

Supplementary Material (ESI)

A novel Prins cascade process for the stereoselective synthesis of oxa-bicycles

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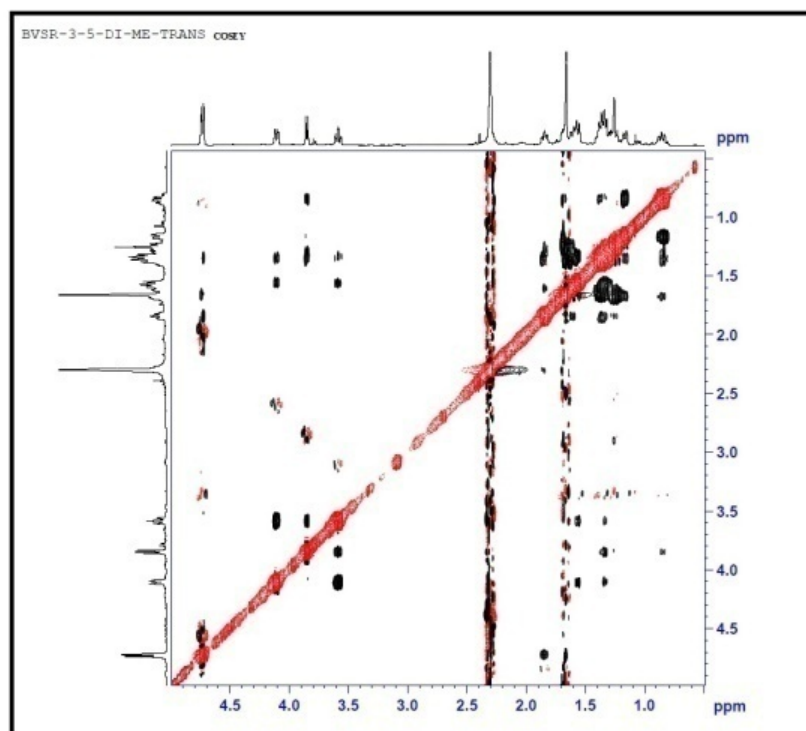
1. ¹H NMR and NOE studies of products **3c, **4h**, **5a** and **6e****

The structures of compounds **3c**, **4h**, **5a** and **6e** 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.

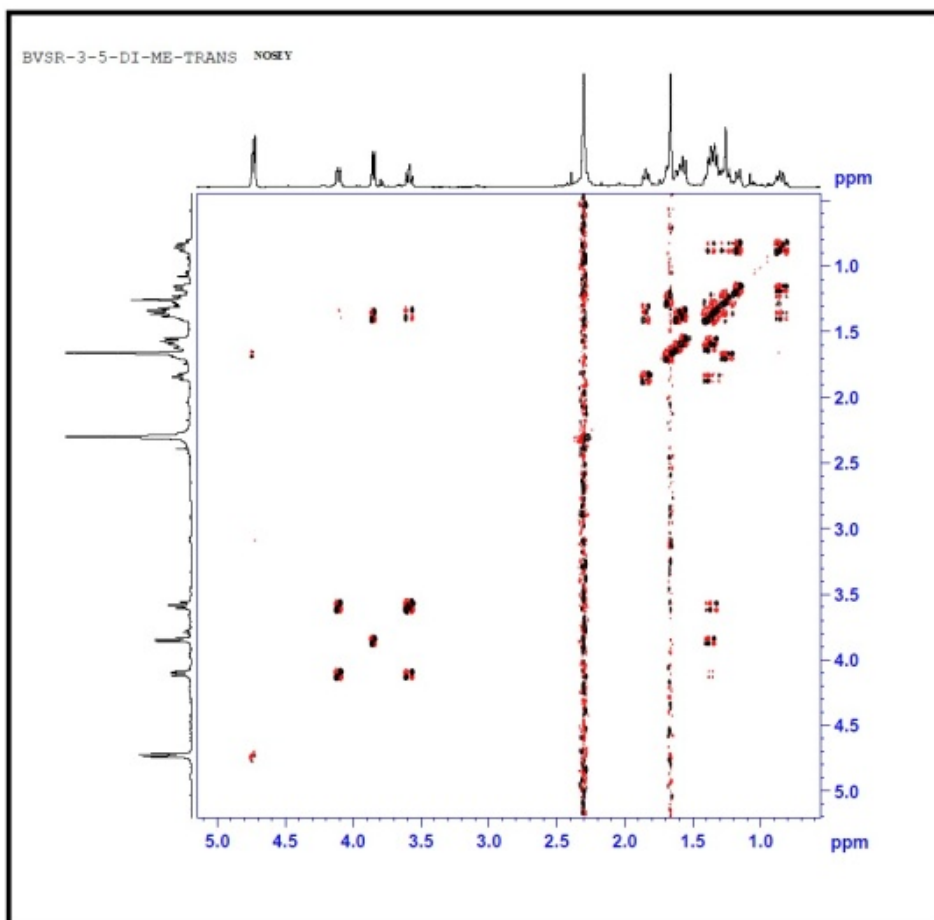
Compound **3c (Table 2, entry 3):**

The distinctive doublet at 3.84 ppm in **3c** due to 1-H was used initiate the assignments with the help of DQF-COSY and NOESY experiments. From the one dimensional ¹H NMR experiments, large coupling constants like: $^3J_{1-H/9-H} = 9.2$, $^3J_{2-H(\text{pro-R})/3-H(\text{pro-S})} = 13.6$, $^3J_{4-H/5-H} = 13.0$, $^3J_{5-H/6-H(\text{pro-R})} = 9.7$, $^3J_{6-H(\text{pro-R})/7-H(\text{pro-R})} = 13.0$, $^3J_{7-H(\text{pro-R})/8-H(\text{pro-S})} = 13.0$, $^3J_{8-H(\text{pro-S})/9-H} = 11.7$ Hz, imply the di-axial disposition of the participating protons, which are consistent with

the structure having both the six-membered rings in chair conformation as shown in the Figure 2. Further support for the proposed structure was derived from small equatorial-equatorial and axial-equatorial couplings like: ${}^3J_{2\text{-H}(\text{pro-S})/3\text{-H}(\text{pro-R})} = 4.5$, ${}^3J_{2\text{-H}(\text{pro-S})/3\text{-H}(\text{pro-S})} = 1.6$, ${}^3J_{2\text{-H}(\text{pro-R})/3\text{-H}(\text{pro-R})} = 2.3$, ${}^3J_{3\text{-H}(\text{pro-R})/4\text{-H}} = 5.3$, ${}^3J_{5\text{-H}/6\text{-H}(\text{pro-S})} = 3.5$, ${}^3J_{6\text{-H}(\text{pro-S})/7\text{-H}(\text{pro-S})} = 3.5$, ${}^3J_{6\text{-H}(\text{pro-R})/7\text{-H}(\text{pro-S})} = 3.5$, ${}^3J_{7\text{-H}(\text{pro-R})/8\text{-H}(\text{pro-R})} = 3.7$, ${}^3J_{7\text{-H}(\text{pro-S})/8\text{-H}(\text{pro-R})} = 3.7$ Hz (some other couplings constants could not be obtained due to spectral overlap and the resulting complexity). Finally the characteristic NOE correlations, 1-H/2-H(pro-R), 1-H/4-H, 1-H/8-H(pro-S), 2-H(pro-R)/4-H, 3-H(pro-S)/5-H, 3-H(pro-S)/9-H, 4-H/6-H(pro-R), 4-H/8-H(pro-S), 5-H/7-H(pro-R) and 6-H(pro-R)/8-H(pro-S) provide emphatic support for the structure, with the two six-membered ring taking ${}^9\text{C}_{2\text{C}}$ and ${}^9\text{C}_{6\text{C}}$ chair conformations. The 1-H/4-H, and 3-H(pro-S)/9-H, imply *anti* conformation of 4-H and 9-H and thus a *trans* fusion of the two six membered rings. The energy minimized structure adequately supports the proposed structure of **3c**.



NOESY (**3c**)



DQF-COSY (**3c**)

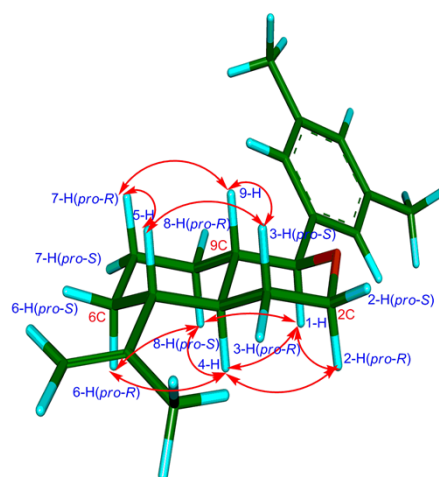
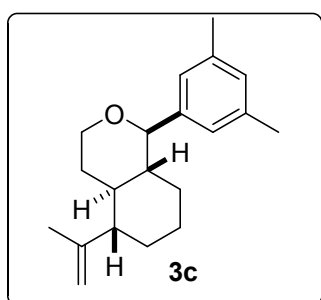
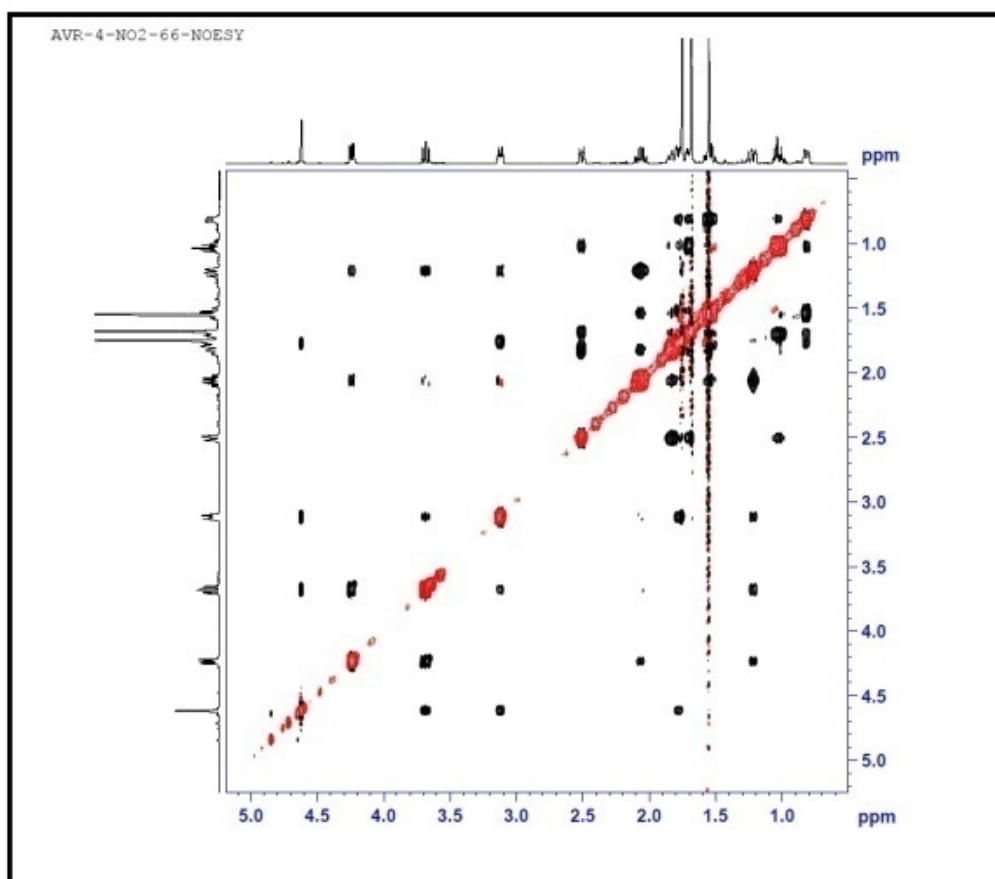


Figure 2. Energy minimized structure and characteristic nOe correlations of **3c**

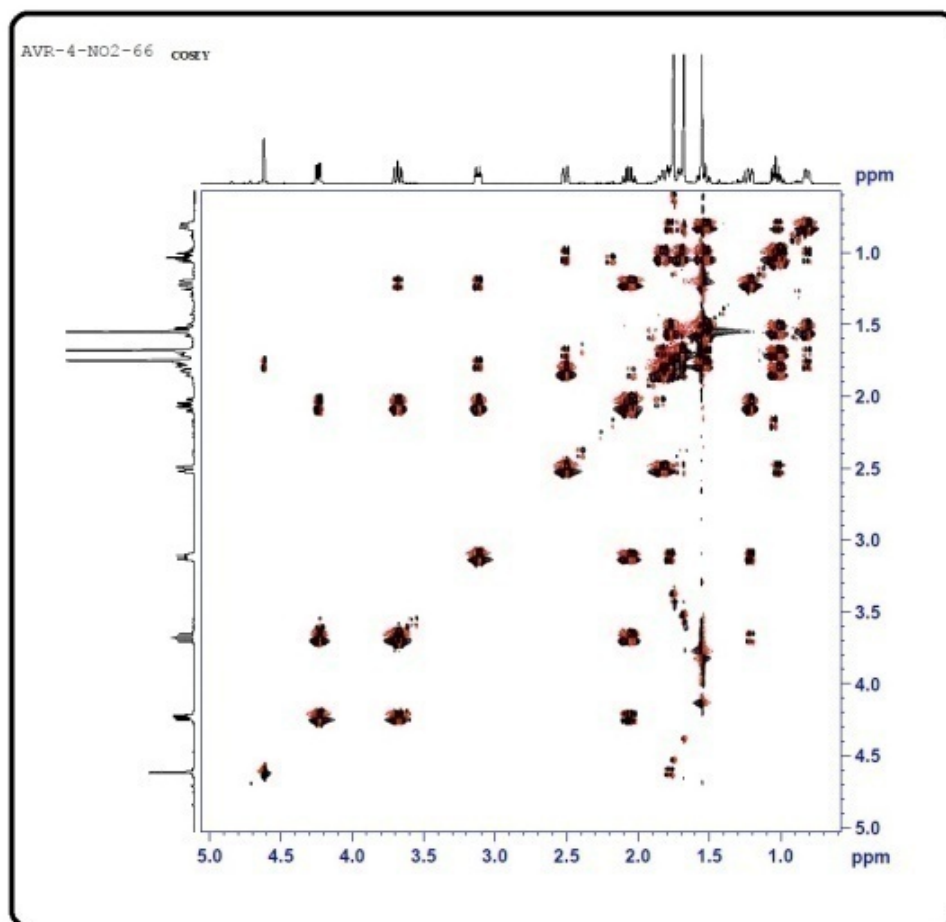
Proton	(δ) ppm	multiplicity	3J values (Hz)
1-H	3.84	d	$^3J_{1-H/9-H} = 9.2$
2-H(pro- <i>S</i>)	4.11	ddd	$^3J_{2-H(\text{pro-}S)/2-H(\text{pro-}R)} = 11.6$ $^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}R)} = 4.5$ $^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}S)} = 1.6$
2-H(pro- <i>R</i>)	3.58	ddd	$^3J_{2-H(\text{pro-}R)/2-H(\text{pro-}S)} = 11.6$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}R)} = 2.3$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}S)} = 13.6$
3-H(pro- <i>R</i>)	1.56	m	$^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}R)} = 4.5$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}R)} = 2.3$ $^3J_{3-H(\text{pro-}S)/3-H(\text{pro-}R)} = 13.4$ $^3J_{3-H(\text{pro-}R)/4-H} = 5.3$
3-H(pro- <i>S</i>)	1.34	m	$^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}S)} = 1.6$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}S)} = 13.6$ $^3J_{3-H(\text{pro-}R)/3-H(\text{pro-}S)} = 13.4$ $^3J_{3-H(\text{pro-}S)/4-H} = *$
4-H	1.28	m	$^3J_{3-H(\text{pro-}S)/4-H} = *$ $^3J_{3-H(\text{pro-}R)/4-H} = 5.3$ $^3J_{4-H/5-H} = 13.0$ $^3J_{4-H/9-H} = *$
5-H	1.84	ddd	$^3J_{5-H/4-H} = 13.0$ $^3J_{5-H/6-H(\text{pro-}S)} = 3.5$ $^3J_{5-H/6-H(\text{pro-}R)} = 9.7$
6-H(pro- <i>S</i>)	1.61	m	$^3J_{5-H/6-H(\text{pro-}S)} = 3.5$ $^3J_{6-H(\text{pro-}R)/6-H(\text{pro-}S)} = 13.0$ $^3J_{6-H(\text{pro-}S)/7-H(\text{pro-}S)} = 3.5$ $^3J_{6-H(\text{pro-}S)/7-H(\text{pro-}R)} = 3.6$ $^3J_{6-H(\text{pro-}S)/10-H} = 1.6$
6-H(pro- <i>R</i>)	1.37	tdd	$^3J_{5-H/6-H(\text{pro-}R)} = 9.7$ $^3J_{6-H(\text{pro-}S)/6-H(\text{pro-}R)} = 13.0$ $^3J_{6-H(\text{pro-}R)/7-H(\text{pro-}S)} = 3.5$ $^3J_{6-H(\text{pro-}R)/7-H(\text{pro-}R)} = 13.0$ $^3J_{6-H(\text{pro-}S)/7-H(\text{pro-}S)} = 3.5$
7-H(pro- <i>S</i>)	1.68	m	$^3J_{6-H(\text{pro-}R)/7-H(\text{pro-}S)} = 3.5$ $^3J_{6-H(\text{pro-}S)/7-H(\text{pro-}S)} = 3.5$ $^3J_{7-H(\text{pro-}R)/7-H(\text{pro-}S)} = 13.0$ $^3J_{7-H(\text{pro-}S)/8-H(\text{pro-}S)} = 3.7$ $^3J_{7-H(\text{pro-}S)/8-H(\text{pro-}R)} = 3.7$
7-H(pro- <i>R</i>)	1.23	qt	$^3J_{6-H(\text{pro-}S)/7-H(\text{pro-}R)} = 3.6$ $^3J_{6-H(\text{pro-}R)/7-H(\text{pro-}R)} = 13.0$ $^3J_{7-H(\text{pro-}S)/7-H(\text{pro-}R)} = 13.0$ $^3J_{7-H(\text{pro-}R)/8-H(\text{pro-}R)} = 3.7$ $^3J_{7-H(\text{pro-}R)/8-H(\text{pro-}S)} = 13.0$
8-H(pro- <i>R</i>)	1.16	dq	$^3J_{7-H(\text{pro-}R)/8-H(\text{pro-}R)} = 3.7$ $^3J_{7-H(\text{pro-}S)/8-H(\text{pro-}R)} = 3.7$ $^3J_{8-H(\text{pro-}S)/8-H(\text{pro-}R)} = 12.8$ $^3J_{8-H(\text{pro-}R)/9-H} = 3.7$
8-H(pro- <i>S</i>)	0.84	m	$^3J_{7-H(\text{pro-}R)/8-H(\text{pro-}S)} = 3.7$ $^3J_{7-H(\text{pro-}S)/8-H(\text{pro-}R)} = 12.8$ $^3J_{8-H(\text{pro-}S)/8-H(\text{pro-}R)} = 12.8$ $^3J_{8-H(\text{pro-}S)/9-H} = 11.7$
9-H	1.36	m	$^3J_{4-H/9-H} = *$ $^3J_{8-H(\text{pro-}S)/9-H} = 11.7$ $^3J_{8-H(\text{pro-}R)/9-H} = 3.7$

Compound 4h (Table 2, entry 8):

The doublet at 4.62 ppm in **4h** due to 1-H is unique and was utilized to make the assignments with the help of DQF-COSY and NOESY experiments. From the one dimensional ^1H NMR experiments, several large diaxial couplings like: $^3J_{2\text{-H}(\text{pro-S})/3\text{-H}(\text{pro-R})}=12.8$, $^3J_{3\text{-H}(\text{pro-R})/4\text{-H}}=12.8$, $^3J_{7\text{-H}(\text{pro-S})/8\text{-H}}=13.3$ are observed suggesting their chair conformations. Small couplings like: $^3J_{1\text{-H}/8\text{-H}}=2.8$, $^3J_{2\text{-H}(\text{pro-R})/3\text{-H}(\text{pro-S})}=1.2$, $^3J_{2\text{-H}(\text{pro-R})/3\text{-H}(\text{pro-R})}=5.2$, $^3J_{2\text{-H}(\text{pro-S})/3\text{-H}(\text{pro-S})}=2.6$, $^3J_{3\text{-H}(\text{pro-S})/4\text{-H}}=4.9$, $^3J_{4\text{-H}/8\text{-H}}=4.9$, $^3J_{5\text{-H}(\text{pro-S})/6\text{-H}(\text{pro-R})}=3.8$, $^3J_{5\text{-H}(\text{pro-S})/6\text{-H}(\text{pro-S})}=4.3$, $^3J_{6\text{-H}(\text{pro-R})/7\text{-H}(\text{pro-S})}=4.8$ and $^3J_{7\text{-H}(\text{pro-R})/8\text{-H}}=3.8$ Hz, consistent with small equatorial-equatorial and axial-equatorial couplings, support the energy minimized structure in the Figure 3. Spectral overlaps resulting in the complexity in the spectrum does not permit determination of several couplings in the six-membered ring. However, characteristic nOe correlations, 1-H/2-H(pro-S), 1-H/4-H, 2-H(pro-S)/4-H, 3-H(pro-R)/5-H(pro-R), 3-H(pro-R)/7-H(pro-S), 5-H(pro-R)/7-H(pro-R) and 6-H(pro-S)/8-H, provide unequivocal support for the structure, with the two six membered rings taking $^8\text{C}_{2\text{C}}$ and $^5\text{C}_{8\text{C}}$ chair conformations. Small value of $^3J_{4\text{-H}/8\text{-H}}=4.9$ Hz further validate the *cis* fusion of the two six-membered rings.



NOESY(**4h**)



DQF-COSY (**4h**)

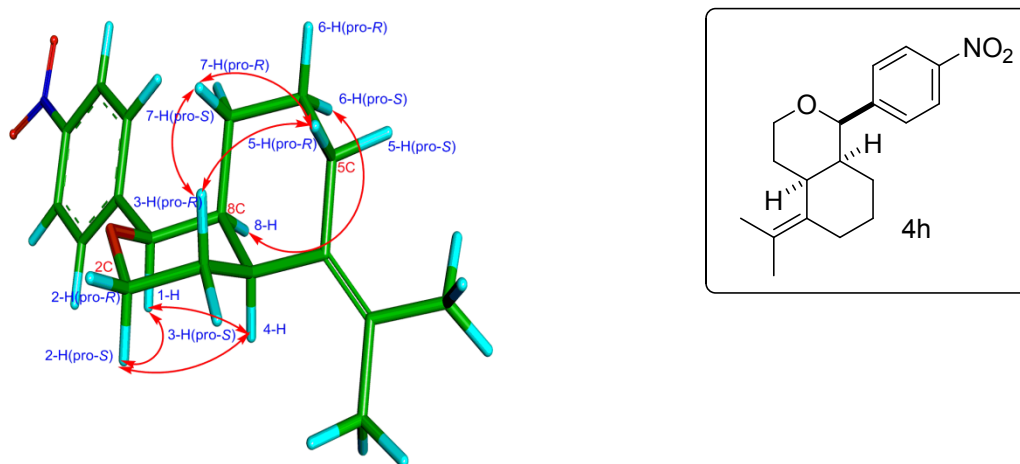


Figure 3. Energy minimized structure and characteristic nOe correlations of **4h**

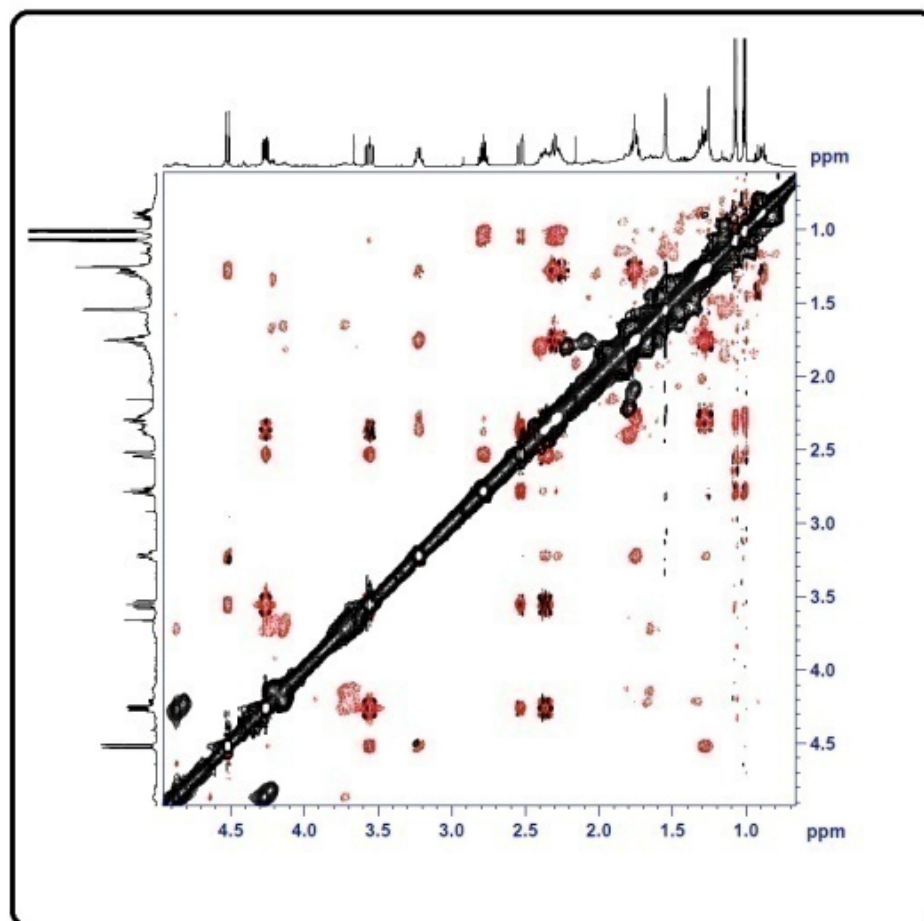
Proton	(δ) ppm	multiplicity	3J values (Hz)
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1-H	4.62	d	${}^3J_{1-H/8-H} = 2.8$
2-H(pro-R)	4.24	ddd	${}^3J_{2-H(\text{pro-S})/2-H(\text{pro-R})} = 11.5$ ${}^3J_{2-H(\text{pro-R})/3-H(\text{pro-S})} = 1.2$ ${}^3J_{2-H(\text{pro-R})/3-H(\text{pro-R})} = 5.2$
2-H(pro-S)	3.68	ddd	${}^3J_{2-H(\text{pro-S})/2-H(\text{pro-R})} = 11.5$ ${}^3J_{2-H(\text{pro-S})/3-H(\text{pro-S})} = 2.6$ ${}^3J_{2-H(\text{pro-S})/3-H(\text{pro-R})} = 12.8$
3-H(pro-S)	1.21	m	${}^3J_{2-H(\text{pro-S})/3-H(\text{pro-S})} = 2.6$ ${}^3J_{2-H(\text{pro-R})/3-H(\text{pro-S})} = 1.2$ ${}^3J_{3-H(\text{pro-R})/3-H(\text{pro-S})} = 12.8$ ${}^3J_{3-H(\text{pro-S})/4-H} = *$
3-H(pro-R)	2.09	qd	${}^3J_{2-H(\text{pro-R})/3-H(\text{pro-R})} = 5.2$ ${}^3J_{2-H(\text{pro-S})/3-H(\text{pro-R})} = 12.8$ ${}^3J_{3-H(\text{pro-S})/3-H(\text{pro-R})} = 12.8$ ${}^3J_{3-H(\text{pro-R})/4-H} = 12.8$
4-H	3.12	dt	${}^3J_{3-H(\text{pro-S})/4-H} = 4.9$ ${}^3J_{3-H(\text{pro-R})/4-H} = 12.8$ ${}^3J_{4-H/8-H} = 4.9$ ${}^3J_{4-H/CH_3} = 2.0$
5-H(pro-S)	2.51	m	${}^3J_{5-H(\text{pro-R})/5-H(\text{pro-S})} = 14.7$ ${}^3J_{5-H(\text{pro-S})/6-H(\text{pro-R})} = 3.8$ ${}^3J_{5-H(\text{pro-S})/6-H(\text{pro-S})} = 4.3$ ${}^3J_{5-H(\text{pro-S})/CH_3} = 1.0$
5-H(pro-R)	1.84	m	${}^3J_{5-H(\text{pro-R})/6-H(\text{pro-R})} = *$ ${}^3J_{5-H(\text{pro-R})/6-H(\text{pro-S})} = *$ ${}^3J_{5-H(\text{pro-R})/5-H(\text{pro-S})} = 14.7$
6-H(pro-R)	1.70	m	${}^3J_{5-H(\text{pro-S})/6-H(\text{pro-R})} = 3.8$ ${}^3J_{5-H(\text{pro-R})/6-H(\text{pro-R})} = *$ ${}^3J_{6-H/6-H(\text{pro-R})} = 13.3$ ${}^3J_{6-H(\text{pro-R})/7-H(\text{pro-S})} = 4.8$ ${}^3J_{6-H(\text{pro-R})/7-H(\text{pro-R})} = *$
6-H(pro-S)	1.02	qt	${}^3J_{6-H(\text{pro-S})/5-H} = 3.8$ ${}^3J_{6-H(\text{pro-S})/5-H'} = 13.3$ ${}^3J_{6-H(\text{pro-S})/6-H(\text{pro-R})} = 13.3$ ${}^3J_{6-H(\text{pro-S})/7-H(\text{pro-R})} = 3.8$ ${}^3J_{6-H(\text{pro-S})/7-H(\text{pro-S})} = 13.3$
7-H(pro-S)	1.52	m	${}^3J_{6-H(\text{pro-S})/7-H(\text{pro-S})} = 13.3$ ${}^3J_{6-H(\text{pro-R})/7-H(\text{pro-S})} = 4.8$ ${}^3J_{7-H(\text{pro-R})/7-H(\text{pro-S})} = 13.3$ ${}^3J_{7-H(\text{pro-S})/8-H} = 13.3$
7-H(pro-R)	0.81	m	${}^3J_{6-H(\text{pro-S})/7-H(\text{pro-R})} = 3.8$ ${}^3J_{6-H(\text{pro-R})/7-H(\text{pro-R})} = *$ ${}^3J_{7-H(\text{pro-R})/7-H(\text{pro-S})} = 13.3$ ${}^3J_{7-H(\text{pro-R})/8-H} = 3.8$
8-H	1.78	m	${}^3J_{1-H/8-H} = 2.8$ ${}^3J_{4-H/8-H} = 4.9$ ${}^3J_{7-H(\text{pro-S})/8-H} = 13.3$ ${}^3J_{7-H(\text{pro-R})/8-H} = 3.8$

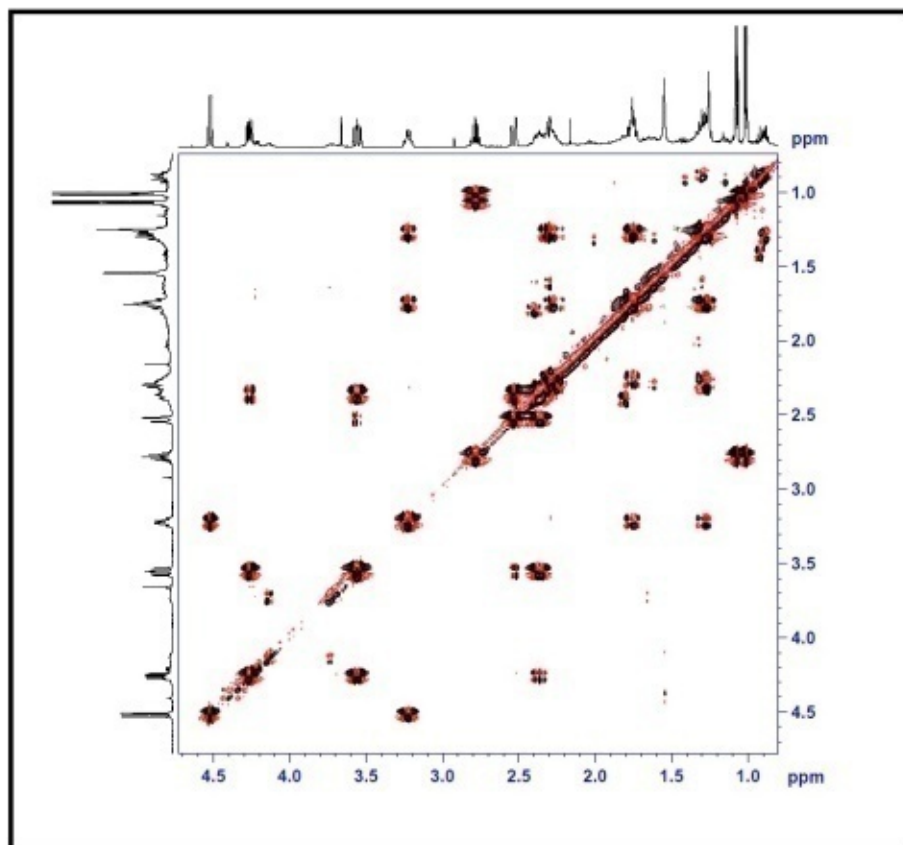
Compound 5a (Table 3, entry 1):

The assignments in **5a** were started with the unique doublet at 4.52 ppm due to 1-H, using DQF-COSY and NOESY experiments. The coupling constants, ${}^3J_{1-H/7-H} = 10.2$, ${}^3J_{2-H(\text{pro-R})/3-H(\text{pro-S})} = 12.6$, ${}^3J_{2-H(\text{pro-S})/3-H(\text{pro-S})} = 5.8$, ${}^3J_{2-H(\text{pro-R})/3-H(\text{pro-R})} = 5.8$, ${}^3J_{2-H(\text{pro-S})/3-H(\text{pro-R})} = 1.0$ Hz along with the nOe correlations 1-H/2-H(pro-R) and 3-H(pro-S)/7-H provide ample

support for a ${}^3\text{C}_{1\text{C}}$ chair form for the six-membered ring. The couplings: ${}^3J_{5\text{-H}(\text{pro-S})/6\text{-H}(\text{pro-S})} = 8.4$, ${}^3J_{5\text{-H}(\text{pro-S})/6\text{-H}(\text{pro-R})} = 4.2$, ${}^3J_{5\text{-H}(\text{pro-R})/6\text{-H}(\text{pro-R})} = 2.7$, ${}^3J_{6\text{-H}(\text{pro-S})/7\text{-H}} = 10.2$, ${}^3J_{6\text{-H}(\text{pro-R})/7\text{-H}} = 8.2$ Hz and the nOe correlations, 1-H/6-H(pro-S), and 5-H(pro-S)/7-H, justify an envelop conformation in the five-membered cyclopentene ring. The energy minimized structure is shown in Figure 4.



DQF-COSY(**5a**)



NOESY (**5a**)

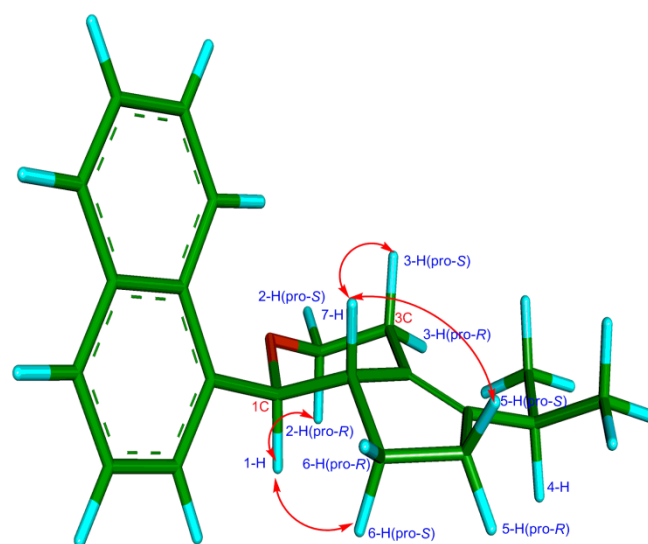
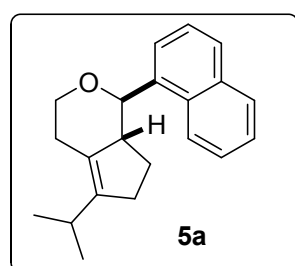
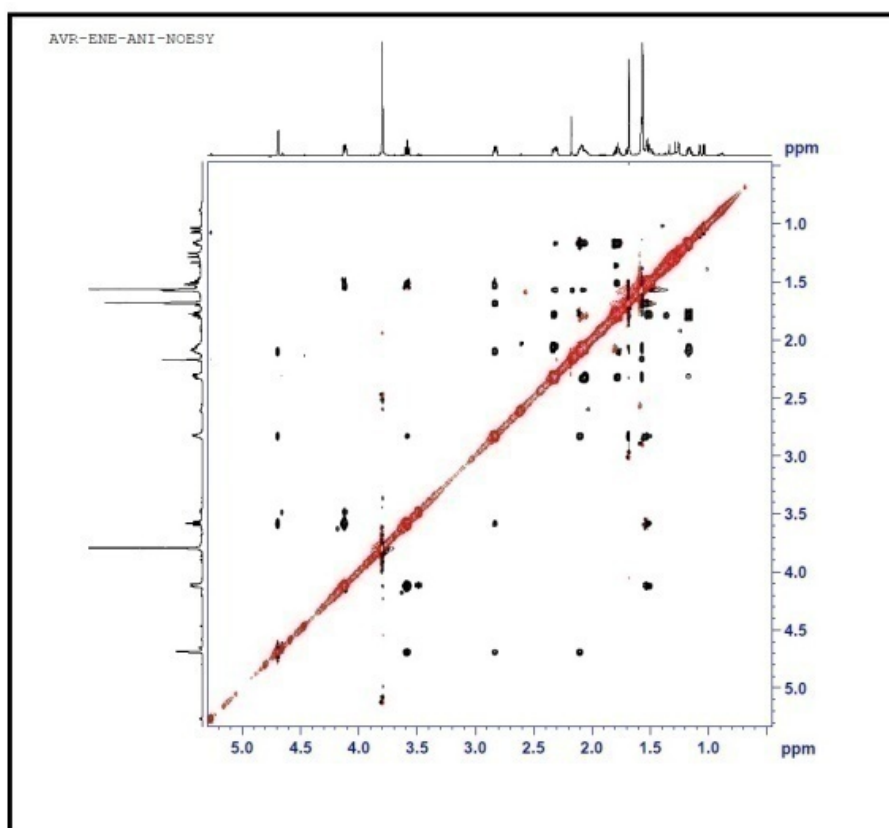


Figure 4. Energy-minimized structure and characteristic nOe correlations of of **5a**

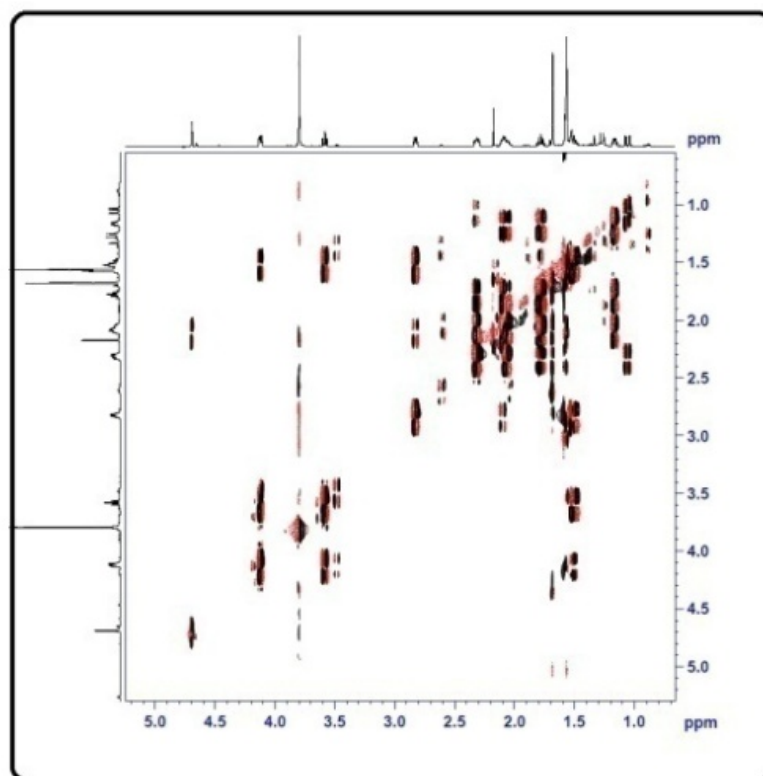
Proton	(δ) ppm	multiplicity	3J values (Hz)
1-H	4.52	d	$^3J_{1-H/7-H} = 10.2$
2-H(pro-S)	4.26	ddd	$^3J_{2-H(\text{pro-S})/2-H(\text{pro-S})} = 10.8$ $^3J_{2-H(\text{pro-S})/3-H(\text{pro-R})} = 1.0$ $^3J_{2-H(\text{pro-S})/3-H(\text{pro-S})} = 5.8$
2-H(pro-R)	3.56	ddd	$^3J_{2-H(\text{pro-R})/2-H(\text{pro-S})} = 10.8$ $^3J_{2-H(\text{pro-R})/3-H(\text{pro-R})} = 2.8$ $^3J_{2-H(\text{pro-R})/3-H(\text{pro-S})} = 12.6$
3-H(pro-R)	2.53	dd	$^3J_{2-H(\text{pro-S})/3-H(\text{pro-R})} = 1.0$ $^3J_{2-H(\text{pro-R})/3-H(\text{pro-R})} = 2.8$ $^3J_{3-H(\text{pro-S})/3-H(\text{pro-R})} = 14.1$
3-H(pro-S)	2.36	m	$^3J_{2-H(\text{pro-S})/3-H(\text{pro-S})} = 5.8$ $^3J_{2-H(\text{pro-R})/3-H(\text{pro-S})} = 12.6$ $^3J_{3-H(\text{pro-R})/3-H(\text{pro-S})} = 14.1$ $^3J_{3-H(\text{pro-S})/7-H} = 2.0$
4-H	2.78	sp	$^3J_{4-H/\text{CH}_3} = 7.0$
5-H(pro-S)	2.28	m	$^3J_{5-H(\text{pro-S})/5-H(\text{pro-R})} = 15.3$ $^3J_{5-H(\text{pro-S})/6-H(\text{pro-S})} = 8.4$ $^3J_{5-H(\text{pro-S})/6-H(\text{pro-R})} = 4.2$ $^3J_{5-H(\text{pro-S})/7-H} = 2.3$
5-H(pro-R)	1.25	m	$^3J_{5-H(\text{pro-S})/5-H(\text{pro-R})} = 15.3$ $^3J_{5-H(\text{pro-R})/6-H(\text{pro-S})} = *$ $^3J_{5-H(\text{pro-R})/6-H(\text{pro-R})} = 2.7$
6-H(pro-S)	1.28	m	$^3J_{5-H(\text{pro-S})/6-H(\text{pro-S})} = 8.4$ $^3J_{5-H(\text{pro-R})/6-H(\text{pro-S})} = *$ $^3J_{6-H(\text{pro-S})/6-H(\text{pro-R})} = 13.2$ $^3J_{6-H(\text{pro-S})/7-H} = 10.2$
6-H(pro-R)	1.76	m	$^3J_{5-H(\text{pro-S})/6-H(\text{pro-R})} = 4.2$ $^3J_{5-H(\text{pro-R})/6-H(\text{pro-R})} = 2.7$ $^3J_{6-H(\text{pro-S})/6-H(\text{pro-R})} = 13.2$ $^3J_{6-H(\text{pro-R})/7-H} = 8.2$
7-H	3.22	m	$^3J_{1-H/7-H} = 10.2$ $^3J_{3-H(\text{pro-S})/7-H} = 2.0$ $^3J_{6-H(\text{pro-S})/7-H} = 10.2$ $^3J_{6-H(\text{pro-R})/7-H} = 8.2$ $^3J_{5-H(\text{pro-R})/7-H} = 2.3$
Ha1	7.56	dd	$^3J_{\text{Ha1}/\text{Ha2}} = 7.2$ $^3J_{\text{Ha1}/\text{Ha3}} = 1.2$
Ha2	7.44	dd	$^3J_{\text{Ha1}/\text{Ha2}} = 7.2$ $^3J_{\text{Ha2}/\text{Ha3}} = 8.2$
Ha3	7.79	dd	$^3J_{\text{Ha2}/\text{Ha3}} = 8.2$ $^3J_{\text{Ha1}/\text{Ha3}} = 1.2$
Ha4	7.84	dd	$^3J_{\text{Ha4}/\text{Ha5}} = 8.2$ $^3J_{\text{Ha4}/\text{Ha6}} = 1.4$
Ha5	7.46	dd	$^3J_{\text{Ha4}/\text{Ha5}} = 8.2$ $^3J_{\text{Ha5}/\text{Ha6}} = 6.6$
Ha6	7.50	m	$^3J_{\text{Ha4}/\text{Ha6}} = 1.4$ $^3J_{\text{Ha5}/\text{Ha6}} = 6.6$ $^3J_{\text{Ha6}/\text{Ha7}} = 8.4$
Ha7	8.30	d	$^3J_{\text{Ha6}/\text{Ha7}} = 8.4$

Compound 6e (Table 3, entry 5):

The doublet at 4.69 ppm in **6e** due to 1-H was used to initiate the assignments with the help of DQF-COSY and NOESY experiments. From the one dimensional ^1H NMR experiments, the coupling constants, $^3J_{1\text{-H}/7\text{-H}} = 3.0$, $^3J_{2\text{-H}(\text{pro-}R)/3\text{-H}(\text{pro-}S)} = 12.1$, $^3J_{2\text{-H}(\text{pro-}S)/3\text{-H}(\text{pro-}R)} = 1.6$, $^3J_{2\text{-H}(\text{pro-}R)/3\text{-H}(\text{pro-}R)} = 2.8$, $^3J_{2\text{-H}(\text{pro-}S)/3\text{-H}(\text{pro-}S)} = 4.6$, $^3J_{3\text{-H}(\text{pro-}R)/4\text{-H}} = 6.0$, $^3J_{3\text{-H}(\text{pro-}S)/4\text{-H}} = 12.1$, $^3J_{4\text{-H}/7\text{-H}} = 6.0$, are consistent with a $^{13}\text{C}_{2\text{C}}$ chair conformation of the six-membered ring. The *cis* fusion of the five-six membered rings is implied by $^3J_{4\text{-H}/7\text{-H}} = 6.0$. Other couplings in the five membered ring like: $^3J_{5\text{-H}(\text{pro-}R)/6\text{-H}(\text{pro-}R)} = 9.4$, $^3J_{5\text{-H}(\text{pro-}R)/6\text{-H}(\text{pro-}S)} = 8.3$, $^3J_{5\text{-H}(\text{pro-}S)/6\text{-H}(\text{pro-}R)} = 10.0$, $^3J_{5\text{-H}(\text{pro-}S)/6\text{-H}(\text{pro-}S)} = 1.1$, $^3J_{6\text{-H}(\text{pro-}S)/7\text{-H}} = 6.3$ Hz and $^3J_{6\text{-H}(\text{pro-}R)/7\text{-H}} = 12.4$ Hz in conformity with envelop conformation of five-membered cyclopentane ring. The characteristic nOe correlations 1-H/2-H(pro-R), 1-H/4-H, 2-H(pro-R)/4-H and 3-H(pro-S)/6-H(pro-R), along with the above deductions are in conformity with *cis*-fusion of the two six-five membered rings. The energy-minimized structure is shown in Figure 5.



NOESY (6f)



DQF-COSY(6f)

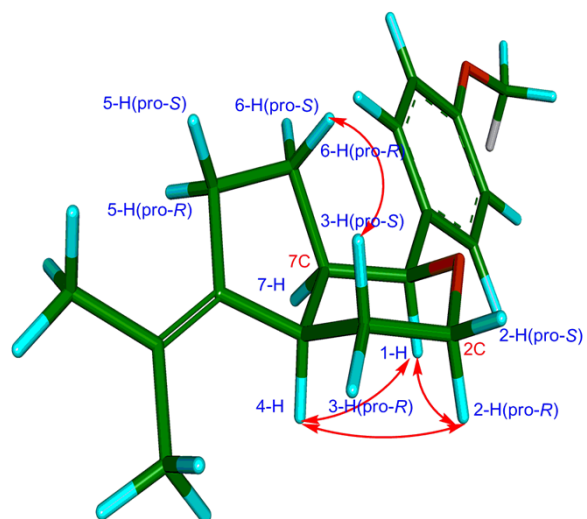
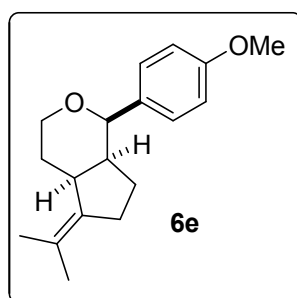


Figure 5. Energy minimized structure and characteristic nOe correlations of **6e**

Proton	(δ) ppm	multiplicity	3J values (Hz)
1-H	4.69	d	$^3J_{1-H/7-H} = 3.0$
2-H(pro- <i>S</i>)	4.11	ddd	$^3J_{2-H(\text{pro-}S)/2-H(\text{pro-}R)} = 11.5$ $^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}R)} = 1.6$ $^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}S)} = 4.6$
2-H(pro- <i>R</i>)	3.58	dt	$^3J_{2-H(\text{pro-}R)/2-H(\text{pro-}R)} = 11.5$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}R)} = 2.8$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}S)} = 12.1$
3-H(pro- <i>R</i>)	1.52	m	$^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}R)} = 1.6$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}R)} = 2.8$ $^3J_{3-H(\text{pro-}S)/3-H(\text{pro-}R)} = 14.0$ $^3J_{3-H(\text{pro-}R)/4-H} = 6.0$
3-H(pro- <i>S</i>)	1.47	m	$^3J_{2-H(\text{pro-}S)/3-H(\text{pro-}S)} = 4.6$ $^3J_{2-H(\text{pro-}R)/3-H(\text{pro-}S)} = 12.1$ $^3J_{3-H(\text{pro-}R)/3-H(\text{pro-}S)} = 14.0$ $^3J_{3-H(\text{pro-}S)/4-H} = 12.1$
4-H	2.82	td	$^3J_{3-H(\text{pro-}R)/4-H} = 6.0$ $^3J_{3-H(\text{pro-}S)/4-H} = 12.1$ $^3J_{4-H/7-H} = 6.0$
5-H(pro- <i>S</i>)	2.31	ddd	$^3J_{5-H(\text{pro-}S)/5-H(\text{pro-}R)} = 16.4$ $^3J_{5-H(\text{pro-}S)/6-H(\text{pro-}R)} = 10.0$ $^3J_{5-H(\text{pro-}S)/6-H(\text{pro-}S)} = 1.1$
5-H(pro- <i>R</i>)	2.05	m	$^3J_{5-H(\text{pro-}S)/5-H(\text{pro-}R)} = 16.4$ $^3J_{5-H(\text{pro-}R)/6-H(\text{pro-}R)} = 9.4$ $^3J_{5-H(\text{pro-}R)/6-H(\text{pro-}S)} = 8.3$ $^3J_{5-H(\text{pro-}R)/\text{CH}_3} = 2.0$
6-H(pro- <i>R</i>)	1.77	tdd	$^3J_{5-H(\text{pro-}S)/6-H(\text{pro-}R)} = 10.0$ $^3J_{5-H(\text{pro-}R)/6-H(\text{pro-}R)} = 9.4$ $^3J_{6-H(\text{pro-}R)/6-H(\text{pro-}S)} = 12.7$ $^3J_{6-H(\text{pro-}R)/7-H} = 12.4$
6-H(pro- <i>S</i>)	1.16	m	$^3J_{5-H(\text{pro-}S)/6-H(\text{pro-}S)} = 1.1$ $^3J_{5-H(\text{pro-}R)/6-H(\text{pro-}S)} = 8.3$ $^3J_{6-H(\text{pro-}R)/6-H(\text{pro-}S)} = 12.7$ $^3J_{6-H(\text{pro-}S)/7-H} = 6.3$
7-H	2.10	m	$^3J_{1-H/7-H} = 3.0$ $^3J_{4-H/7-H} = 6.0$ $^3J_{6-H(\text{pro-}R)/7-H} = 12.4$ $^3J_{6-H(\text{pro-}S)/7-H} = 6.3$

*coupling constants could not be obtained due to spectral complexity.

2. Computational methods

Quantum chemical calculations are performed on the reactants, intermediates (In), transition states (TS) and products to understand the underlying mechanism for the Prins reaction. As model reactants, that may enable us not only to understand the mechanism for the reaction but also compare the reactivity of *E* and *Z* isomers, the structures in entries 1 and 8 from Table 2 (nitrobenzaldehyde) and entries 3 and 6 from Table 3 (chlorobenzaldehyde) are considered. Calculations, on all the structures considered, are performed at B3LYP/6-31G(d) and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) levels of theory using PCM solvent (toluene)

phase. The reaction profiles thus generated are depicted in Figures 2 and 3 for nitro and chloro substitutions respectively. All the calculations are performed using Gaussian 09 programme package.¹ The results discussed here are at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory unless specified. The intermediate, *E/Z*, that forms after initial attack of the activated aldehyde and the dienol is considered as a starting point for understanding the reaction paths, as depicted in Figures 2 and 3. Considering nitrobenzaldehyde, *E/Z* undergoes Prins cyclization thereby forming **In1** (9.5/11.7 kcal/mol) via **TS1** (23.3/22.6 kcal/mol). **In1** then undergoes an ene cyclization forming **In2** (-13.0/-13.9 kcal/mol) via **TS2** (10.8/8.4 kcal/mol). **In2** finally undergoes a proton elimination and forms the observed product. Similarly for chlorobenzaldehyde, *E/Z* undergoes Prins cyclization forming **In1** (4.9/6.9 kcal/mol), via **TS1** (19.9/21.3 kcal/mol), which then undergoes an ene cyclization forming **In2** (-8.9/-8.5 kcal/mol) via **TS2** (13.1/10.8 kcal/mol) and in turn forms the final product. After understanding the mechanism for the reaction, we aimed to look at the reason for the variation in the yields of the formed products. Considering the relative stabilities of *E* and *Z* it is clear that *E* is lower in energy by -1.5/-1.3 kcal/mol compared to *Z* for nitro/chloro benzaldehyde. This may result in *E-Z* isomerisation, which in turn might be a reason for the formation of the observed major and minor products.

References

1. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

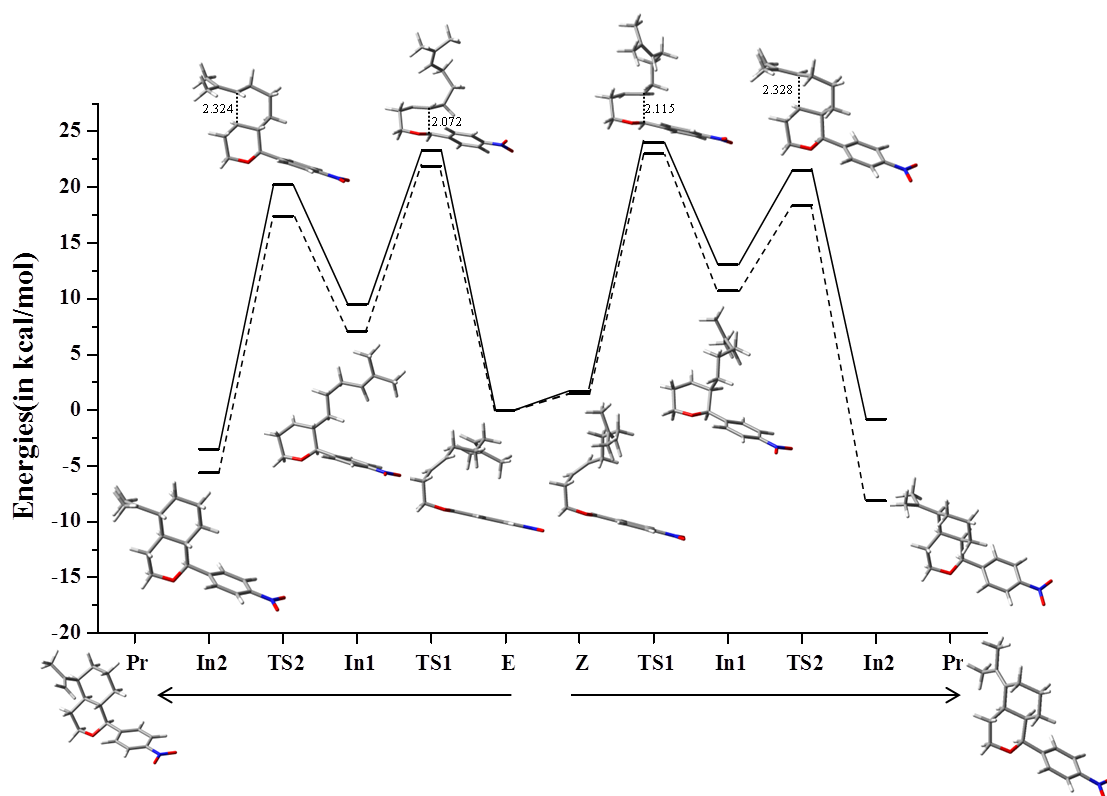


Figure 2. Reaction profile for the Prins reaction at B3LYP/6-31G(d)(dotted lines) and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)(thick lines)

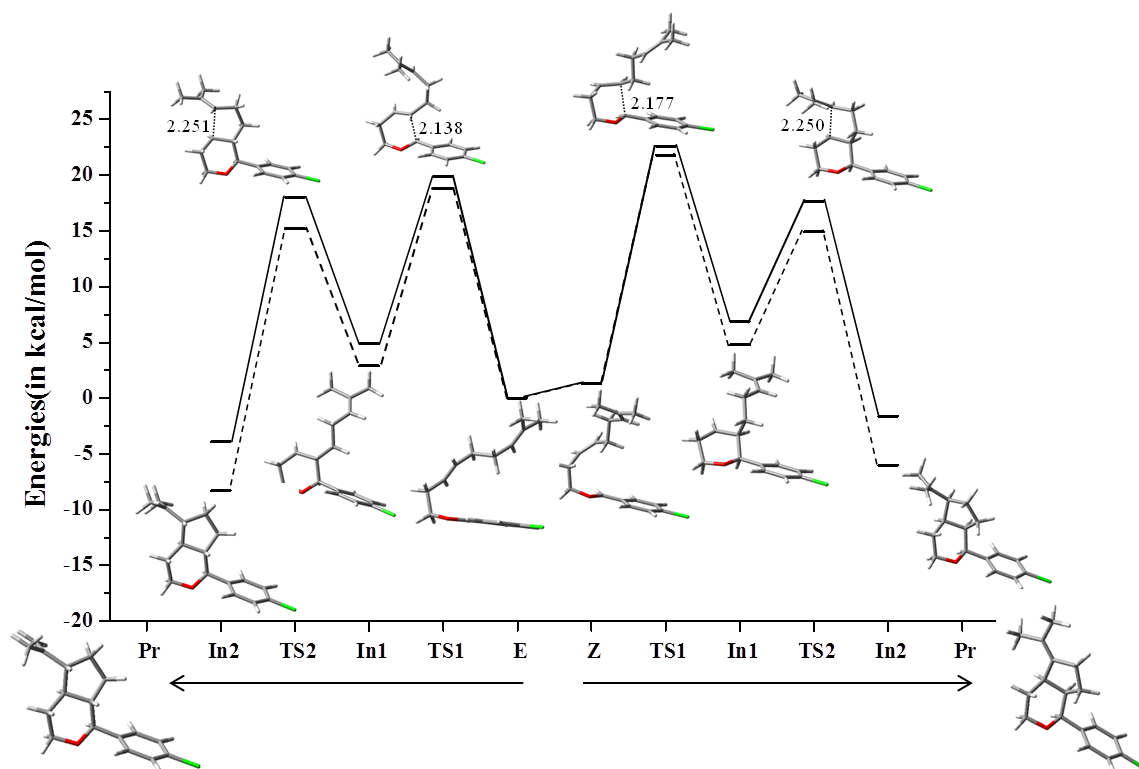
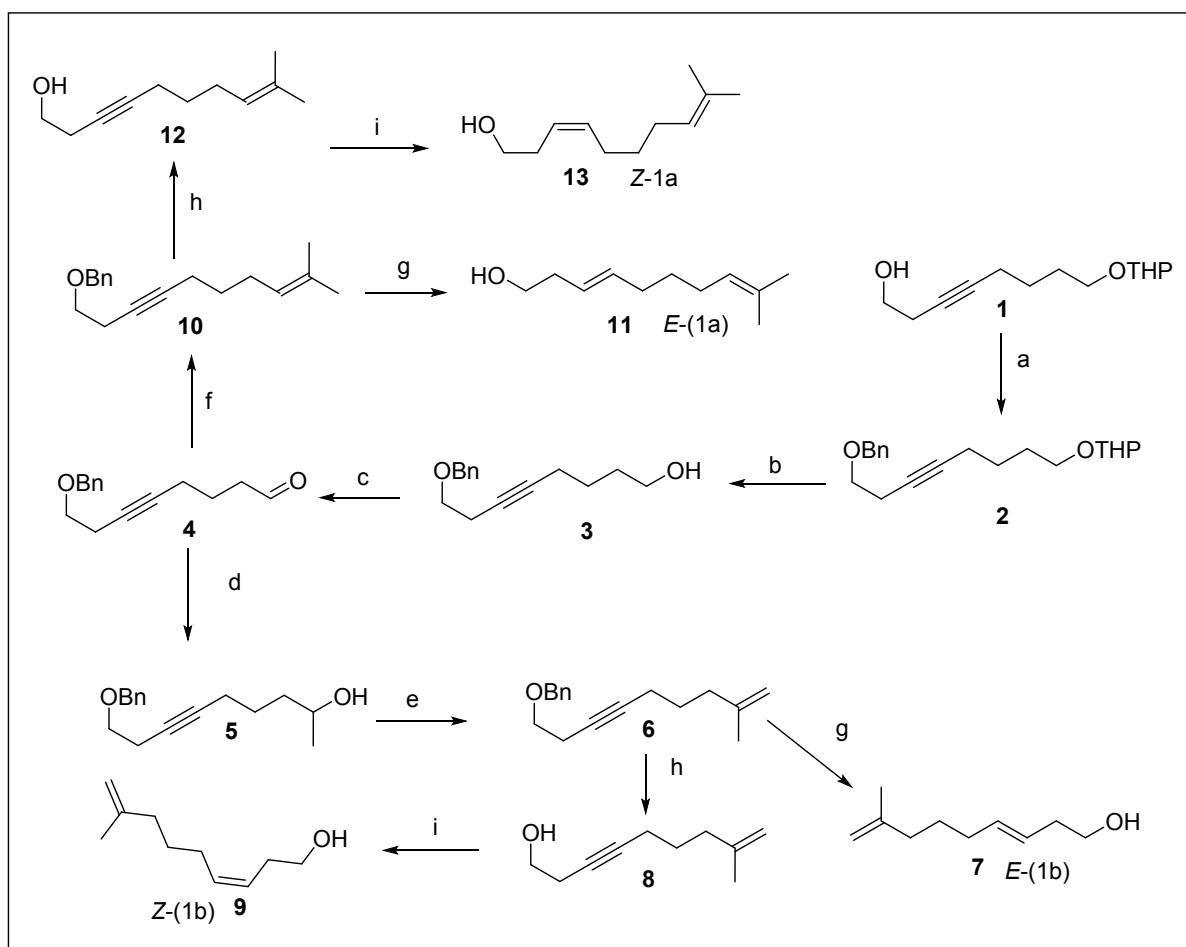


Figure 3. Reaction profile for the Prins reaction using chlorobenzaldehyde at B3LYP/6-31G(d)(dotted lines) and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) (thick lines)

3. General methods

Dichloromethane was dried according to a standard literature procedure. Reactions were performed in an oven-dried round bottom flask, the flasks were fitted with rubber septa and the reactions were conducted under nitrogen atmosphere. Glass syringes were used to transfer the 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 vapors and/or by exposure to methanolic acidic solution of *p*-anisaldehyde (anis) followed by heating (<1 min) on a hot plate (~250°C). Organic solvents were concentrated on rotary evaporator at 35–40 °C. IR spectra were recorded on FT-IR spectrometer. ¹H NMR and ¹³C NMR (proton-decoupled) spectra were recorded in CDCl₃ on 300, 500 600, or 700 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 Electron impact-mass spectrometry (EI-MS).

4. Preparation of the starting material



Reagents and conditions:

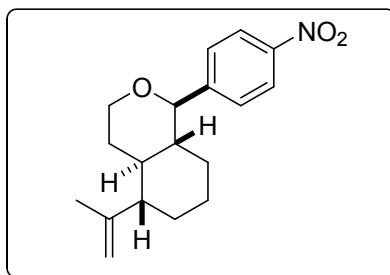
(a) BnBr, NaH, dry THF, 0 °C-r.t, 4h, 95%. (b) Amberlyst-15[®], methanol, 3h, 90%. (c) PCC, DCM, 0 °C, 2h, 90%. (d) CH₃MgBr, dry THF, 0 °C, 3h, 86% (e) i) PCC, DCM, 0 °C, 2h, 90%. ii) *n*-BuLi, C₁Wittig salt, dry THF, -78 °C, 8h, 80%. (f) *n*-BuLi, dry THF, Isopropyltriphenylphosphoniumbromide, -78 °C, 6h, 82%. (g) Li/liq.NH₃, dry ether, -78 °C. (h) Li/naphthalene, dry THF, - 20 °C,2h, 95%. (i) Ni(OAc)₂.4H₂O, NaBH₄, C₂H₅OH, H₂ gas, 2h, 90%.

5. Typical procedure for Prins cascade cyclization

To a stirred solution of (*E/Z*)-9-methyldeca-3,8-dien-1-ol (**1a-b**) or (*E/Z*)-8-methylnona-3, 8-dien-1-ol (**1c-d**) (0.50 mmol) and aldehyde (0.525 mmol) in anhydrous toluene (5 mL) at -10 °C was added AgSbF₆ (20 mol%) under nitrogen atmosphere. The resulting mixture was allowed to stir at room temperature for the specified time (24-30 h). After completion of the reaction as indicated by TLC, the mixture was quenched with saturated NaHCO₃ 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 Na₂SO₄ 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 (**3-6**) (Table 2, Table 3).

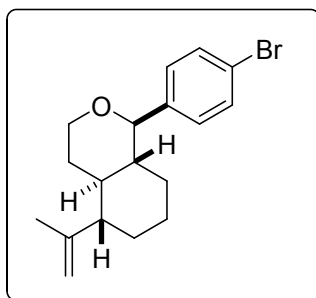
6. Characterization data of products (3a-g, 4h-j,5a-c ,6d-f, 1a-b)

(1*R**,4*aR**,8*aR**)-1-(4-Nitrophenyl)-5-(prop-1-en-2-yl)octahydro-1*H*-isochromene (**3a**; Table 2, entry 1):



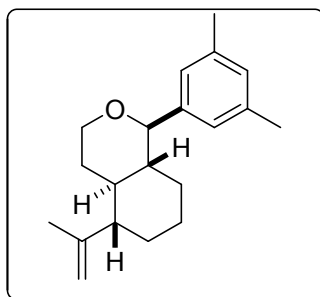
Yield, 128 mg, 90%; Viscous liquid; ¹H NMR (500MHz, CDCl₃): δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 4.74 (d, *J* = 8.3 Hz, 2H), 4.14 (dd, *J* = 4.5, 10.5 Hz, 1H), 4.04 (d, *J* = 9.0 Hz, 1H), 3.61(td, *J* = 11.3, 2.2 Hz, 1H), 1.89-1.78 (m, 1H), 1.74-1.70 (m, 2H), 1.66 (s, 3H), 1.46-1.17 (m, 6H), 1.07(d, *J* = 11.3, 1H), 0.99-.87(m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 148.6, 147.4, 147.2, 128.1, 123.4, 111.5, 84.4, 68.7, 51.5, 47.7, 42.6, 31.8, 30.7, 27.7, 25.3, 18.8; ; IR (KBr): ν_{max} 3075, 2927, 1608, 1522, 1350, 1257, 1091, 1013, 886, 696, 593 cm⁻¹; EI-MS: *m/z* 301 (M)⁺; EI -HRMS (TOF-EI) calcd for C₁₈H₂₃NO₃: 301.1678, Found 301.1677.

(1*R**,4*aR**,8*aR**)-1-(4-Bromophenyl)-5-(prop-1-en-2-yl)octahydro-1*H*-isochromene (**3b**; Table 2, entry 2):



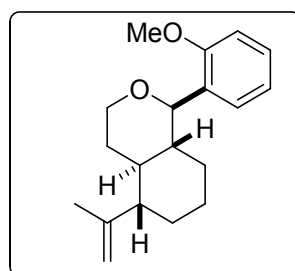
Yield, 140 mg, 85%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.73 (d, *J* = 10.6 Hz, 2H), 4.10 (dd, *J* = 2.4, 11.2 Hz, 2H), 3.89 (d, *J* = 9.1 Hz, 1H), 3.59 (td, *J* = 11.7, 2.1 Hz, 1H), 1.86-1.80 (m, 1H), 1.71-1.67 (m, 1H), 1.66 (s, 3H), 1.63-1.58 (m, 2H), 1.39-1.18 (m, 5H), 1.11 (dd, *J* = 1.9, 12.9 Hz, 1H), 0.89-0.81 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 147.5, 140.2, 131.2, 129.0, 121.4, 111.3, 84.8, 68.7, 51.6, 47.5, 42.8, 32.0, 30.8, 27.8, 25.4; IR (KBr): ν_{max} 3436, 2927, 2147, 1587, 1491, 1454, 1226, 1150, 1117, 819, 641 cm⁻¹; EI-MS: *m/z* 334 (M)⁺; EI-HRMS (TOF-EI) calcd for C₁₈H₂₃BrO: 334.0932, Found 334.0934.

(1*R**,4*aR**,8*aR**)-1-(3,5-Dimethylphenyl)-5-(prop-1-en-2-yl)octahydro-1*H*-isochromene, (**3c**;
Table 2, entry 3):



Yield, 110 mg, 78%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 6.91-6.88 (m, 3H), 4.73 (d, *J* = 8.0 Hz, 2H), 4.11 (ddd, *J* = 11.6, 4.5, 1.6 Hz, 1H), 3.84 (d, *J* = 9.2 Hz, 1H), 3.58 (ddd, *J* = 13.6, 11.6, 2.3 Hz, 1H), 2.23 (s, 6H), 1.84 (ddd, *J* = 13.0, 9.7, 3.5 Hz, 1H), 1.68 (m, *J* = 13.0, 3.7, 3.5 Hz, 1H), 1.61 (m, *J* = 13.0, 3.6, 3.5, 1.6 Hz, 1H), 1.59 (s, 3H), 1.56 (m, *J* = 13.4, 5.3, 4.5, 2.3 Hz, 1H), 1.37 (tdd, *J* = 13.0, 9.7, 3.5 Hz, 1H), 1.36 (m, *J* = 11.7, 3.7 Hz, 1H), 1.34 (m, *J* = 13.6, 13.4, 1.6 Hz, 1H), 1.28 (m, *J* = 13.0, 5.3 Hz, 1H), 1.23 (qt, *J* = 13.0, 3.7, 3.6 Hz, 1H), 1.16 (dq, *J* = 12.8, 3.7 Hz, 1H), 0.84 (m, *J* = 12.8, 11.7, 3.7 Hz, 1H).; ¹³C NMR (125 MHz, CDCl₃): δ 141.0, 137.6, 129.2, 125.1, 111.1, 85.7, 68.8, 51.6, 47.1, 42.9, 32.0, 30.9, 28.0, 25.5, 21.3, 18.9; IR (KBr): ν_{max} 3436, 2927, 2147, 1587, 1491, 1454, 1226, 1150, 1117, 819, 641 cm⁻¹; EI-MS: *m/z* 284 (M)⁺; EI-HRMS (TOF-EI) calcd for C₂₀H₂₈O: 284.2140, Found 284.2143

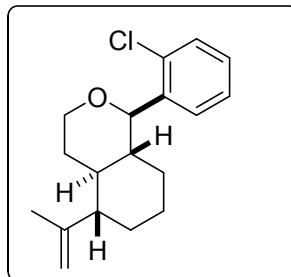
(1*R**,4*aR**,8*aR**)-1-(2-Methoxyphenyl)-5-(prop-1-en-2-yl)octahydro-1*H*-isochromene (**3d**;
Table 2, entry 4):



Yield, 107 mg, 75%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.73 (dd, *J* = 2.7, 2.7 Hz, 2H), 4.56 (d, *J* = 9.0 Hz, 1H), 4.10 (dd, *J* = 4.5, 10.5 Hz, 1H), 3.8 1(s, 3H), 3.63 (td, *J* = 10.5, 1.51 Hz, 1H), 1.89-1.79 (m, 1H), 1.70-1.61 (m, 1H), 1.66 (s, 3H), 1.65-1.54 (m, 2H), 1.47-1.09 (m, 6H), 1.04-0.83 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 156.7, 147.9, 130.0, 128.2, 127.4, 120.9, 111.0, 110.2, 68.9, 55.4, 51.7, 42.9, 32.1, 31.0, 29.7, 27.2, 25.6,

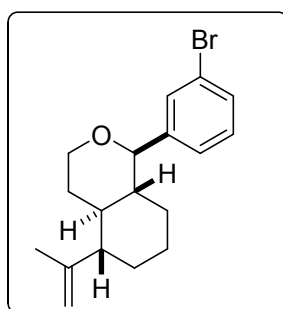
18.8; IR (KBr): ν_{\max} 3451, 2928, 1613, 1514, 1246, 1137, 1095, 832, 770, 696, 525 cm^{-1} ; EI-MS: m/z 286 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: 286.1932, Found 286.1933.

(1*R**,4*aR**,8*aR**)-1-(2-Chlorophenyl)-5-(prop-1-en-2-yl)octahydro-1*H*-isochromene (3e; Table 2, entry 5):



Yield, 117 mg, 81%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.52 (d, $J = 7.5$ Hz, 1H), 7.33 (m, 2H), 7.21 (dt, $J = 6.0, 1.5$ Hz, 1H), 4.76 (d, $J = 4.6$ Hz, 2H), 4.62 (d, $J = 9.0$ Hz, 1H), 4.13 (dd, $J = 4.5, 11.3$ Hz, 1H), 3.67 (td, $J = 9.8, 2.2$ Hz, 1H), 1.91-1.80 (m, 1H), 1.78-1.71 (m, 1H), 1.69 (s, 3H), 1.66-1.55 (m, 2H), 1.49-1.05 (m, 6H), 0.93-0.84 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.6, 139.1, 133.4, 128.9, 128.4, 127.1, 111.2, 76.7, 68.9, 51.6, 42.6, 31.9, 30.9, 29.6, 27.1, 25.5, 18.8; IR (KBr): ν_{\max} 3447, 2926, 1625, 1519, 1250, 1066, 825, 771, 659 cm^{-1} ; EI-MS: m/z 290 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{18}\text{H}_{23}\text{ClO}$: 290.1437, Found, 290.1436

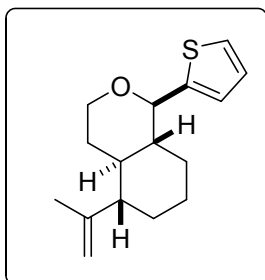
(1*R**,4*aR**,8*aR**)-1-(3-Bromophenyl)-5-(prop-1-en-2-yl)octahydro-1*H*-isochromene (3f; Table 2, entry 6):



Yield 133 mg 80%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.48 (t, $J = 1.5$ Hz, 1H), 7.40 (tt, $J = 1.9, 1.8$ Hz, 1H), 7.20 (d, $J = 3.0$ Hz, 1H), 7.18 (s, 1H), 4.74 (d, $J = 1.90$ Hz, H), 4.72 (d, $J = 1.89$ Hz), 4.11 (dd, $J = 11.2, 4.4$ Hz, 1H), 3.89 (d, $J = 9.0$ Hz, 1H), 3.59 (td, $J = 11.5, 2.1$ Hz, 1H), 1.86-1.80 (m, 1H), 1.72-1.67 (m, 1H), 1.66 (s, 3H), 1.63 (dd, $J = 1.0, 3.2$ Hz, 1H), 1.61-1.58 (m, 1H), 1.42-1.18 (m, 6H), 1.13 (dd, $J = 1.6, 13.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.5, 143.5, 130.7, 130.3, 129.6, 126.0, 122.4, 111.3, 84.8, 68.8, 51.5,

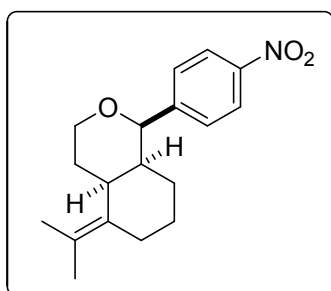
47.5, 42.1, 31.9, 30.7, 27.8, 25.3, 18.8; R (KBr): ν_{\max} 3436, 2998, 2937, 2147, 1587, 1454, 1226, 1150, 1117, 1035, 819 774, 641 cm^{-1} ; EI-MS: m/z 334 (M)⁺; EI-HRMS (TOF-EI) calcd for C₁₈H₂₃BrO: 334.0932, Found 334.0936.

(1*R**,4*aR**,8*aR**)-5-(Prop-1-en-2-yl)-1-(thiophen-2-yl)octahydro-1*H*-isochromene (**3g**; Table 2, entry 7):



Yield, 95 mg, 73%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 7.28-7.24 (m, 1H), 6.97-6.92 (m, 2H), 4.73 (d, J = 4.5 Hz, 2H), 4.26 (d, J = 9.0 Hz, 1H), 4.12 (dd, J = 11.3, 2.2 Hz, 1H), 3.60 (ddd, J = 11.3, 9.0, 3.0 Hz, 1H), 1.90-1.80 (m, 1H), 1.77-1.52 (m, 3H), 1.66 (s, 3H), 1.45-1.21 (m, 6H), 1.01-0.80 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 128.3, 126.0, 125.2, 124.8, 113.7, 111.3, 80.5, 68.3, 51.5, 48.5, 32.0, 30.6, 29.6, 28.0, 25.4, 18.9; IR (KBr): ν_{\max} 3441, 2925, 1643, 1534, 1321, 1143, 956, 864, 765, 645 cm^{-1} ; EI-MS: m/z 262 (M)⁺; EI-HRMS (TOF-EI) calcd for C₁₆H₂₂OS: 262.1391, Found 262.1390.

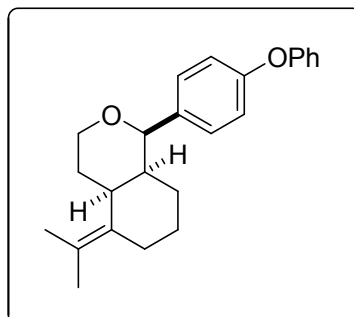
(1*R**,4*aS**,8*aS**)-1-(4-Nitrophenyl)-5-(propan-2-ylidene)octahydro-1*H*-isochromene (**4h**; Table 2, entry 8):



Yield, 133 mg, 89%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 8.18 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 4.62 (d, J = 2.2 Hz, 1H), 4.24 (dd, J = 11.4, 4.7 Hz, 1H), 3.68 (ddd, J = 11.5, 12.8, 2.6 Hz, 1H), 3.12 (dt, J = 12.8, 4.9, 4.9, 2.0 Hz, 1H), 2.54-2.48 (m, 1H), 2.09 (qd, J = 12.9, 5.2 Hz, 1H), 1.87-1.76 (m, 1H), 1.75 (s, 3H), 1.68 (s, 3H), 1.73-1.69 (m, 1H), 1.58-1.48 (m, 1H), 1.24-1.19 (m, 1H), 1.02 (qt, J = 13.3, 3.8 Hz, 1H), 0.82-0.78 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 145.8, 140.2, 131.5, 128.1, 127.6, 114.9, 87.8, 68.3, 51.9, 29.6, 27.1, 26.6, 24.9, 21.8, 21.1; IR (KBr): ν_{\max} 3445, 2295, 1602, 1523, 1462, 1345, 1187, 1095,

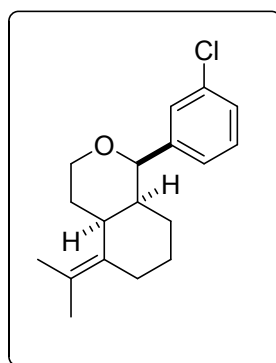
966, 710, 585 cm^{-1} ; EI-MS: m/z 301(M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_3$: 301.1678, Found 301.1681.

(1*R**,4*aS**,8*aS**)-1-(4-Phenoxyphenyl)-5-(propan-2-ylidene)octahydro-1*H*-isochromene (**4i**; Table 2, entry 9):



Yield, 147 mg, 85%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.33 (t, $J = 2.2$ Hz, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 7.24 (m, 1H), 7.23 (d, $J = 8.2$ Hz, 1H), 7.07 (tt, $J = 7.4, 1.0$ Hz, 1H), 7.00-6.95 (m, 4H), 4.53 (d, $J = 2.4$ Hz, 1H), 4.22 (dd, $J = 11.1, 4.8$ Hz, 1H), 3.67 (td, $J = 12.6, 11.4, 2.5$ Hz, 1H), 3.10 (dt, $J = 12.6, 4.2$ Hz, 1H), 2.54-2.48 (m, 1H), 2.06 (qd, $J = 12.9, 4.8$ Hz, 1H), 1.88-1.80 (m, 1H), 1.75 (s, 3H), 1.73-1.70 (m, 1H), 1.68 (s, 3H), 1.58-1.54 (m, 1H), 1.35-1.13 (m, 1H), 1.20-1.16 (m, 1H), 1.06-1.01 (m, 2H); ^{13}C NMR(125MHz, CDCl_3): δ 157.5, 155.5, 136.8, 133.8, 130.8, 129.6, 126.7, 122.8, 121.8, 118.6, 118.5, 82.1, 69.0, 42.7, 39.0, 29.7, 26.4, 25.4, 25.2, 20.3, 19.7, 19.6; IR (KBr): ν_{max} 3448, 2928, 1590, 1506, 1288, 1239, 1093, 868, 750, 692 cm^{-1} ; EI-MS: m/z 348 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2$: 348.2089, Found 348.2090.

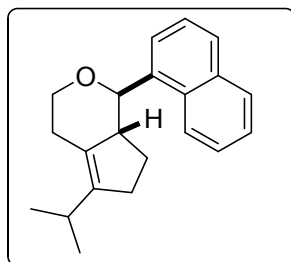
(1*R**,4*aS**,8*aS**)-1-(3-Chlorophenyl)-5-(propan-2-ylidene)octahydro-1*H*-isochromene (**4j**; Table 2, entry 10):



Yield, 117 mg, 81%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.32-7.09 (m, 4H), 4.51 (d, $J = 2.2$ Hz, 1H), 4.22 (dd, $J = 11.1, 4.7$ Hz, 1H), 3.66 (td, $J = 11.9, 2.5$ Hz, 1H), 3.08 (dt, $J = 12.6, 4.2$ Hz, 1H), 2.53-2.47 (m, 1H), 2.05 (qd, $J = 12.9, 5.1$ Hz, 1H), 1.87-1.78 (m, 1H), 1.74 (s, 3H), 1.73-1.68 (m, 1H), 1.68 (s, 3H), 1.61-1.56 (m, 1H), 1.53 (dd, $J = 13.1, 3.8$ Hz,

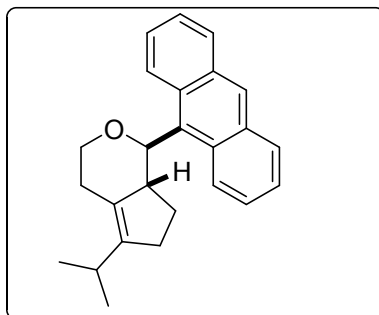
1H), 1.20-1.15(m, 1H), 1.09-0.99 (m, 1H), 0.90-0.85 (m, 1H); ¹³C NMR(125 MHz , CDCl₃): δ 143.9, 133.9, 133.6, 129.1, 126.6, 125.6, 123.4, 121.9, 81.7, 68.9, 42.5, 38.9, 29.6, 26.3, 25.3, 20.3, 19.6; IR (KBr): ν_{max} 3419, 2913, 1654, 1574, 1519, 1324, 1169, 897, 789, 747 cm⁻¹; EI-MS: *m/z* 290 (M)⁺; EI-HRMS (TOF-EI) calcd for C₁₈H₂₃ClO: 290.1437, Found 290.1438.

(1*R**,7*aR**)-5-Isopropyl-1-(naphthalen-1-yl)-1,3,4,6,7,7*a*-hexahydrocyclopenta[*c*]pyran (5*a*; Table 3, entry 1):



Yield, 118 mg, 81%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.79 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.56 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.50 (m, *J* = 8.4, 6.6, 1.4 Hz 1H), 7.46 (dd, *J* = 8.2, 6.6 Hz, 1H), 7.44 (dd, *J* = 8.2, 7.2 Hz, 1H), 4.52 (d, *J* = 10.2 Hz, 1H), 4.26 (ddd, *J* = 10.8, 5.8, 1.0 Hz, 1H), 3.56 (ddd, *J* = 12.6, 10.8, 2.8 Hz, 1H), 3.28-3.20 (m, 1H), 2.78 (sp, *J* = 7.0 Hz, 1H), 2.53 (dd, *J* = 14.1, 2.8, 1.0 Hz, 1H), 2.43-2.24 (m, 1H), 1.83-1.71 (m, 1H), 1.33-1.22 (m, 2H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H); ¹³CNMR(125MHz ,CDCl₃): δ 136.3, 134.1, 131.9, 130.7, 128.8, 128.5, 125.8, 125.4, 125.2, 124.8, 124.5, 76.8, 68.6, 50.4, 29.7, 27.3, 26.7, 25.4, 21.9, 21.2; IR (KBr): ν_{max} 3435, 2925, 2853, 1458, 1270, 1126, 1099, 856, 816, 772, 745, 657 cm⁻¹; EI-MS: *m/z* 292 (M)⁺; EI-HRMS (TOF-EI) calcd for C₂₁H₂₄O: 292.1827, Found 292.1828.

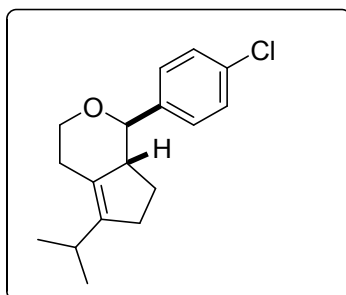
(1*R**,7*aR**)-1-(Anthracen-9-yl)-5-isopropyl-1,3,4,6,7,7*a*-hexahydrocyclopenta[*c*]pyran (5*b*; Table 3, entry 2):



Yield, 133 mg, 78%; Viscous liquid; ¹H NMR (500 MHz, CDCl₃): δ 9.17 (d, *J* = 8.3 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.40 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.49-7.40 (m, 4H), 5.47 (d, *J*

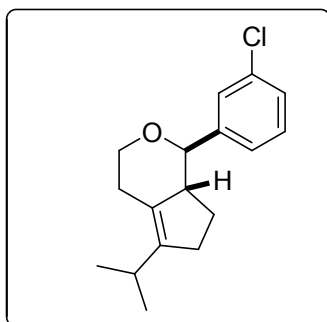
= 10.3 Hz, 1H), 4.43 (ddd, $J = 6.8, 5.6, 3.9$ Hz, 1H), 3.62 (td, $J = 17.3, 8.7, 3.3$ Hz, 2H), 2.82 (sp, $J = 6.8$ Hz, 1H), 2.65-2.54 (m, 2H), 2.32-2.23 (m, 1H), 2.15-2.06 (m, 1H), 1.34-1.28 (m, 2H), 1.11 (d, $J = 6.8$ Hz, 3H), 1.00 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 141.3, 132.1, 132.3, 129.8, 129.2, 129.0, 128.1, 127.6, 125.6, 124.7, 124.4, 123.8, 83.5, 69.1, 51.1, 29.6, 27.5, 26.7, 25.6, 21.7, 21.2; IR (KBr): ν_{max} 3453, 3051, 2925, 1642, 1457, 1371, 1262, 1098, 905, 778, 701 cm^{-1} ; EI-MS: m/z 342 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{25}\text{H}_{26}\text{O}$: 342.1983, Found 342.1984.

(1*R**,7*aR**)-1-(3-Chlorophenyl)-5-isopropyl-1,3,4,6,7,7*a*-hexahydrocyclopenta[*c*]pyran (**5c**; Table 3, entry 3):



Yield, 115 mg, 84%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.16 (d, $J = 8.3$ Hz, 2H), 6.66 (d, $J = 8.3$ Hz, 2H), 4.17 (dd, $J = 11.1, 5.3$ Hz, 1H), 3.71 (d, $J = 9.9$ Hz, 1H), 3.38 (td, $J = 12.0, 10.3, 2.7$ Hz, 1H), 2.73 (sp, $J = 6.5$ Hz, 1H), 2.41 (dd, $J = 14.1, 2.4$ Hz, 1H), 2.32-2.20 (m, 2H), 1.76-1.66 (m, 2H), 1.64-1.53 (m, 2H), 1.03 (d, $J = 6.8$, 3H), 0.98 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 145.8, 140.2, 131.5, 130.9, 128.1, 114.9, 87.9, 68.3, 51.9, 29.5, 27.1, 26.6, 24.9, 21.8, 21.1; IR (KBr): ν_{max} 3447, 2926, 1625, 1519, 1250, 1066, 825, 771, 567 cm^{-1} ; EI-MS: m/z 276 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{17}\text{H}_{21}\text{ClO}$: 276.1281, Found 276.1285.

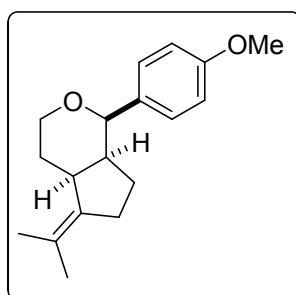
(1*R**,7*aR**)-1-(3-Chlorophenyl)-5-isopropyl-1,3,4,6,7,7*a*-hexahydrocyclopenta[*c*]pyran (**5d**; Table 3, entry 4):



Yield, 113 mg, 82%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.28-7.22 (m, 4H), 4.19 (ddd, $J = 10.0, 5.7, 1.0$ Hz, 1H), 3.81 (d, $J = 9.9$ Hz, 1H), 3.39 (td, $J = 9.7, 2.8, 1.3$ Hz, 1H),

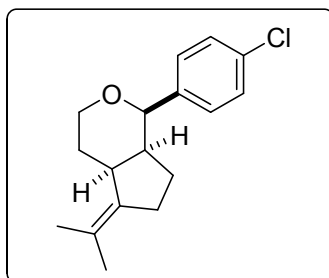
2.71 (sp, $J = 6.8$ Hz, 1H), 2.44 (dd, $J = 11.7, 1.9$ Hz, 1H), 2.36-2.22 (m, 2H), 1.96-1.91 (m, 1H), 1.76-1.69 (m, 1H), 1.35-1.23 (m, 2H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR(125MHz, CDCl_3): δ 134.2, 130.2, 129.5, 127.8, 127.7, 127.0, 125.0, 87.2, 68.3, 52.4, 29.5, 27.0, 26.7, 24.9, 21.8, 21.0. IR (KBr): ν_{max} 3447, 2926, 1625, 1519, 1250, 1066, 825, 771, 567 cm^{-1} ; EI-MS: m/z 276 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{17}\text{H}_{21}\text{ClO}$: 276.1281, Found 276.1283.

(1*R**,4*aS**,7*aS**)-1-(4-Methoxyphenyl)-5-(propan-2-ylidene)octahydrocyclopenta[*c*]pyran (6e; Table 3, entry 5):



Yield, 108 mg, 80%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.21(d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 4.69 (d, $J = 3.0$ Hz, 1H), 4.11(ddd, $J = 11.5, 4.6, 1.6$ Hz, 1H), 3.80 (s, 3H), 3.58 (dt, $J = 12.1, 11.5, 2.8$ Hz, 1H), 2.82 (td, $J = 12.1, 6.0$ Hz, 1H), 2.31 (ddd, $J = 16.4, 10.0, 2.1$ Hz, 1H), 2.12- 2.03 (m, 2H), 1.68 (s, 3H), 1.56 (s, 3H), 1.77 (tdd, $J = 12.7, 12.4, 9.4, 1.0$ Hz, 1H), 1.54-1.46 (m, 2H), 1.19 -1.14 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 158.3, 138.8, 134.7, 126.4, 121.5, 113.4, 78.6, 68.2, 55.2, 45.4, 40.7, 28.2, 26.2, 22.2, 20.6; IR (KBr): ν_{max} 3426, 2929, 1602, 1455, 1262, 1158, 1044, 770, 700 cm^{-1} ; EI-MS: m/z 272 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2$: 272.1776 (M^+), Found 270.1775.

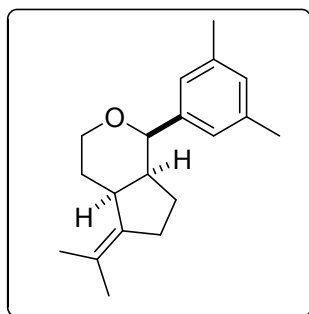
(1*R**,4*aS**,7*aS**)-1-(4-Chlorophenyl)-5-(propan-2-ylidene)octahydrocyclopenta[*c*]pyran (6f; Table 3, entry 6):



Yield, 113 mg, 82%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 7.35-7.16 (m, 4H), 4.71 (d, $J = 3.0$ Hz, 1H), 4.12 (ddd, $J = 11.4, 3.0, 1.3$ Hz, 1H), 3.57 (dt, $J = 12.2, 11.4, 2.4$ Hz, 1H), 2.83 (td, $J = 11.9, 6.1, 5.7$ Hz, 1H), 2.31 (ddd, $J = 16.9, 11.7, 2.5$ Hz, 1H), 2.13-2.00 (m, 2H), 1.77-1.64 (m, 1H), 1.68 (s, 3H), 1.56 (s, 3H), 1.54-1.43 (m, 1H), 1.13-1.02 (m, 2H);

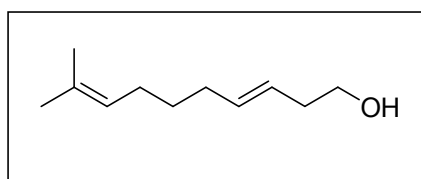
^{13}C NMR (125 MHz, CDCl_3): δ 140.9, 138.5, 132.1, 128.1, 126.6, 121.7, 78.2, 69.0, 45.0, 40.7, 29.6, 28.1, 26.1, 22.0, 20.6 ; IR (KBr): ν_{max} 3440, 2925, 1603, 1513, 1248, 1171, 1032, 832, 611 cm^{-1} ; EI-MS: m/z 276 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{17}\text{H}_{21}\text{ClO}$: 276.1281 (M^+), Found 276.1280.

(1*R**,4*aS**,7*aS**)-1-(3,5-Dimethylphenyl)-5-(propan-2-ylidene)octahydrocyclopenta[*c*]pyran (**6g**; Table 3, entry 7):



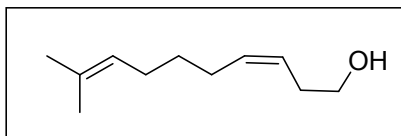
Yield, 105 mg, 78%; Viscous liquid; ^1H NMR (500 MHz, CDCl_3): δ 6.91(s, 2H), 6.85 (s, 1H), 4.67 (d, $J = 3.0$ Hz, 1H), 4.13 (ddd, $J = 13.3, 9.1, 2.3$ Hz, 1H), 3.57 (td, $J = 11.4, 3.5$ Hz, 1H), 2.53 (dt, $J = 12.2, 5.6$ Hz, 1H), 2.31-2.25 (m, 1H), 2.30 (s, 6H), 2.15-2.04 (m, 2H), 1.78 (tdd, $J = 11.9, 10.0, 12.5, 1.2$ Hz, 1H), 1.68 (s, 3H), 1.57 (s, 3H), 1.54-1.50 (m, 1H), 1.21-1.14 (m, 1H), 0.94-0.86 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 142.2, 138.8, 128.1, 123.0, 121.4, 79.0, 68.1, 45.1, 40.8, 28.2, 26.2, 22.2, 21.3, 20.6, 20.5; IR (KBr): ν_{max} 3447, 2926, 1640, 1520, 1312, 1109, 954, 876, 764, 654 cm^{-1} ; EI-MS: m/z 270 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{19}\text{H}_{26}\text{O}$: 270.1983 (M^+), Found 270.1982.

(*E*)-9-Methyldeca-3,8-dien-1-ol (*E*-1a)



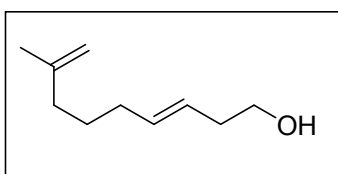
Liquid; ^1H NMR (500 MHz, CDCl_3): δ 5.59-5.52 (m, 1H), 5.54-5.32 (m, 1H), 5.10 (t, $J = 7.1$ Hz, 1H), 4.68 (d, $J = 15.1$ Hz, 1H), 3.63 (t, $J = 5.8$ Hz, 2H), 2.27 (dd, $J = 12.6, 6.4$ Hz, 2H), 2.06-1.94 (m, 4H), 1.69 (s, 3H), 1.60 (m, 3H), 1.46-1.34 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 134.0, 125.8, 124.3, 109.6, 62.0, 35.9, 32.0, 29.5, 27.4, 25.6, 17.6; EI-MS: m/z 168 (M^+); EI-HRMS (TOF-EI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}$: 168.1514 (M^+), Found 168.1517.

(*Z*)-9-Methyldeca-3,8-dien-1-ol (*Z*-1a)



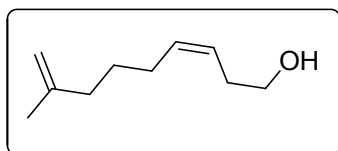
Liquid; ^1H NMR (500 MHz, CDCl_3): δ 5.65-5.51 (m, 1H), 5.43-5.31 (m, 1H), 5.11 (t, $J = 7.0$ Hz, 1H), 4.68 (dd, $J = 14.3, 5.8$ Hz, 1H), 3.65 (t, $J = 6.6$ Hz, 2H), 2.33 (dd, $J = 13.4, 6.9$ Hz, 2H), 2.13-1.94 (m, 4H), 1.69 (s, 3H), 1.60 (s, 3H), 1.48-1.32 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 133.2, 125.1, 124.3, 109.7, 62.3, 37.6, 30.8, 29.8, 27.6, 25.6, 17.6 ; EI-MS: m/z 168 (M) $^+$; EI-HRMS (TOF-EI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}$: 168.1514 (M) $^+$, Found 168.1516.

(E)-8-Methylnona-3,8-dien-1-ol (E-1b)



Liquid; ^1H NMR (500 MHz, CDCl_3): δ 5.60-5.52 (m, 1H), 5.44-5.35 (m, 1H), 4.68 (d, $J = 20.1$ Hz, 2H), 3.64 (t, $J = 6.4$ Hz), 2.27 (q, $J = 6.3$ Hz, 2H), 2.04-1.98 (m, 4H), 1.71 (s, 3H), 1.54-1.46 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 145.7, 133.8, 126.0, 109.8, 62.0, 37.2, 35.8, 32.2, 27.3, 22.3; EI-MS: m/z 154 (M) $^+$; EI-HRMS (TOF-EI) calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: 154.1358 (M) $^+$, Found 154.1360.

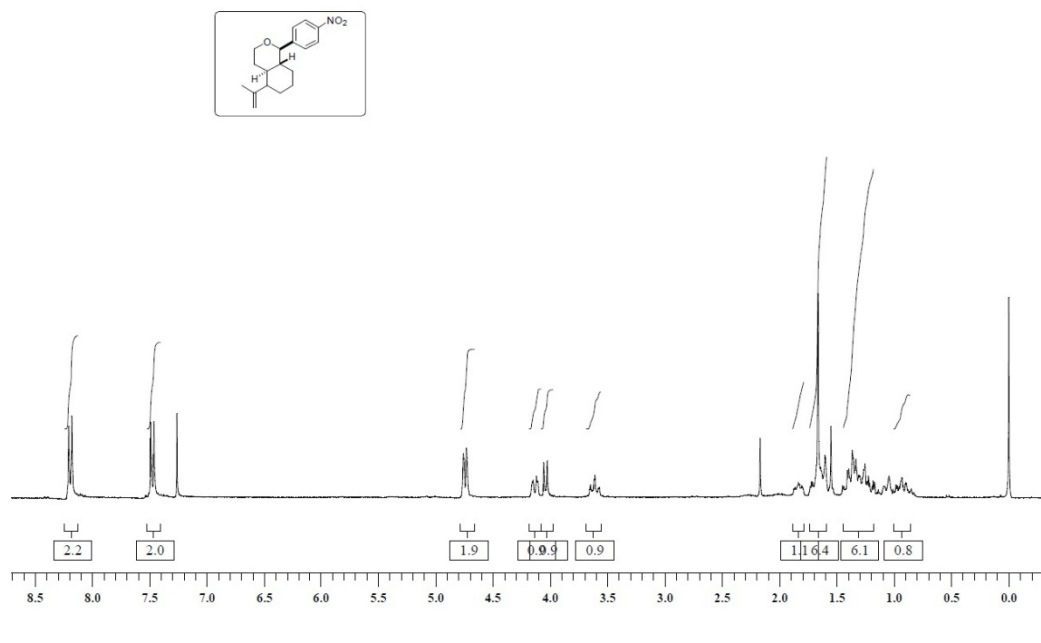
(Z)-8-Methylnona-3,8-dien-1-ol (Z-1b)



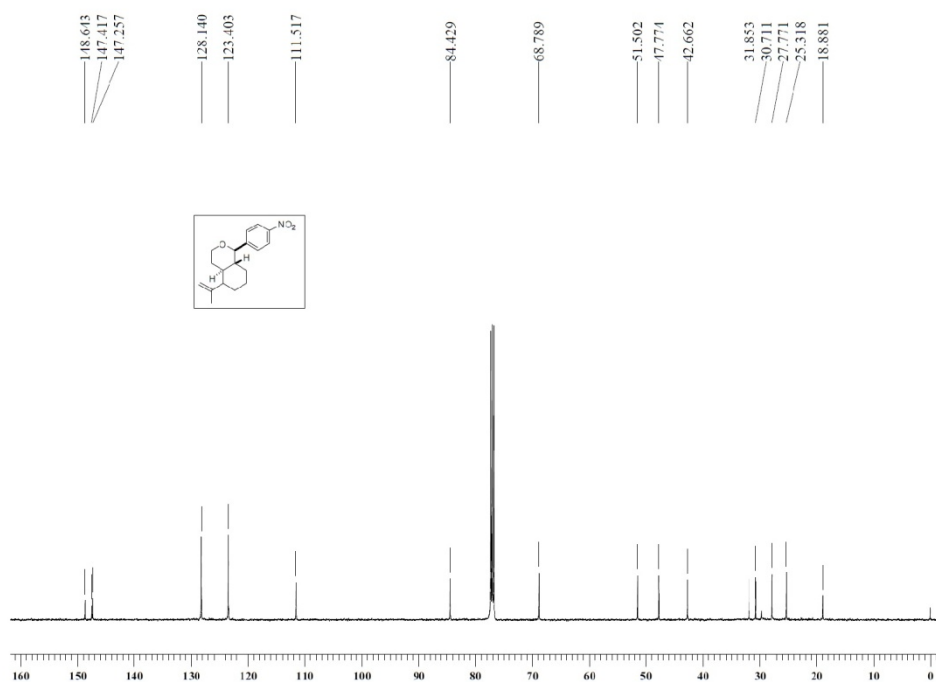
Liquid; ^1H NMR (500 MHz, CDCl_3): δ 5.61-5.52 (m, 1H), 5.42-5.32 (m, 1H), 4.69 (d, $J = 15.7$ Hz, 2H), 3.64 (t, $J = 6.5$ Hz, 2H), 2.33 (d, $J = 6.5$ Hz, 2H), 2.10-1.98 (m, 4H), 1.71 (s, 3H), 1.54-1.47 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 145.6, 132.8, 125.3, 109.8, 62.2, 37.2, 30.7, 27.5, 26.8, 22.2; EI-MS: m/z 154 (M) $^+$; EI-HRMS (TOF-EI) calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: 154.1358 (M) $^+$, Found 154.1363.

7. Copies of ^1H & ^{13}C NMR spectra of products (3a-g, 4h-j, 5a-d, 6e-g, 1a-b).

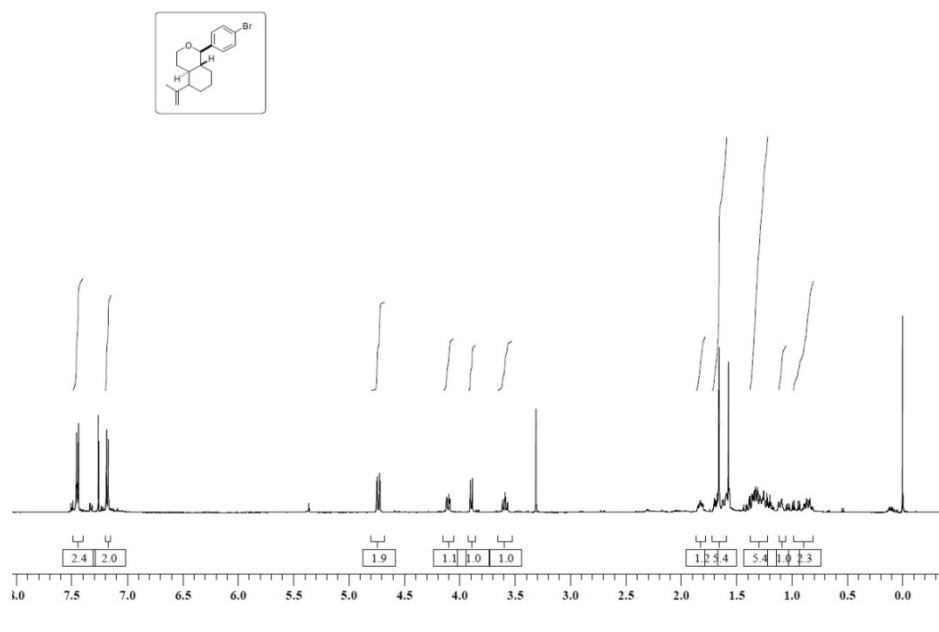
^1H NMR spectrum of 3a (Table 2, entry 1)



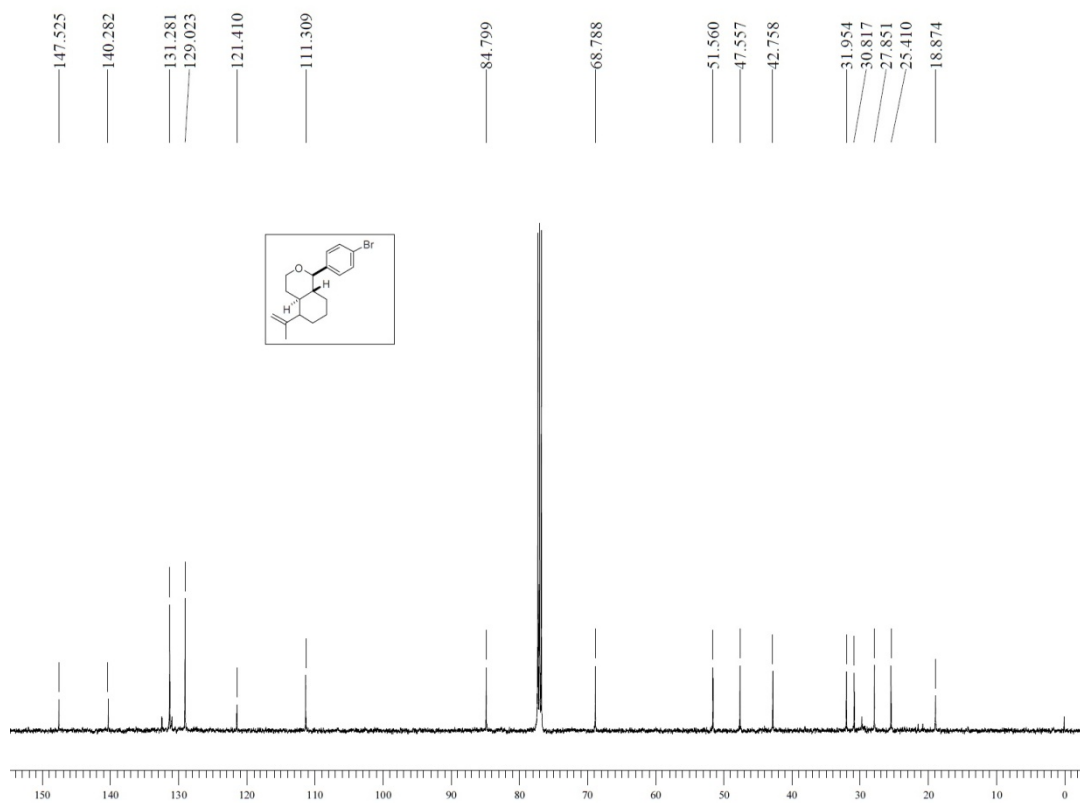
^{13}C NMR spectrum of 3a (Table 2, entry 1)



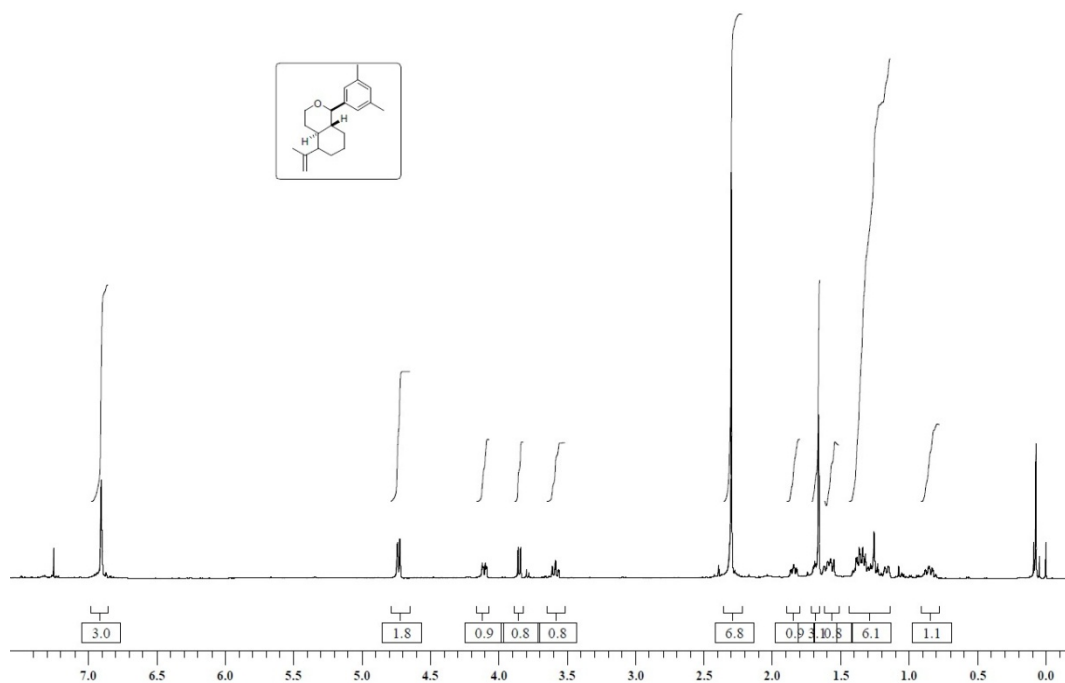
¹H NMR spectrum of 3b (Table 2, entry 2)



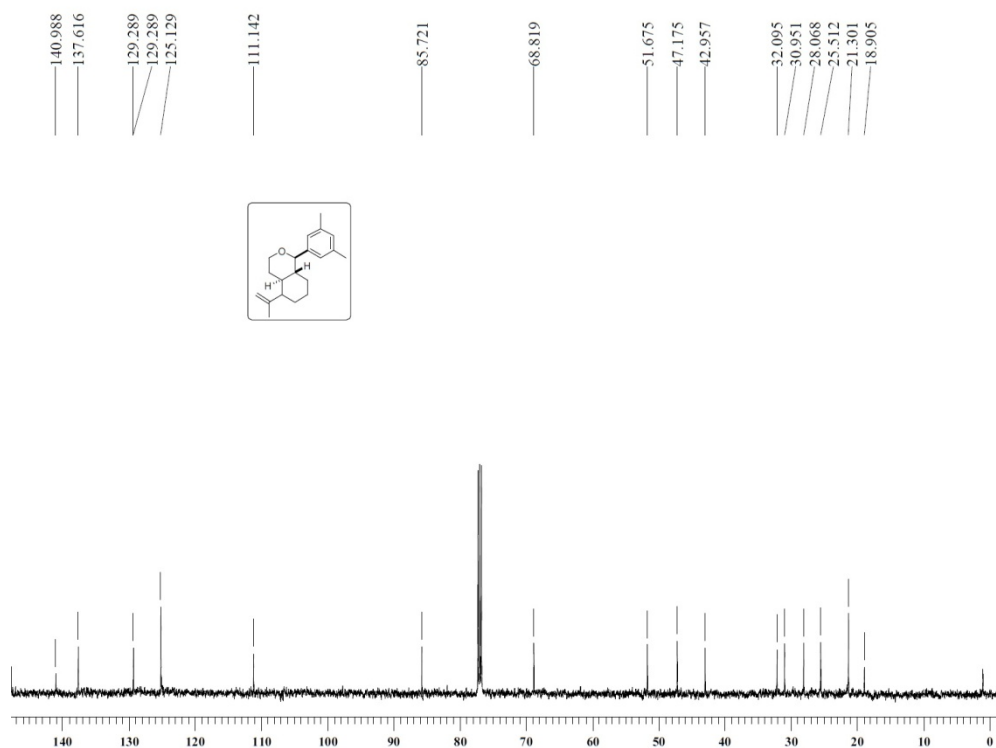
¹³C NMR spectrum of 3b (Table 2, entry 2)



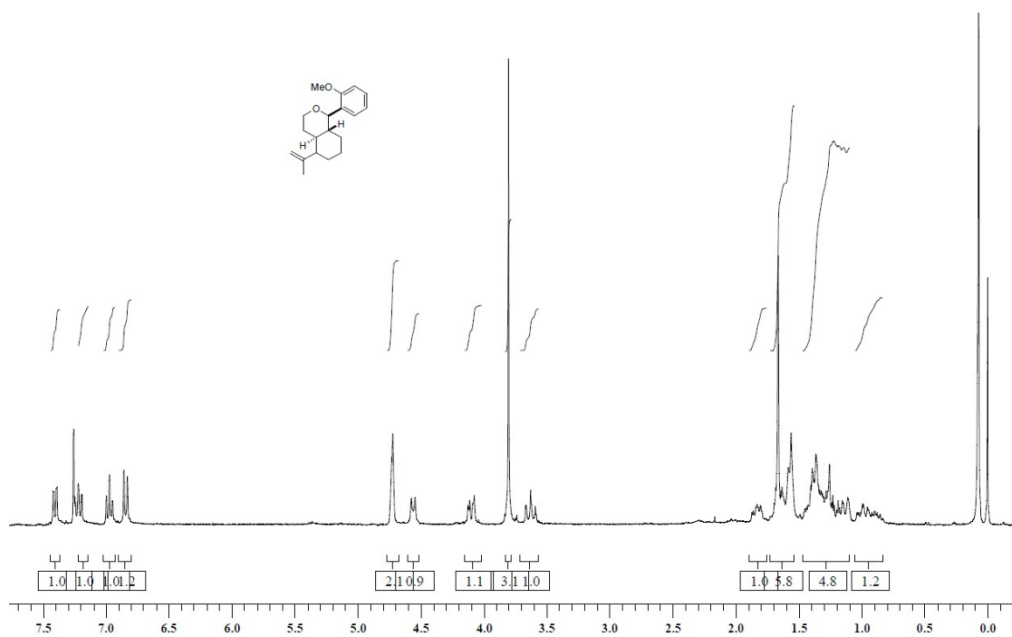
¹H NMR spectrum of 3c (Table 2, entry 3)



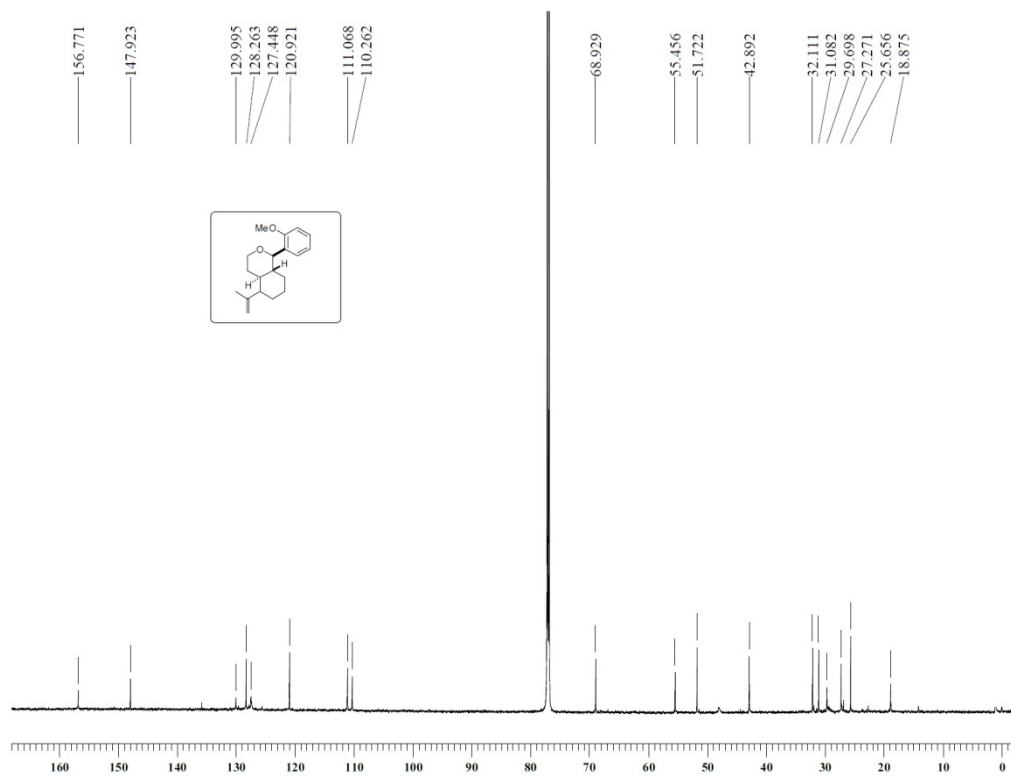
¹³C NMR spectrum of 3c (Table 2, entry 3)



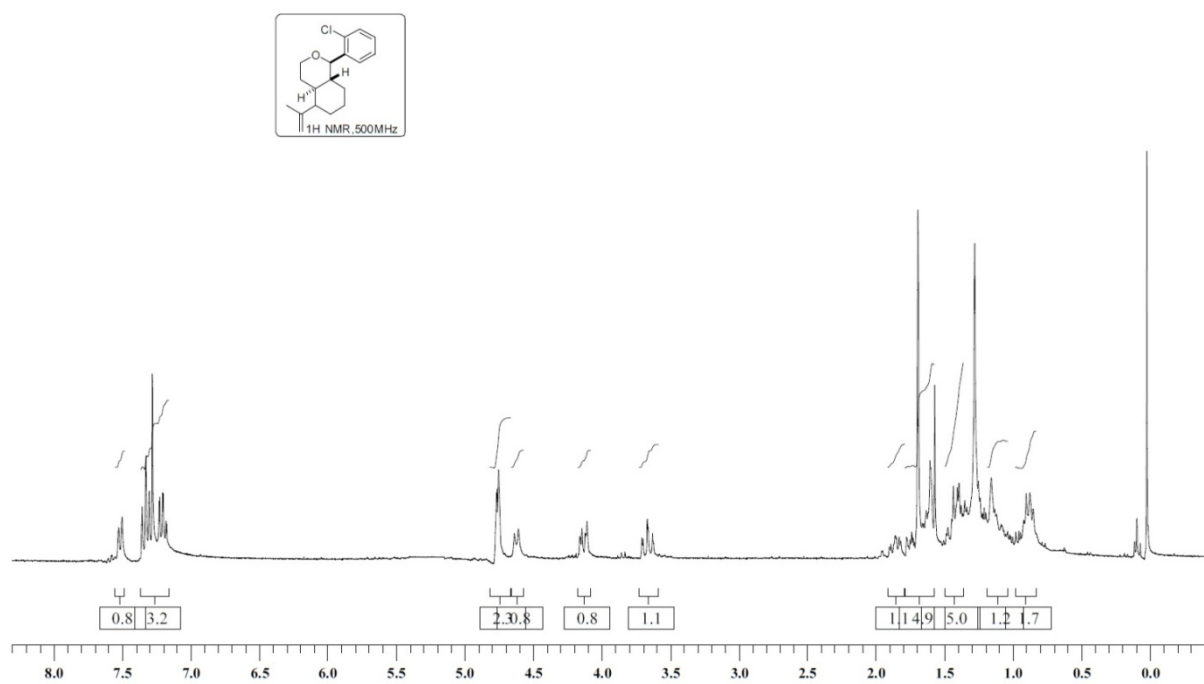
¹H NMR spectrum of 3d (Table 2, entry 4)



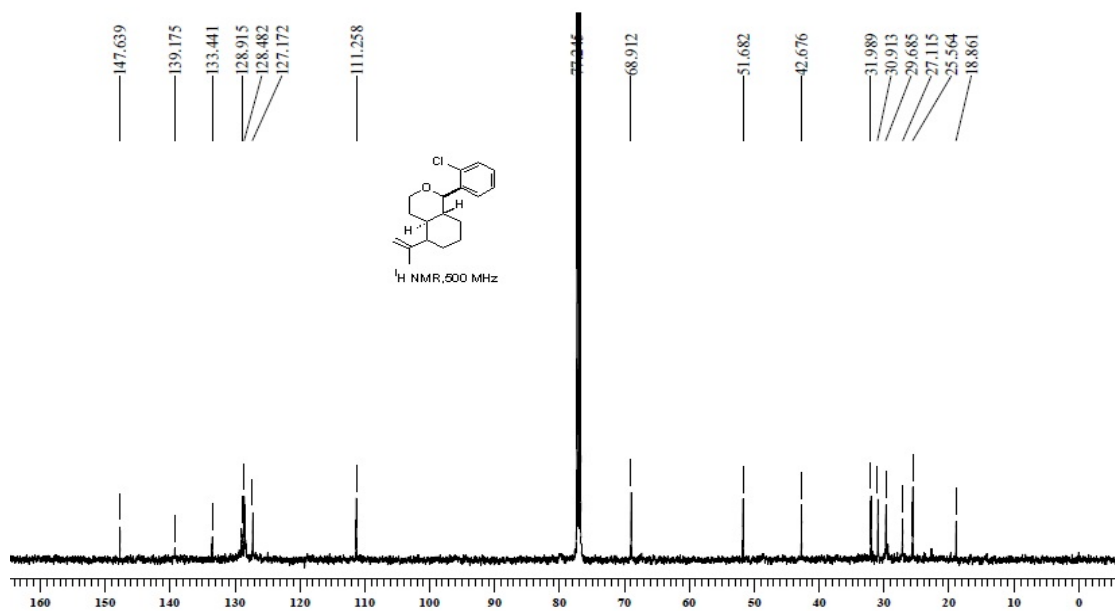
¹³C NMR spectrum of 3d (Table 2, entry 4)



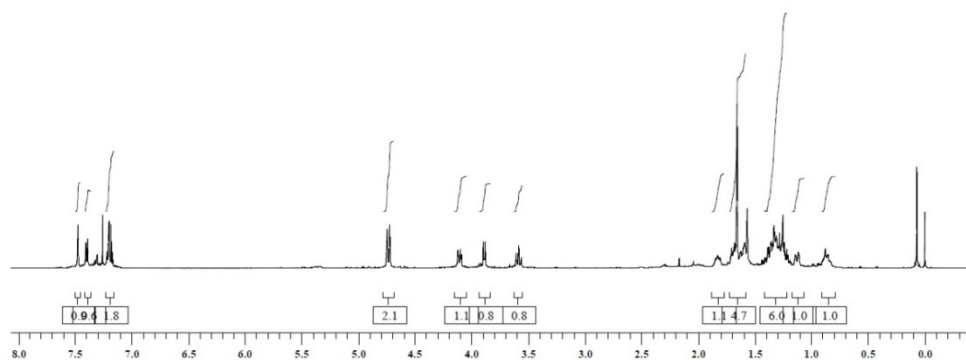
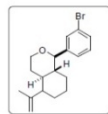
¹H NMR spectrum of 3e (Table 2, entry 5)



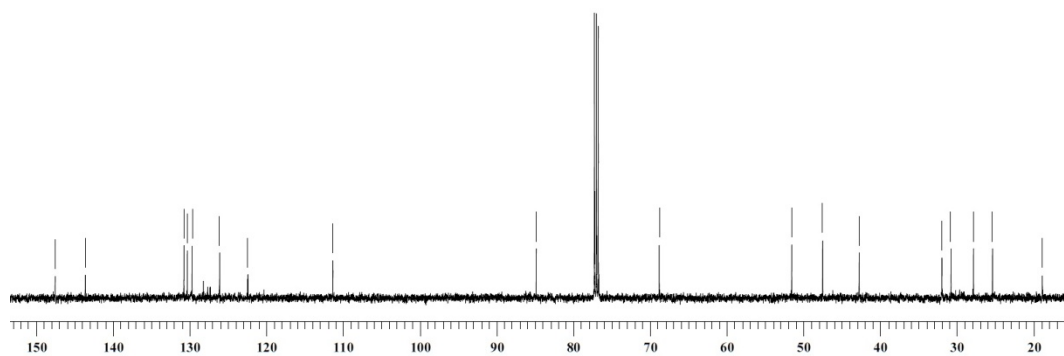
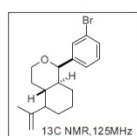
¹³C NMR spectrum of 3e (Table 2, entry 5)



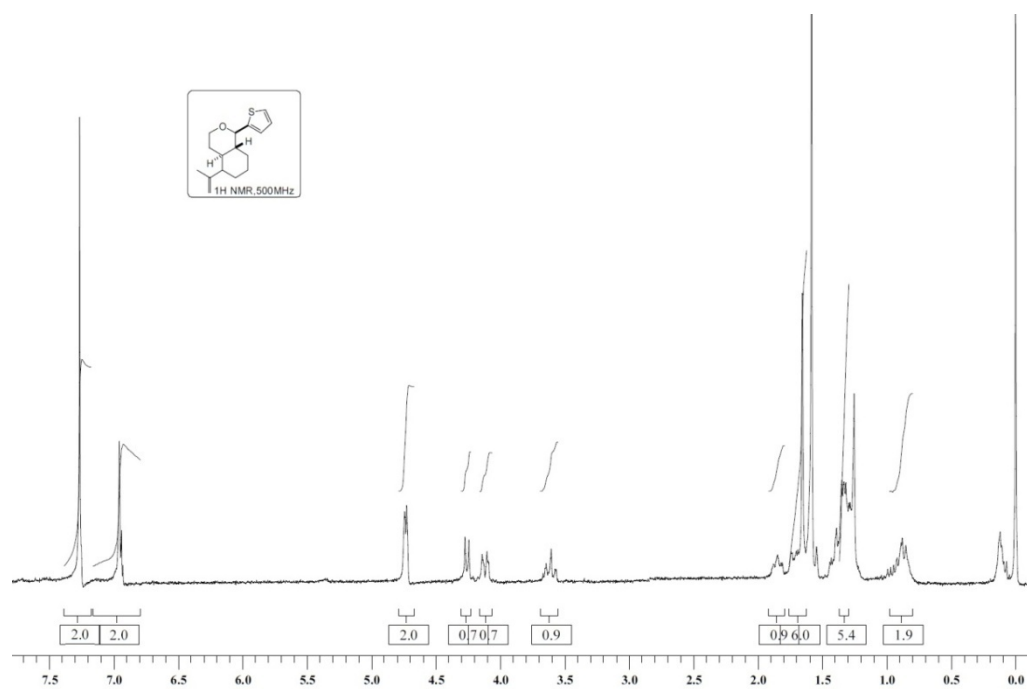
¹H NMR spectrum of 3f (Table 2, entry 6)



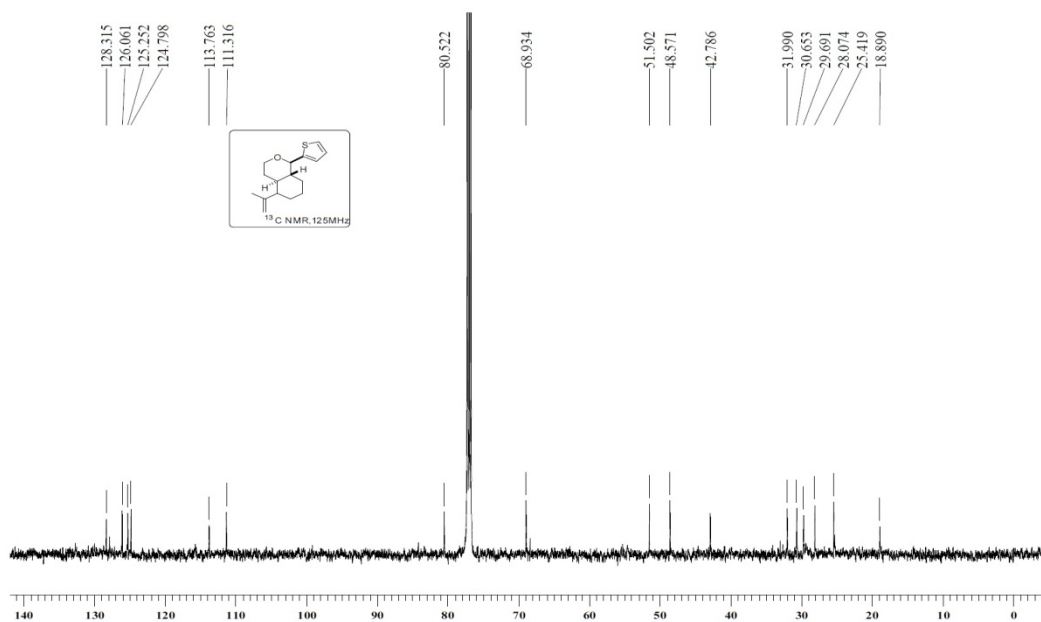
¹³C NMR spectrum of 3f (Table 2, entry 6)



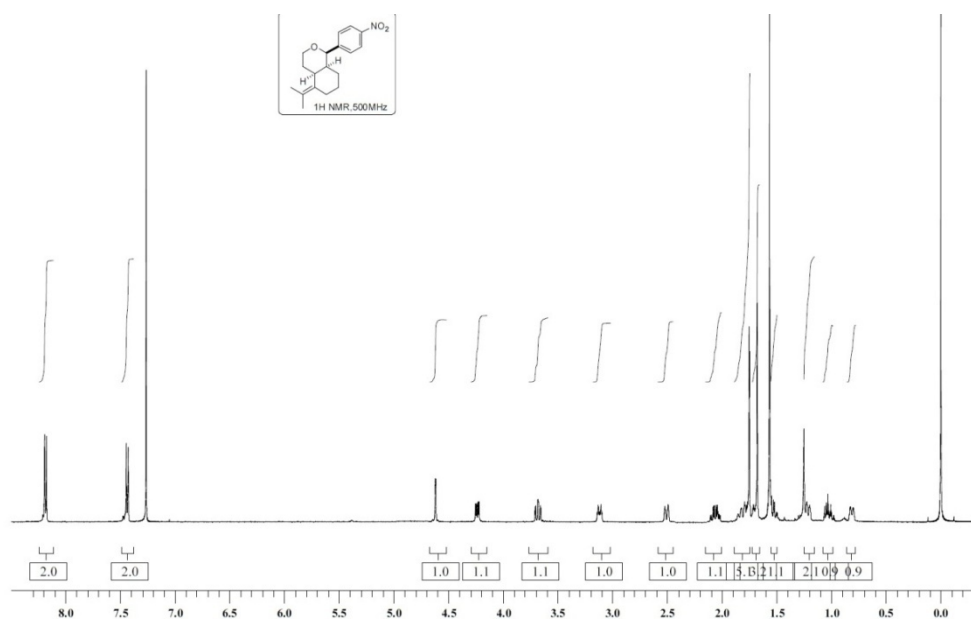
¹H NMR spectrum of 3g (Table 2, entry 7)



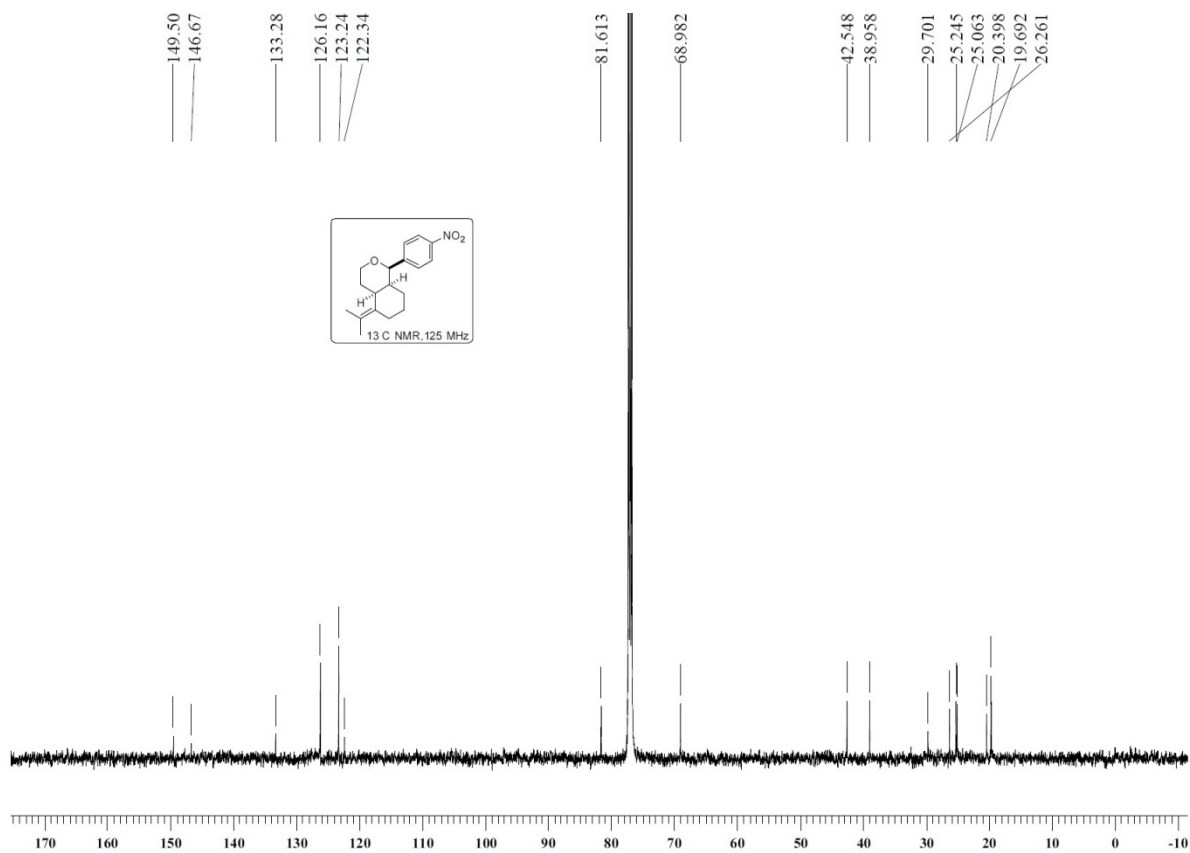
¹³C NMR spectrum of 3g (Table 2, entry 7)



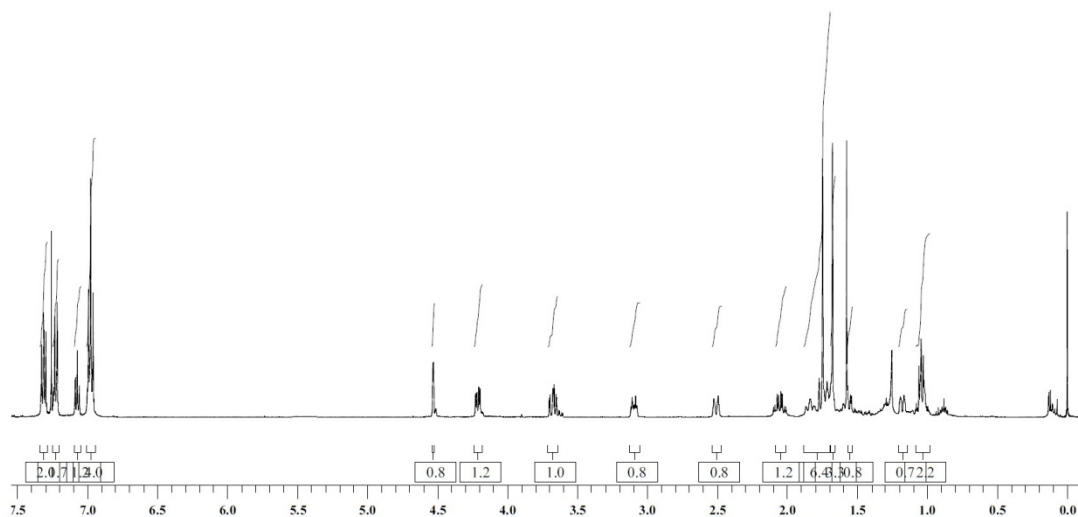
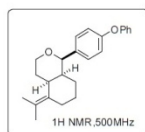
¹H NMR spectrum of 4h (Table 2, entry 8)



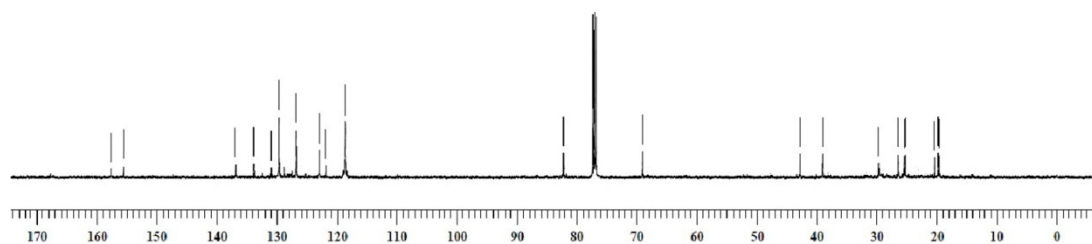
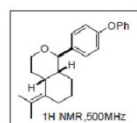
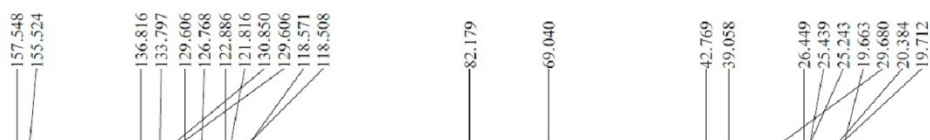
¹³C NMR spectrum of 4h (Table 2, entry 8)



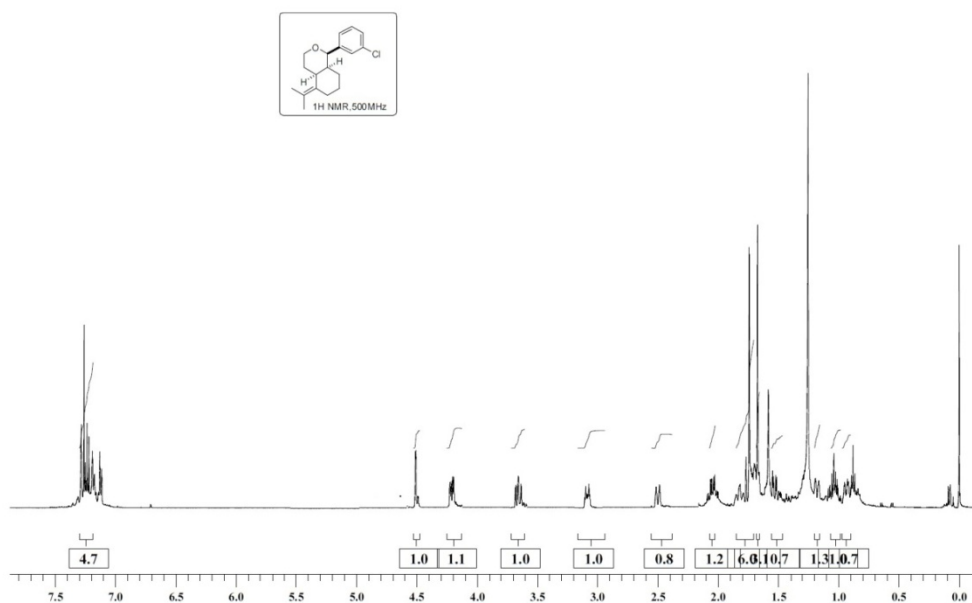
¹H NMR spectrum of 4i (Table 2, entry 9)



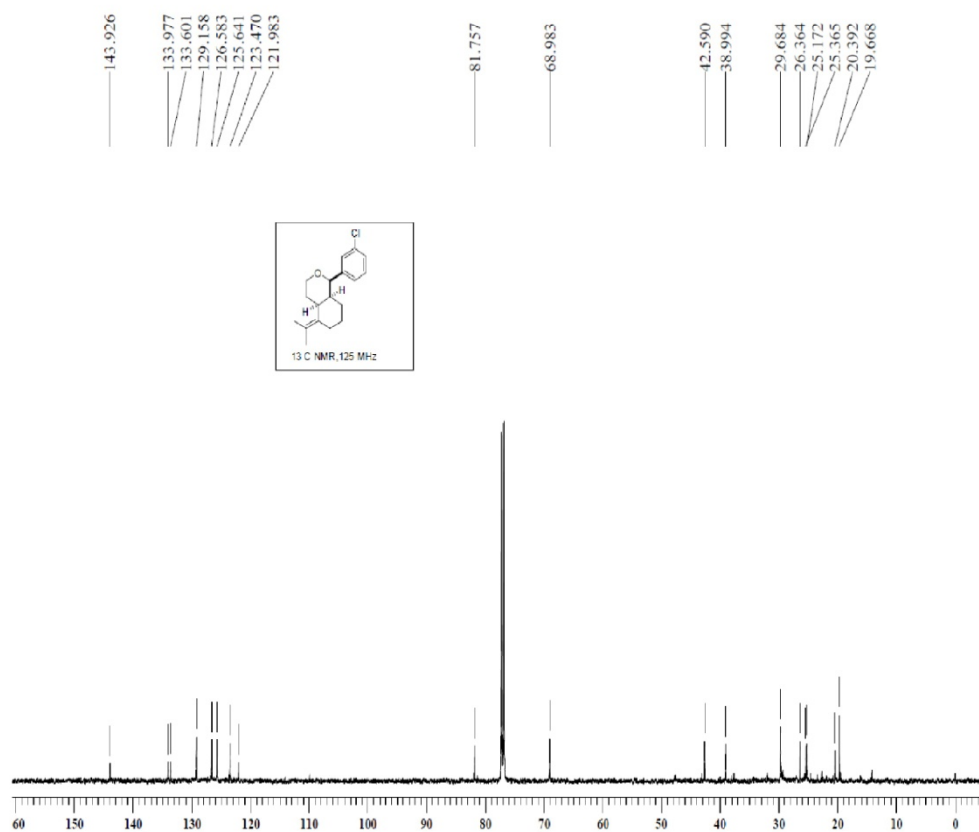
¹³C NMR spectrum of 4i (Table 2, entry 9)



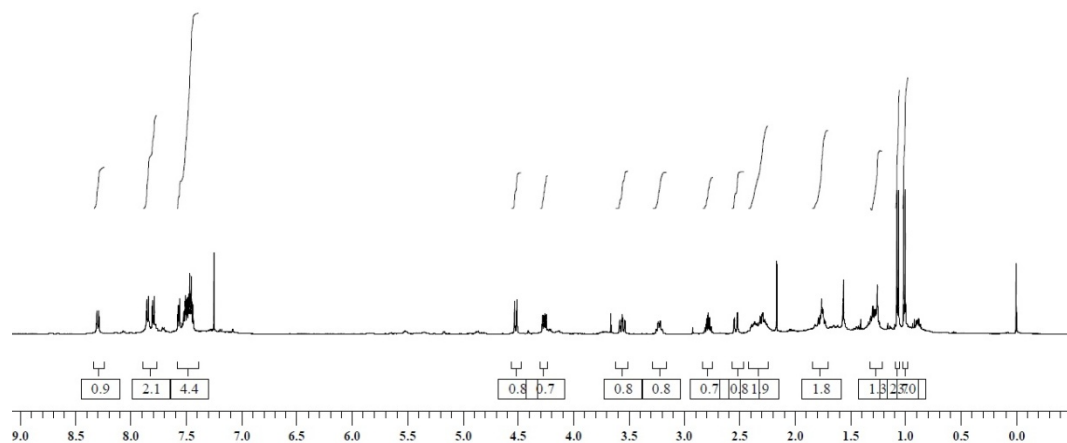
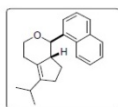
¹H NMR spectrum of 4j (Table 2, entry 10)



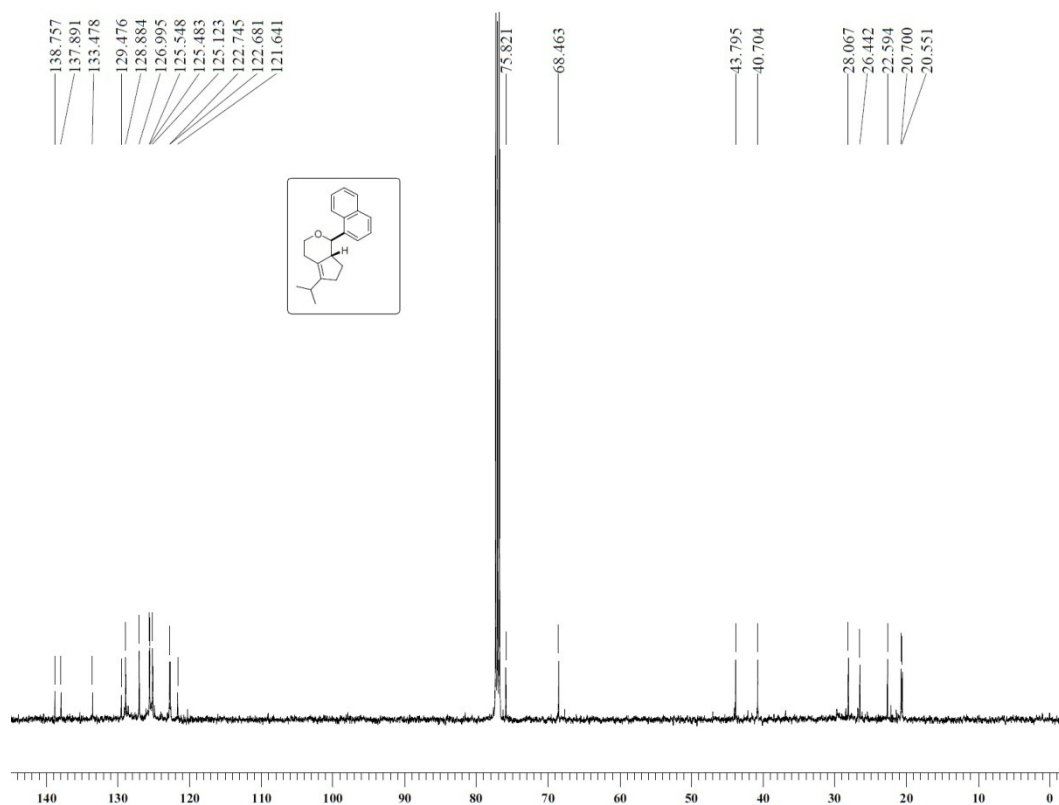
¹³C NMR spectrum of 4j (Table 2, entry 10)



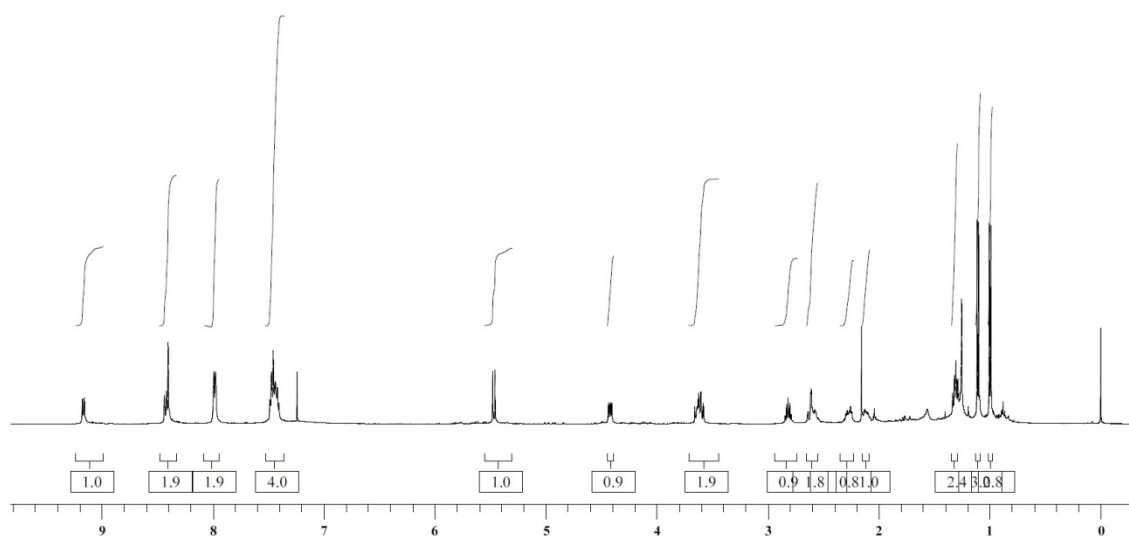
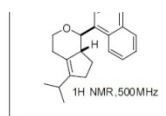
¹H NMR spectrum of 5a (Table 3, entry 1)



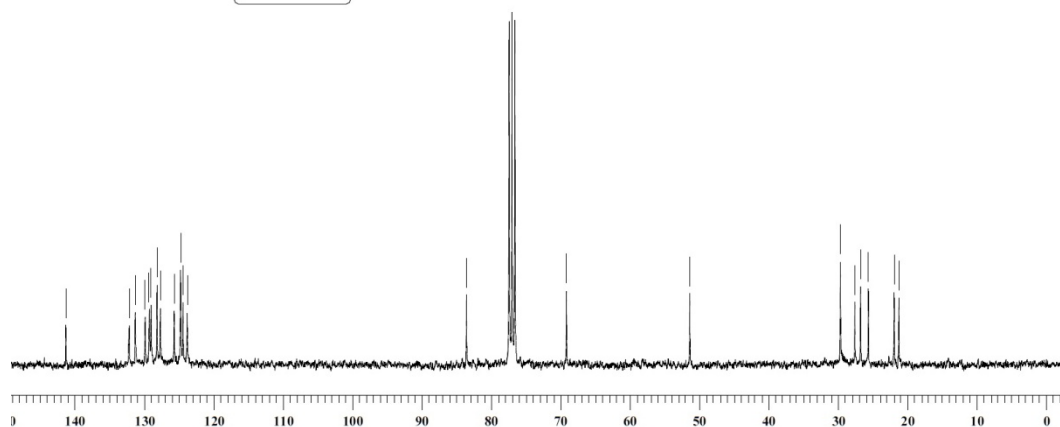
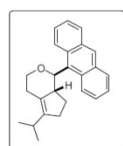
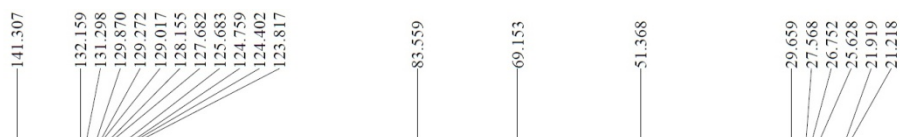
¹³C NMR spectrum of 5a (Table 3, entry 1)



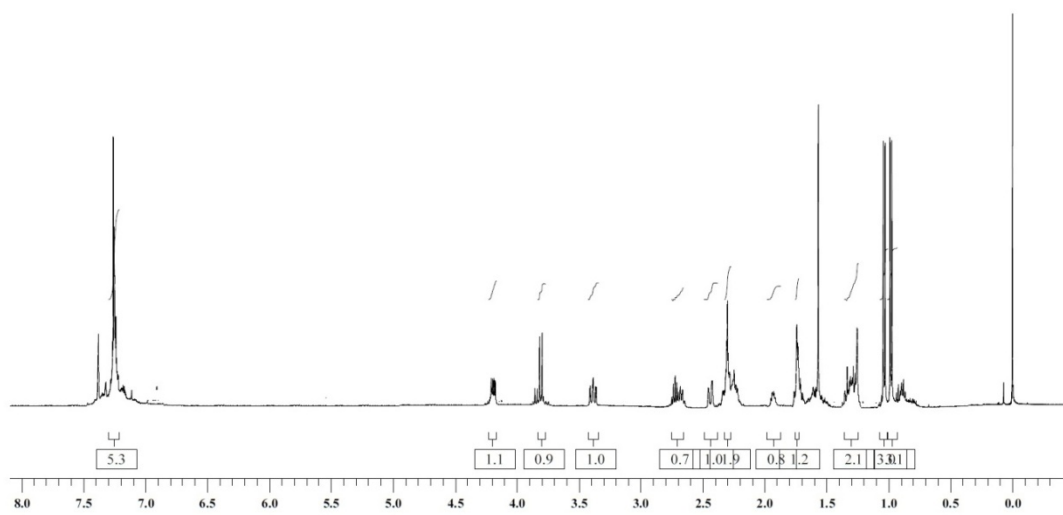
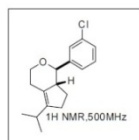
¹H NMR spectrum of 5b (Table 3, entry 2)



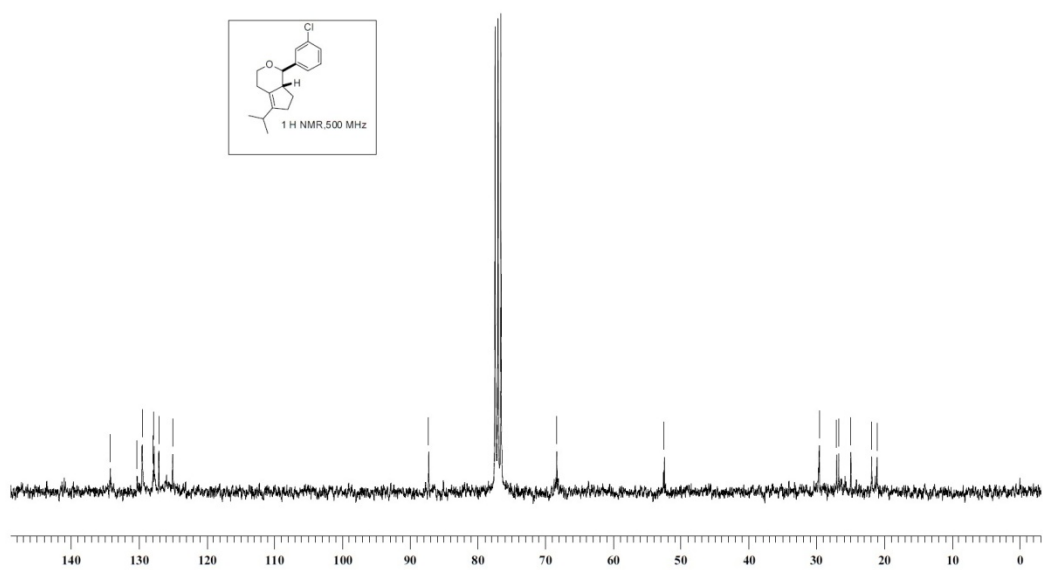
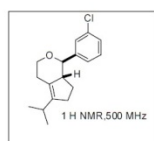
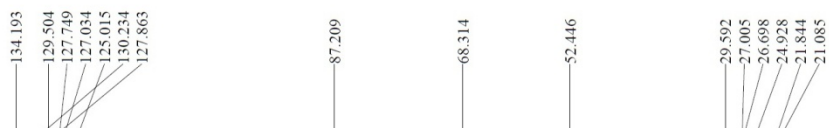
¹H NMR spectrum of 5b (Table 3, entry 2)



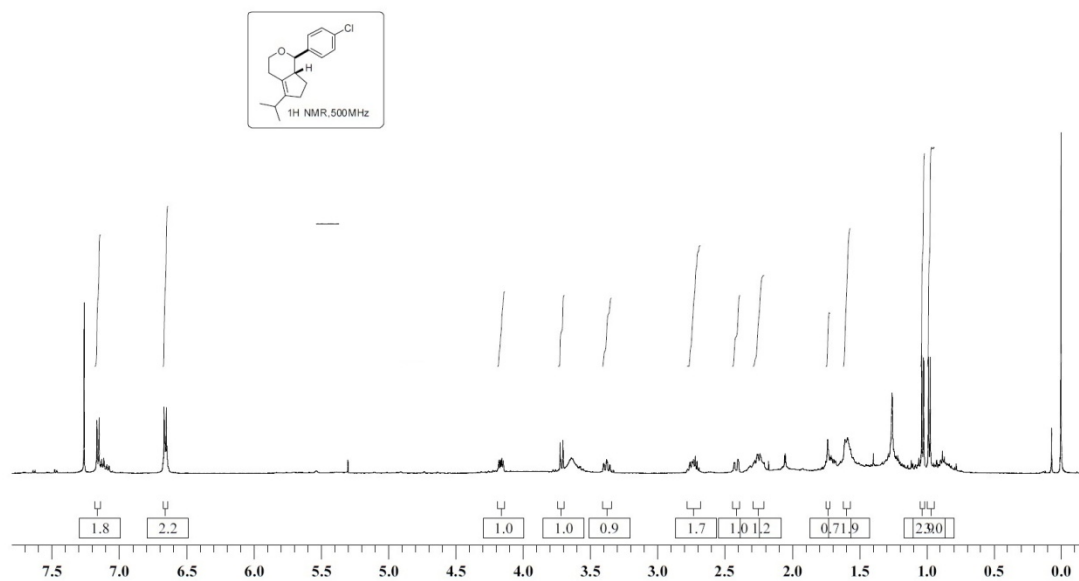
¹H NMR spectrum of 5c (Table 3, entry 3)



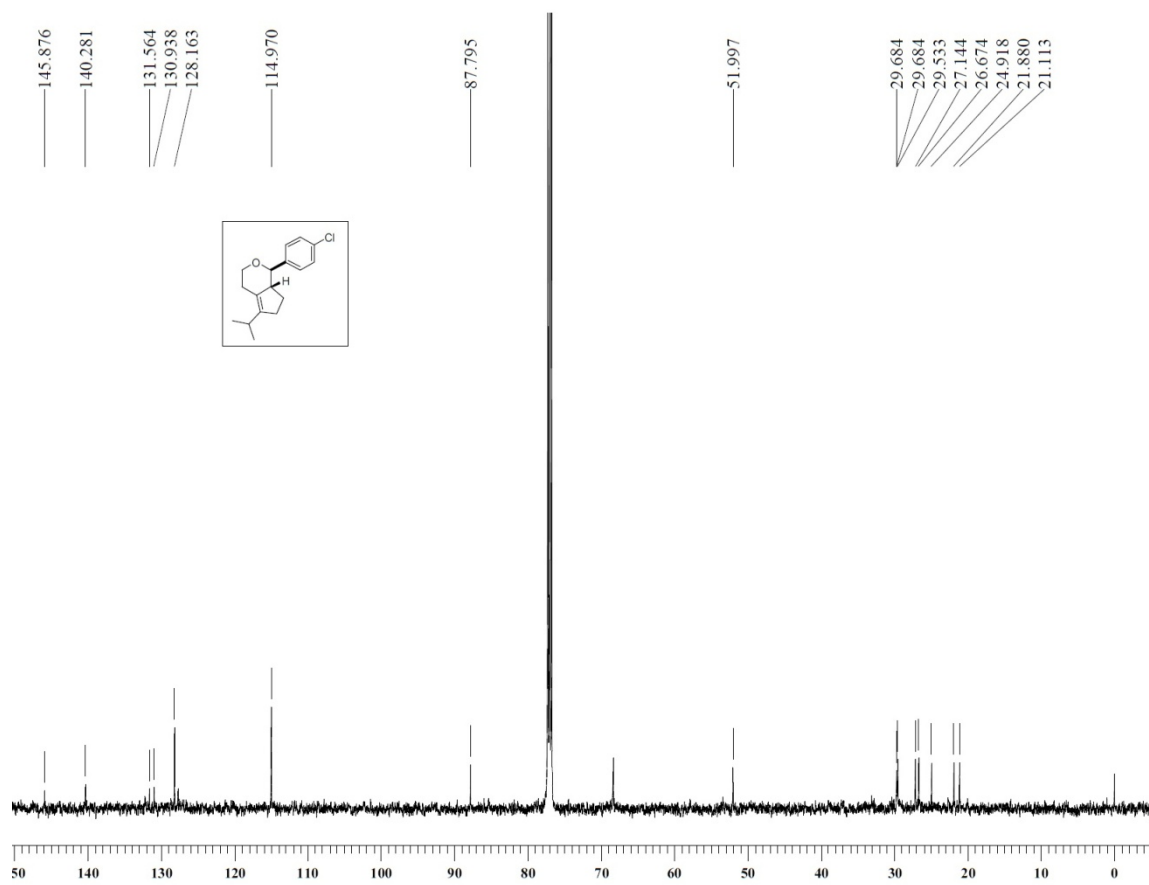
¹³C NMR spectrum of 5c (Table 3, entry 3)



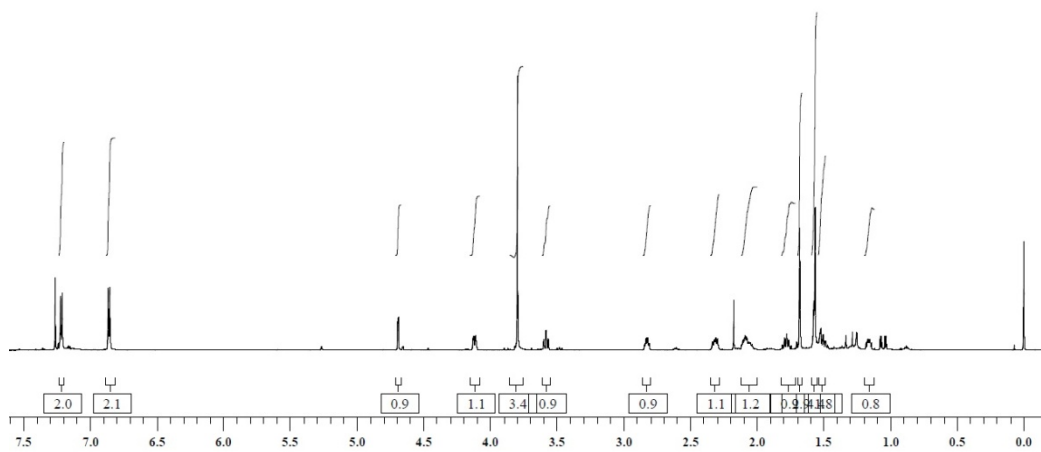
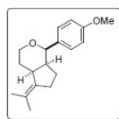
¹H NMR spectrum of 5d (Table 3, entry 4)



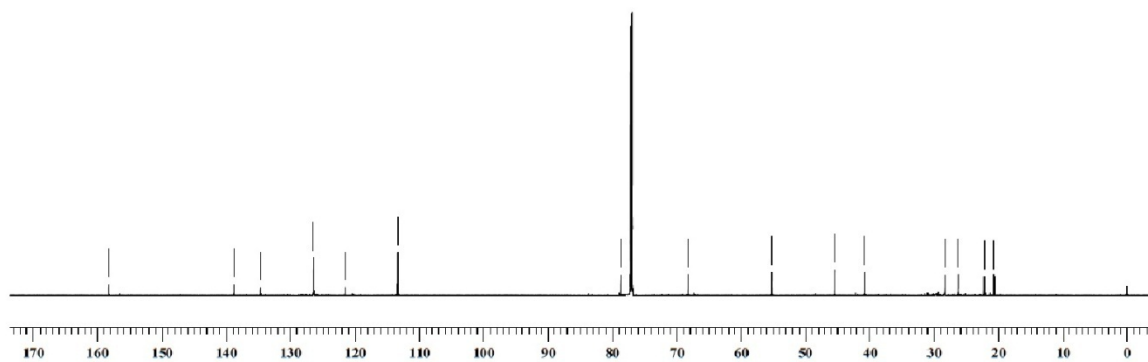
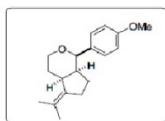
¹³C NMR spectrum of 5d (Table 3, entry 4)



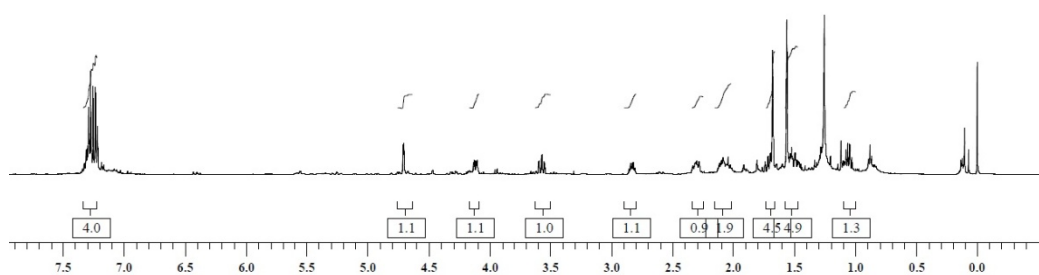
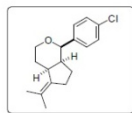
¹H NMR spectrum of 6e (Table 3, entry 5)



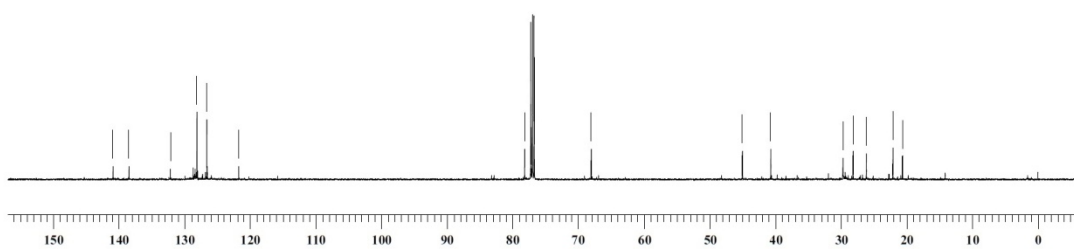
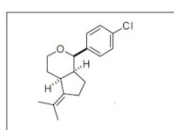
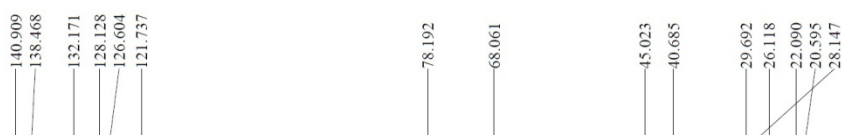
¹³C NMR spectrum of 6e (Table 3, entry 5)



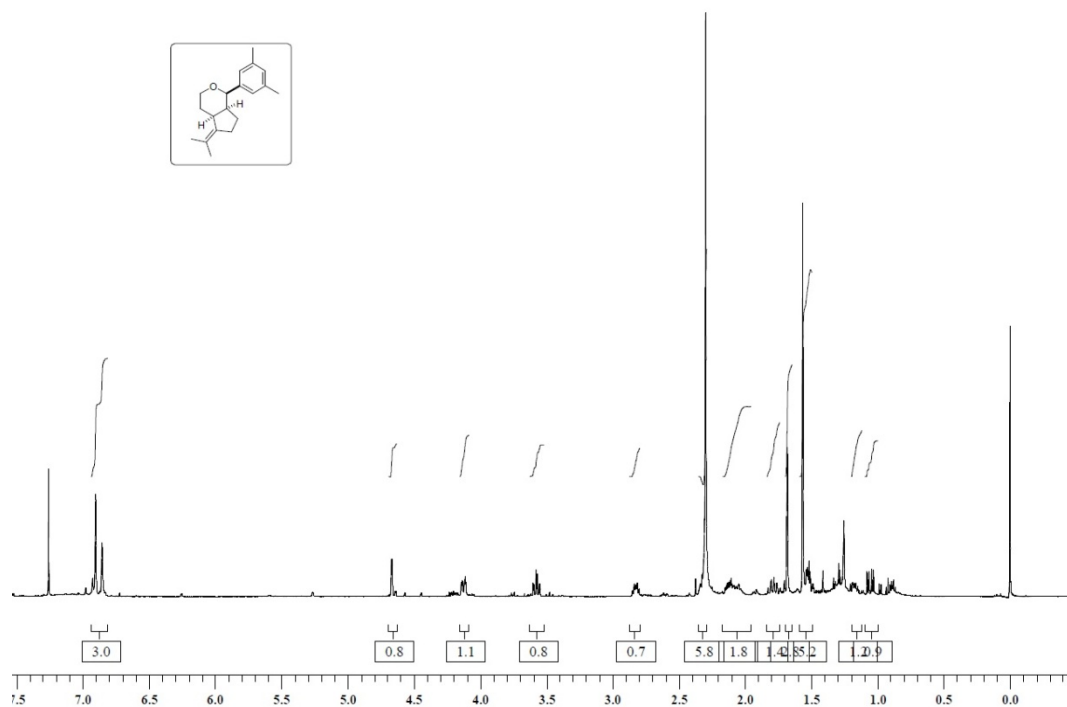
¹H NMR spectrum of 6f (Table 3, entry 6)



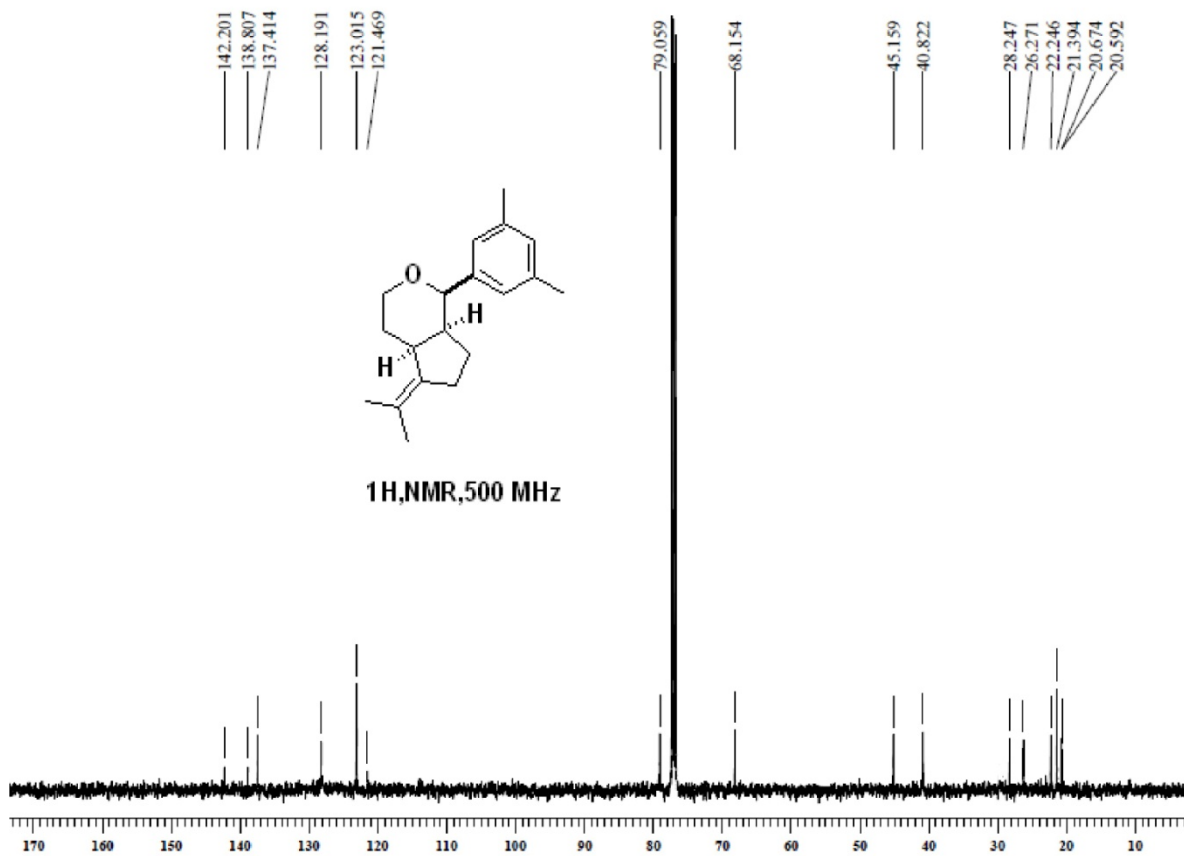
¹³C NMR spectrum of 6f (Table 3, entry 6)



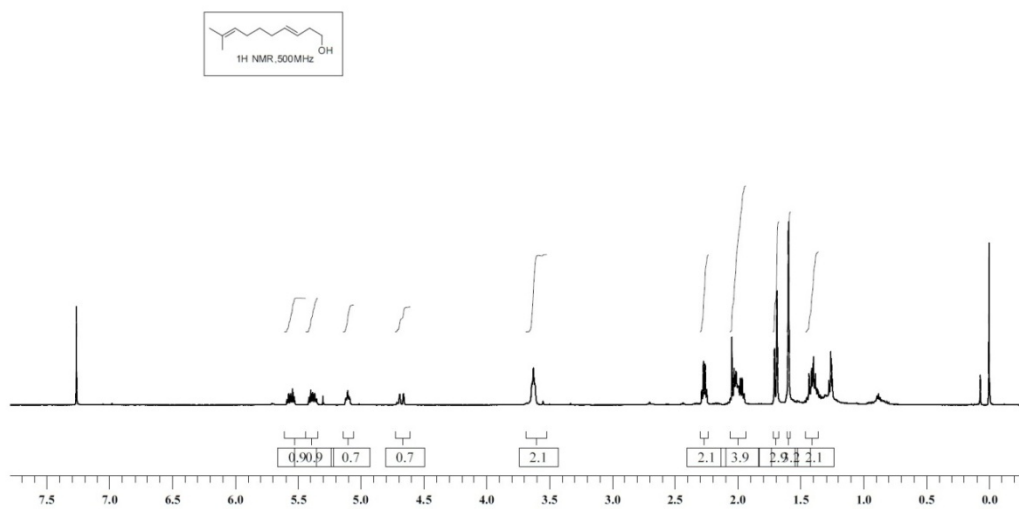
¹H NMR spectrum of 6g (Table 3, entry 7)



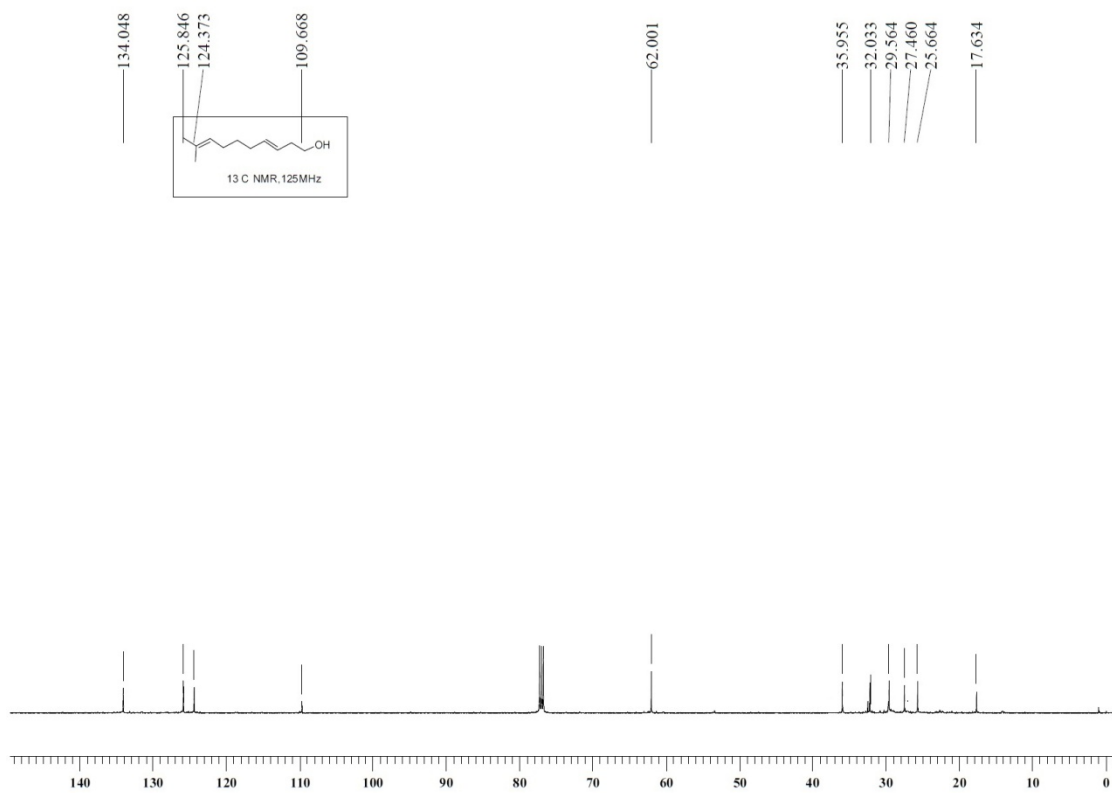
¹³C NMR spectrum of 6g (Table 3, entry 7)



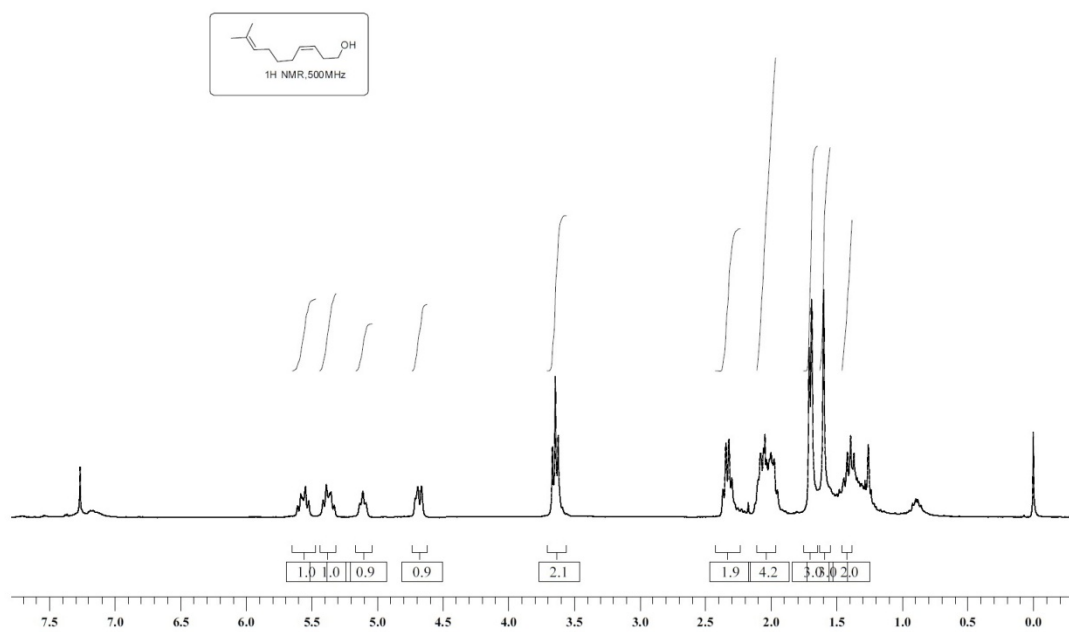
¹H NMR spectrum of E-(1a)



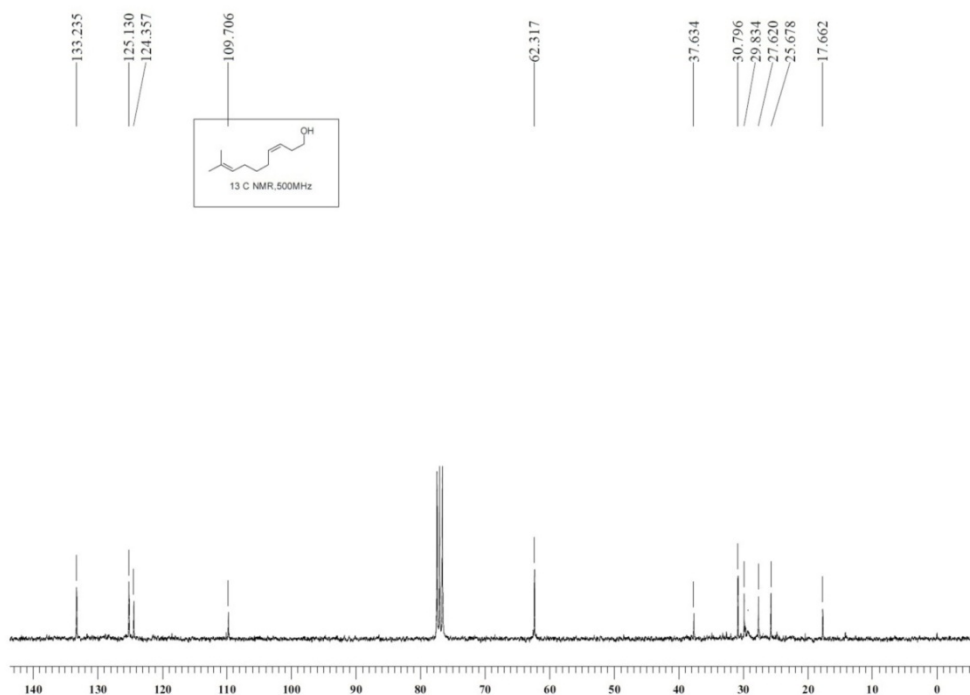
¹³C NMR spectrum of E-(1a)



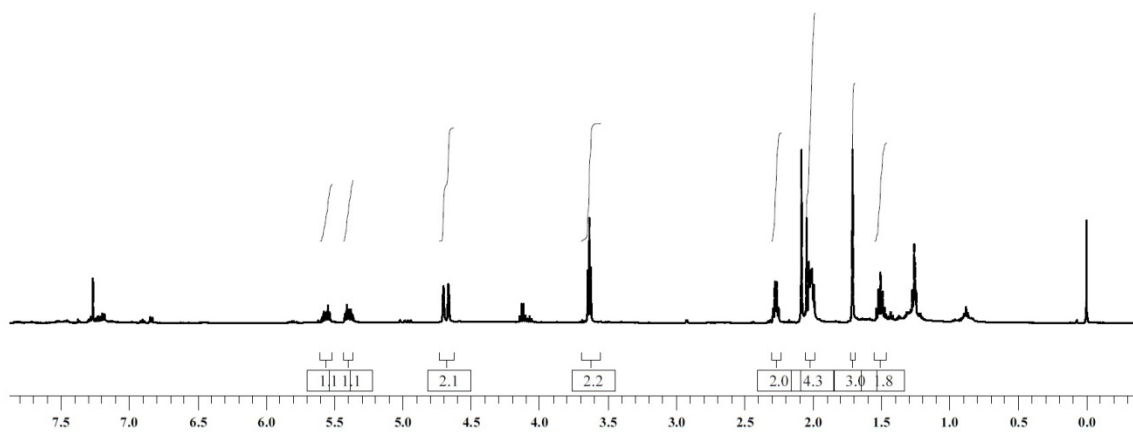
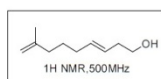
¹H NMR spectrum Z-(1a)



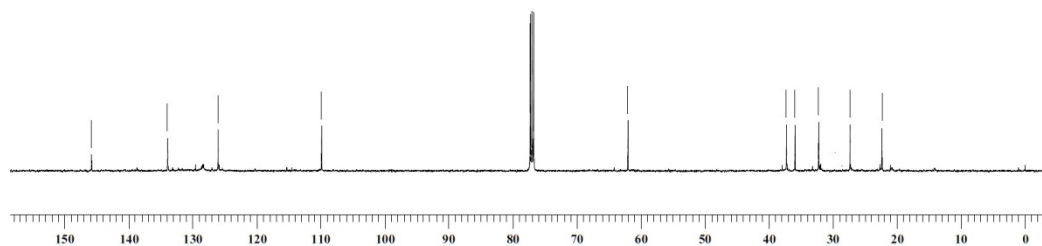
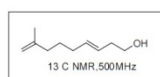
¹³C NMR spectrum Z-(1a)



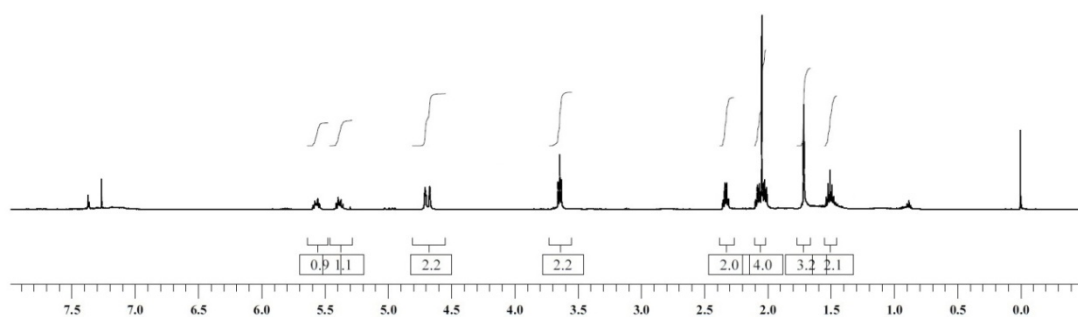
¹H NMR spectrum E-(1b)



¹³C NMR spectrum E-(1b)



¹H NMR spectrum Z-(1b)



¹³C NMR spectrum Z-(1b)

