SUPPORTING INFORMATION

Switching the regioselectivity *via* indium(III) and gold(I) catalysis: A post-Ugi intramolecular hydroarylation to azepino- and azocino-[cd]indolone

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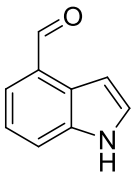
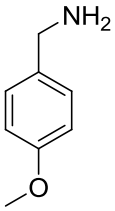
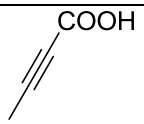
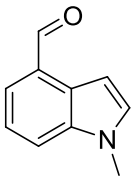
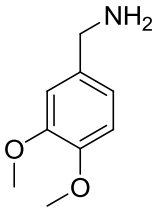
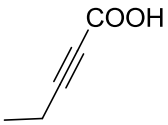
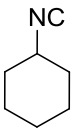
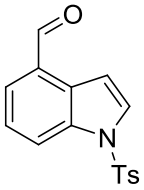
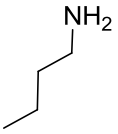
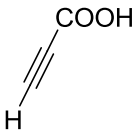
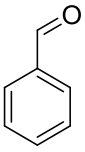
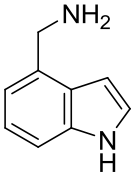
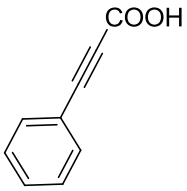
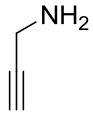
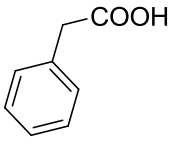
Table of Contents

General Experimental Methods

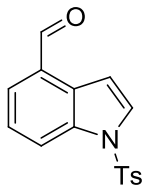
NMR spectra were recorded on a 400 MHz & 300 MHz instrument using $CDCl_3$ and DMSO-d_6 as solvent unless and otherwise stated. The ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. For the Mass spectrometry, ion source temperature 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.

Table 1. Starting materials

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

Synthesis of 1-tosyl-1*H*-indole-4-carbaldehyde (1c)

To a stirred mixture of sodium hydroxide (416 mg, 3 equiv.), tetra-*n*-butylammonium bisulfate (35 mg), and methylene chloride (10 ml) was added 4-formylindole (500 mg, 3.446 mmol), followed at once by a solution of *p*-toluenesulfonyl chloride (821 mg, 1.25 equiv.) in 5 ml of methylene chloride. During additions, the internal temperature was maintained at 5-10^{o}. The reaction mixture was stirred at this temperature for 30 minutes and completion of reaction was checked using TLC. After completion of the reaction, the mixture was diluted with dichloromethane (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 obtained residue which was subjected to silica gel column chromatography (15% Ethylacetate in heptane) to afford the desired product **1c** as solid.



White solid, Yield 73% (750 mg), Melting point; 143-145 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.27 (d, *J*= 8.2Hz, 1H), 7.78-7.71 (m, 4H), 7.50-7.48 (m, 2H), 7.24 (d, *J*= 8.2Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2, 145.4, 135.3, 134.9, 130.0, 129.4(2), 128.9, 128.8, 126.8, 124.2, 119.2, 108.4, 21.5.

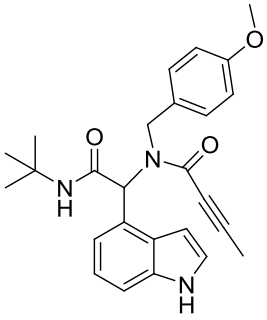
HRMS calculated for $C_{16}H_{13}NO_3S$ 299.0616, found 299.0603.

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

To a solution of carbaldehyde **1a-d** (200mg, 1 equiv) in methanol (3 mL) were added successively Na_2SO_4 (0.3g), amine **2a-e** (1.2 equiv), acid **3a-e** (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 ^{o}C temperature for 12-24 in closed vial. 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 obtained residue which was subjected to silica gel column chromatography (80 % EtOAc in Heptane) to afford the desired product **5a-k** as solid.

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



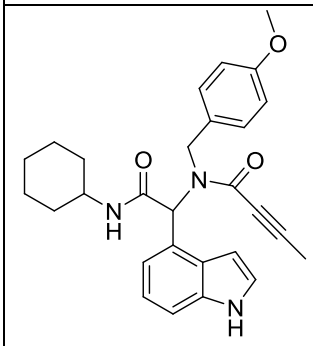
N-(2-(*tert*-butylamino)-1-(1*H*-indol-4-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5a)**

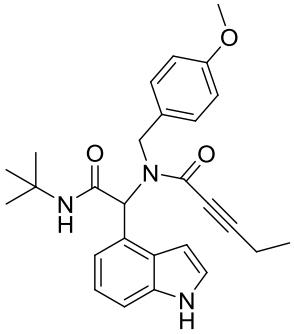
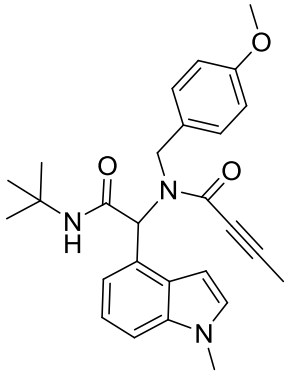
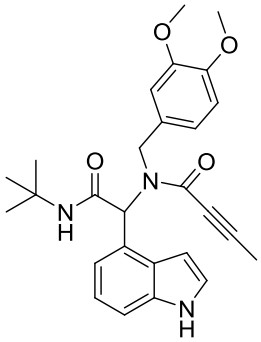
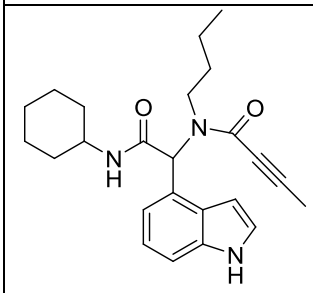
Offwhite solid, Yield 98% (mixture of rotamers ~ 1:1). Melting point: 105-107^{o}C.

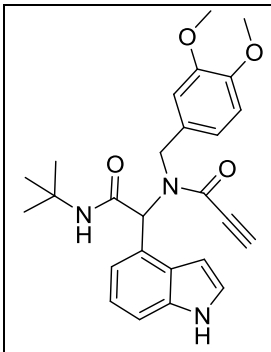
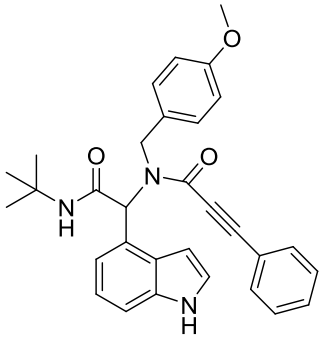
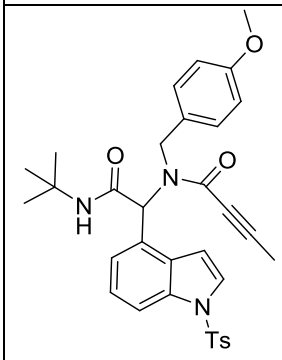
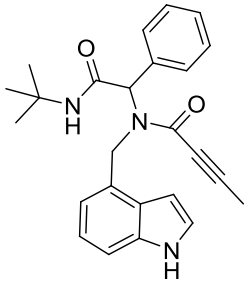
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (bs, 0.35H), 8.22 (bs, 0.64H), 7.40 (d, *J*= 8.0Hz, 0.34H), 7.26-7.06 (m, 4H), 6.90 (d, *J*= 8.1Hz, 0.66H), 6.69-6.60 (m, 2H), 6.46-6.43 (m, 2.39H), 6.35 (s, 0.63H), 5.48 (s, 1H), 4.94 (d, *J*= 16.2Hz, 0.67H), 4.68-4.56 (m, 1H), 3.88 (d, *J*= 15.0Hz, 0.32H), 3.70-3.65 (m, 3H), 2.06 (s, 1H), 1.90 (m, 2H), 1.29 (s, 6H), 1.19 (s, 3H).

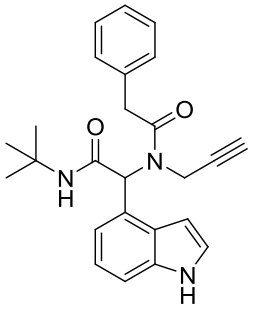
^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 168.5, 158.7, 158.1, 156.4, 156.2, 136.0, 135.7, 130.2, 130.1, 129.7, 128.2(2), 125.8, 125.6, 125.4, 125.0, 121.6, 120.5(2), 113.6, 113.0, 112.3, 111.9, 100.5, 100.0, 91.7, 90.2, 74.1, 73.4, 66.2, 60.1, 55.2, 55.1, 51.6, 51.4, 50.6, 45.3, 28.5, 28.3, 4.0.

HRMS calculated for $C_{26}H_{29}N_3O_3$ 431.2209, found 431.2208.

Structure	Data
	*N*-(2-(cyclohexylamino)-1-(1*H*-indol-4-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5b)** Offwhite solid, Yield 87%, Melting point: 84-86 ^{o}C. **HRMS** calculated for $C_{28}H_{31}N_3O_3$ 457.2365, found 332.1527 (M-125).

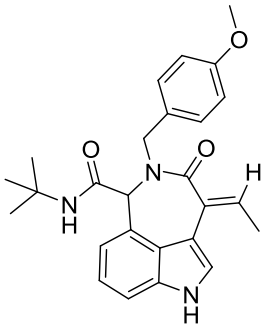
	*N*-(2-(*tert*-butylamino)-1-(1*H*-indol-4-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)pent-2-ynamide **(5c)** Offwhite solid, Yield 80%, Melting point: 69-71^{o}C. **HRMS** calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2344.
	*N*-(2-(*tert*-butylamino)-1-(1-methyl-1*H*-indol-4-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5d)** Yellow solid, Yield 93%, Melting point: 59-61^{o}C. **HRMS** calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2369.
	*N*-(2-(*tert*-butylamino)-1-(1*H*-indol-4-yl)-2-oxoethyl)-*N*-(3,4-dimethoxybenzyl)but-2-ynamide **(5e)** Offwhite solid, Yield 92%, Melting point: 129-131^{o}C. **HRMS** calculated for $C_{27}H_{31}N_3O_4$ 461.2315, found 461.2319.
	*N*-butyl-*N*-(2-(cyclohexylamino)-1-(1*H*-indol-4-yl)-2-oxoethyl)but-2-ynamide **(5f)** Yellow solid, Yield 62%, Melting point: 206-208 ^{o}C. **HRMS** calculated for $C_{24}H_{31}N_3O_2$ 393.2416, found 393.2429.

	N-(2-(tert-butylamino)-1-(1H-indol-4-yl)-2-oxoethyl)-N-(3,4-dimethoxybenzyl)propiolamide **(5g)** Offwhite solid, Yield 91%, Melting point: 135-137 ^{o}C. **HRMS** calculated for $C_{26}H_{29}N_3O_4$ 447.2158, found 447.2180.
	*N*-(2-(*tert*-butylamino)-1-(1*H*-indol-4-yl)-2-oxoethyl)-*N*-(4-methoxybenzyl)-3-phenylpropiolamide **(5h)** Offwhite solid, Yield 76%, Melting point: 85-87 ^{o}C. **HRMS** calculated for $C_{31}H_{31}N_3O_3$ 493.2365, found 493.2360.
	*N*-(2-(*tert*-butylamino)-2-oxo-1-(1-tosyl-1*H*-indol-4-yl)ethyl)-*N*-(4-methoxybenzyl)but-2-ynamide **(5i)** White solid, Yield 68%, Melting point: 91-93 ^{o}C. **HRMS** calculated for $C_{33}H_{35}N_3O_5S$ 585.2297, found 485.1051 (M-100).
	*N*-((1*H*-indol-4-yl)methyl)-N-(2-(*tert*-butylamino)-2-oxo-1-phenylethyl)but-2-ynamide **(5j)** White solid, Yield 84%, Melting point: 83-85 ^{o}C. **HRMS** calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2117.

	*N-tert*-butyl-2-(1*H*-indol-4-yl)-2-(2-phenyl-*N*-(prop-2-ynyl)acetamido)acetamide **(5k)** Offwhite solid, Yield 64%, Melting point: 80-82 ^{o}C. **HRMS** calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2098.

Mehod A: General procedure for $In(OTf)_3$ catalyzed cyclization.

To a glass vial $In(OTf)_3$ (10 mol%) were loaded along with dry dichloroethane (2 mL). Ugi product **5a-j (**0.25 mmol**)** was added. The reaction vial was evacuated-backfilled with argon (4 cycles) and was stirred at 100 ^{o}C 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 (3% methanol in dichloromethane) to afford compound **6a-j**.



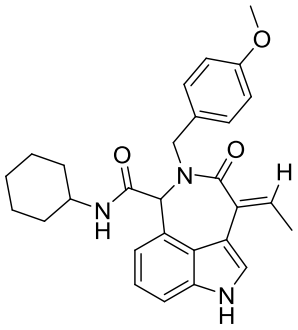
(*E*)-*N*-*tert*-butyl-3-ethylidene-5-(4-methoxybenzyl)-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6a)**

Yellow solid, Yield 80%, Melting point: 103-105 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.28 (s, 1H), 8.08 (s, 1H), 7.42-7.39 (m, 2H), 7.29 (d, *J*= 8.6Hz, 1H), 7.19 (d, *J*= 8.5Hz, 2H), 6.89-6.72 (m, 4H), 5.38 (s, 1H), 4.93 (d, *J*= 15.2Hz, 1H), 4.19 (d, *J*= 15.2Hz, 1H), 3.67 (s, 3H), 2.11 (d, *J*= 7.6Hz, 3H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.5, 166.1, 158.3, 134.6, 130.5, 129.7, 128.6, 128.2, 126.0, 124.4, 123.2, 122.2, 120.4, 113.6, 110.8, 99.8, 62.9, 55.0, 50.5, 48.4, 28.2, 15.5.

HRMS calculated for $C_{26}H_{29}N_3O_3$ 431.2209, found 431.2179.



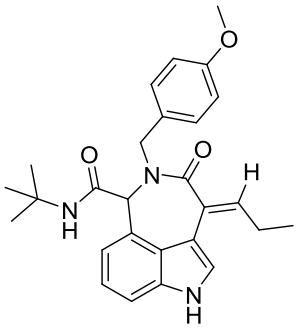
(*E*)-*N*-cyclohexyl-3-ethylidene-5-(4-methoxybenzyl)-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6b)**

Offwhite solid, Yield 70%, Melting point: 108-110 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.28 (s, 1H), 8.25 (d, *J*= 8.0Hz, 1H), 7.41-7.38 (m, 2H), 7.27 (d, *J*= 8.6Hz, 1H), 7.17 (d, *J*= 8.5Hz, 2H), 6.84-6.71 (m, 4H), 5.31 (s, 1H), 4.94 (d, *J*= 15.0Hz, 1H), 4.16 (d, *J*= 15.0Hz, 1H), 3.68 (s, 3H), 3.33 (m, 1H), 2.09 (d, *J*= 7.5Hz, 3H), 1.62-1.42 (m, 5H), 1.12-1.09 (m, 5H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.2, 166.4, 158.3, 134.6, 130.6, 129.4, 128.7, 128.4, 126.0, 124.4, 123.0, 122.3, 120.4, 113.6, 110.8, 99.8, 62.3, 54.9, 48.4, 47.9, 32.2, 32.0, 25.1, 24.2, 24.1, 15.4.

HRMS calculated for $C_{28}H_{31}N_3O_3$ 457.2365, found 457.2349.



(*E*)-*N*-*tert*-butyl-5-(4-methoxybenzyl)-4-oxo-3-propylidene-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6c)**

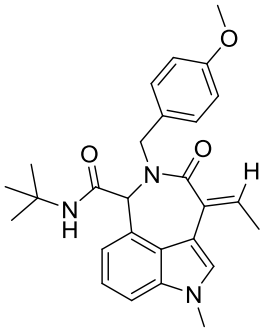
Brown solid, Yield 69%, Melting point: 77-79 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.29 (bs, 1H), 8.06 (s, 1H), 7.41-7.39 (m, 2H), 7.24-7.18 (m, 3H), 6.84-6.81 (m, 3H), 6.60 (t, *J*= 7.5Hz, 1H), 5.38 (s, 1H), 4.95 (d, *J*= 15.0Hz, 1H), 4.17

(d, *J*= 15.0Hz, 1H), 3.67 (s, 3H), 2.68-2.58 (m, 1H), 1.64-1.58 (m, 1H), 1.24 (t, *J*= 7.1Hz, 3H), 1.11 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.5, 166.2, 158.3, 135.6, 134.7, 129.7, 129.0, 128.6, 126.0, 124.4, 123.2, 122.4, 120.2, 113.6, 110.9, 99.9, 63.0, 55.0, 50.5, 48.4, 28.2, 22.4, 14.2.

HRMS calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2398.



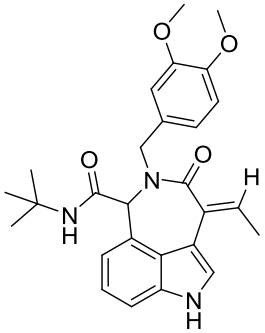
(*E*)-*N*-*tert*-butyl-3-ethylidene-5-(4-methoxybenzyl)-1-methyl-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6d)**

Yellow solid, Yield 80%, Melting point: 75-77 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.06 (s, 1H), 7.46-7.33 (m, 3H), 7.17 (d, *J*= 7.6Hz, 2H), 6.82-6.76 (m, 4H), 5.38 (s, 1H), 4.93 (d, *J*= 15.2Hz, 1H), 4.19 (d, *J*= 15.2Hz, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.11 (d, *J*= 7.1Hz, 3H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.5, 166.2, 158.3, 135.1, 130.4, 130.3, 129.7, 128.6, 124.7, 123.5, 122.4, 120.4, 113.6, 109.2, 99.1, 62.8, 55.0, 50.5, 48.4, 32.6, 28.2, 15.5.

HRMS calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2393.



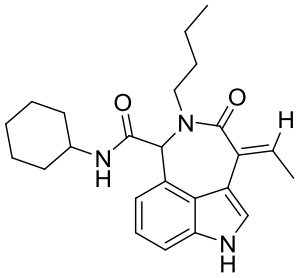
(*E*)-*N*-*tert*-butyl-5-(3,4-dimethoxybenzyl)-3-ethylidene-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6e)**

White solid, Yield 89%, Melting point: 219-221 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.28 (bs, 1H), 8.00 (s, 1H), 7.42-7.39 (m, 2H), 7.29 (d, *J*= 8.5Hz, 1H), 6.89 (s, 1H), 6.83-6.81 (m, 2H), 6.74-6.71 (m, 2H), 5.38 (s, 1H), 4.91 (d, *J*= 15.4Hz, 1H), 4.24 (d, *J*= 15.4Hz, 1H), 3.66-3.64 (m, 6H), 2.11 (d, *J*= 7.6Hz, 3H), 1.09 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.5, 166.3, 148.5, 147.9, 134.6, 130.6, 130.1, 128.3, 126.0, 124.4, 123.3, 122.3, 120.4, 119.1, 111.7, 111.6, 110.8, 99.8, 63.0, 55.5, 55.3, 50.5, 48.7, 28.2, 15.5.

HRMS calculated for $C_{27}H_{31}N_3O_4$ 461.2315, found 461.2323.



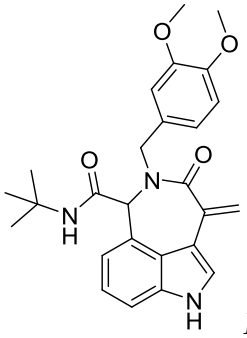
(*E*)-5-butyl-*N*-cyclohexyl-3-ethylidene-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6f)**

Brown solid, Yield 86%, Melting point: 95-97 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ11.28 (bs, 1H), 8.36 (d, *J*= 7.5Hz, 1H), 7.41-7.38 (m, 2H), 7.25 (d, *J*= 8.4Hz, 1H), 6.88 (s, 1H), 6.67 (q, *J*= 7.4Hz, 1H), 5.33(s, 1H), 3.60-3.58 (m, 1H), 3.33 (m, 1H), 3.22 (m, 1H), 2.06 (d, *J*= 7.3Hz, 3H), 1.78-1.48 (m, 7H), 1.23-1.15 (m, 7H), 0.87 (t, *J*= 6.7Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.8, 166.0, 134.6, 130.7, 127.8, 126.0, 124.4, 123.1, 122.4, 120.3, 110.7, 99.7, 62.3, 47.8, 45.8, 32.2, 32.0, 29.4, 25.1, 24.2, 24.1, 19.7, 15.4, 13.7.

HRMS calculated for $C_{24}H_{31}N_3O_2$ 393.2416, found 393.2411.



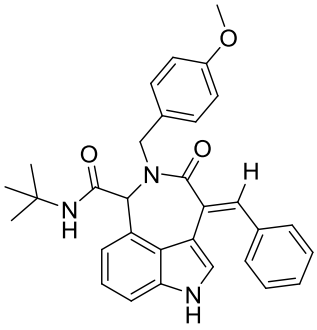
N-*tert*-butyl-5-(3,4-dimethoxybenzyl)-3-methylene-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6g)**

Yellow solid, Yield 86%, Melting point: 99-101 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.31 (bs, 1H), 8.18 (s, 1H), 7.48-7.39 (m, 3H), 6.93-6.77 (m, 4H), 6.13 (s, 1H), 5.97 (s, 1H), 5.46 (s, 1H), 5.04 (d, *J*= 15.3Hz, 1H), 4.16 (d, *J*= 15.3Hz, 1H), 3.69 (s, 6H), 1.09 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.3, 164.1, 148.6, 147.9, 136.2, 135.3, 129.8, 125.8, 123.8, 122.6, 122.0, 119.1, 117.4, 115.0, 112.0, 111.8, 111.7, 100.3, 63.1, 55.5, 55.4, 50.6, 48.4, 28.2.

HRMS calculated for $C_{26}H_{29}N_3O_4$ 447.2158, found 447.2145.



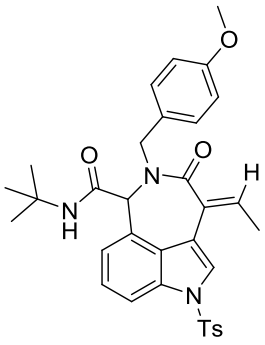
(*E*)-3-benzylidene-*N*-*tert*-butyl-5-(4-methoxybenzyl)-4-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6h)**

Yellow solid, Yield 60%, Melting point: 108-110 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.28 (s, 1H), 8.08 (s, 1H), 7.49 (s, 1H), 7.36 (m, 3H), 7.29-7.21 (m, 5H), 7.08 (d, *J*= 8.6Hz, 1H), 6.92-6.83 (m, 4H), 5.46 (s, 1H), 4.95 (d, *J*= 15.1Hz, 1H), 4.30 (d, *J*= 15.1Hz, 1H), 3.68 (s, 3H), 1.14 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.5, 166.0, 158.4, 136.8, 134.8, 130.7, 129.5, 129.2, 128.9, 128.7, 128.2, 127.6, 126.0, 124.4, 121.6, 120.9, 113.7, 110.6, 100.0, 63.0, 55.0, 50.6, 48.6, 28.2.

HRMS calculated for $C_{31}H_{31}N_3O_3$ 493.2365, found 496.2379.



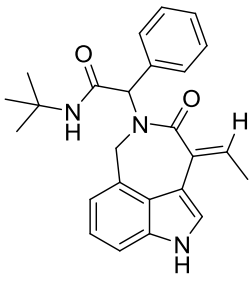
(*E*)-*N*-*tert*-butyl-3-ethylidene-5-(4-methoxybenzyl)-4-oxo-1-tosyl-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide **(6i)**

Offwhite solid, Yield 73%, Melting point: 199-201 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.09 (s, 1H), 7.92 (m, 4H), 7.54 (d, *J*= 8.5Hz, 1H), 7.39 (d, *J*= 7.8Hz, 2H), 7.24 (bs, 1H), 7.18 (d, *J*= 7.8Hz, 2H), 6.89-6.81 (m, 3H), 5.34 (s, 1H), 4.77 (d, *J*= 14.7Hz, 1H), 4.29 (d, *J*= 14.7Hz, 1H), 3.67 (s, 3H), 2.31 (s, 3H), 2.11 (d, *J*= 7.4Hz, 3H), 1.03 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 166.9, 165.6, 158.4, 145.7, 134.0, 132.5, 131.3, 130.3, 129.4, 129.3, 128.8, 127.6, 127.1, 126.8, 124.6, 123.7, 113.6, 112.2, 107.0, 62.3, 55.0, 50.6, 48.7, 28.1, 21.0, 15.5.

HRMS calculated for $C_{33}H_{35}N_3O_5S$ 585.2297, found 585.2273.



(*E*)-*N*-*tert*-butyl-2-(3-ethylidene-4-oxo-3,4-dihydro-1*H*-azepino[5,4,3-*cd*]indol-5(6*H*)-yl)-2-phenylacetamide **(6j)**

White solid, Yield 77%, Melting point: 267-269 ^{o}C.

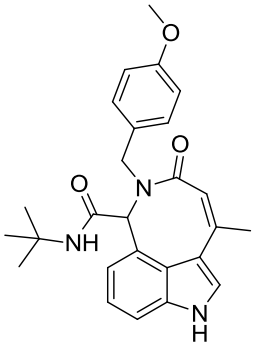
^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.27 (bs, 1H), 8.03 (s, 1H), 7.39-7.23 (m, 8H), 6.76 (q, *J*= 7.5Hz, 1H), 6.37 (s, 1H), 6.05 (s, 1H), 4.88 (d, *J*= 16.0Hz, 1H), 4.09 (d, *J*= 16.0Hz, 1H), 2.08 (d, *J*= 7.4Hz, 3H), 1.28 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 168.9, 167.1, 136.6, 134.5, 131.0, 129.8, 128.6, 128.5, 127.7, 126.0, 124.4, 124.0, 121.4, 120.2, 110.2, 98.4, 59.3, 50.4, 44.1, 28.4, 15.2.

HRMS calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2112.

Method B: General procedure for (IPr)AuNTf$_2$ catalyzed cyclization.

To a glass vial (IPr)AuCl (10 mol%) and AgNTf$_2$ (10 mol%) were loaded along with dry dichloroethane (2 mL). Ugi product **5a-j (**0.25 mmol**)** was added and the reaction vial was evacuated-backfilled with argon (4 cycles) and was stirred at 100 ^{o}C 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 (5% methanol in dichloromethane) to afford compound **7a-h,j**.



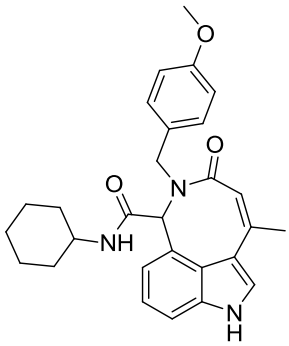
(*Z*)-*N*-*tert*-butyl-6-(4-methoxybenzyl)-3-methyl-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7a)**

Grey solid, Yield 78%, Melting point: 247-249 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (bs, 1H), 7.37-7.30 (m, 4H), 7.16 (s, 1H), 6.84 (d, *J*= 7.2Hz, 2H), 6.32 (s, 1H), 6.21 (s, 1H), 5.24 (s, 1H), 5.16-5.09 (m, 2H), 4.32 (d, *J*= 14.3Hz, 1H), 3.80 (s, 3H), 2.28 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 167.2, 159.3, 145.0, 136.1, 130.3, 129.0, 128.1, 127.9, 127.3, 125.6, 123.2, 121.0, 114.4, 111.3, 100.0, 60.7, 55.3, 51.4, 51.3, 28.2, 24.4.

HRMS calculated for $C_{26}H_{29}N_3O_3$ 431.2209, found 461.2319.



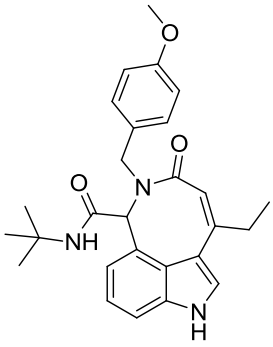
(*Z*)-*N*-cyclohexyl-6-(4-methoxybenzyl)-3-methyl-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7b)**

Brown solid, Yield 68%, Melting point: 204-206 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.26 (bs, 1H), 7.41-7.34 (m, 2H), 7.26-7.18 (m, 3H), 6.71 (d, *J*= 7.6Hz, 2H), 6.57 (s, 1H), 6.14 (d, *J*= 7.4Hz, 1H), 5.95 (s, 1H), 5.47 (s, 1H), 4.61 (s, 2H), 3.65 (s, 3H), 3.47 (m, 1H), 2.18 (s, 3H), 1.61-1.49 (m, 5H), 1.18-0.96 (m, 5H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.4, 166.1, 158.3, 155.5, 143.2, 136.0, 129.7, 128.4, 127.4, 126.9, 126.1, 123.1, 120.1, 113.5, 111.1, 100.0, 61.1, 54.9, 51.5, 47.9, 34.8, 31.9, 31.7, 25.0, 24.6, 23.9.

HRMS calculated for $C_{28}H_{31}N_3O_3$ 457.2365, found 457.2360.



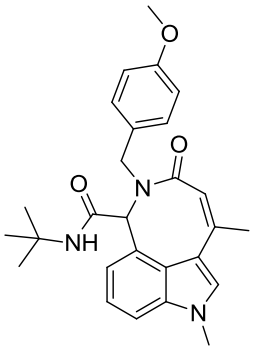
(*Z*)-*N*-*tert*-butyl-3-ethyl-6-(4-methoxybenzyl)-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7c)**

Offwhite solid, Yield 76%, Melting point: 95-97 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.30 (bs, 1H), 7.43-7.25 (m, 6H), 6.81 (d, *J*= 8.4Hz, 2H), 5.95 (s, 1H), 5.44 (s, 1H), 5.34 (s, 1H), 4.83 (d, *J*= 14.1Hz, 1H), 4.31 (d, *J*= 14.1Hz, 1H), 3.69 (s, 3H), 2.72-2.56 (m, 2H), 1.03-0.96 (m, 12H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.4, 166.1, 158.6, 149.0, 135.8, 130.0, 129.7, 129.1, 127.7, 126.2, 125.8, 121.1, 119.8, 113.9, 111.1, 100.0, 61.7, 55.0, 51.4, 50.5, 29.5, 28.0, 12.4.

HRMS calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2387.



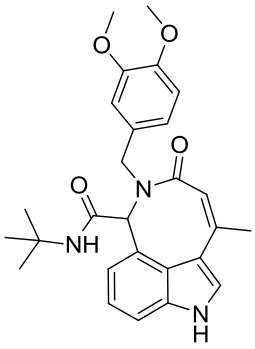
(*Z*)-*N*-*tert*-butyl-6-(4-methoxybenzyl)-1,3-dimethyl-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7d)**

Yellow solid, Yield 75%, Melting point: 66-68 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.47 (d, *J*= 8.2Hz, 1H), 7.36-7.26 (m, 4H), 6.76 (d, *J*= 7.8Hz, 2H), 6.68 (s, 1H), 6.00 (s, 1H), 5.46 (s, 1H), 5.23 (s, 1H), 4.69 (d, *J*= 14.3Hz, 1H), 4.49 (d, *J*= 14.3Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 2.21 (s, 3H), 1.04 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 172.8, 171.2, 163.7, 148.6, 141.6, 135.9, 135.0(2), 133.9, 132.8, 132.3, 128.5, 125.4, 119.0, 114.8, 104.5, 66.6, 60.2, 56.8, 55.8, 37.9, 33.1, 29.2.

HRMS calculated for $C_{27}H_{31}N_3O_3$ 445.2365, found 445.2397.



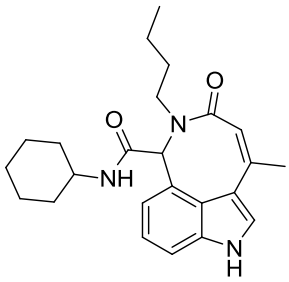
(*Z*)-*N*-*tert*-butyl-6-(3,4-dimethoxybenzyl)-3-methyl-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7e)**

Offwhite solid, Yield 76%, Melting point: 263-265 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.96 (bs, 1H), 7.91 (s, 1H), 7.37 (d, *J*= 7.6Hz, 1H), 7.17-6.96 (m, 6H), 6.37 (s, 1H), 6.19 (s, 1H), 4.13 (dd, *J*= 15.3Hz, 2H), 3.74-3.64 (m, 6H), 2.20 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 174.6, 170.6, 153.6, 153.1, 152.3, 148.1, 140.7, 135.5, 134.9, 134.2, 130.1, 128.4, 125.5, 123.6, 116.6, 114.7, 104.6, 97.8, 63.2, 60.8, 59.6, 55.6, 33.7, 29.0.

HRMS calculated for $C_{27}H_{31}N_3O_4$ 461.2315, found 461.2313.



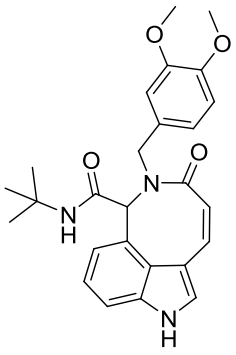
(*Z*)-6-butyl-*N*-cyclohexyl-3-methyl-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7f)**

Brown solid, Yield 40%, Melting point: 88-90 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.30 (bs, 1H), 7.43 (m, 2H), 7.25 (d, *J*= 8.8Hz, 1H), 6.94 (s, 1H), 6.42 (d, *J*= 8.2Hz, 1H), 5.88 (s, 1H), 5.52 (s, 1H), 3.73 (m, 1H), 3.53 (m, 1H), 2.16 (s, 3H), 1.54 (m, 5H), 1.32-1.11 (m, 9H), 0.65 (t, *J*= 6.8Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.6, 165.7, 142.4, 136.8, 136.0, 128.9, 127.2, 127.0, 126.2, 123.6, 120.1, 111.1, 100.4, 61.1, 48.0, 32.0, 31.8, 29.8, 25.0, 24.8, 23.8, 19.2, 13.5.

HRMS calculated for $C_{24}H_{31}N_3O_2$ 393.2416, found 393.2424.



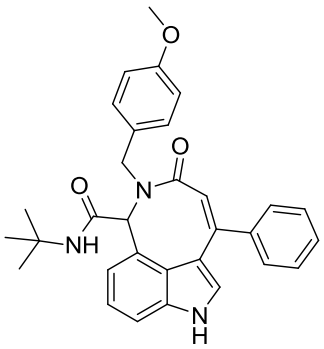
(*Z*)-*N*-*tert*-butyl-6-(3,4-dimethoxybenzyl)-5-oxo-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7g)**

Brown solid, Yield 40%, Melting point: 97-99 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.22 (bs, 1H), 8.06 (s, 1H), 7.41 (d, *J*= 8.2Hz, 1H), 7.30 (s, 1H), 7.18-7.12 (m, 2H), 7.00 (d, *J*= 7.2Hz, 1H), 6.79 (s, 1H), 6.56 (s, 1H), 6.23-6.20 (m, 2H), 6.10 (s, 1H), 4.85 (d, *J*= 17.5Hz, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 3.57 (d, *J*= 17.5Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 169.2, 162.4, 149.4, 148.3, 135.7, 134.1, 127.4, 127.2, 125.6, 123.3, 122.0, 120.8, 118.7, 116.4, 111.6, 108.3, 106.1, 99.2, 57.8, 55.6, 55.4, 50.4, 46.5, 28.4.

HRMS calculated for $C_{26}H_{29}N_3O_4$ 447.2158, found 447.2161.



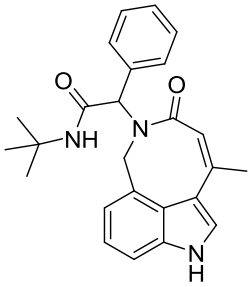
(*Z*)-*N*-*tert*-butyl-6-(4-methoxybenzyl)-5-oxo-3-phenyl-1,5,6,7-tetrahydroazocino[5,4,3-*cd*]indole-7-carboxamide **(7h)**

Brown solid, Yield 44%, Melting point: 130-132 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.34 (bs, 1H), 7.38-7.30 (m, 10H), 6.75 (m, 3H), 6.14 (s, 1H), 5.67-5.61 (m, 2H), 4.78 (d, *J*= 14.6Hz, 1H), 4.54 (d, *J*= 14.6Hz, 1H), 3.67 (s, 3H), 0.94 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.5, 166.2, 147.7, 141.9, 136.1, 129.9, 129.8, 129.5, 128.6, 128.3, 128.1, 127.4, 126.3, 126.2, 123.1(2), 113.7, 110.9, 100.2, 61.9, 55.0, 51.8, 50.7, 27.8.

HRMS calculated for $C_{31}H_{31}N_3O_3$ 493.2365, found 493.2369.



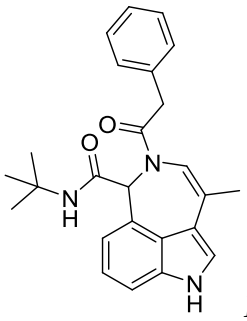
(*Z*)-*N*-*tert*-butyl-2-(3-methyl-5-oxoazocino[5,4,3-*cd*]indol-6(1*H*,5*H*,7*H*)-yl)-2-phenylacetamide **(7j)**

White solid, Yield 81%, Melting point: 253-255 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.10 (bs, 1H), 7.32-7.12 (m, 10H), 6.24 (s, 1H), 6.01 (s, 1H), 4.51-4.28 (m, 2H), 2.32 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 167.2, 144.9, 136.4, 135.8, 129.1, 128.9, 128.6, 128.2, 127.7, 125.6, 125.3, 122.3, 120.0, 110.7, 99.8, 61.2, 50.2, 43.7, 28.2, 24.8.

HRMS calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2104.



N-*tert*-butyl-3-methyl-5-(2-phenylacetyl)-5,6-dihydro-1*H*-azepino[5,4,3-*cd*]indole-6-carboxamide (**6k**)

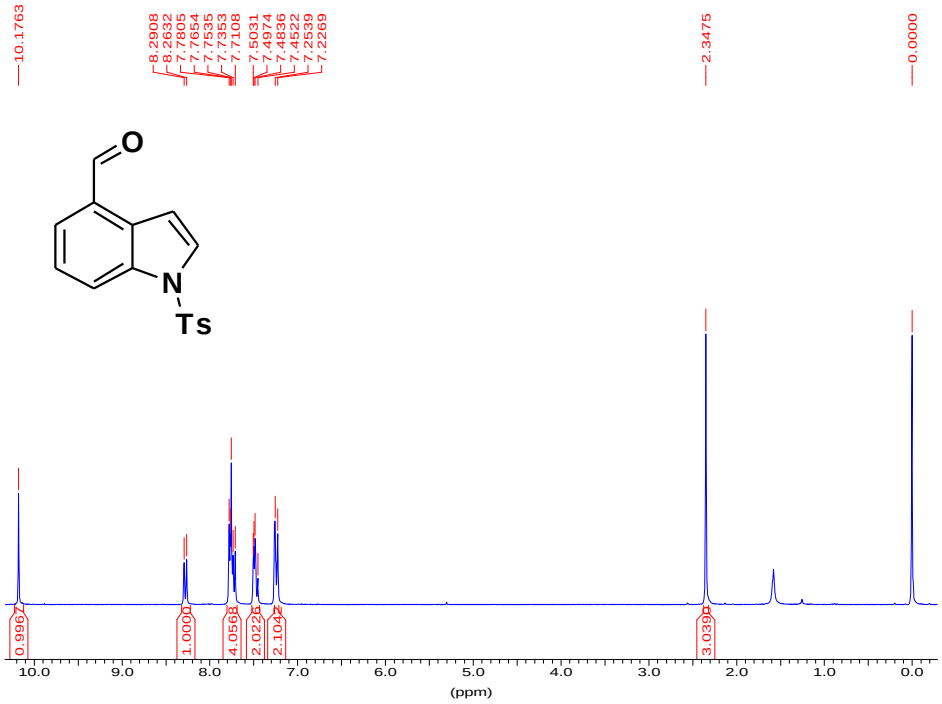
Grey solid, Yield 62% (Method A); 70% (Method B), Melting point: 85-87 ^{o}C.

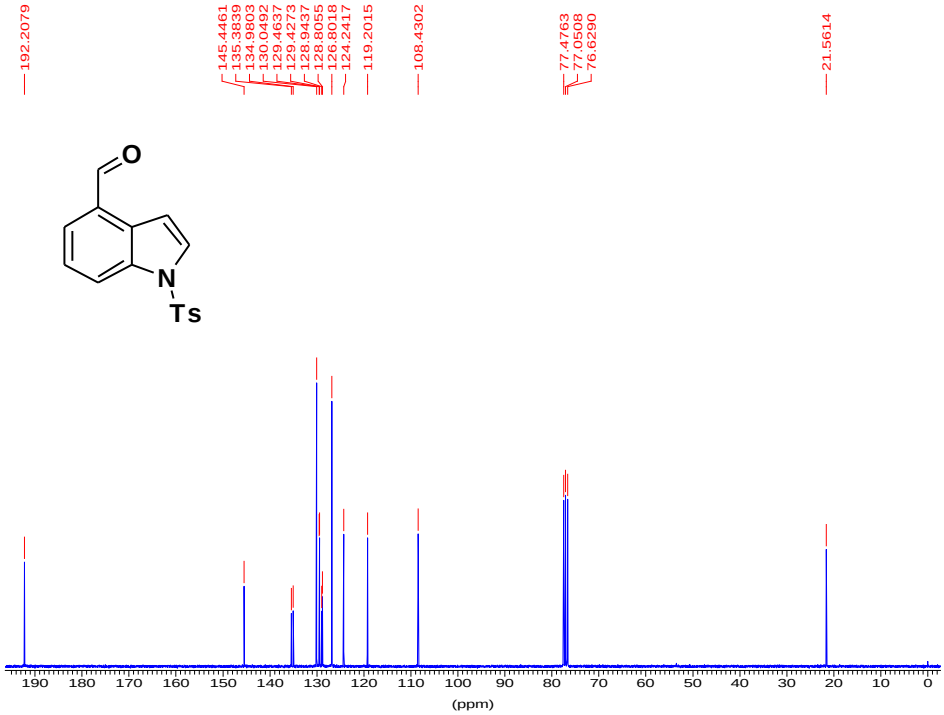
^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.42 (bs, 1H), 7.48 (s, 1H), 7.34 (d, *J*= 8.1Hz, 1H), 7.17-7.09 (m, 6H), 6.95 (d, *J*= 7.1Hz, 1H), 6.35 (m, 3H), 3.79 (d, *J*= 15.5Hz, 1H), 3.65 (d, *J*= 15.5Hz, 1H), 2.08 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 169.7, 167.4, 136.3, 135.4, 130.8, 129.3, 127.9, 126.2, 125.4, 123.7, 123.5, 121.4, 120.1, 119.2, 114.4, 111.2, 61.5, 50.3, 40.8, 28.2, 18.1.

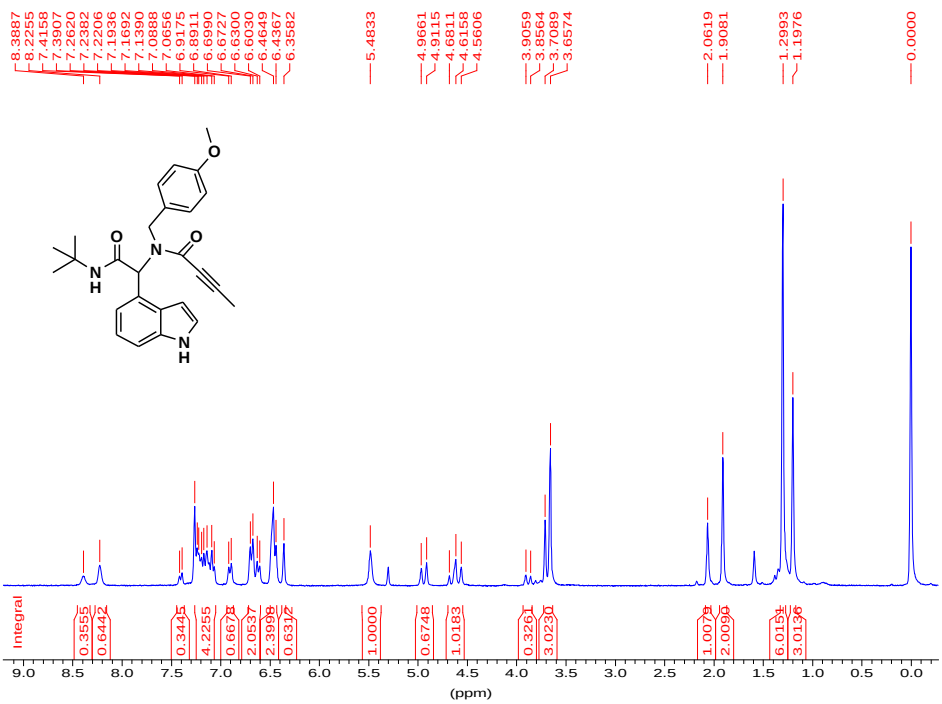
HRMS calculated for $C_{25}H_{27}N_3O_2$ 401.2103, found 401.2124.

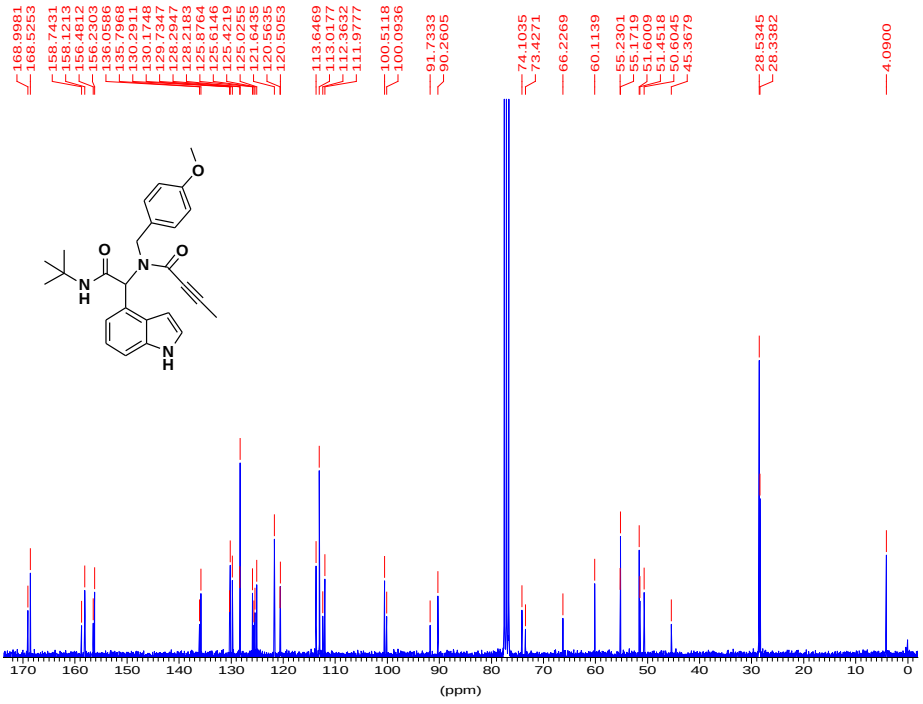
^{1}H and ^{13}C NMR spectra of compound **1c** (300 MHz, $CDCl_3$)



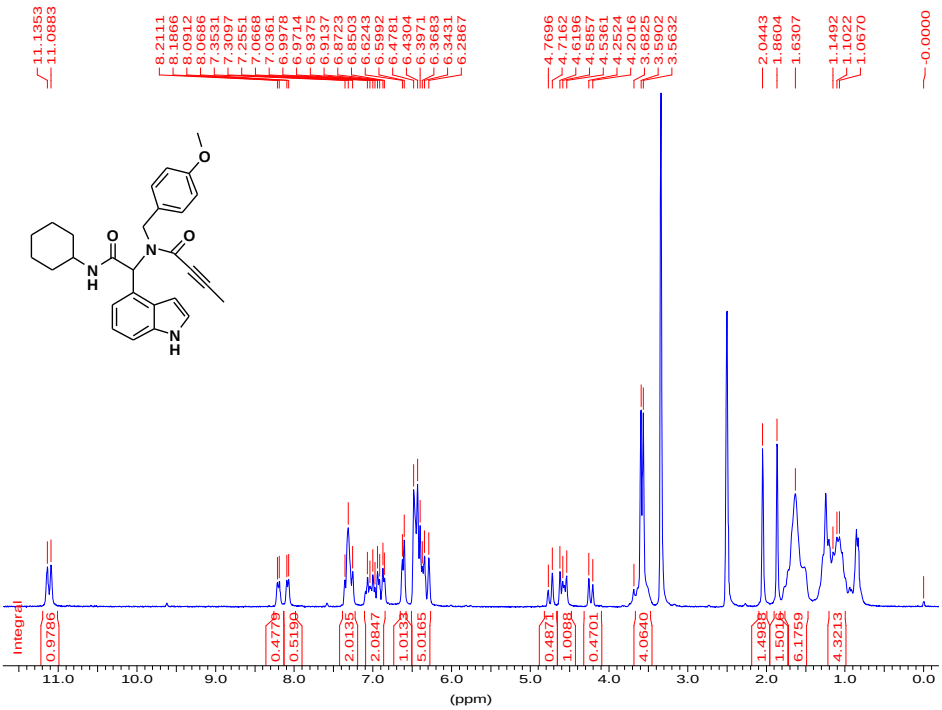


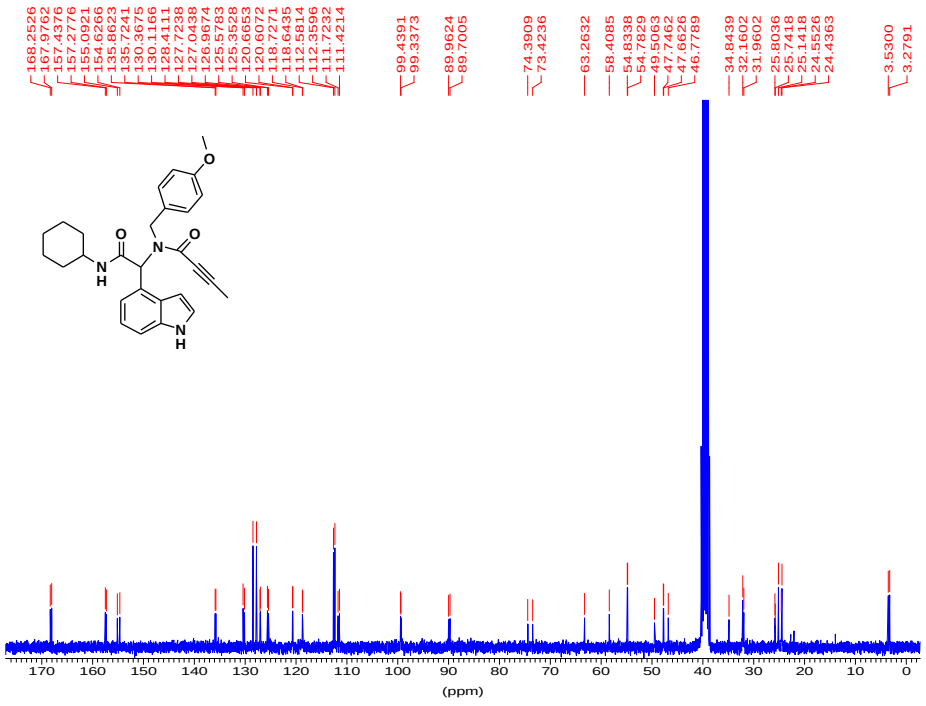
^{1}H and ^{13}C NMR spectra of compound **5a** (300 MHz, $CDCl_3$)



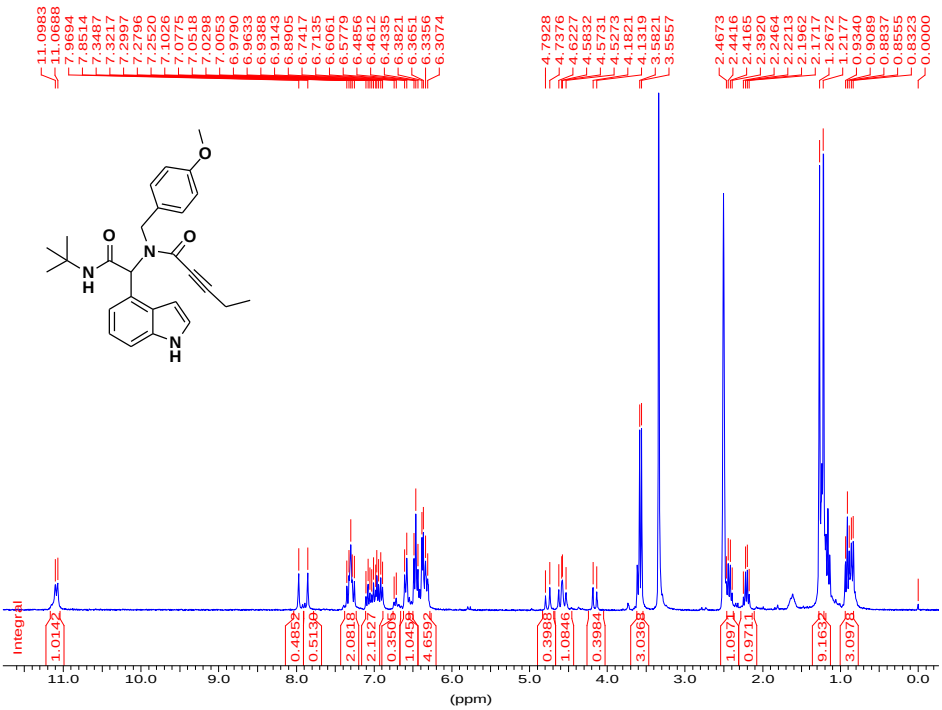


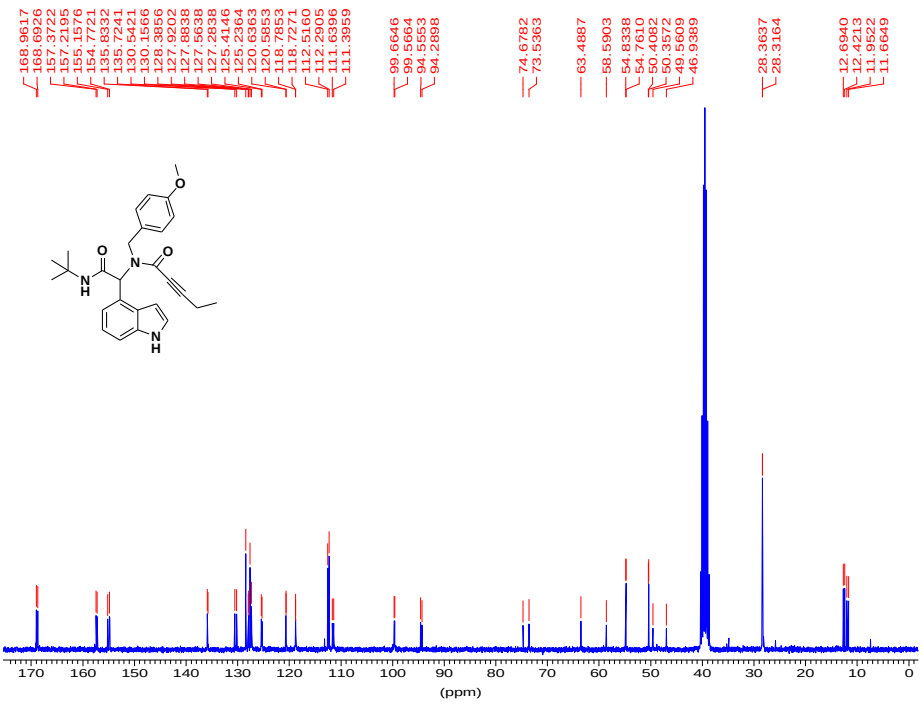
^{1}H and ^{13}C NMR spectra of compound **5b** (300 MHz, DMSO-d_6)



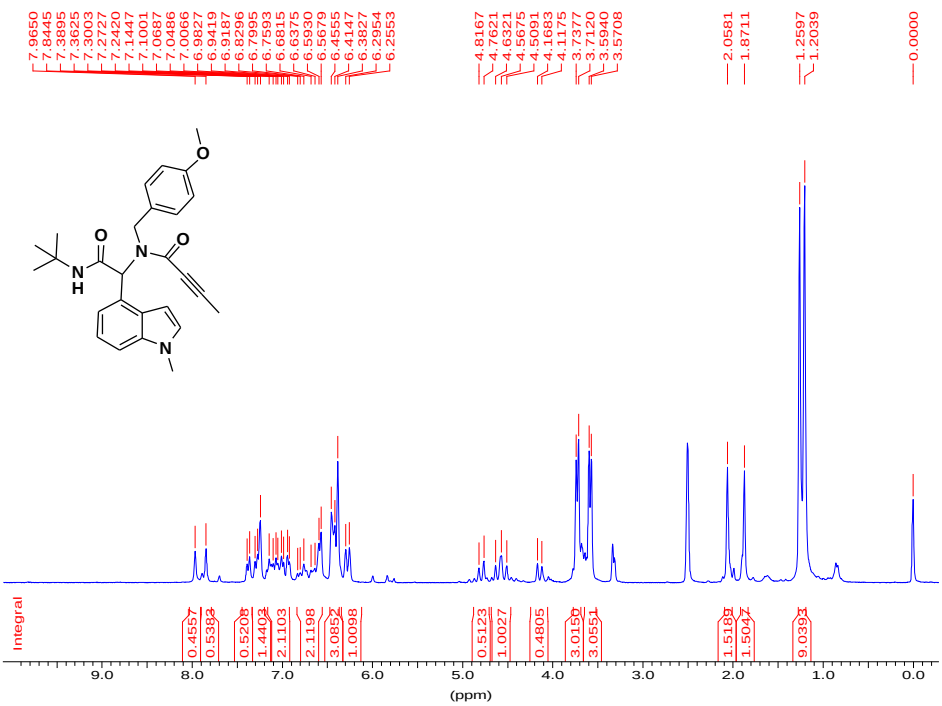


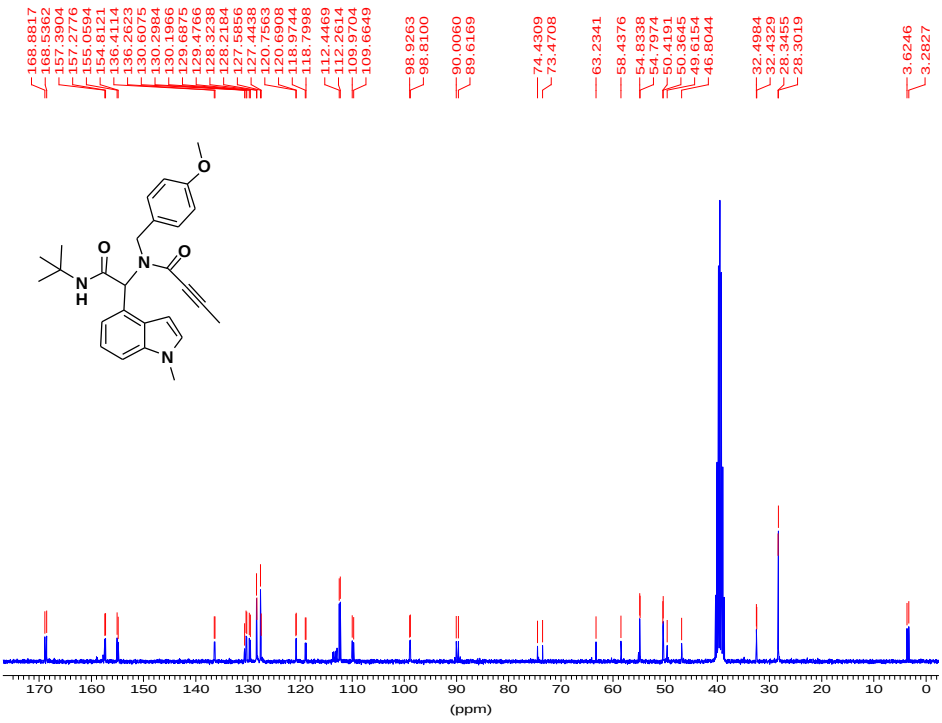
^{1}H and ^{13}C NMR spectra of compound **5c** (300 MHz, DMSO-d_6)



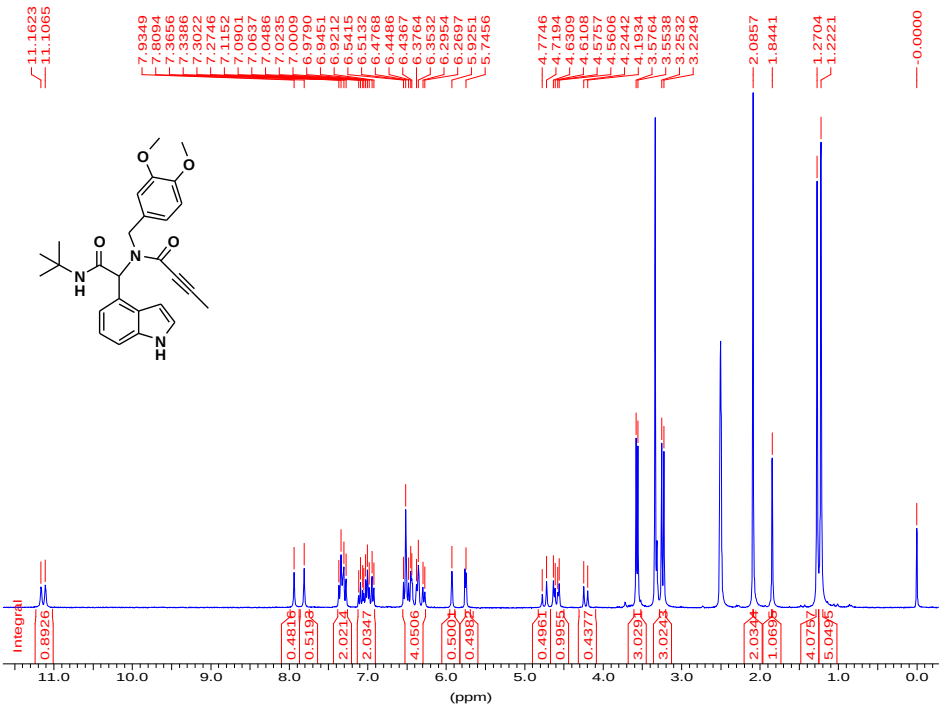


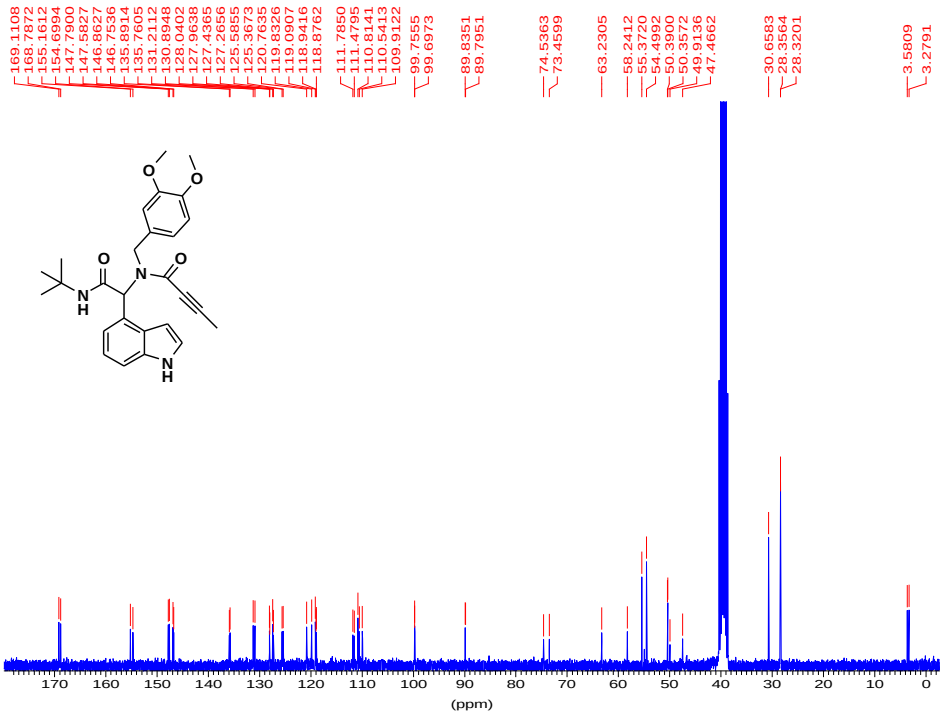
^{1}H and ^{13}C NMR spectra of compound **5d** (300 MHz, DMSO-d_6)



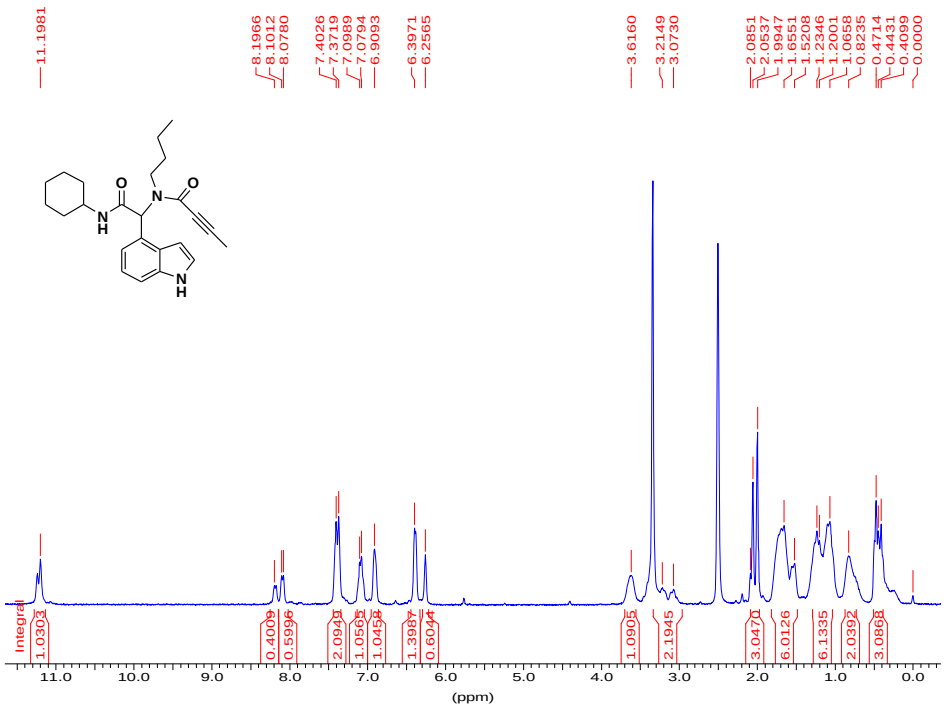


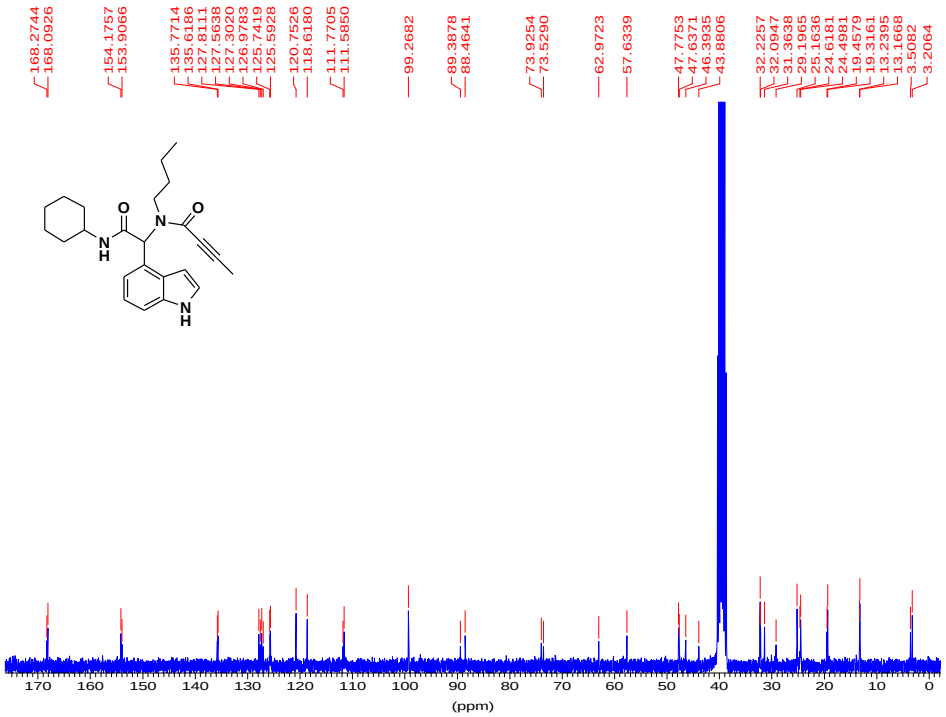
^{1}H and ^{13}C NMR spectra of compound **5e** (300 MHz, DMSO-d_6)



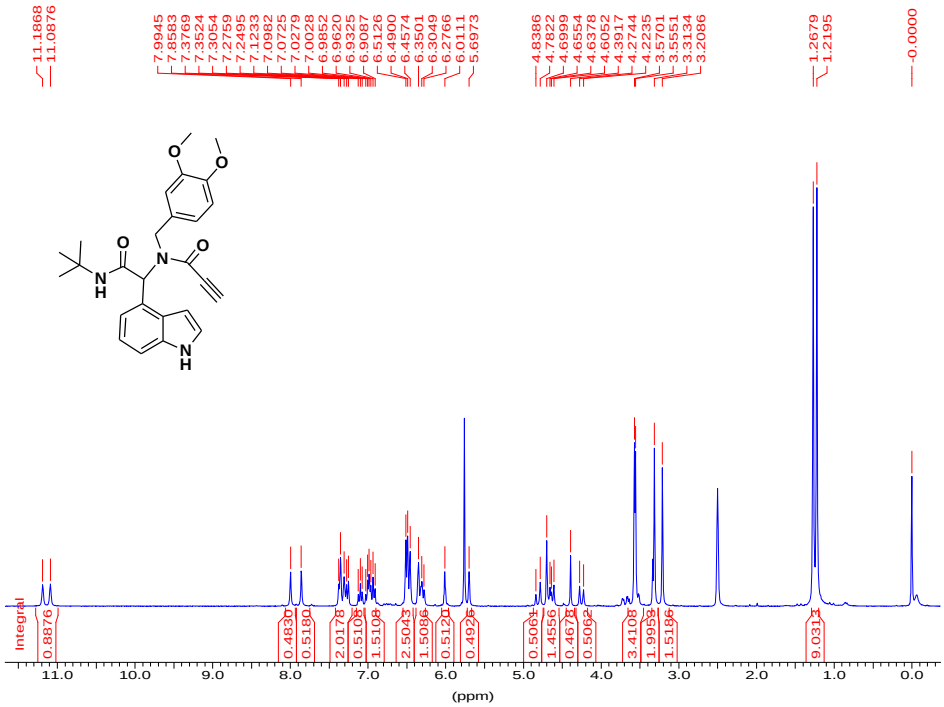


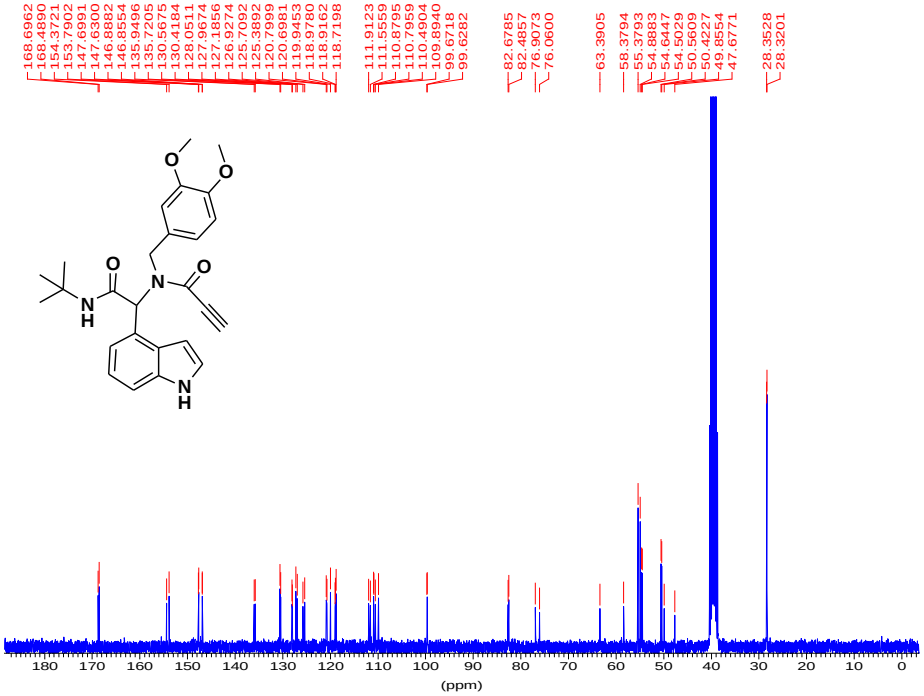
^{1}H and ^{13}C NMR spectra of compound **5f** (300 MHz, DMSO-d_6)



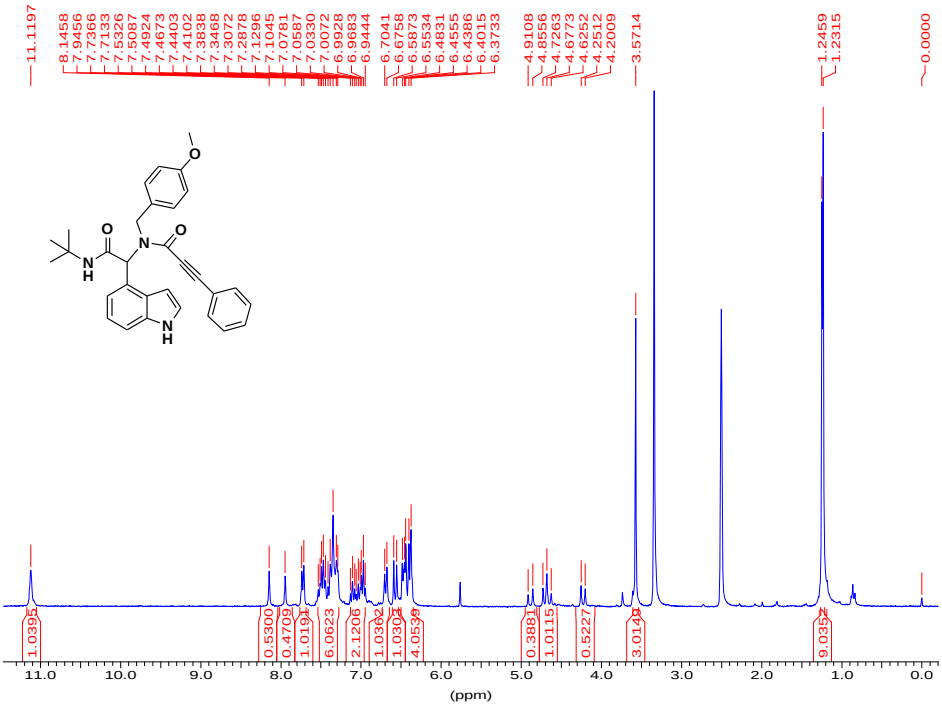


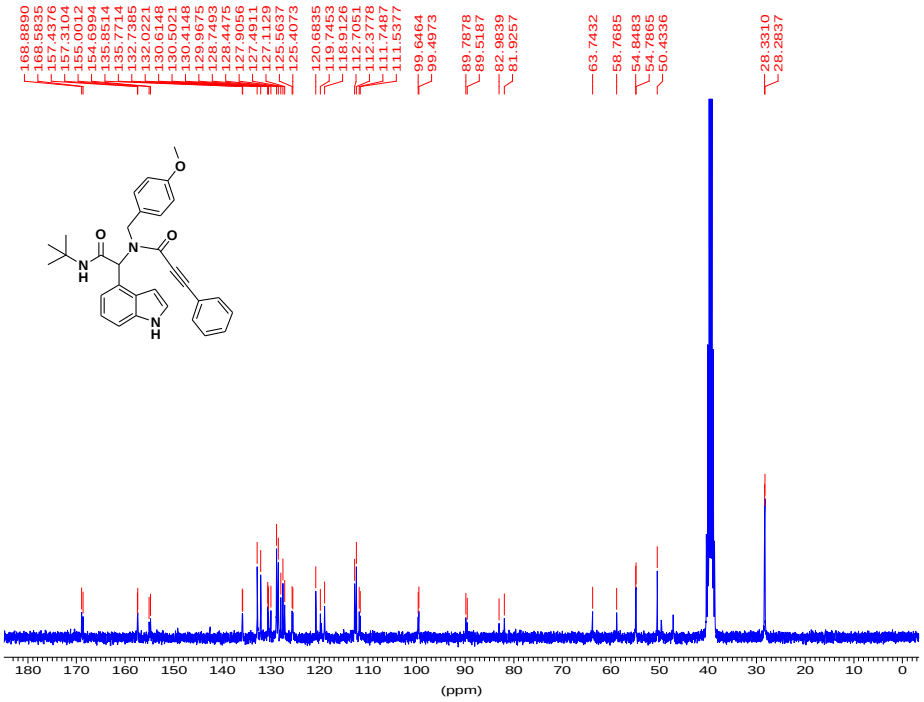
^{1}H and ^{13}C NMR spectra of compound **5g** (300 MHz, DMSO-d_6)



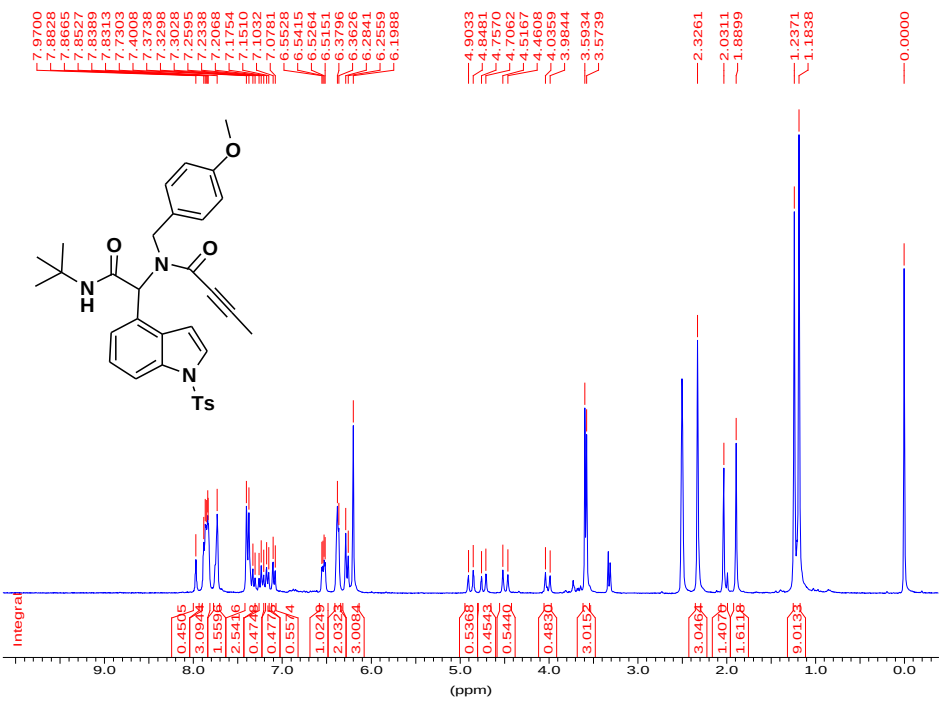


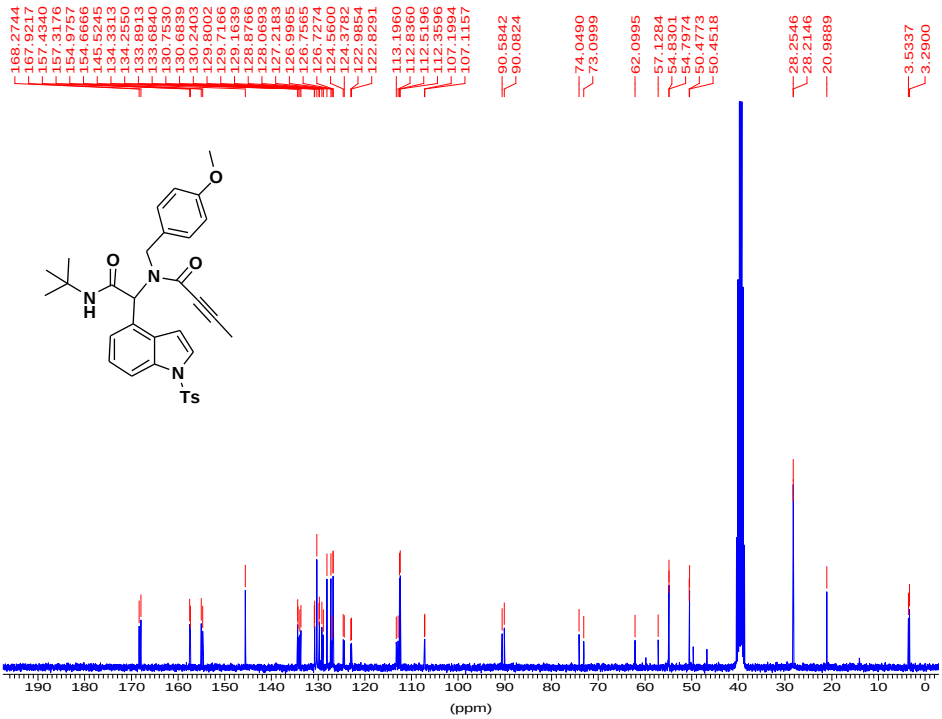
^{1}H and ^{13}C NMR spectra of compound **5h** (300 MHz, DMSO-d_6)



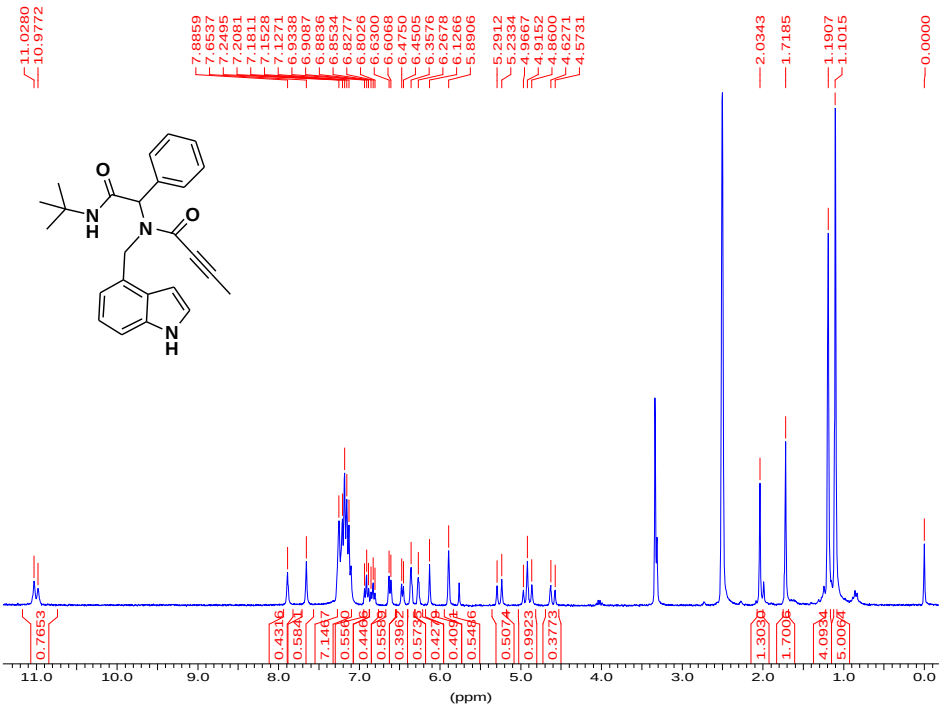


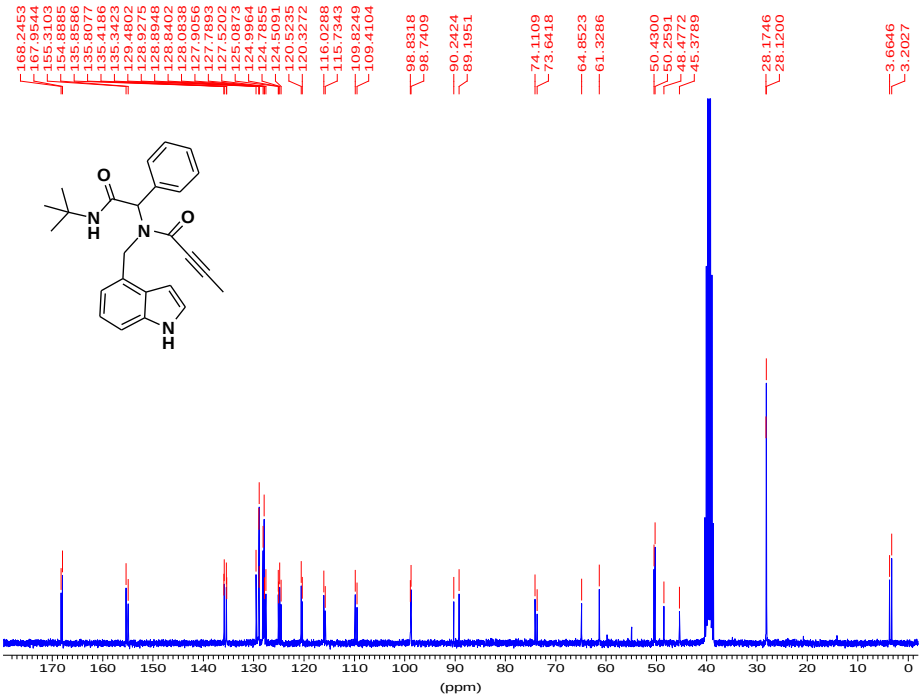
^{1}H and ^{13}C NMR spectra of compound **5i** (300 MHz, DMSO-d_6)



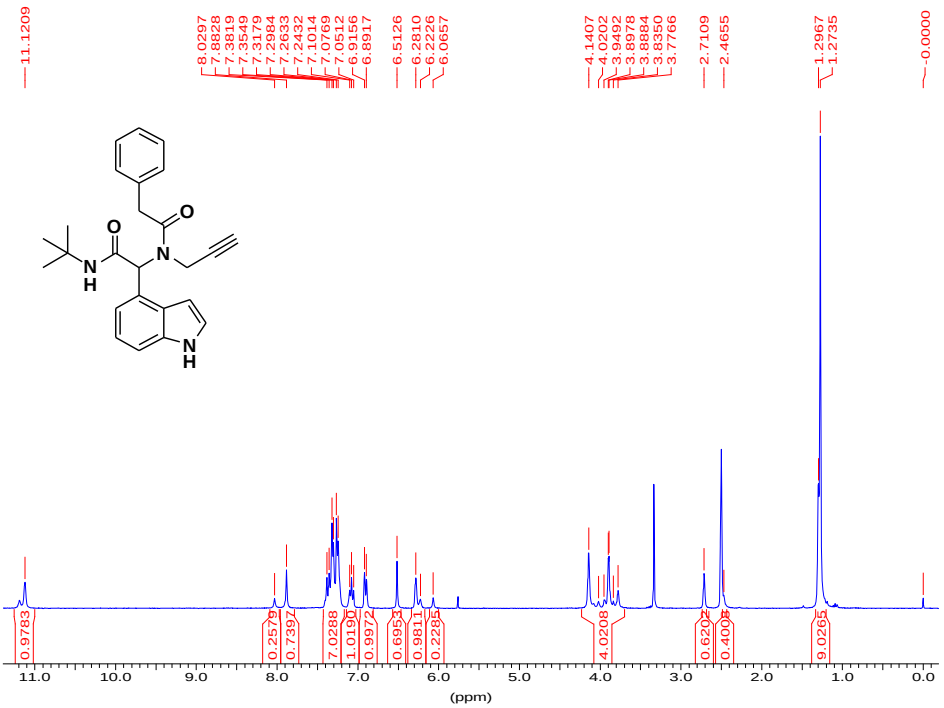


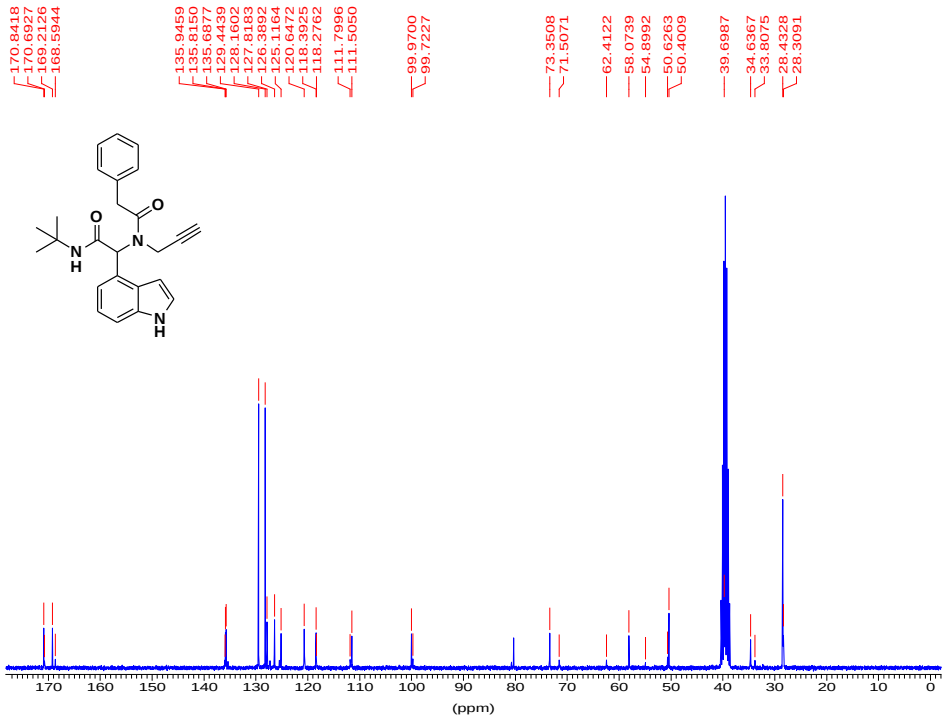
^{1}H and ^{13}C NMR spectra of compound **5j** (300 MHz, DMSO-d_6)



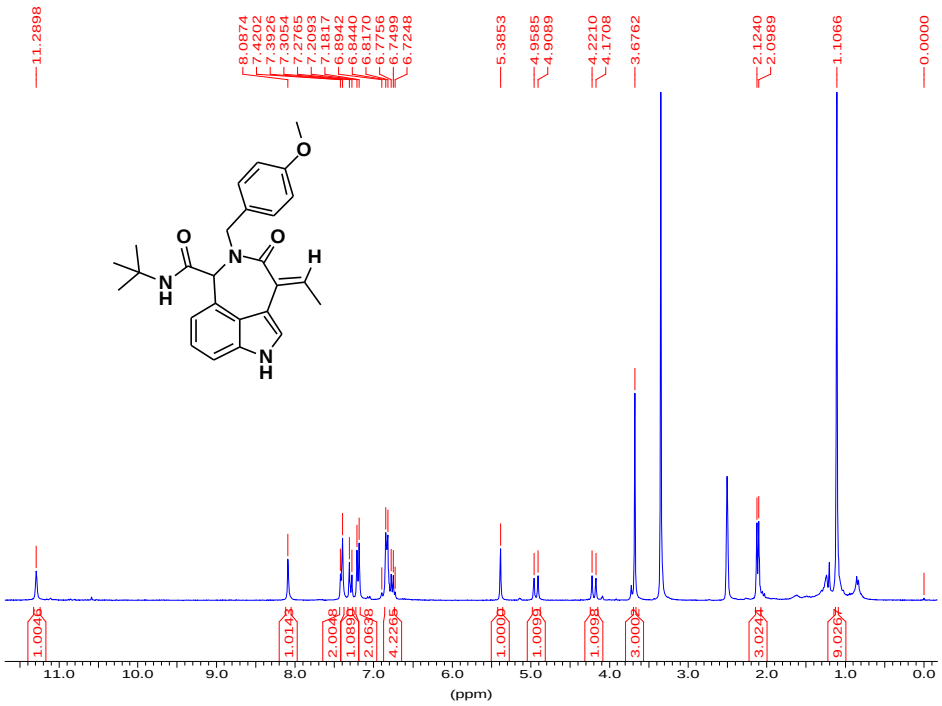


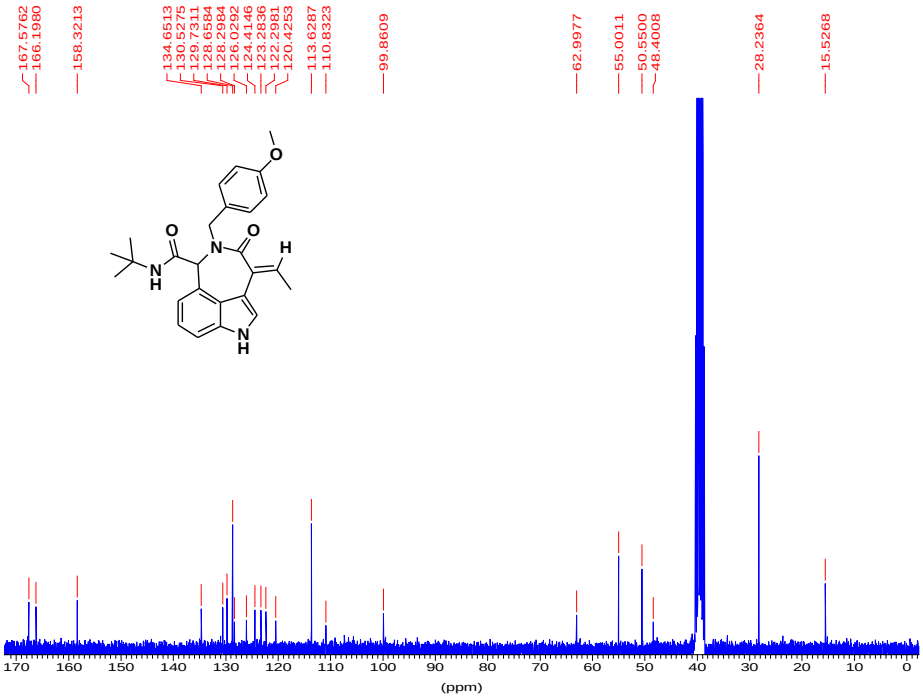
^{1}H and ^{13}C NMR spectra of compound **5k** (300 MHz, DMSO-d_6)



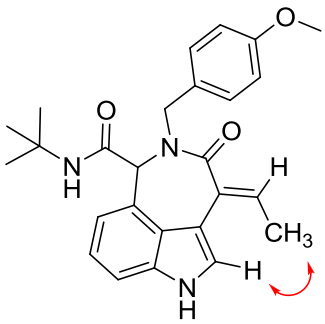


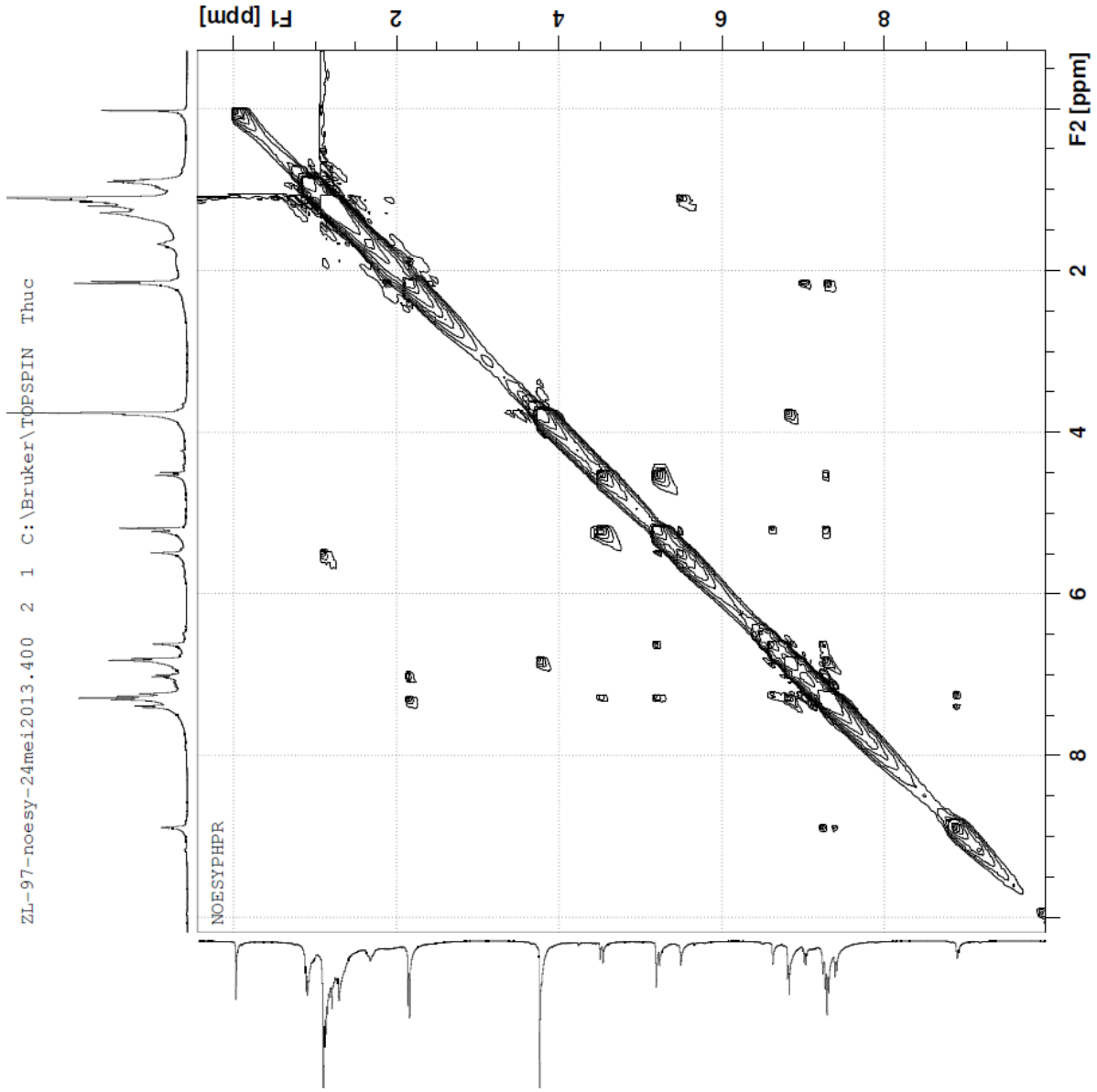
^{1}H and ^{13}C NMR spectra of compound **6a** (300 MHz, DMSO-d_6)



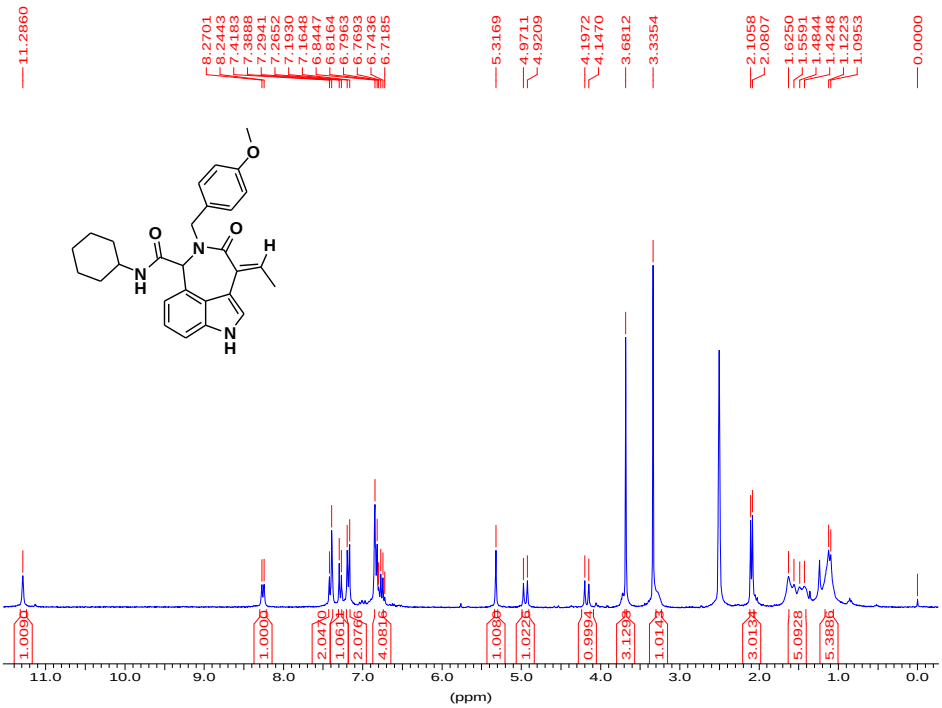


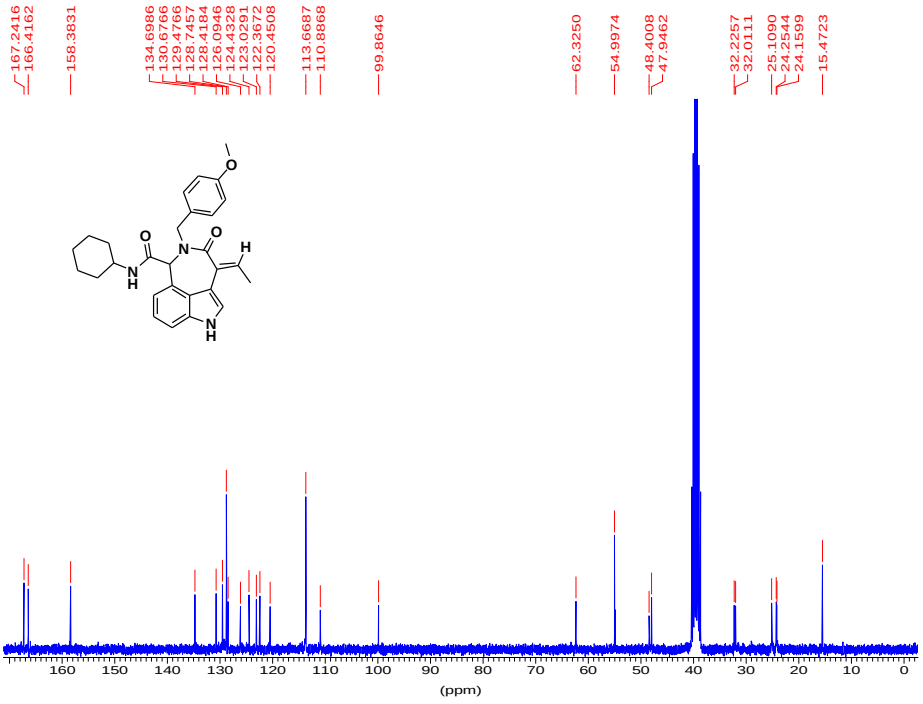
NOESY NMR spectra of compound **6a** (400 MHz, $CDCl_3$)



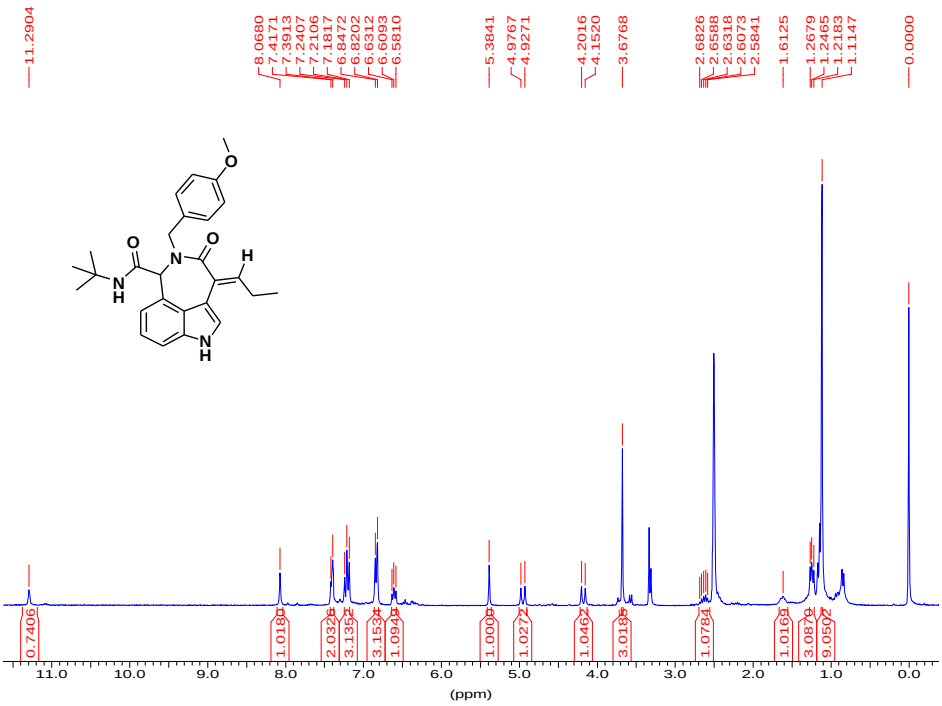


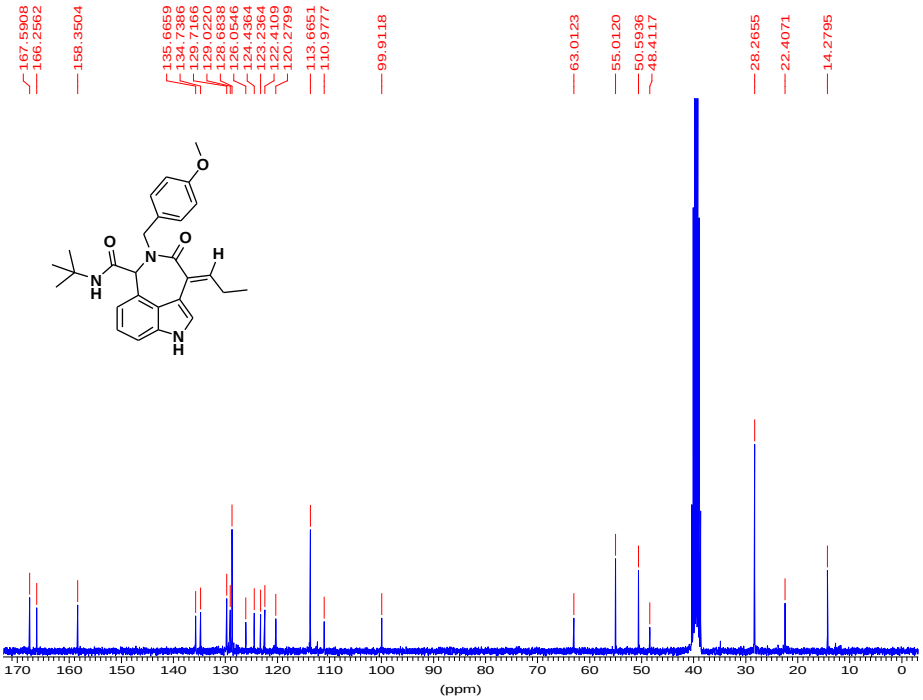
^{1}H and ^{13}C NMR spectra of compound **6b** (300 MHz, DMSO-d_6)



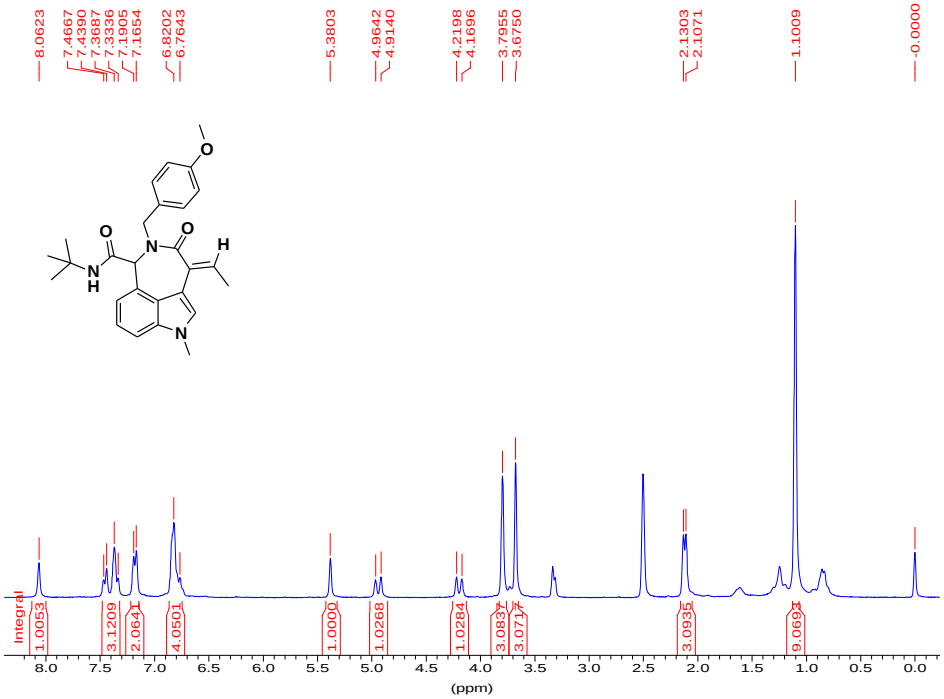


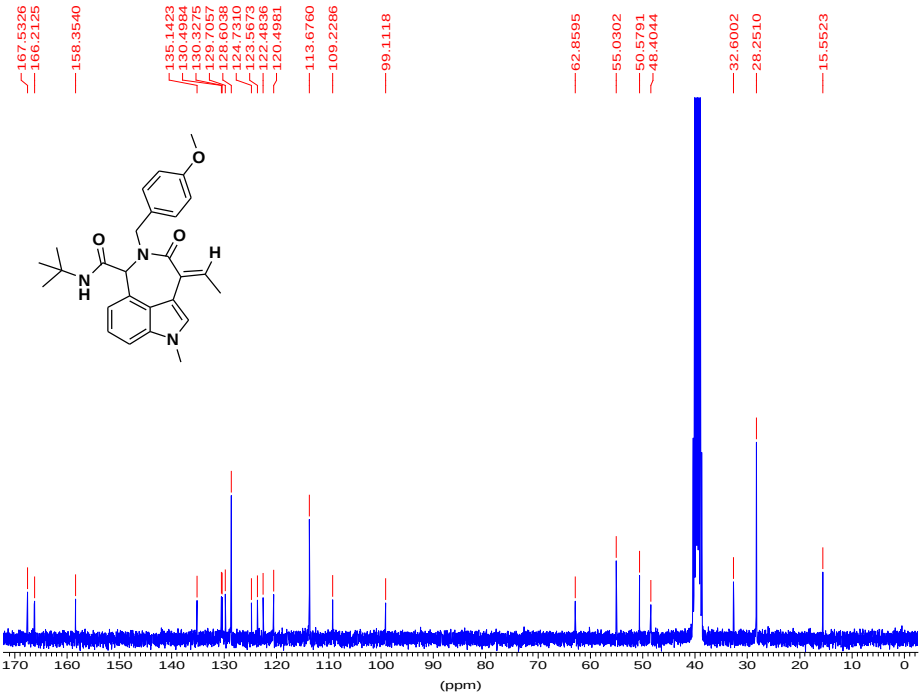
^{1}H and ^{13}C NMR spectra of compound **6c** (300 MHz, DMSO-d_6)



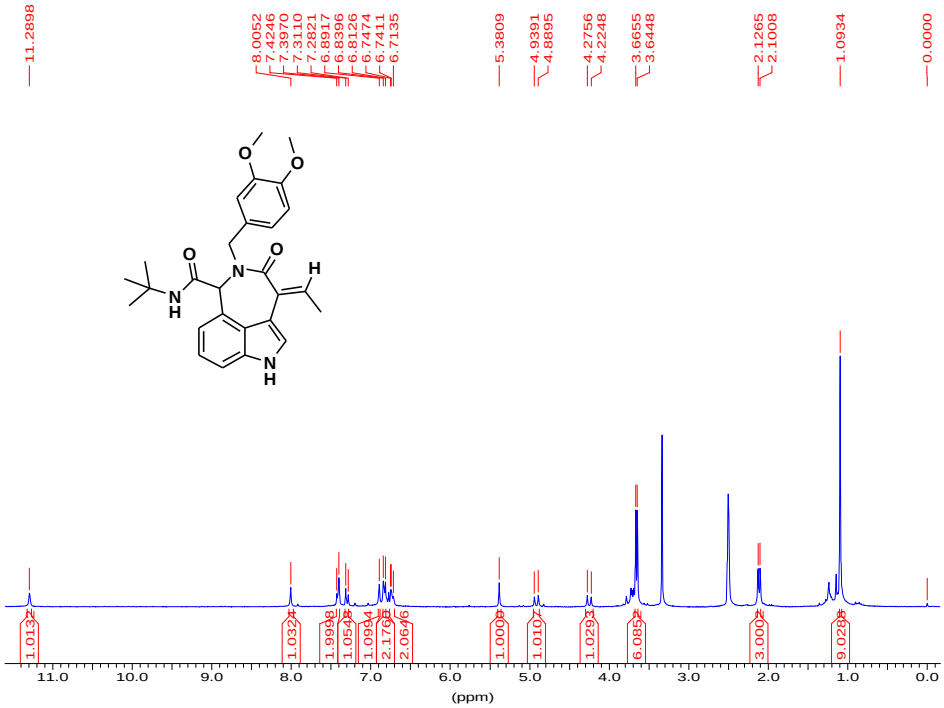


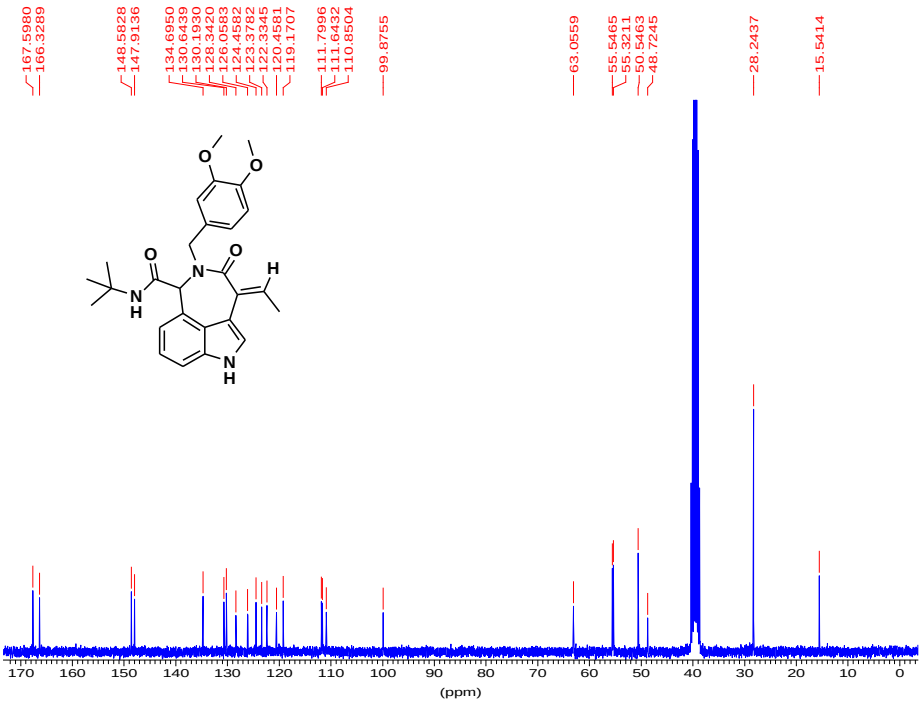
^{1}H and ^{13}C NMR spectra of compound **6d** (300 MHz, DMSO-d_6)



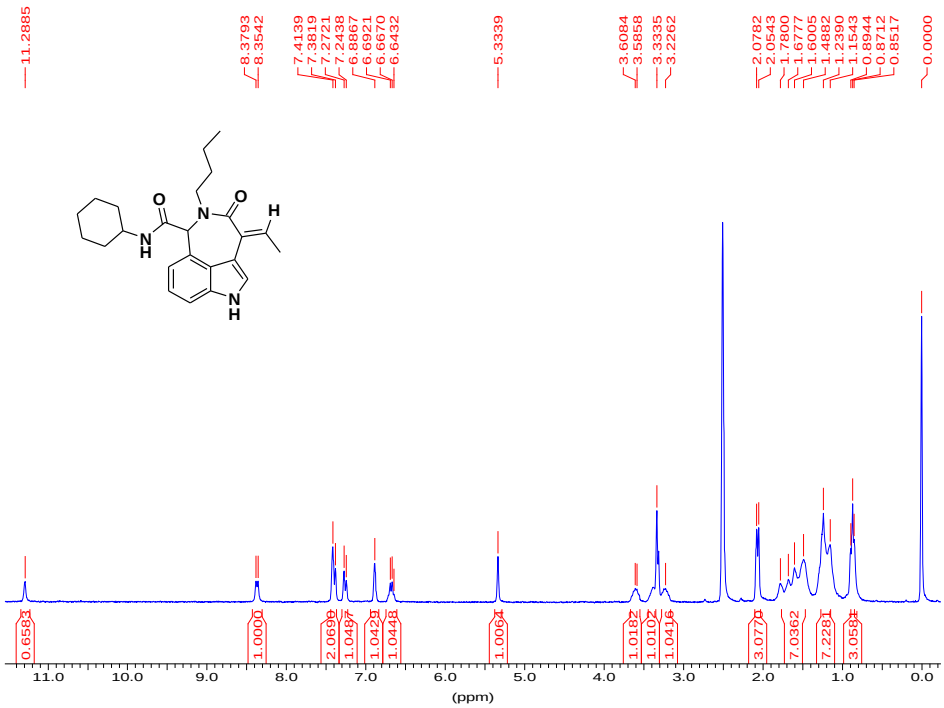


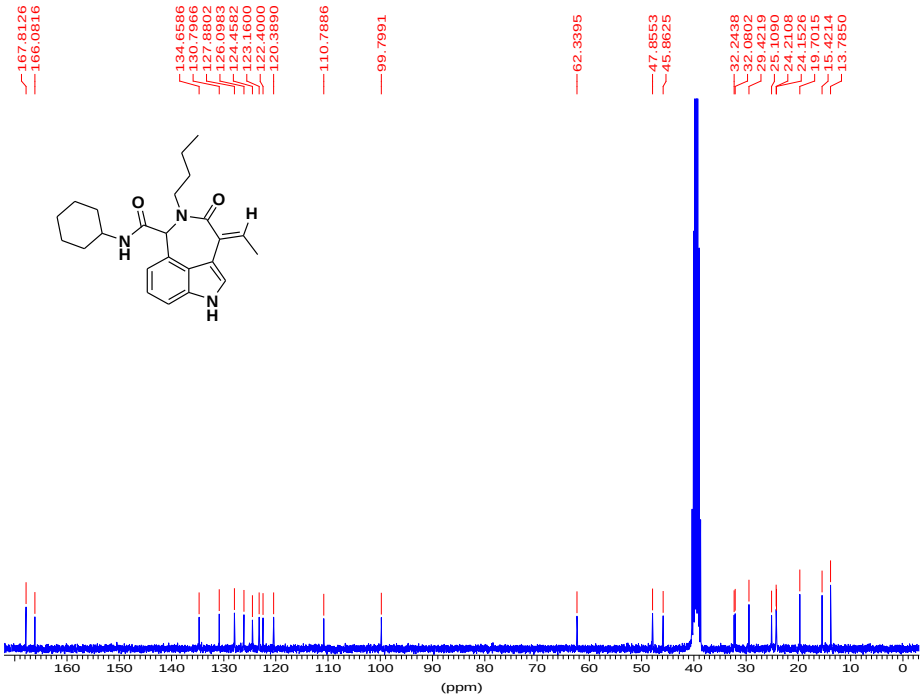
^{1}H and ^{13}C NMR spectra of compound **6e** (300 MHz, DMSO-d_6)



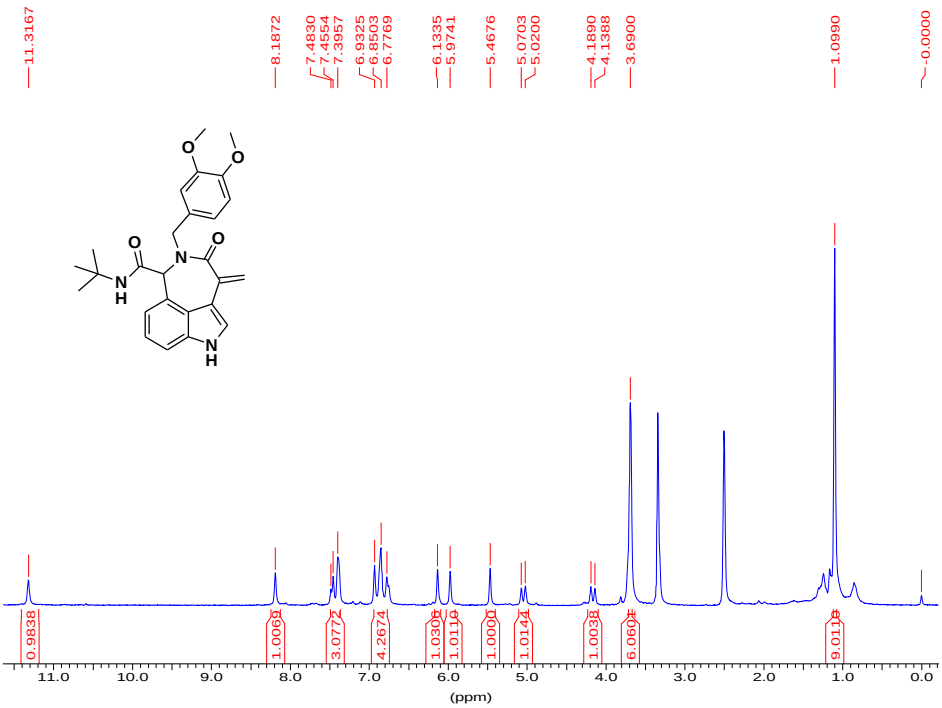


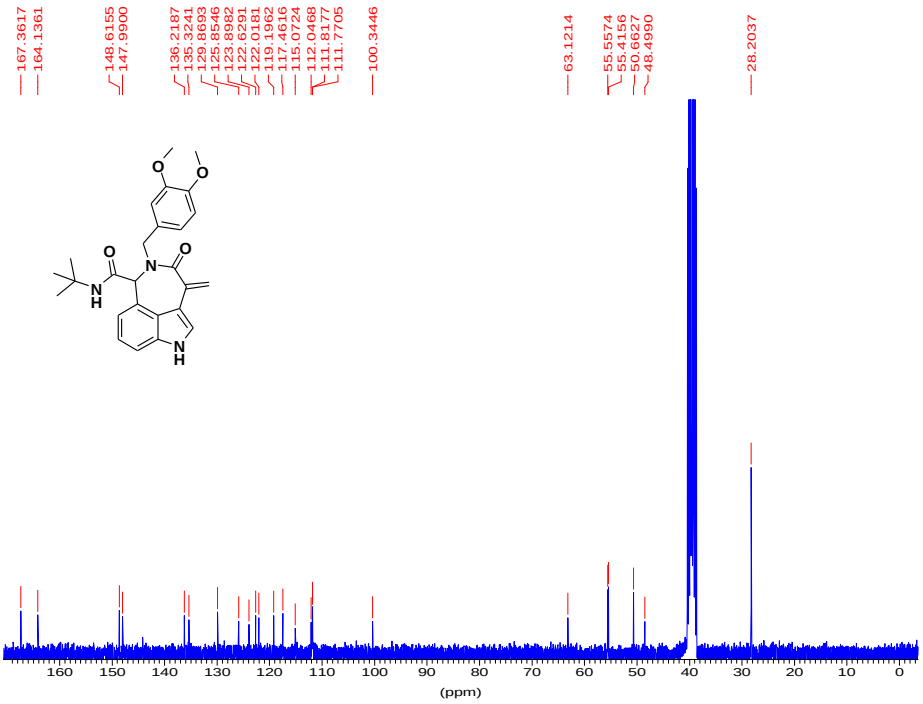
^{1}H and ^{13}C NMR spectra of compound **6f** (300 MHz, DMSO-d_6)



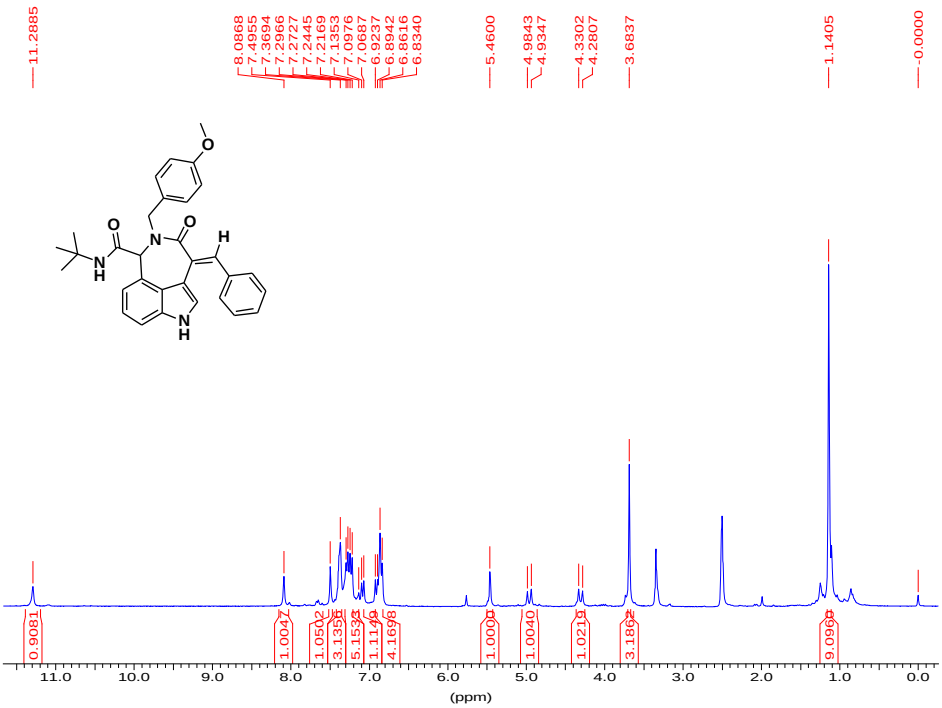


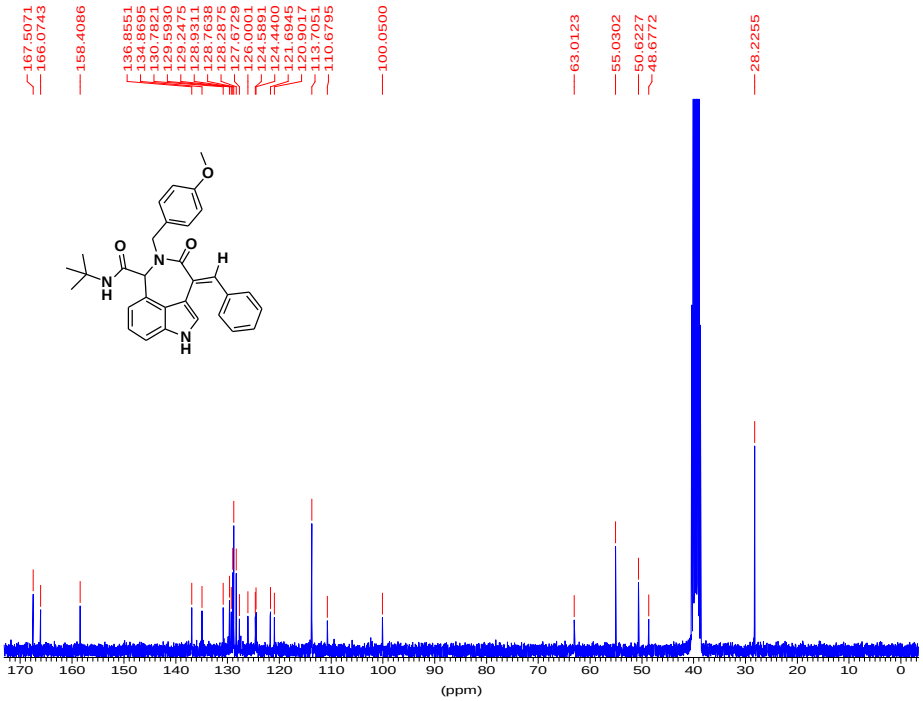
^{1}H and ^{13}C NMR spectra of compound **6g** (300 MHz, DMSO-d_6)



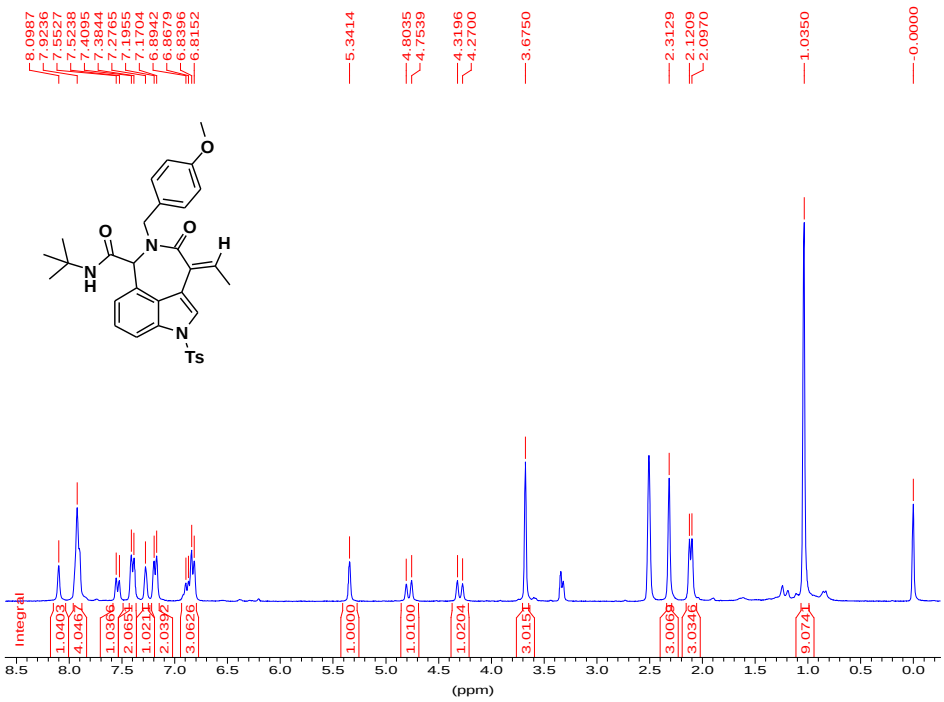


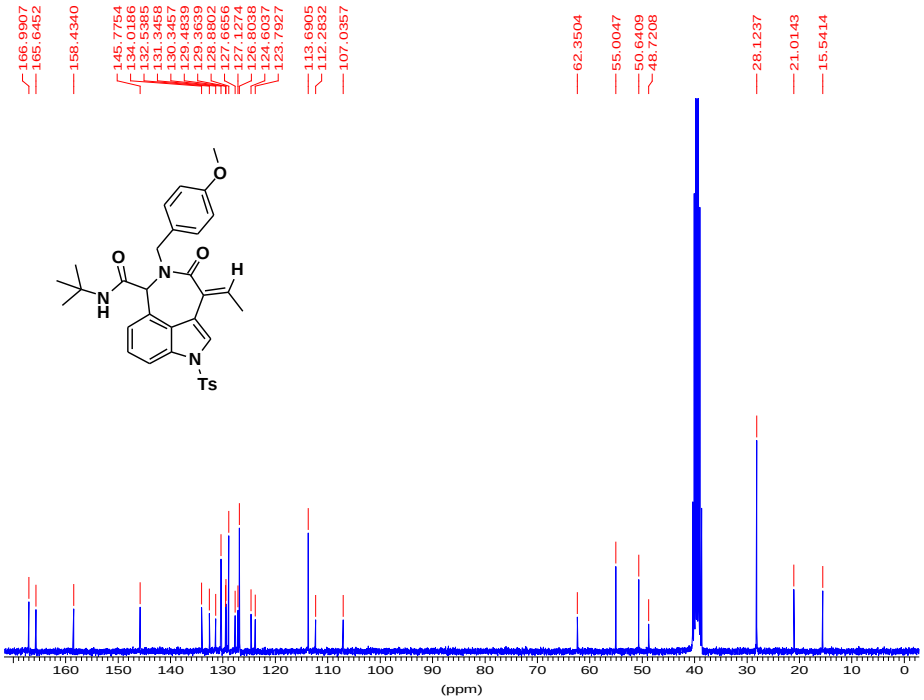
^{1}H and ^{13}C NMR spectra of compound **6h** (300 MHz, DMSO-d_6)



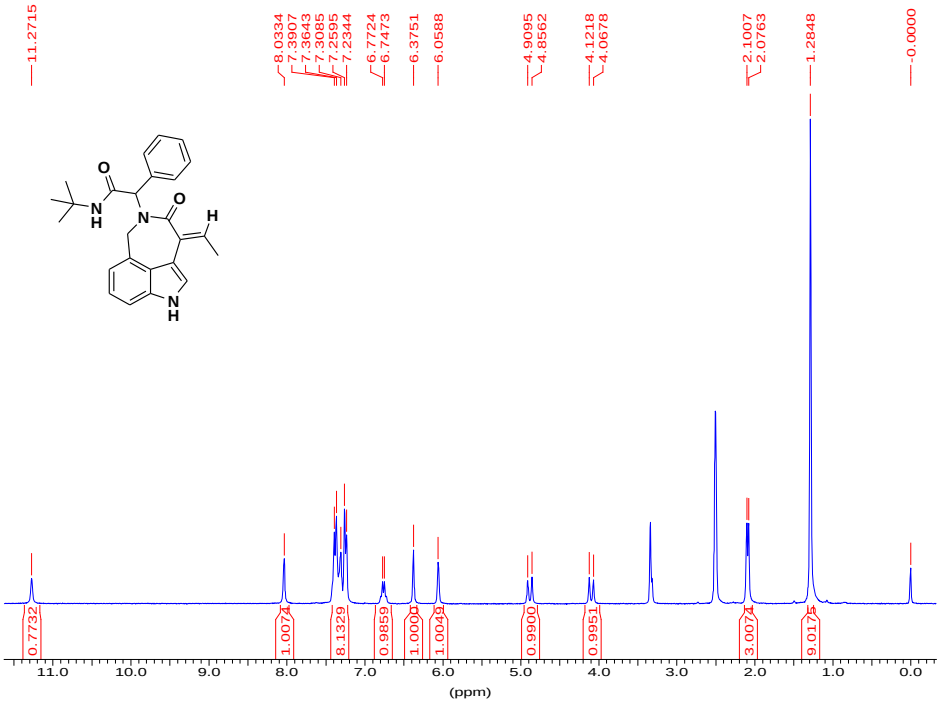


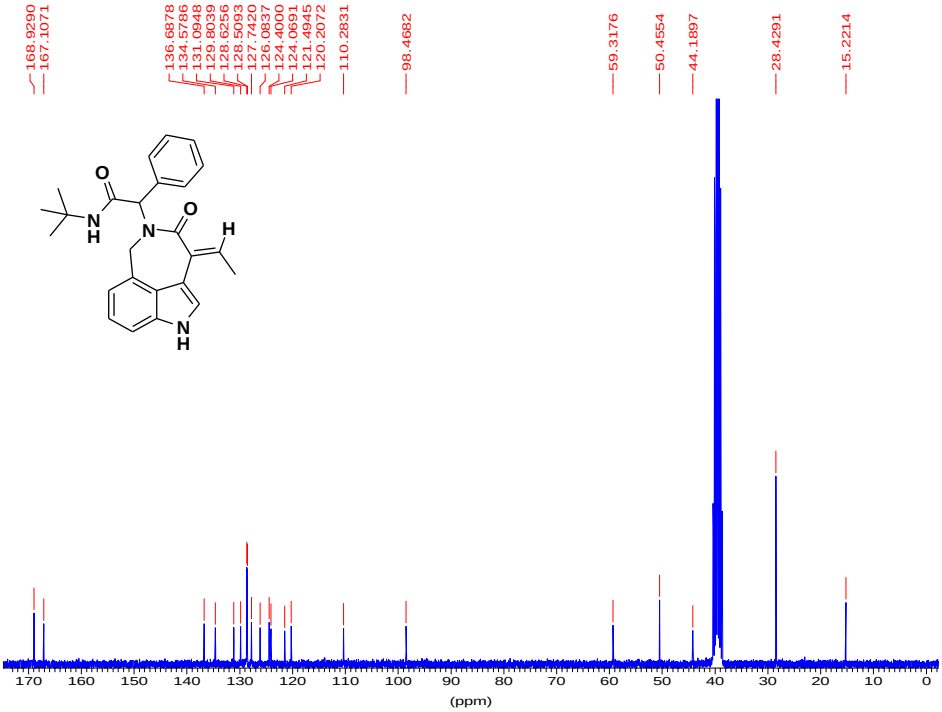
^{1}H and ^{13}C NMR spectra of compound **6i** (300 MHz, DMSO-d_6)



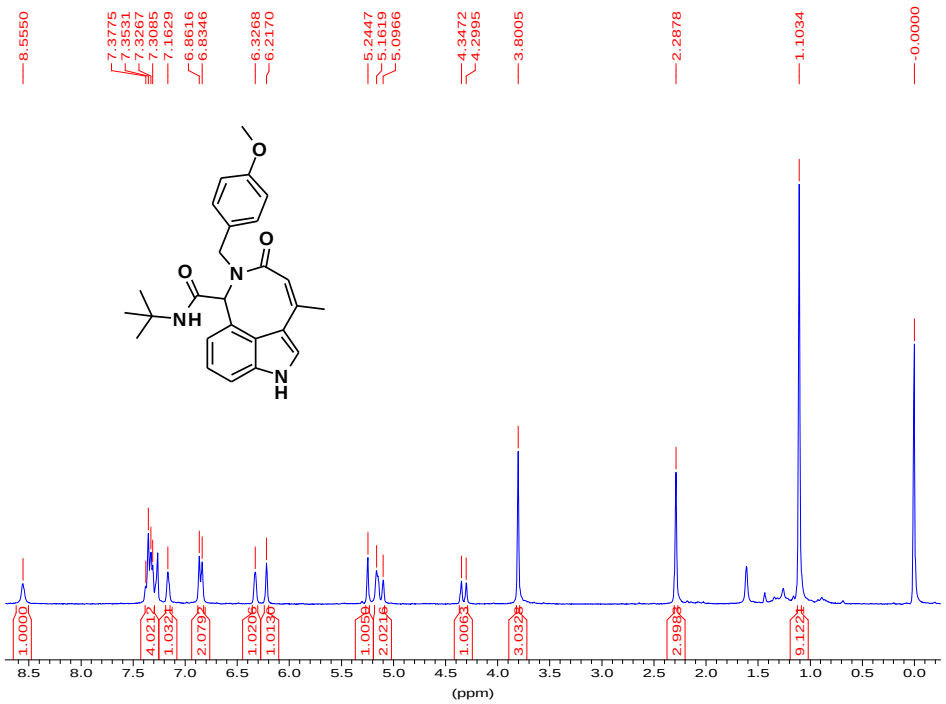


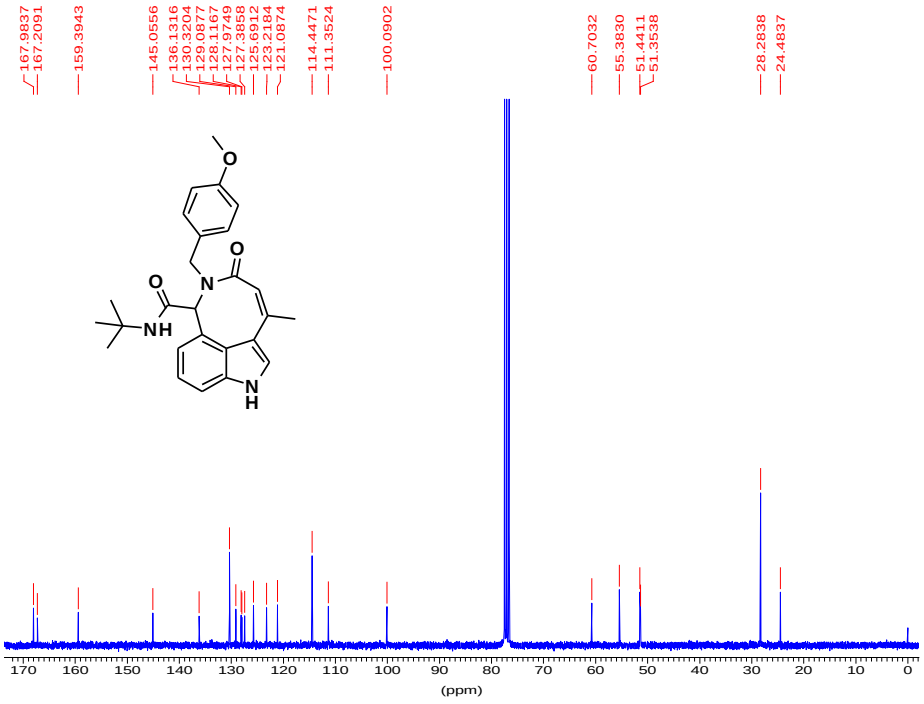
^{1}H and ^{13}C NMR spectra of compound **6j** (300 MHz, DMSO-d_6)



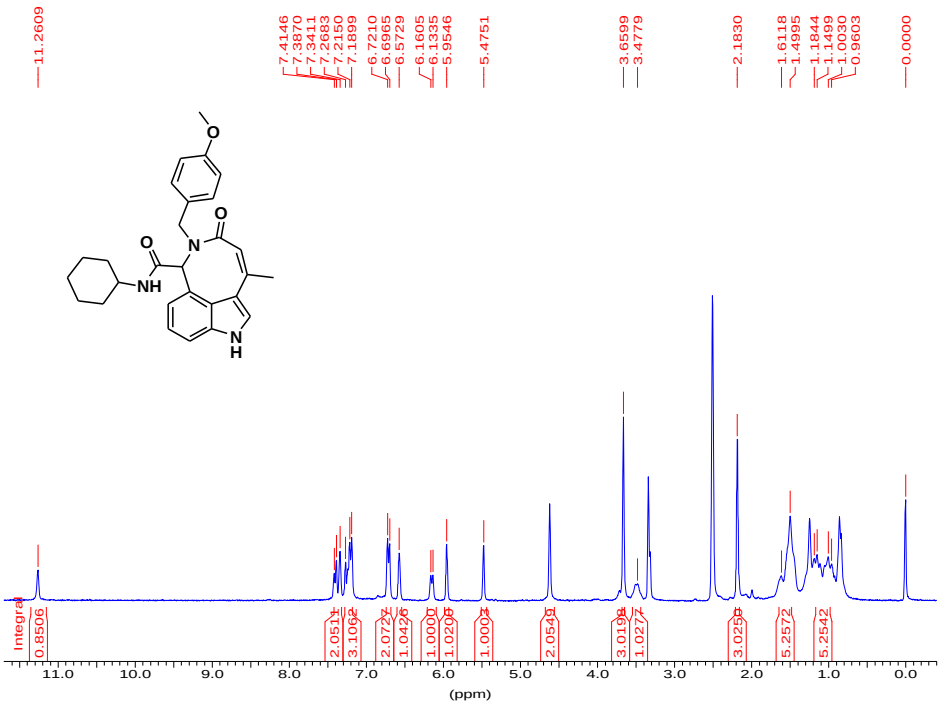


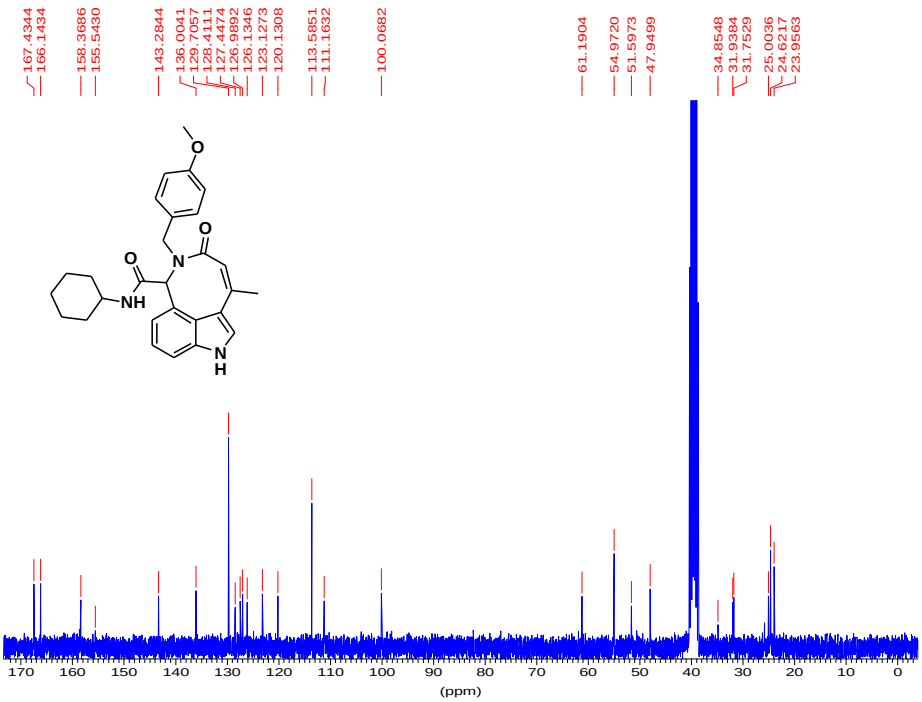
^{1}H and ^{13}C NMR spectra of compound **7a** (300 MHz, DMSO-d_6)



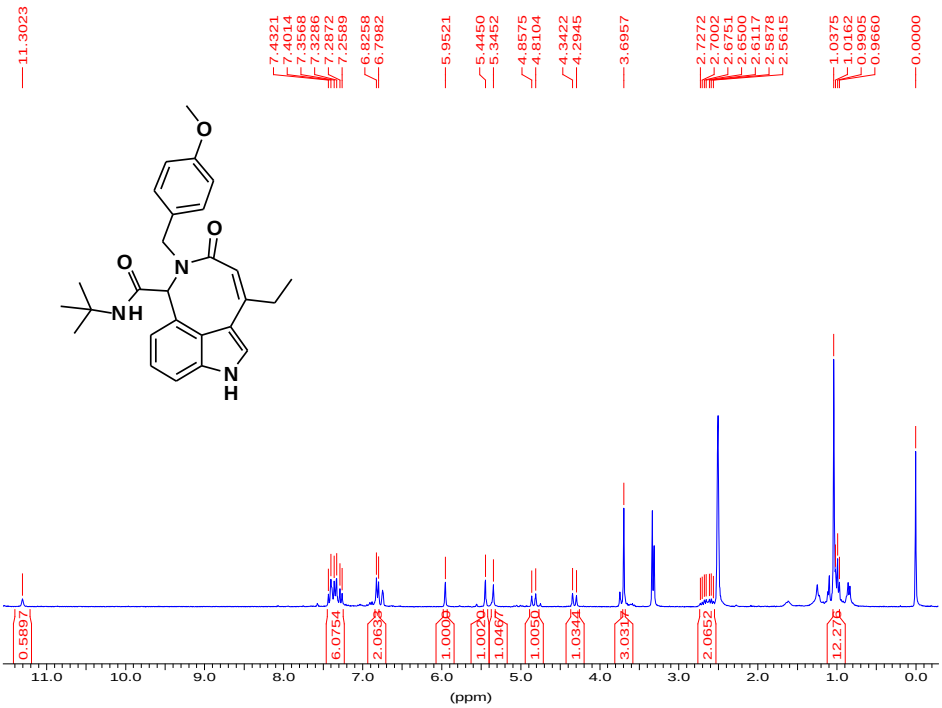


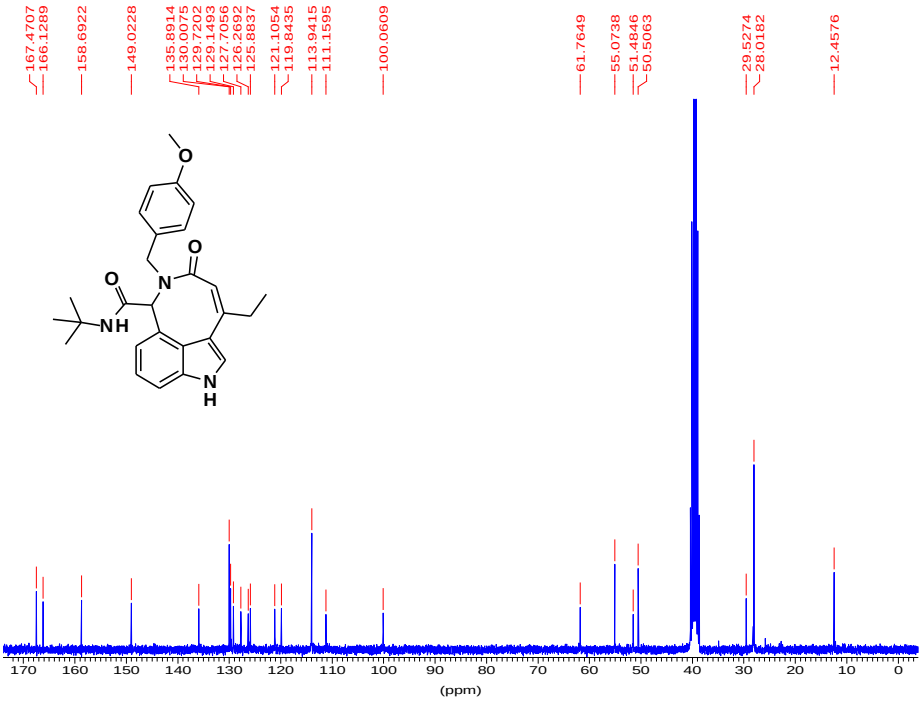
^{1}H and ^{13}C NMR spectra of compound **7b** (300 MHz, DMSO-d_6)



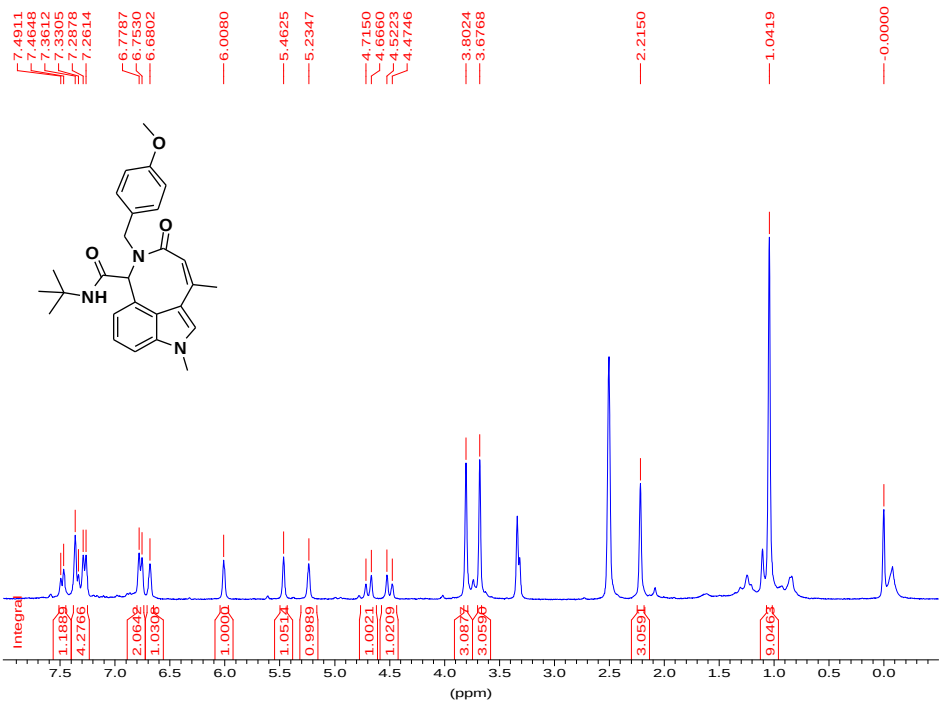


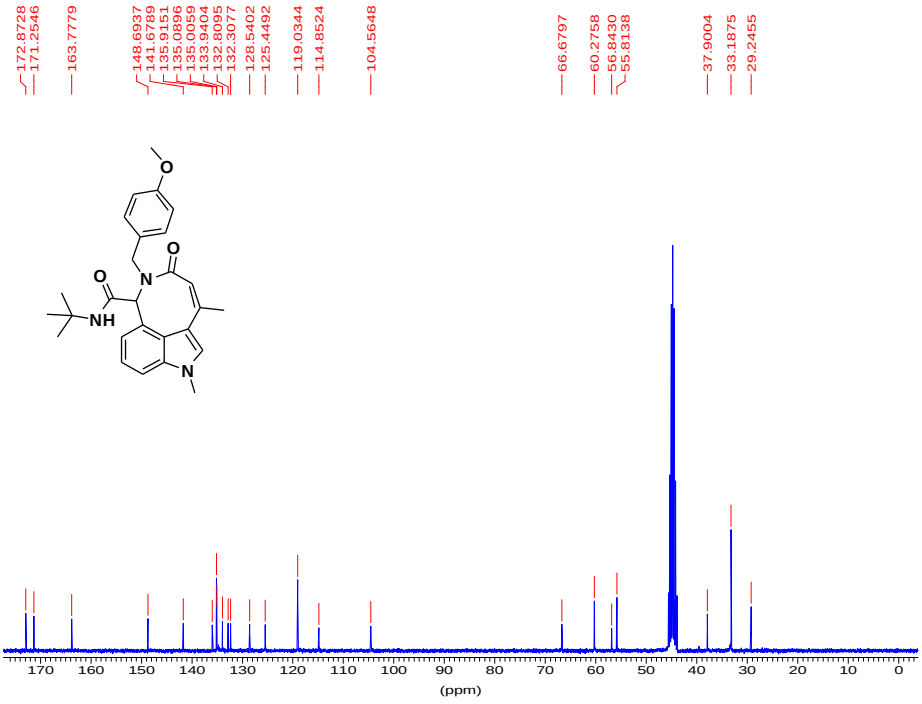
^{1}H and ^{13}C NMR spectra of compound **7c** (300 MHz, DMSO-d_6)



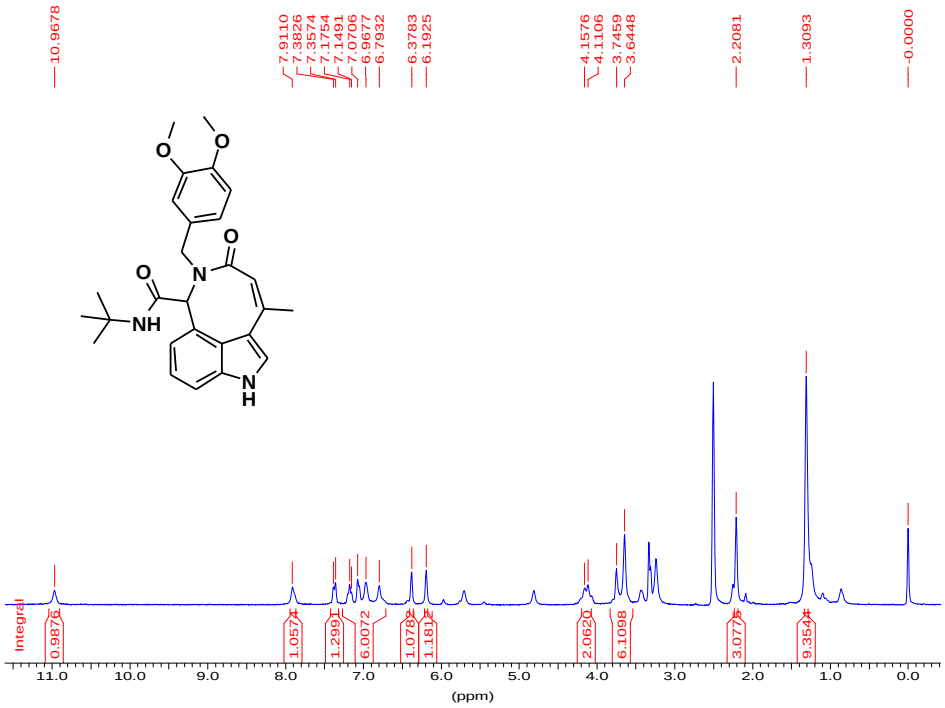


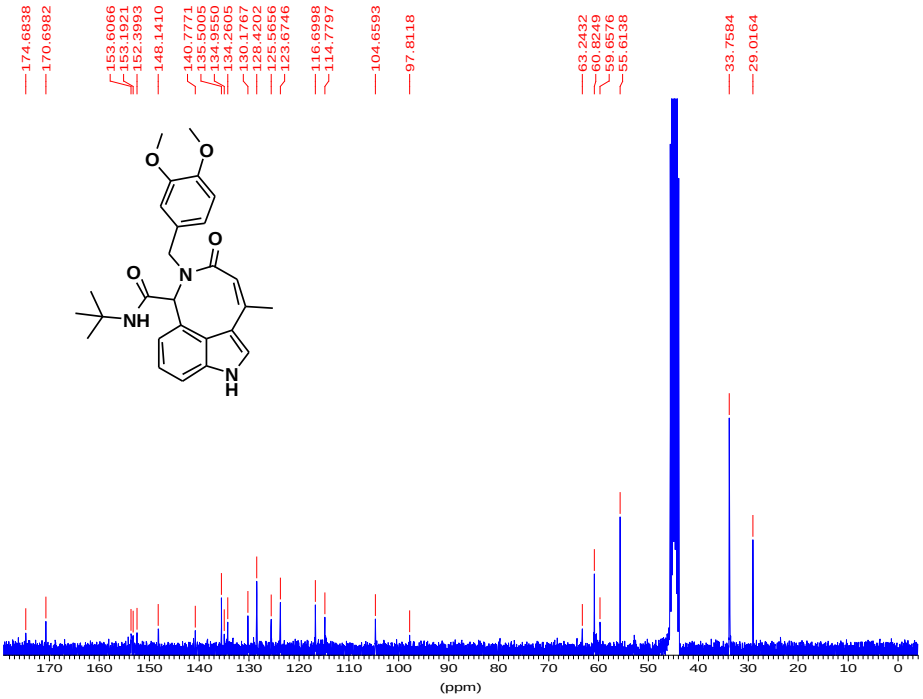
^{1}H and ^{13}C NMR spectra of compound **7d** (300 MHz, DMSO-d_6)



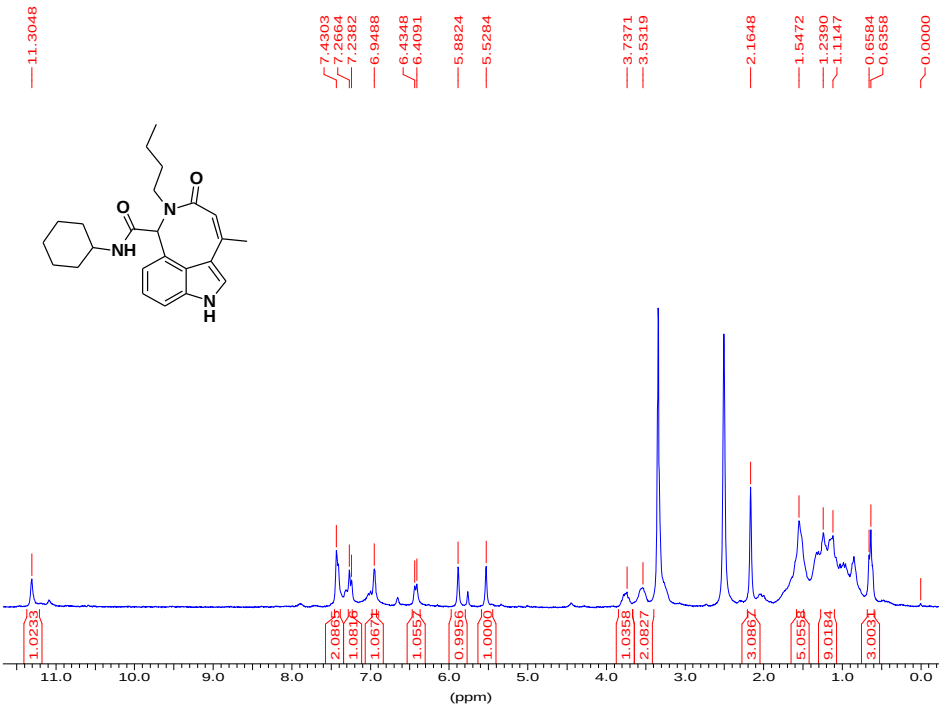


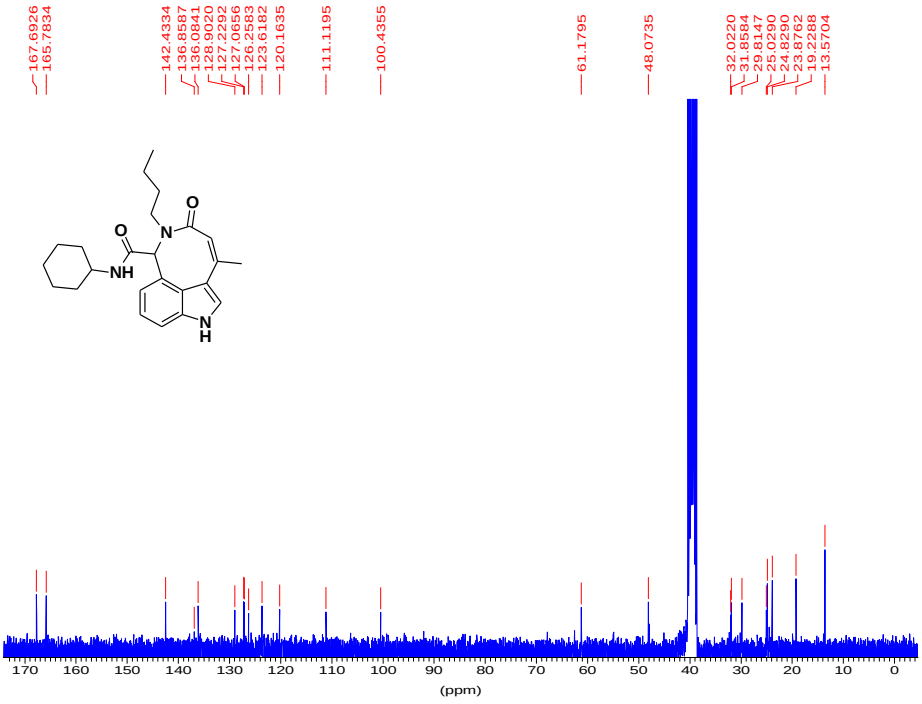
^{1}H and ^{13}C NMR spectra of compound **7e** (300 MHz, DMSO-d_6)



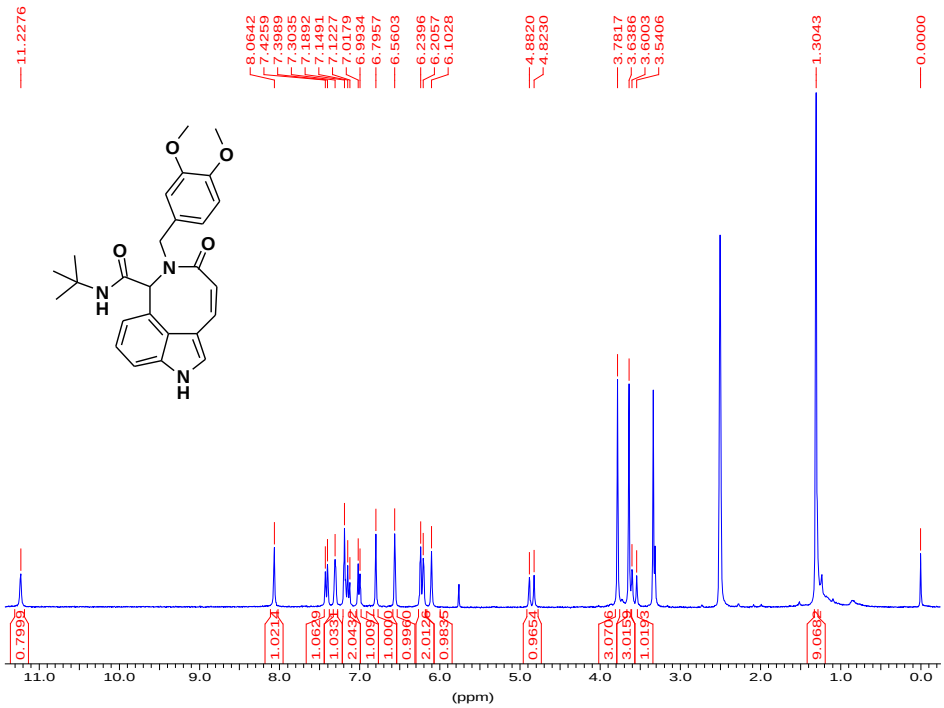


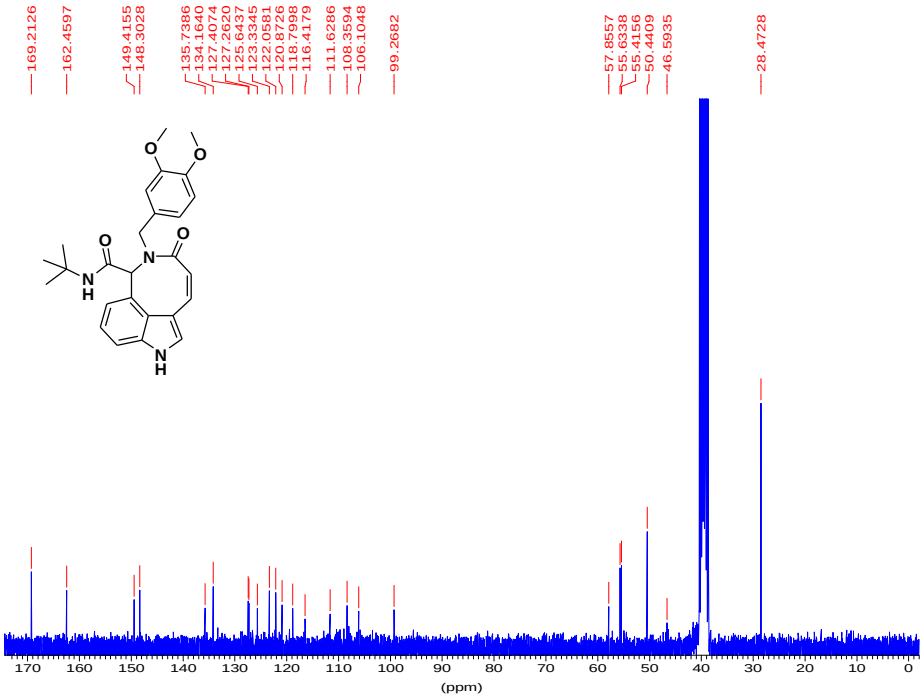
^{1}H and ^{13}C NMR spectra of compound **7f** (300 MHz, DMSO-d_6)



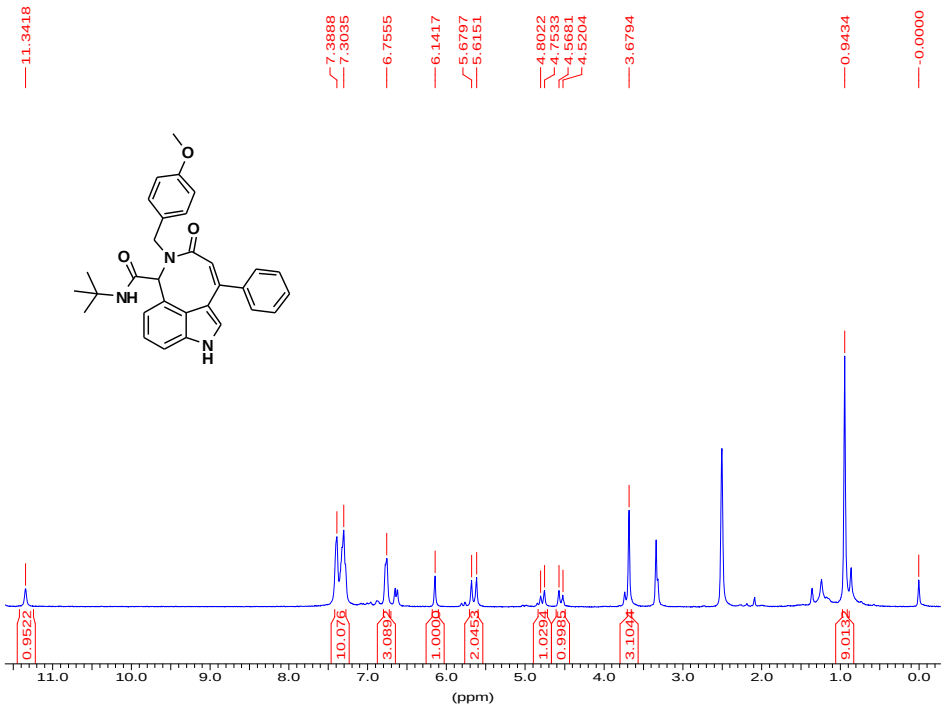


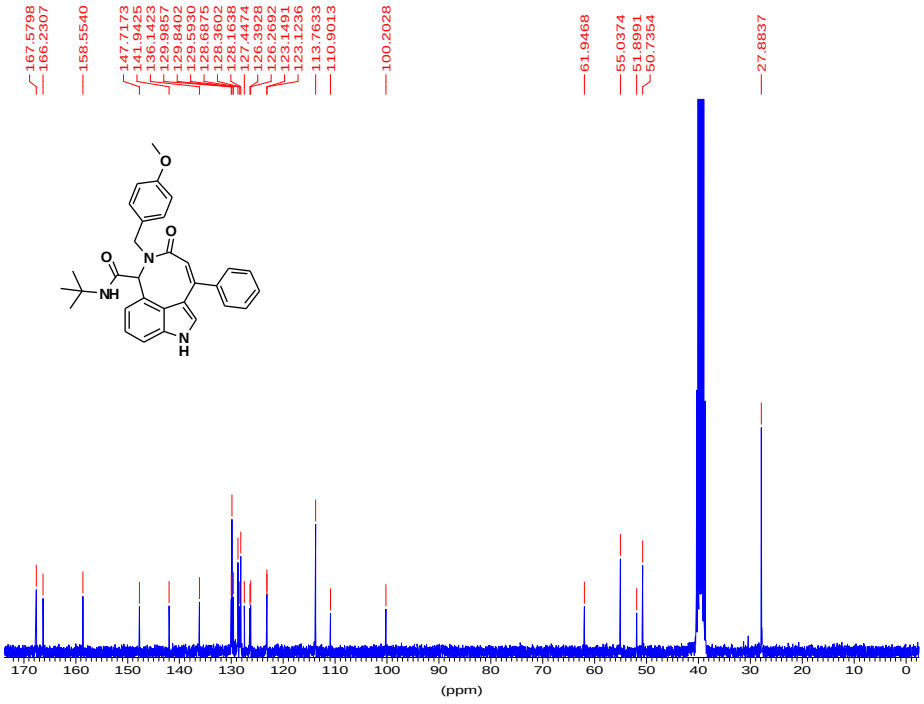
^{1}H and ^{13}C NMR spectra of compound **7g** (300 MHz, DMSO-d_6)



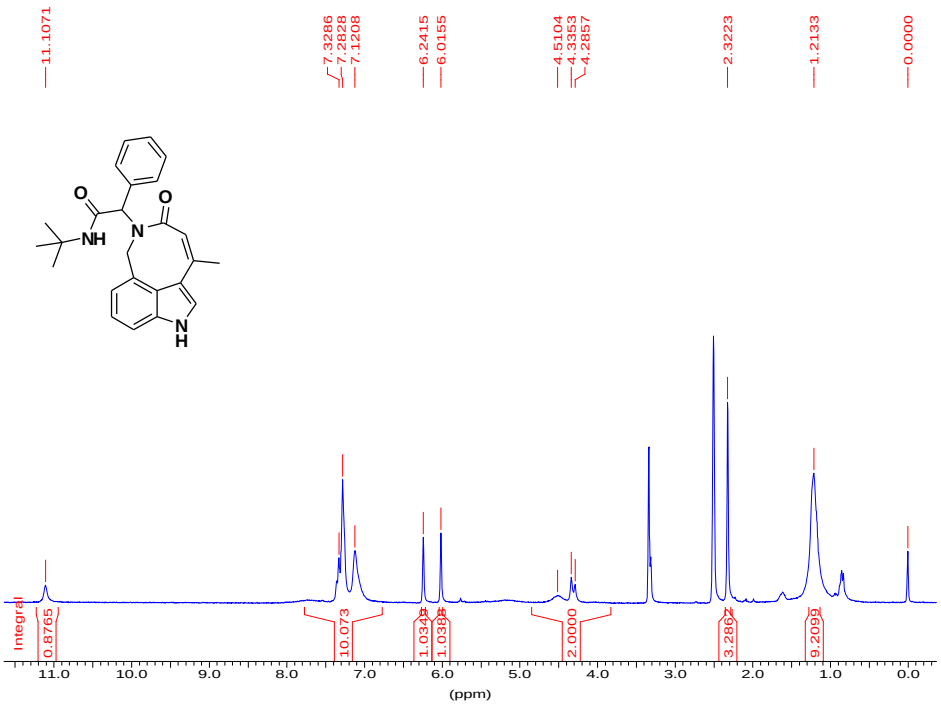


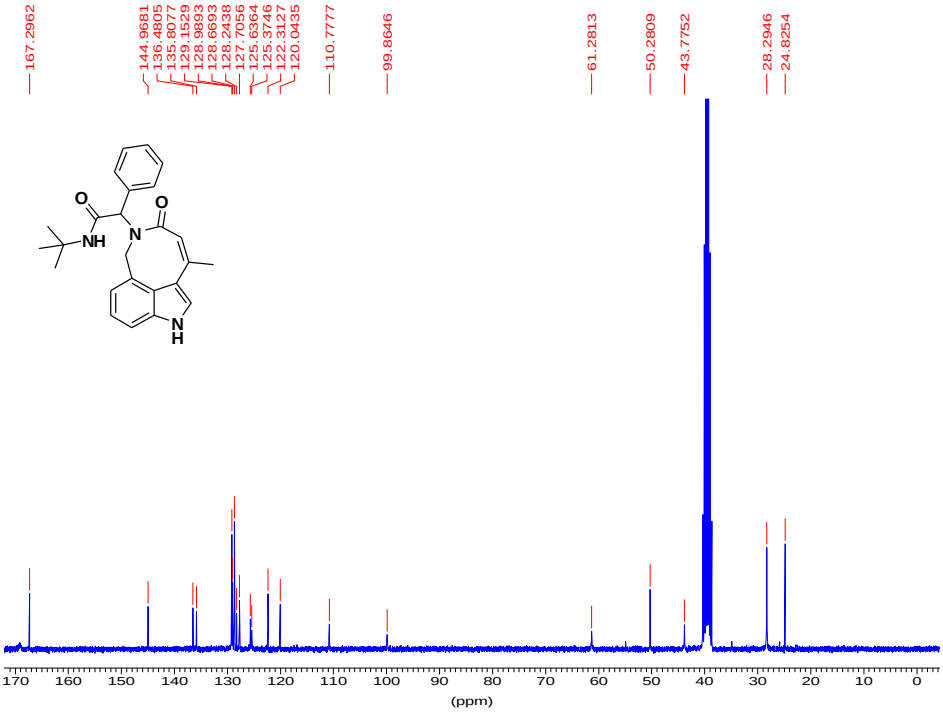
^{1}H and ^{13}C NMR spectra of compound **7h** (300 MHz, DMSO-d_6)





^{1}H and ^{13}C NMR spectra of compound **7j** (300 MHz, DMSO-d_6)





^{1}H and ^{13}C NMR spectra of compound **6k** (300 MHz, DMSO-d_6)