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# Supporting Information



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# Highly Stereoselective Ring Expansion Reactions Mediated by Attractive, Non-bonded Cation–*n* Interactions

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**Supporting Information**

Computational section

Azide synthesis

Experimental section

$^{1}H$ and $^{13}C$ NMR spectra

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### A Note about Compound Designations.

All compounds that are discussed in the main body of the text are identified by bold numbers **1-12** in the Supporting Information. Virtual compounds created in silico for ab initio studies are designated by capitol bold letters **A** – **F** in both the text and the Supporting Information. Throughout, lower case bold letters are added to indicate stereoisomers; for a few in silico compounds additional Greek bold letters are used to indicate rotational conformers. Synthetic intermediates or other compounds that are only discussed in the Supporting Information are designated as **SI1**, **SI2**, etc.

### Crystallographic Data

The stereostructures of compounds *ent*-**3c**, *ent*-**3d, SI-10** (analogue of compound **5**), **SI-11** (analogue of compound **11**) were verified by X-ray crystallography. The details of these analuses can be accessed through CCDC entries 647651 (*ent*-**3c**), 647652 (**SI-10**), 647654 (**SI-11**), and 683831 (*ent*-**3d**) contain the supplementary crystallographic data for this paper. Note that the X-ray structures for racemic compounds **3c** and **3d** were solved in forms enantiomeric to those depicted in the paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

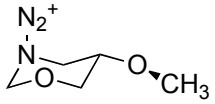
## Computational Data Contents

## Computational Methodology

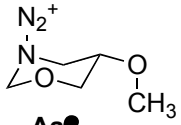
The Gaussian98[1] and Gaussian03 programs were used to perform optimization, single point, and frequency calculations. Only the Gaussian03 program was used for the solvent calculations. The levels of theory and basis sets utilized were MP2/6-31G*, and MP2/6-311+G**//MP2/6-31G*. Frequency calculations were performed to confirm the identity of minima. The MP2/6-31G* frequencies were then scaled based on the recommendations of Scott and Radom[2] and used to convert the electronic energies to free energies. All of the solvent calculations were single points at the MP2/6-311+G**//MP2/6-31G* level of theory and used the CPCM method with a dielectric of 8.93, which is that of dichloromethane, the experimental solvent.

In calculations for the (methoxymethyl)hydroxyethyl azides, the initial conformational searches used a model system in which the *tert*–butylcyclohexane ring was substituted with hydrogens. The hydrogens were then replaced with methyl groups in all located minima and reoptimized. Not surprisingly, some conformers were no longer minima on the potential energy surface due to new steric interactions. All located minima along with their energies are listed below.

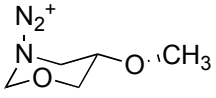
**Table 1S**. Total Energies (HF) and Relative Energies (kcal/mol) of the Heteroatom-Substituted Cyclohexane Intermediate Model System, **A**, for R = Methoxy (**α**, **β** and **γ** are different rotational conformers of the methoxy group)



**Aaα**



**Aaβ**



**Aaγ**

| | MP2/6-31G(d) | | MP2/6-311+G(d,p)// MP2/6-31G(d) | | MP2/6-311+G(d,p)// MP2/6-31G(d) CPCM | |
|---|---|---|---|---|---|---|
| Conformer | Total Energy | Rel. E | Total Energy | Rel. E | Total Energy | Rel. E |
| **Aaα** | -509.3607392 | 6.7 | -509.6502942 | 6.5 | -509.7284358 | 4.4 |
| **Aaβ** | -509.3537409 | 11.0 | -509.6434077 | 10.8 | -509.7234012 | 7.6 |
| **Aaγ** | -509.3600171 | 7.1 | -509.6493108 | 7.1 | -509.7277374 | 4.9 |
| **Abα** | -509.3713410 | 0.0 | -509.6605836 | 0.0 | -509.7354688 | 0.0 |
| **Abγ** | -509.3694586 | 1.2 | -509.6577753 | 1.8 | -509.7341690 | 0.8 |
| **Acα** | -509.3560575 | 9.6 | -509.6456783 | 9.4 | -509.7246449 | 6.8 |
| **Acβ** | -509.3485749 | 14.3 | -509.6383574 | 13.9 | -509.7196747 | 9.9 |
| **Ad** | CNL | — | CNL | — | CNL | — |

**Table 2S**. Total Energies (HF) and Relative Energies (kcal/mol) of the Heteroatom-Substituted Cyclopentane Intermediate Model System, **C**, for R = $CH_2OCH_3$ (**1**, **2**, **3**, **4**, **5**, and **6** are different conformers of the five-membered ring)

| | MP2/6-31G(d) | | MP2/6-311+G(d,p)// MP2/6-31G(d) | | MP2/6-311+G(d,p)// MP2/6-31G(d) CPCM | |
|---|---|---|---|---|---|---|
| Conformer | Total Energy | Rel. E | Total Energy | Rel. E | Total Energy | Rel. E |
| **Ca1** | -587.724808 | 0.0 | -588.072203 | 0.0 | -588.139453 | 0.0 |
| **Ca2** | -587.711118 | 8.6 | -588.060392 | 7.4 | -588.132327 | 4.5 |
| **Ca3** | -587.715968 | 5.5 | -588.064355 | 4.9 | -588.132812 | 4.2 |
| **Cb4** | -587.716059 | 5.5 | -588.064108 | 5.1 | -588.132618 | 4.3 |
| **Cb5** | -587.705800 | 11.9 | -588.054558 | 11.1 | -588.126999 | 7.8 |
| **Cb6** | -587.710967 | 8.7 | -588.059338 | 8.1 | -588.128691 | 6.8 |
| **Cb7** | -587.711884 | 8.1 | -588.060850 | 7.1 | -588.130136 | 5.8 |

**Table 3S**. Total Energies (HF) and Relative Energies (kcal/mol) of the Heteroatom-Substituted Cyclopentane Intermediate Model System, **E**, for R = $CH_2OCH_3$ (**1**, **2**, **3**, **4**, **5**, **6**, and **7** are different conformers of the five-membered ring)

| | MP2/6-31G(d) | | MP2/6-311+G(d,p)// MP2/6-31G(d) | | MP2/6-311+G(d,p)// MP2/6-31G(d) CPCM | |
|---|---|---|---|---|---|---|
| Conformer | Total Energy | Rel. E | Total Energy | Rel. E | Total Energy | Rel. E |
| **Eaı** | -587.722221 | 0.0 | -588.071031 | 0.0 | -588.137952 | 0.0 |
| **Ea2** | -587.721498 | 0.5 | -588.070231 | 0.5 | -588.136688 | 0.8 |
| **Ea3** | -587.719873 | 1.5 | -588.068568 | 1.5 | -588.136437 | 1.0 |
| **Eb4** | -587.720915 | 0.8 | -588.069906 | 0.7 | -588.136496 | 0.9 |
| **Eb5** | -587.713206 | 5.7 | -588.062282 | 5.5 | -588.131721 | 3.9 |
| **Eb6** | -587.712890 | 5.9 | -588.062160 | 5.6 | -588.132392 | 3.5 |

**Table 4S**. Corrections (HF) Based on MP2/6-31G* Frequencies Used to Convert Energies to Free Energies for $N_2^+$ Axial Conformers

| Compound | **a, R equat.** | **b, R axial** |
|---|---|---|
| **A (α)** | 0.155696 | 0.156735 |
| **C (1, 4)** | 0.209666 | 0.208964 |
| **E (1, 4)** | 0.209467 | 0.209030 |

**Table 5S**. MP2/6-31G* Cartesian Coordinates for **Aaα**

| Atom | X | Y | Z |
|---|---|---|---|
| O | -0.6308 | -1.5957 | 0.6501 |
| C | 0.7476 | -1.3352 | 0.2868 |
| C | 0.9409 | 0.1654 | 0.0613 |
| C | -0.0386 | 0.6743 | -0.9985 |
| N | -1.4367 | 0.1933 | -0.6961 |
| C | -1.4860 | -1.3115 | -0.3826 |
| H | 1.0090 | -1.8854 | -0.6266 |
| H | 1.3475 | -1.7076 | 1.1169 |
| H | 0.1937 | 0.2426 | -1.9759 |
| H | -0.0441 | 1.7631 | -1.0861 |
| H | -1.2093 | -1.7558 | -1.3466 |
| H | -2.5090 | -1.5640 | -0.1004 |
| N | -2.0457 | 0.9002 | 0.1992 |
| N | -2.6796 | 1.5450 | 0.9053 |
| O | 2.2011 | 0.4508 | -0.4899 |
| H | 0.7741 | 0.7029 | 1.0094 |
| C | 3.2450 | 0.6209 | 0.4873 |
| H | 4.1396 | 0.8652 | -0.0820 |
| H | 3.4145 | -0.2974 | 1.0570 |
| H | 3.0018 | 1.4427 | 1.1688 |

**Table 6S**. MP2/6-31G* Cartesian Coordinates for **Ab**

| Atom | X | Y | Z |
|---|---|---|---|
| O | -1.8064 | -0.5450 | 1.4017 |
| C | -1.7379 | 0.8688 | 1.0968 |
| C | -0.8248 | 1.1513 | -0.1017 |
| C | -1.3779 | 0.3428 | -1.2854 |
| N | -1.4931 | -1.1086 | -0.8981 |
| C | -2.3351 | -1.2764 | 0.3666 |
| H | -2.7533 | 1.2395 | 0.8945 |
| H | -1.3699 | 1.3469 | 2.0056 |
| H | -2.4077 | 0.6136 | -1.5442 |
| H | -0.7659 | 0.4059 | -2.1874 |
| H | -3.3233 | -0.9398 | 0.0269 |
| H | -2.3466 | -2.3338 | 0.6352 |
| N | -0.3476 | -1.7233 | -0.8107 |
| N | 0.5648 | -2.4180 | -0.8497 |
| C | 0.6151 | 0.7043 | 0.1234 |
| C | 1.5323 | 0.8385 | -0.9360 |
| C | 2.8414 | 0.3739 | -0.8168 |
| C | 3.2639 | -0.2288 | 0.3710 |
| C | 2.3747 | -0.3354 | 1.4419 |
| C | 1.0615 | 0.1250 | 1.3228 |
| H | 1.2384 | 1.3245 | -1.8649 |
| H | 3.5327 | 0.4899 | -1.6475 |
| H | 4.2827 | -0.5945 | 0.4667 |
| H | 2.7015 | -0.7809 | 2.3779 |
| H | 0.3936 | 0.0036 | 2.1687 |
| C | -0.9139 | 2.6464 | -0.4332 |
| H | -1.9517 | 2.9546 | -0.6009 |
| H | -0.5063 | 3.2301 | 0.3967 |
| H | -0.3354 | 2.8889 | -1.3277 |

**Table 7S**. MP2/6-31G* Cartesian Coordinates for **Ca1**

| Atom | X | Y | Z |
|---|---|---|---|
| N | 0.8158 | 0.5051 | -0.8692 |
| C | 1.4423 | -0.0376 | 0.4544 |
| C | 0.2279 | -0.6714 | -1.5912 |
| O | 0.8405 | -1.3096 | 0.5836 |
| C | -0.1256 | -1.6120 | -0.4371 |
| H | 1.0300 | -1.0547 | -2.2241 |
| H | -0.6183 | -0.3563 | -2.2042 |
| N | 0.0376 | 1.5225 | -0.7442 |
| N | -0.5292 | 2.5158 | -0.6966 |
| H | 0.0295 | -2.6579 | -0.7225 |
| C | -1.5385 | -1.4187 | 0.0707 |
| H | -2.2518 | -1.8659 | -0.6393 |
| H | -1.6462 | -1.9240 | 1.0398 |
| O | -1.7591 | -0.0195 | 0.1885 |
| C | -3.0701 | 0.2784 | 0.6968 |

| | | | |
|---|---|---|---|
| H | -3.1468 | 1.3647 | 0.7404 |
| H | -3.8405 | -0.1201 | 0.0285 |
| H | -3.1975 | -0.1427 | 1.6990 |
| C | 1.1014 | 0.8450 | 1.6329 |
| H | 0.0197 | 0.8925 | 1.7688 |
| H | 1.5401 | 0.3789 | 2.5182 |
| H | 1.5320 | 1.8455 | 1.5311 |
| C | 2.9233 | -0.1875 | 0.1842 |
| H | 3.4018 | 0.7877 | 0.0689 |
| H | 3.3687 | -0.7082 | 1.0358 |
| H | 3.0934 | -0.7884 | -0.7117 |

**Table 8S**. MP2/6-31G* Cartesian Coordinates for **Cb4**

| Atom | X | Y | Z |
|---|---|---|---|
| N | 1.2417 | -0.3618 | -0.7230 |
| C | 0.8716 | 0.9407 | 0.0936 |
| O | 0.1233 | 0.4028 | 1.1472 |
| C | -0.5205 | -0.8491 | 0.8135 |
| C | 0.0569 | -1.2717 | -0.5513 |
| H | 0.3716 | -2.3163 | -0.6042 |
| H | -0.6174 | -1.0408 | -1.3753 |
| C | -2.0338 | -0.7413 | 0.7982 |
| H | -2.4625 | -1.7568 | 0.8196 |
| H | -2.3521 | -0.2197 | 1.7118 |
| O | -2.4281 | -0.0482 | -0.3666 |
| C | -3.8461 | 0.1638 | -0.4099 |
| H | -4.3807 | -0.7924 | -0.3978 |
| H | -4.1710 | 0.7764 | 0.4378 |
| H | -4.0488 | 0.6869 | -1.3431 |
| N | 2.3669 | -0.8948 | -0.3907 |
| N | 3.4239 | -1.3158 | -0.2279 |
| H | -0.2237 | -1.5492 | 1.6028 |
| C | 2.1039 | 1.6122 | 0.6492 |
| H | 2.7693 | 1.9498 | -0.1496 |
| H | 1.7703 | 2.4894 | 1.2082 |
| H | 2.6332 | 0.9603 | 1.3481 |
| C | 0.0803 | 1.7969 | -0.8707 |
| H | -0.8153 | 1.2825 | -1.2166 |
| H | -0.2396 | 2.6850 | -0.3184 |
| H | 0.7047 | 2.1063 | -1.7118 |

**Table 9S**. MP2/6-31G* Cartesian Coordinates for **Ea1**

| Atom | X | Y | Z |
|---|---|---|---|
| O | 1.6901 | 1.3889 | -0.1217 |
| C | 1.6673 | 0.0108 | -0.2997 |
| C | 0.3522 | 1.8798 | 0.0112 |
| N | 0.5106 | -0.3235 | 0.7547 |
| C | -0.3066 | 0.9247 | 1.0187 |
| H | 0.4239 | 2.8971 | 0.3977 |
| H | -0.1853 | 1.8736 | -0.9406 |

| | | | |
|---|---|---|---|
| N | -0.1029 | -1.4317 | 0.6252 |
| N | -0.5681 | -2.4805 | 0.5772 |
| C | -1.7902 | 0.6980 | 0.7966 |
| H | -2.2151 | 0.0450 | 1.5760 |
| H | -2.2998 | 1.6711 | 0.8716 |
| O | -1.9172 | 0.1218 | -0.4866 |
| C | -3.2910 | -0.1130 | -0.8451 |
| H | -3.7633 | -0.7995 | -0.1340 |
| H | -3.2728 | -0.5604 | -1.8372 |
| H | -3.8459 | 0.8300 | -0.8722 |
| H | -0.0918 | 1.2154 | 2.0511 |
| C | 2.9595 | -0.5824 | 0.1953 |
| H | 3.7615 | -0.2556 | -0.4723 |
| H | 2.9228 | -1.6747 | 0.1806 |
| H | 3.1703 | -0.2266 | 1.2045 |
| C | 1.2275 | -0.4470 | -1.6749 |
| H | 0.2315 | -0.0829 | -1.9302 |
| H | 1.2395 | -1.5384 | -1.7473 |
| H | 1.9520 | -0.0544 | -2.3935 |

**Table 10S**. MP2/6-31G* Cartesian Coordinates for **Eb4**

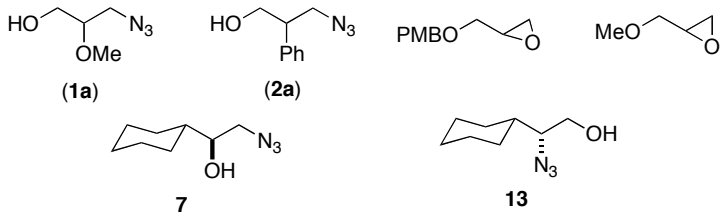
| Atom | X | Y | Z |
|---|---|---|---|
| O | 1.8786 | -1.1704 | -0.5758 |
| C | 0.6690 | -1.9153 | -0.3899 |
| C | -0.4251 | -0.8681 | -0.5955 |
| N | 0.2533 | 0.2830 | 0.0976 |
| C | 1.8175 | 0.0155 | 0.1623 |
| H | 0.6155 | -2.3683 | 0.6067 |
| H | 0.6492 | -2.6948 | -1.1519 |
| H | -0.5294 | -0.6185 | -1.6571 |
| C | -1.7778 | -1.0931 | 0.0394 |
| N | -0.1541 | 1.4633 | -0.1595 |
| N | -0.4901 | 2.5526 | -0.2989 |
| C | -2.3016 | -1.9053 | -0.4875 |
| C | -1.6673 | -1.3744 | 1.0976 |
| O | -2.4377 | 0.1479 | -0.1032 |
| C | -3.7781 | 0.1224 | 0.4134 |
| H | -3.7754 | -0.1173 | 1.4821 |
| H | -4.1826 | 1.1211 | 0.2580 |
| H | -4.3835 | -0.6106 | -0.1292 |
| C | 2.5966 | 1.0864 | -0.5593 |
| H | 2.2590 | 1.1787 | -1.5941 |
| H | 2.5338 | 2.0493 | -0.0454 |
| H | 3.6450 | 0.7778 | -0.5698 |
| C | 2.1597 | -0.1463 | 1.6274 |
| H | 1.9980 | 0.7897 | 2.1679 |
| H | 1.5616 | -0.9304 | 2.0945 |
| H | 3.2164 | -0.4179 | 1.7001 |

**General Information**. All commercial materials were used as supplied unless otherwise noted. $^{1}H$ and $^{13}C$ NMR spectra were recorded on Bruker instruments in $CDCl_3$ at 400 MHz for $^{1}H$ and and 125 MHz for $^{13}C$. IR spectrum was taken on a FT/IR-8000S. Dry flasks (noted) were flame dried under vacuum. Solvents were dried using an Innovative Technologies Pure-Solv solvent system.

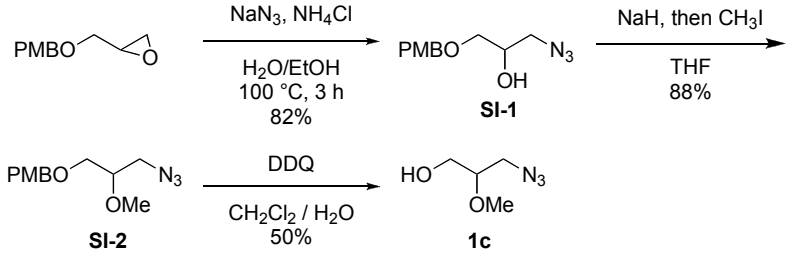
## List of Known Compounds

The following azides and intermediates are known: 3-azido-2-methoxypropan-1-ol (**1a**)[3], 3-azido-2-phenylpropan-1-ol (**2a**)[3], 2-azido-1-cyclohexylethanol (**7**), 2-azido-2-cyclohexylethanol (**13**), 2-(4′-methoxybenzyloxy)methyl oxirane[4], 3-methoxypropane-1,2-diol (**SI-4**).[5]

**Figure S1**: Known intermediates and compounds.

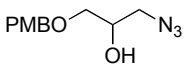



**Scheme S1**. *Synthesis of* **1c**.



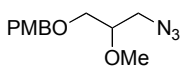

3-Azido-2-methoxy-propan-1-ol (±)-**1c** was prepared in three steps from commercially available starting materials (Scheme S1). Taking into consideration that (±)-**1c** is a low molecular weight azide and therefore volatile, the synthesis entailed a protection/deprotection strategy to increase the molecular weight and subsequent ability to handle the intermediates during the synthesis. Hence, 2-

(4′-methoxybenzyloxy)methyl oxirane[4] underwent nucleophilic ring opening with sodium azide in water/ethanol (1:1) to afford the PMB-protected alcohol (±)-**SI-1** as a single regioisomer. Deprotonation of the secondary alcohol by sodium hydride followed by O-alkylation with iodomethane then gave the desired PMB-protected azide (±)-**SI-2**. Deprotection of the PMB protecting group by DDQ in water/dichloromethane (1:18) gave (±)-**1c** in 37% overall yield over three steps.




**SI-1**

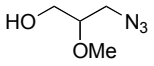
(±)-**1-Azido-3-(4′-methoxybenzyloxy)propan-2-ol (SI-1)**. To a stirred solution of 2-(4′-methoxybenzyloxy)methyl oxirane[4] (2.0 g, 10.3 mmol) in 10.3 mL EtOH and 2.5 mL $H_2O$ at room temperature, $NaN_3$ (0.80 g, 12.4 mmol) and $NH_4Cl$ (0.72 g, 13.4 mmol) were added. After 10 min, the mixture was heated to reflux for 1 h and then allowed to cool to room temperature, diluted with $H_2O$, and extracted with $Et_2O$ (4 × 20 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to an oil that was purified by column chromatography (5-33% EtOAc/hexane) to provide a **SI6** as a colorless oil (2.0 g, 82%); $R_f$ = 0.40 (33% EtOAc/hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 2H), 6.87 (m, 2H), 4.46 (s, 2H), 3.91 (m, 1H), 3.78 (s, 3H), 3.45 (m, 2H), 3.33 (m, 2H), 2.77 (br s, 1H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 159.4, 129.7, 129.5, 113.9, 73.2, 71.0, 69.7, 55.3, 53.5. IR (neat) 3450, 2100 cm$^{-1}$. MS (ES+) *m/z* 260 $[M]^+$; HRMS (ES+) calcd for $C_{11}H_{15}N_3O_3Na$ $[M+1]^+$ 260.1011, found 260.1025.




**SI-2**

(±)-**1-(3′-Azido-2′-methoxypropoxy)methyl-4-methoxybenzene (SI-2)**. A solution of compound **SI-1** (1.00 g, 4.2 mmol) in anhydrous THF (10 ml) was added to a suspension of NaH (60%, 0.19 g, 4.8 mmol) via a cannula, and the resulting solution stirred for 1 h. Iodomethane (0.53

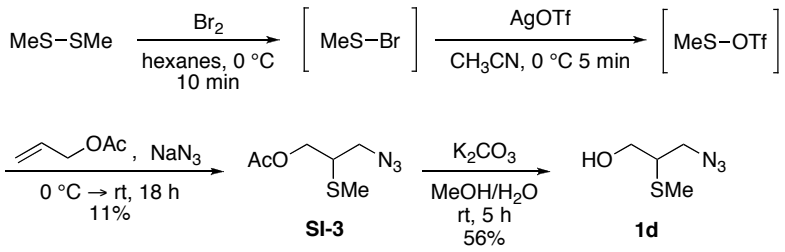
mL, 8.4 mmol) was added dropwise and the reaction mixture was stirred for 45 min, cooled to 0 °C in an ice bath, quenched slowly with $H_2O$, and extracted with $Et_2O$ (4 × 10 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to a yellow oil that was purified by column chromatography (25% EtOAc/hexane) to provide **SI7** as a colorless oil (0.94 g 88%); $R_f$ = 0.73 (33% EtOAc/hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 6.90 (m, 2H), 4.49 (s, 2H), 3.82 (s, 3H), 3.52 (m, 3H), 3.48 (s, 3H), 3.40 (m, 2H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 159.3, 130.0, 129.3, 113.8, 79.3, 73.1, 68.7, 57.8, 55.2, 51.6. IR (neat) 2960, 2110 cm$^{-1}$. MS (ES+) *m/z* 251 $[M]^+$; HRMS (ES+) calcd for $C_{12}H_{17}N_3O_3$ $[M+1]^+$ 251.1270, found 251.1272.



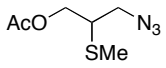

**1c**

(±)-**3-Azido-2-methoxypropan-1-ol (1c)**. DDQ (1.00 g, 4.6 mmol) was added to a stirred mixture of **SI-2** (0.66 g, 3.5 mmol) in $CH_2Cl_2$ (66.7 mL) and $H_2O$ (3.70 mL) at room temperature. After 3 h the reaction was quenched slowly with saturated $NaHCO_3$ (20 mL) followed by of $H_2O$ (40 mL) and then extracted with $CH_2Cl_2$ (5 × 20 mL). The combined organic layers were washed with saturated $NaHCO_3$, water, brine, dried ($Na_2SO_4$), and then concentrated to a yellow oil that was purified by column chromatography (20-80% $Et_2O$/pentane) to provide a colorless oil (0.35 g 75%). $R_f$ = 0.19 (33% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.68 (dd, *J* = 4.2, 3.9 Hz, 1H), 3.58 (dd, *J* = 4.8, 4.5 Hz, 1H), 3.45 (s, 3H), 3.39 (m, 3H), 2.74 (br s, 1H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 80.5, 61.6, 57.8, 50.8. IR (neat) 3440, 2960, 2110 cm$^{-1}$. MS (FAB) *m/z* 131 $[M+1]^+$; HRMS calcd for $C_4H_{10}N_3O_3$ $[M+1]^+$ 131.0695, found 131.0681.

**Scheme S3**. *Synthesis of methylthio-substituted hydroxyalkyl azide* **1d**.



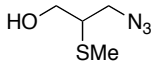

*Preparation of Methyl trifluoromethanesulfono(thioperoxoate).*[6] A flame dried 1000 mL RBF equipped with a magnetic stirring bar and distilled hexanes (200 mL) was cooled to 0 °C under argon and bromine (42.4 mmol, 2.2 mL) was added. Methyl disulfide (42.4 mmol, 3.8 mL) was added to the cooled reaction mixture drop wise with an addition funnel slowly over a period of 5 minutes. After an additional stirring of 10 minutes, the cooled reaction mixture is diluted with 500 mL of dry acetonitrile and silver trifluoromethanesulfonate (84.92 mmol, 22.6 g) was added in one portion to the solution and then the flask was covered in aluminum foil.[6] The crude reaction mixture containing methyl trifluoromethanesulfono(thioperoxoate) was taken forward without purification or isolation.




**SI-3**

(±)-**3-Azido-2-(methylthio)propyl ethanoate (SI-3)**. Allyl acetate (77.2 mmol, 8.3 mL) was added to the cooled flask in which methyl trifluoromethanesulfono(thioperoxoate) (84.93 mmol, 16.7 g) was prepared in situ, followed by addition of sodium azide (308.2 mmol, 20.07 g) in one portion. The reaction mixture was covered in aluminum foil and allowed to heat to room temperature over a period of 18-24 hours, after which time the reaction was filtered through a fritted funnel containing potassium carbonate. The mother liquor was concentrated under reduced pressure and directly adsorbed onto silica gel, which could be purified by column chromatography (3-25 $Et_2O$/pentane) to provide **SI-3** as tan tinted oil (1.90 g, 11%). $R_f$ = 0.34 (25% EtOAc/hexanes). $^1H$ NMR (400 MHz,

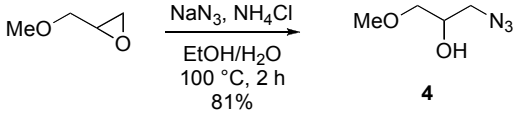
$CDCl_3$) δ 4.35-4.30 (dd, *J* = 16.0, 4.4 Hz, 1H), 4.18-4.13 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.55 (d, *J* = 6.0 Hz, 2H), 2.97-2.93 (m, 1H), 2.19 (s, 3H), 2.09 (s, 3H). $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ 170.5, 63.6, 52.2, 45.4, 20.8, 14.4. IR (neat) 2100, 1741, 1232 $cm^{-1}$. Attempts to detect a molecular ion in the MS of this compound were unsuccessful (FAB and ESI).




**1d**

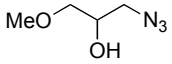
**(±)-3-Azido-2-(methylthio)propan-1-ol (1d)**. To a 100 mL round bottom flask containing **SI-3** (5.2 mmol, 0.99 g) and a magnetic stirring bar was added deionized water (25 mL) and methanol (mL) at room temperature, follwed by the addition of anhydrous $K_2CO_3$ (20.9 mmol, 2.9 g) in one portion. The resulting solution was allowed to stir at room temperature for a duration of 4 hours at which time the solution was diluted with water (50 mL) and extracted with $Et_2O$ (4x's @ 50 mL each time). The combined organic layers were washed with water (1x @ 20 mL) and brine (1X @ 35 mL), and concentrated to give a yellow oil which could then be purified by column chromatography (40%-80% $Et_2O$/pentane) to give **1d** as a colorless oil (0.43 g, 56%). $R_f$ = 0.26 (25% EtOAc/hexanes). $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.84-3.78 (m, 1H), 3.74-3.68 (m, 1H), 3.62-3.51 (m, 2H), 2.91-2.84 (m, 1H), 2.18 (s, 3H). $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ 61.7, 52.2, 49.4, 13.9. IR (neat) 3404, 2920, 2100 $cm^{-1}$. Attempts to detect a molecular ion in the MS of this compound were unsuccessful (FAB and ESI).

**Scheme S4**. *Synthesis of* **4**.




**4**

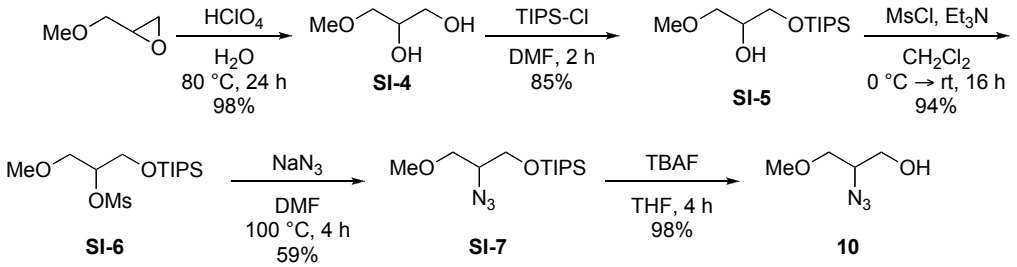
Azide (±)-**4** was synthesized in 81% yield by treatment of glycidyl methyl ether (TCI America) with sodium azide in EtOH/$H_2O$ (Scheme S4).




**4**

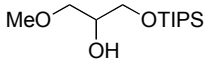
(±)-**1-Azido-3-methoxypropan-2-ol** (**4**). $NH_4Cl$ (1.20 g, 22.1 mmol) and $NaN_3$ (1.30 g, 20.4 mmol) were added sequentially to a solution of racemic glycidyl methyl ether (TCI America, 1.53 mL, 5.7 mmol) in EtOH (23 mL) and $H_2O$ (23 mL), which was then heated to reflux. After 2 h the reaction was allowed to cool to room temperature, diluted with $H_2O$ (20 mL), and extracted with $Et_2O$ (5 × 30 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to a yellow oil that was purified by column chromatography (20-50% $Et_2O$/pentane) to provide a colorless oil (0.61 g, 81%). $R_f$ = 0.65 (50% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.89 (m, 1H), 3.38 (m, 2H), 3.35 (s, 3H), 3.31 (m, 2H), 3.20 (br s, 1H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 73.9, 69.4, 59.1, 53.4. IR (neat) 3420, 2950, 2110 cm$^{-1}$. Attempts to detect a molecular ion in the MS of this compound were unsuccessful (FAB and ESI).

**Scheme S8**. *Synthesis of **10**.*



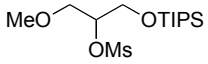

The synthesis of azide (±)-**10** was accomplished in five steps in 45% overall yield. Glycidyl methyl ether (TCI America) was treated with perchloric acid in water to give the known 1,2-diol **SI-4**.[5]

The primary alcohol was then protected with triisopropylsilyl chloride to give alcohol **SI-5**, and subsequent mesylation of the secondary alcohol gave intermediate **SI-6**. Displacement of the mesylated alcohol with sodium azide gave the TIPS-protected azide **SI-7**. Deprotection by tetrabutylammonium fluoride gave azide **10** in 46% overall yield from the 1,2-diol.




**SI-5**

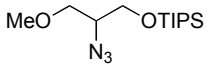
**(±)-1-Methoxy-3-triisopropylsilyloxypropan-2-ol** (**SI-5**). Imidazole (5.10 g, 75.4 mmol) was added to a stirred solution of glycidyl methyl ether (TCI America, 4.00 g, 37.7 mmol) in DMF (75 mL), which was then allowed to stir for 10 min at room temperature, TIPS-Cl (8.90 mL, 41.5 mmol) was then added over 5 min. After 2 h the reaction was diluted with $H_2O$ (40 mL) and extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to a colorless oil that was purified by column chromatography (20-30% EtOAc/hexanes) to provide **SI-5** as colorless oil (8.4 g, 85%). $R_f$ = 0.81 (50% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.83 (m, 1H), 3.73 (m, 2H), 3.46 (m, 2H), 3.38 (s, 3H), 1.07 (m, 21H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 73.5, 70.6, 64.3, 59.1, 17.7, 11.9. IR (neat) 2950, 2880 cm$^{-1}$. MS (ES+) *m/z* 285 $[M+1]^+$; HRMS (ES+) calcd for $C_{13}H_{30}O_3SiNa$ $[M+1]^+$ 285.1862, found 285.1889.




**SI-6**

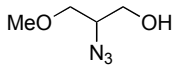
(±)-**1-Methoxy-3-triisopropylsilyloxypropan-2-yl methanesulfonate** (**SI-6**). Triethylamine (8.6 mL, 61.9 mmol) and methanesulfonyl chloride (4.8 mL, 61.9 mmol) were added sequentially to a mixture of **SI-5** (8.10 g, 30.9 mmol) in anhydrous $CH_2Cl_2$ (77 mL) at 0 °C. The reaction was allowed to slowly warm to room temperature and stirred for 16 h. Saturated $NH_4Cl$ (50 mL) and $H_2O$ (55 mL)

were added and the solution was extracted with $CH_2Cl_2$ (4 × 45 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), concentrated, and purified by column chromatography (10-15% $Et_2O$/pentane) to provide **SI-6** as a colorless oil (9.94 g, 94%). $R_f$ = 0.60 (25% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 4.75 (m, 1H), 3.90 (m, 2H), 3.66 (m, 2H), 3.40 (s, 3H), 3.10 (s, 3H), 1.07 (m, 21H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 81.7, 71.7, 62.9, 59.2, 38.3, 17.8, 11.6. IR (neat) 2960, 2890, 1340 cm$^{-1}$. MS (ES+) *m/z* 341 $[M+1]^+$; HRMS (ES+) calcd for $C_{13}H_{33}O_5SSi$ $[M+1]^+$ 341.1818, found 341.1810.




**SI-7**

(±)-**2-Azido-3-methoxypropoxytriisopropylsilane** (**SI-7**). $NaN_3$ (6.78 g, 104 mmol) was added to a stirred solution of **SI-6** (7.10 g 20.9 mmol) in DMF (42 mL). The solution was heated to 100 °C for 7 h after which it was allowed to cool to room temperature, diluted with $H_2O$ (50 mL), and extracted with $Et_2O$ (4 × 20 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to a colorless oil that was purified by column chromatography (5% $Et_2O$/pentane) to provide **SI-7** a colorless oil (3.56 g, 59%). $R_f$ = 0.90 (25% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.87 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.81 (dd, *J* = 10.2, 5.8 Hz, 1H), 3.55 (m, 3H), 3.40 (s, 3H), 1.10 (m, 21H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 71.6, 63.7, 62.4, 59.2, 17.9, 11.9. IR (neat) 2960, 2880, 2100, 1120 cm$^{-1}$. MS (ES+) *m/z* 288 $[M+1]^+$; HRMS (ES+) calcd for $C_{13}H_{30}N_3O_2Si$ $[M+1]^+$ 288.2115, found 288.2107.




**10**

(±)-**2-Azido-3-methoxypropan-1-ol** (**10**). Tetrabutylammonium fluoride (1 M in THF, 4.20 mL, 16.1 mmol) was added dropwise to a stirred solution of **SI-7** (3.60 g, 12.4 mmol) in anhydrous THF (250 mL). After 5 h of stirring at room temperature the solution was diluted with $H_2O$ (60 mL) and extracted with $Et_2O$ (4 × 20 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to a yellow oil that was purified by column chromatography (20-80% $Et_2O$/pentane) to provide **10** as a colorless oil (1.59 g, 98%). $R_f$ = 0.30 (20% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.69 (m, 1H), 3.61 (m, 2H), 3.51 (m, 2H), 3.36 (s, 3H), 3.18 (br s, 1H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 72.3, 62.4, 62.3, 59.2. IR (neat) 3410, 2950, 2100 cm$^{-1}$. Attempts to detect a molecular ion in the MS of this compound were unsuccessful (FAB and ESI).

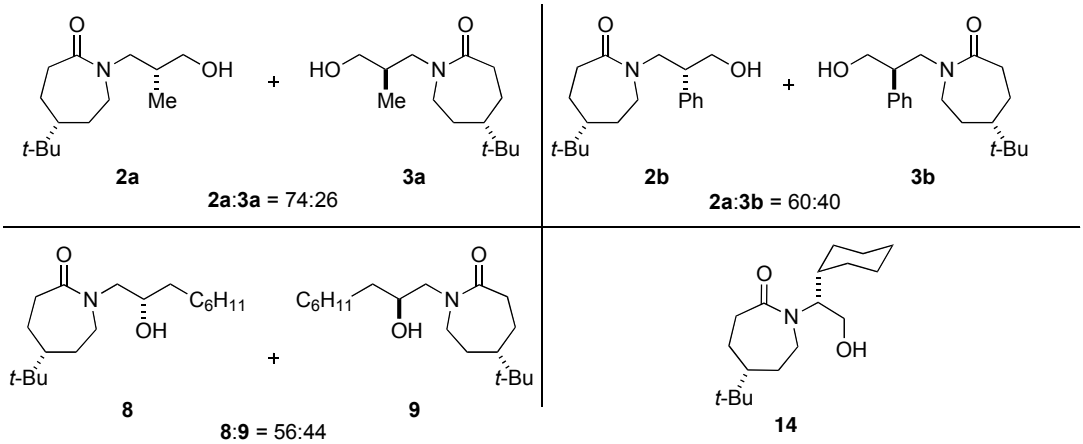
## Ring Expansion Reactions

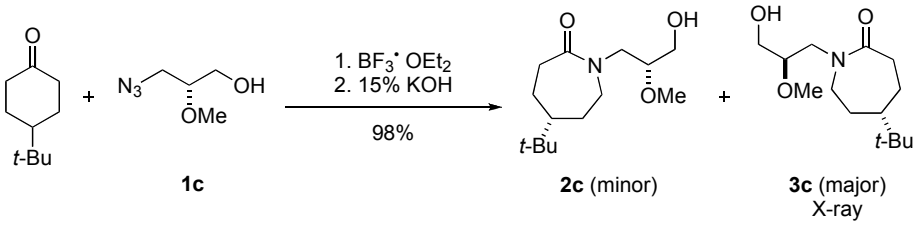
**General procedure for the synthesis of *N*-alkylated caprolactams**. A solution of 4-*tert*-butylcyclohexanone in anhydrous $CH_2Cl_2$ (0.04 M) was cooled to -78 °C and $BF_3$•$OEt_2$ (5.0 equiv) was added. After 30 min a solution of hydroxyalkyl azide (1.2 equiv) in anhydrous $CH_2Cl_2$ (0.04 M) was added to the cooled solution drop wise via a cannula. The reaction mixture was allowed to warm to room temperature slowly over 18–24 h at which time it was concentrated under reduced pressure and 15% KOH was added slowly to the residual oil. The reaction mixture was stirred vigorously at room temperature for 30 min and then partitioned between $CH_2Cl_2$ and $H_2O$. The organic layer was washed with water, brine, dried ($Na_2SO_4$) and concentrated to an oil.

Diastereoselectivities were determined from crude reaction mixtures by HPLC or GC. Diastereomers were separated by column chromatography, preparative TLC, or crystallization; see individual examples for details. Once crystals were obtained they were identified as a particular isomer by HPLC, GC or LCMS comparison with the crude reaction mixture.

Lactams **1a**, **1b**, **2a**, **2b** in Sahasrabudhe et al.[3] and **8**, **9**, and **14** in Katz et al.[7] have been previously reported. The full experimental information regarding these compounds is provided in the Supporting Information of these respective publications.

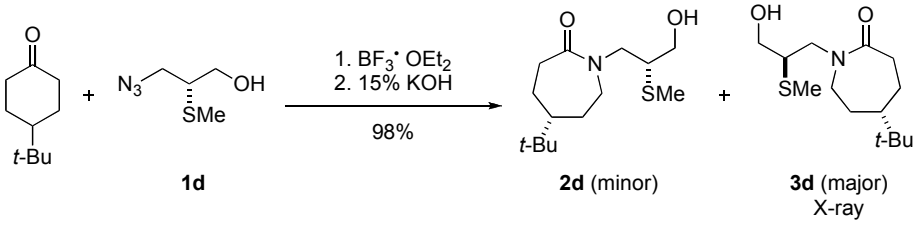
**Figure S2**. Lactams and diastereomeric ratios that have been previously reported.






- Ratio (±)-**2c**:(±)-**3c** = 4:96
- Diastereomeric ratio determined by $^{1}H$ and $^{13}C$ NMR, and GC ($t_R$ major: 27.7, $t_R$ minor: 27.1; Carbowax; 80 – 250 °C at 5 °C/min).
- *ent*-**3c** was recrystallized from $Et_2O$.

**5-*tert*-Butyl-1-(3′-hydroxy-2′-methoxypropyl)azepan-2-one**. **Compound** (±)-**3c**: white solid (0.54 g, 98%). Mp 114.2-116.8 ˚C. $R_f$ = 0.38 (100% EtOAc). $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 4.13 (m, 1H), 3.73 (m, 1H), 3.43 (m, 9H), 2.50 (m, 2H), 1.92 (m, 2H), 1.17 (m, 3H), 0.82 (s, 9H). $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ 177.6, 80.3, 59.5, 57.4, 51.5, 51.1, 47.7, 35.9, 33.0, 28.9, 27.5, 24.1. IR (neat) 3400, 2985, 1630 $cm^{-1}$. MS (ES+) *m/z* 280 $[M+Na]^+$; HRMS (ES+) calcd for $C_{14}H_{27}NO_3Na$ $[M+Na]^+$ 280.1889, found 280.1905. The X-ray for this compound can be obtained from the CCDC (647651); the structure of this racemic compound was arbitrarily solved as the enantiomer of **3c** depicted above. **Compound** (±)-**2c**: $^{13}C$ NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 80.2, 59.6, 57.3, 51.4, 47.9, 36.1, 28.6, 24.2.

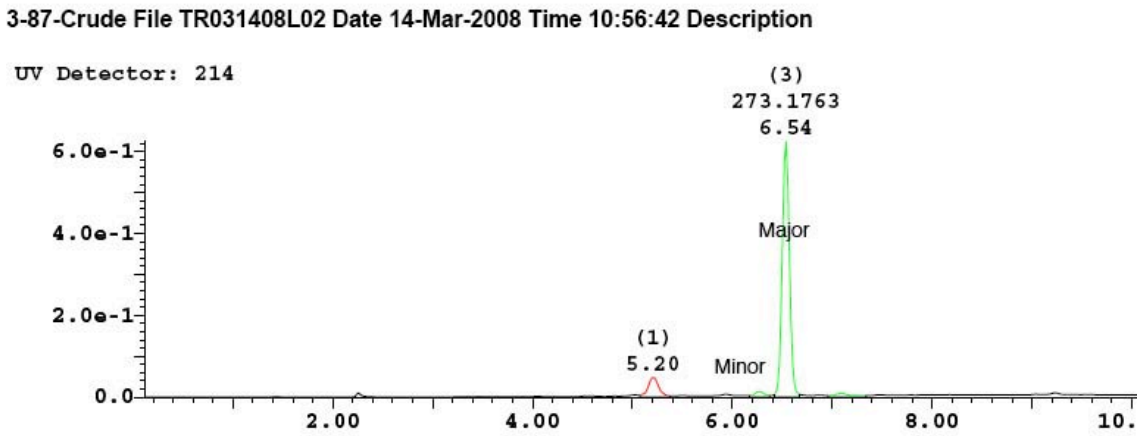



- Ratio (±)-**2d**:(±)-**3d** = 1.8:98.2
- Diastereomeric ratio determined by $^{1}H$ and $^{13}C$ NMR, and LCMS of crude reaction mixture ($t_R$ minor: 6.27 (MS 273.18), $t_R$ major: 6.54 (MS 273.18); Xterra MS C-18 column (5 μM, 4.6 × 150 mm) @ 10% $CH_3CN$ to 100% $CH_3CN$.
- *ent*-**3d** was recrystallized from $CH_2Cl_2$/hexanes.

**5-*tert*-Butyl-1-(3′-hydroxy-2′-(methylthio)propyl)azepan-2-one**. **Compound** (±)-**3d**: white solid (0.82 g, 98%). Mp 86.2-88.4 ˚C. $R_f$ = 0.5 (100% EtOAc). $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 4.48 (t, *J* =

14.4, 7.2, 1H), 3.86 (d, $J$ = 14 Hz, 1H), 3.66 (m, 1H), 3.57-3.39 (m, 3 Hz), 2.81 (m, 1H), 2.57 (m, 2 Hz) 2.15 (s, 3H), 1.99 (m, 2 H), 1.29-1.11 (m, 4 H), 0.87 (s, 9H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 177.6, 61.2, 51.5, 51.2, 48.8, 48.4, 36.0, 33.1, 29.4, 27.5, 24.1, 14.6. IR (neat) 3367, 2952, 1625 $cm^{-1}$. MS (ES+) *m/z* 273 $[M]^+$; HRMS (ES+) calcd for $C_{14}H_{28}NO_2S$ $[M+H]^+$ 274.1841, found 278.1852. The X-ray for this compound can be obtained from the CCDC (683831); the structure of this racemic compound was arbitrarily solved as the enantiomer of **3d** depicted above. **Compound** (±)-**2d:** a high resolution MS was obtained from the LCMS separated data. MS (ES+) *m/z* 273 $[M]^+$; HRMS (ES+) calcd for $C_{14}H_{28}NO_2S$ $[M+H]^+$ 274.1841, found 278.1849.

**Figure S3**. Chromatogram obtained from LCMS of the crude reaction to give **2d** and **3d**, respectively.

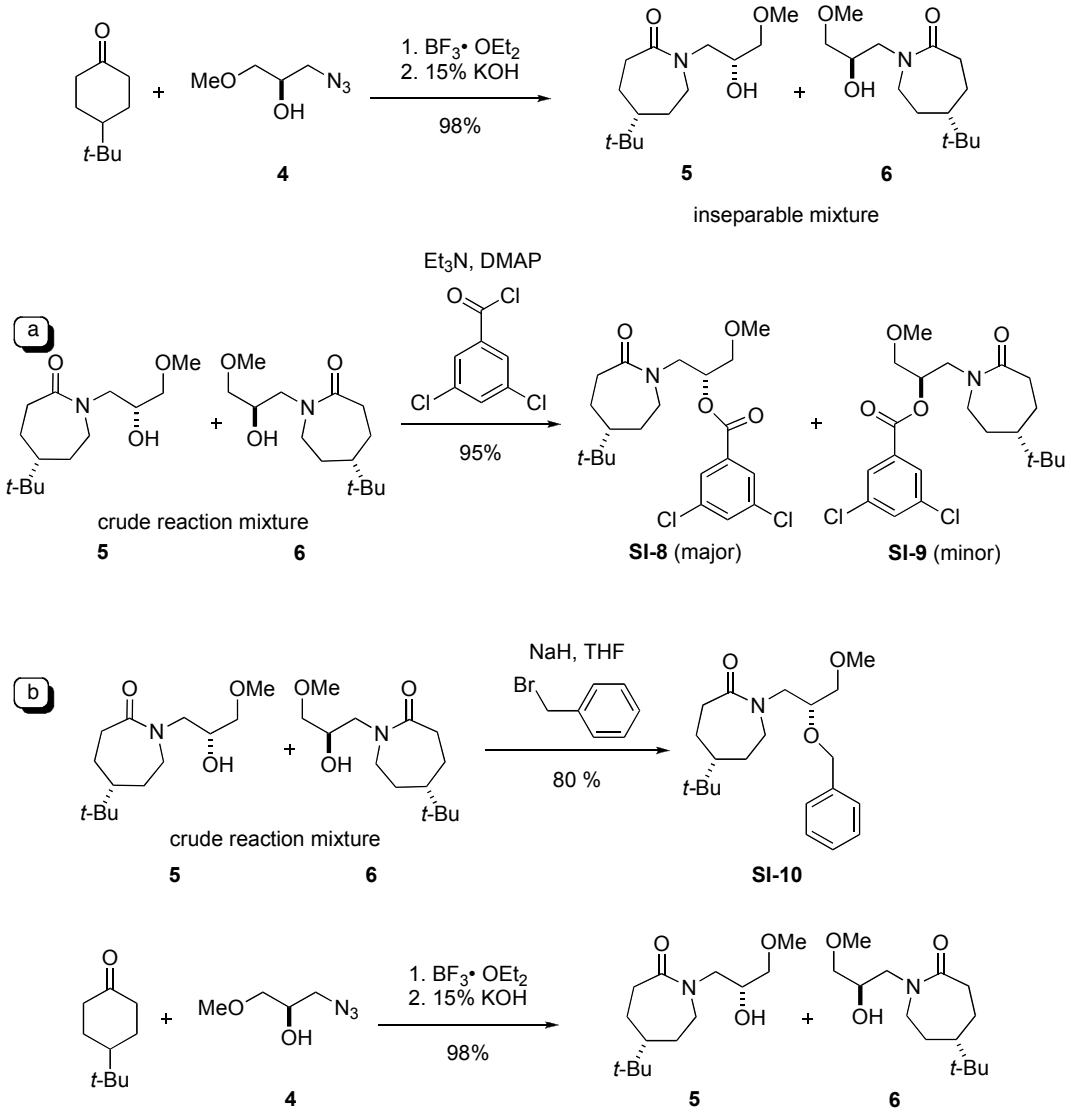



| eak Number | Time | AreaAbs | Area %Total | Height | Mass Found |
|---|---|---|---|---|---|
| 1 | 5.21 | 4951 | 8.62 | 43895 | |
| 2 | 6.27 | 914 | 1.59 | 10401 | 273.18 |
| 3 | 6.54 | 50950 | 88.72 | 617986 | 273.18 |

The ring expansion reaction of **4** and 4-*tert*-butyl-cyclohexanone gave a 98% yield of an inseparable mixture (by chromatography, HPLC, and GC) of lactams **5** and **6**. Acylation of the secondary alcohol by DMAP, $Et_3N$, and 3,5-dichlorobenzoic acid gave easily separable lactams **SI-8** and **SI-9** (Scheme S9a), from which a ratio was obtained by HPLC. Unfortunately, all attempts to obtain crystals from either the crude reaction mixture or the acylated products proved unsuccessful. However, it proved possible to benzylate the crude reaction mixture of **5** and **6** to afford a single crystalline product **SI-10** by recrystallization in ca. 80% yield (Scheme S6b; the fact that a single

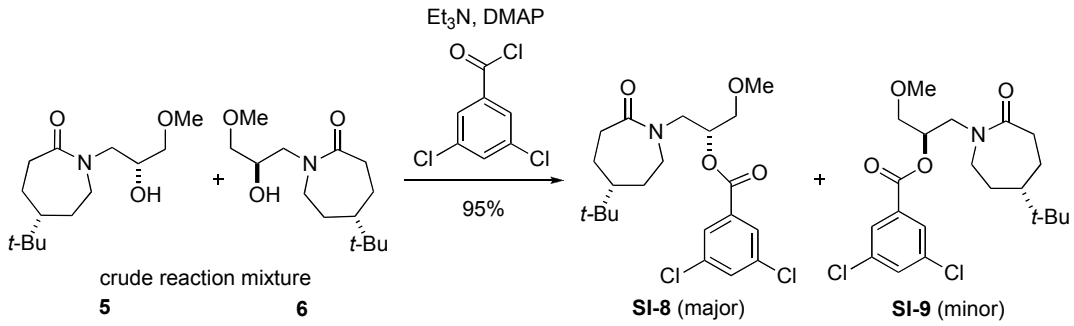
crystalline product could be obtained in such high yield from the 97:3 mixture of **5** and **6** clearly identifies it as a derivative of the major isomer). The structure of **SI-10** was solved by X-ray crystallography, thus proving the stereostructure of the major isomer **5**.

**Scheme S6**. Determination of diastereomeric ratio and structure of **5** and **6**.



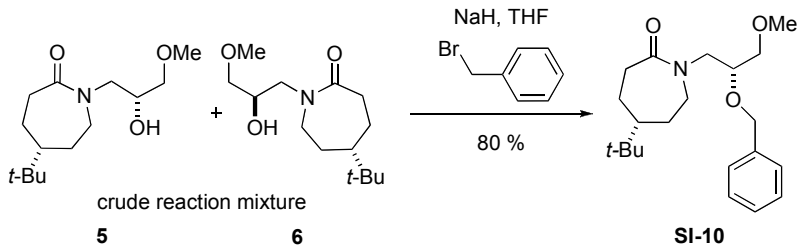

- Ratio (±)-**5** : (±)-**6** 97:3
- Diastereomeric excess determined by $^{1}$H– and $^{13}$C–NMR, and HPLC of **SI-8**/**SI-9** ($t_R$ major: 88.7, $t_R$ minor: 91.4; Phenomenex C18; 10 to 80% gradient ACN/$H_2O$ over 130 min; flow rate 1.0 mL/min; 40 °C isothermal; UV 254 nm).
- **SI-10** (**5** benzyl derivative) was recrystallized from hexanes

**5-*tert*-Butyl-1-(2′-hydroxy-3′-methoxypropyl)azepan-2-one** (two isomers **5**,**6**): colorless oil (0.52 g, 98%). $R_f$ = 0.41 (70% EtOAc/hexanes). **Major Isomer** (**5**): $^1$H NMR (400 MHz, $CDCl_3$) δ 4.02 (m, 1H), 3.86 (s, 1H), 3.47 (m, 2H), 3.32 (m, 7H), 2.48 (m, 2H), 1.87 (s, 2H), 0.95 (s, 3H), 0.79 (s, 9H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 177.7, 74.4, 70.2, 59.0, 52.5, 51.2, 50.8, 36.1, 33.1, 29.6, 27.5, 24.0. **Minor Isomer (6)**: $^{13}$C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 177.6, 74.5, 69.9, 52.7, 51.4, 50.8, 29.1. IR (neat) 3405, 2980, 2890, 1630 cm$^{-1}$. MS (ES+) *m/z* 280.2 $[M+Na]^+$; HRMS (ES+) calcd for $C_{14}H_{27}NO_3Na$ $[M+Na]^+$ 280.1889, found 280.1902.




**1-(5'-*tert*-Butyl-2'-oxoazepan-1'-yl)-3-methoxypropan-2-yl 3,5-dichlorobenzoate**. Triethylamine (1.58 ml, 11.3 mmol) and 4-di(methylamino)pyridine (0.02 g, 0.2 mmol) were added to a stirred solution of **5** and **6** (0.16 g, 0.60 mmol) in anhydrous $CH_2Cl_2$ (19 ml, 0.2 M), which was then cooled to 0 ˚C. After 10 min of stirring at 0 ˚C, 3,5-dichlorobenzoic acid (1.03 g, 4.97 mmol) was added to the homogenous solution and allowed to slowly warm to room temperature. After 18–24 h of stirring at room temperature, the solution was quenched with saturated $NH_4Cl$, then diluted with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (4 × 20 mL). The combined organic layers were washed with brine, dried ($Na_2SO_4$), and concentrated to an orange oil that was purified by column chromatography (20-70% EtOAc/hexanes) to provide pure compounds **SI-8** and **SI-9**. **Compound** (±)-**SI-8**: colorless oil (1.47 g, 96%). $R_f$ = 0.50 (50% EtOAc/hexanes). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H), 7.33 (t, *J* =4.0 Hz, 1Hz), 5.21 (m, 1H), 3.54 (m, 2H), 3.44 (d, *J* = 4.8 Hz, 1H), 3.30 (m, 1H), 3.20 (m, 1H),

3.17 (s, 3H), 2.34 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.26 (t, *J* = 11.6 Hz, 1H), 1.73 (m, 2H), 1.01 (m, 3H), 0.63 (s, 9H), 0.59 (s, 1H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 177.7, 163.4, 135.0, 132.7, 132.6, 127.9, 73.0, 71.8, 59.0, 51.1, 50.0, 48.4, 36.0, 32.8, 30.5, 29.5, 27.3. IR (neat) 2970, 1730, 1650, 1540 cm$^{-1}$. MS (ES+) *m/z* 430.2 $[M+1]^+$; HRMS (ES+) calcd for $C_{21}H_{30}Cl_2NO_4$ $[M+1]^+$ 430.1552, found 430.1532. **Compound** (±)-**SI-9**: $^{13}$C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 177.2, 163.9, 135.3, 132.9, 132.8, 128.1, 72.8, 71.9, 60.2, 51.2, 50.1, 48.7, 36.1, 32.9, 29.6, 27.4, 23.9.

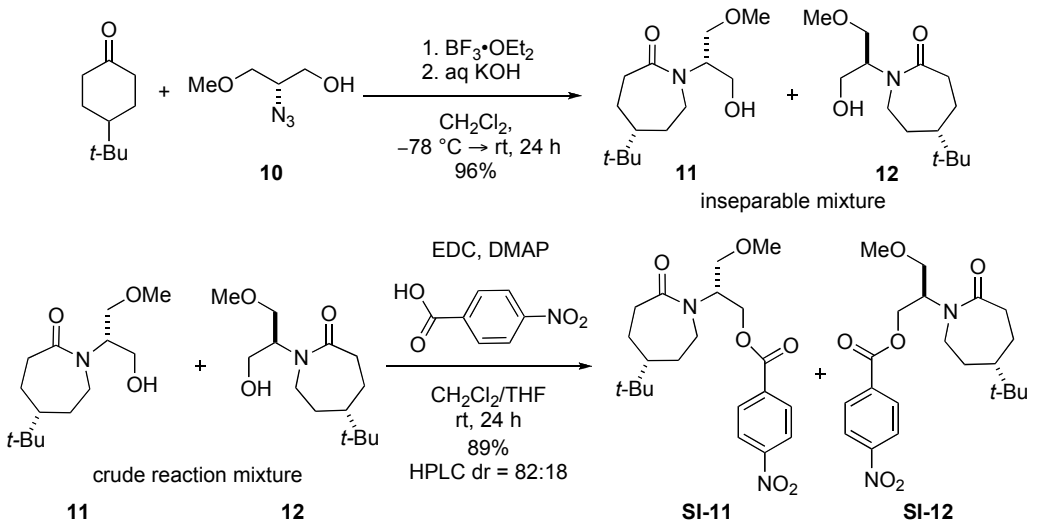


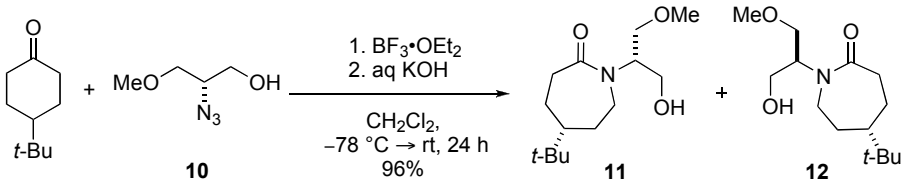

**1-(2′-Benzyloxy-3′-methoxypropyl)-5-*tert*-butylazepan-2-one**. A crude reaction mixture of **5** and **6** (1.0 g, 4.2 mmol) in anhydrous THF (1.5 mL) was added to a flask containing NaH (60%, 0.48 g, 14.0 mmol) via a cannula, and the resulting murky solution was stirred for 30 min. Benzyl bromide (0.66 mL, 5.6 mmol) was added dropwise and the reaction mixture was stirred for an additional 30 min, at which time the reaction was quenched slowly with $H_2O$ (35 mL), and extracted with $Et_2O$ (4 × 40 mL). The combined organic layers were washed with water, brine, dried ($Na_2SO_4$), and concentrated to a yellow oil. Excess benzyl bromide was removed in vacuo and the resulting off-white solid was purified by crystallization from hot hexanes to give colorless crystals (1.24 g, 80%). A single diastereomer **SI-10** was isolated in 80% yield, providing sufficient evidence that **5** is indeed the major diastereomer from the ring expansion reaction. The minor diastereomer resulting from alkylation of **6** was not observed or isolated from the mother liquor. **Compound** (±)-**SI-10**: $R_f$ = 0.34 (70% EtOAc/hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 2H), 7.29 (m, 3H), 5.21 (m, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 12 Hz, 1H), 3.82 (m, 2H), 3.54 (dd, *J* = 10.8, 3.6 Hz 1H), 3.46

(dd, $J$ = 10.4, 4.8 Hz 1H), 3.40 (m, 5H), 3.22 (dd, $J$ = 13.6, 7.6 Hz, 1H), 2.51 (dd, $J$ = 14, 7.2 Hz, 1H), 2.40 (m, 1H), 1.90 (m, 2H), 1.20 (m, 3H), 0.86 (s, 9H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 176.0, 138.6, 128.3, 127.8, 127.6, 73.3, 72.3, 59.3, 51.6, 51.0, 50.2, 36.4, 33.1, 29.1, 27.6, 24.1. IR (neat) 3000, 1655, 1460 cm$^{-1}$. MS (ES+) *m/z* 370.2 $[M+1]^+$; HRMS (ES+) calcd for $C_{21}H_{33}NO_3Na$ $[M+Na]^+$ 370.2358, found 370.2358. The X-ray for this compound can be obtained from the CCDC (647652).

**The ring expansion reaction of 10 and 4-*tert*-butyl-cyclohexanone** gave a 96% yield of an inseparable mixture (by chromatography, HPLC, and GC) of **11** and **12**. Acylation of the secondary alcohol by 4-nitrobenzoic acid, DMAP, and $Et_3N$ and gave easily separable lactams **SI-11** and **SI-12** (Scheme S10), from which a ratio was obtained by HPLC. This method also provided structure of **SI-11** which could be solved by X-ray crystallography, thus proving the stereostructure of the major isomer **11**.

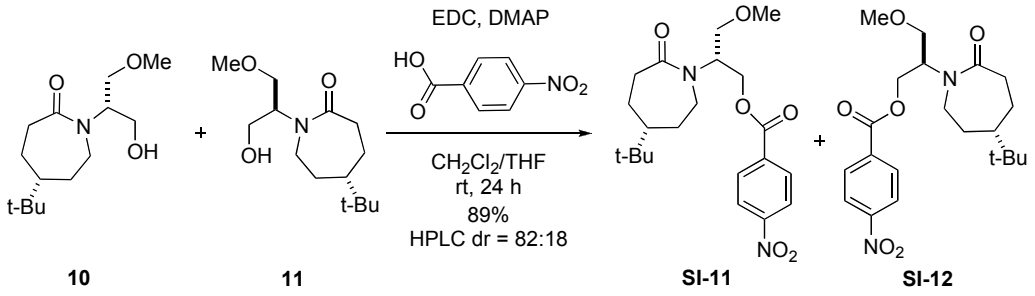
**Scheme S10**. Determination of diastereomeric ratio and structure of **11**,**12**.






- Ratio (±)-**11** : (±)-**12** 83:17
- Diastereomeric excess determined by $^{1}$H– and $^{13}$C–NMR, and HPLC of **SI-11**/**SI-12** ($t_R$ minor: 56.200, $t_R$ minor: 58.377; Phenomenex C18; 5 to 95% gradient ACN/$H_2O$ over 95 min; flow rate 1.0 mL/min; 40 °C isothermal; UV 254 nm).
- **SI-11** (*p*-$NO_2$-benzoylated **11**) was recrystallized from EtOH/Acetone/$H_2O$

**5-*tert*-Butyl-1-(1′-hydroxy-3′-methoxypropan-2′-yl)azepan-2-one** (two isomers **11**,**12**): colorless oil (0.62 g, 96%). $R_f$ = 0.40 (70% EtOAc/hexanes). **Major isomer** (**11**): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.49 (m, 1H), 3.7 (m, 1H), 3.57 (m, 5H), 3.28 (m, 4H), 2.50 (t, *J* = 3.10 Hz, 2H), 1.90 (m, 2H), 1.12 (m, 3H), 0.81 (s, 9H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 177.3, 71.0, 61.6, 58.7, 56.8, 51.3, 45.6, 36.6, 32.9, 29.5, 27.5, 24.1. **Minor isomer** (**12**): $^{13}$C NMR (100.6 MHz, $CDCl_3$, diagnostic peaks only) δ 177.1, 70.9, 61.9, 58.8, 58.2, 56.8, 51.3, 45.6, 36.6, 32.9, 29.5, 27.5, 24.1. IR (neat) 3405, 2980, 2890, 1630 cm$^{-1}$. MS (ES+) *m/z* 280.2 [M+ Na]$^+$; HRMS (ES+) calcd for $C_{14}H_{27}NO_3Na$ [M+Na]$^+$ 280.1889, found 280.1893.




**2-(5′-*tert*-Butyl-2′-oxoazepan-1′-yl)-3-methoxypropyl 4-nitrobenzoate** (**SI-11**, **SI-12**). 4-Nitrobenzoic acid (0.11 g, 0.7 mmol) and 4-dimethylaminopyridine (0.01 g, 0.10 mmol) were added to a stirred solution of **10** and **11** (0.16 g, 0.6 mmol) in anhydrous THF/$CH_2Cl_2$ (1:1, 4 mL) and then

cooled to 0 ˚C. After 10 min of stirring at 0 ˚C, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide, (EDC) (0.13 g, 0.6 mmol) was added to the homogenous solution, which was allowed to warm to room temperature and strirred 18–24 h. The solution was then quenched with 1M aq HCl, diluted with $H_2O$ (20 mL), and extracted with $CH_2Cl_2$ (4 × 20 mL). The combined organic layers were washed with saturated $NaHCO_3$ and brine, then dried ($Na_2SO_4$), and concentrated to a yellow oil. Purification by chromatography (40-100% EtOAc/hexanes) provided pure compounds **SI-11** and **SI-12**. **Compound** (±)-**SI-11**: white solid (0.27 g, 81%). $R_f$ = 0.68 (50% EtOAc/hexanes). Mp 100.5-101.4 ˚C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H), 5.09 (m, 1H), 4.61 (dd, *J* = 11.6, 8.4 Hz, 1H), 4.46 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.66 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.58 (m, 2H), 3.34 (m, 4H), 2.58 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.44 (m, 1H), 1.97 (dd, *J* = 11.2, 8.0 Hz, 2H), 1.24 (m, 3H), 0.86 (s, 9H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 176.6, 164.3, 150.6, 135.2, 130.8, 132.6, 127.9, 71.2, 63.4, 52.4, 51.3, 44.8, 36.5, 33.0, 29.9, 27.5, 24.2. IR (neat) 2990, 1740, 1655 cm$^{-1}$. MS (ES+) *m/z* 407.2 $[M+1]^+$; HRMS (ES+) calcd for $C_{21}H_{30}N_2O_6Na$ $[M+ Na]^+$: 429.2001, found 429.2010. The X-ray for this compound can be obtained from the CCDC (647654).

**Compound** (±)-**SI-12**: white solid (0.06 g, 19%). $R_f$ = 0.31 (50% EtOAc/hexanes). Mp 90.1-91.6 ˚C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 5.16 (m, 1H), 4.54 (d, *J* = 6.8 Hz, 2H), 3.66 (dd, *J* = 8.8 Hz, 2H), 3.66 (s, 1H), 3.57 (m, 1H), 3.36 (s, 3H), 2.62 (m, 2H), 1.97 (m, 1H), 1.14 (m, 4H), 0.77 (s, 9H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 176.7, 164.3, 150.7, 135.1, 130.8, 123.6, 71.6, 63.6, 59.1, 52.1, 51.3, 44.5, 36.5, 33.0, 29.9, 27.4, 24.2. IR (neat), 2990, 1740, 1645, 1545 cm$^{-1}$. MS (ES+) *m/z* 407.2 $[M+Na]^+$; HRMS (ES+) calcd for $C_{21}H_{30}N_2O_6Na$ $[M+Na]^+$ 429.2001, found 429.2001.

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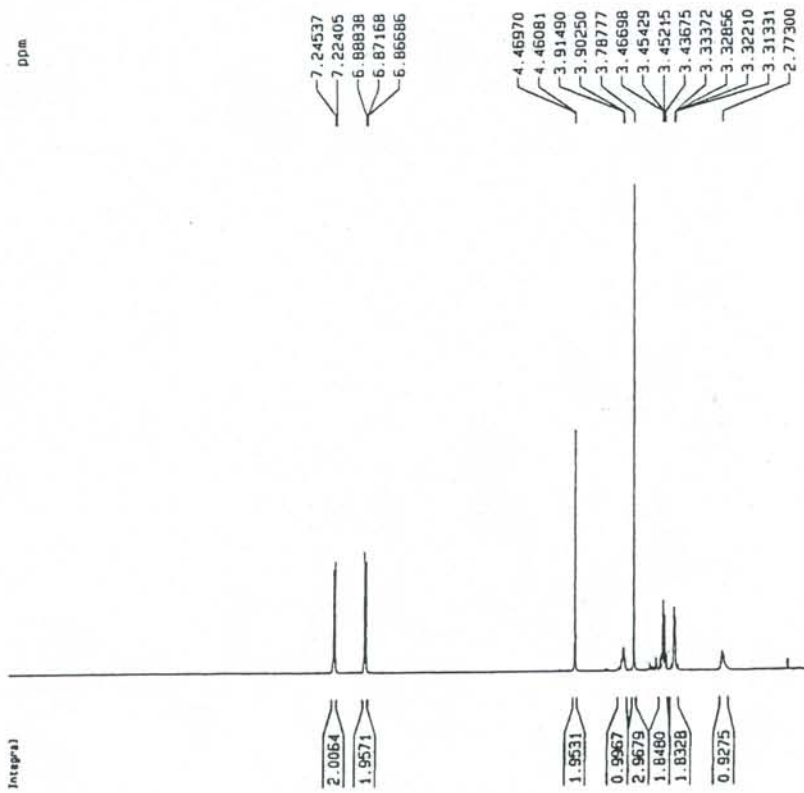


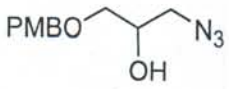


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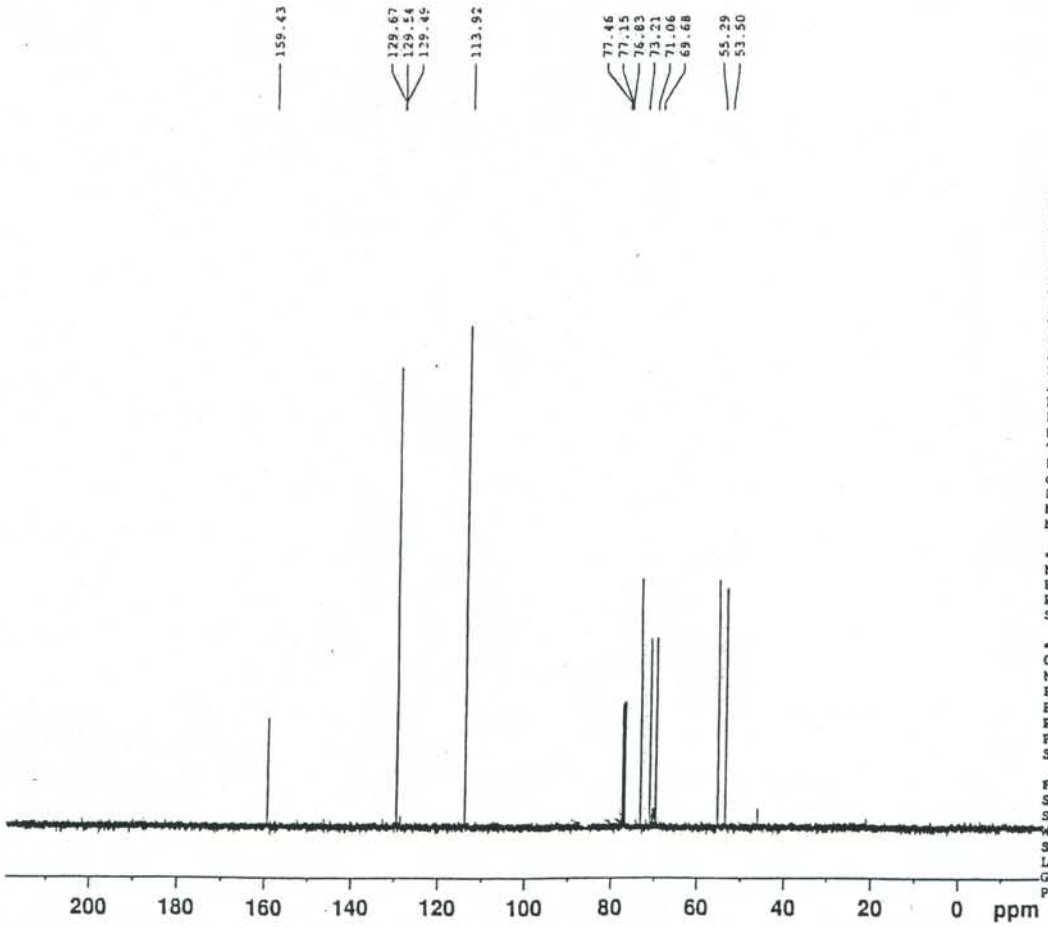


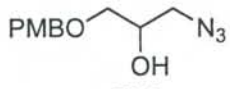


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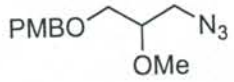


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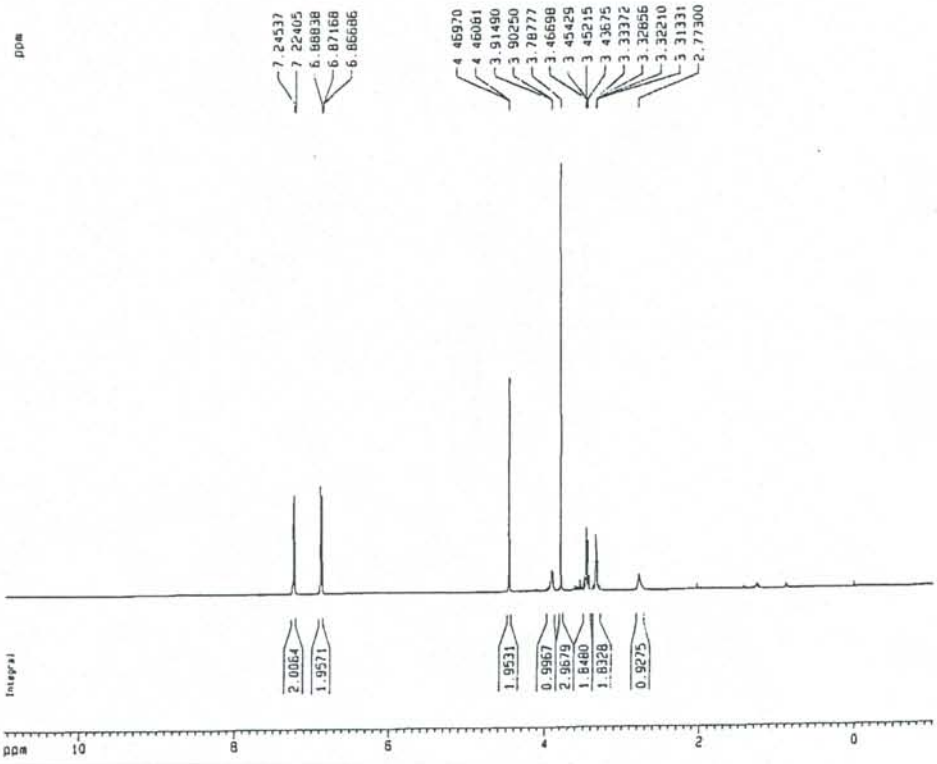


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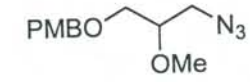


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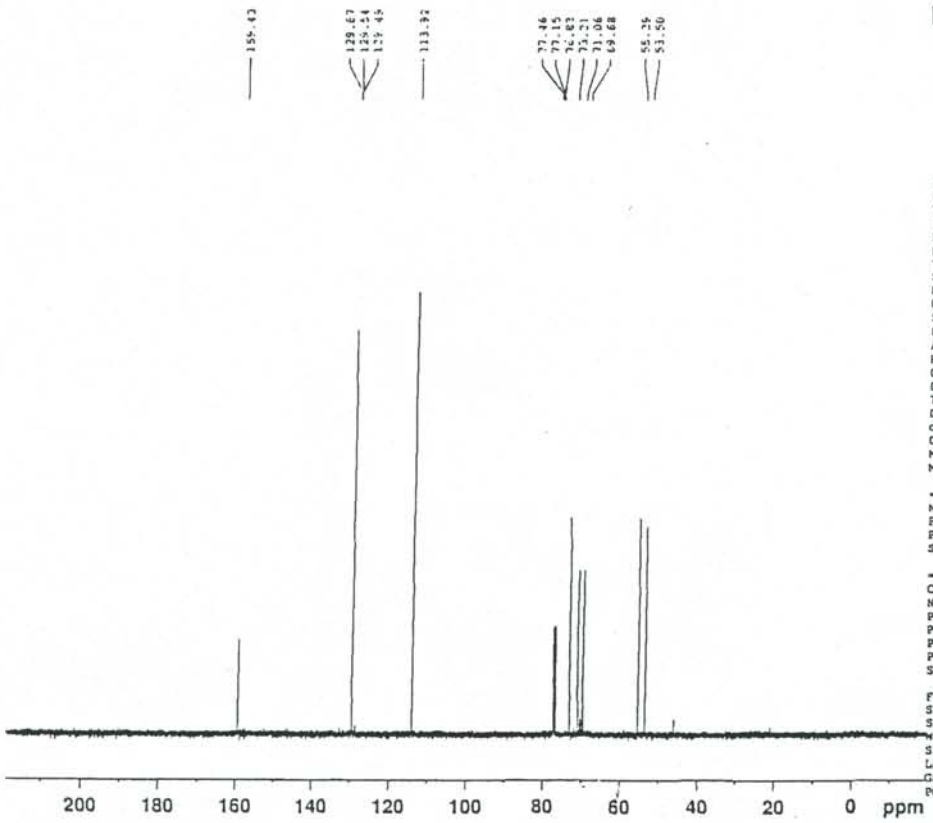


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PL13               120.00 dB
SFO2          400.1316005 MHz

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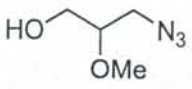
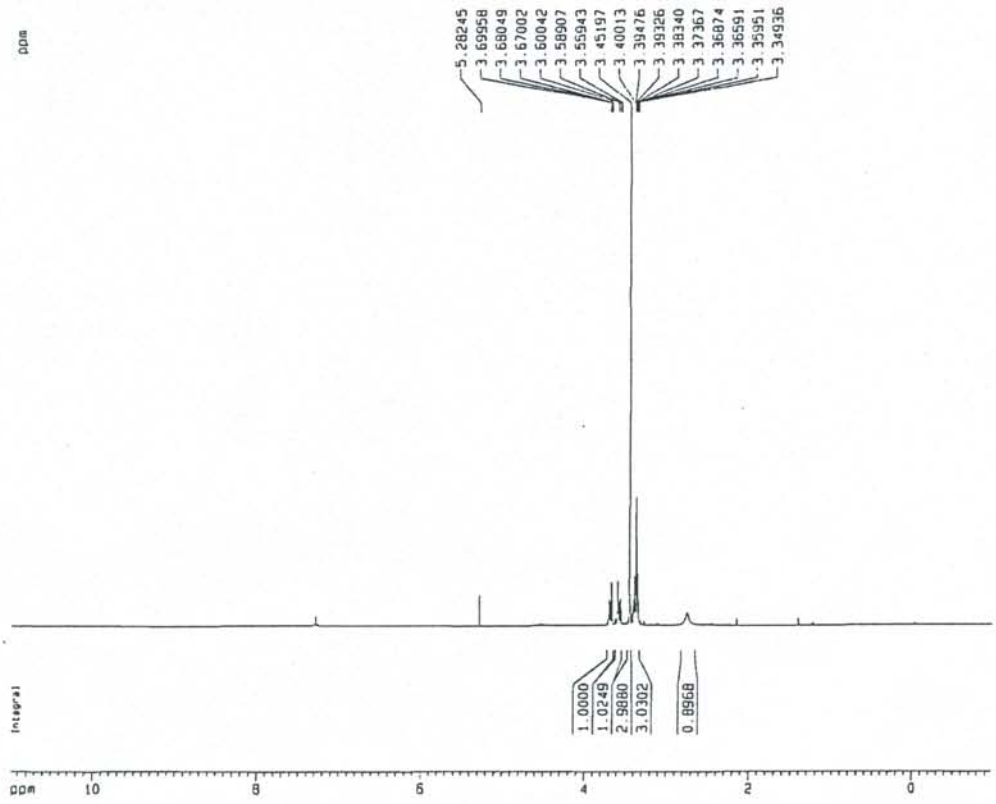
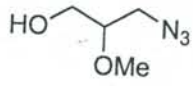


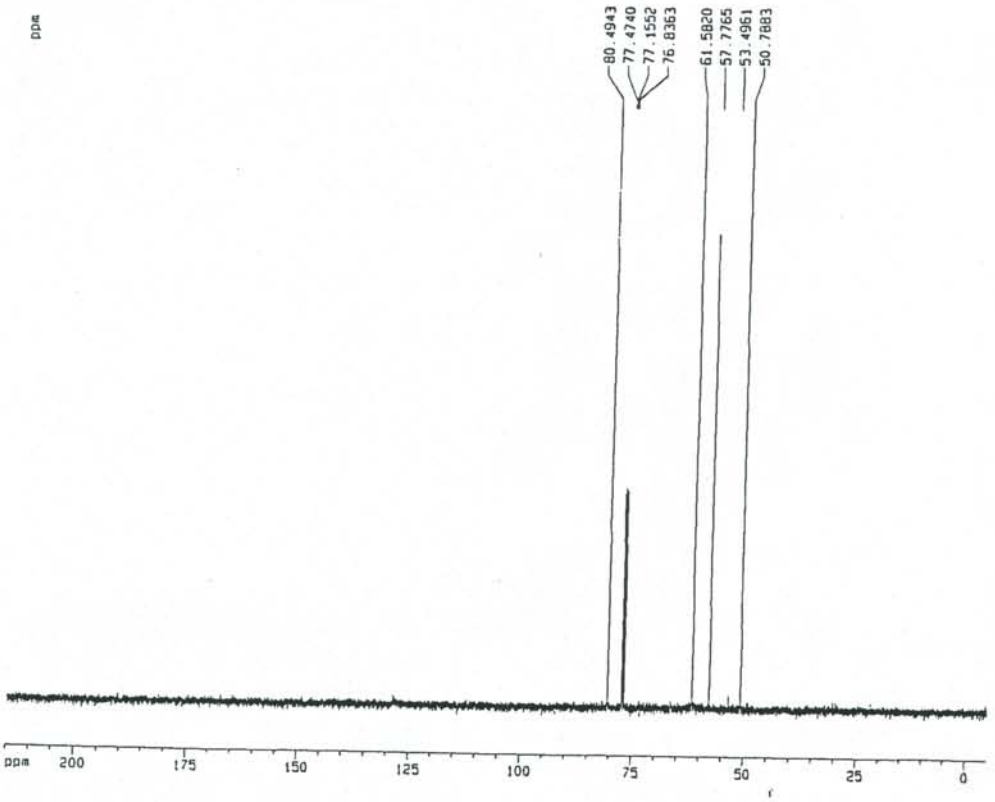

**1c**



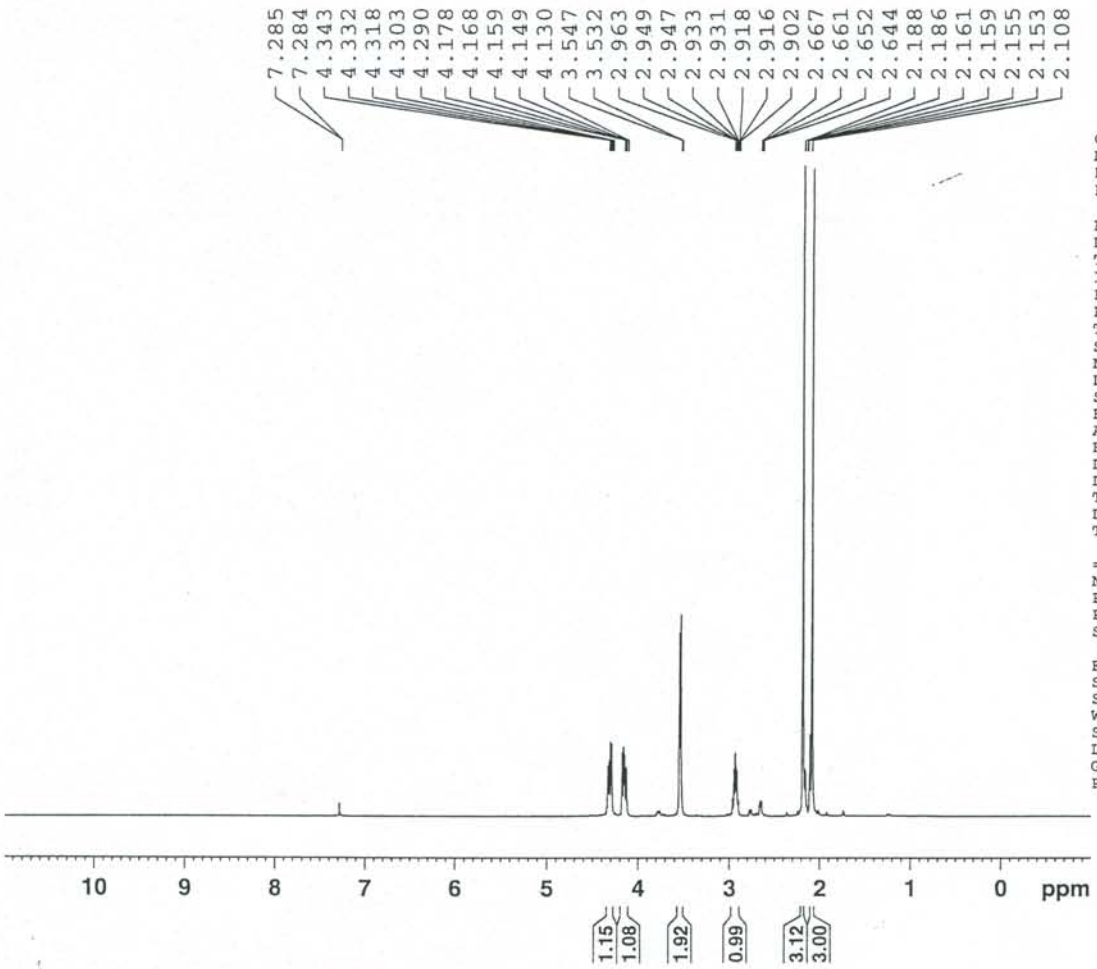

```
--- Acquisition Parameters
Date_                20050920
Time                    14.40
INSTRUM                 spect
PROBHD   5 mm QNP 1H/15
PULPROG                 zg30
TD                     32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                       50.8
DW                    104.400 usec
DE                      6.00 usec
TE                     296.9 K
D1                  1.00000000 sec
HCREST              0.00000000 sec
HCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       7.05 usec
PL1                     -3.00 dB
SFO1              400.1320007 MHz

F2 - Processing parameters
SI                         32768
SF                  400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
CY                       0.00 cm
F1P                    11.000 ppm
F1                   4401.43 Hz
F2P                   -1.000 ppm
F2                    -400.13 Hz
PPMCM                0.50000 ppm/cm
HZCM                240.07800 Hz/cm
```

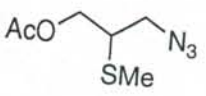



**1c**




```
F2 - Acquisition Parameters
Date_                20050920
Time                    14.43
INSTRUM                 spect
PROBHD   5 mm QNP 1H/15
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        104
DS                          4
SWH                 23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                       2048
DW                    20.850 usec
DE                     6.00 usec
TE                     297.0 K
D1                  0.15000001 sec
d11                 0.03000000 sec
DELTA               0.05000000 sec
HCREST              0.00000000 sec
HCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                       7.20 usec
PL1                     -2.00 dB
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                       1H
PCPD2                   98.40 usec
PL2                     -3.00 dB
PL12                    19.96 dB
PL13                   120.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127690 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
CY                       0.00 cm
F1P                   215.000 ppm
F1                   21631.75 Hz
F2P                    -5.000 ppm
F2                    -503.06 Hz
PPMCM               11.00000 ppm/cm
HZCM                1106.74048 Hz/cm
```




**SI-3**

C
N
E
I

F2 - Acquisition Parameters

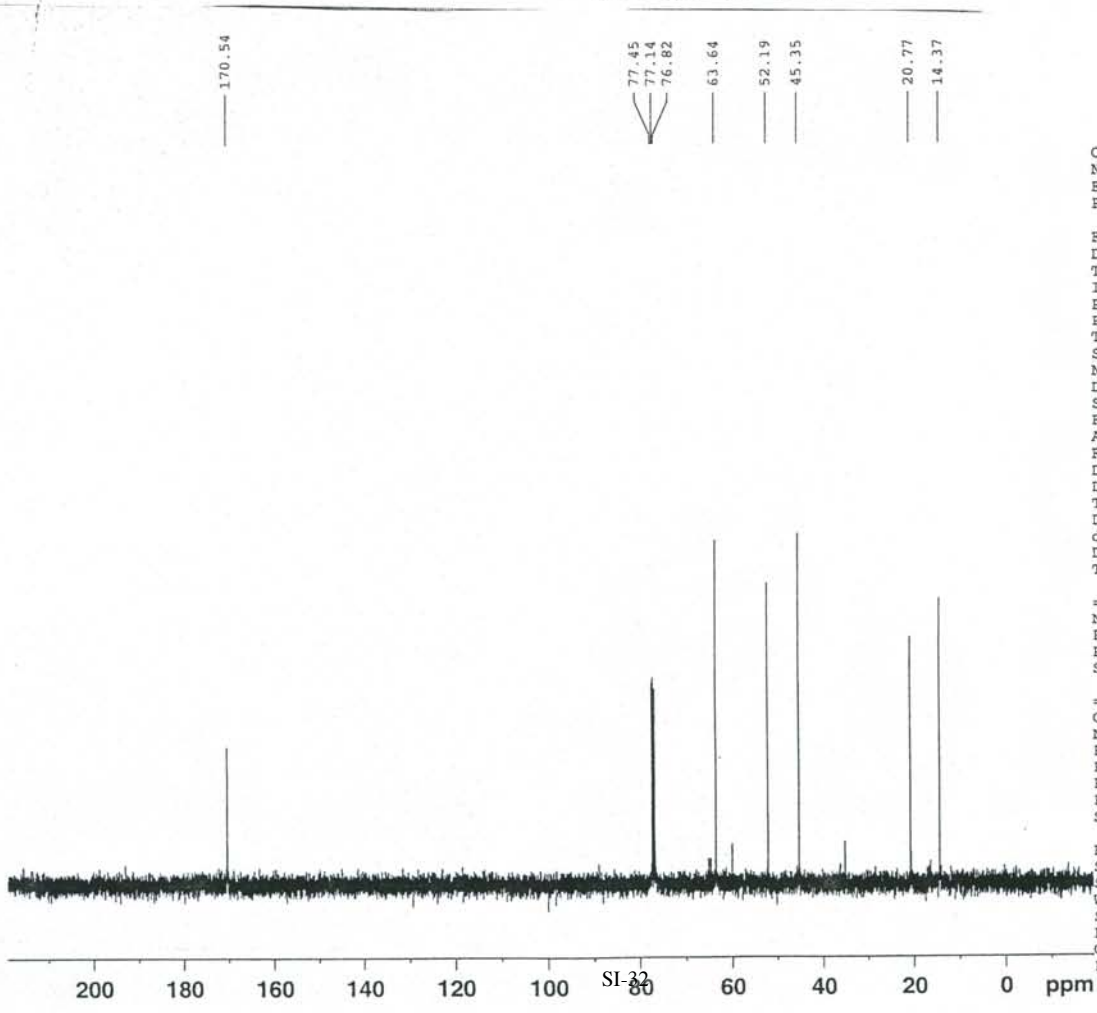
| | |
|---|---|
| Date_ | 20080317 |
| Time | 13.44 |
| INSTRUM | drx400 |
| PROBHD | 5 mm QNP 1H/13 |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.126314 Hz |
| AQ | 3.9584243 sec |
| RG | 90.5 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 296.2 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

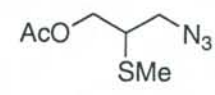
======== CHANNEL f1 ========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 10.50 usec |
| PL1 | -5.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300000 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |




**SI-3**

Cu
NA
EX
PR

_B

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20080317 |
| Time | 12.55 |
| INSTRUM | drx400 |
| PROBHD | 5 mm QNP 1H/13 |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 28 |
| DS | 4 |
| SWH | 23980.814 Hz |
| FIDRES | 0.365918 Hz |
| AQ | 1.3664756 sec |
| RG | 6502 |
| DW | 20.850 usec |
| DE | 6.00 usec |
| TE | 296.2 K |
| D1 | 2.00000000 sec |
| d11 | 0.03000000 sec |
| DELTA | 1.89999998 sec |
| TD0 | 1 |

======== CHANNEL f1 ========

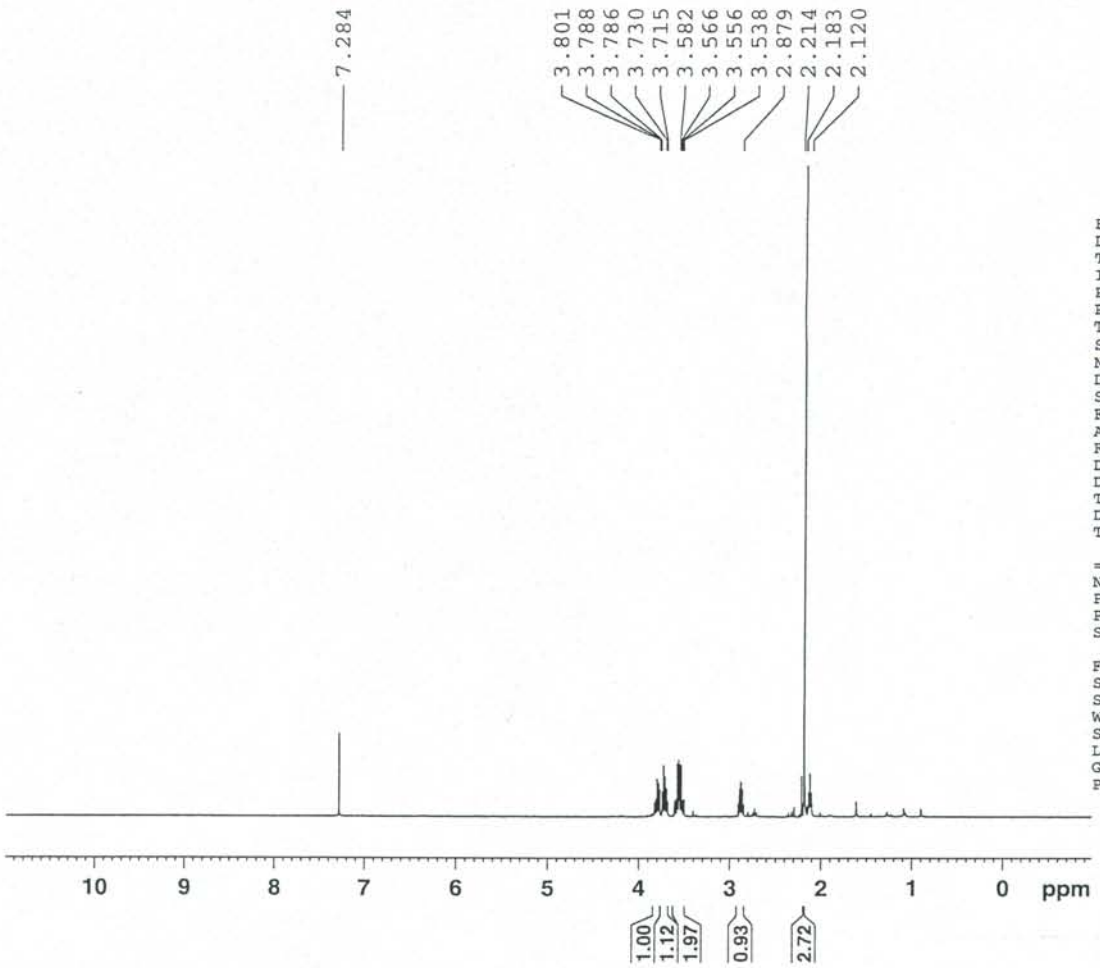
| | |
|---|---|
| NUC1 | 13C |
| P1 | 9.85 usec |
| PL1 | -2.00 dB |
| SFO1 | 100.6228298 MHz |

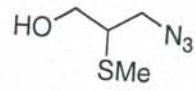
======== CHANNEL f2 ========

| | |
|---|---|
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 100.00 usec |
| PL2 | -5.00 dB |
| PL12 | 14.58 dB |
| PL13 | 16.00 dB |
| SFO2 | 400.1316005 MHz |

F2 - Processing parameters

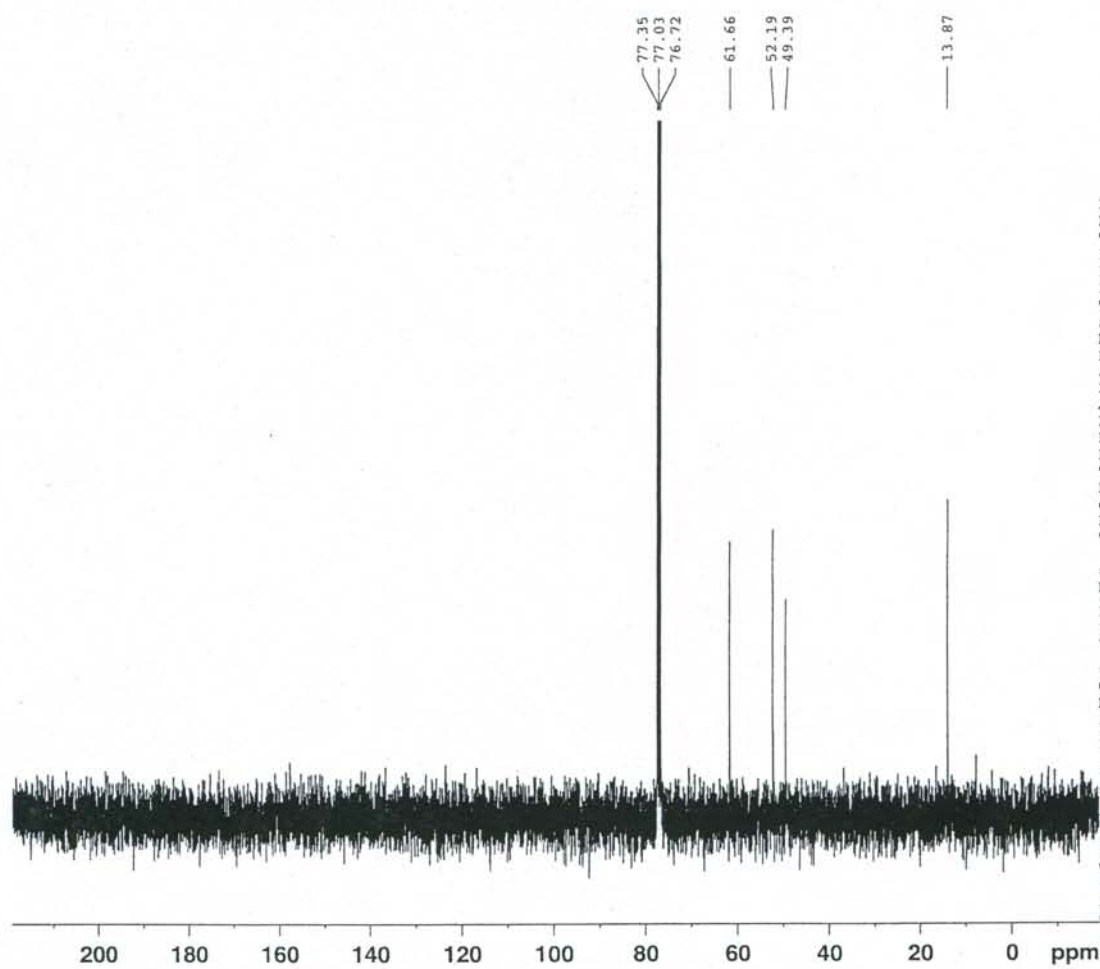
| | |
|---|---|
| SI | 32768 |
| SF | 100.6127690 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

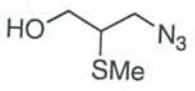



**1d**

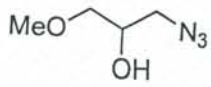
```
F2 - Acquisition Parameters
Date_              20080318
Time                 10.18
INSTRUM             drx400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      9
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                  406.4
DW                 60.400 usec
DE                  6.00 usec
TE                 296.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.50 usec
PL1                 -5.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF             400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



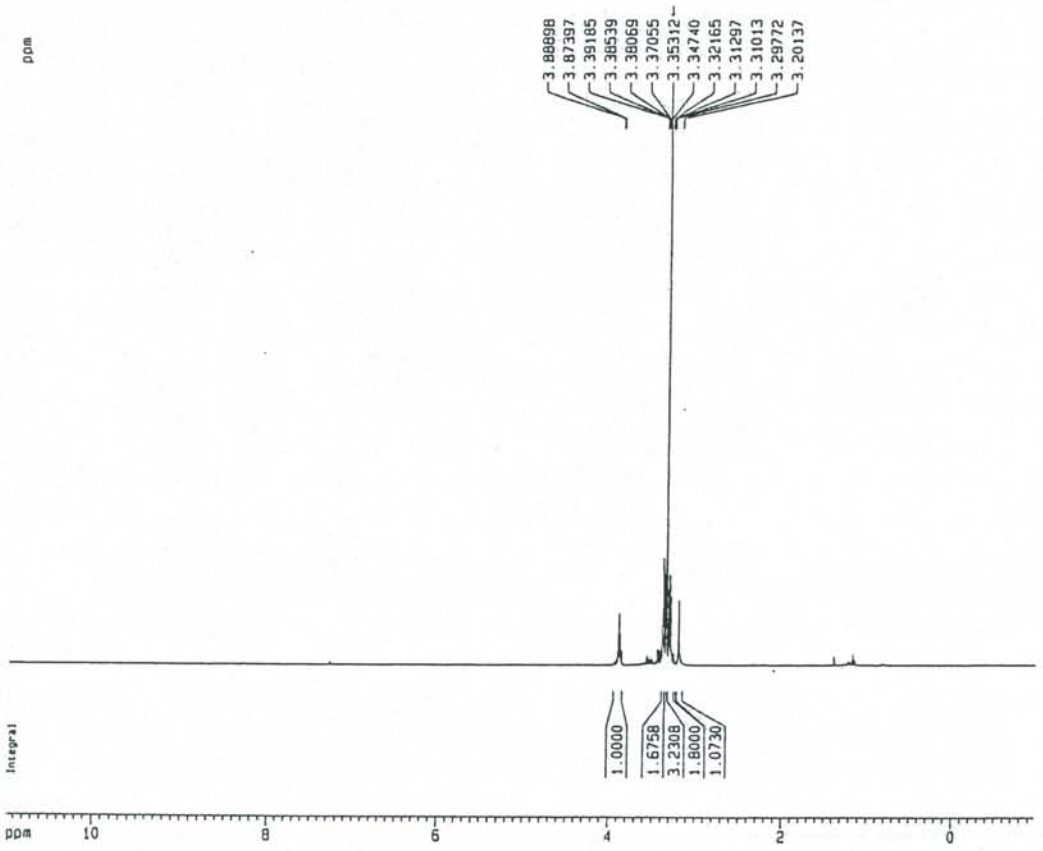




**1d**

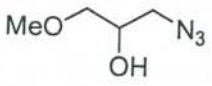
```
F2 - Acquisition Parameters
Date_              20080318
Time                 10.22
INSTRUM             drx400
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     88
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                  6.00 usec
TE                 296.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.85 usec
PL1                 -2.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                14.58 dB
PL13                16.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF             100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



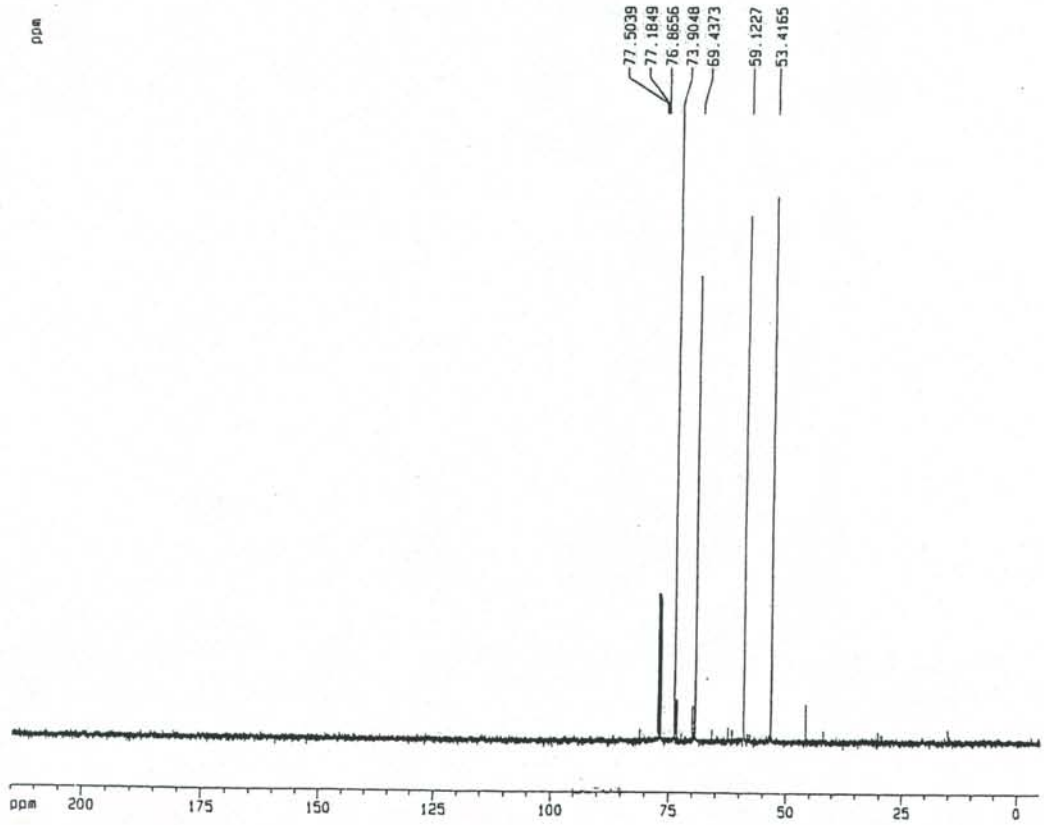

4



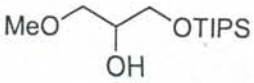

```
F2 - Acquisition Parameters
Date_              20051229
Time                 10.16
INSTRUM              spect
PROBHD  5 mm QNP 1H/15
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              4789.272 Hz
FIDRES           0.146157 Hz
AQ               3.4210291 sec
RG                      32
DW                104.400 usec
DE                  6.00 usec
TE                 295.8 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.05 usec
PL1                 -3.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                      32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                    0.00 cm
F1P                  11.000 ppm
F1                 4401.43 Hz
F2P                  -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.60000 ppm/cm
HZCM             240.07800 Hz/cm
```



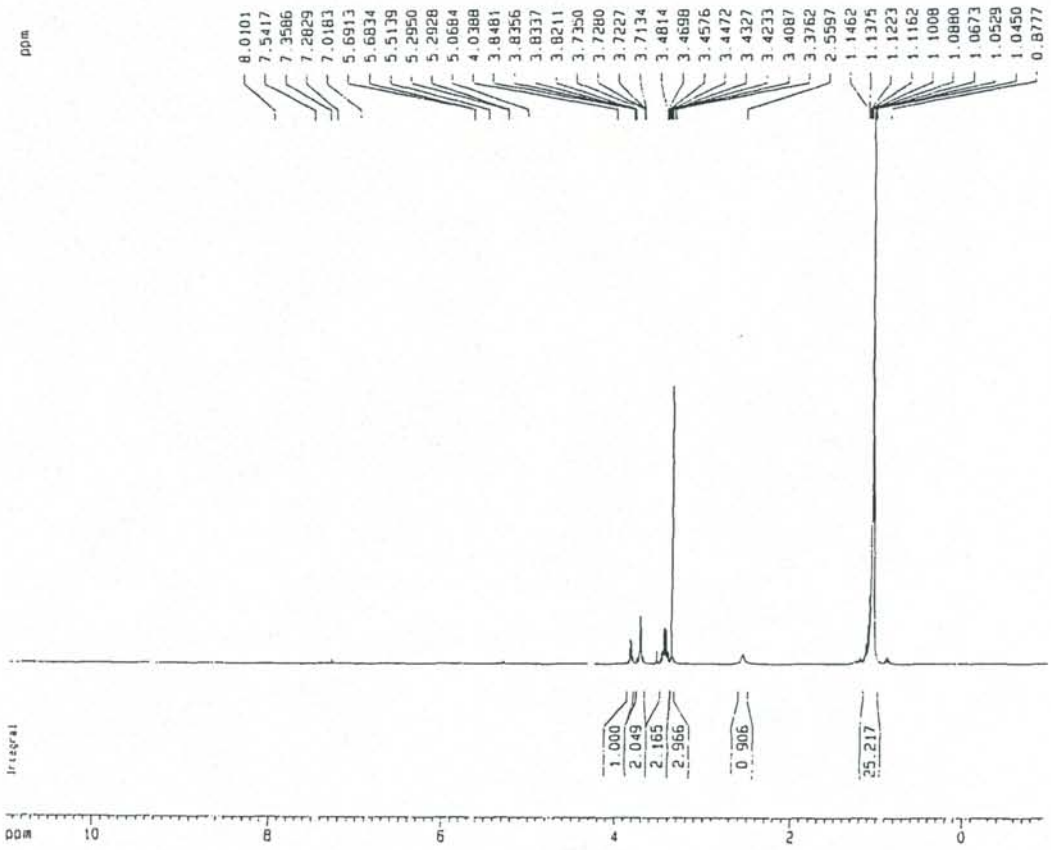

4



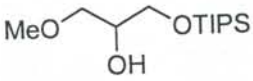

```
PROBHD  3 mm BBO 1H/19
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      71
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                    2048
DW                20.850 usec
DE                   6.00 usec
TE                 298.0 K
D1               0.15000001 sec
d11              0.03000000 sec
DELTA            0.85000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   7.20 usec
PL1                 -2.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               98.40 usec
PL2                 -3.00 dB
PL12                19.96 dB
PL13                120.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
CY                    0.00 cm
F1P                  215.000 ppm
F1                 21631.75 Hz
F2P                  -5.000 ppm
F2                 -503.06 Hz
PPMCM              11.00000 ppm/cm
HZCM             1106.74048 Hz/cm
```



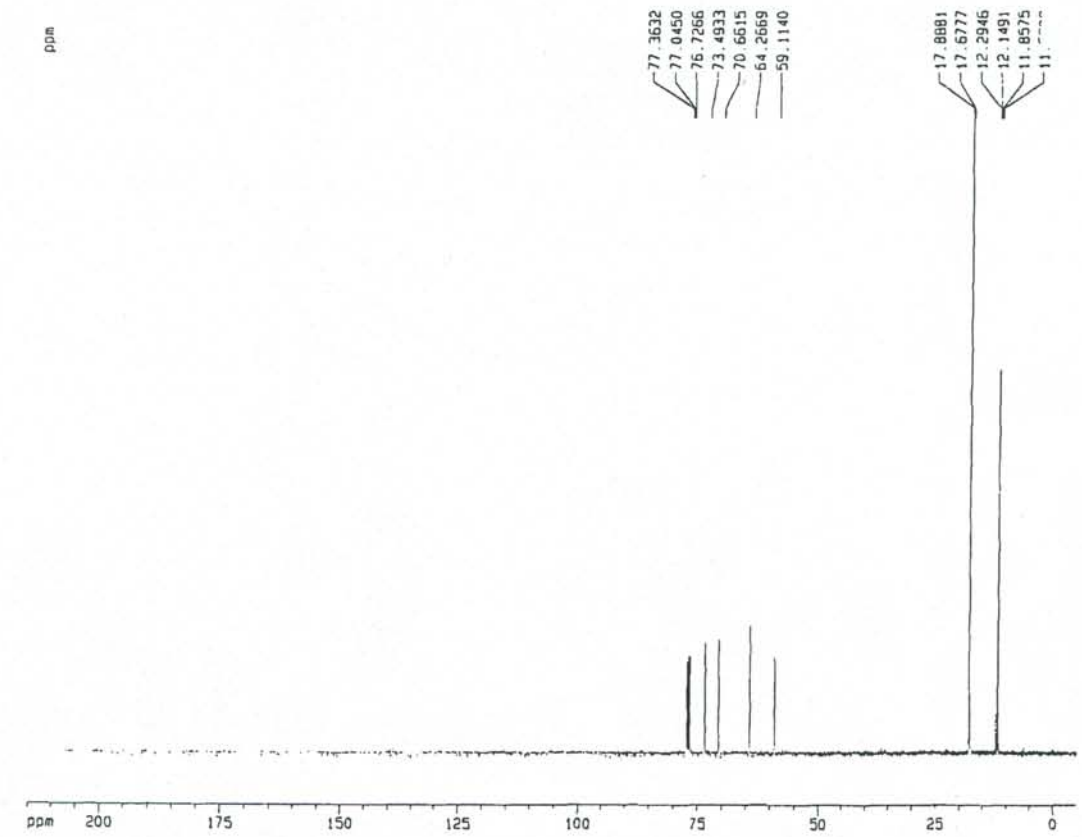

**SI-5**



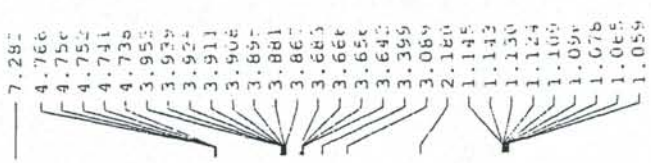

```
F2 - Acquisition Parameters
Date_              20060108
Time                  17.20
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              4789.272 Hz
FIDRES           0.146157 Hz
AQ               3.4210291 sec
RG                      32
DW                104.400 usec
DE                  6.00 usec
TE                 296.6 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

-------- CHANNEL f1 --------
NUC1                   1H
P1                  7.05 usec
PL1                -3.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                   0.00 cm
F1P                11.000 ppm
F1               4401.43 Hz
F2P                -1.000 ppm
F2               -400.13 Hz
PPMCM             0.60000 ppm/cm
HZCM            240.07800 Hz/cm
```

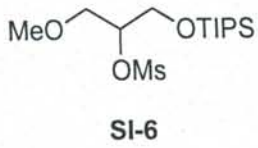



**SI-5**

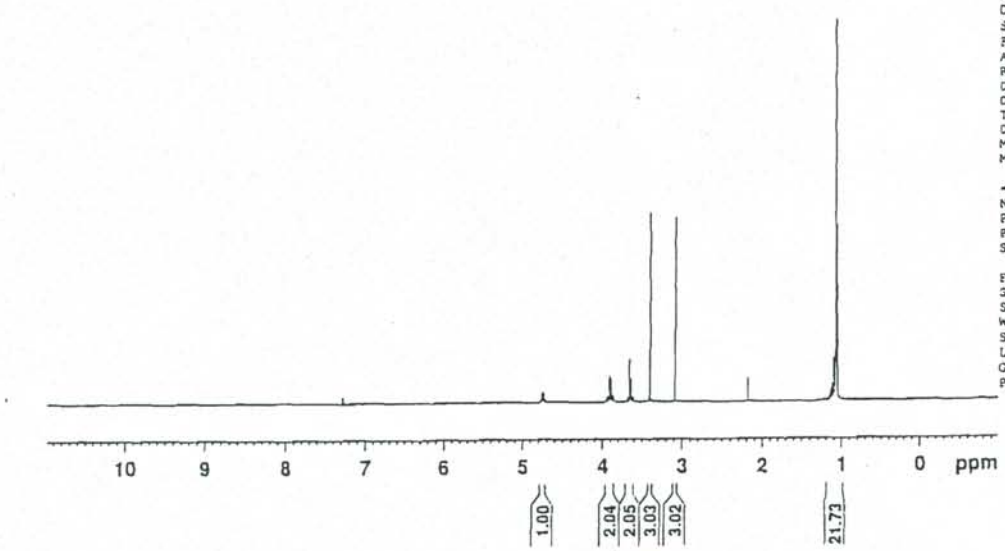



```
F2 - Acquisition Parameters
Date_              20060108
Time                  17.23
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                    2048
DW                20.850 usec
DE                  6.00 usec
TE                 296.8 K
D1               0.15000001 sec
d11              0.03000000 sec
DELTA            0.05000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

-------- CHANNEL f1 --------
NUC1                   13C
P1                  7.20 usec
PL1                -2.00 dB
SFO1          100.6226258 MHz

-------- CHANNEL f2 --------
CPDPRG2            waltz16
NUC2                   1H
PCPD2              96.40 usec
PL2                -3.00 dB
PL12               15.96 dB
PL13              120.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
CY                   0.00 cm
F1P               215.000 ppm
F1              21631.75 Hz
F2P                -5.000 ppm
F2               -503.08 Hz
PPMCM            11.00000 ppm/cm
HZCM            1106.74048 Hz/cm
```

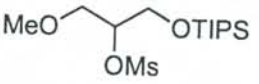




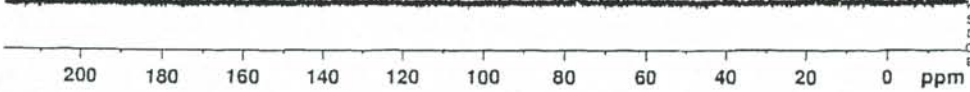

**SI-6**



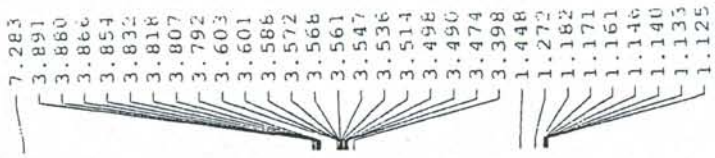

```
F2 - Acquisition Parameters
Date_              20060111
Time                  23.23
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                      64
DW                 104.400 usec
DE                   6.00 usec
TE                  295.8 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

-------- CHANNEL f1 --------
NUC1                    1H
P1                    7.05 usec
PL1                  -3.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

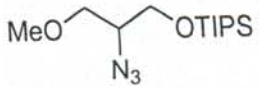



**SI-6**

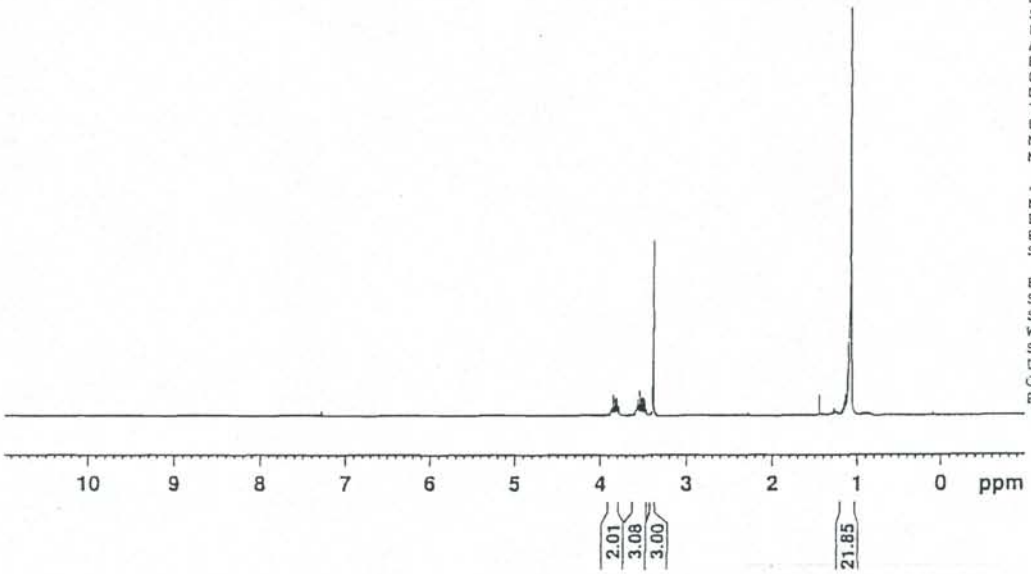

```
F2 - Acquisition Parameters
Date_              20060111
Time                  23.27
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     117
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                    2048
DW                 20.850 usec
DE                   6.00 usec
TE                  296.0 K
D1                0.15000001 sec
d11               0.03000000 sec
DELTA             0.05000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

-------- CHANNEL f1 --------
NUC1                    13C
P1                    7.20 usec
PL1                  -2.00 dB
SFO1          100.6228298 MHz

-------- CHANNEL f2 --------
CPDPRG2             waltz16
NUC2                    1H
PCPD2                98.40 usec
PL2                  -3.00 dB
PL12                 19.96 dB
PL13                120.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

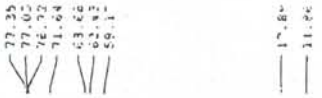


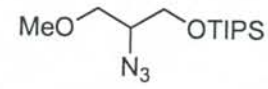




**SI-7**

```
F2 - Acquisition Parameters
Date_              20060112
Time                 21.41
INSTRUM              spect
PROBHD   5 mm QNP 1H/15
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                    50.8
DW                 104.400 usec
DE                   6.00 usec
TE                  296.1 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.05 usec
PL1                  -3.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

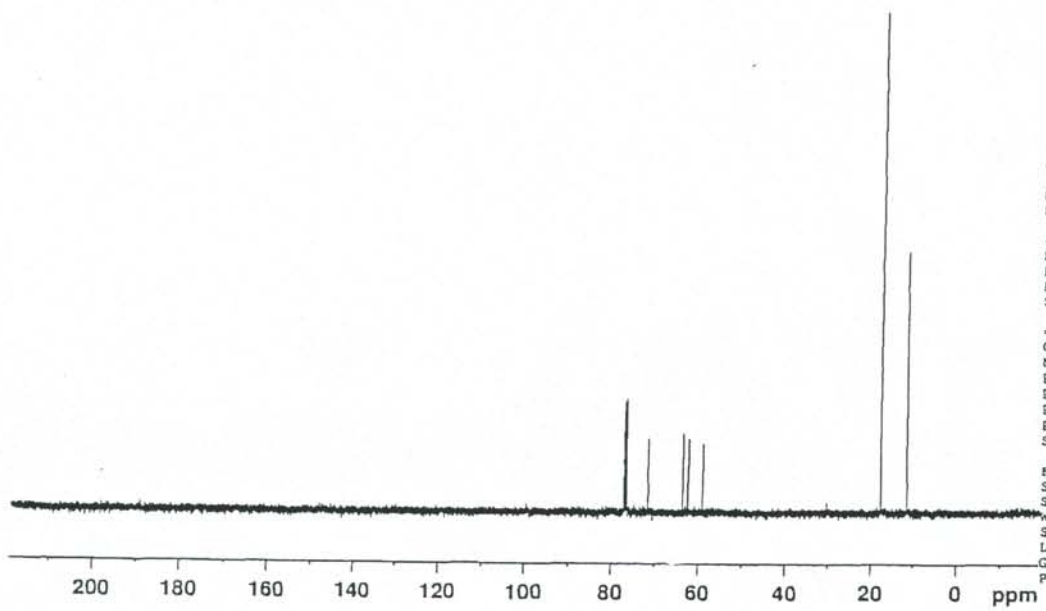


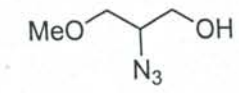





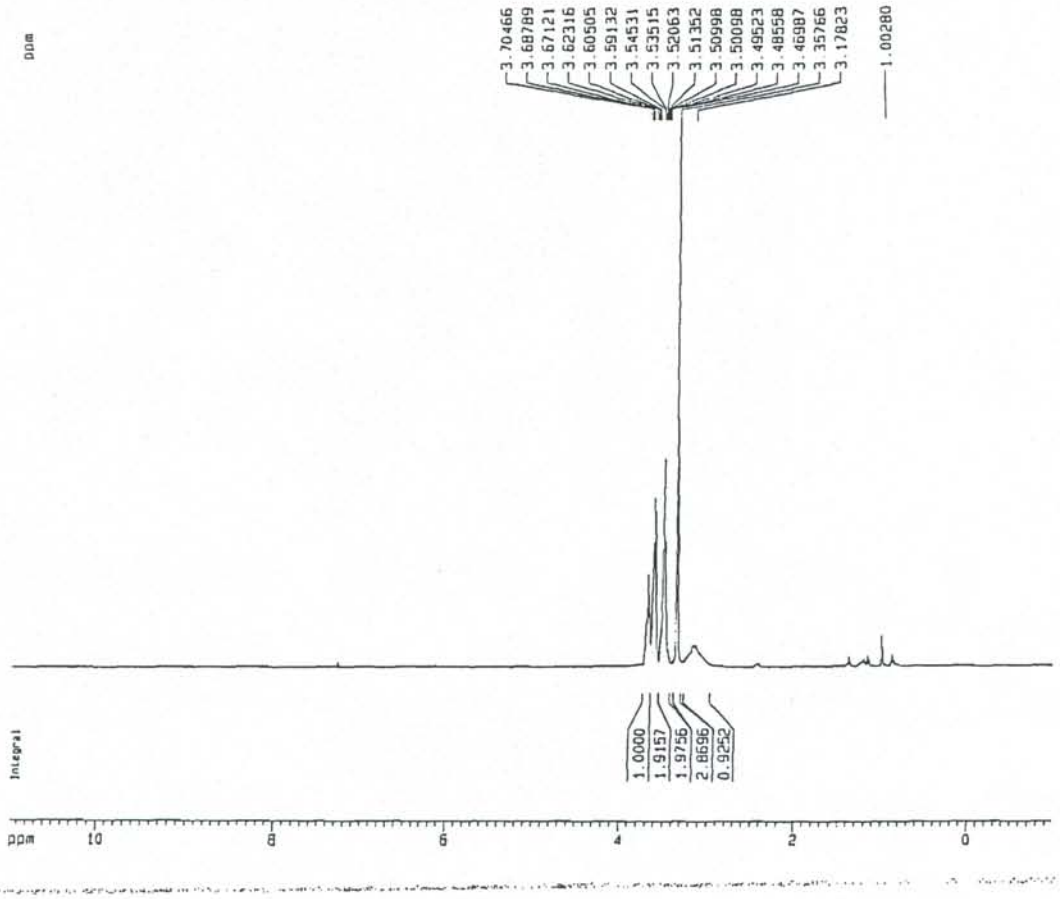

**SI-7**

```
F2 - Acquisition Parameters
Date_              20060112
Time                 21.44
INSTRUM              spect
PROBHD   5 mm QNP 1H/15
PULPROG            zgpg30
TD                  65536
SOLVENT              CDCl3
NS                     103
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                    2048
DW                 20.850 usec
DE                   6.00 usec
TE                  296.3 K
D1              0.15000001 sec
d11             0.03000000 sec
DELTA           0.05000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   7.20 usec
PL1                  -2.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                98.40 usec
PL2                  -3.00 dB
PL12                 19.96 dB
PL13                120.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

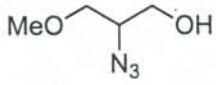




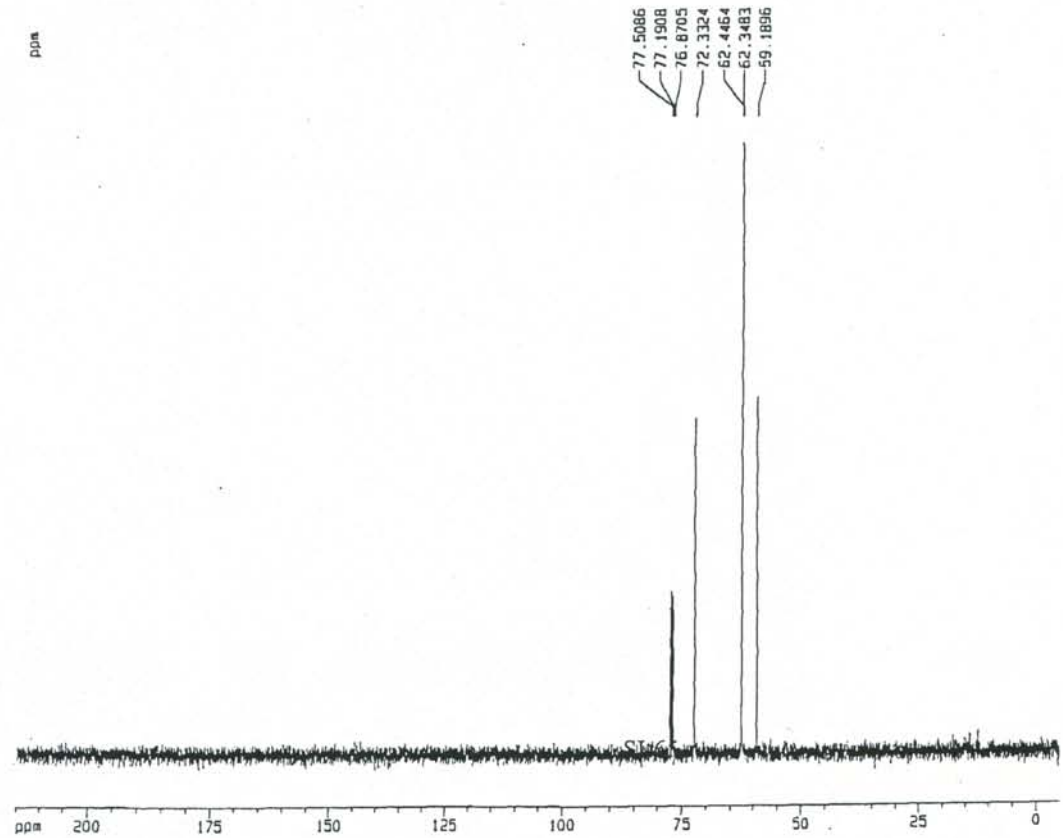

**10**



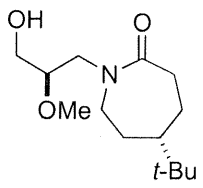

```
F2 - Acquisition Parameters
Date_              20060116
Time                  20.58
INSTRUM                spect
PROBHD   5 mm QNP 1H/15
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                4789.272 Hz
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                        32
DW                   104.400 usec
DE                     6.00 usec
TE                    295.7 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

-------- CHANNEL f1 --------
NUC1                      1H
P1                      7.05 usec
PL1                    -3.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                       20.00 cm
CY                        0.00 cm
F1P                      11.003 ppm
F1                     4401.43 Hz
F2P                     -1.000 ppm
F2                      -400.13 Hz
PPMCM                  0.80000 ppm/cm
HZCM                 240.07800 Hz/cm
```




**10**



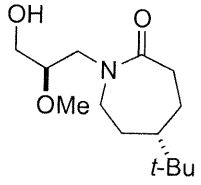

```
F2 - Acquisition Parameters
Date_              20060116
Time                  21.00
INSTRUM                spect
PROBHD   5 mm QNP 1H/15
PULPROG             zgpg30
TD                    65536
SOLVENT                CDCl3
NS                        91
DS                         4
SWH                23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 sec
RG                      2048
DW                   20.850 usec
DE                     6.00 usec
TE                    295.8 K
D1                 0.15000001 sec
d11                0.03000000 sec
DELTA              0.05000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

-------- CHANNEL f1 --------
NUC1                      13C
P1                      7.20 usec
PL1                    -2.00 dB
SFO1             100.6228298 MHz

-------- CHANNEL f2 --------
CPDPRG2                waltz16
NUC2                      1H
PCPD2                  98.40 usec
PL2                    -3.00 dB
PL12                   19.96 dB
PL13                  120.00 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127690 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                       20.00 cm
CY                        8.00 cm
F1P                     215.000 ppm
F1                   21631.75 Hz
F2P                     -5.000 ppm
F2                     -503.06 Hz
PPMCM                 11.20000 ppm/cm
HZCM                1106.74048 Hz/cm
```



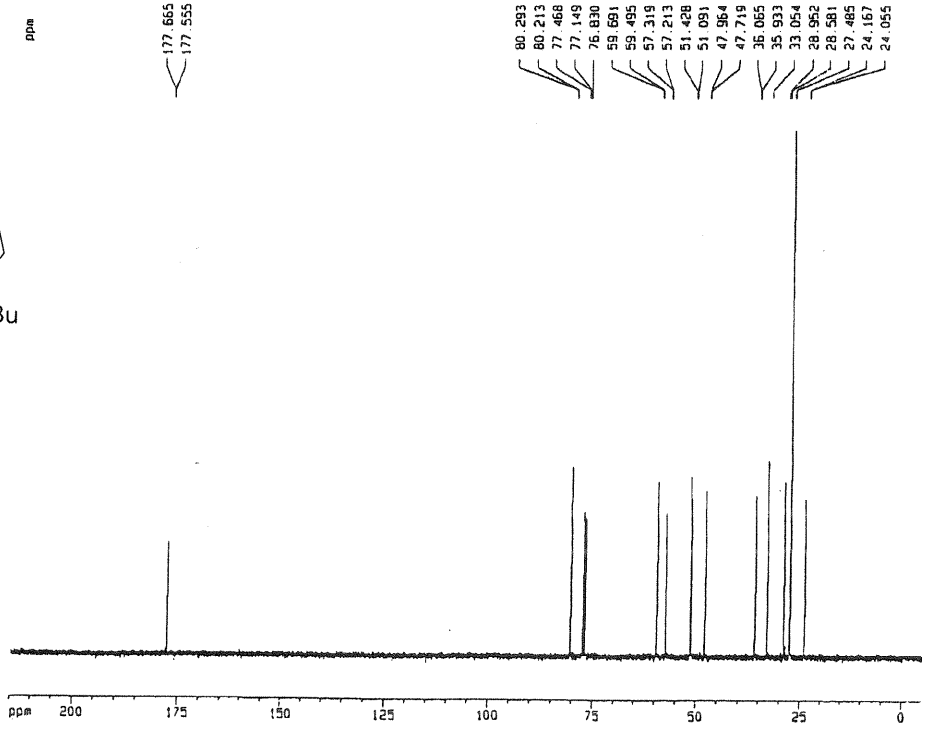

**3c** (major)
X-ray



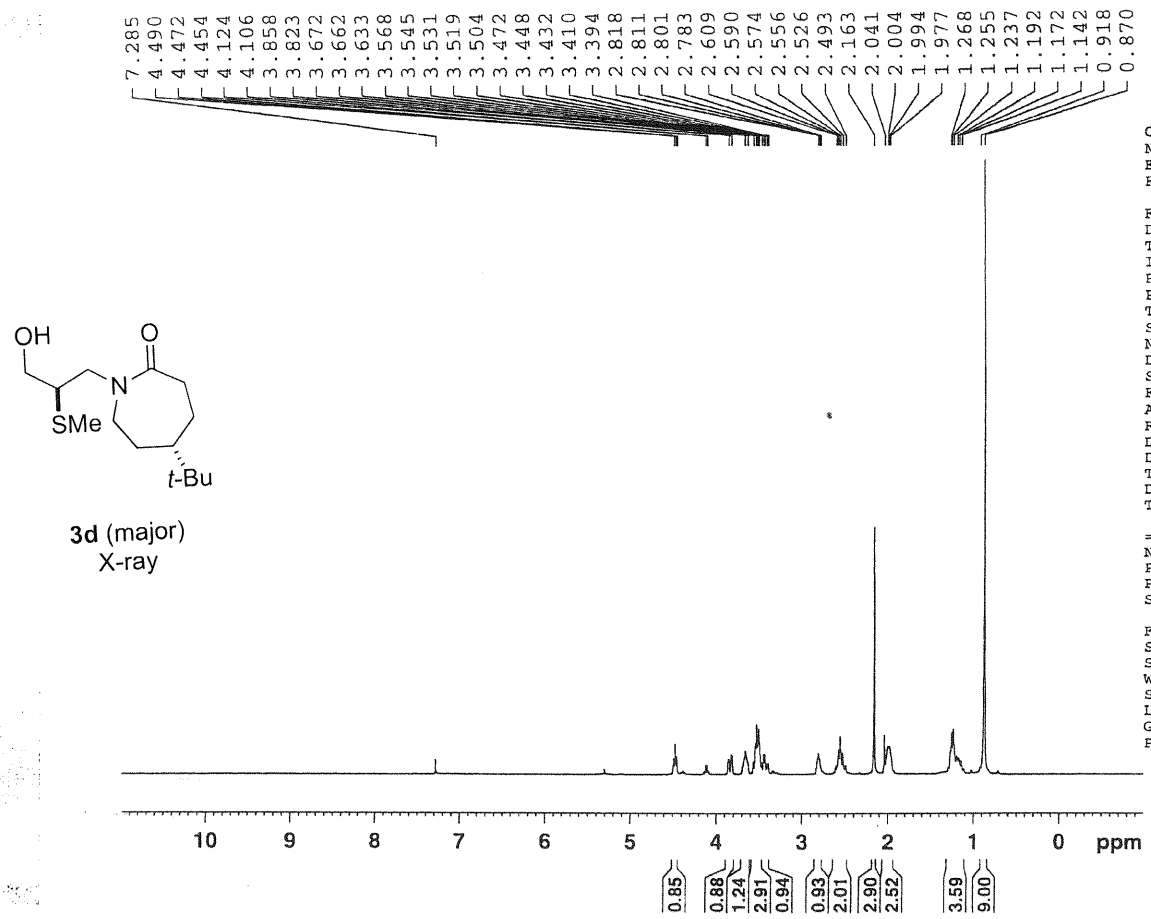

```
F2 - Acquisition Parameters
Date_              20050821
Time                  17.22
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG               zg30
TD                   32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                       32
DW                 104.400 usec
DE                   6.00 usec
TE                  296.6 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

-------- CHANNEL f1 --------
NUC1                     1H
P1                    7.05 usec
PL1                  -3.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                       32768
SF           400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
CY                     0.00 cm
F1P                  11.000 ppm
F1                 4401.43 Hz
F2P                 -1.000 ppm
F2                 -400.13 Hz
PPMCM                0.80000 ppm/cm
HZCM               240.07800 Hz/cm
```




**3c** (major)
X-ray

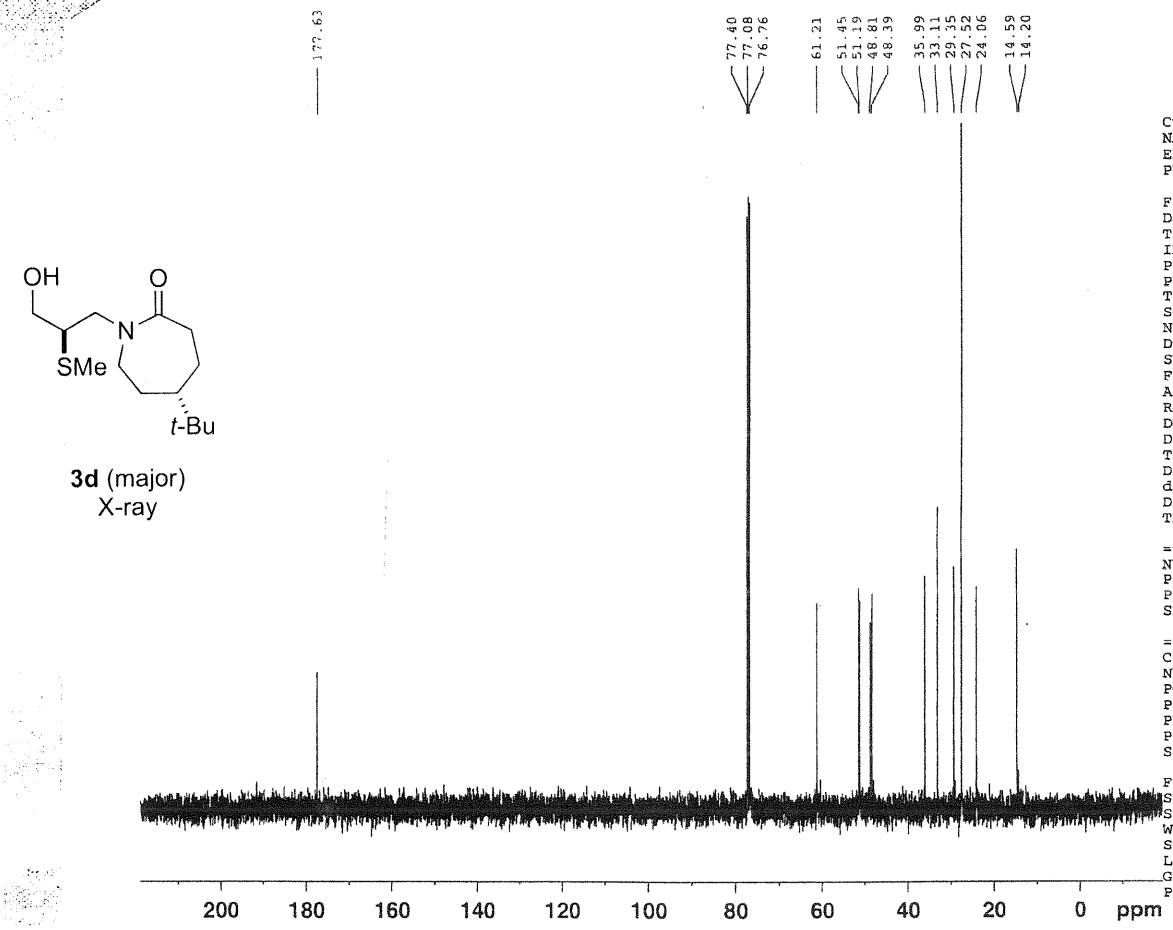



```
F2 - Acquisition Parameters
Date_              20050821
Time                  17.23
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG           zgpg30
TD                   65536
SOLVENT               CDCl3
NS                       76
DS                        4
SWH              23980.814 Hz
FIDRES            0.365818 Hz
AQ                1.3664756 sec
RG                     2048
DW                 20.850 usec
DE                   6.00 usec
TE                  298.7 K
D1                0.15000001 sec
d11               0.03000000 sec
DELTA             0.09000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

-------- CHANNEL f1 --------
NUC1                    13C
P1                   7.20 usec
PL1                  -2.00 dB
SFO1           100.6228298 MHz

-------- CHANNEL f2 --------
CPDPRG2             waltz16
NUC2                     1H
PCPD2                98.40 usec
PL2                  -3.00 dB
PL12                 19.96 dB
PL13                120.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF           100.6127690 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                    20.00 cm
CY                     0.00 cm
F1P                 215.000 ppm
F1                21631.75 Hz
F2P                  -5.000 ppm
F2                 -503.06 Hz
PPMCM                11.00000 ppm/cm
HZCM              1106.74048 Hz/cm
```



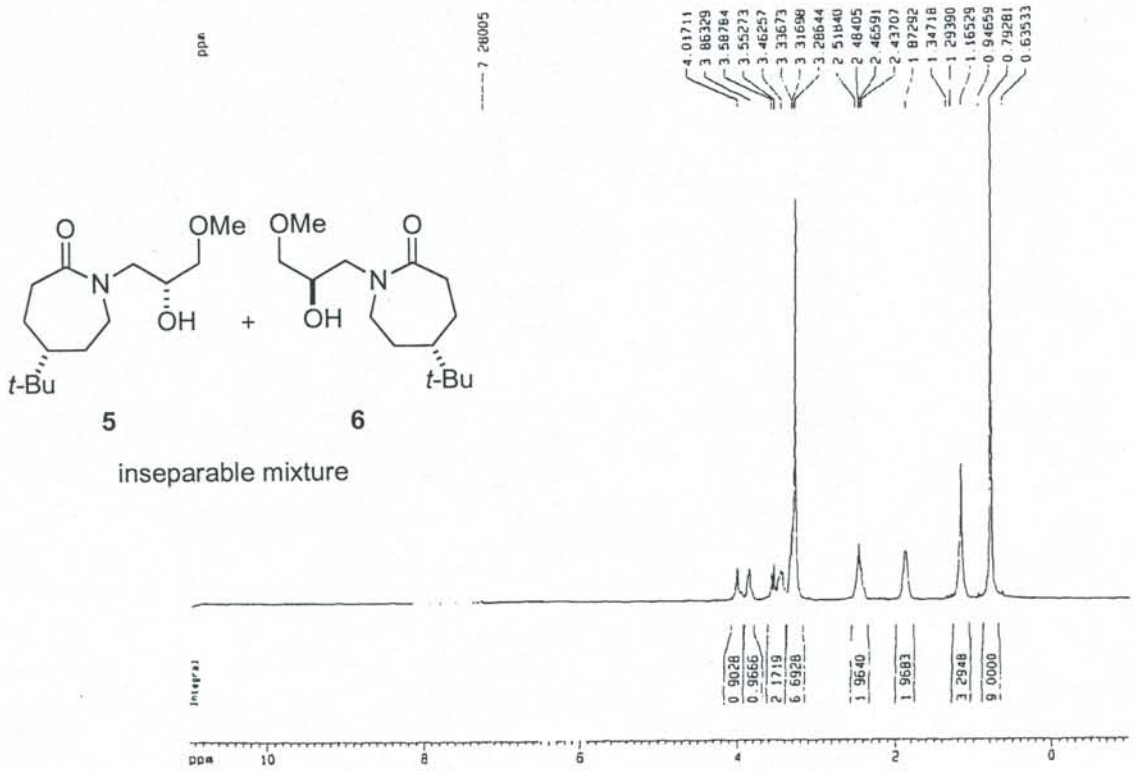

**3d** (major)
X-ray

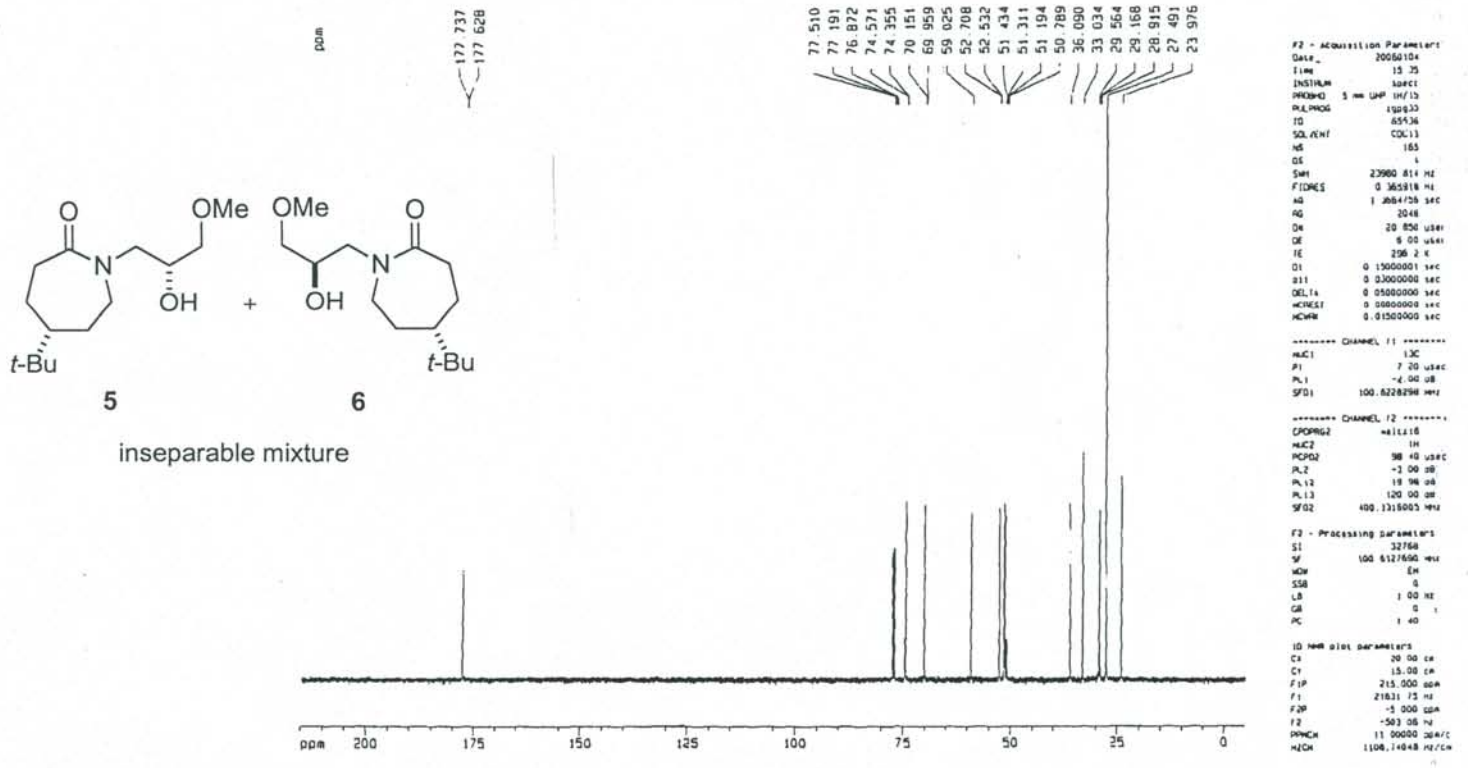
```
Current Data Parameters
NAME      TR_3_87_Column
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080227
Time               11.19
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   11
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 80.6
DW               60.400 usec
DE                6.00 usec
TE               296.2 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.50 usec
PL1               -5.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                 1.00
```

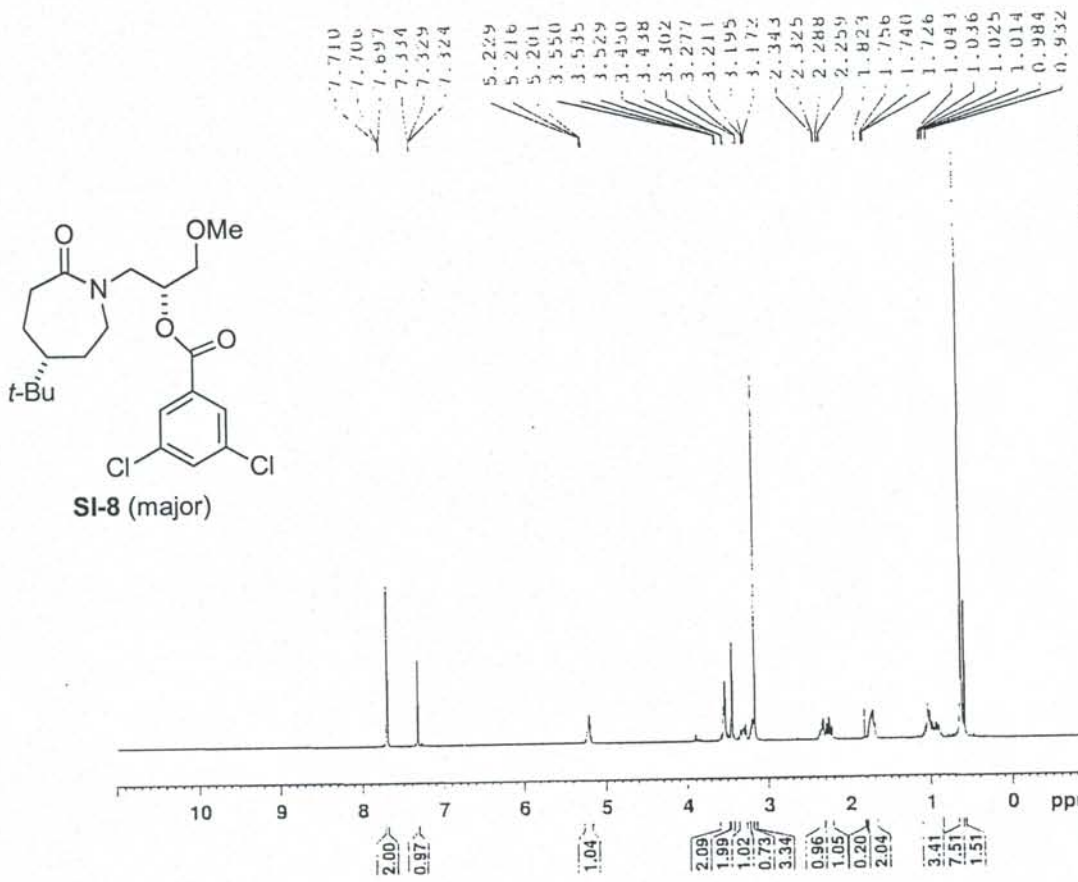



**3d** (major)
X-ray

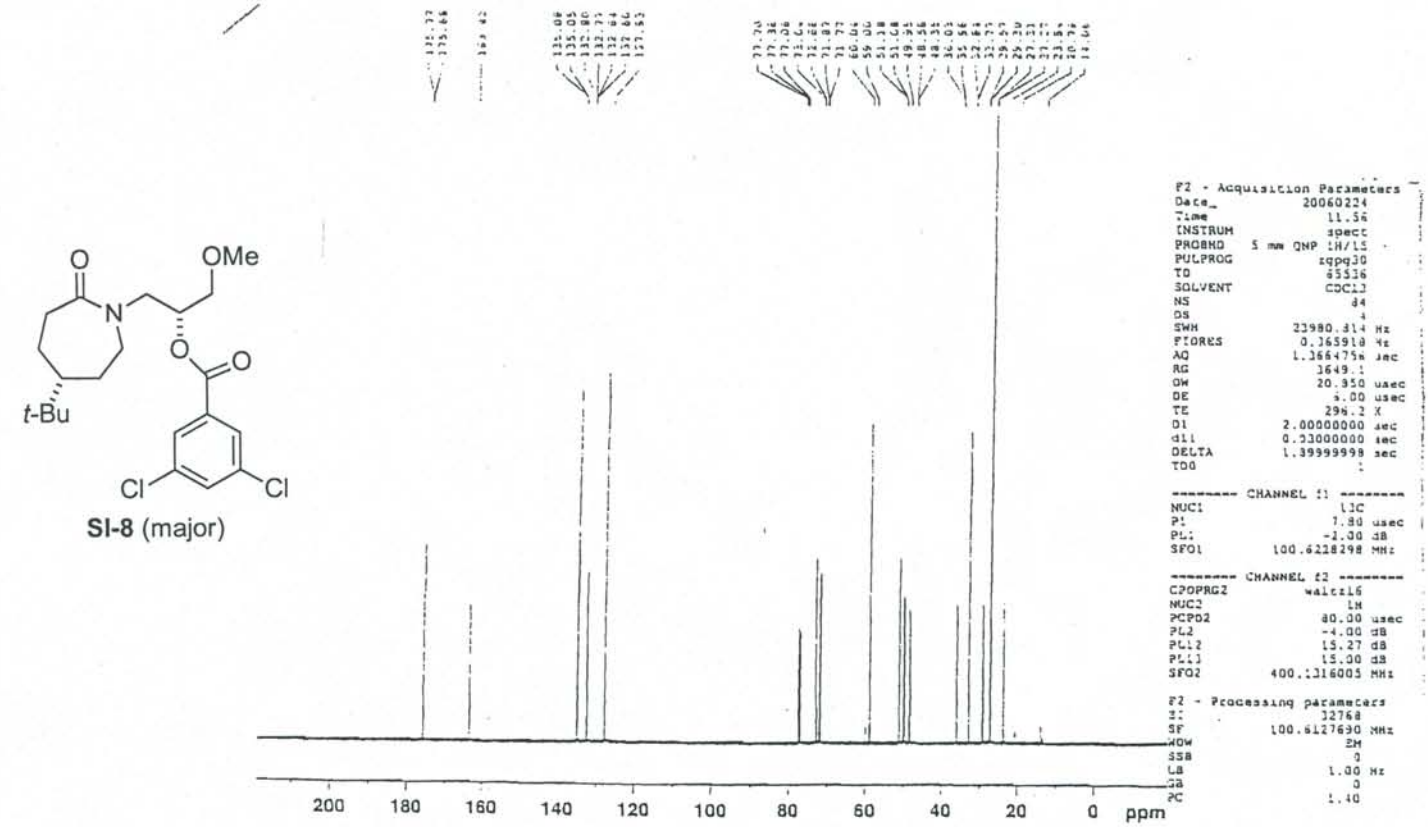
```
Current Data Parameters
NAME      TR_3_87_Column
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080227
Time               11.24
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   50
DS                    4
SWH           23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG                 4096
DW               20.850 usec
DE                6.00 usec
TE               296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.85 usec
PL1               -2.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               -5.00 dB
PL12              14.58 dB
PL13              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                 1.40
```


OMe
OH
t-Bu
OMe
OH
t-Bu
5
6
inseparable mixture
ppm
Integral

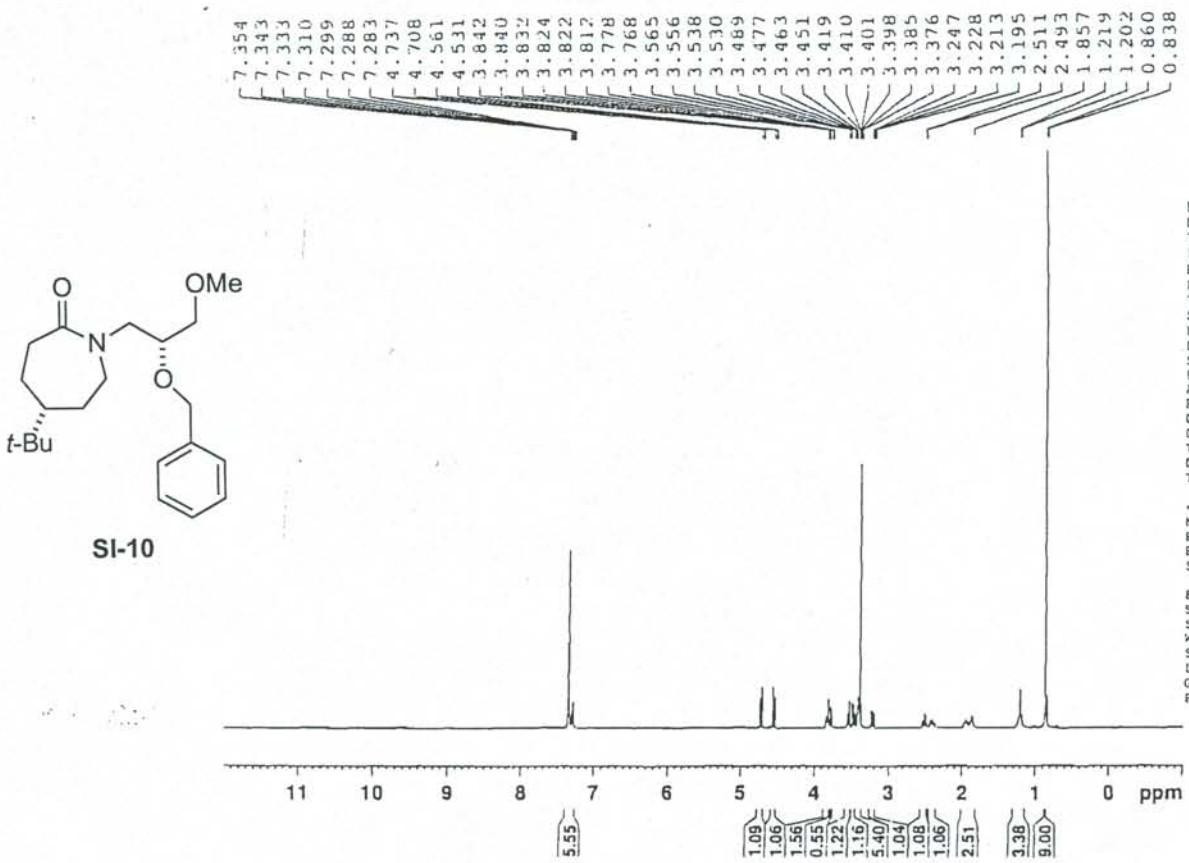

OMe
OH
t-Bu
OMe
OH
t-Bu
5
6
inseparable mixture
ppm

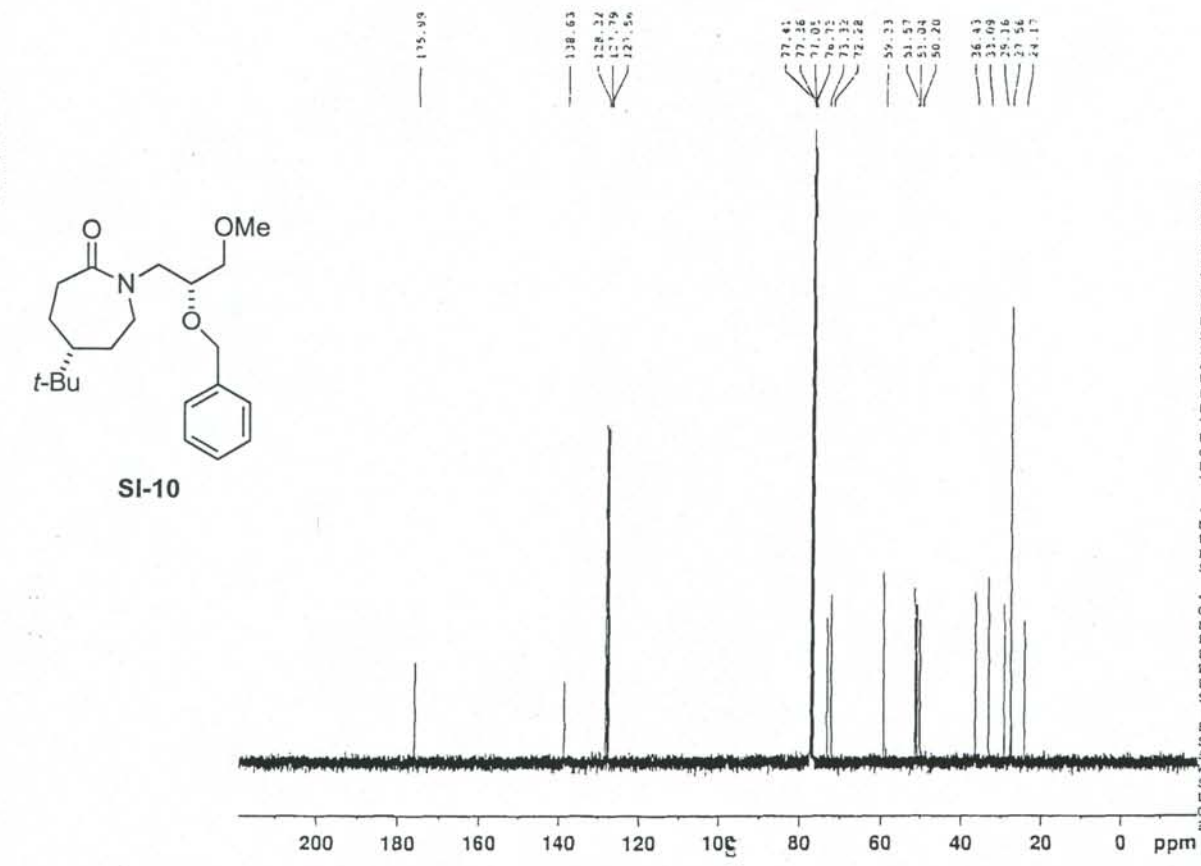


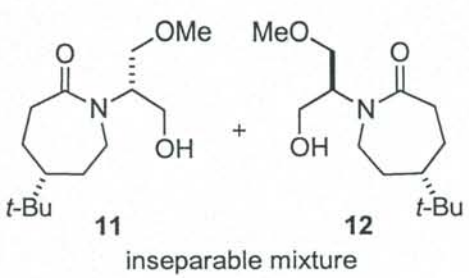

```
Current Data Parameters
NAME          TPR.1.253_major
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20060224
Time                  11.49
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               3278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                     10.1
DW                  60.400 usec
DE                   6.00 usec
TE                  295.7 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.70 usec
PL1                 -4.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



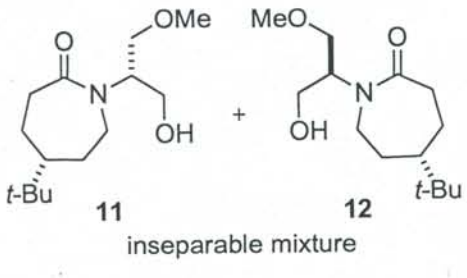

```
F2 - Acquisition Parameters
Date_              20060224
Time                  11.56
INSTRUM               spect
PROBHD   5 mm QNP 1H/15
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      84
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                   1649.1
DW                  20.850 usec
DE                   6.00 usec
TE                  298.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.39999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   7.80 usec
PL1                 -2.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -4.00 dB
PL12                15.27 dB
PL13                15.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

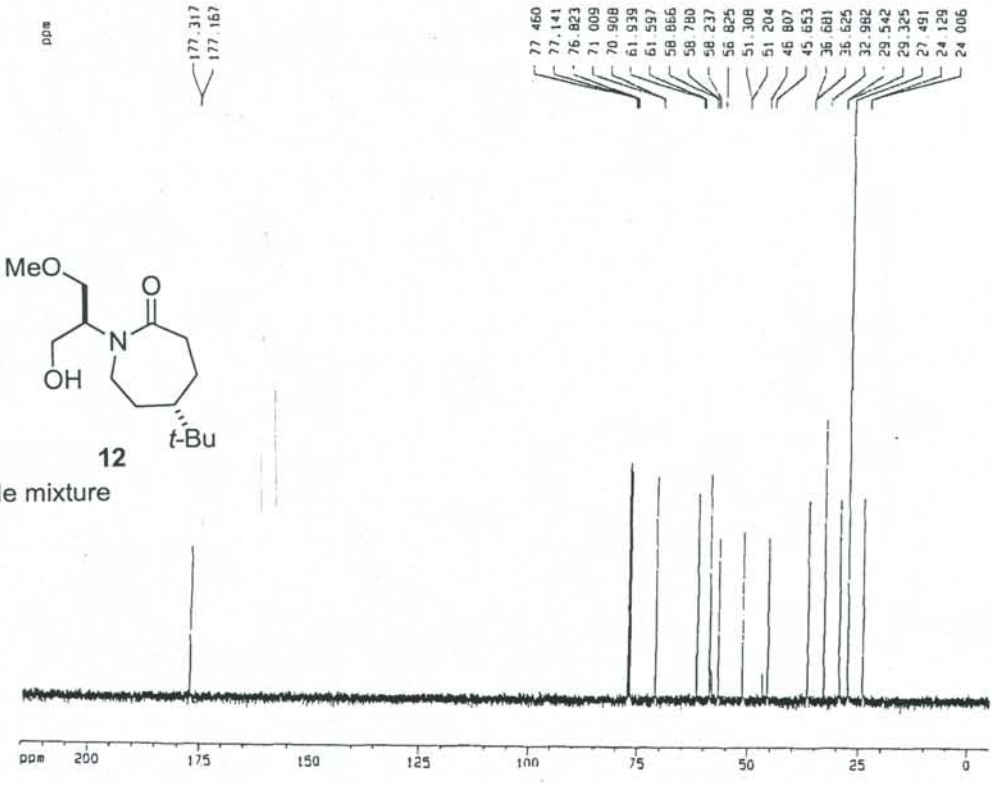

7.354
7.343
7.333
7.310
7.299
7.288
7.283
4.737
4.708
4.561
4.531
3.842
3.840
3.832
3.824
3.822
3.817
3.778
3.768
3.565
3.556
3.538
3.530
3.489
3.477
3.463
3.451
3.419
3.410
3.401
3.398
3.385
3.376
3.247
3.228
3.213
3.195
2.511
2.493
1.857
1.219
1.202
0.860
0.838
O
OMe
N
O
t-Bu
SI-10
F2 - Acquisition Parameters
Date_ 20061113
Time 14.01
INSTRUM spect
PROBHD 5 mm QNP 1H/15
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 8.70 usec
PL1 -4.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11 10 9 8 7 6 5 4 3 2 1 0 ppm
5.55 1.09 1.06 1.56 0.55 1.22 1.16 5.40 1.04 1.08 1.06 2.51 3.38 9.00

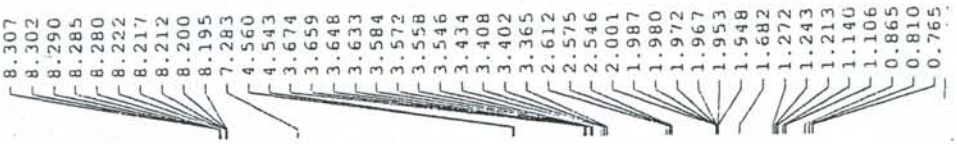

175.99
138.63
128.32
127.79
126.56
77.41
77.36
77.05
76.72
73.32
72.28
59.33
31.57
31.04
30.20
26.43
25.69
25.16
23.56
23.17
O
OMe
N
O
t-Bu
SI-10
F2 - Acquisition Parameters
Date_ 20061113
Time 14.03
INSTRUM spect
PROBHD 5 mm QNP 1H/15
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 147
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 10321.3
DW 20.850 usec
DE 6.00 usec
TE 298.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 7.80 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 15.27 dB
PL13 15.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

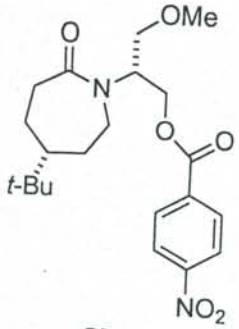

OMe
MeO
O
N
OH
t-Bu
11
12
inseparable mixture


ppm
Integral
1.000
0.211
1.205
2.681
1.119
2.532
5.022
2.477
2.472
3.854
11.273

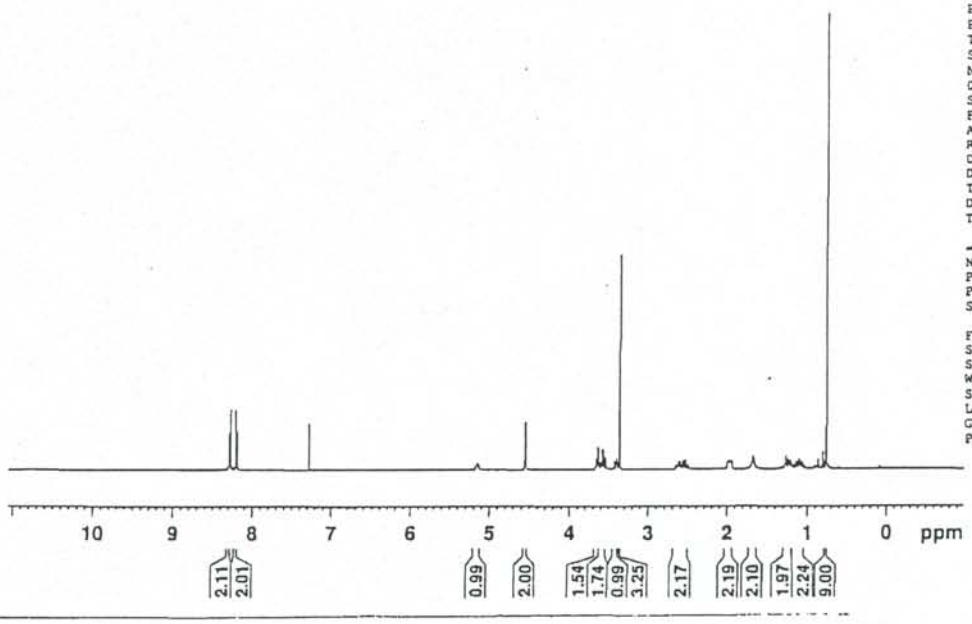

OMe
MeO
O
N
OH
t-Bu
11
12
inseparable mixture


ppm
177.317
177.167
77.460
77.141
76.823
71.009
70.908
61.939
61.597
58.866
58.780
58.237
56.825
51.308
51.204
46.807
45.653
36.681
36.625
32.982
29.542
29.325
27.491
24.129
24.006

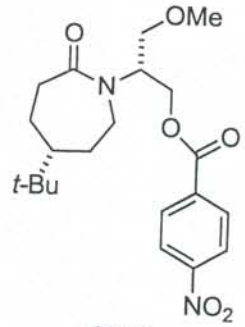


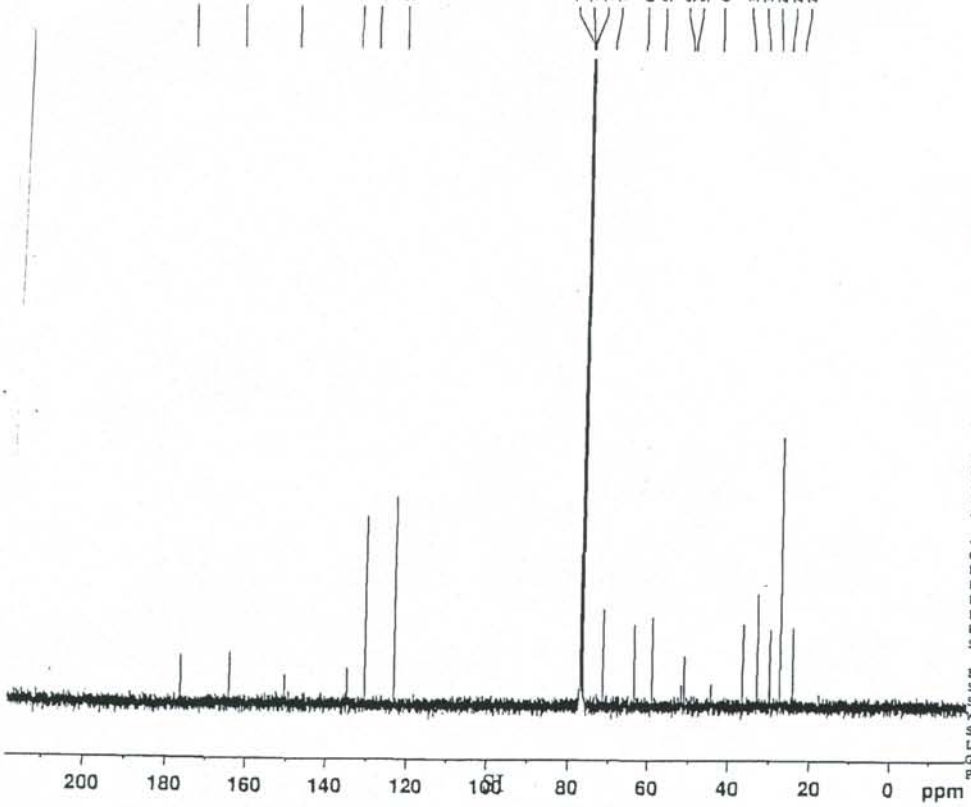

SI-11



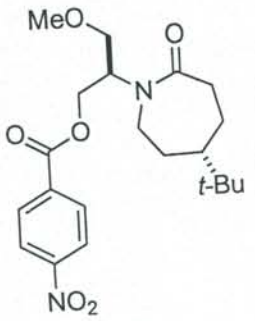

```
F2 - Acquisition Parameters
Date_              20060731
Time                  17.50
INSTRUM               spect
PROBHD    5 mm QNP 1H/15
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                     256
DW                  60.400 usec
DE                   6.00 usec
TE                  297.1 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.70 usec
PL1                 -4.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

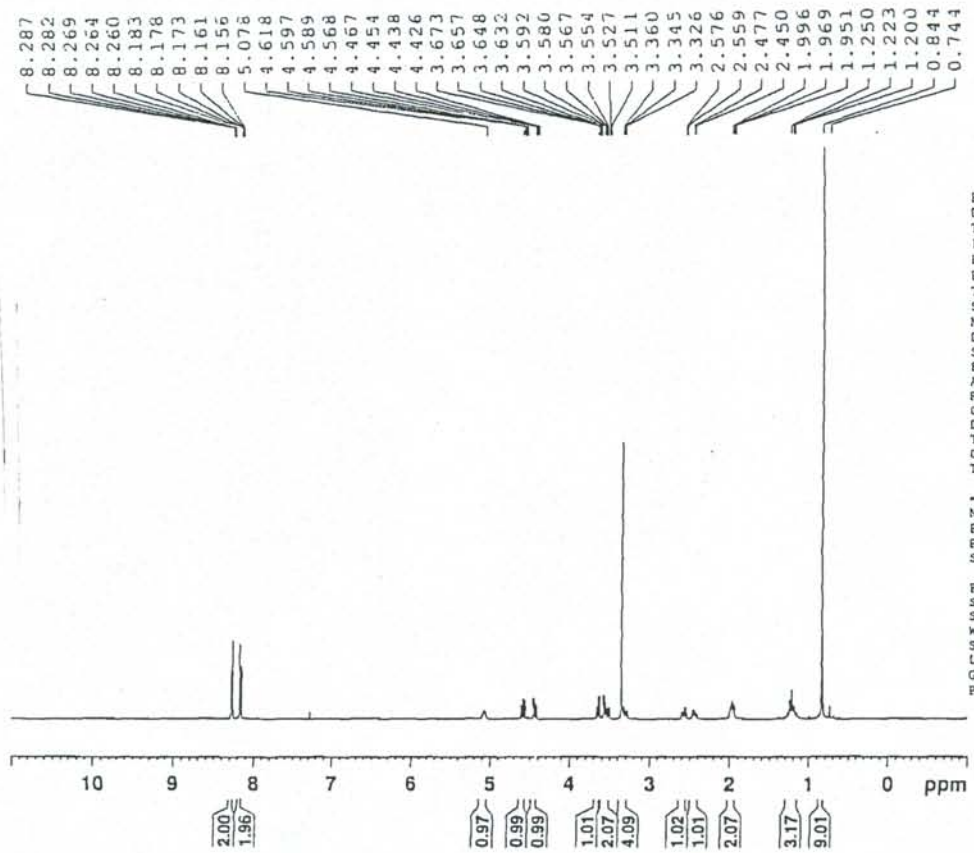

SI-11




```
f2 - Acquisition Parameters
Date_              20060731
Time                  17.55
INSTRUM               spect
PROBHD    5 mm QNP 1H/15
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     816
DS                       4
SWH               23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                   4597.6
DW                  20.850 usec
DE                   6.00 usec
TE                  297.6 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   7.80 usec
PL1                 -2.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -4.00 dB
PL12                15.27 dB
PL13                15.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```




SI-12




F2 - Acquisition Parameters

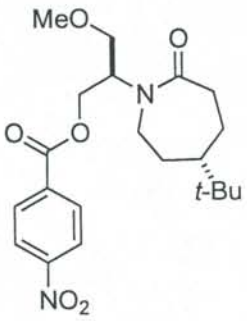
| | |
|---|---|
| Date_ | 20060731 |
| Time | 17.40 |
| INSTRUM | spect |
| PROBHD | 5 mm QNP 1H/15 |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.126314 Hz |
| AQ | 3.9584243 sec |
| RG | 64 |
| DW | 60.400 use |
| DE | 6.00 use |
| TE | 297.0 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |

-------- CHANNEL f1 --------

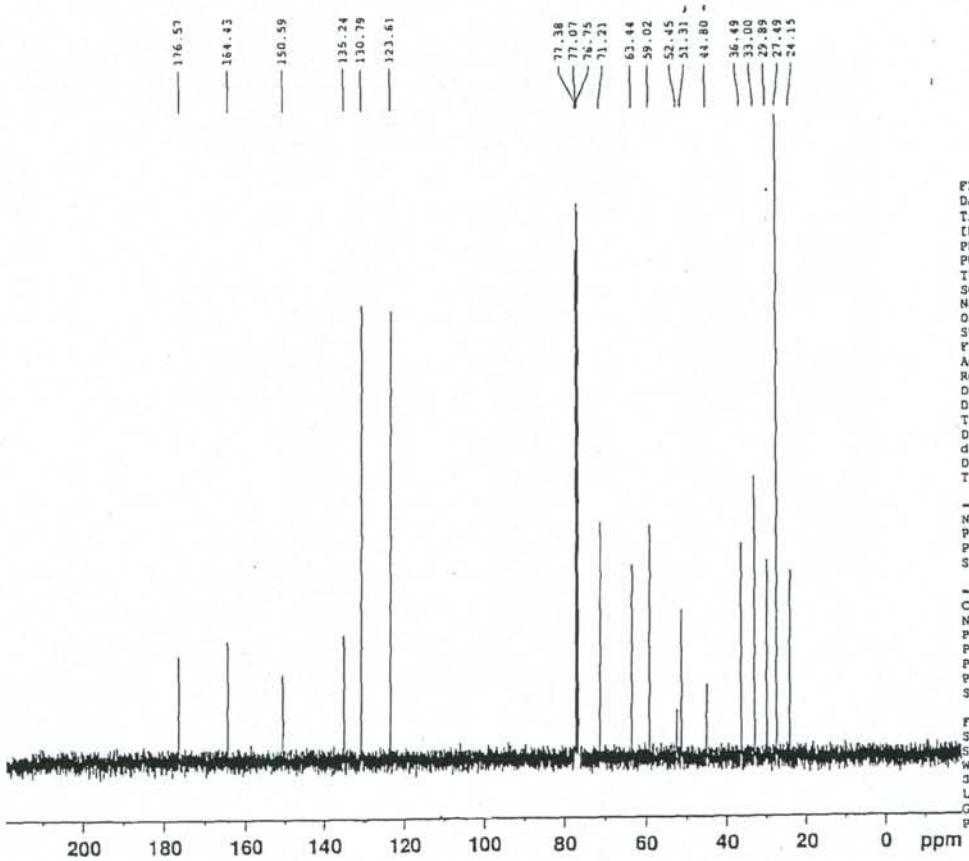
| | |
|---|---|
| NUC1 | 1H |
| P1 | 8.70 use |
| PL1 | -4.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300000 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |




SI-12




F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20060731 |
| Time | 17.42 |
| INSTRUM | spect |
| PROBHD | 5 mm QNP 1H/15 |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 62 |
| DS | 4 |
| SWH | 23980.814 Hz |
| FIDRES | 0.365918 Hz |
| AQ | 1.3664756 sec |
| RG | 2896.3 |
| DW | 20.850 use |
| DE | 6.00 use |
| TE | 297.2 K |
| D1 | 2.00000000 sec |
| d11 | 0.03000000 sec |
| DELTA | 1.89999998 sec |
| TD0 | 1 |

-------- CHANNEL f1 --------

| | |
|---|---|
| NUC1 | 13C |
| P1 | 7.80 use |
| PL1 | -2.00 dB |
| SFO1 | 100.6228298 MHz |

-------- CHANNEL f2 --------

| | |
|---|---|
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 use |
| PL2 | -4.00 dB |
| PL12 | 15.27 dB |
| PL13 | 15.00 dB |
| SFO2 | 400.1316005 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 100.6127690 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |