Supporting Information for

Stereoselective synthesis of octahydrocyclohepta[*c*]pyran-6(1*H*)-one scaffolds through a Prins/alkynylation/hydration sequence

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General

Dichloroethane was dried according to standard literature procedure. Reactions were performed in oven-dried round bottom flask, the flasks were fitted with rubber septa and reactions were conducted under nitrogen atmosphere. Glass syringes were used to transfer solvent. Crude products were purified by column chromatography on silica gel of 100-200 mesh. Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to iodine vapours and/or by exposure to methanolic acidic solution of *p*-anisaldehyde (anis) followed by heating (<1 min) on a hot plate (~250°C). Organic solutions were concentrated on rotary evaporator at 35–40°C. IR spectra were recorded on FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR (proton-decoupled) spectra were recorded in $CDCl_3$ solvent on 300, and 500 MHz NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS

as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra were recorded on mass spectrometer by atmospheric pressure chemical ionization (APCI) technique. and Electron impact-mass spectrometry (EI-MS).

2. **NOE studies of products 4i and 5j**

The structures of compounds **4i** and **5j** were derived by extensive NMR experiments including 2-D Nuclear Overhauser Effect Spectroscopy (NOESY) and Double Quantum Filtered Correlation Spectroscopy (DQFCOSY), Hetero-nuclear Single Quantum Correlations (HSQC) and Hetero-nuclear Multiple Bond Correlation (HMBC) experiments.

Compound 4i (Table 2, entry i):

The unique doublet at 4.51 ppm in **4i** was assigned as 1-H and was subsequently used to make assignments of other protons with the help of DQF-COSY and NOESY experiments. The coupling constants, $^{3}J_{1\text{-H/9-H}}$ = 2.5, $^{3}J_{2\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$=12.3, $^{3}J_{2\text{-H(pro-}S\text{)/3-H(pro-}S\text{)}}$=2.6, $^{3}J_{3\text{-H(pro-}R\text{)/4-H}}$= 13.2, $^{3}J_{4\text{-H/9-H}}$=3.7 Hz and the NOE correlation 1-H/4-H, 1-H/2-H(pro-*S*) and 2-H(pro-*S*)/4-H, are consistent with $^{C9}C_{C2}$ chair conformation of the six-membered ring. Similarly, in the seven-membered ring the diaxial coupling constants: $^{3}J_{6\text{-H(pro-}R\text{)/7-H (pro-}S\text{)}}$ =12.3, $^{3}J_{7\text{-H(pro-}S\text{)/8-H(pro-}S\text{)}}$= 14.5 and $^{3}J_{8\text{-H(pro-}S\text{)/9-H}}$ =11.0 Hz and small couplings like: $^{3}J_{4\text{-H/5-H(pro-}R\text{)}}$ = 3.3, $^{3}J_{4\text{-H/9-H}}$ = 3.7, $^{3}J_{6\text{-H(pro-}S\text{)/7-H(pro-}R\text{)}}$ = 4.2, $^{3}J_{6\text{-H(pro-}S\text{)/7-H(pro-}S\text{)}}$ = 4.2, $^{3}J_{6\text{-H(pro-}R\text{)/7-H(pro-}R\text{)}}$ = 4.5, $^{3}J_{7\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = 2.0 and $^{3}J_{8\text{-H(pro-}R\text{)/9-H}}$ =3.7 Hz provide ample evidence of the energy minimized structure shown in Figure 2. The NOE correlations, 3-H(pro-*R*)/6-H(pro-*R*), 3-H(pro-*R*)/8-H(pro-*S*), 6-H(pro-*R*)/8-H(pro-*S*), 5-H(pro-*R*)/7-H(pro-*S*), 5-H(pro-*R*)/9-H, and 7-H(pro-*S*)/9-H, are consistent with the above structure.

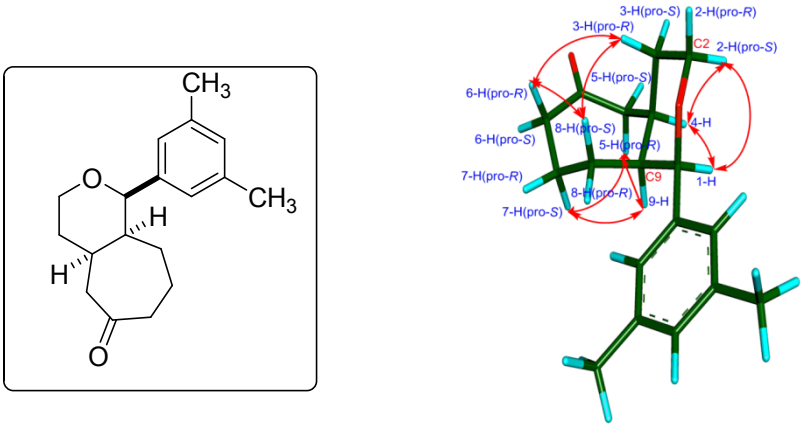
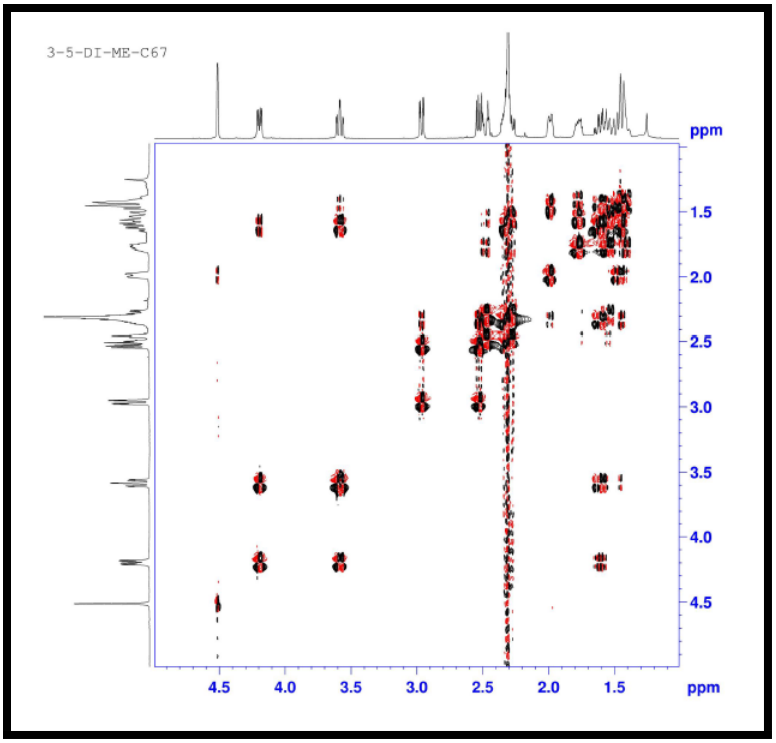
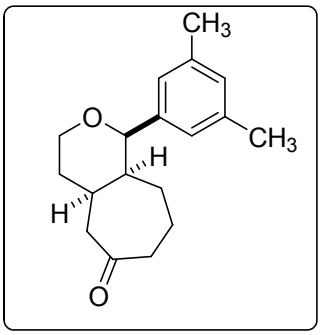


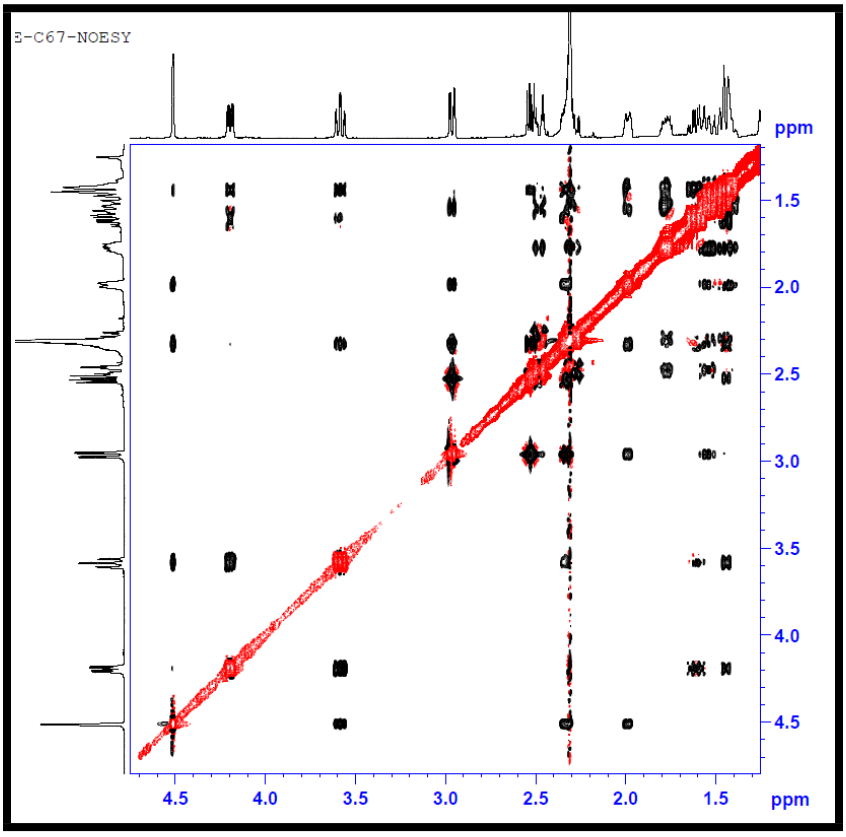
Figure 1. Energy minimized structure of **4i** along with the characteristic NOE correlations shown as double headed arrows

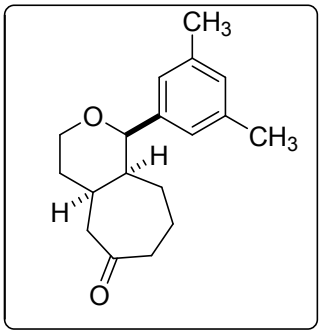
Proton	(δ) ppm	multiplicity	^3J values (Hz)
1-H	4.51	d	$^3J_{1\text{-H/9-H}}$ = 2.5
2-H(pro-*S*)	3.58	ddd	$^3J_{2\text{-H(pro-}S\text{)/2-H(pro-}R\text{)}}$ =11.5 $^3J_{2\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ =12.3 $^3J_{2\text{-H(pro-}S\text{)/3-H(pro-}S\text{)}}$ =2.6
2-H(pro-*R*)	4.20	ddd	$^3J_{2\text{-H(pro-}R\text{)/2-H(pro-}S\text{)}}$ = 11.5 $^3J_{2\text{-H(pro-}R\text{)/3-H(pro-}R\text{)}}$ = 5.0 $^3J_{2\text{-H(pro-}R\text{)/3-H(pro-}S\text{)}}$ = 1.2
3-H(pro-*R*)	1.61	m	$^3J_{2\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ =12.3 $^3J_{2\text{-H(pro-}R\text{)/3-H(pro-}R\text{)}}$ =5.0 $^3J_{3\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ = 13.2 $^3J_{3\text{-H(pro-}R\text{)/4-H}}$ = 13.2
3-H(pro-*S*)	1.44	m	$^3J_{2\text{-H(pro-}S\text{)/3-H(pro-}S\text{)}}$ = 2.6 $^3J_{2\text{-H(pro-}R\text{)/3-H(pro-}S\text{)}}$ = 1.2 $^3J_{3\text{-H(pro-}R\text{)/3-H(pro-}S\text{)}}$ = $^3J_{3\text{-H(pro-}S\text{)/4-H}}$ =
4-H	1.34	m	$^3J_{3\text{-H(pro-}S\text{)/4-H}}$ = $^3J_{3\text{-H(pro-}R\text{)/4-H}}$ = $^3J_{4\text{-H/5-H(pro-}R\text{)}}$ = 3.3 $^3J_{4\text{-H/5-H(pro-}S\text{)}}$ = 6.7 $^3J_{4\text{-H/9-H}}$ =3.7
5-H(pro-*S*)	2.97	dd	$^3J_{5\text{-H(pro-}S\text{)/4-H}}$ = 6.7 $^3J_{5\text{-H(pro-}S\text{)/5-H(pro-}R\text{)}}$= 12.5
5-H(pro-*R*)	2.53	dd	$^3J_{5\text{-H(pro-}R\text{)/4-H}}$ = 3.3 $^3J_{5\text{-H(pro-}R\text{)/5-H(pro-}S\text{)}}$ = 12.5
6-H(pro-*S*)	2.48	dt	$^3J_{6\text{-H(pro-}R\text{)/6-H(pro-}S\text{)}}$ = 18.8 $^3J_{6\text{-H(pro-}S\text{)/7-H (pro-}S\text{)}}$ = 4.2 $^3J_{6\text{-H(pro-}S\text{)/7-H(pro-}R\text{)}}$ =4.2
6-H(pro-*R*)	2.28	m	$^3J_{6\text{-H(pro-}S\text{) /6-H(pro-}R\text{)}}$ = 18.8 $^3J_{6\text{-H(pro-}R\text{)/7-H (pro-}S\text{)}}$ = 12.3 $^3J_{6\text{-H(pro-}R\text{)/7-H(pro-}R\text{)}}$ = 4.5
7-H(pro-*S*)	1.55	m	$^3J_{6\text{-H(pro-}R\text{)/7-H(pro-}S\text{)}}$ = 12.3 $^3J_{6\text{-H(pro-}S\text{) /7-H(pro-}S\text{)}}$ = 4.5 $^3J_{7\text{-H(pro-}R\text{)/7-H(pro-}S\text{)}}$ = 16.4 $^3J_{7\text{-H(pro-}S\text{) /8-H(pro-}S\text{)}}$ =14.5 $^3J_{7\text{-H(pro-}S\text{) /8-H (pro-}R\text{)}}$=2.0
7-H(pro-*R*)	1.77	m	$^3J_{6\text{-H(pro-}S\text{)/7-H(pro-}R\text{)}}$ = $^3J_{6\text{-H(pro-}R\text{)/7-H(pro-}R\text{)}}$ = $^3J_{7\text{-H(pro-}S\text{)/7-H(pro-}R\text{)}}$ = $^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}R\text{)}}$ = $^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}S\text{)}}$ =
8-H(pro-*R*)	1.49	m	$^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}R\text{)}}$ = $^3J_{7\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = $^3J_{8\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = $^3J_{8\text{-H(pro-}R\text{)/9-H}}$ = 3.7
8-H(pro-*S*)	1.42	m	$^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}S\text{)}}$ = $^3J_{7\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = $^3J_{8\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$= $^3J_{8\text{-H(pro-}S\text{)/9-H}}$ = 11.0
9-H	1.98	m	$^3J_{1\text{-H/9-H}}$ = 2.5 $^3J_{4\text{-H/9-H}}$ = 3.7 $^3J_{8\text{-H(pro-}S\text{)/9-H}}$ = 11.0 $^3J_{8\text{-H(pro-}R\text{)/9-H}}$ = 3.7





Correlation spectroscopy (COSY)-(4i; Table 2)





Nuclear Overhauser effect spectroscopy (NOESY)-4i,Table 2

Compound 5j (Table 2, entry j):

The structures of both the compounds were deduced from extensive NMR studies including DQF COSY and NOESY experiments. For **5j**, there are three double doublets (dd) in the 3.26 - 4.45 ppm region, which could arise from 1-H, 2-H (pro-*R*) and 2-H(pro-*S*). In the DQF COSY experiments, 2-H(pro-*R*) and 2-H(pro-*S*), exhibit correlations with each other and thus can be distinguished from 1-H. Thus 1-H, appearing at 4.45 ppm, displays cross peaks with 9-H(pro-*R*) and 9-H(pro-*S*) (having resonances below 2 ppm). Further 1-H also shows strong NOE correlations with aromatic protons. The unique assignment of 1-H, was used to initiate the assignments of other protons resonances. From the one dimensional ^{1}H NMR experiments, the large diaxial-couplings like: $^{3}J_{\text{1-H/9-H(pro-}R\text{)}} = 11.5$, $^{3}J_{\text{2-H(pro-}R\text{)/3-H}} = 10.8$ and $^{3}J_{\text{8-H/9-H(pro-}R\text{)}} = 11.5$ Hz and small equatorial - equatorial and axial - equatorial couplings, $^{3}J_{\text{2-H(pro-}S\text{)/3-H}} = 4.2$, $^{3}J_{\text{1-H/9-H(pro-}S\text{)}} = 2.3$ Hz, in addition to the NOE correlations, 1-H/2-H(pro-*R*), 1-H/8-H, 2-H(pro-*R*)/8-H, 3-H/9-H(pro-*R*), are consistent with $^{C9}C_{C2}$ chair conformation of six membered ring. For the seven membered ring, a chair conformation is indicated by the intra-ring NOE correlations, 3-H/5-H(pro-*R*), 3-H/7-H(pro-*S*), 4-H(pro-*R*)/8-H, 4-H(pro-*R*)/6-H(pro-*S*), 4-H(pro-*R*)/8-H, and 5-H(pro-*R*)/7-H(pro-*S*). Large diaxial coupling constants, $^{3}J_{\text{4-H(pro-}R\text{)/5-H(pro-}R\text{)}} = 11.6$, $^{3}J_{\text{5-H(pro-}R\text{)/6-H(pro-}S\text{)}} = 12.5$, $^{3}J_{\text{7-H(pro-S)/8-H}} = 11.2$ Hz and small couplings like: $^{3}J_{\text{4-H(pro-}R\text{)/5-H(pro-}S\text{)}} = 1.8$, $^{3}J_{\text{5-H(pro-}S\text{) /6-H(pro-}S\text{)}} = 4.2$, $^{3}J_{\text{5-H(pro-}R\text{)/6-H(pro-}R\text{)}} = 4.2$, $^{3}J_{\text{5-H(pro-}S\text{) /6-H(pro-}R\text{)}} = 4.2$, and $^{3}J_{\text{7-H(pro-}R\text{)/8-H}} = 1.8$ Hz provide emphatic support for the chair conformation clearly seen in the energy minimized structure of **5j** in the Figure **2**. Further confirmation of the structure is deduced from the inter-ring correlations 2-H(pro-*R*)/4-H(pro-*R*) and 7-H(pro-*S*)/9-H(pro-*R*).

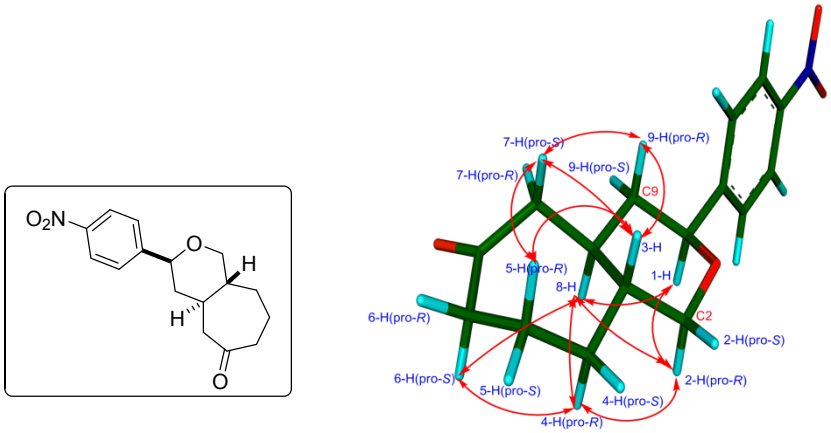
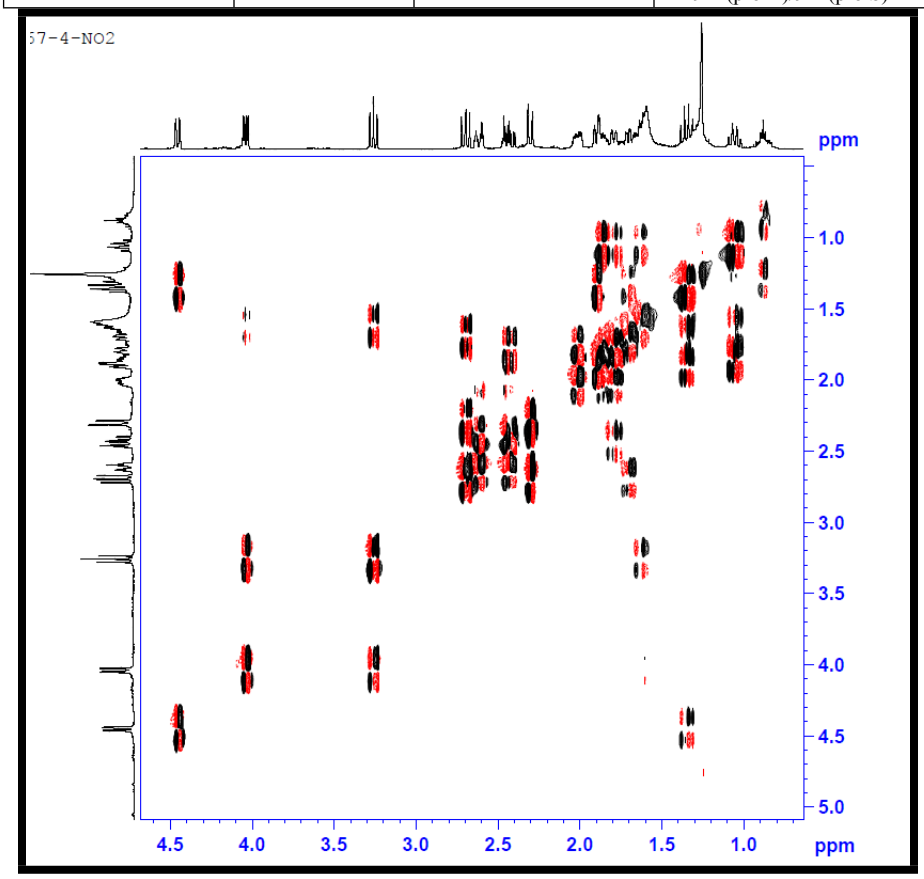
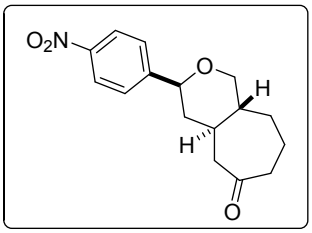


Figure **2**. Energy minimized structure of **5j** along with the characteristic NOE correlations shown as double headed arrows.

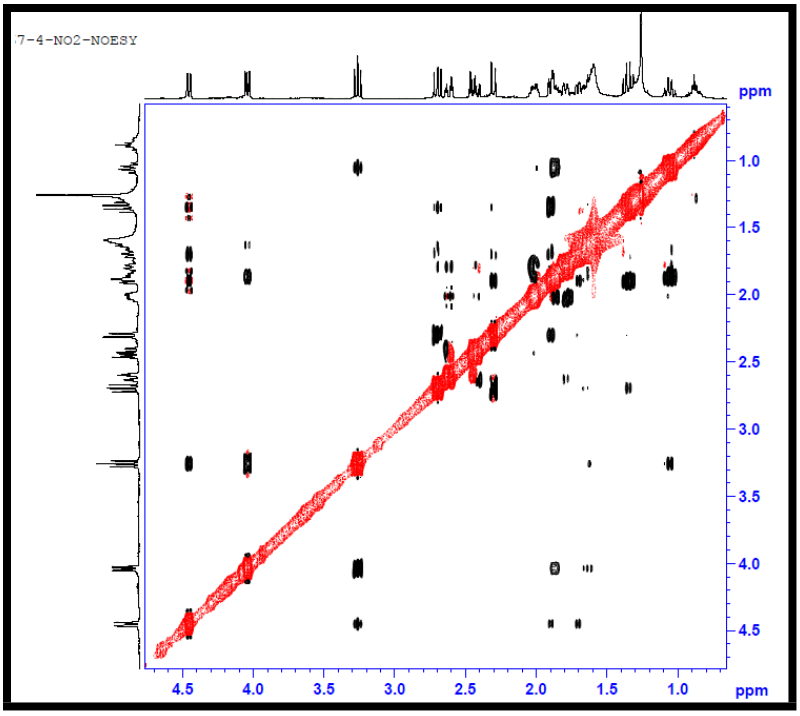
Proton	(δ) ppm	multiplicity	^3J values (Hz)
1-H	4.45	dd	$^3J_{1\text{-H}/9\text{-H(pro-}R\text{)}}$ = 11.5 $^3J_{1\text{-H}/9\text{-H(pro-}S\text{)}}$ = 2.3
2-H(pro-*S*)	4.04	dd	$^3J_{2\text{-H(pro-}S\text{)}/2\text{-H(pro-}R\text{)}}$ = 11.6 $^3J_{2\text{-H(pro-}S\text{)}/3\text{-H}}$ = 4.2
2-H(pro-*R*)	3.26	dd	$^3J_{2\text{-H(pro-}R\text{)}/2\text{-H(pro-}S\text{)}}$ = 11.6 $^3J_{2\text{-H(pro-}R\text{)}/3\text{-H}}$ = 10.8
3-H	1.62	m	$^3J_{2\text{-H(pro-}R\text{)}/3\text{-H}}$ = 10.8 $^3J_{2\text{-H(pro-}S\text{)}/3\text{-H}}$ = 4.2 $^3J_{4\text{-H(pro-}S\text{)}/3\text{-H}}$ = $^3J_{4\text{-H(pro-}R\text{)}/3\text{-H}}$ = $^3J_{3\text{-H}/8\text{-H}}$ =
4-H(pro-*R*)	1.05	m	$^3J_{4\text{-H(pro-}R\text{)}/3\text{-H}}$ =11.6 $^3J_{4\text{-H(pro-}R\text{)}/5\text{-H(pro-}R\text{)}}$= 11.6 $^3J_{4\text{-H(pro-}R\text{)}/5\text{-H(pro-}S\text{)}}$ = 1.8 $^3J_{4\text{-H(pro-}R\text{)}/4\text{-H(pro-S)}}$ = 13.8
4-H(pro-*S*)	1.79	m	$^3J_{4\text{-H(pro-}S\text{)}/3\text{-H}}$ = 11.6 $^3J_{4\text{-H(pro-}S\text{)}/5\text{-H(pro-}S\text{)}}$ = $^3J_{4\text{-H(pro-}S\text{)}/5\text{-H(pro-}S\text{)}}$ = $^3J_{4\text{-H(pro-}R\text{)}/4\text{-H(pro-S)}}$ =
5-H(pro-*S*)	2.01	m	$^3J_{4\text{-H(pro-S)}/5\text{-H(pro-}S\text{)}}$ = $^3J_{4\text{-H(pro-}R\text{)}/5\text{-H(pro-}S\text{)}}$ = $^3J_{5\text{-H(pro-}S\text{)}/6\text{-H (pro-}S\text{)}}$ = $^3J_{5\text{-H(pro-}S\text{)}/6\text{-H(pro-}R\text{)}}$ = $^3J_{5\text{-H(pro-}S\text{)}/5\text{-H(pro-}R\text{)}}$ =
5-H(pro-*R*)	1.84	m	$^3J_{4\text{-H(pro-S)}/5\text{-H(pro-R)}}$ = $^3J_{4\text{-H(pro-}R\text{)}/5\text{-H(pro-}R\text{)}}$ = $^3J_{5\text{-H(pro-}R\text{)}/6\text{-H (pro-}S\text{)}}$ = 12.5 $^3J_{5\text{-H(pro-}R\text{)}/6\text{-H(pro-}R\text{)}}$ = 4.2 $^3J_{5\text{-H(pro-}S\text{)}/5\text{-H(pro-}R\text{)}}$ =
6-H(pro-*S*)	2.43	ddd	$^3J_{5\text{-H(pro-}R\text{)}/6\text{-H(pro-}S\text{)}}$ = 12.5 $^3J_{5\text{-H(pro-}S\text{)}/6\text{-H(pro-}S\text{)}}$ = 4.2 $^3J_{6\text{-H(pro-S)}/6\text{-H(pro-R)}}$ =17.7
6-H(pro-*R*)	2.61	dt	$^3J_{5\text{-H(pro-}R\text{)}/6\text{-H(pro-}R\text{)}}$ = 4.2 $^3J_{5\text{-H(pro-}S\text{)}/6\text{-H(pro-}R\text{)}}$ = 4.2 $^3J_{6\text{-H(pro-S)}/6\text{-H(pro-R)}}$ = 17.1
7-H(pro-*R*)	2.30	dd	$^3J_{7\text{-H(pro-}R\text{)}/8\text{-H}}$ =1.8 $^3J_{7\text{-H(pro-}S\text{)}/7\text{-H(pro-}R\text{)}}$ = 13.6
7-H(pro-*S*)	2.70	dd	$^3J_{7\text{-H(pro-S)}/8\text{-H}}$ = 11.2 $^3J_{7\text{-H(pro-}S\text{)}/7\text{-H(pro-}R\text{)}}$ =13.6
8-H	1.69	m	$^3J_{3\text{-H}/8\text{-H}}$ =

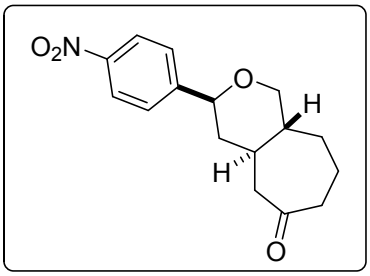
			$^{3}J_{8\text{-H}/9\text{-H(pro-}R\text{)}}$ = $^{3}J_{8\text{-H}/9\text{-H(pro-}S\text{)}}$ = $^{3}J_{7\text{-H(pro-S)}/8\text{-H}}$ = 11.2 $^{3}J_{7\text{-H(pro-}R\text{)}/8\text{-H}}$ = 1.8
9-H(pro-*S*)	1.89		$^{3}J_{1\text{-H}/9\text{-H(pro-}S\text{)}}$ = 2.3 $^{3}J_{8\text{-H}/9\text{-H(pro-}S\text{)}}$ = 3.6 $^{3}J_{9\text{-H(pro-}R\text{)}/9\text{-H(pro-}S\text{)}}$ = 13.4
9-H(pro-*R*)	1.35		$^{3}J_{1\text{-H}/9\text{-H(pro-}R\text{)}}$ = 11.5 $^{3}J_{8\text{-H}/9\text{-H(pro-}R\text{)}}$ = 11.5 $^{3}J_{9\text{-H(pro-}R\text{)}/9\text{-H(pro-}S\text{)}}$ = 13.4





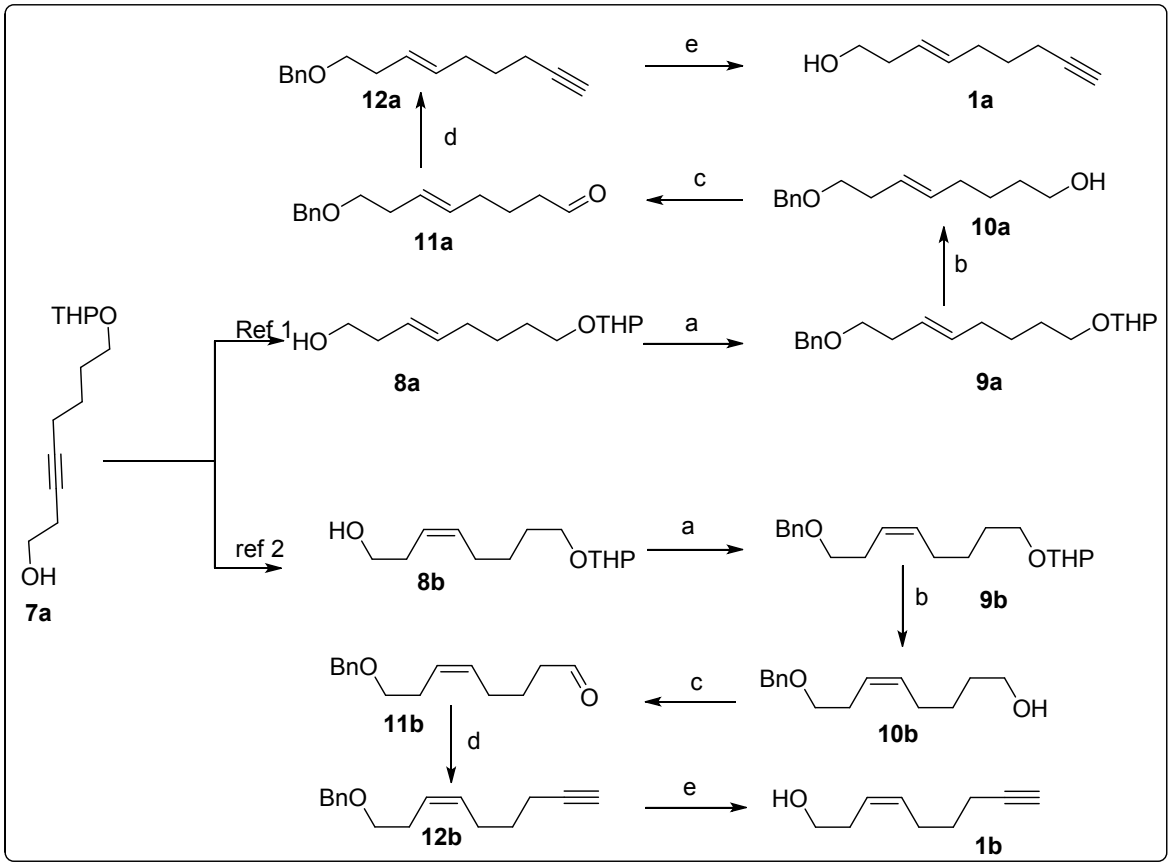
Correlation spectroscopy (COSY)- (5j; Table 2





Nuclear Overhauser effect spectroscopy (NOESY)-5j,Table 2

3. Preparation of (*E/Z*)-non-3-en-8-yn-1-ol (1a/1b)



Scheme 4. Reagents and conditions: (a) NaH, BnBr, dry THF, 0 ^{o}C-r.t, 3h, 90-95%; (b) Amberlyst 15®, methanol, 3h, 88-90%; (c) PCC, DCM, 0 ^{o}C-r.t, 2h, 85-90% (d) Ohira-Bestmann reagent, 2h, 65-70%; (e) Li/naphthalene, dry THF, -20 ^{o}C, 70-75%.

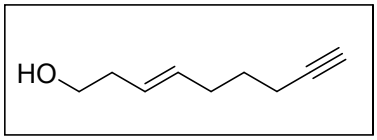
Experimental procedure: To a stirred suspension of NaH (23 mmol, 1.05 equiv) in anhydrous THF (90 mL) was added a solution of (*E*/*Z*)-8-(tetrahydro-2*H*-pyran-2-yloxy)oct-3-en-1-ol **8(a/b)** (5.0 g, 22 mmol) in dry THF (30 mL) at 0 °C. After 30 min, benzyl bromide (22 mmol, 1 equiv) and a catalytic amount of tetrabutylammonium iodide were added and the mixture was stirred at room temperature for 6 h. After completion, as indicated by TLC, the mixture was quenched with 30 mL of ice water and extracted with ethyl aceate (3x20 mL). The combined organic extracts were washed with brine (2x30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford the corresponding (*E/Z*)-2-(8-(benzyloxy)oct-5-enyloxy)tetrahydro-2*H*-pyran **9(a/b)** as liquid in 90% (6.2 g) yield. To a stirred solution of the above (*E/Z*)-2-(8-(benzyloxy)oct-5-enyloxy)tetrahydro-2*H*-pyran **9(a/b)** in methanol (15 mL) was added Amberlyst 15® (5 g) and the mixture was stirred for 2-3h at ambient temperature. After completion, the mixture was filtered, washed with methanol and the filtrate was concentrated *in vacuo*. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford the pure (*E/Z)*-8-(benzyloxy)oct-5-en-1-ol **10(a/b)** as liquid in 90% (4.1 g) yield. The above alcohol **10** was dissolved in dry dichloromethane and then PCC (27 mmol) was added portionwise and the temperature was raised to room temperature and the mixture was stirred for 2-3h at ambient temperature. After completion, the resulting mixture was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford the pure (*E/Z*)-8-(benzyloxy)oct-5-enal **11(a/b)** (3.6 g). The above aldehyde (15.5 mmol) was dissolved in

methanol and then treated with K_2CO_3 followed by a solution of diazo compound in methanol at 0 ^oC and the resulting mixture was stirred for 2h at 0 °C. After completion, as indicated by TLC, the mixture was purified by flash column chromatography over silica gel (ethyl acetate/*n*-hexane) to obtain the pure alkyne **12(a/b)** (2.5 g) as colorless liquid. The above benzyl ether (11 mmol) was added to a blue colored solution of lithium metal (3 equiv) and naphthalene (4 equiv) in dry THF at – 20 ^oC. After completion, as indicated by TLC, it was quenched with ammonium chloride, diluted with 20 mL water and extracted with ethyl acetate (3x20 mL). The combined organic extracts were washed with brine (2x30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacum. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to furnish the corresponding pure eneynol **1(a/b)** as colorless liquid.

References:

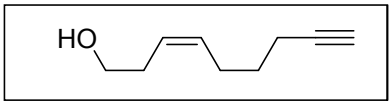
1. Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226.
2. Dukink, J.; Speckai, W. N. *Tetrahedron.* **1978**, *34*, 173.

(*E*)-Non-3-en-8-yn-1-ol (1a):



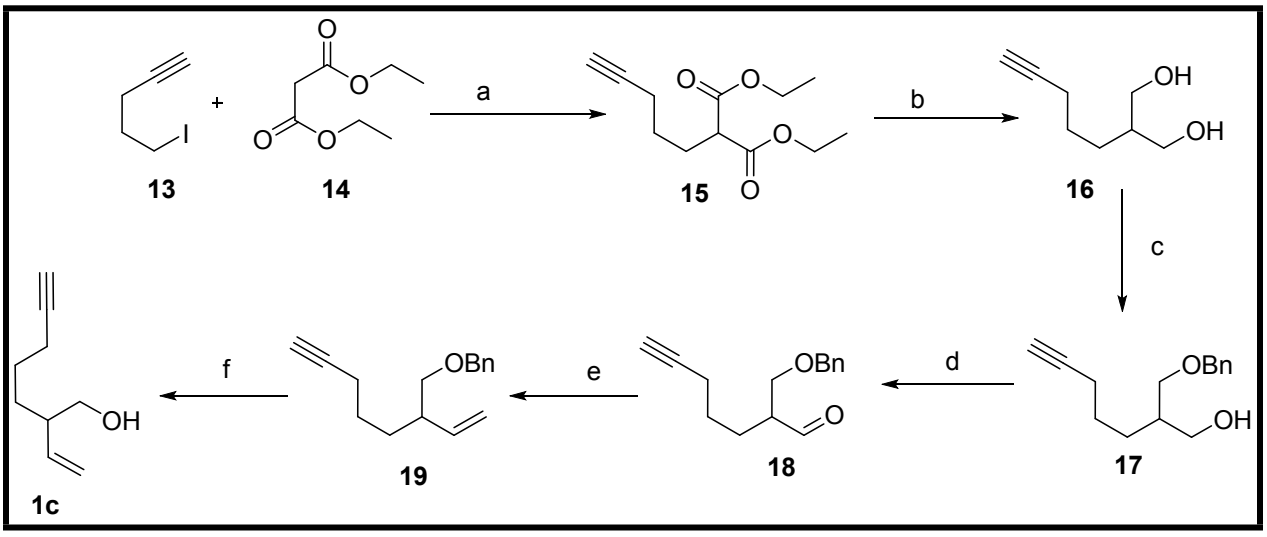
Viscous liquid; ^1H NMR (500 MHz, $CDCl_3$): δ 5.63 (m, 2H), 3.72-3.59 (m, 2H), 2.47-2.10 (m, 6H), 1.96 (t. *J* = 4.5 Hz, 1H), 1.78-1.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.8, 126.9, 84.2, 68.3, 61.9, 35.8, 31.4, 27.9, 17.7; IR (KBr): ν_{max} 3304, 2935, 2116, 1431, 1219, 1047, 969, 771, 634; EI-MS: *m/z* 138 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_9H_{14}O$: 138.1045 $(M)^+$, Found, 138.1047.

(*Z*)-Non-3-en-8-yn-1-ol (1b):



Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.59-5.36 (m, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 2.36 (q, *J* = 6.8 Hz, 2H), 2.25-2.16 (m, 4H), 1.97 (t, *J* = 2.2 Hz, 1H), 1.66-1.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.6, 126.3, 84.3, 68.4, 62.2, 30.7, 28.1, 26.1, 17.7; IR (KBr): ν_{max} 3302, 3010, 2937, 2116, 1626, 1432, 1048, 872, 635; EI-MS: *m/z* 138 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_9H_{14}O$: 138.1045 $(M)^+$, Found, 138.1049.

Preparation of 2-Vinylhept-6-yn-1-ol (1c):



Scheme 5. Reagents and **conditions**: a) NaH, dry THF, 0 °C –r.t, 10h, 85%; b) LAH, dry THF, 0 °C –r.t, 10h, 80%; c) NaH, BnBr, TBAI, dry THF, 0 °C –r.t, 10h, 95%; d) IBX, DMSO, DCM, 2h, 90%; e) LHMDS, Ph_3PCH_3Br, -78 °C-r.t, 10h, 70%; f) Li/naphthalene, dry THF, -20 °C, 2h, 90%.

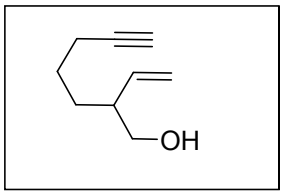
Experimental procedure for 1c:

To a cooled solution of sodium hydride (34.4 mmol, 1.1 equiv) in dry DMF (75 mL), dimethyl malonate **14** (5.0 g, 31.2 mmol) was added dropwise with continuous stirring under nitrogen atmosphere. After stirring for 30 min, the resulting solid suspension was diluted with 30 mL dry DMF and stirred at room temperature. After stirring for another 15 min, iodo compound **13** (7.25 g, 37.4 mmol) was added by dissolving it in minimum quantity of dry DMF at r.t. The mixture was stirred for overnight. After completion, as indicated by TLC, the mixture was quenched with ice water (50 mL) and extracted with ether (3x60 mL). The organic layer was washed with brine (2x30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford the diester **15** (7.0g) as a pure product. To a cooled suspension of lithium aluminum hydride (8.3 g, 84.9 mmol) in anhydrous tetrahydrofuran (150 mL), a solution of diester **15** (7.0 g, 298 mmol) in 10-15 mL of dry THF was added dropwise with stirring under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 2-3h, and the excess of lithium aluminum hydride was quenched by adding anhydrous sodium sulphate and left it overnight. The mixture was then filtered through celite and the residue was washed with hot ethyl acetate. The filtrate was dried over anhydrous Na_2SO_4 and concentrated in vacuo and the resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford the corresponding diol **16**. To a stirred suspension of NaH (30 mmol, 1.05 equiv) in anhydrous THF (80 mL) was added a solution of diol **16** (4.1 g, 29.4 mmol) in dry THF (20 mL) at 0 °C. After 30 min, benzyl bromide (30 mmol, 1 equiv) and a catalytic amount of tetrabutyl ammonium iodide were added and the mixture was stirred at room temperature for 12 h. After completion, as indicated by TLC, the mixture was quenched with ice water and extracted with ethyl aceate (3x60 mL). The combined organic extracts were washed with brine (2x30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting

crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford the monobenzyl ether **17** as a liquid in 95% (6.4 g) yield. To a stirred solution of monobenzyl ether (27.4 mmol) in dry DCM (80 mL) was added Dess-Martin periodinane (18.6 g, 43.8 mmol) at 0 °C under nitrogen atmosphere. The resulting mixture was stirred for 2h at 0 °C. After completion, as indicated by TLC, the reaction was quenched with saturated $NaHCO_3$ solution (40 mL) and extracted with DCM (3x30 mL). The combined organic extracts were washed with brine (2x20 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo to get the crude aldehyde which was quickly purified by flash column chromatography over silica gel (ethyl acetate/*n*-hexane) to obtain the pure aldehyde (5.6 g, 90% yield), which was immediately used for the next reaction. To a stirred suspension of C1 Wittig salt i.e. PPh_3CH_3Br (17.40 g, 49 mmol, 2 equiv.) in dry THF (60 mL) was added LHMDS (32 mL 1M in toluene, 1.5 equiv) at -20 °C. The reaction was stirred at 0 °C for 1h. After complete generation of the ylide, a solution of the above aldehyde **18** in 40 mL dry THF was added at -70 °C. The mixture was stirred for 1h at -70 ^oC. After completion, as indicated by TLC, it was quenched with ice water, diluted with 50 mL water and extracted with ethyl acetate (3x60 mL). The combined organic extracts were washed with brine (2 x 60 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to furnish the corresponding pure olefin **19** as a colorless liquid. The above benzyl ether **19** at – 20 ^oC was added to a blue coloured solution of lithium (3 equiv.) and naphthalene (4 equiv.) in dry THF. After completion of the reaction, as indicated by TLC, it was quenched with ammonium chloride, diluted with 60 mL water and extracted with ethyl acetate (3x40 mL). The combined organic extracts were washed with brine (2 x 40 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. The resulting crude product was purified by column chromatography

(silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to furnish the pure olefin **1c** as a colorless liquid

2-Vinylhept-6-yn-1-ol (1f)



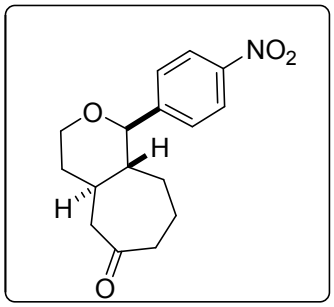
Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.63-5.54 (m, 1H), 5.18 (dd, *J* = 11.3, 13.5 Hz, 2H), 3.61-3.55 (m, 1H), 3.44 (t, *J* = 8.2 Hz, 1H), 2.27-2.15 (m, 3H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.73-1.32 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.4, 117.3, 84.1, 68.3, 65.4, 6.4, 29.5, 25.8, 18.2; IR (KBr): ν_{max} 3432, 3027, 2927, 1603, 1491, 1453, 1383, 1031, 917, 750, 701, 632; EI-MS: *m/z* 138 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_9H_{14}O$: 138.1045 $(M)^+$, Found, 138.1048.

4. Typical procedure for Prins cascade cyclization

To a stirred solution of (*E/Z*)-9-methyldeca-3,8-dien-1-ol (**1a/1b**) or 2-vinylhept-6-yn-1-ol (**1c**) (0.50 mmol) and aldehyde (0.525 mmol) were added $BF_3.OEt_2$ and CuCl (10 mol% each) in dichloroethane at -10 ^{o}C and the temperature was slowly raised to room temperature for the specified time (24-30 h). After completion, as indicated by TLC, the mixture was quenched with saturated $NaHCO_3$ solution (0.5 mL), diluted with water (2-3 mL) and extracted with dichloromethane (2x5 mL). The combined organic phases were washed with brine (3x2 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradients to afford the pure products (Table 2).

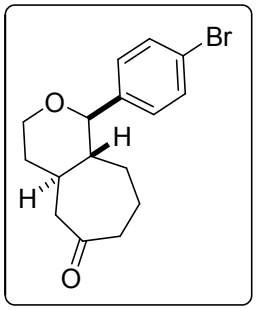
5. Characterization data of products (3a-e, 4f-i and 5j-l)

1-(4-Nitrophenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**3a**; Table 2, entry a)



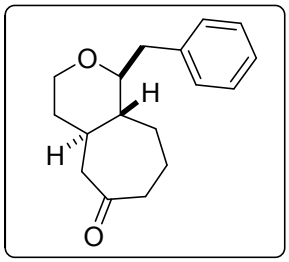
Yield, 90 %; Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 4.46 (d, *J* = 9.8 Hz, 1H), 4.04 (dd, *J* = 4.5, 12.0 Hz, 1H), 3.26 (t, *J* = 11.3 Hz, 1H), 2.68 (dd, *J* = 3.0, 13.0 Hz, 1H), 2.62 (dt, *J* = 4.5, 4.5, 13.6 Hz, 1H), 2.46 (dd, *J* = 4.5, 12.8, 1H), 2.29 (dd, *J* = 13.6 Hz, 1H), 2.09-1.99 (m, 1H),1.99-1.52 (m, 5H), 1.42-1.17 (m , 2H); ^{13}C NMR(125MHz , $CDCl_3$): δ 212.7, 149.5, 147.1, 126.3, 123.5, 78.3, 73.1, 50.4, 45.3, 43.5, 41.7, 38.6, 31.3, 22.2; IR (KBr): ν_{max} 3064, 2926, 1693, 1525, 1438, 1349, 1171, 1102, 1046, 808, 742, 682 cm^{-1}; ESI-MS: *m/z* 289 $(M)^+$; ESI-HRMS calcd for $C_{16}H_{19}NO_4$: 289.1314, Found 289.1319.

1-(4-Bromophenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**3b**; Table 2, entry b)



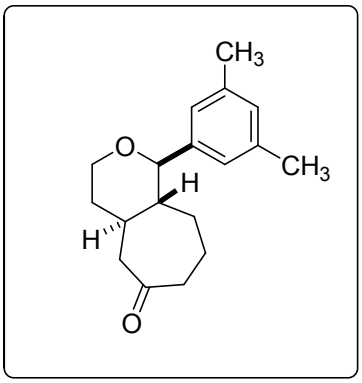
Yield, 85%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz), 4.08 (dd, *J* = 3.2, 10.5 Hz, 1H), 3.85 (d, *J* = 9.4 Hz, 1H), 3.59 (td, *J* = 3.9, 11.1 Hz, 1H), 2.76 (dd, *J* = 3.0, 10.5 Hz, 1H), 2.41-2.27 (m, 2H), 1.85-1.33 (m, 8H), 0.98-0.78 (m, 1H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.3, 139.9, 131.5, 129.2, 121.8, 84.7, 68.0, 51.1, 43.2, 38.6, 34.6, 31.5, 29.7, 22.1; IR (KBr): ν_{max} 3436, 2998, 2937, 1698, 1587, 1491, 1454, 1327, 1226, 1150, 1117, 1035, 949, 819, 774 cm^{-1}; EI-MS: *m/z* 322 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_{16}H_{20}O_2Br$: 322.0638, Found 322.0639.

1-Benzyloctahydrocyclohepta[*c*]pyran-6(1*H*)-one (**3c**; Table 2, entry c)



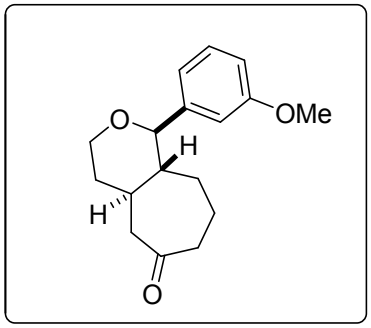
Yield, 71%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.19 (m ,5H), 3.92 (ddd, *J* = 1.5, 4.5, 11.5 Hz, 1H), 3.64 (t, *J* = 6.2 Hz, 1H), 3.33 (td, *J* = 2.4, 11.6, 14.0 Hz, 1H), 3.24 (td, *J* = *J* = 2.7, 6.7, 9.1 Hz, 1H), 3.10 (dd, *J* = 2.7, 14.6 Hz, 1H), 2.70-2.64 (m, 1H),2.55 (td, *J* = 3.8, 17.8 Hz, 1H), 2.40 (td, *J* = 3.9, 12.4 Hz, 1H), 2.30-2.12 (m, 2H), 2.05-1.93 (m, 1H), 1.76-1.46 (m, 5H), 1.32-1.25 (m, 1H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.5, 139.1, 129.3, 128.0, 126.0, 81.9, 67.5, 50.8, 49.4, 43.1, 39.6, 38.4, 34.8, 31,7, 22.3; IR (KBr): ν_{max} 3447, 3027, 1699, 1602, 1454, 1383, 1247, 1110, 771, 700 cm^{-1}; EI-MS:: *m/z* 258 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_{17}H_{22}O_2$: 258.1620, Found 258.1619.

1-(3, 5-Dimethylphenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**3d**; Table 2, entry d)



Yield, 85%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95-6.91 (m, 3H), 4.08 (ddd, *J* = 2.5, 3.2, 13.2 Hz, 1H), 3.81 (d, *J* = 9.3 Hz, 1H), 3.58 (ddd, *J* = 4.5, 6.1, 11.7 Hz, 1H), 2.79 (dd, *J* = 3.3, 10.0 Hz, 1H), 2.51 (dt, *J* = 3.8, 3.8, 18.0 Hz, 1H), 2.31-2.27 (m, 2H), 2.31 (s, 6H), 1.82-1.51 (m, 6H) :^{13}C NMR (125MHz , $CDCl_3$): δ 213.5, 140.6, 137.8, 129.6, 125.2, 85.6, 68.0, 50.8, 50.7, 43.3, 38.7, 34.8, 31.7, 22.2, 21.3: IR (KBr): ν_{max} 2926, 2853, 1698, 1608, 1458, 1376, 1240, 1087, 849, 749 cm^{-1}; EI-MS: *m/z* 272 $(M)^{+}$; EI-HRMS (TOF-EI) calcd for $C_{18}H_{24}O_2$: 272.1776, Found 272.1778.

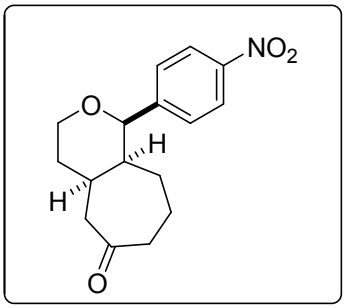
1-(3-Methoxyphenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**3e**; Table 2, entry e)



Yield, 78%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (m, 1H), 6.92-6.81 (m, 3H), 4.10 (dd, *J* = 3.3, 10.7 Hz, 1H), 3.86 (d, *J* = 9.5 Hz, 1H), 3.82 (s, 3H), 3.62-3.56 (m, 1H), 2.77 (dd, *J* = 3.0, 10.2 Hz, 1H), 2.52 (dt, *J* = 4.1, 18.0 Hz, 1H), 2.39-2.31 (m, 2H), 1.82-1.51 (m, 7H), 0.96-0.86 (m, 1H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.5, 159.6, 142.4, 129.4, 120.0, 113.4,

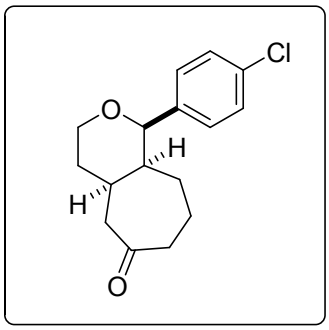
112.9, 85.4, 68.0, 55.2, 51.0, 50.6, 43.2, 38.7, 34.7, 31.6, 22.2; IR (KBr): ν_{max} 3446, 2929, 2851, 1698, 1603, 1440, 1261, 1158, 1042, 761, 700 cm^{-1}; ES-MS *m/z* 274 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_{17}H_{22}O_3$: 274.1569, Found 274.1574.

1-(4-Nitrophenyl) octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**4f**; Table 2, entry f)



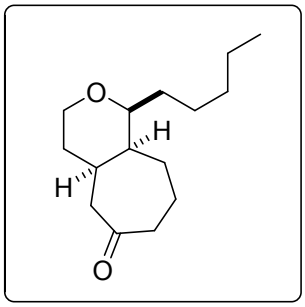
Yield, 93%; Viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 4.66 (d, *J* = 1.5 Hz,1H), 4.25 (dd, *J* = 4.5, 11.3 hz, 1H), 3.62 (td, *J* = 3.0, 12.0 Hz, 1H), 3.01 (dd, *J* = 3.0, 12.8 Hz, 1H), 2.61-2.45 (M, 2H), 2.43-2.23 (m, 2H), 2.12-2.03 (m, 1H), 1.83-1.40 (m, 6H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.2, 148.8, 146.8, 126.1, 123.3, 82.0, 68.9, 48.0, 46.38, 43.8, 36.2, 26.4, 22.9, 22.4; IR (KBr): ν_{max} 3564, 2929, 1698, 1604, 1518, 1345, 1174, 1096, 852, 771 cm^{-1}; ESI-MS: *m/z* 289 $(M)^+$; ESI-HRMS calcd for $C_{16}H_{19}NO_4$: 289.1314, Found 289.1316.

1-(4-Chlorophenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**4g**; Table 2, entry g)



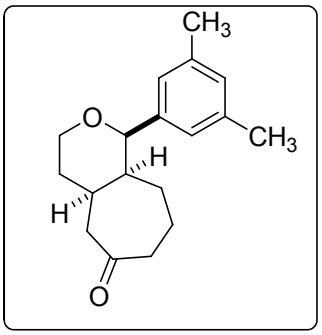
Yield, 85 %; Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31(d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 4.55 (d, *J* = 1.5 Hz, 1H), 4.19 (ddd, *J* = 3.7, 7.5, 1.5 Hz, 1H), 3.60 (td, *J* = 3.0, 12.9 Hz, 1H), 2.58-2.42 (m, 2H), 2.40-2.21 (m, 2H), 2.06-1.93 (m, 1H), 182-1.31 (m, 6H), ^{13}C NMR(125MHz , $CDCl_3$): δ 213.5, 139.8, 132.2, 128.2, 126.6, 82.2, 68.9, 48.2, 46.5, 43.9, 36.3, 29.6, 26.5, 22.7: IR (KBr): ν_{max} 3458, 2930, 2856, 1698, 1599, 1491, 1403, 1267, 1174, 1091, 1015, 805, 736, 674 cm^{-1}; EI-MS: *m/z* 278 $(M)^+$; EI-HRMS (TOF-EI) calcd for $C_{16}H_{19}ClO_2$: 278.1074, Found 278.1077.

1-Pentyloctahydrocyclohepta[*c*]pyran-6(1*H*)-one (**4h**; Table 2, entry h)



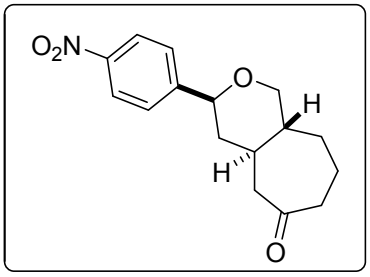
Yield, 65%; Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02 (dd, *J* = 3.0, 9.8 Hz, 1H), 3.42 (td, *J* = 2.6, 11.7 Hz, 1H), 3.31 (t, *J* = 5.28 Hz, 1H), 2.92 (dd, *J* = 3.4, 12.4 Hz, 1H), 2.58-2.40 (m, 2H), 2.39-2.23 (m, 2H), 2.13-1.89 (m, 1H), 1.82-1.21 (M, 11H), 0.98-0.82 (m, 6H); ^{13}C NMR (125MHz , $CDCl_3$): δ 214.1, 82.0, 68.8, 48.4, 44.2, 43.8, 36.5, 31.9, 29.6, 27.0, 25.8, 22.6, 22.5, 14.0 : IR (KBr): ν_{max} 3450, 2928, 2860, 1699, 1459, 1371, 1176, 1090, 759 cm^{-1}; EI -MS: *m/z* 238 $(M)^+$; EI-HRMS calcd for $C_{15}H_{26}O_2$: 238.1933, Found 238.1936.

1-(3, 5-Dimethylphenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**4i**; Table 2, entry i)



Yield, 85%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.90 (m, 3H), 4.52 (d, *J* = 2.3 Hz, 1H), 4.20 (dd, *J* = 5.2, 12.0 Hz, 1H), 3,59 (td, *J* = 3.0, 12.0 Hz, 1H), 2.97 (dd, *J* = 3.0, 12.0 Hz, 1H), 2.57-2.44 (m, 2H), 2.40-2.23 (m, 2H), 2.31 (s, 6H), 2.04-1.95 (m,1H), 1.84 (m, 1H), 1.69-1.39 (m, 5H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.6, 140.9, 137.2, 128.0, 122.7, 82.8, 68.7, 48.0, 46.4, 43.7, 36.1, 26.4, 22.6, 22.4, 21.0; IR (KBr): ν_{max} 3007, 2939, 1697, 1604, 1457, 1361, 1223, 1178, 1094, 1061, 851, 734, 509 cm^{-1}; EI-MS: *m/z* 272 $(M)^{+}$; EI-HRMS calcd for $C_{18}H_{24}O_2$: 272.1776, Found 272.1778.

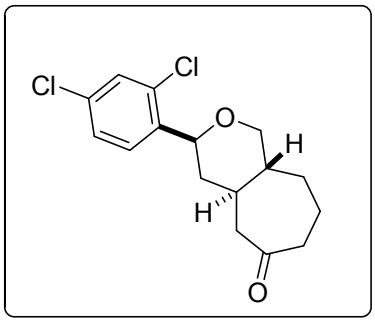
3-(4-Nitrophenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**5j**; Table 2, entry j)



Yield, 90%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 4.45 (dd, *J* = 1.9, 11.3 Hz, 1H),4.04 (dd, *J* = 4.2, 11.7 Hz, 1H), 3.26 (t, *J* = 11.0 Hz, 1H), 2.69 (dd, *J* = 2.3, 11.1 Hz, 1H), 2.61 (dt, *J* = 3.4, 13.1, 17.7 Hz, 1H), 2.48-2.39 (m, 2H), 2.30 (dd, *J* = 1.2, 13.4 Hz, 1H), 2.05-1.97 (m, 1H), 1.92-1.54 (m, 5H), 1.10 -1.01 (M, 1H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.5, 159.6, 142.4, 129.3, 120.0, 85.5, 68.0, 51.1, 50.6, 43.3, 38.7,

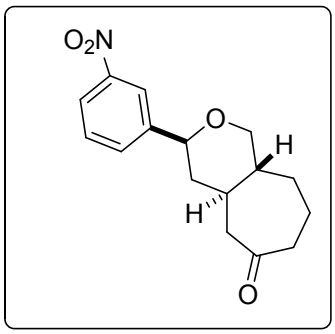
34.7, 31.6, 22.2 ; IR (KBr): ν_{max} 3446, 2926, 1718, 1604, 1522, 1347, 1094, 907, 754, 554 cm^{-1}; ESI-MS: *m/z* 289 $(M)^+$; ESI-HRMS calcd for $C_{16}H_{19}NO_4$: 289.1314, Found 289.1318.

3-(2, 4-Dichlorophenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**5k**; Table 2, entry k)



Yield, 85%; Viscous liquid; ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.3 Hz, 1H), 7.38-7.31 (m, 1H), 7.27-7.23 (m, 1H), 4.65 (d, *J* = 10.9 Hz, 1H), 4.01 (dd, *J* = 4.1, 11.6, Hz, 1H), 3.27 (m, td, *J* = 3.8, 11.2 Hz, 1H), 2,69-2.54 (m, 2H), 2,48-2.38 (m, 2H), 2.29 (d, *J* = 13.6 Hz, 1H), 2.04-1.55 (m, 7H), 1.27-1.07 (m, 1H); ^{13}C NMR(125MHz , $CDCl_3$): δ 213.0, 138.6, 133.3, 132.0, 128.9, 127.4, 75.7, 73.2, 50.4, 45.4, 43.6, 40.0, 38.4, 31.4, 22.3; IR (KBr): ν_{max} 3404, 2928, 2860, 1699, 1590, 1474, 1367, 1176, 1097, 865, 823, 779 cm^{-1}; ESI -MS: *m/z* 312 $(M)^+$; ESI-HRMS calcd for $C_{16}H_{18}O_2Cl_2$: 312.0684, Found 312.0691.

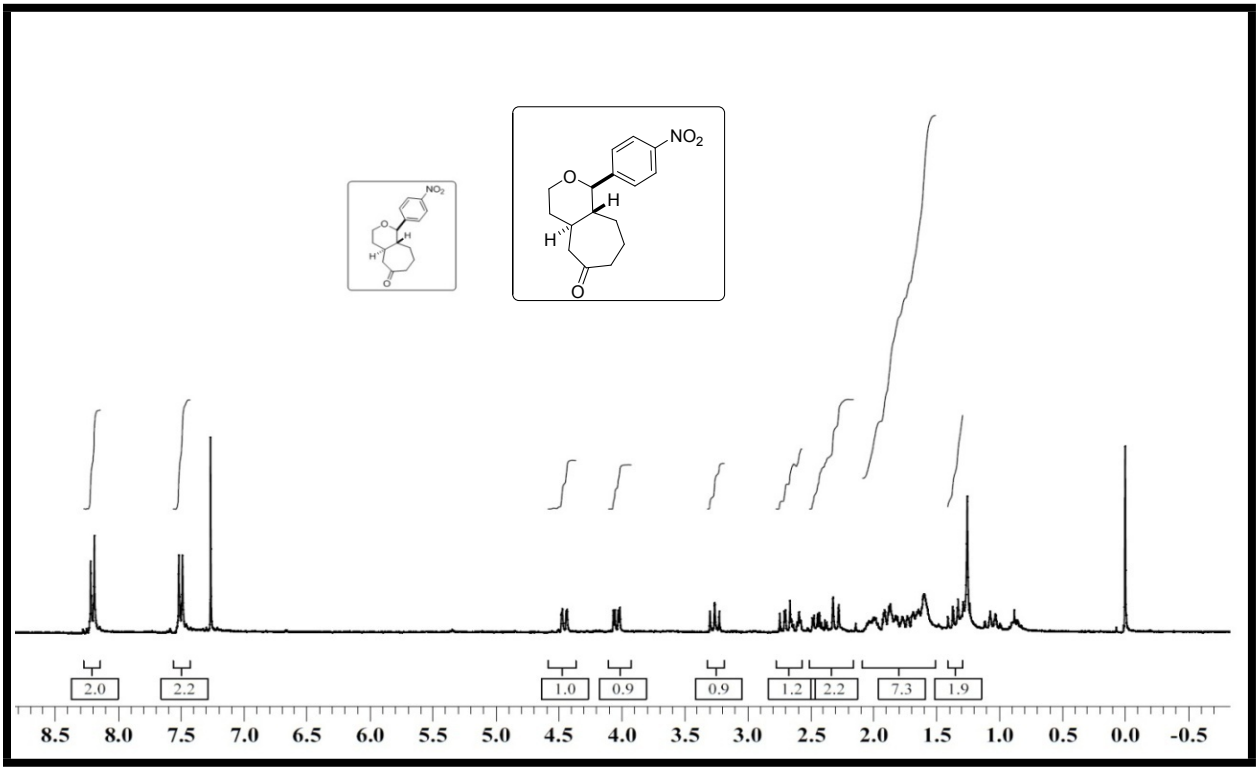
3-(3-Nitrophenyl)octahydrocyclohepta[*c*]pyran-6(1*H*)-one (**5l**; Table 2, entry l)



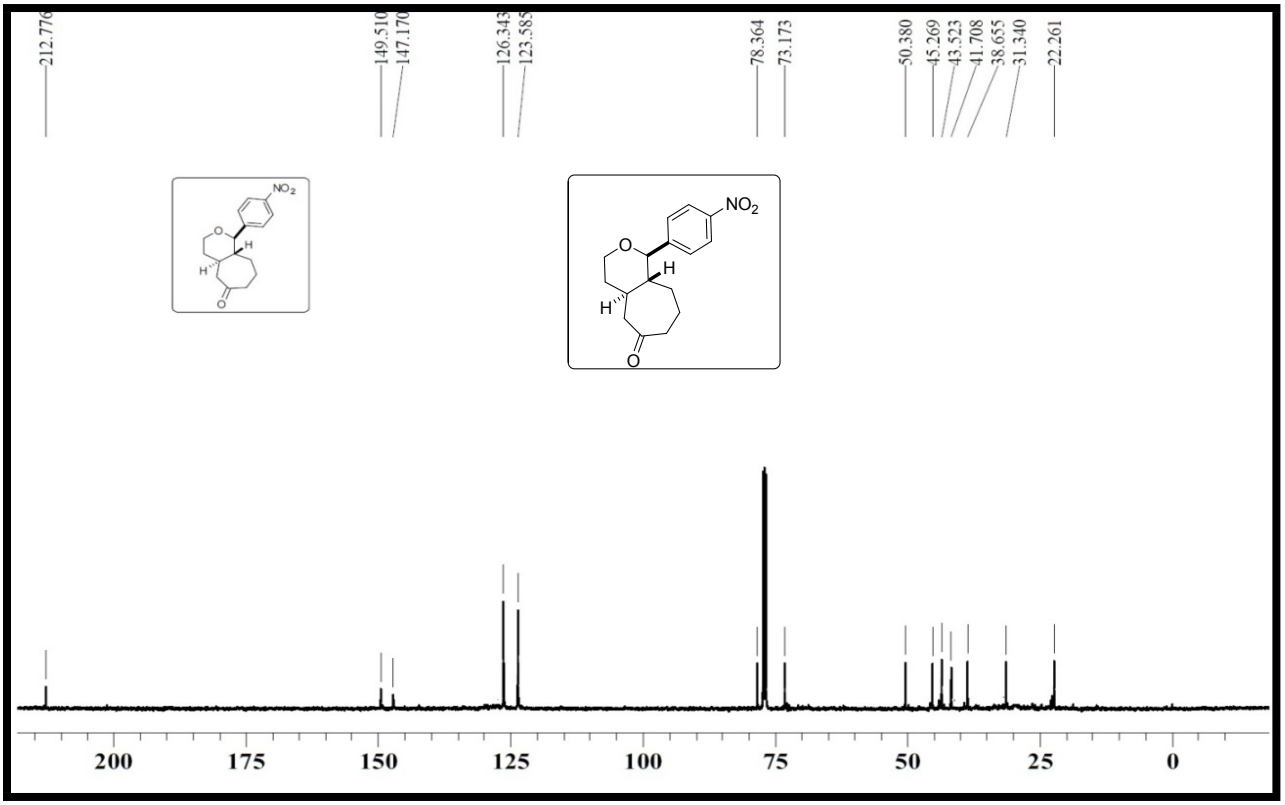
Yield, 87%; Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.18-8.12 (m, 1H), 7.68-7.63 (m, 1H), 7.55 (m, 1H), 4.45 (dd, *J* = 2.1, 11.4 Hz, 1H), 4.04 (dd, *J* = 4.1, 11.9 Hz, 1H), 3.27 (t, *J* = 10.8 Hz, 1H), 2.71 (dd, *J* = 2.2, 11.1 Hz, 1H), 2.66-2.40 (m, 2H), 2.31 (dd, *J* = 1.3, 13.4 Hz, 1H), 2.05-1.96 (m, 1H), 1.94 (m, 7H); ^{13}C NMR(125MHz , $CDCl_3$): δ 212.8, 148.3, 144.6, 135.2, 133.6, 131.8, 129.9, 78.2, 73.2, 50.4, 45.3, 41.6, 38.6, 31.3, 22.6; IR (KBr): ν_{max} 3446, 2929, 1698, 1603, 1440, 1261, 1158, 1042, 761 cm^{-1}; ESI-MS: *m/z* 289 $(M)^{+}$; EI-HRMS calcd for $C_{16}H_{19}NO_4$: 289.1314, Found 289.1316.

5. Copies of ^{1}H and ^{13}C NMR spectra of products and starting materials

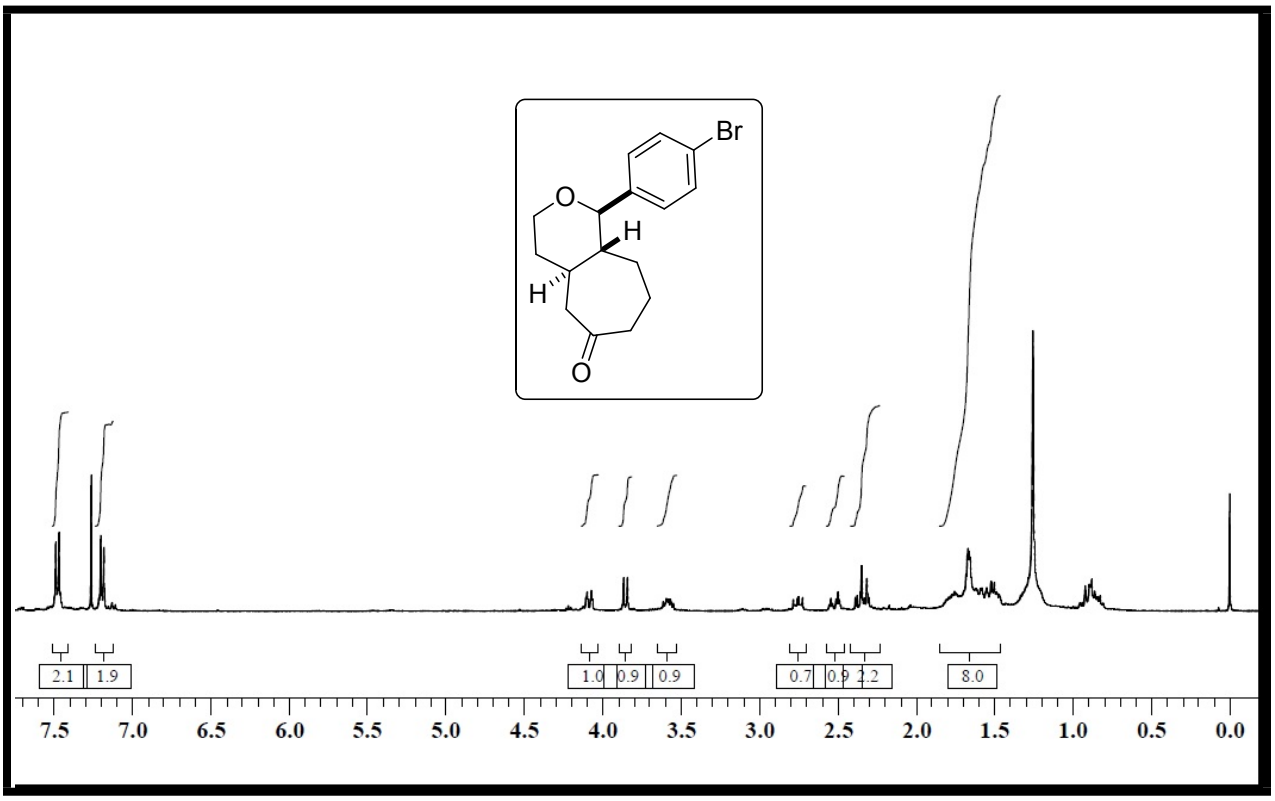
^{1}H NMR spectrum of 3a (Table 2, entry a), 300MHz, $CDCl_3$



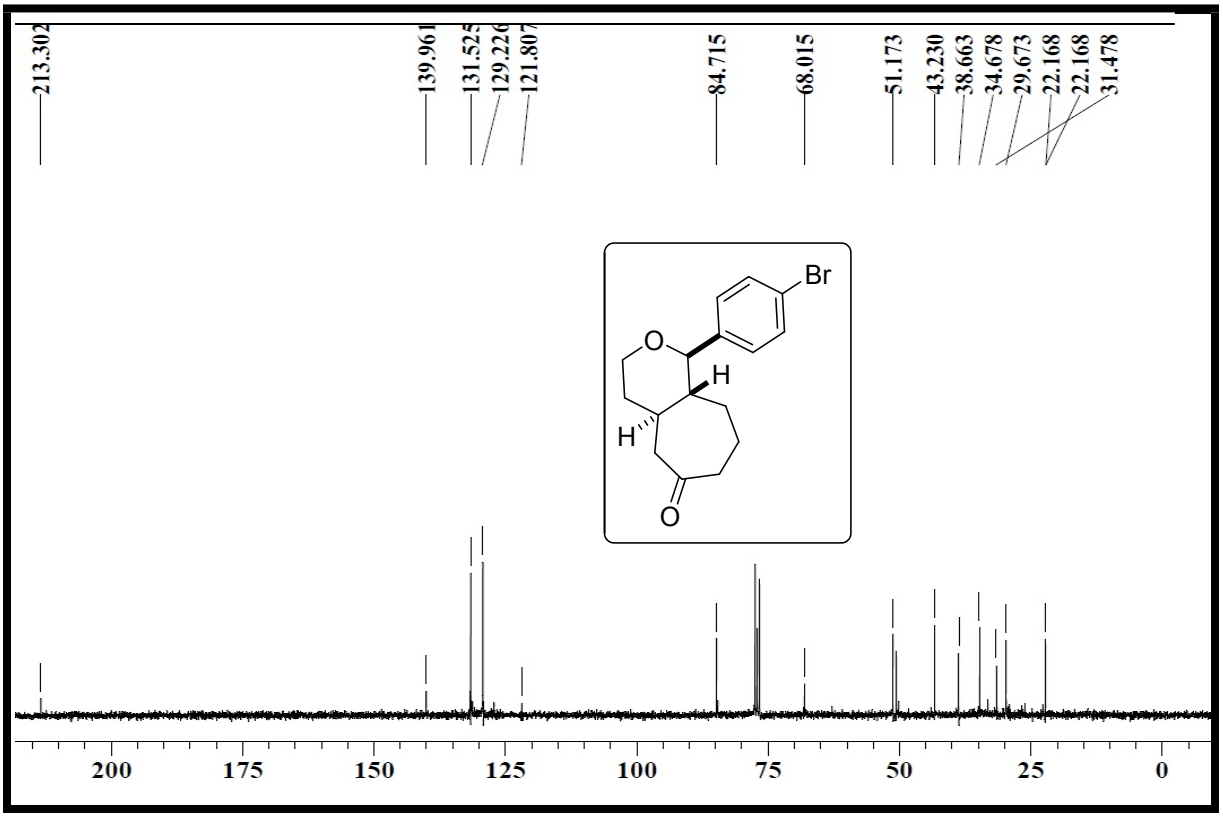
^{13}C NMR spectrum of 3a (Table 2, entry a), 125MHz, $CDCl_3$



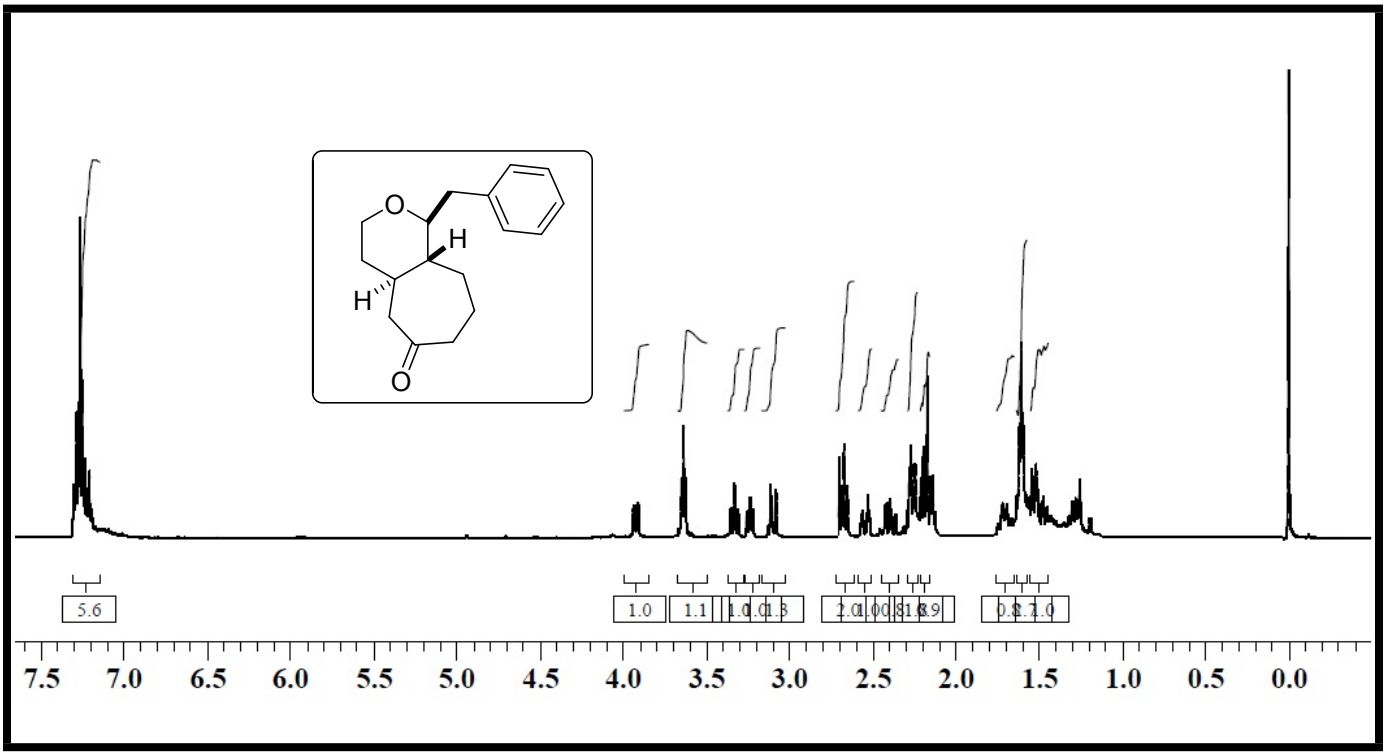
^{1}H NMR spectrum of 3b (Table 2, entry b), 300MHz, $CDCl_3$



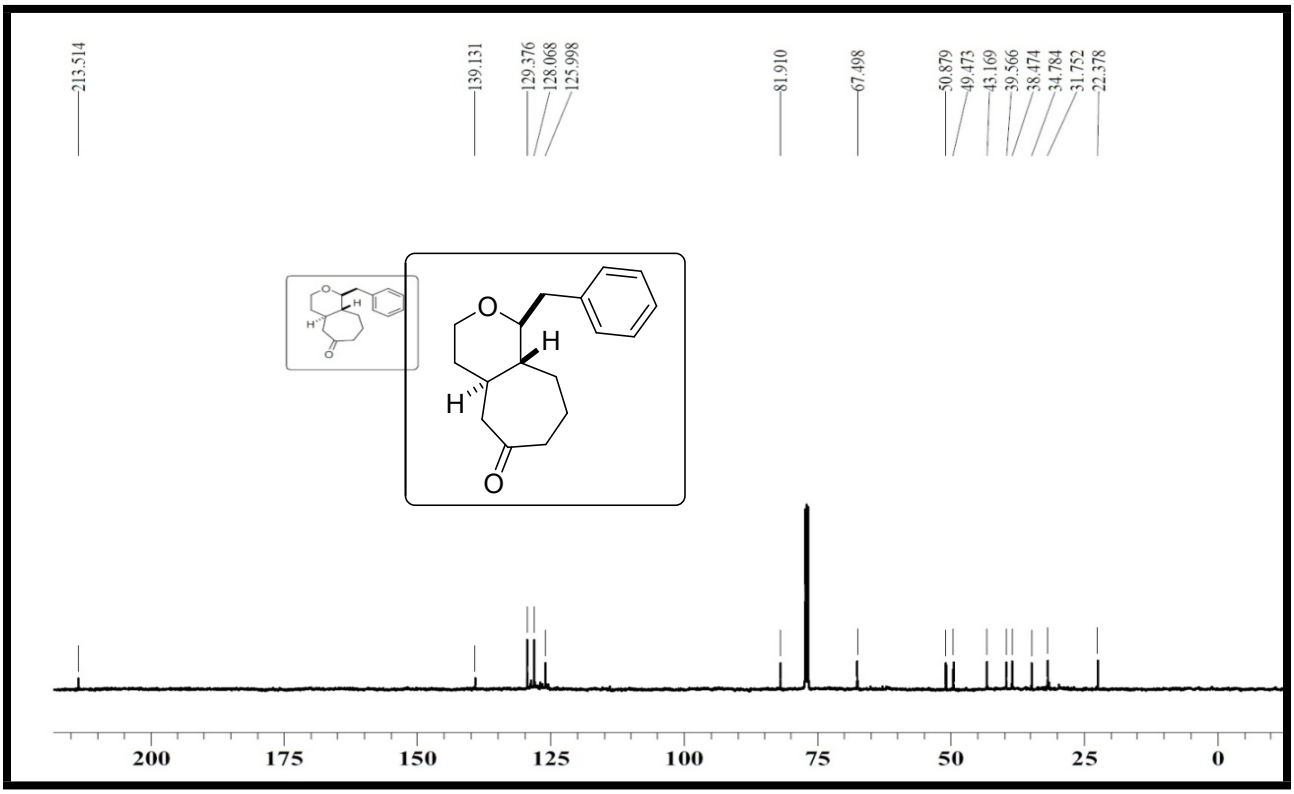
^{13}C NMR spectrum of 3b(Table 2, entry b), 125MHz, $CDCl_3$



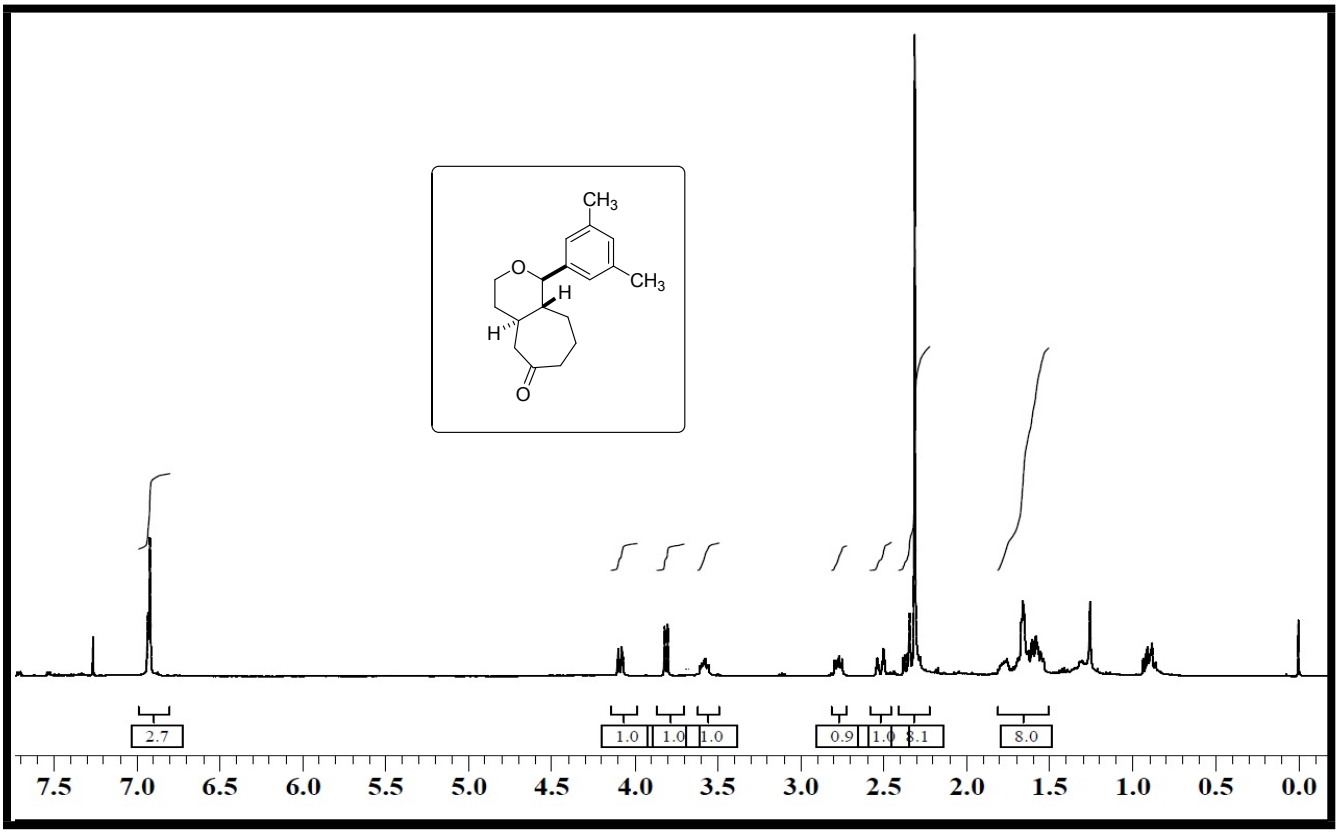
^{1}H NMR spectrum of 3c (Table 2, entry c), 300MHz, $CDCl_3$



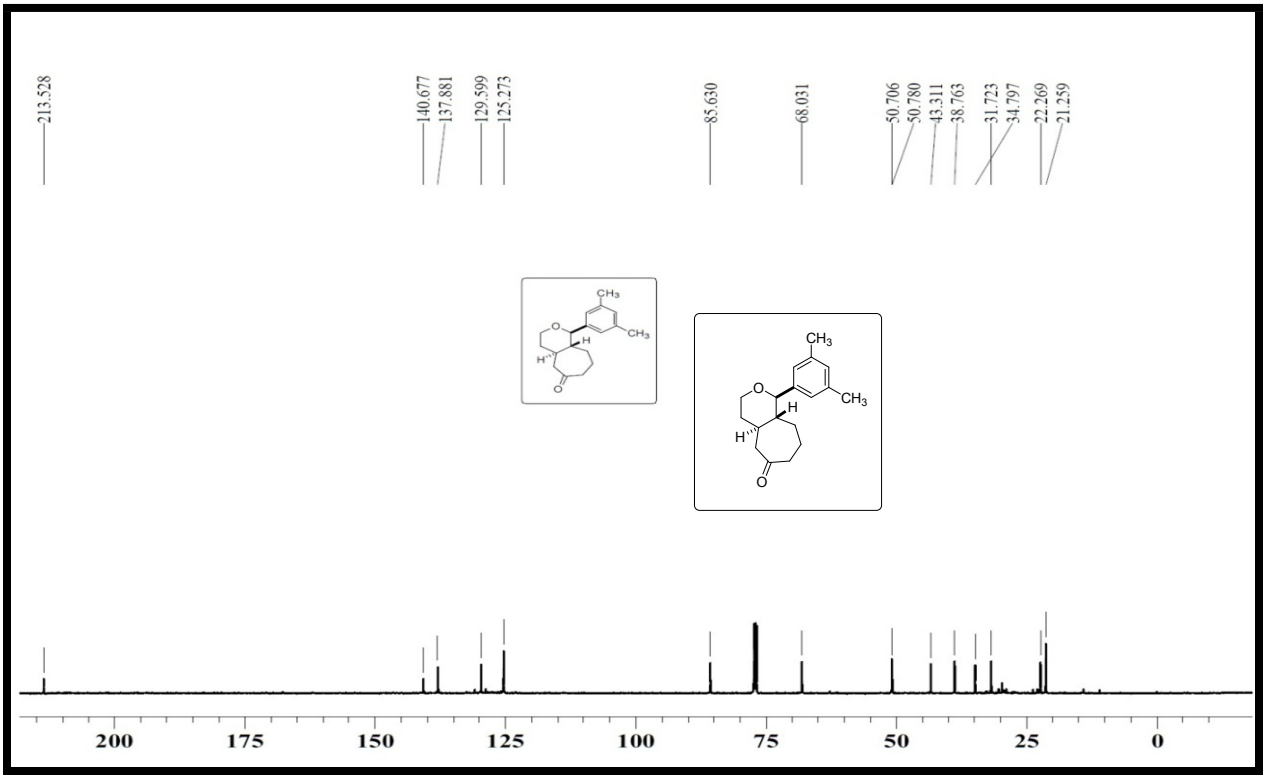
^{13}C NMR spectrum of 3c (Table 2, entry c), 125MHz, $CDCl_3$



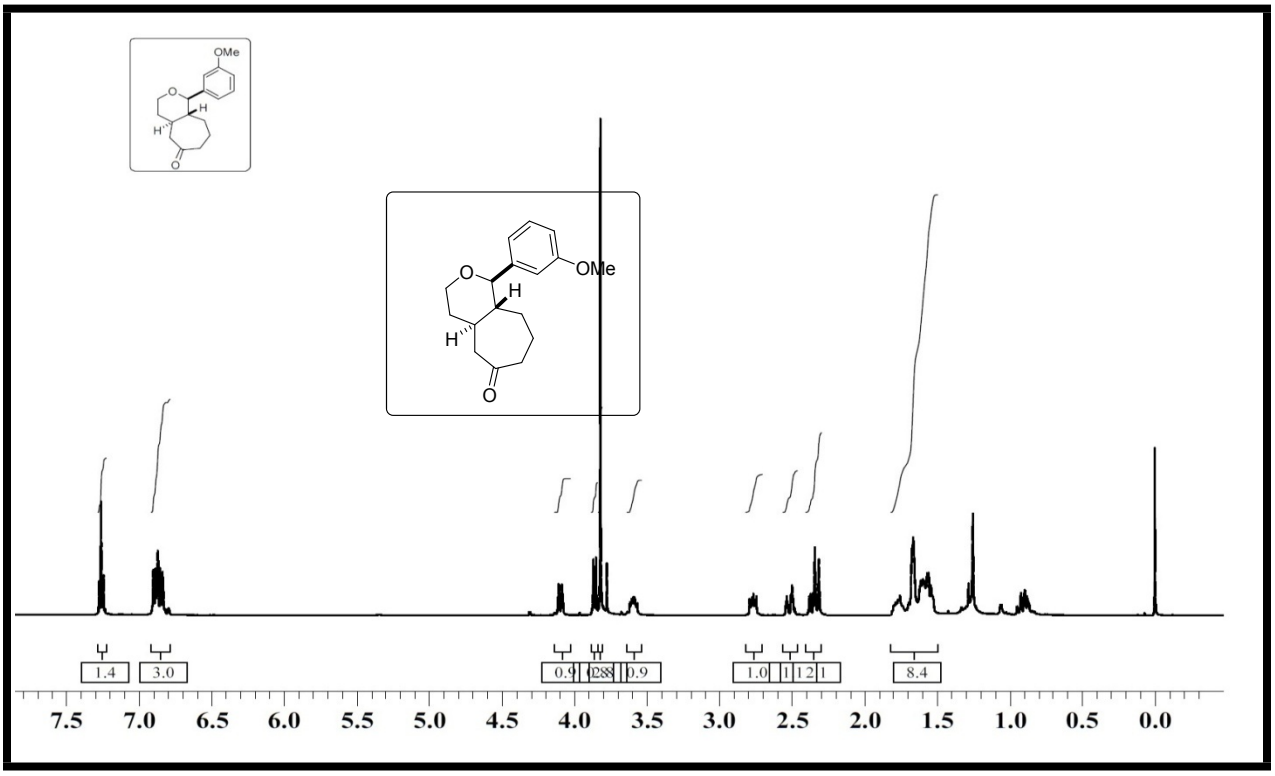
^{1}H NMR spectrum of 3d (Table 2, entry d), 500MHz, $CDCl_3$



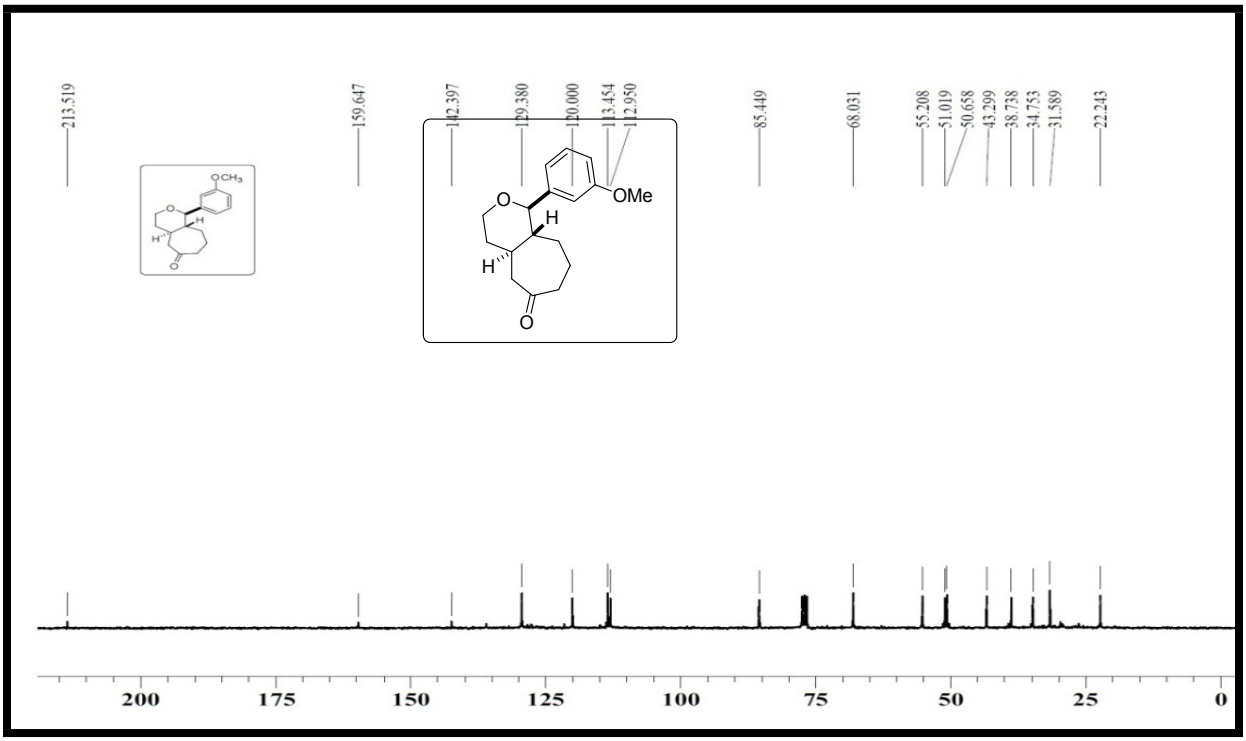
^{13}C NMR spectrum of 3d (Table 2, entry d), 125MHz, $CDCl_3$



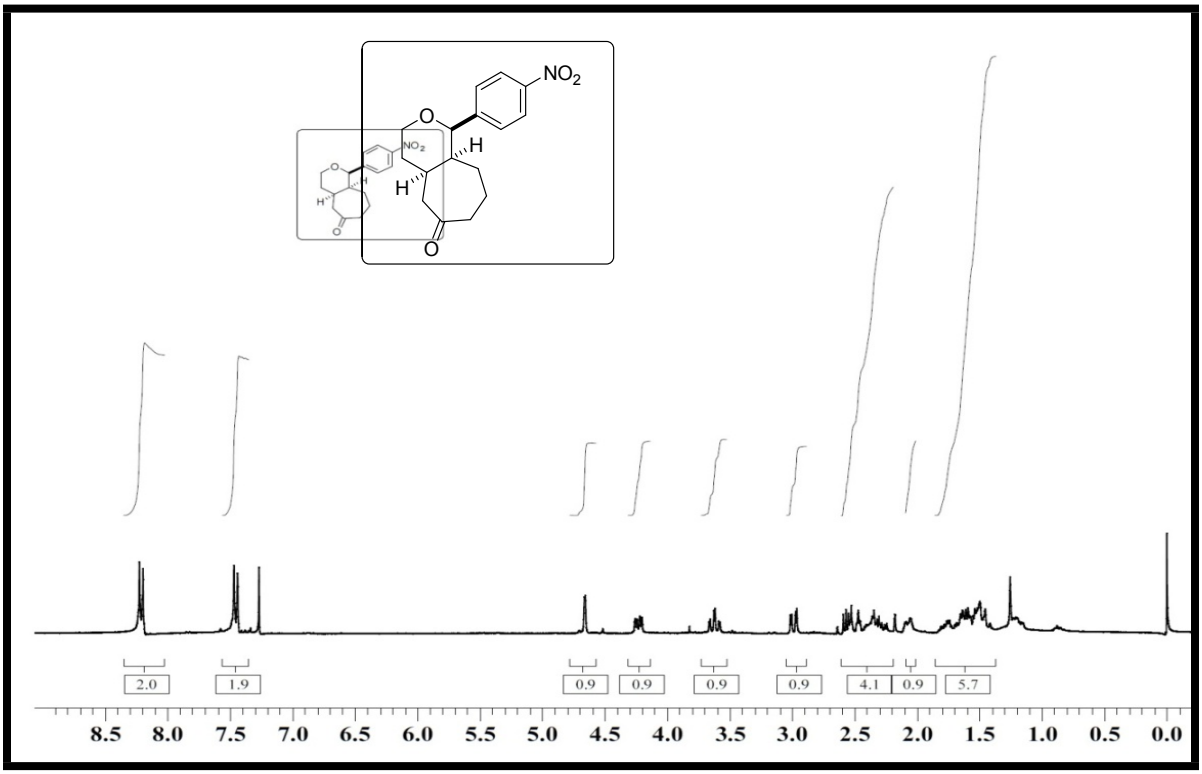
^{1}H NMR spectrum of 3e (Table 2, entry e), 500MHz, $CDCl_3$



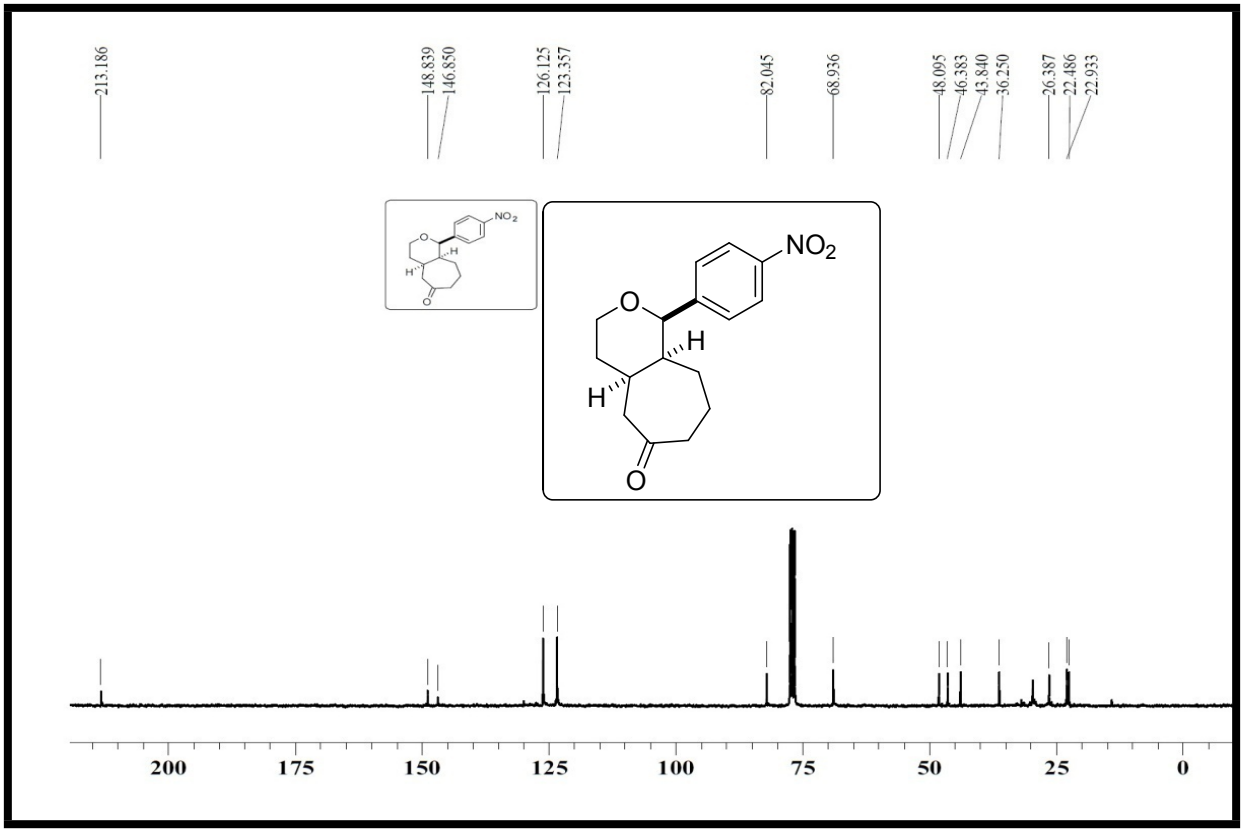
^{13}C NMR spectrum of 3e (Table 2, entry e), 125MHz, $CDCl_3$



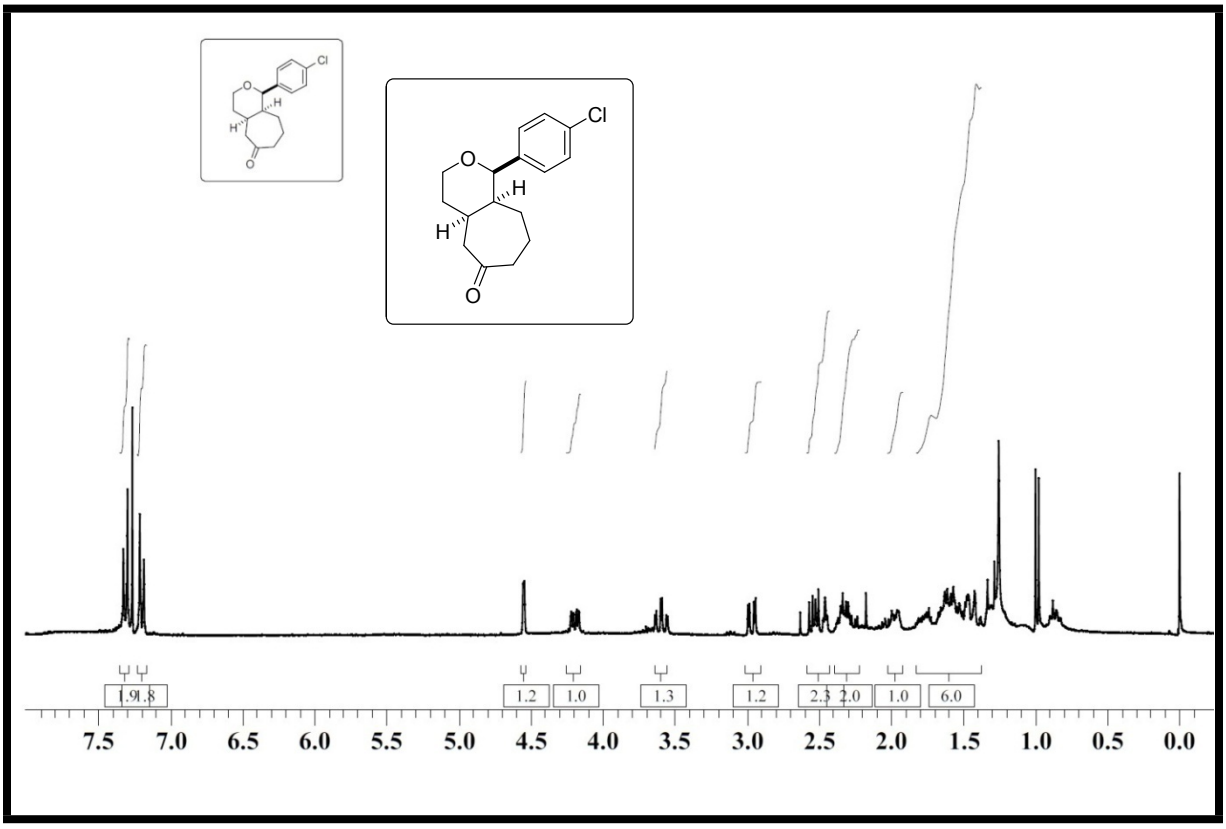
^{1}H NMR spectrum of 4f (Table 2, entry f), 300MHz, $CDCl_3$



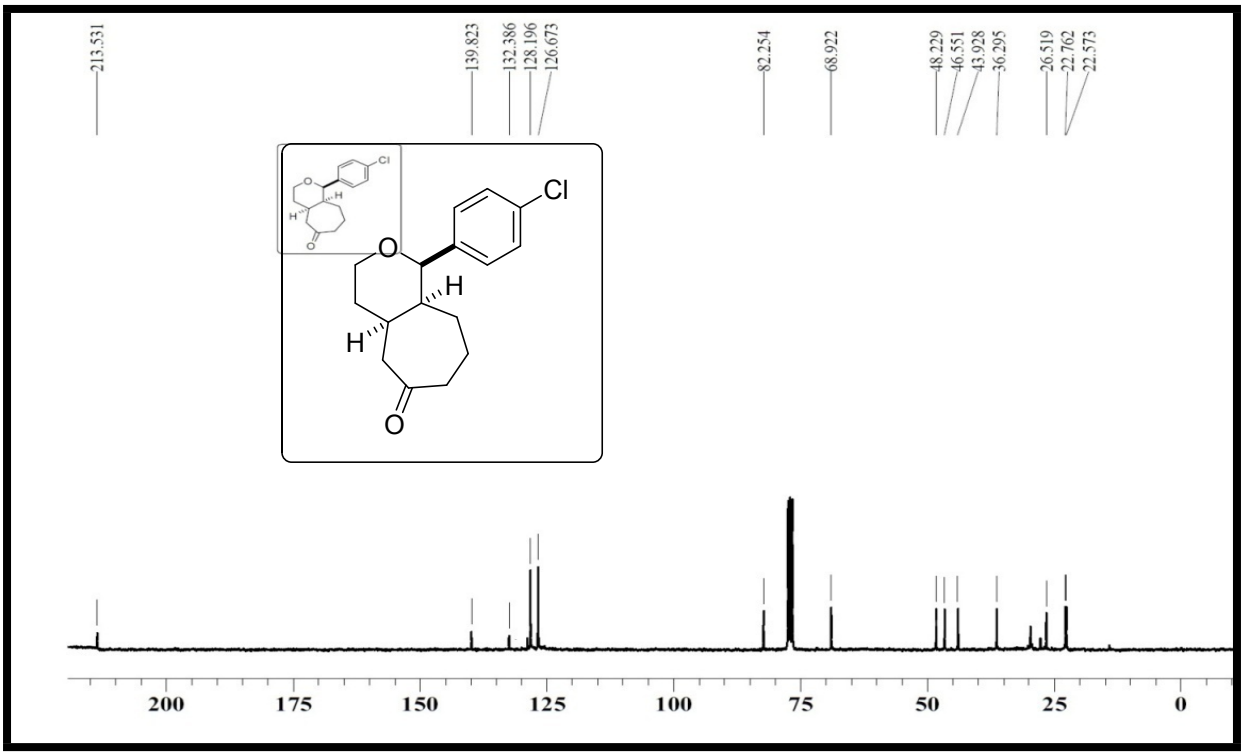
^{13}C NMR spectrum of 4f(Table 2, entry f), 125MHz, $CDCl_3$



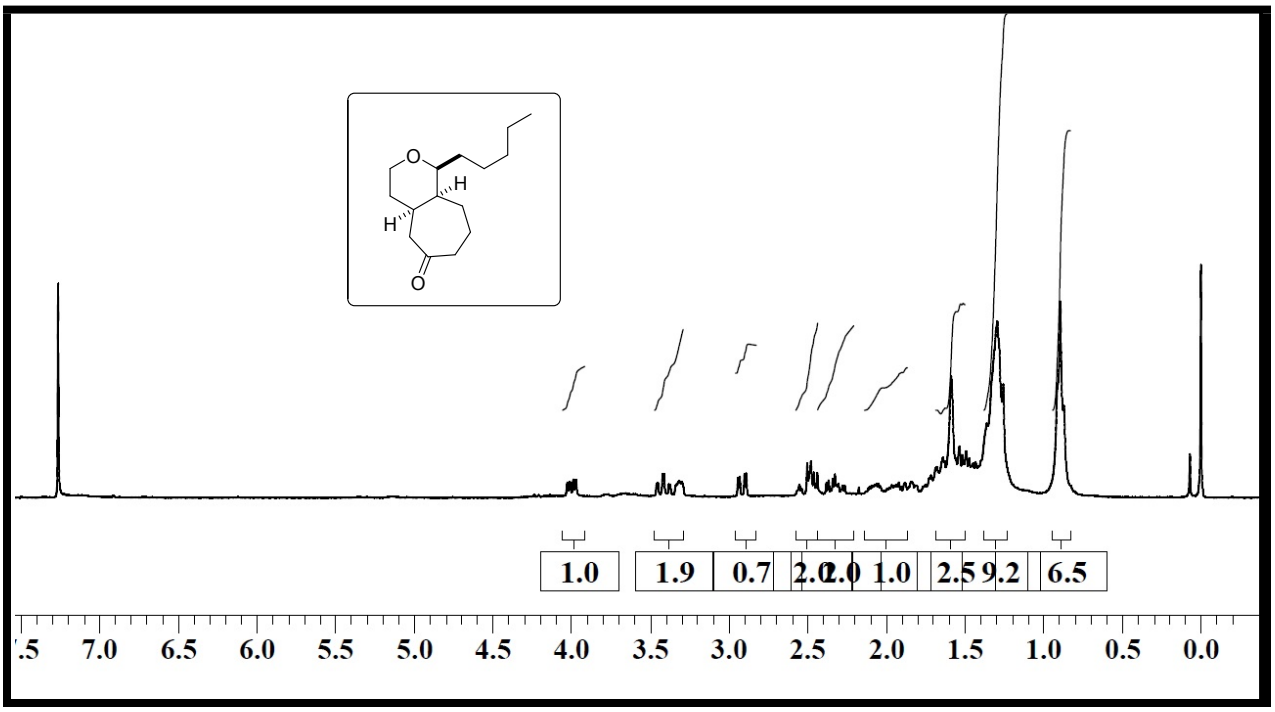
^{1}H NMR spectrum of 4g (Table 2, entry g), 300MHz, $CDCl_3$



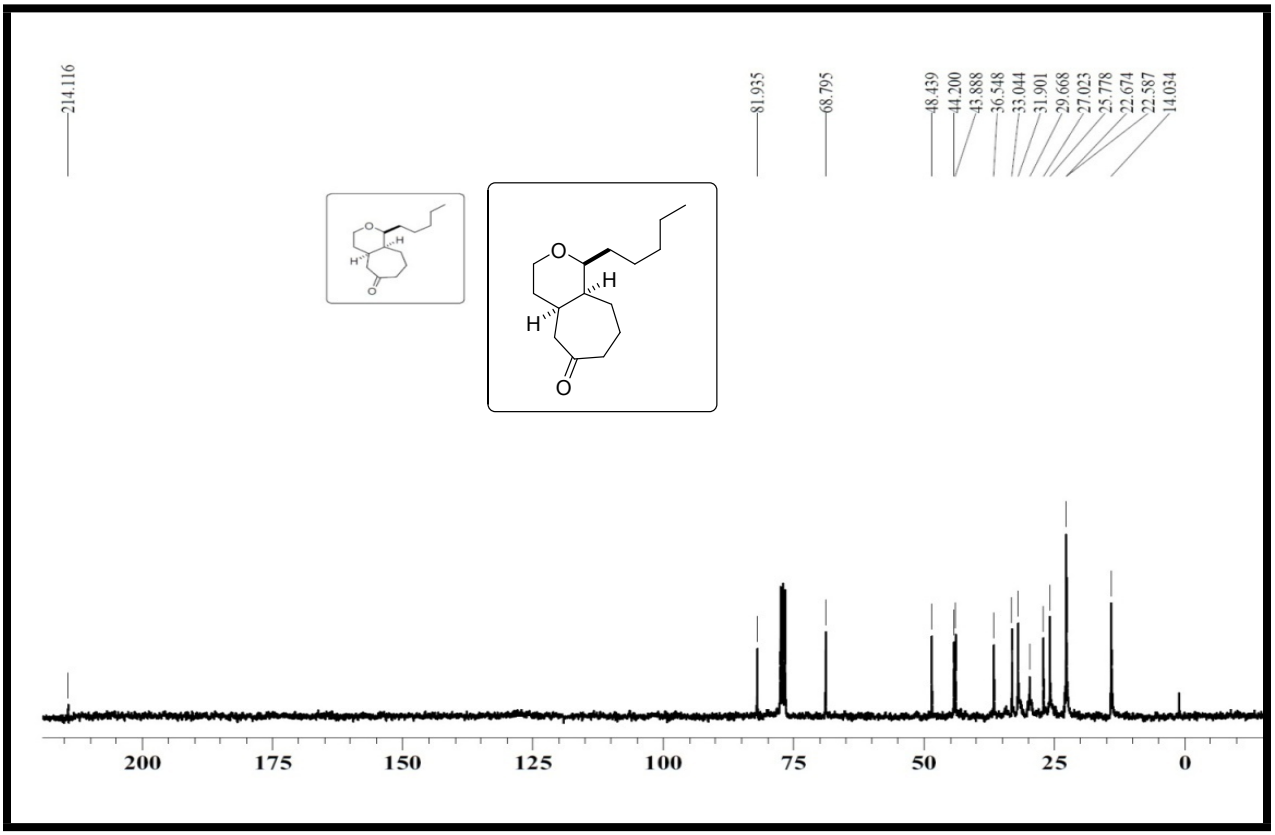
^{13}C NMR spectrum of 4g (Table 2, entry g), 125MHz, $CDCl_3$



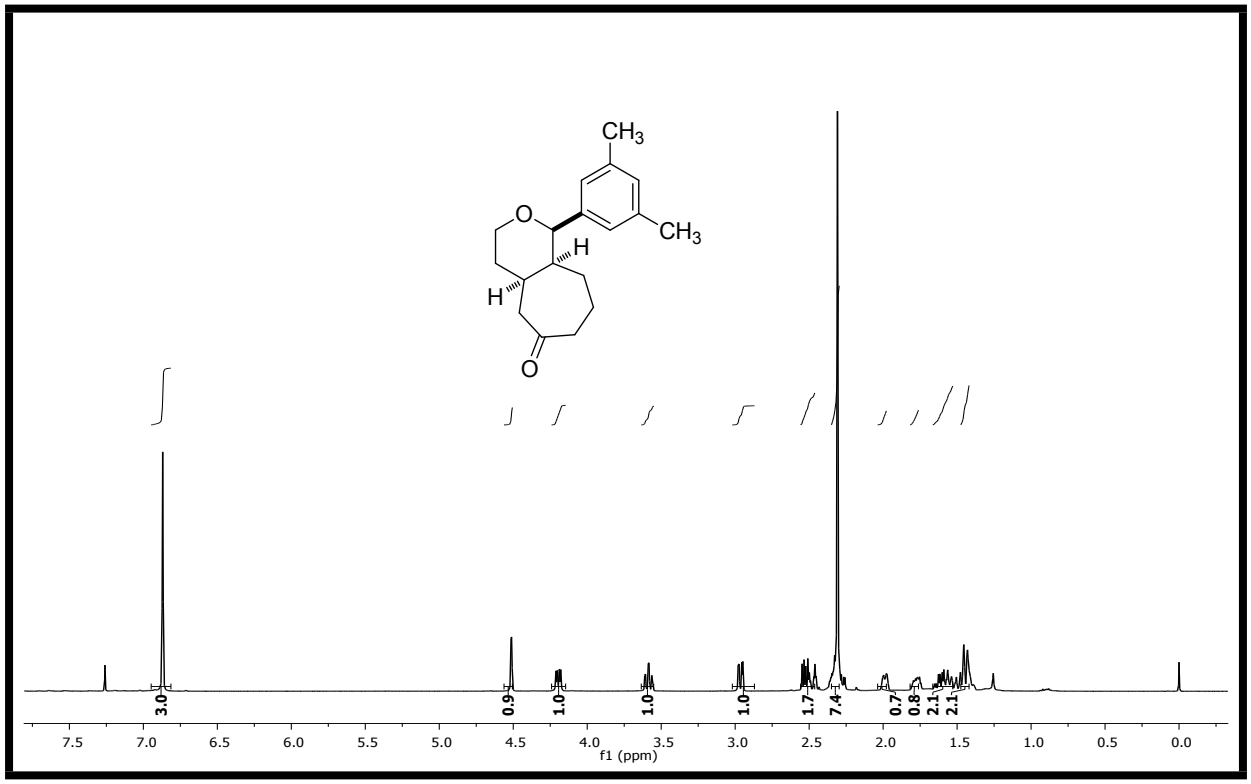
^{1}H NMR spectrum of 4i (Table 2, entry i), 300MHz, $CDCl_3$



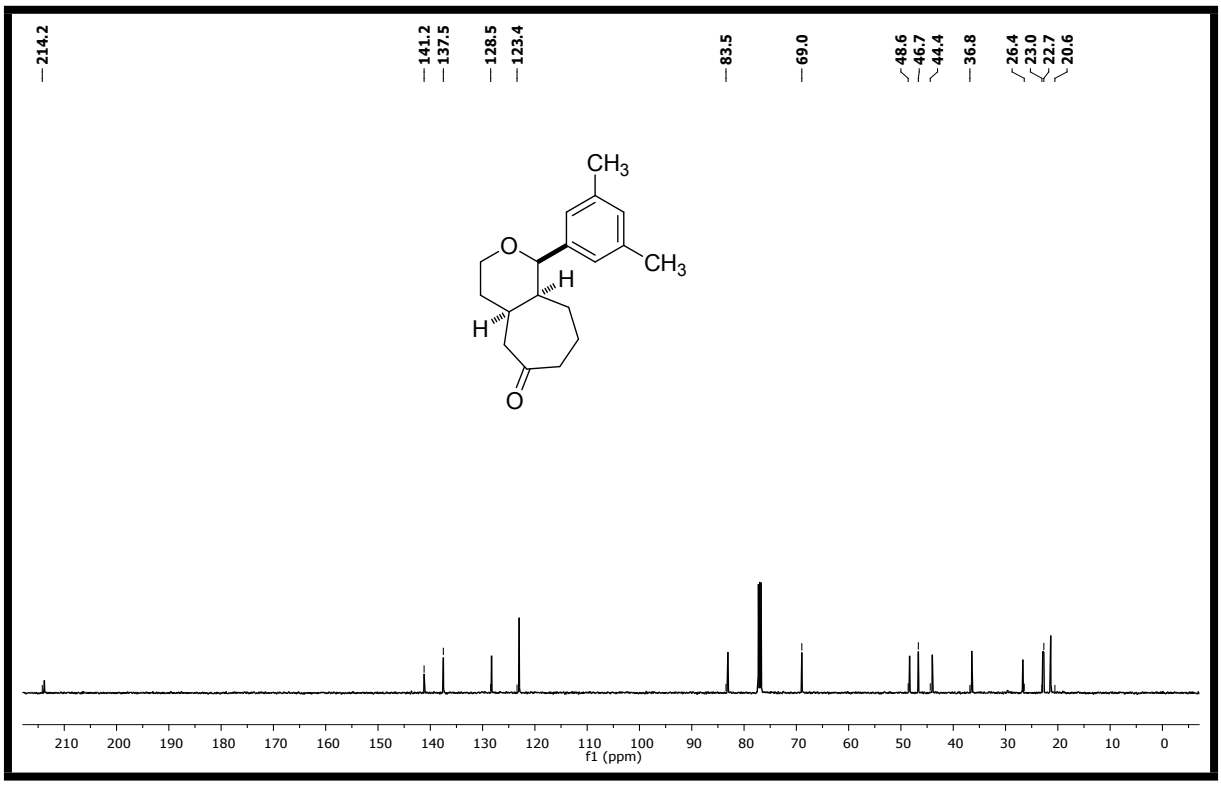
^{13}C NMR spectrum of 4i (Table 2, entry i), 125MHz, $CDCl_3$



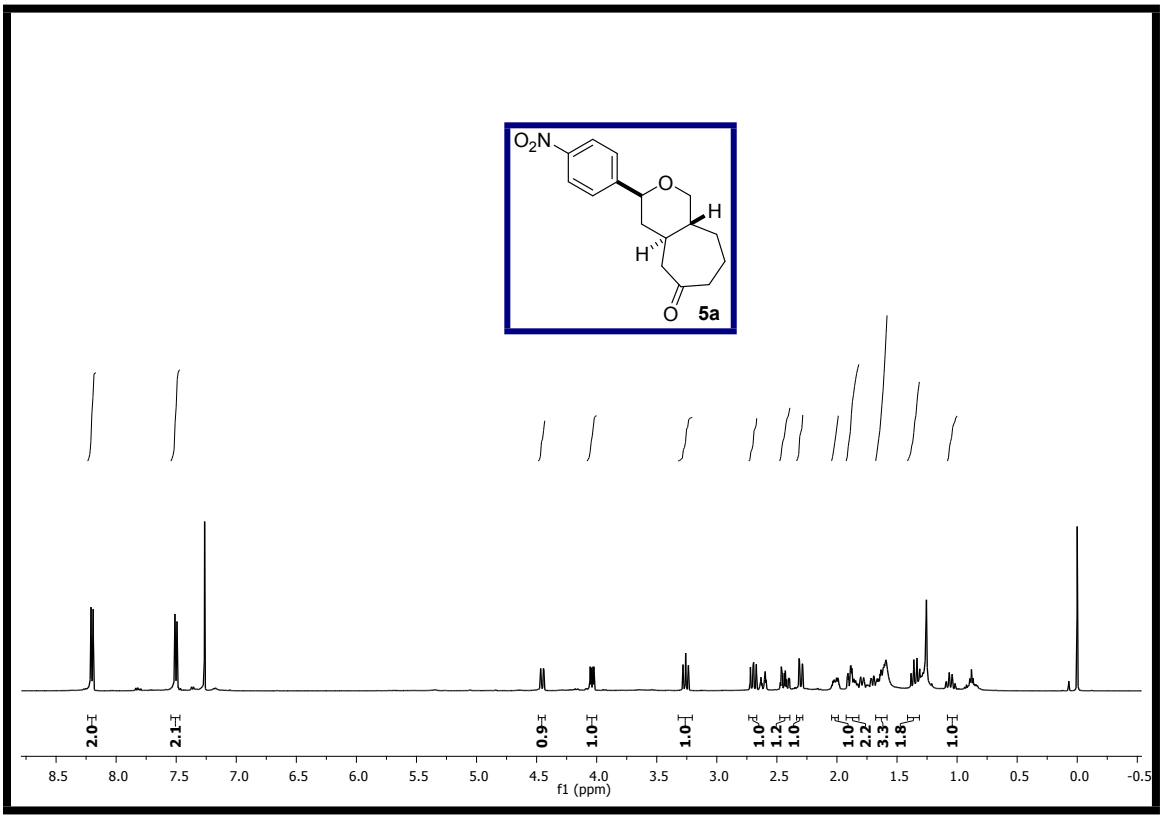
H NMR spectrum of 4h (Table 2, entry h), 300MHz, $CDCl_3$



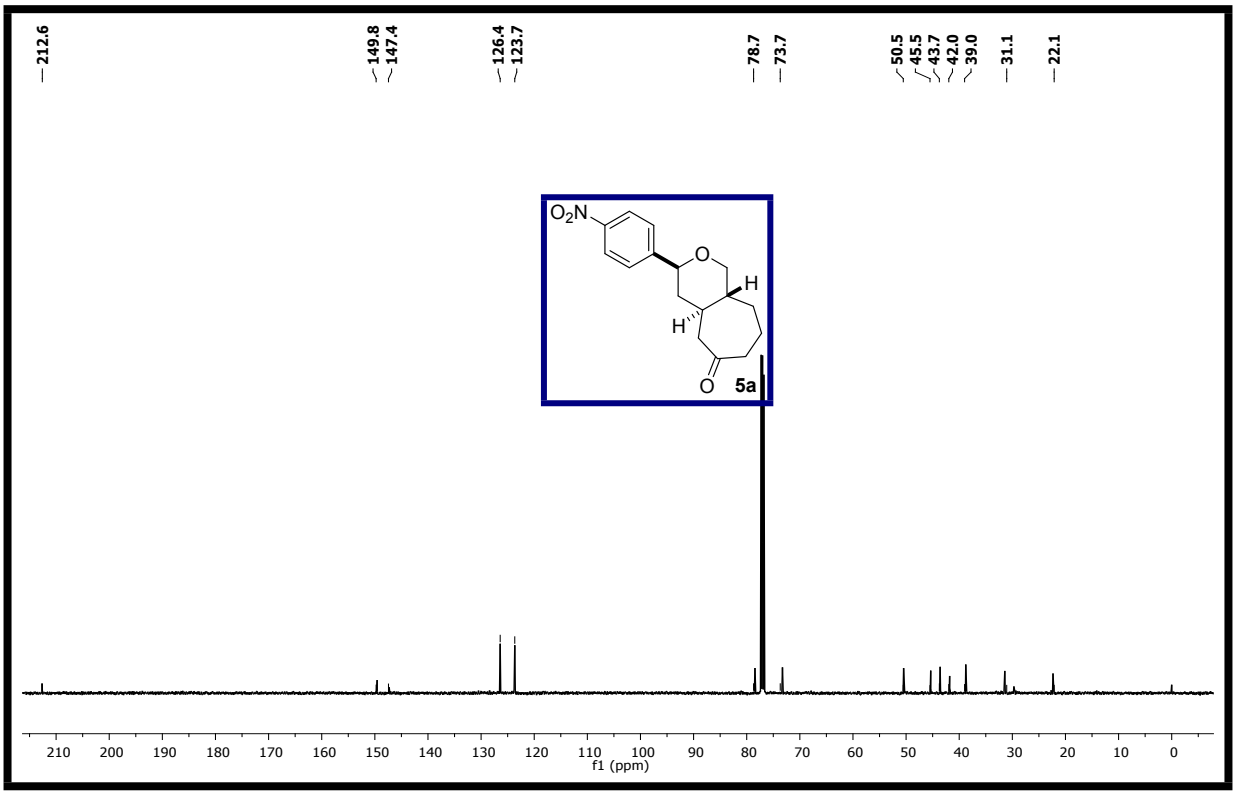
^{13}C NMR spectrum of 4h (Table 2, entry h), 125MHz, $CDCl_3$



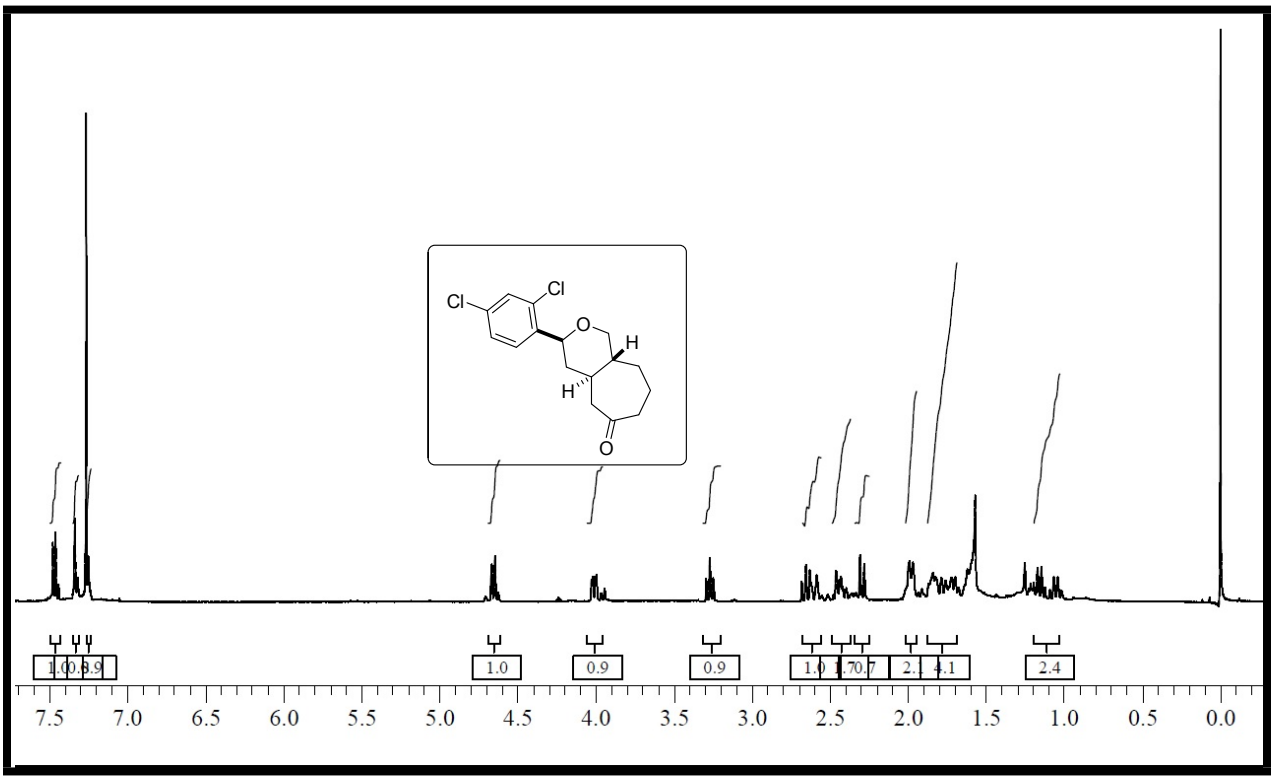
^{1}H NMR spectrum of 5j (Table 2, entry j), 500MHz, $CDCl_3$



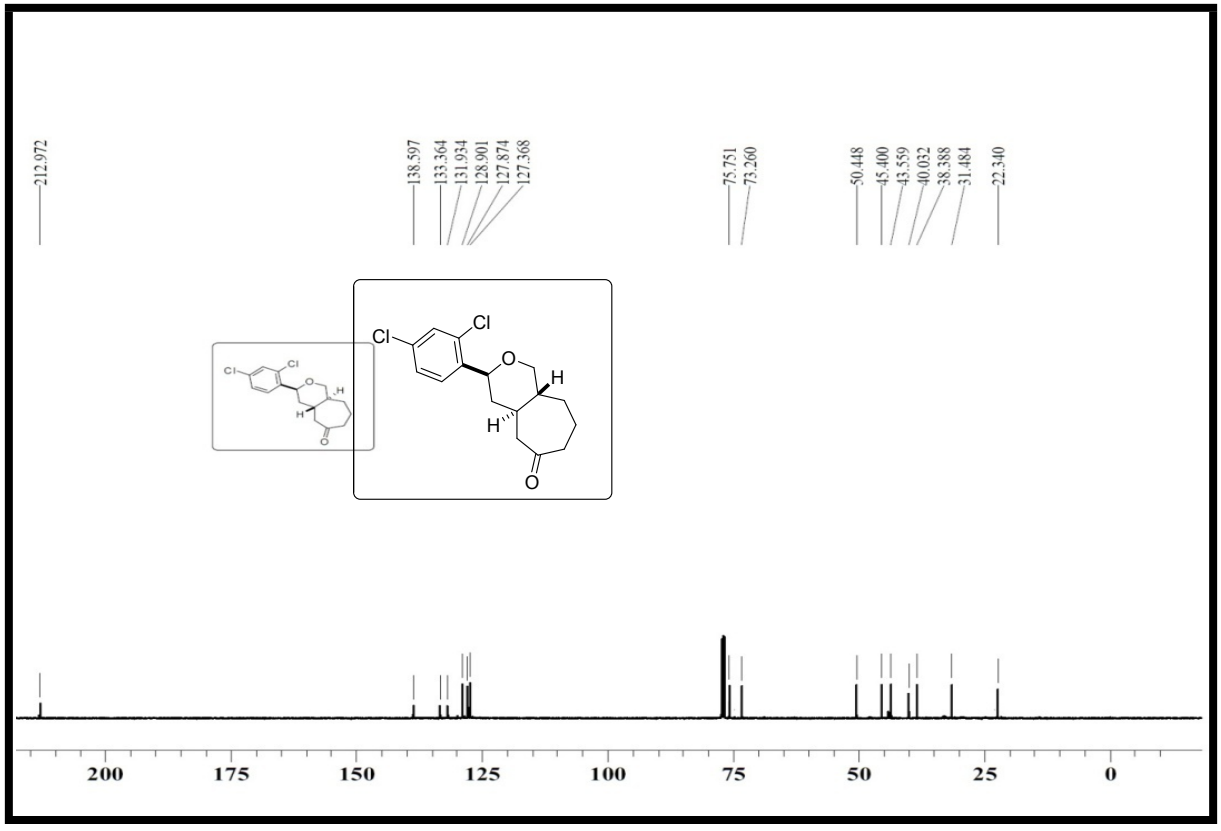
^{13}C NMR spectrum of 5j (Table 2, entry j), 125MHz, $CDCl_3$



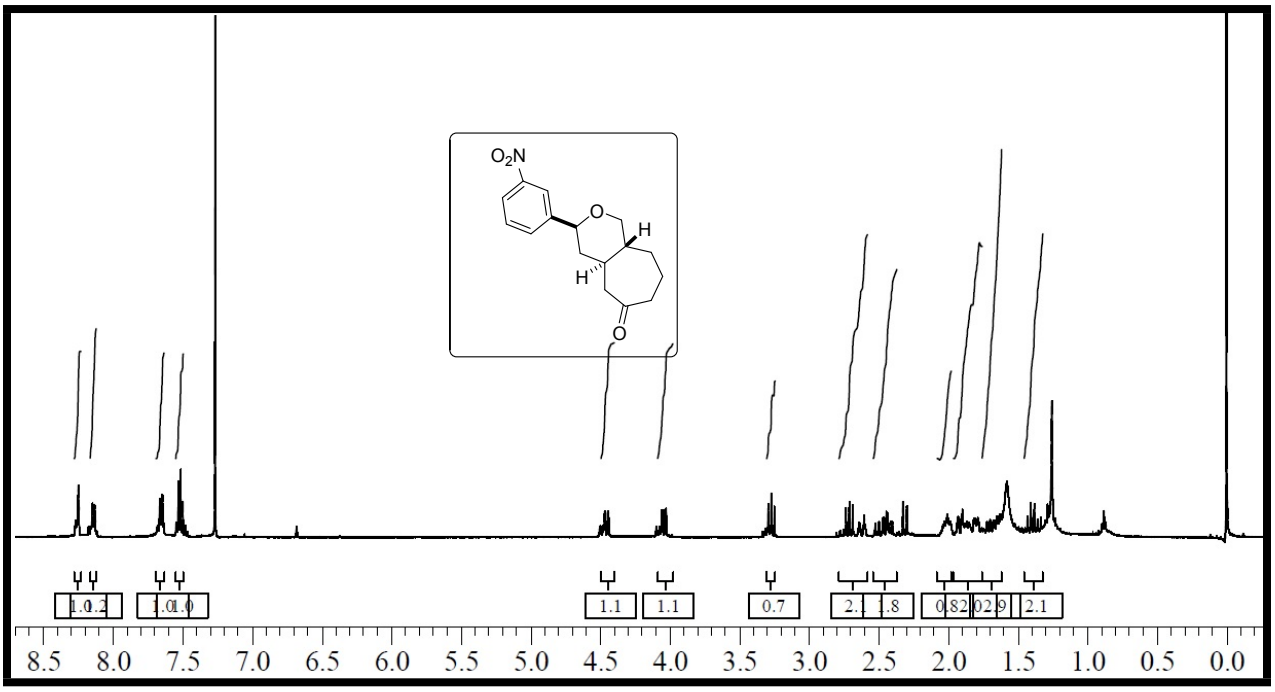
^{1}H NMR spectrum of 5k (Table 2, entry k), 500MHz, $CDCl_3$



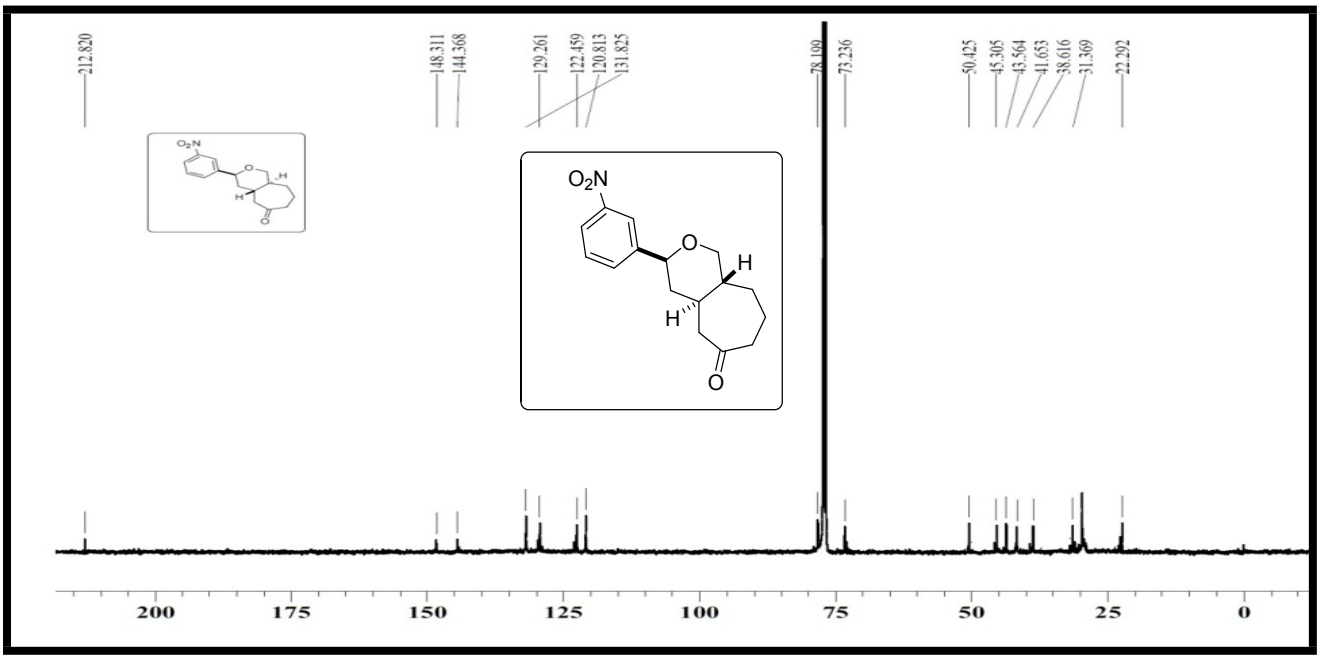
^{13}C NMR spectrum of 5k (Table 2, entry k), 125MHz, $CDCl_3$



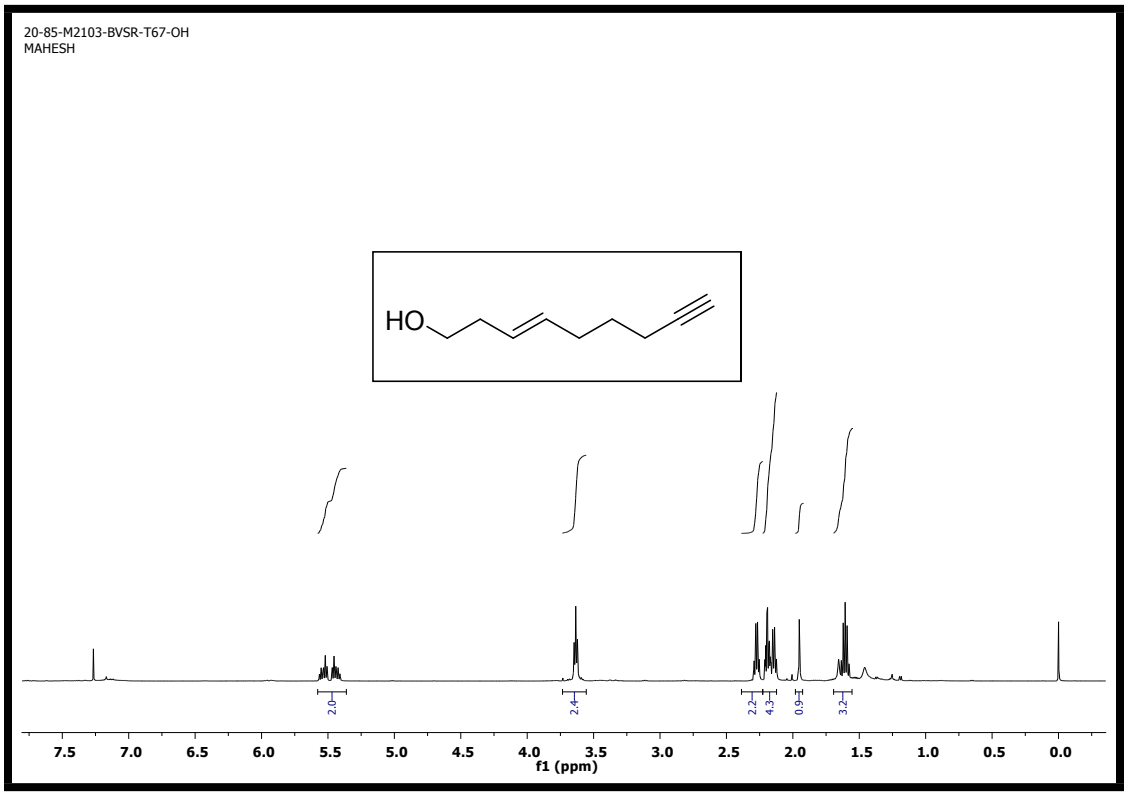
^{1}H NMR spectrum of 5l (Table 2, entry l), 300MHz, $CDCl_3$



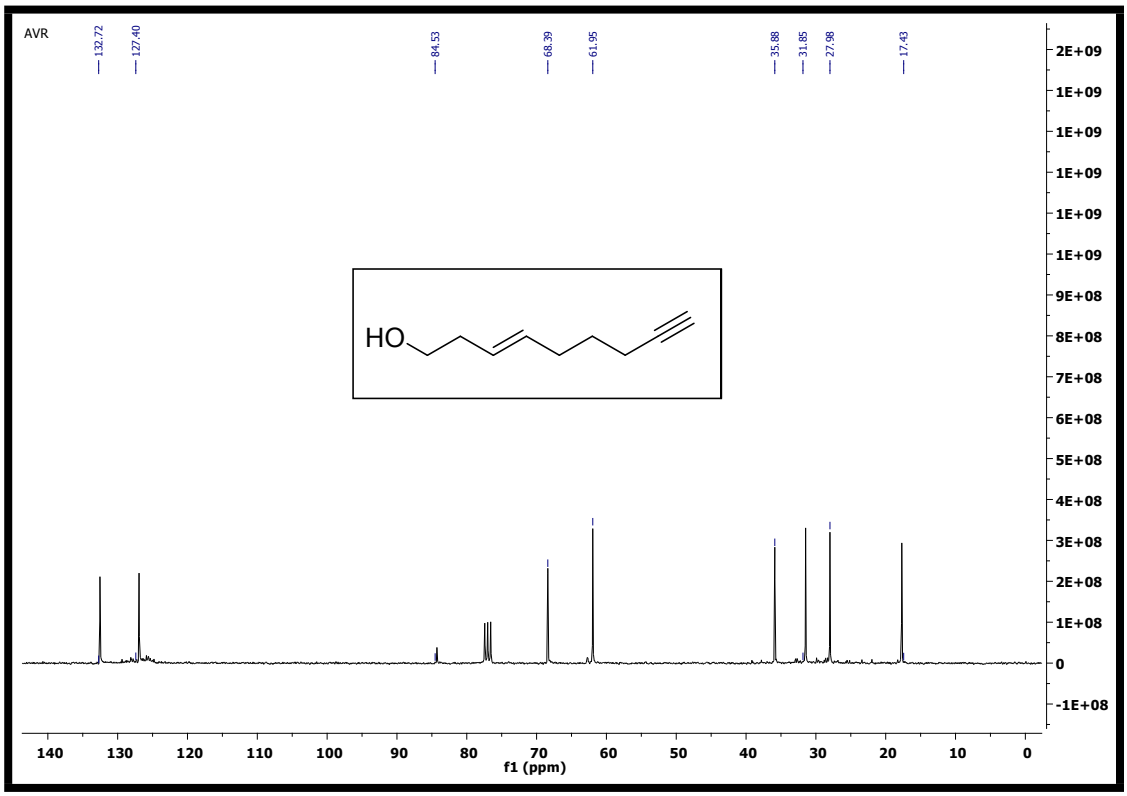
^{1}H NMR spectrum of 5l (Table 2, entry l), 300MHz, $CDCl_3$



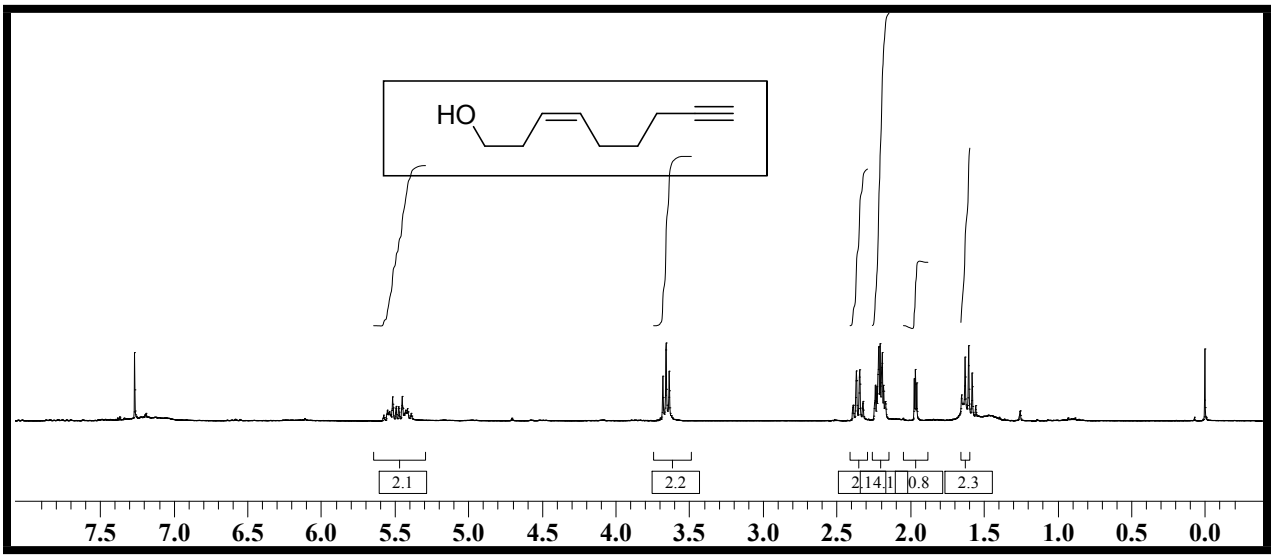
^{1}H NMR spectrum of 1a, 500MHz, $CDCl_3$



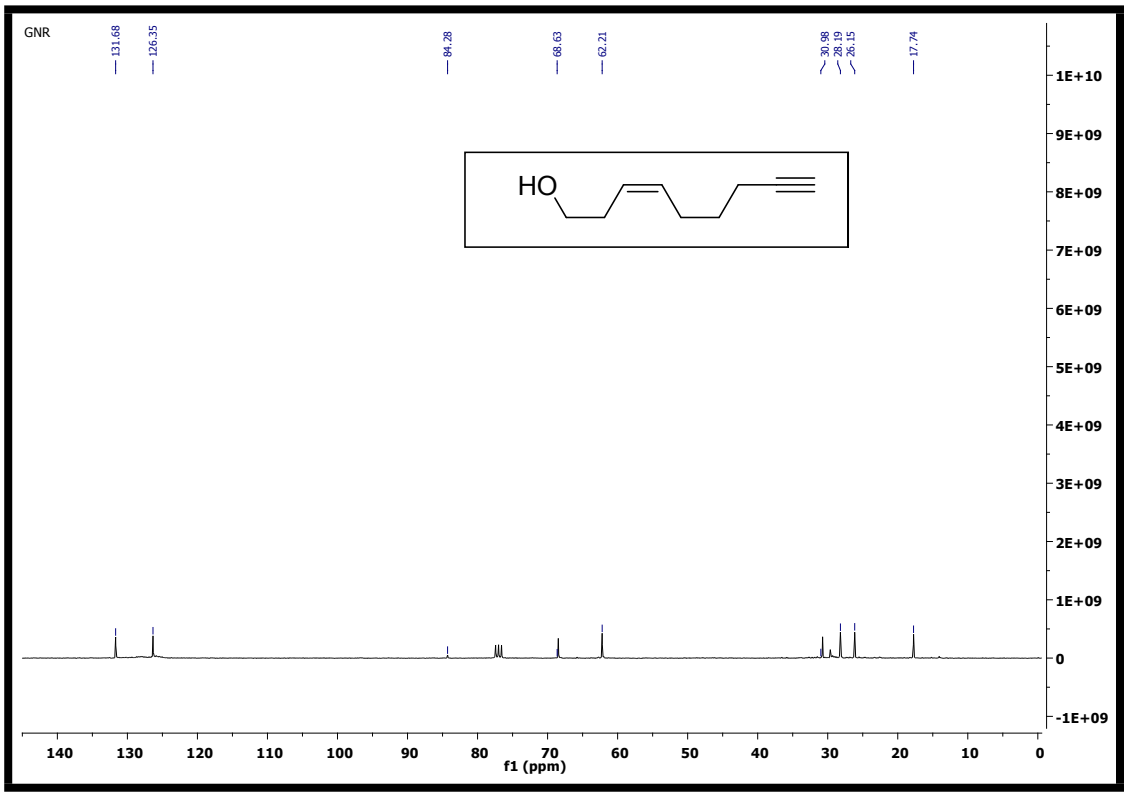
^{13} C NMR spectrum of 1a,125MHz, $CDCl_3$



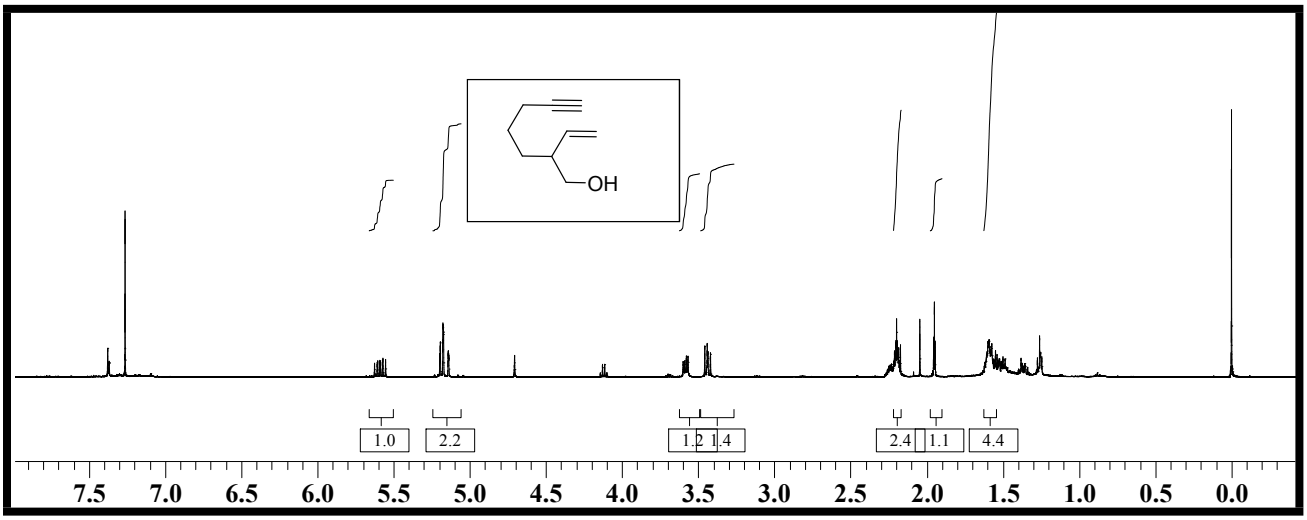
^{1}H NMR spectrum of 1b , 500MHz, $CDCl_3$



^{13} C NMR spectrum of 1b, 125 MHz, $CDCl_3$



^{1}H NMR spectrum of 1c, 500MHz, $CDCl_3$



^{13}C NMR spectrum of 1c (Table 2) 125MHz, $CDCl_3$