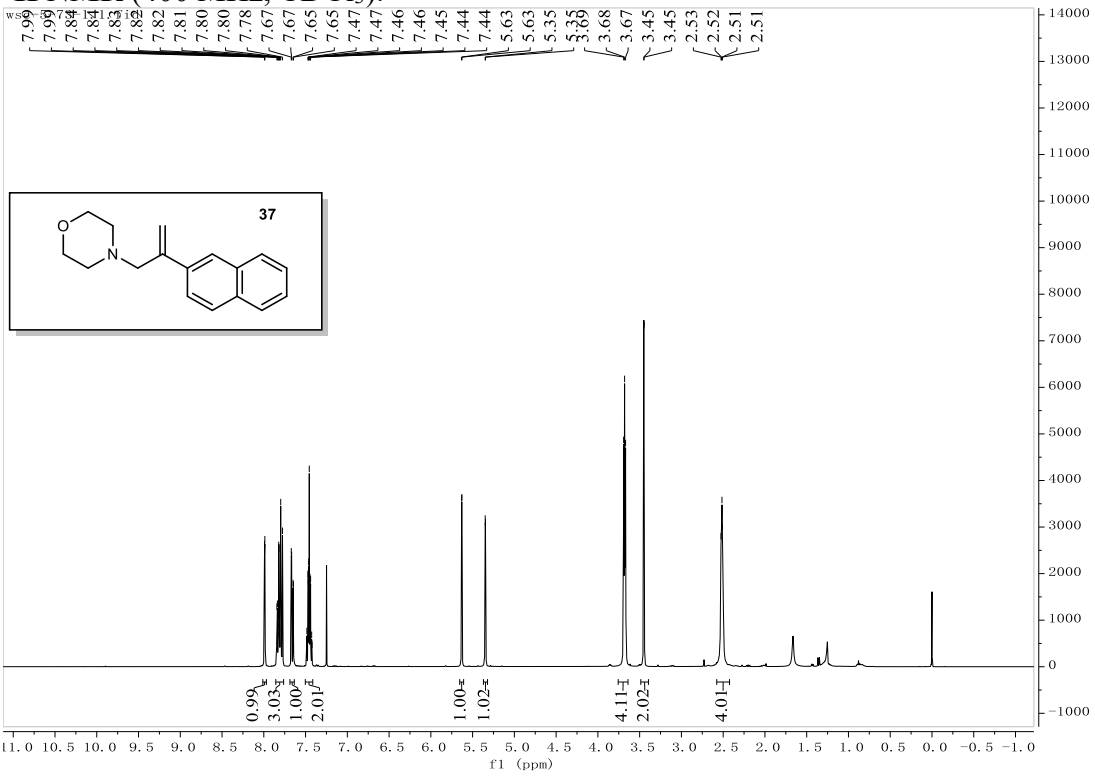

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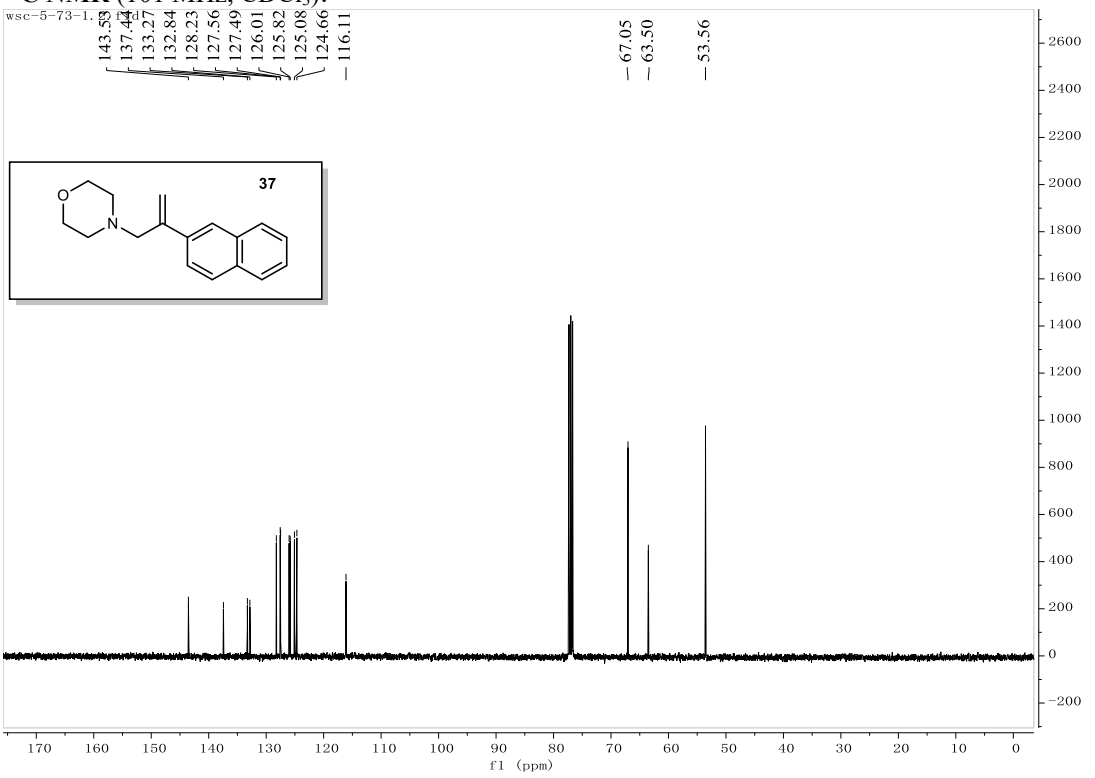
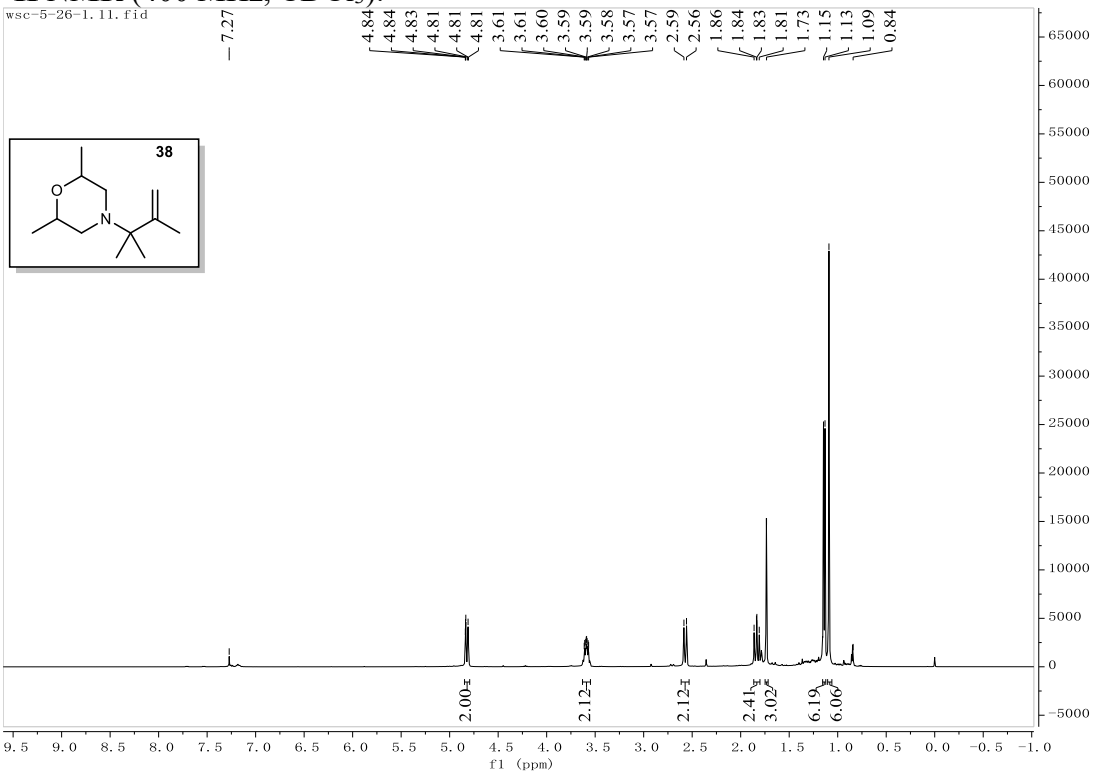
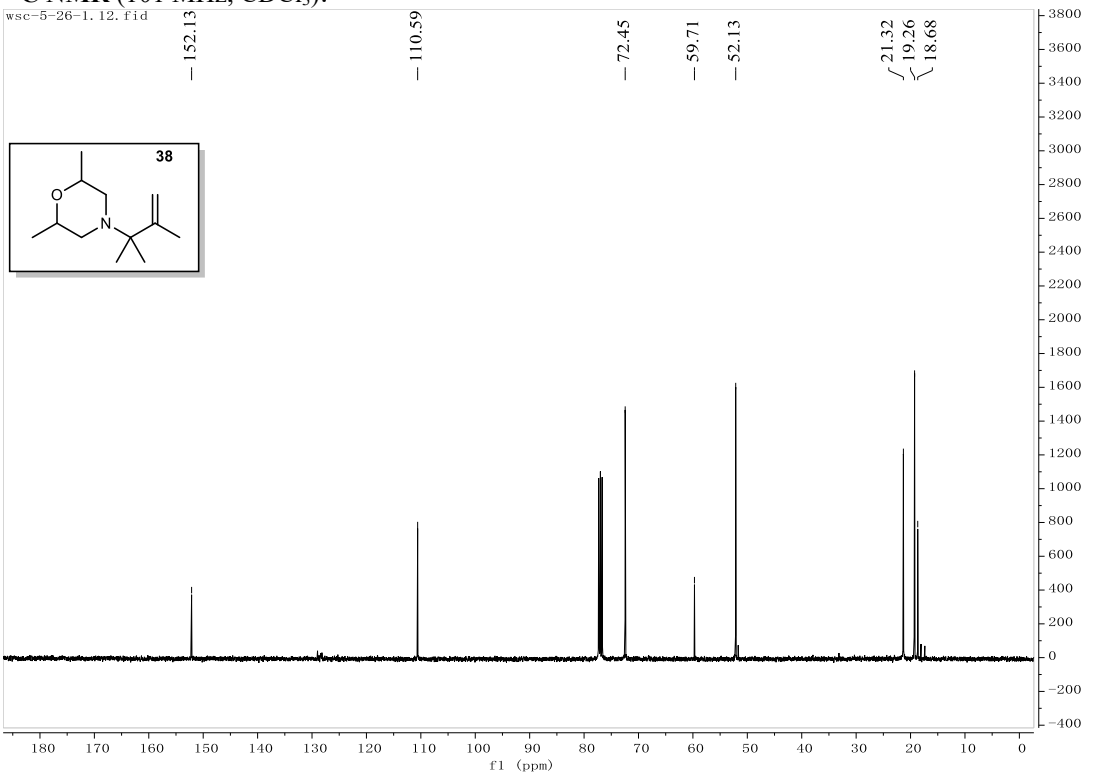


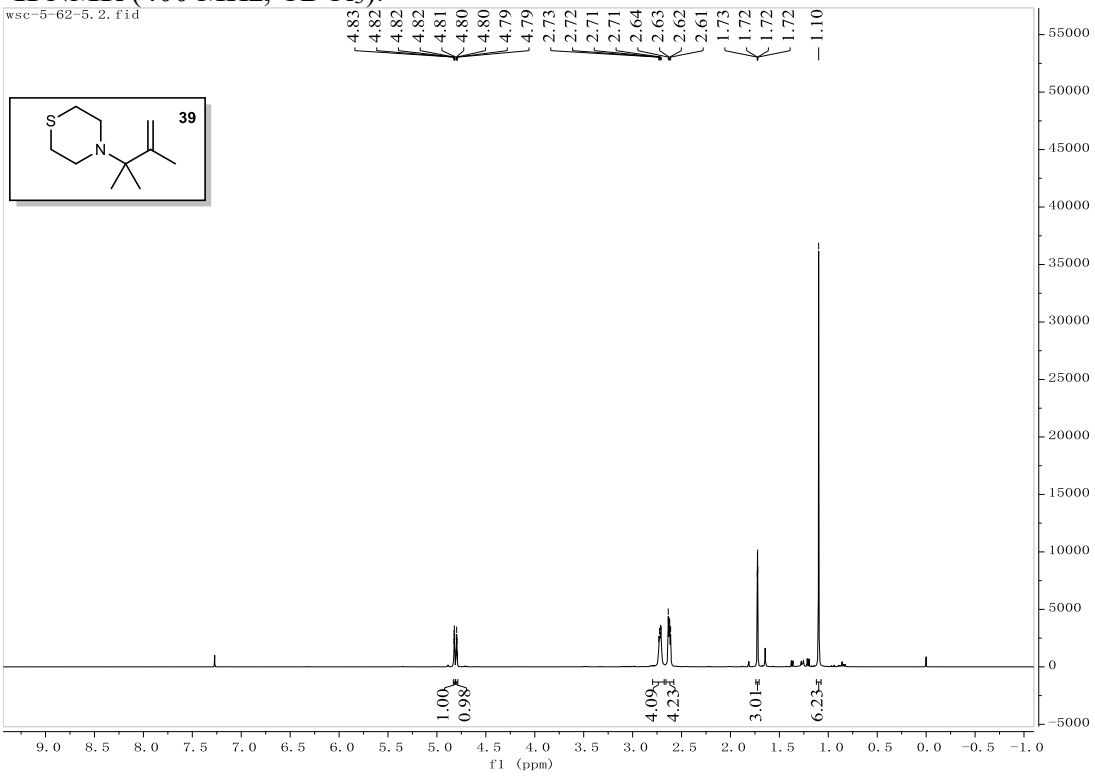
^{1}H NMR (400 MHz, $CDCl_3$):



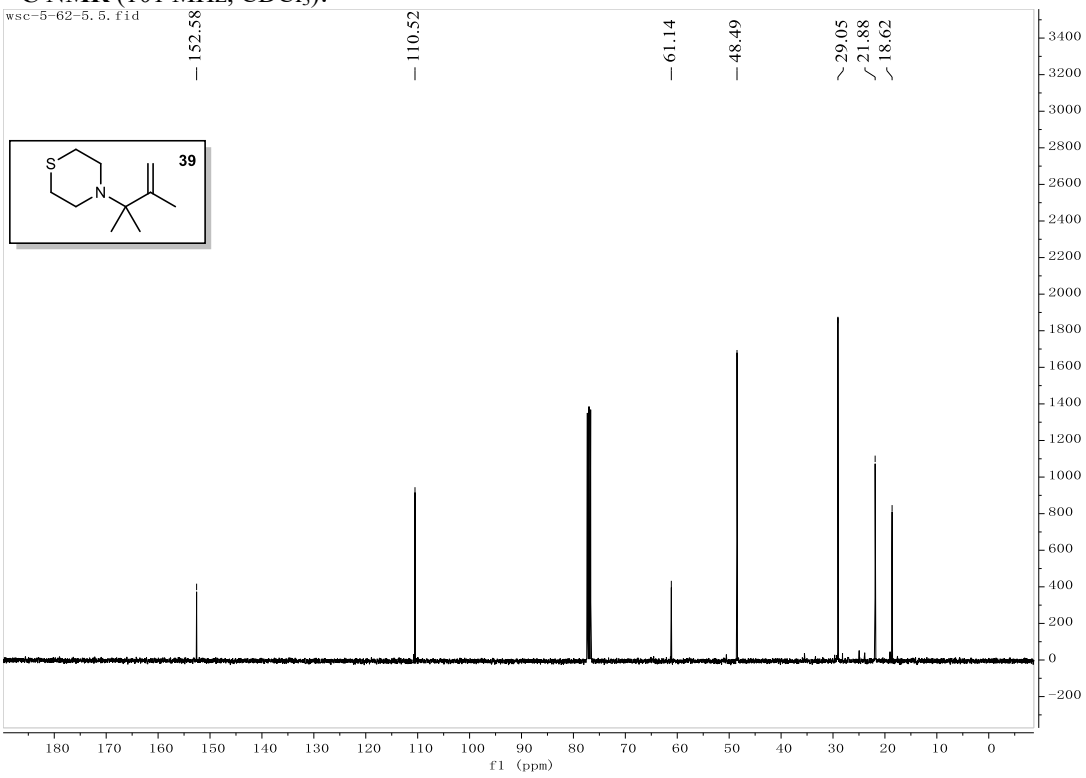
^{13}C NMR (101 MHz, $CDCl_3$):



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



^{13}C NMR (101 MHz, $CDCl_3$):



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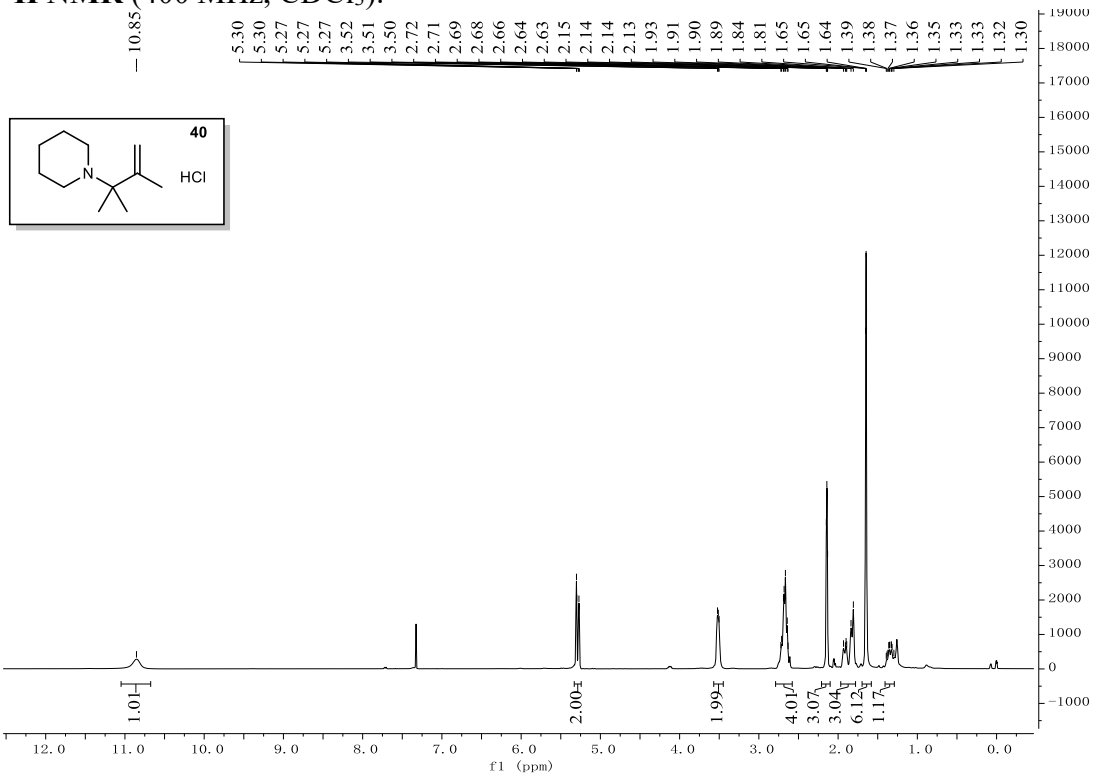
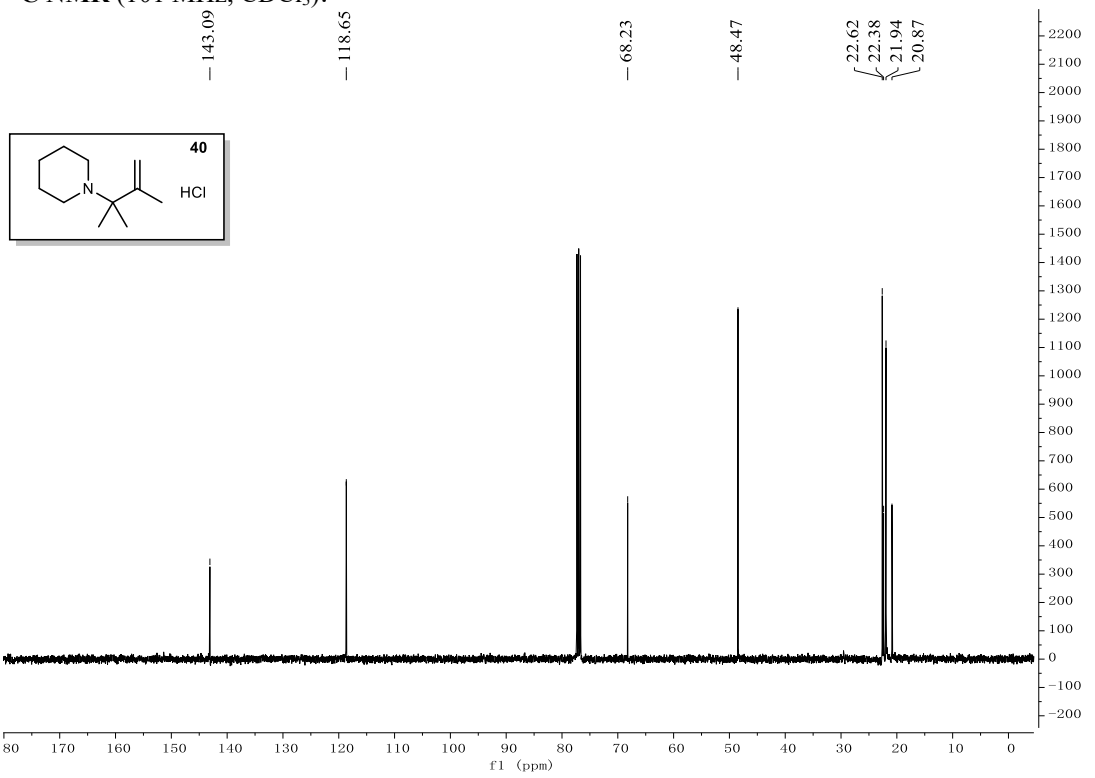
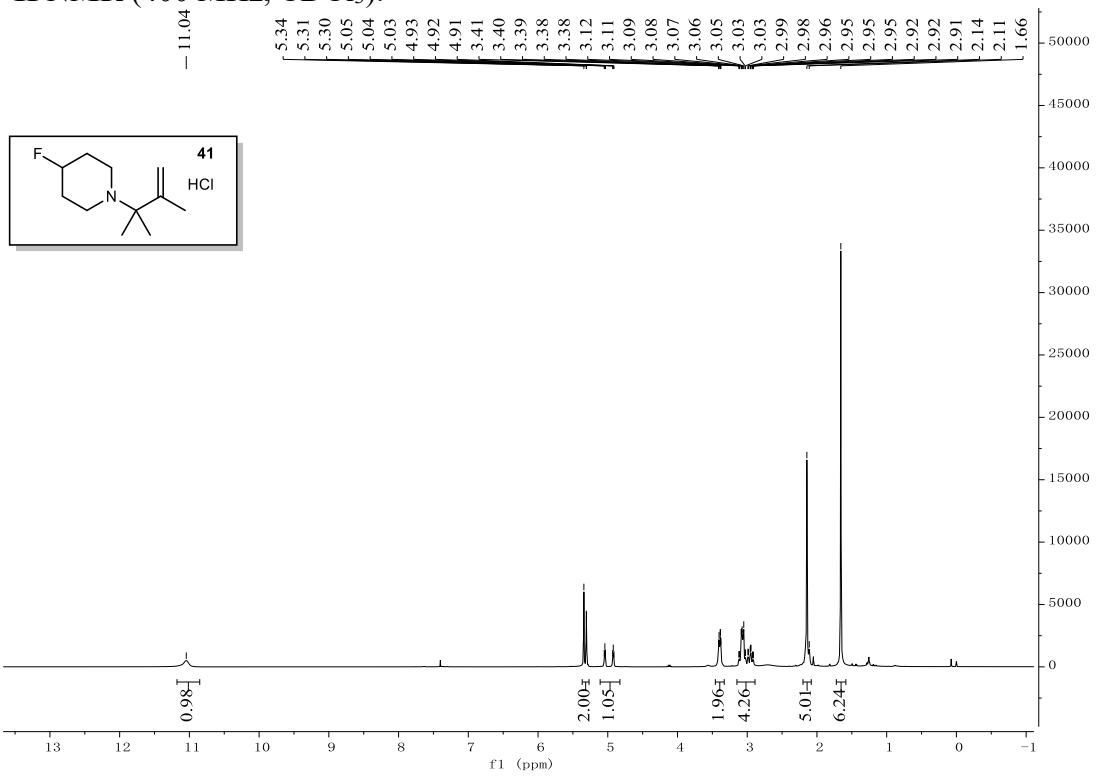


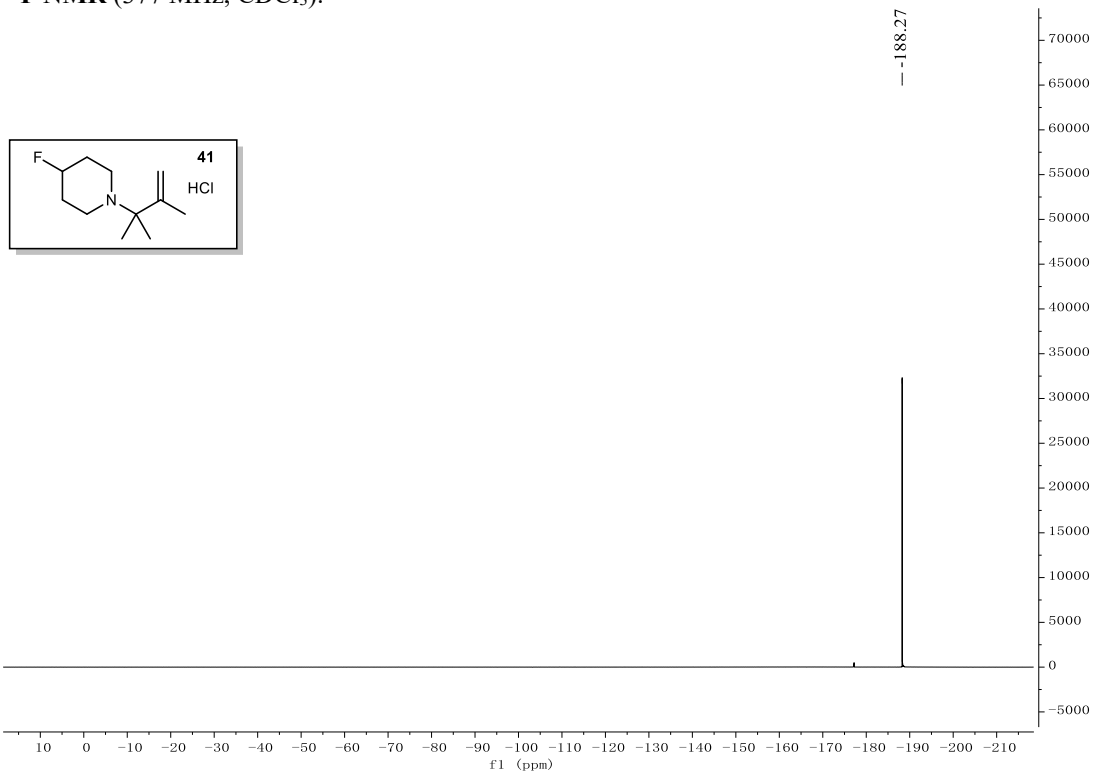
^{13}C NMR (101 MHz, $CDCl_3$):



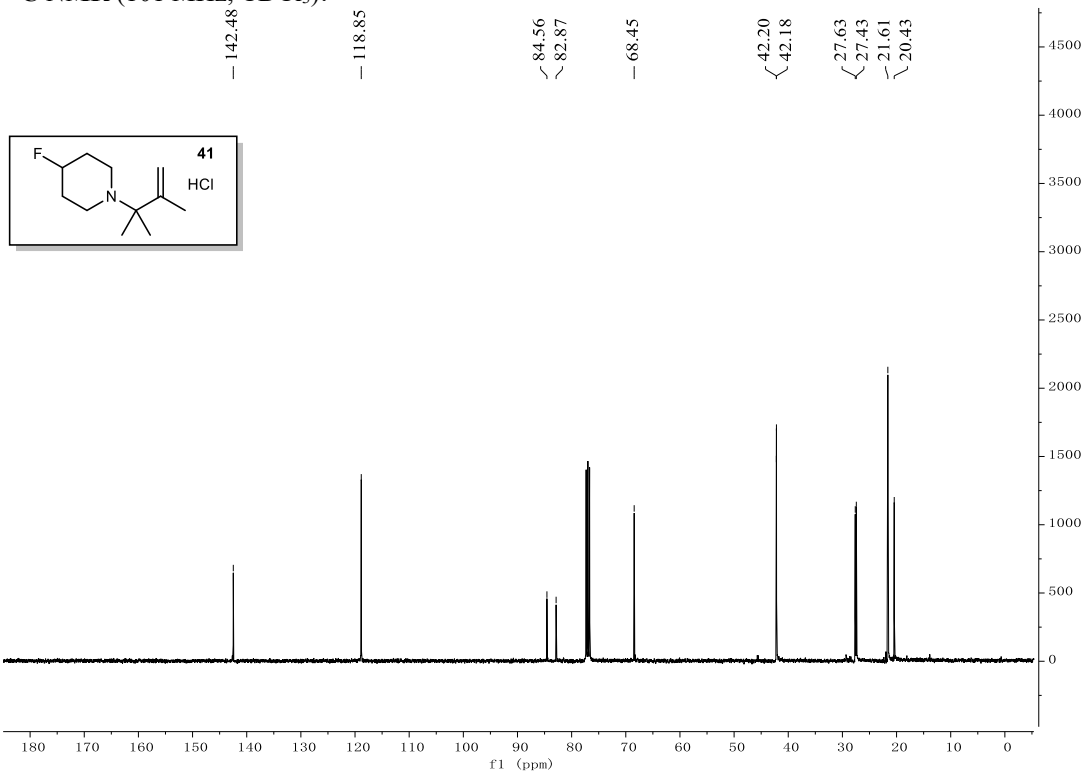
^{1}H NMR (400 MHz, $CDCl_3$):



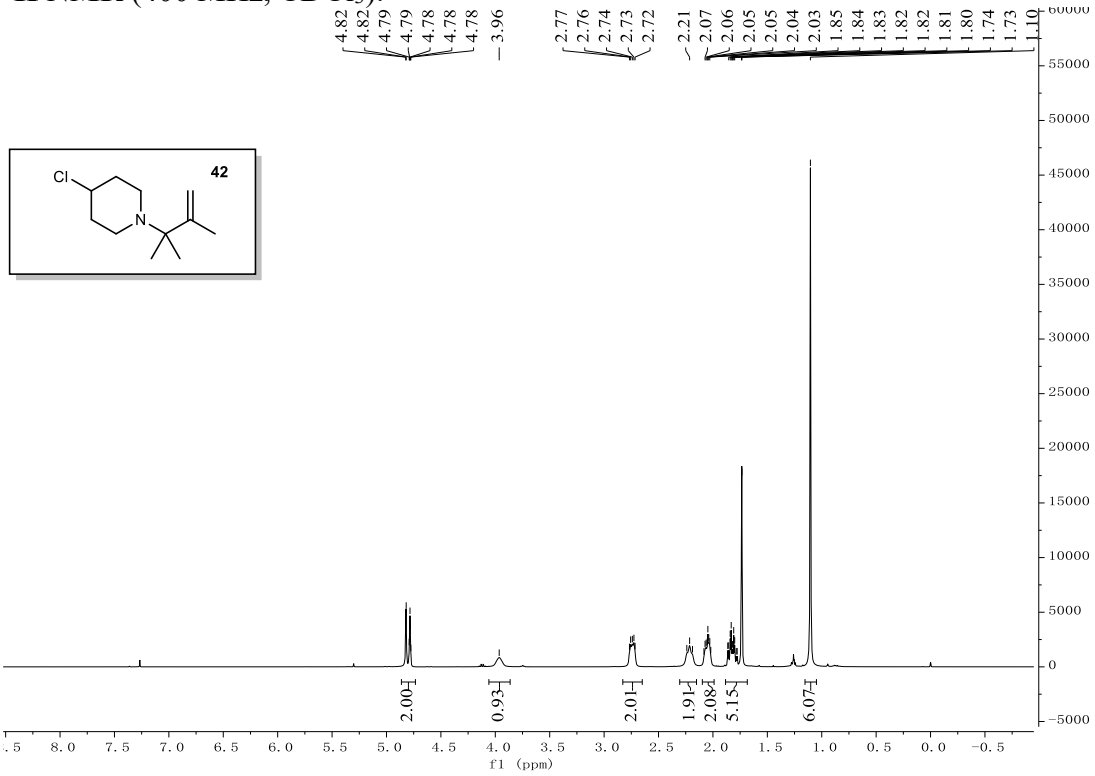
^{19}F NMR (377 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):



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



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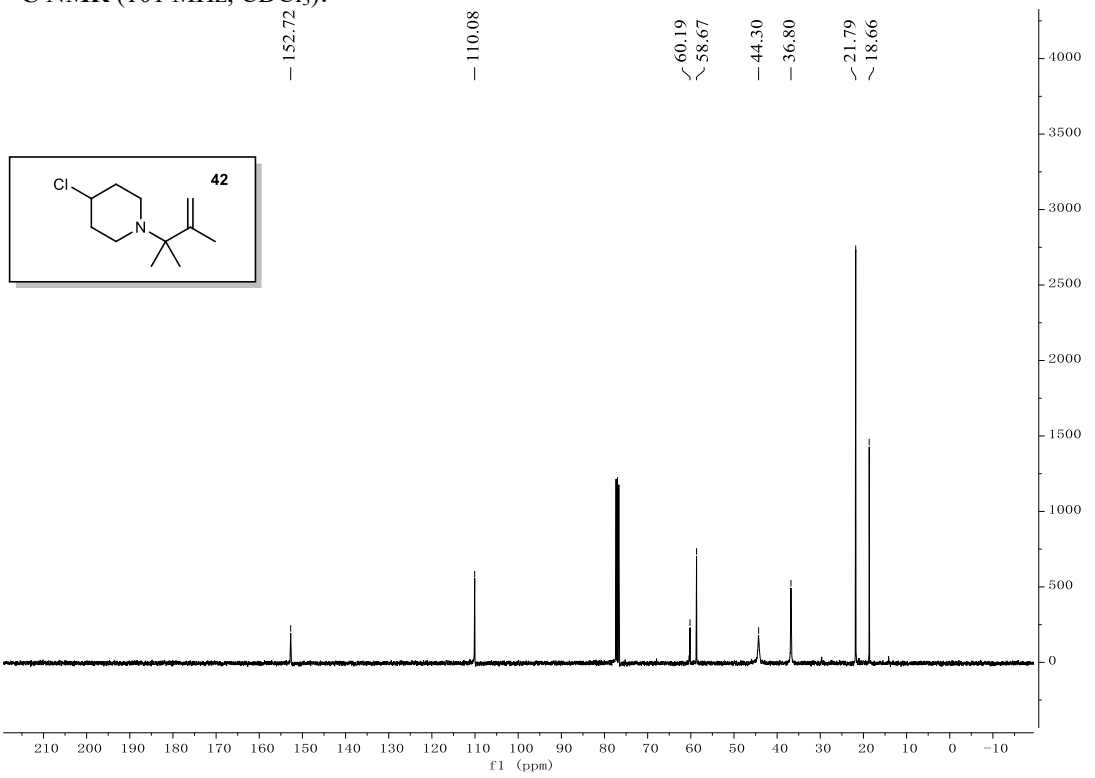

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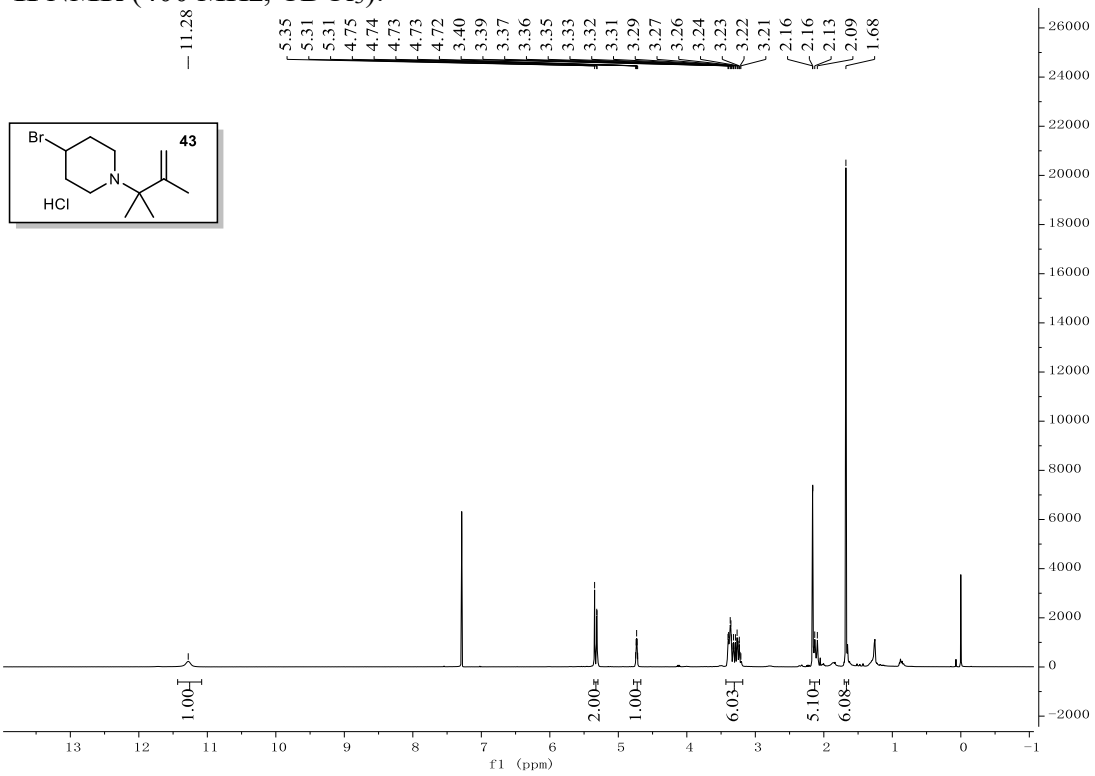

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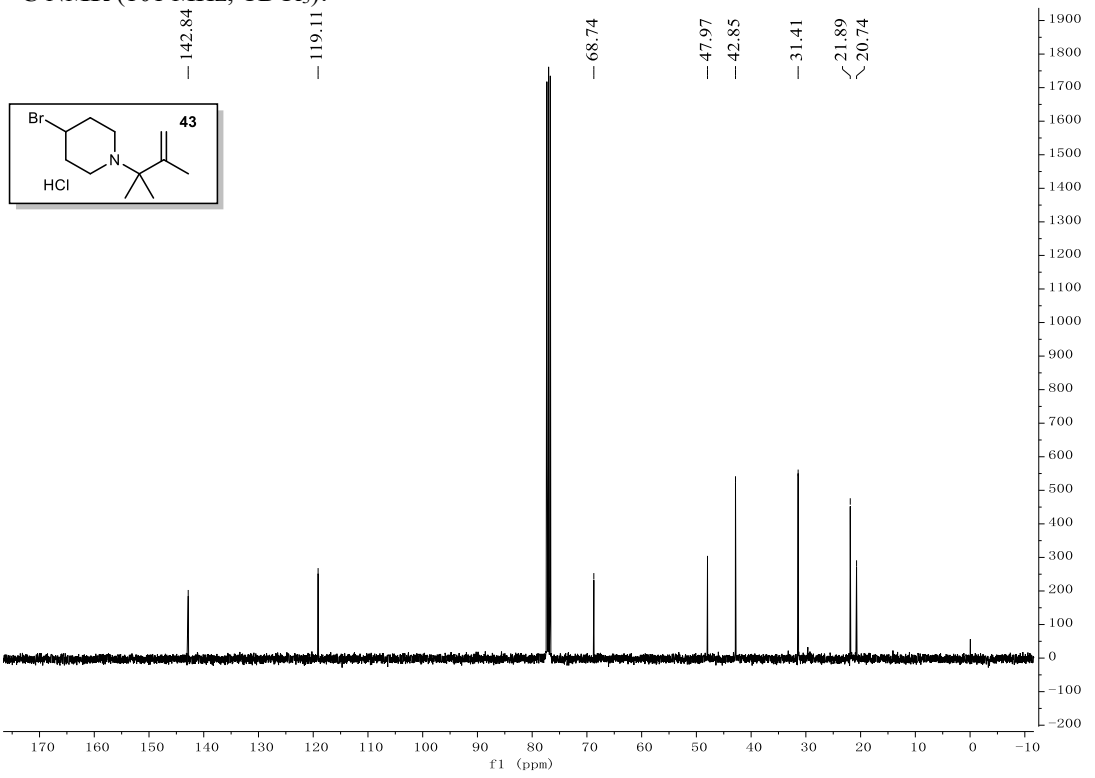

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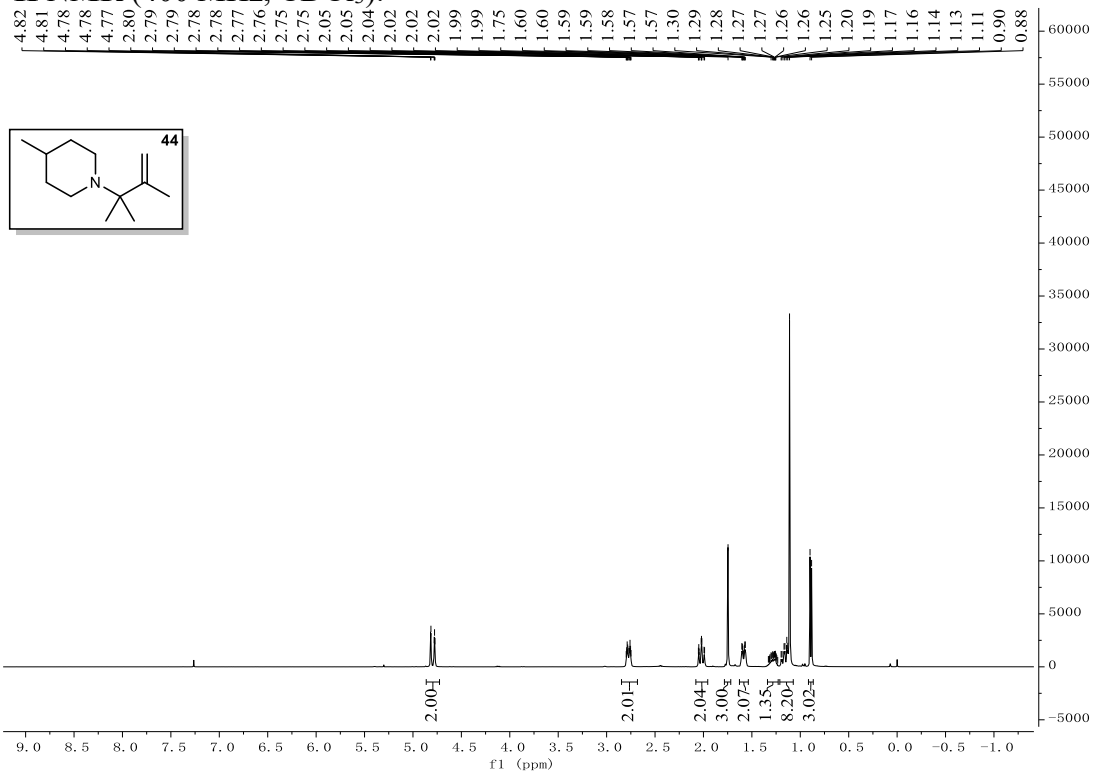

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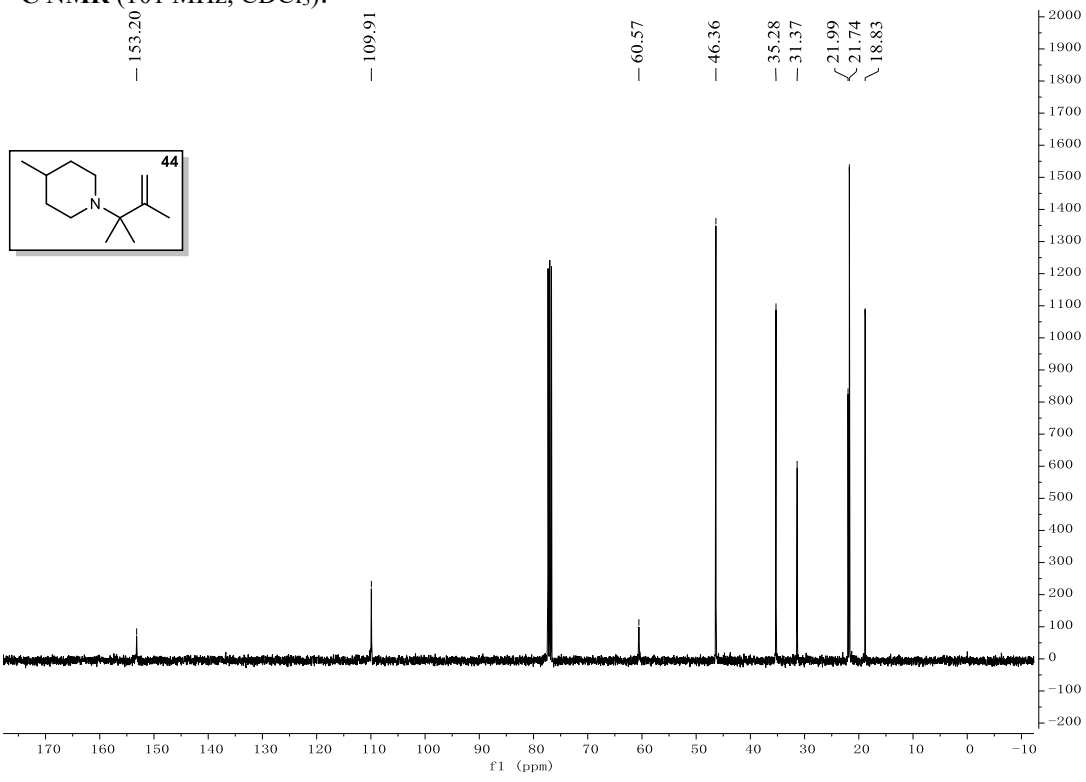

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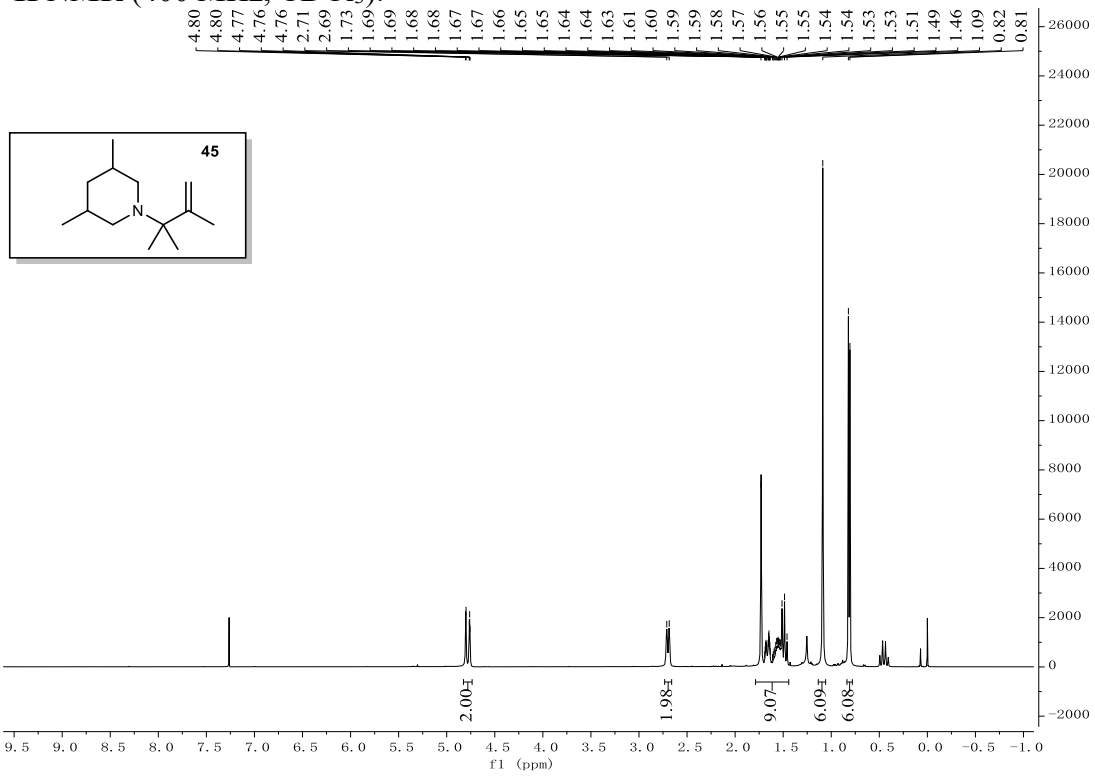

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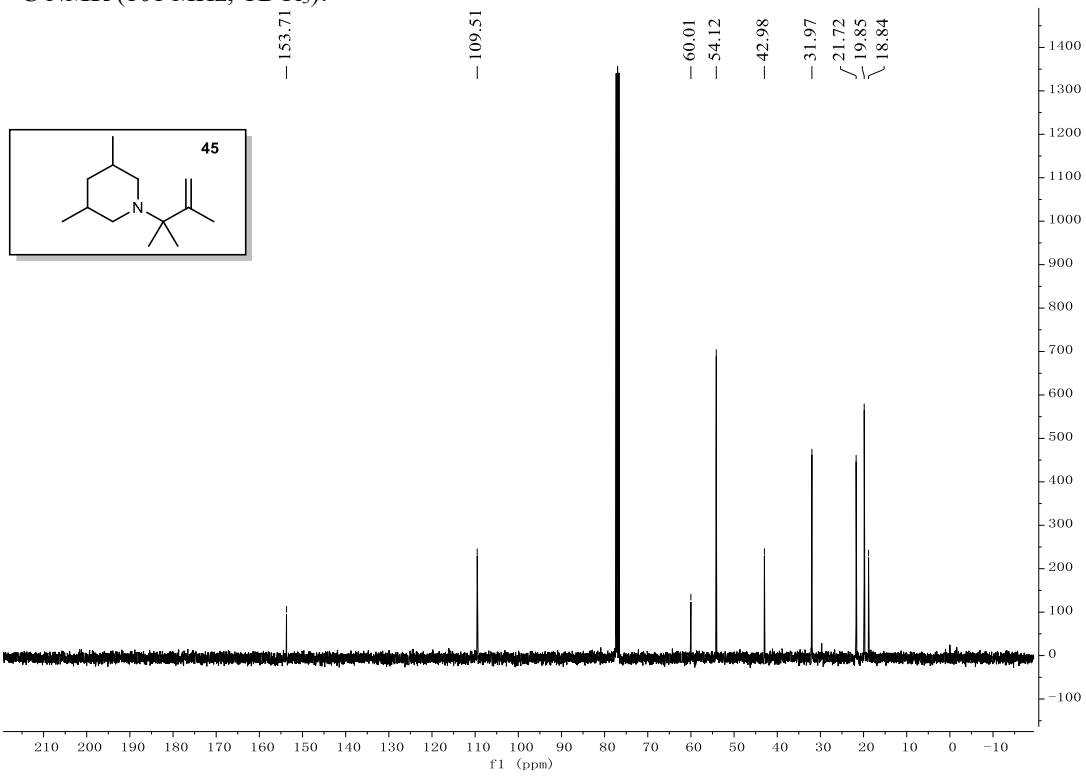

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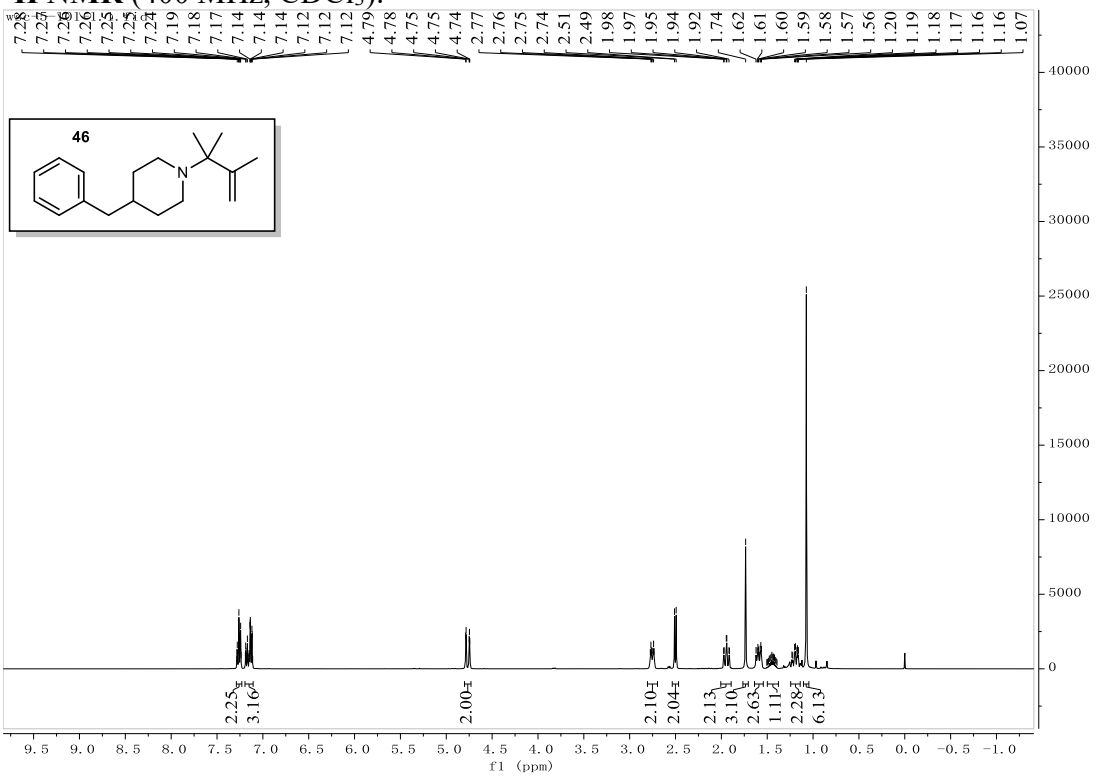

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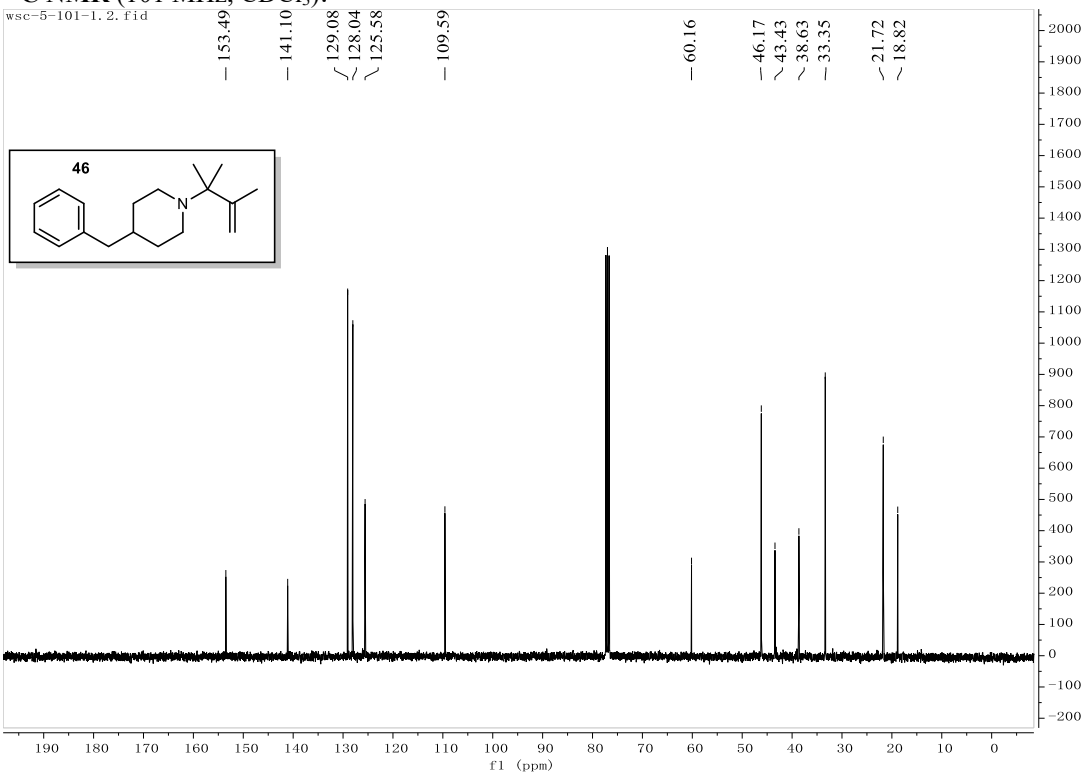

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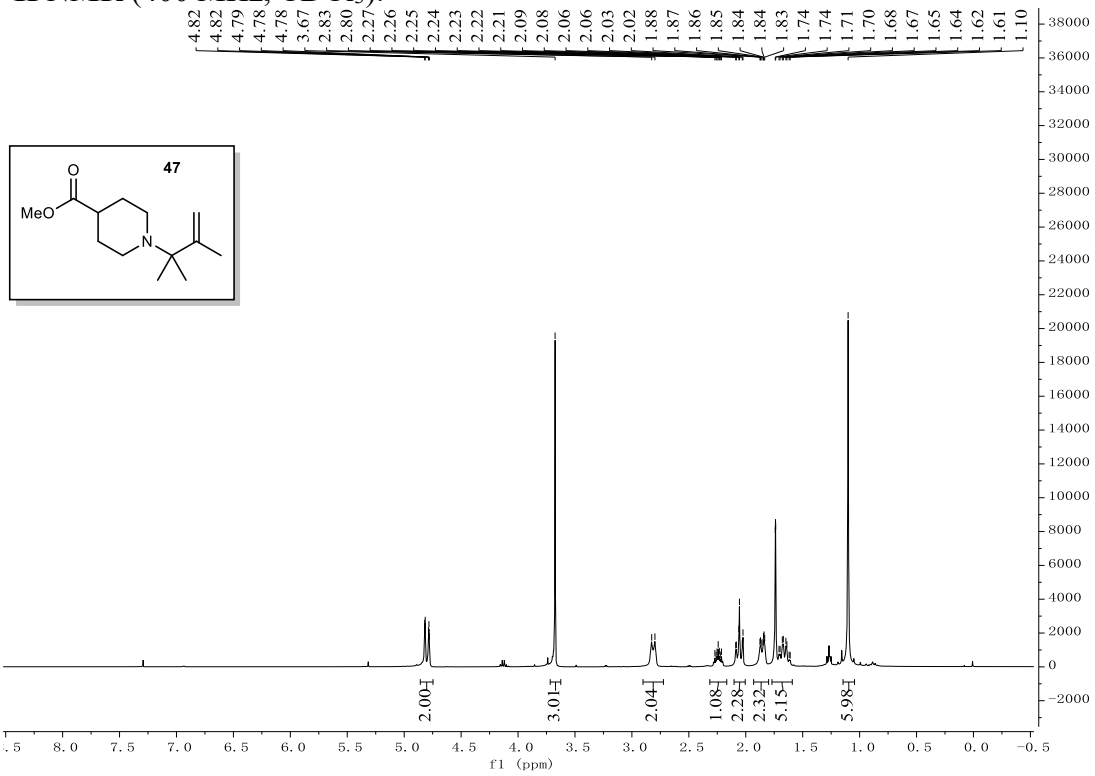

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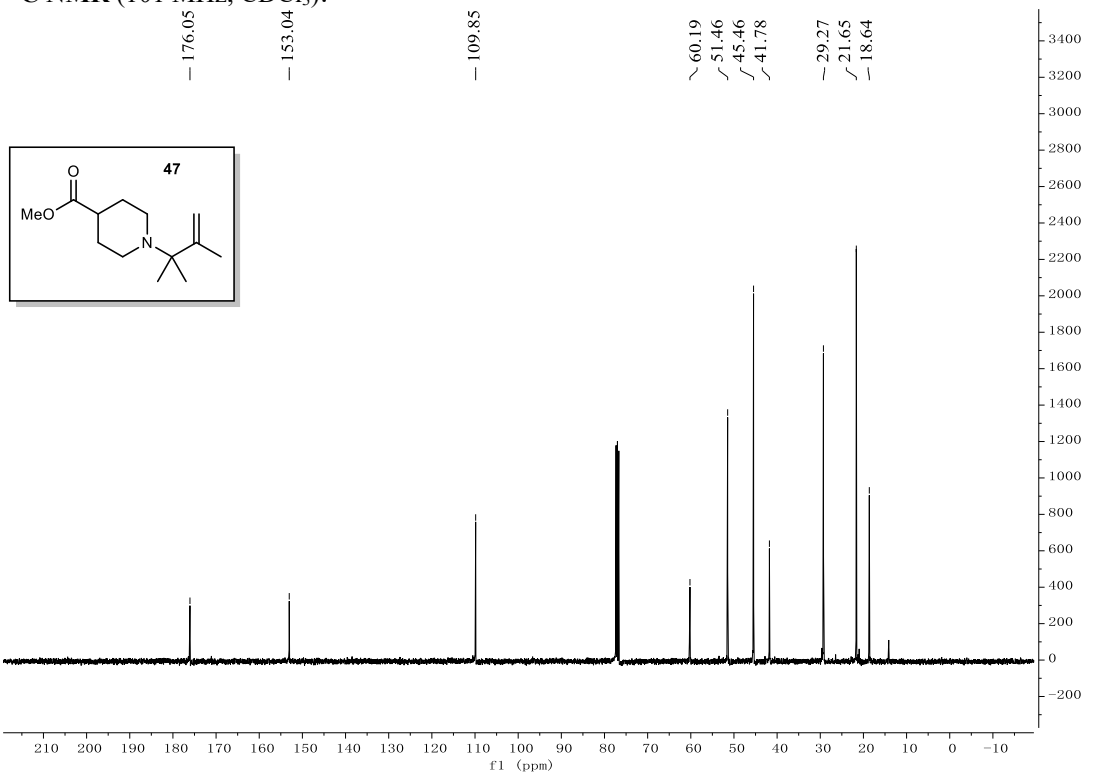

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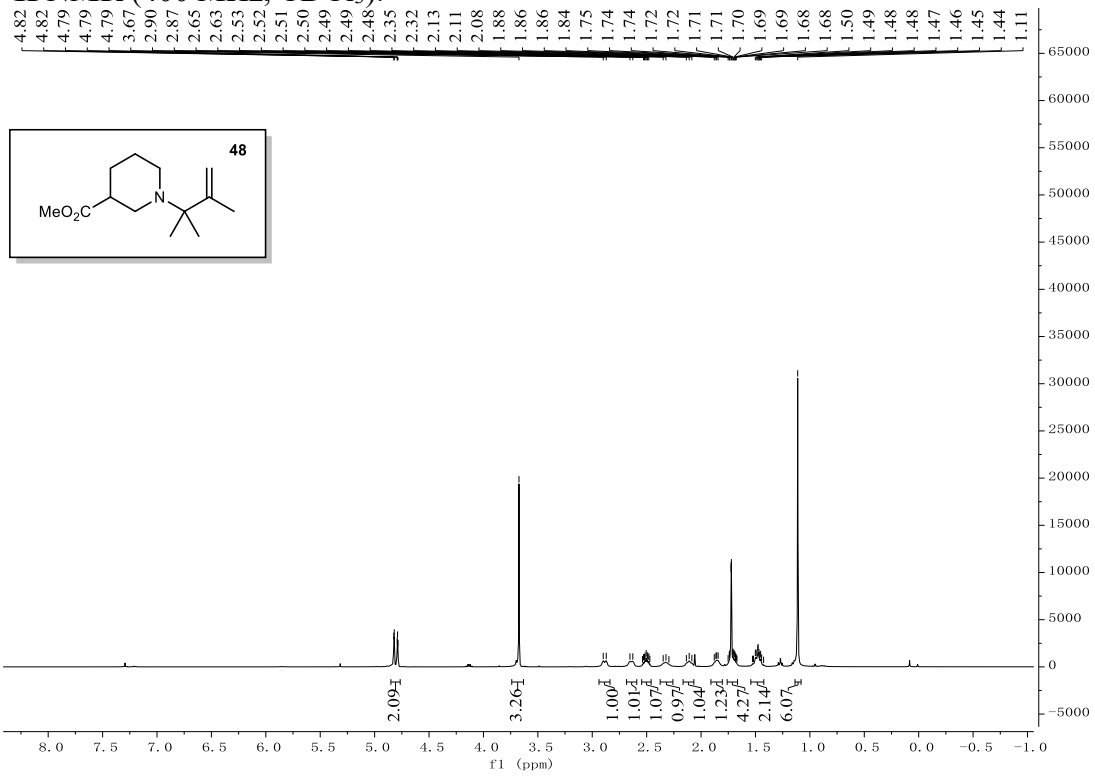

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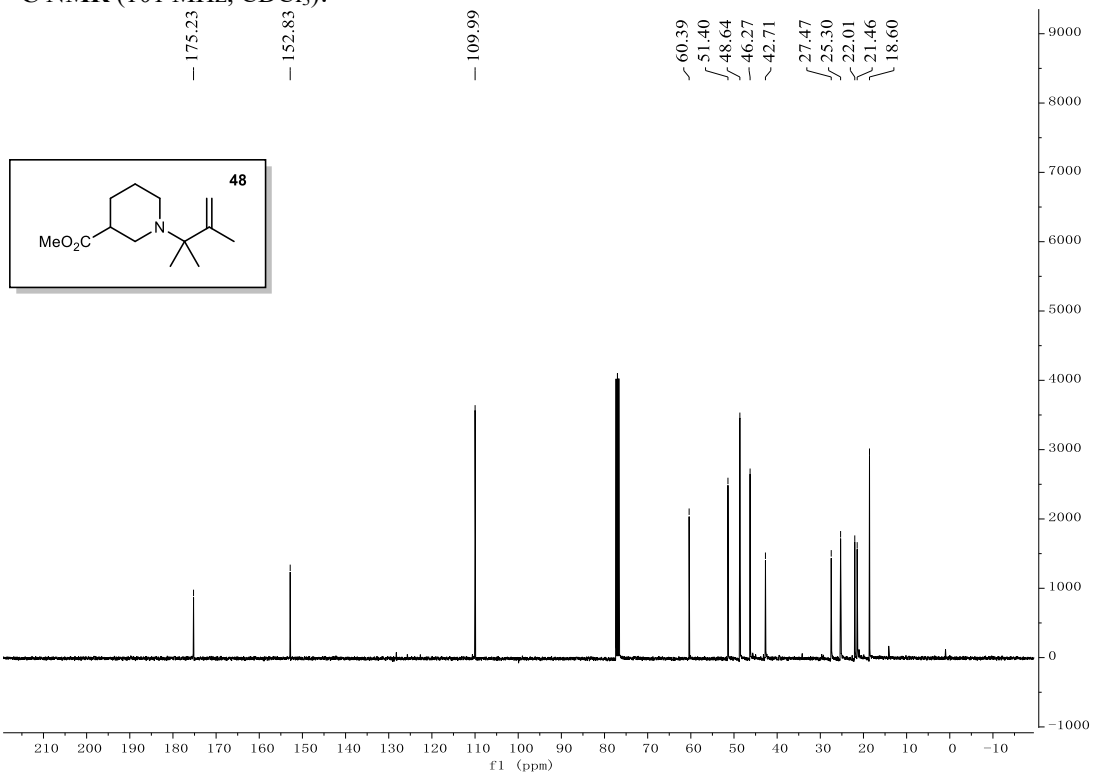

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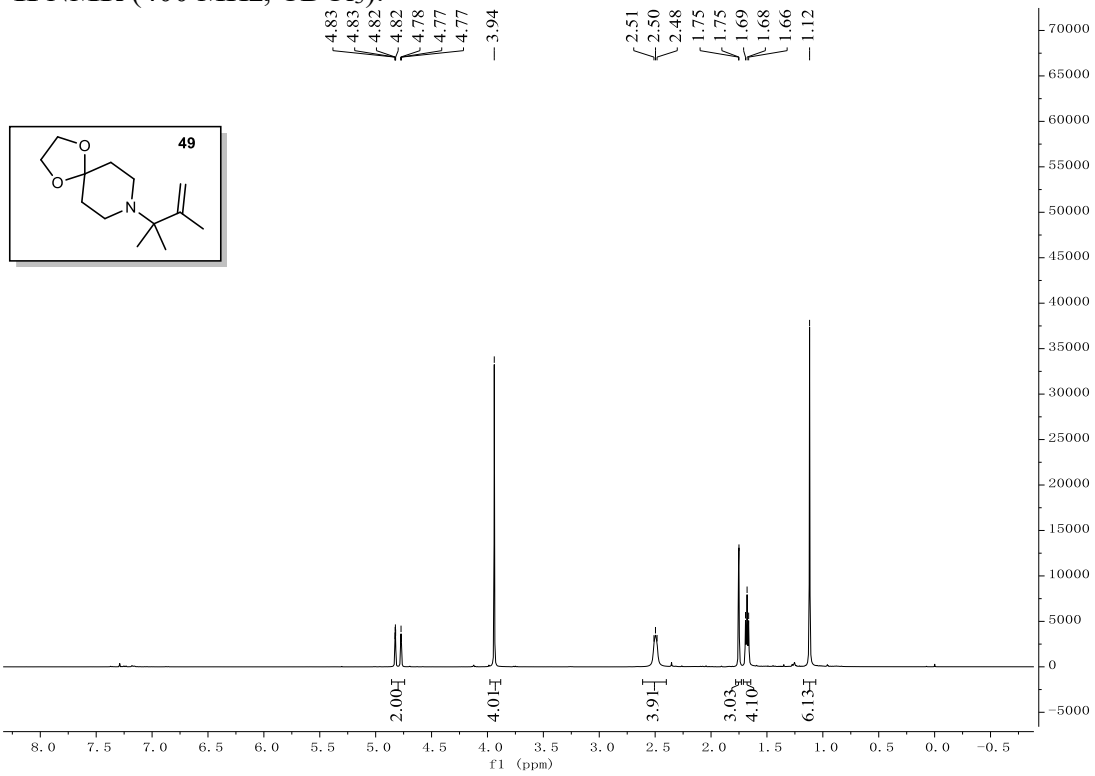

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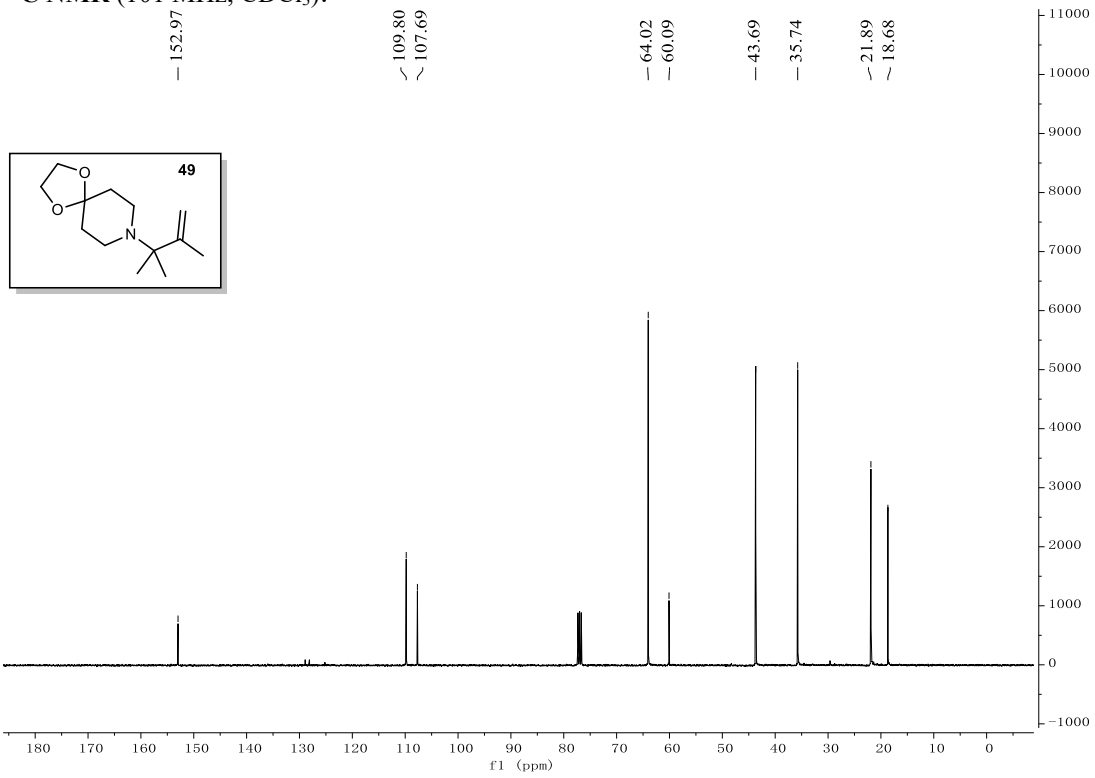

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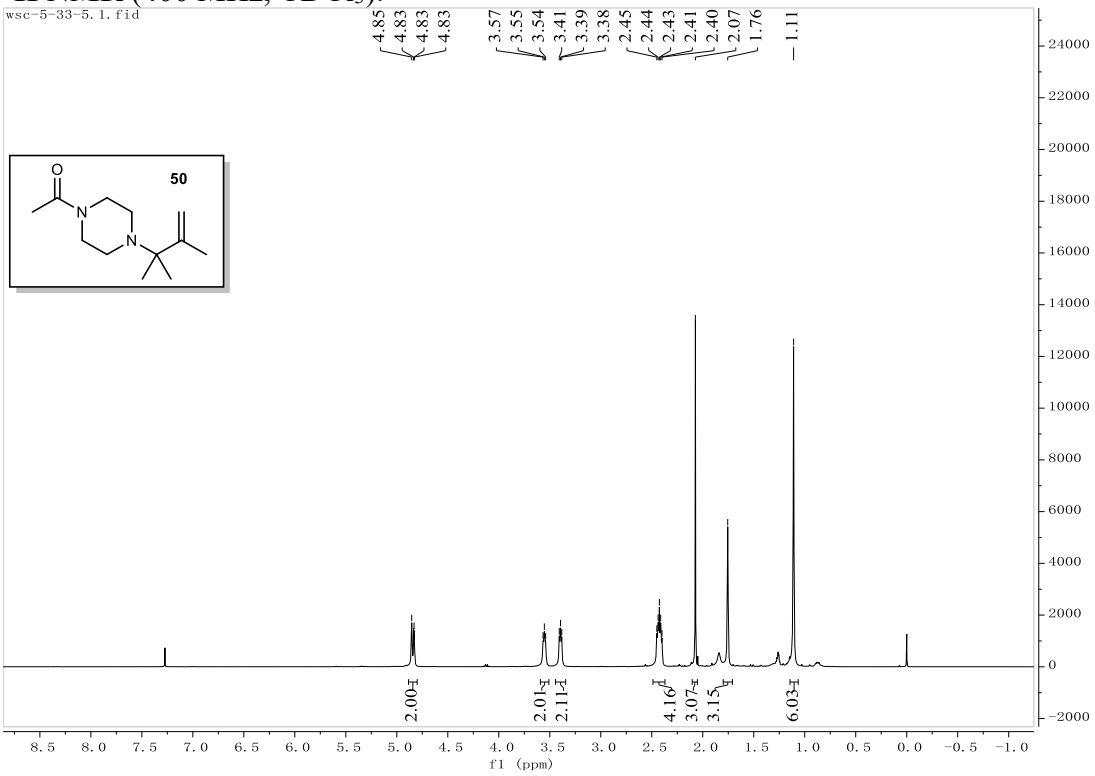

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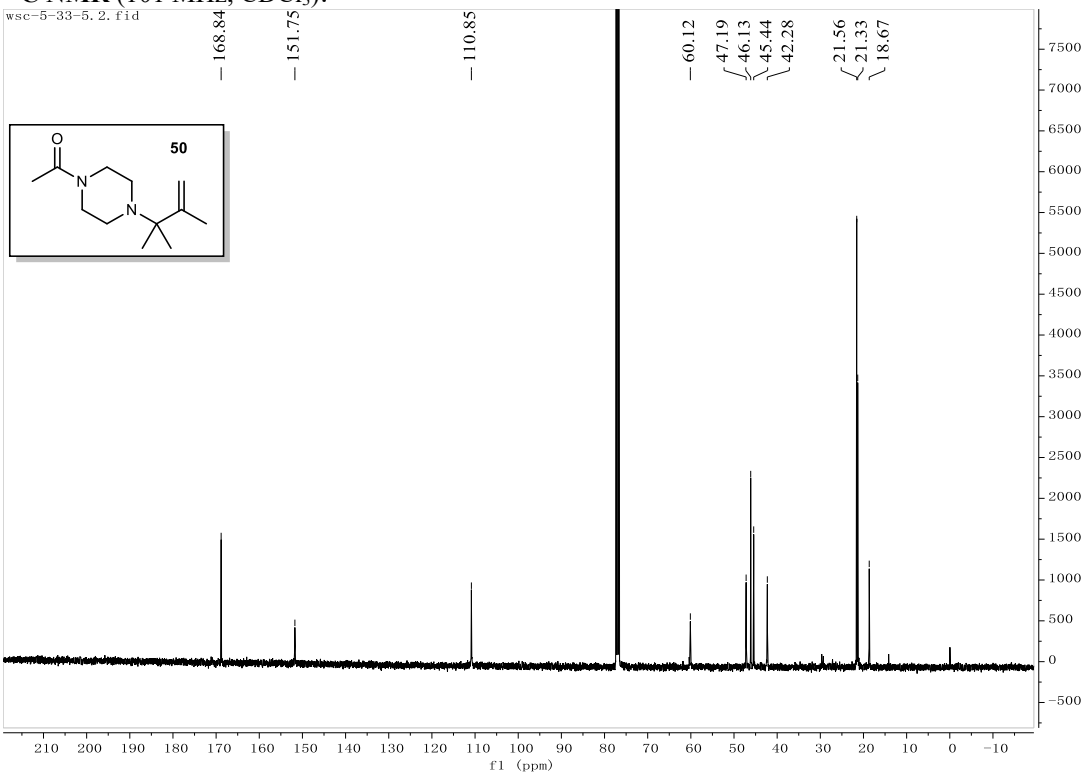

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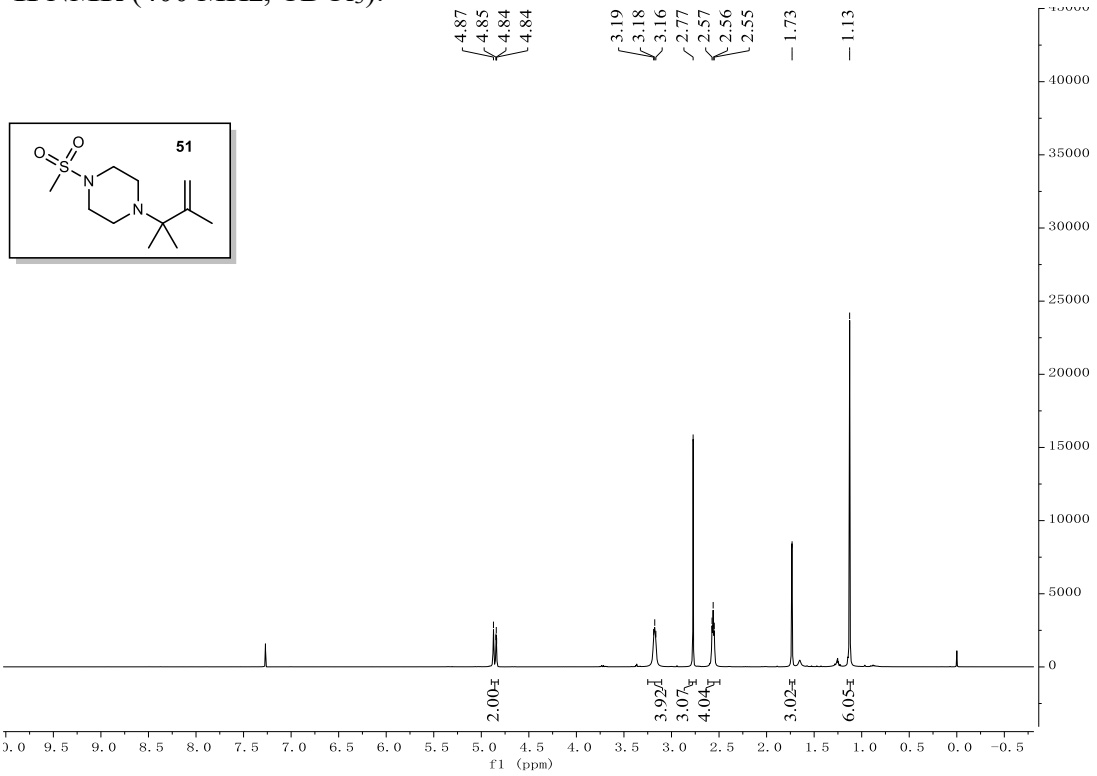

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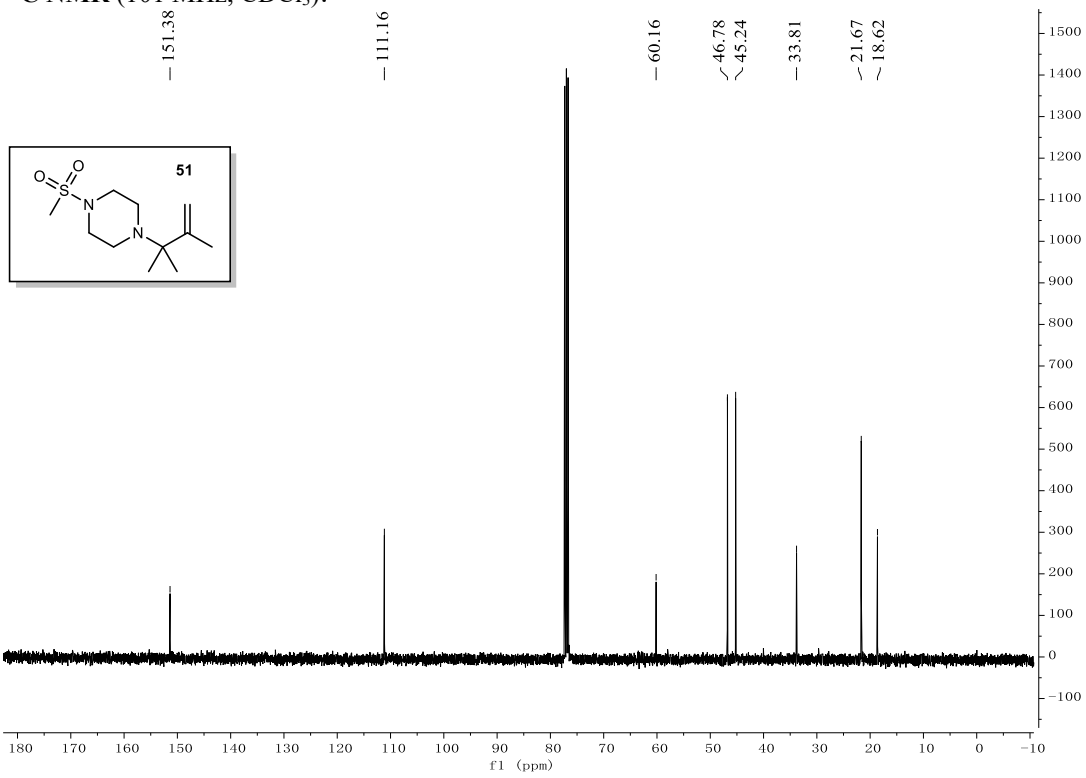

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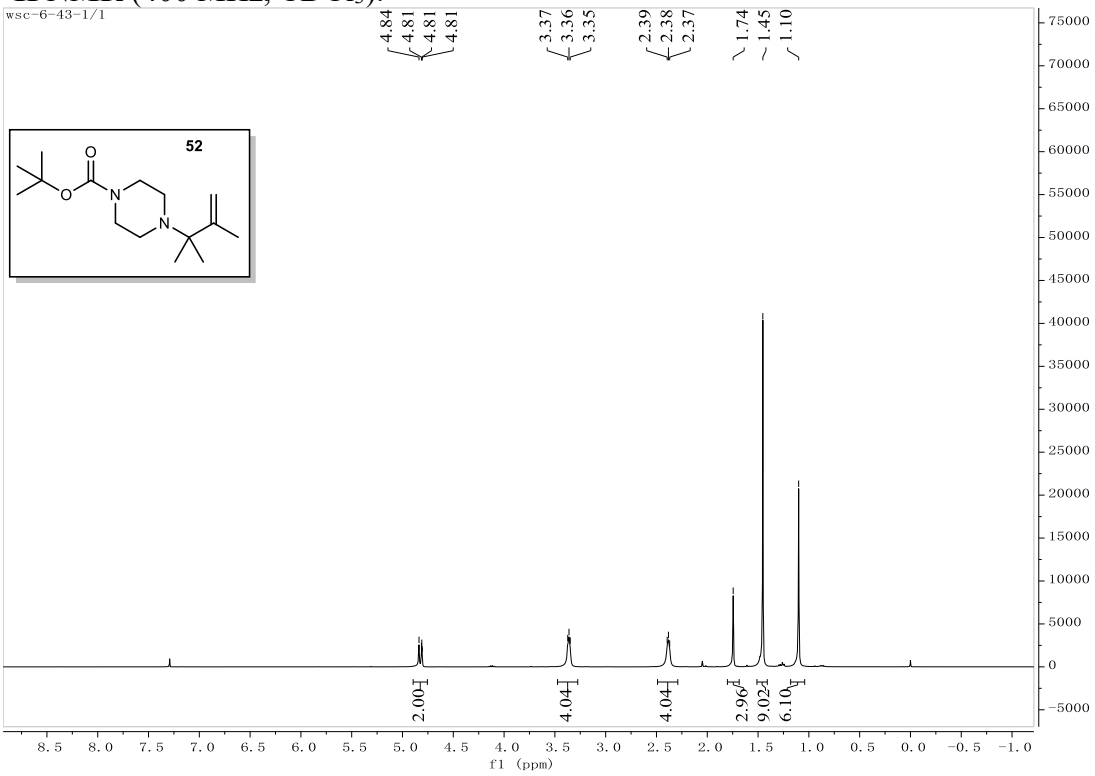

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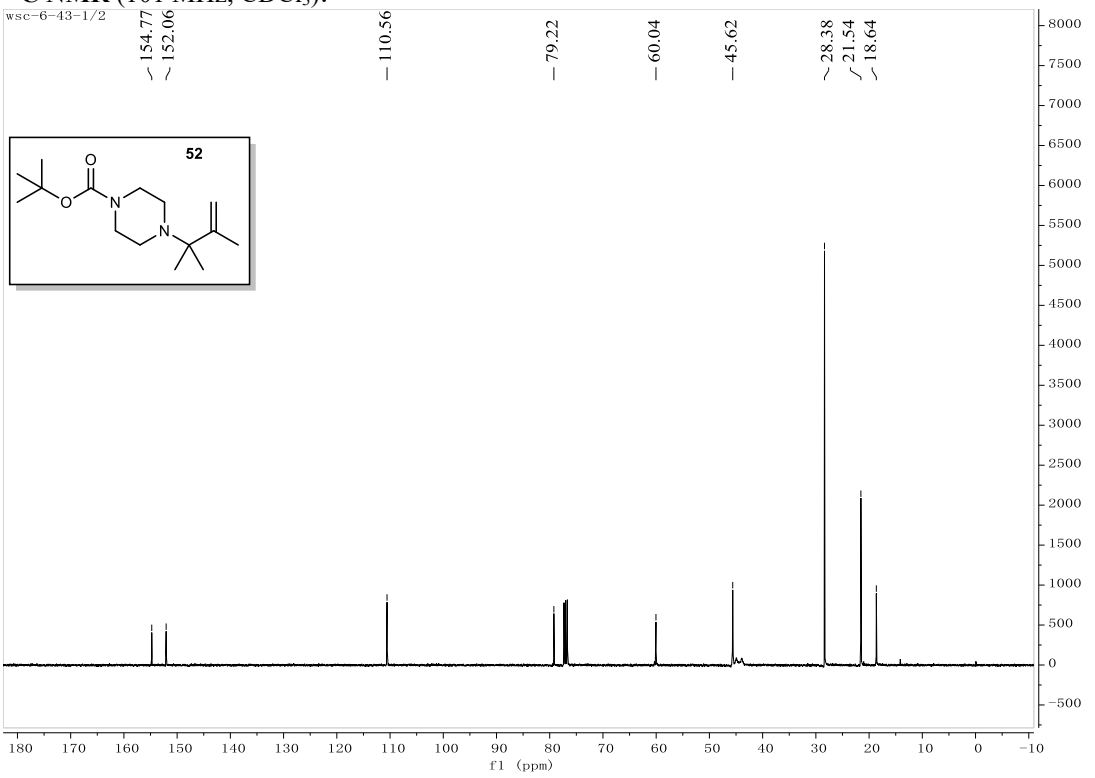

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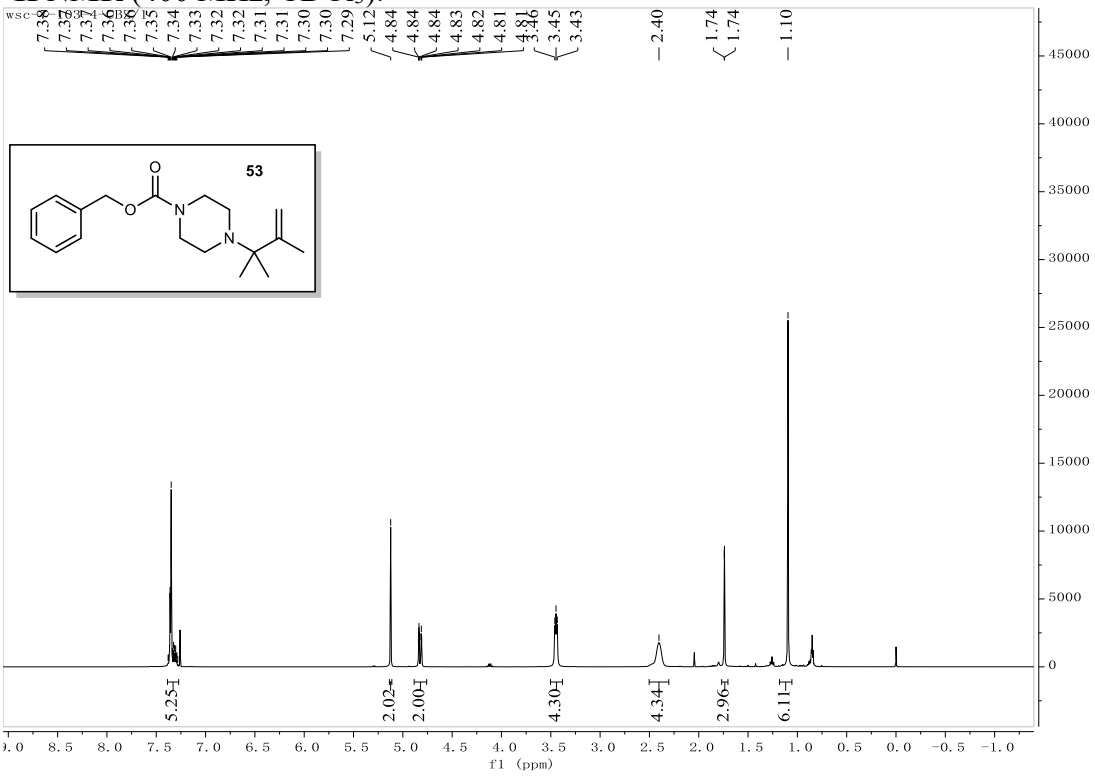

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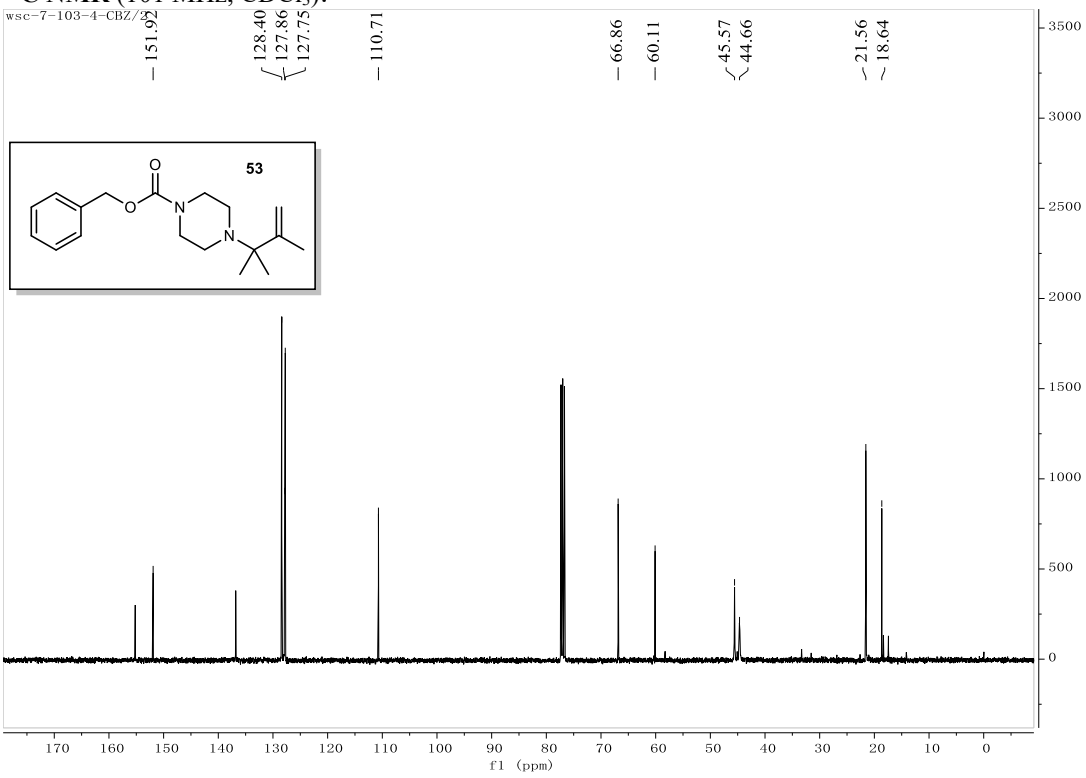

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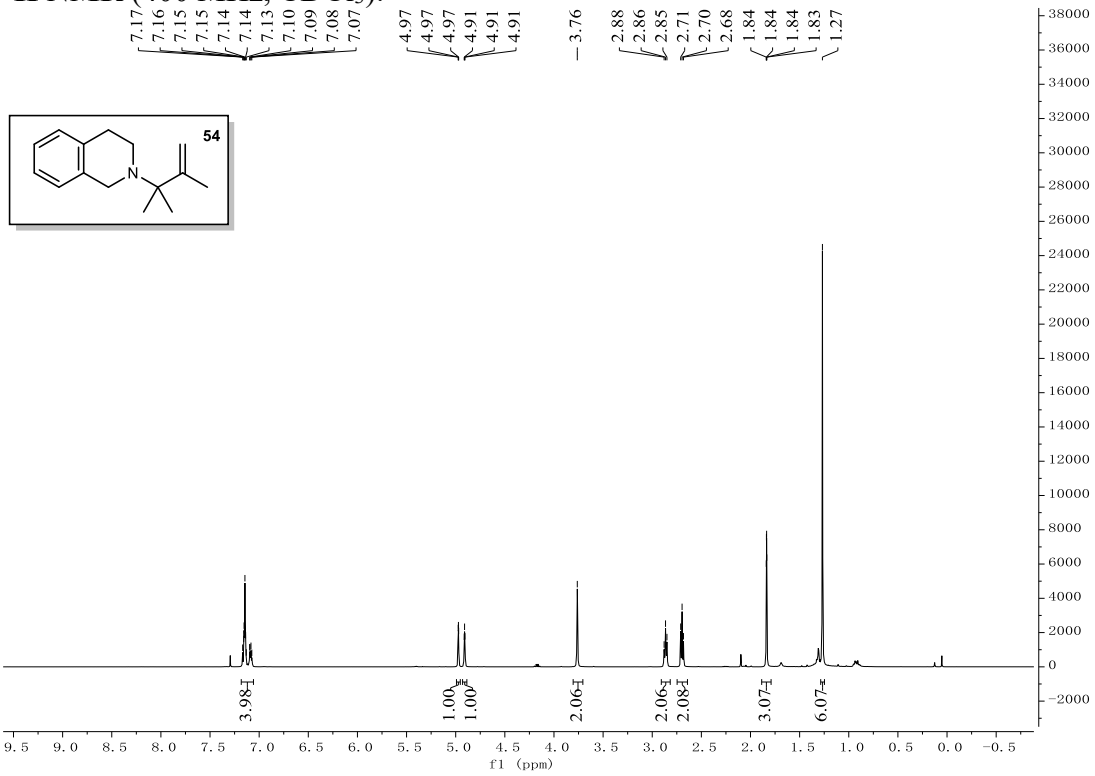

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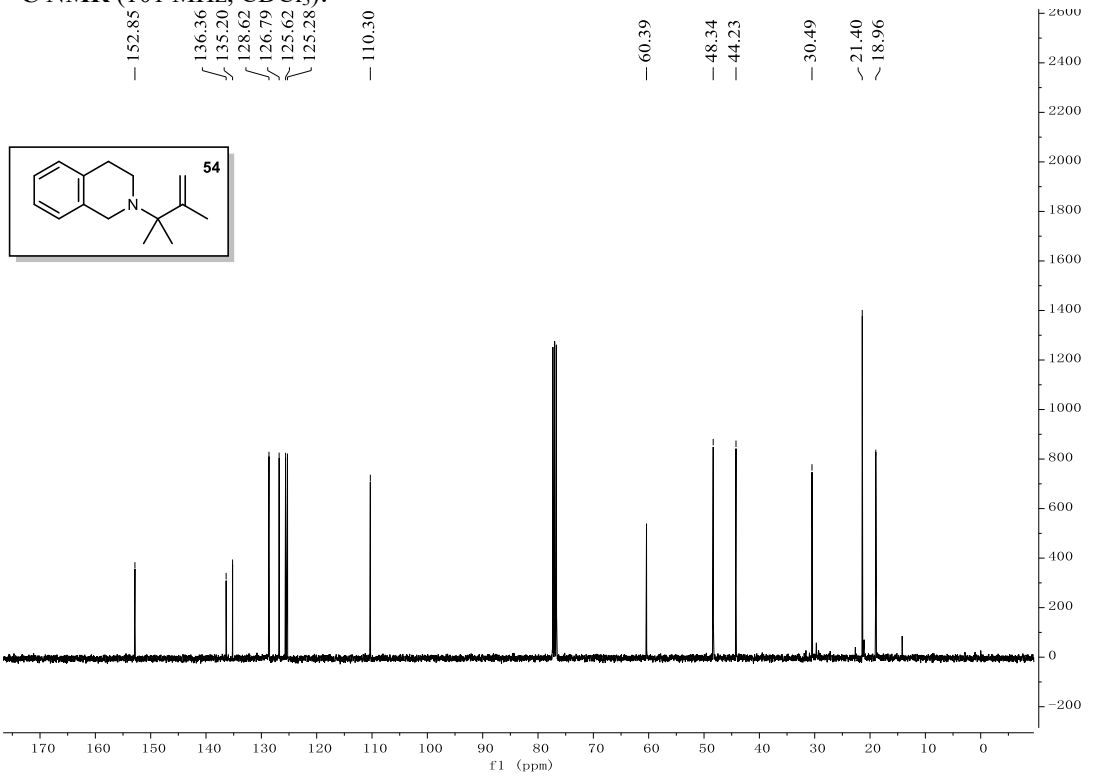

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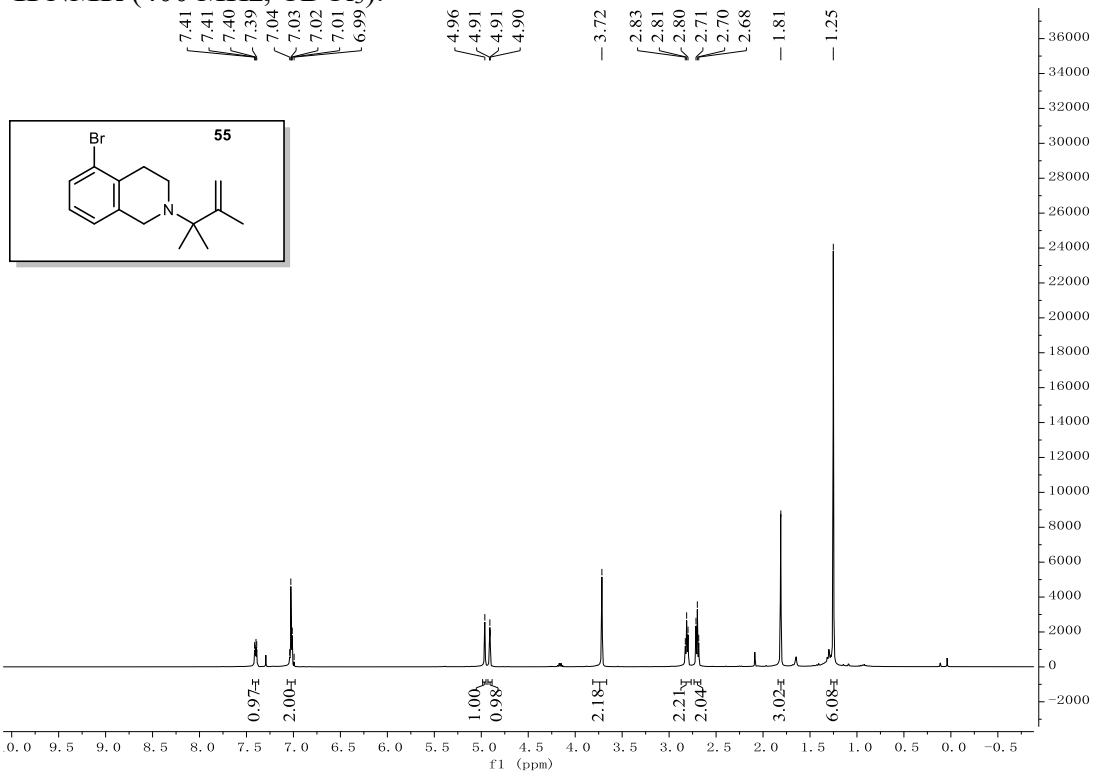

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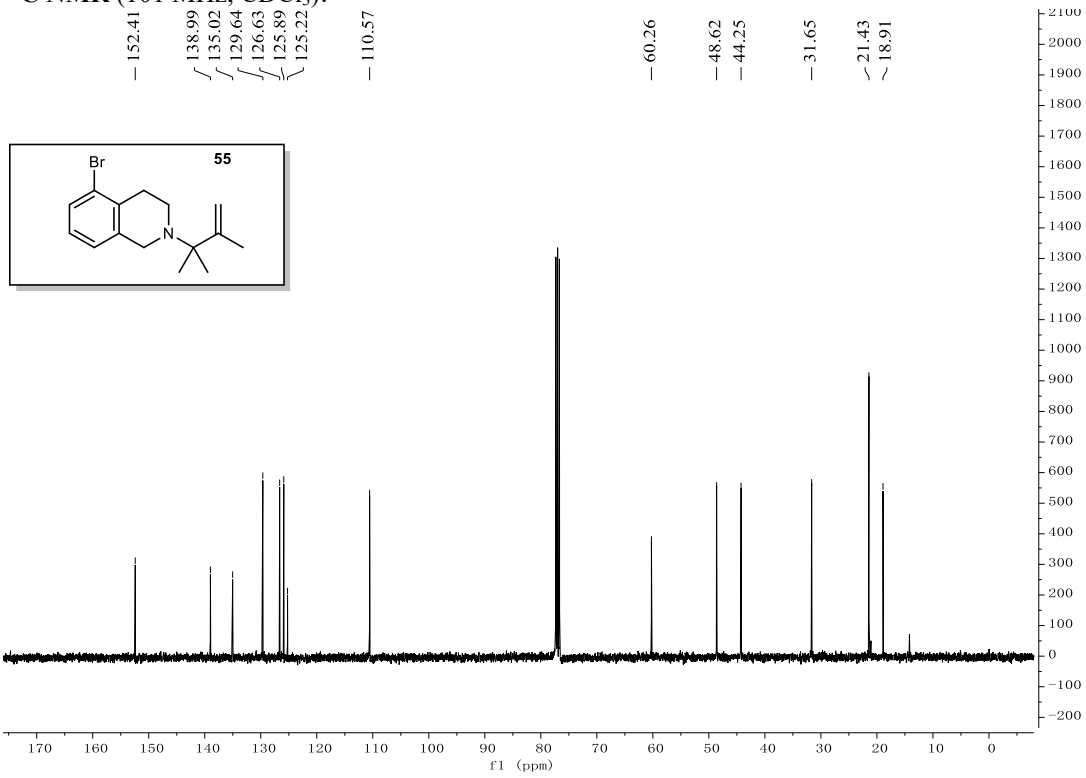

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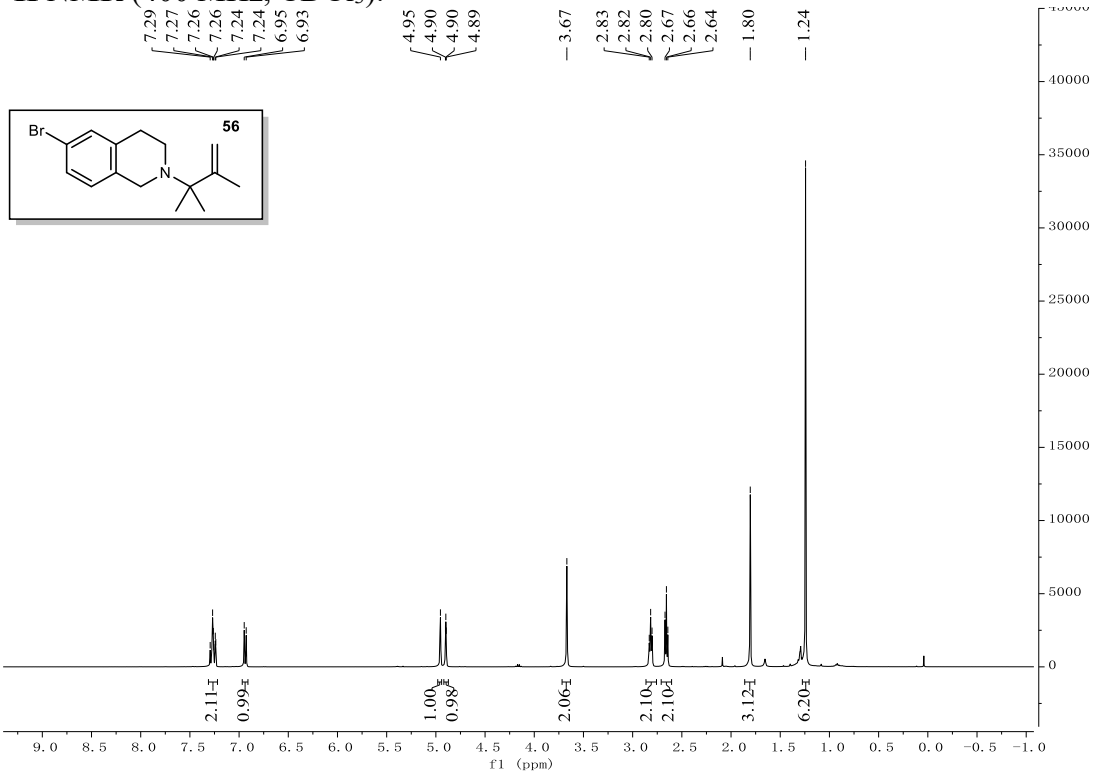

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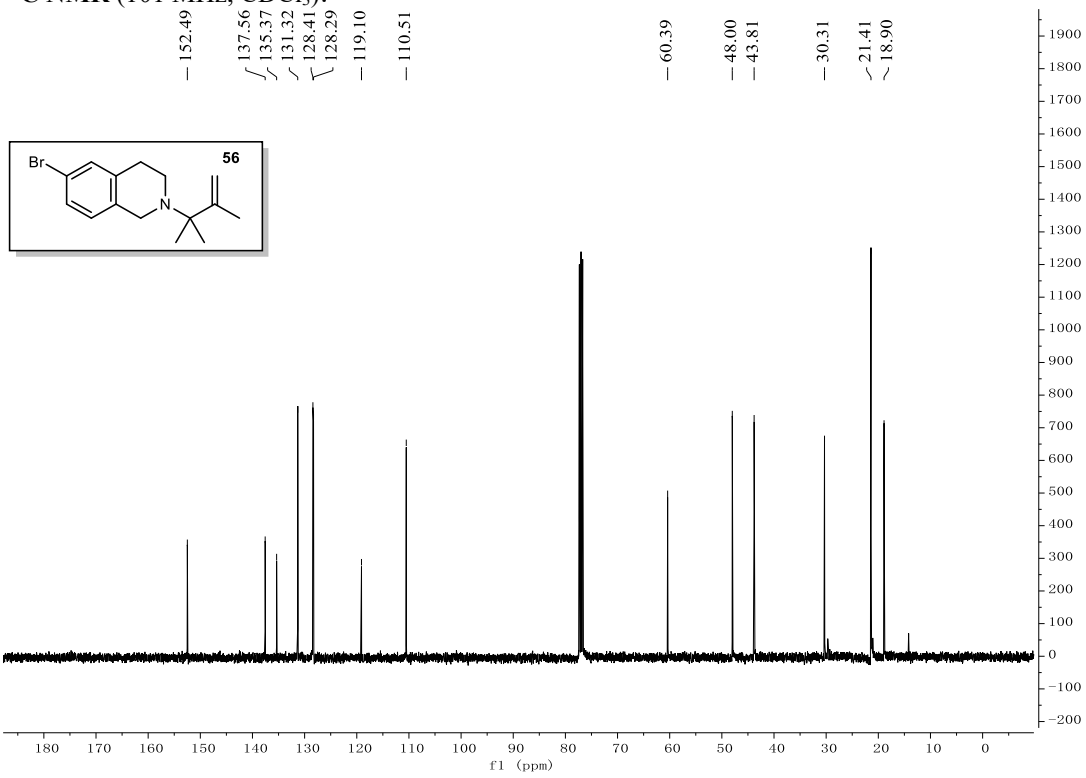

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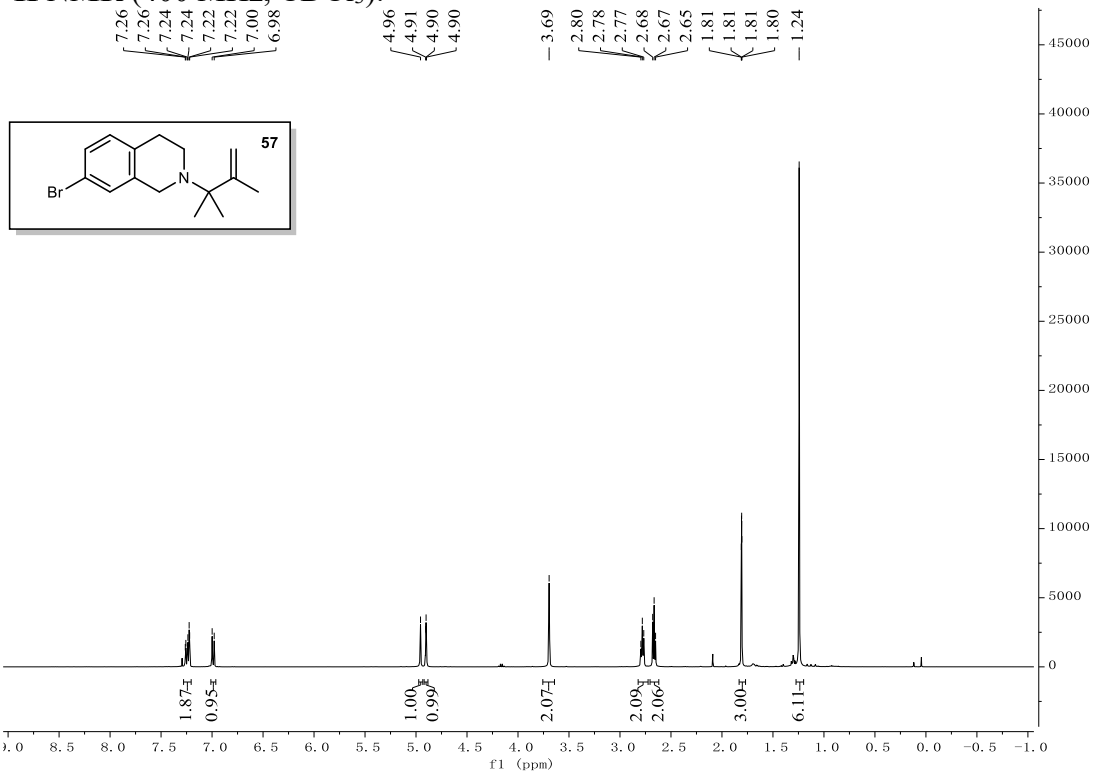

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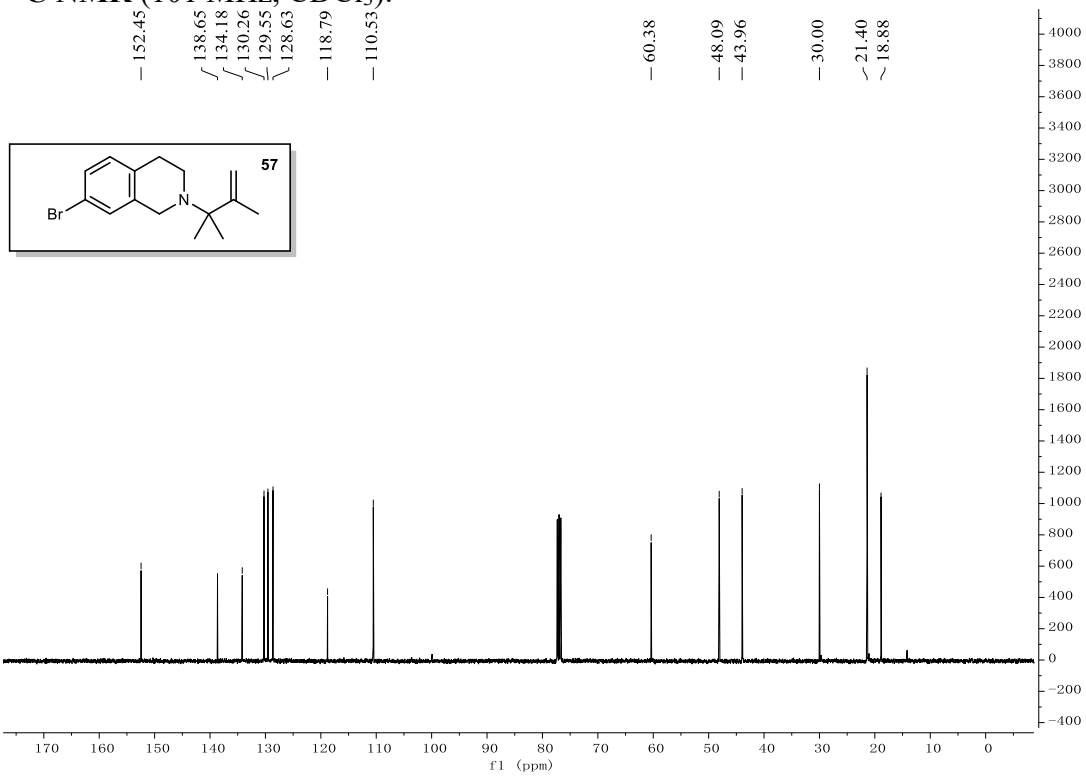

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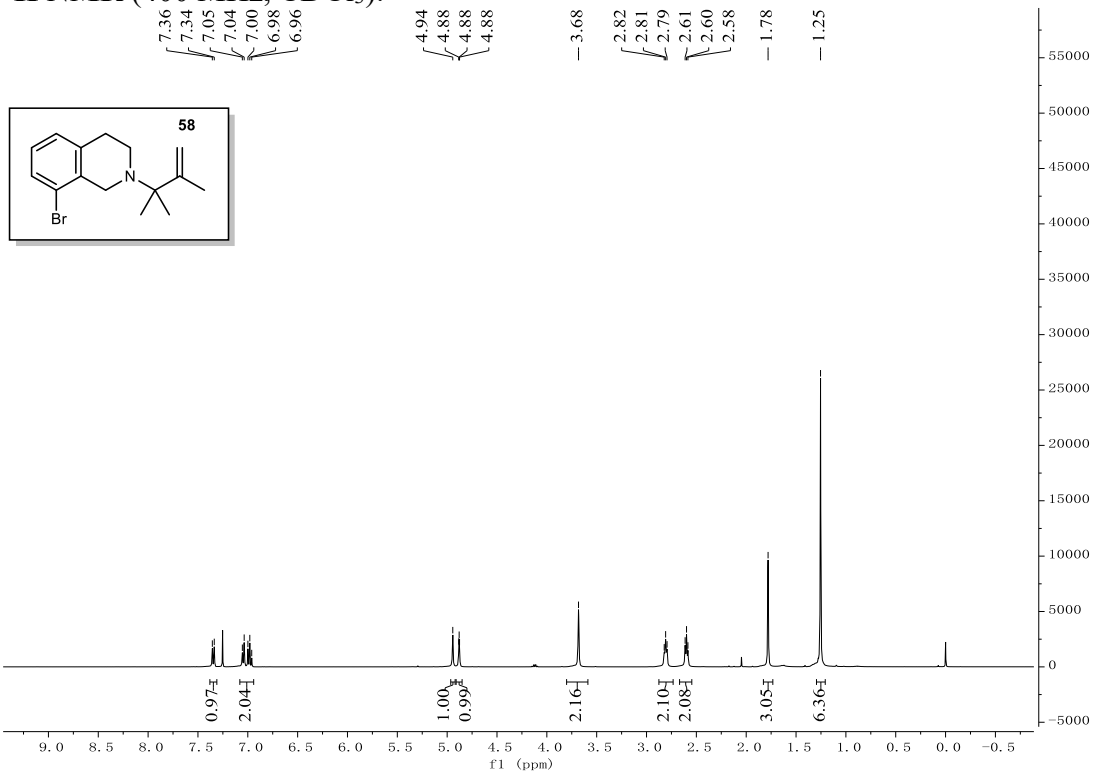

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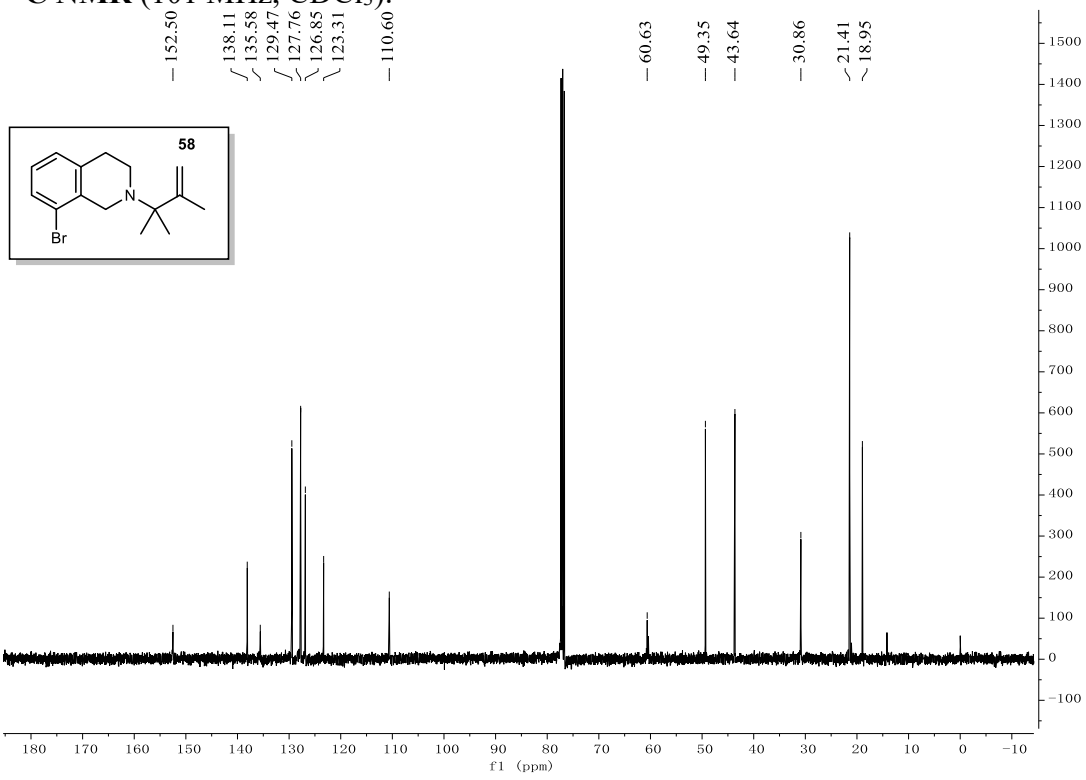

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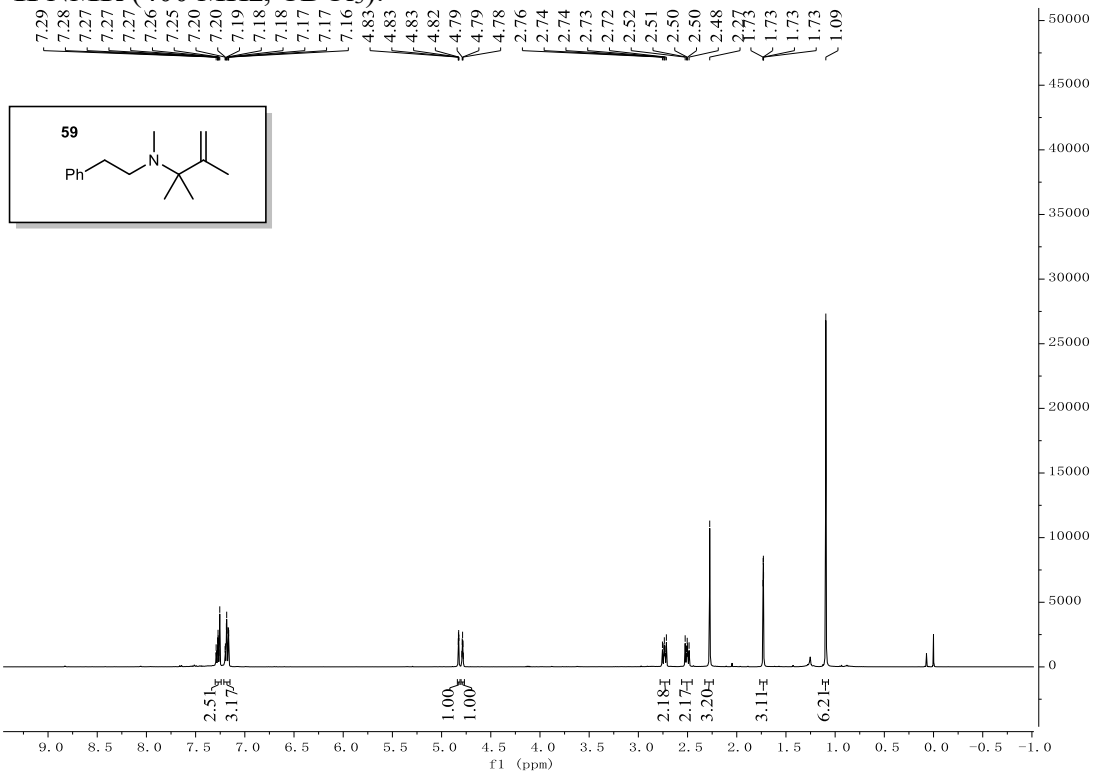

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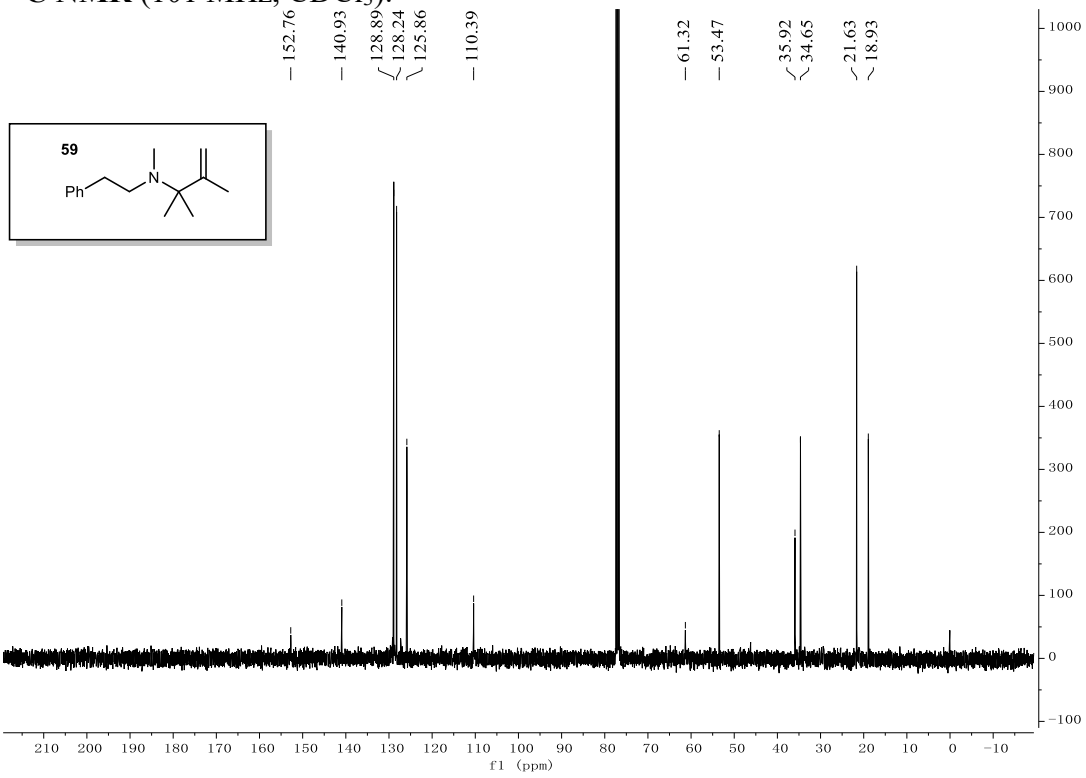

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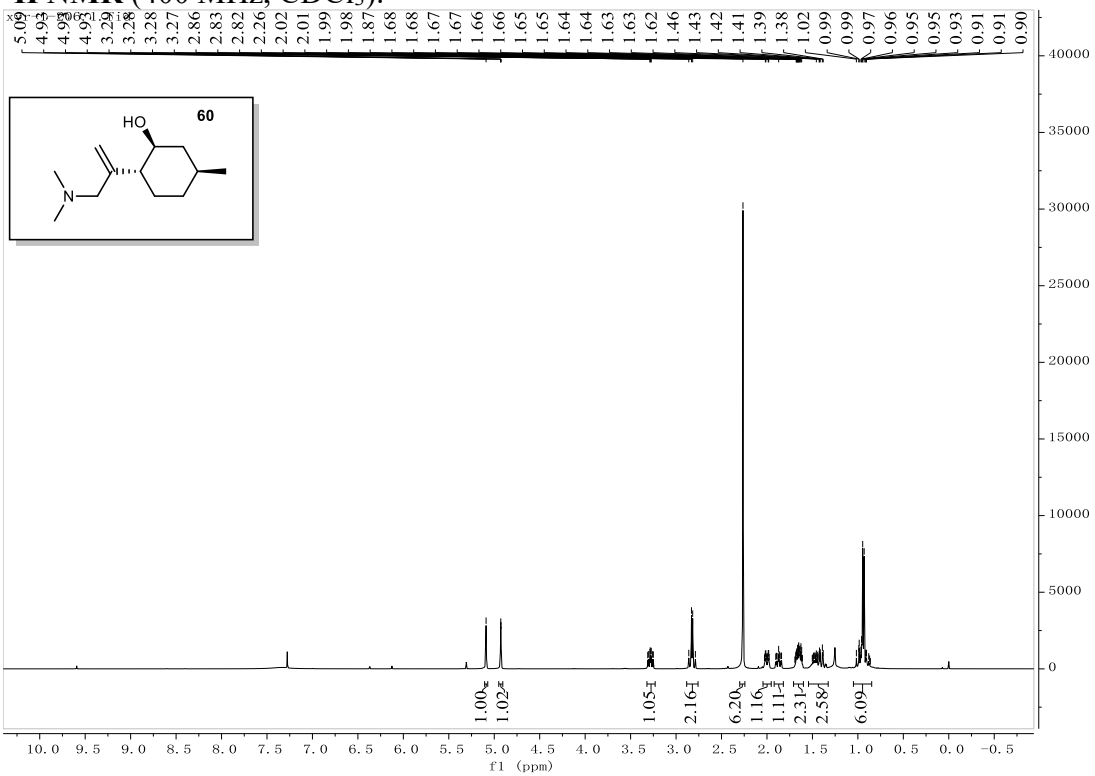

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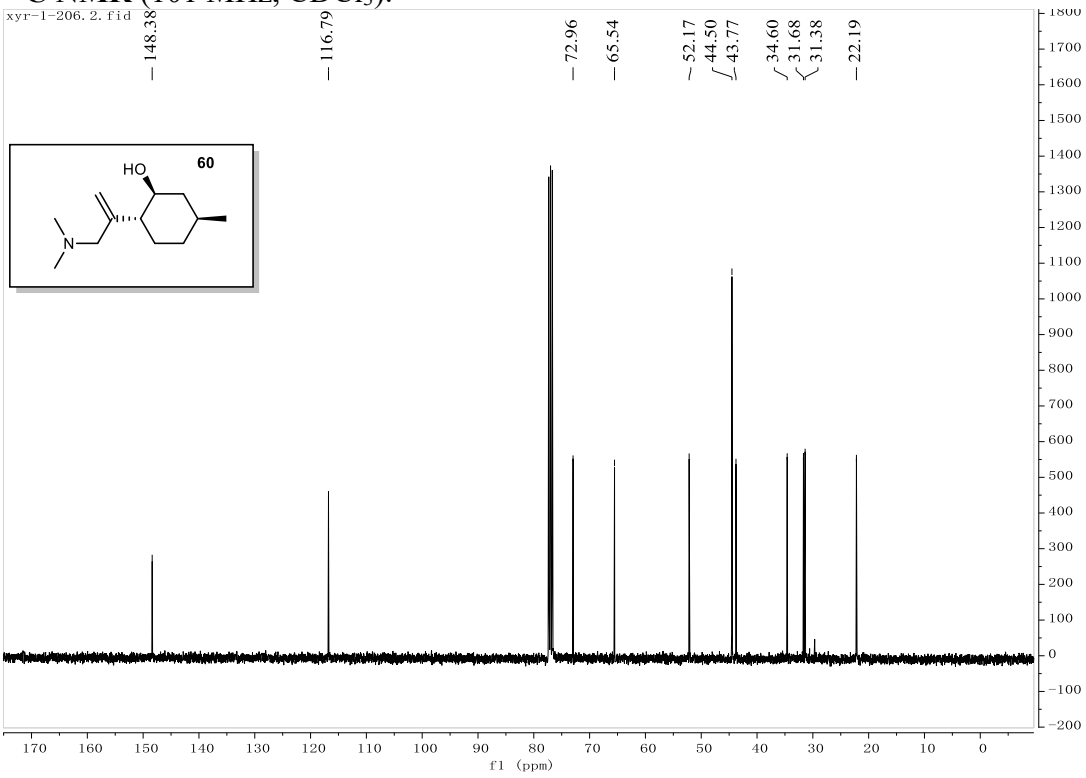

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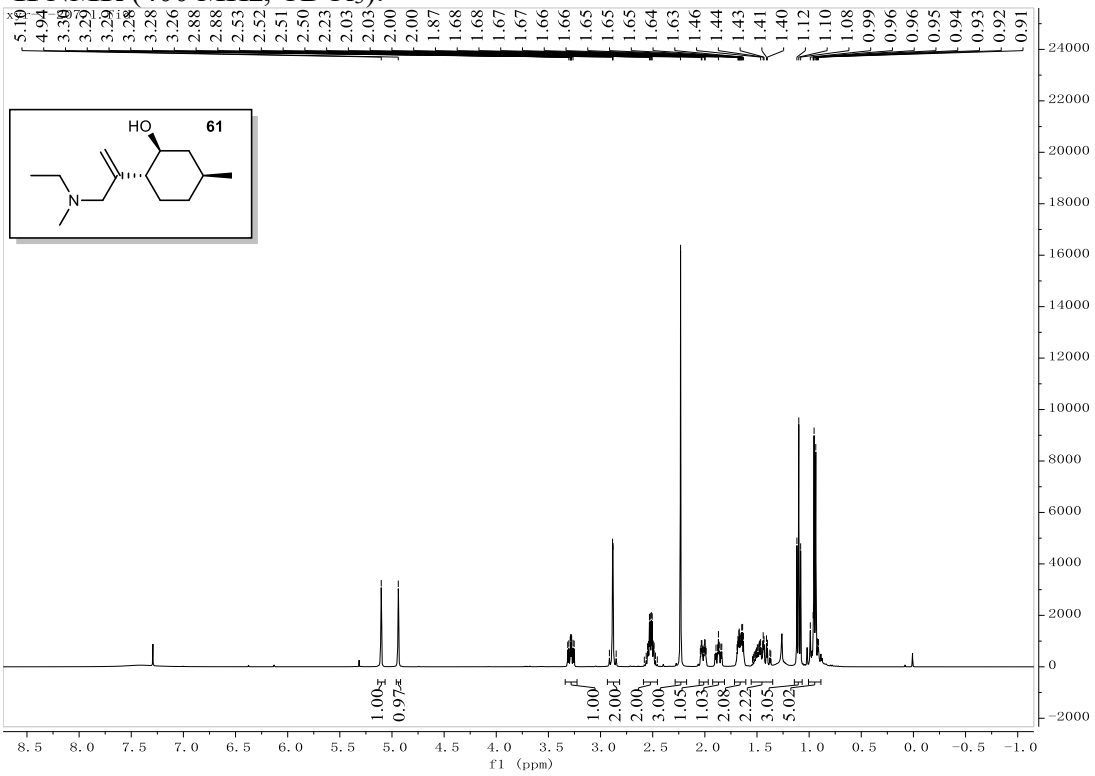

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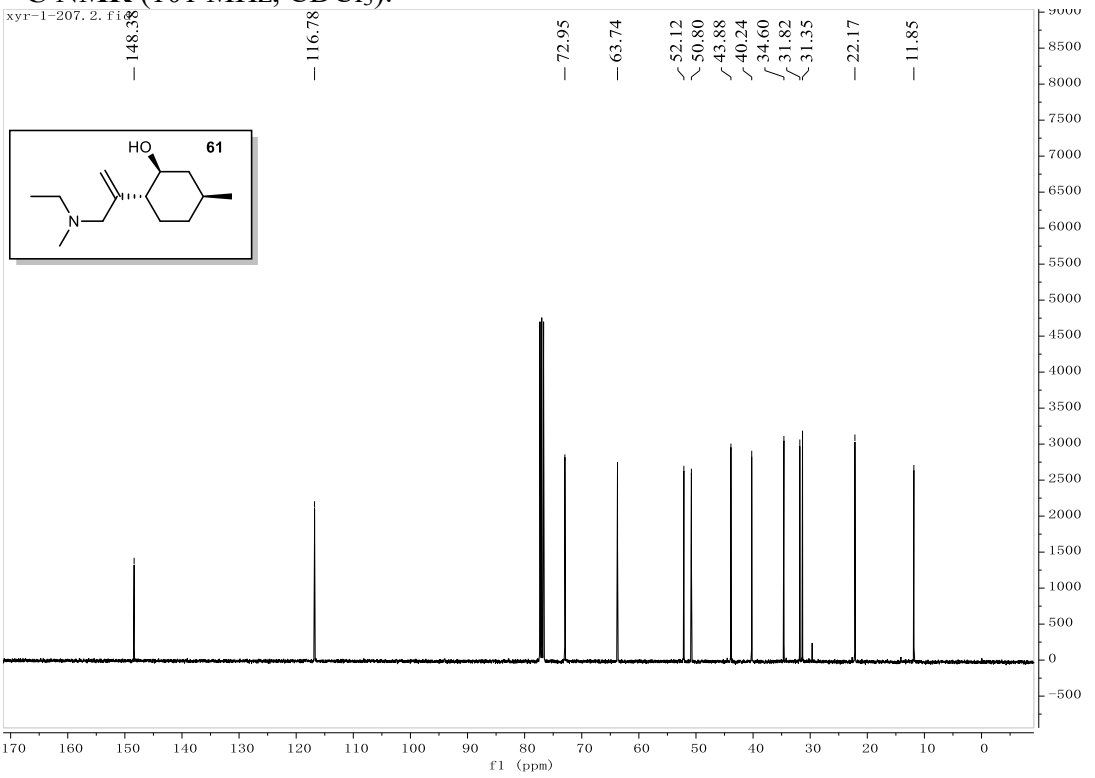

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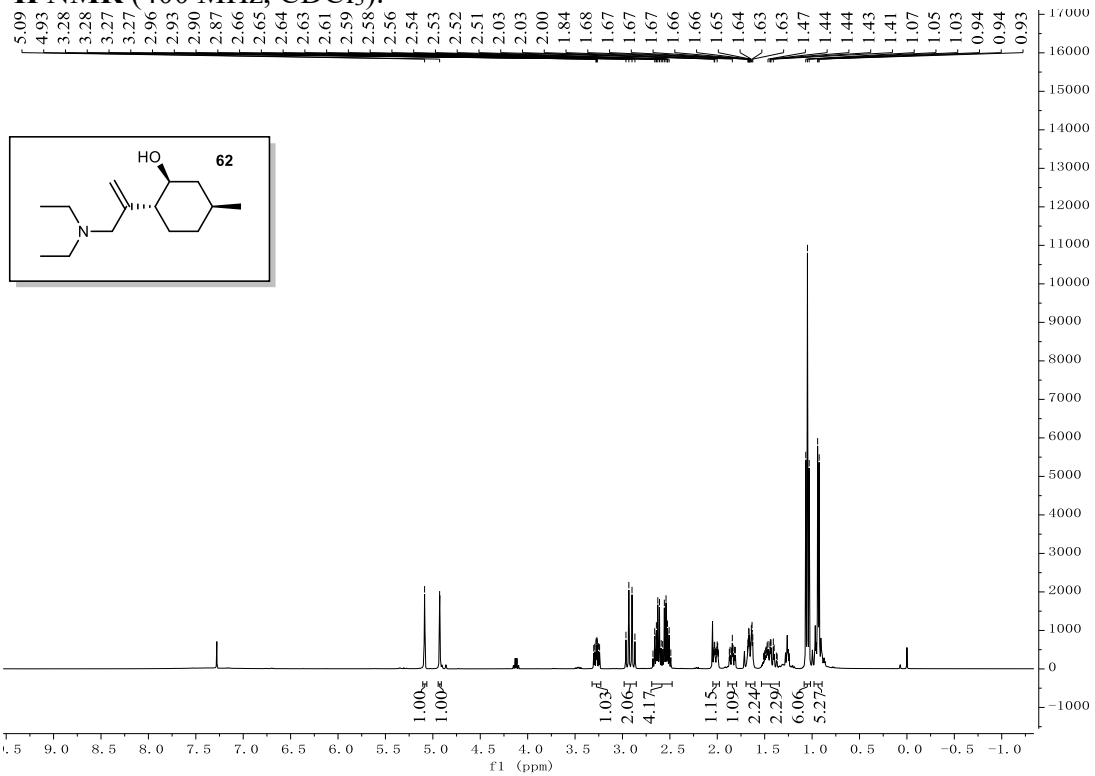

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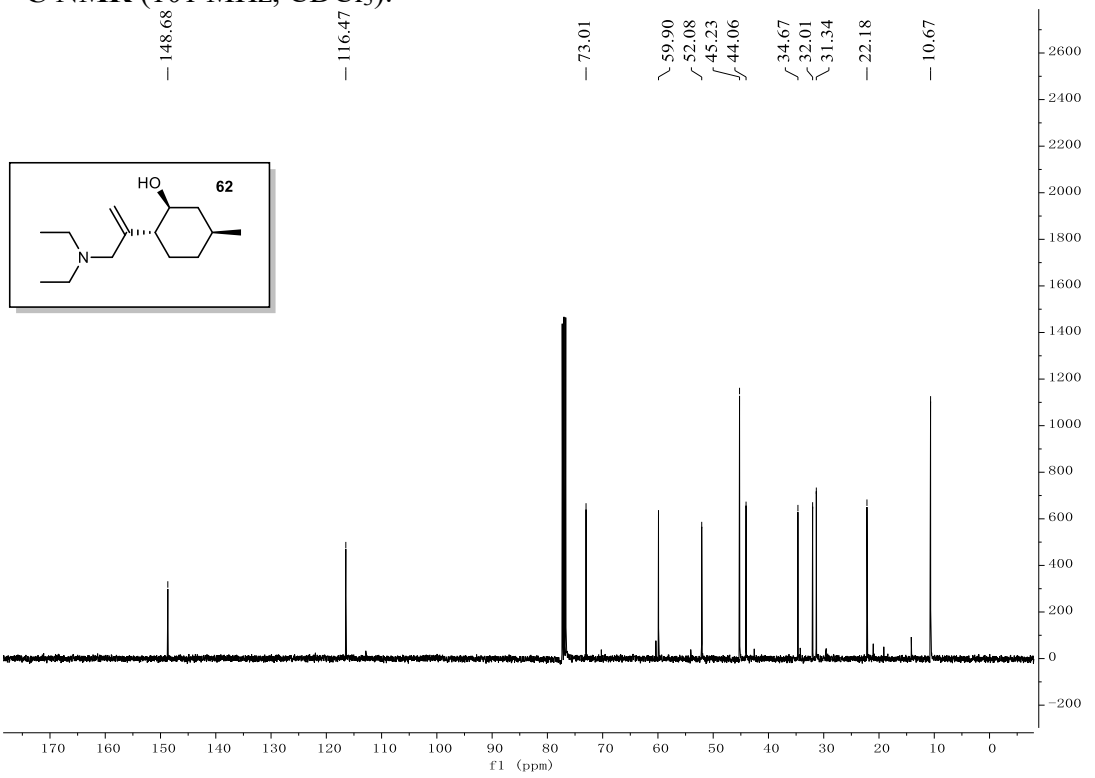

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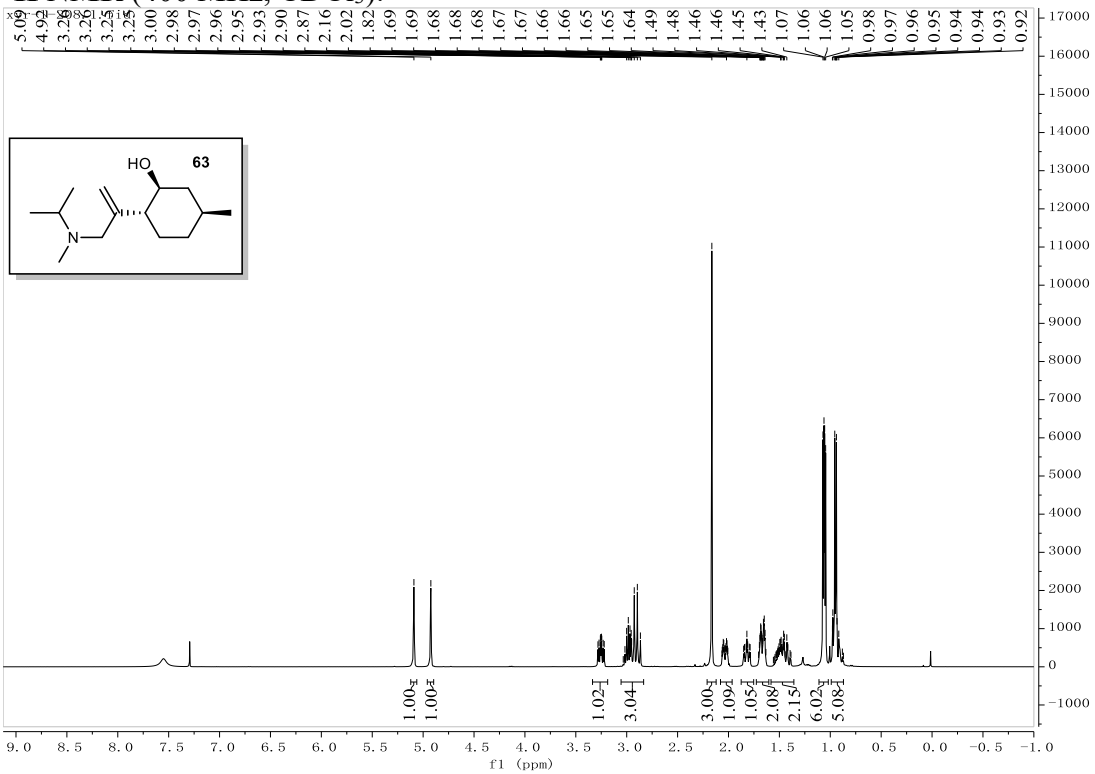

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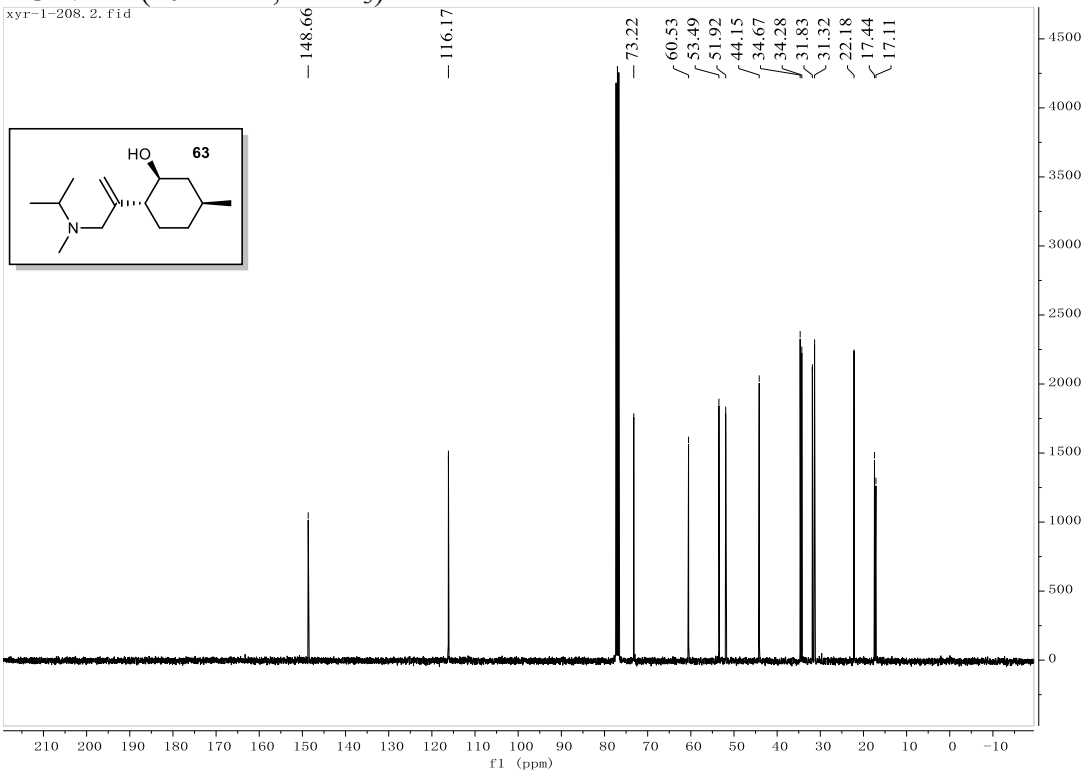
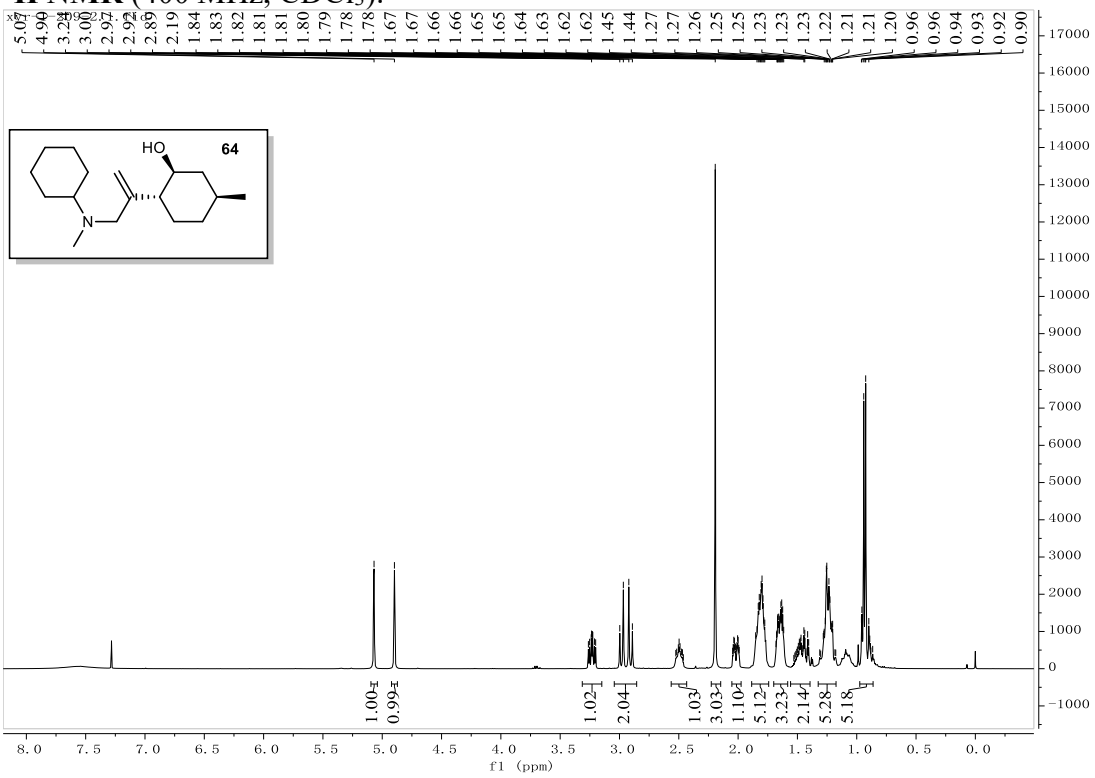
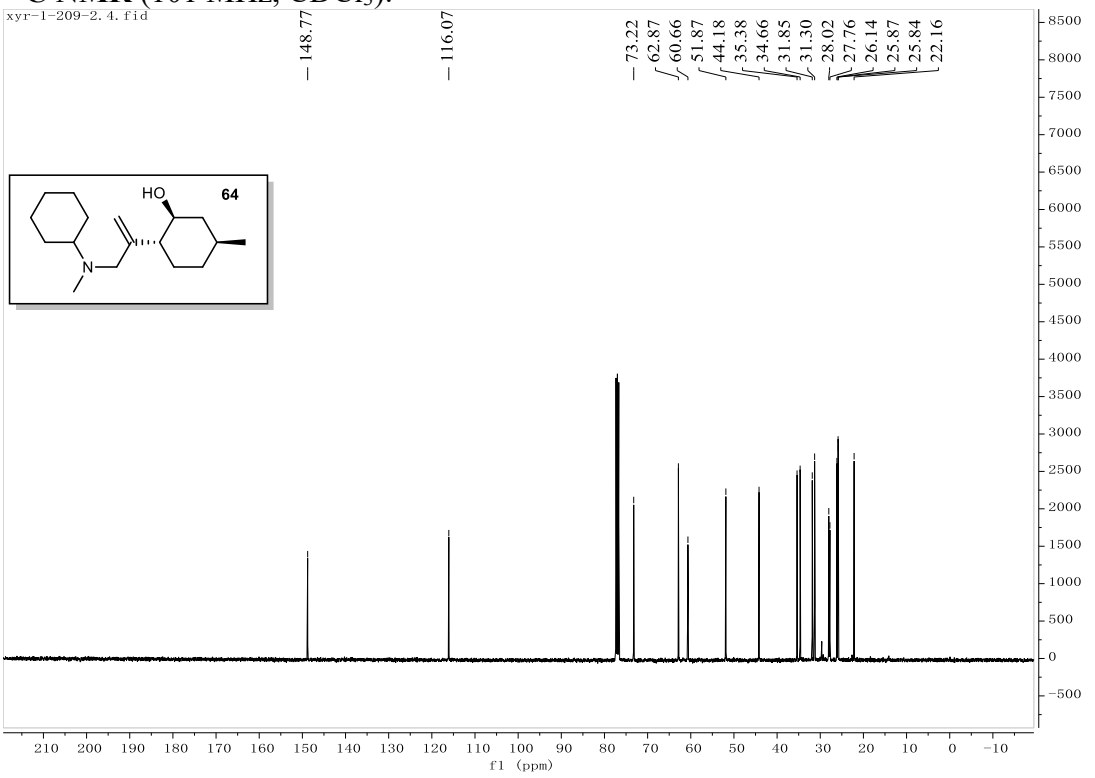


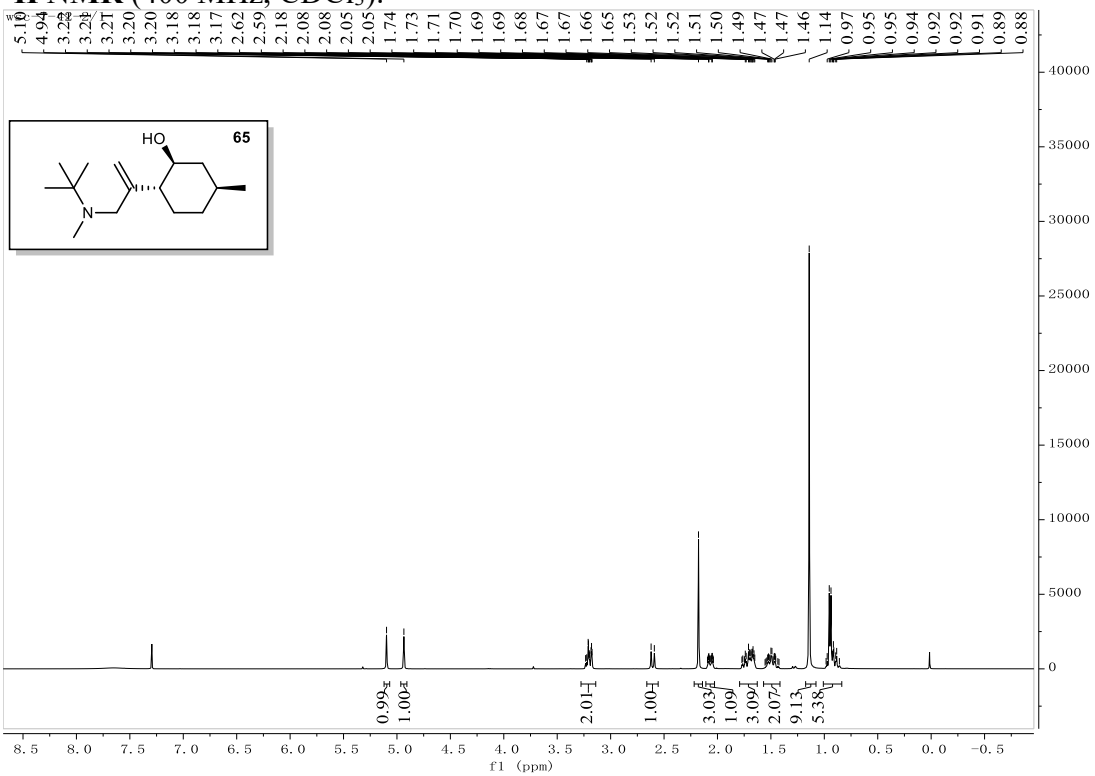
^{1}H NMR (400 MHz, $CDCl_3$):



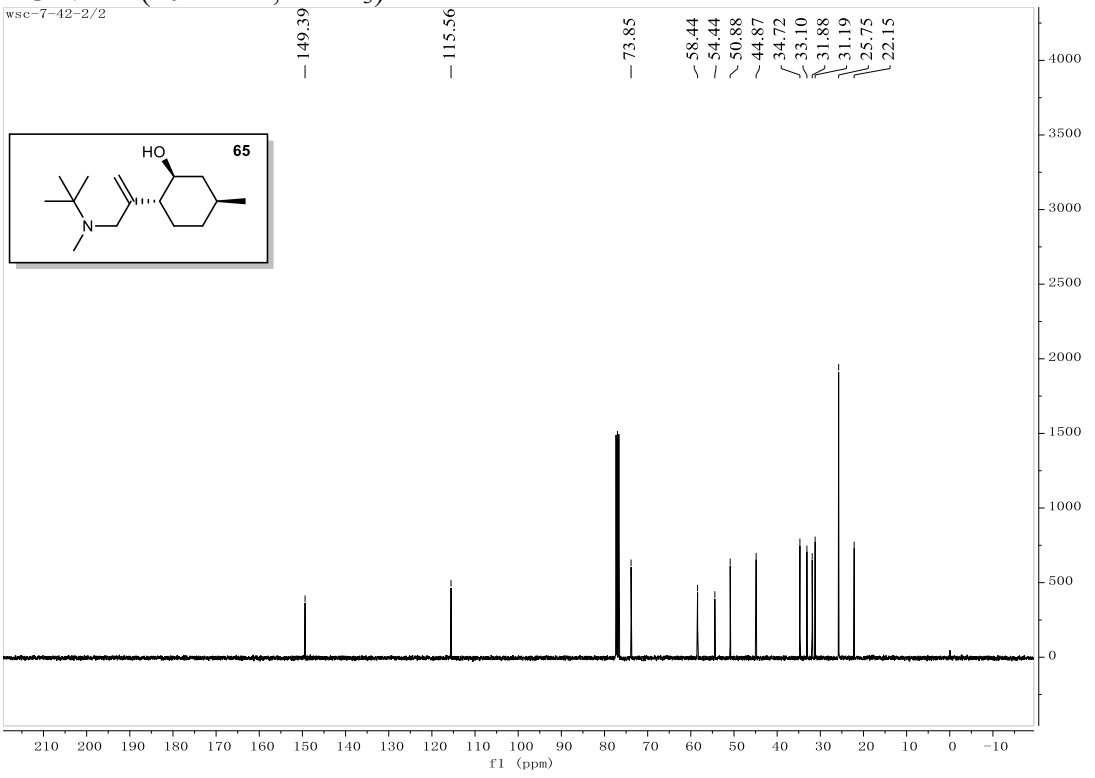
^{13}C NMR (101 MHz, $CDCl_3$):



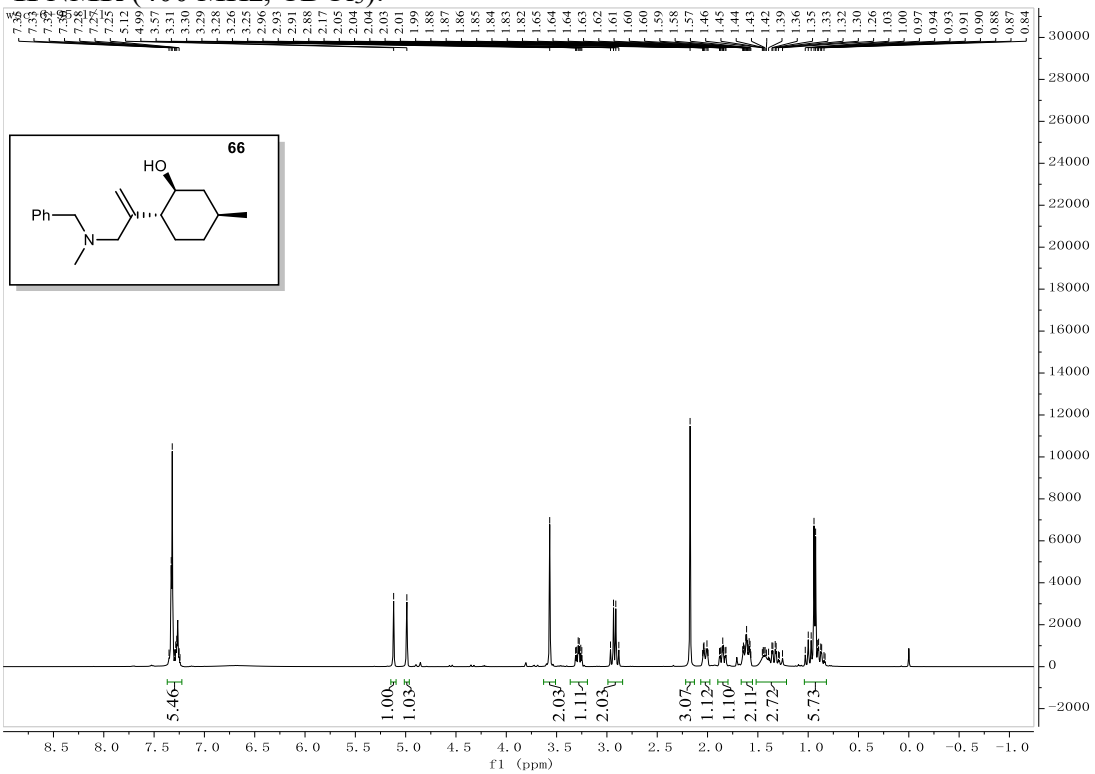
^{1}H NMR (400 MHz, $CDCl_3$):



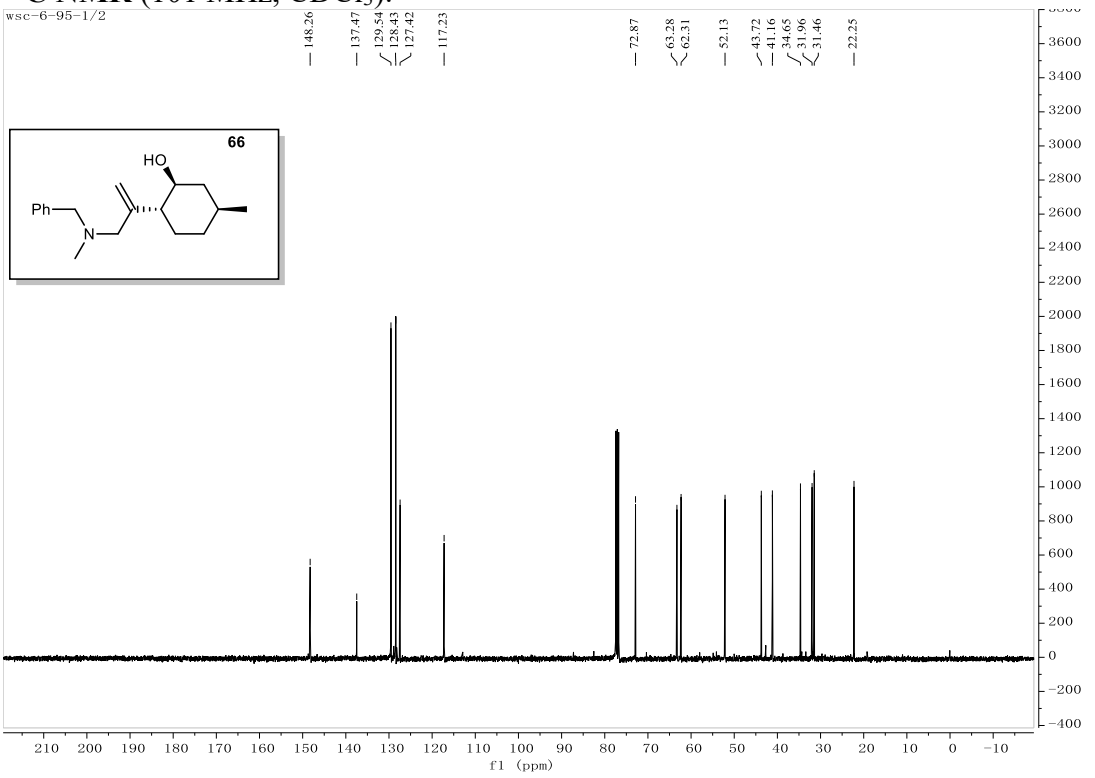
^{13}C NMR (101 MHz, $CDCl_3$):



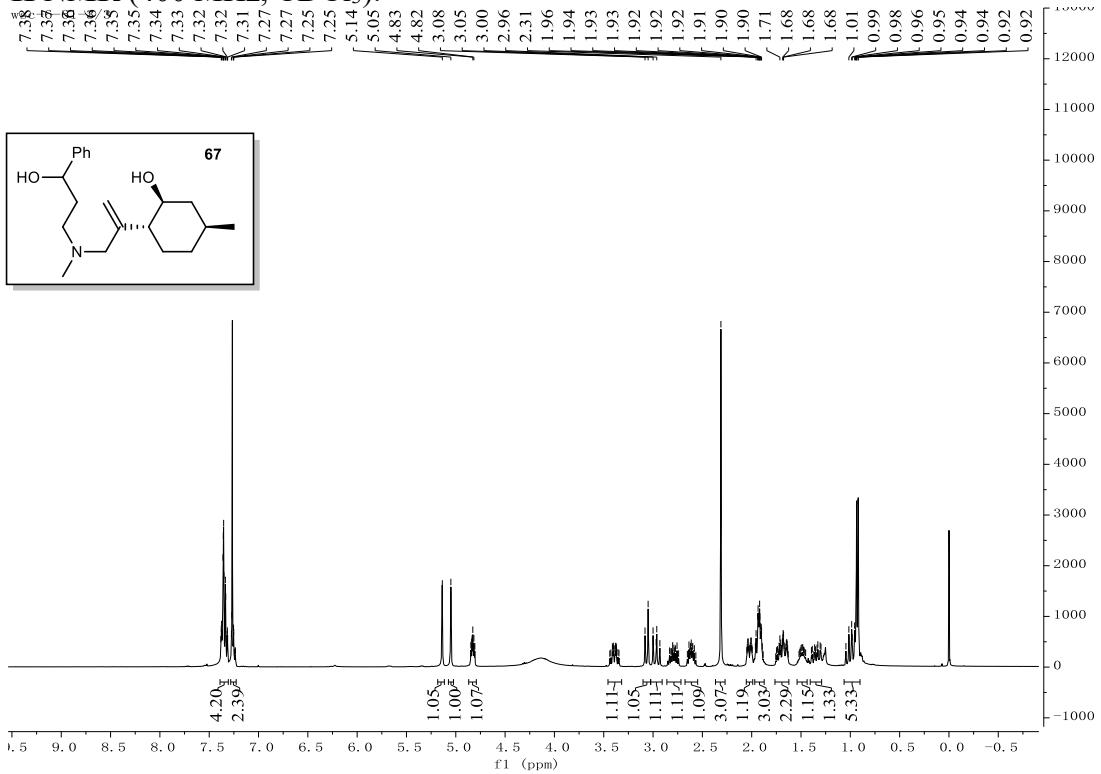
^{1}H NMR (400 MHz, $CDCl_3$):



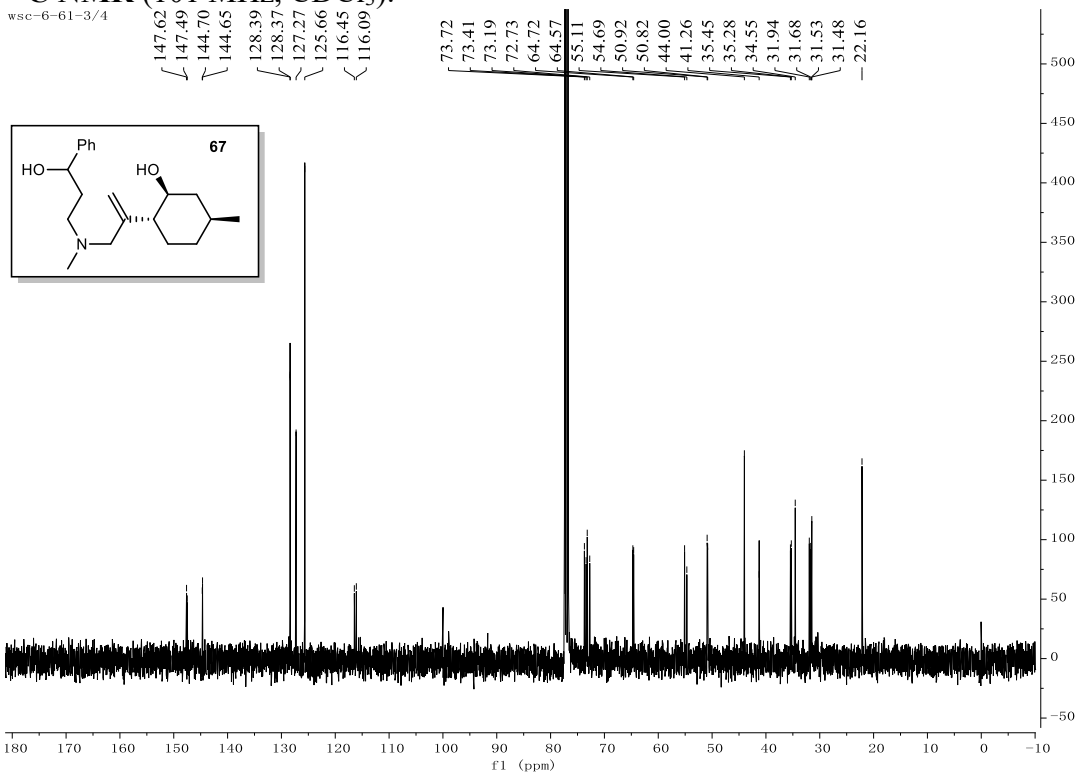
^{13}C NMR (101 MHz, $CDCl_3$):



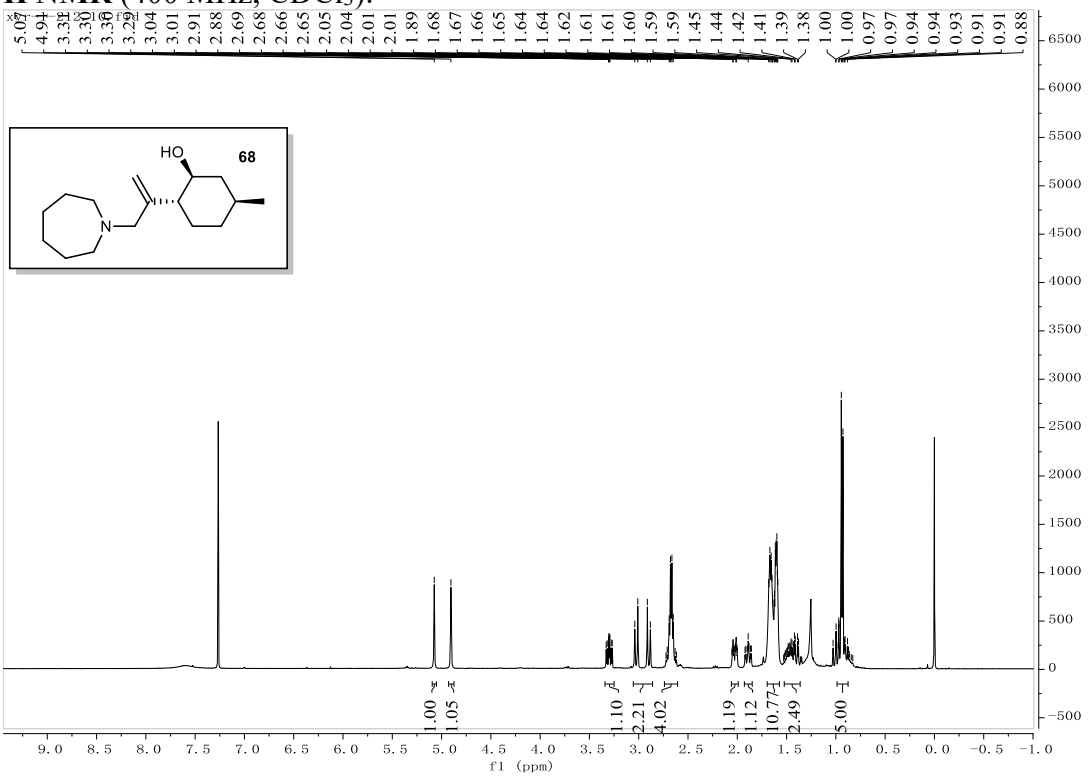
^{1}H NMR (400 MHz, $CDCl_3$):



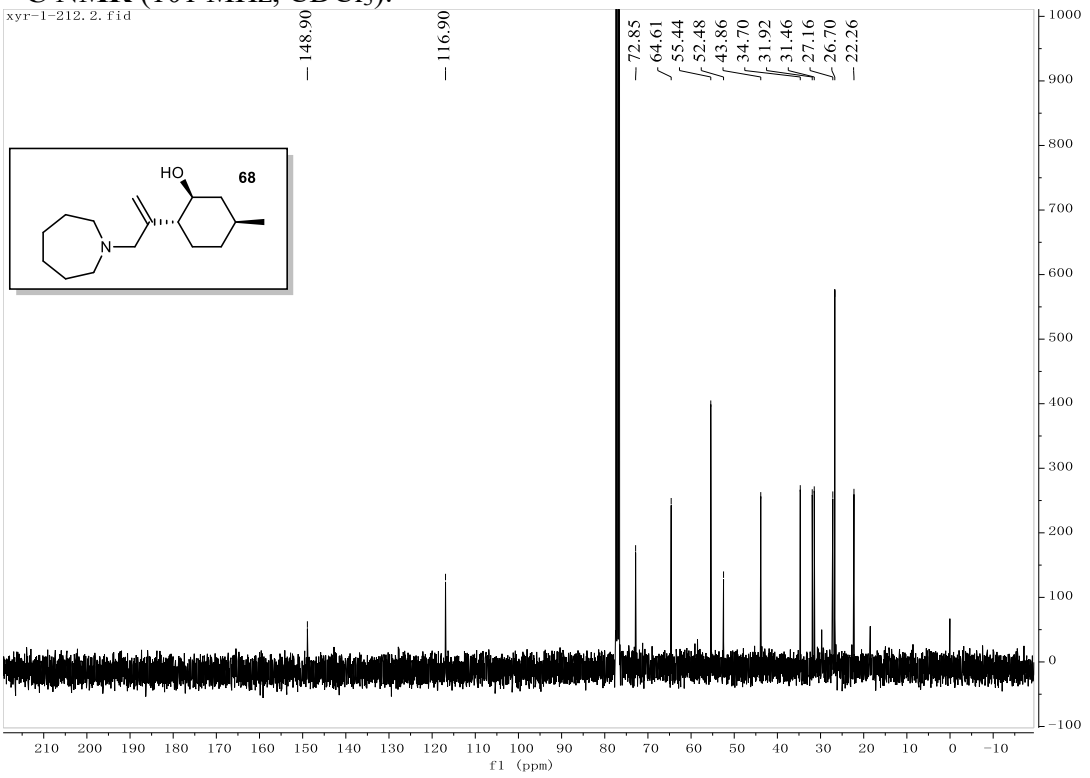
^{13}C NMR (101 MHz, $CDCl_3$):



H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):



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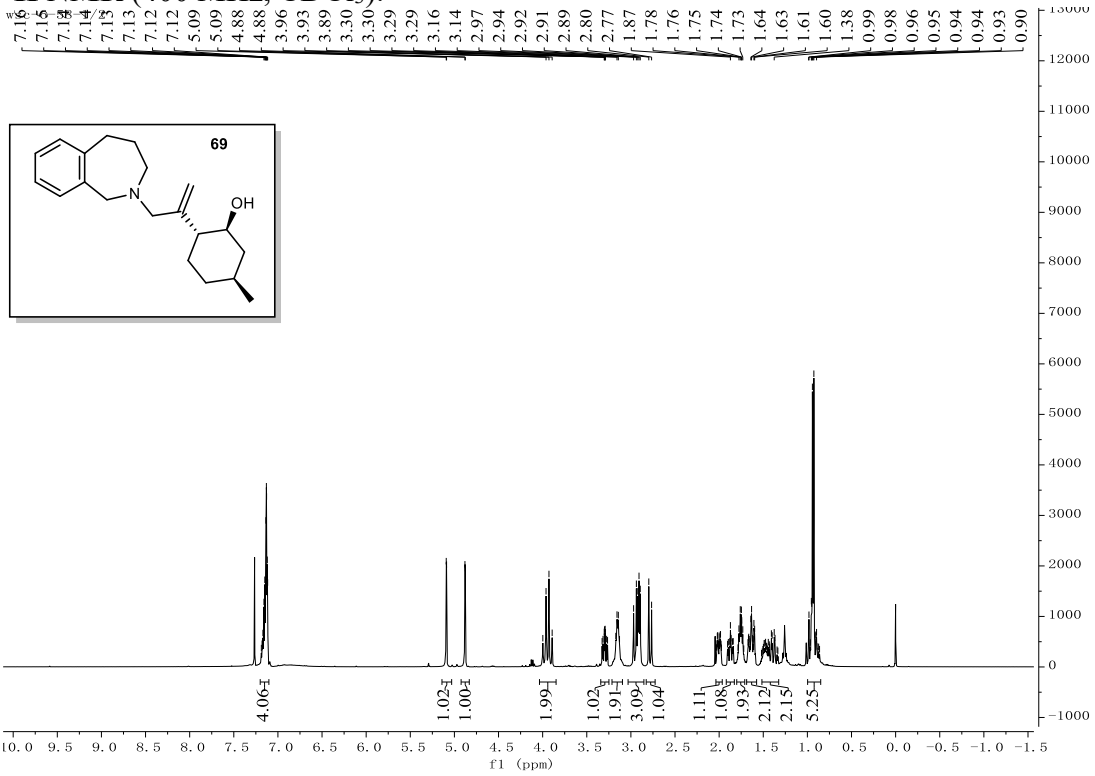

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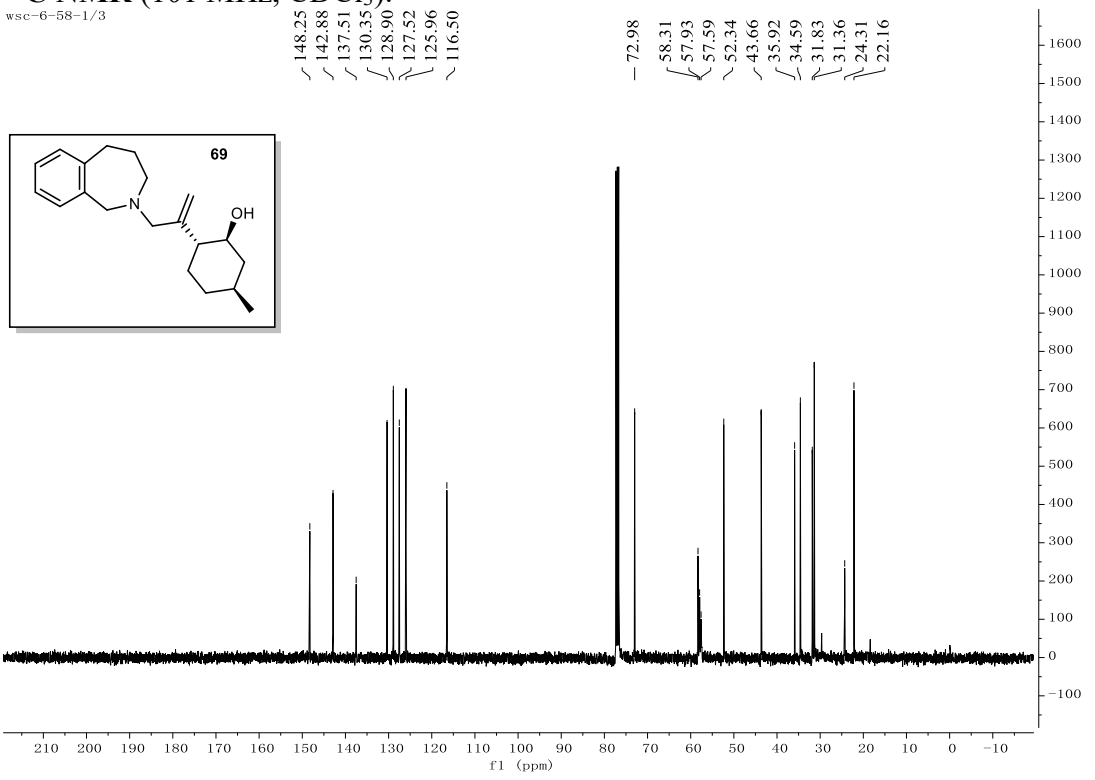

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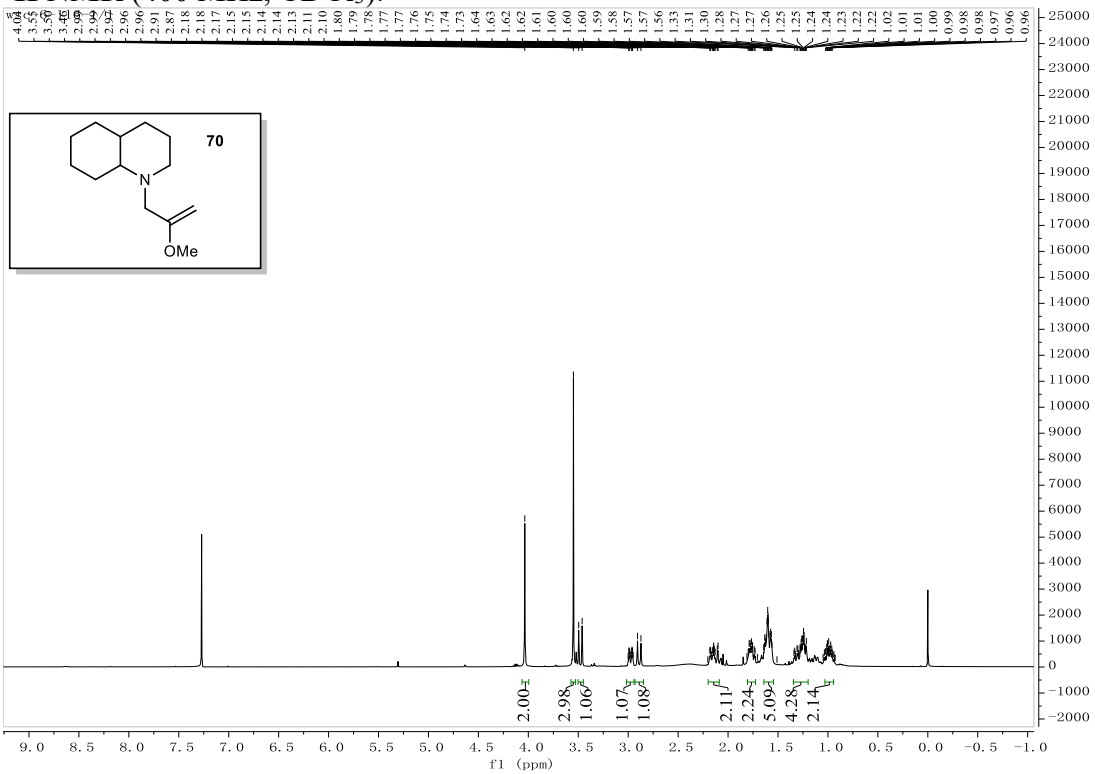

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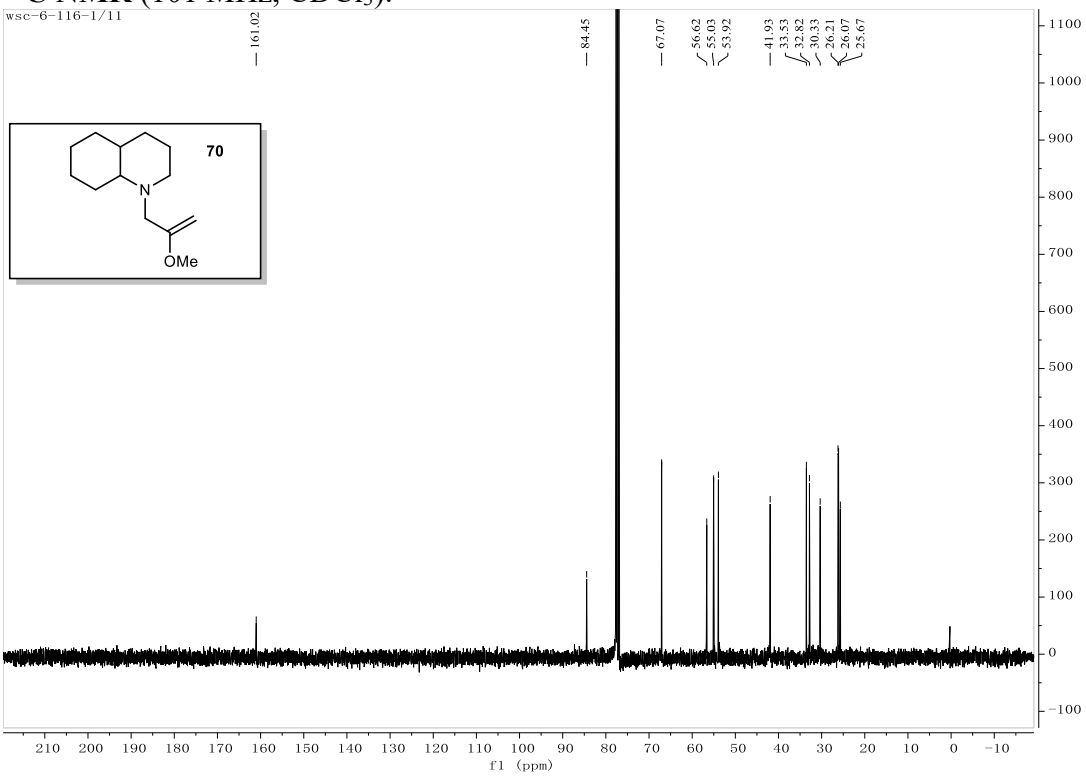

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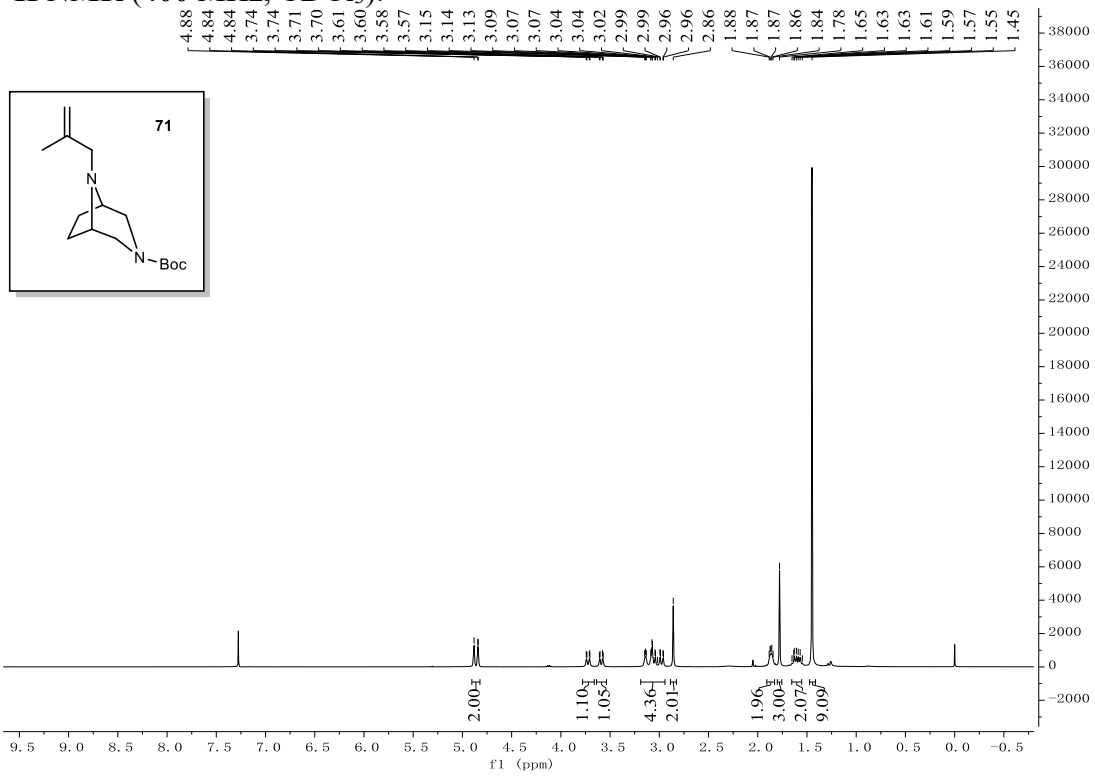

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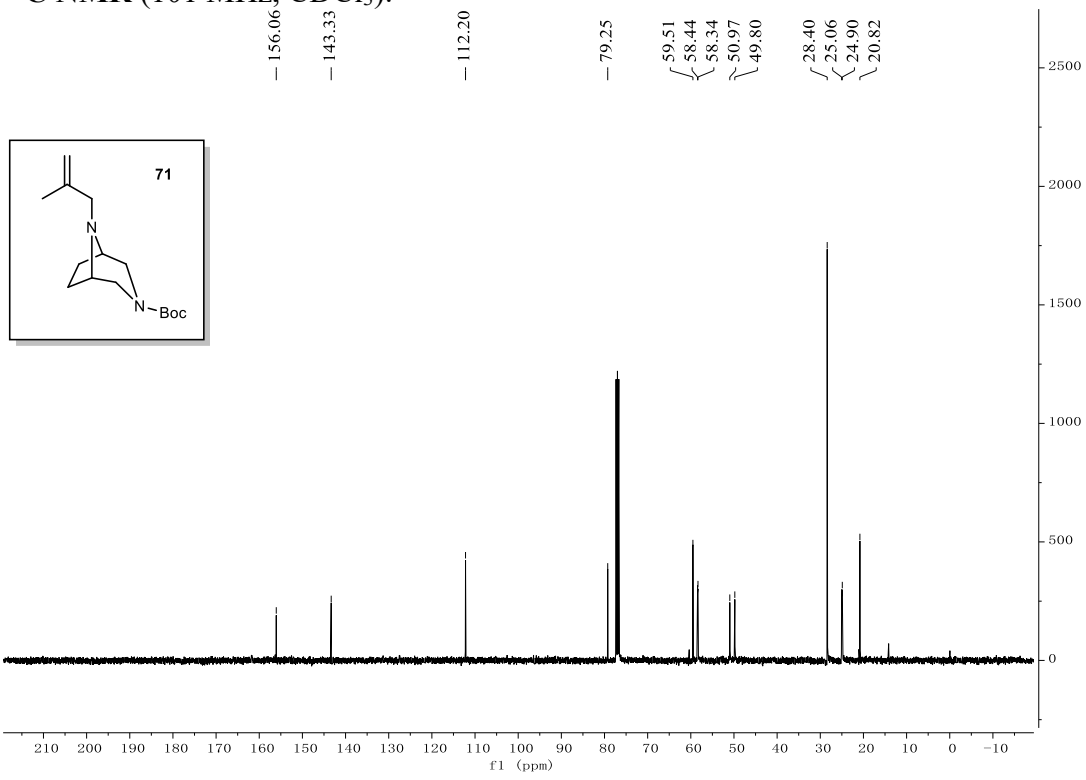

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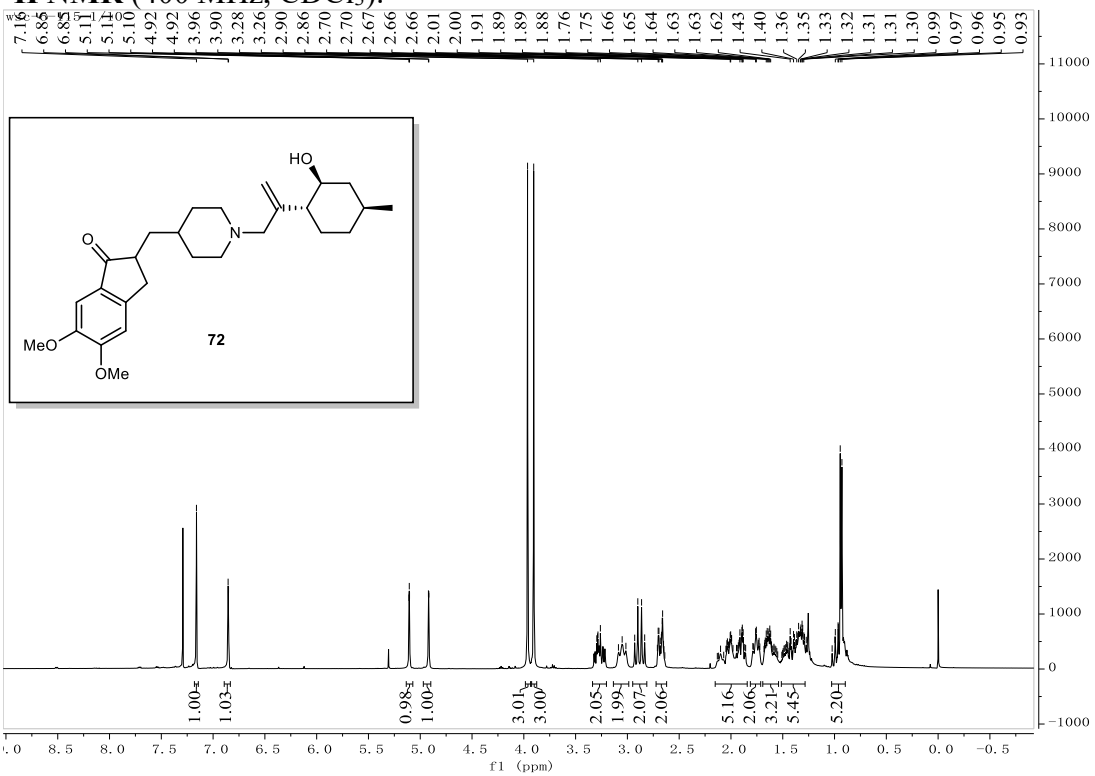

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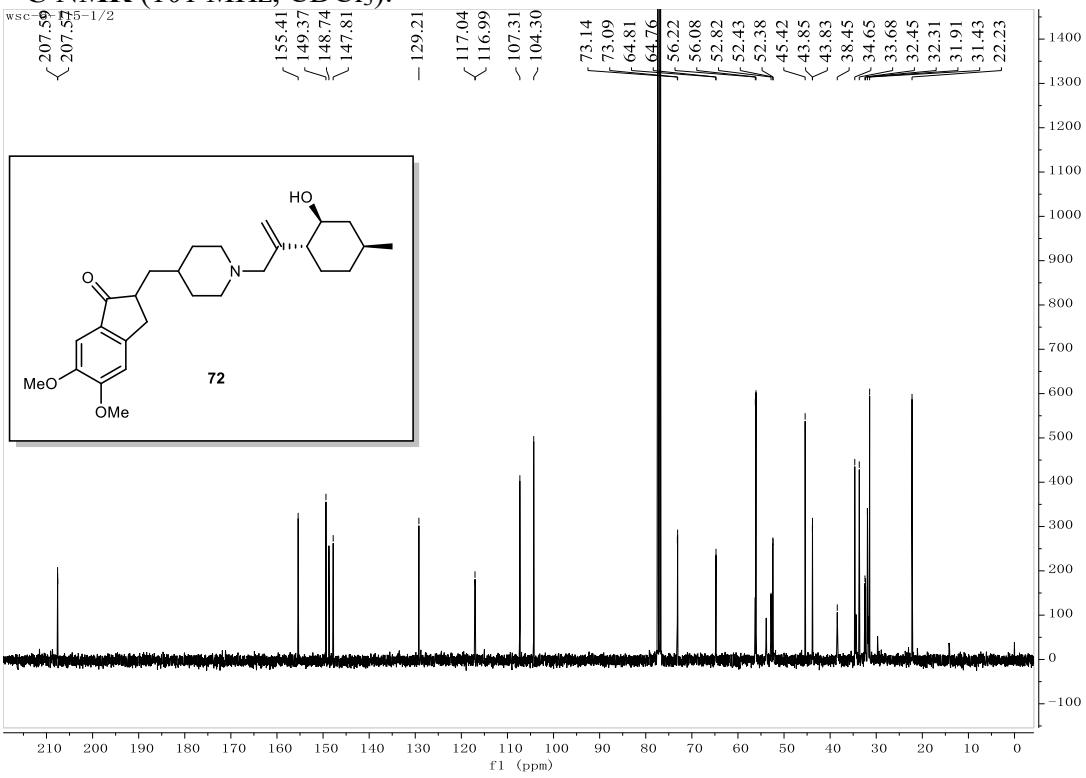
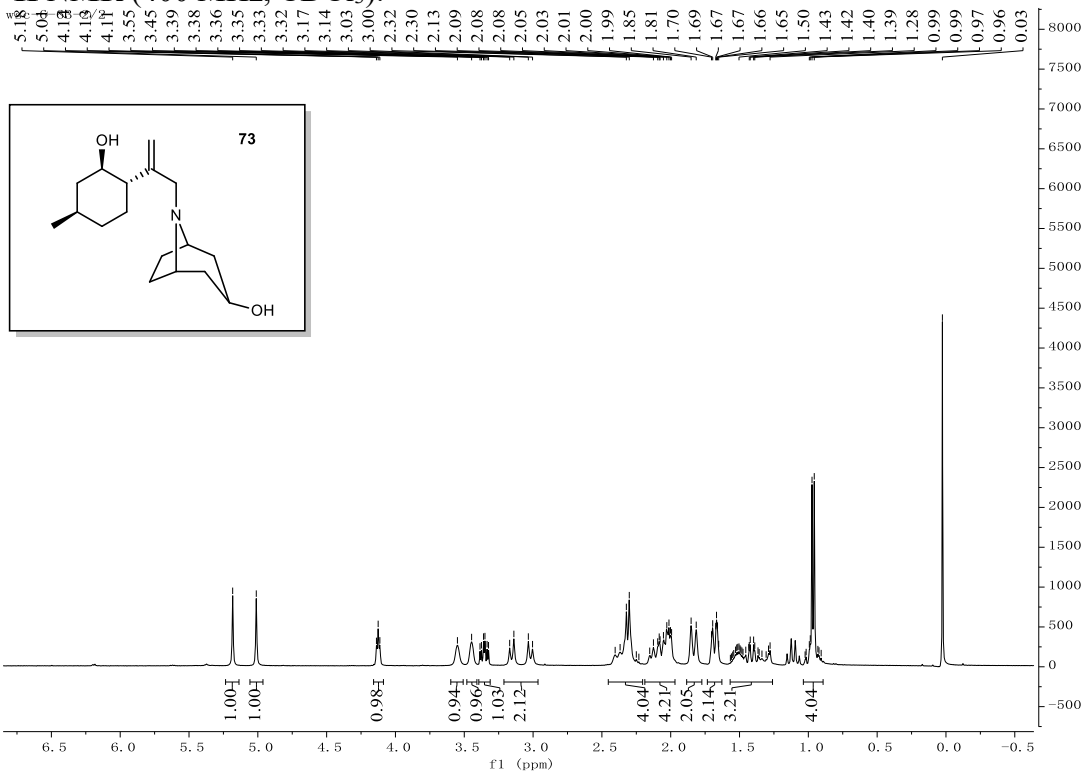


^{1}H NMR (400 MHz, $CDCl_3$):



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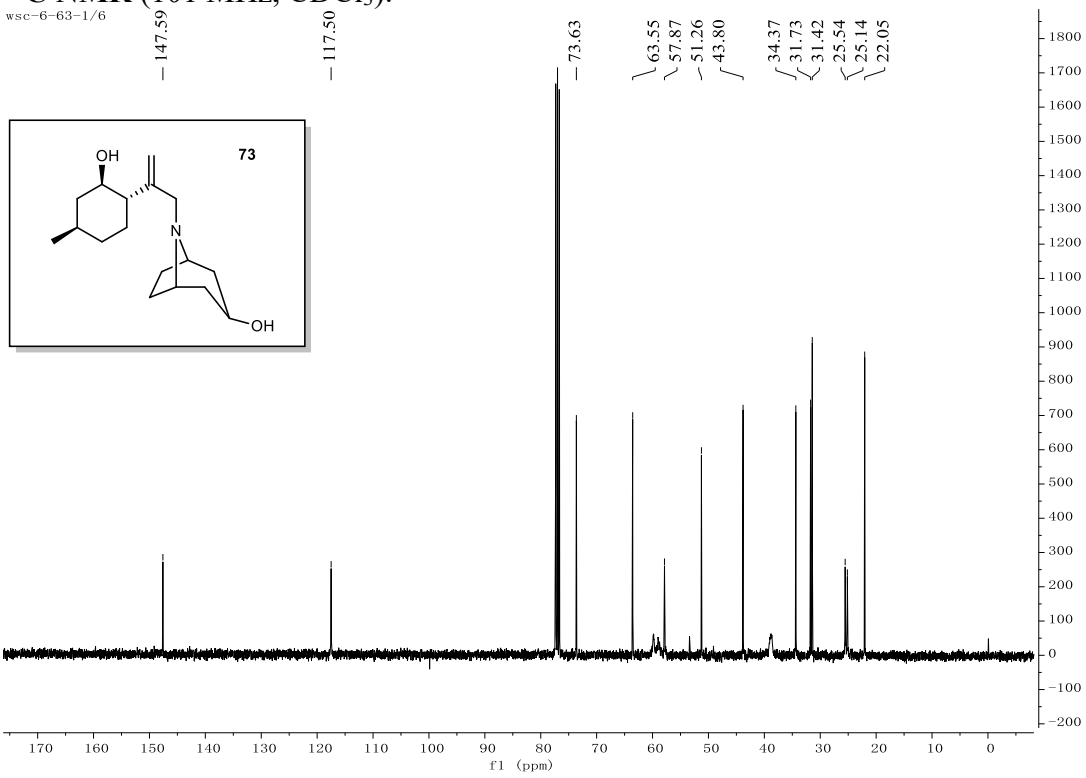

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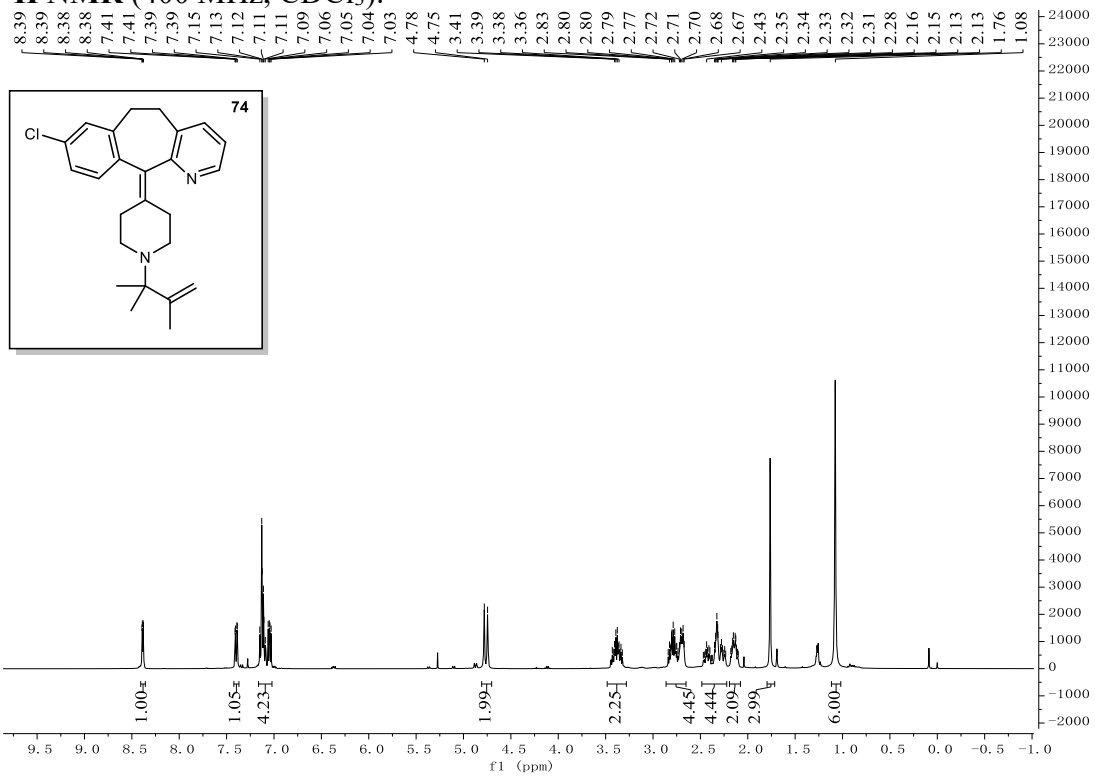

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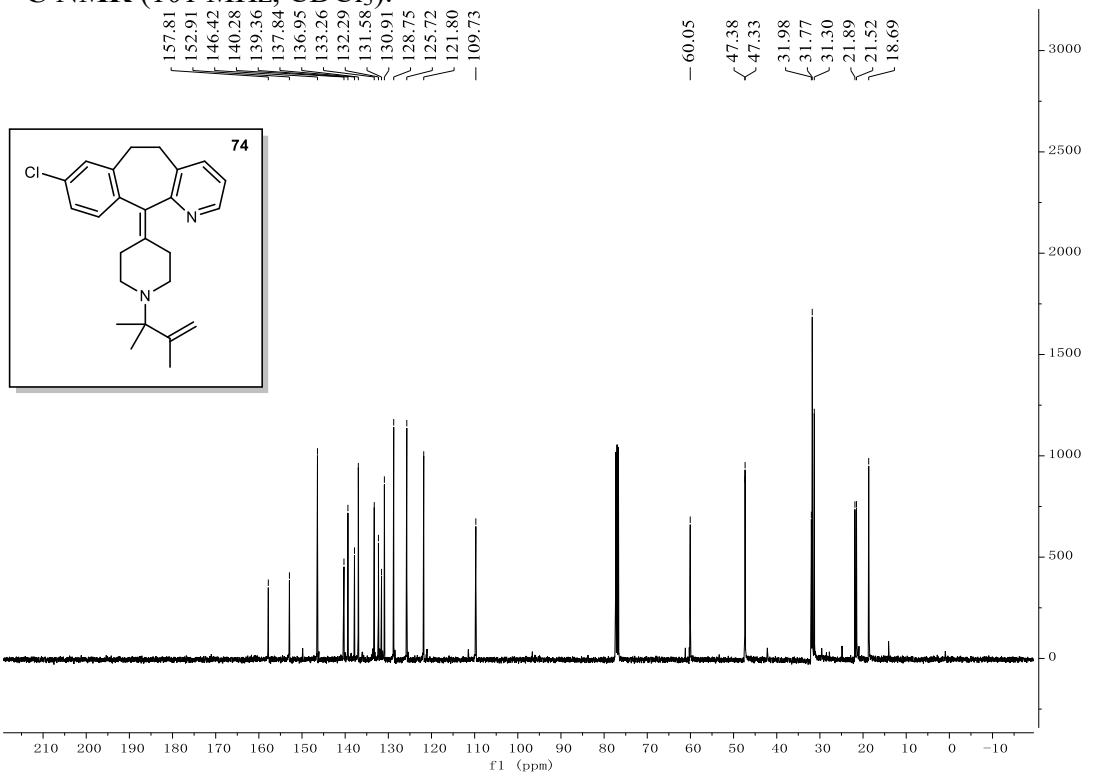

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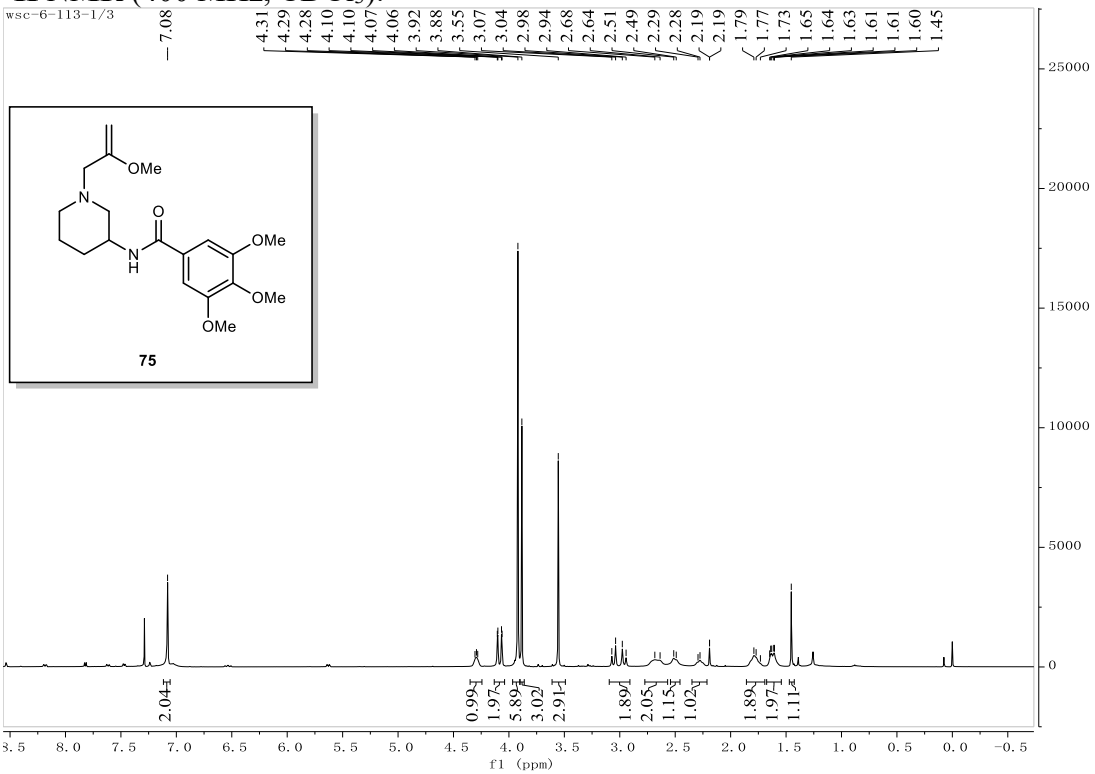
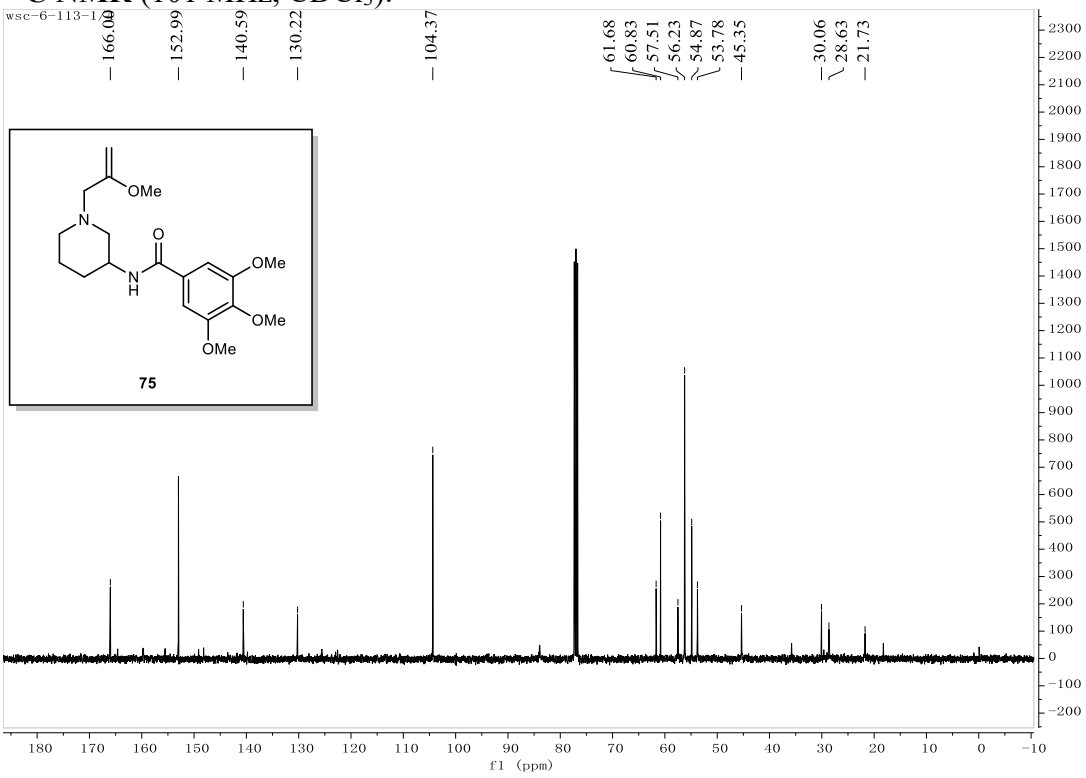
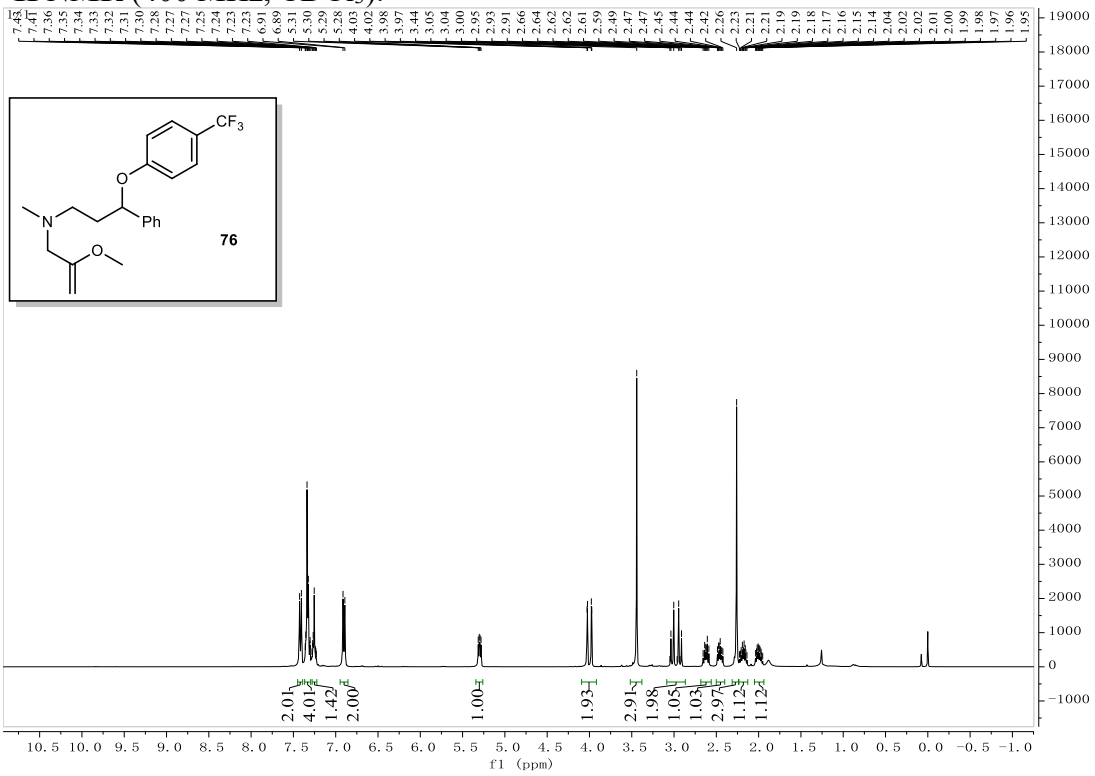


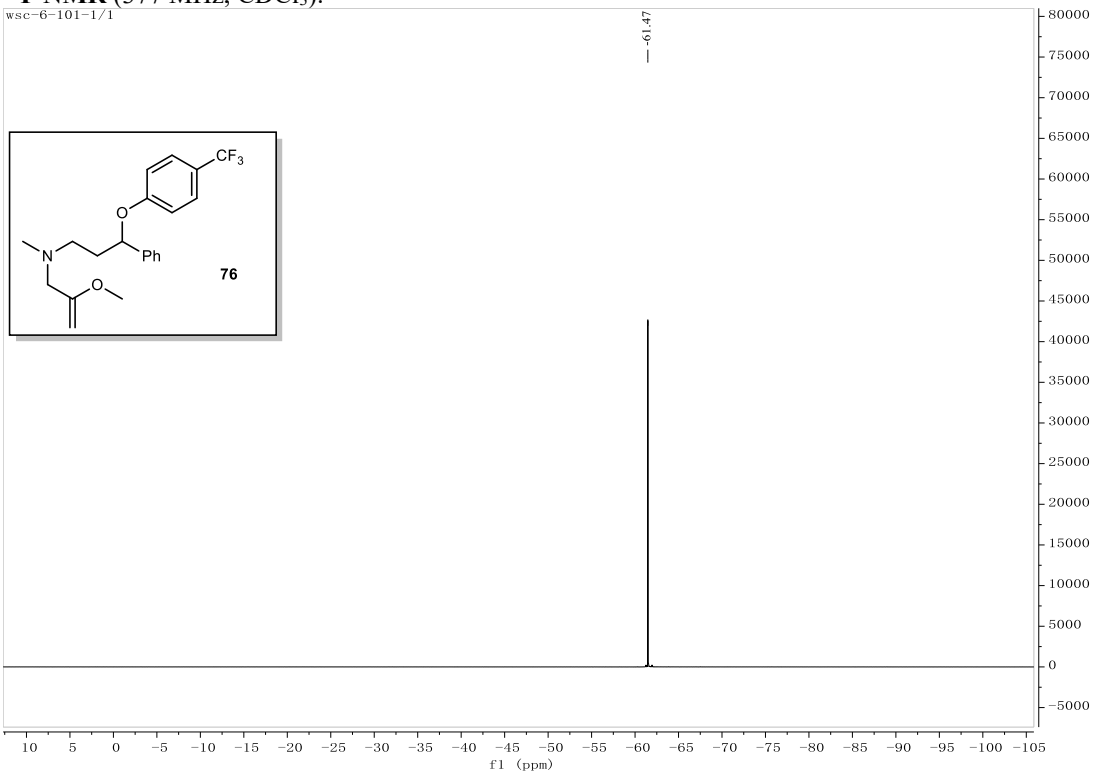
^{13}C NMR (101 MHz, $CDCl_3$):



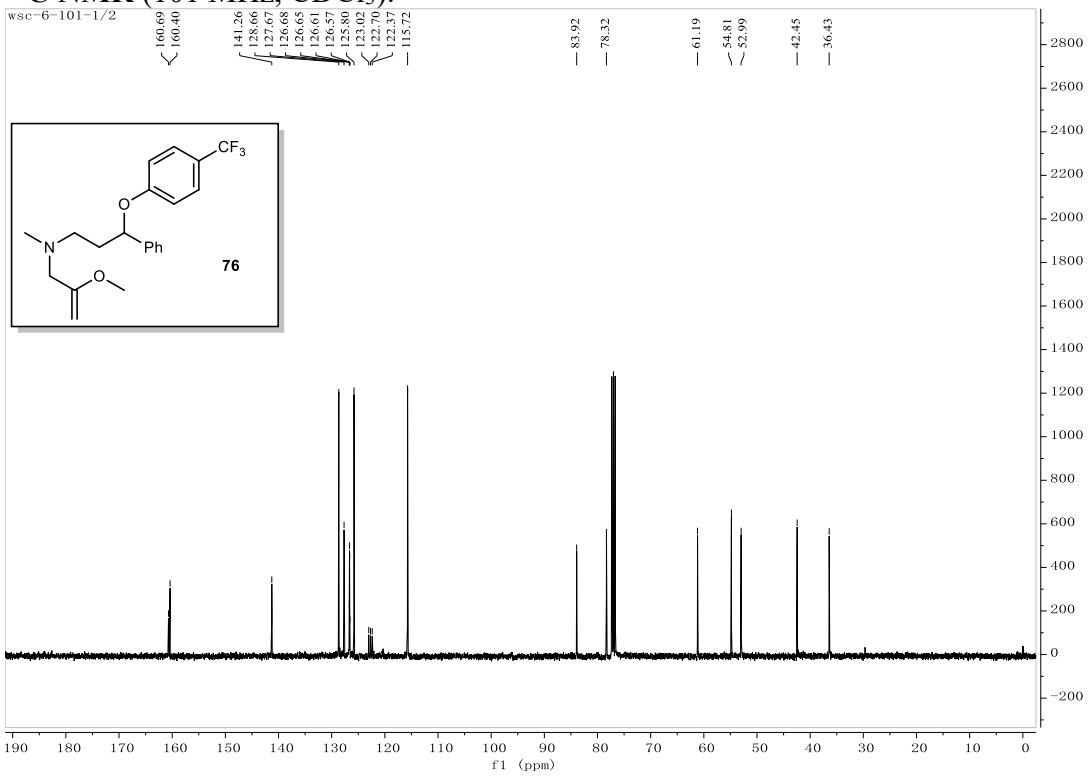
^{1}H NMR (400 MHz, $CDCl_3$):



^{19}F NMR (377 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):



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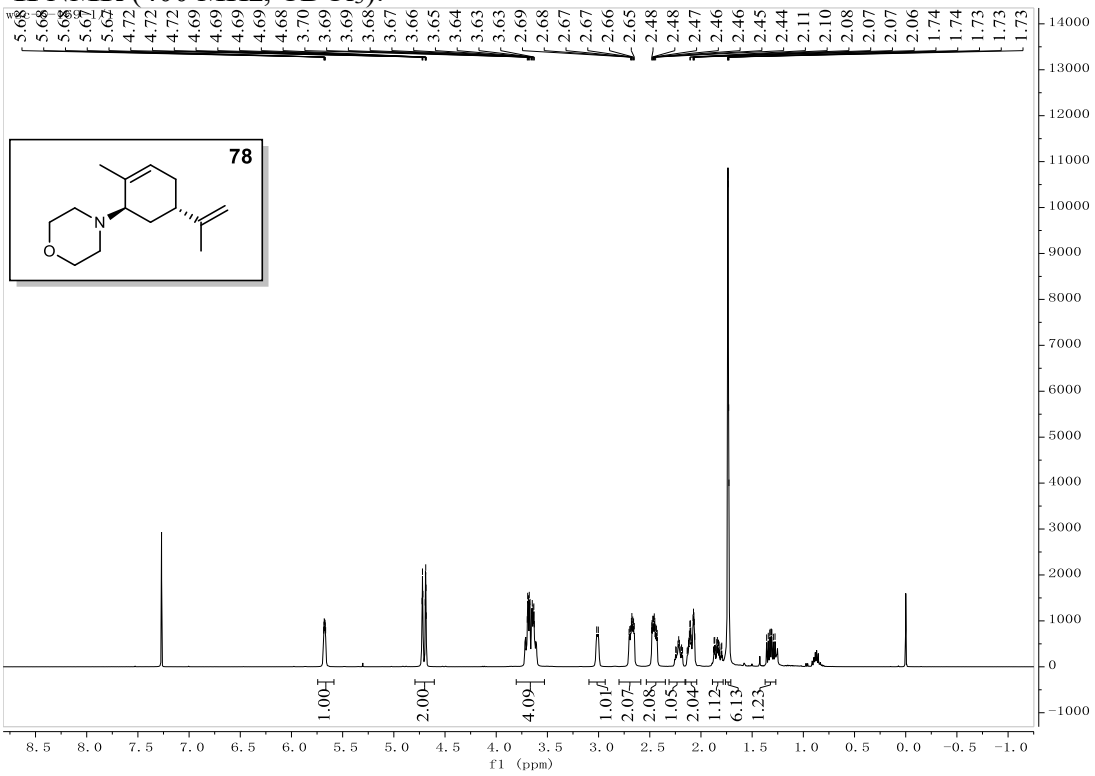

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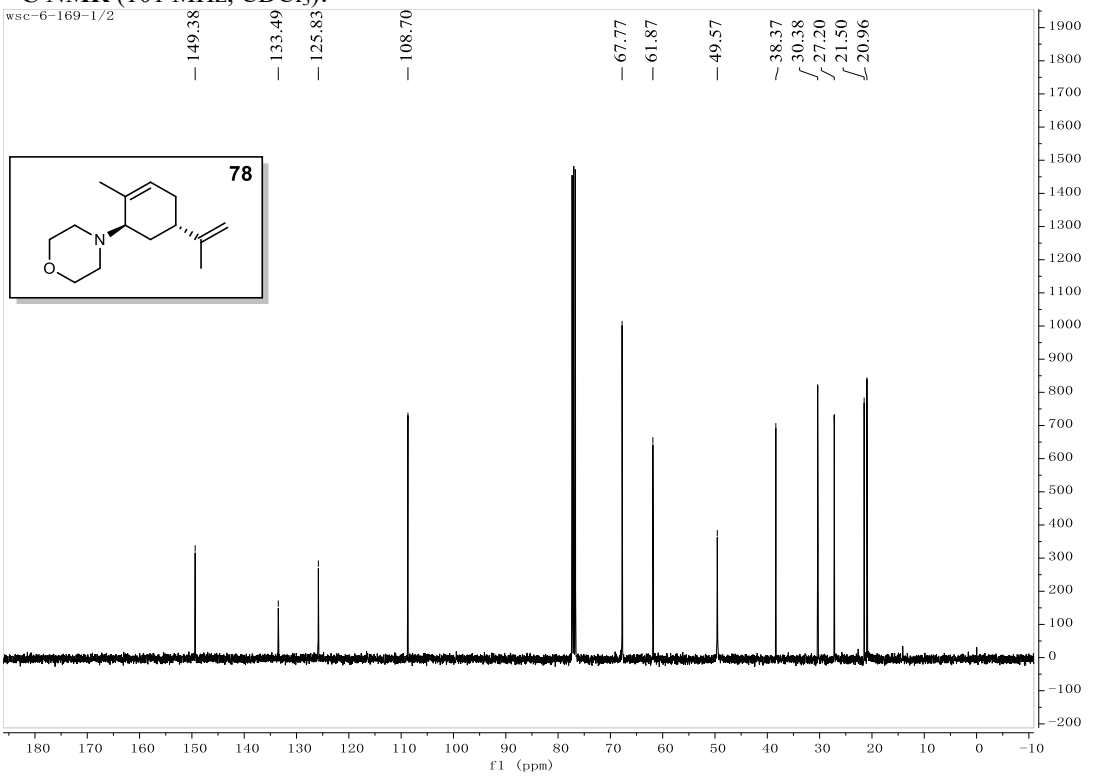

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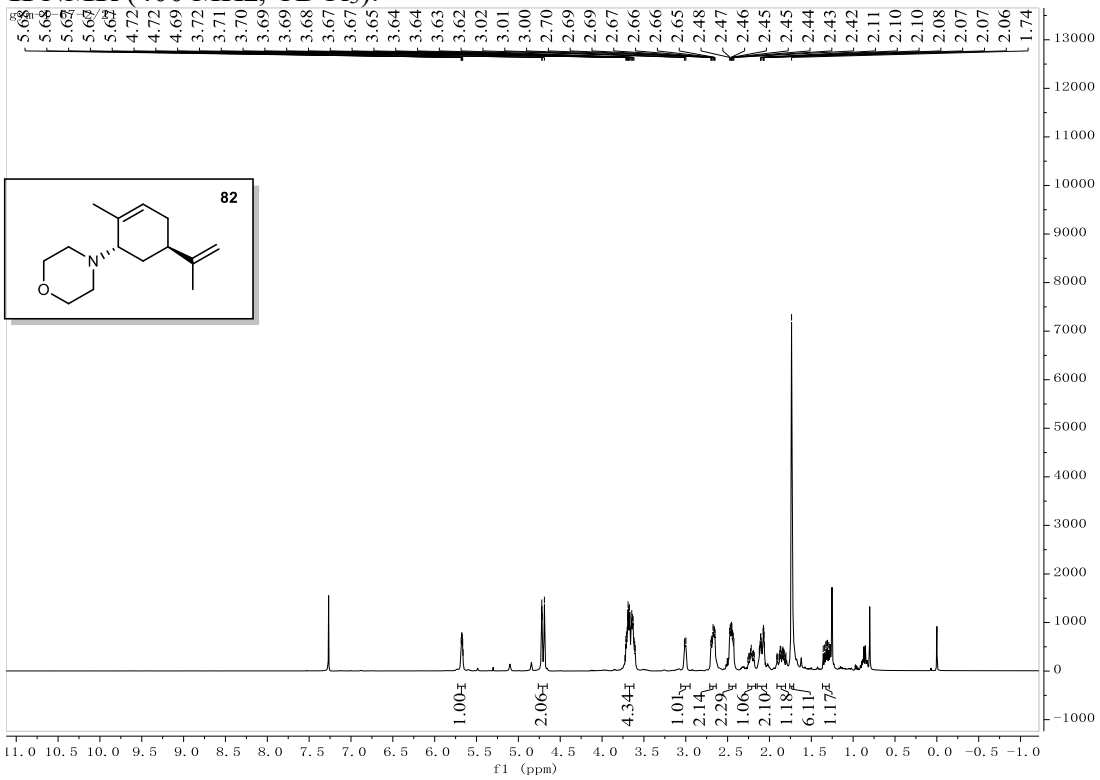

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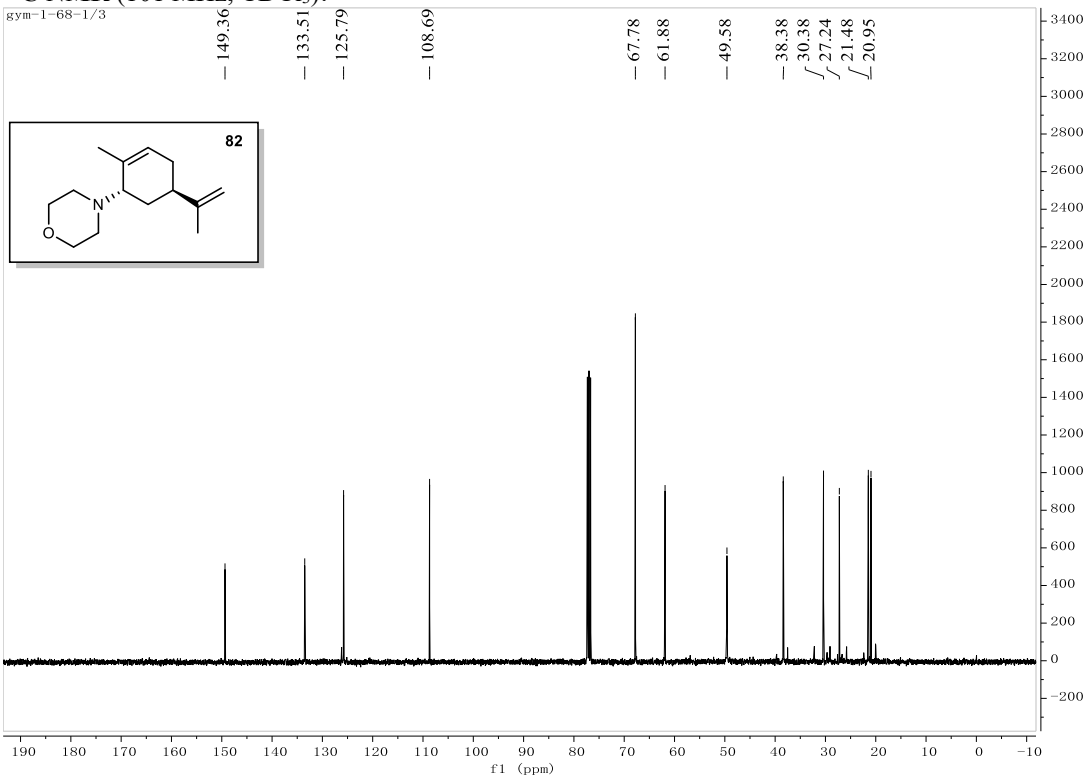

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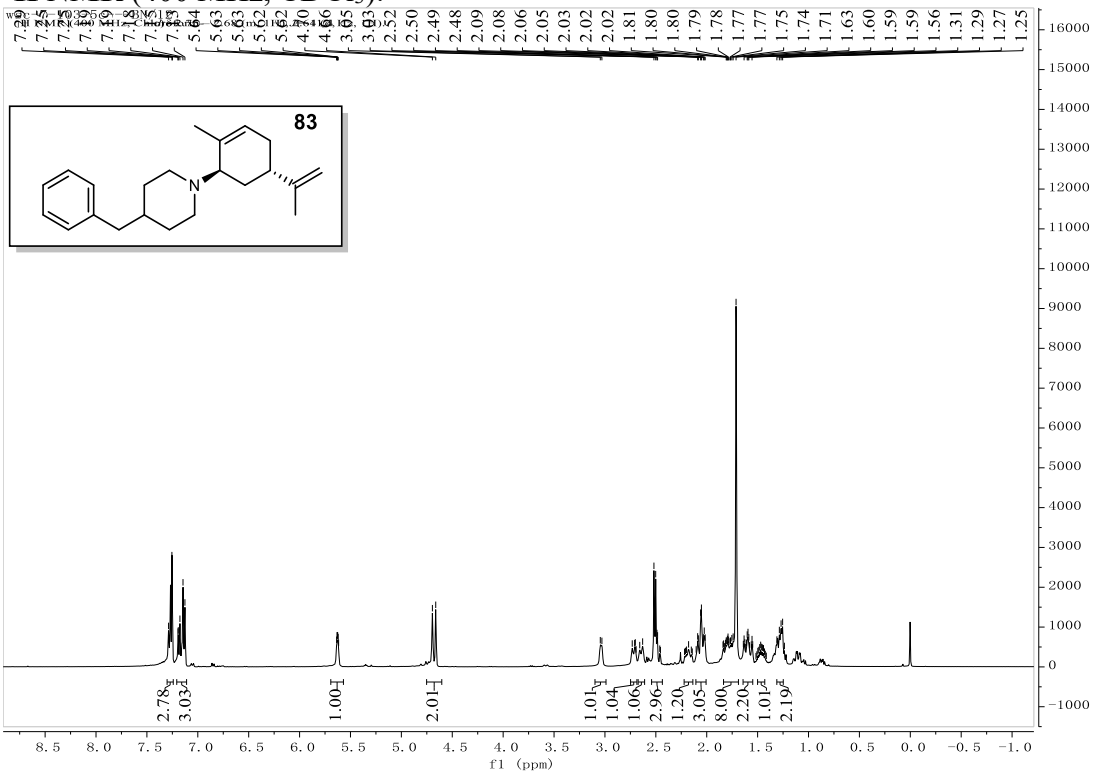

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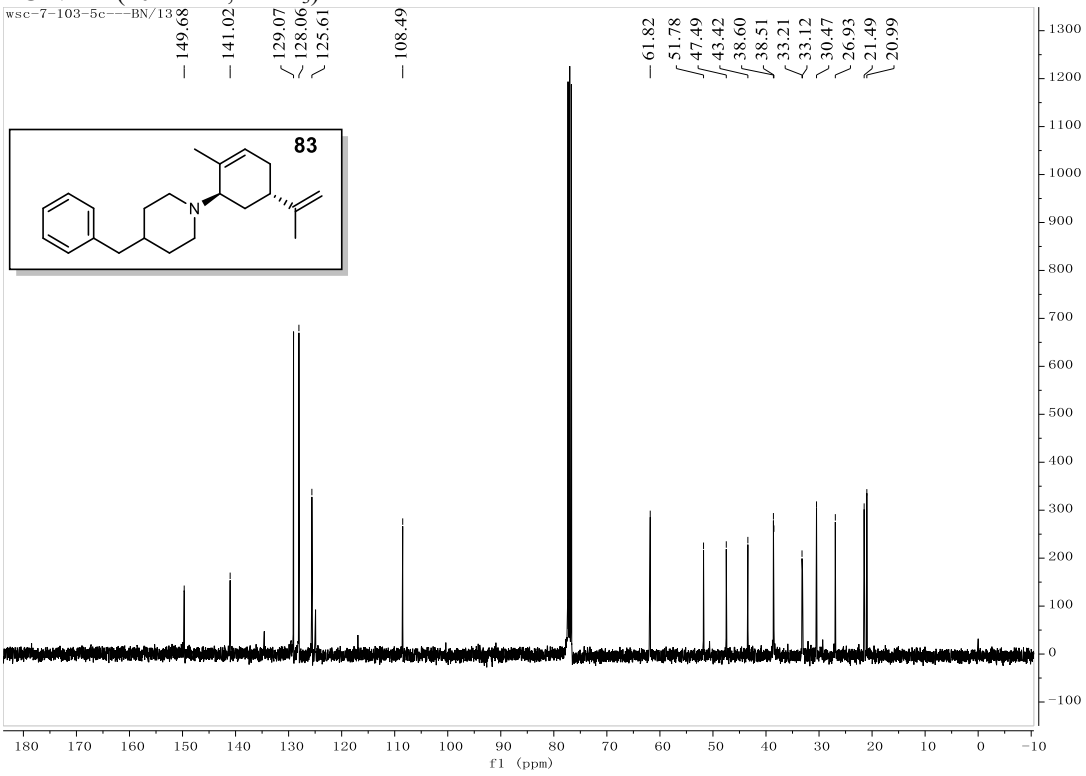

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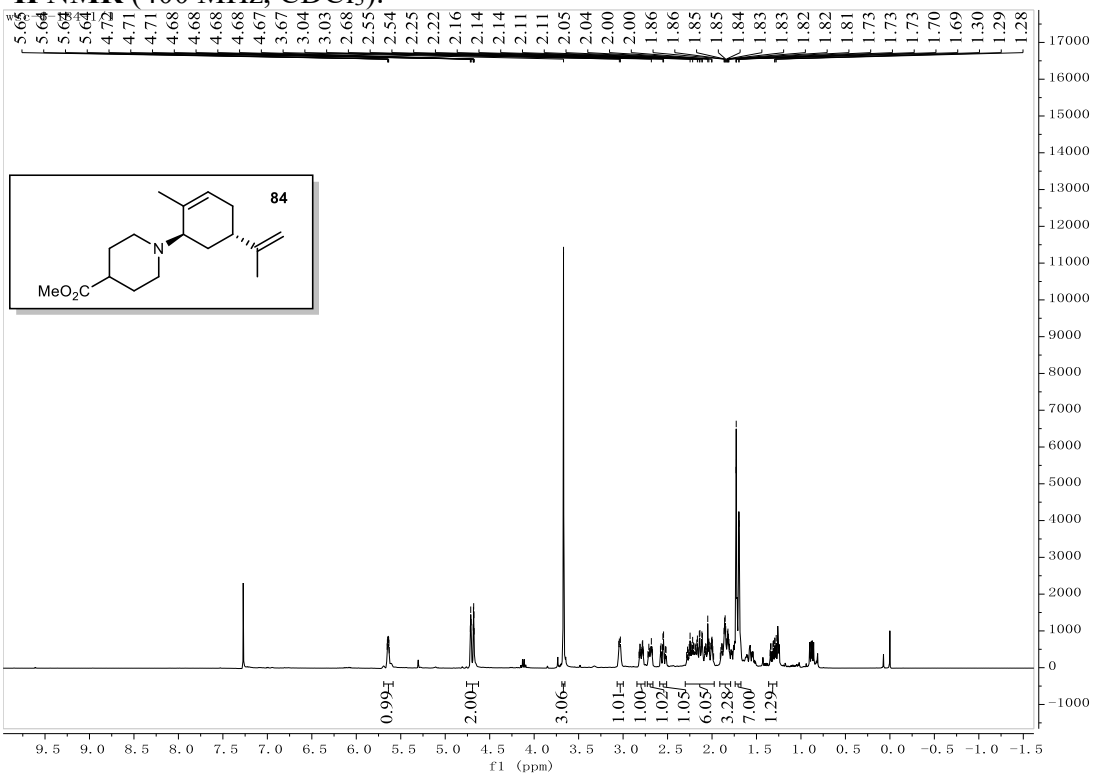

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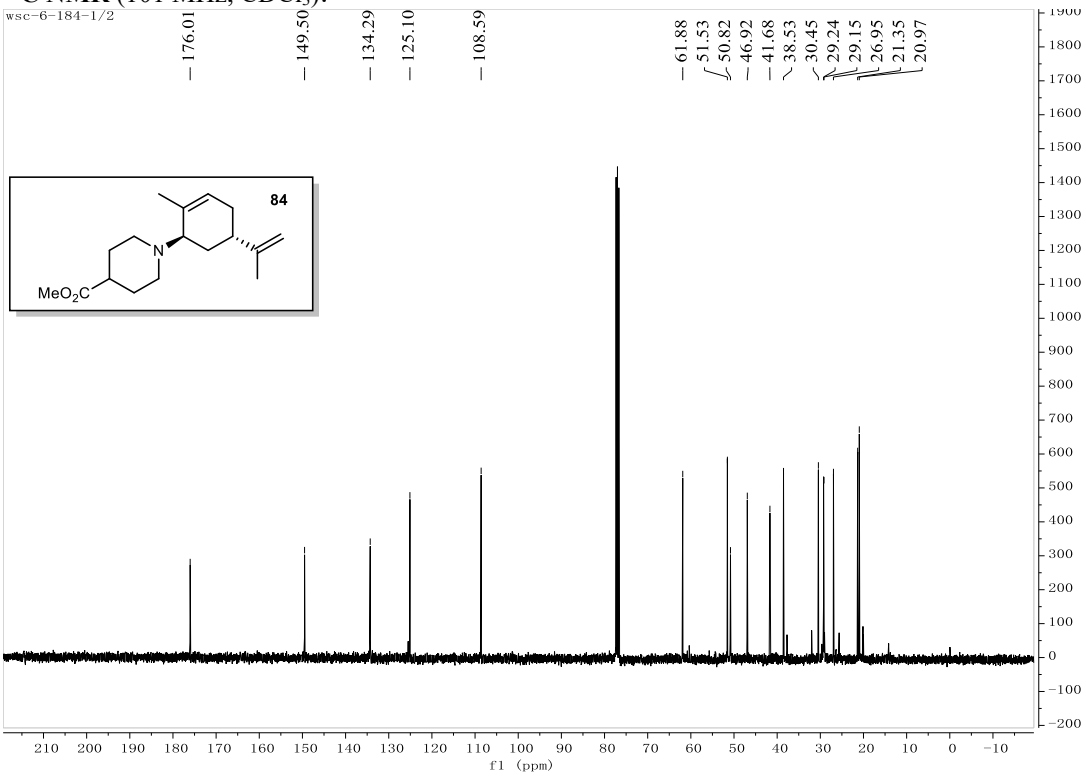

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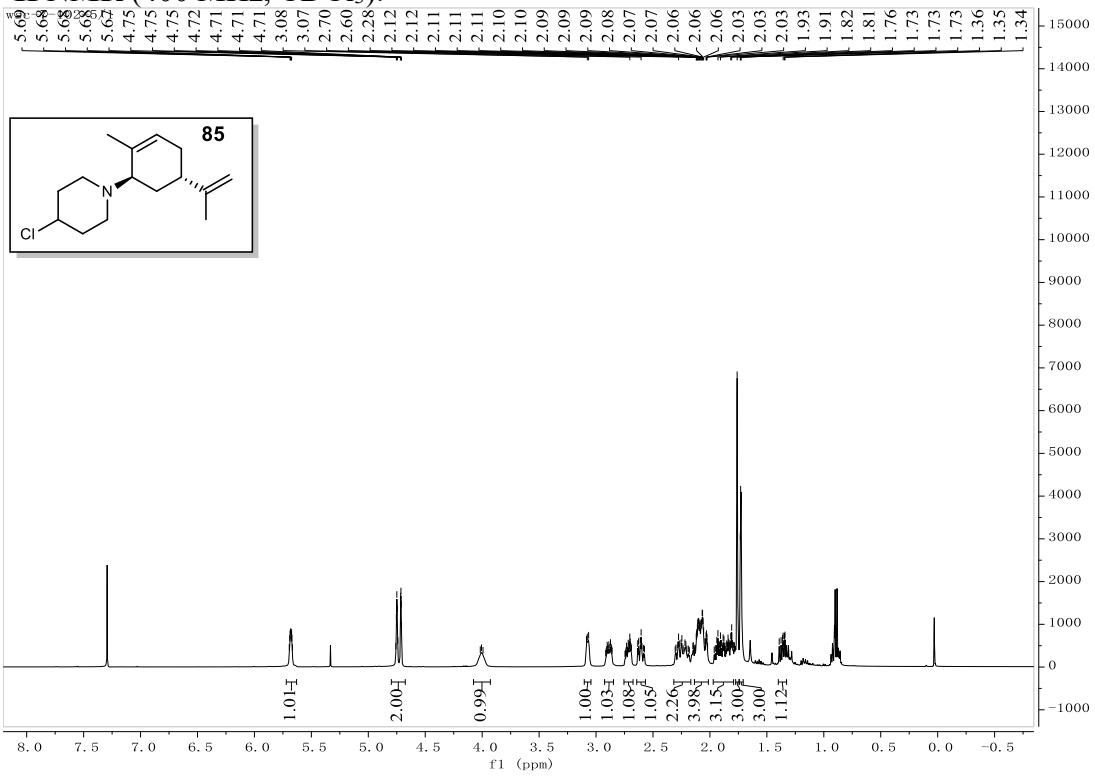

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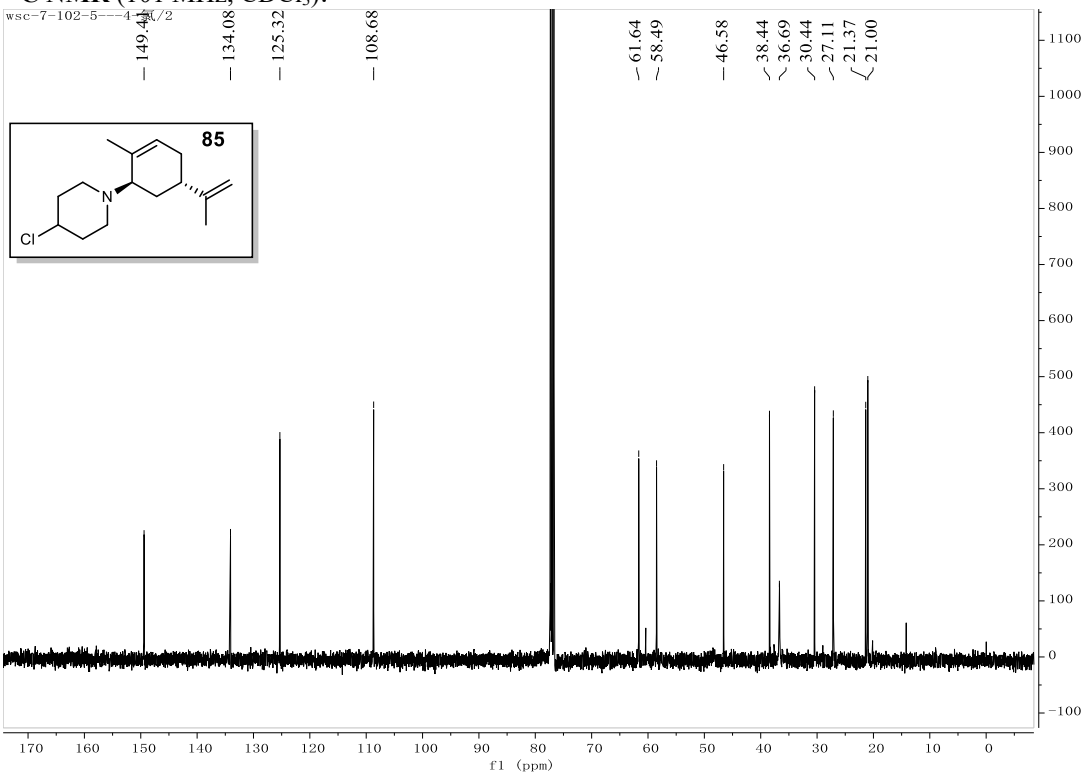

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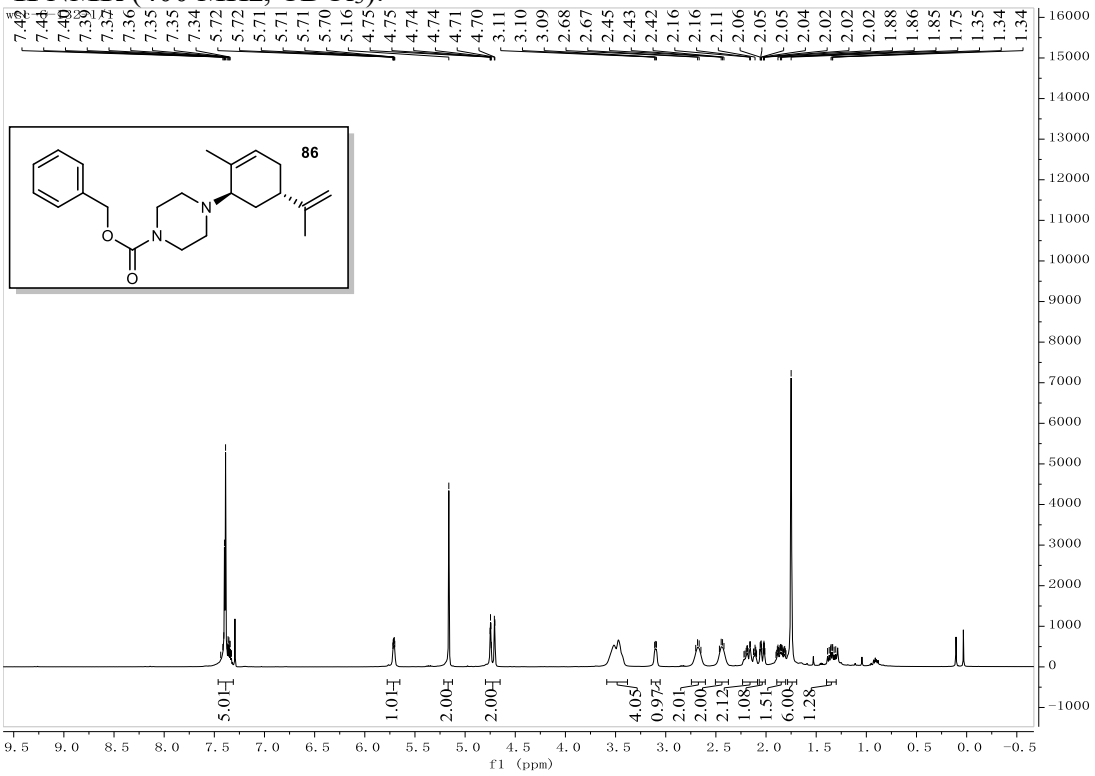

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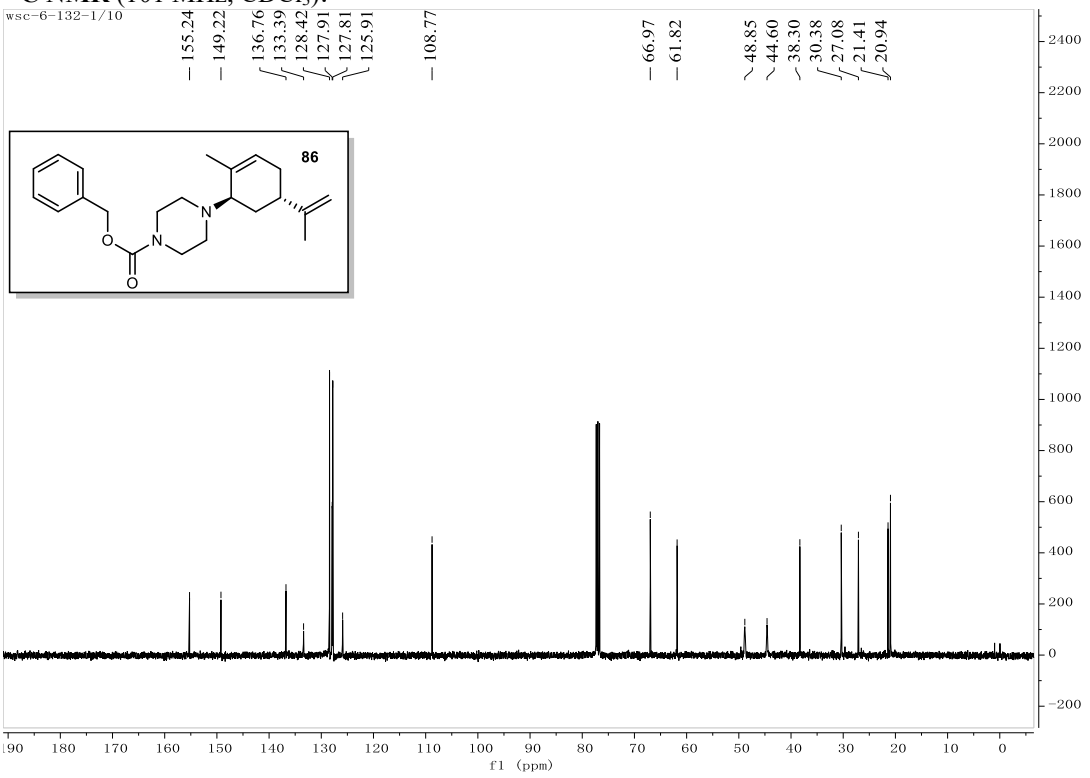

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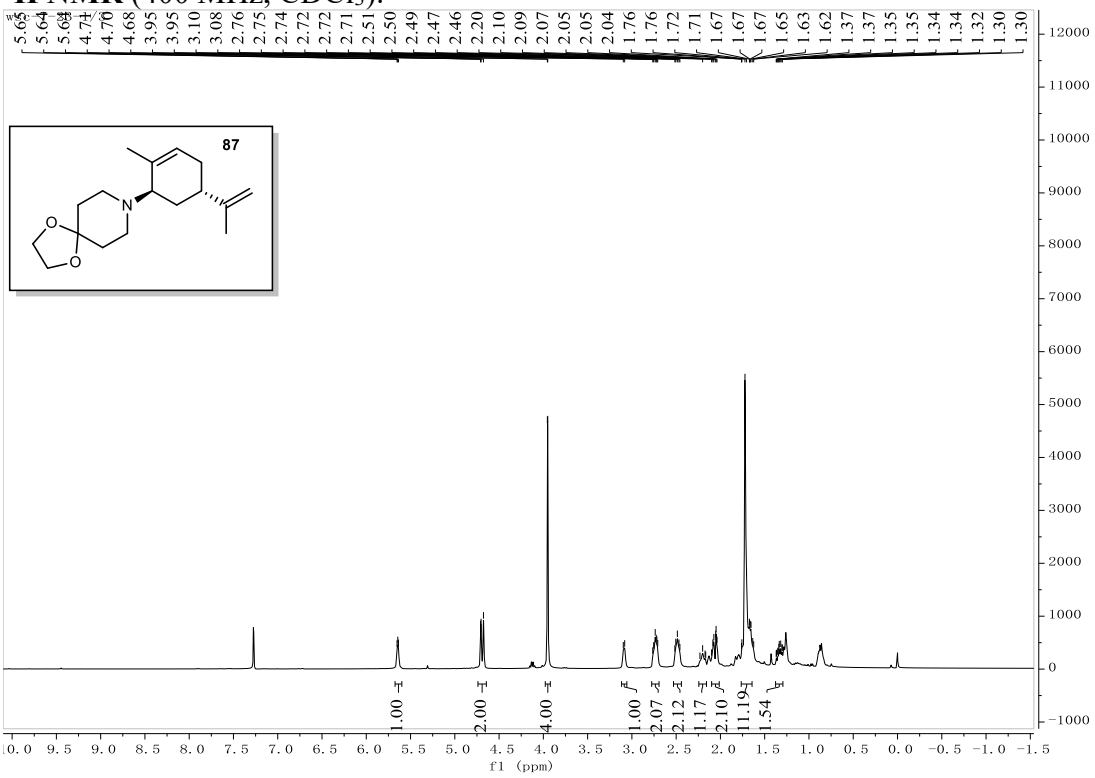

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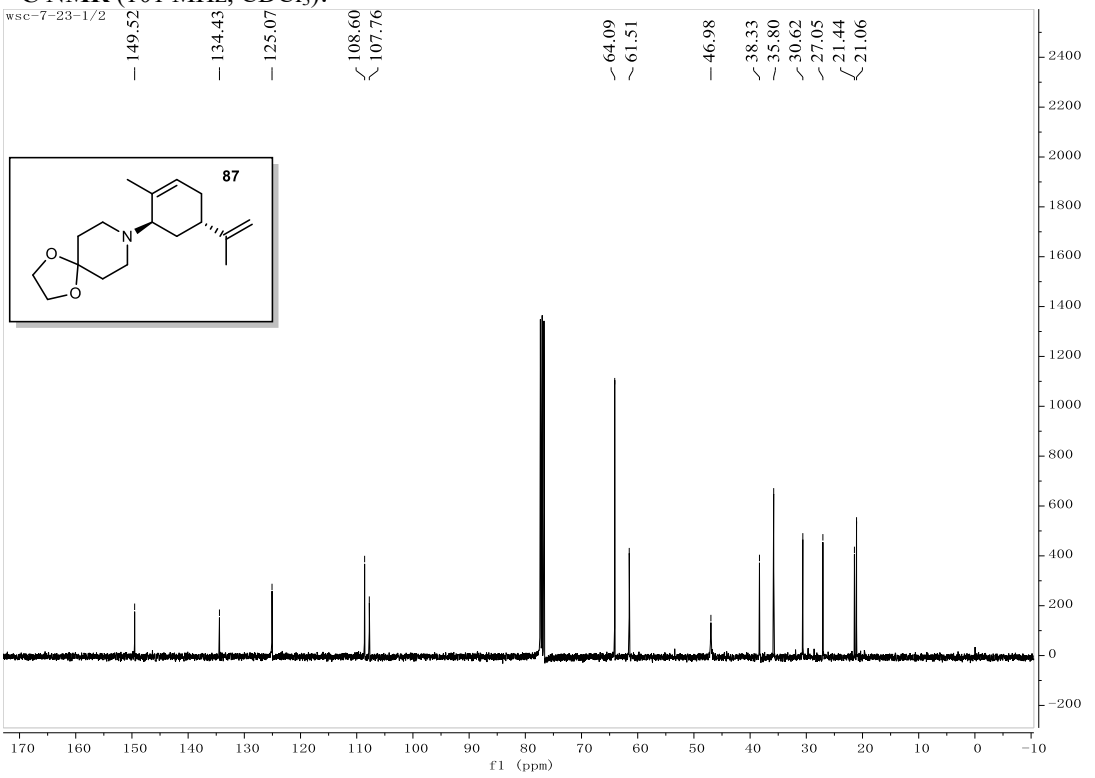

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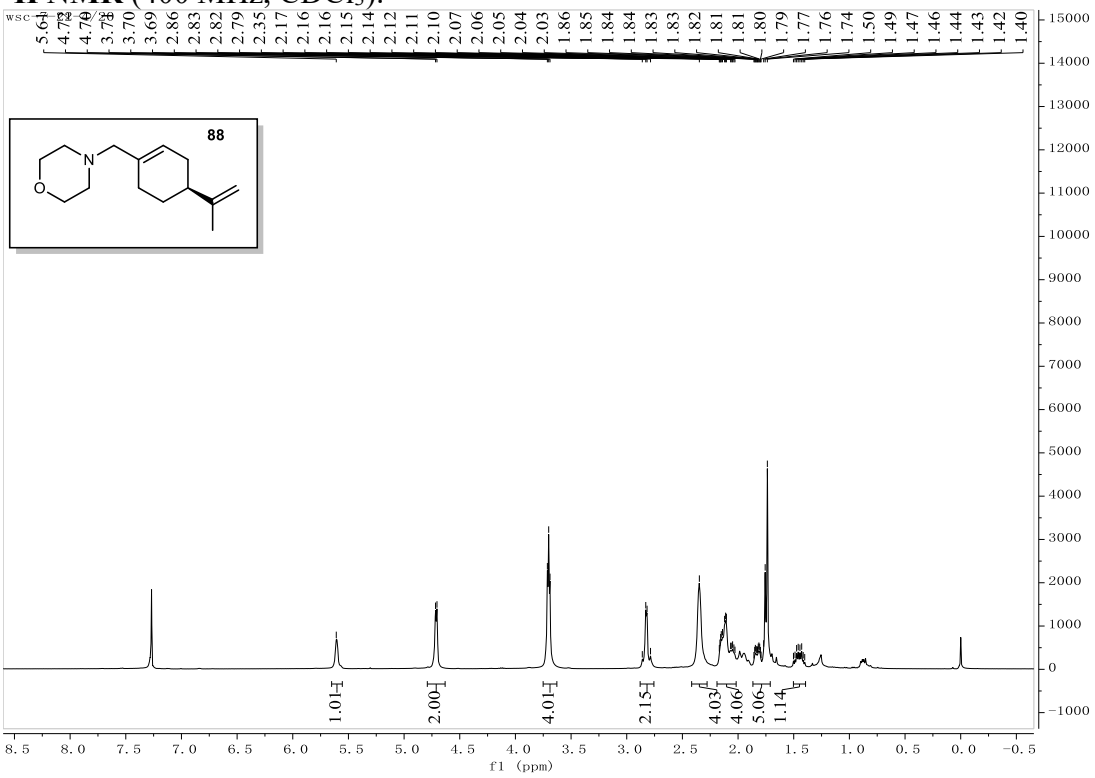

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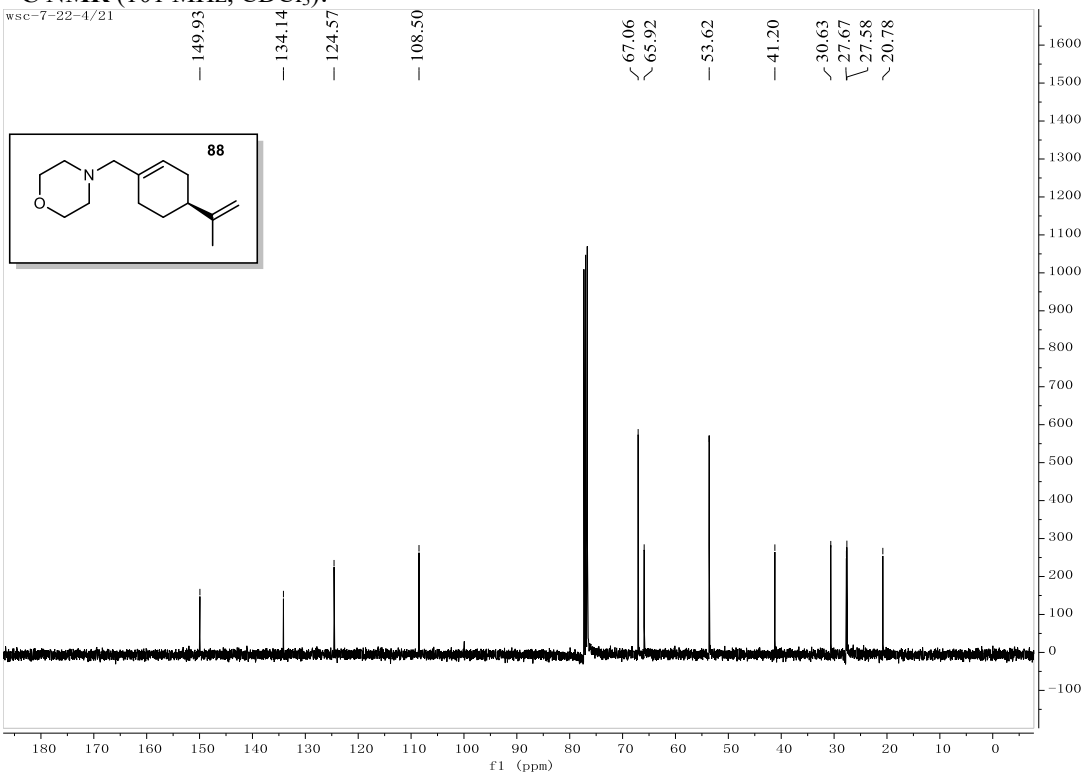

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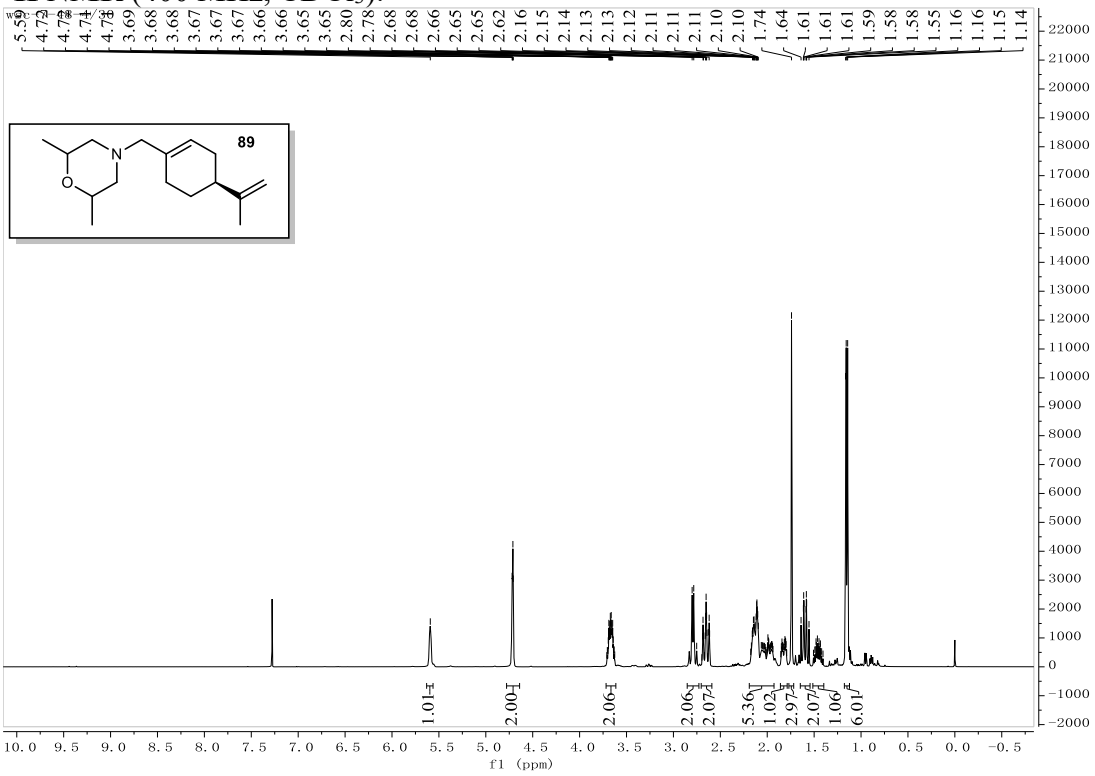

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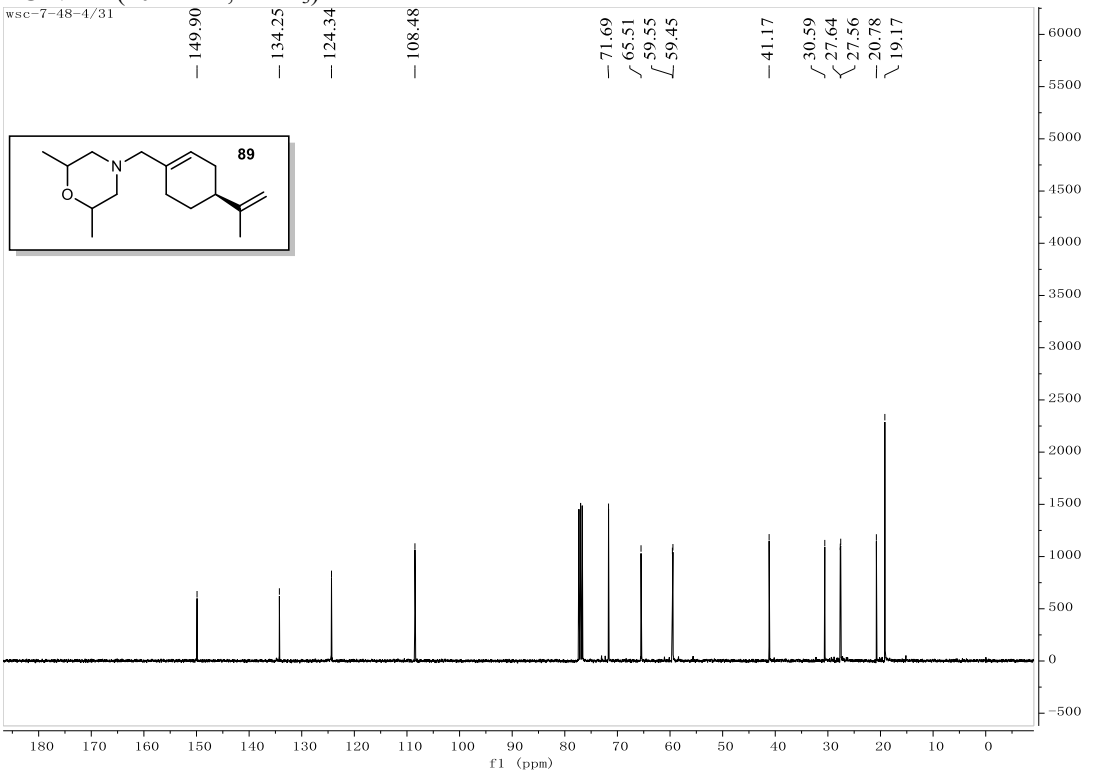

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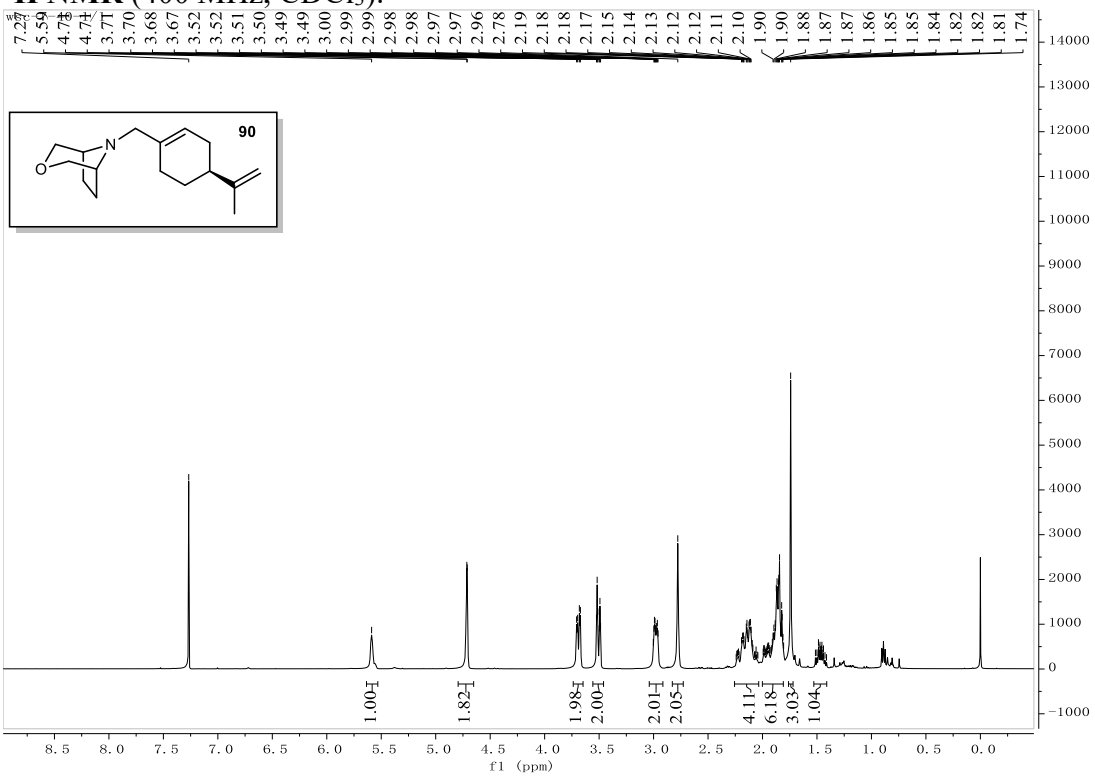

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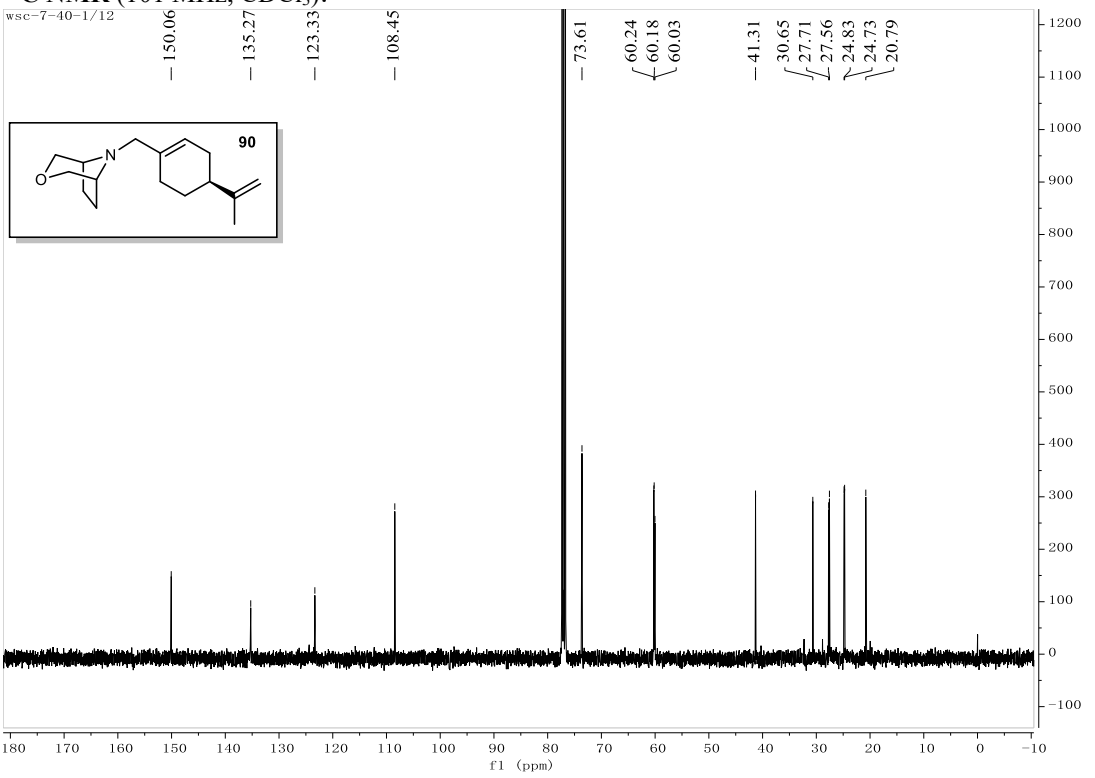

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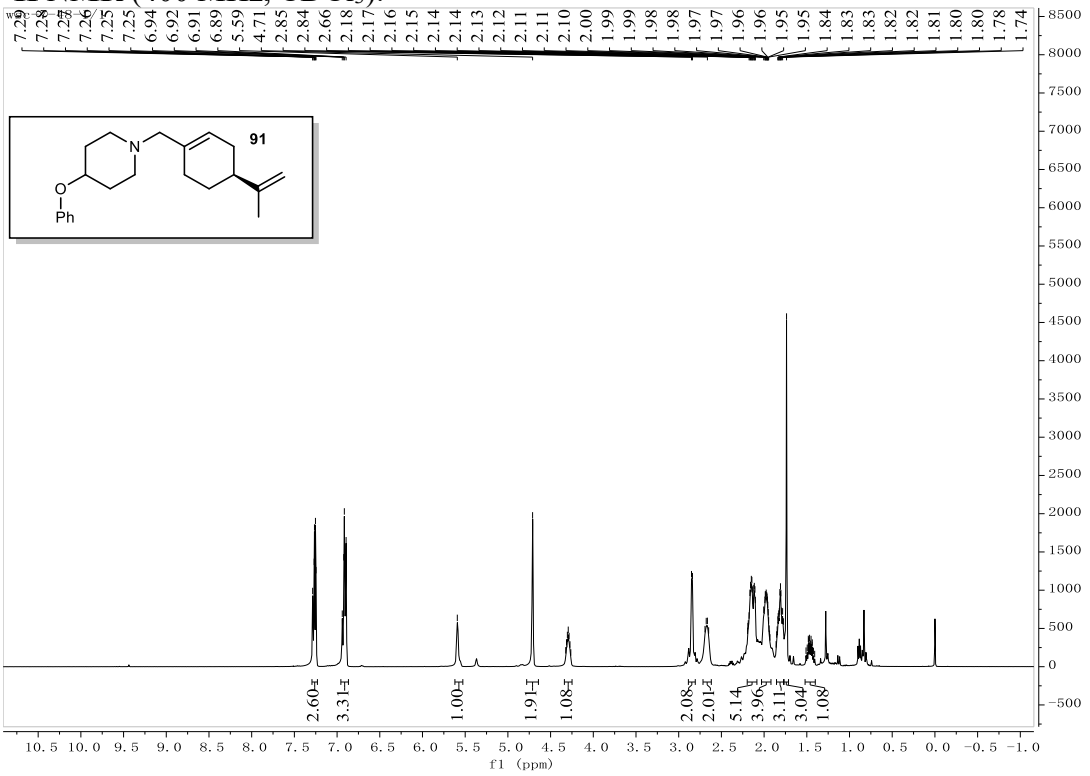

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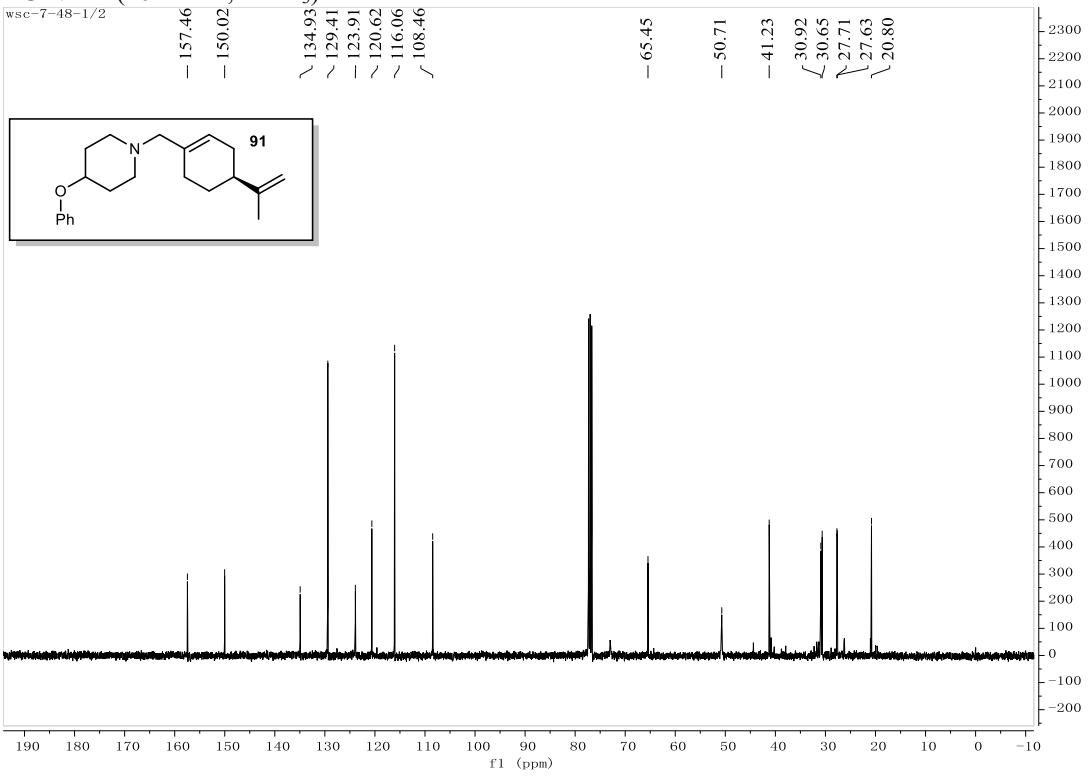

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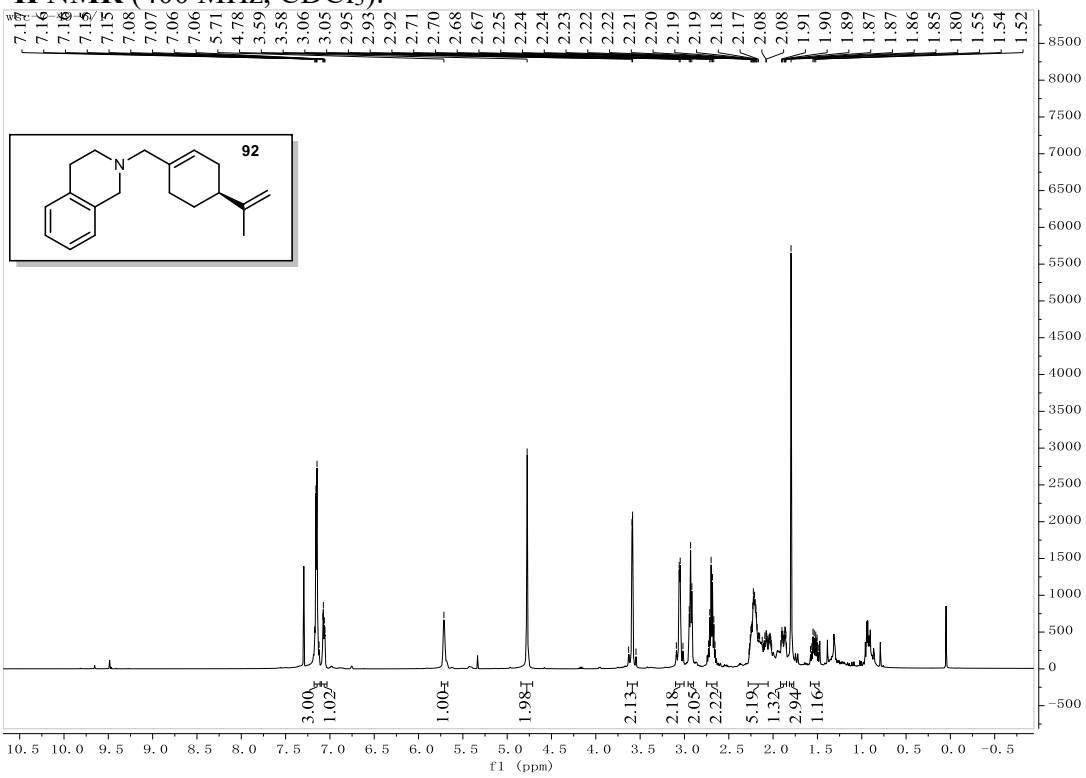

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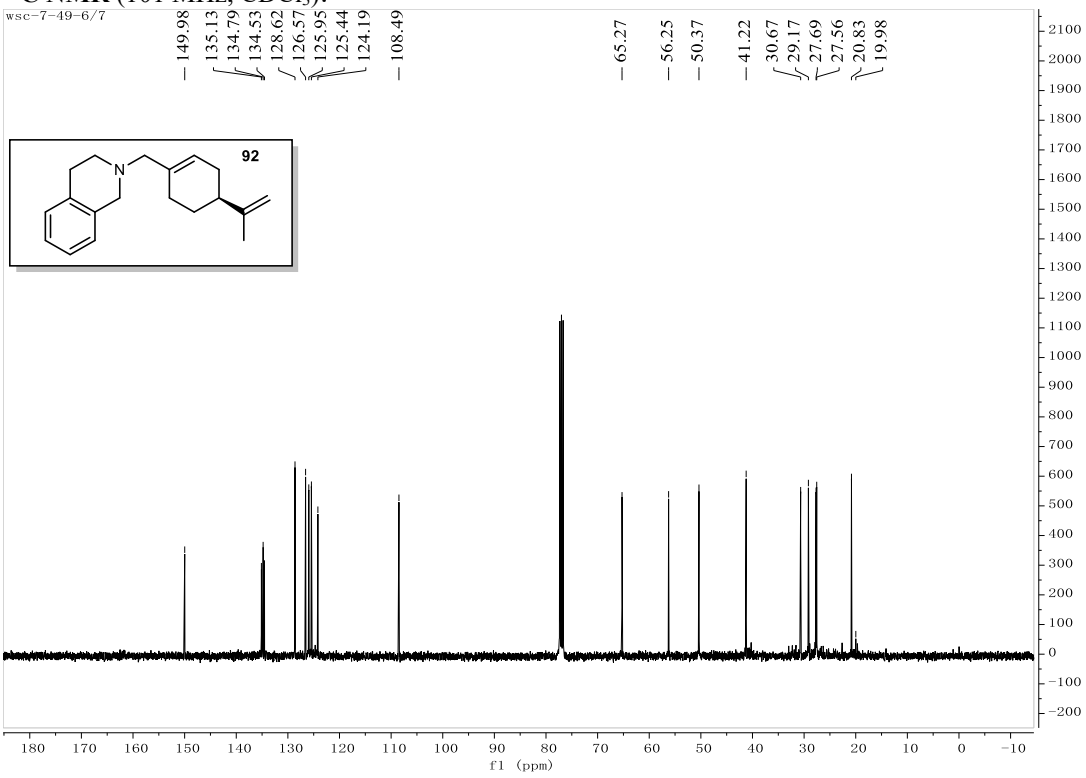

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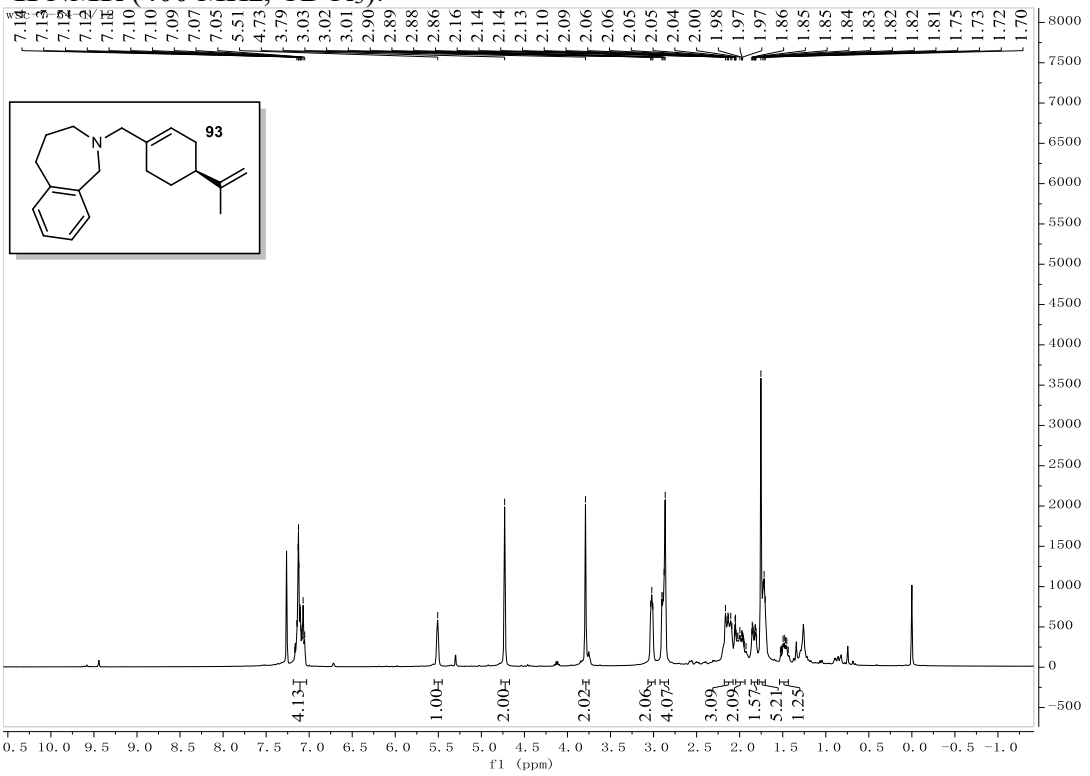

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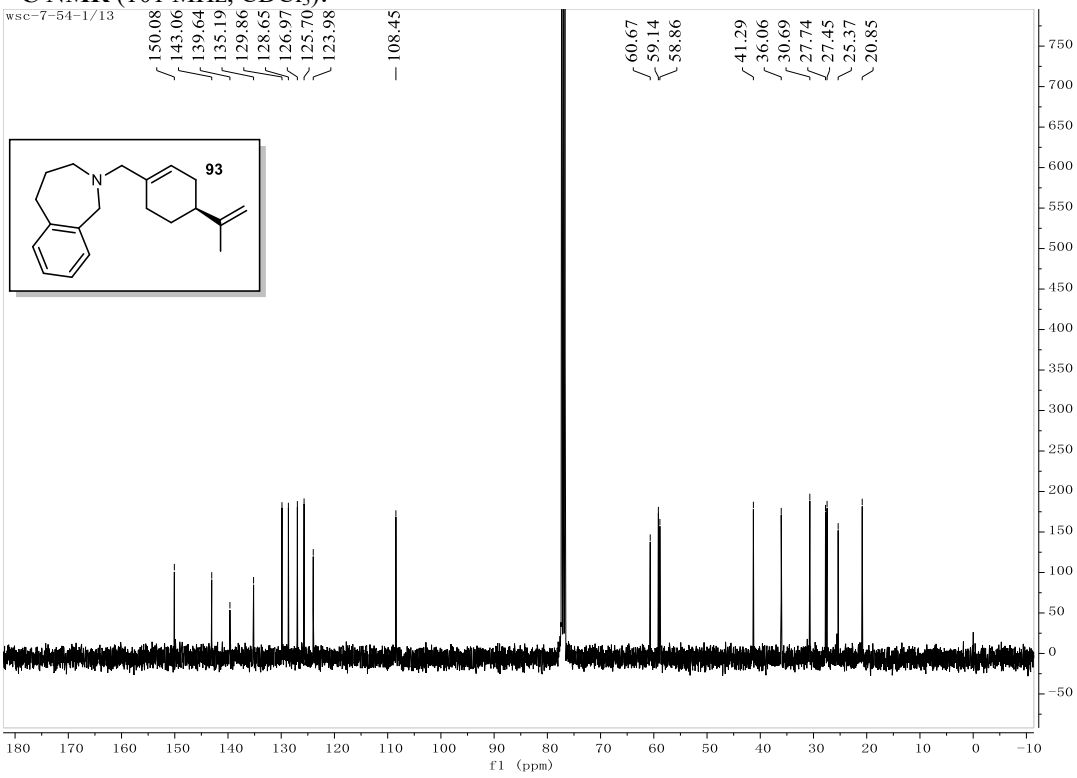
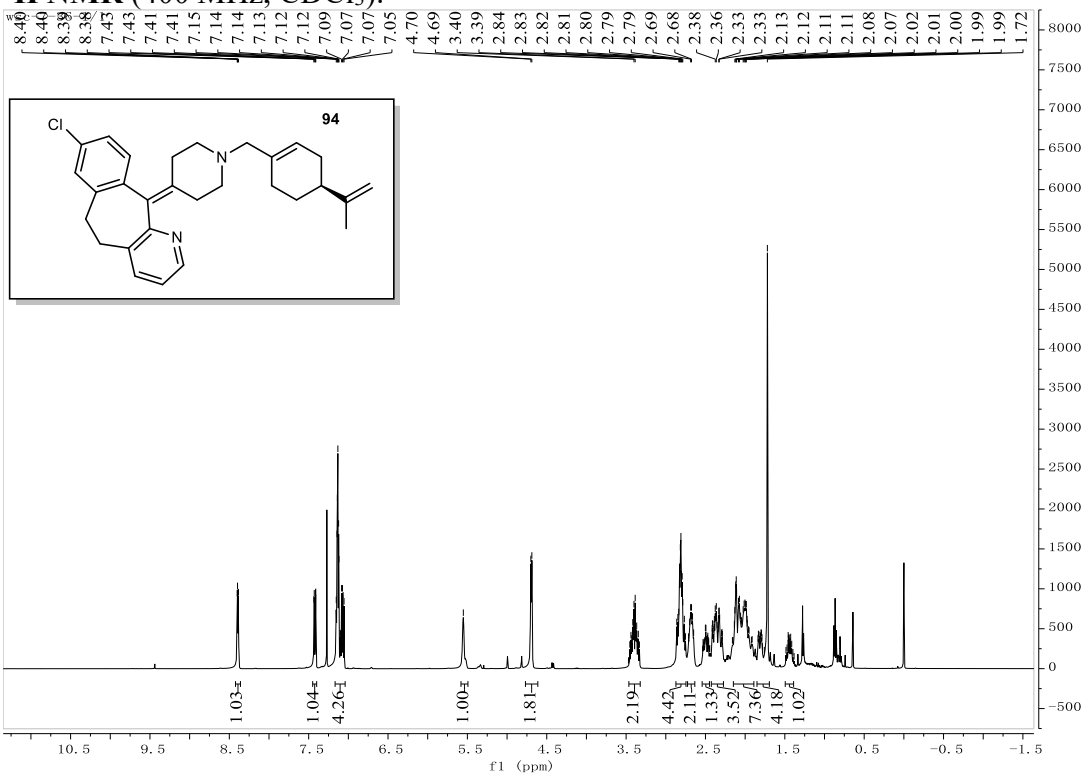


^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):