Supporting Information (SI)

Ruthenium-Catalyzed *ortho* Alkenylation of Aromatics with Alkenes at Room Temperature with Hydrogen Evolution

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Experimental Section

General Procedure for the Alkenylation of Aromatic amides, oximes and anilides with Alkenes catalyzed by Ruthenium Complex.

A 15-mL pressure tube with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added aromatic amides or oximes or anilides **1** or **4** or **6** (100 mg), alkenes **2** (2.0equiv), acetic acid (2.0 equiv) and 1,2-dichloroethane (3.0 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at room temperature (~ 24 °C) for 24 h. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure alkenylated product **3** or **5** or **7**.

The alkenylation reaction can also be done in a round bottom flask under the nitrogen atmosphere.

Note: a) For substrate **3ha**, AcOH (4.0 equiv) was used. b) For compound **3aj**, 1,4-dioxane solvent was used and the reaction was done at 100 °C.

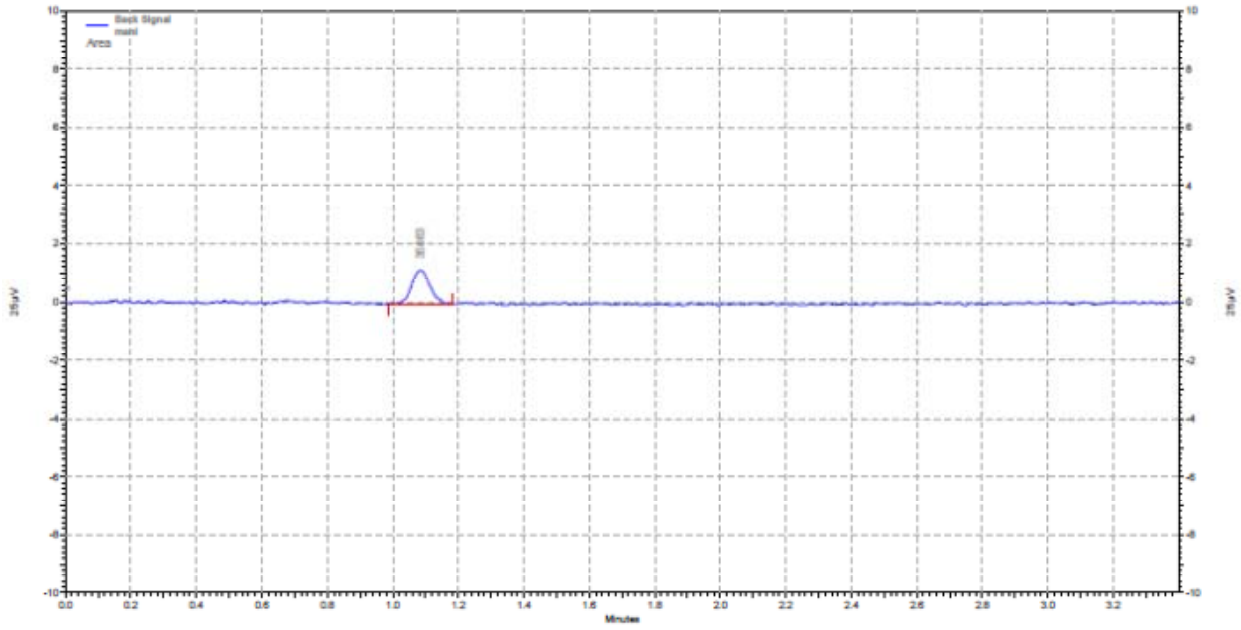
Procedure for the 1.0 Gram Scale Reaction of *N*-methyl benzamide (1a) with methyl acrylate (2a).

A 50 mL single neck round bottom flask with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the flask, were then added *N*-methyl benzamide (**1a**) (1.0 gram), methyl acrylate (**2a**) (2.0 equiv), acetic acid (2.0 equiv) and 1,2-dichloroethane (15.0 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the nitrogen balloon was kept on the septum. The reaction mixture was allowed to stir at room temperature for 24 h. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure alkenylated product **3aa** in 79% yield.

Procedure for the Determination of H_2 gas Evolution by GC.

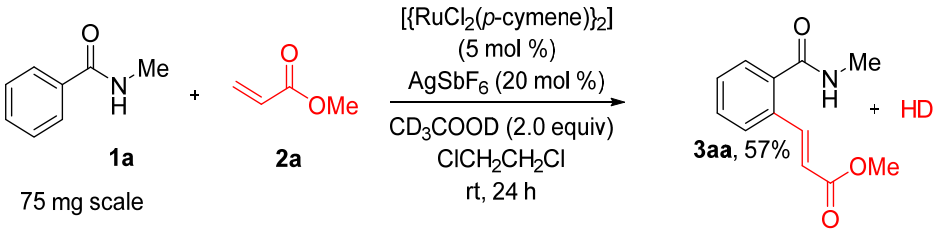
A 25-mL schlenk tube with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added *N*-methyl benzamide (**1a**) (100 mg), methyl acrylate (**2a**) (2.0 equiv), acetic acid (2.0 equiv) and 1,2-dichloroethane (3.0 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was completely covered by Teflon tape. Then, the reaction mixture was allowed to stir at room temperature (~ 24 °C) for 24 h. After that, the gaseous reaction mixture was taken by the syringe and injected into the gas chromatograph (GC) equipped with a TCD detector (Agilent 7890). The characteristic peak for H_2 gas was observed in the exact region (retention time 1-1.2 minutes).

Gas Chromatograph Spectrum



Procedure for the Determination of HD Evolution by Isotope-Ratio Mass Spectrometry (IR-MS).

A 10-mL glass tube with a screw cap containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added *N*-methyl benzamide (**1a**) (75 mg), methyl acrylate (**2a**) (2.0 equiv), acetic acid (2.0 equiv) and 1,2-dichloroethane (2.0 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. Then, the reaction mixture was allowed to stir at room temperature (~ 24 °C) for 24 h. IR-MS (Delta V Plus model) analysis was done with the reaction mixture.



In the spectra, brown line indicating the molecular mass is 2 and it is for H_2 gas.

The green line indicating that the molecular mass is 3 and it is for HD gas.

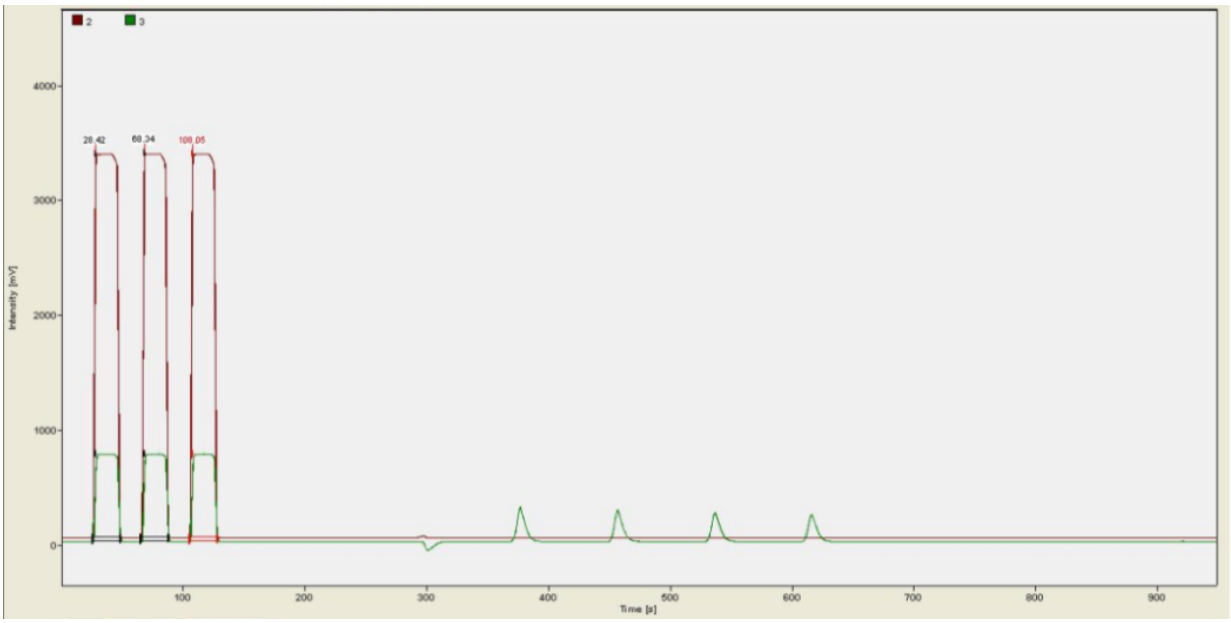
The first 3 peaks are corresponding to the reference gas. The reference gas has both (H_2+HD) mixtures. So that, we observed both brown and green colour peak in a particular ratio. The remaining 4 peaks are corresponding to the reaction mixture. Here, only green colour peaks are observed which clearly indicates that HD gas was formed in the reaction. Generally, in the IR-MS analysis, the instrument takes reference gas 3 times and the reaction mixture gas for 4 times consecutively. Thus, we have observed 3 peaks in the reference region followed by 4 peaks for the reaction mixture.

(**Notes**: It is important to note that the intensity of HD detection in the IR-MS spectrum for the four consecutive injection of reaction mixture is in decreasing order (see the spectra 1 and 2). It is expected that in the first injection concentration of HD is high and in the following peaks intensity could decrease a little bit.

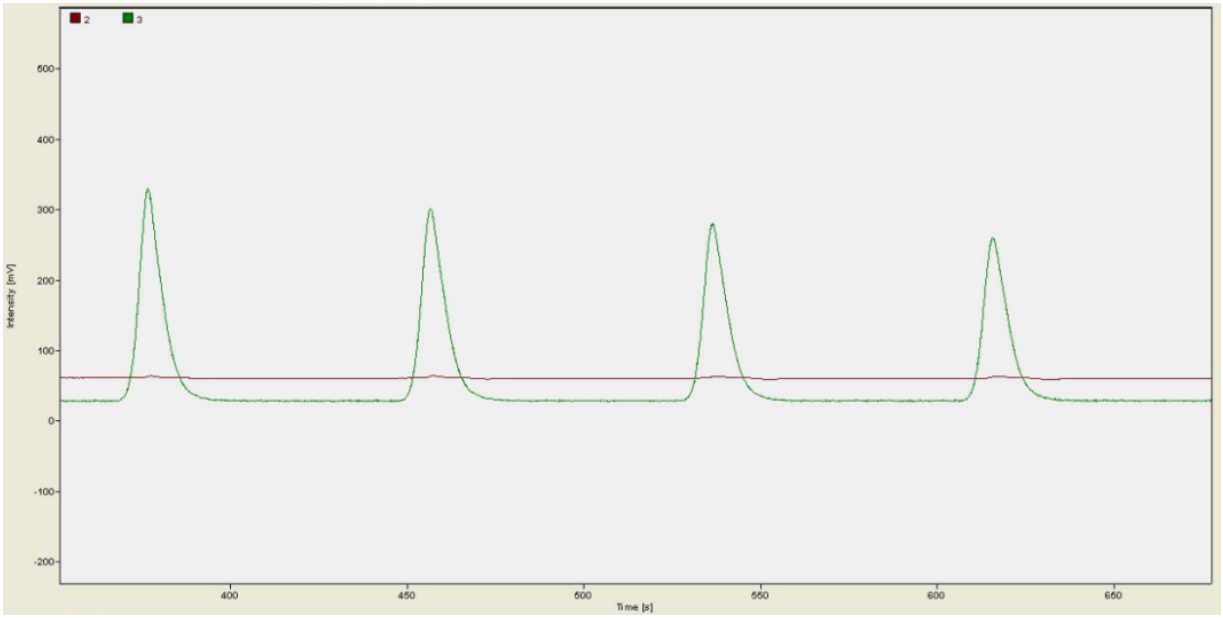
Next, we have tried the same reaction in 150 mg scale of *N*-methyl benzamide (**1a**). Previously, we have done in 75 mg scale corresponding to **1a**. Interestingly, the intensity of HD gas is also increased almost twice in the IR-MS spectra (see spectra 1 and 2). For 75 mg

scale reaction, the intensity of HD gas was around 330 mV. For 150 mg scale reaction, the intensity of HD gas was increased 750 mV. This result clearly indicates that the amount of HD gas production in the reaction is highly depends on the concentration of the reaction.

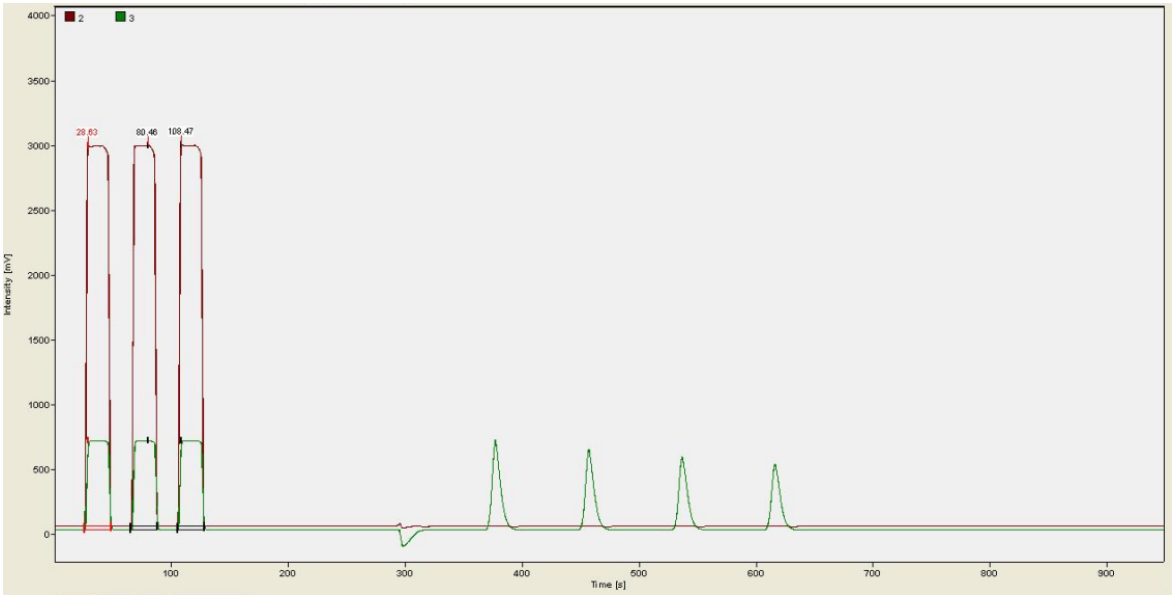
IR-MS Spectra of 75 mg scale reaction (spectra 1)



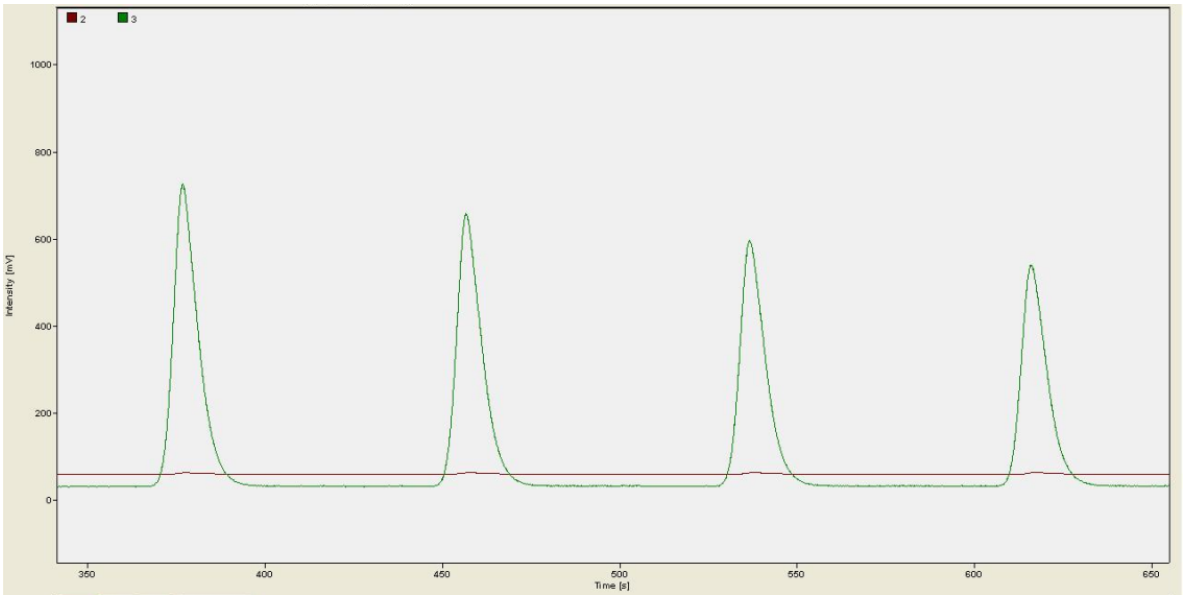
Maximized area for characteristic peak in spectra 1



IR-MS Spectra of 150 mg scale reaction (spectra 2)

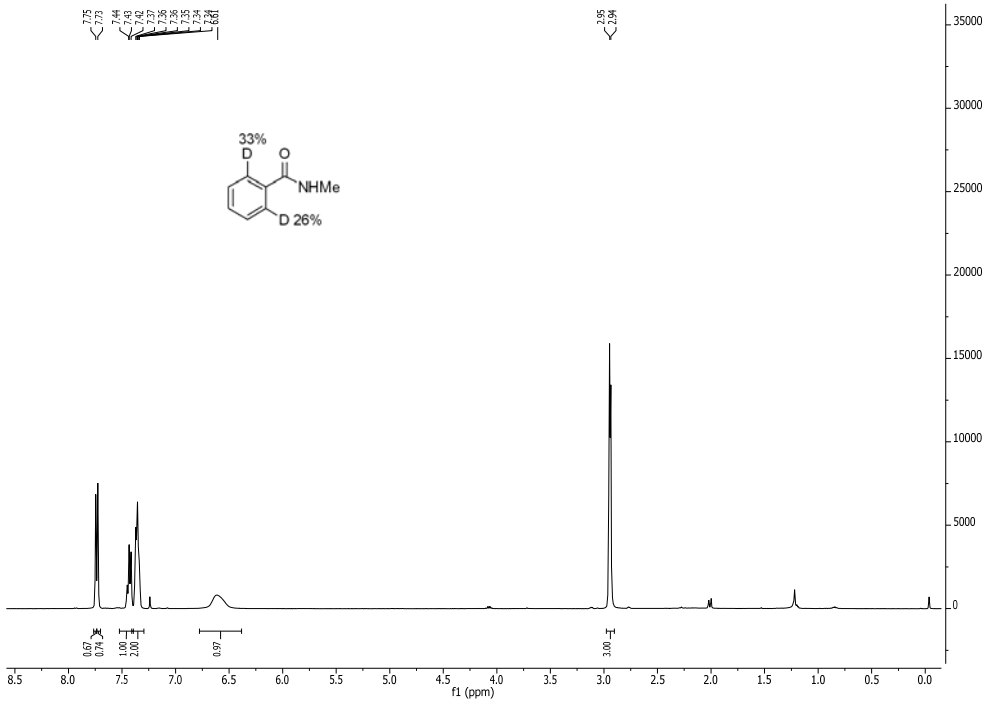


Maximized area for characteristic peak in spectra 2

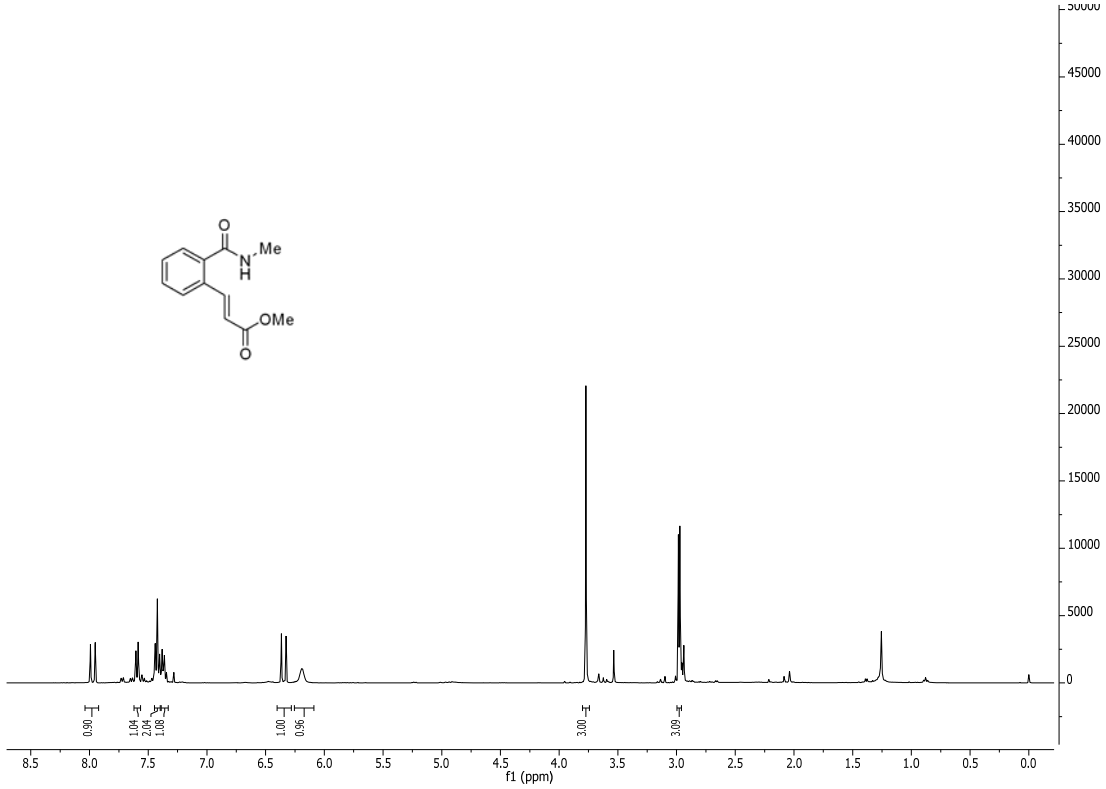


NMR Spectra of the HD Evolution reaction mixture.

^{1}H NMR Spectra of Compound **1a** obtained at the end of the reaction. Deuterium incorporation was observed at both ortho carbons of **1a**.

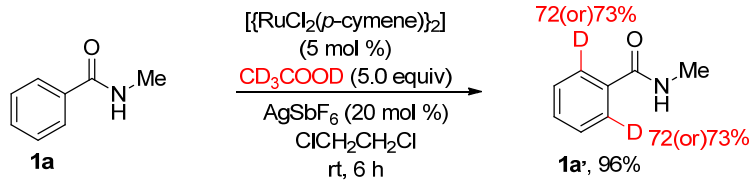


^{1}H NMR Spectra of Compound **3aa** obtained at the end of the reaction. No deuterium incorporation was observed in the compound.

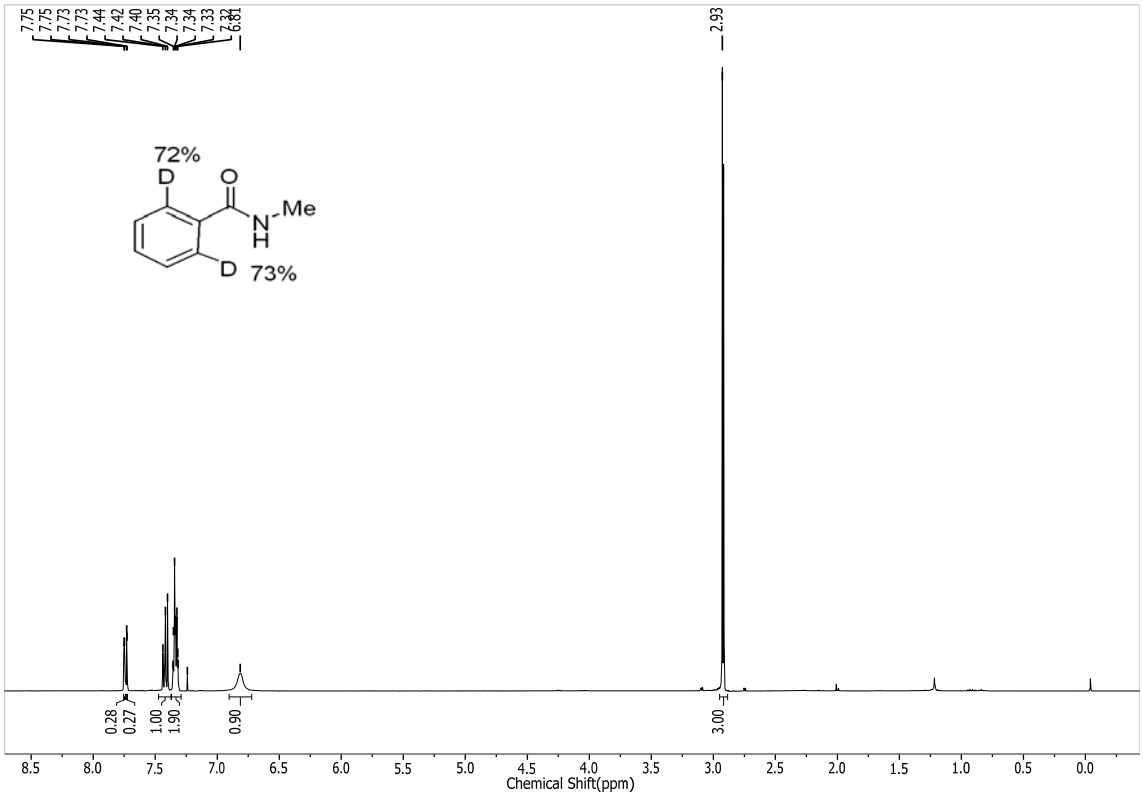


Deuterium studies

To know the feasibility of C-H bond activation of aromatic amide at room temperature, the following deuterium labelling experiment was done. Treatment of **1a** with CD_3COOD in the presence of $[\{RuCl_2(p\text{-cymene})\}_2]$ (5.0 mol %) and $AgSbF_6$ (20 mol %) in 1,2-dichloroethane at room temperature for 6 h gave product **1a'** in 96% yield with 72% and 73% of deuterium incorporation at the both *ortho* carbons. It clearly indicates that the *ortho* C-H bond cleavage of aromatic amide in intermediate **9** is a reversible process.



^{1}H NMR Spectra of Compound **1a'.**

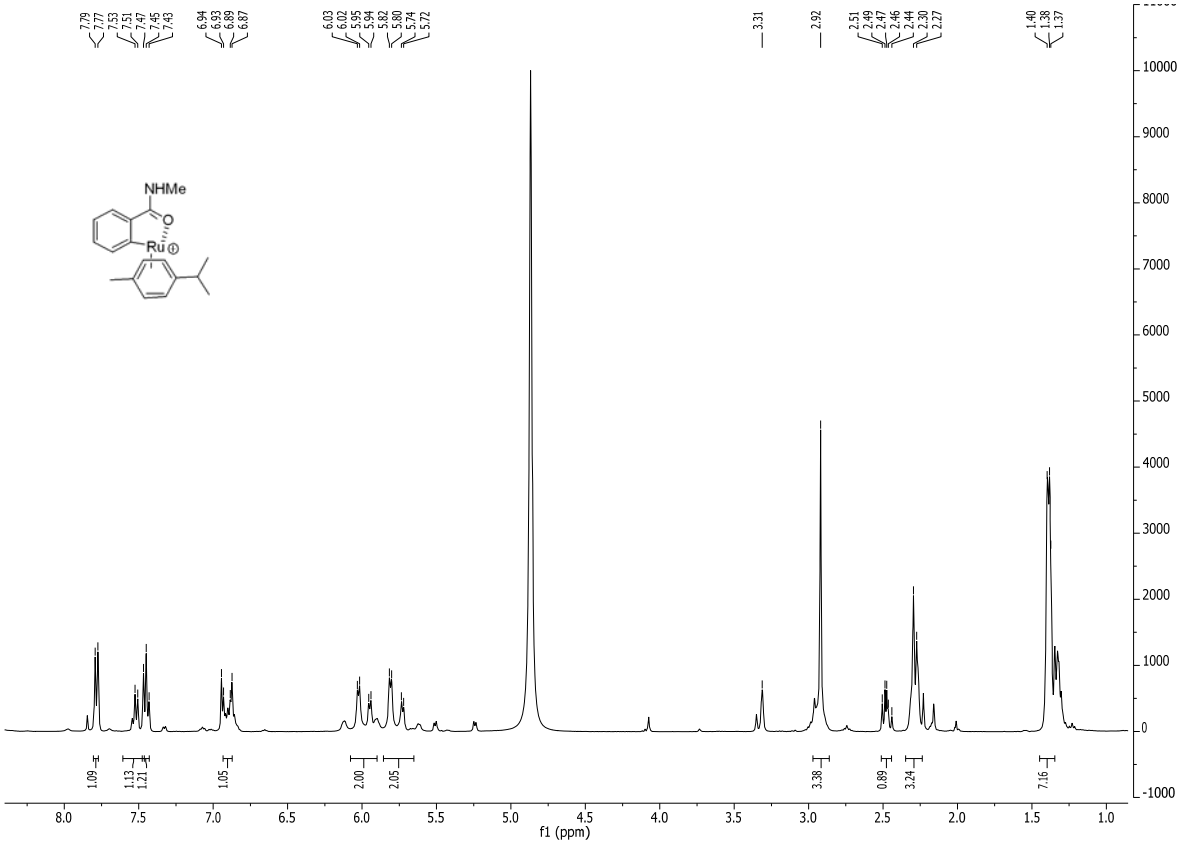


Procedure for the Preparation of a Five-Membered Ruthenacycle Intermediate 9.

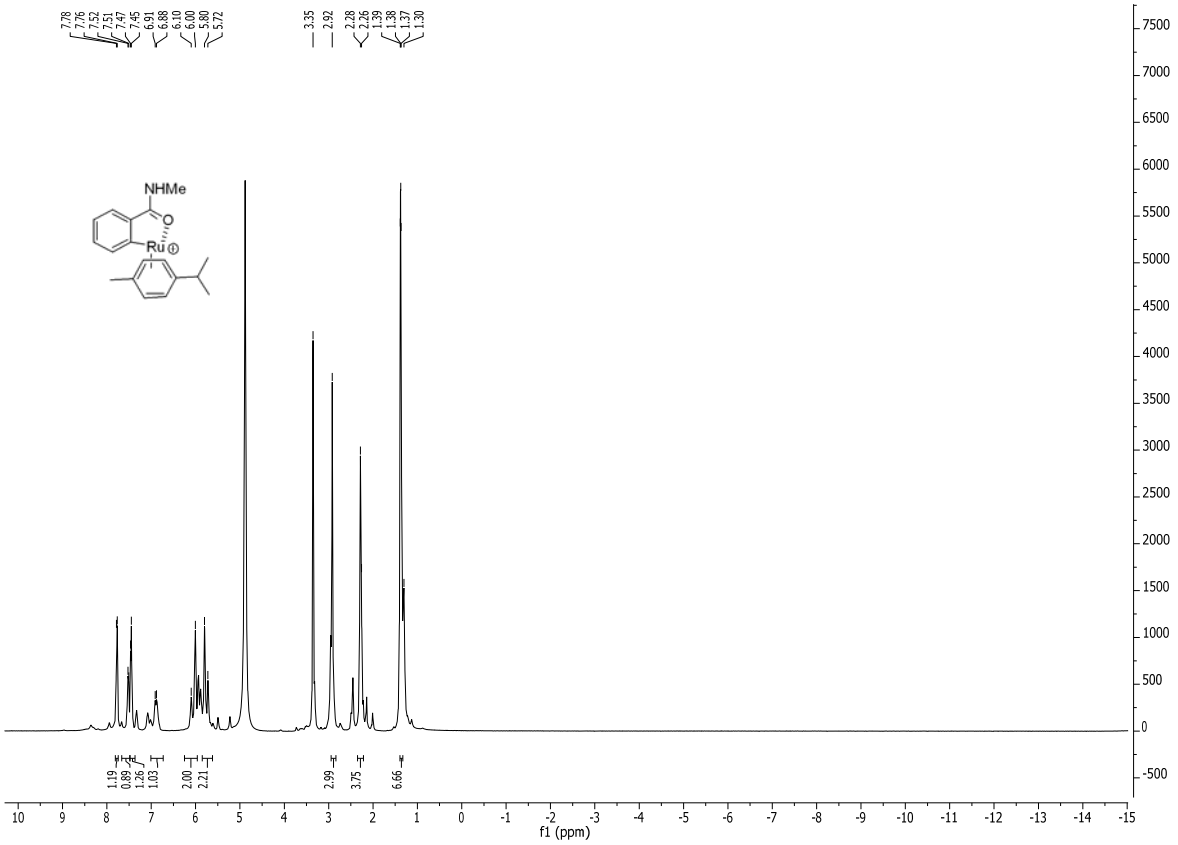
A 25-mL schlenk tube with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (50 mg), and $AgSbF_6$ (4.0 equiv) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added benzamide **1a** (1.0 equiv), AcOH (2.0 equiv) and $ClCH_2CH_2Cl$ (2.0 mL) via syringe and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that the septum was completely covered by Teflon tape. Then, the reaction mixture was allowed to stir at room temperature for 24 h. After the reaction mixture was diluted with methanol, filtered through Celite and the filtrate was concentrated and taken for further analysis without any further purification. We have tried to get a single crystal. However, we could not make it. The NMR spectra was recorded with the crude reaction mixture without further purification.

NMR Data

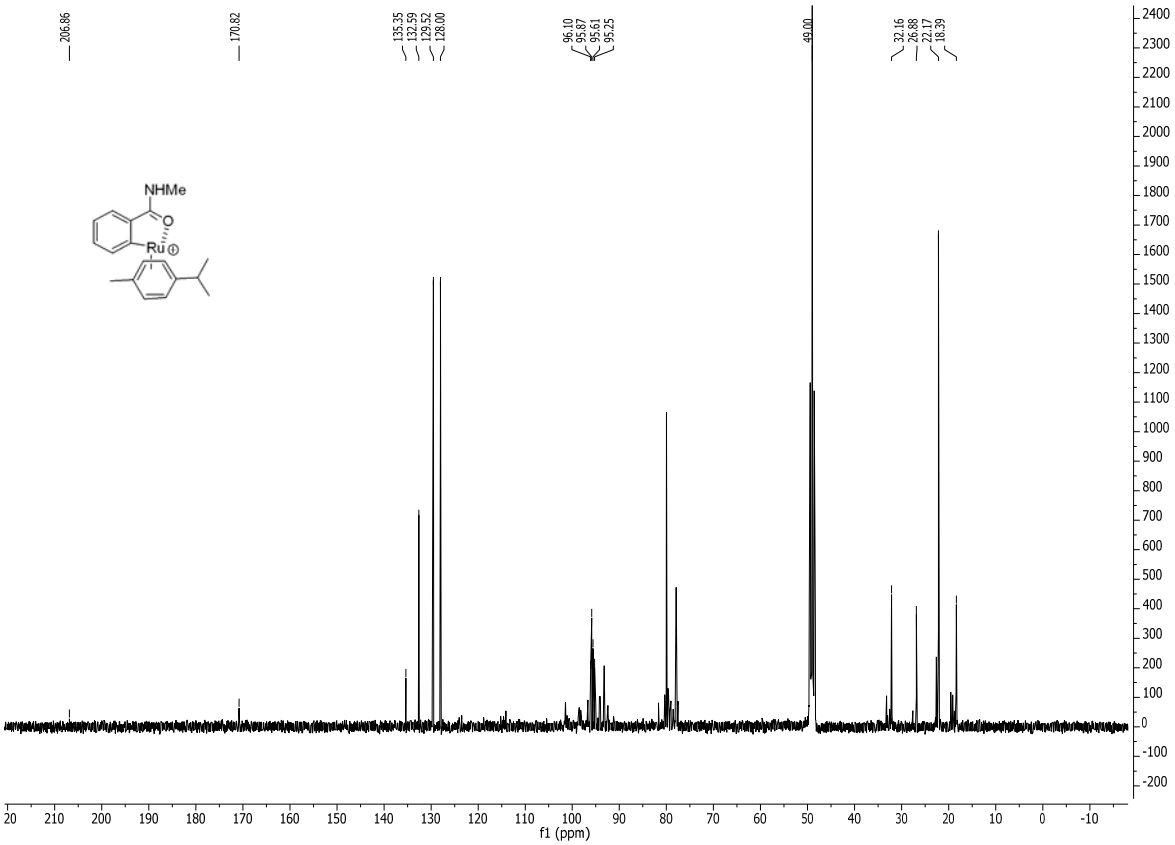
^{1}H NMR Spectra of Complex **9.**



^{1}H NMR Spectra of Complex **9** (Included negative region).

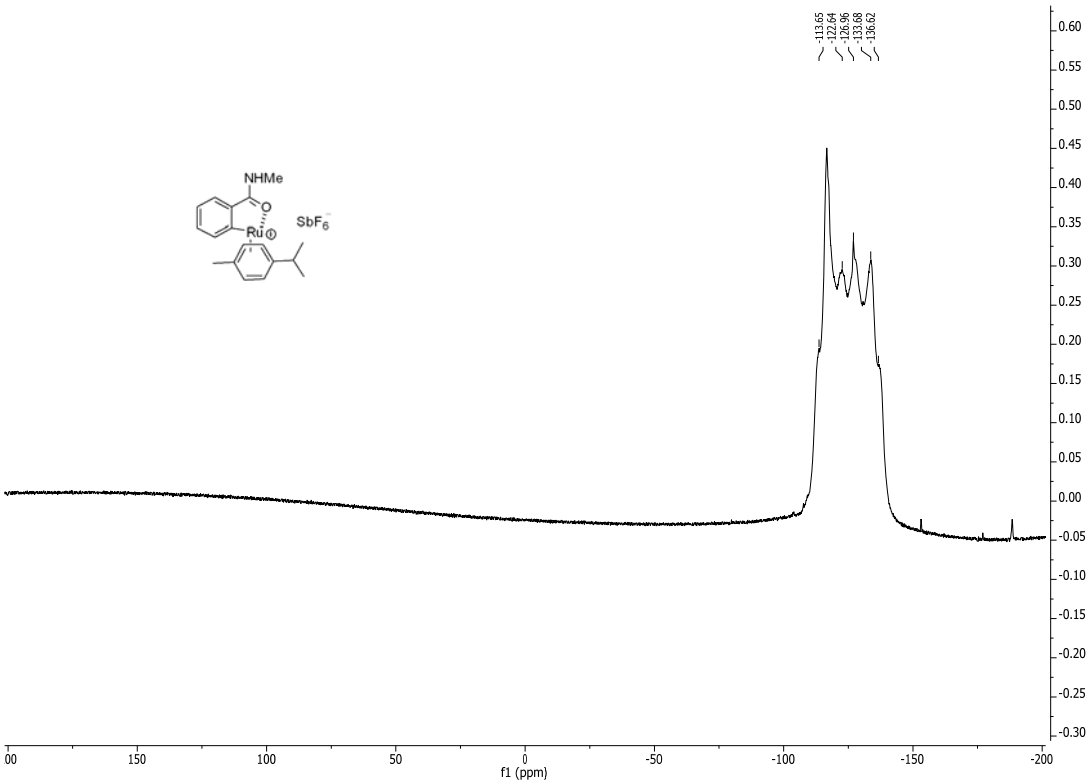


^{13}C NMR Spectra of Complex **9**

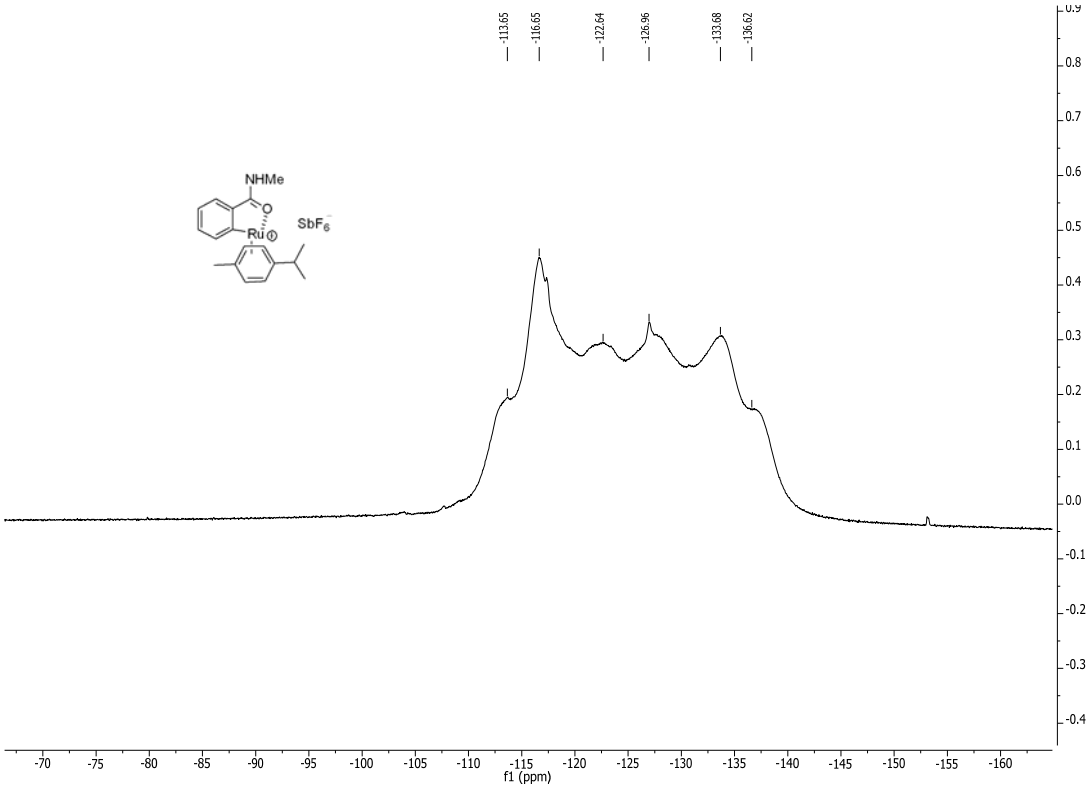


Note: In ^{13}C NMR, a characteristic C-Ru peak found at δ 206.86 due to the deshilding of C-Ru.

^{19}F NMR Spectra of Complex **9**



^{19}F NMR Spectra of Complex **9** (expansion)

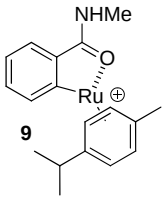


MALDI-TOF spectra of complex 9

Chemical formula of complex **9**: **[**$C_{18}H_{22}NORu$]

Calculated mass: 370.0739

Found: 370.1141



9

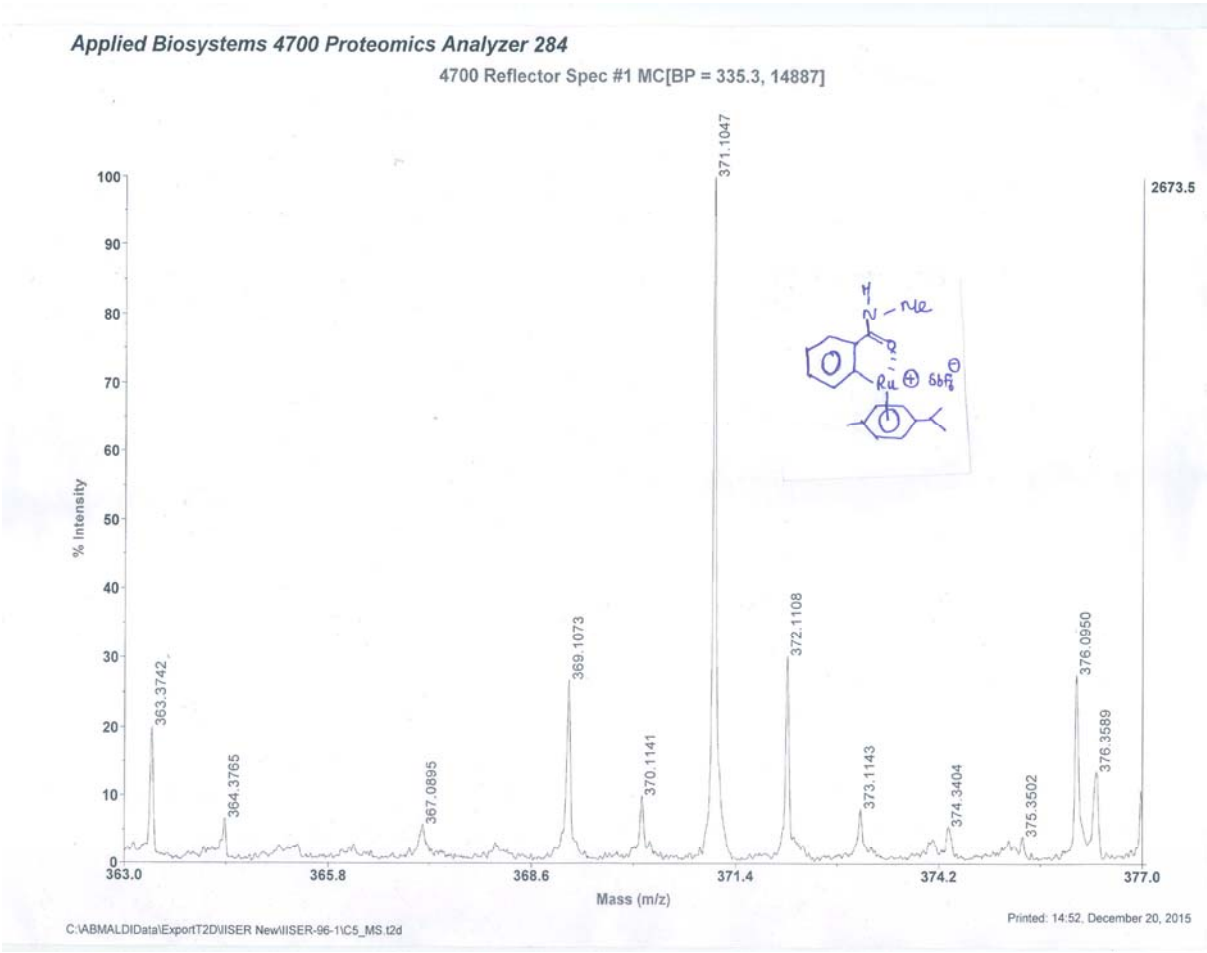
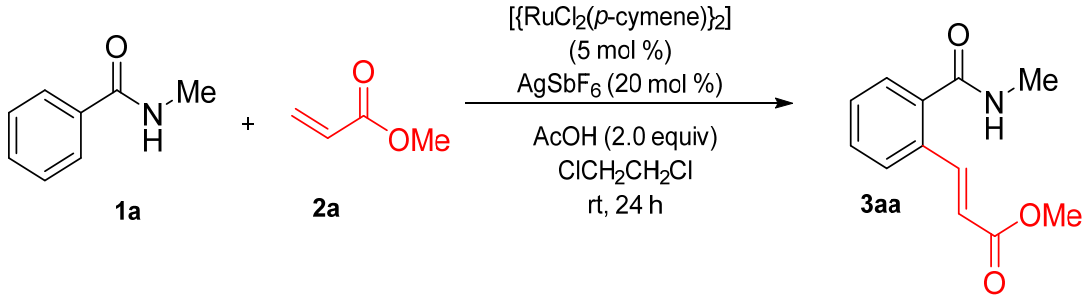


Table S1. Optimization Studies[a]



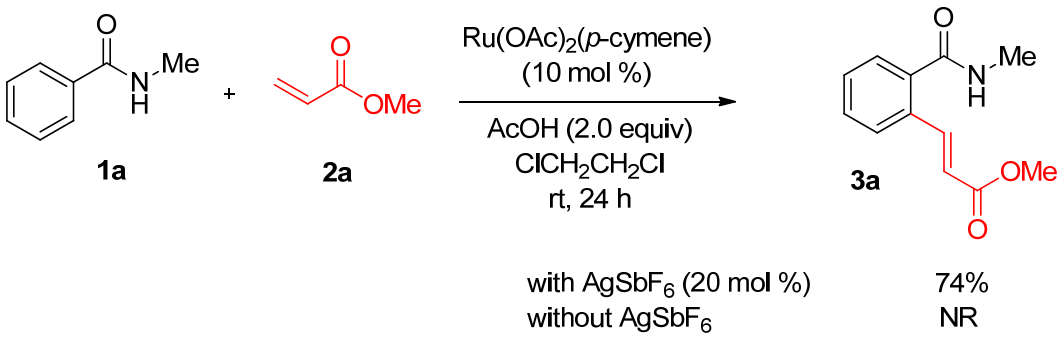
Entry	Solvent	Acid source	Additive	Yield of **3aa** (%)[b]
1	Acetonitrile	Acetic acid (2.0equiv)	$AgSbF_6$	NR
2	Methanol	Acetic acid (2.0 equiv)	$AgSbF_6$	NR
3	THF	Acetic acid (2.0 equiv)	$AgSbF_6$	52
4	DME	Acetic acid (2.0 equiv)	$AgSbF_6$	54
5	1,4-dioxane	Acetic acid (2.0 equiv)	$AgSbF_6$	40
6	DMF	Acetic acid (2.0 equiv)	$AgSbF_6$	NR
7	Water	Acetic acid (2.0 equiv)	$AgSbF_6$	NR
8	Toluene	Acetic acid (2.0 equiv)	$AgSbF_6$	NR
9	$ClCH_2CH_2Cl$	Acetic acid (2.0 equiv)	$AgSbF_6$	81
10	$ClCH_2CH_2Cl$	Acetic acid (1.0 equiv)	$AgSbF_6$	74
11	$ClCH_2CH_2Cl$	Pivalic acid (2.0 equiv)	$AgSbF_6$	69
12	$ClCH_2CH_2Cl$	Adamantane carboxylic acid (1.0 equiv)	$AgSbF_6$	61
13	$ClCH_2CH_2Cl$	Mesitylinic acid (1.0 equiv)	$AgSbF_6$	64
14	$ClCH_2CH_2Cl$	Benzoic acid (1.0 equiv)	$AgSbF_6$	38
15	$ClCH_2CH_2Cl$	Acetic acid (2.0 equiv)	AgOTf	64
16	$ClCH_2CH_2Cl$	Acetic acid (2.0 equiv)	$AgBF_4$	52
17	$ClCH_2CH_2Cl$	Acetic acid (2.0 equiv)	KPF_6	NR
18	$ClCH_2CH_2Cl$	Acetic acid (2.0 equiv)	$CuBF_4$	NR

[a]All reactions were carried out under the following conditions: **1a** (100 mg), **2a** (2.0equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (5mol %), additive (20 mol %) andsolvent (3.0 mL) at rt for 24 h under the N_2 atmosphere. [b] Isolated yield.

Note: The catalytic reaction was tried without ruthenium and $AgSbF_6$. No product **3aa** was observed in the reaction.

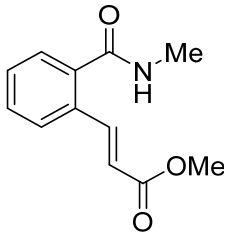
We have tried the *ortho* alkenylation of **1a** with methyl acrylate (**2a**) in the presence of a catalytic amount of $Ru(OAc)_2$(*p*-cymene) (10 mol %), $AgSbF_6$ (20 mol %) and AcOH (2.0 equiv) in $ClCH_2CH_2Cl$ at room temperature for 24 h. In the reaction, the expected *ortho* alkenylated benzamide **3aa** was observed in 74% yield. But, the same reaction does not

proceed without $AgSbF_6$. This result clearly reveals that the $AgSbF_6$ is crucial for the reaction. In the reaction, $AgSbF_6$ acts as a halogen scavenger as well as forming the active cationic ruthenium species **8** for the catalytic reaction.



Spectral Data of All Compounds.

Methyl (*E*)-3-(2-(methylcarbamoyl)phenyl)acrylate (3aa).



White solid; eluent (29% ethylacetate in hexanes).The reaction scale is 100mg (**1a)**, 132mg of product was isolated and yield is 81%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, *J* = 16.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 2.92 (s, 3H).

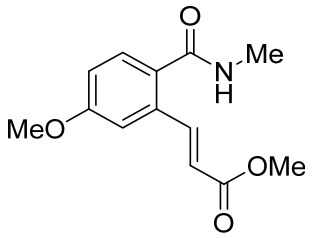
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5,166.9, 142.1, 136.9, 132.5, 130.1, 129.7, 127.4, 126.9, 119.9, 51.6, 26.7.

HRMS (ESI): calc. for [($C_{12}H_{13}NO_3$)Na] (M+Na) 242.0793, measured 242.0798.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3281, 2978, 2360, 1705, 1628, 1545, 1264, 1040, 763.

Rf (hexane/ethyl acetate = 2:1): 0.31.

Methyl (*E*)-3-(5-methoxy-2-(methylcarbamoyl)phenyl)acrylate (3ba).



White solid; eluent (32% ethylacetate in hexanes).The reaction scale is 100mg (**1b)**, 69mg of product was isolated and yield is 46%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.0Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.33 (d, *J* = 16.0.Hz, 1H), 5.84 (s, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 2.97 (d, *J* = 4.0 Hz, 3H).

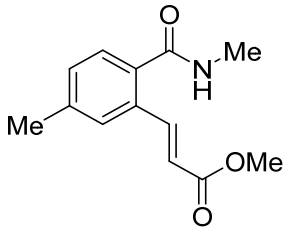
^{13}C NMR ($CDCl_3$, 100 MHz):δ168.9, 166.8, 160.9, 142.5, 134.9, 129.5, 129.3, 120.5, 115.3, 112.2, 55.4, 51.8, 26.9.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_4$)Na] (M+Na) 272.0899, measured 272.0906.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3301, 3080, 2948, 1710, 1624, 1540, 1284, 1033, 863.

Rf (hexane/ethyl acetate = 1:1): 0.61.

Methyl (*E*)-3-(5-methyl-2-(methylcarbamoyl)phenyl)acrylate (3ca).



White solid; eluent (29% ethylacetate in hexanes).The reaction scale is 100mg (**1c**), 122mg of product was isolated and yield is 78%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, *J* = 16.0 Hz, 1H), 7.37 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.15 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.00 (s, 1H), 3.75 (s, 3H), 2.95 (d, *J* = 4.0 Hz, 3H), 2.34 (s, 3H).

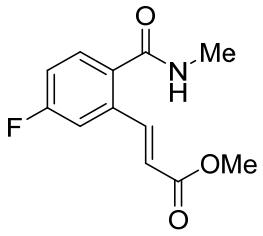
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 166.9, 142.3, 140.5, 134.2, 132.8, 130.5, 127.7, 127.6, 120.0, 51.7, 26.9, 21.3.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_3$)Na] (M+Na) 256.0950, measured 256.0954.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3294, 2950, 1707, 1627, 1545, 1432, 1219, 1034, 705.

Rf (hexane/ethyl acetate = 1:1): 0.65.

Methyl (*E*)-3-(5-fluoro-2-(methylcarbamoyl)phenyl)acrylate (3da).



White solid; eluent (27% ethylacetate in hexanes).The reaction scale is 100mg (**1d**), 110mg of product was isolated and yield is 71%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, *J* = 16.0 Hz, 1H), 7.47 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.29 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.07 (td, *J* = 8.0, 4.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.11 (s, 1H), 3.80 (s, 3H), 3.00 (d, *J* = 4.0 Hz, 3H).

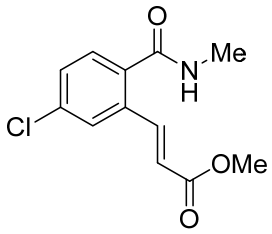
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 166.5, 164.6, 162.1, 141.0 and 140.9 (F-coupling), 135.4, 133.2, 129.7, 121.4, 116.8 and 116.6(F-coupling), 113.9 and 113.6(F-coupling), 51.9, 26.9.

HRMS (ESI): calc. for [($C_{12}H_{12}FNO_3$)Na] (M+Na) 260.0699, measured 260.0711.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3285, 3079, 2923, 1718, 1633, 1550, 1318, 1265, 1162, 1010.

Rf (hexane/ethyl acetate = 2:1): 0.32.

Methyl (*E*)-3-(5-chloro-2-(methylcarbamoyl)phenyl)acrylate (3ea).



White solid; eluent (26% ethylacetate in hexanes).The reaction scale is 100mg (**1e**), 96mg of product was isolated and yield is 64%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 16.0 Hz, 1H), 7.55 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 5.92 (s, 1H), 3.77 (s, 3H), 2.98 (d, *J* = 6.0 Hz, 3H).

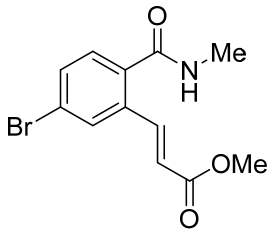
^{13}C NMR ($CDCl_3$, 100 MHz):δ168.3, 166.5, 140.7, 136.4, 135.2, 134.6, 129.7, 128.9, 127.1, 121.5, 51.9, 26.9.

HRMS (ESI): calc. for [($C_{12}H_{12}ClNO_3$)H] (M+H) 254.0584, measured 254.0593.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3280, 2947, 1717, 1634, 1554, 1264, 1040.

Rf (hexane/ethyl acetate = 2:1): 0.37.

Methyl (*E*)-3-(5-bromo-2-(methylcarbamoyl)phenyl)acrylate (3fa).



Pale yellow solid; eluent (29% ethylacetate in hexanes).The reaction scale is 100mg (**1f**), 85mg of product was isolated and yield is 61%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 16.0 Hz, 1H), 7.74 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.25 (m, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.08 (s, 1H), 3.81 (s, 3H), 3.00 (d, *J* = 6.0 Hz, 3H).

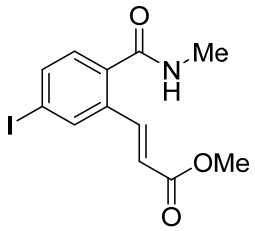
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.3, 166.5, 140.6, 135.6, 134.8, 132.6, 130.0, 129.1, 124.6, 121.5, 51.9, 26.9.

HRMS (ESI): calc. for [($C_{12}H_{12}BrNO_3$)Na] (M+Na) 319.9898, measured 319.9912.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3281, 3075, 2947, 1719, 1637, 1555, 1312, 1167, 1006.

Rf (hexane/ethyl acetate = 2:1): 0.34.

Methyl (*E*)-3-(5-iodo-2-(methylcarbamoyl)phenyl)acrylate (3ga).



White solid; eluent (28% ethylacetate in hexanes).The reaction scale is 100mg (**1g**), 73mg of product was isolated and yield is 55%.

^{1}H NMR (DMSO d_6, 400 MHz):δ 8.48 (d, J = 4.0 Hz, 1H), 8.25 (d, J = 4.0 Hz, 1H), 7.83 (dd, J = 8.0, 4.0 Hz, 1H), 7.78 (d, J = 16.0 Hz, 1H), 7.22 (d, J = 8.0Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H), 3.72 (s, 3H), 2.76 (d, J = 4.0 Hz, 3H).

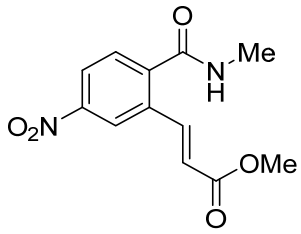
^{13}C NMR (DMSO d_6, 100 MHz): δ 167.8, 166.3, 140.5, 140.91, 138.4, 136.9, 133.9, 129.5, 120.5, 96.7, 51.6, 26.1.

HRMS (ESI): calc. for [($C_{12}H_{12}INO_3$)Na] (M+Na) 367.9760, measured 367.9764.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3288, 2957, 1719, 1634, 1554, 1264, 1042.

Rf (hexane/ethyl acetate = 2:1): 0.33.

Methyl (*E*)-3-(2-(methylcarbamoyl)-5-nitrophenyl)acrylate (3ha).



White solid; eluent (27% ethylacetate in hexanes).The reaction scale is 100mg (**1h**), 78mg of product was isolated and yield is 53%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, J = 4.0 Hz, 1H), 8.21 (dd, J = 8.0, 4.0 Hz, 1H), 7.90 (d, J = 16.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.09 (s, 1H), 3.79 (s, 3H), 3.02 (d, J = 4.0 Hz, 3H).

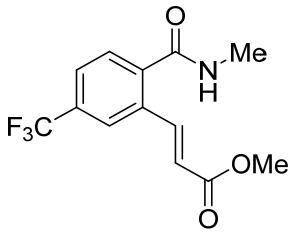
^{13}C NMR (DMSO d_6, 100 MHz):δ166.9, 166.1, 148.3, 142.9, 139.7, 133.4, 129.3, 128.6, 124.3, 123.5, 122.2, 121.8, 51.8, 26.1.

HRMS (ESI): calc. for [($C_{12}H_{12}N_2O_5$)Na] (M+Na) 287.0644, measured 287.0651.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3292,3081, 2949, 1714, 1638, 1549, 1279, 788.

Rf (hexane/ethyl acetate = 2:1): 0.39.

Methyl (*E*)-3-(2-(methylcarbamoyl)-5-(trifluoromethyl)phenyl)acrylate (3ia).



White solid; eluent (31% ethylacetate in hexanes).The reaction scale is 100mg (**1i**), 98 mg of product was isolated and yield is 69%.

^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.82 (s, 1H),7.61 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.56 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.94 (s, 1H), 3.78 (s, 3H), 3.01 (d, *J* = 8.0 Hz, 3H).

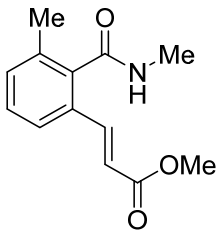
^{13}C NMR ($CDCl_3$, 100 MHz):δ168.0, 166.4, 140.4, 139.9, 133.6, 132.7, 132.3, 128.2, 126.3 and 126.2, (F-coupling), 124.1, 122.2, 51.9, 26.9.

HRMS (ESI): calc. for [($C_{13}H_{12}F_3NO_3$)H] (M+H) 288.0848, measured 288.0856.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3283, 2939, 1718, 1631, 1554, 1264, 1162.

Rf (hexane/ethyl acetate = 2:1): 0.31.

Methyl (*E*)-3-(3-methyl-2-(methylcarbamoyl)phenyl)acrylate (3ja).



White solid; eluent (29% ethylacetate in hexanes).The reaction scale is 100mg (**1j**), 109mg of product was isolated and yield is 70%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 5.74 (s, 1H), 3.75 (s, 3H), 3.02 (d, *J* = 4.0 Hz, 3H), 2.32 (s, 3H).

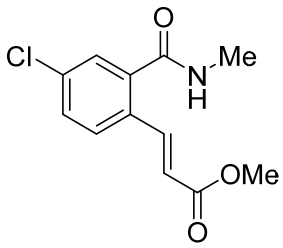
^{13}C NMR ($CDCl_3$, 100 MHz): δ169.6, 166.9, 141.7, 138.1, 135.3, 131.8, 131.4, 129.0, 123.8, 120.0, 51.7, 26.5, 19.1.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_3$)H] (M+H) 256.0950, measured 256.0958.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3293, 2949, 1707, 1634, 1545, 1214, 1034.

Rf (hexane/ethyl acetate = 2:1): 0.38.

Methyl (*E*)-3-(4-chloro-2-(methylcarbamoyl)phenyl)acrylate (3ka).



White solid; eluent (27% ethylacetate in hexanes).The reaction scale is 100mg (**1k**), 101mg of product was isolated and yield is 68%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 5.95 (s, 1H), 3.77 (s, 3H), 2.99 (d, *J* = 4.0 Hz, 3H).

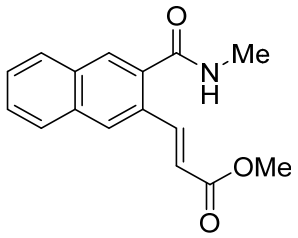
^{13}C NMR ($CDCl_3$, 100 MHz):δ167.8, 166.6, 140.8, 138.4, 135.8, 131.2, 130.4, 128.5, 127.8, 120.8, 51.8, 26.9.

HRMS (ESI): calc. for [($C_{12}H_{12}ClNO_3$)Na] (M+Na) 276.0403, measured 276.0407.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3280, 2947, 1718, 1631, 1559, 1312, 1040.

Rf (hexane/ethyl acetate = 2:1): 0.41.

Methyl (*E*)-3-(2-(methylcarbamoyl)naphthalen-2-yl)acrylate (3la).



White solid; eluent (26% ethylacetate in hexanes).The reaction scale is 100mg (**1l**), 114mg of product was isolated and yield is 78%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 16.0 Hz, 1H),8.03 (s, 1H), 7.91 (s, 1H), 7.83(dd, *J* = 8.0, 4.0 Hz, 1H), 7.79 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.52 (t, *J* = 4.0 Hz, 1H), 7.53 (t, *J* = 4.0 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.06 (s, 1H), 3.79 (s, 3H), 3.04 (d, *J* = 8.0 Hz, 3H).

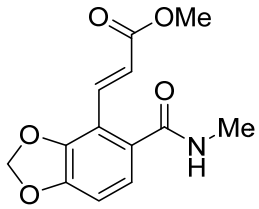
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 166.9, 142.6, 136.9, 133.9, 133.4, 132.9, 130.1, 128.2, 128.0, 127.8, 127.7, 127.5, 120.0, 51.7, 26.9.

HRMS (ESI): calc. for [($C_{16}H_{15}NO_3$)Na] (M+Na) 292.0950, measured 292.0958.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3279, 3054, 2941, 1710, 1624, 1545, 1302, 1159, 1034, 747.

Rf (hexane/ethyl acetate = 2:1): 0.33.

Methyl (*E*)-3-(5-(methylcarbamoyl)benzo[*d*][1,3]dioxol-4-yl)acrylate (3ma).



White solid; eluent (32% ethylacetate in hexanes).The reaction scale is 100 mg (**1m**), 91 mg of product was isolated and yield is 62%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.27 (s, 1H), 6.05 (s, 2H), 3.74 (d, *J* = 4.0 Hz, 3H), 2.93 (d, *J* = 4.0 Hz, 3H).

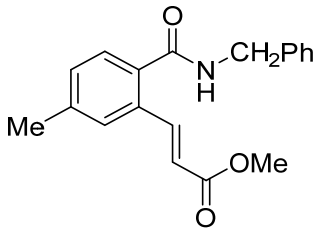
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 167.4, 149.1, 147.1, 136.6, 130.8, 123.1, 121.7, 115.7, 108.6, 101.9, 51.7, 26.9.

HRMS (ESI): calc. for [($C_{13}H_{13}NO_5$)Na] (M+Na) 286.0691, measured 286.0702.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3295, 2947, 1707, 1635, 1548,1449, 1301, 1170, 901, 823.

Rf (hexane/ethyl acetate = 1:1): 0.41.

Methyl (*E*)-3-(2-(benzylcarbamoyl)-5-methylphenyl)acrylate (3na).



White solid; eluent (28% ethylacetate in hexanes).The reaction scale is 100mg (**1n**), 70mg of product was isolated and yield is 51%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, *J* = 16.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 4.0 Hz, 3H), 7.33 (s, 1H), 7.28 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.16 (d,*J* = 8.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.14 (s, 1H), 4.60 (s, 2H), 3.76 (s, 3H), 2.35 (s, 3H).

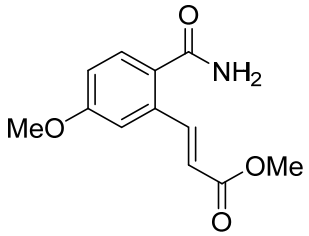
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.5, 166.9, 142.4, 140.6, 137.8, 133.9, 132.9, 130.5, 128.8, 127.9, 127.8, 127.7, 127.6, 120.2, 51.7, 44.2, 21.3.

HRMS (ESI): calc. for [($C_{19}H_{19}NO_3$)H] (M+H) 310.1443, measured 310.1454.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3311, 2937, 1724, 1628, 1543, 1310, 1130, 975, 760.

Rf (hexane/ethyl acetate = 2:1): 0.40.

Methyl (*E)*-3-(2-carbamoyl-5-methoxyphenyl)acrylate (3oa).



White solid; eluent (34% ethylacetate in hexanes).The reaction scale is 100 mg (**1o**), 111 mg of product was isolated and yield is 86%.

^{1}H NMR (DMSO d_6, 400 MHz): δ 8.07 (d, J = 16.0 Hz, 1H), 7.85 (s, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.42 (s, 1H), 7.35 (d, J = 4.0 Hz, 1H), 7.02 (dd, J = 8.0, 4.0 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H).

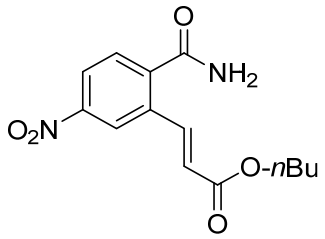
^{13}C NMR (DMSO d_6, 100 MHz): δ 169.8, 166.7, 160.2, 142.6, 133.9, 130.1, 129.6, 119.3, 115.7, 111.5, 55.6, 51.6.

HRMS (ESI): calc. for [($C_{12}H_{13}NO_4$)H] (M+H) 236.0923, measured 236.0932.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3322, 2927, 1721, 1638, 1541, 1319, 1130, 975, 860.

Rf (hexane/ethyl acetate = 1:1): 0.32.

Butyl (*E*)-3-(2-carbamoyl-5-methoxyphenyl)acrylate (3pb).



White solid; eluent (34% ethylacetate in hexanes).The reaction scale is 100 mg (**1p**), 131 mg of product was isolated and yield is 88%.

^{1}H NMR (DMSO d_6,400 MHz): δ 8.65 (d, J = 4.0 Hz, 1H), 8.27 (dd, J = 8.0, 4.0 Hz, 1H), 8.22 (s, 1H), 7.93 (s, 1H), 7.88 (d, J = 16.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 16.0 Hz, 1H), 4.17 (t, J = 8.0 Hz, 2H), 1.63 (quintet, J = 8.0 Hz, 2H), 1.38 (m, 2H), 0.92 (t, J = 8.0 Hz, 3H).

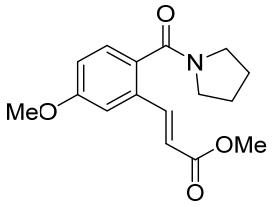
^{13}C NMR (DMSO d_6, 100 MHz): δ 168.6, 165.7, 148.2, 143.2, 139.6, 133.1, 129.0, 124.2, 122.4, 121.7, 64.0, 30.2, 18.6, 13.5.

HRMS (ESI): calc. for [($C_{14}H_{16}N_2O_5$)Na] (M+Na) 315.0957, measured 315.0962.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3322, 2837, 1734, 1618, 1541, 1319, 1137, 979, 761.

Rf (hexane/ethyl acetate = 1:1): 0.31.

Methyl (*E*)-3-(5-methoxy-2-(pyrrolidine-1-carbonyl)phenyl)acrylate (3qa).



Colourless liquid; eluent (26% ethylacetate in hexanes).The reaction scale is 100mg (**1q**), 85 mg of product was isolated and yield is 60%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 4.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.65 (t, *J* = 4.0 Hz, 2H), 3.54 (t, *J* = 4.0 Hz, 2H), 1.93 (q, *J* = 4.0 Hz, 2H), 1.82 (q, *J* = 4.0 Hz, 2H).

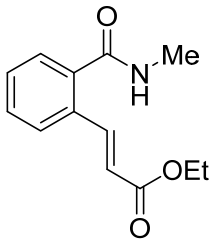
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 166.8, 159.9, 141.5, 132.4, 131.1, 128.3, 120.2, 115.9, 111.5, 55.4, 51.7, 48.6, 45.7, 25.9, 24.5.

HRMS (ESI): calc. for [($C_{16}H_{19}NO_4$)H] (M+H) 290.1392, measured 290.1397.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3434, 2954, 1710, 1599, 1429, 1310, 1169, 1031, 828.

Rf (hexane/ethyl acetate = 2:1): 0.29.

Ethyl (*E*)-3-(2-(methylcarbamoyl)phenyl)acrylate (3ac).



White solid; eluent (31% ethylacetate in hexanes).The reaction scale is 100mg (**1a**), 138mg of product was isolated and yield is 80%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 16.0 Hz, 1H), 7.57 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.34 (td, *J* = 8.0, 4.0 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.99 (s, 1H), 4.21 (q, *J* = 8.0 Hz, 2H), 2.97 (d, *J* = 4.0 Hz, 3H), 1.29 (t, *J* = 8.0 Hz, 3H).

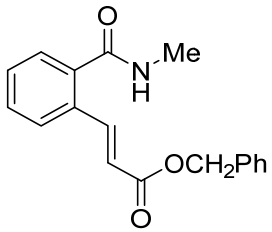
^{13}C NMR ($CDCl_3$, 100 MHz): δ169.3, 166.5, 141.8, 137.2, 132.7, 130.2, 129.7, 127.6, 127.1, 120.8, 60.5, 26.8, 14.2.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_3$)Na] (M+Na) 256.0950, measured 256.0957.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3281, 3065, 2978, 1705, 1628, 1545, 1432, 1264, 1040, 765.

Rf (hexane/ethyl acetate = 2:1): 0.38.

Benzyl (*E*)-3-(2-(methylcarbamoyl)phenyl)acrylate (3ad).



White solid;eluent (28% ethylacetate in hexanes).The reaction scale is 100mg (**1a**), 166mg of product was isolated and yield is 76%.

^{1}H NMR ($CDCl_3$, 400 MHz):δ8.02 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 4.0 Hz, 1H), 7.45 (td, *J* = 8.0, 4.0 Hz, 1H), 7.41 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.39 (t,*J* = 4.0 Hz, 3H), 7.36 (dt, *J* = 8.0, 4.0 Hz, 2H), 7.33 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.85 (s, 1H), 5.23 (s, 2H), 2.99 (d, *J* = 4.0 Hz, 3H).

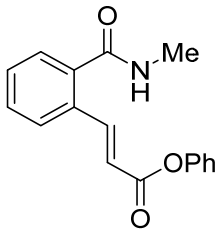
^{13}C NMR ($CDCl_3$, 100 MHz): δ169.2, 166.2, 142.4, 137.2, 135.9, 132.6, 131.3, 130.2, 129.8, 128.5, 128.4, 128.2, 127.6, 127.1, 126.8, 120.3, 66.3, 26.8.

HRMS (ESI): calc. for [($C_{18}H_{17}NO_3$)Na] (M+Na) 318.1106, measured 318.1112.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3311, 2937, 1724, 1628, 1543, 1310, 1130, 975, 760.

Rf (hexane/ethyl acetate = 2:1): 0.38.

Phenyl (*E*)-3-(2-(methylcarbamoyl)phenyl)acrylate (3ae).



White solid; eluent (27% ethylacetate in hexanes).The reaction scale is 100mg (**1a**), 148mg of product was isolated and yield is 71%.

^{1}H NMR ($CDCl_3$, 400 MHz):δ8.22 (d, *J* = 16.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.19 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.18 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 5.96 (s, 1H), 3.04 (d, *J* = 4.0 Hz, 3H).

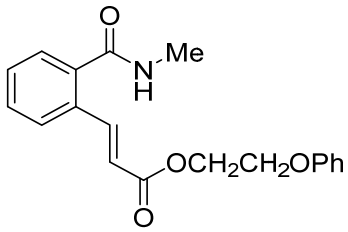
^{13}C NMR ($CDCl_3$, 100 MHz):δ169.2, 164.9, 150.7, 143.8, 137.3, 132.6, 130.4, 130.2, 129.4, 127.6, 127.3, 125.7, 121.6, 119.8, 26.9.

HRMS (ESI): calc. for [($C_{17}H_{15}NO_3$)Na] (M+Na) 304.0950, measured 304.0953.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3310, 3068, 2935, 1728, 1631, 1543, 1310, 1138, 975, 766.

Rf (hexane/ethyl acetate = 2:1): 0.39.

2-Phenoxyethyl (*E*)-3-(2-(methylcarbamoyl)phenyl)acrylate (3af).



White solid; eluent (31% ethylacetate in hexanes).The reaction scale is 100mg (**1a**), 146mg of product was isolated and yield is 61%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.48-7.38 (m, 3H) 7.32 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.29 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.00 (d,*J* = 4.0 Hz, 1H),, 6.97-6.94 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.03 (s, 1H), 4.56 (t, *J* = 4.0 Hz, 2H), 4.25 (t, *J* = 4.0 Hz, 2H), 2.99 (d, *J* = 4.0 Hz, 3H).

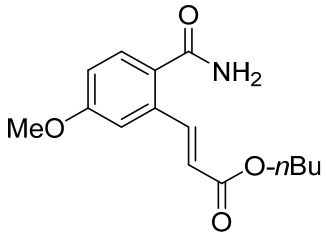
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 166.3, 158.4, 142.6, 137.0, 132.5, 130.3, 129.9, 129.5, 127.6, 127.1, 121.1, 120.0, 114.6, 65.8, 62.9, 26.9.

HRMS (ESI): calc. for [($C_{19}H_{19}NO_4$)H] (M+H) 326.1392, measured 326.1400.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3312, 3057, 2931, 1725, 1637, 1540, 1310, 1138, 975, 760.

Rf(hexane/ethyl acetate = 2:1): 0.29.

Butyl (*E*)-3-(2-carbamoyl-5-methoxyphenyl)acrylate (3ob).



White solid; eluent (34% ethylacetate in hexanes).The reaction scale is 100 mg (**1o**), 139 mg of product was isolated and yield is 91%.

^{1}H NMR (DMSO d_6, 400 MHz): δ 8.07 (d, J = 16.0 Hz, 1H), 7.85 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.37 (d, J = 4.0 Hz, 1H), 7.02 (dd, J = 8.0, 4.0 Hz, 1H), 6.63 (d, J = 16.0 Hz, 1H), 4.15 (t, J = 8.0 Hz, 2H), 3.84 (s, 3H), 1.62 (quintet, J = 8.0 Hz, 2H), 1.38 (m, 2H), 0.91 (t, J = 8.0 Hz, 3H).

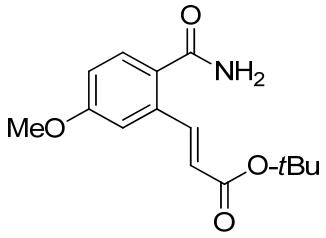
^{13}C NMR (DMSO d_6, 100 MHz): δ 169.9, 166.4, 160.2, 142.6, 134.0, 130.2, 129.7, 119.6, 115.9, 111.4, 63.9, 55.7, 30.5, 18.7, 14.0.

HRMS (ESI): calc. for [($C_{15}H_{19}NO_4$)Na] (M+Na) 300.1212, measured 300.1216.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3323, 2939, 1728, 1627, 1541, 1319, 1127, 968, 758.

Rf (hexane/ethyl acetate = 1:1): 0.29.

***tert*-Butyl (*E*)-3-(2-carbamoyl-5-methoxyphenyl)acrylate (3og)**.



White solid; eluent (34% ethylacetate in hexanes).The reaction scale is 100 mg (**1o**), 134 mg of product was isolated and yield is 88%.

^{1}H NMR (DMSO d_6, 400 MHz): δ 7.99 (d, J = 16.0 Hz, 1H), 7.83 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.44 (s, 1H), 7.33 (d, J = 4.0 Hz, 1H), 6.99 (dd, J = 8.0, 4.0 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 1.48 (s, 9H).

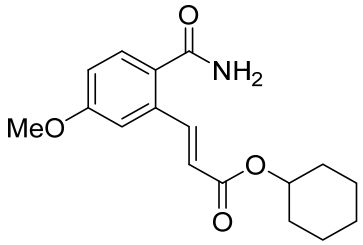
^{13}CNMR(DMSO d_6, 100 MHz): δ 169.9, 165.6, 160.2, 141.8, 134.0, 130.2, 129.6, 121.2, 115.8, 111.1, 80.1, 55.6, 28.1.

HRMS (ESI): calc. for [($C_{15}H_{19}NO_4$)Na] (M+Na) 300.1212, measured 300.1216.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3319, 2934, 1729, 1618, 1549, 1318, 1134, 971, 769.

Rf (hexane/ethyl acetate = 1:1): 0.29.

Cyclohexyl (*E*)-3-(2-carbamoyl-5-methoxyphenyl)acrylate (3oh).



White solid; eluent (34% ethylacetate in hexanes).The reaction scale is 100 mg (**1o**), 150 mg of product was isolated and yield is 90%.

^{1}H NMR (DMSO d_6, 400 MHz): δ 8.07 (d, J = 16.0 Hz, 1H), 7.85 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.37 (d, J = 4.0 Hz, 1H), 7.01 (dd, J = 8.0, 4.0 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 4.78 (m, 1H), 3.84 (s, 3H), 1.87 - 1.83 (m, 2H), 1.72 - 1.69 (m, 2H), 1.54 - 1.47 (m, 1H), 1.40 (quintet, J = 4.0 Hz, 4H), 1.29 - 1.24 (m, 1H).

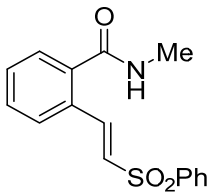
^{13}C NMR (DMSO d_6, 100 MHz): δ 169.9, 165.7, 160.2, 142.5, 134.0, 130.2, 129.6, 119.9, 116.0, 111.3, 72.2, 55.6, 31.4, 25.2, 23.5.

HRMS (ESI): calc. for [($C_{17}H_{21}NO_4$)Na] (M+Na) 326.1368, measured 326.1378.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3319, 2927, 1722, 1625, 1545, 1310, 1130, 981, 860.

Rf (hexane/ethyl acetate = 1:1): 0.30.

(*E*)-N-Methyl-2-(2-(phenylsulfonyl)vinyl)benzamide (3ai).



White solid; eluent (35% ethylacetate in hexanes).The reaction scale is 100mg (**1a**), 131mg of product was isolated and yield is 59%.

^{1}H NMR (DMSO d_6,400 MHz): δ 8.51 (s, 1H), 7.91 (dd, J = 8.0, 4.0 Hz, 1H), 7.90(d, J = 12.0 Hz, 1H), 7.85 (t, J = 4.0 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 2H), 7.57 (d, J = 12.0 Hz, 1H), 7.50 – 7.48 (m, 3H),2.79 (d, J = 4.0 Hz, 3H).

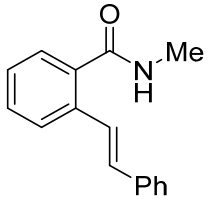
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 140.5, 140.3, 136.9, 133.5, 130.9, 130.7, 130.6, 129.5, 129.3, 128.6, 127.8, 127.7, 27.1.

HRMS (ESI): calc. for [($C_{16}H_{15}NO_3S$)Na] (M+Na) 324.0670, measured 324.0676.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3210, 3053, 2925, 2363, 1694, 1642, 1616, 1296, 1135, 1075, 999, 741.

Rf(hexane/ethyl acetate = 1:1): 0.39.

(*E*)-*N*-Methyl-2-styrylbenzamide (3aj).



White solid; eluent (29% ethylacetate in hexanes).The reaction scale is 100mg (**1a**), 76mg of product was isolated and yield is 43%.

^{1}H NMR ($CDCl_3$, 400 MHz):δ7.72 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H),7.43 (d, *J* = 4.0 Hz, 1H),7.40 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H),7.27 (t, *J* = 8.0 Hz, 2H),7.04 (d, *J* = 16.0 Hz, 2H), 5.81 (s, 1H), 3.00 (d, *J* = 4.0 Hz, 3H).

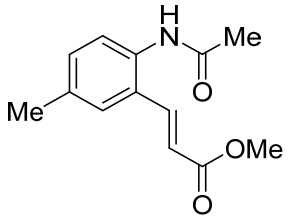
^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.4, 135.3, 135.1, 134.7, 127.1, 121.8, 120.3, 120.0, 117.8, 110.6, 110.3, 61.6, 31.9, 15.8.

HRMS (ESI): calc. for [($C_{16}H_{15}NO$)H] (M+H) 238.1232, measured 238.1231.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3309, 3052, 2930, 2361, 1625, 1527, 1310, 1154, 953, 755.

Rf (hexane/ethyl acetate = 2:1): 0.32.

Methyl (*E*)-3-(2-acetamido-5-methylphenyl)acrylate (5aa).



White solid; eluent (31% ethylacetate in hexanes).The reaction scale is 100mg (**4a**), 91mg of product was isolated and yield is 58%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ7.79 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.35 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H), 2.21 (s, 3H).

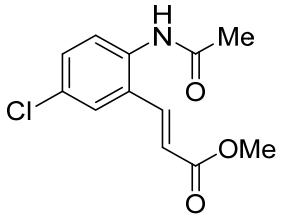
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.2, 167.7, 139.8, 135.7, 133.4, 131.5, 127.9, 127.2, 125.7, 119.4, 51.7, 23.8, 20.9.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_3$)Na] (M+Na) 256.0950, measured 256.0960.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3265, 3068, 2950, 1703, 1647, 1526, 1430, 1268, 1229,1030, 974, 815.

Rf (hexane/ethyl acetate = 2:1): 0.28.

Methyl (*E*)-3-(2-acetamido-5-chlorophenyl)acrylate (5ba).



White solid; eluent (29% ethylacetate in hexanes).The reaction scale is 100mg (**4b**), 70mg of product was isolated and yield is 47%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 16.0 Hz, 1H), 7.49 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.22 (s, 3H).

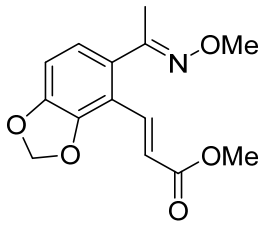
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 166.8, 138.2, 134.3, 131.2, 130.6, 128.9, 126.7, 126.4, 121.4, 51.9, 24.1.

HRMS (ESI): calc. for [($C_{12}H_{12}ClNO_3$)Na] (M+Na) 276.0403, measured 276.0406.

FT-IR $\tilde{\nu}$ (cm^{-1}): 3268, 3080, 2950, 1710, 1653, 1517, 1517, 1268, 1229,1022, 973, 819.

Rf (hexane/ethyl acetate = 2:1): 0.31.

Methyl(*E*)-3-(5-((E)-1-(methoxyimino)ethyl)benzo[*d*][1,3]dioxol-4-yl)acrylate (7aa).



White solid; eluent (7% ethylacetate in hexanes).The reaction scale is 100mg (**6a**), 80mg of product was isolated and yield is 56%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ7.70 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.05 (s, 2H), 3.95 (s, 3H), 3.77 (s, 3H), 2.15 (s, 3H).

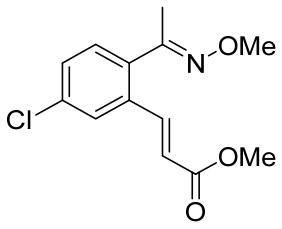
^{13}C NMR ($CDCl_3$, 100 MHz): δ167.7, 155.1, 147.9, 147.2, 137.8, 132.3, 122.5, 122.2, 115.9, 109.1, 101.7, 61.9, 51.6, 17.1.

HRMS (ESI): calc. for [($C_{14}H_{15}NO_5$)H] (M+H) 278.1028, measured 278.1034.

FT-IR $\tilde{\nu}$ (cm^{-1}): 2902, 1713, 1629, 1526, 1463, 1244, 1181, 1038, 864, 809.

Rf (hexane/ethyl acetate = 90:10): 0.31.

Methyl (*E*)-3-(5-chloro-2-((*E*)-1-(methoxyimino)ethyl)phenyl)acrylate (7ba).



Colourless liquid; eluent (5% ethylacetate in hexanes).The reaction scale is 100mg (**6b**), 61mg of product was isolated and yield is 42%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ7.86 (d, *J* = 16.0 Hz, 1H), 7.56 (s, 1H), 7.34 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 3.97 (s, 3H), 3.79 (s, 3H), 2.16 (s, 3H).

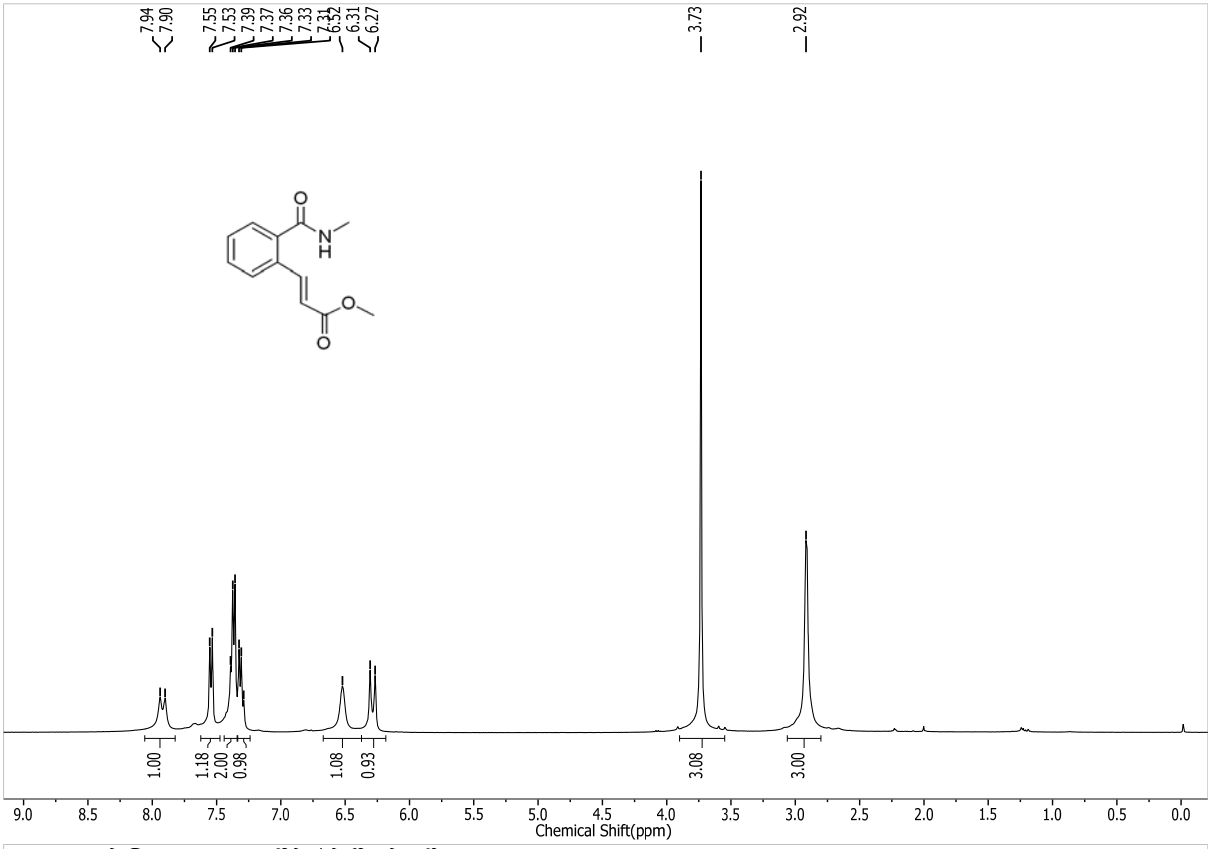
^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 154.3, 142.3, 136.2, 134.8, 134.7, 130.1, 129.7, 127.1, 120.2, 62.2, 51.8, 16.3.

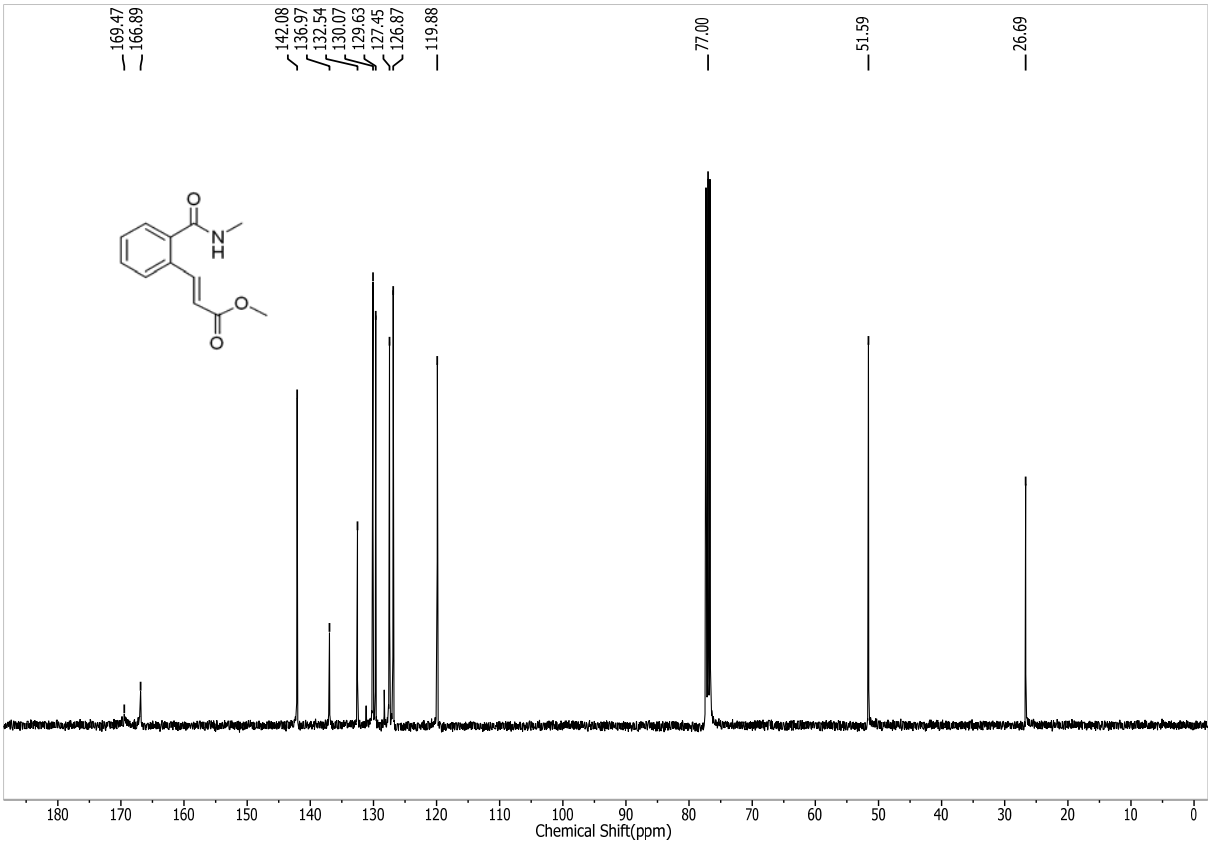
HRMS (ESI): calc. for [($C_{13}H_{14}ClNO_3$)H] (M+H) 268.0740, measured 268.0745.

FT-IR $\tilde{\nu}$ (cm^{-1}): 2892, 1719, 1620, 1521, 1469, 1241, 1181, 1038, 864, 817.

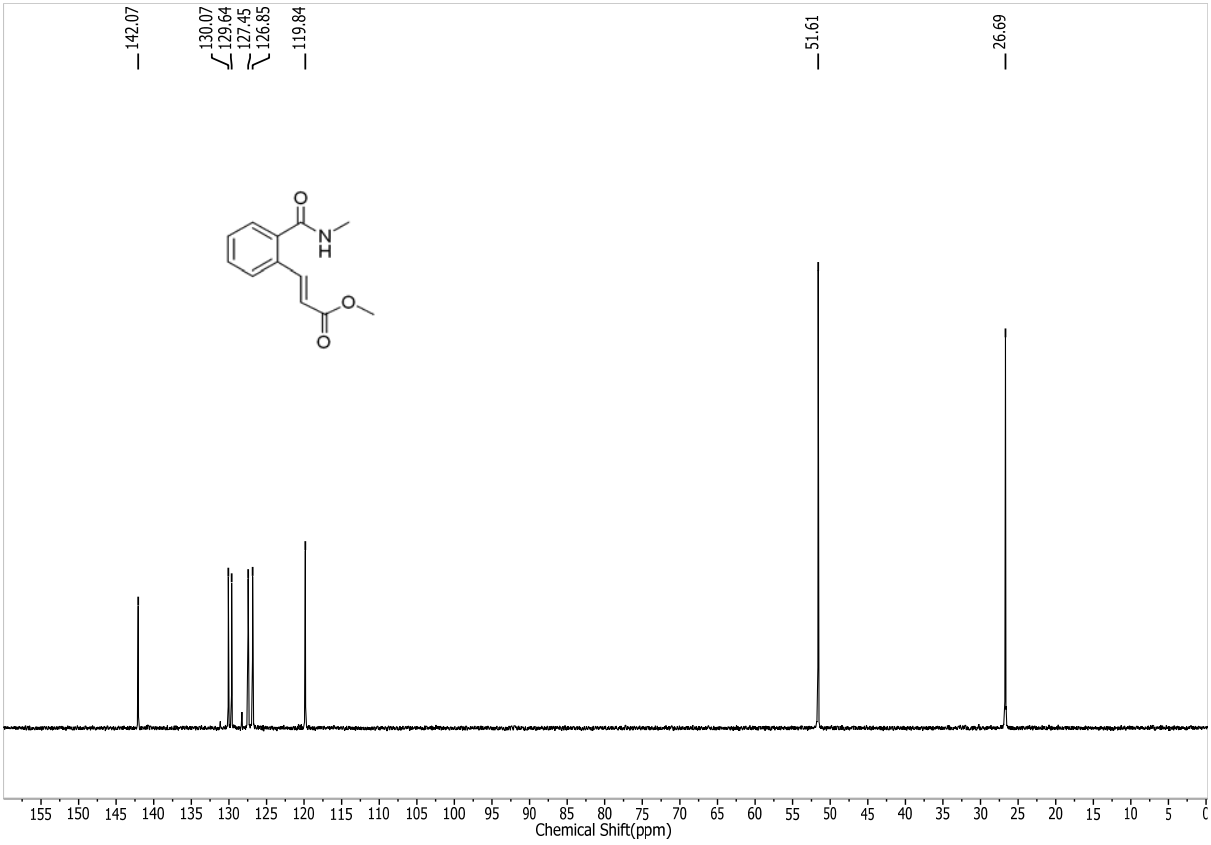
Rf (hexane/ethyl acetate = 90:10): 0.53.

^{1}H and ^{13}C NMR Spectra of Compound **3aa.**

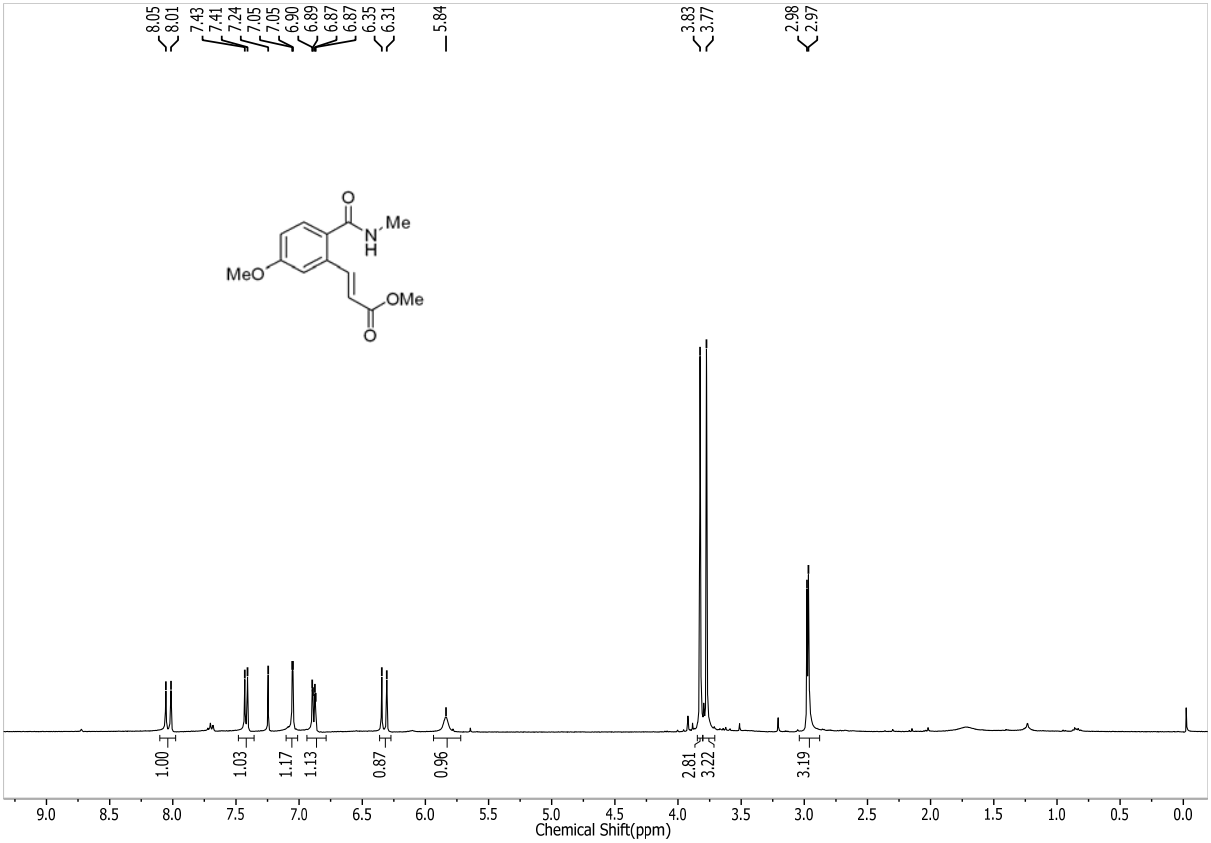


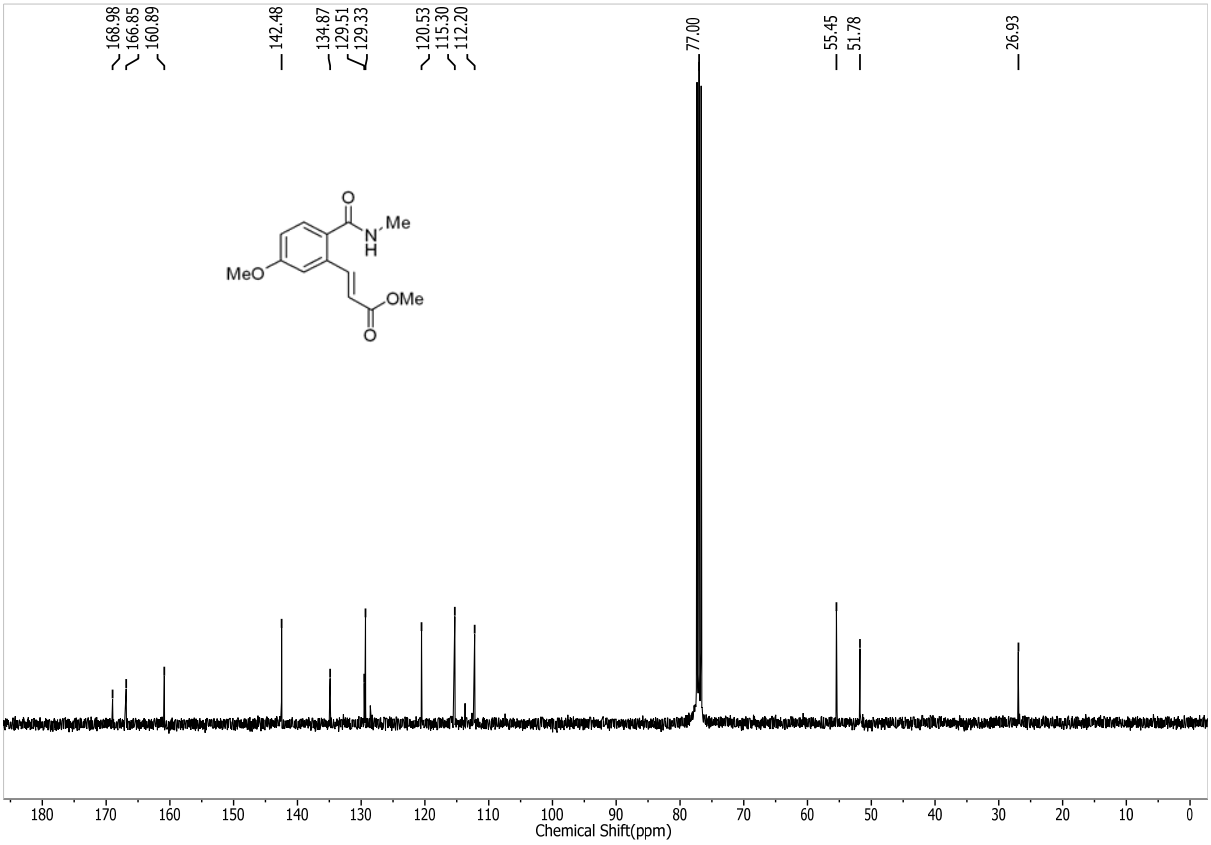


DEPT (135) NMR Spectrum of Compound **3aa.**

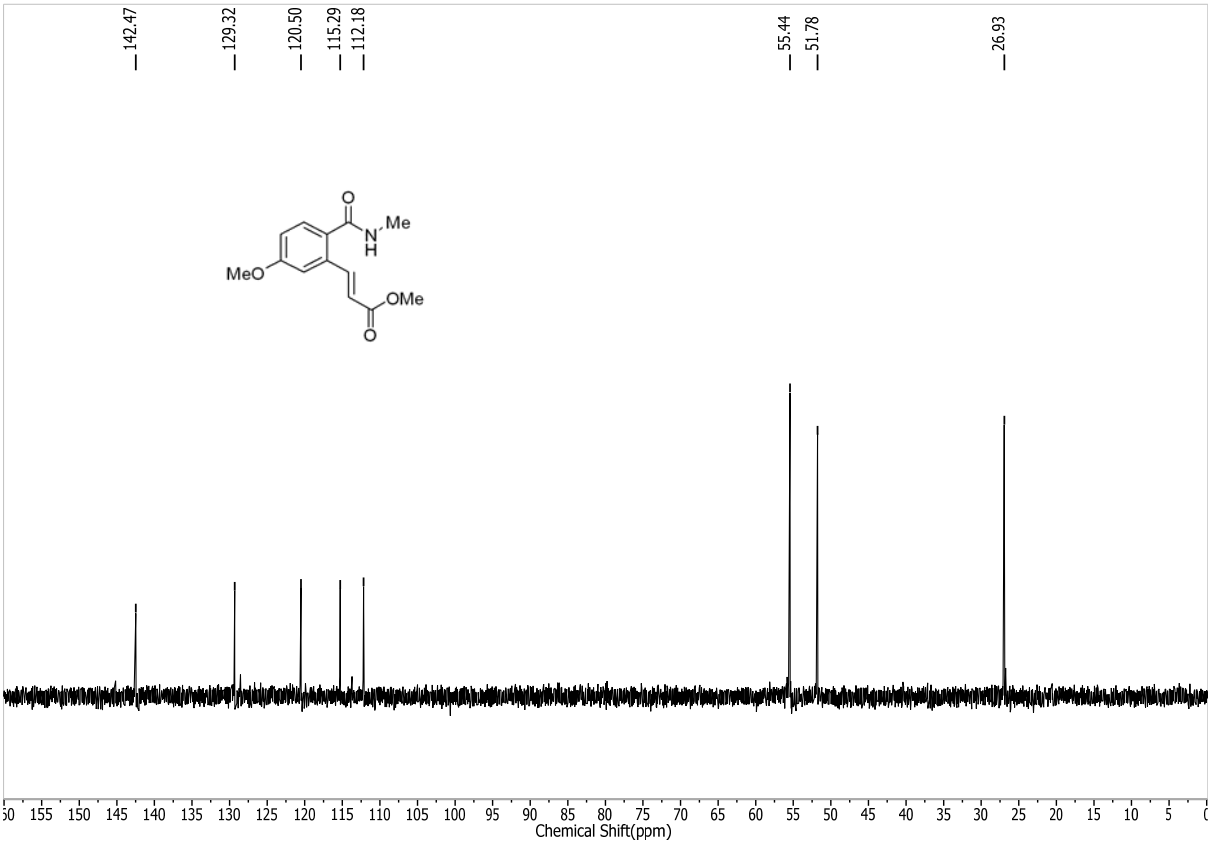


^{1}H and ^{13}C NMR Spectra of Compound **3ba.**

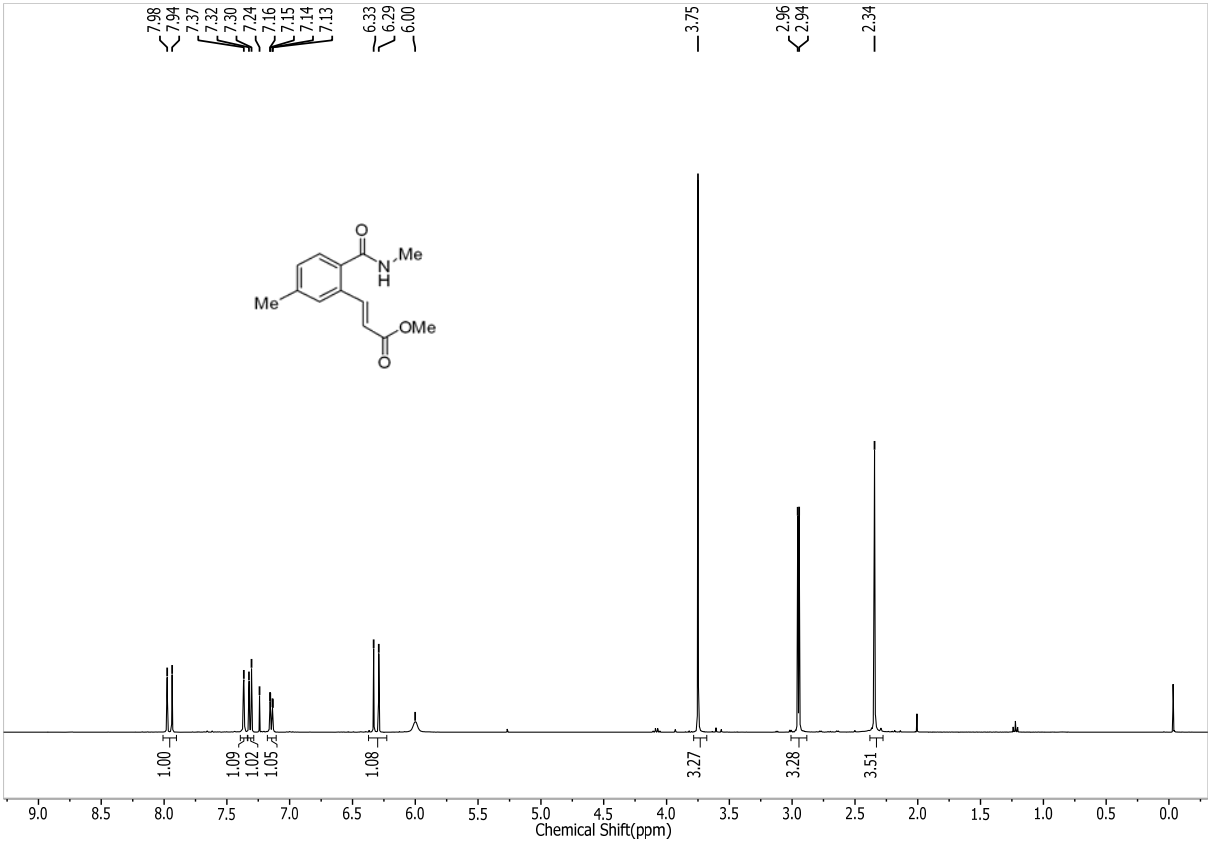


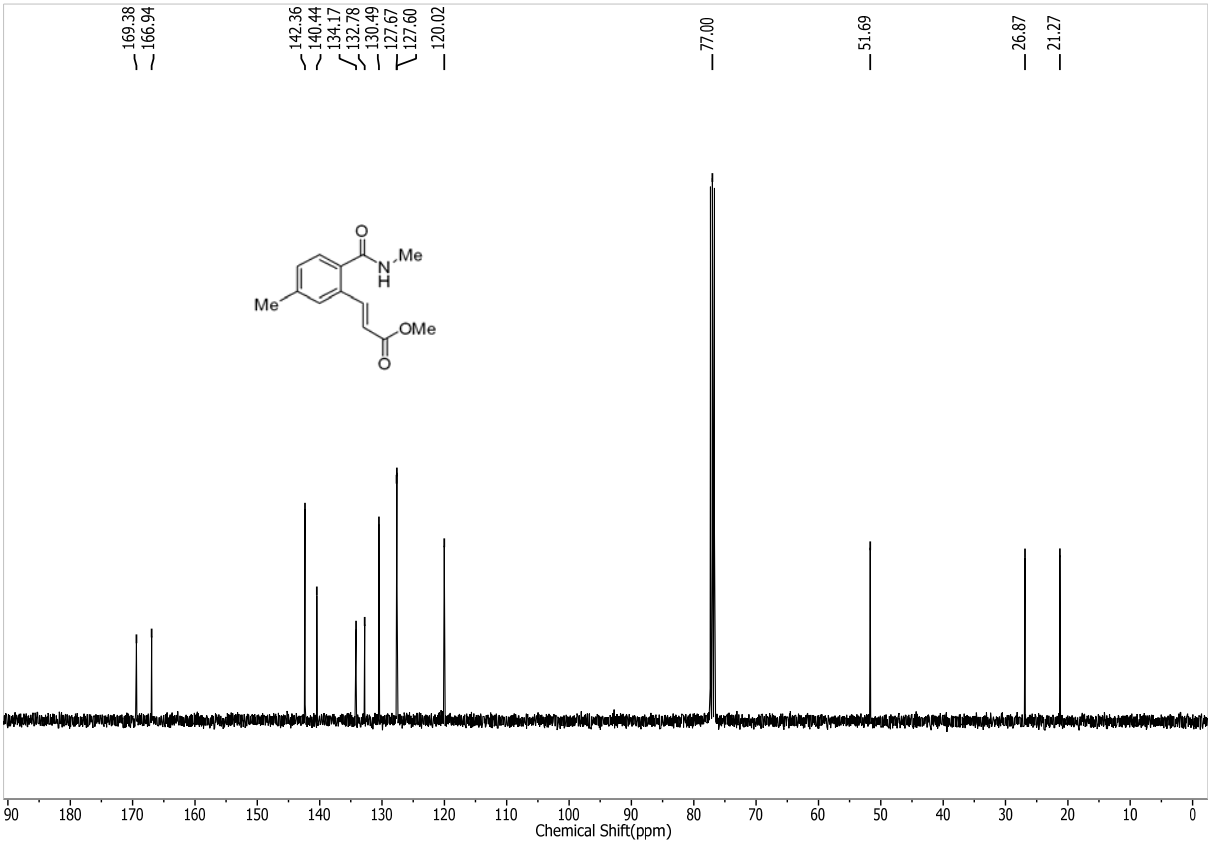


DEPT (135) NMR Spectrum of Compound **3ba.**

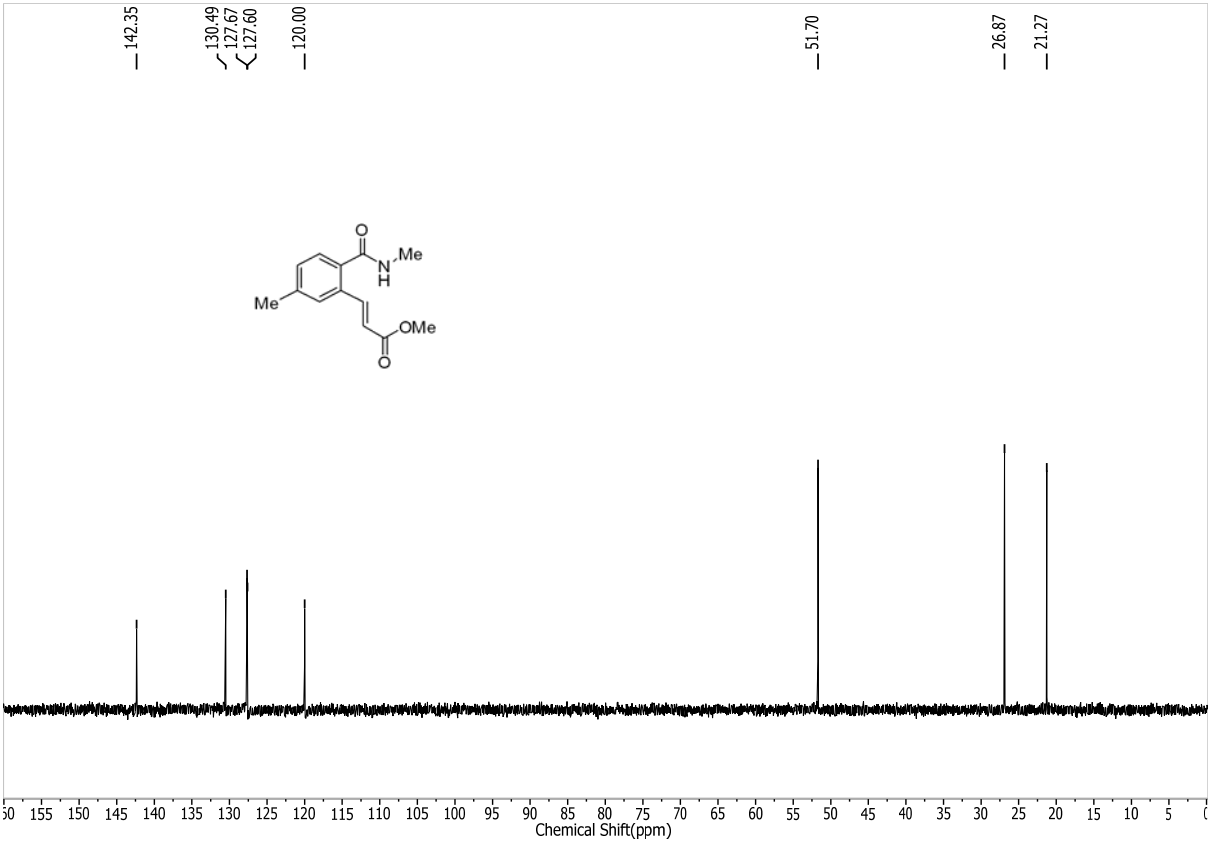


^{1}H and ^{13}C NMR Spectra of Compound **3ca.**

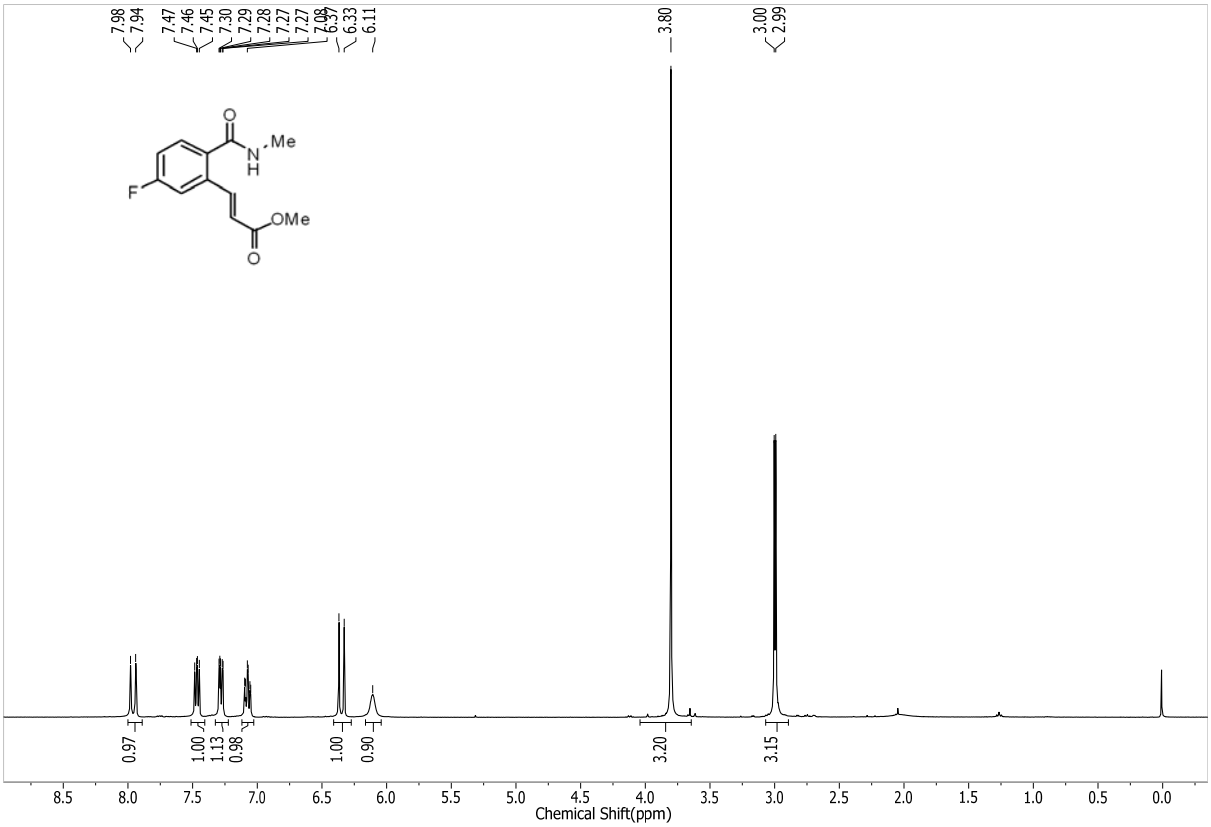


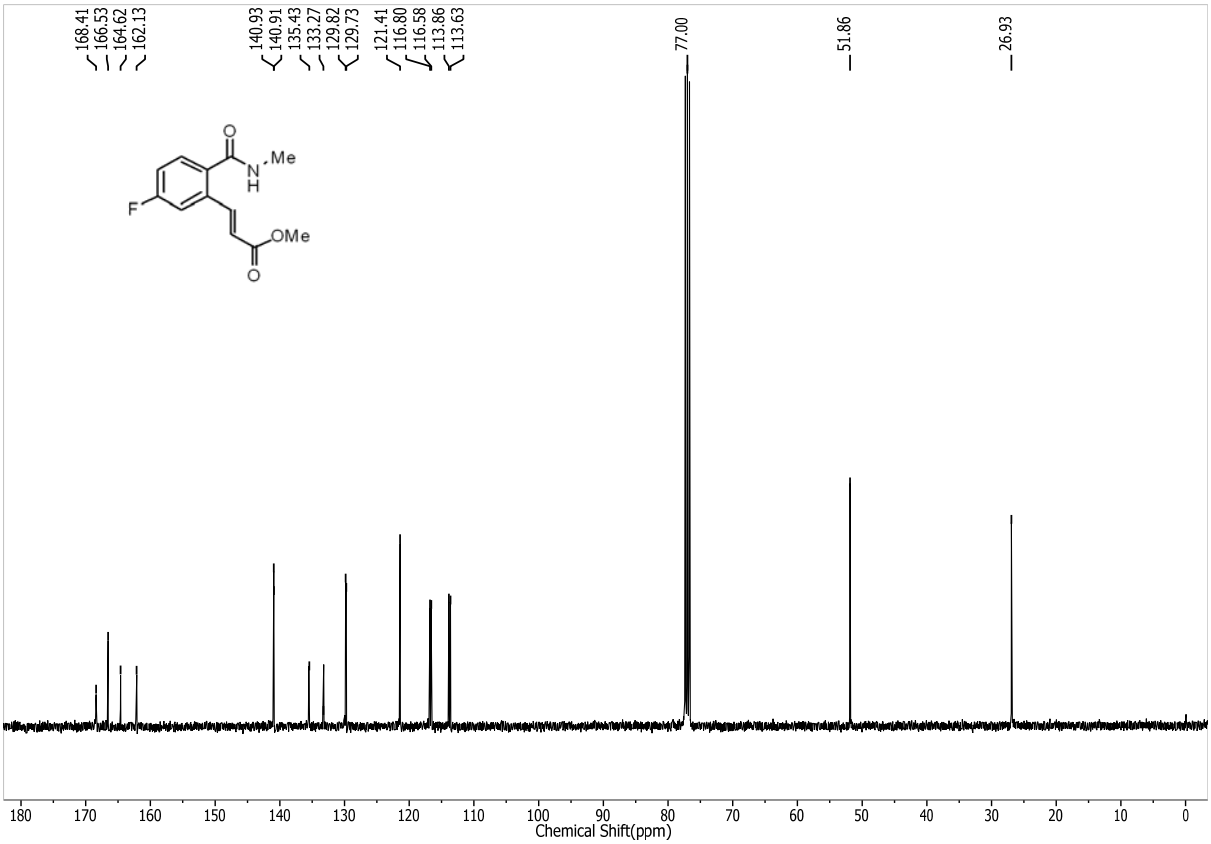


DEPT (135) NMR Spectrum of Compound **3ca.**

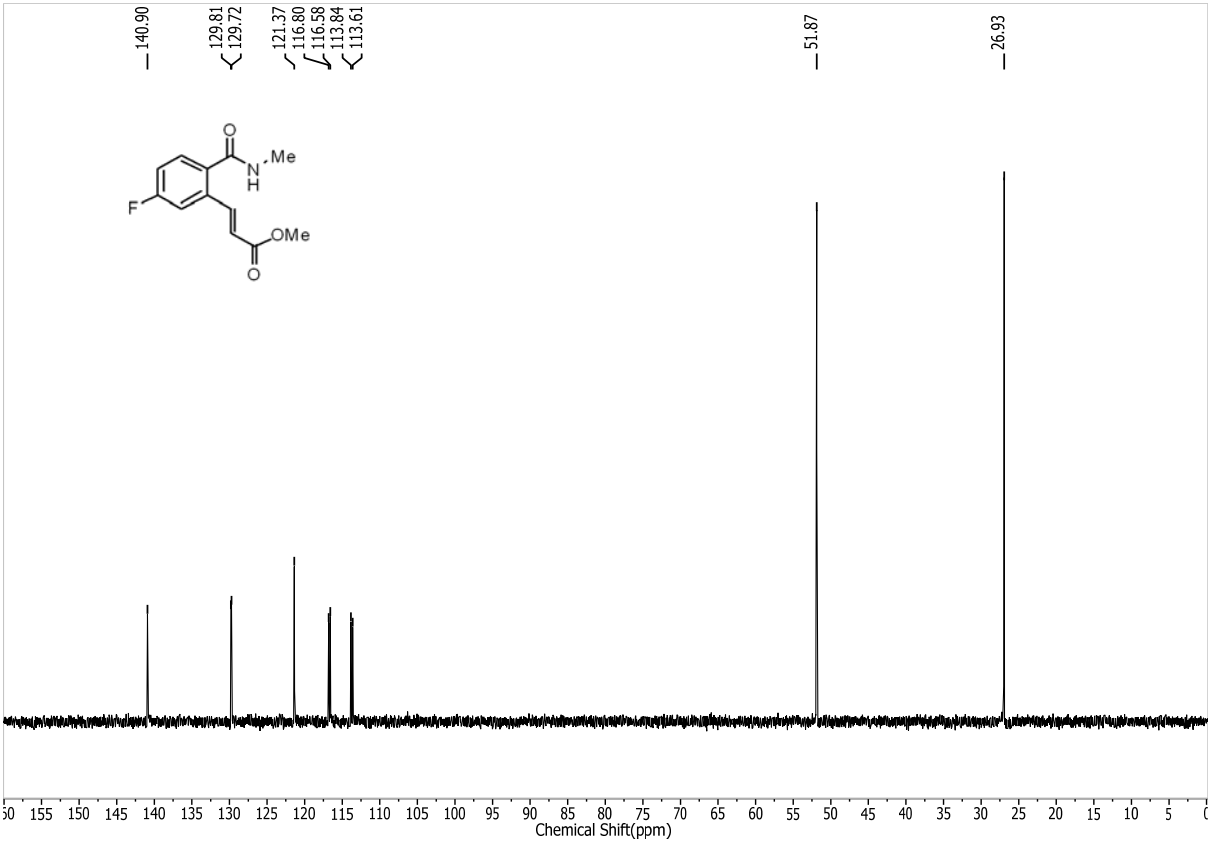


^{1}H and ^{13}C NMR Spectra of Compound **3da.**

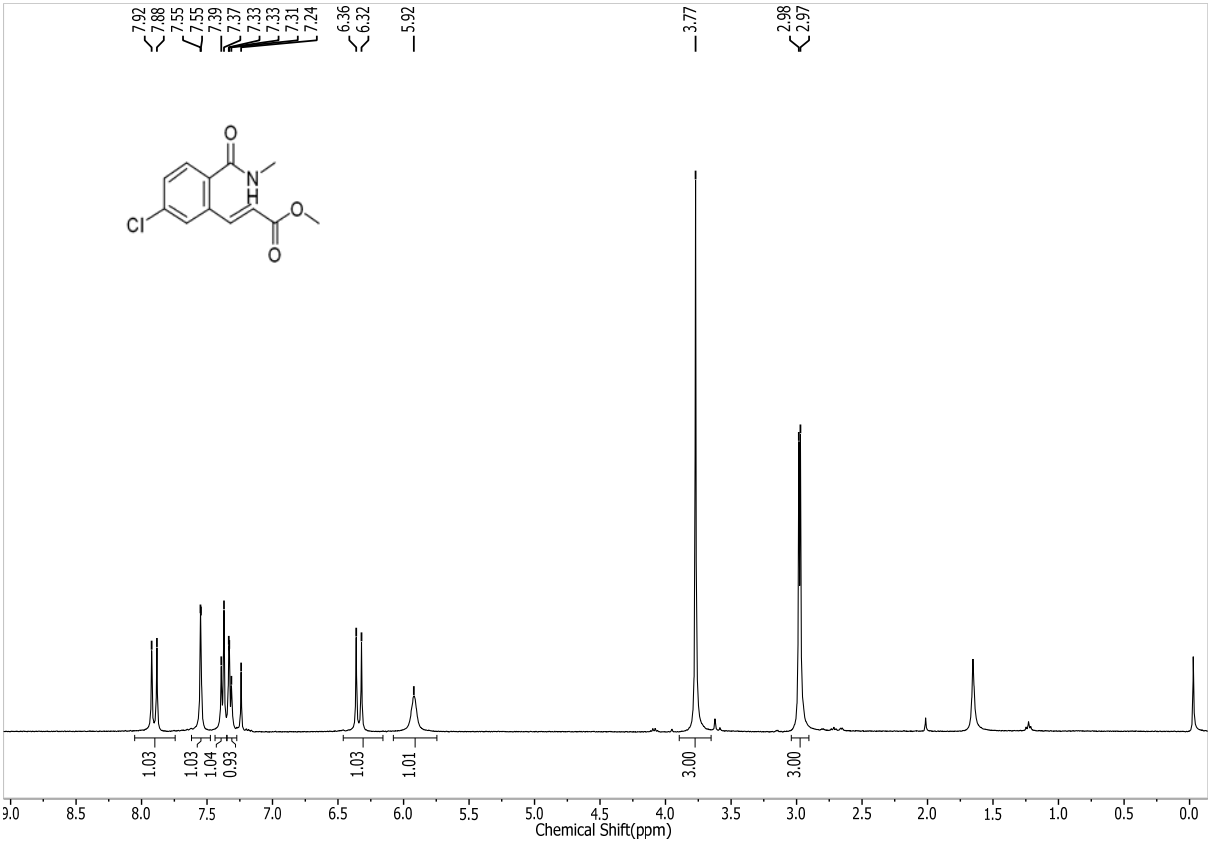


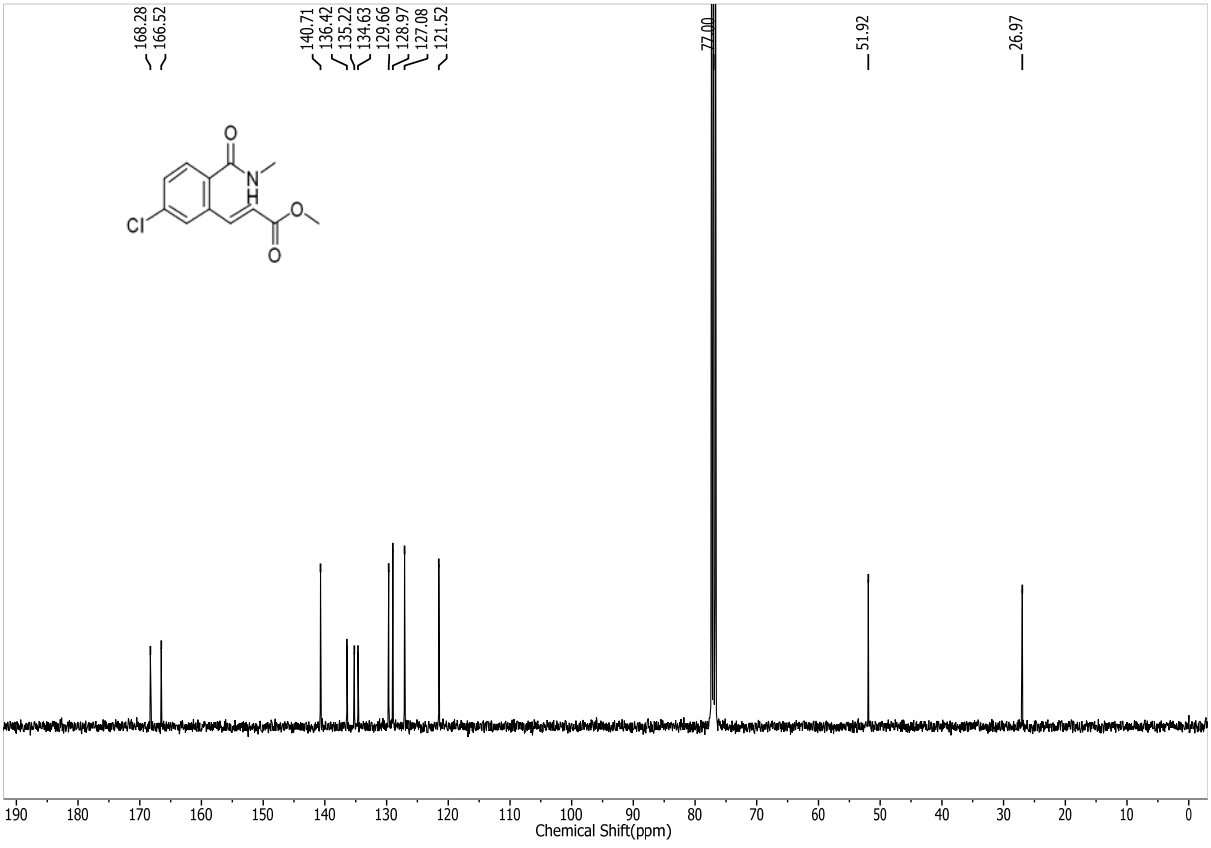


DEPT (135) NMR Spectrum of Compound **3da.**

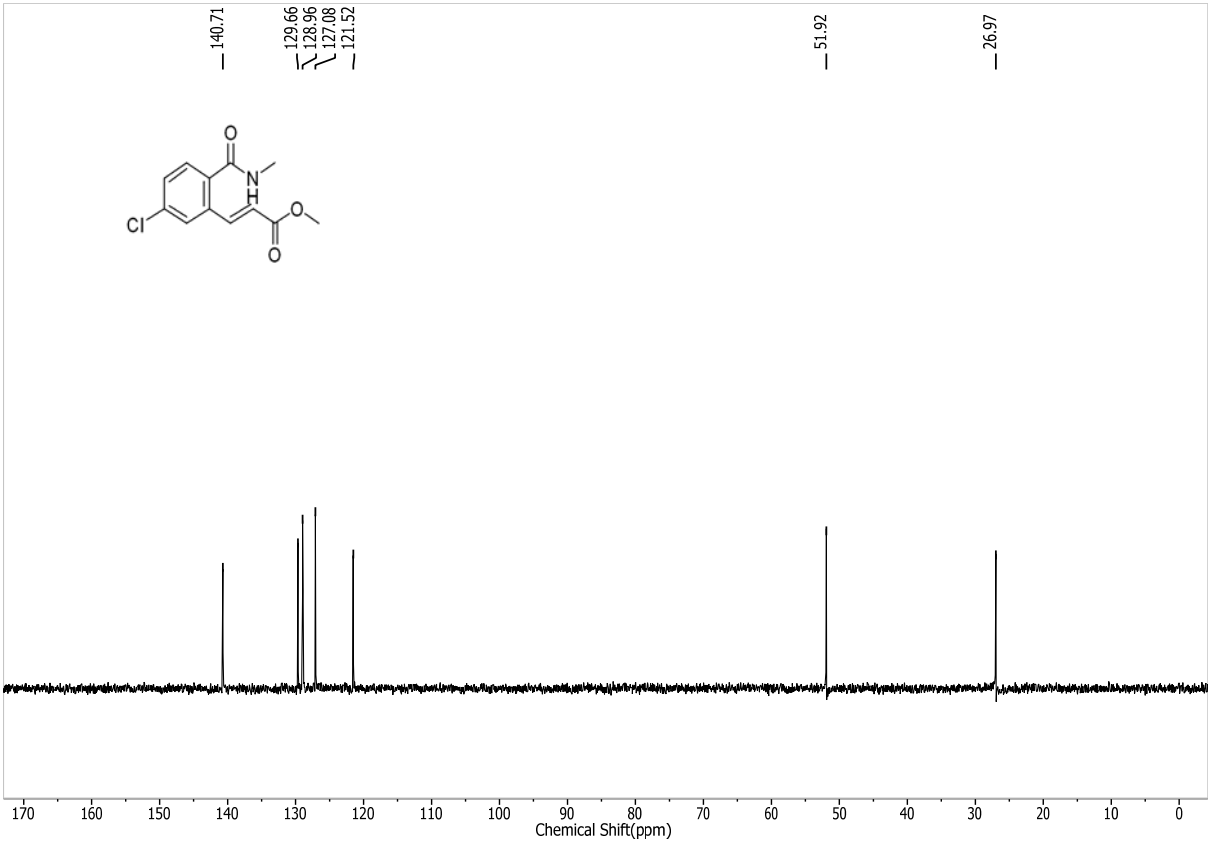


^{1}H and ^{13}C NMR Spectra of Compound **3ea.**

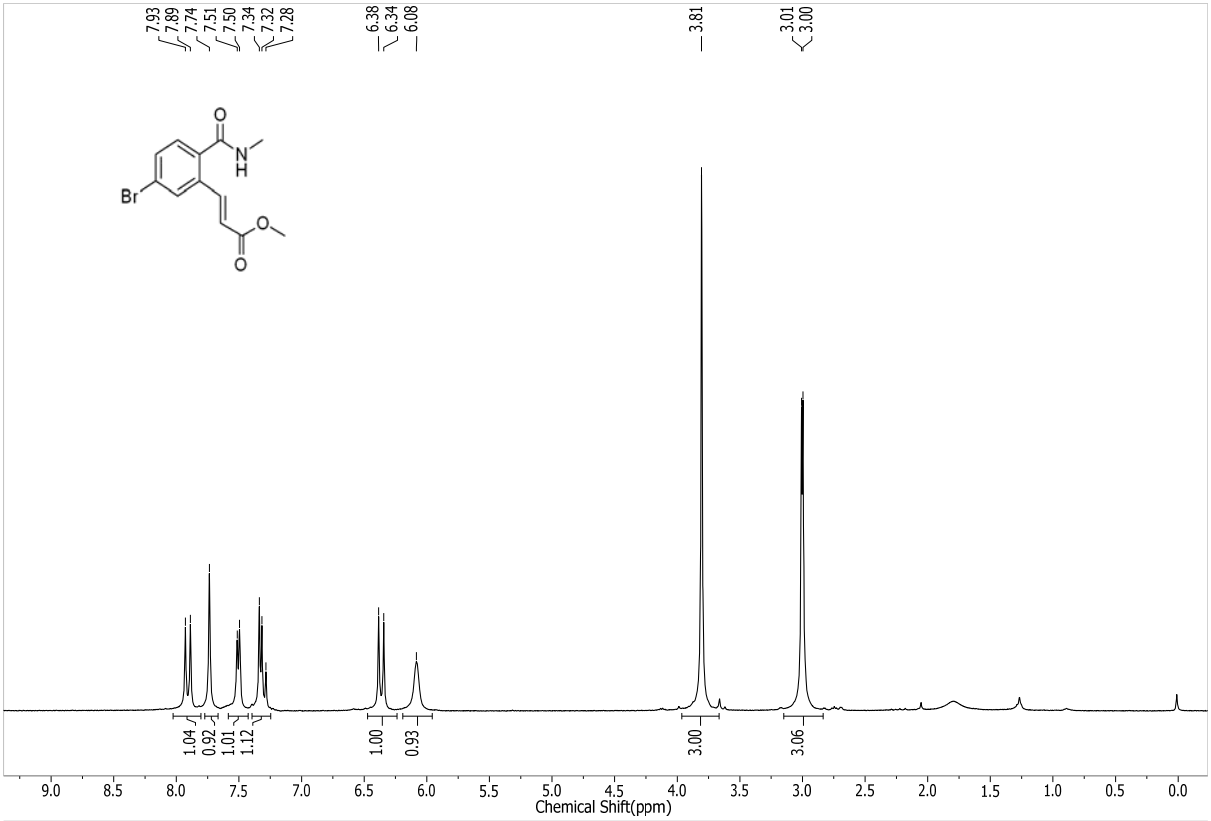


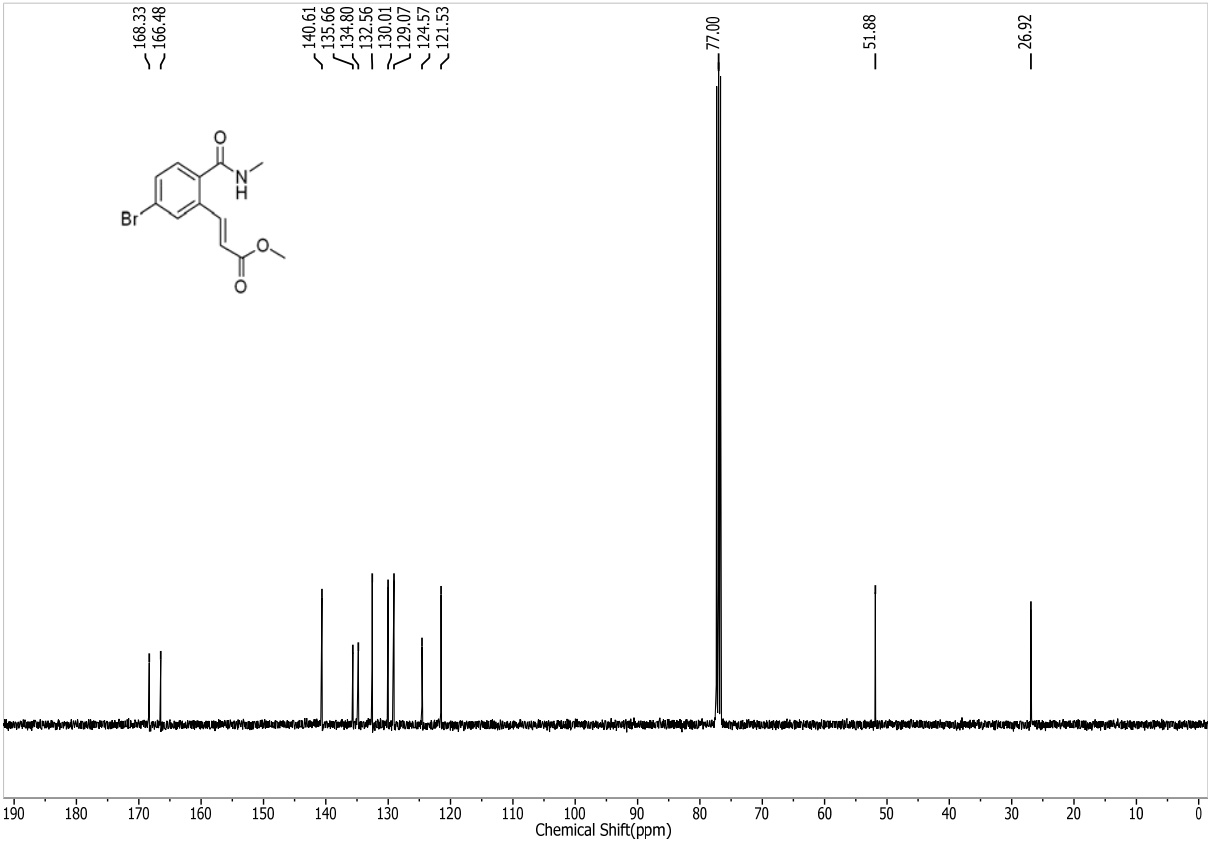


DEPT (135) NMR Spectrum of Compound **3ea.**

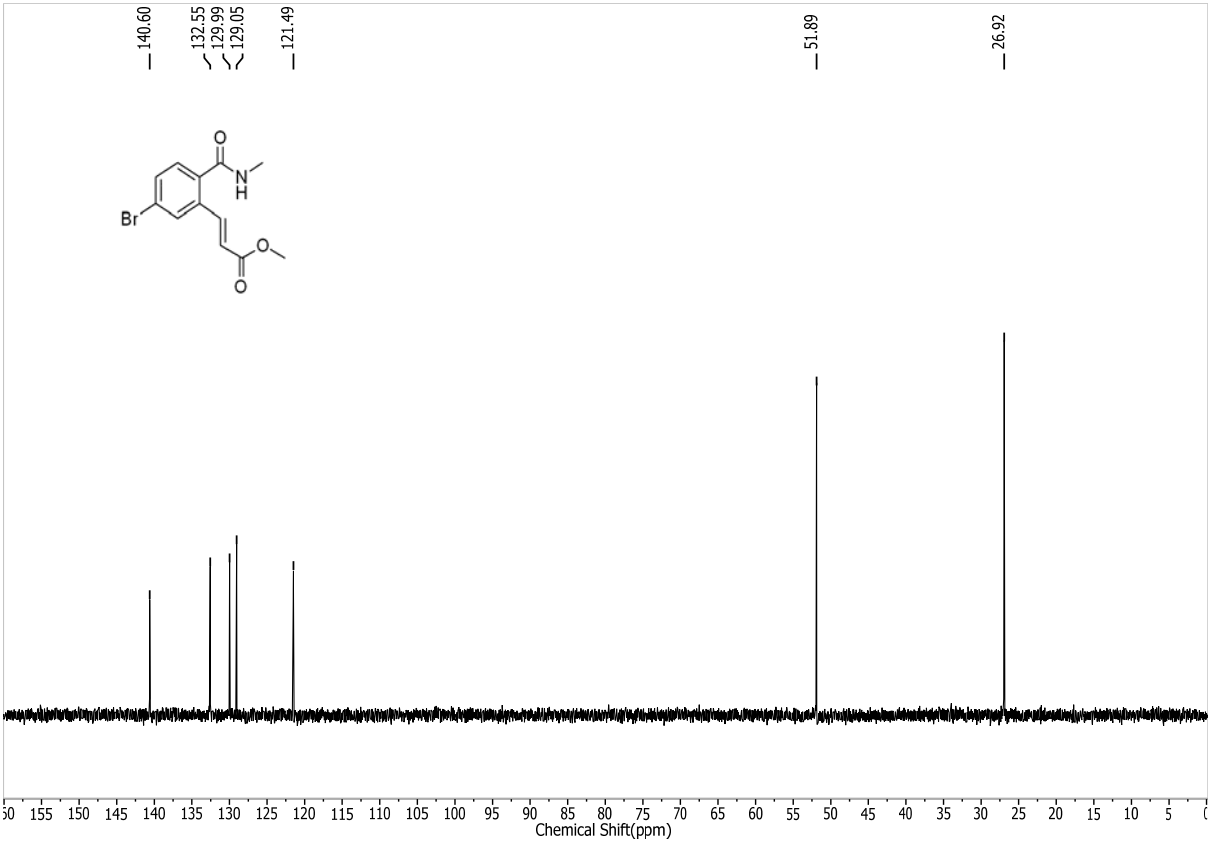


^{1}H and ^{13}C NMR Spectra of Compound **3fa.**

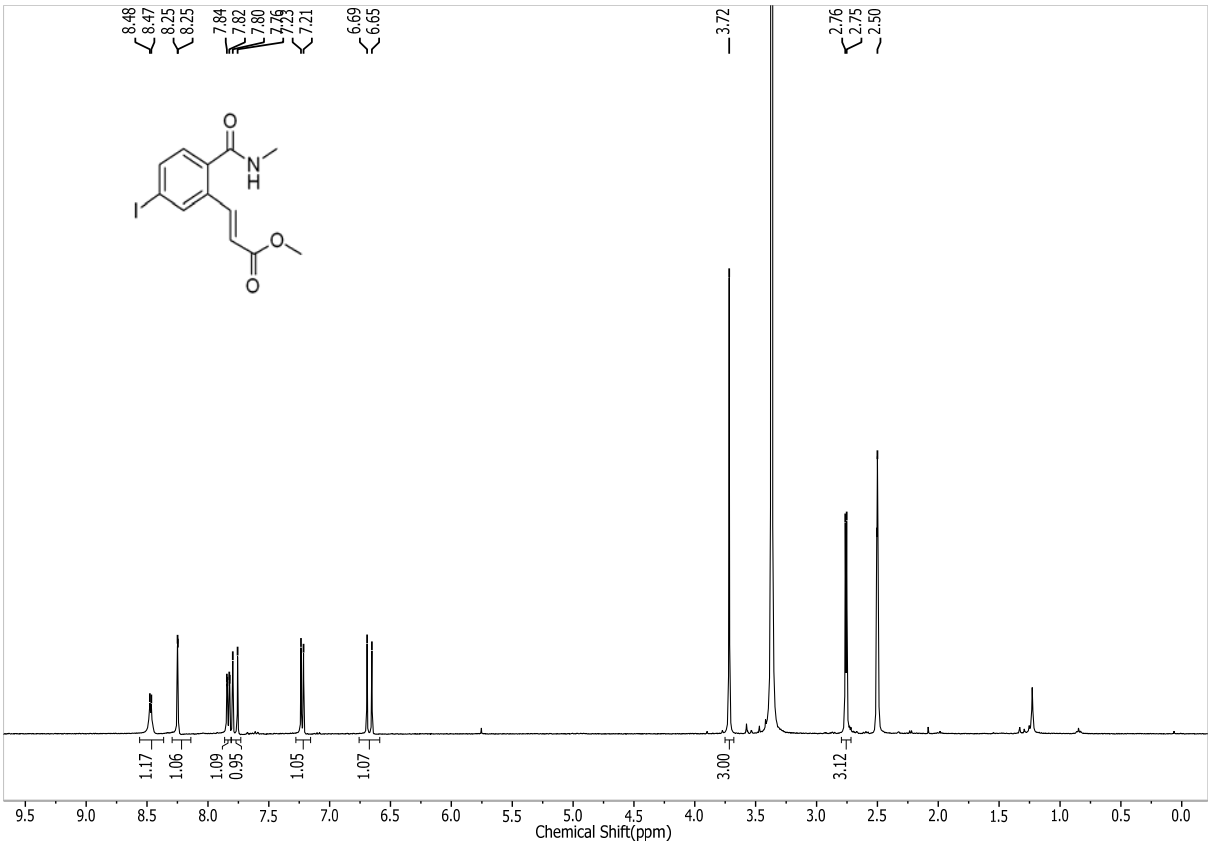


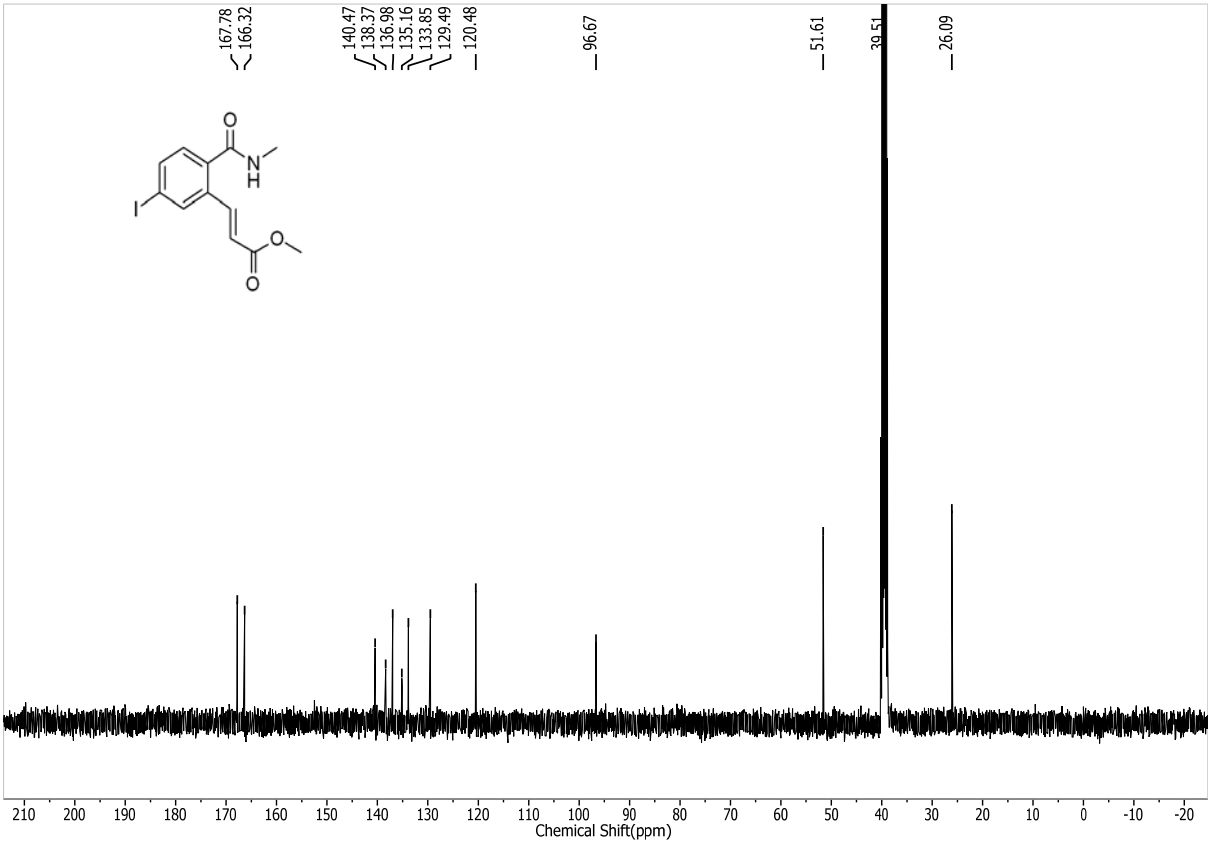


DEPT (135) NMR Spectrum of Compound **3fa.**

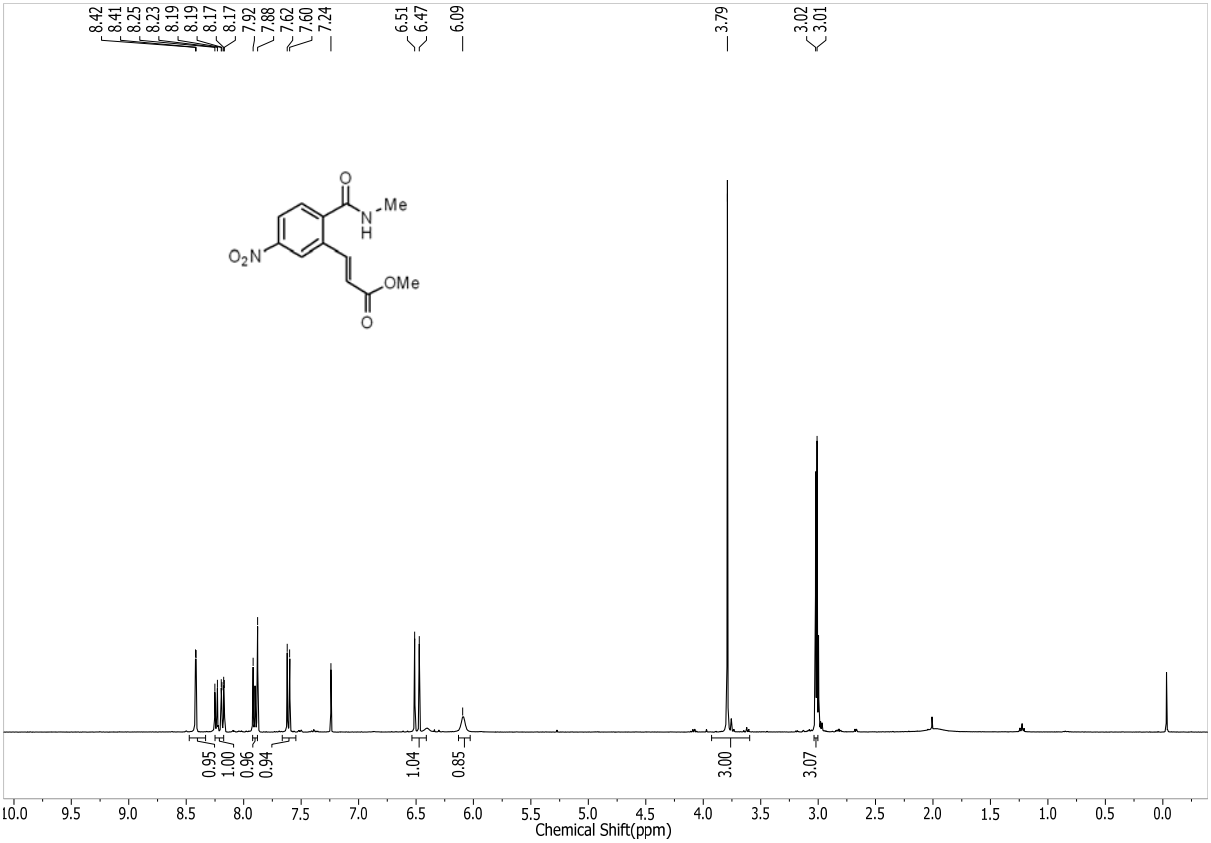


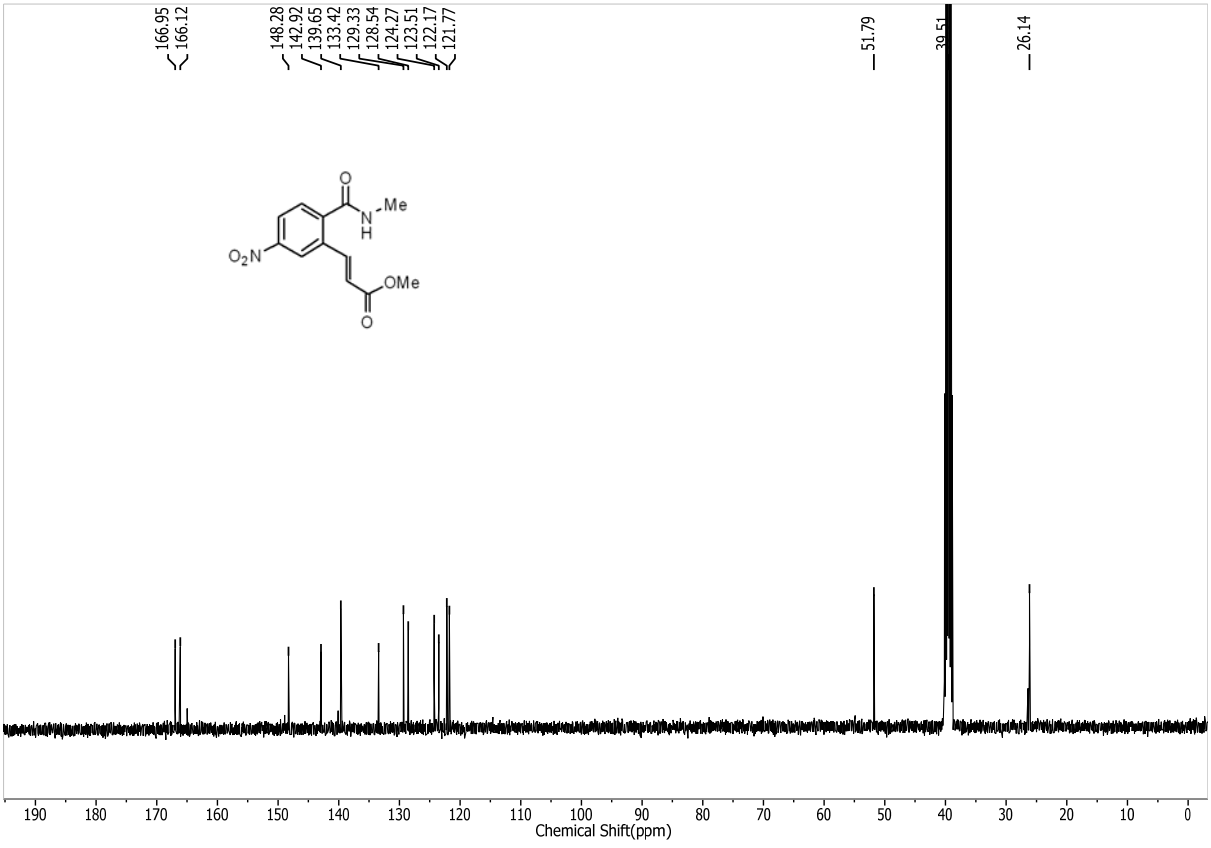
^{1}H and ^{13}C NMR Spectra of Compound **3ga.**



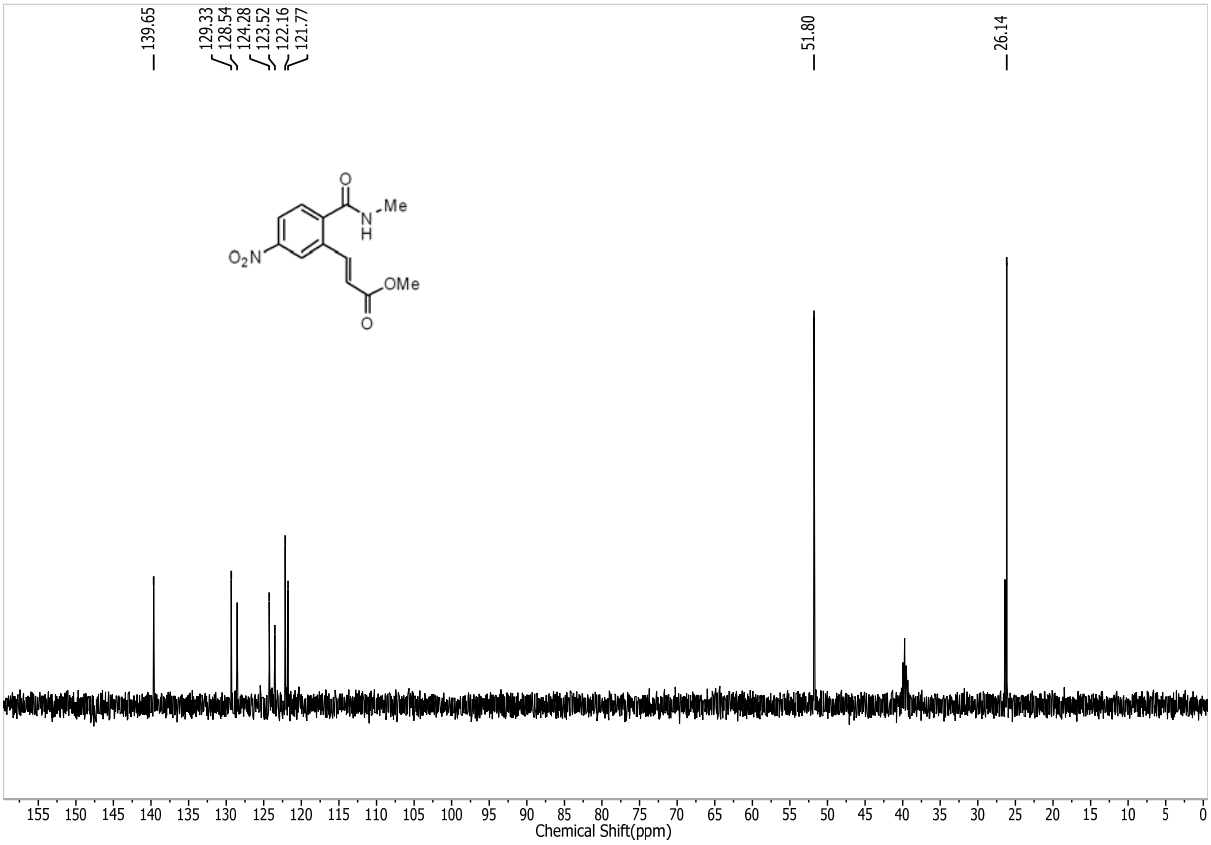


^{1}H and ^{13}C NMR Spectra of Compound **3ha.**

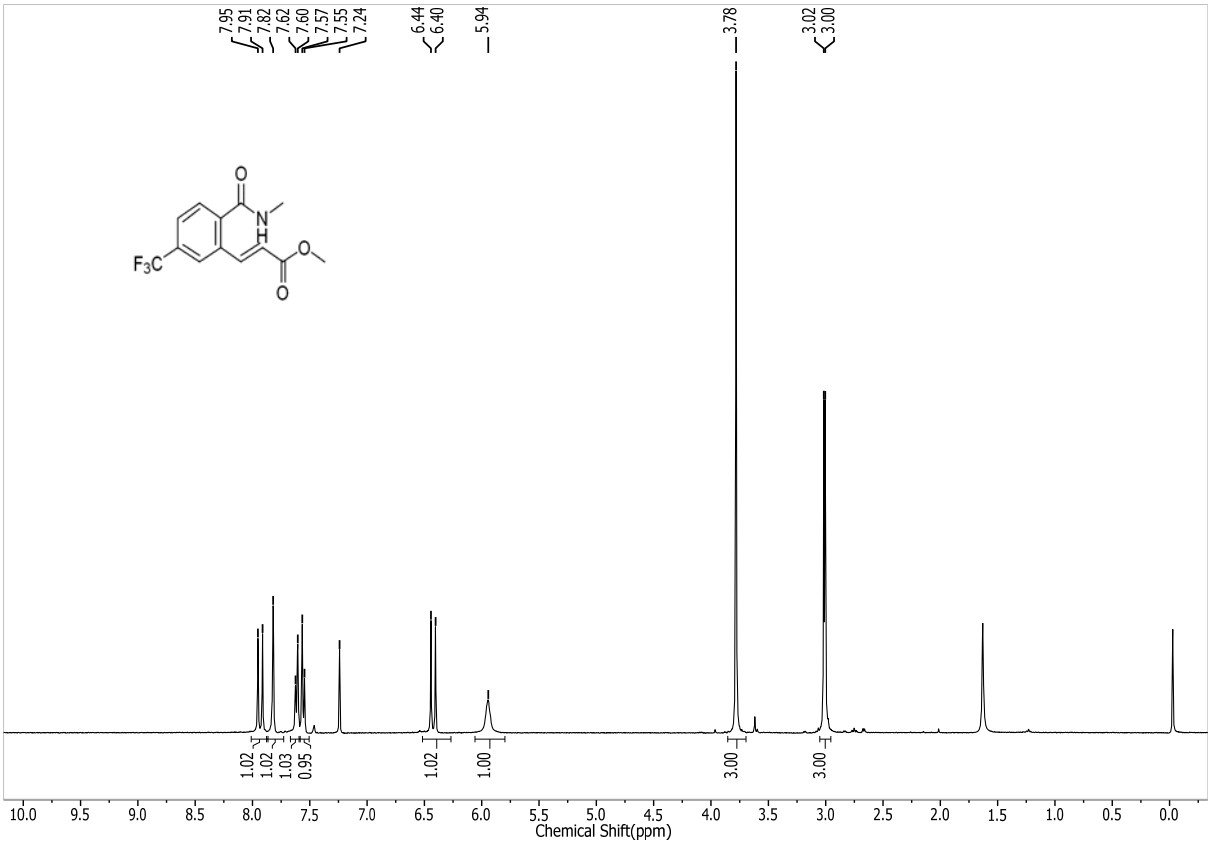


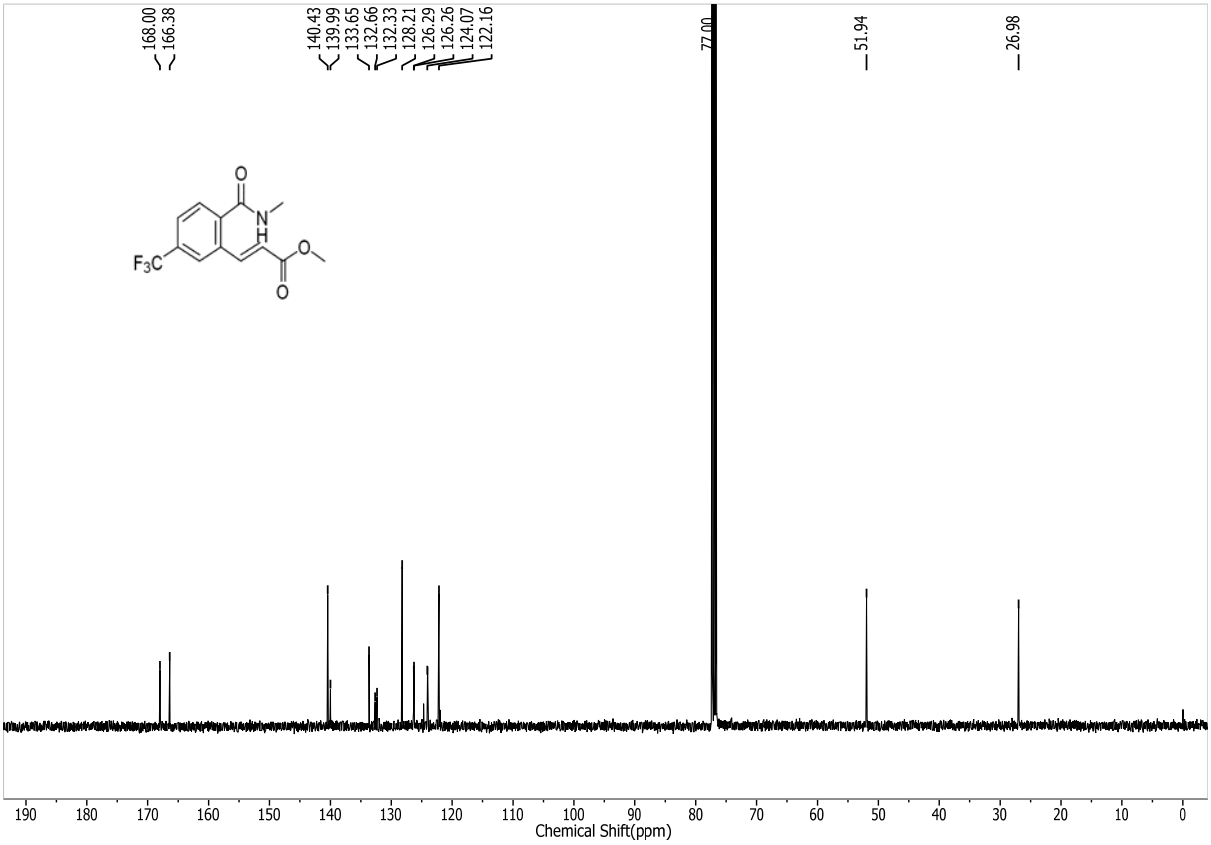


DEPT (135) NMR Spectrum of Compound **3ha.**

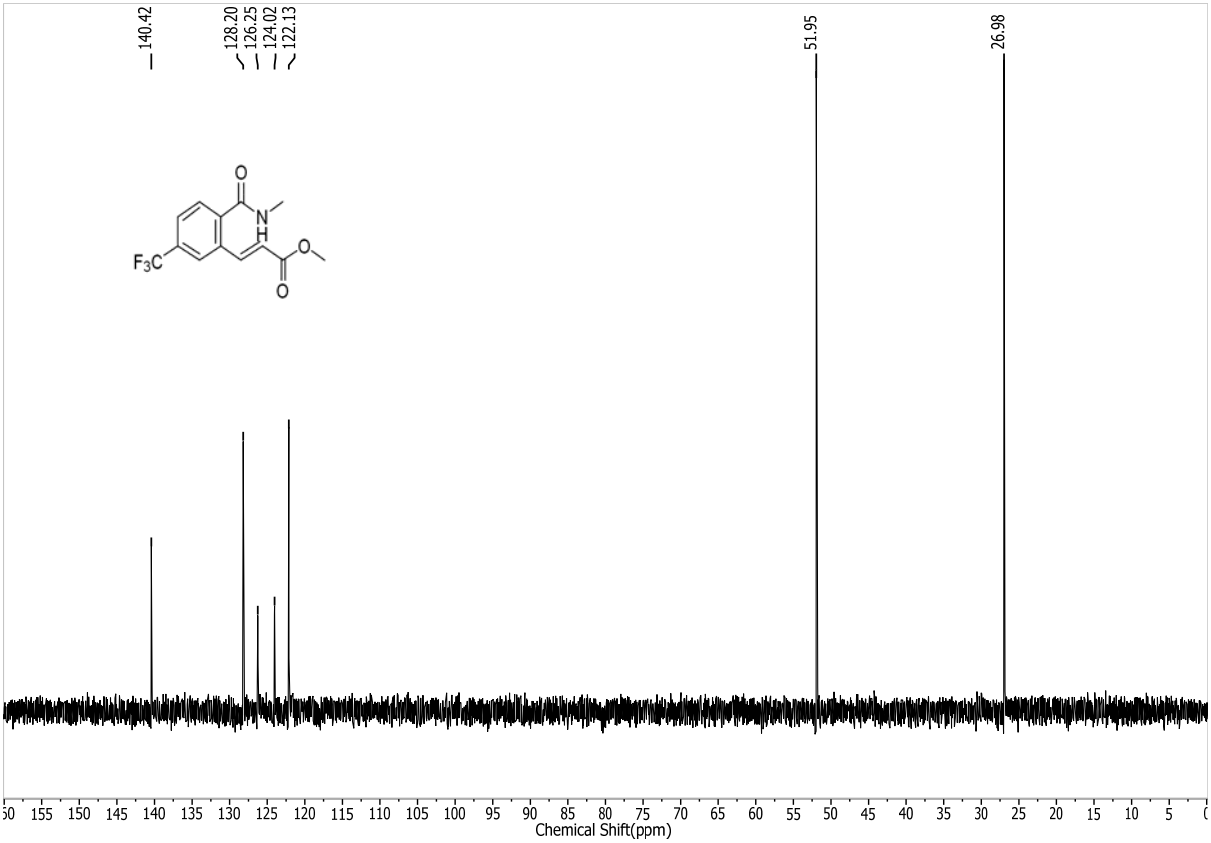


^{1}H and ^{13}C NMR Spectra of Compound **3ia.**

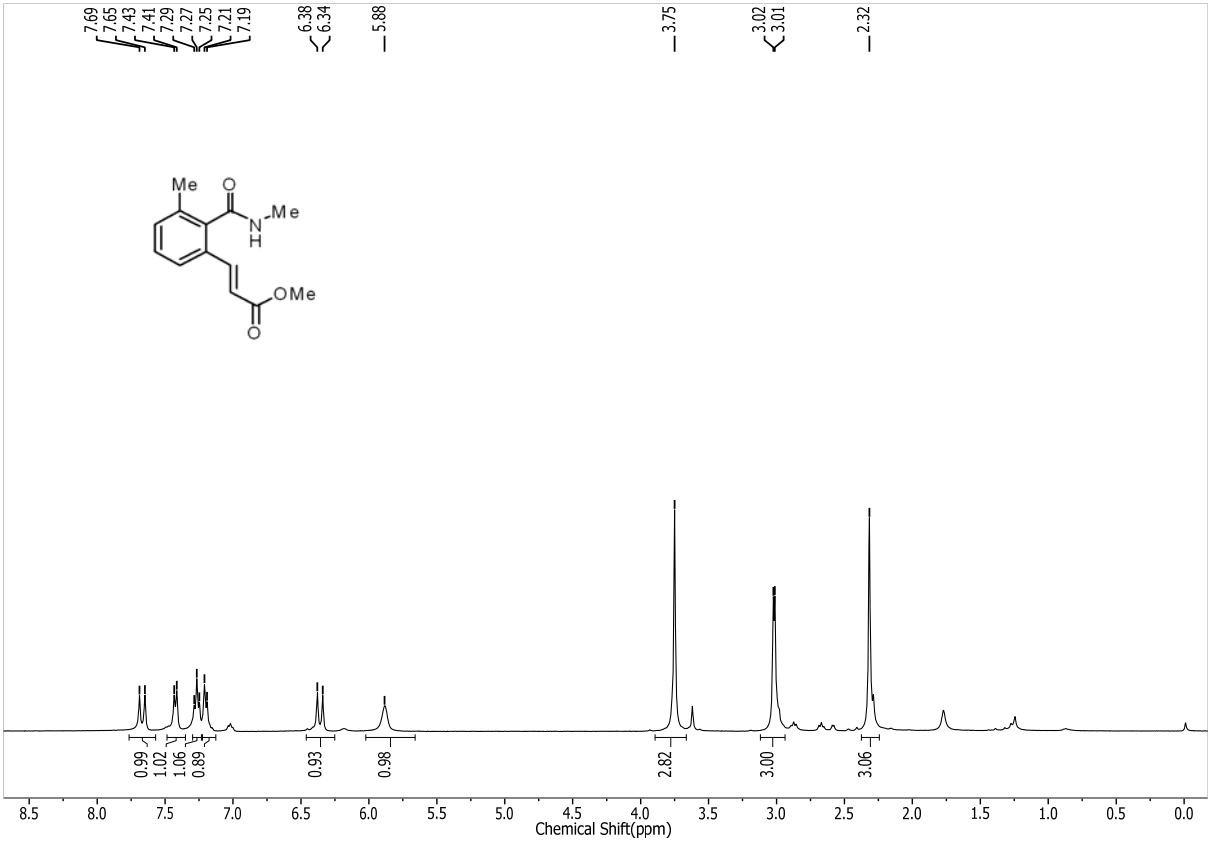


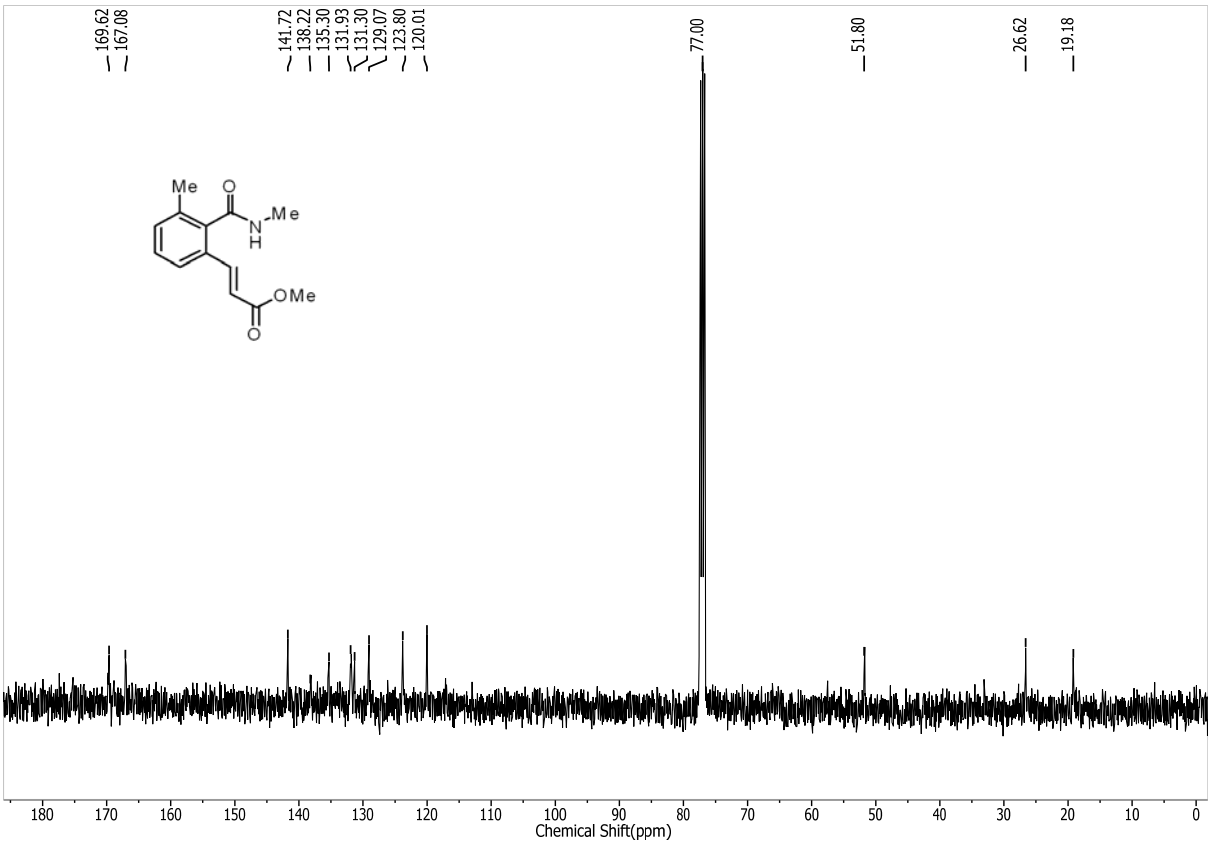


DEPT (135) NMR Spectrum of Compound **3ia.**

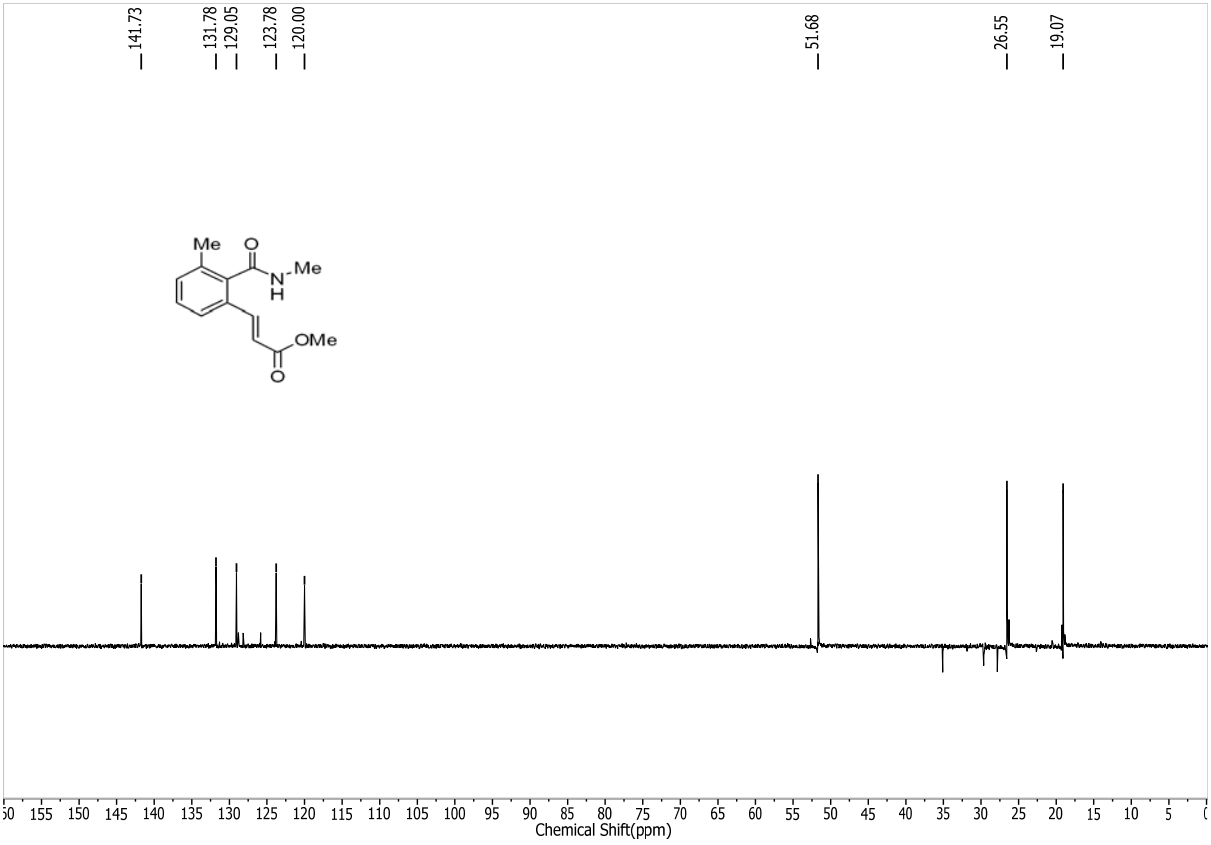


^{1}H and ^{13}C NMR Spectra of Compound **3ja.**

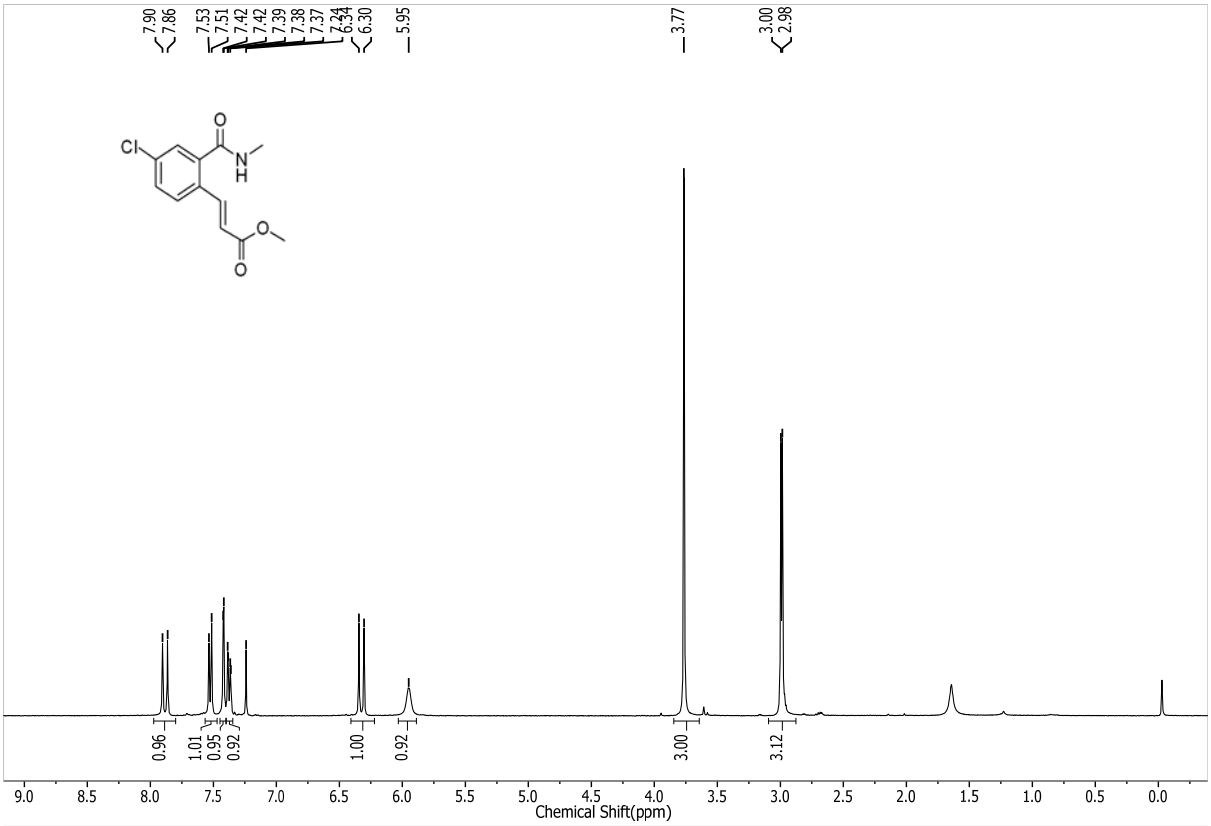


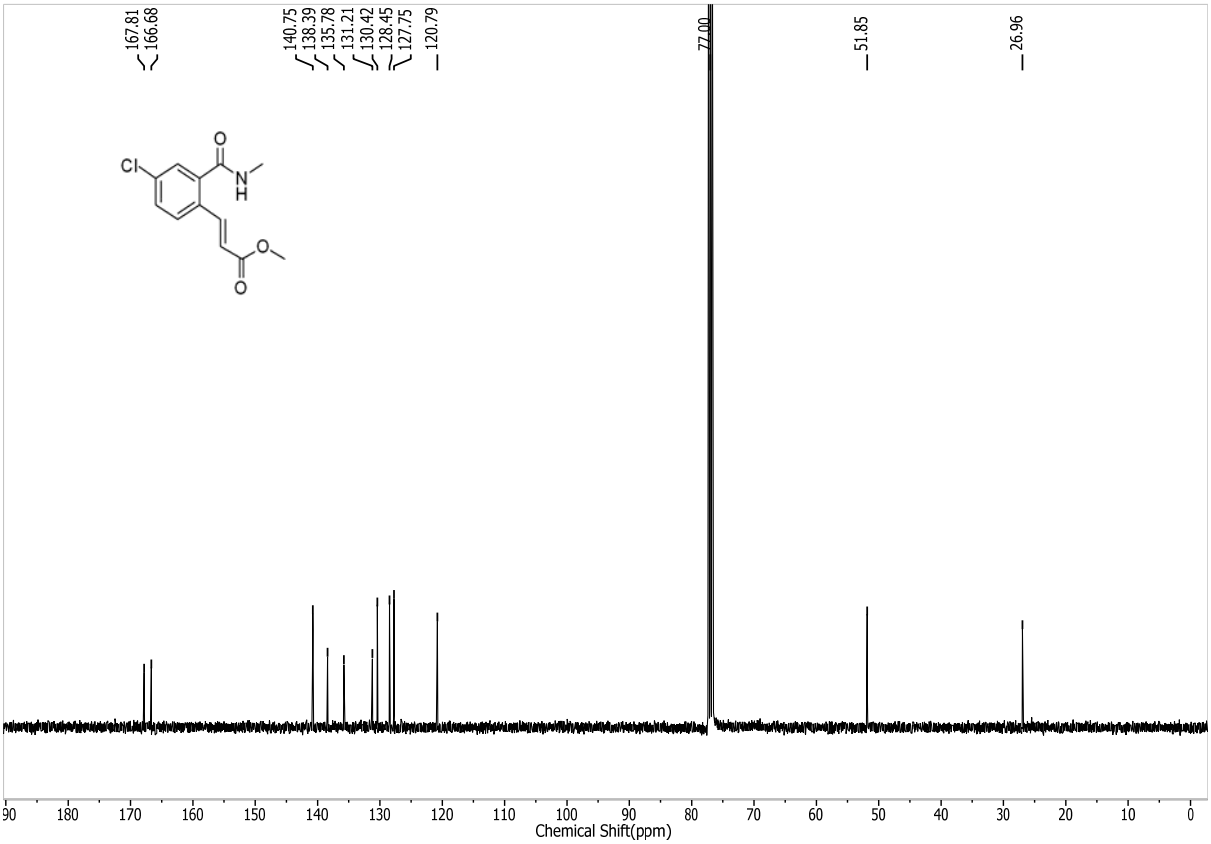


DEPT (135) NMR Spectrum of Compound **3ja.**

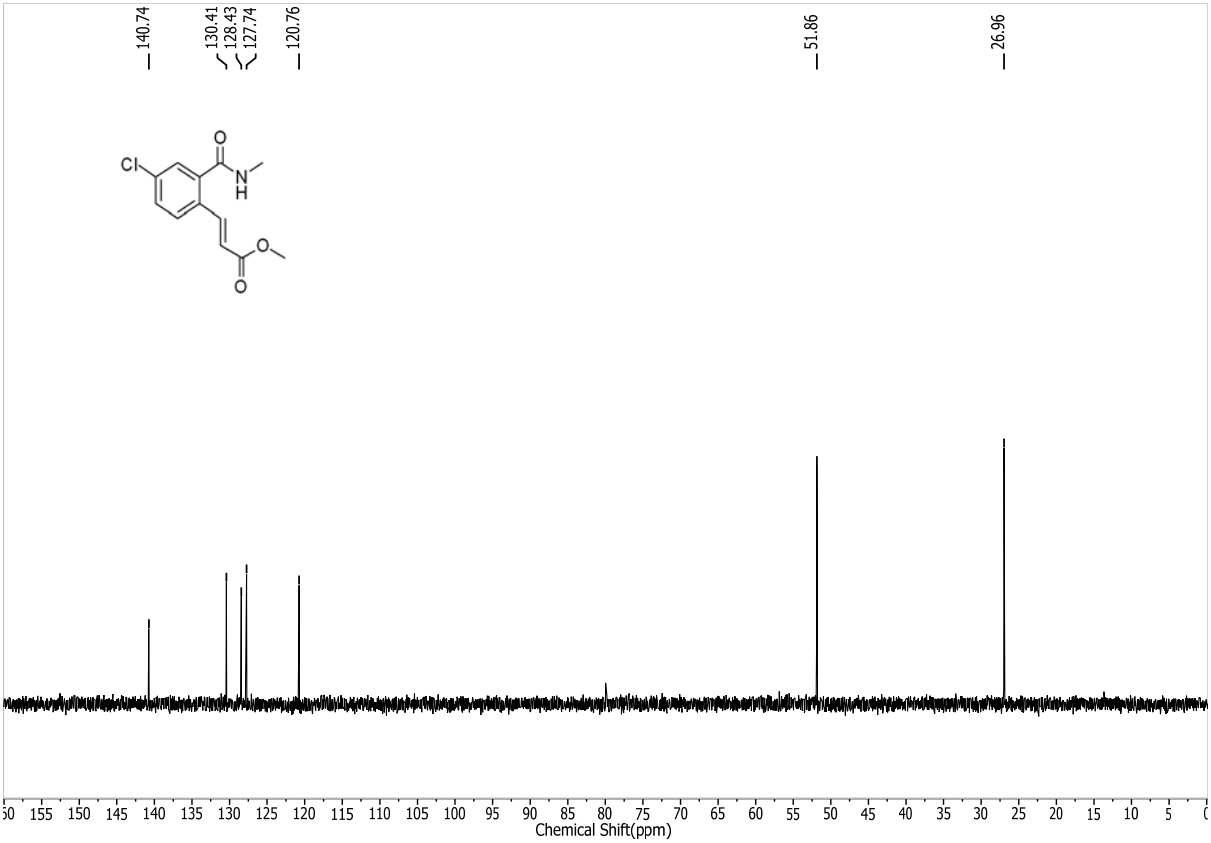


^{1}H and ^{13}C NMR Spectra of Compound **3ka.**

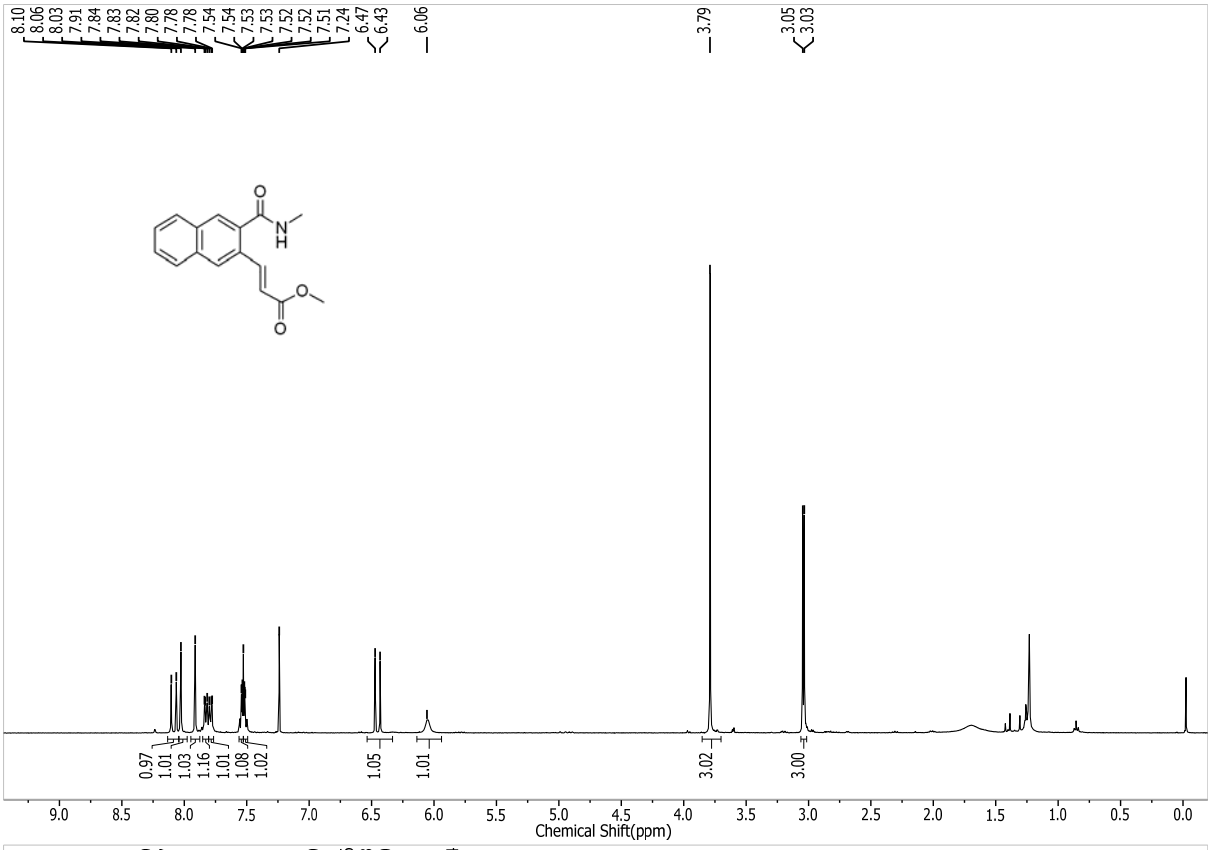


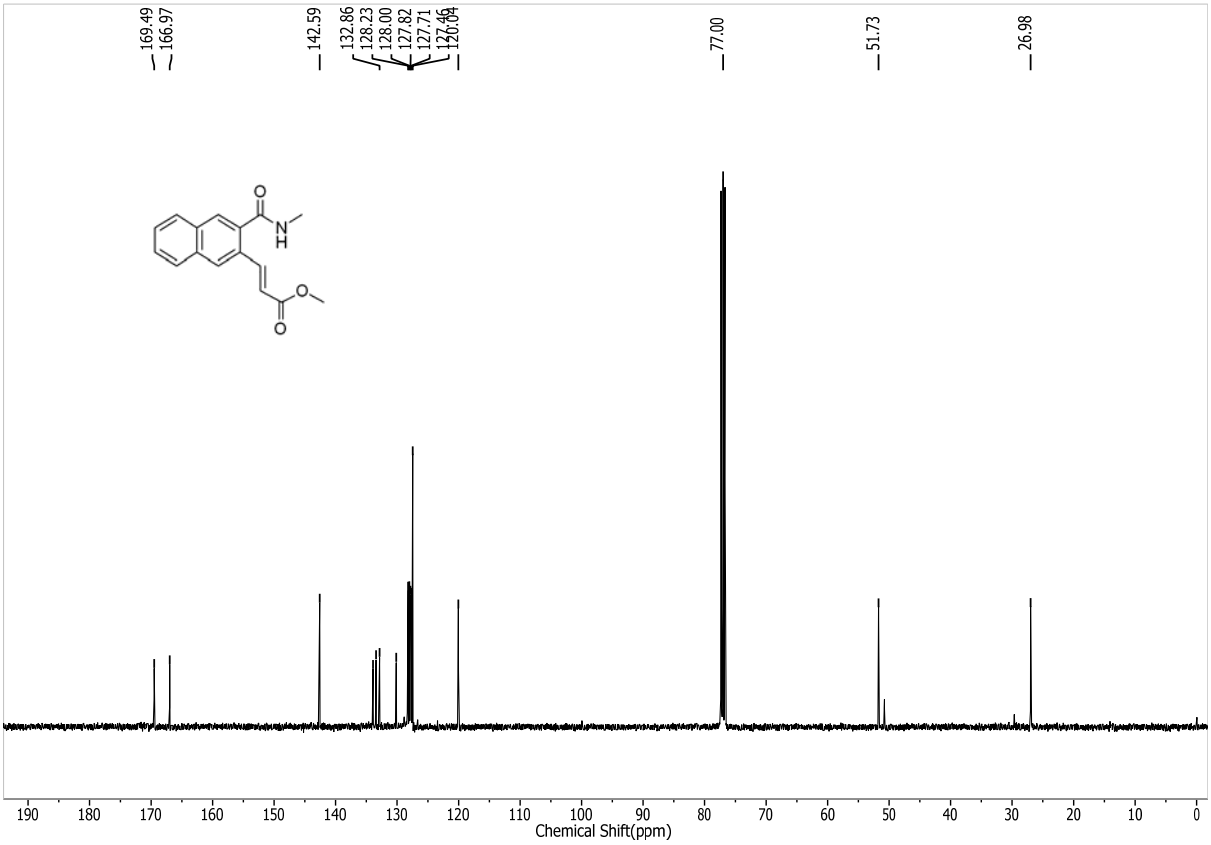


DEPT (135) NMR Spectrum of Compound **3ka.**

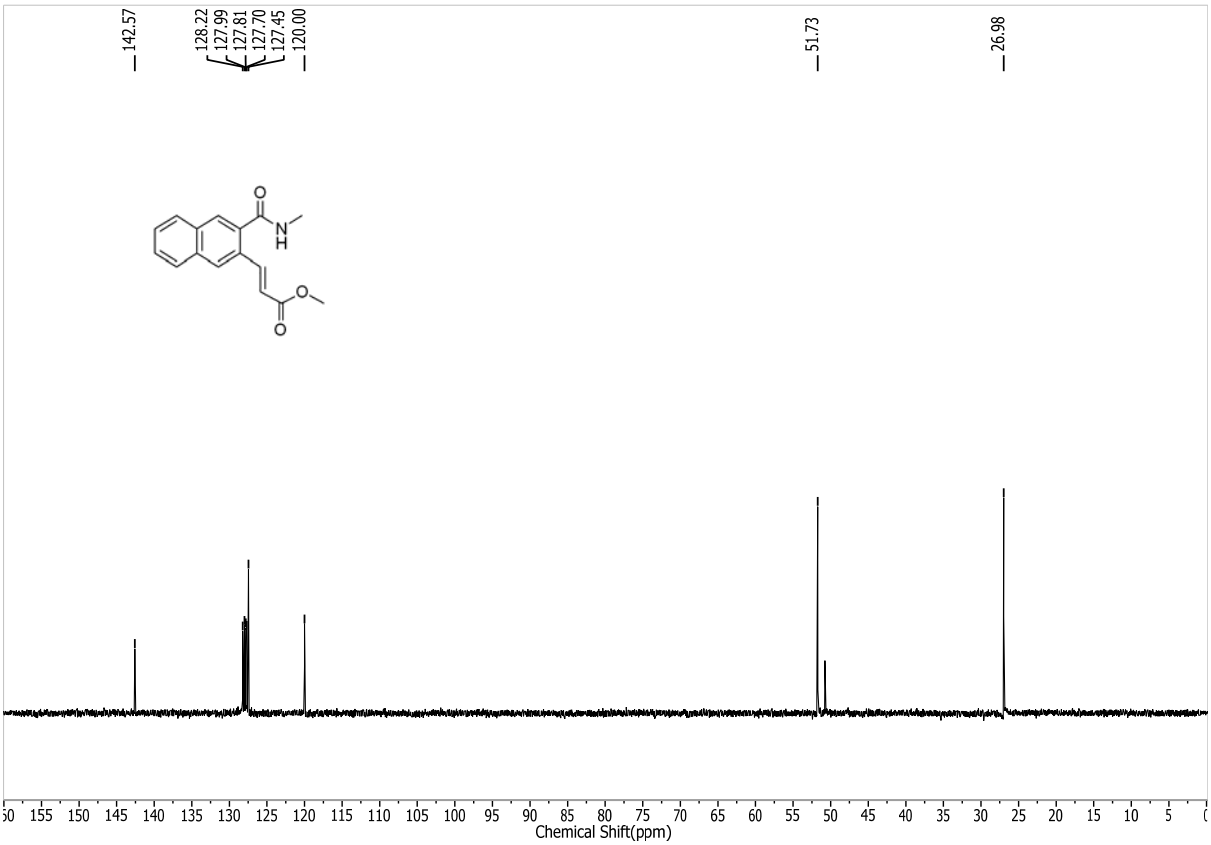


^{1}H and ^{13}C NMR Spectra of Compound **3la.**

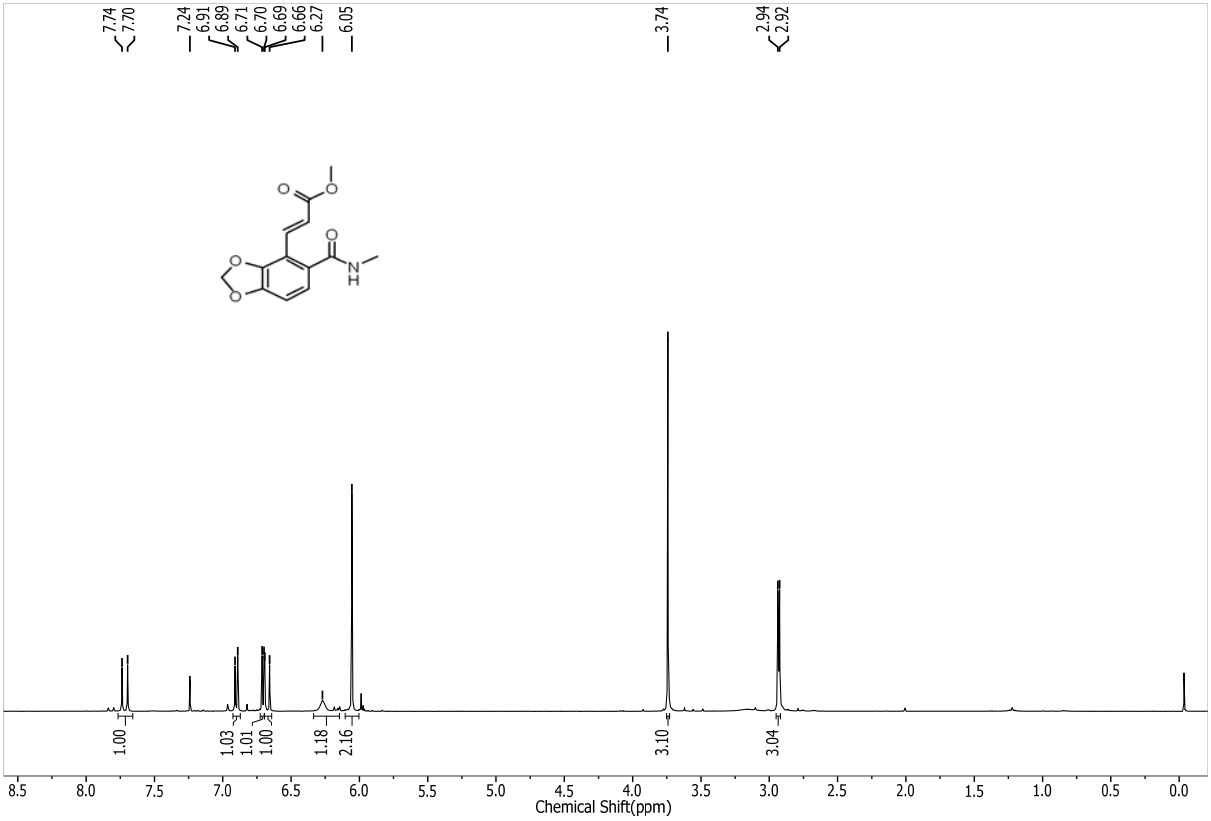


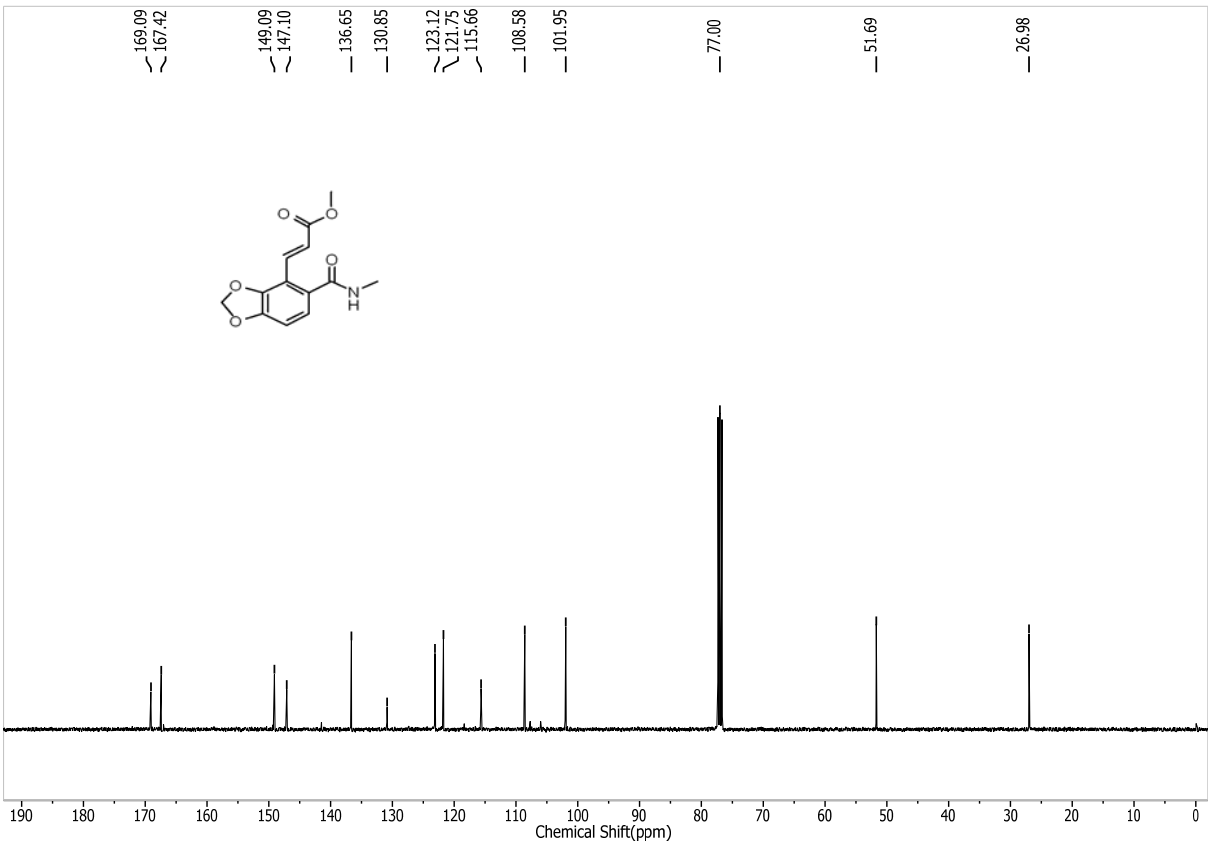


DEPT (135) NMR Spectrum of Compound **3la.**

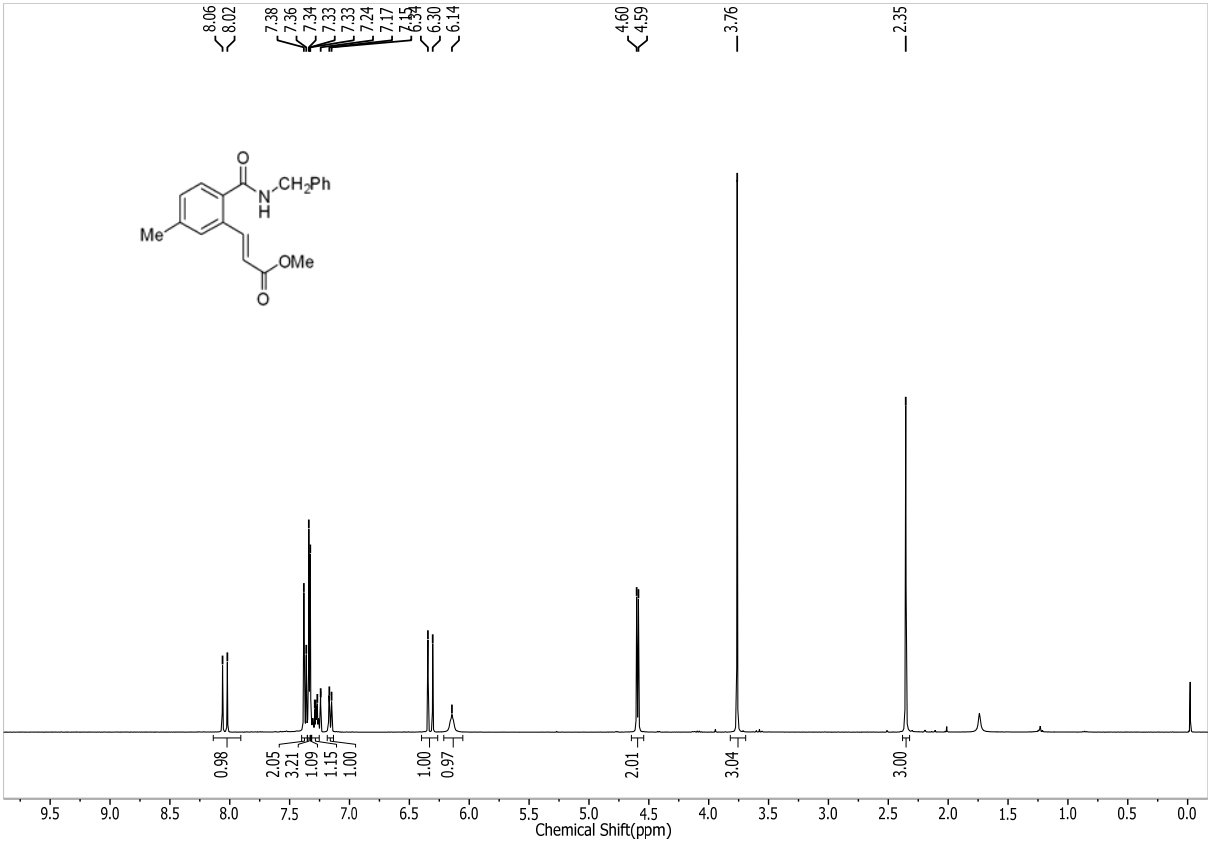


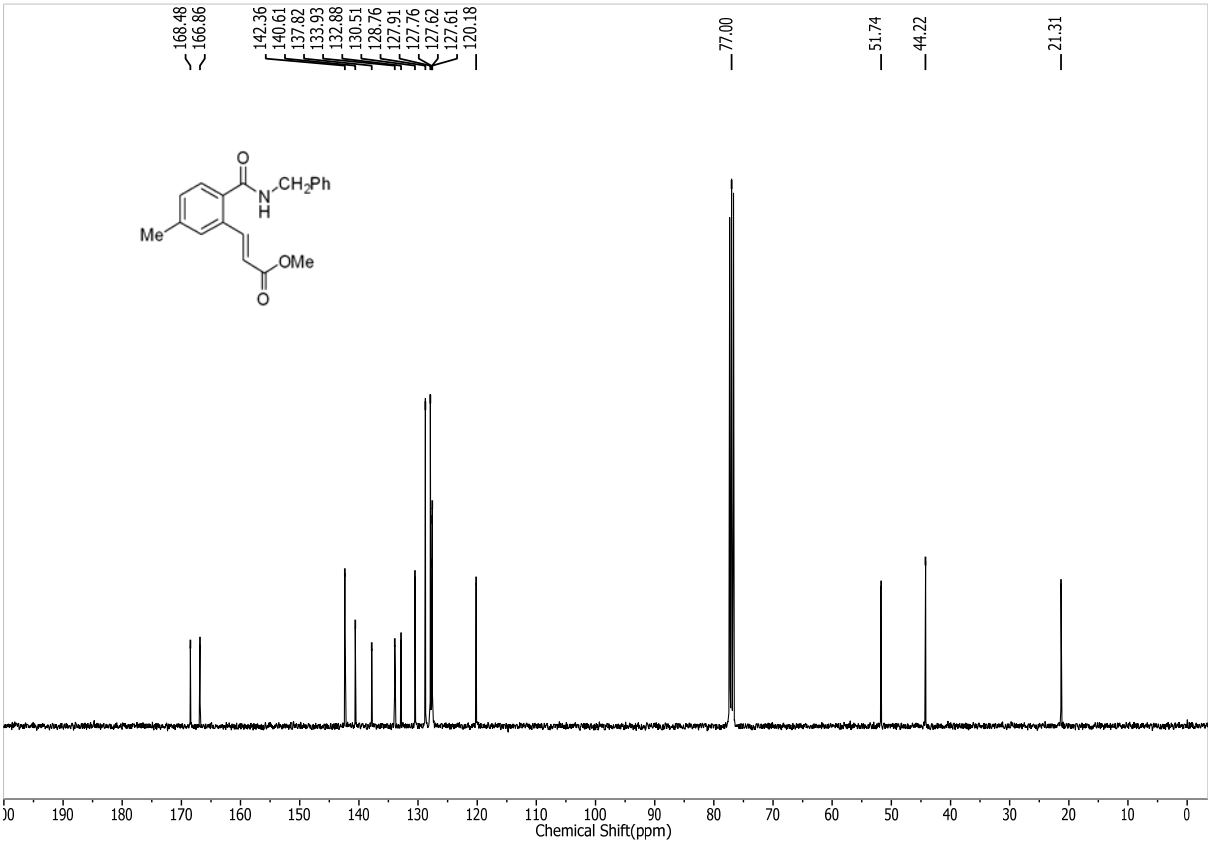
^{1}H and ^{13}C NMR Spectra of Compound **3ma.**



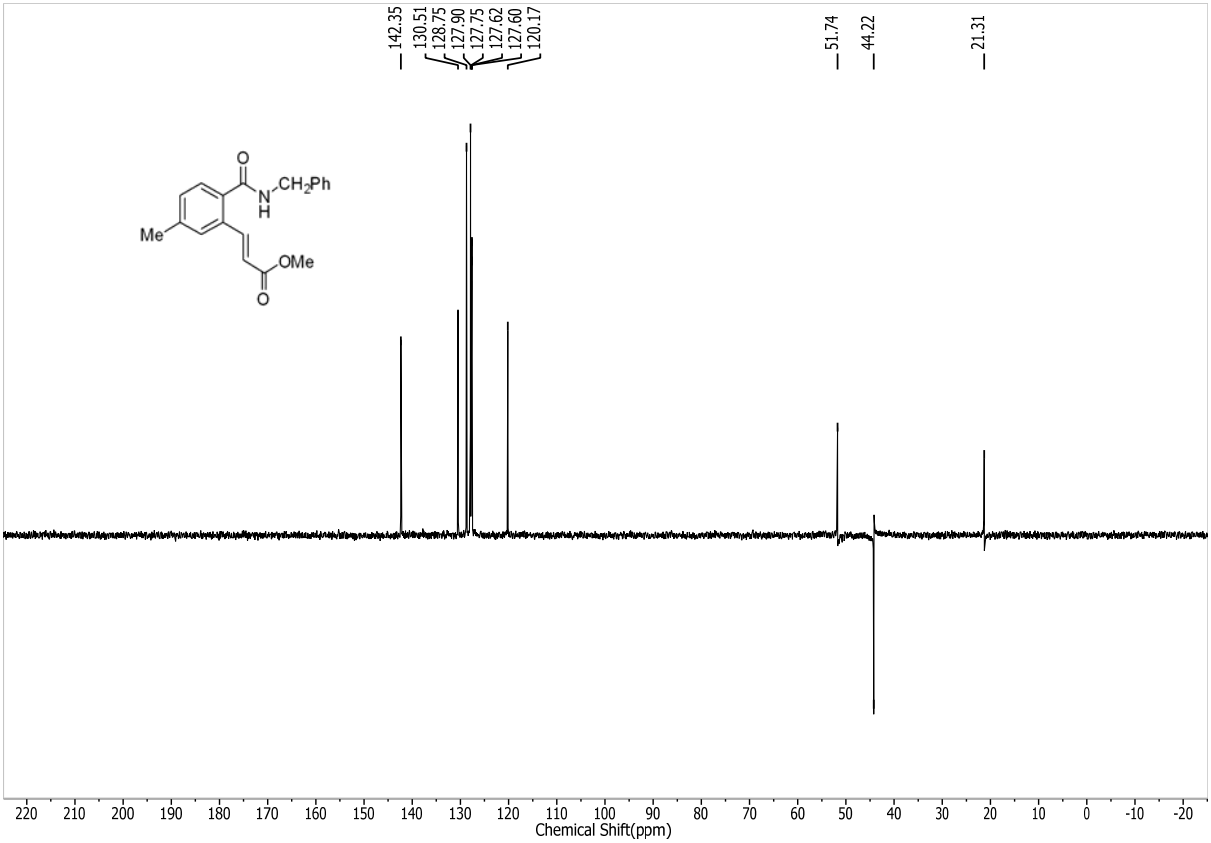


^{1}H and ^{13}C NMR Spectra of Compound **3na.**

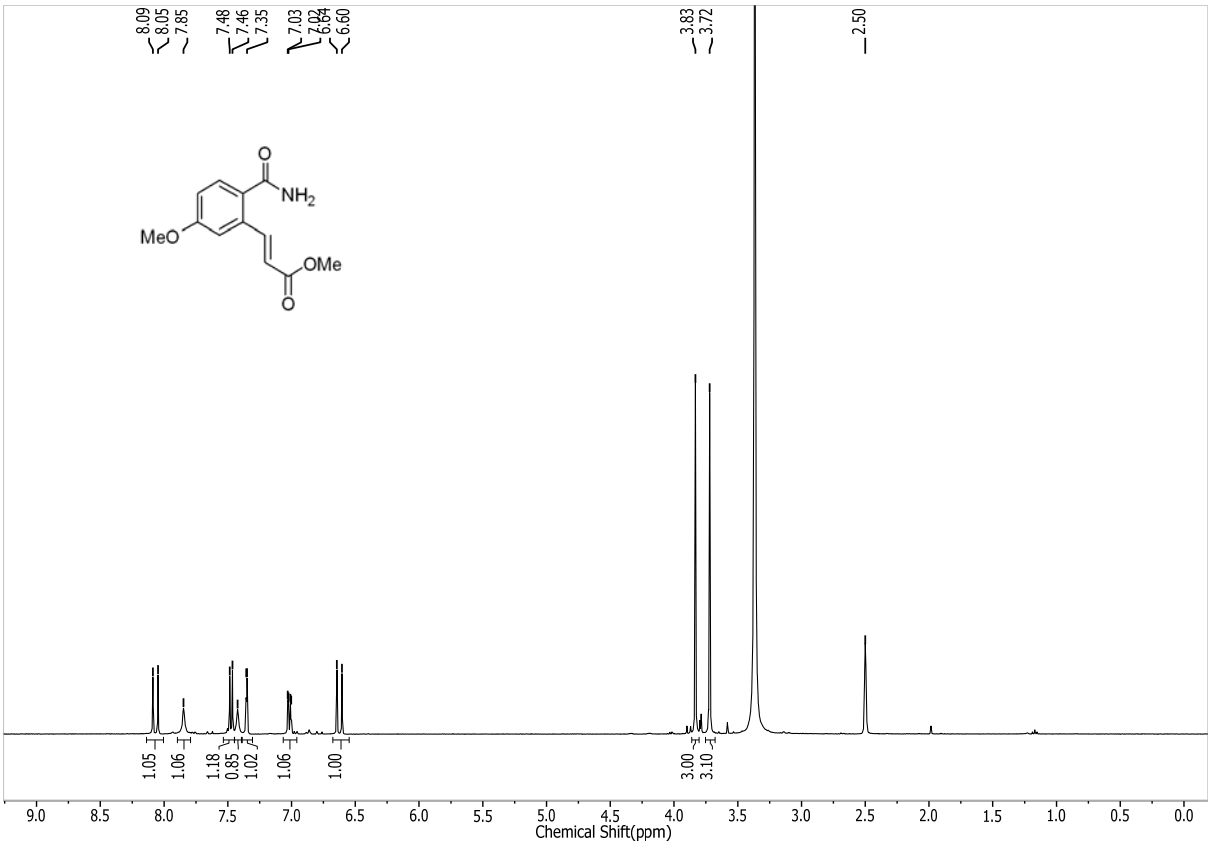


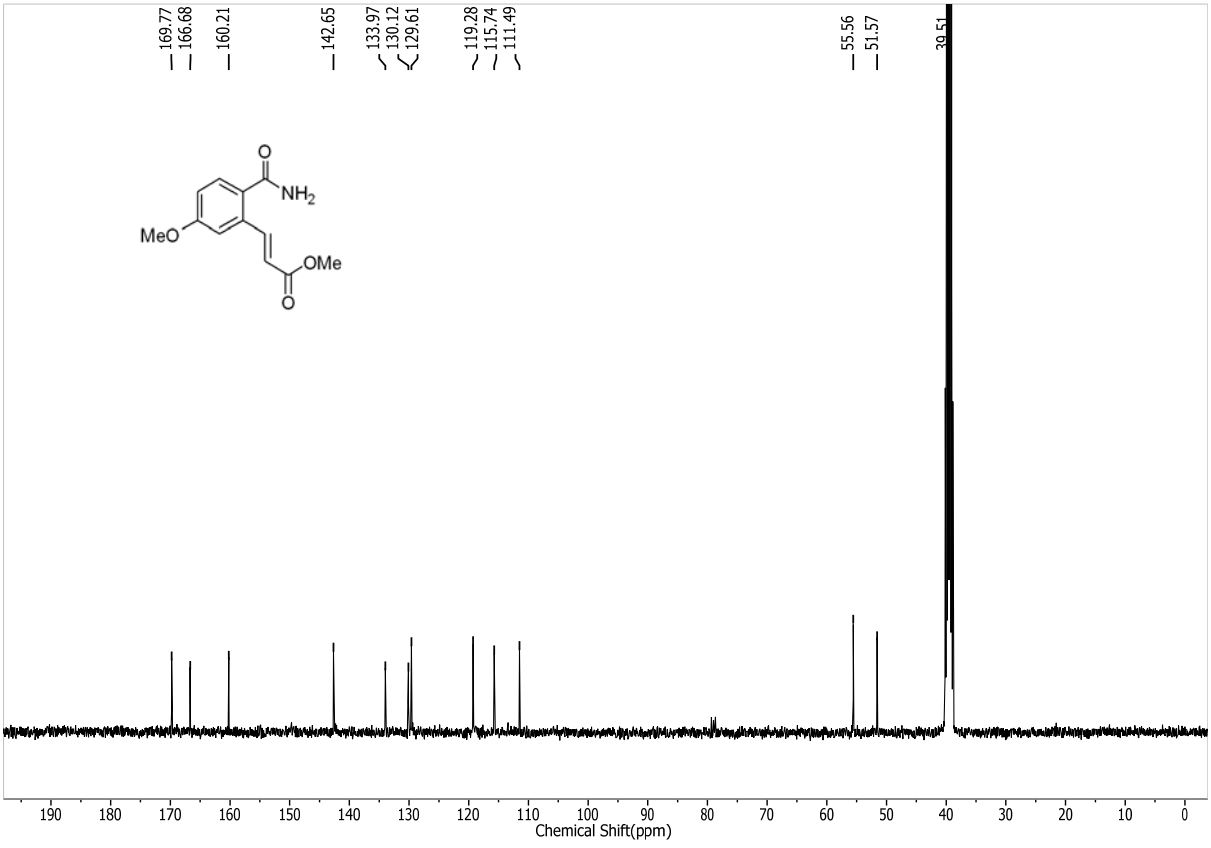


DEPT (135) NMR Spectrum of Compound **3na.**

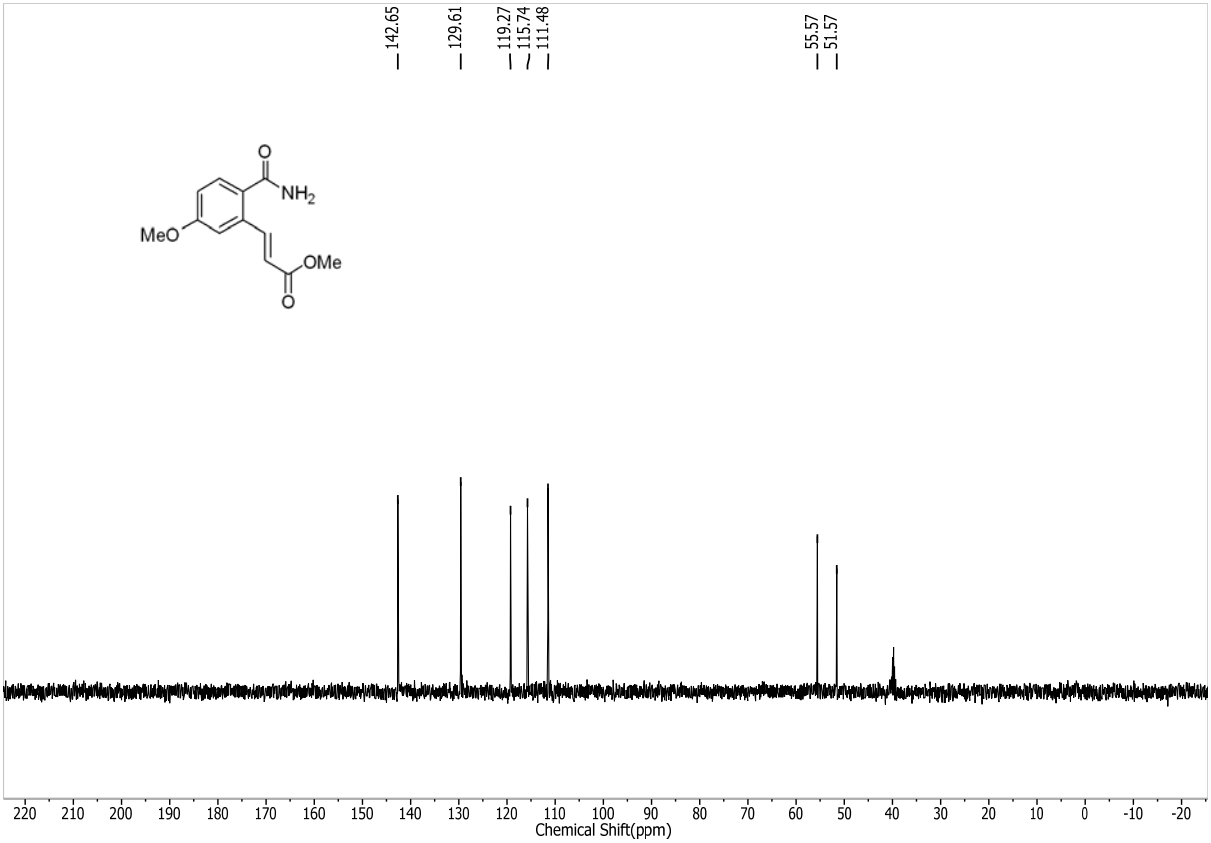


^{1}H and ^{13}C NMR Spectra of Compound **3oa.**

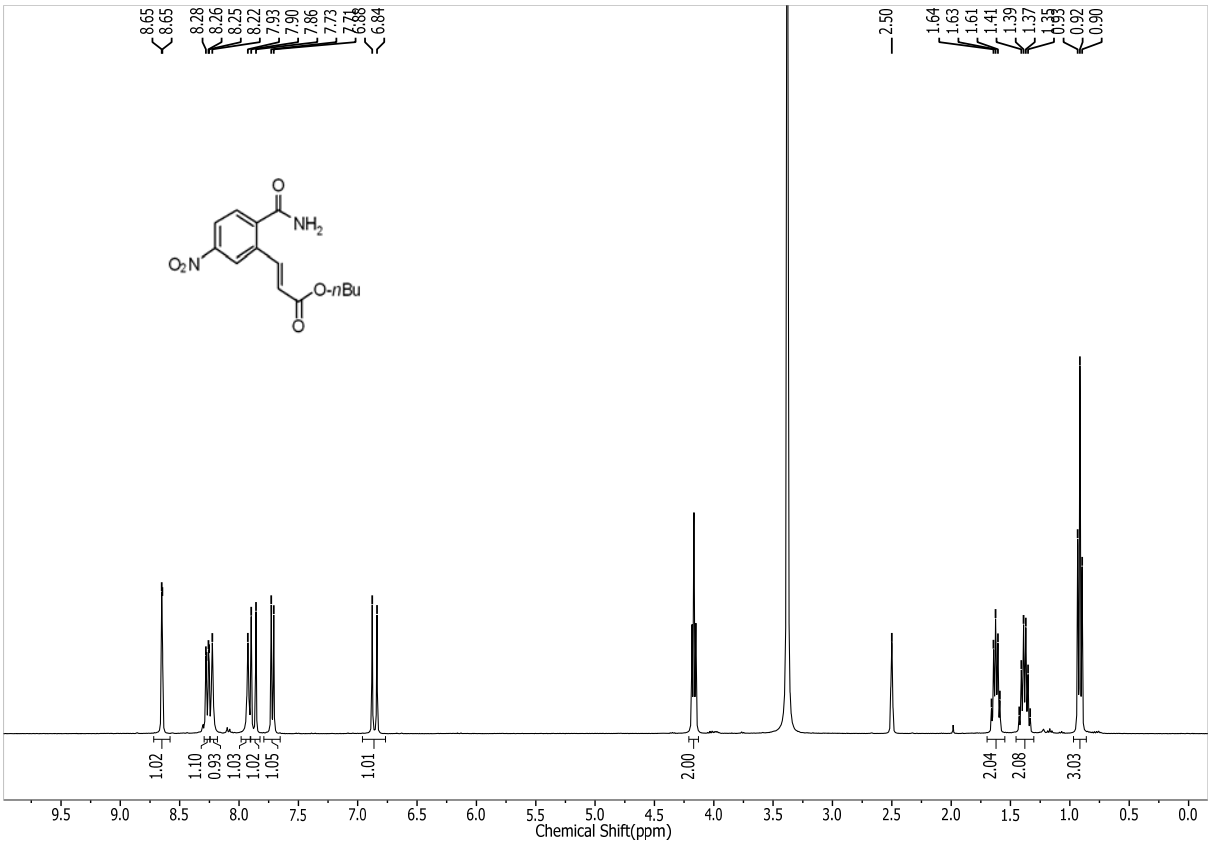


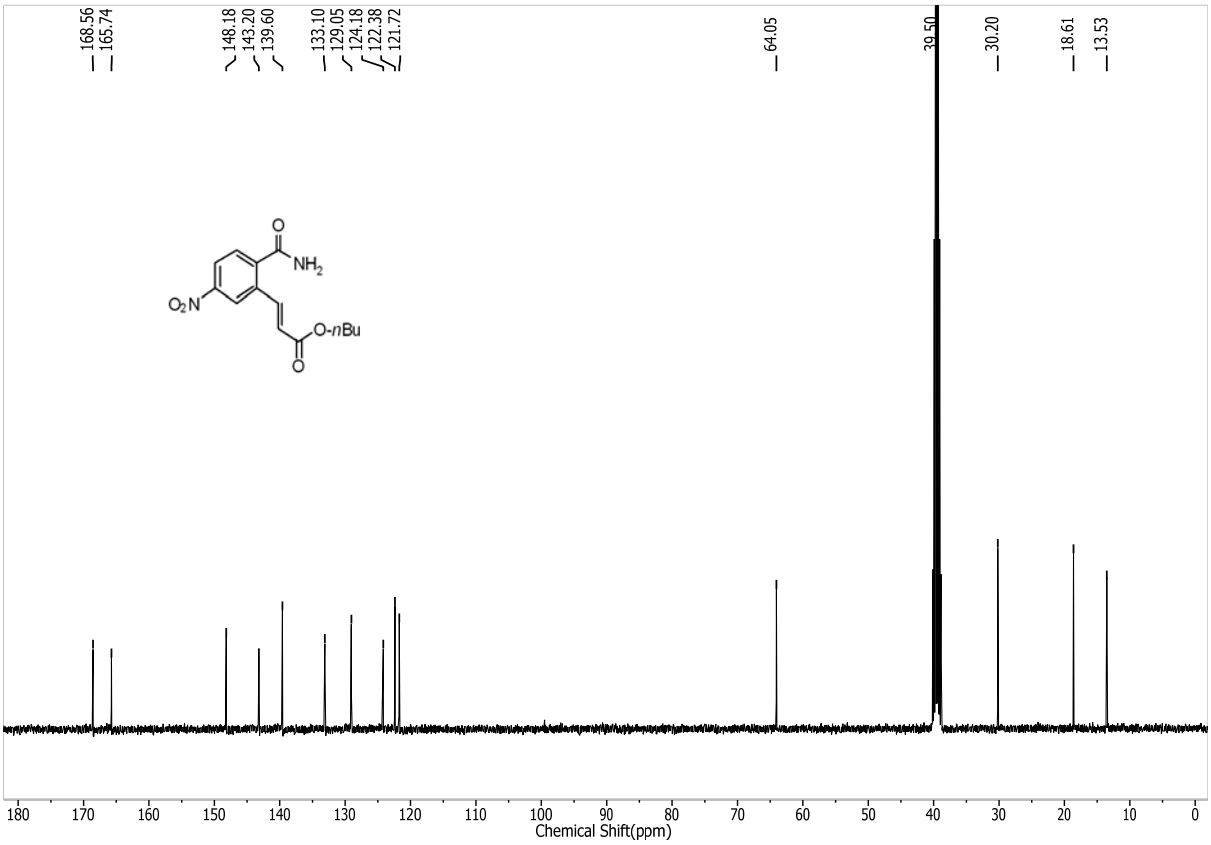


DEPT (135) NMR Spectrum of Compound **3oa.**

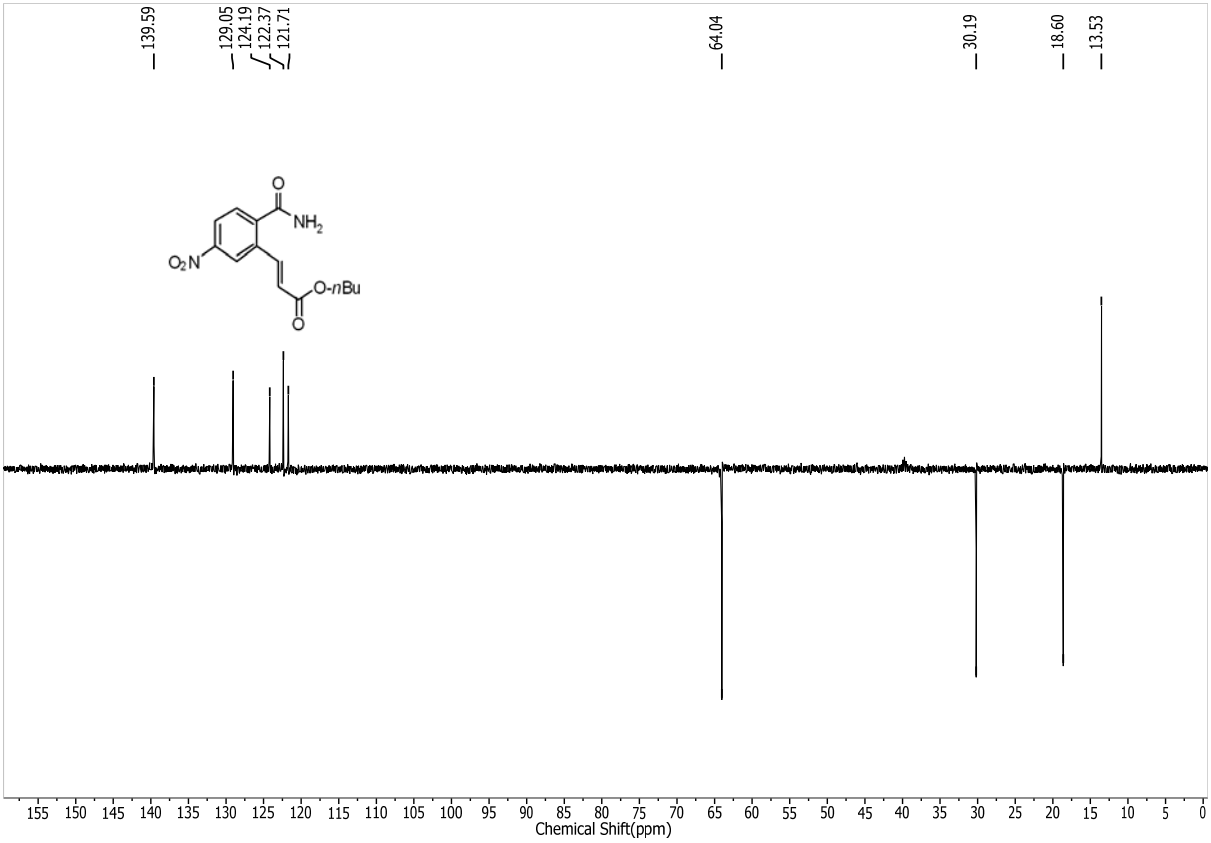


^{1}H and ^{13}C NMR Spectra of Compound **3pb.**

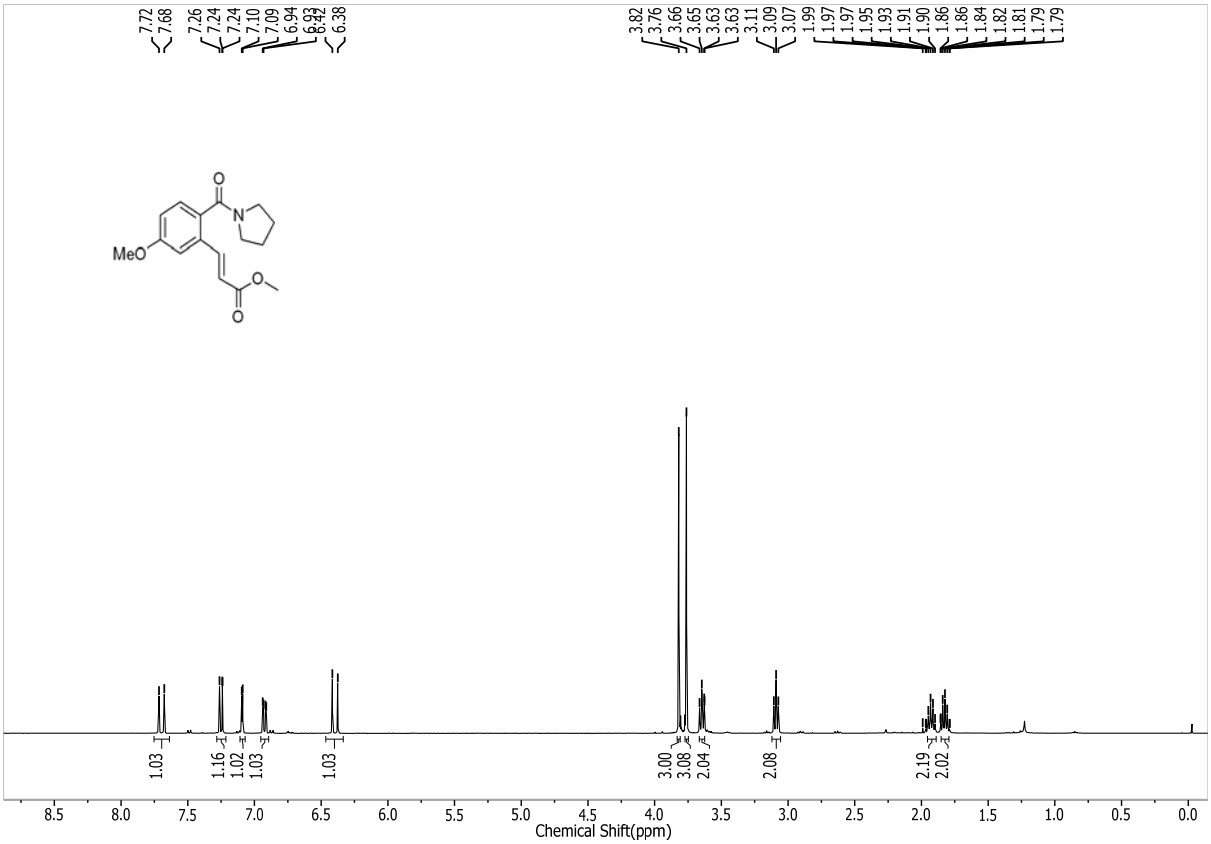


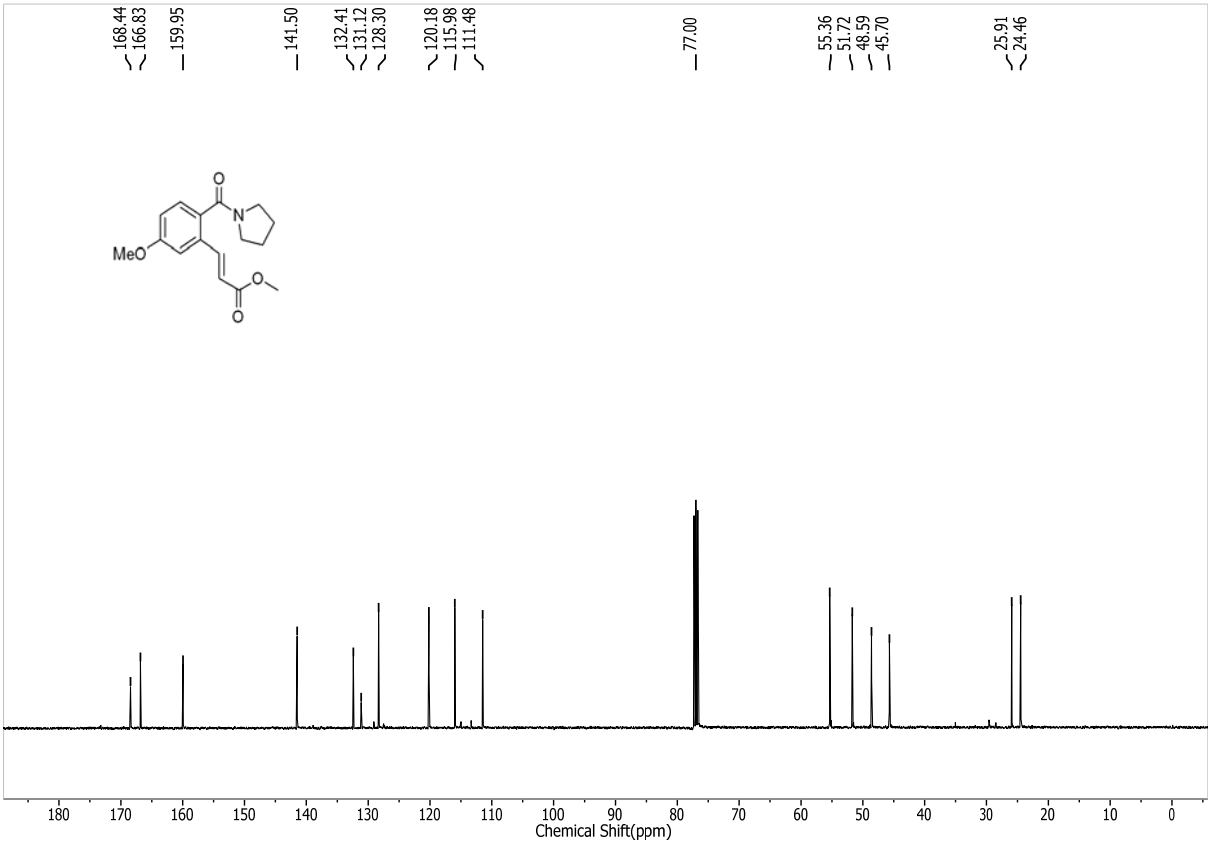


DEPT (135) NMR Spectrum of Compound **3pb.**

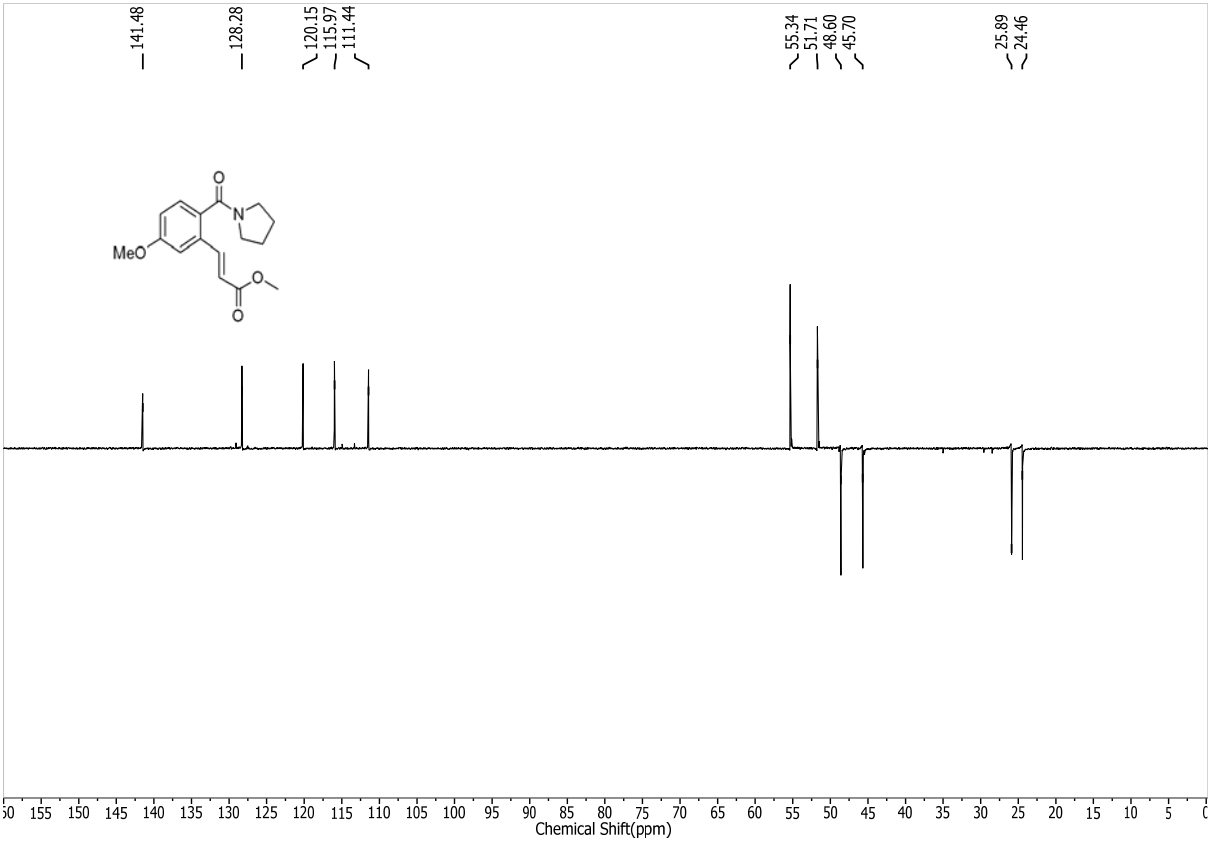


^{1}H and ^{13}C NMR Spectra of Compound **3qa.**

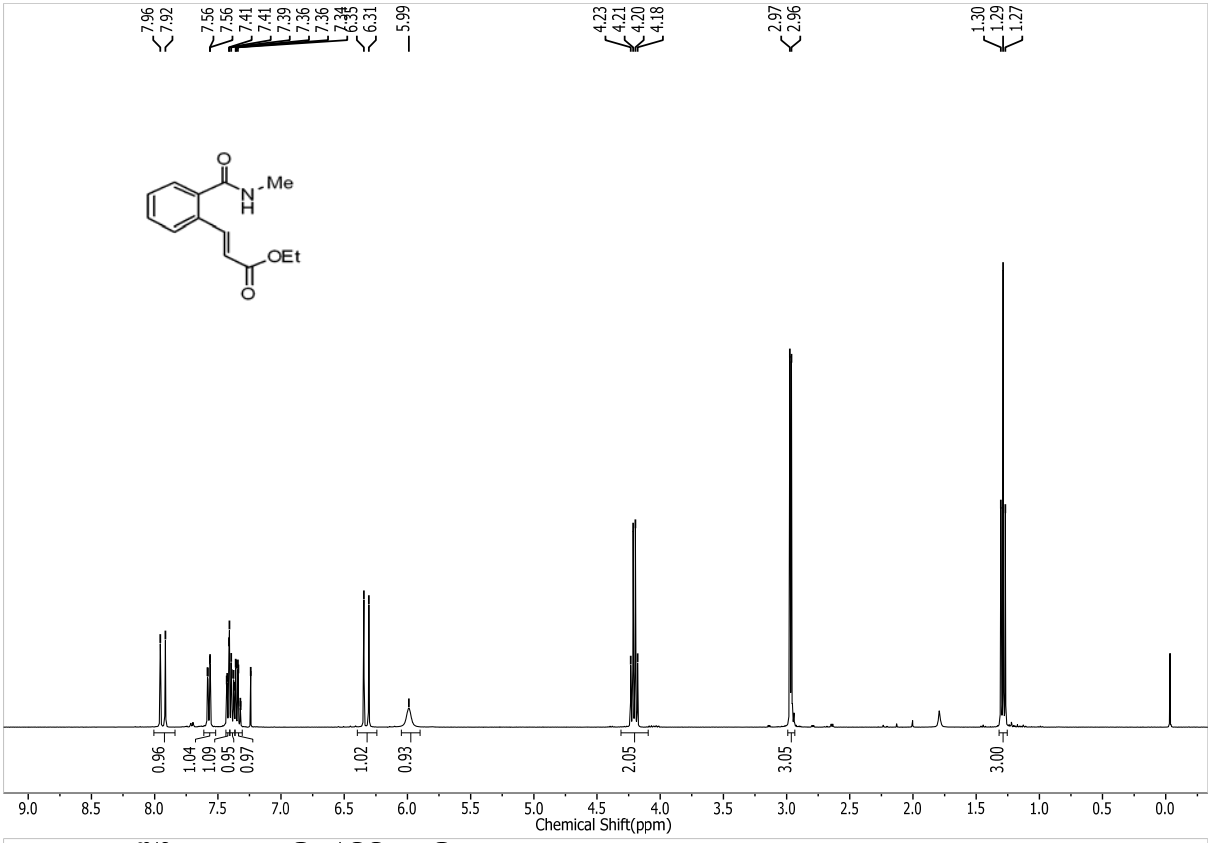


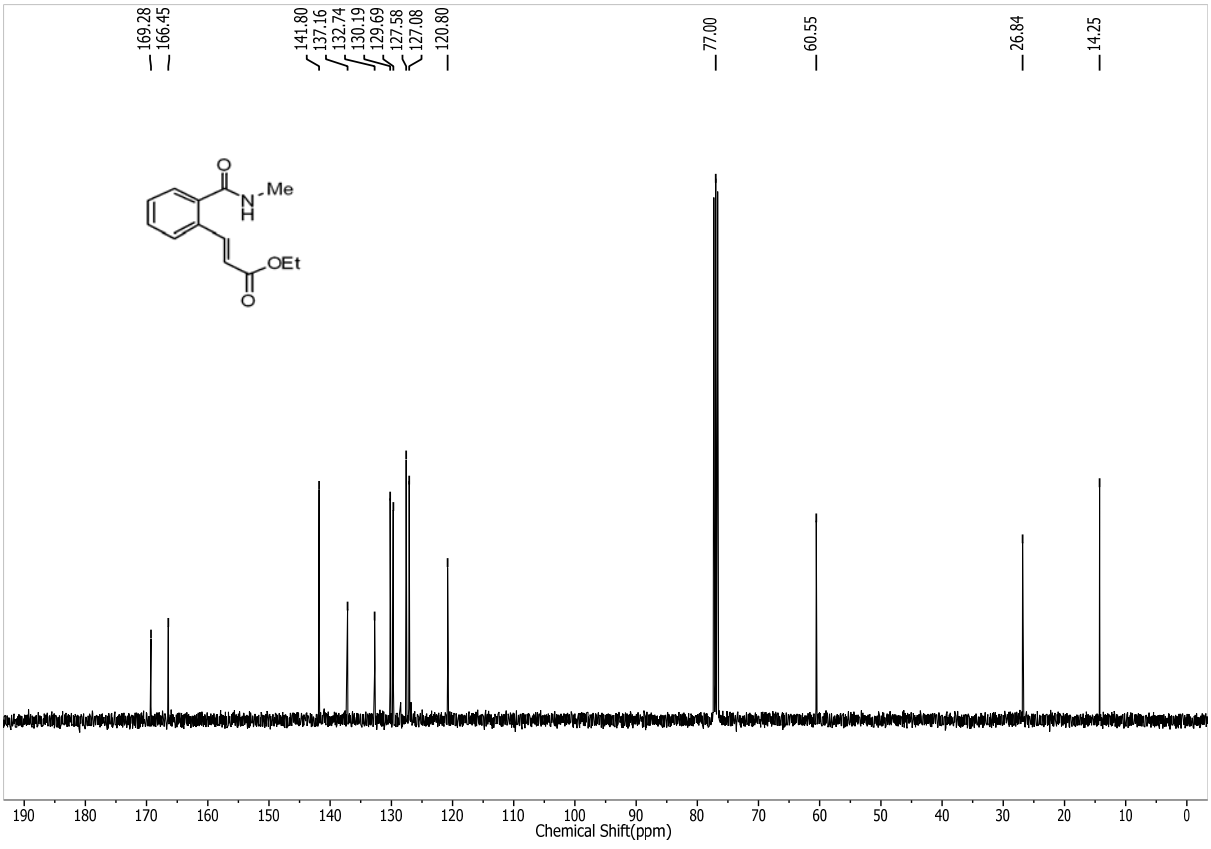


DEPT (135) NMR Spectrum of Compound **3qa.**

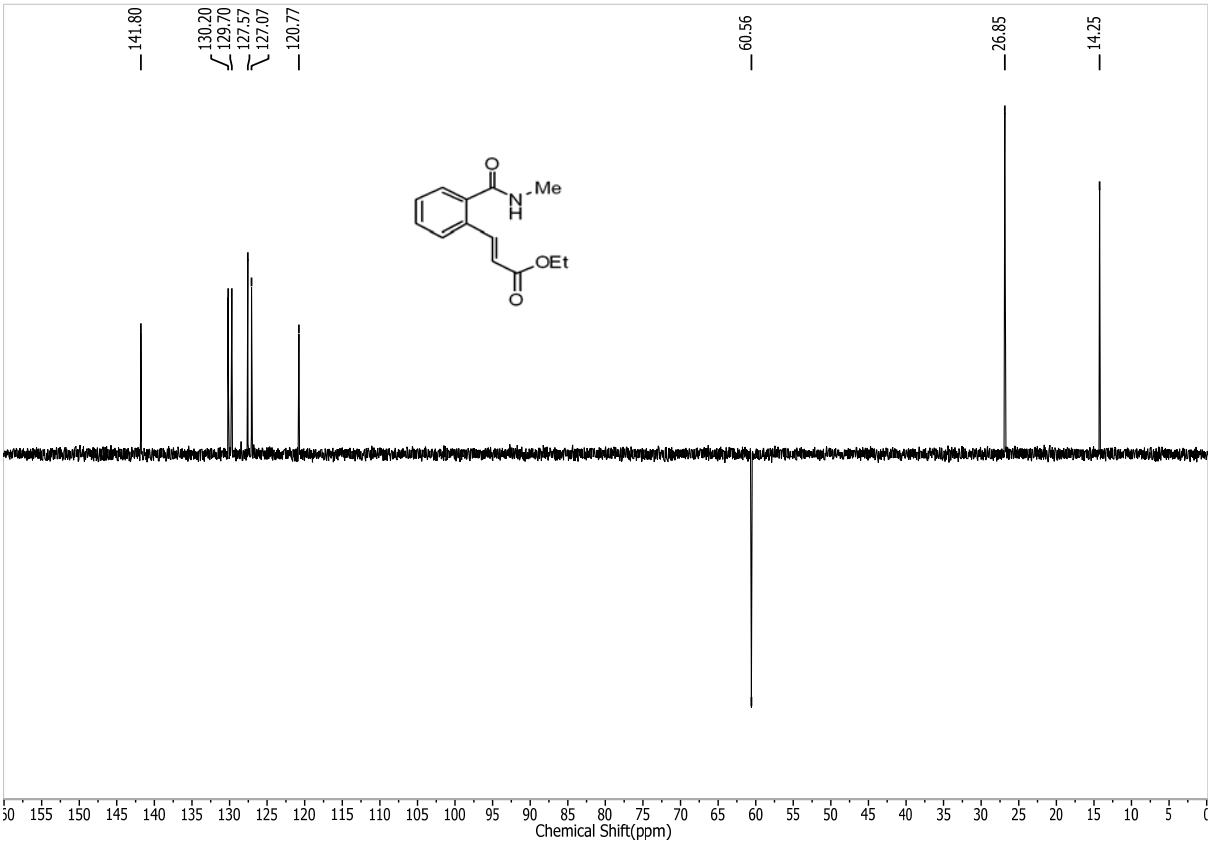


^{1}H and ^{13}C NMR Spectra of Compound **3ac.**

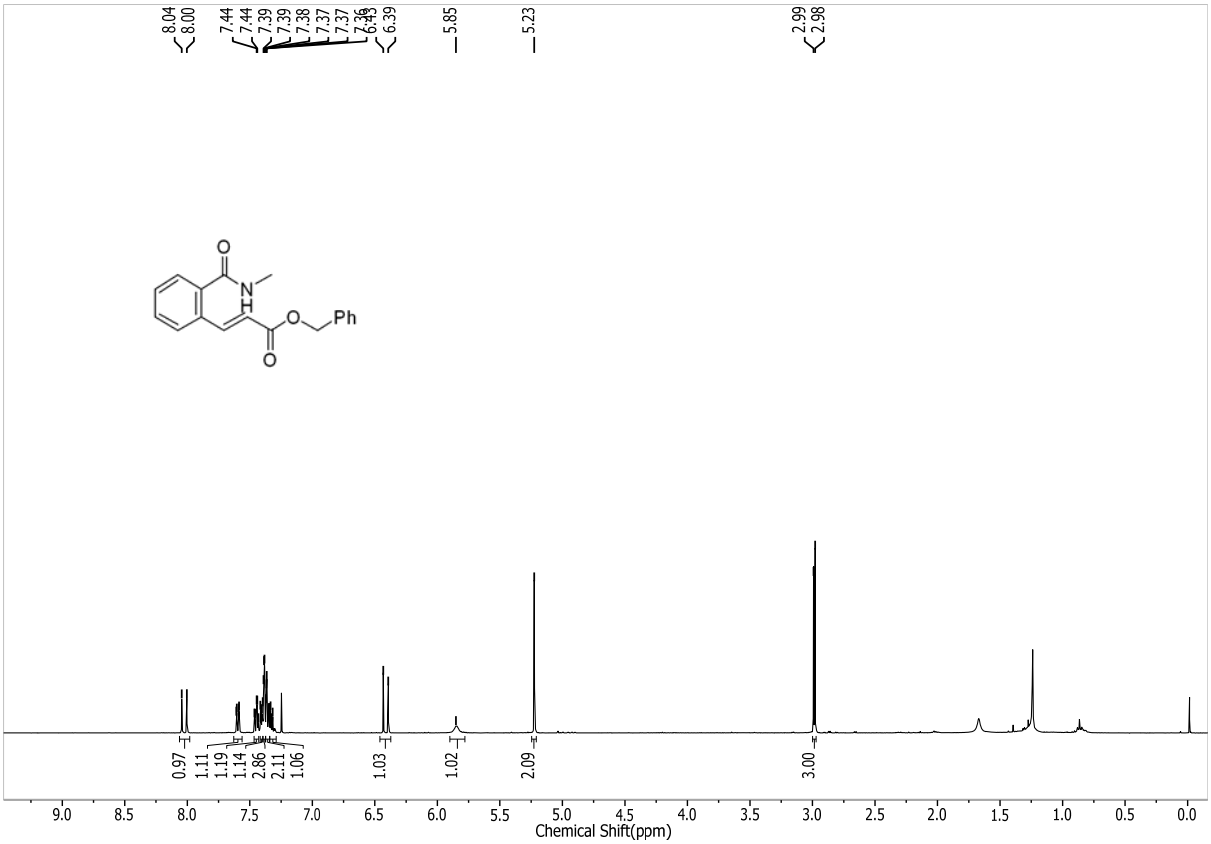


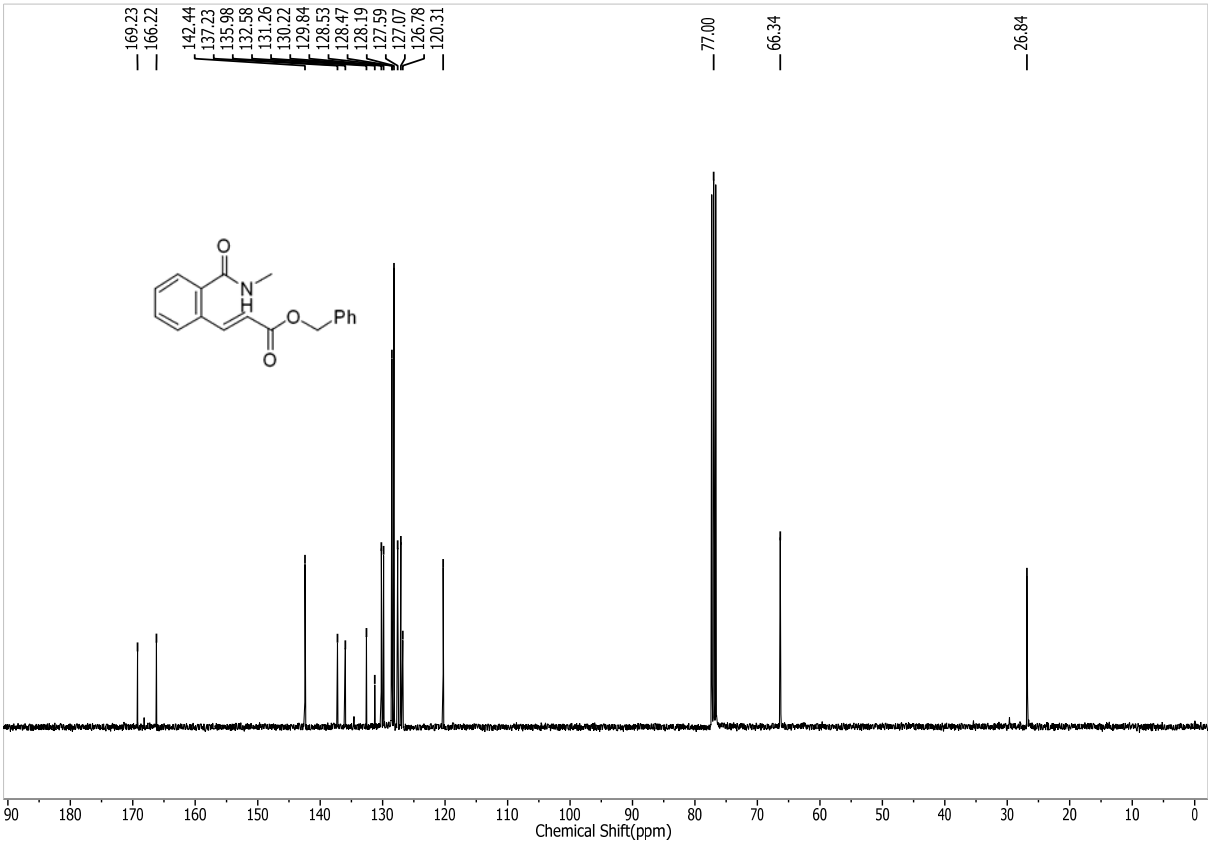


DEPT (135) NMR Spectrum of Compound **3ac.**

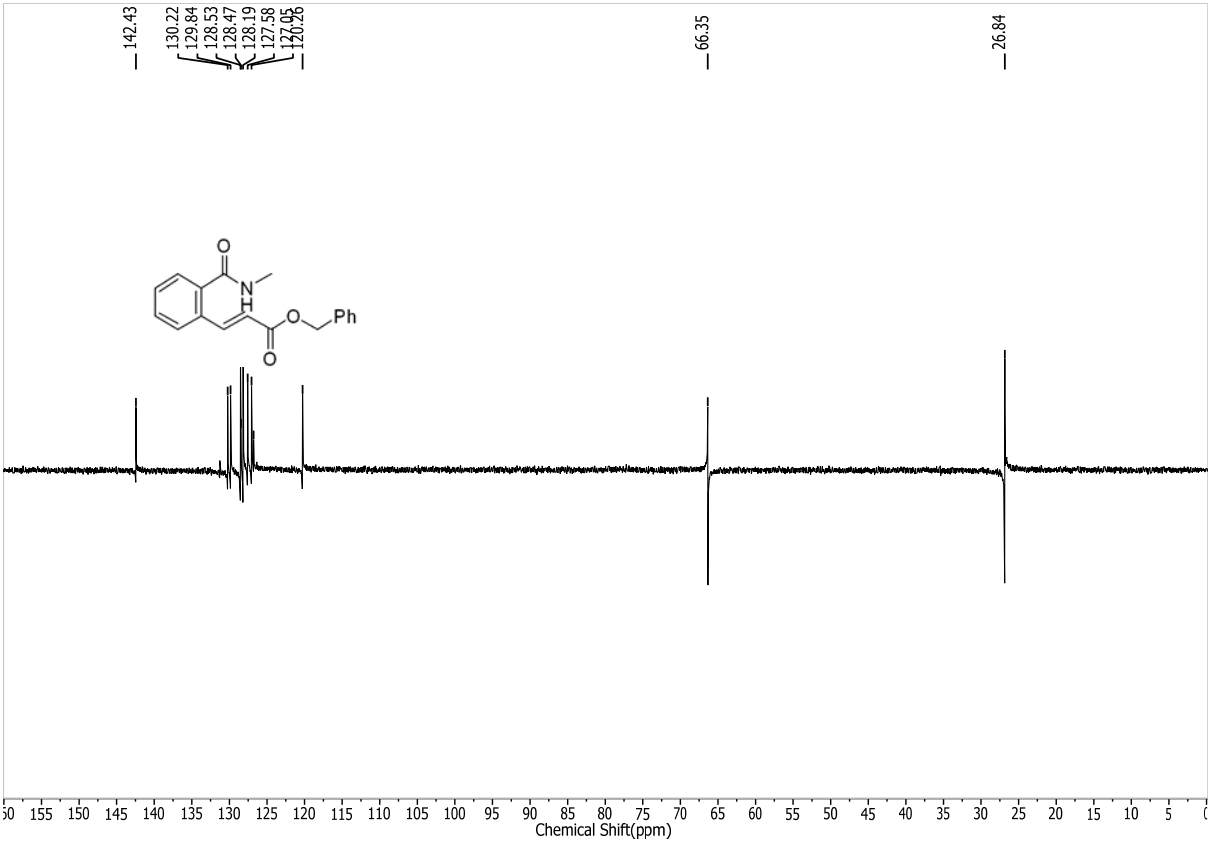


^{1}H and ^{13}C NMR Spectra of Compound **3ad.**

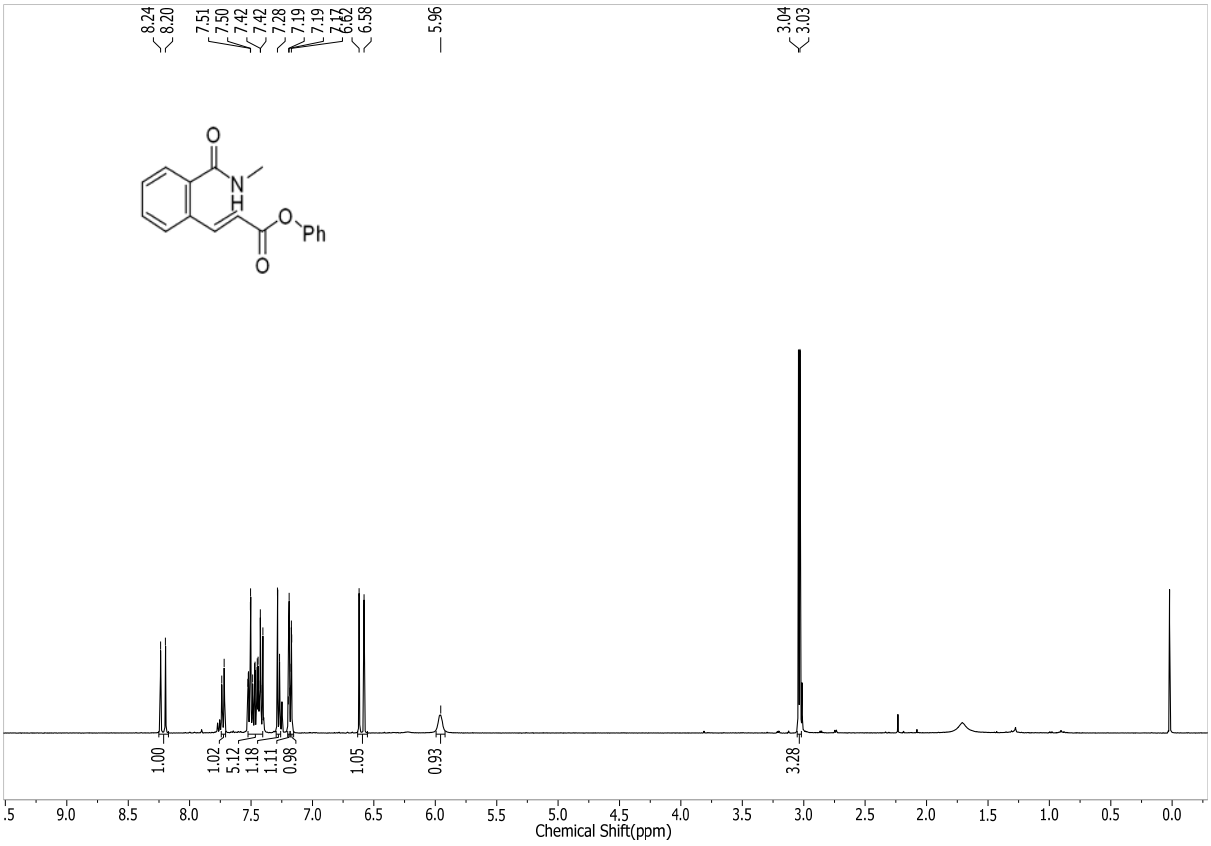


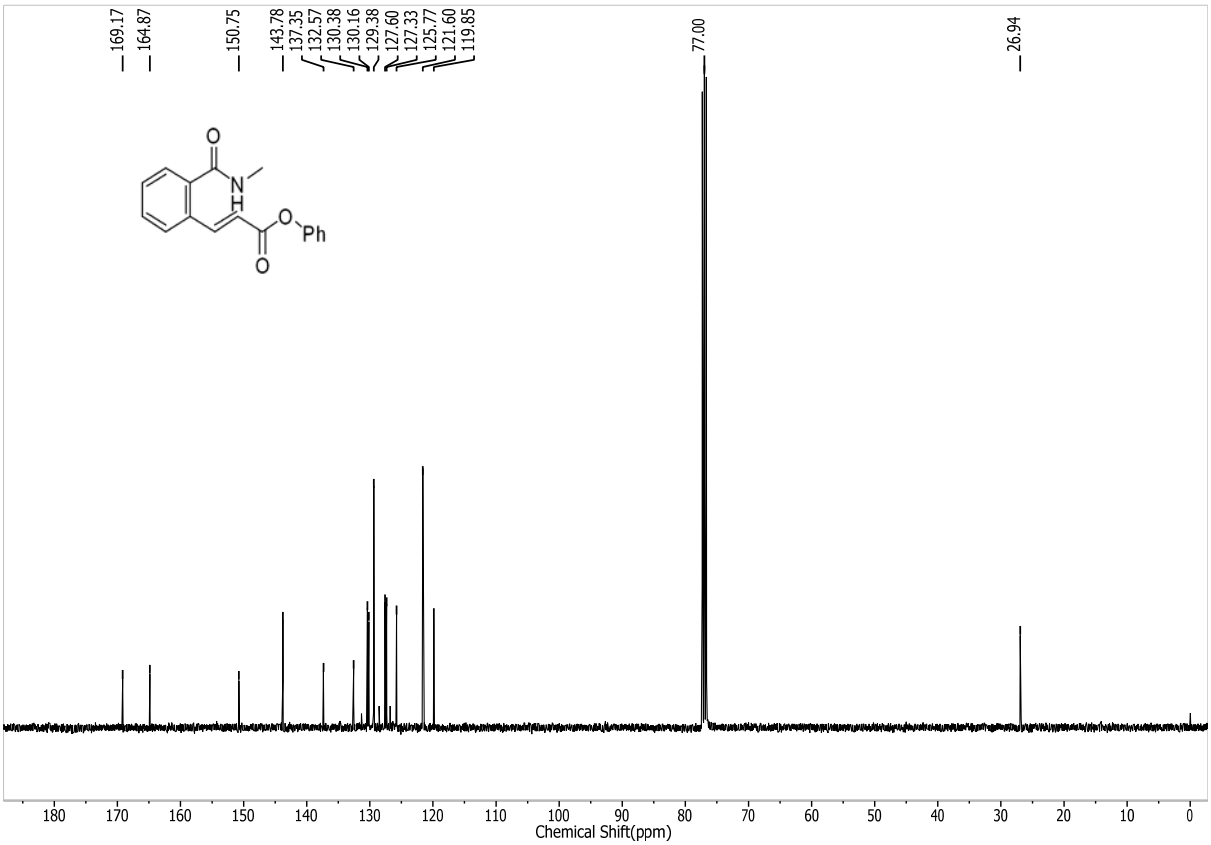


DEPT (135) NMR Spectrum of Compound **3ad.**

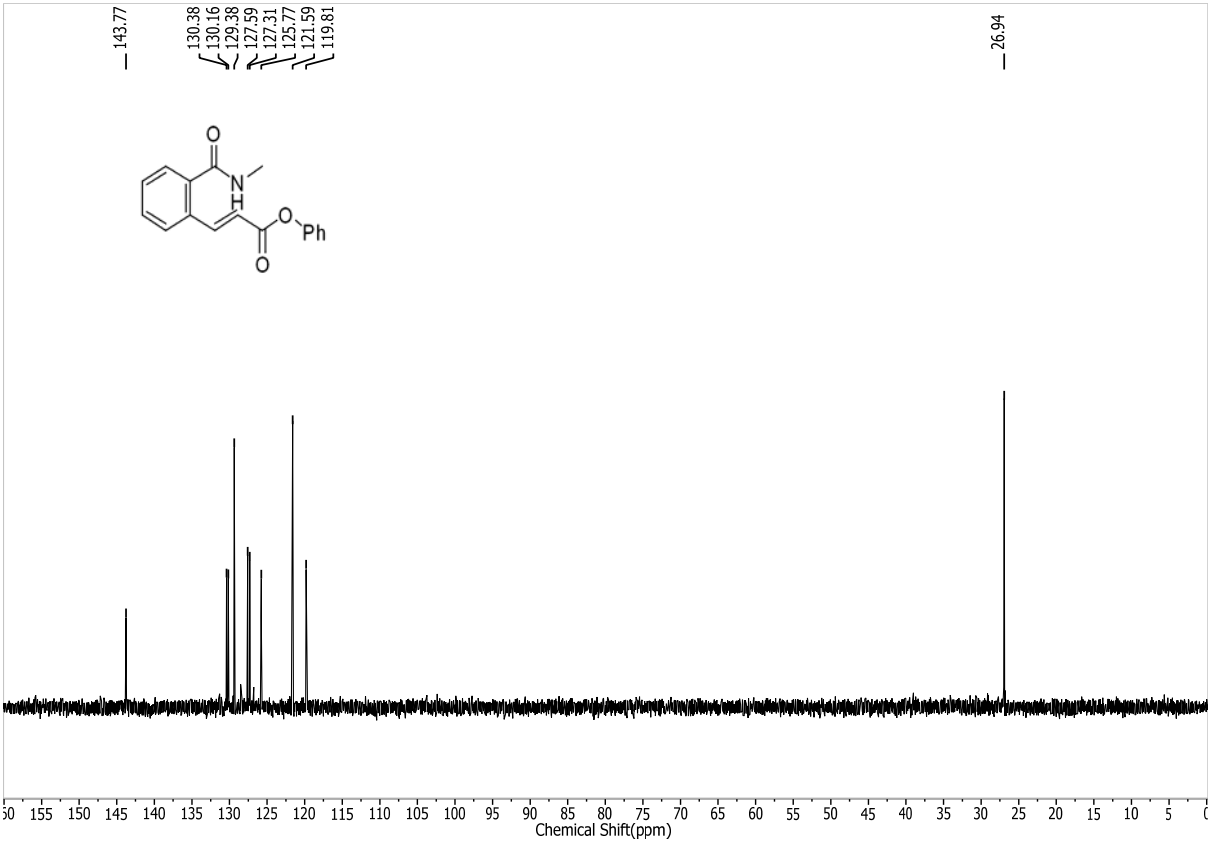


^{1}H and ^{13}C NMR Spectra of Compound **3ae.**

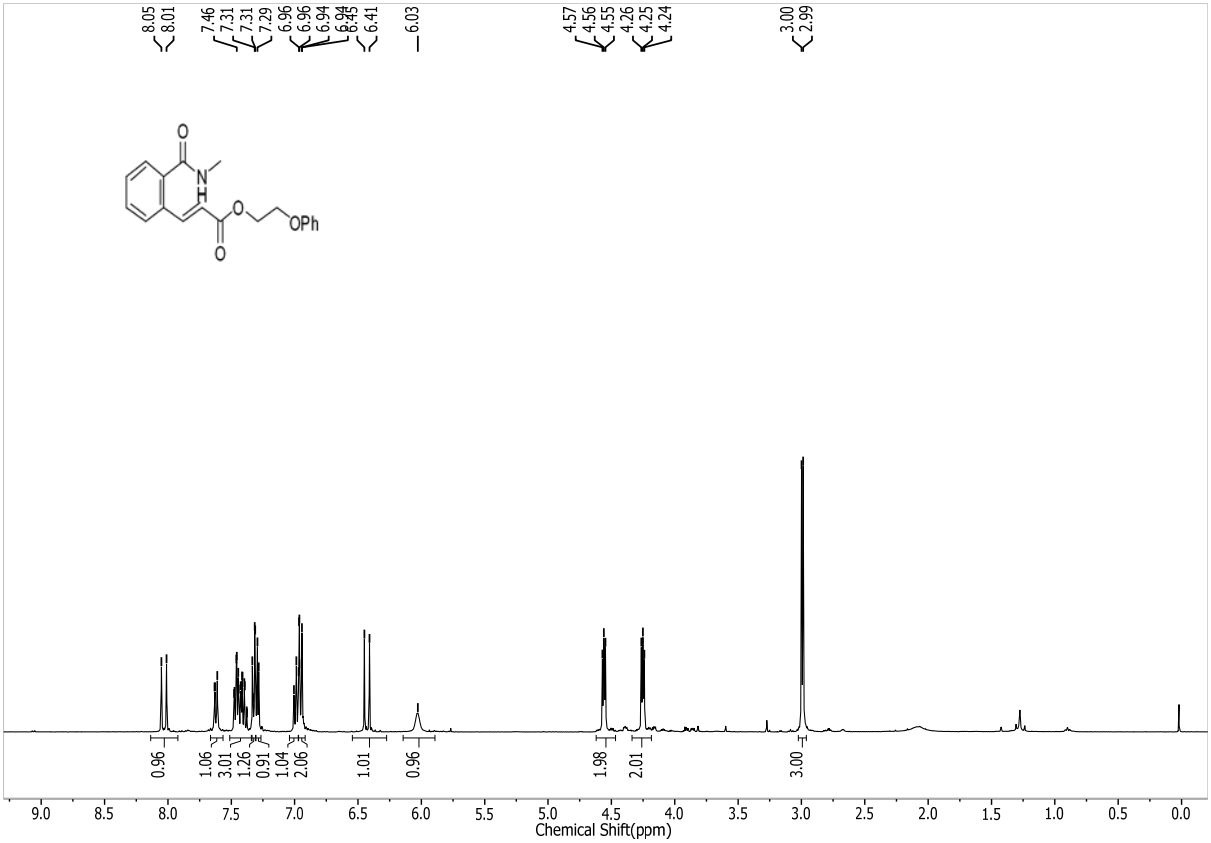


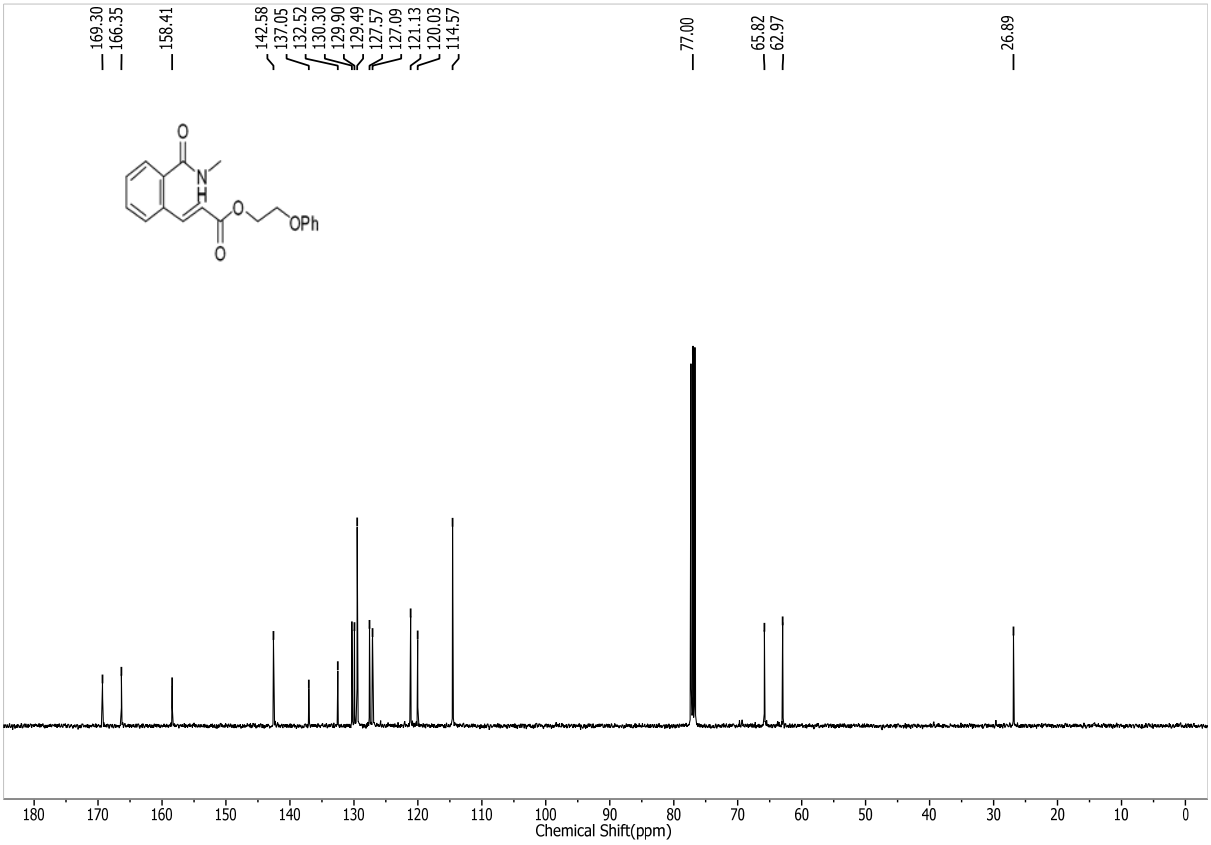


DEPT (135) NMR Spectrum of Compound **3ae.**

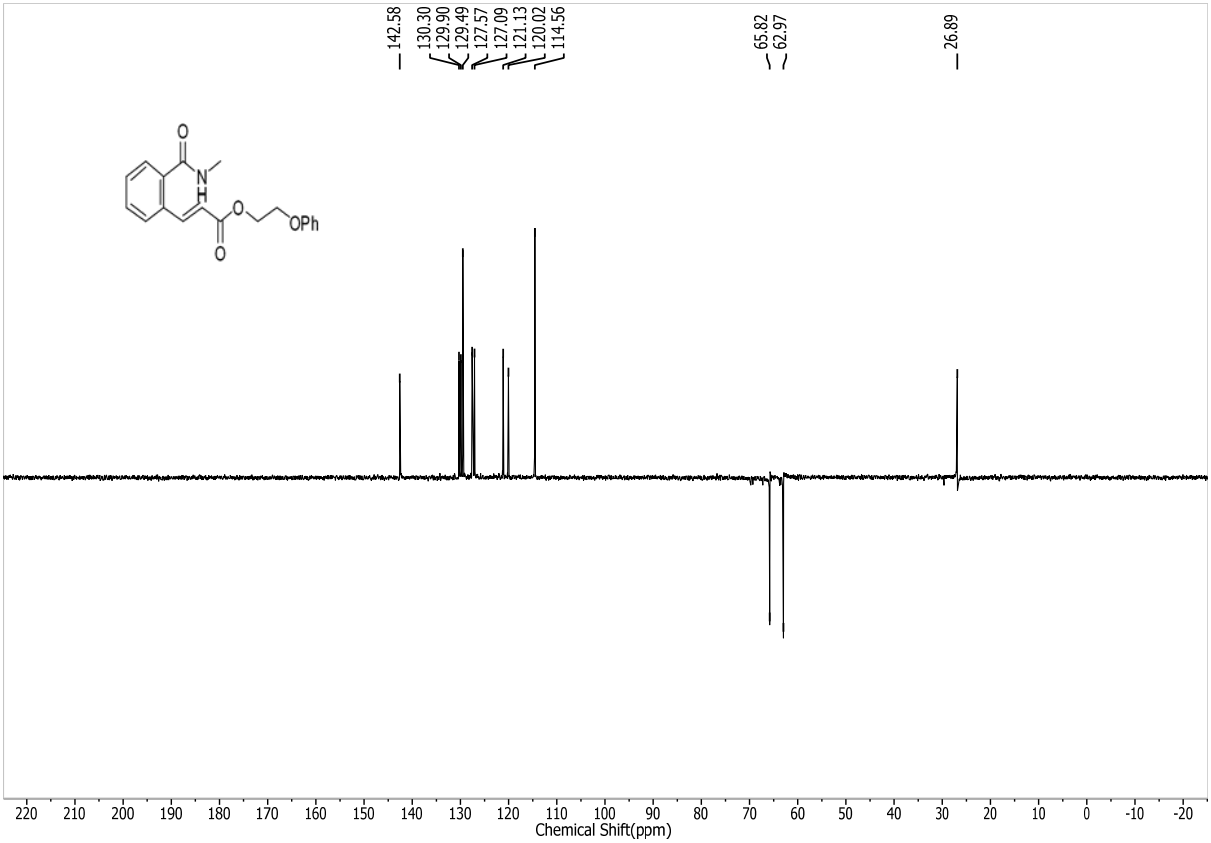


^{1}H and ^{13}C NMR Spectra of Compound **3af.**

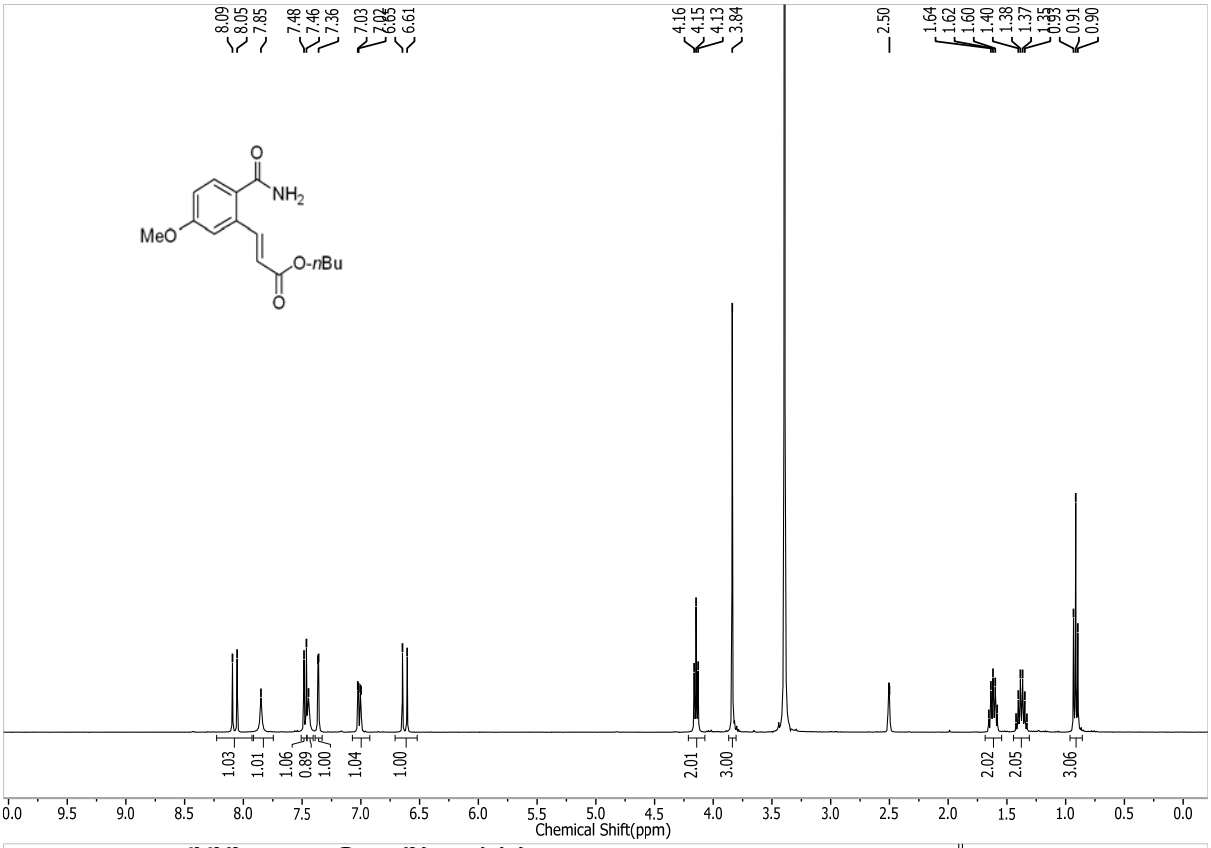


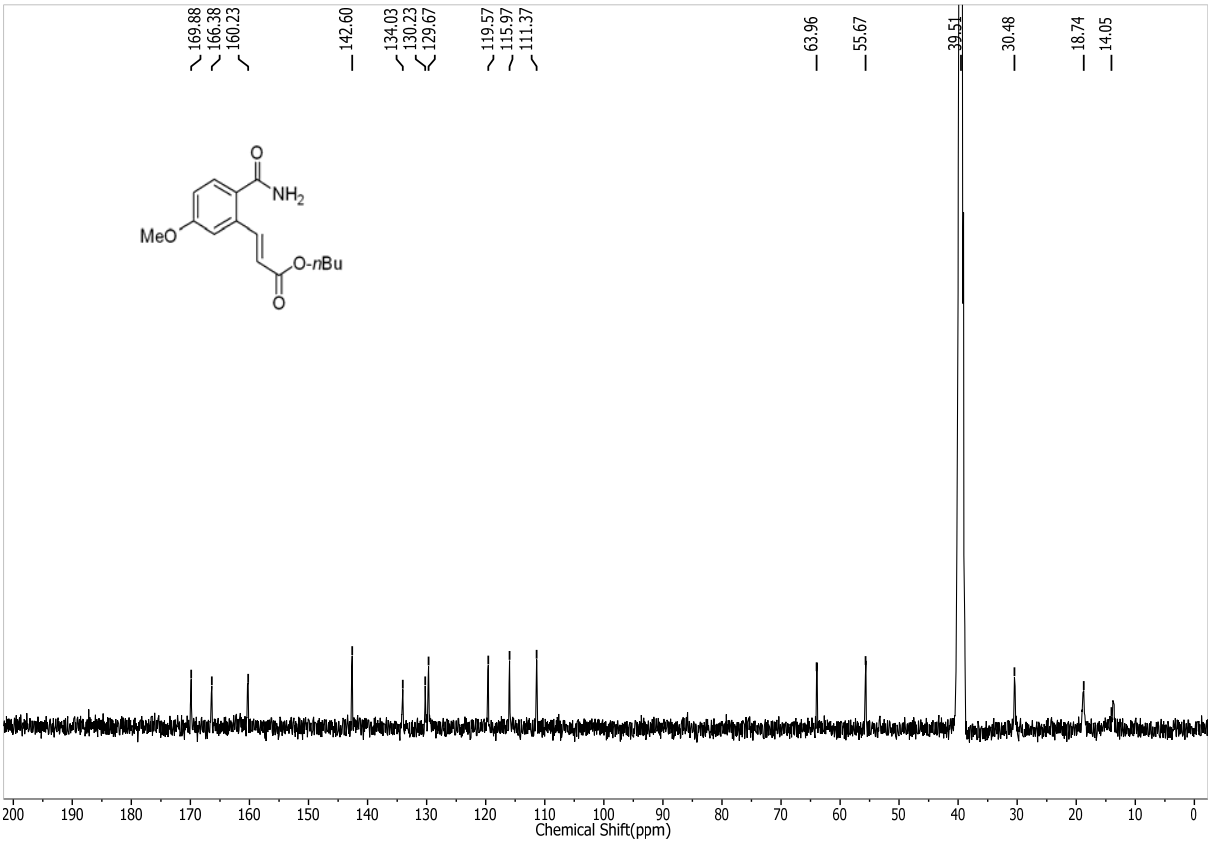


DEPT (135) NMR Spectrum of Compound **3af.**

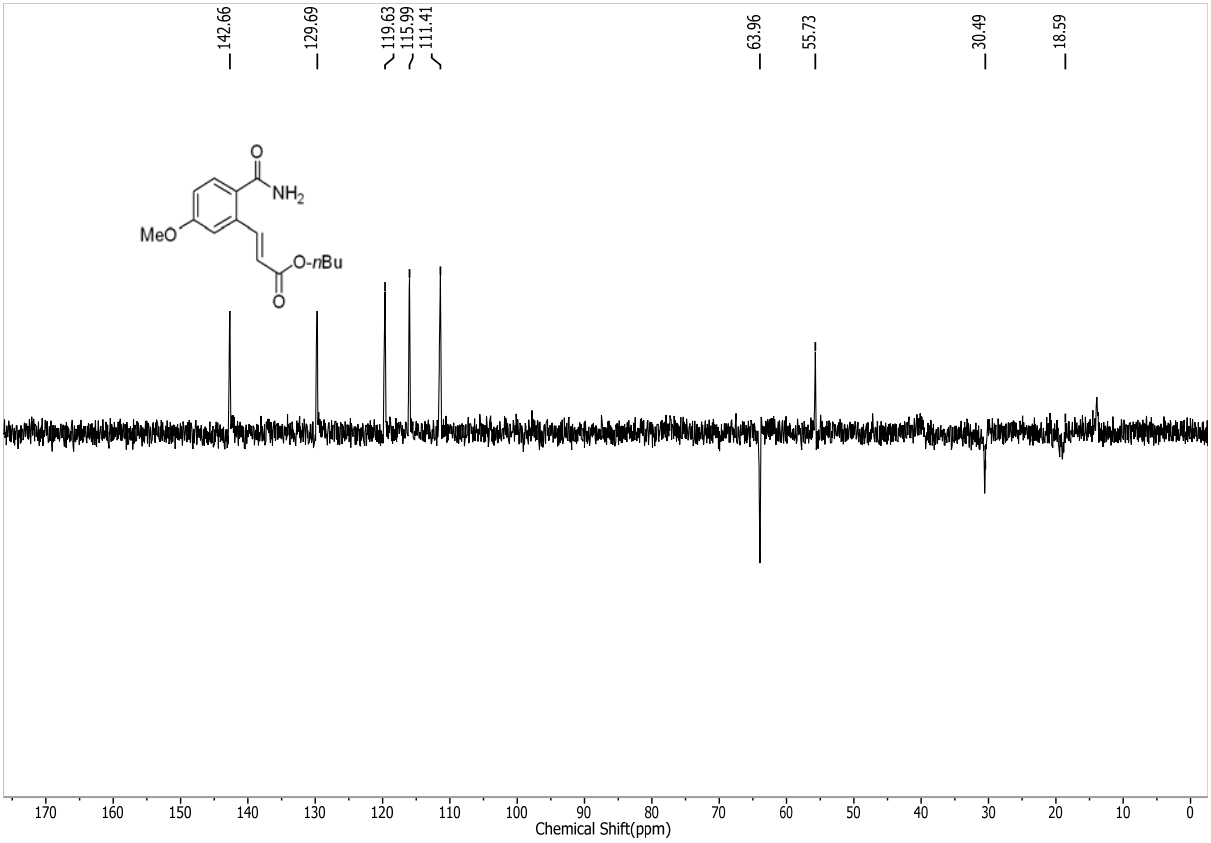


^{1}H and ^{13}C NMR Spectra of Compound **3ob.**

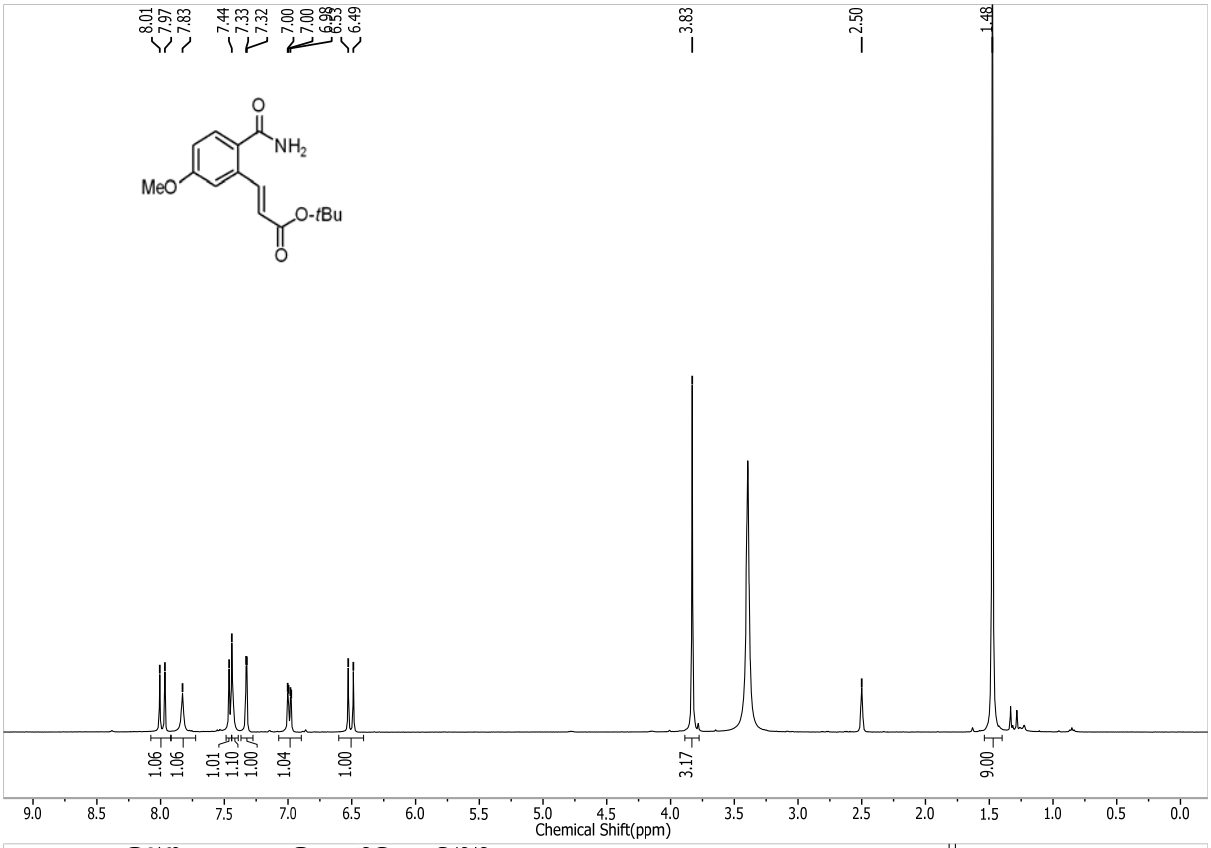


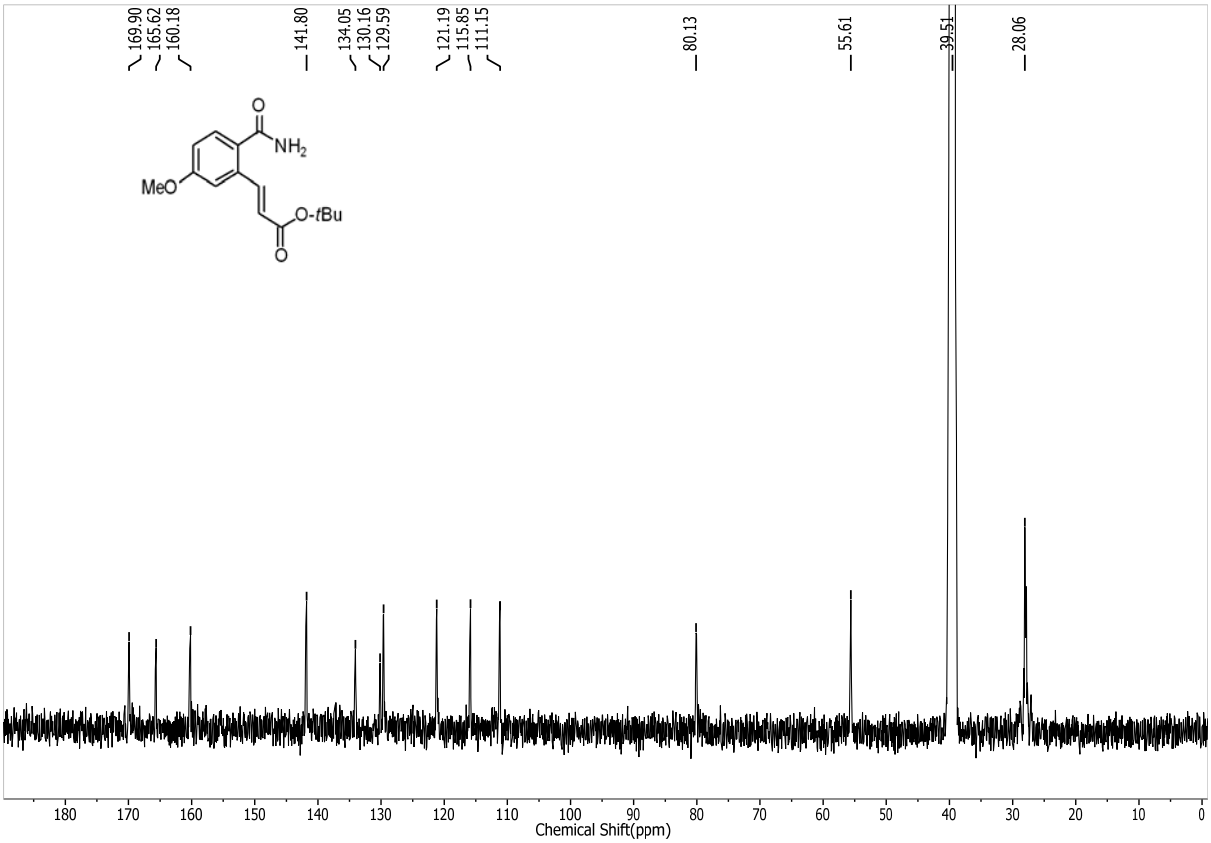


DEPT (135) NMR Spectrum of Compound **3ob.**

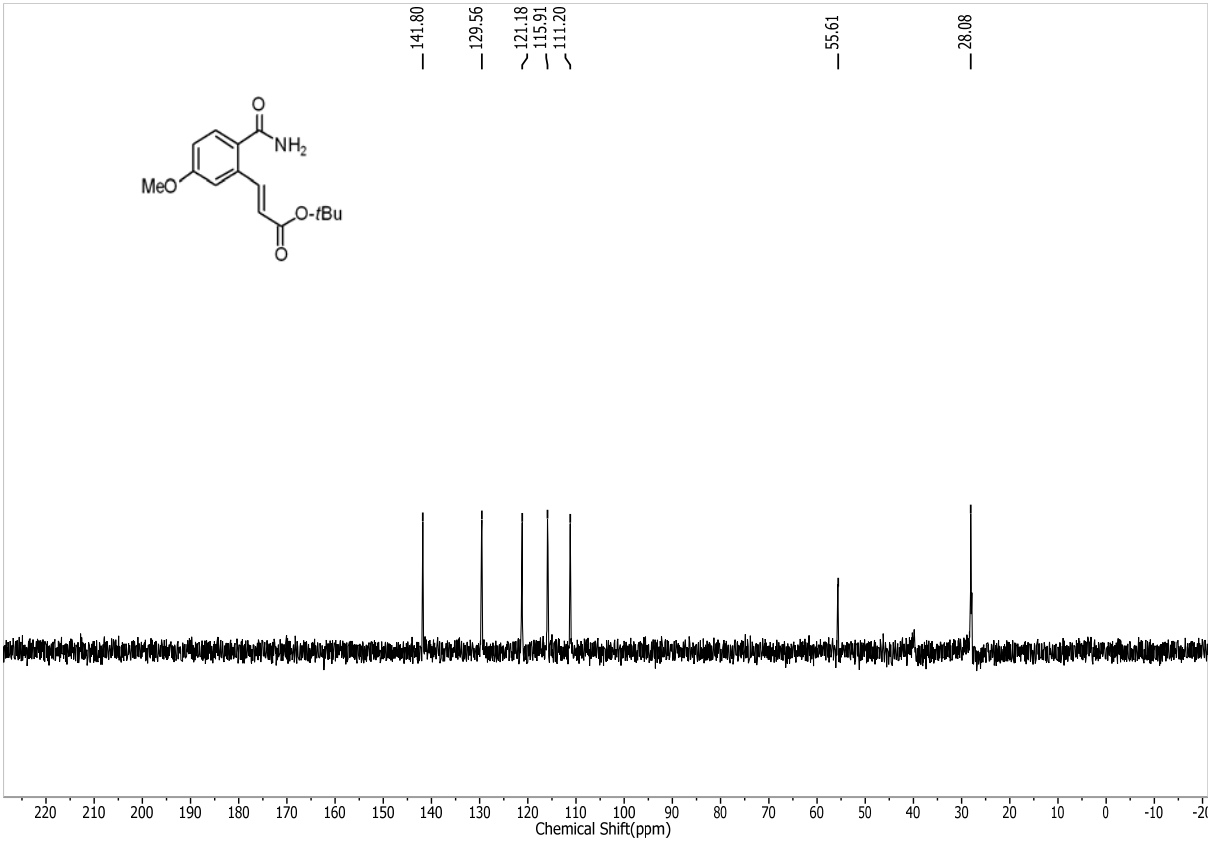


^{1}H and ^{13}C NMR Spectra of Compound **3og.**

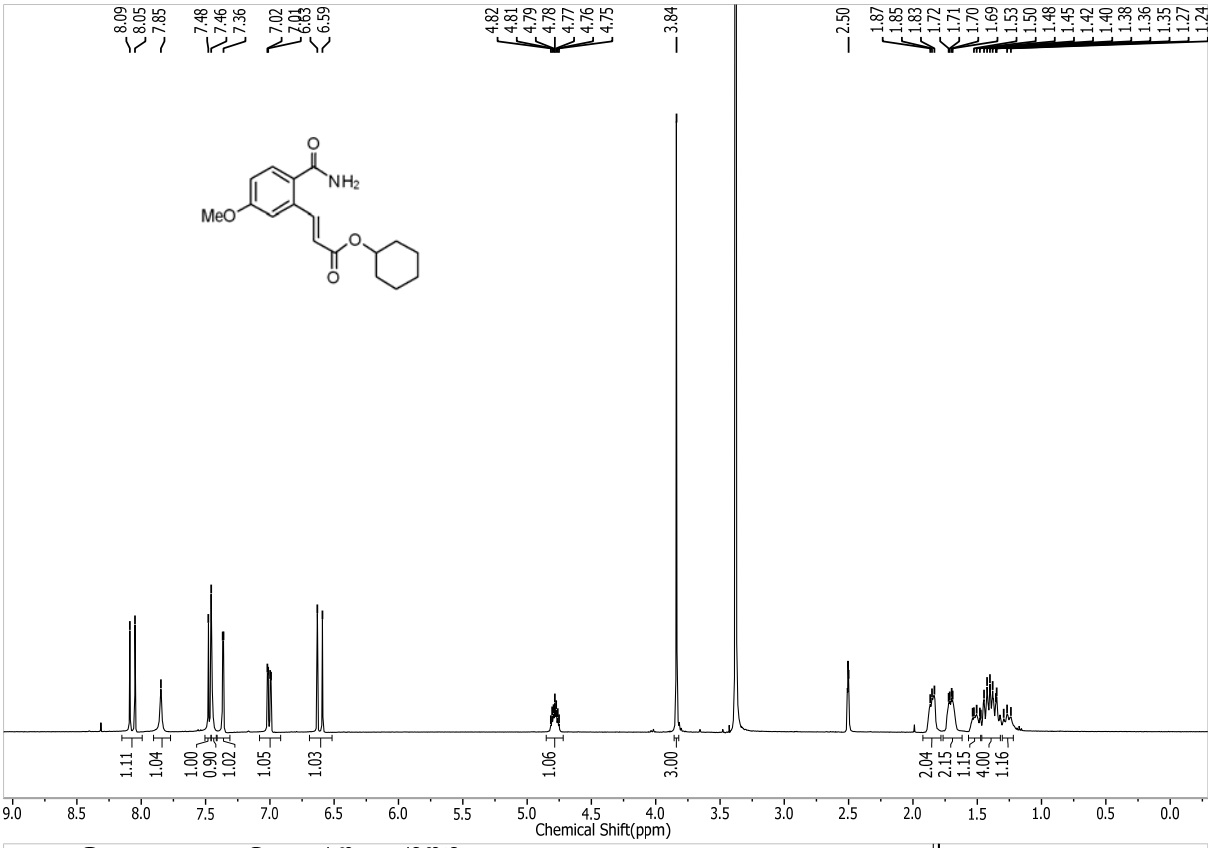


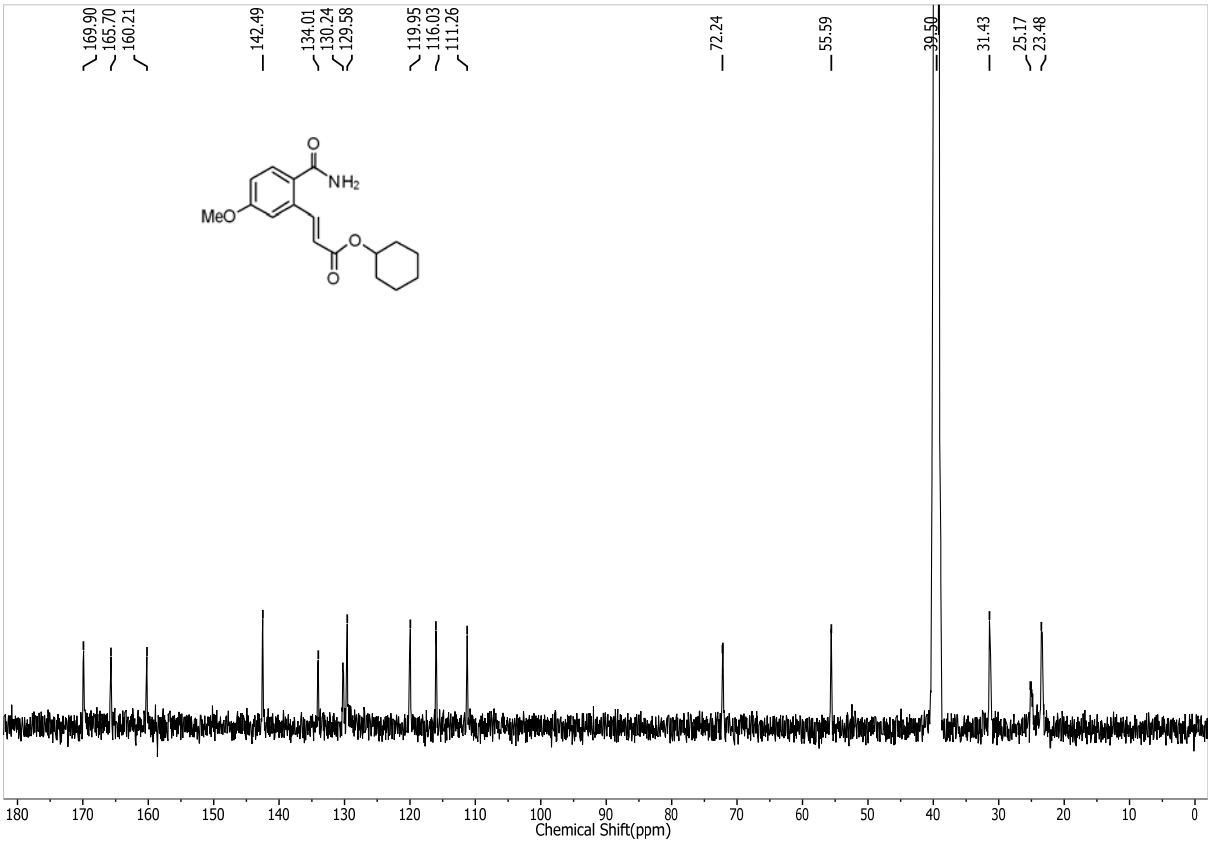


DEPT (135) NMR Spectrum of Compound **3og.**

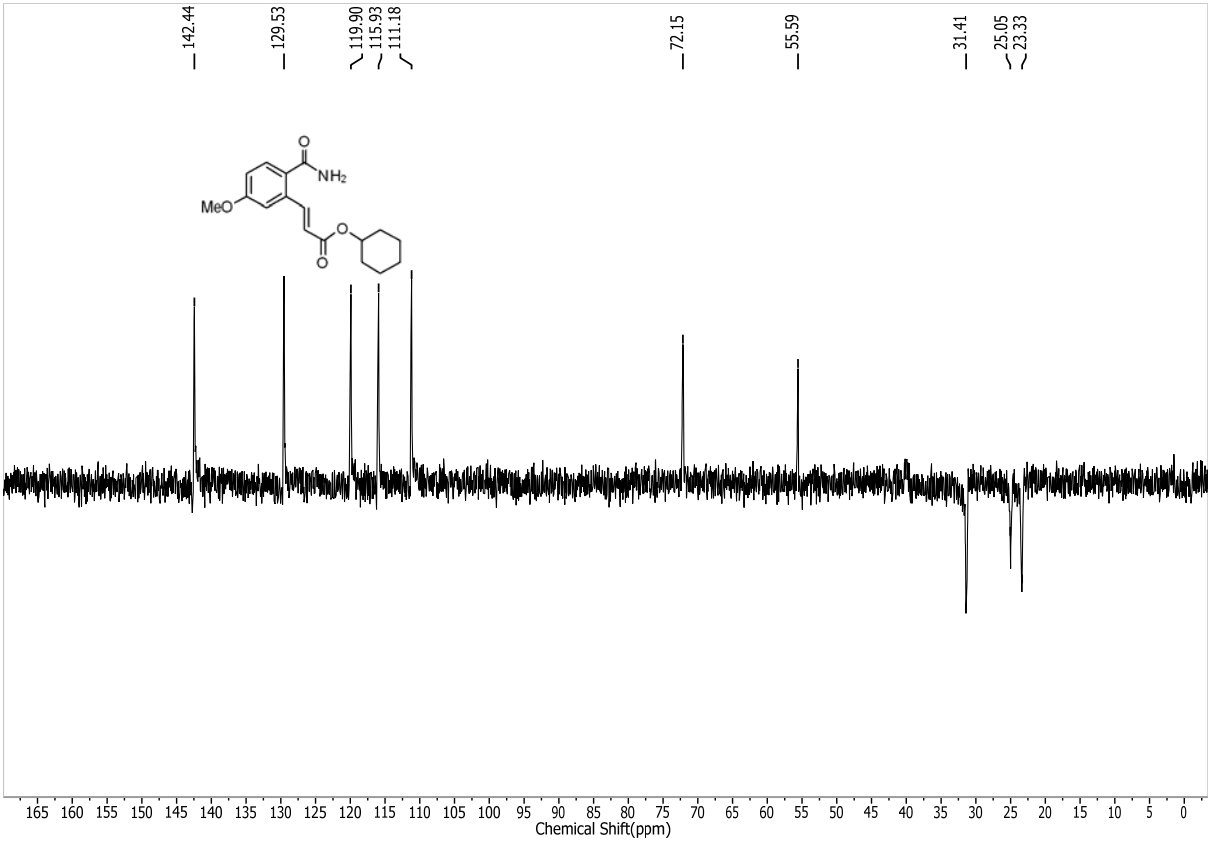


^{1}H and ^{13}C NMR Spectra of Compound **3oh.**

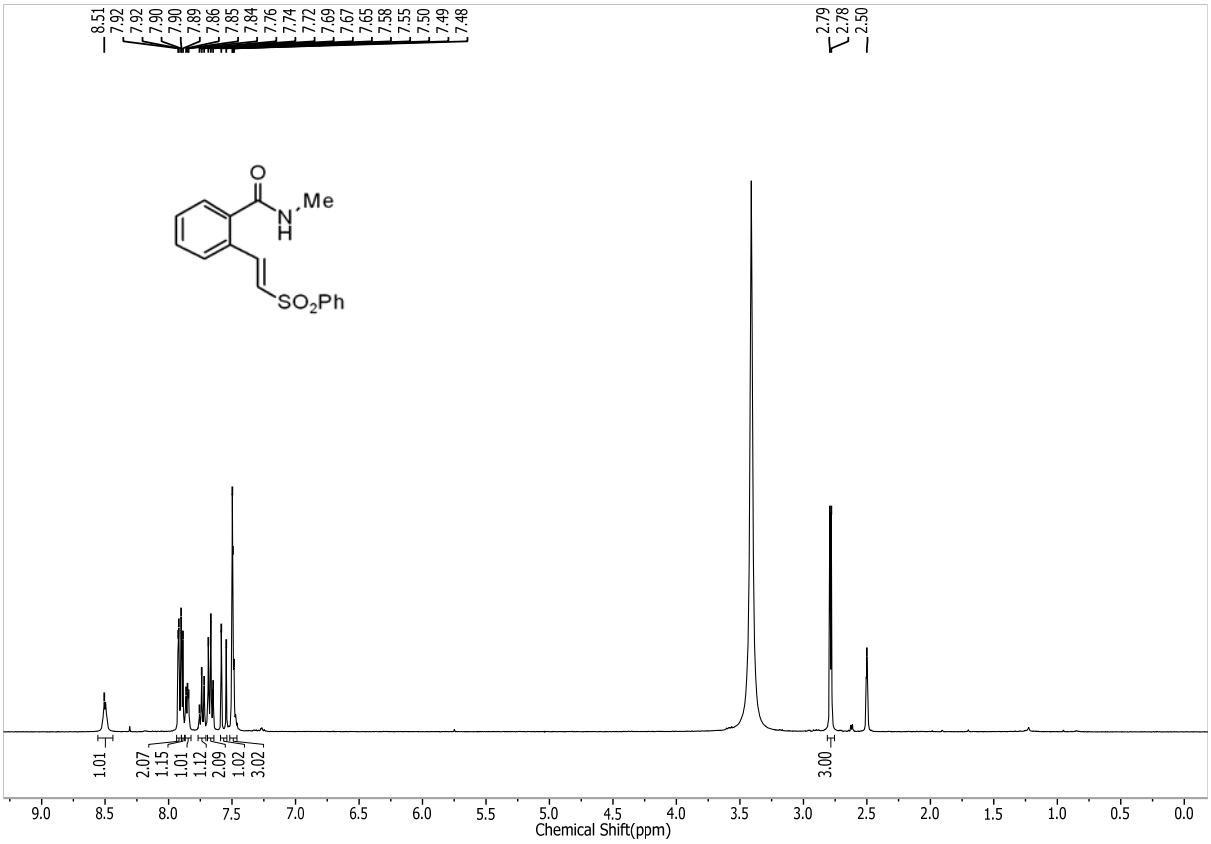


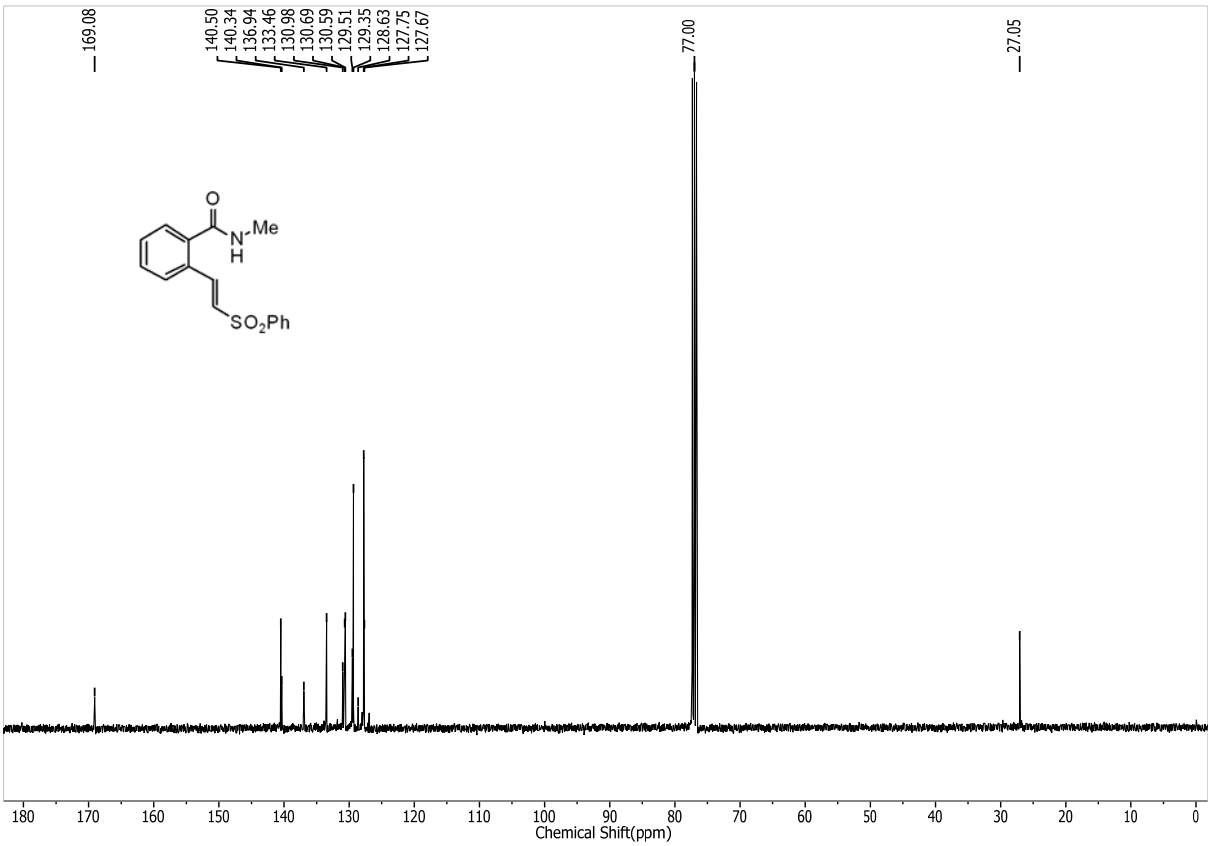


DEPT (135) NMR Spectrum of Compound **3oh.**

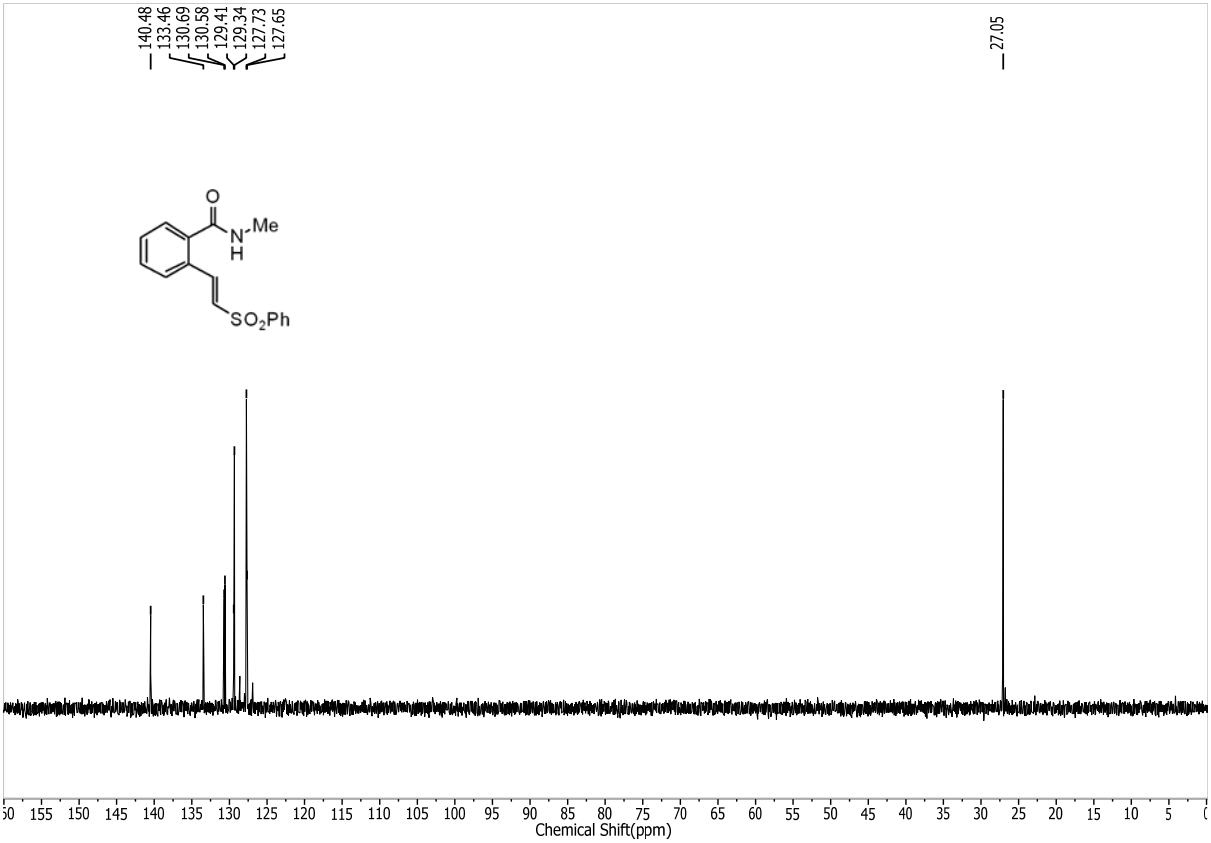


^{1}H and ^{13}C NMR Spectra of Compound **3ai.**

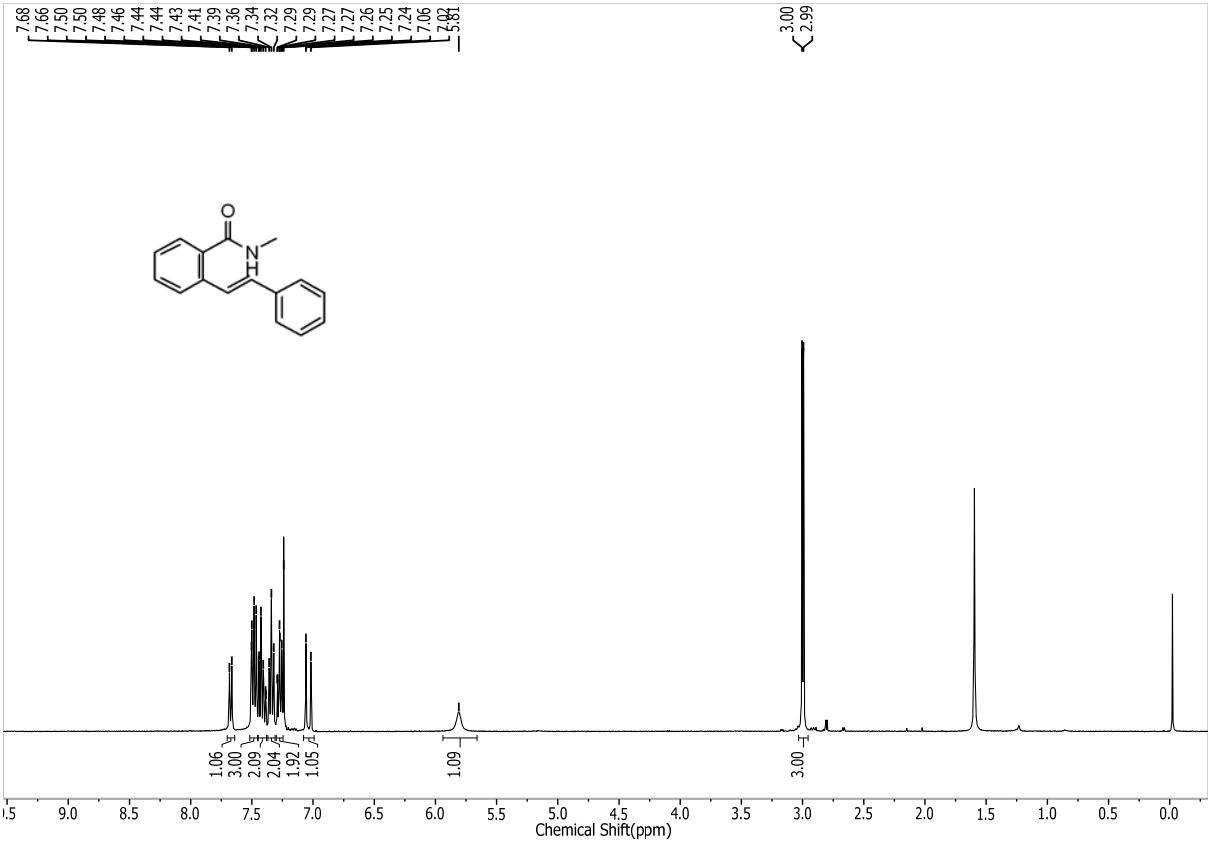


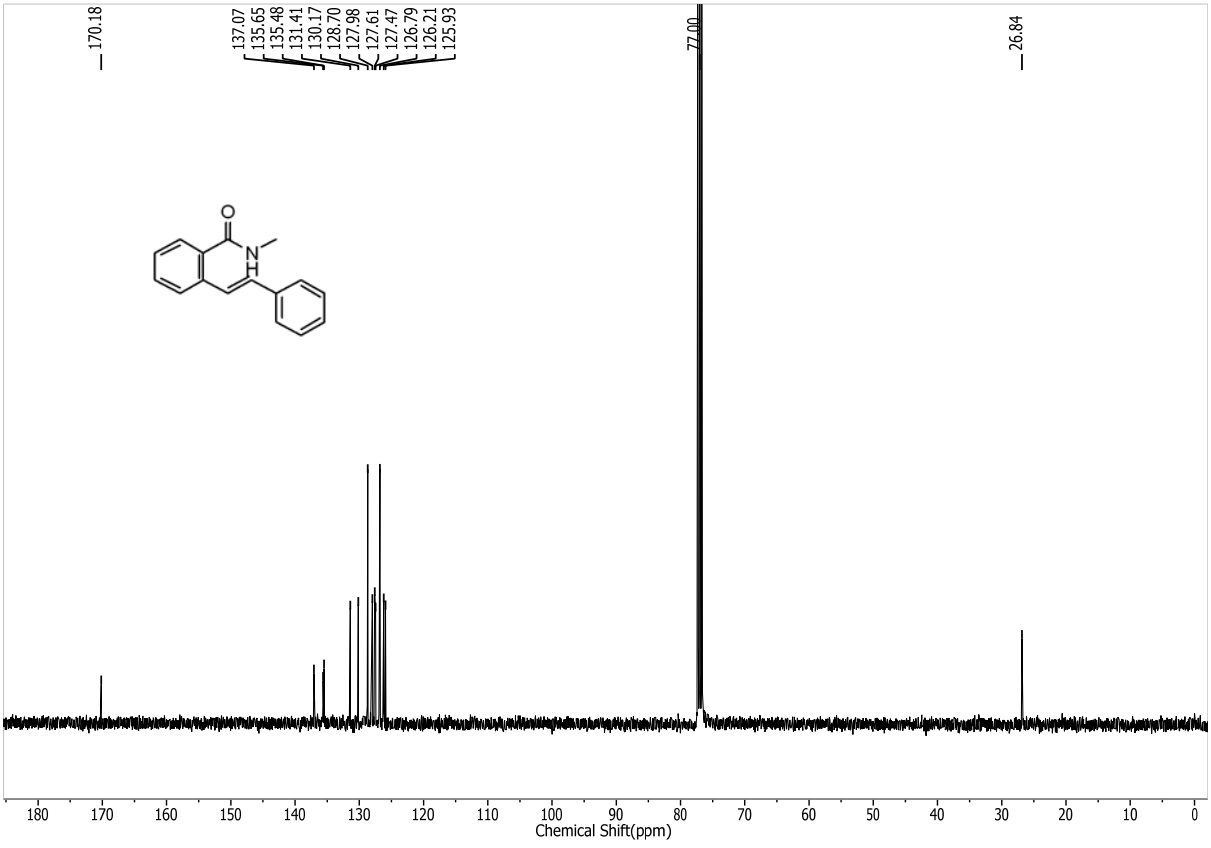


DEPT (135) NMR Spectrum of Compound **3ai.**

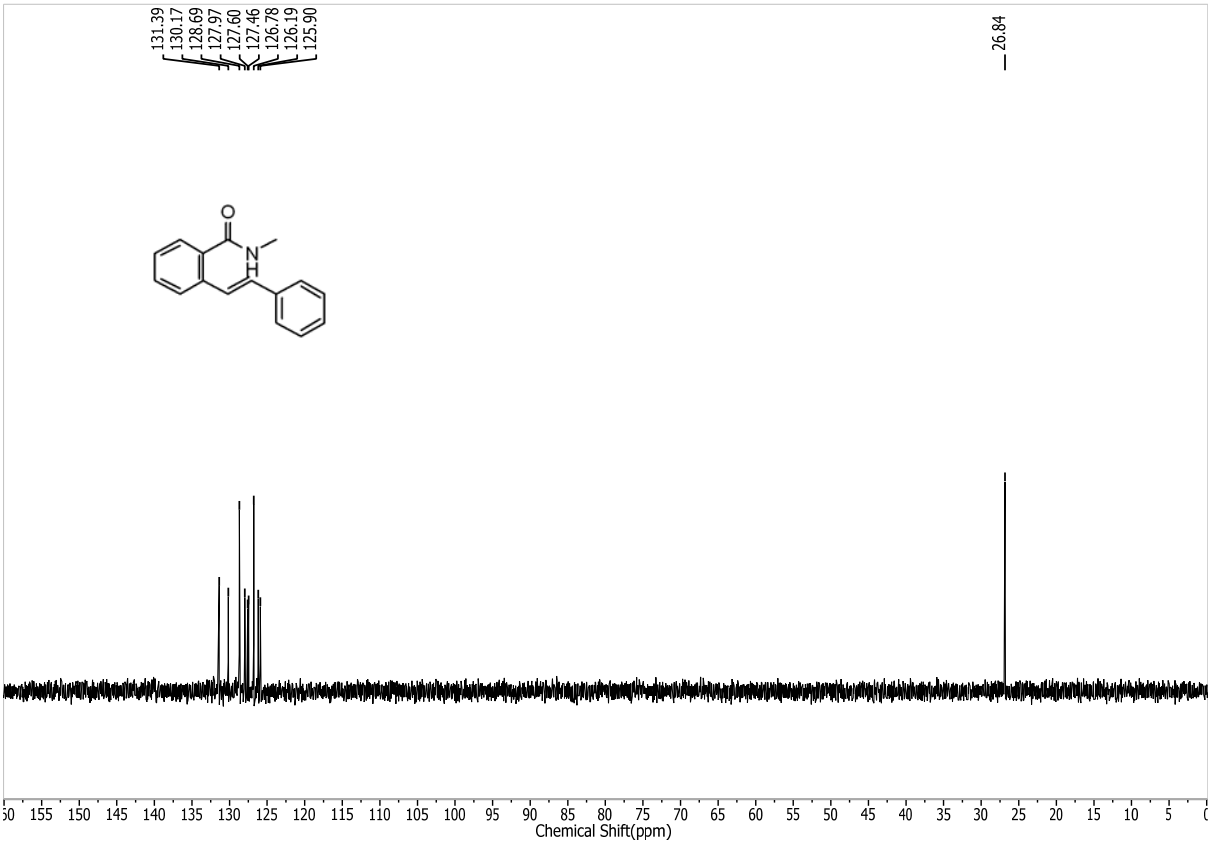


^{1}H and ^{13}C NMR Spectra of Compound **3aj.**

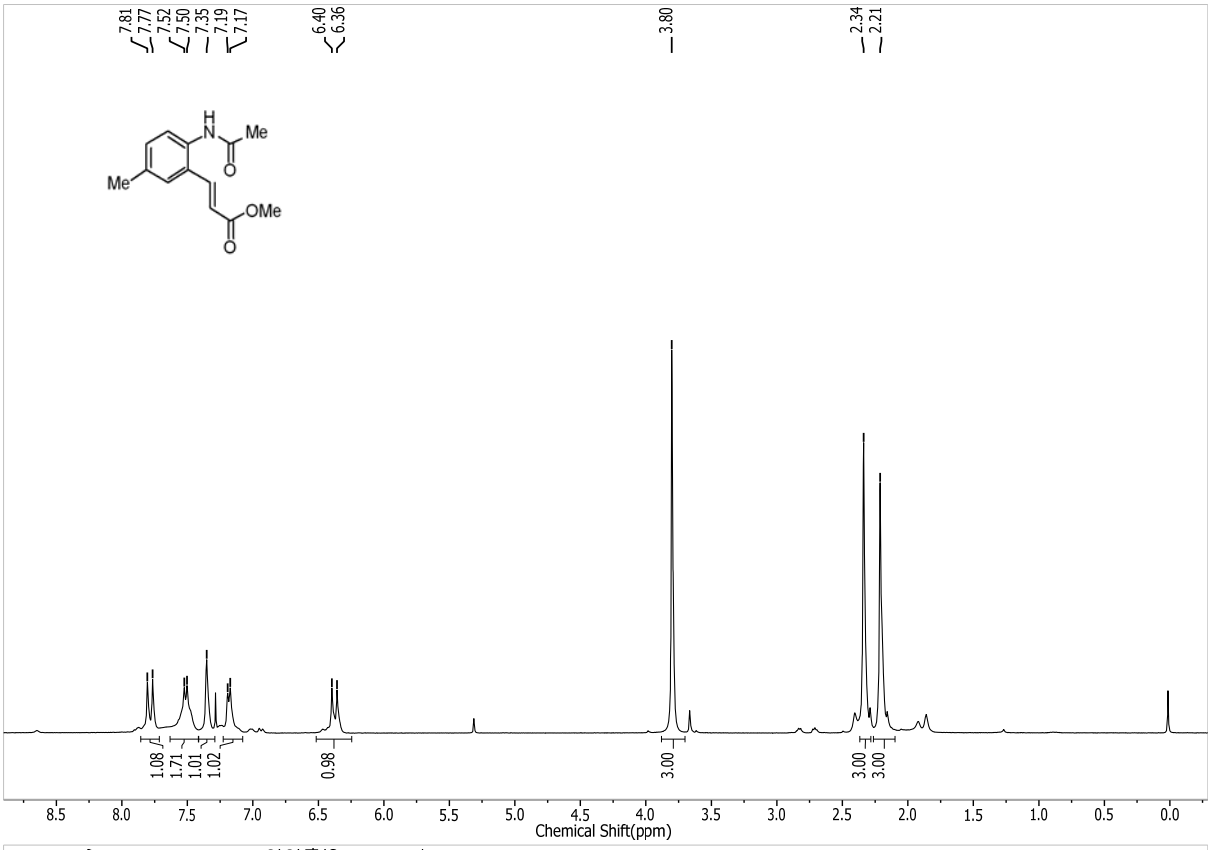


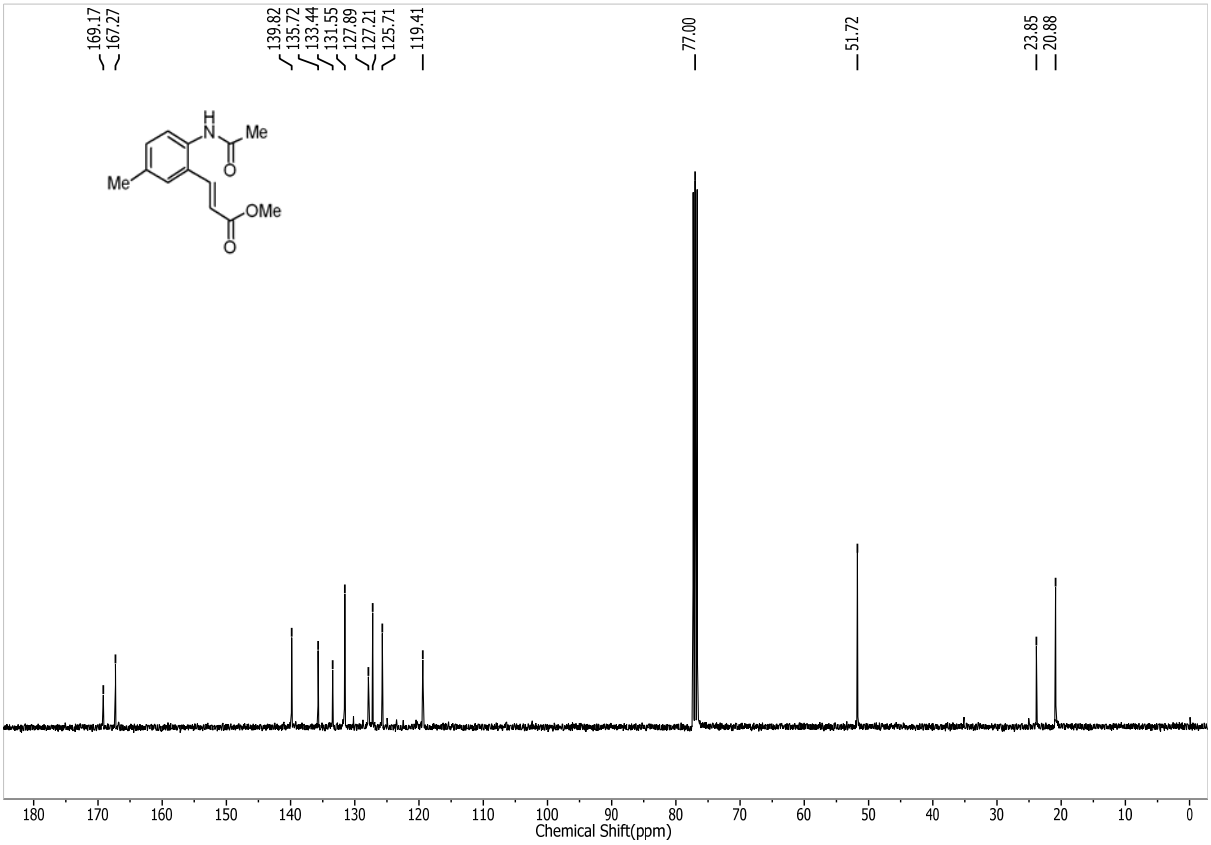


DEPT (135) NMR Spectrum of Compound **3aj.**

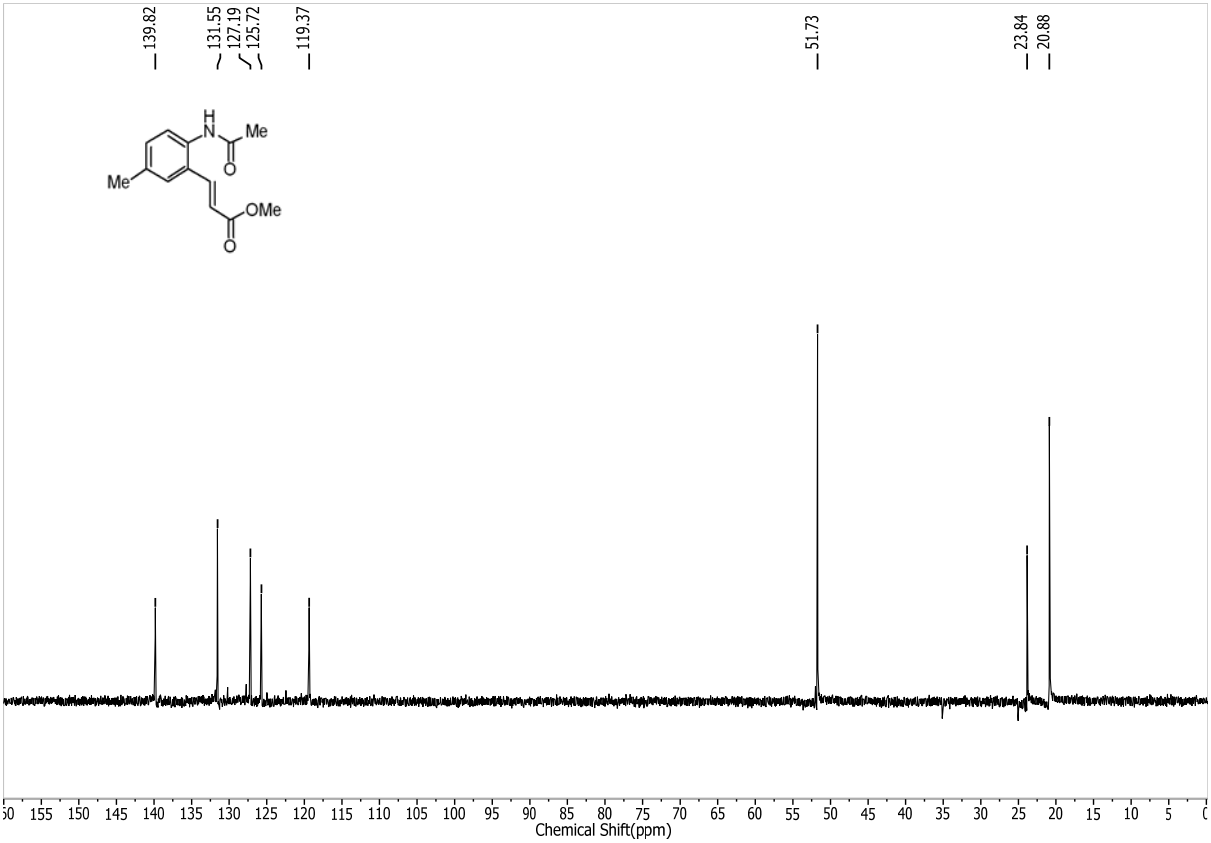


^{1}H and ^{13}C NMR Spectra of Compound **5aa.**

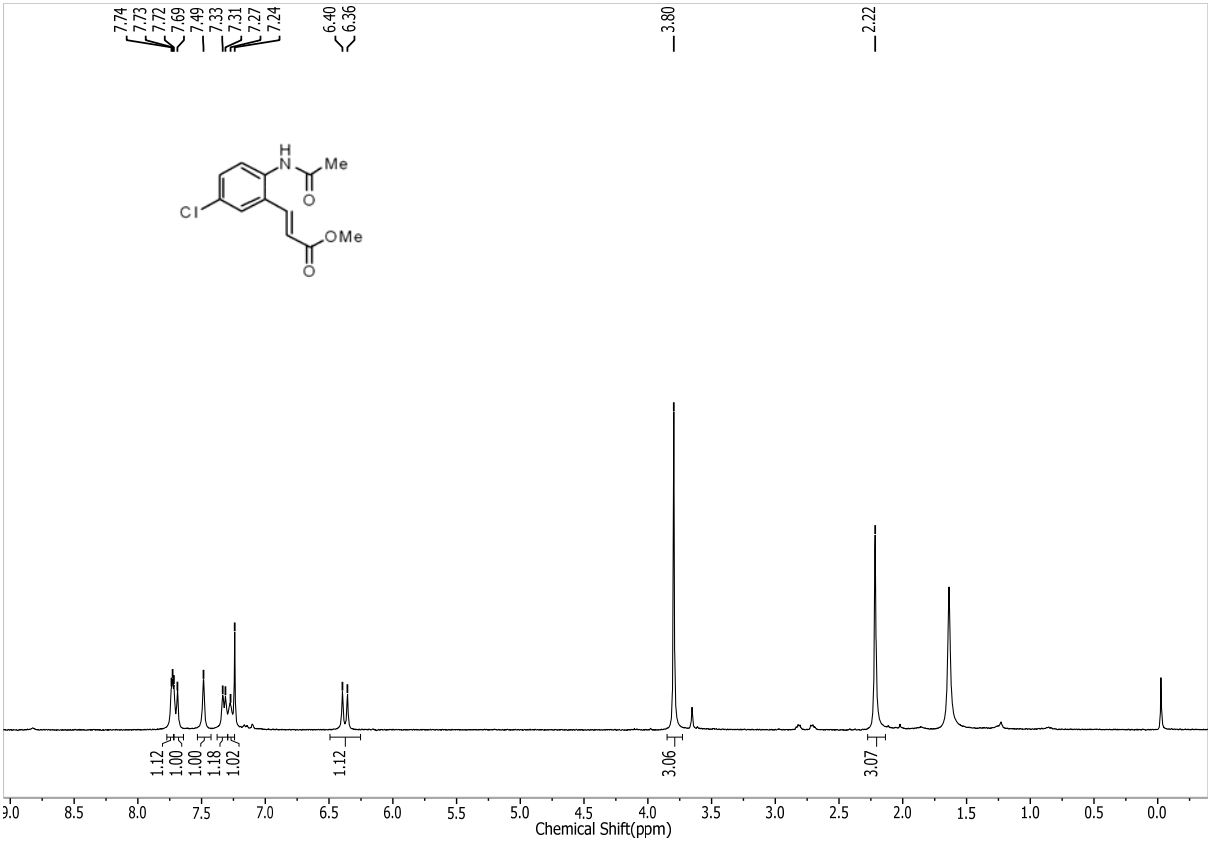


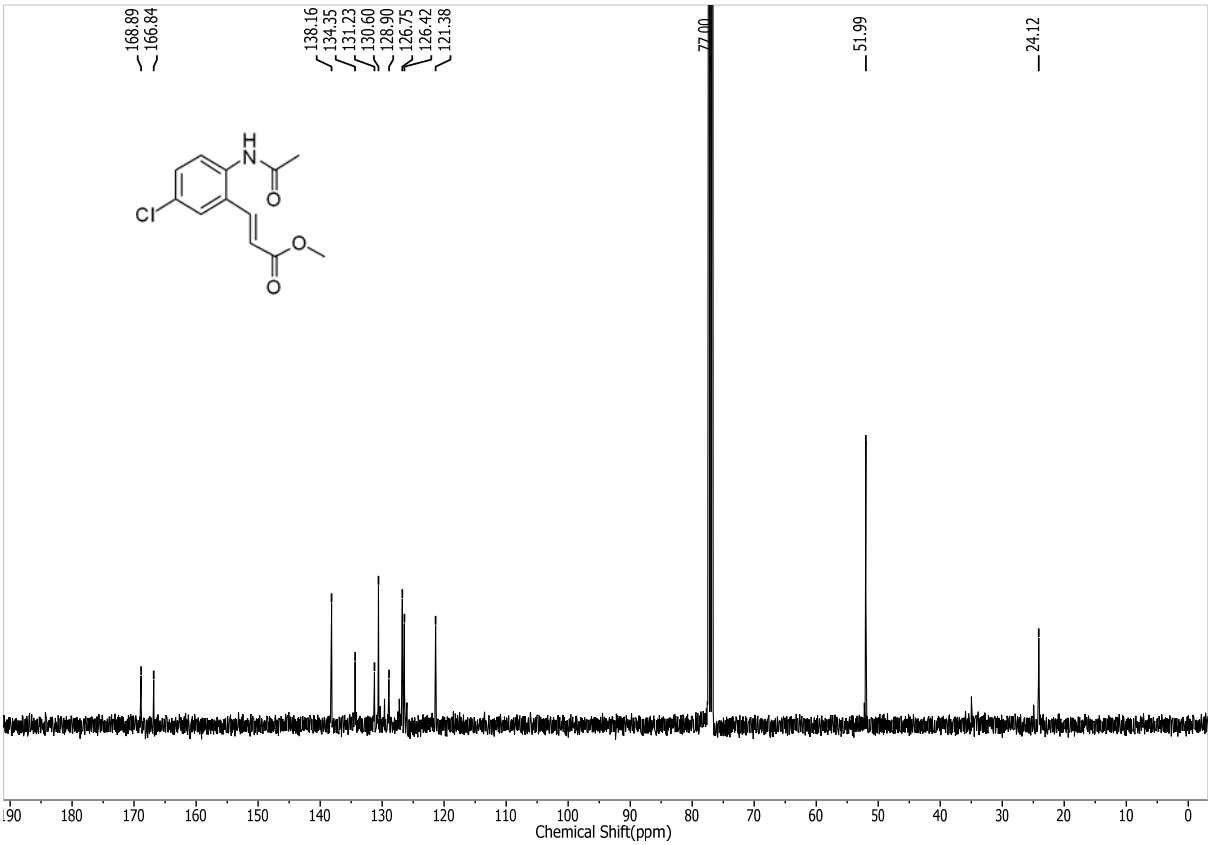


DEPT (135) NMR Spectrum of Compound **5aa.**

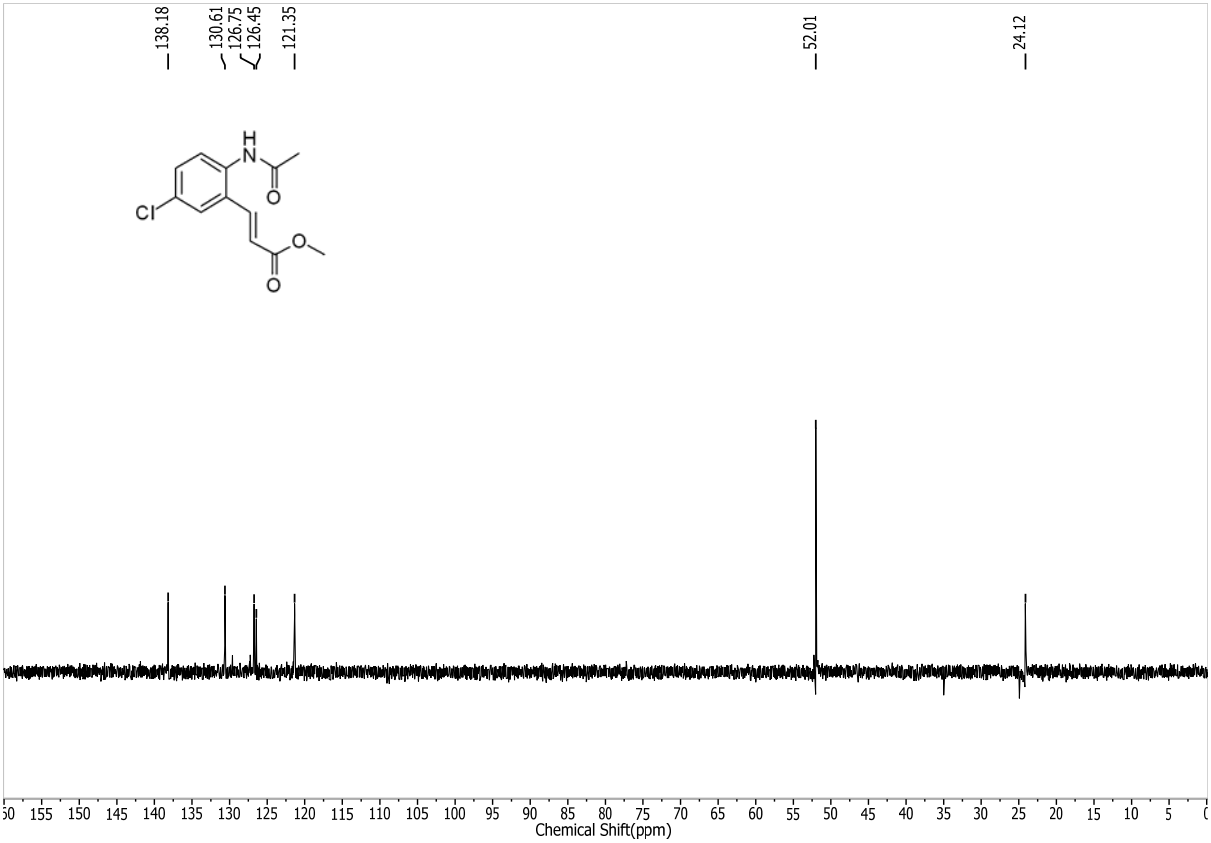


^{1}H and ^{13}C NMR Spectra of Compound **5ba.**

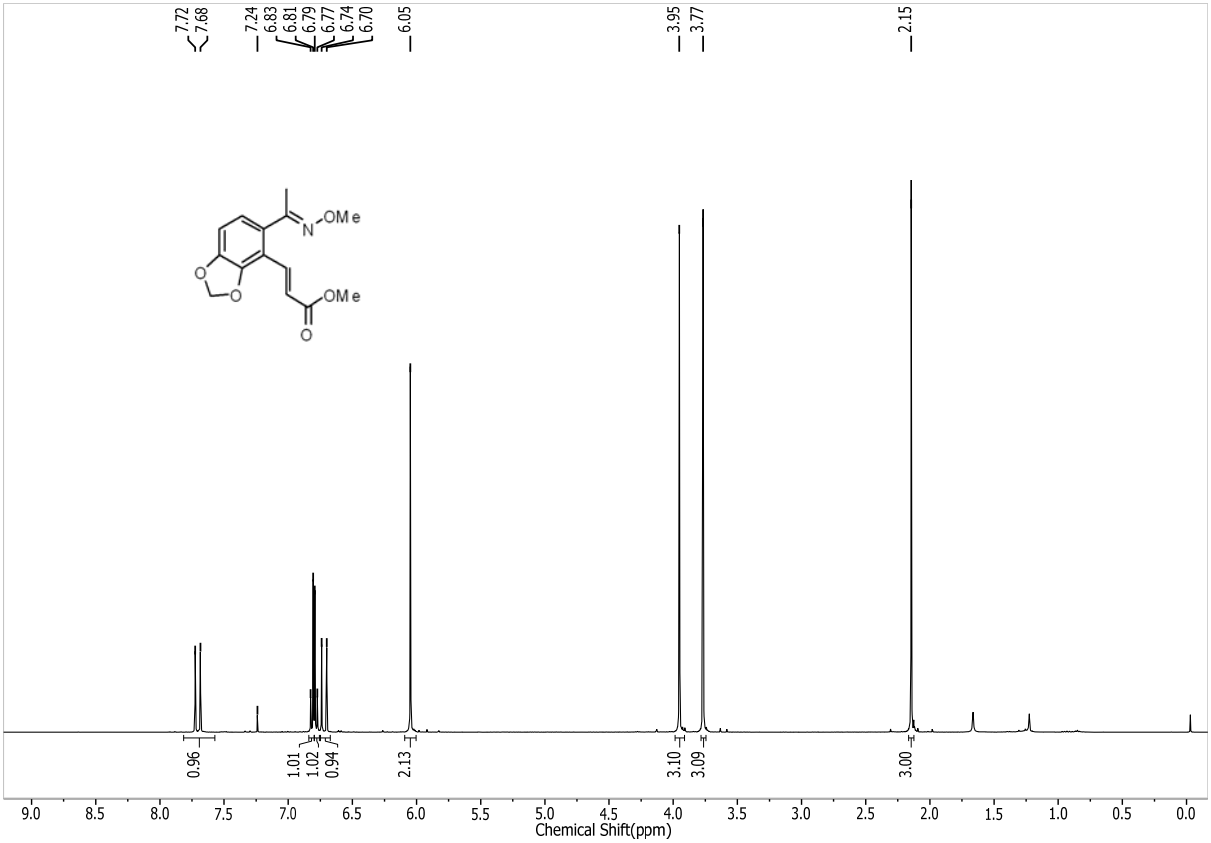


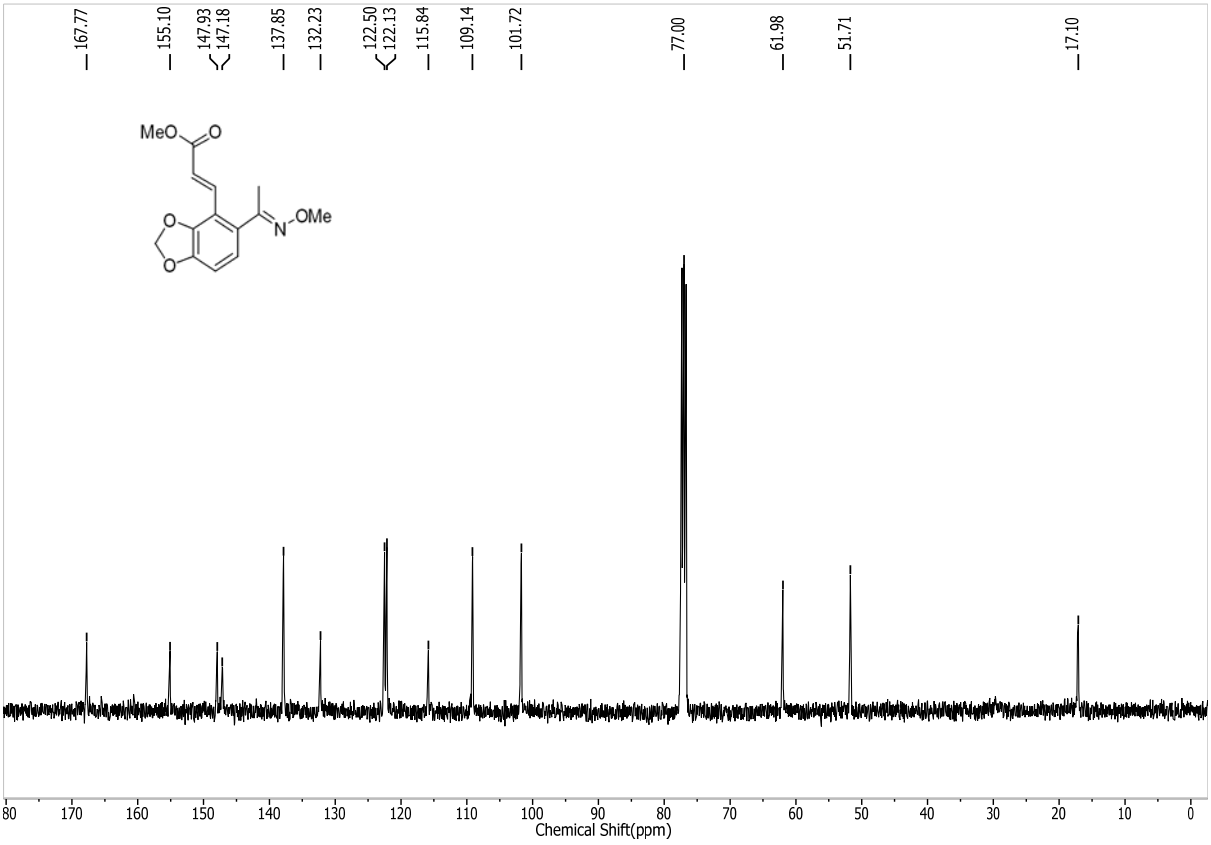


DEPT (135) NMR Spectrum of Compound **5ba.**

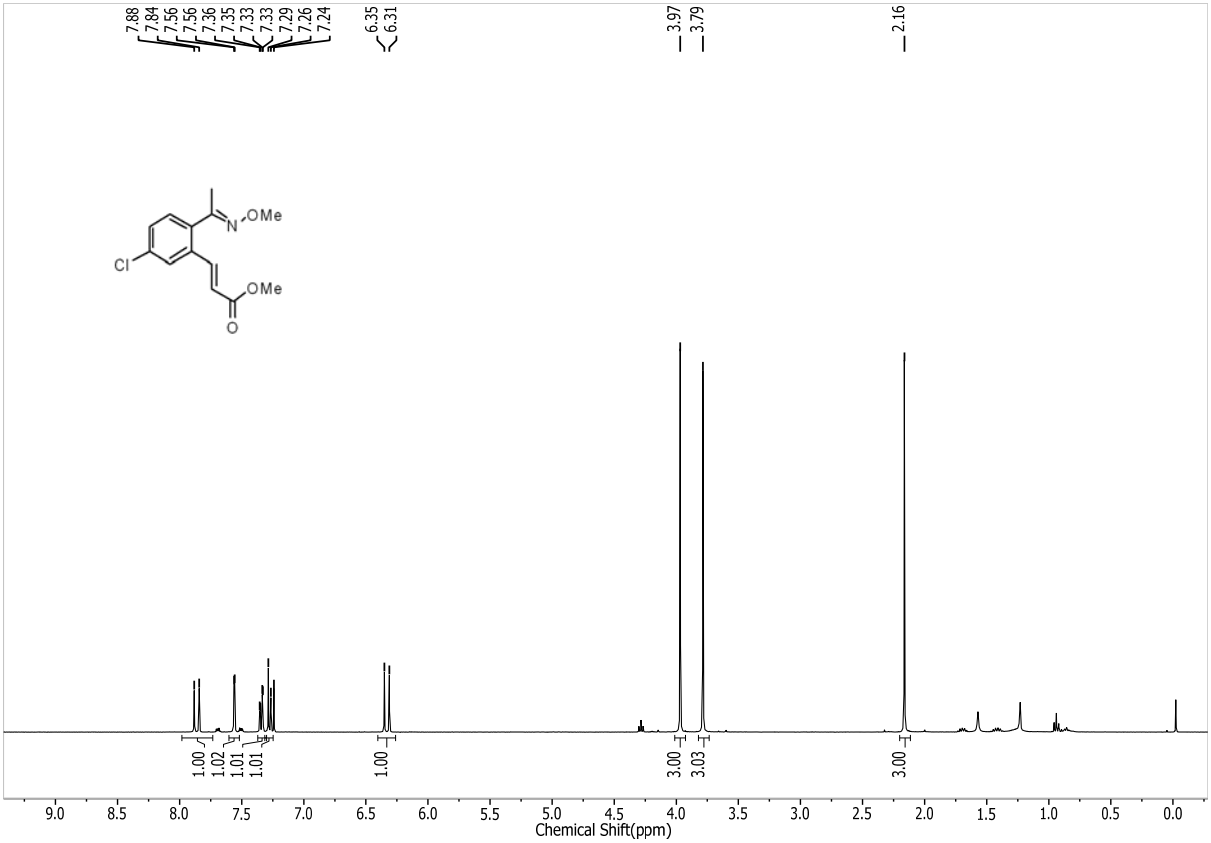


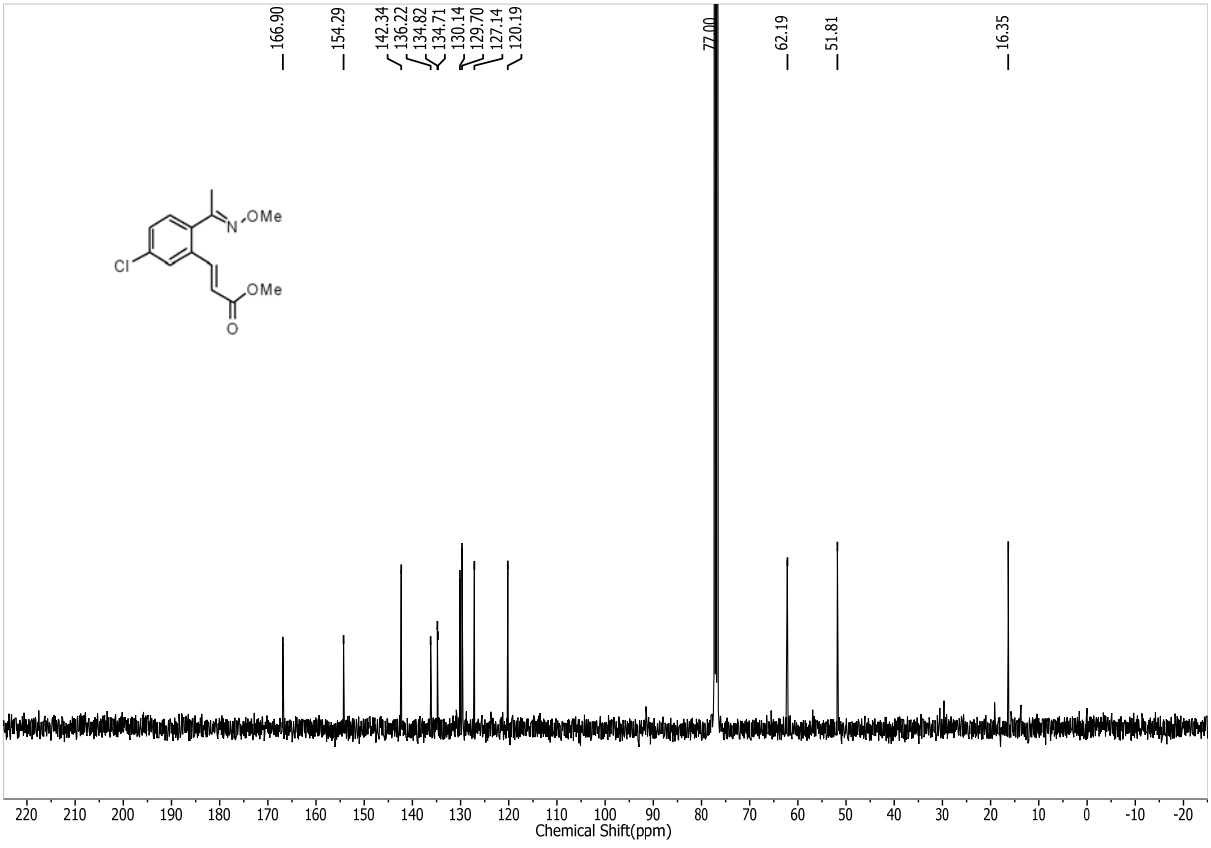
^{1}H and ^{13}C NMR Spectra of Compound **7aa.**





^{1}H and ^{13}C NMR Spectra of Compound **7ba.**





DEPT (135) NMR Spectrum of Compound **7ba.**