Stereocontrol in an intermolecular Schmidt reaction of equilibrating hydroxyalkyl allylic azides

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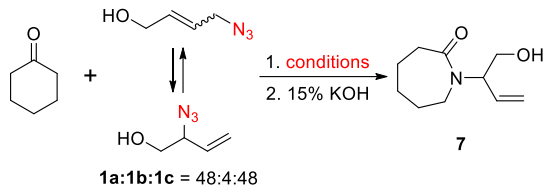
Contents

1. Reaction condition optimization

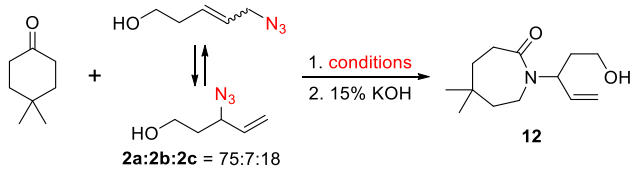
Table S1. Condition optimization for the Schmidt reaction of allylic azide **1**.[a]



Entry	Equiv. of allylic azide 1	Catalyst	Equiv. of Catalyst	Solvent	Isolated Yield
1	2.0	$SnCl_4$	3.0	DCM	45%
2	2.0	$SnCl_4$	3.0	DCE	61%
3	2.0	$BF_3{\cdot}Et_2O$	3.0	DCM	66%
4	2.0	$BF_3{\cdot}Et_2O$	3.0	DCE	50%
5	2.0	$TiCl_4$	3.0	DCM	35%
6	2.0	$TiCl_4$	3.0	DCE	30%
7	**2.0**	**$BF_3{\cdot}Et_2O$**	**3.0**	**HFIP**	**80%**
8	2.0	CF_3SO_3H	3.0	HFIP	60%
9	2.0	$TiCl_4$	3.0	HFIP	48%
10	2.0	$Ti[OCH(CF_3)_2]_4$	3.0	HFIP	54%
11	2.0	$(CF_3SO_2)_2NH$	3.0	HFIP	messy
12	2.0	$BF_3{\cdot}Et_2O$	1.5	HFIP	74%
13	1.5	$BF_3{\cdot}Et_2O$	1.1	HFIP	62%
14	1.5	$BF_3{\cdot}Et_2O$	1.3	HFIP	64%

[a] Conditions: 1. cyclohexanone (0.3 mmol, 1.0 equiv.), allylic azide **1**, catalyst, solvent (0.5 mL), 90 °C, 10-15 h; 2. 15% aq. KOH (5.4 mL/mmol).

Table S2. Condition optimization for the Schmidt reaction of allylic azide **2**.[a]



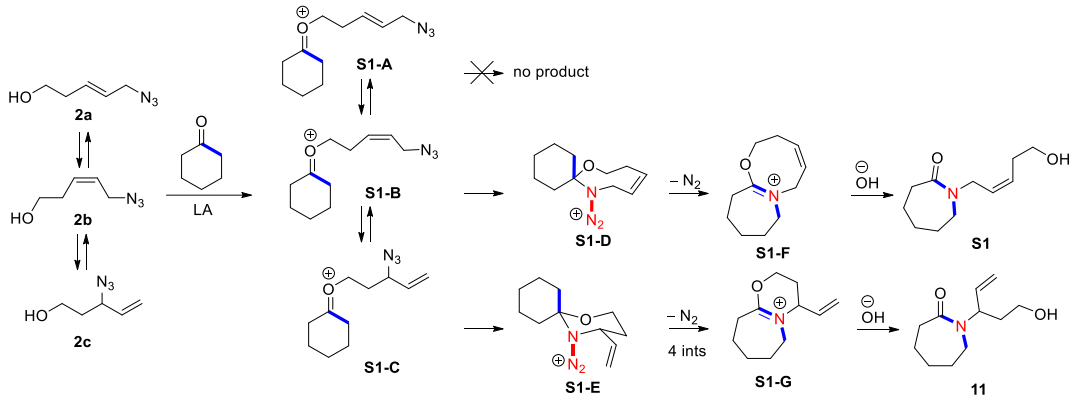
Entry	Catalyst	Equiv. of Catalyst	Isolated Yield
1	$BF_3{\cdot}Et_2O$	1.5	40%
2	$BF_3{\cdot}Et_2O$	3.0	40%
3	$SnCl_4$	1.5	46%
4	CF_3SO_3H	1.5	30%
5	$(CF_3SO_2)_2NH$	1.5	Messy
6	$TiCl_4$ (aq)	1.5	58%
7	$TiCl_4$	1.5	64%
8	**$Ti[OCH(CF_3)_2]_4$**	**1.5**	**81%**

[a] Conditions: 1. 4,4-dimethylcyclohexanone (0.3 mmol, 1.0 equiv.), allylic azide **2** (2.0 equiv.), catalyst, HFIP (0.5 mL), 90 °C, 10-15 h; 2. 15% aq. KOH (5.4 mL/mmol).

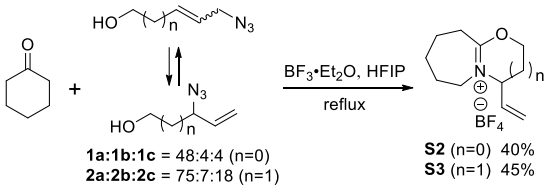
2. Detailed information of mechanistic insights and computational study

Mechanistically, all the isomers of allylic azide can react with ketone to form the dehydration intermediates under the acidic catalysis (Scheme S1, SI). The isomer **a**-derived dehydration intermediate cannot further form the hemiaminal due to the long distance between azide and oxonium ion. Similarly, the 8-memerbered ring hemiaminal derived from cis isomer **b** is difficult to be formed. The internal isomer **c** is perfect to afford the productive intermediate with 6-membered ring, and further ring expansion gives iminium ether, which is hydrolysed in basic condition to give *N*-hydroxyalk-1-en-3-yl lactam. The full conversion of allylic azides confirms that isomers **a** and **b** both rearrange to isomer **c** in this domino reaction, and the formation of lactams with chiral *N*-substituent increases the complexity of the original Schmidt products. The iminium ether tetrafluoroborates can be obtained with 40-45% yields if the hydrolysis is not conducted (Scheme S2, SI), further confirming the above mechanistic explanation.

Scheme S1. Pathways for 1,3-allylic rearrangement/Schmidt reactions of ketone.



Scheme S2. Syntheses of iminium ethers.

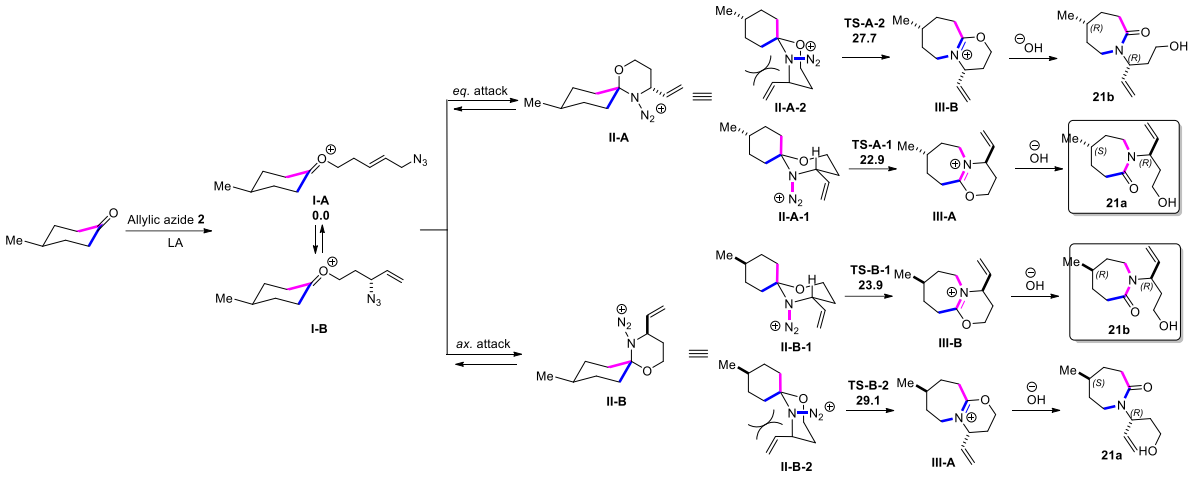


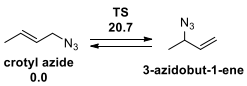
Computational study

All structures were optimized using B3LYP[S1] as implemented in GAUSSIAN16[S2] with the def2svp[S3] basis set including Grimme's D3 dispersion corrections[S4], along with treatment of solvent effects using the SMD[S5] solvation model. Experimentally, reactions were run in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), but calculations were conducted in 2,2,2-trifluoroethanol with eps=16.7 (dielectric constant of HFIP)[S6] and epsinf=1.626 (square of HFIP's refractive index 1.275). Based on the optimized structures, vibrational frequencies were calculated at the same level of theory to characterize the stationary points on the potential energy surface and evaluate zero-point vibrational energies (ZPVEs) and thermal Gibbs free energy corrections at 298.15 K. The single-point energies were computed at B3LYP-D3/def2-TZVP[S3,S7] level of theory, including HFIP effect. Gibbs free energies obtained at the B3LYP-D3/def2-TZVP/SMD(HFIP)//B3LYP-D3/def2-SVP/SMD(HFIP) level are discussed in the main text. Extensive conformational searches for intermediate **I-A** (Scheme S3**)** were conducted to ensure that the lowest energy conformers were located. Intrinsic reaction coordinate (IRC) calculations of the transition states were performed to verify their locations in the potential energy surface. The overall barrier from **I-A** to **TS-A-1** is 22.9 kcal/mol, which is higher than 20.7 kcal/mol

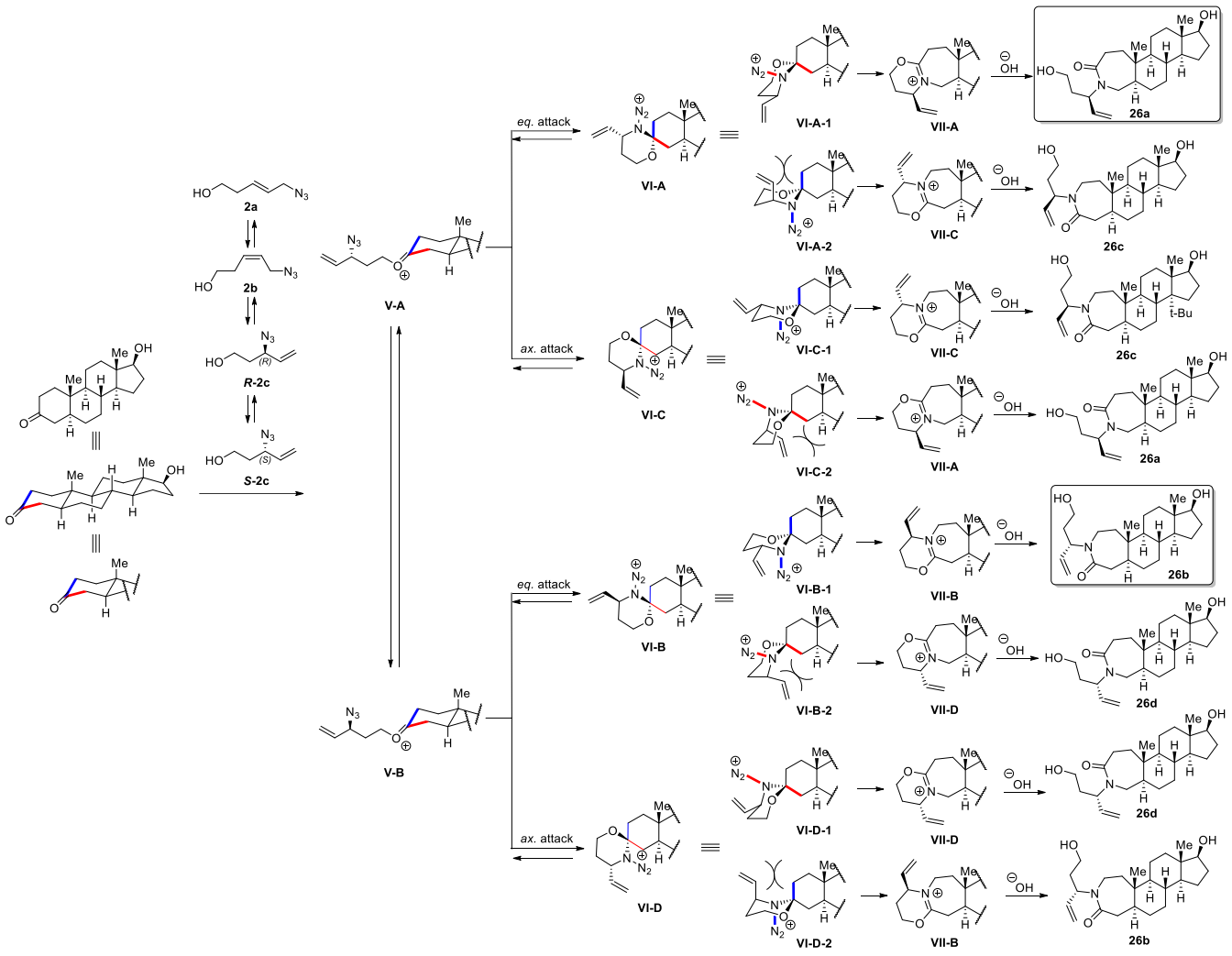
calculated for the allylic azide rearrangement, and therefore the overall diastereoselectivity is controlled by the alkyl migration/N_2 loss transition state structures.

Scheme S3. Pathways for 1,3-allylic rearrangement/Schmidt reactions of prochiral ketone.





Scheme S4. Pathways for 1,3-allylic rearrangement/Schmidt reactions of unsymmetrical ketone.


2a
2b
R-2c
S-2c
V-A
V-B
eq. attack
ax. attack
VI-A
VI-C
VI-B
VI-D
VI-A-1
VI-A-2
VI-C-1
VI-C-2
VI-B-1
VI-B-2
VI-D-1
VI-D-2
VII-A
VII-C
VII-B
VII-D
26a
26c
26d
26b

3. General information

NMR spectra was recorded on an Agilent DD2 400 MHz spectrometer in deuterated solvents (400 MHz for ^{1}H and 101 MHz for ^{13}C). Chemical shifts in ^{1}H NMR spectra are reported in ppm on the δ scale from an internal standard of TMS. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of deuterated solvents on the δ scale.

High resolution mass spectrometry (HRMS) was performed on Bruker UHR-TOF maXis and are reported as m/z. Infrared spectrometry (IR) was performed on Bruker Tensor 27 and are reported as cm^{-1}. Thin layer chromatography (TLC) was performed using TLC silica gel plates HSG F254 (Jiangyou) and visualized using UV light, or potassium permanganate. Silica gel column chromatography was carried out using 200-300 mesh silica gel (Jiangyou) on Biotage Isolera one.

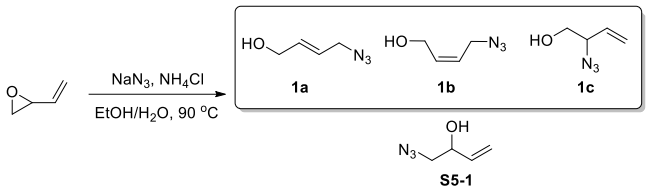
Dichloromethane, THF, and toluene were purified by passage through solvent purification columns. DCE was purchased as "Extra dry" from Energy Chemical. HFIP was purchased with 99.5% purity from Energy Chemical. Unless otherwise noted, all other purchased reagents and solvents were used as received, without further purification.

AZIDE SAFETY NOTICE:

Although organic azides are known to have the potentially explosive nature, no issues were encountered in the course of this work. Precautions are necessary to ensure the safe conditions of all the operations. All the azide-containing waste and aqueous solutions were treated with a large excess amount of aqueous sodium hypochlorite before pouring in the special waste containers. For the further information of azide safety, see the corresponding references.[S1]

4. Experimental Procedures

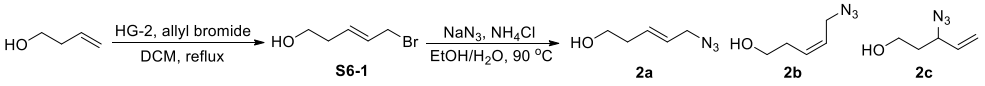
Scheme S5. Preparation of compound **1**.



(*E*)-4-Azidobut-2-en-1-ol (**1a**), **(*Z*)-4-azidobut-2-en-1-ol** (**1b**), **2-azidobut-3-en-1-ol** (**1c**), and **1-azidobut-3-en-2-ol** (**S5-1**).[S8] To a solution of 2-vinyloxirane (2.16 g, 30.8 mmol) and ammonium chloride (4.92 g, 92.4 mmol) in a mixed solvent of ethanol (88 mL) and water (11 mL), was added sodium azide (3.00 g, 46.1 mmol). The resulting mixture was refluxed for 16 h. After cooling to room temperature, water and ethyl acetate were added. After separation, the aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated. The residue was purified by silica gel column chromatography (10 – 20% EtOAc/PE) to afford **S5-1** (70 mg, 2%) as a colorless oil and a mixture of azides **1a**, **1b** and **1c** (1.57 g, 45%, 48:4:48 ratio) as a colorless oil. Azide **1a**, **1b** and **1c**: R_f = 0.25 (20% EtOAc/PE). Azide **1a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 – 5.88 (m, 1H), 5.80 – 5.73 (m, 1H), 4.19 (d, *J* = 6.4 Hz, 2H), 3.79 (d, *J* = 6.4 Hz, 2H), 2.28 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 124.1, 62.5, 52.2. Azide **1b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (d, *J* = 6.8 Hz, 2H), 3.87 (d, *J* = 6.8 Hz, 2H), 2.12 (br, 1H). Azide **1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.73 (m, 1H), 5.43 – 5.36 (m, 2H), 4.07 – 4.03 (m, 1H), 3.67 – 3.63 (m, 1H), 3.57 – 3.53 (m, 1H), 2.54 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 120.2, 66.4, 64.6. Azide **S5-1**: R_f = 0.40 (20% EtOAc/PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.85 (m, 1H), 5.41 (dt, *J* = 17.2 Hz, 1.2 Hz, 1H), 5.28 (dt, *J* = 10.4 Hz, 1.2 Hz, 1H), 4.34 (br, 1H), 3.40 (dd, *J* = 3.6 Hz, 12.3 Hz, 1H), 3.33 (dd, *J* = 7.2 Hz, 12.3 Hz, 1H), 2.08 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 117.2, 72.0, 56.4.

Scheme S6. Preparation of compound **2**.

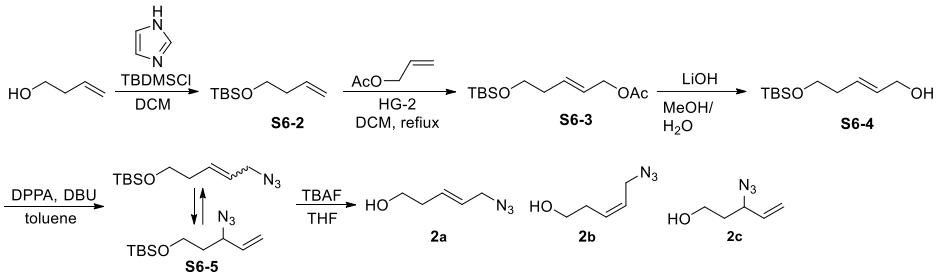
Method I:



5-Bromopent-3-en-1-ol (**S6-1**). To a solution of Hoveyda-Grubbs catalyst 2nd generation (HG-2, 0.17 mmol) in dichloromethane (5 mL) under N_2 atmosphere at room temperature was added a solution of but-3-en-1-ol (500 mg, 6.93 mmol) and allyl bromide (2.5 g, 20.8 mmol) in dichloromethane (10 mL) slowly. The reaction mixture was stirred overnight. The solvent was concentrated in vacuum and the residue was purified by chromatography (0 – 20% EtOAc/PE) to afford bromide **S6-1** (285 mg, 25%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 – 5.70 (m, 2H), 3.94 (d, *J* = 6.5 Hz, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.93 (br, 1H), 2.34 (q, *J* = 6.1 Hz, 2H).

(*E*)-5-Azidopent-3-en-1-ol (**2a**), **(*Z*)-5-azidopent -3-en-1-ol** (**2b**) and **3-azidopent-4-en-1-ol** (**2c**). Following the procedure of Liu et al.,[S9] to a solution of the above bromide **S6-1** (285 mg, 1.74 mmol) and ammonium chloride (279 mg, 5.21 mmol) in a mixed solvent of ethanol (32 mL) and water (4 mL), was added sodium azide (170 mg, 2.61 mmol). The resulting mixture was refluxed overnight. After cooling to room temperature, water and ethyl acetate were added. After separation, the aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated. The residue was purified by silica gel column chromatography (10 – 30% EtOAc/PE) to afford a mixture of azides **2a**, **2b** and **2c** (88 mg, 40%, 75:7:18 ratio) as a colorless oil.

Method II:



(But-3-en-1-yloxy)(*tert*-butyl)dimethylsilane (**S6-2**). To a cooled solution of but-3-en-1-ol (20.0 g, 0.277 mol) in dry CH_2Cl_2 (500 mL) at 0 °C was added imidazole (32.1 g, 0.471 mol), and the resulting mixture was stirred for 10 min. To this solution was added *tert*-butyldimethylchlorosilane (56.9 g, 0.377 mol), and the resulting mixture was stirred overnight at room temperature. After completion of the reaction, the reaction was diluted with water and extracted into dichloromethane. The organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (0 – 3% DCM/PE) to afford **S6-2** (29.0 g, 56%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 – 5.61 (m, 1H), 5.24 – 4.86 (m, 2H), 3.65 (t, *J* = 6.8 Hz, 2H), 2.27 (q, *J* = 6.8 Hz, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-yl acetate (**S6-3**). To a solution of Hoveyda-Grubbs catalyst 2nd generation (HG-2, 0.67 mmol) in dichloromethane (45 mL) under N_2 atmosphere at room temperature was added a solution of **S6-2** (5.00 g, 26.8 mmol) and allyl acetate (13.4 g, 134 mmol) in dichloromethane (45 mL) slowly. The reaction mixture was stirred overnight. The solvent was concentrated in vacuum and the residue was purified by chromatography to afford **S6-3** (4.83 g, 70%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.70 (m, 1H), 5.67 – 5.55 (m, 1H), 4.49 (d, *J* = 6.3 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.26 (q, *J* = 6.7 Hz, 2H), 2.04 (s, 3H), 0.87 (s, 9H), 0.03 (s, 6H).

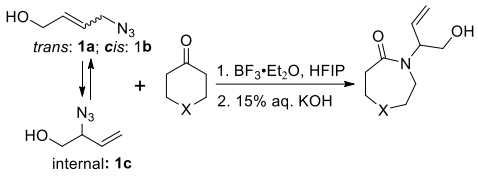
(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-ol (**S6-4**)**.** To a solution of **S6-3** (8.30 g, 32.1 mmol) in a mixed solvent of methanol (70 mL) and water (23 mL) was added lithium hydroxide monohydrate (6.74 g, 160 mmol) at room temperature until **S6-3** was consumed. The reaction was quenched by the addition of saturated ammonium chloride solution. The resulting solution was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum to give alcohol **S6-4** (6.2 g, 90%) as a colorless oil without further purification.

(*E*)-((5-Azidopent-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (**S6-5a**), **(*Z*)-((5-azidopent-3-en-1-yl) oxy)(*tert*-butyl)dimethylsilane** (**S6-5b**) and **((3-azidopent-4-en-1-yl)oxy)(*tert*-butyl)dimethylsilane** (**S6-5c**). A mixture of the above alcohol **S6-4** (6.20 g, 28.7 mmol) and DPPA (18.9 g, 68.8 mmol) was dissolved in dry toluene (60 mL). The mixture was cooled to 0 ℃ under N_2 and neat DBU (10.5 g, 68.8 mmol) was added. The reaction mixture was stirred overnight at room temperature. To the reaction mixture was added hydrochloric acid (0.1 M) dropwise until colorless. The resulting mixture was partitioned between ethyl acetate and brine, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (0 – 5% EtOAc/PE) to afford a mixture of **S6-5a**, **S6-5b** and **S6-5c** (2.40 g, 35%, 50:18:32 ratio) as a colorless oil. Azide **6-5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.70 (m, 1H), 5.64 – 5.51 (m, 1H), 3.73 – 3.68 (m, 2H), 3.67 – 3.63 (m, 2H), 2.31 (tdd, *J* = 7.9, 6.1, 1.2 Hz, 2H), 0.88 (s, 9H), 0.04 (s, 6H). Azide **6-5b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (d, *J* = 7.4 Hz, 1H). Azide **6-5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.70 (m, 1H), 5.33 – 5.23 (m, 2H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.68 – 3.60 (m, 2H), 1.71

(dt, *J* = 6.9, 5.8 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H).

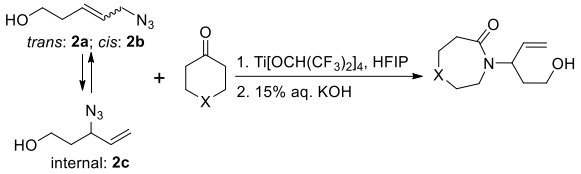
(*E*)-5-Azidopent-3-en-1-ol (**2a**), **(*Z*)-5-azidopent -3-en-1-ol** (**2b**) and **3-azidopent-4-en-1-ol** (**2c**). To a solution of **S6-5** (2.40 g, 9.94 mmol) in dry THF (50 mL) was added tetrabutylammonium fluoride (1 mol/L in THF, 19.9 mL, 19.9 mmol) and stirred for 5 h at room temperature. The reaction was quenched by addition of saturated ammonium chloride solution. The resulting solution was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (10 – 30% EtOAc/PE) to afford a mixture of azides **2a**, **2b** and **2c** (945 mg, 75%, 75:7:18 ratio) as a colorless oil. R_f = 0.45 (30% EtOAc/PE). Azide **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.73 (m, 1H), 5.69 – 5.60 (m, 1H), 3.75 (d, *J* = 6.4 Hz, 2H), 3.69 (q, *J* = 6.0 Hz, 2H), 2.36 (q, *J* = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 125.7, 61.71, 52.7, 35.5. Azide **2b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 124.9, 61.78, 47.2, 30.9. Azide **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 17.2, 10.2, 7.7 Hz, 1H), 5.34 (dt, *J* = 11.1, 1.0 Hz, 1H), 5.31 (dt, *J* = 4.1, 0.9 Hz, 1H), 4.10 (q, *J* = 7.4 Hz, 1H), 3.80 – 3.68 (m, 2H), 2.00 (t, *J* = 4.5 Hz, 1H), 1.81 – 1.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 118.5, 62.3, 59.3, 36.7.

General procedure A: Schmidt reaction of allyllic azides 1.



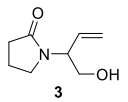
Under argon atmosphere, to a solution of allylic azides (0.6 mmol, 2.0 equiv.) and cyclic ketone (0.3 mmol, 1.0 equiv.) in HFIP (0.5 mL) was added BF_3•Et_2O (0.9 mmol, 3.0 equiv.) dropwise. The reaction mixture was heated to reflux for 10-15 h. After cooling to room temperature, the resulting mixture was treated with an aqueous solution of 15% KOH (5.4 mL/mmol) and was stirred vigorously at room temperature for 1 h. Then the reaction mixture was poured into water and extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography (0 – 5% MeOH/DCM) to afford a target product.

General procedure B: Schmidt reaction of allyllic azides 2.



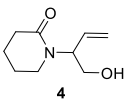
Preparation of $Ti[OCH(CF_3)_2]_4$: To a cooled solution of excessive HFIP at 0 ℃ was added $TiCl_4$ (1 mol/L in DCM) dropwise and stirred for 7 h at room temperature. The residue was concentrated under vacuum to give $Ti[OCH(CF_3)_2]_4$ as a brown oil without further purification.

Under argon atmosphere, to a solution of allylic azides (0.6 mmol, 2.0 equiv.) and cyclic ketone (0.3 mmol, 1.0 equiv.) in HFIP (0.5 mL) was added $Ti[OCH(CF_3)_2]_4$ (0.45 mmol, 1.5 equiv.) dropwise. The reaction mixture was heated to reflux for 10-15 h. After cooling to room temperature, the resulting mixture was treated with an aqueous solution of 15% KOH (5.4 mL/mmol) and was stirred vigorously at room temperature for 1 h. Then the reaction mixture was poured into water and extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography (0 – 5% MeOH/DCM) to afford a target product.



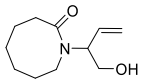
3

1-(1-Hydroxybut-3-en-2-yl)pyrrolidin-2-one (**3**). According to General procedure A, a mixture of cyclobutanone (38.8 mg, 0.554 mmol), allylic azides **1** (125 mg, 1.11mmol) and BF_3•Et_2O (236 mg, 1.66 mmol) in dry HFIP (1.0 mL) afforded the title product **3** (64.1 mg, 75%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3738, 3610, 3210, 3111, 2906, 2405, 1517 cm^{-1}; HRMS (ESI) m/z calculated for $C_8H_{14}NO_2$ $(M+H)^+$: 156.1019, Found: 156.1021; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (ddd, *J* = 17.0, 10.5, 6.1 Hz, 1H), 5.27 – 5.12 (m, 2H), 4.55 – 4.46 (m, 1H), 3.85 (br, 1H), 3.77 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.71 – 3.64 (m, 1H), 3.48 – 3.37 (m, 1H), 3.37 – 3.29 (m, 1H), 2.45 – 2.35 (m, 2H), 2.08 – 1.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.19, 132.39, 118.02, 62.33, 56.97, 44.64, 31.47, 18.21.



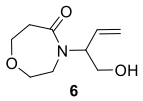
4

1-(1-Hydroxybut-3-en-2-yl)piperidin-2-one (**4**). According to General procedure A, a mixture of cyclopentanone (43.7 mg, 0.519 mmol), allylic azides **1** (117 mg, 1.04 mmol) and BF_3•Et_2O (221 mg, 1.56 mmol) in dry HFIP (1.0 mL) afforded the title product **4** (48.0 mg, 55%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3640, 3480, 3305, 3088, 2943, 2393 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{15}NNaO_2$ $(M+Na)^+$: 192.0995, Found: 192.1000; ^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 16.6, 10.6, 5.7 Hz, 1H), 5.25 – 5.07 (m, 2H), 5.04 – 4.94 (m, 1H), 3.87 (br, 1H), 3.78 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.70 (dd, *J* = 11.5, 8.8 Hz, 1H), 3.27 – 3.15 (m, 2H), 2.46 – 2.34 (m, 2H), 1.86 – 1.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.31, 132.83, 117.85, 61.96, 58.51, 43.93, 32.42, 23.06, 20.76.



5

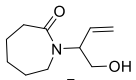
1-(1-Hydroxybut-3-en-2-yl)azocan-2-one (**5**). According to General procedure A, a mixture of cycloheptanone (43.7 mg, 0.519 mmol), allylic azides **1** (117 mg, 1.04 mmol) and BF_3•Et_2O (221 mg, 1.56 mmol) in dry HFIP (1.0 mL) afforded the title product **5** (40.8 mg, 40%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3752, 3445, 3103, 3008, 2381, 1634 cm^{-1}; HRMS (ESI) m/z calculated for $C_{11}H_{20}NO_2$ $(M+H)^+$: 198.1488, Found: 198.1488; ^1H NMR (400 MHz, $CDCl_3$) δ 5.98 (ddd, *J* = 17.4, 10.6, 6.8 Hz, 1H), 5.29 – 5.15 (m, 2H), 4.51 (q, *J* = 6.4 Hz, 1H), 3.85 (br, 1H), 3.86 – 3.74 (m, 2H), 3.53 – 3.37 (m, 2H), 2.56 – 2.46 (m, 2H), 1.80 (p, *J* = 5.6 Hz, 2H), 1.71 – 1.47 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.42, 133.64, 118.06, 64.25, 62.18, 47.00, 34.54, 30.69, 28.46, 26.10, 24.53.



6

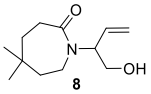
4-(1-Hydroxybut-3-en-2-yl)-1,4-oxazepan-5-one (**6**). According to General procedure A, a mixture of tetrahydro-4*H*-pyran-4-one (55.4 mg, 0.554 mmol), allylic azides **1** (125 mg, 1.11 mmol) and BF_3•Et_2O (236 mg, 1.66 mmol) in dry HFIP (1.0 mL) afforded the title product **6** (41.0 mg, 40%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3709, 3484, 3375, 3109, 2886, 2782, 2531 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{16}NO_3$ $(M+H)^+$: 186.1124, Found: 186.1126; ^1H NMR (400 MHz, $CDCl_3$) δ 5.72 (ddd, *J* = 17.5, 10.8, 5.3 Hz, 1H), 5.31 – 5.19 (m,

2H), 5.19 – 5.13 (m, 1H), 3.85 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.81 – 3.78 (m, 2H), 3.76 (dd, *J* = 5.0, 3.3 Hz, 1H), 3.72 – 3.59 (m, 2H), 3.42 (t, *J* = 4.1 Hz, 2H), 2.86 – 2.78 (m, 2H), 2.77 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.90, 133.16, 118.76, 70.60, 65.30, 62.34, 57.77, 47.02, 41.33.



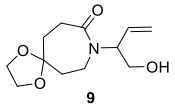
7

1-(1-Hydroxybut-3-en-2-yl)azepan-2-one (**7**). According to General procedure A, a mixture of cyclohexanone (54.4 mg, 0.554 mmol), allylic azides **1** (125 mg, 1.11 mmol) and BF_3•Et_2O (236 mg, 1.66 mmol) in dry HFIP (1.0 mL) afforded the title product **7** (81.2 mg, 80%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3105, 3044, 2884, 2775, 1515, 1356, 1280 cm^{-1}; HRMS (ESI) m/z calculated for $C_{10}H_{18}NO_2$ $(M+H)^+$: 184.1332, Found: 184.1329; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddd, *J* = 17.5, 10.8, 5.5 Hz, 1H), 5.22 (dt, *J* = 10.7, 1.5 Hz, 1H), 5.17 (dt, *J* = 17.5, 1.5 Hz, 1H), 5.14 – 5.06 (m, 1H), 3.78 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.62 (dd, *J* = 11.4, 8.7 Hz, 1H), 3.38 (br, 1H), 3.30 – 3.22 (m, 2H), 2.59 – 2.51 (m, 2H), 1.74 – 1.53 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.53 , 133.61, 118.18, 62.47, 58.19, 45.08, 37.43, 29.88, 28.80, 23.29.



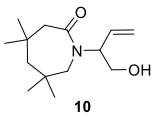
8

1-(1-Hydroxybut-3-en-2-yl)-5,5-dimethylazepan-2-one (**8**). According to General procedure A, a mixture of 4,4-dimethylcyclohexan-1-one (35.0 mg, 0.277 mmol), allylic azides **1** (62.7 mg, 0.554 mmol) and BF_3•Et_2O (118 mg, 0.831 mmol) in dry HFIP (0.5 mL) afforded the title product **8** (42.2 mg, 72%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3610, 3110, 3043, 2626, 2265, 1525, 1436 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{21}NNaO_2$ $(M+Na)^+$: 234.1464, Found: 234.1467; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 17.6, 10.8, 5.6 Hz, 1H), 5.31 – 5.15 (m, 2H), 5.12 – 5.04 (m, 1H), 3.83 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.66 (t, *J* = 10.1 Hz, 1H), 3.31 – 3.18 (m, 2H), 2.85 (br, 1H), 2.58 – 2.46 (m, 2H), 1.52 – 1.33 (m, 4H), 0.95 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.41, 133.52, 118.35, 62.92, 58.55, 41.65, 40.76, 36.09, 32.82, 32.30, 28.65.



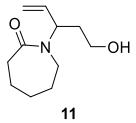
9

8-(1-Hydroxybut-3-en-2-yl)-1,4-dioxa-8-azaspiro[4.6]undecan-9-one (**9**). According to General procedure A, a mixture of 1,4-dioxaspiro[4.5]decan-8-one (43.3 mg, 0.277 mmol), allylic azides **1** (62.7 mg, 0.554 mmol) and BF_3•Et_2O (118 mg, 0.831 mmol) in dry HFIP (0.5 mL) afforded the title product **9** (35 mg, 53%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3706, 3483, 3371, 3111, 3046, 2774, 2274 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{20}NO_4$ $(M+H)^+$: 242.1386, Found: 242.1382; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 17.6, 10.7, 5.5 Hz, 1H), 5.31 – 5.15 (m, 2H), 5.17 – 5.07 (m, 1H), 4.00 – 3.92 (m, 2H), 3.96 – 3.90 (m, 2H), 3.82 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.65 (dd, *J* = 11.4, 8.7 Hz, 1H), 3.42 – 3.28 (m, 2H), 2.82 (br, 1H), 2.67 – 2.57 (m, 2H), 1.91 – 1.68 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.52, 133.32, 118.49, 108.86, 64.56, 64.51, 62.59, 58.23, 40.26, 38.53, 33.08, 32.01.



10

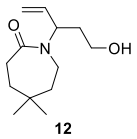
1-(1-Hydroxybut-3-en-2-yl)-4,4,6,6-tetramethylazepan-2-one (**10**). According to General procedure A, a mixture of 3,3,5,5-tetramethylcyclohexan-1-one (42.7 mg, 0.277 mmol), allylic azides **1** (62.7 mg, 0.554 mmol) and BF_3•Et_2O (118 mg, 0.831 mmol) in dry HFIP (0.5 mL) afforded the title product **10** (39.5 mg, 60%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3558, 3111, 3047, 2595, 1519, 1406, 1354 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{26}NO_2$ $(M+H)^+$: 240.1958, Found: 240.1961; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (ddd, *J* = 17.2, 10.5, 6.5 Hz, 1H), 5.25 (dt, *J* = 10.5, 1.3 Hz, 1H), 5.14 (dt, *J* = 17.4, 1.4 Hz, 1H), 4.46 – 4.35 (m, 1H), 3.89 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.83 – 3.74 (m, 1H), 3.70 (br, 1H), 3.22 (d, *J* = 15.1 Hz, 1H), 2.99 (d, *J* = 15.1 Hz, 1H), 2.53 (d, *J* = 13.6 Hz, 1H), 2.40 (d, *J* = 13.7 Hz, 1H), 1.44 – 1.33 (m, 2H), 1.04 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.59, 133.50, 117.89, 65.03, 63.92, 58.80, 56.49, 49.75, 34.33, 31.99, 31.86, 29.69, 29.59, 28.13.



11

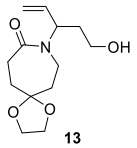
1-(5-Hydroxypent-1-en-3-yl)azepan-2-one (**11**). According to General procedure B, a mixture of cyclohexanone (27.2 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded the title product **11** (43.7 mg, 80%) as a colorless

oil after column chromatography (0 - 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3427, 2932, 2861, 2716, 1638, 1477 cm^{-1}; HRMS (ESI) m/z calculated for $C_{11}H_{20}NO_2$ $(M+H)^+$: 198.1449, Found: 198.1442; ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 16.4, 10.9, 4.8 Hz, 1H), 5.29 – 5.19 (m, 3H), 3.79 (br, 1H), 3.60 (d, *J* = 10.8 Hz, 1H), 3.41 – 3.31 (m, 1H), 3.14 (q, *J* = 6.7, 5.6 Hz, 2H), 2.61 – 2.46 (m, 2H), 1.98 – 1.68 (m, 1H), 1.71 – 1.44 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.71, 136.94, 117.57, 58.07, 51.68, 43.86, 37.29, 32.47, 29.96, 29.05, 23.42.



12

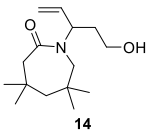
1-(5-Hydroxypent-1-en-3-yl)-5,5-dimethylazepan-2-one (**12**). According to General procedure B, a mixture of 4,4-dimethylcyclohexan-1-one (35.0 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded the title product **12** (51.0 mg, 81%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3111, 3043, 2761, 2686, 1520, 1402, 1351 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_{24}NO_2$ $(M+H)^+$: 226.1801, Found: 226.1798; ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 17.3, 10.8, 4.9 Hz, 1H), 5.29 – 5.21 (m, 2H), 5.19 (dd, *J* = 2.8, 1.8 Hz, 1H), 3.80 (br, 1H), 3.61 (d, *J* = 11.7 Hz, 1H), 3.36 (td, *J* = 11.7, 2.8 Hz, 1H), 3.14 – 3.04 (m, 2H), 2.58 – 2.44 (m, 2H), 1.94 – 1.89 (m, 1H), 1.57 – 1.49 (m, 1H), 1.49 – 1.40 (m, 2H), 1.37 – 1.25 (m, 2H), 0.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.52, 136.88, 117.64, 58.07, 51.60, 41.77, 39.22, 36.10, 32.49, 32.46, 32.31, 29.38, 28.06.



13

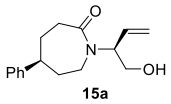
8-(5-Hydroxypent-1-en-3-yl)-1,4-dioxa-8-azaspiro[4.6]undecan-9-one (**13**). According to General procedure B, a mixture of 1,4-dioxaspiro[4.5]decan-8-one (43.3 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded the title product **13** (36 mg, 51%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3635, 3308, 2394, 2322, 1703 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_{22}NO_4$ $(M+H)^+$: 256.1543, Found: 256.1541; ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.5, 10.8, 5.4 Hz, 1H), 5.35 – 5.23 (m, 3H), 4.10 – 3.78 (m, 4H), 3.64 (d, *J* = 17.1 Hz, 2H), 3.36 (td, *J* = 11.1,

2.7 Hz, 1H), 3.31 – 3.13 (m, 2H), 2.68 (ddd, *J* = 14.6, 8.4, 4.1 Hz, 1H), 2.60 (ddd, *J* = 14.6, 7.4, 3.8 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.87 – 1.80 (m, 2H), 1.77 – 1.65 (m, 2H), 1.49 (ddd, *J* = 14.5, 8.4, 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.87, 136.58, 118.04, 108.66, 64.67, 64.54, 58.05, 51.66, 38.88, 38.83, 33.20, 32.53, 31.76.

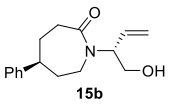


14

1-(5-Hydroxypent-1-en-3-yl)-4,4,6,6-tetramethylazepan-2-one (**14**). According to General procedure B, a mixture of 3,3,5,5-tetramethylcyclohexan-1-one (42.7 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded the title product **14** (47.6 mg, 68%) as a colorless oil after column chromatography (0 - 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3110, 3047, 2527, 1514, 1405, 1356, 1292 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{27}NNaO_2$ $(M+Na)^+$: 276.1934, Found: 276.1937; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 17.7, 10.1, 6.0 Hz, 1H), 5.32 – 5.23 (m, 2H), 5.23 – 5.19 (m, 1H), 3.63 (br, 1H), 3.60 (s, 1H), 3.39 – 3.31 (m, 1H), 3.04 – 2.85 (m, 2H), 2.59 – 2.41 (m, 2H), 1.94 – 1.85 (m, 1H), 1.54 (td, *J* = 12.2, 11.4, 1.8 Hz, 1H), 1.45 – 1.32 (m, 2H), 1.06 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.96, 137.49, 117.65, 58.15, 56.69, 53.73, 52.75, 49.74, 34.06, 33.09, 32.83, 31.91, 30.73, 28.58, 28.26.



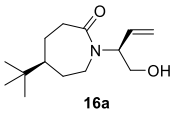
15a



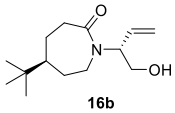
15b

(*S)-1-((*S**)-1-Hydroxybut-3-en-2-yl)-5-phenylazepan-2-one** (**15a**) and **(*S**)-1-((*R**)-1-hydroxy but-3-en-2-yl)-5-phenylazepan-2-one** (**15b**). According to General procedure A, a mixture of 4-phenylcyclohexan-1-one (70 mg, 0.402 mmol), allylic azides **1** (90.9 mg, 0.803 mmol) and BF_3•Et_2O (171 mg, 1.21 mmol) in dry HFIP (0.8 mL) afforded the title product **15a** (52.1 mg, 50%) as a white solid and **15b** (16.7 mg, 16%) as a white solid after column chromatography (0 – 5% MeOH/DCM). Compound **15a**: R_f = 0.30 (5% MeOH/DCM), IR (KBr): 3845, 3435, 2928, 2866, 1954, 1640 cm^{-1}; HRMS (ESI) m/z calculated for $C_{16}H_{22}NO_2$ $(M+H)^+$: 260.1645, Found: 260.1651; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.05 (m, 5H), 5.84 (ddd, *J* = 17.1, 10.9, 6.1 Hz, 1H), 5.37 – 5.23 (m, 2H), 5.19 – 5.08

(m, 1H), 3.85 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.75 – 3.65 (m, 1H), 3.53 – 3.33 (m, 2H), 3.04 (br, 1H), 2.83 – 2.63 (m, 3H), 2.07 – 1.96 (m, 2H), 1.86 – 1.71 (m, 1H), 1.68 – 1.53 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.98, 145.96, 133.40, 128.58(2C), 126.65(2C), 126.51, 119.09, 62.82, 58.50, 48.06, 44.27, 36.93, 36.91, 30.62. Compound **15b**: R_f = 0.35 (5% MeOH/DCM), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 5H), 5.78 (ddd, *J* = 17.6, 10.7, 5.2 Hz, 1H), 5.31 – 5.12 (m, 3H), 3.91 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.70 (t, *J* = 10.2 Hz, 1H), 3.52 – 3.35 (m, 2H), 2.82 – 2.57 (m, 4H), 2.09 – 1.94 (m, 2H), 1.89 – 1.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.86, 146.03, 133.55, 128.55(2C), 126.73(2C), 126.48, 118.04, 62.83, 58.28, 48.28, 44.63, 36.71, 36.22, 30.75.

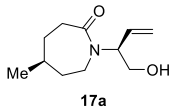


16a

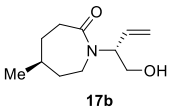


16b

(*S)-5-(*tert*-Butyl)-1-((*S**)-1-hydroxybut-3-en-2-yl)azepan-2-one** (**16a**) and **(*S**)-5-(*tert*-butyl) -1-((*R**)-1-hydroxybut-3-en-2-yl)azepan-2-one** (**16b**). According to General procedure A, a mixture of 4-(*tert*-butyl)cyclohexan-1-one (50 mg, 0.324 mmol), allylic azides **1** (73.3 mg, 0.648 mmol) and BF_3•Et_2O (138 mg, 0.972 mmol) in dry HFIP (0.6 mL) afforded the title product **16a** (26.4 mg, 34%) as a white solid and **16b** (8.5 mg, 11%) as a white solid after column chromatography (0 – 5% MeOH/DCM). Compound **16a**: R_f = 0.30 (5% MeOH/DCM); IR (KBr): 3005, 2888, 2662, 1512, 1402, 1352, 1283 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{25}NNaO_2$ $(M+Na)^+$: 262.1777, Found: 262.1782; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.5, 10.7, 6.0 Hz, 1H), 5.33 – 5.19 (m, 2H), 5.09 – 4.98 (m, 1H), 3.83 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.67 (dd, *J* = 11.3, 8.6 Hz, 1H), 3.37 – 3.22 (m, 2H), 2.88 (br, 1H), 2.67 – 2.56 (m, 1H), 2.58 – 2.47 (m, 1H), 2.01 – 1.91 (m, 2H), 1.30 – 1.19 (m, 2H), 1.16 – 1.05 (m, 1H), 0.86 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.54, 133.49, 118.77, 62.96, 58.59, 51.49, 44.60, 36.76, 33.03, 30.11, 27.49 (3C), 24.16. Compound **16b**: R_f = 0.35 (5% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 17.4, 10.8, 5.2 Hz, 1H), 5.32 – 5.12 (m, 2H), 5.14 – 5.06 (m, 1H), 3.85 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.70 (d, *J* = 11.4 Hz, 1H), 3.31 (qd, *J* = 15.7, 7.5 Hz, 2H), 2.68 (br, 1H), 2.67 – 2.46 (m, 2H), 2.03 – 1.92 (m, 2H), 1.35 – 1.17 (m, 3H), 0.86 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.29, 133.59, 117.90, 62.99, 58.53, 51.58, 45.03, 36.53, 33.03, 29.74, 27.52 (3C), 24.08.

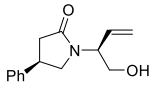


17a

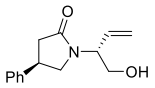


17b

(*S)-1-((*S**)-1-Hydroxybut-3-en-2-yl)-5-methylazepan-2-one** (**17a**) and **(*S**)-1-((*R**)-1-hydroxy but-3-en-2-yl)-5-methylazepan-2-one** (**17b**). According to General procedure A, a mixture of 4-methylcyclohexan-1-one (62 mg, 0.554 mmol), allylic azides **1** (125 mg, 1.11 mmol) and BF_3•Et_2O (236 mg, 1.66 mmol) in dry HFIP (1.0 mL) afforded the title product **17a** (63.2 mg, 58%) as a colorless oil and **17b** (19.6 mg, 18%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). Compound **17a**: R_f = 0.30 (5% MeOH/DCM); IR (KBr): 3681, 3412, 2948, 2392, 1850, 1720, 1601 cm^{-1}; HRMS (ESI) m/z calculated for $C_{11}H_{20}NO_2$ $(M+H)^+$: 198.1488, Found: 198.1488; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddd, *J* = 17.1, 10.8, 6.0 Hz, 1H), 5.26 – 5.15 (m, 2H), 5.08 – 4.98 (m, 1H), 3.74 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.65 – 3.54 (m, 1H), 3.51 (br, 1H), 3.29 – 3.17 (m, 2H), 2.56 – 2.48 (m, 2H), 1.80 – 1.70 (m, 2H), 1.68 – 1.55 (m, 1H), 1.27 – 1.14 (m, 1H), 1.10 – 0.98 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.11, 133.64, 118.60, 62.47, 58.15, 43.78, 37.24, 36.31, 36.00, 31.28, 22.50. Compound **17b**: R_f = 0.35 (5% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 17.8, 10.8, 5.0 Hz, 1H), 5.28 – 5.19 (m, 1H), 5.21 – 5.06 (m, 2H), 3.89 – 3.79 (m, 1H), 3.72 – 3.60 (m, 1H), 3.34 – 3.25 (m, 2H), 2.80 (br, 1H), 2.63 – 2.51 (m, 2H), 1.87 – 1.73 (m, 2H), 1.71 – 1.59 (m, 1H), 1.33 – 1.20 (m, 2H), 0.94 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.16, 133.66, 117.86, 62.86, 58.38, 44.39, 36.91, 36.27, 36.24, 31.27, 22.51.



18a



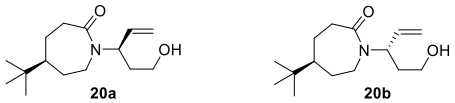
18b

(*R)-1-((*S**)-1-Hydroxybut-3-en-2-yl)-4-phenylpyrrolidin-2-one** (**18a**) and **(*R**)-1-((*R**)-1-hydroxy but-3-en-2-yl)-4-phenylpyrrolidin-2-one** (**18b**). According to General procedure A, a mixture of 3-phenylcyclobutan-1-one (70.1 mg, 0.479 mmol), allylic azides **1** (108 mg, 0.958 mmol) and BF_3•Et_2O (204 mg, 1.44 mmol) in dry HFIP (0.9 mL) afforded the title product **18a** (44.4 mg, 40%) as a colorless oil and **18b** (18.9 mg, 17%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). Compound **18a**: R_f = 0.30 (5% MeOH/DCM); IR (KBr): 3323, 2933, 2875, 2385, 1685, 1487, 1432 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{18}NO_2$ $(M+H)^+$: 232.1332, Found: 232.1332; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 2H), 7.28 – 7.06 (m, 3H), 5.77 (ddd, *J* = 17.2, 10.6, 6.5 Hz, 1H), 5.30 – 5.17 (m, 2H), 4.66 – 4.56 (m, 1H), 3.84 (dd, *J* = 9.7, 8.2 Hz, 2H), 3.79 – 3.67 (m, 2H), 3.65 – 3.56 (m, 1H), 3.37 (dd, *J* = 9.7, 6.7 Hz, 1H), 2.87 (dd, *J* = 16.9, 9.0 Hz, 1H), 2.62 (dd, *J* = 16.9, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.02, 142.37, 132.19, 128.85(2C), 127.07, 126.68(2C), 118.75, 62.40, 57.07,

51.98, 39.27, 37.39. Compound **18b**: R_f = 0.35 (5% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.09 (m, 5H), 5.81 (ddd, *J* = 17.0, 10.6, 6.2 Hz, 1H), 5.34 – 5.16 (m, 2H), 4.64 – 4.53 (m, 1H), 3.85 (dd, *J* = 11.7, 4.3 Hz, 1H), 3.79 – 3.66 (m, 2H), 3.63 – 3.54 (m, 1H), 3.47 (dd, *J* = 9.3, 7.8 Hz, 1H), 3.32 (br, 1H), 2.85 (dd, *J* = 16.8, 8.8 Hz, 1H), 2.64 (dd, *J* = 16.8, 9.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.98, 141.73, 132.25, 128.84(2C), 127.12, 126.81(2C), 118.40, 62.60, 57.29, 52.04, 39.34, 37.87.

19a **19b**

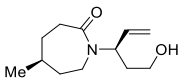
(*S)-1-((*R**)-5-Hydroxypent-1-en-3-yl)-5-phenylazepan-2-one** (**19a**) and **(*S**)-1-((*S**)-5-hydroxy pent-1-en-3-yl)-5-phenylazepan-2-one** (**19b**). According to General procedure B, a mixture of 4-phenylcyclohexan-1-one (48.3 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded a mixture of compounds **19a** and **19b** (37.9 mg, 50%, 10:1 ratio) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3409, 2931, 2866, 1635, 1481 cm^{-1}; HRMS (ESI) m/z calculated for $C_{17}H_{24}NO_2$ $(M+H)^+$: 274.1801, Found: 274.1803. Compound **19a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.08 (m, 3H), 5.93 (ddd, *J* = 17.5, 10.5, 5.3 Hz, 1H), 5.36 – 5.22 (m, 3H), 3.77 (br, 1H), 3.68 – 3.57 (m, 1H), 3.42 – 3.30 (m, 1H), 3.30 – 3.17 (m, 2H), 2.80 – 2.67 (m, 3H), 2.06 – 1.86 (m, 3H), 1.86 – 1.71 (m, 1H), 1.64 – 1.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.56, 145.71, 136.16, 128.62 (2C), 126.61, 126.59 (2C), 118.41, 58.07, 52.01, 48.18, 43.00, 36.77, 36.49, 32.36, 30.53. Compound **19b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.4, 10.7, 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.62, 128.67, 126.68, 117.82, 58.44, 43.43, 36.21, 32.59.



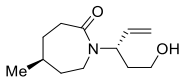
20a **20b**

(*S)-5-(*tert*-Butyl)-1-((*R**)-5-hydroxypent-1-en-3-yl)azepan-2-one** (**20a**) and **(*S**)-5-(*tert*-butyl) -1-((*S**)-5-hydroxypent-1-en-3-yl)azepan-2-one** (**20b**). According to General procedure B, a mixture of 4-(*tert*-butyl)cyclohexan-1-one (80.4 mg, 0.554 mmol), allylic azides **2** (140.8 mg, 1.11 mmol) and $Ti[OCH(CF_3)_2]_4$ (595 mg, 0.831 mmol) in dry HFIP (1.0 mL) afforded a mixture of compounds **20a** and **20b** (58.9 mg, 42%, 15:1 ratio) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3452, 3083, 2355, 2237, 1852, 1640 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{28}NO_2$ $(M+H)^+$: 254.2114, Found: 254.2116. Compound **20a** : ^{1}H NMR (400 MHz,

$CDCl_3$) δ 5.88 (ddd, *J* = 17.7, 10.2, 5.2 Hz, 1H), 5.31 – 5.20 (m, 2H), 5.24 – 5.13 (m, 1H), 3.81 (br, 1H), 3.63 – 3.54 (m, 1H), 3.29 (td, *J* = 11.8, 2.8 Hz, 1H), 3.17 (ddd, *J* = 15.1, 6.6, 1.8 Hz, 1H), 3.03 (dd, *J* = 15.0, 10.6 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.54 – 2.42 (m, 1H), 2.01 – 1.84 (m, 3H), 1.47 (ddt, *J* = 14.4, 11.9, 2.6 Hz, 1H), 1.32 – 1.17 (m, 2H), 1.13 – 1.00 (m, 1H), 0.84 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.63, 136.76, 117.79, 57.94, 51.80, 51.51, 43.05, 36.53, 33.05, 32.40, 30.11, 27.48 (3C), 24.24. Compound **20b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 17.5, 10.6, 4.7 Hz, 1H), 3.46 (td, *J* = 11.5, 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.16, 117.35, 58.17, 51.44, 43.35, 36.14, 32.66, 29.91, 27.46, 24.11.

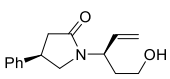


21a

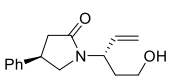


21b

(*S)-1-((*R**)-5-Hydroxypent-1-en-3-yl)-5-methylazepan-2-one** (**21a**) and **(*S**)-1-((*S**)-5-hydroxy pent-1-en-3-yl)-5-methylazepan-2-one** (**21b**). According to General procedure B, a mixture of 4-methylcyclohexan-1-one (31.0 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded a mixture of compounds **21a** and **21b** (43.9 mg, 75%, 10:1 ratio) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3368, 2923, 2869, 1631, 1445 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{22}NO_2$ $(M+H)^+$: 212.1645, Found: 212.1641. Compound **21a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.5, 10.4, 5.3 Hz, 1H), 5.19 (dddd, *J* = 18.5, 16.5, 4.1, 2.4 Hz, 3H), 3.82 (br, 1H), 3.55 (d, *J* = 11.4 Hz, 1H), 3.28 (td, *J* = 11.7, 2.9 Hz, 1H), 3.16 – 3.00 (m, 2H), 2.59 – 2.47 (m, 2H), 1.86 (tdd, *J* = 11.2, 5.1, 3.5 Hz, 1H), 1.82 – 1.68 (m, 2H), 1.64 –1.58 (m, 1H), 1.52 – 1.39 (m, 1H), 1.22 (dtd, *J* = 14.2, 11.3, 3.3 Hz, 1H), 1.12 – 0.94 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.41, 136.67, 117.75, 57.95, 51.61, 42.60, 37.23, 36.32, 36.19, 32.41, 31.27, 22.60. Compound **21b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddd, *J* = 17.4, 10.7, 4.6 Hz, 1H), 3.44 (td, *J* = 11.4, 3.1 Hz, 1H), 3.23 – 3.14 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.11, 117.32, 58.22, 51.64, 42.87, 37.13, 35.85, 32.62, 31.27, 22.39.

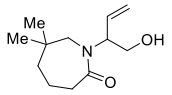


22a

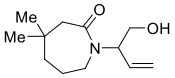


22b

(*R)-1-((*R**)-5-Hydroxypent-1-en-3-yl)-4-phenylpyrrolidin-2-one** (**22a**) and **(*R**)-1-((*S**) -5-hydroxypent-1-en-3-yl)-4-phenylpyrrolidin-2-one** (**22b**). According to General procedure B, a mixture of 3-phenylcyclobutan-1-one (40.5 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded a mixture of compounds **22a** and **22b** (39.4 mg, 58%, 2:1 ratio) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3845, 3435, 2928, 2866, 1954, 1640 cm^{-1}; HRMS (ESI) m/z calculated for $C_{15}H_{19}NNaO_2$ $(M+Na)^+$: 246.1488, Found: 246.1484; Compounds **22a** and **22b**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H), 7.28 – 7.17 (m, 5H), 5.91 – 5.80 (m, 1H), 5.84 – 5.74 (m, 1H), 5.32 – 5.15 (m, 4H), 4.94 – 4.83 (m, 2H), 3.76 – 3.39 (m, 9H), 3.34 (dd, *J* = 9.1, 6.1 Hz, 2H), 3.18 (dd, *J* = 9.7, 7.6 Hz, 2H), 2.94 – 2.80 (m, 2H), 2.64 (ddd, *J* = 17.0, 8.6, 3.1 Hz, 2H), 1.98 – 1.85 (m, 2H), 1.77 – 1.63 (m, 2H). Compound **22a**:^{13}C NMR (101 MHz, $CDCl_3$) δ 174.82, 142.06, 135.27, 128.88(2C), 127.17, 126.64(2C), 118.21, 58.38, 50.26, 49.67, 38.93, 37.47, 33.15. Compound **22b**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.62, 135.54, 128.90(2C), 127.20, 126.71(2C), 117.85, 58.30, 50.18, 49.48, 38.64, 37.43, 32.98.



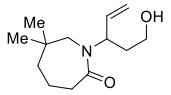
23a



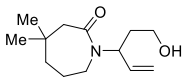
23b

1-(1-Hydroxybut-3-en-2-yl)-6,6-dimethylazepan-2-one (**23a**) and **1-(1-hydroxybut-3-en-2-yl) -4,4-dimethylazepan-2-one** (**23b**). According to General procedure A, a mixture of 3,3-dimethylcyclohexan-1-one (65.5 mg, 0.519 mmol), allylic azides **1** (117.3 mg, 1.037 mmol) and BF_3•Et_2O (221 mg, 1.56 mmol) in dry HFIP (1.0 mL) afforded a mixture of compounds **23a** and **23b** (70 mg, 64%, 1.05:1 ratio) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3838, 3477, 2952, 2314, 1642, 1476 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{22}NO_2$ $(M+H)^+$: 212.1645, Found: 212.1648; Compound **23a** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 17.2, 10.6, 6.4 Hz, 1H), 3.14 (d, *J* = 15.1 Hz, 1H), 2.95 (d, *J* = 15.1 Hz, 1H), 0.88 (s, 3H), 0.87 (s, 3H). Compound **23b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.71 (ddd, *J* = 17.7, 10.7, 5.4 Hz, 1H), 0.95 (s, 3H), 0.88 (s, 3H). The rest peaks: ^1H NMR (400 MHz, $CDCl_3$) δ 5.24 – 5.07 (m, 5H), 4.58 – 4.46 (m, 1H), 3.87 – 3.76 (m, 3H), 3.75 – 3.66 (m, 1H), 3.64 – 3.55 (m, 1H), 3.37 (br, 1H), 3.30 – 3.17 (m, 2H), 2.56 – 2.37 (m, 4H), 1.76 – 1.55 (m, 4H), 1.56 – 1.34 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.29, 174.95, 133.91, 133.66, 118.10, 117.89, 77.38, 77.07, 76.75, 63.50, 63.28, 62.58,

58.05, 58.01, 49.60, 44.97, 43.70, 38.03, 32.76, 30.55, 27.67, 25.66, 25.33, 19.63.

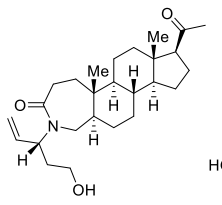


24a

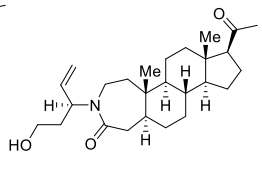


24b

1-(5-Hydroxypent-1-en-3-yl)-6,6-dimethylazepan-2-one (**24a**) and **1-(5-hydroxypent-1-en-3-yl) -4,4-dimethylazepan-2-one** (**24b**). According to General procedure B, a mixture of 3,3-dimethylcyclohexan-1-one (48.3 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and $Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded a mixture of compounds **24a** and **24b** (31.2 mg, 60%, 1.5:1 ratio) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3404, 3080, 2951, 1632, 1472 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_{24}NO_2$ $(M+H)^+$: 226.1762, Found: 226.1767. Compound **24a** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (td, *J* = 10.5, 2.7 Hz, 2H), 3.02 – 2.77 (m, 2H), 0.878 (s, 3H), 0.874 (s, 3H). Compound **24b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 – 3.68 (m, 1H), 3.47 – 3.36 (m, 1H), 2.61 – 2.34 (m, 2H), 1.00 (s, 3H), 0.98 (s, 3H). The rest peaks: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.79 (m, 2.5H), 5.27 – 5.16 (m, 7.5H), 3.57 (br, 4H), 3.17 – 3.05 (m, 2H), 2.61 – 2.34 (m, 3H), 1.95 – 1.83 (m, 3H), 1.72 – 1.57 (m, 5H), 1.57 – 1.42 (m, 6H), 1.42 – 1.32 (m, 1.5H). Compound **24a**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.71, 137.61, 117.54, 58.14, 52.59, 49.57, 44.19, 43.61, 38.06, 32.62, 28.65, 19.57. Compound **24b**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.23, 136.84, 117.72, 58.16, 53.88, 51.86, 44.18, 43.78, 32.90, 30.56, 25.55, 25.19.



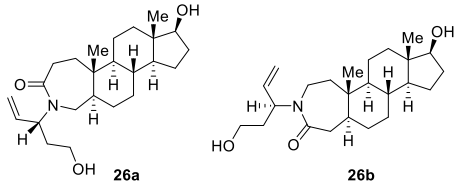
25a



25b

(5a*R*,5b*S*,7a*S*,8*S*,10a*S*,10b*R*,12a*R*)-8-Acetyl-2-((*R*)-5-hydroxypent-1-en-3-yl)-5a,7a-dimethyl hexadecahydrocyclopenta[5,6]naphtho[2,1-c]azepin-3(2*H*)-one (**25a**) and **(5a*S*,5b*S*,7a*S*,8*S*,10a*S*, 10b*R*,12a*S*)-8-acetyl-3-((*S*)-5-hydroxypent-1-en-3-yl)-5a,7a-dimethylhexadecahydrocyclopenta [5,6]naphtho[1,2-d]azepin-2(1*H*)-one** (**25b**). According to General procedure B, a mixture of 5α-pregnane-3,20-dione (87.7 mg, 0.277 mmol), allylic azides **2** (70.5 mg, 0.554 mmol) and

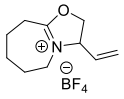
$Ti[OCH(CF_3)_2]_4$ (298 mg, 0.416 mmol) in dry HFIP (0.5 mL) afforded the title product **25a** as a white solid (35.7 mg, 31%) and **25b** (27.6 mg, 24%) as a white solid after column chromatography (0 – 5% MeOH/DCM). Compound **25a**: R_f = 0.30 (5% MeOH/DCM); IR (KBr): 3730, 2931, 1702, 1627 cm^{-1}; HRMS (ESI) m/z calculated for $C_{26}H_{42}NO_3$ $(M+H)^+$: 416.3159, Found: 416.3171; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 17.4, 10.6, 5.4 Hz, 1H), 5.31 – 5.20 (m, 2H), 5.23 – 5.12 (m, 1H), 3.73 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.57 (s, 1H), 3.33 – 3.13 (m, 2H), 2.98 – 2.57 (m, 2H), 2.56 – 2.33 (m, 3H), 2.21 – 2.08 (m, 1H), 2.08 (s, 3H), 1.99 (dt, *J* = 12.4, 3.5 Hz, 1H), 1.87 (ttd, *J* = 15.5, 7.4, 6.3, 2.9 Hz, 2H), 1.64 (tdd, *J* = 16.9, 13.6, 8.0 Hz, 4H), 1.51 – 1.07 (m, 9H), 0.98 – 0.88 (m, 1H), 0.86 (s, 3H), 0.74 (ddd, *J* = 12.1, 10.4, 4.1 Hz, 1H), 0.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.40, 177.04, 136.75, 117.88, 63.63, 57.94, 56.52, 53.69, 51.53, 49.40, 45.16, 43.90, 38.89, 38.05, 35.72, 34.95, 32.43, 32.27, 31.70, 31.46, 27.08, 24.30, 22.73, 20.94, 13.36, 12.15. Compound **25b**: R_f = 0.35 (5% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddd, *J* = 17.7, 10.4, 5.2 Hz, 1H), 5.32 – 5.22 (m, 2H), 5.22 – 5.12 (m, 1H), 3.77 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.60 (s, 1H), 3.25 (ddd, *J* = 27.3, 13.7, 10.4 Hz, 2H), 2.95 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.82 (dd, *J* = 14.9, 10.8 Hz, 1H), 2.49 (t, *J* = 8.8 Hz, 1H), 2.10 (s, 3H), 2.01 (dd, *J* = 13.5, 10.2 Hz, 2H), 1.98 – 1.84 (m, 1H), 1.78 (dd, *J* = 14.3, 6.3 Hz, 1H), 1.75 – 1.20 (m, 12H), 1.23 – 1.04 (m, 3H), 0.95 (td, *J* = 12.6, 4.5 Hz, 1H), 0.88 (s, 3H), 0.76 (td, *J* = 11.6, 11.0, 4.0 Hz, 1H), 0.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.47, 177.27, 136.76, 117.86, 63.66, 57.92, 56.47, 54.01, 51.48, 43.85, 43.42, 41.77, 40.14, 38.92, 38.87, 38.30, 34.70, 32.31, 31.85, 31.45, 30.75, 24.30, 22.83, 21.22, 13.34, 12.07.



(5a*R*,5b*S*,7a*S*,8*S*,10a*S*,10b*R*,12a*R*)-8-Hydroxy-2-((*R*)-5-hydroxypent-1-en-3-yl)-5a,7a-dimethyl hexadecahydrocyclopenta[5,6]naphtho[2,1-c]azepin-3(2*H*)-one (**26a**) and **(5a*S*,5b*S*,7a*S*,8*S*,10a*S*, 10b*R*,12a*S*)-8-hydroxy-3-((*S*)-5-hydroxypent-1-en-3-yl)-5a,7a-dimethylhexadecahydrocyclopenta [5,6]naphtho[1,2-d]azepin-2(1*H*)-one** (**26b**). According to General procedure B, a mixture of stanolone (110 mg, 0.379 mmol), allylic azides **2** (96.3 mg, 0.757 mmol) and $Ti[OCH(CF_3)_2]_4$ (407 mg, 0.568 mmol) in dry HFIP (0.8 mL) afforded the title product **26a** (66.4 mg, 45%) as a colorless oil and **26b** (44.3 mg, 30%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). Compound **26a**:

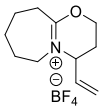
R_f = 0.30 (5% MeOH/DCM); IR (KBr): 3752, 2925, 1701 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H_{40}NO_3$ $(M+H)^+$: 390.3002, Found: 390.3015; ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.5, 10.6, 5.4 Hz, 1H), 5.31 – 5.20 (m, 2H), 5.21 – 5.11 (m, 1H), 3.79 (s, 1H), 3.57 (q, *J* = 8.0, 7.5 Hz, 2H), 3.33 – 3.14 (m, 2H), 2.66 (ddd, *J* = 14.8, 13.1, 1.5 Hz, 1H), 2.50 – 2.34 (m, 2H), 2.08 – 1.73 (m, 5H), 1.73 – 1.07 (m, 12H), 1.07 – 0.74 (m, 6H), 0.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.14, 136.71, 117.88, 81.59, 57.93, 53.95, 51.53, 50.89, 49.46, 45.21, 42.72, 38.11, 36.60, 35.73, 35.01, 32.40, 32.27, 31.34, 30.34, 27.07, 23.27, 20.54, 12.18, 11.09. Compound **26b**: R_f = 0.35 (5% MeOH/DCM); ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 17.7, 10.4, 5.2 Hz, 1H), 5.31 – 5.20 (m, 2H), 5.19 – 5.09 (m, 1H), 3.58 (t, *J* = 8.5 Hz, 2H), 3.32 – 3.14 (m, 2H), 2.92 (m, 1H), 2.80 (dd, *J* = 14.9, 10.7 Hz, 1H), 2.12 – 1.59 (m, 7H), 1.61 – 1.13 (m, 10H), 1.14 – 0.95 (m, 2H), 0.95 – 0.74 (m, 5H), 0.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.30, 136.69, 117.85, 81.66, 57.91, 54.28, 51.49, 50.87, 43.50, 42.65, 41.77, 40.15, 38.95, 38.34, 36.63, 34.75, 32.29, 31.47, 30.73, 30.43, 23.27, 20.82, 12.08, 11.06.

Scheme S2. Syntheses of iminium ethers.



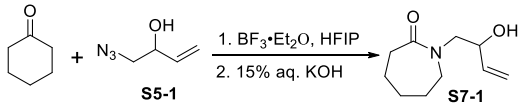
S2

3-Vinyl-3,5,6,7,8,9-hexahydro-2H-oxazolo[3,2-*a*]azepin-4-ium tetrafluoroborate (**S2**). Under argon atmosphere, to a solution of allylic azides **1** (184 mg, 1.630 mmol) and cyclic ketone (80 mg, 0.815 mmol) in HFIP (2.0 mL) was added BF_3•Et_2O (175 mg, 1.22 mmol) dropwise. The reaction mixture was heated to reflux for 12 h. After cooling to room temperature, the residue was purified by silica gel column chromatography (2 – 10% MeOH/DCM) to afford the title product **S2** (82.5 mg, 40%) as a pale yellow solid. R_f = 0.5 (10% MeOH/DCM); IR (KBr): 3123, 2889, 2782, 2202, 1522, 1468 cm^{-1}; HRMS (ESI) m/z calculated for $C_{10}H_{16}NO^+$ $(M–BF_4)^+$: 166.1226, Found: 166.1247; ^1H NMR (400 MHz, $CDCl_3$) δ 5.97 (dt, *J* = 16.9, 9.6 Hz, 1H), 5.70 – 5.48 (m, 2H), 5.21 – 5.09 (m, 1H), 5.03 (q, *J* = 9.4 Hz, 1H), 4.63 (t, *J* = 8.7 Hz, 1H), 3.70 (dd, *J* = 15.2, 8.3 Hz, 1H), 3.57 (dd, *J* = 14.8, 8.0 Hz, 1H), 3.02 – 2.79 (m, 1H), 1.99 – 1.62 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.82, 130.49, 126.32, 75.89, 67.92, 46.33, 28.67, 27.94, 25.26, 21.11.



S3

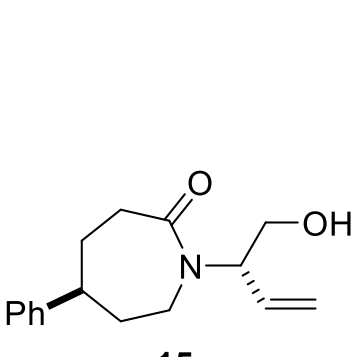
4-Vinyl-2,3,4,6,7,8,9,10-octahydro-[1,3]oxazino[3,2-*a*]azepin-5-ium tetrafluoroborate (**S3**) . Under argon atmosphere, to a solution of allylic azides **2** (181 mg, 1.43 mmol) and cyclic ketone (70 mg, 0.713 mmol) in HFIP (1.3 mL) was added BF_3•Et_2O (304 mg, 2.14 mmol) dropwise. The reaction mixture was heated to reflux for 12 h. After cooling to room temperature, the residue was purified by silica gel column chromatography (2 – 10% MeOH/DCM) to afford the title product **S3** (85.7 mg, 45%) as a pale yellow solid. R_f = 0.5 (10% MeOH/DCM); IR (KBr): 3450, 2930, 2863, 2341, 1639, 1480 cm^{-1}; HRMS (ESI) m/z calculated for $C_{11}H_{18}NO^+$ $(M–BF_4)^+$: 180.1383, Found: 180.1387; ^1H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddd, J = 17.5, 10.3, 7.6 Hz, 1H), 5.57 – 5.37 (m, 2H), 4.72 – 4.61 (m, 1H), 4.46 (td, *J* = 10.9, 3.2 Hz, 1H), 4.38 (dt, *J* = 8.6, 4.8 Hz, 1H), 3.85 (dd, *J* = 15.1, 8.7 Hz, 1H), 3.74 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.92 (dt, *J* = 7.2, 4.3 Hz, 2H), 2.51 (ddt, *J* = 15.1, 10.0, 4.8 Hz, 1H), 2.15 (dq, *J* = 14.8, 3.9 Hz, 1H), 1.92 – 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.17, 132.49, 122.31, 65.93, 60.92, 54.34, 34.40, 28.70, 25.44, 25.40, 21.81.



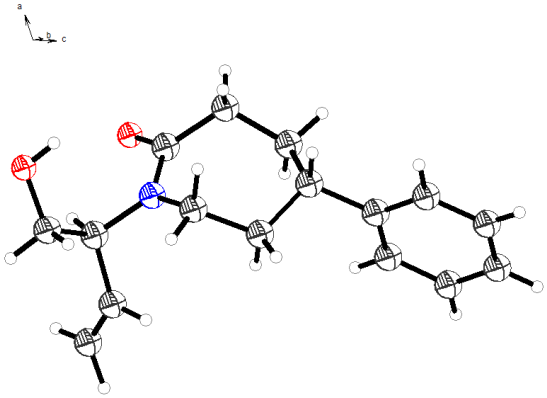
S5-1 S7-1

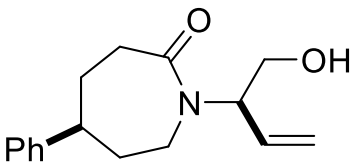
1-(2-Hydroxybut-3-en-1-yl)azepan-2-one (**S7-1**). According to the general procedure A, a mixture of ketone (28.2 mg, 0.287 mmol), allylic azides **S5-1** (65 mg, 0.575 mmol) and BF_3•Et_2O (122 mg, 0.862 mmol) in dry HFIP (0.5 mL) afforded the iminium ethers. The iminium ethers was treated with an aqueous solution of 15% KOH (1.5 mL) afforded the title product **S7-1** (45.3 mg, 86%) as a colorless oil after column chromatography (0 – 5% MeOH/DCM). R_f = 0.3 (5% MeOH/DCM); IR (KBr): 3016, 2778, 1503, 1356, 1282 cm^{-1}; HRMS (ESI) m/z calculated for $C_{10}H_{18}NO_2$ $(M+H)^+$: 184.1332, Found: 184.1329; ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 17.3, 10.5, 5.6 Hz, 1H), 5.32 (dt, *J* = 17.1, 1.6 Hz, 1H), 5.13 (dt, *J* = 10.4, 1.5 Hz, 1H), 4.28 (d, *J* = 7.4 Hz, 1H), 3.92 (s, 1H), 3.54 – 3.40 (m, 2H), 3.39 (dd, *J* = 5.8, 3.9 Hz, 3H), 2.56 – 2.47 (m, 2H), 1.75 – 1.57 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.18, 138.49, 115.62, 72.56, 55.84, 51.91, 37.01, 29.81, 28.09, 23.20.

5. X-ray crystal structures of 15a, 15b, 26a and 26b.

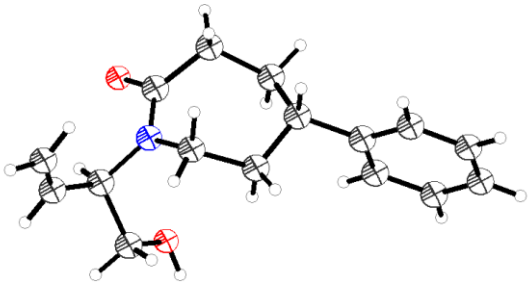


15a
(CCDC2176978)



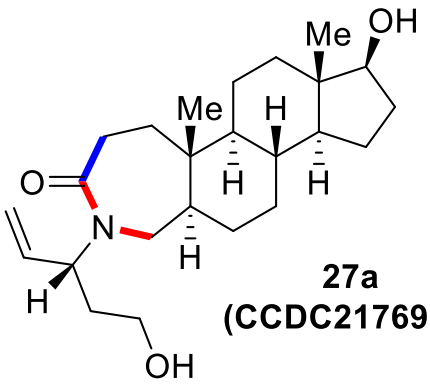


15b
(CCDC2176979)

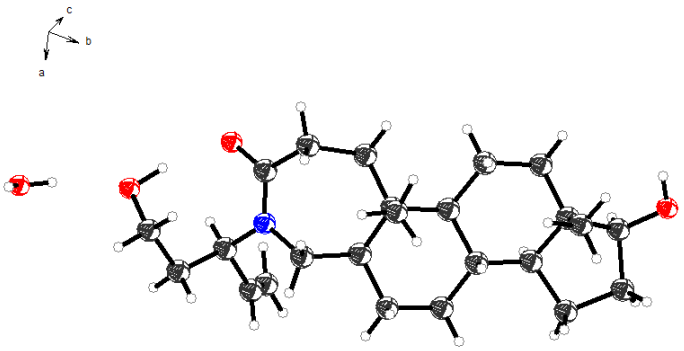


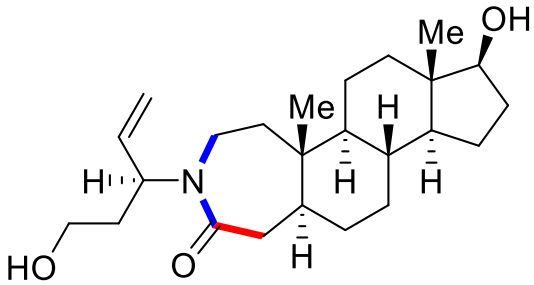
Phase	**15a**	**15b**
Empirical formula	$C_{16}H_{21}NO_2$	$C_{16}H_{21}NO_2$
Formula weight	259.34	259.34
T/K	273.15	296
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
Unit cell dimensions	a = 21.9697(13) Å α = 90 °. b = 6.3504(3) Å β = 114.886 °. c = 23.5320(13) Å γ= 90 °.	a = 5.6228(6) Å α = 88.886 °. b = 11.5801(11) Å β = 84.246 °. c = 22.772(2) Å γ= 83.434 °.
V(Å^3)	2978.3(3)	1465.6(3)
Z, Calculated density(g/cm^3)	8 1.157	2 1.175
Absorption coefficient(mm^{-1})	0.076	0.077
F(000)	1120.0	560.0
Crystal size(mm^3)	0.2×0.2×0.2	0.2×0.2×0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)

2Θ range for data collection(°)	4.26 to 55.096	1.798 to 54.848
Limiting indices	-26 ≤ h ≤ 28, -8 ≤ k ≤ 8, -30 ≤ l ≤ 29	-6 ≤ h ≤ 7, -15 ≤ k ≤ 14, -29 ≤ l ≤ 29
Reflections collected/ unique	18551 [R_{int} = 0.0497, Rsigma = 0.0495]	18551 [R_{int} = 0.0497, Rsigma = 0.0495]
Data/ restraints / parameters	3419/0/184	3419/0/181
Goodness-of-fit on F^2	1.018	1.019
Final R indices [I>2σ(I)]	R_1 = 0.0568, wR_2 = 0.1242	R_1 = 0.0579, wR_2 = 0.1468
R indices (all data)	R_1 = 0.1169, wR_2 = 0.1466	R_1 = 0.1179, wR_2 = 0.1743
Largest diff. peak and hole/(e.Å^{-3})	0.15 and -0.18	0.14 and -0.17

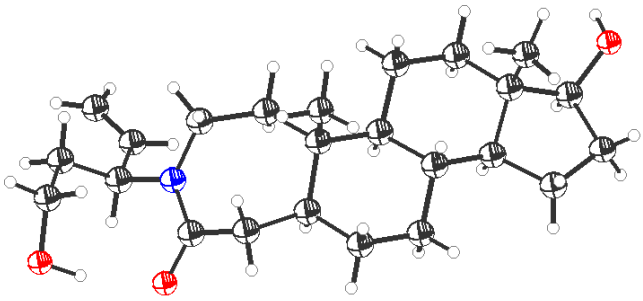


27a
(CCDC2176980)





28a
(CCDC 2176981)



Phase	**27a**	**28a**
Empirical formula	$C_{24}H_{39}NO_3$	$C_{24}H_{39}NO_3$
Formula weight	389.56	389.56
T/K	296.15	273.15
Crystal system	orthorhombic	orthorhombic
Space group	$R2_12_12_1$	$P2_12_12_1$
Unit cell dimensions	a = 6.3720(6) Å α = 90 °. b = 21.111(2) Å β = 90 °. c = 17.2221(17) Å γ= 90 °.	a = 10.4856(19) Å α = 90 °. b = 14.332(2) Å β = 90 °. c = 14.635(2) Å γ= 90 °.
V(Å^3)	2316.7(4)	2199.5(6)
Z, Calculated density(g/cm^3)	4 1.169	4 1.176
Absorption coefficient(mm^{-1})	0.078	0.076
F(000)	896.0	856.0
Crystal size(mm^3)	0.2×0.2×0.2	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection (°)	3.052 to 54.888	3.978 to 55.014
Limiting indices	-7 ≤ h ≤ 8, -27 ≤ k ≤ 27, -21 ≤ l ≤ 22	-13 ≤ h ≤ 13, -18 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected/ unique	22020 [R_{int} = 0.1009, R_{sigma} = 0.1650]	19927 [R_{int} = 0.0467, R_{sigma} = 0.0603]
Data/ restraints / parameters	5292/0/292	5028/0/273
Goodness-of-fit on F^2	0.977	1.022
Final R indices [I>2σ(I)]	R_1 = 0.0612, wR_2 = 0.0916	R_1 = 0.0510, wR_2 = 0.0946
R indices (all data)	R_1 = 0.2102, wR_2 = 0.1196	R_1 = 0.1041, wR_2 = 0.1096
Largest diff. peak and hole/(e.Å^{-3})	0.16 and -0.15	0.14 and -0.16

6. Reference

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7. Cartesian coordinates of the DFT-optimized structures

TS-A-1

E_{sol} optimization: -708.037052 a.u.

E_{sol} single-point: -708.8224521 a.u.

G_{sol} thermo-corrected: -708.5528101 a.u.

C	1.02377100	-0.74687600	1.15793300
C	2.47006800	-1.04844100	0.75792700
C	1.13499300	1.34587600	-0.26557800
C	2.58964200	1.03708600	-0.61664200
C	3.29023700	0.21398200	0.47278500
C	0.32269300	0.06993100	0.00004500
N	-0.97782100	0.38592700	0.57851300
C	-2.02243400	-0.64142600	0.49685200
C	-2.03490200	-1.36610200	-0.84646700
C	-0.62442900	-1.76935000	-1.24713400
O	0.25059800	-0.63597900	-1.20478300
C	-3.32439000	-0.10169300	1.02055000
C	-4.51452600	-0.28300600	0.44212200
C	4.73110700	-0.12085100	0.08960300
N	-1.62712800	1.67703700	-0.30722600
N	-2.01013500	2.70785400	-0.40197300
H	0.47812900	-1.68081800	1.34601600
H	0.99053900	-0.14454900	2.07665500
H	2.92353400	-1.62351900	1.58274500
H	2.47426300	-1.70022800	-0.13219700
H	1.07576400	1.98429400	0.62895700
H	0.65551800	1.87221700	-1.10652800
H	3.12194700	1.98822600	-0.77954000
H	2.62174800	0.48264300	-1.56997500
H	3.30404500	0.82065900	1.39816800
H	-1.63385700	-1.32693200	1.28388800
H	-2.68017000	-2.25397000	-0.78481800
H	-2.45953500	-0.68622600	-1.60484000
H	-0.59485200	-2.12714200	-2.28496600
H	-0.24060800	-2.57495000	-0.59801500
H	-3.23929300	0.46610900	1.95386800
H	-5.41803100	0.13615200	0.89456600
H	-4.64485200	-0.84830900	-0.48487700
H	5.31703300	0.79441300	-0.09604000
H	5.23643600	-0.68960000	0.88751700
H	4.76206500	-0.73114600	-0.82949300

TS-B-1

E_{sol} optimization: -708.035215 a.u.

E_{sol} single-point: -708.8207095 a.u.

G_{sol} thermo-corrected: -708.5513045 a.u.

C	-1.29883500	0.36324100	1.43969000
C	-2.32351400	-0.63731000	0.91044200
C	-1.06570700	1.34565900	-0.86719500
C	-2.12593300	0.37798700	-1.38411700
C	-3.10220300	-0.07848300	-0.28921100
C	-0.26832600	0.81222900	0.39365700
N	0.49782300	-0.30600400	-0.13696800
C	1.77393500	-0.01110100	-0.79463800
C	2.57220100	1.06939000	-0.07306900
C	1.67224200	2.24556600	0.27049800
O	0.51752400	1.80055600	0.99252200
C	2.47706200	-1.28920400	-1.15722800
C	3.78171700	-1.51628800	-0.98277900
C	-4.11856300	-1.08523500	-0.82564500
N	0.95402000	-1.28658400	1.17341200
N	0.91859000	-2.22520900	1.75335100
H	-1.79890000	1.28790000	1.76459700
H	-0.75129400	-0.01474800	2.31757500
H	-1.82887100	-1.58116600	0.61980100
H	-3.01816100	-0.89207800	1.72724900
H	-1.52824800	2.26252800	-0.46805800
H	-0.37521500	1.64720100	-1.66542600
H	-1.64138200	-0.50420400	-1.83622000
H	-2.68075200	0.88204700	-2.19288600
H	-3.64764800	0.81825900	0.06077500
H	1.37228000	0.40161600	-1.74738600
H	2.99299800	0.63610700	0.85060900
H	3.40696300	1.40267900	-0.70595700
H	1.36788300	2.79177900	-0.63883900

H	2.18313700	2.95333600	0.93706100
H	1.83221300	-2.05402100	-1.60427200
H	4.45991100	-0.77566900	-0.54991000
H	4.22141400	-2.47228300	-1.28192700
H	-3.61545600	-1.99924600	-1.18599800
H	-4.83631200	-1.38394200	-0.04401100
H	-4.69225200	-0.66466400	-1.66795400

TS-A-2

E_{sol} optimization: -708.029822 a.u.

E_{sol} single-point: -708.8151582 a.u.

G_{sol} thermo-corrected: -708.5451952 a.u.

C	1.16533200	1.42815100	-0.18165600
C	2.56374700	1.02151100	0.27433800
C	0.64493300	-0.96584500	-0.80854100
C	2.03939000	-1.35264500	-0.31086100
C	3.07023300	-0.22964000	-0.45755600
C	0.13962600	0.29962200	0.00778900
N	-1.11444700	0.63161600	-0.63460100
C	-2.35753100	-0.05024700	-0.17357000
C	-2.34978600	-0.29785800	1.33421800
C	-1.00534700	-0.82899700	1.80827000
O	0.04106700	0.05207200	1.37958600
C	-2.52116100	-1.23862200	-1.11179900
C	-2.76250100	-2.49403800	-0.72858300
C	4.44927800	-0.65643600	0.04389200
N	-1.43464100	2.26089400	-0.26745200
N	-1.76176400	3.27658200	-0.55050500
H	1.16598000	1.71900400	-1.24297400
H	0.81145900	2.28418700	0.41812100
H	3.25027500	1.86689100	0.10511900

H	2.54914100	0.82948200	1.36047100
H	-0.05686100	-1.79592300	-0.67940300
H	0.66489500	-0.70317800	-1.87517300
H	2.35151500	-2.23859600	-0.88962200
H	1.97647100	-1.66194000	0.74613600
H	3.14663800	0.01670200	-1.53358900
H	-3.17927900	0.63185200	-0.44249100
H	-3.16584400	-0.97966200	1.61178500
H	-2.54443200	0.66637200	1.83212500
H	-0.81548300	-1.85139100	1.44217300
H	-0.94995800	-0.84403700	2.90489100
H	-2.49006700	-0.97629800	-2.17385200
H	-2.79175900	-2.80413100	0.31932600
H	-2.95360700	-3.26733900	-1.47871400
H	4.81921800	-1.53907100	-0.50337000
H	4.41465900	-0.91591000	1.11607900
H	5.18719800	0.15302300	-0.08145900

TS-B-2

E_{sol} optimization: -708.02798 a.u.

E_{sol} single-point: -708.8134284 a.u.

G_{sol} thermo-corrected: -708.5429834 a.u.

C	1.23105700	1.14592900	1.05290600
C	2.41615100	0.84694800	0.13961300
C	0.47049800	-1.24645100	0.84978000
C	1.67947000	-1.55351000	-0.02484500
C	2.86715900	-0.61704400	0.24517100
C	-0.00436600	0.27352100	0.78159600
N	-0.48185200	0.42542800	-0.57260100
C	-1.89613800	0.08210900	-0.88320200
C	-2.83805700	0.43198200	0.26748800
C	-2.25657600	0.01655600	1.60973800

O	-0.94515600	0.57621500	1.76782900
C	-1.84028900	-1.35771200	-1.37807600
C	-2.61706300	-2.35234100	-0.94429000
C	4.04375200	-0.91582500	-0.68231400
N	-0.39659800	2.07979500	-0.95597200
N	-0.07849500	2.89673000	-1.62742200
H	1.49587700	0.95809600	2.10389500
H	0.90911900	2.19976400	0.99724800
H	2.16516600	1.07873300	-0.91077800
H	3.24581000	1.51905800	0.41297700
H	0.71442600	-1.34871300	1.91919100
H	-0.36873900	-1.91355800	0.62761200
H	1.39614100	-1.49541300	-1.08949700
H	1.97766100	-2.59808200	0.16623300
H	3.19032800	-0.78822400	1.28933800
H	-2.15077100	0.67330800	-1.77713400
H	-2.97620300	1.52563800	0.26561800
H	-3.82427900	-0.02497600	0.10499200
H	-2.85207500	0.41923200	2.43994700
H	-2.21524700	-1.07957000	1.71938300
H	-1.13058600	-1.52055800	-2.19496600
H	-3.33307800	-2.23844900	-0.12618400
H	-2.56364400	-3.33548100	-1.42161700
H	3.76415400	-0.75510900	-1.73795400
H	4.90375600	-0.26279100	-0.46028200
H	4.37845800	-1.96126500	-0.58008800

I-A

E_{sol} optimization: -708.073252 a.u.

E_{sol} single-point: -708.8585992 a.u.

G_{sol} thermo-corrected: -708.5893482 a.u.

C	3.38305000	-0.05896100	0.18245400
C	2.34922800	-0.81464500	1.02844300
C	1.19942400	0.09121200	1.48620400
C	0.65296700	0.97357500	0.42619100
C	1.53578600	1.51949800	-0.62690600
C	2.68714500	0.58304200	-1.02475600
O	-0.55757500	1.31863100	0.58401600
C	-1.31531100	2.24075900	-0.27699000
C	-2.78581500	1.99454700	0.02622200
C	-3.16167200	0.58931600	-0.35182900
C	-3.19553900	-0.43315600	0.51213900
C	-3.27535300	-1.86505400	0.07551400
N	-1.90234900	-2.46665700	0.01789300
N	-1.06839500	-1.84283500	-0.61490600
N	-0.23206300	-1.30693100	-1.17758200
H	3.80435000	0.75313300	0.80495300
H	1.93861700	-1.65166000	0.43949500
H	2.82267000	-1.25202700	1.92067600
H	0.37201200	-0.45171200	1.96668300
H	1.57712900	0.81618300	2.23768700
H	0.96178400	1.86848700	-1.49529600
H	1.94121700	2.43458200	-0.14262100
H	2.28503300	-0.21022000	-1.67620100
H	3.40617200	1.16029200	-1.62547800
H	-0.98411400	3.25522200	-0.01290700
H	-1.06782700	2.02393000	-1.32499700
H	-2.96732900	2.18590400	1.09575100
H	-3.35718800	2.73850700	-0.55266800
H	-3.30041200	0.39123200	-1.42291500
H	-3.02075600	-0.25464400	1.57998500

H	-3.83063900	-2.49268900	0.78313600
H	-3.74275700	-1.96030800	-0.91866000
C	4.52392700	-0.97656500	-0.25581600
H	5.27597900	-0.42600200	-0.84417000
H	5.03380300	-1.42105200	0.61442700
H	4.14548000	-1.80266000	-0.88204800

Crotyl azide

E_{sol} optimization: -320.58206 a.u.

E_{sol} single-point: -320.9478077 a.u.

G_{sol} thermo-corrected: -320.8689467 a.u.

C	-2.87060100	0.67689000	-0.14630900
C	-1.63624000	0.02414300	0.39357000
C	-0.76599100	-0.70482600	-0.31799700
C	0.47137800	-1.32543600	0.26024100
N	1.72086500	-0.70340000	-0.26534600
N	1.86651500	0.49328700	-0.05911300
N	2.09349300	1.60146200	0.07767900
H	-2.84684600	1.76690500	0.03206500
H	-2.99213600	0.50472400	-1.22746900
H	-3.77258000	0.30054900	0.36891600
H	-1.44771500	0.15984500	1.46785300
H	-0.91958000	-0.84823500	-1.39533200
H	0.46892400	-1.26241700	1.36202700
H	0.55254300	-2.38543500	-0.01763000

Transition state from crotyl azide to 3-azidobut-1-ene

E_{sol} optimization: -320.54508 a.u.

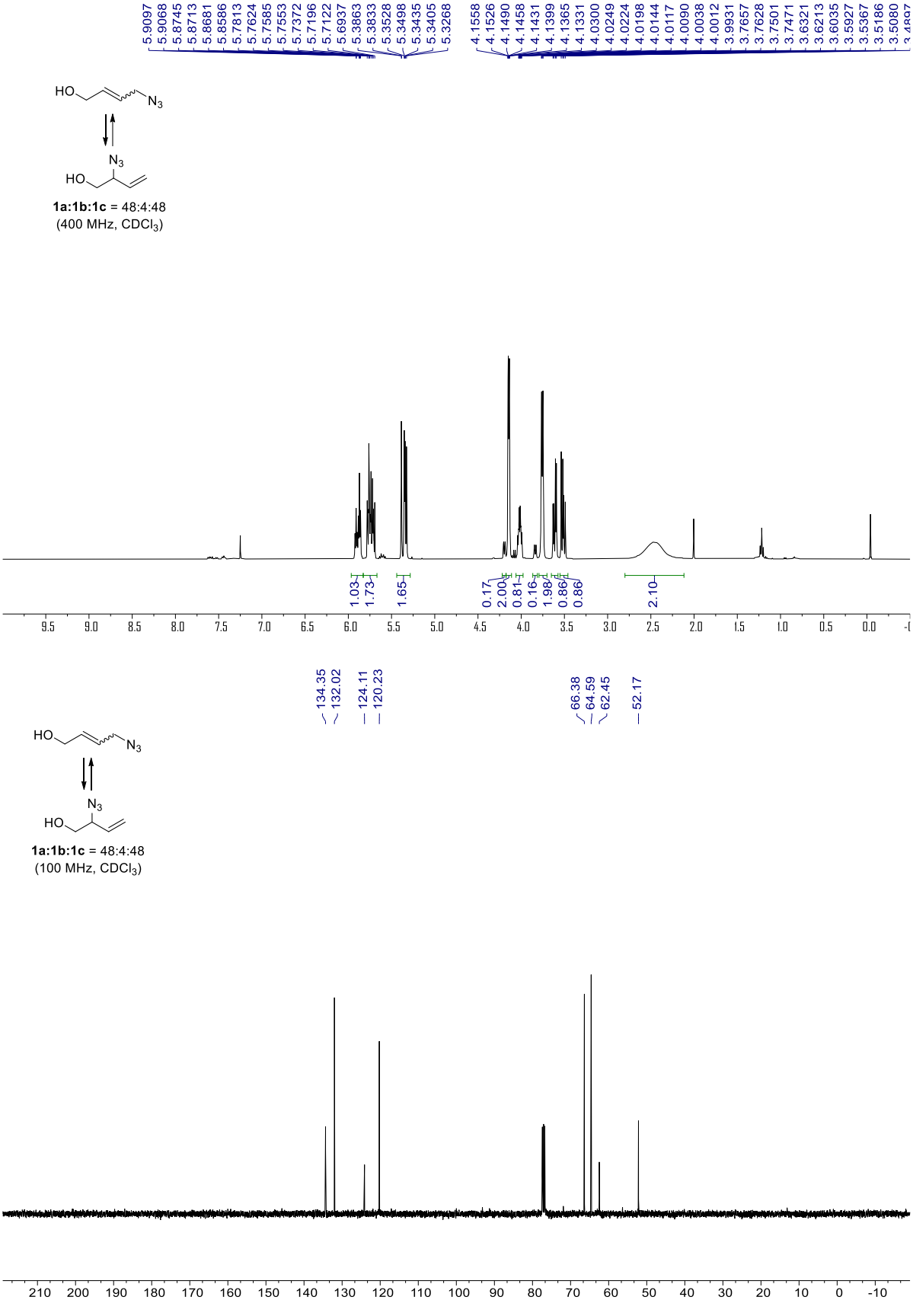
E_{sol} single-point: -320.9148068 a.u.

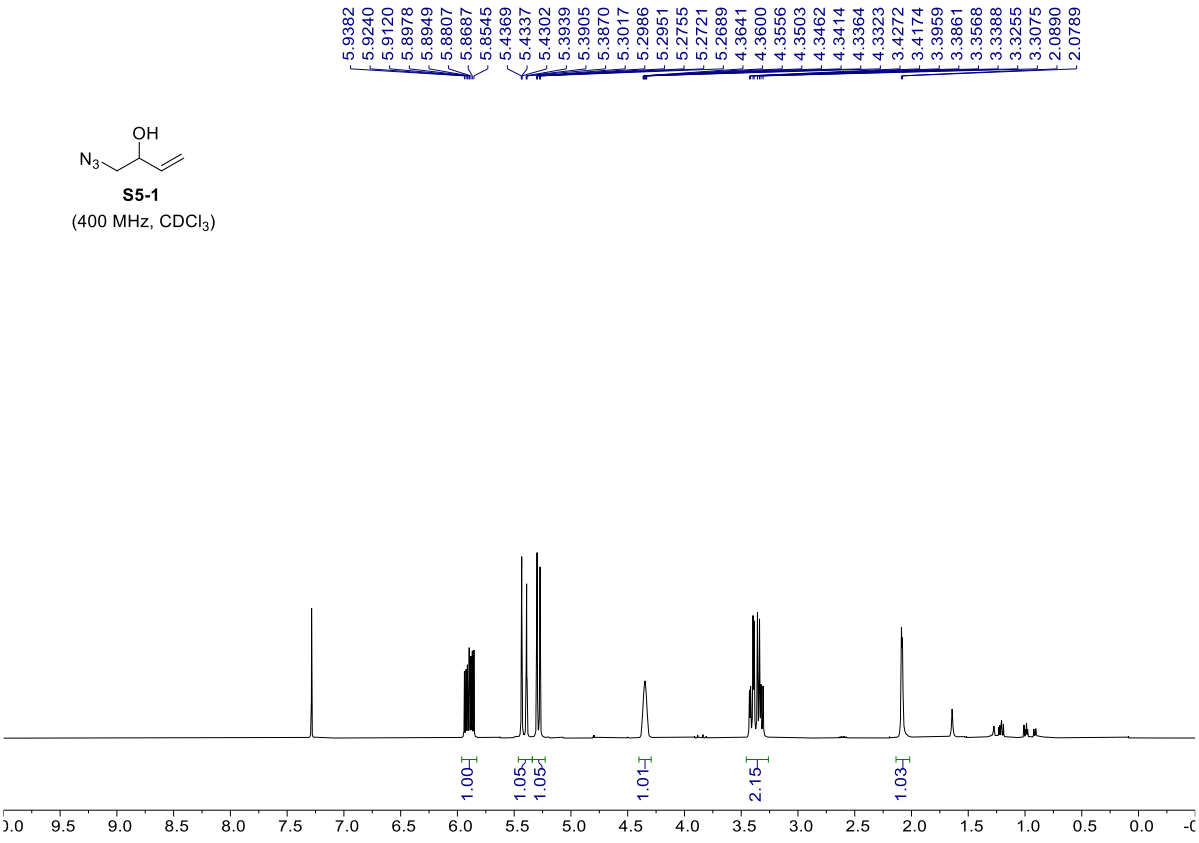
G_{sol} thermo-corrected: -320.8359038 a.u.

C	2.42052500	-0.21365200	-0.11611800
C	1.09307500	0.24813300	0.38087100

C	0.28374800	1.15628300	-0.30879900
C	-0.95251600	1.53853700	0.18877900
N	-2.11210500	-0.31913700	-0.13957500
N	-1.19178000	-1.05309900	-0.05787000
N	-0.13183700	-1.56348800	0.03371100
H	2.65598400	-1.22177900	0.25513100
H	2.47467400	-0.20718800	-1.21512000
H	3.20127800	0.46669700	0.27197300
H	0.89982600	0.11388000	1.45053700
H	0.53119200	1.38603100	-1.35157900
H	-1.17472400	1.44030100	1.25427100
H	-1.60717100	2.19631500	-0.38747200

8. Copies of ^{1}H NMR and ^{13}C NMR




5.9382
5.9240
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5.4337
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5.3939
5.3905
5.3870
5.3017
5.2986
5.2951
5.2755
5.2721
5.2689
4.3641
4.3600
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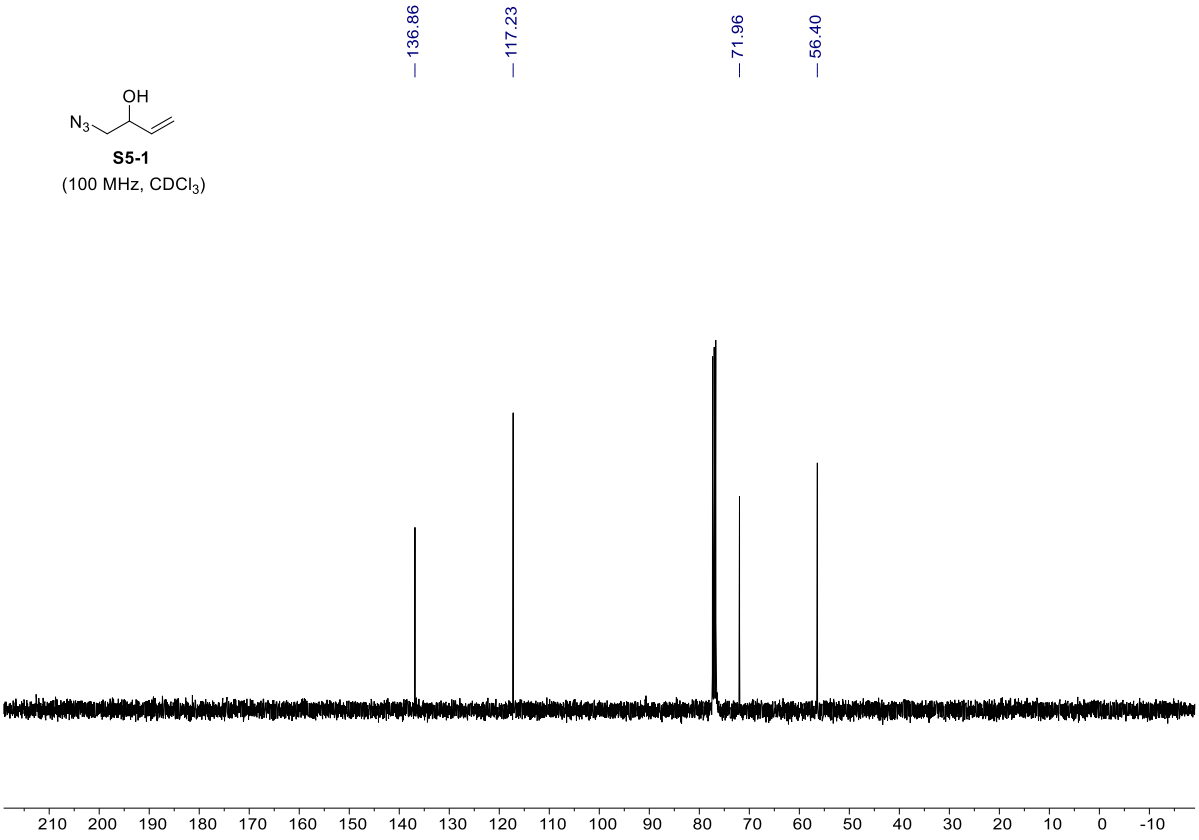
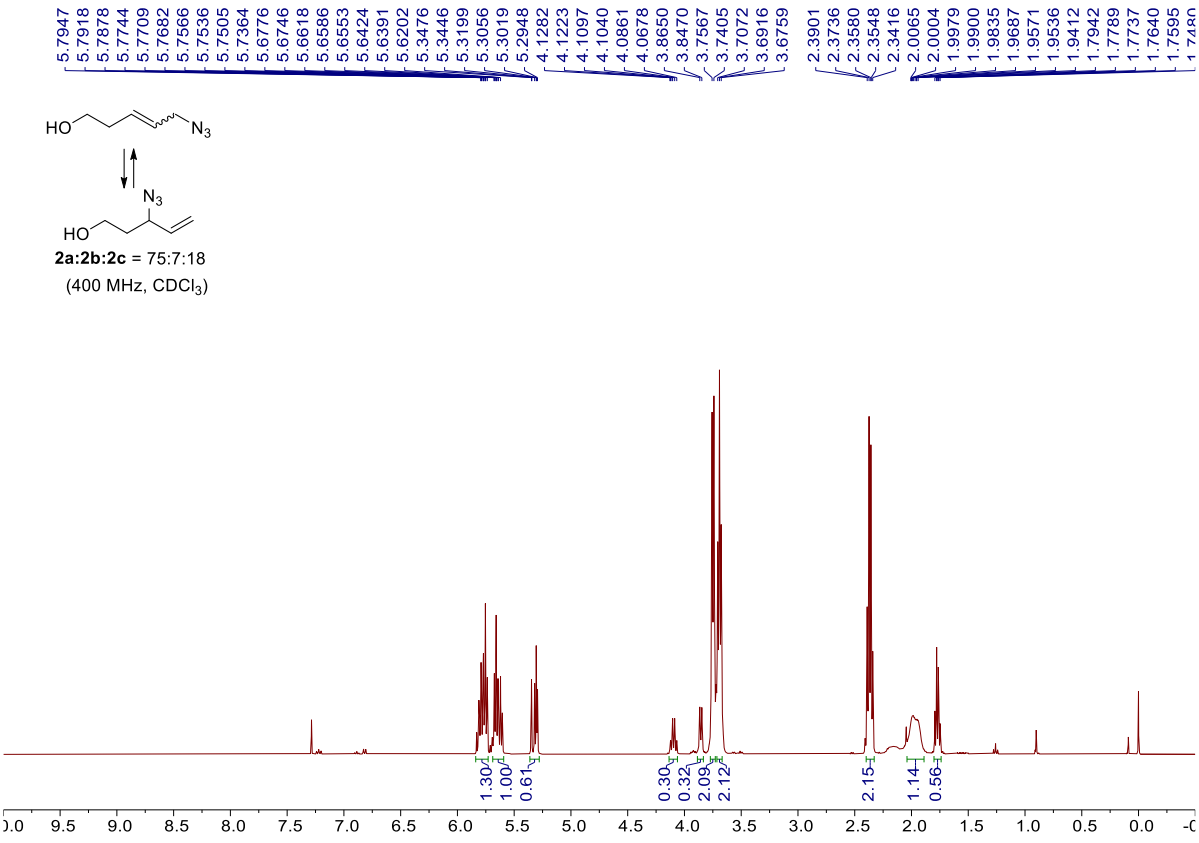
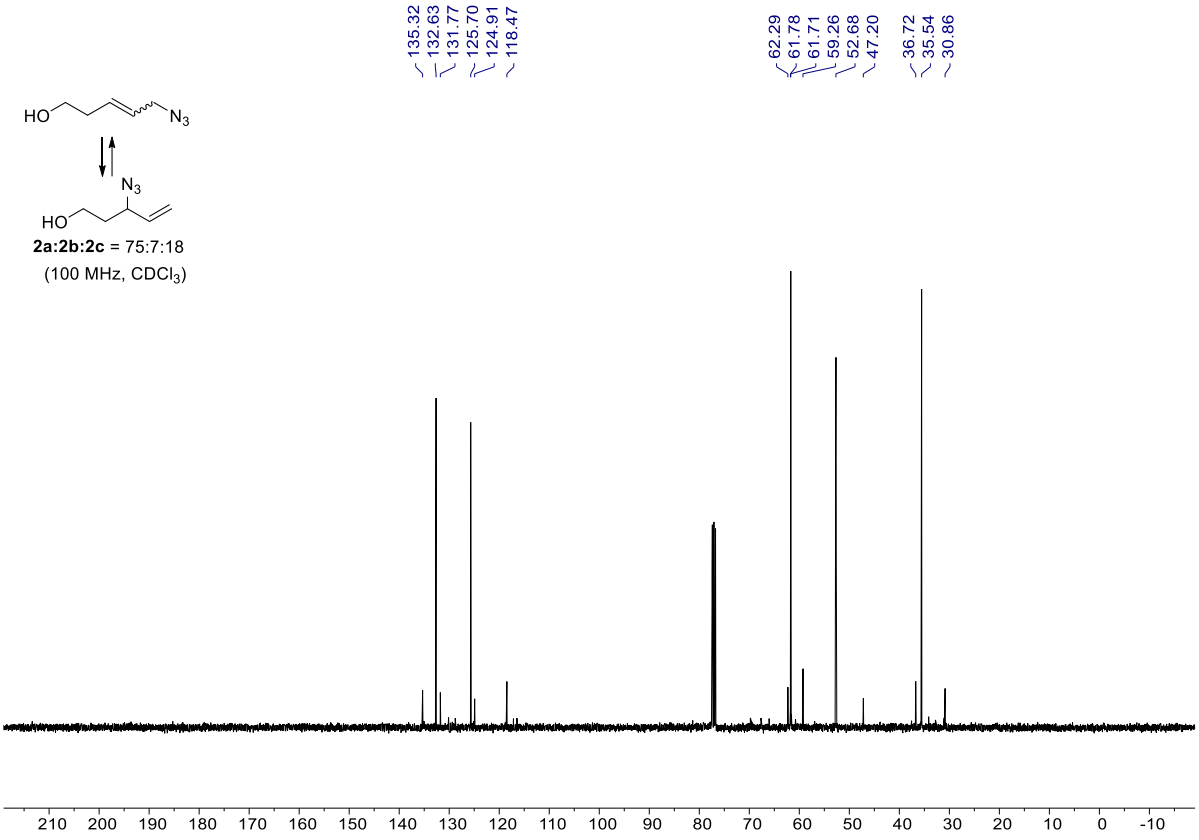
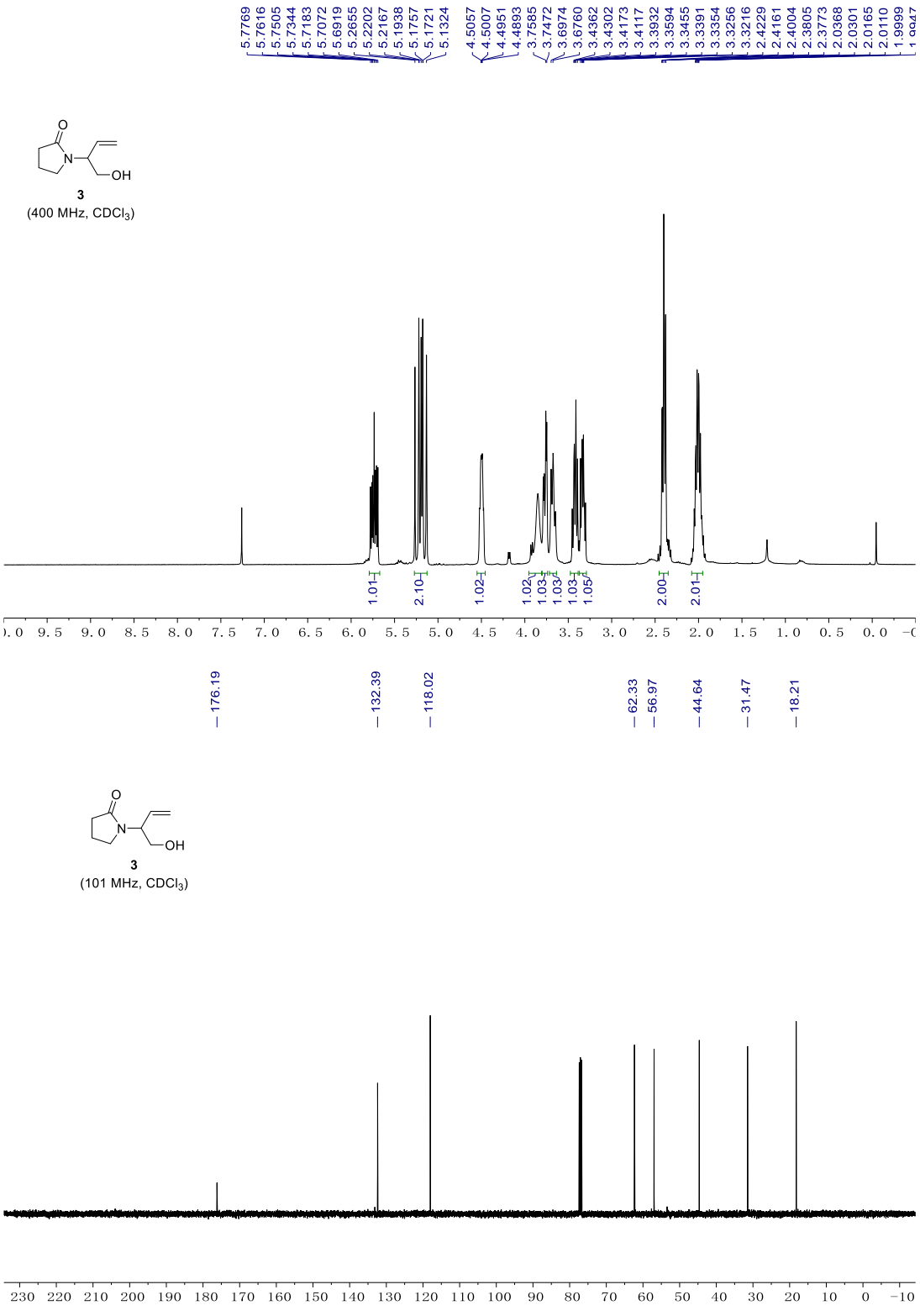
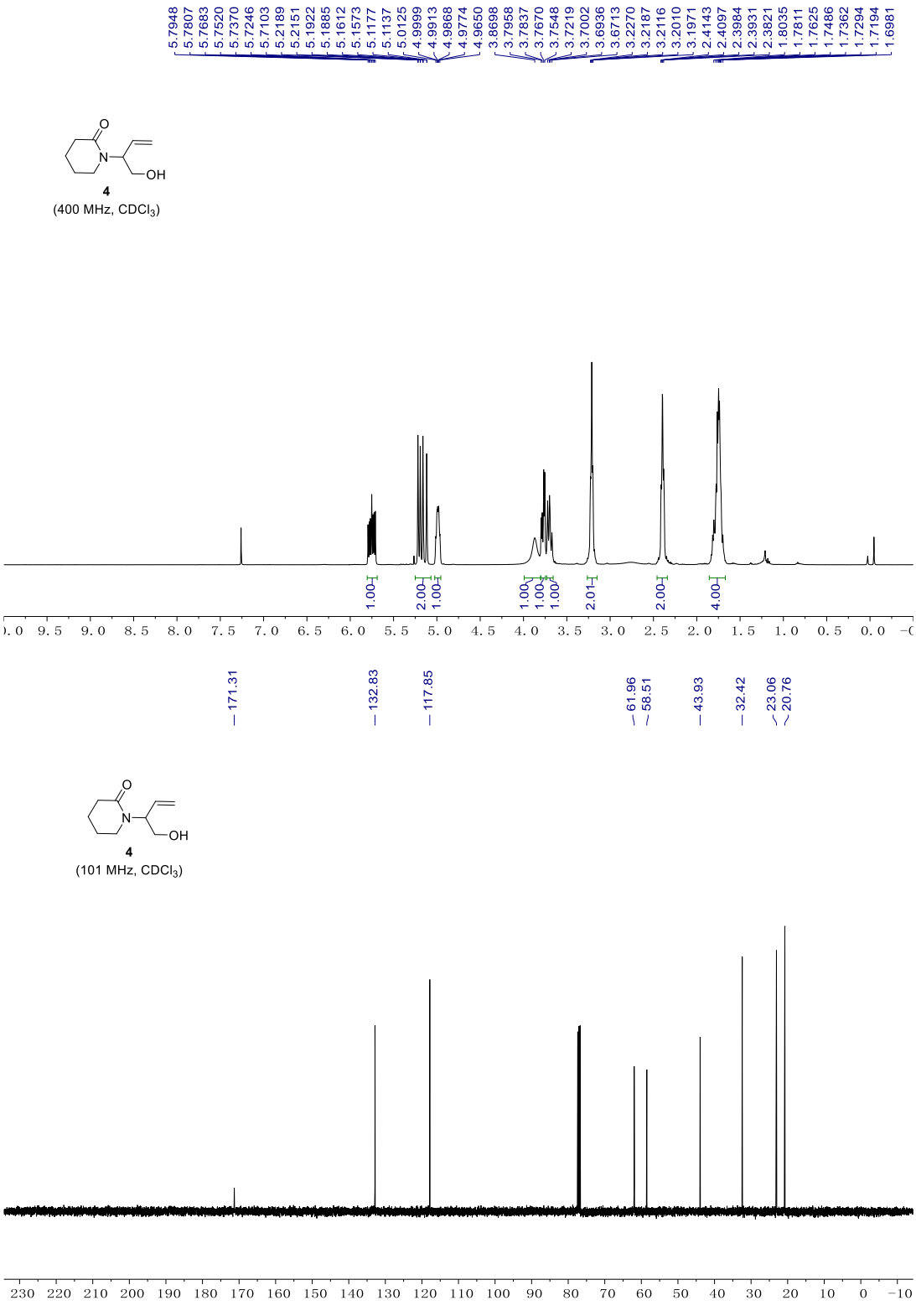
3.3959
3.3861
3.3568
3.3388
3.3255
3.3075
2.0890
2.0789
OH
N3
S5-1
(400 MHz, CDCl3)
1.00
1.05
1.05
1.01
2.15
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

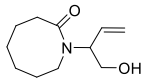

136.86
117.23
71.96
56.40
OH
N3
S5-1
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


5.7947
5.7918
5.7878
5.7744
5.7709
5.7682
5.7566
5.7536
5.7505
5.7364
5.6776
5.6746
5.6618
5.6586
5.6553
5.6424
5.6391
5.6202
5.3476
5.3446
5.3199
5.3056
5.3019
5.2948
4.1282
4.1223
4.1097
4.1040
4.0861
4.0678
3.8650
3.8470
3.7567
3.7405
3.7072
3.6916
3.6759
2.3901
2.3736
2.3580
2.3548
2.3416
2.0065
2.0004
1.9979
1.9900
1.9835
1.9687
1.9571
1.9536
1.9412
1.7942
1.7789
1.7737
1.7640
1.7595
HO
N3
N3
HO
2a:2b:2c = 75:7:18
(400 MHz, CDCl3)
1.30
1.00
0.61
0.30
0.32
2.09
2.12
2.15
1.14
0.56
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

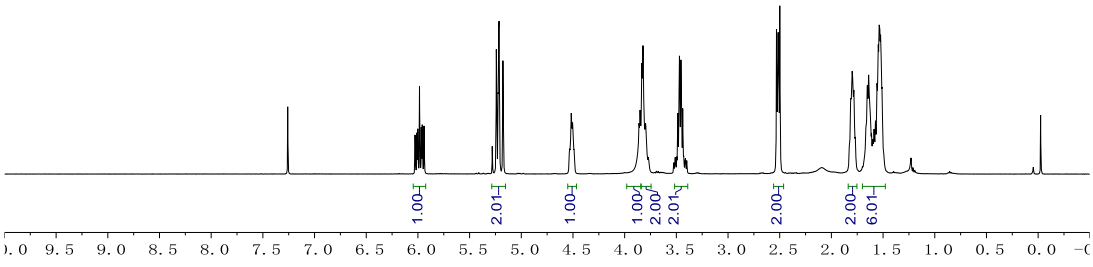

135.32
132.63
131.77
125.70
124.91
118.47
62.29
61.78
61.71
59.26
52.68
47.20
36.72
35.54
30.86
HO
N3
N3
HO
2a:2b:2c = 75:7:18
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

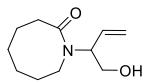

5.7769
5.7616
5.7505
5.7344
5.7183
5.7072
5.6919
5.2655
5.2202
5.2167
5.1938
5.1757
5.1721
5.1324
4.5057
4.5007
4.4951
4.4893
3.7585
3.7472
3.6974
3.6760
3.4362
3.4302
3.4173
3.4117
3.3932
3.3594
3.3455
3.3391
3.3354
3.3256
3.3216
2.4229
2.4161
2.4004
2.3805
2.3773
2.0368
2.0301
2.0165
2.0110
1.9999
O
N
OH
3
(400 MHz, CDCl3)
1.01
2.10
1.02
1.02
1.03
1.03
1.03
1.05
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
176.19
132.39
118.02
62.33
56.97
44.64
31.47
18.21
O
N
OH
3
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


5.7948
5.7807
5.7683
5.7520
5.7370
5.7246
5.7103
5.2189
5.2151
5.1922
5.1885
5.1612
5.1573
5.1177
5.1137
5.0125
4.9999
4.9913
4.9868
4.9774
4.9650
3.8698
3.7958
3.7837
3.7670
3.7548
3.7219
3.7002
3.6936
3.6713
3.2270
3.2187
3.2116
3.2010
3.1971
2.4143
2.4097
2.3984
2.3931
2.3821
1.8035
1.7811
1.7625
1.7486
1.7362
1.7294
1.7194
1.6981
O
N
OH
4
(400 MHz, CDCl3)
1.00
2.00
1.00
1.00
1.00
1.00
2.01
2.00
4.00
171.31
132.83
117.85
61.96
58.51
43.93
32.42
23.06
20.76
O
N
OH
4
(101 MHz, CDCl3)

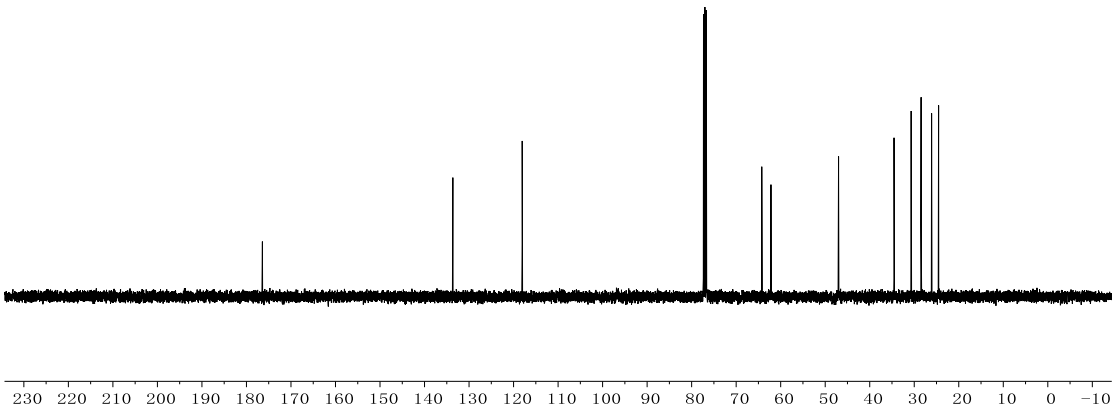


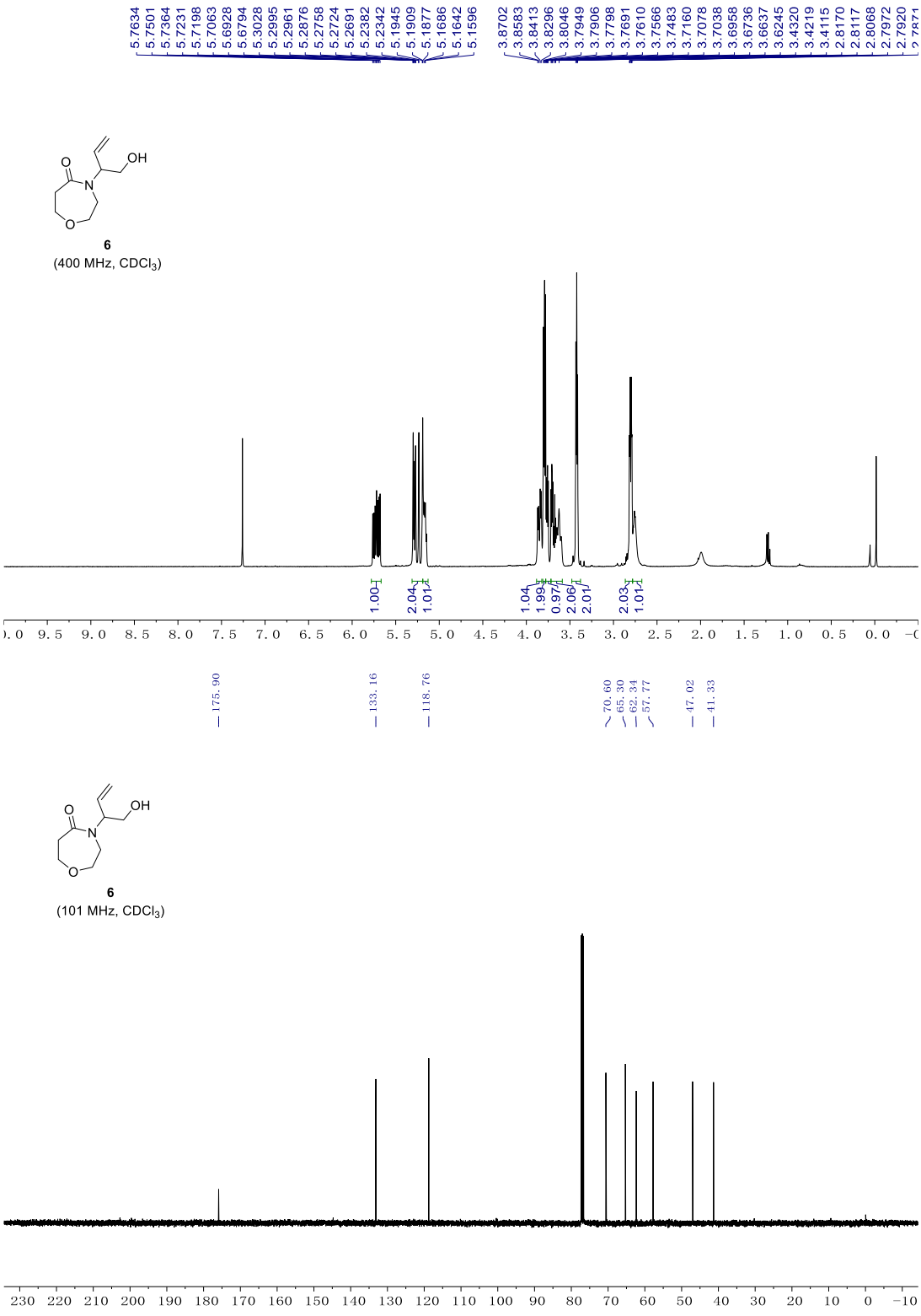
5
(400 MHz, $CDCl_3$)

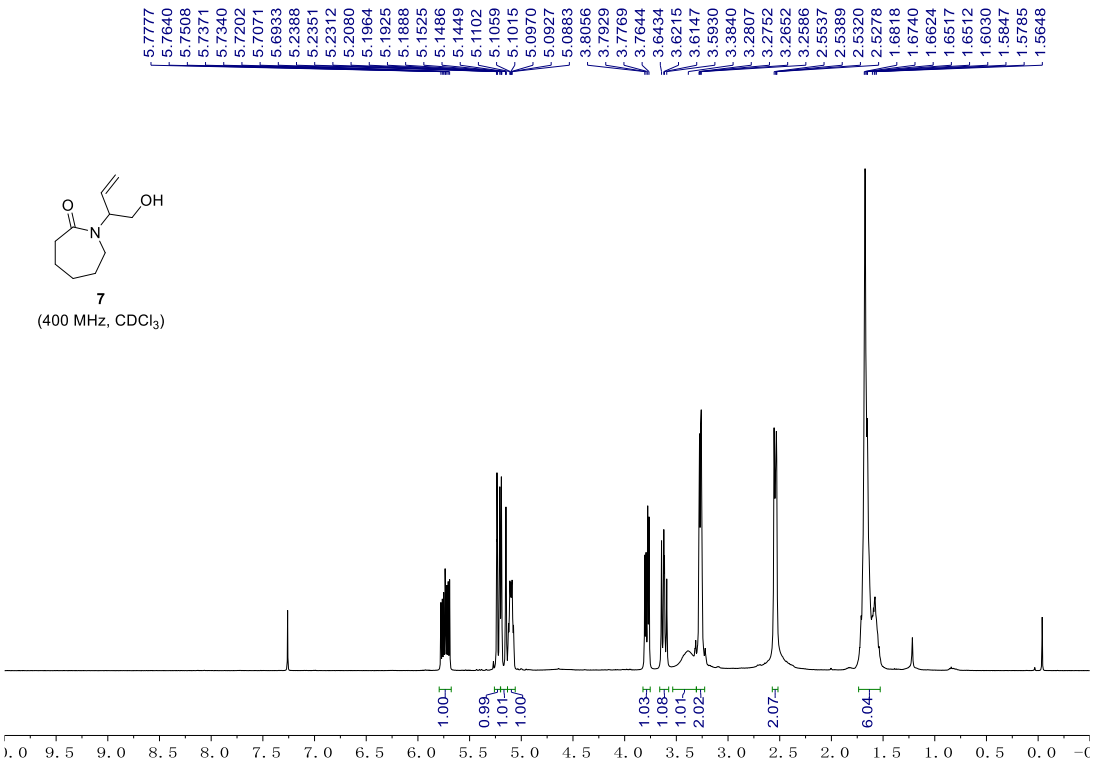


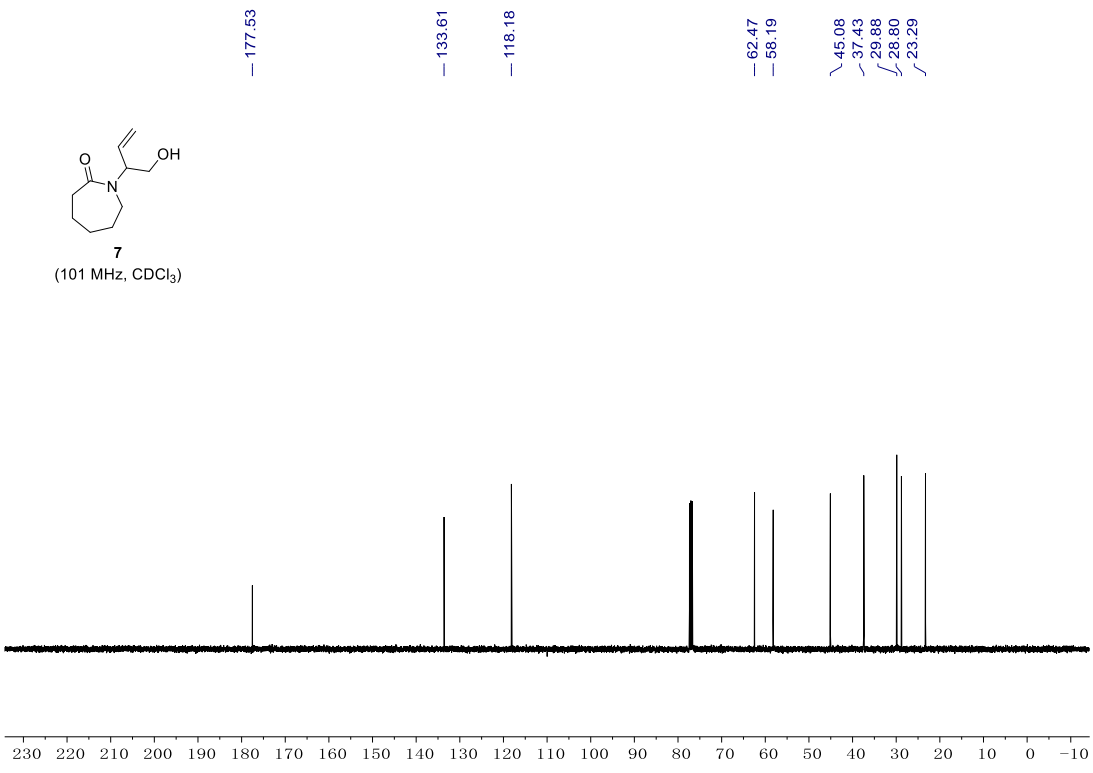


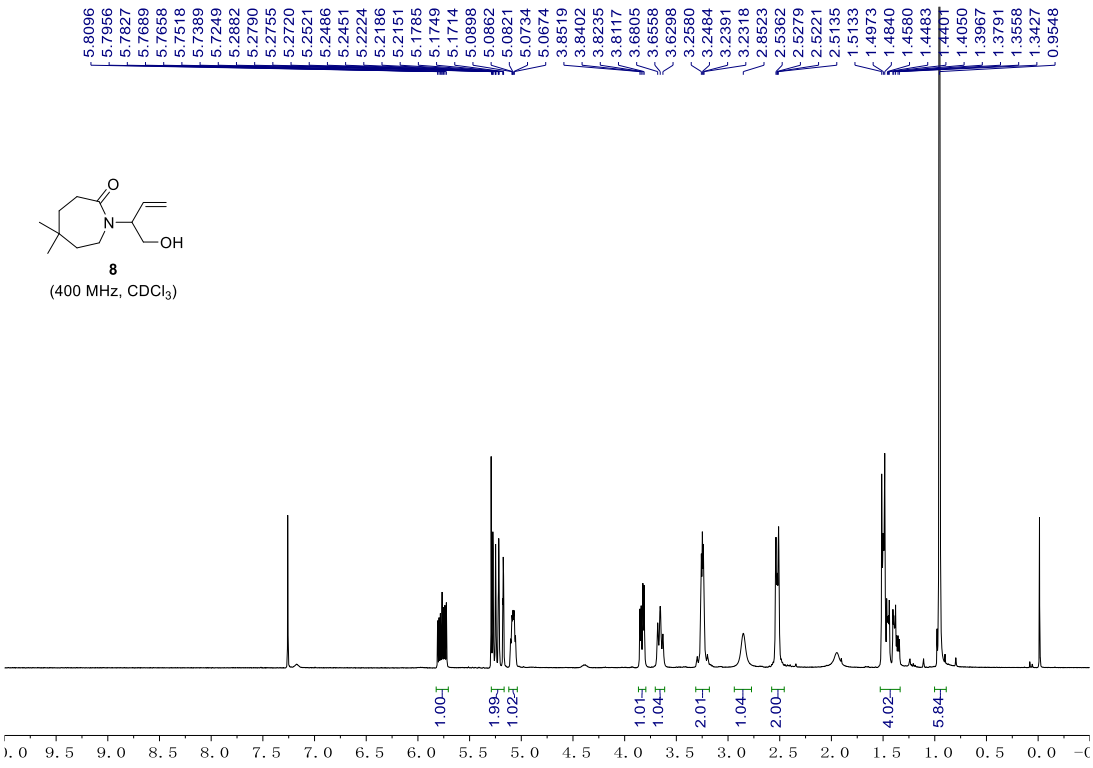
5
(101 MHz, $CDCl_3$)

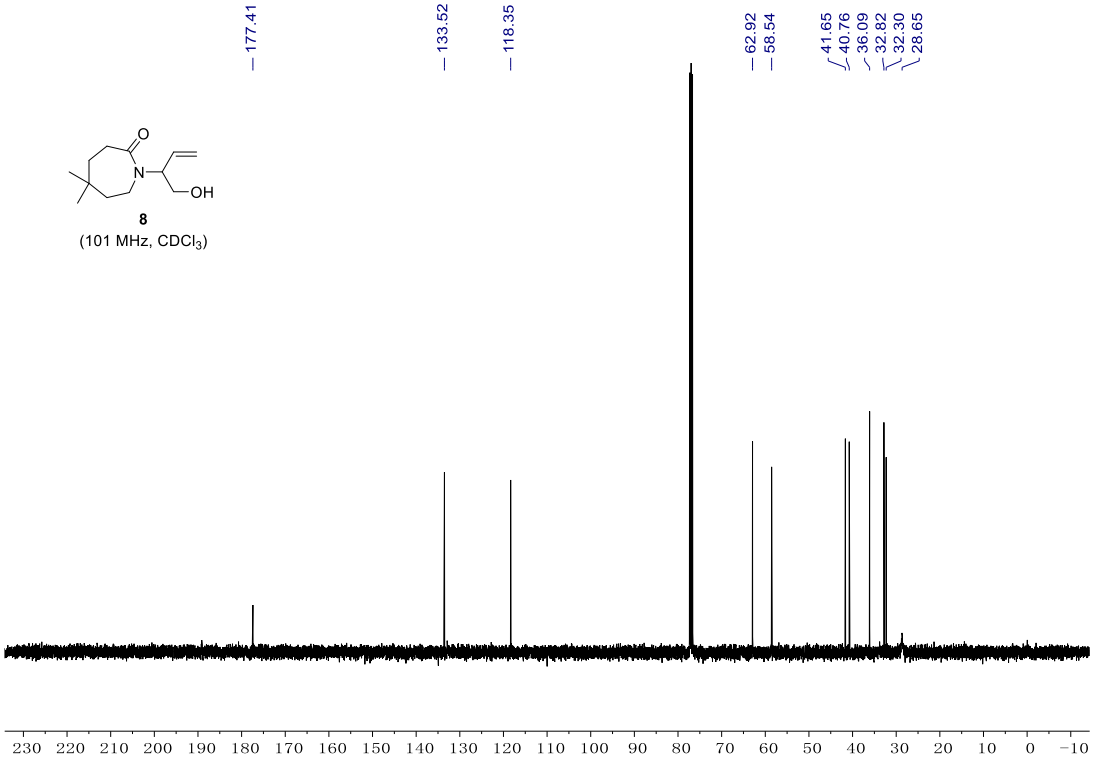


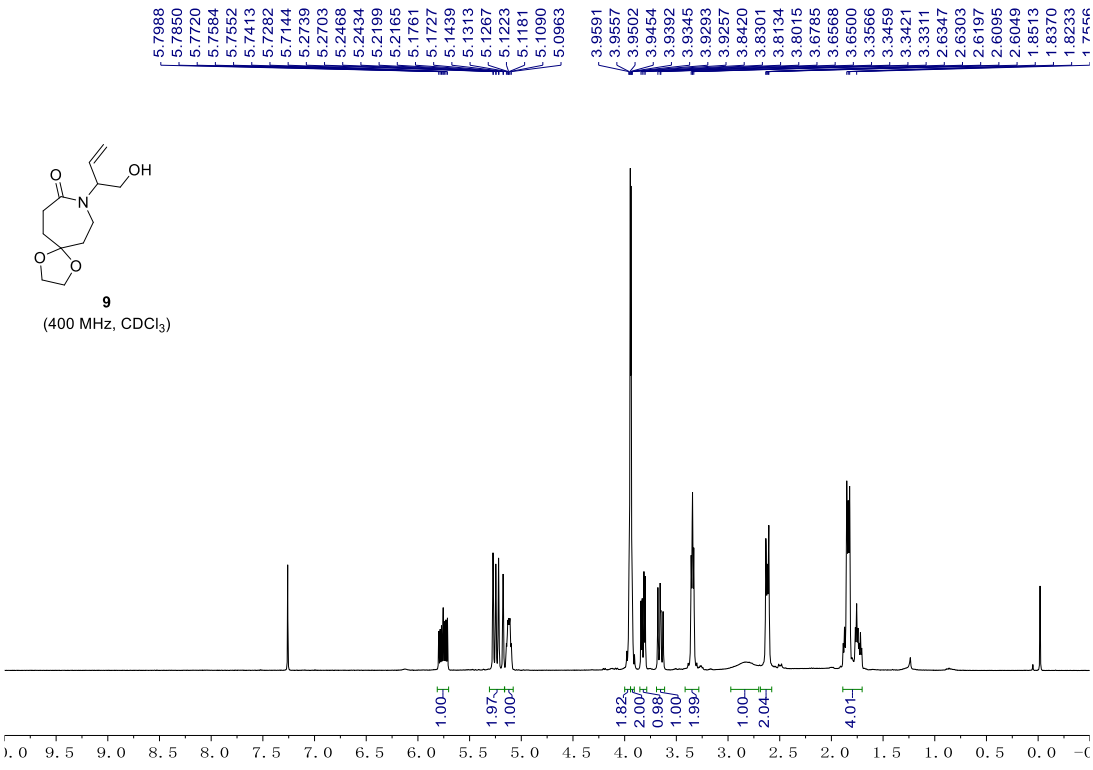

6
(400 MHz, CDCl3)
6
(101 MHz, CDCl3)

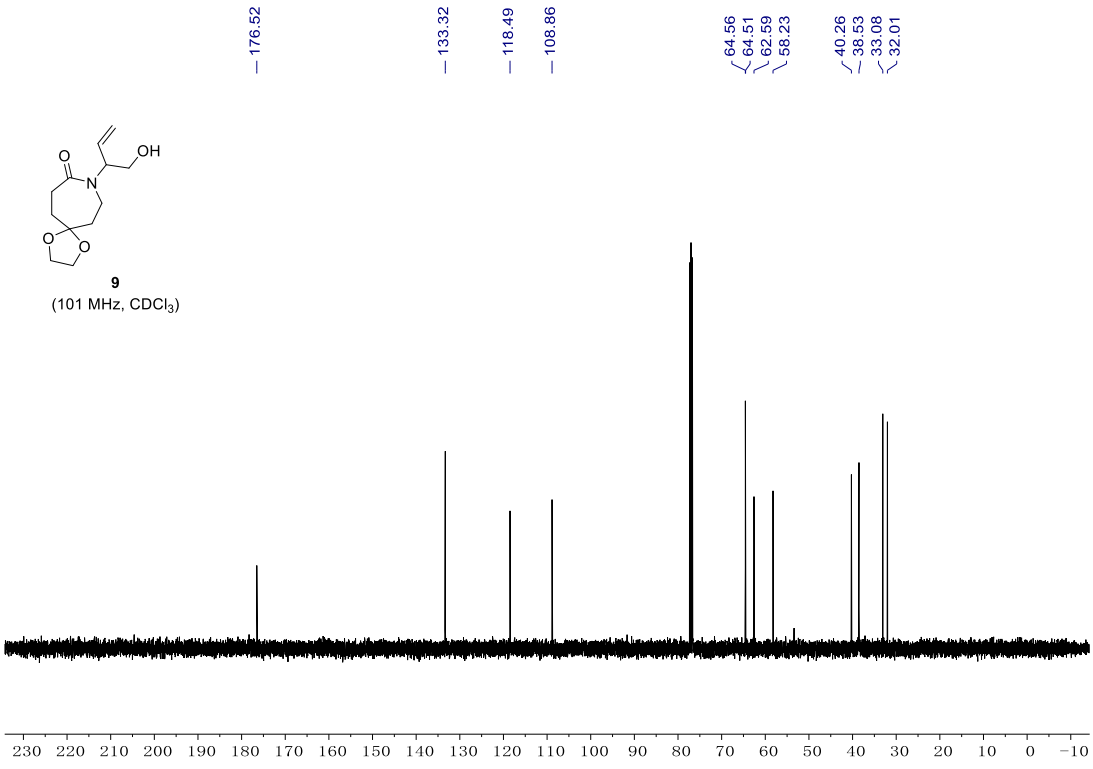

5.7777
5.7640
5.7508
5.7371
5.7340
5.7202
5.7071
5.6933
5.2388
5.2351
5.2312
5.2080
5.1964
5.1925
5.1888
5.1525
5.1486
5.1449
5.1102
5.1059
5.1015
5.0970
5.0927
5.0883
3.8056
3.7929
3.7769
3.7644
3.6434
3.6215
3.6147
3.5930
3.3840
3.2807
3.2752
3.2652
3.2586
2.5537
2.5389
2.5320
2.5278
1.6818
1.6740
1.6624
1.6517
1.6512
1.6030
1.5847
1.5785
1.5648
OH
O
N
7
(400 MHz, CDCl3)
1.00
0.99
1.01
1.00
1.03
1.08
1.01
2.02
2.07
6.04

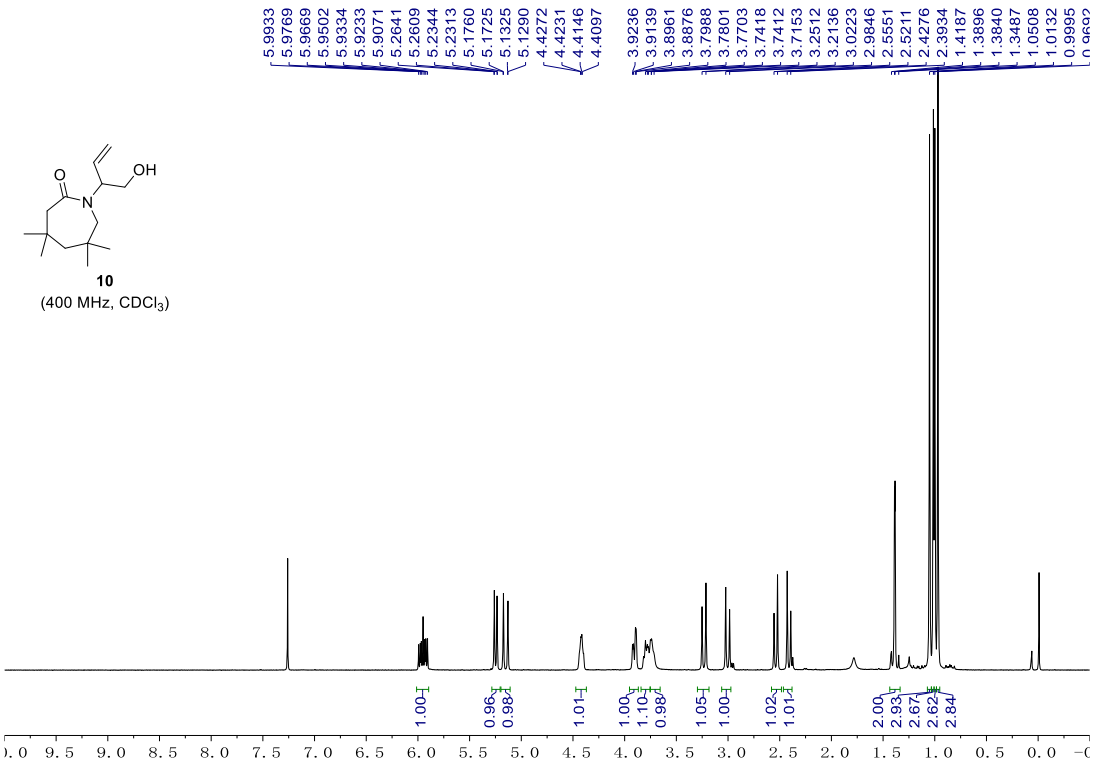

177.53
133.61
118.18
62.47
58.19
45.08
37.43
29.88
28.80
23.29
OH
O
N
7
(101 MHz, CDCl3)

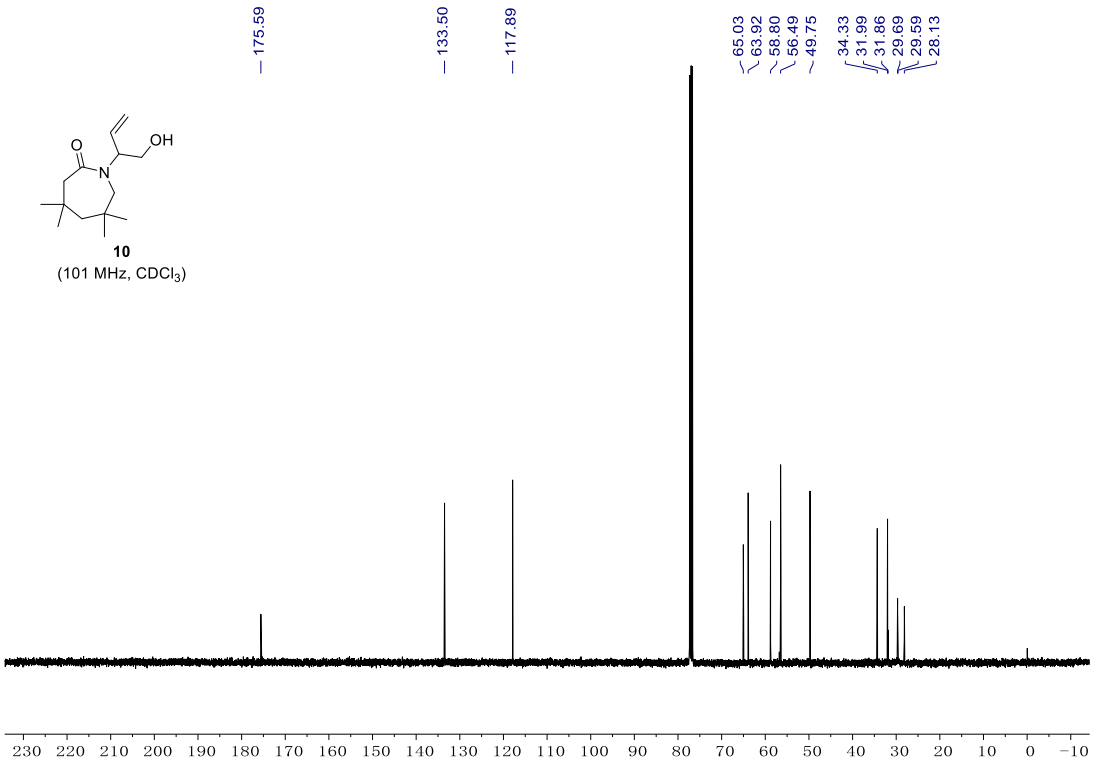

5.8096
5.7956
5.7827
5.7689
5.7658
5.7518
5.7389
5.7249
5.2882
5.2790
5.2755
5.2720
5.2521
5.2486
5.2451
5.2224
5.2186
5.2151
5.1785
5.1749
5.1714
5.0898
5.0862
5.0821
5.0734
5.0674
3.8519
3.8402
3.8235
3.8117
3.6805
3.6558
3.6298
3.2580
3.2484
3.2391
3.2318
2.8523
2.5362
2.5279
2.5221
2.5135
1.5133
1.4973
1.4840
1.4580
1.4483
1.4401
1.4050
1.3967
1.3791
1.3558
1.3427
0.9548
O
N
OH
8
(400 MHz, CDCl3)
1.00
1.99
1.02
1.01
1.04
2.01
1.04
2.00
4.02
5.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

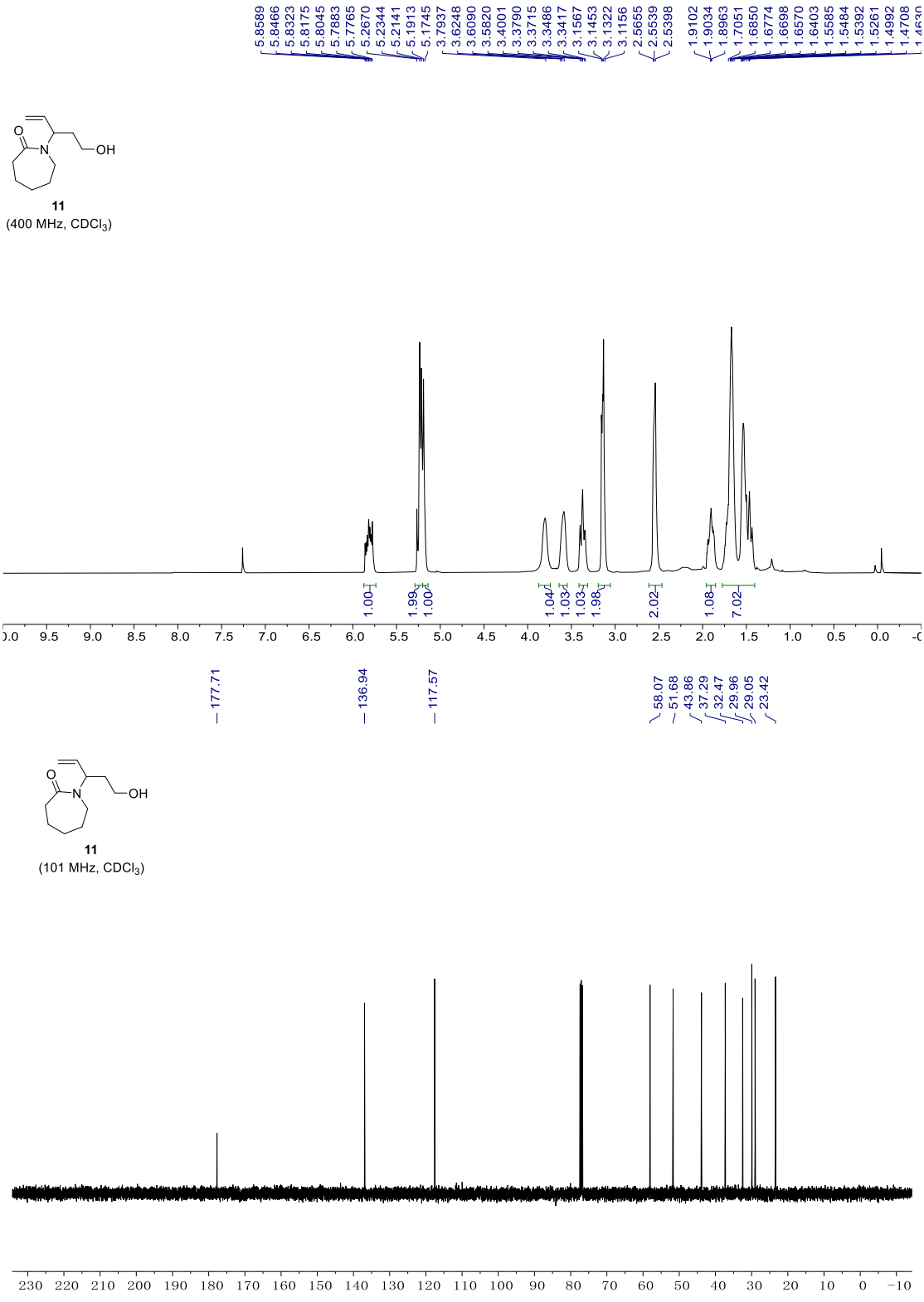

177.41
133.52
118.35
62.92
58.54
41.65
40.76
36.09
32.82
32.30
28.65
O
N
OH
8
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

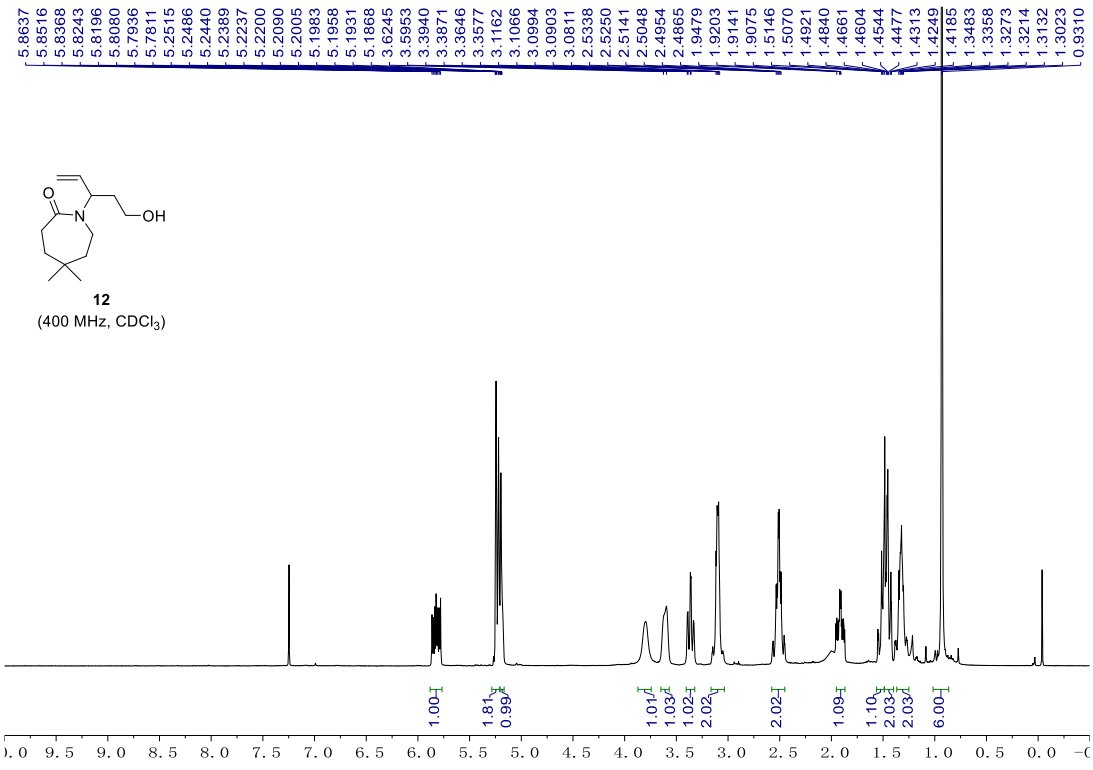

5.7988
5.7850
5.7720
5.7584
5.7552
5.7413
5.7282
5.7144
5.2739
5.2703
5.2468
5.2434
5.2199
5.2165
5.1761
5.1727
5.1439
5.1313
5.1267
5.1223
5.1181
5.1090
5.0963
3.9591
3.9557
3.9502
3.9454
3.9392
3.9345
3.9293
3.9257
3.8420
3.8301
3.8134
3.8015
3.6785
3.6568
3.6500
3.5566
3.3459
3.3421
3.3311
2.6347
2.6303
2.6197
2.6095
2.6049
1.8513
1.8370
1.8233
OH
O
N
O
O
9
(400 MHz, CDCl3)
1.00
1.97
1.00
1.82
2.00
0.98
1.00
1.99
1.00
2.04
4.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

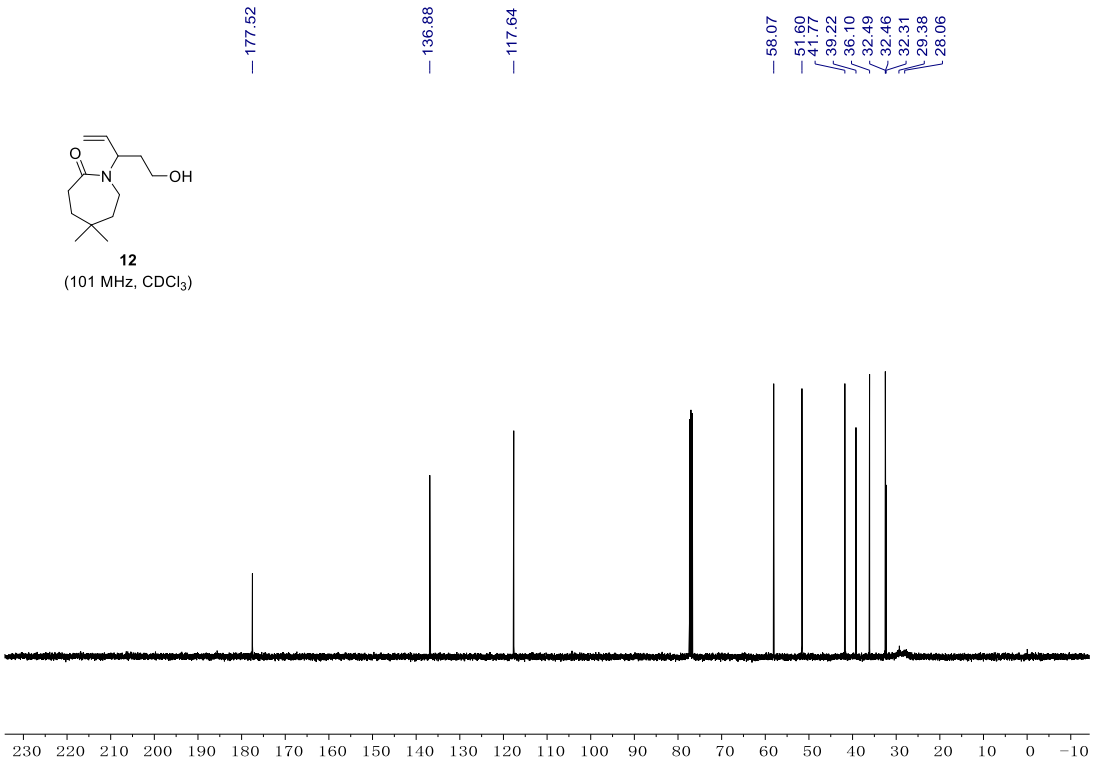

176.52
133.32
118.49
108.86
64.56
64.51
62.59
58.23
40.26
38.53
33.08
32.01
OH
O
N
O
O
9
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

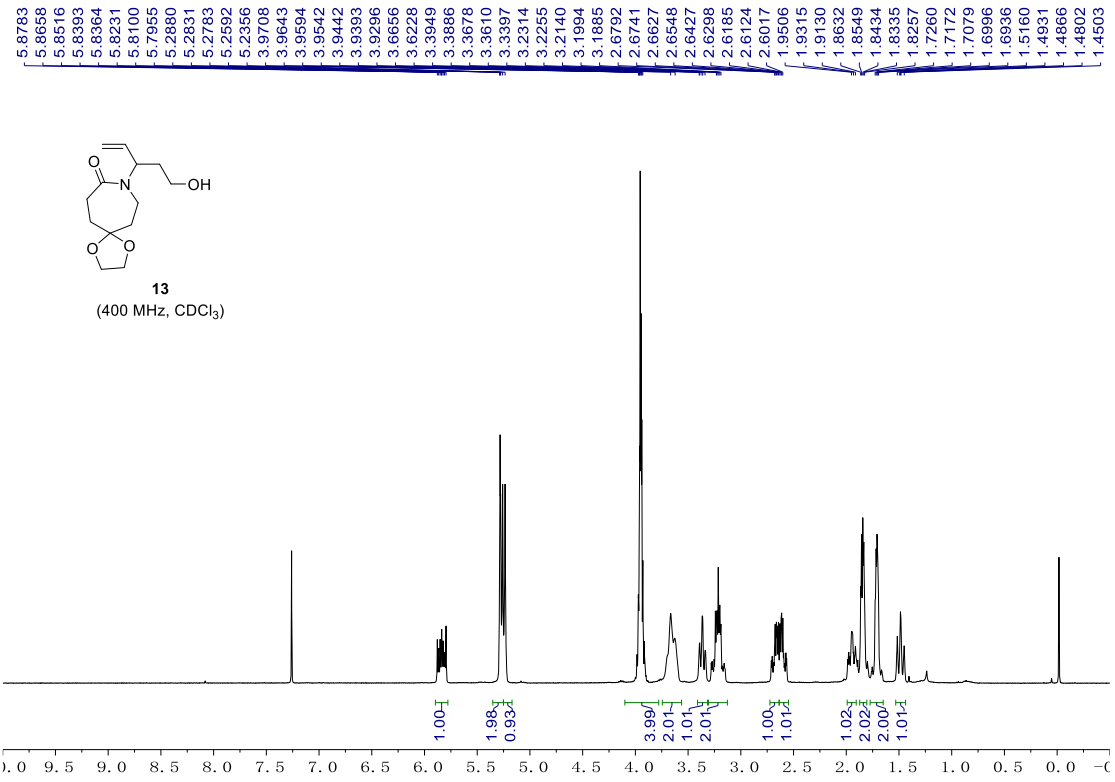

10
(400 MHz, $CDCl_3$)

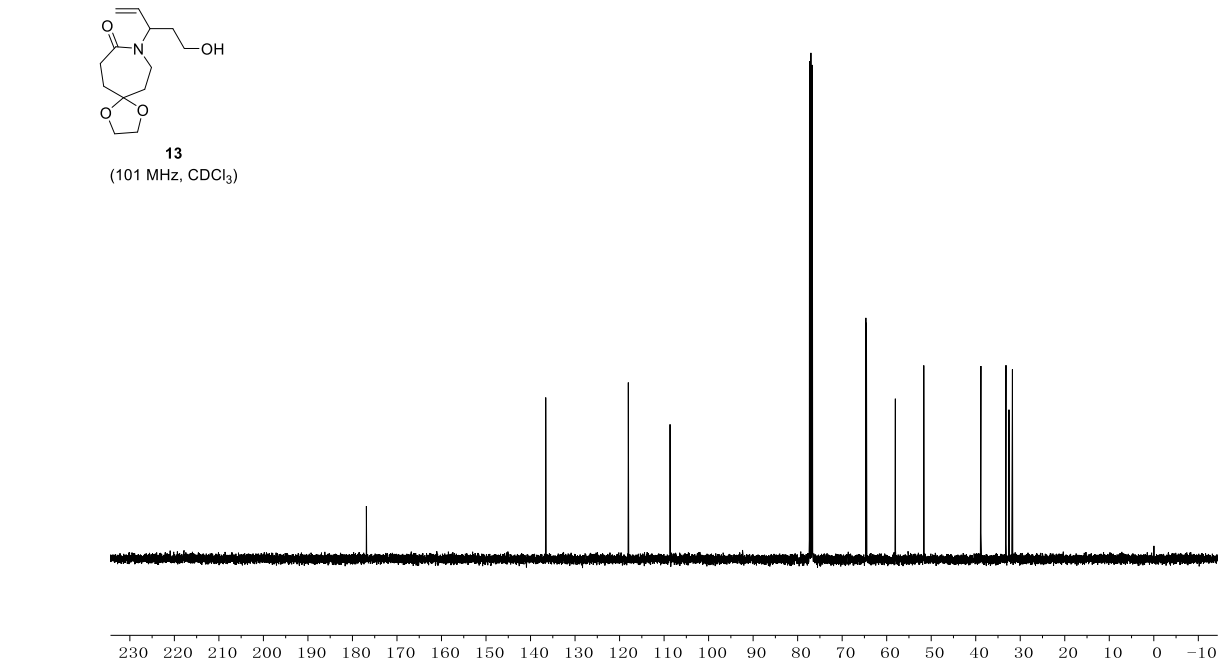

10
(101 MHz, $CDCl_3$)

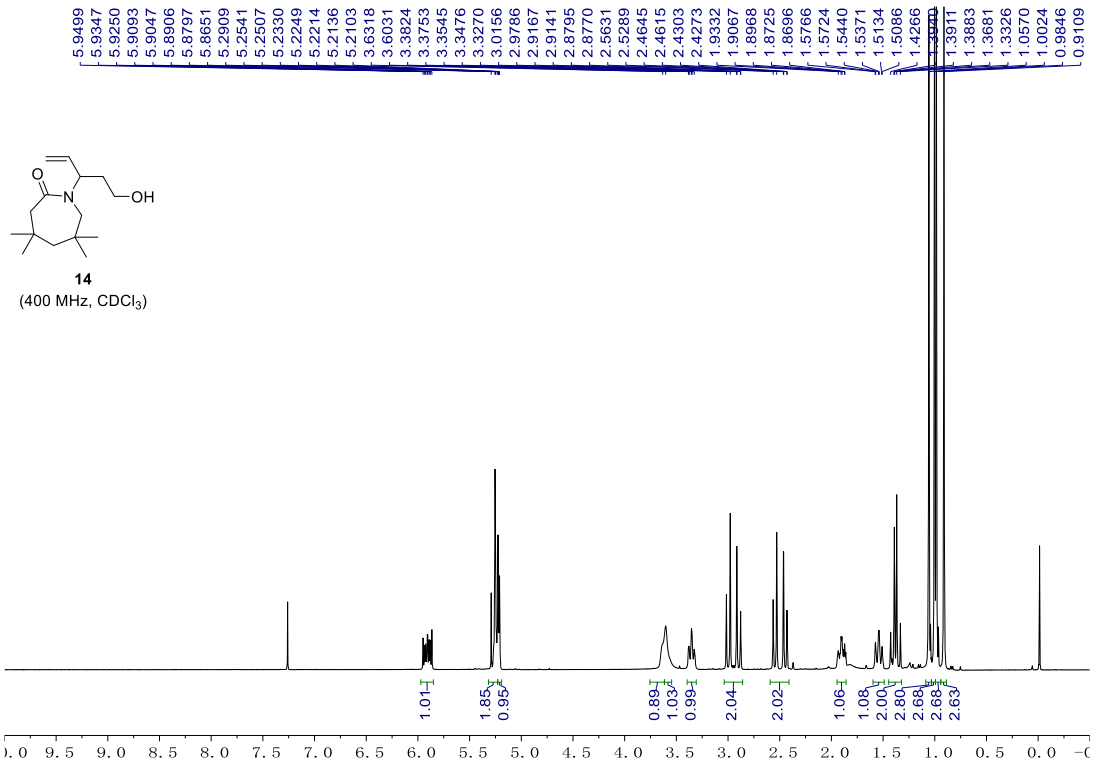

5.8589
5.8466
5.8323
5.8175
5.8045
5.7883
5.7765
5.2670
5.2344
5.2141
5.1913
5.1745
3.7937
3.6248
3.6090
3.5820
3.4001
3.3790
3.3715
3.3486
3.3417
3.1567
3.1453
3.1322
3.1156
2.5655
2.5539
2.5398
1.9102
1.9034
1.8963
1.7051
1.6850
1.6774
1.6698
1.6570
1.6403
1.5585
1.5484
1.5392
1.5261
1.4992
1.4708
O
N
OH
11
(400 MHz, CDCl3)
1.00
1.99
1.00
1.04
1.03
1.03
1.98
2.02
1.08
7.02
177.71
136.94
117.57
58.07
51.68
43.86
37.29
32.47
29.96
29.05
23.42
O
N
OH
11
(101 MHz, CDCl3)

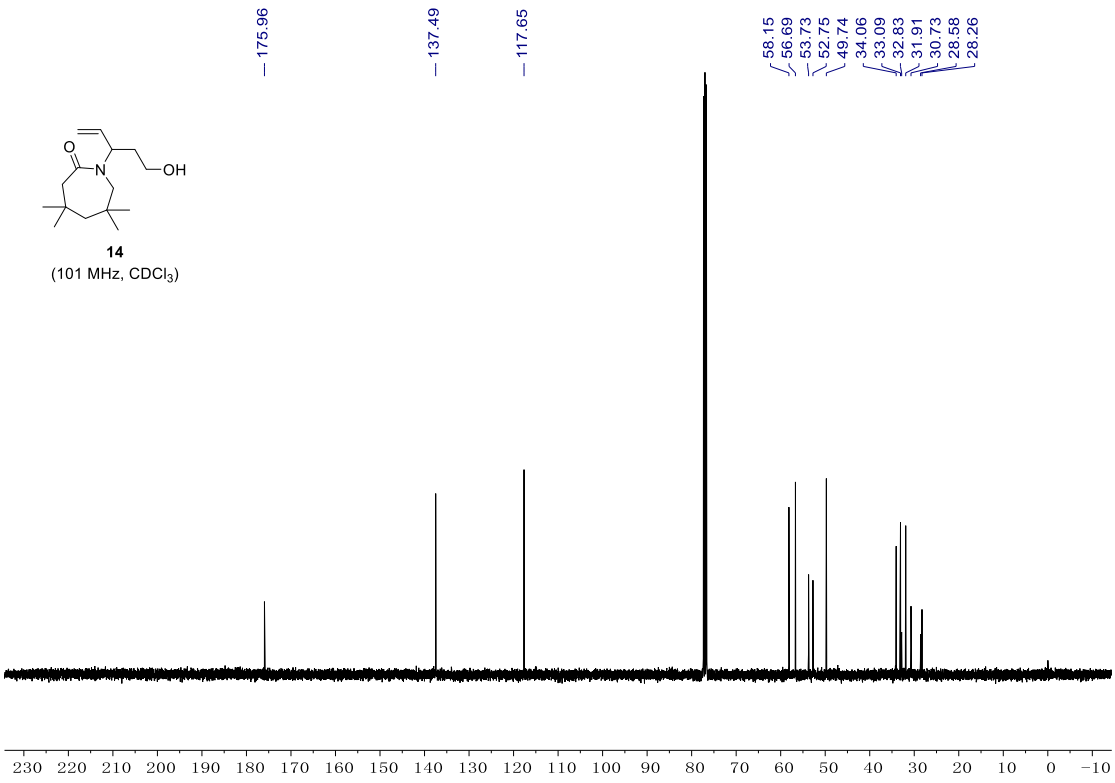

5.8637
5.8516
5.8368
5.8243
5.8196
5.8080
5.7936
5.7811
5.2515
5.2486
5.2440
5.2389
5.2237
5.2200
5.2090
5.2005
5.1983
5.1958
5.1931
5.1868
3.6245
3.5953
3.3940
3.3871
3.3646
3.3577
3.1162
3.1066
3.0994
3.0903
3.0811
2.5338
2.5250
2.5141
2.5048
2.4954
2.4865
1.9479
1.9203
1.9141
1.9075
1.5146
1.5070
1.4921
1.4840
1.4661
1.4604
1.4544
1.4477
1.4313
1.4249
1.4185
1.3483
1.3358
1.3273
1.3214
1.3132
1.3023
0.9310
O
N
OH
12
(400 MHz, CDCl3)
1.00
1.81
0.99
1.01
1.03
1.02
2.02
2.02
1.09
1.10
2.03
2.03
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

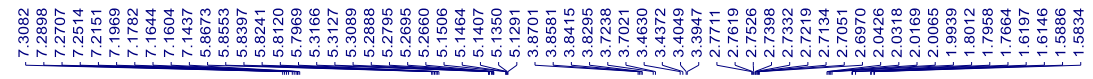

177.52
136.88
117.64
58.07
51.60
41.77
39.22
36.10
32.49
32.46
32.31
29.38
28.06
O
N
OH
12
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

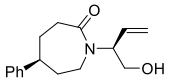

5.8783
5.8658
5.8516
5.8393
5.8364
5.8231
5.8100
5.7955
5.2880
5.2831
5.2783
5.2592
5.2356
3.9708
3.9643
3.9594
3.9542
3.9442
3.9393
3.9296
3.6656
3.6228
3.3949
3.3886
3.3678
3.3610
3.3397
3.3314
3.2255
3.2140
3.1994
3.1885
2.6792
2.6741
2.6627
2.6548
2.6427
2.6298
2.6185
2.6124
2.6017
1.9506
1.9315
1.9130
1.8632
1.8549
1.8434
1.8335
1.8257
1.7260
1.7172
1.7079
1.6996
1.6936
1.5160
1.4931
1.4866
1.4802
1.4503
OH
13
(400 MHz, CDCl3)
1.00
1.98
0.93
3.99
2.01
1.01
2.01
1.00
1.01
1.02
2.02
2.00
1.01


176.87
136.58
118.04
108.66
64.67
64.54
58.05
51.66
38.88
38.83
33.20
32.53
31.76
OH
13
(101 MHz, CDCl3)

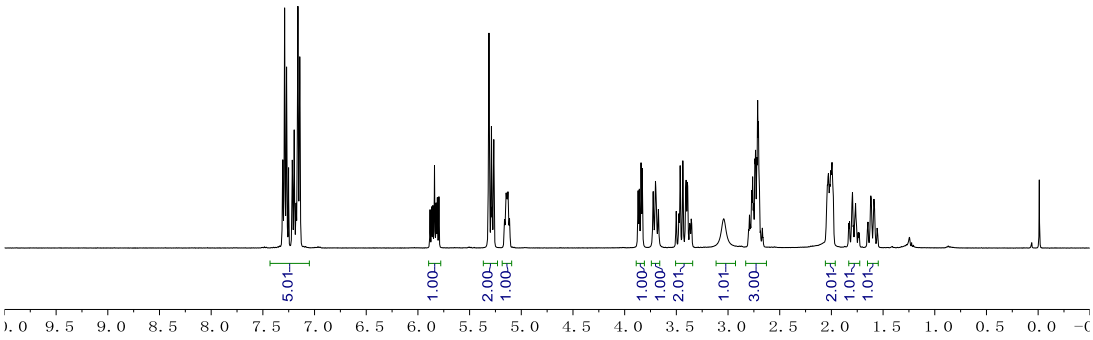

5.9499
5.9347
5.9250
5.9093
5.9047
5.8906
5.8797
5.8651
5.2909
5.2541
5.2507
5.2330
5.2249
5.2214
5.2136
5.2103
3.6318
3.6031
3.3824
3.3753
3.3545
3.3476
3.3270
3.0156
2.9786
2.9167
2.9141
2.8795
2.8770
2.5631
2.5289
2.4645
2.4615
2.4303
2.4273
1.9332
1.9067
1.8968
1.8725
1.8696
1.5766
1.5724
1.5440
1.5371
1.5134
1.5086
1.4266
1.3911
1.3883
1.3681
1.3326
1.0570
1.0024
0.9846
0.9109
O
N
OH
14
(400 MHz, CDCl3)
1.01
1.85
0.95
0.89
1.03
0.99
2.04
2.02
1.06
1.08
2.00
2.80
2.68
2.68
2.63

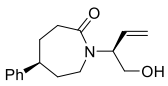

175.96
137.49
117.65
58.15
56.69
53.73
52.75
49.74
34.06
33.09
32.83
31.91
30.73
28.58
28.26
O
N
OH
14
(101 MHz, CDCl3)



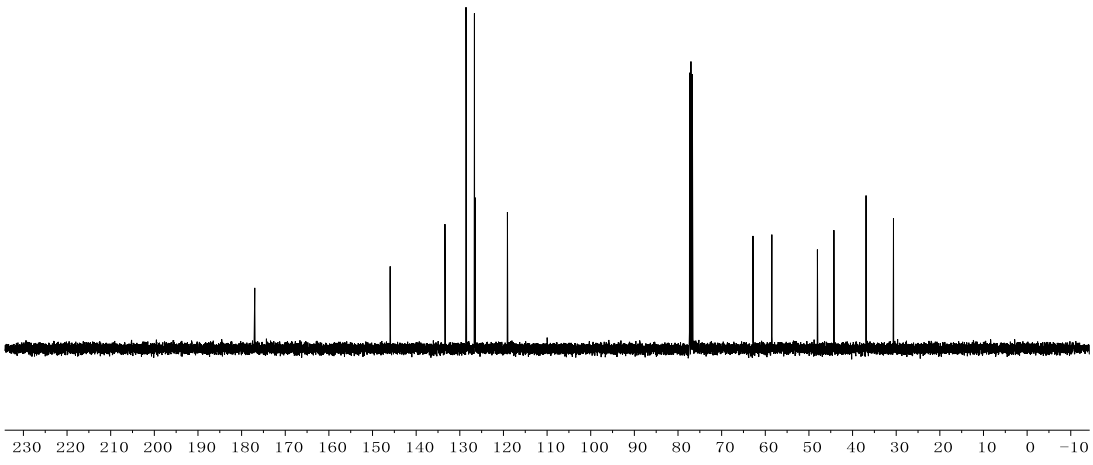


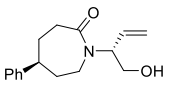
15a
(400 MHz, $CDCl_3$)



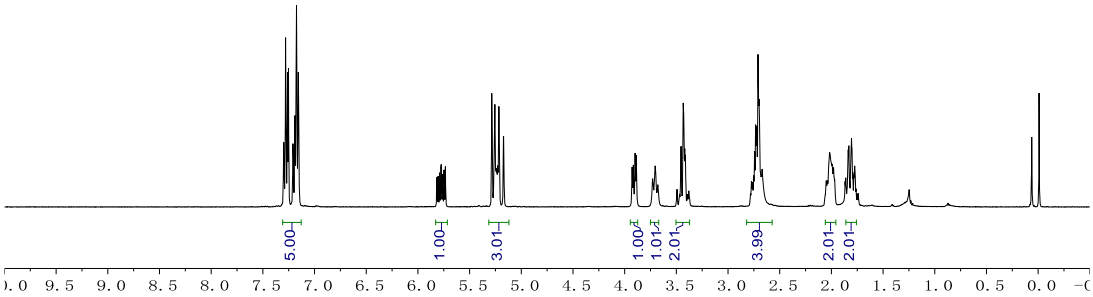


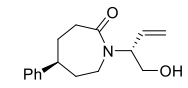
15a
(101 MHz, $CDCl_3$)



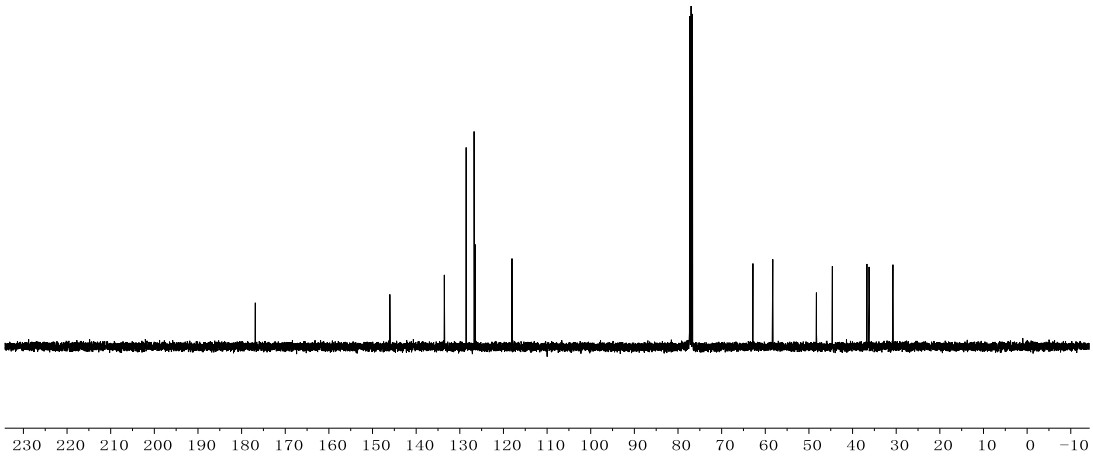


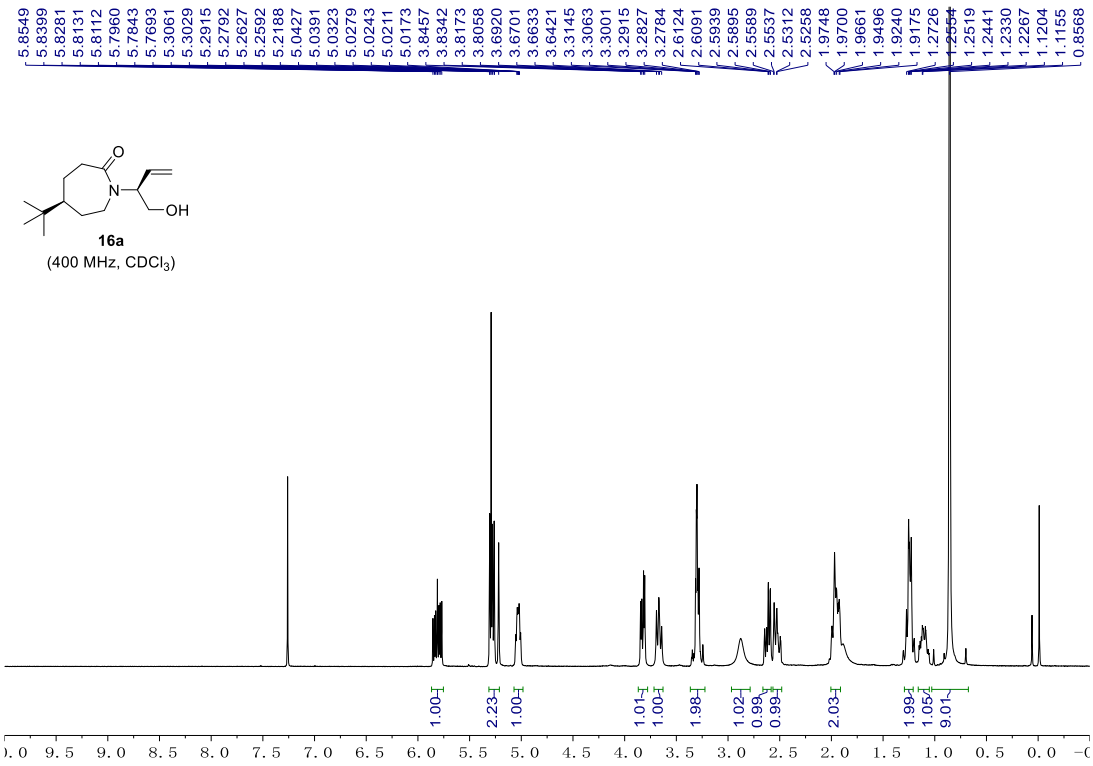
15b
(400 MHz, $CDCl_3$)

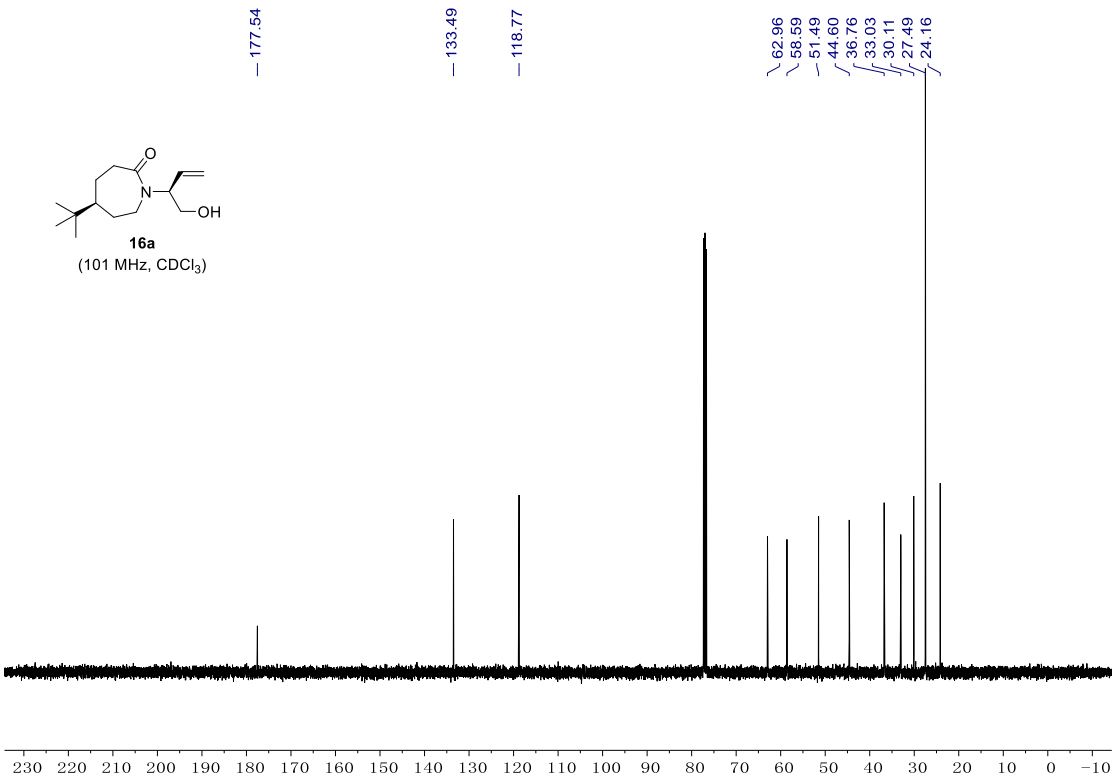


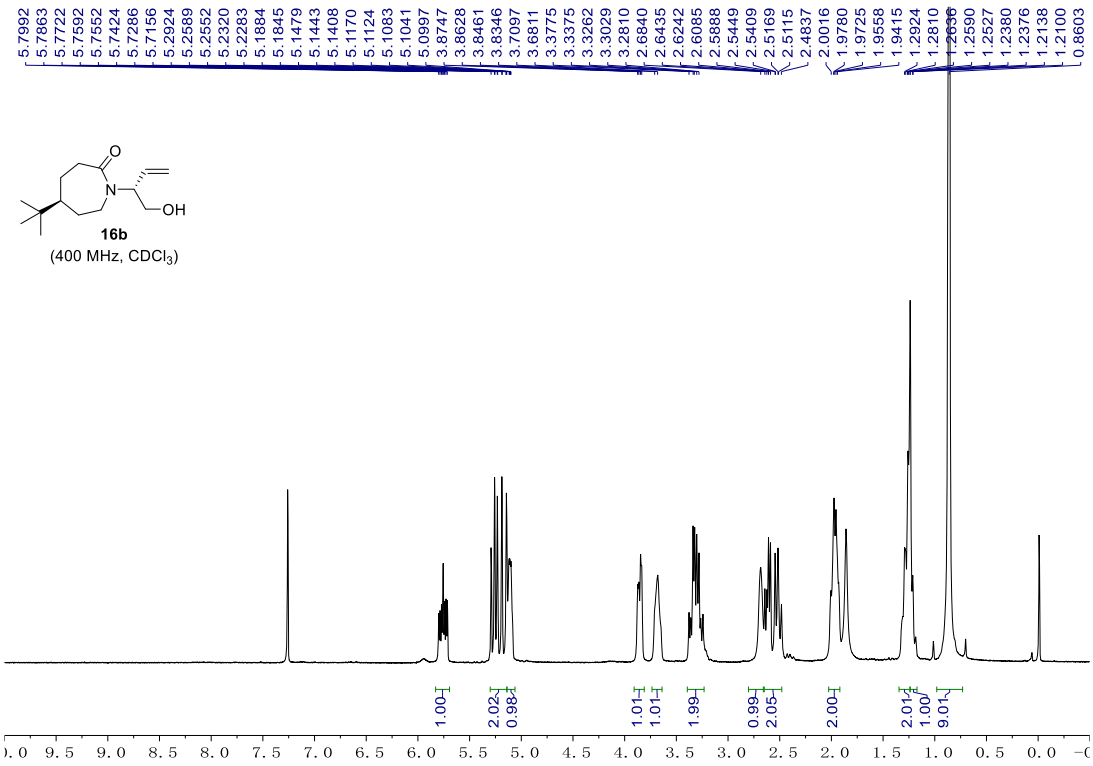


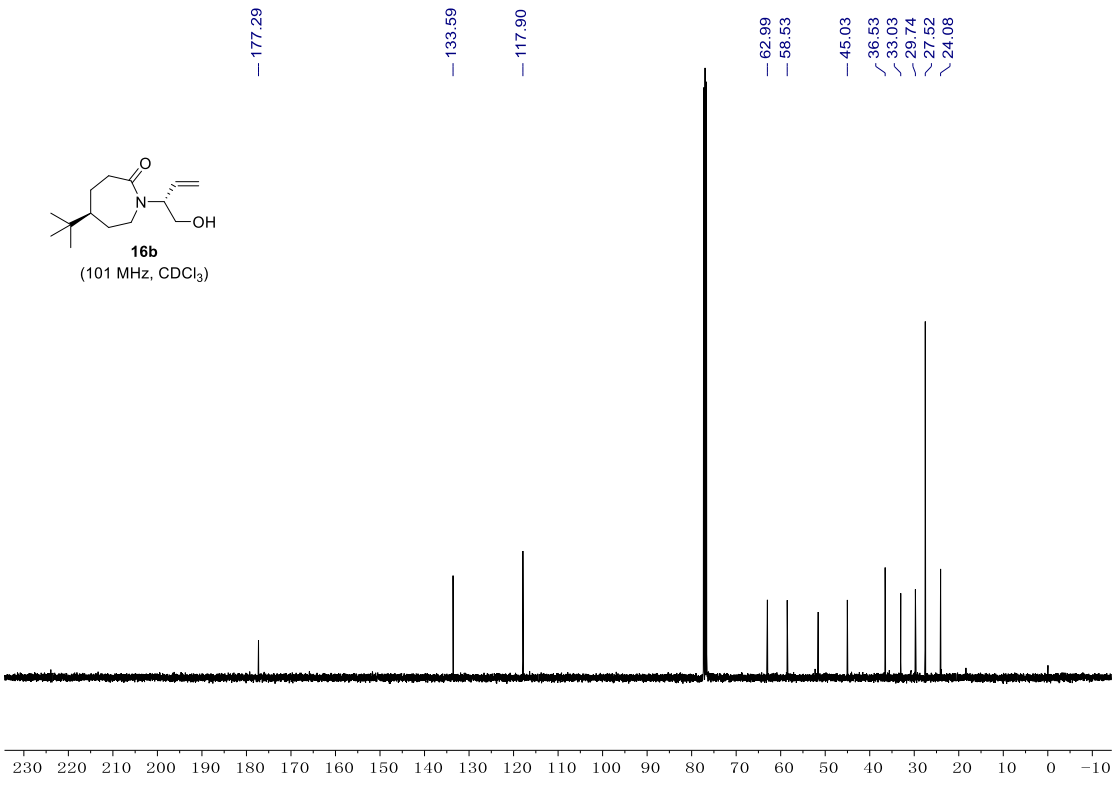
15b
(101 MHz, $CDCl_3$)

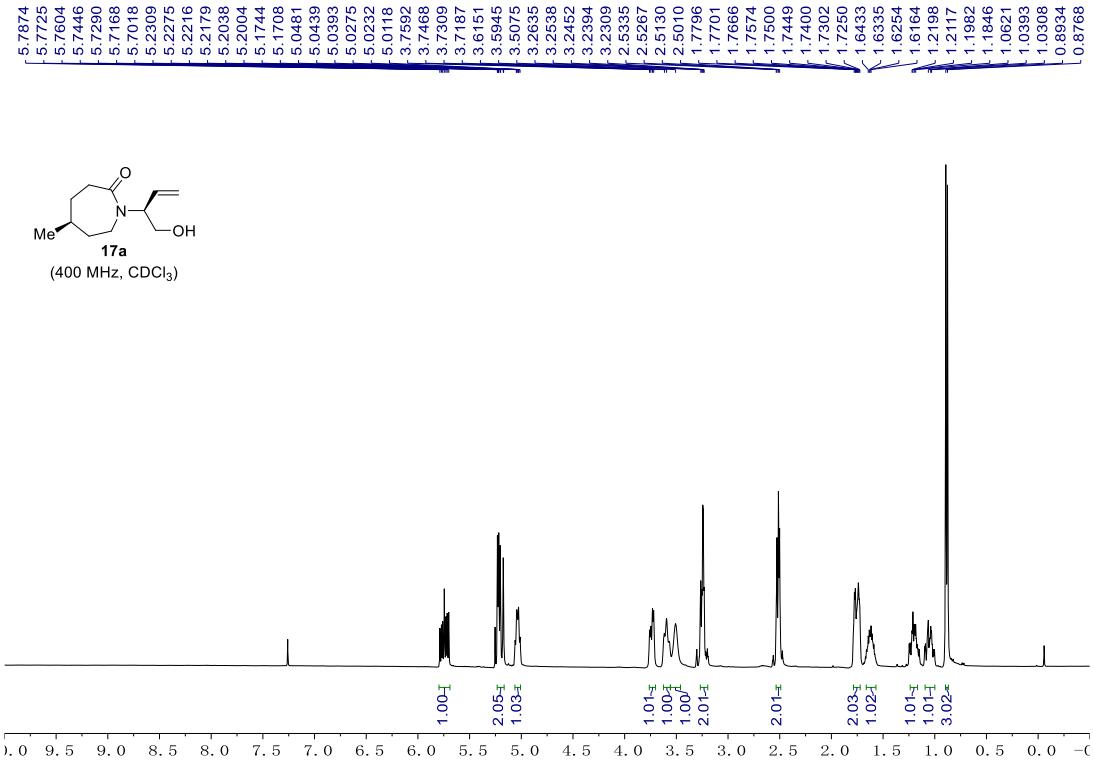


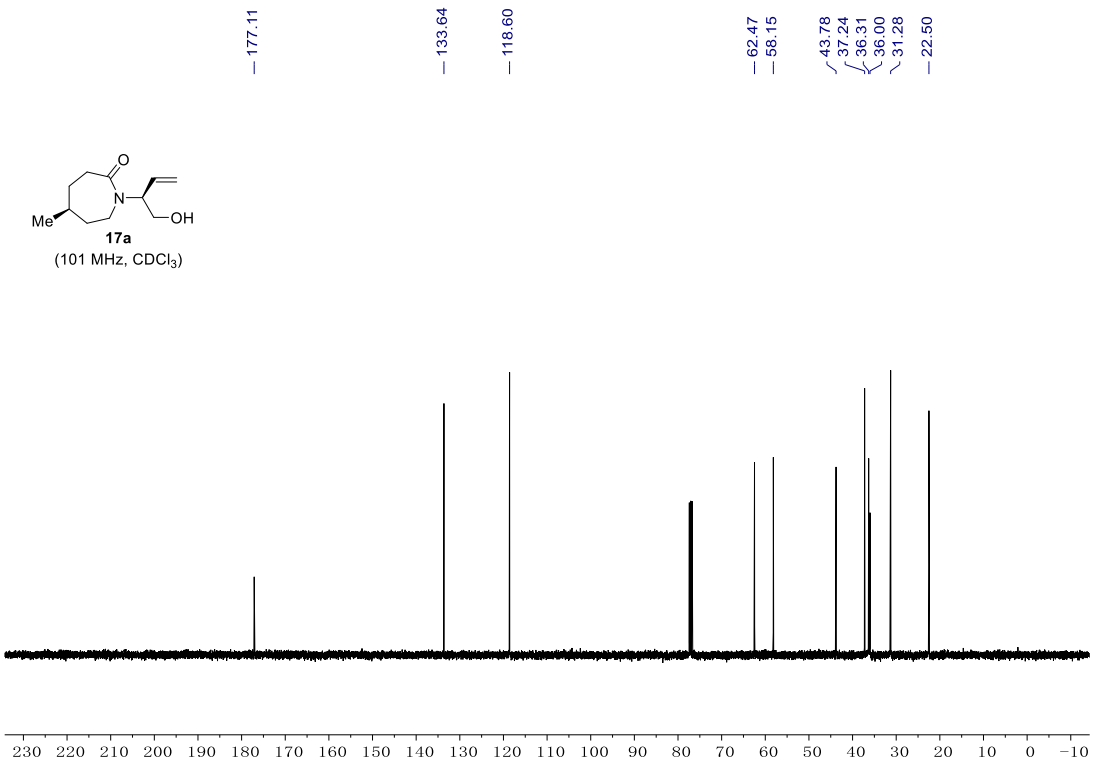

5.8549
5.8399
5.8281
5.8131
5.8112
5.7960
5.7843
5.7693
5.3061
5.3029
5.2915
5.2792
5.2627
5.2592
5.2188
5.0427
5.0391
5.0323
5.0279
5.0243
5.0211
5.0173
3.8457
3.8342
3.8173
3.8058
3.6920
3.6701
3.6633
3.6421
3.3145
3.3063
3.3001
3.2915
3.2827
3.2784
2.6124
2.6091
2.5939
2.5895
2.5589
2.5537
2.5312
2.5258
1.9748
1.9700
1.9661
1.9496
1.9240
1.9175
1.2726
1.2554
1.2519
1.2441
1.2330
1.2267
1.1204
1.1155
0.8568
O
N
OH
16a
(400 MHz, CDCl3)
1.00
2.23
1.00
1.01
1.00
1.98
1.02
0.99
0.99
2.03
1.99
1.05
9.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

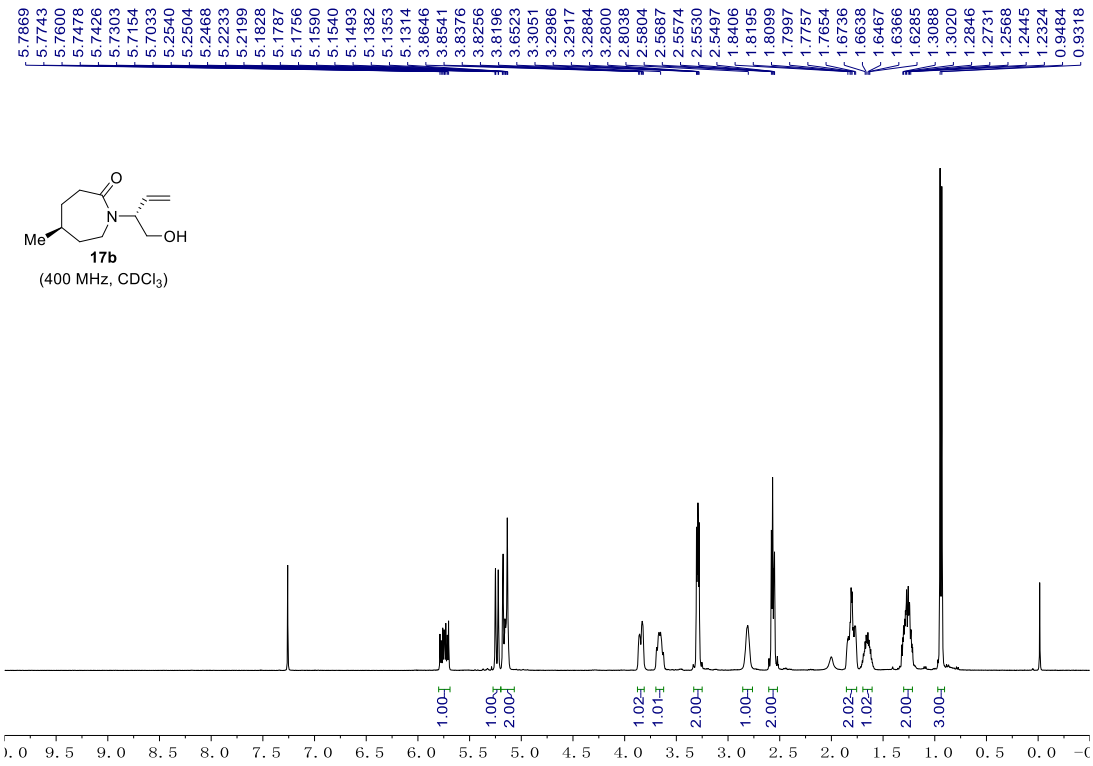

177.54
133.49
118.77
62.96
58.59
51.49
44.60
36.76
33.03
30.11
27.49
24.16
O
N
OH
16a
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

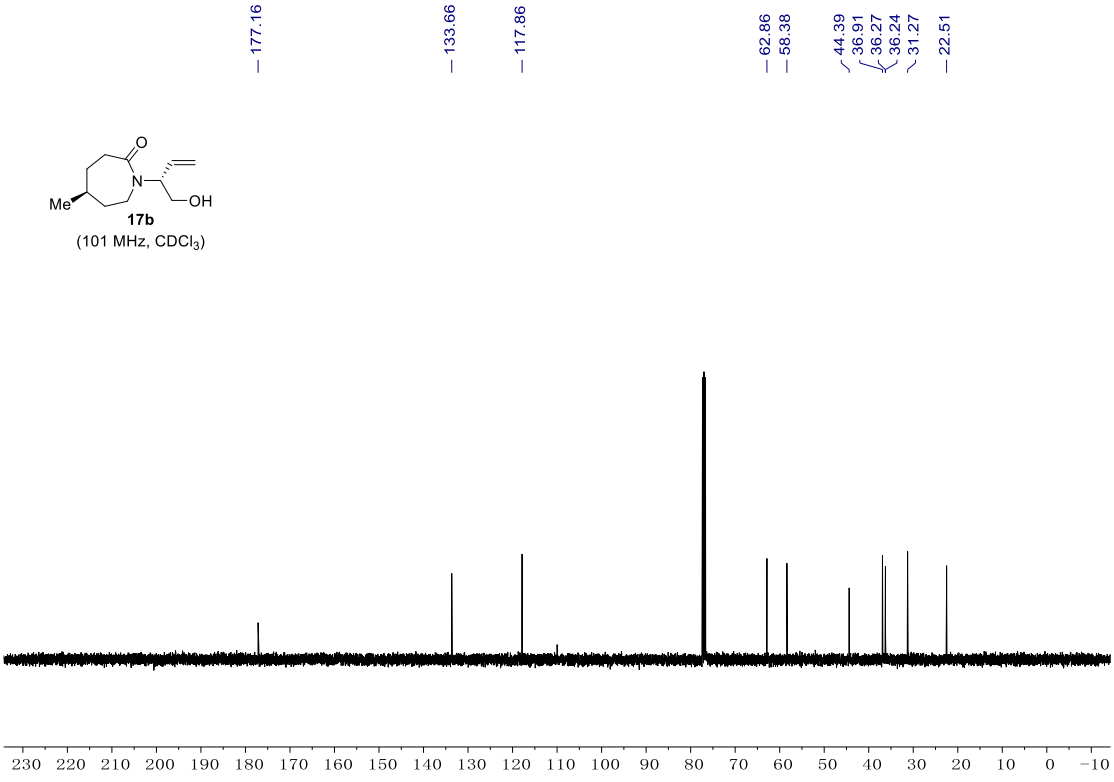

5.7992
5.7863
5.7722
5.7592
5.7552
5.7424
5.7286
5.7156
5.2924
5.2589
5.2552
5.2320
5.2283
5.1884
5.1845
5.1479
5.1443
5.1408
5.1170
5.1124
5.1083
5.1041
5.0997
3.8747
3.8628
3.8461
3.8346
3.7097
3.6811
3.3775
3.3375
3.3262
3.3029
3.2810
2.6840
2.6435
2.6242
2.6085
2.5888
2.5449
2.5409
2.5169
2.5115
2.4837
2.0016
1.9780
1.9725
1.9558
1.9415
1.2924
1.2810
1.2636
1.2590
1.2527
1.2380
1.2376
1.2138
1.2100
0.8603
O
N
OH
16b
(400 MHz, CDCl3)
1.00
2.02
0.98
1.01
1.01
1.99
0.99
2.05
2.00
2.01
1.00
9.01

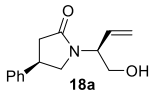

177.29
133.59
117.90
62.99
58.53
45.03
36.53
33.03
29.74
27.52
24.08
O
N
OH
16b
(101 MHz, CDCl3)


5.7874
5.7725
5.7604
5.7446
5.7290
5.7168
5.7018
5.2309
5.2275
5.2216
5.2179
5.2038
5.2004
5.1744
5.1708
5.0481
5.0439
5.0393
5.0275
5.0232
5.0118
3.7592
3.7468
3.7309
3.7187
3.6151
3.5945
3.5075
3.2635
3.2538
3.2452
3.2394
3.2309
2.5335
2.5267
2.5130
2.5010
1.7796
1.7701
1.7666
1.7574
1.7500
1.7449
1.7400
1.7302
1.7250
1.6433
1.6335
1.6254
1.6164
1.2198
1.2117
1.1982
1.1846
1.0621
1.0393
1.0308
0.8934
0.8768
O
N
Me
OH
17a
(400 MHz, CDCl3)
1.00
2.05
1.03
1.01
1.00
1.00
2.01
2.01
2.03
1.02
1.01
1.01
3.02


177.11
133.64
118.60
62.47
58.15
43.78
37.24
36.31
36.00
31.28
22.50
O
N
Me
OH
17a
(101 MHz, CDCl3)

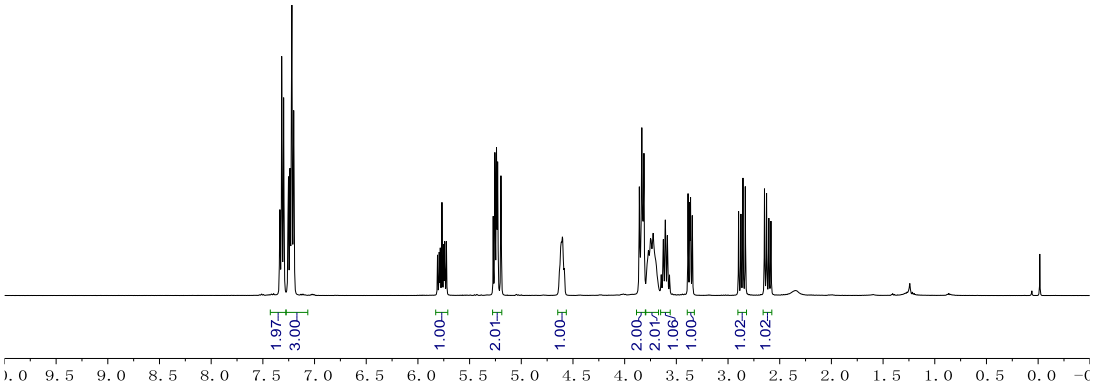

5.7869
5.7743
5.7600
5.7478
5.7426
5.7303
5.7154
5.7033
5.2540
5.2504
5.2468
5.2233
5.2199
5.1828
5.1787
5.1756
5.1590
5.1540
5.1493
5.1382
5.1353
5.1314
3.8646
3.8541
3.8376
3.8256
3.8196
3.6523
3.3051
3.2986
3.2917
3.2884
3.2800
2.8038
2.5804
2.5687
2.5574
2.5530
2.5497
1.8406
1.8195
1.8099
1.7997
1.7757
1.7654
1.6736
1.6638
1.6467
1.6366
1.6285
1.3088
1.3020
1.2846
1.2731
1.2568
1.2445
1.2324
0.9484
0.9318
O
N
OH
Me
17b
(400 MHz, CDCl3)
1.00
1.00
2.00
1.02
1.01
2.00
1.00
2.00
2.02
1.02
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

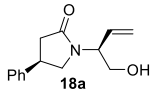

177.16
133.66
117.86
62.86
58.38
44.39
36.91
36.27
36.24
31.27
22.51
O
N
OH
Me
17b
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10



18a

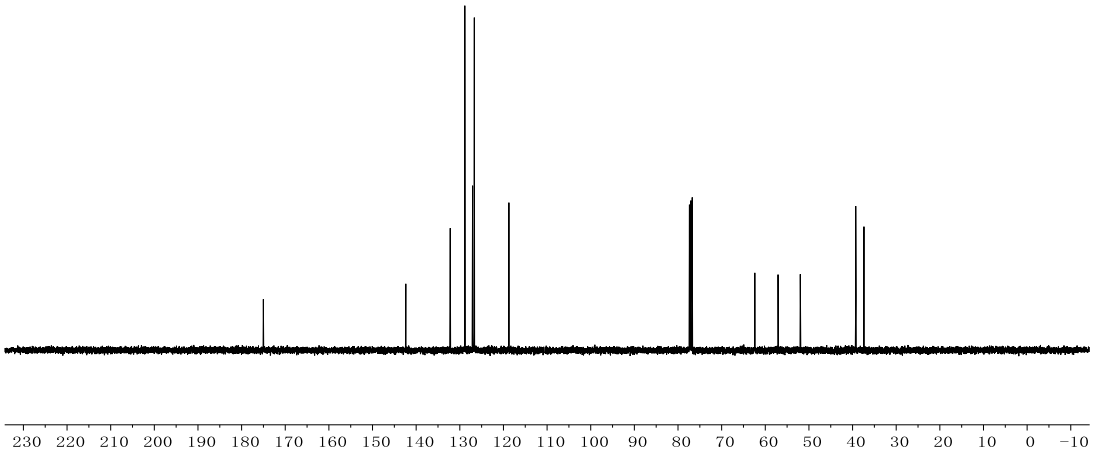
(400 MHz, $CDCl_3$)

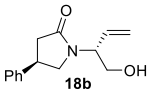




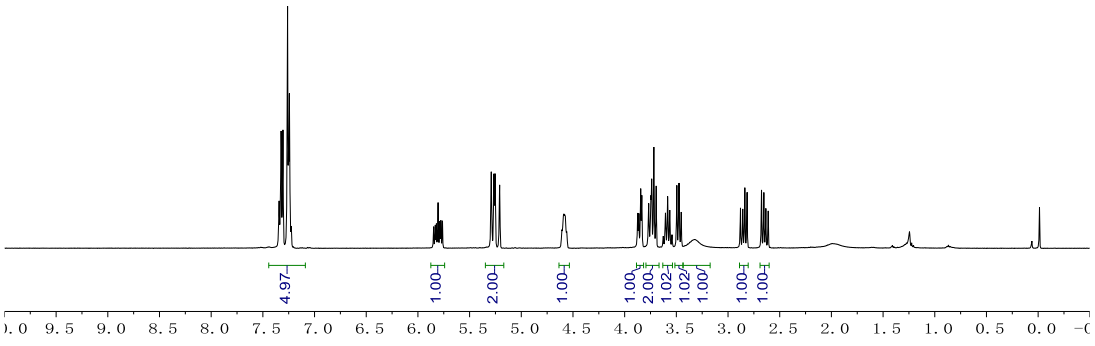
18a

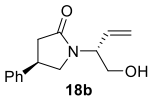
(101 MHz, $CDCl_3$)



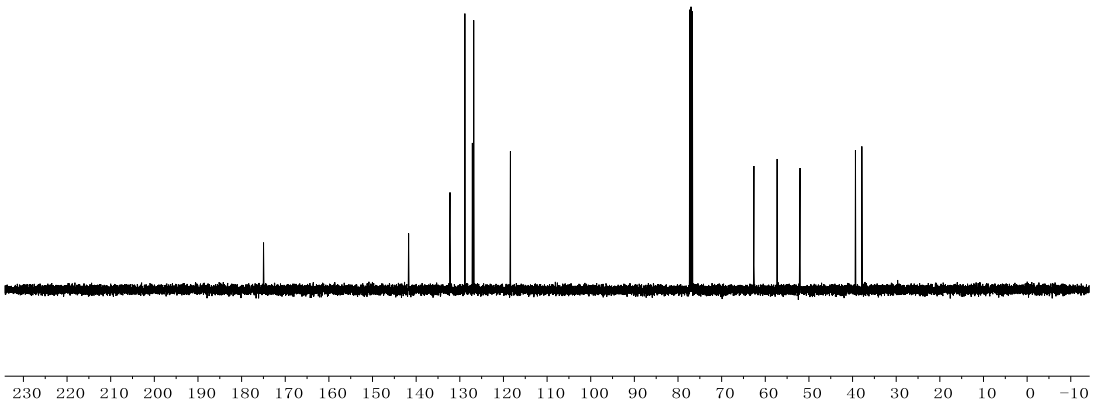


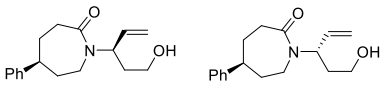
18b
(400 MHz, $CDCl_3$)



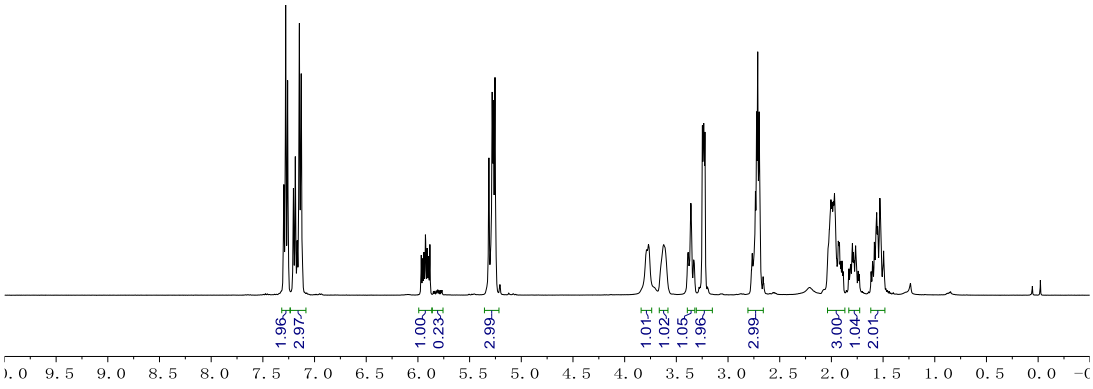


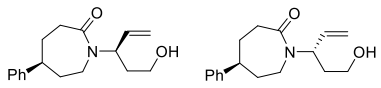
18b
(101 MHz, $CDCl_3$)



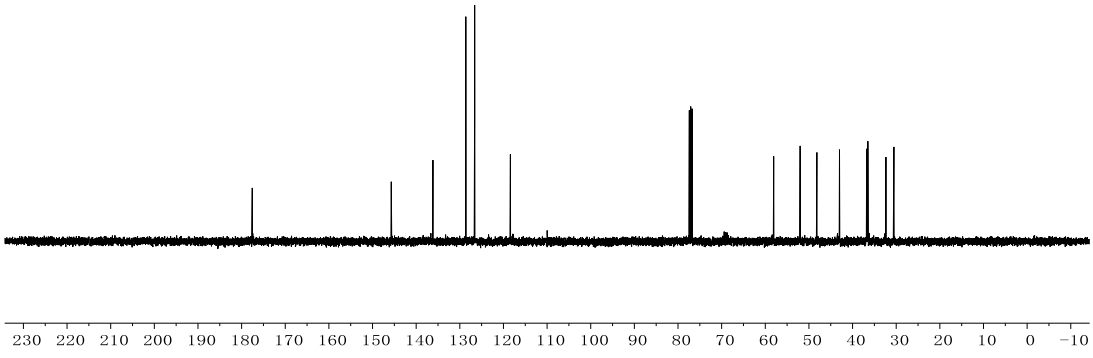


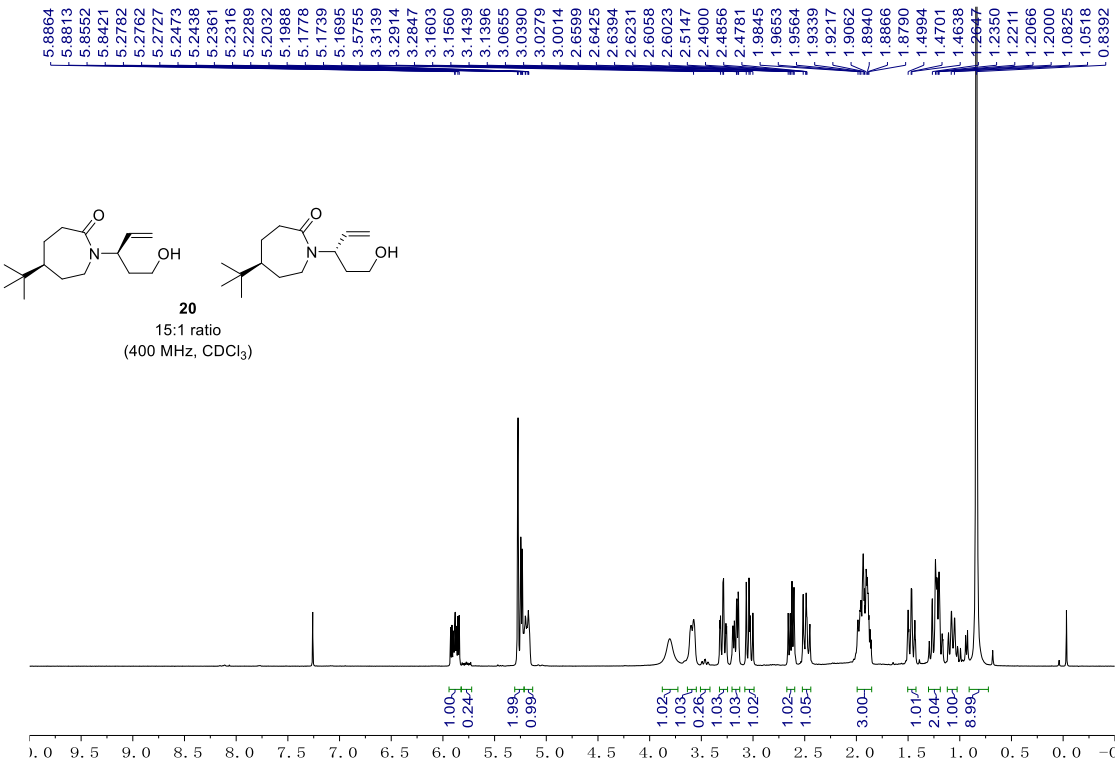
19
10:1 ratio
(400 MHz, $CDCl_3$)



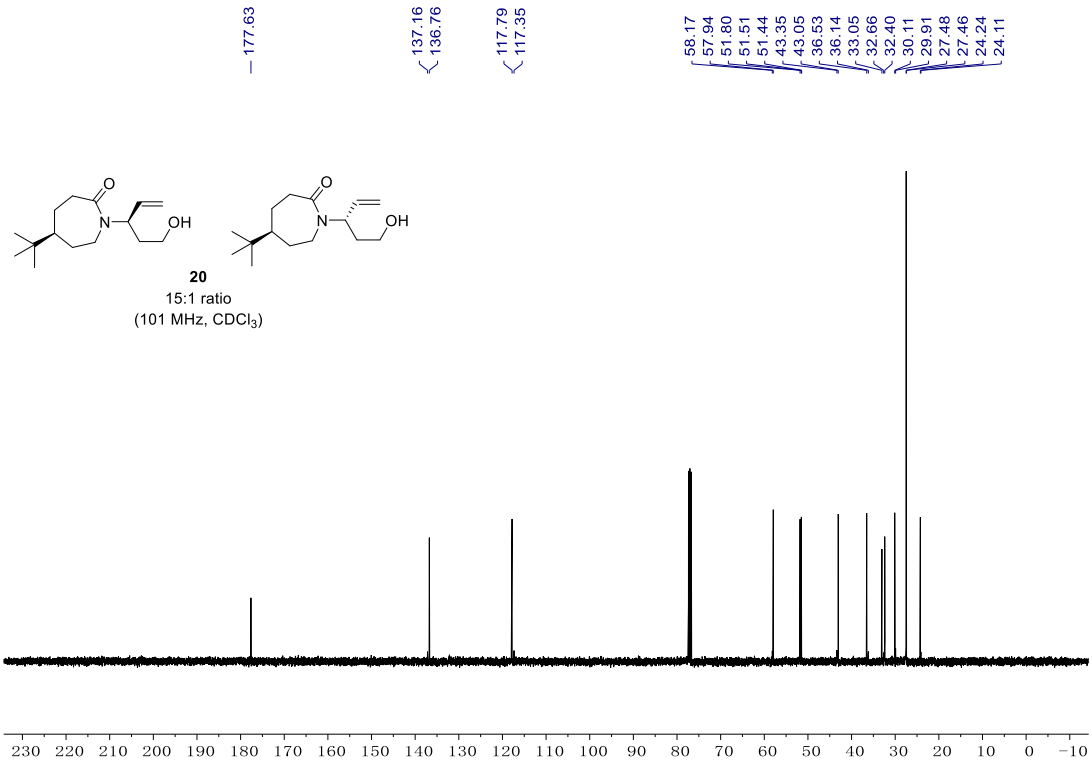


19
10:1 ratio
(101 MHz, $CDCl_3$)

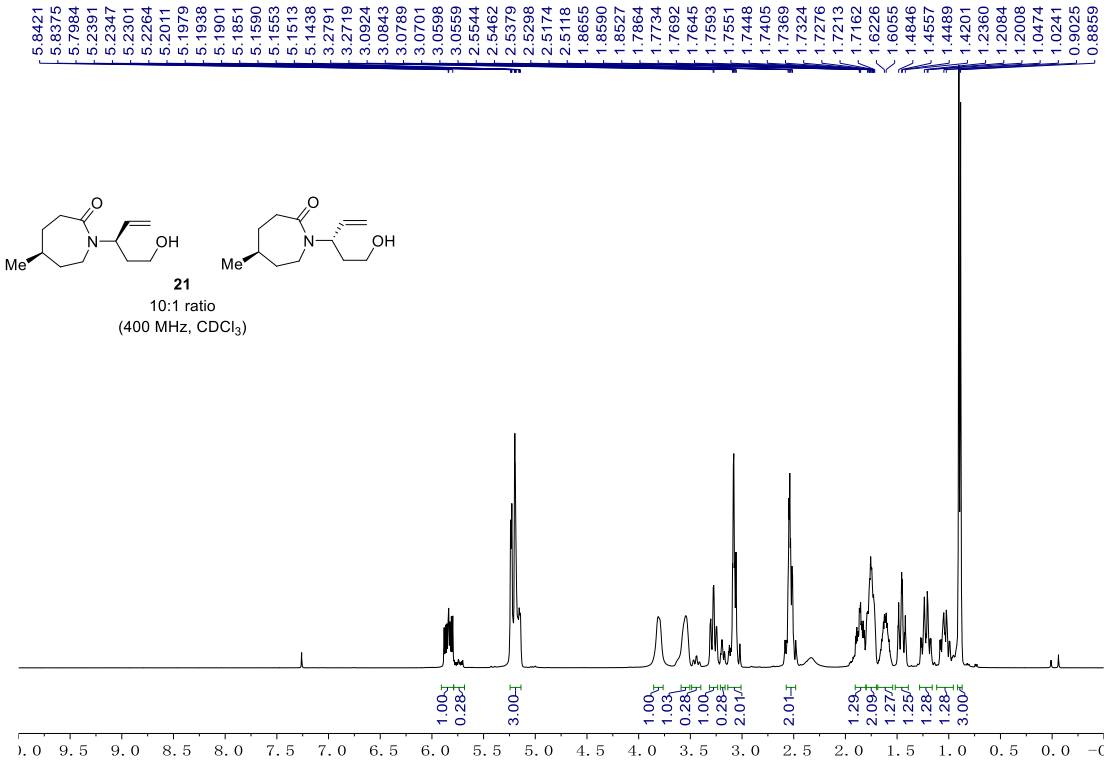


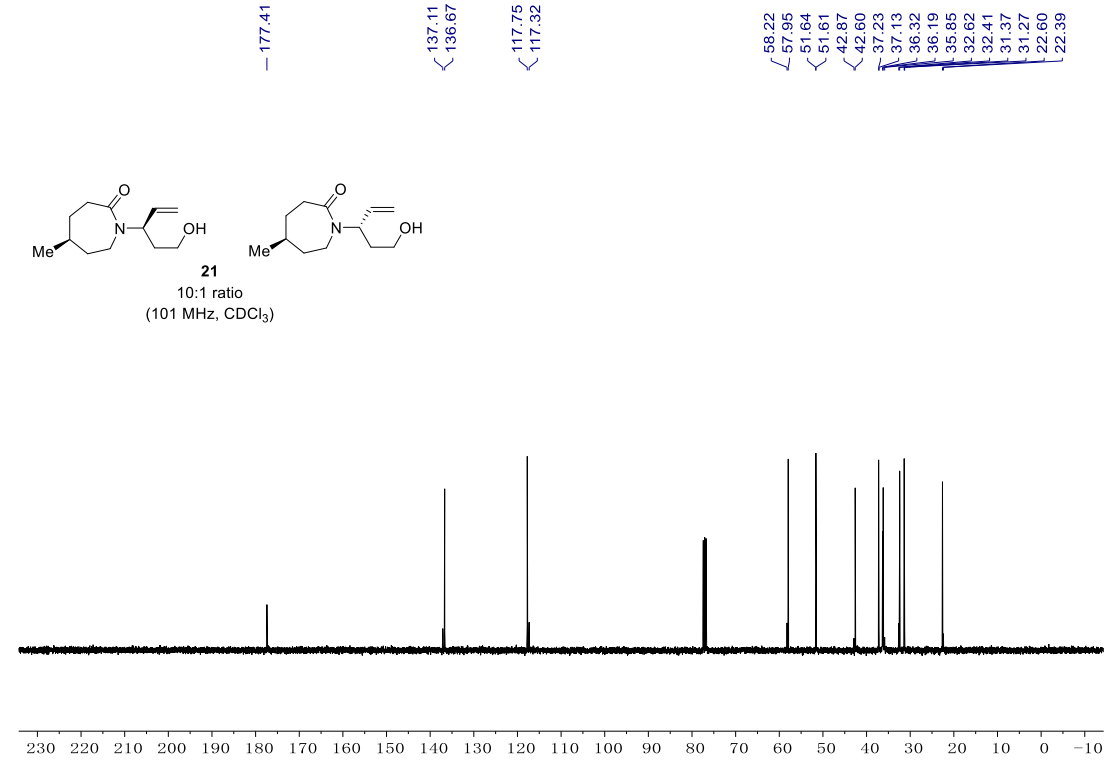


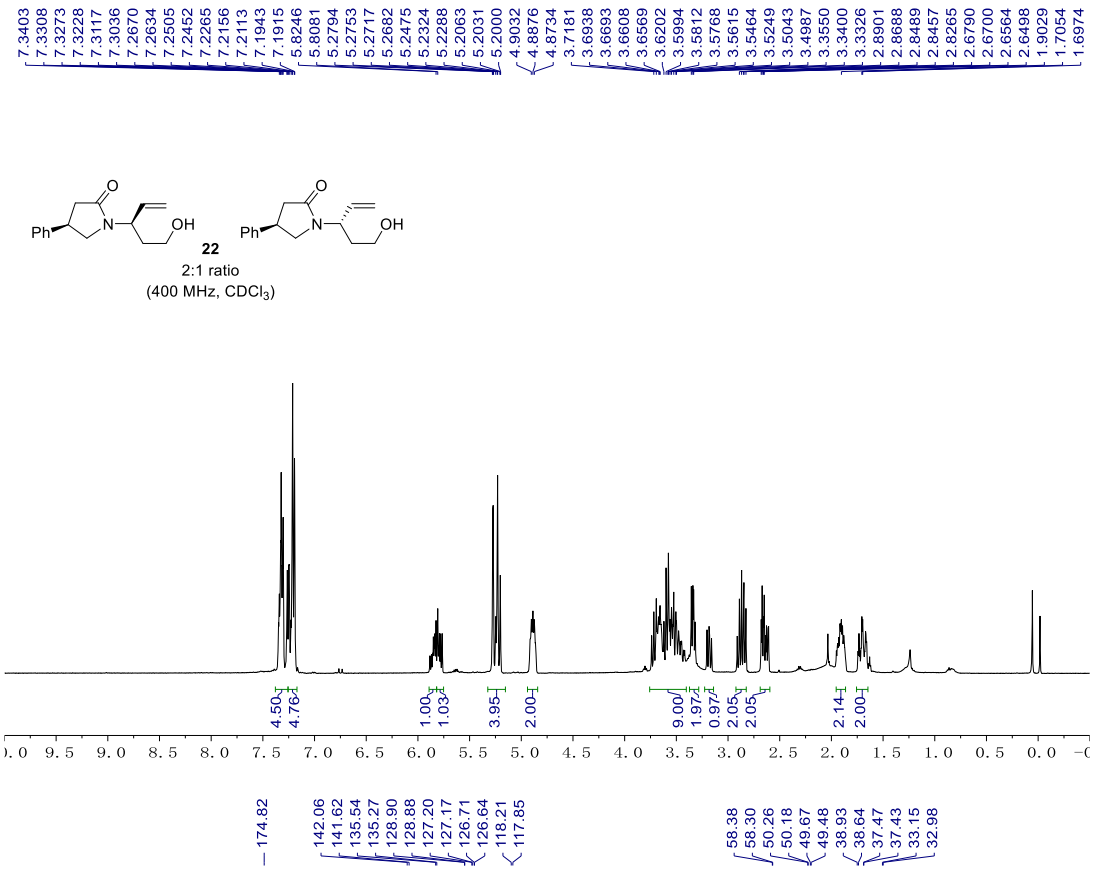
20
15:1 ratio
(400 MHz, $CDCl_3$)

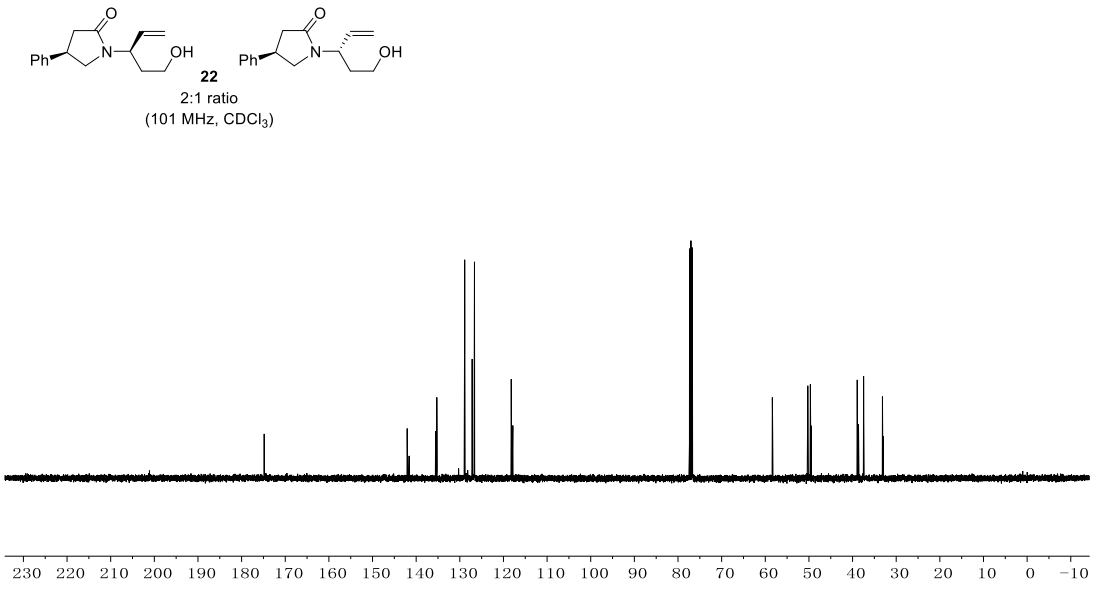


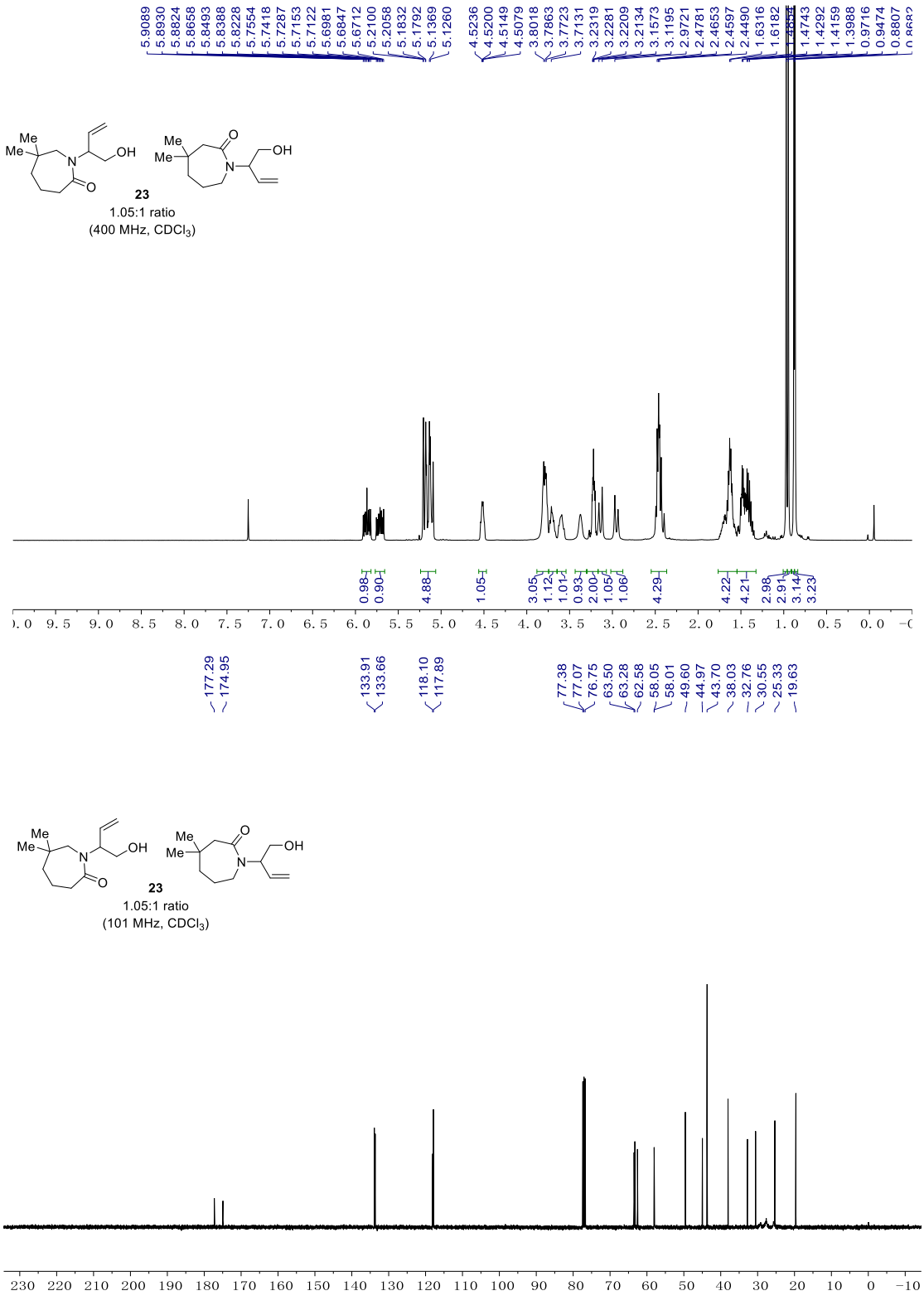
20
15:1 ratio
(101 MHz, $CDCl_3$)

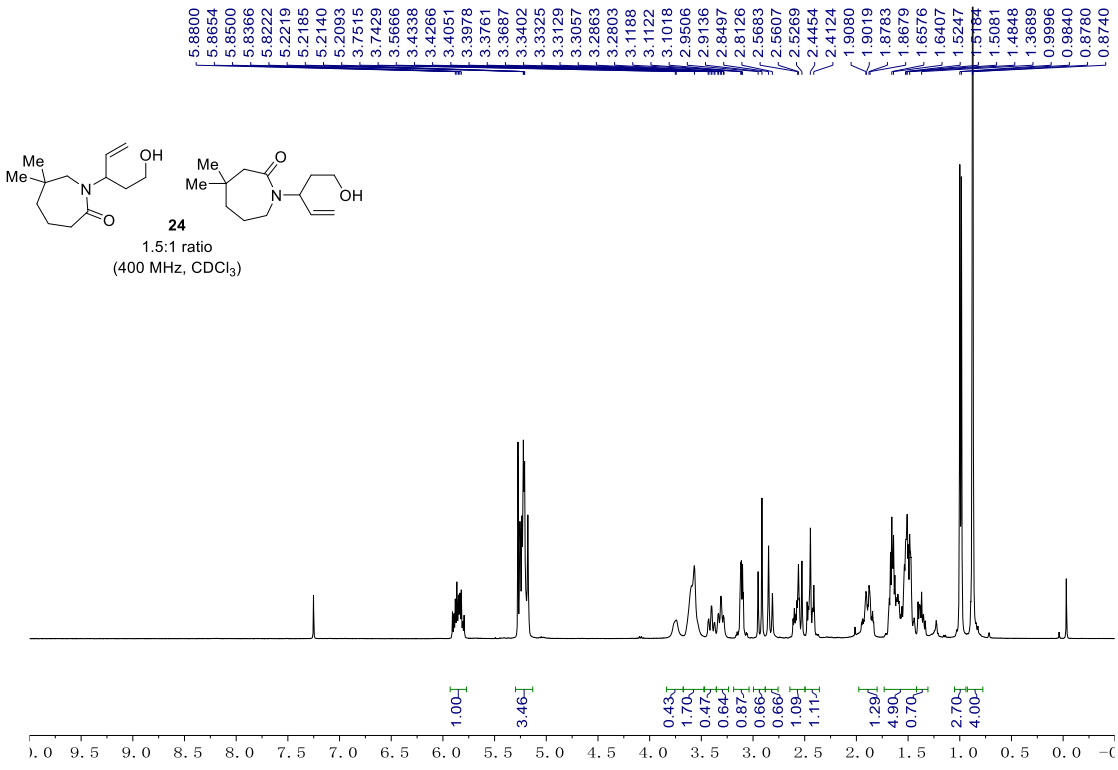

5.8421
5.8375
5.7984
5.2391
5.2347
5.2301
5.2264
5.2011
5.1979
5.1938
5.1901
5.1851
5.1590
5.1553
5.1513
5.1438
3.2791
3.2719
3.0924
3.0843
3.0789
3.0701
3.0598
3.0559
2.5544
2.5462
2.5379
2.5298
2.5174
2.5118
1.8655
1.8590
1.8527
1.7864
1.7734
1.7692
1.7645
1.7593
1.7551
1.7448
1.7405
1.7369
1.7324
1.7276
1.7213
1.7162
1.6226
1.6055
1.4846
1.4557
1.4489
1.4201
1.2360
1.2084
1.2008
1.0474
1.0241
0.9025
0.8859
Me
OH
21
10:1 ratio
(400 MHz, CDCl3)
1.00
0.28
3.00
1.00
1.03
0.28
1.00
0.28
2.01
2.01
1.29
2.09
1.27
1.25
1.28
1.28
3.00

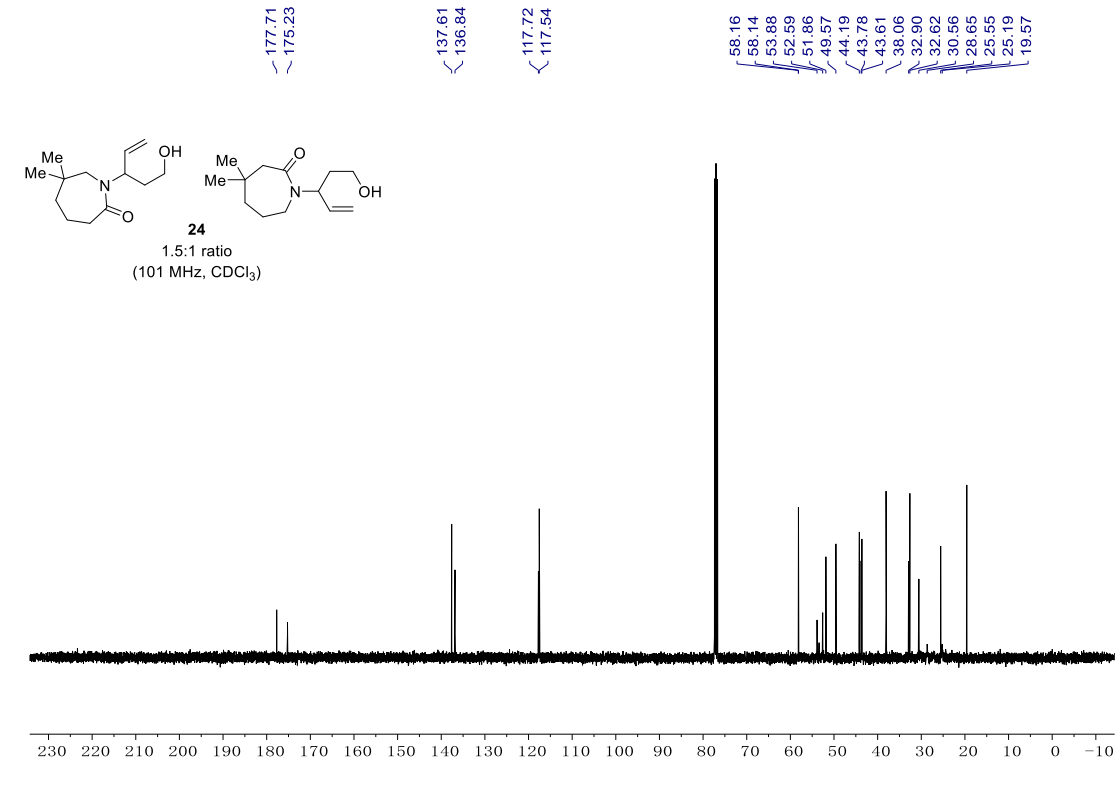

177.41
137.11
136.67
117.75
117.32
58.22
57.95
51.64
51.61
42.87
42.60
37.23
37.13
36.32
36.19
35.85
32.62
32.41
31.37
31.27
22.60
22.39
Me
OH
21
10:1 ratio
(101 MHz, CDCl3)

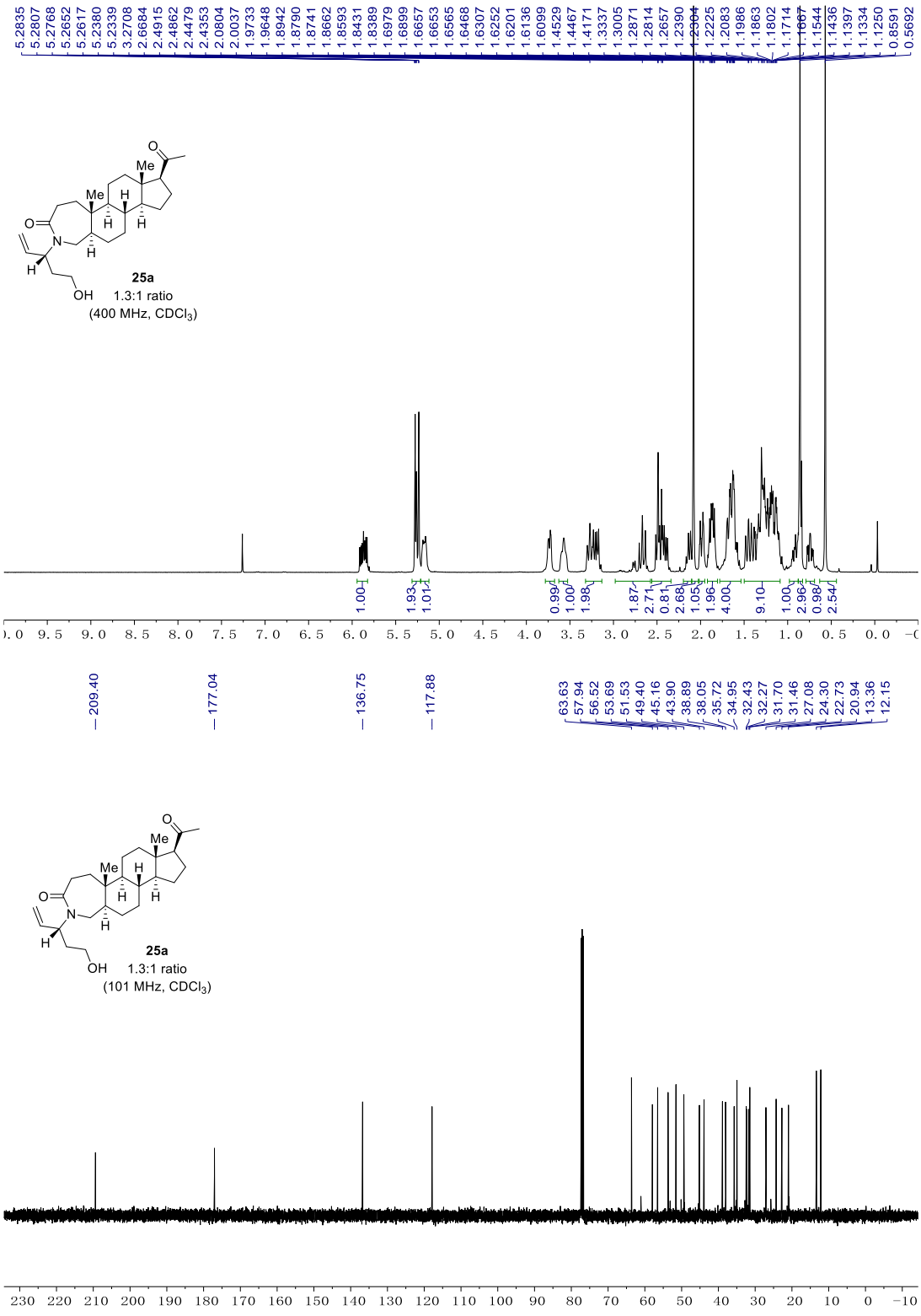

22
2:1 ratio
(400 MHz, CDCl3)

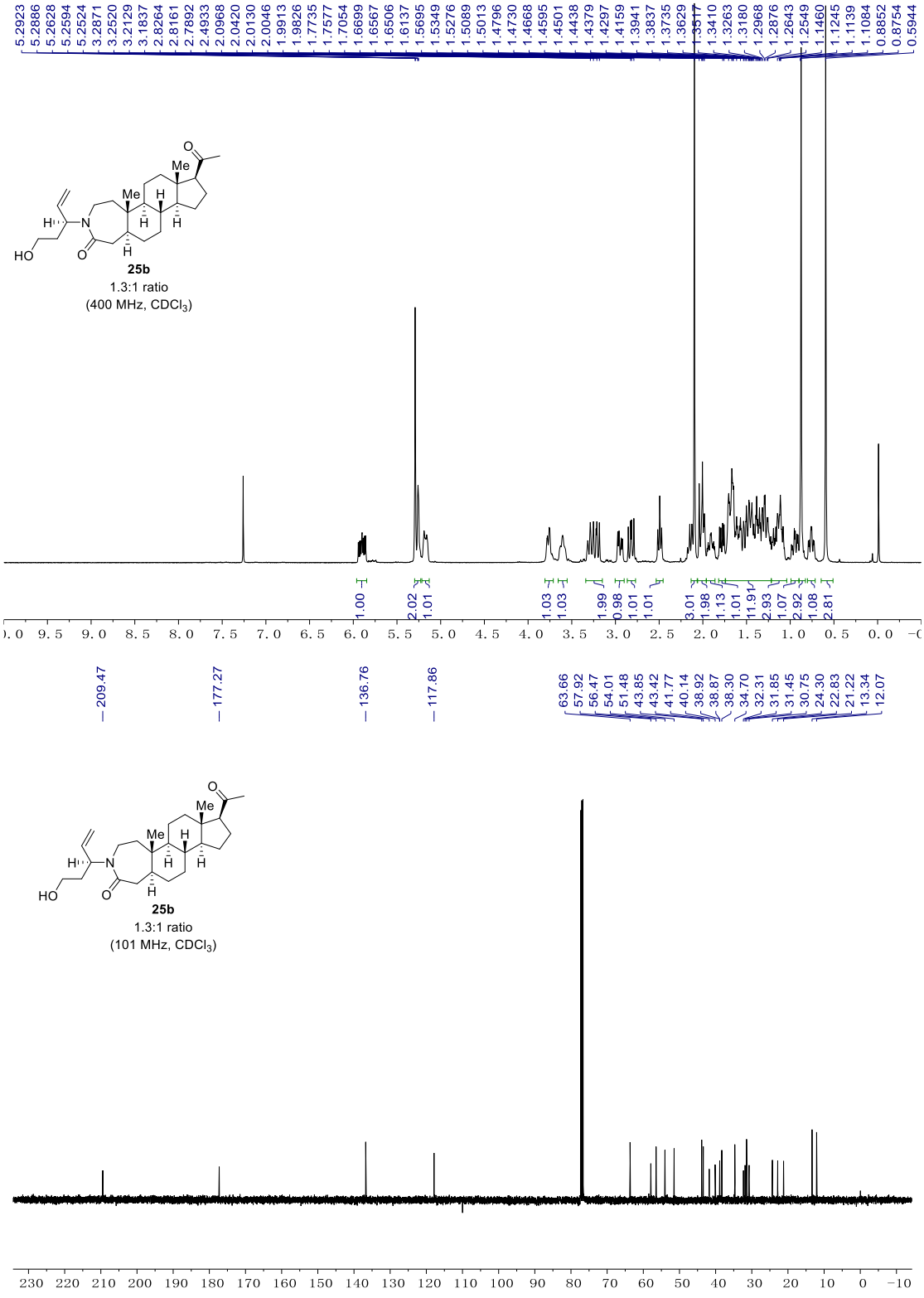

22
2:1 ratio
(101 MHz, CDCl3)

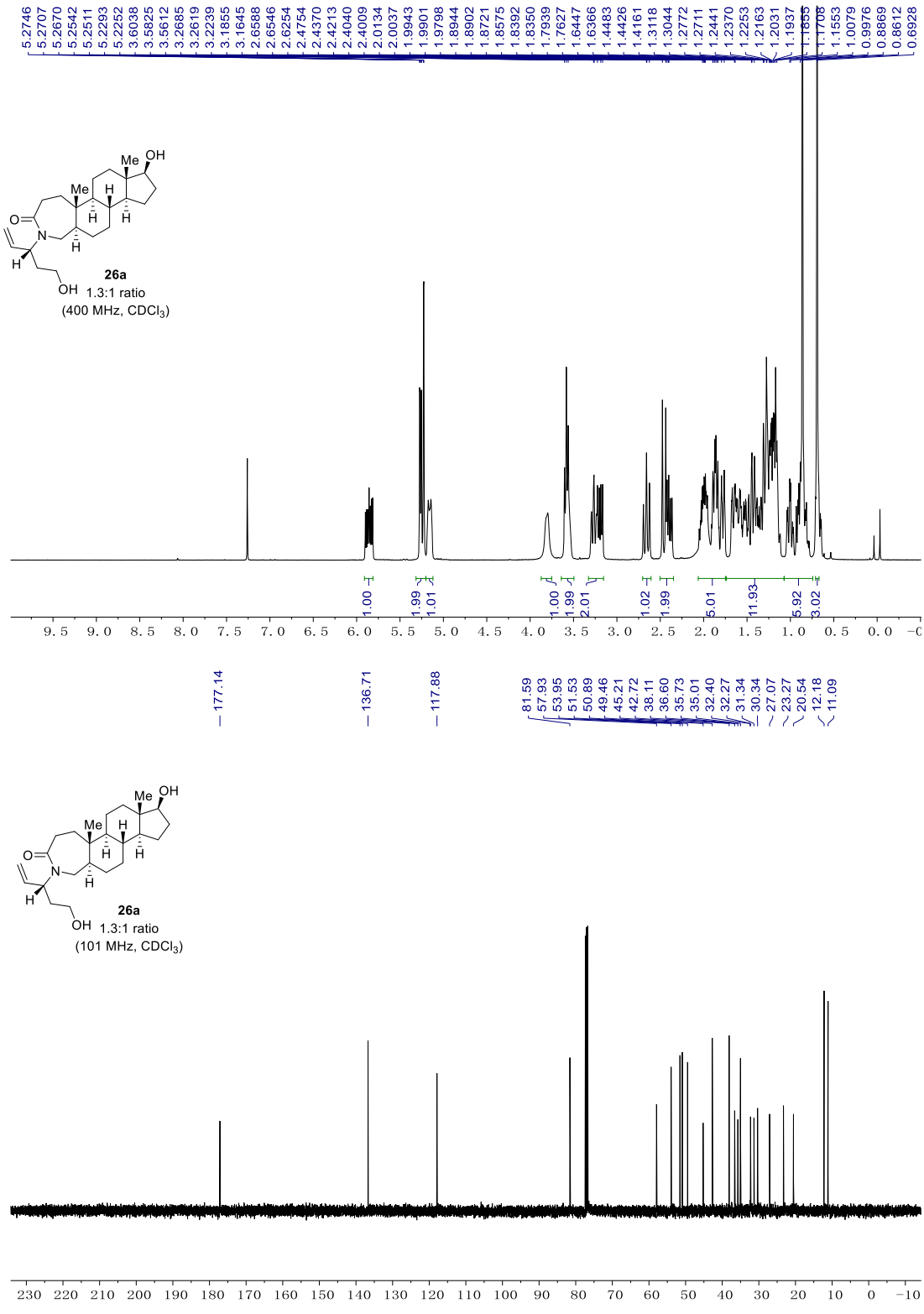

23
1.05:1 ratio
(400 MHz, CDCl3)
23
1.05:1 ratio
(101 MHz, CDCl3)

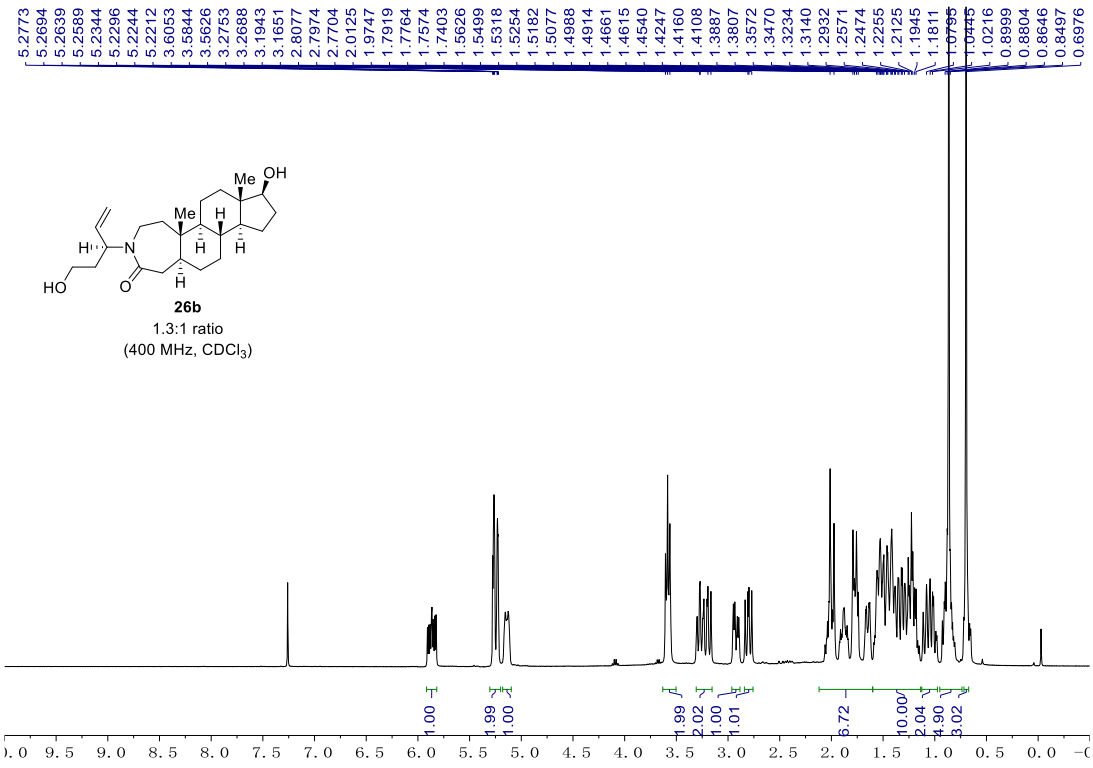

5.8800
5.8654
5.8500
5.8366
5.8222
5.2219
5.2185
5.2140
5.2093
3.7515
3.7429
3.5666
3.4338
3.4266
3.4051
3.3978
3.3761
3.3687
3.3402
3.3325
3.3129
3.3057
3.2863
3.2803
3.1188
3.1122
3.1018
2.9506
2.9136
2.8497
2.8126
2.5683
2.5607
2.5269
2.4454
2.4124
1.9080
1.9019
1.8783
1.8679
1.6576
1.6407
1.5247
1.5184
1.5081
1.4848
1.3689
0.9996
0.9840
0.8780
0.8740
Me
Me
N
O
OH
Me
Me
O
N
OH
24
1.5:1 ratio
(400 MHz, CDCl3)
1.00
3.46
0.43
1.70
0.47
0.64
0.87
0.66
0.66
1.09
1.11
1.29
4.90
0.70
2.70
4.00


177.71
175.23
137.61
136.84
117.72
117.54
58.16
58.14
53.88
52.59
51.86
49.57
44.19
43.78
43.61
38.06
32.90
32.62
30.56
28.65
25.55
25.19
19.57
Me
Me
N
O
OH
Me
Me
O
N
OH
24
1.5:1 ratio
(101 MHz, CDCl3)

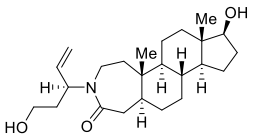

25a
1.3:1 ratio
(400 MHz, CDCl3)
25a
1.3:1 ratio
(101 MHz, CDCl3)


25b
1.3:1 ratio
(400 MHz, CDCl3)
25b
1.3:1 ratio
(101 MHz, CDCl3)

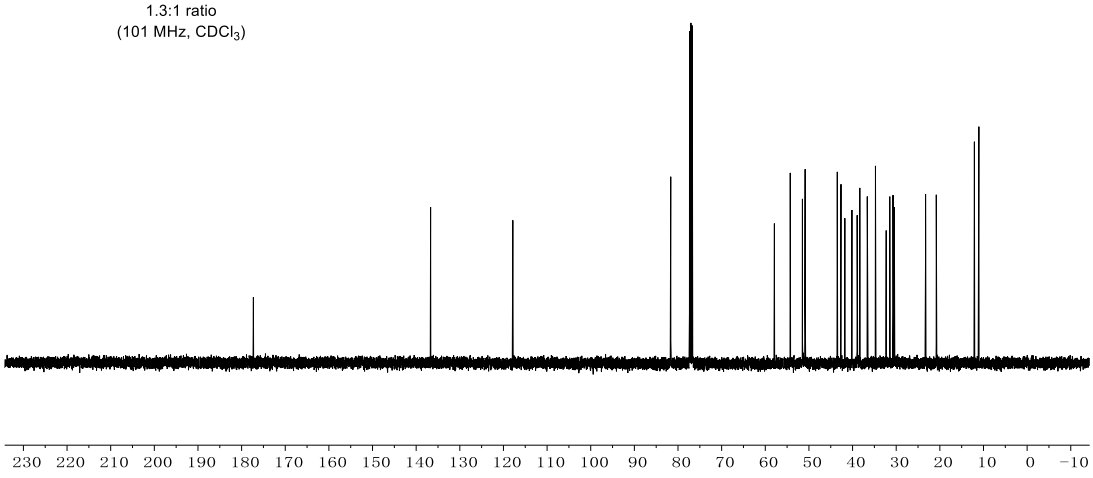

26a
1.3:1 ratio
(400 MHz, CDCl3)
26a
1.3:1 ratio
(101 MHz, CDCl3)

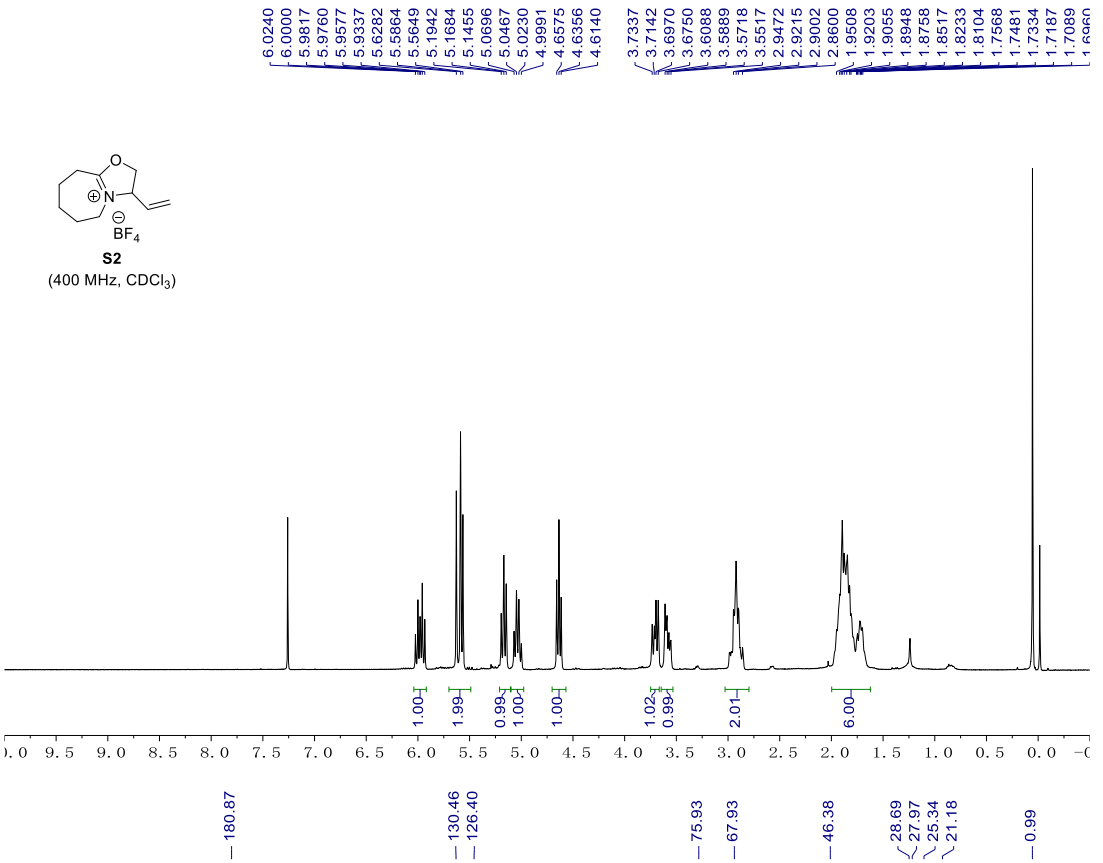


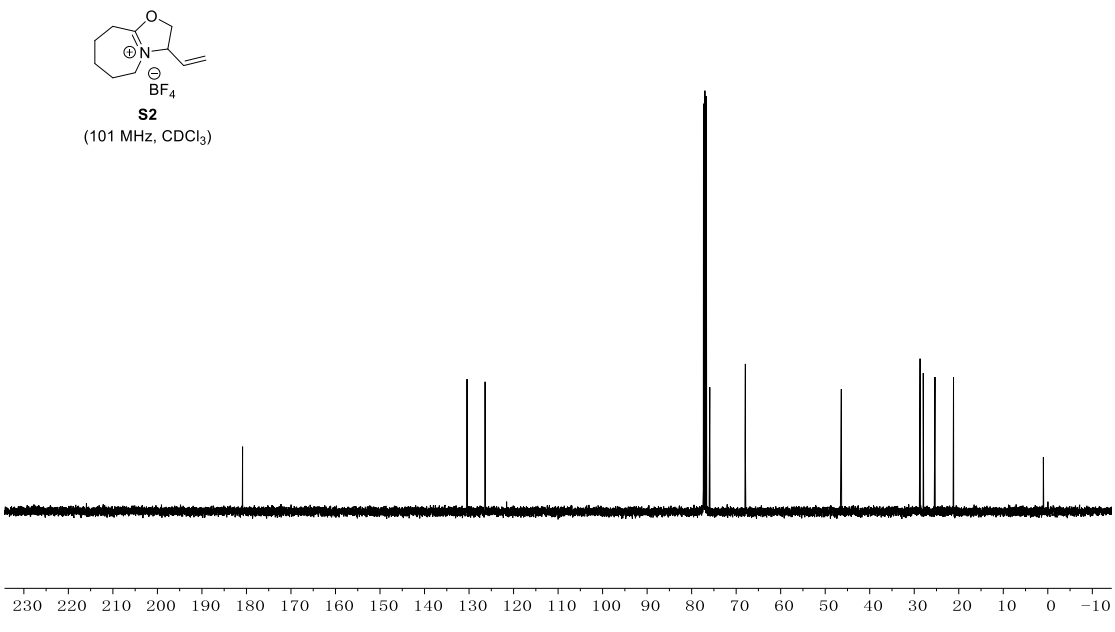
26b
1.3:1 ratio
(400 MHz, $CDCl_3$)

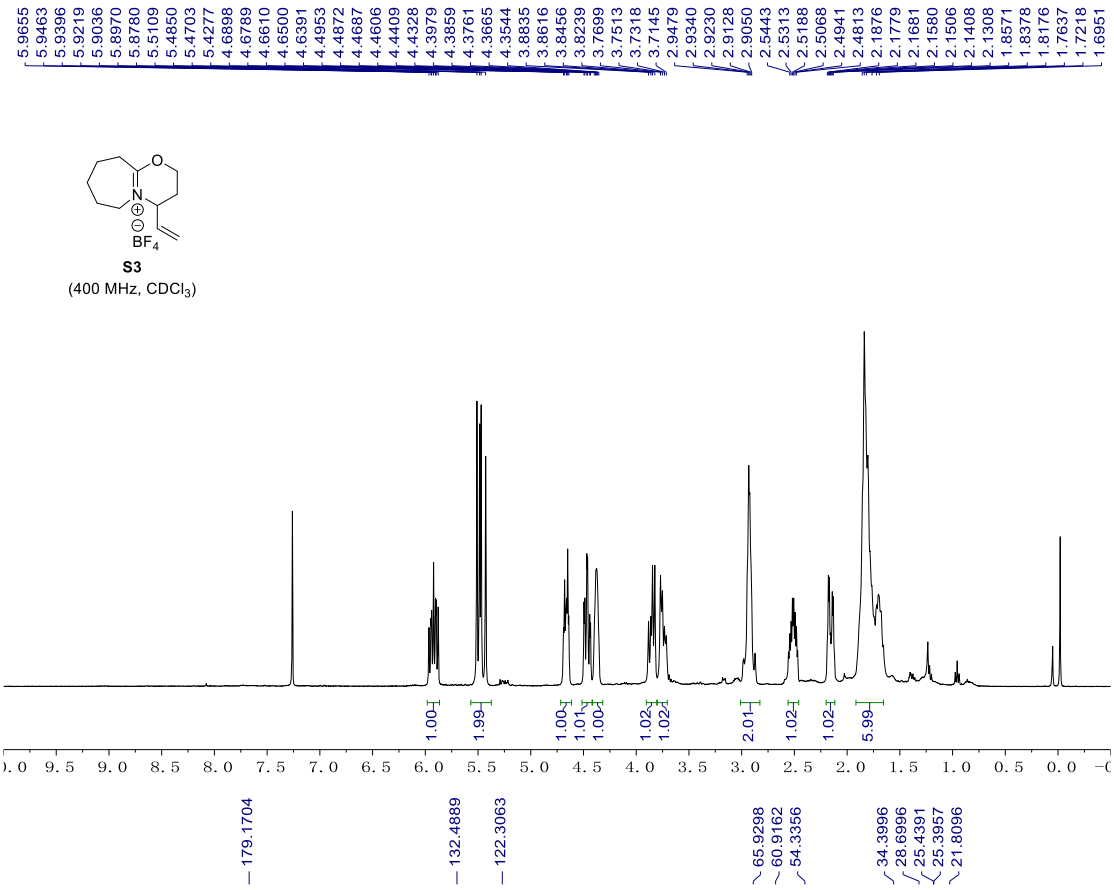


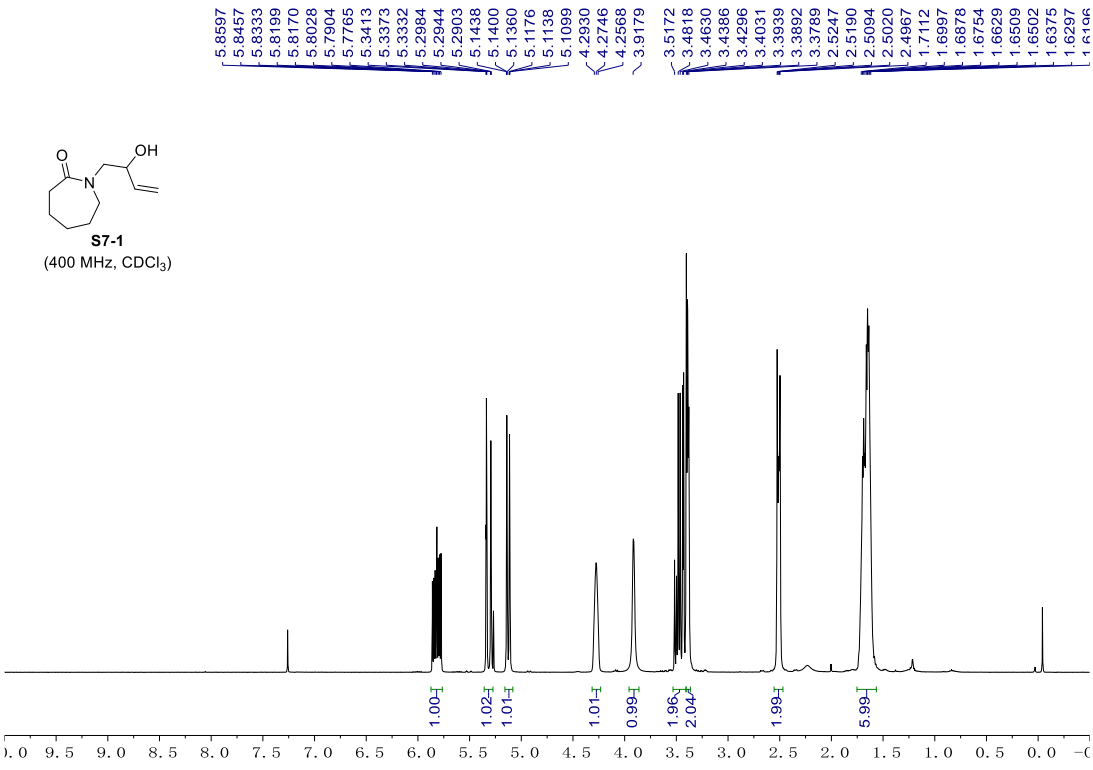
26b
1.3:1 ratio
(101 MHz, $CDCl_3$)

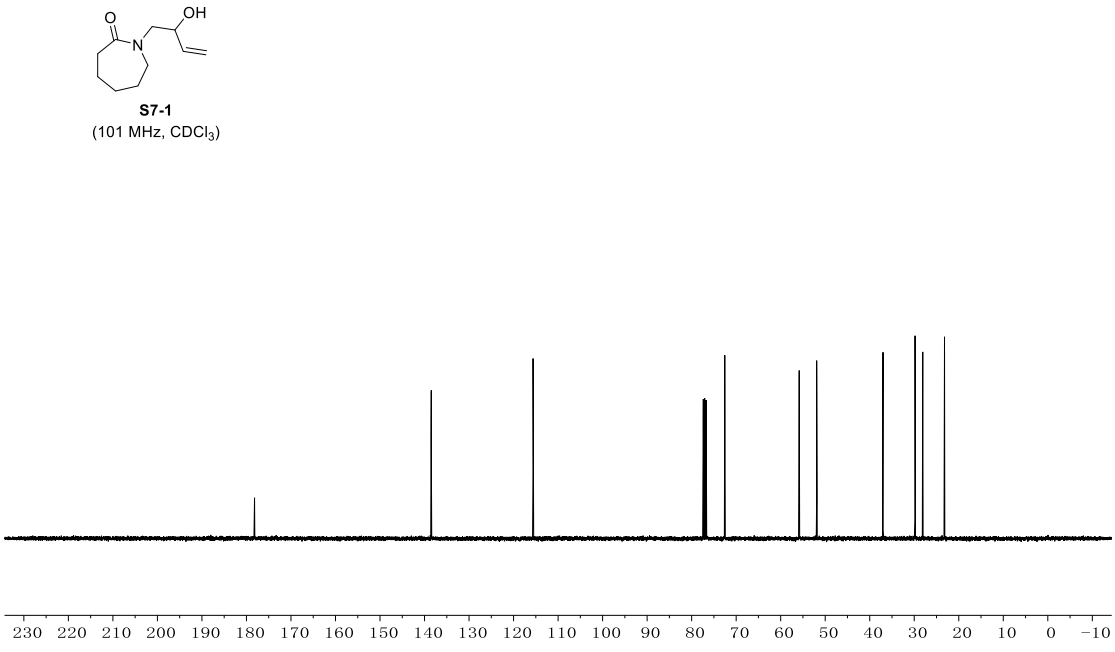



6.0240
6.0000
5.9817
5.9760
5.9577
5.9337
5.6282
5.5864
5.5649
5.1942
5.1684
5.1455
5.0696
5.0467
5.0230
4.9991
4.6575
4.6356
4.6140
3.7337
3.7142
3.6970
3.6750
3.6088
3.5889
3.5718
3.5517
2.9472
2.9215
2.9002
2.8600
1.9508
1.9203
1.9055
1.8948
1.8758
1.8517
1.8233
1.8104
1.7568
1.7481
1.7334
1.7187
1.7089
BF4
S2
(400 MHz, CDCl3)
1.00
1.99
0.99
1.00
1.00
1.02
0.99
2.01
6.00


180.87
130.46
126.40
75.93
67.93
46.38
28.69
27.97
25.34
21.18
0.99
BF4
S2
(101 MHz, CDCl3)


5.9655
5.9463
5.9396
5.9219
5.9036
5.8970
5.8780
5.5109
5.4850
5.4703
5.4277
4.6898
4.6789
4.6610
4.6500
4.6391
4.4953
4.4872
4.4687
4.4606
4.4409
4.4328
4.3979
4.3859
4.3761
4.3665
4.3544
3.8835
3.8616
3.8456
3.8239
3.7699
3.7513
3.7318
3.7145
2.9479
2.9340
2.9230
2.9128
2.9050
2.5443
2.5313
2.5188
2.5068
2.4941
2.4813
2.1876
2.1779
2.1681
2.1580
2.1506
2.1408
2.1308
1.8571
1.8378
1.8176
1.7637
1.7218
1.6951
O
N
BF4
S3
(400 MHz, CDCl3)
1.00
1.99
1.00
1.01
1.00
1.02
1.02
2.01
1.02
1.02
5.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
179.1704
132.4889
122.3063
65.9298
60.9162
54.3356
34.3996
28.6996
25.4391
25.3957
21.8096
O
N
BF4
S3
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


S7-1
(400 MHz, $CDCl_3$)


S7-1
(101 MHz, $CDCl_3$)