Temperature-Controlled Redox-Neutral Ruthenium(II)-Catalyzed Regioselective Allylation of Benzamides with Allylic Acetates

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Supporting Information (SI)

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Experimental Section

General Procedure for the Allylation of Aromatic amides with Allylic Acetates Catalyzed by a Ruthenium Complex

A 15-mL pressure tube with septum containing amide **1** (100 mg), [{$RuCl_2$(*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, was then added 1,2-dichloroethane (1.0 mL) via syringe. After that, allylic acetate **2** (2.0-2.5 equiv) and 1,2-dichloroethane (2.0 mL) were added 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 rt for 16-36 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 (for some compounds CH_2Cl_2 and MeOH combination were used. It has been mentioned in the substrates below) as eluent to give pure **3**.

Note: Liquid amide reactants are added after adding 1.0 mL of solvent. For product **3aa,** 2.0 equiv of allyl acetate (**2a**) was used.

General Procedure for the Alkenylation of Aromatic amides with Allylic Acetates catalyzed by Ruthenium Complex.

A 15-mL pressure tube with septum containing amide **1** (100 mg), [{$RuCl_2$(*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, was then added 1,2-dichloroethane (1.0 mL) via syringe. After that, allylacetate **2a** (1.2-2.0 equiv) and 1,2-dichloroethane (2.0 mL) were added 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 100-120 °C for 12-20 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 (for some compounds CH_2Cl_2 and MeOH combination were used. It has been mentioned in the substrates below) to give pure **4**.

Note: For products **4ba-4ga,** 1.2 equiv of allylacetate (**2a**) and products **4ja-4qa,** 2.0 equiv of allylacetate (**2a**) was used. Reaction temperature is 120 °C for products **4fa, 4ga, 4la, 4ma, 4na** and **4pa**.

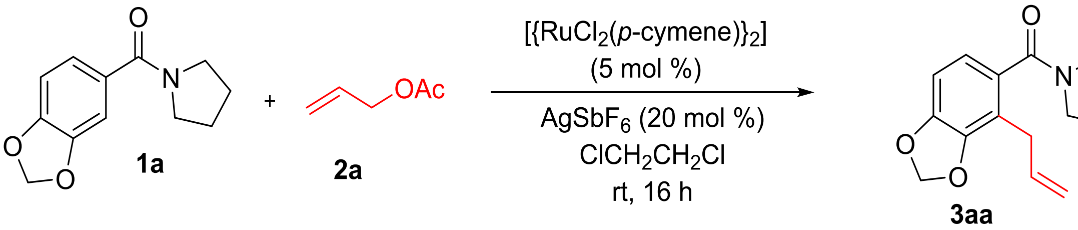
General Procedure for the Synthesis of Isochromanone Derivatives.

ortho Allylated aromatic amides (**3**) (50 mg) was taken in a 10-mL sealed tube and dissolved with 0.5 mL of 1,4 dioxane and 2.0 mL of 6N HCl. Then, the reaction mixture heated at 110°C for 12 h. After cooling to ambient temperature, water was poured into the reaction mixture and extracted with ethyl acetate. The organic layer was washed with brine solution and dried over Na_2SO_4. The solution was concentrated under the reduced pressure. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure **5.**

General Procedure for the Synthesis of Isobenzofuranone Derivatives.

ortho Vinylated aromatic amides (**4**) (50 mg) was taken in a 10-mL sealed tube and dissolved with 0.5 mL of 1,4-dioxane and 2.0 mL of 6N HCl. Then the reaction mixture heated at 120°C for 12 h. After cooling to ambient temperature, water was poured in to the reaction mixture and extracted with ethyl acetate. The organic layer was washed with brine solution and dried over Na_2SO_4. The solution was concentrated under the reduced pressure. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure **6**.

Table S1. Optimization Studies[a]



Entry	Solvent	Allyl source	Additive	Yield of **3aa** (%)[b]
1	*Iso*-propanol	Allyl acetate (2.0equiv)	$AgSbF_6$	38
2	Methanol	Allyl acetate (2.0equiv)	$AgSbF_6$	44
3	THF	Allyl acetate (2.0equiv)	$AgSbF_6$	68
4	DME	Allyl acetate (2.0equiv)	$AgSbF_6$	66
5	DMF	Allyl acetate (2.0equiv)	$AgSbF_6$	NR
6	DMSO	Allyl acetate (2.0 equiv)	$AgSbF_6$	NR
4	Toluene	Allyl acetate (2.0 equiv)	$AgSbF_6$	NR
8	1,4 Dioxane	Allyl acetate (2.0 equiv)	$AgSbF_6$	50
9	CH_3CN	Allyl acetate (2.0 equiv)	$AgSbF_6$	NR
10	$ClCH_2CH_2Cl$	Allyl acetate (2.0 equiv)	$AgSbF_6$	81
11	$ClCH_2CH_2Cl$	Allyl acetate (2.0 equiv)	AgOTf	71
12	$ClCH_2CH_2Cl$	Allyl acetate (2.0 equiv)	$AgBF_4$	69
13	$ClCH_2CH_2Cl$	Allyl acetate (2.0 equiv)	KPF_6	NR
14	$ClCH_2CH_2Cl$	Allyl bromide (2.0 equiv)	$AgSbF_6$	NR
15	$ClCH_2CH_2Cl$	Allyl carbonate (2.0 equiv)	$AgSbF_6$	NR
16	$ClCH_2CH_2Cl$	Allyl alcohol (2.0 equiv)	$AgSbF_6$	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 16 h under the N_2 atmosphere. [b] Isolated yield.

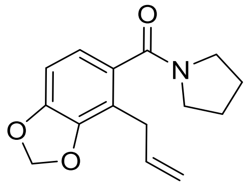
Note: The catalytic reaction was tried without ruthenium and $AgSbF_6$. No product **3aa** was observed in the reaction.

Initially, the allylation reaction was screened with various additives, solvents and allyl sources. The allylation reaction of **1a** with **2a** was tried in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) in various solvents such as *iso*-PrOH, MeOH, 1,4-dioxane, THF, DME, $ClCH_2CH_2Cl$, methanol, toluene, CH_3CN, DMSO, DMF and water at room temperature for 16 h (entries 1-10). Among them, $ClCH_2CH_2Cl$ was very effective, yielding product **3aa** in 81% yield (entry 10). *iso*-PrOH, MeOH, THF, DME and 1,4-dioxane were partially effective, providing product **3aa** in 38%, 44%, 68%, 66% and 50% yields, respectively. Remaining solvents were not effective. Further, the allylation reaction was examined with various additives such as $AgSbF_6$, $AgBF_4$, AgOTf, KPF_6 and $CuBF_4$ (entries 10-13) Among them, $AgSbF_6$ was effective, affording product **3aa** in 81% yield. $AgBF_4$ and AgOTf were partially effective, providing product **3aa** in 69% and 71% yields, respectively. KPF_6 and $CuBF_4$ were not effective. The catalytic reaction was also tested with other allyl sources such as allyl bromide, allyl alcohol and allyl carbonate. However, in these reactions, no allylated product **3aa** was observed (entries 14-16).

We have tried the *ortho* alkenylation of 4-methoxy-*N*-methylbenzamide **(1h)** with allyl acetate (**2a**) in the presence of a catalytic amount of $Ru(OAc)_2$(*p*-cymene) (10 mol %), $AgSbF_6$ (20 mol %) in $ClCH_2CH_2Cl$ at room temperature for 36 h. In the reaction, the expected *ortho* alkenylated benzamide **3ha** was observed in 52% 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.

(4-Allylbenzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3aa).



The representative general procedure was followed using **1a** (100 mg), **2a** (2.0 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 96 mg and yield is 81%. Colorless solid; eluent (30% ethylacetate in hexane).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.89 – 5.77 (m, 1H), 4.98 (dq, *J* = 16.0, 4.0 Hz, 1H), 4.93 (dt, *J* = 12.0, 4.0 Hz, 1H), 3.53 (t, *J*= 8.0 Hz, 2H), 3.36 (d, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 1.87 (p, *J* = 8.0 Hz, 2H), 1.75 (p, *J* = 8.0 Hz, 2H).

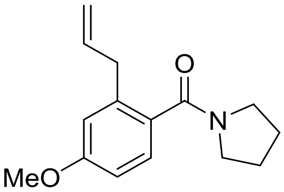
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 147.3, 146.2, 135.2, 131.8, 119.7, 118.6, 115.5, 106.3, 100.9, 48.9, 45.4, 30.9, 25.9, 24.5.

HRMS (ESI): calc. for [($C_{15}H_{17}NO_3$)H] (M+H) 260.1287, measured 260.1289.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3011, 2931, 2817, 1651, 1425, 1317, 1049, 918, 871, 668.

Rf (hexane/ethyl acetate = 70:30): 0.23.

(2-Allyl-4-methoxyphenyl)(pyrrolidin-1-yl)methanone (3ba).



The representative general procedure was followed using **1b** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 85 mg and yield is 71%. Colorless solid; eluent (28% ethylacetate in hexane).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (d, *J* = 8.0Hz, 1H),6.74 (d, *J* = 4.0Hz, 1H),6.71 (dd, *J* = 8.0, 4.0 Hz, 1H),5.90 -5.80 (m, 1H), 5.06 – 4.97 (m, 2H), 3.76 (s, 3H), 3.57 (t, *J* = 8.0Hz,2H), 3.34 (d, *J* = 8.0Hz, 2H), 3.11 (d, *J* = 8.0Hz, 2H), 1.88 (p, *J* = 4.0Hz, 2H), 1.79 (p, *J* = 4.0Hz, 2 H).

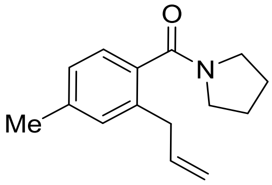
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 159.8, 138.3, 136.5, 130.2, 127.4, 115.9, 115.3, 111.3, 55.2, 48.8, 45.4, 37.5, 25.9, 24.5.

HRMS (ESI): calc. for [($C_{15}H_{19}NO_2$)H] (M+H) 246.1494, measured 246.1502.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2978, 2901, 1614, 1579, 1468, 1219, 1031, 858, 744, 598.

Rf (hexane/ethyl acetate = 70:30): 0.31.

(2-Allyl-4-methylphenyl)(pyrrolidin-1-yl)methanone (3ca).



The representative general procedure was followed using **1c** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 76 mg and yield is 63%. Colorless solid; eluent (30% ethylacetate in hexane).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.02 (dq, *J* = 16.0, 4.0 Hz, 1H), 4.98 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.58 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H).

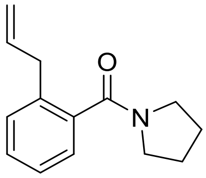
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 138.7, 136.9, 136.1, 134.8, 130.4, 126.8, 125.9, 115.7, 48.7, 45.3, 37.3, 25.9, 24.5, 21.2.

HRMS (ESI): calc. for [($C_{15}H_{19}NO$)H] (M+H) 230.1545, measured 230.1553.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661.

Rf (hexane/ethyl acetate = 70:30): 0.38.

(2-Allylphenyl)(pyrrolidin-1-yl)methanone (3da).



The representative general procedure was followed using **1d** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 85 mg and yield is 69%. Colorless solid; eluent (30% ethylacetate in hexane).

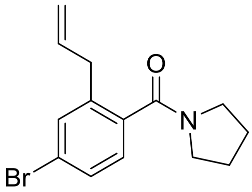
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.31 (td, *J* = 8.0, 4.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J* = 8.0, 4.0 Hz, 2H),5.94 -5.86 (m, 1H), 5.09 – 5.01 (m, 2H), 3.63 (t, *J* = 8.0Hz,2H), 3.44 (d, *J* = 8.0Hz,2H), 3.14 (t, *J* = 8.0Hz,2H), 1.94 (p, *J* = 4.0Hz,2H), 1.84 (p, *J* = 4.0Hz,2 H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.6, 138.7, 136.4, 135.7, 132.8, 129.4, 127.5,122.9, 116.7,48.7, 45.5, 37.1, 25.9, 24.5.

HRMS (ESI): calc. for [(C$_{14}$H$_{17}$NO)H] (M+H) 216.1388, measured 216.1395.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2979, 1614, 1570, 1413, 1261, 1048, 879, 717, 628.

Rf (hexane/ethyl acetate = 70:30): 0.31.

(2-Allyl-4-bromophenyl)(pyrrolidin-1-yl)methanone (3ea).



The representative general procedure was followed using **1e** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 77 mg and yield is 66%. Colorless solid; eluent (24% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.38 (d, *J* = 4.0Hz,1H),7.34 (dd, *J* = 8.0, 4.0 Hz,1H),7.05 (d, *J* = 8.0Hz,1H),5.88 -5.78 (m, 1H), 5.08 – 5.02 (m, 2H), 3.58 (t, *J* = 8.0Hz,2H), 3.37 (d, *J* = 8.0Hz,2H), 3.09 (t, *J* = 8.0Hz,2H), 1.90 (p, *J* = 4.0Hz,2H), 1.81 (p, *J* = 4.0Hz,2H).

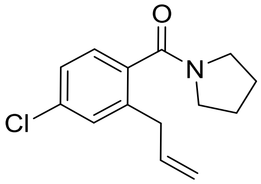
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 137.5, 136.7, 136.1, 129.8, 128.9, 126.2, 125.9, 115.8, 48.7, 45.3, 37.4, 25.9, 24.5.

HRMS (ESI): calc. for [($C_{14}H_{16}BrNO$)H] (M+H) 294.0494, measured 294.0495.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3078, 2931, 1634, 1589, 1463, 1259, 1041, 874, 747, 668.

Rf (hexane/ethyl acetate = 70:30): 0.29.

(2-Allyl-4-chlorophenyl)(pyrrolidin-1-yl)methanone(3fa).



The representative general procedure was followed using **1f** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 73 mg and yield is 61%. Colorless solid; eluent (30% ethylacetate in hexane).

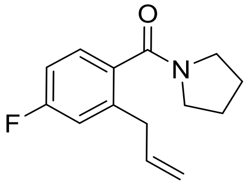
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (d, *J* = 4.0 Hz, 1H), 7.17 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.05 (dq, *J* = 12.0, 4.0 Hz, 1H), 5.02 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.37 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ168.5, 138.5, 135.9, 135.7, 134.6, 129.8, 127.3, 126.4, 116.7, 48.6, 45.4, 37.1, 25.9, 24.5.

HRMS (ESI): calc. for [($C_{14}H_{16}ClNO$)H] (M+H) 250.0999, measured 250.1003.

Rf (hexane/ethyl acetate = 70:30): 0.31.

(2-Allyl-4-Fluorophenyl)(pyrrolidin-1-yl)methanone (3ga).



The representative general procedure was followed using **1g** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 62 mg and yield is 52%. Colorless liquid; eluent (25% ethylacetate in hexane).

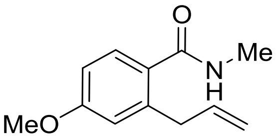
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.16 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.89 (td, *J* = 8.0, 4.0 Hz, 1H), 5.88 – 5.79 (m, 1H), 5.06 (dq, *J* = 8.0, 4.0 Hz, 1H), 5.03 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.59 (t, *J* = 8.0 Hz, 2H), 3.39 (d, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 1.91 (p, *J* = 8.0 Hz, 2H), 1.81 (p, *J* = 8.0 Hz, 2H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.9, 163.9, 161.5, 139.4 and 139.3 (F-coupling), 135.8, 133.6, 127.8 and 127.7 (F-coupling), 116.7 and 116.5(F-coupling), 113.3 and 113.1 (F-coupling), 48.7, 45.5, 37.2, 25.9, 24.4.

HRMS (ESI): calc. for [($C_{14}H_{16}FNO$)H] (M+H) 234.1294, measured 234.1299.

Rf (hexane/ethyl acetate = 70:30): 0.33.

2-Allyl-4-methoxy-*N*-methylbenzamide (3ha).



The representative general procedure was followed using **1h** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 63 mg and yield is 51%. Colorless solid; eluent (30% ethylacetate in hexanes).

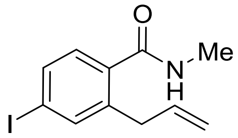
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.33(d, *J* = 8.0Hz, 1H), 6.73 – 6.69 (m, 2H), 6.02 – 5.92 (m, 1H), 5.87 (s, 1H), 5.05 (dq, *J* = 8.0, 4.0 Hz, 1H), 5.0 (dq, *J* = 12.0, 4.0 Hz, 1H), 3.78 (s, 3H), 3.53 (d, *J* = 8.0 Hz, 2H), 2.91 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 170.2, 160.7, 139.9, 137.5, 129.0, 128.9, 116.0, 115.9, 111.3, 55.2, 37.8, 26.6.

HRMS (ESI): calc. for [($C_{12}H_{15}NO_2$)H] (M+H) 206.1181, measured 206.1187.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3289, 2922, 1630, 1536, 1403, 1157, 1041, 999.

2-Allyl-4-iodo-*N*-methylbenzamide(3ia).



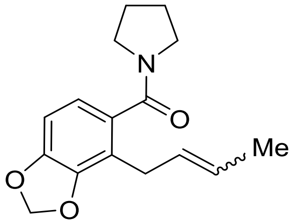
The representative general procedure was followed using **1i** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 49 mg and yield is 42%. Colorless solid; eluent (30% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.57 (d, *J* = 4.0Hz,1H), 7.54 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.06 (d, *J* = 8.0Hz,1H),5.98 (s, 1H), 5.96 – 5.86 (m, 1H), 5.07 (dq, *J* = 8.0, 4.0 Hz, 1H), 4.99 (dq, *J* = 12.0, 4.0 Hz, 1H), 3.44 (d, *J* = 8.0Hz,2H), 2.91 (d, *J* = 4.0Hz,3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 169.7, 139.8, 139.2, 136.7, 135.9, 135.4, 128.7, 116.7, 96.3 37.1, 26.6.

HRMS (ESI): calc. for [($C_{11}H_{12}INO$)H] (M+H) 302.0042, measured 302.0049.

(4-(But-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ab).



The representative general procedure was followed using **1a** (100 mg), **2b** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 98 mg and yield is 78%. Colorless liquid; eluent (27% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): **E isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.51 – 5.34 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J*= 8.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 1.64 (d, *J* = 8.0 Hz, 3H).

Z isomer: δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.51 – 5.34 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.29 (d, *J* = 4.0 Hz, 1H), 3.13 (t, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 1.58 (d, *J* = 4.0 Hz, 1H).

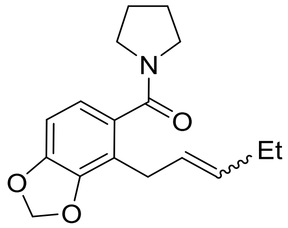
^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.2, 147.3, 146.1, 131.7, 127.7, 127.1, 126.3, 124.8, 106.2, 100.9, 48.9, 45.4, 29.8, 25.9, 24.6, 12.8. **Z isomer:** δ 169.1, 147.3, 146.1, 131.7, 127.7, 126.3, 119.8, 119.7, 106.2, 100.9, 48.9, 45.4, 29.6, 25.9, 24.6, 17.8.

HRMS (ESI): calc. for [($C_{16}H_{19}NO_3$)H] (M+H) 274.1443, measured 274.1446.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2989, 2717, 1637, 1485, 1212, 1041, 908, 875, 652.

Rf (hexane/ethyl acetate = 70:30): 0.23.

(4-(Pent-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ac).



The representative general procedure was followed using **1a** (100 mg), **2c** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 101 mg and yield is 77%. Colorless liquid; eluent (30% ethylacetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H),6.63 (d, *J* = 8.0 Hz, 1H),5.93 (s, 2H), 5.38 – 5.32 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.08 (p, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 3H).**Z isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H),6.63 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.48 – 5.43 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.08 (p, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 3H).

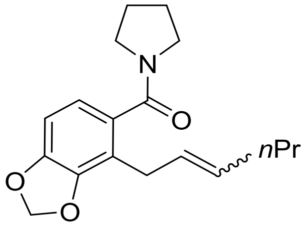
^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.1, 147.3, 146.1, 133.4, 132.6, 131.7, 125.5, 119.9, 106.1, 100.9, 48.9, 45.4, 25.9, 24.8, 24.6, 20.5, 14.1. **Z isomer:** δ 170.7, 147.3, 146.1, 130.5, 125.4, 125.3, 119.7, 119.6, 106.1, 100.9, 48.9, 45.4, 39.0, 34.7, 29.8, 25.9, 25.4, 24.9, 24.8, 24.6, 20.5, 14.1, 13.5.

HRMS (ESI): calc. for [($C_{17}H_{21}NO_3$)H] (M+H) 288.1600, measured 288.1610.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2948, 2811, 1616, 1435, 1212, 1021, 905, 875, 669.

Rf (hexane/ethyl acetate = 70:30): 0.23.

(4-(Hex-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ad).



The representative general procedure was followed using **1a** (100 mg), **2d** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 103 mg and yield is 76%. Colorless liquid; eluent (26% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): **E isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 5.38 – 5.33 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.36 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.05 (q, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J* = 8.0 Hz, 2H), 5.38 – 5.33 (m, 2H), 0.87 (t, *J* = 8.0 Hz, 3H).

Z isomer: δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 5.47 – 5.41 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.05 (q, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J* = 8.0 Hz, 2H), 5.38 – 5.33 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): **E isomer:** δ 170.7, 147.2, 146.0, 131.7, 130.8, 126.2, 126.0, 119.7, 106.2, 100.9, 48.8, 45.4, 29.2, 25.8, 24.9, 24.5, 22.7, 13.7.

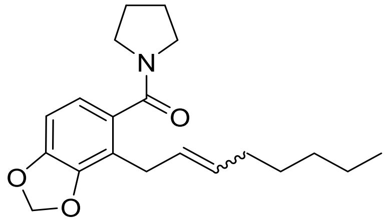
Z isomer: δ 169.1, 147.2, 146.0, 130.4, 126.5, 120.1, 119.9, 119.7, 106.2, 100.9, 48.8, 39.0, 34.7, 34.5, 29.9, 25.0, 22.4, 13.6.

HRMS (ESI): calc. for [(C$_{18}$H$_{23}$NO$_3$)H] (M+H) 302.1756, measured 302.1762.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2967, 2819, 1614, 1435, 1312, 1041, 908, 818, 695.

Rf (hexane/ethyl acetate = 70:30): 0.29.

(4-(Oct-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ae).



The representative general procedure was followed using **1a** (100 mg), **2e** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 102 mg and yield is 68%. Colorless liquid; eluent (28% ethylacetate in hexane).

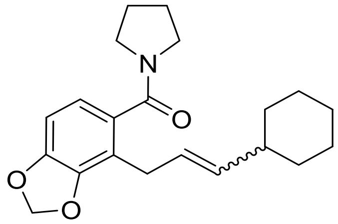
^{1}H NMR (CDCl$_3$, 400 MHz): **E isomer:** δ 6.65 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.37 – 5.35 (m, 2H), 3.54 (t, *J* = 8.0 Hz, 2H), 3.35 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.06 (q, *J* = 8.0 Hz, 2H), 1.88 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J*= 8.0 Hz, 2H), 1.36 – 1.16 (m, 6H), 0.84 (t, *J* = 8.0 Hz, 3H). **Z isomer:** δ 6.65 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.43 – 5.40 (m, 1H), 3.54 (t, *J* = 8.0 Hz, 2H), 3.29 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.06 (q, *J* = 8.0 Hz, 2H), 1.88 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J*= 8.0 Hz, 2H), 1.36 – 1.16 (m, 6H), 0.84 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): **E isomer:** δ 169.1, 147.2, 146.1, 131.7, 131.1, 125.9, 119.9, 119.7, 106.1, 100.9, 48.8, 45.4, 31.4, 29.2, 27.1, 25.9, 24.9, 24.5, 22.5, 13.9. **Z isomer:**δ 169.1, 147.2, 146.1, 131.9, 131.1, 126.2, 119.9, 119.7, 106.1, 100.9, 48.8, 36.5, 34.7, 32.4, 31.3, 29.9, 29.6, 28.9, 22.4, 13.9.

HRMS (ESI): calc. for [($C_{20}H_{27}NO_3$)H] (M+H) 330.2069, measured 330.2077.

Rf (hexane/ethyl acetate = 70:30): 0.23.

(4-(3-Cyclohexylallyl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3af).



The representative general procedure was followed using **1a** (100 mg), **2f** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 96 mg and yield is 62%. Colorless liquid; eluent (30% ethyl acetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.67 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.31 – 5.18 (m, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.38 (d, *J* = 8.0 Hz, 2H), 3.16 (t, *J* = 8.0 Hz, 2H), 2.39 – 2.32 (m, 1H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H), 1.68 – 1.56 (m, 6H), 1.35 – 1.19 (m, 2H), 1.19 – 1.07 (m, 2H), 1.07 – 0.93 (m, 2H).

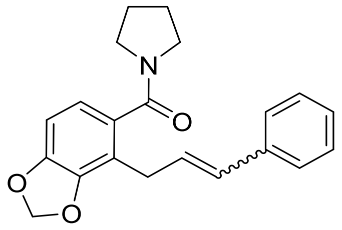
Z isomer: δ 6.67 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.41 – 5.38 (m, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.30 (d, *J* = 8.0 Hz, 2H), 3.16 (t, *J* = 8.0 Hz, 2H), 2.39 – 2.32 (m, 1H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H), 1.68 – 1.56 (m, 6H), 1.35 – 1.19 (m, 2H), 1.19 – 1.07 (m, 2H), 1.07 – 0.93 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.1, 147.3, 146.1, 137.1, 131.7, 124.3, 120.2, 119.8, 106.2, 100.9, 48.9, 45.5, 36.2, 33.1, 26.0, 25.9, 25.8, 25.1, 24.6. **Z isomer:** δ 169.1, 137.9, 137.8, 137.1, 130.5, 124.1, 123.9, 119.8, 106.2, 100.9, 48.9, 45.5, 40.5, 39.1, 34.8, 32.9, 30.2, 29.6, 26.1.

HRMS (ESI): calc. for [($C_{21}H_{27}NO_3$)H] (M+H) 342.2069, measured 342.2073.

Rf (hexane/ethyl acetate = 98:2): 0.63.

(4-(3-Phenylallyl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ag).



The representative general procedure was followed using **1a** (100 mg), **2g** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 113 mg and yield is 74%. Colorless liquid; eluent (27% ethylacetate in hexanes).

^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 7.35 – 7.17 (m, 6H), 6.67 (s, 2H), 6.43 (dt, *J* = 12.0, 4.0 Hz, 1H), 5.94 (s, 2H), 5.74 (dt, *J* = 12.0, 8.0 Hz, 1H), 3.68 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 1.74 – 1.62 (m, 4H).

Z isomer: δ 7.35 – 7.17 (m, 6H), 6.67 (s, 2H), 6.43 (dt, *J* = 12.0, 4.0 Hz, 1H), 5.94 (s, 2H), 5.74 (dt, *J* = 12.0, 8.0 Hz, 1H), 3.56 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.52 (t, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 1.74 – 1.62 (m, 4H).

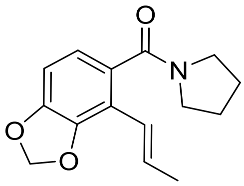
^{13}C NMR (CDCl$_3$, 100 MHz): **E isomer:** δ 168.7, 147.3, 145.9, 136.8, 131.9, 129.4, 128.7, 128.1, 126.7, 119.6, 119.1, 106.6, 101.0, 48.6, 45.5, 26.5, 25.7, 24.3.

Z isomer: δ 168.9, 146.1, 137.1, 131.7, 131.1, 128.4, 127.1, 126.6, 125.9, 119.9, 118.8, 106.2, 101.0, 49.0, 45.1, 29.9, 29.6, 25.6.

HRMS (ESI): calc. for [($C_{21}H_{21}NO_3$)H] (M+H) 336.1600, measured 336.1607.

Rf (hexane/ethyl acetate = 70:30): 0.27.

(*E*)-(4-(Prop-1-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (4aa).



The representative general procedure was followed using **1a** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100°C for12 h. The desired product was isolated in 89 mg and yield is 76%. Colorless solid; eluent (30% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.71 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.55 (dq, *J* = 16.0, 8.0 Hz, 1H), 6.22(dq, *J* = 16.0, 4.0 Hz, 1H), 5.98 (s, 2H), 3.61 (t, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 1.91 (p, *J* = 8.0 Hz, 2H), 1.84 (dd, *J* = 8.0, 4.0 Hz, 3H), 1.84 – 1.78 (m, 2H).

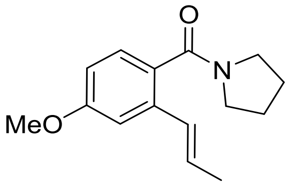
^{13}C NMR (CDCl$_3$, 100 MHz): δ 169.1, 147.6, 144.8, 132.6, 130.7, 122.9, 119.9, 117.5, 106.6, 100.9, 48.4, 45.5, 25.9, 24.6, 19.4.

HRMS (ESI): calc. for [($C_{15}H_{17}NO_3$)H] (M+H) 260.1287, measured 260.1289.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2881, 2797, 1647, 1435, 1312, 1041, 918, 874, 680.

Rf (hexane/ethyl acetate = 70:30): 0.22.

(*E*)-(4-Methoxy-2-(prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ba).



The representative general procedure was followed using **1b** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100°C for12 h. The desired product was isolated in 88 mg and yield is 74%. Colorless solid; eluent (28% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.13 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 6.74 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.25 – 6.16 (m, 1H), 3.79 (s, 3H), 3.62 (t, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H), 1.91 (p, *J* = 8.0 Hz, 2H), 1.83 (dd, *J* = 8.0, 4.0 Hz, 2H), 1.82 – 1.77 (m, 2H).

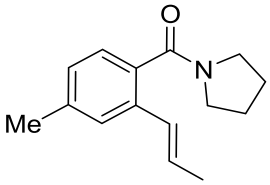
^{13}C NMR (CDCl$_3$, 100 MHz): δ 169.7, 159.8, 135.9, 129.1, 128.5, 127.8, 127.6, 112.6, 110.4, 55.2, 48.3, 45.5, 25.9, 24.6, 18.7.

HRMS (ESI): calc. for [($C_{15}H_{19}NO_2$)H] (M+H) 246.1494, measured 246.1502.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661.

Rf (hexane/ethyl acetate = 70:30): 0.32.

(*E*)-(4-Methyl-2-(prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ca).



The representative general procedure was followed using **1c** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100°C for12 h. The desired product was isolated in 98 mg and yield is 81%. Colorless solid; eluent (28% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.25 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.23- 6.15 (m, 1H), 3.61 (t, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.81 (dd, *J* = 8.0, 4.0 Hz, 3H), 1.81 – 1.75(m, 2 H).

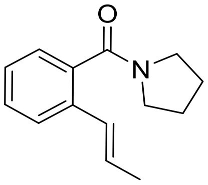
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 138.5, 133.9, 133.3, 127.9, 127.6, 127.5, 126.0, 125.9, 48.2, 45.4, 25.8, 24.5, 21.3, 18.7.

HRMS (ESI): calc. for [($C_{15}H_{19}NO$)H] (M+H) 230.1545, measured 230.1553.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2942, 2617, 1647, 1415, 1317, 1047, 918, 875, 598.

Rf (hexane/ethyl acetate = 70:30): 0.29.

(*E*)-(2-(Prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4da).



The representative general procedure was followed using **1d** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100 °C for 12 h. The desired product was isolated in 92 mg and yield is 75%. Colorless solid; eluent (27% ethylacetate in hexanes).

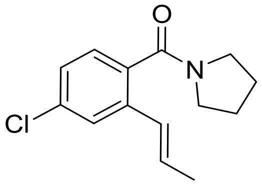
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 8.0Hz,1H),7.24 -7.18 (m, 1H), 7.12 (t, *J* = 4.0Hz,2H),6.33 (d, *J* = 16.0Hz,1H),6.20 -6.13(m, 1H), 3.57 (t, *J* = 8.0Hz,2 H), 3.00 (t, *J* = 8.0Hz,2 H), 1.85 (p, *J* = 4.0Hz,2 H), 1.77(dt, *J* = 8.0, 4.0Hz,3 H), 1.76 – 1.72 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 135.8, 133.8, 128.7, 128.2, 127.4, 126.7, 125.8, 125.2, 48.0, 45.2, 25.7, 24.4, 18.6.

HRMS (ESI): calc. for [($C_{14}H_{17}NO$)H] (M+H) 216.1388, measured 216.1395.

Rf (hexane/ethyl acetate = 70:30): 0.33.

(*E*)-(4-Chloro-2-(prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4fa).



The representative general procedure was followed using **1f** (100 mg), **2a** (1.2 equiv) and the reaction was done at 120°C for12 h. The desired product was isolated in 86 mg and yield is 73%. Colorless solid; eluent (28% ethylacetate in hexanes).

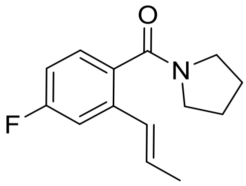
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.45 (d, *J* = 4.0 Hz, 1H), 7.17 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.21 (m, 1H), 3.63 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 1.93 (p, *J* = 6.5 Hz, 2H), 1.85 (dd, *J* = 8.0, 2.0 Hz, 3H), 1.84 – 1.78 (m, 2H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.7, 136.1, 134.8, 134.5, 129.3, 127.6, 126.9, 126.6, 125.5, 48.2, 45.5, 25.9, 24.6, 18.7.

HRMS (ESI): calc. for [($C_{14}H_{16}ClNO$)H] (M+H) 250.0999, measured 250.1003.

Rf (hexane/ethyl acetate = 70:30): 0.29.

(*E*)-(4-Fluoro-2-(Prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ga).



The representative general procedure was followed using **1g** (100 mg), **2a** (1.2 equiv) and the reaction was done at 120°C for12 h. The desired product was isolated in 75 mg and yield is 62%. Colorless solid; eluent (28% ethylacetate in hexanes).

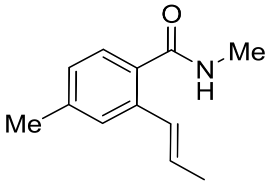
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.17 (d, *J* = 8.0Hz,1H),7.13 (dd, *J* = 8.0, 4.0Hz,1H),6.88(dt, *J* = 8.0, 4.0 Hz,1H),6.35 (d, *J* = 16.0Hz,1H),6.27 -6.18(m, 1H), 3.61 (t, *J* = 8.0Hz,2H), 3.06 (t, *J* = 8.0Hz,2H), 1.91 (p, *J* = 4.0Hz,2H), 1.83(dd, *J* = 8.0, 4.0Hz,3H), 1.81 – 1.77(m, 2H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.9, 164.1 and 161.6 (F-coupling), 136.8 and 136.7 (F-coupling), 132.1, 129.8, 128.1 and 127.9 (F-coupling), 126.7, 114.0 and 113.8 (F-coupling), 111.9 and 111.7 (F-coupling), 48.3, 45.5, 25.9, 24.5, 18.7.

HRMS (ESI): calc. for [($C_{14}H_{16}FNO$)H] (M+H) 234.1294, measured 234.1299.

Rf (hexane/ethyl acetate = 98:2): 0.63.

(*E*)-*N*,4-Dimethyl-2-(prop-1-en-1-yl)benzamide (4ja).



The representative general procedure was followed using **1j** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 79 mg and yield is 63%. White Colour solid; eluent (0.3% methanol in DCM).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, *J* = 4.0Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 8.0Hz, 1H), 6.67 (dd, *J* = 16.0, 4.0 Hz, 1H), 6.20-6.11 (m, 1H), 5.81 (s, 1H), 2.95 (d, *J* = 4.0 Hz,3 H), 2.32 (s, 3 H), 1.86 (dd, *J* = 8.0, 4.0Hz, 3 H).

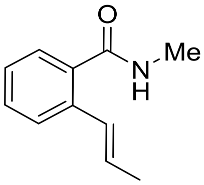
^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3, 139.9, 135.9, 132.0, 128.6, 128.4, 127.5, 127.4, 126.9, 26.7, 21.3, 18.7.

HRMS (ESI): calc. for $[(C_{12}H_{15}NO)H]$ (M+H) 190.1232, measured 190.1236.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3289, 2922, 1630, 1536, 1403, 1157, 1041, 999.

Rf (hexane/ethyl acetate = 70:30): 0.27.

(*E*)-*N*-Methyl-2-(prop-1-en-1-yl)benzamide(4ka).



The representative general procedure was followed using **1k** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 84 mg and yield is 65%. White Colour solid; eluent (0.3% methanol in DCM).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, *J* = 4.0Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H),7.16 (t, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 12.0Hz, 1H), 6.20-6.11 (m, 1H), 5.92 (s, 1 H), 2.93(d, *J* = 4.0 Hz, 3 H), 1.85 (dd, *J* = 8.0, 4.0Hz, 3 H).

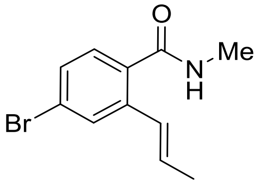
^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3, 135.8, 134.8, 129.8, 128.6, 128.3, 127.3, 126.6, 126.1, 26.6, 18.6.

HRMS (ESI): calc. for $[(C_{11}H_{13}NO)H]$ (M+H) 176.1075, measured 176.1073.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3294, 2935, 1635, 1546, 1444, 1319, 1005, 954, 687.

Rf (hexane/ethyl acetate = 70:30): 0.21.

(*E*)-4-Bromo-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4la).



The representative general procedure was followed using **1l** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120°C for 20 h. The desired product was isolated in 66 mg and yield is 56%. Colorless solid; eluent (0.3% methanol in DCM).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 4.0Hz, 1 H), 7.31 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 6.60 (dd, *J* = 16.0, 4.0 Hz, 1 H), 6.23-6.14 (m, 1 H), 5.83 (s, 1 H), 2.96(d, *J* = 4.0 Hz,3 H), 1.87 (dd, *J* = 8.0, 4.0Hz, 3 H).

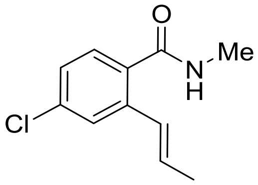
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 137.9, 133.5, 130.3, 129.6, 129.2, 128.9, 127.2, 124.3, 26.7, 18.7.

HRMS (ESI): calc. for $[(C_{11}H_{12}BrNO)H]$ (M+H) 254.0181, measured 254.0188.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3282, 2945, 2817, 1635, 1547, 1441, 1312, 1041, 935, 875, 661.

Rf (hexane/ethyl acetate = 70:30): 0.29.

(*E*)-4-Chloro-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4ma).



The representative general procedure was followed using **1m** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120 °C for 20 h. The desired product was isolated in 66 mg and yield is 54%. Colorless solid; eluent (0.3% methanol in DCM).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, *J* = 4.0Hz, 1 H), 7.29 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.14 (dt, *J* = 8.0, 4.0 Hz, 1 H), 6.60 (d, *J* = 16.0Hz, 1 H), 6.23-6.14 (m, 1 H), 5.89 (s, 1 H), 2.94 (dd, *J* =8.0, 4.0 Hz,3 H), 1.87 (d, *J* = 4.0Hz, 3 H).

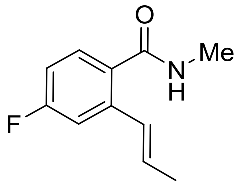
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 137.8, 135.9, 133.1, 130.2, 128.8, 127.3, 126.7, 126.2, 26.7, 18.7.

HRMS (ESI): calc. for [($C_{11}H_{12}ClNO$)H] (M+H) 210.0686, measured 210.0691.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3078, 2931, 1634, 1589, 1463, 1259, 1041, 874, 747, 668.

Rf(hexane/ethyl acetate = 70:30): 0.30.

(*E*)-4-Fluoro-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4na).



The representative general procedure was followed using **1n** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120°C for 20 h. The desired product was isolated in 47 mg and yield is 42%. Colorless solid; eluent (0.3% methanol in DCM).

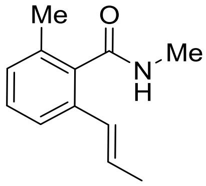
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.88 (td, *J* = 8.0, 4.0 Hz, 1H), 6.67 (dt, *J* = 16.0, 4.0 Hz, 1H), 6.20 (dq, *J* = 12.0, 4.0 Hz, 1H), 5.78(s, 1H), 2.97 (d, *J* = 4.0Hz, 3H), 1.88(dd, *J* = 8.0, 4.0 Hz,3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 164.8, 162.3, 138.7 and 138.6 (F-coupling), 130.9, 130.1, 129.6 and 129.5 (F-coupling), 127.5, 113.8 and 113.6 (F-coupling), 112.8 and 112.6 (F-coupling), 26.8, 18.7.

HRMS (ESI): calc. for [($C_{11}H_{12}FNO$)H] (M+H) 194.0981, measured 194.0988.

Rf(hexane/ethyl acetate = 70:30): 0.31.

(*E*)-*N*,2-Dimethyl-6-(prop-1-en-1-yl)benzamide (4oa).



The representative general procedure was followed using **1o** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 104 mg and yield is 83%. Colorless solid; eluent (0.3% methanol in DCM).

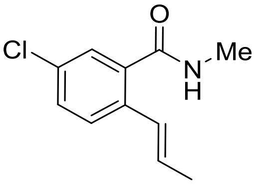
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27 (d, *J* = 8.0Hz, 1 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 4.0 Hz, 1 H), 6.36 (d, *J* = 16.0,Hz, 1 H), 6.19-6.13 (m, 1 H), 5.75 (s, 1 H), 2.95 (d, *J* = 8.0 Hz,3 H), 2.25 (s, 3 H), 1.82 (dd, *J* = 8.0, 4.0Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 135.7, 134.7, 134.5, 128.7, 128.4, 128.2, 127.8, 122.5, 26.4, 19.1, 18.7.

HRMS (ESI): calc. for $[(C_{12}H_{15}NO)H]$ (M+H) 190.1232, measured 190.1236.

Rf (hexane/ethyl acetate = 70:30): 0.28.

(*E*)-5-Chloro-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4pa).



The representative general procedure was followed using **1m** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120°C for 20 h. The desired product was isolated in 64 mg and yield is 51%. Colorless solid; eluent (0.3% methanol in DCM).

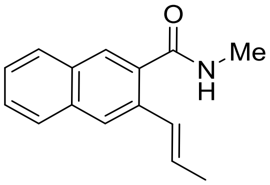
^{1}H NMR ($CDCl_3$, 400 MHz):δ 7.39 (d, *J* = 8.0Hz, 1 H), 7.35 (d, *J* = 4.0 Hz, 1 H), 7.27 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.59 (d, *J* = 16.0Hz, 1 H), 6.21-6.12 (m, 1 H), 5.86 (s, 1 H), 2.96 (d, *J* = 8.0 Hz, 3 H), 1.86 (dd, *J* = 8.0, 4.0Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 136.0, 134.4, 132.4, 130.0, 129.5, 127.6, 127.4, 127.3, 26.7, 18.7.

HRMS (ESI): calc. for [($C_{11}H_{12}ClNO$)H] (M+H) 210.0686, measured 210.0685.

Rf (hexane/ethyl acetate = 70:30): 0.21.

(*E*)-*N*-Methyl-3-(prop-1-en-1-yl)-2-naphthamide (4qa).



The representative general procedure was followed using **1i** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 93 mg and yield is 77%. Colorless solid; eluent (0.3% methanol in DCM).

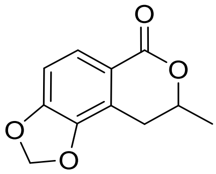
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1 H), 7.86 (s, 1 H), 7.76 (t, *J* = 8.0 Hz,2 H), 7.47 (t, *J* = 8.0 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 16.0Hz, 1 H), 6.31-6.22 (m, 1 H), 5.99 (s, 1 H), 3.01 (d, *J* = 8.0 Hz,3 H), 1.91 (dd, *J* = 8.0, 4.0Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3, 133.9, 133.5, 133.5, 131.6, 128.8, 128.6, 127.9, 127.6, 127.3, 127.2, 126.1, 125.2, 26.8, 18.8.

HRMS (ESI): calc. for [($C_{15}H_{15}NO$)H] (M+H) 226.1232, measured 226.1236.

Rf (hexane/ethyl acetate = 98:2): 0.63.

8-Methyl-8,9-dihydro-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (5a).



The representative general procedure was followed using **3aa** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 25 mg and yield is 64%. Colorless solid; eluent (11% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.45 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J*= 4.0 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 5.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.16 – 2.08 (m, 1H), 1.88 – 1.78 (m, 1H), 0.99 (t, *J* = 8.0 Hz, 3H).

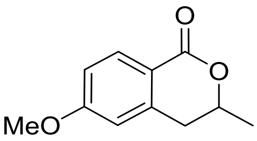
^{13}C NMR (CDCl$_3$, 100 MHz): δ 165.1, 151.6, 143.8, 126.3, 119.8, 118.8, 107.6, 102.3, 74.6, 28.6, 20.9.

HRMS (ESI): calc. for [($C_{11}H_{10}O_4$)H] (M+H) 207.0657, measured 207.0659.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2927, 2854, 1707, 1589, 1232, 1116, 1041, 908, 845, 664.

Rf (hexane/ethyl acetate = 80:20): 0.38.

6-Methoxy-3-methylisochroman-1-one (5b).



The representative general procedure was followed using **3ba** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 27 mg and yield is 61%. Colorless solid; eluent (10% ethyl acetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.02 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 4.0 Hz, 1H),6.67 (d, *J* = 4.0 Hz, 1H), 4.67 – 4.59 (m, 1H), 3.84 (s, 3H), 2.92 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.84 (dd, *J* = 16.0, 4.0 Hz, 1H),1.48 (d, *J* = 8.0 Hz, 3H).

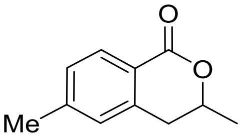
^{13}C NMR (CDCl$_3$, 100 MHz): δ 165.5, 163.7, 141.4, 132.6, 117.5, 113.4, 112.1, 74.7, 55.5, 35.2, 20.9.

HRMS (ESI): calc. for [($C_{11}H_{12}O_3$)H] (M+H) 193.0865, measured 193.0874.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2980, 2935, 1713, 1607, 1458, 1117, 1041, 908, 741, 691.

Rf (hexane/ethyl acetate = 80:20): 0.48.

3,6-Dimethylisochroman-1-one (5c).



The representative general procedure was followed using **3ca** (50 mg) and the reaction was done at 110°C for12 h. The desired product was isolated in 24 mg and yield is 62%. Colorless solid; eluent (10% ethylacetate in hexanes).

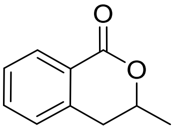
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 4.67 -4.58 (m, 1 H), 2.90 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.83 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.37 (s, 3H), 1.48 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 144.6, 139.1, 130.3, 128.5, 127.8, 122.3, 74.9, 34.9, 21.7, 20.9.

HRMS (ESI): calc. for [($C_{11}H_{12}O_2$)H] (M+H) 177.0916, measured 177.0923.

Rf (hexane/ethyl acetate = 80:20): 0.43.

3-Methylisochroman-1-one (5d).



The representative general procedure was followed using **3da** (50 mg) and the reaction was done at 110°Cfor 12 h. The desired product was isolated in 22 mg and yield is 58%. Colorless solid; eluent (10% ethylacetate in hexanes).

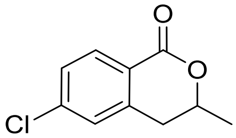
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.51 (td, *J* = 8.0, 4.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.69 -4.64(m, 1 H), 2.96 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.90 (dd, *J* = 16.0, 4.0 Hz, 1H),1.50 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 139.1, 133.6, 130.2, 127.6, 127.2, 124.9, 75.1, 34.9, 20.9.

HRMS (ESI): calc. for [($C_{10}H_{10}O_2$)H] (M+H) 163.0759, measured 163.0770.

Rf (hexane/ethyl acetate = 80:20): 0.43.

6-Chloro-3-methylisochroman-1-one (5ea).



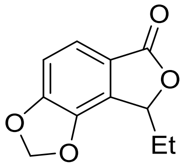
The representative general procedure was followed using **3fa** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 20 mg and yield is 51%. Colorless solid; eluent (10% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.22 (d, *J* = 4.0 Hz, 1H), 4.69 -4.61 (m, 1 H), 2.94 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.87 (dd, *J* = 16.0, 4.0 Hz, 1H),), 1.49 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 164.7, 140.7, 139.9, 131.8, 128.1, 127.4, 123.4, 74.9, 34.6, 20.8.

Rf (hexane/ethyl acetate = 98:2): 0.63.

8-Ethyl-[1,3]dioxolo[4,5-*e*]isobenzofuran-6(8*H*)-one (6a).



The representative general procedure was followed using **4aa** (50 mg) and the reaction was done at 120 °C for 12 h. The desired product was isolated in 25 mg and yield is 61%. Colorless solid; eluent (10% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.45 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J* = 4.0 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 5.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.16 -2.08(m, 1 H), 1.83 (dq, *J* = 12.0, 4.0 Hz, 1H), 0.99 (t, *J* = 8.0 Hz, 3H).

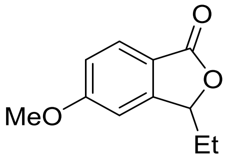
^{13}C NMR (CDCl$_3$, 100 MHz): δ 169.7, 152.4, 141.1, 129.2, 121.3, 120.8, 109.9, 102.6, 79.6, 26.7, 8.8.

HRMS (ESI): calc. for [($C_{11}H_{10}O_4$)H] (M+H) 207.0657, measured 207.0666.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661.

Rf (hexane/ethyl acetate = 80:20): 0.33.

3-Ethyl-5-methoxyisobenzofuran-1(3*H*)-one (6b).



The representative general procedure was followed using **4ba** (50 mg) and the reaction was done at 120 °C for 12 h. The desired product was isolated in 22 mg and yield is 56%. Colorless solid; eluent (12% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.35 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.88 (s, 3H), 2.15 – 2.04 (m, 1H),1.84 – 1.73 (m, 1H), 0.98 (t, *J* = 8.0 Hz, 3H).

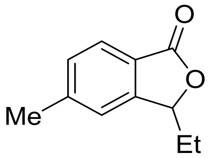
^{13}C NMR (CDCl$_3$, 100 MHz): δ 170.4, 164.6, 152.5, 127.2, 118.7, 116.1, 105.8, 81.5, 55.8, 27.6, 8.7.

HRMS (ESI): calc. for [(C$_{11}$H$_{12}$O$_3$)H] (M+H) 193.0865, measured 193.0874.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2972, 2933, 1702, 1604, 1495, 1255, 1083, 1019, 689.

Rf (hexane/ethyl acetate = 80:20): 0.31.

3-Ethyl-5-methylisobenzofuran-1(3*H*)-one (6ca).



The representative general procedure was followed using **4ca** (50 mg) and the reaction was done at 120 °C for 12 h. The desired product was isolated in 19 mg and yield is 51%. Colorless solid; eluent (12% ethylacetate in hexanes).

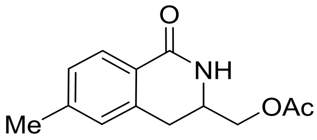
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H), 5.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.46 (s, 3H), 2.13 – 2.02 (m, 1H), 1.81 – 1.74 (m, 1H), 0.96 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 150.3, 145.1, 130.2, 125.4, 123.7, 122.0, 82.0, 27.7, 22.1, 8.8.

HRMS (ESI): calc. for [($C_{11}H_{12}O_2$)H] (M+H) 177.0916, measured 177.0923.

Rf (hexane/ethyl acetate = 80:20): 0.30.

(6-Methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl acetate (11a).



The representative general procedure was followed using **10a** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 58 mg and yield is 41%. Colorless solid; eluent (32% ethylacetate in hexanes).

^{1}H NMR (DMSO *d₆*, 400 MHz): δ 7.96 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 4.08 (dd, *J*= 12.0, 4.0 Hz, 1H), 3.92 (dd, *J*= 12.0, 4.0 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.02 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.81 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.33 (s, 3H), 1.97 (s, 3H).

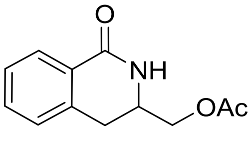
^{13}C NMR (DMSO d_6, 100 MHz): δ 170.3, 164.3, 142.0, 137.2, 128.3, 127.5, 127.0, 126.1, 65.1, 48.7, 29.5, 21.1, 20.6.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_3$)H] (M+H) 234.1130, measured 234.1141.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3300 (broad), 2926, 2315, 1649, 1615, 1454, 1337, 1080, 657.

Rf (hexane/ethyl acetate = 60:40): 0.23.

(1-Oxo-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl acetate (11b).

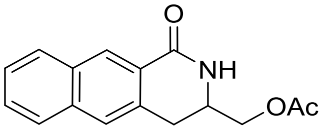


The representative general procedure was followed using **10b** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 55 mg and yield is 38%. Colorless solid; eluent (32% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 4.24 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.05 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.02 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.89 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.06 (s, 3H).
IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661.

Rf (hexane/ethyl acetate = 60:40): 0.24.

(1-Oxo-1,2,3,4-tetrahydrobenzo[g]isoquinolin-3-yl)methyl acetate (11c).



The representative general procedure was followed using **10c** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 63 mg and yield is 47%. Colorless solid; eluent (32% ethylacetate in hexanes).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.62 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.53 (d, *J* = 8.20 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 4.27 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.07 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.02 – 3.98 (m, 1H), 3.20 (dd, *J* = 16.0, 4.0 Hz, 1H), 3.04 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.06 (s, 3H).
^{13}C NMR (CDCl$_3$, 100 MHz): δ 170.7, 166.3, 135.4, 132.3, 132.1, 129.6, 129.4, 128.7, 128.5, 127.1, 126.3, 126.2, 65.9, 50.2, 30.6, 20.7.

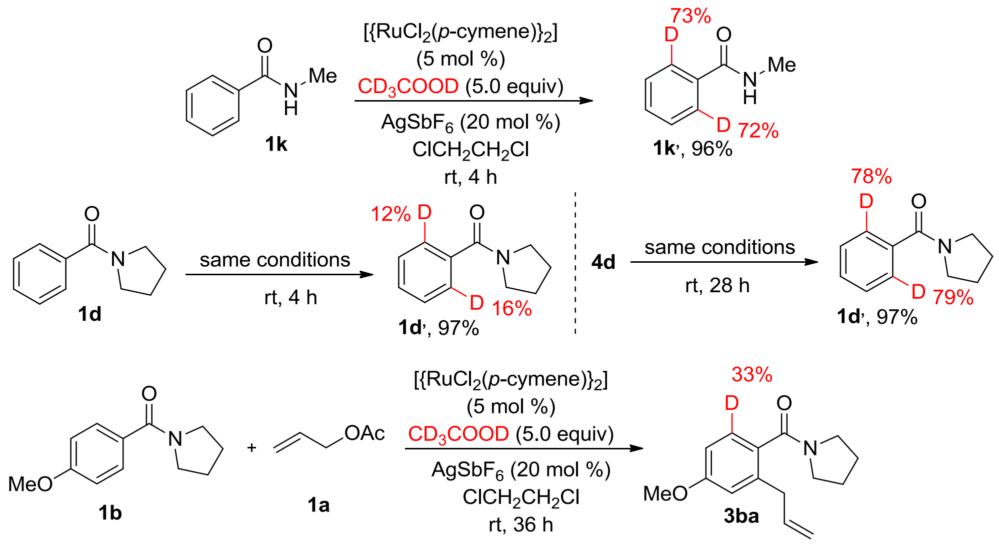
HRMS (ESI): calc. for [(C$_{16}$H$_{16}$NO$_3$)H] (M+H) 270.1130, measured 270.1140.

IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3267 (broad), 1734, 1727, 1656, 1413, 1229, 1042, 730.

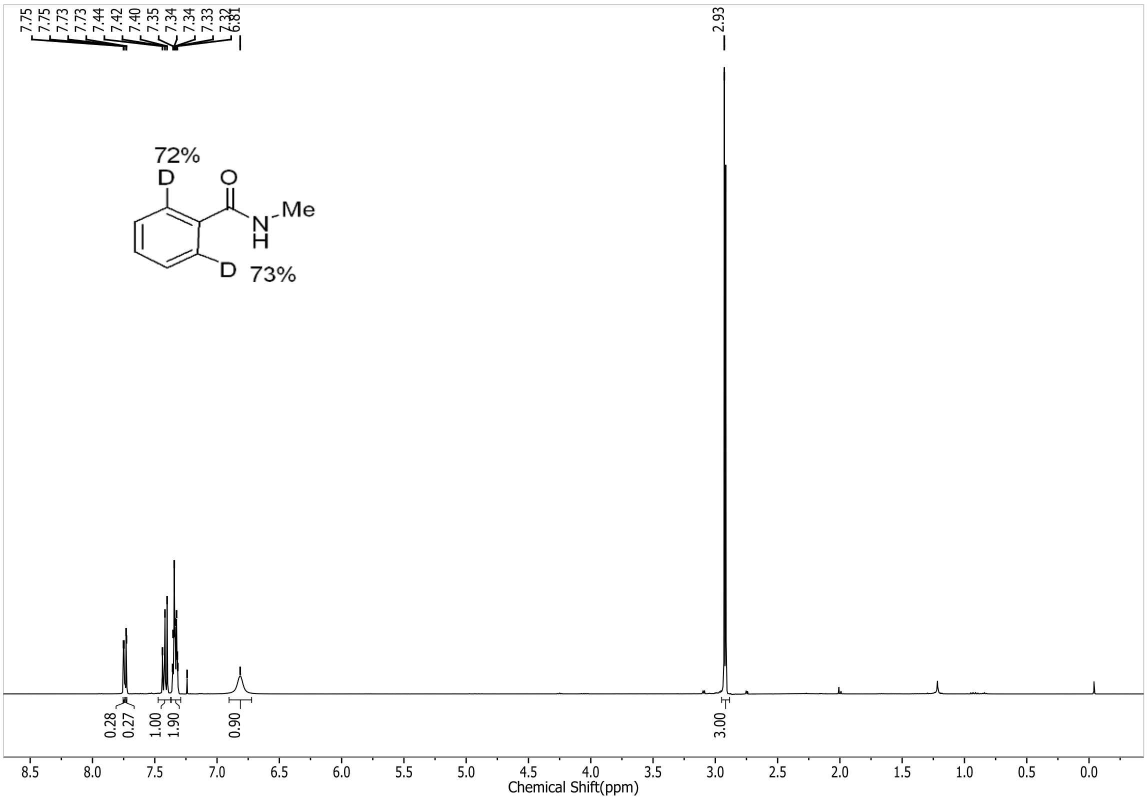
Rf (hexane/ethyl acetate = 60:40): 0.28.

Deuterium Studies

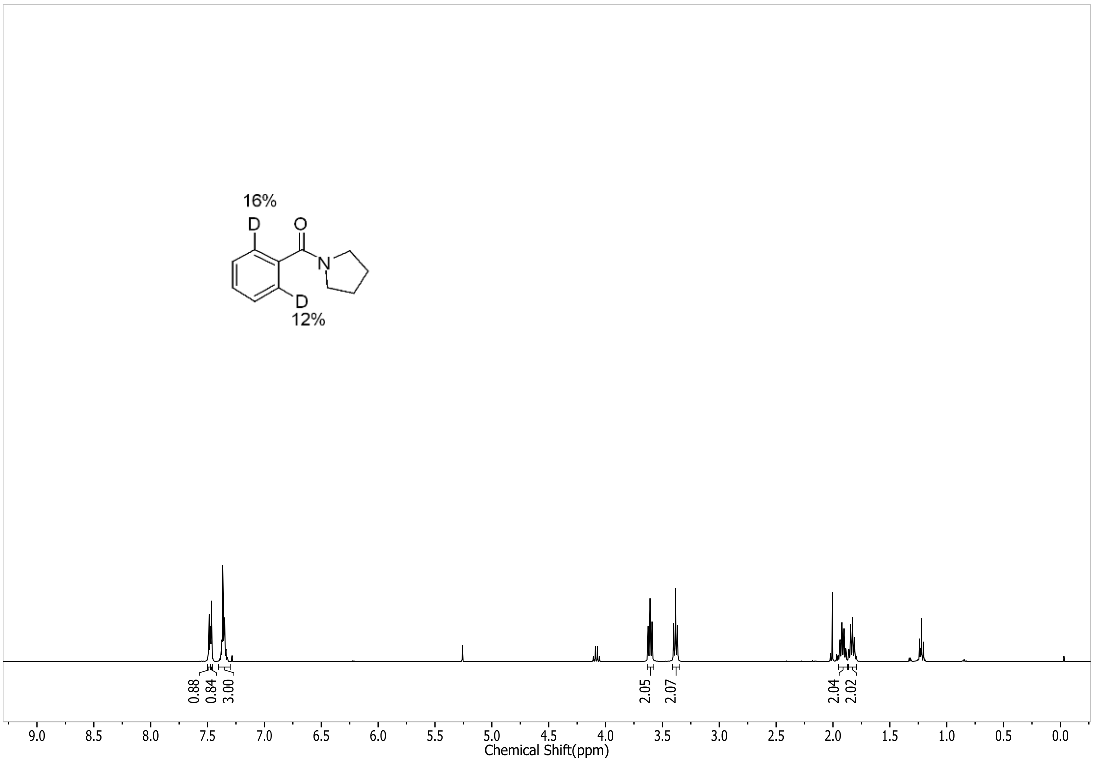
To know the feasibility of C-H bond activation of *N*-methyl benzamide and *N*,*N*-disubstituted benzamide at room temperature, the following deuterium labelling experiment was done. Treatment of **1k**with CD_3COOD in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) in 1,2-dichloroethane at room temperature for 4 h gave product **1k‘** in 96% yield with 72% and 73% of deuterium incorporation at the both *ortho* carbons. But, *N*,*N*-disubstituted benzamide **1d** under similar reaction conditions provided product **1d‘** in 97% yield with 12% and 16% of deuterium incorporation at the both *ortho* carbons. The maximum deuterium incorporation at the both *ortho* carbons of product **1d‘** in 78% and 79% were observed at room temperature for 28 h. Based on these dueterium studies, we concluded that the C-H bond of *N*-methyl benzamides can be activated at room temperature within 4 h. But, the allylation step needs a longer reaction time or the higher reaction temperature. In the case of weak directing group such as *N*,*N*-disubstituted benzamide, the C-H bond activation can also be done at room temperature, but the process is slow and needs a longer reaction time. In addition when *N*,*N*-disubstituted benzamide**1b** was treated with allyl acetate **(2a)** in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %), $AgSbF_6$ (20 mol %) and CD_3COOD (2.0 equiv)in 1,2-dichloroethane (DCE) at room temperature for 36 h, *ortho* allylated benzamide **3ba** was observed in 69% yield along with 33% deuterium incorporation at the *ortho* carbon. This results clearly indicates that the *ortho* C-H bond cleavage of aromatic amide in intermediate **8** is a reversible process.

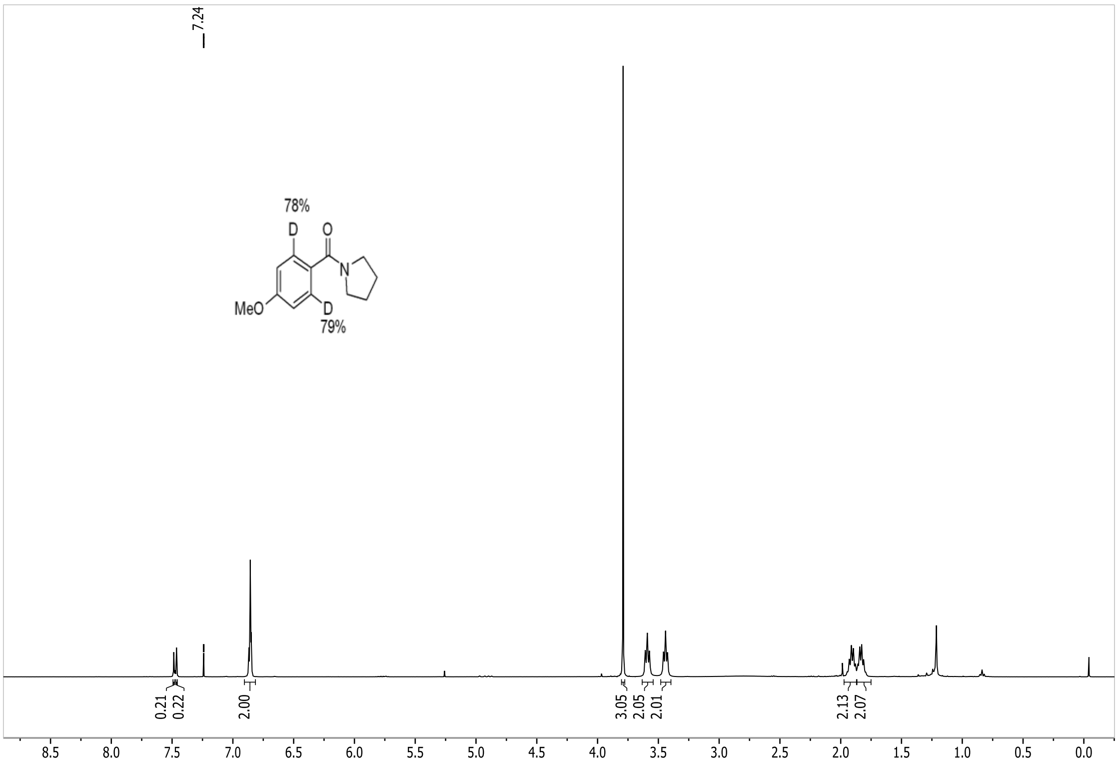


^{1}H NMR Spectra of Compound **1k'.**

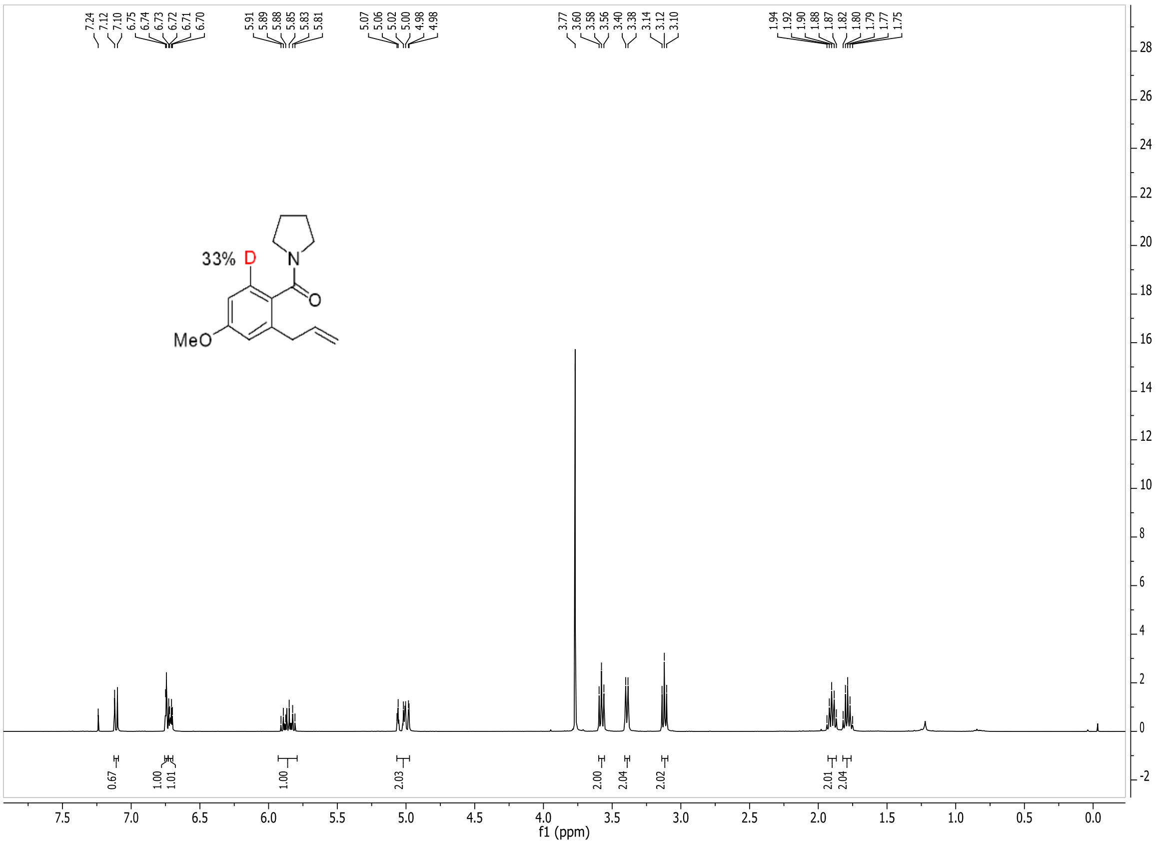


^{1}H NMR Spectra of Compound **1b'**





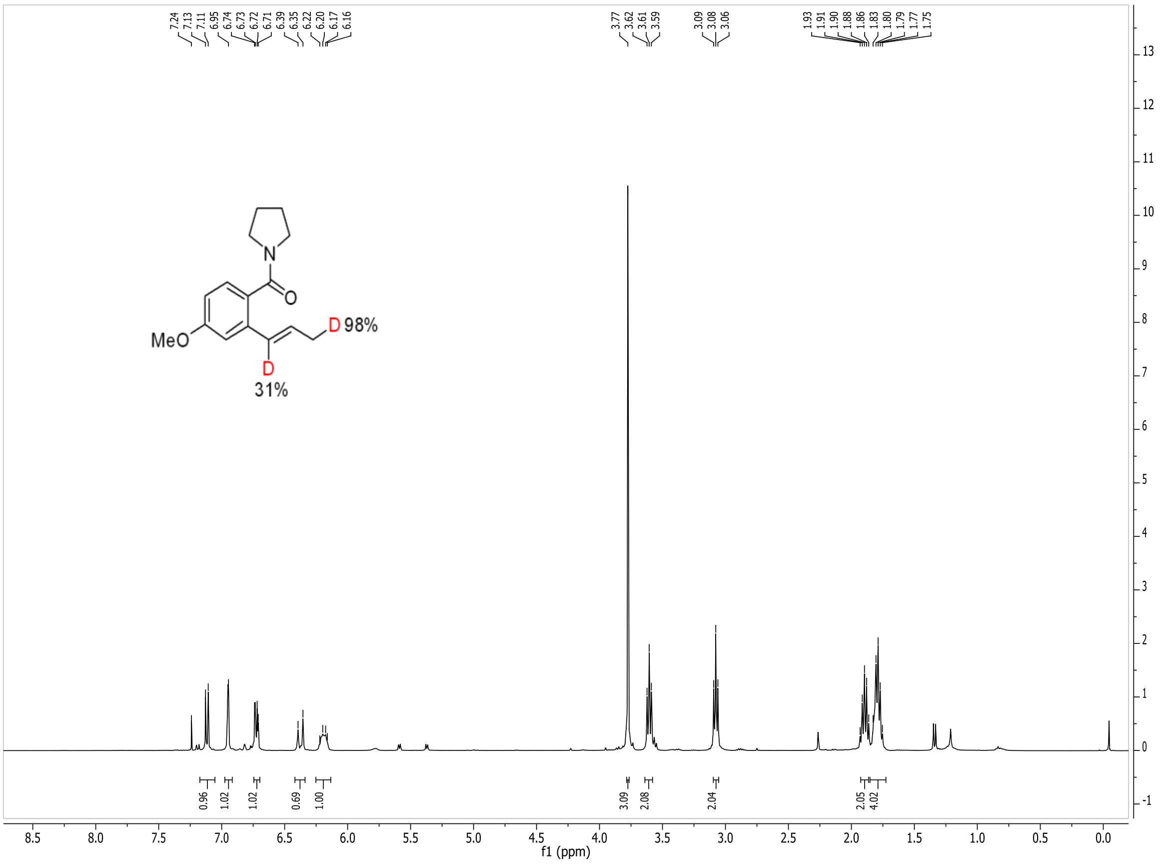
^{1}H and ^{13}C NMR Spectra of Compound **3ba’.**



Mechanistic Studies for Double Bond Isomerization Reaction.

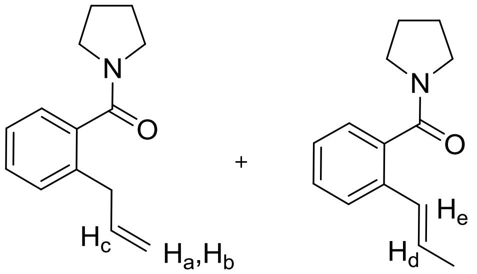
When *ortho* allylated benzamide **3ba** was treated with CD_3COOD (2.0 equiv) in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %), $AgSbF_6$ (20 mol %) in 1,2-dichloroethane (DCE) at 100°C for 12 h, *ortho* vinylated benzamide **4ba** was observed in 92% yield along with 96% deuterium incorporation at the CH_3 group attached with the vinyl carbon and 31% deuterium incorporation was observed at the α position of the vinylic carbon.

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



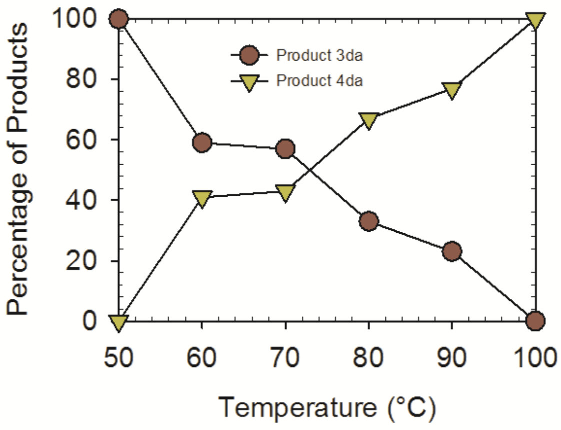
Mechanistic Studies for Double Bond Isomerization Reaction.

The reaction temperature is crucial for the isomerization reaction so the temperature effect for the conversion of **3ad** to **4ad** was studied completely. The reaction was carried out at different temperature such as 50 °C, 60 °C, 70 °C, 80 °C, 90 °C and 100 °C at standard reaction condition. Benzamide **1d** was treated with allyl acetate **(2a)** in the presence of [{RuCl$_2$(*p*-cymene)}$_2$] (5.0 mol %) and AgSbF$_6$ (20 mol %) in 1,2-dichloroethane (DCE) at mentioned temperature for 36 h, Then, the reaction mixture was diluted with CH$_2$Cl$_2$, filtered through Celite and the filtrate was concentrated. The crude residue was purified by column chromatography to find out the yield. Later, ^{1}H NMR analysis was done and the percentage of the product **3da** and **4da** was determined by using ^{1}H NMR integration method. The characteristic proton for the both of the compounds **3da** and **4da** was analyzed in the crude ^{1}H NMR data and the ratio of the products were calculated based on the integration. The product yields are isolated yields**.**

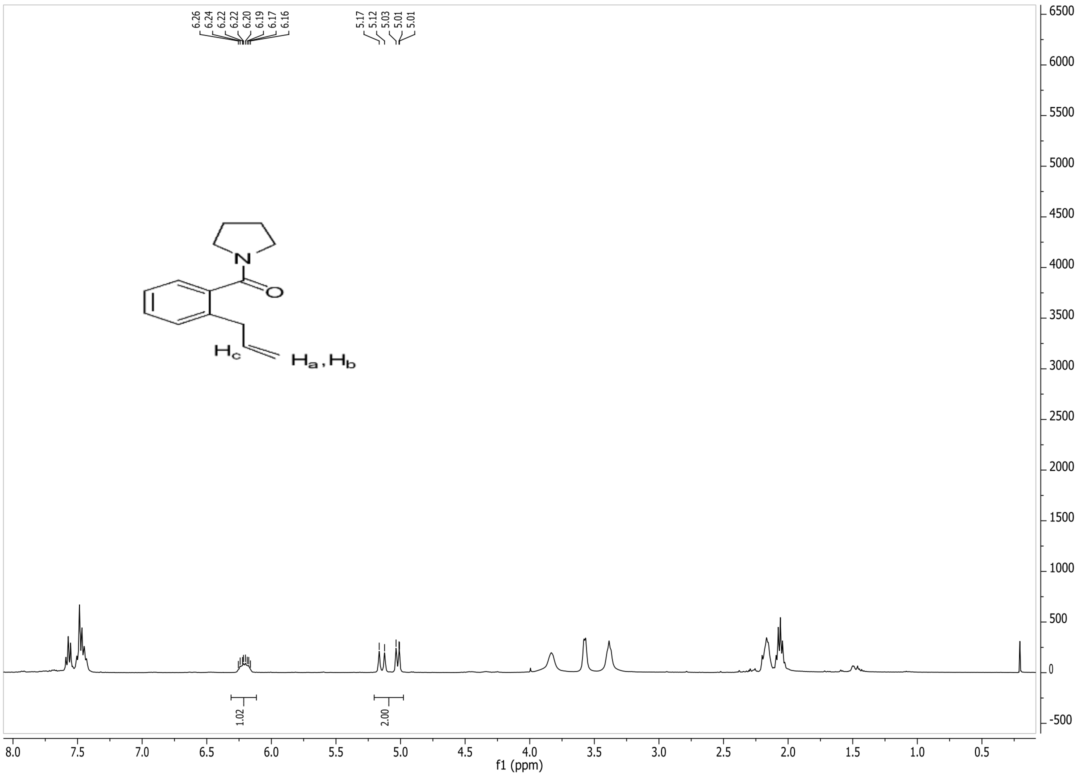


H_a, H_b 5.09 – 5.01 (m, 2H); H_c 5.94 -5.86 (m, 1H); H_d 6.20 -6.13 (m, 1H); H_e 6.33 (d, *J* = 16.0 Hz, 1H).

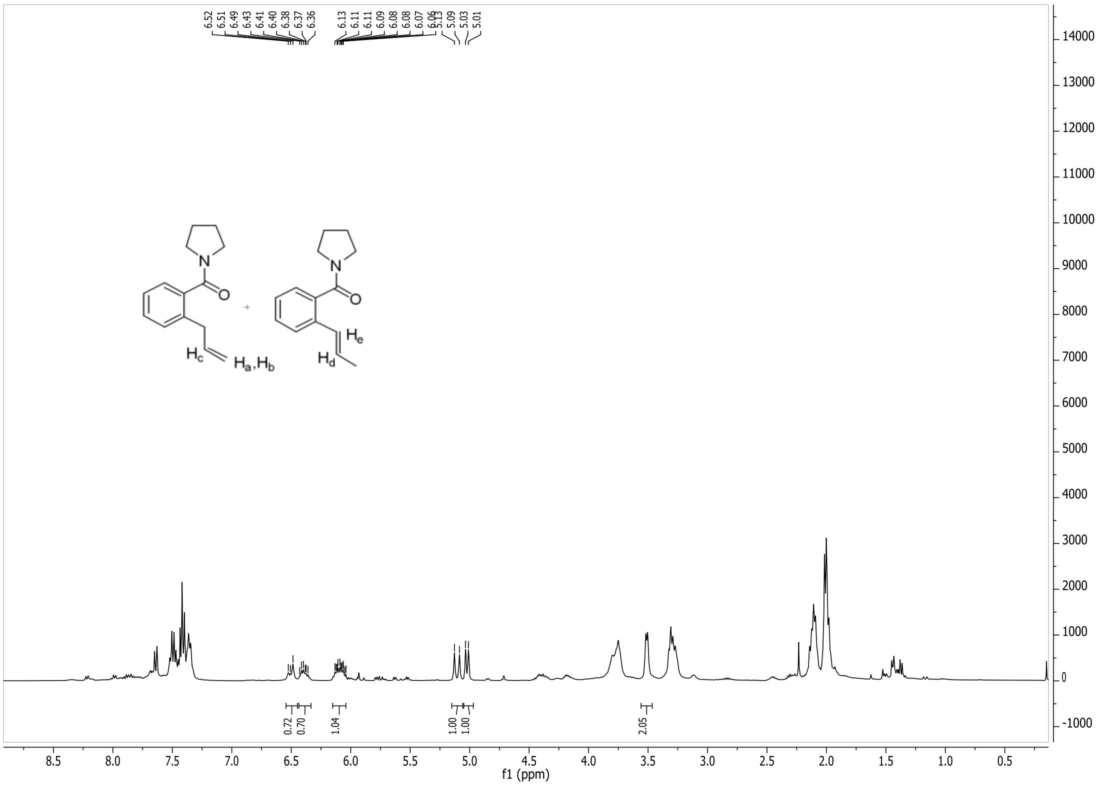
Sl.no	Reaction temperature (°C)	Ratio of the products in ^{1}H NMR **(3da : 4da)**	Percentage of the products **(3da : 4da)**
1	50 °C	1 : 0	100 : 0
2	60 °C	1 : 0.7	59 : 41
3	70 °C	1 : 0.75	57 : 43
4	80 °C	1 : 2	33 : 77
5	90 °C	1 : 3.5	22 : 88
6	100 °C	0 : 1	0 : 100



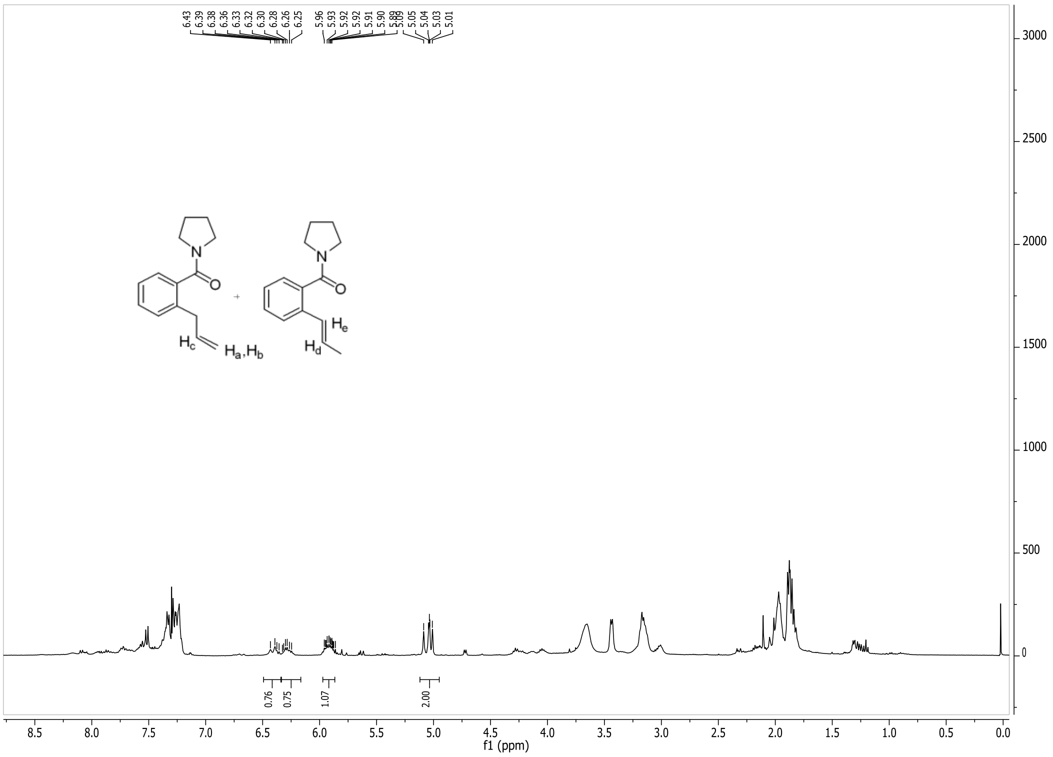
^{1}H NMR Spectra of Crude reaction mixture **3d** at 50 °C.



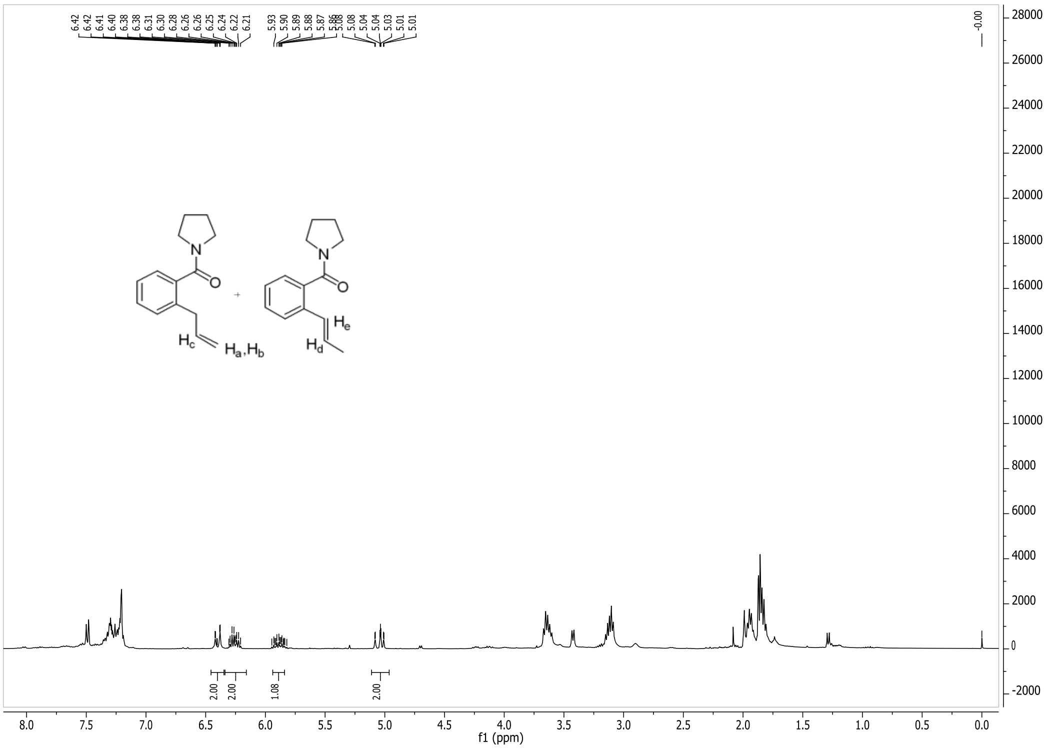
^{1}H NMR Spectra of Crude reaction mixture **3d** at 60 °C.



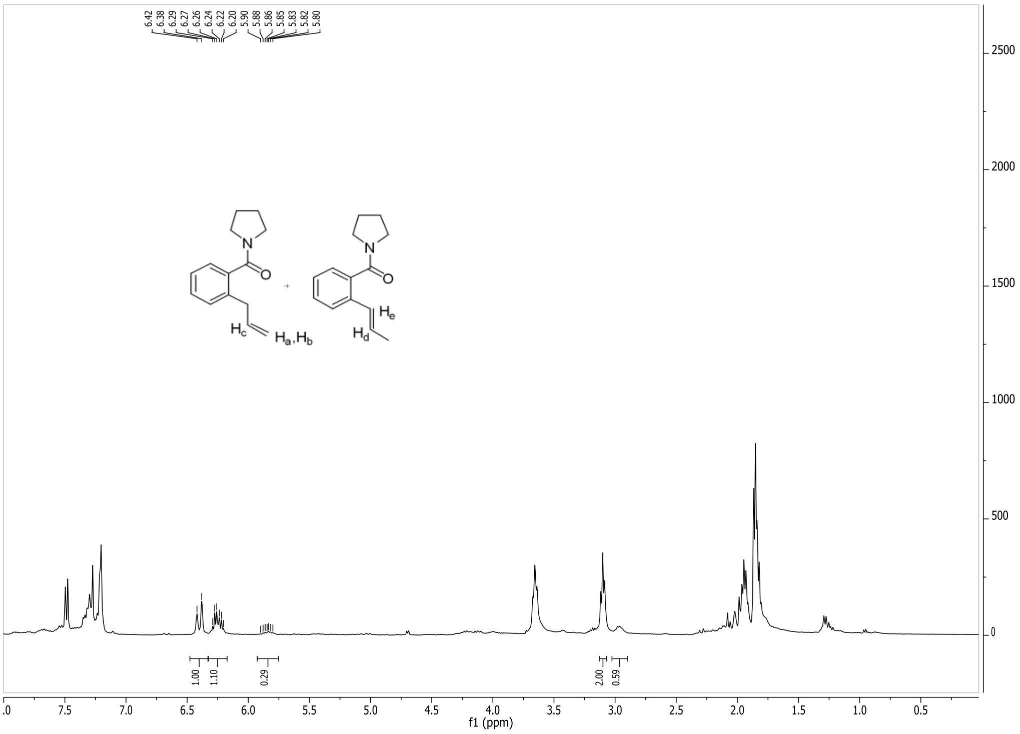
^{1}H NMR Spectra of Crude reaction mixture **3d** at 70 °C.



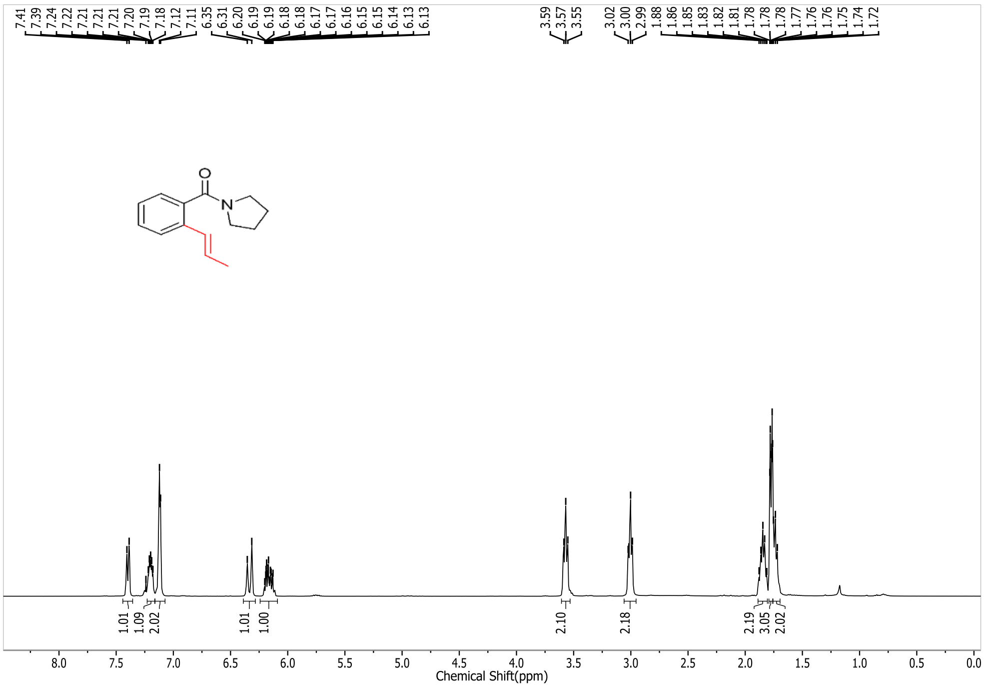
^{1}H NMR Spectra of Crude reaction mixture **3d** at 80 °C.



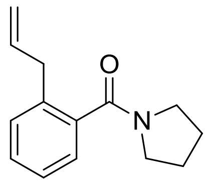
^{1}H NMR Spectra of Crude reaction mixture **3d** at 90°C.



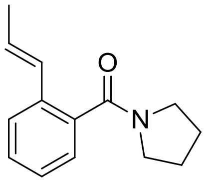
^{1}H NMR Spectra of compound **4ad** at 100°C.



The energy of the molecules calculated by using DFT calculations.



3da



4da

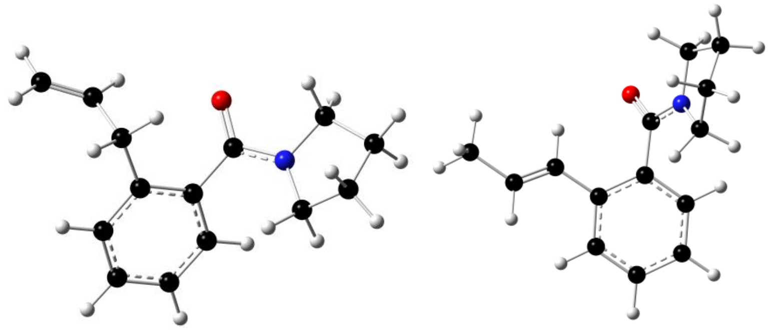


Figure X. B3LYP/6-31G

(a) Optimized structure of compound **3da** (b) Optimized structure of compound **4da**

Molecule	Energy	
Compound **3da**	-673.69625741a.u	-18332.2 eV
Compound **4da**	-673.70553985a.u	-18332.4 eV

ΔE = 0.2 eV = 19.29706 kJ/mol

Compound **4da** is 19.2 kJ/mol is stabilized than Compound **3da**.

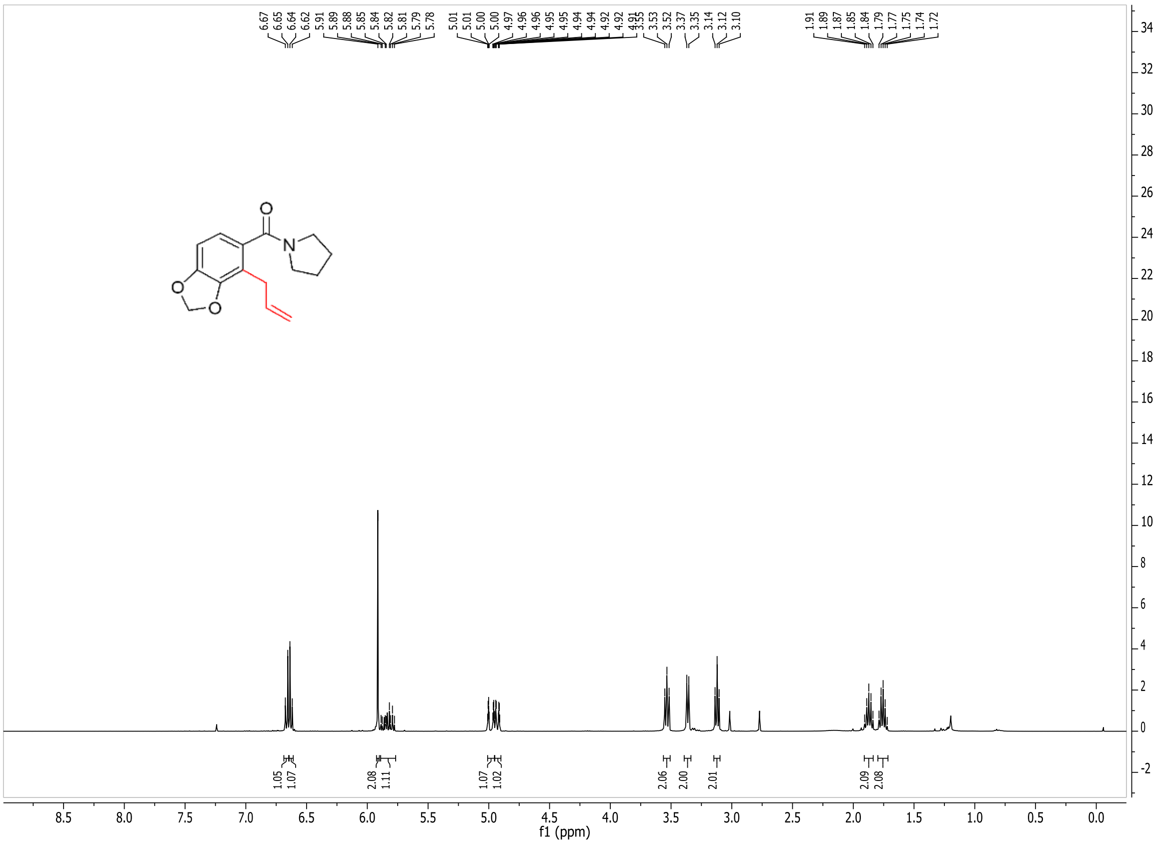
Computational Details:

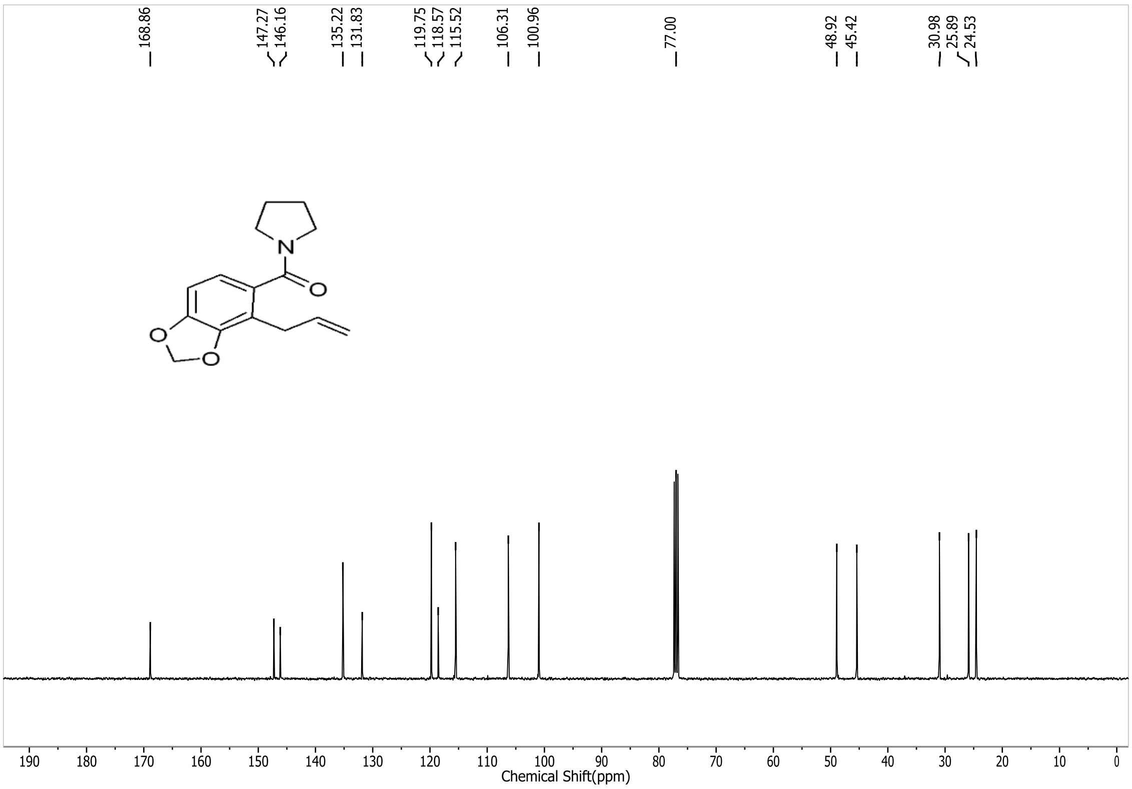
The ground state geometries were optimized without symmetry constraints using the B3LYP functional^2 in combination with the 6-31G(d) basis set^2 with the program package Gaussian 09 Revision C. 01.^{3} The optimized geometries were confirmed to be local minima by performing vibrational frequency calculations and obtaining only positive (real) frequencies.

References:

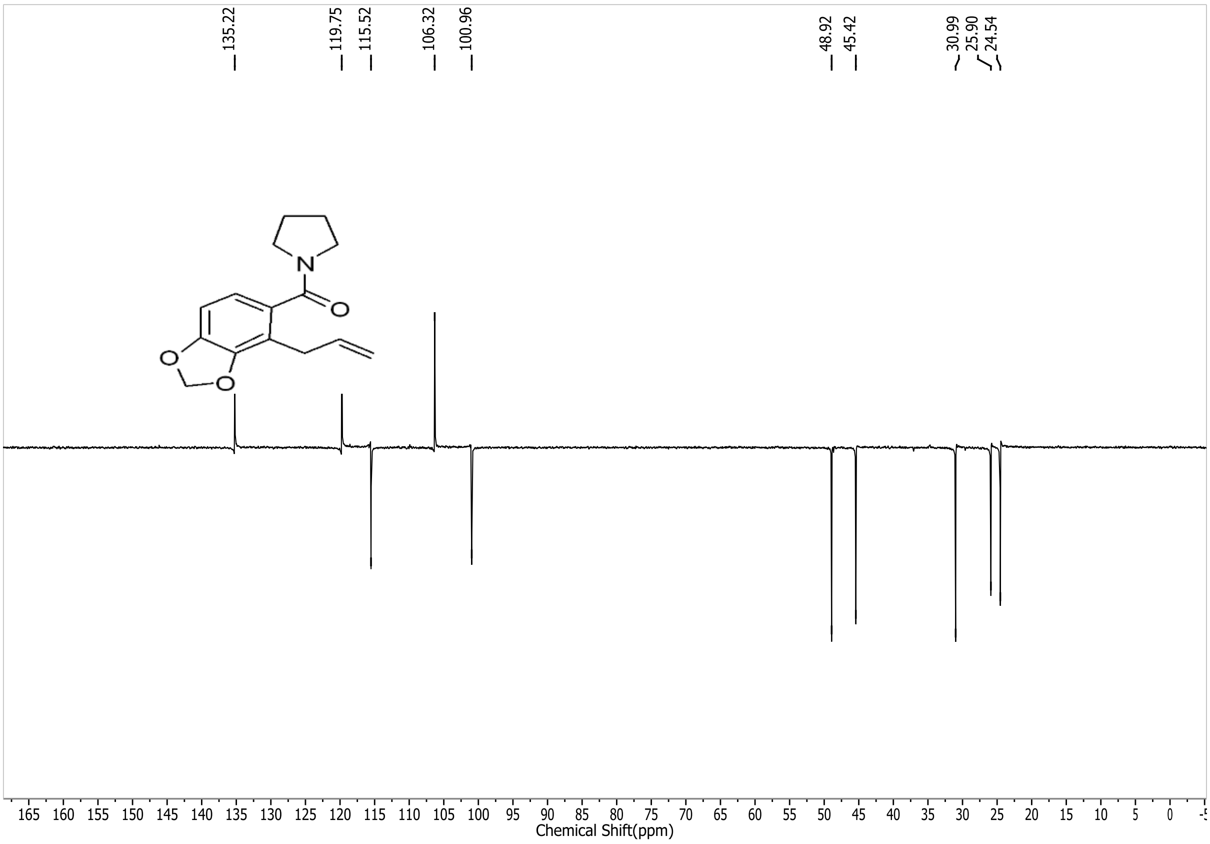
1. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
2. (a) G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, 1991, **94**, 6081; (b) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193.
3. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

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

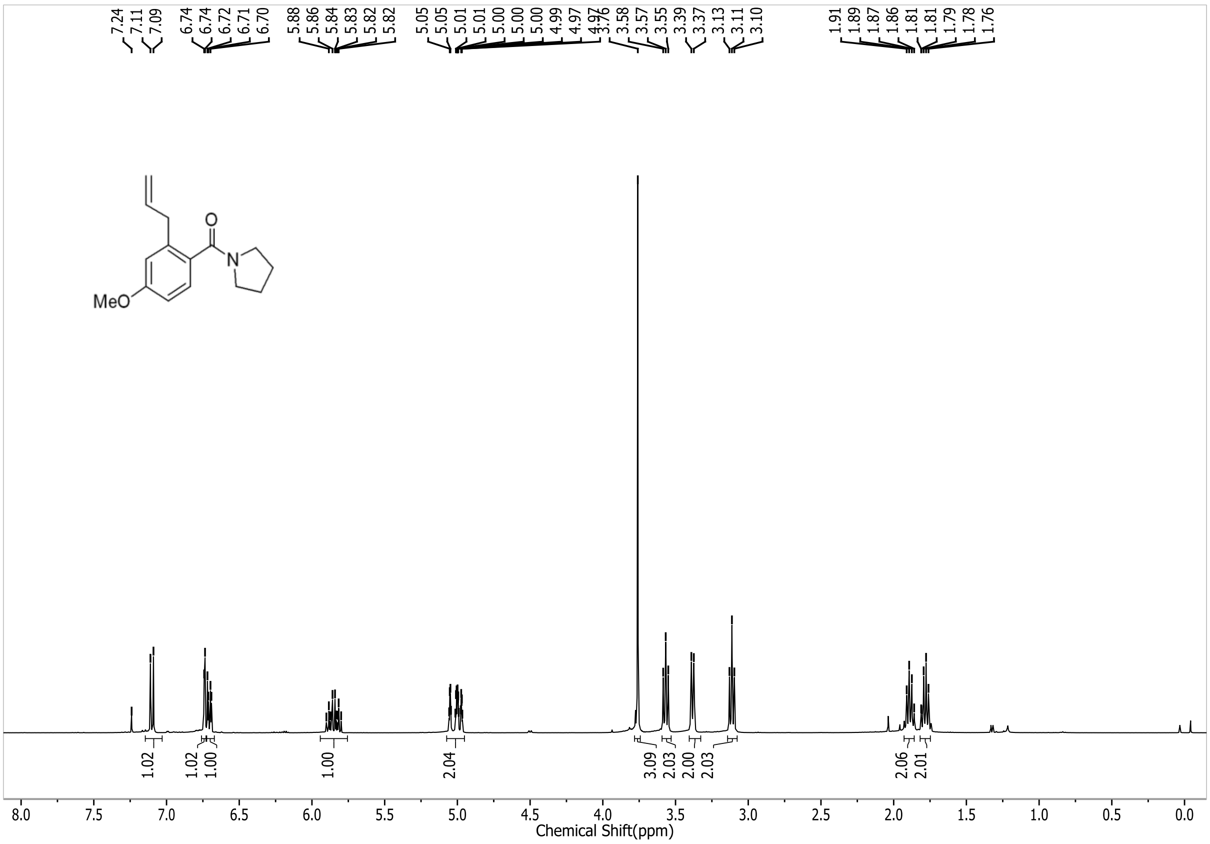


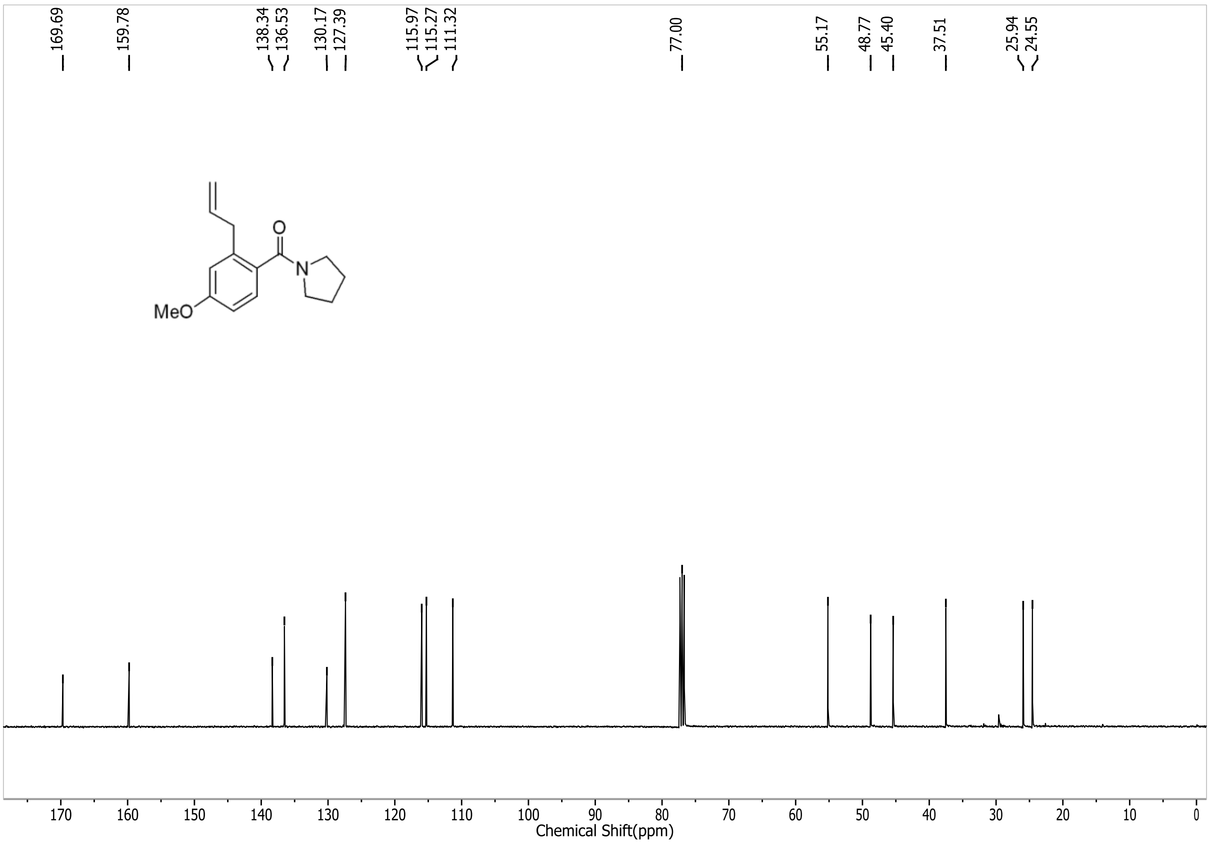


DEPT (135) NMR Spectrum of Compound **3aa.**

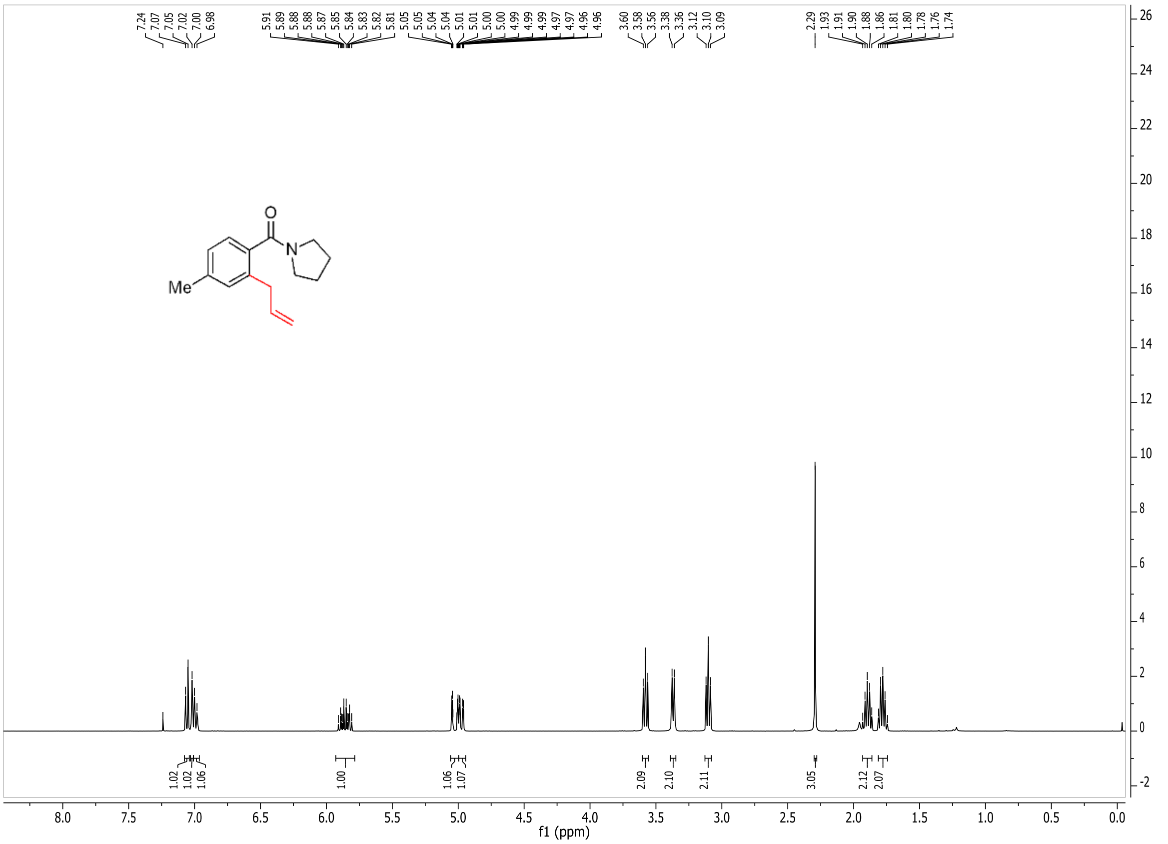


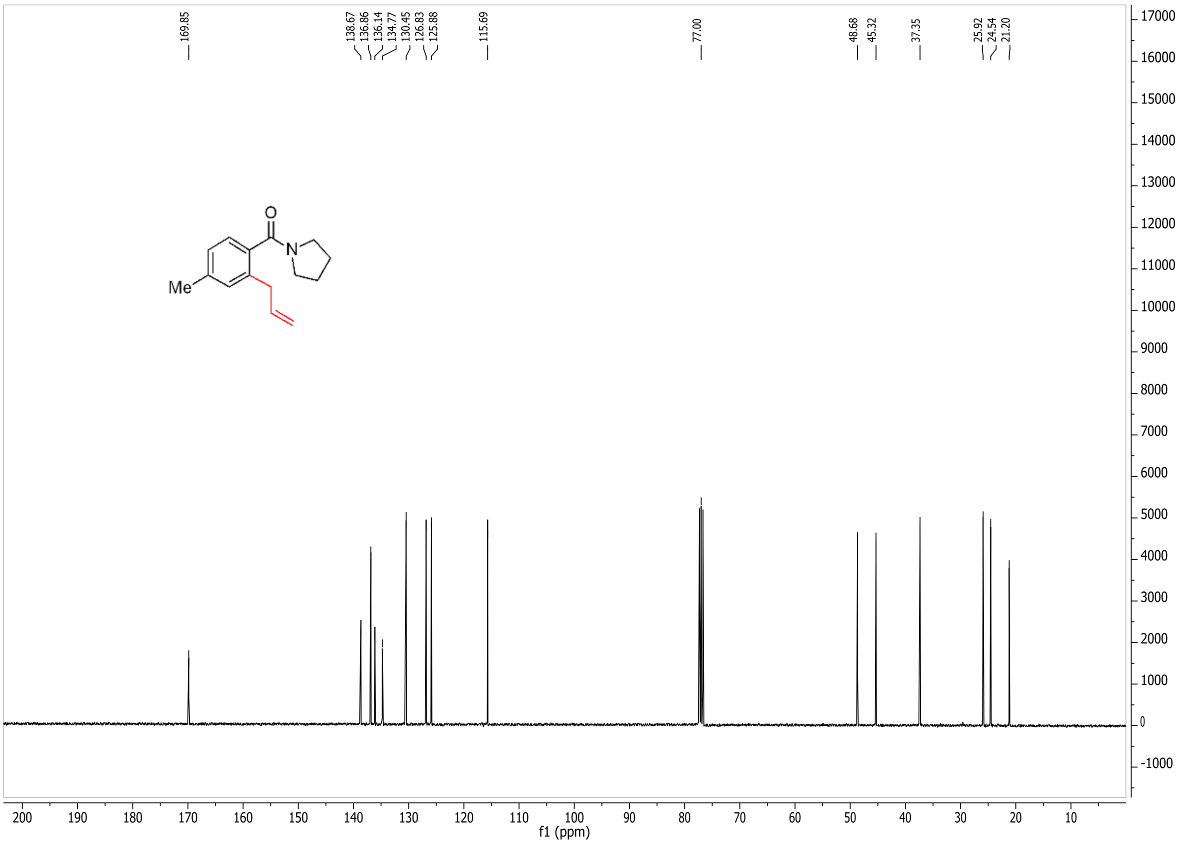
^{1}H and ^{13}C NMR Spectra of Compound **3ba.**



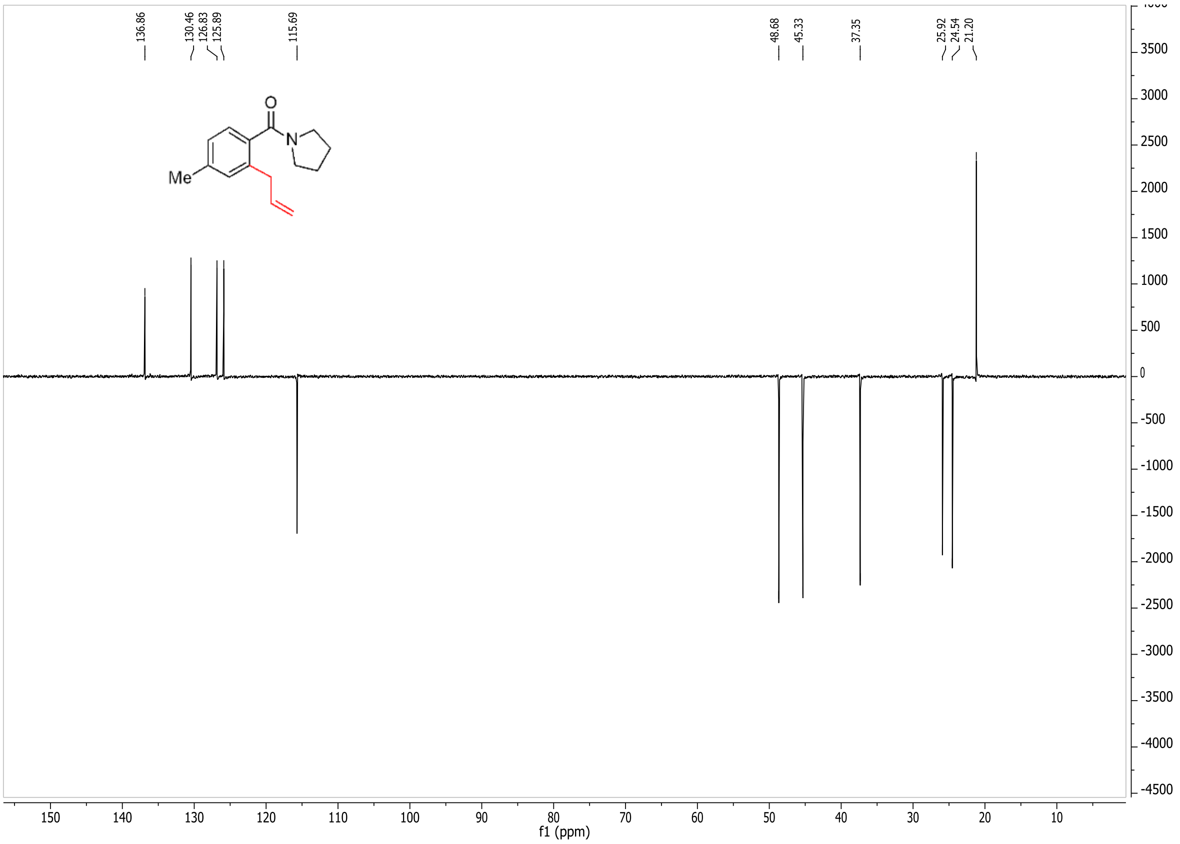


^{1}H and ^{13}C NMR Spectra of Compound **3ca.**

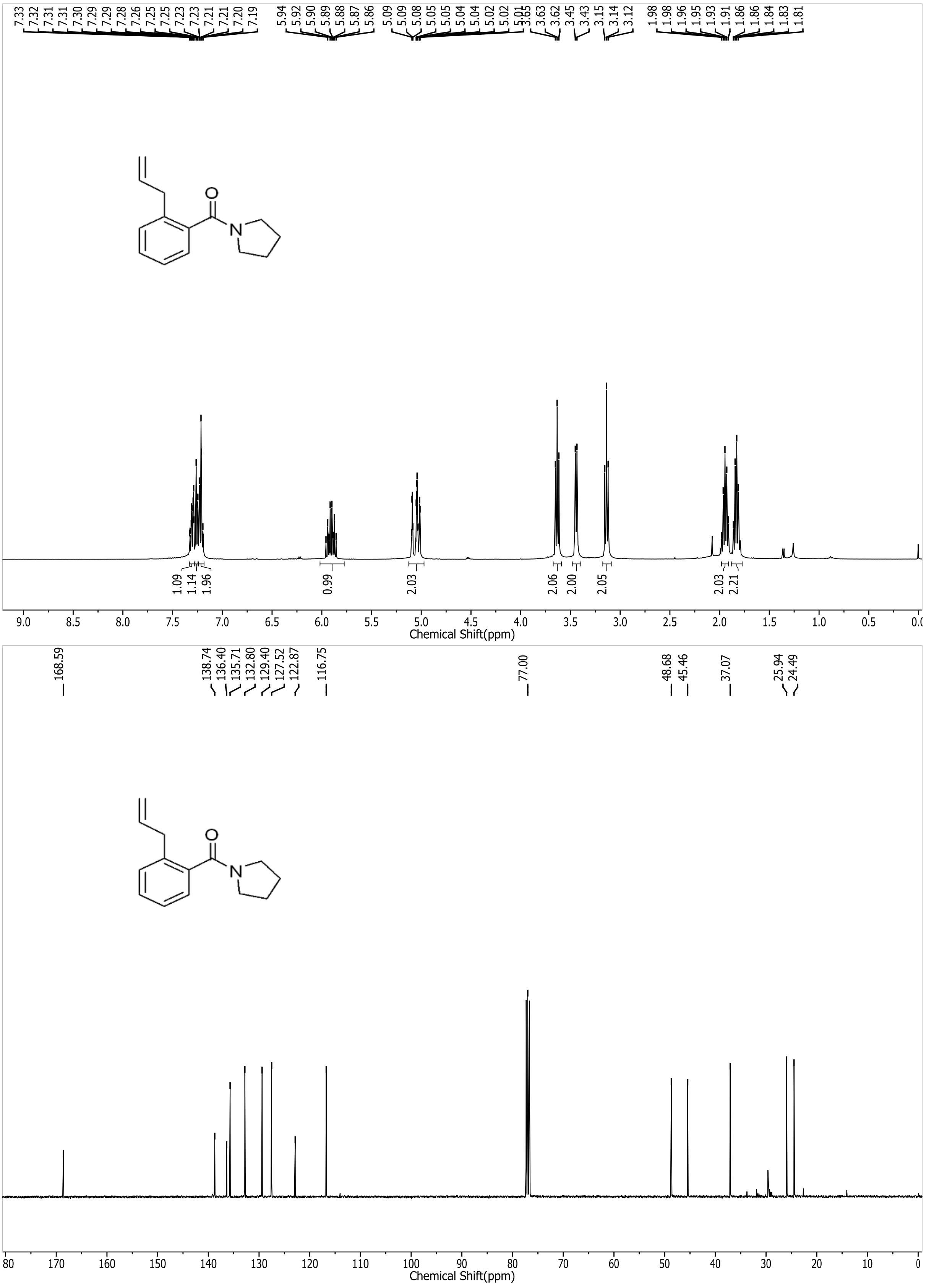




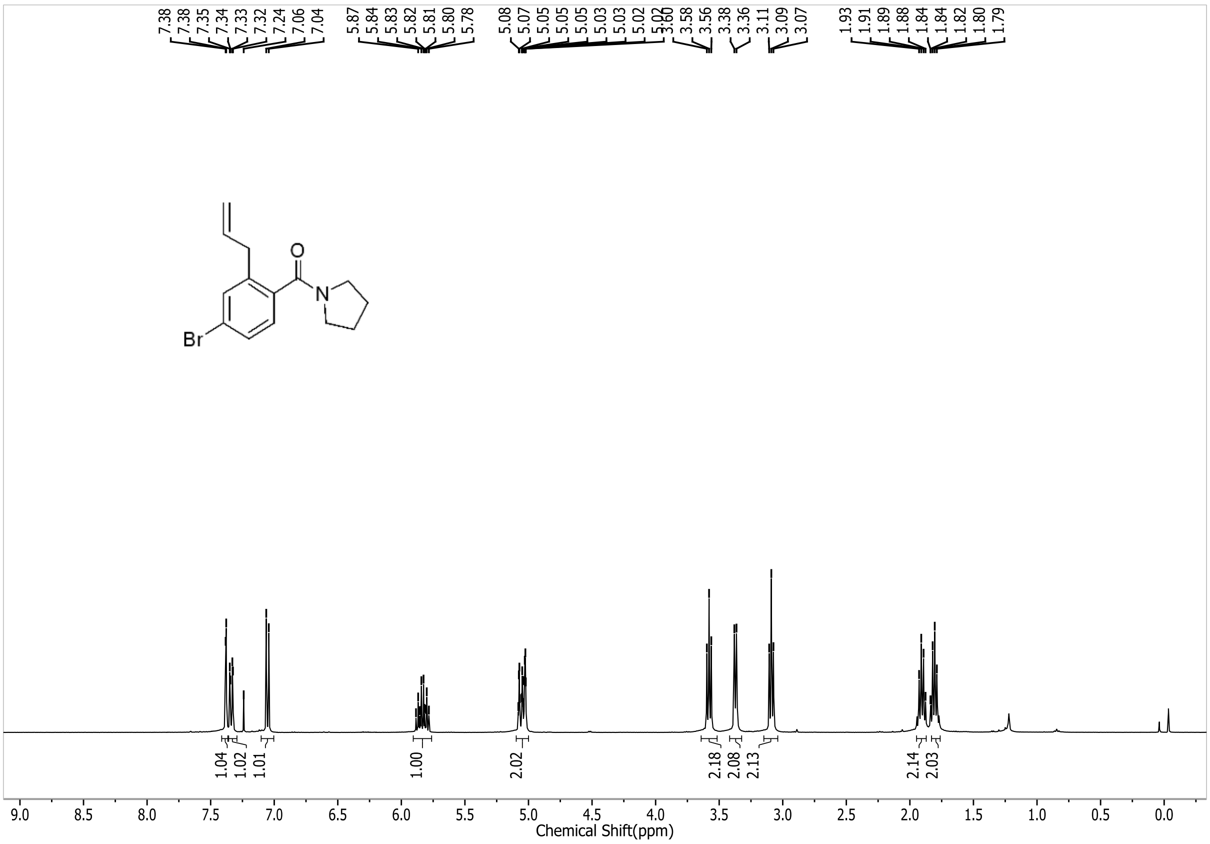
DEPT (135) NMR Spectrum of Compound **3ca.**

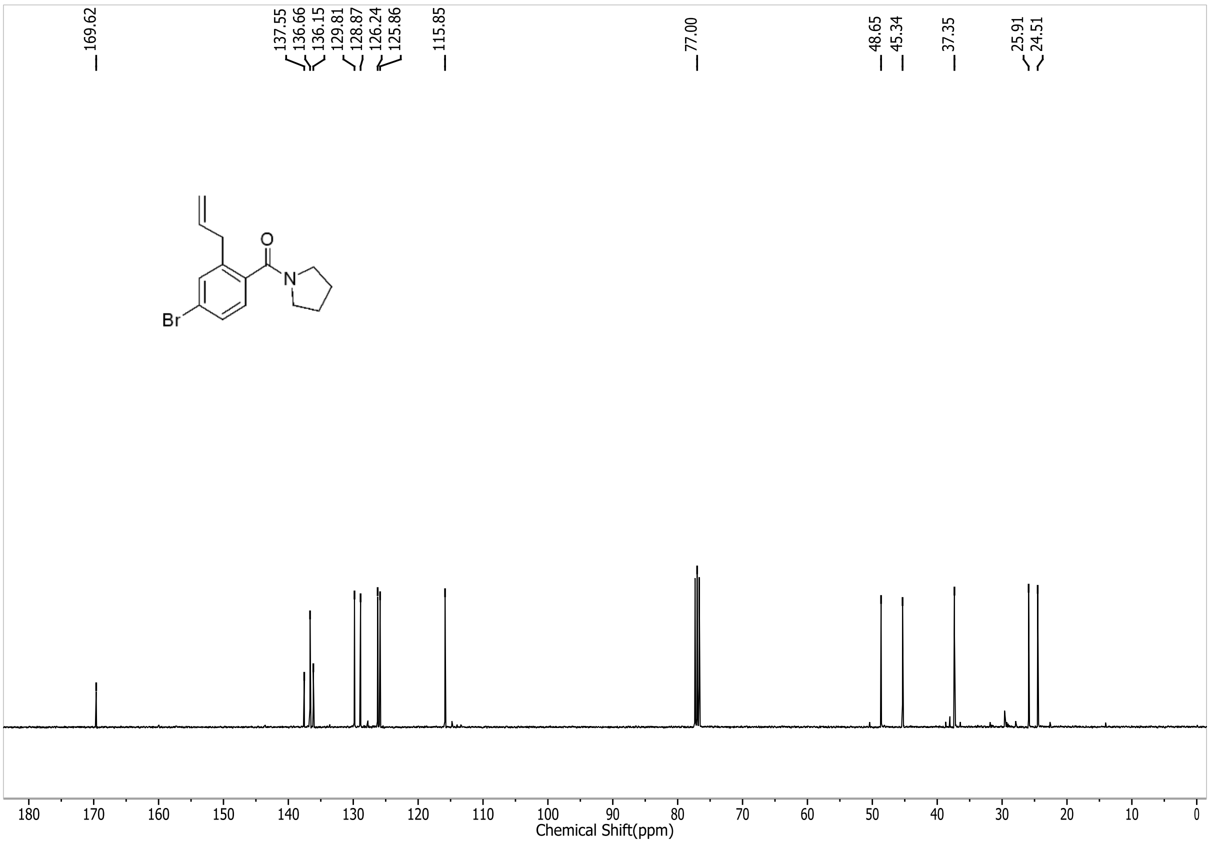


^{1}H and ^{13}C NMR Spectra of Compound **3da.**

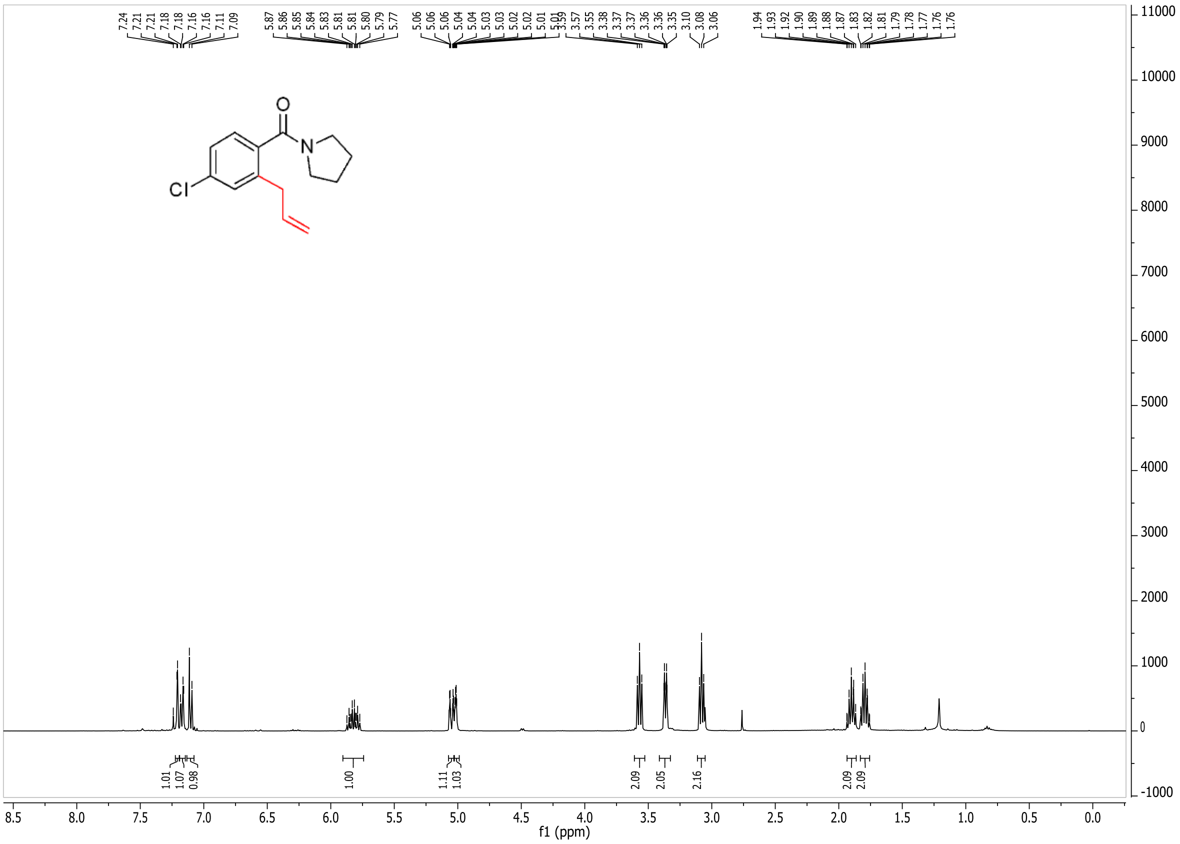


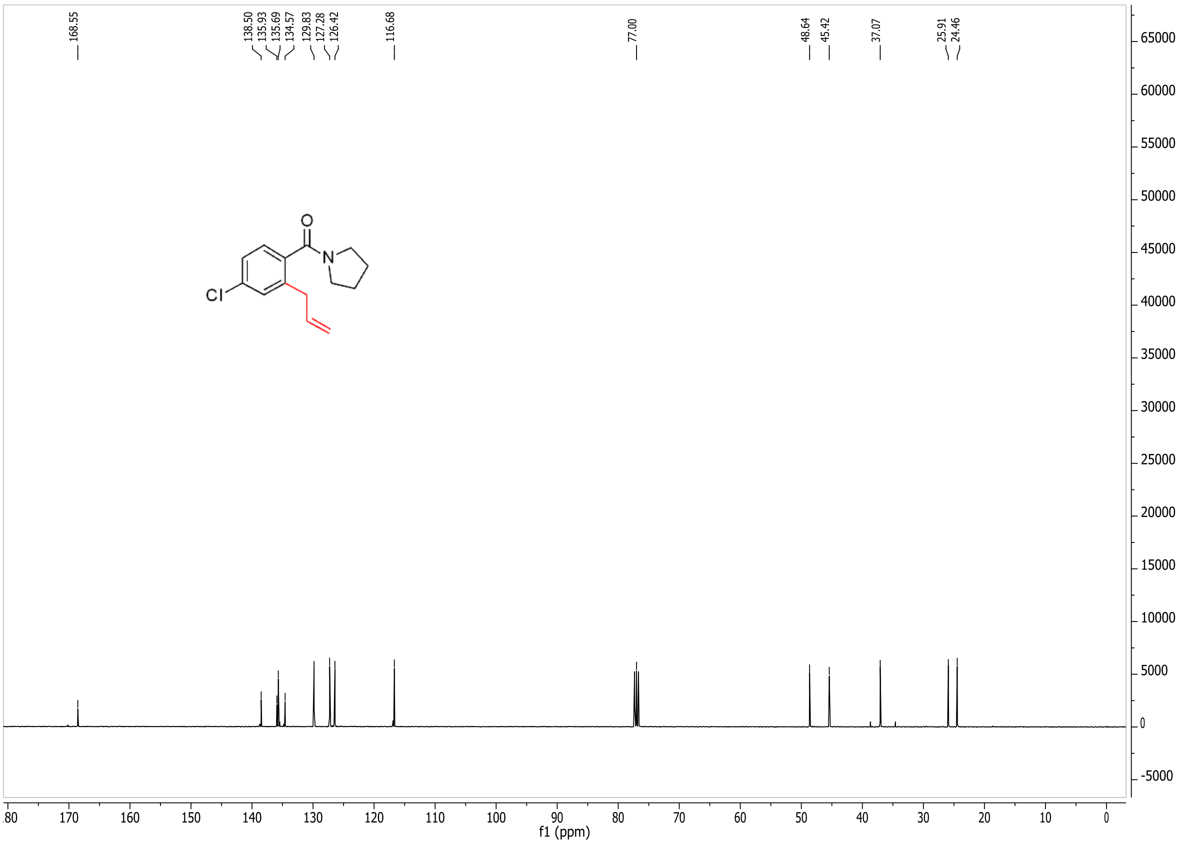
^{1}H and ^{13}C NMR Spectra of Compound **3ea.**



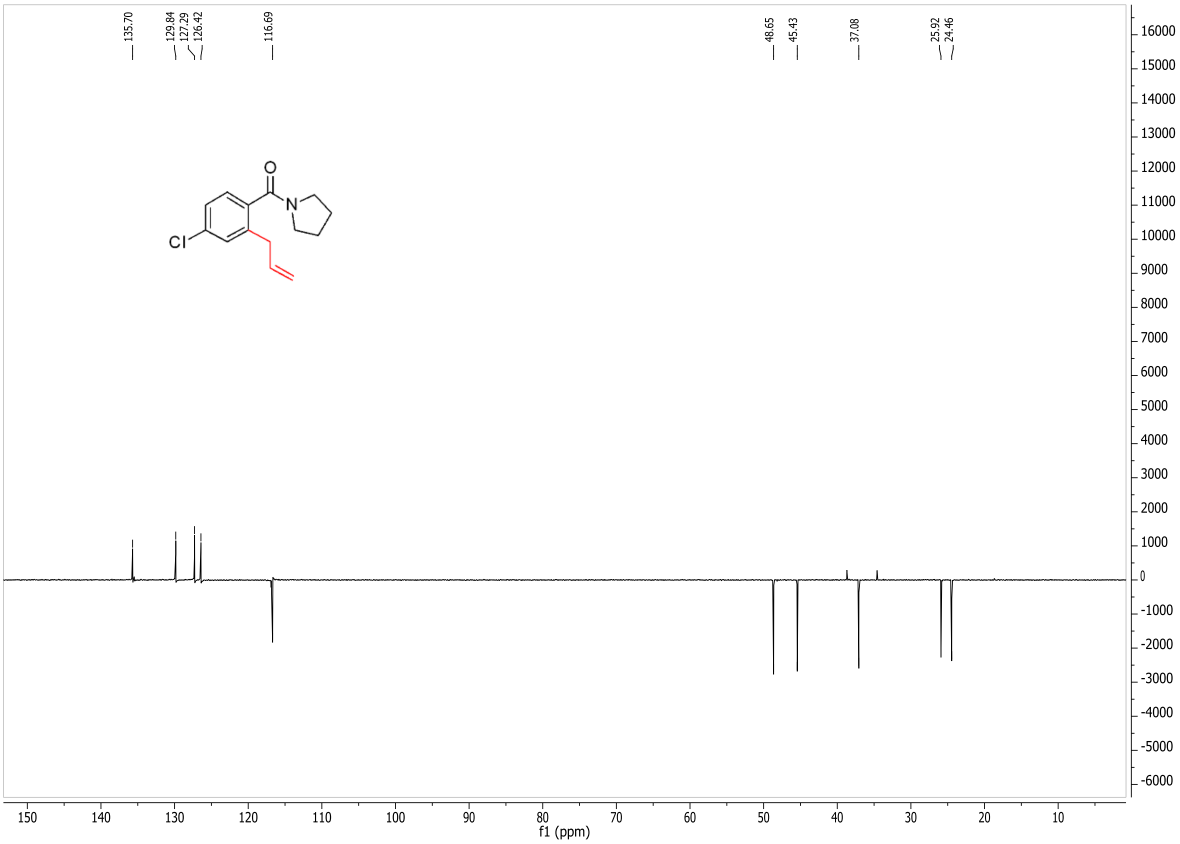


^{1}H and ^{13}C NMR Spectra of Compound **3fa.**

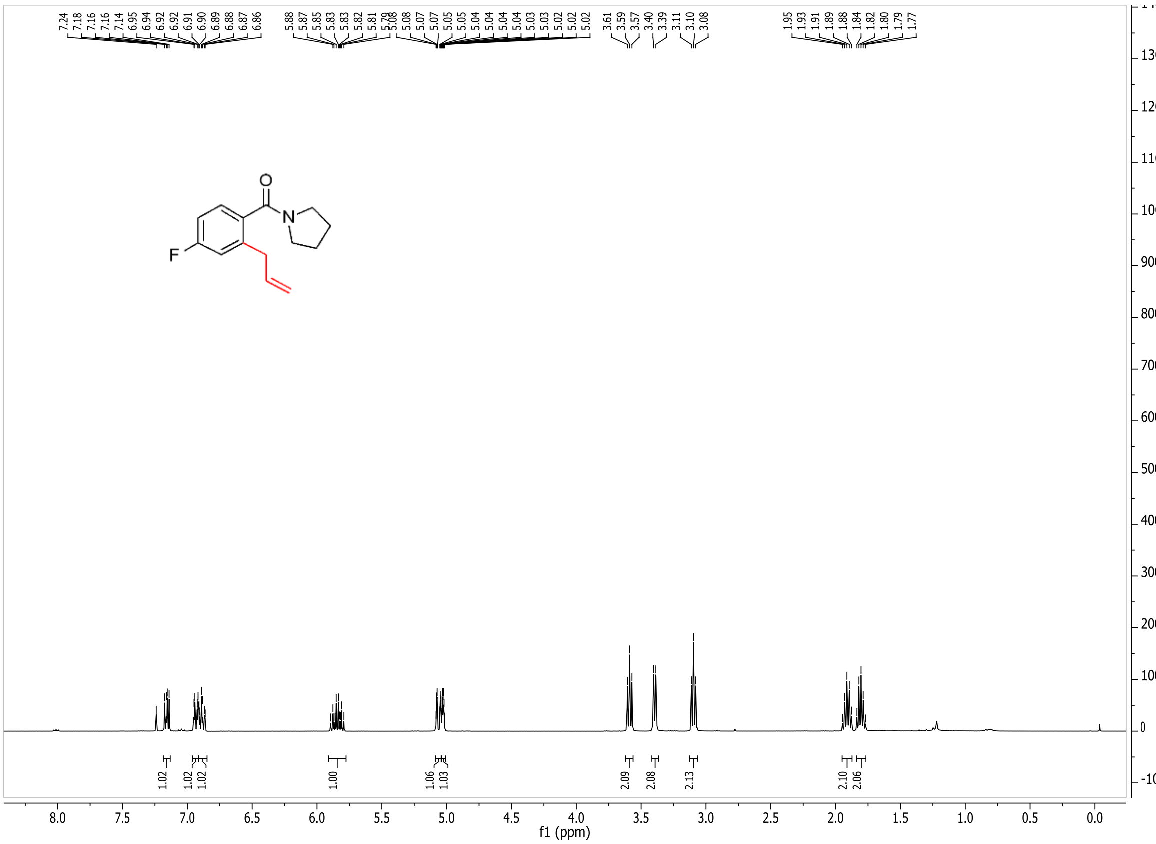


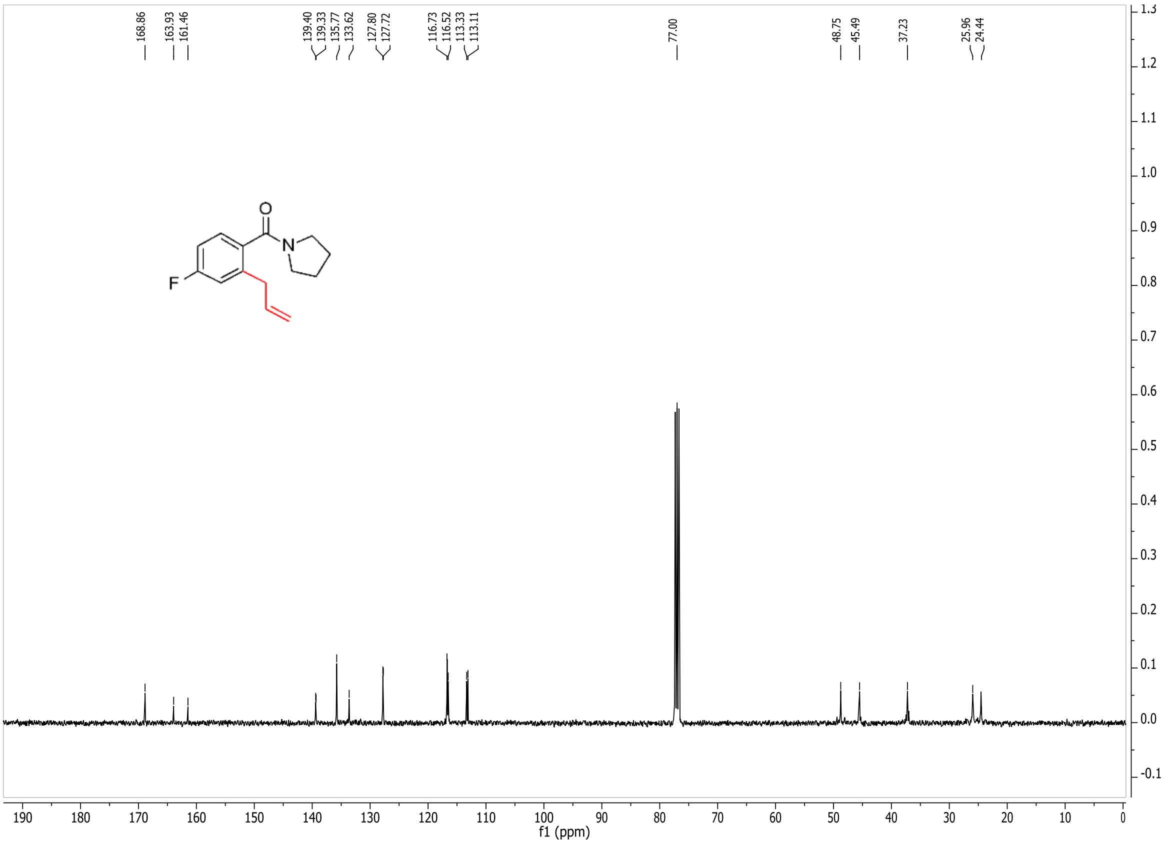


DEPT (135) NMR Spectrum of Compound **3fa.**

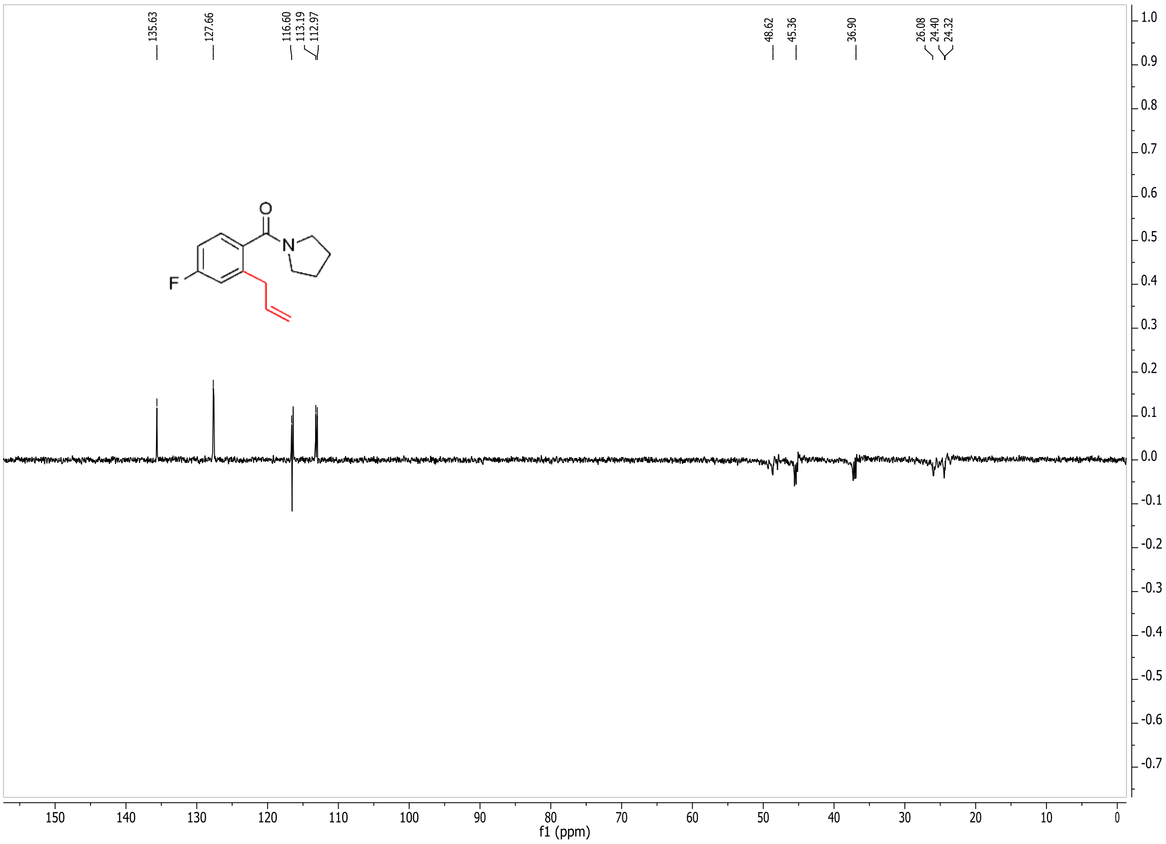


^{1}H and ^{13}C NMR Spectra of Compound **3ga.**

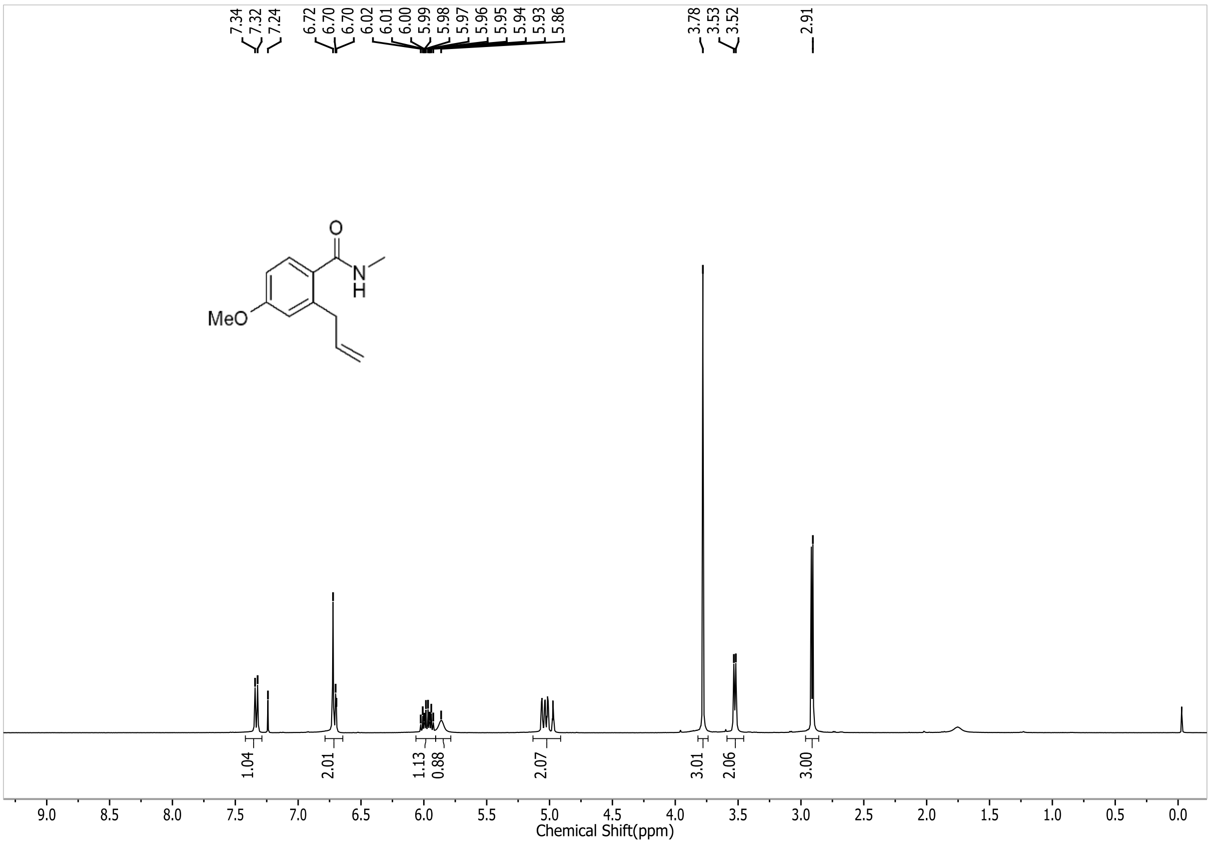


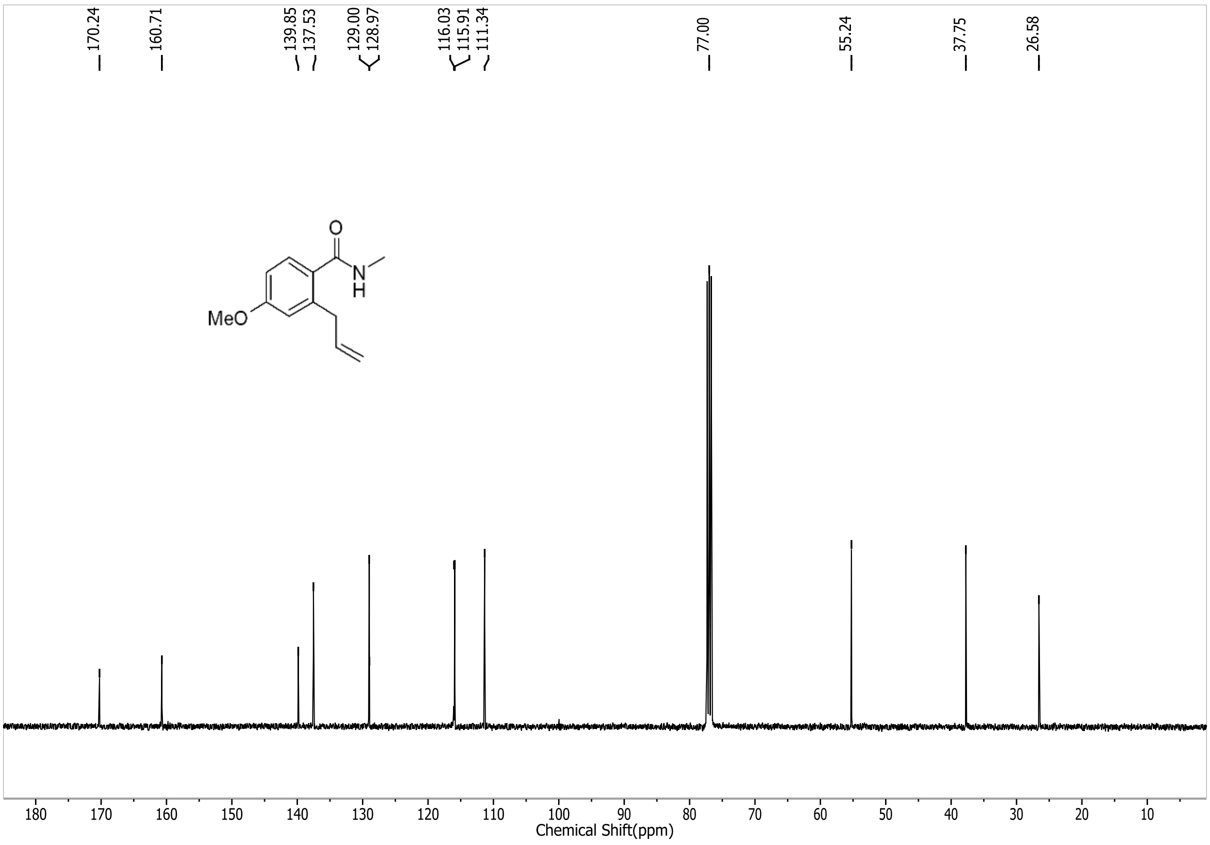


DEPT (135) NMR Spectrum of Compound **3ga.**

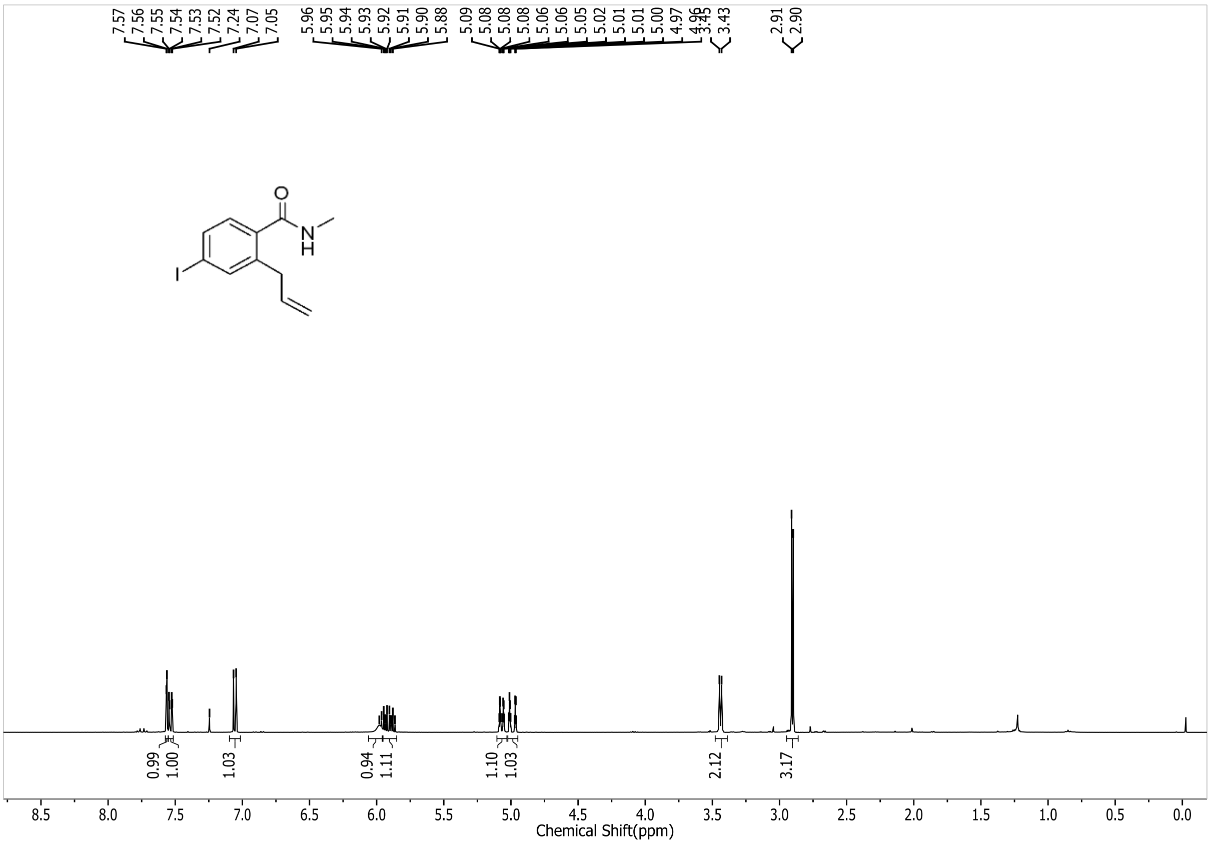


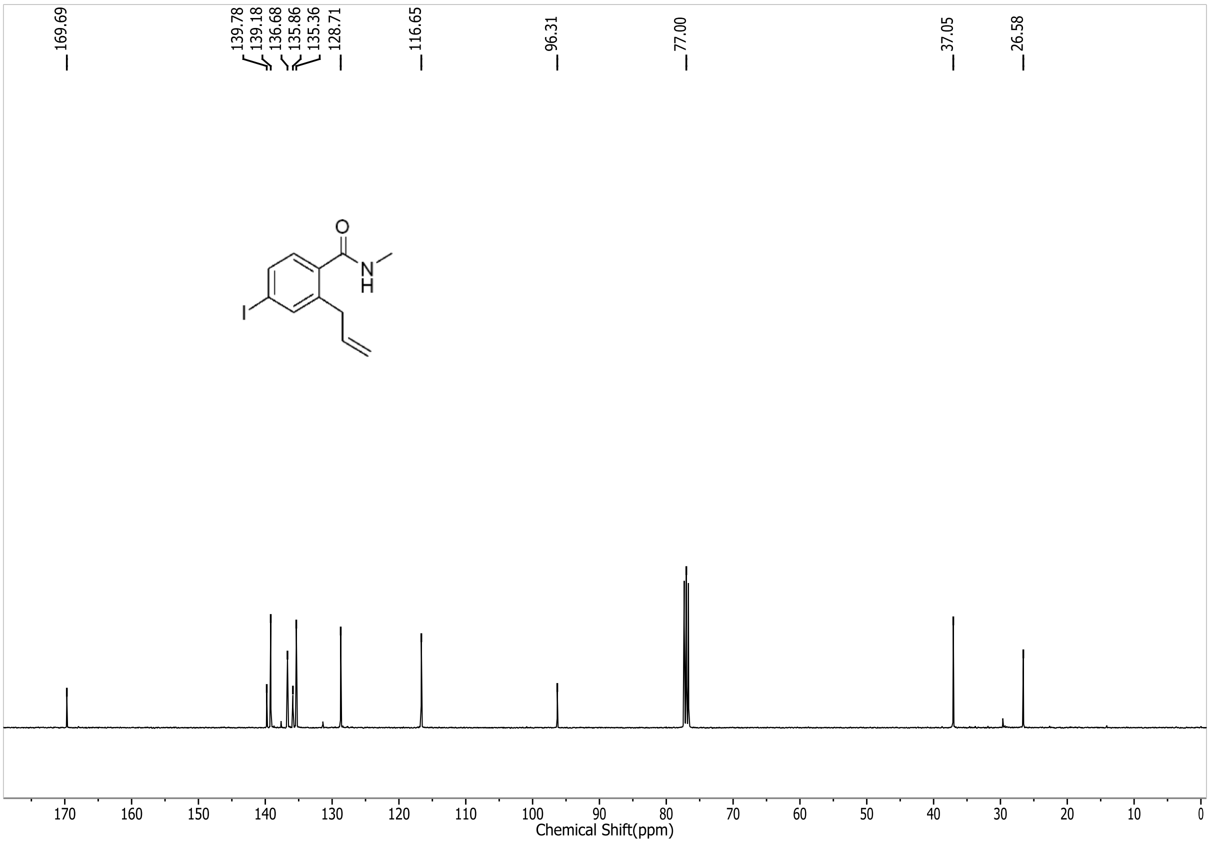
^{1}H and ^{13}C NMR Spectra of Compound **3ha.**



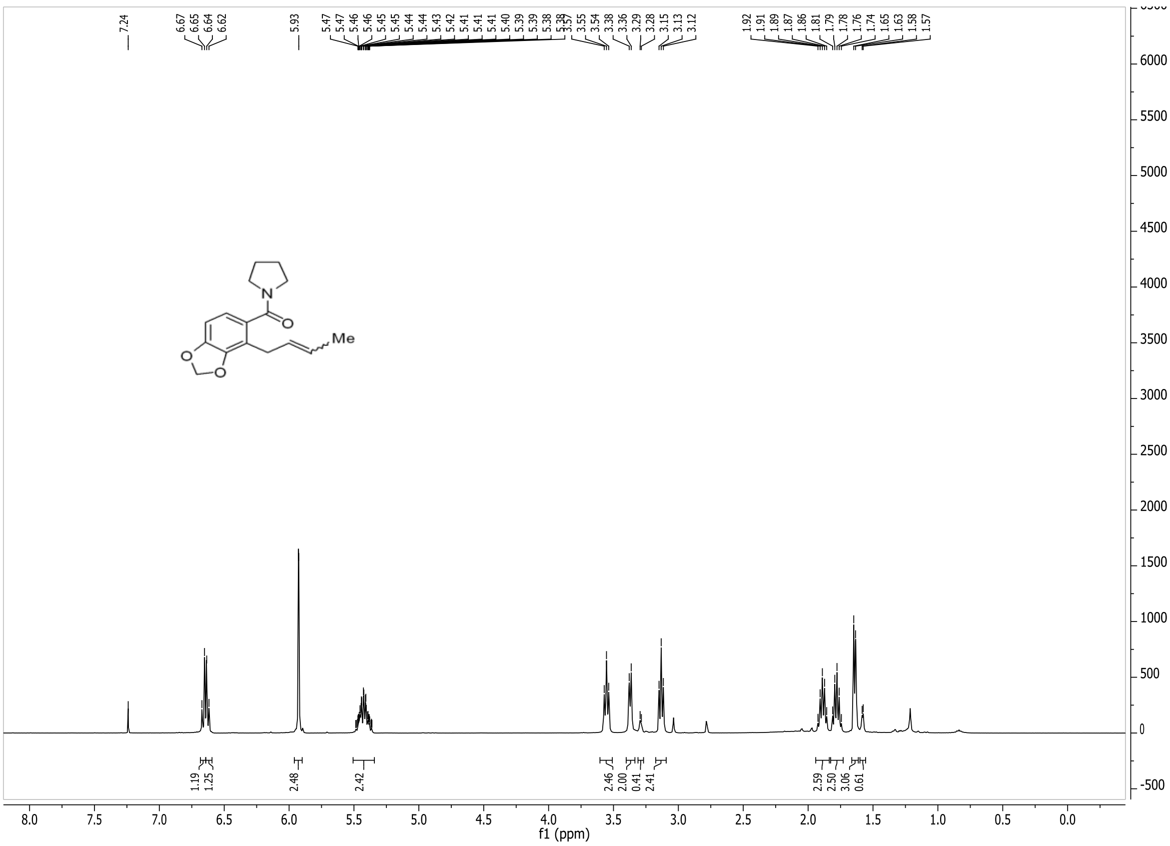


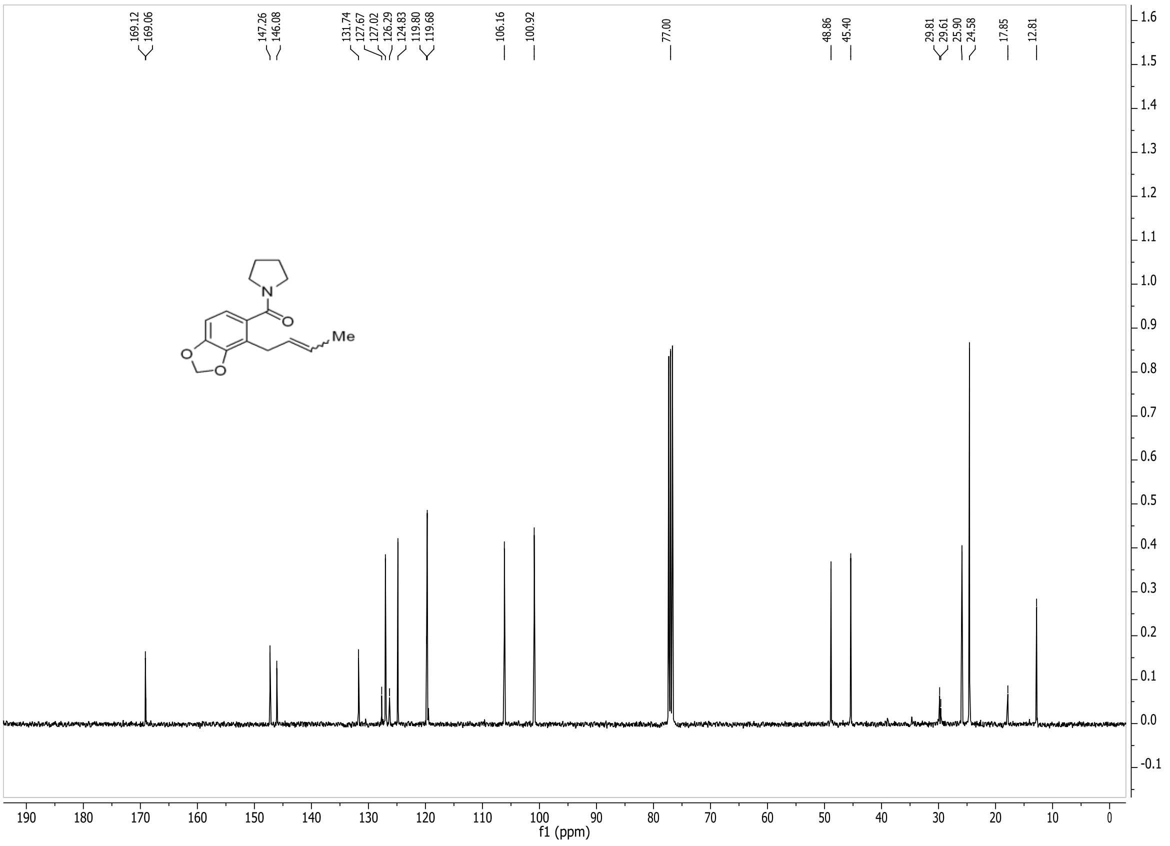
^{1}H and ^{13}C NMR Spectra of Compound **3ia.**



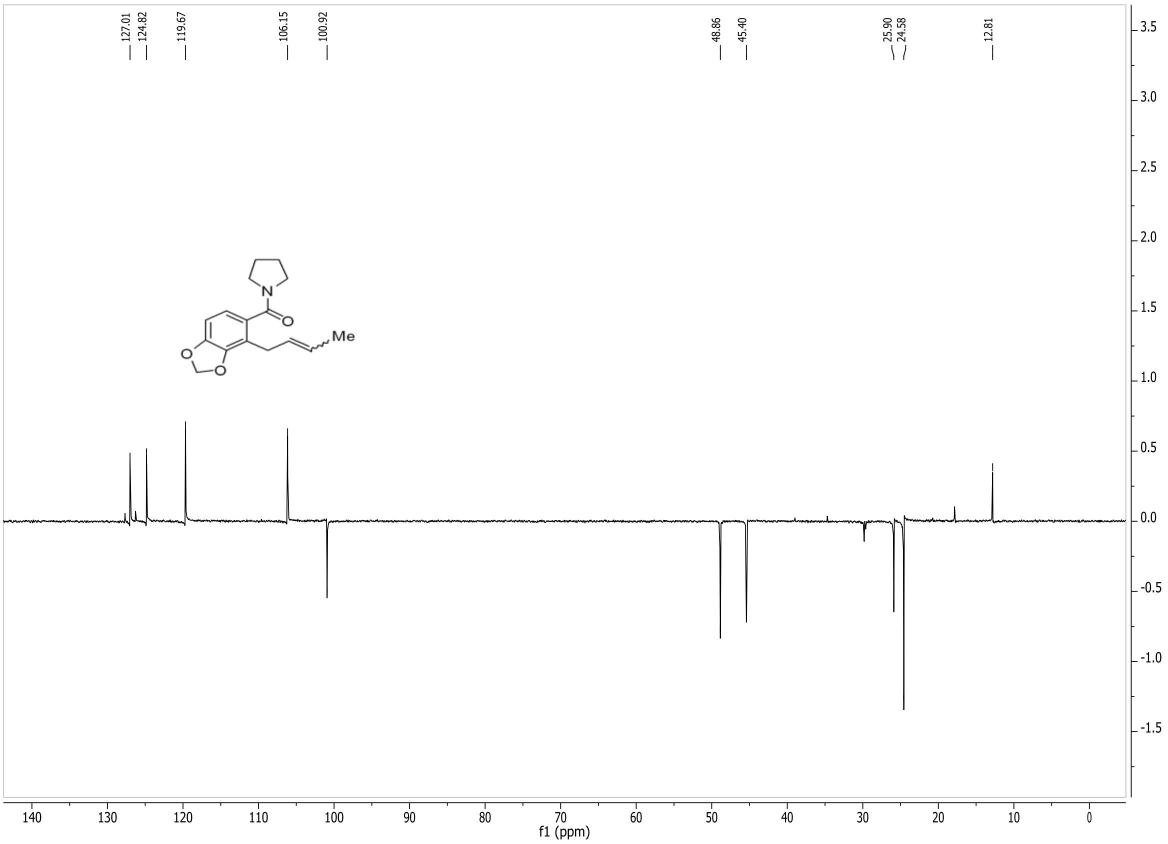


^{1}H and ^{13}C NMR Spectra of Compound **3ab.**

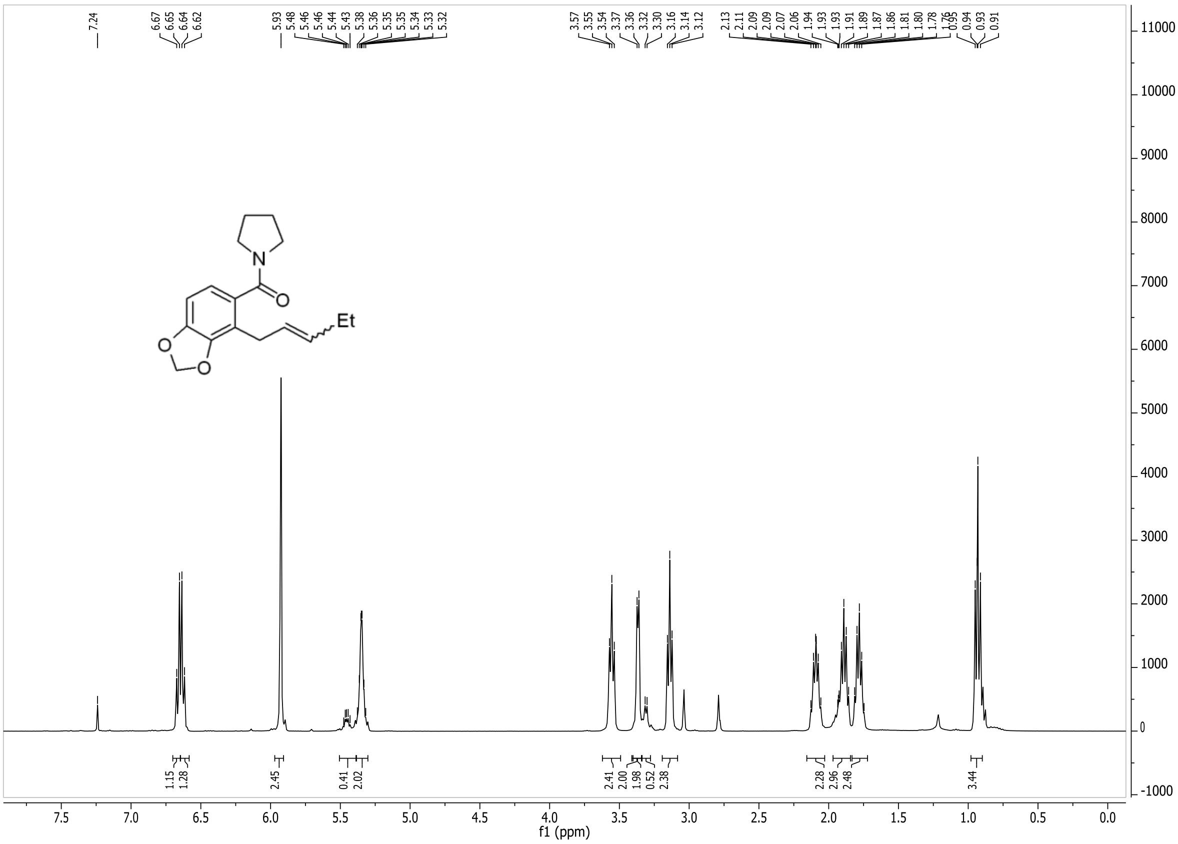


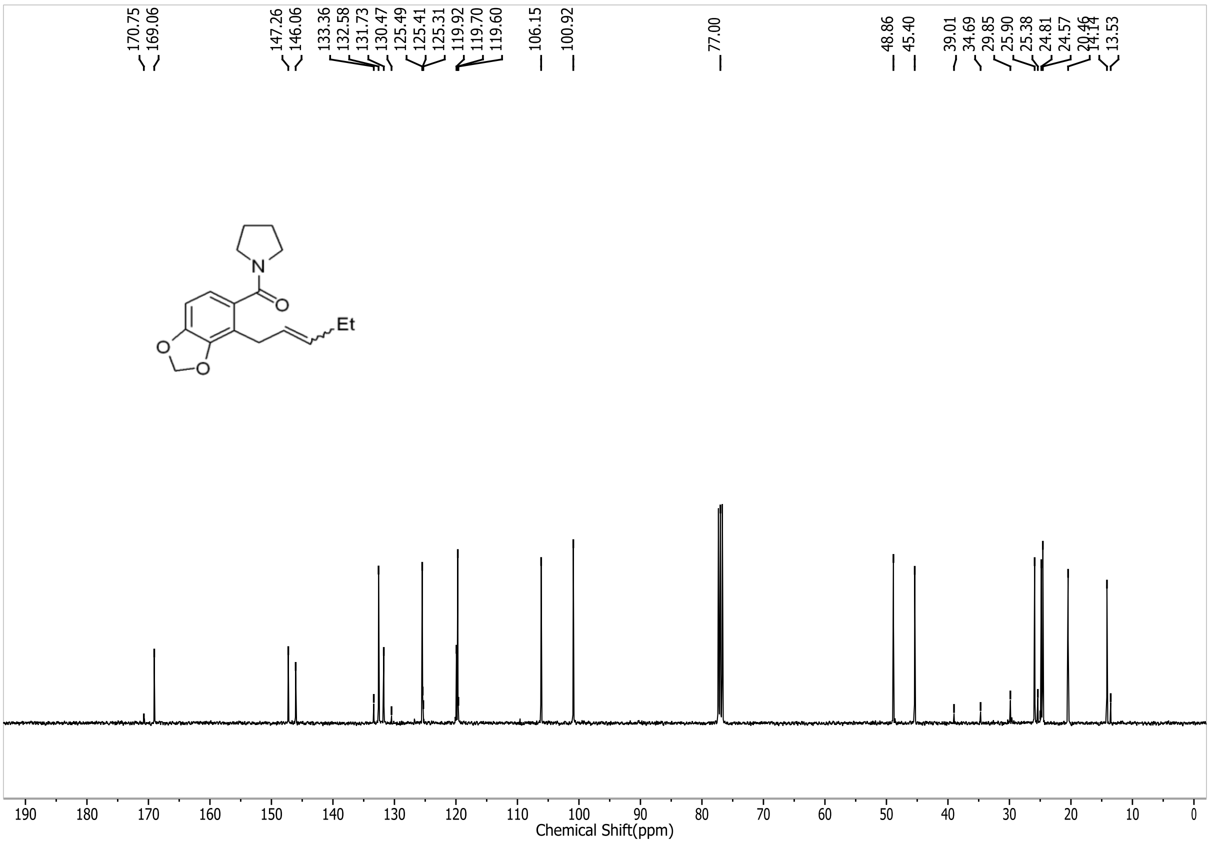


DEPT (135) NMR Spectrum of Compound **3ab.**

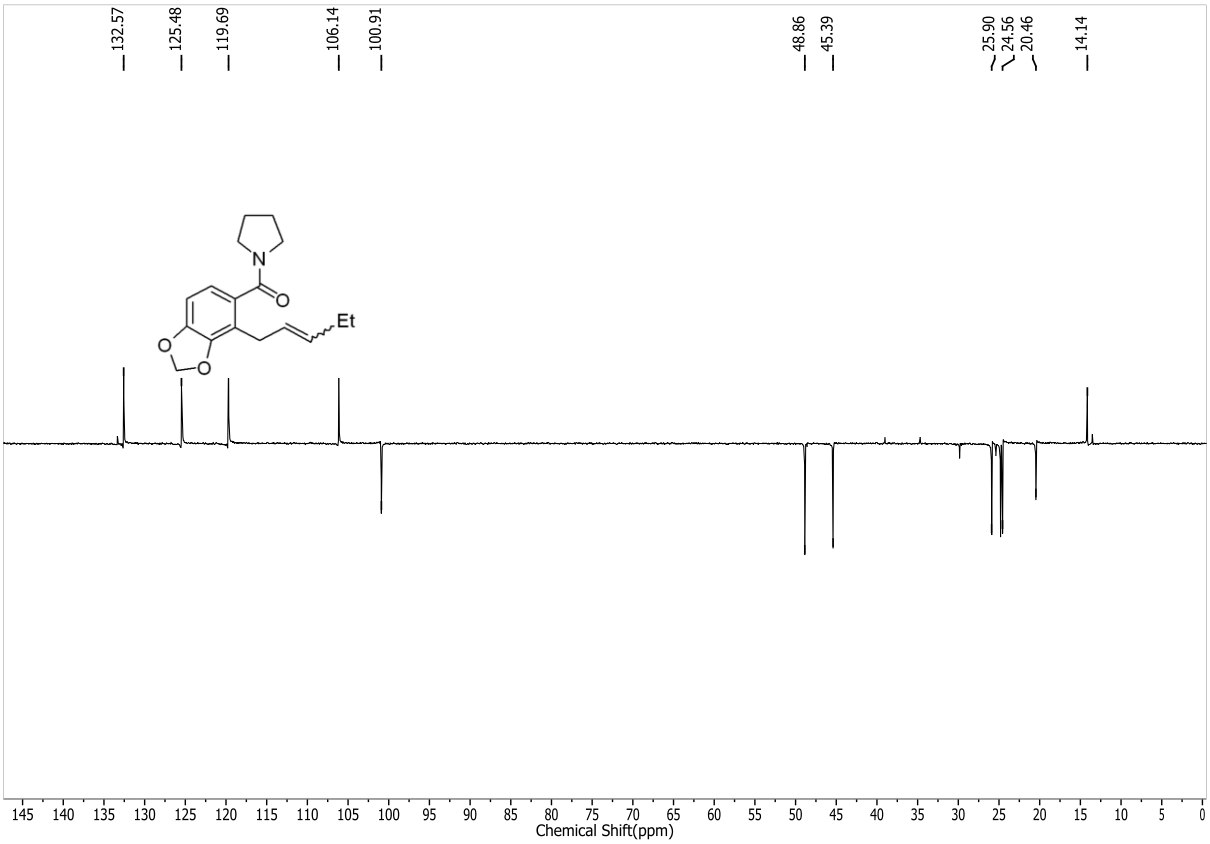


^{1}H and ^{13}C NMR Spectra of Compound **3ac.**

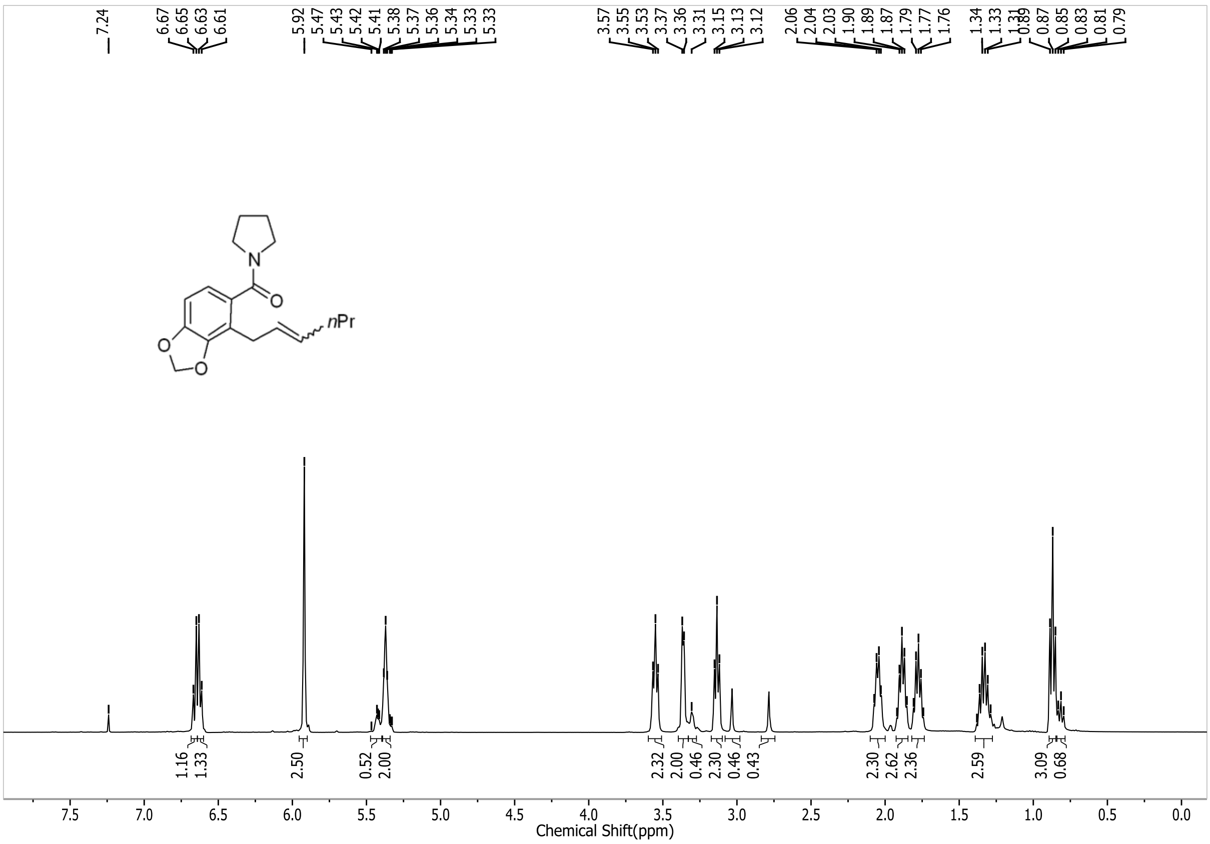


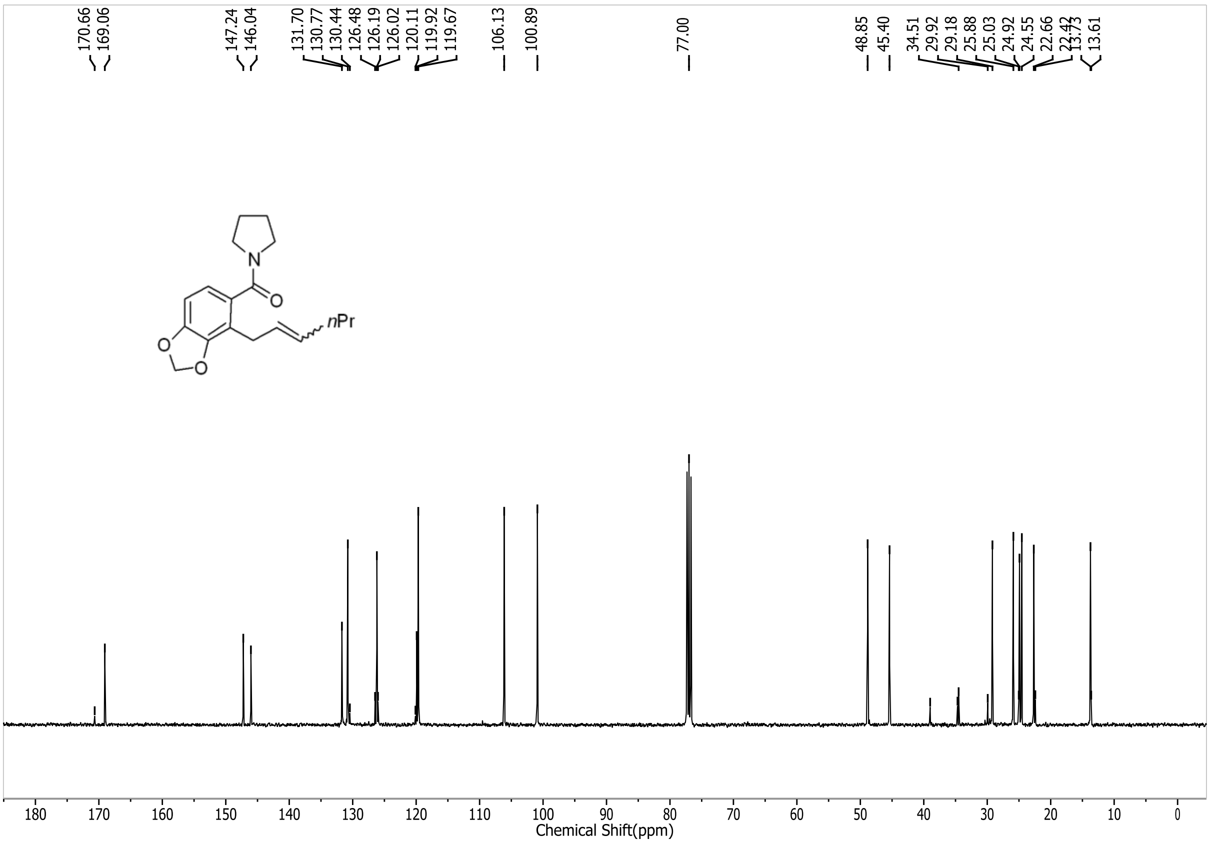


DEPT (135) NMR Spectrum of Compound **3ac.**

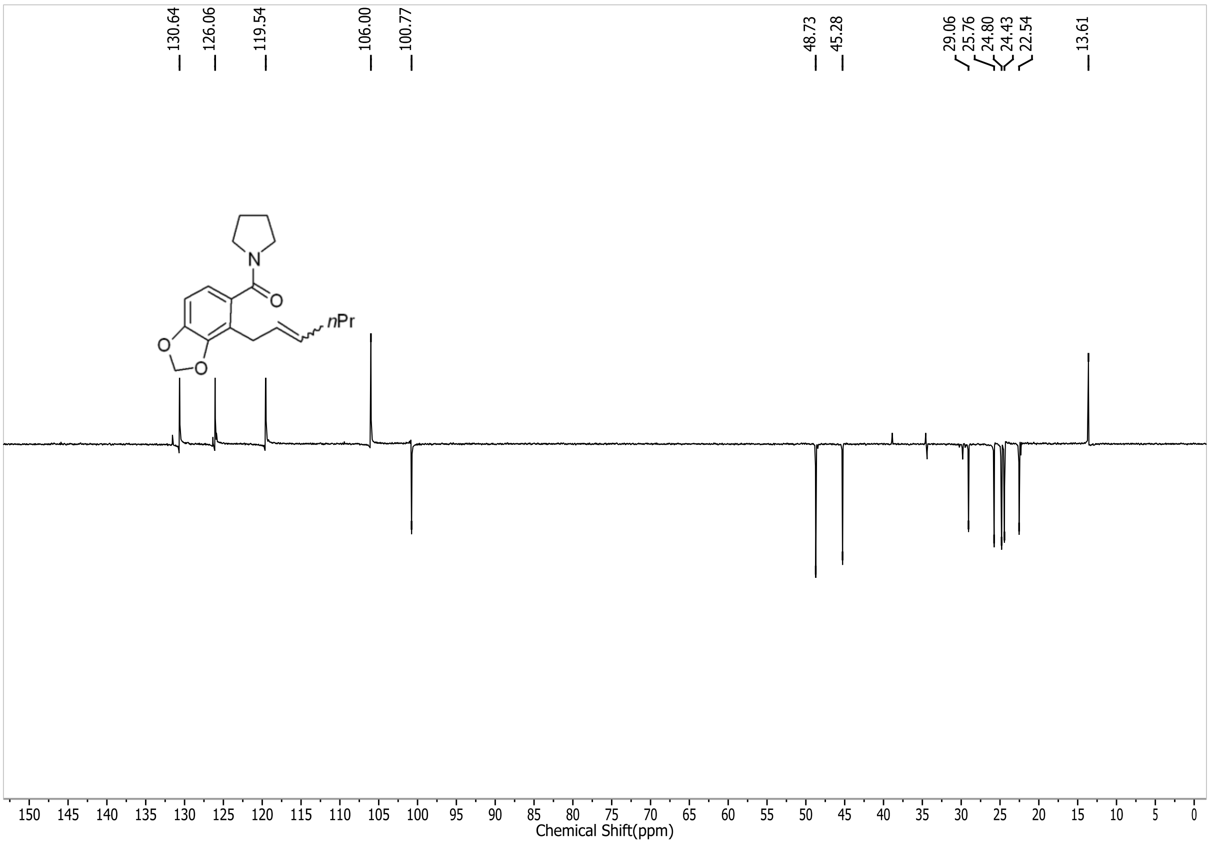


^{1}H and ^{13}C NMR Spectra of Compound **3ad.**

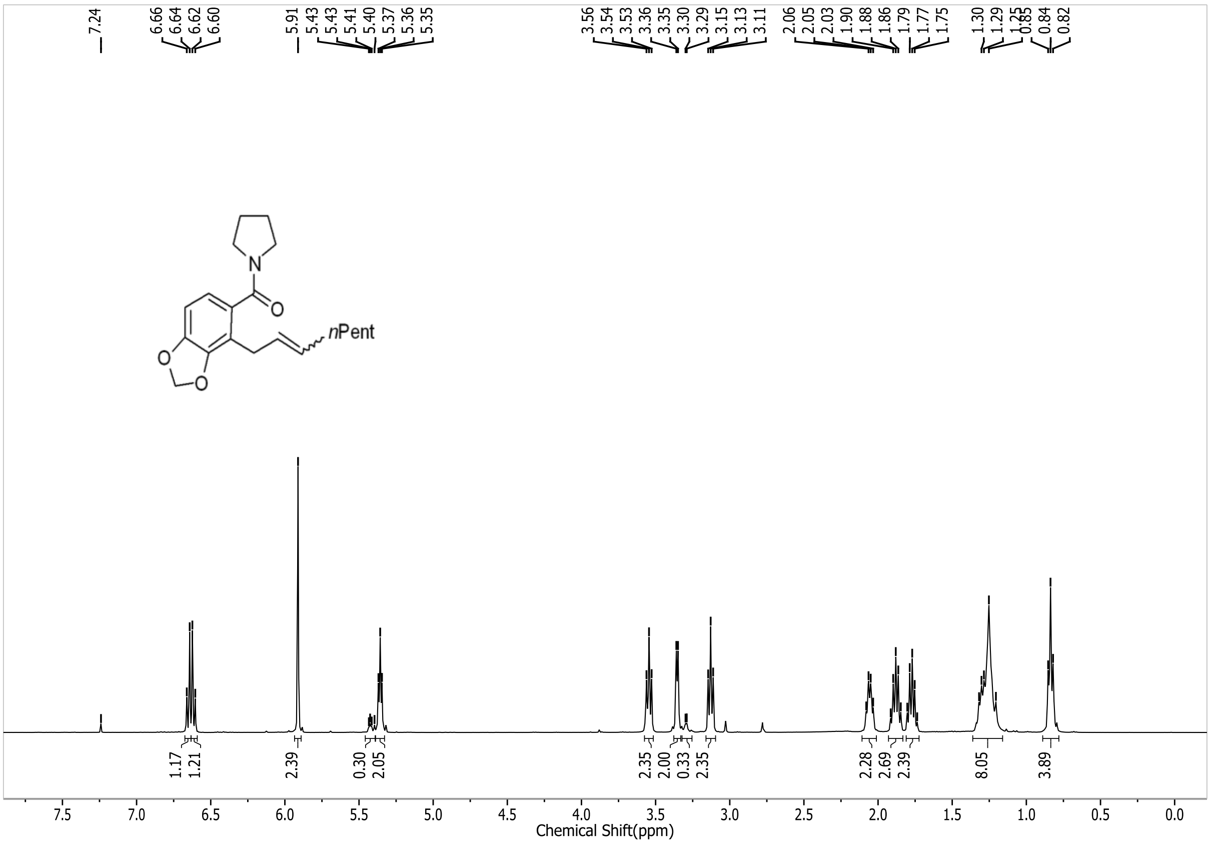


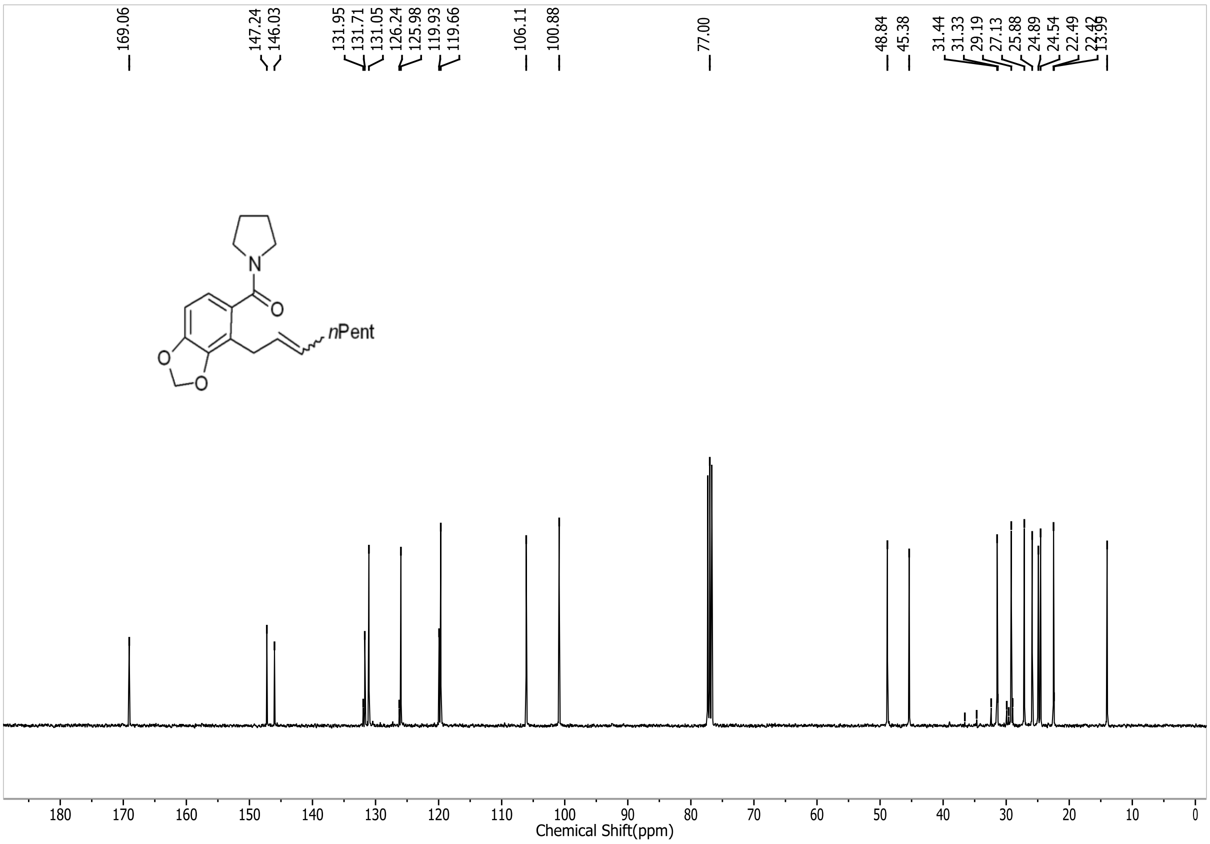


DEPT (135) NMR Spectrum of Compound **3ad.**

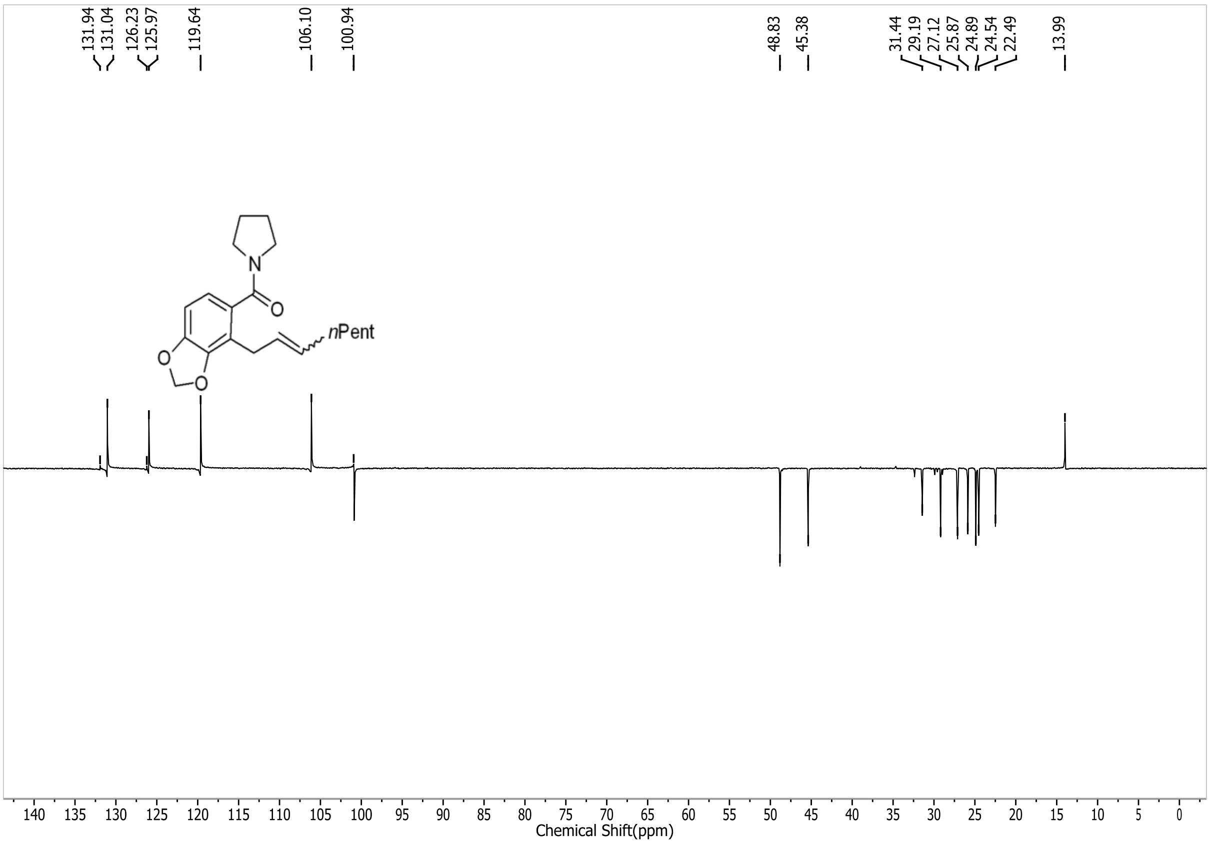


^{1}H and ^{13}C NMR Spectra of Compound **3ae.**

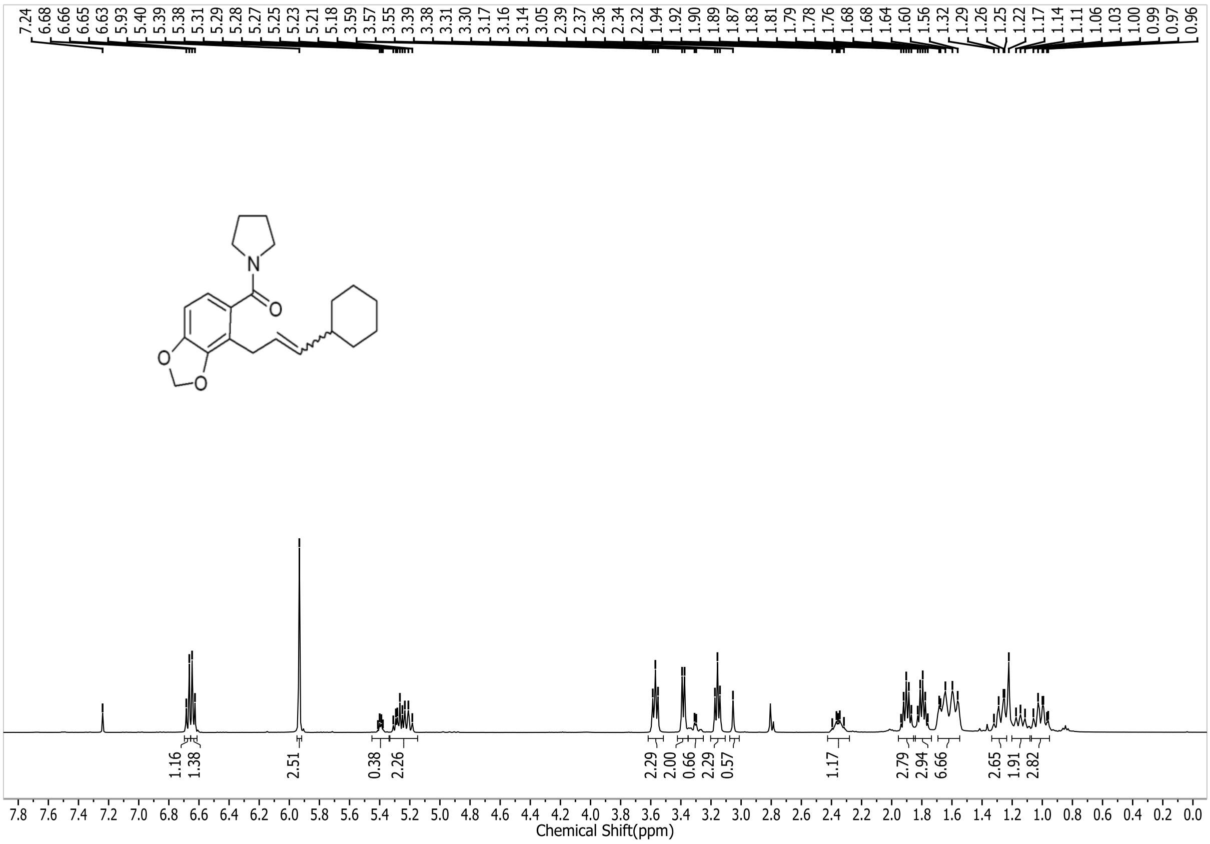


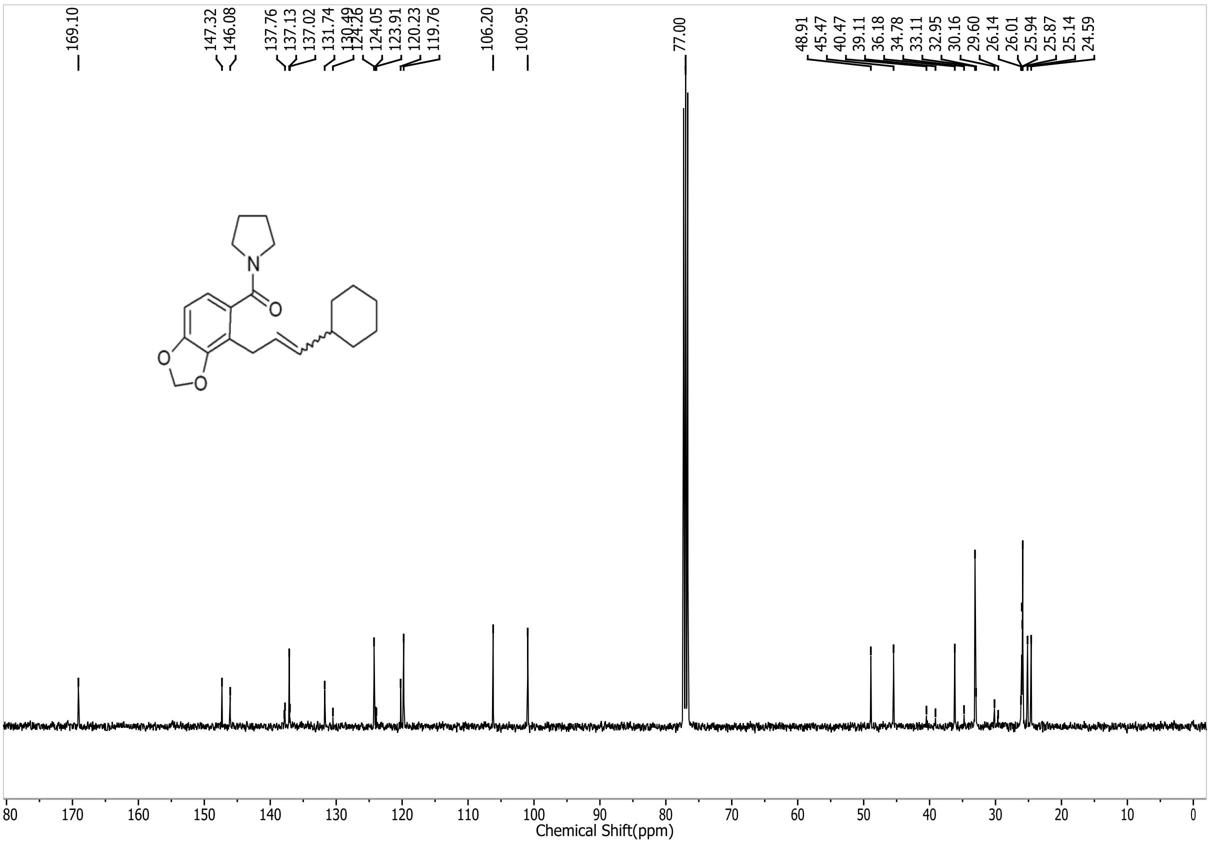


DEPT (135) NMR Spectrum of Compound **3ae.**

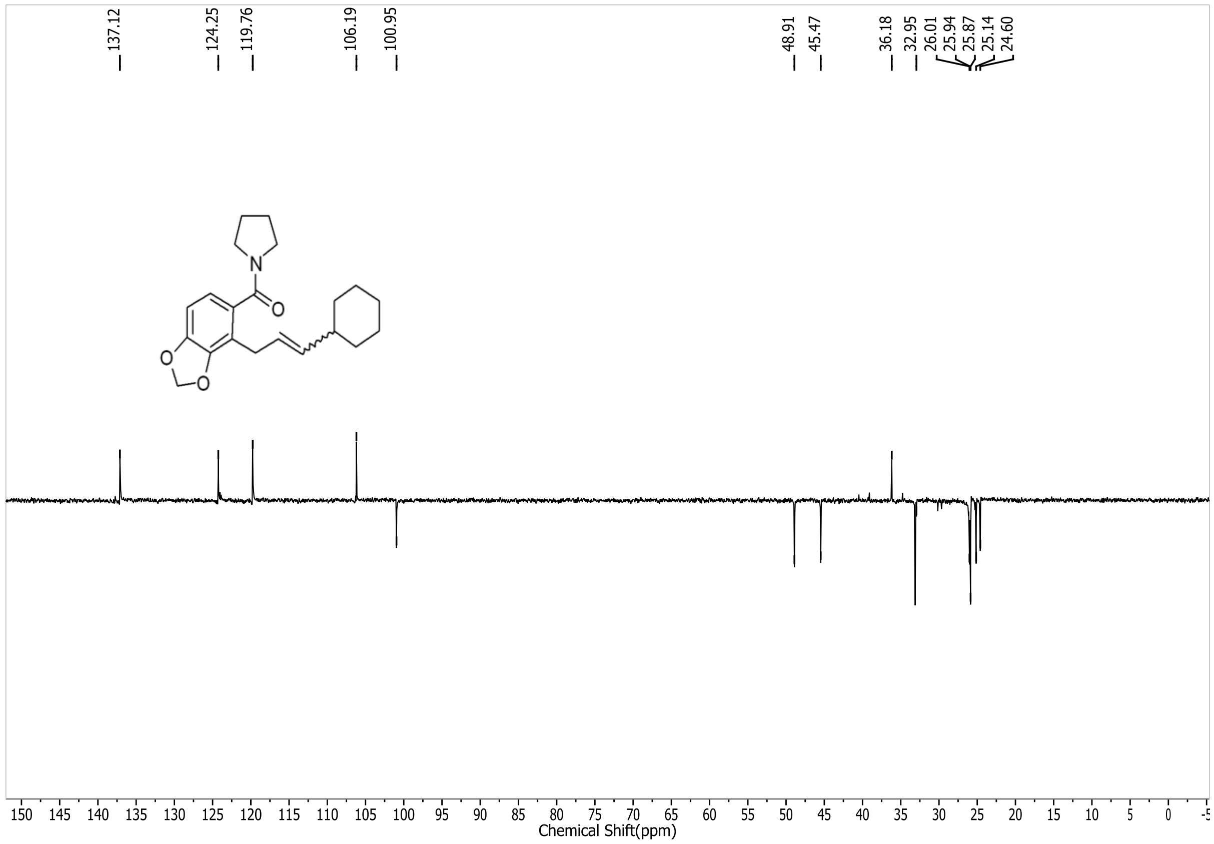


^{1}H and ^{13}C NMR Spectra of Compound **3af.**

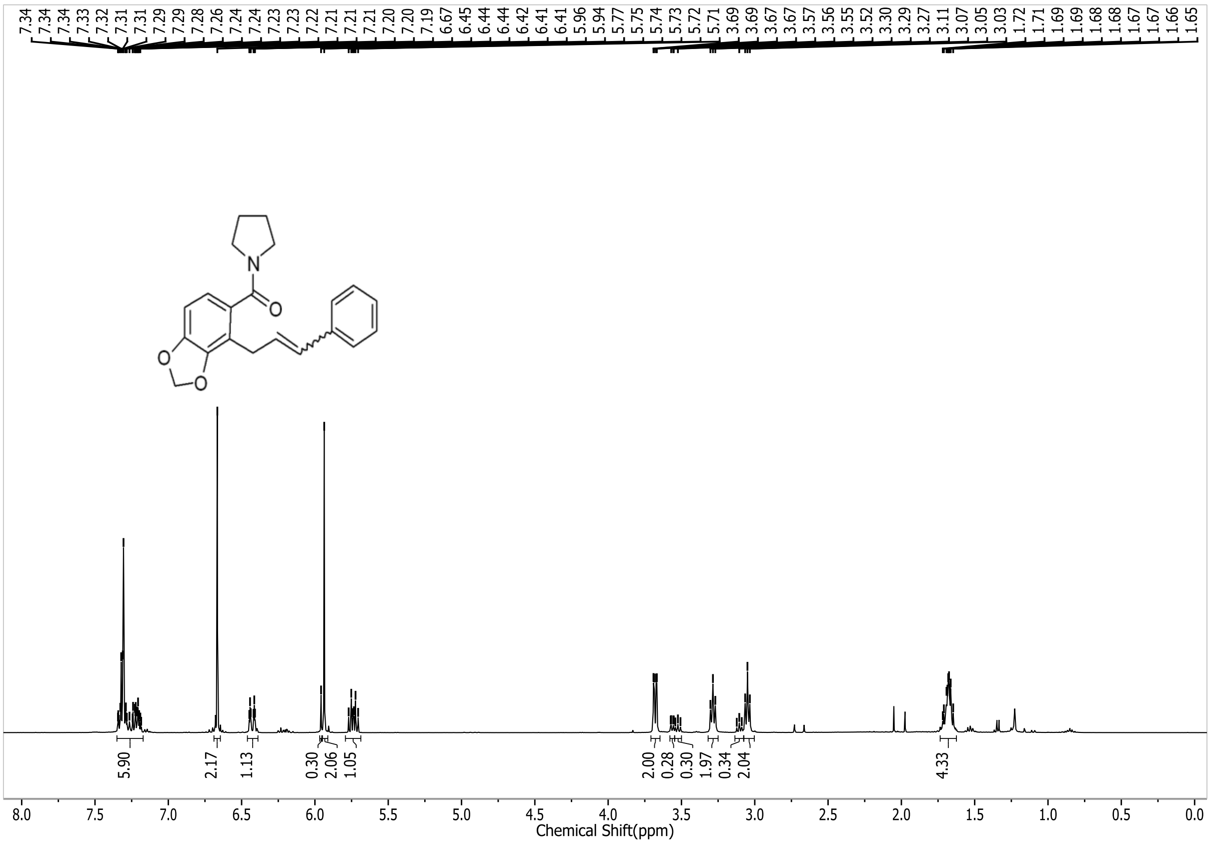


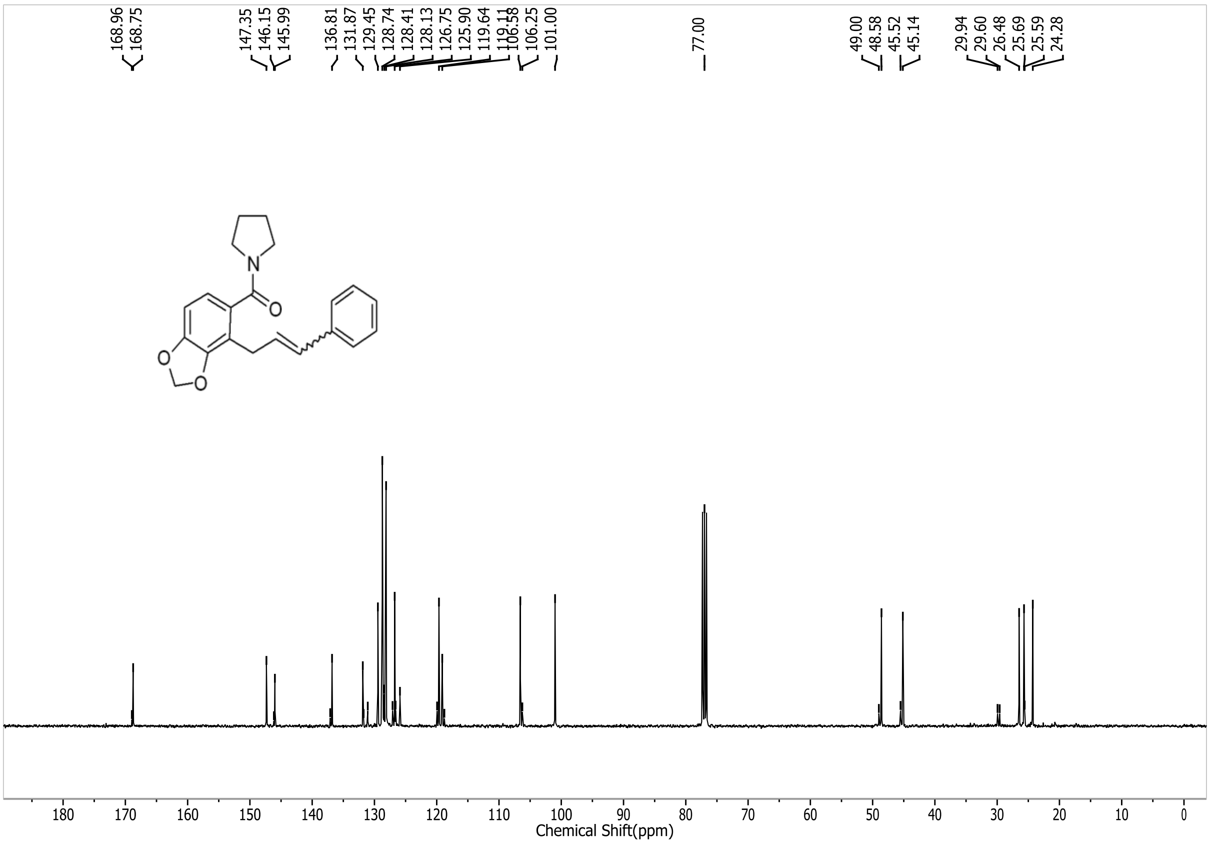


DEPT (135) NMR Spectrum of Compound **3af.**



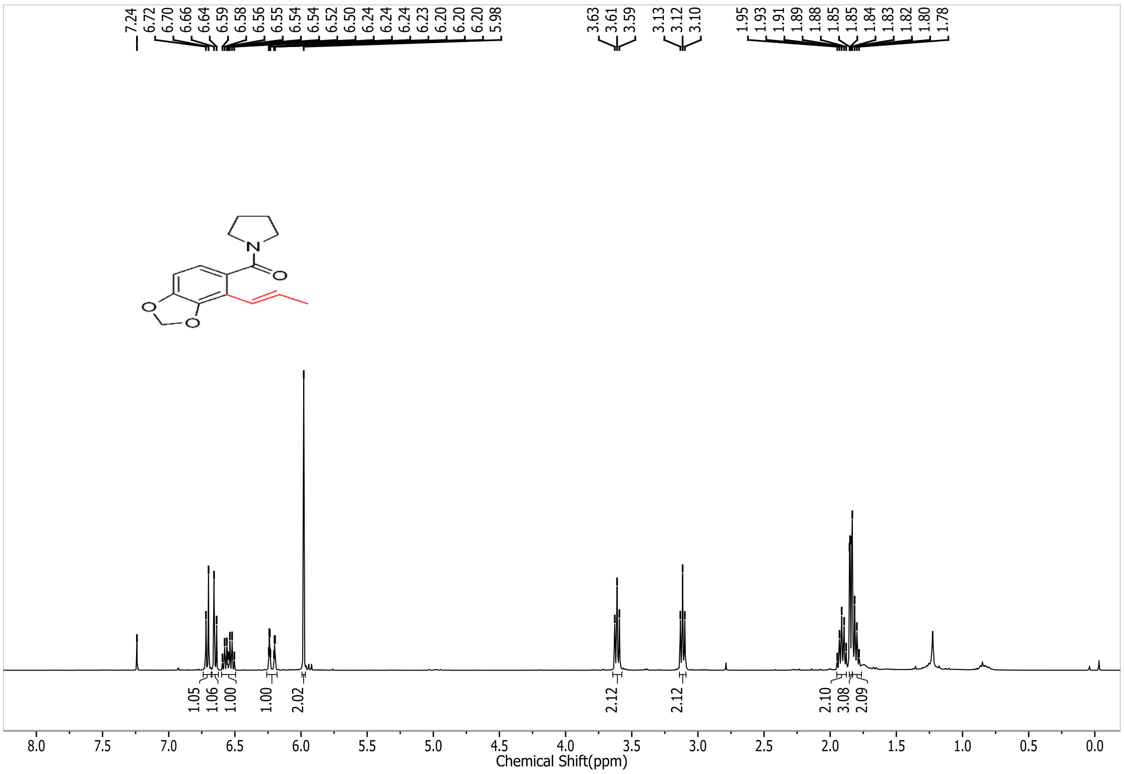
^{1}H and ^{13}C NMR Spectra of Compound **3ag.**

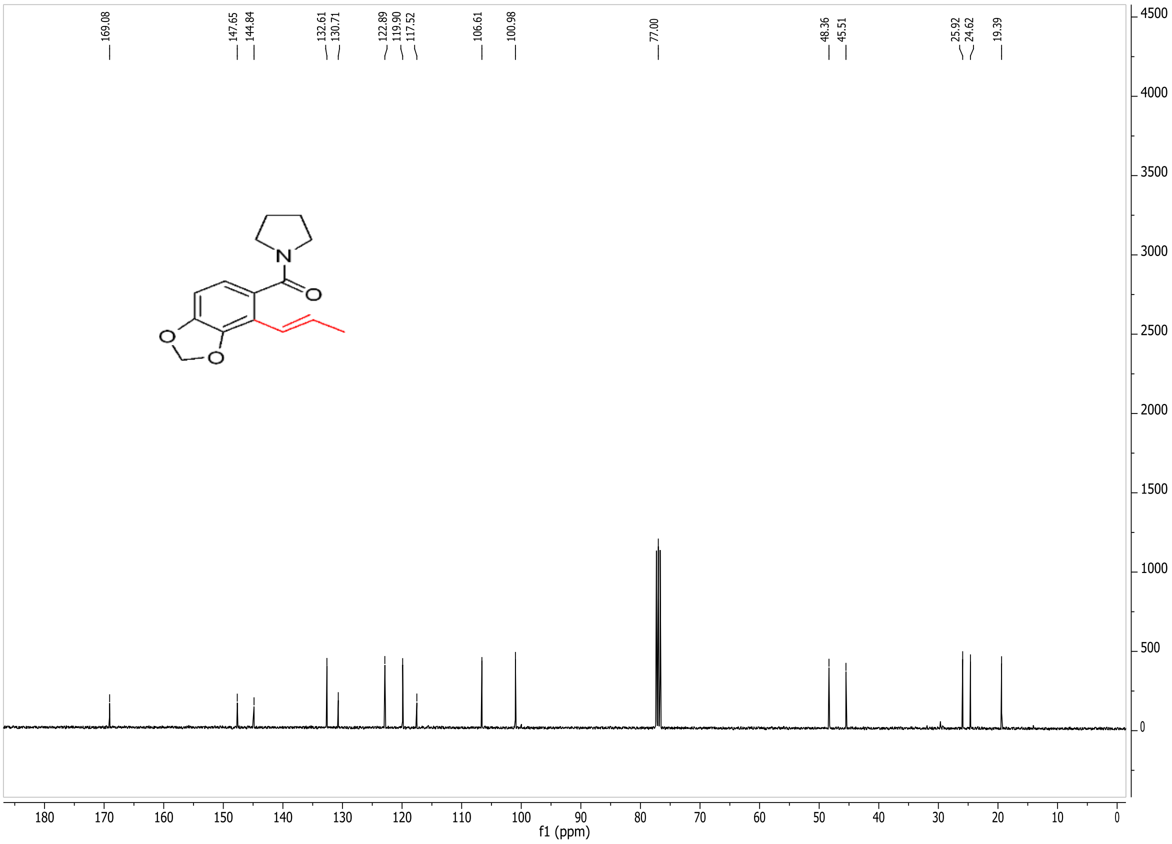




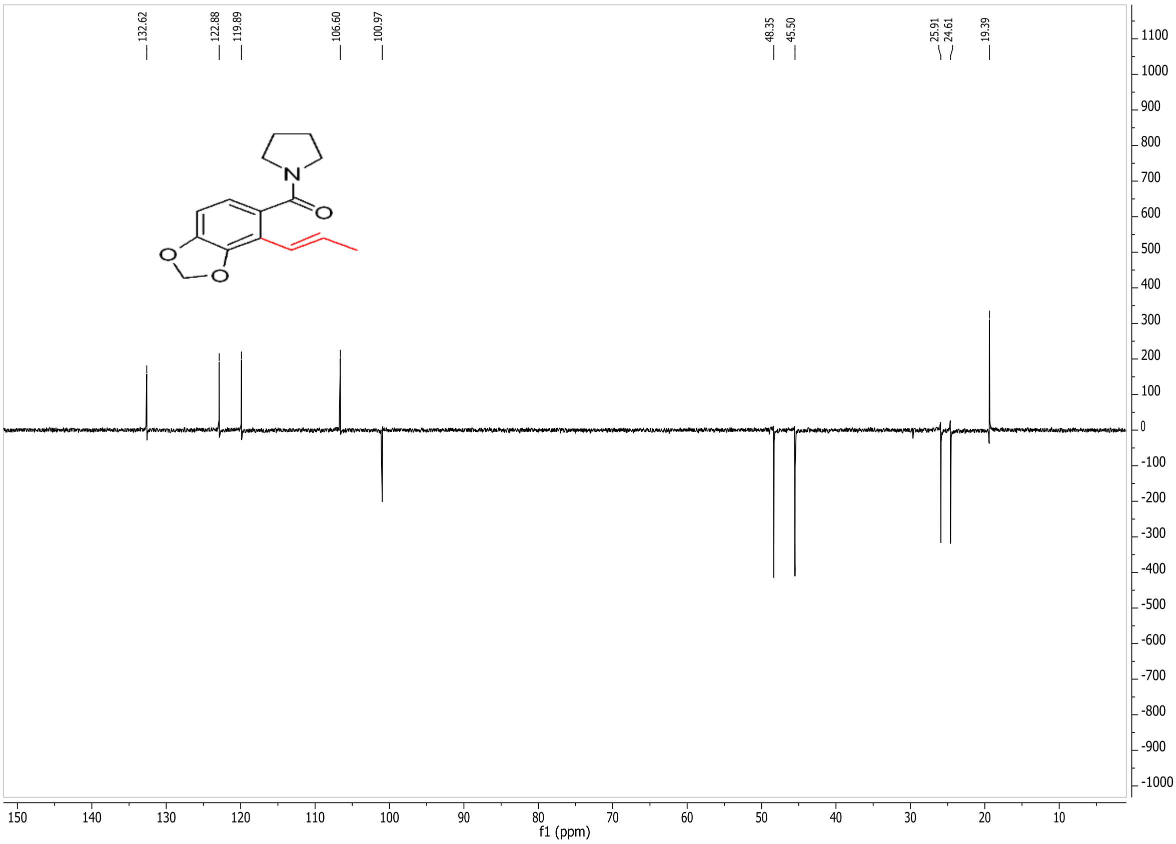
DEPT (135) NMR Spectrum of Compound **3ag.**

^{1}H and ^{13}C NMR Spectra of Compound **4aa.**

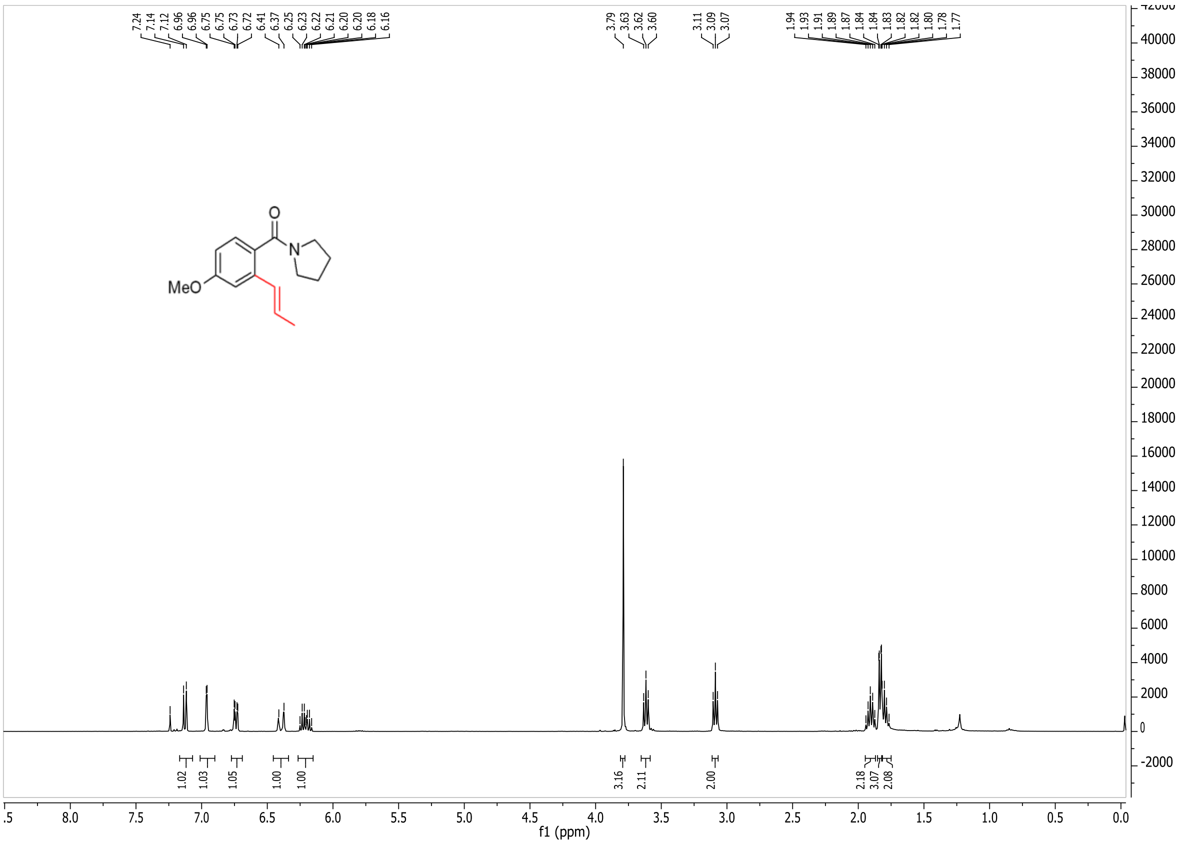


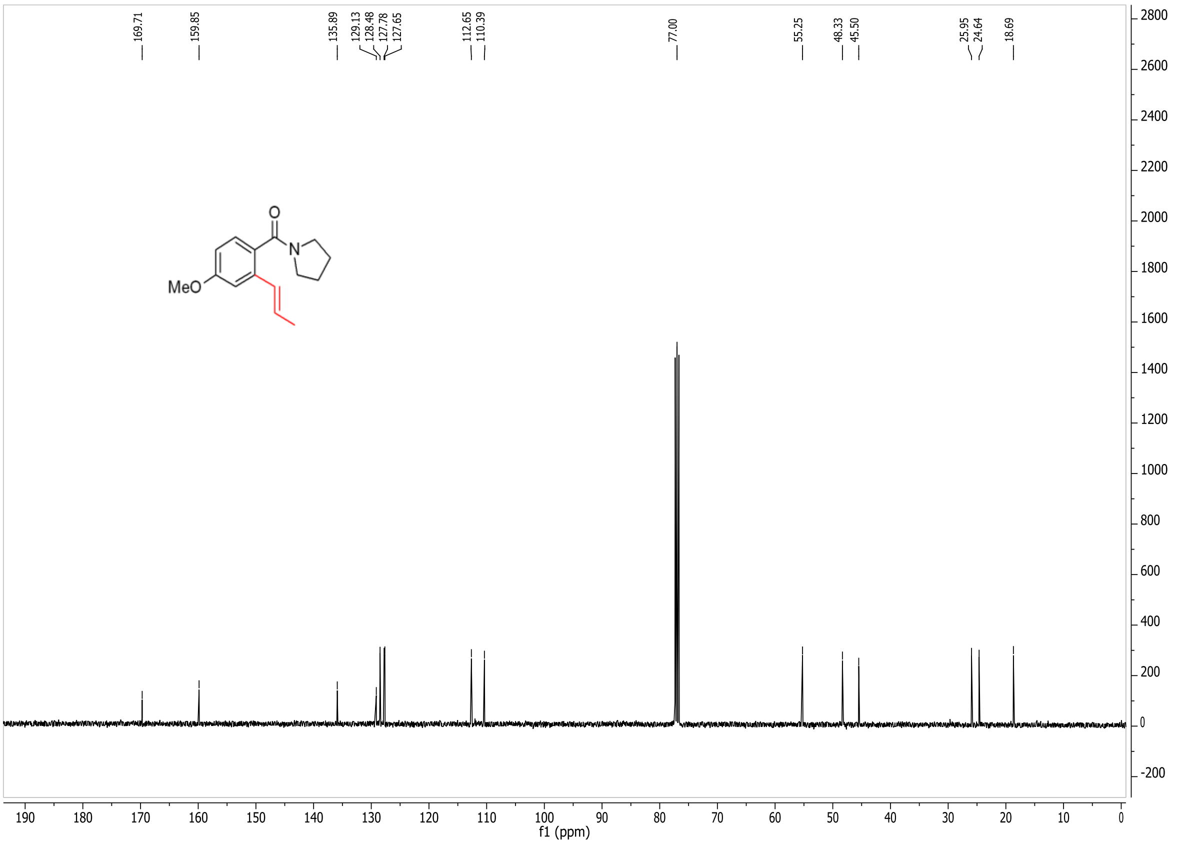


DEPT (135) NMR Spectrum of Compound **4aa.**

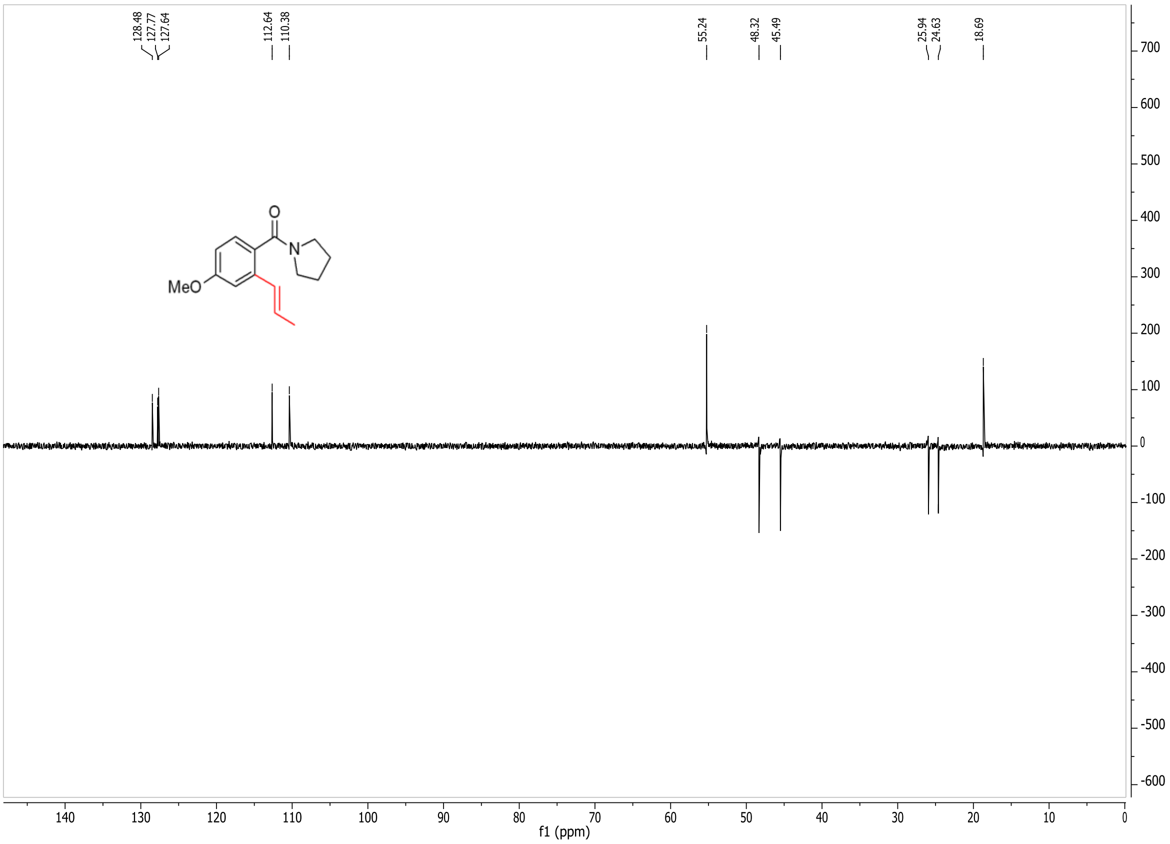


^{1}H and ^{13}C NMR Spectra of Compound **4ba.**

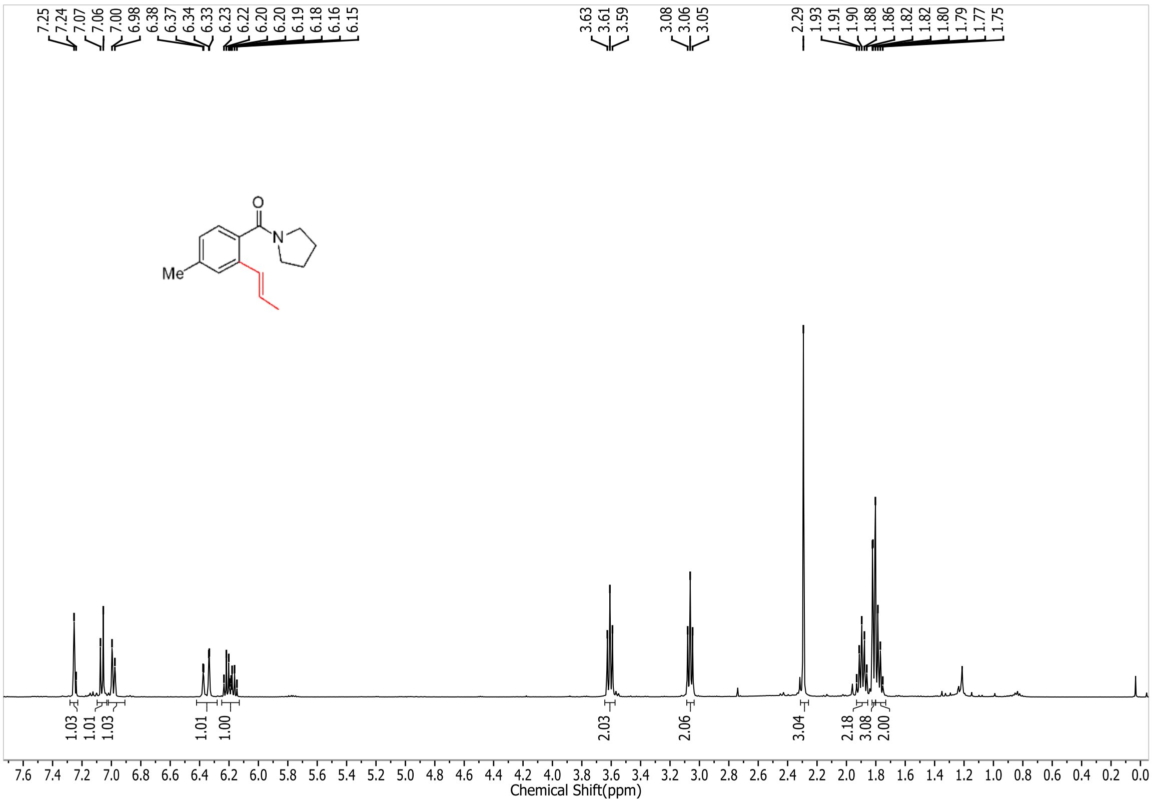


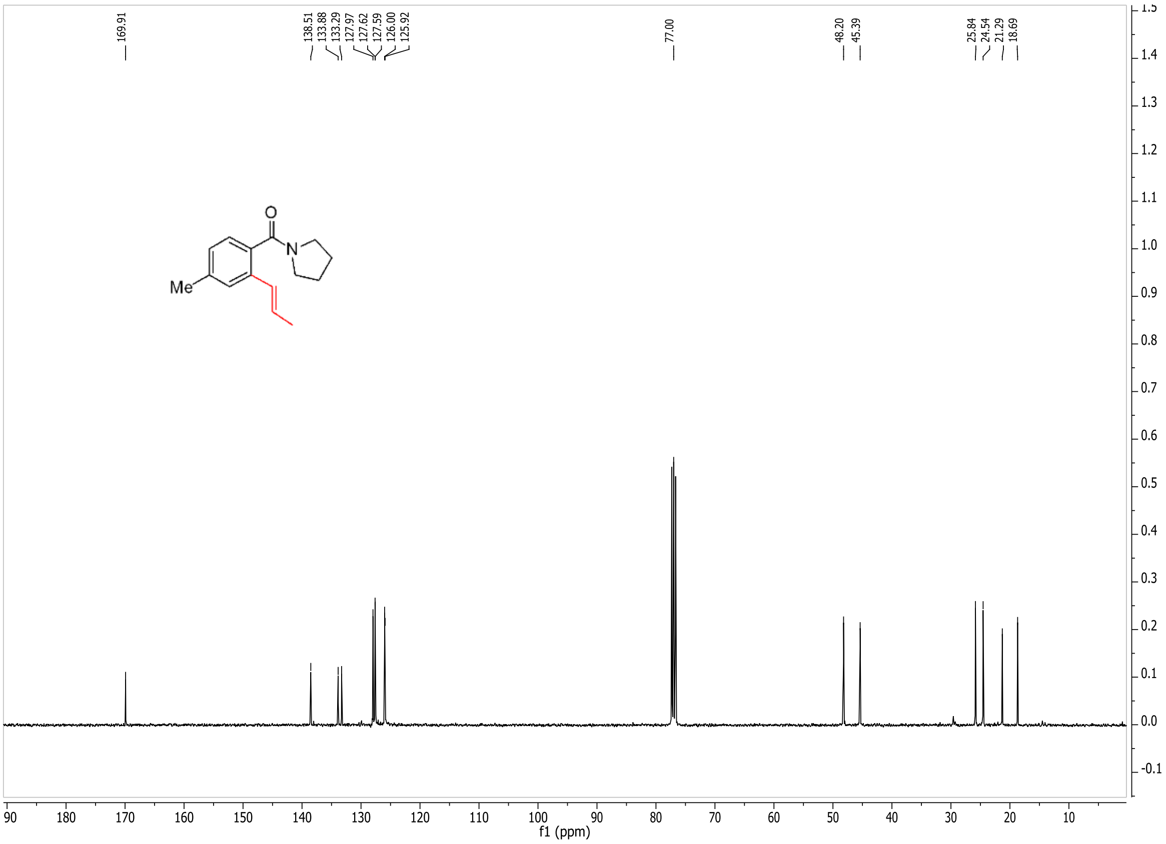


DEPT (135) NMR Spectrum of Compound **4ca.**



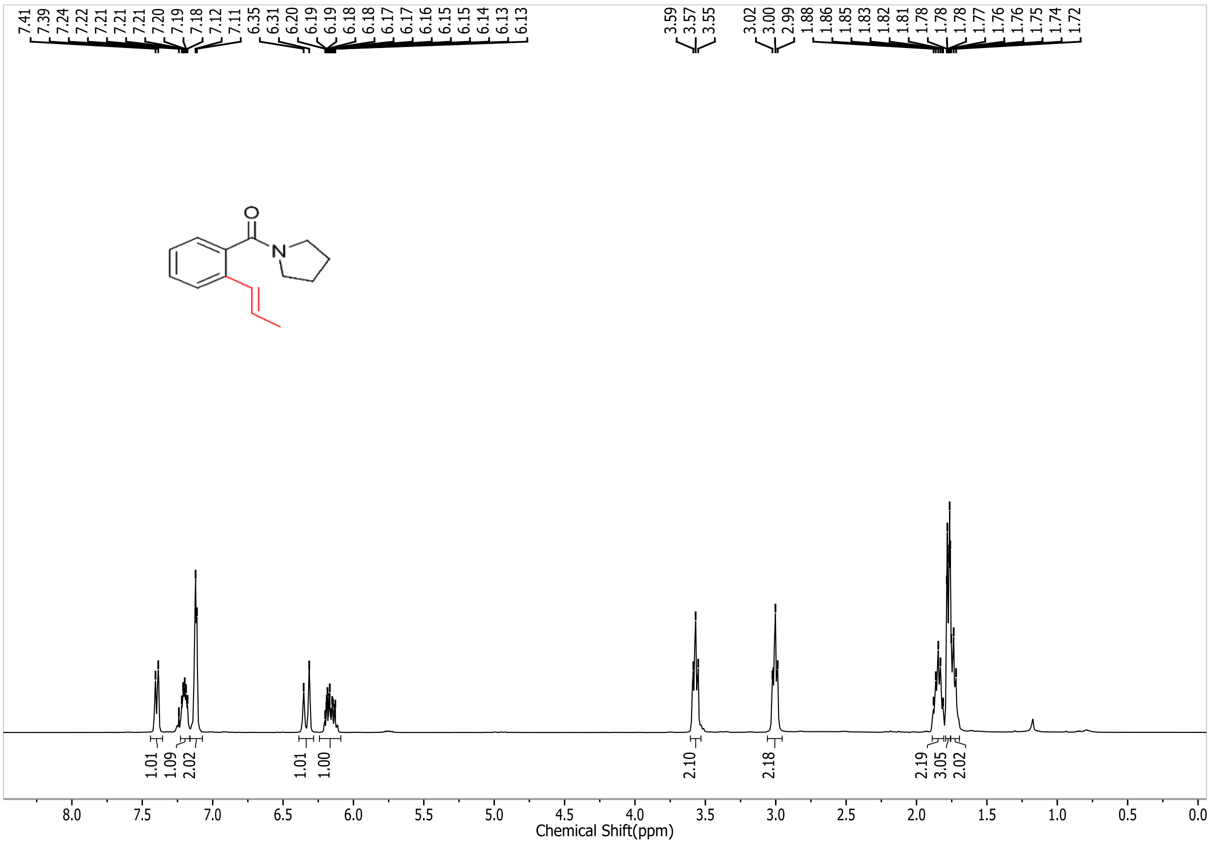
^{1}H and ^{13}C NMR Spectra of Compound **4da.**

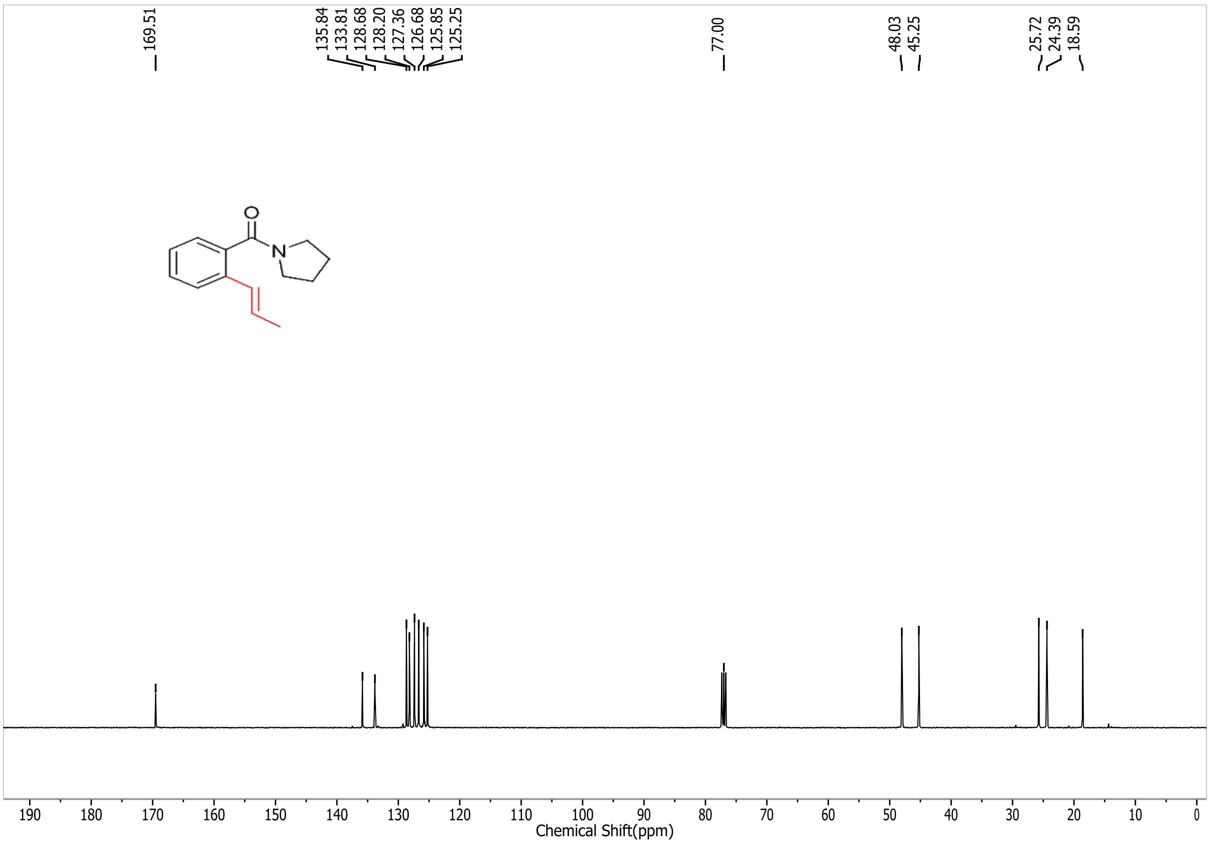




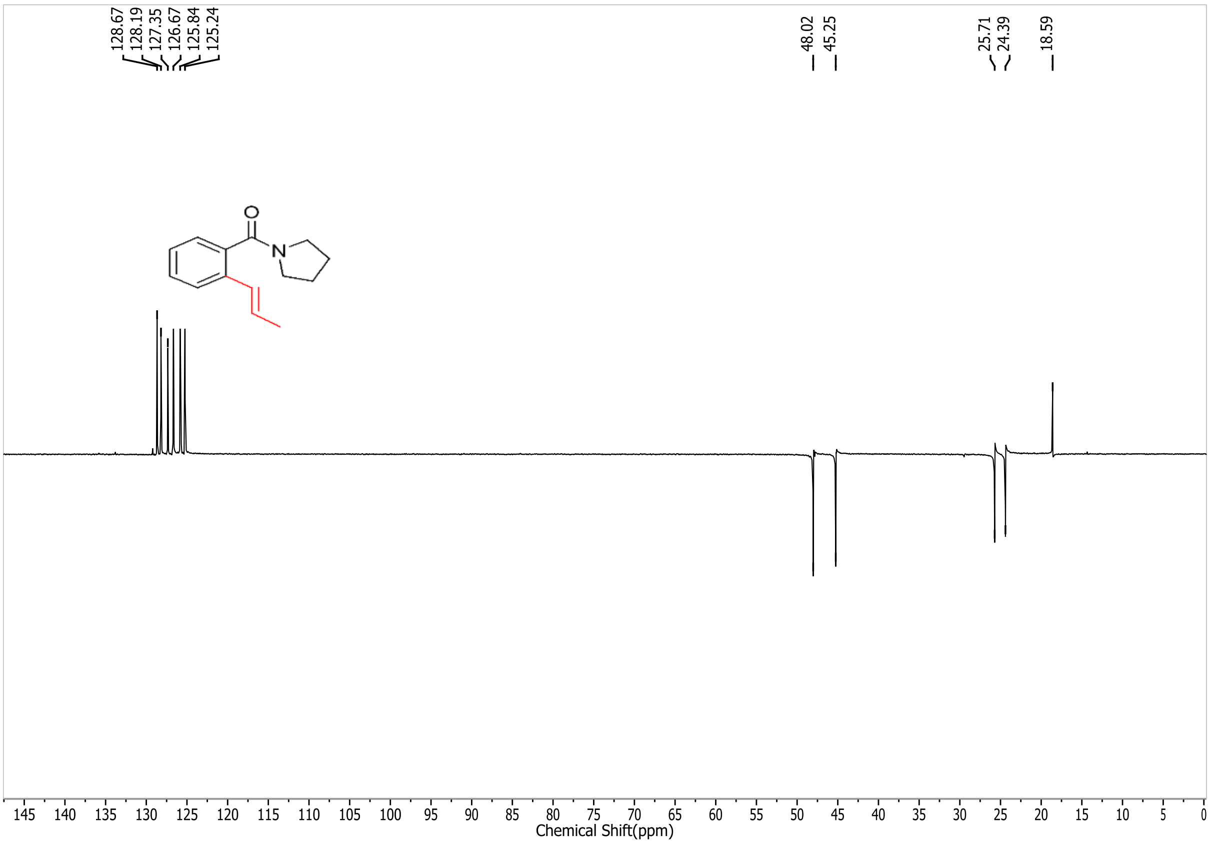
DEPT (135) NMR Spectrum of Compound **4da.**

^{1}H and ^{13}C NMR Spectra of Compound **4ea.**

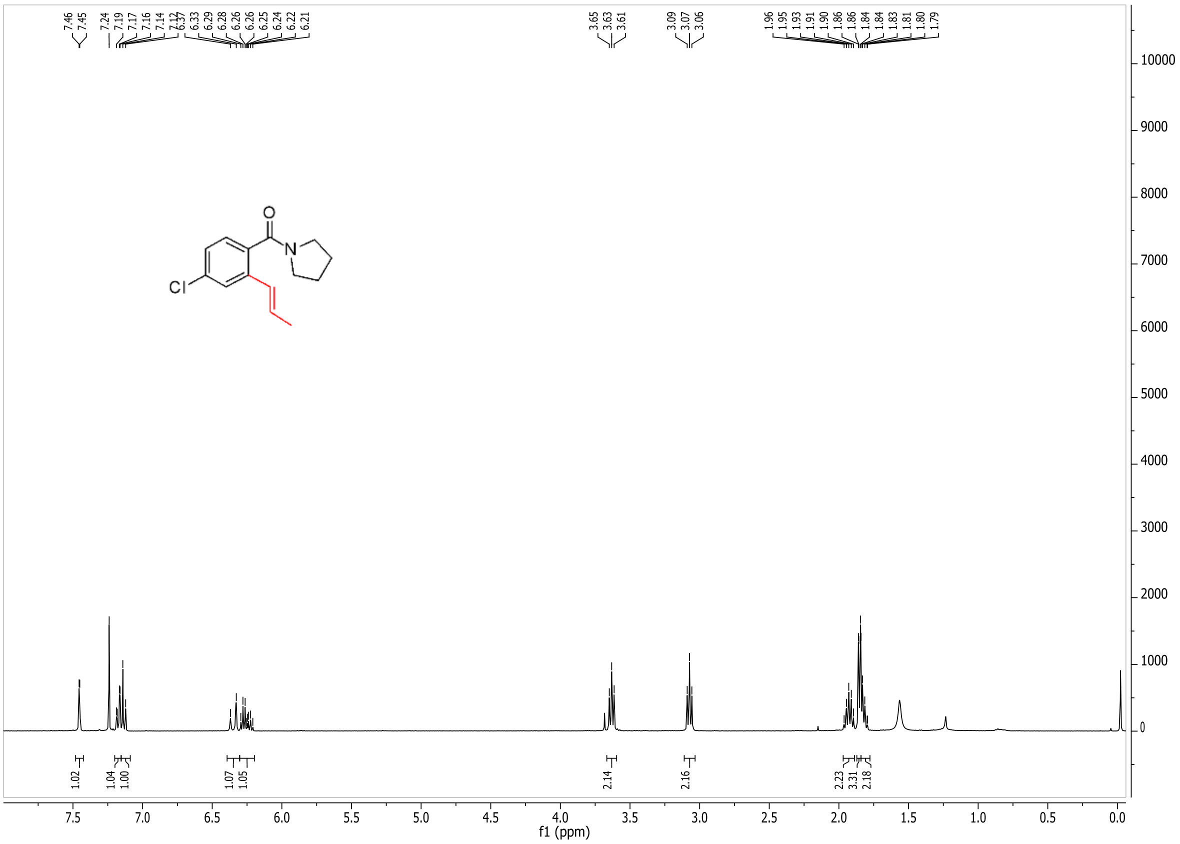


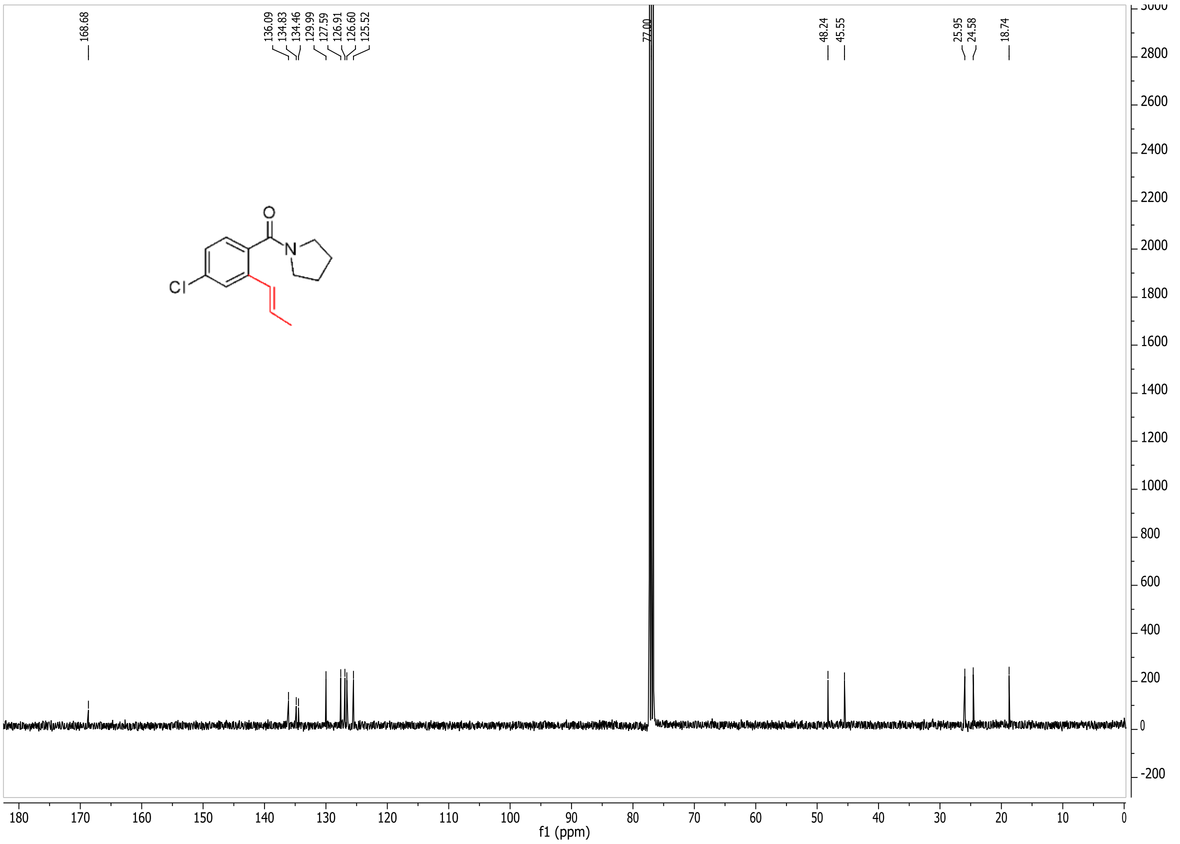


DEPT (135) NMR Spectrum of Compound **4ea.**

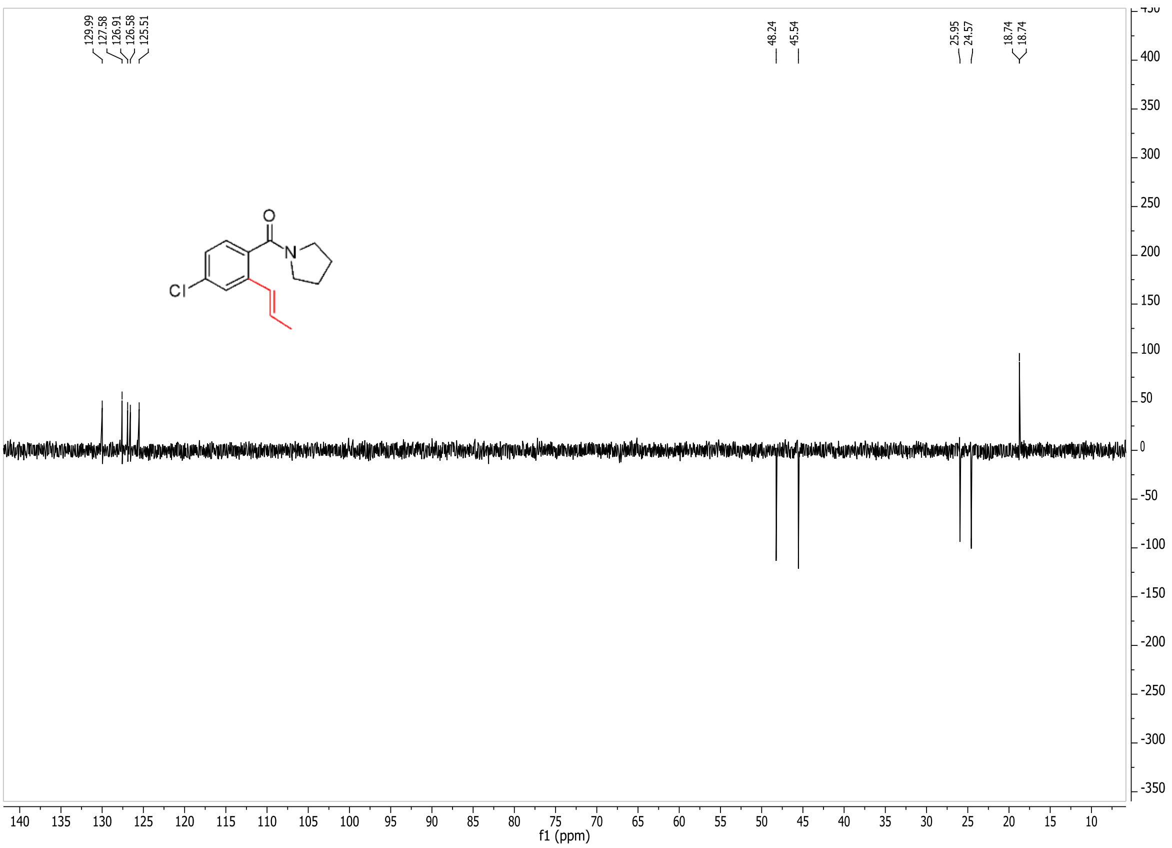


^{1}H and ^{13}C NMR Spectra of Compound **4fa.**

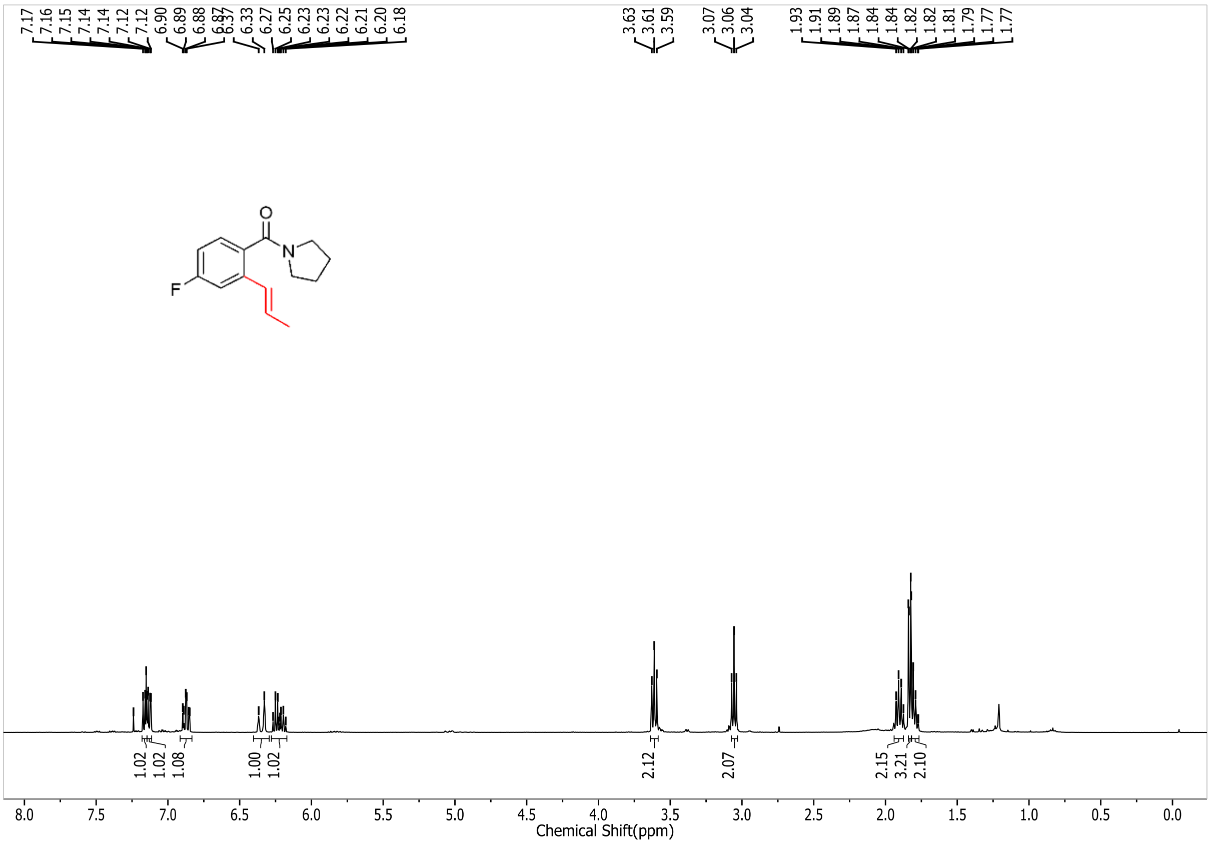


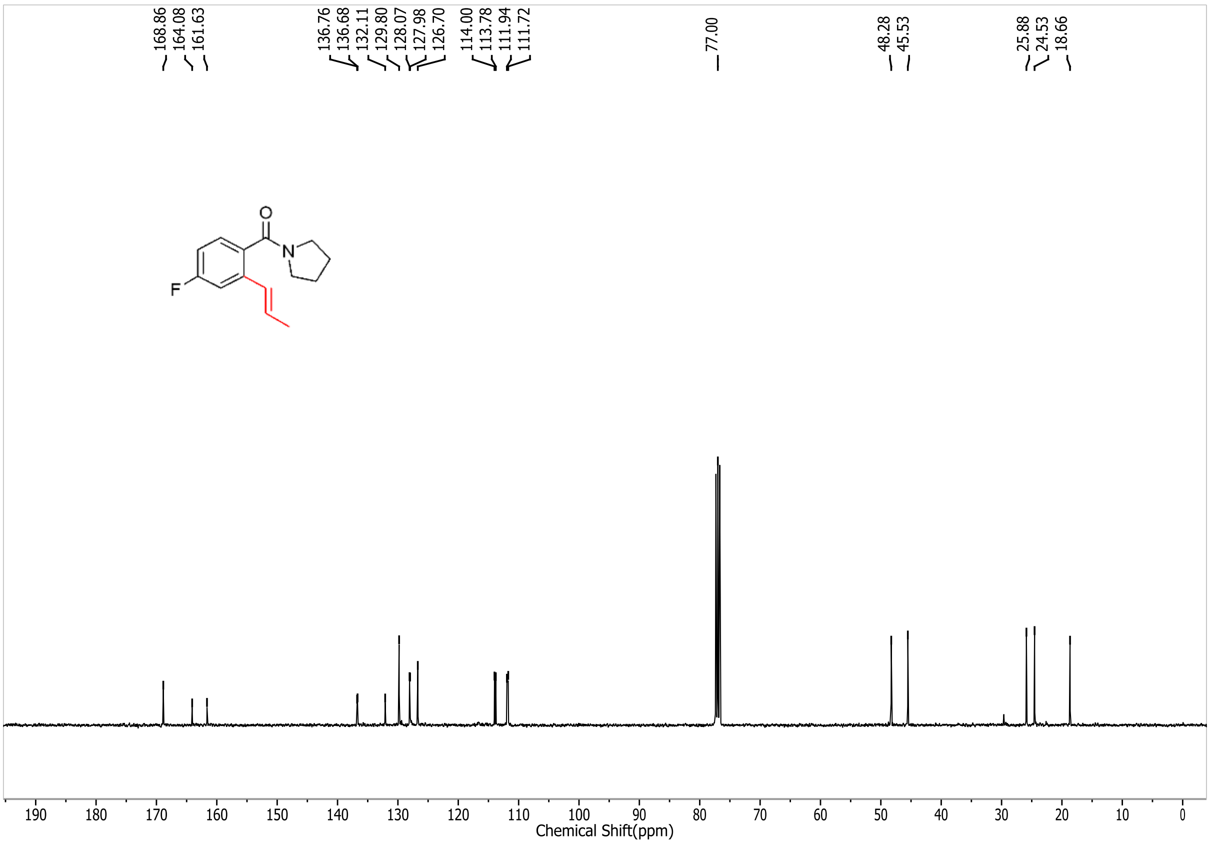


DEPT (135) NMR Spectrum of Compound **4fa.**

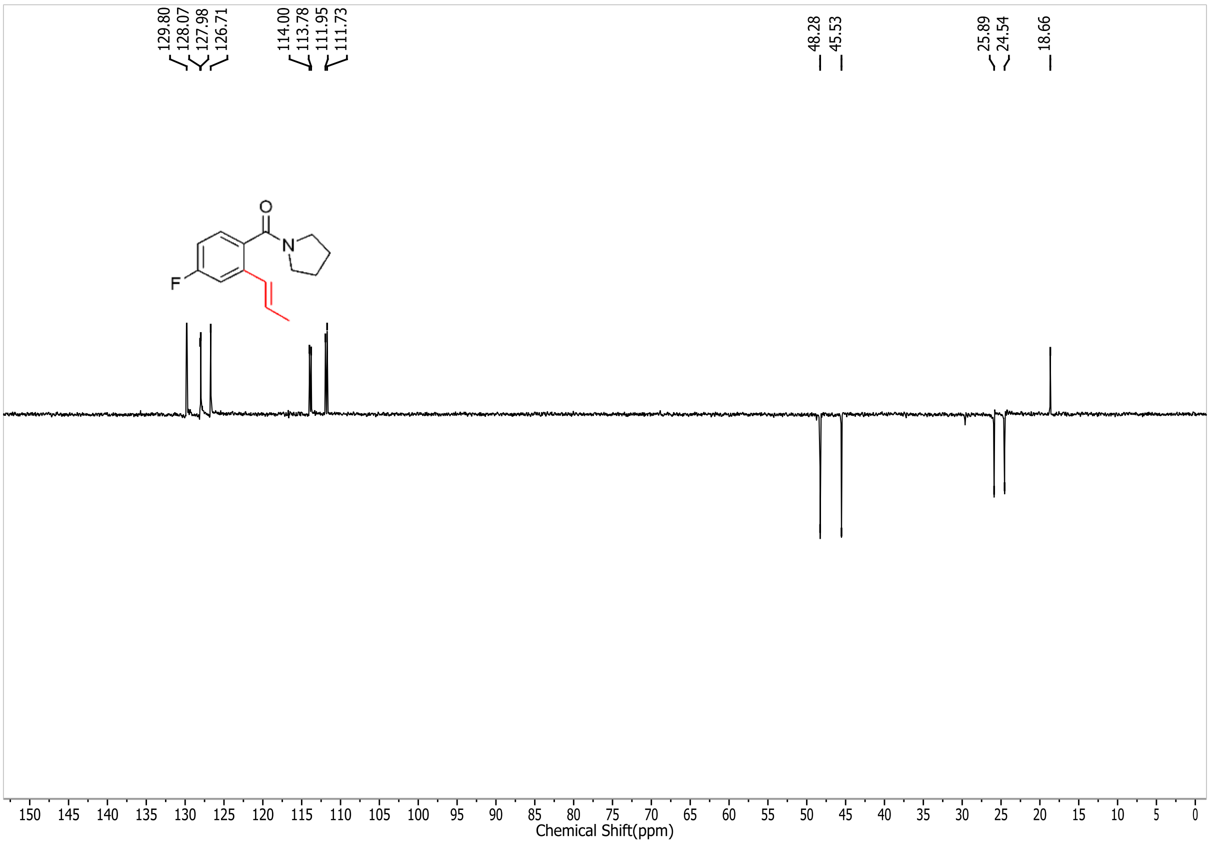


^1H and ^{13}C NMR Spectra of Compound **4ga.**

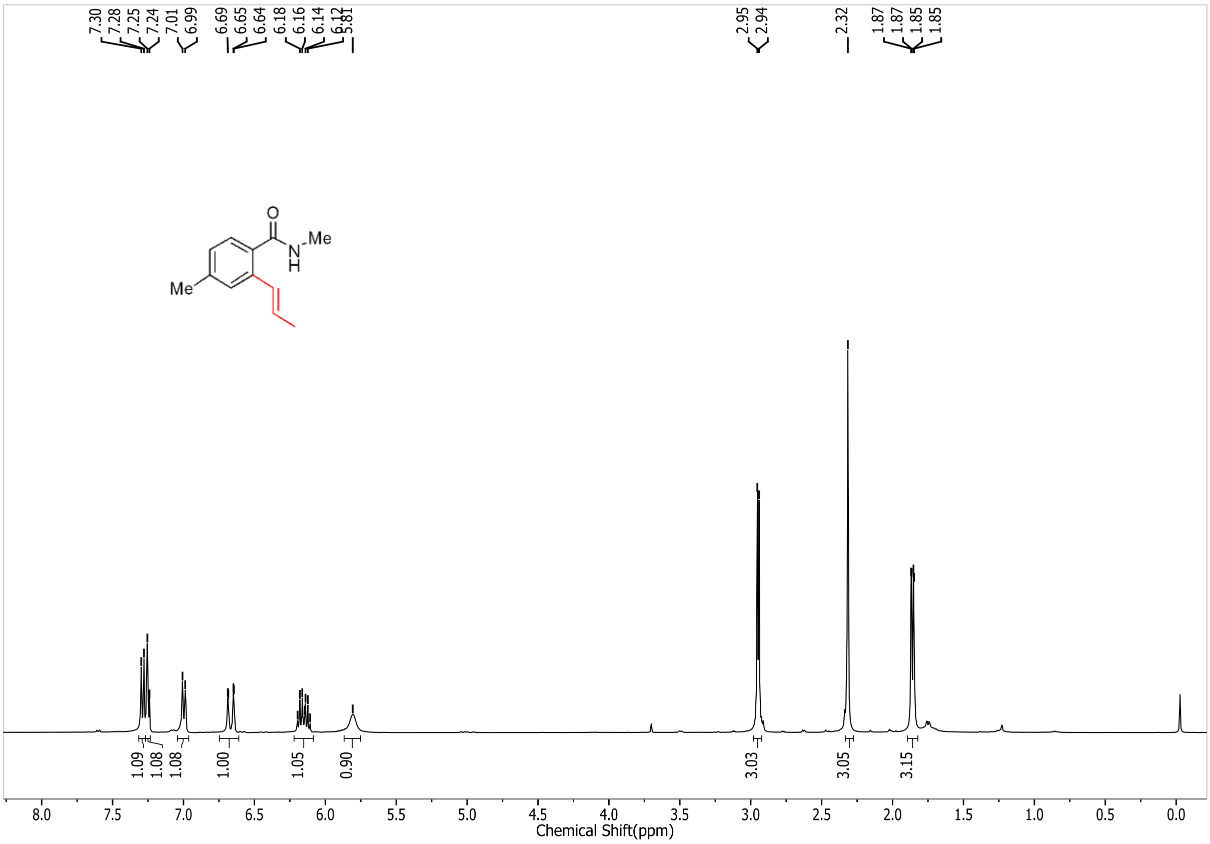


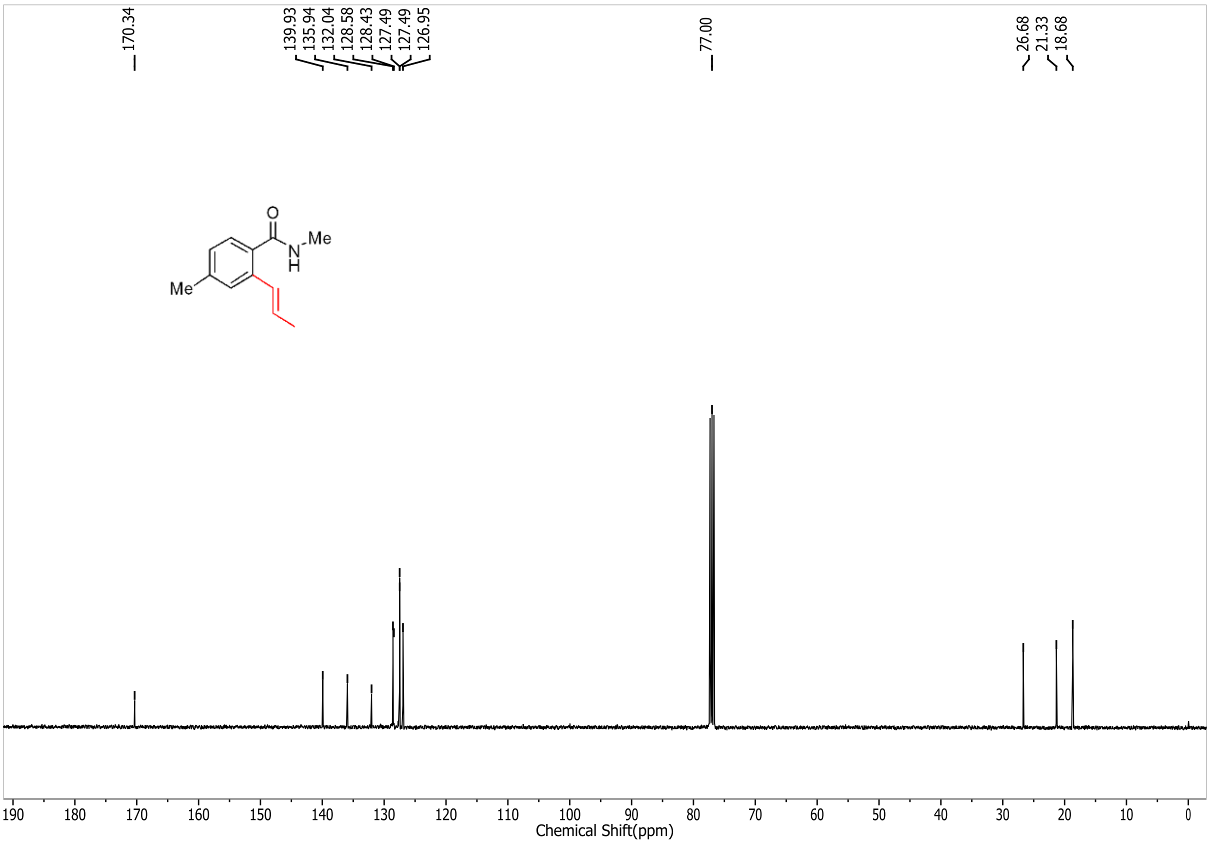


DEPT (135) NMR Spectrum of Compound **4ga.**



^{1}H and ^{13}C NMR Spectra of Compound **4ja.**





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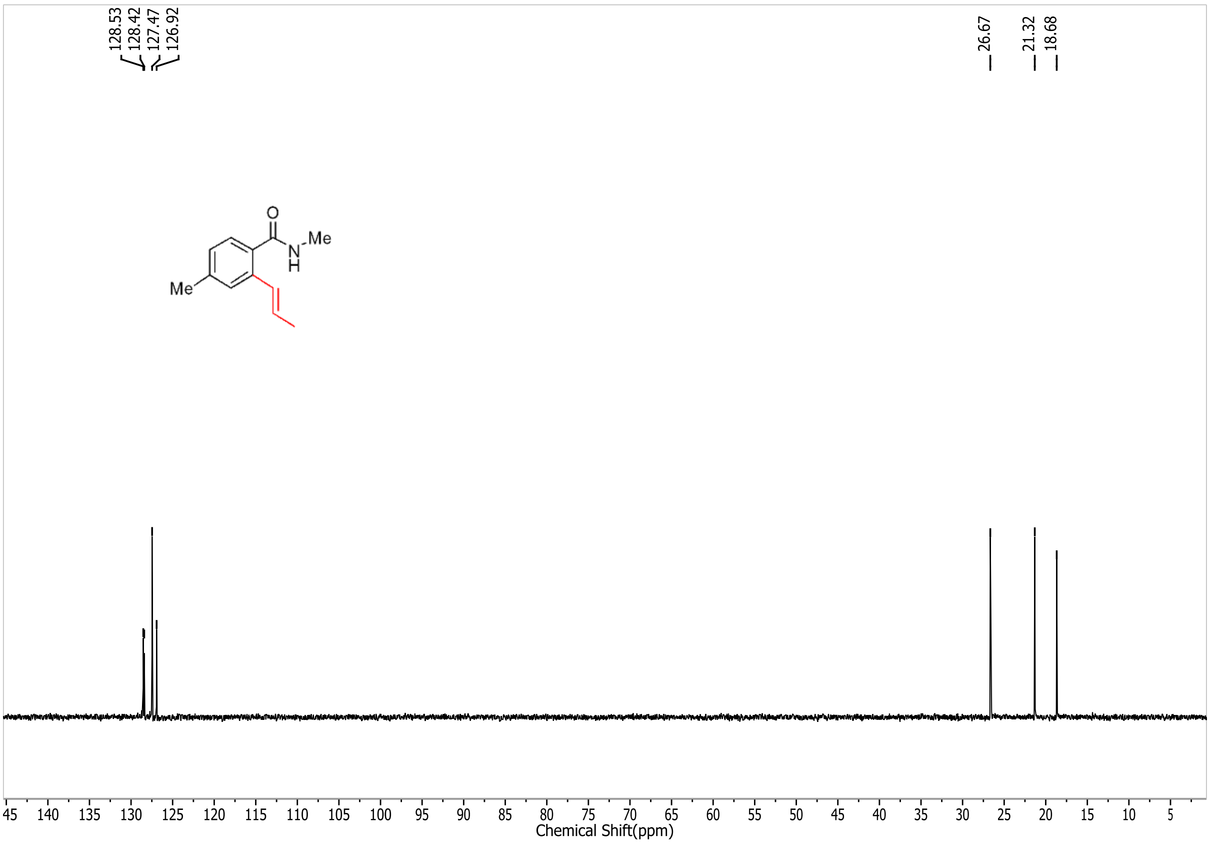
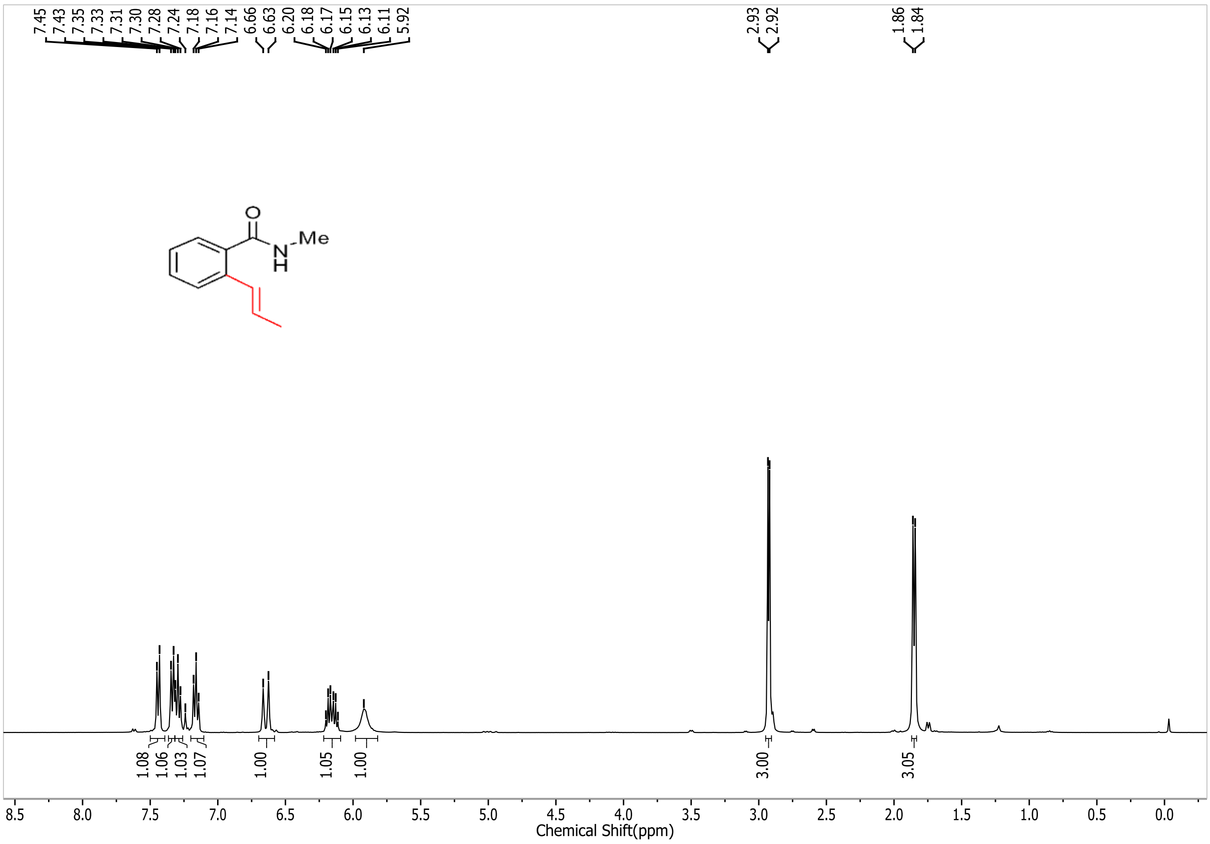
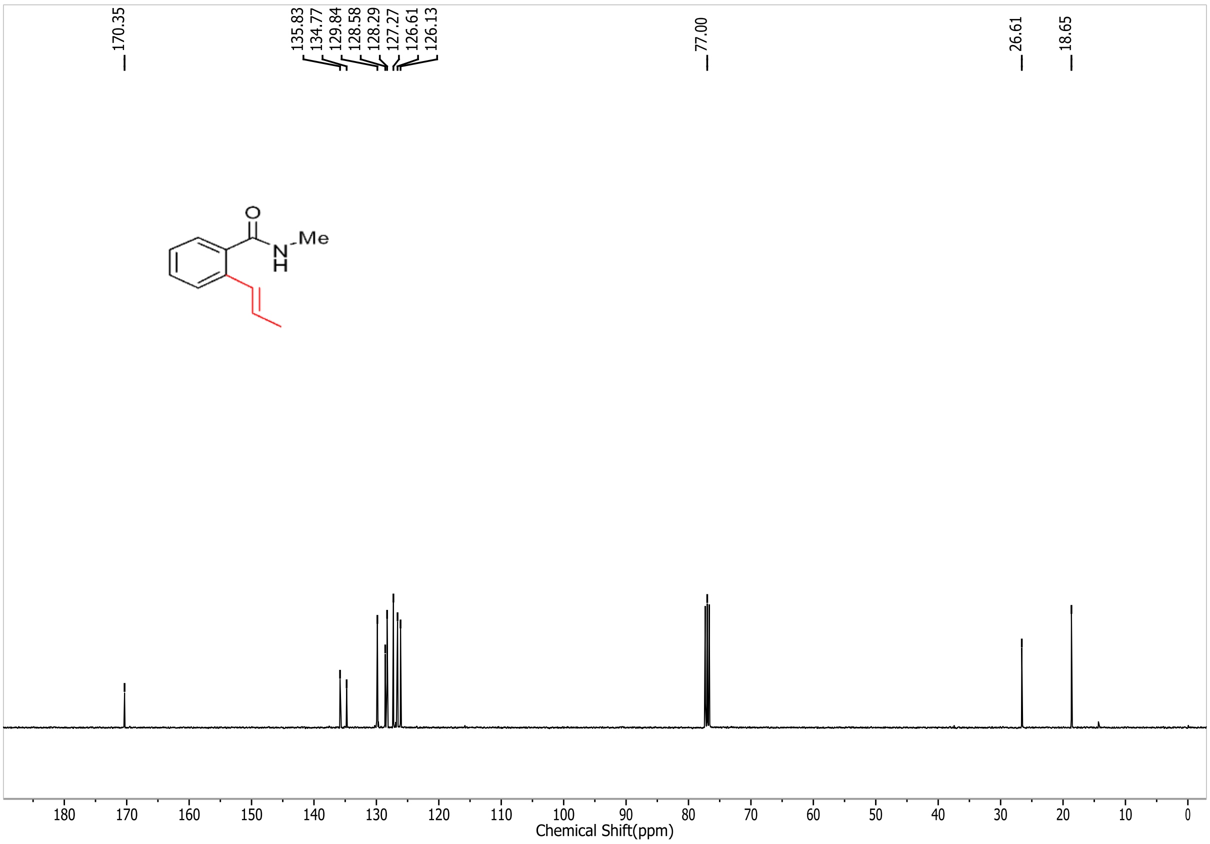
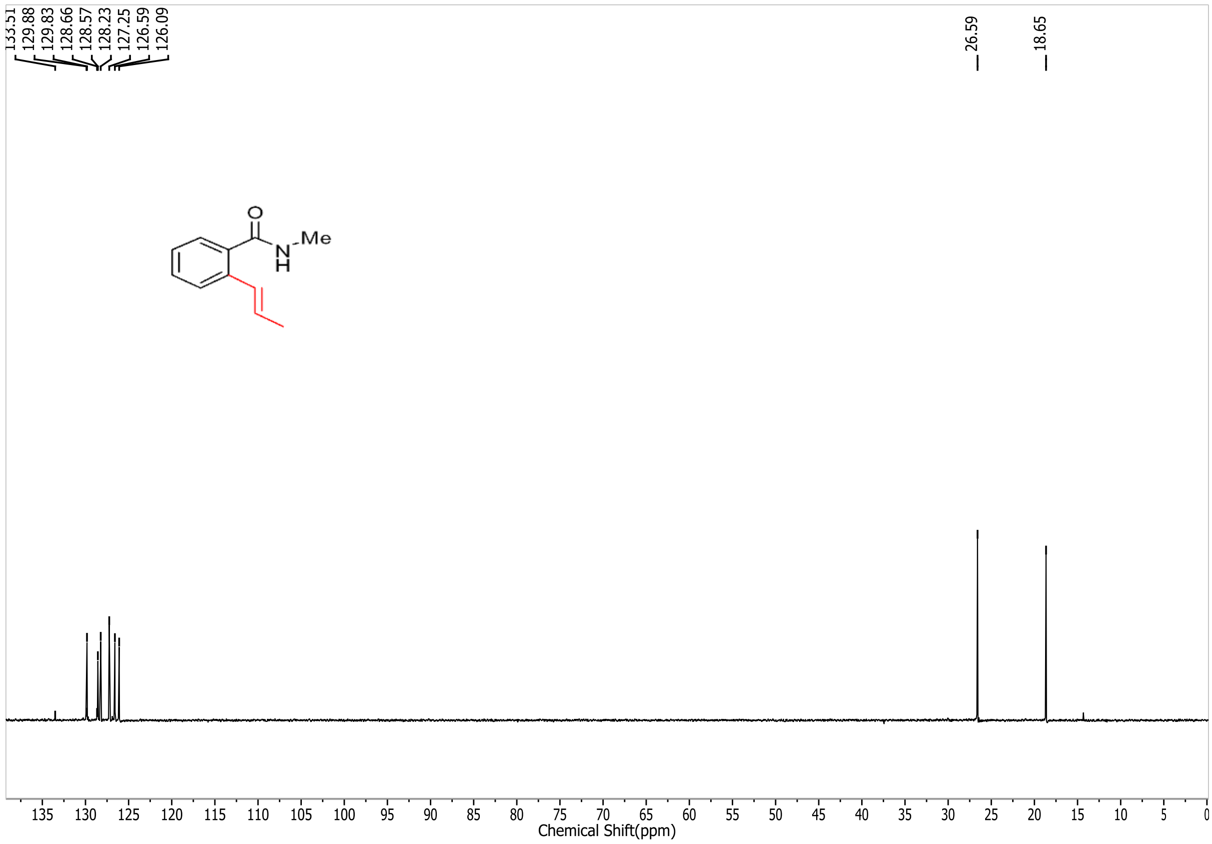


^{1}H and ^{13}C NMR Spectra of Compound **4ka.**

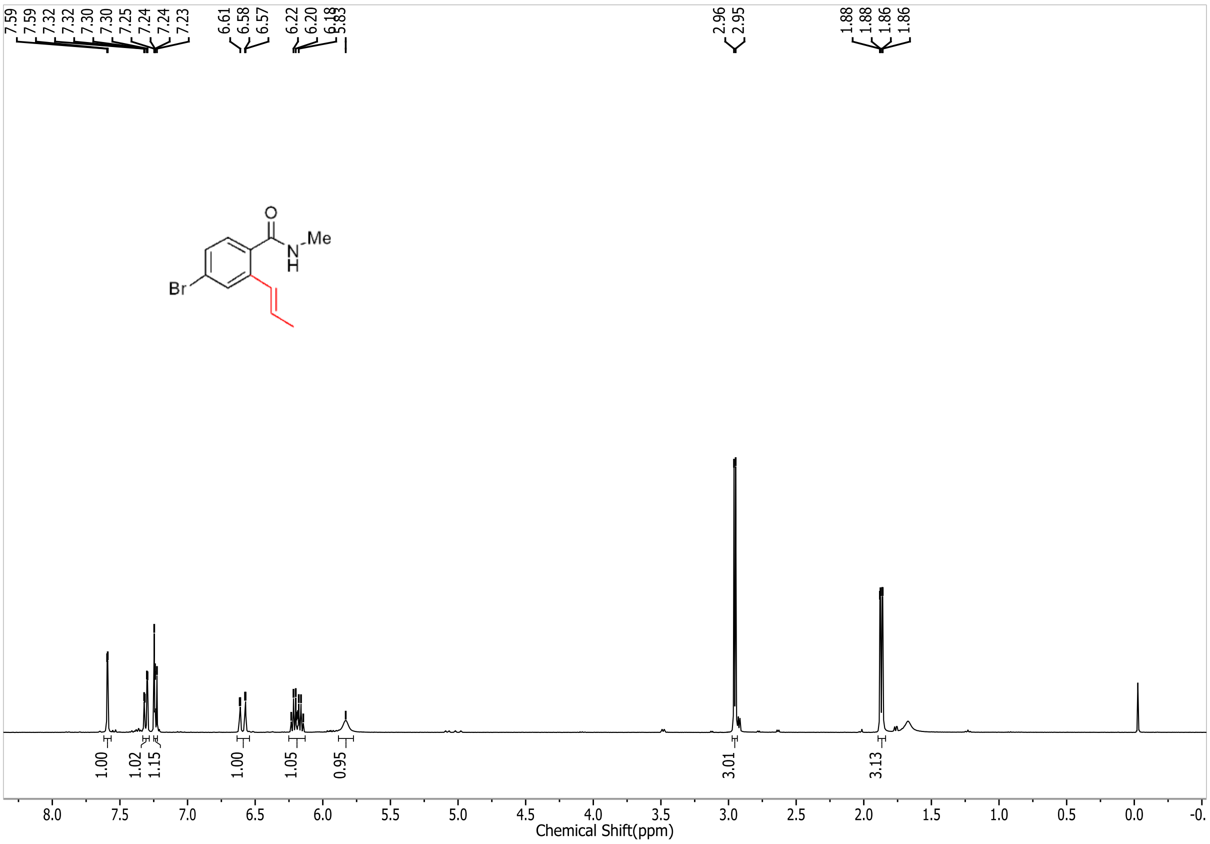


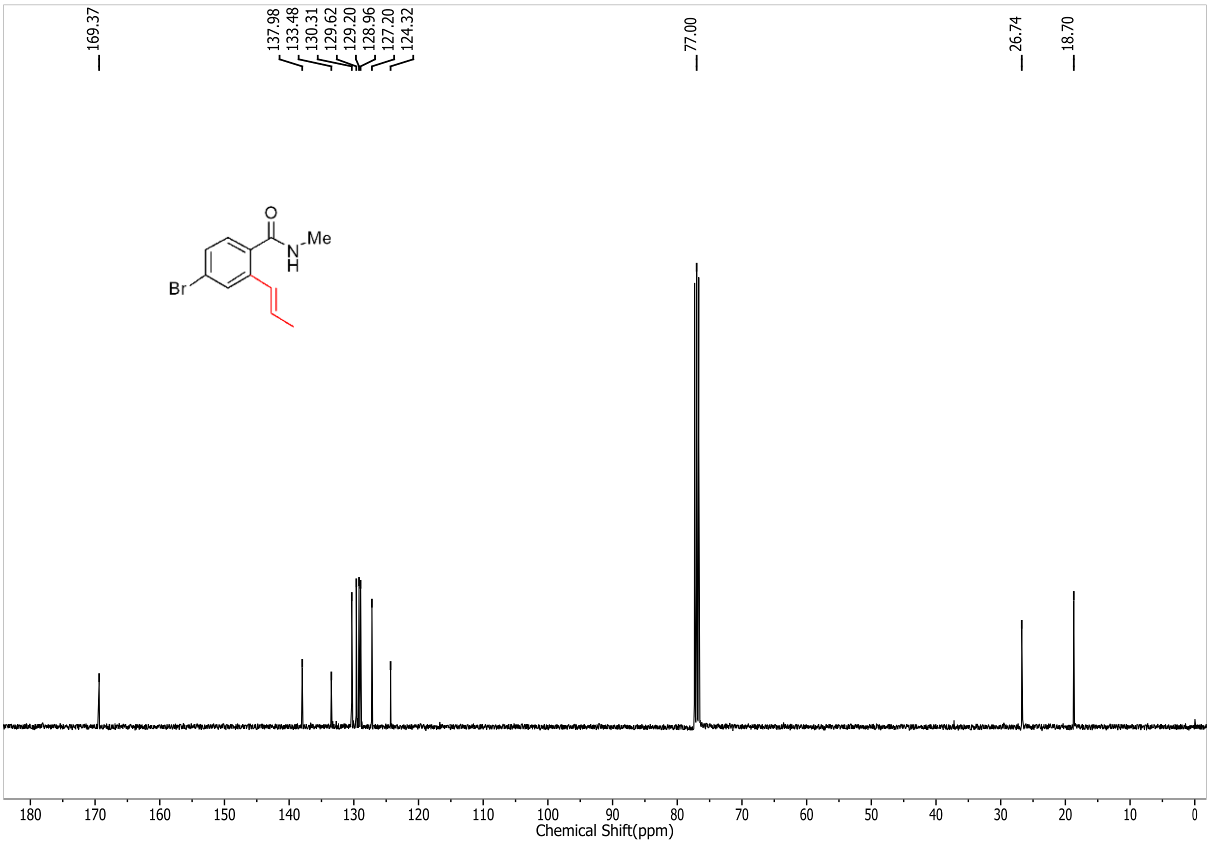


DEPT (135) NMR Spectrum of Compound **4ka.**



^{1}H and ^{13}C NMR Spectra of Compound **4la.**





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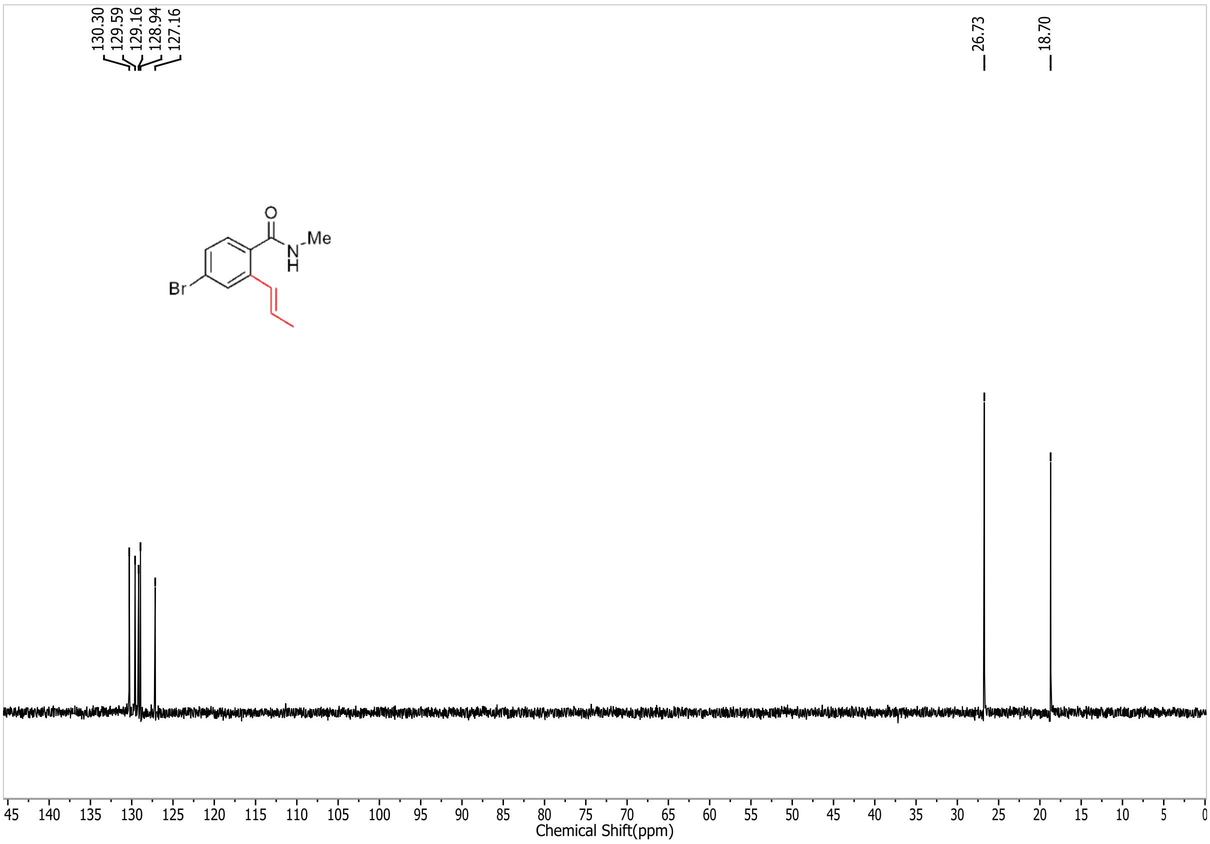
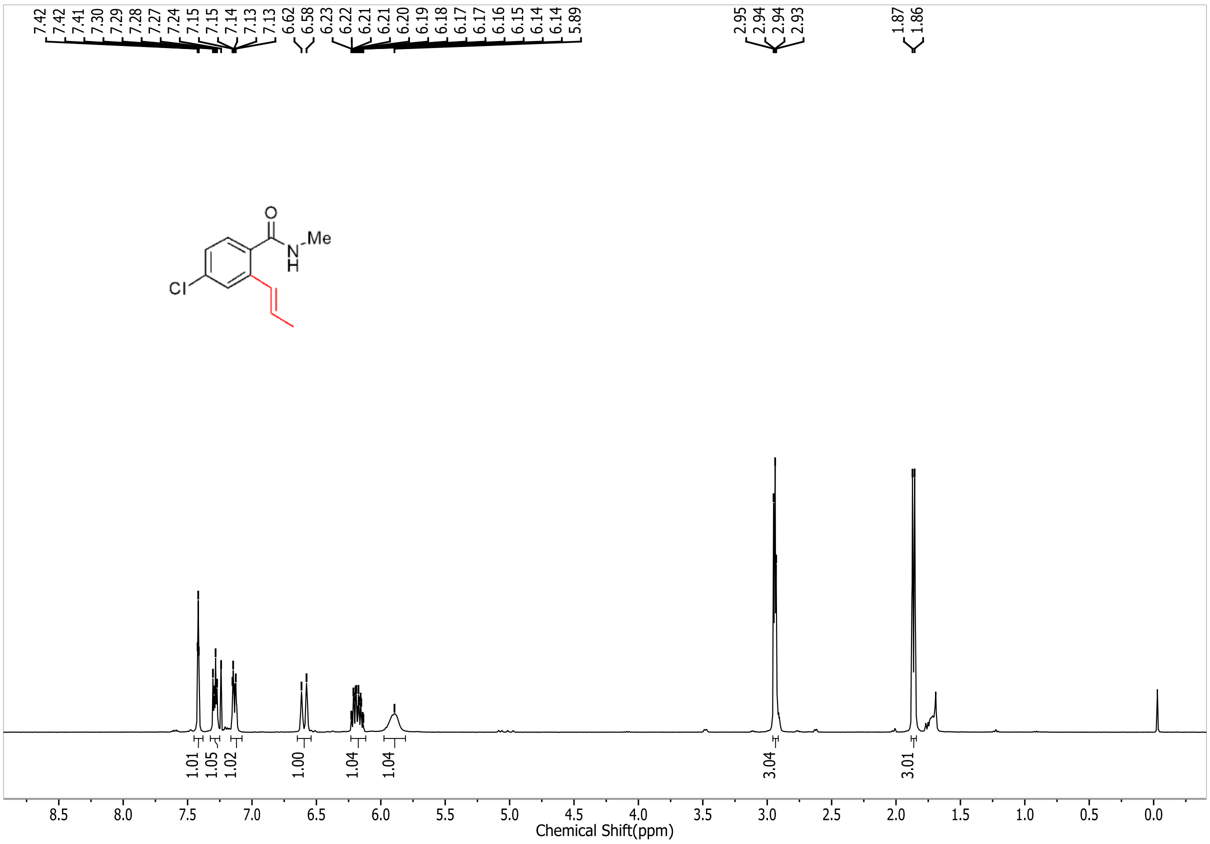
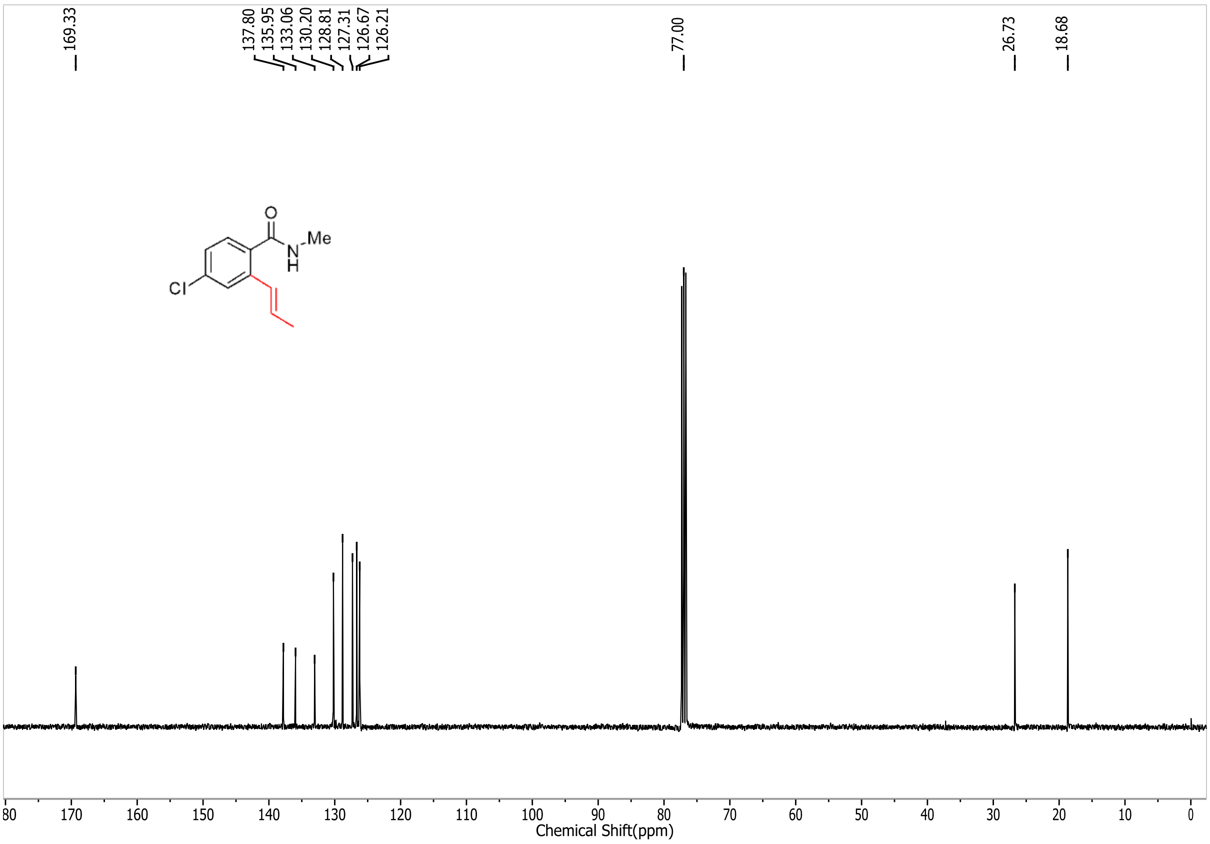
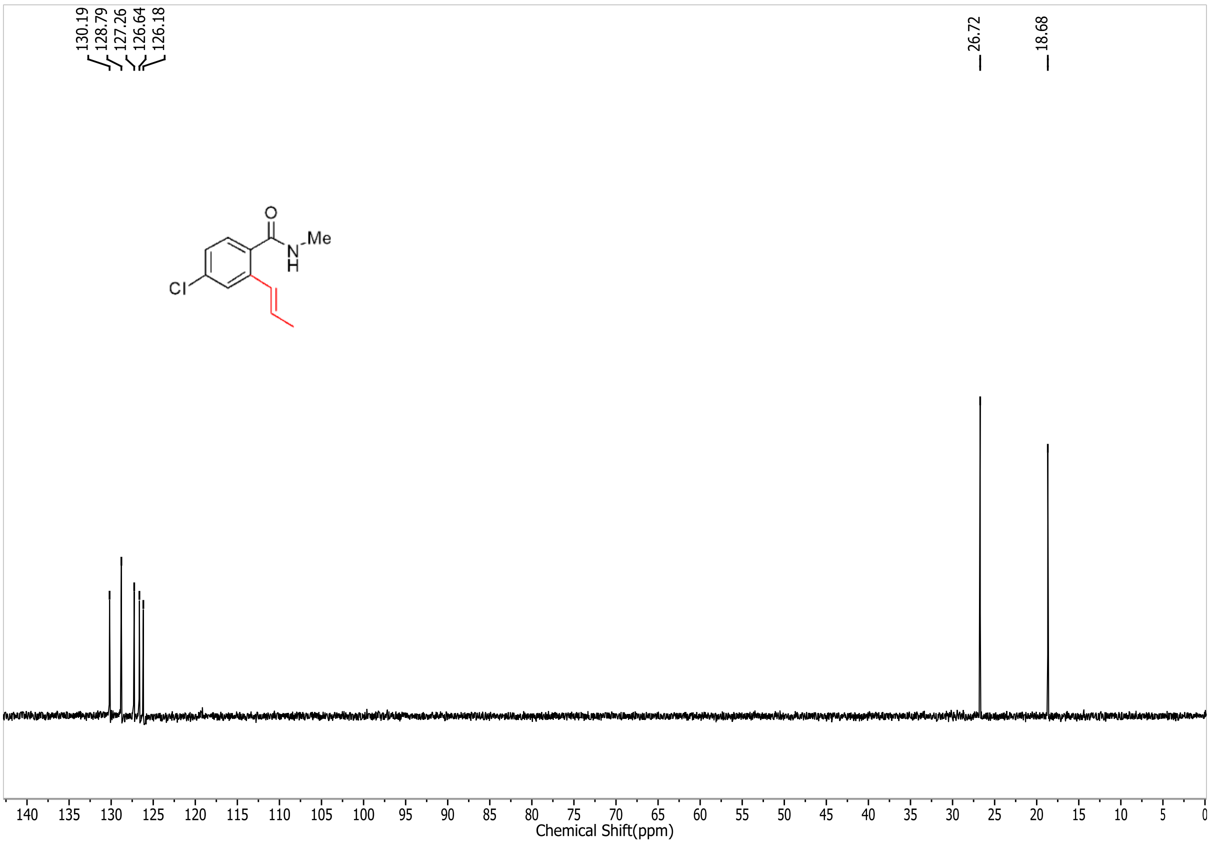


^{1}H and ^{13}C NMR Spectra of Compound **4ma.**

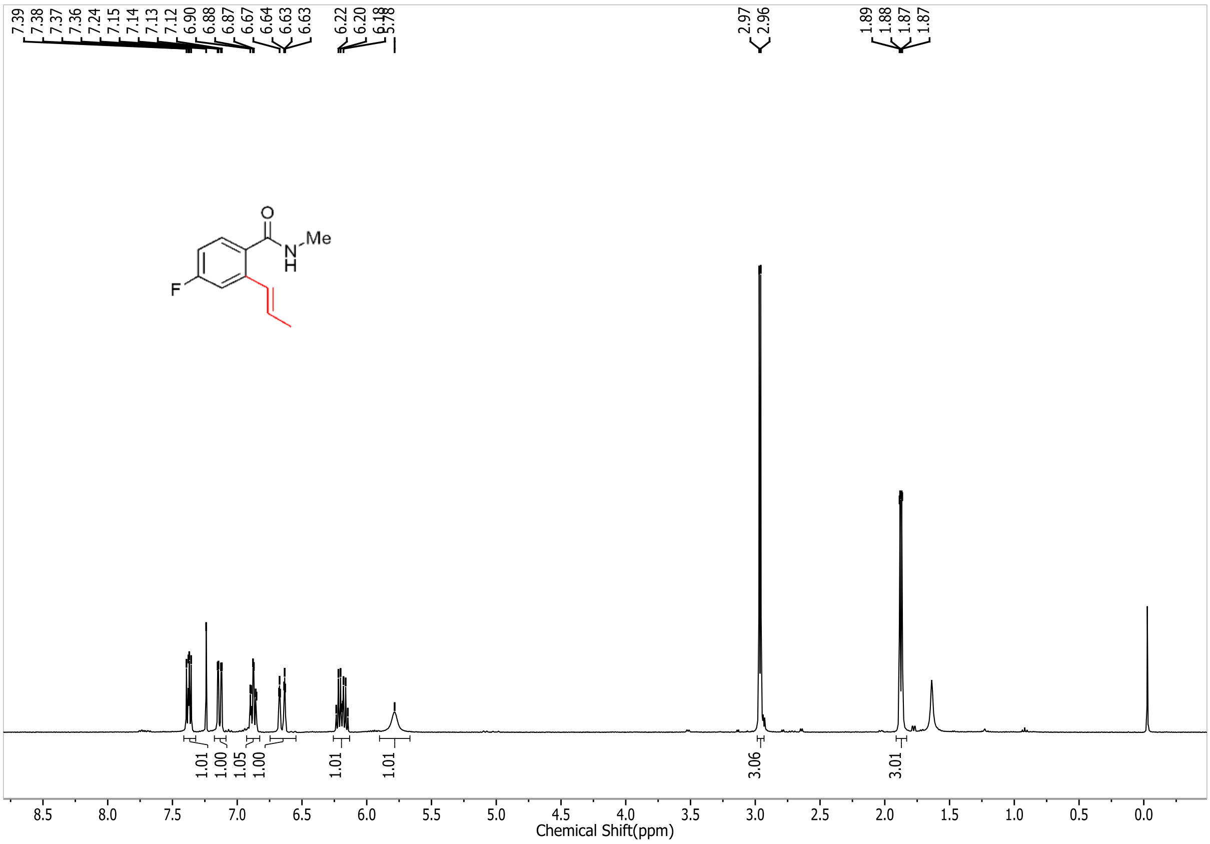


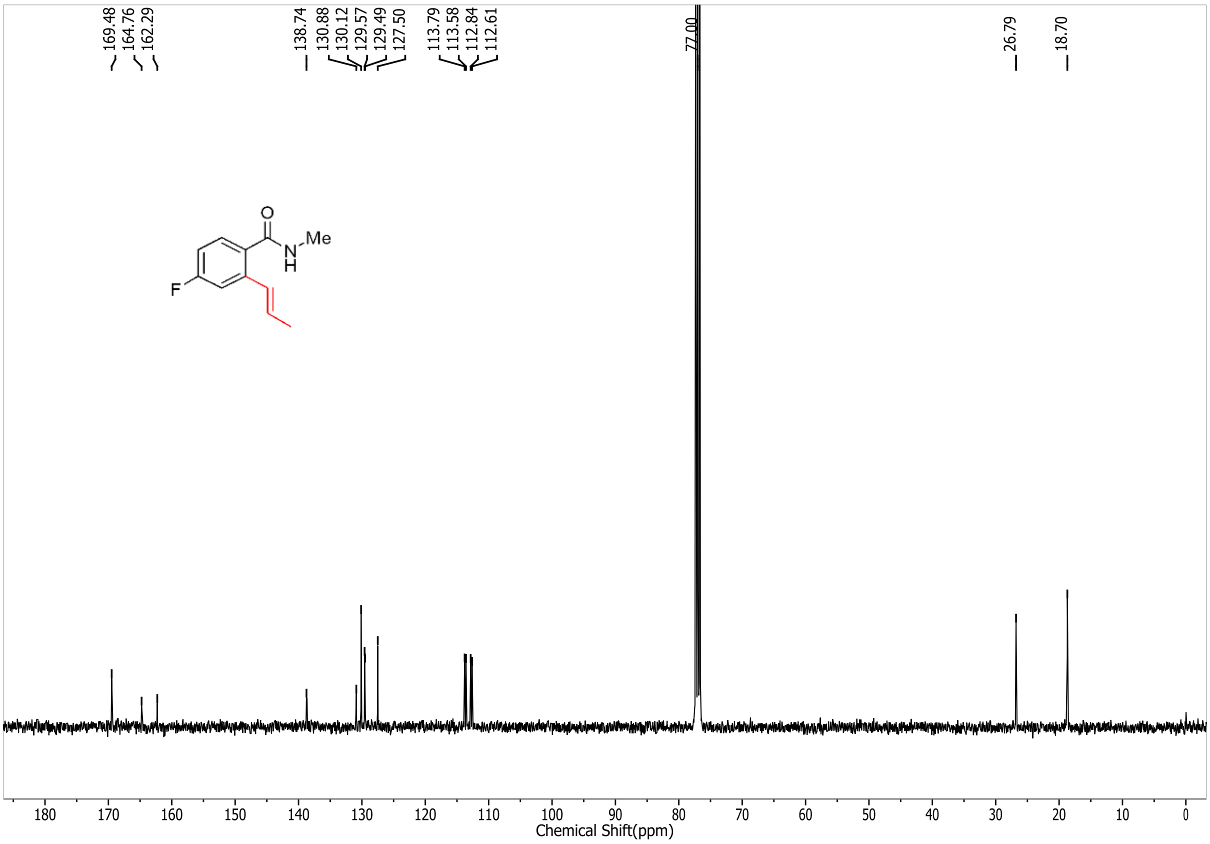


DEPT (135) NMR Spectrum of Compound **4ma.**

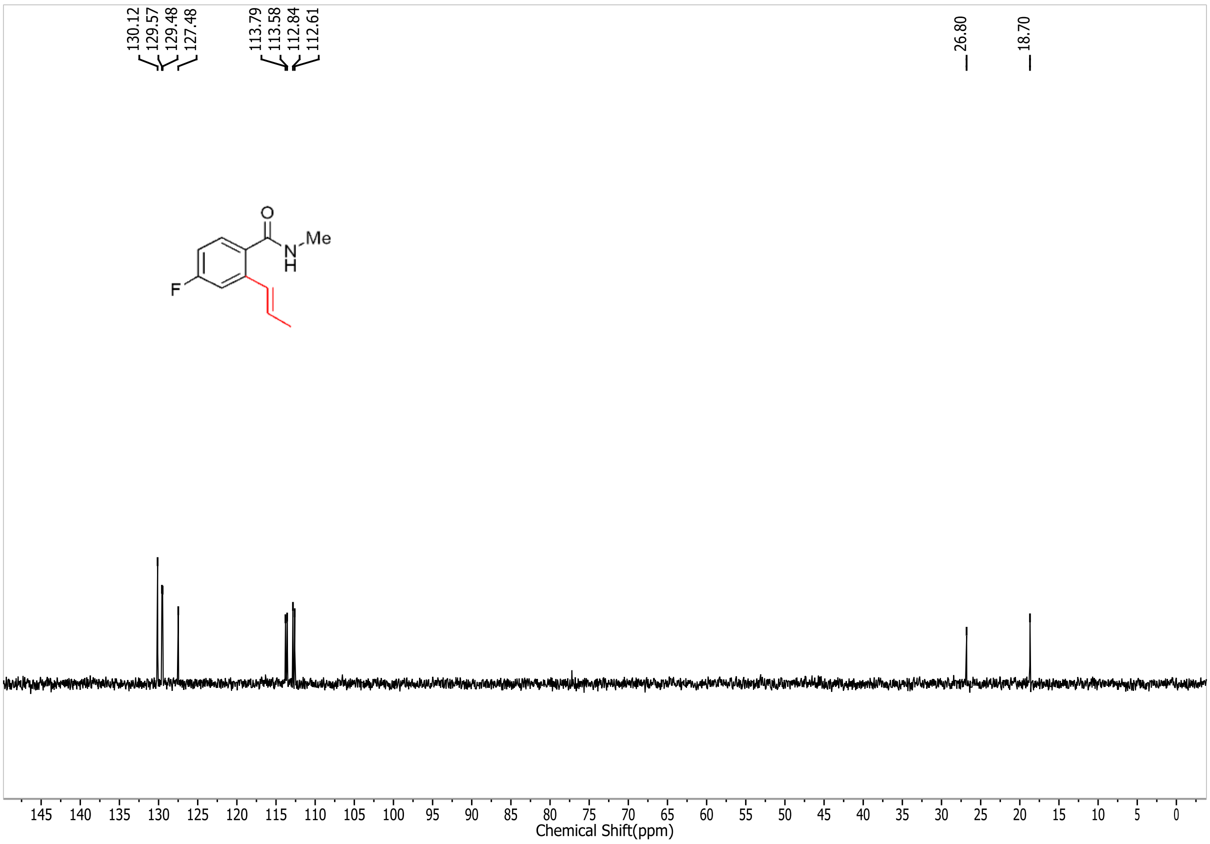


^{1}H and ^{13}C NMR Spectra of Compound **4na.**

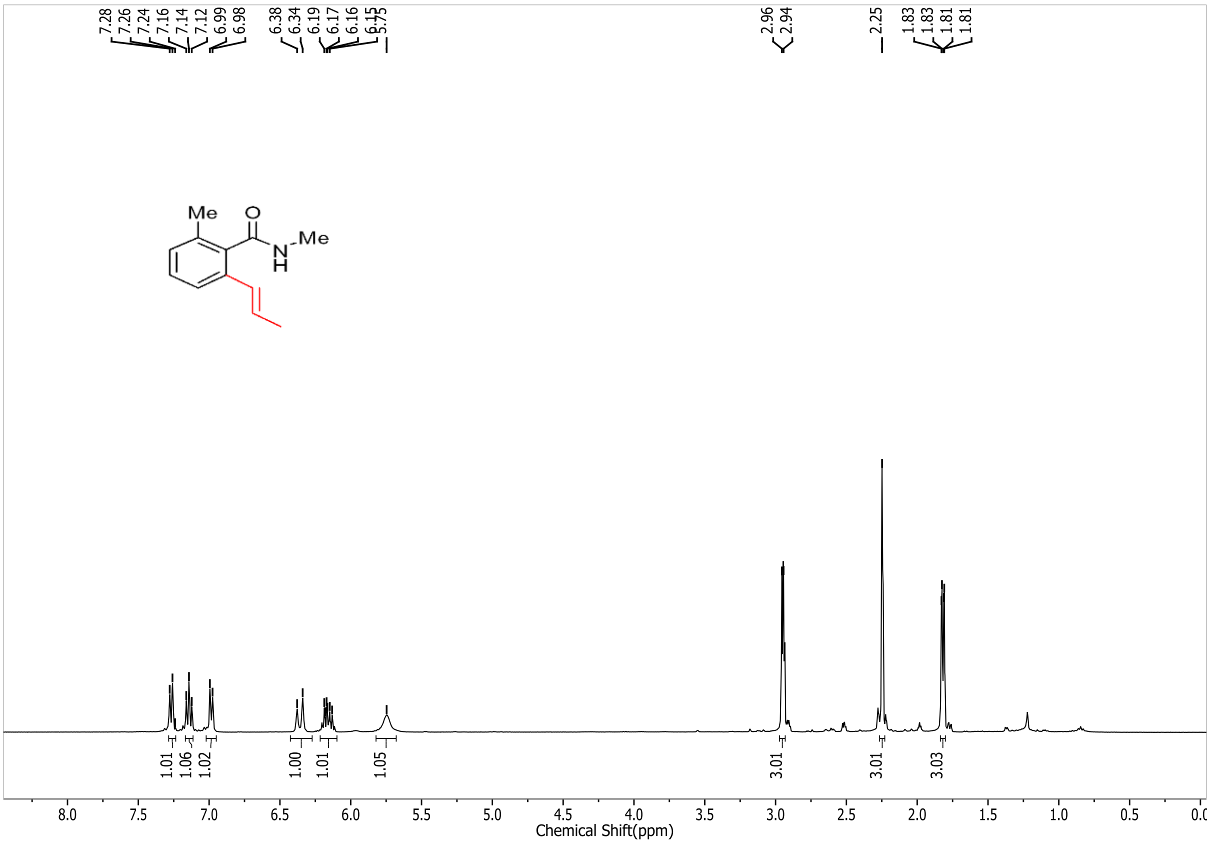


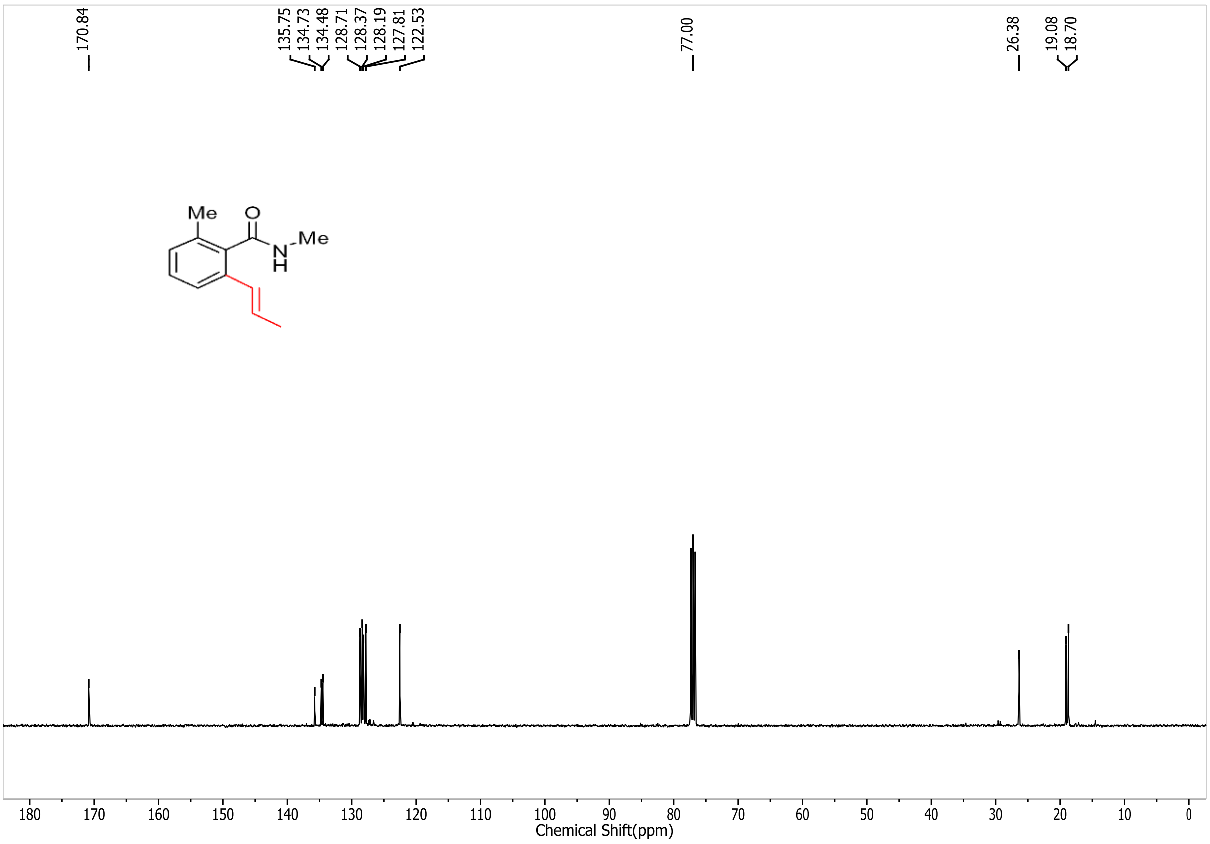


DEPT (135) NMR Spectrum of Compound **4na.**

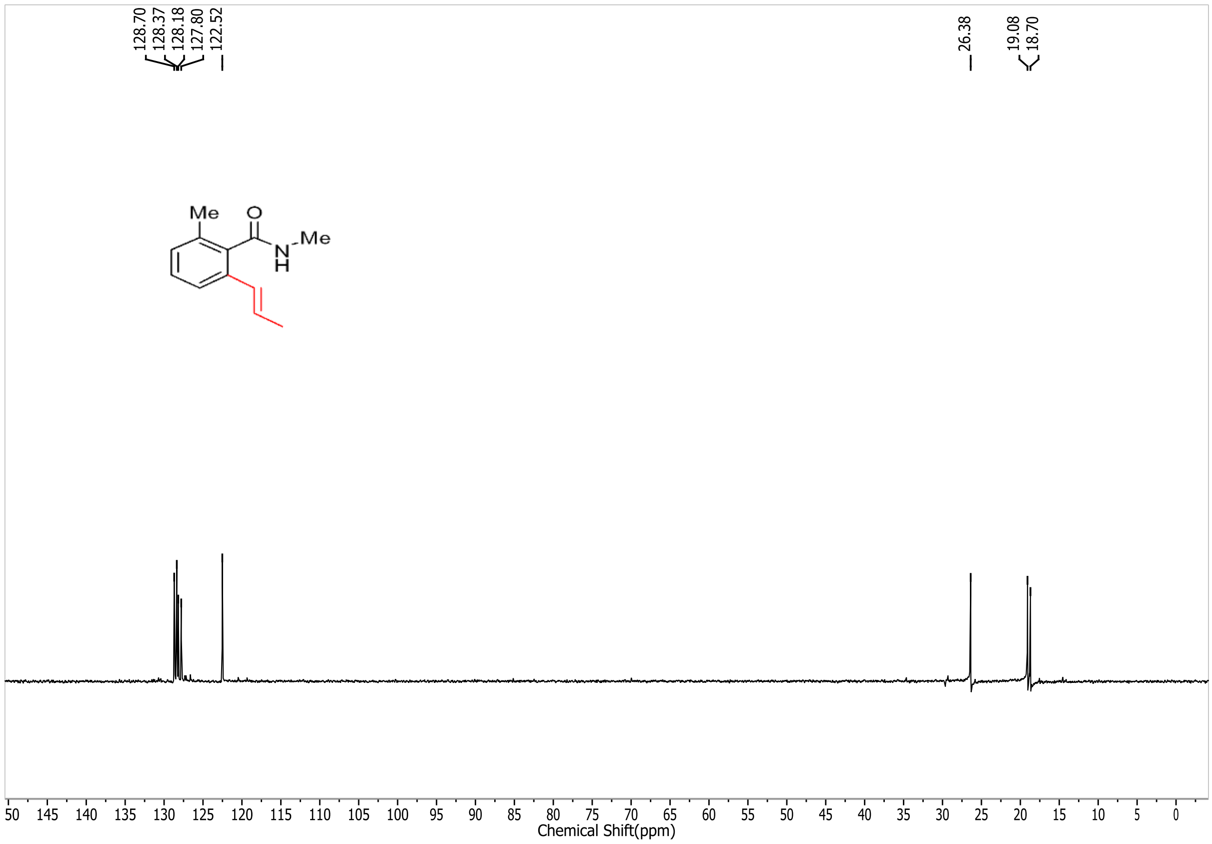


^{1}H and ^{13}C NMR Spectra of Compound **4oa.**

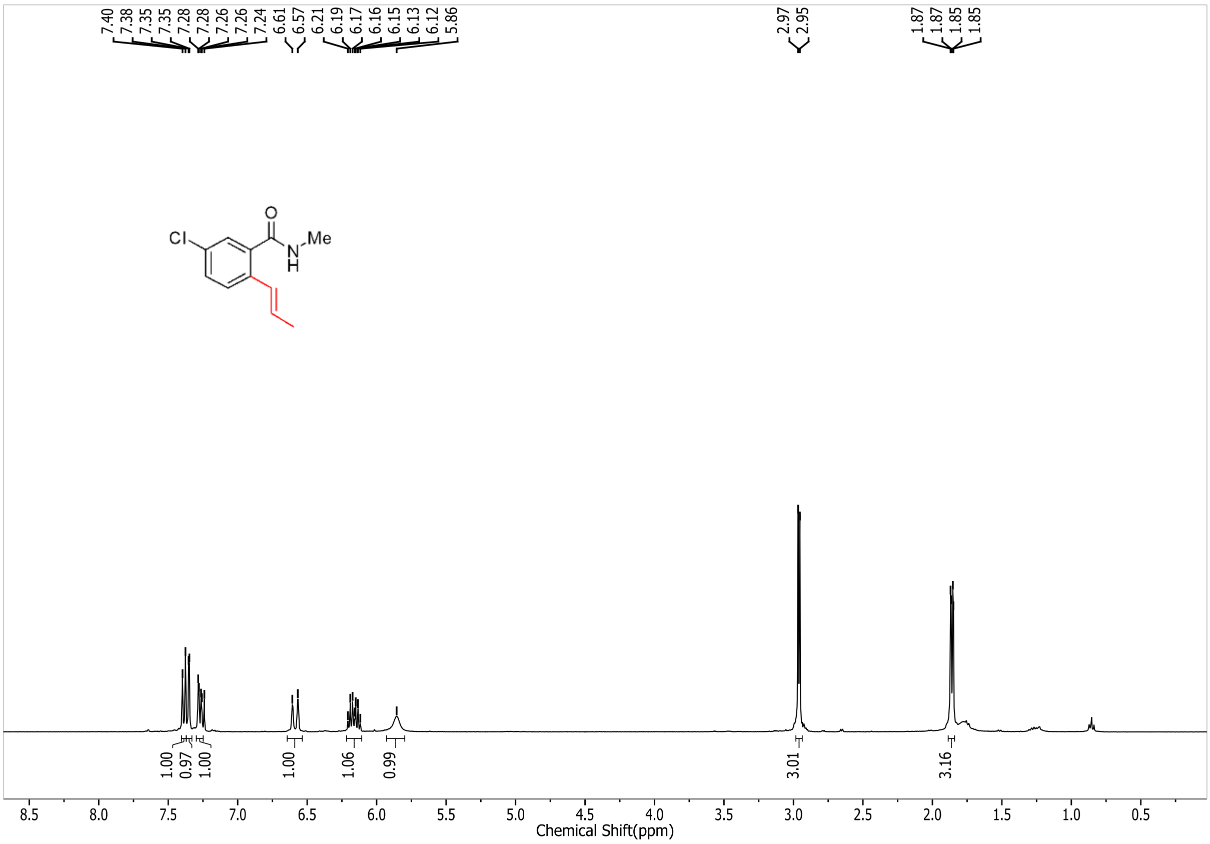


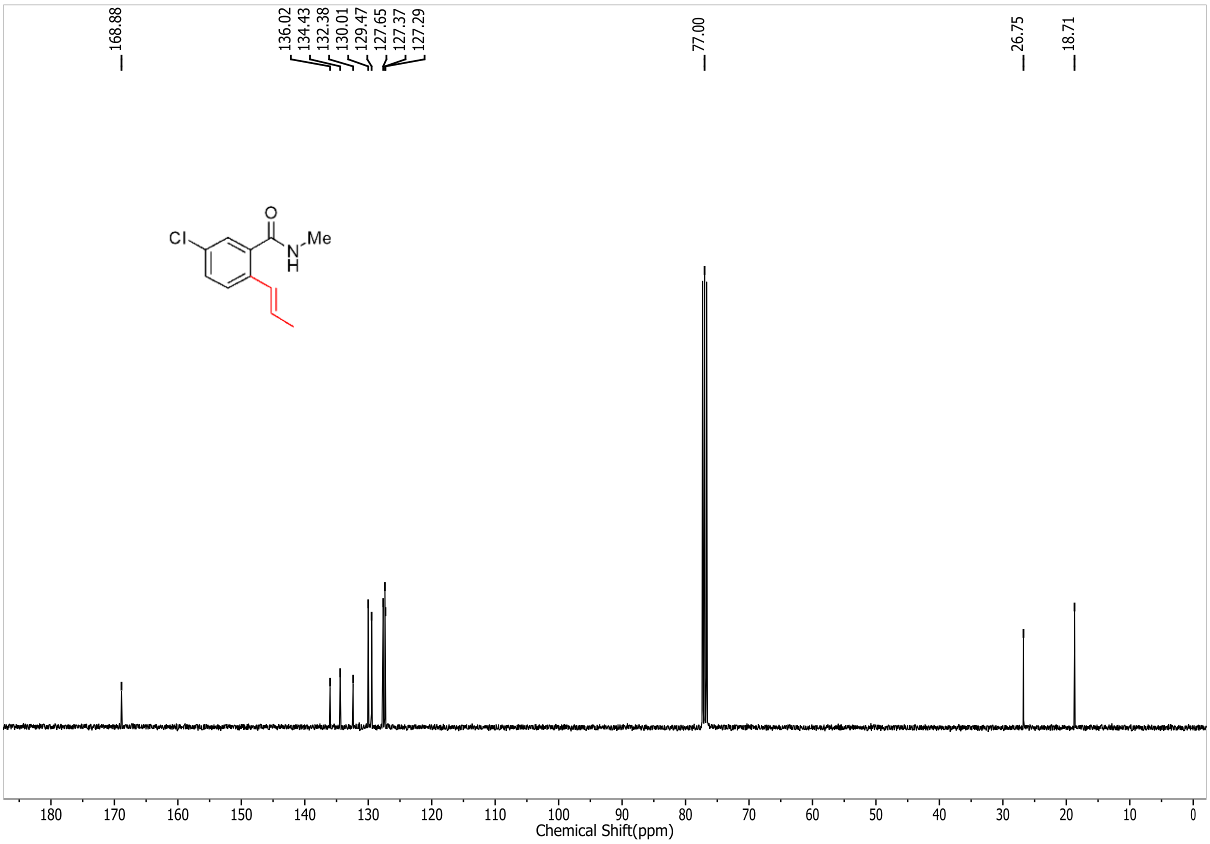


DEPT (135) NMR Spectrum of Compound **4oa.**

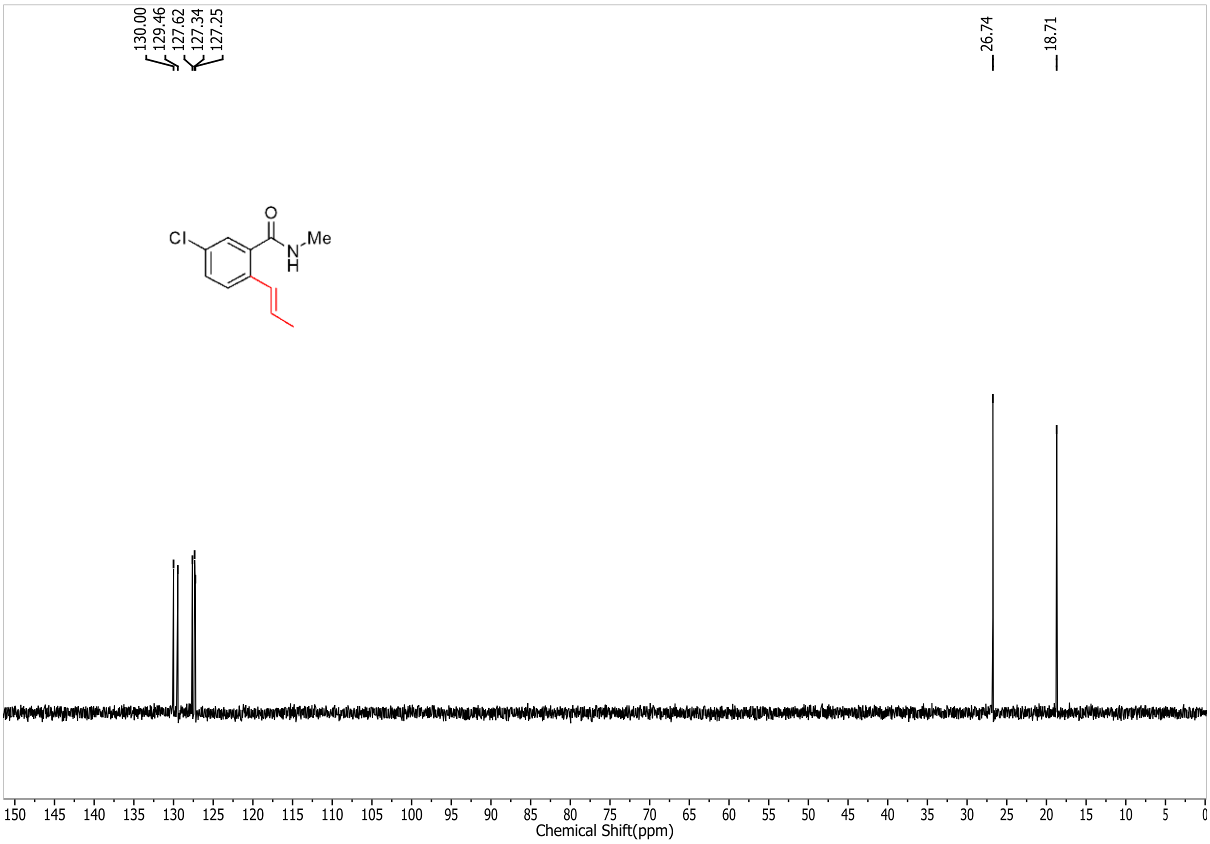


^{1}H and ^{13}C NMR Spectra of Compound **4pa.**





DEPT (135) NMR Spectrum of Compound **4pa.**



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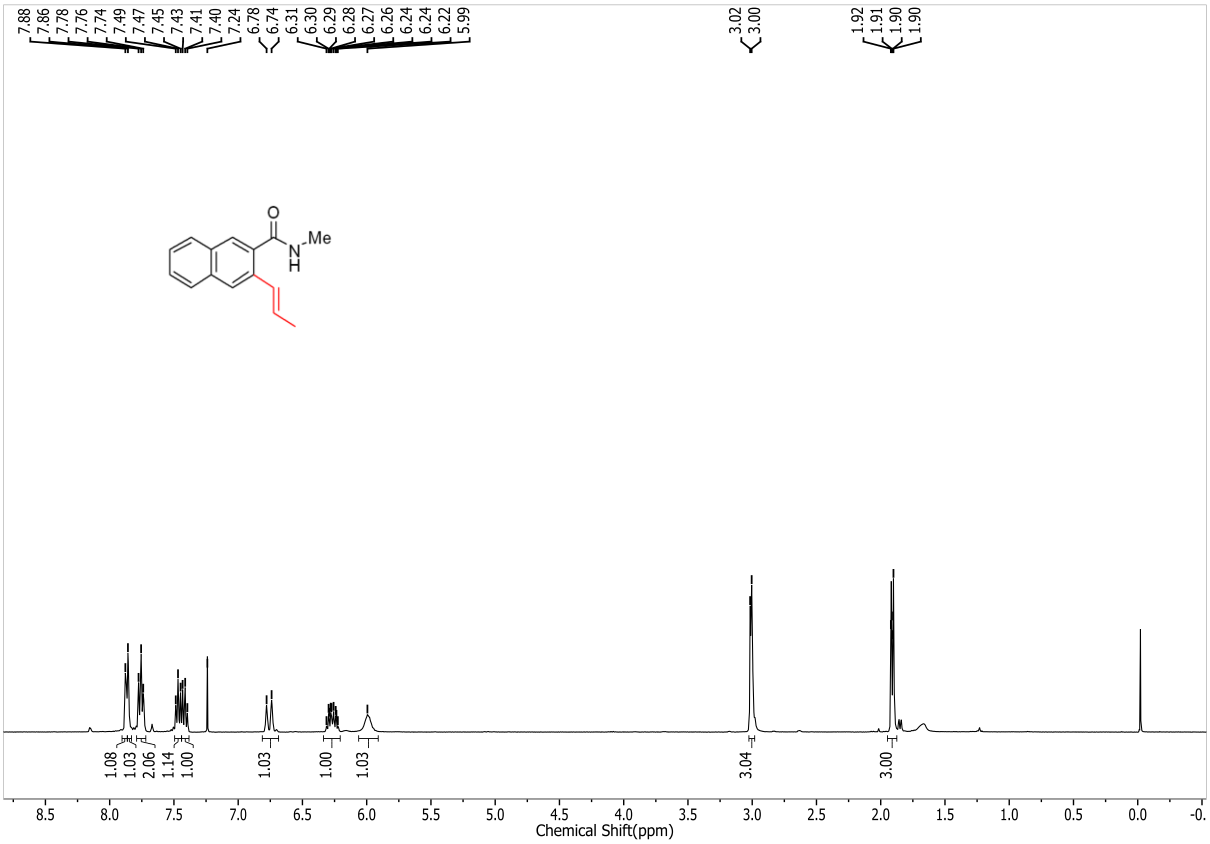
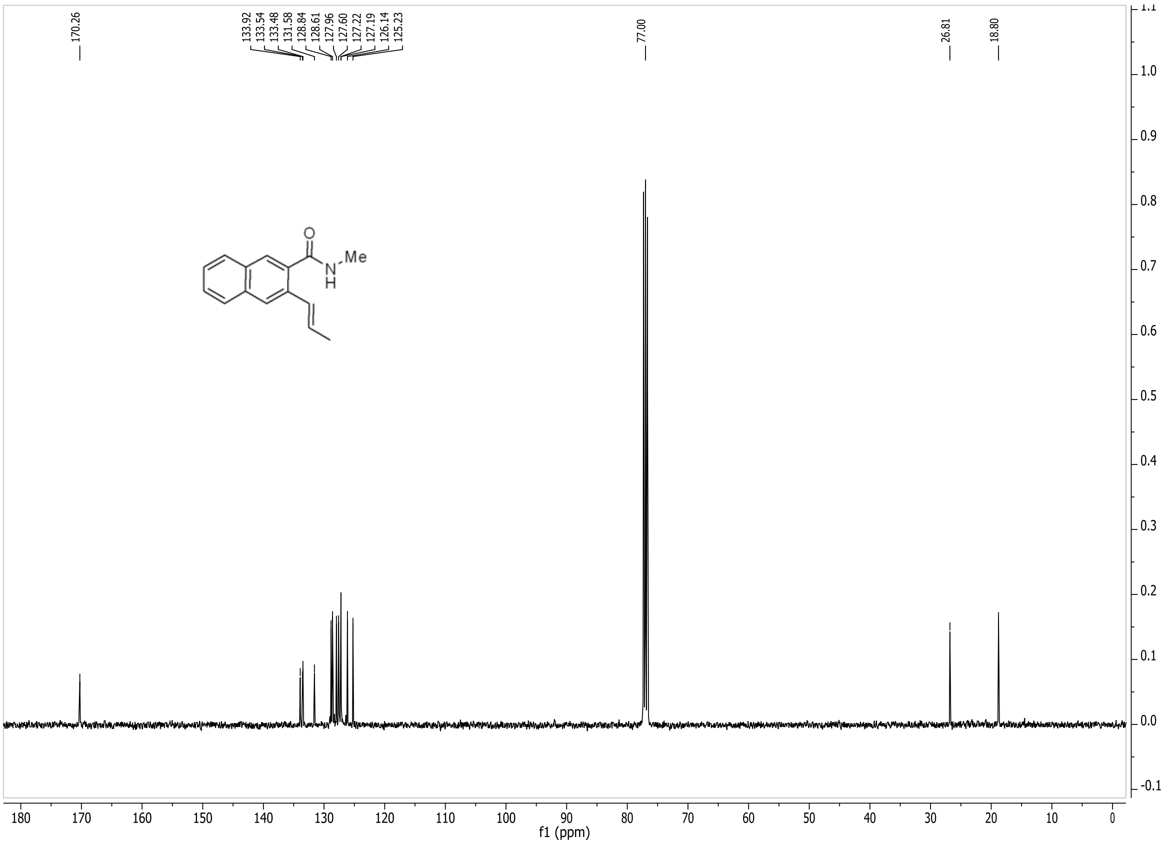
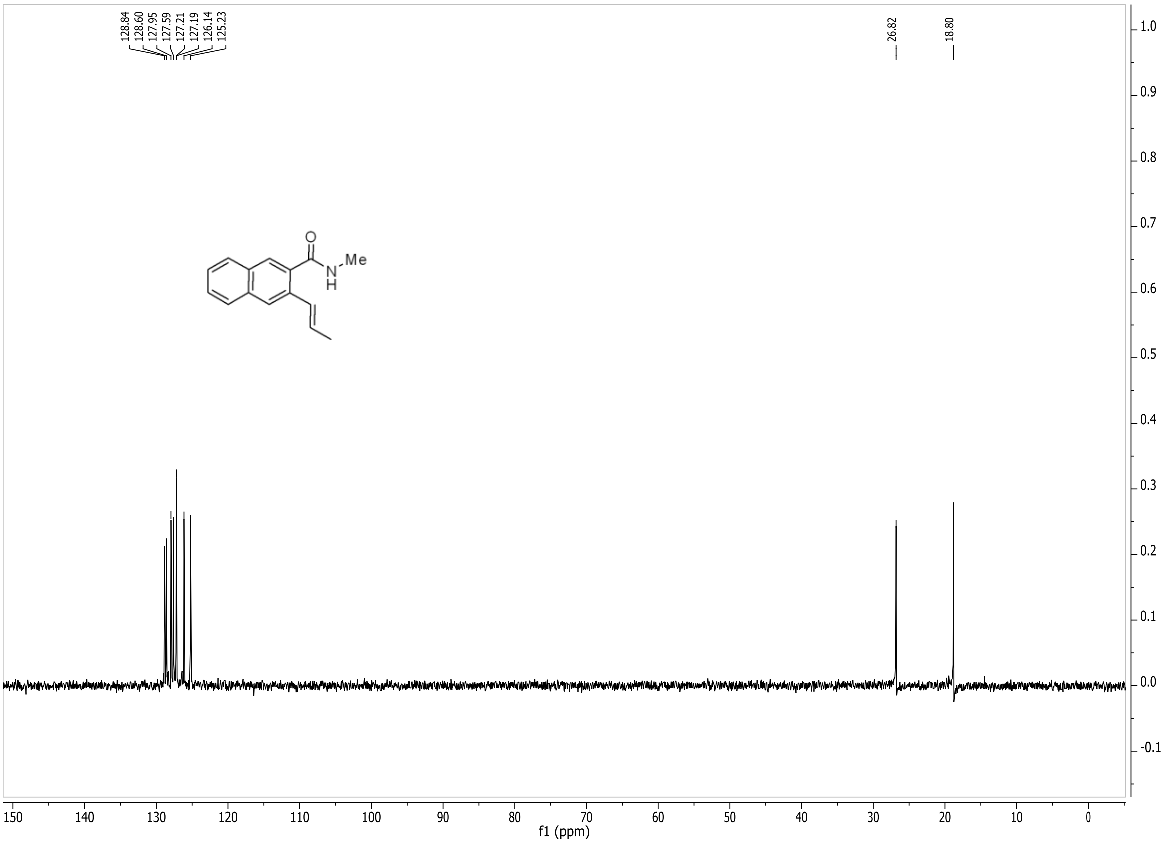
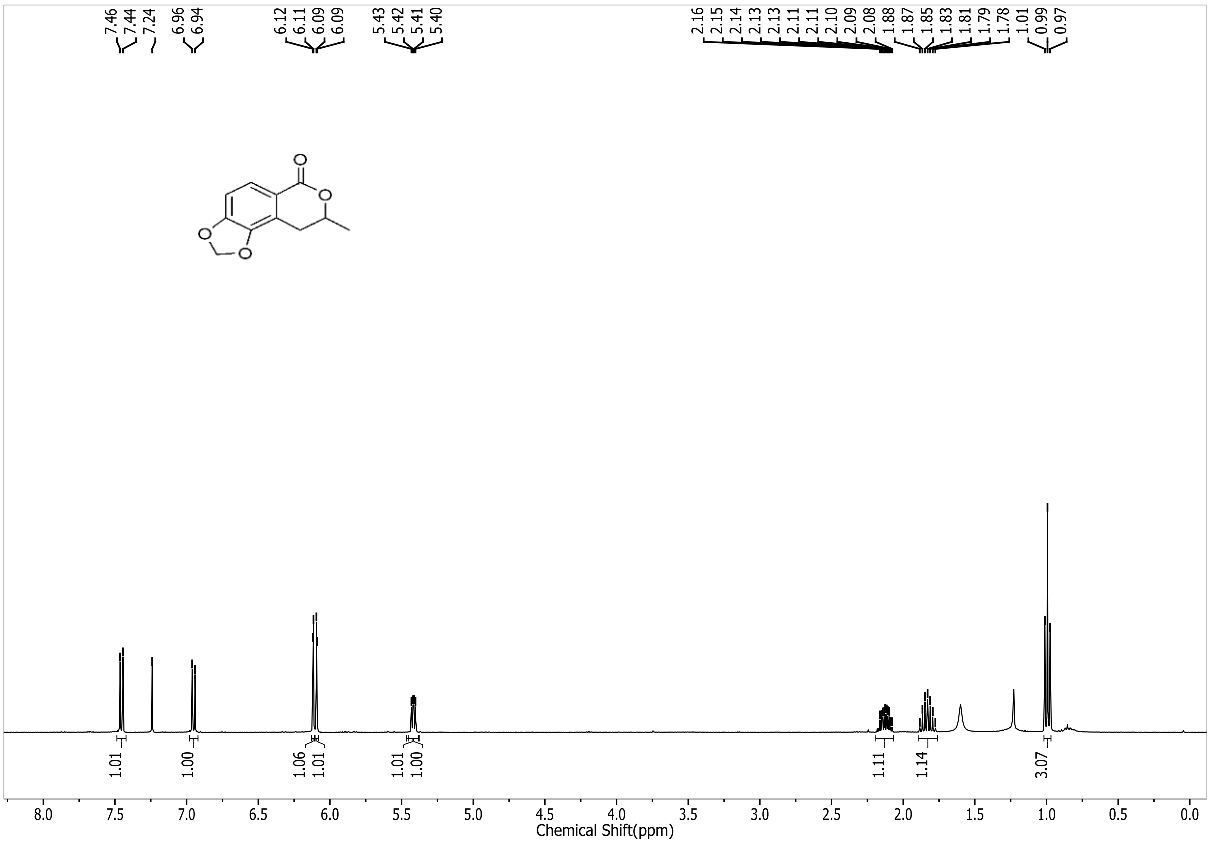


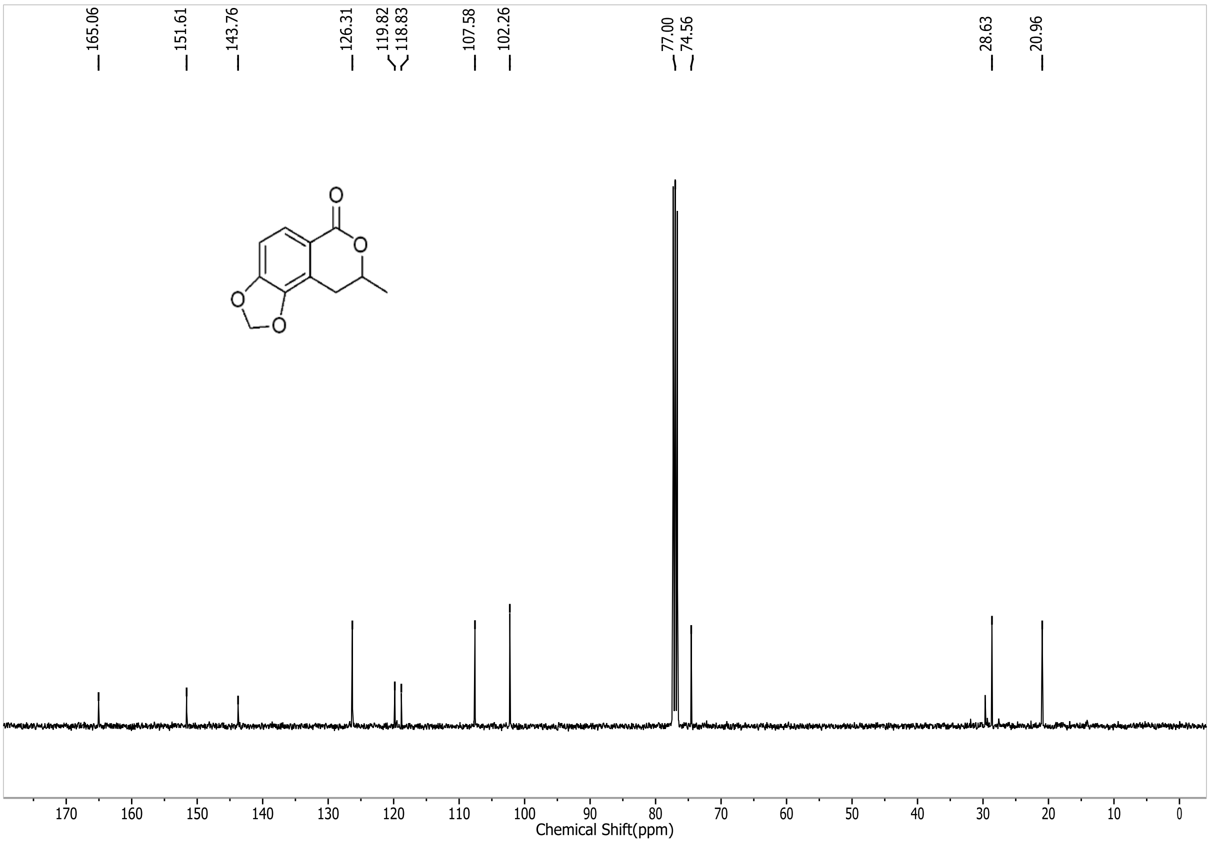


DEPT (135) NMR Spectrum of Compound **4qa.**

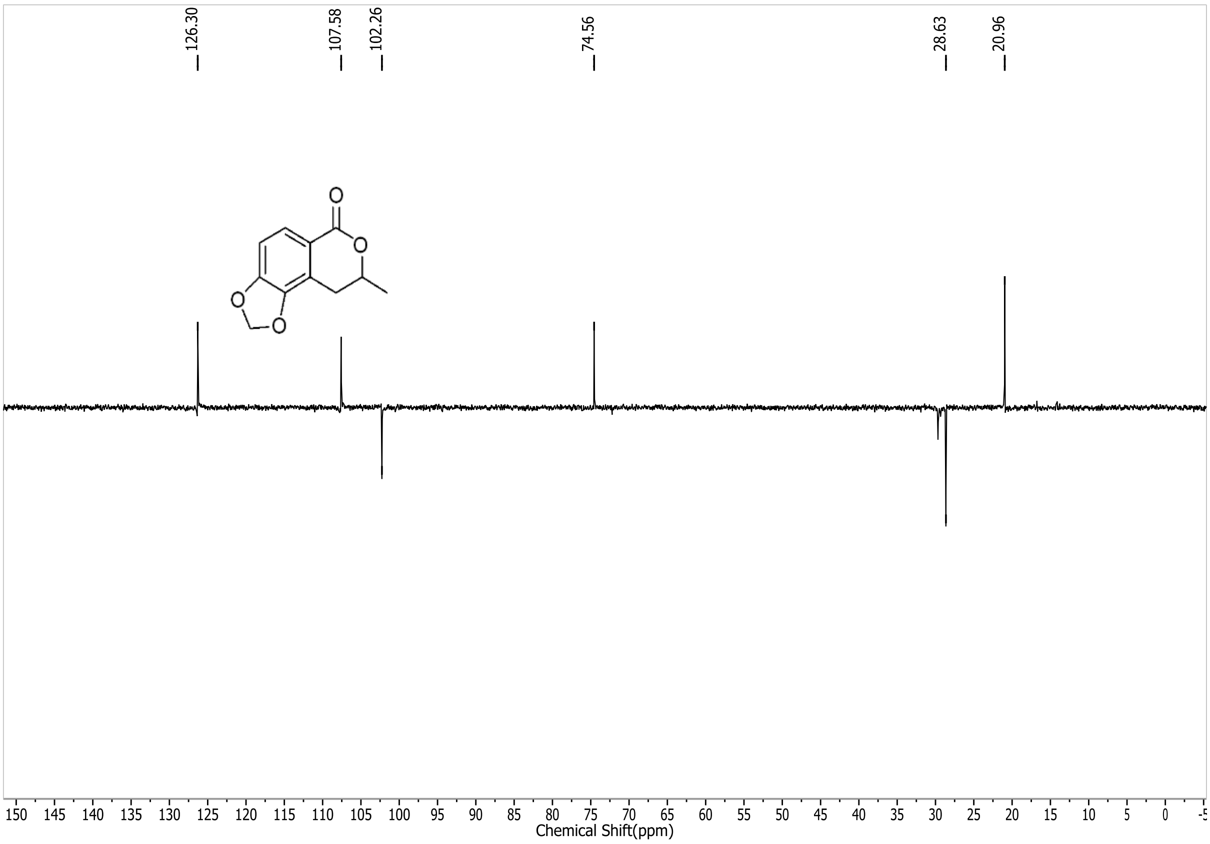


^{1}H and ^{13}C NMR Spectra of Compound **5a.**

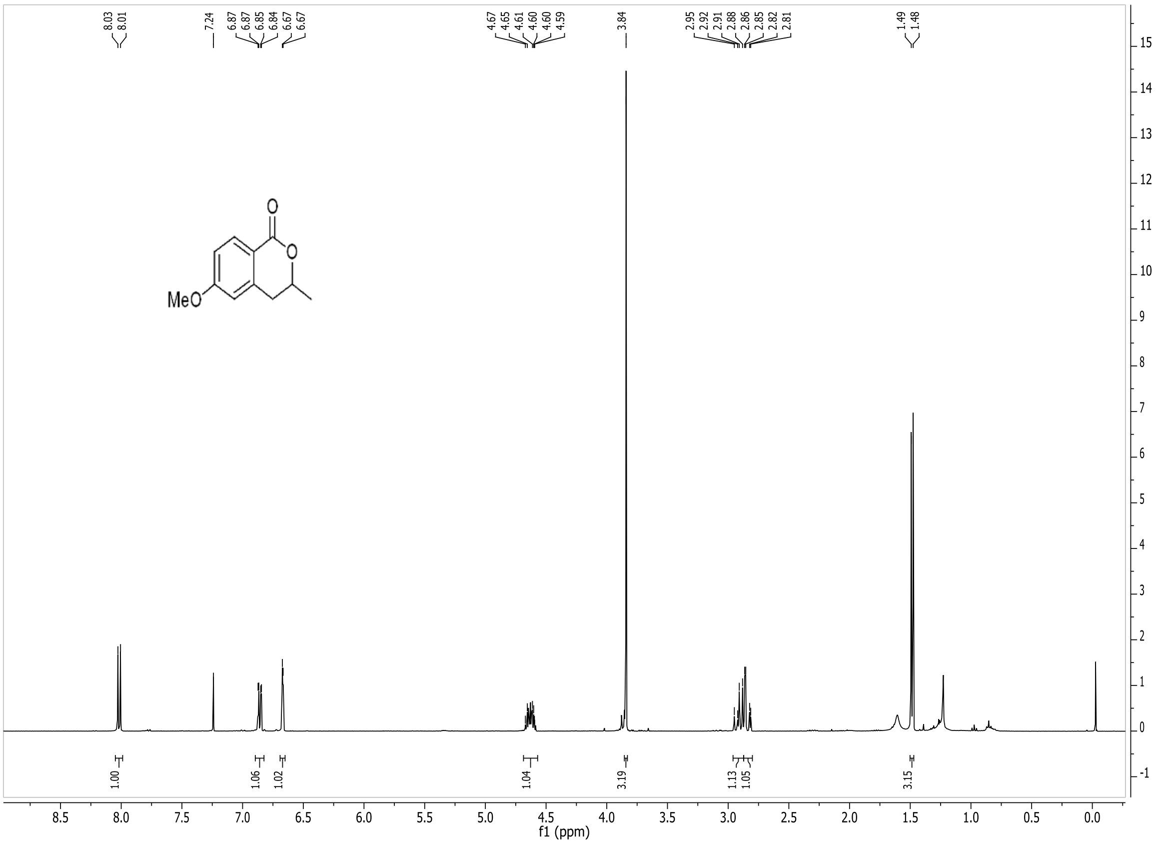


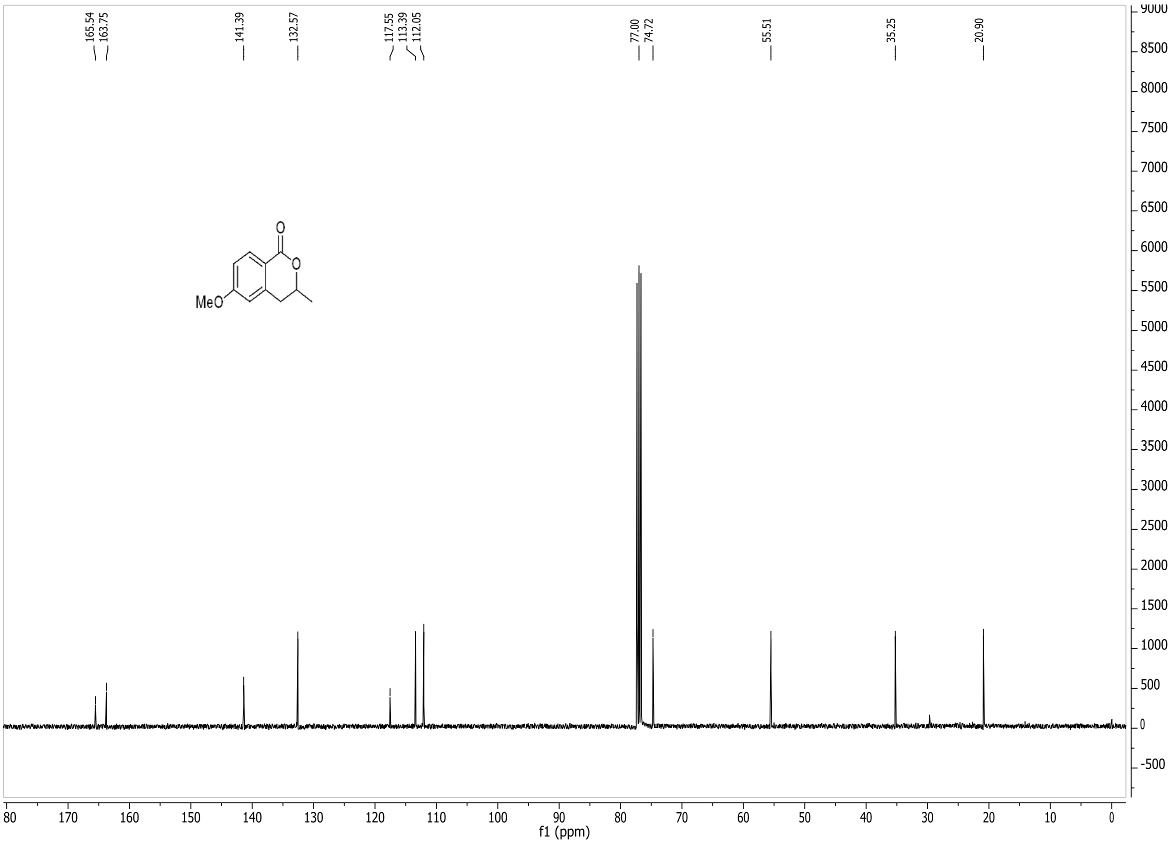


DEPT (135) NMR Spectrum of Compound **5a.**

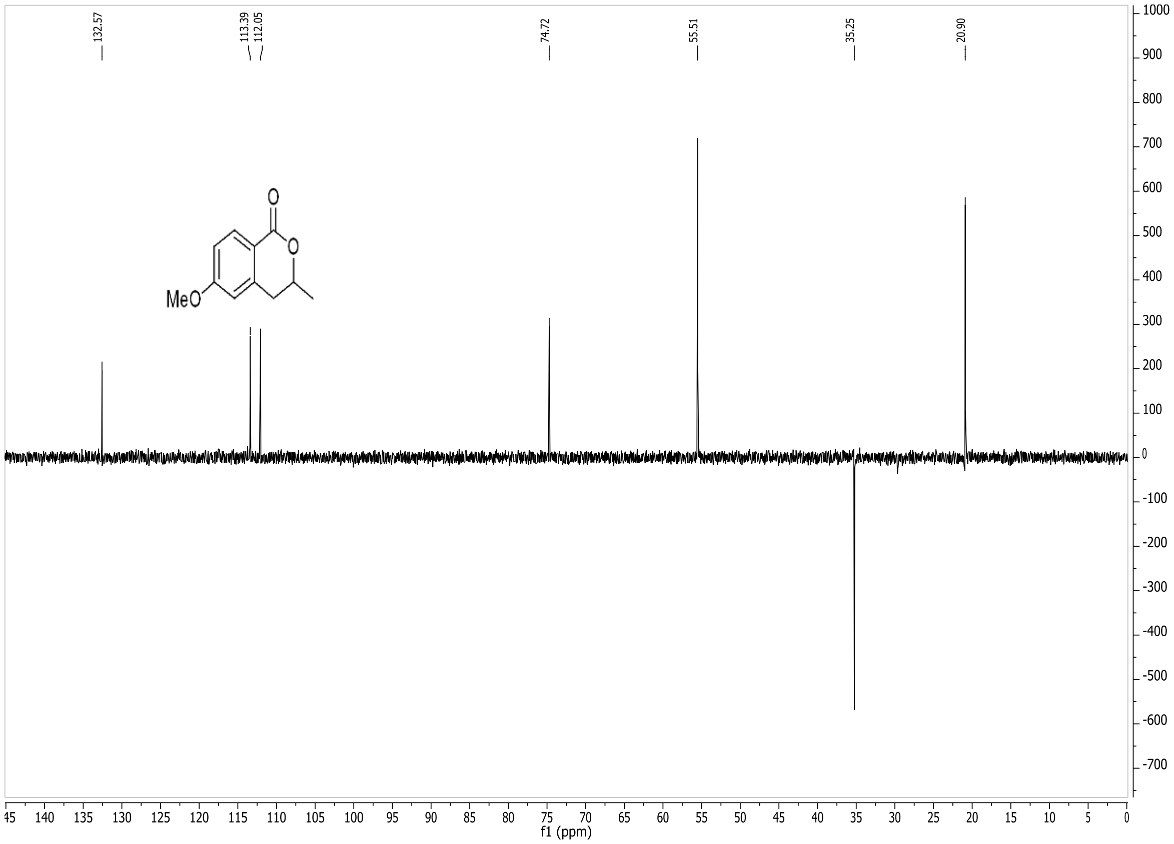


^{1}H and ^{13}C NMR Spectra of Compound **5b.**

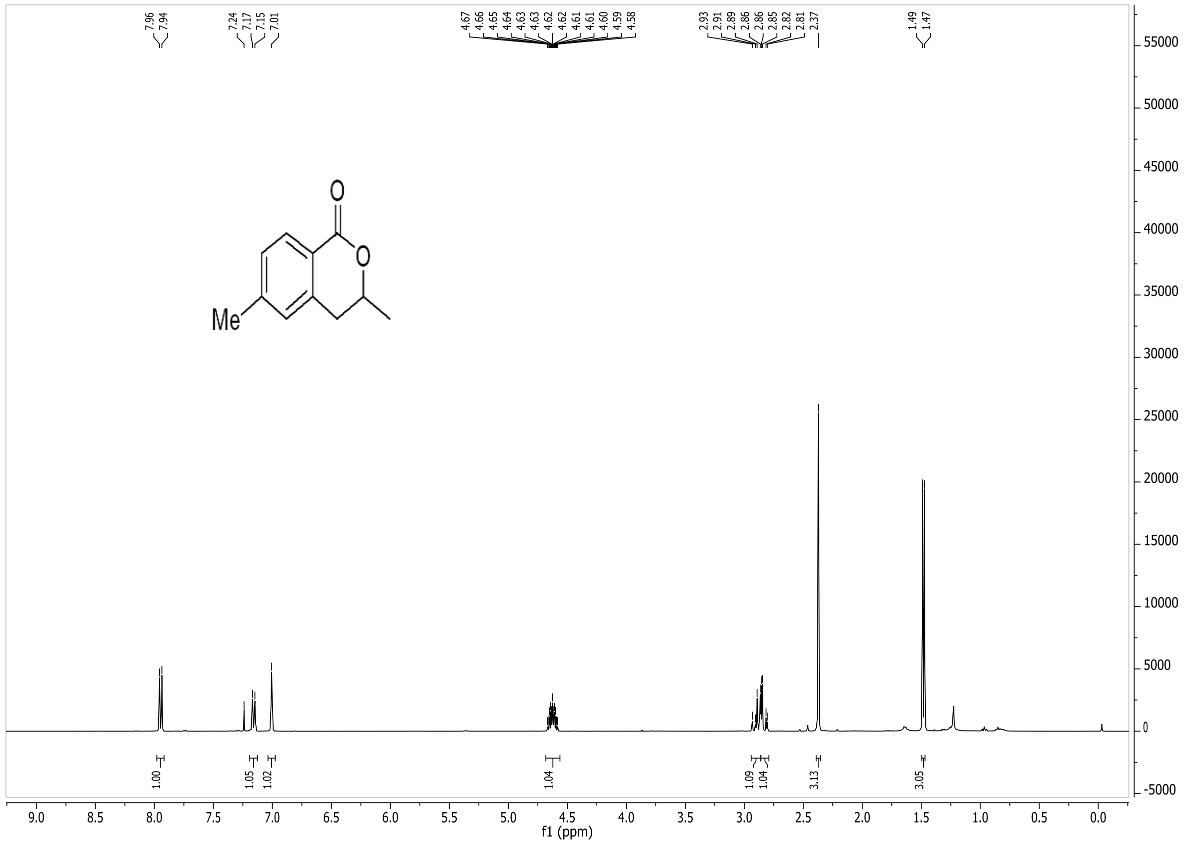


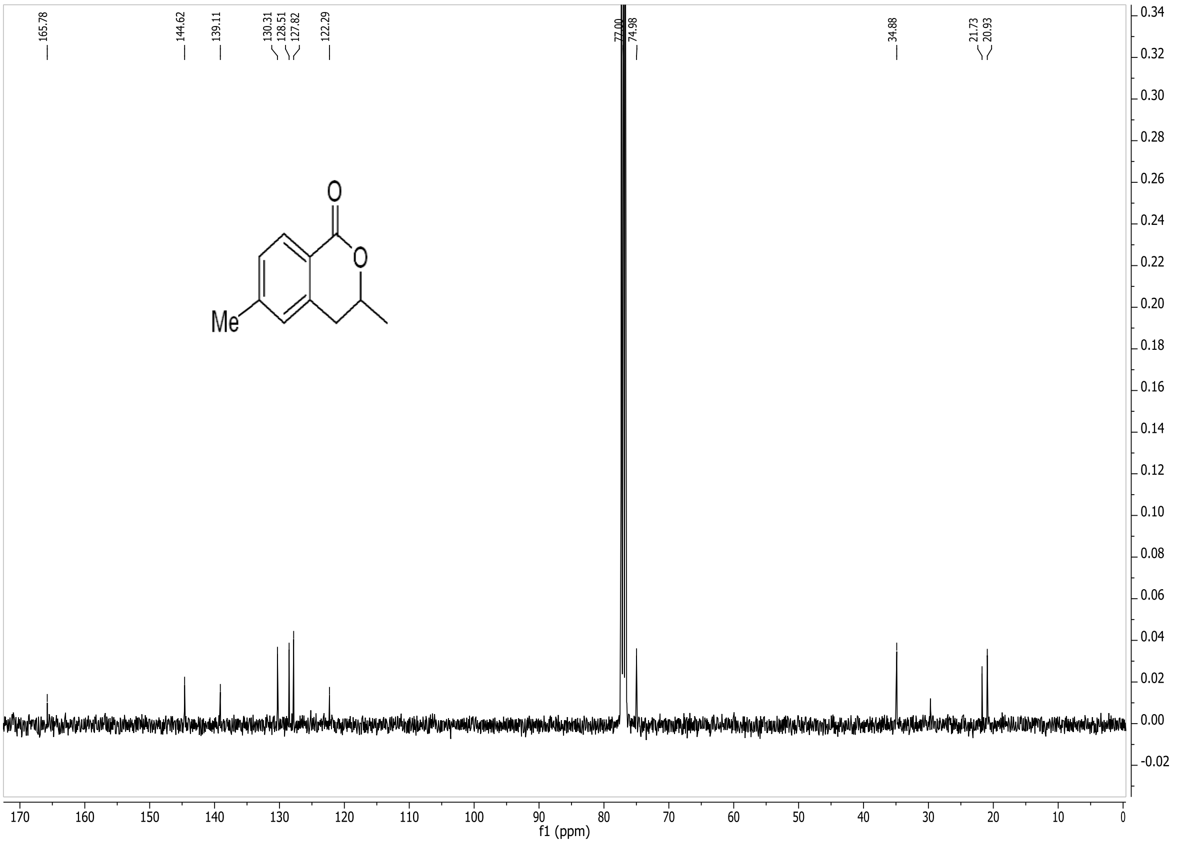


DEPT (135) NMR Spectrum of Compound **5b.**

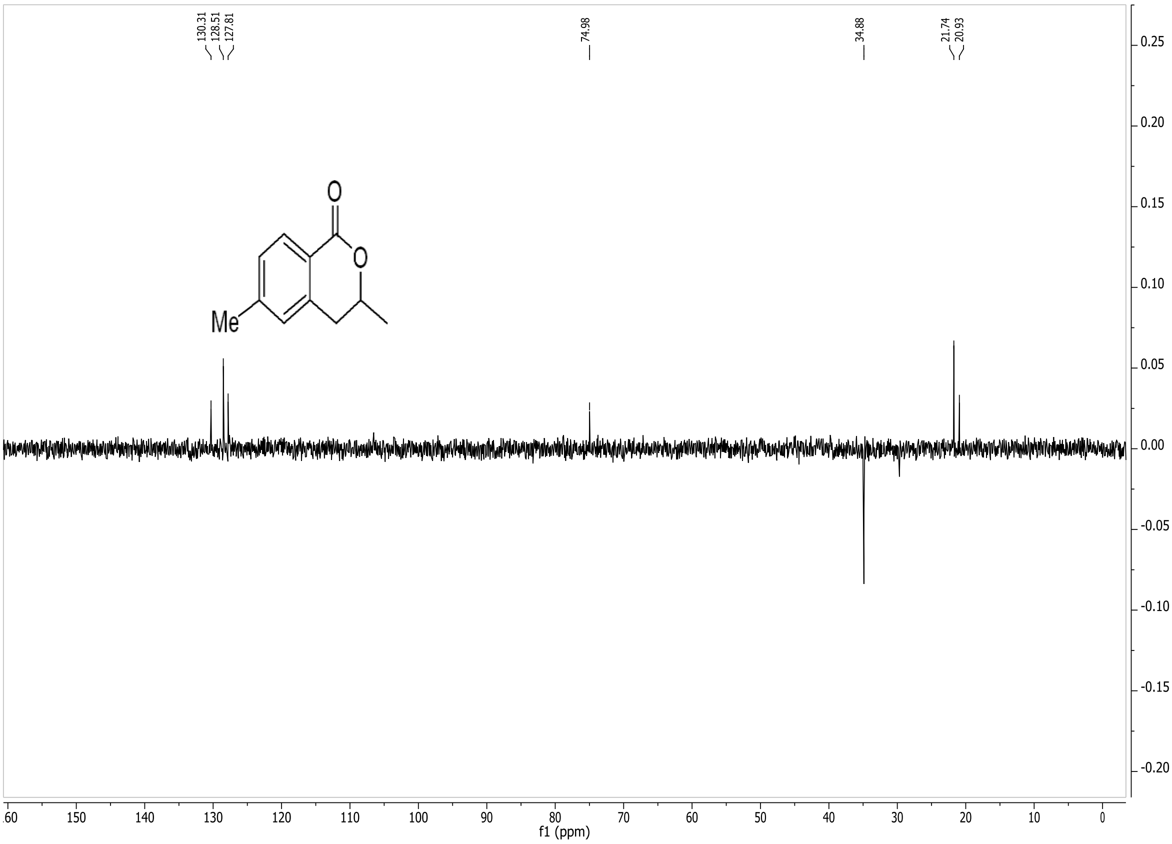


^{1}H and ^{13}C NMR Spectra of Compound **5c.**

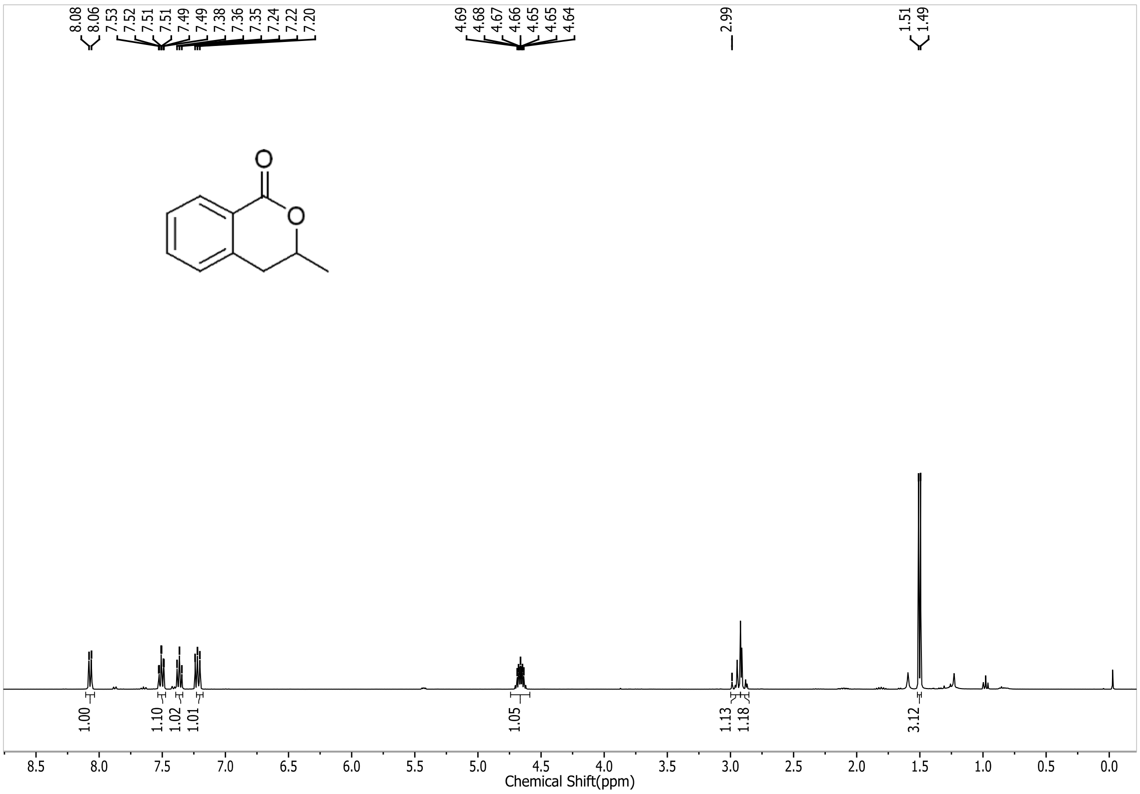


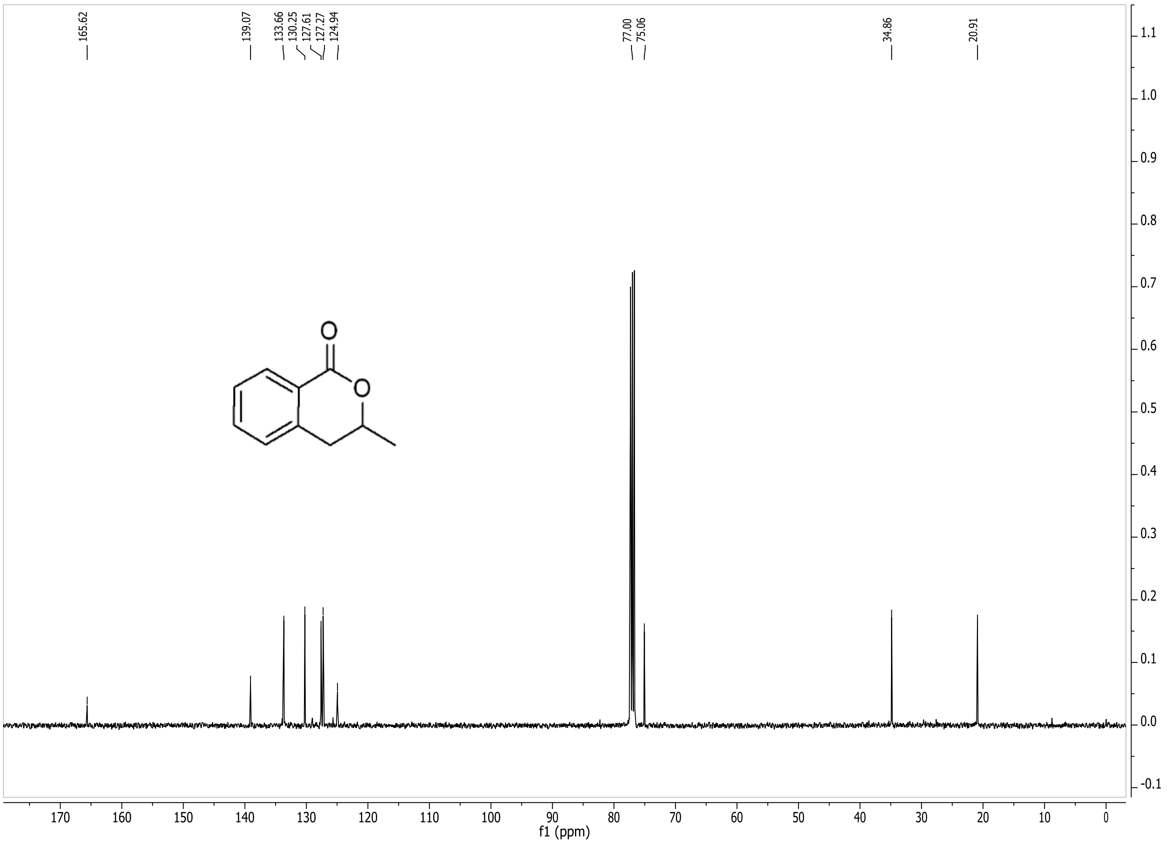


DEPT (135) NMR Spectrum of Compound **5c.**

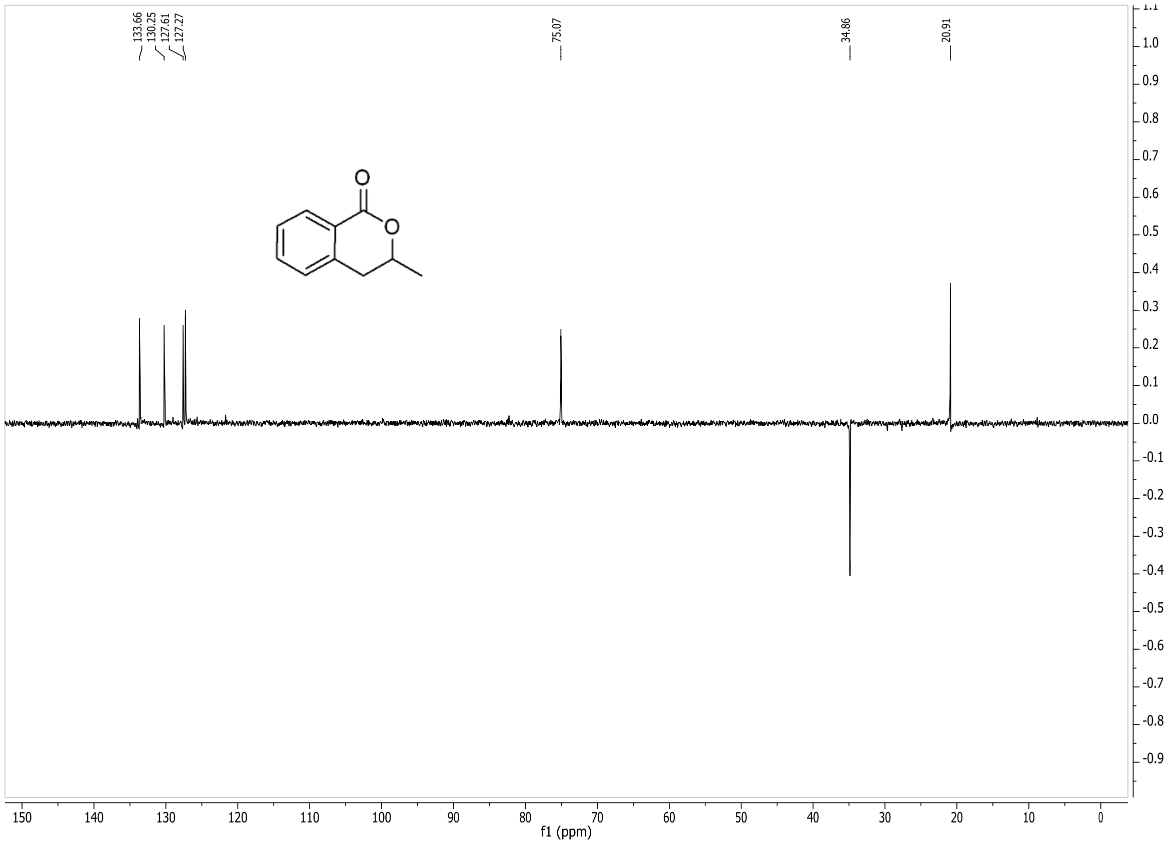


^{1}H and ^{13}C NMR Spectra of Compound **5d.**

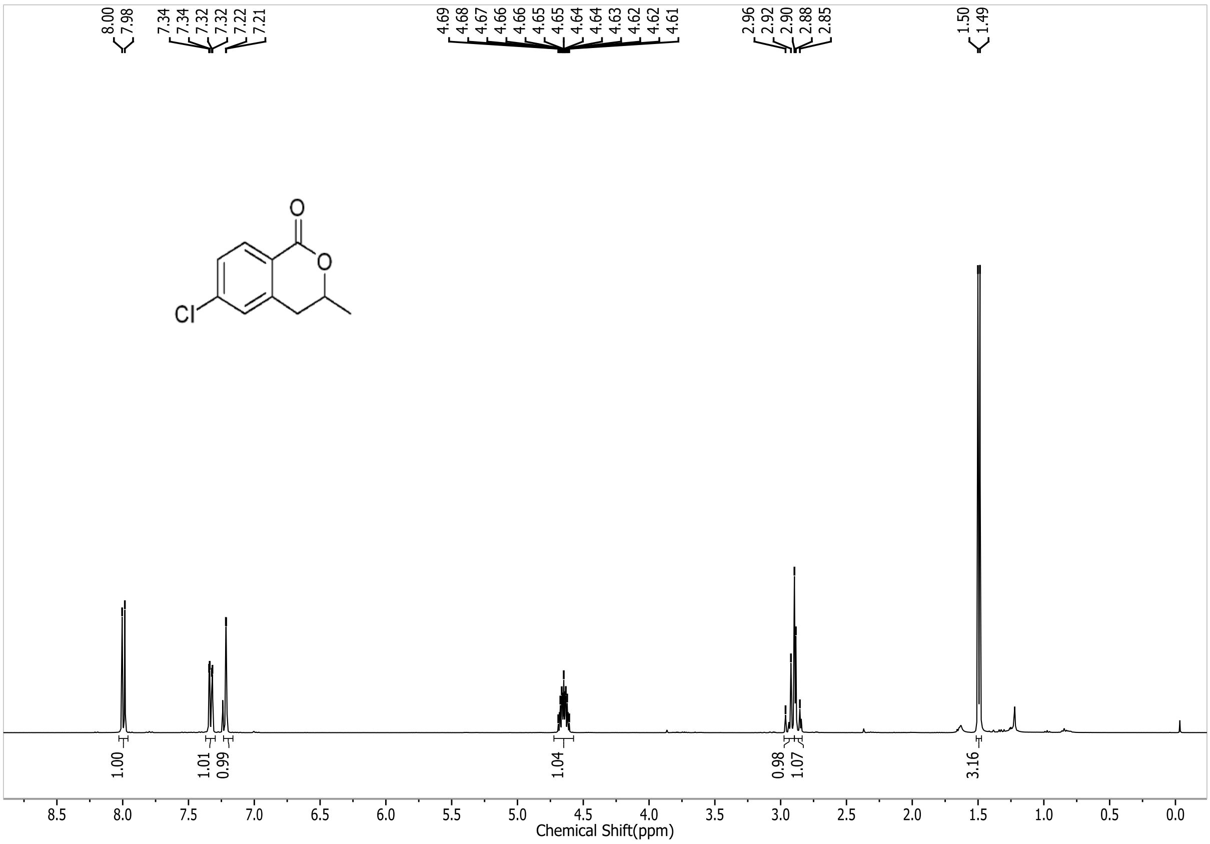


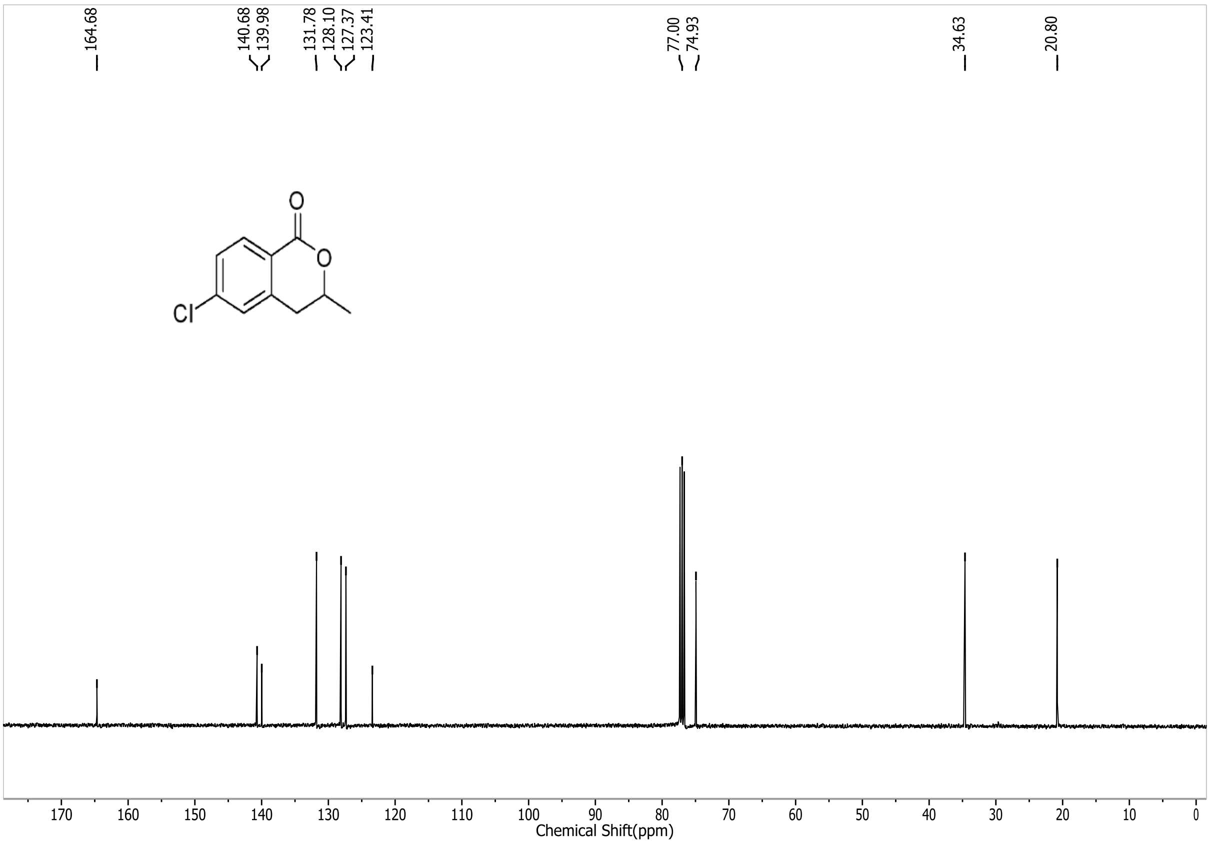


DEPT (135) NMR Spectrum of Compound **5d.**

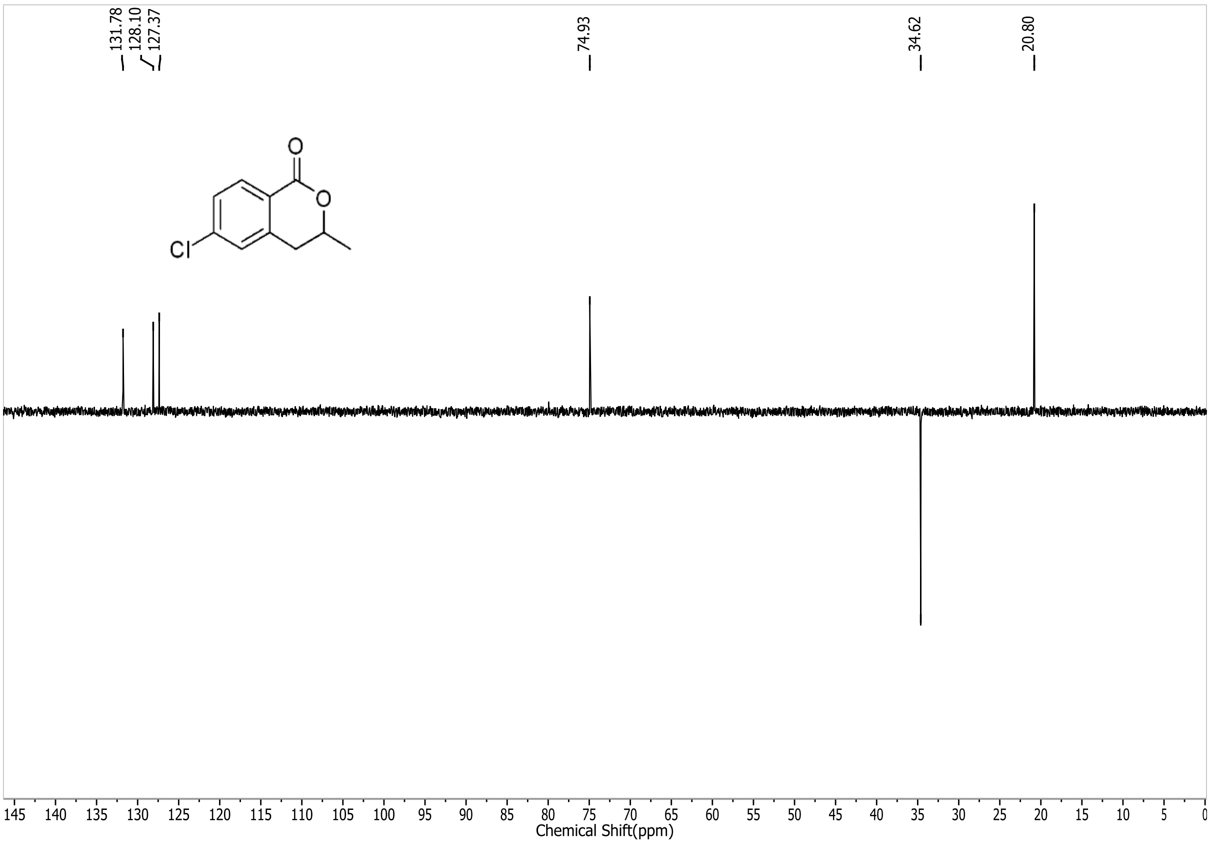


^{1}H and ^{13}C NMR Spectra of Compound **5e.**

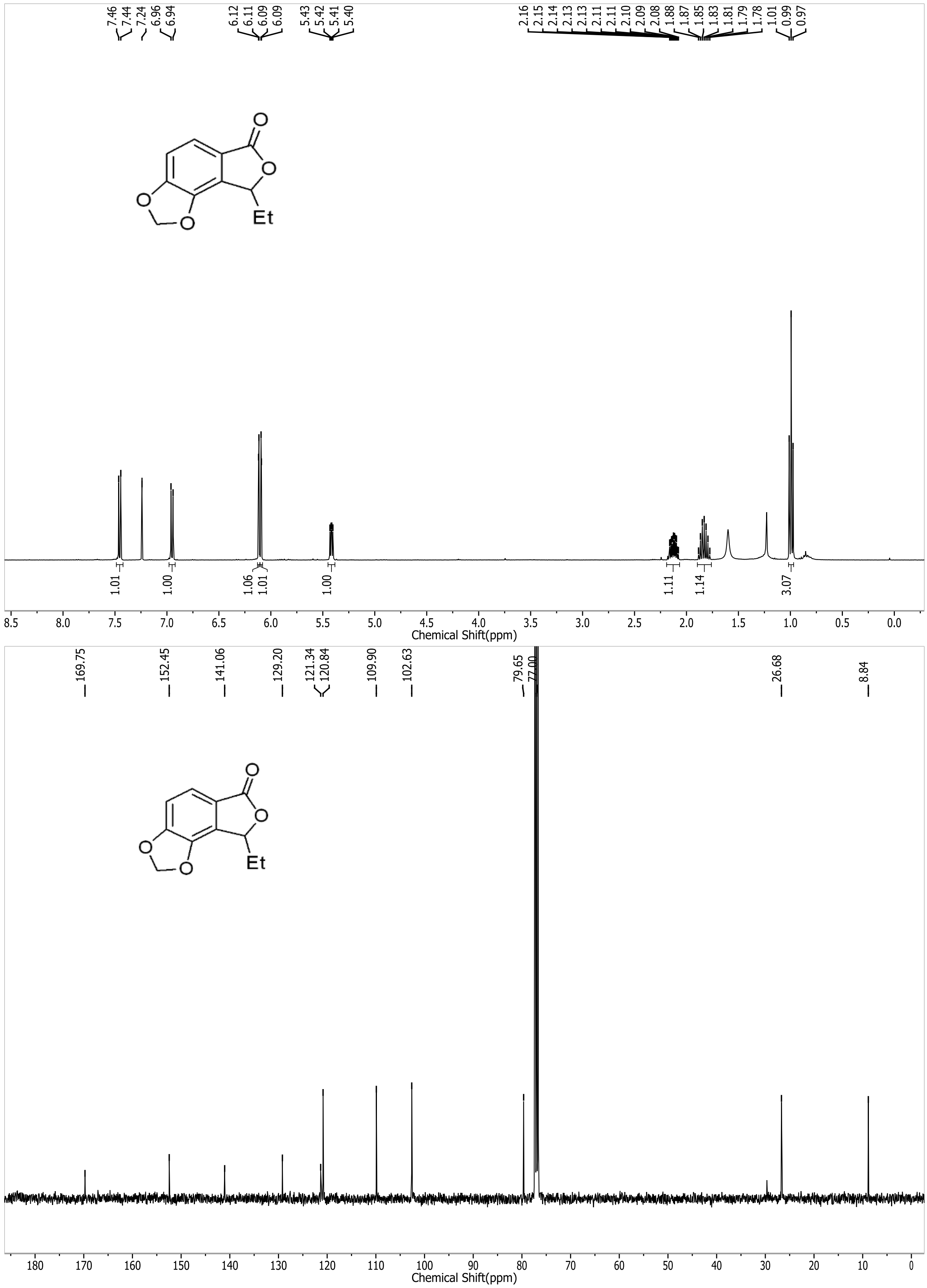




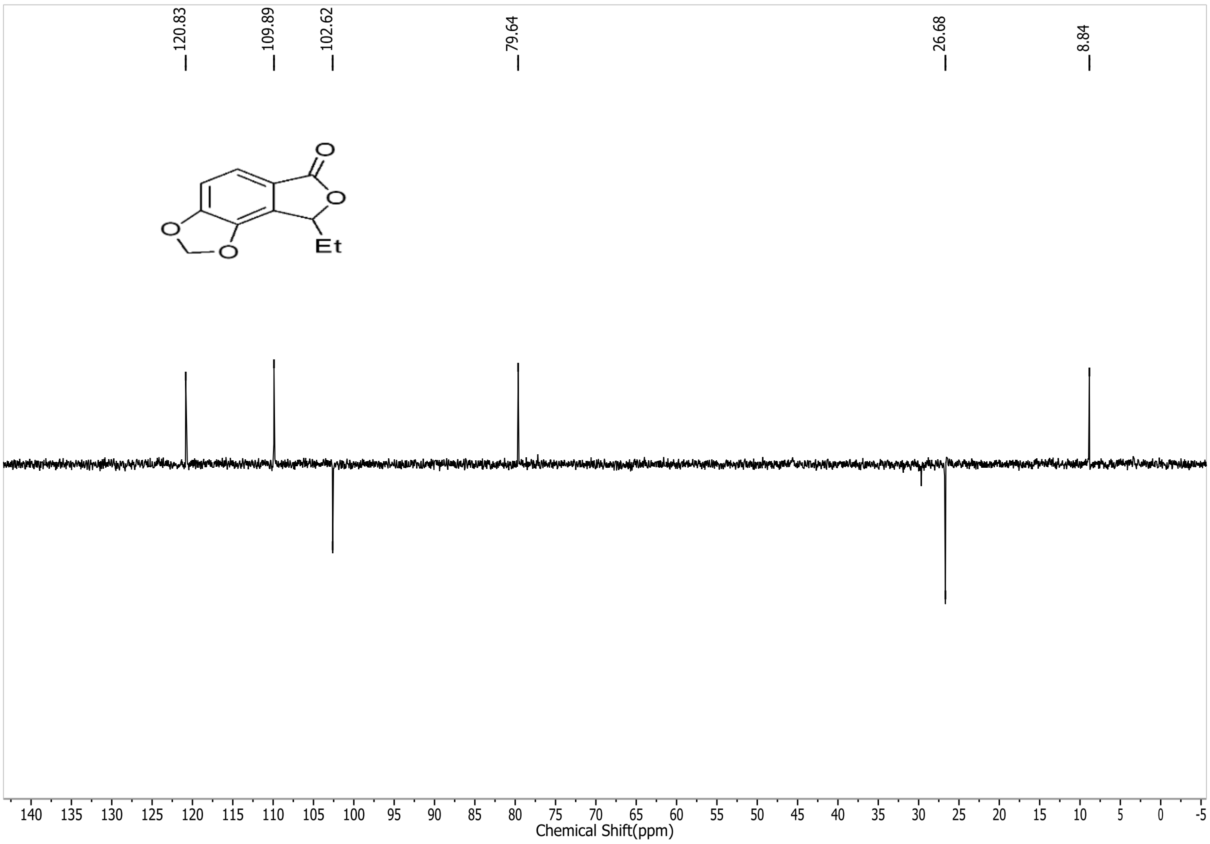
DEPT (135) NMR Spectrum of Compound **5e.**



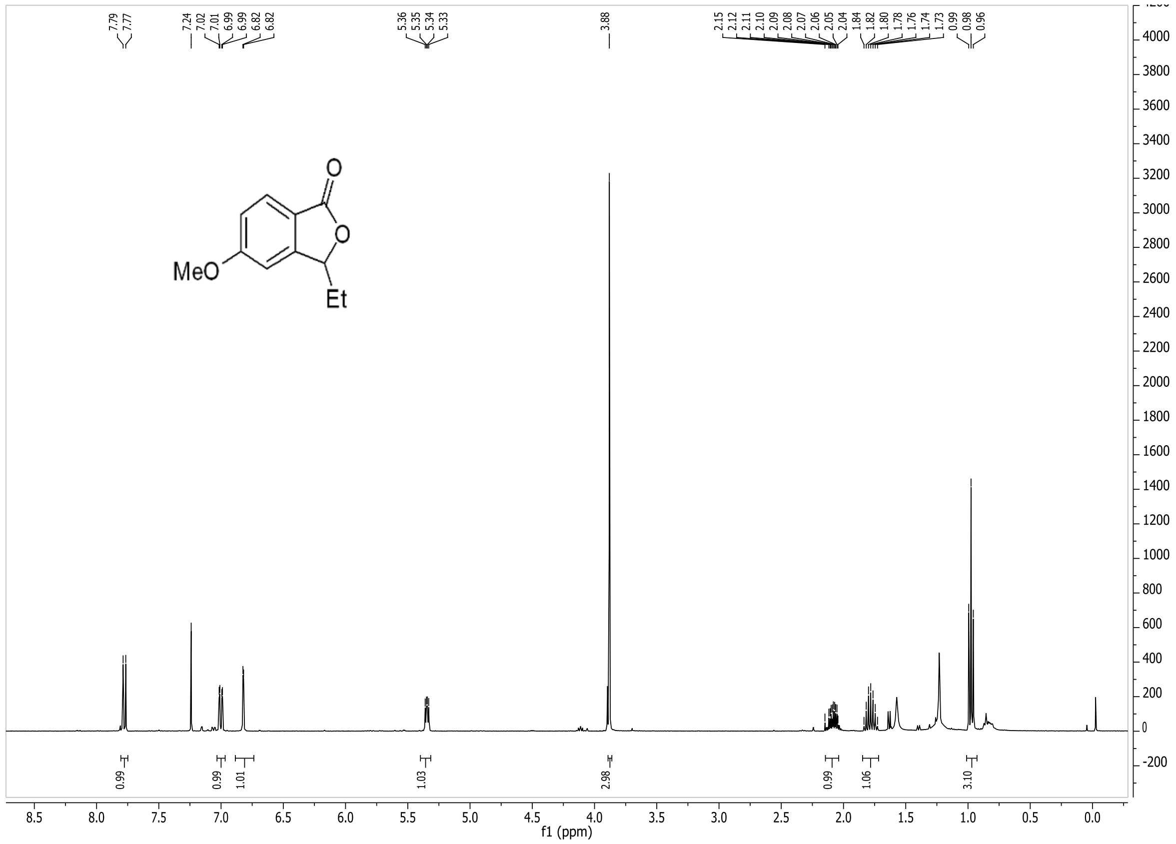
^{1}H and ^{13}C NMR Spectra of Compound **6a.**

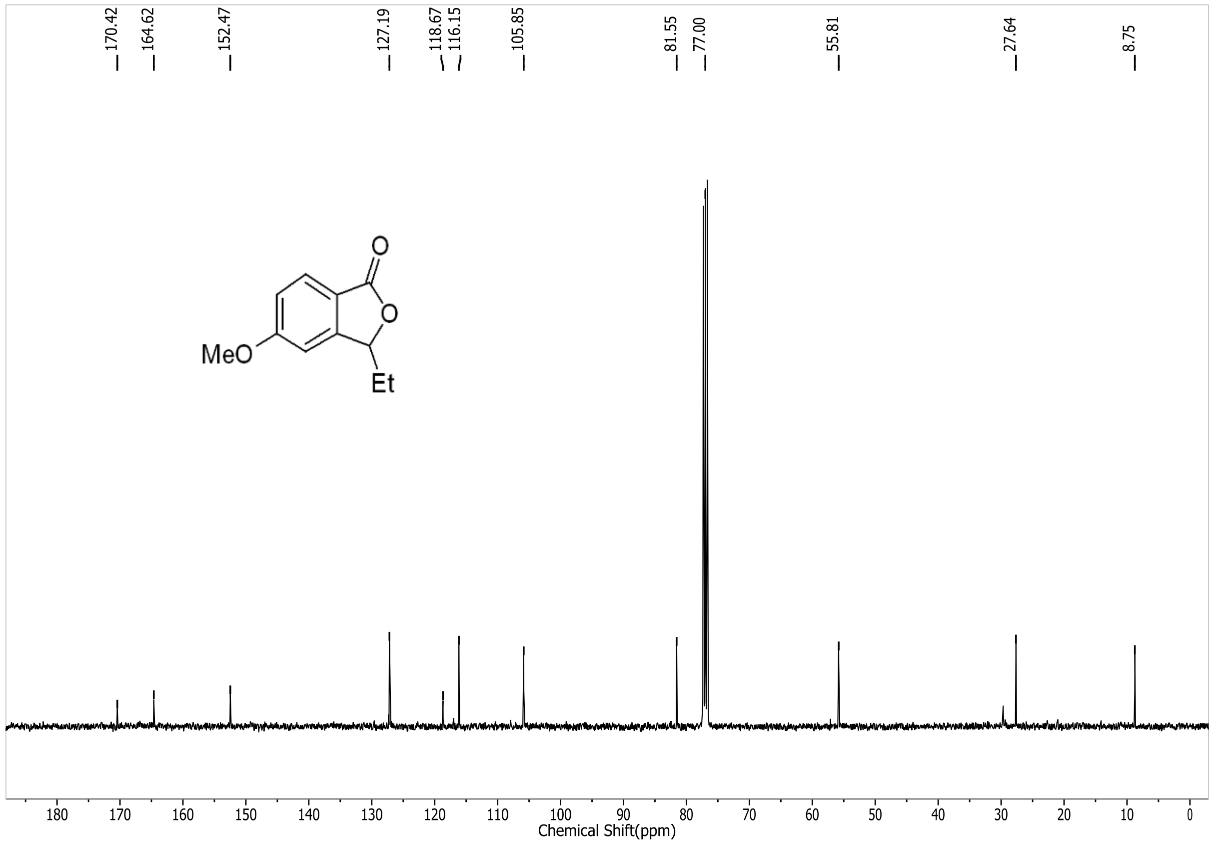


DEPT (135) NMR Spectrum of Compound **6a.**

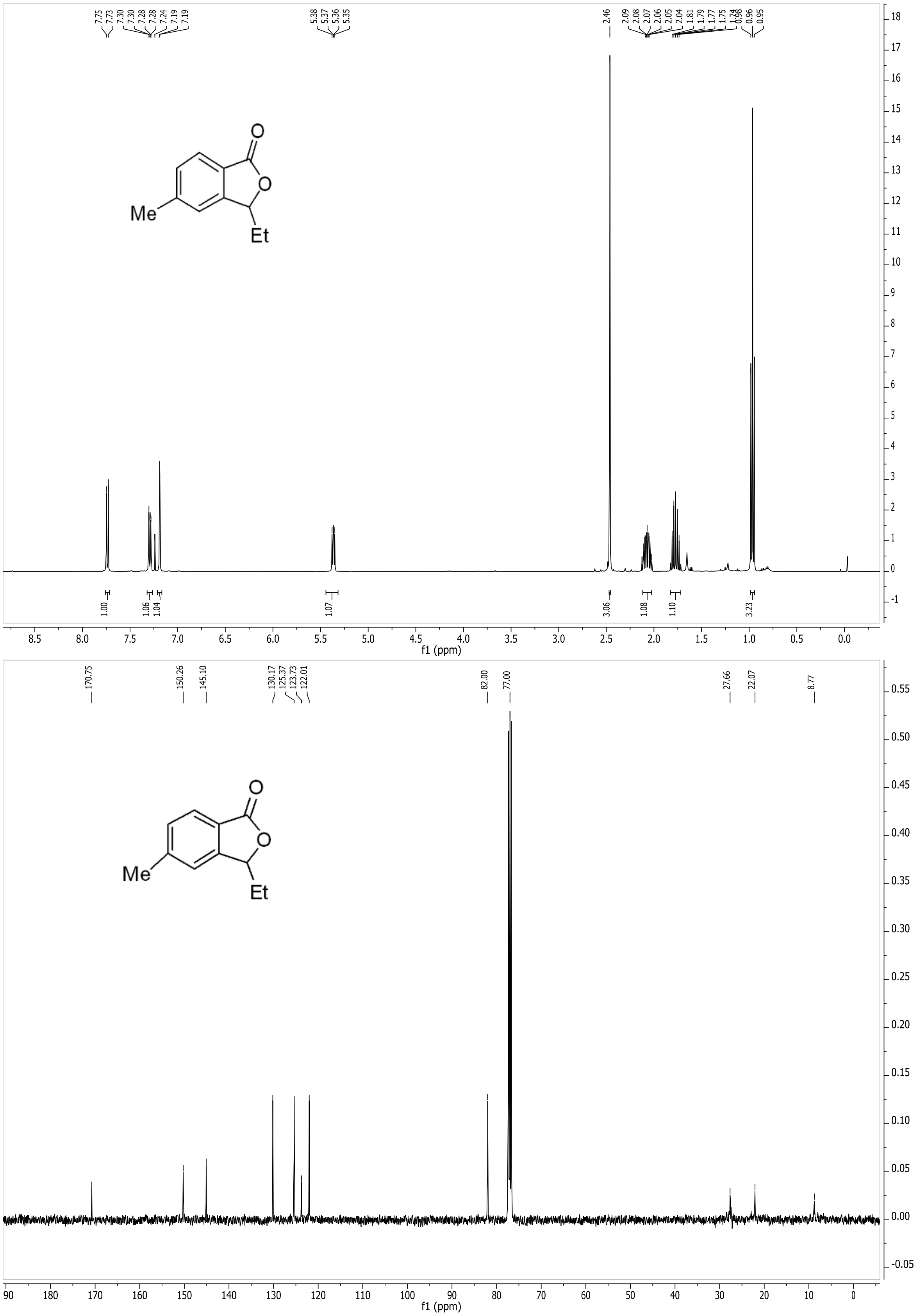


^{1}H and ^{13}C NMR Spectra of Compound 6**b.**

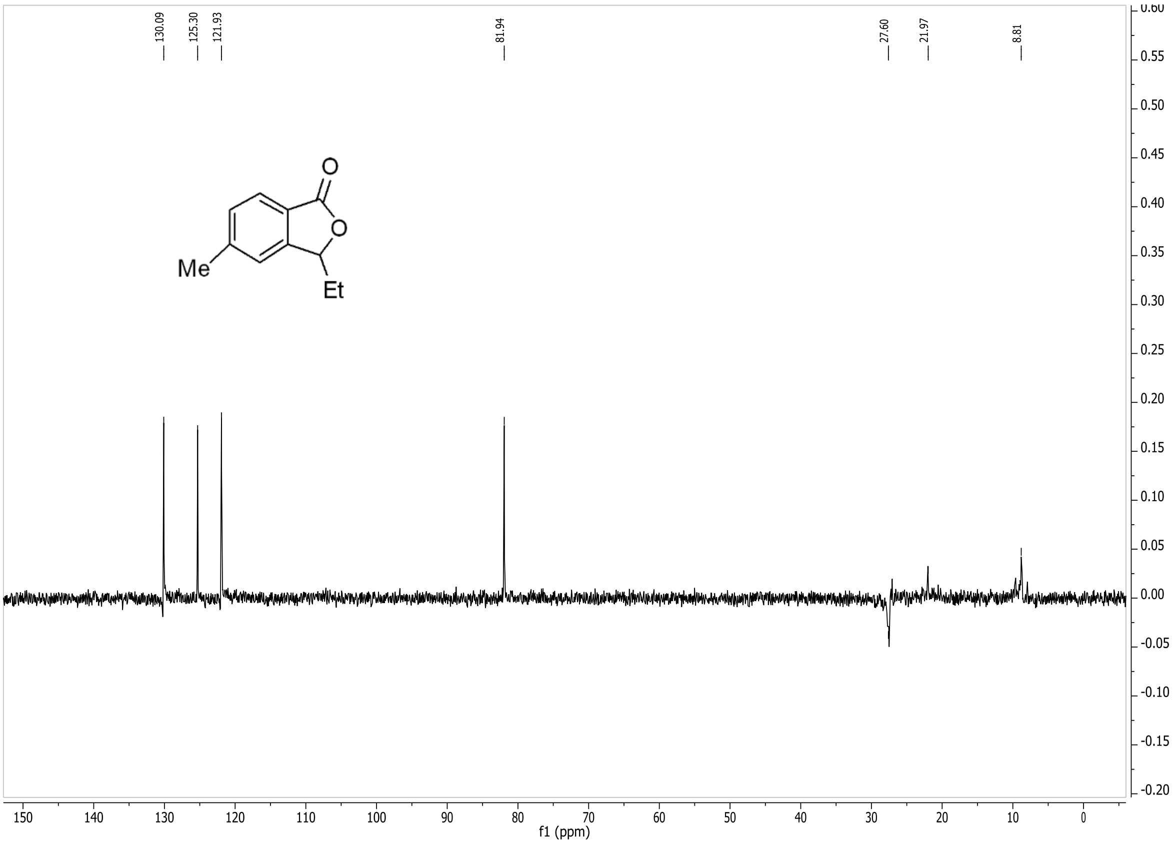




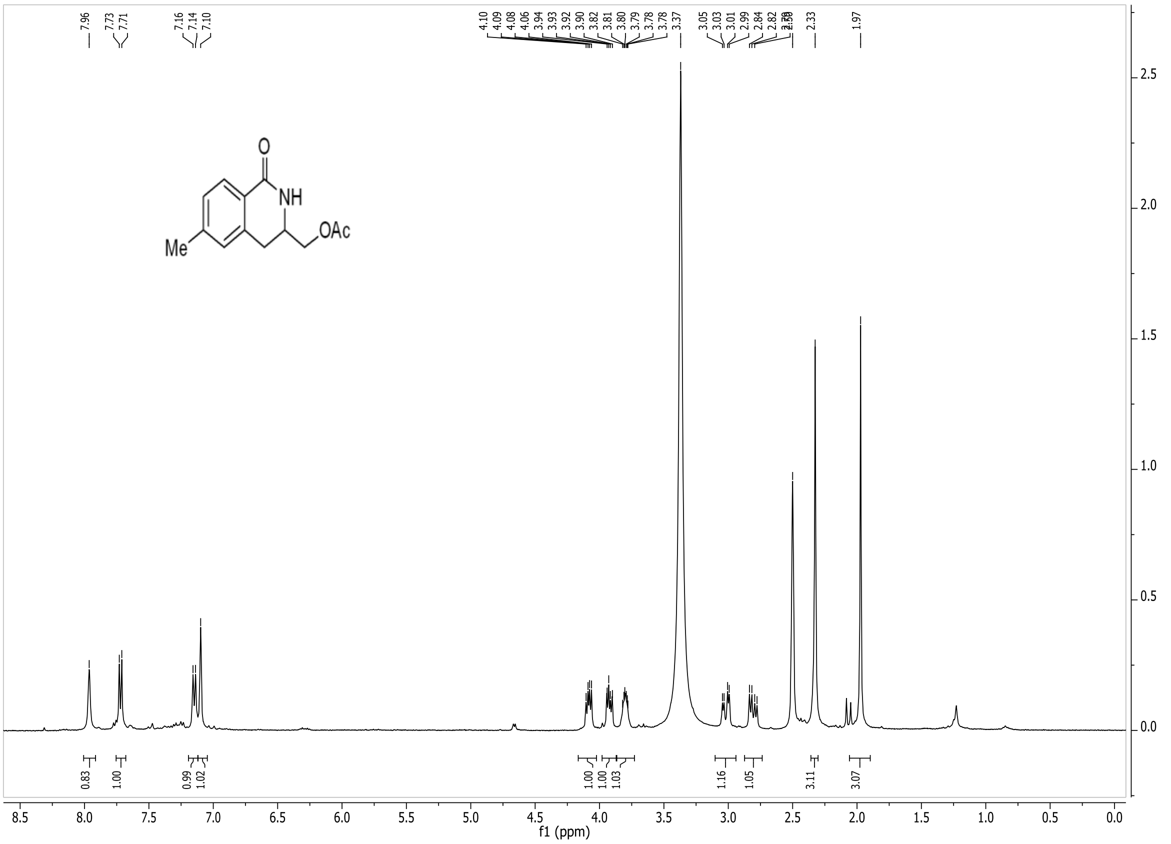
^{1}H and ^{13}C NMR Spectra of Compound **6c.**

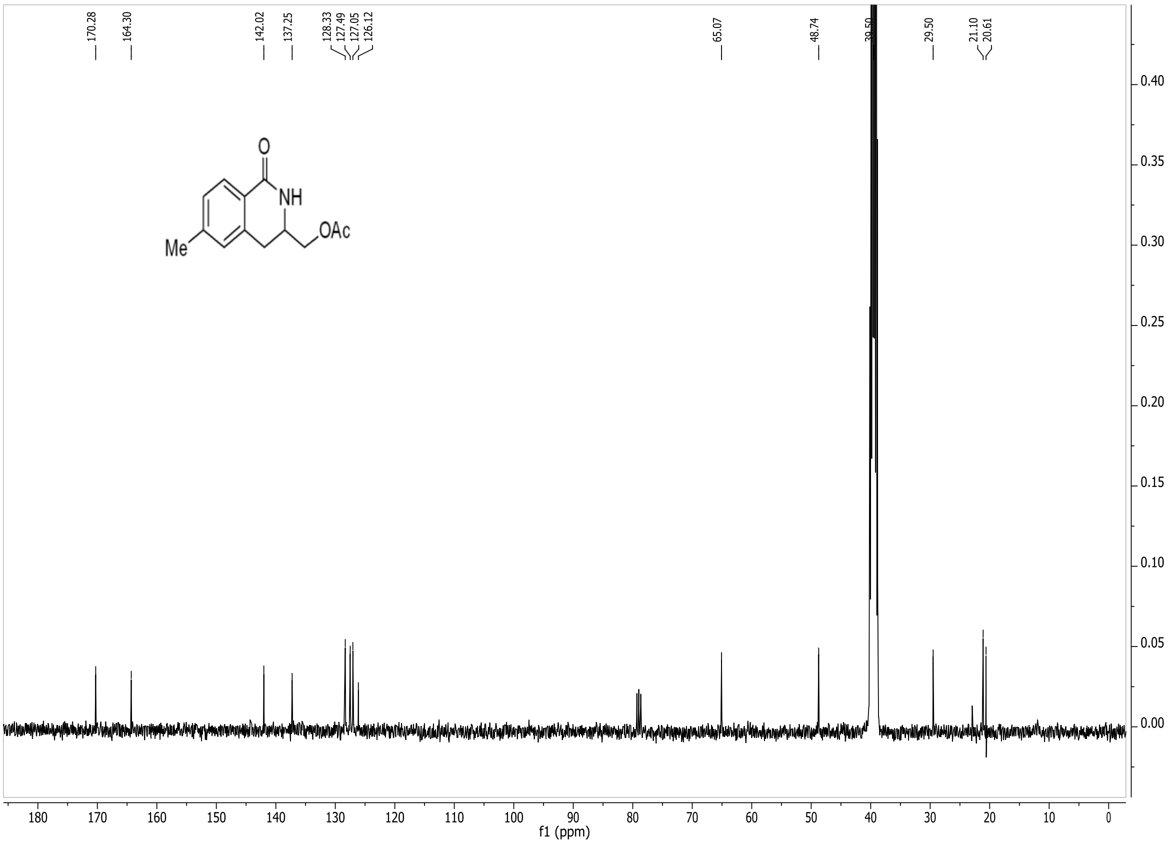


DEPT (135) NMR Spectrum of Compound **6c.**

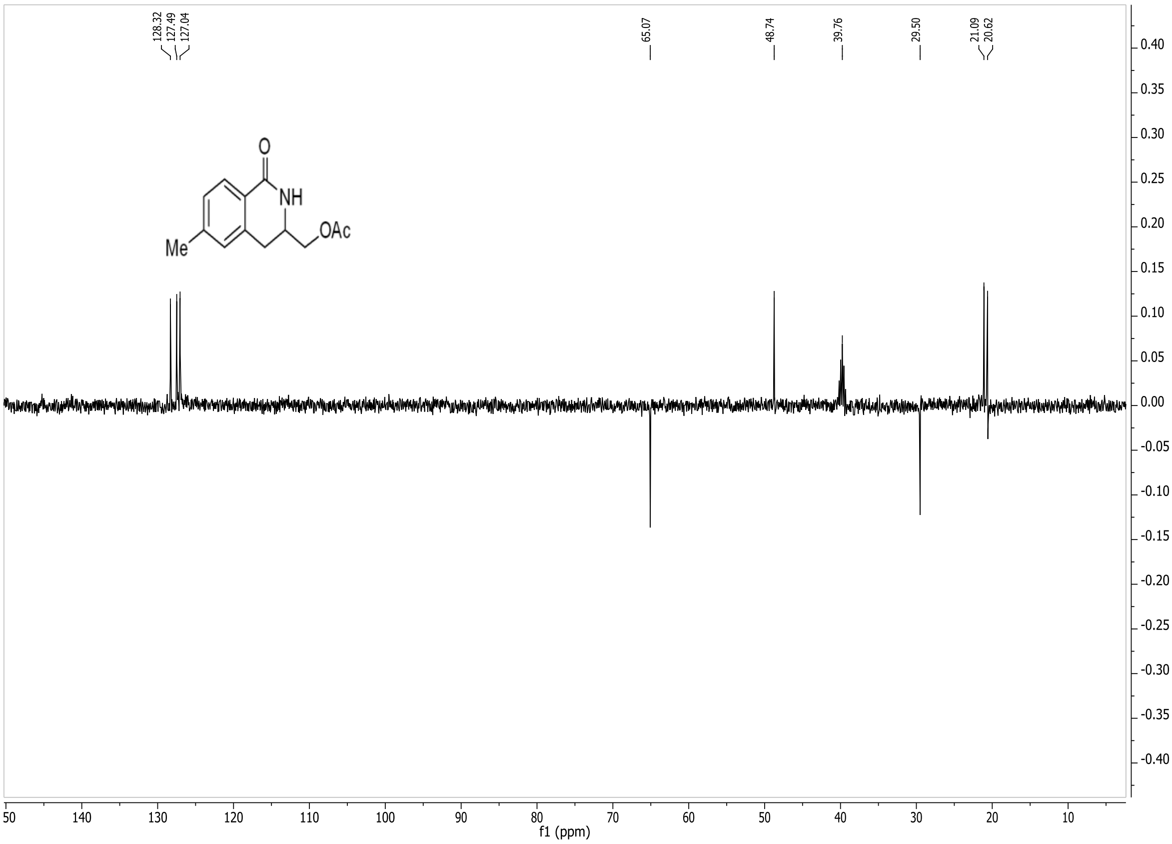


^{1}H and ^{13}C NMR Spectra of Compound **11a.**

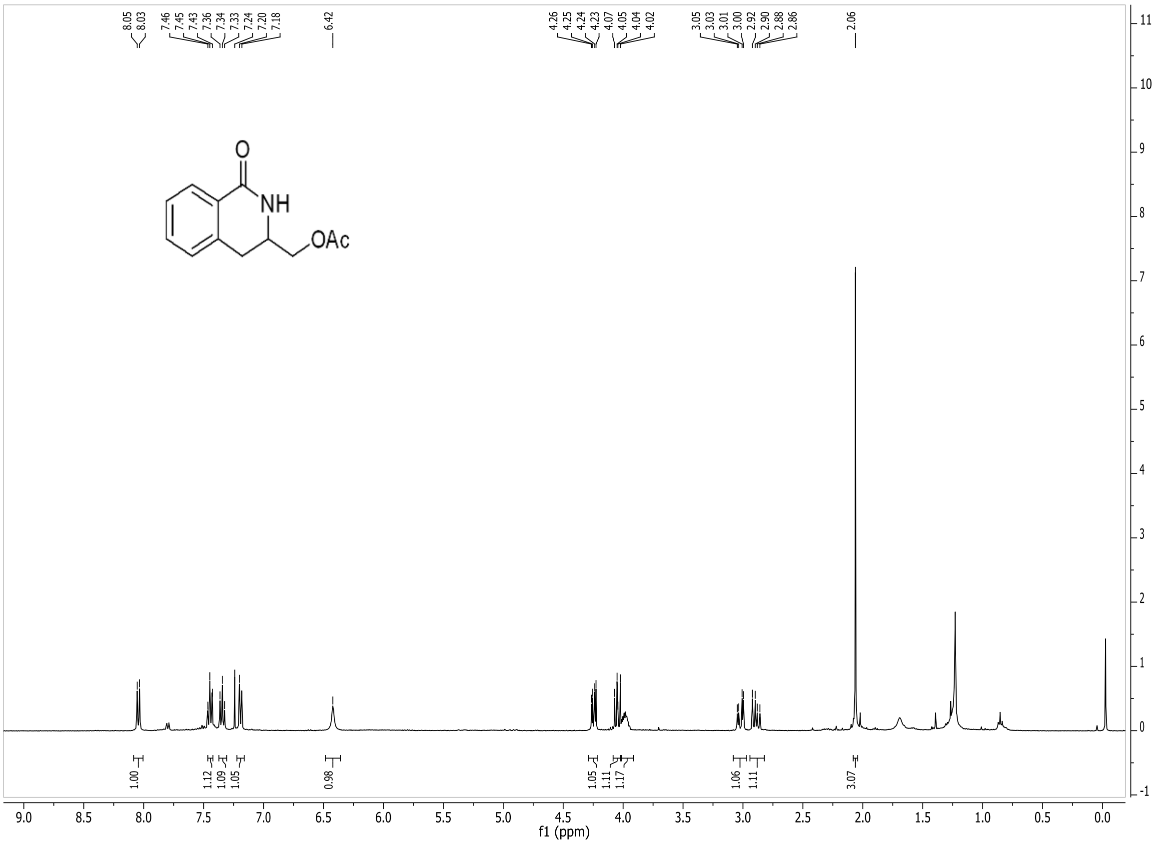




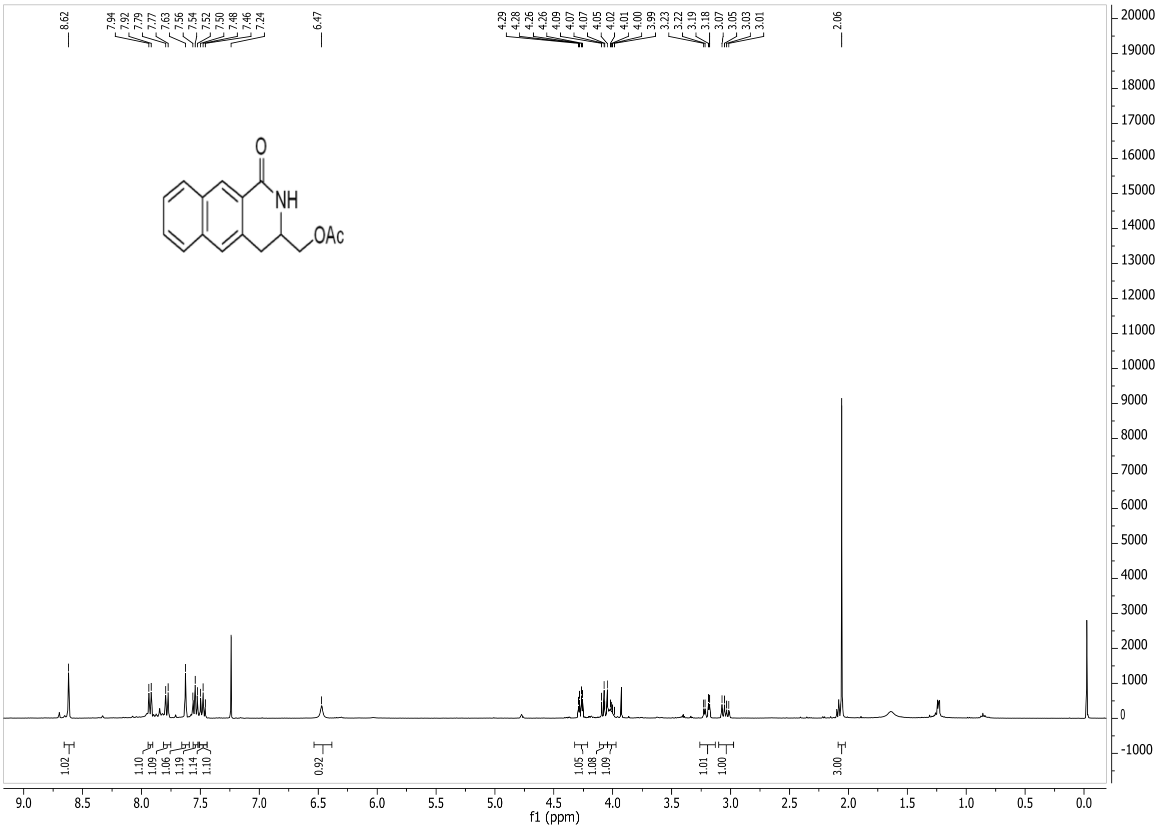
DEPT (135) NMR Spectrum of Compound **11a.**

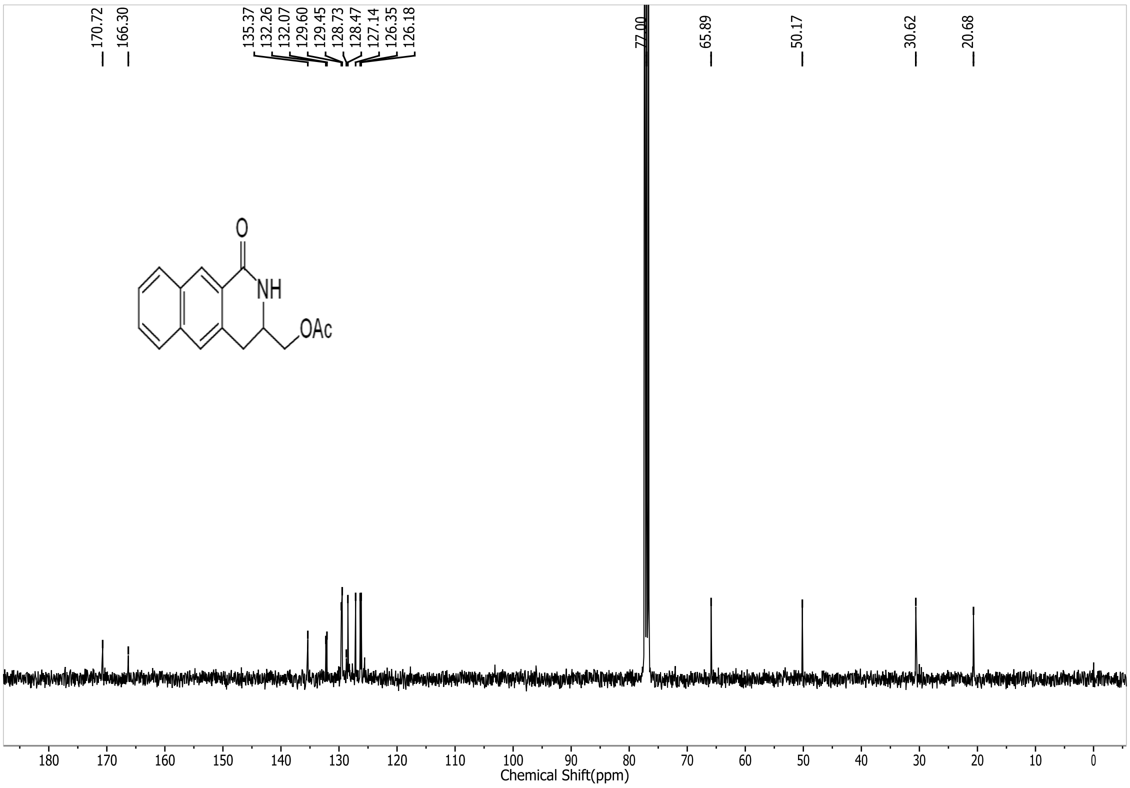


^{1}H and ^{13}C NMR Spectra of Compound **11b.**



^{1}H and ^{13}C NMR Spectra of Compound **11c.**





DEPT (135) NMR Spectrum of Compound **11c.**