Supporting Information (SI)

Rhodium(III)-Catalyzed Aerobic Oxidative C-H Olefination of Unsaturated Acrylamides with Unactivated Olefins

*Ravichandran Logeswaran and Masilamani Jeganmohan**

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

Email: *mjeganmohan@iitm.ac.in*

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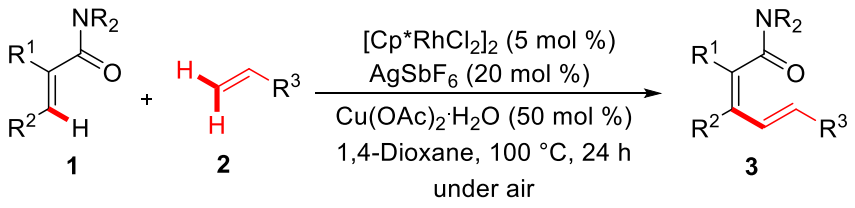
Experimental Section

General Information: All reactions were carried out under the air atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Dry solvents were used for the reaction. Column chromatographical purifications were performed using SiO_2 (120-200 mesh ASTM) from Avra Pvt. Ltd., India. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. $[Rh(Cp^*)Cl_2]_2$,[1] was prepared according to literature procedures. Commercially available. Alkenes **2a**-**2e**, metal salts and other chemicals were purchased from0 Sigma-Aldrich and Spectrochem. Pvt. Ltd., India. and used without further purification. Starting materials **1a**-**1p**[2], 2-(But-3-en-1-yl)isoindoline-1,3-dione(**2f**)[3], 2-(but-3-en-1-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide(**2g**)[3], ethyl pent-4-enoate(**2h**)[4], 4-(but-3-en-1-yloxy)-2H-chromen-2-one(**2i**)[5], dec-9-en-1-yl acetate(**2j**)[6] and pent-4-en-1-yl benzoate(**2k**)[6] were prepared by known literature procedures.

1. General Procedure for C-H Olefination of Acrylamide with Unactivated Olefins



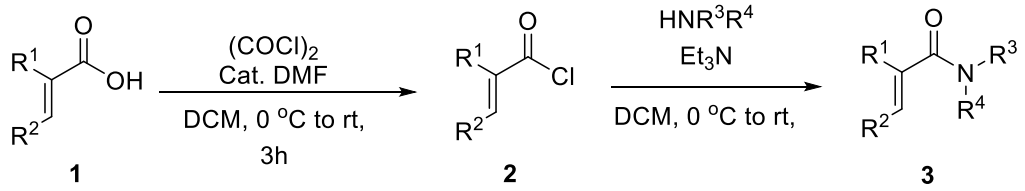
$[Cp^*RhCl_2]_2$ (5.0 mol %), $Cu(OAc)_2{\cdot}H_2O$ (50 mol %) and $AgSbF_6$ (20 mol %) were taken in a 15 mL Schlenk tube ($AgSbF_6$ was taken inside the glove box). 1,4-Dioxane (1.0 mL) was added to the reaction mixture via syringe. Then, acrylamide **1** (50 mg, 1 equiv), alkene **2** (3 equiv), were added to the solution in sequence and followed by the addition of 1,4-Dioxane (2.0 mL). After that, the tube was sealed using screw cap under air and the reaction mixture was allowed to stir at 100 °C for 24 h in oil bath. After cooling to the ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure product **3.** In case of functionalized olefins **2f**-**2j** (2.0 equiv) was used. The ratio of regioisomer was calculated by ^1H NMR analysis.

Procedure for the synthesis of 3aa in 1 mmol Scale.

$[Cp^*RhCl_2]_2$ (5.0 mol %, 30.9 mg), $Cu(OAc)_2 \cdot H_2O$ (50 mol %, 100mg) and $AgSbF_6$ (20 mol %, 69 mg) were taken in a 15 mL Schlenk tube ($AgSbF_6$ was taken inside the glove box). 1,4-Dioxane (1.0 mL) was added to the reaction mixture via syringe. Then, acrylamide **1a** (1 mmol, 139 mg), alkene **2a** (3 mmol, 331 mg), were added to the solution in sequence and followed by the addition of 1,4-Dioxane (3.0 mL). After that, the tube was sealed using screw cap under air and the reaction mixture was allowed to stir at 100 °C for 24 h in oil bath. After cooling to the ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure product **3aa** in 71% (175 mg).

Substrate synthesis

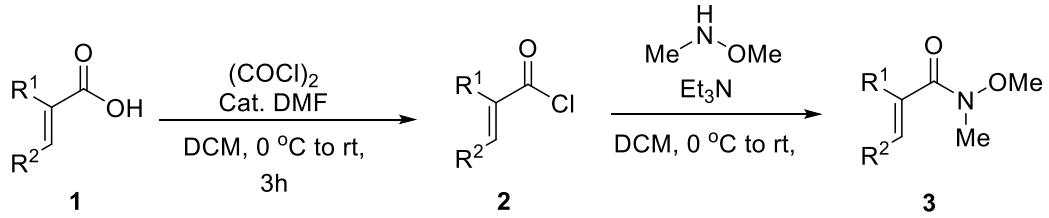
General reaction procedure for acrylamides 1a-1i, 1m-1p[2]



To a solution of the carboxylic acid **1** (20 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) at 0 °C was added dropwise $(COCl)_2$ (20 mmol, 1.0 equiv.) followed by a catalytic amount of DMF (0.1 mL). The reaction was allowed to stir at rt for 3 h. The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride **2**, which was used directly for the next step without futher purification.

The acid chloride was added dropwise to a solution of amine (20 mmol, 1.0 equiv.) and Et_3N (24 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL). The mixture was stirred overnight at room temperature. Then the mixture was diluted with CH_2Cl_2 , washed successively with water, satured aqueous $NaHCO_3$, and brine. The organic layer was dried over $NaSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography, eluting with EtOAc/hexane, to afford corresponding acrylamides **3**.

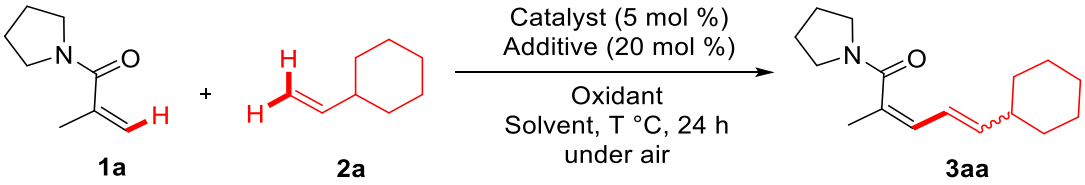
General reaction procedure for acrylamides 1k-1l[2d]



To a solution of the carboxylic acid **1** (20.0 mmol, 1.0 eq.) in dry CH_2Cl_2 (20 mL) at 0 ^oC was added dropwise $(COCl)_2$ (20 mmol, 1 eq.) followed by a catalytic amount of DMF (2 drops). The reaction was allowed to stir at rt for 3 h. The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride **2**, which was used directly for the next step without futher purification.

To a solution of *N*-methoxy methylamine hydrochloride salt (22 mmol, 1.1 equiv) was added dropwise Et_3N (42 mmol, 2.1 equiv) in dry CH_2Cl_2 (20 mL) at 0 ^oC. Acid chloride **2** was then added dropwise to the solution. The mixture was stirred overnight at room temperature. Then the mixture was diluted with CH_2Cl_2 , washed successively with water, satured aqueous $NaHCO_3$, and brine. The organic layer was dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography, eluting with EtOAc/hexane, to afford corresponding acrylamides **3**.

Table S1. Optimization Studies[a]



1a **2a** **3aa**

Entry	Catalyst	Additive	Oxidant	Solvent	Temperature (°C)	Yield **3aa** (%)[b]
1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	1,4-dioxane	100	51
2	$[Cp^*RhCl_2]_2$	$AgSbF_6$	Ag_2O	1,4-dioxane	100	32
3	$[Cp^*RhCl_2]_2$	$AgSbF_6$	Ag_2CO_3	1,4-dioxane	100	16
4	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	72
5	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	1,4-dioxane	100	67
6	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	72[c]
7	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,2-dichloroethane	100	45[c]
8	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	DMF	100	27[c]
9	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,2-dichlorobenzene	100	53[c]
10	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	2,2,2-Trifluoroethanol	100	trace[c]
11	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	Acetonitrile	100	trace[c]
12	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	Methanol	100	49[c]
13	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,2-Dimethoxyethane	100	47[c]
14	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	53[c, d]
15	$[Cp^*RhCl_2]_2$	$AgBF_4$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	48[c]
16	$[Cp^*RhCl_2]_2$	AgOTf	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	25[c]
17	$[Cp^*RhCl_2]_2$	$NaSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	trace[c]
18	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	rt	NR[c]
19	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	68[c, e]
20	$[RuCl_2(p\text{-cymene})]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[c]
21	$Cp^*Co(CO)I_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[c]
22	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[c]
23	-	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[c]
24	$[Cp^*RhCl_2]_2$	-	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[c]
25	$[Cp^*RhCl_2]_2$	$AgSbF_6$	-	1,4-dioxane	100	NR[c]
26	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	48[c, e]
27	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[f]
28	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	NR[g]
29	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	45[h]

30	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	41[i]
31	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	60	30
32	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	65[j]
33	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	1,4-dioxane	100	69[k]

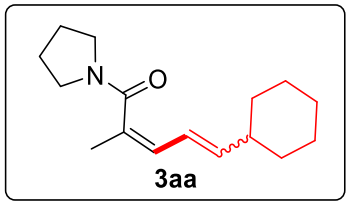
[a]All reactions were carried out under the following conditions: **1a** (50 mg), **2a** (3.0 equiv), Catalyst (5 mol %), Additive (20 mol %), Oxidant (1.0 equiv) in Solvent (3 mL) at T °C for 24 h under air. [b]Isolated yields. [c]50 mol % of $Cu(OAc)_2{\cdot}H_2O$ was used under air. [d]Under N_2 [e]2.5 mol% of $[Cp^*RhCl_2]_2$ was used. [f]1,10-phenanthroline (20 mol %) was used. [g]2,2-bipyridyl (20 mol %) was used. [h]PPh_3 (20 mol %) was used. [i]*N*-Boc-L-phenylalanine (20 mol %). [j]20 mol % of $Cu(OAc)_2.H_2O$ was used. [j]2 equiv. of $Cu(OAc)_2.H_2O$ was used.

Reference:

1) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.
2) (a) Zhang, J.; Loh, T.-P. *Chem. Commun.* **2012**, *48*, 11232. (b) L. Ackermann, A.V. Lygin, N. Hofmann, *Org. Lett.* **2011**, 13, 3278-3281. (c) Jiang, B.; Zhao, M.; Li, S.-S.; Xu, Y.- H.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2018**, *57*, 555− 559 (d) Lan, Y.; Fan, P.; Liu, X.-W.; Meng, F.-F.; Ahmad, T.; Xu, Y.-H.; Loh, T.-P. *Chem. Commun.* **2017**, *53*, 12353.
3) Lu, M.-Z.; Chen, X.-R.; Xu, H.; Dai, H.-X.; Yu, J.-Q *Chem. Sci.* **2018**, *9*, 1311−1316.
4) Harris, J. R.; Waetzig, S. R.; Woerpel, K. A. *Org. Lett.* **2009**, *11*, 3290–3293.
5) Kong, W.; An, H.; Song, Q. *Chem. Commun.* **2017**, *53*, 8968
6) Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J, *J. Am. Chem. Soc.* **2011**, *133*, 16410−16413.

Spectral Data of Compounds

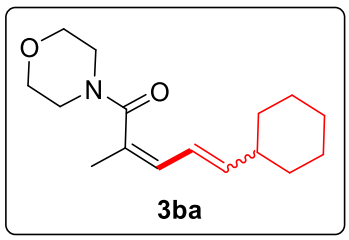
(2*Z*)-5-Cyclohexyl-2-methyl-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one (3aa).



3aa

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 6:1 and the yield is 72% (64 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, *J* = 11.7 Hz, 1H), 5.76 (t, *J* = 11.3 Hz, 1H), 5.29 (t, *J* = 10.2 Hz, 1H), 3.53 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 6.8 Hz, 2 H), 2.47 – 2.38 (m, 1H), 1.98 (s, 3H), 1.92 – 1.86 (m, 4H), 1.75 – 1.68 (m, 4H), 1.32 – 1.06 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 139.5, 134.3, 123.2, 122.4, 47.1, 45.0, 36.7, 33.2, 25.9, 25.8, 24.5, 20.2. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{16}H_{26}NO$ 248.2009; Found 248.2008.

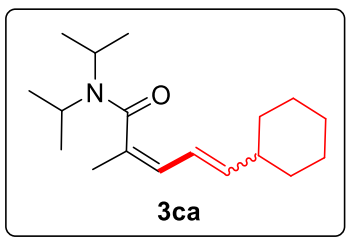
(2*Z*)-5-Cyclohexyl-2-methyl-1-morpholinopenta-2,4-dien-1-one (3ba).



3ba

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 4:1 and the yield is 67% (57 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, *J* = 11.4 Hz, 1H), 5.76 (t, *J* = 11.4 Hz, 1H), 5.29 (t, *J* = 10.2 Hz, 1H), 3.54 (dd, *J* = 7.1, 1.8 Hz, 2H), 3.34 – 3.31 (m, 2H), 2.48 – 2.37 (m, 1H), 1.98 (s, 3H), 1.91 – 1.89 (m, 4H), 1.75 – 1.68 (m, 4H), 1.31 – 1.06 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 139.6, 134.3, 123.2, 122.3, 47.1, 45.1, 36.7, 33.2, 32.8, 25.9, 25.8, 24.6, 24.5, 20.3. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{16}H_{26}NO_2$ 264.1958; Found 264.1954.

(2*Z*)-5-Cyclohexyl-*N*,*N*-diisopropyl-2-methylpenta-2,4-dienamide (3ca).

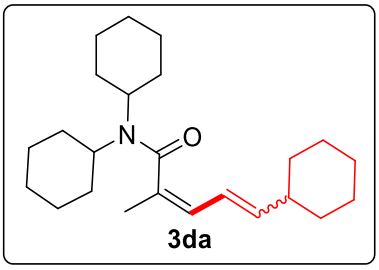


3ca

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of E/Z in the ratio of 3:1 and the yield is 70% (57 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, *J* = 11.7 Hz, 1H), 5.82 (t, *J* = 11.3 Hz, 1H), 5.57 5.23 (t, *J* = 10.2 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.43 – 3.34 (m, 1H), 2.45 – 2.35 (m, 1H), 1.92 (s, 3H), 1.70 – 1.59 (m, 6H), 1.35 – 1.22 (m, 6H), 1.13 (d, *J* = 6.6 Hz, 12H), 1.09 (d, *J* = 6.7

Hz, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 138.4, 135.0, 122.6, 122.2, 50.6, 45.5, 40.7, 36.6, 33.2, 32.7, 26.1, 26.0, 25.8, 20.7, 20.6, 20.6, 20.4. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{18}H_{32}NO$ 278.2478: Found 278.2471.

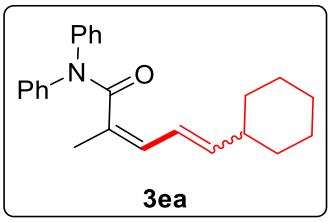
(2*Z*)-*N*,*N*,5-Tricyclohexyl-2-methylpenta-2,4-dienamide (3da).



3da

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 20:1 and the yield is 59% (42 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (d, *J* = 11.6 Hz, 1H), 5.84 (t, *J* = 11.2 Hz, 1H), 5.22 (t, *J* = 10.2 Hz, 1H), 3.49 (t, *J* = 11.7 Hz, 1H), 2.91 (t, *J* = 11.7 Hz, 1H), 2.41 (m, 1H), 1.92 (s, 3H), 1.84 – 1.40 (m, 20H), 1.36 – 1.02 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 138.3, 135.2, 122.7, 122.0, 59.6, 55.7, 36.6, 29.9, 26.6, 26.0, 25.8, 25.3, 25.3, 20.9. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{24}H_{40}NO$ 358.3104; Found 358.3104.

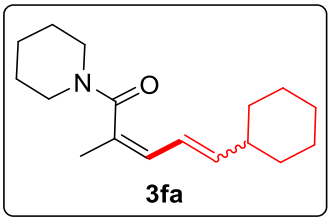
(2*Z*)-5-Cyclohexyl-2-methyl-*N*,*N*-diphenylpenta-2,4-dienamide (3ea).



3ea

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 18:1 and the yield is 38% (28 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 5H), 7.25 – 7.20 (m, *J* = 6.3 Hz, 5H), 6.21 (t, *J* = 11.3 Hz, 1H), 6.09 (d, *J* = 11.8 Hz, 1H), 5.36 (t, *J* = 10.2 Hz, 1H), 2.34 – 2.27 (m, 1H), 1.83 (s, 3H), 1.72 – 1.66 (m, 2H), 1.56 – 1.49 (m, 2H), 1.26 – 1.09 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 142.5, 140.1, 133.3, 128.9, 126.4, 122.7, 36.5, 33.1, 32.7, 25.9, 25.7, 20.9. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{24}H_{28}NO$ 346.2165; Found 346.2164.

(2*Z*)-5-Cyclohexyl-2-methyl-1-(piperidin-1-yl)penta-2,4-dien-1-one (3fa).

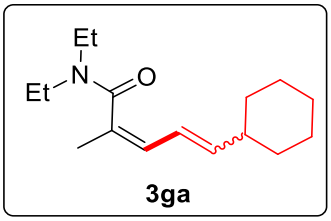


3fa

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 4:1 and the yield is 61% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (d, *J* = 11.6 Hz, 1H), 5.76 (t, *J* = 11.3 Hz, 1H), 5.25 (t, *J* = 10.3 Hz, 1H), 3.64 – 3.56 (m, 2H), 3.37 – 3.31 (m, 2H), 2.45 – 2.34 (m, 1H), 1.94 (s,

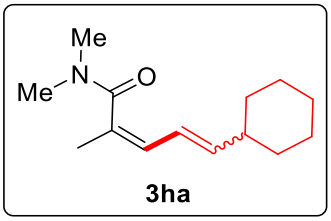
3H), 1.72 – 1.55 (m, 4H), 1.53 – 1.49 (m, 2H), 1.32 – 1.01 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 139.1, 133.1, 123.3, 122.3, 47.3, 41.9, 41.9, 40.8, 36.6, 33.1, 32.7, 26.7, 26.7, 26.0, 25.9, 25.7, 25.7, 25.6, 24.5, 20.8, 20.5. HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{17}H_{27}NONa$ 284.1985; Found 284.1990.

(2*Z*)-5-Cyclohexyl-*N*,*N*-diethyl-2-methylpenta-2,4-dienamide (3ga).



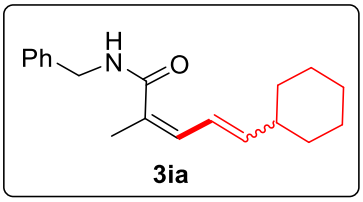
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 3:1 and the yield is 58% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 11.7 Hz, 1H), 5.74 (t, *J* = 11.3 Hz, 1H), 5.25 (t, *J* = 10.2 Hz, 1H), 3.48 – 3.43 (m, 2H), 3.31 – 3.26 (m, 2H), 2.46 – 2.36 (m, 1H), 1.96 (s, 3H), 1.72 – 1.59 (m, 4H), 1.33 – 1.02 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 139.1, 133.5, 123.1, 122.3, 42.3, 40.7, 38.2, 36.6, 33.1, 32.6, 26.0, 25.9, 25.7, 21.0, 20.6, 14.3, 12.8. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{16}H_{28}NO$ 250.2165; Found 250.2168.

(2*Z*)-5-Cyclohexyl-*N*,N,2-trimethylpenta-2,4-dienamide (3ha).



Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 2:1 and the yield is 51% (50 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 – 6.21 (m, 1H), 5.92 (m, 1H), 5.86 – 5.79 (m, 1H), 5.70 (t, *J* = 11.4 Hz, 1H), 5.64 (d, *J* = 7.2 Hz, 1H), 5.28 (t, *J* = 10.3 Hz, 1H), 3.00 (s, 3H), 2.95 (s, 3H), 2.41 (m, 1H), 1.96 (s, 3H), 1.74 – 1.58 (m, 4H), 1.31 – 1.04 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 142.1, 139.5, 133.0, 131.0, 128.8, 123.7, 123.6, 122.2, 41.0, 37.6, 37.5, 36.6, 34.2, 34.1, 33.1, 32.8, 26.0, 25.9, 25.9, 25.8, 20.6, 20.3. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{14}H_{24}NO$ 222.1852: Found 222.1853.

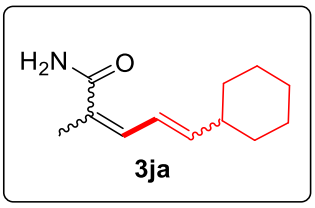
(2*Z*)-*N*-Benzyl-5-cyclohexyl-2-methylpenta-2,4-dienamide (3ia).



Prepared according to General Procedure 1. Colorless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 4:1 and the yield is 37% (30mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 6.43 (d, *J* = 11.7 Hz, 1H), 6.28

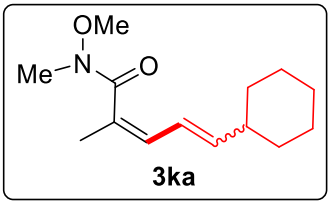
(t, *J* = 11.3 Hz, 1H), 5.87 (s, 1H), 5.38 (t, *J* = 10.3 Hz, 1H), 4.54 – 4.52 (m, 2H), 2.48 – 2.39 (m, 2H), 2.34 (t, *J* = 7.5 Hz, 1H), 2.02 (s, 3H), 1.75 – 1.55 (m, 4H), 1.34 – 1.04 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ. 169.9, 141.3, 134.0, 132.1, 128.8, 127.9, 127.6, 127.4, 122.1, 43.6, 36.5, 33.1, 32.5, 29.7, 25.9, 25.8, 21.2. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{19}H_{26}NO$ 284.2009; Found 284.2007

(2Z)-5-Cyclohexyl-2-methylpenta-2,4-dienamide (3ja).



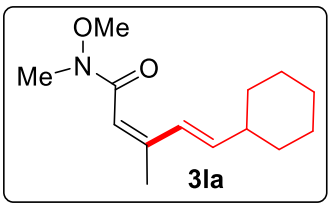
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 2:1 and the yield is 44% (50 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (dd, *J* = 15.2, 11.2 Hz, 1H), 6.65 (br, 1H), 6.49 (t, *J* = 15.2 Hz, 1H), 5.77 (dd, *J* = 15.2, 7.2 Hz, 1H), 5.62 (br, 1H), 2.17 (d, *J* = 5.8 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.96 (s, 3H), 1.77 – 1.58 (m, 4H), 1.40 – 1.25 (m, 4H), 1.20 – 1.06 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 184.1, 172.5, 172.3, 145.9, 142.2, 140.9, 136.8, 136.3, 132.7, 130.3, 129.1, 127.3, 124.2, 122.2, 121.6, 41.0, 38.5, 36.5, 33.0, 32.6, 26.0, 25.8, 25.7, 24.6, 22.3, 21.1, 20.8. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{12}H_{20}NO$ 194.1539; Found 194.1533.

(2*Z*)-5-Cyclohexyl-*N*-methoxy-*N*,2-dimethylpenta-2,4-dienamide (3ka).



Prepared according to General Procedure 1. Colorless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 2:1 and the yield is 65% (60 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (d, *J* = 11.7 Hz, 1H), 5.86 (t, *J* = 11.3 Hz, 1H), 5.30 (t, *J* = 10.1 Hz, 1H), 3.65 (s, 5.3H), 3.24 (s, 2H), 3.23 (s, 3H), 2.48 – 2.38 (m, 1H), 1.99 (s, 3H), 1.69 – 1.58 (m, 4H), 1.35 – 1.01 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 139.3, 129.9, 124.3, 122.4, 40.8, 36.6, 33.1, 32.7, 26.0, 25.9, 25.8, 25.8, 25.7, 20.2, 20.0. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{14}H_{24}NO_2$ 238.1802; Found 238.1807.

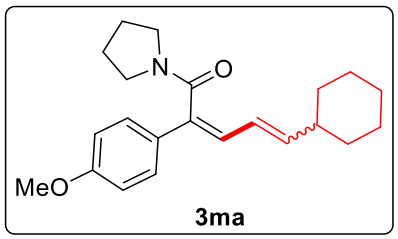
(2*Z*,4*E*)-5-Cyclohexyl-*N*-methoxy-*N*,3-dimethylpenta-2,4-dienamide (3la).



Prepared according to General Procedure 1. Colorless liquid; Eluent (15% ethyl acetate in hexane). Isolated yield is 40% (37 mg, single isomer). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d,

J = 15.8 Hz, 1H), 6.06 (s, 1H), 6.00 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.68 (s, 3H), 3.22 (s, 3H), 2.11 (s, 1H), 2.01 (s, 3H), 1.75 (m, 4H), 1.34 – 1.08 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 143.3, 125.8, 114.4, 61.5, 41.4, 32.7, 26.1, 25.9, 21.3. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{14}H_{24}NO_2$ 238.1802; Found 238.1800.

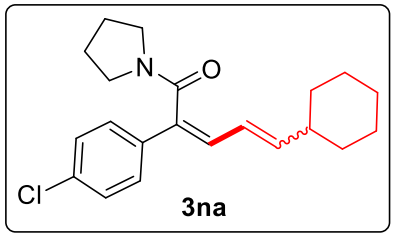
(2*Z*)-5-Cyclohexyl-2-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one (3ma).



3ma

Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 2:1 and the yield is 84% (62 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 1H), 6.86 (t, *J* = 9.1 Hz, 2H), 6.77 (d, *J* = 11.8 Hz, 1H), 5.97 (t, *J* = 11.3 Hz, 1H), 5.44 (t, *J* = 10.3 Hz, 1H), 3.80 (s, 3H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.20 (t, *J* = 6.5 Hz, 2H), 2.56-2.50 (m, 1H), 1.92 – 1.88 (m, 2H), 1.84 – 1.79 (m, 2H), 1.75 – 1.65 (m, 4H), 1.33 – 1.06 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.1, 168.8, 168.7, 159.4, 159.2, 144.3, 141.5, 137.5, 135.9, 128.4, 128.4, 126.8, 126.6, 125.8, 124.3, 122.8, 120.3, 55.3, 55.2, 47.2, 47.2, 45.1, 41.2, 36.9, 33.2, 32.8, 27.1, 26.0, 25.9, 25.8, 25.8, 25.7, 24.6, 24.5. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{22}H_{30}NO_2$ 340.2271; Found 340.2268.

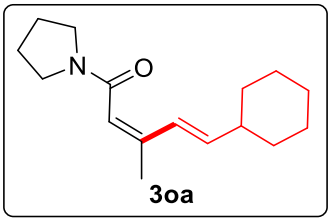
(2*Z*)-2-(4-Chlorophenyl)-5-cyclohexyl-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one (3na).



3na

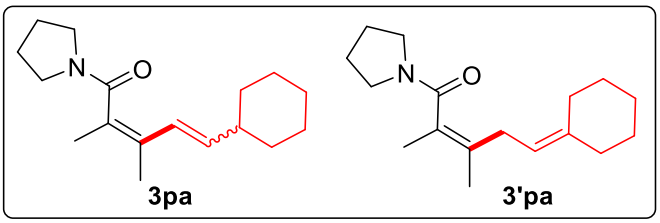
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of *E*/*Z* in the ratio of 3:1 and the yield is 69% (50 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 6.54 (d, *J* = 11.0 Hz, 1H), 6.11 (dd, *J* = 14.8, 11.2 Hz, 1H), 5.91 (dd, *J* = 15.0, 7.2 Hz, 1H), 3.66 – 3.61 (m, 2H), 3.20 – 3.15 (m, 2H), 2.11 – 2.01 (m, 1H), 1.97 – 1.89 (m, 2H), 1.86 – 1.80 (m, 2H), 1.73 – 1.65 (m, 4H), 1.20 – 1.07 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 146.1, 135.1, 134.4, 133.4, 131.3, 129.3, 129.1, 129.0, 128.9, 128.2, 126.9, 126.6, 124.1, 122.5, 47.2, 45.2, 41.2, 33.1, 32.6, 29.7, 26.0, 25.8, 25.8, 25.7, 24.5. HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{21}H_{26}ClNONa$ 366.1595; Found 366.1592.

(2*Z*,4*E*)-5-Cyclohexyl-2-methyl-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one (3oa).



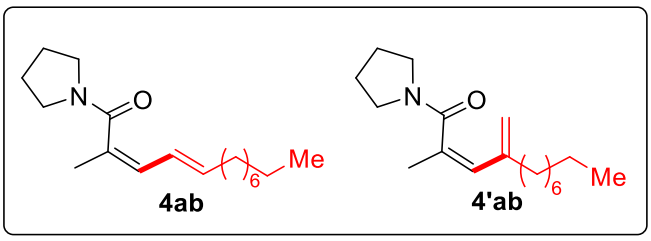
Prepared according to General Procedure 1. Colourless liquid; Eluent (20% ethyl acetate in hexane). Isolated yield is 45% (40 mg, single isomer). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 5.91 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.74 (s, 1H), 3.51 (t, *J* = 6.8 Hz, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.14 – 2.05 (m, 1H), 1.94 (s, 3H), 1.91 – 1.84 (m, 4H), 1.77 – 1.68 (m, 4H), 1.29 – 1.09 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.9, 142.2, 125.9, 118.7, 47.0, 45.4, 41.3, 32.7, 26.2, 26.1, 26.0, 24.4, 20.8. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{16}H_{26}NO$ 248.2009; Found 248.2007.

(2*Z*)-5-Cyclohexyl-2,3-dimethyl-1-(pyrrolidin-1-yl)penta-2,4-dien-1-one (3pa)/(*Z*)-5-Cyclohexylidene-2,3-dimethyl-1-(pyrrolidin-1-yl)pent-2-en-1-one (3'pa).



Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **3pa**/**3'pa** in the ratio of 5:1 and the yield is 54% (46 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 – 6.00 (m, 1H), 5.63 (dd, *J* = 15.6, 7.2 Hz, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.24 (t, *J* = 6.5 Hz, 2H), 1.89 (s, 3H), 1.88 – 1.82 (m, 4H), 1.75 (s, 3H), 1.71 – 1.51 (m, 4H), 1.28 – 1.02 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 138.3, 137.2, 130.2, 129.7, 126.7, 126.4, 47.0, 45.0, 41.1, 33.5, 33.1, 26.1, 25.9, 25.9, 25.9, 25.8, 24.6, 15.9, 13.2. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{17}H_{28}NO$ 262.2165; Found 262.2164.

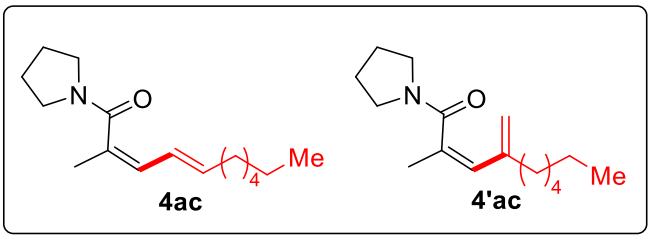
(2*Z*,4*E*)-2-Methyl-1-(pyrrolidin-1-yl)trideca-2,4-dien-1-one (4ab)/(*Z*)-2-Methyl-4-methylene-1-(pyrrolidin-1-yl)dodec-2-en-1-one (4'ab).



Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **4ab**/**4'ab** in the ratio of 3:1 and the yield is 59% (59 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 – 5.83 (m, 2H), 5.72 – 5.65 (m, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.33 – 3.27 (m, 2H), 2.04 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.92 (s, 3H), 1.90 – 1.85 (m, 4H), 1.45 – 1.24 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

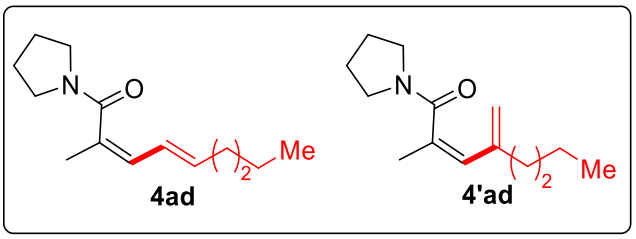
170.4, 144.6, 136.4, 134.2, 133.7, 133.0, 132.2, 128.4, 128.2, 126.3, 124.2, 113.7, 47.2, 47.1, 46.8, 45.1, 45.0, 35.2, 32.7, 31.8, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 28.3, 27.6, 25.9, 25.9, 24.5, 24.4, 22.6, 21.6, 20.0,14.0. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{18}H_{32}NO$ 278.2478; Found 278.2482.

(2*Z*,4*E*)-2-Methyl-1-(pyrrolidin-1-yl)undeca-2,4-dien-1-one (4ac)/(*Z*)-2-Methyl-4-methylene-1-(pyrrolidin-1-yl)dec-2-en-1-one (4'ac).



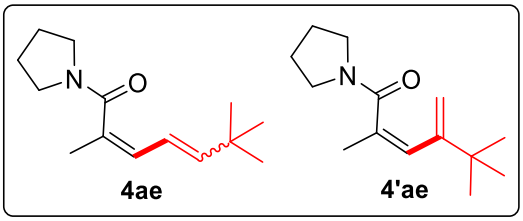
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **4ac**/**4'ac** in the ratio of 7:1 and the yield is 67% (60 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96 – 5.82 (m, 2H), 5.72 – 5.65 (m, 1H), 3.54 (t, *J* = 6.6 Hz, 2H), 3.34 – 3.29 (m, 2H), 2.07 – 2.02 (m, 2H), 1.92 (s, 3H), 1.91 – 1.87 (m, 4H), 1.37 – 1.26 (m, 8H), 0.89 – 0.85 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 136.5, 133.8, 132.2, 128.2, 126.3, 123.0, 113.8, 47.2, 45.1, 32.7, 31.7, 29.2, 28.8, 25.9, 24.5, 22.6, 20.0, 14.1. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{16}H_{28}NO$ 250.2165; Found 250.2167.

(2*Z*,4*E*)-2-Methyl-1-(pyrrolidin-1-yl)nona-2,4-dien-1-one (4ad)/(*Z*)-2-Methyl-4-methylene-1-(pyrrolidin-1-yl)oct-2-en-1-one (4'ad).



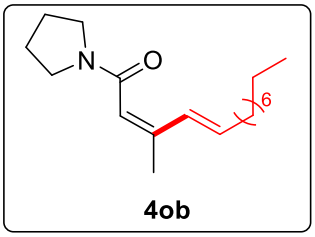
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **4ad**/**4'ad** in the ratio of 3:1 and the yield is 68% (54 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 – 5.82 (m, 2H), 5.73 – 5.65 (m, 1H), 3.56 – 3.51 (m, 2H), 3.33 – 3.28 (m, 2H), 2.08 – 2.03 (m, 2H), 1.92 (s, 3H), 1.91 – 1.86 (m, 4H), 1.33 – 1.24 (m, 4H), 0.90 – 0.85 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 144.6, 136.4, 132.2, 128.5, 128.2, 126.3, 124.2, 123.0, 113.8, 47.2, 46.9, 45.2, 45.0, 34.9, 32.3, 31.3, 30.4, 27.3, 25.9, 25.9, 24.5, 24.4, 22.4, 22.1, 21.6, 20.0, 13.9, 13.9. HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{14}H_{23}NONa$ 244.1672; Found 244.1677.

(2*Z*,4*E*)-2,6,6-Trimethyl-1-(pyrrolidin-1-yl)hepta-2,4-dien-1-one (4ae)/(*Z*)-2,5,5-Trimethyl-4-methylene-1-(pyrrolidin-1-yl)hex-2-en-1-one (4'ae).



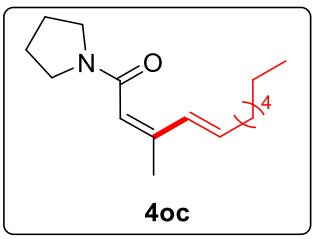
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **4ae**/**4'ae** in the ratio of 4:1 and the yield is 44% (35 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 – 5.80 (m, 2H), 5.73 (d, *J* = 14.7 Hz, 1H), 3.55 – 3.45 (m, 4H), 3.34 – 3.28 (m, 4H), 1.93 (s, 3H), 1.91 – 1.81 (m, 4H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 147.1, 143.0, 135.6, 132.5, 132.2, 128.5, 125.8, 123.7, 122.6, 121.3, 110.0, 47.19, 46.80, 45.0, 45.0, 44.0, 42.1, 33.2, 31.4, 29.5, 29.4, 27.4, 27.3, 26.0, 26.0, 24.6, 20.0. HRMS (ESI-TOF) m/z : $(M+H)^+$ Calcd for $C_{14}H_{24}NO$ 222.1852; Found 222.1855.

(2*Z*,4*E*)-2-Methyl-1-(pyrrolidin-1-yl)trideca-2,4-dien-1-one (4ob).



Prepared according to General Procedure 1. Colourless liquid; Eluent (20% ethyl acetate in hexane). Isolated yield is 50% (50 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 14 Hz, 1H), 6.04 – 5.94 (m, 1H), 5.74 (s, 1H), 5.22 (s, 1H), 5.04 (s, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 2.16 (m, 2H), 1.95 (s, 3H), 1.94 – 1.85 (m, 4H), 1.46 – 1.27 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.6, 137.0, 128.1, 118.7, 47.1, 45.5, 33.3, 31.9, 29.5, 29.4, 29.3, 26.2, 24.4, 22.7, 20.9, 14.1. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{18}H_{32}NO$ 278.2478; Found 278.2475.

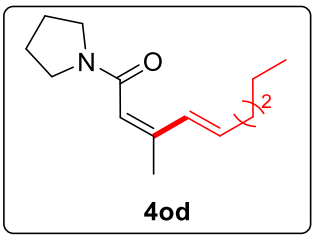
(2*Z*,4*E*)-3-Methyl-1-(pyrrolidin-1-yl)undeca-2,4-dien-1-one (4oc).



Prepared according to General Procedure 1. Colourless liquid; Eluent (20% ethyl acetate in hexane). Isolated yield is 45% (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 16.3 Hz, 1H), 6.04 – 5.93 (m, 1H), 5.73 (s, 1H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 2.20 – 2.09 (m, 2H), 1.94 (s, 3H), 1.93 – 1.82 (m, 4H), 1.45 – 1.35 (m, 2H), 1.33 – 1.26 (m, 8H), 0.87 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 144.6, 136.9, 128.1, 118.6,

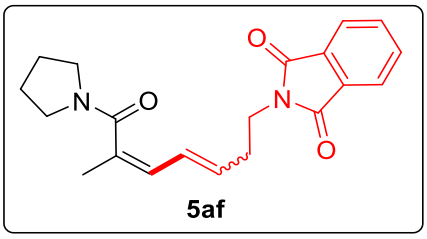
47.1, 45.4, 33.2, 31.7, 29.2, 29.0, 26.1, 24.4, 22.6, 20.9, 14.1. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{16}H_{28}NO$ 250.2165; Found 250.2169.

(2*Z*,4*E*)-3-Methyl-1-(pyrrolidin-1-yl)nona-2,4-dien-1-one (4od).



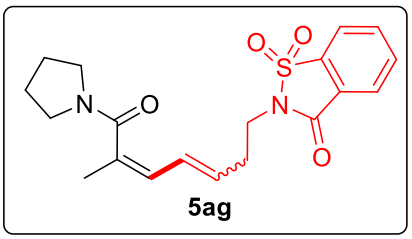
Prepared according to General Procedure 1. Colourless liquid; Eluent (20% ethyl acetate in hexane). Isolated yield is 49% (39 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 1H), 6.00 (dd, *J* = 15.1, 7.9 Hz, 1H), 5.74 (s, 1H), 3.52 (t, *J* = 6.1 Hz, 2H), 3.43 (t, *J* = 5.9 Hz, 2.2H), 2.20 – 2.12 (m, 2H), 1.95 (s, 3H), 1.93 – 1.84 (m, 4H), 1.45 – 1.27 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 144.6, 136.8, 128.2, 118.7, 47.0, 45.4, 32.9, 31.4, 26.2, 24.4, 22.4, 20.8, 13.9. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{14}H_{24}NO$ 222.1852; Found 278.1855.

2-((5*Z*)-6-Methyl-7-oxo-7-(pyrrolidin-1-yl)hepta-3,5-dien-1-yl)isoindoline-1,3-dione (5af).



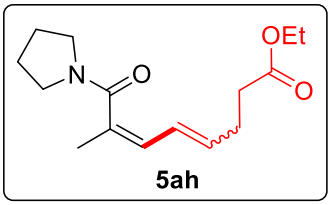
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of E/Z in the ratio of 4:1 and the yield is 66% (80 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.68 – 7.61 (m, 2H), 5.93 – 5.80 (m, 2H), 5.60 (dt, *J* = 14.5, 7.2 Hz, 1H), 3.68 (t, *J* = 6.9 Hz, 2H), 3.43 (t, *J* = 7.1 Hz, 2H), 3.10 (t, *J* = 6.7 Hz, 2H), 2.44 – 2.36 (m, 2H), 1.83 (s, 3H), 1.73 – 1.64 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 168.2, 133.9, 133.5, 132.0, 131.3, 128.7, 128.1, 127.8, 127.2, 123.2, 122.4, 47.2, 47.0, 45.1, 45.1, 37.3, 37.3, 32.0, 26.6, 25.8, 24.4, 24.4, 21.0, 20.1, 19.9, 14.2. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{20}H_{23}N_2O_3$ 339.1703; Found 339.1706.

2-((5*Z*)-6-Methyl-7-oxo-7-(pyrrolidin-1-yl)hepta-3,5-dien-1-yl)benzo[d]isothiazol-3(2*H*)-one 1,1-dioxide (5ag).



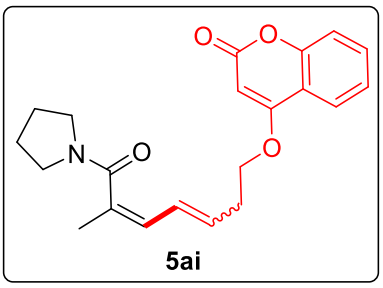
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of E/Z in the ratio of 2.5:1 and the yield is 59% (78 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.93 – 7.80 (m, 3H), 6.04 – 5.90 (m, 2H), 5.80 – 5.68 (m, 1H), 3.83 (t, *J* = 7.0 Hz, 2H), 3.54 (t, *J* = 7.3 Hz, 2H), 3.24 (t, *J* = 6.4 Hz, 2H), 2.66 – 2.60 (m, 2H), 1.91 (s, 3H), 1.89 – 1.83 (m, 2H), 1.80 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 158.8, 137.6, 134.8, 134.4, 131.9, 131.6, 129.0, 128.8, 128.3, 127.2, 127.2, 127.0, 125.2, 125.1, 123.6, 120.9, 120.8, 47.7, 47.6, 45.9, 45.7, 38.6, 38.5, 31.7, 26.8, 25.7, 25.6, 24.3, 24.3, 20.0, 19.6. HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{19}H_{22}N_2O_4SNa$ 397.1192; Found 397.1192.

Ethyl (6*Z*)-7-methyl-8-oxo-8-(pyrrolidin-1-yl)octa-4,6-dienoate (5ah).



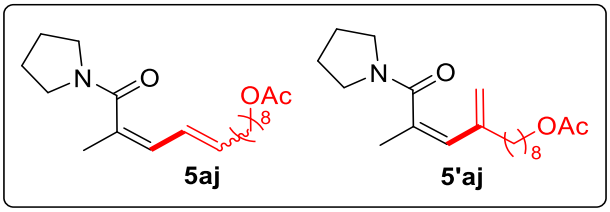
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of E/Z in the ratio of 2:1 and the yield is 72% (72 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00 – 5.86 (m, 2H), 5.71 – 5.64 (m, 1H), 4.14 – 4.09 (m, 2H), 3.55 – 3.50 (m, 2H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.36 (m, 2H), 1.91 (s, 3H), 1.90 – 1.84 (m, 4H), 1.27 – 1.22 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 170.2, 133.5, 130.6, 127.7, 127.4, 125.5, 122.5, 60.4, 60.3, 47.2, 47.1, 45.0, 34.1, 33.9, 27.9, 25.9, 24.5, 23.1, 20.2, 19.9, 14.2. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{15}H_{24}NO_3$ 266.1751; Found 266.1750.

4-(((5*Z*)-6-Methyl-7-oxo-7-(pyrrolidin-1-yl)hepta-3,5-dien-1-yl)oxy)-2H-chromen-2-one (5ai).



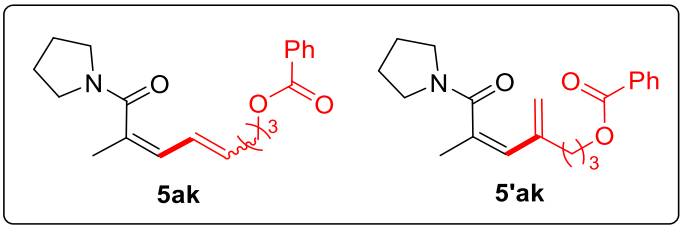
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **5ai**/**5'ai** in the ratio of 4:1 and the yield is 54% (69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.12 (m, 1H), 5.94 (d, *J* = 11.0 Hz, 1H), 5.80 – 5.70 (m, 1H), 5.65 (s, 1H), 4.15 (q, *J* = 6.1 Hz, 2H), 3.56 – 3.49 (m, 2H), 3.30 (t, *J* = 5.5 Hz, 2H), 2.68 (q, *J* = 6.4 Hz, 2H), 1.94 (s, 3H), 1.87 (s, 4H). δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 165.5, 162.9, 153.3, 134.6, 132.4, 129.7, 129.4, 127.4, 123.9, 123.0, 122.2, 118.8, 116.7, 115.6, 90.5, 68.4, 60.4, 47.2, 45.1, 31.8, 29.7, 27.0, 25.9, 24.4, 21.0, 20.0, 14.2. HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{21}H_{23}NO_4Na$ 376.1519; Found 376.1515.

(9*E*,11*Z*)-12-Methyl-13-oxo-13-(pyrrolidin-1-yl)trideca-9,11-dien-1-yl acetate (5aj)/(*Z*)-11-Methyl-9-methylene-12-oxo-12-(pyrrolidin-1-yl)dodec-10-en-1-yl acetate (5'aj).



Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **5aj**/**5'aj** in the ratio of 6:1 and the yield is 68% (82 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 – 5.83 (m, 2H), 5.70 – 5.62 (m, 1H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.30 (t, *J* = 6.3 Hz, 2H), 2.06 – 2.00 (m, 5H), 1.90 (s, 3H), 1.89 – 1.84 (m, 4H), 1.61 – 1.56 (m, 2H), 1.35 – 1.24 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 170.4, 144.6, 136.2, 133.5, 133.0, 132.3, 128.3, 128.1, 126.3, 124.3, 122.9, 113.8, 64.5, 64.5, 47.1, 47.0, 46.8, 45.1, 45.0, 35.1, 32.6, 29.4, 29.3, 29.3, 29.1, 29.1, 29.1, 29.0, 29.0, 28.5, 28.5, 28.5, 28.2, 27.5, 25.9, 25.8, 24.5, 24.4, 24.3, 21.5, 20.9, 20.2, 19.9. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{20}H_{34}NO_3$ 336.2533; Found 336.2533.

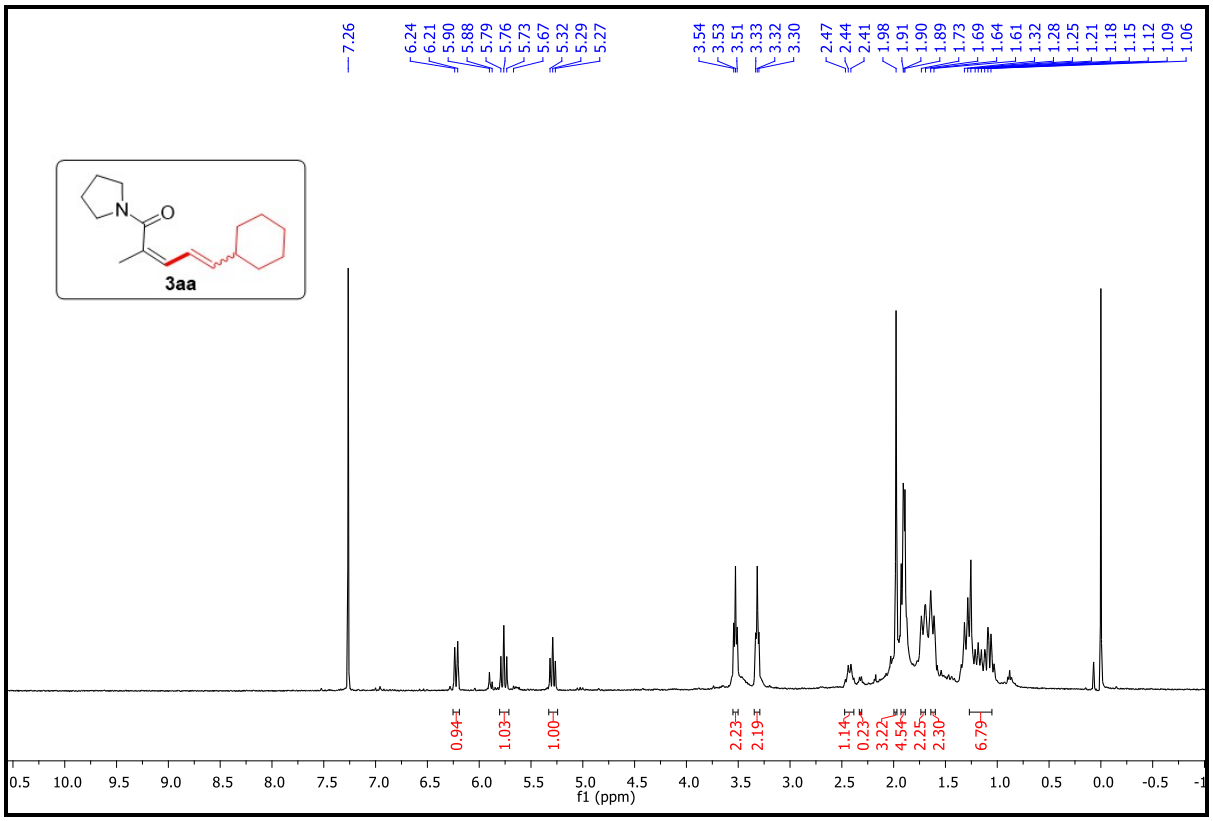
(4*E*,6*Z*)-7-Methyl-8-oxo-8-(pyrrolidin-1-yl)octa-4,6-dien-1-yl benzoate (5ak)/(Z)-11-(*Z*)-6-Methyl-4-methylene-7-oxo-7-(pyrrolidin-1-yl)hept-5-en-1-yl benzoate (5'ak).



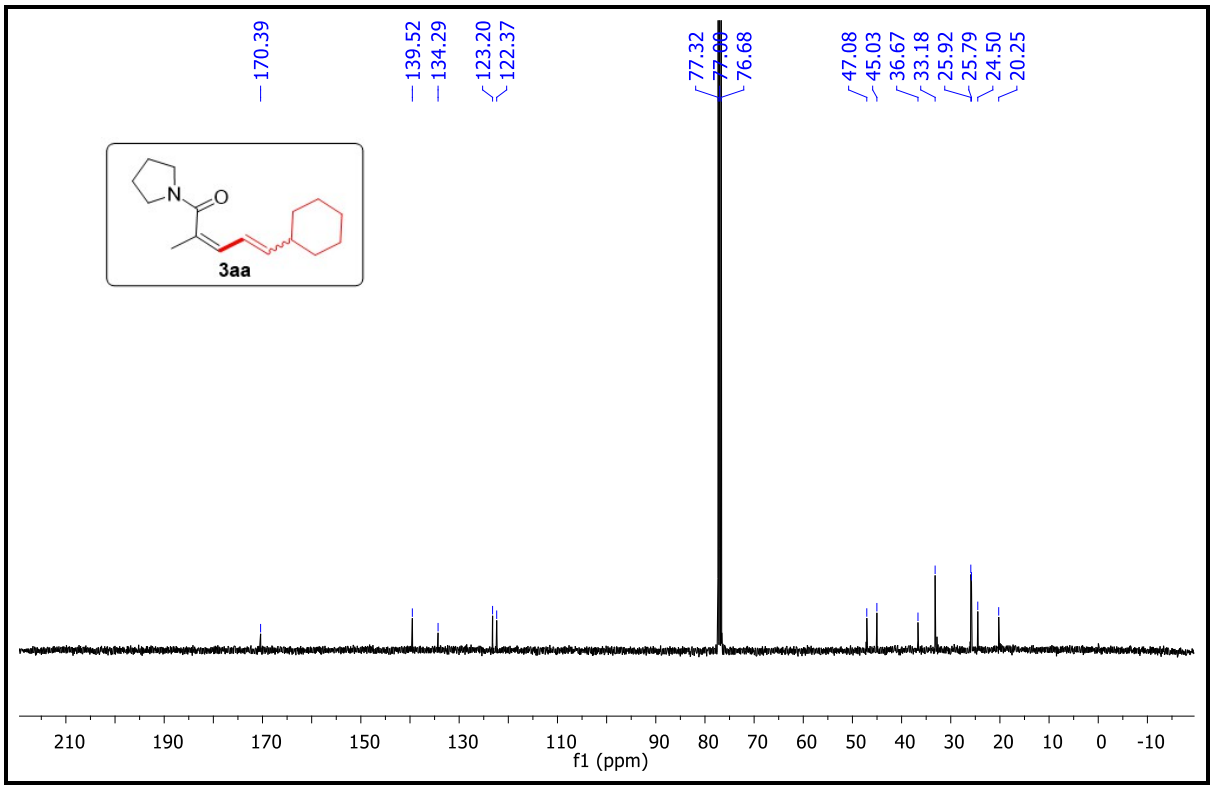
Prepared according to General Procedure 1. Colourless liquid; Eluent (30% ethyl acetate in hexane). Isolated as an inseparable mixture of **5ak**/**5'ak** in the ratio of 5:1 and the yield is 69% (78 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (t, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 6.02 – 5.90 (m, 2H), 5.74 – 5.66 (m, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.52 – 3.47 (m, 2H), 3.30 – 3.26 (m, 2H), 2.24 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.92 (s, 3H), 1.88 – 1.82 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 166.5, 134.3, 133.2, 132.9, 131.4, 130.3, 129.5, 128.3, 127.8, 127.3, 125.5, 122.5, 114.7, 64.1, 64.0, 47.2, 47.1, 45.1, 45.0, 31.5, 29.1, 28.4, 28.2, 27.4, 25.9, 25.8, 24.4, 24.4, 24.0, 21.6, 20.1, 19.9. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{20}H_{26}NO_3$ 328.1907; Found 328.1908.

Copies of ^{1}H, $^{13}C\{1H\}$ NMR and DEPT-135 Spectra

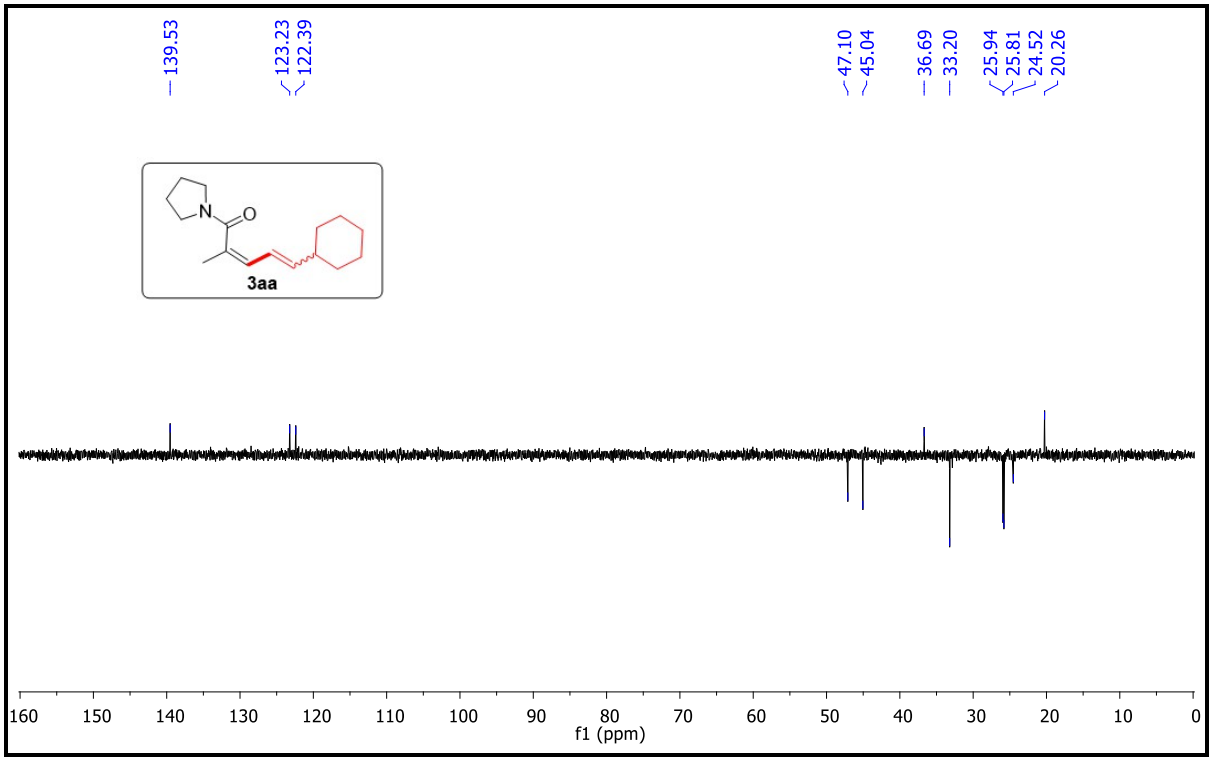
^{1}H NMR spectra of compound **3aa** in $CDCl_3$ at 400 MHz



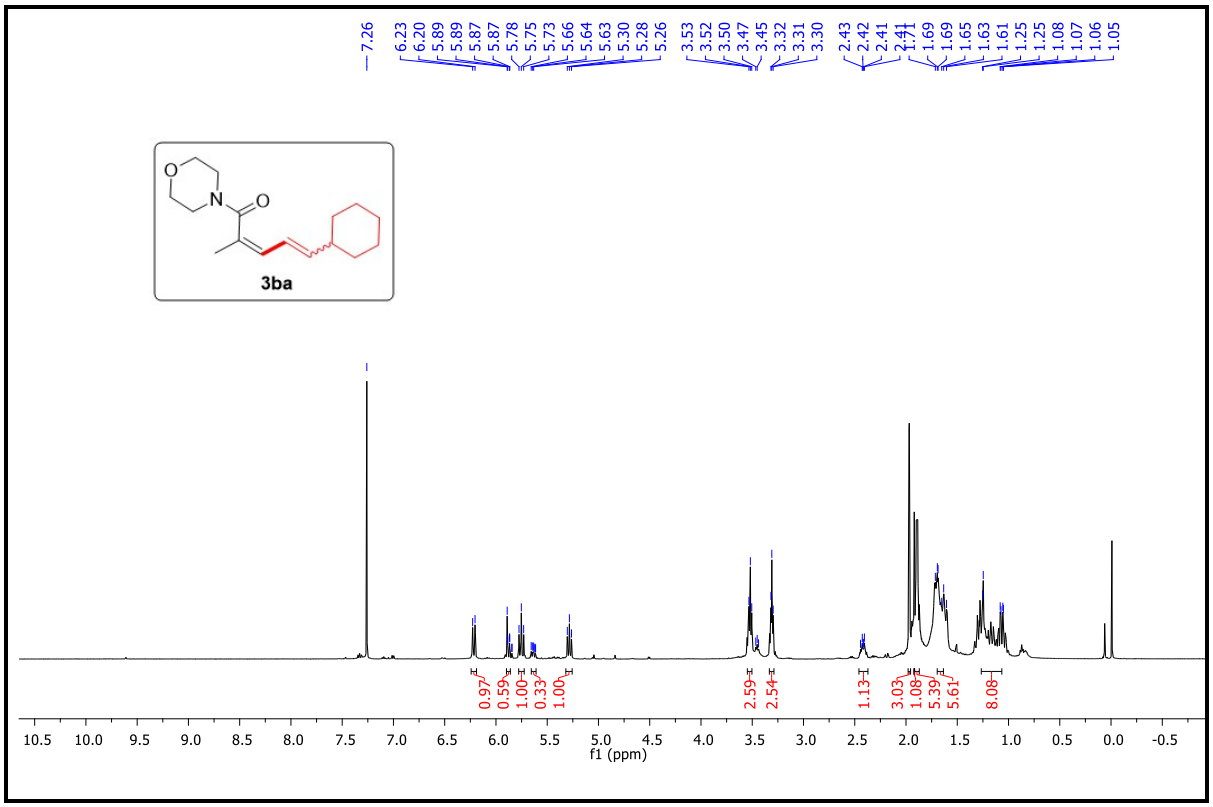
^{13}C NMR spectra of compound **3aa** in $CDCl_3$ at 101 MHz



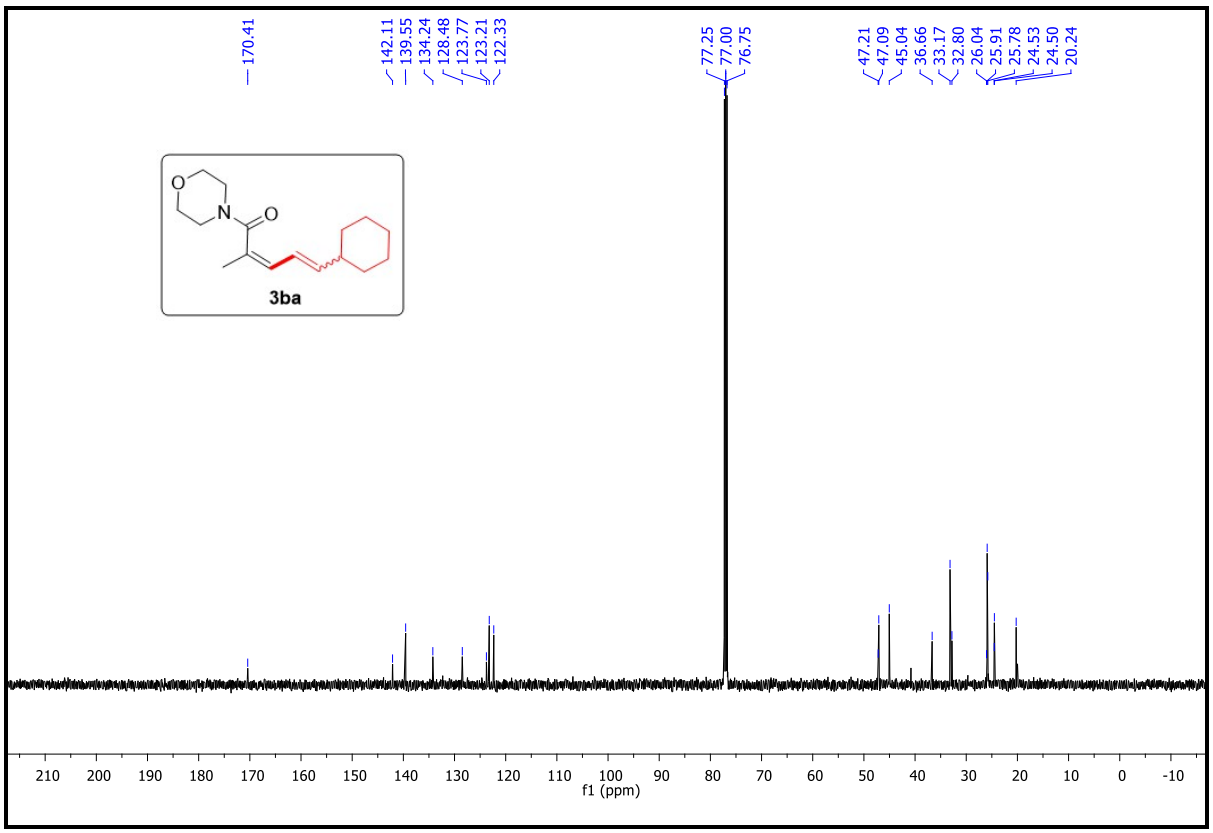
DEPT 135 NMR spectra of compound **3aa** in $CDCl_3$ at 101 MHz



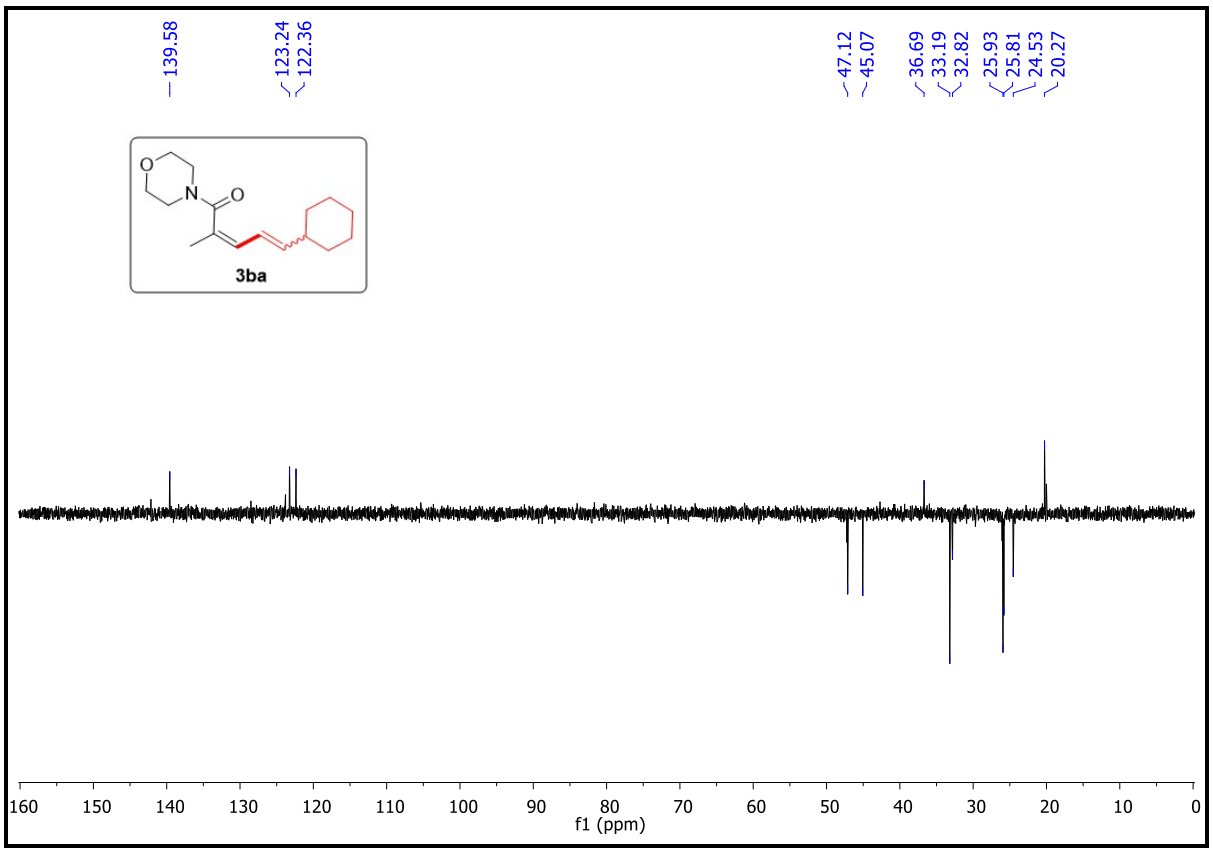
^{1}H NMR spectra of compound **3ba** in $CDCl_3$ at 400 MHz



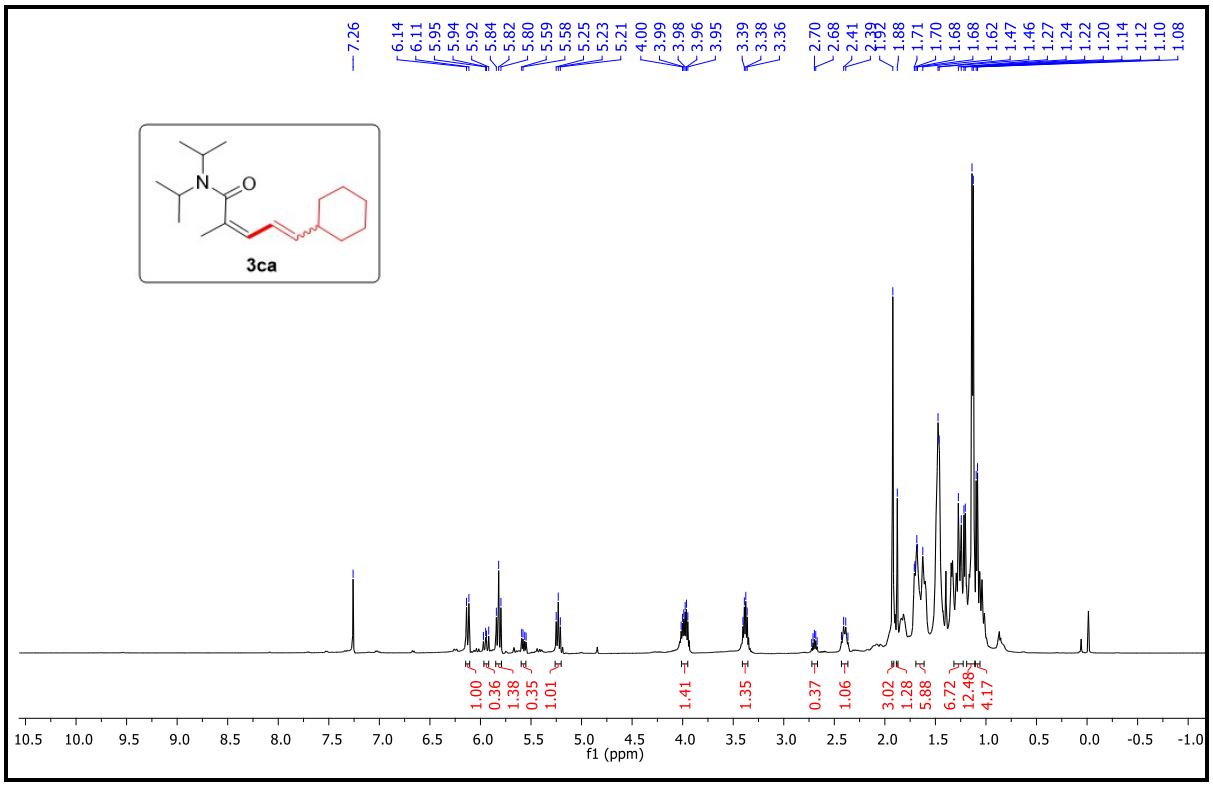
^{13}C NMR spectra of compound **3ba** in $CDCl_3$ at 101 MHz



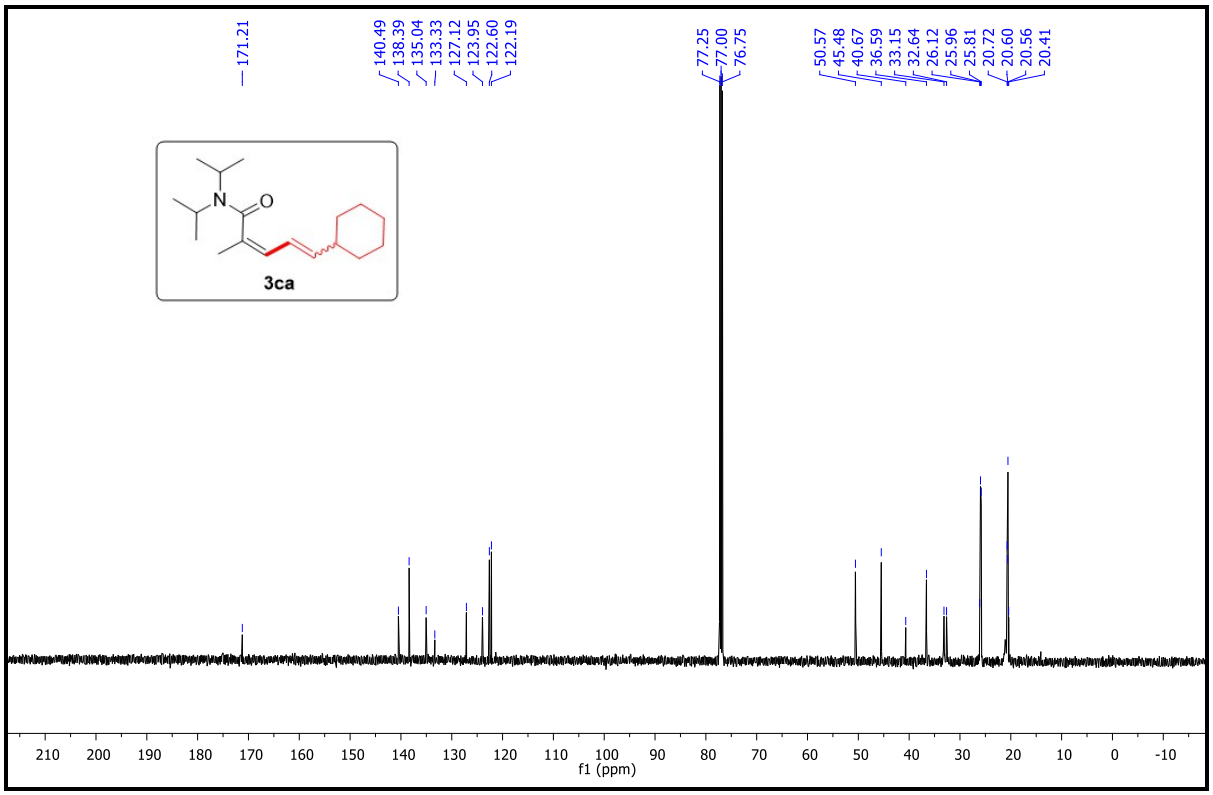
DEPT 135 NMR spectra of compound **3ba** in $CDCl_3$ at 101 MHz



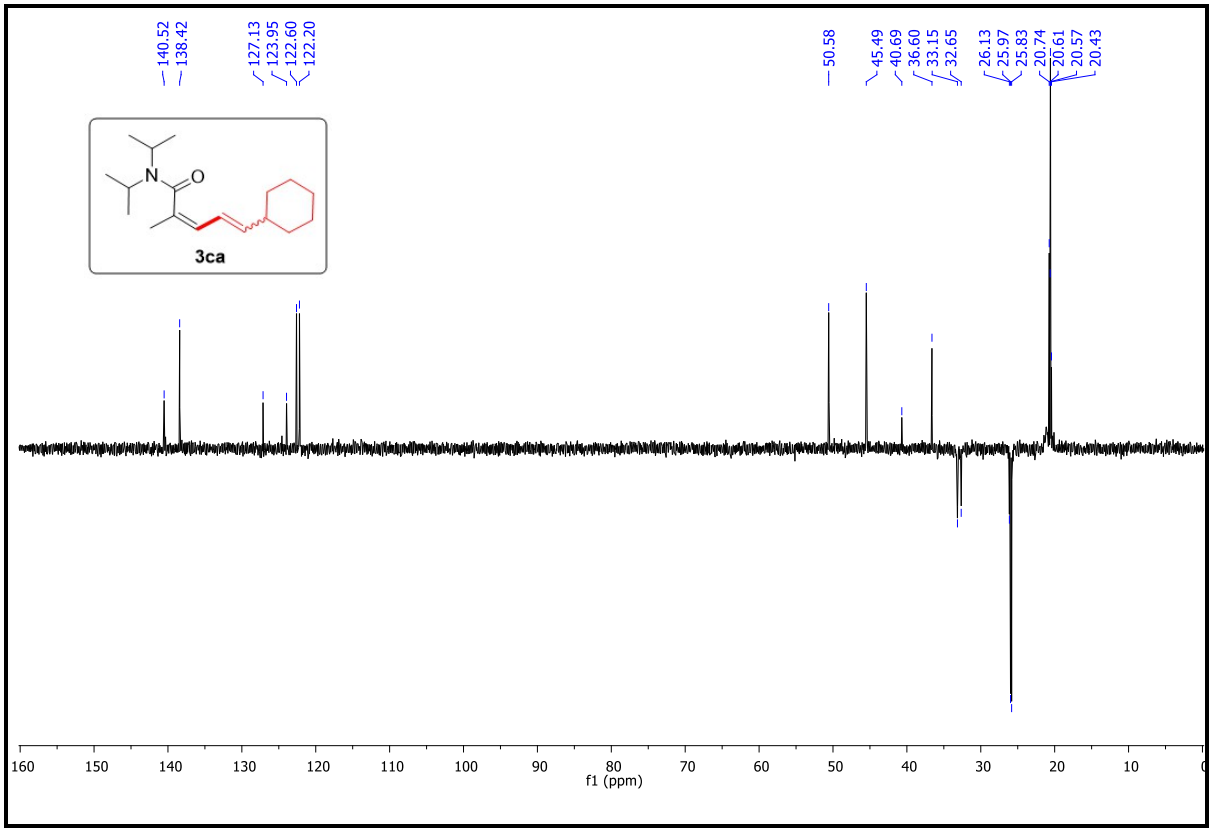
^{1}H NMR spectra of compound **3ca** in $CDCl_3$ at 500 MHz



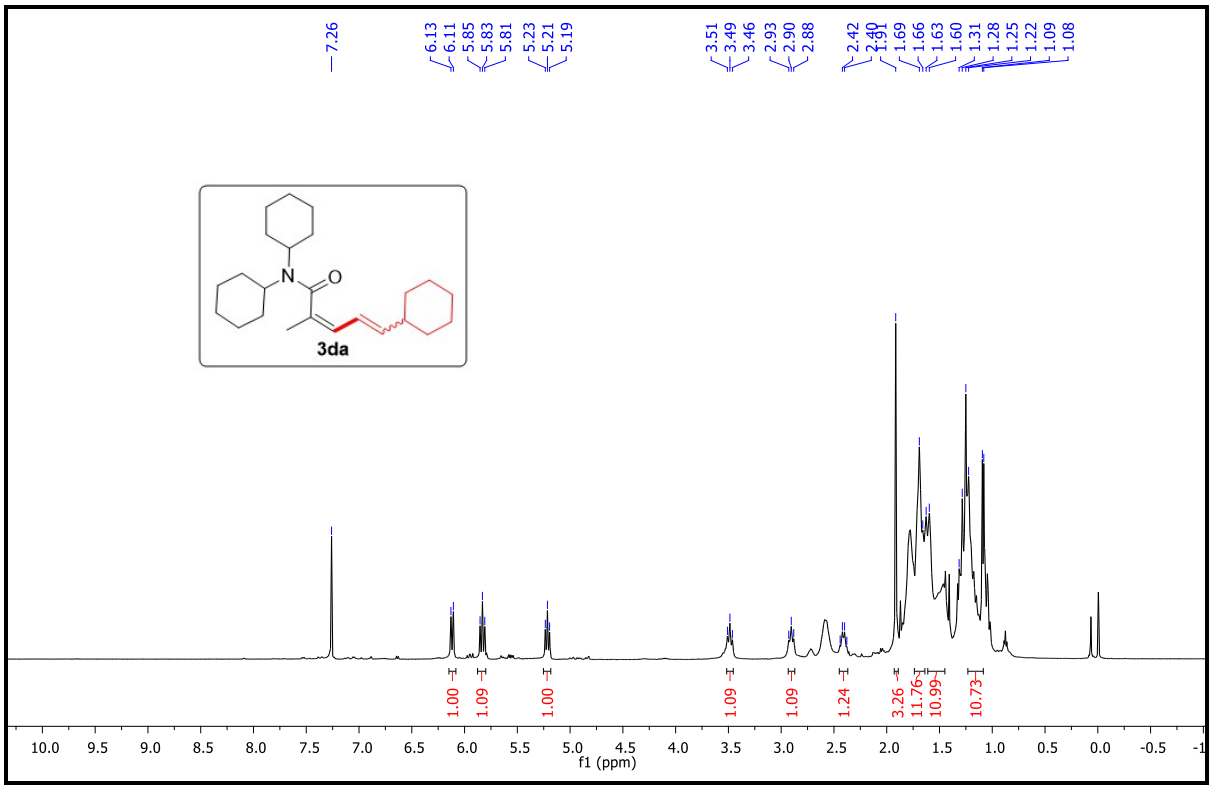
^{13}C NMR spectra of compound **3ca** in $CDCl_3$ at 126 MHz



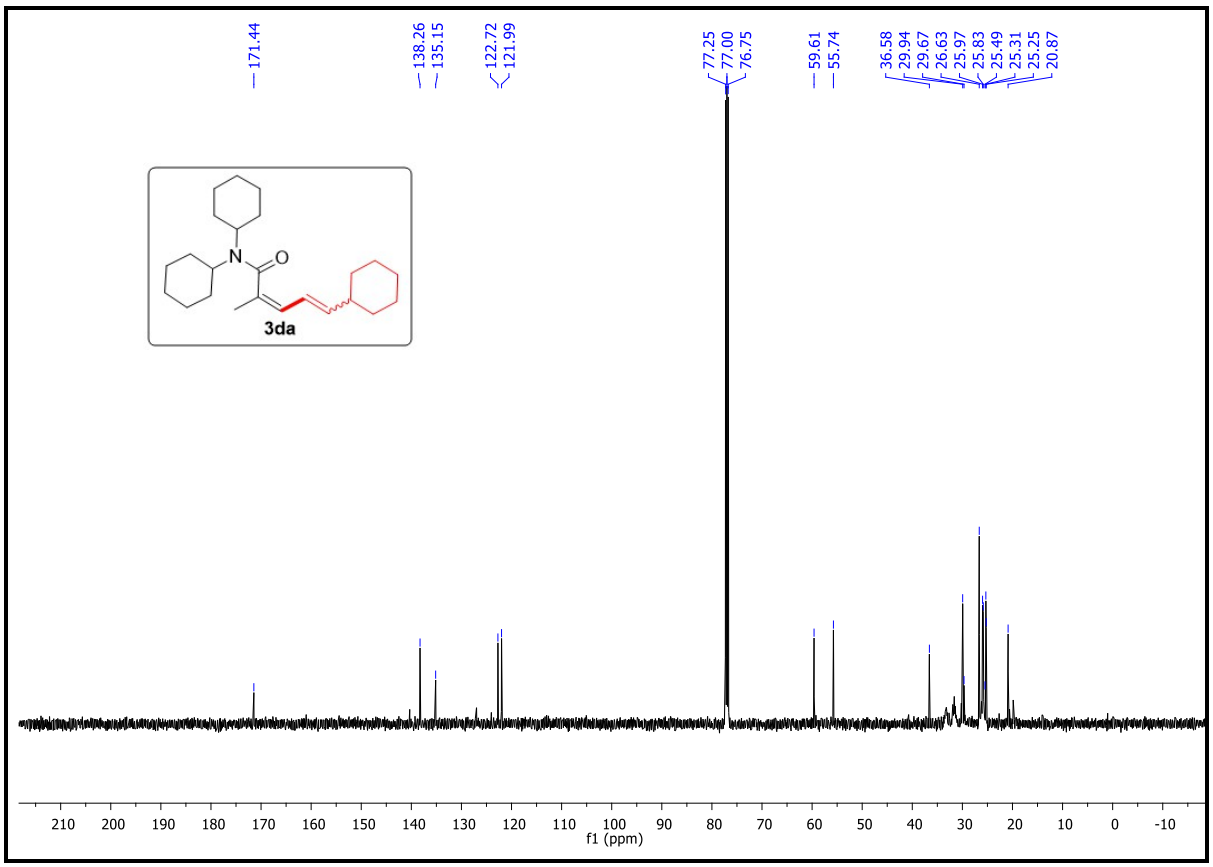
DEPT 135 NMR spectra of compound **3ca** in $CDCl_3$ at 126 MHz



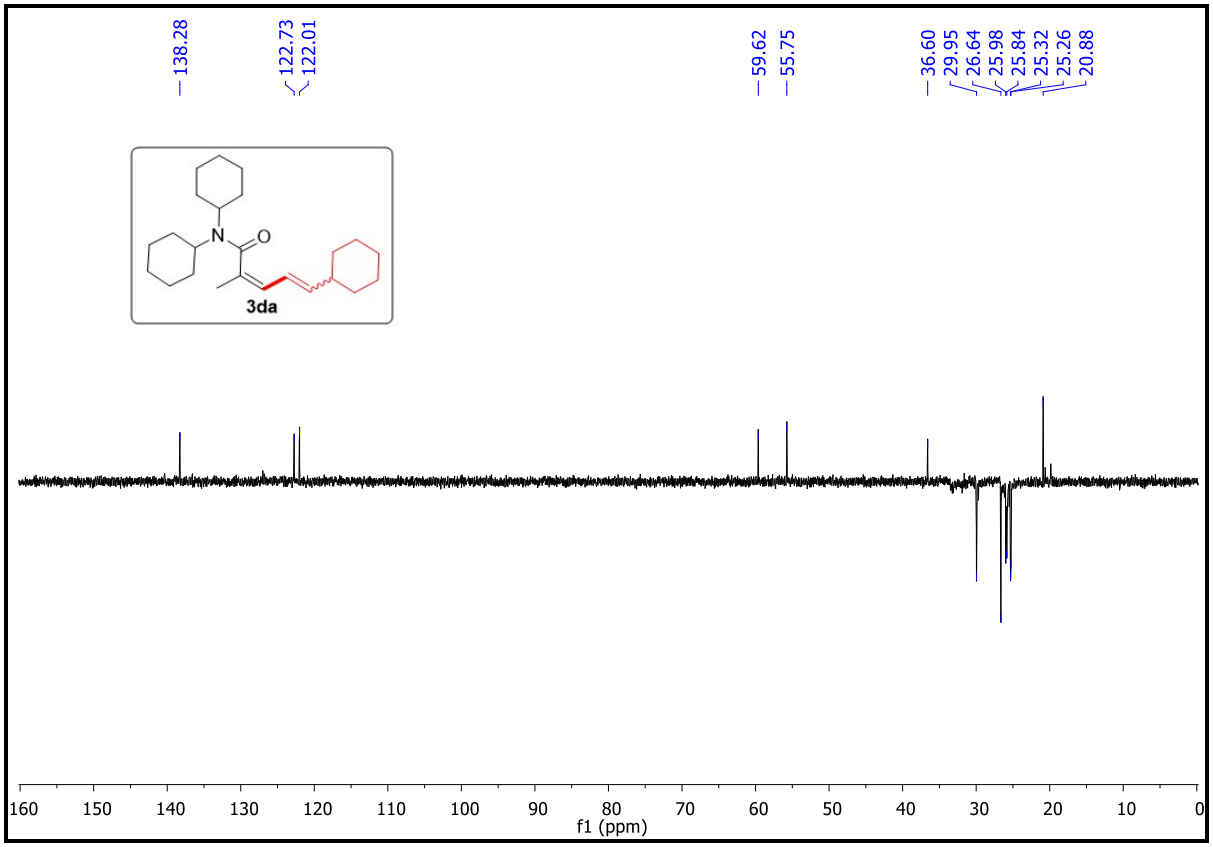
^{1}H NMR spectra of compound **3da** in $CDCl_3$ at 400 MHz



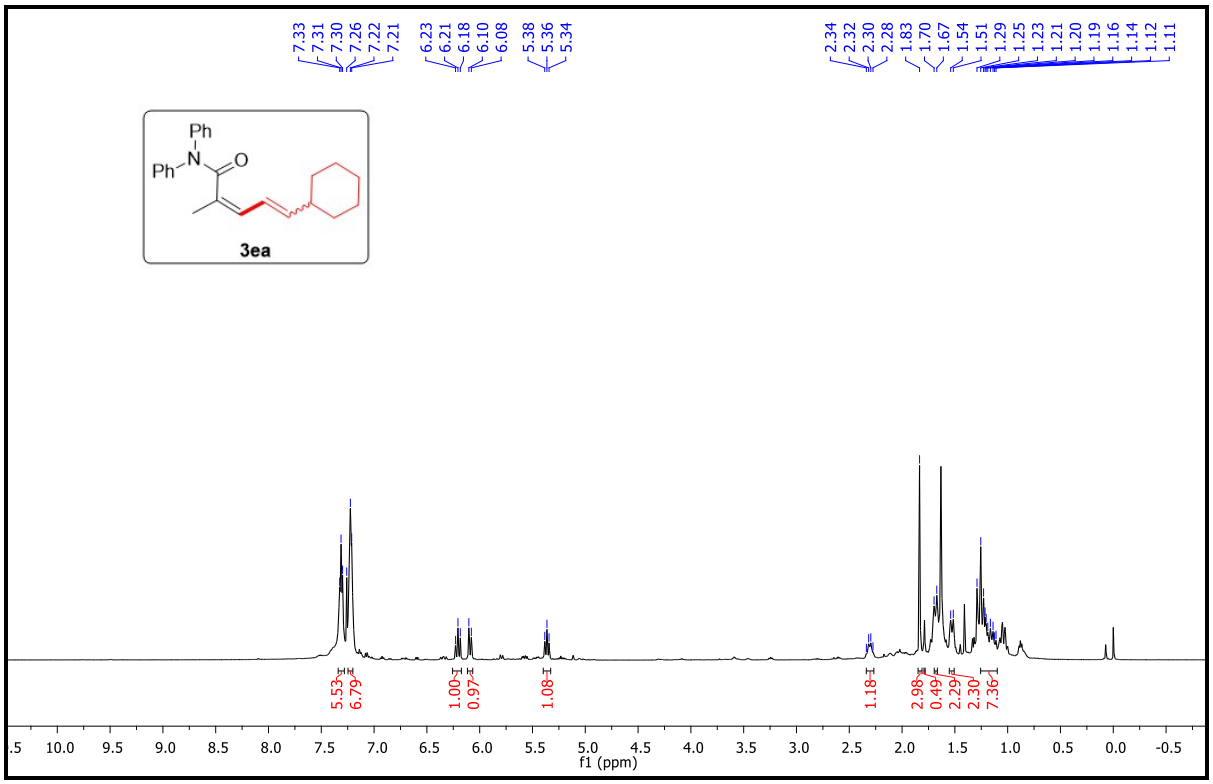
^{13}C NMR spectra of compound **3da** in $CDCl_3$ at 101 MHz



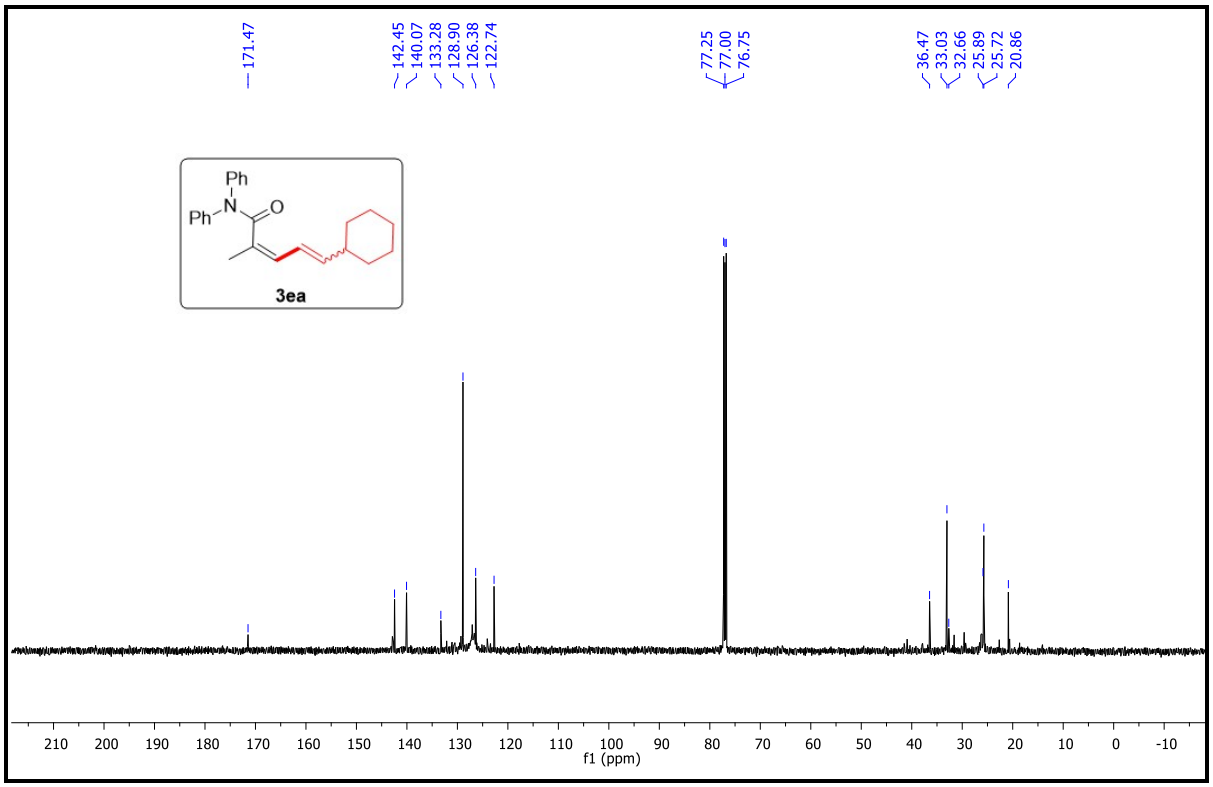
DEPT 135 NMR spectra of compound **3da** in $CDCl_3$ at 101 MHz



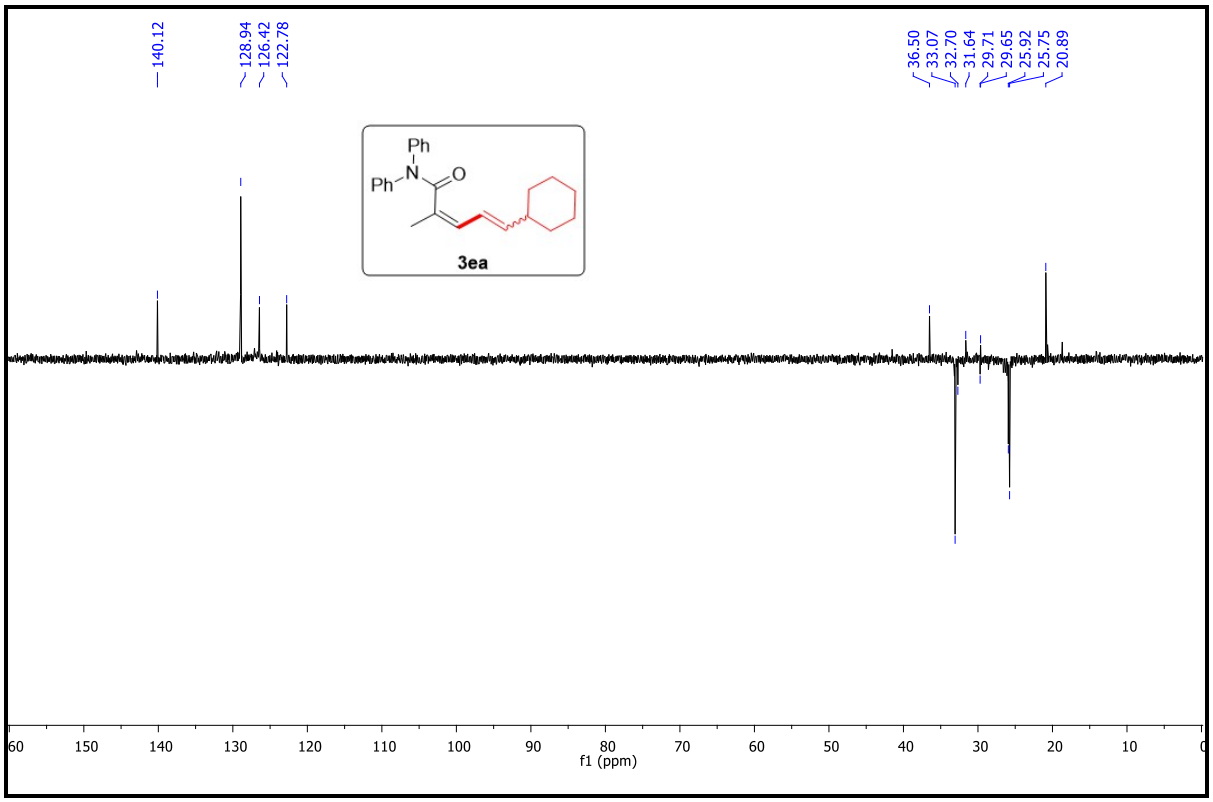
^{1}H NMR spectra of compound **3ea** in $CDCl_3$ at 500 MHz



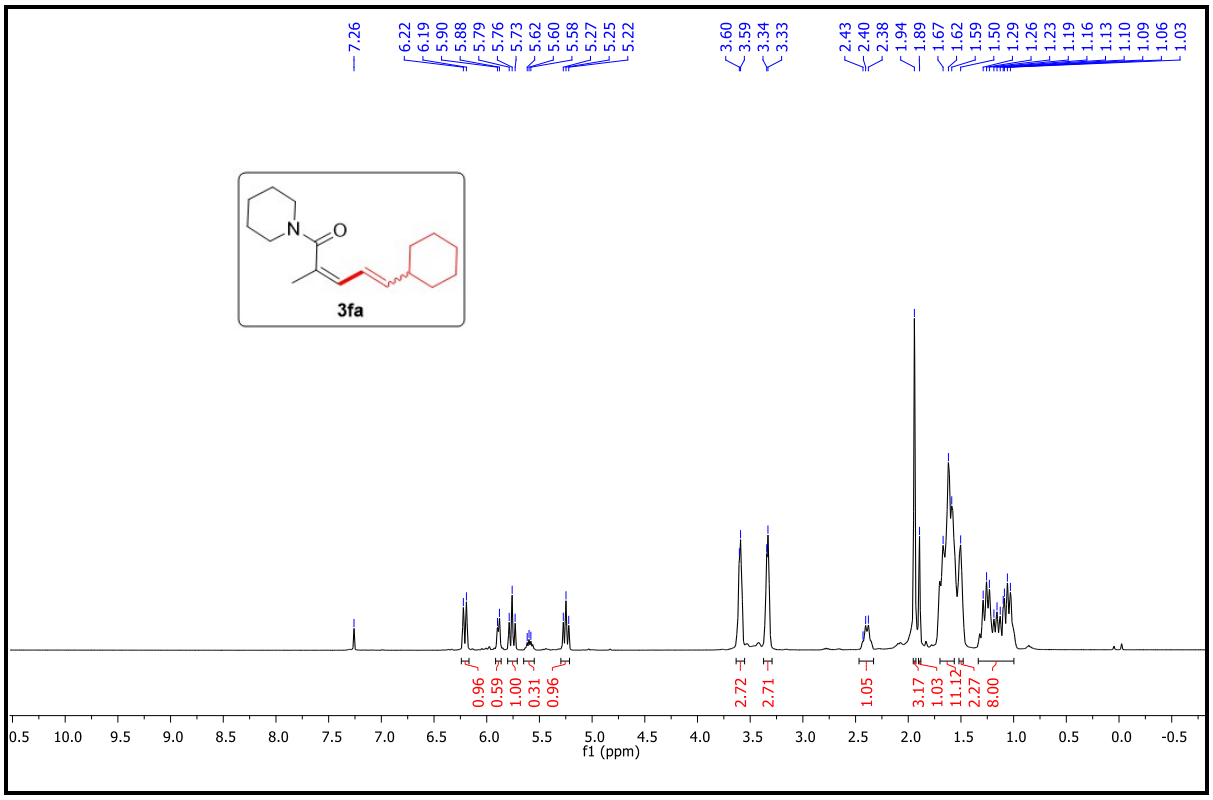
^{13}C NMR spectra of compound **3ea** in $CDCl_3$ at 126 MHz



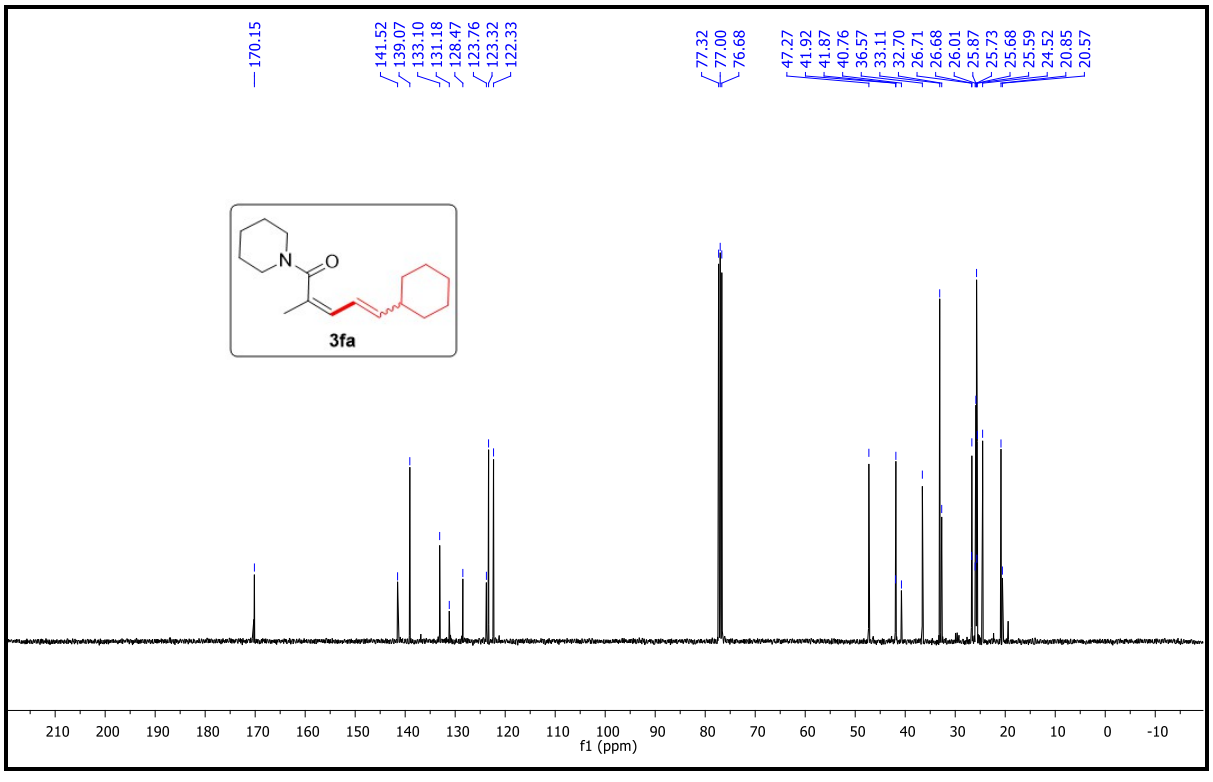
DEPT 135 NMR spectra of compound **3ea** in $CDCl_3$ at 126 MHz



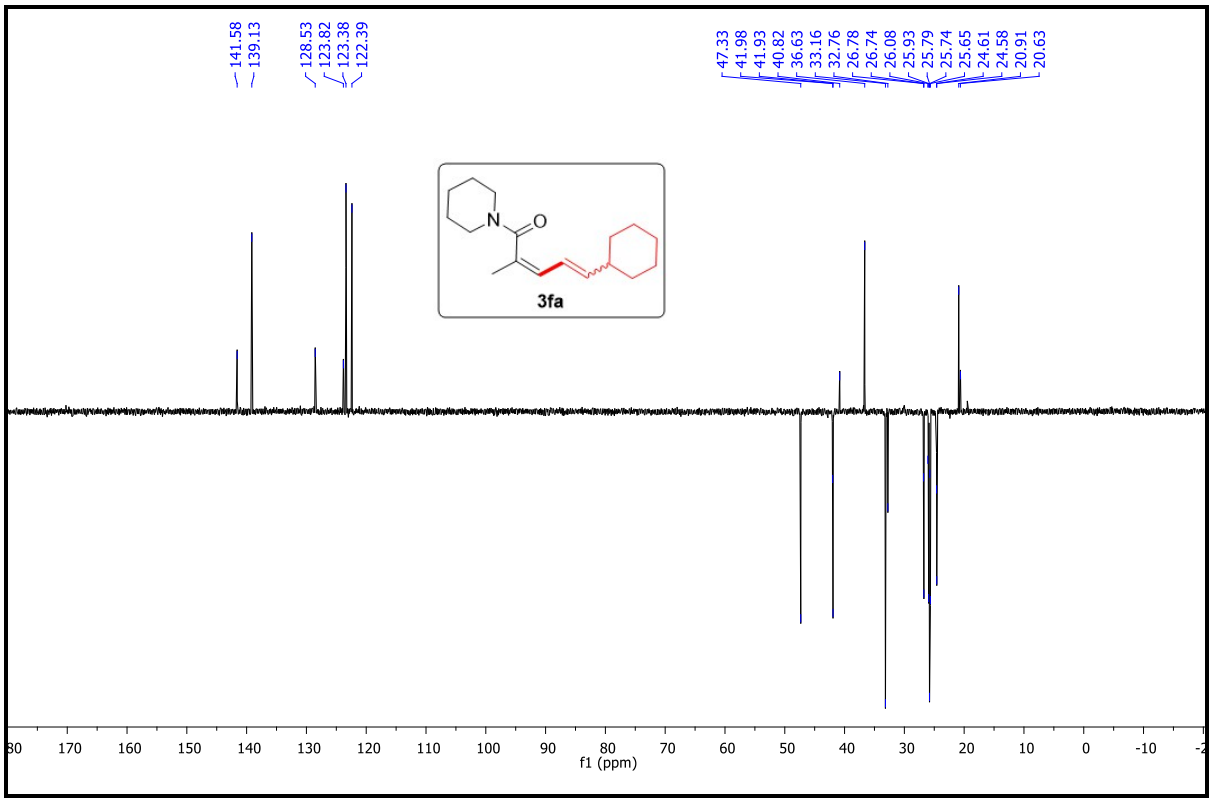
^{1}H NMR spectra of compound **3fa** in $CDCl_3$ at 400 MHz



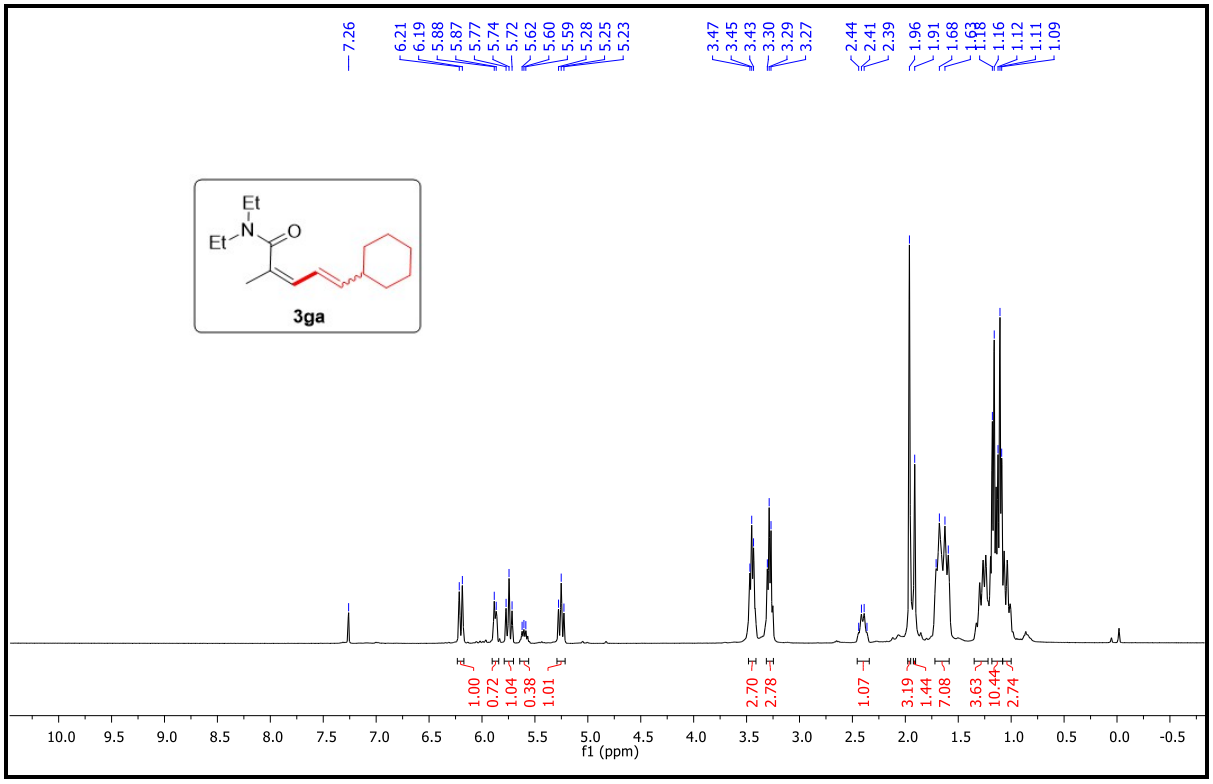
^{13}C NMR spectra of compound **3fa** in $CDCl_3$ at 101 MHz



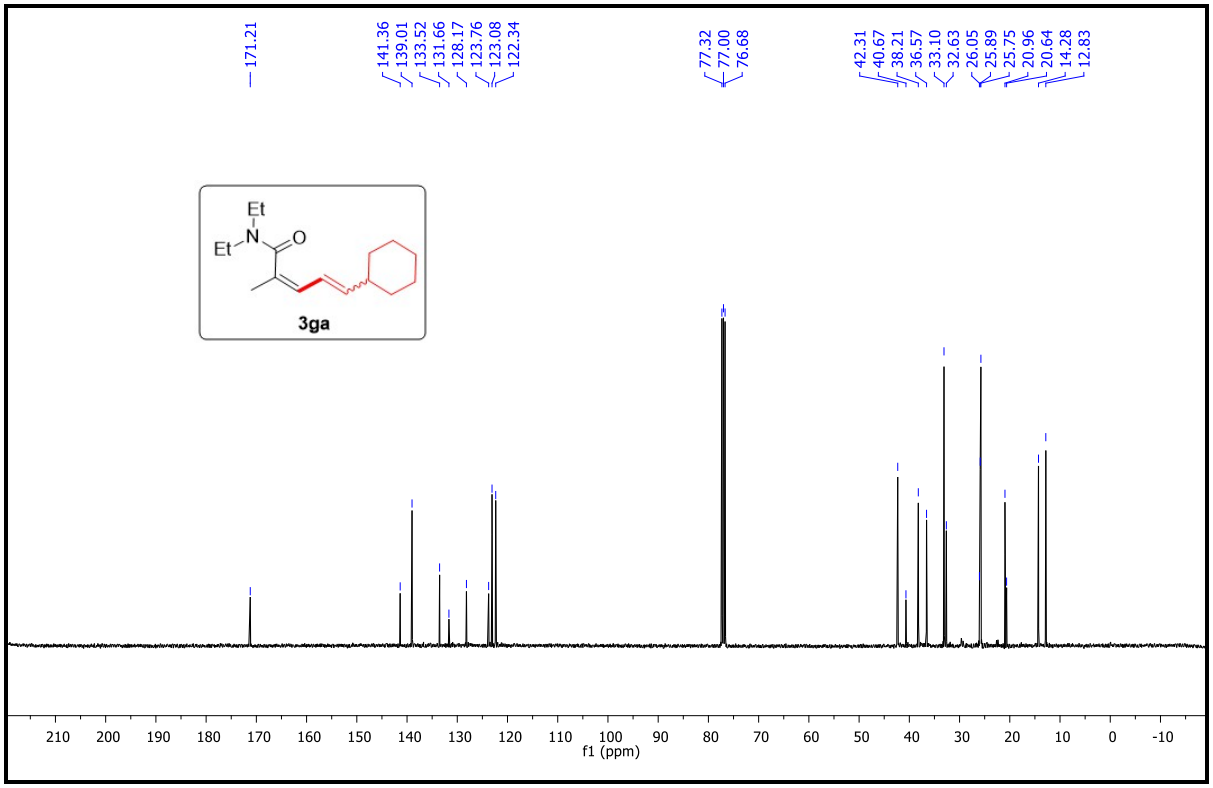
DEPT 135 NMR spectra of compound **3fa** in $CDCl_3$ at 101 MHz



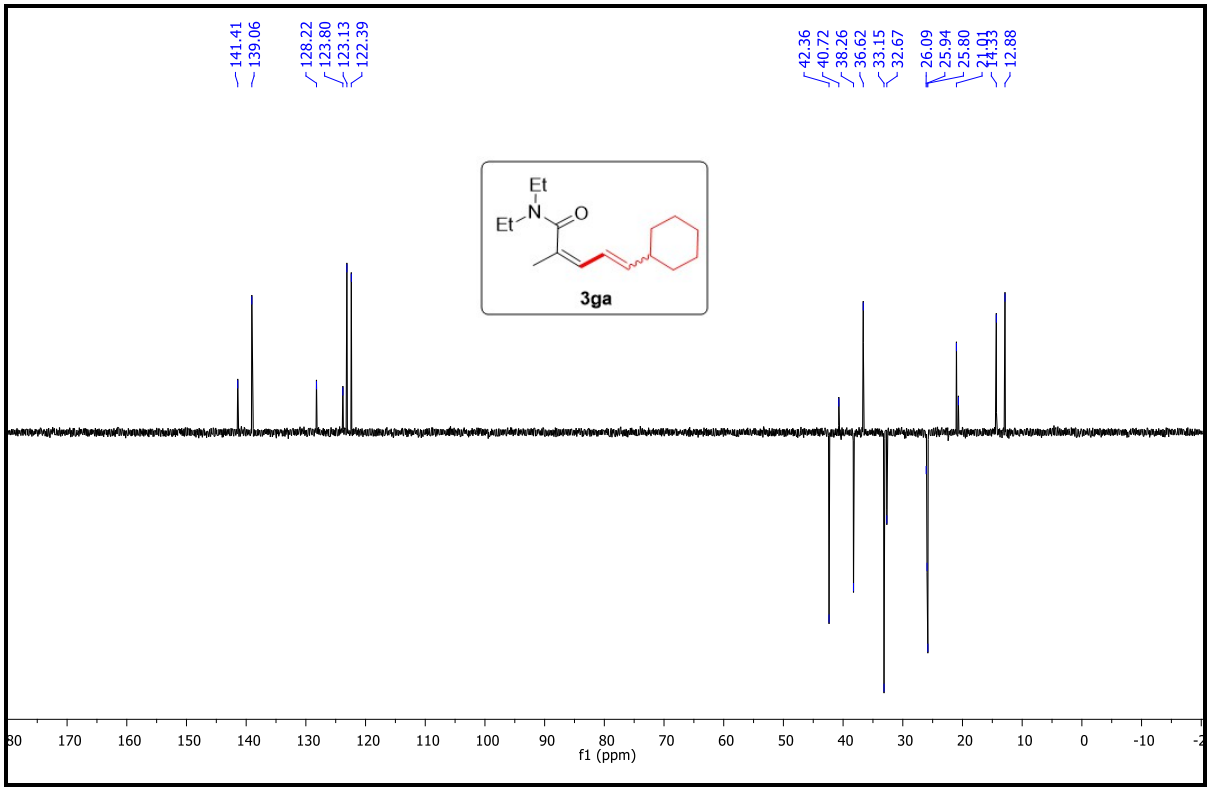
^{1}H NMR spectra of compound **3ga** in $CDCl_3$ at 400 MHz



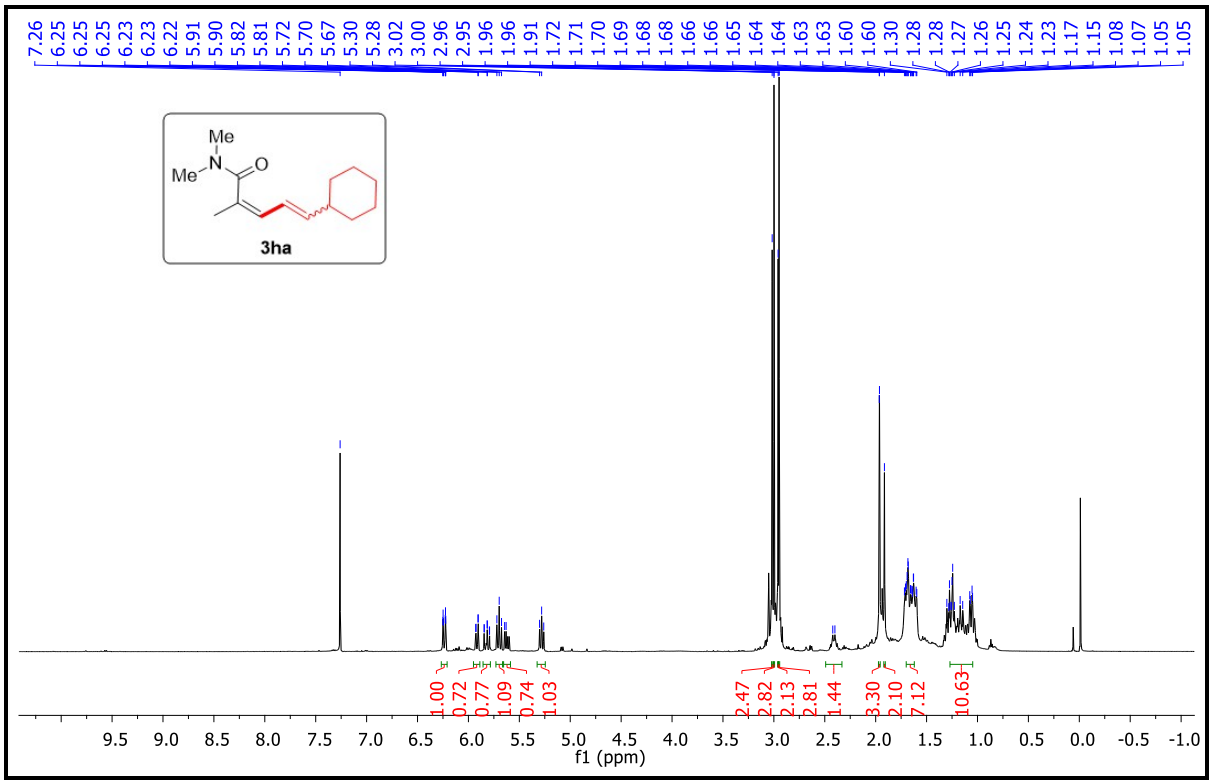
^{13}C NMR spectra of compound **3ga** in $CDCl_3$ at 101 MHz



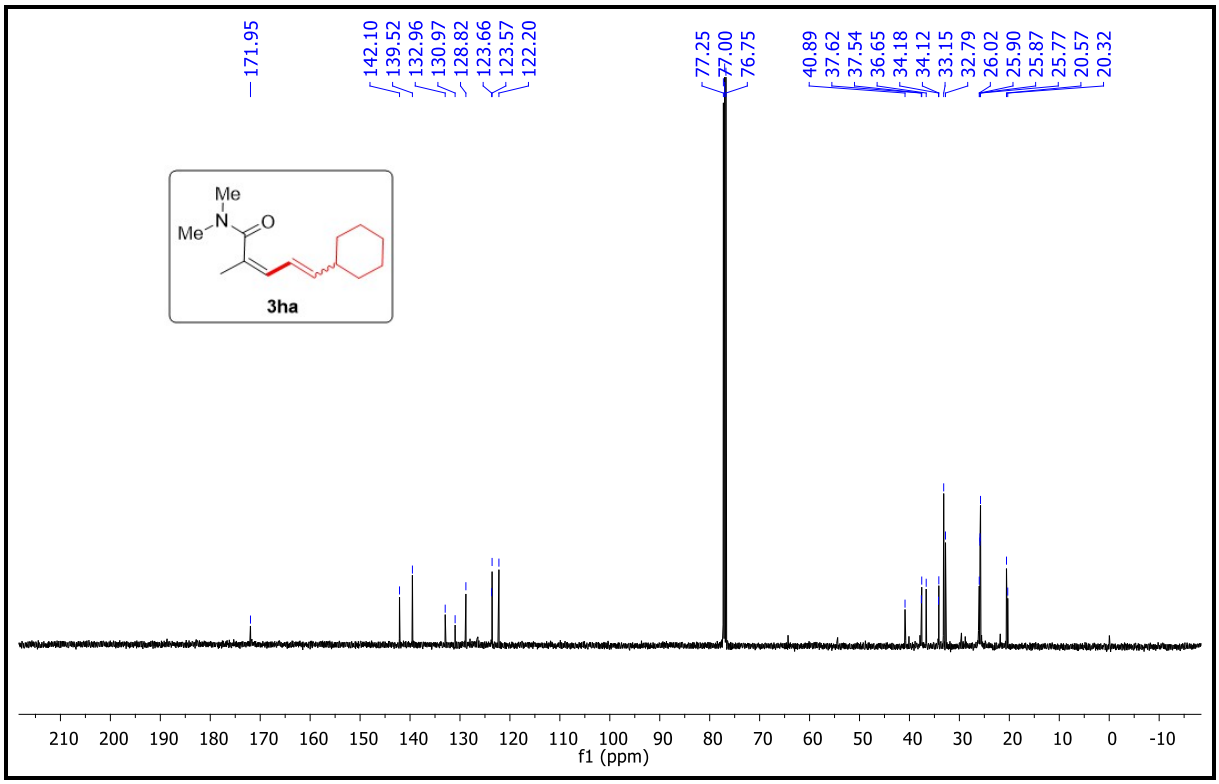
DEPT 135 NMR spectra of compound **3ga** in $CDCl_3$ at 101 MHz



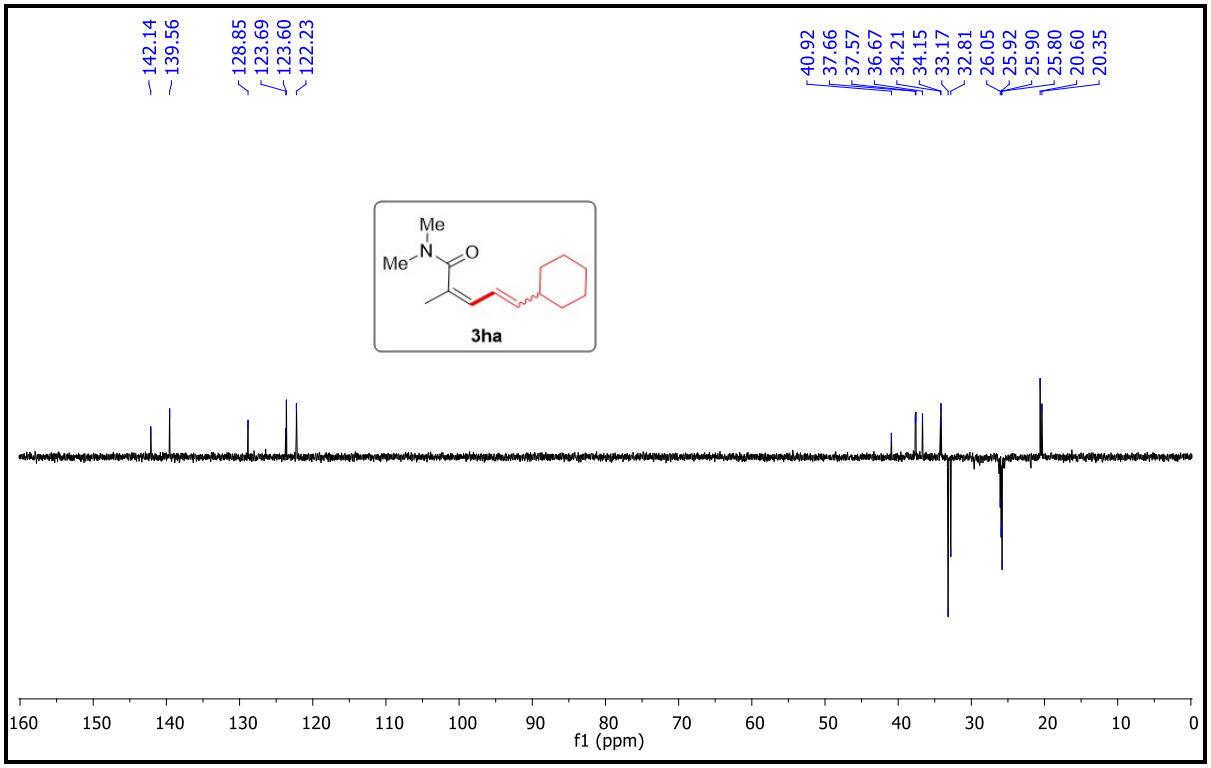
^{1}H NMR spectra of compound **3ha** in $CDCl_3$ at 500 MHz



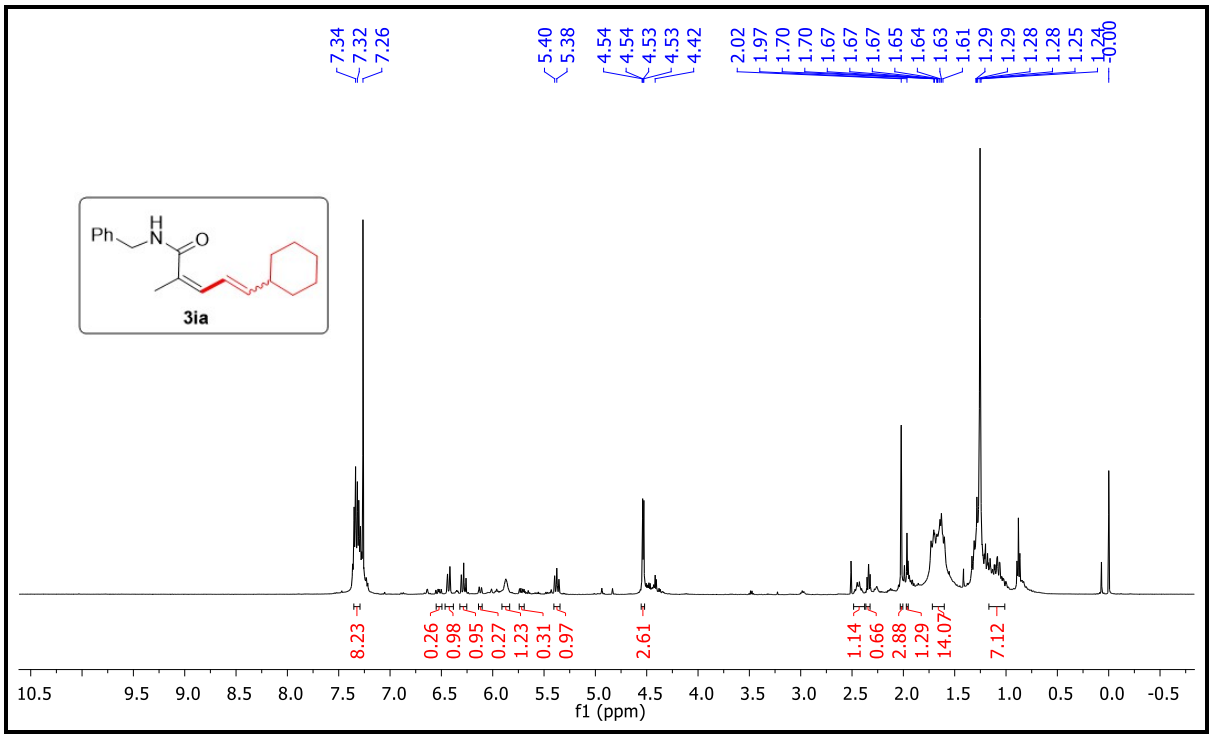
^{13}C NMR spectra of compound **3ha** in $CDCl_3$ at 126 MHz



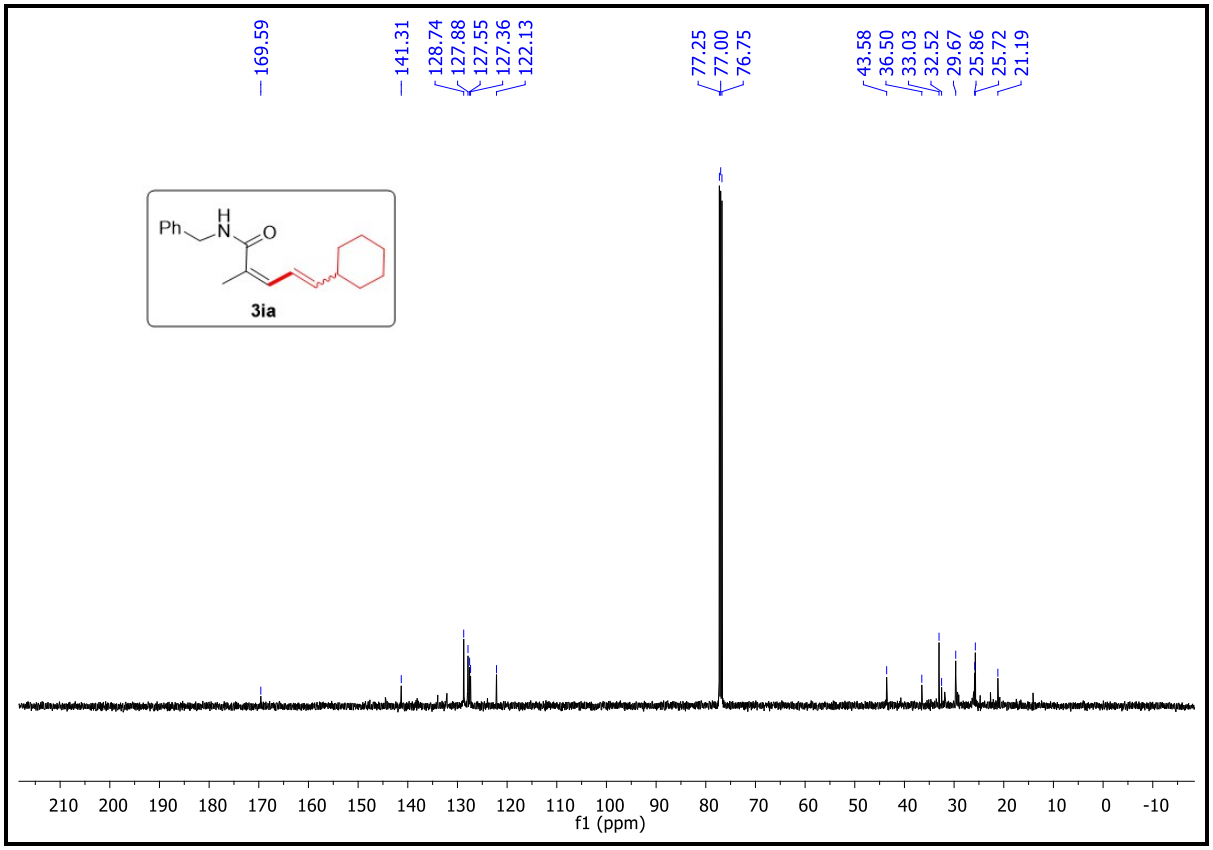
DEPT 135 NMR spectra of compound **3ha** in $CDCl_3$ at 126 MHz



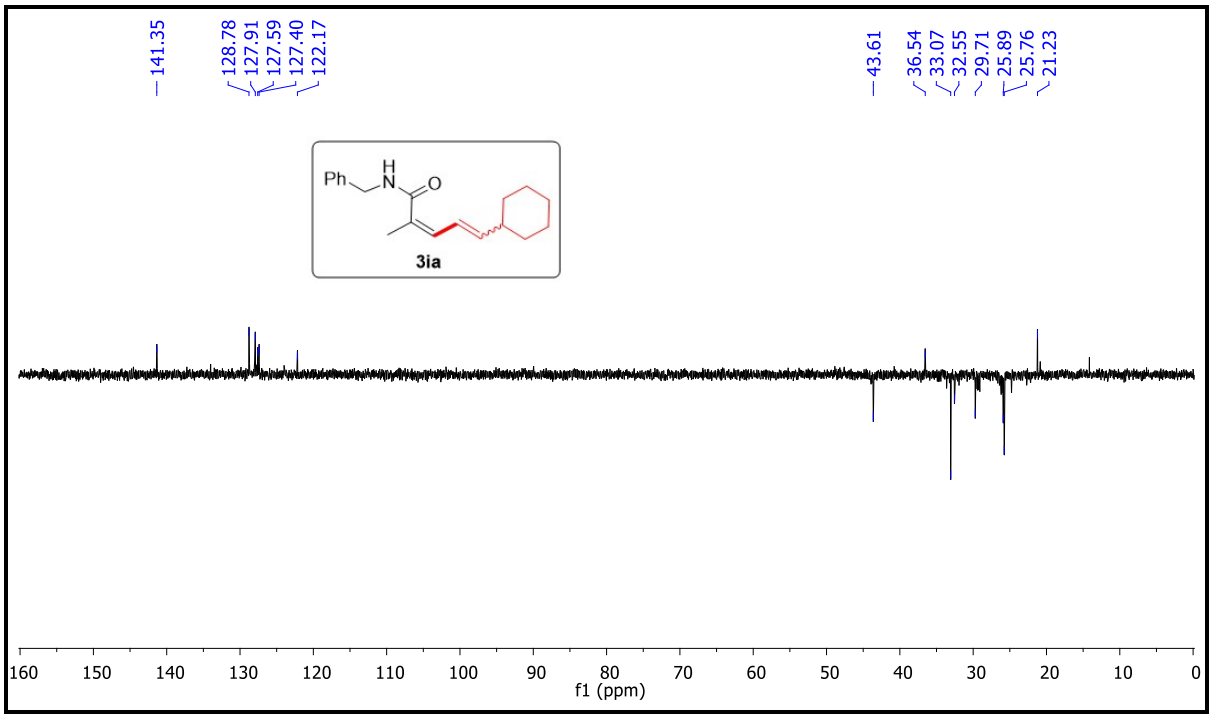
^{1}H NMR spectra of compound **3ia** in $CDCl_3$ at 500 MHz



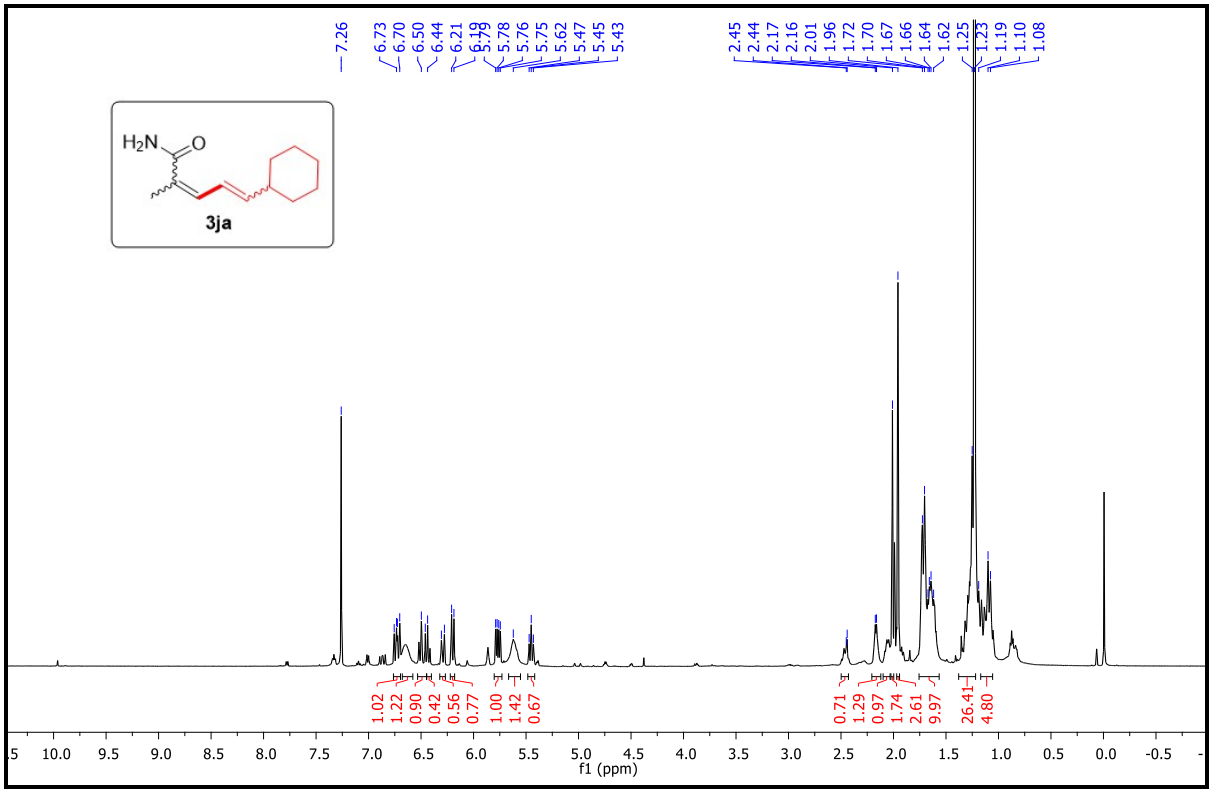
^{13}C NMR spectra of compound **3ia** in $CDCl_3$ at 126 MHz



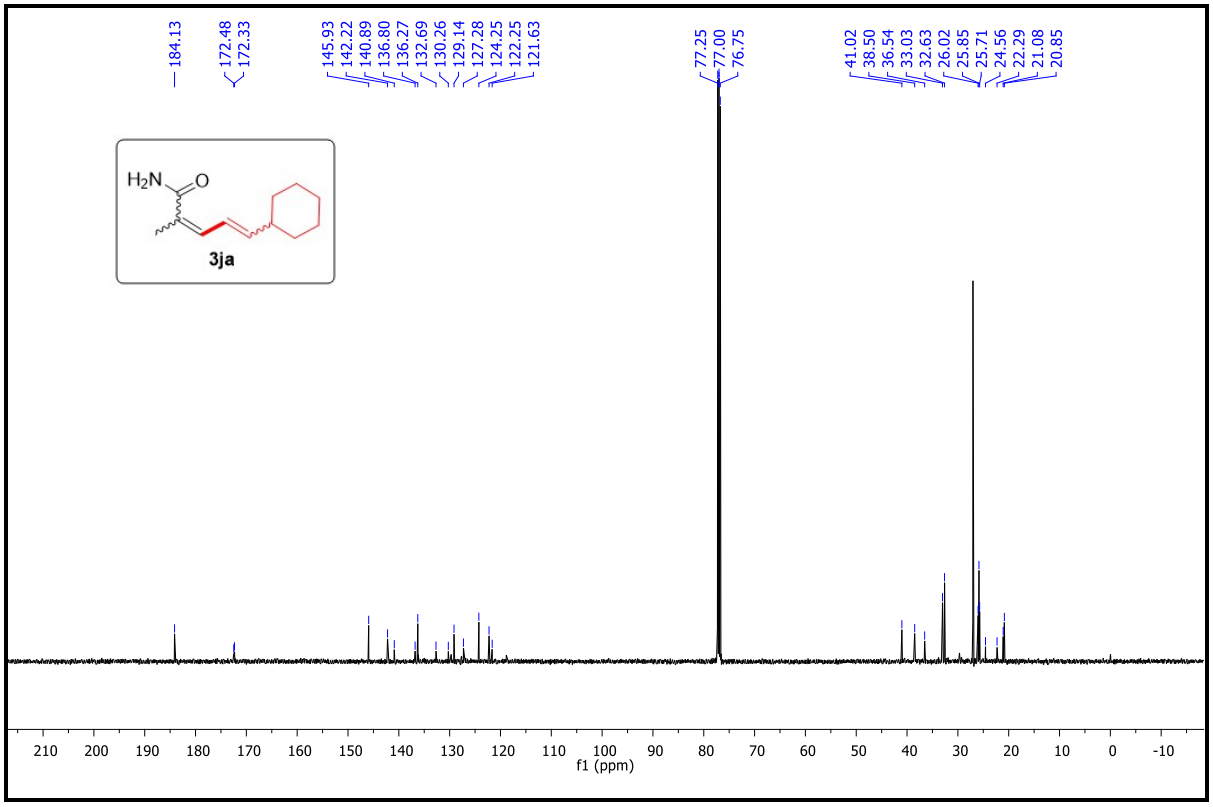
DEPT 135 NMR spectra of compound **3ia** in $CDCl_3$ at 126 MHz



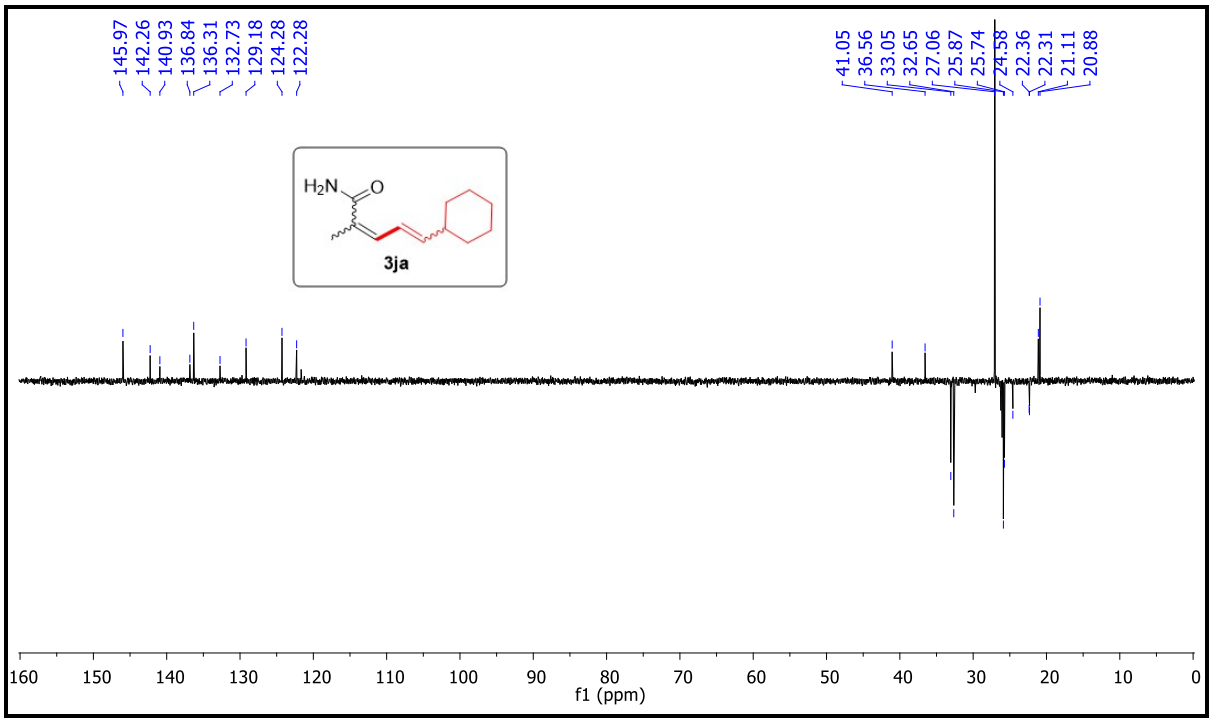
^{1}H NMR spectra of compound **3ja** in $CDCl_3$ at 500 MHz



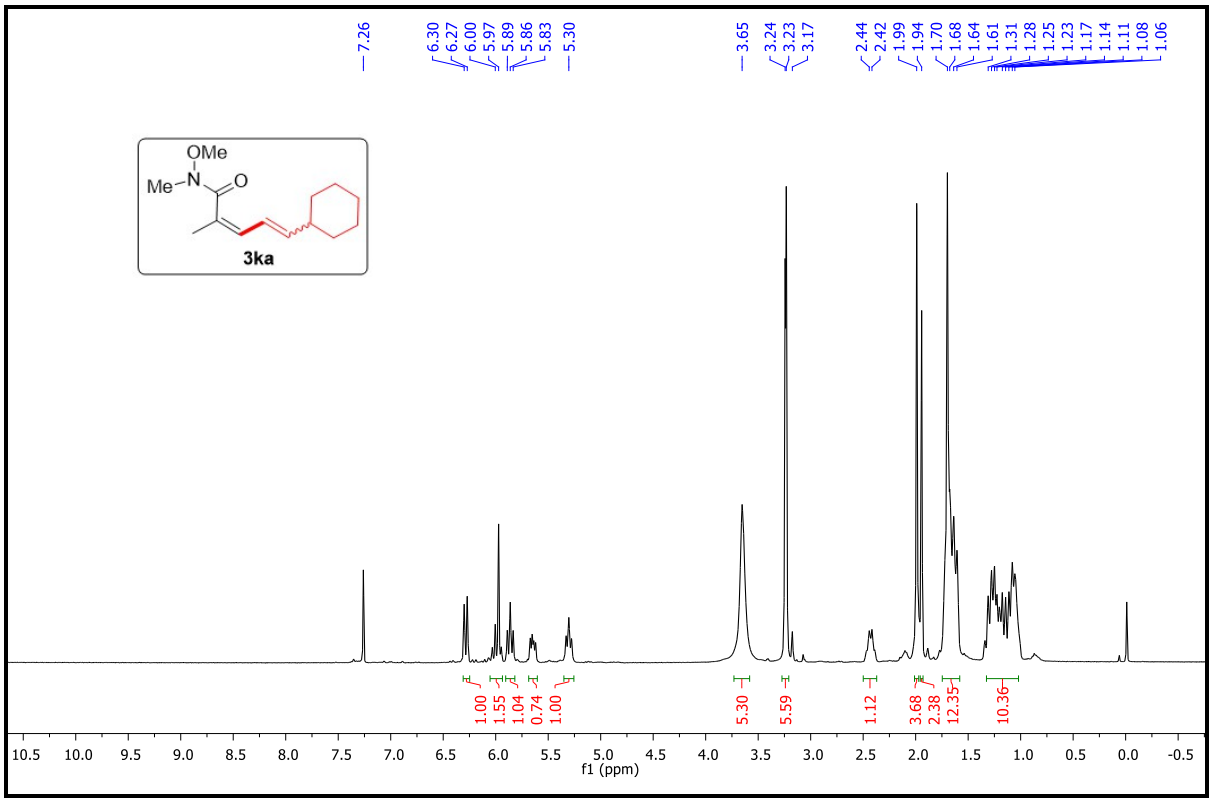
^{13}C NMR spectra of compound **3ja** in $CDCl_3$ at 126 MHz



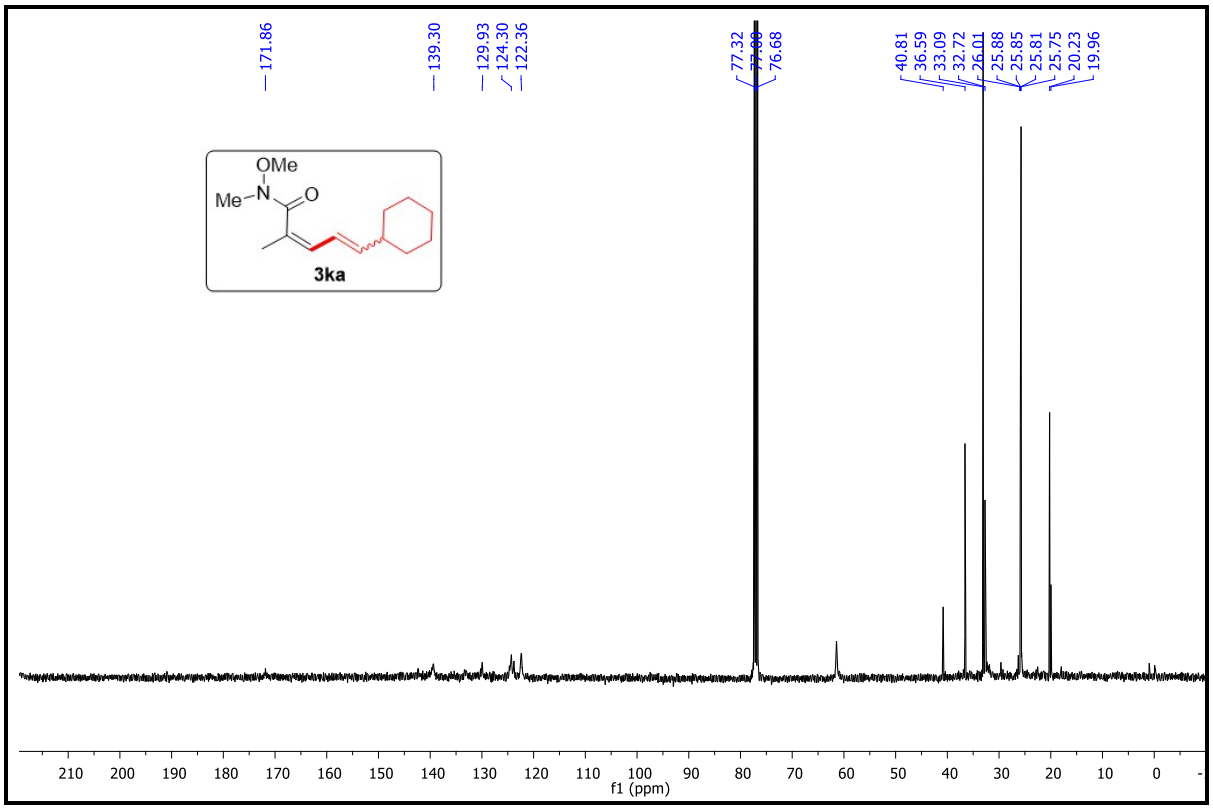
DEPT 135 NMR spectra of compound **3ja** in $CDCl_3$ at 126 MHz



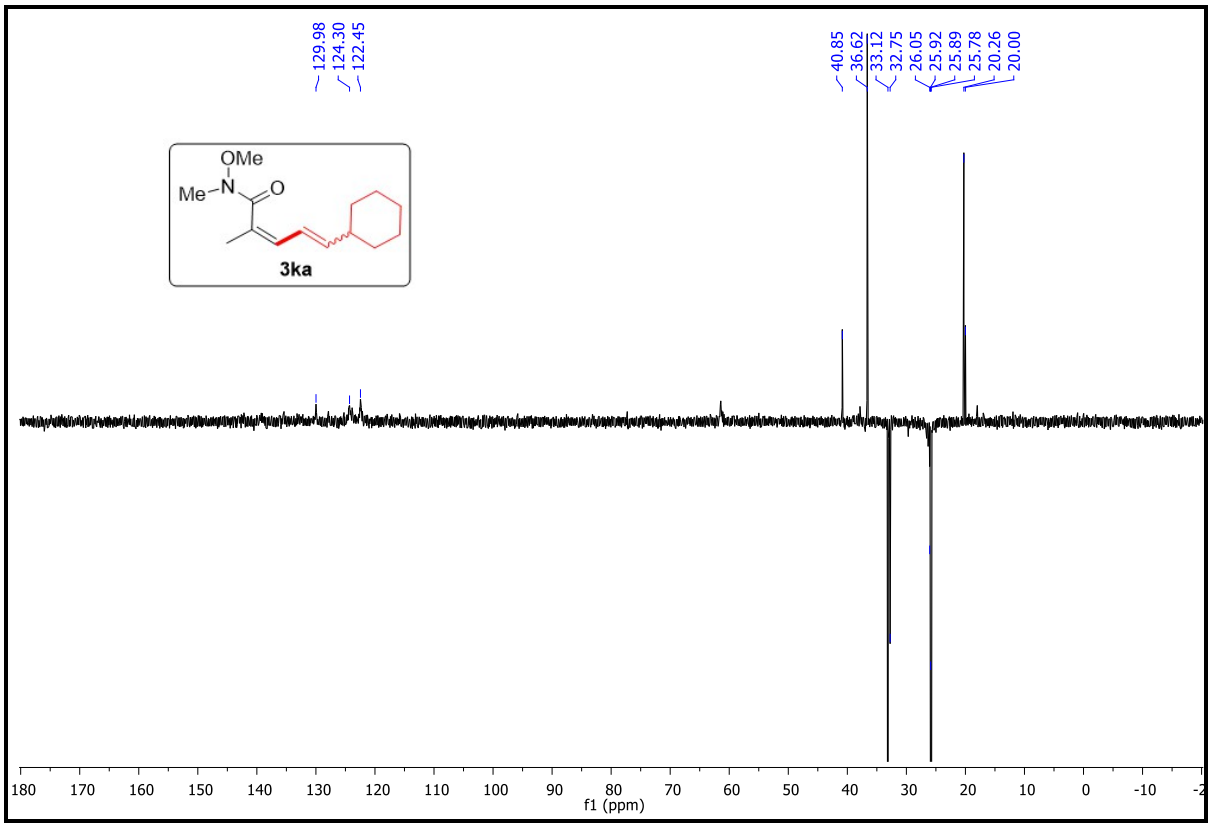
^{1}H NMR spectra of compound **3ka** in $CDCl_3$ at 400 MHz



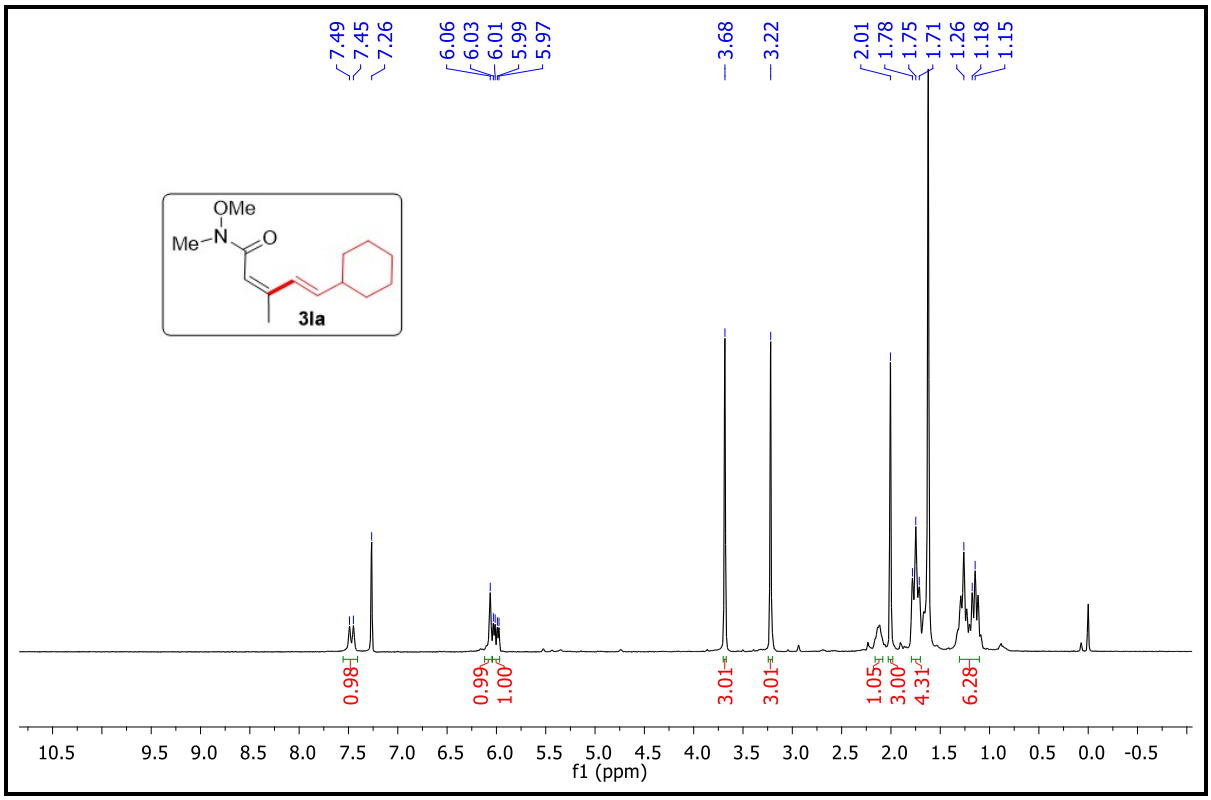
^{13}C NMR spectra of compound **3ka** in $CDCl_3$ at 101 MHz



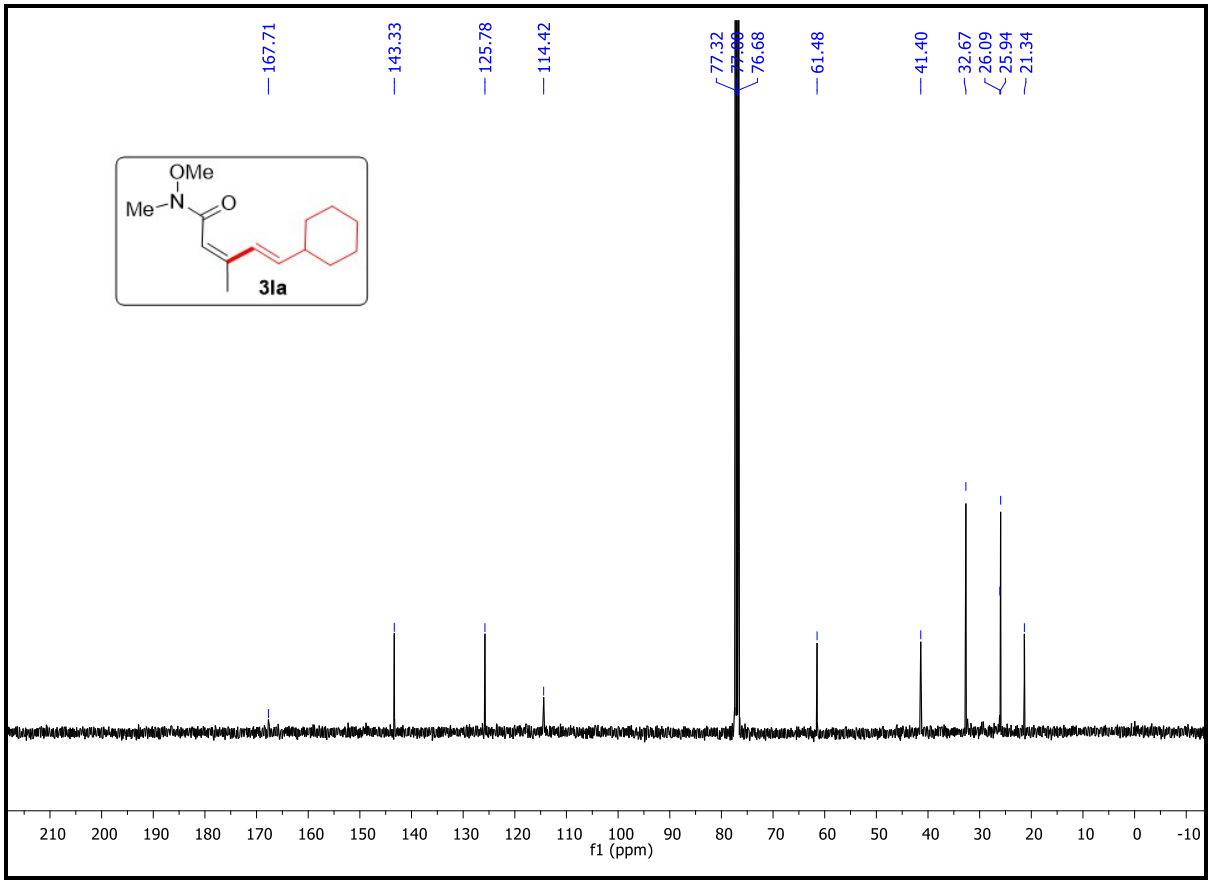
DEPT 135 NMR spectra of compound **3ka** in $CDCl_3$ at 101 MHz



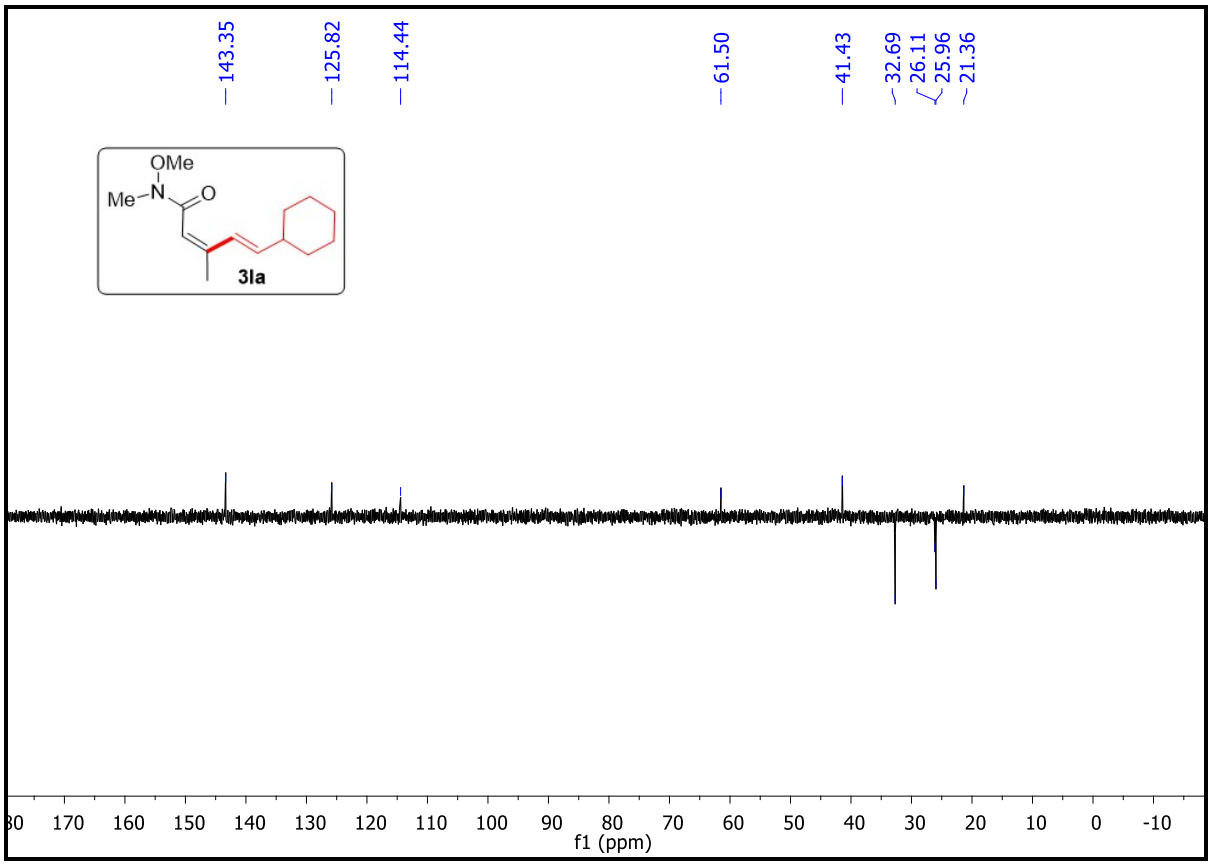
^{1}H NMR spectra of compound **3la** in $CDCl_3$ at 400 MHz



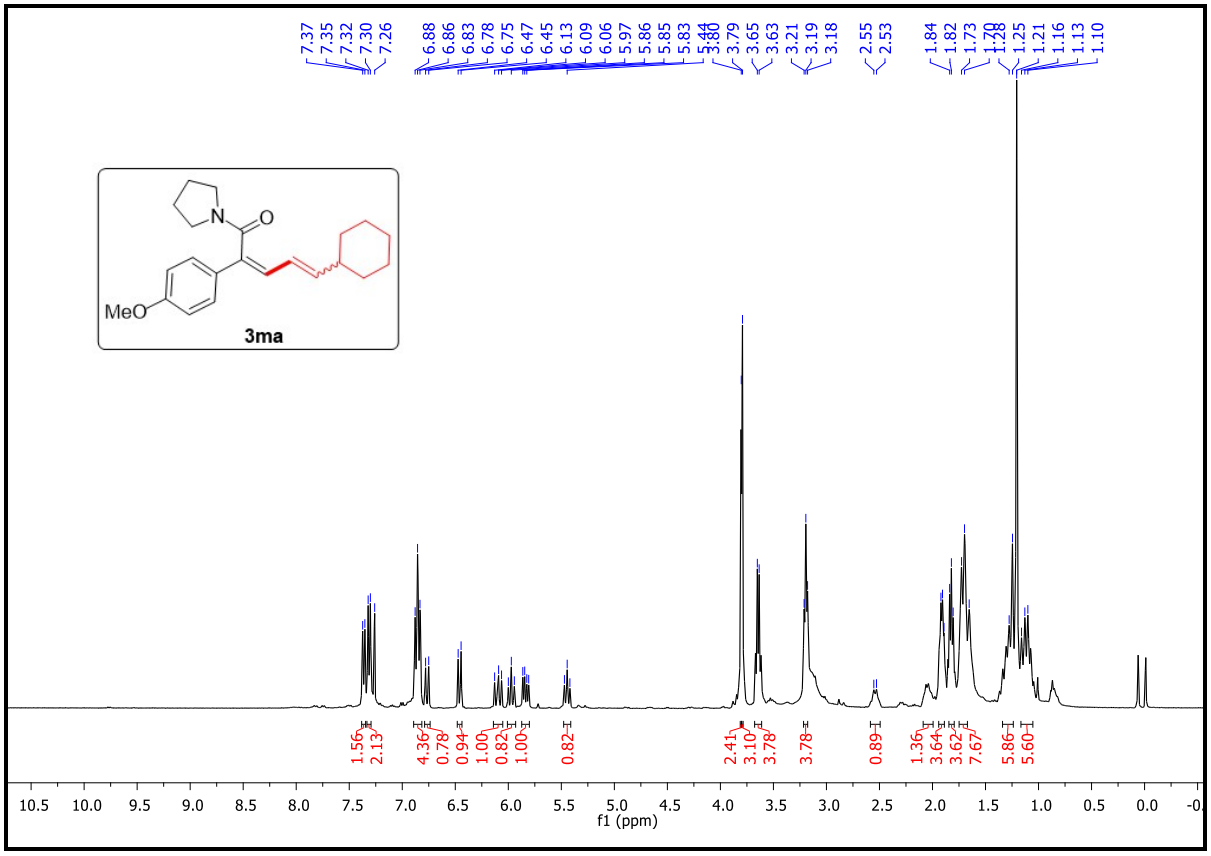
^{13}C NMR spectra of compound **3la** in $CDCl_3$ at 101 MHz



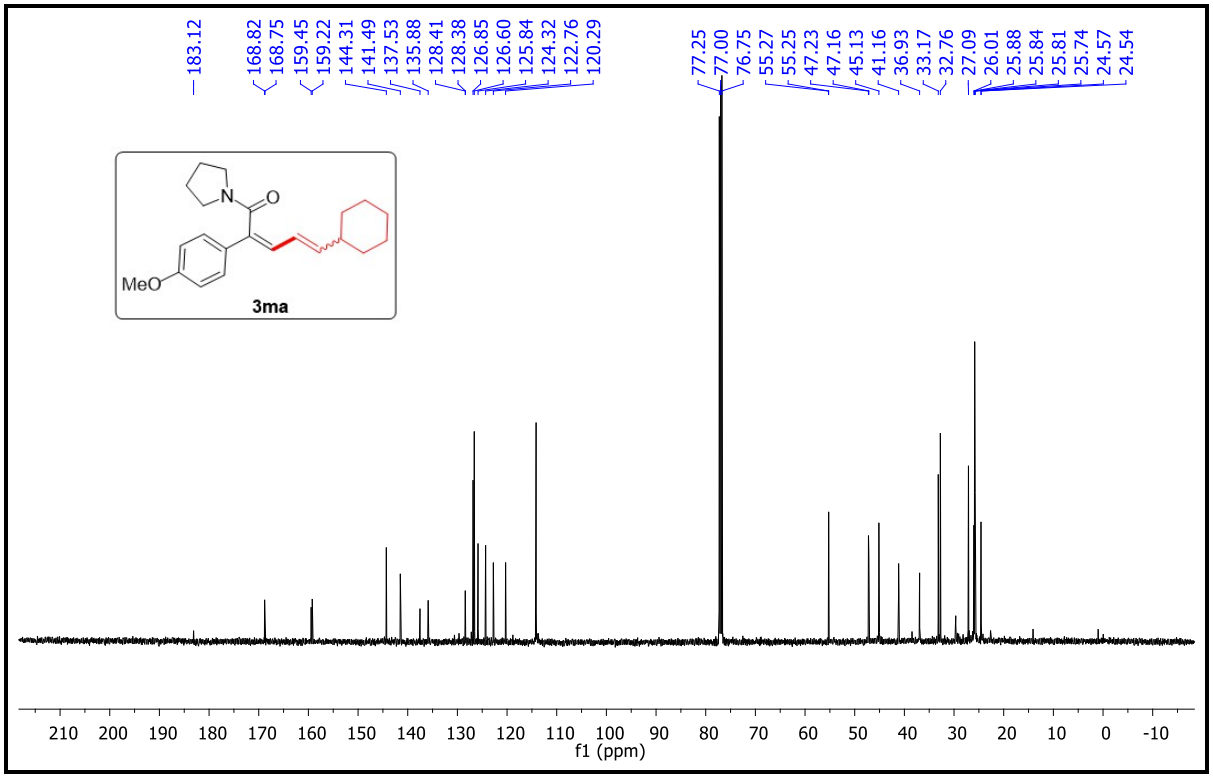
DEPT 135 NMR spectra of compound **3la** in $CDCl_3$ at 101 MHz



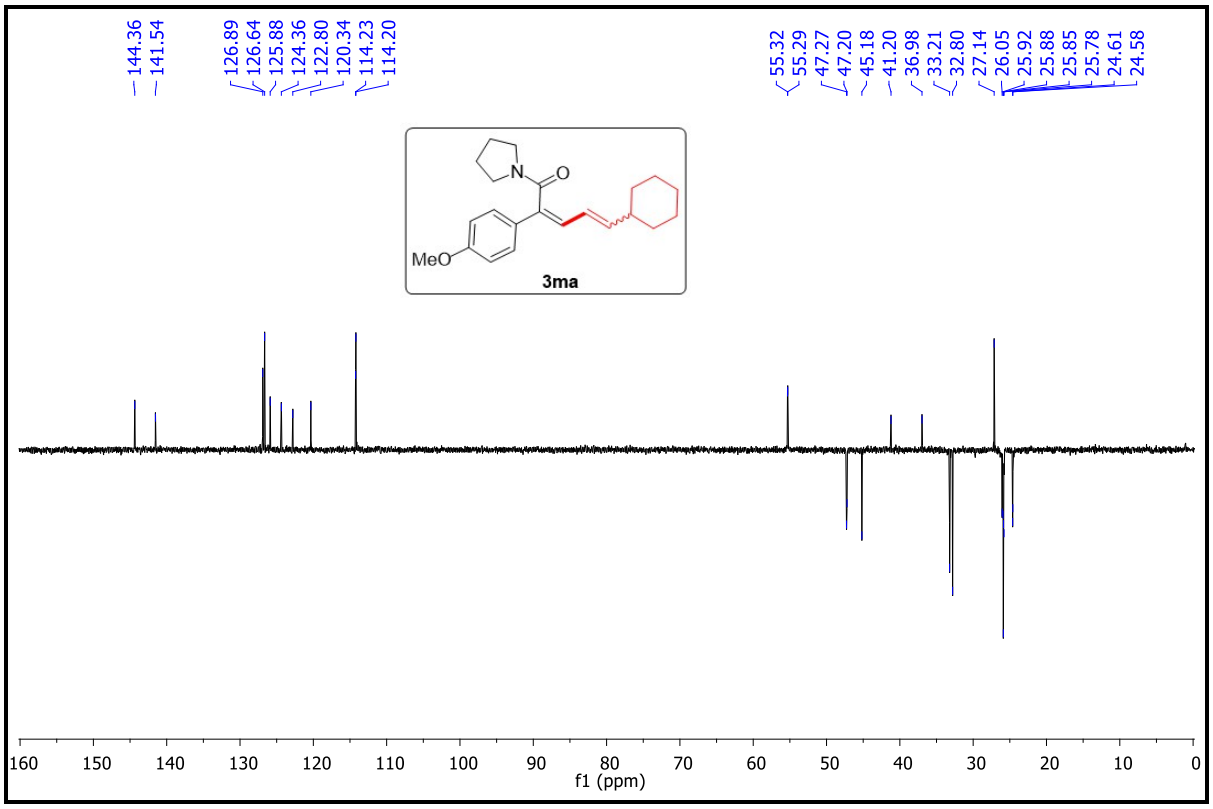
^{1}H NMR spectra of compound **3ma** in $CDCl_3$ at 500 MHz



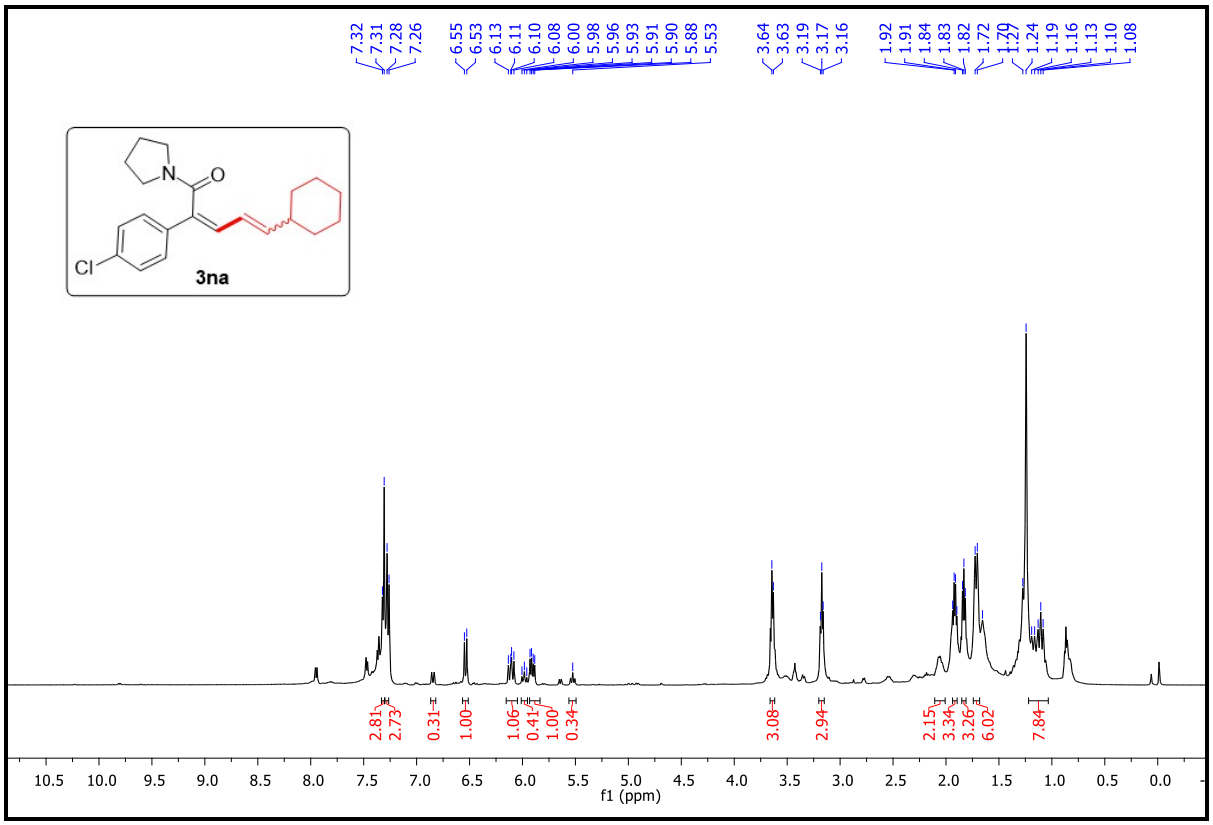
^{13}C NMR spectra of compound **3ma** in $CDCl_3$ at 126 MHz



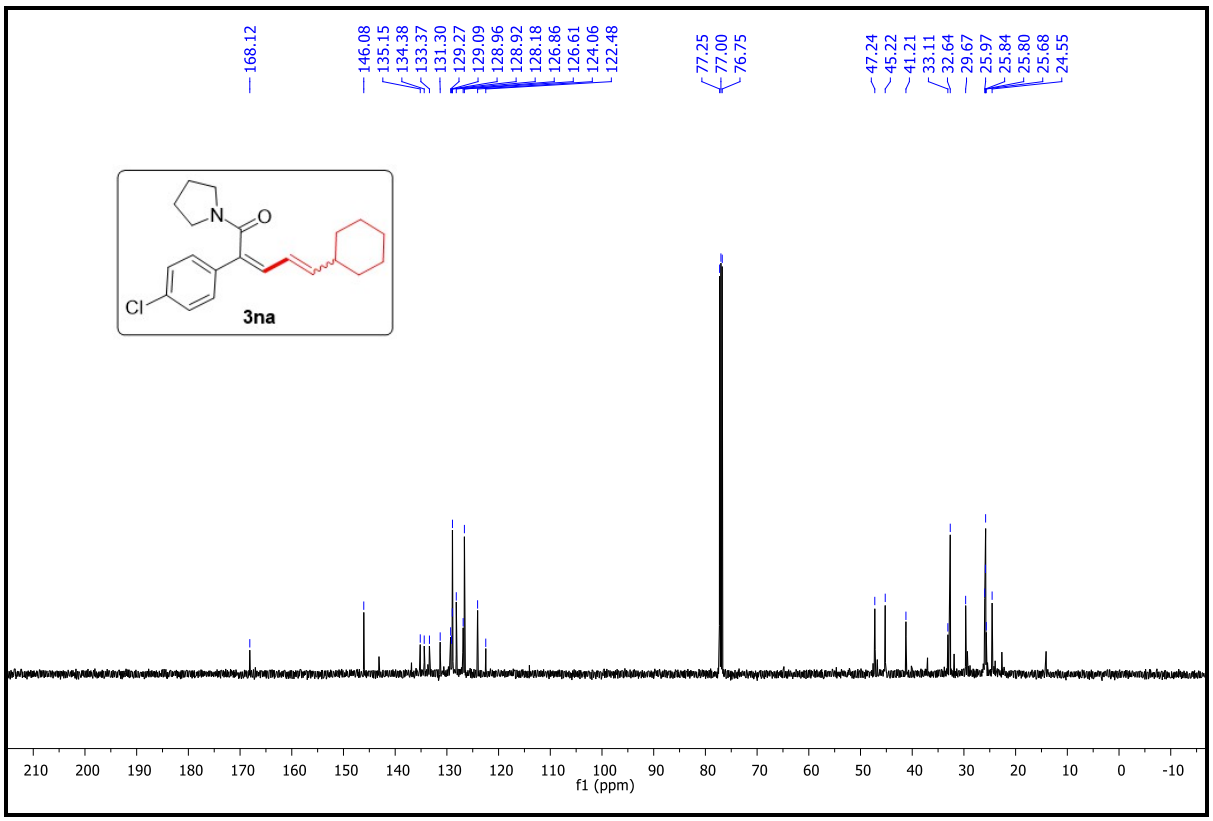
DEPT 135 NMR spectra of compound **3ma** in $CDCl_3$ at 126 MHz



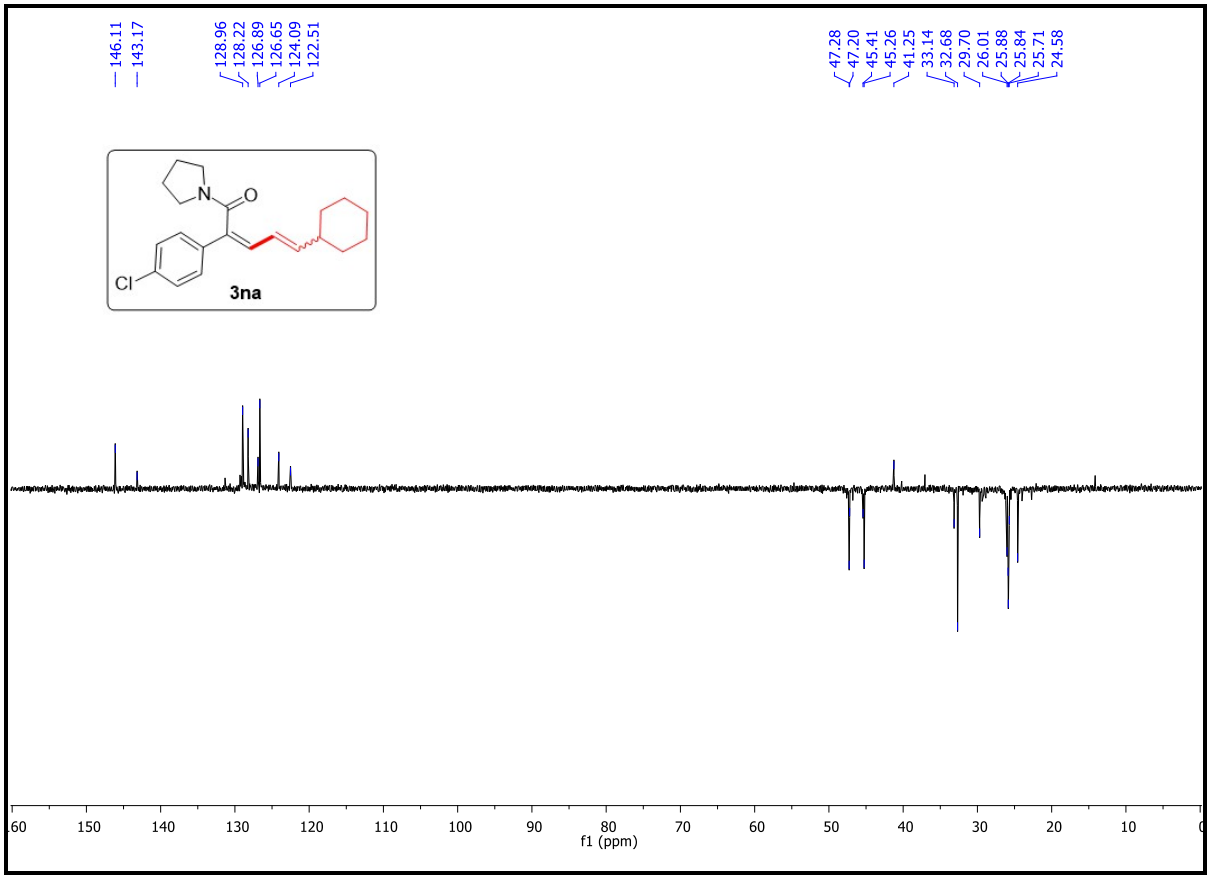
^{1}H NMR spectra of compound **3na** in $CDCl_3$ at 500 MHz



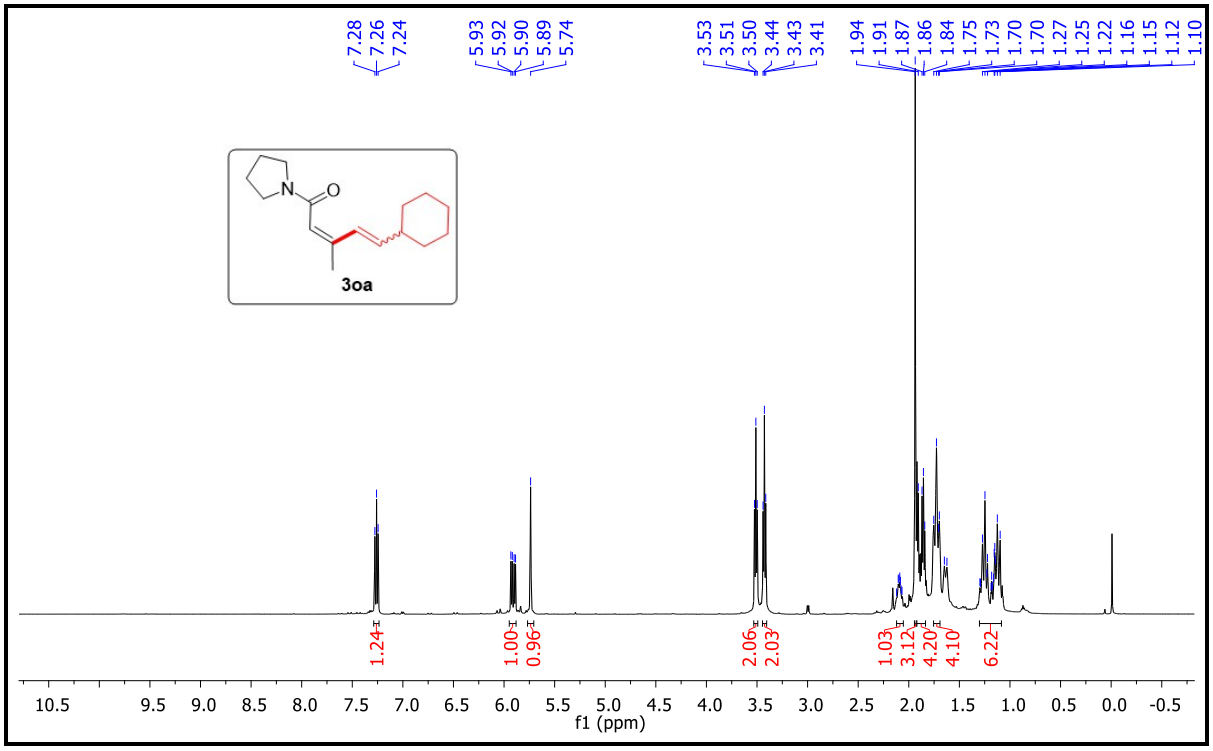
^{13}C NMR spectra of compound **3na** in $CDCl_3$ at 126 MHz



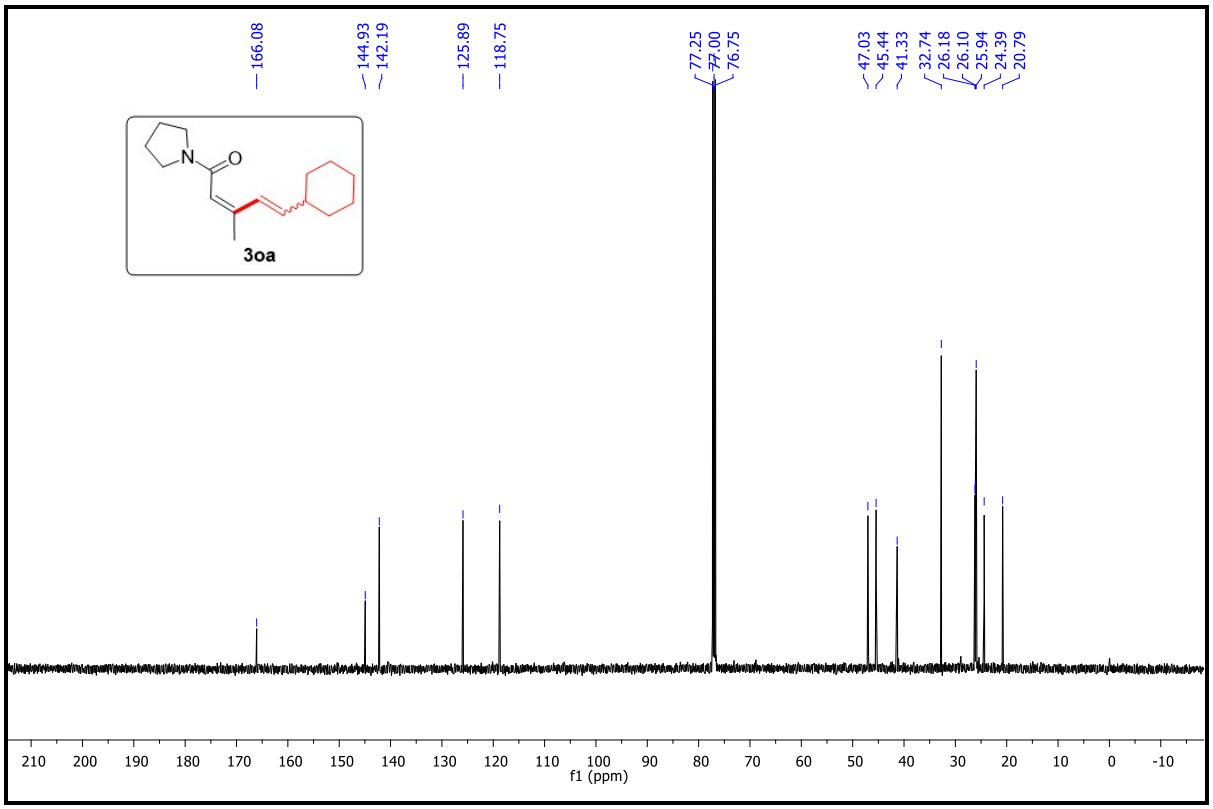
DEPT 135 NMR spectra of compound **3na** in $CDCl_3$ at 126 MHz



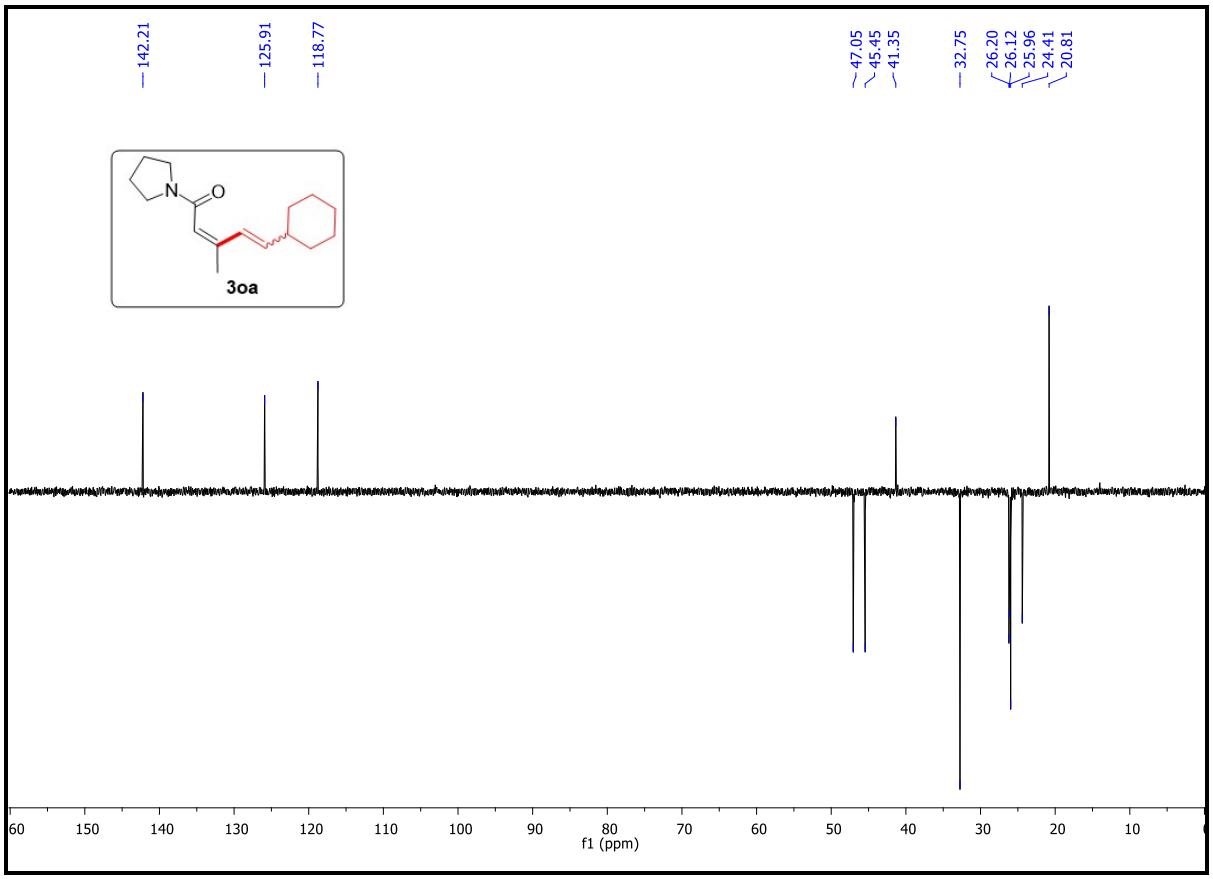
^{1}H NMR spectra of compound **3oa** in $CDCl_3$ at 500 MHz



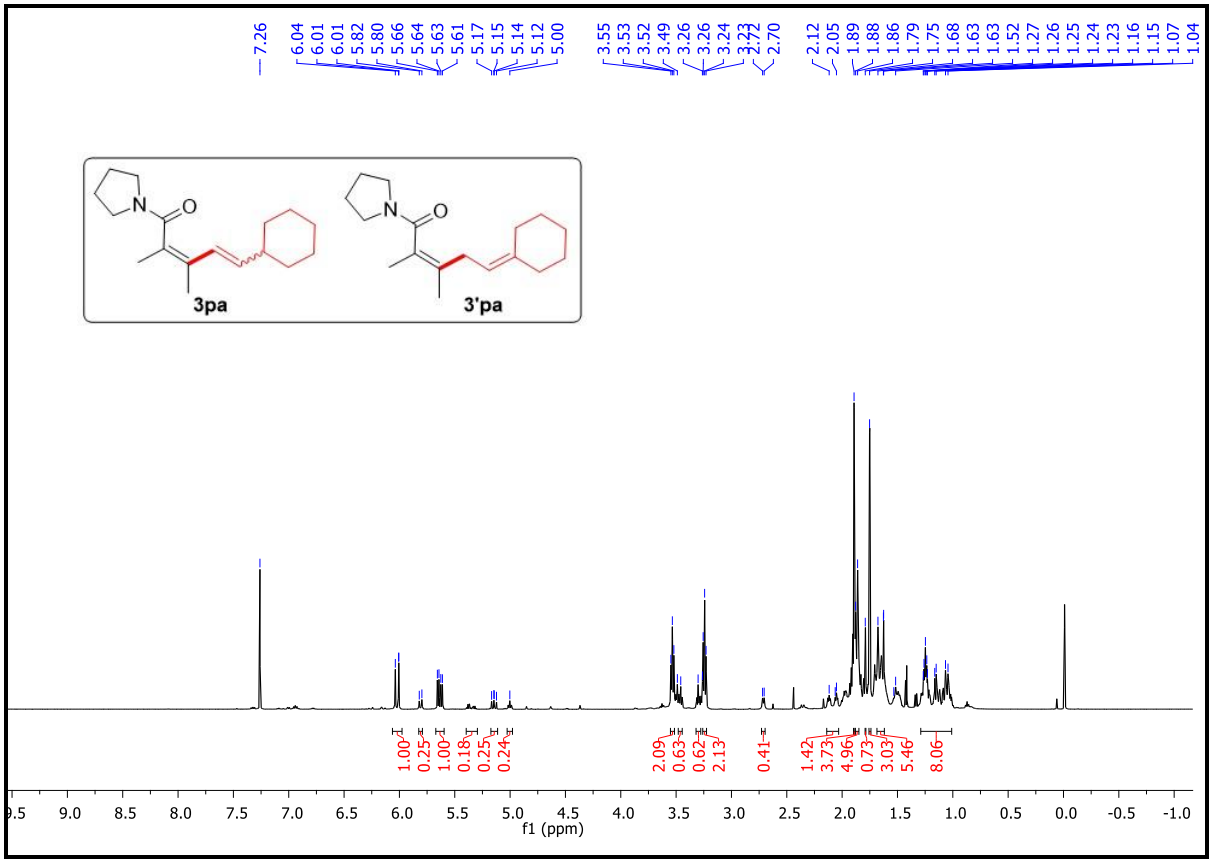
^{13}C NMR spectra of compound **3oa** in $CDCl_3$ at 126 MHz



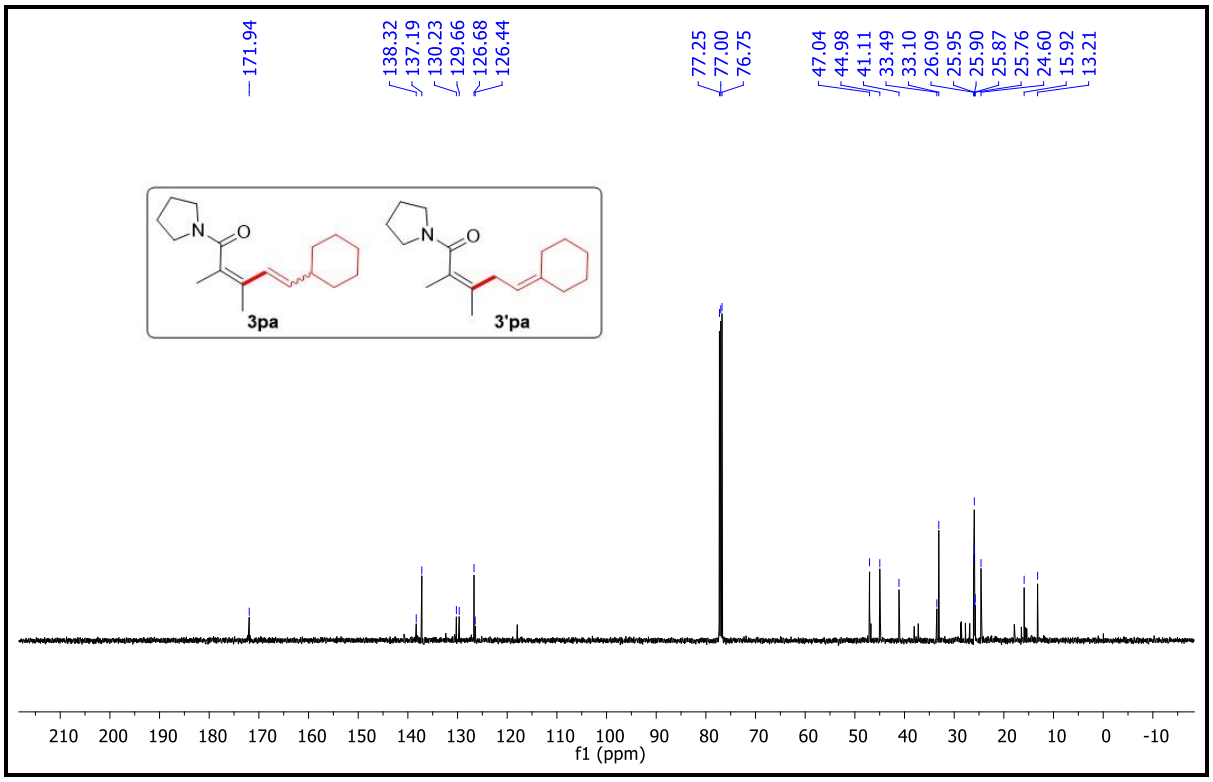
DEPT 135 NMR spectra of compound **3oa** in $CDCl_3$ at 126 MHz



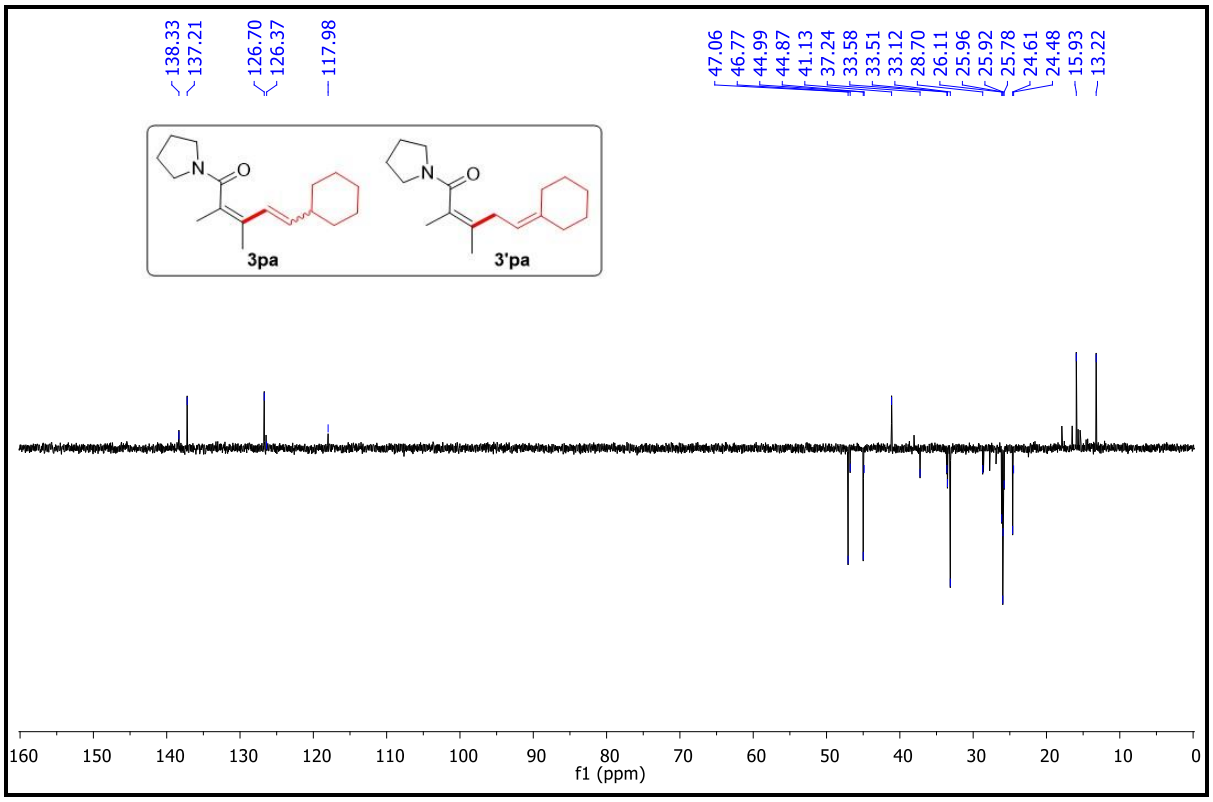
^{1}H NMR spectra of compound **3pa** in $CDCl_3$ at 500 MHz



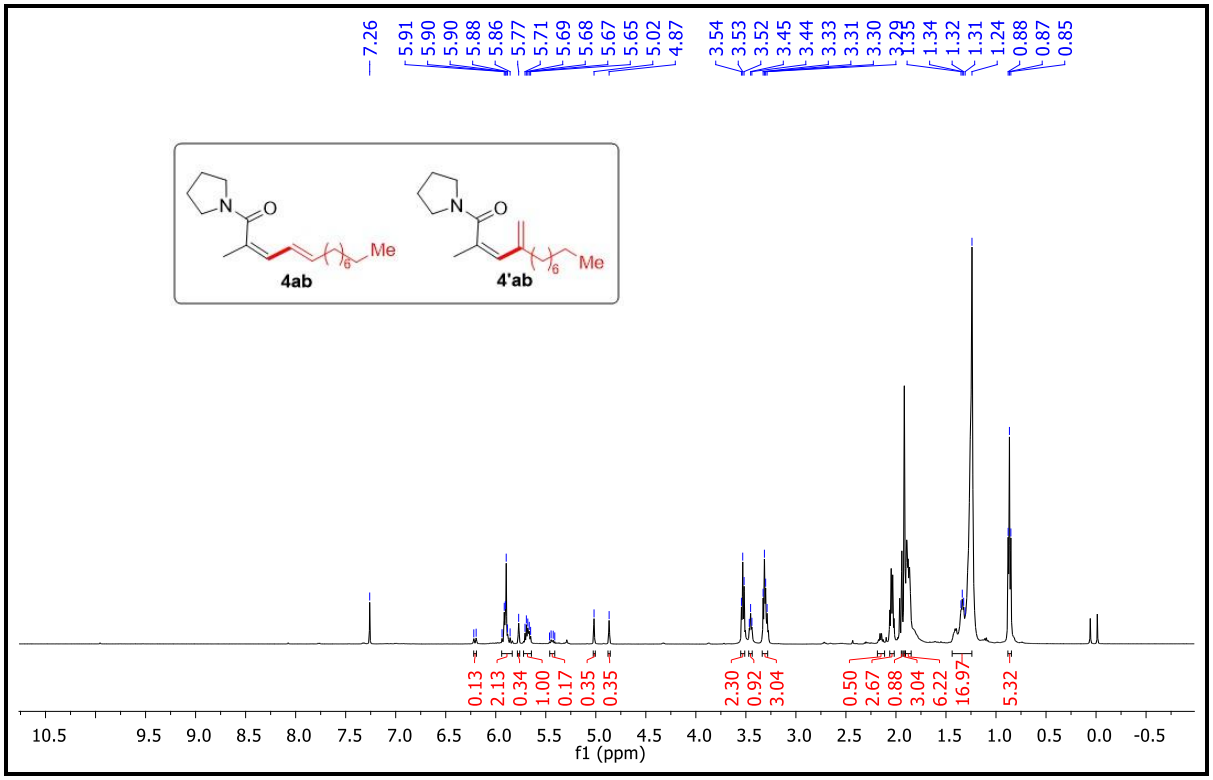
^{13}C NMR spectra of compound **3pa** in $CDCl_3$ at 126 MHz



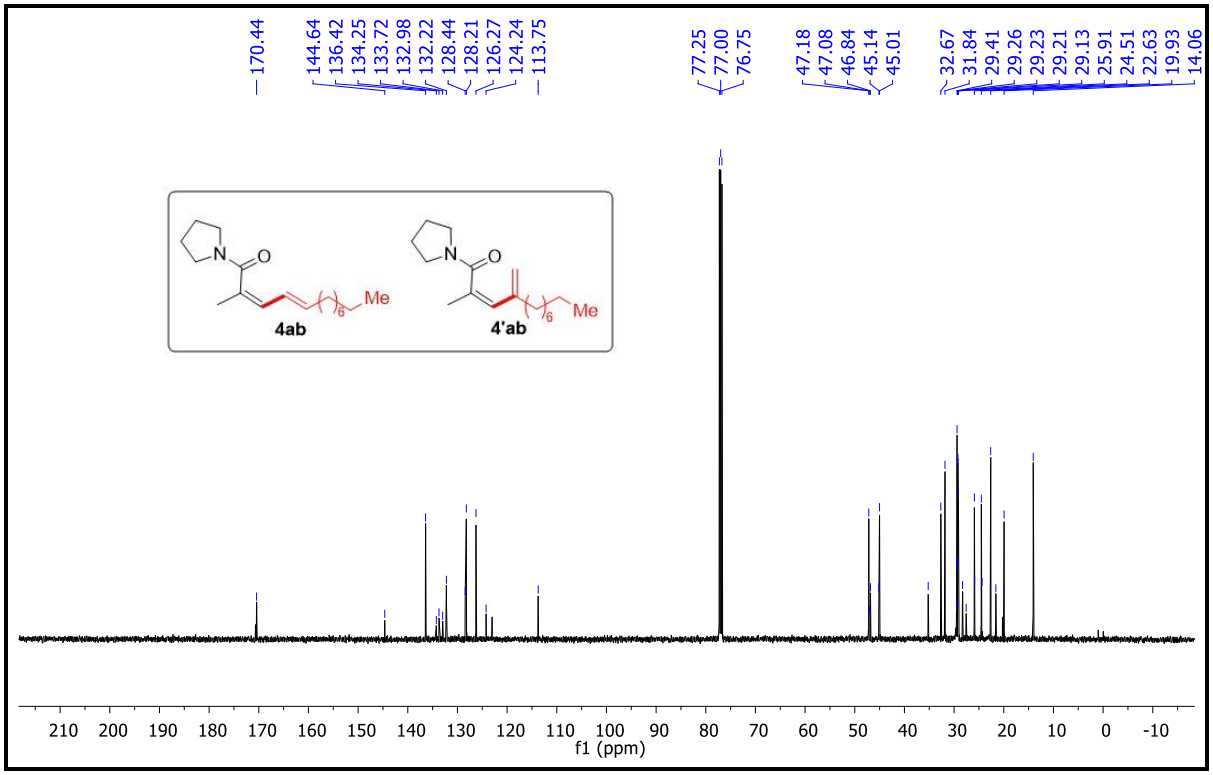
DEPT 135 NMR spectra of compound **3pa** in $CDCl_3$ at 126 MHz



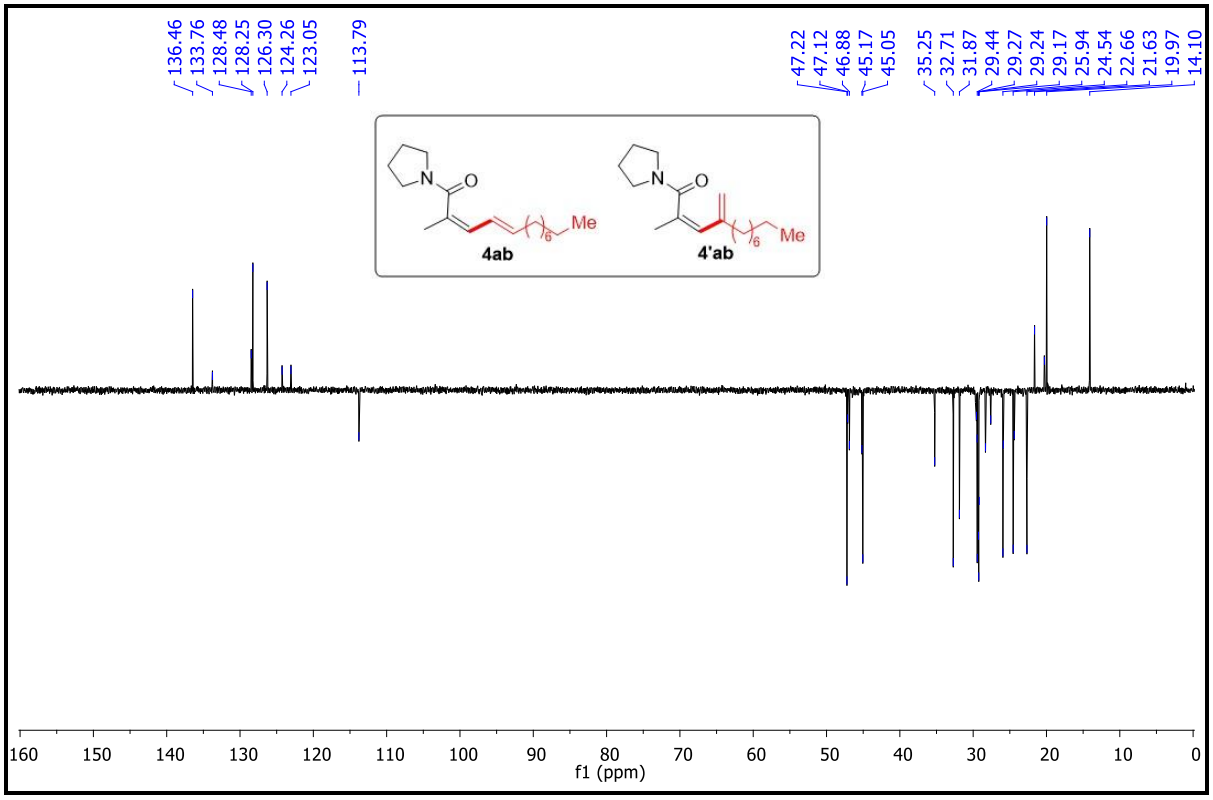
^{1}H NMR spectra of compound **4ab** in $CDCl_3$ at 500 MHz



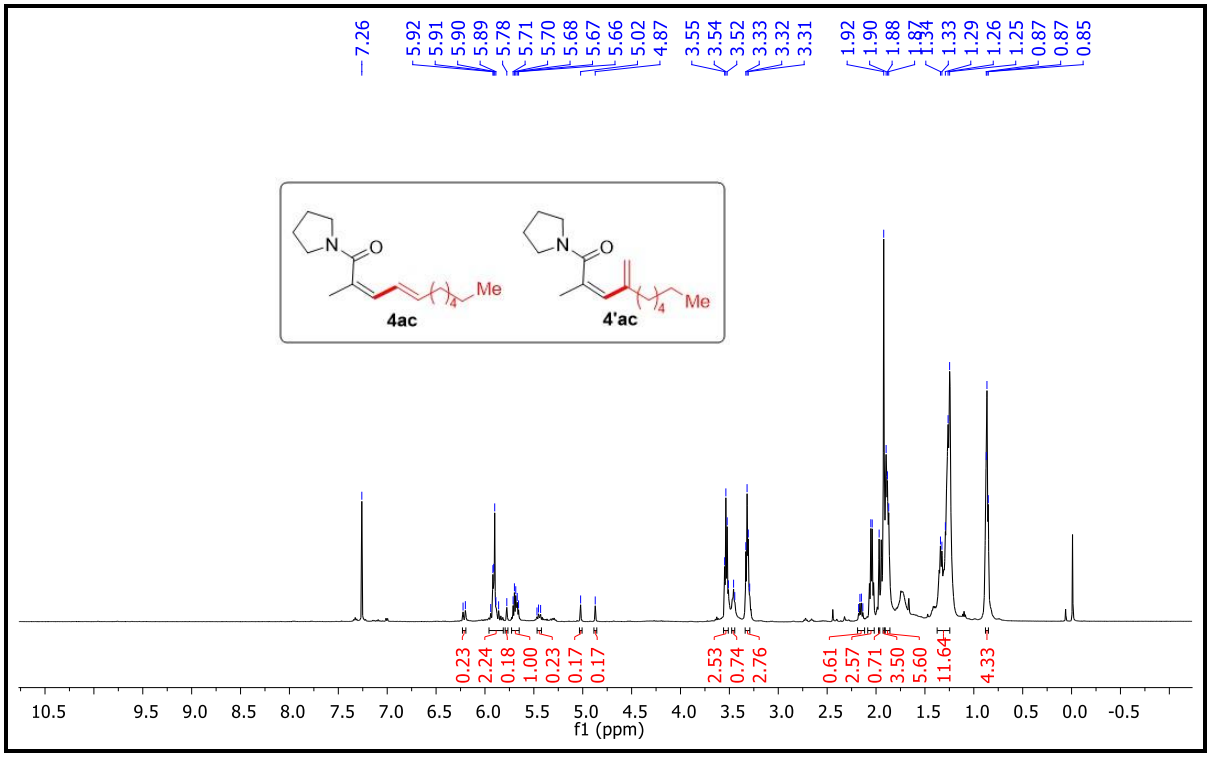
^{13}C NMR spectra of compound **4ab** in $CDCl_3$ at 126 MHz



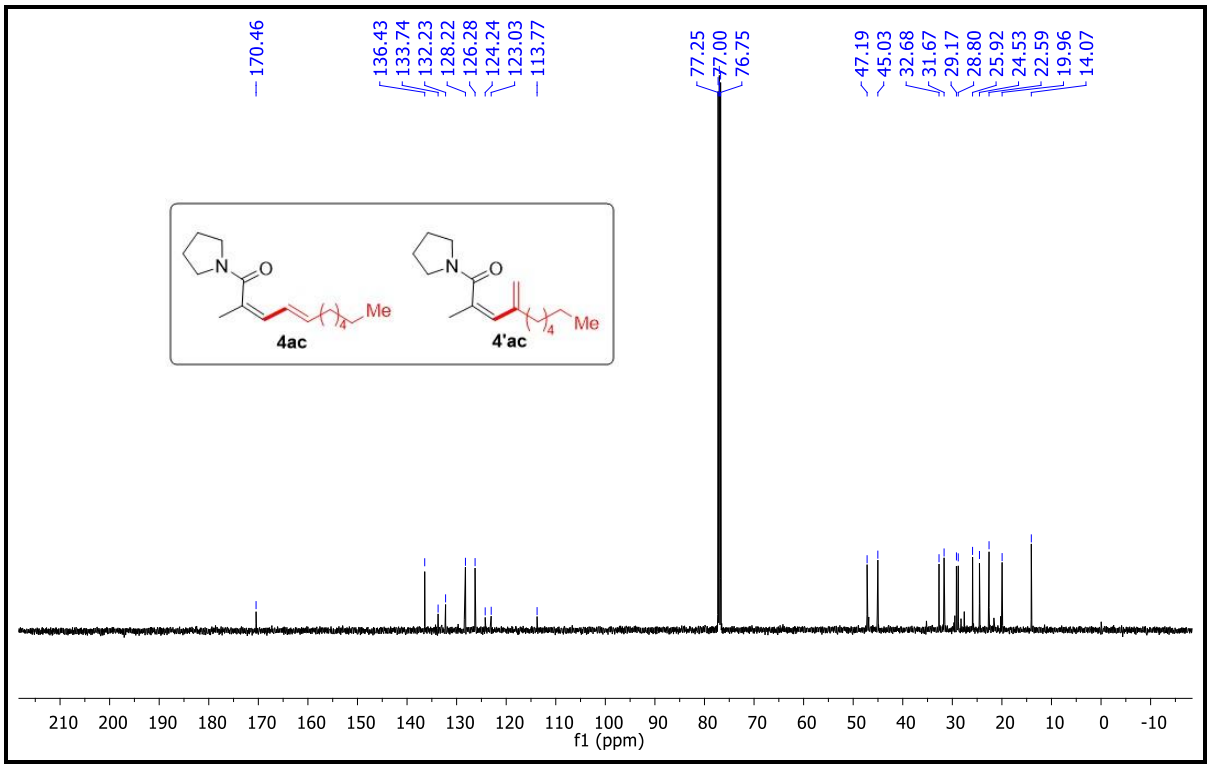
DEPT 135 NMR spectra of compound **4ab** in $CDCl_3$ at 126 MHz



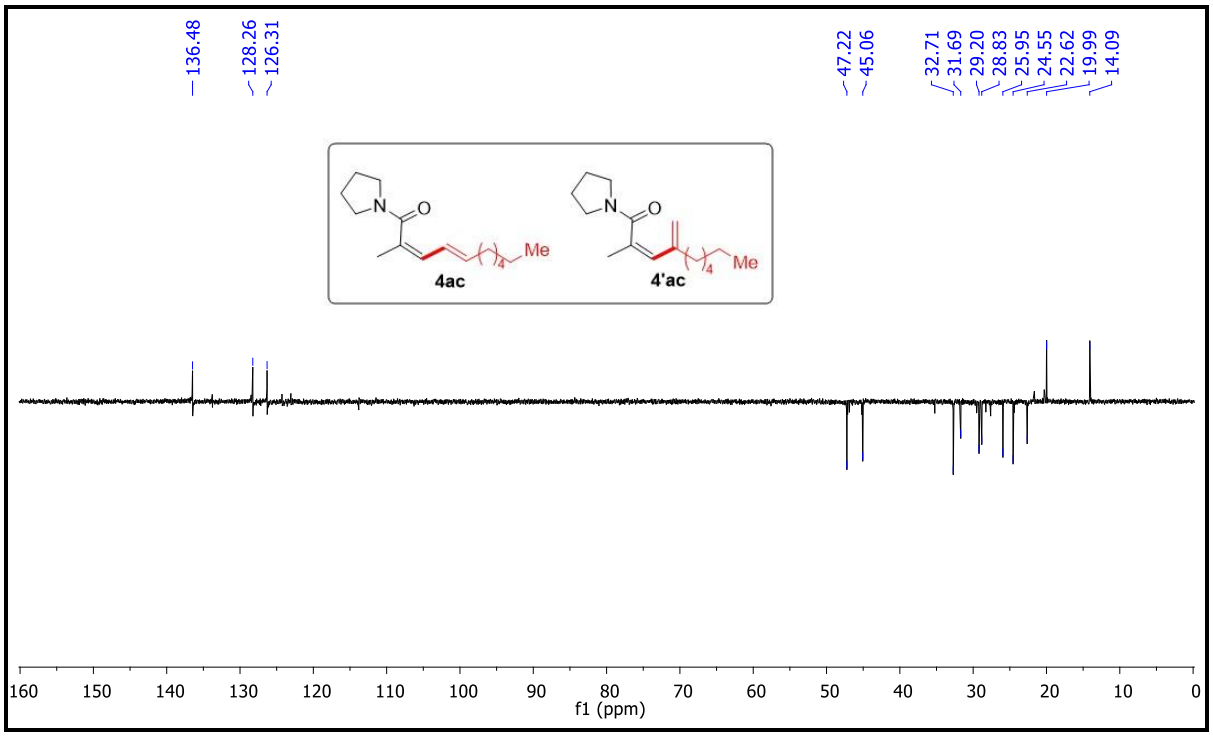
^{1}H NMR spectra of compound **4ac** in $CDCl_3$ at 500 MHz



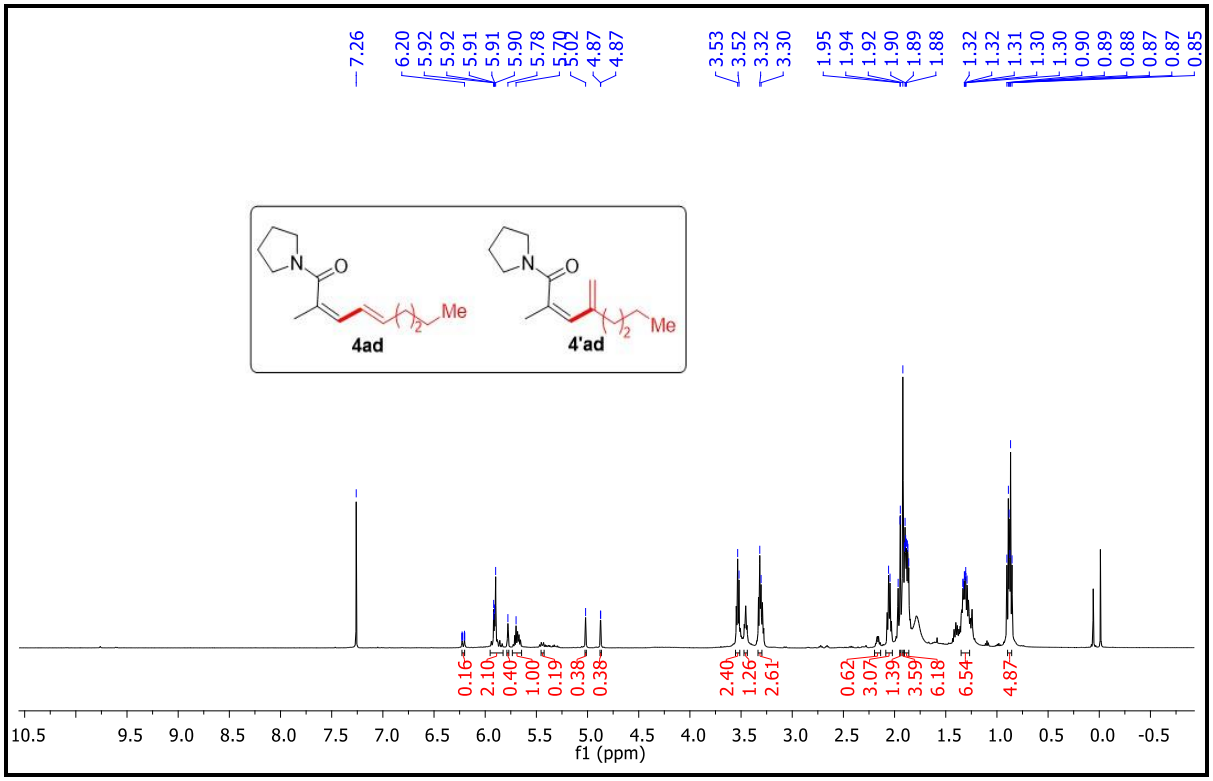
^{13}C NMR spectra of compound **4ac** in $CDCl_3$ at 126 MHz



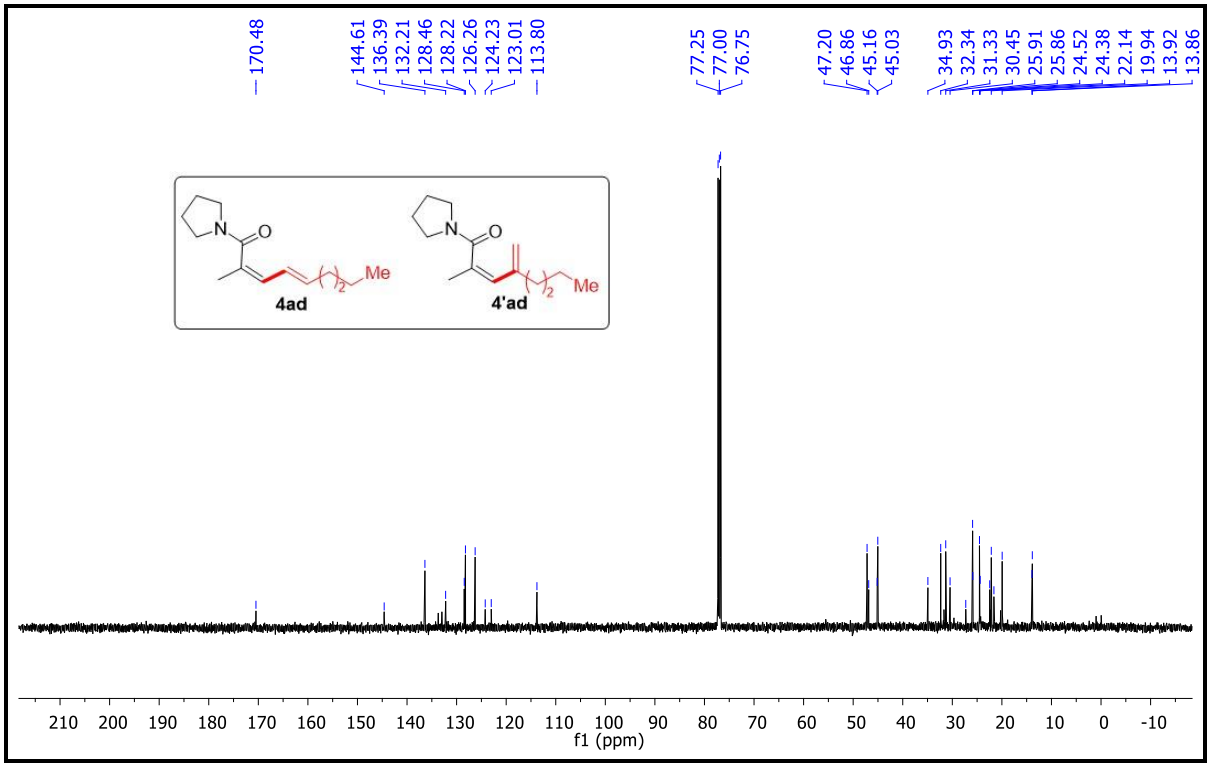
DEPT 135 NMR spectra of compound **4ac** in $CDCl_3$ at 126 MHz



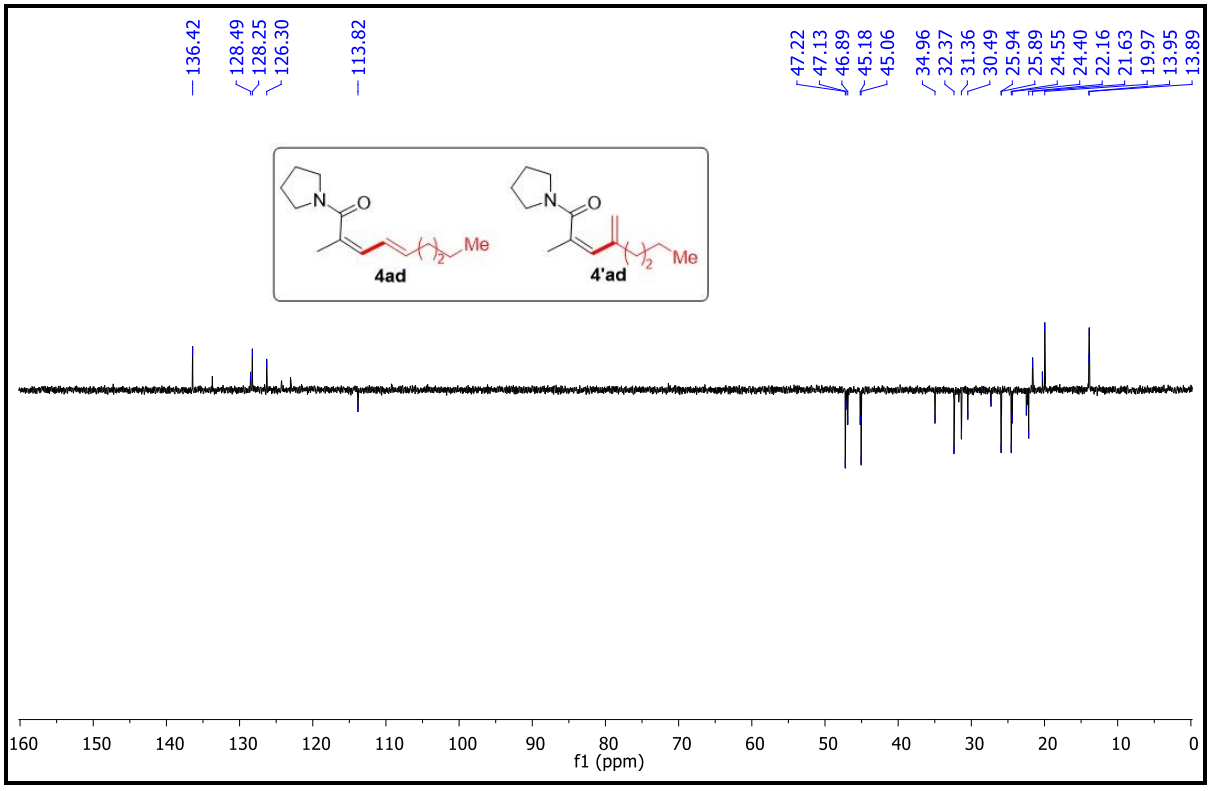
^{1}H NMR spectra of compound **4ad** in $CDCl_3$ at 500 MHz



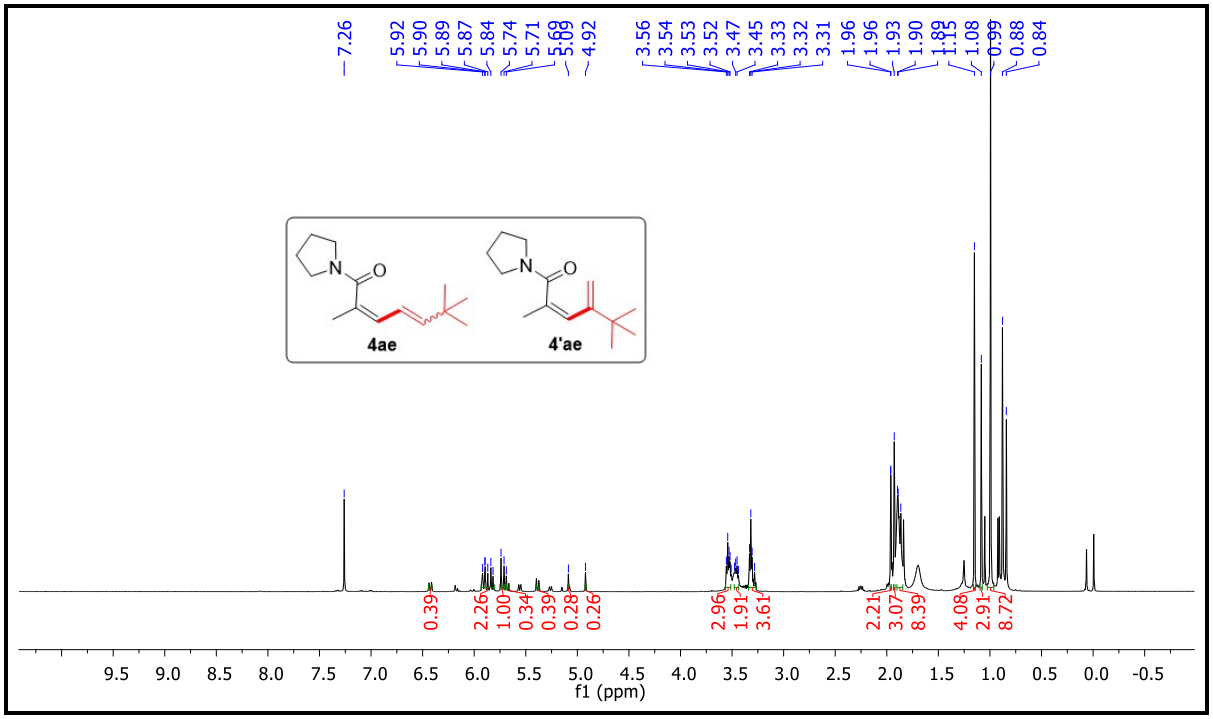
^{13}C NMR spectra of compound **4ad** in $CDCl_3$ at 126 MHz



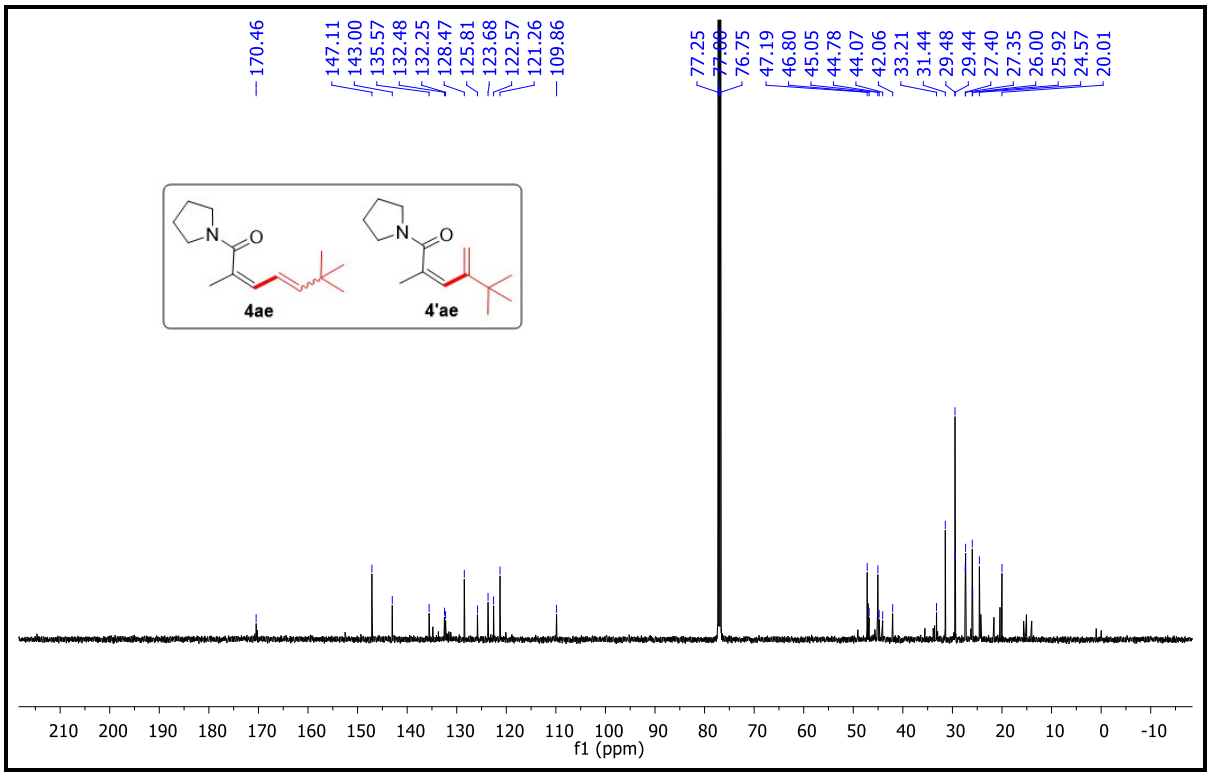
DEPT 135 NMR spectra of compound **4ad** in $CDCl_3$ at 126 MHz



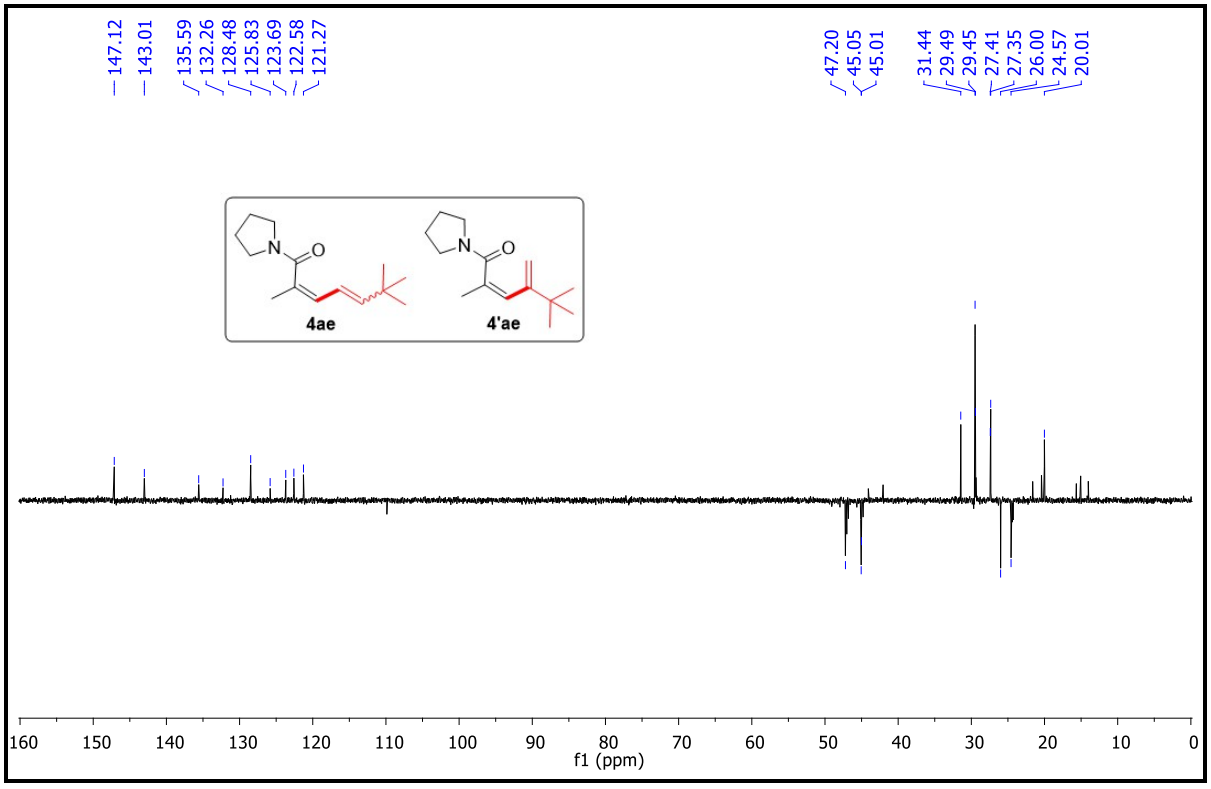
^{1}H NMR spectra of compound **4ae** in $CDCl_3$ at 500 MHz



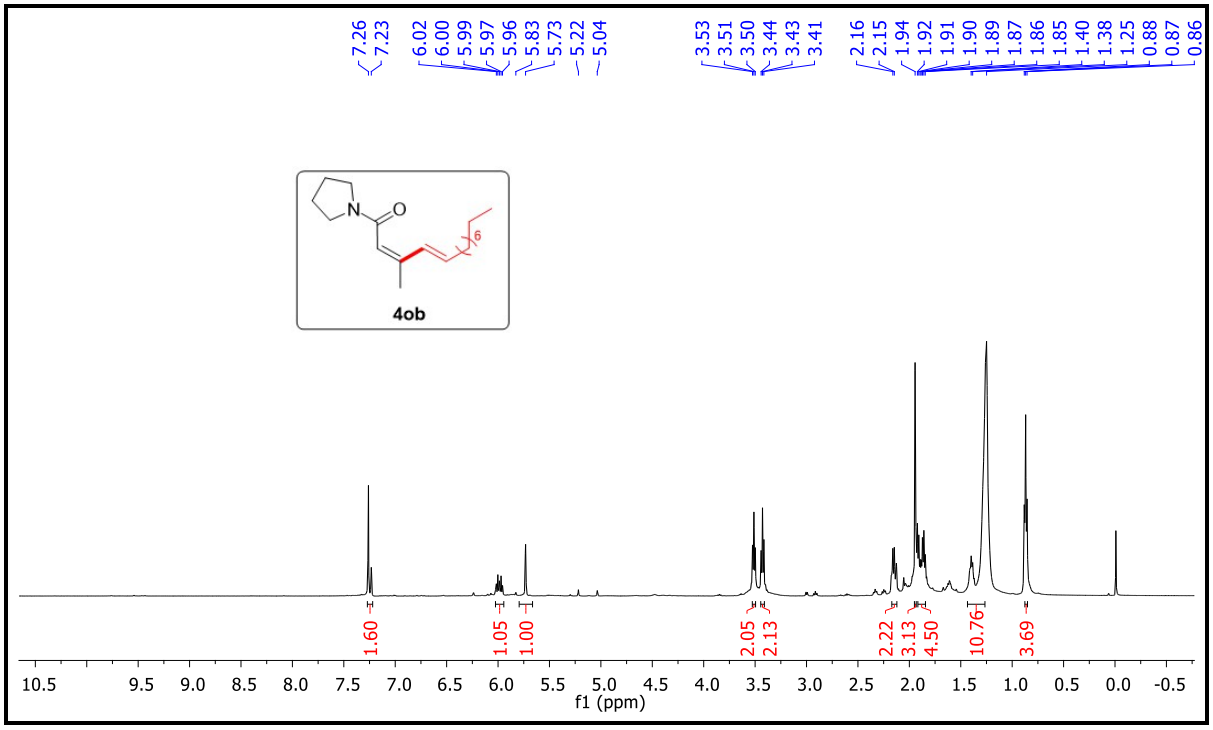
^{13}C NMR spectra of compound **4ae** in $CDCl_3$ at 126 MHz



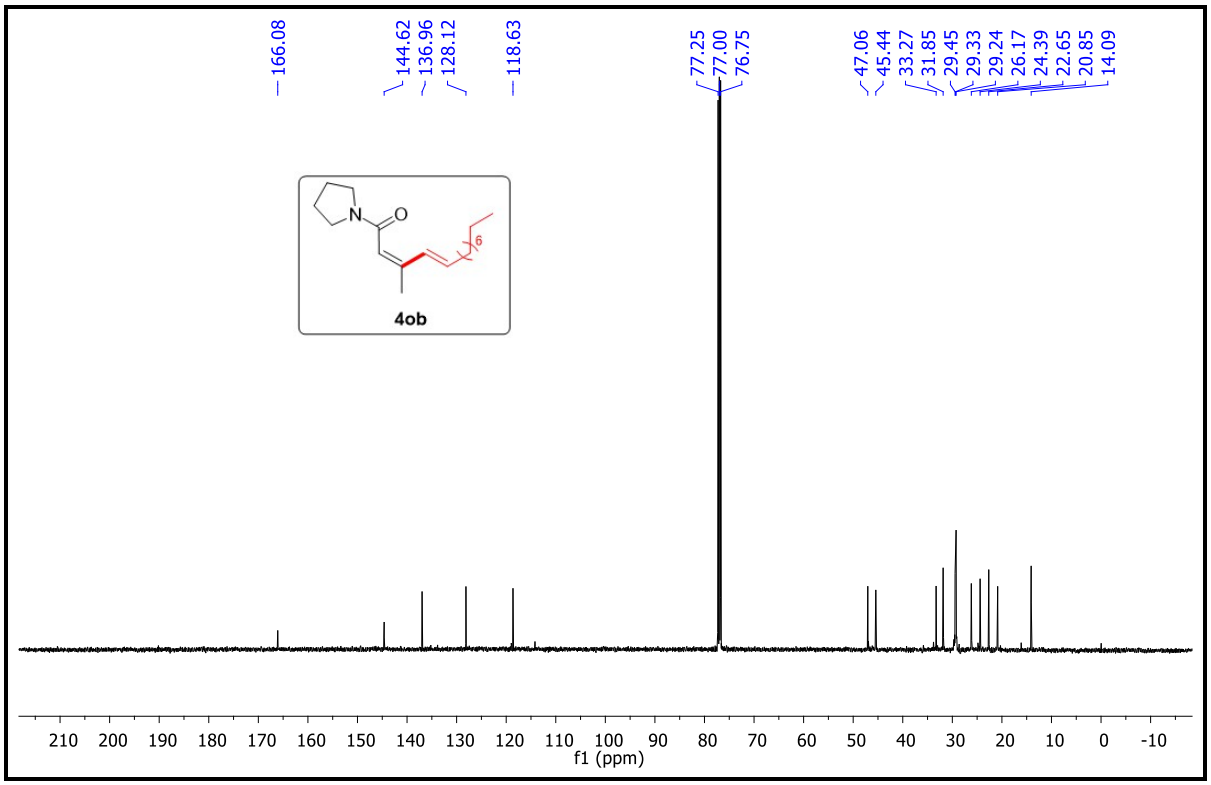
DEPT 135 NMR spectra of compound **4ae** in $CDCl_3$ at 126 MHz



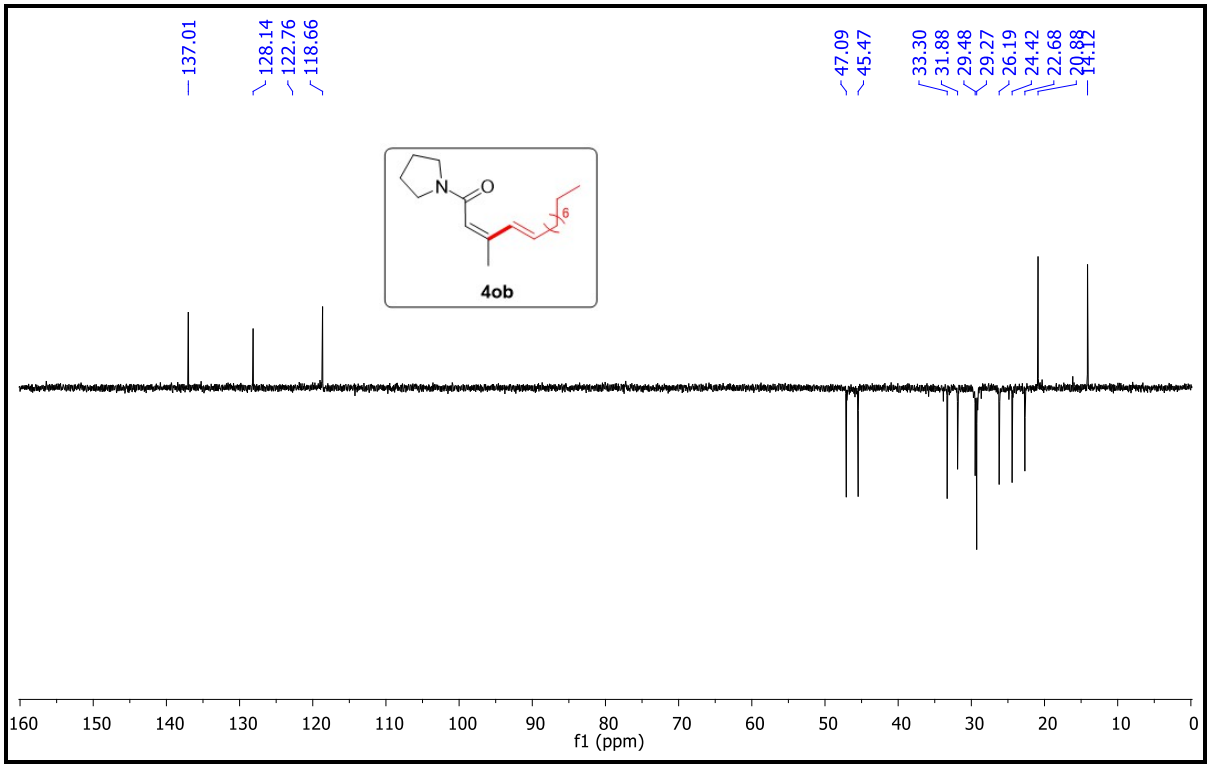
^{1}H NMR spectra of compound **4ob** in $CDCl_3$ at 500 MHz



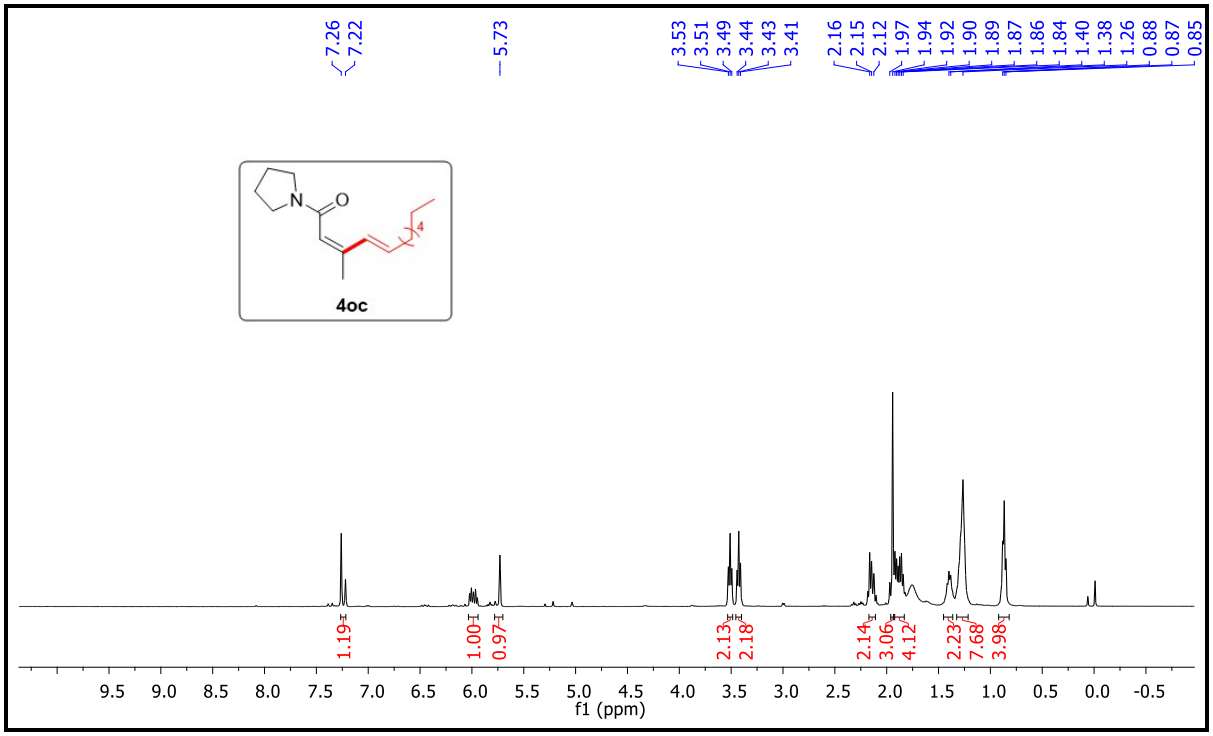
^{13}C NMR spectra of compound **4ob** in $CDCl_3$ at 126 MHz



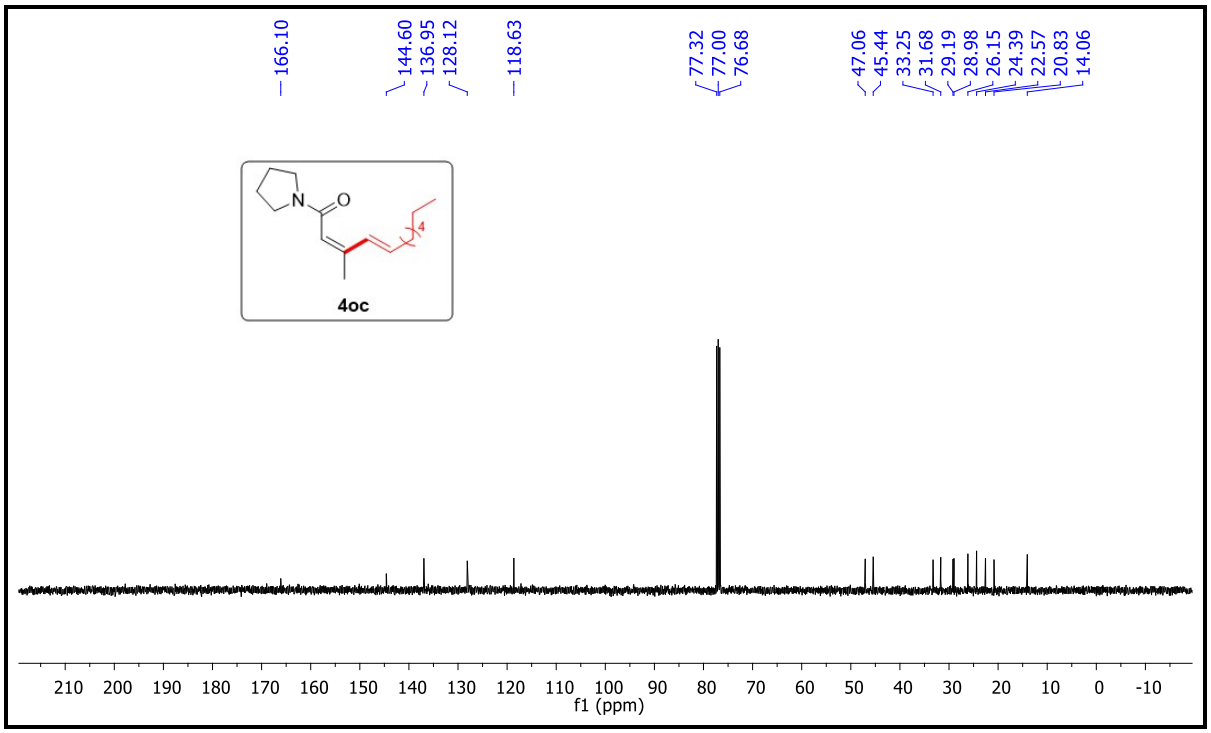
DEPT 135 NMR spectra of compound **4ob** in $CDCl_3$ at 126 MHz



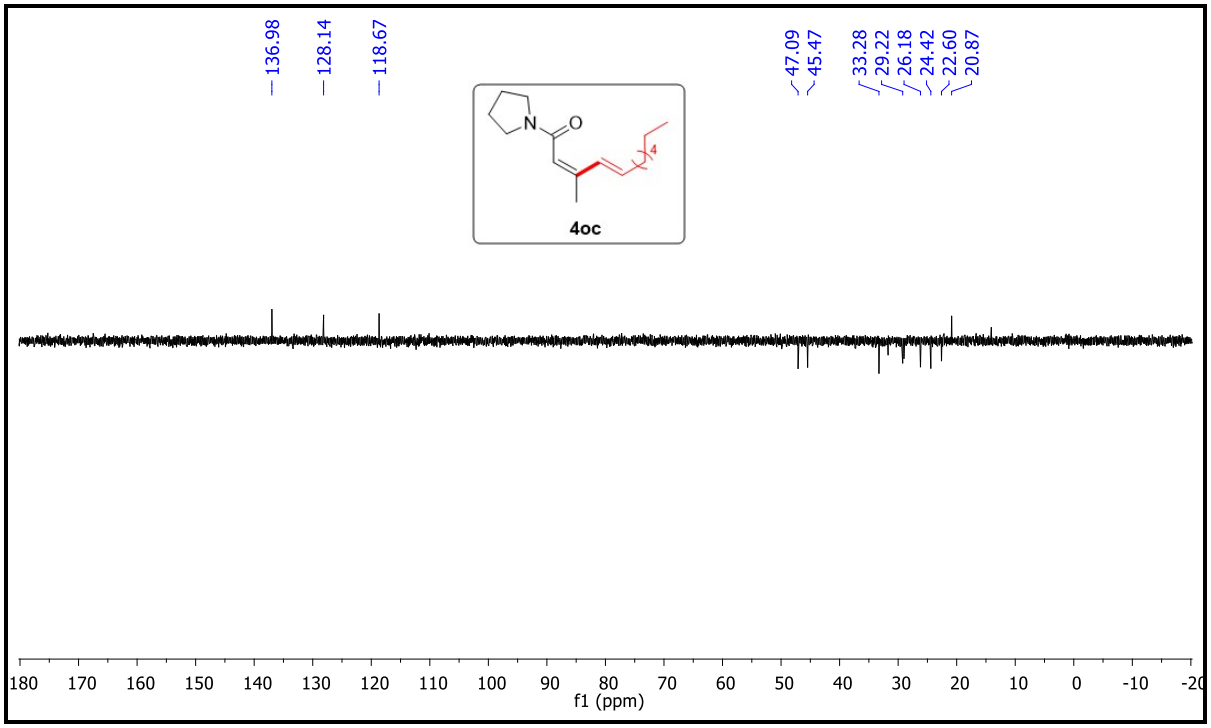
^{1}H NMR spectra of compound **4oc** in $CDCl_3$ at 400 MHz



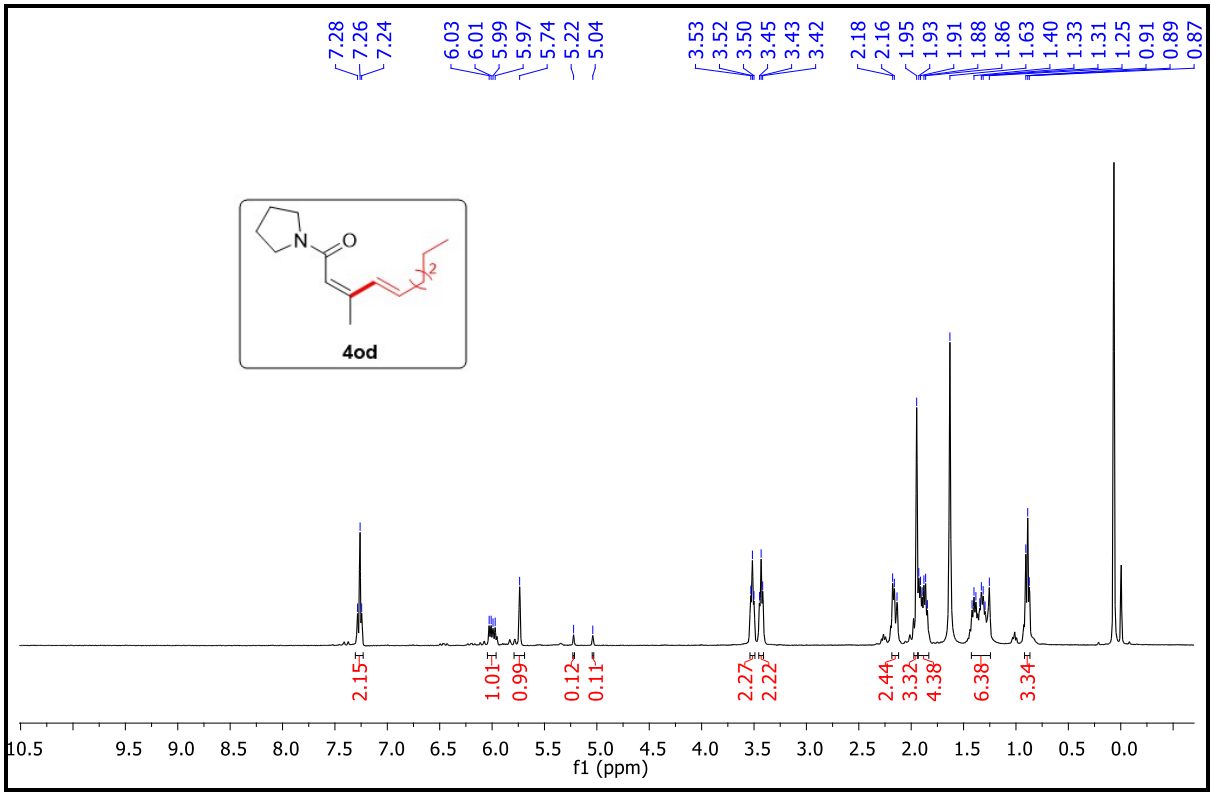
^{13}C NMR spectra of compound **4oc** in $CDCl_3$ at 101 MHz



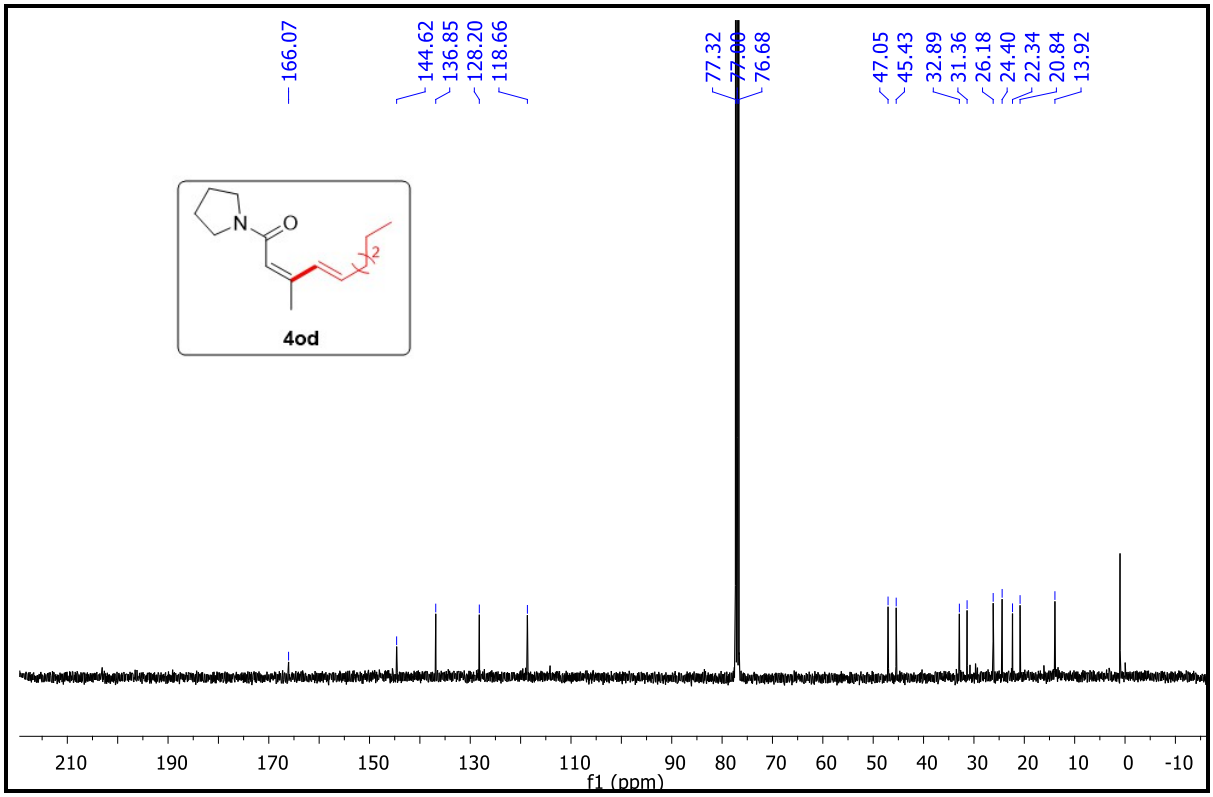
DEPT 135 NMR spectra of compound **4oc** in $CDCl_3$ at 101 MHz



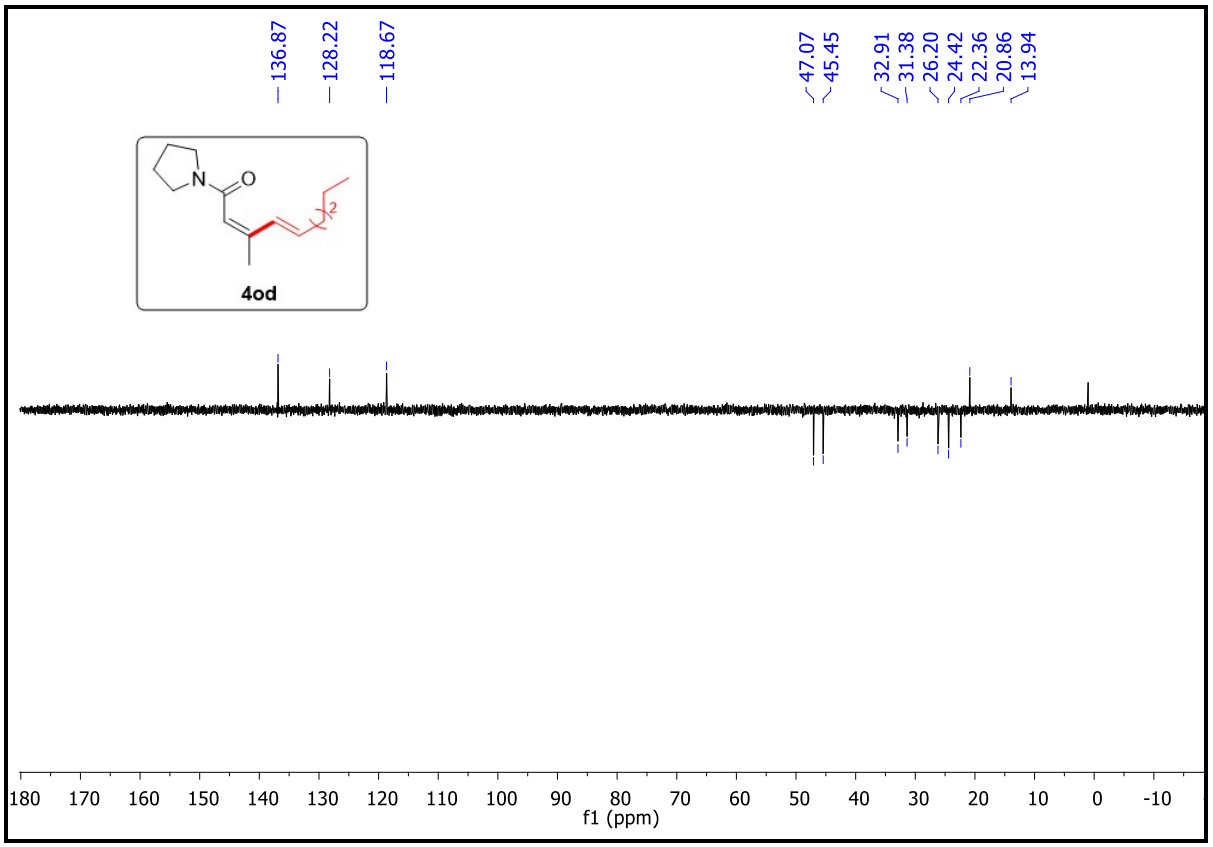
^{1}H NMR spectra of compound **4od** in $CDCl_3$ at 400 MHz



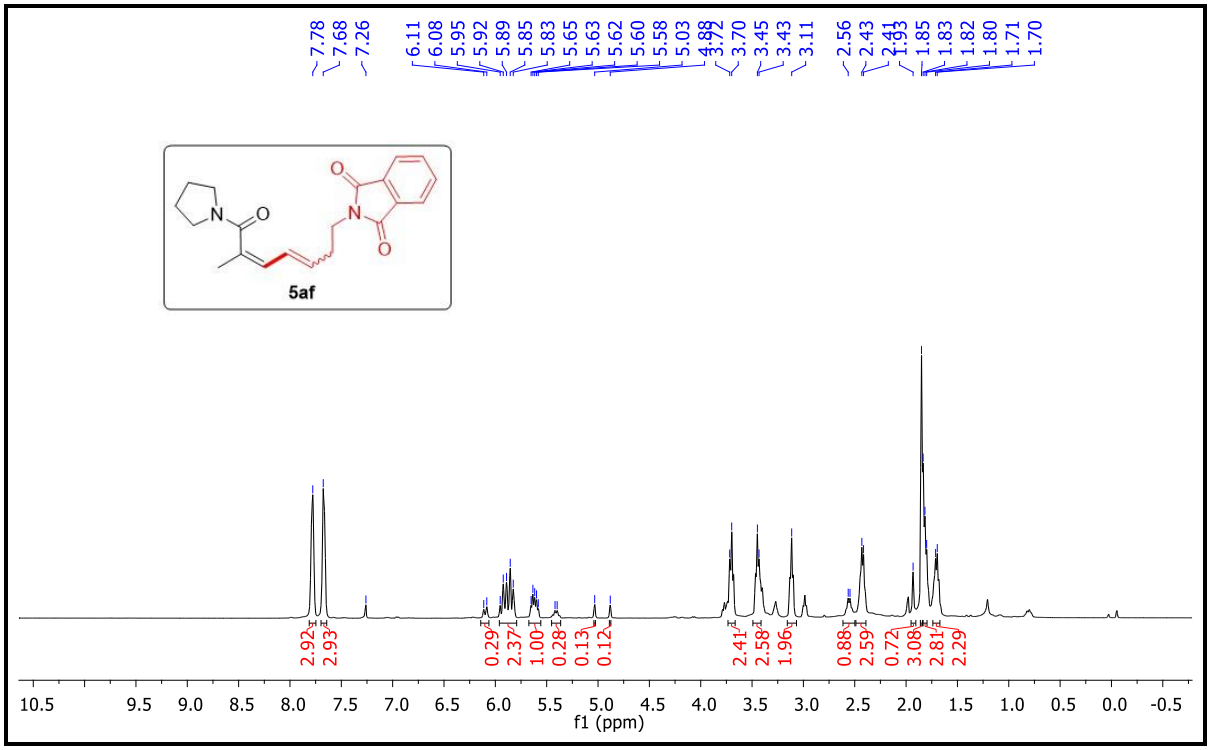
^{13}C NMR spectra of compound **4od** in $CDCl_3$ at 101 MHz



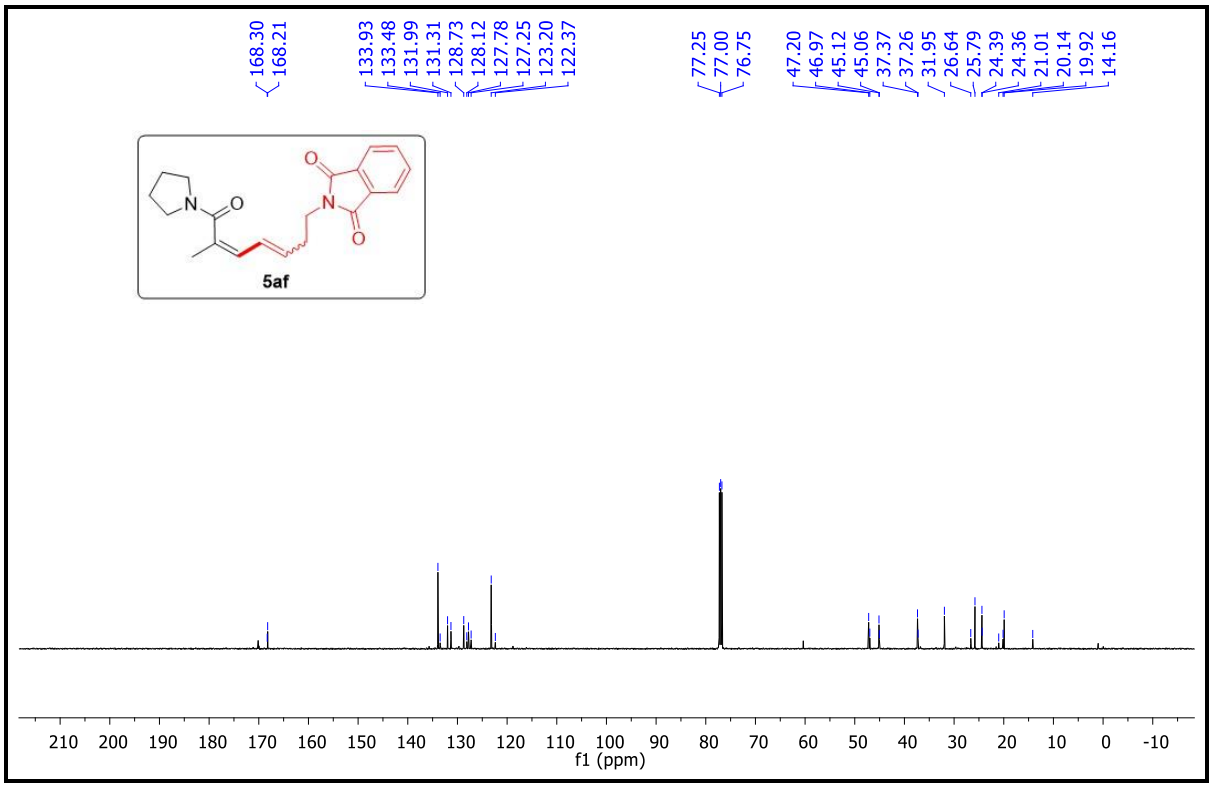
DEPT 135 NMR spectra of compound **4od** in $CDCl_3$ at 101 MHz



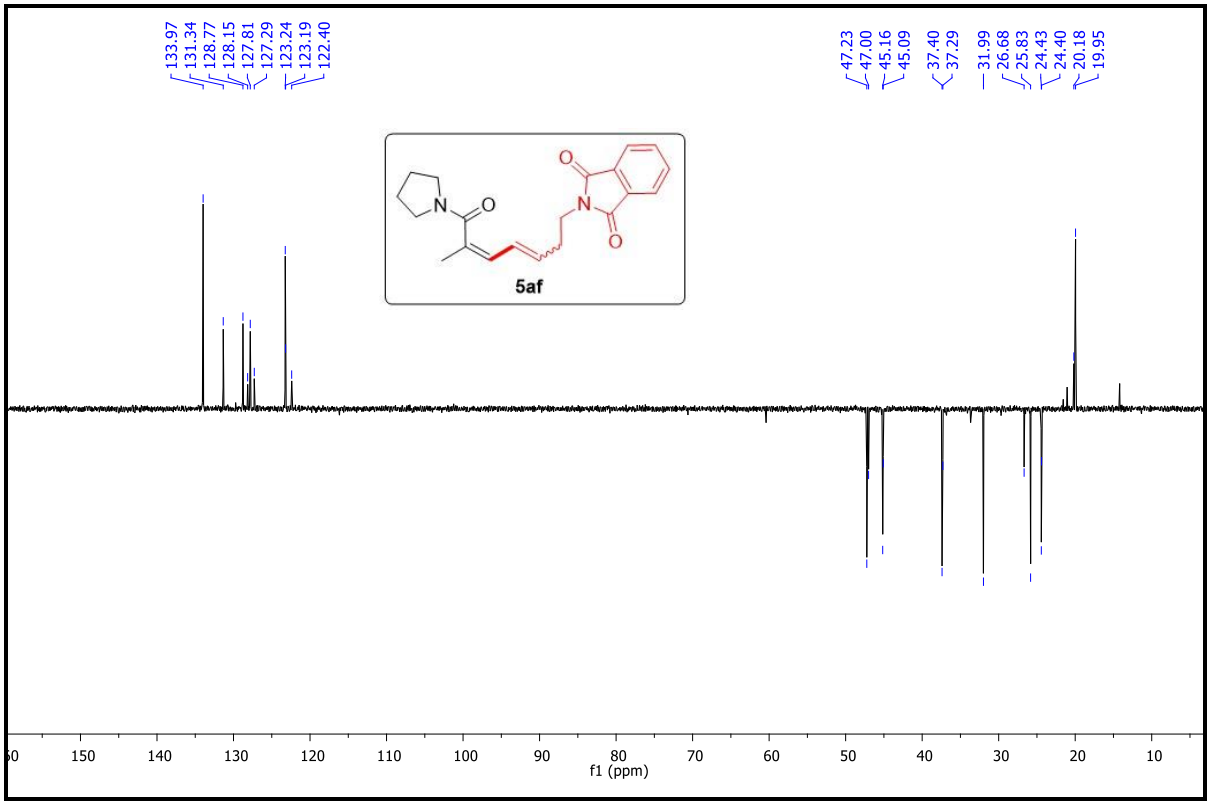
^{1}H NMR spectra of compound **5af** in $CDCl_3$ at 500 MHz



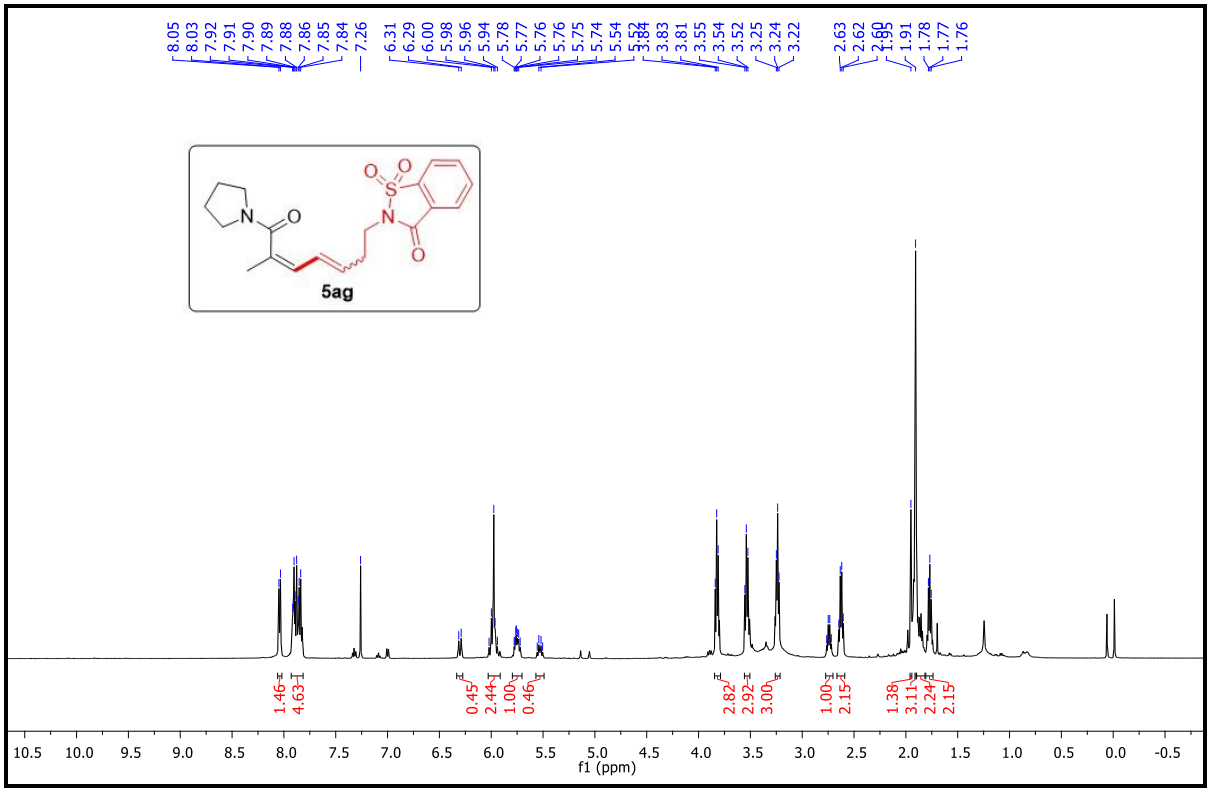
^{13}C NMR spectra of compound **5af** in $CDCl_3$ at 126 MHz



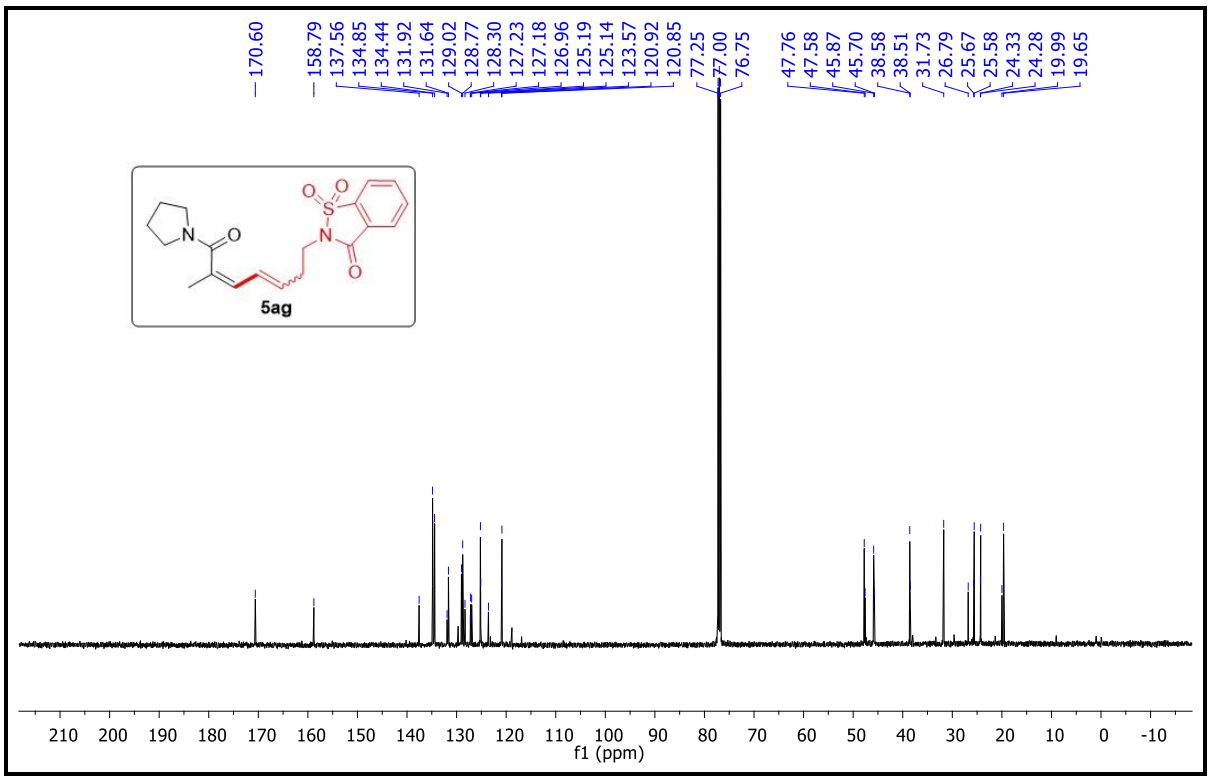
DEPT 135 NMR spectra of compound **5af** in $CDCl_3$ at 126 MHz



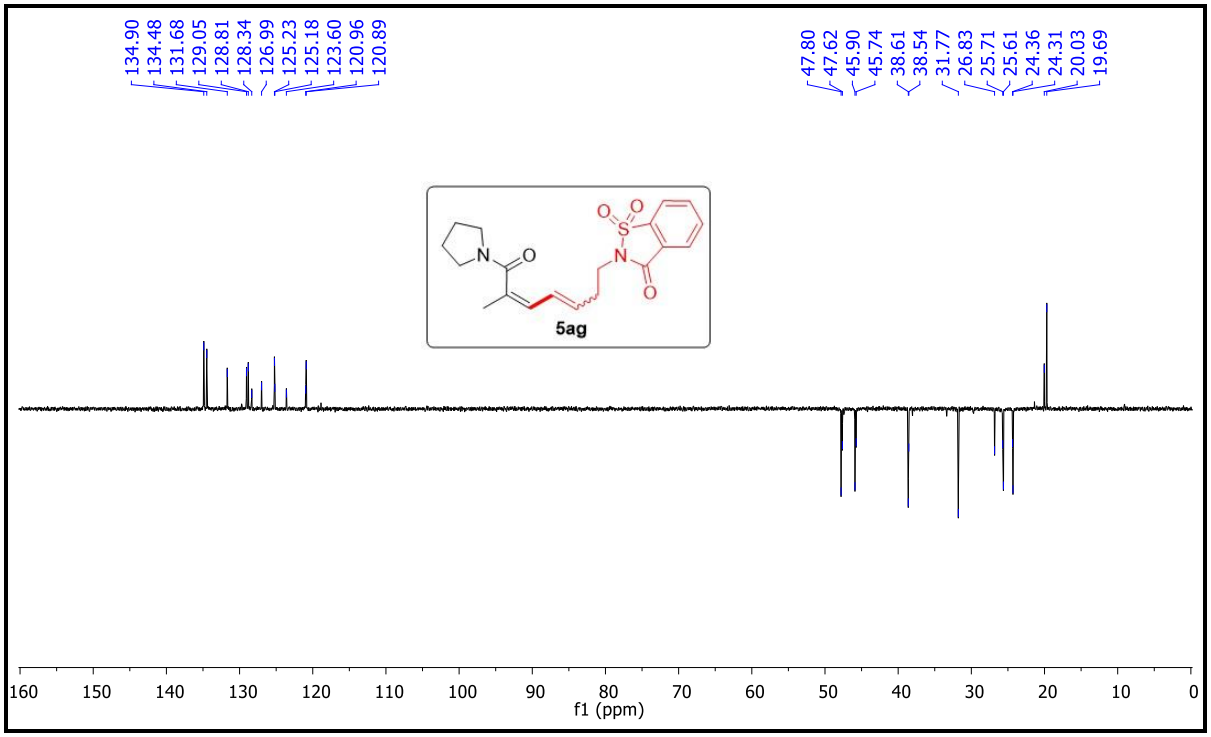
^{1}H NMR spectra of compound **5ag** in $CDCl_3$ at 500 MHz



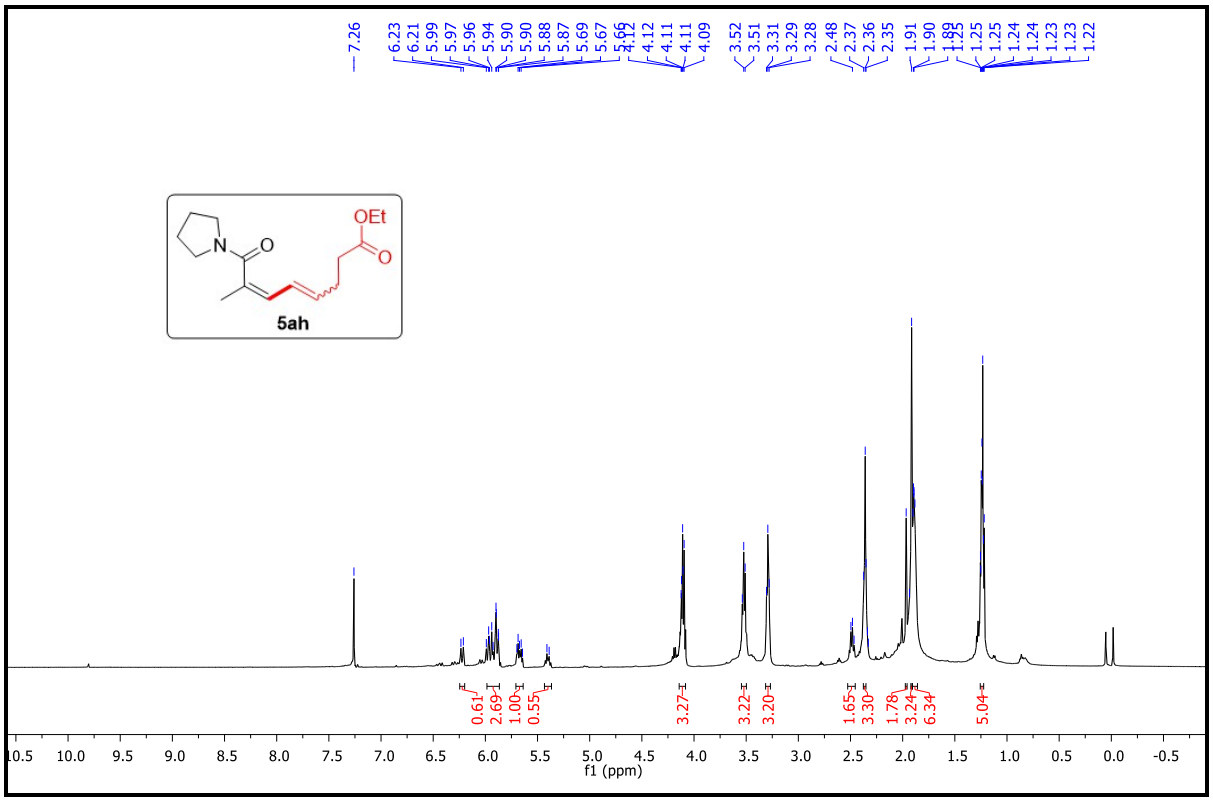
^{13}C NMR spectra of compound **5ag** in $CDCl_3$ at 126 MHz



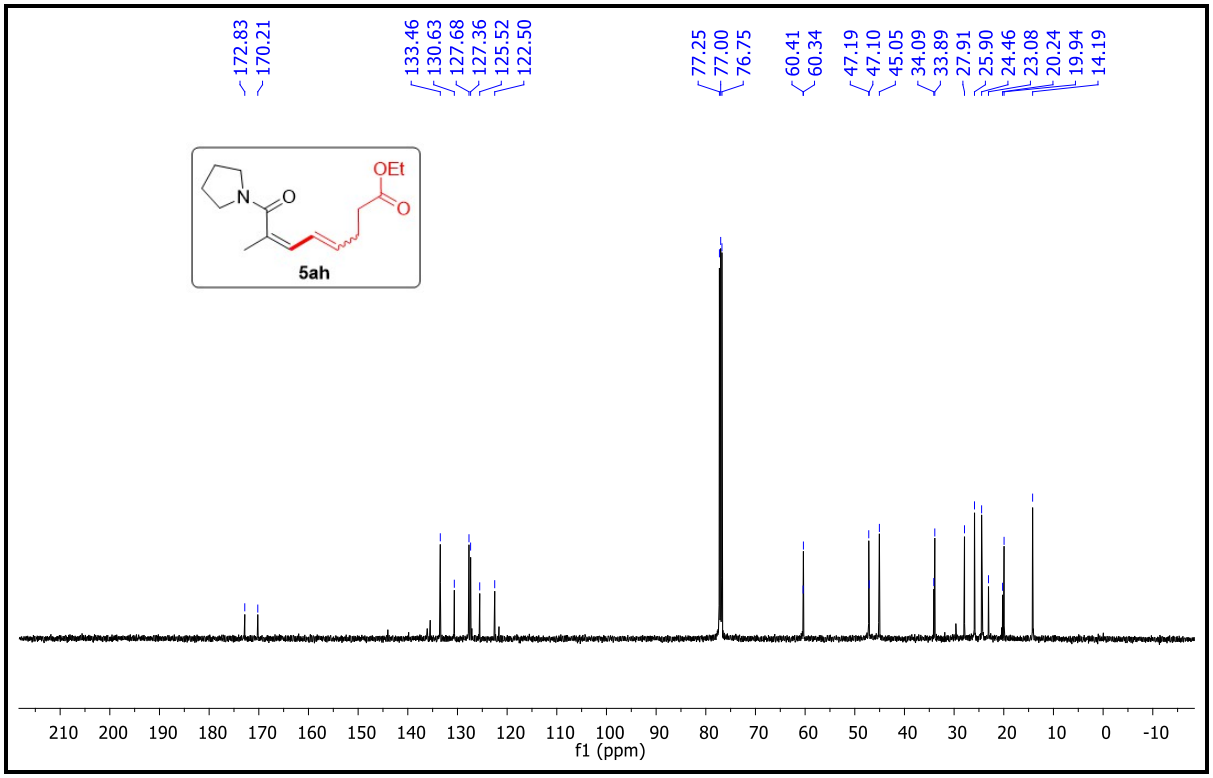
DEPT 135 NMR spectra of compound **5ag** in $CDCl_3$ at 126 MHz



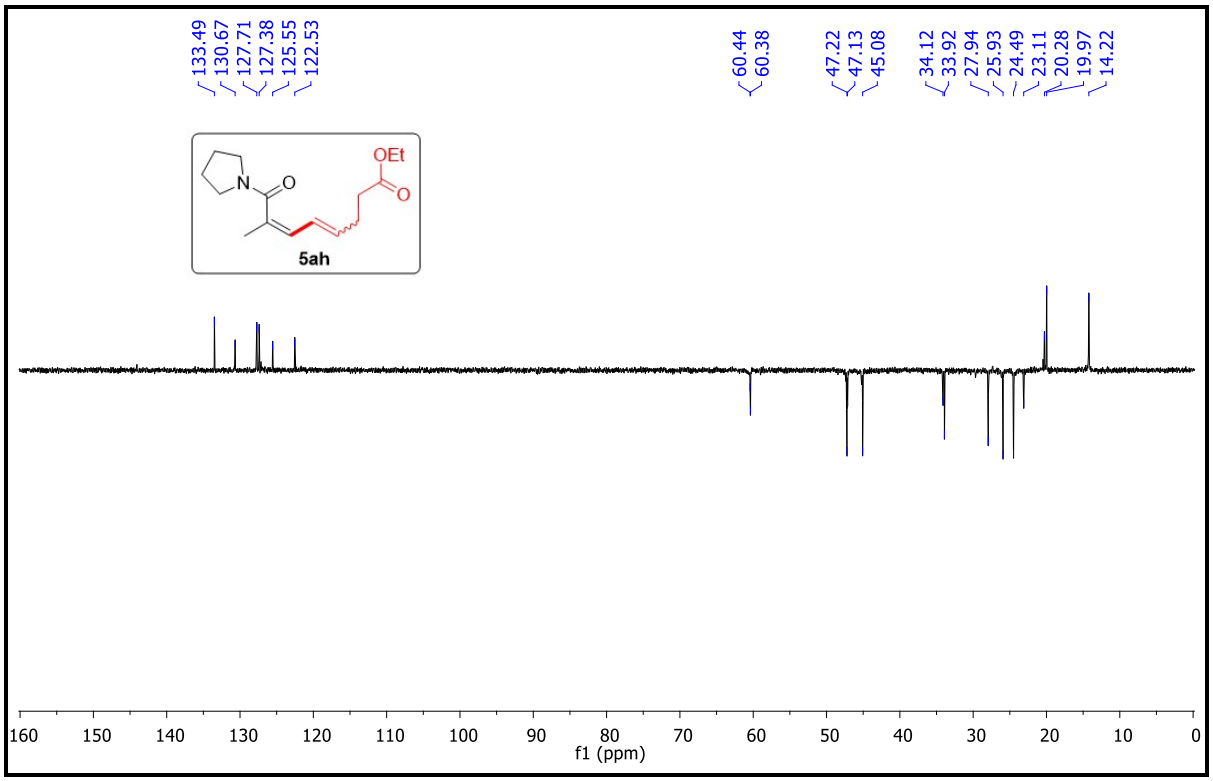
^{1}H NMR spectra of compound **5ah** in $CDCl_3$ at 500 MHz



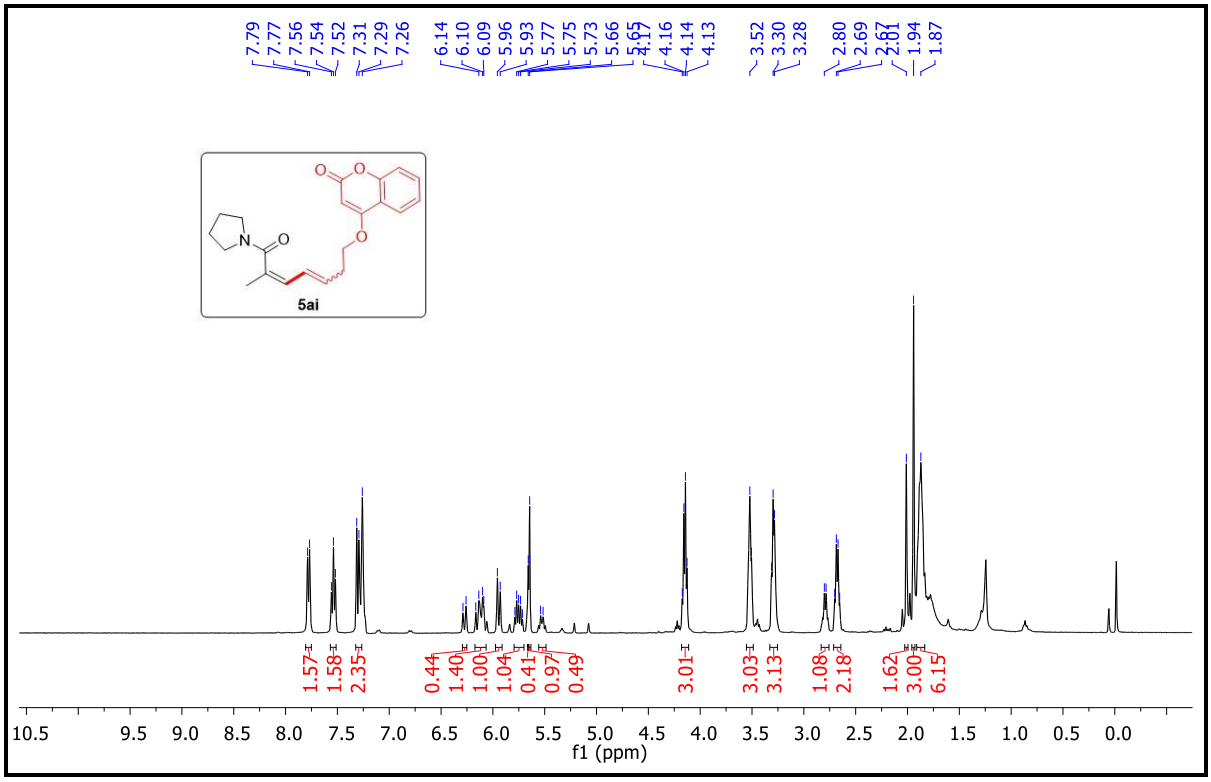
^{13}C NMR spectra of compound **5ah** in $CDCl_3$ at 126 MHz



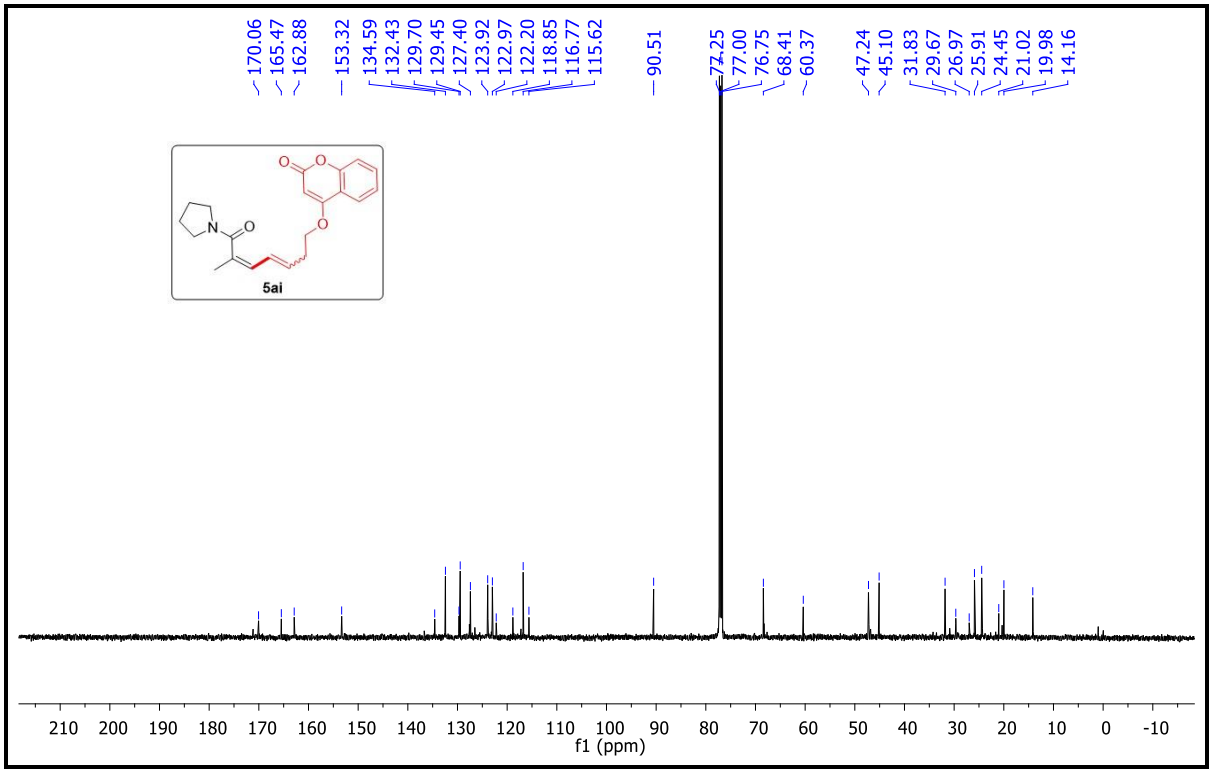
DEPT 135 NMR spectra of compound **5ah** in $CDCl_3$ at 126 MHz



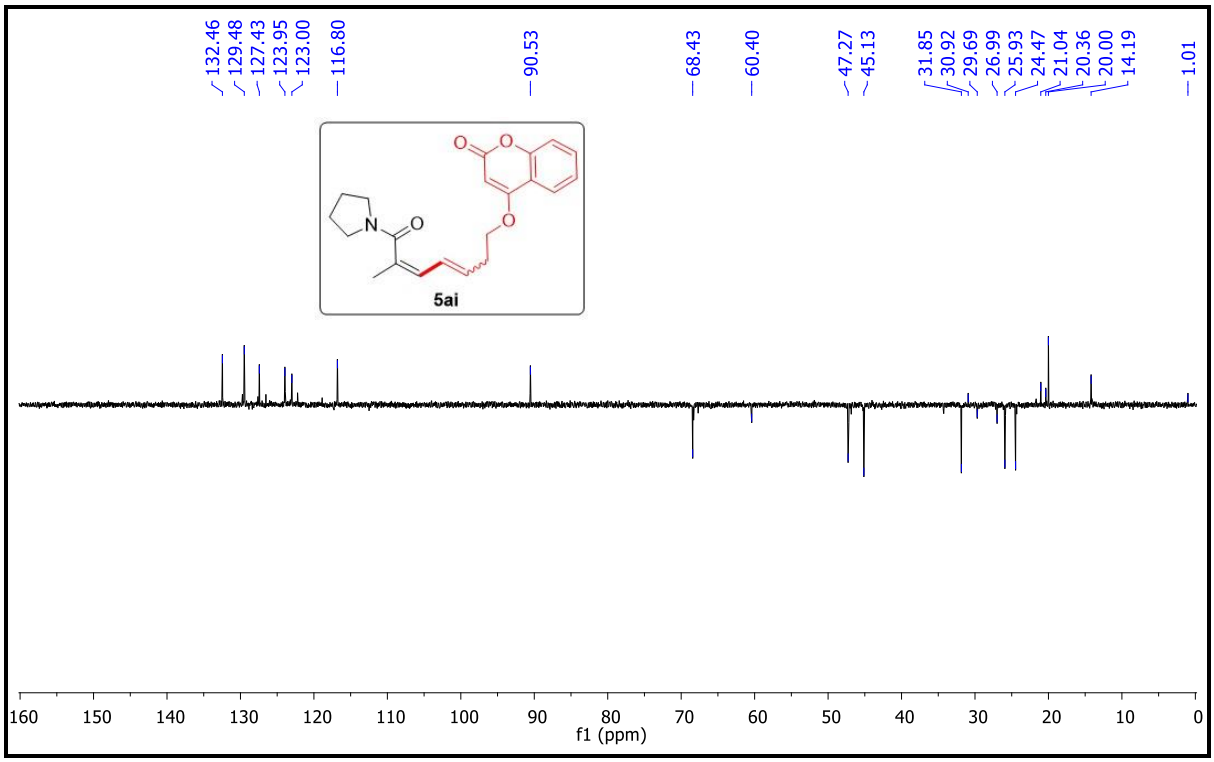
^{1}H NMR spectra of compound **5ai** in $CDCl_3$ at 400 MHz



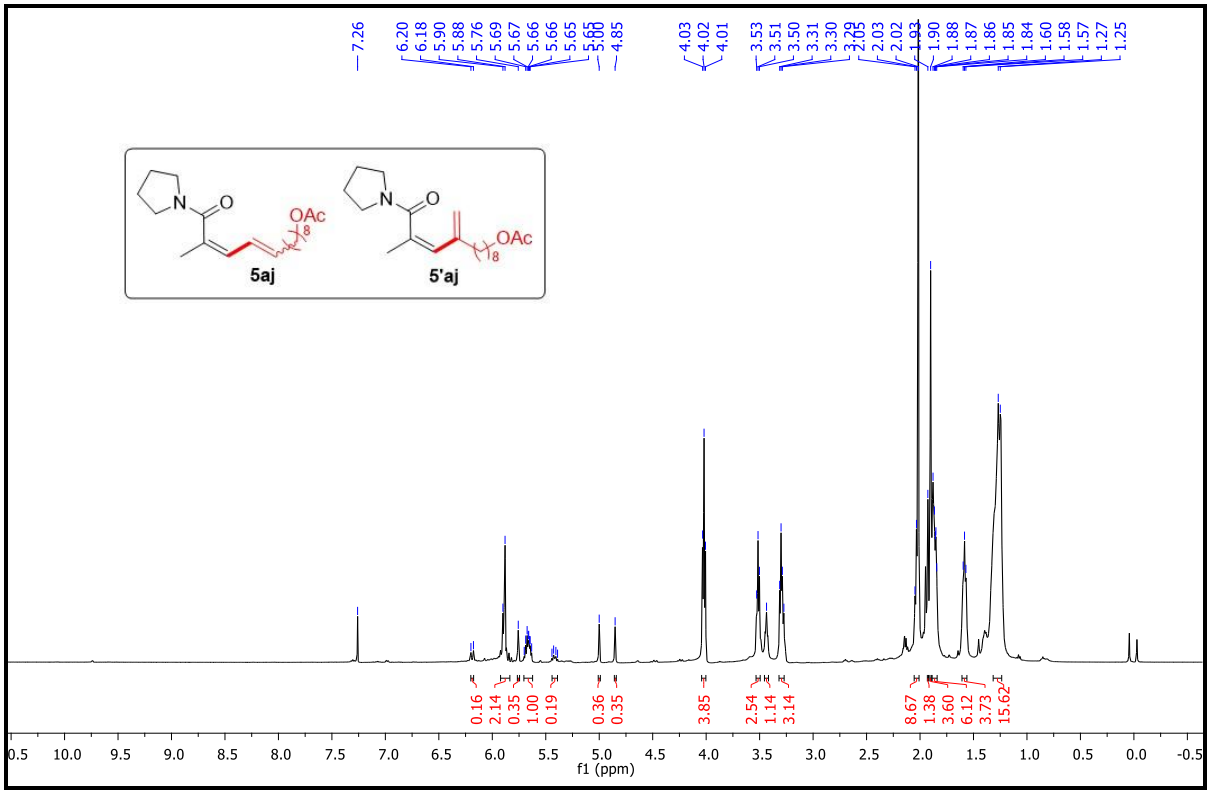
^{13}C NMR spectra of compound **5ai** in $CDCl_3$ at 101 MHz



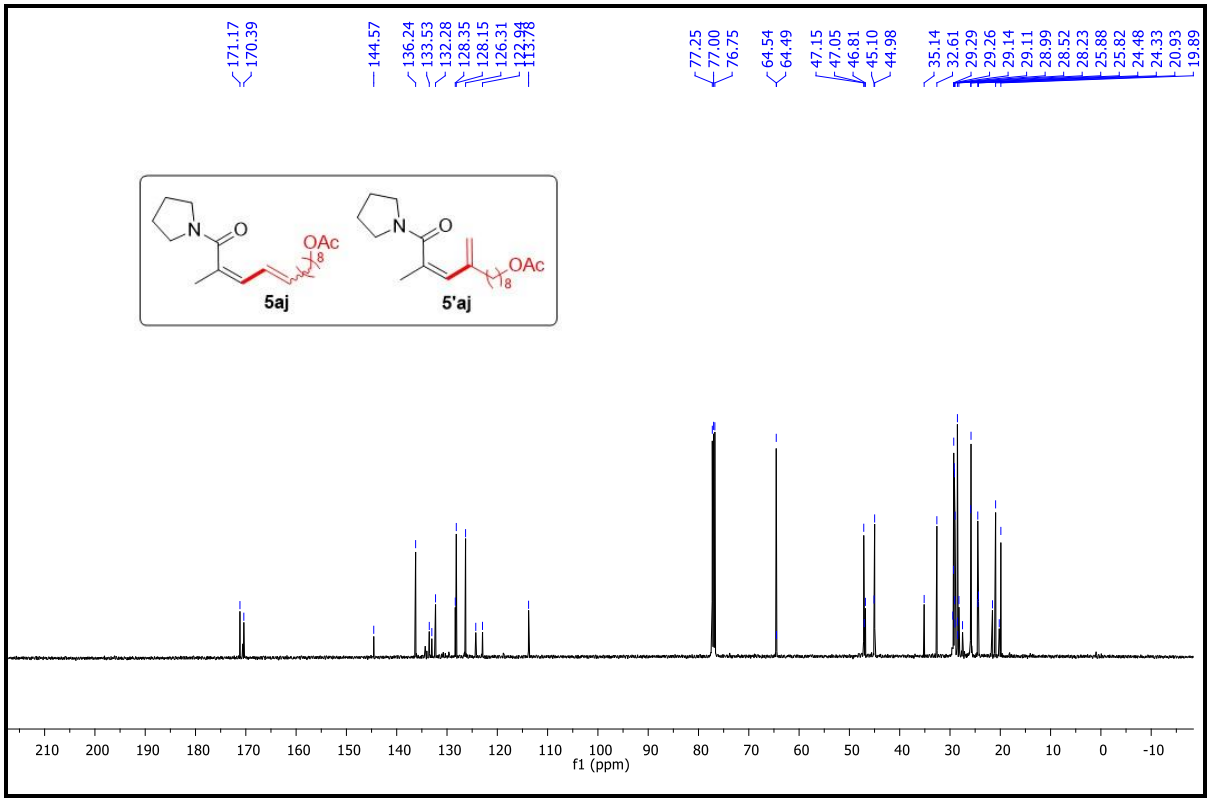
DEPT 135 NMR spectra of compound **5ai** in $CDCl_3$ at 101 MHz



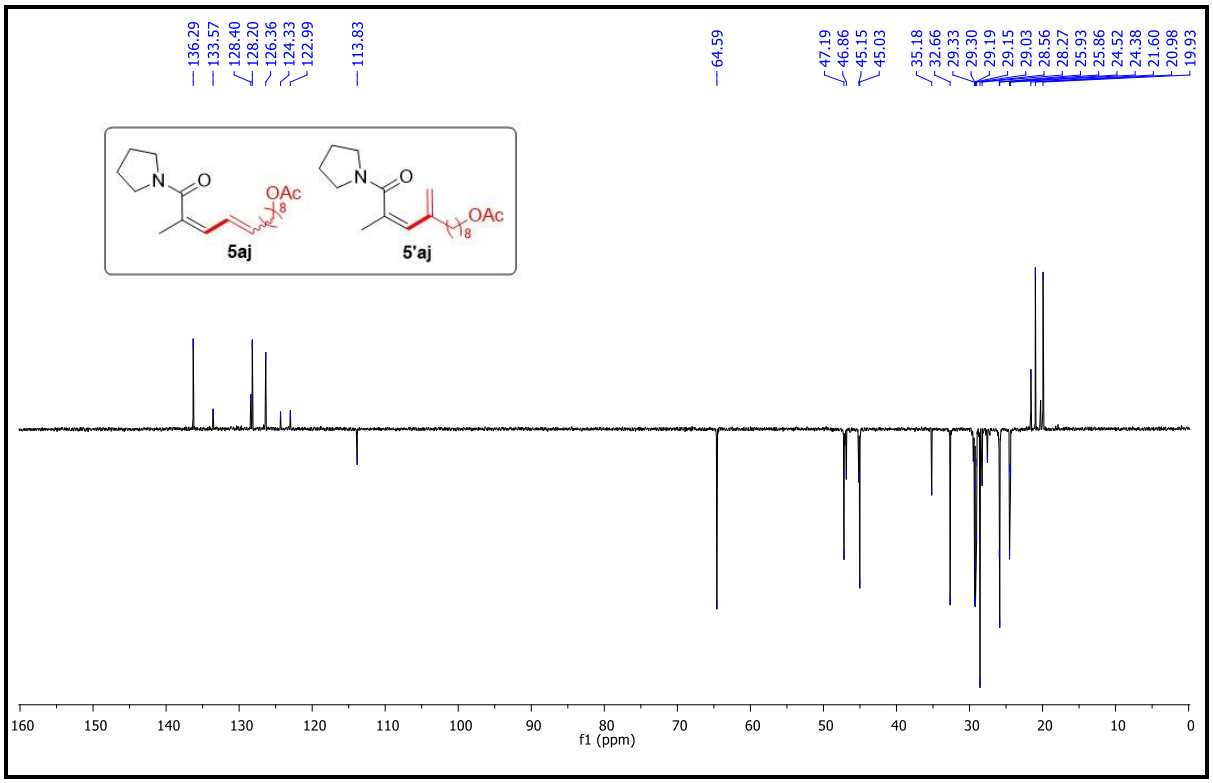
^{1}H NMR spectra of compound **5aj** in $CDCl_3$ at 500 MHz



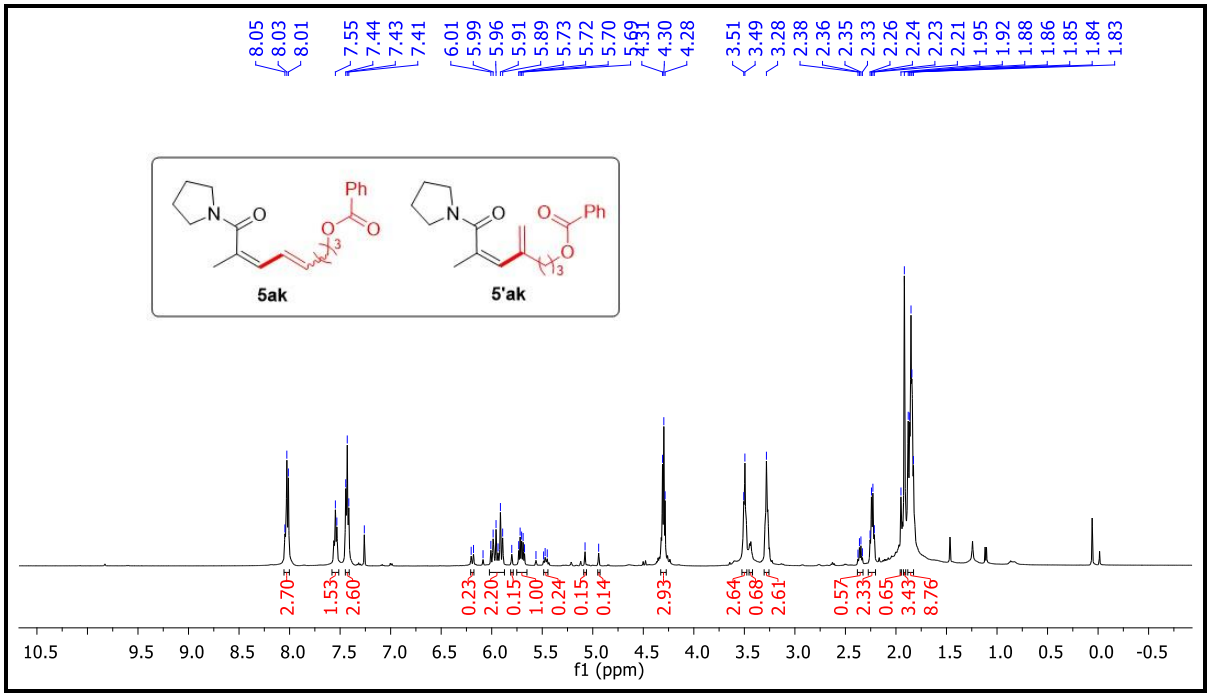
^{13}C NMR spectra of compound **5aj** in $CDCl_3$ at 126 MHz



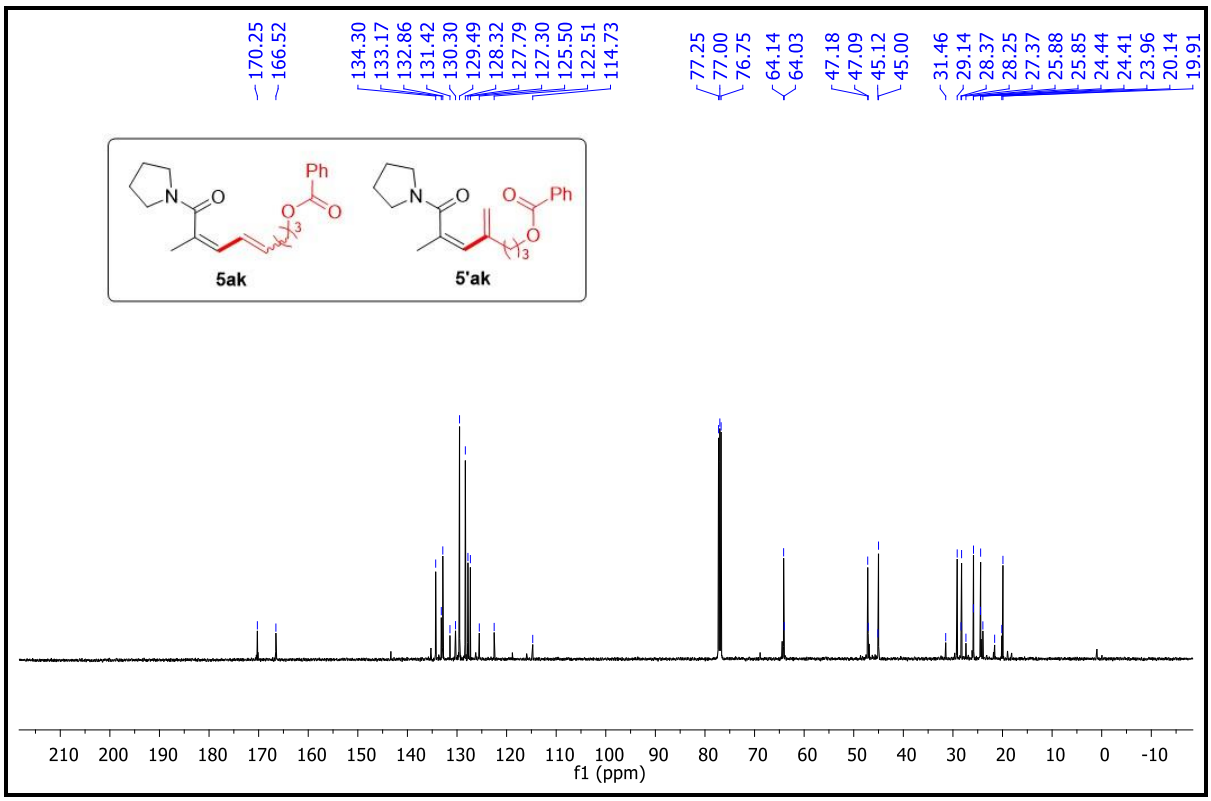
DEPT 135 NMR spectra of compound **5aj** in $CDCl_3$ at 126 MHz



^{1}H NMR spectra of compound **5ak** in $CDCl_3$ at 500 MHz



^{13}C NMR spectra of compound **5ak** in $CDCl_3$ at 126 MHz



DEPT 135 NMR spectra of compound **5ak** in $CDCl_3$ at 126 MHz