Supporting Information

Facile solvolysis of a surprisingly twisted tertiary amide.

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Materials and Methods

Materials: Dichloromethane (EMD, OmniSolve® High Purity) was dried by the method described by Pangborn et al.[1] Oxalyl chloride (Alfa Aesar, 98%),-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid (Santa Cruz Biotech), 4-aminopyridine (Alfa Aesar, 98%), 4-methylaminopyridine (Alfa Aesar, 99%), dimethylamine (Acros Organics, 2.0 M in THF), sodium *t*-butoxide (Acros Organics, 98%), deuterochloroform (Cambridge Isotopes, 99.8% D +0.05% V/V TMS) and deuteromethanol (Cambridge Isotopes, 99.8% D +0.05% V/V TMS) were used as received.

General methods:

Synthesis of methyl 4-(methyl(pyridin-4-yl)carbamoyl)bicyclo[2.2.2]octane-1-carboxylate (**1**): A 15 mL round bottom flask was equipped with a Teflon-coated magnetic stirbar and charged with 4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid (100 mg, 473 µmol). The flask was sealed with a rubber septum and purged with dry nitrogen for 5 minutes before attaching a balloon filled with dry nitrogen. Dichloromethane (anhydrous, 4.30 mL) was added by syringe and the stirplate was set to 200 rpm. Catalytic dimethylformamide (anhydrous, 25 µL) was added by syringe after 5 minutes of stirring at 20 °C. The flask was then placed in an ice bath at 0 °C, and allowed to cool for 5 minutes. Oxalyl chloride (45 µL, 525 µmol, 1.11 equiv.) was added dropwise by syringe over the course of 30 seconds. The flask was stirred at 0 °C for 2 minutes, and then removed from the ice bath and stirred for 45 minutes at 20 °C. The reaction was cooled to 0°C and a solution of 4-methylaminopyridine (70.4 mg, 651 µmol, 1.38 equiv.) and triethylamine (140 µL, 1.01 mmol, 2.14 equiv.) in dichloromethane (anhydrous, 1.50 mL) was added dropwise by syringe over the course of 3 minutes. The reaction stirred at 0°C for 5 minutes, then stirred at 20 °C for 16 hours.

The reaction mixture was transferred to a separatory funnel containing 5% aqueous sodium bicarbonate (50 mL) and extracted with dichloromethane (3 × 50 mL). The organic extracts were combined and dried over anhydrous sodium sulfate before being concentrated under reduced pressure. The crude product was purified by silica chromatography using an isocratic eluent of 2 % triethylamine in dichloromethane. The pure amide was isolated as a white crystalline solid (108.7 mg, 360 µmol, 76.1%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J_{HH} = 6.4 Hz, 2H,), 7.10 (d, J_{HH} = 6.4 Hz, 2H,), 3.55 (s, 3H, OCH_3), 3.17 (s, 3H, NCH_3) 1.72–1.59 (m, 12H,). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 177.2, 152.9, 151.4, 123.1, 51.7, 46.2, 41.9, 41.0, 38.4, 28.9, 27.9. IR (diamond, thin film) cm^{-1} 2949 (m), 2871 (m), 1720 (s, ester), 1638 (s, amide), 1583 (s), 1256 (s), 728 (s), 591 (s).

Synthesis of methyl 4-(pyridin-4-ylcarbamoyl)bicyclo[2.2.2]octane-1-carboxylate (**2**): The synthesis, workup and purification procedures were the same as for the

synthesis of **1**, but using 4-aminopyridine instead of 4-methylaminopyridine. The product was isolated as a white crystalline solid (58.6%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J_{HH} = 6.4 Hz, 2H,), 8.07 (br, 1H, N-H), 7.54 (d, J_{HH} = 6.4 Hz, 2H,), 3.61 (s, 3H, OCH_3), 1.91–1.78 (m, 12H). (400 MHz, $CDCl_3$) δ 177.6, 176.2, 150.8, 145.1, 113.8, 52.0, 40.3, 38.7, 28.2, 27.9. IR (diamond, thin film) cm^{-1} 3230 (w), 3162 (w), 2951 (m), 2871 (m), 1717 (s, ester), 1675 (s, amide), 1588 (s), 1507 (s), 1327 (s), 1252 (s), 1078 (s), 908 (s), 724 (s), 645 (s), 573 (s), 537 (s).

Synthesis of methyl 4-(dimethylcarbamoyl)bicyclo[2.2.2]octane-1-carboxylate (**3**): The synthesis, workup and purification procedures were the same as for the synthesis of **1**, but using 4.0 equiv of dimethylamine instead of 4-methylaminopyridine and triethylamine. The product was isolated as a white crystalline solid (82.2%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 3H, OCH_3), 2.98 (s, 6H N-CH_3), 1.91–1.85 (m, 6H), 1.81–1.74 (m, 6H). (400 MHz, $CDCl_3$) δ 178.0, 176.2, 51.7, 39.6, 38.9, 38.6, 28.0, 27.6. IR (diamond, thin film) cm^{-1} 2949 (m), 2920 (m), 2868 (m), 1714 (s), 1614 (s), 1379 (s), 1254 (s), 1070 (s).

*Solvolysis of compounds **1**–**3**:* Solutions (100 mM, 600 μL) of the amides in deuteromethanol were prepared in 1-dram vials, and then transferred to 5 mm NMR tubes. For each, sample, a ^{1}H NMR spectrum (8 scans) was taken at 22 °C. Then the tube was ejected from the spectrometer. A solution of sodium *t*-butoxide in deuteromethanol (300 mM, 200 μL) was added in one portion. The NMR tube was turned up-side-down and right-side-up 3 times to mix the contents before being inserted into the spectrometer, for 4 successive ^{1}H NMR spectra. The first spectrum was finished approximately 5 minutes after butoxide addition, the next three occurred at 20, 40 and 60 minutes after butoxide addition. This process was repeated for samples of each compound. (see spectra on pages S7–S9)

X-ray crystallography

Low-temperature diffraction data (ω-scans) were collected for (1) on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD or for (2) on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate with Mo Kα radiation (λ = 0.71073 Å) for the both structures. Data was processed and absorption corrected with CrystalClear.[2] All structures were solved by direct methods using SHELXT and were refined against F^2 on all data by full-matrix least squares with SHELXL.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The Fourier map of (**1**) revealed two crystallographically independent but chemically identical molecules in the asymmetric unit that are related by a pseudo-inversion center. Attempts to find a higher symmetry space group did not reveal any alternate choices. In the crystallographic modeling of (**2**), hydrogen H1 was found in the difference map and

freely refined. Atoms H1 and H13 participate in hydrogen bonding. H13 was geometrically placed, but the donor/acceptor distance of C13/O1 was freely refined. The donor/acceptor pair that involved H1 was between N1 and N2_$1, where _$1 denotes the symmetry operation x-1/2, -y+1/2, z+1/2. The full numbering scheme of (**1**) and (**2**) can be found below. Full details of the X-ray structure determination are in the CIF included as Supporting Information. CCDC number 1423262 (**1**) and 1423261 (**2**) contain the supplementary crystallographic data for this paper.

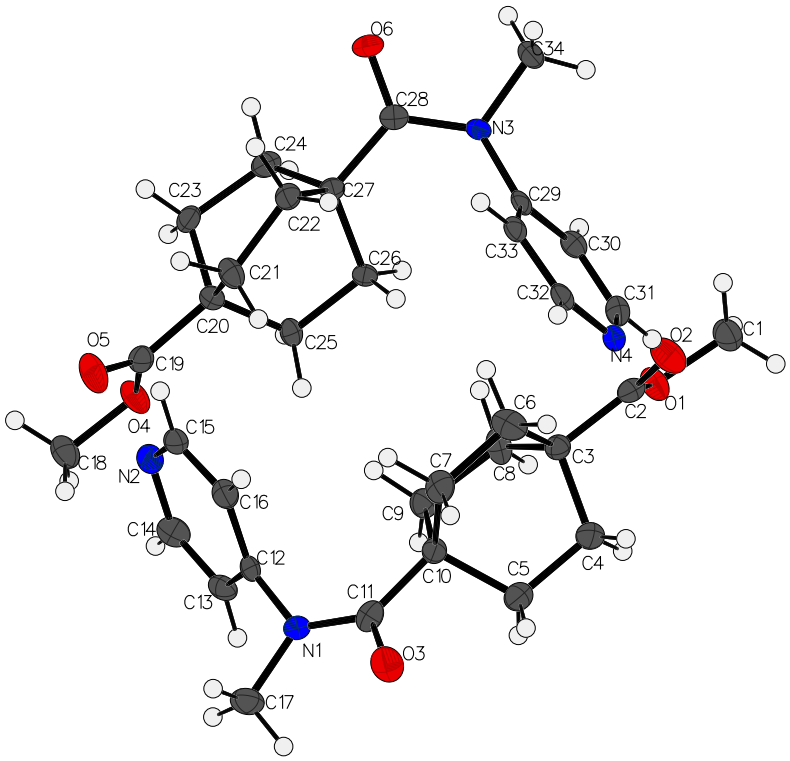


Figure S1. The full numbering scheme of the asymmetric unit of (**1**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as arbitrary spheres.

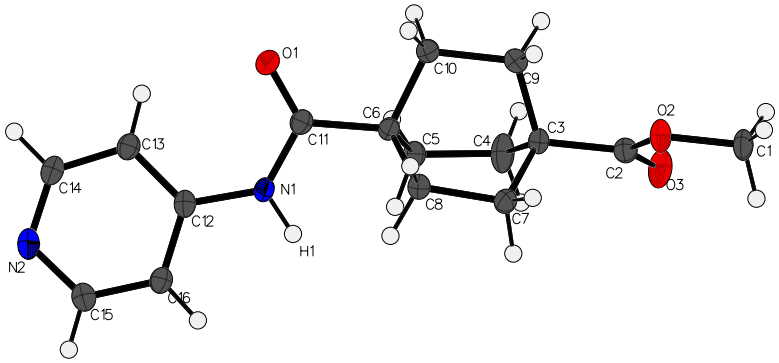


Figure S2. The full numbering scheme of asymmetric unit in (**2**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as arbitrary spheres.

Table S1. Crystallographic Parameters of (**1**) and (**2**)

Identification code	(**1**)		(**2**)	
Empirical formula	$C_{17}H_{22}N_2O_3$		$C_{16}H_{20}N_2O_3$	
Formula weight	302.36		207.21	
Temperature	93(2) K		93(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Triclinic		Monoclinic	
Space group	$P\bar{1}$		P $2_1/n$	
Unit cell dimensions	a = 7.1666(8) Å	α=75.729(5)°	a=6.53400(10)Å	α = 90°
	b = 10.5180(12)Å	β=82.329(6)°	b =25.7728(5) Å	β=97.402(7)°
	c = 20.800(3) Å	γ=82.895(6)°	c = 8.4563(6) Å	γ = 90°
Volume	1499.1(3) $Å^3$		1412.17(11) $Å^3$	
Z	4		4	
Absorption coefficient	0.092 mm^{-1}		0.073 mm^{-1}	
F(000)	648		436	
Crystal size	0.320 x 0.200 x 0.190 mm^3		0.210 x 0.200 x 0.190 mm^3	
Crystal color and habit	Colorless Prism		Colorless Block	
Theta range for data collection	3.049 to 25.025°.		3.162 to 27.485°.	
Index ranges	$-8 \le h \le 8, -12 \le k \le 12, -24 \le l \le 24$		$-8 \le h \le 8, -33 \le k \le 33, -10 \le l \le 10$	
Reflections collected	12190		38962	
Independent reflections	5281 [R(int) = 0.0728]		3235 [R(int) = 0.0500]	
Observed reflections (I > 2σ (I))	3493		2638	
Completeness to theta = 25.242°	99.6 %		99.9 %	
Max. and min. transmission	0.983 and 0.820		0.986 and 0.902	
Data / restraints / parameters	5281 / 0 / 401		3235 / 0 / 195	
Goodness-of-fit on F^2	1.130		1.145	
Final R indices [I>2σ (I)]	R1 = 0.0837, wR2 = 0.1191		R1 = 0.0414, wR2 = 0.1033	
R indices (all data)	R1 = 0.1399, wR2 = 0.1324		R1 = 0.0506, wR2 = 0.1081	
Largest diff. peak and hole	0.233 and -0.230 e.$Å^{-3}$		0.374 and -0.221 e.$Å^{-3}$	

Computational Details

All computations were performed with the Gaussian 09[4] suite of programs. Structural models of the two conformers 1 & 2, as well as the two truncated model structures 12 & 13 (Cartesian coordinates given in SI) were prepared by DFT optimization in gas phase using a generalized gradient approximation (GGA) functional : B3LYP[5,6] & a hybrid meta-GGA functional : ωB97XD[7–10] with 6-31+G(2d,p)[11] basis set.

For the truncated model structures, default Gaussian 09 values were adopted for the numerical integration grids and self-consistent-field (SCF) and geometry optimization convergence criteria, whereas for the bent & extended conformers, a quadratically convergent SCF procedure[12] was used.

Complete list of xyz coordinates for optimized structures

Structure	bent-12	
Functional	B3LYP	
Basis set	6-31+G(2d,p)	
Energy	-495.514900	

O	3.21319200	-0.04372400	0.01964400
N	1.02663000	0.49276800	-0.18945300
N	-3.13329700	-0.27865300	0.05871600
C	2.04757700	-0.39054200	0.13323900
C	-0.35816000	0.21188100	-0.09461400
C	-1.21630800	1.08629500	0.58333900
H	-0.83286700	1.97081000	1.07903700
C	-2.57789200	0.79680000	0.62736900
H	-3.25527500	1.46406000	1.15518200
C	-2.30851000	-1.10339000	-0.59493600
H	-2.76962700	-1.96722200	-1.06809700
C	-0.93458500	-0.90391300	-0.71064100
H	-0.33249400	-1.59397900	-1.28877100
C	1.43160000	1.86069500	-0.53870500
H	0.62081800	2.34169000	-1.08692900
H	2.32423700	1.81298900	-1.16265400
H	1.67385900	2.45168100	0.35185300
C	1.69890900	-1.76866600	0.66387700
H	0.77103300	-1.79559500	1.23778400
H	1.61144000	-2.48167100	-0.16213200
H	2.53422200	-2.08674500	1.28916700

	Structure	bent-12	
	Functional	ωB97XD	
	Basis set	6-31+G(2d,p)	
	Energy	-495.349217	
O	3.19582900	-0.07158500	0.06117200
N	1.03256400	0.48259100	-0.21922600
N	-3.11231000	-0.26009000	0.07679100
C	2.02802800	-0.40182400	0.14408800
C	-0.35124600	0.21712500	-0.11493200
C	-1.18219000	1.06874000	0.61183400
H	-0.77819700	1.93074700	1.13012600
C	-2.54106800	0.78721800	0.67174800
H	-3.20311100	1.43597900	1.23904000
C	-2.31059000	-1.06193200	-0.62374400
H	-2.78764700	-1.90512600	-1.11635500
C	-0.94200100	-0.86655200	-0.76094900
H	-0.35114400	-1.53625600	-1.37365200
C	1.45062400	1.83857900	-0.56414600
H	0.62831200	2.34158600	-1.07438300
H	2.31612500	1.78737500	-1.22535900
H	1.73726400	2.41047100	0.32503600
C	1.63802700	-1.76599100	0.67213700
H	0.71476000	-1.75616500	1.25426700
H	1.51201000	-2.46930600	-0.15585400
H	2.46571700	-2.11632400	1.28858400

	Structure	extended-12	
	Functional	B3LYP	
	Basis set	6-31+G(2d,p)	
	Energy	-495.511833	
O	-1.61353600	-1.68645300	-0.46853500
N	-0.98558800	0.42119800	0.16883100
N	3.19989300	-0.26350000	-0.05942800
C	-1.92818700	-0.55259100	-0.15353000
C	0.40801800	0.16123200	0.07321200
C	1.28336300	1.16713700	-0.35660700
H	0.92237700	2.13991100	-0.66741600
C	2.65068700	0.90373500	-0.40282100
H	3.33566200	1.67908300	-0.73886300
C	2.35473600	-1.21812200	0.34849100
H	2.80583700	-2.16662600	0.63025900
C	0.97357700	-1.06867700	0.43392300

H	0.35786600	-1.89064800	0.76558100
C	-1.39214900	1.80181000	0.44224700
H	-2.34432700	1.81680100	0.96984000
H	-1.49055500	2.40082600	-0.47197000
H	-0.64831000	2.27074800	1.08835800
C	-3.39156500	-0.14335500	-0.10422600
H	-3.60269300	0.72343400	-0.73832900
H	-3.97254300	-0.99572100	-0.45496000
H	-3.70604100	0.10291500	0.91582500

Structure	extended-12
Functional	ωB97XD
Basis set	6-31+G(2d,p)
Energy	-495.345181

O	-1.58612000	-1.67256600	-0.50397200
N	-0.98525600	0.41341600	0.19122700
N	3.18369500	-0.25401900	-0.06964300
C	-1.91183300	-0.55373100	-0.16629400
C	0.40444600	0.16140100	0.08506100
C	1.26349900	1.15571800	-0.38422800
H	0.89050700	2.11593600	-0.71985800
C	2.62756100	0.89743000	-0.43848900
H	3.30635400	1.66374300	-0.80421800
C	2.35109000	-1.19763400	0.37463400
H	2.81079800	-2.13494700	0.67638700
C	0.97465700	-1.05082600	0.47465900
H	0.36444400	-1.86389900	0.83873200
C	-1.39620200	1.78260000	0.47637200
H	-2.33417000	1.78867600	1.03025300
H	-1.52358900	2.38062500	-0.43421500
H	-0.64019000	2.25586800	1.10465400
C	-3.37275900	-0.15178600	-0.11992200
H	-3.57583100	0.74191300	-0.71656300
H	-3.94772500	-0.98876200	-0.51300800
H	-3.69345900	0.04656300	0.90776100

Structure	bent-13
Functional	B3LYP
Basis set	6-31+G(2d,p)
Energy	-456.233444

O	-3.29493100	-0.76551600	-0.16890000
N	-1.05466700	-0.74737600	-0.21707900

N	3.01724200	0.34726200	0.07096400
C	-2.27491800	-0.11869600	-0.00622200
C	0.27681500	-0.32666600	-0.11278600
C	1.25658700	-1.29444900	0.15809600
H	0.97814800	-2.33201000	0.31511000
C	2.58956200	-0.91062700	0.23440800
H	3.35392600	-1.65474200	0.44533000
C	2.07953800	1.26041400	-0.19589500
H	2.43155300	2.27890000	-0.34353600
C	0.71704600	0.98830900	-0.30796900
H	0.03833500	1.78743500	-0.56918200
C	-2.30884200	1.32354800	0.44385100
H	-1.52695400	1.55530700	1.17111800
H	-2.18877700	1.99228500	-0.41509500
H	-3.29174500	1.50363100	0.87980200
H	-1.18778600	-1.73687000	-0.39044800

Structure	bent-13
Functional	ωB97XD
Basis set	6-31+G(2d,p)
Energy	-456.077836

O	-3.29577000	-0.69965100	-0.19506600
N	-1.06260500	-0.74628100	-0.28853000
N	2.98781300	0.34535100	0.09427300
C	-2.25476000	-0.10615500	-0.00412500
C	0.26872100	-0.33893600	-0.15249100
C	1.23081300	-1.29053200	0.19449100
H	0.94743300	-2.31914100	0.39112700
C	2.55757500	-0.90074600	0.29738200
H	3.31462000	-1.63164300	0.56834300
C	2.06387400	1.24235600	-0.24598900
H	2.42253900	2.25238900	-0.42674900
C	0.71112500	0.96170400	-0.39513000
H	0.03596900	1.74048400	-0.72160600
C	-2.22668400	1.29174200	0.56352300
H	-1.38960800	1.45431600	1.24589400
H	-2.16187700	2.02389500	-0.24677000
H	-3.17203500	1.44641400	1.08295500
H	-1.21131900	-1.71958800	-0.51882800

Structure	extended-13
Functional	B3LYP
Basis set	6-31+G(2d,p)

Energy -456.237923

O	-2.11709400	1.38575400	-0.00440800
N	-1.05250800	-0.64313000	-0.00561000
N	3.06882400	0.26659200	0.00346300
C	-2.17115300	0.17077400	-0.00303900
C	0.30266300	-0.28590300	-0.00286500
C	1.25496900	-1.31592400	-0.00230900
H	0.94910600	-2.35863500	-0.00391700
C	2.60495900	-0.98853900	0.00100000
H	3.35206600	-1.77891900	0.00120700
C	2.14981400	1.23774600	0.00308400
H	2.53292900	2.25562400	0.00511100
C	0.77064600	1.03364400	-0.00015300
H	0.08346700	1.86588600	-0.00128300
C	-3.48366100	-0.59441000	0.00731000
H	-3.59181300	-1.16401900	0.93704500
H	-4.30103900	0.12182100	-0.06877900
H	-3.54092400	-1.29888100	-0.82978200
H	-1.23066000	-1.63747200	-0.00749200

Structure extended-13
Functional ωB97XD
Basis set 6-31+G(2d,p)
Energy -456.081231

O	-2.10472200	1.38006100	-0.00805000
N	-1.05042000	-0.64551200	-0.01190400
N	3.05768100	0.26871300	0.00705800
C	-2.16152600	0.17031700	-0.00726500
C	0.30135700	-0.28731000	-0.00545600
C	1.25169000	-1.31282200	-0.00419900
H	0.95033100	-2.35620100	-0.00804300
C	2.59705800	-0.98320400	0.00199700
H	3.34563800	-1.77109300	0.00296800
C	2.13955400	1.23437600	0.00568600
H	2.52119000	2.25220600	0.00978300
C	0.76429700	1.02883500	-0.00058000
H	0.07655000	1.86058500	-0.00176900
C	-3.47251600	-0.58928400	0.01427700
H	-3.60368700	-1.08316000	0.98251200
H	-4.28468900	0.12072100	-0.13453400
H	-3.50705200	-1.35390600	-0.76759400
H	-1.23082600	-1.63749200	-0.01176700

Structure	bent-1
Functional	B3LYP
Basis set	6-31+G(2d,p)
Energy	-996.004505

O	-4.34176000	-0.65171800	-0.93964900
O	-4.32858200	-0.89147900	1.29488600
O	1.46493900	2.95301100	0.29514400
N	2.62630900	1.14327000	-0.36197700
N	3.77212000	-2.89560400	0.22447400
C	-5.67427300	-1.18950500	-0.96183500
H	-5.96671300	-1.20051400	-2.01182400
H	-6.35064200	-0.55854700	-0.38006500
H	-5.68501000	-2.20066800	-0.54787800
C	-3.76641400	-0.55155800	0.27926700
C	-2.36167800	0.02614400	0.19578500
C	-1.70276300	0.04505300	1.58959300
H	-1.52113800	-0.98447800	1.91607900
H	-2.38973800	0.48001000	2.31980100
C	-0.37689800	0.84915500	1.53500900
H	0.39054700	0.33994700	2.12641500
H	-0.50023900	1.84505300	1.97089500
C	-2.38839300	1.47689000	-0.34686700
H	-3.00408000	1.53119100	-1.24839100
H	-2.85221500	2.13059600	0.40092300
C	-0.94062900	1.93797800	-0.65017800
H	-0.74851400	1.90975900	-1.72959700
H	-0.78526400	2.96648200	-0.32441600
C	-1.47693800	-0.81033600	-0.76294000
H	-1.83315500	-0.67589700	-1.78811900
H	-1.57121100	-1.87712600	-0.53297800
C	0.00834000	-0.37091700	-0.62608400
H	0.54913100	-1.11870100	-0.04406800
H	0.47776000	-0.33579000	-1.61417700
C	0.08906600	1.01167700	0.06237900
C	1.44360800	1.75682800	0.03790200
C	2.96993400	-0.22733700	-0.16105800
C	3.40459600	-1.01164300	-1.23181200
H	3.42690000	-0.60562200	-2.23738800
C	3.78976100	-2.32739400	-0.98738000
H	4.12282200	-2.95875100	-1.80768100
C	3.36926300	-2.13341400	1.24523100
H	3.37085200	-2.60366900	2.22581000
C	2.97144500	-0.80281100	1.11076400
H	2.67832500	-0.22574100	1.98057800

C	3.78094300	2.04228500	-0.52764100
H	4.19299000	2.34693600	0.44188600
H	3.46765600	2.93899600	-1.06189300
H	4.55133400	1.51778700	-1.09524300

Structure	bent-1
Functional	ωB97XD
Basis set	6-31+G(2d,p)
Energy	-995.709380

O	-4.27835600	-0.64055600	-0.91192800
O	-4.26090400	-0.82658400	1.31666200
O	1.52148600	2.96754900	0.23897600
N	2.64981600	1.12708400	-0.35769900
N	3.50672200	-2.96444500	0.22265200
C	-5.61283600	-1.14361200	-0.91363900
H	-5.90988800	-1.18515800	-1.96101500
H	-6.27318100	-0.47806300	-0.35263200
H	-5.64785700	-2.13900500	-0.46481300
C	-3.70058600	-0.52197800	0.29362500
C	-2.29785100	0.04365900	0.19114900
C	-1.58077800	-0.04655900	1.54662800
H	-1.36209500	-1.09711200	1.76619000
H	-2.24251600	0.30561000	2.34082900
C	-0.28073400	0.78688600	1.50332000
H	0.51327100	0.26081500	2.03995900
H	-0.41387800	1.75407700	1.99760500
C	-2.34931800	1.52782000	-0.22932700
H	-3.01500100	1.65478300	-1.08714200
H	-2.76333900	2.11873200	0.59513000
C	-0.92250500	2.00112300	-0.57804400
H	-0.78135000	2.02923000	-1.66474900
H	-0.74873700	3.01033300	-0.20579800
C	-1.46310100	-0.70564300	-0.86724500
H	-1.84753200	-0.46826800	-1.86303100
H	-1.56511800	-1.78757800	-0.73659100
C	0.02288800	-0.29734800	-0.73042100
H	0.55749100	-1.08406200	-0.19525200
H	0.48347500	-0.21160600	-1.71957400
C	0.12726100	1.03947700	0.03280800
C	1.48117300	1.77290000	0.00135300
C	2.91792000	-0.25552000	-0.15659100
C	3.24463300	-1.07252300	-1.23367700
H	3.25354500	-0.67232500	-2.24128100
C	3.52566900	-2.41028100	-0.99125000

H	3.77089400	-3.07477700	-1.81537800
C	3.21924200	-2.16614000	1.24934400
H	3.22133600	-2.62944800	2.23227800
C	2.93301300	-0.81113400	1.11743400
H	2.72504100	-0.20140600	1.98908700
C	3.84435100	1.96392700	-0.46431200
H	4.24680100	2.21556000	0.52396000
H	3.59307100	2.89057600	-0.97919400
H	4.60134700	1.41702900	-1.02986500

Structure extended-1
Functional B3LYP
Basis set 6-31+G(2d,p)
Energy -996.001891

O	-4.98874900	0.80367600	-0.40537900
O	-4.99107000	-1.31595400	0.34155900
O	1.70973100	1.23508300	1.07893900
N	2.19277200	-0.47556500	-0.29806100
N	6.32994200	0.40952400	0.03563900
C	-6.42194000	0.74503500	-0.49821600
H	-6.73046400	1.72479500	-0.86266100
H	-6.85991300	0.54264500	0.48209300
H	-6.72762700	-0.03934800	-1.19481800
C	-4.37972500	-0.31626800	0.04106000
C	-2.86897200	-0.14911800	0.10960900
C	-2.19968100	-1.46980400	0.53978600
H	-2.29715200	-2.20288400	-0.26884500
H	-2.72372300	-1.89333900	1.39991700
C	-0.70720500	-1.21545700	0.87555300
H	-0.10377700	-2.06970700	0.56110200
H	-0.56555100	-1.13114900	1.95888700
C	-2.47560900	0.94800900	1.13053900
H	-3.06275900	1.85304700	0.95520700
H	-2.71928000	0.59888500	2.14078500
C	-0.95977100	1.25175200	1.00529000
H	-0.79753500	2.19983000	0.48313900
H	-0.50408100	1.36684800	1.98939600
C	-2.29946400	0.27123600	-1.26892300
H	-2.63887000	1.28356800	-1.50389200
H	-2.69035100	-0.38492300	-2.05435700
C	-0.74683700	0.19704000	-1.24010900
H	-0.41644500	-0.66572400	-1.82009400
H	-0.32098500	1.08214800	-1.72596700
C	-0.24104900	0.11833700	0.22697500

C	1.28396200	0.34011100	0.36244800
C	3.58495700	-0.14778500	-0.15800600
C	4.45373600	-1.03448500	0.47503500
H	4.08477200	-1.95376800	0.91761400
C	5.80862200	-0.71119800	0.54265100
H	6.50530500	-1.38665700	1.03371000
C	5.48343500	1.25640700	-0.56150300
H	5.92113000	2.16669000	-0.96418900
C	4.11490900	1.02773400	-0.68678100
H	3.47497400	1.75553400	-1.17118700
C	1.91873300	-1.55152000	-1.25225200
H	1.94771000	-1.18868600	-2.28769900
H	0.95428100	-2.01390600	-1.06705800
H	2.68344200	-2.32420900	-1.14402400

Structure	extended-1
Functional	ωB97XD
Basis set	6-31+G(2d,p)
Energy	-995.703217

O	-4.95933100	-0.81908900	0.32871600
O	-4.95145400	1.34399000	-0.24119800
O	1.71437300	-1.18492900	-1.12060600
N	2.16772400	0.45594600	0.33161700
N	6.28742600	-0.38056600	-0.08125100
C	-6.38092100	-0.76003900	0.42858600
H	-6.69581400	-1.75909600	0.72806800
H	-6.82195900	-0.49258200	-0.53444800
H	-6.68245800	-0.02245600	1.17580200
C	-4.34932000	0.32242500	-0.02362800
C	-2.84478500	0.15295500	-0.10255100
C	-2.16773300	1.49438200	-0.42259700
H	-2.23909400	2.15214800	0.45081100
H	-2.69740800	1.99928100	-1.23354200
C	-0.69276300	1.24433500	-0.80288700
H	-0.07015400	2.07458000	-0.46341900
H	-0.57582900	1.20636800	-1.89145000
C	-2.45628500	-0.85955500	-1.20028000
H	-3.06346000	-1.76378900	-1.11348800
H	-2.66700800	-0.41993900	-2.18162800
C	-0.95614100	-1.20192800	-1.06400800
H	-0.82248300	-2.17322300	-0.57767000
H	-0.48430700	-1.28404900	-2.04356700
C	-2.28810200	-0.38111500	1.23470800
H	-2.60686500	-1.41849200	1.36725900

H	-2.70026100	0.18933900	2.07340000
C	-0.74477500	-0.27014100	1.22612500
H	-0.44394800	0.58015800	1.83955600
H	-0.29869200	-1.16141100	1.68018500
C	-0.23838000	-0.11894100	-0.22865000
C	1.27770300	-0.33184200	-0.36821600
C	3.55541300	0.14473900	0.16792900
C	4.37131500	0.97450800	-0.58798800
H	3.95802000	1.83555000	-1.10136700
C	5.72469900	0.66878000	-0.67894400
H	6.38682300	1.29838400	-1.26740700
C	5.48882300	-1.17111300	0.63693300
H	5.96310700	-2.02553700	1.11223800
C	4.12566900	-0.95431500	0.79565600
H	3.51709000	-1.63329100	1.38126700
C	1.89454200	1.44876300	1.36096200
H	1.89044000	1.00165800	2.36242100
H	0.94543300	1.95055600	1.19350000
H	2.68031700	2.20702900	1.32870700

Structure	bent-2
Functional	B3LYP
Basis set	6-31+G(2d,p)
Energy	-956.723628

O	-4.17411700	-0.84469900	-0.94011400
O	-4.11550000	-1.11171000	1.29096200
O	1.40214100	3.16088300	0.13408700
N	2.65913600	1.38151800	-0.34578300
N	4.52735200	-2.37998800	0.15076200
C	-5.46054200	-1.48566800	-0.95723600
H	-5.76300000	-1.50374300	-2.00423100
H	-6.17755400	-0.91858200	-0.35871200
H	-5.38668100	-2.50063800	-0.55945000
C	-3.59482900	-0.71566800	0.27361200
C	-2.23945300	-0.03097300	0.18208900
C	-1.58284100	0.05364000	1.57481200
H	-1.31230600	-0.95419900	1.90717300
H	-2.30251500	0.43254100	2.30470500
C	-0.33195800	0.96789800	1.51193000
H	0.46857200	0.54737200	2.12840500
H	-0.54665800	1.96080400	1.91896500
C	-2.37574300	1.40657100	-0.37877200
H	-2.99217800	1.40237700	-1.28114400
H	-2.88900500	2.03318400	0.35986500

C	-0.96633300	1.97214600	-0.68806000
H	-0.77102000	1.94463500	-1.76657600
H	-0.88711800	3.01377300	-0.37642700
C	-1.29463400	-0.81106100	-0.76838900
H	-1.65874800	-0.71339700	-1.79493500
H	-1.31072100	-1.87940000	-0.52719800
C	0.15275200	-0.26102400	-0.63422100
H	0.74757500	-0.95848800	-0.04369000
H	0.62408400	-0.20094100	-1.62082800
C	0.12601900	1.13222600	0.03643700
C	1.43002700	1.94929500	-0.01724500
C	3.23081200	0.10266800	-0.16779000
C	4.10995100	-0.38787900	-1.13924800
H	4.29802300	0.17725700	-2.04623200
C	4.72777600	-1.61807900	-0.93023400
H	5.41245800	-2.01413800	-1.67647100
C	3.69249400	-1.89859900	1.07759100
H	3.54808800	-2.51693100	1.96047400
C	3.03609600	-0.67355200	0.97813700
H	2.40674700	-0.32607300	1.78787500
H	3.32878200	2.11643200	-0.54637900

Structure	bent-2
Functional	ωB97XD
Basis set	6-31+G(2d,p)
Energy	-956.436918

O	-4.05122000	-0.84402700	-0.85711700
O	-3.92555800	-1.09123800	1.36233200
O	1.47880700	3.25154000	-0.05766100
N	2.73017100	1.42438000	-0.24719500
N	3.99328300	-2.58557200	0.10030400
C	-5.33429100	-1.46650600	-0.82322800
H	-5.66679300	-1.51230000	-1.85969400
H	-6.02927200	-0.87476500	-0.22271500
H	-5.26104300	-2.47010300	-0.39803400
C	-3.43825800	-0.70716500	0.32875100
C	-2.09882800	-0.01089100	0.19112300
C	-1.32281200	-0.06951300	1.51563800
H	-0.99691000	-1.09957600	1.69548800
H	-1.98180900	0.19764800	2.34443900
C	-0.10893900	0.88442900	1.44930400
H	0.75242700	0.42225900	1.93700300
H	-0.31271500	1.82040600	1.97923700
C	-2.30729800	1.47311400	-0.17979100

H	-3.01365900	1.55896900	-1.00964000
H	-2.74708700	1.99558500	0.67697500
C	-0.94653700	2.09415000	-0.56076500
H	-0.85140700	2.17932800	-1.64900500
H	-0.85079600	3.10205500	-0.15711100
C	-1.24167600	-0.65018200	-0.92070400
H	-1.68715900	-0.42410700	-1.89320100
H	-1.23530000	-1.74000700	-0.81829400
C	0.20269500	-0.10483600	-0.82763400
H	0.83261000	-0.84732900	-0.33453100
H	0.61612600	0.05049000	-1.82954900
C	0.20747900	1.21571300	-0.02896000
C	1.50254200	2.03544500	-0.10438400
C	3.13839100	0.06999000	-0.12073300
C	3.55084400	-0.64315700	-1.24091500
H	3.52626700	-0.18295100	-2.22193800
C	3.96603200	-1.95919000	-1.07644700
H	4.28521900	-2.54166400	-1.93654100
C	3.61658600	-1.88535400	1.16971200
H	3.65932400	-2.40491100	2.12309900
C	3.19518100	-0.56081700	1.11689100
H	2.92318300	-0.02994900	2.02129800
H	3.47170900	2.10767800	-0.32661800

Structure	extended-2
Functional	B3LYP
Basis set	6-31+G(2d,p)
Energy	-956.738829

O	4.79813100	0.67732000	-0.77500000
O	4.90508100	-0.13042800	1.31986400
O	-1.71797300	-1.88455800	-0.32951700
N	-2.22282300	0.31950100	-0.02531100
N	-6.44181600	0.46049900	0.01579800
C	6.22024600	0.88700800	-0.73996800
H	6.47490800	1.31763300	-1.70825500
H	6.74180900	-0.06143300	-0.59083700
H	6.48532300	1.57193200	0.06890800
C	4.25192100	0.14749700	0.34107200
C	2.74904900	-0.04903300	0.19615200
C	2.14078400	-0.53794500	1.52503700
H	2.23681500	0.25180300	2.27743600
H	2.71287800	-1.38896500	1.90225100
C	0.65275300	-0.92400500	1.31338900
H	0.03422100	-0.51486800	2.12026100

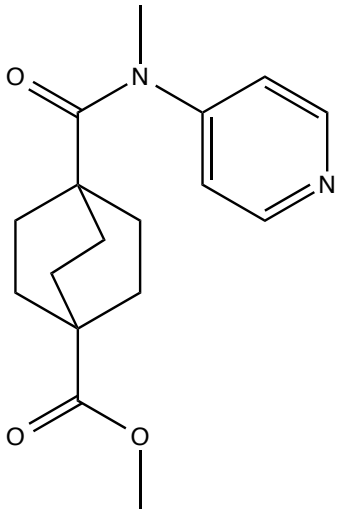
H	0.51759800	-2.00902800	1.33428700
C	2.44374800	-1.10210500	-0.90128700
H	2.99074400	-0.85812700	-1.81551200
H	2.80189500	-2.08110200	-0.56340800
C	0.91704000	-1.14464400	-1.17502200
H	0.68728400	-0.67775500	-2.14038900
H	0.55610800	-2.17334400	-1.22679200
C	2.05744700	1.27777400	-0.20875000
H	2.37713700	1.55986800	-1.21522500
H	2.37161700	2.08503500	0.46126800
C	0.51189700	1.10473600	-0.15224500
H	0.11995200	1.64207300	0.72141000
H	0.06280500	1.55556000	-1.04520600
C	0.15052100	-0.39509100	-0.05856700
C	-1.34485900	-0.73515000	-0.16648500
C	-3.62506400	0.30605700	-0.01995000
C	-4.28981100	1.53032700	0.14709500
H	-3.73272500	2.45536400	0.26804700
C	-5.67855800	1.55053200	0.15749500
H	-6.20412100	2.49390200	0.28673800
C	-5.79520900	-0.69891700	-0.14292700
H	-6.42105500	-1.58101100	-0.25759800
C	-4.40875200	-0.84447300	-0.17006500
H	-3.95155600	-1.81278100	-0.30333400
H	-1.80999100	1.23117200	0.09991200

Structure	extended-2
Functional	ωB97XD
Basis set	6-31+G(2d,p)
Energy	-956.448045

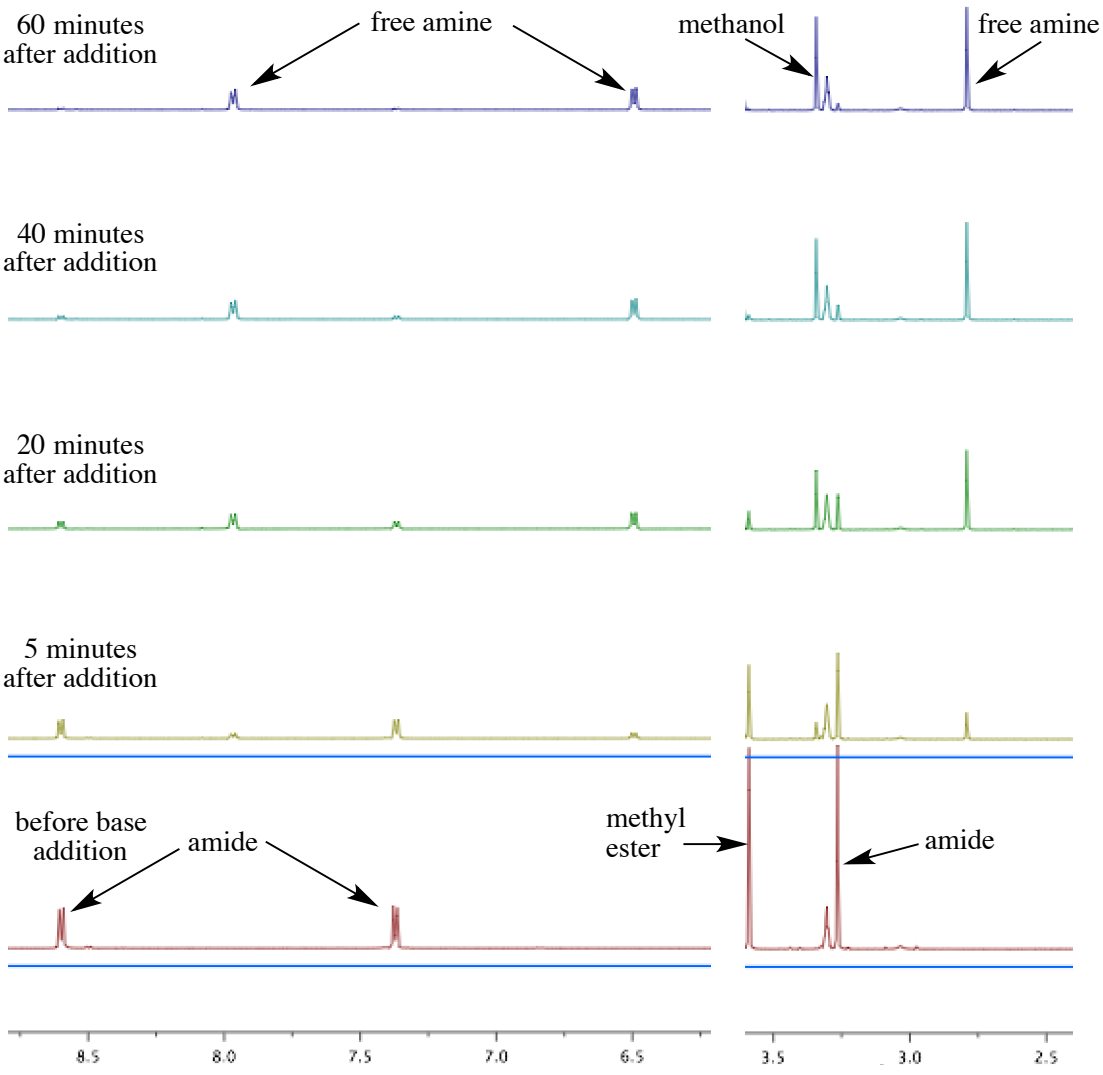
O	4.80450400	0.44799600	-0.83021200
O	4.81753000	0.24935600	1.39805800
O	-1.71019900	-1.91387700	-0.19353900
N	-2.20079300	0.30458600	-0.08950000
N	-6.40492400	0.45797600	0.01575100
C	6.21295700	0.67399700	-0.79117500
H	6.51652500	0.81125500	-1.82829800
H	6.72481000	-0.18472100	-0.35090800
H	6.44154400	1.56610600	-0.20338100
C	4.21321000	0.23901300	0.35548200
C	2.72337100	-0.00267600	0.20440700
C	2.06378400	-0.16020300	1.58234200
H	2.09748300	0.79938600	2.10837800
H	2.63613800	-0.86400100	2.19056000

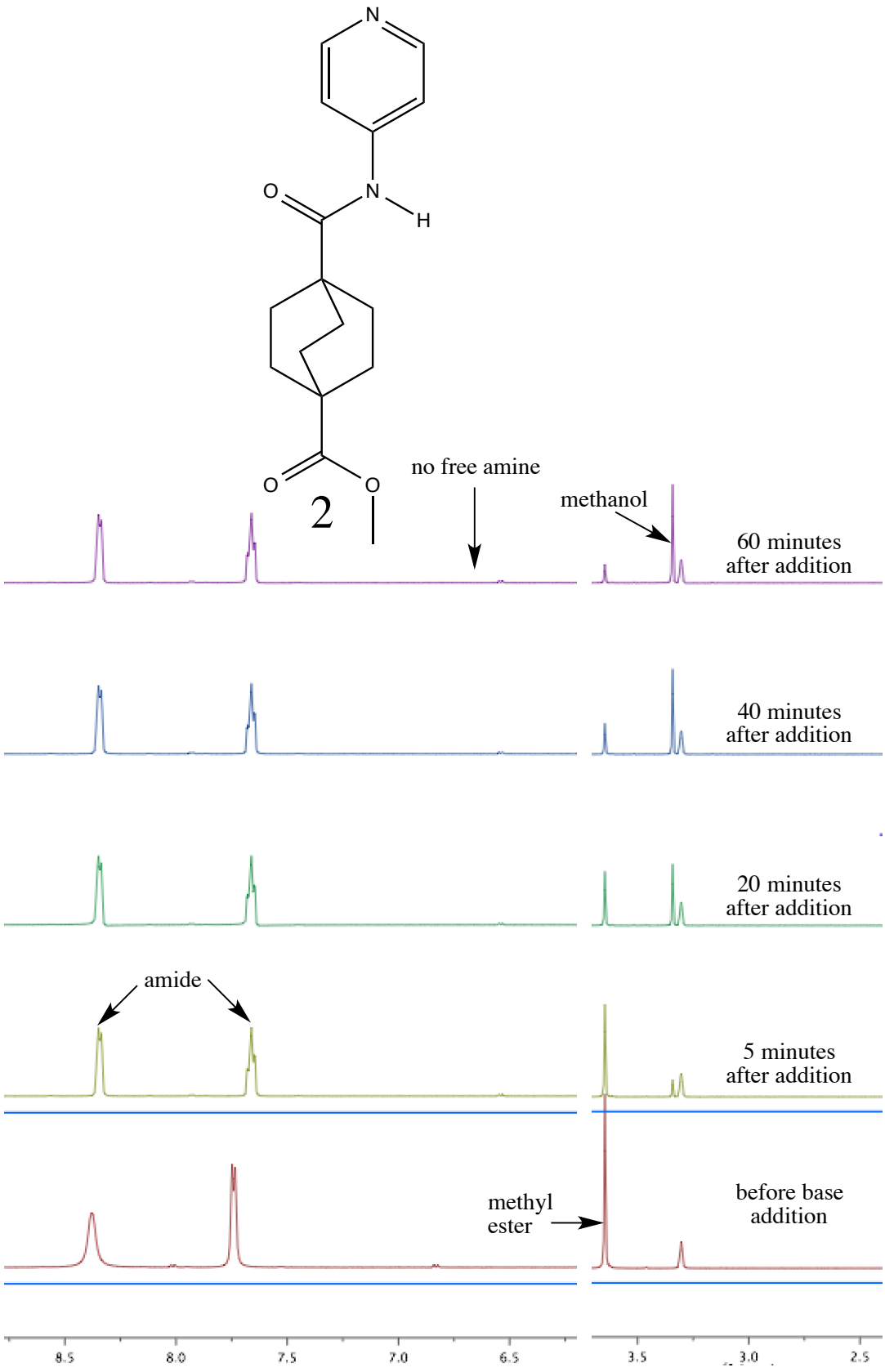
C	0.60655300	-0.64277800	1.40488900
H	-0.05830600	-0.11075600	2.09385900
H	0.51044100	-1.70891700	1.63014400
C	2.45674600	-1.28446800	-0.61497400
H	3.06196000	-1.28317200	-1.52473400
H	2.76173300	-2.15433600	-0.02279000
C	0.95416000	-1.36243800	-0.96501700
H	0.78719100	-1.08193300	-2.01127100
H	0.57420300	-2.37791000	-0.84335500
C	2.05596500	1.17811300	-0.53335500
H	2.38008000	1.18026700	-1.57754900
H	2.37694900	2.12875600	-0.09617500
C	0.51750200	1.03803200	-0.43790800
H	0.14306000	1.73424500	0.32436800
H	0.06037500	1.31443700	-1.39454000
C	0.15354800	-0.41019400	-0.05706400
C	-1.33391200	-0.76089300	-0.13924400
C	-3.59885100	0.29528900	-0.05913900
C	-4.25598700	1.52708000	0.02024900
H	-3.69808700	2.45814700	0.05633300
C	-5.64045900	1.55059300	0.05433500
H	-6.16210400	2.50202900	0.11762500
C	-5.76399500	-0.70754200	-0.06135000
H	-6.39220300	-1.59420600	-0.09274300
C	-4.38206800	-0.85836400	-0.10231500
H	-3.92898600	-1.83557600	-0.16643700
H	-1.78260600	1.21981900	-0.04827700

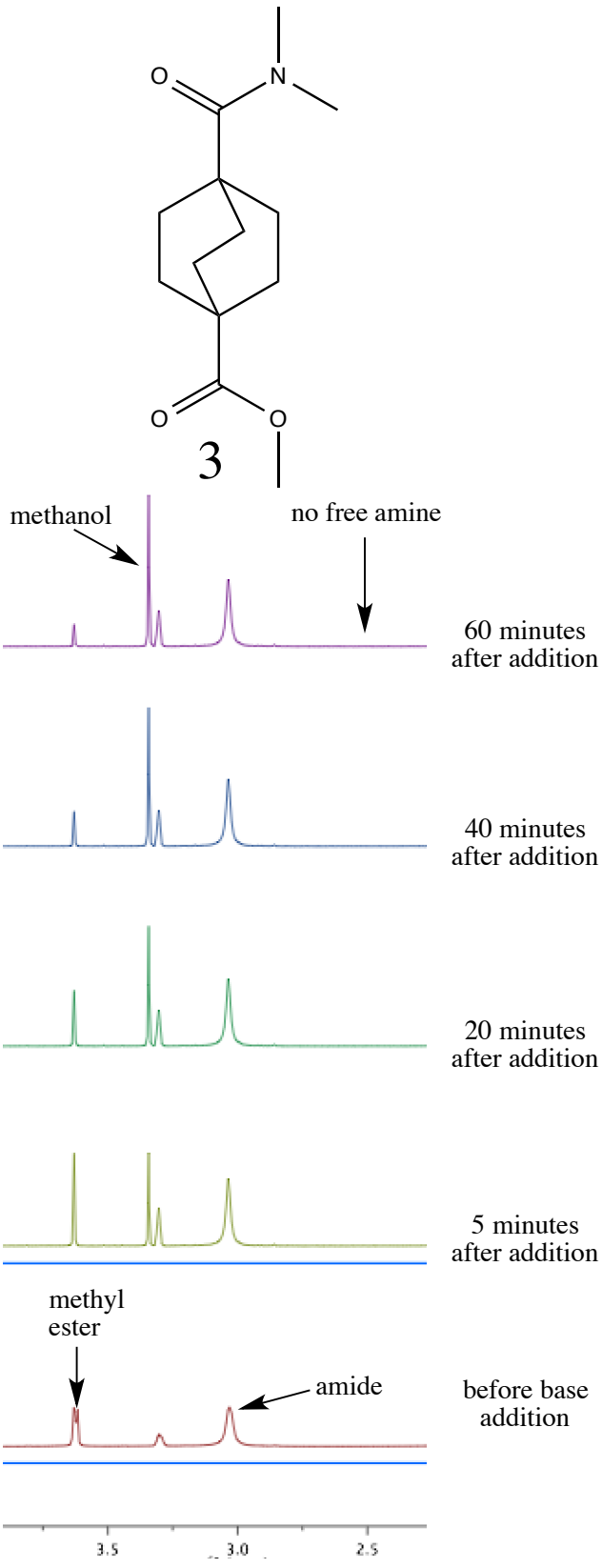
Solvolysis Kinetics



1

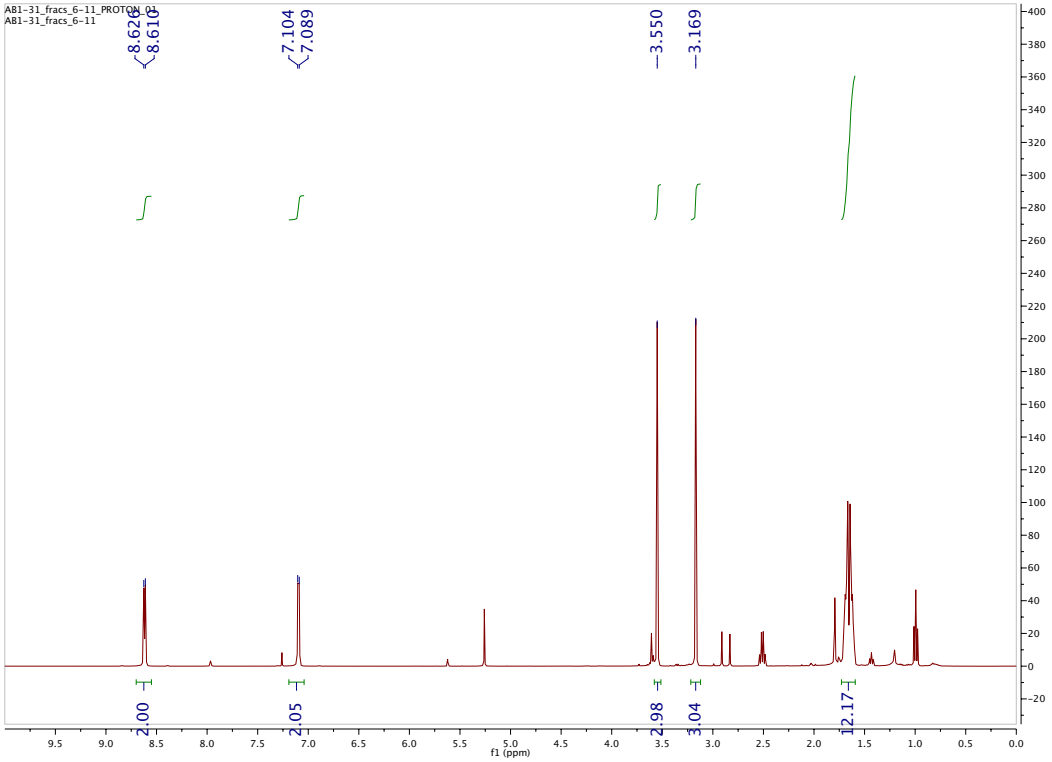



N
O
N
H
O
O
2
no free amine
methanol
60 minutes
after addition
40 minutes
after addition
20 minutes
after addition
amide
5 minutes
after addition
methyl
ester
before base
addition
8.5
8.0
7.5
7.0
6.5
3.5
3.0
2.5

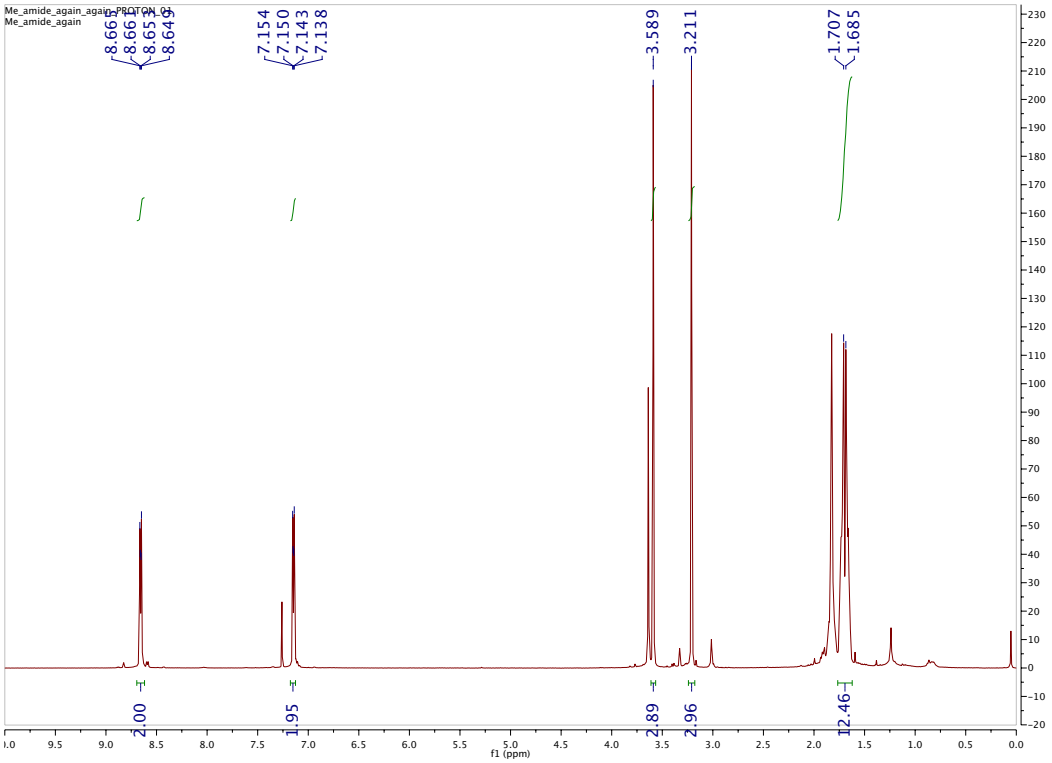

O
N
O
O
3
methanol
no free amine
60 minutes
after addition
40 minutes
after addition
20 minutes
after addition
5 minutes
after addition
methyl
ester
amide
before base
addition
3.5
3.0
2.5

Spectral Library

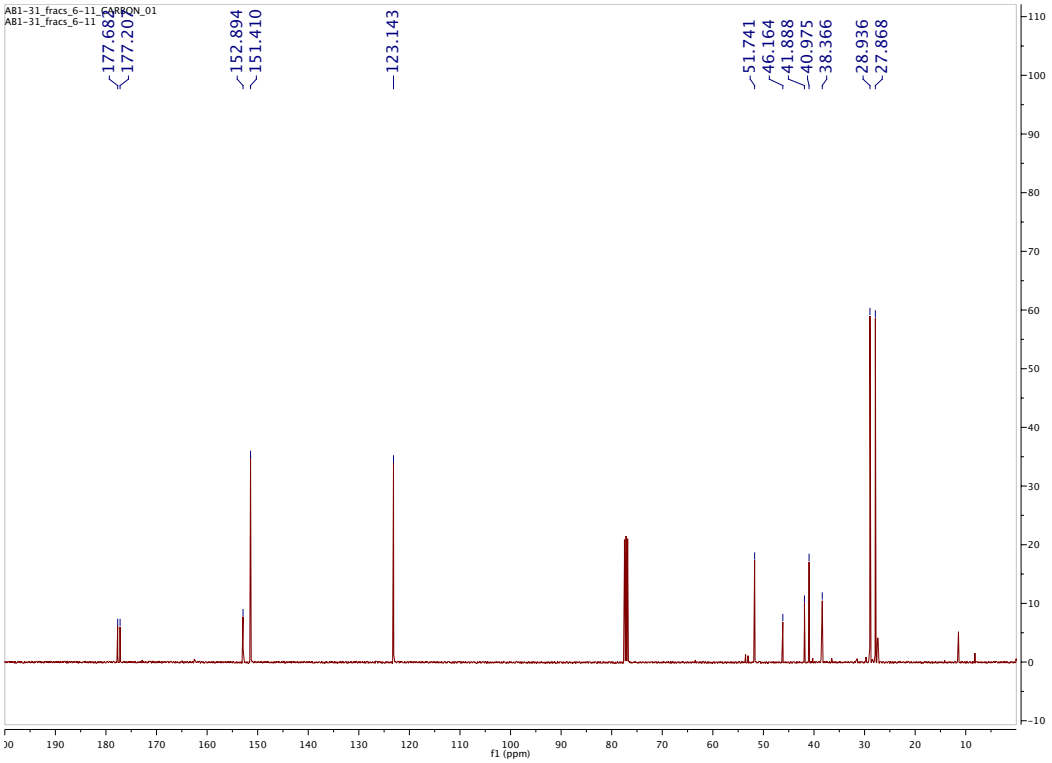
1 ^{1}H (some solvent contamination)



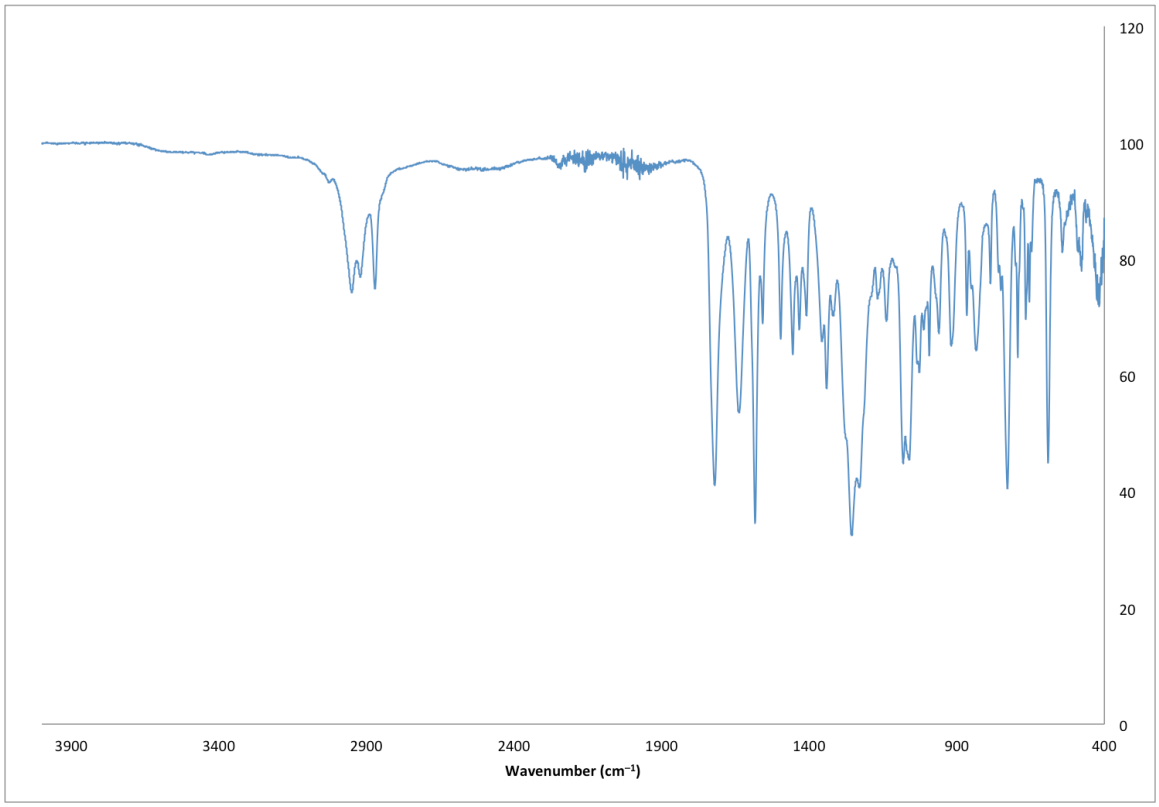
1 ^{1}H (some decomposition)



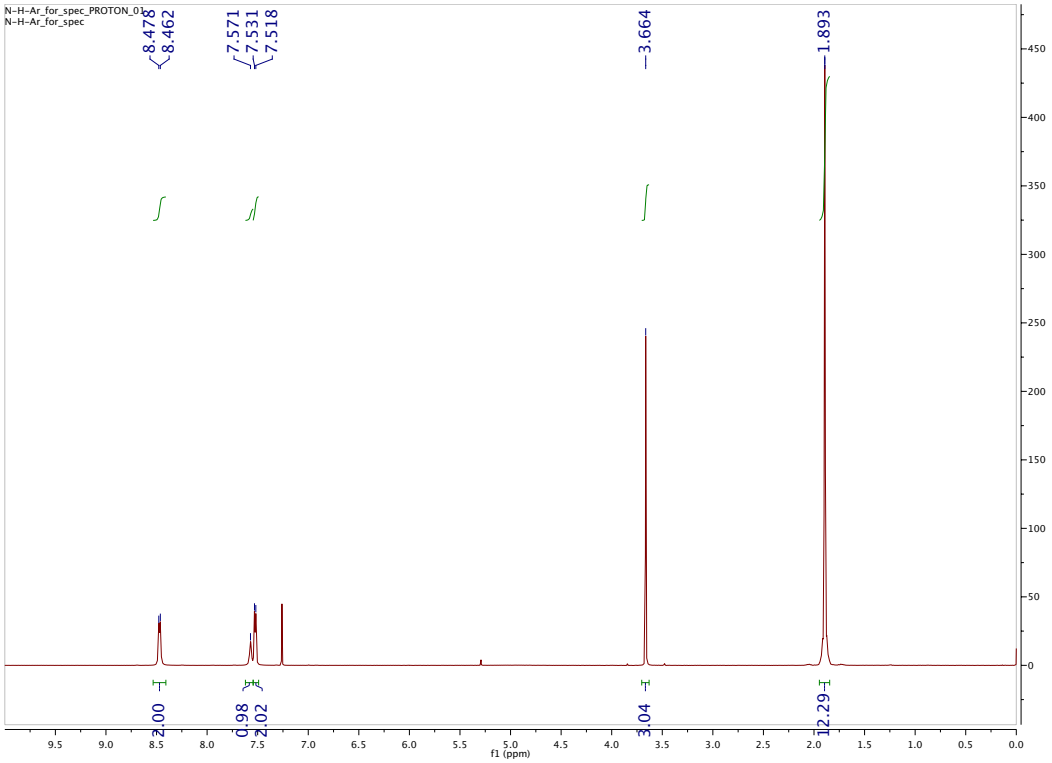
1 ^{13}C


AB1-31_fracs_6-11_CARBON_01
AB1-31_fracs_6-11_CARBON_01
177.684
177.207
152.894
151.410
123.143
51.741
46.164
41.888
40.975
38.366
28.936
27.868
f1 (ppm)

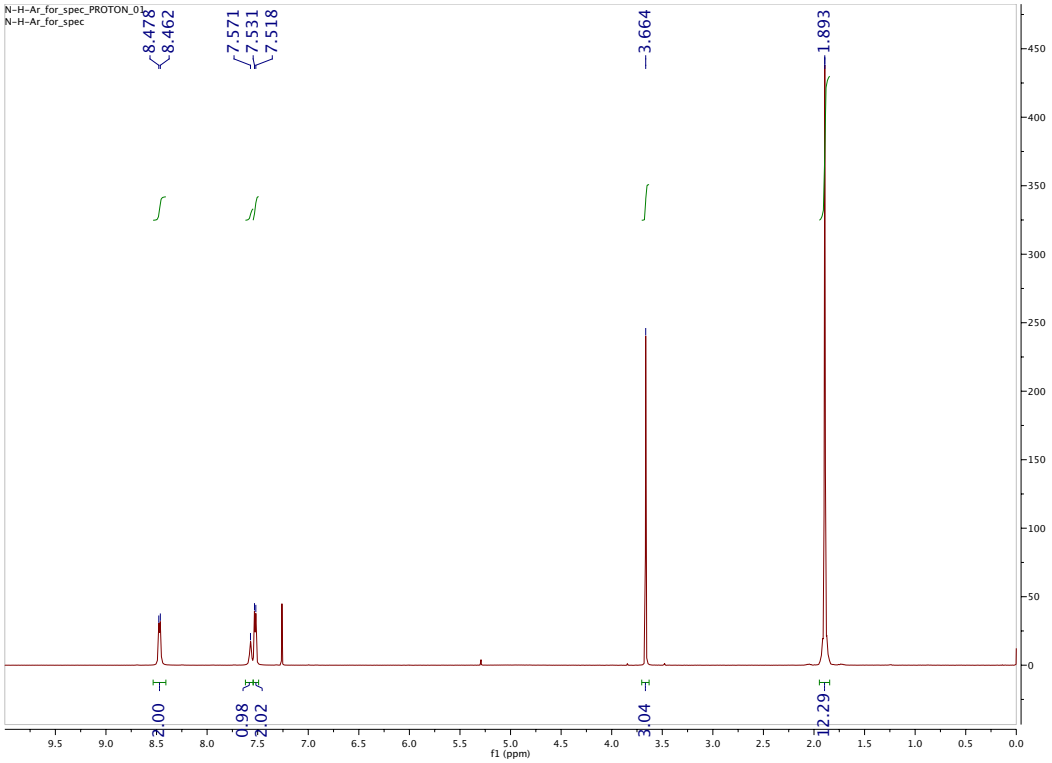
1 IR


Wavenumber (cm⁻¹)

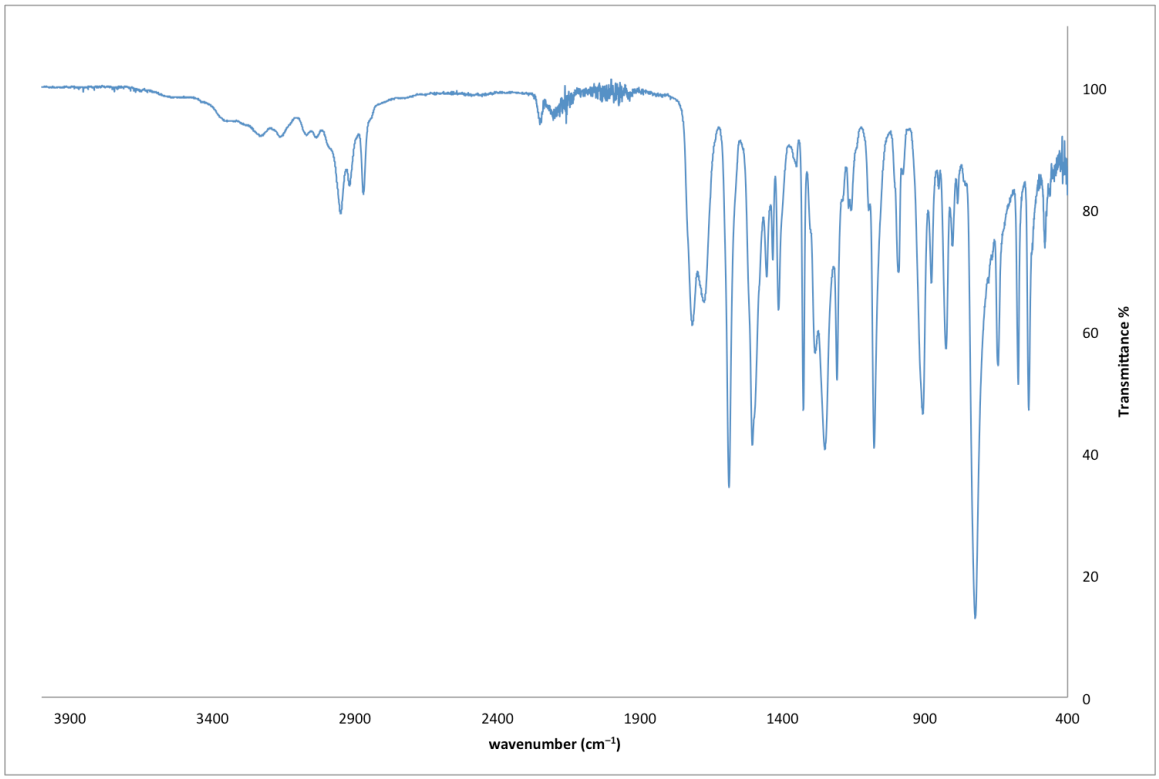
2 ^{1}H


N-H-Ar_for_spec_PROTON_01
N-H-Ar_for_spec
8.478
8.462
7.571
7.531
7.518
3.664
1.893
2.00
0.98
2.02
3.04
12.29
f1 (ppm)

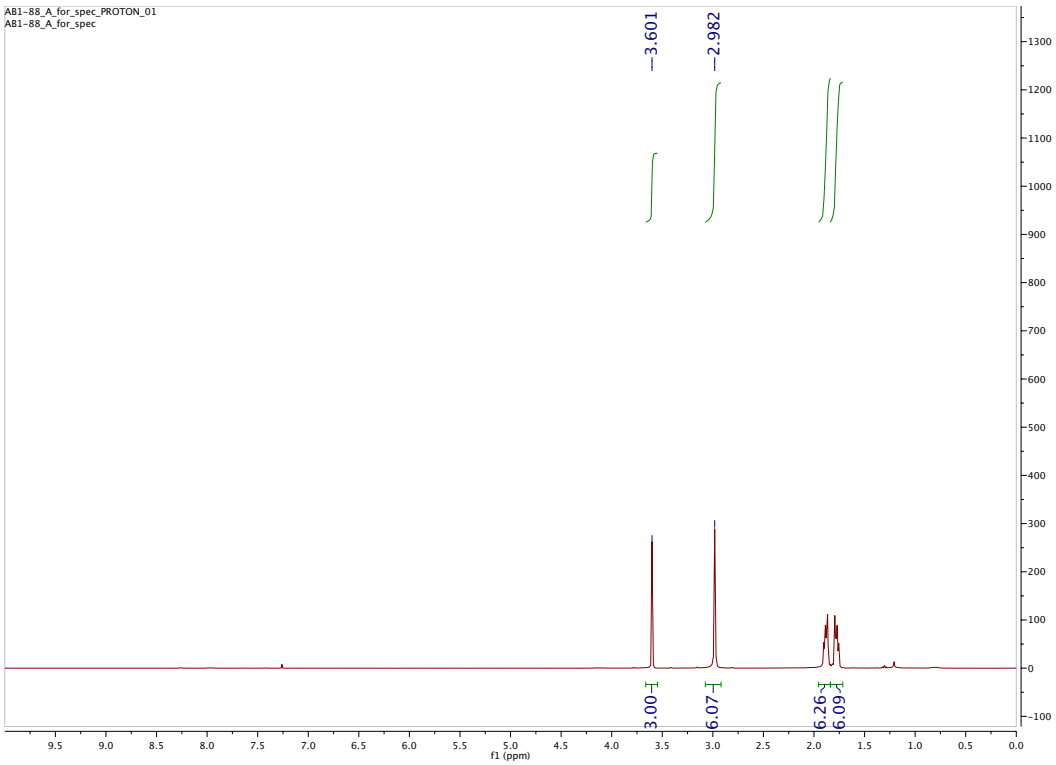
2 ^{13}C


N-H-Ar_for_spec_PROTON_01
N-H-Ar_for_spec
8.478
8.462
7.571
7.531
7.518
3.664
1.893
2.00
0.98
2.02
3.04
12.29
f1 (ppm)

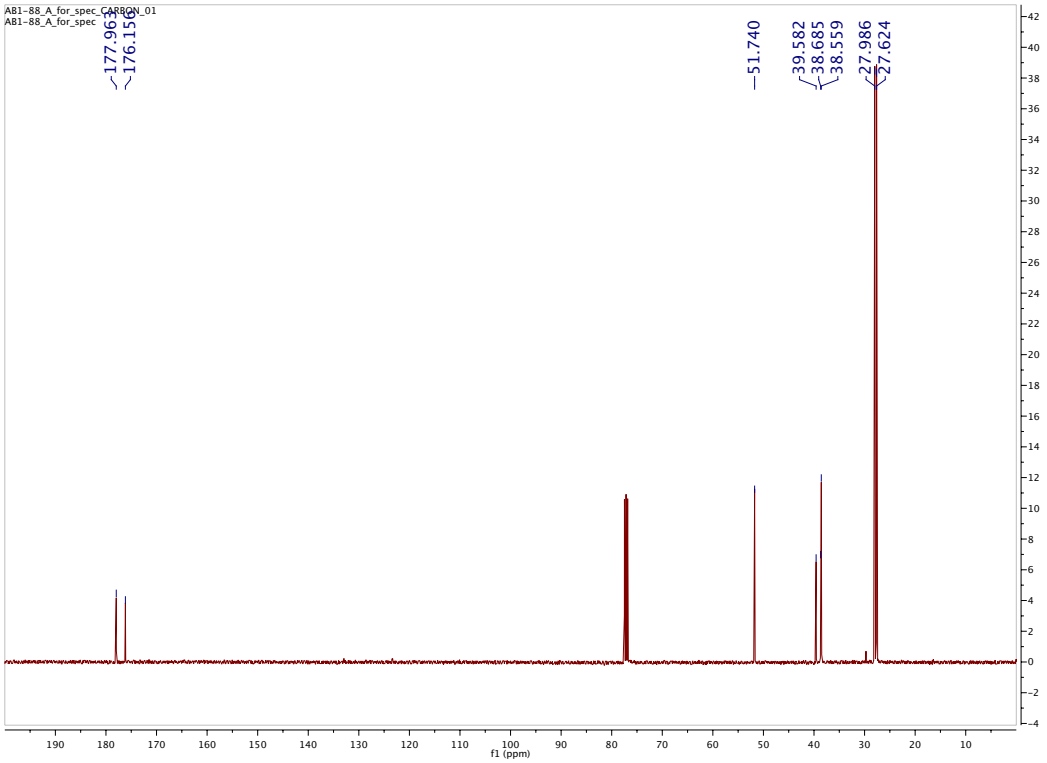
2 IR


100
80
60
40
20
0
Transmittance %
3900
3400
2900
2400
1900
1400
900
400
wavenumber (cm⁻¹)

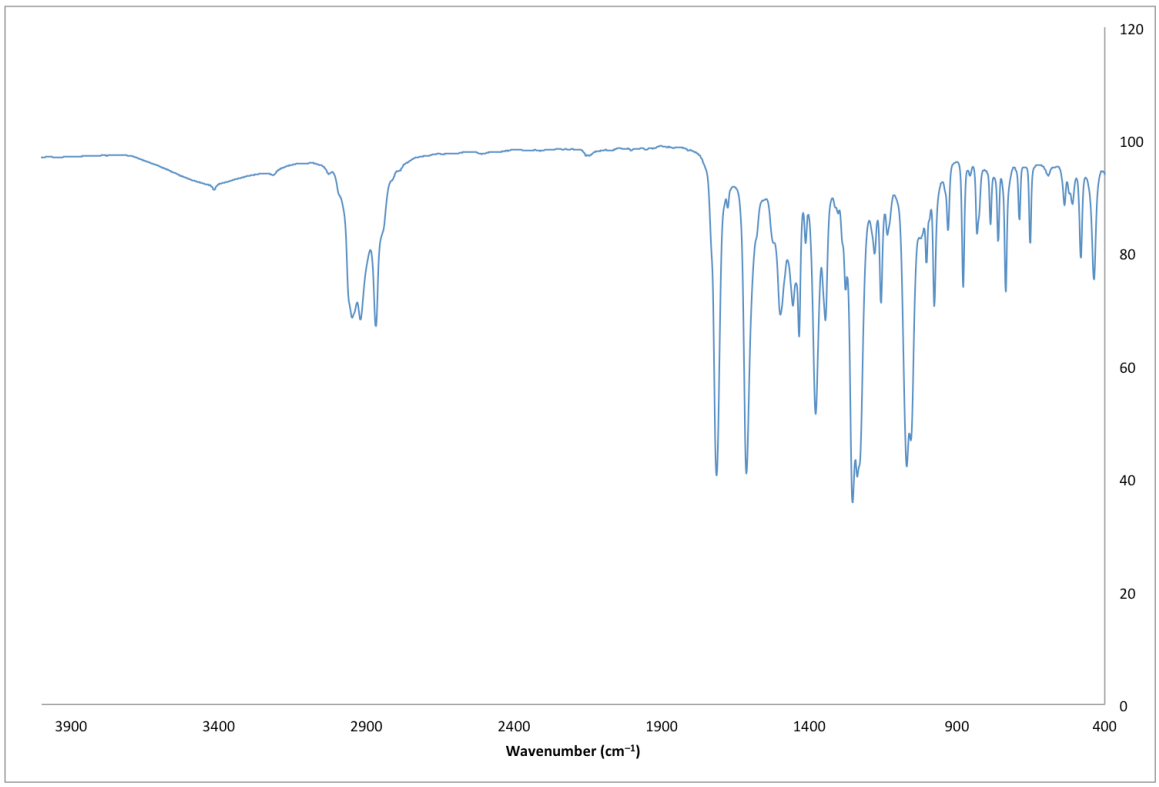
3 ^{1}H


AB1-88_A_for_spec_PROTON_01
AB1-88_A_for_spec
3.601
2.982
3.00
6.07
6.26
6.09
f1 (ppm)

3 ^{13}C


AB1-88_A_for_spec_CARBON_01
AB1-88_A_for_spec
177.963
176.150
51.740
39.582
38.685
38.559
27.986
27.624
f1 (ppm)

3 IR


Wavenumber (cm⁻¹)

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