Supporting Information

Synthesis of Chiral Seven-membered β-Substituted Lactams *via* Rh-catalyzed Asymmetric Hydrogenation

Yi Huang,[†] Pan Li,[†] Xiu-Qin Dong,[†]* Xumu Zhang[‡,†]*

[†]Key Laboratory of Biomedical Polymers, Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, 430072, P. R. China

[‡] Department of Chemistry and Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, P. R. China.

Email: zhangxm@sustc.edu.cn, xiuqindong@ whu.edu.cn

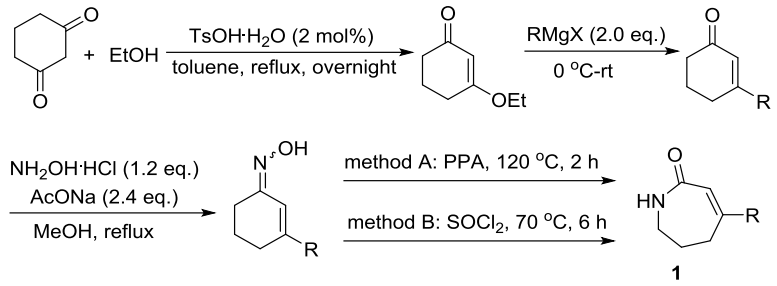
Contents

I. General remarks

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or in the argon-filled glovebox. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers without further purification. The anhydrous CH_2Cl_2 and MeOH (superdry solvent, 99.9%, water $\leq$ 30 ppm, with molecular sieves.) were purchased from J&K Chemical Technology company and transferred by syringe. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ADVANCE III (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.0 ppm (for ^{13}C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR and ^{1}H NMR analyses were run with decoupling. Enantiomeric excess values were determined by Daicel chiral column on an Agilent 1260 Series HPLC instrument. Optical rotations $[\alpha]_D$ were measured on a PERKIN ELMER polarimeter 343 instrument. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000& Bruker Compact TOF mass spectrometer. The substrate 4-phenyl-1,5,6,7-tetrahydro-2H-azepin-2-one **1a** and its analogues were synthesized according to the literatures. [1-6] Compound **2f** was transformed into N-*p*-chlorobenzoyl protected lactam **3** for the determination of absolute configuration. The absolute configuration of lactam **3** is (*R*), which was determined by X-ray analysis. [7] The absolute configurations of other hydrogenation products were assigned by analogy.

II. General procedure for the preparation of substrates

General procedure for the synthesis of 1a and its analogues:



The 3-ethoxy-2-cyclohexen-1-one was synthesized according to the following procedures. [1] To a solution of 1,3-cyclohexanedione (100 mmol, 11.2 g, 1.0 equiv.) in toluene (50 mL) was added EtOH (760 mmol, 44 mL, 7.6 equiv.), *p*-TsOH·H_2O (2 mmol, 0.02 equiv.) at ambient temperature. The flask was equipped with a reflux condenser and placed in oil bath maintained at 130 °C overnight. The reaction mixture was allowed to cool down to ambient temperature and the solvent was removed in *vacuo* to give orange oil. The crude product was dissolved in CH_2Cl_2 and neutralized with aqueous NaOH (0.1 M). The organic phase and aqueous phase were separated, and the organic phases were combined, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography using PE/EA (V: V = 10:1) as eluent to afford pure product as pale orange or colorless oil (11.7 g, 84% yield).

The corresponding cyclic unsaturated ketone was obtained according to the following procedure. [1-2] A flame-dried flask was charged with THF solution (30 mL) of corresponding Grignard reagent (2.0 equiv., 60 mmol) and cooled to 0 °C. 3-ethoxy-2-cyclohexen-1-one (1.0 equiv., 4.2 g, 30 mmol) was added to the solution dropwise. Once the addition was completed, the reaction mixture was warmed to room temperature and stirred for 2 h until the completion of the disappearance of starting material. The reaction mixture was placed in an ice bath and 0.2 M aqueous H_2SO_4 was added to quench the reaction, and then extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column

chromatography using PE/EA (10:1, V: V) as eluent to give desired product as yellow solid.

The oximes were obtained from corresponding ketone according to the following procedures. [3] The product corresponding ketone from last step (1.0 equiv., 20 mmol) was dissolved in MeOH (20 mL), and successive addition of hydroxylamine hydrochloride (1.2 equiv., 24 mmol, 1.7 g) and sodium acetate trihydrate (2.4 equiv., 48 mmol, 6.5 g). The flask was equipped with a reflux condenser and placed in oil bath maintained at 70 ^{o}C overnight or for 4 h. The reaction mixture was allowed to cool down to ambient temperature, washed with brine and extracted with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4, and the solvent was removed from the mixture under reduced pressure. The resulting crude product was used for next step directly without further purification.

Method A for the synthesis of seven-membered β-substituted α,β-unsaturated lactams. [4]

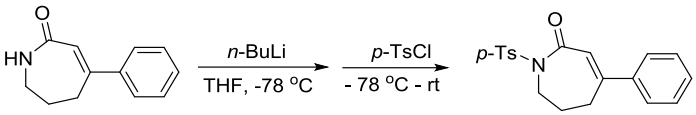
To PPA (polyphosphoric acid, 10 mL) at 120 ^{o}C was added the oxime (12.8 mmol) by portionwise over 5 min. The mixture was stirred at this temperature for 2 h resulting in a deep red-brown syrup. The syrup was poured slowly into ice water and then neutralized with 1 M aqueous $NaHCO_3$, extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4. The resulting crude product was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to provide crude product, and the finally desired product was obtained after recrystallization from diethyl ether and CH_2Cl_2.

Method B for the synthesis of seven-membered β-substituted α,β-unsaturated lactams. [5]

A solution of thionyl chloride (16 equiv.) in 1,4-dioxane was added dropwise into a stirred solution of oxime (1.0 equiv.) in 1,4-dioxane (0.5 M) in a 10 mL round-bottom flask at 0 ^{o}C. The resulting mixture was then placed at 70 ^{o}C and stirred for 6 h. The

mixture was concentrated under *vacuo* and diluted with CH_2Cl_2 and then the reaction was quenched with saturated aqueous sodium bicarbonate to adjust pH ≈ 7. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent, and after which, recrystallized in CH_2Cl_2 and petroleum ether to provide the desired product as brown solid.

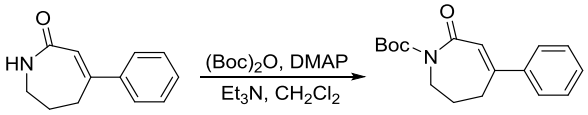
Method C for the synthesis of N-*p*-Ts seven-membered β-phenyl substituted α,β-unsaturated lactam 1j.



1a **1j**

n-BuLi (2.4 M in hexane, 0.1 mL, 1.1 eq.) was added into the THF (1.0 mL) solution of β-phenyl substituted α,β-unsaturated lactam **1a** (0.21 mmol, 39.3 mg, 1.0 eq.) at -78 °C under N_2 atmosphere and stirred for 1 h, and 1.0 mL THF solution of *p*-TsCl (0.23 mmol, 44.0 mg, 1.1 eq.) was transferred into this reaction mixture at the same temperature under N_2 atmosphere. After stirring at -78 °C for another 5 min, the cooling bath was removed and warmed to room temperature and stirred for 1 h under N_2 atmosphere. The reaction mixture was subjected to flash column chromatography directly and the finally desired product N-Ts β-phenyl substituted α,β-unsaturated lactam **1j** was obtained as white solid (58.0 mg, 81% yield).

Method D for the synthesis of N-Boc seven-membered β-phenyl substituted α,β-unsaturated lactam 1k. [6]

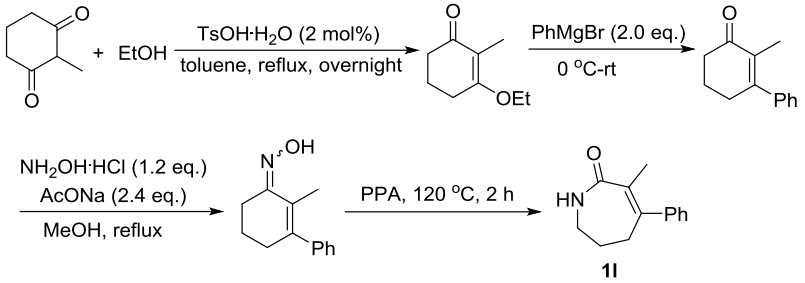


1a **1k**

The N-Boc substituted lactam was synthesized according to the following procedures: **1a** (2.0 mmol), DMAP (0.1 eq., 0.2 mmol), and NEt_3 (1.5 eq., 3.0 mmol) were dissolved in CH_2Cl_2 (4.0 mL), followed by addition of $(Boc)_2O$ (2.0 eq., 4.0

mmol). The reaction mixture was stirred at room temperature for another 5 h. The reaction mixture was subjected to flash column chromatography directly and the finally desired N-Boc product **1k** was obtained as white solid (487 mg, 85% yield).

Method E for the synthesis of tetrasubstituted (3-methyl-4-phenyl-1,5,6,7-tetrahydro-2*H*-azepin-2one) lactam 1l



1l

The 3-ethoxy-2-methyl-2-cyclohexen-1-one was synthesized according to the following procedures. To a solution of 2-methyl-1,3-cyclohexanedione (50 mmol, 6.3 g, 1.0 equiv.) in toluene (30 mL) was added EtOH (380 mmol, 22 mL, 7.6 equiv.), *p*-TsOH·H_2O (1 mmol, 0.02 equiv.) at ambient temperature. The flask was equipped with a reflux condenser and placed in oil bath maintained at 130 °C overnight. The reaction mixture was allowed to cool down to ambient temperature and the solvent was removed in *vacuo* to give orange oil. The crude product was dissolved in CH_2Cl_2 and neutralized with aqueous NaOH (0.1 M). The organic phase and aqueous phase were separated, and the organic phases were combined, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography using PE/EA (V: V = 10:1) as eluent to afford pure product as yellow solid (2.6 g, 34% yield).

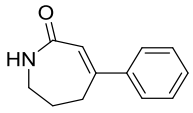
The cyclic unsaturated ketone 2-methyl-3-phenyl-2-cyclohexen-1-one was obtained according to the following procedure. A flame-dried flask was charged with THF solution (15 mL) of phenylmagnesium bromide (2.0 equiv., 34 mmol) and cooled to 0 °C. 3-ethoxy-2-methyl-2-cyclohexen-1-one (1.0 equiv., 2.6 g, 17 mmol) was added to the solution dropwise. Once the addition was completed, the reaction mixture was warmed to room temperature and stirred for 2 h until the completion of the

disappearance of starting material. The reaction mixture was placed in an ice bath and 0.2 M aqueous H_2SO_4 was added to quench the reaction, and then extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography using PE/EA (10:1, V: V) as eluent to give desired product as yellow viscous oil (1.6 g, 51% yield).

The oximes were obtained from corresponding ketone according to the following procedures. The product corresponding ketone from last step (1.0 equiv., 8.6 mmol, 1.6 g) was dissolved in MeOH (20 mL), and successive addition of hydroxylamine hydrochloride (1.2 equiv., 10.3 mmol, 716 mg) and sodium acetate trihydrate (2.4 equiv., 20.6 mmol, 2.8 g). The flask was equipped with a reflux condenser and placed in oil bath maintained at 70 ^oC overnight or for 4 h. The reaction mixture was allowed to cool down to ambient temperature, washed with brine and extracted with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4, and the solvent was removed from the mixture under reduced pressure. The resulting crude product was used for next step directly without further purification (1.65 g white solid, 95% yield).

To PPA (polyphosphoric acid, 10 mL) at 120 ^oC was added the oxime (8.2 mmol, 1.65 g) by portionwise over 5 min. The mixture was stirred at this temperature for 2 h resulting in a deep red-brown syrup. The syrup was poured slowly into ice water and then neutralized with 1 M aqueous $NaHCO_3$, extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4. The resulting crude product was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to provide crude product, and the finally desired product was obtained as colorless crystal after recrystallization from diethyl ether and CH_2Cl_2 (677 mg, 41% yield).

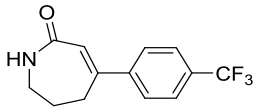
4-phenyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1a**



Brown solid; M. P. 133-134 ^oC; Total yield 38%; It was obtained according to

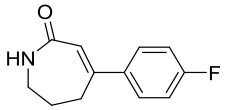
method A. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.47-7.44 (m, 2H), 7.40-7.32 (m, 3H), 6.19 (s, 1H), 3.36-3.32 (m, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.15-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.50, 150.42, 141.47, 128.50, 126.17, 122.75, 40.24, 30.81, 29.58. ESI-HRMS calculated for $C_{12}H_{13}NONa^+$ ($[M+Na]^+$): 210.0889; Found: 210.0890.

4-(4-(trifluoromethyl)phenyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1b**



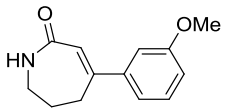
Dark brown solid; M. P. 140-141 ºC; Total yield 12%; It was obtained according to method B. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.64 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.28 (brs, 1H), 6.22 (s, 1H), 3.38-3.34 (m, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.18-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 171.74, 148.98, 145.14, 130.42 (q, *J* = 32.0 Hz), 126.59, 125.54 (q, *J* = 4.0 Hz), 124.47, 122.55, 40.22, 30.95, 29.42. ESI-HRMS calculated for $C_{13}H_{12}F_3NONa^+$ ($[M+Na]^+$): 278.0763; Found: 278.0766.

4-(4-fluorophenyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1c**



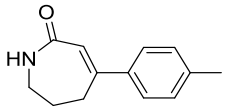
Yellow solid; M. P. 150-152 ºC; Total yield 45%. It was obtained according to method A. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.45-7.41 (m, 2H), 7.15 (brs, 1H), 7.08-7.04 (m, 2H), 6.14 (s, 1H), 3.36-3.32 (m, 2H), 2.78 (t, *J* = 4.0 Hz, 2H), 2.15-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.22, 162.87 (d, *J* = 247.0 Hz), 149.37, 137.52 (d, *J* = 3.0 Hz), 127.98 (d, *J* = 8.0 Hz), 122.74 (d, *J* = 1.0 Hz), 115.46 (d, *J* = 21.0 Hz), 40.26, 31.00, 29.42. ESI-HRMS calculated for $C_{12}H_{12}FNONa^+$ ($[M+Na]^+$): 228.0795; Found: 228.0797.

4-(3-methoxyphenyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1d**



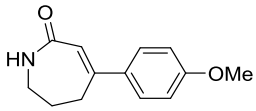
Dark brown solid; M. P. 101-102 ºC; Total yield 14%. It was obtained according to method B. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.49 (brs, 1H), 7.31-7.27 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.91-6.88 (m, 1H), 6.19 (s, 1H), 3.83 (s, 3H), 3.35-3.31 (m, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.14-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.48, 159.52, 150.29, 142.96, 129.48, 122.81, 118.60, 113.92, 111.83, 55.21, 40.20, 30.86, 29.57. ESI-HRMS calculated for $C_{13}H_{15}NO_2Na^+$ ($[M+Na]^+$): 240.0995; Found: 240.0998.

4-(*p*-tolyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1e**



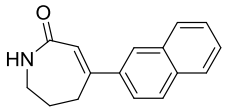
Dark brown solid; M. P. 147-148 ºC; Total yield 13%. It was obtained according to method B. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.36 (d, *J* = 8.0 Hz, 2H), 7.19-7.17 (m, 3H), 6.17 (s, 1H), 3.34-3.30 (m, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.14-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.63, 150.36, 138.62, 138.48, 129.21, 126.10, 121.97, 40.31, 30.71, 29.57, 21.10. ESI-HRMS calculated for $C_{13}H_{15}NONa^+$ ($[M+Na]^+$): 224.1046; Found: 224.1049.

4-(4-methoxyphenyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1f**



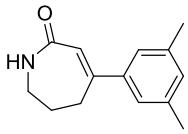
Pale brown solid; M. P. 122-123 ºC; Total yield 27%. It was obtained according to method A. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.42 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.78 (brs, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 3.35-3.30 (m, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.13-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.60, 160.01, 149.91, 133.58, 127.53, 121.13, 113.88, 55.31, 40.37, 30.61, 29.52. ESI-HRMS calculated for $C_{13}H_{15}NO_2Na^+$ ($[M+Na]^+$): 240.0995; Found: 240.0999.

4-(2-naphthenyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1g**



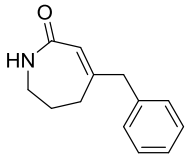
White solid; M. P. 170-172 ^{o}C; Total yield 45%. It was obtained according to method A. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.92 (s, 1H), 7.86-7.82 (m, 3H), 7.60-7.57 (m, 2H), 7.52-7.49 (m, 2H), 6.34 (s, 1H), 3.40-3.35 (m, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.20-2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.38, 150.23, 138.65, 133.15, 133.08, 128.28, 128.25, 127.54, 126.52, 126.49, 125.49, 124.08, 123.19, 40.35, 30.79, 29.62. ESI-HRMS calculated for $C_{16}H_{15}NONa^{+}$ ([M+Na]$^{+}$): 260.1046; Found: 260.1050.

4-(3,5-dimethylphenyl)-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1h**



White solid; M. P. 206-208 ^{o}C; Total yield 8%. It was obtained according to method A. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.07 (s, 2H), 6.99 (s, 1H), 6.70 (brs, 1H), 6.16 (d, *J* = 4.0 Hz, 1H), 3.35-3.30 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 6H), 2.14-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 172.35, 150.77, 141.59, 138.08, 130.20, 124.14, 122.45, 40.40, 30.95, 29.59, 21.29. ESI-HRMS calculated for $C_{14}H_{17}NONa^{+}$ ([M+Na]$^{+}$): 238.1202; Found: 238.1205.

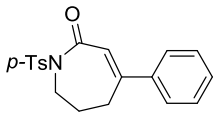
4-benzyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1i**



Brown solid; M. P. 120-121 ^{o}C; Total yield 2%. It was obtained according to method A. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.32-7.28 (m, 2H), 7.25-7.19 (m, 3H), 6.57 (brs, 1H), 5.84 (s, 1H), 3.45 (s, 2H), 3.21-3.17 (m, 2H), 2.31 (t, *J* = 8.0 Hz, 2H),

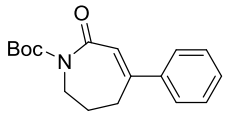
1.84-1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 171.41, 152.76, 138.10, 128.98, 128.57, 126.71, 122.87, 46.28, 40.86, 31.92, 28.55. ESI-HRMS calculated for $C_{13}H_{15}NONa^+$ ([M+Na]$^+$): 224.1046; Found: 224.1046.

4-phenyl-1-tosyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one **1j**



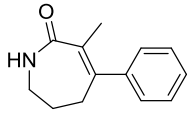
White solid; M. P. 94-97 ºC; Total yield 31%. It was obtained according to method A and C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.98 (d, *J* = 8.0 Hz, 2H), 7.40-7.33 (m, 7H), 6.09 (s, 1H), 4.00 (t, *J* = 8.0 Hz, 2H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.29-2.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 169.11, 151.96, 144.68, 140.04, 136.24, 129.39, 129.33, 128.77, 128.55, 126.26, 122.01, 45.00, 28.89, 28.33, 21.65. ESI-HRMS calculated for $C_{19}H_{19}NO_3SNa^+$ ([M+Na]$^+$): 364.0978; Found: 364.0984.

tert-butyl 7-oxo-5-phenyl-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate **1k**



White solid; M. P. 52-54 ºC; Total yield 32%. It was obtained according to method A and D. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.47-7.44 (m, 2H), 7.42-7.35 (m, 3H), 6.24 (s, 1H), 3.85 (t, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.13-2.07 (m, 2H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 170.27, 151.99, 150.46, 140.55, 129.05, 128.70, 126.30, 123.72, 82.77, 43.46, 28.19, 28.06, 27.00. ESI-HRMS calculated for $C_{17}H_{21}NO_3Na^+$ ([M+Na]$^+$): 310.1414; Found: 310.1410.

2-methyl-3-phenyl-1,5,6,7-tatrahydro-2*H*-azepin-2-one **1l**



White crystal; M. P. 130-132 ºC; Total yield 7%; It was obtained according to method E. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.75 (brs, 1H), 7.35 (t, *J* = 7.2 Hz,

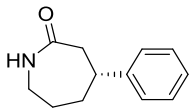
2H), 7.27-7.20 (m, 3H), 2.55 (q, *J* = 7.2 Hz, 4H), 2.25-2.18 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 176.31, 141.61, 130.60, 129.07, 128.41, 128.20, 126.59, 34.11, 32.33, 29.78, 18.71. ESI-HRMS calculated for $C_{13}H_{15}NONa^+$ ($[M+Na]^+$): 224.1051; Found: 224.1045.

III. General procedure for the Rh-catalyzed asymmetric hydrogenation

In an argon-filled glove-box, a solution of ZhaoPhos **L1** (6.6 mol%) and $Rh(NBD)_2BF_4$ (6.0 mol%) in the total volume of 0.5 mL of anhydrous CH_2Cl_2 and MeOH (V/V = 1:1) was stirred at room temperature for 2.0 h. 0.2 mmol substrate **1** was transferred into the resulting catalytic complex to make the concentration of substrate 0.4 M. And then stirred for another 5 min. The vials were transferred into autoclave, which was then charged with 50 atm H_2 and stirred at room temperature for 48 h. The hydrogen gas was released carefully and the solution was concentrated and purified through a short celite column on silica gel to remove the metal complex. The product was analyzed by ^{1}H NMR spectra for conversion-determination and purification by flash column chromatography using PE/EA (V: V = 1: 5) to provide desired hydrogenation product, which was further analyzed by chiral HPLC for ee values determination.

The absolute configuration of product **2f** was determined by the X-ray analysis of its N-*p*-chlorobenzoyl derivative **3**, [7] and the others were determined by analogy.

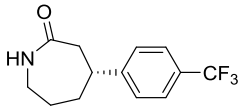
(*R*)-4-phenylazepan-2-one **2a**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) to provide desired hydrogenation product as brown solid; M. P. 174-177 ^oC; >99% conv.; 37.1 mg, 98% yield; 93% ee; $[\alpha]_D^{20}$ = -49.40 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 11.3 min

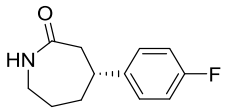
(minor), t_R = 12.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.32-7.29 (m, 2H), 7.23-7.18 (m, 3H), 6.34 (brs, 1H), 3.38-3.25 (m, 2H), 2.97-2.85 (m, 2H), 2.61 (d, *J* = 12.0 Hz, 1H), 2.15-2.11 (m, 1H), 1.99-1.92 (m, 1H), 1.83-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.13, 146.86, 128.59, 126.41, 126.32, 43.61, 42.65, 40.66, 39.31, 29.73. ESI-HRMS calculated for $C_{12}H_{15}NONa^+$ ($[M+Na]^+$): 212.1046; Found: 212.1048.

(*R*)-4-(4-(trifluoromethyl)phenyl)azepan-2-one **2b**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as orange solid; M. P. 142-144 ^{o}C; >99% conv.; 50.4 mg, 98% yield; 93% ee; $[\alpha]_D^{20}$ = -38.70 (c = 1.2, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 13.8 min (minor), t_R = 12.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.66 (brs, 1H), 3.40-3.26 (m, 2H), 2.99-2.92 (m, 2H), 2.62-2.57 (m, 1H), 2.14-2.10 (m, 1H), 2.00-1.96 (m, 1H), 1.86-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 176.70, 150.67, 128.75 (q, *J* = 33.0 Hz), 126.72, 125.60 (q, *J* = 4.0 Hz), 124.11 (d, *J* = 270.0 Hz), 43.25, 42.50, 40.51, 39.04, 29.56. ESI-HRMS calculated for $C_{13}H_{14}F_3NONa^+$ ($[M+Na]^+$): 280.0920; Found: 280.0919.

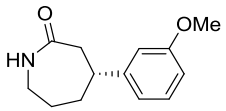
(*R*)-4-(4-fluorophenyl)azepan-2-one **2c**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1:5) as eluent to give desired hydrogenation product as orange solid; M. P. 189-190 ^{o}C; >99% conv.; 40.6 mg, 98% yield; 91% ee; $[\alpha]_D^{20}$ = -37.14 (c = 0.7, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralpak AD-H column, hexane:

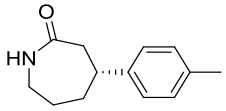
isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 13.3 min (minor), t_R = 14.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.17-7.13 (m, 2H), 7.02-6.97 (m, 2H), 6.50 (brs, 1H), 3.35-3.27 (m, 2H), 2.94-2.87 (m, 2H), 2.58-2.55 (m, 1H), 2.12-2.09 (m, 1H), 1.98-1.93 (m, 1H), 1.76-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 176.93, 161.32 (d, *J* = 243.0 Hz), 142.55 (d, *J* = 4.0 Hz), 127.72 (d, *J* = 8.0 Hz), 115.33 (d, *J* = 21.0 Hz), 43.78, 42.58, 39.95, 39.40, 29.64. ESI-HRMS calculated for $C_{12}H_{14}FNONa^+$ ($[M+Na]^+$): 230.0952; Found: 230.0954.

(*R*)-4-(3-methoxyphenyl)azepan-2-one **2d**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as orange solid; M. P. 108-110 ^{o}C; >99% conv.; 42.5 mg, 97% yield; 86% ee; $[\alpha]_D^{20}$ = -12.73 (c = 1.1, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 21.8 min (minor), t_R = 28.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.22 (t, *J* = 8.0 Hz, 1H), 6.79-6.73 (m, 3H), 6.45 (brs, 1H), 3.80 (s, 3H), 3.38-3.25 (m, 2H), 2.95-2.82 (m, 2H), 2.62-2.59 (m, 1H), 2.15-2.12 (m, 1H), 1.98-1.93 (m, 1H), 1.83-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.27, 159.66, 148.48, 129.60, 118.69, 112.34, 111.45, 55.16, 43.55, 42.65, 40.69, 39.16, 29.66. ESI-HRMS calculated for $C_{13}H_{17}NO_2Na^+$ ($[M+Na]^+$): 242.1151; Found: 242.1153.

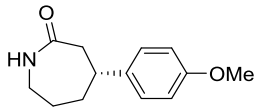
(*R*)-4-(*p*-tolyl)azepan-2-one **2e**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as orange solid; M. P. 139-140 ^{o}C; >99% conv.; 39.8 mg, 98% yield; 87% ee; $[\alpha]_D^{20}$ = -31.81 (c = 0.72, $CHCl_3$);

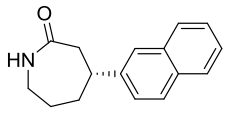
The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 13.0 min (minor), t_R = 13.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.13-7.07 (m, 4H), 6.47 (brs, 1H), 3.39-3.23 (m, 2H), 2.95-2.82 (m, 2H), 2.60-2.57 (m, 1H), 2.32 (s, 3H), 2.12-2.09 (m, 1H), 1.95-1.92 (m, 1H), 1.81-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.29, 143.93, 135.89, 129.23, 126.17, 43.75, 42.64, 40.22, 39.38, 29.72, 20.96. ESI-HRMS calculated for $C_{13}H_{17}NONa^+$ ([M+Na]$^+$): 226.1202; Found: 226.1204.

(*R*)-4-(4-methoxyphenyl)azepan-2-one **2f**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as brown solid; M. P. 138-139 ºC; >99% conv.; 43.4 mg, 99% yield; 88% ee; $[\alpha]_D^{20}$ = -44.22 (c = 1.31, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 40.9 min (minor), t_R = 43.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.13-7.09 (m, 2H), 6.86-6.82 (m, 2H), 6.63 (brs, 1H), 3.79 (s, 3H), 3.35-3.24 (m, 2H), 2.93-2.81 (m, 2H), 2.57 (d, *J* = 12.0 Hz, 1H), 2.12-2.09 (m, 1H), 1.95-1.91 (m, 1H), 1.80-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.40, 157.94, 139.11, 127.22, 113.85, 55.19, 43.95, 42.59, 39.79, 39.44, 29.67. ESI-HRMS calculated for $C_{13}H_{17}NO_2Na^+$ ([M+Na]$^+$): 242.1151; Found: 242.1156.

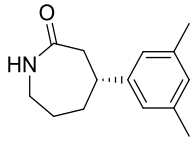
(*R*)-4-(2-naphthenyl)azepan-2-one **2g**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as white solid; M. P. 176-178

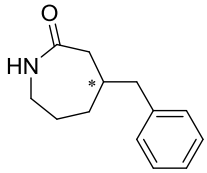
^{o}C; >99% conv.; 47.8 mg, 99% yield; 93% ee; $[\alpha]_D^{20}$ = -55.02 (c = 1.43, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 43.4 min (minor), t_R = 45.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.82-7.78 (m, 3H), 7.62 (s, 1H), 7.48-7.41 (m, 2H), 7.35-7.33 (m, 1H), 6.52 (brs, 1H), 3.39-3.29 (m, 2H), 3.06-2.99 (m, 2H), 2.70 (d, *J* = 12.0 Hz, 1H), 2.20 (d, *J* = 12.0 Hz, 1H), 2.00-1.69 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.15, 144.26, 133.50, 132.20, 128.29, 127.61, 127.56, 126.07, 125.46, 125.26, 124.38, 43.70, 42.66, 40.75, 39.15, 29.78. ESI-HRMS calculated for $C_{16}H_{17}NONa^+$ ($[M+Na]^+$): 262.1202; Found: 262.1204.

(*R*)-4-(3,5-dimethylphenyl)azepan-2-one **2h**



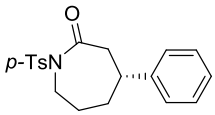
The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as white solid; M. P. 156-157 ^{o}C. >99% conv.; 43.4 mg, 99% yield; 96% ee; $[\alpha]_D^{20}$ = -28.64 (c = 0.43, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 24.9 min (minor), t_R = 31.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 6.85 (s, 1H), 6.80 (s, 2H), 6.77 (brs, 1H), 3.37-3.23 (m, 2H), 2.93-2.77 (m, 2H), 2.56 (d, *J* = 16.0 Hz, 1H), 2.29 (s, 6H), 2.13-2.09 (m, 1H), 1.95-1.89 (m, 1H), 1.82-1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.45, 146.89, 137.99, 127.95, 124.13, 43.86, 42.58, 40.53, 39.10, 29.73, 21.26. ESI-HRMS calculated for $C_{14}H_{19}NONa^+$ ($[M+Na]^+$): 240.1359; Found: 240.1360.

(+)-4-benzylazepan-2-one **2i**



The title compound was purified by flash column chromatography using PE/EA (V: V = 1: 5) as eluent to give desired hydrogenation product as brown solid; M. P. 110-111 ^{o}C; 86% conv.; 33.7 mg; 83% yield; 84% ee; $[\alpha]_D^{20}$ = 1.91 (c = 0.21, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 90: 10; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 17.2 min (minor), t_R = 15.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.30-7.26 (m, 3H), 7.22-7.18 (m, 1H), 7.16-7.14 (m, 1H), 6.15 (brs, 1H), 3.22-3.19 (m, 2H), 2.75-2.70 (m, 1H), 2.57-2.41 (m, 3H), 2.01-1.97 (m, 1H), 1.88-1.78 (m, 2H), 1.53-1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.35, 139.76, 129.18, 128.35, 126.17, 43.16, 42.76, 42.39, 35.86, 35.66, 28.60. ESI-HRMS calculated for $C_{13}H_{17}NONa^+$ ($[M+Na]^+$): 226.1202; Found: 226.1202.

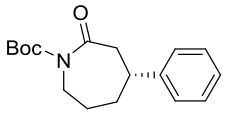
(*R*)-4-phenyl-1-tosylazepan-2-one **2j**



The title compound was purified by flash column chromatography using PE/EA (V: V = 5: 1) as eluent to give the desired hydrogenation product as white solid; M. P. 113-115 ^{o}C; >99% conv.; 68.3 mg; 99% yield; >99% ee; $[\alpha]_D^{20}$ = -1.47 (c = 1.77, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel AD-H column, hexane: isopropanol = 95: 5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 70.5 min (minor), t_R = 84.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.91 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.69-4.63 (m, 1H), 3.65-3.59 (m, 1H), 3.03-2.97 (m, 1H), 2.86-2.84 (m, 1H), 2.68 (d, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 2.19-2.05 (m, 2H), 1.79-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 173.16, 145.79, 144.63, 136.41, 129.31, 128.72, 128.55, 126.70, 126.21, 46.08, 45.62, 40.50, 38.03, 29.23, 21.66. ESI-HRMS calculated

for $C_{19}H_{21}NO_3SNa^+$ ([M+Na]$^+$): 366.1134; Found: 366.1143.

tert-butyl (*R*)-2-oxo-4-phenylazepane-1-carboxylate **2k**



The title compound was purified by flash column chromatography using PE/EA (V: V = 5: 1) as eluent to give the desired hydrogenation product as white solid; M. P. 71-72 ºC; >99% conv; 17.4 mg; 30% yield (70% Boc group was removed, determined by ^{1}H crude NMR); 99% ee; $[\alpha]_D^{20}$ = -39.70 (c = 0.68, $CHCl_3$); The enantiomeric excess was determined by HPLC on chiralcel OD-H column, hexane: isopropanol = 98: 2; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R = 16.2 min (minor), t_R = 19.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.32-7.28 (m, 2H), 7.23-7.16 (m, 3H), 4.33 (dd, *J* = 6.4 Hz, *J* = 15.2 Hz, 1H), 3.43 (dd, *J* = 10.0 Hz, *J* = 15.2 Hz, 1H), 3.13-3.07 (m, 1H), 2.95 (t, *J* = 11.6 Hz, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.09-2.04 (m, 2H), 1.81-1.63 (m, 2H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 173.96, 152.80, 146.34, 128.62, 126.50, 126.28, 82.97, 46.33, 45.70, 41.06, 37.97, 28.46, 27.98. ESI-HRMS calculated for $C_{17}H_{23}NO_3Na^+$ ([M+Na]$^+$): 312.1570; Found: 312.1567.

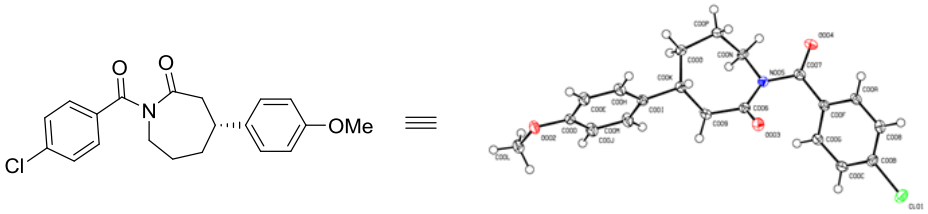
IV. Gram-scale asymmetric hydrogenation of model substrate

In an argon-filled glove box, a solution of $Rh(NBD)_2BF_4$ (6.0 mol%) and ZhaoPhos **L1** (6.6 mol%) in anhydrous CH_2Cl_2 and MeOH (1: 1, V: V) was stirred at room temperature for 2 h at least. 0.51g model substrate **1a** (2.72 mmol) was transferred into the resulting complex to make the concentration 0.4 M, and stirred at the same temperature for another 5 min, and then was transferred into autoclave. 50 atm of H_2 was charged and stirred at room temperature for 48 h. The hydrogen gas was released carefully and the solution was concentrated and purified through a short celite column on silica gel to remove the metal complex. The product was analyzed by ^{1}H NMR spectra for conversion-determination and purification by flash column chromatography using PE/EA (V: V = 1: 5) to provide desired hydrogenation product **2a** (97%

conversion, 95% yield), which was further analyzed by chiral HPLC for ee values determination (92% ee).

V. Transformation for hydrogenation product 2f

(*R*)-1-(4-chlorobenzoyl)-4-(4-methoxyphenyl)azepan-2-one **3**



The title compound was synthesized *via* following procedures: *n*-BuLi (1.1 equiv., 2.4 M in hexane, 0.11 mL, 0.275 mmol) was added dropwise to the THF (1.0 mL) solution of desired product **2f** (1.0 equiv., 54.8 mg, 0.25 mmol) at -78 ^{o}C over 5 min. The resulting mixture was stirred at this temperature for 1 h, after which, the corresponding 4-chlorobenzoyl chloride (1.1 equiv., 0.275 mmol, 48.1 mg) was added in one portion. And the resulting reaction mixture was warmed to ambient temperature and stirred for overnight. After concentrating in *vacuo*, the resulting precipitate was directly subjected to flash column chromatography on silica gel using petroleum/ethyl acetate (V: V = 5: 1) to provide the desired corresponding product **3**. The enantiomeric excess was determined by chiral HPLC, and absolute configuration was determined as (*R*) by X-ray crystallography; 70% isolated yield; 63.0 mg; 86% ee; $[\alpha]_D^{20}$ = -2.54 (c = 1.18, $CHCl_3$); M. P. 123-125 ^{o}C. The enantiomeric excess was determined by chiral HPLC on chiralpak AD-H column, hexane/isopropanol = 90:10; flow rate = 1.0 ml/min; UV detection at 254 nm; t_R = 26.9 min (minor), t_R = 31.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.45 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.52 (dd, *J* = 4.0, 12.0 Hz, 1H), 3.80 (s, 3H), 3.58 (dd, *J* = 8.0, 12.0 Hz, 1H), 3.21-3.15 (m, 1H), 3.02-2.96 (m, 1H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.22-2.12 (m, 2H), 1.92-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 175.89, 173.08, 158.24, 137.74, 137.59, 134.80, 129.24, 128.43, 127.30, 114.07, 55.25,

45.75, 45.00, 40.29, 38.07, 28.69. ESI-HRMS calculated for $C_{20}H_{20}ClNO_3Na^+$ ($[M+Na]^+$): 380.1024; Found: 380.1025.

VI. Reference

[1] M. Zhou, T.-L. Liu, M. Cao, X. Zhang. *Org. Lett*. 2014, **16**, 3484.

[2] N. J. A. Martin, B. List, *J. Am. Chem. Soc.* 2006, **128**, 13368.

[3] W. P. Hong, A. V. Iosub and S. S. Stahl, *J. Am. Chem. Soc.* 2013, **135**, 13664.

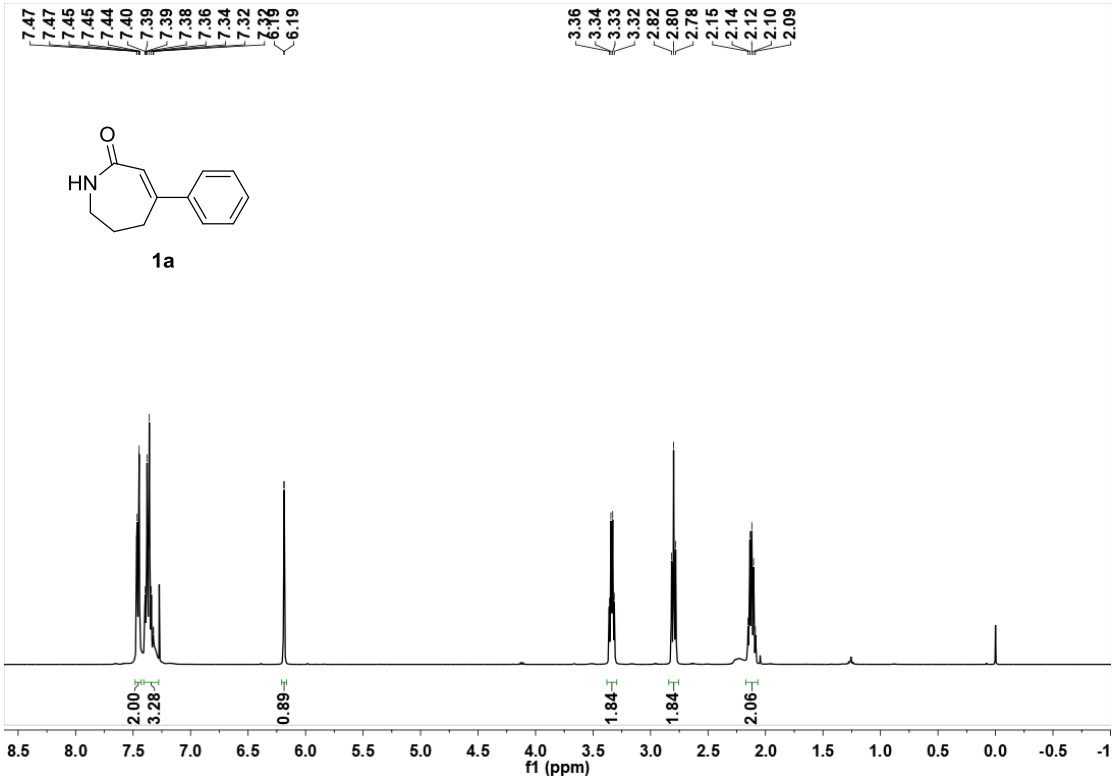
[4] J. W. Lyga, *J. Heterocyclic Chem.* 1996, **33**, 1631.

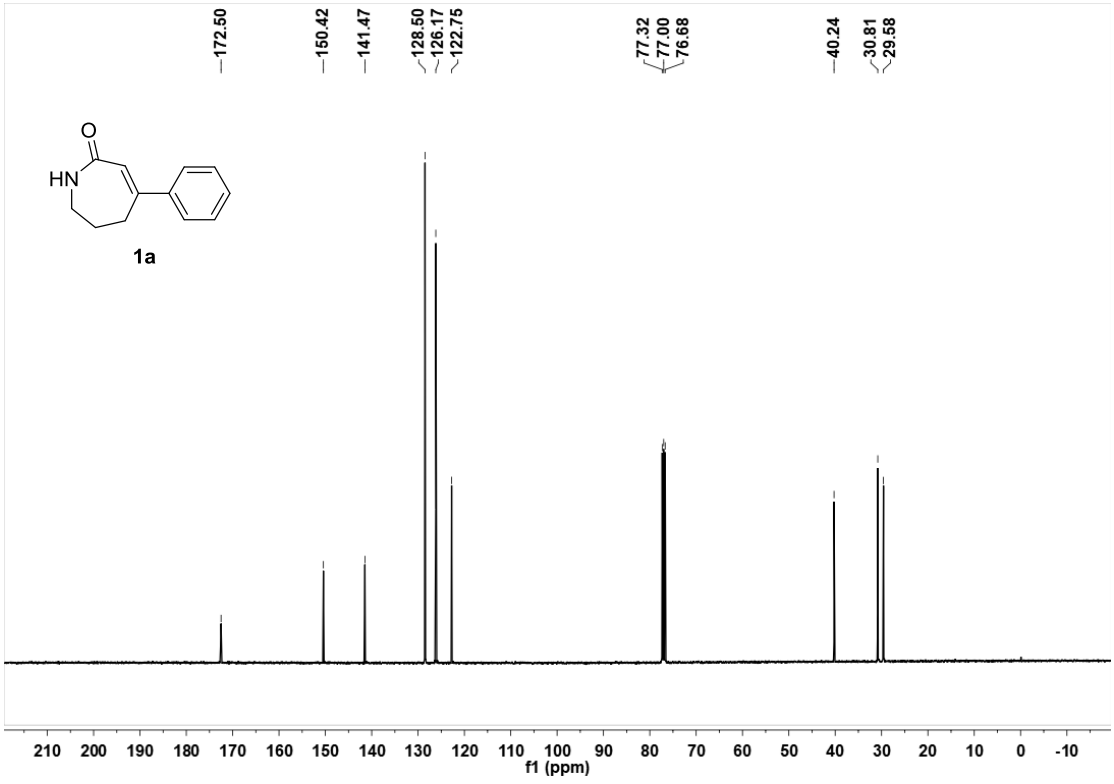
[5] J. Zhao, J. L. Brosmer, Q. Tang, Z. Yang, K. N. Houk, P. L. Diaconescu, O. Kwon. *J. Am. Chem. Soc*. 2017, **139**, 9807.

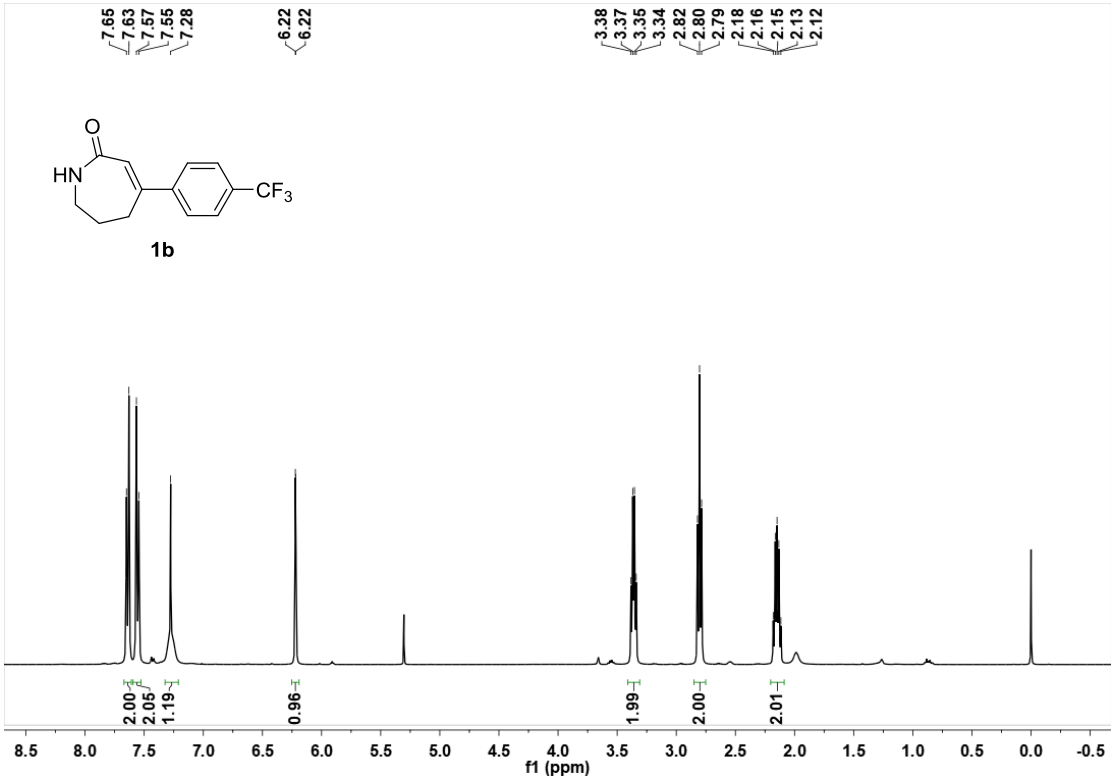
[6] X. Liu, Z. Han, Z. Wang, K. Ding. *Angew. Chem. Int. Ed.* 2014, **53**, 1978.

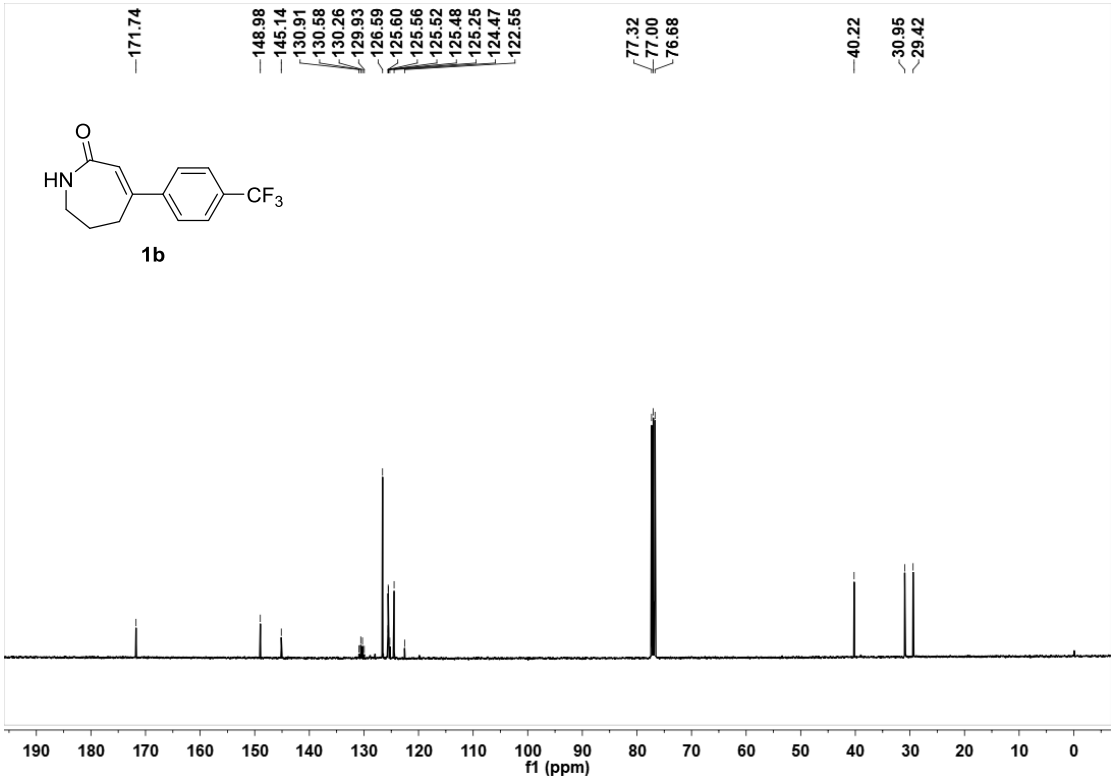
[7] The X-ray crystal data of N-*p*-chlorobenzoyl **2f** derivative compound **3** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1855329. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: +44 (1223)336033 or Email: deposit@ccdc.cam.ac.uk].

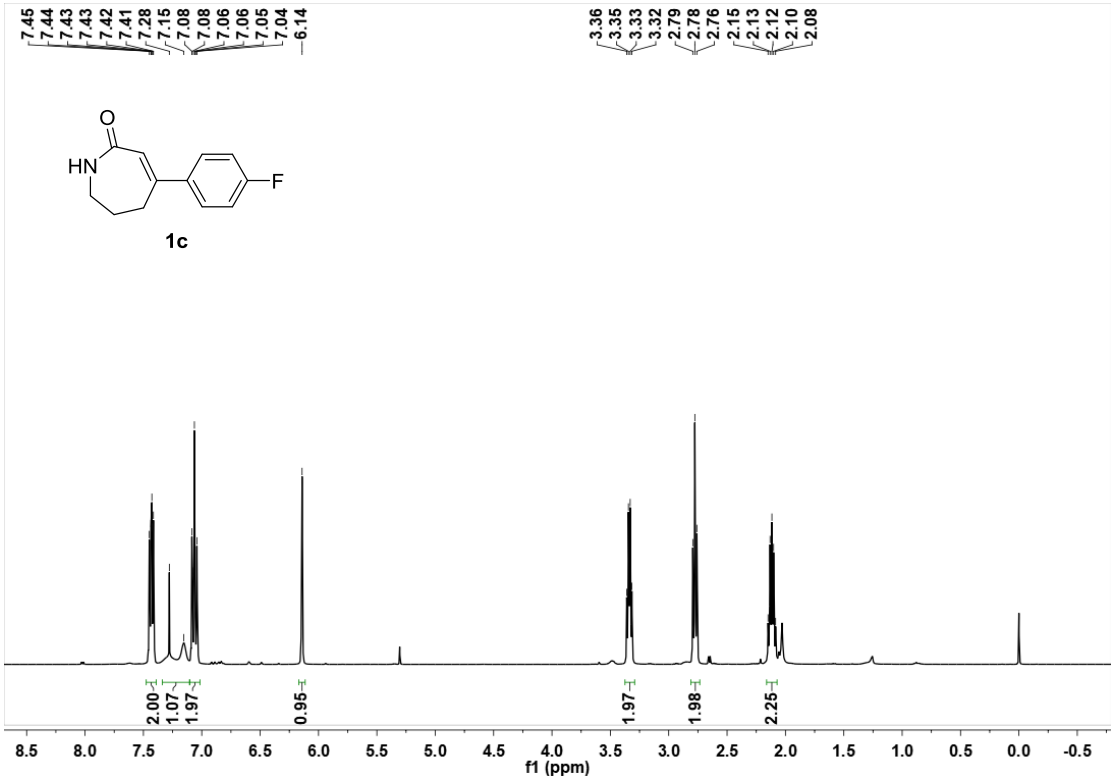
VII. NMR spectra

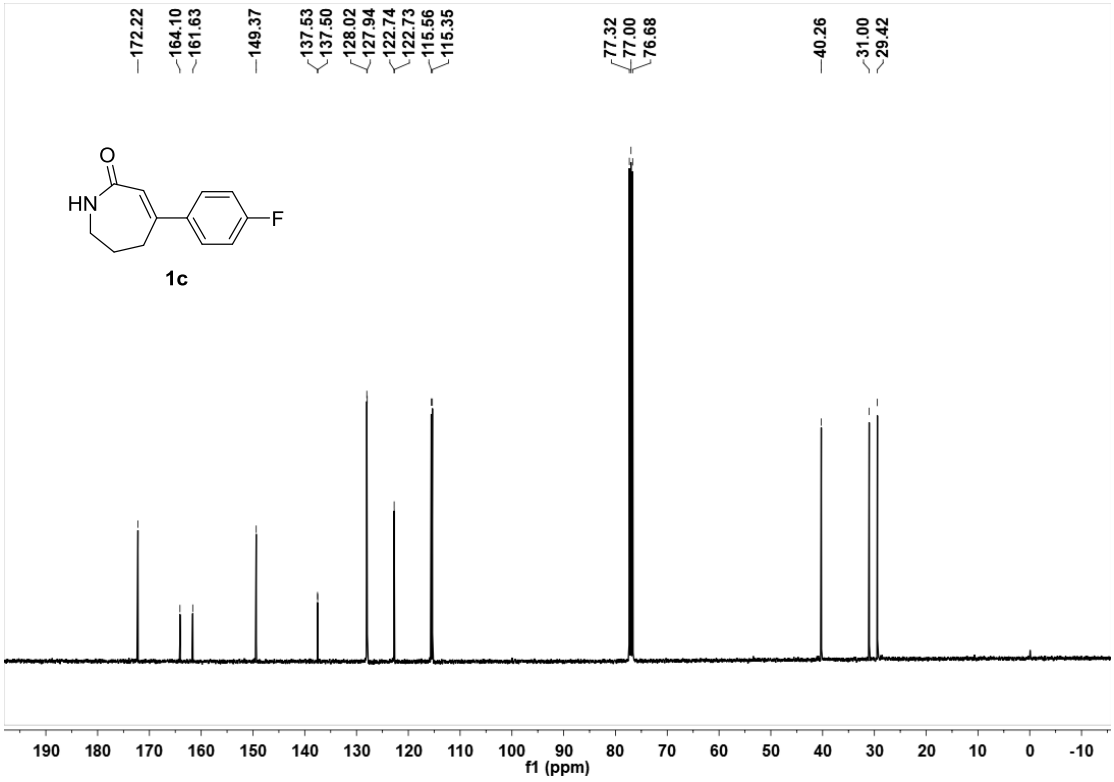


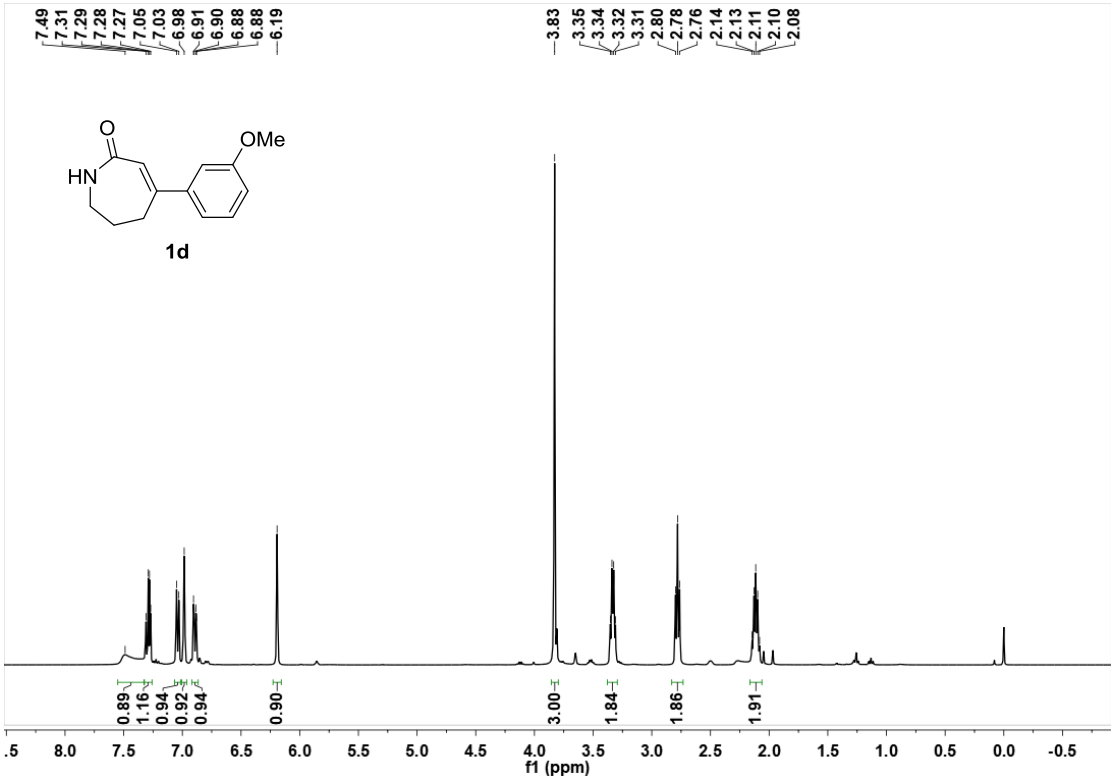


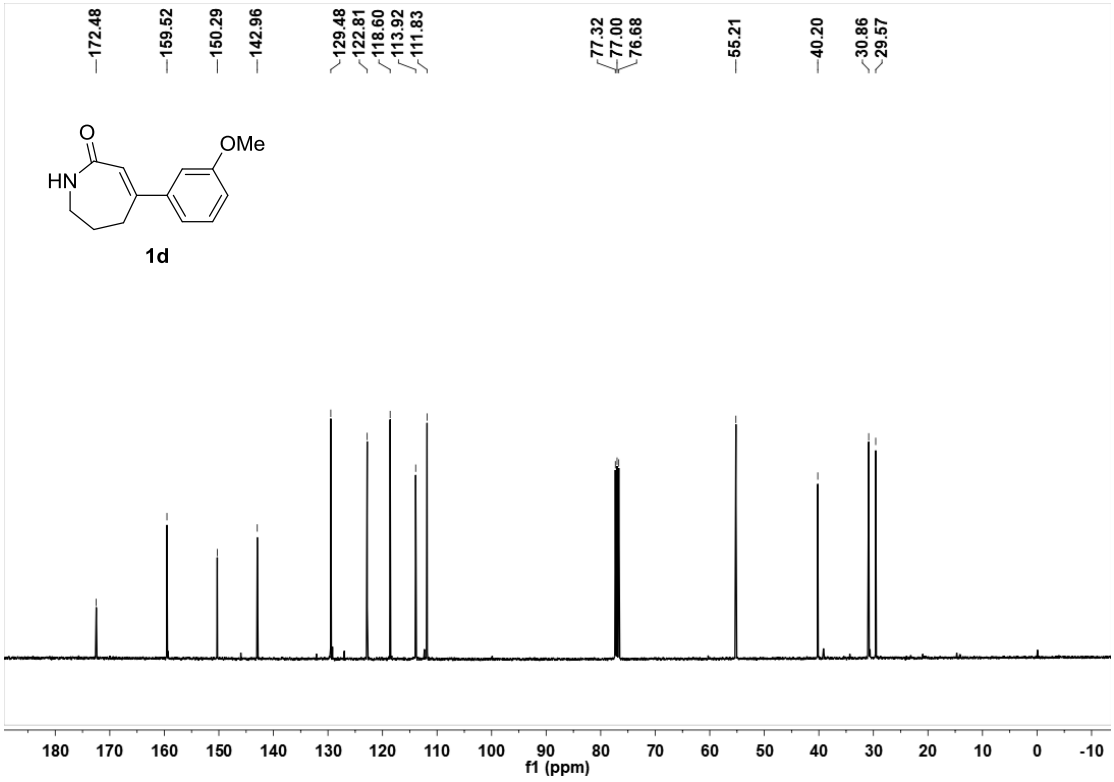

7.65
7.63
7.57
7.55
7.28
6.22
6.22
3.38
3.37
3.35
3.34
2.82
2.80
2.79
2.18
2.16
2.15
2.13
2.12
O
HN
CF3
1b
2.00
2.05
1.19
0.96
1.99
2.00
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

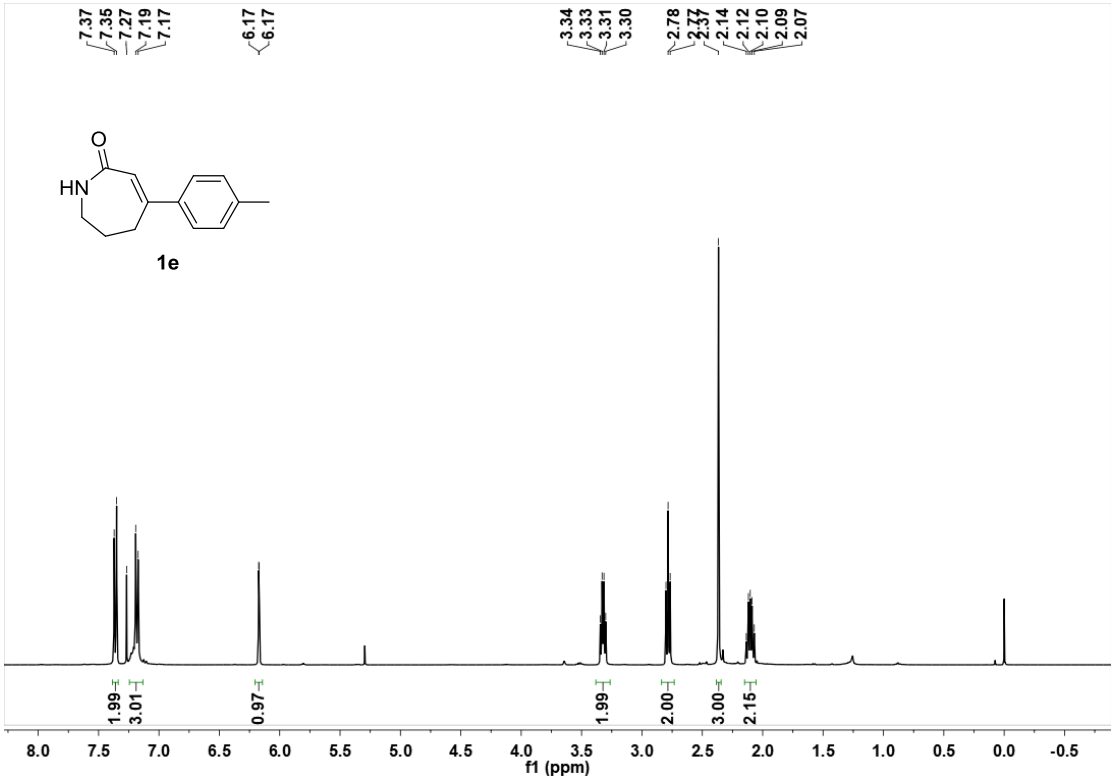

171.74
148.98
145.14
130.91
130.58
130.26
129.93
126.59
125.60
125.56
125.52
125.48
125.25
124.47
122.55
77.32
77.00
76.68
40.22
30.95
29.42
O
HN
CF3
1b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

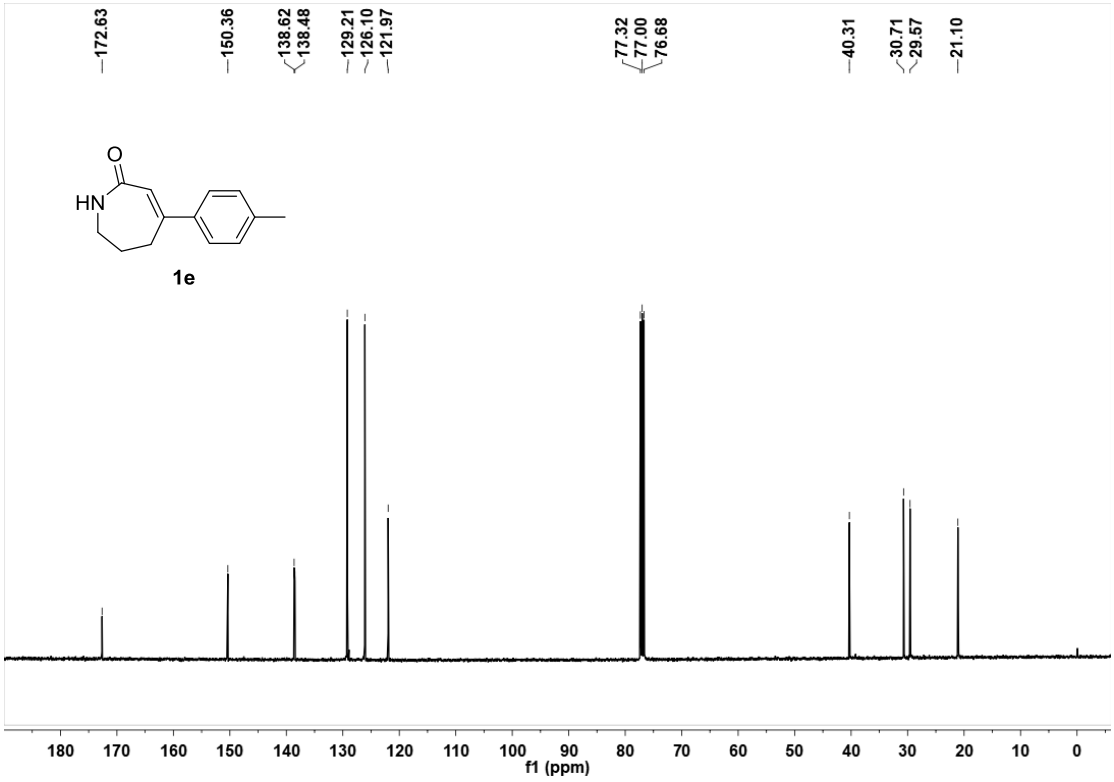

7.45
7.44
7.43
7.43
7.42
7.41
7.28
7.15
7.08
7.08
7.06
7.06
7.05
7.04
6.14
3.36
3.35
3.33
3.32
2.79
2.78
2.76
2.15
2.13
2.12
2.10
2.08
O
HN
F
1c
2.00
1.07
1.97
0.95
1.97
1.98
2.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

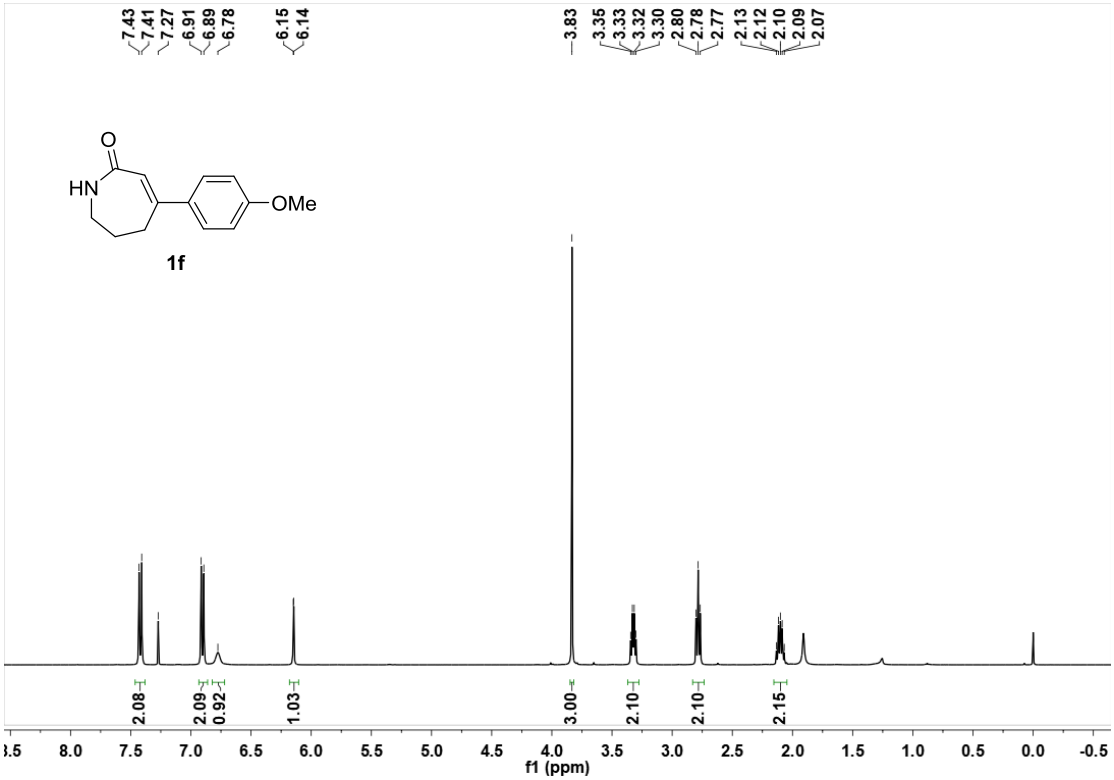

172.22
164.10
161.63
149.37
137.53
137.50
128.02
127.94
122.74
122.73
115.56
115.35
77.32
77.00
76.68
40.26
31.00
29.42
O
HN
F
1c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

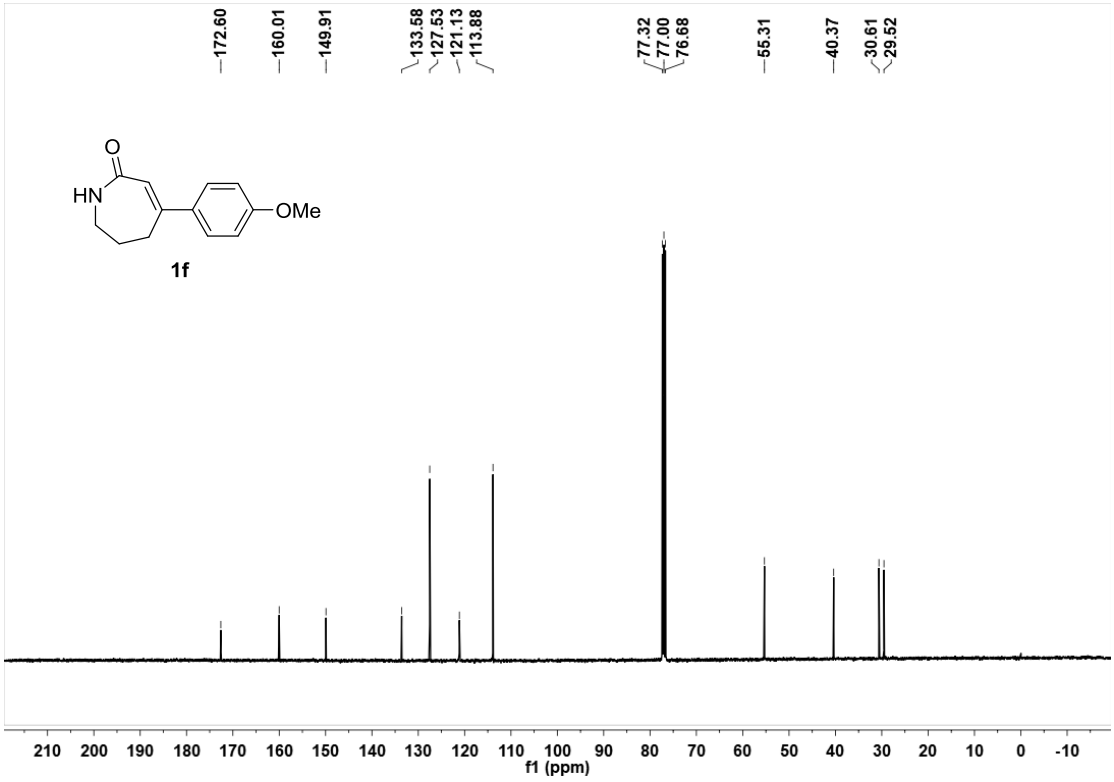

7.49
7.31
7.29
7.28
7.27
7.05
7.03
6.98
6.91
6.90
6.88
6.88
6.19
3.83
3.35
3.34
3.32
3.31
2.80
2.78
2.76
2.14
2.13
2.11
2.10
2.08
O
HN
OMe
1d
0.89
1.16
0.94
0.92
0.94
0.90
3.00
1.84
1.86
1.91
f1 (ppm)

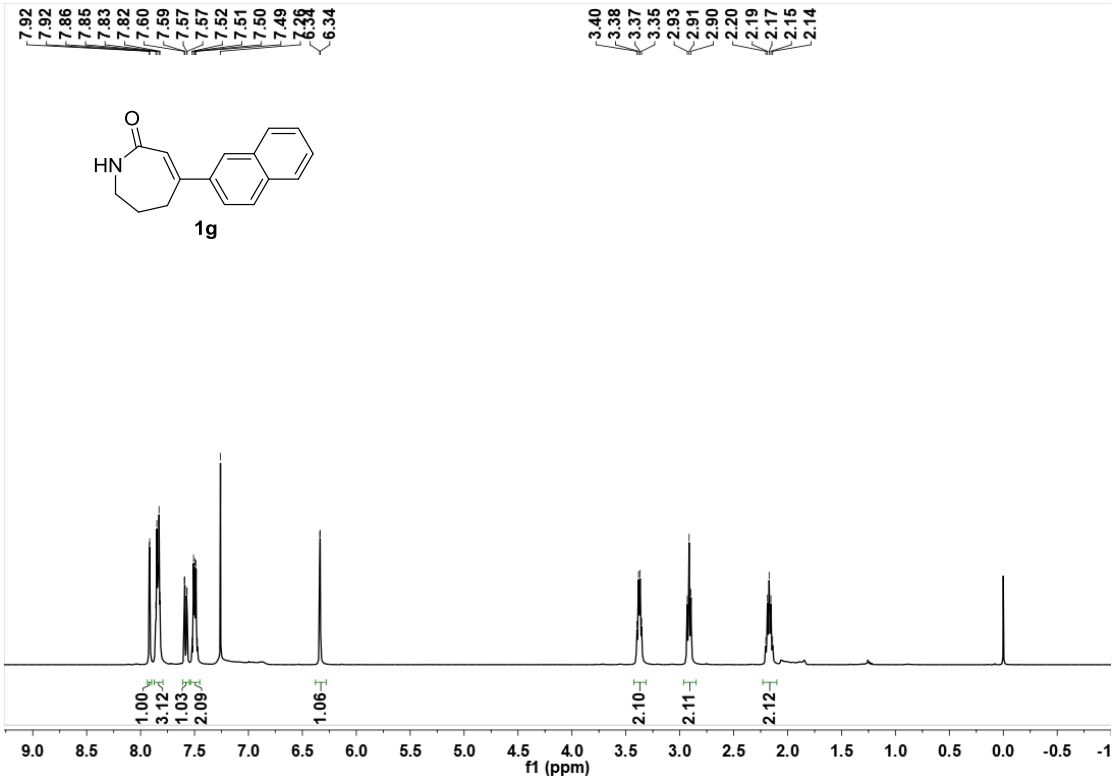

172.48
159.52
150.29
142.96
129.48
122.81
118.60
113.92
111.83
77.32
77.00
76.68
55.21
40.20
30.86
29.57
O
HN
OMe
1d
f1 (ppm)

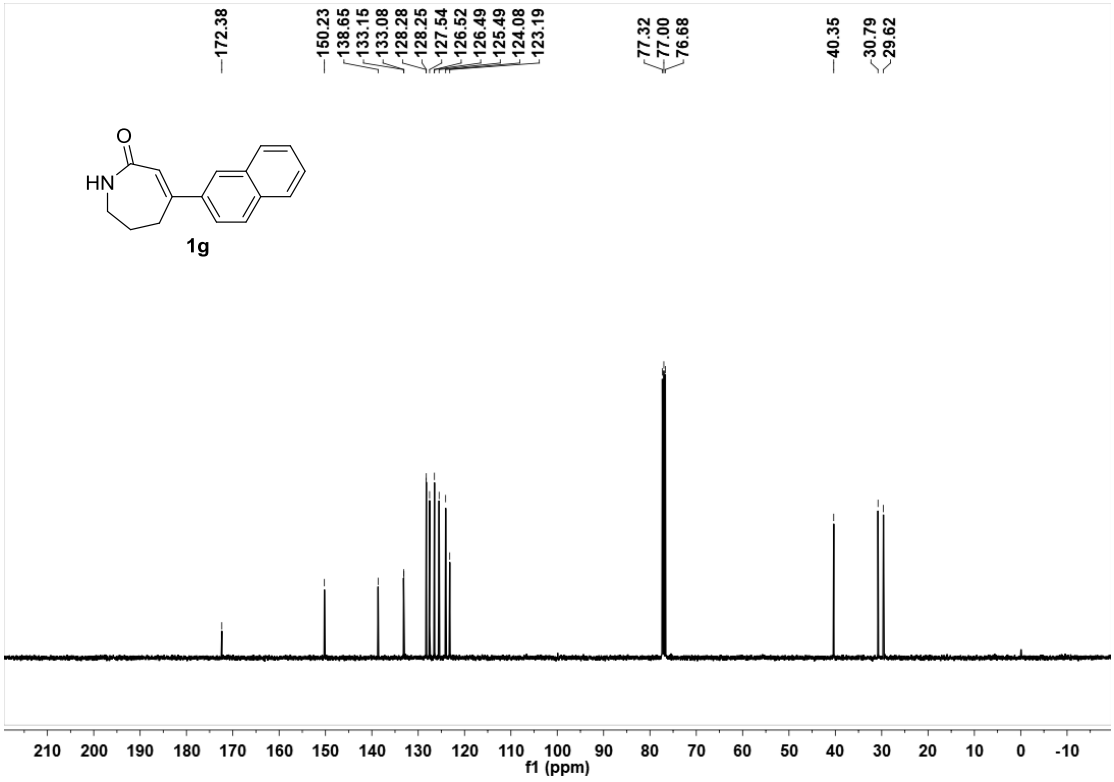

7.37
7.35
7.27
7.19
7.17
6.17
6.17
3.34
3.33
3.31
3.30
2.78
2.37
2.14
2.12
2.10
2.09
2.07
O
HN
1e
1.99
3.01
0.97
1.99
2.00
3.00
2.15
f1 (ppm)

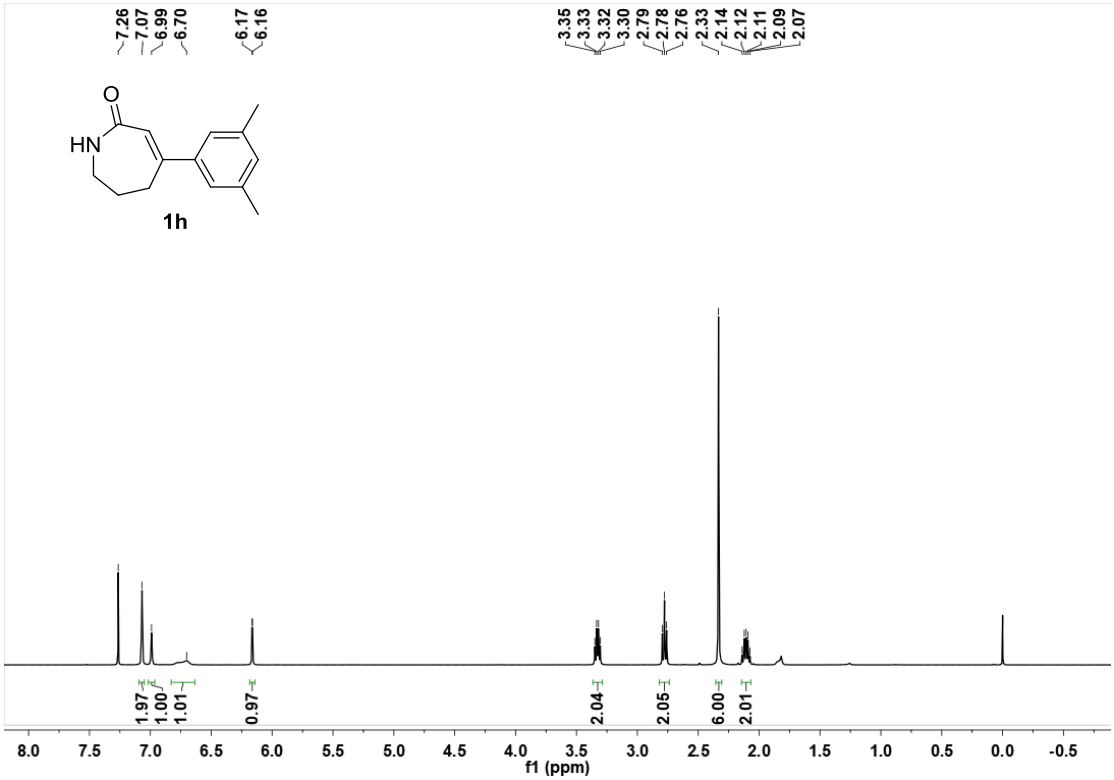

172.63
150.36
138.62
138.48
129.21
126.10
121.97
77.32
77.00
76.68
40.31
30.71
29.57
21.10
O
HN
1e
f1 (ppm)

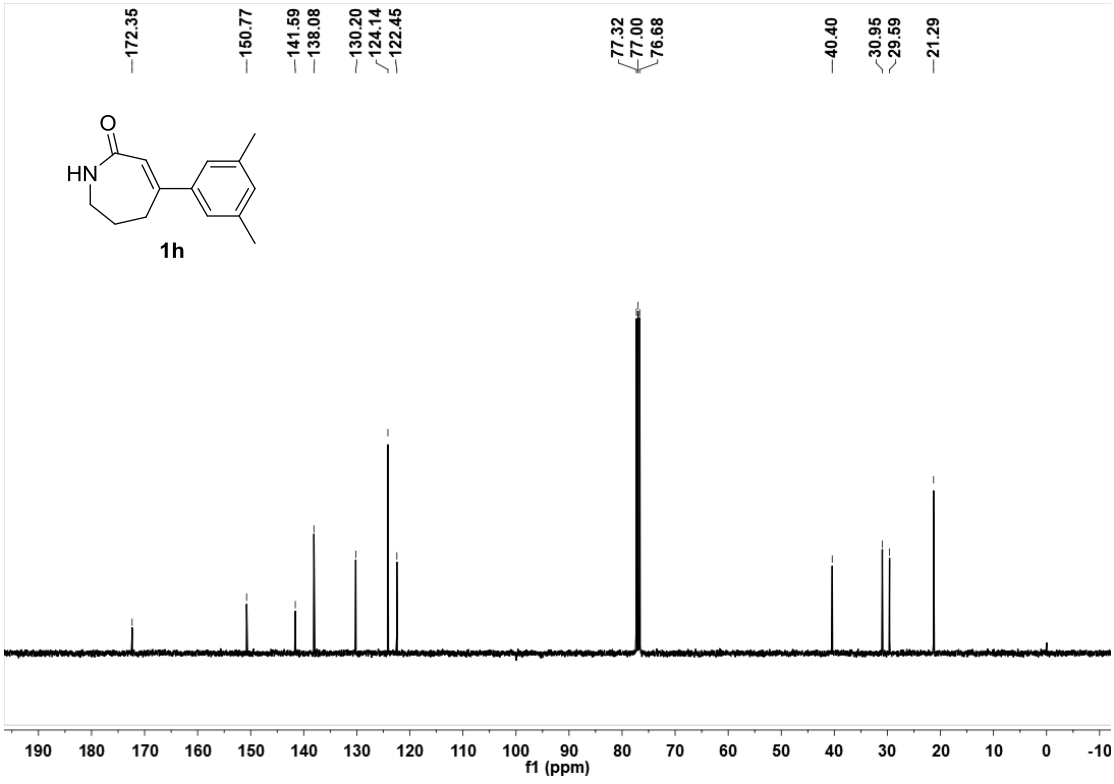

7.43
7.41
7.27
6.91
6.89
6.78
6.15
6.14
3.83
3.35
3.33
3.32
3.30
2.80
2.78
2.77
2.13
2.12
2.10
2.09
2.07
O
HN
OMe
1f
2.08
2.09
0.92
1.03
3.00
2.10
2.10
2.15
f1 (ppm)

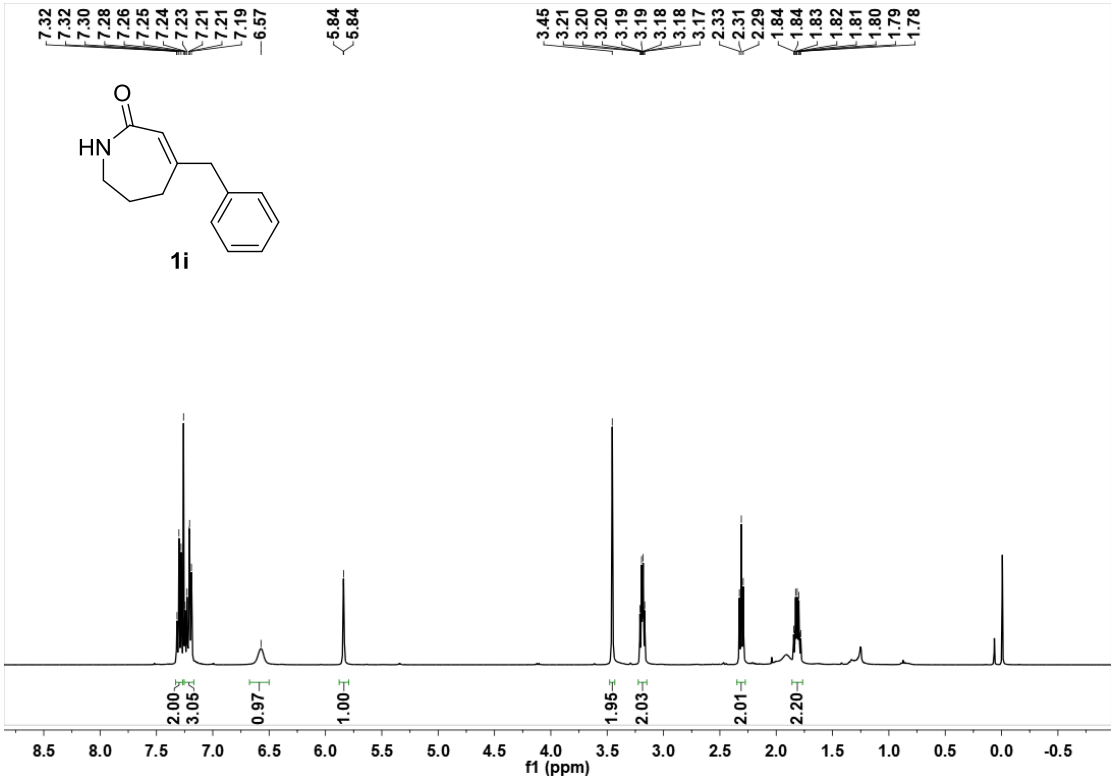

172.60
160.01
149.91
133.58
127.53
121.13
113.88
77.32
77.00
76.68
55.31
40.37
30.61
29.52
O
HN
OMe
1f
f1 (ppm)

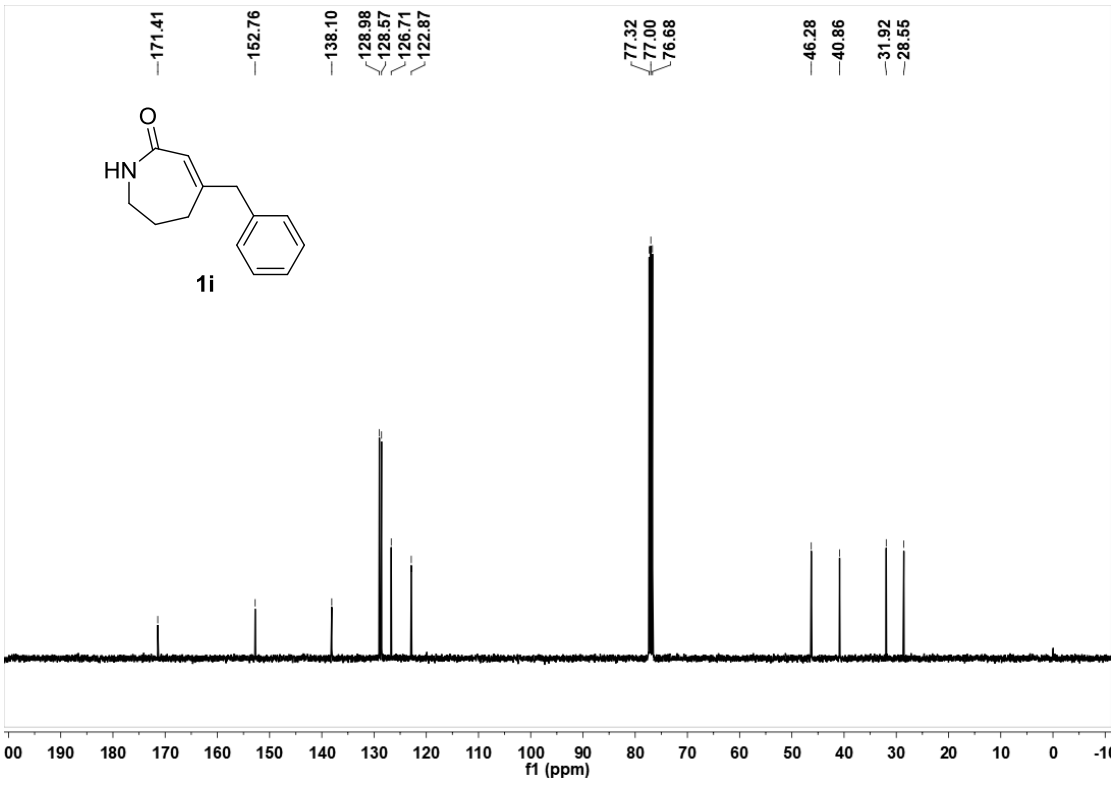

7.92
7.92
7.86
7.85
7.83
7.82
7.60
7.59
7.57
7.57
7.52
7.51
7.50
7.49
6.34
6.34
3.40
3.38
3.37
3.35
2.93
2.91
2.90
2.20
2.19
2.17
2.15
2.14
O
HN
1g
1.00
3.12
1.03
2.09
1.06
2.10
2.11
2.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

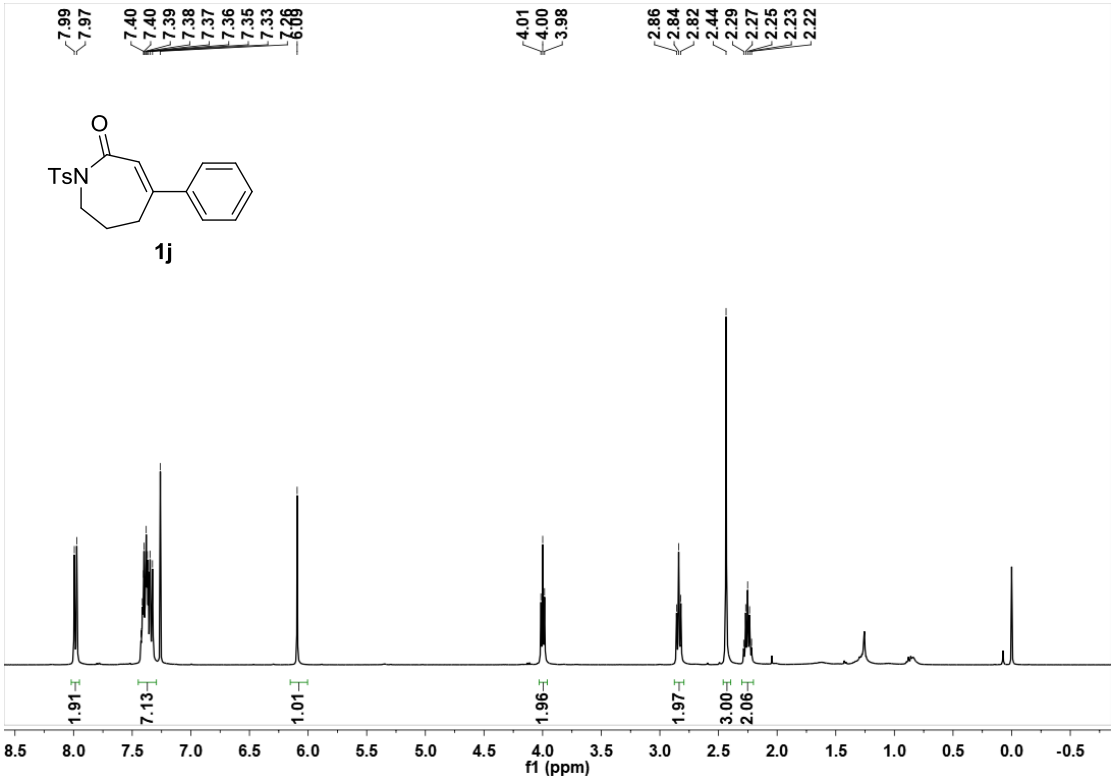

172.38
150.23
138.65
133.15
133.08
128.28
128.25
127.54
126.52
126.49
125.49
124.08
123.19
77.32
77.00
76.68
40.35
30.79
29.62
O
HN
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

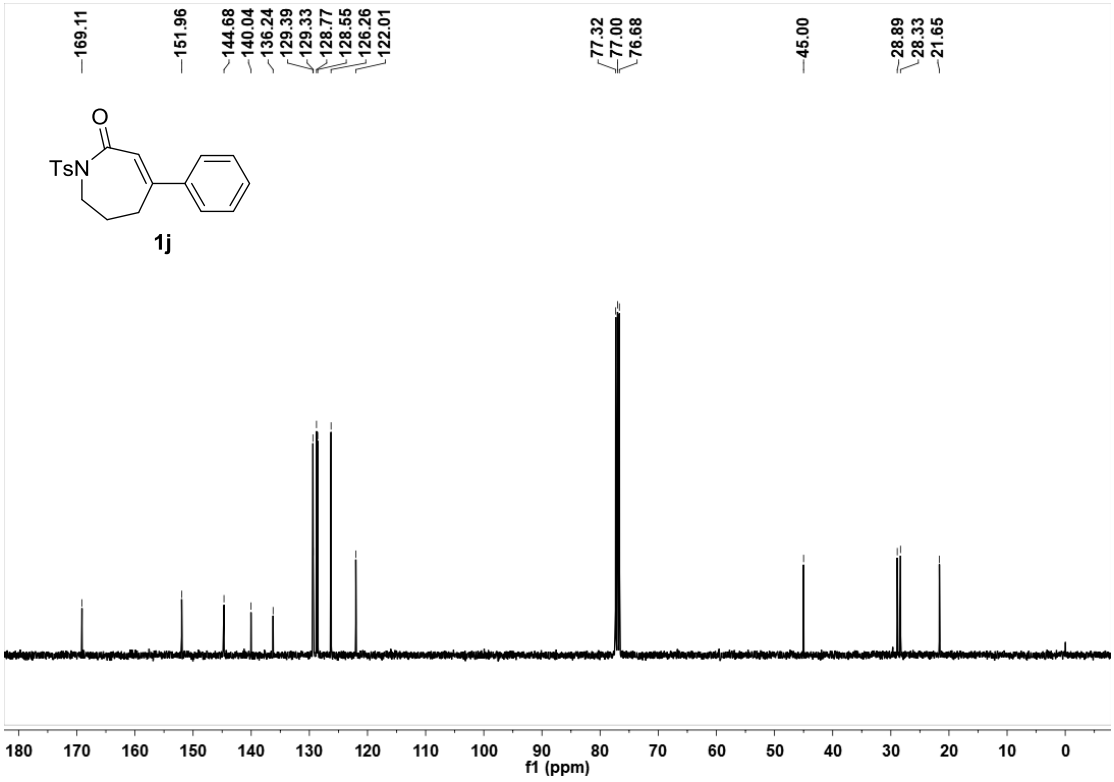

7.26
7.07
6.99
6.70
6.17
6.16
3.35
3.33
3.32
3.30
2.79
2.78
2.76
2.33
2.14
2.12
2.11
2.09
2.07
O
HN
1h
1.97
1.00
1.01
0.97
2.04
2.05
6.00
2.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

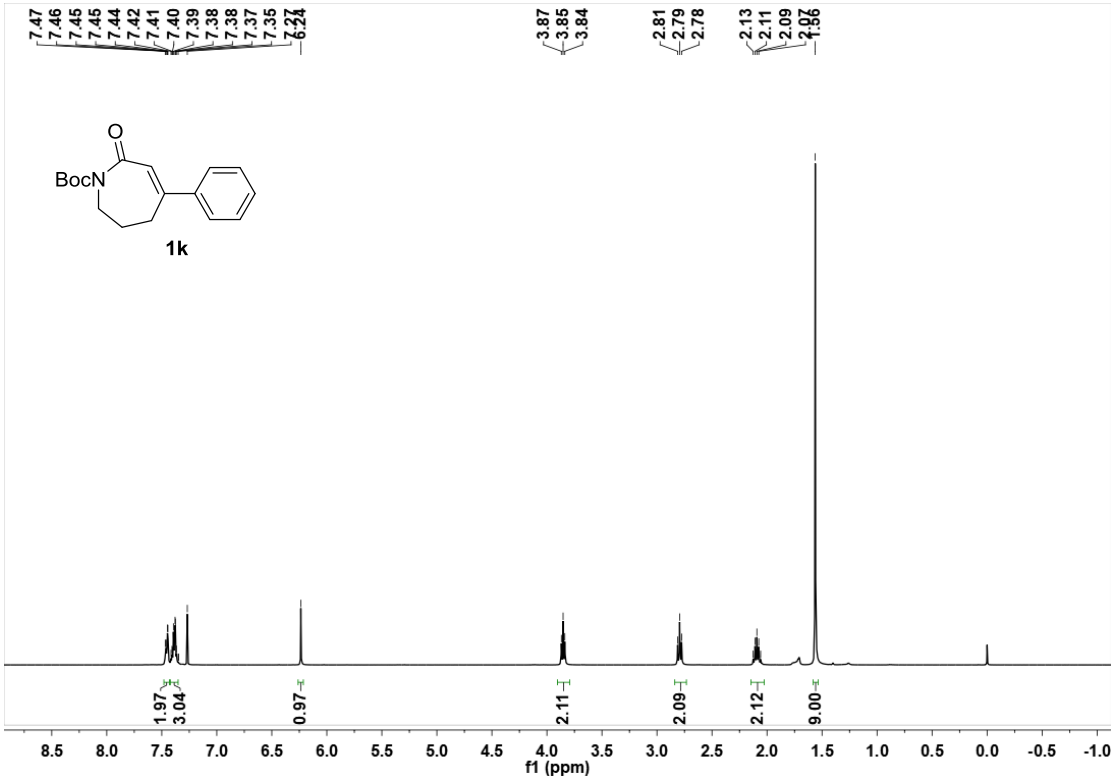

172.35
150.77
141.59
138.08
130.20
124.14
122.45
77.32
77.00
76.68
40.40
30.95
29.59
21.29
O
HN
1h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

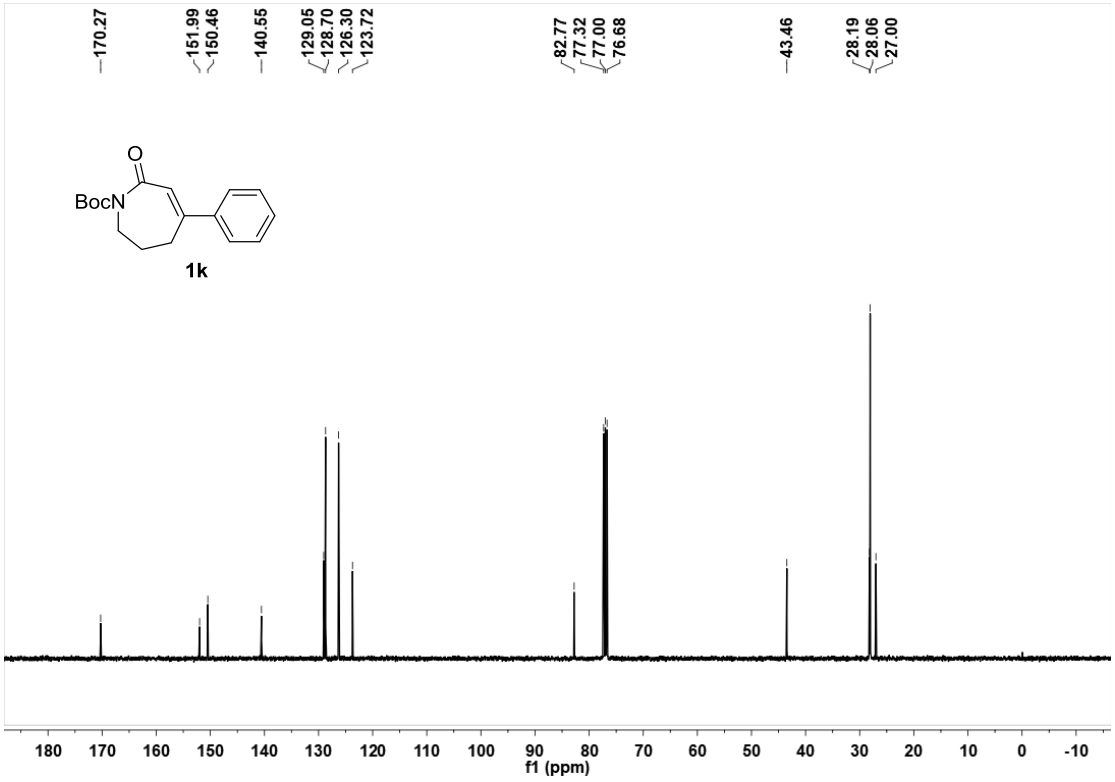

7.32
7.32
7.30
7.28
7.26
7.25
7.24
7.23
7.21
7.21
7.19
6.57
5.84
5.84
3.45
3.21
3.20
3.20
3.19
3.19
3.18
3.18
3.17
2.33
2.31
2.29
1.84
1.84
1.83
1.82
1.81
1.80
1.79
1.78
O
HN
1i
2.00
3.05
0.97
1.00
1.95
2.03
2.01
2.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

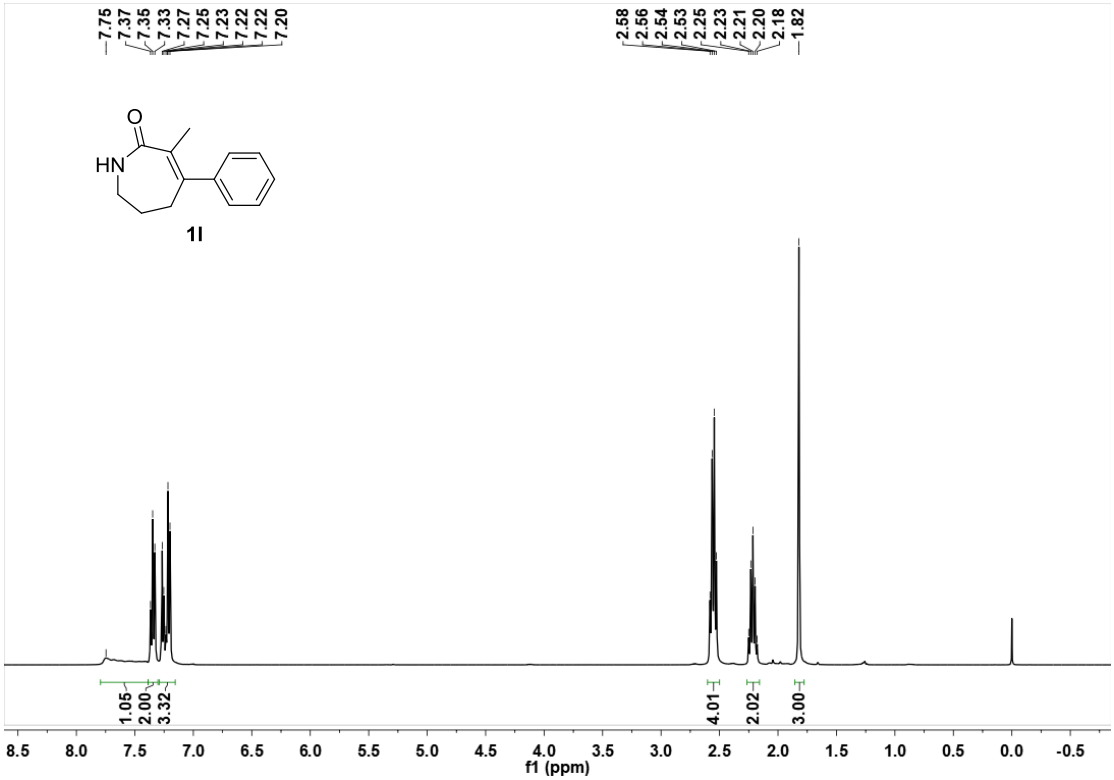

171.41
152.76
138.10
128.98
128.57
126.71
122.87
77.32
77.00
76.68
46.28
40.86
31.92
28.55
O
HN
1i
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

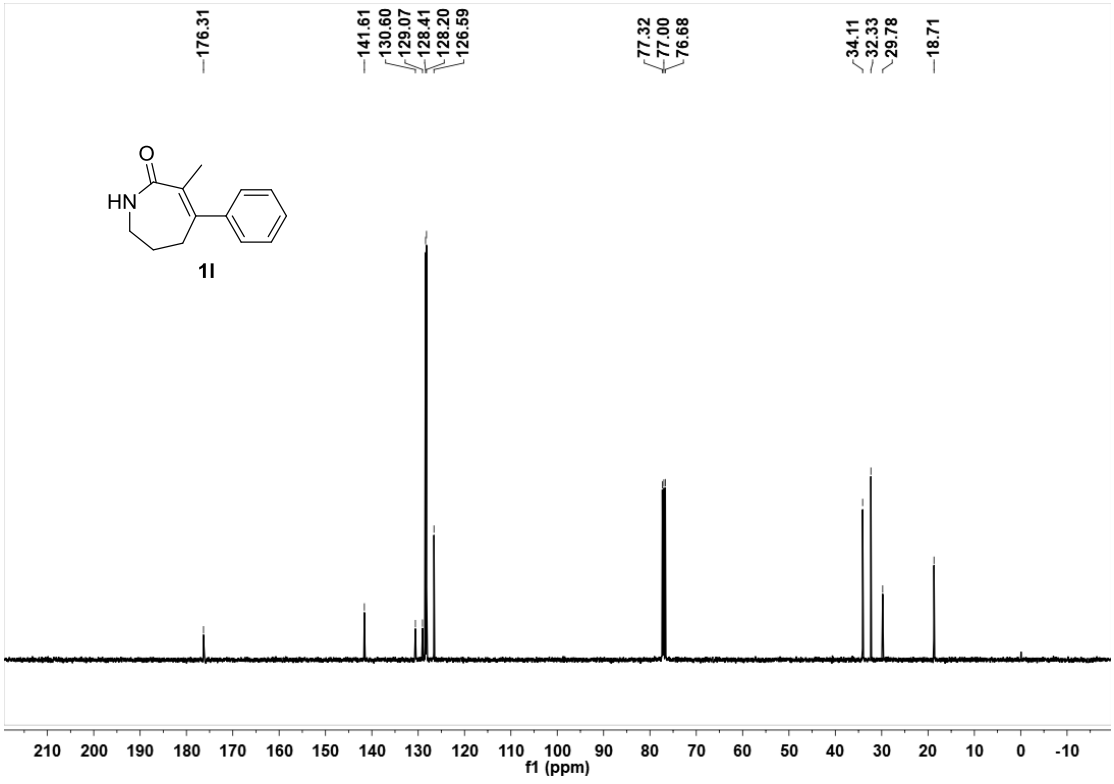

7.99
7.97
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.33
4.01
4.00
3.98
2.86
2.84
2.82
2.44
2.29
2.27
2.25
2.23
2.22
O
TsN
1j
1.91
7.13
1.01
1.96
1.97
3.00
2.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

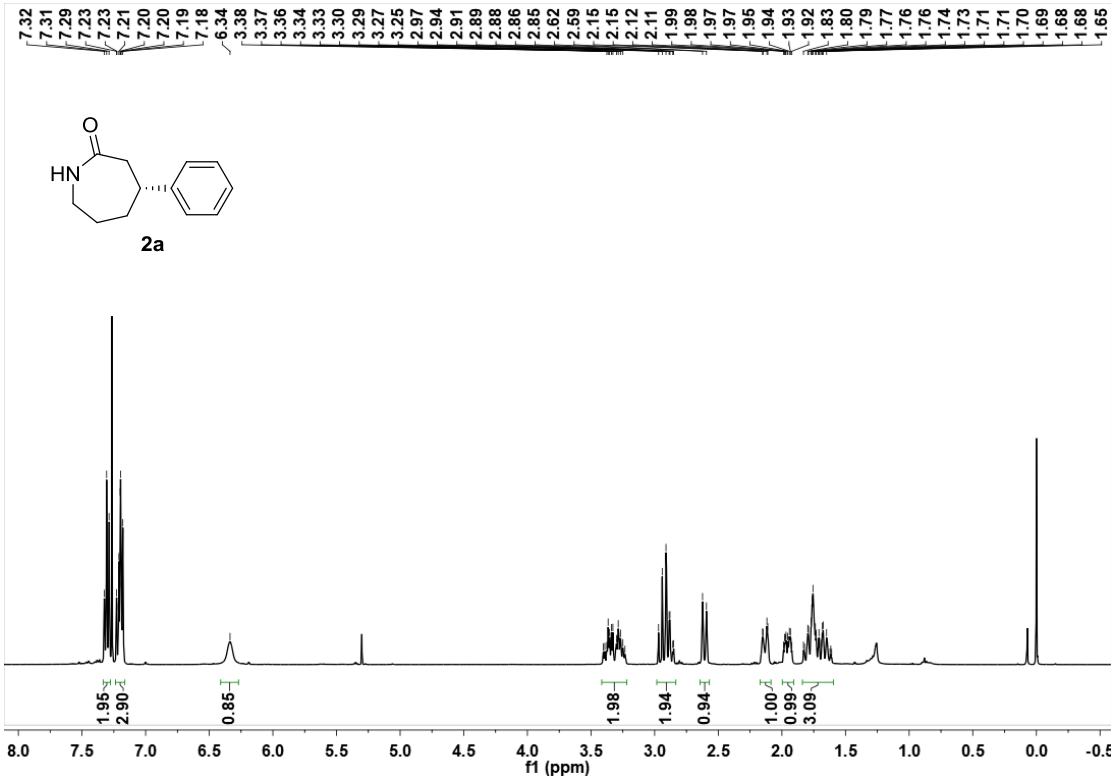

169.11
151.96
144.68
140.04
136.24
129.39
129.33
128.77
128.55
126.26
122.01
77.32
77.00
76.68
45.00
28.89
28.33
21.65
O
TsN
1j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

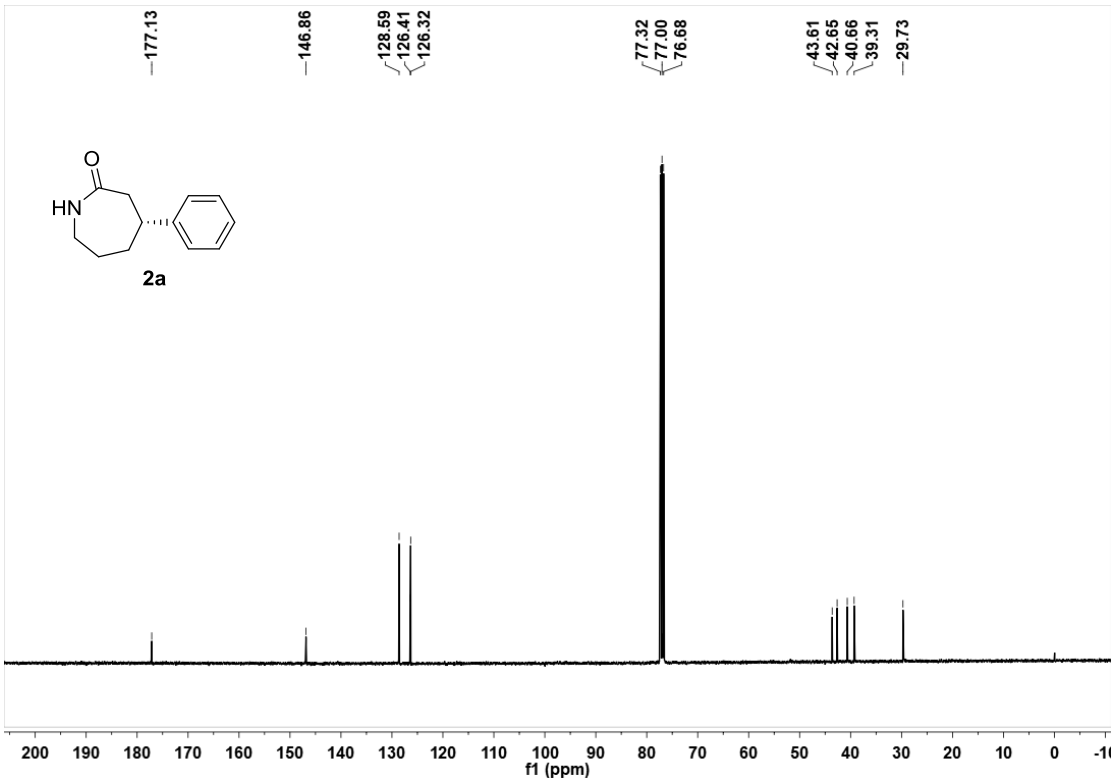

7.47
7.46
7.45
7.45
7.44
7.42
7.41
7.40
7.39
7.38
7.38
7.37
7.35
3.87
3.85
3.84
2.81
2.79
2.78
2.13
2.11
2.09
1.56
O
BocN
1k
1.97
3.04
0.97
2.11
2.09
2.12
9.00
f1 (ppm)

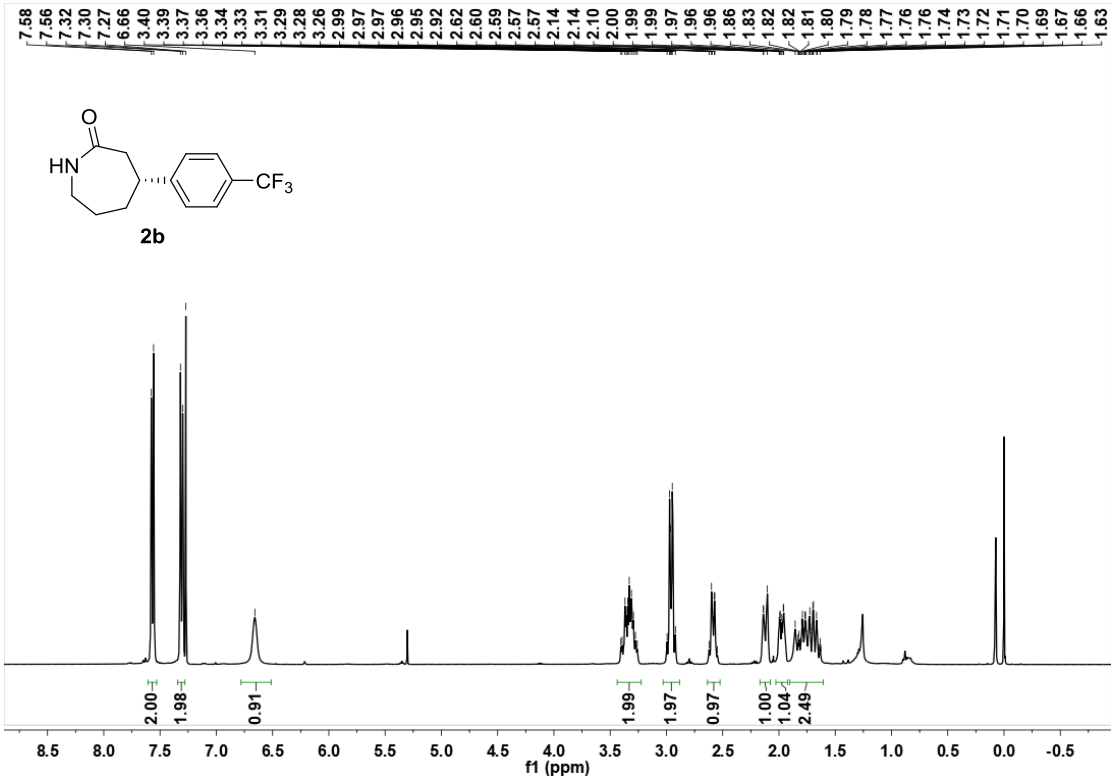

170.27
151.99
150.46
140.55
129.05
128.70
126.30
123.72
82.77
77.32
77.00
76.68
43.46
28.19
28.06
27.00
O
BocN
1k
f1 (ppm)

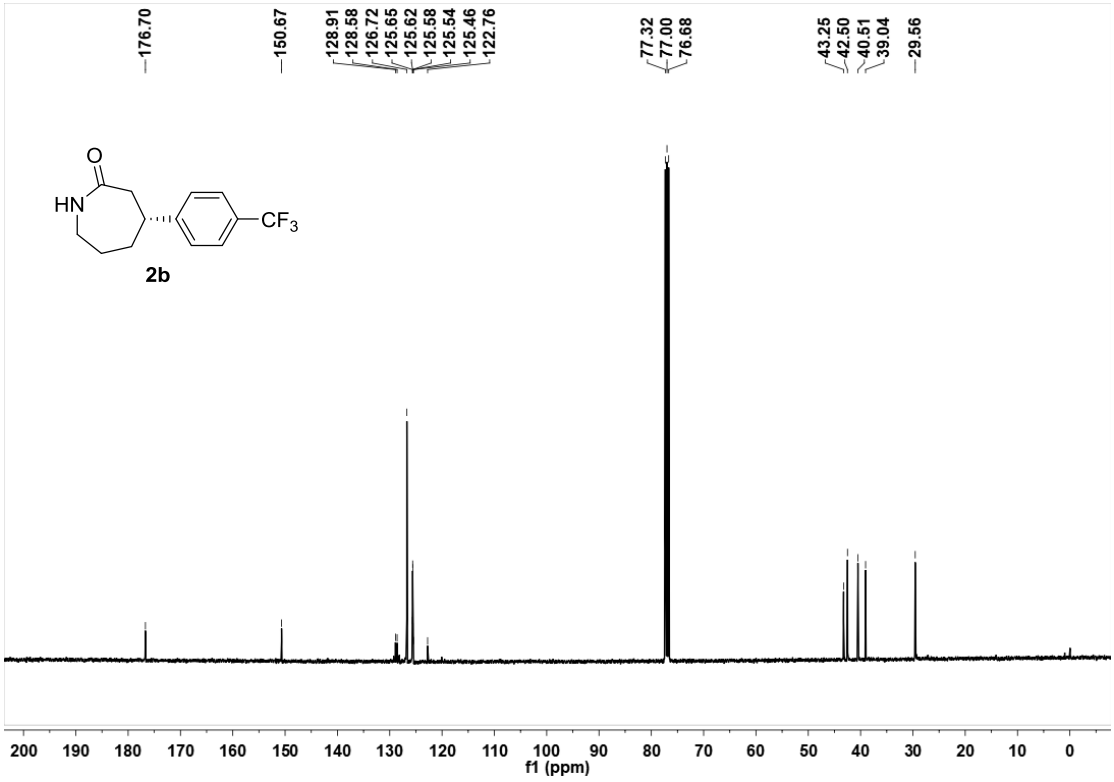

7.75
7.37
7.35
7.33
7.27
7.25
7.23
7.22
7.22
7.20
2.58
2.56
2.54
2.53
2.25
2.23
2.21
2.20
2.18
1.82
O
HN
1l
1.05
2.00
3.32
4.01
2.02
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

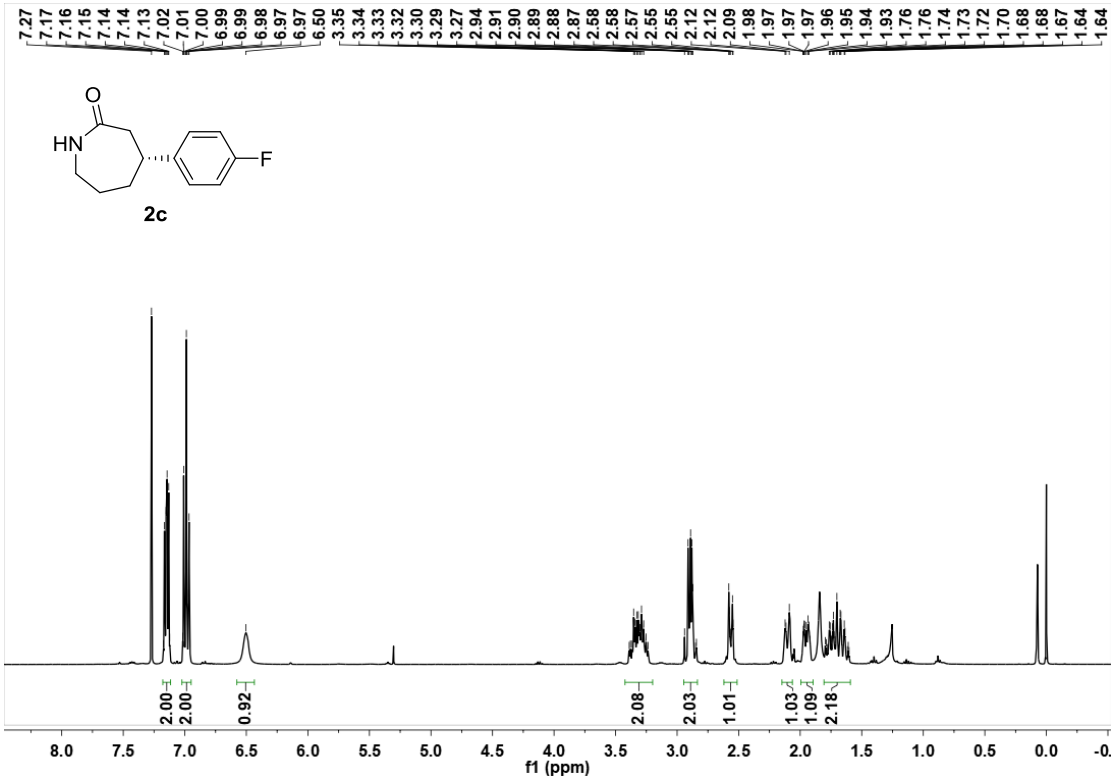

176.31
141.61
130.60
129.07
128.41
128.20
126.59
77.32
77.00
76.68
34.11
32.33
29.78
18.71
O
HN
1l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

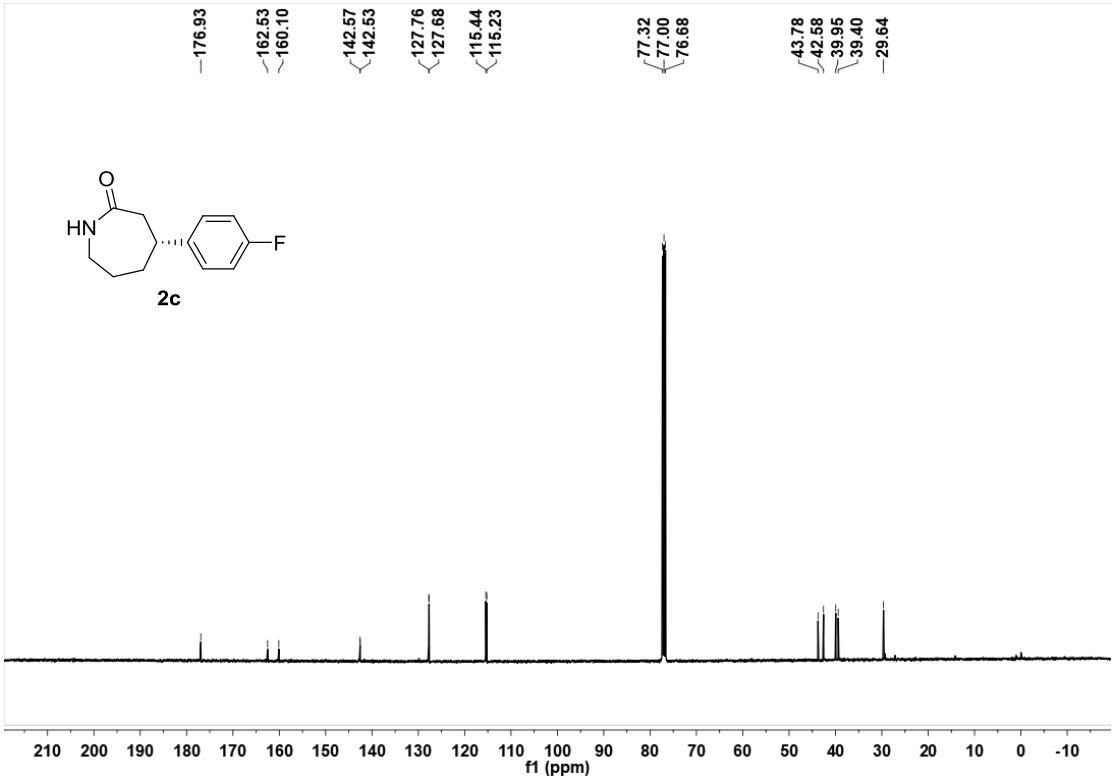

7.32 7.31 7.29 7.23 7.23 7.21 7.20 7.20 7.19 7.18 6.34 3.38 3.37 3.36 3.34 3.33 3.30 3.29 3.27 3.25 2.97 2.94 2.91 2.89 2.88 2.86 2.85 2.62 2.59 2.15 2.15 2.12 2.11 1.99 1.98 1.97 1.97 1.95 1.94 1.93 1.92 1.83 1.80 1.79 1.77 1.76 1.76 1.74 1.73 1.71 1.71 1.70 1.69 1.68 1.68 1.65
HN
O
2a
1.95 2.90 0.85 1.98 1.94 0.94 1.00 0.99 3.09
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
f1 (ppm)

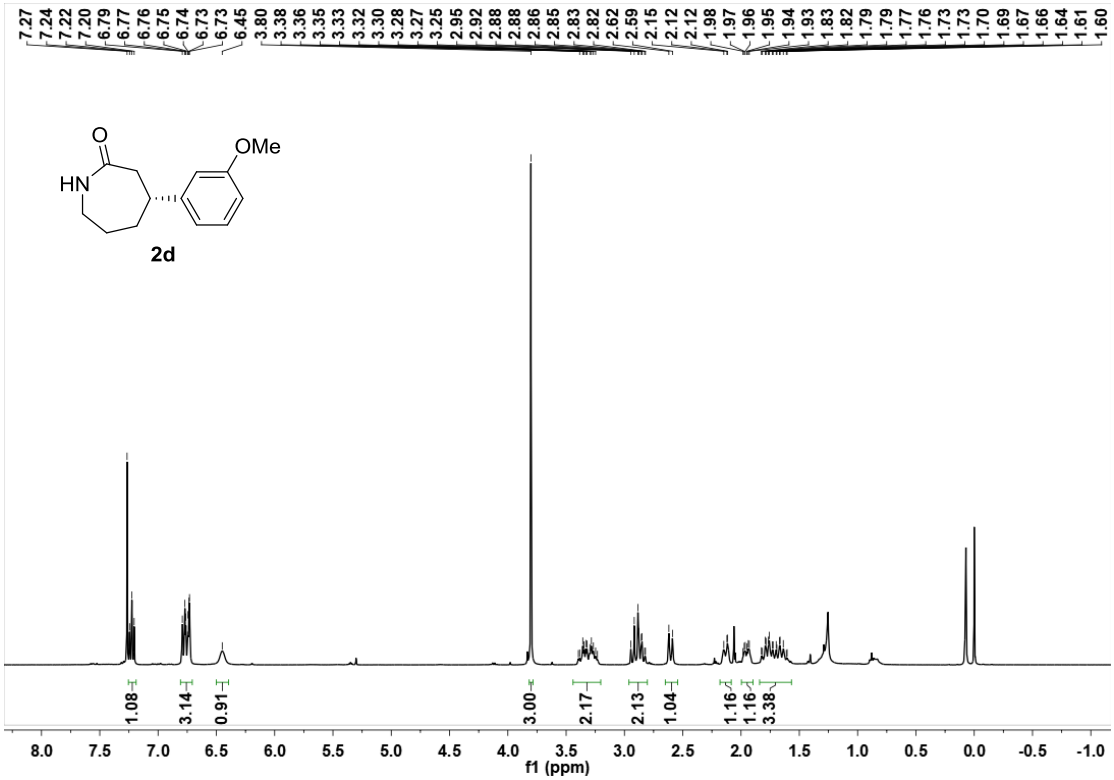

177.13 146.86 128.59 126.41 126.32 77.32 77.00 76.68 43.61 42.65 40.66 39.31 29.73
HN
O
2a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

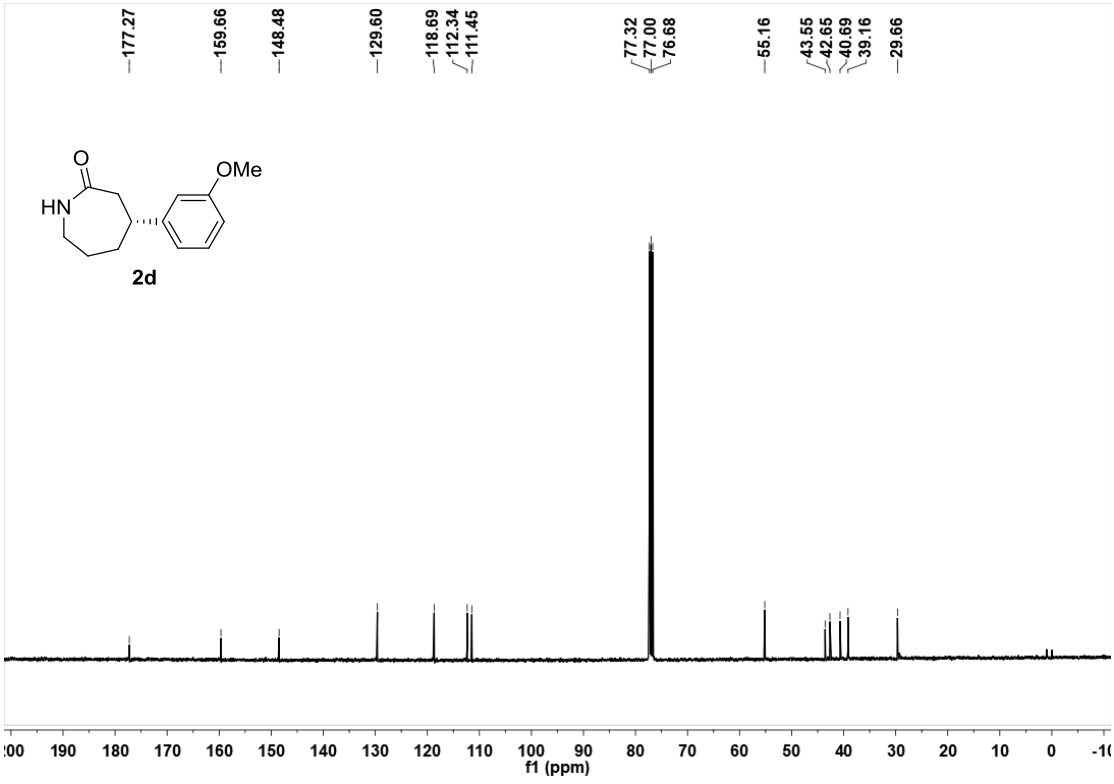

7.58 7.56 7.32 7.30 7.27 6.66 3.40 3.39 3.37 3.36 3.34 3.33 3.31 3.29 3.28 3.26 2.99 2.97 2.97 2.96 2.95 2.92 2.62 2.60 2.59 2.57 2.57 2.14 2.14 2.10 2.00 1.99 1.99 1.97 1.96 1.96 1.86 1.83 1.82 1.82 1.81 1.80 1.79 1.78 1.77 1.76 1.76 1.74 1.73 1.72 1.71 1.70 1.69 1.67 1.66 1.63
HN
O
CF3
2b
2.00 1.98 0.91 1.99 1.97 0.97 1.00 1.04 2.49
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 -0.5
f1 (ppm)

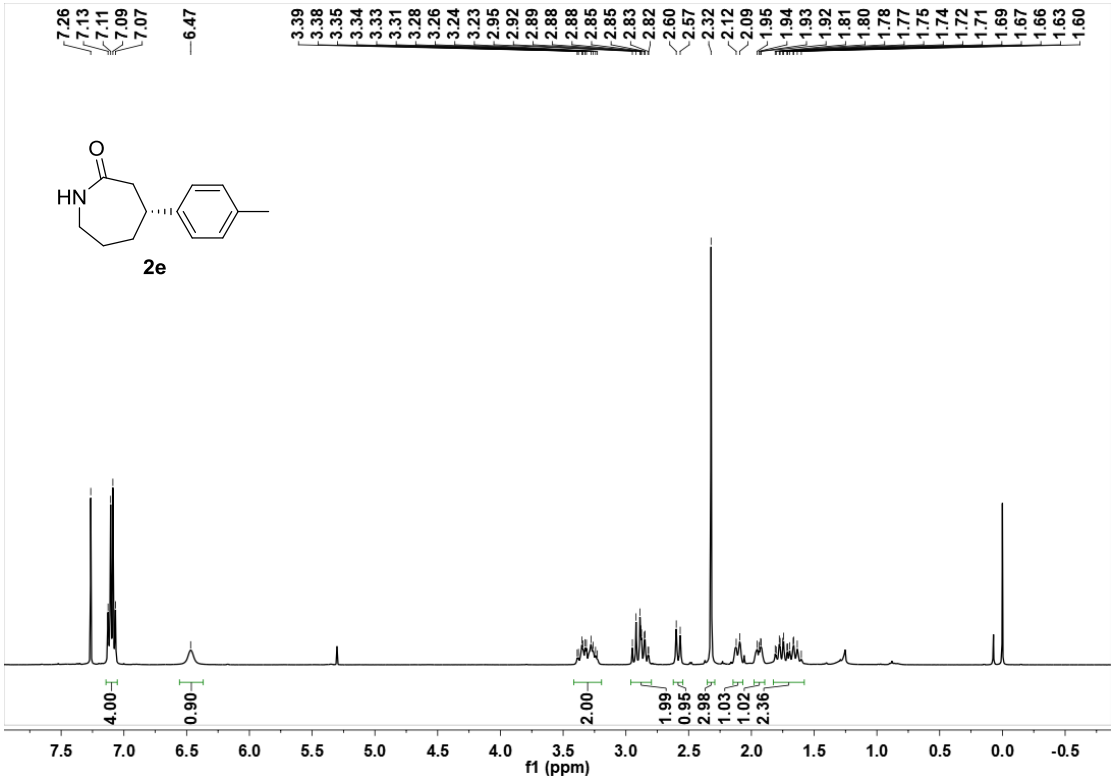

176.70 150.67 128.91 128.58 126.72 125.65 125.62 125.58 125.54 125.46 122.76 77.32 77.00 76.68 43.25 42.50 40.51 39.04 29.56
HN
O
CF3
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

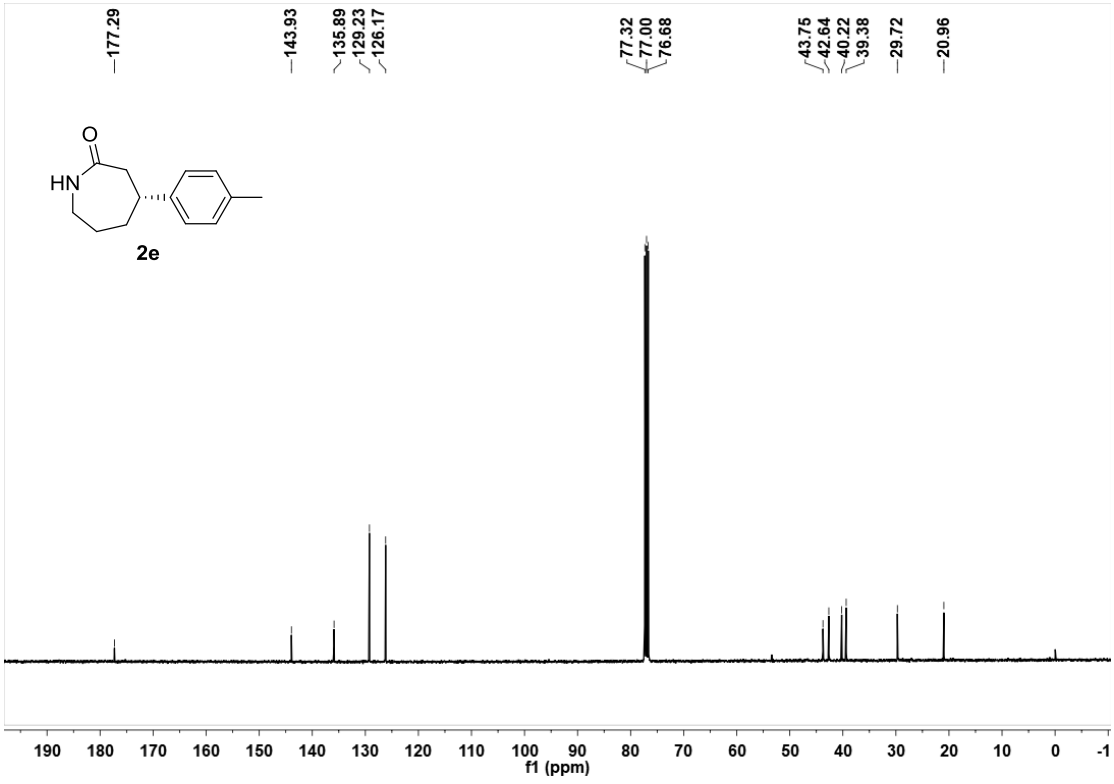

7.27 7.17 7.16 7.15 7.14 7.14 7.13 7.02 7.01 7.00 6.99 6.99 6.98 6.97 6.97 6.50
3.35 3.34 3.33 3.32 3.30 3.29 3.27 2.94 2.91 2.90 2.89 2.88 2.87 2.58 2.58 2.57 2.55 2.55 2.12 2.12 2.09 1.98 1.97 1.97 1.97 1.96 1.95 1.94 1.93 1.76 1.76 1.74 1.73 1.72 1.70 1.68 1.68 1.67 1.64 1.64
O
HN
F
2c
2.00 2.00 0.92 2.08 2.03 1.01 1.03 1.09 2.18
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
f1 (ppm)

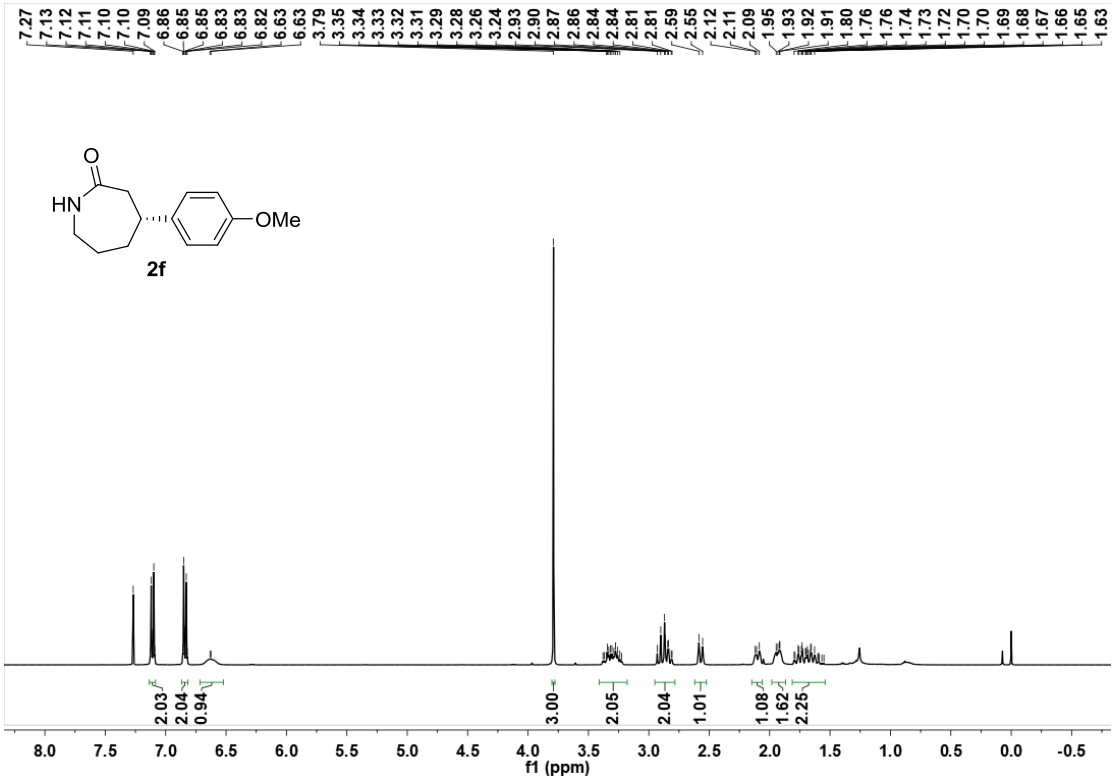

176.93
162.53 160.10
142.57 142.53
127.76 127.68
115.44 115.23
77.32 77.00 76.68
43.78 42.58 39.95 39.40
29.64
O
HN
F
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

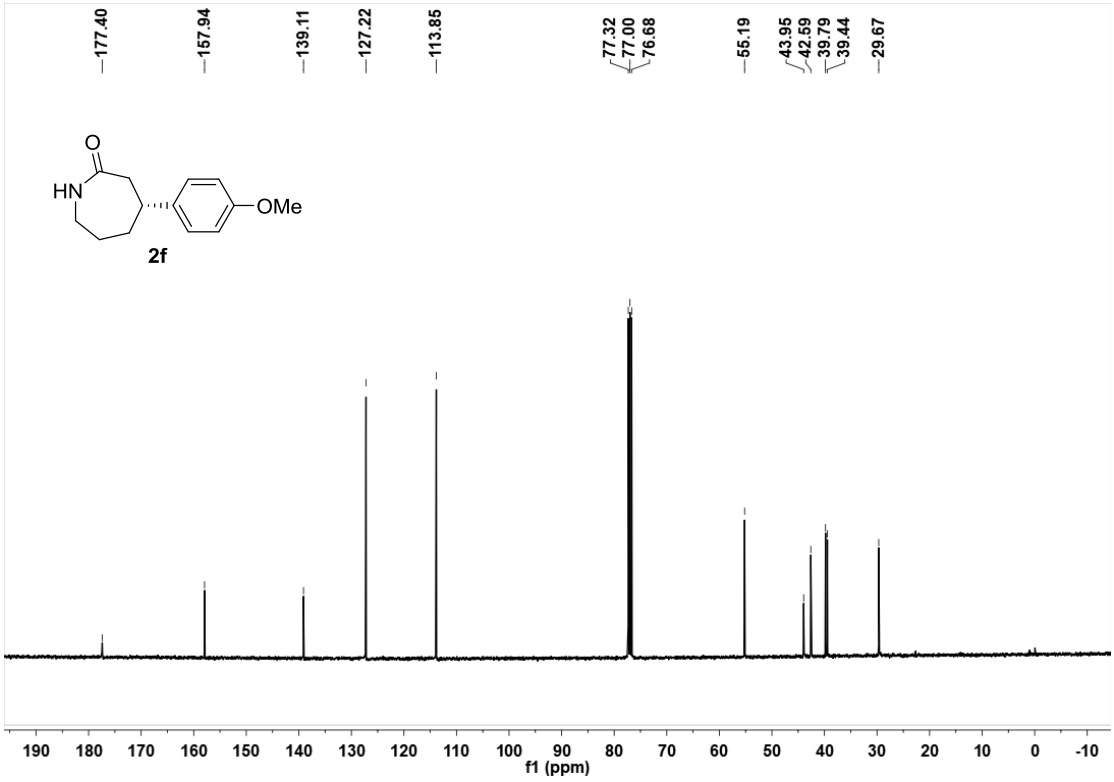

7.27 7.24 7.22 7.20 6.79 6.77 6.76 6.75 6.74 6.73 6.73 6.45 3.80 3.38 3.36 3.35 3.33 3.32 3.30 3.28 3.27 3.25 2.95 2.92 2.88 2.88 2.86 2.85 2.83 2.82 2.62 2.59 2.15 2.12 2.12 1.98 1.97 1.96 1.95 1.94 1.93 1.83 1.82 1.79 1.79 1.77 1.76 1.73 1.73 1.70 1.69 1.67 1.66 1.64 1.61 1.60
O
HN
OMe
2d
1.08 3.14 0.91 3.00 2.17 2.13 1.04 1.16 1.16 3.38
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 -0.5 -1.0
f1 (ppm)

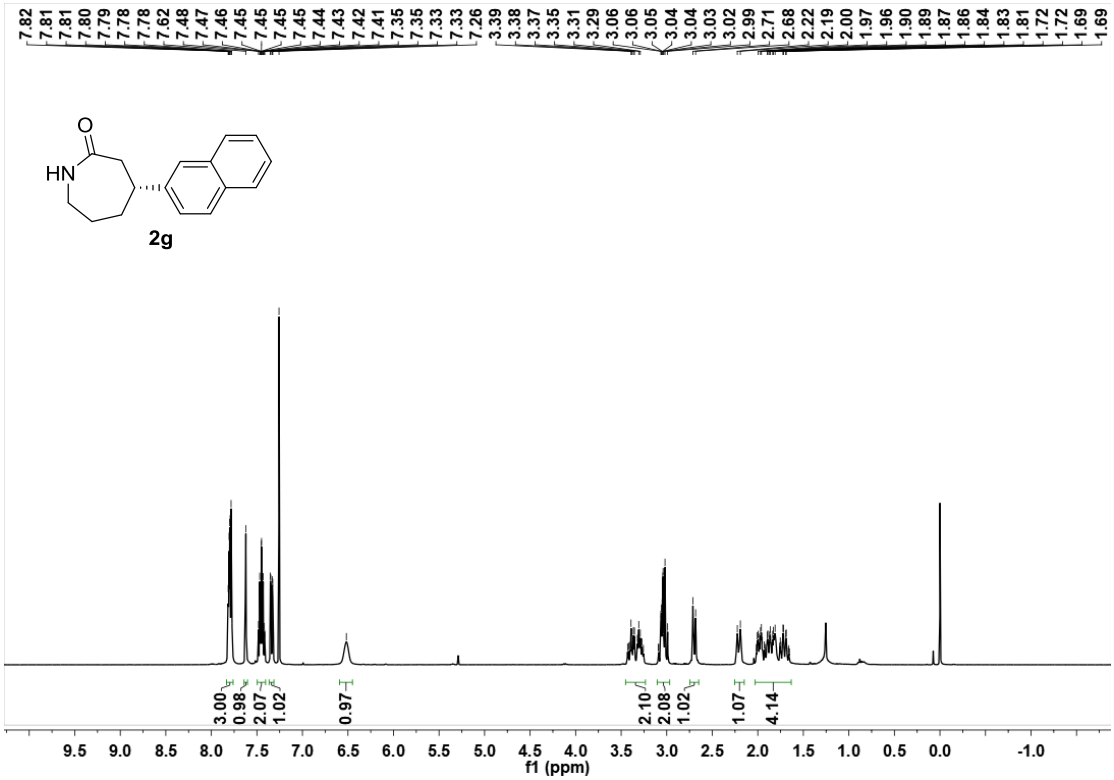

177.27 159.66 148.48 129.60 118.69 112.34 111.45 77.32 77.00 76.68 55.16 43.55 42.65 40.69 39.16 29.66
O
HN
OMe
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

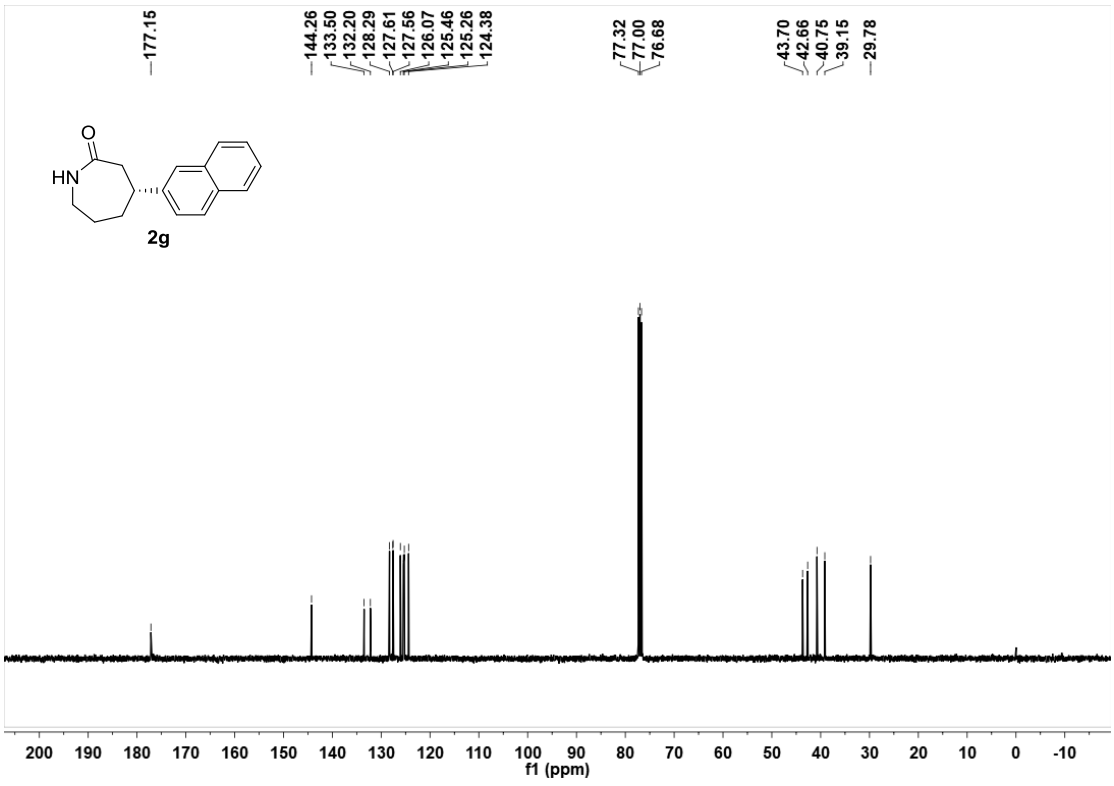

7.26
7.13
7.11
7.09
7.07
6.47
3.39
3.38
3.35
3.34
3.33
3.31
3.28
3.26
3.24
3.23
2.95
2.92
2.89
2.88
2.88
2.85
2.85
2.83
2.82
2.60
2.57
2.32
2.12
2.09
1.95
1.94
1.93
1.92
1.81
1.80
1.78
1.77
1.75
1.74
1.72
1.71
1.69
1.67
1.66
1.63
1.60
HN
O
2e
4.00
0.90
2.00
1.99
0.95
2.98
1.03
1.02
2.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

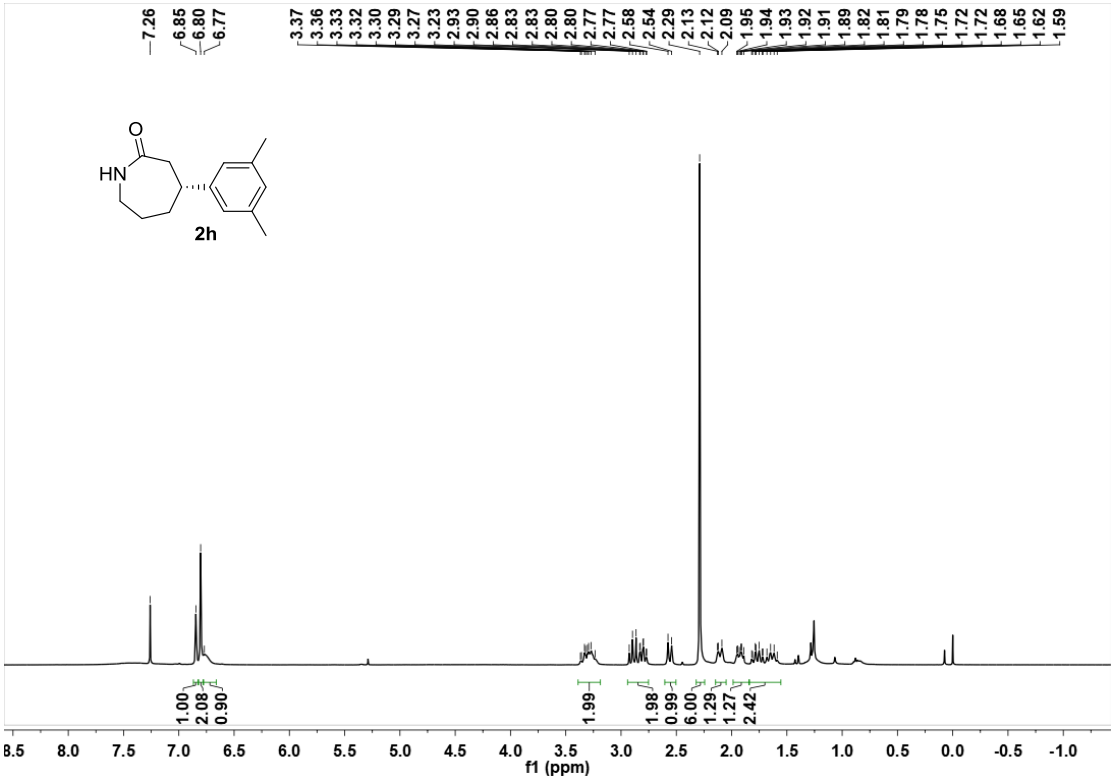

177.29
143.93
135.89
129.23
126.17
77.32
77.00
76.68
43.75
42.64
40.22
39.38
29.72
20.96
HN
O
2e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

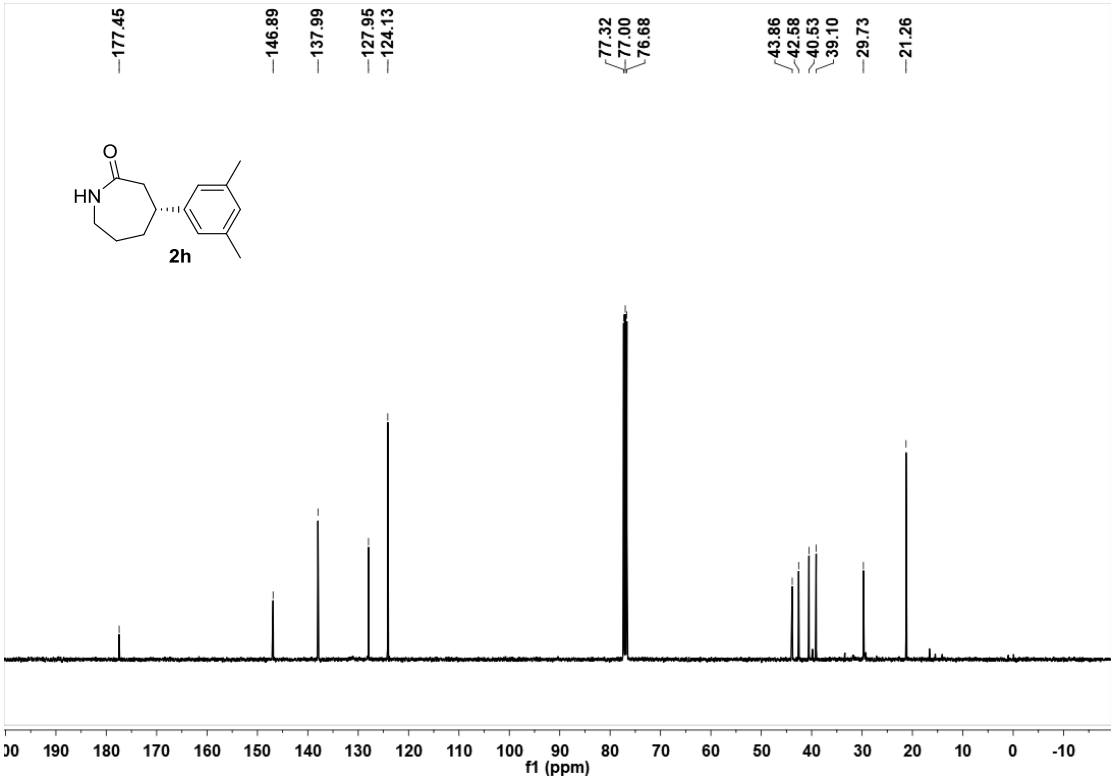

7.27 7.13 7.12 7.11 7.10 7.10 7.09 6.86 6.85 6.85 6.83 6.83 6.82 6.63 6.63 3.79 3.35 3.34 3.33 3.32 3.31 3.29 3.28 3.26 3.24 2.93 2.90 2.87 2.86 2.84 2.84 2.81 2.81 2.59 2.55 2.12 2.11 2.09 1.95 1.93 1.92 1.91 1.80 1.76 1.76 1.74 1.73 1.72 1.70 1.70 1.69 1.68 1.67 1.66 1.65 1.63
HN
O
OMe
2f
2.03 2.04 0.94 3.00 2.05 2.04 1.01 1.08 1.62 2.25
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 -0.5
f1 (ppm)

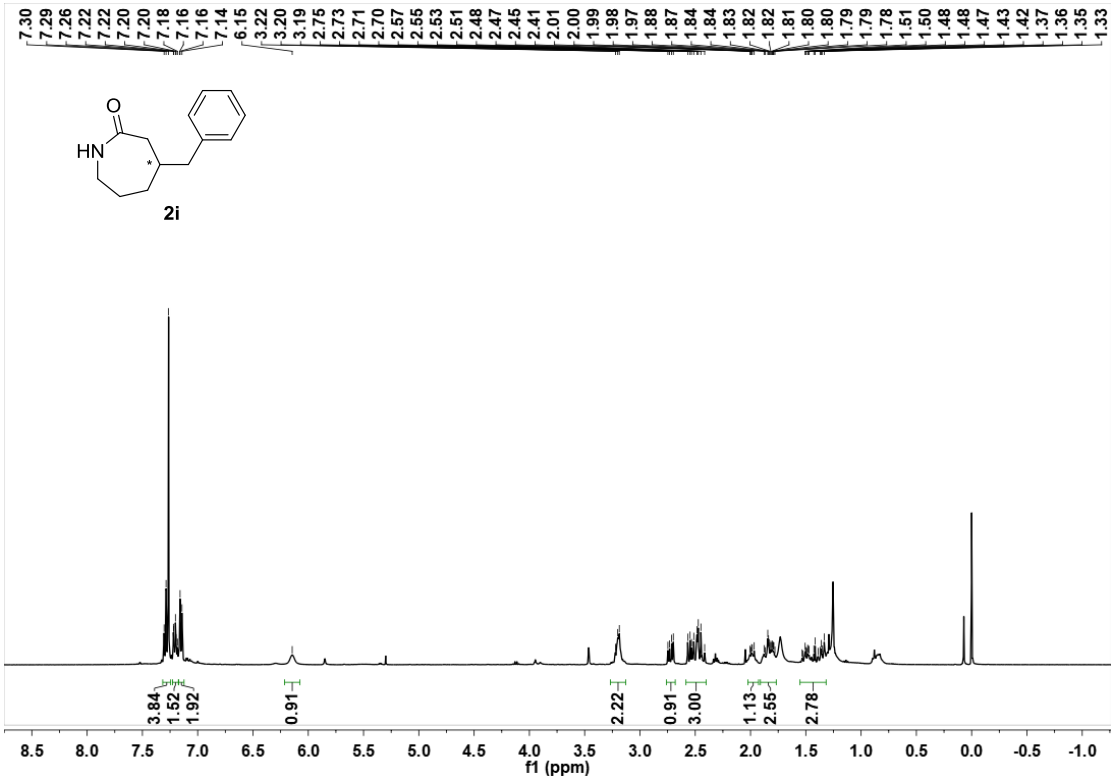

177.40 157.94 139.11 127.22 113.85 77.32 77.00 76.68 55.19 43.95 42.59 39.79 39.44 29.67
HN
O
OMe
2f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

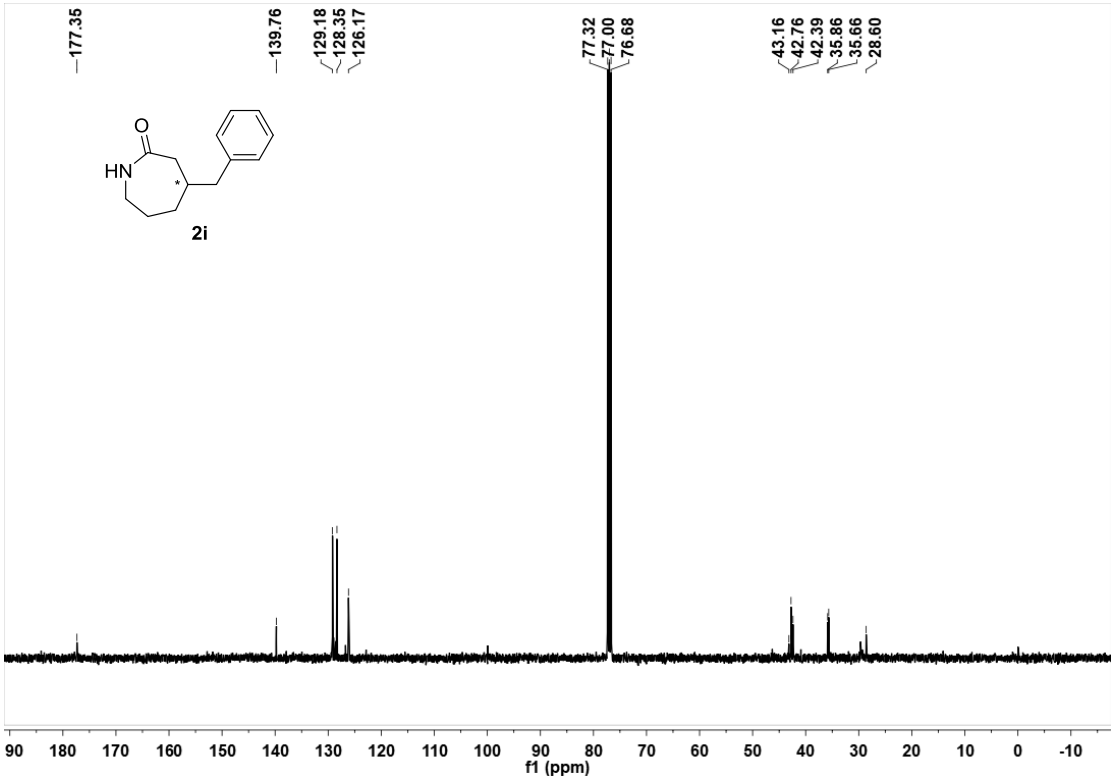

7.82 7.81 7.81 7.80 7.79 7.78 7.78 7.62 7.48 7.47 7.46 7.45 7.45 7.45 7.45 7.44 7.43 7.42 7.41 7.35 7.35 7.33 7.33 7.26
3.39 3.38 3.37 3.35 3.31 3.29 3.06 3.06 3.05 3.04 3.04 3.03 3.02 2.99 2.71 2.68 2.22 2.19 2.00 1.97 1.96 1.90 1.89 1.87 1.86 1.84 1.83 1.81 1.72 1.72 1.69 1.69
HN
O
2g
3.00 0.98 2.07 1.02 0.97 2.10 2.08 1.02 1.07 4.14
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 -1.0
f1 (ppm)

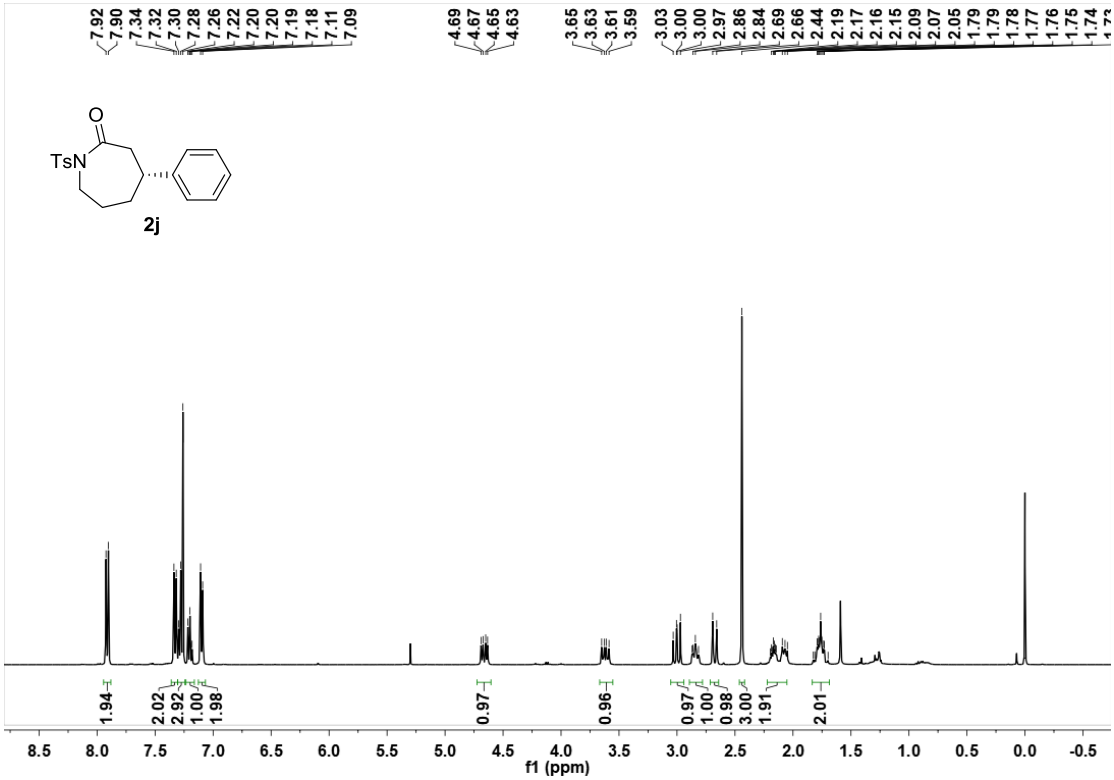

177.15
144.26 133.50 132.20 128.29 127.61 127.56 126.07 125.46 125.26 124.38
77.32 77.00 76.68
43.70 42.66 40.75 39.15 29.78
HN
O
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

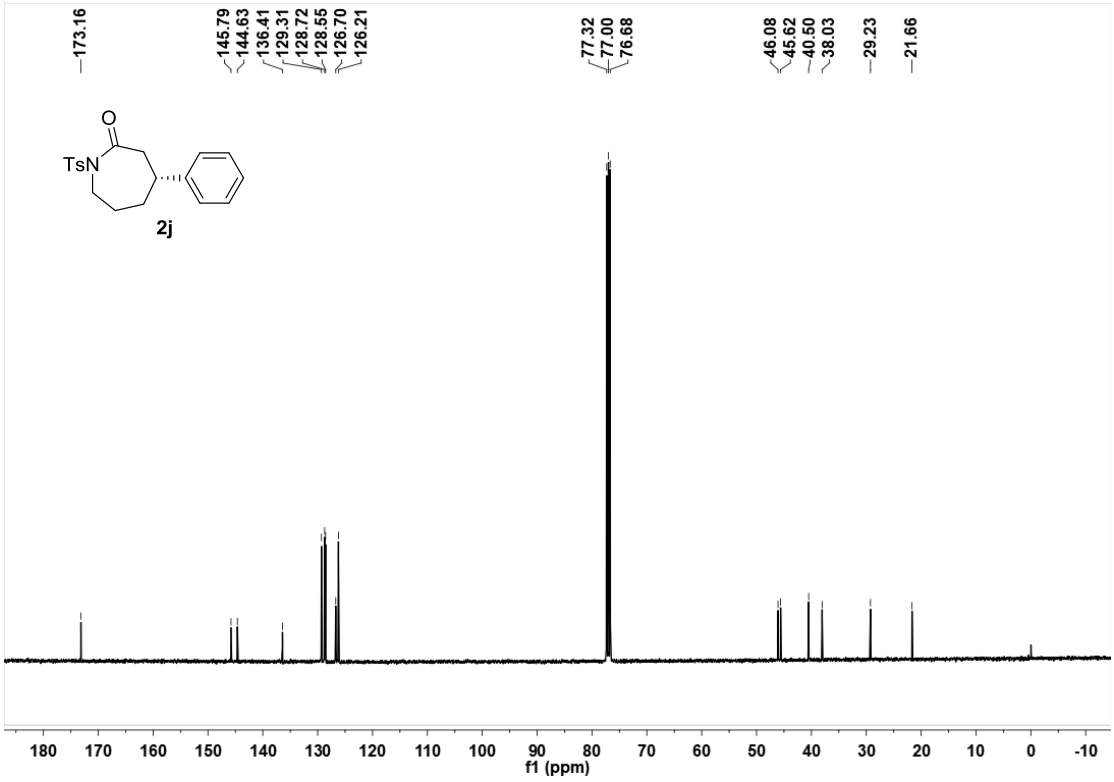

7.26
6.85
6.80
6.77
3.37
3.36
3.33
3.32
3.30
3.29
3.27
3.23
2.93
2.90
2.86
2.83
2.83
2.80
2.80
2.77
2.77
2.58
2.54
2.29
2.13
2.12
2.09
1.95
1.94
1.93
1.92
1.91
1.89
1.82
1.81
1.79
1.78
1.75
1.72
1.72
1.68
1.65
1.62
1.59
O
HN
2h
1.00
2.08
0.90
1.99
1.98
0.99
6.00
1.29
1.27
2.42
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

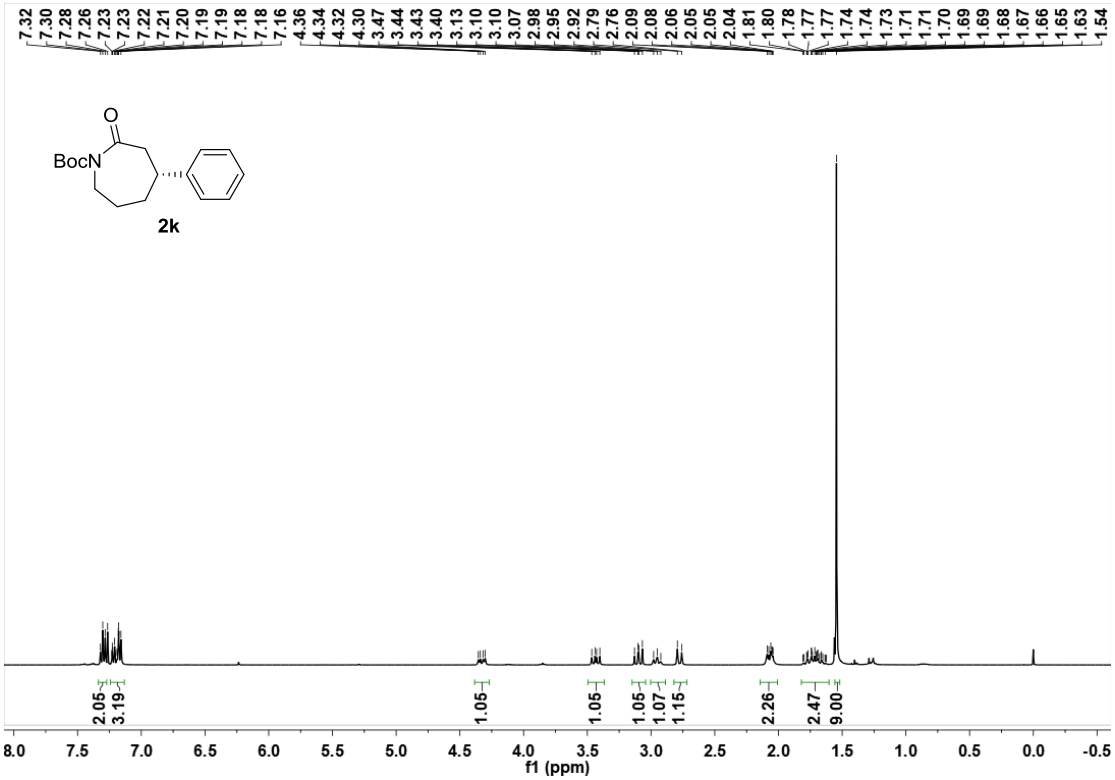

177.45
146.89
137.99
127.95
124.13
77.32
77.00
76.68
43.86
42.58
40.53
39.10
29.73
21.26
O
HN
2h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

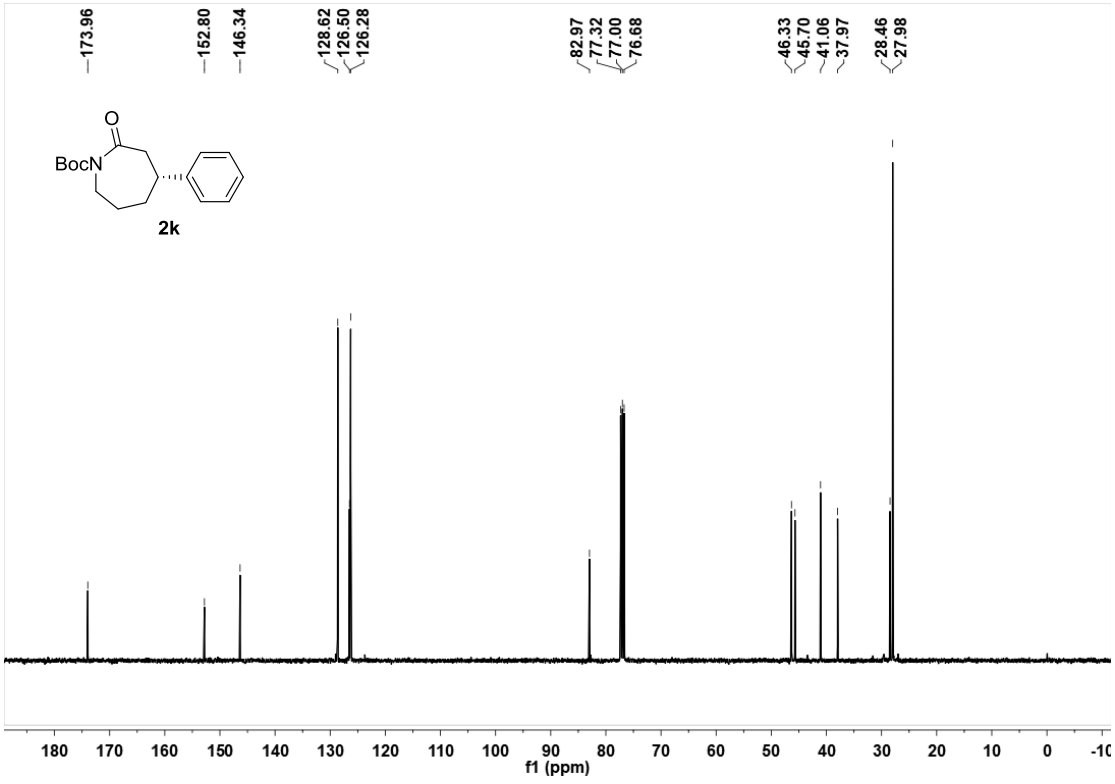

7.30 7.29 7.26 7.22 7.22 7.20 7.20 7.18 7.16 7.16 7.14 6.15 3.22 3.20 3.19 2.75 2.73 2.71 2.70 2.57 2.55 2.53 2.51 2.48 2.47 2.45 2.41 2.01 2.00 1.99 1.98 1.97 1.88 1.87 1.84 1.84 1.83 1.82 1.82 1.81 1.80 1.80 1.79 1.79 1.78 1.51 1.50 1.48 1.48 1.47 1.43 1.42 1.37 1.36 1.35 1.33
O
HN
*
2i
3.84 1.52 1.92 0.91 2.22 0.91 3.00 1.13 2.55 2.78
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 -0.5 -1.0
f1 (ppm)

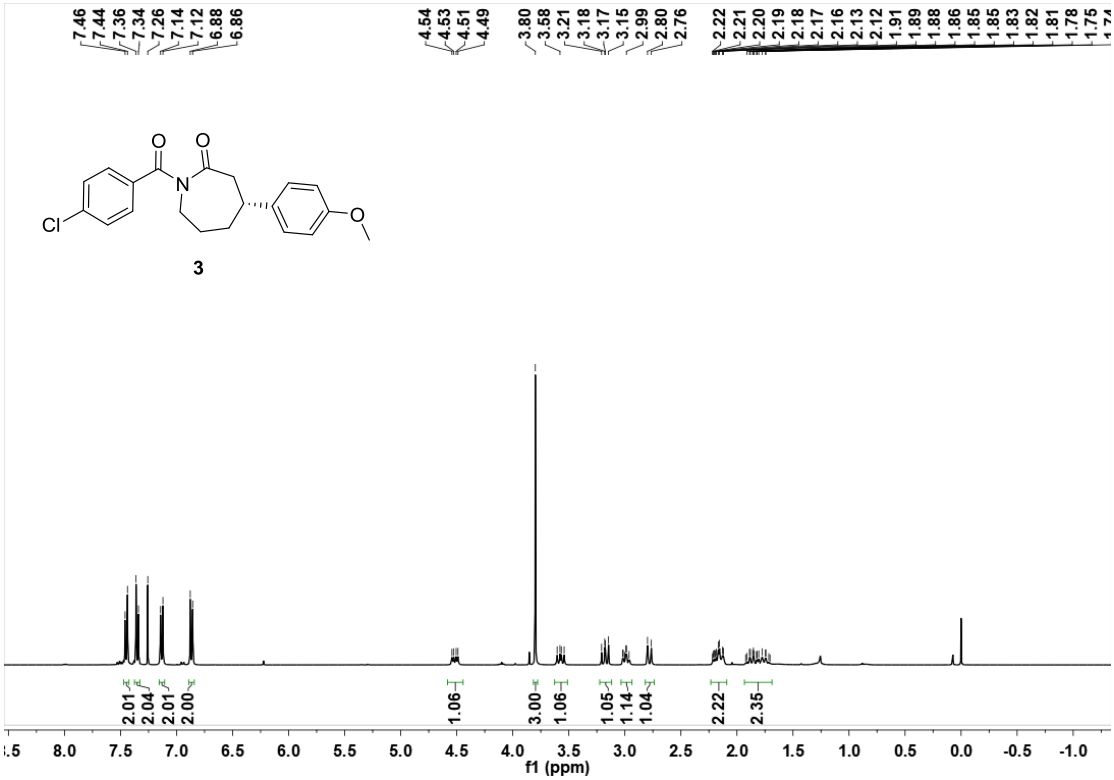

177.35 139.76 129.18 128.35 126.17 77.32 77.00 76.68 43.16 42.76 42.39 35.86 35.66 28.60
O
HN
*
2i
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

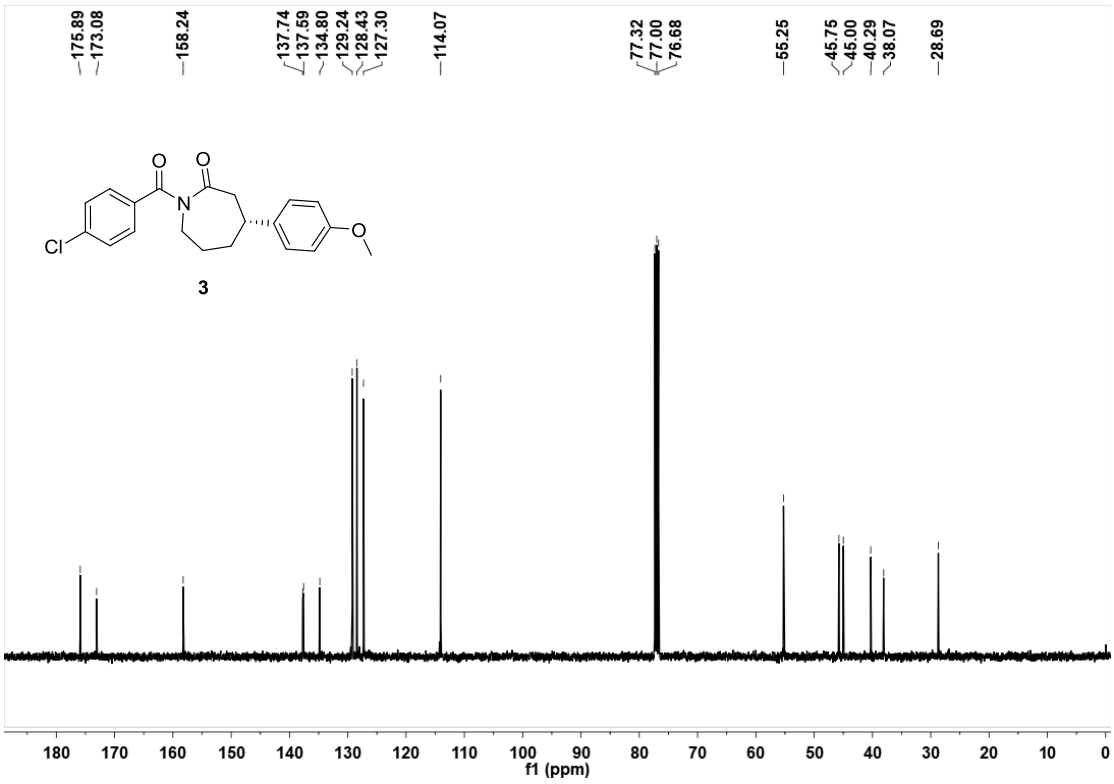

7.92
7.90
7.34
7.32
7.30
7.28
7.26
7.22
7.20
7.20
7.19
7.18
7.11
7.09
4.69
4.67
4.65
4.63
3.65
3.63
3.61
3.59
3.03
3.00
3.00
2.97
2.86
2.84
2.69
2.66
2.44
2.19
2.17
2.16
2.15
2.09
2.07
2.05
1.79
1.79
1.78
1.77
1.76
1.75
1.74
O
TsN
2j
1.94
2.02
2.92
1.00
1.98
0.97
0.96
0.97
1.00
0.98
3.00
1.91
2.01
8.5
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
-0.5
f1 (ppm)


173.16
145.79
144.63
136.41
129.31
128.72
128.55
126.70
126.21
77.32
77.00
76.68
46.08
45.62
40.50
38.03
29.23
21.66
O
TsN
2j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.32 7.30 7.28 7.26 7.23 7.23 7.22 7.21 7.20 7.19 7.19 7.18 7.18 7.16 4.36 4.34 4.32 4.30 3.47 3.44 3.43 3.40 3.13 3.10 3.10 3.07 2.98 2.95 2.92 2.79 2.76 2.09 2.08 2.06 2.05 2.05 2.04 1.81 1.80 1.78 1.77 1.77 1.74 1.74 1.73 1.71 1.71 1.70 1.69 1.69 1.68 1.67 1.66 1.65 1.63 1.54
O
BocN
2k
2.05 3.19 1.05 1.05 1.05 1.07 1.15 2.26 2.47 9.00
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 -0.5
f1 (ppm)


173.96 152.80 146.34 128.62 126.50 126.28 82.97 77.32 77.00 76.68 46.33 45.70 41.06 37.97 28.46 27.98
O
BocN
2k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

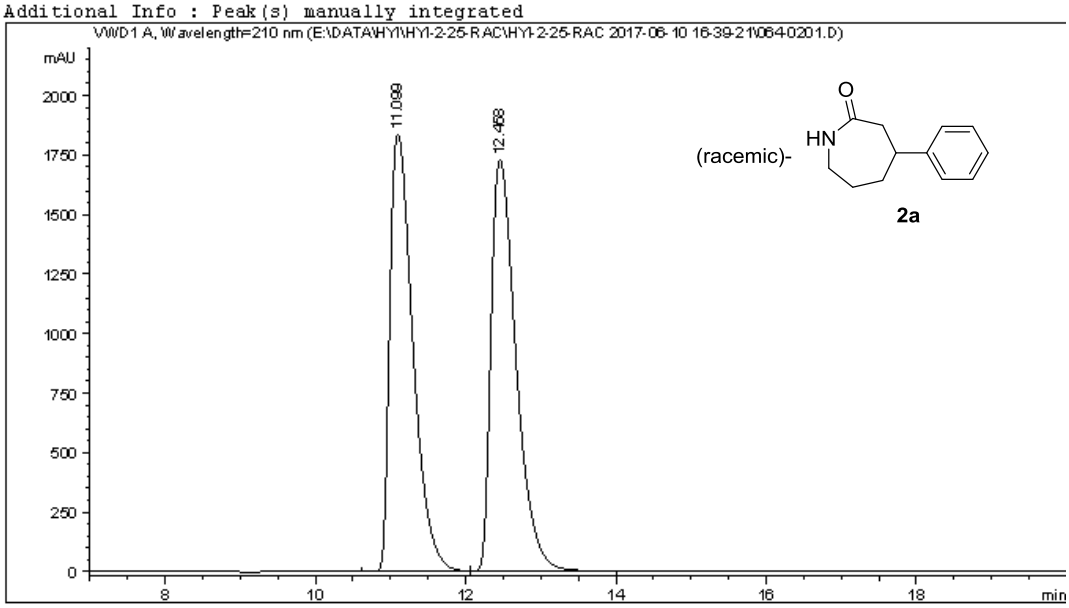

7.46
7.44
7.36
7.34
7.26
7.14
7.12
6.88
6.86
4.54
4.53
4.51
4.49
3.80
3.58
3.21
3.18
3.17
3.15
2.99
2.80
2.76
2.22
2.21
2.20
2.19
2.18
2.17
2.16
2.13
2.12
1.91
1.89
1.88
1.86
1.85
1.85
1.83
1.82
1.81
1.78
1.75
O
O
N
Cl
O
3
2.01
2.04
2.01
2.00
1.06
3.00
1.06
1.05
1.14
1.04
2.22
2.35
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


175.89
173.08
158.24
137.74
137.59
134.80
129.24
128.43
127.30
114.07
77.32
77.00
76.68
55.25
45.75
45.00
40.29
38.07
28.69
O
O
N
Cl
O
3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

VIII. HPLC spectra

Data File E:\DATA\HYI\HYI-2-25-RAC\HYI-2-25-RAC 2017-06-10 16-39-21\064-0201.D
Sample Name: HYI-2-25-RAC-AD

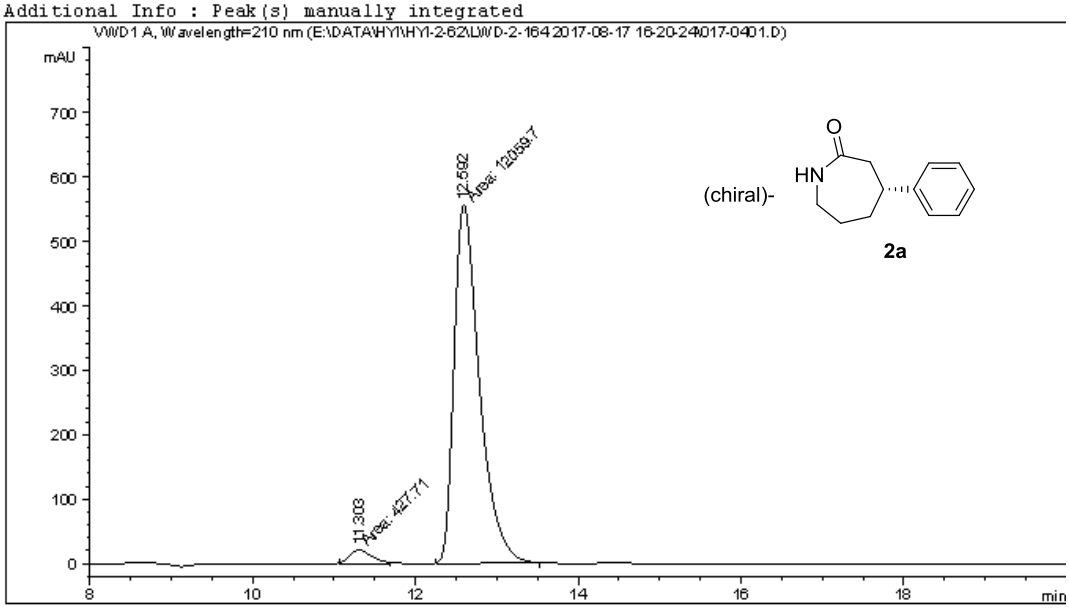
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 64
    Injection Date  : 6/10/2017 6:04:36 PM                Inj :   1
                                                  Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-2-25-RAC\HYI-2-25-RAC 2017-06-10 16-39-21\VWD-ADH(1-2)-
                      90-10-1.0-210NM-60MIN.M
    Last changed    : 6/10/2017 6:55:22 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\HYI\HYI-2-25-RAC\HYI-2-25-RAC 2017-06-10 16-39-21\VWD-ADH(1-2)-
                      90-10-1.0-210NM-60MIN.M (Sequence Method)
    Last changed    : 12/22/2017 12:00:25 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.099 VB    0.3308 3.91619e4  1836.01221  49.4965
       2  12.458 BB    0.3567 3.99587e4  1728.76416  50.5035

    Totals :                  7.91206e4  3564.77637

    ======================================================================
```

Data File E:\DATA\HYI\HYI-2-62\LWD-2-164 2017-08-17 16-20-24\017-0401.D
Sample Name: HYI-2-62-3

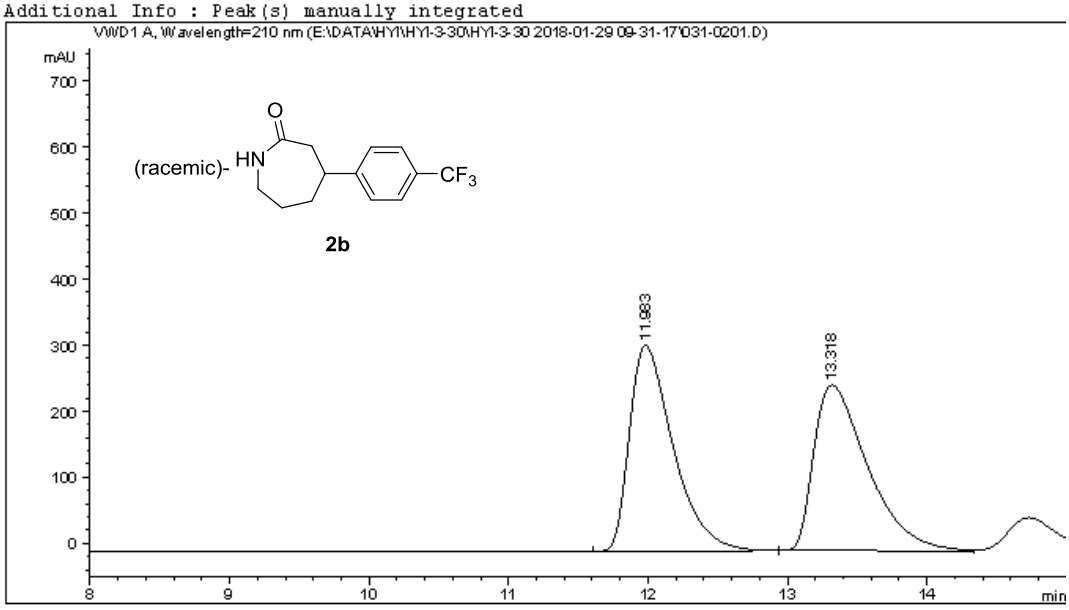
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 17
    Injection Date  : 8/17/2017 5:33:53 PM               Inj :   1
                                                   Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-2-62\LWD-2-164 2017-08-17 16-20-24\VWD-AD(1-2)-90-10-1ML
                      -210NM-20MIN-10UL.M
    Last changed    : 8/17/2017 4:20:25 PM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-2-62\LWD-2-164 2017-08-17 16-20-24\VWD-AD(1-2)-90-10-1ML
                      -210NM-20MIN-10UL.M (Sequence Method)
    Last changed    : 12/22/2017 12:08:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  11.303 MM    0.3210  427.70978   22.20485   3.4251
       2  12.592 MM    0.3617 1.20597e4   555.66443  96.5749

    Totals :                  1.24874e4   577.86928


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\HYI\HYI-3-30\HYI-3-30 2018-01-29 09-31-17\031-0201.D
Sample Name: HYI-3-30-4

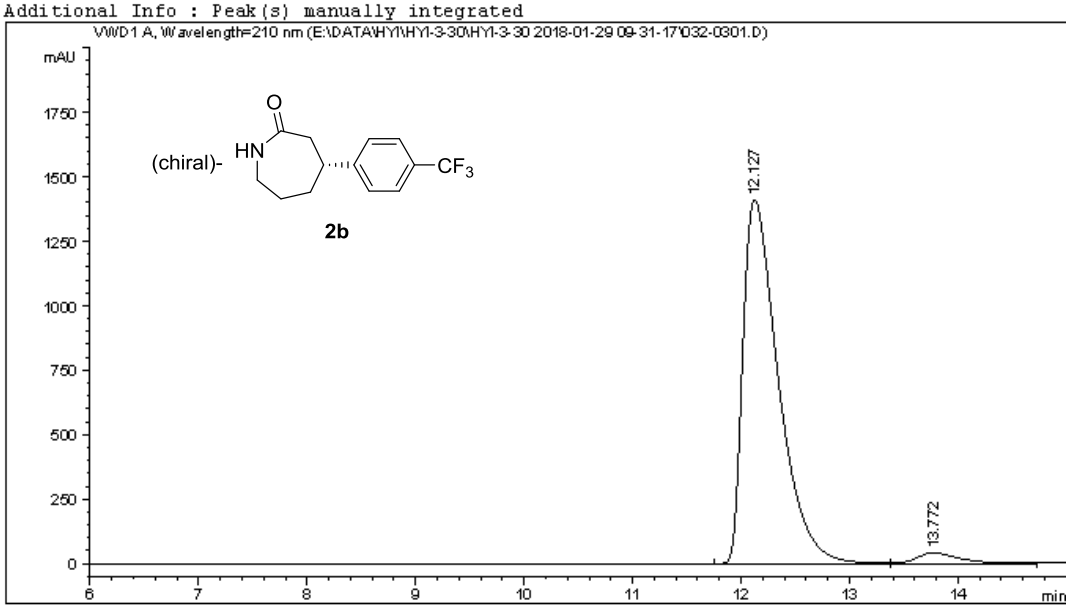
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 31
    Injection Date  : 1/29/2018 10:33:48 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-3-30\HYI-3-30 2018-01-29 09-31-17\VWD-AD(1-2)-90-10-1.
                      0ML-5UL-210NM-20MIN.M
    Last changed    : 1/29/2018 9:31:17 AM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-3-30\HYI-3-30 2018-01-29 09-31-17\VWD-AD(1-2)-90-10-1.
                      0ML-5UL-210NM-20MIN.M (Sequence Method)
    Last changed    : 1/31/2018 10:22:51 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.983 BB    0.3297 6773.45410  311.46817  50.2503
       2  13.318 BV    0.4060 6705.96289  250.73395  49.7497

    Totals :                  1.34794e4   562.20212


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\HYI\HYI-3-30\HYI-3-30 2018-01-29 09-31-17\032-0301.D
Sample Name: HYI-3-30-5

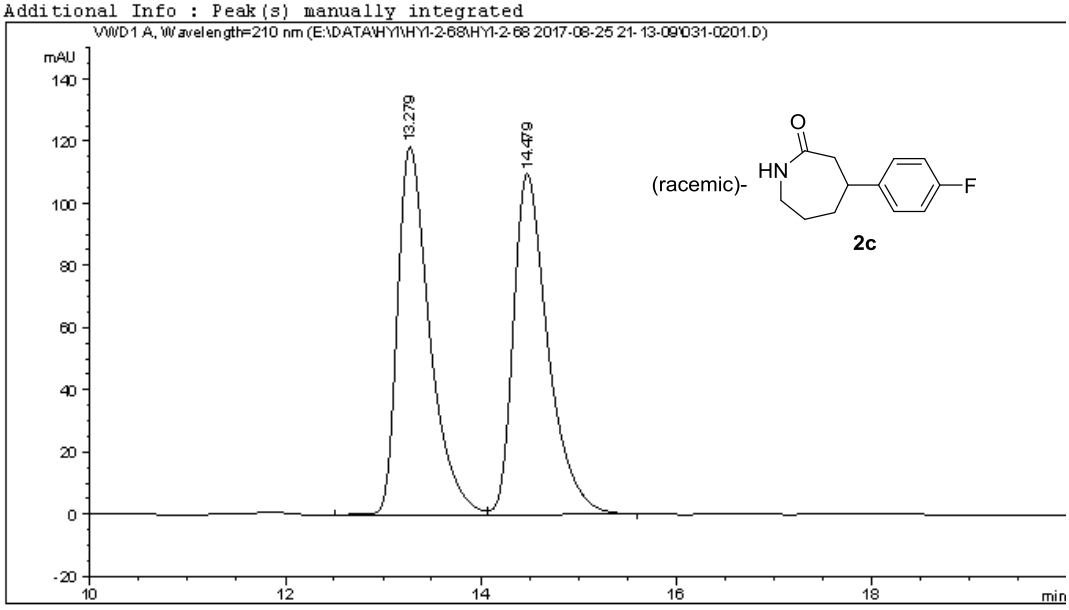
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 32
    Injection Date  : 1/29/2018 10:54:34 AM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-3-30\HYI-3-30 2018-01-29 09-31-17\VWD-AD(1-2)-90-10-1.
                      0ML-5UL-210NM-20MIN.M
    Last changed    : 1/29/2018 9:31:17 AM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-3-30\HYI-3-30 2018-01-29 09-31-17\VWD-AD(1-2)-90-10-1.
                      0ML-5UL-210NM-20MIN.M (Sequence Method)
    Last changed    : 1/29/2018 3:22:11 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.127 BV    0.3450 3.19150e4  1410.55725  96.6787
       2  13.772 VV    0.4132 1096.39819   39.94759   3.3213

    Totals :                  3.30114e4  1450.50484


    ==================================================================
                            *** End of Report ***
```

Data File E:\DATA\HYI\HYI-2-68\HYI-2-68 2017-08-25 21-13-09\031-0201.D
Sample Name: HYI-2-68-2

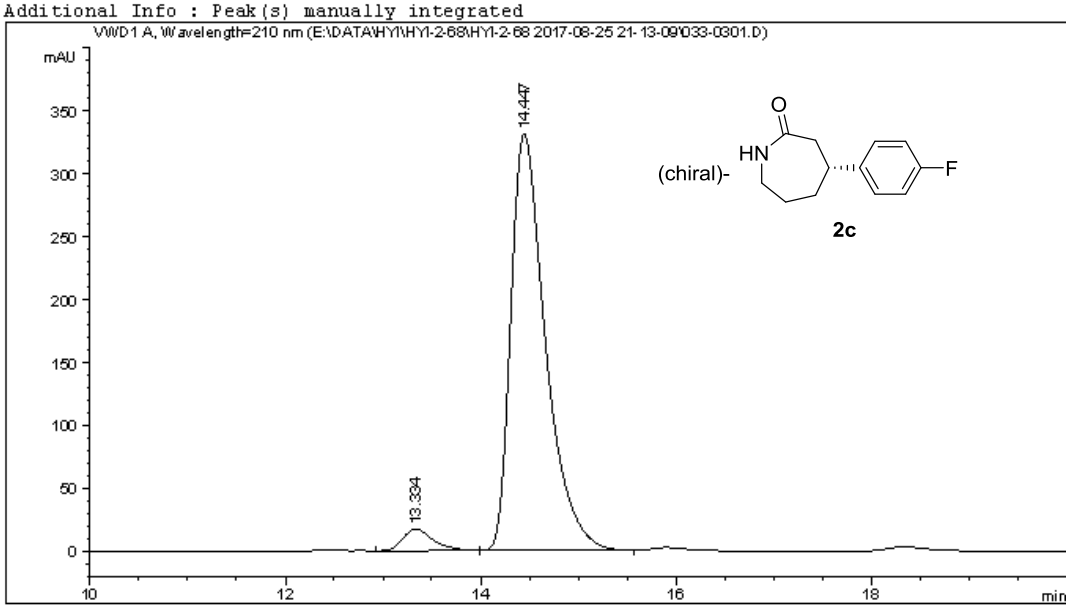
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 31
    Injection Date  : 8/25/2017 10:14:55 PM              Inj :   1
                                                   Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-2-68\HYI-2-68 2017-08-25 21-13-09\VWD-AD(1-2)-90-10-1ML-
                      210NM-20MIN-10UL.M
    Last changed    : 8/25/2017 9:13:09 PM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-2-68\HYI-2-68 2017-08-25 21-13-09\VWD-AD(1-2)-90-10-1ML-
                      210NM-20MIN-10UL.M (Sequence Method)
    Last changed    : 12/22/2017 12:11:53 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                          Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.279 BV    0.3460 2708.44067  118.36437  50.1114
       2  14.479 VB    0.3710 2696.39868  109.61091  49.8886

    Totals :                  5404.83936  227.97528


    ==================================================================
                          *** End of Report ***
```

Data File E:\DATA\HYI\HYI-2-68\HYI-2-68 2017-08-25 21-13-09\033-0301.D
Sample Name: HYI-2-68-1

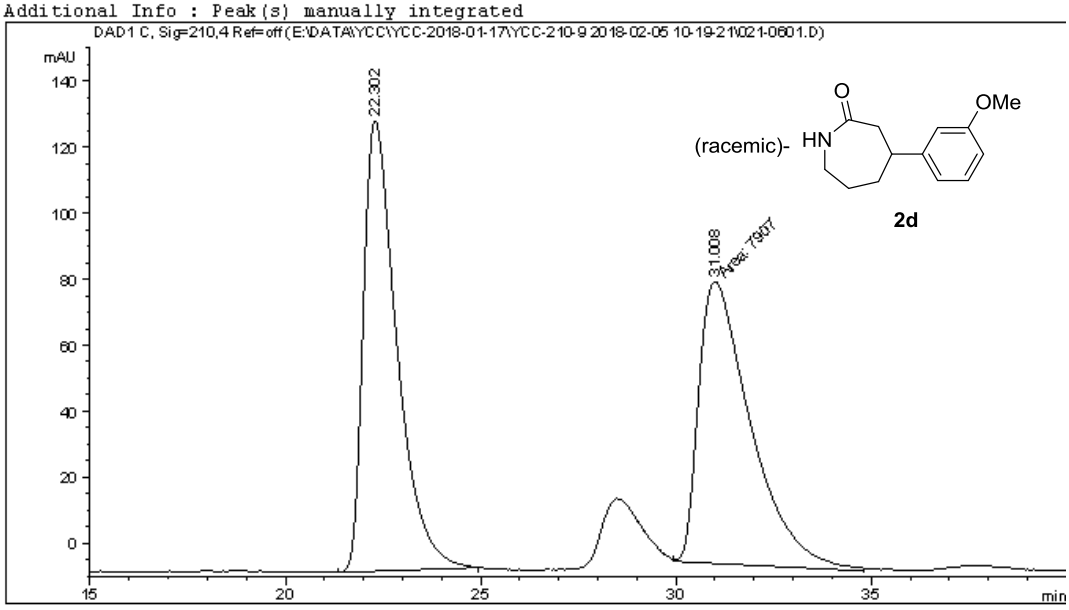
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 33
    Injection Date  : 8/25/2017 10:35:46 PM               Inj :   1
                                                   Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-2-68\HYI-2-68 2017-08-25 21-13-09\VWD-AD(1-2)-90-10-1ML-
                      210NM-20MIN-10UL.M
    Last changed    : 8/25/2017 9:13:09 PM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-2-68\HYI-2-68 2017-08-25 21-13-09\VWD-AD(1-2)-90-10-1ML-
                      210NM-20MIN-10UL.M (Sequence Method)
    Last changed    : 12/22/2017 12:15:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.334 BB    0.3293  374.94095   17.27020   4.3904
       2  14.447 BB    0.3737 8165.04102  331.06558  95.6096

    Totals :                  8539.98196  348.33578


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\YCC\YCC-2018-01-17\YCC-210-9 2018-02-05 10-19-21\021-0601.D
Sample Name: HYI-m-OMe-20180205

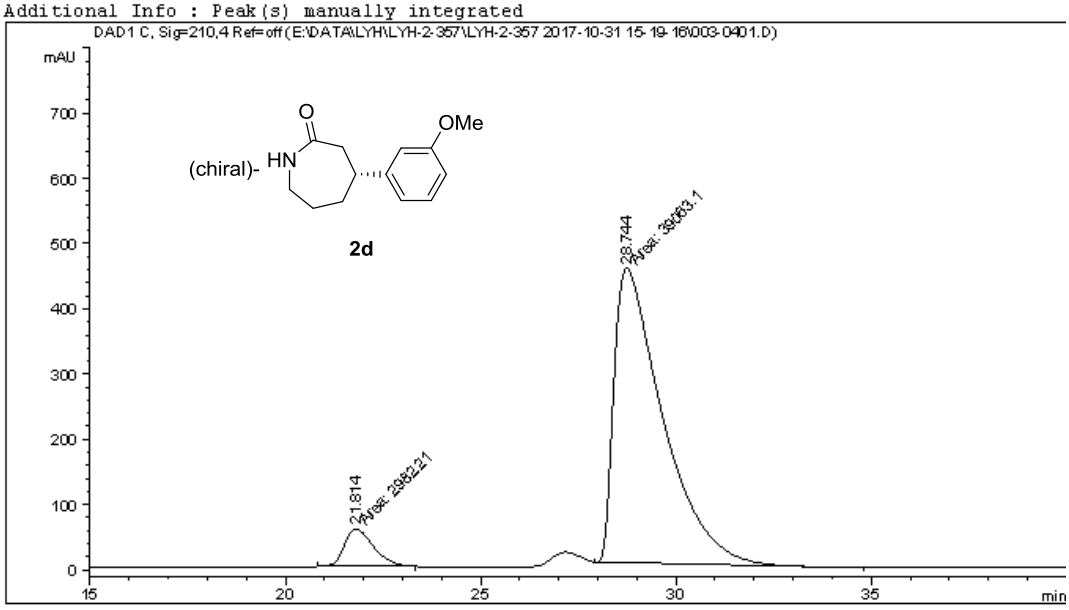
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 21
    Injection Date  : 2/5/2018 12:10:18 PM               Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\YCC\YCC-2018-01-17\YCC-210-9 2018-02-05 10-19-21\DAD-OD(1-2)-90-
                      10-1ML-2UL-ALL-40MIN.M
    Last changed    : 2/5/2018 10:57:54 AM by SYSTEM
    Analysis Method : E:\DATA\YCC\YCC-2018-01-17\YCC-210-9 2018-02-05 10-19-21\DAD-OD(1-2)-90-
                      10-1ML-2UL-ALL-40MIN.M (Sequence Method)
    Last changed    : 2/5/2018 7:23:04 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  22.302 BB    0.8750 8126.89355  136.42274  50.6857
       2  31.008 MM    1.5440 7907.00342   85.35120  49.3143

    Totals :                  1.60339e4   221.77395


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LYH\LYH-2-357\LYH-2-357 2017-10-31 15-19-16\003-0401.D
Sample Name: HYI-2-121-3-OD-CHIRAL

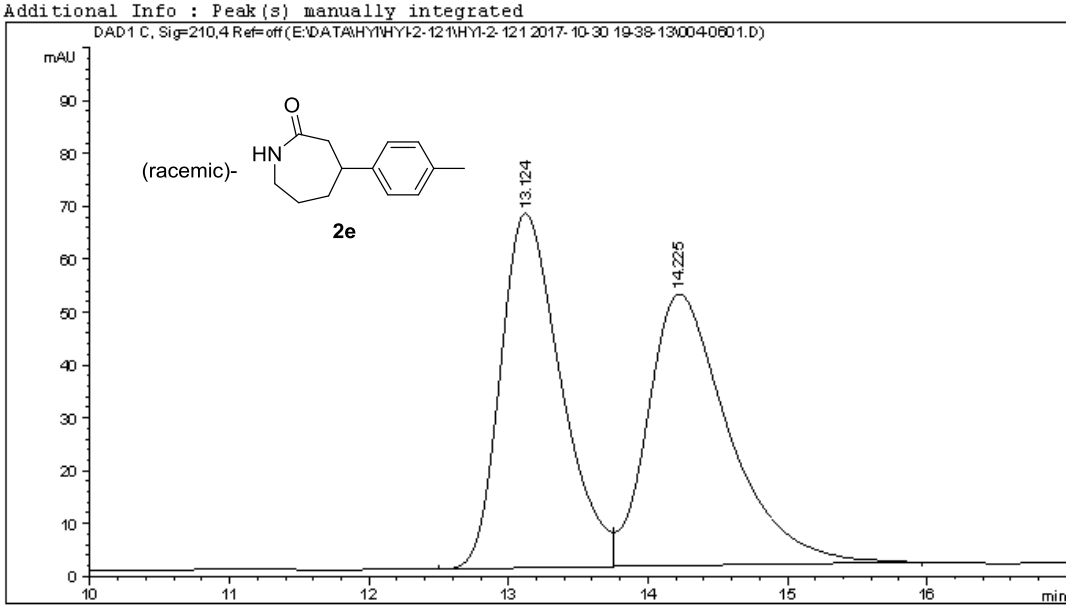
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 3
    Injection Date  : 10/31/2017 6:03:58 PM              Inj :   1
                                                   Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\LYH\LYH-2-357\LYH-2-357 2017-10-31 15-19-16\DAD-OD(1-2)-90-10-1.
                      0ML-10UL-ALL-40MIN.M
    Last changed    : 10/31/2017 3:23:07 PM by SYSTEM
    Analysis Method : E:\DATA\LYH\LYH-2-357\LYH-2-357 2017-10-31 15-19-16\DAD-OD(1-2)-90-10-1.
                      0ML-10UL-ALL-40MIN.M (Sequence Method)
    Last changed    : 1/26/2018 4:31:54 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                          Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.814 MM    0.8629 2982.20972   57.59763   7.0929
       2  28.744 MM    1.4439 3.9063le4   450.90622  92.9071

    Totals :                  4.20453e4   508.50385


    ==================================================================
                          *** End of Report ***
```

Data File E:\DATA\HYI\HYI-2-121\HYI-2-121 2017-10-30 19-38-13\004-0601.D
Sample Name: HYI-2-121-5-RAC

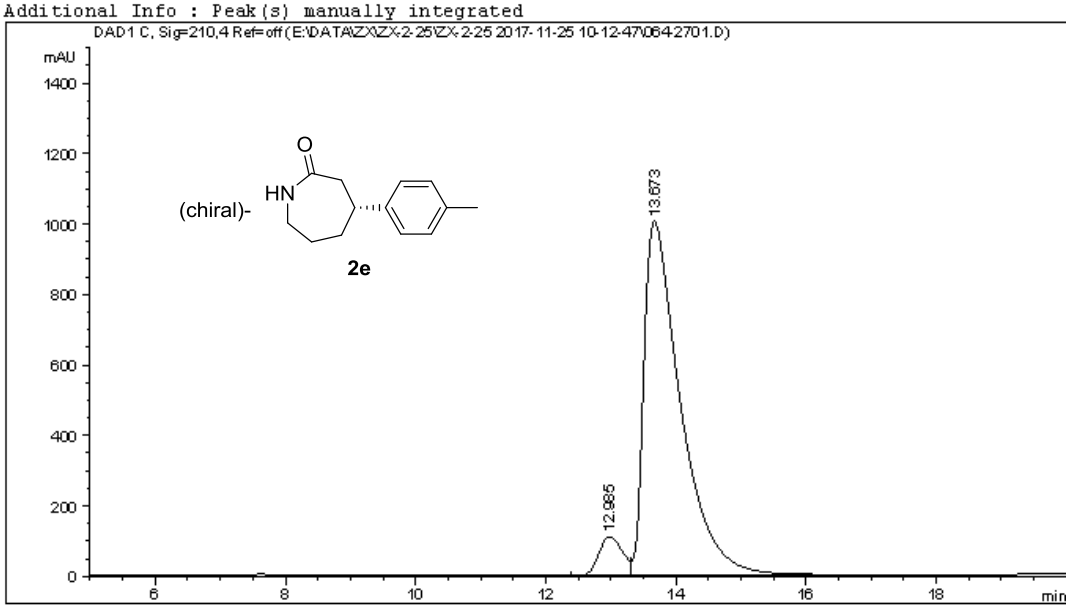
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 4
    Injection Date  : 10/30/2017 10:54:10 PM              Inj :   1
                                                   Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-2-121\HYI-2-121 2017-10-30 19-38-13\DAD-OD(1-2)-90-10-1.
                      0ML-10UL-ALL-40MIN.M
    Last changed    : 10/30/2017 7:38:13 PM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-2-121\HYI-2-121 2017-10-30 19-38-13\DAD-OD(1-2)-90-10-1.
                      0ML-10UL-ALL-40MIN.M (Sequence Method)
    Last changed    : 1/26/2018 4:51:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.124 BV    0.4556 2010.67249   67.09521  49.2823
       2  14.225 VB    0.6017 2069.23608   51.39780  50.7177

    Totals :                  4079.90857  118.49301


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\ZX\ZX-2-25\ZX-2-25 2017-11-25 10-12-47\064-2701.D
Sample Name: HYI-2-142-2

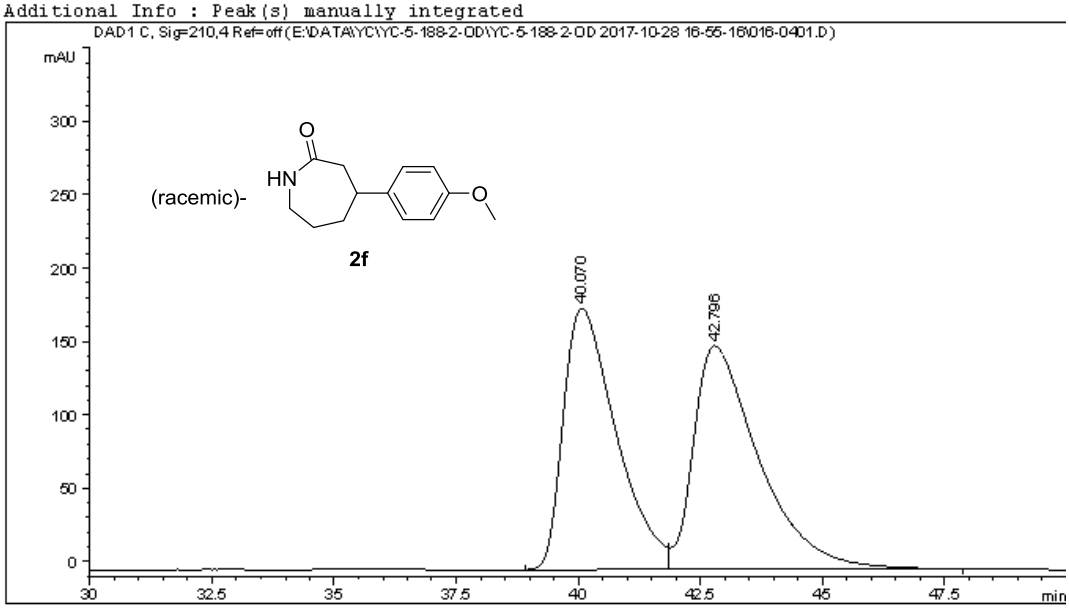
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  27
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 64
    Injection Date  : 11/26/2017 2:28:34 AM                 Inj :  1
                                                    Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\ZX\ZX-2-25\ZX-2-25 2017-11-25 10-12-47\DAD-0D(1-2)-90-10-1.0ML-
                      10UL-ALL-40MIN.M
    Last changed    : 11/25/2017 7:12:07 PM by SYSTEM
    Analysis Method : E:\DATA\ZX\ZX-2-25\ZX-2-25 2017-11-25 10-12-47\DAD-0D(1-2)-90-10-1.0ML-
                      10UL-ALL-40MIN.M (Sequence Method)
    Last changed    : 1/26/2018 4:57:53 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.985 BV    0.3973 2773.65454  110.31618   6.6158
       2  13.673 VB    0.5785 3.91510e4  1005.08282  93.3842

    Totals :                  4.19247e4  1115.39900


    ======================================================================
                            *** End of Report ***
```

Data File E:\DATA\YC\YC-5-188-2-OD\YC-5-188-2-OD 2017-10-28 16-55-16\016-0401.D
Sample Name: HYI-2-100-4-p-OME

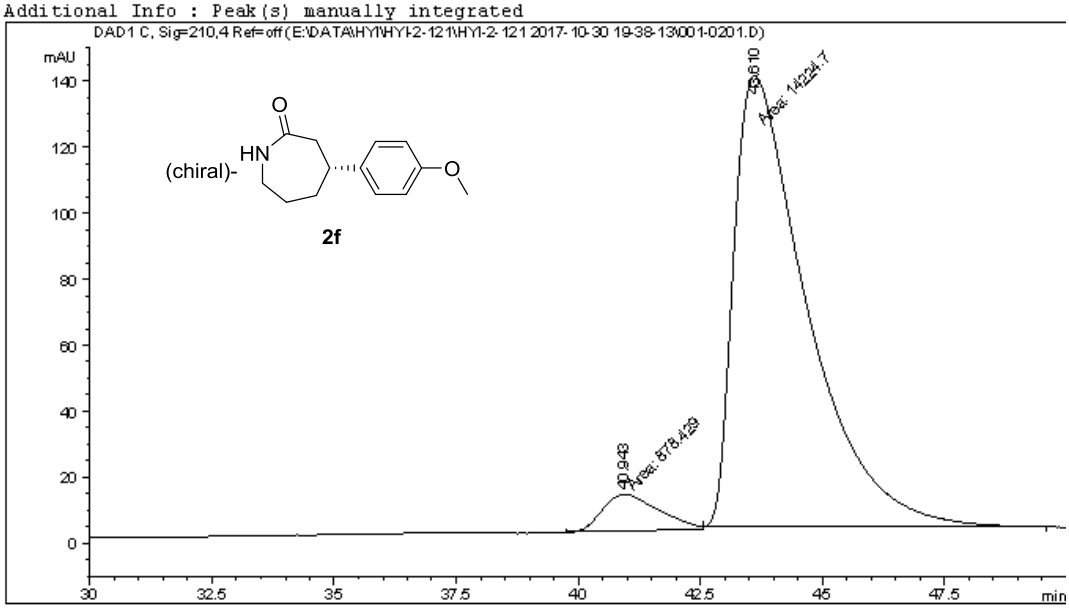
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 16
    Injection Date  : 10/28/2017 6:29:15 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\YC\YC-5-188-2-OD\YC-5-188-2-OD 2017-10-28 16-55-16\DAD-OD(1-2)-
                      90-10-0.5ML-5UL-ALL-50MIN.M
    Last changed    : 10/28/2017 5:22:43 PM by SYSTEM
    Analysis Method : E:\DATA\YC\YC-5-188-2-OD\YC-5-188-2-OD 2017-10-28 16-55-16\DAD-OD(1-2)-
                      90-10-0.5ML-5UL-ALL-50MIN.M (Sequence Method)
    Last changed    : 1/31/2018 10:10:29 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                          Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  40.070 BV    1.0896 1.33866e4   177.95691  48.5011
       2  42.796 VB    1.2974 1.4214le4   152.22879  51.4989

    Totals :                  2.76007e4   330.18570


    ==================================================================
                          *** End of Report ***
```

Data File E:\DATA\HYI\HYI-2-121\HYI-2-121 2017-10-30 19-38-13\001-0201.D
Sample Name: HYI-2-121-1

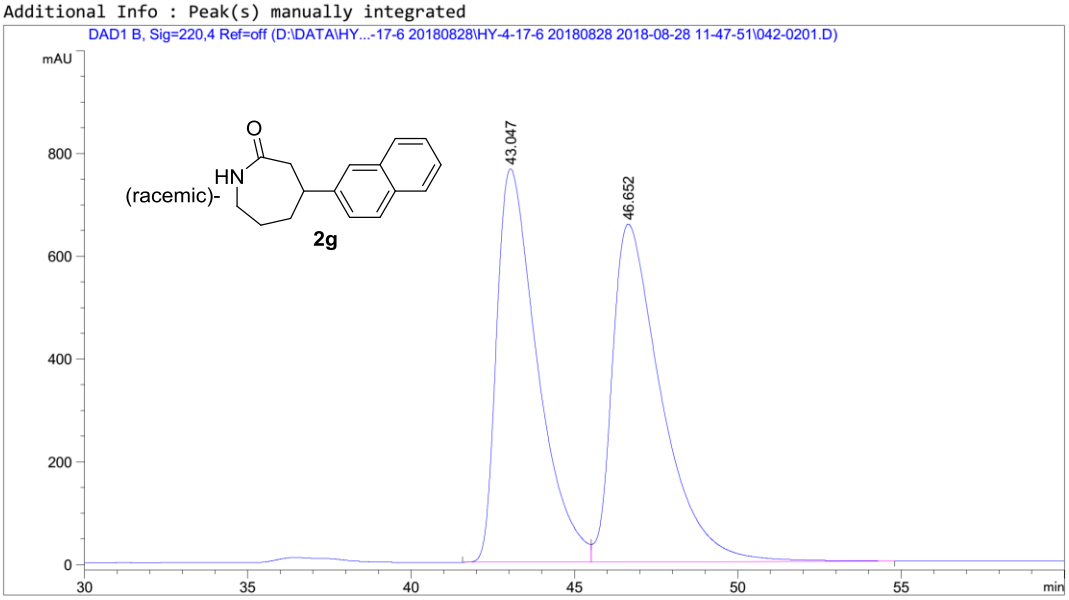
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 1
    Injection Date  : 10/30/2017 8:10:10 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\HYI\HYI-2-121\HYI-2-121 2017-10-30 19-38-13\DAD-OD(1-2)-90-10-0.
                      5ML-5UL-ALL-50MIN.M
    Last changed    : 10/30/2017 7:38:13 PM by SYSTEM
    Analysis Method : E:\DATA\HYI\HYI-2-121\HYI-2-121 2017-10-30 19-38-13\DAD-OD(1-2)-90-10-0.
                      5ML-5UL-ALL-50MIN.M (Sequence Method)
    Last changed    : 1/26/2018 4:20:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  40.943 MM    1.3301  878.42926   11.00687   5.8162
       2  43.610 MM    1.7353 1.42247e4   136.62337  94.1838

    Totals :                  1.51032e4   147.63024


    ======================================================================
                              *** End of Report ***
```

Data File D:\DATA\HY\HY-4-17-6 20180828\HY-4-17-6 20180828 2018-08-28 11-47-51\042-0201.D
Sample Name: HY-4-17-6

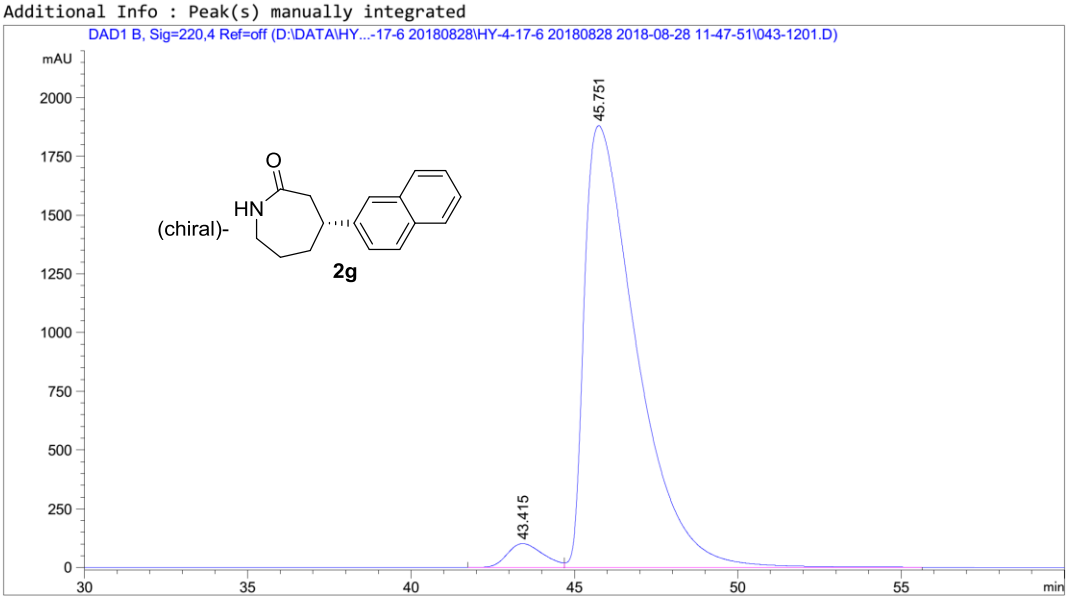
```
======================================================================
Acq. Operator   :                                Seq. Line :   2
Acq. Instrument : Instrument 2                    Location : Vial 42
Injection Date  : 8/28/2018 11:59:56 AM               Inj :   1
                                                 Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\HY\HY-4-17-6 20180828\HY-4-17-6 20180828 2018-08-28 11-47-51\DAD-OD
                  (1-2)-90-10-0.5ML-3UL-ALL-60MIN.M
Last changed    : 8/28/2018 11:44:59 AM
Analysis Method : D:\METHOD\LWD\DAD-OJ(1-6)-85-15-1ML-3UL-ALL-50MIN.M
Last changed    : 9/1/2018 12:24:09 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  43.047 BV    1.2825 6.58445e4   764.77026  49.0214
   2  46.652 VB    1.5342 6.84735e4   656.86407  50.9786

Totals :                  1.34318e5  1421.63434
```

Data File D:\DATA\HY\HY-4-17-6 20180828\HY-4-17-6 20180828 2018-08-28 11-47-51\043-1201.D
Sample Name: HY-4-17-5

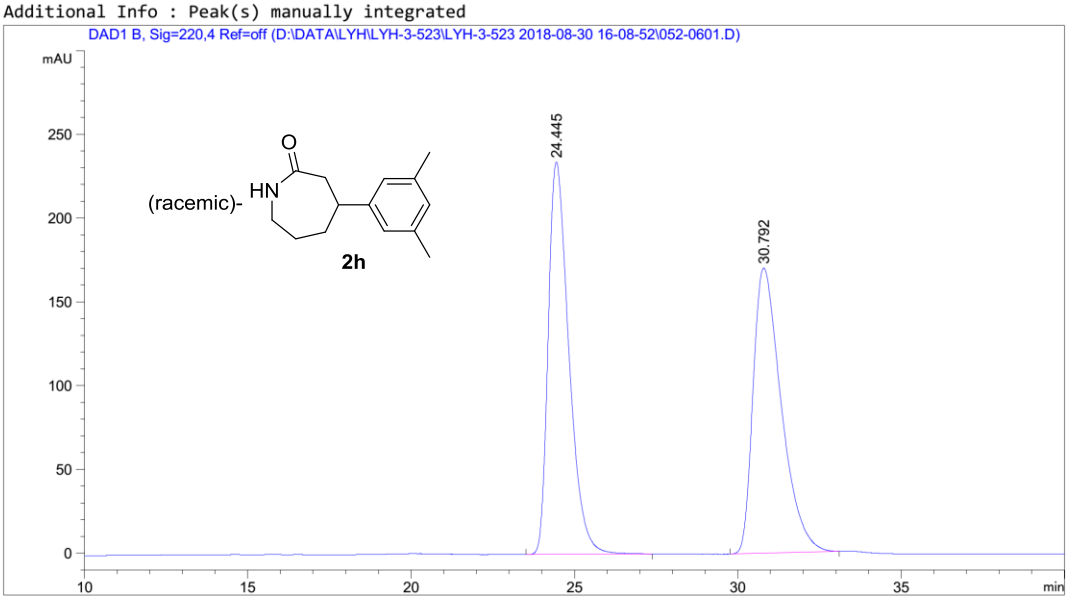
```
======================================================================
Acq. Operator   :                                Seq. Line :  12
Acq. Instrument : Instrument 2                    Location : Vial 43
Injection Date  : 8/28/2018 6:05:28 PM                 Inj :   1
                                                 Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\HY\HY-4-17-6 20180828\HY-4-17-6 20180828 2018-08-28 11-47-51\DAD-OD
                  (1-2)-90-10-0.5ML-3UL-ALL-60MIN.M
Last changed    : 8/28/2018 11:44:59 AM
Analysis Method : D:\METHOD\LWD\DAD-OJ(1-6)-85-15-1ML-3UL-ALL-50MIN.M
Last changed    : 9/1/2018 12:26:01 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  43.415 BV    1.1340 7720.46631  101.43162   3.5864
   2  45.751 VB    1.4496 2.07551e5  1880.57080  96.4136

Totals :                  2.15272e5  1982.00242
```

Data File D:\DATA\LYH\LYH-3-523\LYH-3-523 2018-08-30 16-08-52\052-0601.D
Sample Name: HY-4-21-6

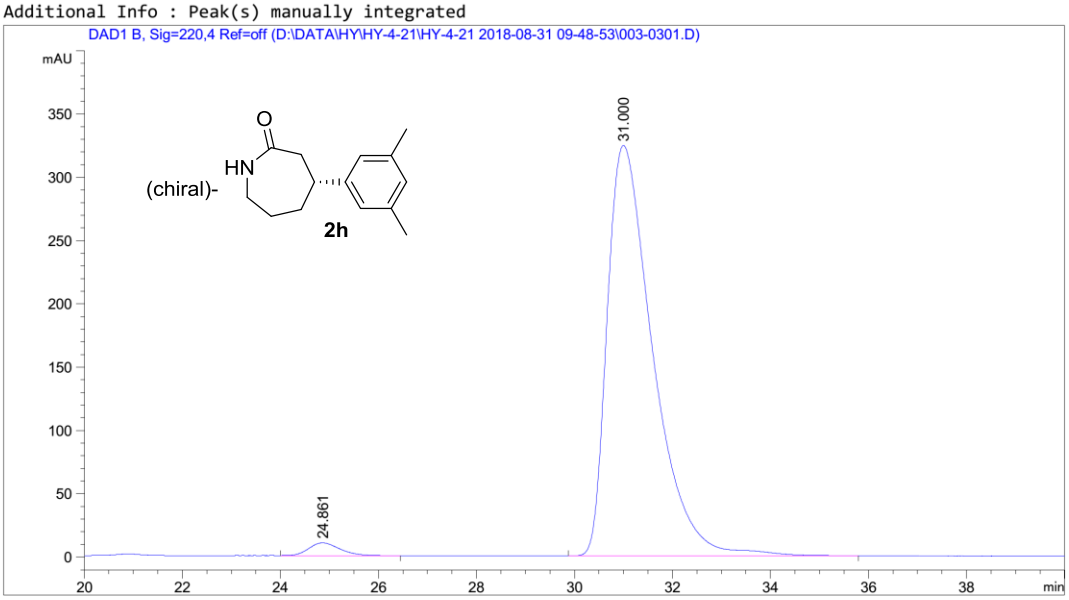
```
======================================================================
Acq. Operator   :                                Seq. Line :   6
Acq. Instrument : Instrument 2                    Location : Vial 52
Injection Date  : 8/30/2018 8:19:50 PM                 Inj :   1
                                                 Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\LYH\LYH-3-523\LYH-3-523 2018-08-30 16-08-52\DAD-OD(1-2)-90-10-0.5ML
                  -3UL-ALL-60MIN.M
Last changed    : 8/28/2018 11:44:59 AM
Analysis Method : D:\METHOD\LWD\DAD-OJ(1-6)-85-15-1ML-3UL-ALL-50MIN.M
Last changed    : 9/1/2018 12:16:19 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.445 BB    0.6744 1.02854e4   234.17816  50.2120
   2  30.792 BB    0.9169 1.01985e4   170.24193  49.7880

Totals :                  2.04839e4   404.42009
```

Data File D:\DATA\HY\HY-4-21\HY-4-21 2018-08-31 09-48-53\003-0301.D
Sample Name: HY-4-21-5

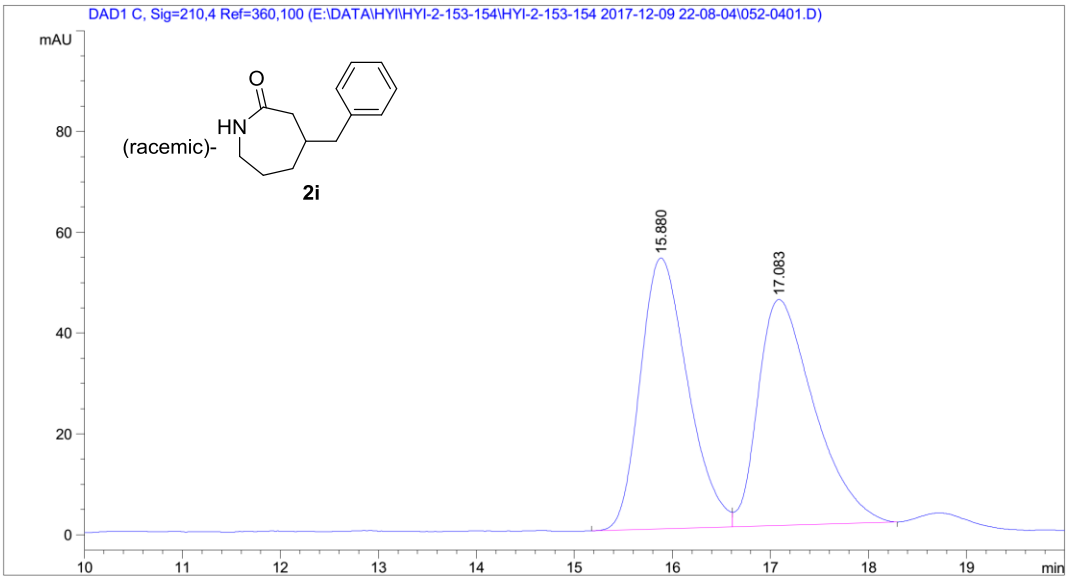
```
======================================================================
Acq. Operator   :                                Seq. Line :   3
Acq. Instrument : Instrument 2                    Location : Vial 3
Injection Date  : 8/31/2018 10:42:20 AM               Inj :   1
                                                 Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\HY\HY-4-21\HY-4-21 2018-08-31 09-48-53\DAD-OD(1-2)-90-10-0.5ML-3UL-
                  ALL-60MIN.M
Last changed    : 8/28/2018 11:44:59 AM
Analysis Method : D:\METHOD\LWD\DAD-OJ(1-6)-85-15-1ML-3UL-ALL-50MIN.M
Last changed    : 9/1/2018 12:20:50 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.861 BB    0.6227  443.65598   10.09456   2.0801
   2  31.000 BB    0.9697 2.08851e4   324.16504  97.9199

Totals :                  2.13288e4   334.25960
```

Data File E:\DATA\HYI\HYI-2-153-154\HYI-2-153-154 2017-12-09 22-08-04\052-0401.D
Sample Name: HYI-2-153-5

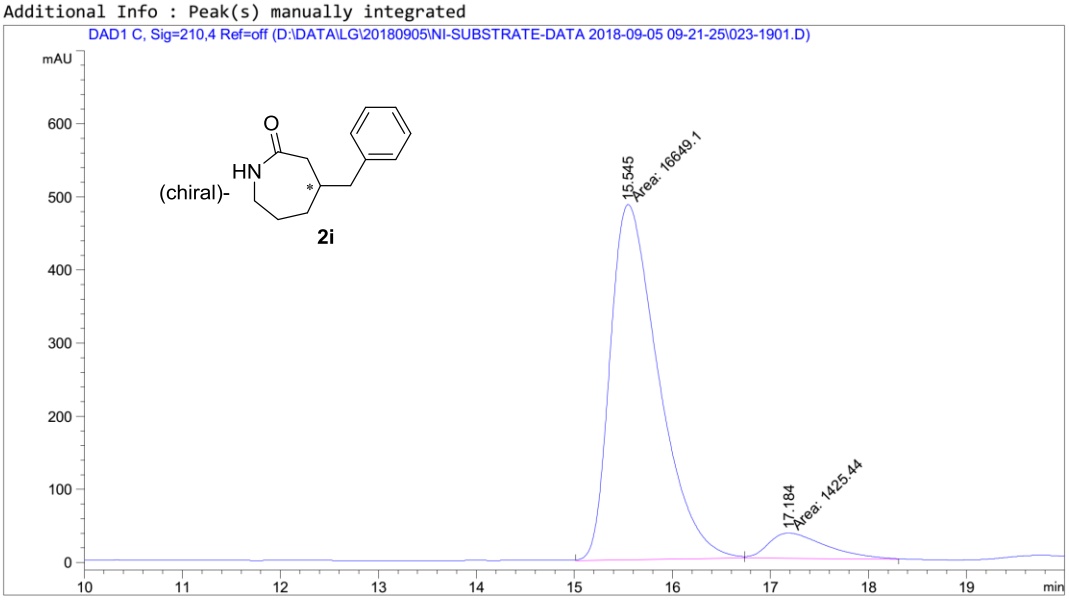
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   4
Acq. Instrument : 1260HPLC-DAD                  Location : Vial 52
Injection Date  : 12/10/2017 12:15:17 AM             Inj :   1
                                               Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\HYI\HYI-2-153-154\HYI-2-153-154 2017-12-09 22-08-04\DAD-OD(1-2)-90-
                  10-1ML-2UL-ALL-60MIN.M
Last changed    : 12/9/2017 10:08:04 PM by SYSTEM
Analysis Method : E:\DATA\HYI\HYI-2-153-154\HYI-2-153-154 2017-12-09 22-08-04\DAD-OD(1-2)-90-
                  10-1ML-2UL-ALL-60MIN.M (Sequence Method)
Last changed    : 9/5/2018 5:40:07 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.880 BV    0.5143 1808.72571   53.78516  50.3141
   2  17.083 VB    0.6007 1786.13989   44.84090  49.6859

Totals :                  3594.86560   98.62606
```

Data File D:\DATA\LG\20180905\NI-SUBSTRATE-DATA 2018-09-05 09-21-25\023-1901.D
Sample Name: HY-4-24-2

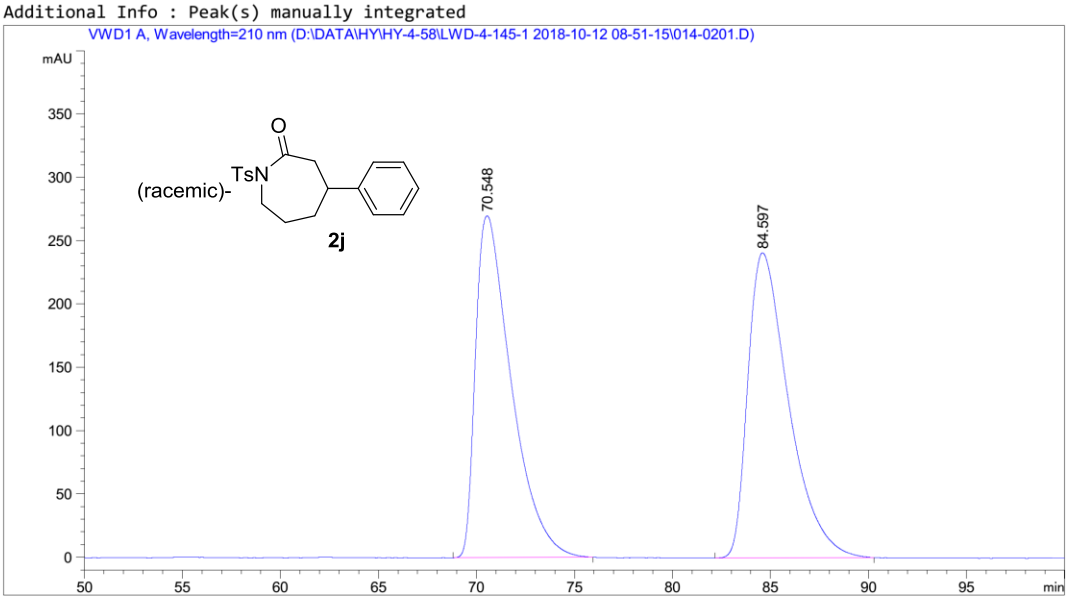
```
=====================================================================
Acq. Operator   :                              Seq. Line :  19
Acq. Instrument : Instrument 2                  Location : Vial 23
Injection Date  : 9/5/2018 2:17:49 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\LG\20180905\NI-SUBSTRATE-DATA 2018-09-05 09-21-25\DAD-OD(1-2)-90-10
                  -1ML-3UL-ALL-30MIN.M
Last changed    : 9/5/2018 9:43:34 AM
Analysis Method : D:\METHOD\CZY\DAD-OD(1-2)-97-3-1ML-5UL-ALL-25MIN.M
Last changed    : 9/5/2018 5:36:10 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.545 MM    0.5711 1.66491e4   485.86322  92.1136
   2  17.184 MM    0.6819 1425.43518   34.83768   7.8864

Totals :                  1.80746e4   520.70090
```

Data File D:\DATA\HY\HY-4-58\LWD-4-145-1 2018-10-12 08-51-15\014-0201.D
Sample Name: Ts-20181012-RAC

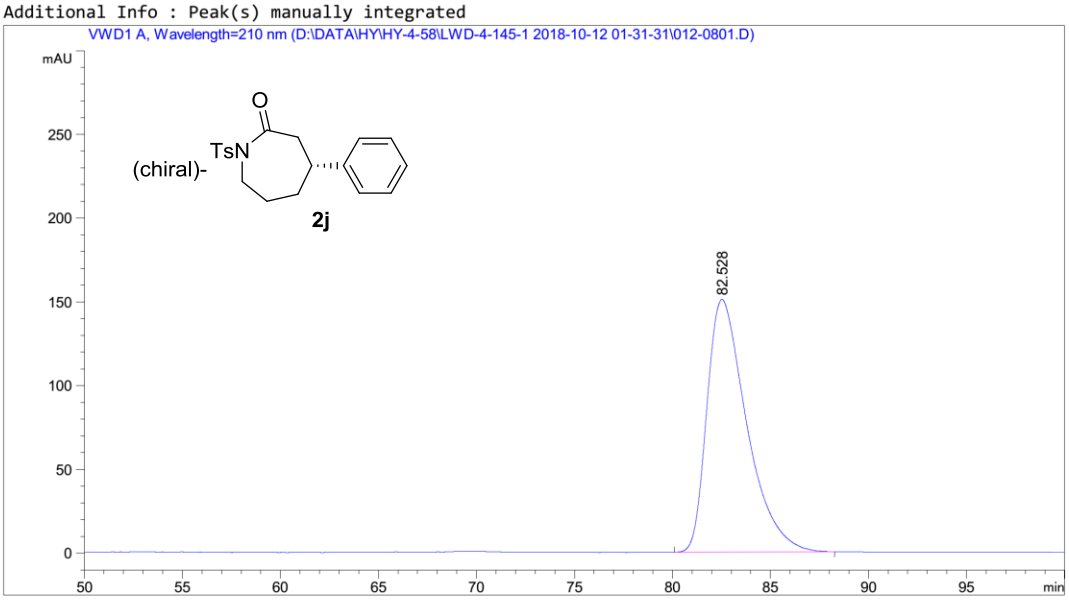
```
======================================================================
Acq. Operator   :                              Seq. Line :   2
Acq. Instrument : Instrument 1                  Location : Vial 14
Injection Date  : 10/12/2018 9:05:25 AM              Inj :   1
                                               Inj Volume : 20.000 µl
Acq. Method     : D:\DATA\HY\HY-4-58\LWD-4-145-1 2018-10-12 08-51-15\VWD-AD(1-2)-95-5-1ML-1UL
                  -210NM-100MIN.M
Last changed    : 10/12/2018 9:05:46 AM
                  (modified after loading)
Analysis Method : D:\DATA\HY\HY-4-58\LWD-4-145-1 2018-10-12 08-51-15\014-0201.D\DA.M (VWD-AD(
                  1-2)-95-5-1ML-1UL-210NM-100MIN.M, From Data File)
Last changed    : 10/12/2018 11:46:28 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  70.548 BB    1.8832 3.42851e4   269.87137  49.5972
   2  84.597 BB    2.0729 3.48420e4   240.97566  50.4028

Totals :                  6.91272e4   510.84703
```

Data File D:\DATA\HY\HY-4-58\LWD-4-145-1 2018-10-12 01-31-31\012-0801.D
Sample Name: HY-4-58-1

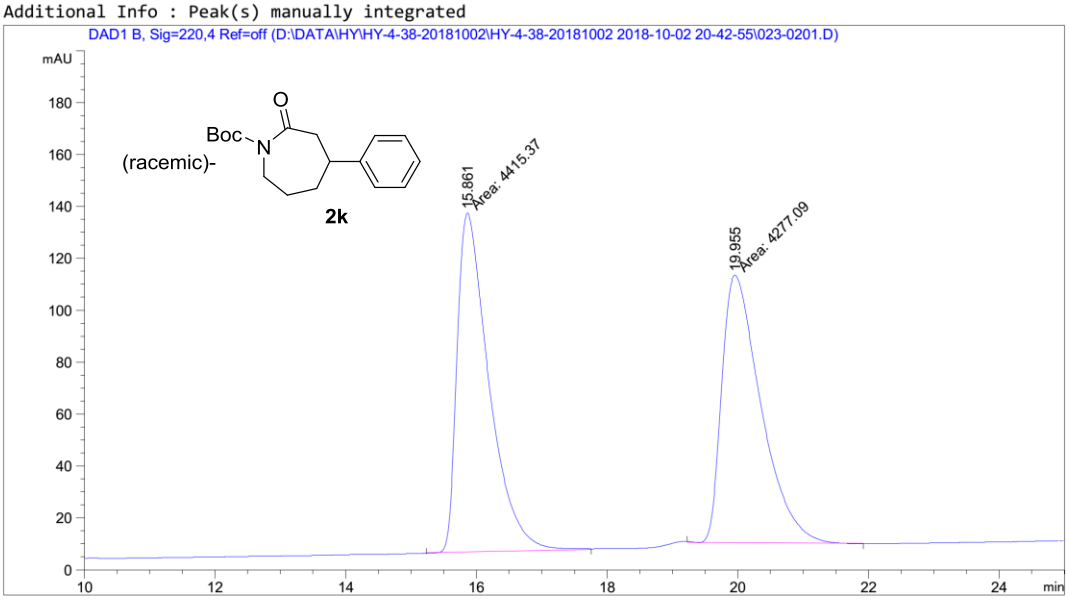
```
======================================================================
Acq. Operator   :                                Seq. Line :   8
Acq. Instrument : Instrument 1                    Location : Vial 12
Injection Date  : 10/12/2018 6:18:32 AM               Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : D:\DATA\HY\HY-4-58\LWD-4-145-1 2018-10-12 01-31-31\VWD-AD(1-2)-95-5-1ML-1UL
                  -210NM-100MIN.M
Last changed    : 10/12/2018 7:48:06 AM
                  (modified after loading)
Analysis Method : D:\DATA\HY\HY-4-58\LWD-4-145-1 2018-10-12 01-31-31\012-0801.D\DA.M (VWD-AD(
                  1-2)-95-5-1ML-1UL-210NM-100MIN.M, From Data File)
Last changed    : 10/12/2018 11:48:06 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  82.528 BB    2.0348 2.12238e4   150.90871 100.0000

Totals :                  2.12238e4   150.90871
```

Data File D:\DATA\HY\HY-4-38-20181002\HY-4-38-20181002 2018-10-02 20-42-55\023-0201.D
Sample Name: HY-4-38-1

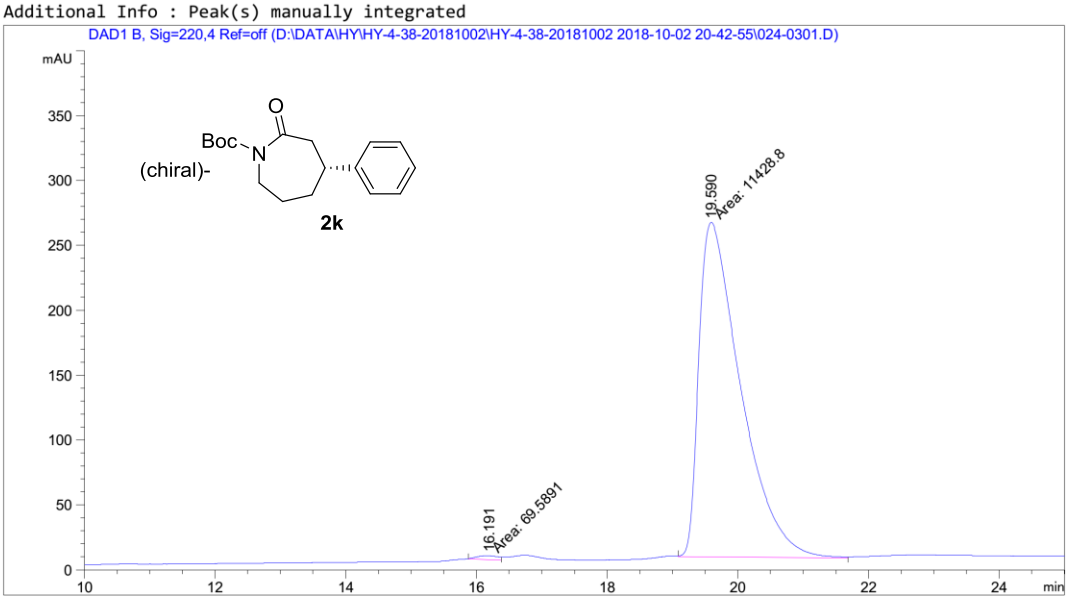
```
======================================================================
Acq. Operator   :                                Seq. Line :   2
Acq. Instrument : Instrument 2                    Location : Vial 23
Injection Date  : 10/2/2018 9:14:58 PM                 Inj :   1
                                                 Inj Volume : 2.000 µl
Acq. Method     : D:\DATA\HY\HY-4-38-20181002\HY-4-38-20181002 2018-10-02 20-42-55\DAD-OD(1-2
                  )-98-2-1ML-1UL-ALL-30MIN.M
Last changed    : 9/29/2018 8:16:43 AM
Analysis Method : D:\METHOD\LWD\DAD-OD(1-2)-80-20-1ML-5UL-ALL-80MIN.M
Last changed    : 10/18/2018 8:19:21 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.861 MM    0.5642 4415.36914  130.43875  50.7954
   2  19.955 MM    0.6923 4277.08545  102.97542  49.2046

Totals :                  8692.45459  233.41417
```

Data File D:\DATA\HY\HY-4-38-20181002\HY-4-38-20181002 2018-10-02 20-42-55\024-0301.D
Sample Name: HY-4-38-2

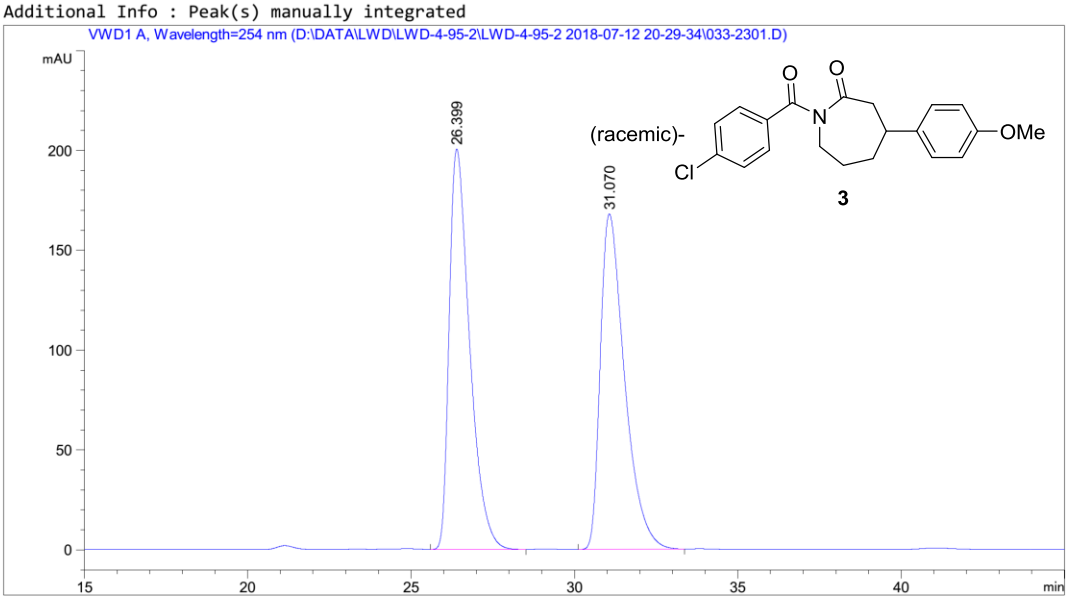
```
======================================================================
Acq. Operator   :                                Seq. Line :   3
Acq. Instrument : Instrument 2                    Location : Vial 24
Injection Date  : 10/2/2018 9:45:55 PM                 Inj :   1
                                                 Inj Volume : 2.000 µl
Acq. Method     : D:\DATA\HY\HY-4-38-20181002\HY-4-38-20181002 2018-10-02 20-42-55\DAD-OD(1-2
                  )-98-2-1ML-1UL-ALL-30MIN.M
Last changed    : 9/29/2018 8:16:43 AM
Analysis Method : D:\METHOD\LWD\DAD-OD(1-2)-80-20-1ML-5UL-ALL-80MIN.M
Last changed    : 10/18/2018 8:26:02 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.191 MM    0.3778   69.58908    3.06972   0.6052
   2  19.590 MM    0.7392 1.14288e4   257.67871  99.3948

Totals :                  1.14984e4   260.74843
```

Data File D:\DATA\LWD\LWD-4-95-2\LWD-4-95-2 2018-07-12 20-29-34\033-2301.D
Sample Name: HY-3-170-RAC

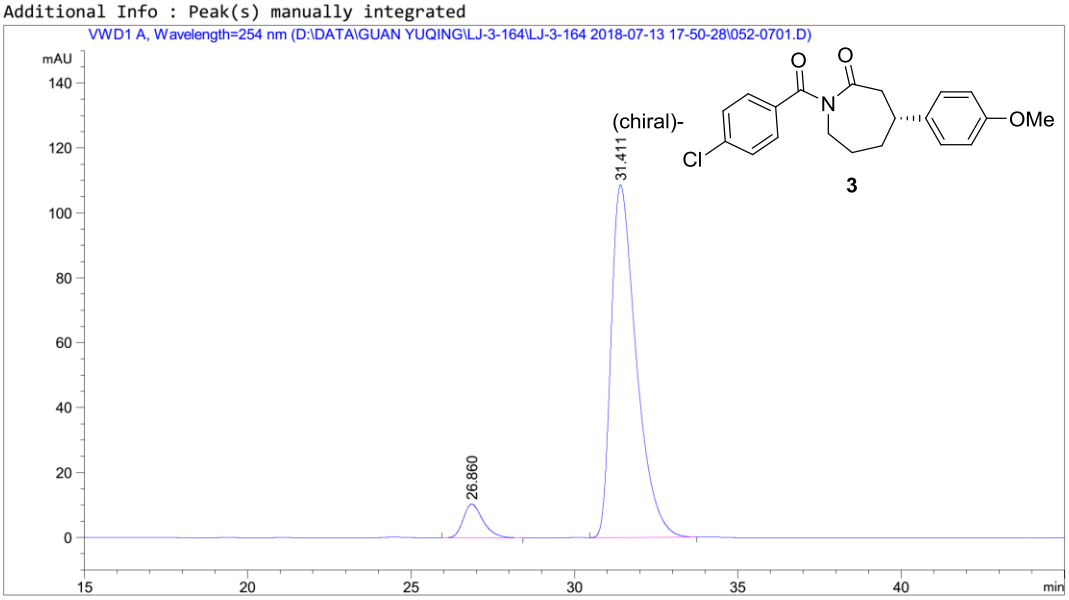
```
======================================================================
Acq. Operator   :                          Seq. Line :  23
Acq. Instrument : Instrument 1              Location : Vial 33
Injection Date  : 7/13/2018 2:31:37 PM           Inj :   1
                                          Inj Volume : 2.000 µl
Acq. Method     : D:\DATA\LWD\LWD-4-95-2\LWD-4-95-2 2018-07-12 20-29-34\VWD-AD(1-2)-90-10-1ML
                  -2UL-254NM-60MIN.M
Last changed    : 7/13/2018 10:23:58 AM
Analysis Method : D:\METHOD\CZY\VWD-AD(1-2)-97-3-1ML-3UL-210NM-10MIN.M
Last changed    : 7/18/2018 11:13:35 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.399 BB    0.6608 8693.81152  200.52046  50.0285
   2  31.070 BB    0.7882 8683.89063  167.96379  49.9715

Totals :                  1.73777e4   368.48425
```

Data File D:\DATA\GUAN YUQING\LJ-3-164\LJ-3-164 2018-07-13 17-50-28\052-0701.D
Sample Name: HY-3-157-CHIRAL

```
======================================================================
Acq. Operator   :                              Seq. Line :   7
Acq. Instrument : Instrument 1                  Location : Vial 52
Injection Date  : 7/14/2018 12:01:38 AM              Inj :   1
                                               Inj Volume : 2.000 µl
Acq. Method     : D:\DATA\GUAN YUQING\LJ-3-164\LJ-3-164 2018-07-13 17-50-28\VWD-AD(1-2)-90-10
                  -1ML-2UL-254NM-60MIN.M
Last changed    : 7/13/2018 10:23:58 AM
Analysis Method : D:\METHOD\CZY\VWD-AD(1-2)-97-3-1ML-3UL-210NM-10MIN.M
Last changed    : 7/18/2018 11:29:30 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.860 BB    0.6374  439.71262   10.41835   7.0320
   2  31.411 BB    0.8134 5813.31201  108.62247  92.9680

Totals :                  6253.02463  119.04082
```