SUPPORTING INFORMATION

Gold(I) and Platinum(II) switch: A post-Ugi intramolecular hydroarylation to pyrrolopyridinones and pyrroloazepinones

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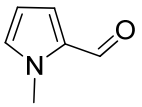
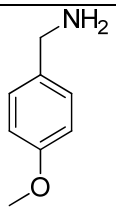
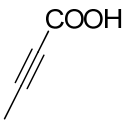
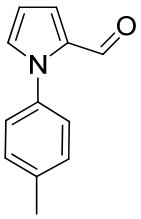
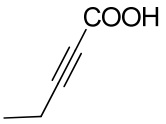
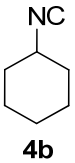
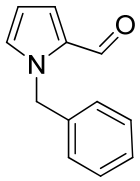
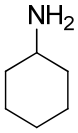
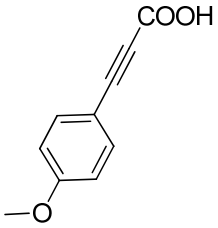
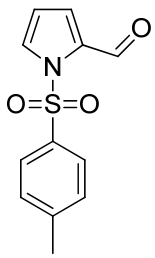
General Experimental Methods

NMR spectra were recorded on a 400 MHz & 300 MHz instrument using $CDCl_3$ and DMSO-d_6 as solvent, stated accordingly. The ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. For the Mass spectrometry, ion source temperature was 150-250 °C, as required. High-resolution EI-mass spectra were performed with a resolution of 10,000. For chromatography, analytical TLC plates and 70-230 mesh silica gel were used. All the solvents and chemicals were purchased and used as available. All the reactions at rt and heating were carried out in a screw capped vial under air.

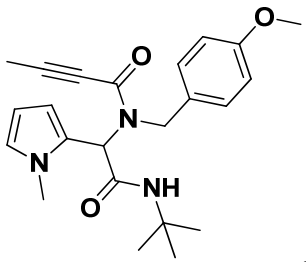
Table 1. Starting materials

Aldehyde	**Amine**	**2-alkynoic acid**	**Isonitrile**
 **1a**	 **2a**	 **3a**	 **4a**
 **1b**	 **2b**	 **3b**	 **4b**
 **1c**	 **2c**	 **3c**	
1d			
 **1e**			

General procedure for synthesis of Ugi products **5a-i**

To a solution of 2-formylpyrrole **1a-e** (1.83 mmol, 1 equiv) in methanol (3 mL) were added successively Na_2SO_4 (0.3g), amine **2a-c** (1.2 equiv), alkynoic acid **3a-c** (1.2 equiv) and isonitrile **4a-b** (1.2 equiv) in a screw capped vial equipped with a magnetic stir bar. The reaction mixture was stirred at 50 ^oC under air for 24-48 h in an oil bath. After completion of the reaction, the mixture was diluted with EtOAc (100 mL) and was extracted with water (50 mL). Organic layer was washed with brine (50 mL), dried over magnesium sulfate and evaporated under reduced pressure to obtain residue which was subjected to silica gel column chromatography (80% EtOAc in Heptane) to afford the desired product **5a-i** as solid.

Ugi products appear as mixture of two rotamers, so ^1H and ^{13}C NMR spectra are not very characteristic. Only representative data for one compound are given.



N-(2-(*tert*-butylamino)-1-(1-methyl-1*H*-pyrrol-2-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5a).**

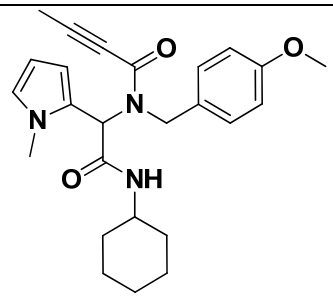
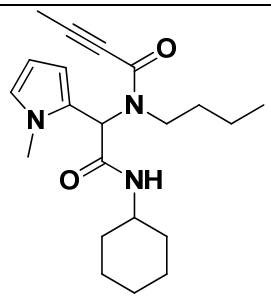
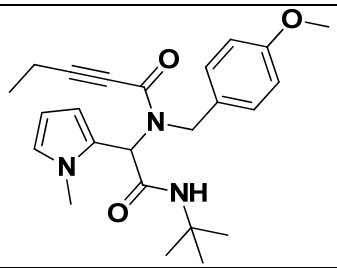
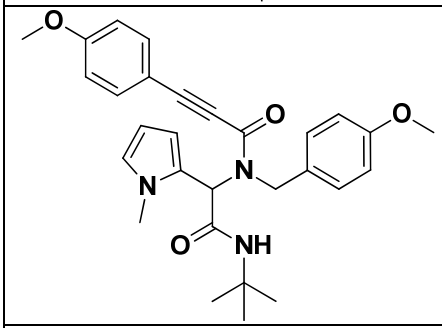
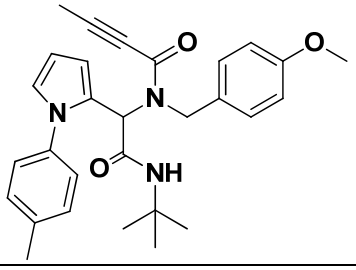
White solid, Yield 83% (mixture of rotamers ~ 1:3). Melting point: 192-194 ^oC.

^1H NMR (300 MHz, $CDCl_3$) δ 6.85 (d, *J*= 8.49Hz, 0.55H), 6.78 (d, *J*= 8.67Hz, 1.51H), 6.66 (m, 2H), 6.51 (m, 0.26H), 6.31 (m, 1.49H), 6.22 (bs, 0.24H), 6.12 (t, 0.25H), 6.02 (t, 0.74H), 5.95 (s, 0.75H), 5.88 (s, 0.26H), 5.53 (bs, 0.78H), 5.44 (bs, 0.25H), 5.01 (d, *J*= 15.84Hz, 0.75H), 4.47 (d, *J*= 15.84Hz, 0.76H), 4.37(d, *J*= 7.53Hz, 0.44H), 3.75 (s, 3H), 3.15 (s, 0.75H), 3.01 (s, 2.27H), 2.01 (m, 3H), 1.33 (s, 6.69H), 1.27 (s, 2.40H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 167.3, 158.7, 158.4, 156.0, 155.6, 130.8, 130.1, 129.8, 129.1, 125.0, 123.7, 123.4, 113.4, 113.2, 111.5, 111.3, 107.5, 91.2, 90.4, 74.2, 73.3, 60.2, 55.2, 53.8, 51.7, 51.6, 49.8, 45.6, 33.3, 33.1, 28.5, 28.4, 4.1(2).

HRMS calculated for $C_{23}H_{29}N_3O_3$ 395.2209, found 395.2207.

Table 2. Ugi products

Struucture	Data
	*N*-(2-(cyclohexylamino)-1-(1-methyl-1*H*-pyrrol-2-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5b)** White solid, Yield 72%, Melting point: 164-166 °C. HRMS calculated for $C_{25}H_{31}N_3O_3$ 421.2365 found 421.2354
	*N*-butyl-*N*-(2-(cyclohexylamino)-1-(1-methyl-1*H*-pyrrol-2-yl)-2-oxoethyl)but-2-ynamide **(5c)** White solid, Yield 87%, Melting point: 118-120 °C. HRMS calculated for $C_{21}H_{31}N_3O_2$ 357.2416 found 357.2418
	*N*-(2-(*tert*-butylamino)-1-(1-methyl-1*H*-pyrrol-2-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)pent-2-ynamide **(5d)** White solid, Yield 69%, Melting point: 152-154 °C. HRMS calculated for $C_{24}H_{31}N_3O_3$ 409.2365 found 409.2350
	*N*-(2-(*tert*-butylamino)-1-(1-methyl-1*H*-pyrrol-2-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)-3-(4-methoxyphenyl)propiolamide **(5e)** White solid, Yield 84%, Melting point: 161-163 °C. HRMS calculated for $C_{29}H_{33}N_3O_4$ 487.2471 found 487.2474
	*N*-(2-(*tert*-butylamino)-2-oxo-1-(1-(*p*-tolyl)-1*H*-pyrrol-2-yl)ethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5f)** Yellow solid, Yield 69%, Melting point: 125-127 °C. HRMS calculated for $C_{29}H_{33}N_3O_3$ 471.2522 found 471.2520

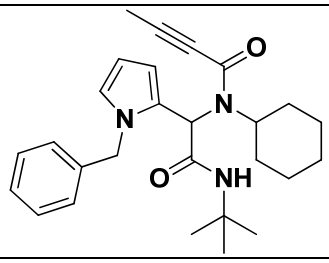
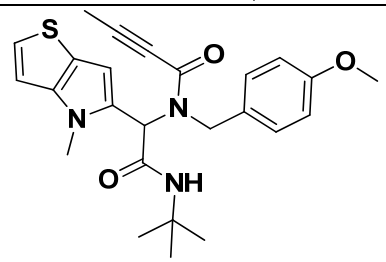
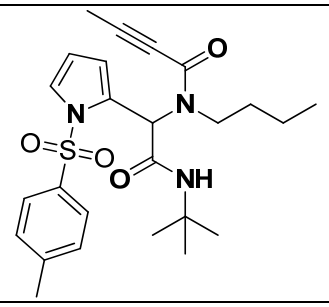
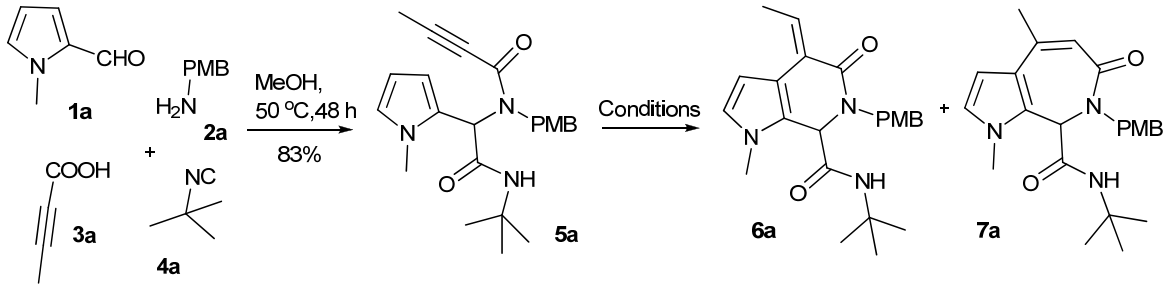
	*N*-(1-(1-benzyl-1*H*-pyrrol-2-yl)-2-(*tert*-butylamino)-2-oxoethyl)-*N*-cyclohexylbut-2-ynamide **(5g)** Offwhite solid, Yield 53%, Melting point: 165-167 ^{o}C. HRMS calculated for $C_{27}H_{35}N_3O_2$ 433.2729 found 433.2730
	*N*-(2-(*tert*-butylamino)-1-(4-methyl-4*H*-thieno[3,2-b]pyrrol-5-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5h)** Offwhite solid, Yield 93%, Melting point: 179-181 ^{o}C. HRMS calculated for $C_{25}H_{29}N_3O_3S$ 451.1930 found 451.1934
	*N*-butyl-*N*-(2-(*tert*-butylamino)-2-oxo-1-(1-tosyl-1*H*-pyrrol-2-yl)ethyl)but-2-ynamide **(5i)** Offwhite solid, Yield 93%, Melting point: 144-146 ^{o}C. HRMS calculated for $C_{29}H_{33}N_3O_5S$ 471.2192 found 371.1401 (M-$C_5H_{10}NO$)

Table I Optimization of the intramolecular hydroarylation[a]

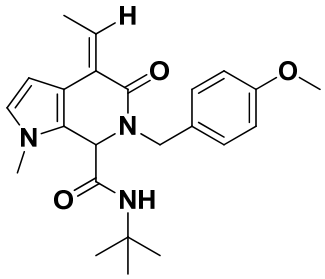


Entry	Catalyst (mol %)	Solvent	Time (h)	Temp °C	Conversion (%) (**6a**/**7a**)[b]
1	AuCl (5)	$CDCl_3$	24	50 °C	25 (0/25)
2	$AuCl_3$ (5)	$CDCl_3$	24	50 °C	35 (0/35)
3	$Au(PPh_3)Cl$ (5)	$CDCl_3$	24	50 °C	0 (0/0)
4	$Au(PPh_3)OTf$ (5)	$CDCl_3$	24	rt	47 (47/0)
5	**$Au(PPh_3)OTf$ (5)**	**$CDCl_3$**	**3**	**50 °C**	**100 (93/0)[c]**
6	$Au(PPh_3)SbF_6$ (5)	$CDCl_3$	24	rt	30 (30/0)
7	AgOTf (5)	$CDCl_3$	24	rt	0 (0/0)
8	AgOTf (5)	$CDCl_3$	24	50 °C	50 (0/50)
9	$PtCl_2$ (5)	$CDCl_3$	24	rt	0 (0/0)
10	**$PtCl_2$ (5)**	**$CDCl_3$**	**14**	**50 °C**	**100 (10/82)[c]**
11	$PtCl_2$ (5)	$CDCl_3$	24	35 °C	10 (0/10)
12	$PtCl_2$ (5)	$CDCl_3$	6	80 °C	100 (25/75)
13	$PtCl_2$ (5)	$CDCl_3$	4	120 °C	100 (35/75)
14	$H_2PtCl_6 \cdot 6H_2O$ (5)	$CDCl_3$	24	rt	0 (0/0)
15	$H_2PtCl_6 \cdot 6H_2O$ (5)	$CDCl_3$	24	50 °C	traces (0/traces)
16	$Au(PPh_3)OTf$ (5)	ACN-d_3	24	50 °C	100 (60/0)[c,d]
17	$Au(PPh_3)OTf$ (5)	THF-d_8	24	50 °C	100 (45/0)[c,d]
18	$Au(PPh_3)OTf$ (5)	Toluene-d_8	24	50 °C	47 (47/0)
19	$PtCl_2$ (5)	ACN-d_3	24	50 °C	0 (0/0)
20	$PtCl_2$ (5)	THF-d_8	24	50 °C	5 (0/5)
21	$PtCl_2$ (5)	Toluene-d_8	24	50 °C	15 (0/15)
22	$Au(PPh_3)OTf$ (2)	$CDCl_3$	24	50 °C	40 (40/0)
23	$PtCl_2$ (2)	$CDCl_3$	48	50 °C	50 (10/40)

[a] All reactions were run on a 0.1 mmol scale of **5a** in a screw capped vial under air. All the reactions in heating were also carried out in screw capped vial under air in an oil bath. [b] Conversion and ratio based on ^{1}H NMR analysis; [c] Isolated yields; [d] Unidentified byproducts formed. PMB = *p*-methoxybenzyl

General procedure for $Au(PPh_3)OTf$ catalyzed cyclization.

To a screw capped vial equipped with a magnetic stir bar was added $Au(PPh_3)Cl$ (5 mol%) and AgOTf (5 mol%) along with chloroform (2 mL). Ugi product **5a-i (**0.2 mmol**)** was added and reaction mixture was stirred at 50 ^{o}C under air in an oil bath until completion. After completion, reaction mixture was partitioned between EtOAc (100 mL) and water (50 mL). Organic layer was washed with brine (50 mL), dried over magnesium sulfate and evaporated under reduced pressure. The residue obtained was purified by silica gel column chromatography (10% diethyl ether in dichloromethane) to afford compound **6a-i**.



(*E*)-*N*-(*tert*-butyl)-4-ethylidene-6-(4-methoxybenzyl)-1-methyl-5-oxo-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6a)**

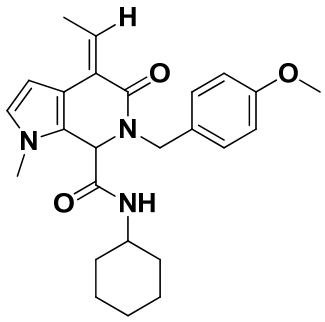
Geometry of *exo*-cyclic double bond was confirmed by NOESY NMR experiment.

Offwhite solid, Yield 93%, Melting point: 160-162 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J*= 8.76Hz, 2H), 6.94 (q, 1H), 6.83 (d, *J*= 8.64Hz, 2H), 6.62 (d, *J*= 2.82Hz, 1H), 6.37 (d, *J*= 3.03Hz, 1H), 5.54 (d, *J*= 14.52Hz, 1H), 5.33 (bs, 1H), 4.84 (s, 1H), 3.90 (d, *J*=14.67Hz, 1H), 3.77 (s, 3H), 3.57 (s, 3H), 2.10 (d, *J*= 7.53, 3H), 1.21 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 164.8, 159.2, 130.1, 129.3, 128.4, 124.5, 123.9, 121.8, 116.0, 114.0, 105.3, 61.3, 55.2, 51.6, 48.7, 34.2, 28.4, 14.8.

HRMS calculated for $C_{23}H_{29}N_3O_3$ 395.2209, found 395.2211.



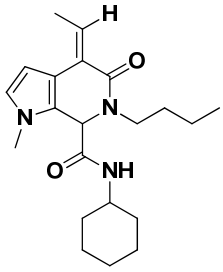
(*E*)-*N*-cyclohexyl-4-ethylidene-6-(4-methoxybenzyl)-1-methyl-5-oxo-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6b**)

White solid, Yield 90%, Melting point: 215-217 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J*= 8.49Hz, 2H), 6.93 (q, 1H), 6.83 (d, *J*= 8.49Hz, 2H), 6.61 (d, *J*= 2.64Hz, 1H), 6.36 (d, *J*= 2.82Hz, 1H), 5.56 (d, *J*= 14.70Hz, 1H), 5.48 (d, *J*= 7.92Hz, 1H), 4.94 (s, 1H), 3.86 (d, *J*=14.67Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H), 2.09 (d, *J*= 7.35, 3H), 2.10-2.07 (m, 1H), 1.60-1.54 (m, 4H), 1.34-1.25 (m, 2H), 1.13-0.95 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 165.1, 159.2, 129.9, 129.3, 128.3, 124.6, 124.0, 121.7, 116.1, 114.0, 105.3, 60.2, 55.2, 48.9, 48.5, 34.4, 32.6, 32.4, 25.3, 24.5(2), 14.8.

HRMS calculated for $C_{25}H_{31}N_3O_3$ 421.2365, found 421.2360.



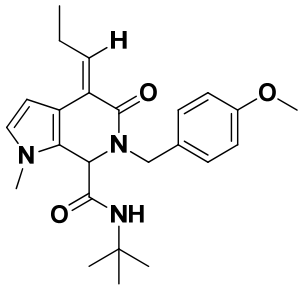
(*E*)-6-butyl-*N*-cyclohexyl-4-ethylidene-1-methyl-5-oxo-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6c**)

White solid, Yield 77%, Melting point: 219-221 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (q, 1H), 6.65 (d, *J*= 2.82Hz, 1H), 6.36 (d, *J*= 3.00Hz, 1H), 5.48 (d, *J*= 7.92Hz, 1H), 5.04 (s, 1H), 4.15-4.05 (m, 1H), 3.73 (s, 3H), 3.65-3.59 (m, 1H), 2.93-2.84 (m, 1H), 2.06 (d, *J*= 7.56, 3H), 1.85-1.82 (m, 1H), 1.66-1.55 (m, 7H), 1.37-1.25 (m, 4H), 1.13-0.99 (m, 2H), 0.92 (t, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 164.9, 128.7, 124.6, 124.1, 121.7, 116.2, 105.3, 61.5, 48.5, 47.3, 34.5, 32.6, 32.4, 29.3, 25.3, 24.5, 24.4, 20.2, 14.8, 13.8.

HRMS calculated for $C_{21}H_{31}N_3O_2$ 357.2416, found 357.2395.



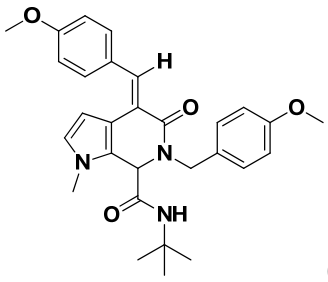
(*E*)-*N*-(*tert*-butyl)-6-(4-methoxybenzyl)-1-methyl-5-oxo-4-propylidene-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6d**)

White solid, Yield 93%, Melting point: 154-156 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J*= 8.64Hz, 2H), 6.84-6.79 (m, 3H), 6.61 (d, *J*= 2.82Hz, 1H), 6.32 (d, *J*= 2.82Hz, 1H), 5.53 (d, *J*= 14.52Hz, 1H), 5.33 (bs, 1H), 4.83 (s, 1H), 3.92 (d, *J*=14.49Hz, 1H), 3.77 (s, 3H), 3.57 (s, 3H), 2.56-2.50 (m, 2H), 1.21-1.15 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 164.9, 159.2, 136.7, 130.1, 128.4, 124.6, 122.4, 121.9, 115.9, 114.0, 105.3, 61.2, 55.2, 51.6, 48.7, 34.2, 28.4, 22.3, 13.6.

HRMS calculated for $C_{24}H_{31}N_3O_3$ 409.2365, found 409.2365.



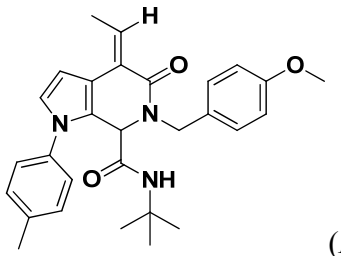
(*E*)-*N*-(*tert*-butyl)-6-(4-methoxybenzyl)-4-(4-methoxybenzylidene)-1-methyl-5-oxo-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6e**)

White solid, Yield 87%, Melting point: 68-70 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J*= 8.64Hz, 2H), 7.15 (d, *J*= 8.64Hz, 2H), 6.89 (d, *J*= 8.86Hz, 2H), 6.83 (d, *J*= 8.49Hz, 2H), 6.48 (d, *J*= 2.82Hz, 1H), 6.20 (s, 1H), 5.93 (d, *J*= 2.82Hz, 1H), 5.54 (bs, 1H), 5.38 (d, *J*= 14.67Hz, 1H), 4.85 (s, 1H), 4.42 (d, *J*=14. 07Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.07 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 167.3, 160.2, 159.3, 143.5, 132.6, 129.9, 129.8, 129.2(2), 122.9, 120.2, 118.2, 114.2, 113.6, 108.4, 55.6, 55.3(2),52.0, 51.7, 33.1, 28.2.

HRMS calculated for $C_{29}H_{33}N_3O_4$ 487.2471, found 487.2488.



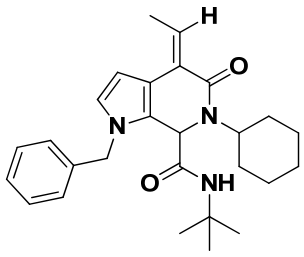
(*E*)-*N*-(*tert*-butyl)-4-ethylidene-6-(4-methoxybenzyl)-5-oxo-1-(*p*-tolyl)-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6f**)

Brown solid, Yield 35%, Melting point: 113-115 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.18 (m, 4H), 7.07-6.96 (m, 3H), 6.86-6.81 (m, 3H), 6.56 (d, *J*= 2.82Hz, 1H), 5.56 (d, *J*= 14.88Hz, 1H), 4.80 (s, 1H), 4.75 (bs, 1H), 3.88 (d, *J*=14.67Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H), 2.14 (d, *J*= 7.53, 3H), 1.06 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 165.1, 159.0, 138.1, 136.1, 130.2, 130.1, 129.8, 128.9, 125.0, 124.4, 124.3, 122.0, 118.3, 113.9, 106.8, 59.5, 55.3, 51.3, 48.4, 28.2, 21.0,14.9.

HRMS calculated for $C_{29}H_{33}N_3O_3$ 471.2522, found 471.2549.



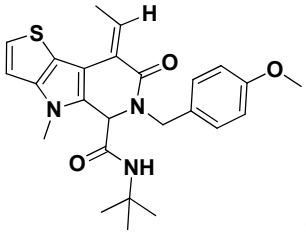
(*E*)-1-benzyl-*N*-(*tert*-butyl)-6-cyclohexyl-4-ethylidene-5-oxo-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6g**)

White solid, Yield 95%, Melting point: 147-149 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.08 (d, *J*= 6.78Hz, 2H), 6.83-6.73 (m, 2H), 6.35 (d, *J*= 2.82Hz, 1H), 5.61 (d, *J*= 15.81Hz, 1H), 5.54 (bs, 1H), 5.12 (d, *J*=15.99Hz, 1H), 4.71 (s, 1H), 4.44 (m, 1H), 2. 07 (d, *J*= 7.53, 3H), 1.76-1.70 (m, 2H), 1.61-1.52 (m, 2H), 1.31-1.25 (m, 4H), 1.19 (s, 9H), 0.96-0.77 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 165.7, 137.5, 128.8, 128.7, 127.6, 126.9, 126.0, 124.1, 123.8, 116.4, 105.4, 57.1, 55.1, 51.6, 51.2, 29.8, 29.4, 28.4, 25.8, 25.5, 25.1, 14.7.

HRMS calculated for $C_{27}H_{35}N_3O_2$ 433.2729, found 433.2725.



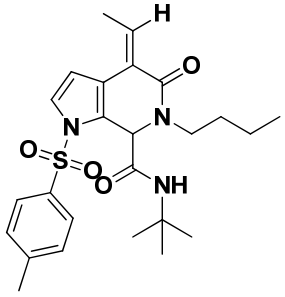
(*E*)-*N*-(*tert*-butyl)-8-ethylidene-6-(4-methoxybenzyl)-4-methyl-7-oxo-5,6,7,8-tetrahydro-4*H*-thieno[2',3':4,5]pyrrolo[2,3-*c*]pyridine-5-carboxamide (**6h**)

Yellow solid, Yield 86%, Melting point: 204-206 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J*= 8.46Hz, 2H), 7.12 (d, *J*= 5.28Hz, 1H), 6.94-6.87 (m, 2H), 6.83 (d, *J*= 8.67Hz, 2H), 5.49-5.44 (m, 2H), 4.89 (s, 1H), 4.01 (d, *J*=14.70Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 2.31 (d, *J*= 7.53, 3H), 1.20 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 165.2, 159.3, 142.4, 129.9, 129.6, 128.1, 127.6, 124.4, 124.2, 118.9, 114.1, 110.1, 108.8, 60.7, 55.2, 51.7, 49.1, 32.6, 28.4, 15.6.

HRMS calculated for $C_{25}H_{29}N_3O_3S$ 451.1930, found 451.1943.



(*E*)-*N*-(*tert*-butyl)-6-butyl-4-ethylidene-5-oxo-1-tosyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine-7-carboxamide (**6i**)

White solid, Yield 72%, Melting point: 114-116 ^{o}C.

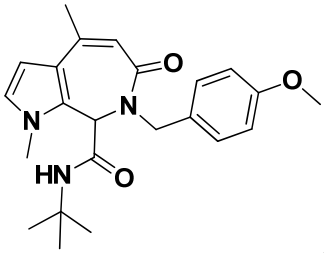
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J*= 8.28Hz, 2H), 7.27 (d, *J*= 8.13Hz, 2H), 6.78 (d, *J*= 4.32Hz, 1H), 6.53 (q, 1H), 5.23 (d, *J*= 4.35Hz, 1H), 4.76 (bs, 1H), 4.52 (s, 1H), 3.90-3.80 (m, 1H), 3.59-3.50 (m, 1H), 2.43 (s, 3H), 1.77-1.67 (m, 2H), 1.48-1.32 (m, 11H), 1.01-0.95 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 165.3, 144.2, 137.3, 136.5, 133.4, 131.6, 129.5, 127.3, 106.3, 72.4, 66.7, 66.1, 55.3, 41.6, 28.5, 27.8, 21.6, 20.1, 13.8, 13.5.

HRMS calculated for $C_{29}H_{33}N_3O_5S$ 471.2192, found 471.2150.

General procedure for $PtCl_2$ catalyzed cyclization.

To a screw capped vial equipped with a magnetic stir bar was added $PtCl_2$ (5 mol%) along with chloroform (2 mL). Ugi product **5a-i (**0.2 mmol**)** was added and reaction mixture was stirred at 50 ^{o}C under air in an oil bath until completion. After completion, reaction mixture was partitioned between EtOAc (100 mL) and water (50 mL). Organic layer was washed with brine (50 mL), dried over magnesium sulfate and evaporated under reduced pressure. The residue obtained was purified by silica gel column chromatography (20% diethyl ether in dichloromethane) to afford compound **7a-d, f-h**.



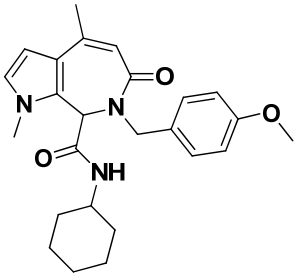
N-(*tert*-butyl)-7-(4-methoxybenzyl)-1,4-dimethyl-6-oxo-1,6,7,8-tetrahydropyrrolo[2,3-*c*]azepine-8-carboxamide (**7a**)

White solid, Yield 82%, Melting point: 110-112 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J*= 8.56Hz, 2H), 6.82 (d, *J*= 8.32Hz, 2H), 6.49(d, *J*= 2.76Hz, 1H), 6.17 (d, *J*= 2.76Hz, 1H), 5.94 (s, 1H), 5.35 (bs, 1H), 5.20 (d, *J*= 14.36Hz, 1H), 4.76 (s, 1H), 4.46 (d, *J*=14.60Hz, 1H), 3.78 (s, 3H), 3.11 (s, 3H), 2.13 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 167.2, 159.3, 141.3, 129.9, 129.3, 128.0, 123.0, 121.3, 118.8, 114.2, 105.9, 55.7, 55.3, 52.0, 51.6, 33.2, 28.3, 22.8.

HRMS calculated for $C_{23}H_{29}N_3O_3$ 395.2209, found 395.2211.



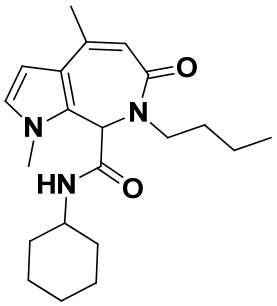
N-cyclohexyl-7-(4-methoxybenzyl)-1,4-dimethyl-6-oxo-1,6,7,8 tetrahydropyrrolo[2,3-*c*]azepine-8-carboxamide (**7b**)

White solid, Yield 60%, Melting point: 153-155 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J*= 8.64Hz, 2H), 6.82 (d, *J*= 8.67Hz, 2H), 6.49(d, *J*= 2.82Hz, 1H), 6.17 (d, *J*= 2.82Hz, 1H), 5.94 (s, 1H), 5.40 (d, *J*= 8.28Hz, 1H), 5.25 (d, *J*= 14.49Hz, 1H), 4.82 (s, 1H), 4.43 (d, *J*=14.49Hz, 1H), 3.78 (s, 3H), 3.67-3.57 (m, 1H), 3.10 (s, 3H), 2.12 (d, *J*=0.75Hz, 3H), 1.70-1.55 (m, 4H), 1.29-1.20 (m, 2H), 0.98-0.86 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 167.0, 159.3, 141.4, 129.9, 129.2, 127.7, 123.0, 121.5, 118.7, 114.3, 105.9, 55.3, 55.1, 51.9, 48.5, 33.2, 32.8, 32.5, 25.3, 24.5(2), 22.9.

HRMS calculated for $C_{25}H_{31}N_3O_3$ 421.2365, found 421.2362.



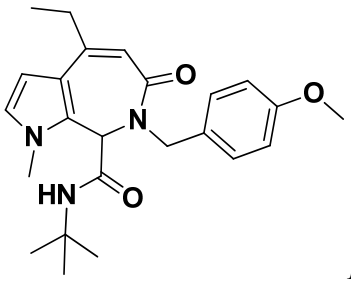
7-butyl-*N*-cyclohexyl-1,4-dimethyl-6-oxo-1,6,7,8-tetrahydropyrrolo[2,3-*c*]azepine-8-carboxamide (**7c**)

White solid, Yield 75%, Melting point: 122-124 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62(d, *J*= 2.82Hz, 1H), 6.19 (d, *J*= 2.85Hz, 1H), 5.86 (s, 1H), 5.68 (d, *J*= 8.07Hz, 1H), 4.88 (s, 1H), 3.89-3.79 (m, 1H), 3.72 (m, 4H), 3.48-3.39 (m, 1H), 2.10 (d, *J*=0.96Hz, 3H), 1.79-1.71 (m, 2H), 1.59-1.54 (m, 5H), 1.33-1.25 (m, 4H), 1.11-1.02 (m, 3H), 0.90 (t, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 167.0, 141.1, 127.8, 123.3, 121.5, 118.8, 106.1, 57.5, 50.3, 48.7, 34.0, 32.8, 32.6, 31.0, 25.3, 24.6, 24.5, 22.9, 20.0, 13.9.

HRMS calculated for $C_{21}H_{31}N_3O_2$ 357.2416, found 357.2405.



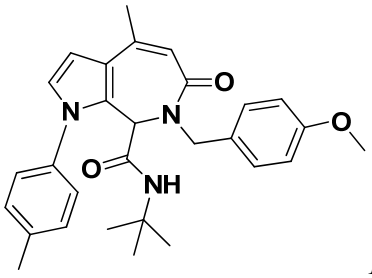
N-(*tert*-butyl)-4-ethyl-7-(4-methoxybenzyl)-1-methyl-6-oxo-1,6,7,8-tetrahydropyrrolo[2,3-*c*]azepine-8-carboxamide (**7d**)

White solid, Yield 83%, Melting point: 126-128 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J*= 8.67Hz, 2H), 6.83 (d, *J*= 8.67Hz, 2H), 6.49(d, *J*= 2.82Hz, 1H), 6.16 (d, *J*= 2.82Hz, 1H), 5.94 (s, 1H), 5.39 (bs, 1H), 5.16 (d, *J*= 14.67Hz, 1H), 4.77 (s, 1H), 4.50 (d, *J*=14.49Hz, 1H), 3.79 (s, 3H), 3.13 (s, 3H), 2.53-2.41 (m, 2H), 1.15-1.10 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 167.2, 159.3, 147.0, 129.9, 129.3, 128.4, 123.0, 120.5, 117.1, 114.3, 105.5, 55.8, 55.3, 52.0, 51.6, 33.2, 29.5, 28.3, 13.2.

HRMS calculated for $C_{24}H_{31}N_3O_3$ 409.2365, found 409.2338.



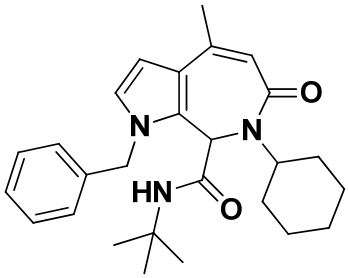
N-(*tert*-butyl)-7-(4-methoxybenzyl)-4-methyl-6-oxo-1-(*p*-tolyl)-1,6,7,8-tetrahydropyrrolo[2,3-*c*]azepine-8-carboxamide (**7f**)

Sticky solid, Yield 63%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J*= 7.92Hz, 2H), 6.97-6.90 (m, 4H), 6.73-6.69 (m, 3H), 6.33 (d, *J*= 2.82Hz, 1H), 5.99 (s, 1H), 5.31 (bs, 1H), 4.73 (s, 1H), 4.67 (d, *J*= 14.49Hz, 1H), 4.53 (d, *J*=14.31Hz, 1H), 3.78 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 1.13 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 167.1, 159.2, 141.2, 138.0, 135.4, 129.9(2), 129.1, 128.4, 125.7, 123.1, 121.8, 119.4, 114.1, 106.9, 56.2, 55.2, 51.9, 51.6, 28.3, 22.9, 21.1.

HRMS calculated for $C_{29}H_{33}N_3O_3$ 471.2522, found 471.2492.



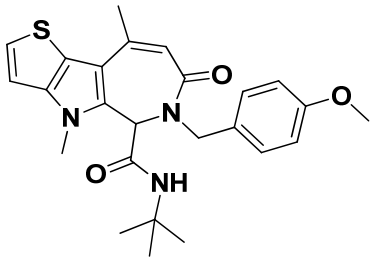
1-benzyl-*N*-(*tert*-butyl)-7-cyclohexyl-4-methyl-6-oxo-1,6,7,8-tetrahydropyrrolo[2,3-*c*]azepine-8-carboxamide (**7g**)

Green solid, Yield 50%, Melting point: 157-159 ^oC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 3H), 7.22-7.19 (m, 2H), 6.75 (d, *J*= 2.64Hz, 1H), 6.26 (d, *J*= 2.61Hz, 1H), 5.89 (s, 1H), 5.32-5.26 (m, 2H), 5.14 (d, *J*= 15.99Hz, 1H), 4.84 (s, 1H), 4.50-4.42 (m, 1H), 2.10 (s, 3H), 1.95-1.92 (m, 1H), 1.81-1.78 (m, 1H), 1.67-1.49 (m, 2H), 1.40-1.25 (m, 4H), 1.10 (s, 9H), 0.97-0.72 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 167.1, 139.8, 136.8, 129.2, 128.6, 128.3, 126.9, 123.3, 122.5, 119.9, 106.4, 54.5, 52.2, 51.4, 51.2, 32.0, 31.0, 28.2, 25.8, 25.6, 25.4, 22.7.

HRMS calculated for $C_{27}H_{35}N_3O_2$ 433.2729, found 433.2711.



N-(*tert*-butyl)-6-(4-methoxybenzyl)-4,9-dimethyl-7-oxo-4,5,6,7-tetrahydrothieno[2',3':4,5]pyrrolo[2,3-*c*]azepine-5-carboxamide (**7h**)

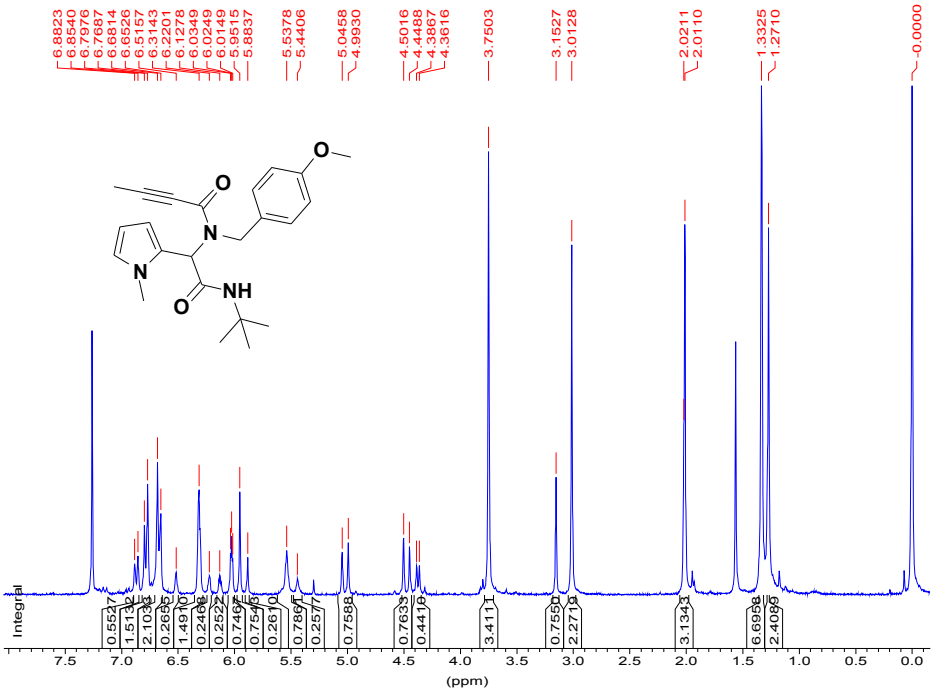
Green solid, Yield 79%, Melting point: 210-212 ^{o}C.

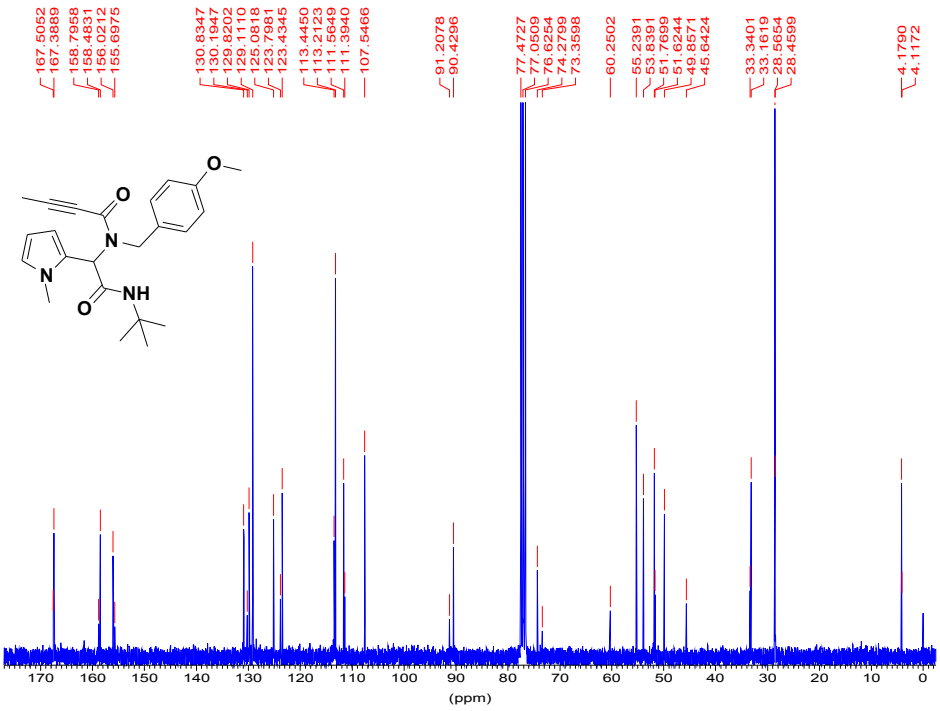
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J*= 8.67Hz, 2H), 7.13 (d, *J*= 5.25Hz, 1H), 6.88-6.82 (m, 3H), 6.00 (s, 1H), 5.46 (bs, 1H), 5.15 (d, *J*= 14.49Hz, 1H), 4.87 (s, 1H), 4.54 (d, *J*=14.49Hz, 1H), 3.79 (s, 3H), 3.28 (s, 3H), 2.30 (d, *J*= 0.93Hz, 3H), 1.16 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 166.7, 159.5, 140.8, 140.3, 132.9, 130.1, 129.0, 124.2, 120.5, 118.7, 114.4(2), 110.2, 56.2, 55.4, 52.0, 51.9, 31.5, 28.4, 23.4.

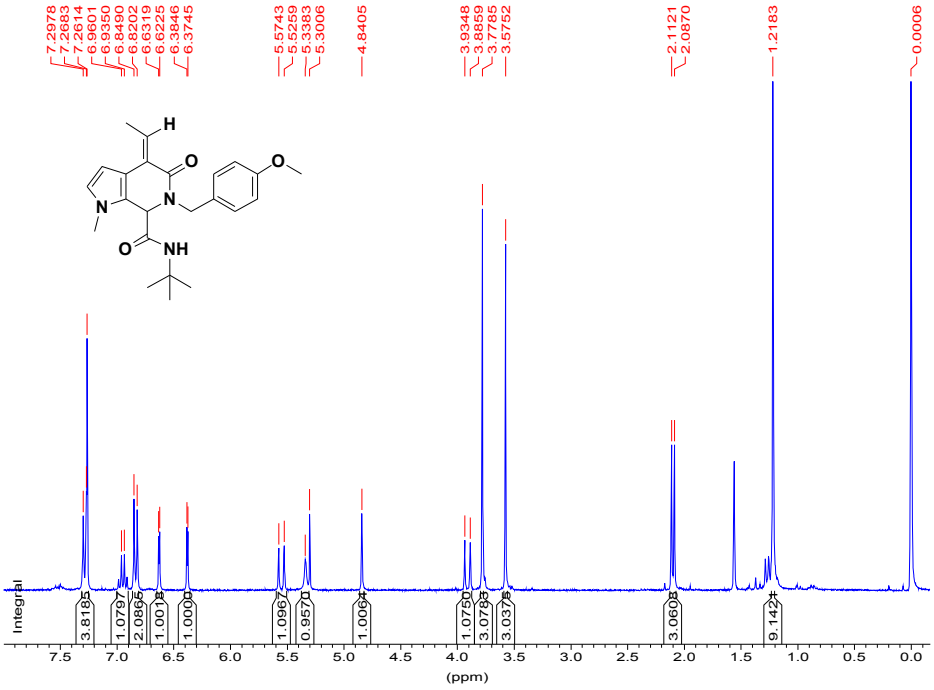
HRMS calculated for $C_{25}H_{29}N_3O_3S$ 451.1930, found 451.1929.

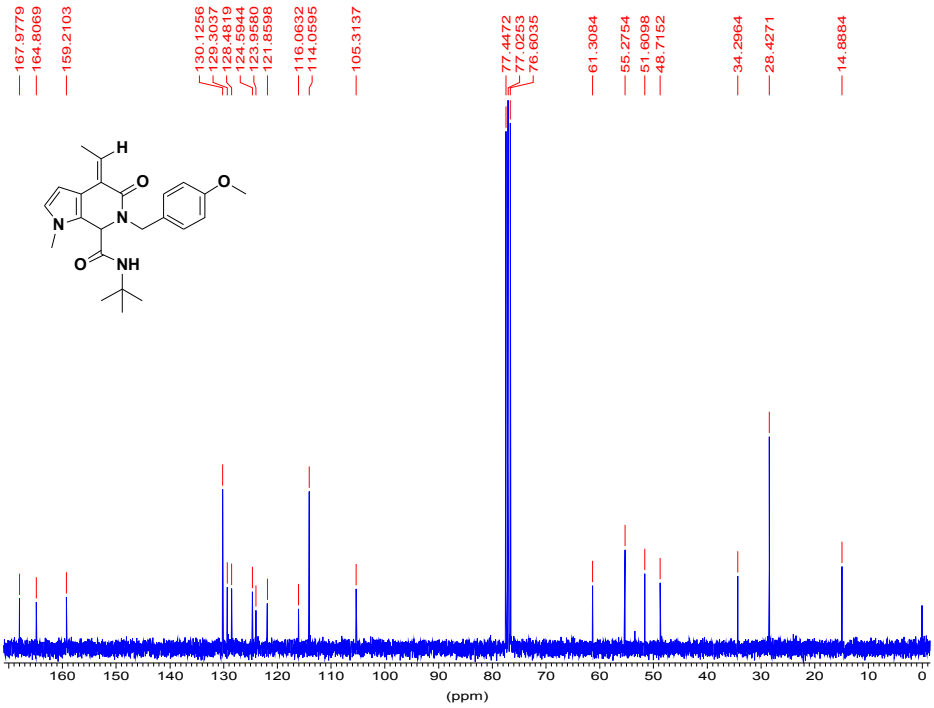
^{1}H and ^{13}C NMR spectra of compound **5a** (300 MHz, $CDCl_3$)



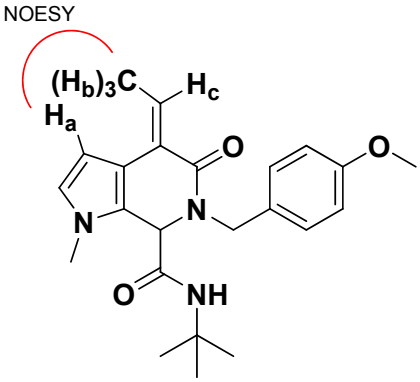


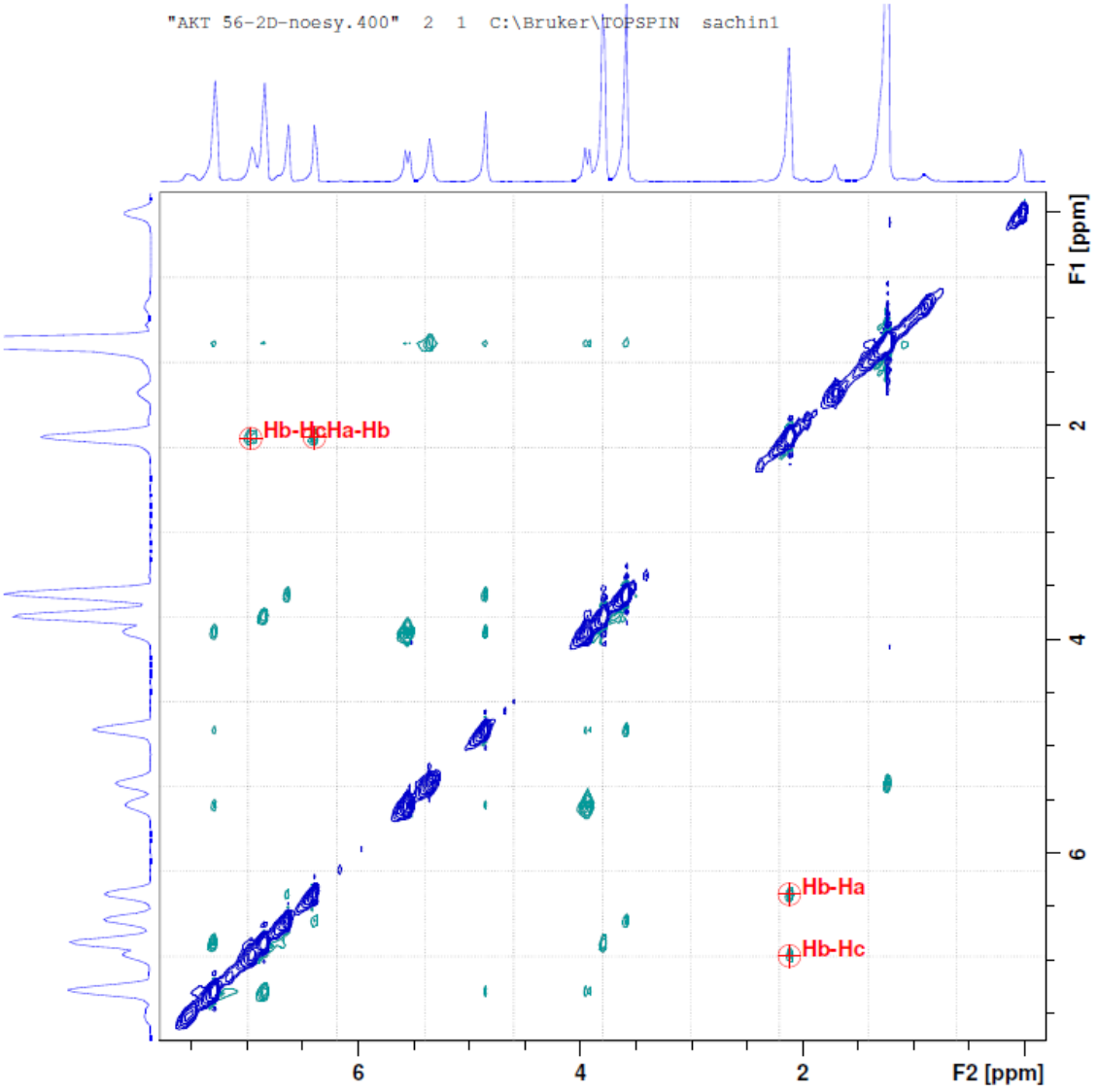
^{1}H and ^{13}C NMR spectra of compound **6a** (300 MHz, $CDCl_3$)



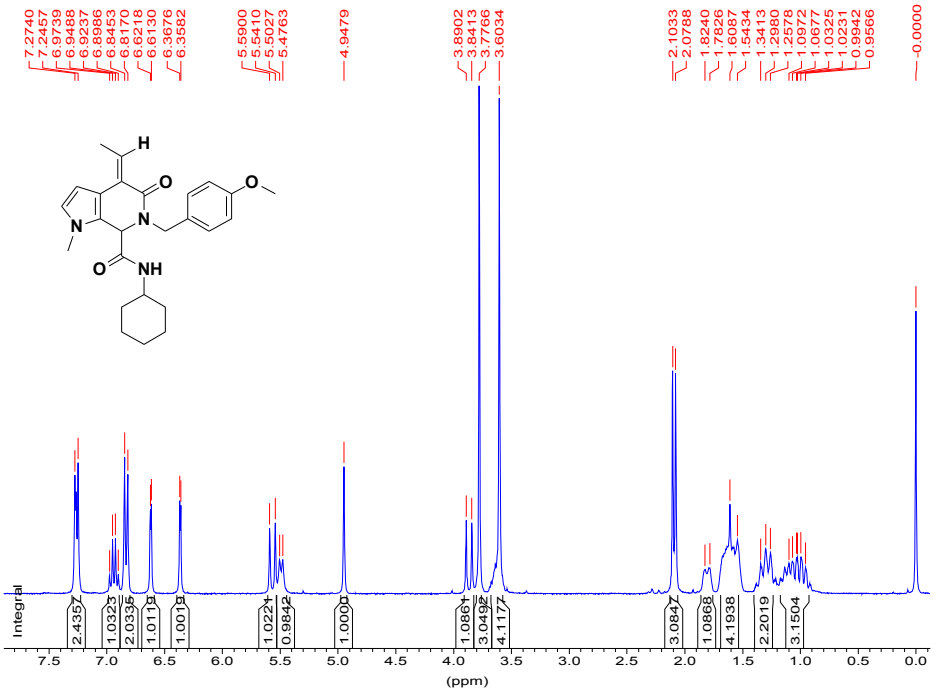


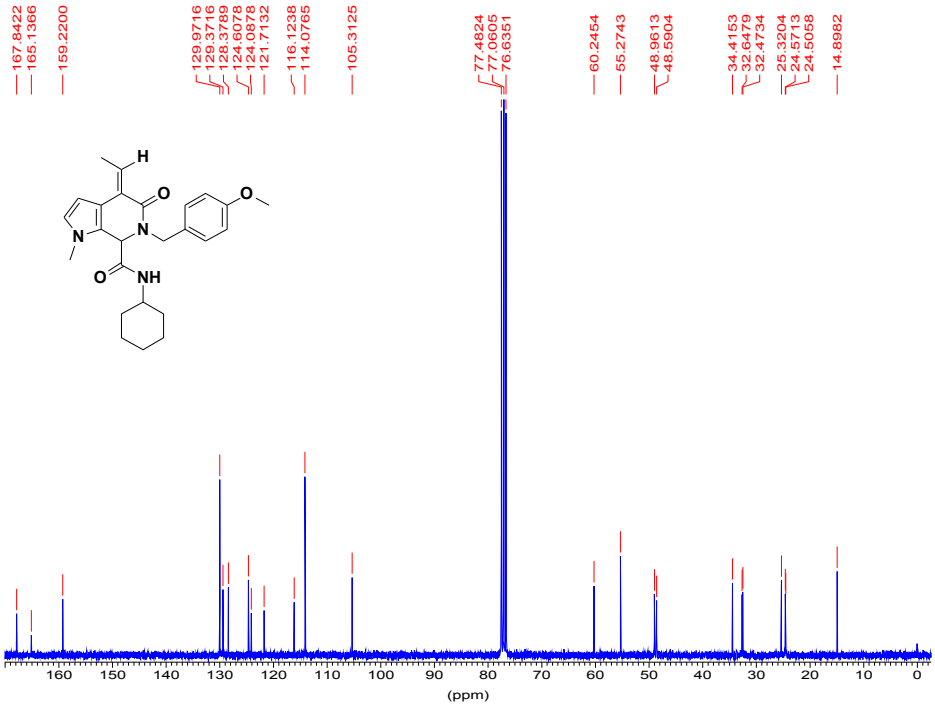
NOESY NMR spectra of compound **6a** (400 MHz, $CDCl_3$).



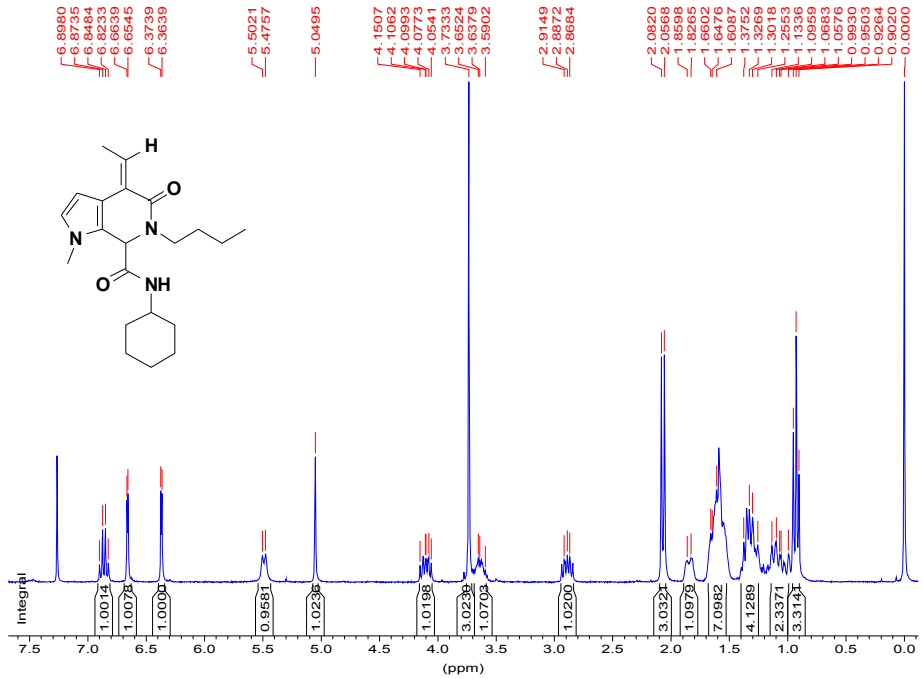


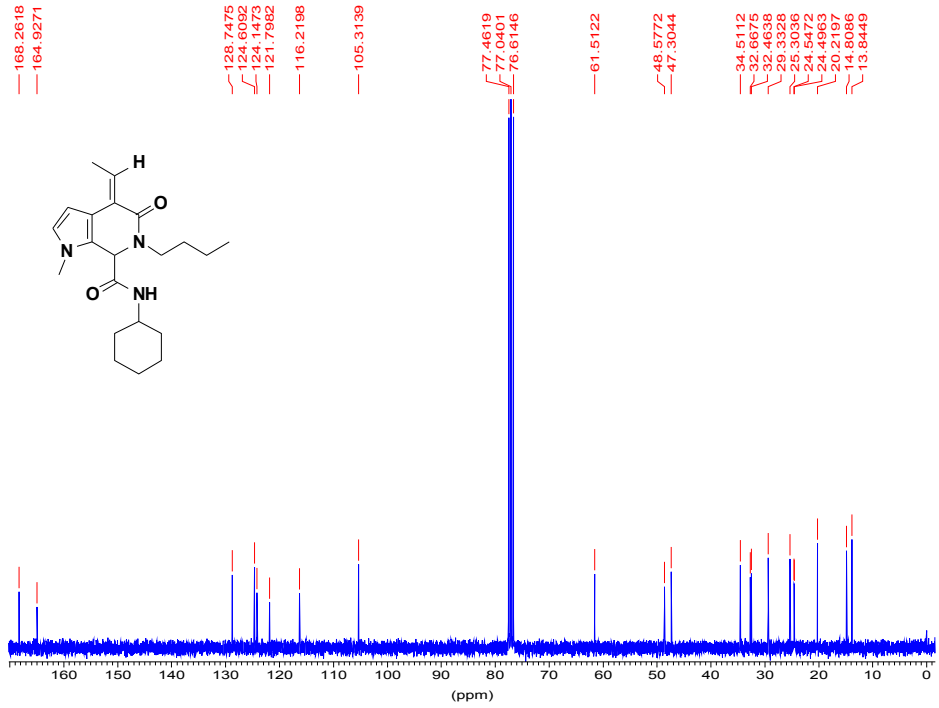
^{1}H and ^{13}C NMR spectra of compound **6b** (300 MHz, $CDCl_3$)



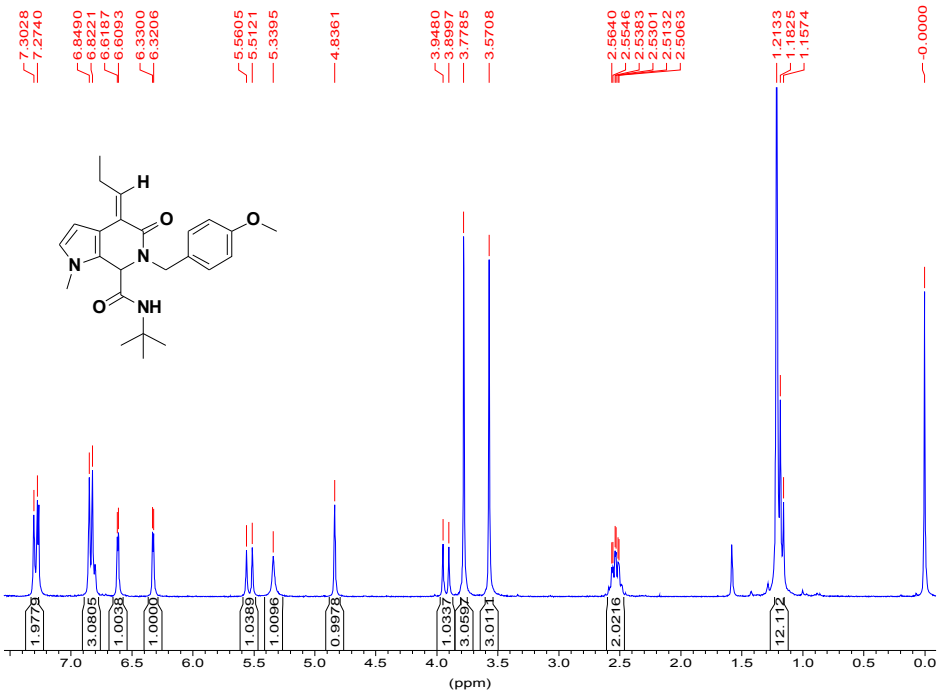


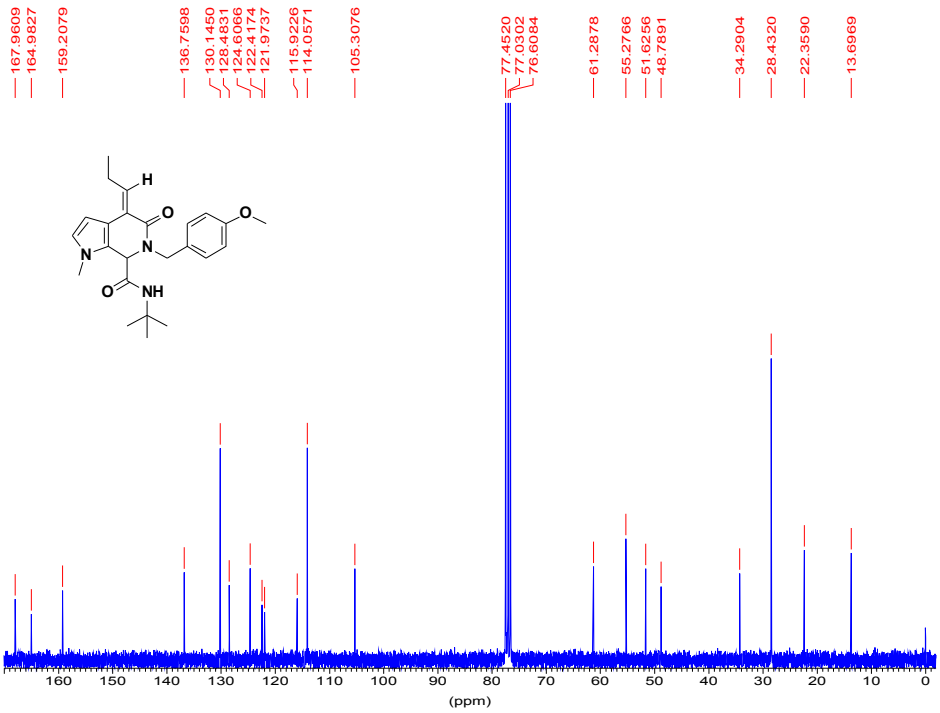
^{1}H and ^{13}C NMR spectra of compound **6c** (300 MHz, $CDCl_3$)



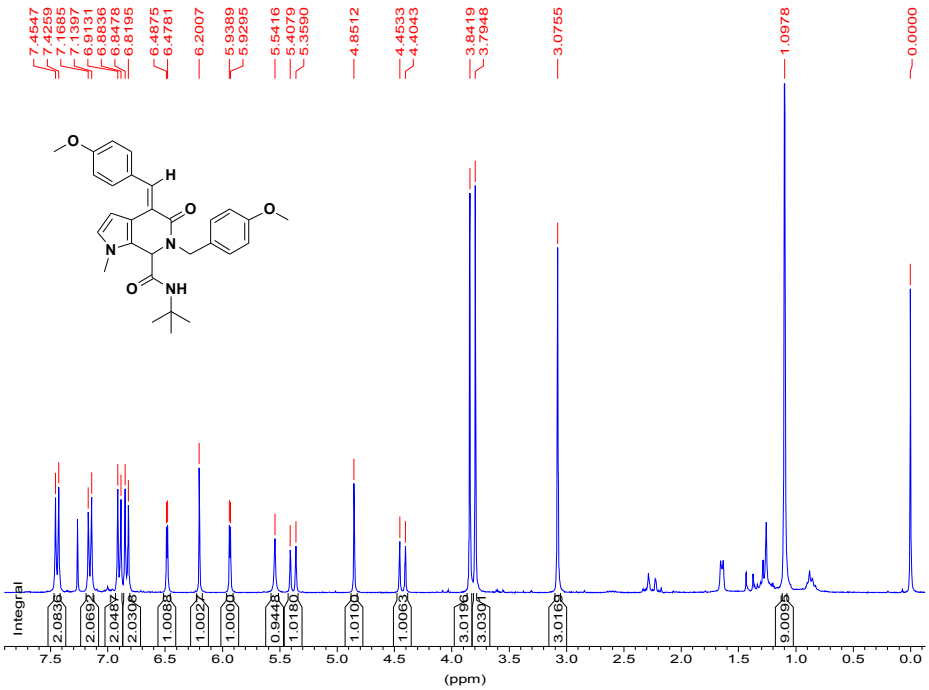


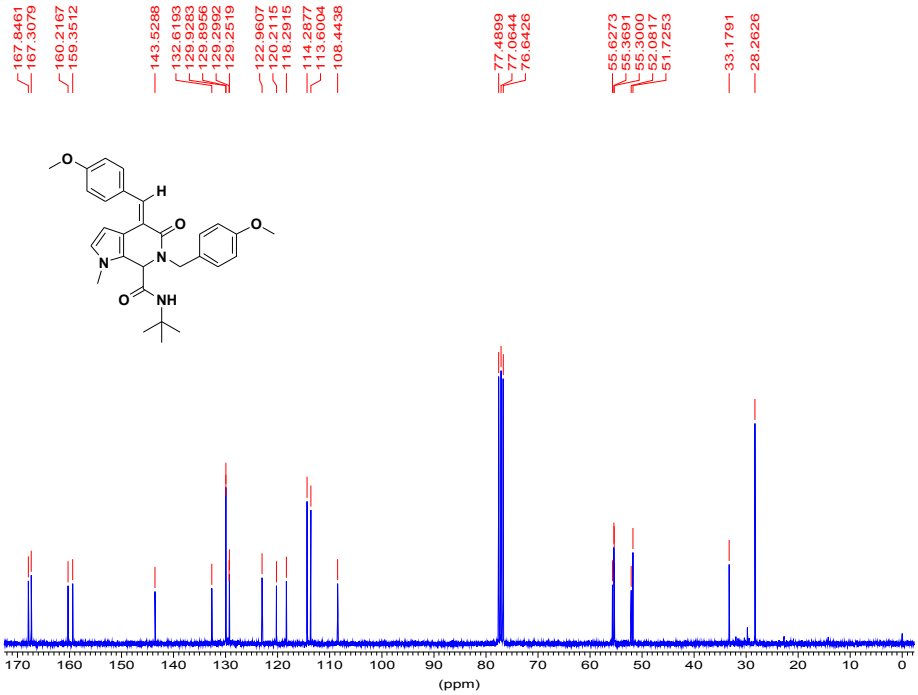
^{1}H and ^{13}C NMR spectra of compound **6d** (300 MHz, $CDCl_3$)



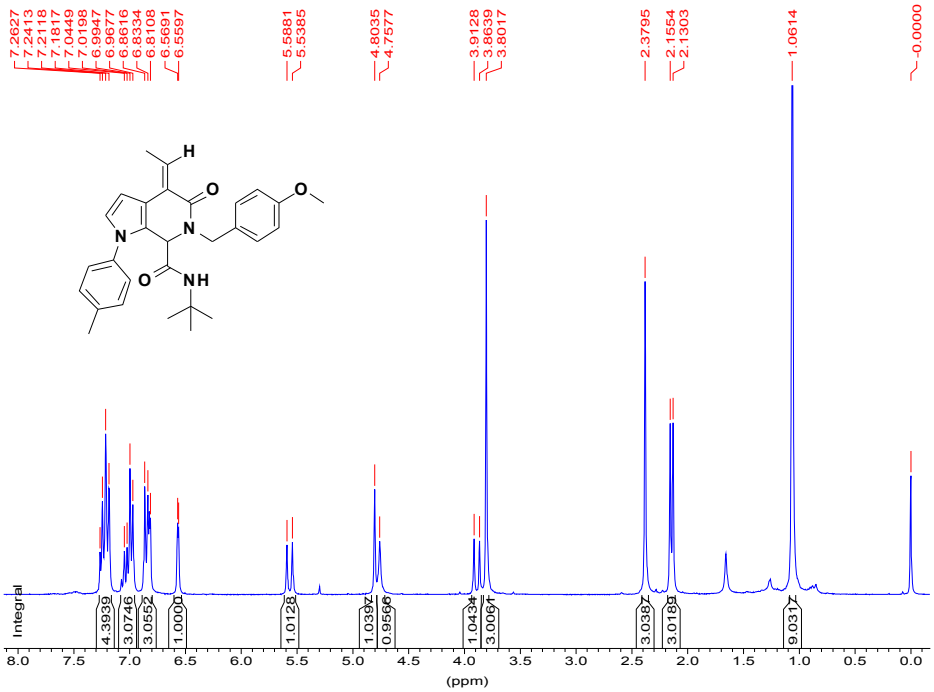


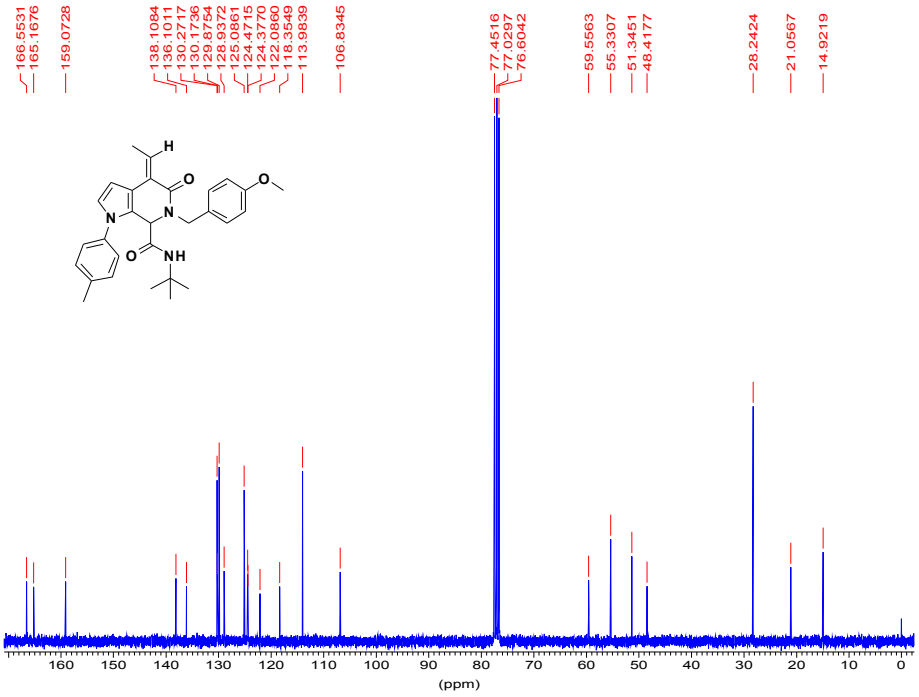
^{1}H and ^{13}C NMR spectra of compound **6e** (300 MHz, $CDCl_3$)



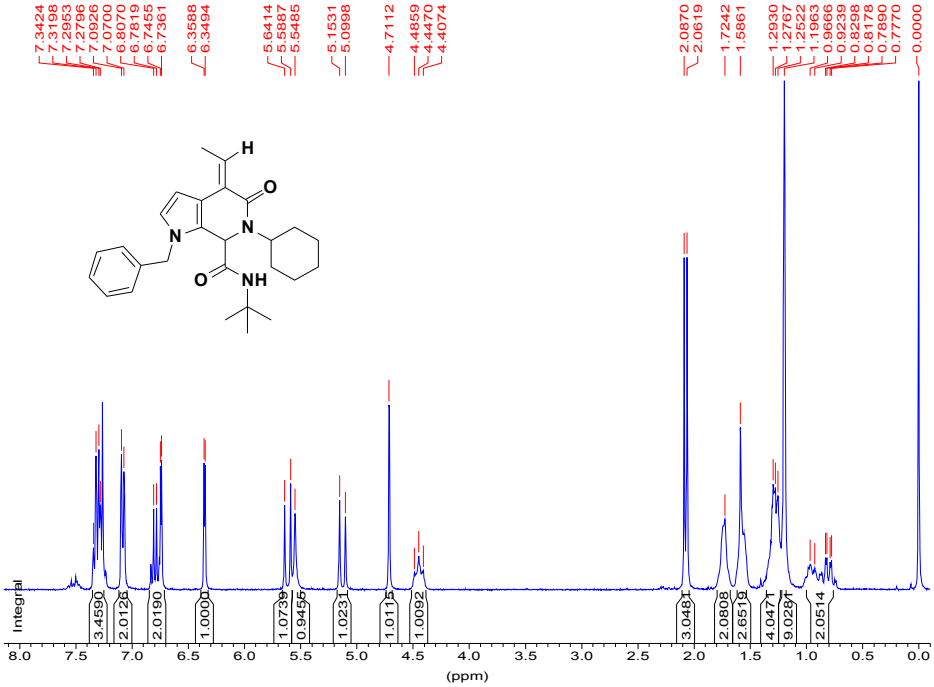


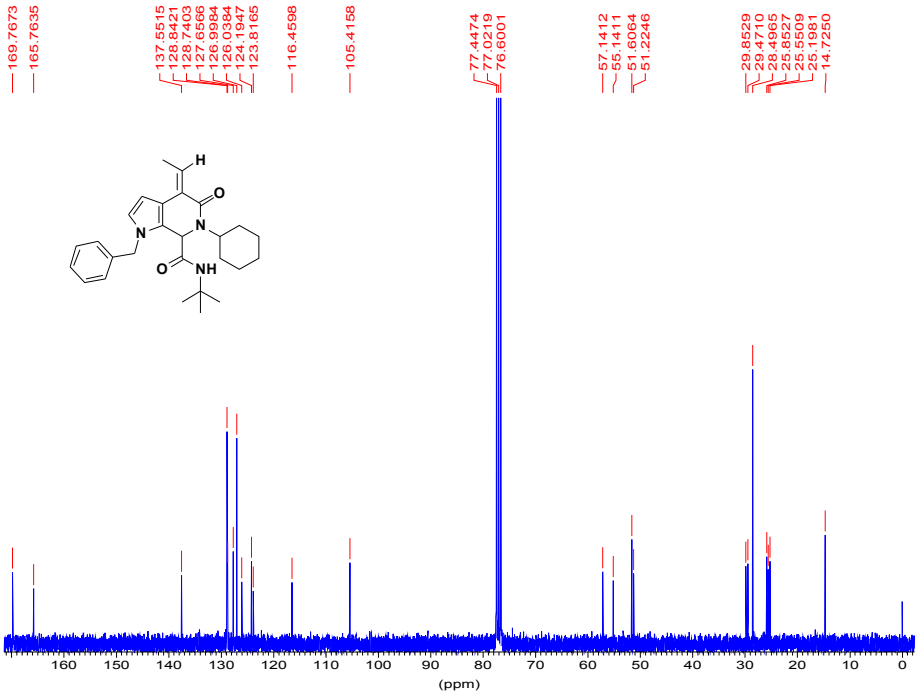
^{1}H and ^{13}C NMR spectra of compound **6f** (300 MHz, $CDCl_3$)



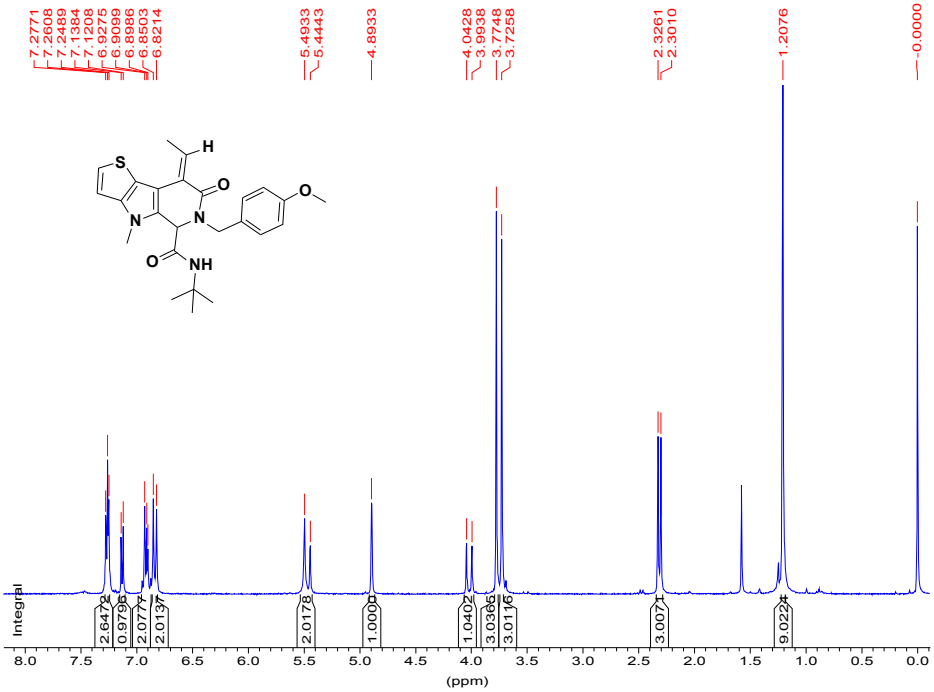


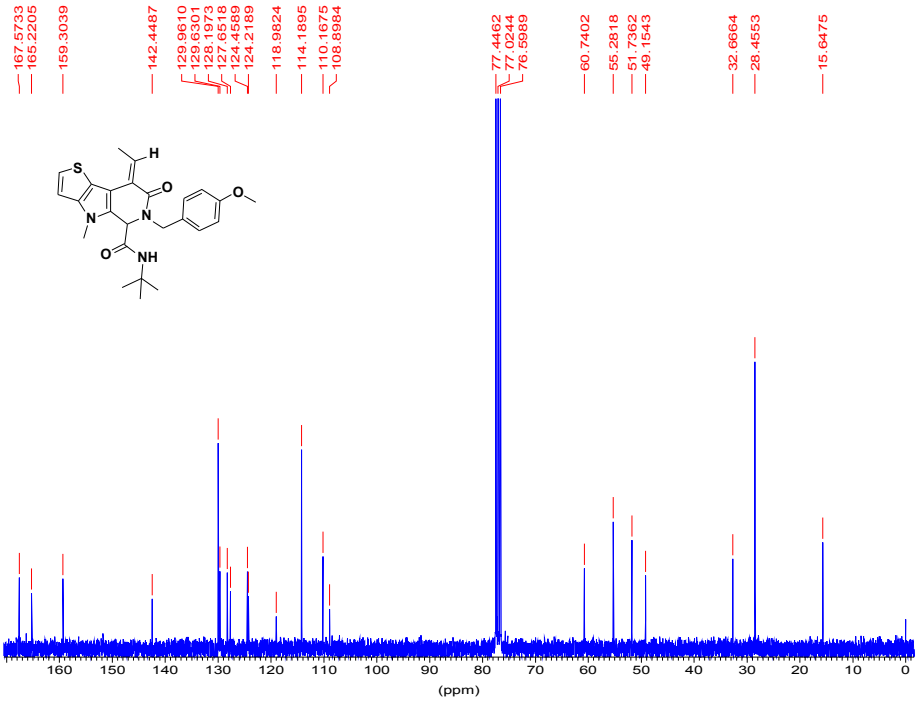
^{1}H and ^{13}C NMR spectra of compound **6g** (300 MHz, $CDCl_3$)



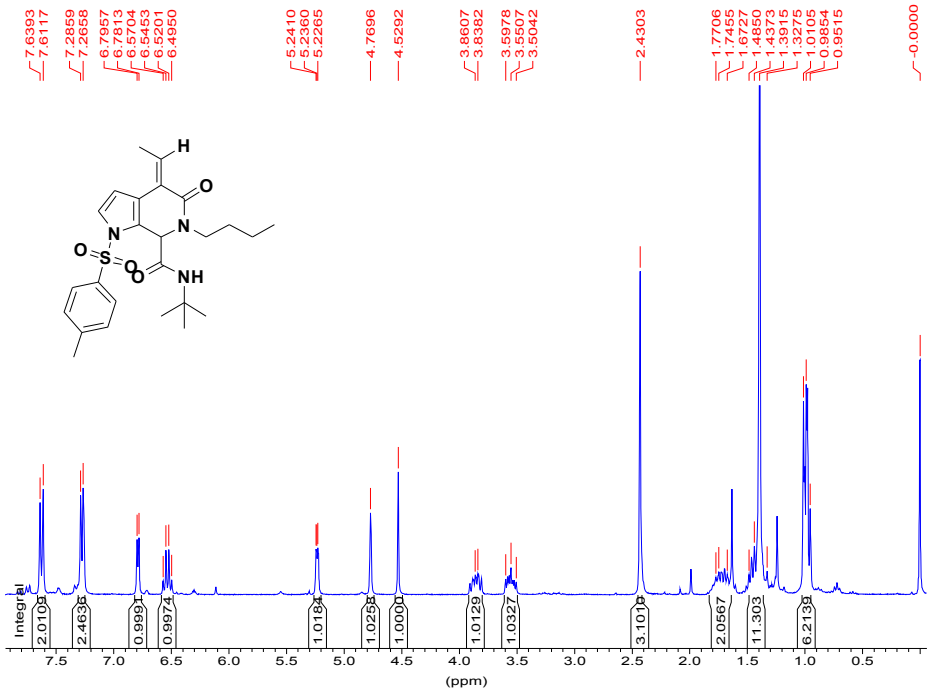


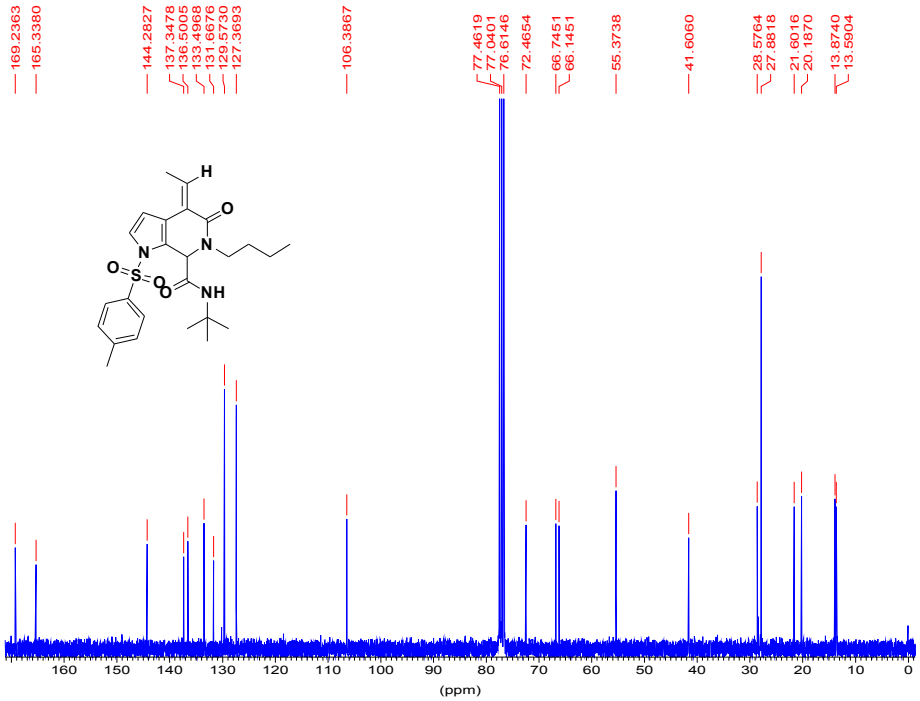
^{1}H and ^{13}C NMR spectra of compound **6h** (300 MHz, $CDCl_3$)



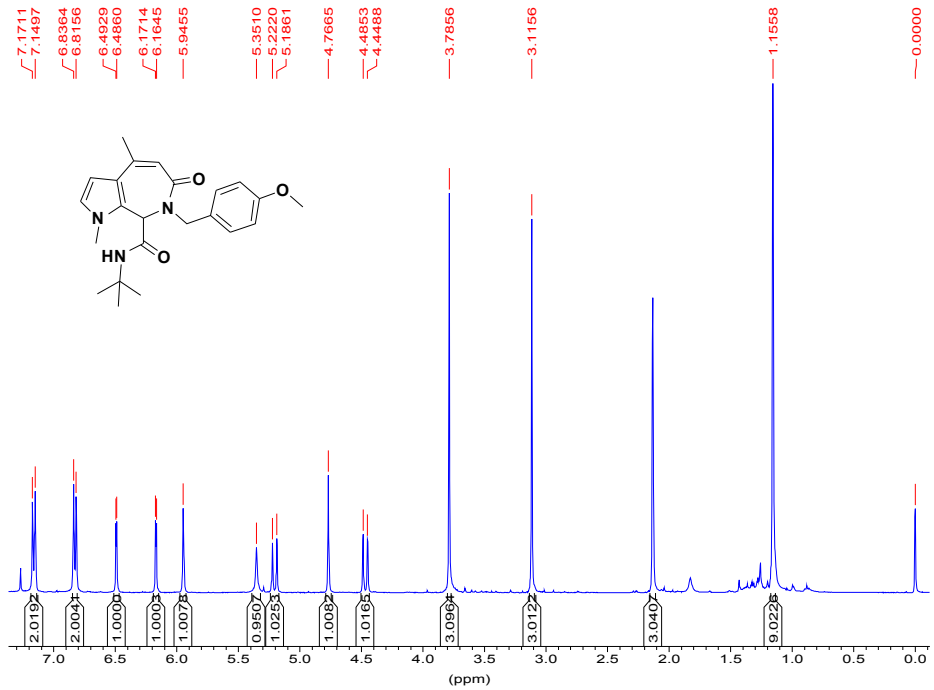


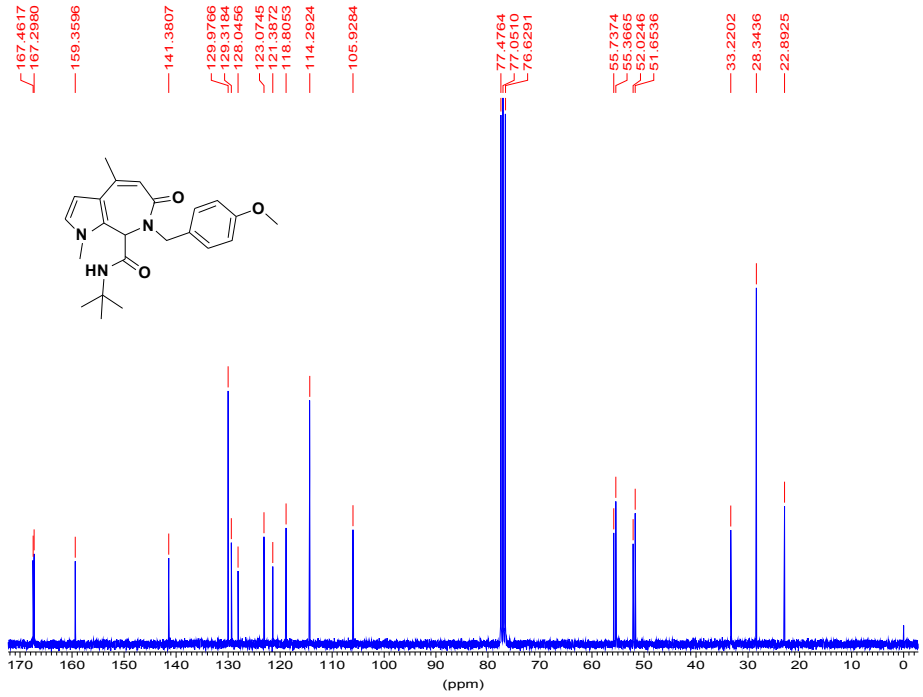
^{1}H and ^{13}C NMR spectra of compound **6i** (300 MHz, $CDCl_3$)



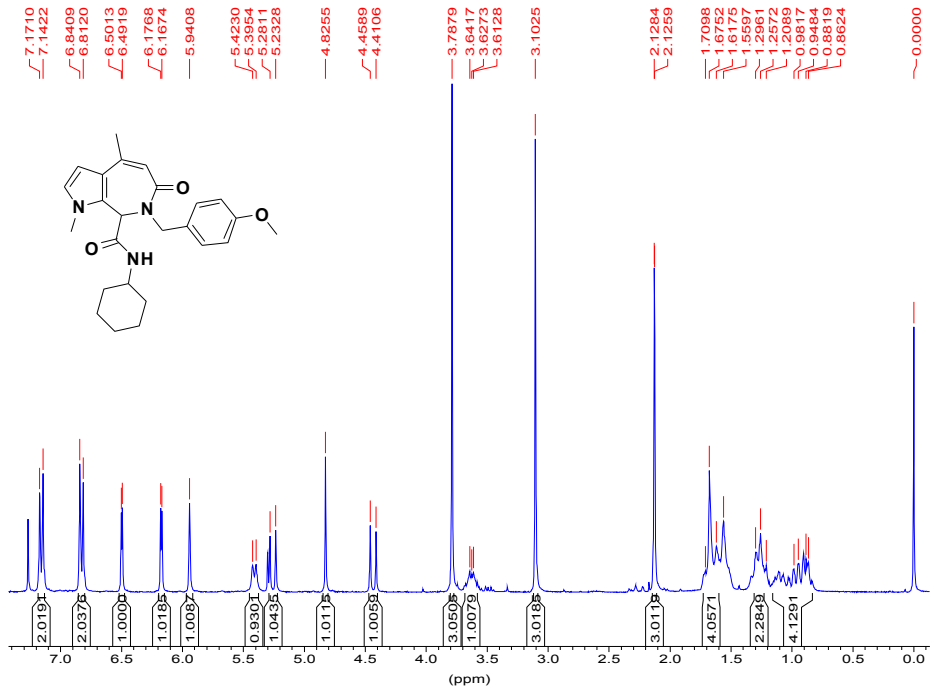


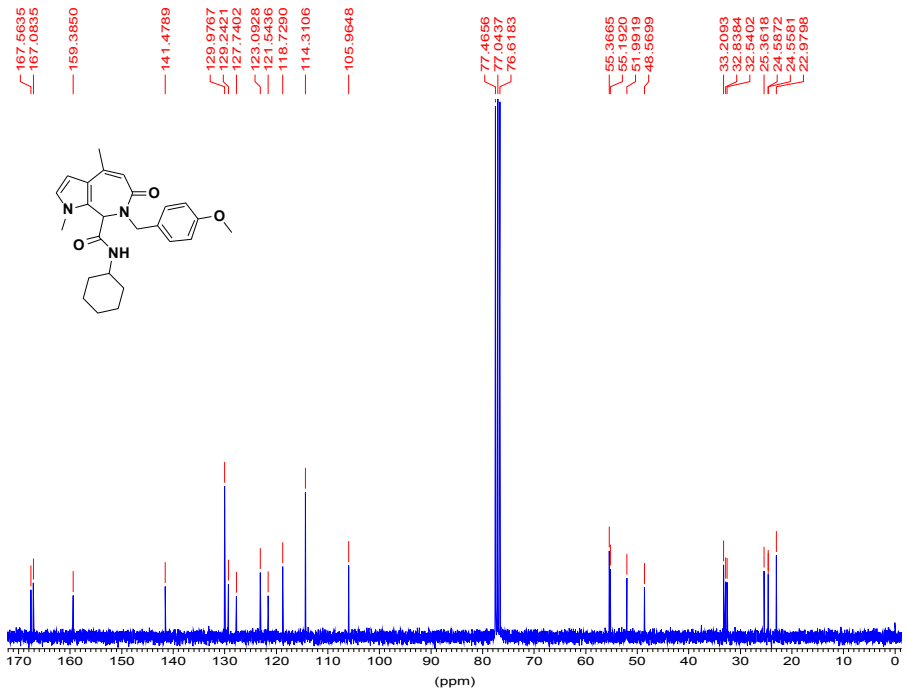
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **7a**



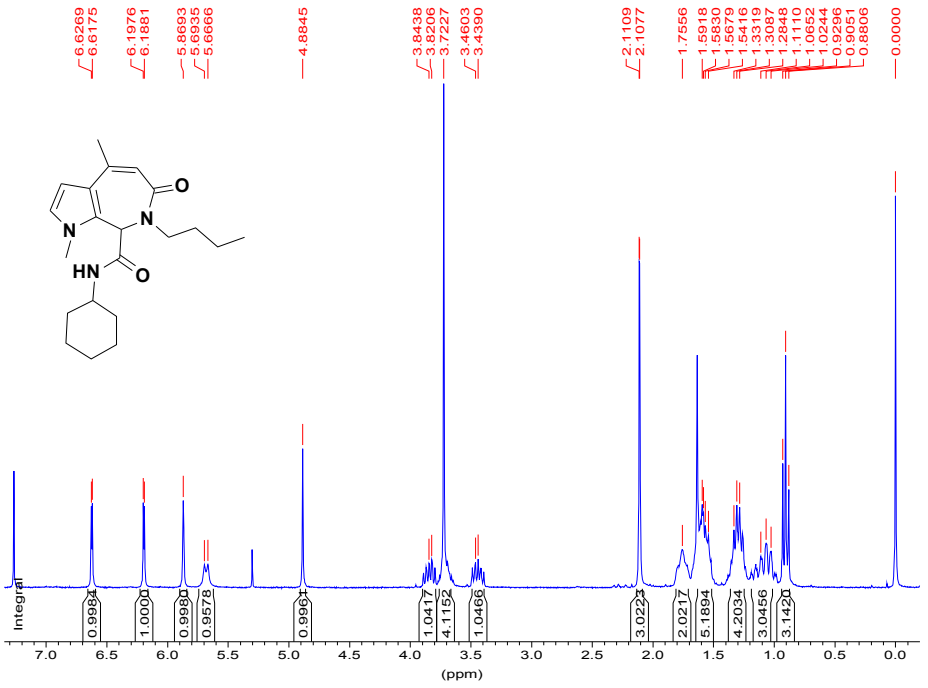


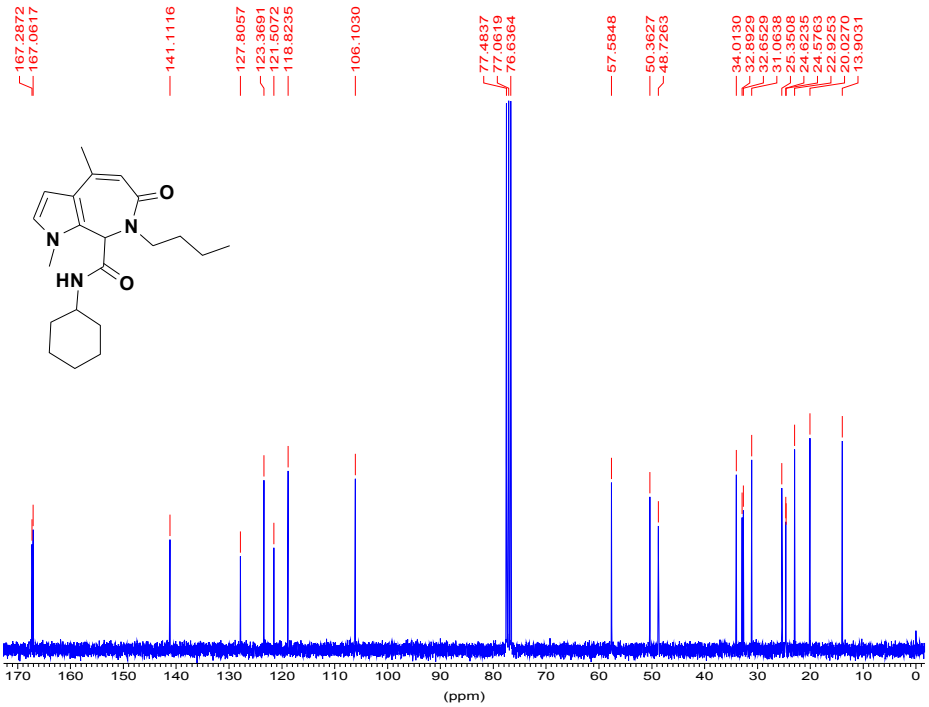
^{1}H and ^{13}C NMR spectra of compound **7b** (300 MHz, $CDCl_3$)



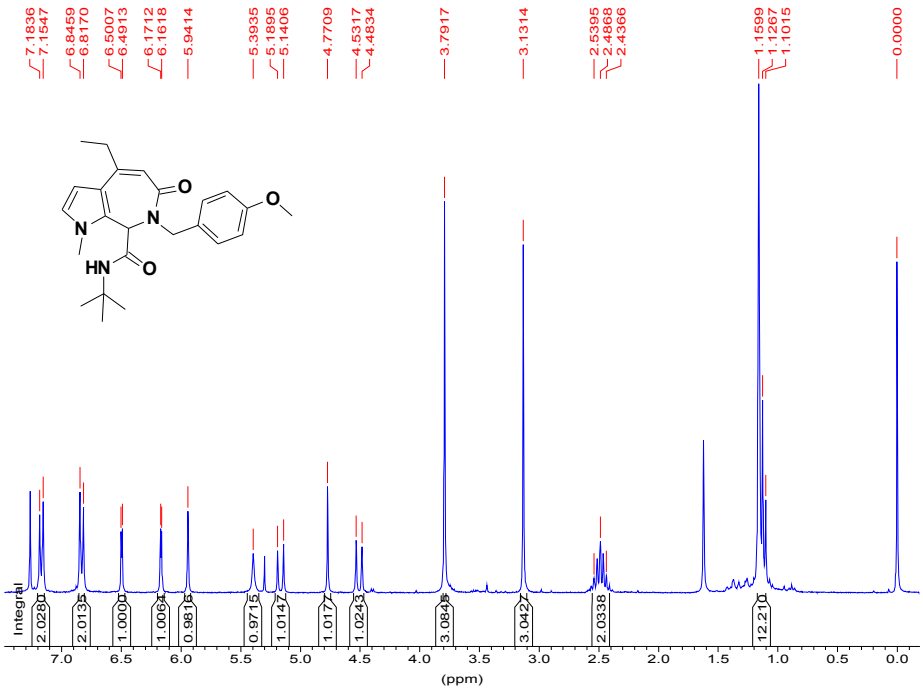


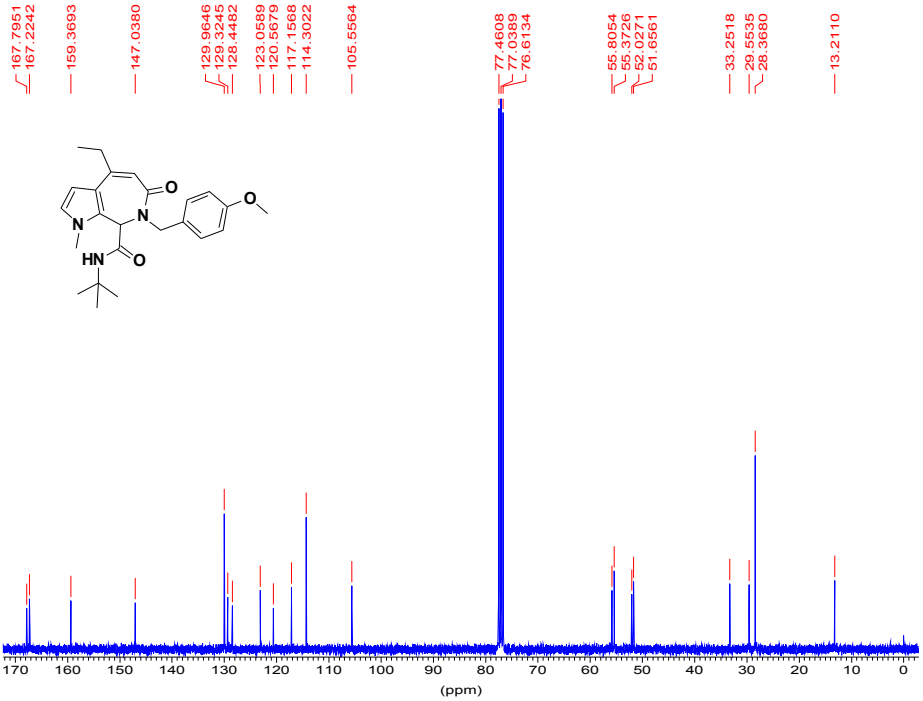
^{1}H and ^{13}C NMR spectra of compound **7c** (300 MHz, $CDCl_3$)



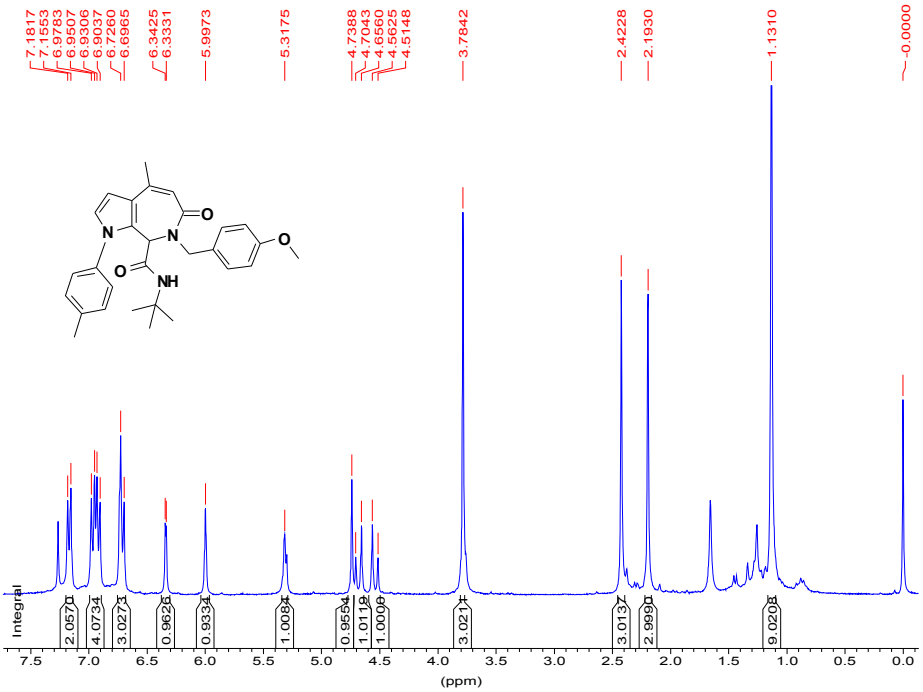


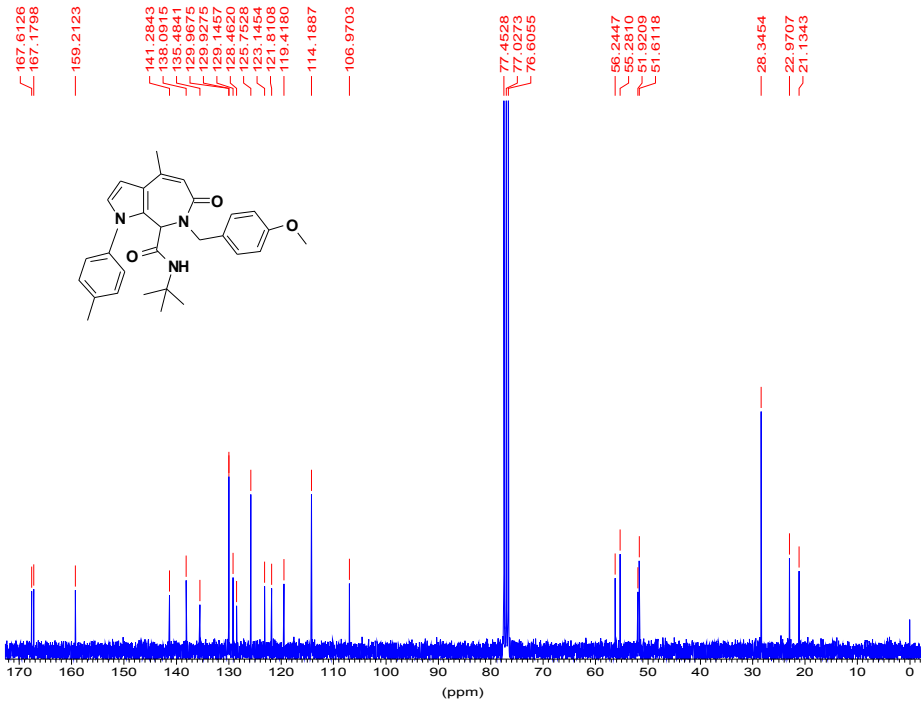
^{1}H and ^{13}C NMR spectra of compound **7d** (300 MHz, $CDCl_3$)



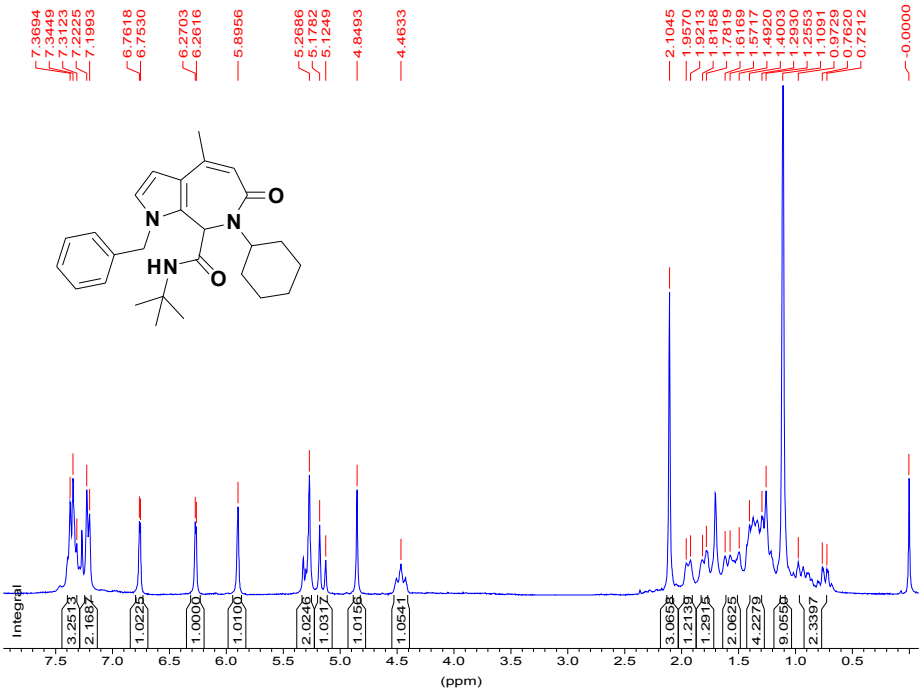


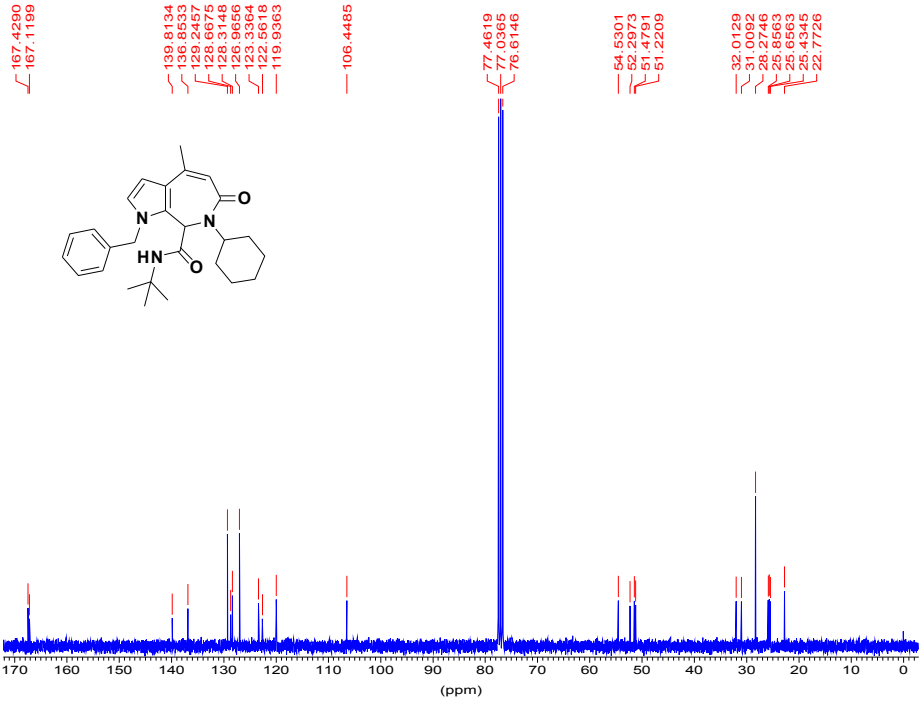
^{1}H and ^{13}C NMR spectra of compound **7f** (300 MHz, $CDCl_3$)





^{1}H and ^{13}C NMR spectra of compound **7g** (300 MHz, $CDCl_3$)





^{1}H and ^{13}C NMR spectra of compound **7h** (300 MHz, $CDCl_3$)