

Supporting Information for

Sequential One-Pot Vilsmeier-Haack and Organocatalyzed Mannich Cyclizations to Functionalized Benzoindolizidines and Benzoquinolizidines

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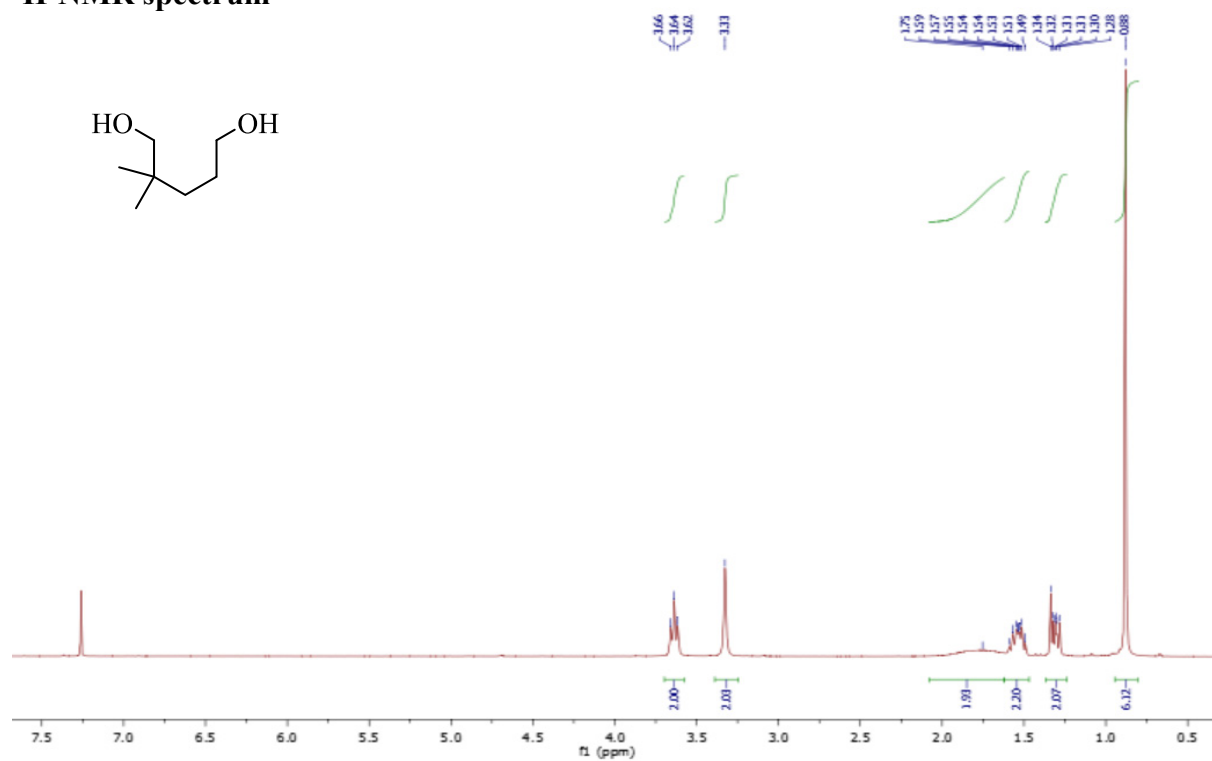
Département de chimie, Université de Sherbrooke, 2500, boulevard de l'Université, Sherbrooke,
Québec, Canada J1K 2R1

Content :

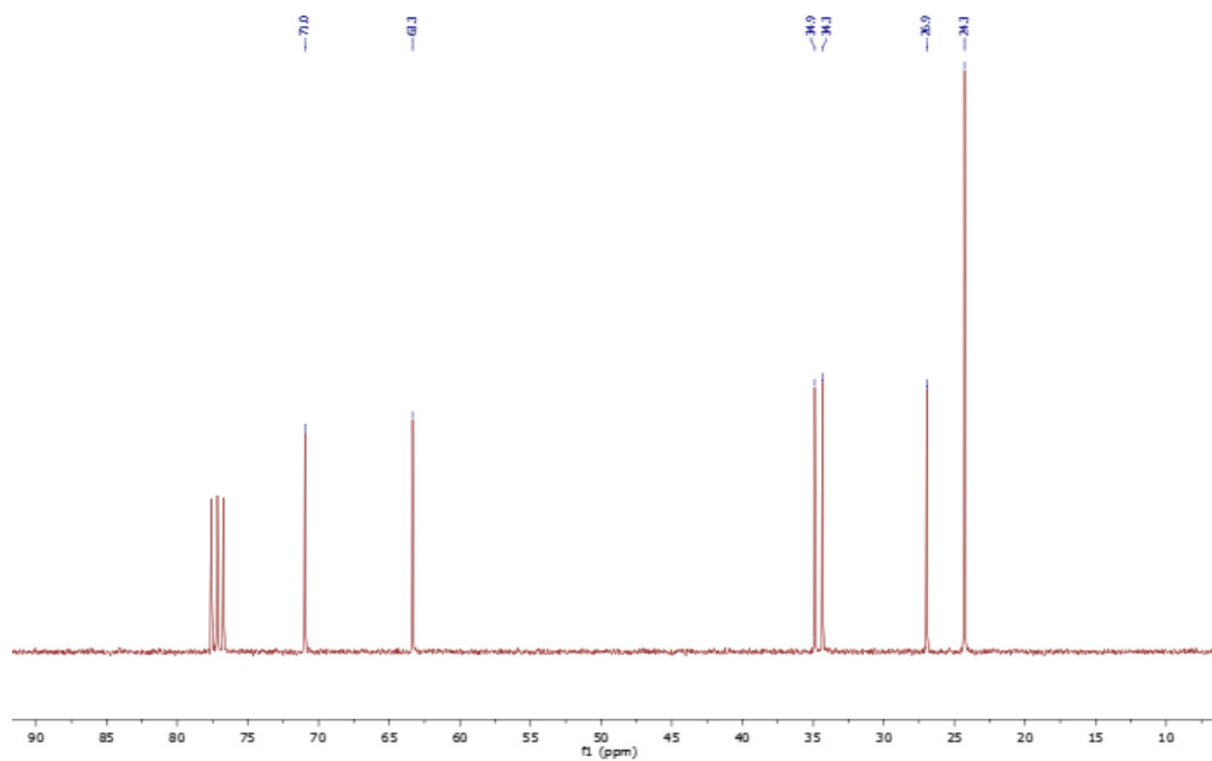
¹ H AND ¹³ C NMR SPECTRA.....	S2
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2,2-Dimethylpentane-1,5-diol (11)

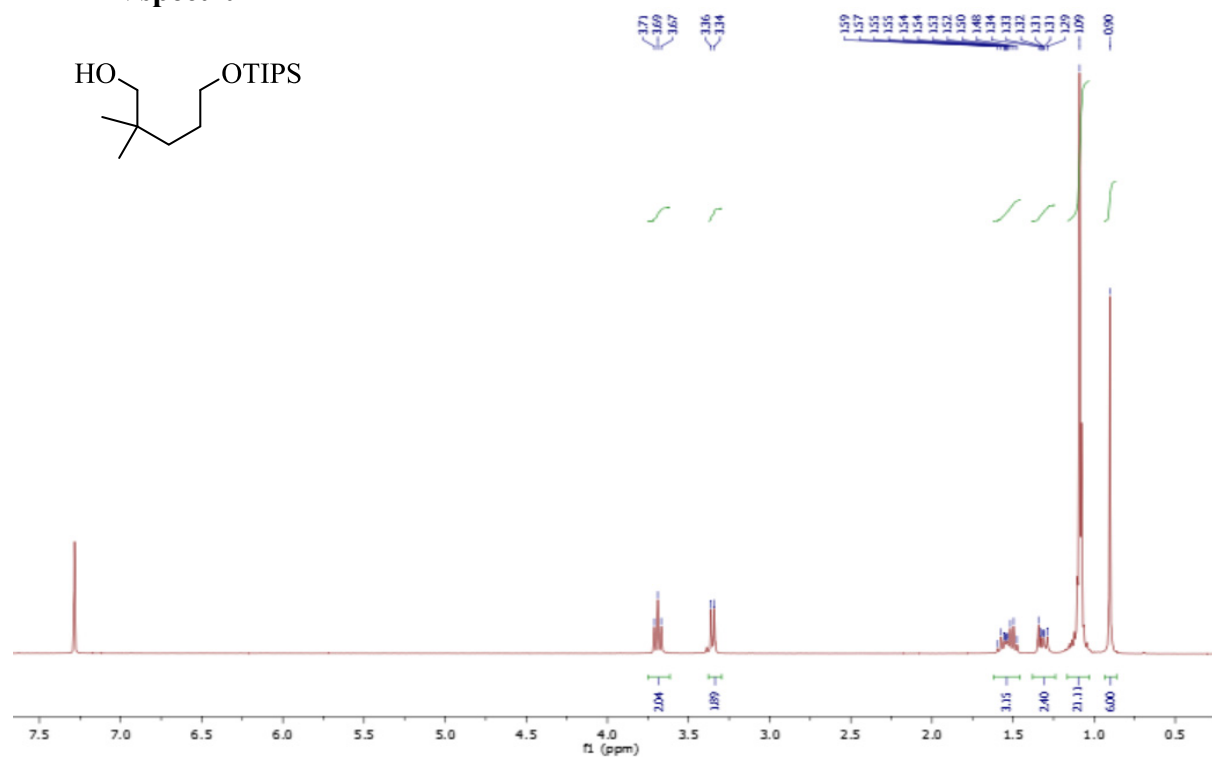
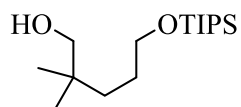
^1H -NMR spectrum



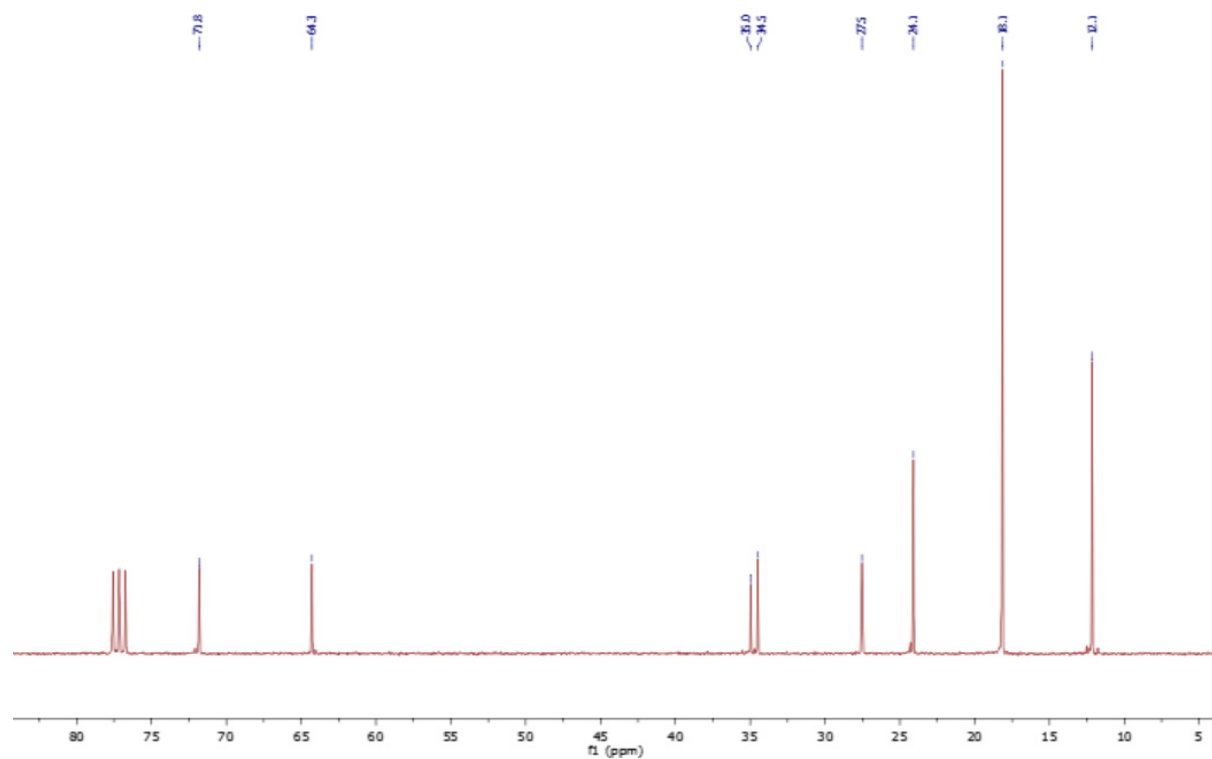
^{13}C -NMR spectrum



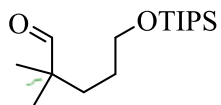
¹H RMN spectrum



¹³C RMN spectrum



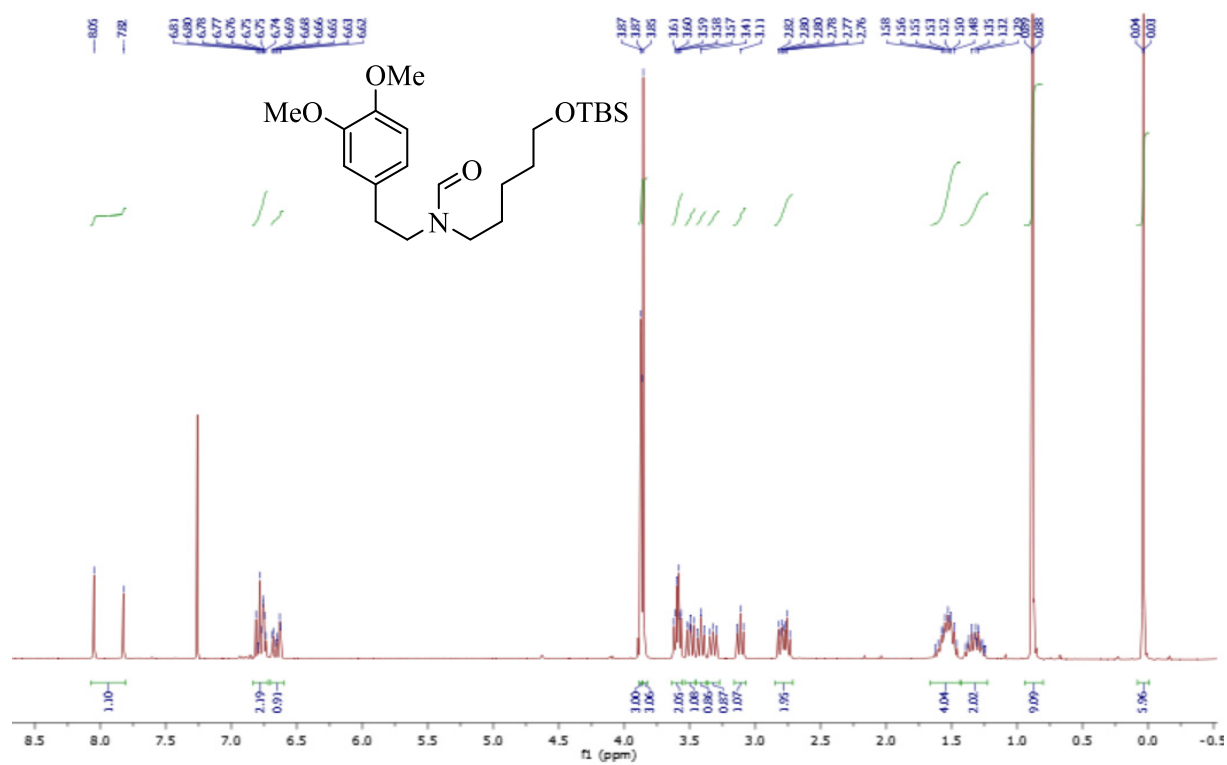
¹H RMN spectrum



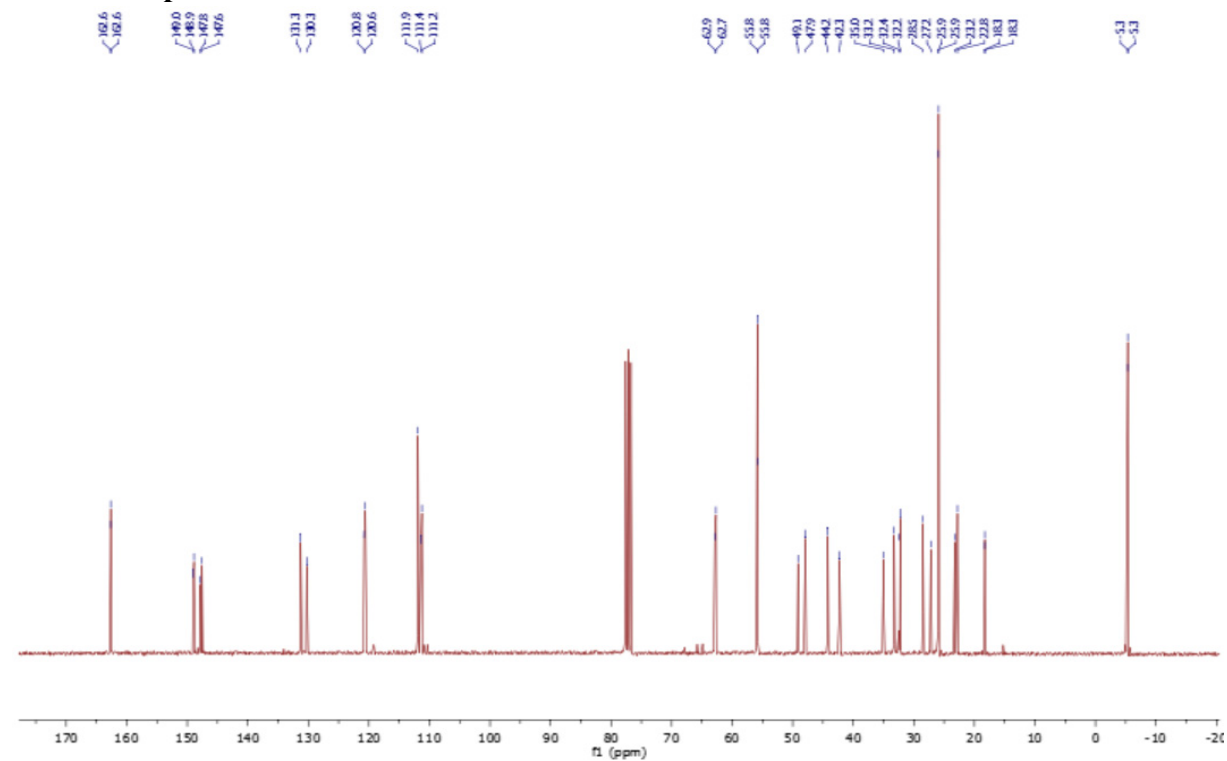
13C NMR spectrum of compound 10a in CDCl₃. The x-axis is labeled 'f1 (ppm)' and ranges from 220 to 0. The spectrum shows several peaks: a small peak at 206.3 ppm, a small peak at 78.3 ppm, a small peak at 63.5 ppm, a small peak at 46.6 ppm, a small peak at 31.5 ppm, a small peak at 27.9 ppm, a small peak at 21.4 ppm, a small peak at 18.1 ppm, and a large peak at 12.1 ppm. The peak at 12.1 ppm is the most intense.

***N*-(5-((*tert*-Butyldimethylsilyl)oxy)pentyl)-*N*-(3,4-dimethoxyphenethyl)formamide (14a)**

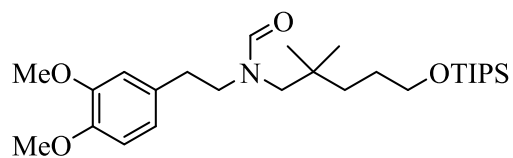
¹H RMN spectrum



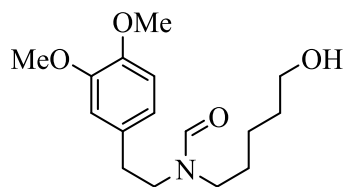
¹³C RMN spectrum



¹H RMN spectrum

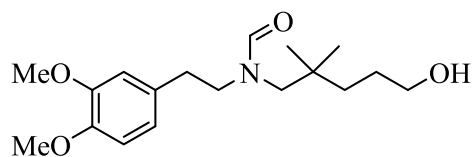


¹H RMN spectrum



¹³C NMR spectrum of compound 10b in CDCl₃. The spectrum shows peaks from 0 to 170 ppm. Key peaks are labeled with their chemical shifts: 162.8, 162.7, 148.9, 147.7, 147.4, 147.1, 131.1, 130.1, 120.7, 120.5, 111.8, 111.3, 111.1, 62.1, 60.0, -55.8, 49.1, 47.8, 44.1, 42.1, 34.8, 33.1, 32.1, 32.0, 28.3, 27.0, 22.9, and 22.6.

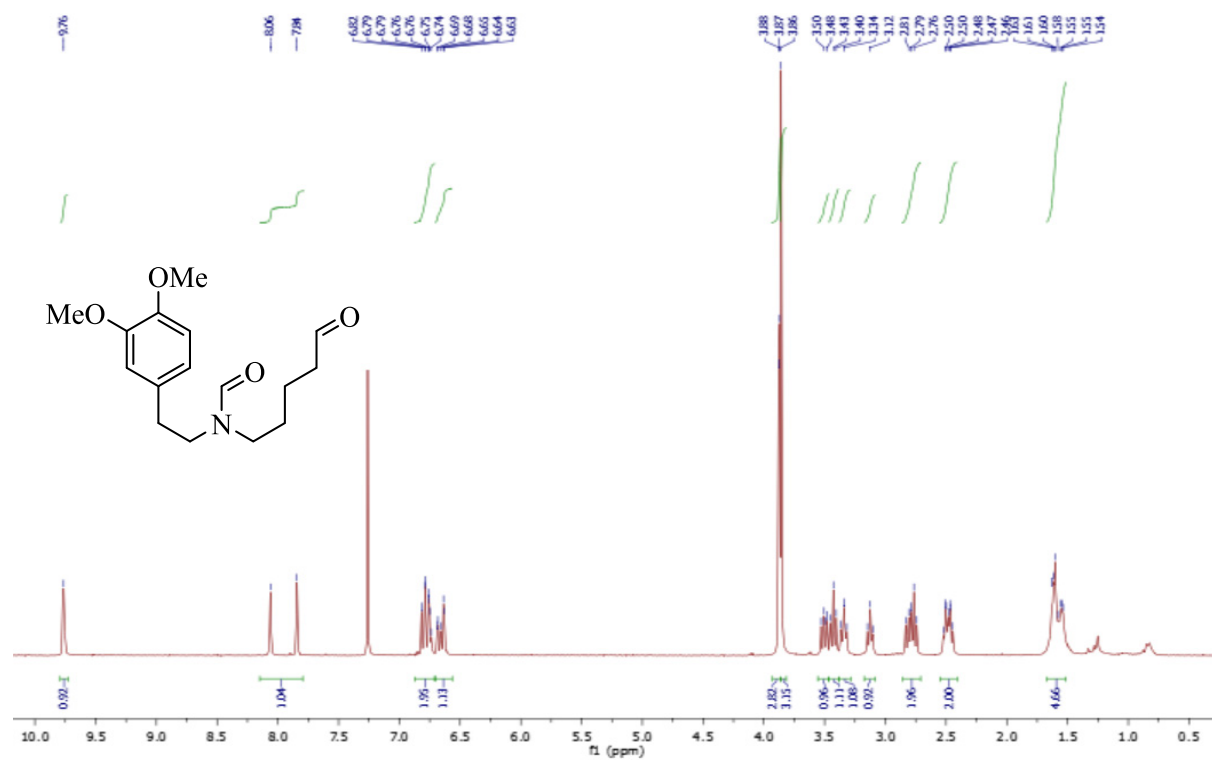
¹H RMN spectrum



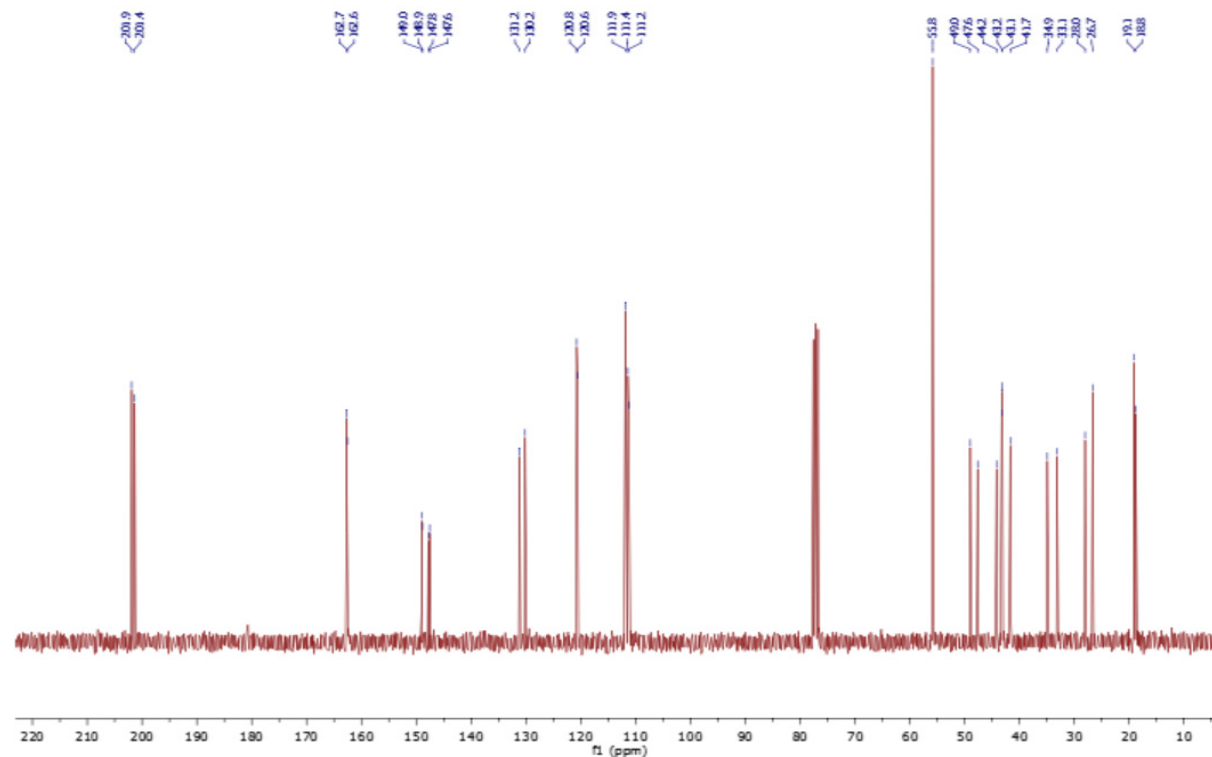
13C NMR spectrum of compound 10a in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from 10 to 170. The spectrum shows several peaks in the aromatic region (110-160 ppm) and aliphatic region (25-65 ppm). A triplet for the CDCl₃ solvent is visible at 77.0 ppm. Labeled peaks are indicated with blue arrows and values: 164.2, 149.3, 148.3, 147.8, 131.5, 130.3, 121.0, 120.8, 119.2, 118.5, 118.4, 111.6, 111.4, 61.3, 58.5, 56.0, 56.0, 50.8, 49.5, 48.0, 36.4, 36.2, 36.2, 35.6, 33.3, 33.1, 32.1, 32.2, 31.4, 25.3.

***N*-(3,4-Dimethoxyphenethyl)-*N*-(5-oxopentyl)formamide (16a)**

¹H RMN spectrum

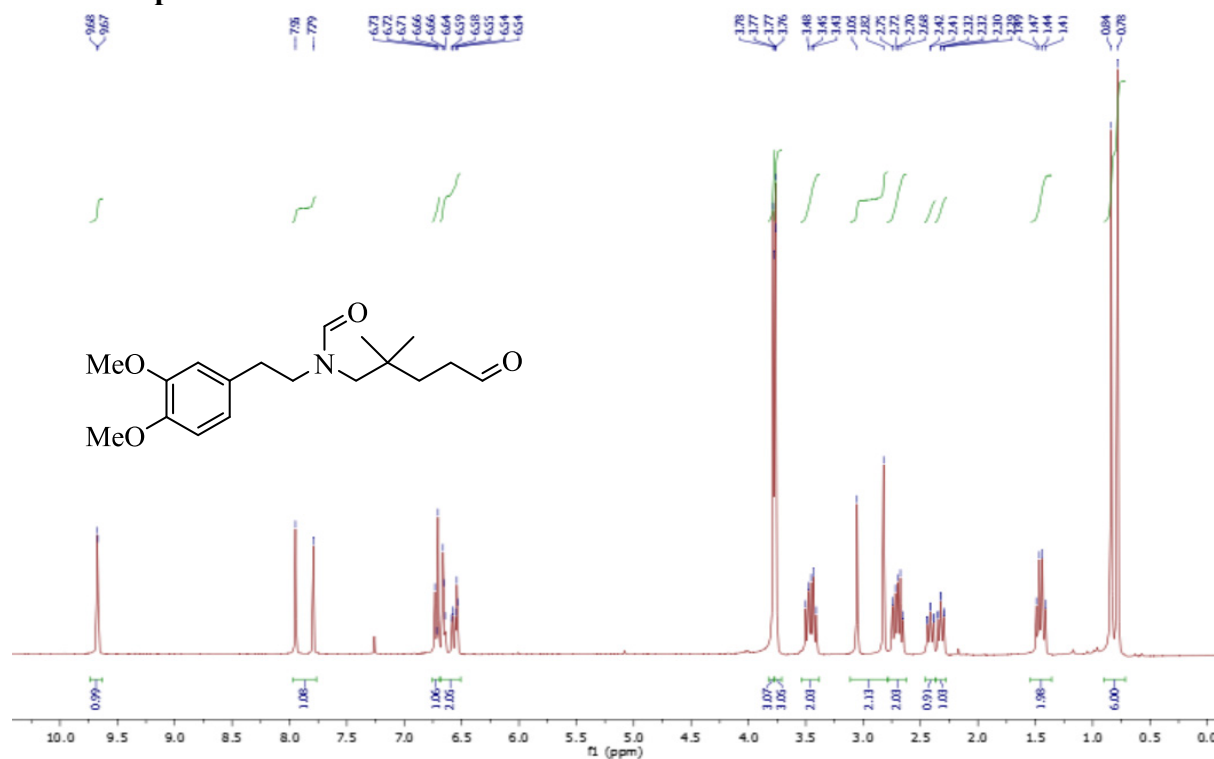


¹³C RMN spectrum

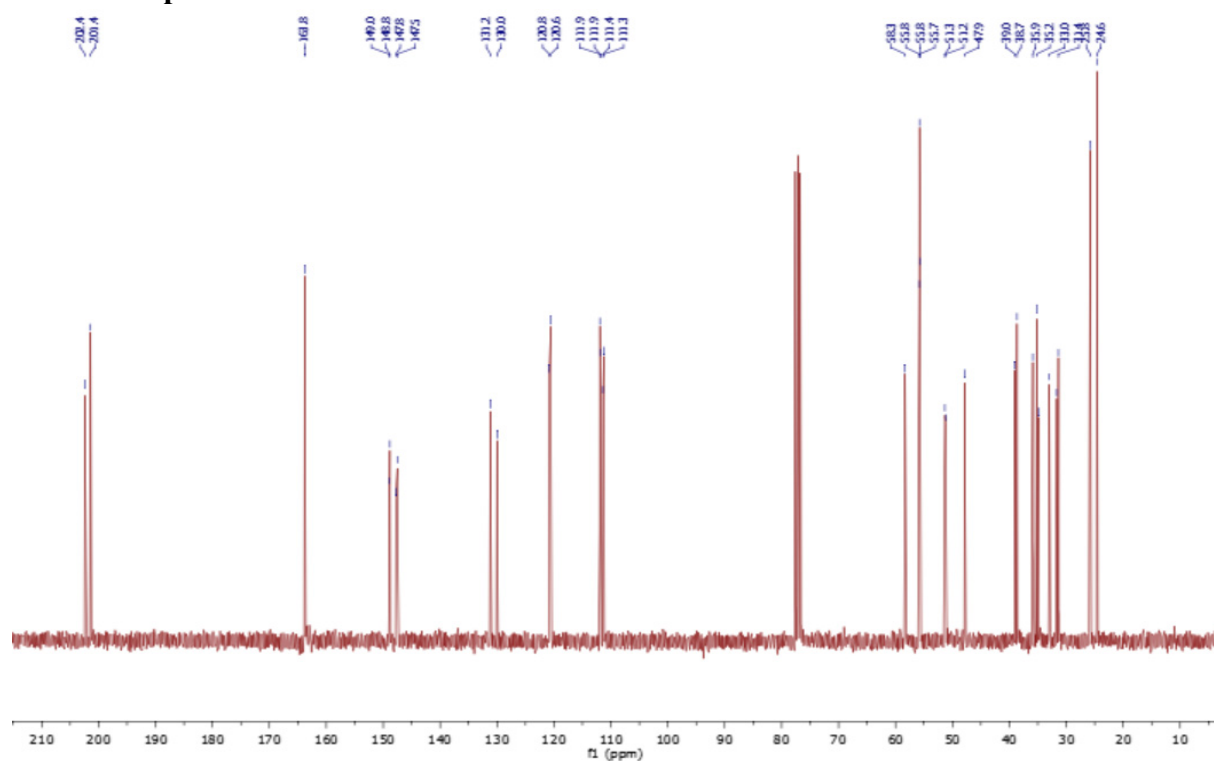


***N*-(3,4-Dimethoxyphenethyl)-*N*-(2,2-dimethyl-5-oxopentyl)formamide (16b)**

¹H RMN spectrum

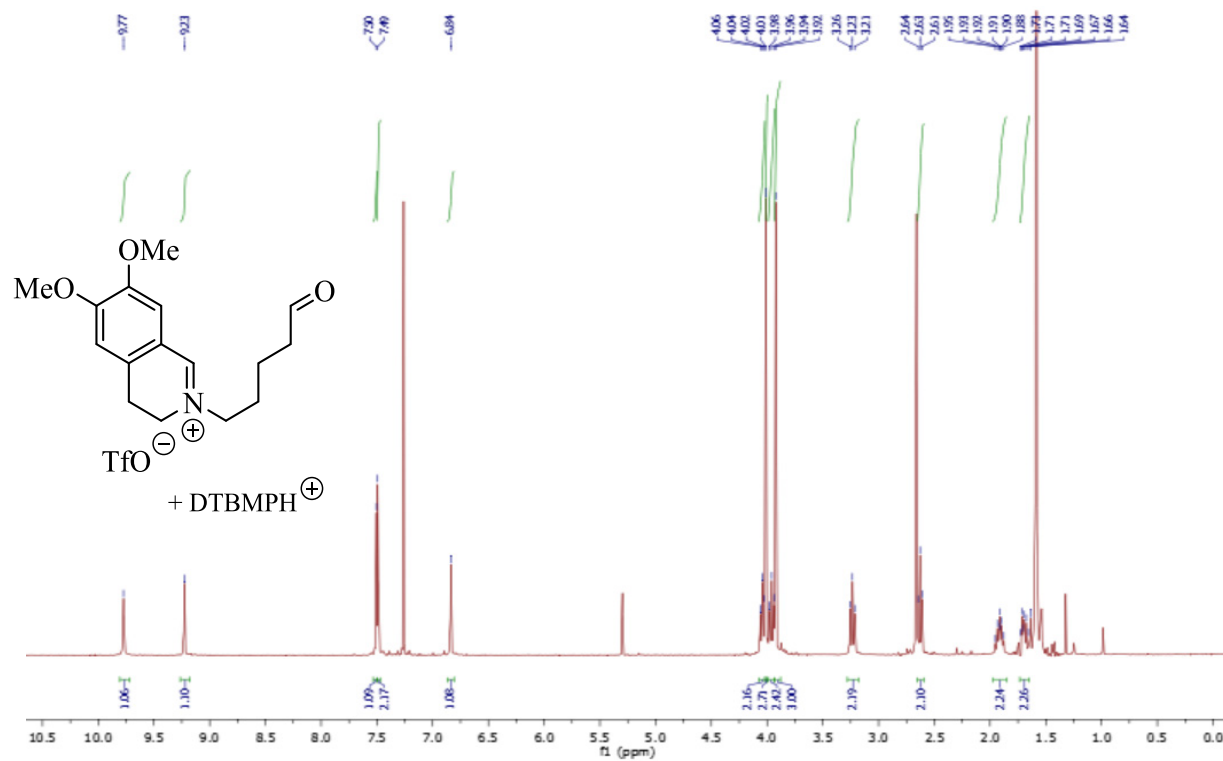


¹³C RMN spectrum



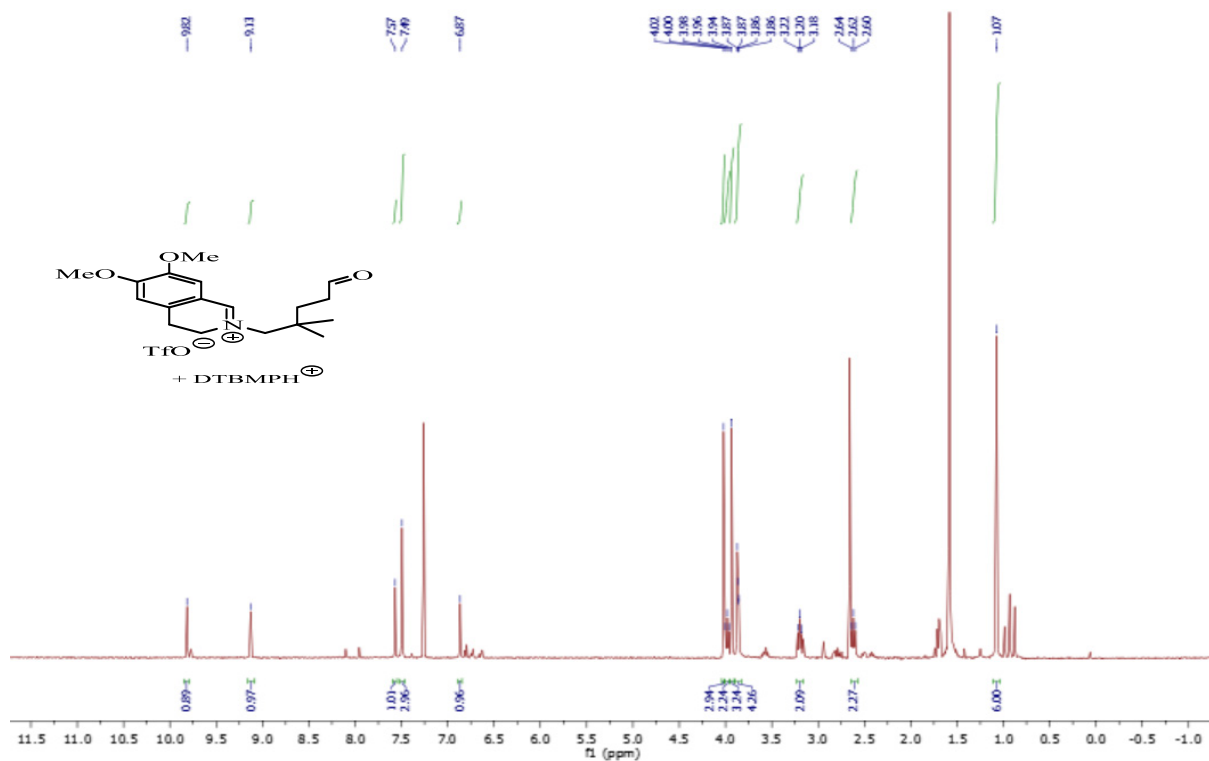
Iminium ion 17a

¹H RMN spectrum



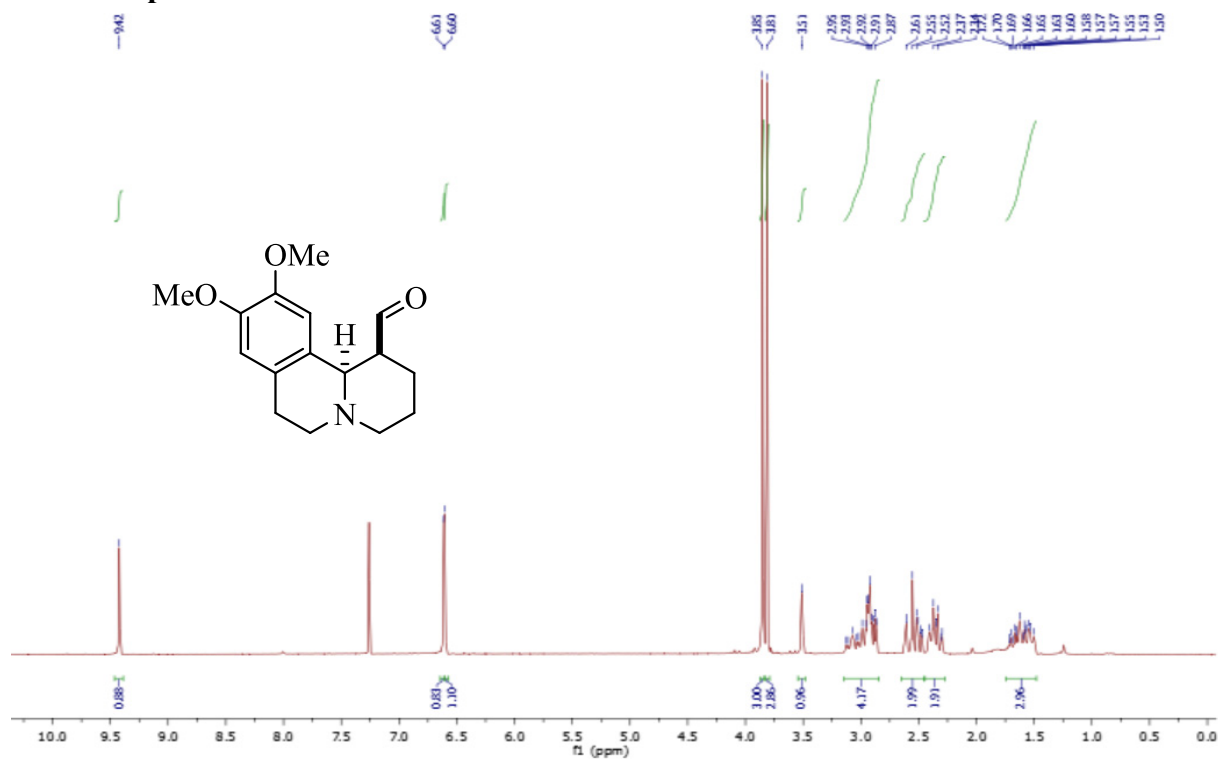
Iminium ion 17b

¹H RMN spectrum

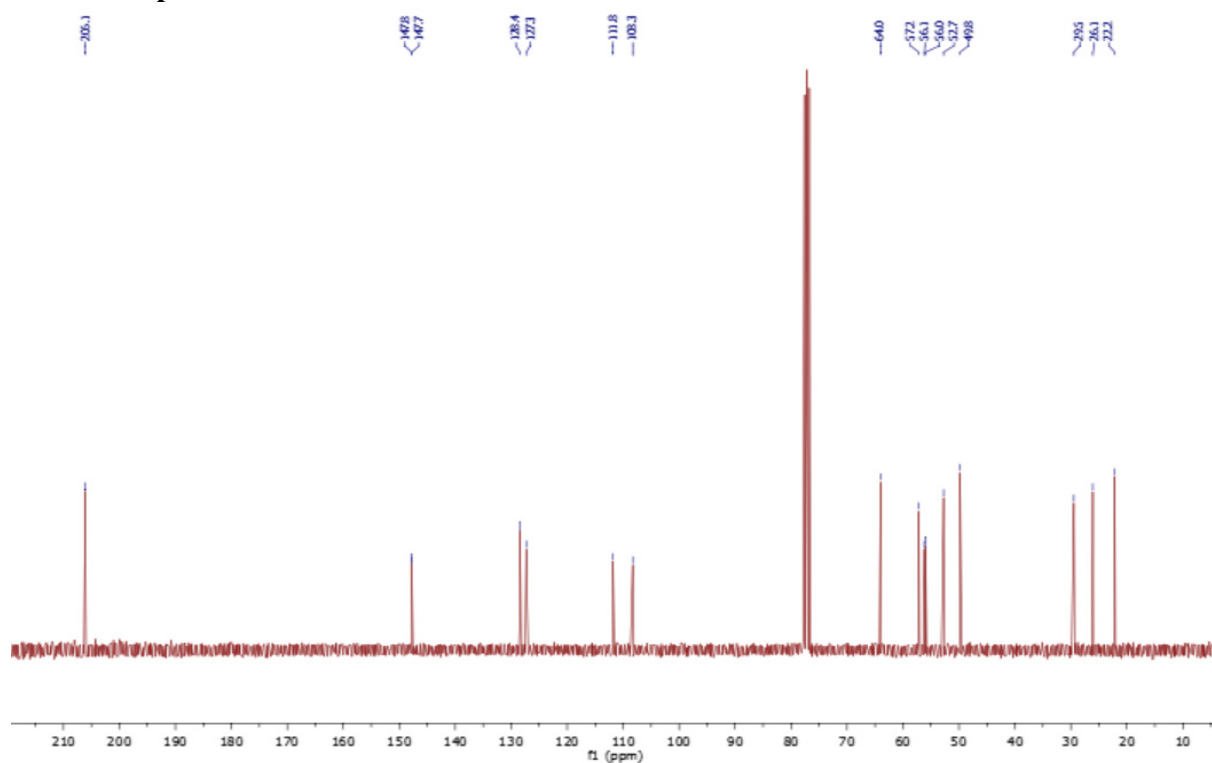


***trans*-9,10-Dimethoxy-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinoline-1-carbaldehyde (18a)**

¹H RMN spectrum

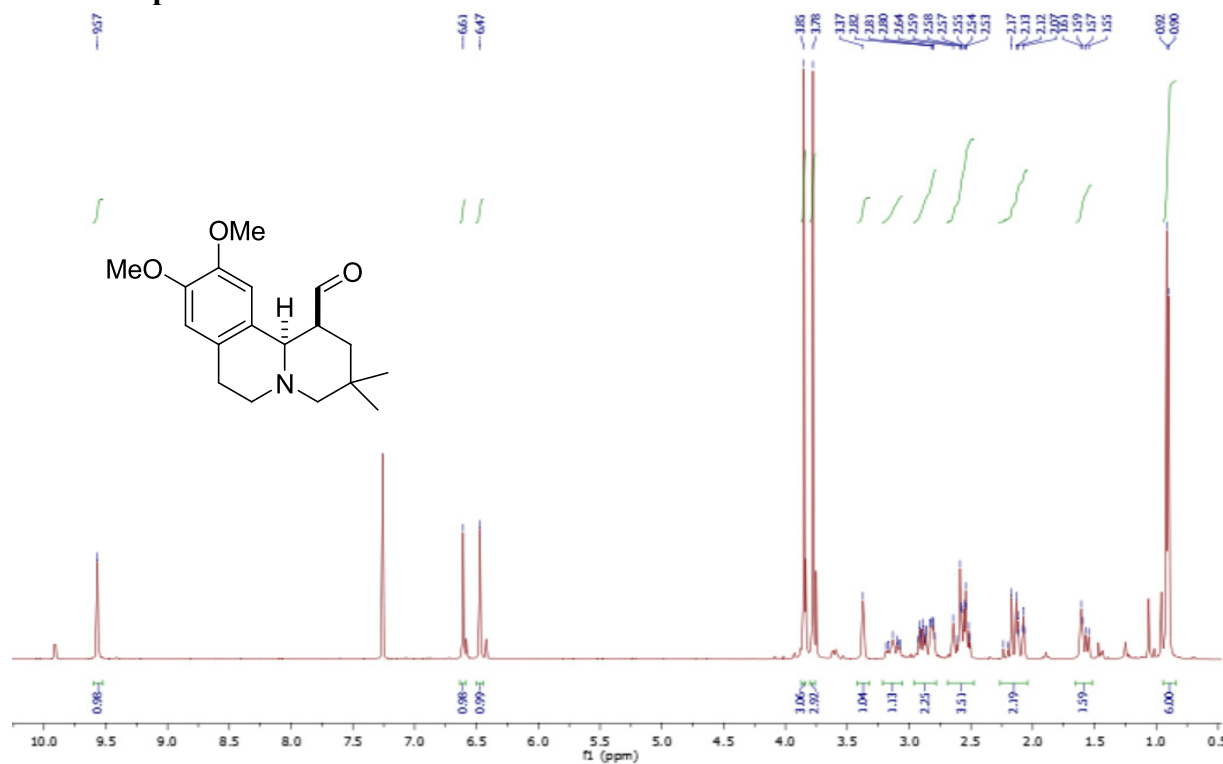


¹³C RMN spectrum

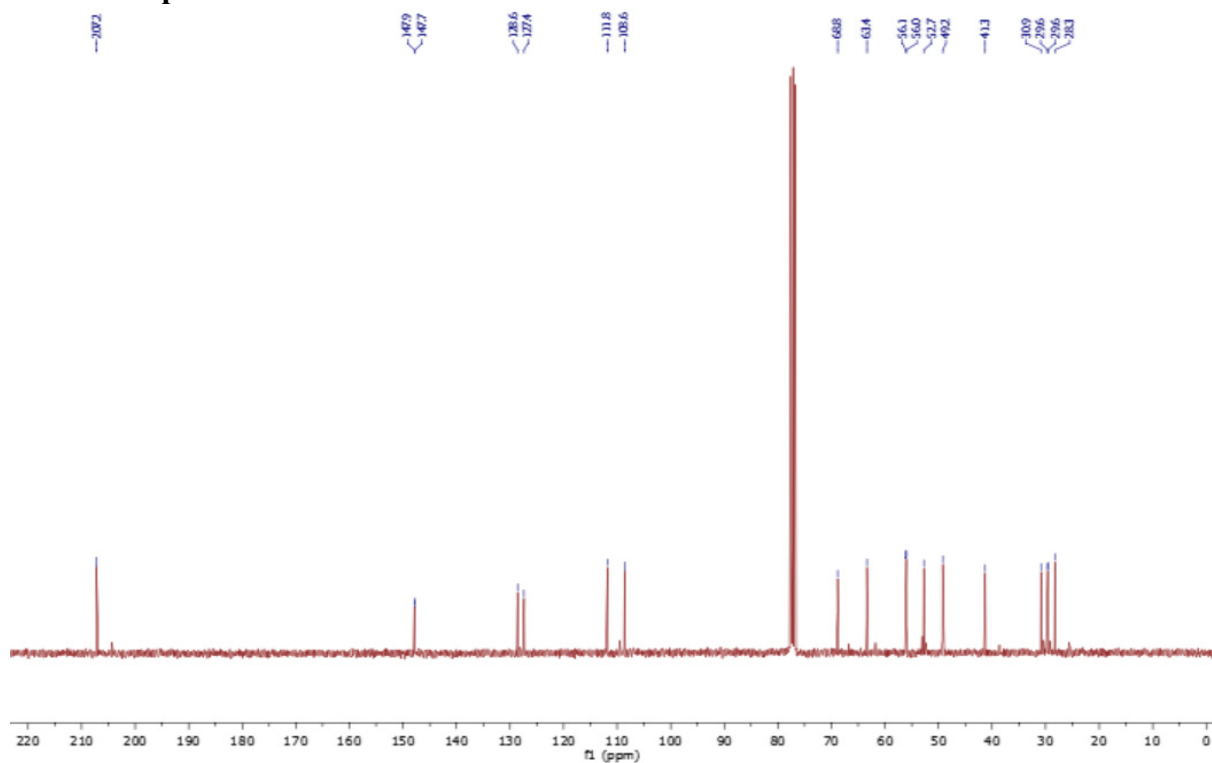


***trans*-9,10-Dimethoxy-3,3-dimethyl-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinoline-1-carbaldehyde (18b)**

¹H RMN spectrum

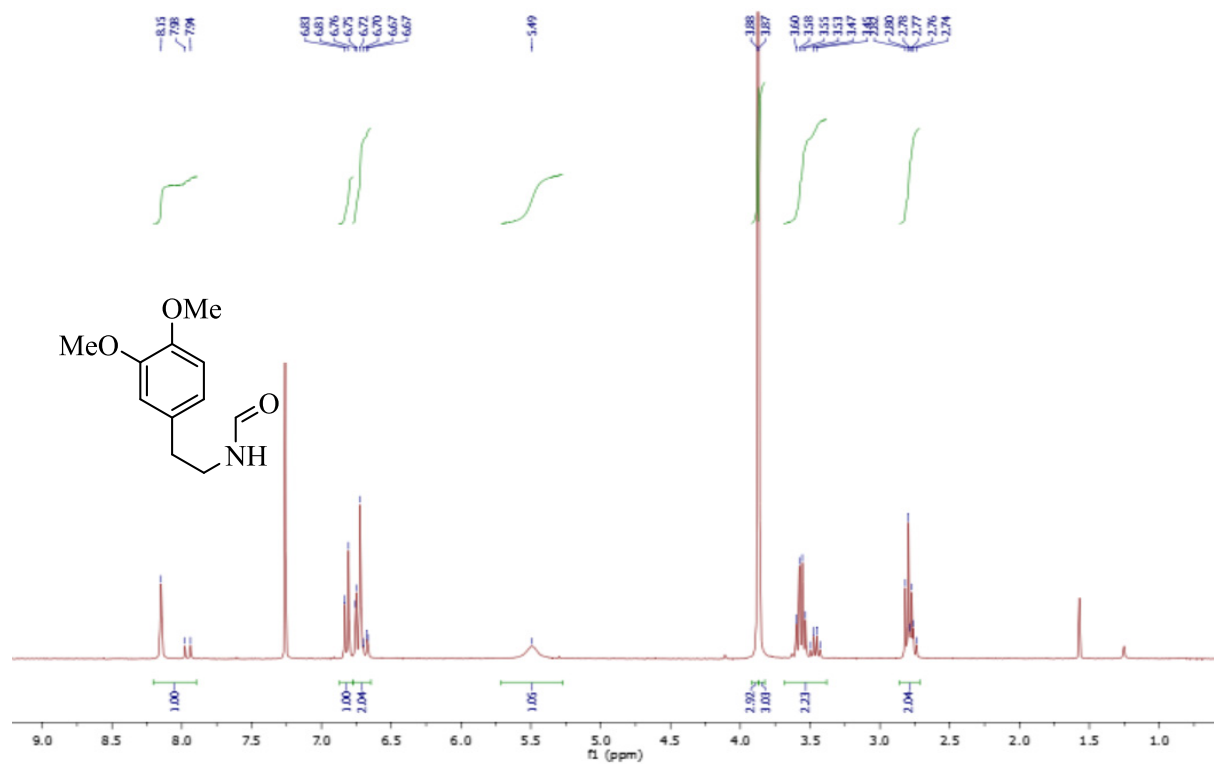


¹³C RMN spectrum

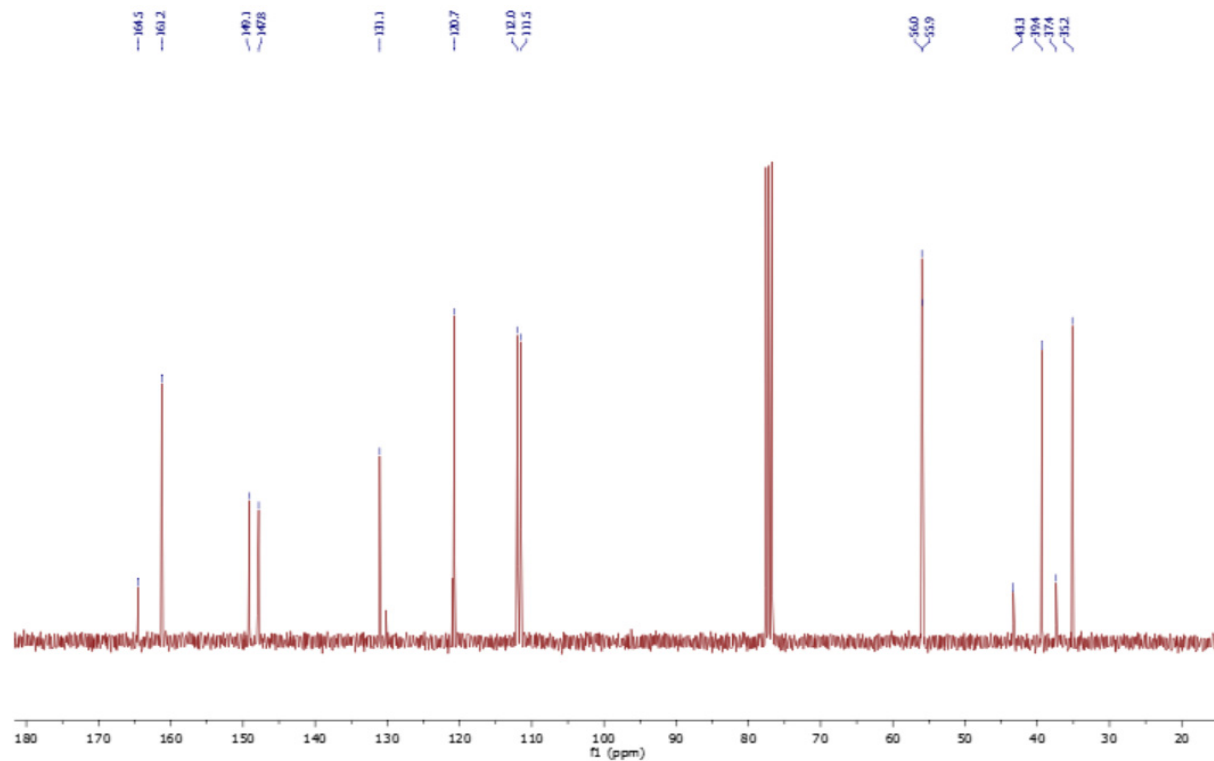


***N*-(3,4-Dimethoxyphenethyl)formamide (19)**

¹H RMN spectrum

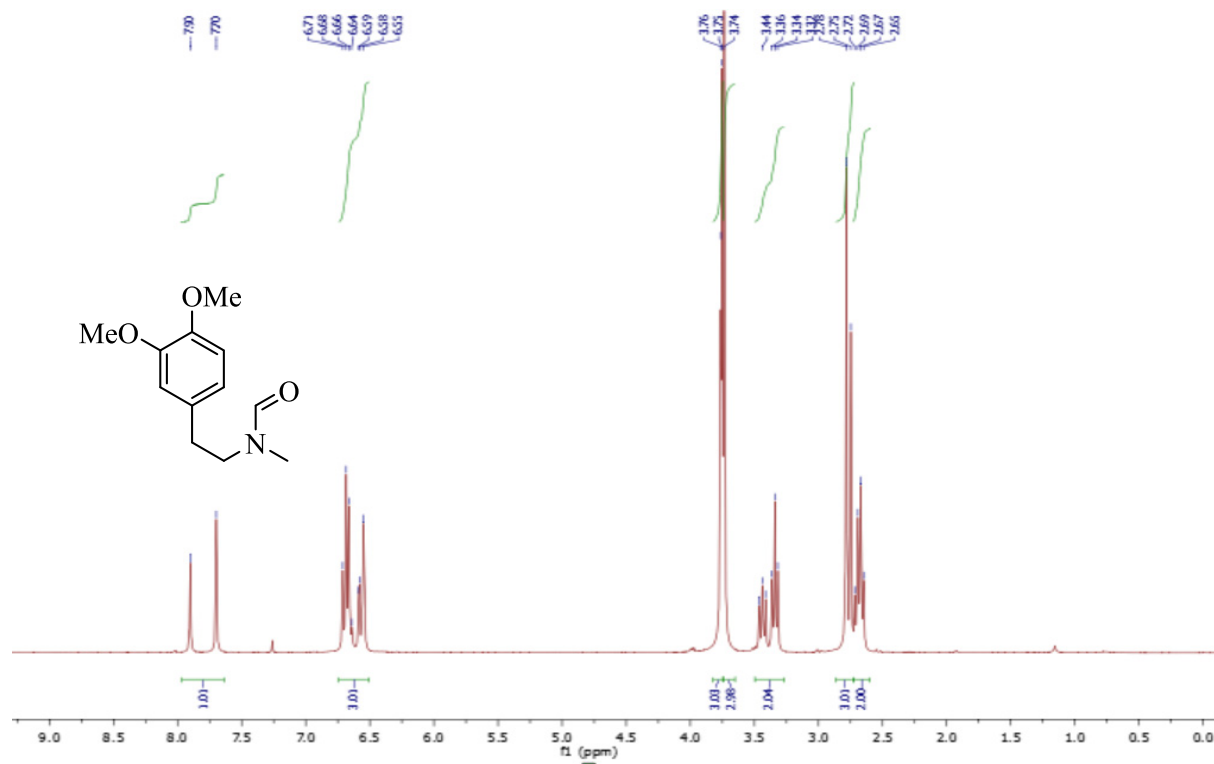


¹³C RMN spectrum

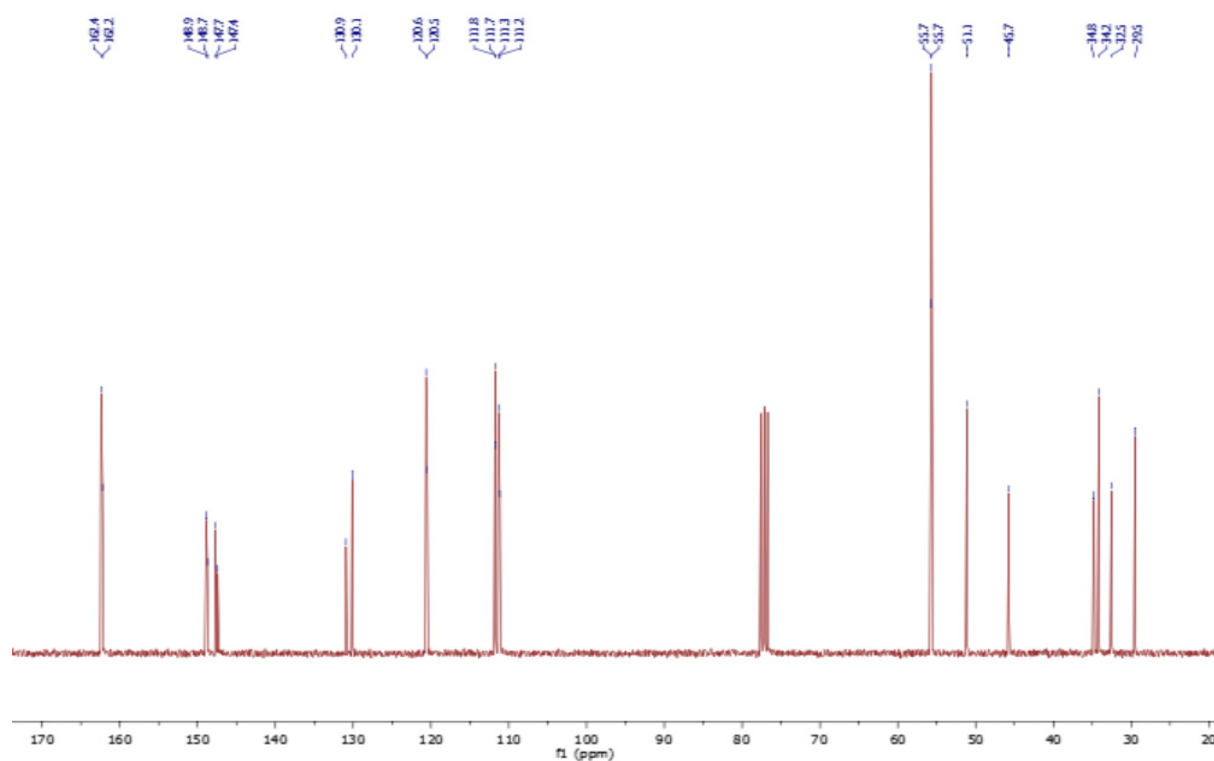


***N*-(3,4-Dimethoxyphenethyl)-*N*-methylformamide (20)**

¹H RMN spectrum

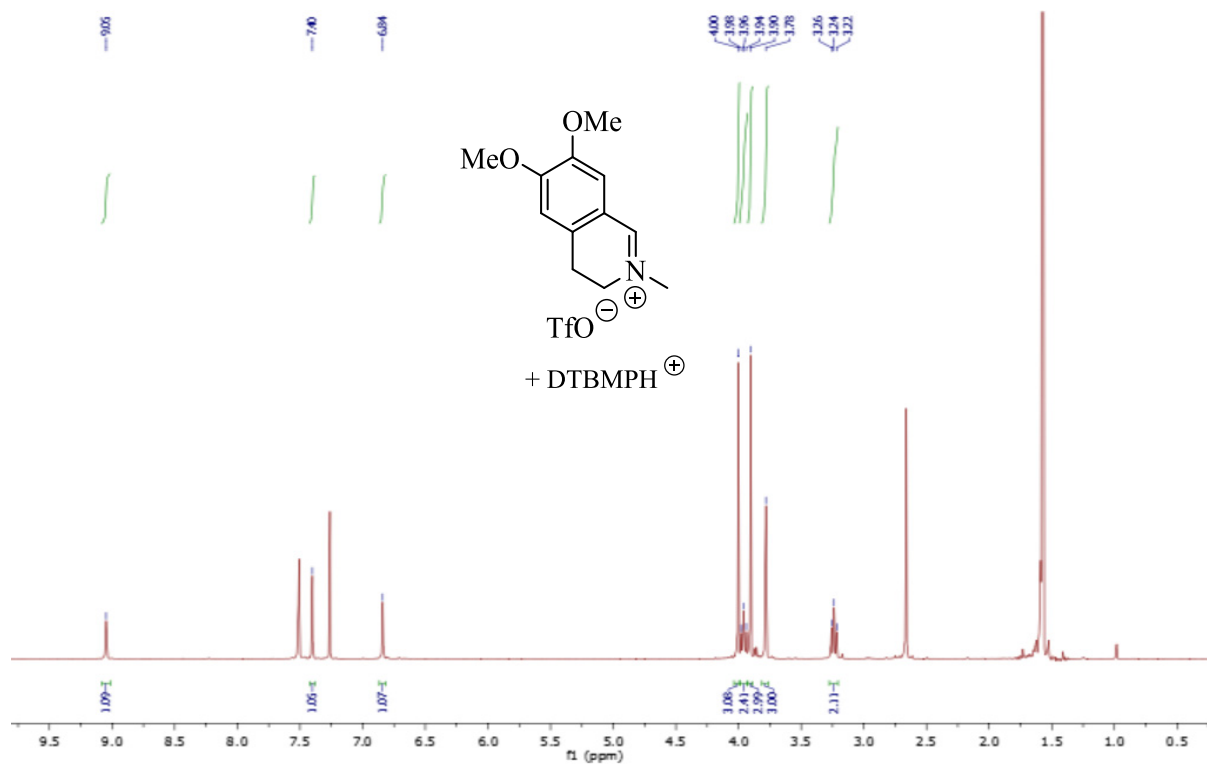


¹³C RMN spectrum



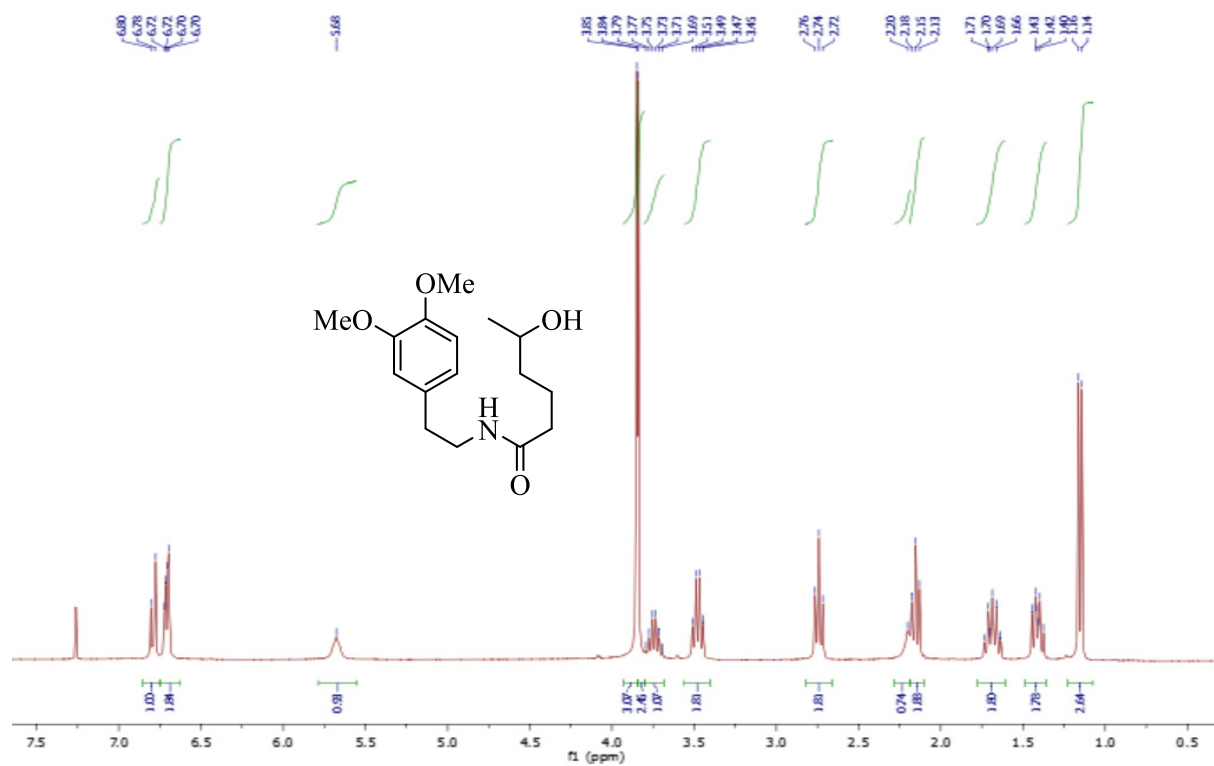
Iminium ion (21)

¹H RMN spectrum

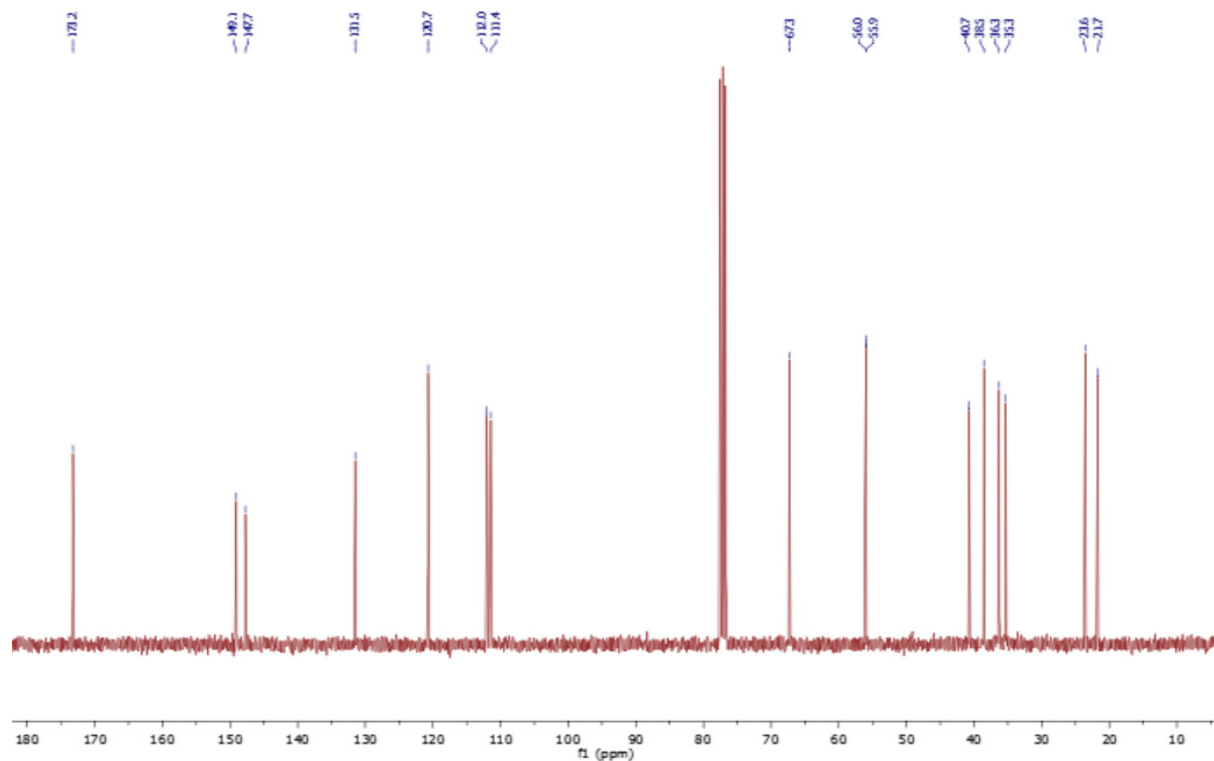


***N*-(3,4-Dimethoxyphenethyl)-5-hydroxyhexanamide (24)**

¹H RMN spectrum

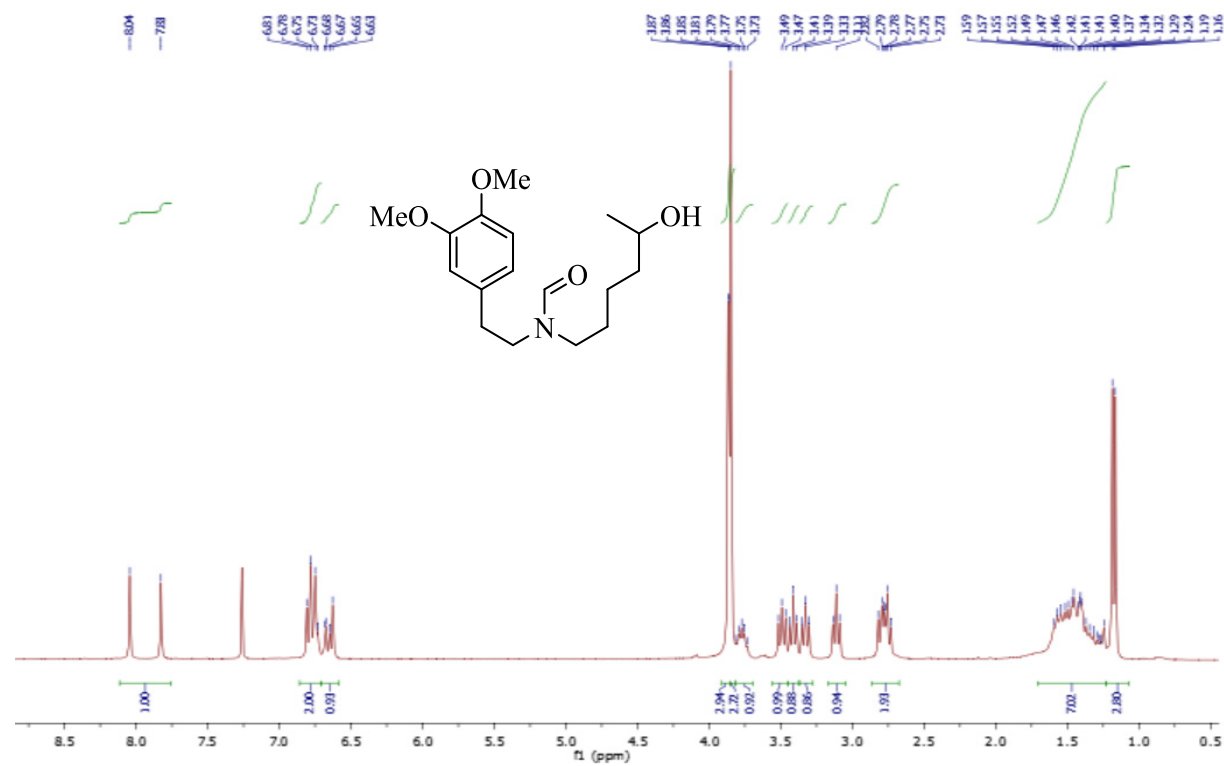


¹³C RMN spectrum

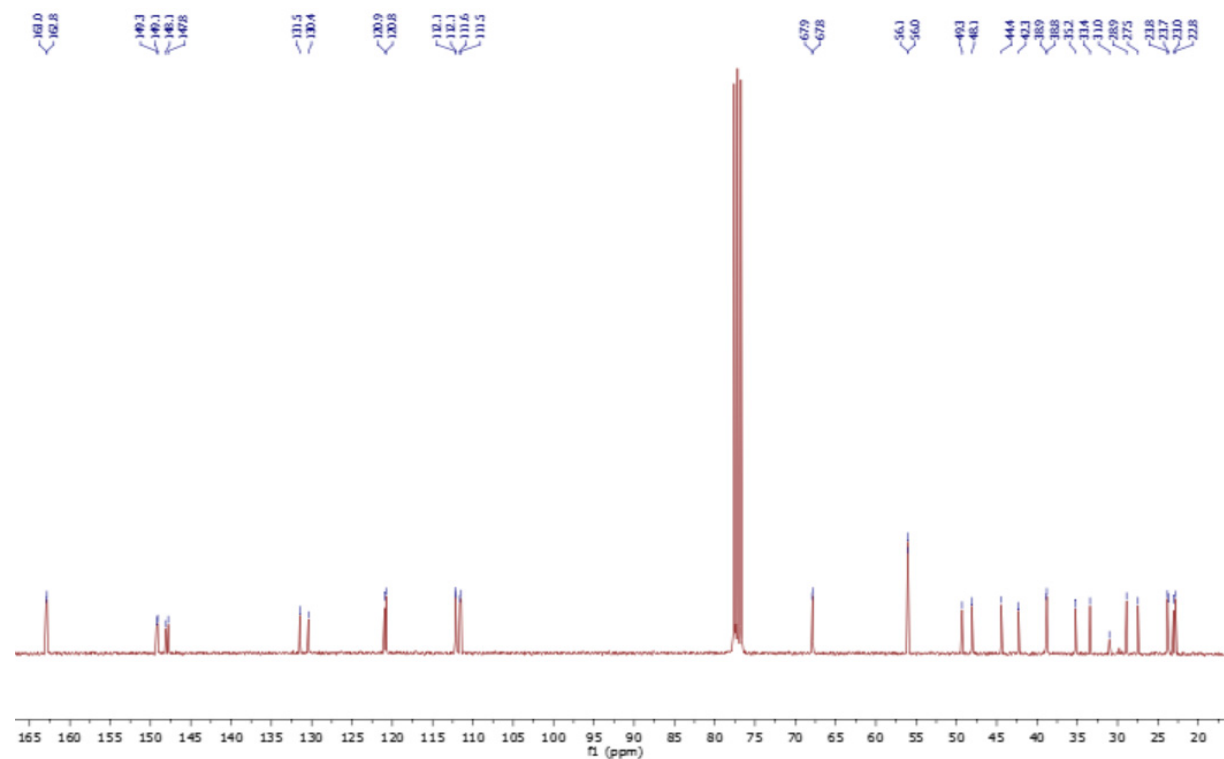


***N*-(3,4-Dimethoxyphenethyl)-*N*-(5-hydroxyhexyl)formamide (27)**

¹H RMN spectrum

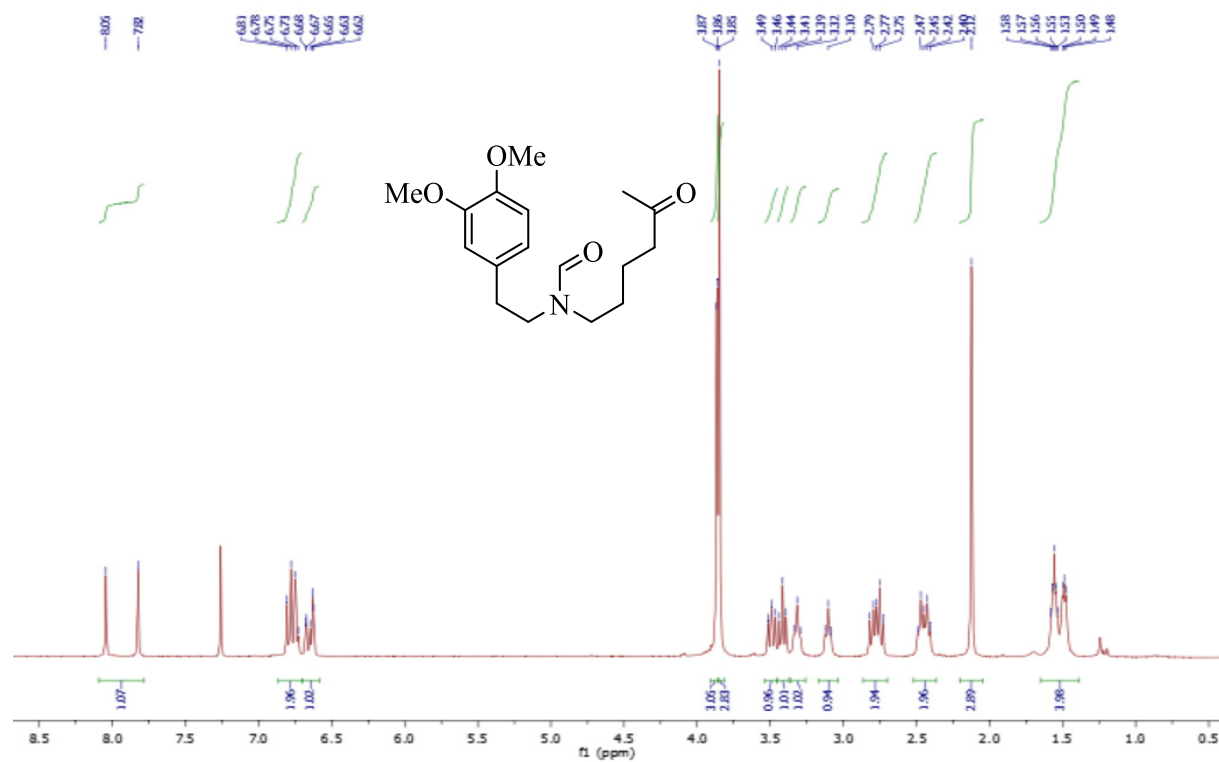


¹³C RMN spectrum

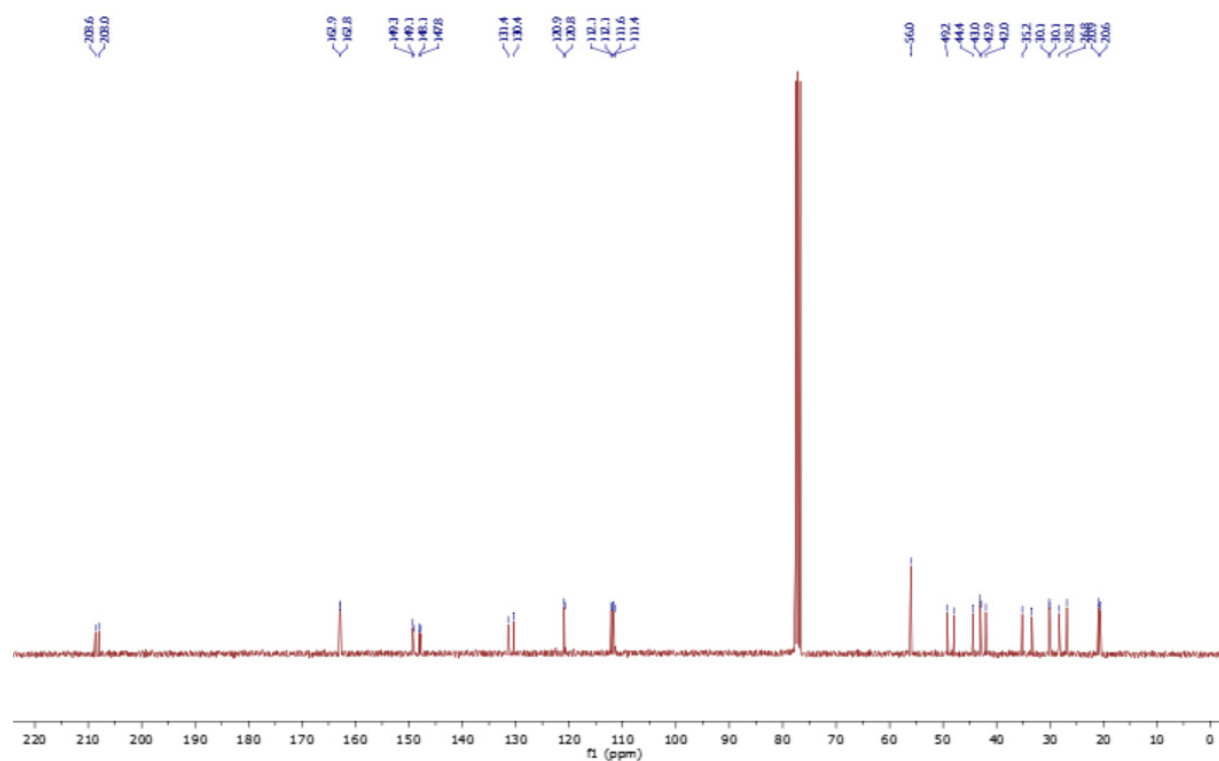


***N*-(3,4-Dimethoxyphenethyl)-*N*-(5-oxohexyl)formamide (28a)**

¹H RMN spectrum

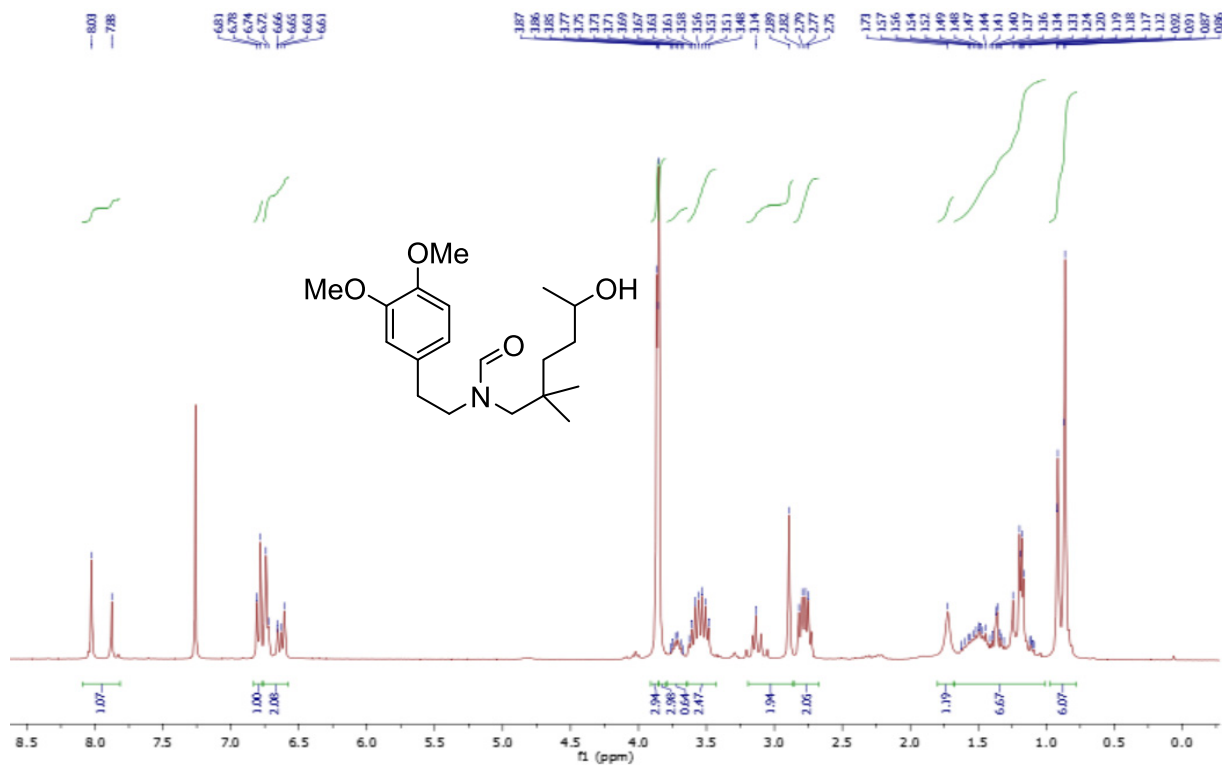


¹³C RMN spectrum

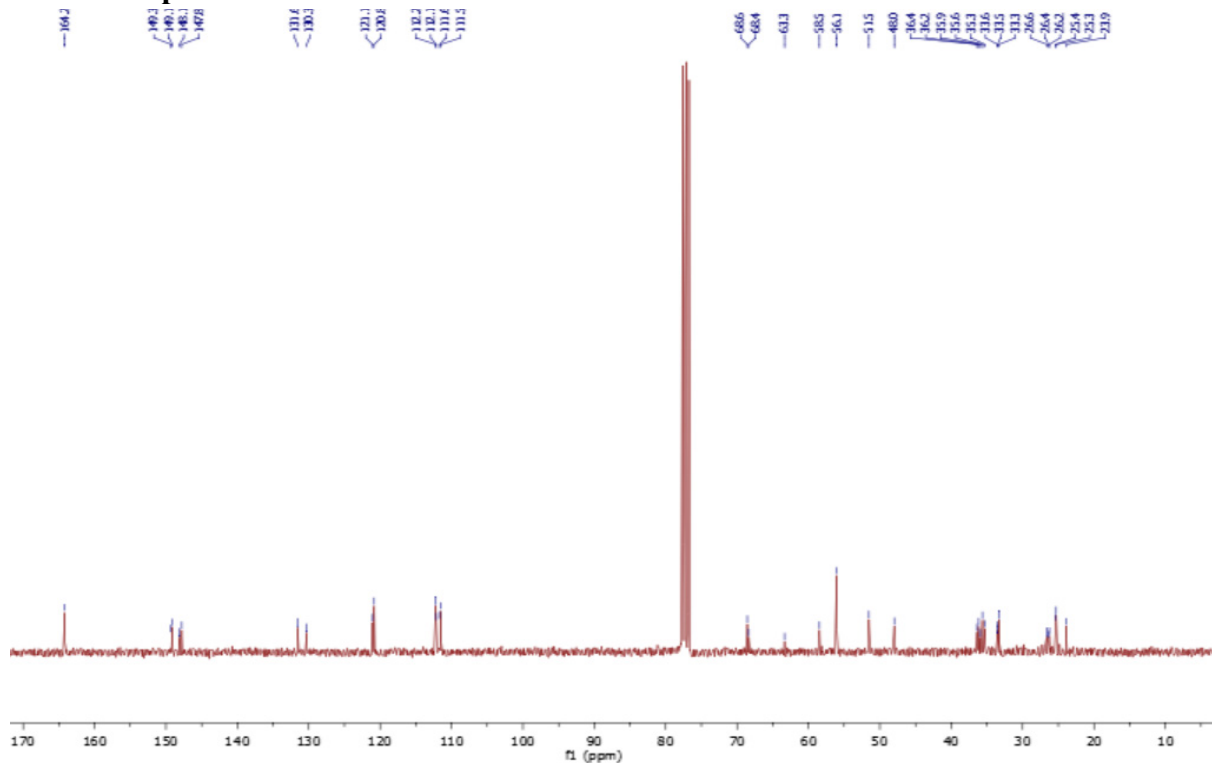


***N*-(3,4-Dimethoxyphenethyl)-*N*-(5-hydroxy-2,2-dimethylhexyl)formamide**

¹H RMN spectrum

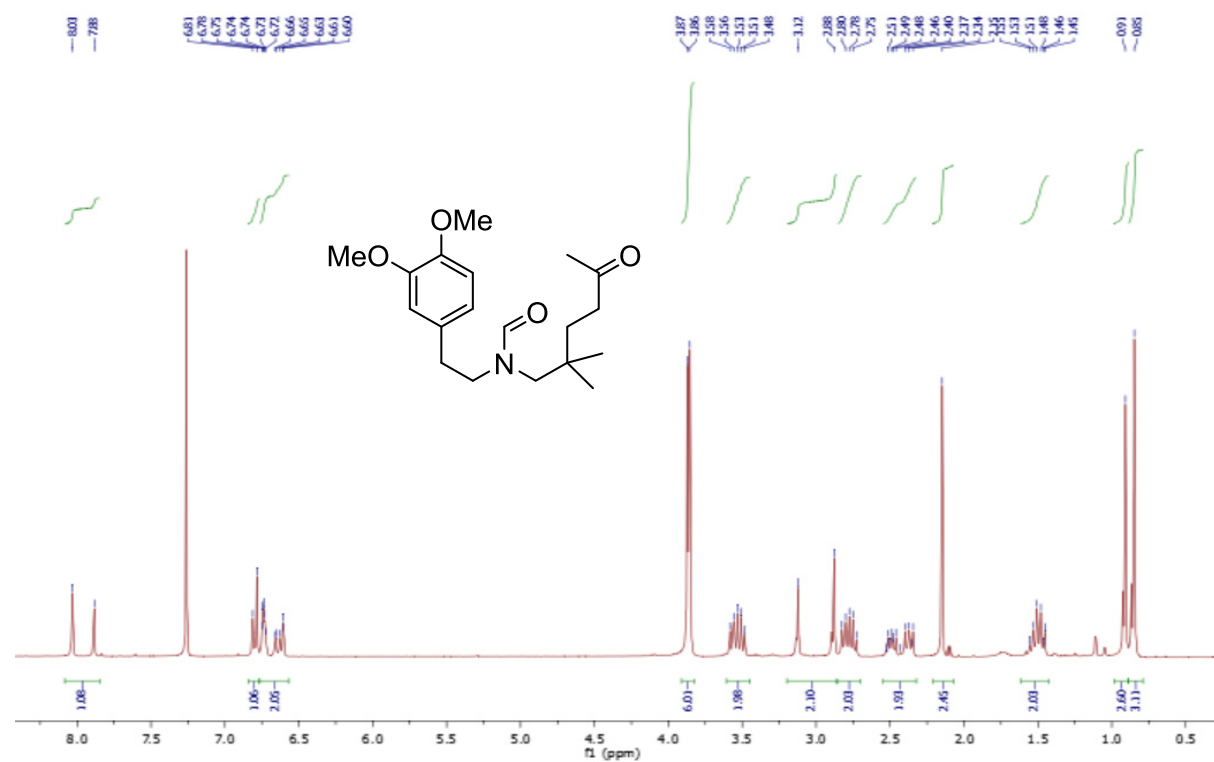


¹³C RMN spectrum

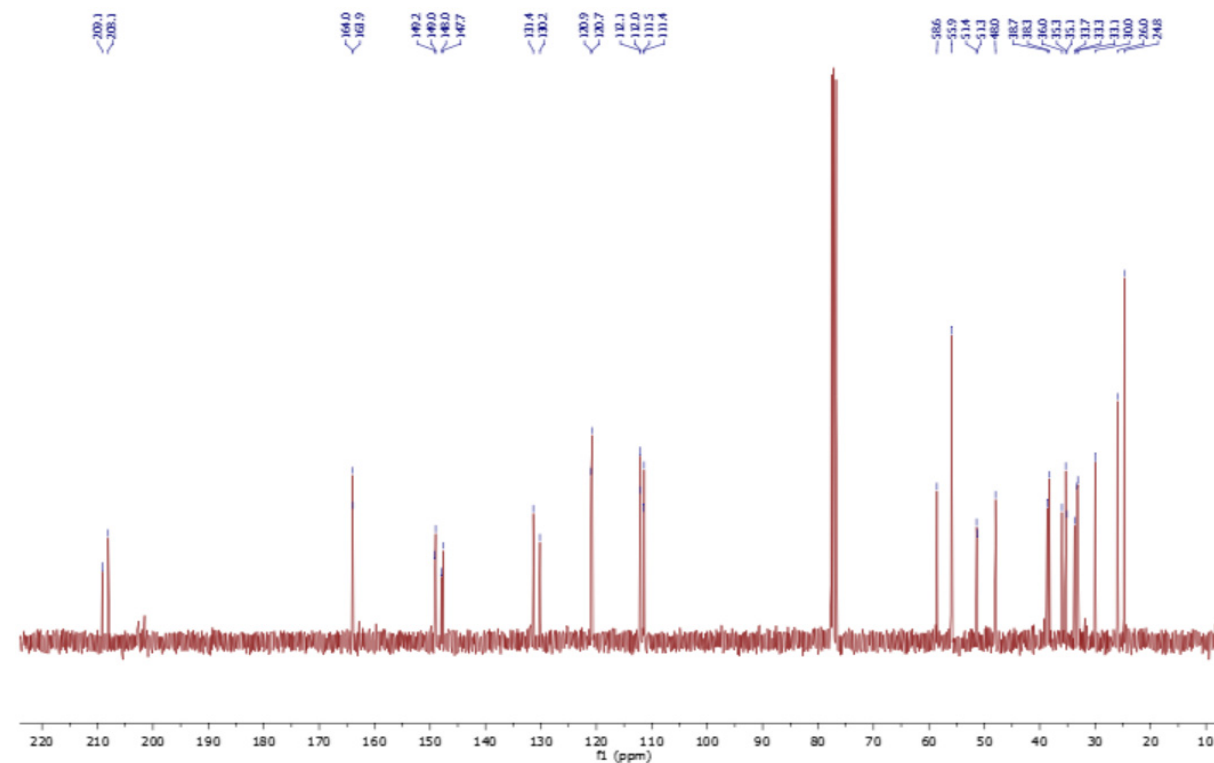


***N*-(3,4-Dimethoxyphenethyl)-*N*-(2,2-dimethyl-5-oxohexyl)formamide (28b)**

¹H RMN spectrum

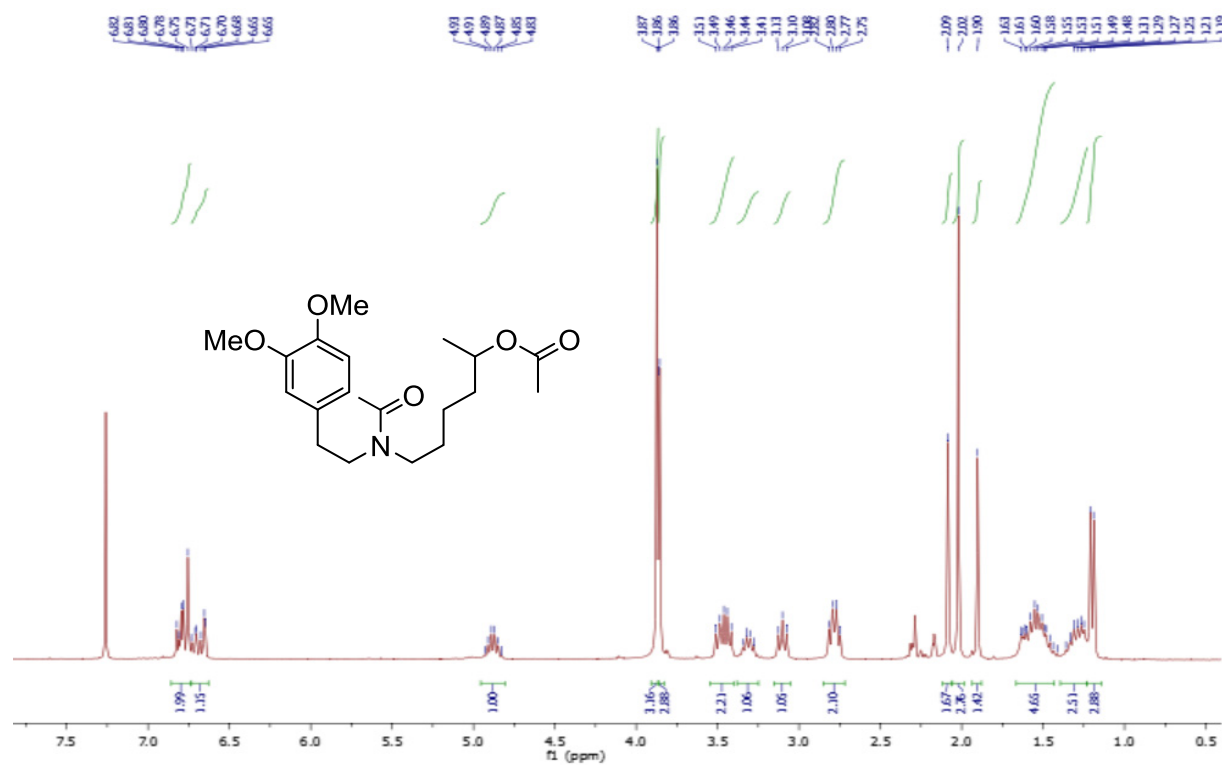


¹³C RMN spectrum

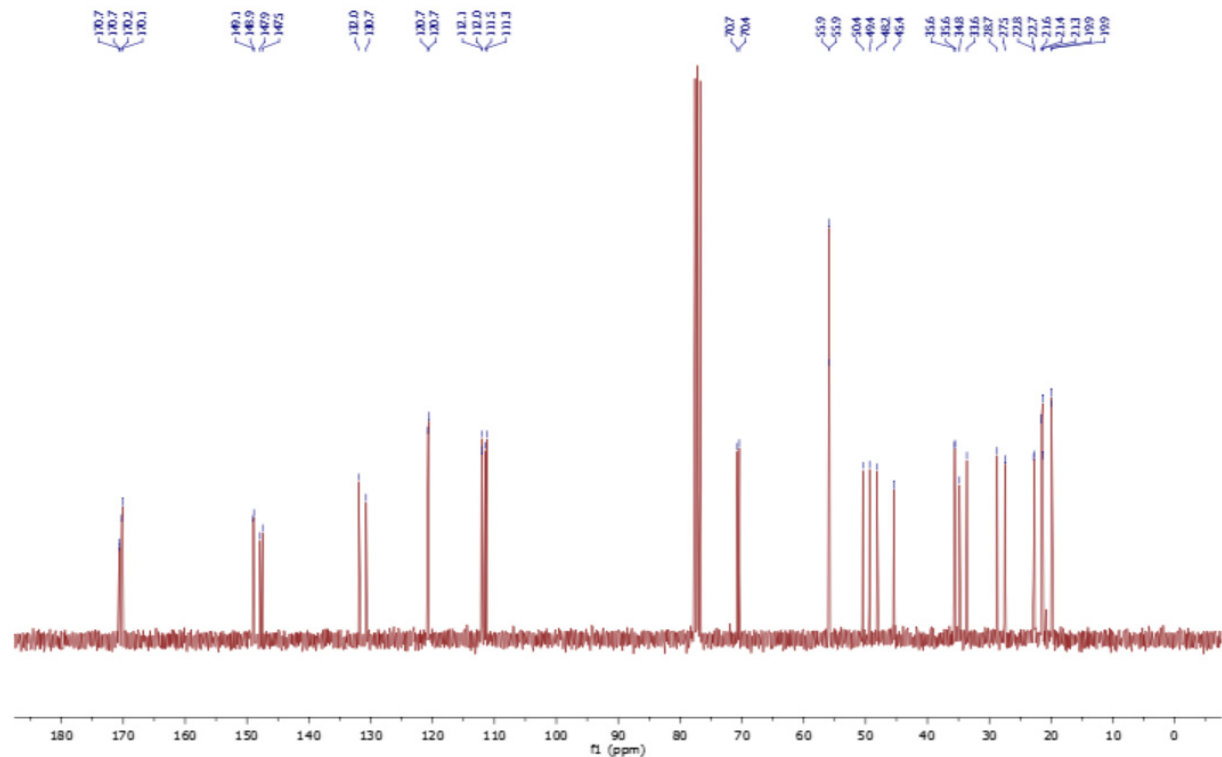


6-(*N*-(3,4-Dimethoxyphenethyl)acetamido)hexan-2-yl acetate

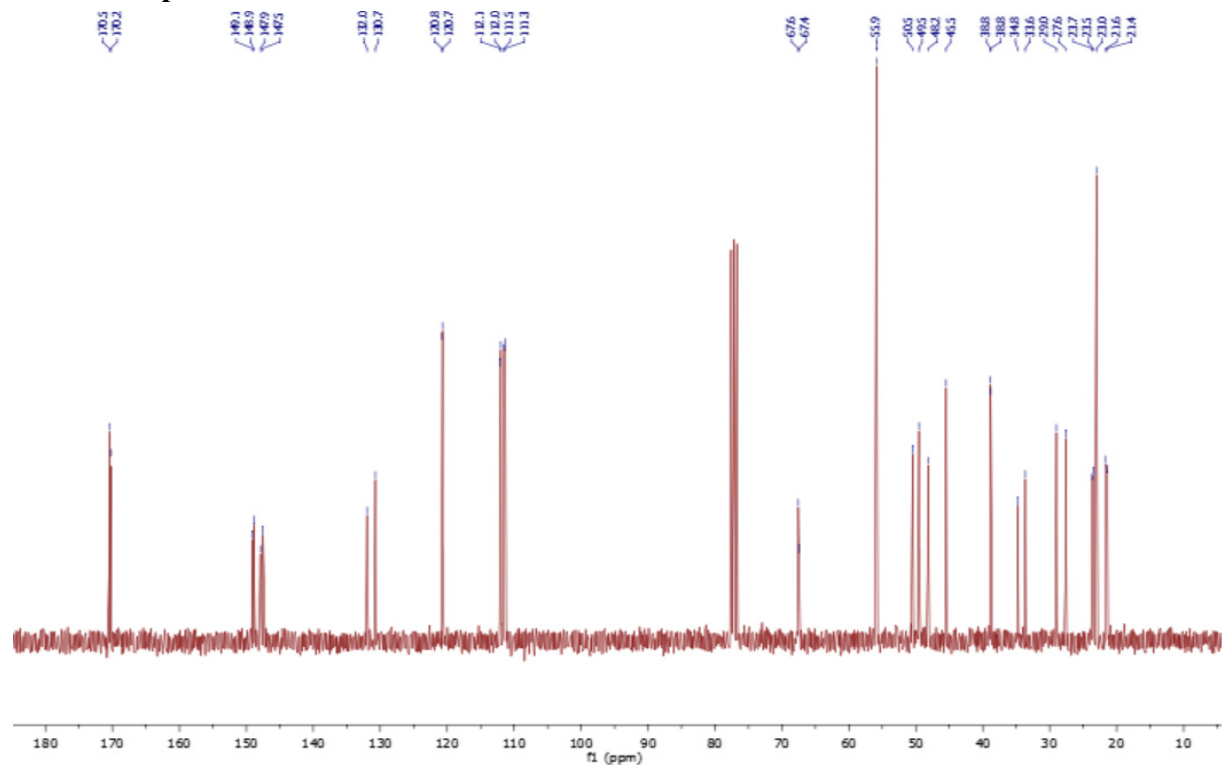
¹H RMN spectrum



¹³C RMN spectrum

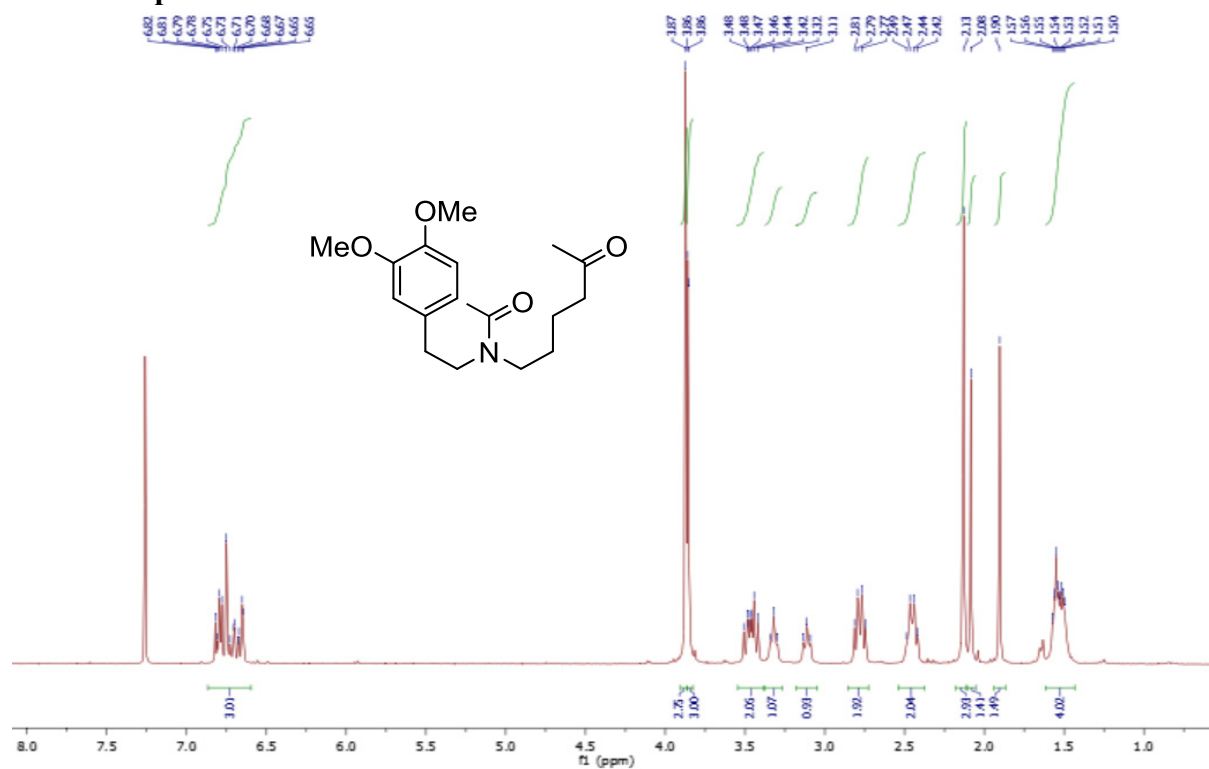


¹H RMN spectrum

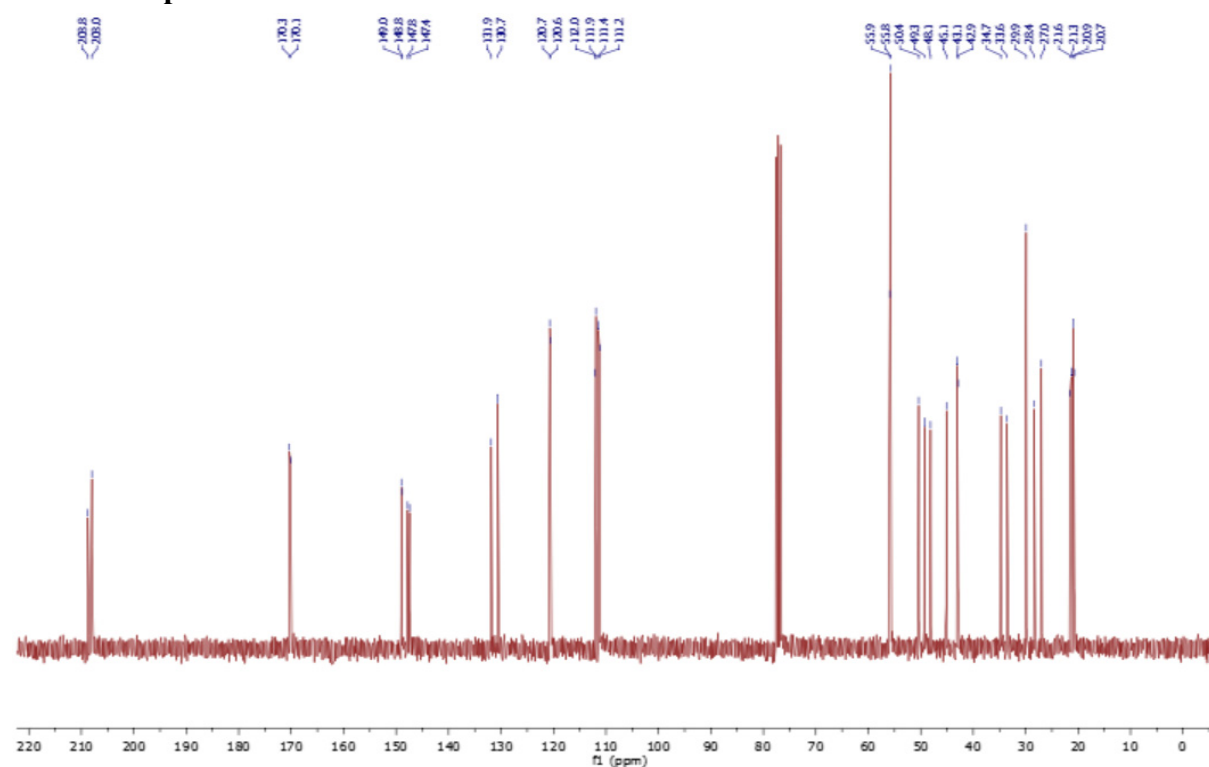


***N*-(3,4-Dimethoxyphenethyl)-*N*-(5-oxohexyl)acetamide (28c)**

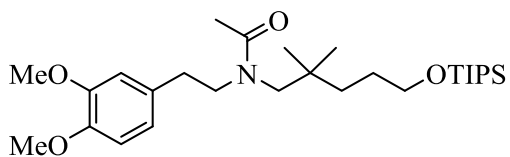
¹H RMN spectrum



¹³C RMN spectrum

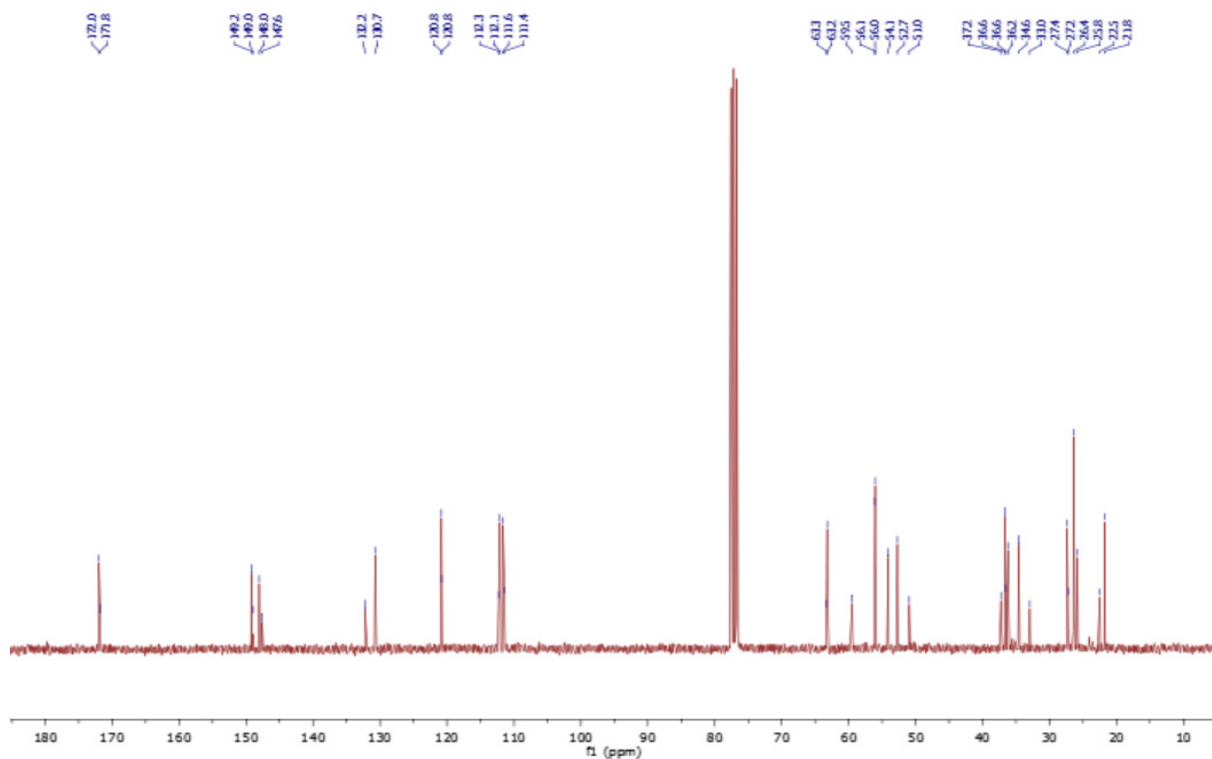


¹H RMN spectrum



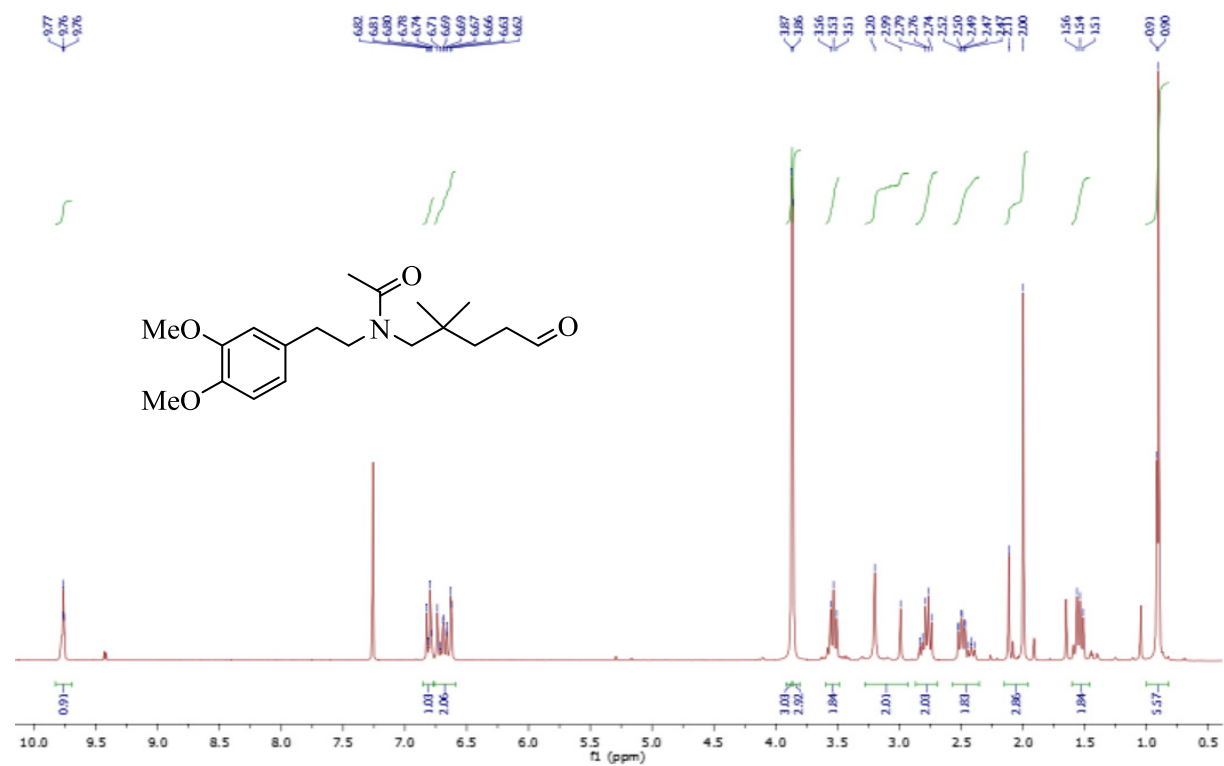
Peak Label	Chemical Shift (ppm)
172.3	172.3
147.6	147.6
147.0	147.0
146.2	146.2
132.3	132.3
130.9	130.9
120.8	120.8
120.5	120.5
112.3	112.3
111.6	111.6
111.4	111.4
77.3	77.3
56.3	56.3
56.1	56.1
54.6	54.6
52.5	52.5
50.9	50.9
37.3	37.3
37.1	37.1
36.7	36.7
36.5	36.5
34.7	34.7
31.0	31.0
27.8	27.8
27.6	27.6
26.1	26.1
25.9	25.9
22.5	22.5
21.7	21.7
18.2	18.2
12.1	12.1
12.1	12.1

¹H RMN spectrum

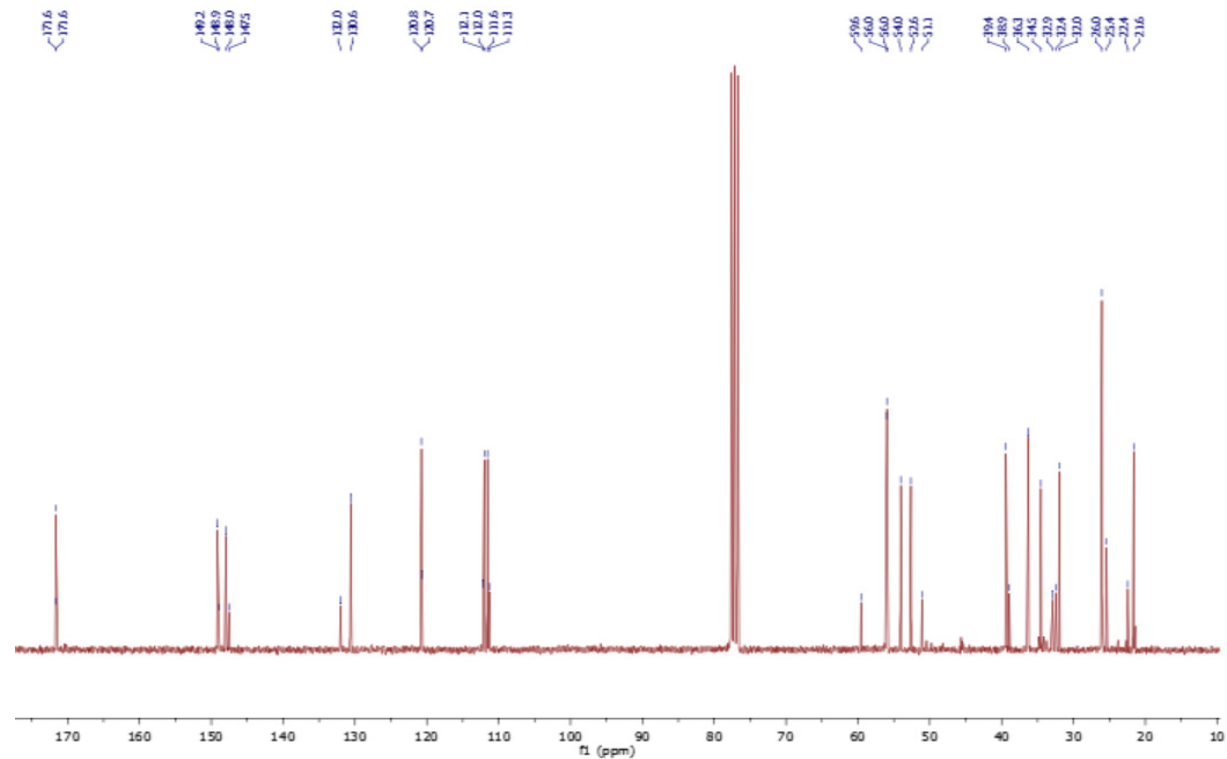


N-(3,4-Dimethoxyphenethyl)-*N*-(2,2-dimethyl-5-oxopentyl)acetamide

¹H RMN spectrum

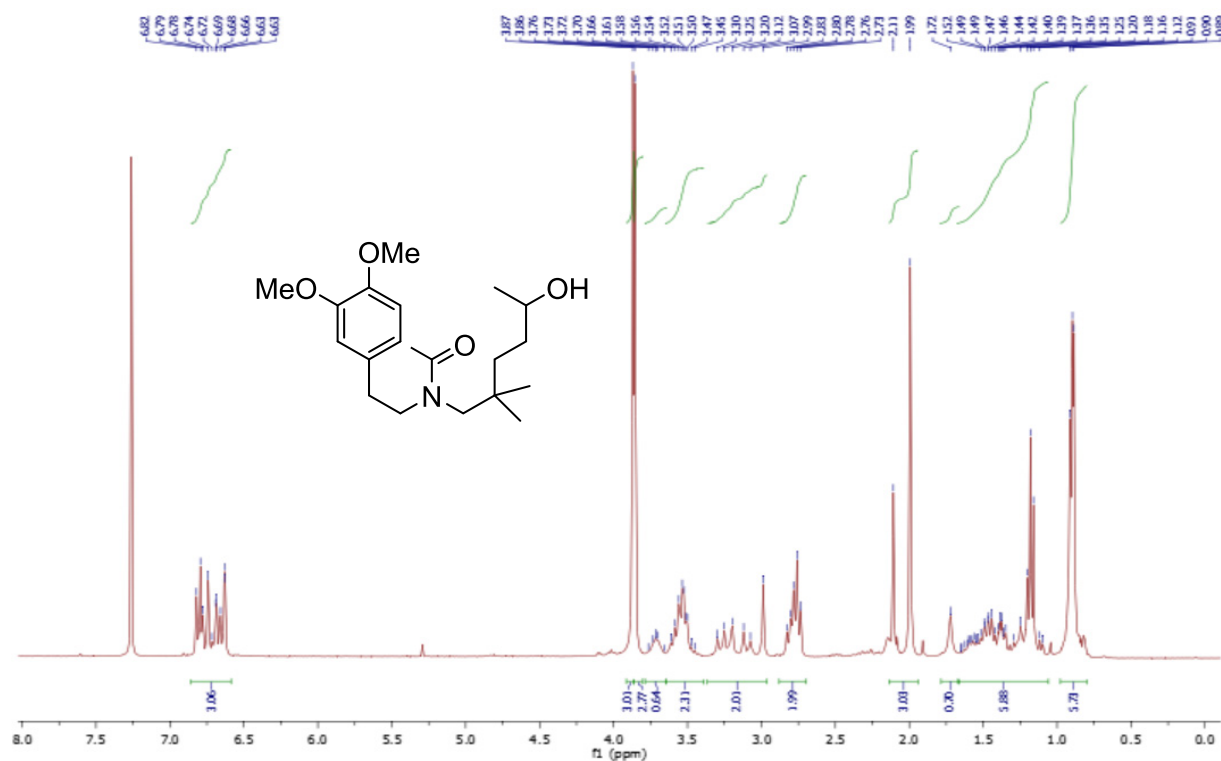


¹³C RMN spectrum

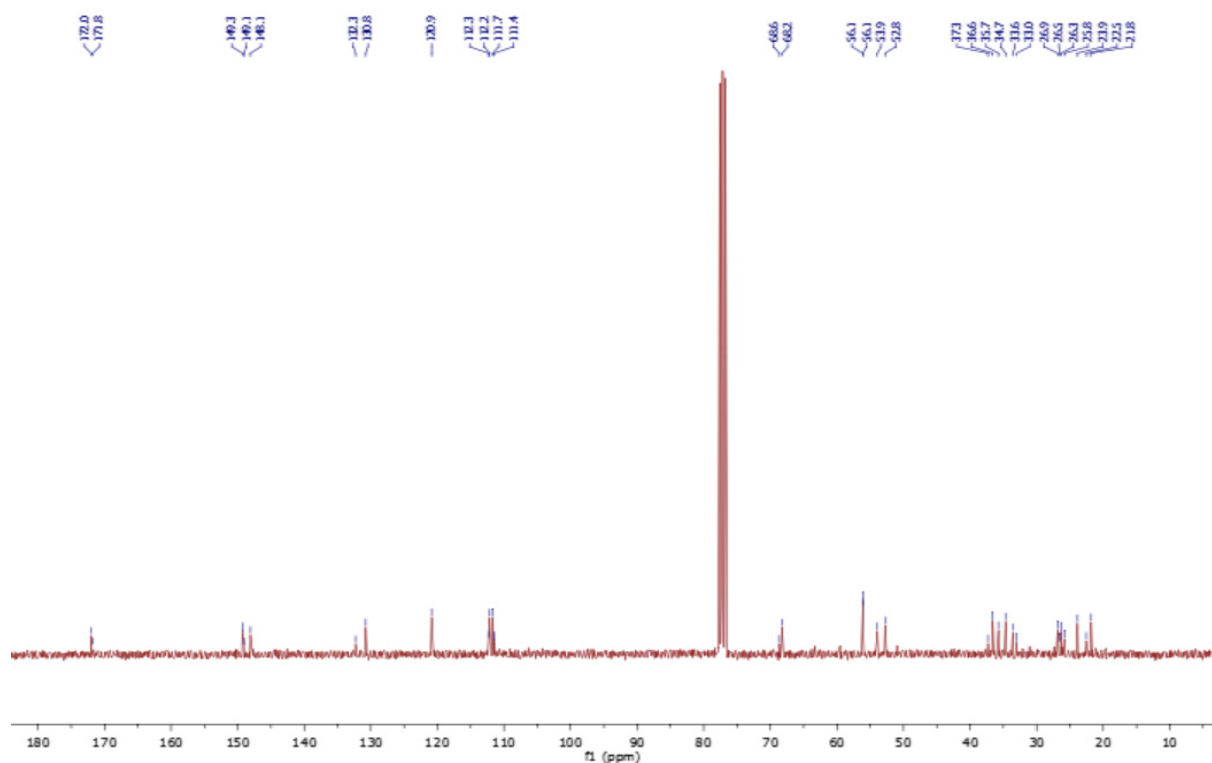


***N*-(3,4-Dimethoxyphenethyl)-*N*-(5-hydroxy-2,2-dimethylhexyl)acetamide**

¹H RMN spectrum

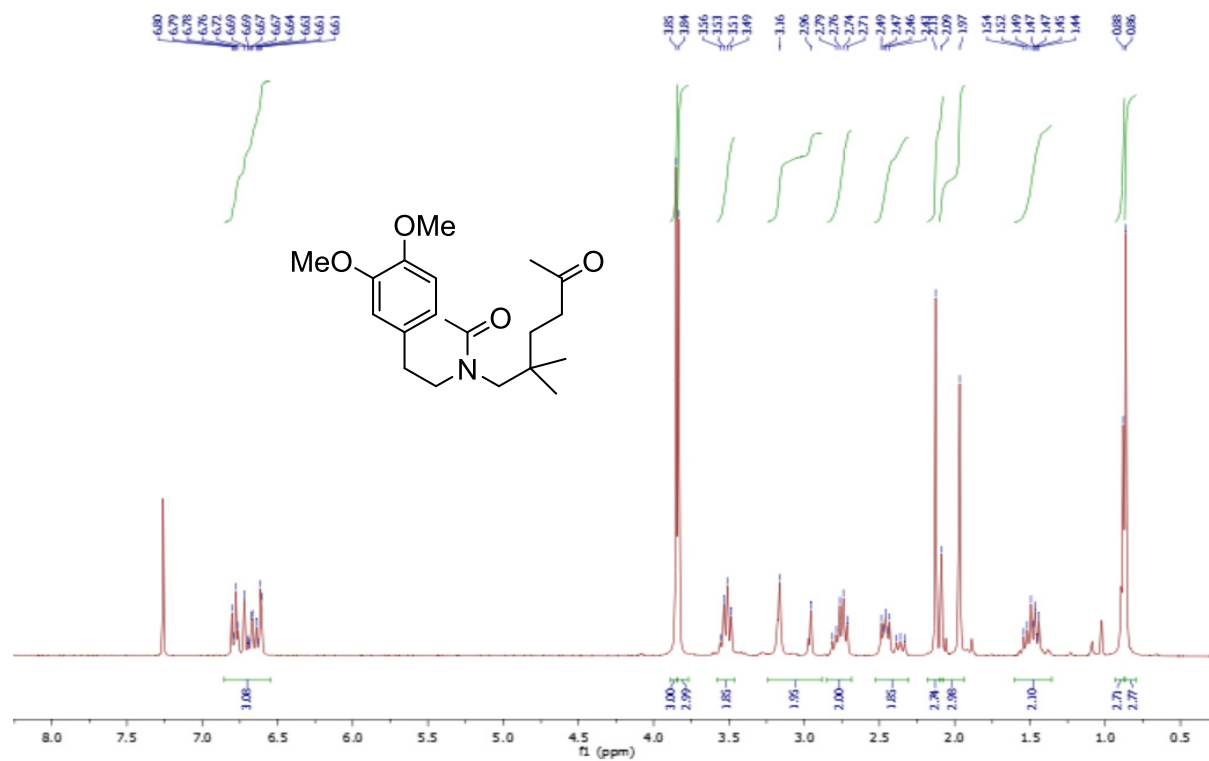


¹³C RMN spectrum

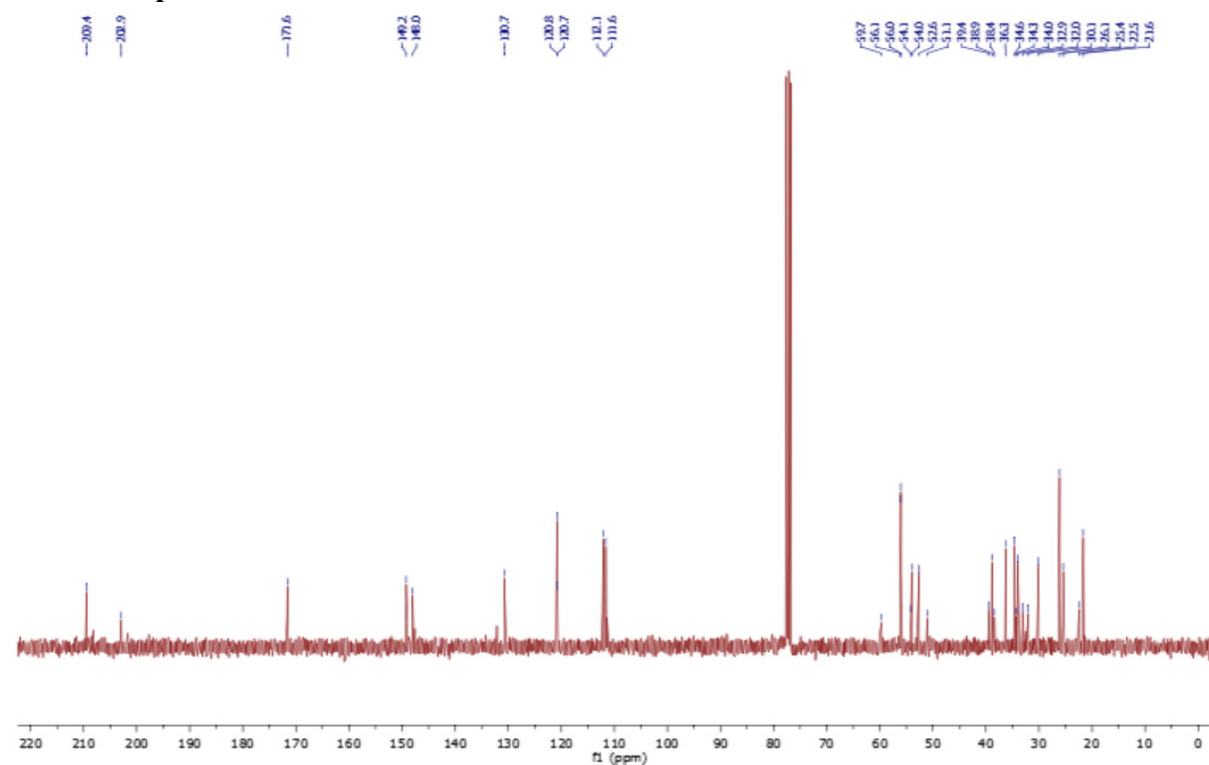


***N*-(3,4-Dimethoxyphenethyl)-*N*-(2,2-dimethyl-5-oxohexyl)acetamide (28d)**

¹H RMN spectrum

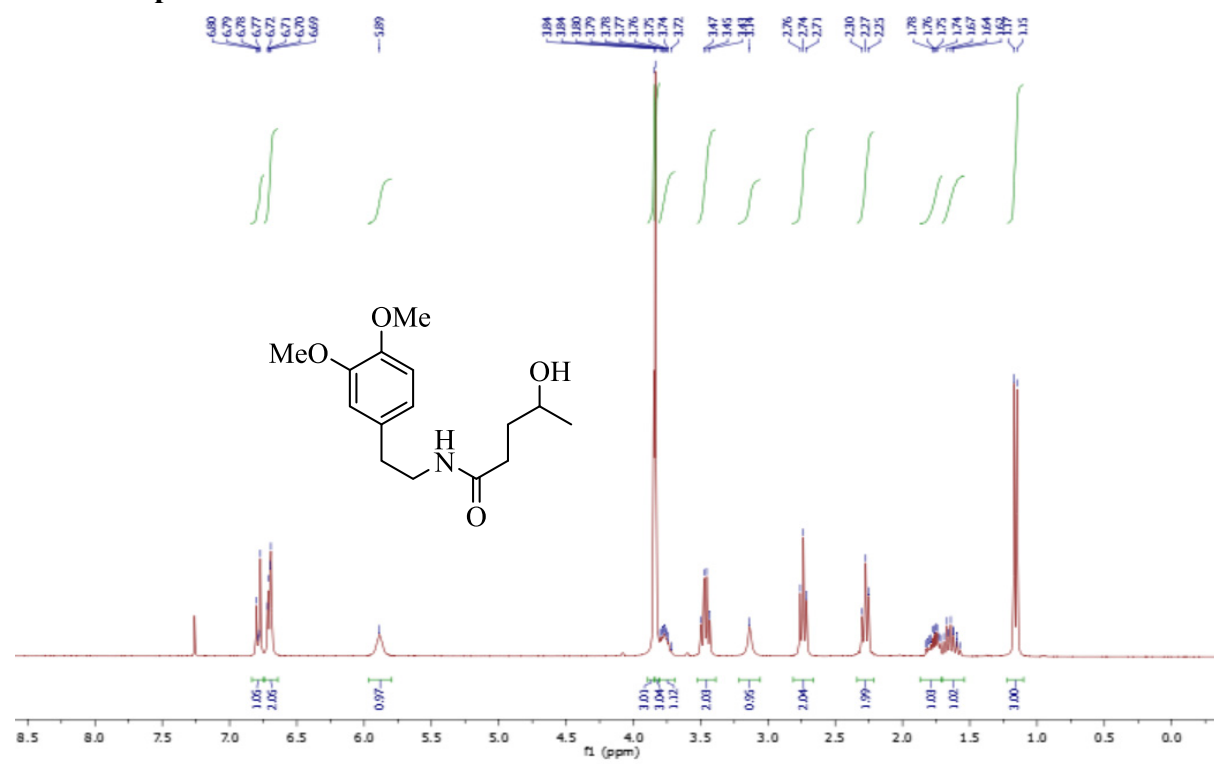


¹³C RMN spectrum



***N*-(3,4-Dimethoxyphenethyl)-*N*-(4-hydroxy)pentanamide**

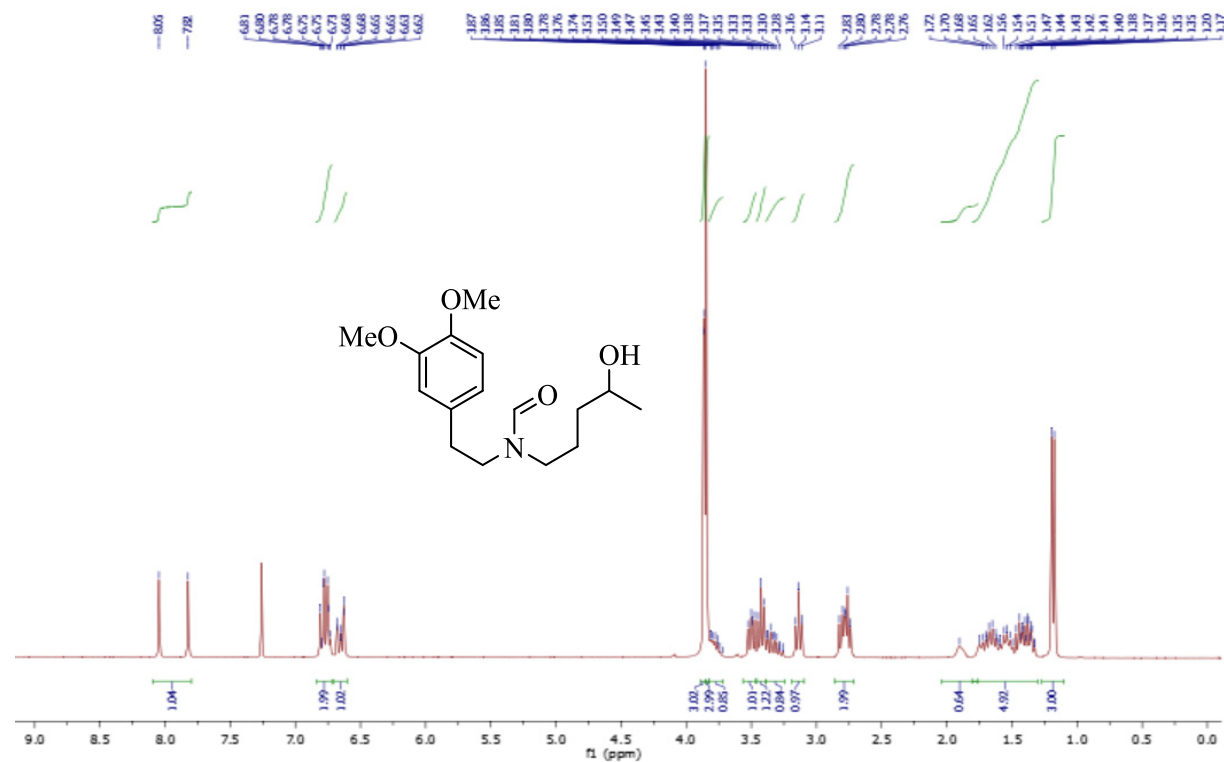
¹H RMN spectrum



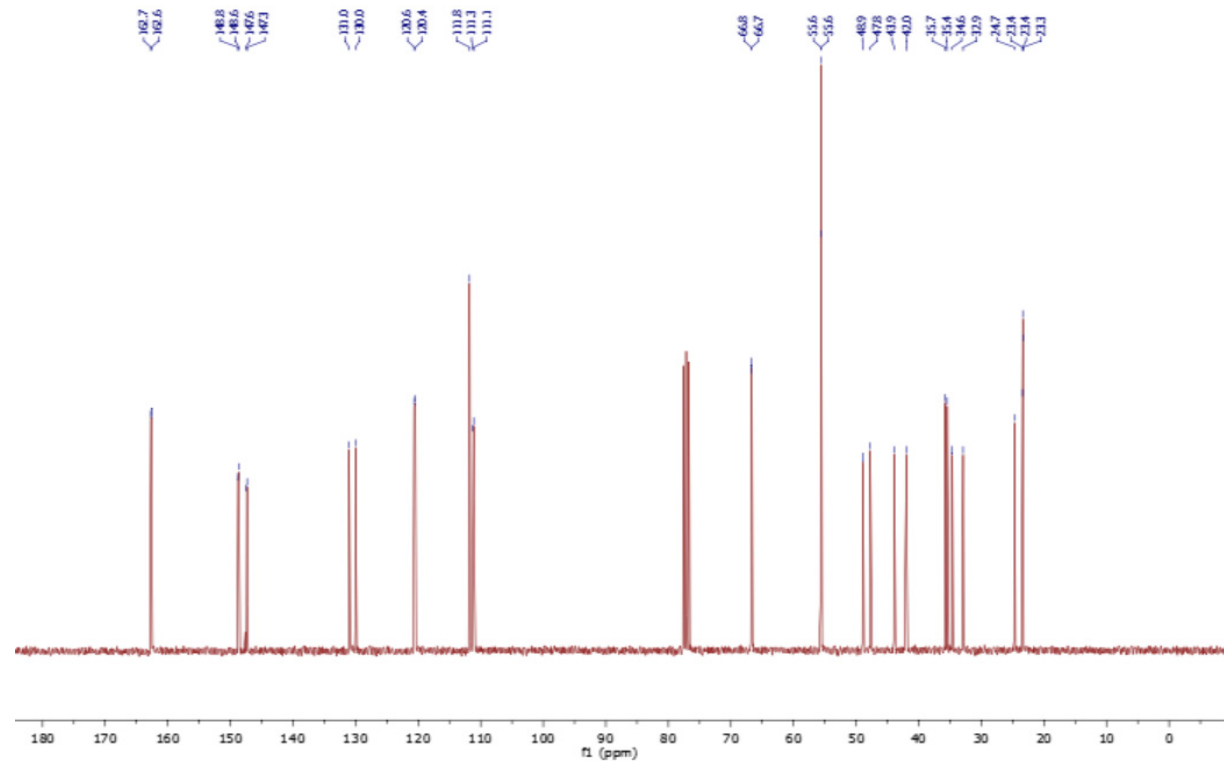
¹³C RMN spectrum

***N*-(3,4-Dimethoxyphenethyl)-*N*-(4-hydroxypentyl)formamide**

¹H RMN spectrum

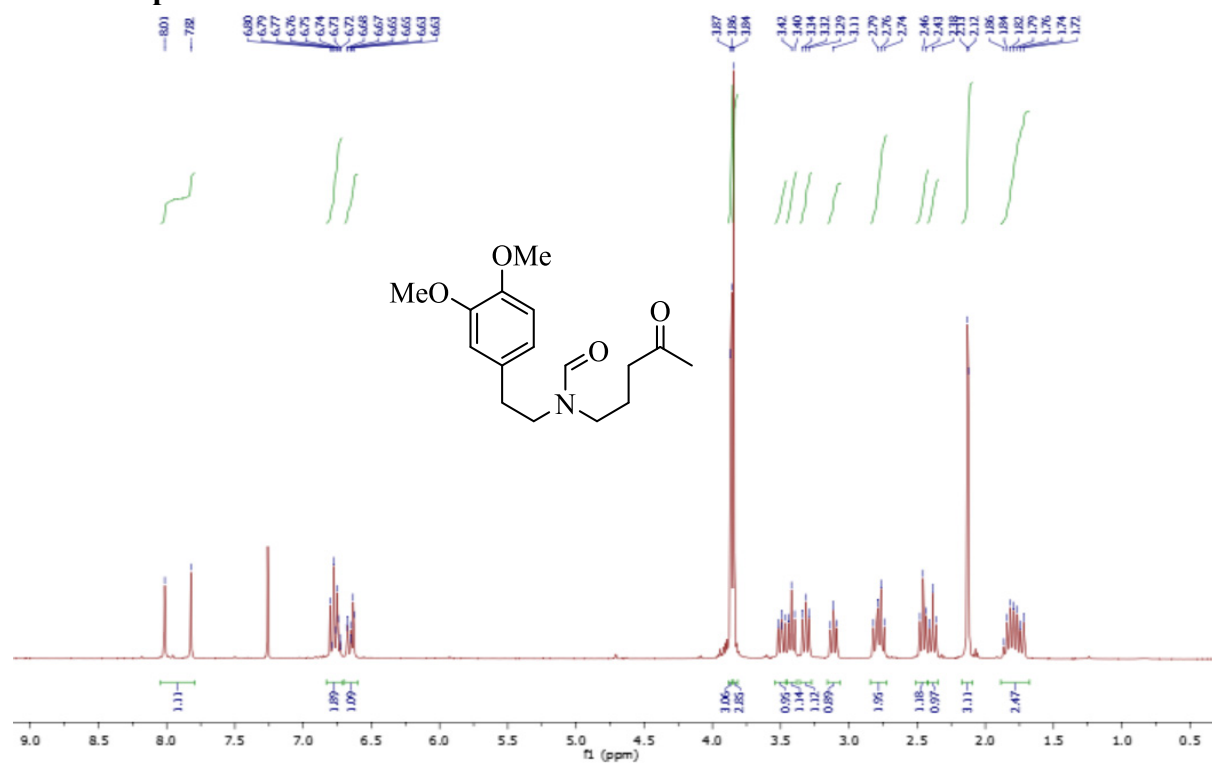


¹³C RMN spectrum

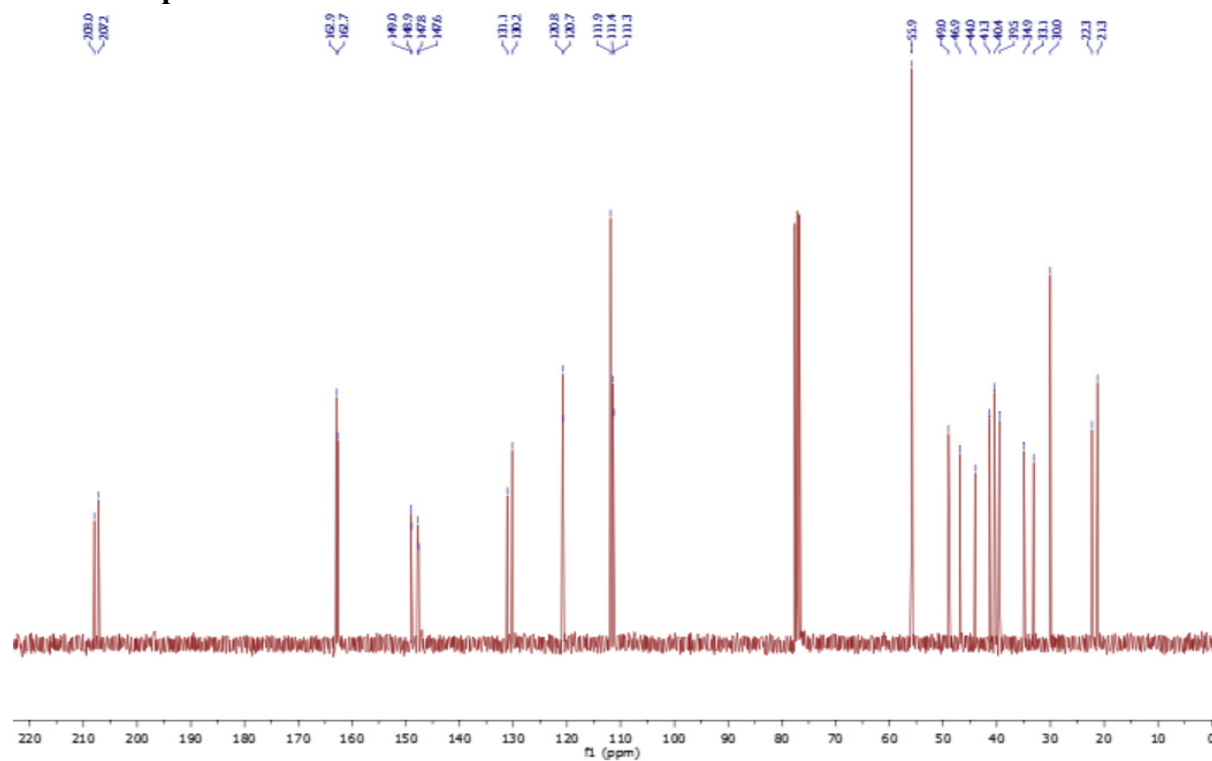


***N*-(3,4-Dimethoxyphenethyl)-*N*-(4-oxopentyl)formamide (28e)**

¹H RMN spectrum

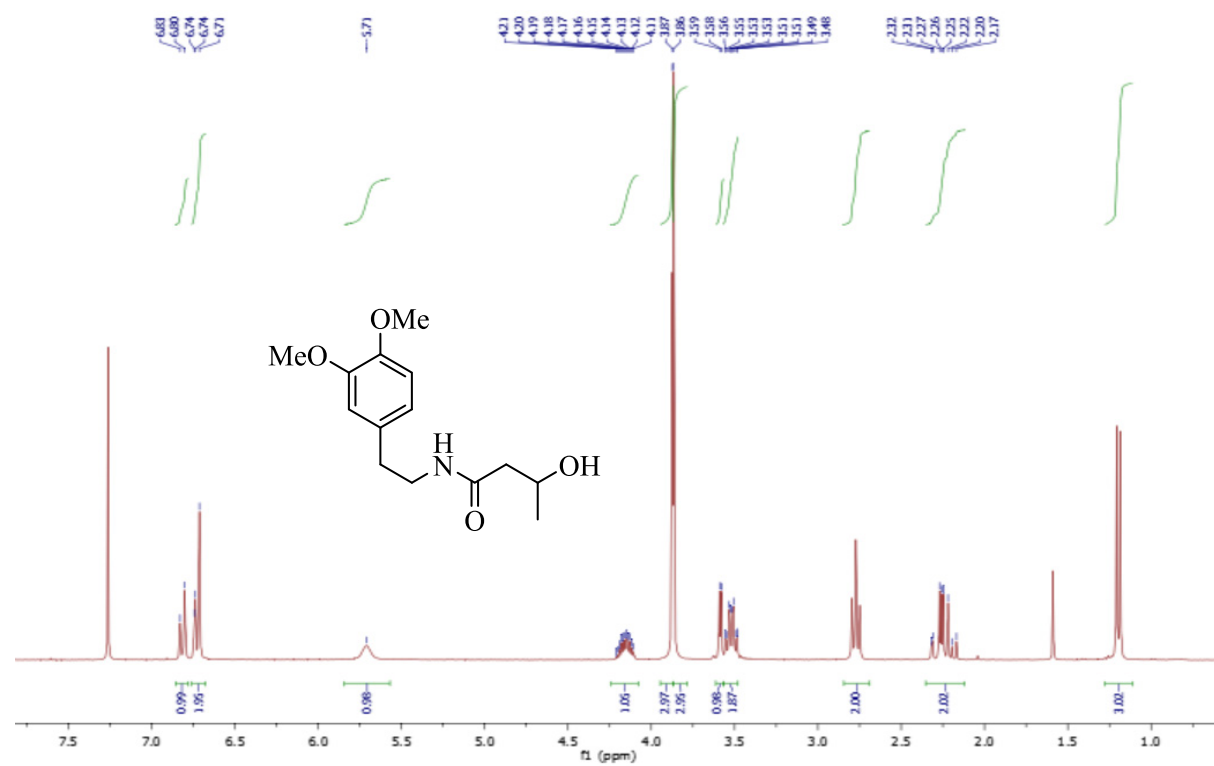


¹³C RMN spectrum

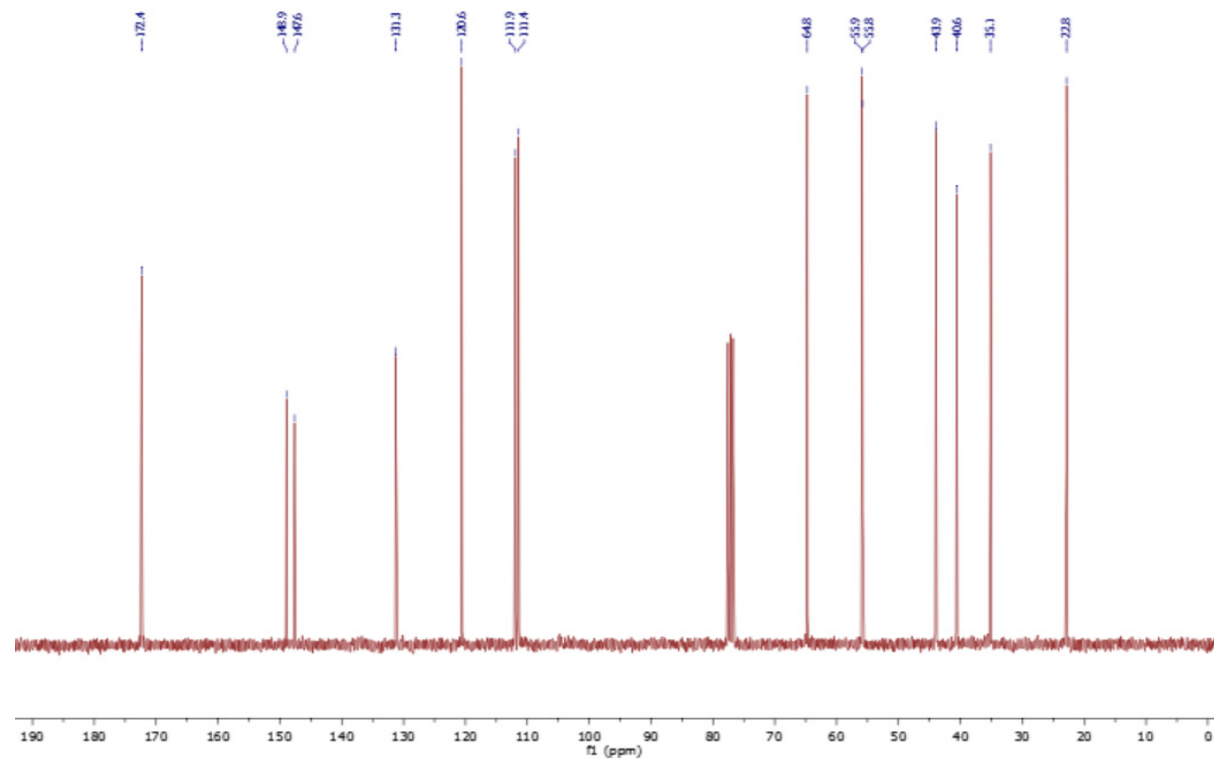


***N*-(3,4-Dimethoxyphenethyl)-3-hydroxybutanamide**

¹H RMN spectrum

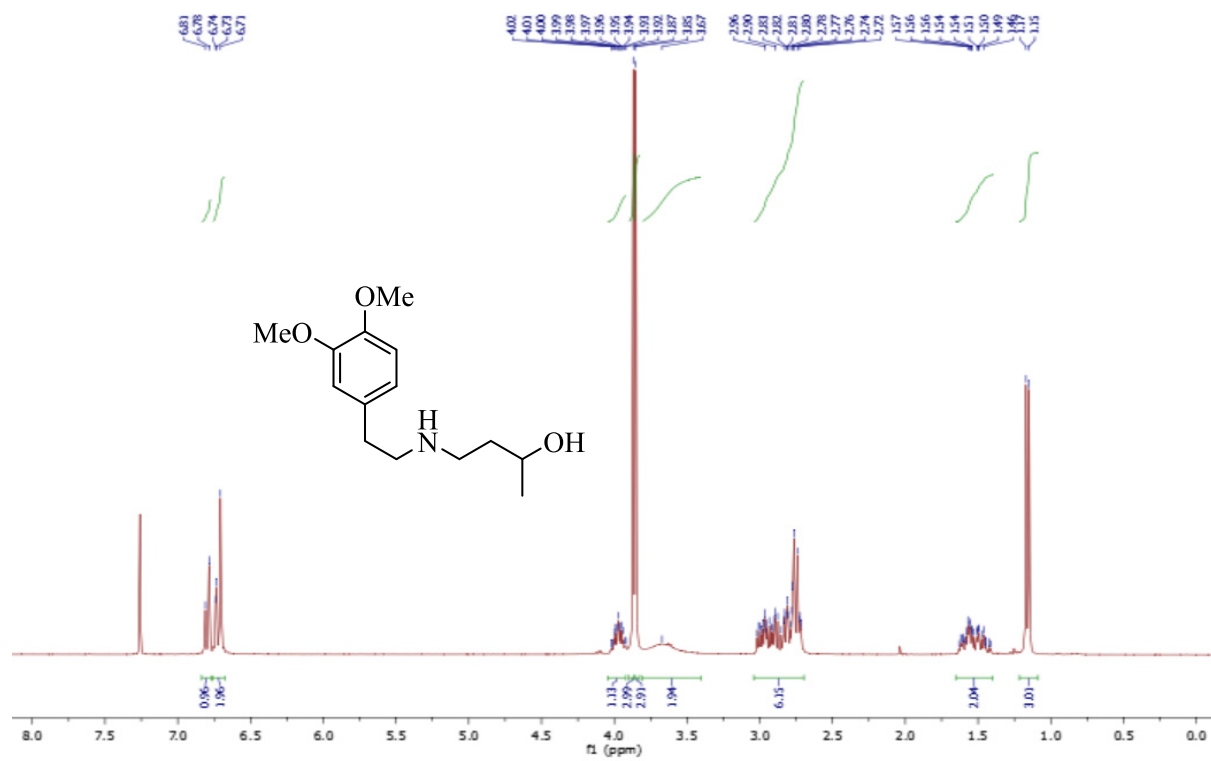


¹³C RMN spectrum

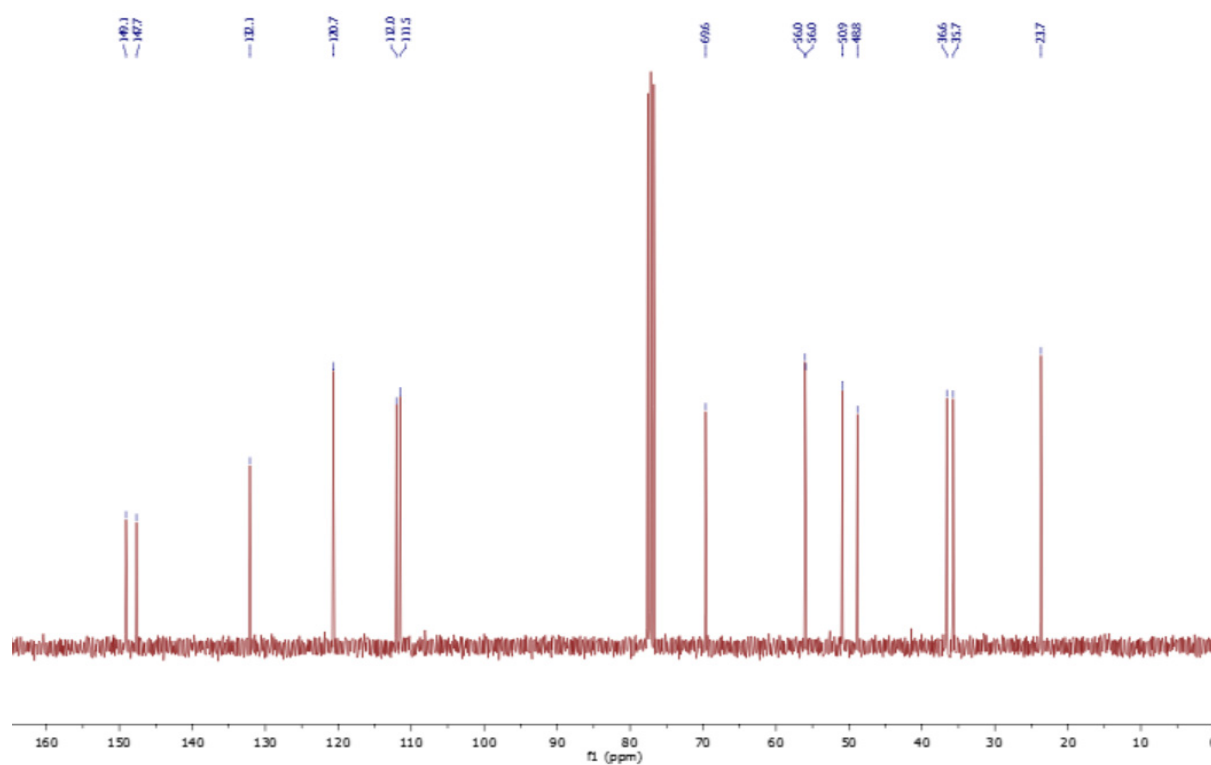


***N*-(3,4-Dimethoxyphenethyl)-*N*-methyl-5-oxohexanamide**

¹H RMN spectrum

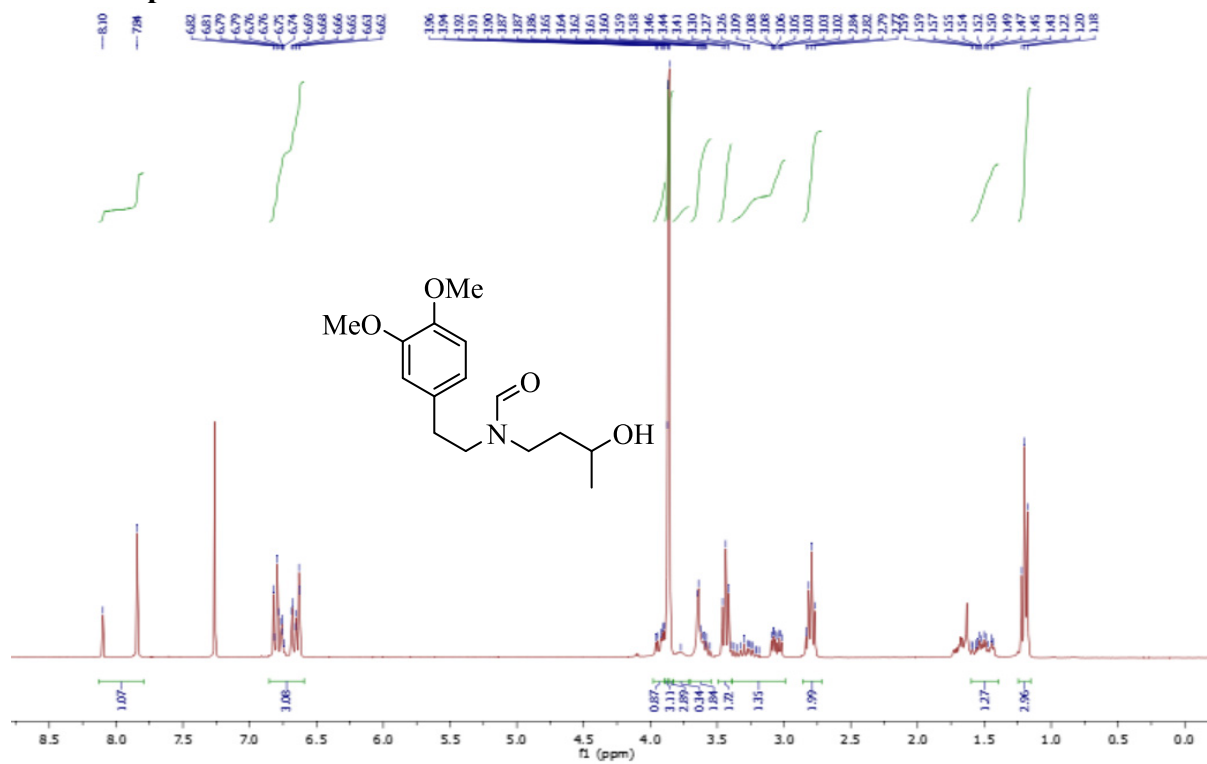


¹³C RMN spectrum

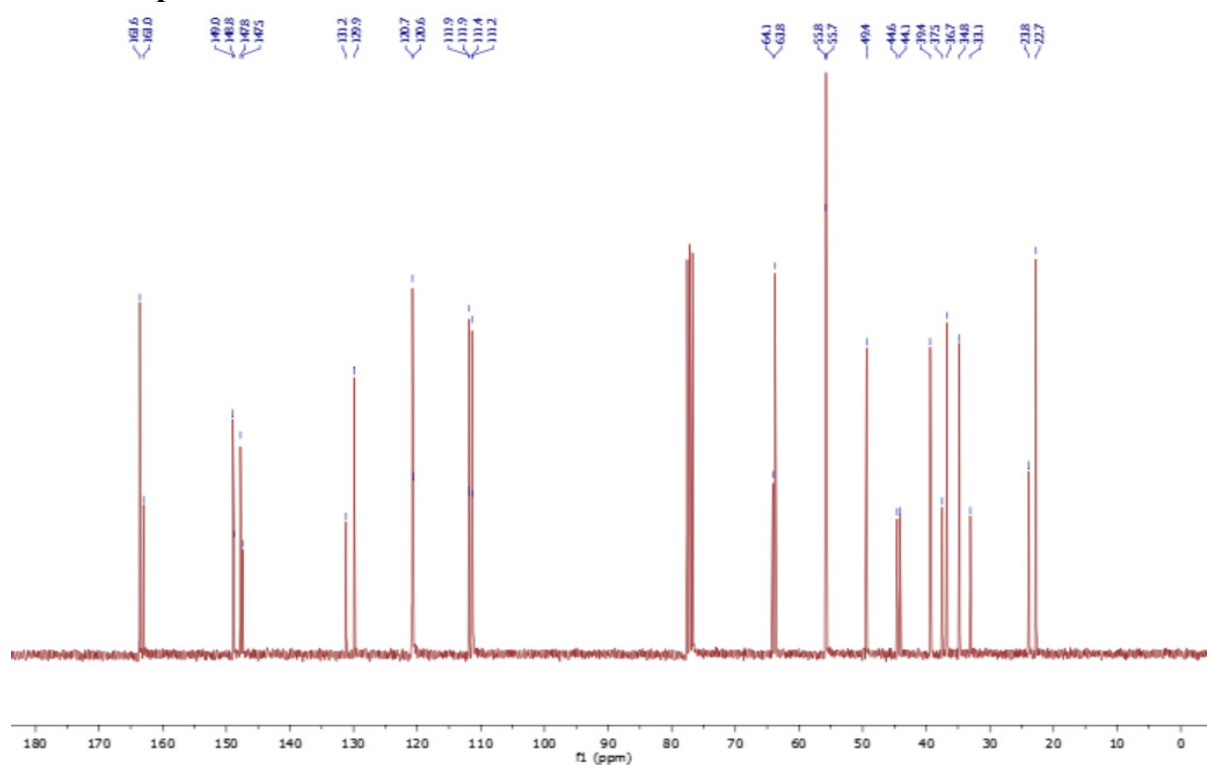


***N*-(3,4-Dimethoxyphenethyl)-*N*-(3-hydroxybutyl)formamide**

¹H RMN spectrum

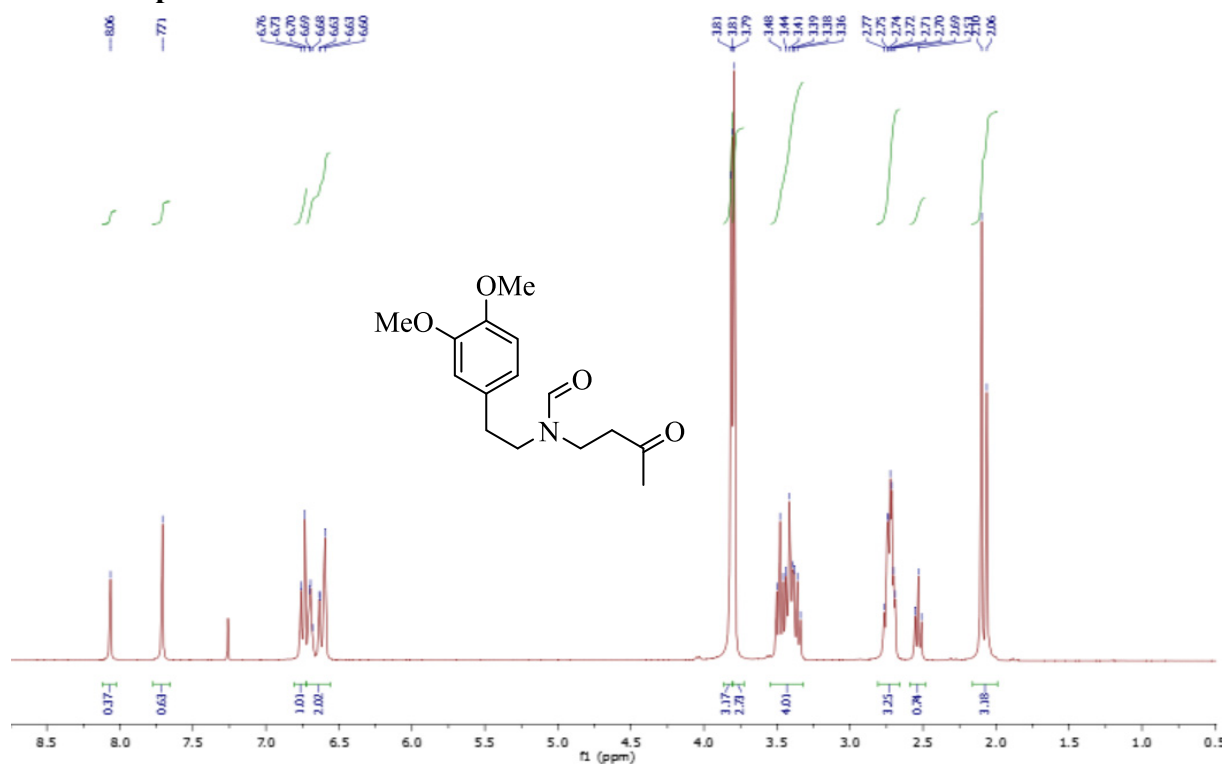


¹³C RMN spectrum

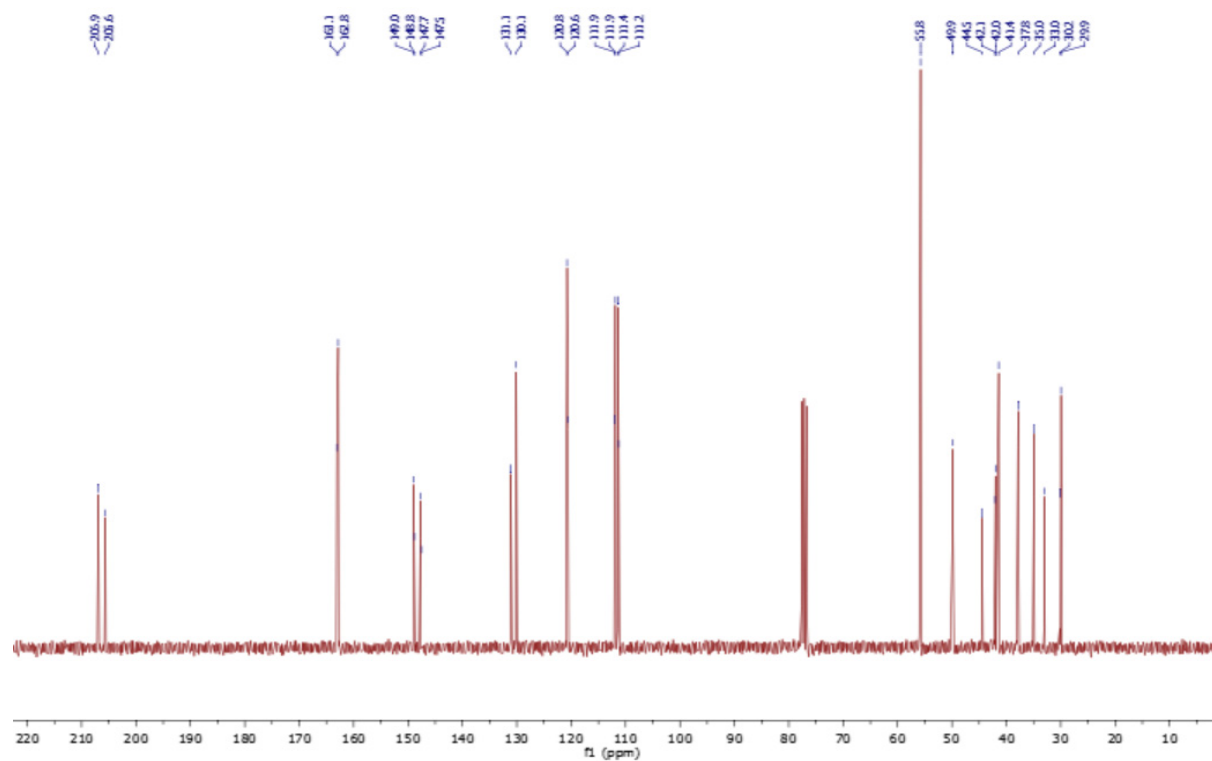


***N*-(3,4-Dimethoxyphenethyl)-*N*-(3-oxobutyl)formamide (28f)**

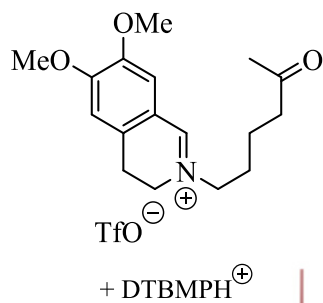
¹H RMN spectrum



¹³C RMN spectrum

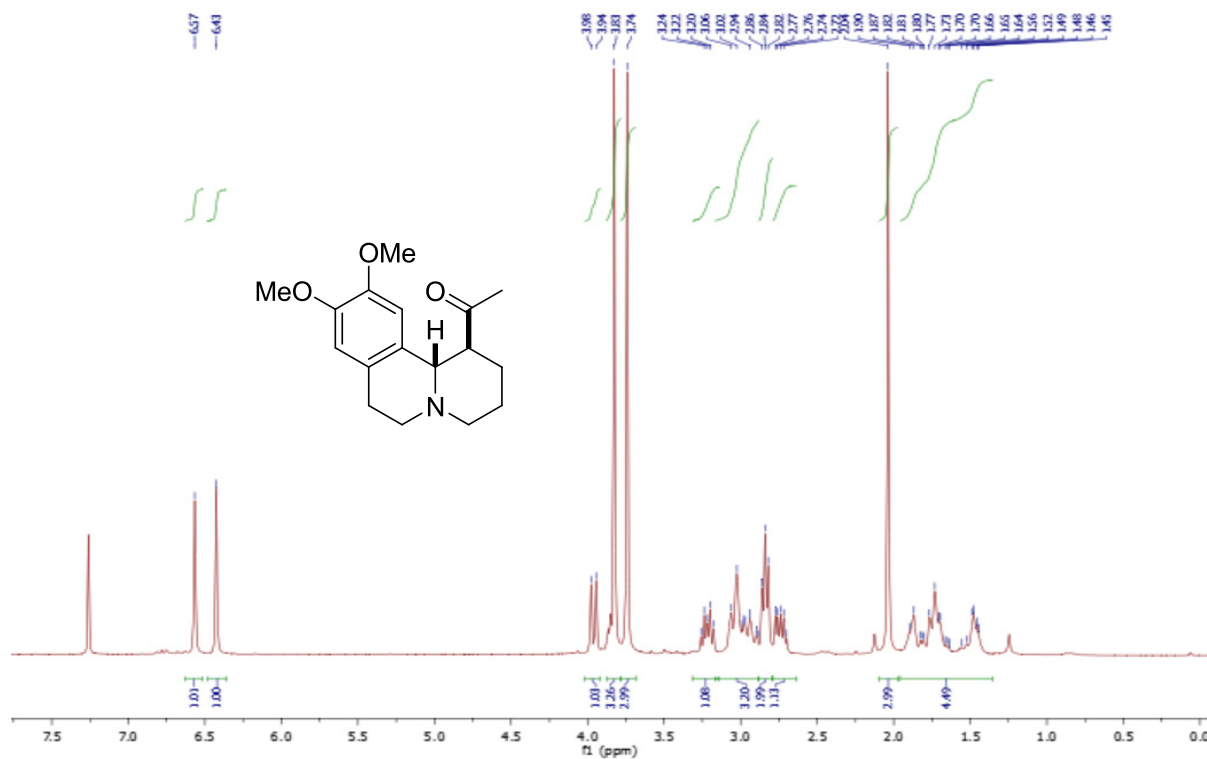


¹H RMN spectrum

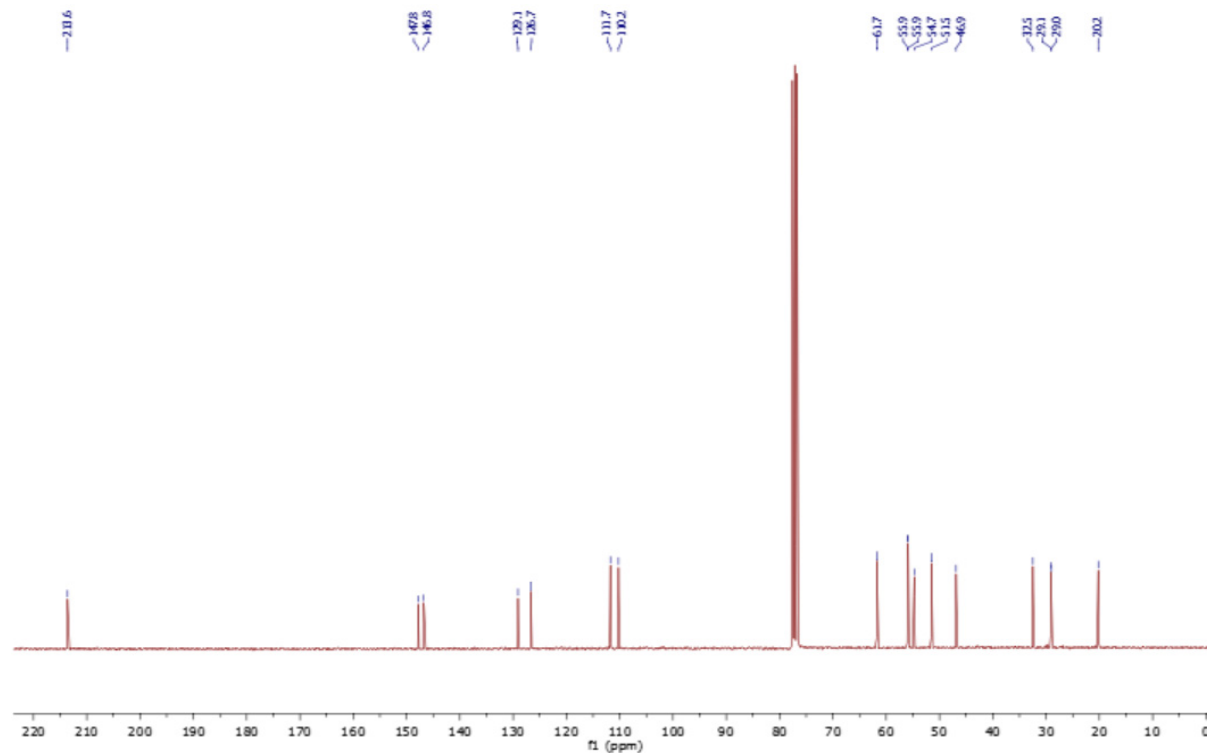


***cis*-1-(9,10-Dimethoxy-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinolin-1-yl)ethan-1-one (30a)**

¹H RMN spectrum

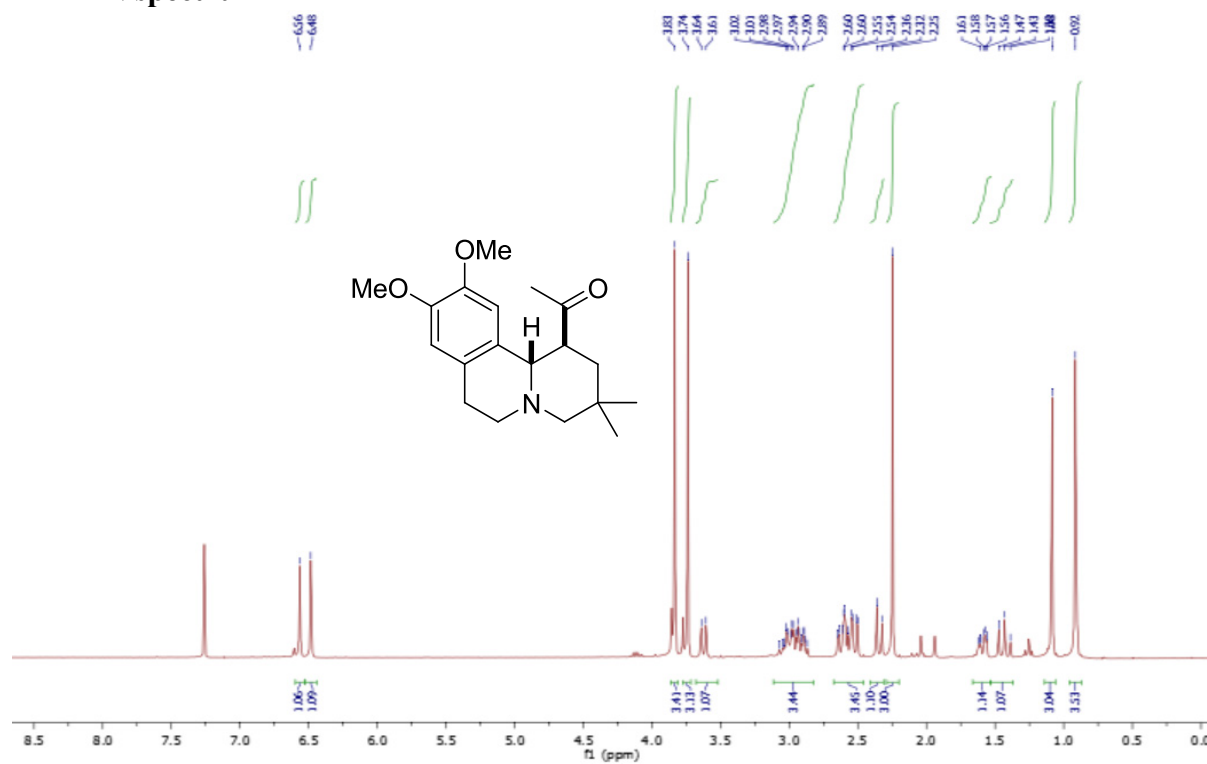


¹³C RMN spectrum

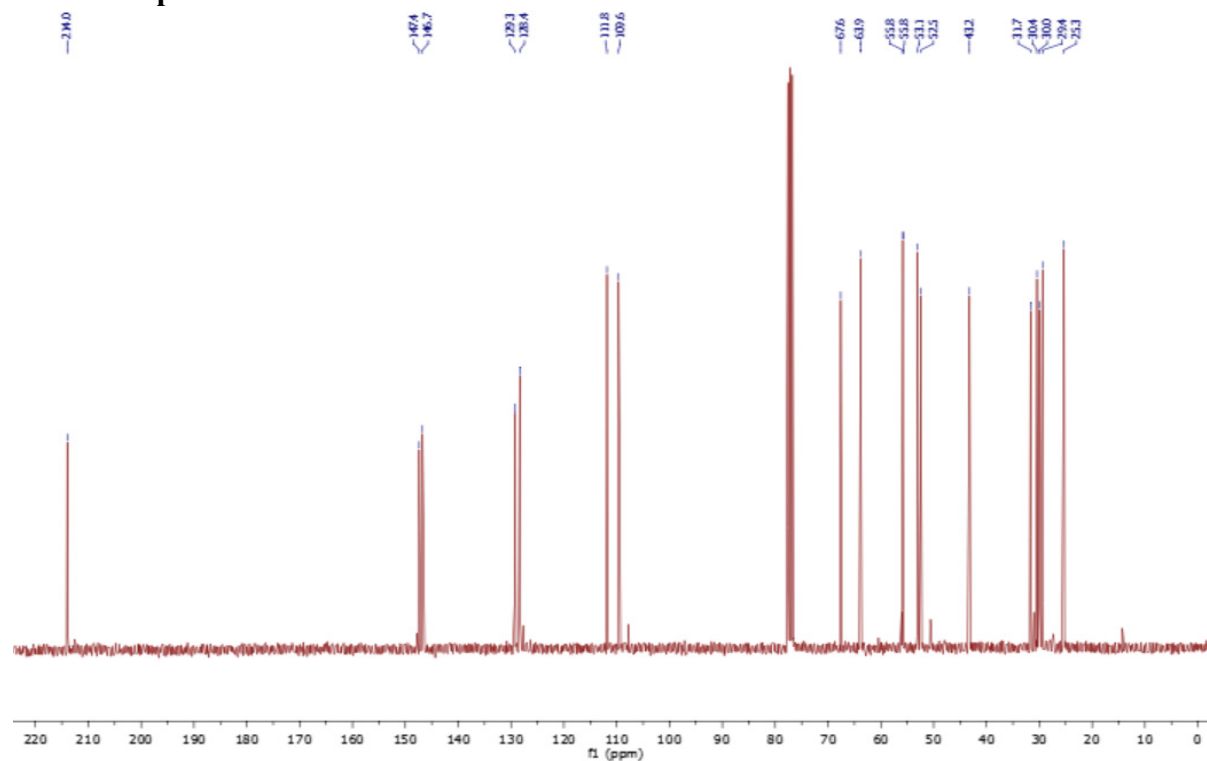


***cis*-1-(9,10-Dimethoxy-3,3-dimethyl-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinolin-1-yl)ethan-1-one (30b)**

¹H RMN spectrum

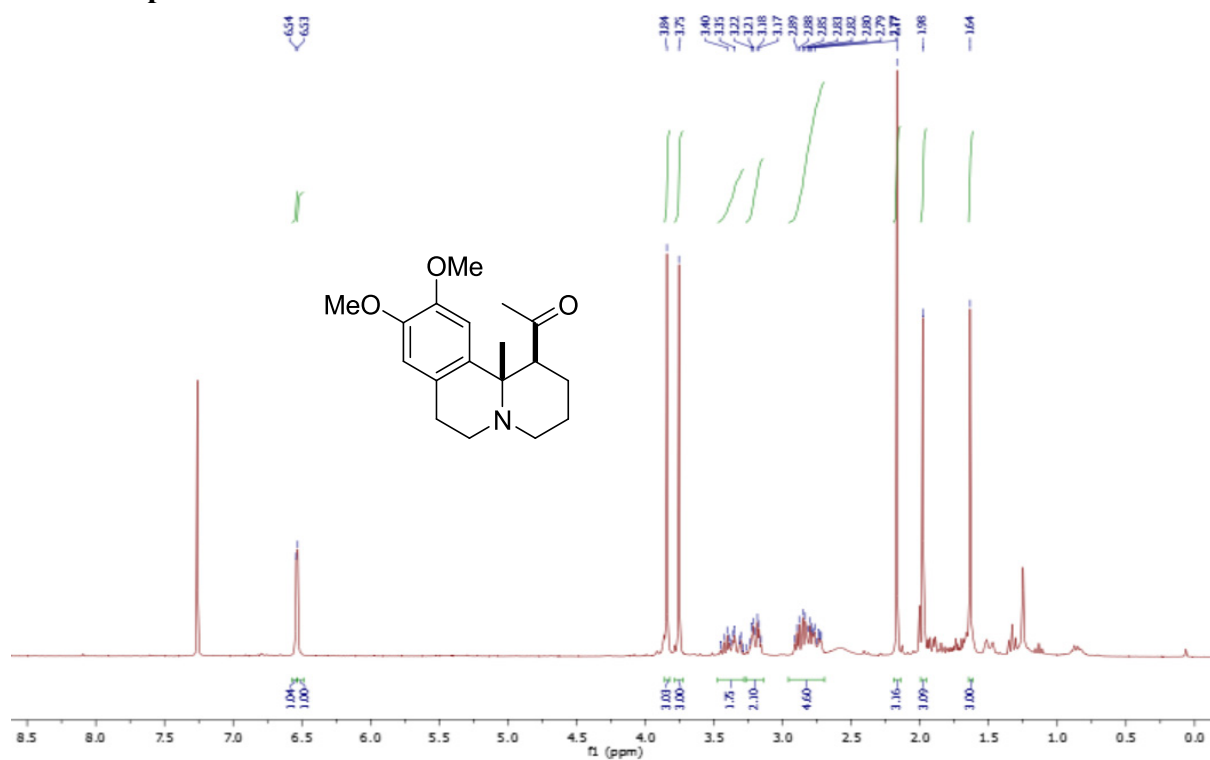


¹³C RMN spectrum

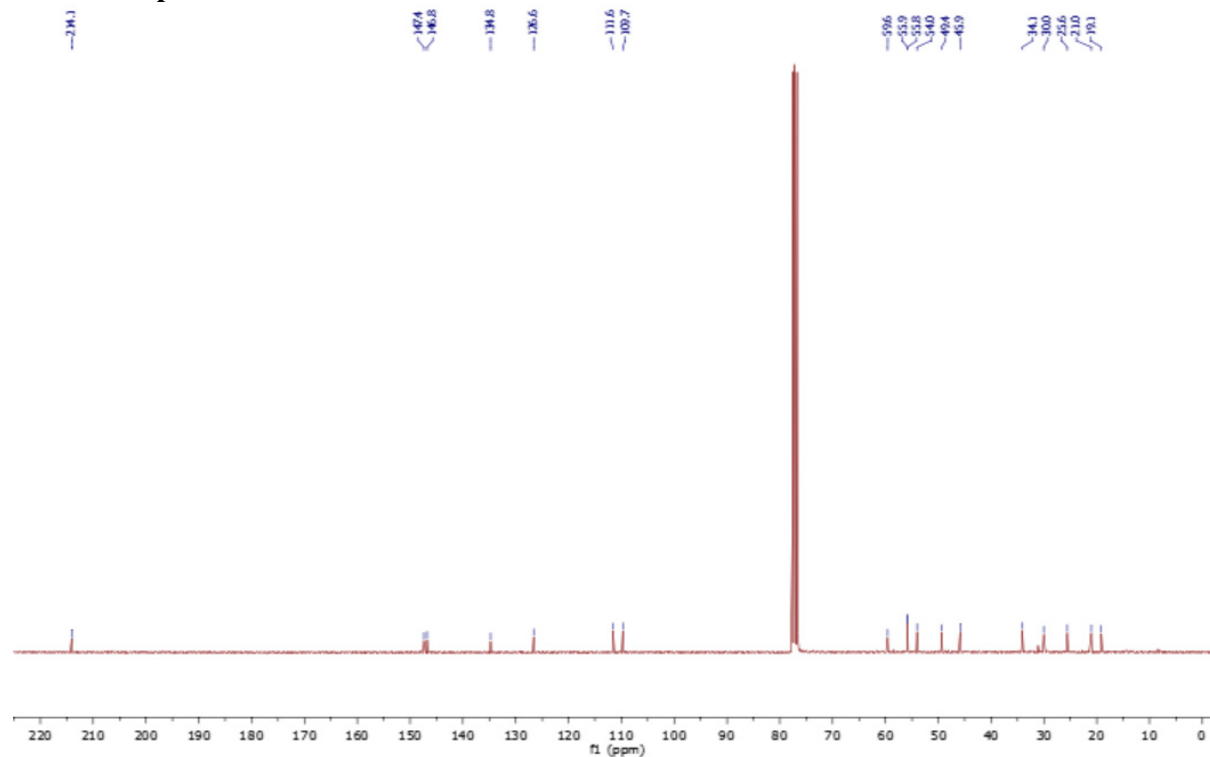


***cis*-1-(9,10-Dimethoxy-11b-methyl-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinolin-1-yl)ethan-1-one (30c)**

¹H RMN spectrum

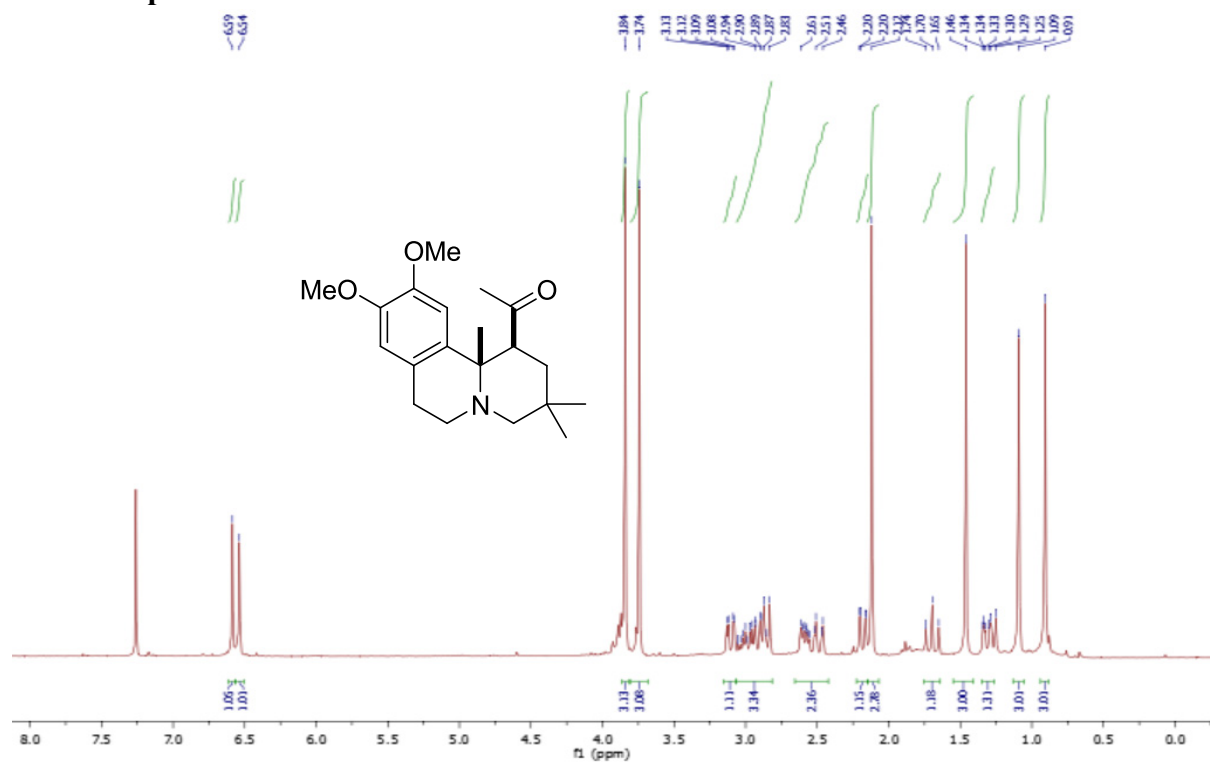


¹³C RMN spectrum

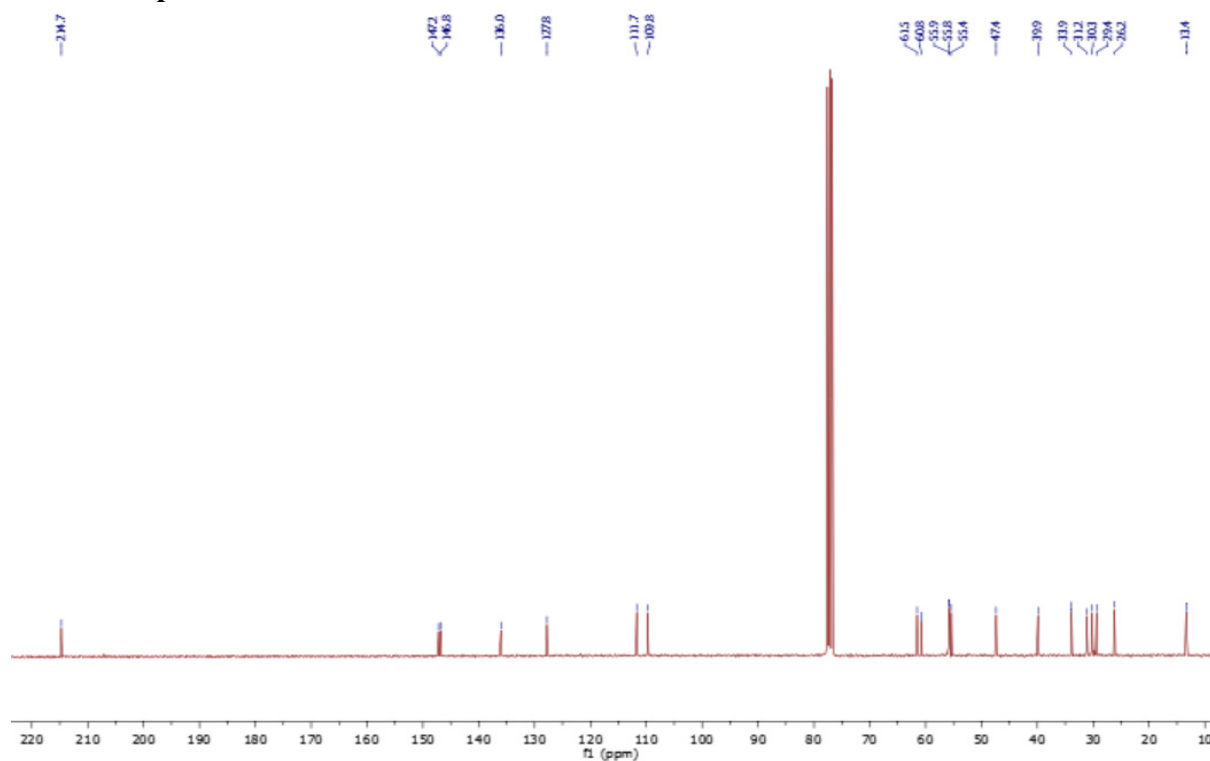


***cis*-1-(9,10-Dimethoxy-3,3,11b-trimethyl-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinolin-1-yl)ethan-1-one (30d)**

¹H RMN spectrum

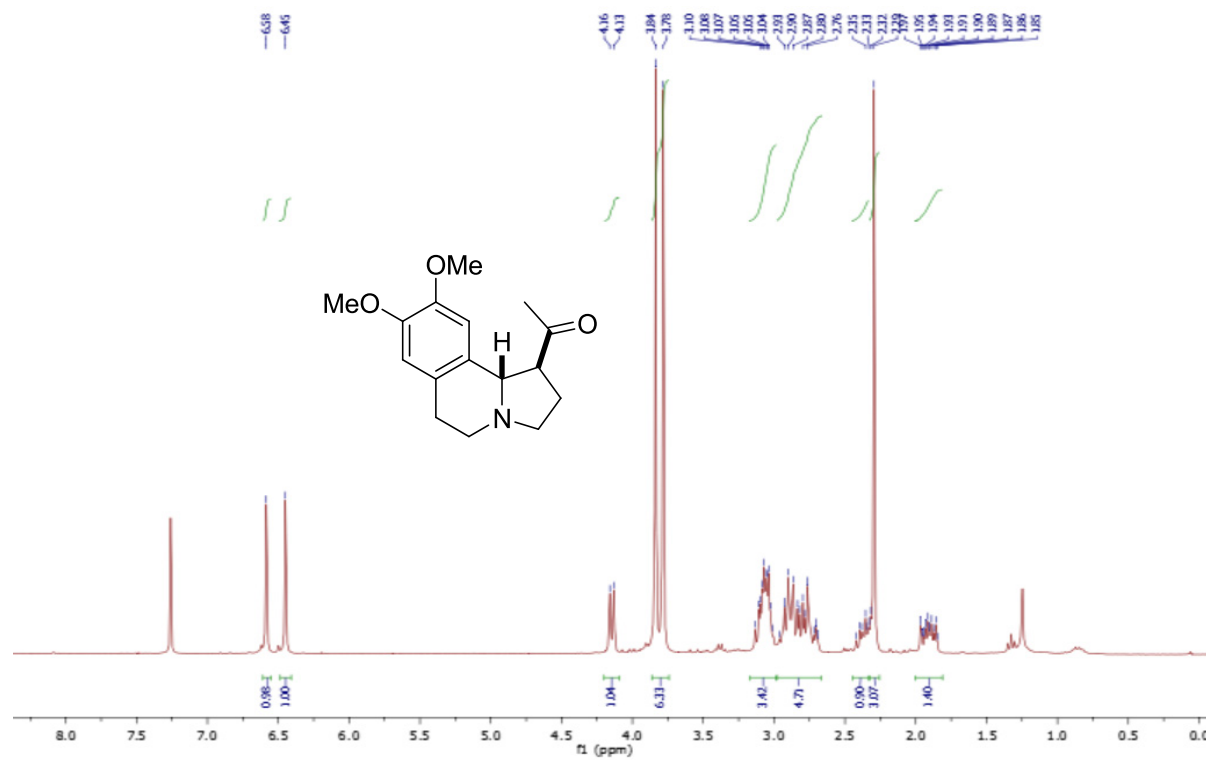


¹³C RMN spectrum

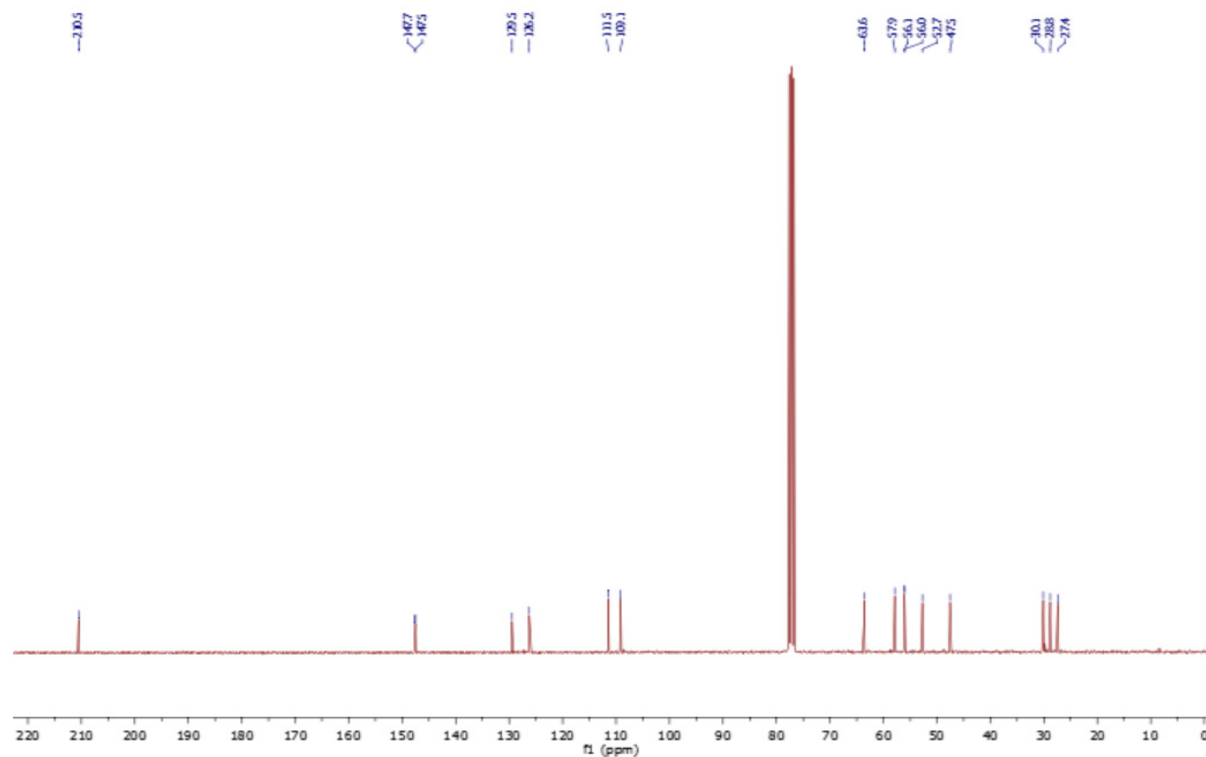


***cis*-1-(8,9-Dimethoxy-1,2,3,5,6,10b-hexahydropyrrolo[2,1-*a*]isoquinolin-1-yl)ethan-1-one (30e)**

¹H RMN spectrum

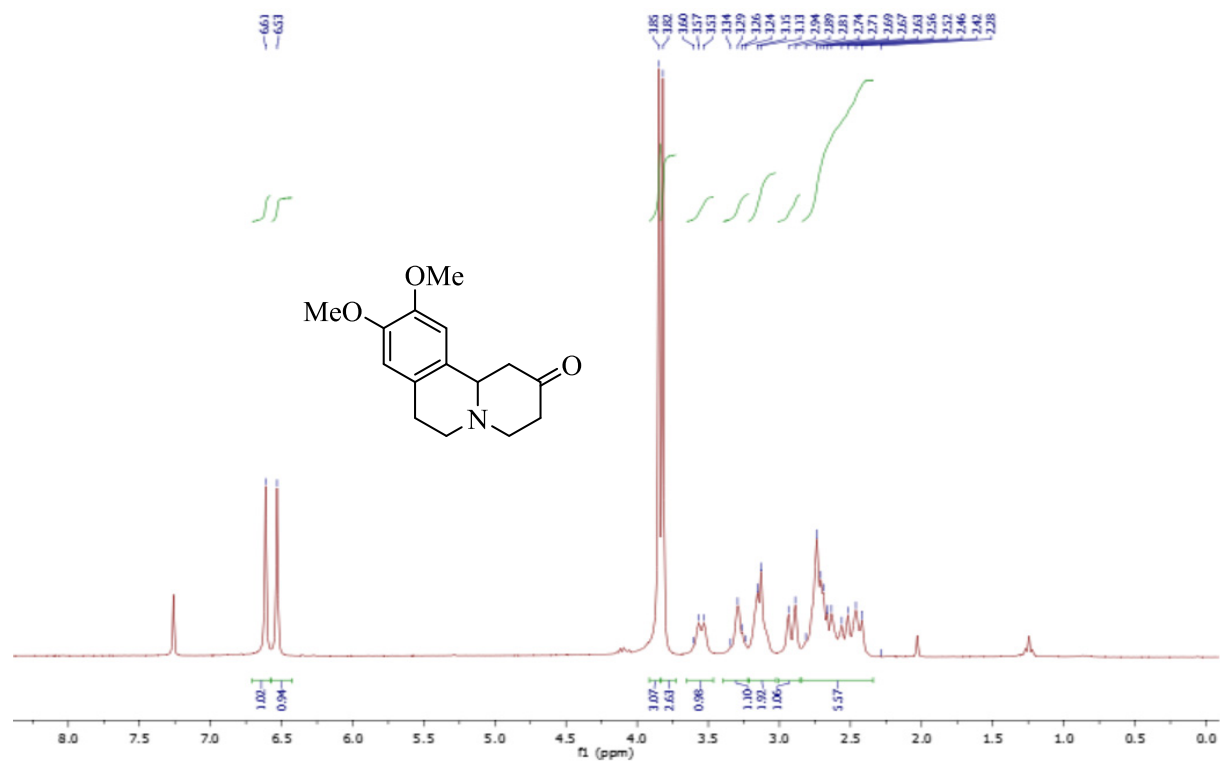


¹³C RMN spectrum

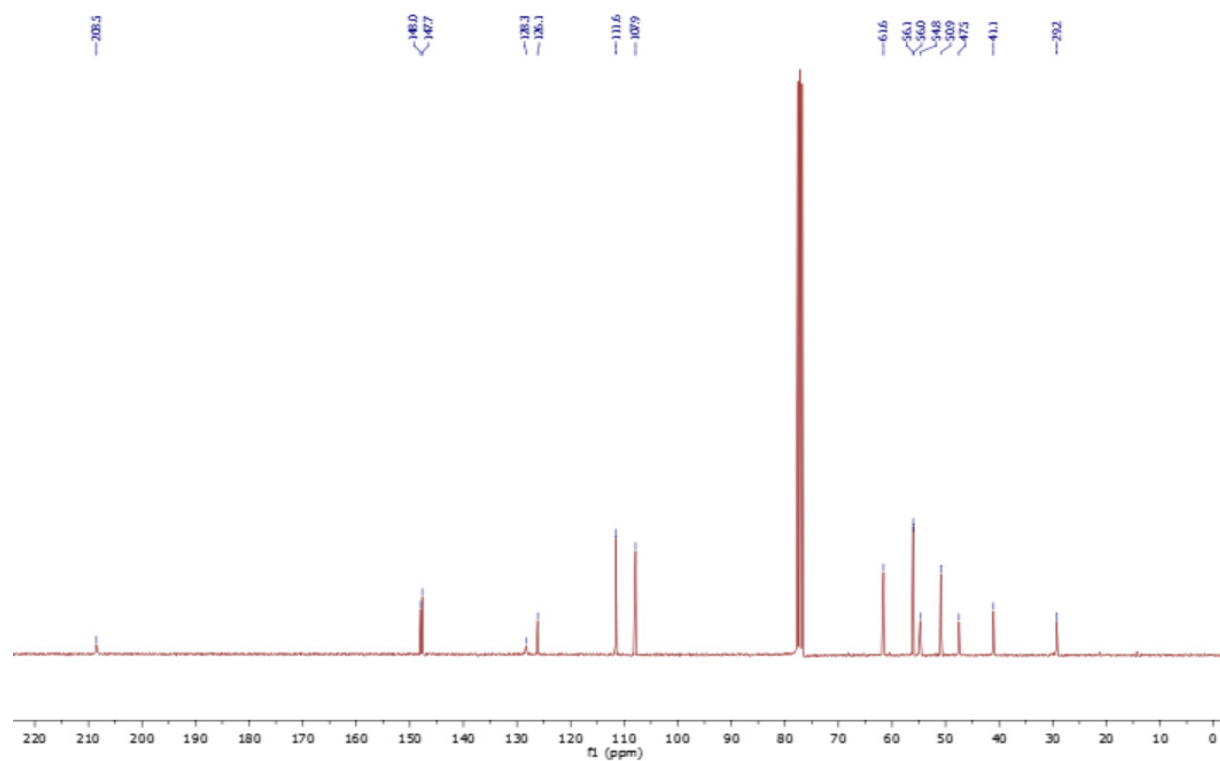


9,10-Dimethoxy-1,3,4,6,7,11b-hexahydro-2*H*-pyrido[2,1-*a*]isoquinolin-2-one (30f)

¹H RMN spectrum

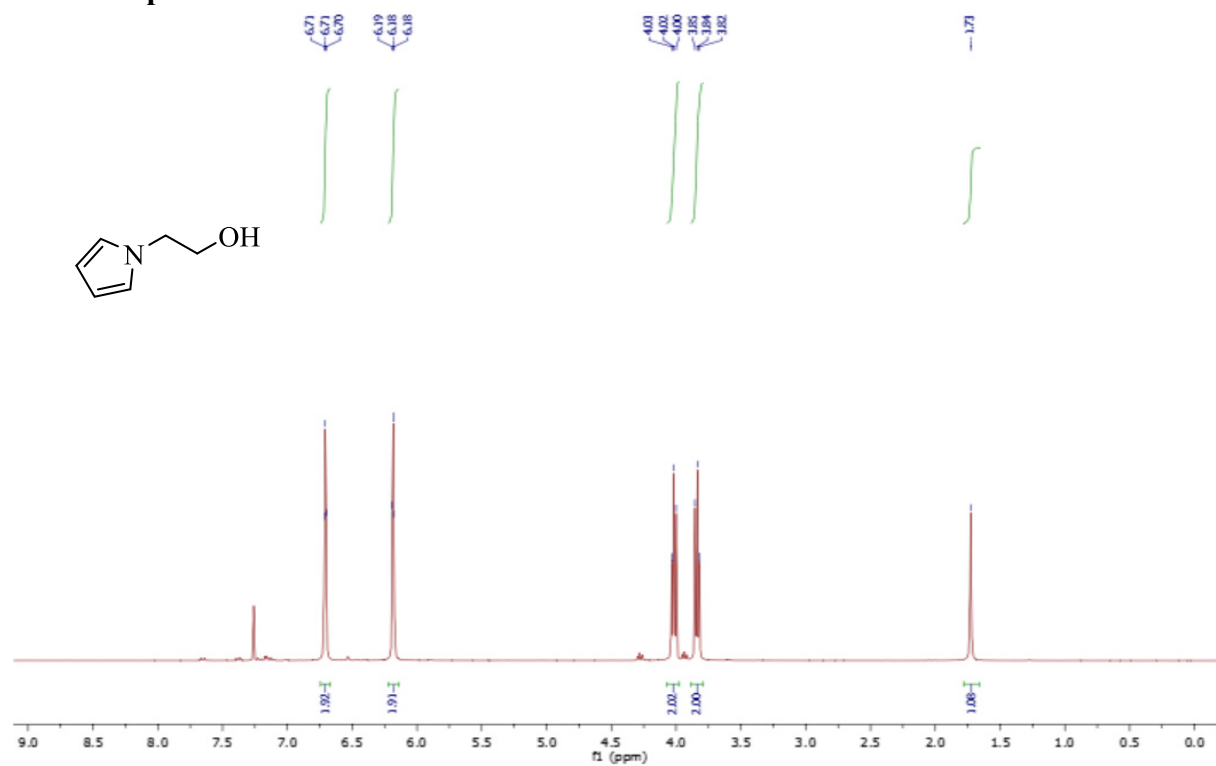


¹³C RMN spectrum

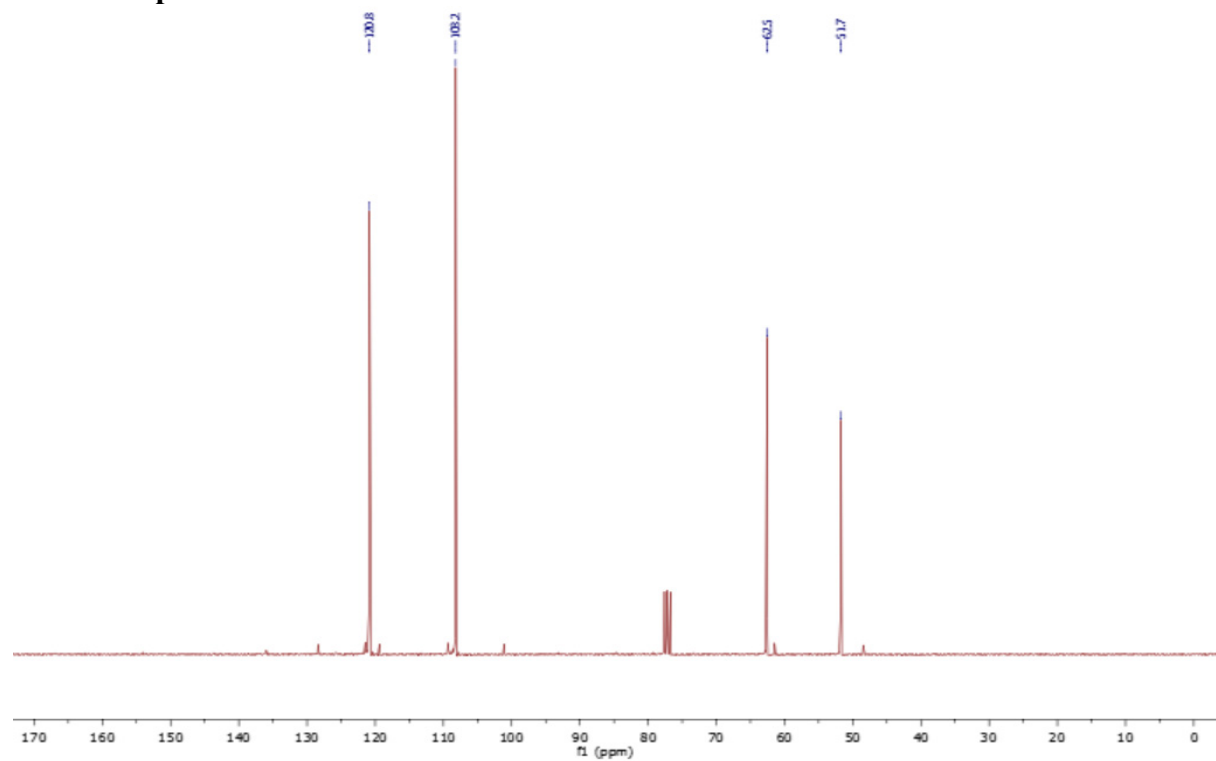


2-(1*H*-Pyrrol-1-yl)ethan-1-ol (36)

¹H RMN spectrum

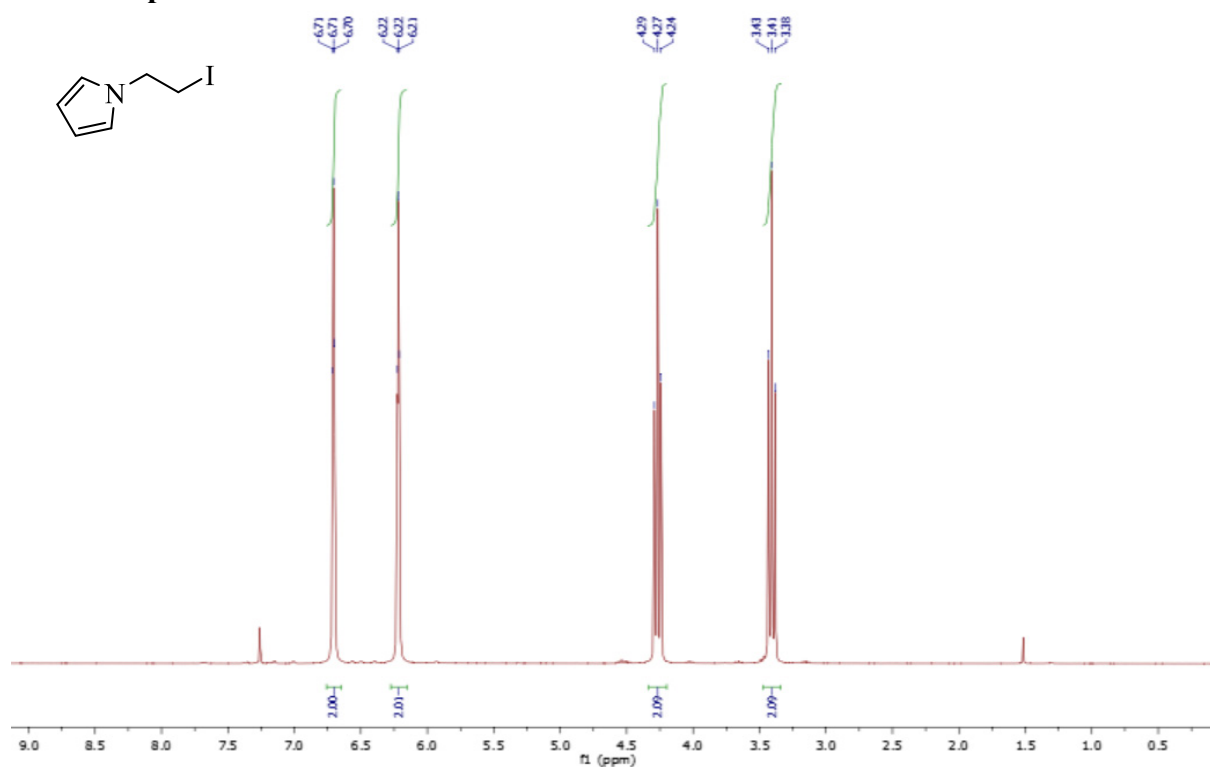


¹³C RMN spectrum

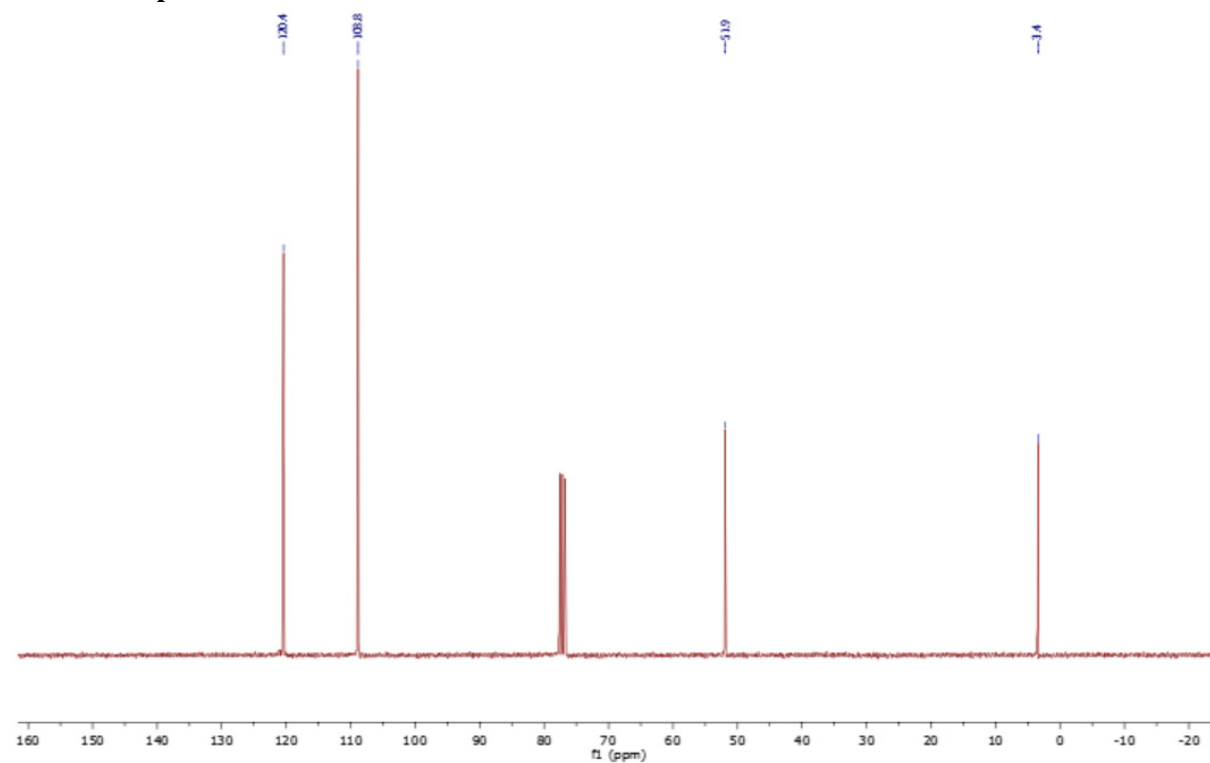


1-(2-Iodoethyl)-1H-pyrrole (37)

¹H RMN spectrum

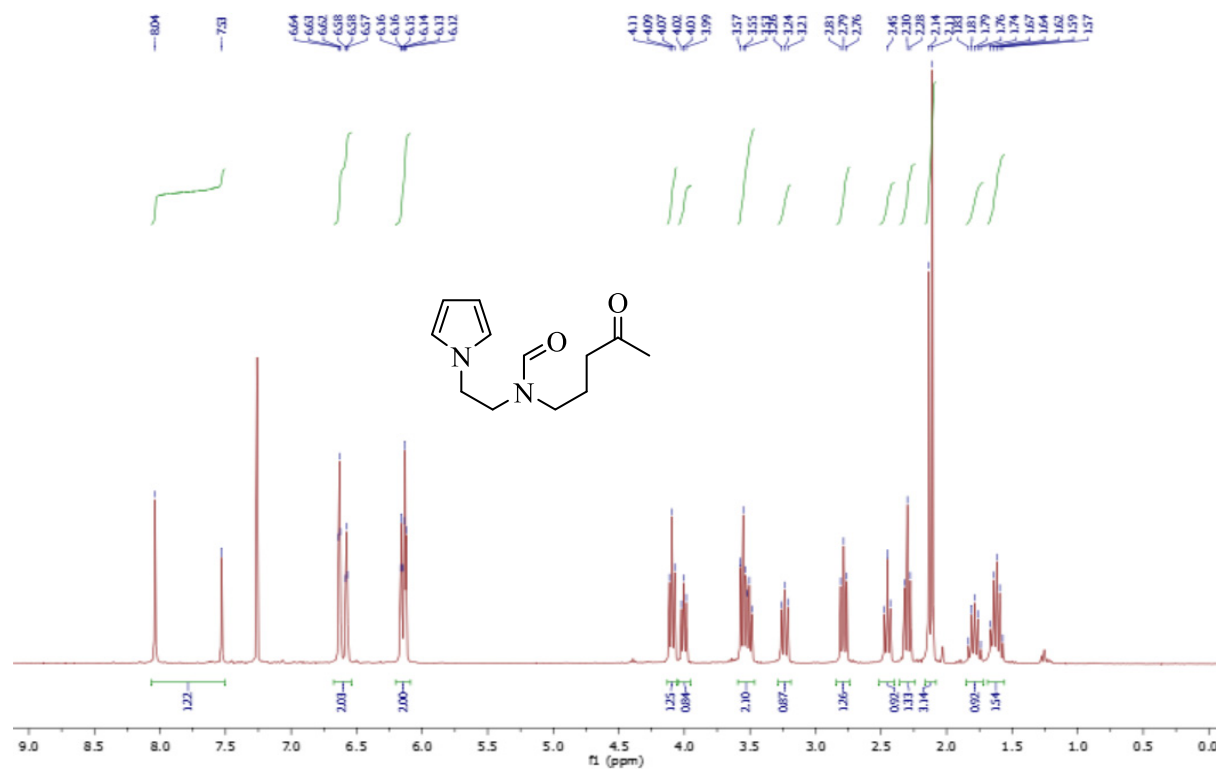


¹³C RMN spectrum

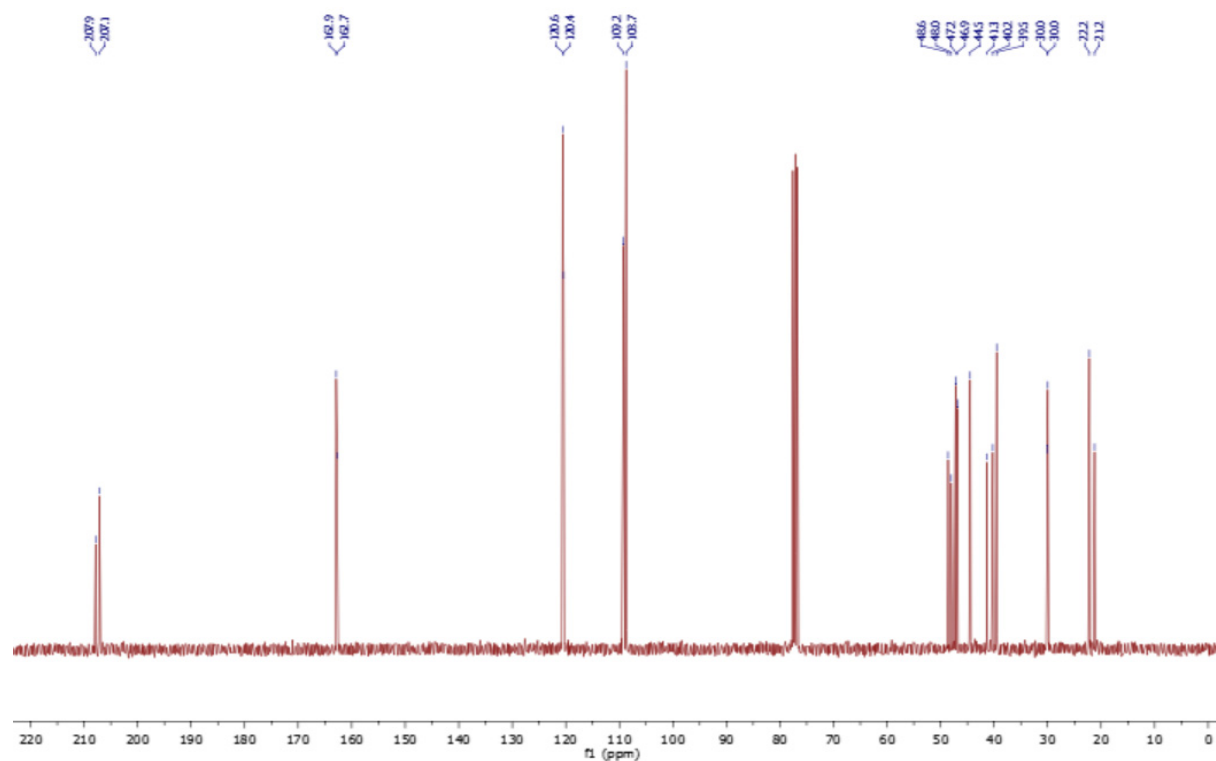


***N*-(2-(1*H*-Pyrrol-1-yl)ethyl)-*N*-(4-oxopentyl)formamide (39a)**

¹H RMN spectrum

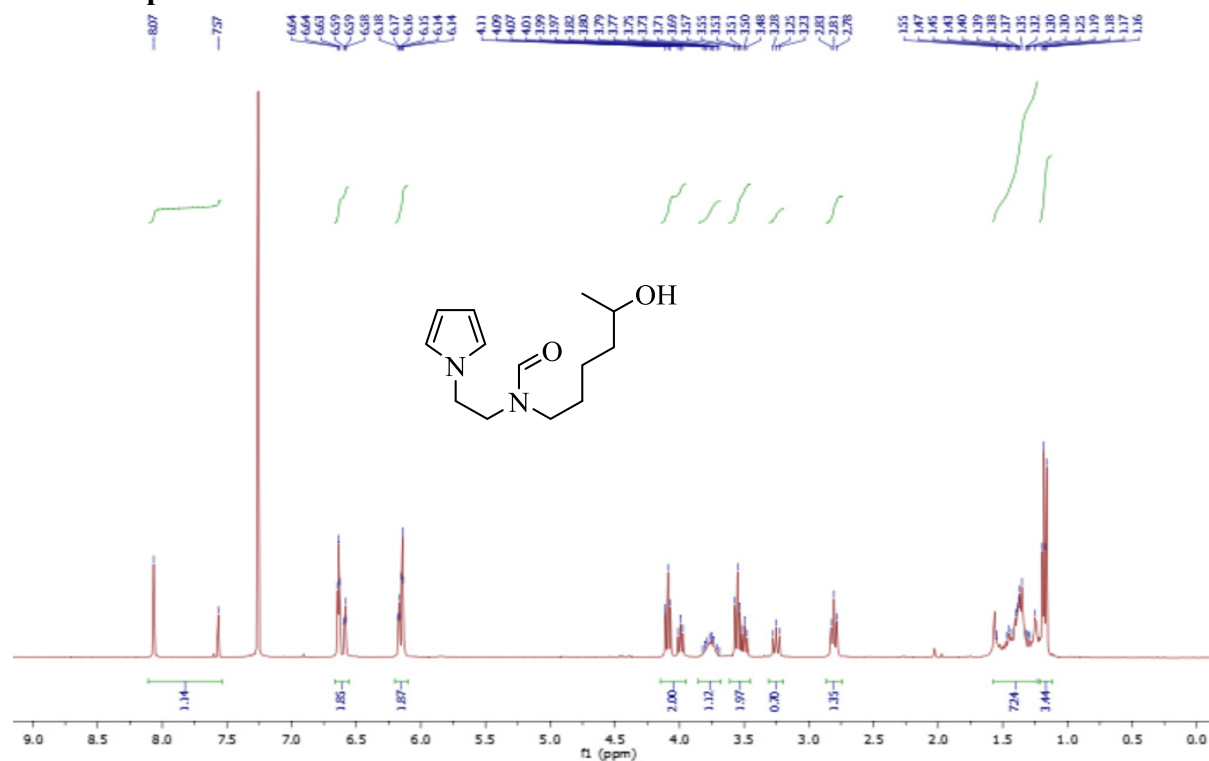


¹³C RMN spectrum

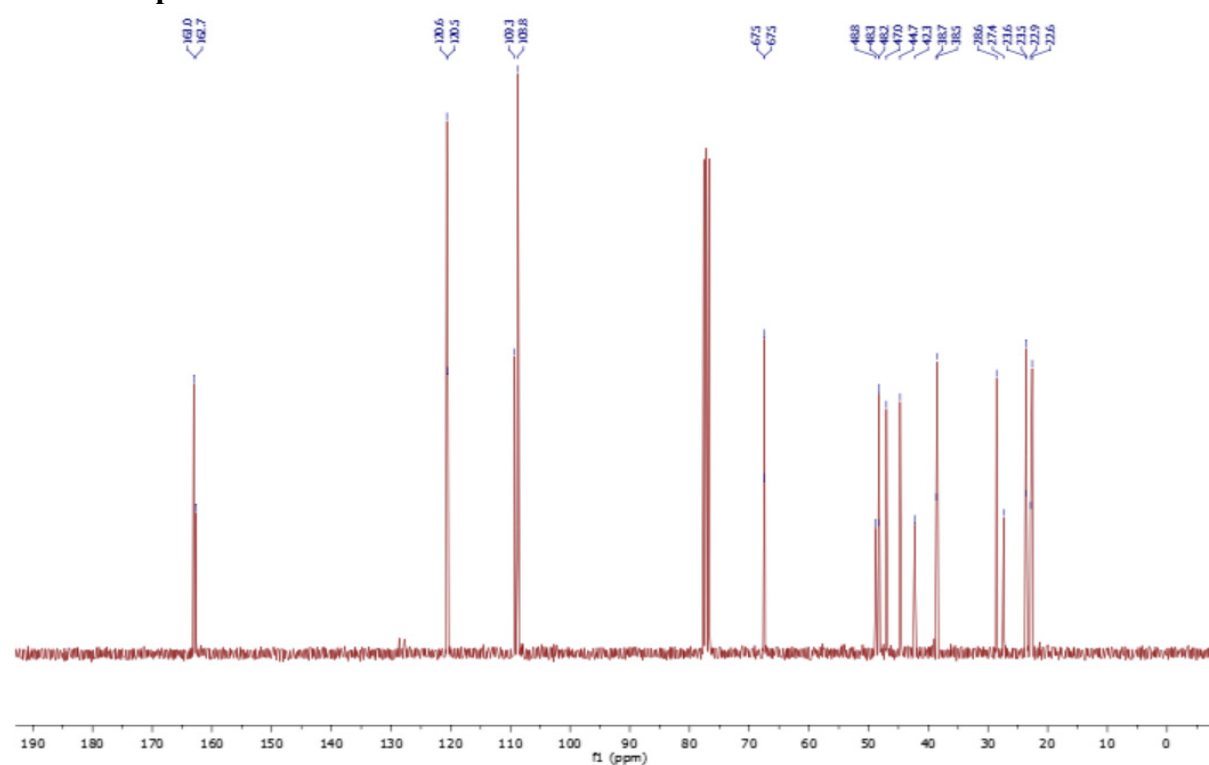


***N*-(2-(1*H*-Pyrrol-1-yl)ethyl)-*N*-(5-hydroxyhexyl)formamide**

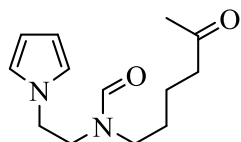
¹H RMN spectrum



¹³C RMN spectrum

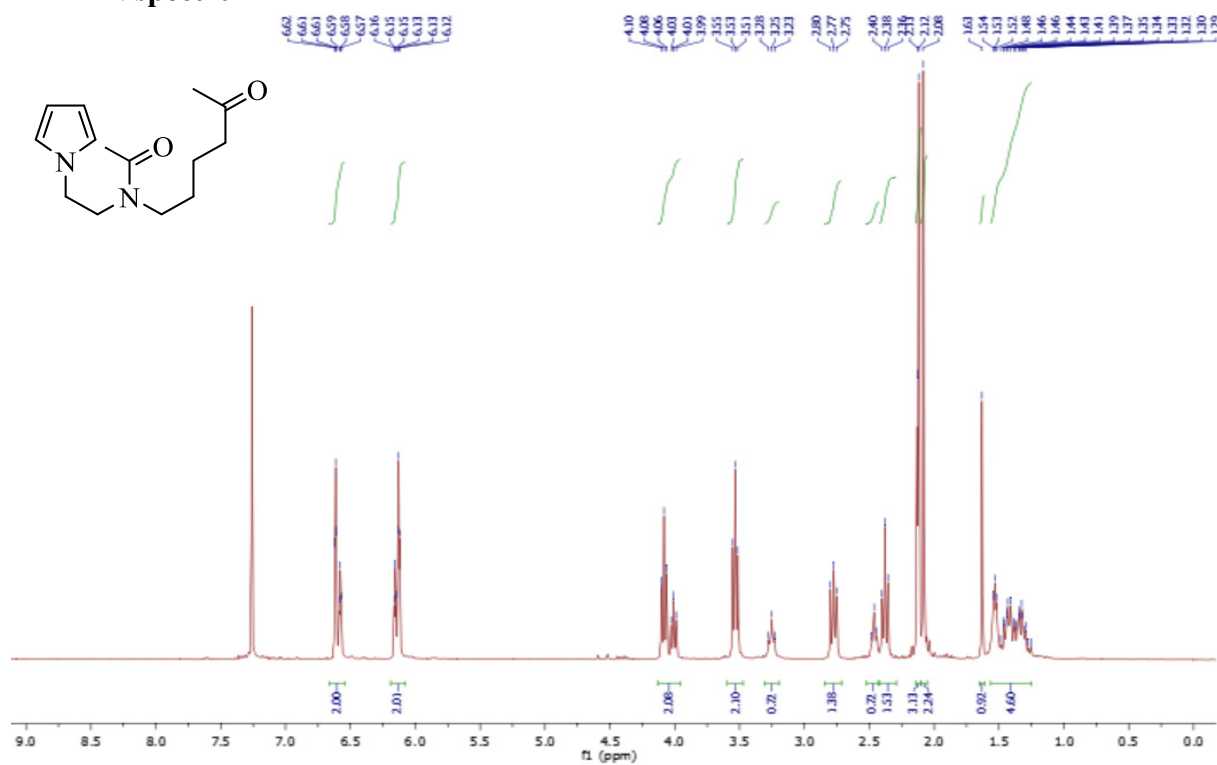


¹H RMN spectrum

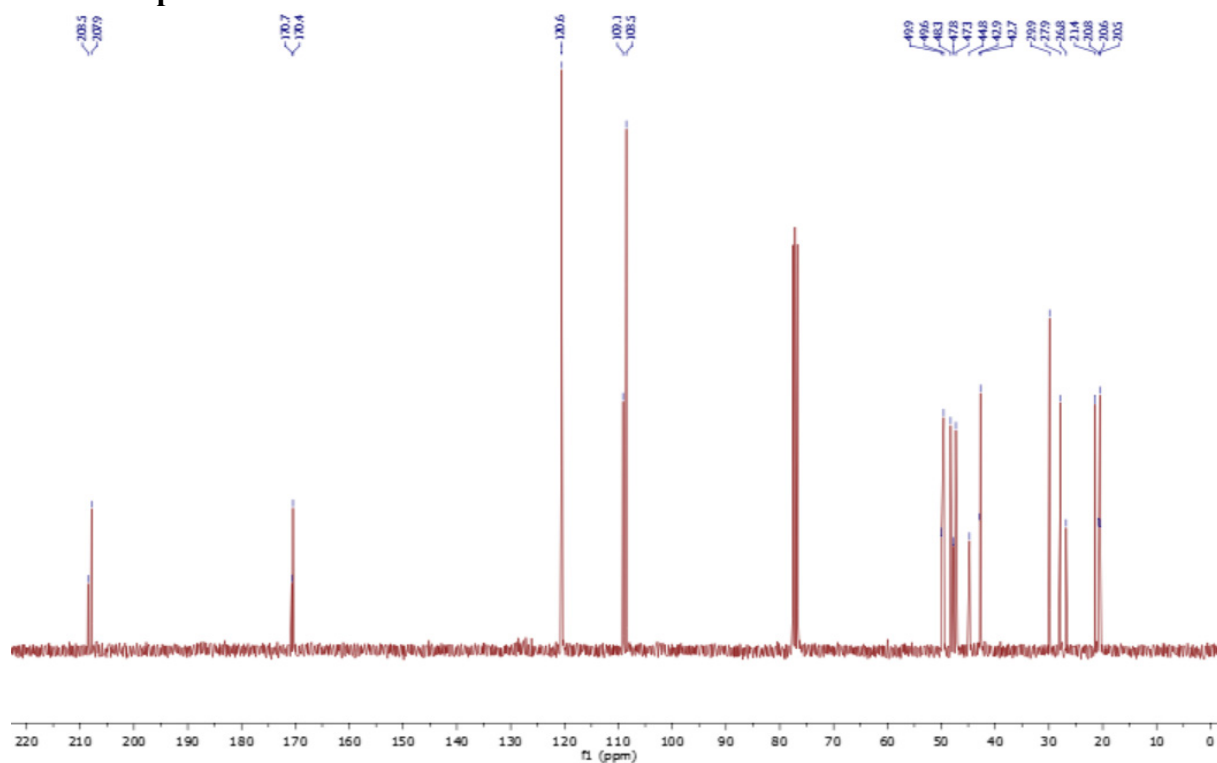


***N*-(2-(1*H*-Pyrrol-1-yl)ethyl)-*N*-(5-oxohexyl)acetamide (39c)**

¹H RMN spectrum

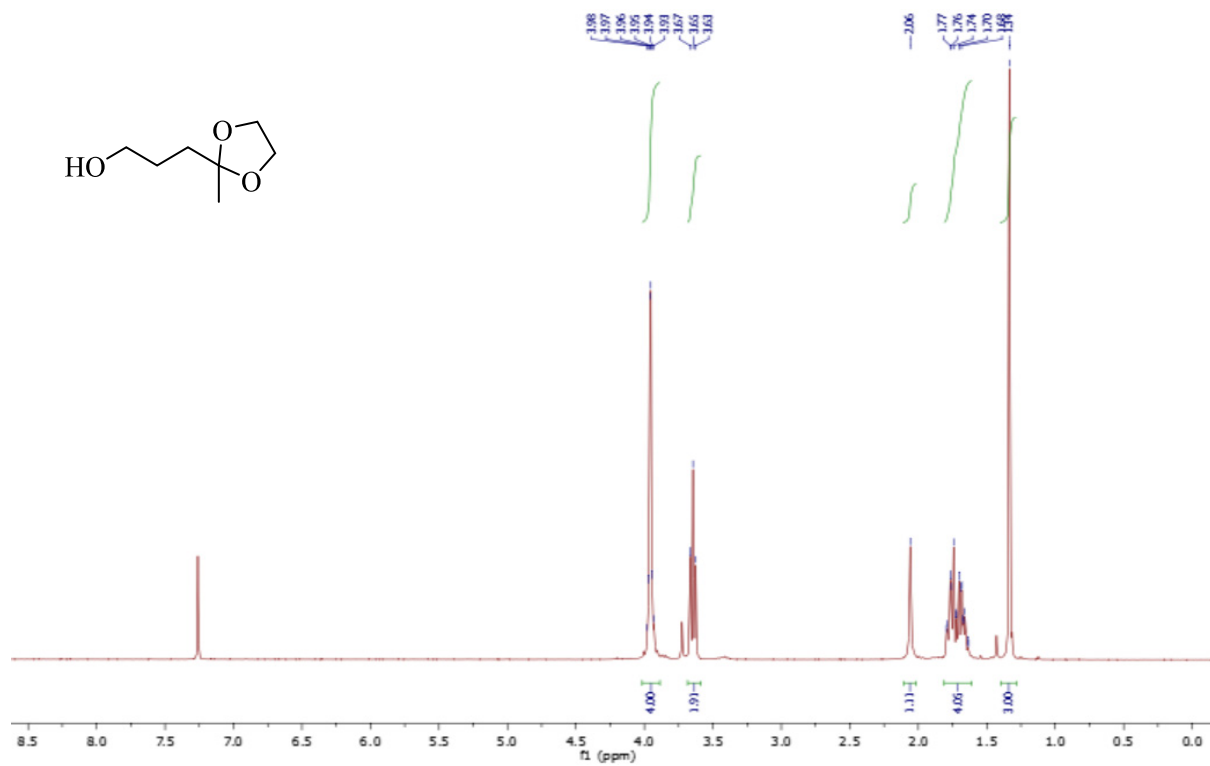


¹³C RMN spectrum

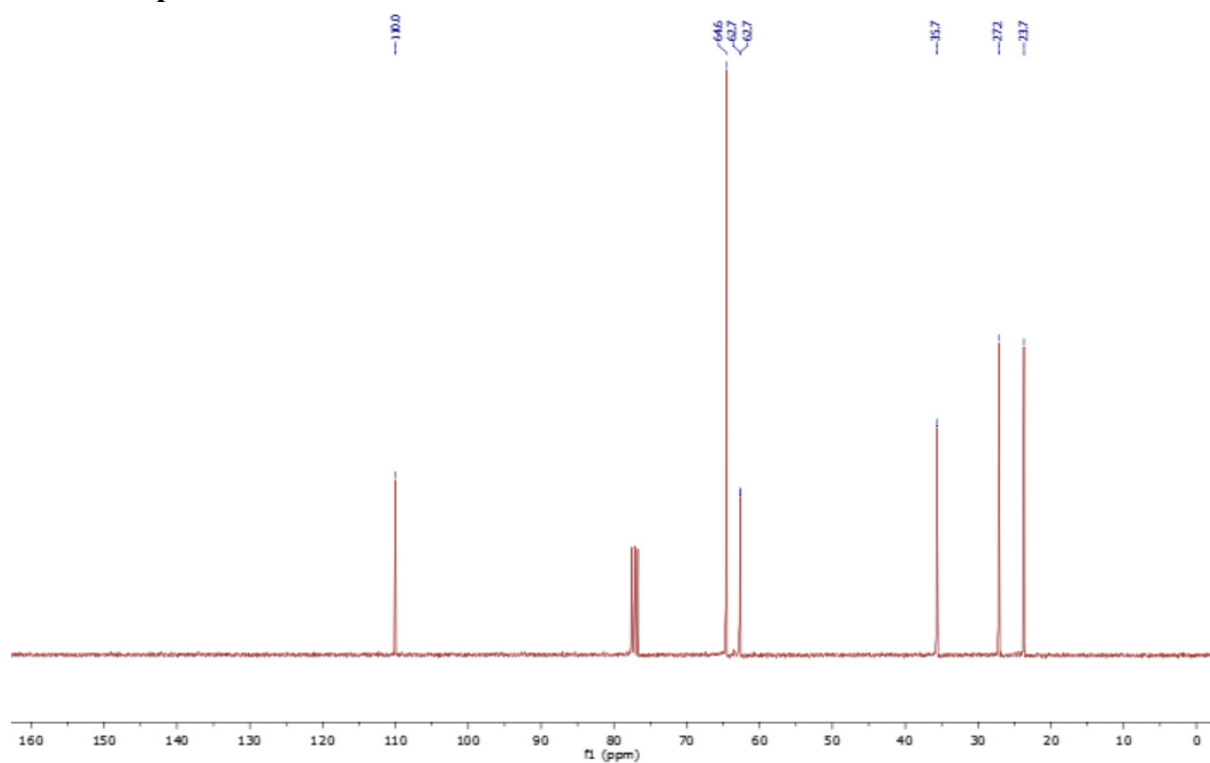


3-(2-Methyl-1,3-dioxolan-2-yl)propan-1-ol (40)

¹H RMN spectrum

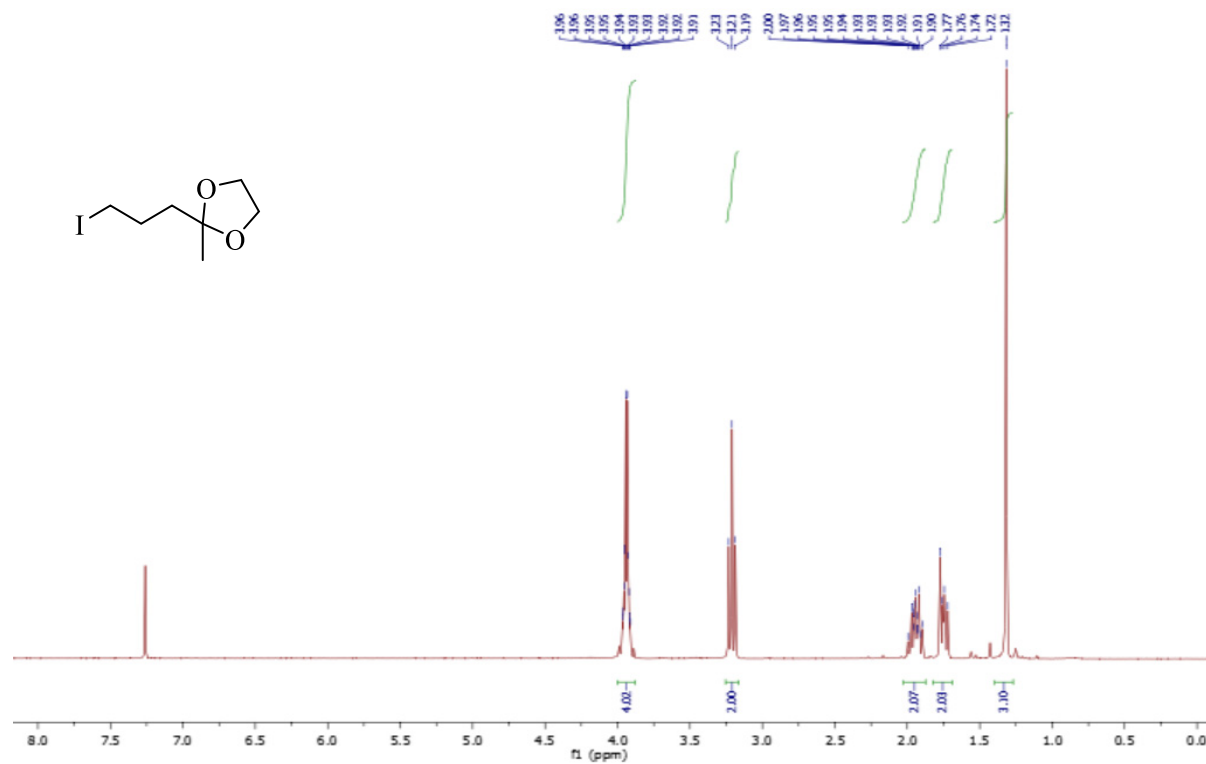


¹³C RMN spectrum

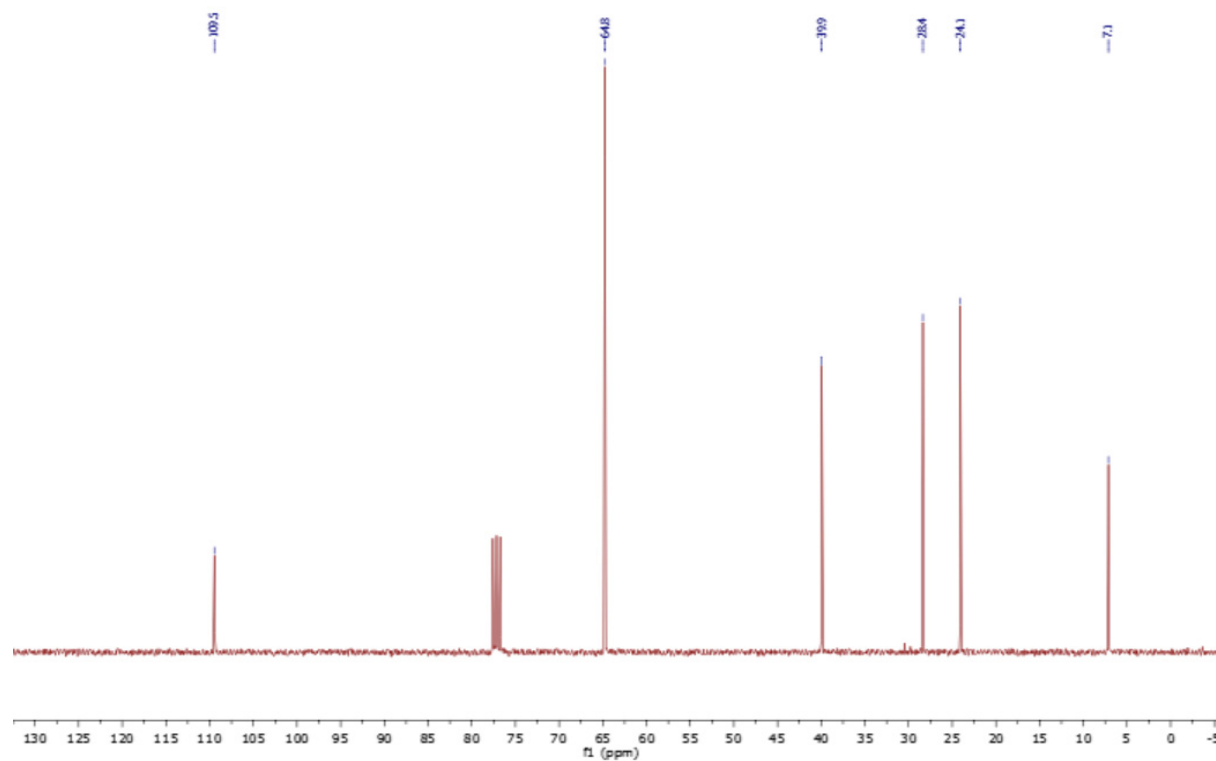


2-(3-Iodopropyl)-2-methyl-1,3-dioxolane (41)

¹H RMN spectrum

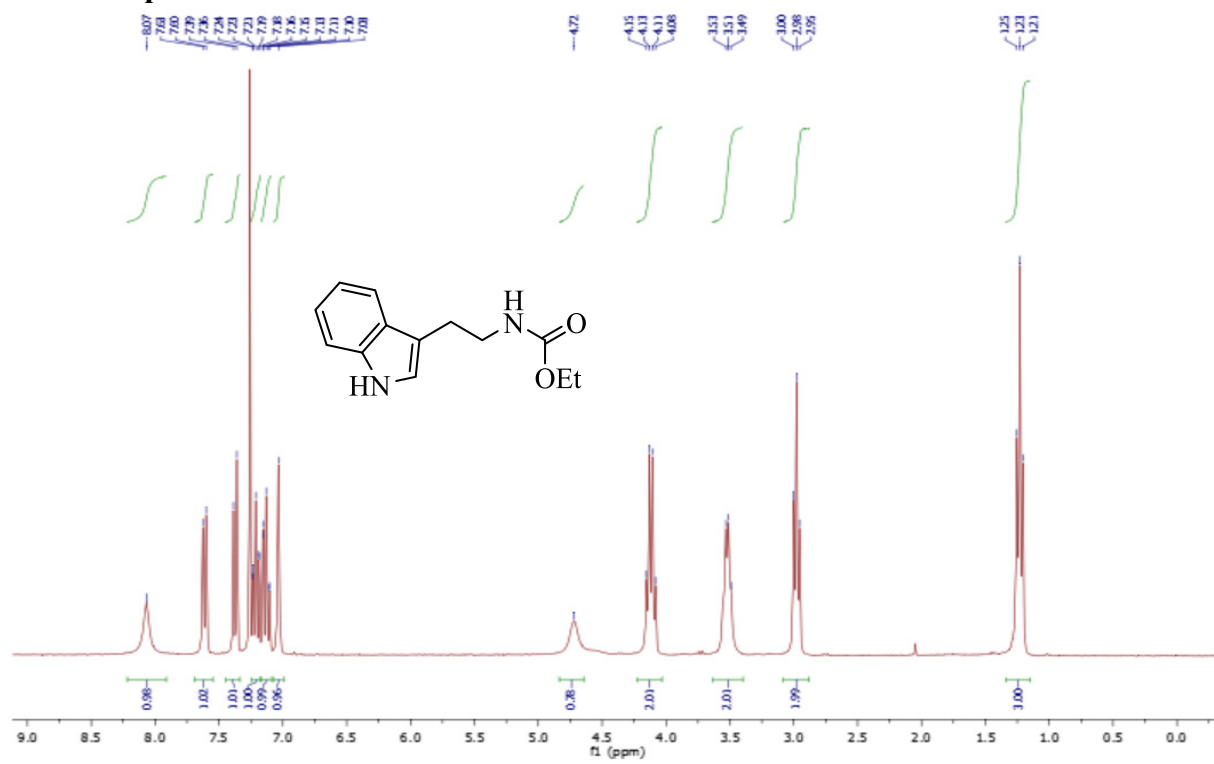


¹³C RMN spectrum

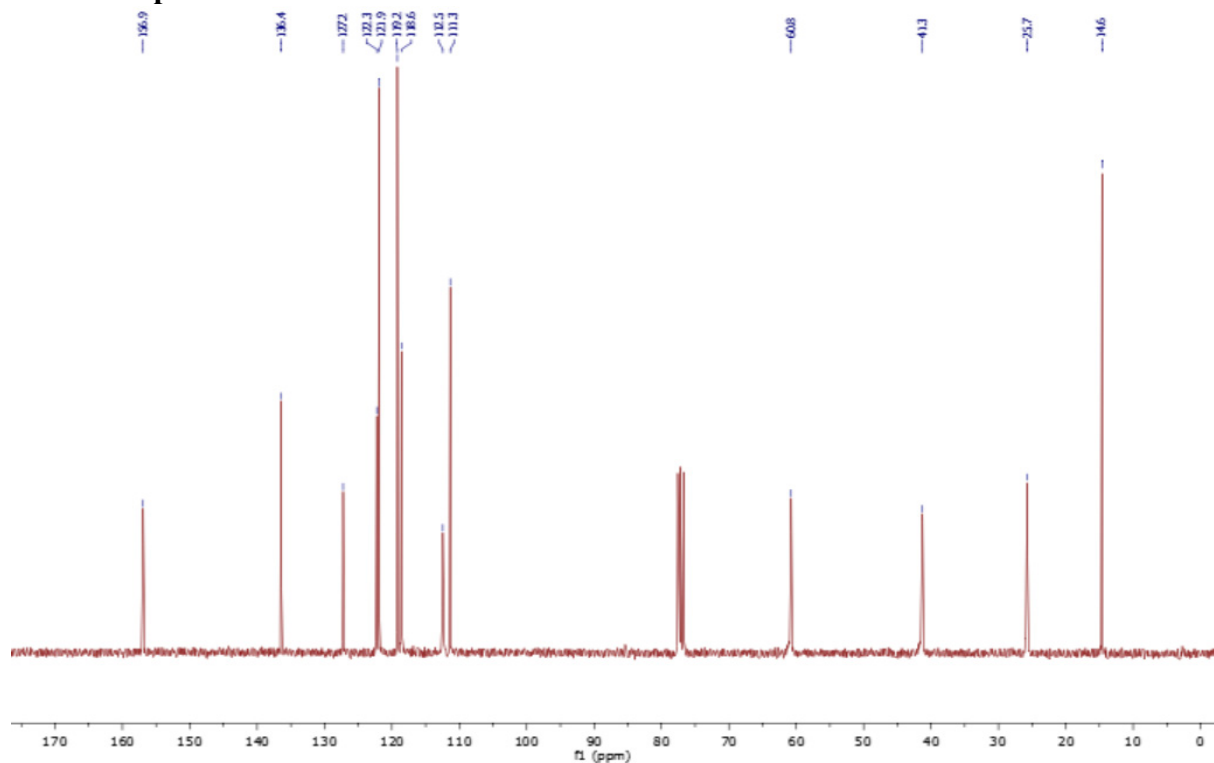


Ethyl (2-(1*H*-indol-3-yl)ethyl)carbamate

¹H RMN spectrum

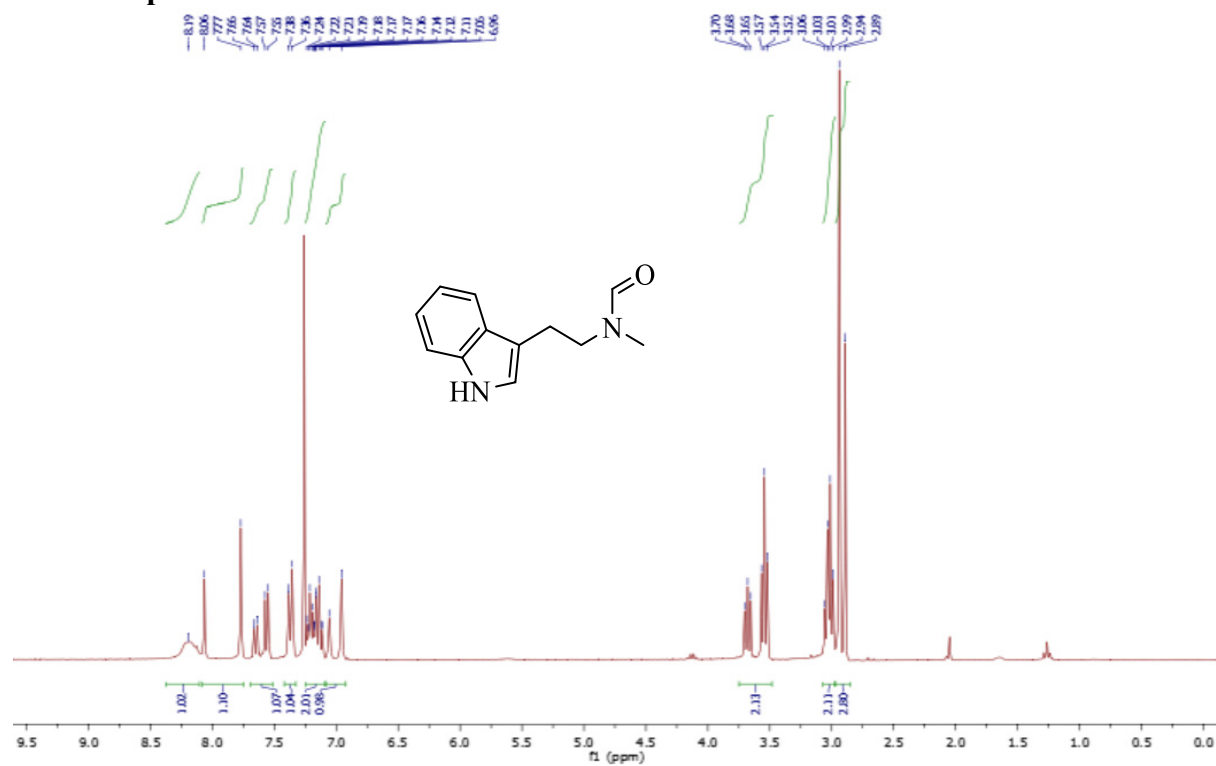


¹³C RMN spectrum

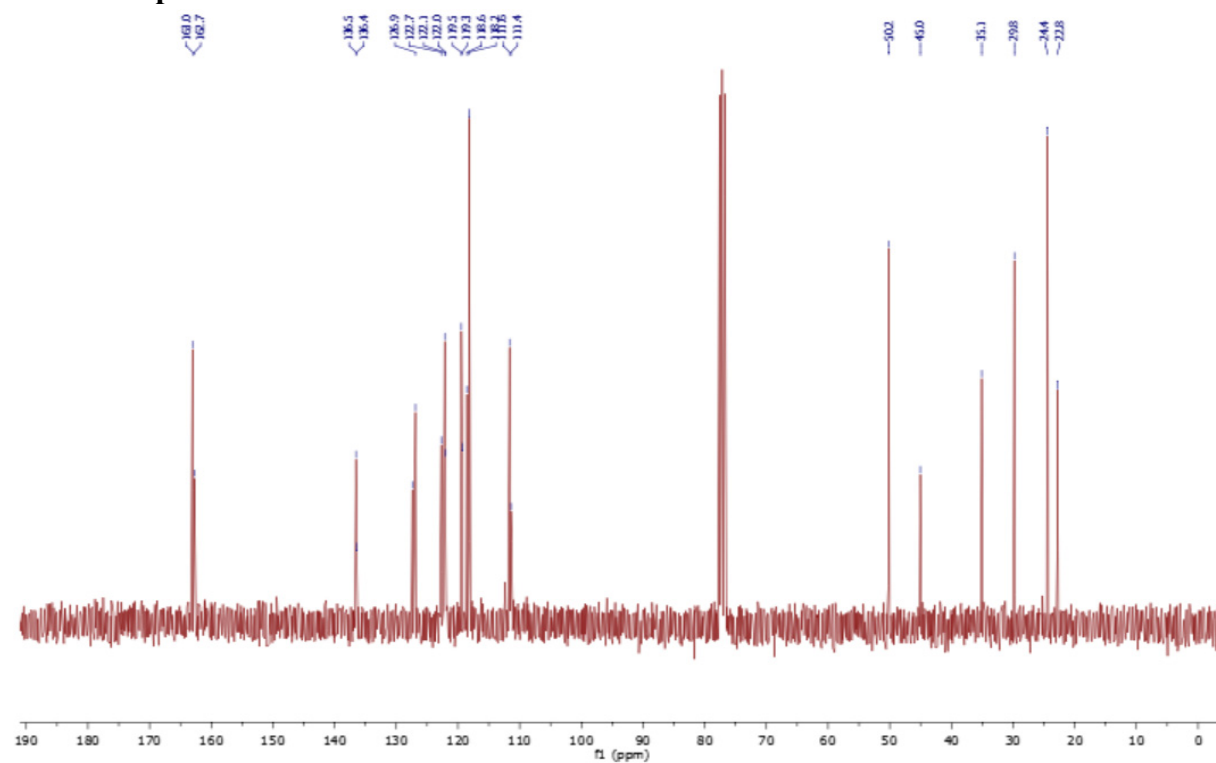


***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-methylformamide (42)**

¹H RMN spectrum

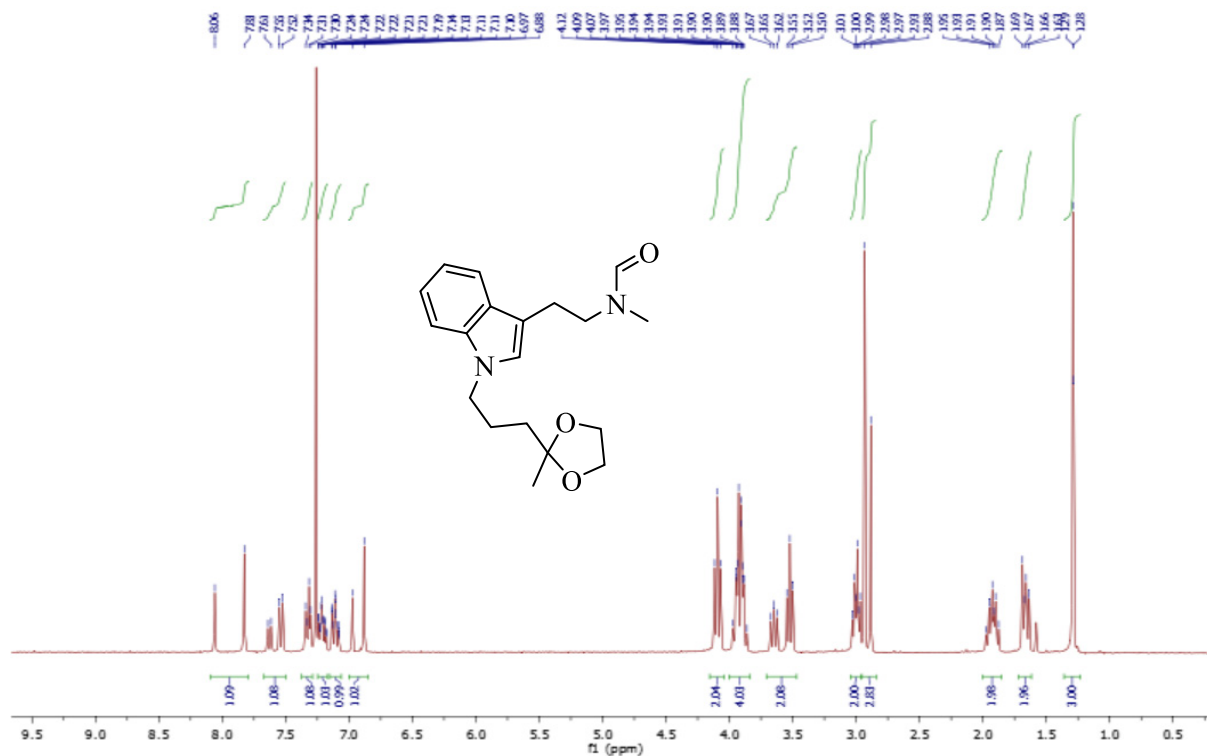


¹³C RMN spectrum

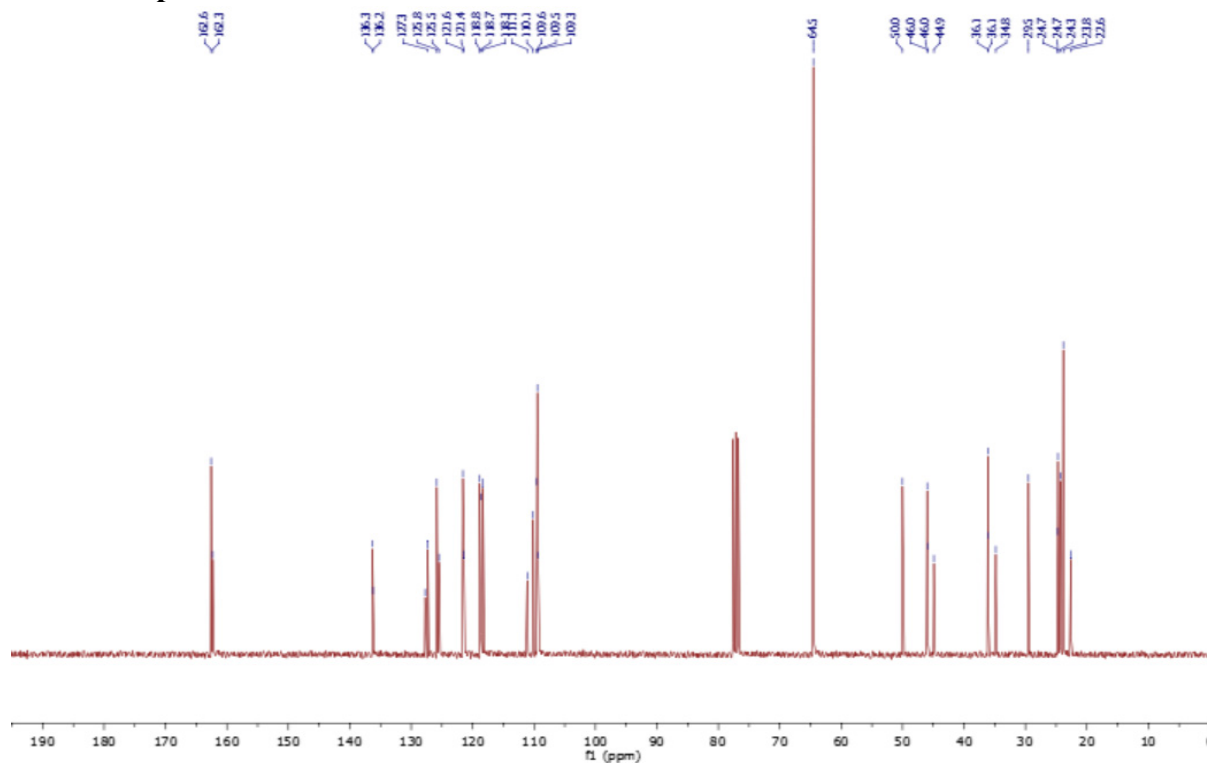


***N*-Methyl-*N*-(2-(1-(3-(2-methyl-1,3-dioxolan-2-yl)propyl)-1*H*-indol-3-yl)ethyl)formamide (43)**

¹H RMN spectrum

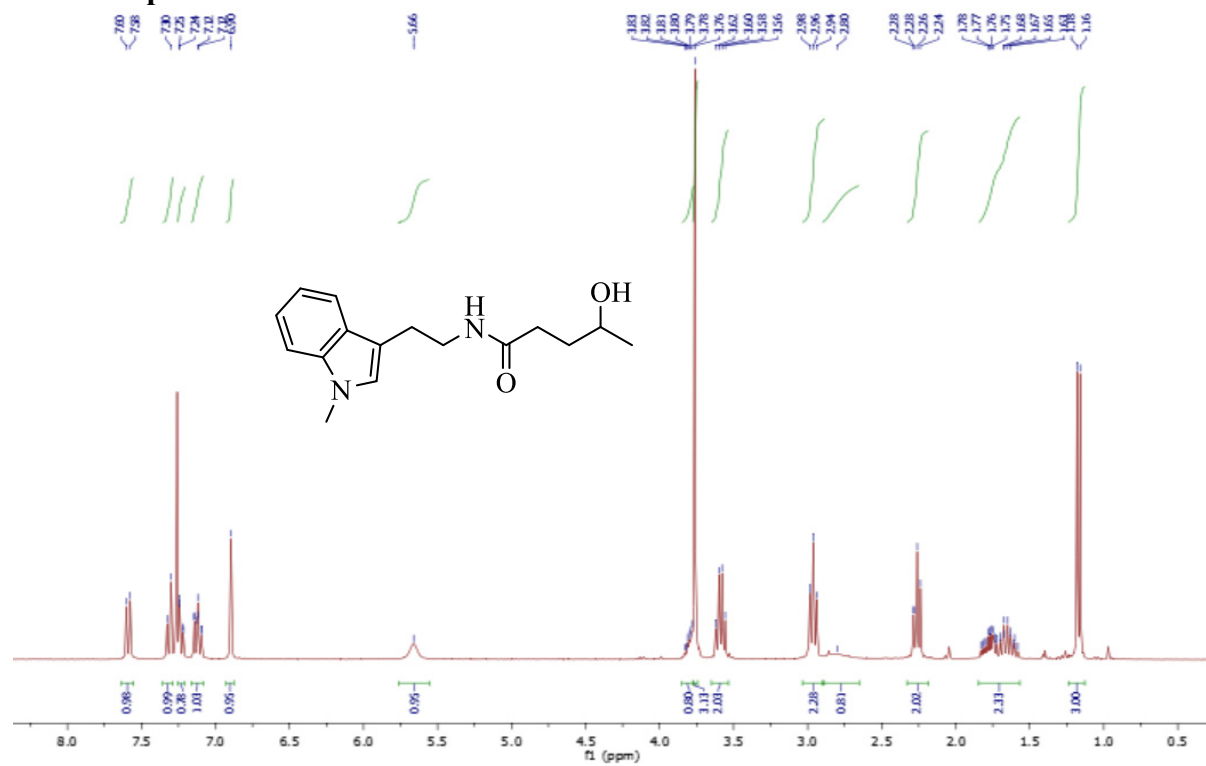


¹³C RMN spectrum

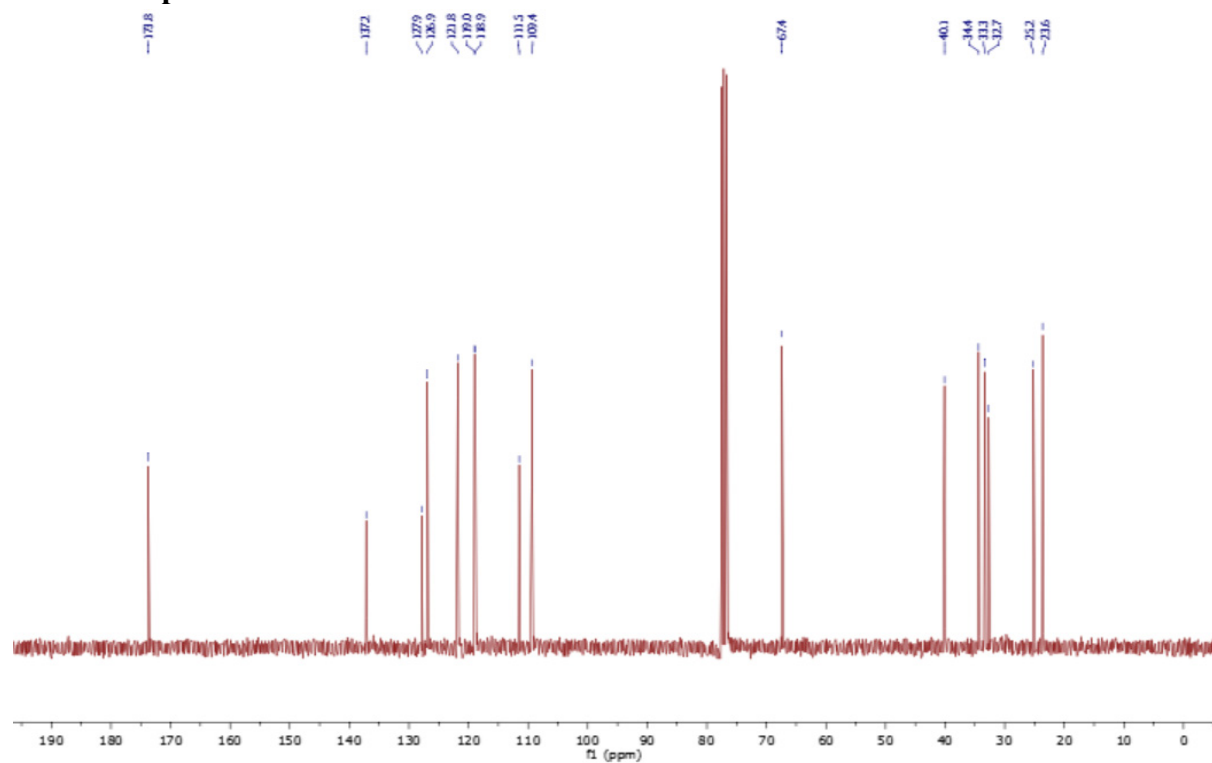


4-Hydroxy-N-(2-(1-methyl-1H-indol-3-yl)ethyl)pentanamide

¹H RMN spectrum

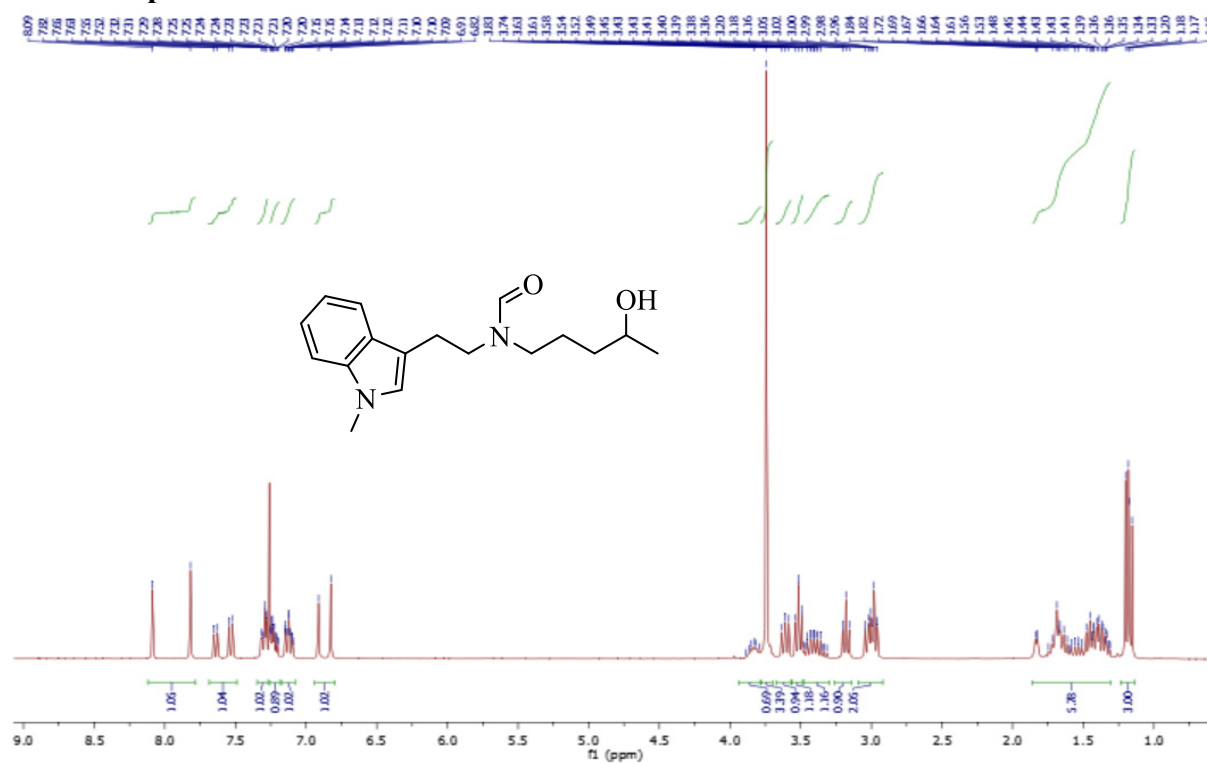


¹³C RMN spectrum

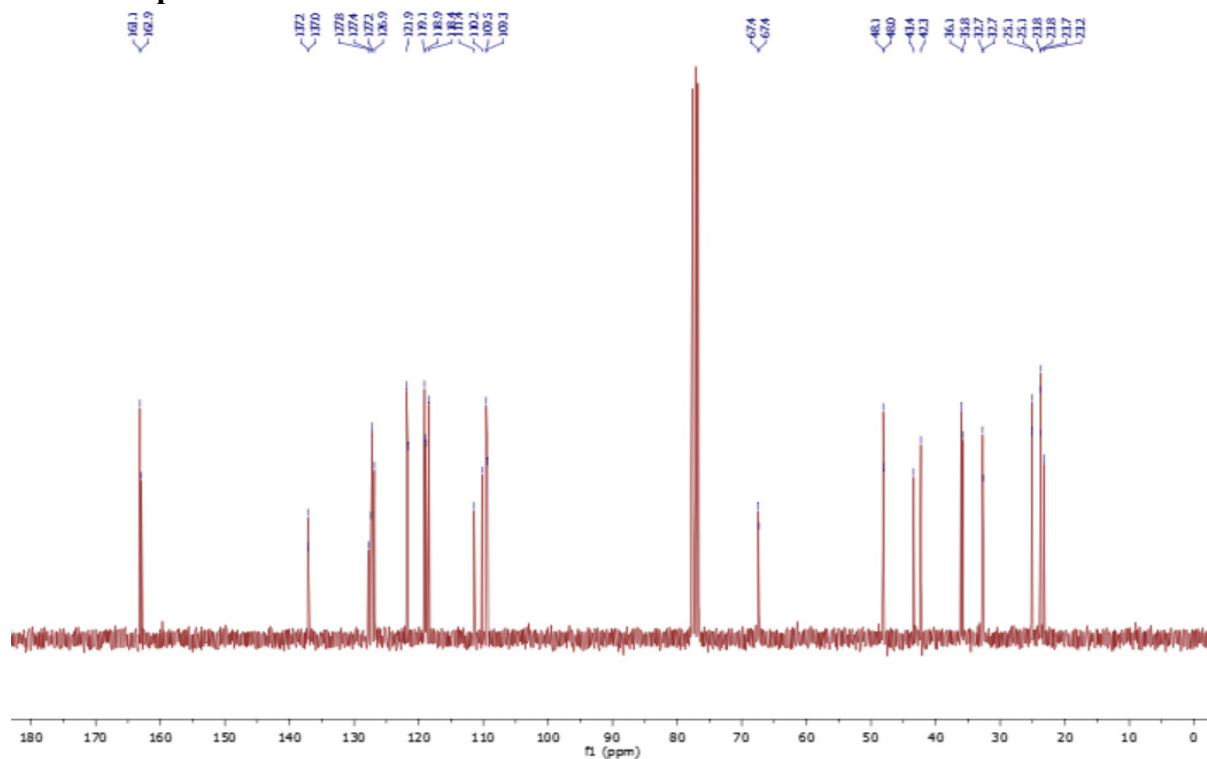


***N*-(4-Hydroxypentyl)-*N*-(2-(1-methyl-1*H*-indol-3-yl)ethyl)formamide**

¹H RMN spectrum

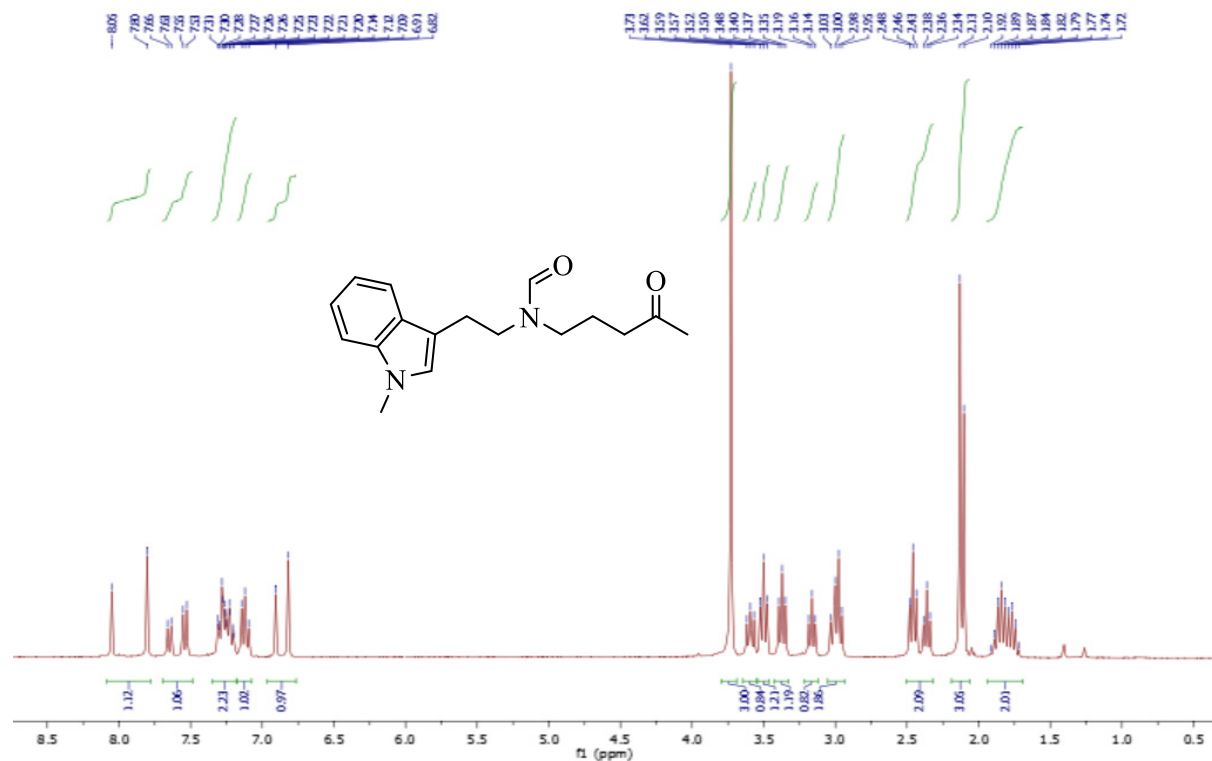


¹³C RMN spectrum

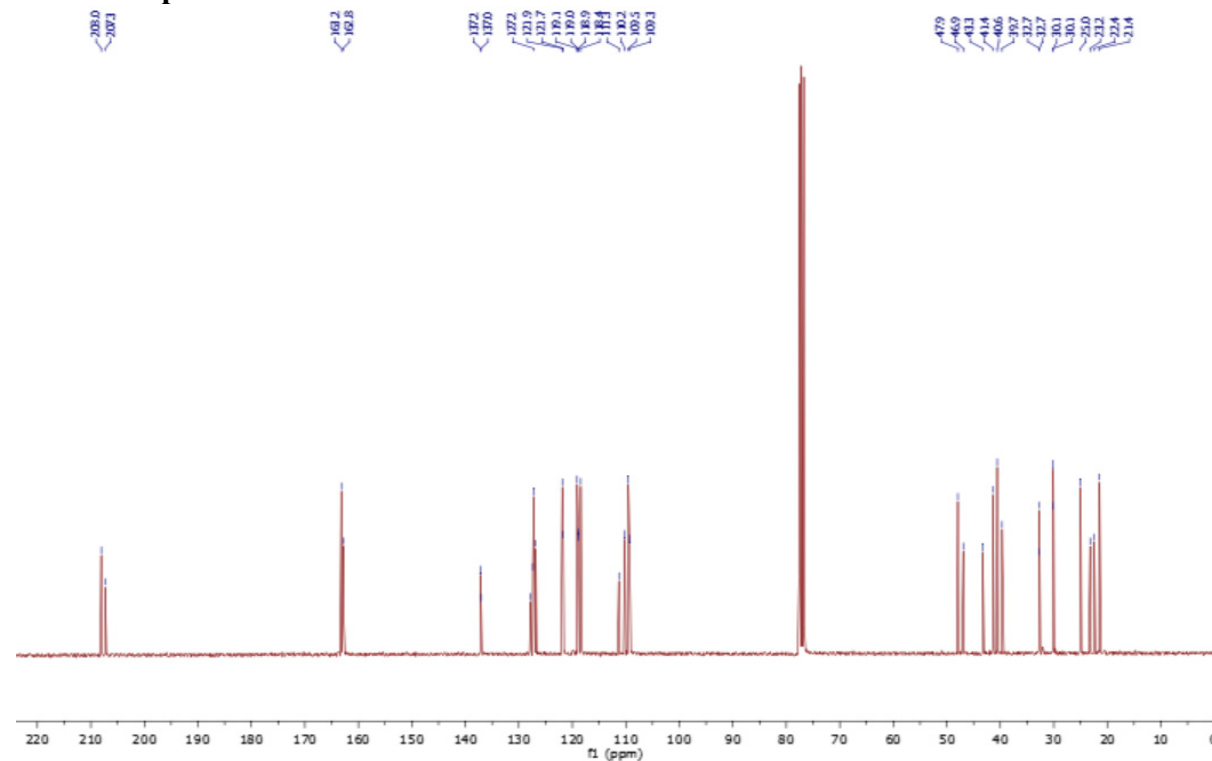


***N*-(2-(1-Methyl-1*H*-indol-3-yl)ethyl)-*N*-(4-oxopentyl)formamide (44a)**

¹H RMN spectrum

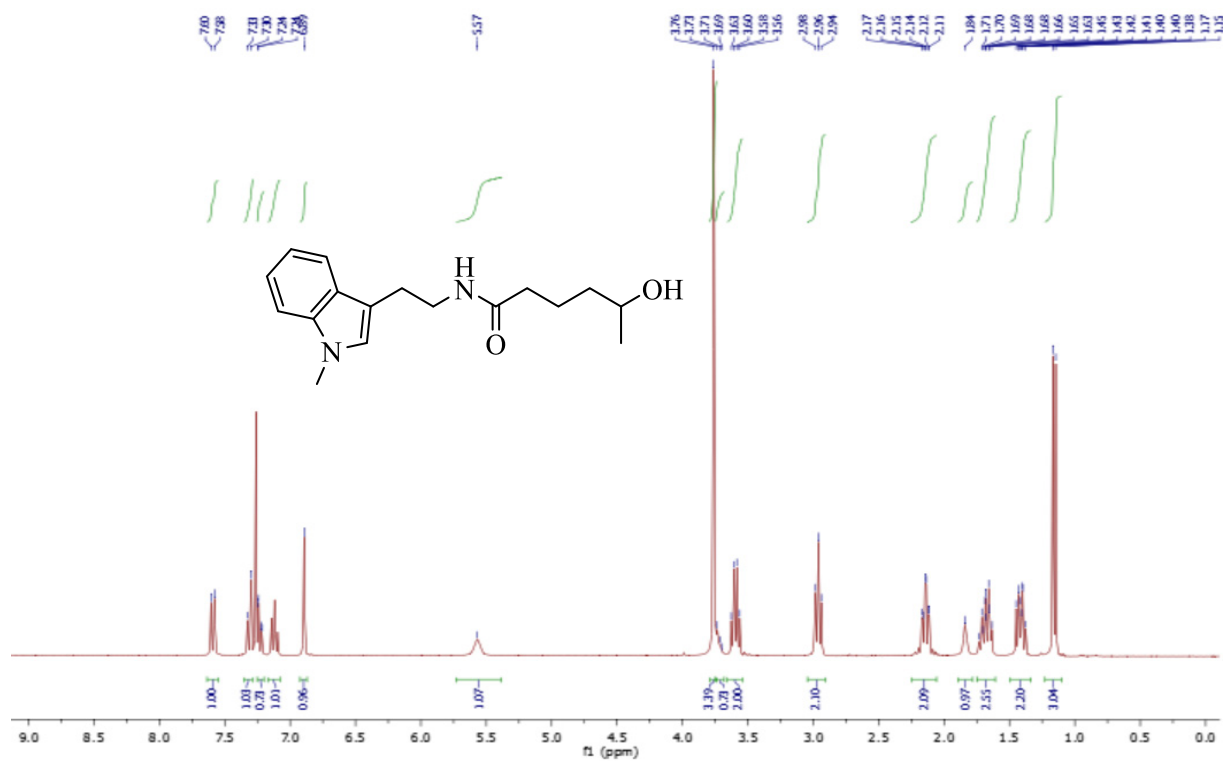


¹³C RMN spectrum

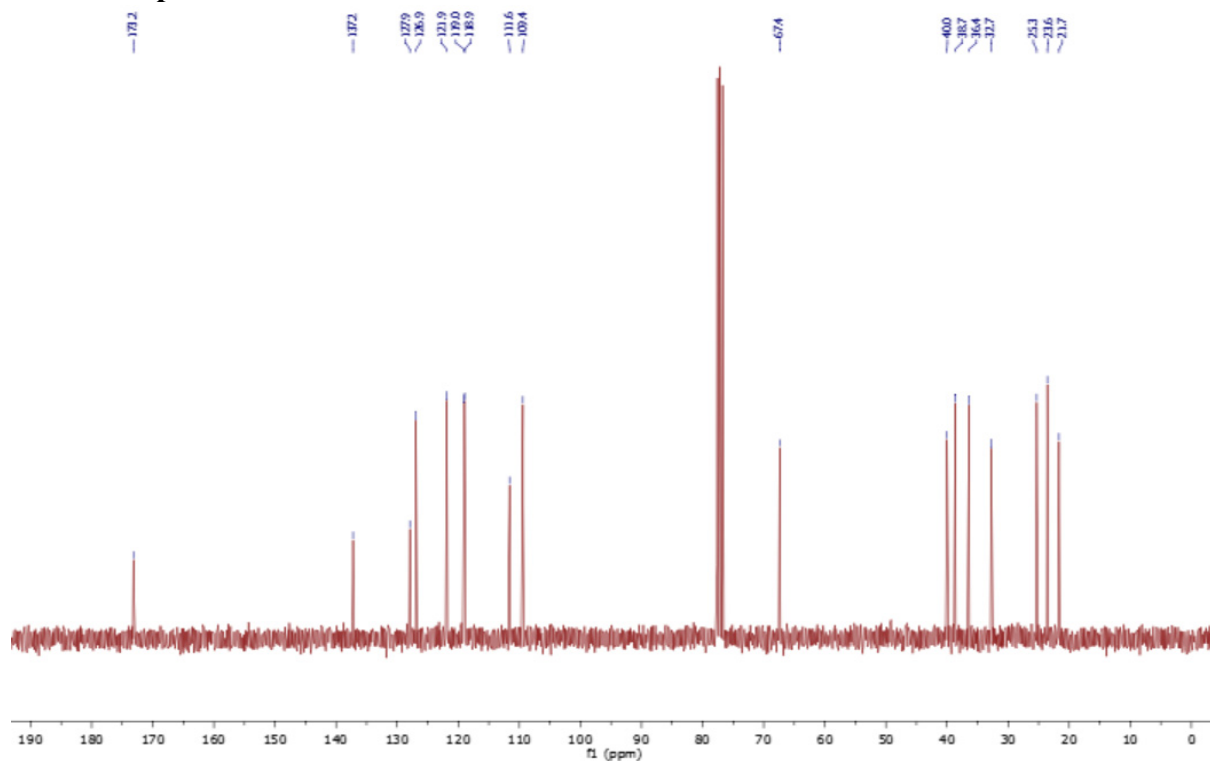


5-Hydroxy-N-(2-(1-methyl-1H-indol-3-yl)ethyl)hexanamide

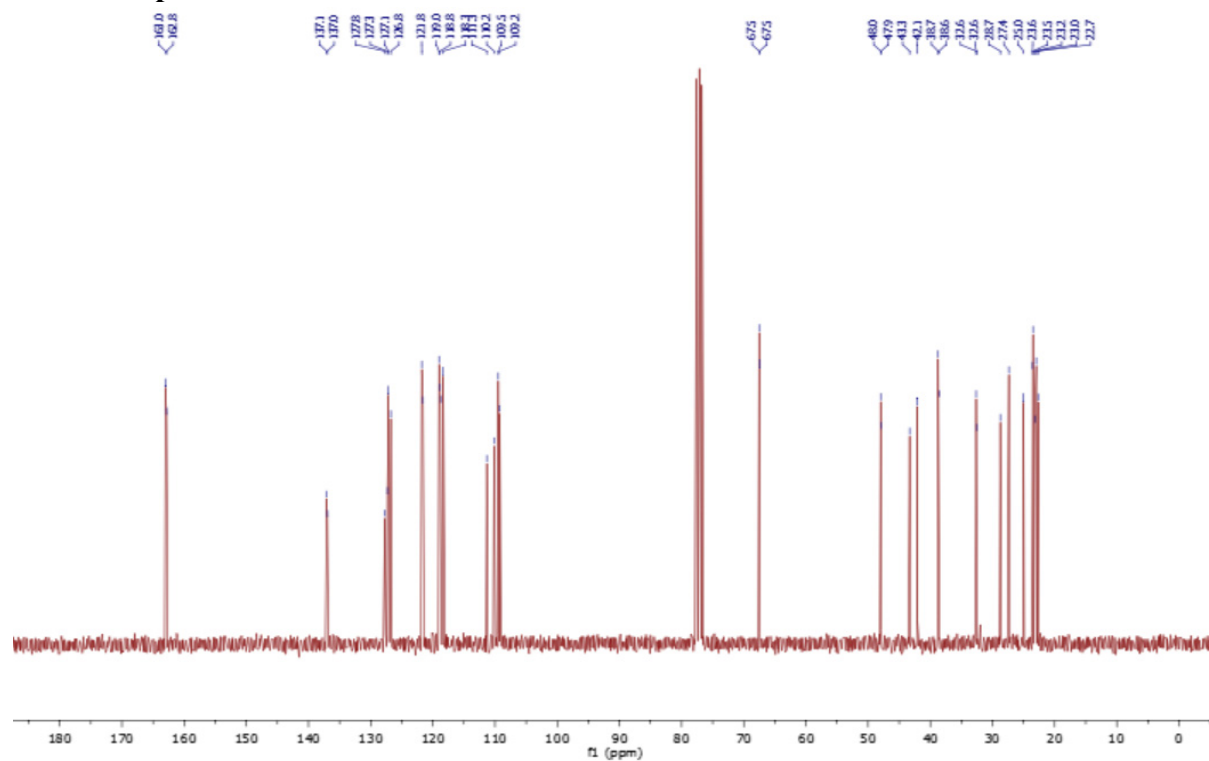
¹H RMN spectrum



¹³C RMN spectrum

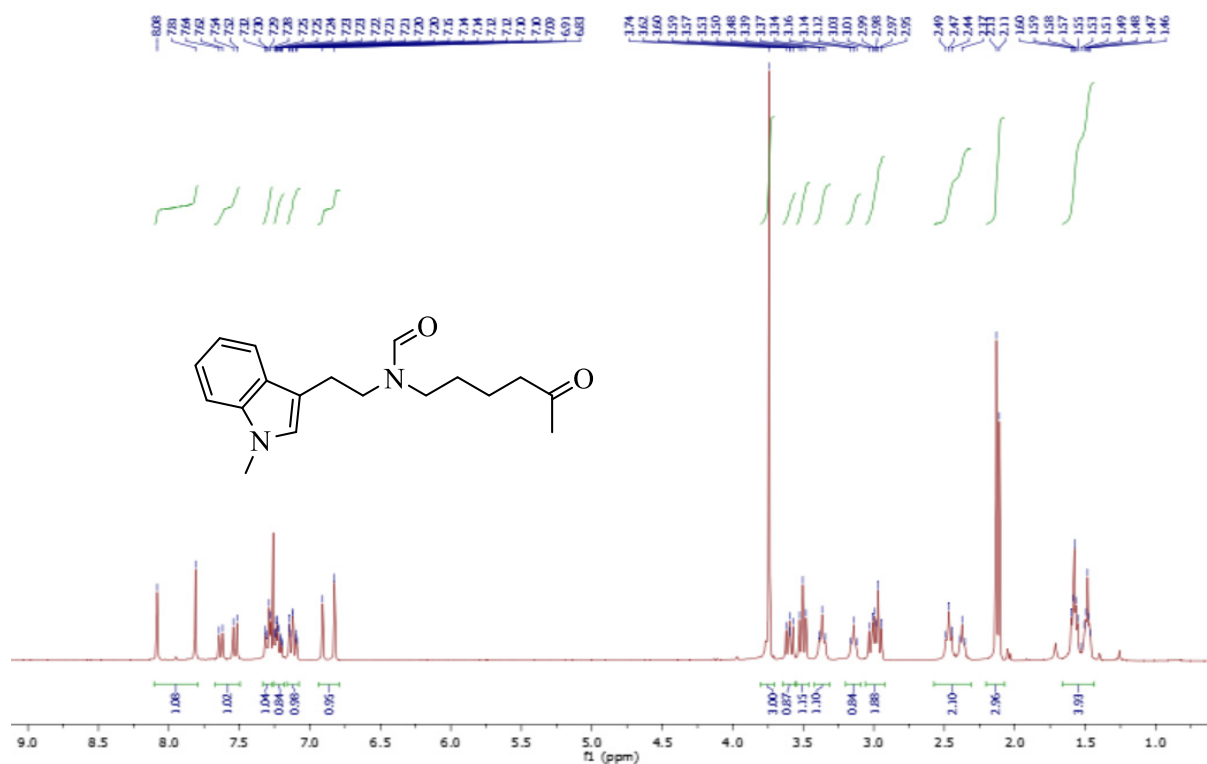


¹H RMN spectrum

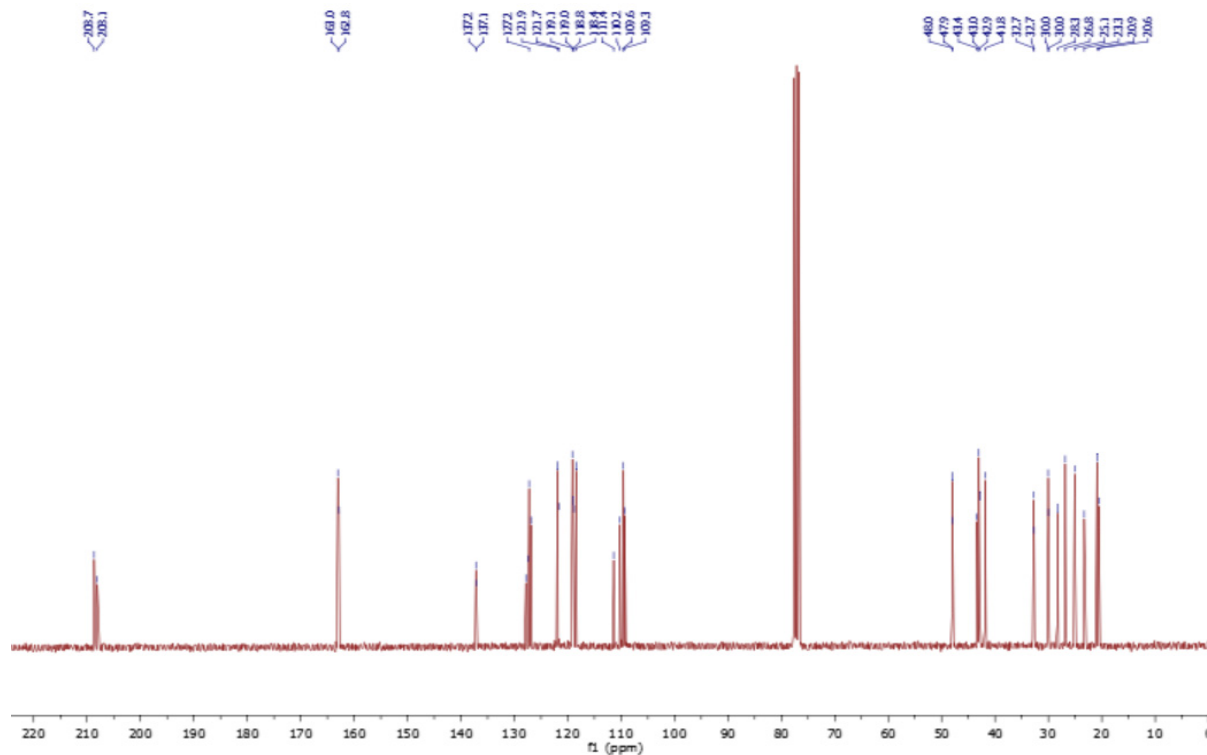


***N*-(2-(1-Methyl-1*H*-indol-3-yl)ethyl)-*N*-(5-oxohexyl)formamide (44b)**

¹H RMN spectrum

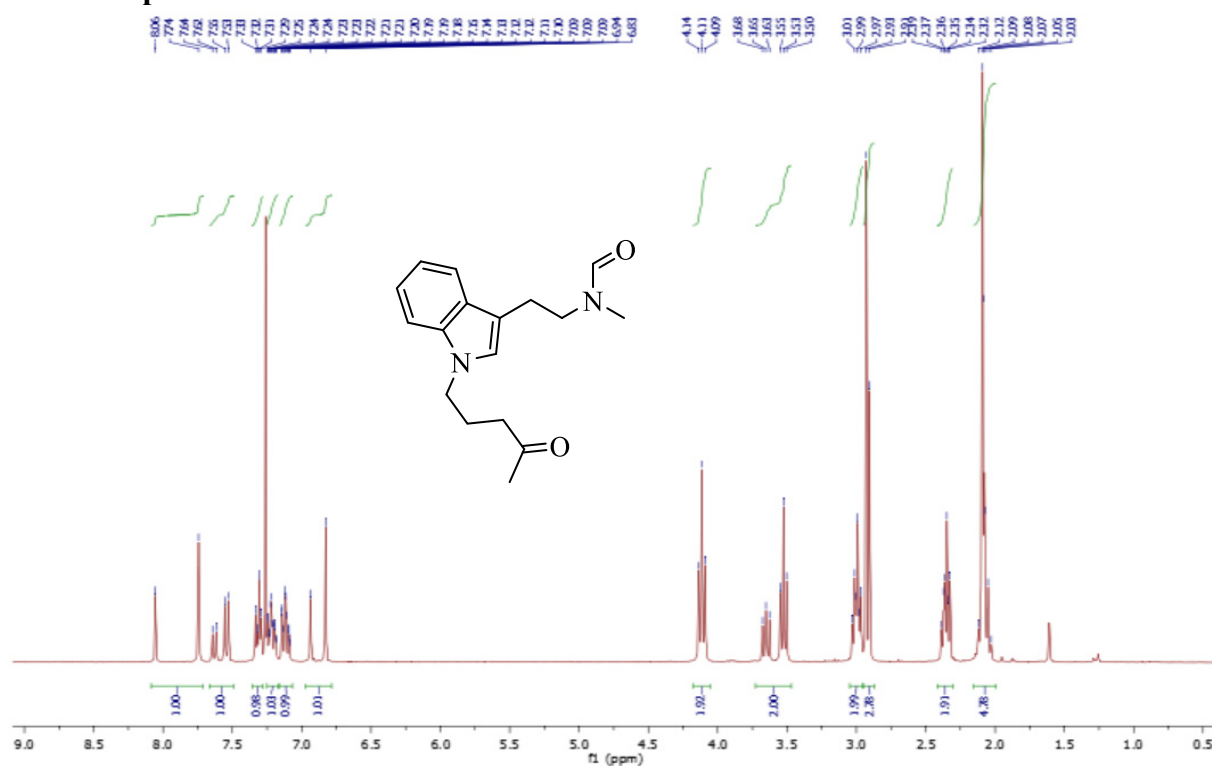


¹³C RMN spectrum

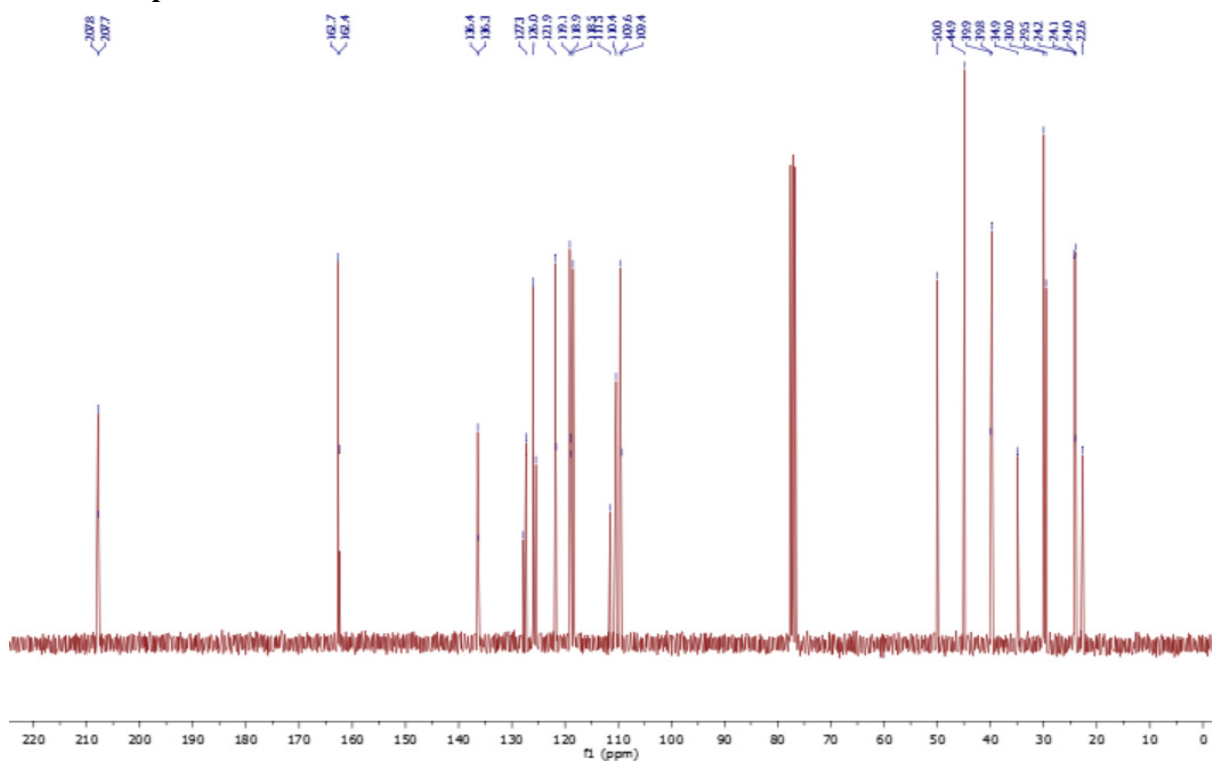


***N*-Methyl-*N*-(2-(1-(4-oxopentyl)-1*H*-indol-3-yl)ethyl)formamide (44c)**

¹H RMN spectrum

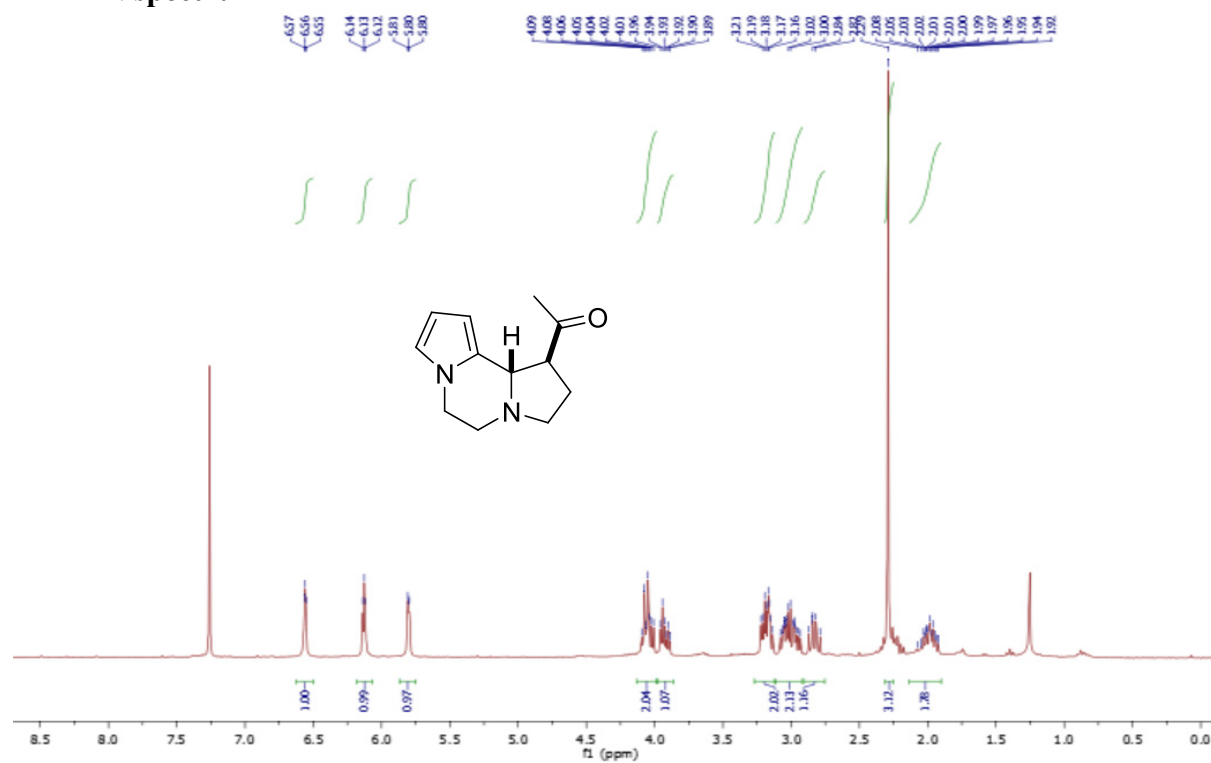


¹³C RMN spectrum

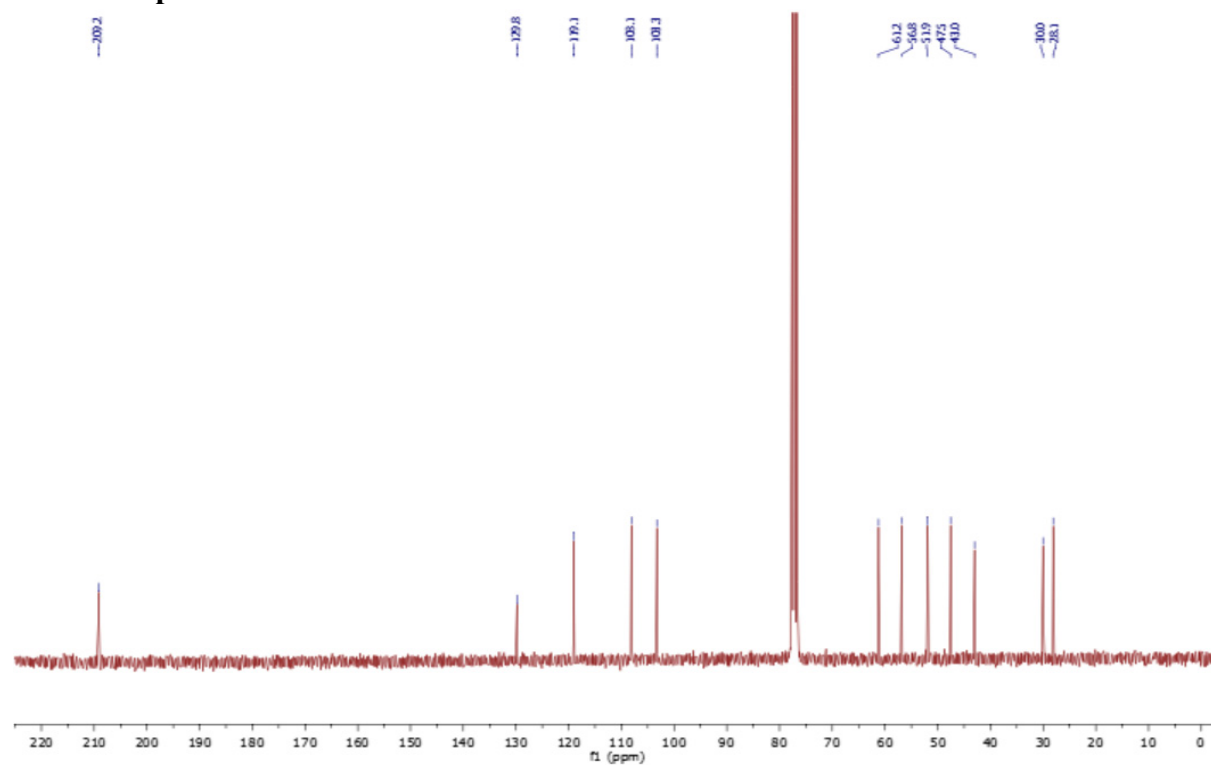


***cis*-1-(1,2,3,5,6,10b-Hexahydroyrrolo[1,2-*a*:2',1'-*c*]pyrazin-1-yl)ethan-1-one (49a)**

¹H RMN spectrum

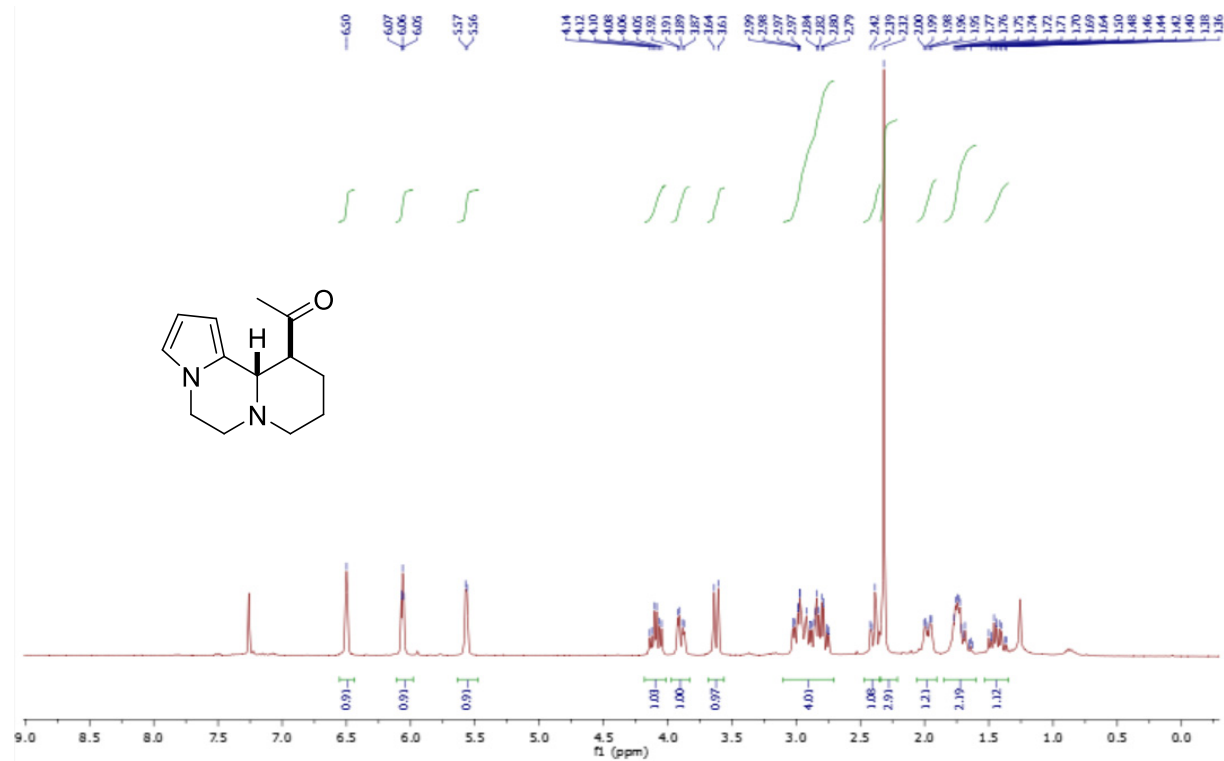


¹³C RMN spectrum

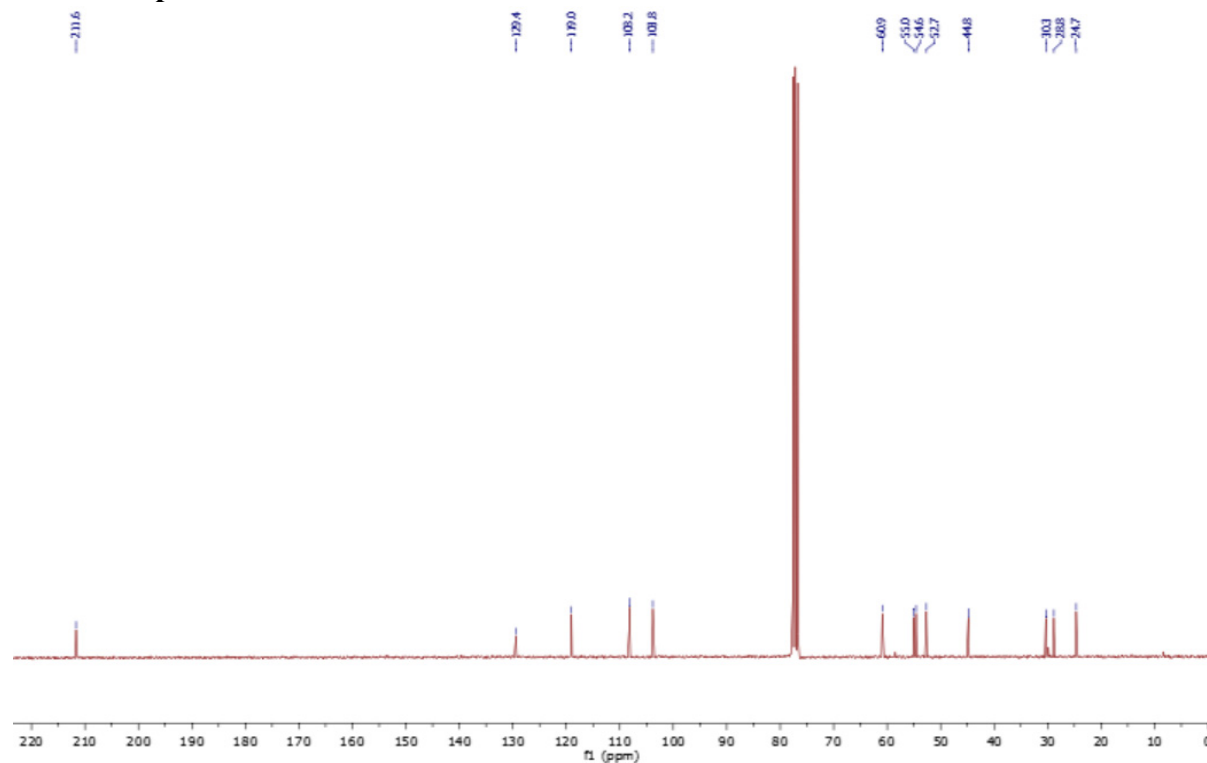


***cis*-1-(5,6,9,10,11,11a-Hexahydro-8*H*-pyrido[1,2-*a*]pyrrolo[2,1-*c*]pyrazin-11-yl)ethan-1-one (49b)**

¹H RMN spectrum

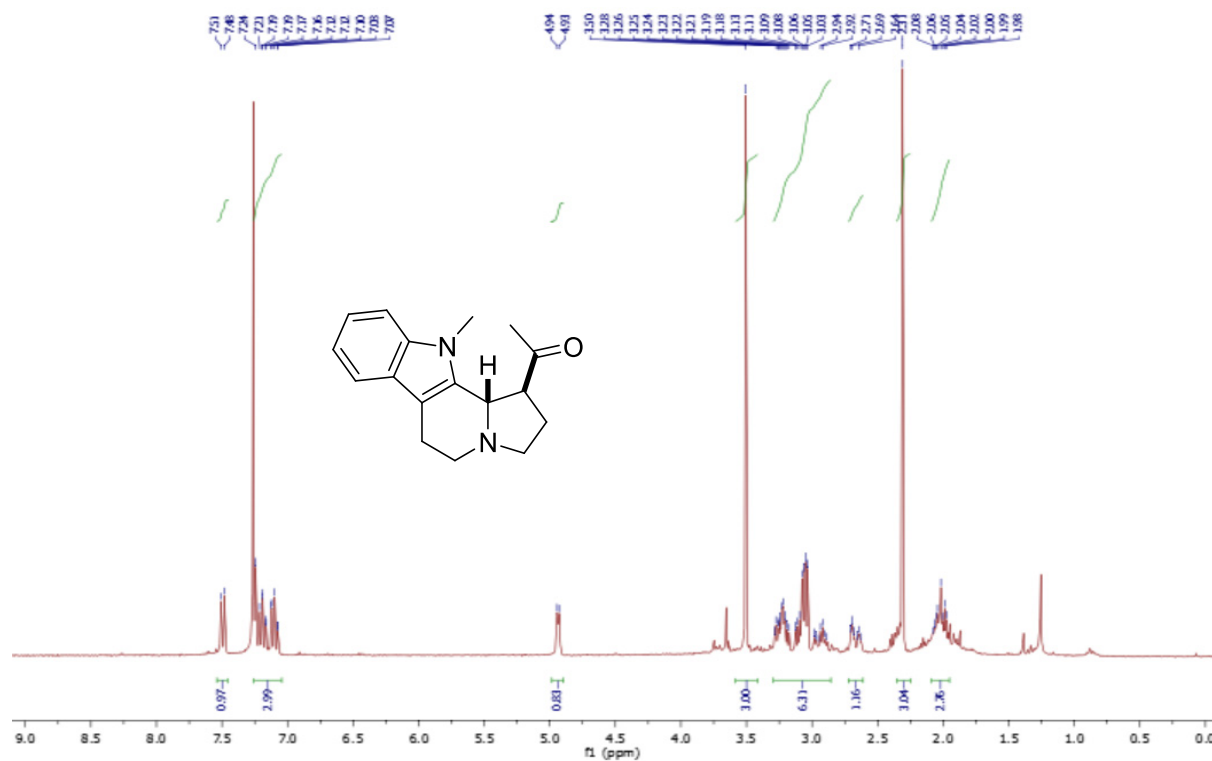


¹³C RMN spectrum

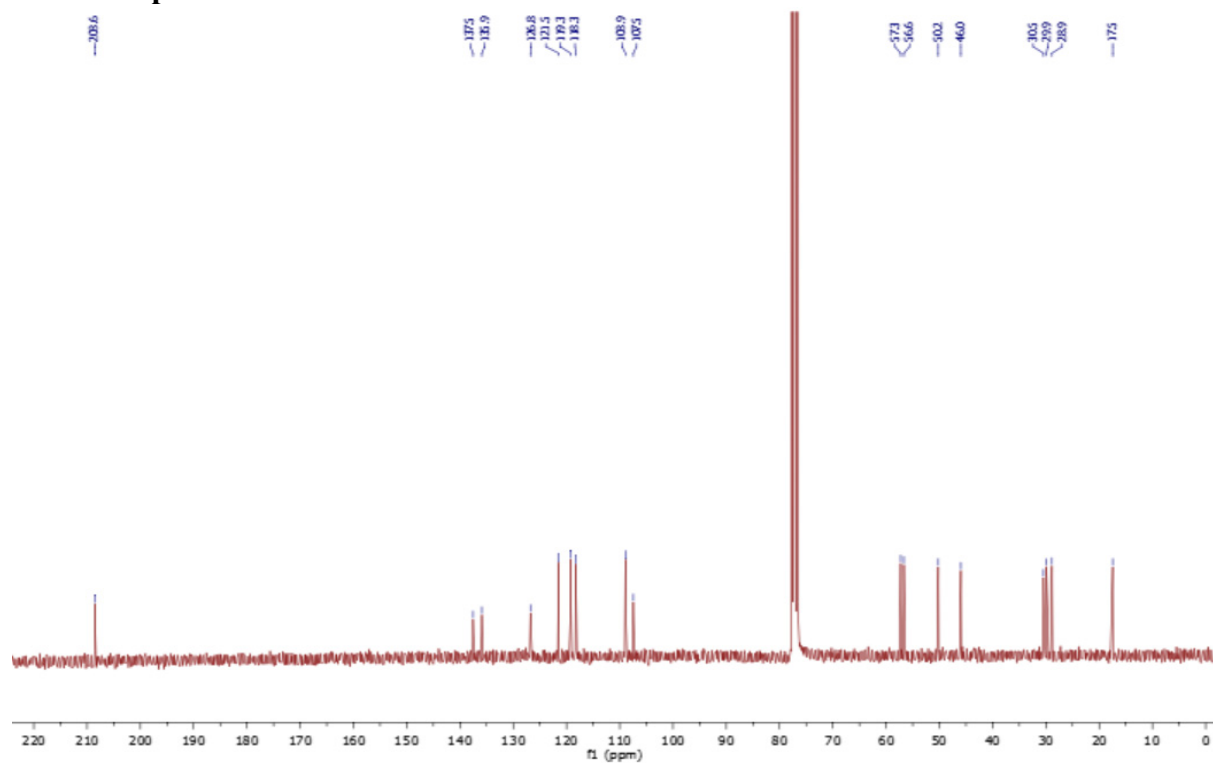


***cis*-1-(11-Methyl-2,3,5,6,11,11b-hexahydro-1*H*-indolizino[8,7-*b*]indol-1-yl)ethan-1-one (50a)**

¹H RMN spectrum

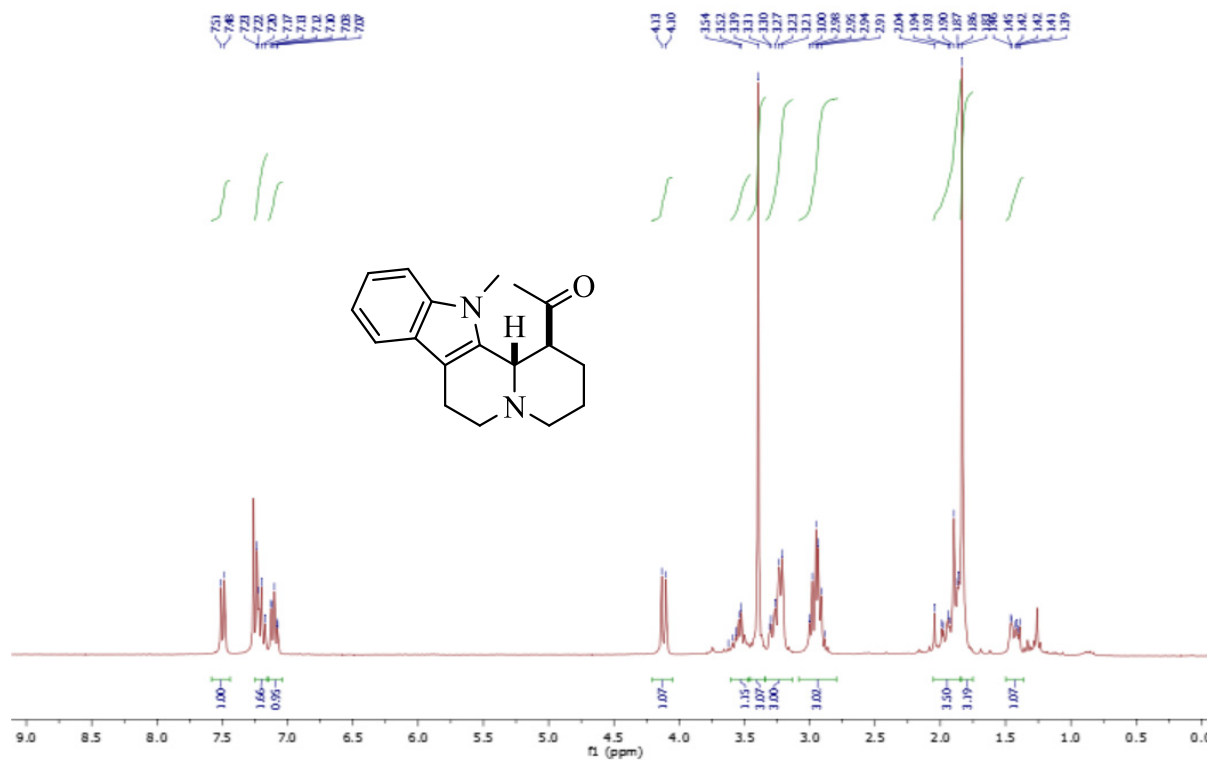


¹³C RMN spectrum

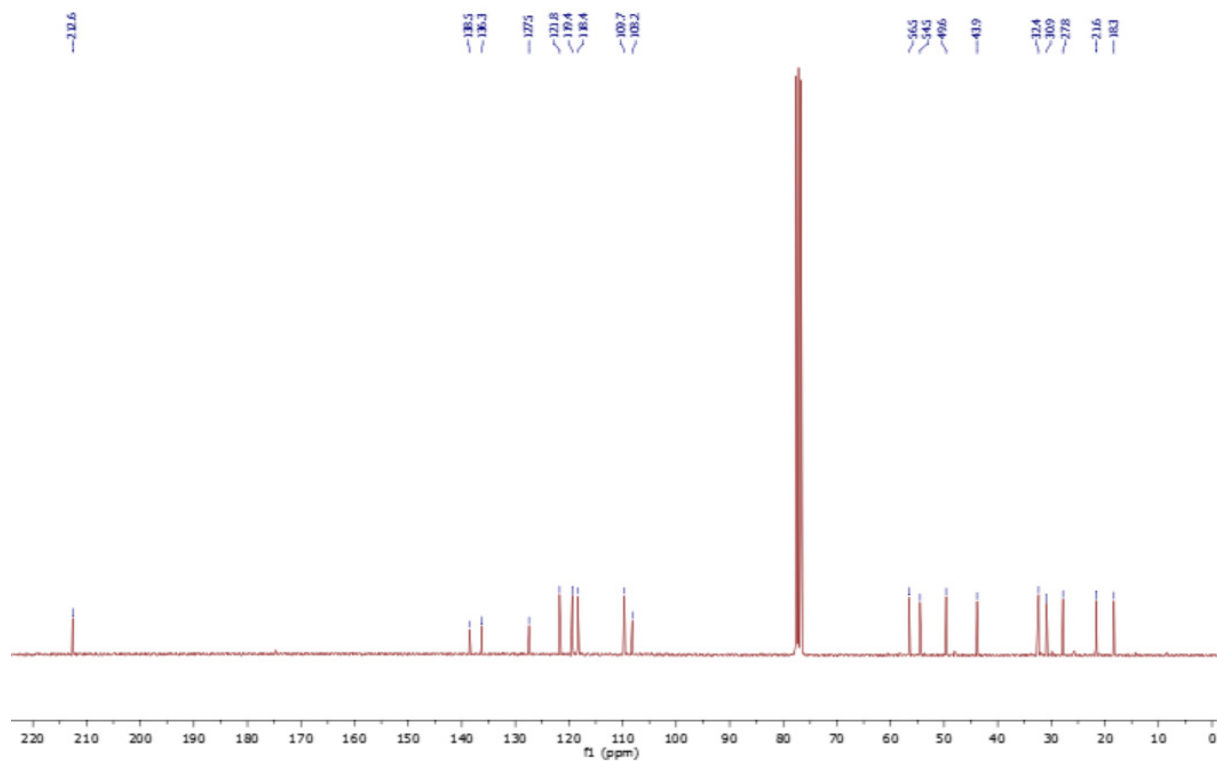


***cis*-1-(12-Methyl-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-1-yl)ethan-1-one (50b)**

¹H RMN spectrum

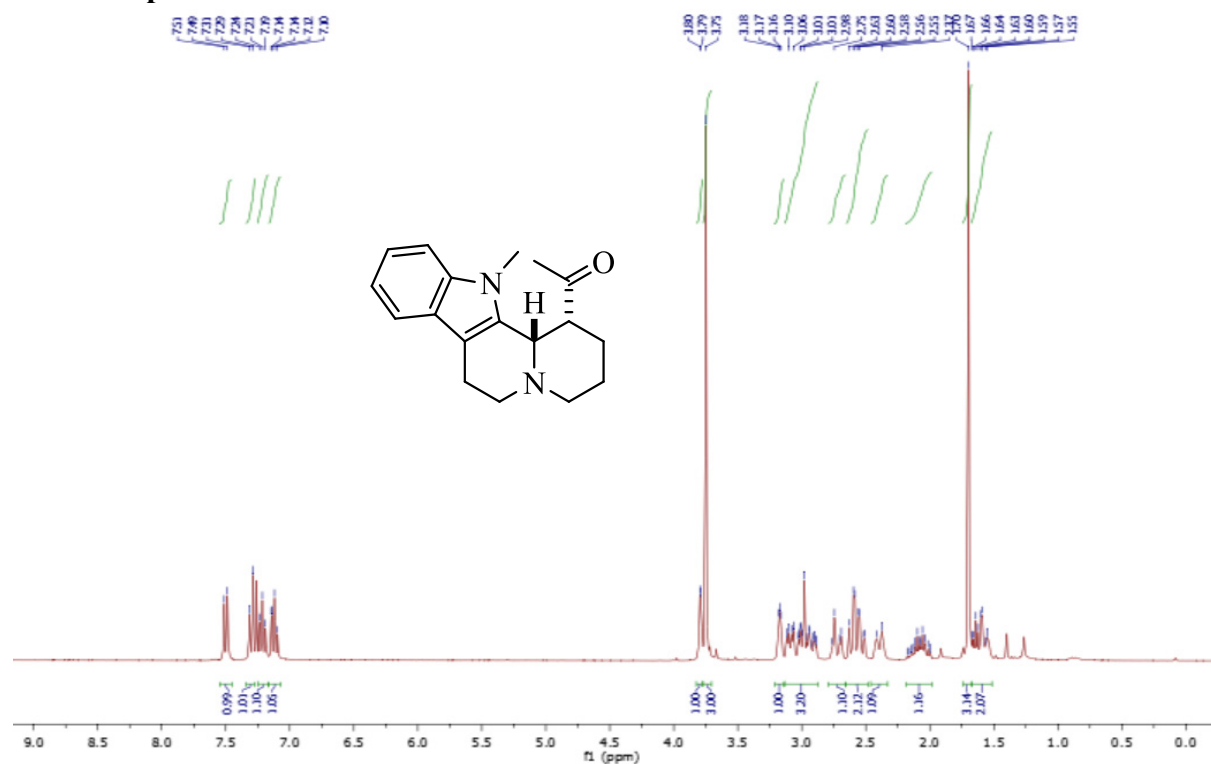


¹³C RMN spectrum

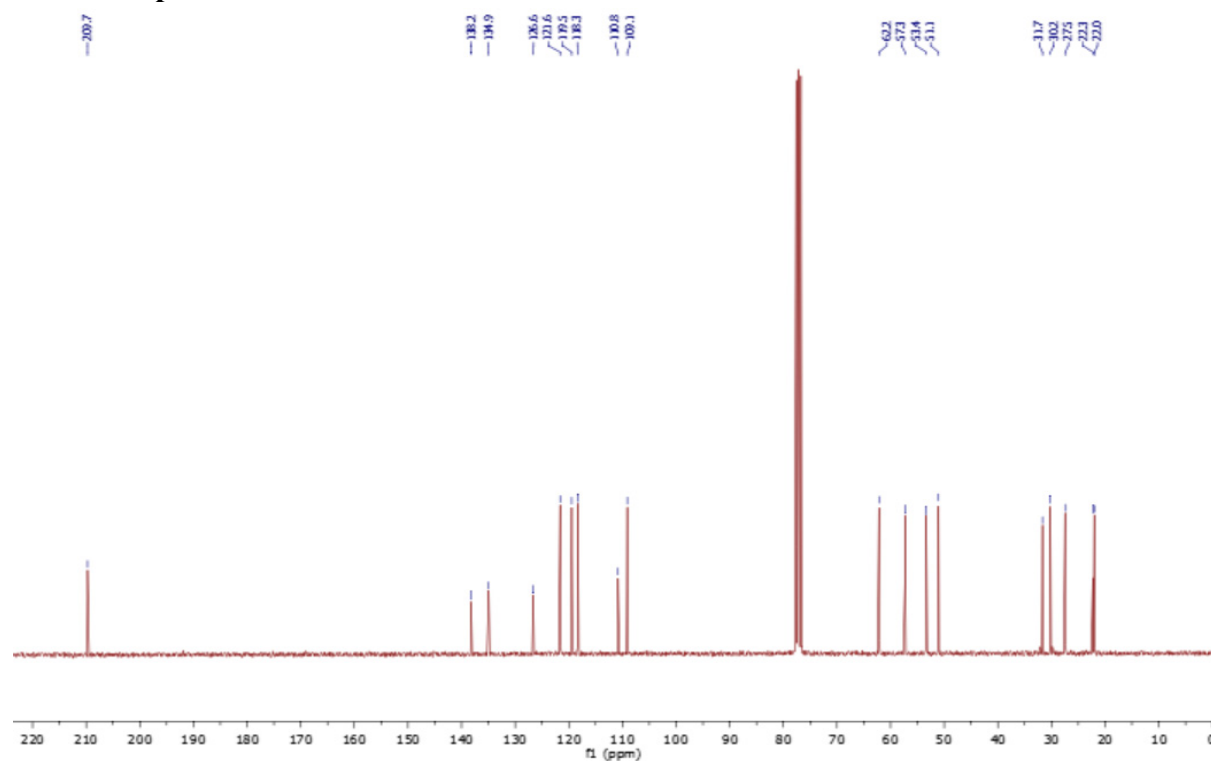


***trans*-1-(12-Methyl-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-1-yl)ethan-1-one (50b)**

¹H RMN spectrum

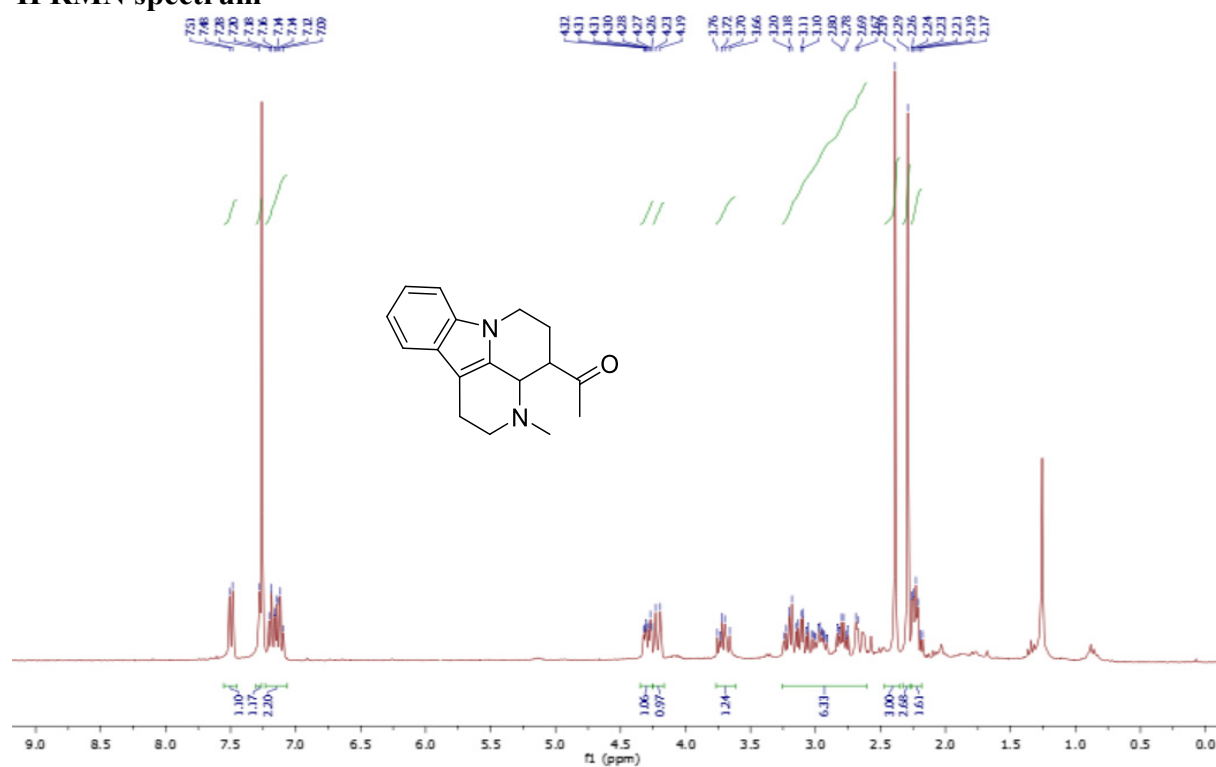


¹³C RMN spectrum



1-(3-Methyl-2,3,3a,4,5,6-hexahydro-1*H*-indolo[3,2,1-*de*][1,5]naphthyridin-4-yl)ethan-1-one (50c)

¹H RMN spectrum



¹³C RMN spectrum

