

Total Synthesis of the Lycopodium Alkaloid Serratezomine A Using Free Radical-Mediated Vinyl Amination to Prepare a β -Stannyl Enamine Linchpin

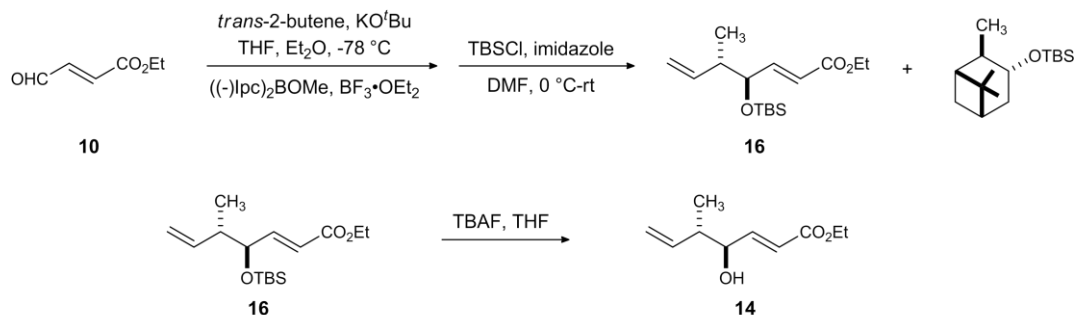
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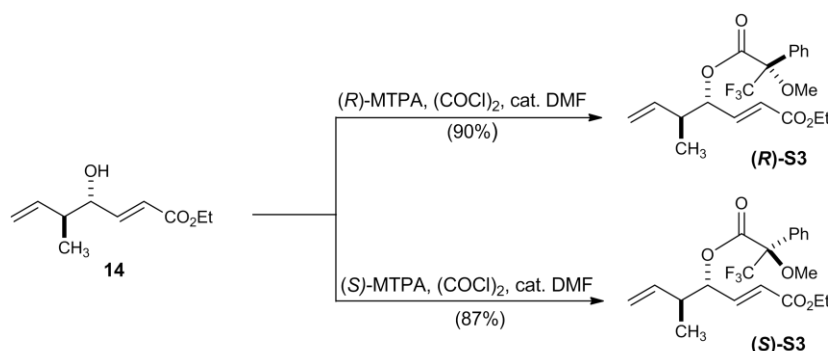
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Structural Elucidation and 2D NMR Data

Mosher Ester Formation and Analysis of Alcohol **14**Scheme 1. Formation of Alcohol **14**

Alcohol **14** was formed via a Brown crotylation of aldehyde **10** (Scheme 1). On small scale, alcohol **14** was separated from the terpene alcohol byproduct (not shown) by column chromatography. On large scale, the terpene alcohol was distilled selectively, leaving some remaining that along with alcohol **14** was carried on through the TBS-protection step to form **16**. Pure **16** was then exposed to TBAF to provide **14** uncontaminated with the terpene alcohol side product.

Initial attempts to determine the *ee* of this reaction with HPLC analysis (Chiral AD, OJ, and OD columns with various solvent systems) proved ineffective as resolution of the peaks did not occur. Using the Mosher ester¹ however, allowed us to determine not only the *ee* of the molecule, but the absolute stereochemistry as well at the carbinol carbon. The Mosher ester derivatives of alcohol **14** were formed using the *R*-MTPA acid and *S*-MTPA acid to form the *R*- and *S*-Mosher esters ((*R*)-**S3** and (*S*)-**S3**), respectively (Scheme 2).

Scheme 2. Formation of the *R*- and *S*-Mosher esters of Alcohol **14**

The Mosher analysis addresses a conformational preference in which the carbonyl proton, ester carbonyl, and the trifluoromethyl groups of the MTPA (Mosher ester) substituent lie in the same plane (Figure 1).² In this conformation, the ¹H NMR signals of protons H_a, H_b, and H_c in the (*R*)-MTPA ester lie upfield relative to those in the (*S*)-MTPA (vice versa for H_x, H_y, H_z) because of shielding by the phenyl group.

¹ Dale, J.A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

² Ohanti, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092.

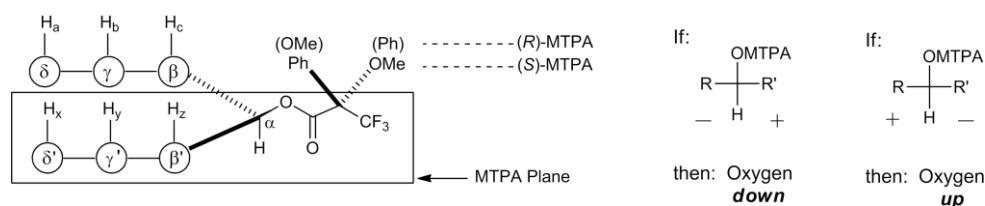


Figure 1. Mosher ester conformational preference

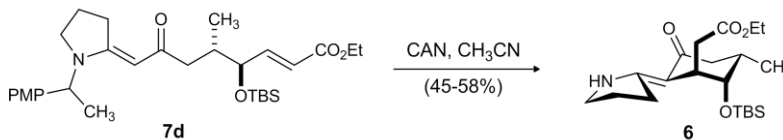
Kakisawa analysis³ of the ^1H NMR chemical shifts (Table 1) of Mosher ester derivatives *R*-**S3** and *S*-**S3** support the assignment of the (*S*) configuration of the alcohol stereocenter. Because the *trans* olefin was used in the crotylation, the *anti*-arrangement of hydroxy and methyl group was assumed. From each Mosher ester formed, a *dr* of 1:0.04 was observed by ^1H NMR, giving the parent alcohol an *ee* of 92.3%.

Table 1. Kakisawa Analysis

Assignment	δ_S (Hz)	δ_R (Hz)	$\delta_S - \delta_R$ (Hz)
A	629.8627	625.6307	4.2320
B	1791.1150	1784.0650	7.0500
C	2836.8903	2809.3605	27.5298
D	2492.7405	2449.3555	43.3850
E	obscured	obscured	obscured
F	492.5650	526.0620	-33.4970
G	2376.3098	2415.9423	-39.6325
H	2128.9872	2156.5133	-27.5261

³ Kusumi, Y.; Hamada, T.; Ishitsuka, M.O.; Ohanti, I., Kakisawa, H. *J. Org. Chem.* **1992**, 57, 1033-1035.

Scheme 3. Formation of Vinylogous Amide **6**



Vinylogous amide **6** was formed by an oxidative deprotection of **7d** which underwent a spontaneous intramolecular Michael addition, setting the new stereocenter at C6 (Scheme 3). Structure **6** contained a vinylogous amide in which the IR showed an NH stretch at 3250 cm^{-1} and a carbonyl stretch at 1609 cm^{-1} indicating a conjugated system (Figure 2). The ^1H NMR and spin-spin decoupling experiments helped to establish the connectivity along the cyclohexanone ring (H6-H9) as well as to the ester side chain (H11). Small coupling constants within H7, which is adjacent to the OTBS group, indicated that it sat in the equatorial conformation, leaving the large OTBS group to be axial. The key NOE correlation came from selective excitation of H6, which is at 2.9 ppm and is free from interference of other hydrogens (Spectrum 1). Excitation of H6 showed a 2.6% NOE to H3 on the pyrrolidine ring (Spectrum 2). The only way for this to occur would be for the vinylogous amide to be in the *cis*-geometry, as shown. In addition, the NH shows up at 10.7 ppm in the ^1H NMR indicating that hydrogen bonding is likely occurring with the carbonyl group.

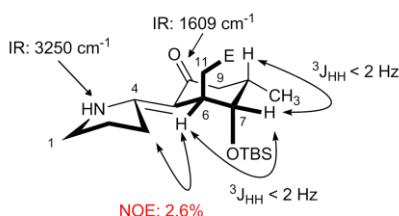
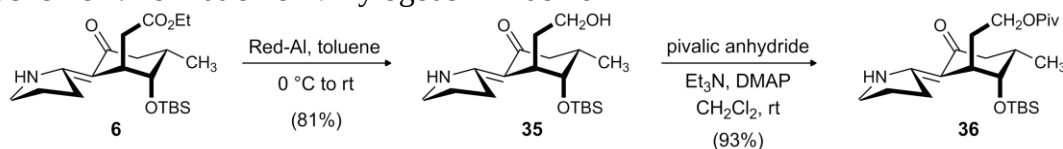
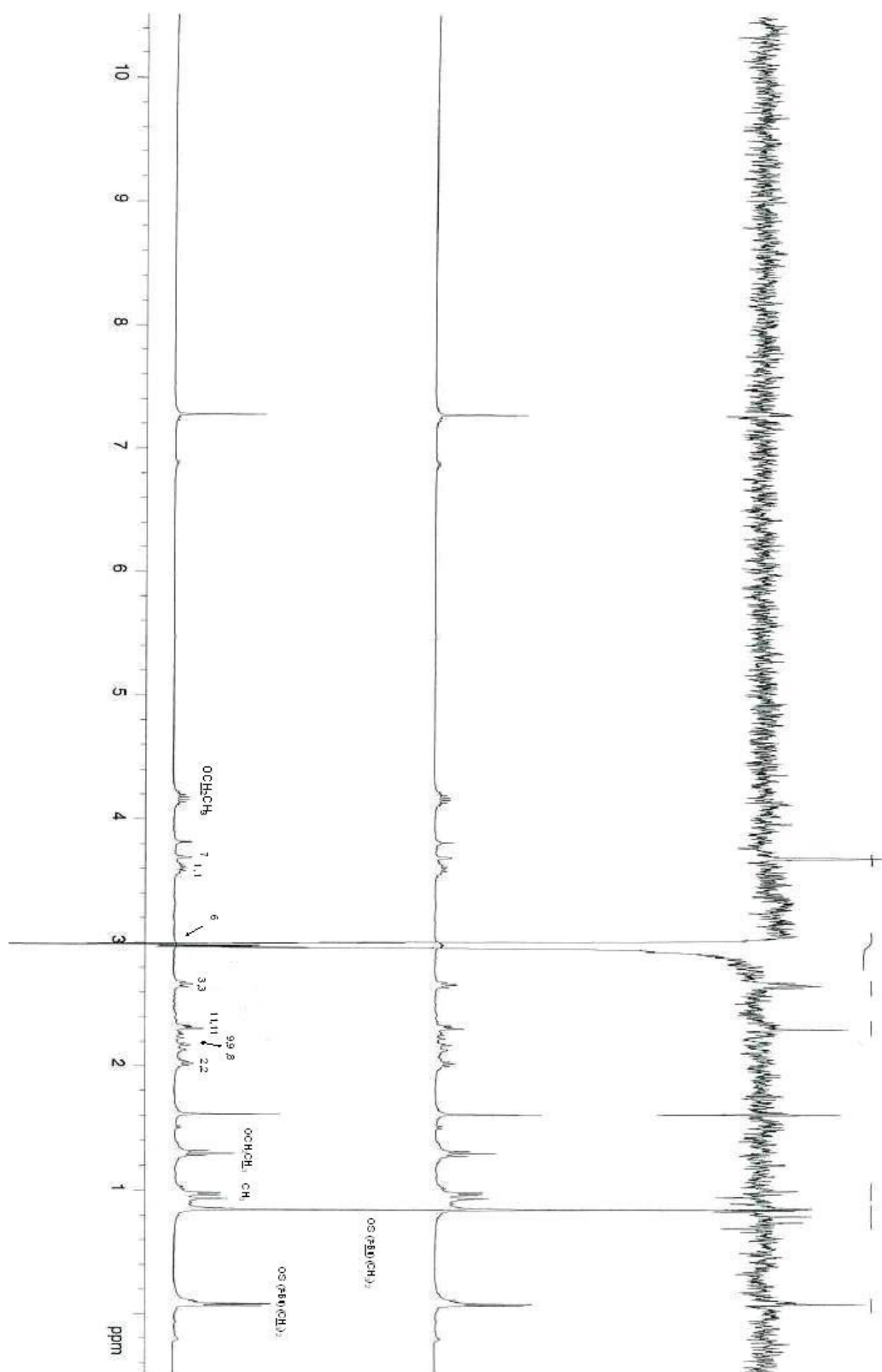


Figure 2. Key data in assigning **6**

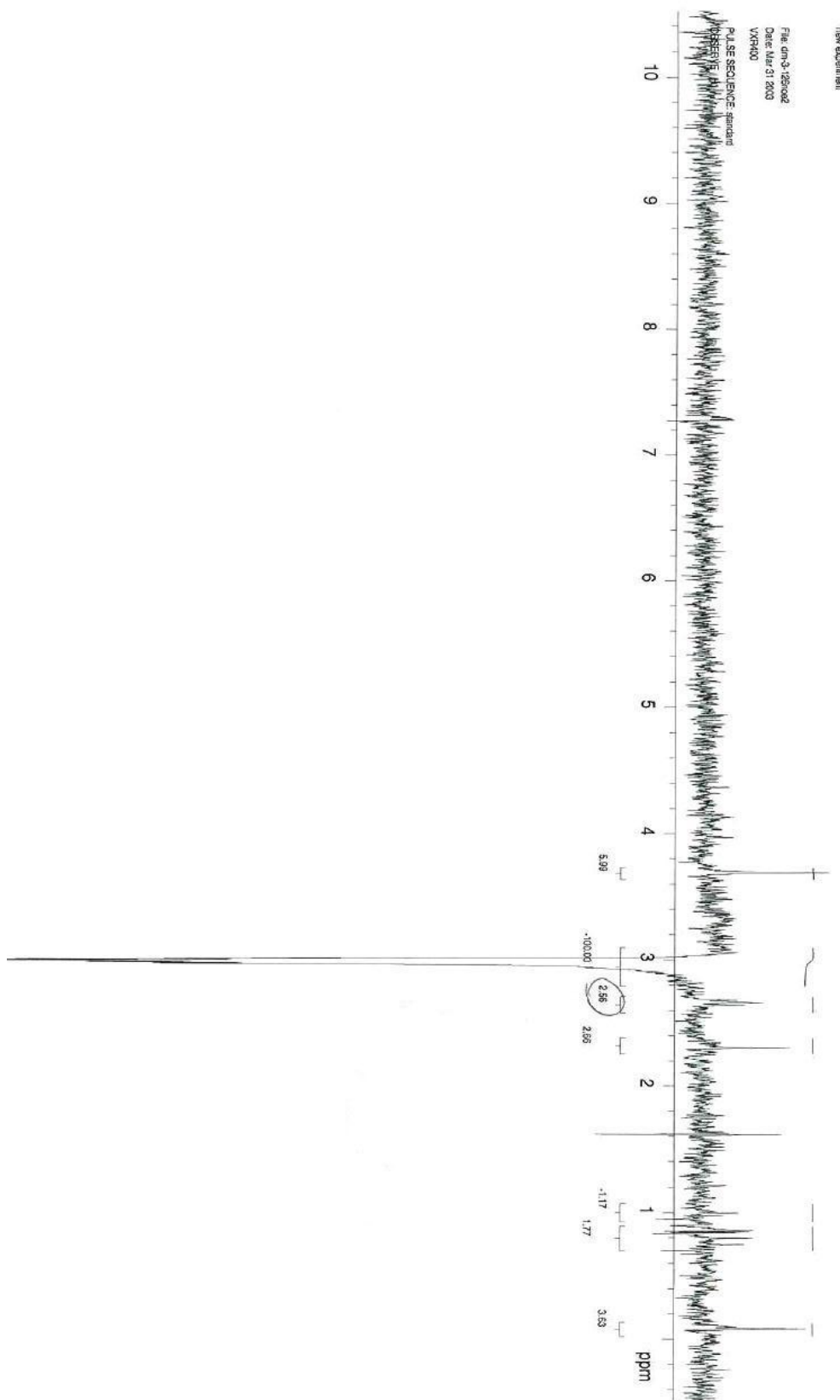
At a later point in the synthesis, the ester of the vinylogous amide was reduced to the alcohol (**35**) and protected as the pivalate (Scheme 4). Pivalate **36** proved to be more stable and easier to handle than **6** and therefore 2D NOESY NMR data was obtained to ensure the vinylogous amide geometry remained in the *cis*-configuration (it could potentially have isomerized during the Red-Al reduction step). The NOESY NMR indicates a crosspeak from the methylene at C3 to the equatorial hydrogen at C6 (Spectrum 3).

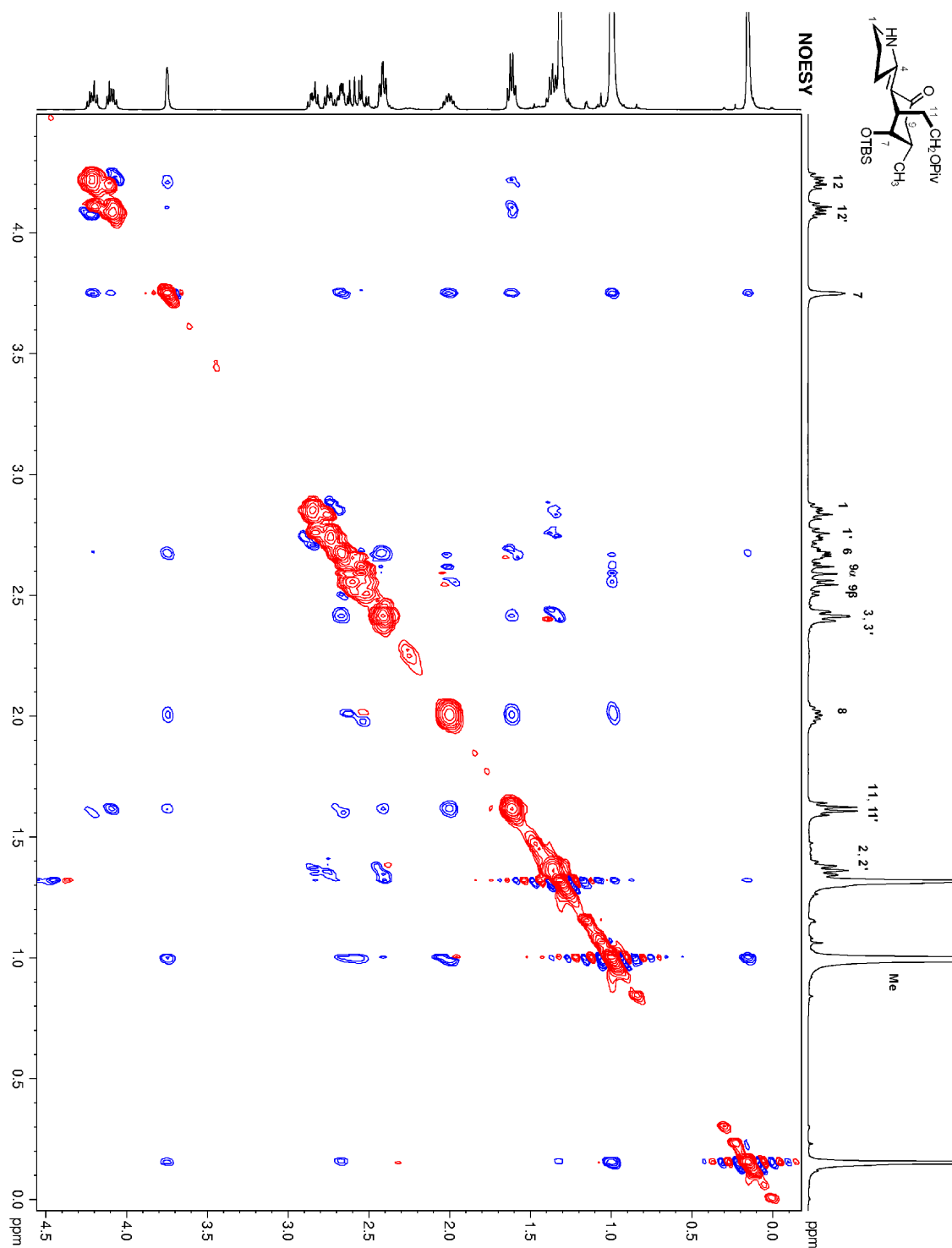
Scheme 4. Formation of Vinylogous Amide **26**



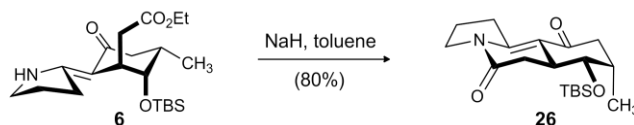
Spectrum 1. 1D NOE (400 MHz, CDCl_3) of H6 in Vinylogous Amide **6**

Spectrum 2. 1D NOE (400 MHz, CDCl_3) of H6 with Integration



Spectrum 3. 2D NOESY (500 MHz, C₆D₆) of Vinylogous Amide **26**

Scheme 5. Reaction to Form Imide **97**



Vinylogous imide **26** was identified as the sole product resulting from exposure of vinylogous amide **6** to any type of basic conditions including even Et₃N-treated silica (Scheme 5). It was evident by ¹H NMR that the proton shifts in the product were dramatically different than the starting material resulting from a new backbone structure. A combination of ¹H NMR, ¹³C NMR, IR, mass spectroscopy, and 2D COSY and NOESY data were utilized to determine the structure of **26**. Preliminary data including IR and ¹³C NMR proved useful in establishing the new functional groups present. The key IR data showed disappearance of the ester stretch at 1732 cm⁻¹ as well as three new strong peaks: 1695, 1664, 1581 cm⁻¹. ¹³C NMR showed four new quaternary carbons at 196, 170, 156, and 107 ppm matching nicely with a conjugated ketone, amide, and enamine, respectively. Mass spectrometry results also supported loss of an ethoxy group, thereby tentatively leading to assignment of the backbone of **26** via cyclization of the nitrogen onto the ester.

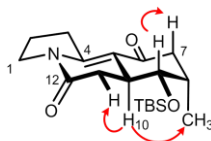
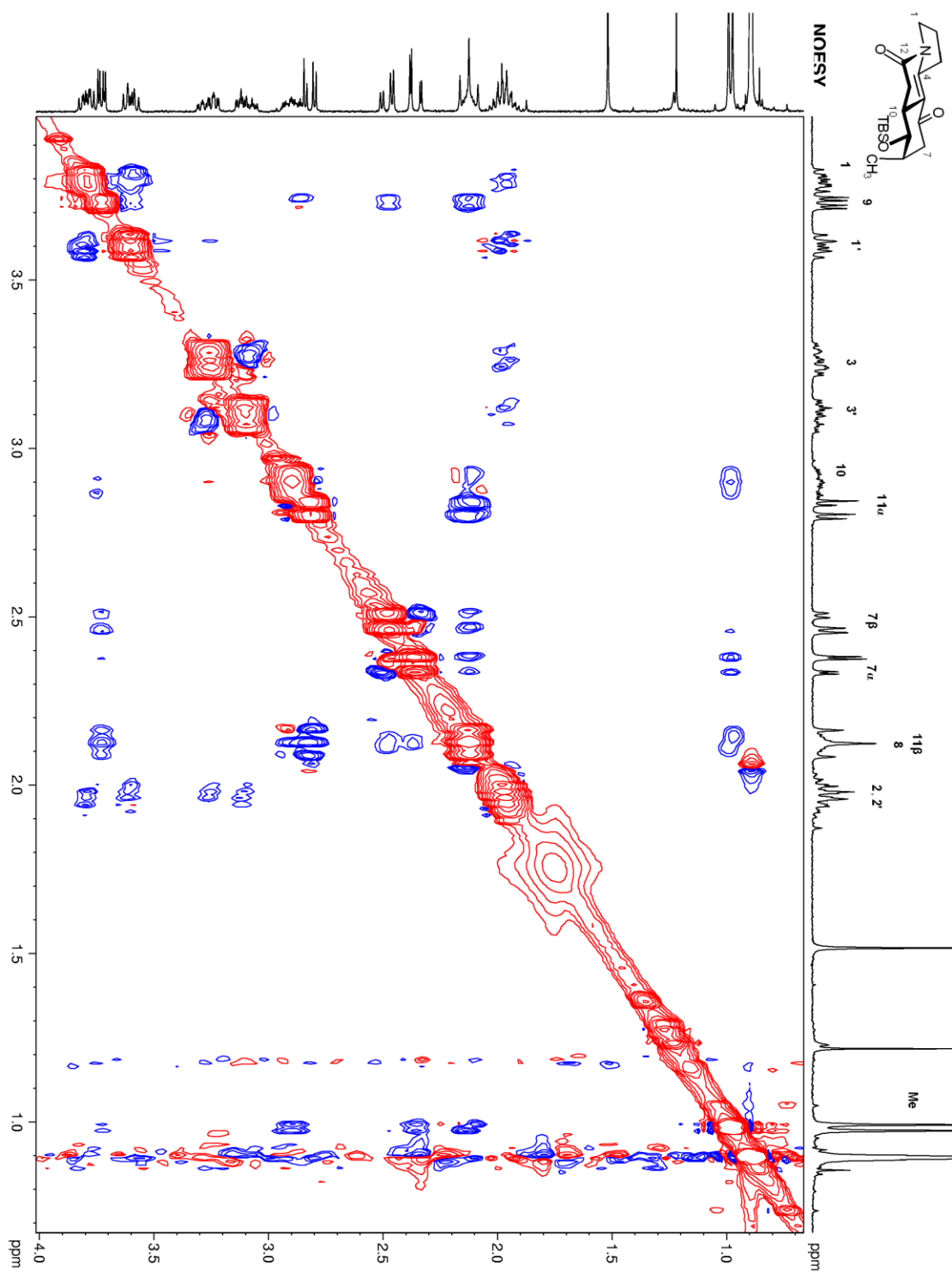
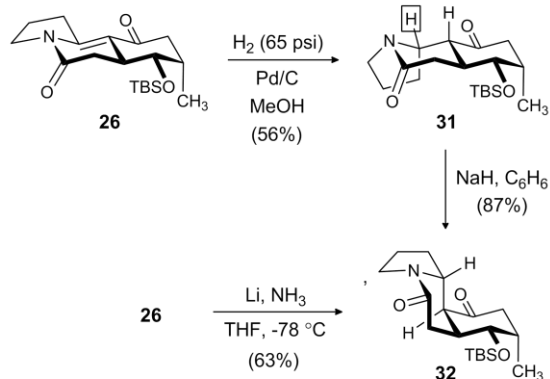


Figure 3. NOESY correlations of imide **26**

COSY established two isolated systems, those including the pyrrolidine ring (H1-H3) and those including 6,6-ring system (H7-H11). The stereocenters at C8-C10 were already set in the starting vinylogous amide and the cyclization to **26** did not result in the formation of new stereocenters. NOESY correlations were still used in confirming the three stereocenters (Figure 3 and Spectrum 4). The cross peak of H10 and CH₃-8 corresponds to a 1,3-diaxial relationship and *cis* arrangement. A second interaction of H10 to H11α was also noted. H11α is in the equatorial conformation due to a coupling constant of ³J_{10,11α} = 5.2 Hz, whereas H11β has two large coupling constants corresponding to the geminal coupling (²J = 16.1 Hz) and axial-axial coupling (³J_{10,11β} = 16.1 Hz). A correlation from H7 to H9 represent the second 1,3-diaxial interaction with H9 also demonstrating a large coupling constant (³J_{9,10} = 9.5 Hz). No NOESY correlations were observed between the pyrrolidine ring hydrogens and the 6,6-ring system.

Spectrum 4. 2D NOESY (500 MHz, CDCl₃) of Imide 26

Scheme 6. Reactions to form ketone epimers **31** and **32**.



Ketone **31** resulted from alkene reduction of imide **26**, thereby setting two new stereocenters at C4 and C5 (Scheme 6). With the disappearance of the alkene, the new ^{13}C NMR peaks clearly represented a ketone (207 ppm) and an amide (169 ppm) functionality. The new 5,6,6-ring system produced two more hydrogens in the ^1H NMR in an already crowded region between 4.2 and 1.2 ppm, therefore requiring two solvents for resolution. First, ^1H - ^1H spin decoupling experiments in C_6D_6 established most of the main skeleton but H5 overlapped with three other hydrogens (H8, H10, and one of H11). The two methylene hydrogens adjacent to the ketone (H7) and amide (H11) could not be distinguished, therefore a spin decoupling experiment in CDCl_3 was run in which the connectivity was fully elucidated.

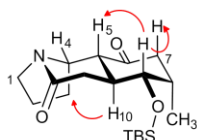


Figure 4. NOESY correlations in **31**

The 2D experiments were then run in C_6D_6 . An HSQC was required to separate the overlapping hydrogens into their respective methines and methylenes (Spectrum 5). A 2D NOESY provided a crosspeak between H9 and H7 β (both axial hydrogens) and from H9 to H5 (Figure 4 and Spectrum 6). The latter crosspeak, though, was not entirely conclusive because of the H5 overlap as described above. Although based on the HSQC, the leftmost part of the multiplet peak corresponds to H5 and this is the same region that the NOESY crosspeak showed a correlation. A second key correlation was noted from the pyrrolidine ring (H3) to H10. Again, H10 was one of the overlapping hydrogens in the multiplet, however, only H10 is close enough to the pyrrolidine ring to be deduced as the correct hydrogen for the observed correlation. The correlation to the pyrrolidine ring would suggest that H4 is β , as shown, but H5 did not show any correlations to H4 in the NOESY. However, a 1D NOE experiment in CDCl_3 could be utilized in which selective excitation of H5 provided an enhancement of 11.5% in H4 and 5.2% in H9 indicating that both H4 and H5 are β .

An interesting observation in the ^1H NMR (C_6D_6) was that H3 α and H3 β were separated by 1.6 ppm! Based on NOESY correlations, H3 β is on the same face as H4 and is the one at 2.18 ppm, whereas H3 α is at 0.60 ppm. Both hydrogens at C3 appear to be experiencing either a shielding (H3 α) or deshielding (H3 β) effect from the nearby ketone carbonyl since the hydrogens at C2 occur, which experience no shielding effects, appear at 1.2 ppm. When building a model of **31**, it can be reasoned that H3 α sits more in the plane of the lone pair of electrons on the oxygen and this results in the upfield shielding of the hydrogen relative to H3 β .

A crystal structure of ketone **31** was later obtained that agreed in both the assigned structure and stereochemistry. Fortunately, a co-crystallization had occurred with a minor impurity in **31** containing a compound consistent with a hydroxyl group at C5 (**S4**, 10% composition within the crystals, Figure 5). The same *cis*-stereochemistry of H4 and C5-OH was observed as in the ketone between H4 and H5.

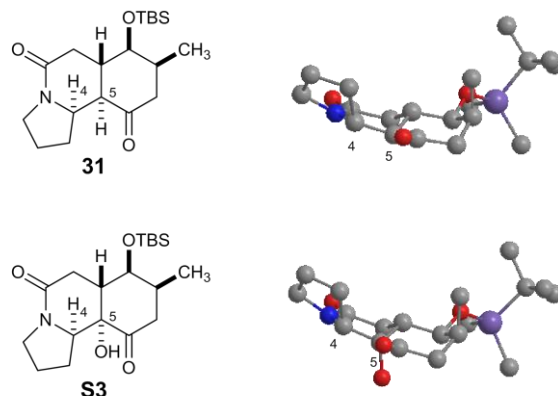


Figure 5. X-ray crystal structures of ketone **31** and α -hydroxyketone **S4**

Ketone **31** could be epimerized with base to form exclusively the epimer **32** at C5 (^{13}C – 209 and 168 ppm, Scheme 6). Again, benzene proved to be a better solvent in terms of separation and therefore was used for subsequent NMR analysis. The *trans*-decalone in **31** was now converted to a *cis*-decalone in **32**, thereby providing two possible ring flip conformations that had to be established (Figure 6). Again, spin decoupling experiments were used to solve the backbone assignments. Note that the ring system is flipped from how it was drawn previously to best show the correlations and therefore the terms α and β will be reversed as well. 2D NOESY correlations helped to provide the 1,3-diaxial interaction between H7 β and H5 and it was noted that H7 β contained two large coupling constants (both geminal and vicinal were 13.2 Hz), also highlighting that it is axial (Spectrum 7). H5 also showed correlations to H4 and H10. The correlation to H4 highlights that while there is a *trans*-relationship with H5, the two hydrogens are in an axial/equatorial relationship. This arrangement also forces the large OTBS group into the axial orientation. In the new *cis*-decalone, H4 occurs at 3.95 ppm, whereas in the previous structure **31**, H4 was at 3.15 ppm. The downfield shift of H4 appears to be due to H4 sitting underneath the carbonyl, therefore falling in the deshielding region of the carbonyl. Also, the CH₂ at C3 no longer experience the pronounced shielding effects of the carbonyl (H3 α , same side as H4, is at 1.40 ppm and H3 β is at 1.05 ppm).

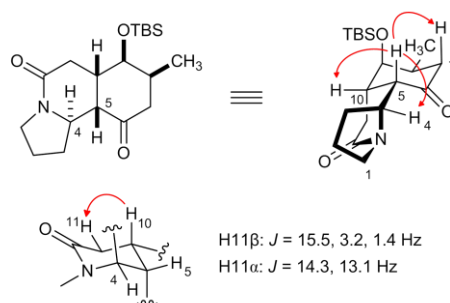
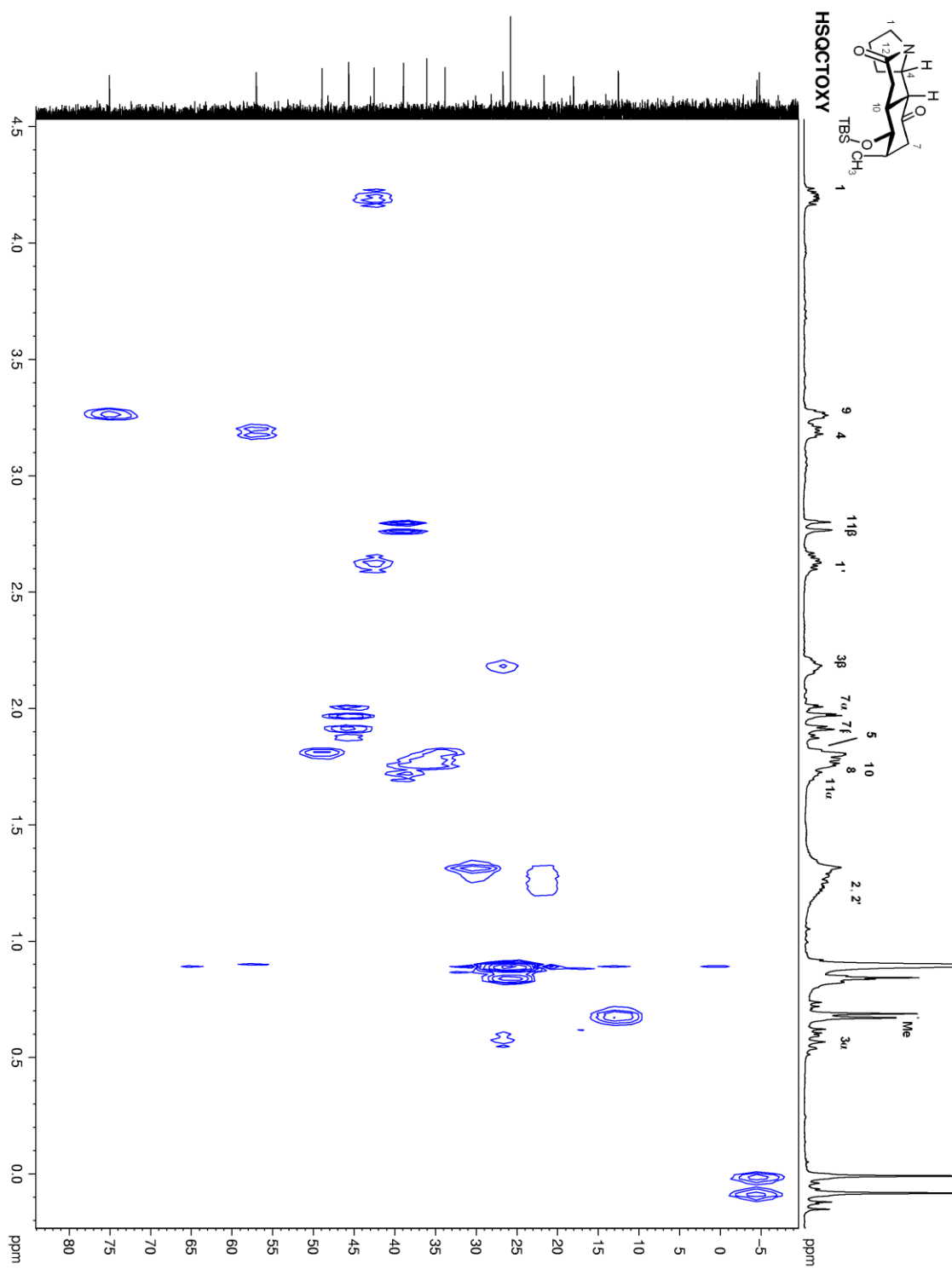
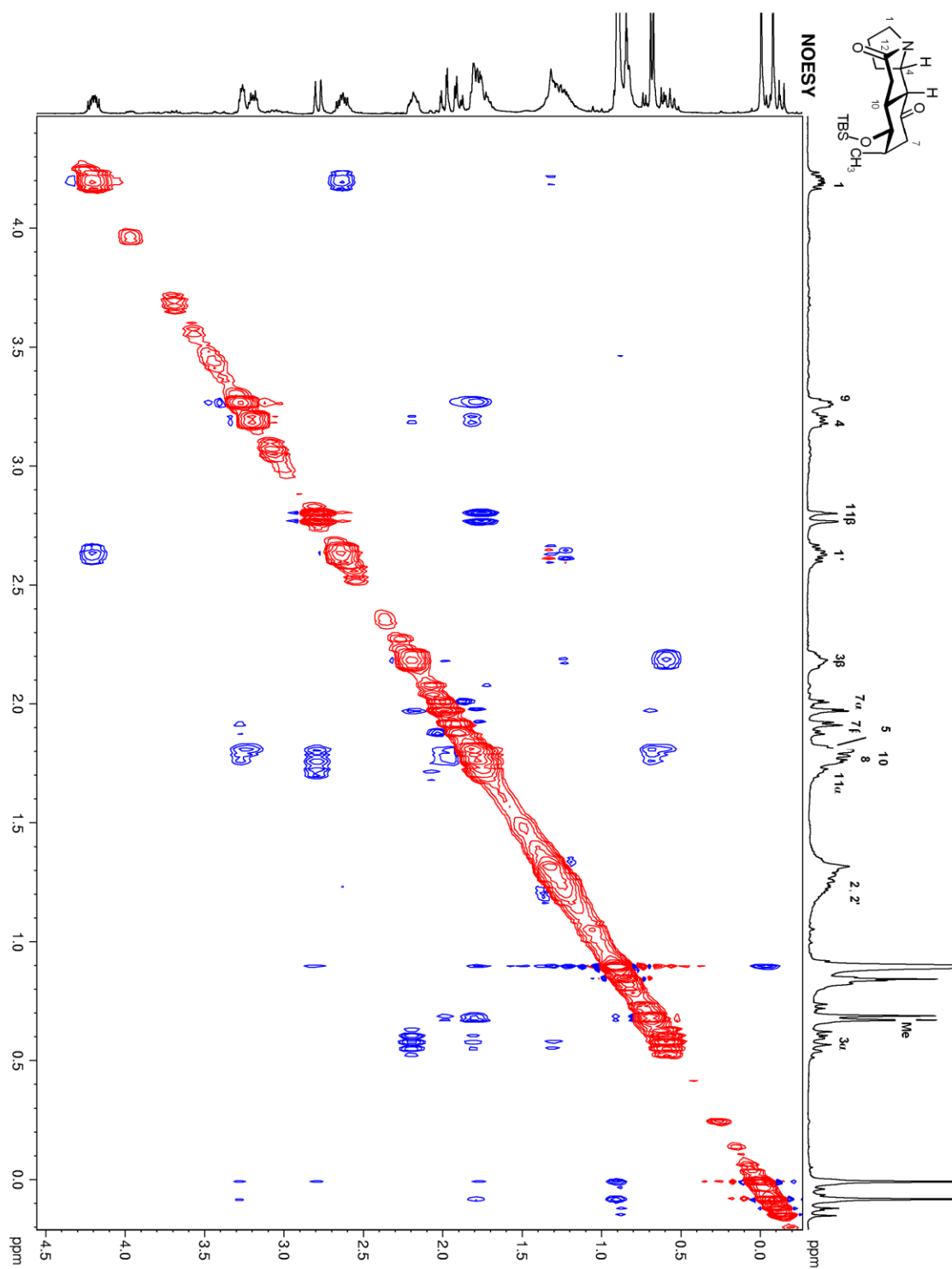


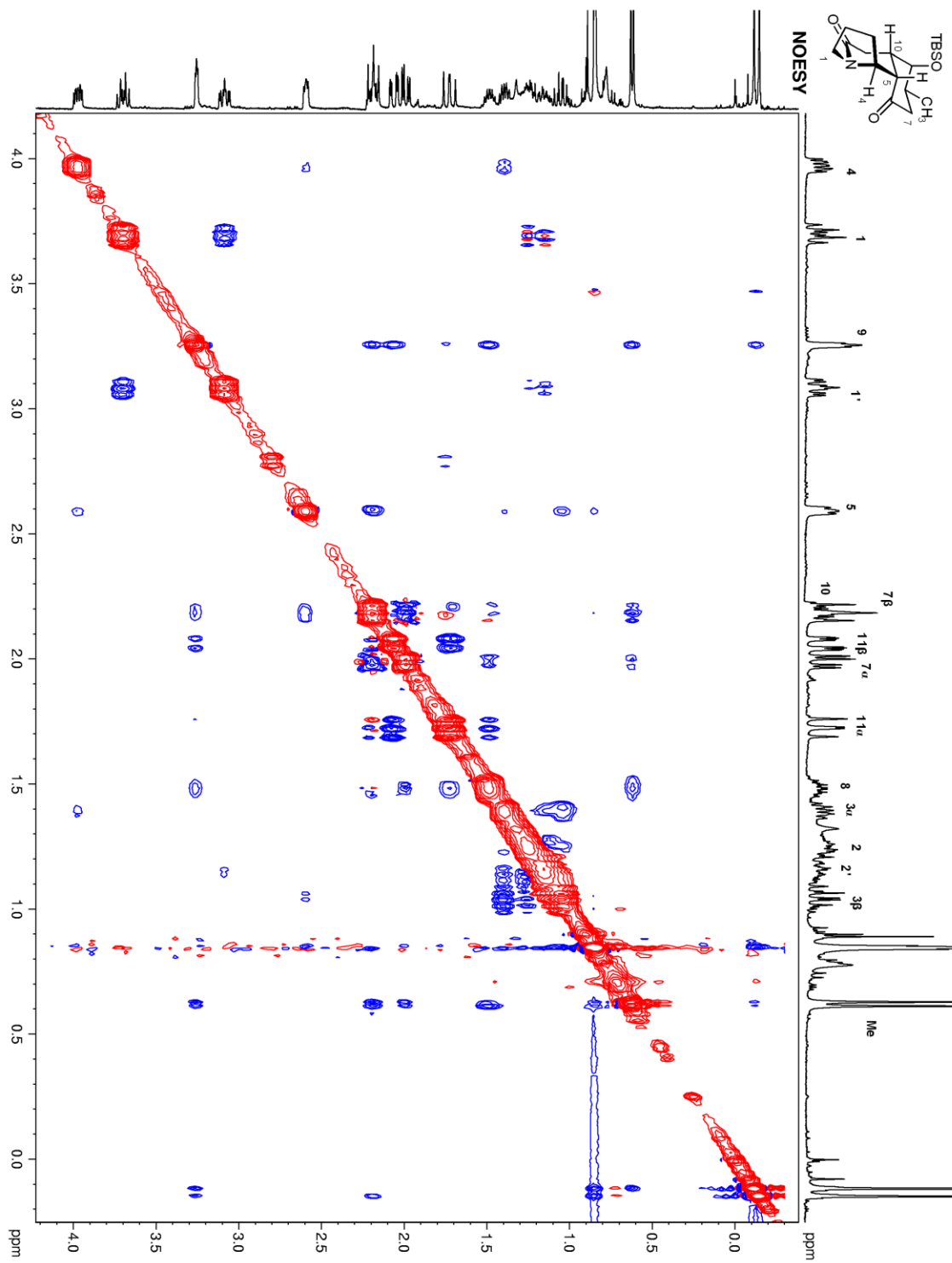
Figure 6. NOESY correlations in ketone isomer **32**

Also noticed in ketone epimer **32** is a W-coupling from H11 β to H5. The lactam portion of **32** is highlighted in Figure 6. A NOESY correlation from H10 to H11 β demonstrated that the two hydrogens were on

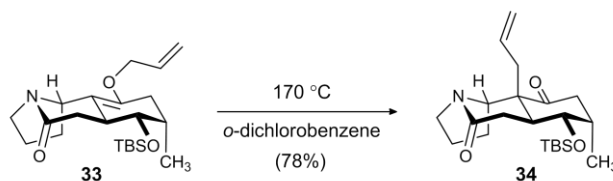
the same face. H11 β is equatorial on the lactam ring, as well as H5, and these two hydrogens are aligned in a conformation such that a W-coupling is noted in H11 β of 1.4 Hz. Unfortunately H5 is broadened such that the same coupling cannot be observed. This is further affirmation of the structure and correct chair assignment of the *cis*-decalone ring system in **32**.

Spectrum 5. 2D HSQC-TOXY (400 MHz, C₆D₆) of Ketone **31**

Spectrum 6. NOESY (400 MHz, C₆D₆) of Ketone **31**

Spectrum 7. NOESY (400 MHz, C₆D₆) of Ketone Epimer 32

Scheme 7. Claisen Rearrangement to Form C-Allyl **34**



C-allyl **34** was obtained from the Claisen rearrangement of allyl vinyl ether **33** in good yield (Scheme 7). The stereochemistry at C4 was known from the ketone precursor (**31**) which was used to form **33**. Therefore the new quaternary allyl stereocenter was the only unknown configuration. Use of COSY in C₆D₆, which provided maximal separation, allowed for determination of the connectivity of three spin systems: H1-H4, H7-H11, and H13-H15 and their subsequent placement along the 5,6,6'-backbone (Spectrum 8). A region from 2.0-2.3 ppm was very crowded and contained six peaks, including the allylic hydrogens (H13 and 13'), H10, H11 α , H7 β , and H3 (see Figure 7 for assignments). First, H7 α was distinguished from H7 β based on the coupling constants which were determined to be 14.8 and 2.6 Hz, indicating that H7 α is equatorial (due to the 2.6 Hz coupling with H8 which is also equatorial). Therefore, H7 β must be axial and hence would be β based on the orientation as drawn. H11 β also separates from the region and contains only large coupling constants pointing towards an axial orientation and hence β . It is also similar in appearance to H11 β from ketone **31**. NOESY correlations in the same solvent were mostly clear, despite the overlap of hydrogens (Spectrum 9). Since H13 resided on the leftmost side of the overlapping region, a NOESY correlation from H4 to H13 could be observed. Furthermore, H9 (which is axial, $J = 9.9, 4.8$ Hz) showed a very broad crosspeak to the right half of the overlapping region, indicating the likelihood of two or more correlations. Out of the possible hydrogens, H3 is too far from H9, H10 is axial and on the opposite face of H9 also making it unlikely, and H11 α is equatorial and likely too far from H9. Therefore, the remaining possible hydrogens are H7 β and H13 – both of which are 1,3-diaxial interactions. The NOESY correlations led to assignment of the allyl group as β .

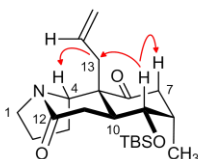
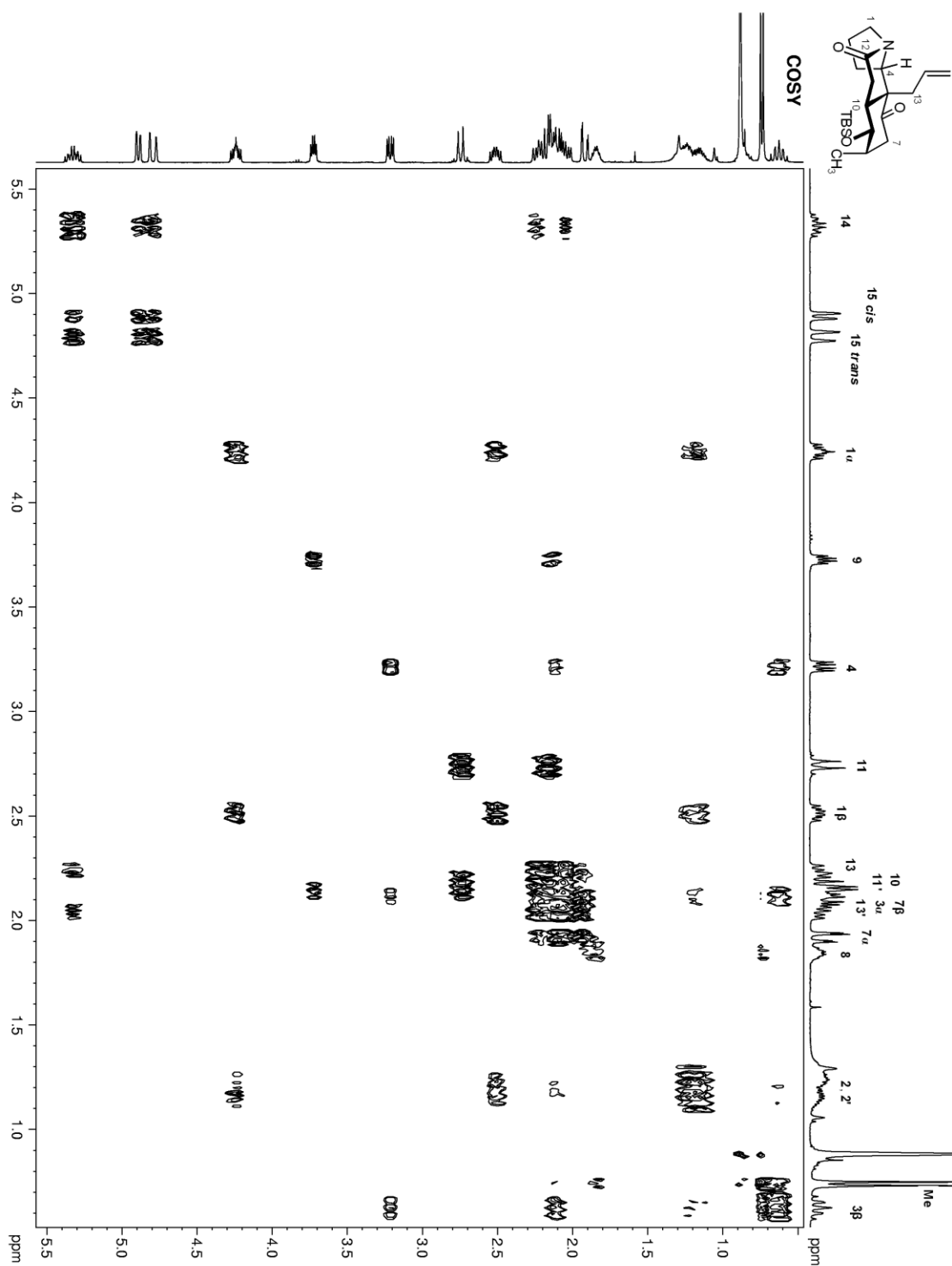
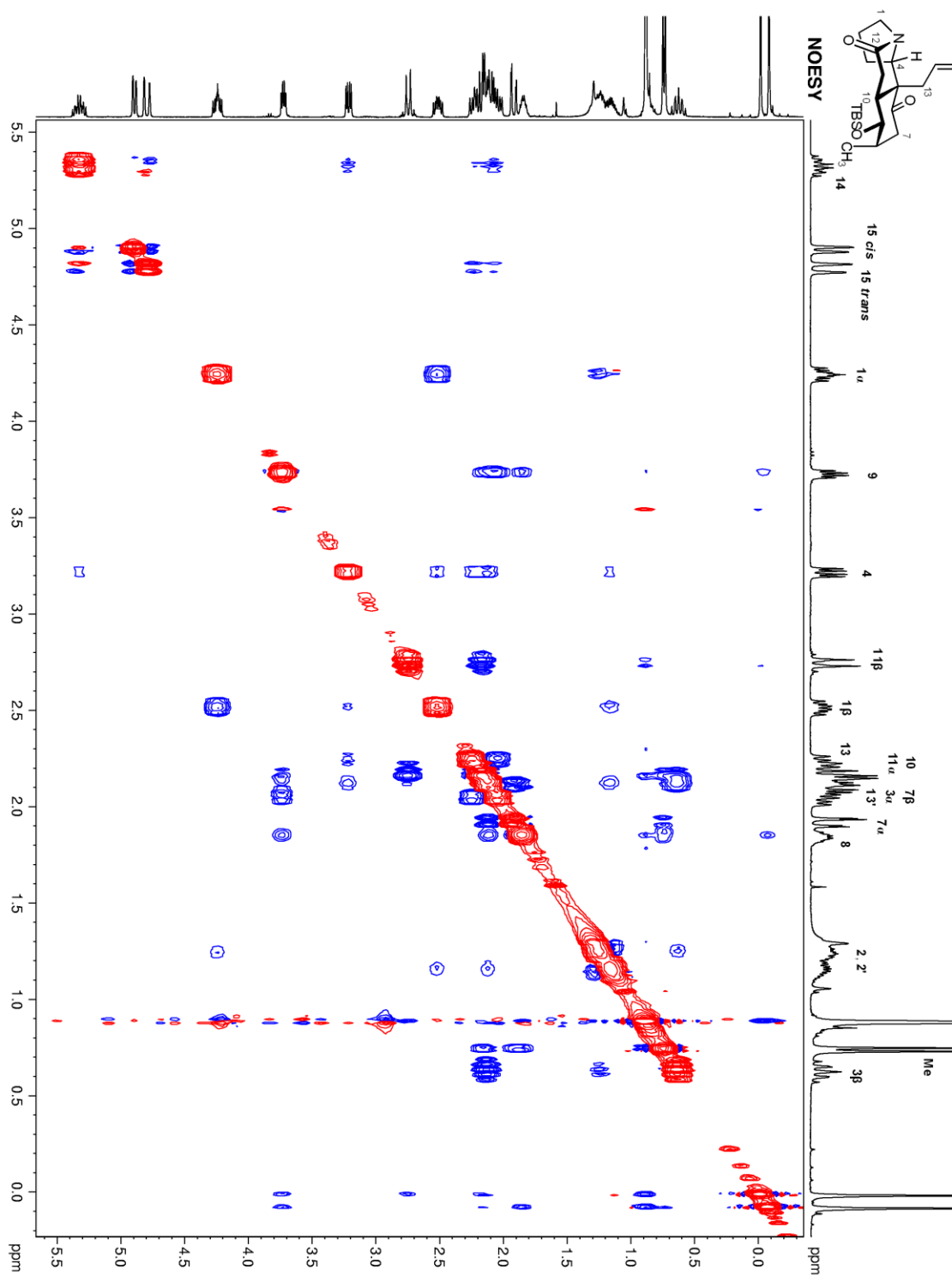
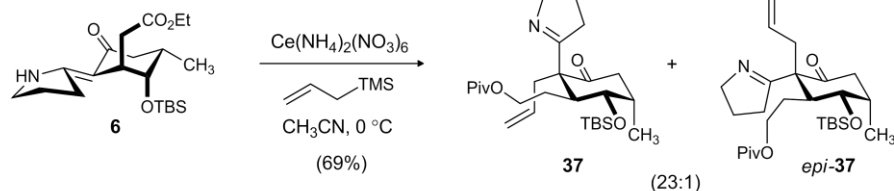


Figure 7. NOESY correlations observed in **34**

Spectrum 8. COSY (400 MHz, C₆D₆) of C-allyl **34**

Spectrum 9. NOESY (400 MHz, C₆D₆) of C-allyl **34**

Scheme 8. Formation of Diastereomers from the Oxidative Allylation



A cerium(IV)-mediated oxidative allylation of **6** was used to form the desired allyl product (**37**) as the main diastereomer, with some of the minor diastereomer (*epi-37*) being observed on a larger reaction scale (Scheme 8). Both structures were fully solved with the aid of 2D NMR techniques. Starting with the main diastereomer (**37**), COSY was used to assign the connectivity along the backbone providing three spin systems: H1-H3, H7-12, and H13-H15. Usually to assign H7-H12, the methyl group is used as a starting point. Due to some overlapping in the regions around 2.4 ppm and 1.7 ppm, an HSQC was also acquired and nicely demonstrates the exact position of the respective hydrogens within the crowded regions (Spectrum 11). This aids in the NOESY assignment as well, for example when a correlation is noted to one side of an overlapping region of peaks, the exact hydrogen can be identified due to the HSQC. With H9 identified at 4.65 ppm, it was determined that it resides in the axial orientation based on the coupling constants ($J = 9.5, 4.0$ Hz, the 9.5 Hz coupling represents $^3J_{9,10}$). A NOESY correlation could be observed between H9 and H7, therefore signifying a 1,3-diaxial interaction and showing that the cyclohexanone ring is in the opposite chair conformation from the starting material (Figure 8 and Spectrum 10). To assign the stereochemistry of the allyl group, a NOESY correlation was noted from the vinyl hydrogen, H14, to H10. Because H10 is in the axial position on the α -face, the allyl group must also be on the α -face and to do so must be in the equatorial position. Further NOESY assignments were made to the diastereotopic allylic methylene hydrogens, such that H13 (3.01 ppm) showed a correlation to H14, which must be on the interior of the allyl group because of the correlation of H14 to H10. Also, H13' (~2.41 ppm, based on the HSQC) displayed a crosspeak to the *trans*-vinyl hydrogen (H15). No correlations could be observed from pyrrolidine hydrogens (H1-H3) to either the cyclohexanone ring or the pivalate side chain. Therefore, it was assumed that the imine nitrogen is pointing towards the cyclohexanone ring. To ensure the placement of the allyl group relative to the backbone, HMBC was used (Spectrum 12). Both the ketone (C8, ^{13}C : 209 ppm) and the imine (C4, ^{13}C : 176 ppm) carbons showed correlations to the allylic methylene hydrogens (H13,13'). C4 also showed a correlation to H10 and then from C10 to the pivalate side chain (H12, 12') and to H9. The 2D correlations fully match that of the desired allylation product (**37**) as the major diastereomer.

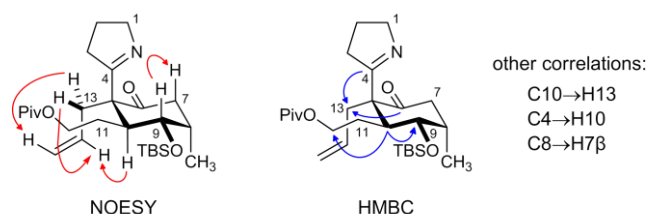


Figure 8. NOESY and HMBC correlations in **37**

Allyl diastereomer *epi-37* was also isolated and identified originally as a diastereomer based on the allyl incorporation in the ^1H NMR and the presence of the ketone (210 ppm) and imine (178 ppm) peaks in the ^{13}C NMR which indicated that the C5 carbon was allylated, rather than the nitrogen or oxygen. The 2D data for the

allyl diastereomer (*epi*-**37**) was also obtained to corroborate the data with the previous assignments and to distinguish the preferred chair conformation. After COSY data was analyzed, H9 was again found to be in the axial orientation ($J = 7.9, 3.5$ Hz) meaning that the cyclohexanone chair was in the same conformation. Therefore, the allyl group should be on the β -face and was expected to show 1,3-diaxial interactions with H9 in the NOESY spectrum (Figure 9 and Spectrum 13). Unfortunately, of the two allylic hydrogens at C13, one shows no correlation to H9 and the other is overlapping with the hydrogens at C7. While a crosspeak is noted from H9 to the overlapping region, it cannot be discerned whether this is due to the allylic methylene or the axial H7. Other NOESY correlations can still be used in the assignment, such as H13 (which is not occluded by other hydrogens) to H11 and also from the pyrrolidine ring hydrogen, H3, to H10. These two correlations demonstrate that *epi*-**37** represents the diastereomer of **37**.

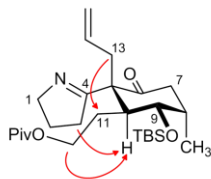
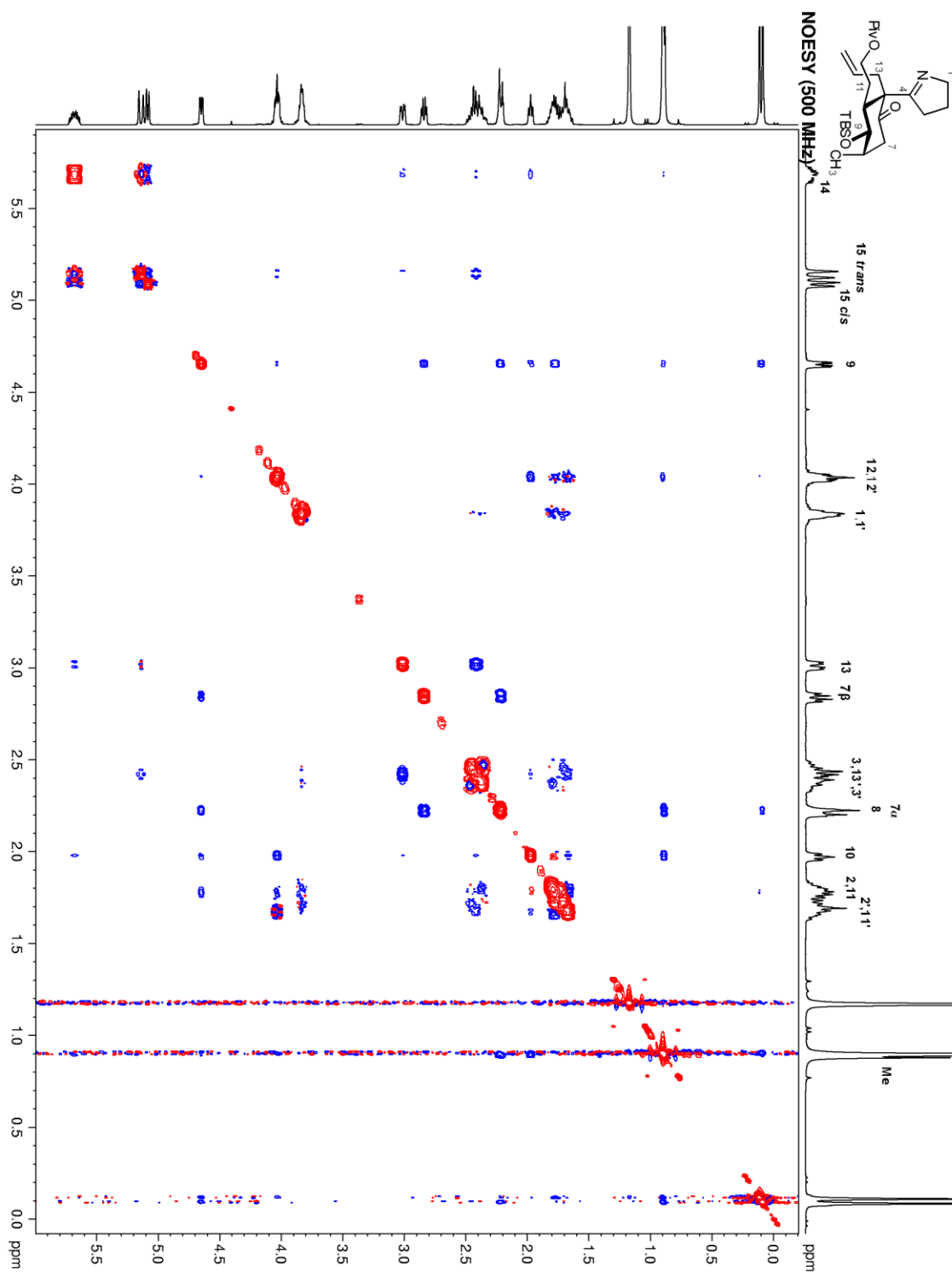
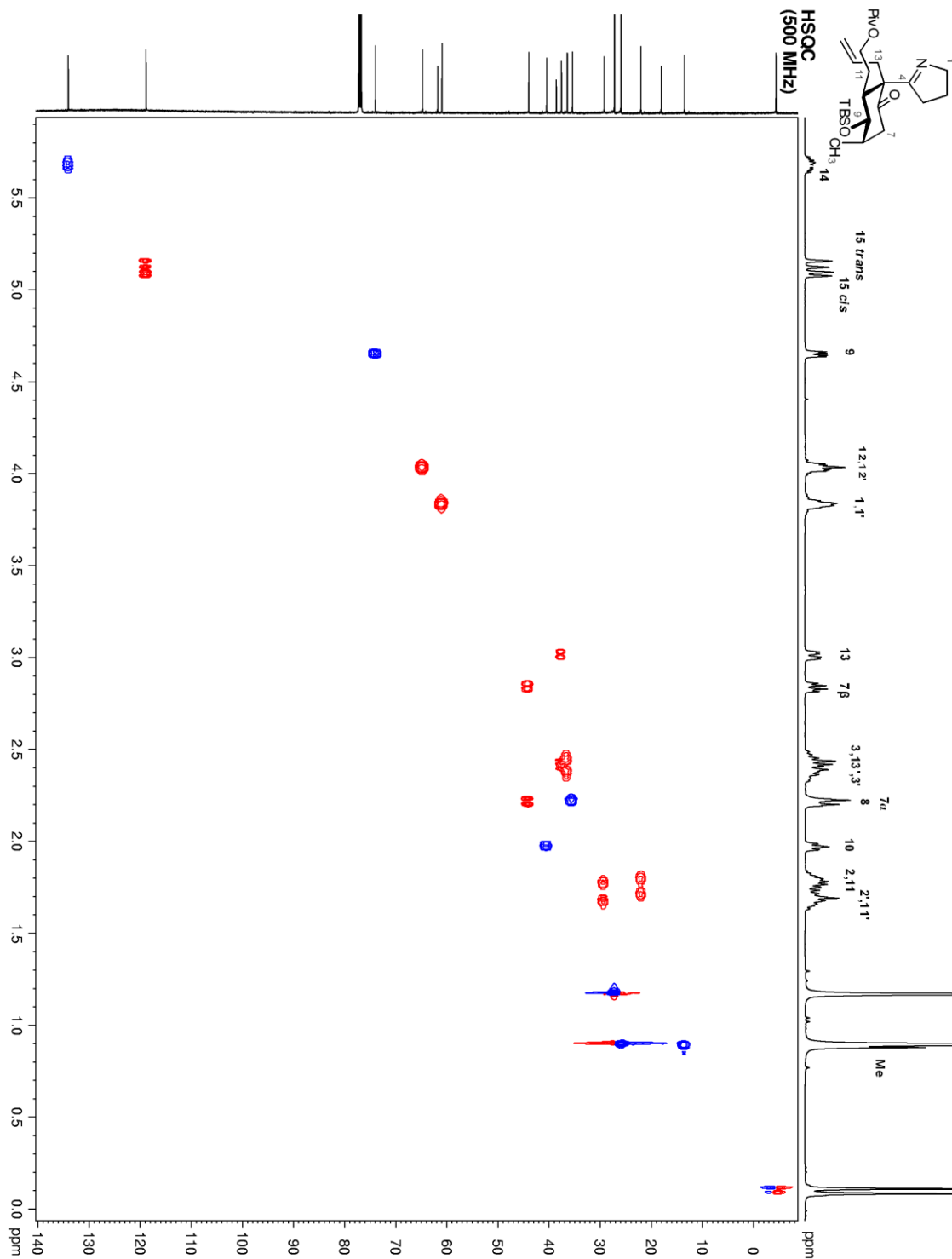
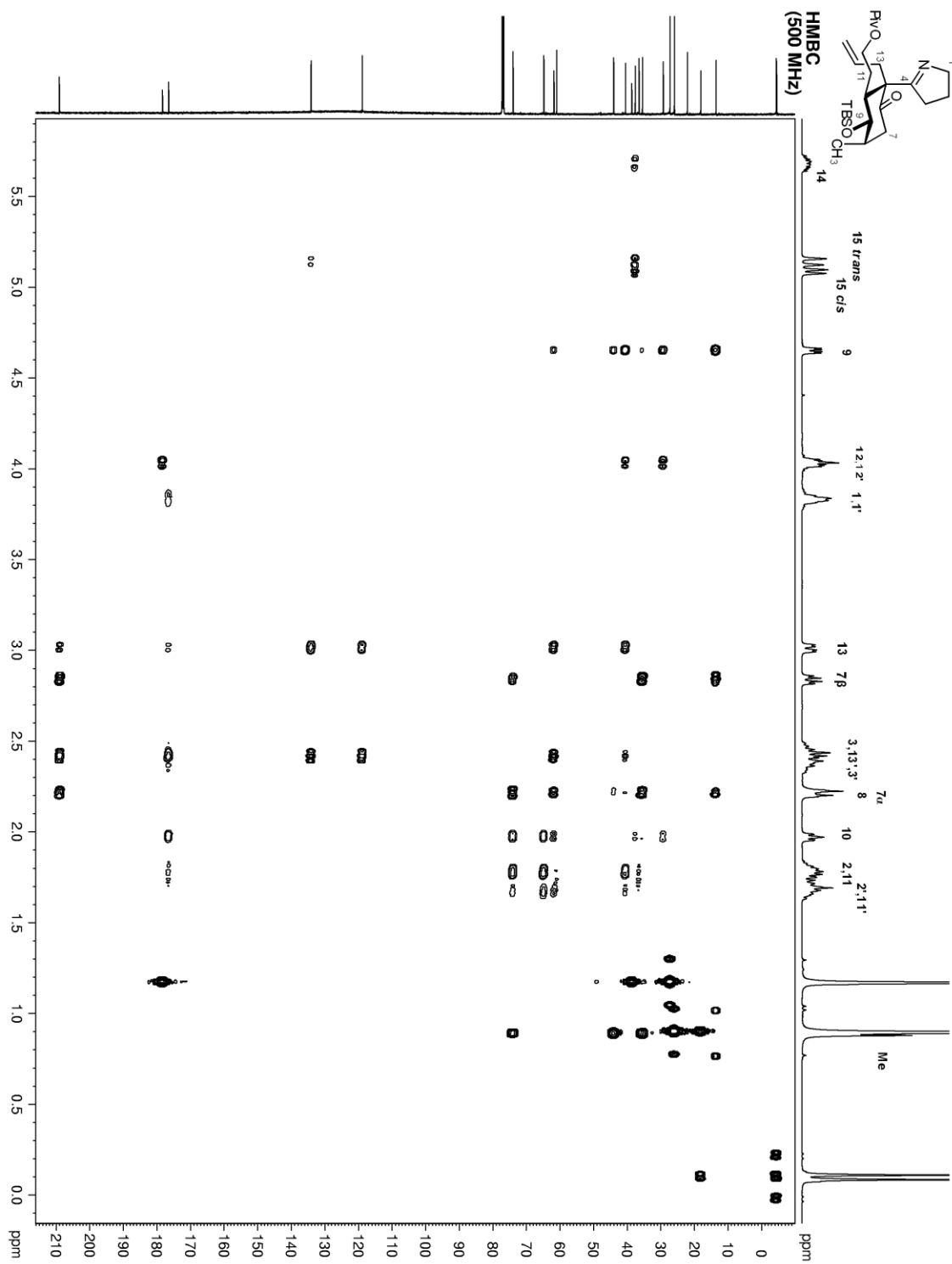
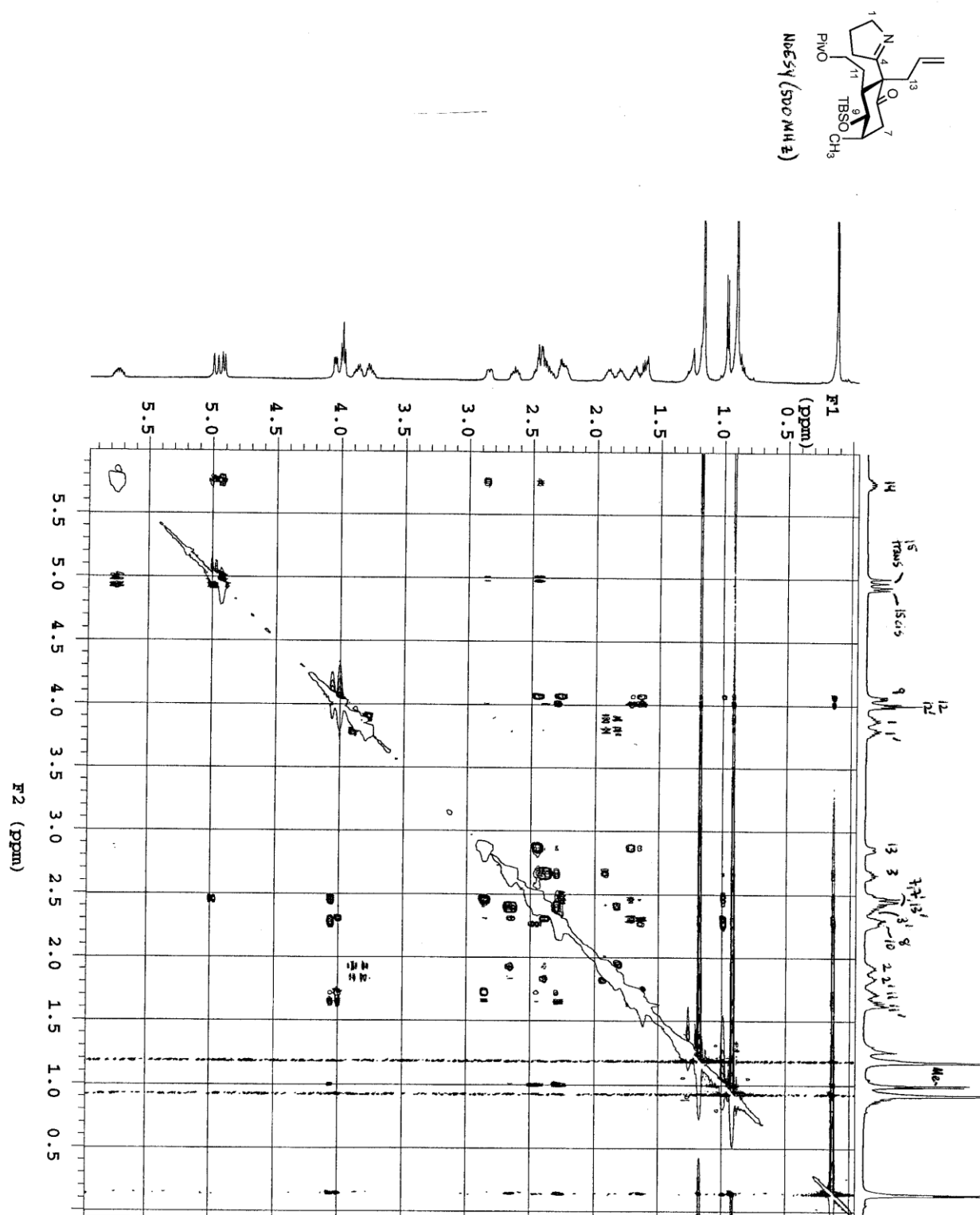


Figure 9. NOESY correlations in *epi*-**37**

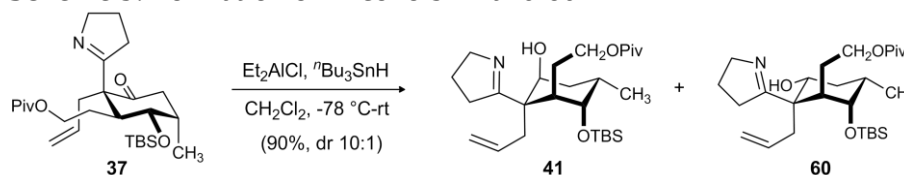


Spectrum 11. HSQC (500 MHz, CDCl₃) of C-allyl **37**

Spectrum 12. HMBC (500 MHz, CDCl₃) of C-allyl **37**

Spectrum 13. NOESY (400 MHz, CDCl₃) of C-allyl Diastereomer *epi*-37

Scheme 9. Formation of Alcohols **41** and **60**



The two secondary alcohols were formed by a directed reduction of ketone **37** using Et_2AlCl and $t\text{Bu}_3\text{SnH}$ (Scheme 9). The β -orientation (**41**) was the favored diastereomer under the directed reduction conditions. This was postulated to occur by binding of both the imine and ketone to the Lewis acid, which would block the top face of the cyclohexanone ring, and then using an external reducing agent, $t\text{Bu}_3\text{SnH}$, to attack from the opposite face. The α -alcohol (**60**) in turn could be favored using NaBH_4 in isopropanol. Reduction was confirmed by loss of the ketone resonance in the ^{13}C NMR at 209 ppm. A broad peak at 3350 in the IR region was also observed indicating the OH group. Both structures could be separated by column chromatography and were subjected to NMR analysis to determine the alcohol stereocenter, beginning with **41**.

A 2D COSY spectrum of **41** indicated three distinct spin systems, including H1-H3 (pyrrolidine), H6-H12 (cyclohexanol ring and pivalate side chain), and H13-H15 (allyl group). Moreover, five hydrogens occur in an overlapping pattern, from 1.75-1.95 ppm. Use of HSQC showed that these peaks (H2 and 2', H7 α , H10, and H11) did not particularly favor either side of the overlapping region and therefore NOESY correlations to this region would be complicated (Spectrum 15). Starting with the other hydrogens, H9, which was axial in the starting material, was now found to be only a broad singlet due to two small couplings which led to an equatorial assignment.⁴ In the NOESY spectrum, H9 also shows a correlation to H12, also pointing towards the same chair assignment (Figure 10 and Spectrum 14). H6 shows the same broad singlet shape in the ^1H NMR as H9 did, suggesting it is also equatorial, although it could be broadened due to the geminal OH and this alone was not confirmation that H6 was equatorial. H6 also showed a NOESY correlation to the vinyl hydrogen (H14). Since the allyl group is α and axial, due to the chair conformation of the cyclohexanol ring, the only way H6 could show a correlation to H14 would be for H6 to be equatorial and therefore α . As mentioned, the overlap region in the ^1H NMR makes it difficult to assign any 1,3-diaxial interactions from H13 or 13' to H7 α . In the NOESY spectrum, a crosspeak from H13 is noted to the overlap region. Therefore of the five hydrogens, it is likely to be either H7 α or H10 (H2 and 2' are too far as well as H11). Upon closer inspection, the shape of the crosspeak in the F2 dimension is well-resolved as shown in . The shape of the crosspeak can often aid in the assignment of crowded regions. The same shaped crosspeak and location was also observed from both H6 and the methyl to the overlapping region. Only H7 α makes sense for the correlation with H6, H13, and the methyl. Therefore this confirms the α -allyl group orientation as the same as the previous assignment and the fact that H6 has NOESY correlations to both H7 α and H7 β also confirms that H6 is equatorial.

⁴ This was also observed in vinylogous amide **6** above when H9 was in the equatorial position.

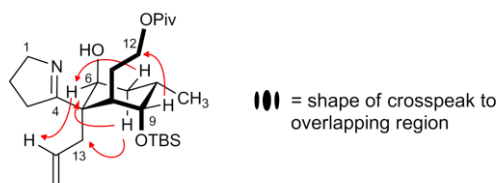


Figure 10. NOESY correlations in **41**

Analysis of the chair conformation of β -alcohol **41** reveals that four substituents reside in the axial position. The implications of this can be seen in the ^1H NMR where the peaks in general are broadened and do not show as much splitting, as they did previously in ketone **37**. With the α -alcohol epimer **63** the peaks are much sharper, even though it sits in the same chair conformation as the β -alcohol, due to only three substituents being axial. COSY was used to assign the peaks in **63** and then NOESY correlations were used to assign that indeed **63** contained the α -alcohol (Figure 11 and Spectrum 16). The hydrogen geminal to the OH, H6, is now axial ($J = 12.1, 3.9$ Hz) and shows correlations to H8, H7 β , and H11. H9 is again a broad singlet, indicating that it is equatorial. Due to the better separation of hydrogens in the ^1H NMR, the NOESY correlation could be observed from H7 α to H13, again asserting that the allyl configuration was correctly assigned in the ketone precursor (**37**).

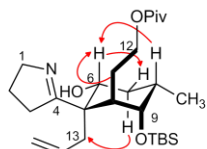
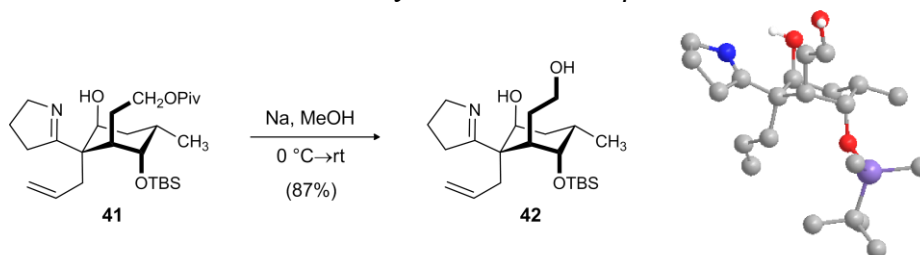
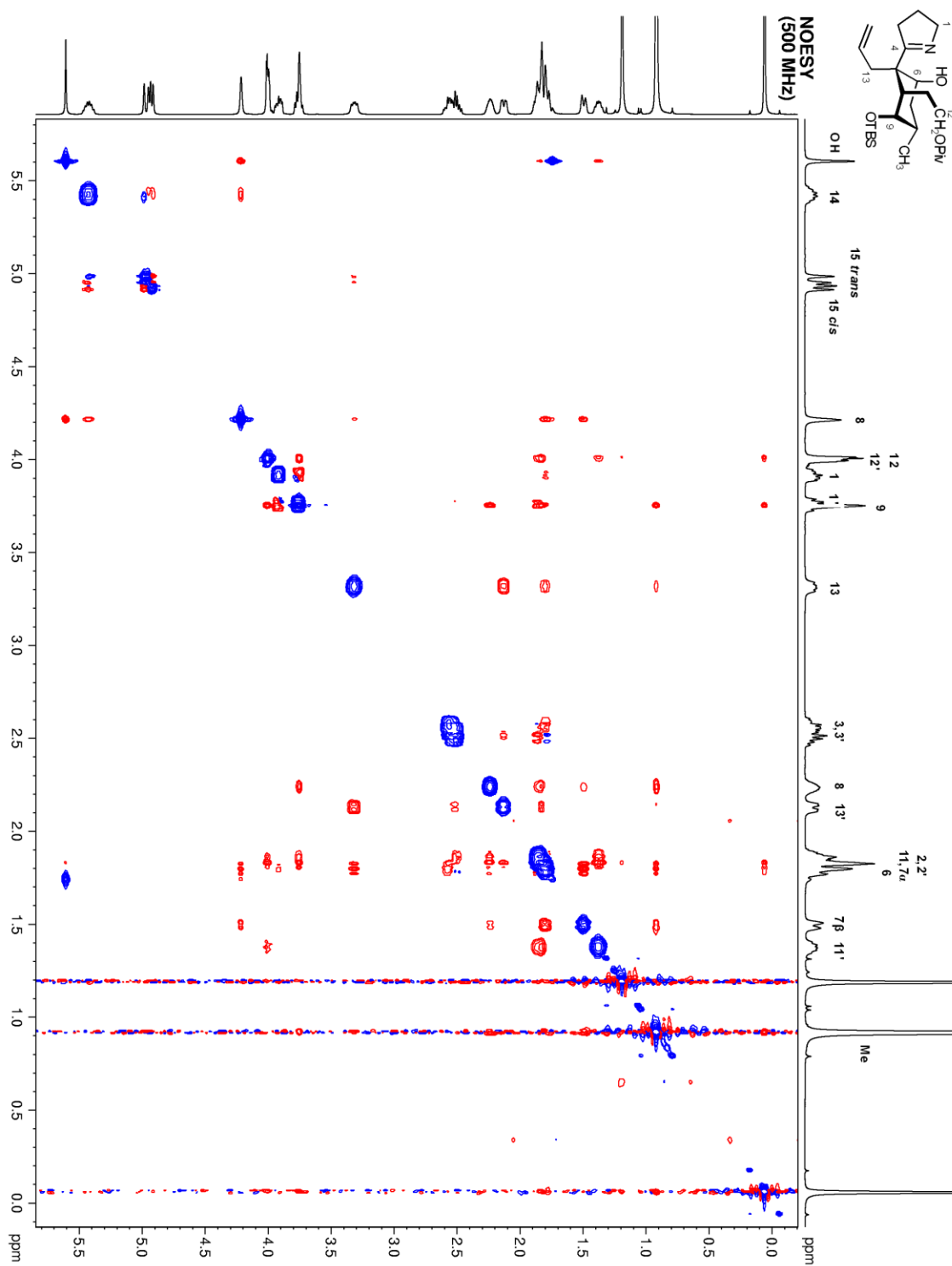


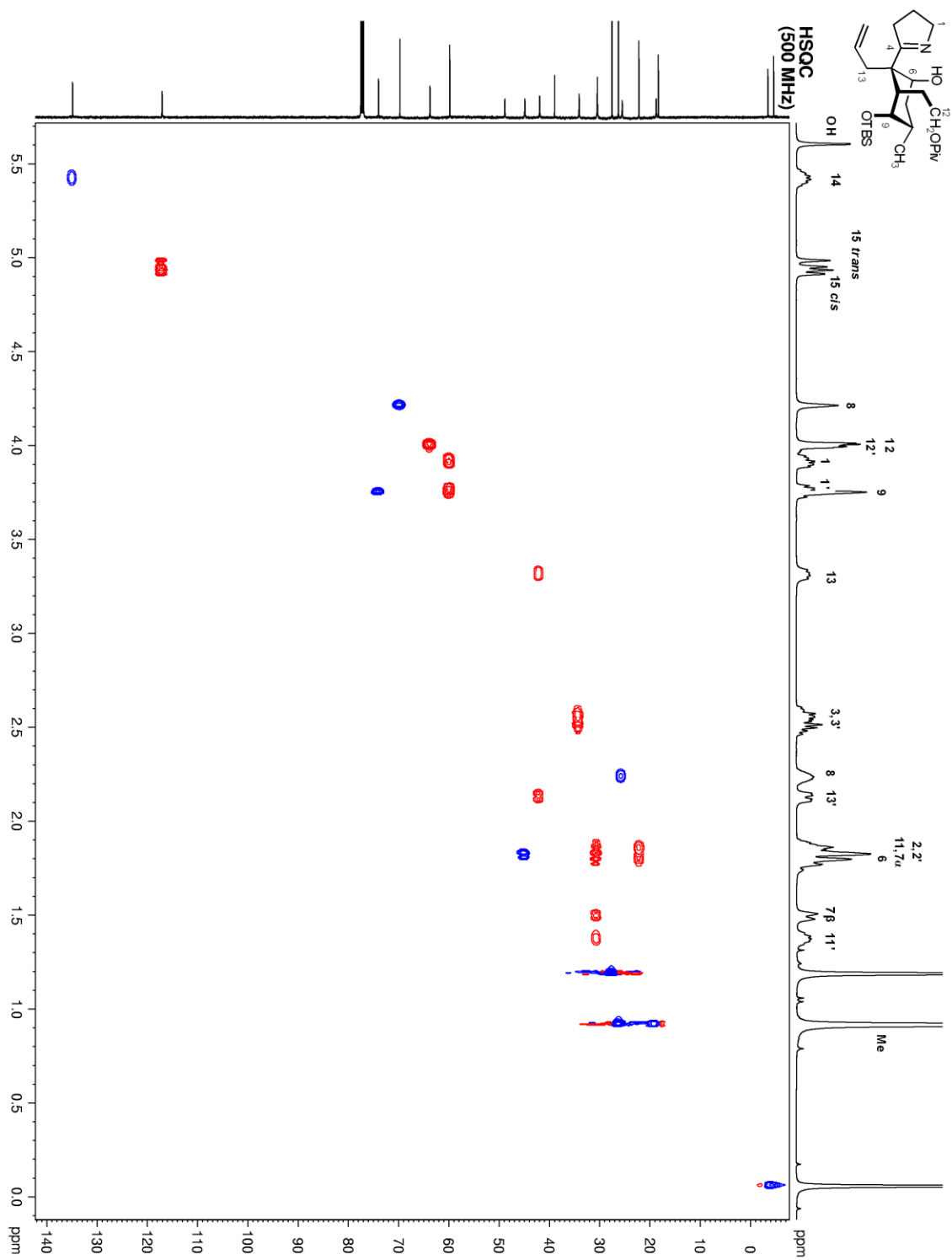
Figure 11. NOESY correlations in α -alcohol **60**

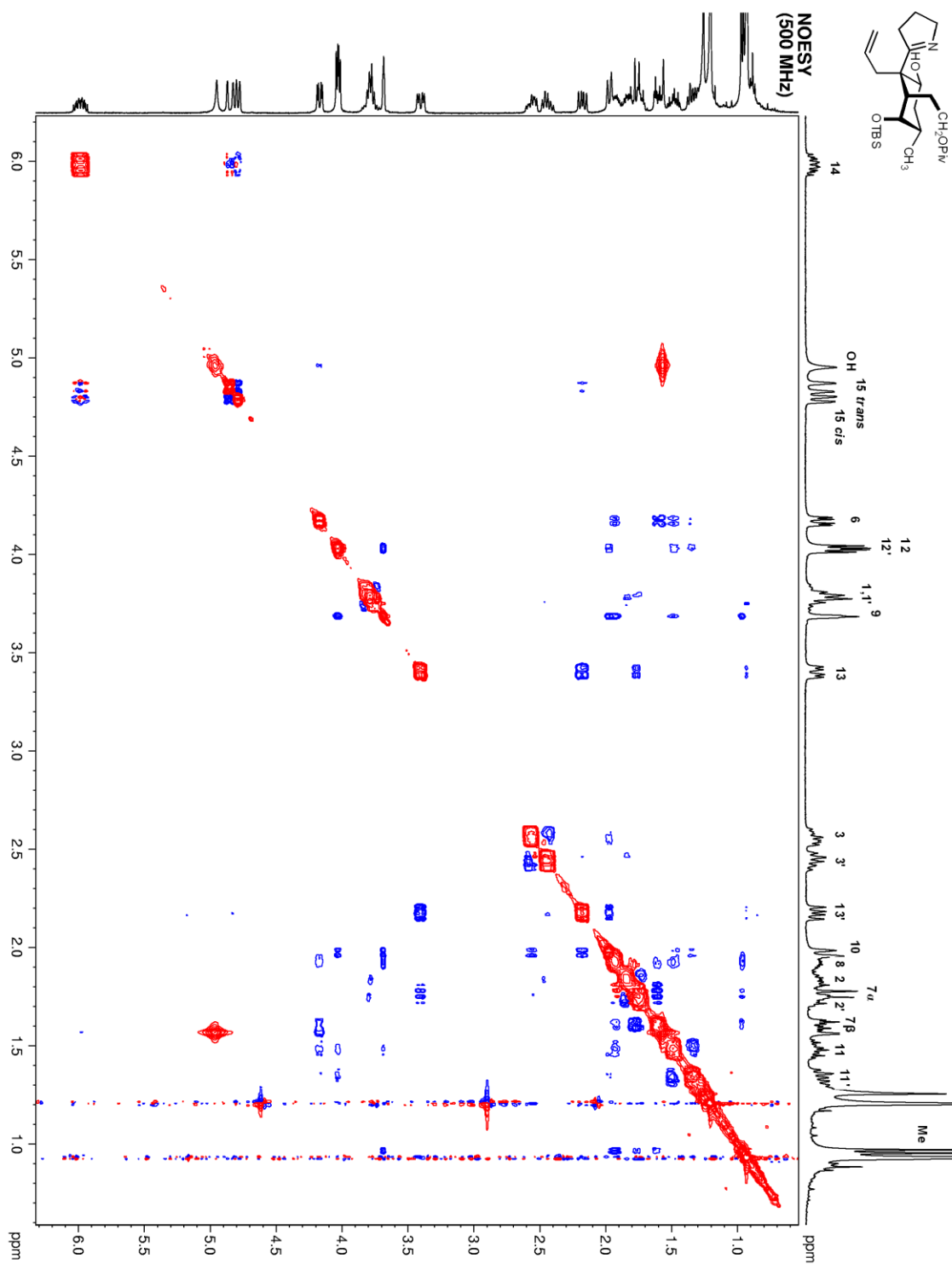
At a later point in the synthesis, we arrived at β -diol (**42**), derived from pivalate deprotection of **41** (Scheme 10). This compound was a solid and could be crystallized sufficiently to obtain an X-ray structure, confirming the assignments made by 2D NMR in the precursor.

Scheme 10. Formation and Crystal Structure of β -diol **42**

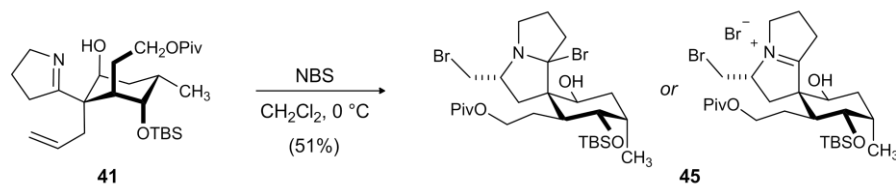


Spectrum 14. NOESY (500 MHz, CDCl₃) of β-alcohol **41**

Spectrum 15. HSQC (500 MHz, CDCl₃) of β -alcohol **41**



Scheme 11. Formation of Dibromide **45**



Exposure of the terminal alkene in β -alcohol **41** to NBS provided a new tricyclic product (**45**, Scheme 11). The ^1H NMR showed two well-resolved dd patterns at 3.4 and 3.5 ppm, which are the methylene adjacent to the bromide. Interestingly, by ^{13}C NMR, two peaks were observed at 179 and 177 ppm, the latter being the pivalate ester. By mass spectrometry, a small peak was observed for the parent mass containing two bromines and loss of one hydrogen. Therefore it appeared that the bromide may not be a counterion to an iminium salt, but rather it had added to the carbon of the iminium. Therefore both structures are shown as possibilities for **45**.

To determine the structure and stereochemistry, COSY was used to assign the backbone, first in CDCl_3 . Unfortunately both H6 and H9 were overlapping with other hydrogens, which made the assignment of the ring flip of the cyclohexanol ring difficult. However, use of 1D TOCSY allowed for both a more definitive assignment of the backbone structure and determination of coupling constants by showing all the hydrogens within the connected spin system of the irradiated hydrogen (Spectrum 19). When H8 was irradiated, H6, H9, H10, and H7 α and β could be discerned whereas before they were obscured by other proton signals. In particular, the coupling constants of H6 and H9 were able to be assigned and were found to be axial (H6: $J = 13.4, 3.8$ Hz; H9: $J = 10.2, 5.4$ Hz).⁵ The coupling constants of the two hydrogens at H7 allowed determination of which was α versus β also based on coupling constants. With confident assignment of the backbone, the NOESY spectrum was used to show the respective diaxial correlations within the cyclohexanol ring (Figure 12 and Spectrum 18). Correlations within the new pyrrolizidine ring could also be observed, demonstrating the relative stereochemistry of the brominated side chain (H15) with H13 α and also H14 with H13 β . Unfortunately, due to overlapping hydrogens, no correlations from the 5,5-ring system to the cyclohexanol ring could be reliably distinguished. Only a very weak crosspeak could be noted from H12 to H13 β and this was not believed to be reliable enough for assignment of stereochemistry at C14. Once the solvent was switched to C_6D_6 , H6 was now free from other hydrogens and a correlation to H13 α could be observed and also from H13 α to H15,15', showing that the bromomethyl group is on the α -face (Spectrum 17). H6 also showed a direct correlation to H15,15'. The configuration at C4, however, could not be determined at this stage.

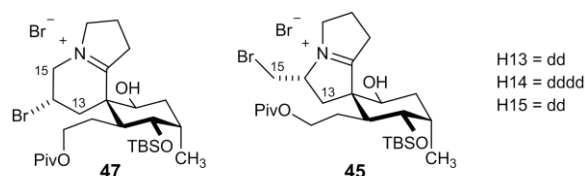


Figure 12. NOESY correlations of **45** in CDCl_3 and C_6D_6

While the assignment above was demonstrated on a 5,5-pyrrolizidine system assuming a 5-*exo*-cyclization, the starting imine could have also formed a 5,6-indolizidine via a 6-*endo*-mode cyclization after the

⁵ The coupling constants that were solved with the aid of 1D TOCSY are denoted with an asterisk in the experimental section.

bromination. We considered this possibility and in the dibromo compound alone, the assignments would not have necessarily led to a conclusive decision. Consider both possible structures, **45** and **47**, focusing in particular on C13-15 (Figure 13). In both structures, one would expect the hydrogens to have similar coupling constants and possibly shifts within the ^1H NMR. In general, a hydrogen adjacent to a bromine might be expected to be further downfield (3-3.5 ppm) whereas that next to a nitrogen around 2.5 ppm, but in this case the nitrogen lone pair is delocalized into the adjacent C-Br bond and would shift any adjacent hydrogens downfield from 2-3 ppm.

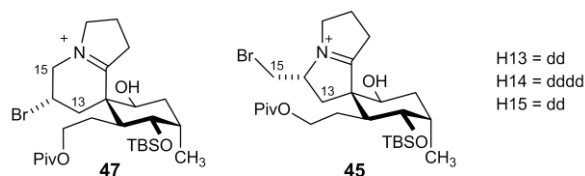
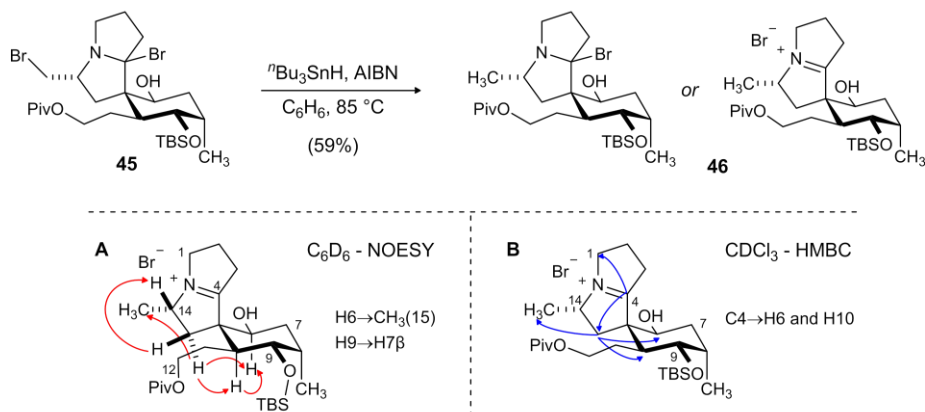


Figure 13. Two plausible dibromide structures

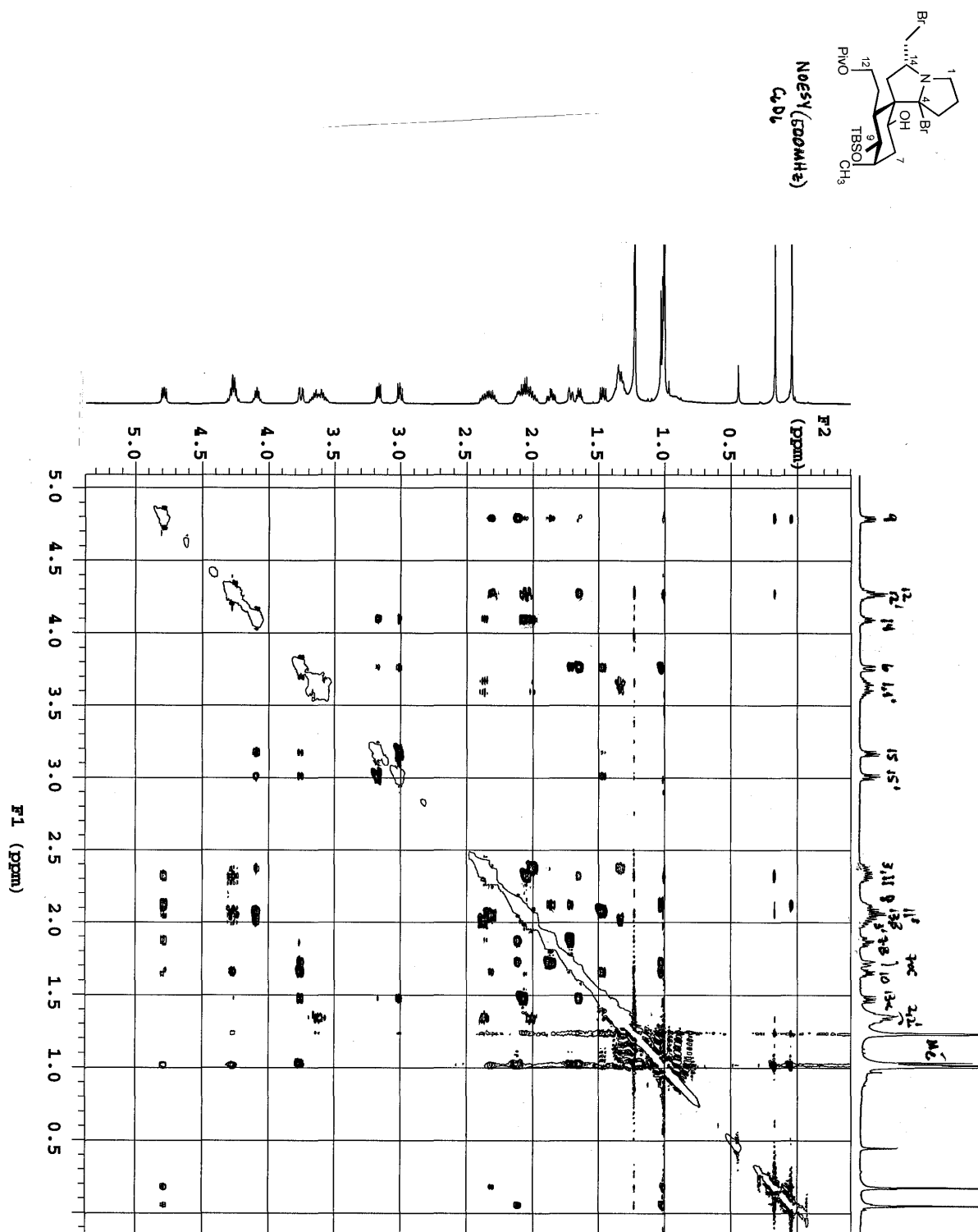
Therefore, to tell the difference between **45** and **47**, a reduction was carried out using $n\text{Bu}_3\text{SnH}$ and AIBN (Scheme 12). In the NMR of the reduced compound (**46**), two noticeable methyl singlets were observed, that from the methyl already present at C8 and the second from C15, leading to assignment of the reduced product as **46** and therefore the dibromide as **45** and not **47**. Notice that **47** would provide a new methylene instead of a methyl group and could be distinguished by ^{13}C DEPT or HSQC. Interestingly, analysis of the **46** showed that the iminium-like carbon at 179 ppm was still present! It is more likely to assume it is the iminium rather than the α -bromoamine.

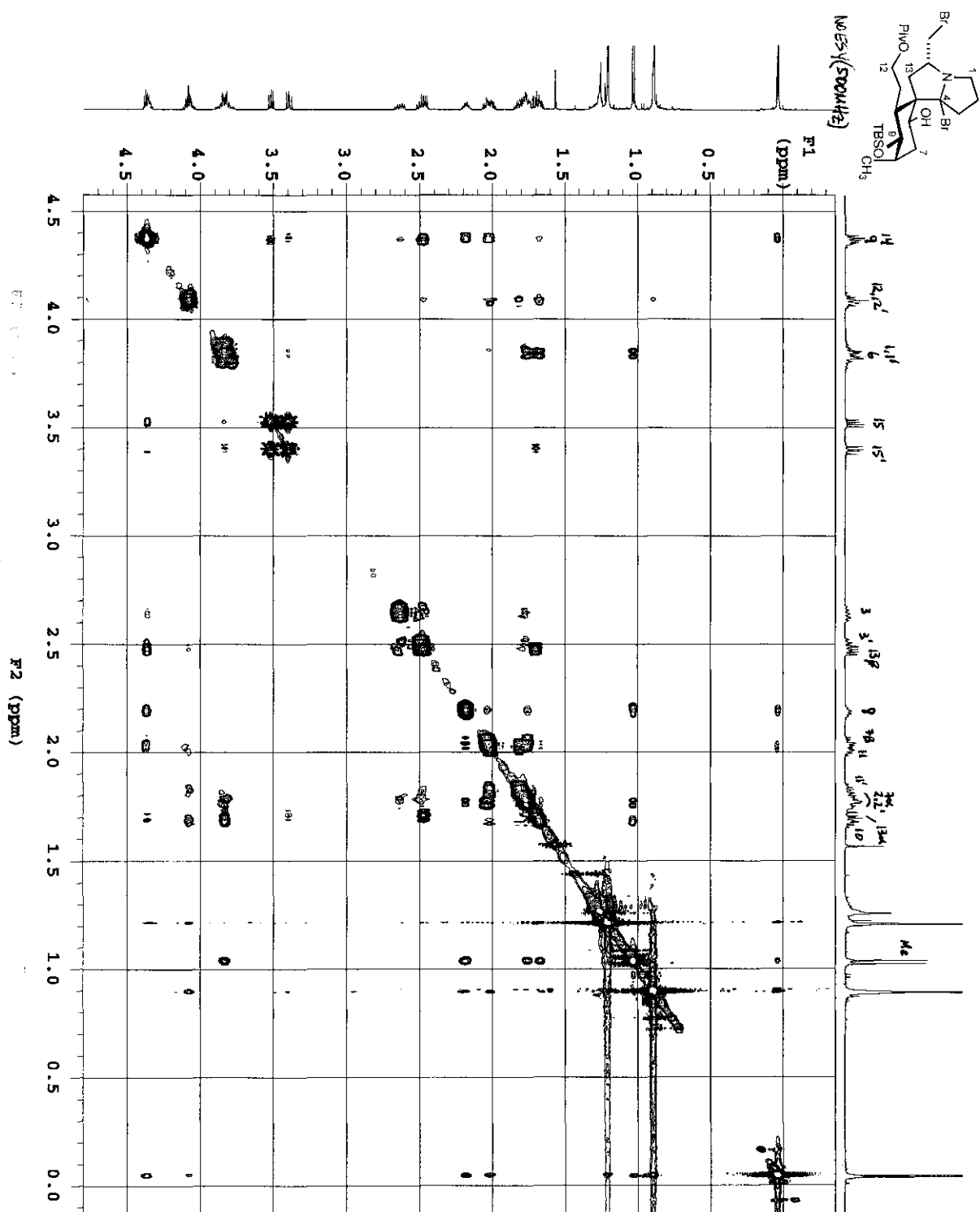
2D NMR analysis was originally performed in C_6D_6 in which the COSY and NOESY were utilized to confirm the structure. NOESY correlations from H6 to both H10 and CH_3 -8 showed that the cyclohexanol ring was in the same chair conformation as the starting dibromide (Spectrum 20). H13 α showed correlations to both H6 and H10 and from H13 α to the CH_3 -15. H13 β , which appears to be pointing more forward and away from the cyclohexanol ring only shows a correlation to H14. These NOESY assignments lead to the same configuration for the C14 stereocenter as was the case for dibromide **45**. COSY correlations from H3 were somewhat misleading due to overlap of the hydrogens and therefore an HSQC was later taken in CDCl_3 (which showed clearer separation of the hydrogens of interest, Spectrum 21). It was found that only five methines existed, that of CH-6, CH-8, CH-9, CH-10, and CH-14 and therefore C4 must be a quaternary carbon.

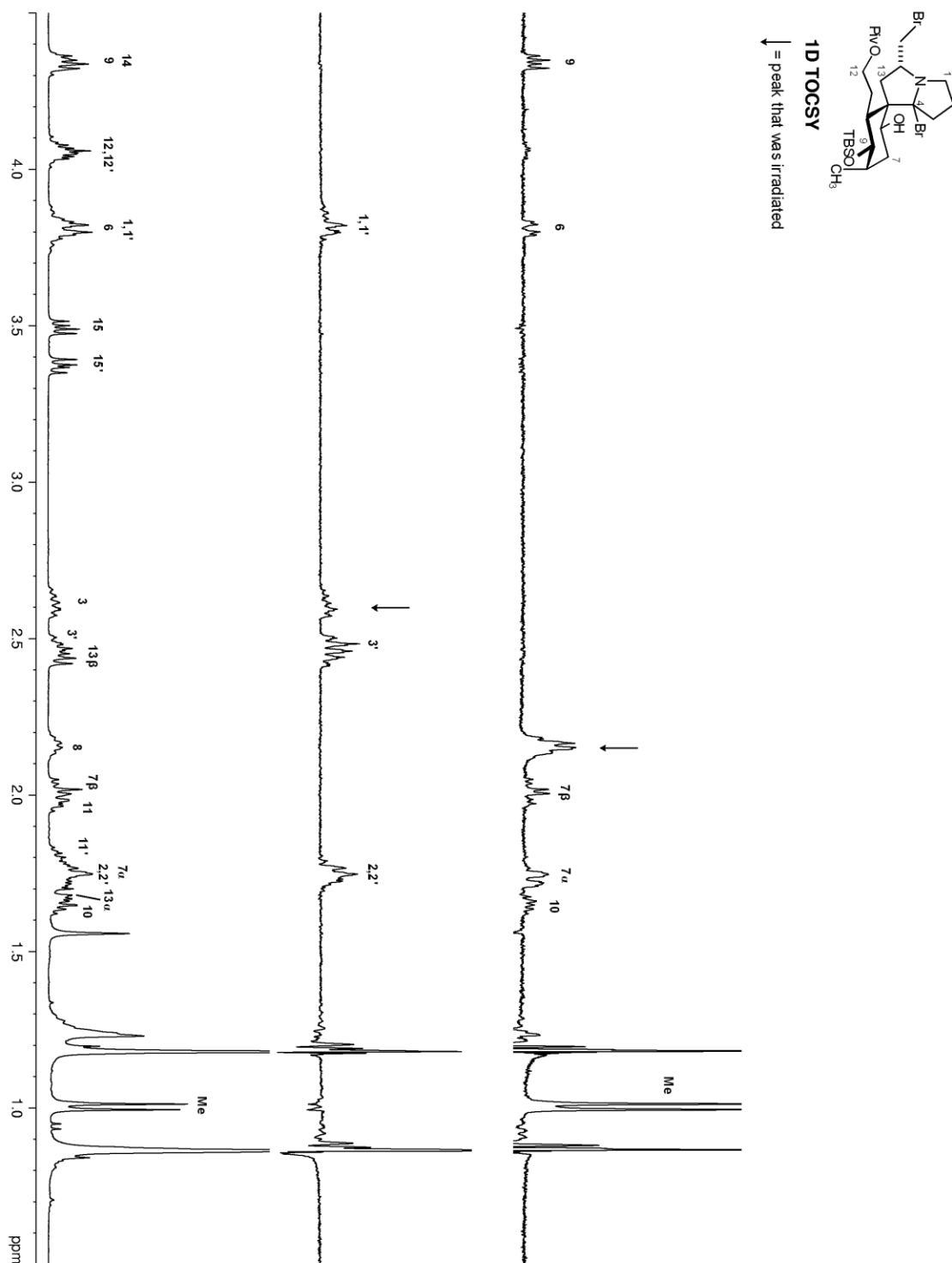
Scheme 12. Reduction of the dibromide for structure elucidation

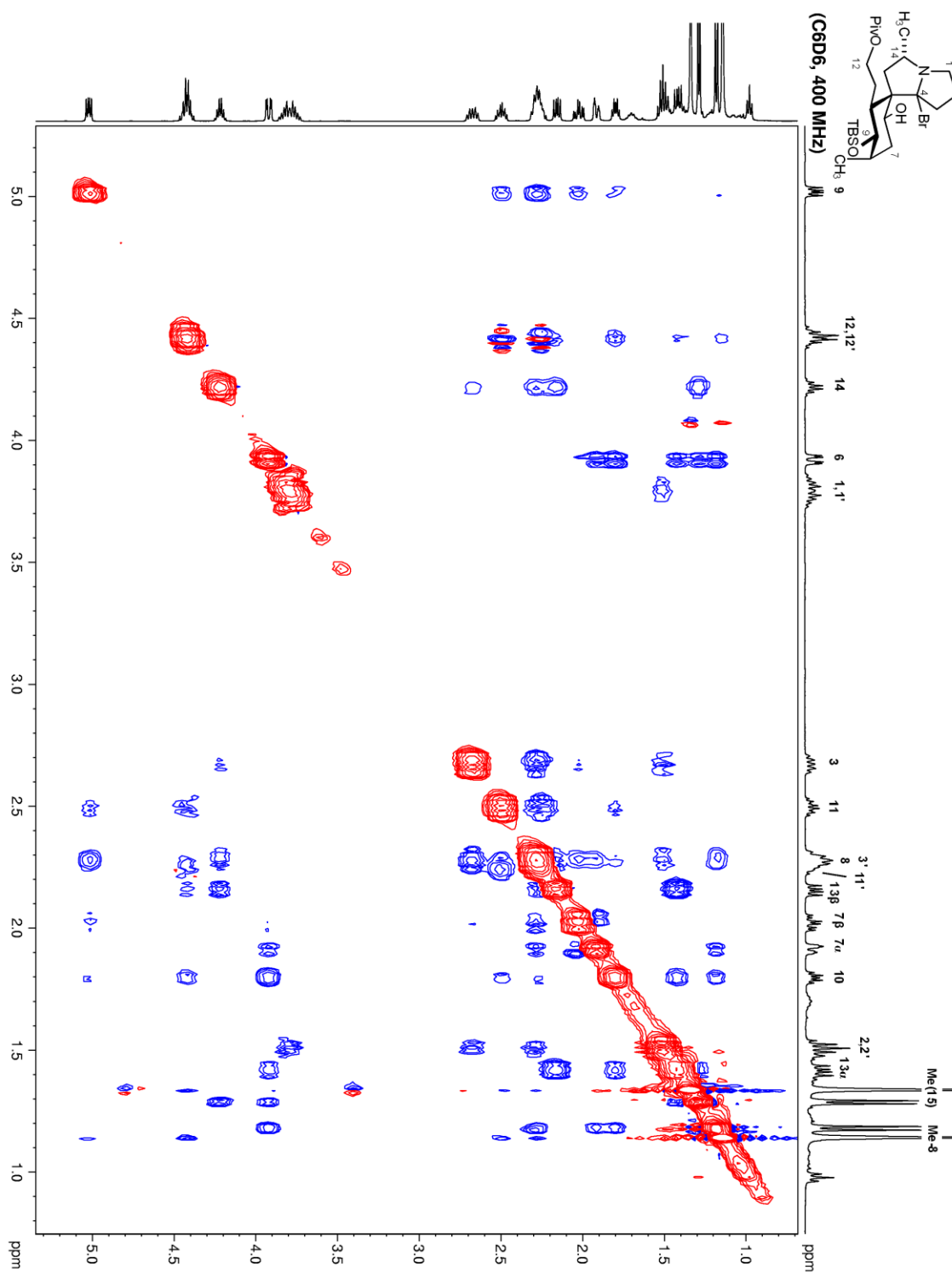


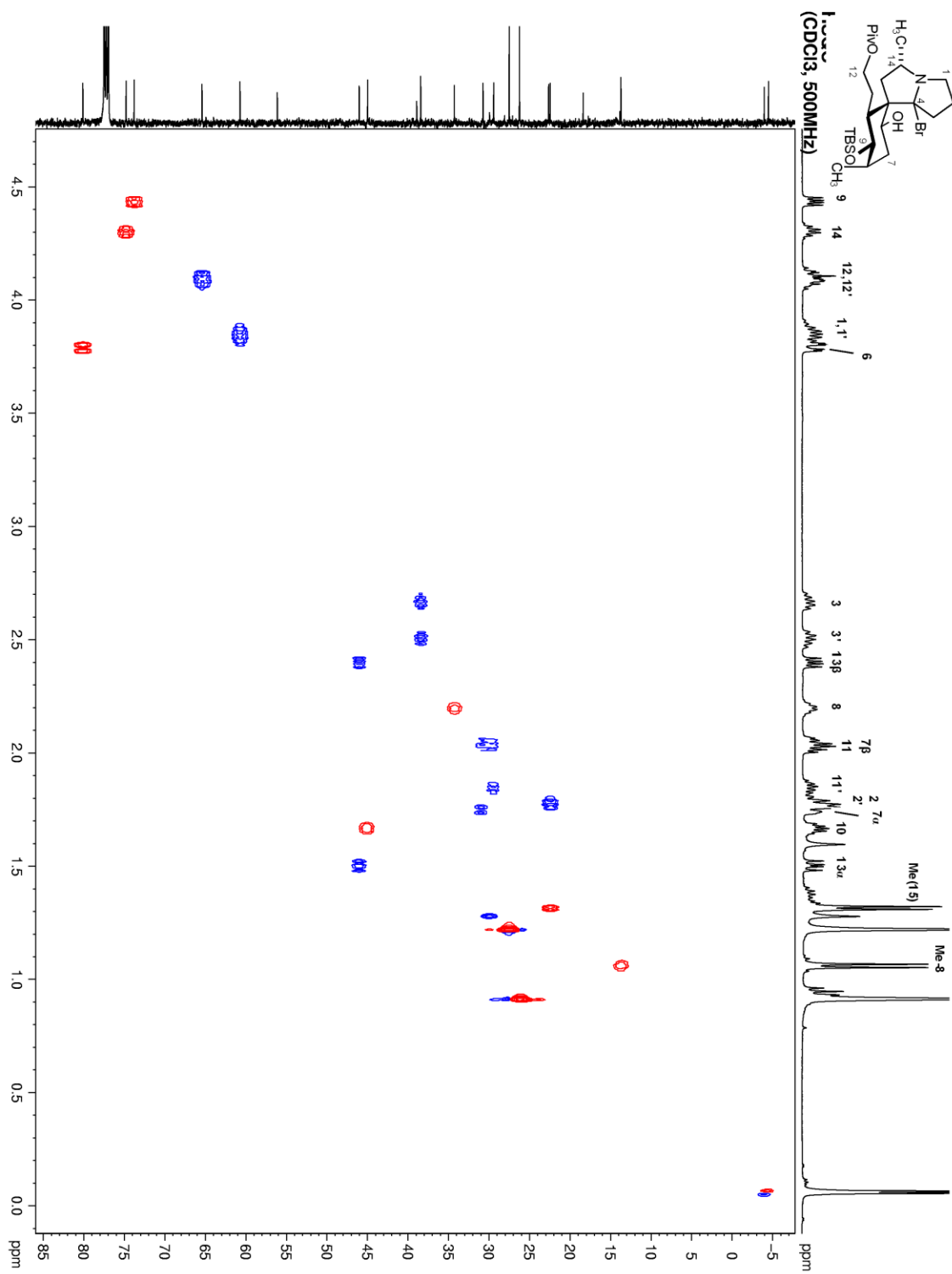
Further evidence was provided by an HMBC, which easily showed correlations from two separate peaks at 177 ppm (pivalate ester) and 179 ppm (Spectrum 22). Tracing the HMBC crosspeaks from C4 highlighted H1, H13, and both H6 and H10. A correlation from C13 to the methyl (CH₃-15) demonstrated that the 5,5-system was still intact, along with an iminium-like carbon at 179 ppm. This time, mass spectrometry results only showed the parent ion without the bromine. It seems as if the **46** would be the iminium compound, but later in our synthesis (see below for compound *epi*-**49**), we isolated another iminium salt. This compound, however, was polar and eluted on silica using MeOH in CH₂Cl₂. Compound **46** is relatively non-polar and elutes easily on silica with EtOAc in hexanes. It is unclear which structure best suits **46**, even with all of the data at hand.

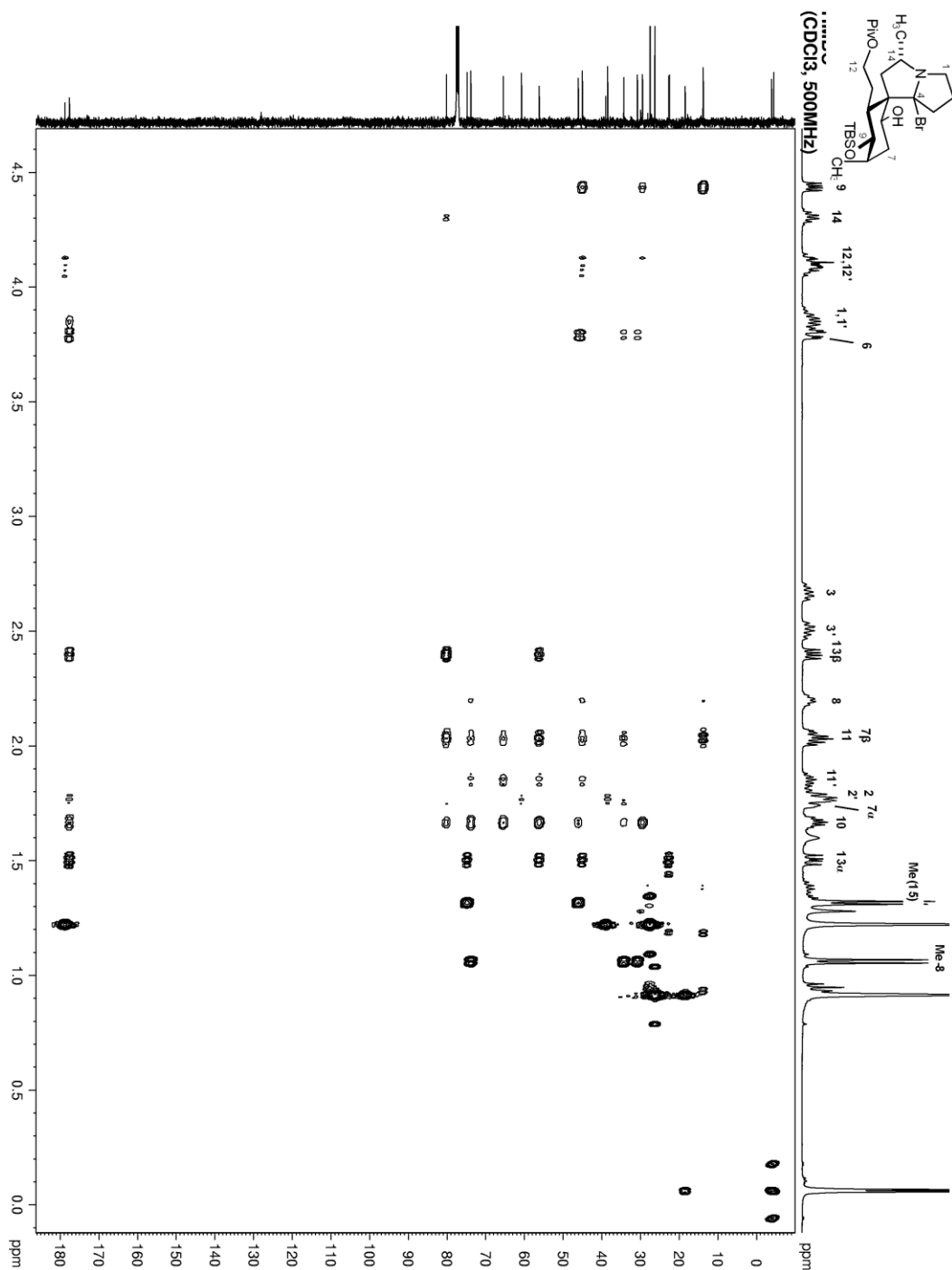
Spectrum 17. NOESY (500 MHz, C₆D₆) of Dibromide 45

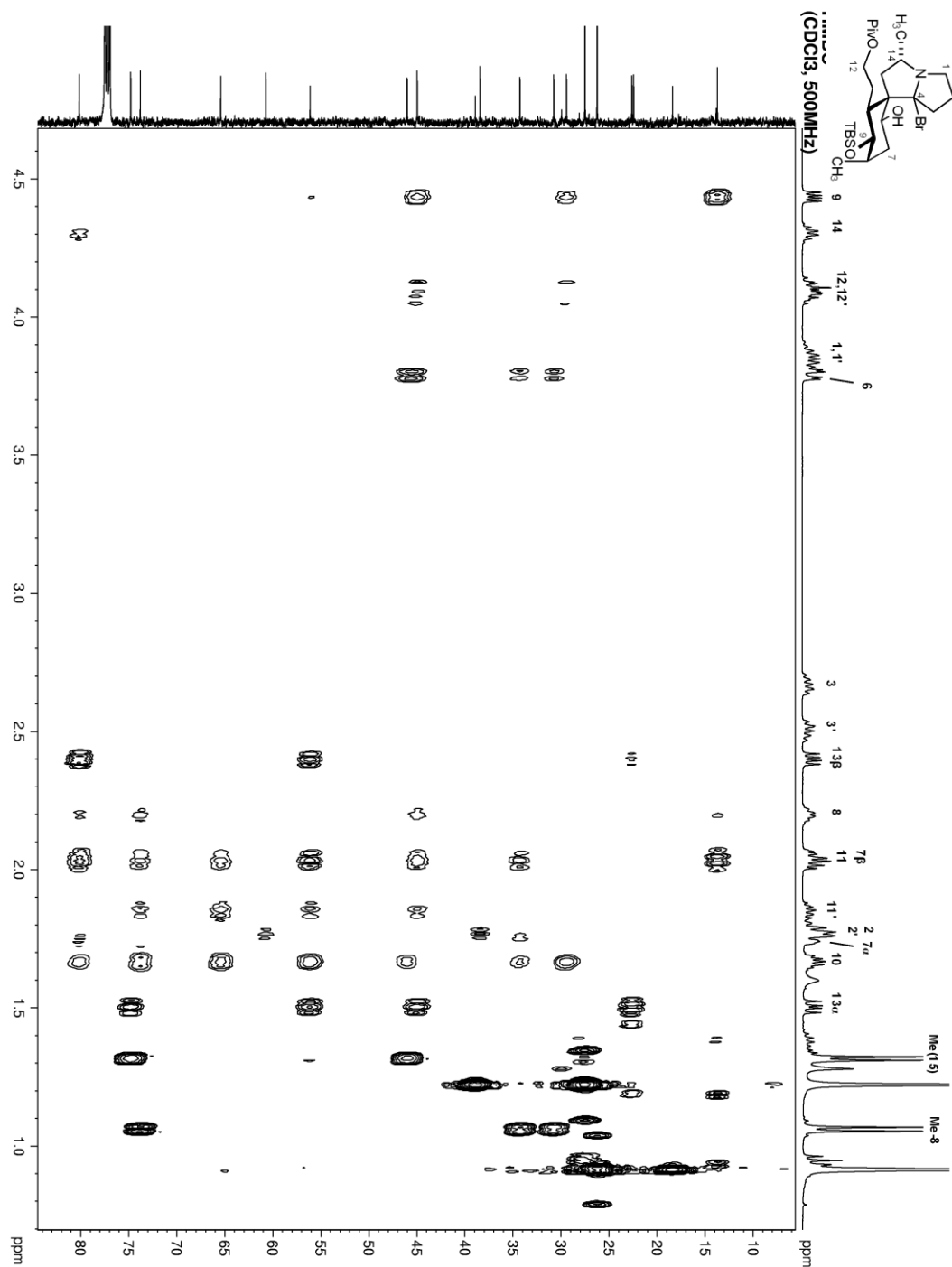
Spectrum 18. NOESY (500 MHz, CDCl₃) of Dibromide 45



Spectrum 20. NOESY (400 MHz, C₆D₆) of the Pyrrolizidine **46**

Spectrum 21. HSQC (500 MHz, CDCl₃) of the Pyrrolizidine **46**

Spectrum 22. HMBC (500 MHz, CDCl₃) of Pyrrolizidine **46**

Spectrum 23. HMBC (500 MHz, CDCl₃) - expanded section of Pyrrolizidine **46**

Ketone **31** and α -Hydroxyketone **S4**

The sample was submitted by Julie Pigza (research group of J. Johnston, Department of Chemistry, Indiana University). A colorless crystal (approximate dimensions $0.30 \times 0.15 \times 0.08 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted at 117(2) K.

Data collection

The data collection was carried out using Mo K α radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Four major sections of frames were collected with 0.30° steps in ω at different ϕ settings and a detector position of -43° in 2θ . Data to a resolution of $0.84 \text{ \AA}$ were considered in the reduction. Final cell constants were calculated from the xyz centroids of 677 strong reflections from the actual data collection after integration (SAINT). The intensity data were corrected for absorption (SADABS).⁶ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The space group C2 was determined based on intensity statistics and systematic absences. The structure was solved using SIR-92⁷ and refined with SHELXL-97.⁸ A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters with the exception of H5a which was refined with a relative isotropic displacement parameter. The displacement parameter of the O5 (at 10%) was restrained so that its Uij components approximate to isotropic behavior. The final full matrix least squares refinement converged to $R1 = 0.0373$ and $wR2 = 0.0845$ (F2, all data). The remaining electron density is minuscule and located on bonds. The Flack parameter is slightly higher than expected, which might be an artifact of the crystal quality.

Structure description

The structure was found as proposed. However, there is a 10 % impurity co-crystallized, in which the molecule has a hydroxy group bound to C5 instead of a hydrogen atom.

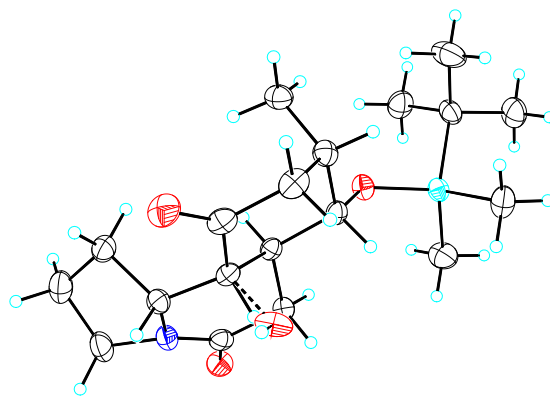


Mounted specimen.

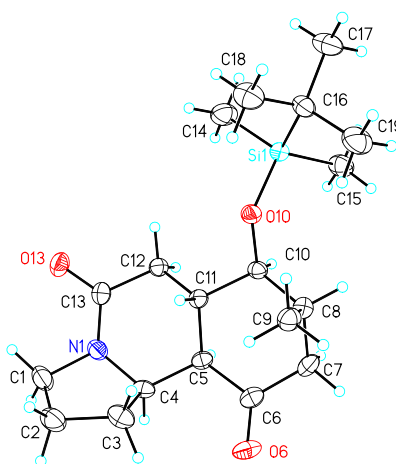
⁶ An empirical correction for absorption anisotropy: Blessing, R. *Acta Cryst.* **1995**, A51, 33.

⁷ SIR-92: Altomare, A.; Cascarno, G.; Giacovazzo, C.; Gualardi, A. *J. Appl. Cryst.* **1993**, 26, 343.

⁸ SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.



Formula unit, disorder at C5 shown.



Formula unit, 90% of the time.

Table 2. Crystal data and structure refinement for 03242.

Empirical formula	C ₁₉ H ₃₃ N O _{3.10} Si
Formula weight	353.07
Crystal color, shape, size	colorless block, 0.30 x 0.15 x 0.08 mm ³
Temperature	117(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 24.705(9) Å α = 90°.
	b = 6.725(3) Å β = 97.458(9)°.
	c = 11.915(4) Å γ = 90°.
Volume	1962.6(13) Å ³
Z	4
Density (calculated)	1.195 Mg/m ³
Absorption coefficient	0.136 mm ⁻¹
F(000)	771

Data collection

Theta range for data collection	2.23 to 25.20°.
Index ranges	-29 ≤ h ≤ 29, -8 ≤ k ≤ 8, -14 ≤ l ≤ 13
Reflections collected	8132
Independent reflections	3440 [R(int) = 0.0411]
Observed Reflections	2986
Completeness to theta = 25.20°	99.2 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9892 and 0.9602
Solution	Direct methods
Refinement method	Full-matrix least-squares on F ²
Weighting scheme	w = [σ ² F _o ² + AP ² + BP] ⁻¹ , with P = (F _o ² + 2 F _c ²)/3, A = 0.0394, B = 0.1408
Data / restraints / parameters	3440 / 7 / 260
Goodness-of-fit on F ²	1.024
Final R indices [I > 2σ(I)]	R1 = 0.0373, wR2 = 0.0793
R indices (all data)	R1 = 0.0482, wR2 = 0.0845
Absolute structure parameter	0.26(13)
Largest diff. peak and hole	0.197 and -0.175 e.Å ⁻³

$$\text{Goodness-of-fit} = [\sum [w(F_o^2 - F_c^2)^2] / N_{\text{observns}} - N_{\text{params}}]^{1/2}, \text{ all data.}$$

$$R1 = \sum (|F_o| - |F_c|) / \sum |F_o|.$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

Table 3. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 03242. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si1	3950(1)	2594(1)	8305(1)	22(1)
N1	1385(1)	2071(3)	8269(2)	24(1)
C1	878(1)	1031(5)	7866(2)	34(1)
C2	738(1)	1734(4)	6640(2)	35(1)
C3	1147(1)	3382(4)	6465(2)	31(1)
C4	1382(1)	3975(4)	7671(2)	23(1)
C5	1934(1)	5010(4)	7833(2)	21(1)
O5	2083(6)	5970(20)	8875(13)	22(6)
C6	1973(1)	6814(4)	7075(2)	25(1)
O6	1578(1)	7549(3)	6530(1)	34(1)
C7	2539(1)	7634(4)	7108(2)	27(1)
C8	2946(1)	6010(4)	6885(2)	24(1)
C9	2821(1)	5182(4)	5691(2)	28(1)
C10	2950(1)	4436(4)	7804(2)	20(1)
O10	3332(1)	2918(3)	7633(1)	23(1)
C11	2393(1)	3474(4)	7804(2)	19(1)
C12	2368(1)	2107(3)	8811(2)	21(1)
O13	1788(1)	-603(3)	9164(1)	29(1)
C13	1823(1)	1085(4)	8770(2)	24(1)
C15	4219(1)	4940(4)	8985(2)	34(1)
C14	3919(1)	677(5)	9410(2)	37(1)
C16	4381(1)	1761(4)	7192(2)	28(1)
C17	4960(1)	1294(5)	7749(2)	38(1)
C18	4138(1)	-88(5)	6591(2)	37(1)
C19	4410(1)	3425(5)	6324(2)	45(1)

Table 4. Bond lengths [Å] and angles [°] for 03242.

Si1-O10	1.6444(15)	Si1-C14	1.852(3)
Si1-C15	1.857(3)	Si1-C16	1.890(2)
N1-C13	1.343(3)	N1-C1	1.460(3)
N1-C4	1.465(3)	C1-C2	1.532(4)
C1-H1A	0.9900	C1-H1B	0.9900
C2-C3	1.532(4)	C2-H2A	0.9900
C2-H2B	0.9900	C3-C4	1.531(3)
C3-H3A	0.9900	C3-H3B	0.9900

C4-C5	1.521(3)	C4-H4A	1.0000
C5-O5	1.406(16)	C5-C6	1.523(3)
C5-C11	1.538(3)	C5-H5A	1.0000
O5-H5O	0.8400	C6-O6	1.207(3)
C6-C7	1.497(3)	C7-C8	1.531(3)
C7-H7A	0.9900	C7-H7B	0.9900
C8-C10	1.522(3)	C8-C9	1.522(3)
C8-H8A	1.0000	C9-H9A	0.9800
C9-H9B	0.9800	C9-H9C	0.9800
C10-O10	1.424(3)	C10-C11	1.518(3)
C10-H10A	1.0000	C11-C12	1.519(3)
C11-H11A	1.0000	C12-C13	1.507(3)
C12-H12A	0.9900	C12-H12B	0.9900
O13-C13	1.236(3)	C15-H15A	0.9800
C15-H15B	0.9800	C15-H15C	0.9800
C14-H14A	0.9800	C14-H14B	0.9800
C14-H14C	0.9800	C16-C18	1.519(4)
C16-C17	1.530(3)	C16-C19	1.532(4)
C17-H17A	0.9800	C17-H17B	0.9800
C17-H17C	0.9800	C18-H18A	0.9800
C18-H18B	0.9800	C18-H18C	0.9800
C19-H19A	0.9800	C19-H19B	0.9800
C19-H19C	0.9800		

O10-Si1-C14	108.46(11)	O10-Si1-C15	110.96(11)
C14-Si1-C15	109.08(14)	O10-Si1-C16	105.64(9)
C14-Si1-C16	111.82(12)	C15-Si1-C16	110.84(12)
C13-N1-C1	121.2(2)	C13-N1-C4	126.85(19)
C1-N1-C4	108.06(19)	N1-C1-C2	104.1(2)
N1-C1-H1A	110.9	C2-C1-H1A	110.9
N1-C1-H1B	110.9	C2-C1-H1B	110.9
H1A-C1-H1B	109.0	C1-C2-C3	106.3(2)
C1-C2-H2A	110.5	C3-C2-H2A	110.5
C1-C2-H2B	110.5	C3-C2-H2B	110.5
H2A-C2-H2B	108.7	C4-C3-C2	103.76(19)
C4-C3-H3A	111.0	C2-C3-H3A	111.0
C4-C3-H3B	111.0	C2-C3-H3B	111.0
H3A-C3-H3B	109.0	N1-C4-C5	113.07(18)
N1-C4-C3	101.9(2)	C5-C4-C3	117.65(19)
N1-C4-H4A	107.9	C5-C4-H4A	107.9
C3-C4-H4A	107.9	O5-C5-C4	116.8(7)
O5-C5-C6	97.3(7)	C4-C5-C6	114.47(18)

O5-C5-C11	102.7(7)	C4-C5-C11	109.94(19)
C6-C5-C11	114.72(18)	O5-C5-H5A	11.5
C4-C5-H5A	105.6	C6-C5-H5A	105.6
C11-C5-H5A	105.6	C5-O5-H5O	109.5
O6-C6-C7	123.4(2)	O6-C6-C5	122.4(2)
C7-C6-C5	114.1(2)	C6-C7-C8	111.4(2)
C6-C7-H7A	109.4	C8-C7-H7A	109.4
C6-C7-H7B	109.4	C8-C7-H7B	109.4
H7A-C7-H7B	108.0	C10-C8-C9	113.6(2)
C10-C8-C7	108.28(19)	C9-C8-C7	111.39(19)
C10-C8-H8A	107.8	C9-C8-H8A	107.8
C7-C8-H8A	107.8	C8-C9-H9A	109.5
C8-C9-H9B	109.5	H9A-C9-H9B	109.5
C8-C9-H9C	109.5	H9A-C9-H9C	109.5
H9B-C9-H9C	109.5	O10-C10-C11	108.15(18)
O10-C10-C8	109.73(17)	C11-C10-C8	112.07(18)
O10-C10-H10A	108.9	C11-C10-H10A	108.9
C8-C10-H10A	108.9	C10-O10-Si1	128.06(14)
C10-C11-C12	112.83(18)	C10-C11-C5	112.57(19)
C12-C11-C5	106.46(17)	C10-C11-H11A	108.3
C12-C11-H11A	108.3	C5-C11-H11A	108.3
C13-C12-C11	112.26(18)	C13-C12-H12A	109.2
C11-C12-H12A	109.2	C13-C12-H12B	109.2
C11-C12-H12B	109.2	H12A-C12-H12B	107.9
O13-C13-N1	122.0(2)	O13-C13-C12	120.9(2)
N1-C13-C12	117.1(2)	Si1-C15-H15A	109.5
Si1-C15-H15B	109.5	H15A-C15-H15B	109.5
Si1-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5	Si1-C14-H14A	109.5
Si1-C14-H14B	109.5	H14A-C14-H14B	109.5
Si1-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5	C18-C16-C17	109.1(2)
C18-C16-C19	109.3(2)	C17-C16-C19	108.6(2)
C18-C16-Si1	110.46(16)	C17-C16-Si1	109.68(18)
C19-C16-Si1	109.73(18)	C16-C17-H17A	109.5
C16-C17-H17B	109.5	H17A-C17-H17B	109.5
C16-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C16-C18-H18A	109.5
C16-C18-H18B	109.5	H18A-C18-H18B	109.5
C16-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C16-C19-H19A	109.5
C16-C19-H19B	109.5	H19A-C19-H19B	109.5

C16-C19-H19C 109.5

H19A-C19-H19C

109.5

H19B-C19-H19C 109.5

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 03242. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si1	19(1)	21(1)	26(1)	1(1)	2(1)	1(1)
N1	20(1)	26(1)	28(1)	-2(1)	2(1)	-2(1)
C1	22(1)	38(2)	42(2)	-5(1)	2(1)	-6(1)
C2	27(1)	38(2)	39(2)	-8(1)	-4(1)	1(1)
C3	25(1)	42(2)	25(1)	-6(1)	0(1)	3(1)
C4	20(1)	25(1)	25(1)	-1(1)	3(1)	6(1)
C5	24(1)	21(1)	17(1)	0(1)	1(1)	3(1)
O5	30(8)	12(8)	26(9)	4(6)	11(6)	6(6)
C6	32(1)	21(1)	23(1)	-4(1)	5(1)	6(1)
O6	37(1)	32(1)	34(1)	9(1)	1(1)	13(1)
C7	37(1)	15(1)	27(1)	1(1)	0(1)	0(1)
C8	24(1)	22(1)	27(1)	1(1)	3(1)	-2(1)
C9	29(1)	28(1)	26(1)	4(1)	7(1)	2(1)
C10	19(1)	20(1)	21(1)	-3(1)	1(1)	1(1)
O10	20(1)	20(1)	29(1)	-3(1)	3(1)	2(1)
C11	21(1)	18(1)	19(1)	-2(1)	1(1)	1(1)
C12	20(1)	19(1)	24(1)	0(1)	2(1)	1(1)
O13	34(1)	24(1)	31(1)	5(1)	4(1)	-6(1)
C13	28(1)	23(1)	21(1)	-5(1)	5(1)	-3(1)
C15	28(1)	36(2)	37(2)	-6(1)	-3(1)	0(1)
C14	35(1)	39(2)	37(2)	13(1)	6(1)	7(1)
C16	20(1)	31(1)	33(1)	4(1)	5(1)	1(1)
C17	25(1)	45(2)	44(2)	-5(2)	2(1)	7(1)
C18	34(1)	42(2)	33(2)	-11(1)	3(1)	4(1)
C19	35(1)	57(2)	47(2)	16(2)	18(1)	8(1)

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 03242.

	x	y	z	U(eq)
H1A	585	1394	8323	40(8)
H1B	931	-428	7900	47(9)
H2A	360	2252	6510	34(7)

H2B	770	621	6109	62(10)
H3A	1437	2882	6038	32(6)
H3B	962	4523	6053	27(6)
H4A	1113	4867	7976	26(6)
H5A	1978	5538	8624	25
H5O	1905	7036	8889	34
H7A	2653	8237	7859	25(6)
H7B	2539	8691	6530	50(9)
H8A	3317	6626	6958	23(6)
H9A	2836	6259	5142	38(7)
H9B	2455	4593	5592	39(7)
H9C	3090	4161	5571	41(8)
H10A	3061	5070	8558	10(5)
H11A	2312	2670	7097	24(6)
H12A	2659	1089	8825	22(6)
H12B	2439	2891	9518	33(7)
H15A	3992	5340	9561	44(9)
H15B	4213	5987	8411	68(11)
H15C	4595	4732	9341	52(9)
H14A	3692	1159	9969	57(9)
H14B	4288	401	9784	69(11)
H14C	3760	-545	9060	65(11)
H17A	5183	874	7168	50(9)
H17B	4948	224	8303	34(7)
H17C	5121	2486	8131	36(7)
H18A	4364	-496	6014	63(10)
H18B	3767	202	6229	42(8)
H18C	4126	-1164	7142	31(7)
H19A	4634	2988	5749	46(8)
H19B	4574	4612	6707	82(13)
H19C	4041	3740	5960	45(8)

Table 7. Torsion angles [°] for 03242.

C13-N1-C1-C2	-128.8(2)	C4-N1-C1-C2	30.4(3)
N1-C1-C2-C3	-7.3(3)	C1-C2-C3-C4	-16.7(3)
C13-N1-C4-C5	-10.5(3)	C1-N1-C4-C5	-168.21(19)
C13-N1-C4-C3	116.7(2)	C1-N1-C4-C3	-41.0(2)
C2-C3-C4-N1	34.2(2)	C2-C3-C4-C5	158.4(2)
N1-C4-C5-O5	-76.8(8)	C3-C4-C5-O5	164.8(8)
N1-C4-C5-C6	170.48(18)	C3-C4-C5-C6	52.1(3)
N1-C4-C5-C11	39.7(2)	C3-C4-C5-C11	-78.8(3)

O5-C5-C6-O6	-112.4(7)	C4-C5-C6-O6	11.5(3)
C11-C5-C6-O6	140.0(2)	O5-C5-C6-C7	65.2(7)
C4-C5-C6-C7	-171.00(19)	C11-C5-C6-C7	-42.5(3)
O6-C6-C7-C8	-130.3(2)	C5-C6-C7-C8	52.3(3)
C6-C7-C8-C10	-60.7(2)	C6-C7-C8-C9	64.9(3)
C9-C8-C10-O10	56.7(2)	C7-C8-C10-O10	-179.01(17)
C9-C8-C10-C11	-63.4(2)	C7-C8-C10-C11	60.8(2)
C11-C10-O10-Si1	-135.62(16)	C8-C10-O10-Si1	101.9(2)
C14-Si1-O10-C10	98.7(2)	C15-Si1-O10-C10	-21.1(2)
C16-Si1-O10-C10	-141.29(18)	O10-C10-C11-C12	66.7(2)
C8-C10-C11-C12	-172.19(19)	O10-C10-C11-C5	-172.75(17)
C8-C10-C11-C5	-51.7(2)	O5-C5-C11-C10	-62.7(7)
C4-C5-C11-C10	172.32(18)	C6-C5-C11-C10	41.6(3)
O5-C5-C11-C12	61.4(7)	C4-C5-C11-C12	-63.6(2)
C6-C5-C11-C12	165.75(18)	C10-C11-C12-C13	-177.19(19)
C5-C11-C12-C13	58.9(2)	C1-N1-C13-O13	-18.1(3)
C4-N1-C13-O13	-173.1(2)	C1-N1-C13-C12	160.5(2)
C4-N1-C13-C12	5.5(3)	C11-C12-C13-O13	148.0(2)
C11-C12-C13-N1	-30.6(3)	O10-Si1-C16-C18	-56.31(19)
C14-Si1-C16-C18	61.5(2)	C15-Si1-C16-C18	-176.57(18)
O10-Si1-C16-C17	-176.54(18)	C14-Si1-C16-C17	-58.7(2)
C15-Si1-C16-C17	63.2(2)	O10-Si1-C16-C19	64.3(2)
C14-Si1-C16-C19	-177.96(19)	C15-Si1-C16-C19	-56.0(2)

Table 8. Hydrogen bonds for 03242 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O5-H5O...O13#1	0.84	1.65	2.452(16)	157.8

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z

The sample was submitted by Julie Pigza (research group of J. Johnston, Department of Chemistry & Vanderbilt Institute of Chemical Biology, Vanderbilt University). A colorless crystal (approximate dimensions $0.28 \times 0.25 \times 0.17 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a diffractometer equipped with an APEX II detector at 150(2) K.

Data collection

The data collection was carried out using Mo K α radiation (graphite monochromator) with a frame time of 5 seconds and a detector distance of 6.0 cm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 4 were collected (6 major sections of frames with 0.50° ω and ϕ scans). Data to a resolution of 0.72 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9874 strong reflections from the actual data collection after integration (SAINT).⁶ The intensity data were corrected for absorption (SADABS).⁷ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The space group P2₁2₁2₁ was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004⁹ and refined with SHELXL-97.⁸ A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0296 and wR2 = 0.0827 (F², all data). The remaining electron density is minuscule and located on bonds.

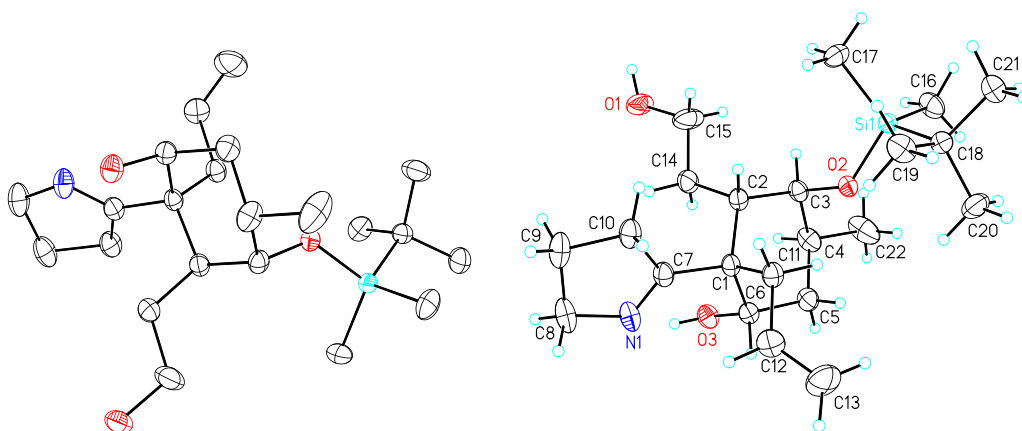
Structure description

The structure was found as proposed, the absolute configuration is established by anomalous scattering. Hydrogen bonding was found and is listed in the tables.



Bulk material.

⁹ Sir2004, A Program for Automatic Solution and Refinement of Crystal Structures: M. C. Burla, R. Caliendo, M. Carnalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Sagna. Vers. 1.0 (2004).



Formula unit.

Table 9. Crystal data and structure refinement for 08005.

Empirical formula	C ₂₂ H ₄₁ N O ₃ Si
Formula weight	395.65
Crystal color, shape, size	colorless block, 0.28 × 0.25 × 0.17 mm ³
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.3755(6) Å α = 90°. b = 10.0021(6) Å β = 90°. c = 25.2346(15) Å γ = 90°.
Volume	2366.4(3) Å ³
Z	4
Density (calculated)	1.111 Mg/m ³
Absorption coefficient	0.119 mm ⁻¹
F(000)	872

Data collection

Theta range for data collection	2.19 to 27.52°.
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -32 ≤ l ≤ 32
Reflections collected	34462
Independent reflections	5434 [R(int) = 0.0226]
Observed Reflections	5231
Completeness to theta = 27.52°	99.9 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9800 and 0.9674
Solution	Direct methods

Refinement method	Full-matrix least-squares on F2
Weighting scheme	$w = [\sigma^2 F_o^2 + AP^2 + BP]^{-1}$, with $P = (F_o^2 + 2 F_c^2)/3$, $A = 0.0551$, $B = 0.4036$
Data / restraints / parameters	5434 / 0 / 252
Goodness-of-fit on F2	0.987
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0814
R indices (all data)	R1 = 0.0310, wR2 = 0.0827
Absolute structure parameter	0.04(8)
Largest diff. peak and hole	0.283 and -0.309 e.Å ⁻³

Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/N_{\text{observns}} - N_{\text{params}}]]^{1/2}$, all data.

$R1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

Table 10. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å²x 103) for 08005. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si1	2472(1)	2113(1)	8165(1)	21(1)
O1	272(1)	3958(1)	10362(1)	41(1)
O2	1281(1)	1172(1)	8473(1)	22(1)
O3	-2157(1)	-407(1)	9653(1)	28(1)
N1	-271(1)	-1477(1)	10334(1)	32(1)
C1	462(1)	-500(1)	9479(1)	21(1)
C2	792(1)	1034(1)	9427(1)	23(1)
C3	331(1)	1616(1)	8883(1)	23(1)
C4	-1209(1)	1239(1)	8739(1)	30(1)
C5	-1404(1)	-275(1)	8751(1)	28(1)
C6	-1069(1)	-864(1)	9294(1)	23(1)
C7	702(1)	-930(1)	10053(1)	24(1)
C8	322(2)	-1814(2)	10863(1)	40(1)
C9	1693(2)	-991(2)	10911(1)	38(1)
C10	2133(2)	-786(1)	10330(1)	31(1)
C11	1546(1)	-1329(1)	9138(1)	24(1)
C12	1275(2)	-2815(1)	9147(1)	31(1)
C13	1127(2)	-3563(2)	8718(1)	49(1)
C14	144(2)	1883(1)	9881(1)	29(1)
C15	699(2)	3276(2)	9902(1)	63(1)
C16	1585(2)	3309(1)	7700(1)	35(1)
C17	3578(2)	3089(1)	8645(1)	32(1)
C18	3594(1)	859(1)	7789(1)	25(1)
C19	4497(2)	39(1)	8184(1)	33(1)
C20	2624(2)	-86(2)	7471(1)	38(1)

C21	4594(2)	1583(2)	7401(1)	35(1)
C22	-1630(2)	1822(2)	8200(1)	49(1)

Table 11. Bond lengths [Å] and angles [°] for 08005.

Si1-O2	1.6554(9)	Si1-C17	1.8701(13)
Si1-C16	1.8710(13)	Si1-C18	1.8913(13)
O1-C15	1.4041(17)	O1-H1O	0.8400
O2-C3	1.4350(14)	O3-C6	1.4398(14)
O3-H3O	0.8400	N1-C7	1.2776(17)
N1-C8	1.4862(17)	C1-C7	1.5287(15)
C1-C6	1.5526(17)	C1-C11	1.5670(16)
C1-C2	1.5712(17)	C2-C3	1.5517(15)
C2-C14	1.5518(16)	C2-H2	1.0000
C3-C4	1.5356(18)	C3-H3	1.0000
C4-C5	1.5258(19)	C4-C22	1.5308(18)
C4-H4	1.0000	C5-C6	1.5236(16)
C5-H5A	0.9900	C5-H5B	0.9900
C6-H6	1.0000	C7-C10	1.5195(18)
C8-C9	1.530(2)	C8-H8A	0.9900
C8-H8B	0.9900	C9-C10	1.5379(18)
C9-H9A	0.9900	C9-H9B	0.9900
C10-H10A	0.9900	C10-H10B	0.9900
C11-C12	1.5088(18)	C11-H11A	0.9900
C11-H11B	0.9900	C12-C13	1.324(2)
C12-H12	0.9500	C13-H13A	0.9500
C13-H13B	0.9500	C14-C15	1.488(2)
C14-H14A	0.9900	C14-H14B	0.9900
C15-H15A	0.9900	C15-H15B	0.9900
C16-H16A	0.9800	C16-H16B	0.9800
C16-H16C	0.9800	C17-H17A	0.9800
C17-H17B	0.9800	C17-H17C	0.9800
C18-C21	1.5370(18)	C18-C20	1.5377(18)
C18-C19	1.5435(18)	C19-H19A	0.9800
C19-H19B	0.9800	C19-H19C	0.9800
C20-H20A	0.9800	C20-H20B	0.9800
C20-H20C	0.9800	C21-H21A	0.9800
C21-H21B	0.9800	C21-H21C	0.9800
C22-H22A	0.9800	C22-H22B	0.9800
C22-H22C	0.9800		

O2-Si1-C17	111.49(5)	O2-Si1-C16	110.99(6)
C17-Si1-C16	108.63(7)	O2-Si1-C18	103.51(5)
C17-Si1-C18	111.29(6)	C16-Si1-C18	110.90(6)
C15-O1-H1O	109.5	C3-O2-Si1	125.55(7)
C6-O3-H3O	109.5	C7-N1-C8	109.12(12)
C7-C1-C6	110.77(10)	C7-C1-C11	106.02(9)
C6-C1-C11	108.12(9)	C7-C1-C2	108.96(9)
C6-C1-C2	112.70(10)	C11-C1-C2	110.05(9)
C3-C2-C14	109.85(10)	C3-C2-C1	112.66(10)
C14-C2-C1	113.31(9)	C3-C2-H2	106.9
C14-C2-H2	106.9	C1-C2-H2	106.9
O2-C3-C4	109.68(10)	O2-C3-C2	110.36(9)
C4-C3-C2	112.31(10)	O2-C3-H3	108.1
C4-C3-H3	108.1	C2-C3-H3	108.1
C5-C4-C22	111.42(13)	C5-C4-C3	110.55(10)
C22-C4-C3	111.09(11)	C5-C4-H4	107.9
C22-C4-H4	107.9	C3-C4-H4	107.9
C6-C5-C4	112.20(11)	C6-C5-H5A	109.2
C4-C5-H5A	109.2	C6-C5-H5B	109.2
C4-C5-H5B	109.2	H5A-C5-H5B	107.9
O3-C6-C5	107.32(10)	O3-C6-C1	113.06(9)
C5-C6-C1	111.69(10)	O3-C6-H6	108.2
C5-C6-H6	108.2	C1-C6-H6	108.2
N1-C7-C10	114.62(11)	N1-C7-C1	122.73(12)
C10-C7-C1	122.61(11)	N1-C8-C9	105.33(11)
N1-C8-H8A	110.7	C9-C8-H8A	110.7
N1-C8-H8B	110.7	C9-C8-H8B	110.7
H8A-C8-H8B	108.8	C8-C9-C10	102.78(11)
C8-C9-H9A	111.2	C10-C9-H9A	111.2
C8-C9-H9B	111.2	C10-C9-H9B	111.2
H9A-C9-H9B	109.1	C7-C10-C9	100.89(11)
C7-C10-H10A	111.6	C9-C10-H10A	111.6
C7-C10-H10B	111.6	C9-C10-H10B	111.6
H10A-C10-H10B	109.4	C12-C11-C1	113.80(11)
C12-C11-H11A	108.8	C1-C11-H11A	108.8
C12-C11-H11B	108.8	C1-C11-H11B	108.8
H11A-C11-H11B	107.7	C13-C12-C11	124.15(14)
C13-C12-H12	117.9	C11-C12-H12	117.9
C12-C13-H13A	120.0	C12-C13-H13B	120.0
H13A-C13-H13B	120.0	C15-C14-C2	113.68(11)

C15-C14-H14A	108.8	C2-C14-H14A	108.8
C15-C14-H14B	108.8	C2-C14-H14B	108.8
H14A-C14-H14B	107.7	O1-C15-C14	112.61(13)
O1-C15-H15A	109.1	C14-C15-H15A	109.1
O1-C15-H15B	109.1	C14-C15-H15B	109.1
H15A-C15-H15B	107.8	Si1-C16-H16A	109.5
Si1-C16-H16B	109.5	H16A-C16-H16B	109.5
Si1-C16-H16C	109.5	H16A-C16-H16C	109.5
H16B-C16-H16C	109.5	Si1-C17-H17A	109.5
Si1-C17-H17B	109.5	H17A-C17-H17B	109.5
Si1-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C21-C18-C20	108.54(11)
C21-C18-C19	109.09(11)	C20-C18-C19	109.55(11)
C21-C18-Si1	110.25(9)	C20-C18-Si1	109.90(9)
C19-C18-Si1	109.48(8)	C18-C19-H19A	109.5
C18-C19-H19B	109.5	H19A-C19-H19B	109.5
C18-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5	C18-C20-H20A	109.5
C18-C20-H20B	109.5	H20A-C20-H20B	109.5
C18-C20-H20C	109.5	H20A-C20-H20C	109.5
H20B-C20-H20C	109.5	C18-C21-H21A	109.5
C18-C21-H21B	109.5	H21A-C21-H21B	109.5
C18-C21-H21C	109.5	H21A-C21-H21C	109.5
H21B-C21-H21C	109.5	C4-C22-H22A	109.5
C4-C22-H22B	109.5	H22A-C22-H22B	109.5
C4-C22-H22C	109.5	H22A-C22-H22C	109.5
H22B-C22-H22C	109.5		

Table 12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 08005. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si1	24(1)	19(1)	19(1)	2(1)	-2(1)	-2(1)
O1	47(1)	36(1)	41(1)	-18(1)	15(1)	-15(1)
O2	25(1)	22(1)	19(1)	2(1)	1(1)	-1(1)
O3	24(1)	31(1)	27(1)	2(1)	5(1)	3(1)
N1	35(1)	40(1)	22(1)	8(1)	2(1)	4(1)
C1	24(1)	21(1)	17(1)	1(1)	0(1)	3(1)
C2	26(1)	22(1)	19(1)	1(1)	2(1)	3(1)
C3	25(1)	21(1)	22(1)	4(1)	1(1)	3(1)

C4	24(1)	32(1)	33(1)	10(1)	-1(1)	4(1)
C5	24(1)	34(1)	25(1)	4(1)	-5(1)	-1(1)
C6	24(1)	23(1)	22(1)	1(1)	2(1)	2(1)
C7	30(1)	22(1)	21(1)	2(1)	1(1)	6(1)
C8	46(1)	52(1)	23(1)	12(1)	2(1)	7(1)
C9	46(1)	49(1)	21(1)	2(1)	-4(1)	13(1)
C10	35(1)	36(1)	23(1)	4(1)	-5(1)	4(1)
C11	26(1)	25(1)	22(1)	0(1)	1(1)	5(1)
C12	33(1)	25(1)	36(1)	2(1)	0(1)	9(1)
C13	62(1)	30(1)	54(1)	-12(1)	0(1)	7(1)
C14	38(1)	25(1)	25(1)	-3(1)	8(1)	0(1)
C15	75(1)	58(1)	54(1)	-36(1)	38(1)	-42(1)
C16	37(1)	34(1)	33(1)	15(1)	-3(1)	1(1)
C17	37(1)	28(1)	31(1)	-7(1)	-4(1)	-5(1)
C18	26(1)	25(1)	24(1)	-2(1)	2(1)	-4(1)
C19	30(1)	29(1)	39(1)	3(1)	6(1)	5(1)
C20	40(1)	36(1)	38(1)	-14(1)	2(1)	-8(1)
C21	35(1)	40(1)	30(1)	1(1)	7(1)	-5(1)
C22	31(1)	61(1)	55(1)	34(1)	-16(1)	-6(1)

Table 13. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 08005.

	x	y	z	U(eq)
H1O	892	4529	10442	62
H3O	-1997	-714	9958	41
H2	1852	1136	9450	27
H3	392	2612	8904	27
H4	-1853	1636	9012	35
H5A	-2400	-495	8655	33
H5B	-770	-688	8483	33
H6	-1137	-1860	9268	27
H8A	533	-2781	10888	48
H8B	-360	-1571	11147	48
H9A	2435	-1486	11110	46
H9B	1511	-126	11089	46
H10A	2551	111	10272	37
H10B	2818	-1477	10212	37
H11A	1501	-1012	8767	29
H11B	2522	-1156	9271	29
H12	1206	-3242	9483	37

H13A	1190	-3166	8376	59
H13B	958	-4495	8751	59
H14A	-905	1913	9837	35
H14B	349	1438	10223	35
H15A	1754	3254	9887	75
H15B	355	3772	9587	75
H16A	907	3865	7897	52
H16B	1075	2807	7425	52
H16C	2307	3880	7534	52
H17A	2974	3742	8828	48
H17B	4338	3558	8454	48
H17C	4002	2479	8905	48
H19A	5111	-581	7988	49
H19B	3864	-468	8419	49
H19C	5088	645	8395	49
H20A	3212	-722	7272	57
H20B	2043	437	7223	57
H20C	1998	-574	7714	57
H21A	5216	929	7227	52
H21B	5177	2232	7595	52
H21C	4026	2051	7133	52
H22A	-2640	1637	8132	73
H22B	-1048	1411	7921	73
H22C	-1472	2790	8202	73

Table 14. Torsion angles [°] for 08005.

C17-Si1-O2-C3	48.91(10)	C16-Si1-O2-C3	-72.33(10)
C18-Si1-O2-C3	168.65(9)	C7-C1-C2-C3	-170.07(10)
C6-C1-C2-C3	-46.69(13)	C11-C1-C2-C3	74.08(12)
C7-C1-C2-C14	-44.58(14)	C6-C1-C2-C14	78.81(12)
C11-C1-C2-C14	-160.42(10)	Si1-O2-C3-C4	127.52(9)
Si1-O2-C3-C2	-108.23(10)	C14-C2-C3-O2	159.72(10)
C1-C2-C3-O2	-72.93(12)	C14-C2-C3-C4	-77.56(12)
C1-C2-C3-C4	49.79(13)	O2-C3-C4-C5	67.58(13)
C2-C3-C4-C5	-55.52(13)	O2-C3-C4-C22	-56.66(15)
C2-C3-C4-C22	-179.76(12)	C22-C4-C5-C6	-176.79(11)
C3-C4-C5-C6	59.16(14)	C4-C5-C6-O3	68.10(13)
C4-C5-C6-C1	-56.35(14)	C7-C1-C6-O3	50.84(13)
C11-C1-C6-O3	166.61(9)	C2-C1-C6-O3	-71.53(12)
C7-C1-C6-C5	172.02(10)	C11-C1-C6-C5	-72.22(12)
C2-C1-C6-C5	49.65(12)	C8-N1-C7-C10	0.03(16)

C8-N1-C7-C1	177.94(12)	C6-C1-C7-N1	-1.84(16)
C11-C1-C7-N1	-118.91(13)	C2-C1-C7-N1	122.68(13)
C6-C1-C7-C10	175.90(11)	C11-C1-C7-C10	58.84(14)
C2-C1-C7-C10	-59.57(14)	C7-N1-C8-C9	16.84(16)
N1-C8-C9-C10	-25.89(15)	N1-C7-C10-C9	-16.50(15)
C1-C7-C10-C9	165.58(11)	C8-C9-C10-C7	24.59(14)
C7-C1-C11-C12	64.53(13)	C6-C1-C11-C12	-54.30(13)
C2-C1-C11-C12	-177.78(10)	C1-C11-C12-C13	126.71(16)
C3-C2-C14-C15	-65.37(18)	C1-C2-C14-C15	167.64(15)
C2-C14-C15-O1	-170.66(15)	O2-Si1-C18-C21	170.00(9)
C17-Si1-C18-C21	-70.14(10)	C16-Si1-C18-C21	50.91(11)
O2-Si1-C18-C20	50.39(10)	C17-Si1-C18-C20	170.25(9)
C16-Si1-C18-C20	-68.70(11)	O2-Si1-C18-C19	-69.99(9)
C17-Si1-C18-C19	49.88(10)	C16-Si1-C18-C19	170.93(9)

Table 15. Hydrogen bonds for 08005 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O1-H1O...O3#1	0.84	2.04	2.8126(14)	152.0
O3-H3O...N1	0.84	2.03	2.6864(15)	135.1

Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, -y+1/2, -z+2$

The sample was submitted by Julie Pigza (research group of J. Johnston, Department of Chemistry & Vanderbilt Institute of Chemical Biology, Vanderbilt University). A colorless crystal (approximate dimensions $0.20 \times 0.10 \times 0.02 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a diffractometer equipped with a detector at 150(2) K.

Data collection

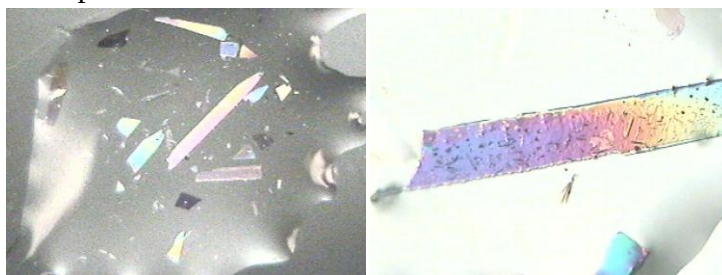
The data collection was carried out using Mo K α radiation (graphite monochromator) with a frame time of 40 seconds and a detector distance of 6.0 cm. A collection strategy was calculated and complete data to a resolution of 0.84 Å with a redundancy of 4 were collected. Seven major sections of frames were collected with 0.50° ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 8729 strong reflections from the actual data collection after integration (SAINT).⁶ The intensity data were corrected for absorption (SADABS).⁶ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

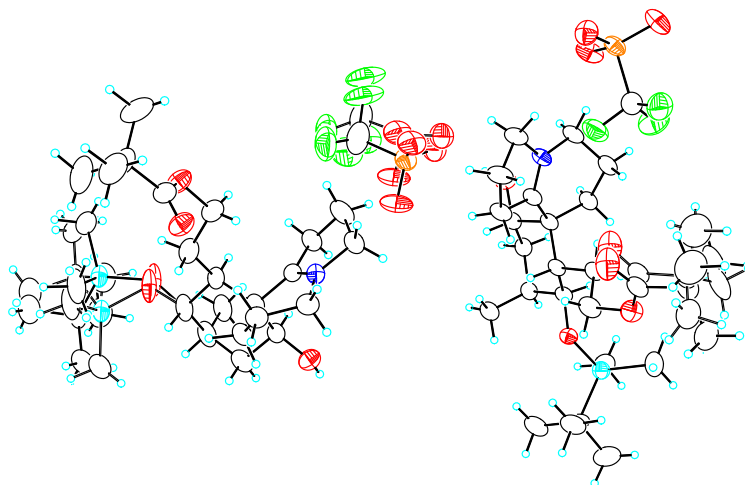
The space group P1 was determined based on intensity statistics and the lack of systematic absences. The structure was solved using SIR-2004⁹ and refined with SHELXL-97.⁸ A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Several side chains and one counterion are disordered over two sites and were refined with a set of restraints and constraints. The final full matrix least squares refinement converged to $R1 = 0.0424$ and $wR2 = 0.1203$ (F^2 , all data). The remaining electron density is located near the disordered triflate.

Structure description

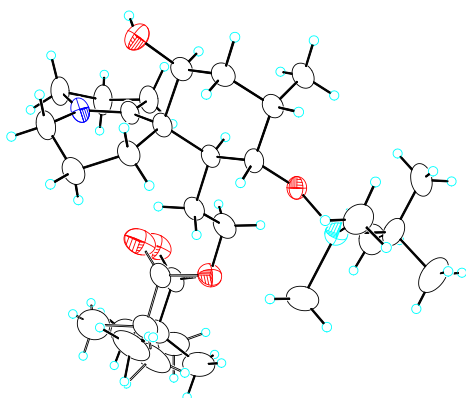
The structure was found as proposed with two formula units in the asymmetric unit. The absolute structure was established by anomalous dispersion.



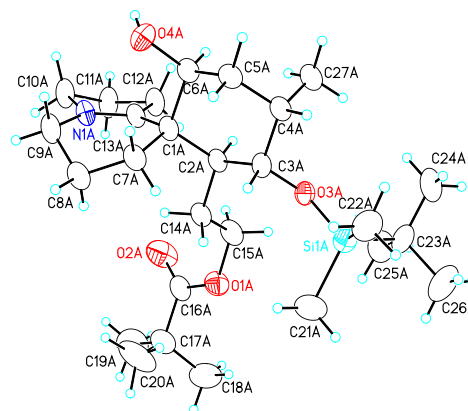
Bulk material.



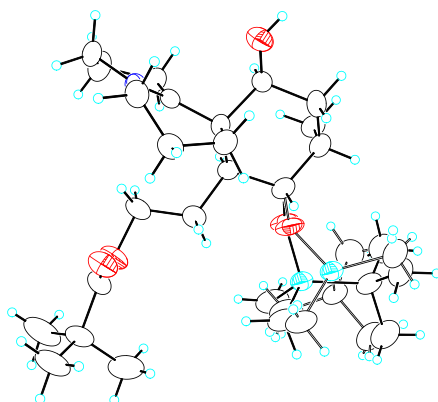
Formula unit.



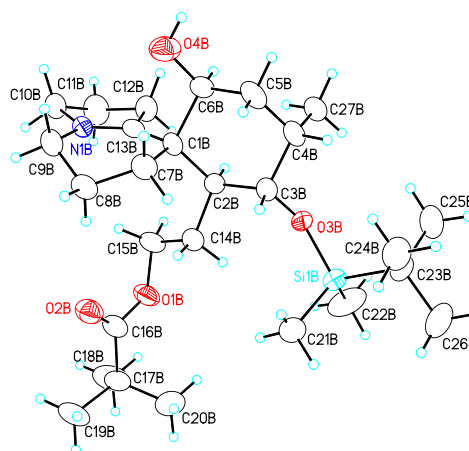
Molecule A.



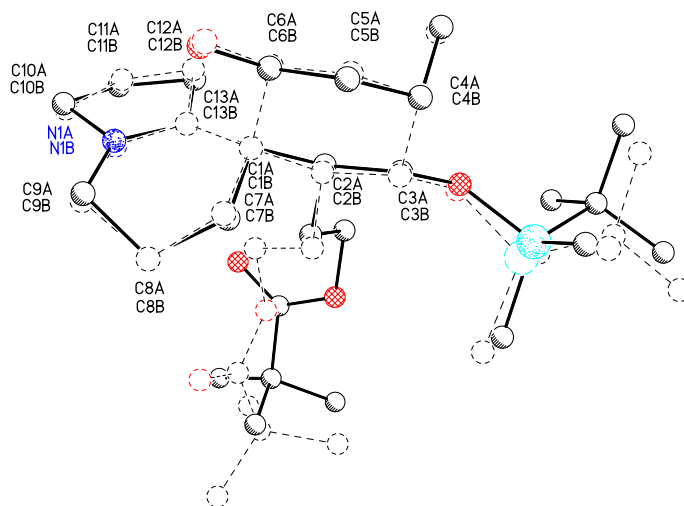
Molecule A, disorder omitted.



Molecule B.



Molecule B, disorder omitted.



LSQ fit of both molecules, disorder and hydrogen atoms omitted, only major site shown; data in Table 24.

Table 16. Crystal data and structure refinement for 07123.

Empirical formula	C ₂₈ H ₅₀ F ₃ N O ₇ S Si	
Formula weight	629.84	
Crystal color, shape, size	colorless plate, 0.20 × 0.10 × 0.02 mm ³	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P1	
Unit cell dimensions	a = 7.8828(4) Å	α = 105.055(1)°.
	b = 10.6926(5) Å	β = 92.644(1)°.
	c = 20.2725(9) Å	γ = 94.146(1)°.
Volume	1642.01(13) Å ³	
Z	2	
Density (calculated)	1.274 Mg/m ³	
Absorption coefficient	0.194 mm ⁻¹	
F(000)	676	

Data collection

Theta range for data collection	1.04 to 25.01°.
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 11, -24 ≤ l ≤ 24
Reflections collected	20883
Independent reflections	9868 [R(int) = 0.0242]
Observed Reflections	8419
Completeness to theta = 25.01°	99.8 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9961 and 0.9621

Solution	Direct methods
Refinement method	Full-matrix least-squares on F ²
Weighting scheme	$w = [\sigma^2 F_o^2 + AP^2 + BP]^{-1}$, with $P = (F_o^2 + 2 F_c^2)/3$, $A = 0.0764$, $B = 0.0953$
Data / restraints / parameters	9868 / 54 / 835
Goodness-of-fit on F ²	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1076
R indices (all data)	R1 = 0.0557, wR2 = 0.1203
Absolute structure parameter	0.03(7)*
Largest diff. peak and hole	0.536 and -0.413 e.Å ⁻³

Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2] / N_{\text{observns}} - N_{\text{params}}]^{1/2}$, all data.

$R1 = \sum (|F_o| - |F_c|) / \sum |F_o|$. $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

* absolute configuration is established

Table 17. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å² x 10³) for 07123. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si1A	1558(1)	10886(1)	6092(1)	35(1)
O1A	6079(3)	8222(3)	5963(1)	42(1)
O3A	2156(3)	10111(2)	5338(1)	30(1)
O4A	-35(3)	6243(2)	2944(1)	37(1)
C1A	1864(4)	6872(3)	3998(2)	28(1)
C2A	2655(4)	8094(3)	4546(2)	27(1)
C3A	1299(4)	8988(3)	4861(2)	28(1)
C4A	191(4)	9393(3)	4325(2)	30(1)
C5A	-590(4)	8165(3)	3800(2)	31(1)
C6A	771(4)	7332(3)	3450(2)	29(1)
C7A	718(4)	5923(3)	4297(2)	32(1)
C8A	1419(4)	4616(3)	4248(2)	37(1)
C9A	1893(5)	4022(3)	3521(2)	37(1)
N1A	3184(3)	4936(3)	3358(1)	30(1)
C10A	4540(4)	4500(3)	2897(2)	38(1)
C11A	5859(4)	5674(3)	3089(2)	42(1)
C12A	4789(4)	6819(3)	3376(2)	35(1)
C13A	3247(4)	6192(3)	3597(2)	28(1)
C14A	3744(4)	7700(3)	5099(2)	32(1)
C15A	5304(4)	8625(4)	5393(2)	42(1)
O2A	7658(10)	6971(8)	5271(4)	63(2)
C16A	7181(9)	7363(6)	5830(4)	33(2)

C17A	7620(10)	6847(7)	6448(4)	46(2)
C18A	8023(8)	7956(7)	7088(3)	64(2)
C19A	9209(12)	6124(9)	6312(4)	95(3)
C20A	6003(12)	6035(10)	6546(5)	94(4)
O2D	7250(40)	6520(30)	5148(12)	63(2)
C16D	6920(30)	6990(20)	5718(11)	33(2)
C17D	7590(30)	6550(20)	6332(11)	46(2)
C18D	9150(20)	7414(19)	6680(9)	64(2)
C19D	8110(30)	5180(20)	6051(11)	95(3)
C20D	6120(30)	6560(30)	6795(14)	94(4)
C21A	2204(6)	10028(5)	6739(2)	58(1)
C22A	-790(5)	11004(4)	6073(2)	49(1)
C23A	2764(5)	12546(4)	6287(2)	43(1)
C24A	2214(6)	13258(4)	5760(2)	55(1)
C25A	4691(5)	12367(4)	6248(2)	55(1)
C26A	2404(8)	13357(5)	7002(2)	77(2)
C27A	1148(4)	10345(3)	3997(2)	37(1)
O1B	10964(3)	8507(3)	-618(1)	47(1)
O2B	13409(3)	9323(3)	5(1)	48(1)
O4B	8178(4)	12695(3)	2333(1)	50(1)
C1B	9031(4)	11495(3)	1204(2)	32(1)
C2B	8532(4)	11235(4)	419(2)	35(1)
C3B	8254(5)	12502(4)	219(2)	46(1)
C4B	6935(5)	13286(4)	639(2)	45(1)
C5B	7531(5)	13594(4)	1401(2)	46(1)
C6B	7683(5)	12353(3)	1625(2)	36(1)
C7B	10839(4)	12188(4)	1425(2)	40(1)
C8B	12177(4)	11323(4)	1573(2)	39(1)
C9B	11532(4)	10555(4)	2059(2)	38(1)
N1B	9876(3)	9875(3)	1796(1)	31(1)
C10B	9269(5)	8683(4)	1985(2)	41(1)
C11B	7767(5)	8129(4)	1472(2)	54(1)
C12B	7203(5)	9319(4)	1268(2)	40(1)
C13B	8774(4)	10239(3)	1407(2)	30(1)
C14B	9848(5)	10524(4)	-45(2)	45(1)
C15B	10005(5)	9119(4)	-43(2)	43(1)
C16B	12686(5)	8732(4)	-525(2)	40(1)
C17B	13510(5)	8164(4)	-1186(2)	48(1)
C18B	12764(7)	6756(6)	-1503(3)	78(2)
C19B	15425(5)	8221(5)	-1030(2)	64(1)
C20B	13127(7)	8997(6)	-1674(3)	79(2)
O3B	7630(20)	12126(19)	-494(5)	56(1)

Si1B	8339(2)	12482(2)	-1203(1)	39(1)
C21B	10714(11)	12582(13)	-1161(11)	67(4)
C22B	7380(20)	11190(12)	-1948(7)	73(3)
C23B	7579(8)	14074(6)	-1252(3)	44(1)
C24B	8500(16)	15225(10)	-694(5)	58(2)
C25B	5675(9)	14097(9)	-1175(4)	66(2)
C26B	7930(20)	14349(12)	-1955(5)	71(4)
O3D	7840(40)	12310(30)	-489(9)	56(1)
Si1D	8639(4)	13452(3)	-850(1)	39(1)
C21D	10840(20)	13090(30)	-1090(20)	67(4)
C22D	8500(30)	15170(18)	-415(8)	58(2)
C23D	7187(12)	12952(10)	-1660(5)	44(1)
C24D	7470(40)	11554(19)	-2047(13)	73(3)
C25D	5324(14)	13018(15)	-1475(7)	66(2)
C26D	7680(40)	13870(20)	-2119(11)	71(4)
C27B	5130(5)	12641(4)	476(2)	50(1)
S1A	3165(2)	6393(1)	1544(1)	47(1)
O5A	1715(6)	5887(4)	1748(2)	72(1)
O6A	3433(5)	7780(3)	1826(2)	67(1)
O7A	4645(5)	5724(4)	1576(2)	64(1)
C28A	2805(9)	6274(8)	664(3)	81(2)
F1A	2382(7)	4969(4)	333(2)	115(2)
F2A	1506(6)	6924(4)	527(2)	99(1)
F3A	4151(6)	6666(4)	376(2)	101(1)
S1D	2714(14)	5691(14)	1274(6)	47(1)
O5D	1670(50)	5420(40)	1730(20)	72(1)
O6D	2540(40)	7100(20)	1495(16)	67(1)
O7D	4520(30)	5570(40)	1290(19)	64(1)
C28D	1990(40)	5700(30)	464(11)	81(2)
F1D	1950(60)	4410(30)	153(17)	115(2)
F2D	630(40)	6400(40)	605(18)	99(1)
F3D	3060(50)	6370(40)	180(18)	101(1)
S1B	5990(1)	1006(1)	3447(1)	35(1)
O5B	5651(4)	-27(3)	3764(2)	54(1)
O6B	4562(3)	1424(3)	3120(2)	49(1)
O7B	7480(3)	891(3)	3055(1)	47(1)
C28B	6610(5)	2400(4)	4168(2)	41(1)
F1B	7890(3)	2193(3)	4572(1)	63(1)
F2B	7123(3)	3449(2)	3963(1)	63(1)
F3B	5312(4)	2722(3)	4555(1)	77(1)

Table 18. Bond lengths [Å] and angles [°] for 07123.

Si1A-O3A	1.648(2)	Si1A-C21A	1.857(4)
Si1A-C22A	1.864(4)	Si1A-C23A	1.888(4)
O1A-C16A	1.296(8)	O1A-C15A	1.458(4)
O1A-C16D	1.50(2)	O3A-C3A	1.432(4)
O4A-C6A	1.423(4)	O4A-H4AO	0.8400
C1A-C13A	1.506(4)	C1A-C2A	1.548(5)
C1A-C7A	1.565(4)	C1A-C6A	1.573(4)
C2A-C3A	1.536(4)	C2A-C14A	1.542(4)
C2A-H2A	1.0000	C3A-C4A	1.531(4)
C3A-H3A	1.0000	C4A-C5A	1.527(5)
C4A-C27A	1.528(5)	C4A-H4A	1.0000
C5A-C6A	1.526(4)	C5A-H5A	0.9900
C5A-H5B	0.9900	C6A-H6A	1.0000
C7A-C8A	1.521(5)	C7A-H7A	0.9900
C7A-H7B	0.9900	C8A-C9A	1.520(5)
C8A-H8A	0.9900	C8A-H8B	0.9900
C9A-N1A	1.467(4)	C9A-H9A	0.9900
C9A-H9B	0.9900	N1A-C13A	1.300(4)
N1A-C10A	1.473(4)	C10A-C11A	1.526(5)
C10A-H10A	0.9900	C10A-H10B	0.9900
C11A-C12A	1.541(4)	C11A-H11A	0.9900
C11A-H11B	0.9900	C12A-C13A	1.488(4)
C12A-H12A	0.9900	C12A-H12B	0.9900
C14A-C15A	1.515(5)	C14A-H14A	0.9900
C14A-H14B	0.9900	C15A-H15A	0.9900
C15A-H15B	0.9900	O2A-C16A	1.191(7)
C16A-C17A	1.529(7)	C17A-C18A	1.517(9)
C17A-C19A	1.518(10)	C17A-C20A	1.540(9)
C18A-H18A	0.9800	C18A-H18B	0.9800
C18A-H18C	0.9800	C19A-H19A	0.9800
C19A-H19B	0.9800	C19A-H19C	0.9800
C20A-H20A	0.9800	C20A-H20B	0.9800
C20A-H20C	0.9800	O2D-C16D	1.183(16)
C16D-C17D	1.530(15)	C17D-C18D	1.509(18)
C17D-C19D	1.515(18)	C17D-C20D	1.526(17)
C18D-H18D	0.9800	C18D-H18E	0.9800
C18D-H18F	0.9800	C19D-H19D	0.9800
C19D-H19E	0.9800	C19D-H19F	0.9800
C20D-H20D	0.9800	C20D-H20E	0.9800
C20D-H20F	0.9800	C21A-H21A	0.9800

C21A-H21B	0.9800	C21A-H21C	0.9800
C22A-H22A	0.9800	C22A-H22B	0.9800
C22A-H22C	0.9800	C23A-C24A	1.529(6)
C23A-C26A	1.534(6)	C23A-C25A	1.547(6)
C24A-H24A	0.9800	C24A-H24B	0.9800
C24A-H24C	0.9800	C25A-H25A	0.9800
C25A-H25B	0.9800	C25A-H25C	0.9800
C26A-H26A	0.9800	C26A-H26B	0.9800
C26A-H26C	0.9800	C27A-H27A	0.9800
C27A-H27B	0.9800	C27A-H27C	0.9800
O1B-C16B	1.357(5)	O1B-C15B	1.455(4)
O2B-C16B	1.191(4)	O4B-C6B	1.415(5)
O4B-H4BO	0.8400	C1B-C13B	1.506(5)
C1B-C7B	1.548(5)	C1B-C2B	1.568(5)
C1B-C6B	1.587(4)	C2B-C3B	1.539(5)
C2B-C14B	1.540(5)	C2B-H2B	1.0000
C3B-O3D	1.413(14)	C3B-O3B	1.446(10)
C3B-C4B	1.533(5)	C3B-H3B	1.0000
C4B-C27B	1.518(6)	C4B-C5B	1.536(6)
C4B-H4B	1.0000	C5B-C6B	1.519(5)
C5B-H5C	0.9900	C5B-H5D	0.9900
C6B-H6B	1.0000	C7B-C8B	1.522(5)
C7B-H7C	0.9900	C7B-H7D	0.9900
C8B-C9B	1.520(5)	C8B-H8C	0.9900
C8B-H8D	0.9900	C9B-N1B	1.454(5)
C9B-H9C	0.9900	C9B-H9D	0.9900
N1B-C13B	1.294(4)	N1B-C10B	1.478(4)
C10B-C11B	1.516(6)	C10B-H10C	0.9900
C10B-H10D	0.9900	C11B-C12B	1.525(5)
C11B-H11C	0.9900	C11B-H11D	0.9900
C12B-C13B	1.493(5)	C12B-H12C	0.9900
C12B-H12D	0.9900	C14B-C15B	1.518(5)
C14B-H14C	0.9900	C14B-H14D	0.9900
C15B-H15C	0.9900	C15B-H15D	0.9900
C16B-C17B	1.516(5)	C17B-C19B	1.522(6)
C17B-C20B	1.528(6)	C17B-C18B	1.537(7)
C18B-H18G	0.9800	C18B-H18H	0.9800
C18B-H18I	0.9800	C19B-H19G	0.9800
C19B-H19H	0.9800	C19B-H19I	0.9800
C20B-H20G	0.9800	C20B-H20H	0.9800
C20B-H20I	0.9800	O3B-Si1B	1.689(8)
Si1B-C22B	1.849(15)	Si1B-C21B	1.864(9)

Si1B-C23B	1.869(6)	C21B-H21D	0.9800
C21B-H21E	0.9800	C21B-H21F	0.9800
C22B-H22D	0.9800	C22B-H22E	0.9800
C22B-H22F	0.9800	C23B-C25B	1.518(9)
C23B-C24B	1.547(13)	C23B-C26B	1.561(9)
C24B-H24D	0.9800	C24B-H24E	0.9800
C24B-H24F	0.9800	C25B-H25D	0.9800
C25B-H25E	0.9800	C25B-H25F	0.9800
C26B-H26D	0.9800	C26B-H26E	0.9800
C26B-H26F	0.9800	O3D-Si1D	1.680(15)
Si1D-C22D	1.834(18)	Si1D-C21D	1.865(14)
Si1D-C23D	1.891(9)	C21D-H21G	0.9800
C21D-H21H	0.9800	C21D-H21I	0.9800
C22D-H22G	0.9800	C22D-H22H	0.9800
C22D-H22I	0.9800	C23D-C25D	1.535(13)
C23D-C24D	1.53(2)	C23D-C26D	1.558(14)
C24D-H24G	0.9800	C24D-H24H	0.9800
C24D-H24I	0.9800	C25D-H25G	0.9800
C25D-H25H	0.9800	C25D-H25I	0.9800
C26D-H26G	0.9800	C26D-H26H	0.9800
C26D-H26I	0.9800	C27B-H27D	0.9800
C27B-H27E	0.9800	C27B-H27F	0.9800
S1A-O5A	1.357(4)	S1A-O7A	1.419(3)
S1A-O6A	1.441(4)	S1A-C28A	1.763(6)
C28A-F3A	1.327(8)	C28A-F2A	1.336(6)
C28A-F1A	1.391(9)	S1D-O5D	1.332(17)
S1D-O7D	1.441(17)	S1D-O6D	1.471(17)
S1D-C28D	1.717(18)	C28D-F3D	1.31(2)
C28D-F2D	1.345(19)	C28D-F1D	1.36(2)
S1B-O5B	1.432(3)	S1B-O6B	1.436(3)
S1B-O7B	1.442(3)	S1B-C28B	1.816(4)
C28B-F3B	1.329(4)	C28B-F2B	1.336(4)
C28B-F1B	1.337(4)		

O3A-Si1A-C21A	109.44(17)	O3A-Si1A-C22A	111.41(16)
C21A-Si1A-C22A	109.9(2)	O3A-Si1A-C23A	104.56(14)
C21A-Si1A-C23A	110.1(2)	C22A-Si1A-C23A	111.35(19)
C16A-O1A-C15A	118.1(4)	C16A-O1A-C16D	15.9(10)
C15A-O1A-C16D	111.4(8)	C3A-O3A-Si1A	127.70(19)
C6A-O4A-H4AO	109.5	C13A-C1A-C2A	109.8(3)
C13A-C1A-C7A	111.7(3)	C2A-C1A-C7A	113.5(3)

C13A-C1A-C6A	103.7(2)	C2A-C1A-C6A	108.2(2)
C7A-C1A-C6A	109.4(3)	C3A-C2A-C14A	111.7(3)
C3A-C2A-C1A	112.1(2)	C14A-C2A-C1A	110.5(2)
C3A-C2A-H2A	107.4	C14A-C2A-H2A	107.4
C1A-C2A-H2A	107.4	O3A-C3A-C4A	110.4(2)
O3A-C3A-C2A	107.9(2)	C4A-C3A-C2A	113.0(3)
O3A-C3A-H3A	108.5	C4A-C3A-H3A	108.5
C2A-C3A-H3A	108.5	C5A-C4A-C27A	112.8(3)
C5A-C4A-C3A	108.4(3)	C27A-C4A-C3A	113.1(3)
C5A-C4A-H4A	107.4	C27A-C4A-H4A	107.4
C3A-C4A-H4A	107.4	C6A-C5A-C4A	111.9(3)
C6A-C5A-H5A	109.2	C4A-C5A-H5A	109.2
C6A-C5A-H5B	109.2	C4A-C5A-H5B	109.2
H5A-C5A-H5B	107.9	O4A-C6A-C5A	109.1(2)
O4A-C6A-C1A	110.5(3)	C5A-C6A-C1A	109.7(3)
O4A-C6A-H6A	109.2	C5A-C6A-H6A	109.2
C1A-C6A-H6A	109.2	C8A-C7A-C1A	114.4(3)
C8A-C7A-H7A	108.7	C1A-C7A-H7A	108.7
C8A-C7A-H7B	108.7	C1A-C7A-H7B	108.7
H7A-C7A-H7B	107.6	C9A-C8A-C7A	110.0(3)
C9A-C8A-H8A	109.7	C7A-C8A-H8A	109.7
C9A-C8A-H8B	109.7	C7A-C8A-H8B	109.7
H8A-C8A-H8B	108.2	N1A-C9A-C8A	107.2(3)
N1A-C9A-H9A	110.3	C8A-C9A-H9A	110.3
N1A-C9A-H9B	110.3	C8A-C9A-H9B	110.3
H9A-C9A-H9B	108.5	C13A-N1A-C9A	124.2(3)
C13A-N1A-C10A	113.5(3)	C9A-N1A-C10A	122.3(3)
N1A-C10A-C11A	102.3(3)	N1A-C10A-H10A	111.3
C11A-C10A-H10A	111.3	N1A-C10A-H10B	111.3
C11A-C10A-H10B	111.3	H10A-C10A-H10B	109.2
C10A-C11A-C12A	103.4(3)	C10A-C11A-H11A	111.1
C12A-C11A-H11A	111.1	C10A-C11A-H11B	111.1
C12A-C11A-H11B	111.1	H11A-C11A-H11B	109.0
C13A-C12A-C11A	103.6(3)	C13A-C12A-H12A	111.0
C11A-C12A-H12A	111.0	C13A-C12A-H12B	111.0
C11A-C12A-H12B	111.0	H12A-C12A-H12B	109.0
N1A-C13A-C12A	110.3(3)	N1A-C13A-C1A	123.0(3)
C12A-C13A-C1A	126.6(3)	C15A-C14A-C2A	114.7(3)
C15A-C14A-H14A	108.6	C2A-C14A-H14A	108.6
C15A-C14A-H14B	108.6	C2A-C14A-H14B	108.6
H14A-C14A-H14B	107.6	O1A-C15A-C14A	108.4(3)
O1A-C15A-H15A	110.0	C14A-C15A-H15A	110.0

O1A-C15A-H15B	110.0	C14A-C15A-H15B	110.0
H15A-C15A-H15B	108.4	O2A-C16A-O1A	122.1(7)
O2A-C16A-C17A	125.7(7)	O1A-C16A-C17A	112.0(6)
C18A-C17A-C19A	107.5(6)	C18A-C17A-C16A	110.8(6)
C19A-C17A-C16A	108.3(6)	C18A-C17A-C20A	108.5(7)
C19A-C17A-C20A	116.0(8)	C16A-C17A-C20A	105.8(6)
O2D-C16D-O1A	126(2)	O2D-C16D-C17D	124(2)
O1A-C16D-C17D	109.6(15)	C18D-C17D-C19D	108.7(18)
C18D-C17D-C20D	113.6(17)	C19D-C17D-C20D	111.3(19)
C18D-C17D-C16D	110.1(16)	C19D-C17D-C16D	106.6(15)
C20D-C17D-C16D	106.4(17)	C17D-C18D-H18D	109.5
C17D-C18D-H18E	109.5	H18D-C18D-H18E	109.5
C17D-C18D-H18F	109.5	H18D-C18D-H18F	109.5
H18E-C18D-H18F	109.5	C17D-C19D-H19D	109.5
C17D-C19D-H19E	109.5	H19D-C19D-H19E	109.5
C17D-C19D-H19F	109.5	H19D-C19D-H19F	109.5
H19E-C19D-H19F	109.5	C17D-C20D-H20D	109.5
C17D-C20D-H20E	109.5	H20D-C20D-H20E	109.5
C17D-C20D-H20F	109.5	H20D-C20D-H20F	109.5
H20E-C20D-H20F	109.5	Si1A-C21A-H21A	109.5
Si1A-C21A-H21B	109.5	H21A-C21A-H21B	109.5
Si1A-C21A-H21C	109.5	H21A-C21A-H21C	109.5
H21B-C21A-H21C	109.5	Si1A-C22A-H22A	109.5
Si1A-C22A-H22B	109.5	H22A-C22A-H22B	109.5
Si1A-C22A-H22C	109.5	H22A-C22A-H22C	109.5
H22B-C22A-H22C	109.5	C24A-C23A-C26A	108.7(4)
C24A-C23A-C25A	109.0(3)	C26A-C23A-C25A	110.3(4)
C24A-C23A-Si1A	110.0(3)	C26A-C23A-Si1A	110.3(3)
C25A-C23A-Si1A	108.4(3)	C23A-C24A-H24A	109.5
C23A-C24A-H24B	109.5	H24A-C24A-H24B	109.5
C23A-C24A-H24C	109.5	H24A-C24A-H24C	109.5
H24B-C24A-H24C	109.5	C23A-C25A-H25A	109.5
C23A-C25A-H25B	109.5	H25A-C25A-H25B	109.5
C23A-C25A-H25C	109.5	H25A-C25A-H25C	109.5
H25B-C25A-H25C	109.5	C23A-C26A-H26A	109.5
C23A-C26A-H26B	109.5	H26A-C26A-H26B	109.5
C23A-C26A-H26C	109.5	H26A-C26A-H26C	109.5
H26B-C26A-H26C	109.5	C4A-C27A-H27A	109.5
C4A-C27A-H27B	109.5	H27A-C27A-H27B	109.5
C4A-C27A-H27C	109.5	H27A-C27A-H27C	109.5
H27B-C27A-H27C	109.5	C16B-O1B-C15B	116.2(3)
C6B-O4B-H4BO	109.5	C13B-C1B-C7B	112.6(3)

C13B-C1B-C2B	109.2(3)	C7B-C1B-C2B	113.8(3)
C13B-C1B-C6B	102.7(3)	C7B-C1B-C6B	108.9(3)
C2B-C1B-C6B	109.0(3)	C3B-C2B-C14B	107.9(3)
C3B-C2B-C1B	111.8(3)	C14B-C2B-C1B	113.8(3)
C3B-C2B-H2B	107.7	C14B-C2B-H2B	107.7
C1B-C2B-H2B	107.7	O3D-C3B-O3B	9.7(11)
O3D-C3B-C4B	110.4(18)	O3B-C3B-C4B	108.6(10)
O3D-C3B-C2B	113.4(15)	O3B-C3B-C2B	106.5(8)
C4B-C3B-C2B	112.7(3)	O3D-C3B-H3B	100.4
O3B-C3B-H3B	109.7	C4B-C3B-H3B	109.7
C2B-C3B-H3B	109.7	C27B-C4B-C3B	113.2(4)
C27B-C4B-C5B	113.6(3)	C3B-C4B-C5B	108.5(3)
C27B-C4B-H4B	107.0	C3B-C4B-H4B	107.0
C5B-C4B-H4B	107.0	C6B-C5B-C4B	111.0(3)
C6B-C5B-H5C	109.4	C4B-C5B-H5C	109.4
C6B-C5B-H5D	109.4	C4B-C5B-H5D	109.4
H5C-C5B-H5D	108.0	O4B-C6B-C5B	108.5(3)
O4B-C6B-C1B	110.3(3)	C5B-C6B-C1B	111.0(3)
O4B-C6B-H6B	109.0	C5B-C6B-H6B	109.0
C1B-C6B-H6B	109.0	C8B-C7B-C1B	115.1(3)
C8B-C7B-H7C	108.5	C1B-C7B-H7C	108.5
C8B-C7B-H7D	108.5	C1B-C7B-H7D	108.5
H7C-C7B-H7D	107.5	C9B-C8B-C7B	110.5(3)
C9B-C8B-H8C	109.6	C7B-C8B-H8C	109.6
C9B-C8B-H8D	109.6	C7B-C8B-H8D	109.6
H8C-C8B-H8D	108.1	N1B-C9B-C8B	109.8(3)
N1B-C9B-H9C	109.7	C8B-C9B-H9C	109.7
N1B-C9B-H9D	109.7	C8B-C9B-H9D	109.7
H9C-C9B-H9D	108.2	C13B-N1B-C9B	125.8(3)
C13B-N1B-C10B	113.1(3)	C9B-N1B-C10B	121.0(3)
N1B-C10B-C11B	103.0(3)	N1B-C10B-H10C	111.2
C11B-C10B-H10C	111.2	N1B-C10B-H10D	111.2
C11B-C10B-H10D	111.2	H10C-C10B-H10D	109.1
C10B-C11B-C12B	103.2(3)	C10B-C11B-H11C	111.1
C12B-C11B-H11C	111.1	C10B-C11B-H11D	111.1
C12B-C11B-H11D	111.1	H11C-C11B-H11D	109.1
C13B-C12B-C11B	103.9(3)	C13B-C12B-H12C	111.0
C11B-C12B-H12C	111.0	C13B-C12B-H12D	111.0
C11B-C12B-H12D	111.0	H12C-C12B-H12D	109.0
N1B-C13B-C12B	109.9(3)	N1B-C13B-C1B	122.8(3)
C12B-C13B-C1B	126.9(3)	C15B-C14B-C2B	116.0(3)
C15B-C14B-H14C	108.3	C2B-C14B-H14C	108.3

C15B-C14B-H14D	108.3	C2B-C14B-H14D	108.3
H14C-C14B-H14D	107.4	O1B-C15B-C14B	108.8(3)
O1B-C15B-H15C	109.9	C14B-C15B-H15C	109.9
O1B-C15B-H15D	109.9	C14B-C15B-H15D	109.9
H15C-C15B-H15D	108.3	O2B-C16B-O1B	123.2(3)
O2B-C16B-C17B	126.2(4)	O1B-C16B-C17B	110.6(3)
C16B-C17B-C19B	108.7(3)	C16B-C17B-C20B	107.5(3)
C19B-C17B-C20B	110.0(4)	C16B-C17B-C18B	110.0(3)
C19B-C17B-C18B	110.7(4)	C20B-C17B-C18B	109.8(4)
C17B-C18B-H18G	109.5	C17B-C18B-H18H	109.5
H18G-C18B-H18H	109.5	C17B-C18B-H18I	109.5
H18G-C18B-H18I	109.5	H18H-C18B-H18I	109.5
C17B-C19B-H19G	109.5	C17B-C19B-H19H	109.5
H19G-C19B-H19H	109.5	C17B-C19B-H19I	109.5
H19G-C19B-H19I	109.5	H19H-C19B-H19I	109.5
C17B-C20B-H20G	109.5	C17B-C20B-H20H	109.5
H20G-C20B-H20H	109.5	C17B-C20B-H20I	109.5
H20G-C20B-H20I	109.5	H20H-C20B-H20I	109.5
C3B-O3B-Si1B	133.4(8)	O3B-Si1B-C22B	107.2(6)
O3B-Si1B-C21B	109.6(7)	C22B-Si1B-C21B	112.0(9)
O3B-Si1B-C23B	108.7(9)	C22B-Si1B-C23B	109.1(5)
C21B-Si1B-C23B	110.1(4)	C25B-C23B-C24B	108.2(7)
C25B-C23B-C26B	107.3(7)	C24B-C23B-C26B	106.4(7)
C25B-C23B-Si1B	111.5(5)	C24B-C23B-Si1B	111.9(5)
C26B-C23B-Si1B	111.2(7)	C3B-O3D-Si1D	117.0(13)
O3D-Si1D-C22D	119.1(14)	O3D-Si1D-C21D	108.5(14)
C22D-Si1D-C21D	112.7(12)	O3D-Si1D-C23D	97.0(7)
C22D-Si1D-C23D	110.5(7)	C21D-Si1D-C23D	107.6(13)
Si1D-C21D-H21G	109.5	Si1D-C21D-H21H	109.5
H21G-C21D-H21H	109.5	Si1D-C21D-H21I	109.5
H21G-C21D-H21I	109.5	H21H-C21D-H21I	109.5
Si1D-C22D-H22G	109.5	Si1D-C22D-H22H	109.5
H22G-C22D-H22H	109.5	Si1D-C22D-H22I	109.5
H22G-C22D-H22I	109.5	H22H-C22D-H22I	109.5
C25D-C23D-C24D	109.6(14)	C25D-C23D-C26D	111.9(14)
C24D-C23D-C26D	108.5(14)	C25D-C23D-Si1D	109.5(7)
C24D-C23D-Si1D	108.9(13)	C26D-C23D-Si1D	108.3(11)
C23D-C24D-H24G	109.5	C23D-C24D-H24H	109.5
H24G-C24D-H24H	109.5	C23D-C24D-H24I	109.5
H24G-C24D-H24I	109.5	H24H-C24D-H24I	109.5
C23D-C25D-H25G	109.5	C23D-C25D-H25H	109.5
H25G-C25D-H25H	109.5	C23D-C25D-H25I	109.5

H25G-C25D-H25I	109.5	H25H-C25D-H25I	109.5
C23D-C26D-H26G	109.5	C23D-C26D-H26H	109.5
H26G-C26D-H26H	109.5	C23D-C26D-H26I	109.5
H26G-C26D-H26I	109.5	H26H-C26D-H26I	109.5
C4B-C27B-H27D	109.5	C4B-C27B-H27E	109.5
H27D-C27B-H27E	109.5	C4B-C27B-H27F	109.5
H27D-C27B-H27F	109.5	H27E-C27B-H27F	109.5
O5A-S1A-O7A	116.7(3)	O5A-S1A-O6A	111.9(2)
O7A-S1A-O6A	114.3(2)	O5A-S1A-C28A	106.9(3)
O7A-S1A-C28A	103.7(2)	O6A-S1A-C28A	101.4(3)
F3A-C28A-F2A	107.5(5)	F3A-C28A-F1A	107.1(5)
F2A-C28A-F1A	107.0(6)	F3A-C28A-S1A	114.2(5)
F2A-C28A-S1A	113.2(4)	F1A-C28A-S1A	107.4(4)
O5D-S1D-O7D	125(2)	O5D-S1D-O6D	93.9(19)
O7D-S1D-O6D	105(2)	O5D-S1D-C28D	122(2)
O7D-S1D-C28D	109.3(16)	O6D-S1D-C28D	88.5(14)
F3D-C28D-F2D	107(2)	F3D-C28D-F1D	111(2)
F2D-C28D-F1D	126(3)	F3D-C28D-S1D	112(2)
F2D-C28D-S1D	100.5(18)	F1D-C28D-S1D	99.1(18)
O5B-S1B-O6B	117.22(17)	O5B-S1B-O7B	114.25(16)
O6B-S1B-O7B	113.76(16)	O5B-S1B-C28B	103.20(18)
O6B-S1B-C28B	102.62(16)	O7B-S1B-C28B	103.24(17)
F3B-C28B-F2B	106.6(3)	F3B-C28B-F1B	107.5(3)
F2B-C28B-F1B	106.7(3)	F3B-C28B-S1B	111.3(3)
F2B-C28B-S1B	111.7(2)	F1B-C28B-S1B	112.7(3)

Table 19. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 07123. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si1A	34(1)	35(1)	35(1)	9(1)	9(1)	0(1)
O1A	35(1)	45(2)	47(1)	14(1)	-9(1)	6(1)
O3A	26(1)	28(1)	35(1)	7(1)	5(1)	4(1)
O4A	27(1)	39(1)	39(1)	0(1)	3(1)	-1(1)
C1A	20(2)	25(2)	42(2)	12(1)	5(1)	3(1)
C2A	20(2)	24(2)	39(2)	12(1)	3(1)	3(1)
C3A	22(2)	24(2)	38(2)	8(1)	6(1)	1(1)
C4A	25(2)	31(2)	38(2)	13(1)	7(1)	10(1)
C5A	20(2)	36(2)	39(2)	14(2)	3(1)	7(1)
C6A	19(2)	31(2)	40(2)	12(2)	3(1)	2(1)

C7A	23(2)	31(2)	45(2)	15(2)	4(1)	1(1)
C8A	29(2)	33(2)	53(2)	19(2)	6(2)	0(1)
C9A	31(2)	25(2)	57(2)	13(2)	11(2)	0(1)
N1A	22(1)	25(2)	46(2)	12(1)	5(1)	3(1)
C10A	26(2)	26(2)	59(2)	7(2)	11(2)	7(1)
C11A	27(2)	29(2)	68(2)	4(2)	12(2)	6(2)
C12A	21(2)	27(2)	56(2)	10(2)	13(2)	4(1)
C13A	19(2)	25(2)	42(2)	11(1)	1(1)	5(1)
C14A	24(2)	30(2)	43(2)	14(2)	0(1)	4(1)
C15A	31(2)	38(2)	58(2)	19(2)	-11(2)	3(2)
O2A	55(5)	86(7)	66(3)	37(4)	26(3)	38(4)
C16A	17(3)	32(5)	54(4)	17(3)	4(2)	-2(3)
C17A	42(2)	48(4)	53(4)	22(3)	-6(2)	2(3)
C18A	55(4)	83(5)	54(3)	26(3)	-12(3)	-6(3)
C19A	116(7)	93(7)	84(5)	26(5)	-15(5)	63(6)
C20A	102(5)	87(9)	106(8)	72(6)	-37(5)	-53(5)
O2D	55(5)	86(7)	66(3)	37(4)	26(3)	38(4)
C16D	17(3)	32(5)	54(4)	17(3)	4(2)	-2(3)
C17D	42(2)	48(4)	53(4)	22(3)	-6(2)	2(3)
C18D	55(4)	83(5)	54(3)	26(3)	-12(3)	-6(3)
C19D	116(7)	93(7)	84(5)	26(5)	-15(5)	63(6)
C20D	102(5)	87(9)	106(8)	72(6)	-37(5)	-53(5)
C21A	67(3)	66(3)	48(2)	28(2)	5(2)	0(2)
C22A	38(2)	59(3)	48(2)	8(2)	16(2)	6(2)
C23A	46(2)	34(2)	42(2)	-5(2)	8(2)	-2(2)
C24A	62(3)	31(2)	75(3)	16(2)	14(2)	7(2)
C25A	45(2)	43(2)	70(3)	10(2)	1(2)	-15(2)
C26A	99(4)	57(3)	60(3)	-10(2)	23(3)	-7(3)
C27A	32(2)	33(2)	49(2)	16(2)	2(2)	7(2)
O1B	35(1)	62(2)	40(1)	1(1)	8(1)	15(1)
O2B	40(2)	56(2)	42(2)	2(1)	6(1)	9(1)
O4B	60(2)	46(2)	42(1)	5(1)	14(1)	9(1)
C1B	28(2)	33(2)	42(2)	17(2)	6(1)	9(1)
C2B	33(2)	43(2)	37(2)	19(2)	10(1)	12(2)
C3B	39(2)	58(3)	56(2)	37(2)	18(2)	20(2)
C4B	33(2)	51(2)	68(2)	36(2)	19(2)	18(2)
C5B	39(2)	35(2)	70(3)	22(2)	18(2)	15(2)
C6B	37(2)	33(2)	41(2)	13(2)	14(2)	10(2)
C7B	35(2)	39(2)	51(2)	19(2)	9(2)	2(2)
C8B	30(2)	41(2)	45(2)	8(2)	5(2)	3(2)
C9B	32(2)	39(2)	44(2)	11(2)	-3(2)	7(2)
N1B	28(1)	34(2)	33(1)	13(1)	4(1)	8(1)

C10B	44(2)	36(2)	50(2)	22(2)	6(2)	12(2)
C11B	49(2)	43(2)	77(3)	29(2)	3(2)	0(2)
C12B	33(2)	41(2)	49(2)	20(2)	-1(2)	-1(2)
C13B	31(2)	30(2)	32(2)	7(1)	10(1)	8(1)
C14B	43(2)	56(3)	42(2)	21(2)	11(2)	21(2)
C15B	36(2)	49(2)	43(2)	6(2)	13(2)	12(2)
C16B	36(2)	39(2)	42(2)	4(2)	9(2)	10(2)
C17B	40(2)	66(3)	38(2)	11(2)	14(2)	14(2)
C18B	69(3)	78(4)	67(3)	-21(3)	25(3)	8(3)
C19B	39(2)	92(4)	58(3)	9(2)	18(2)	19(2)
C20B	69(3)	125(5)	60(3)	45(3)	25(3)	30(3)
O3B	41(5)	96(5)	59(2)	57(2)	28(2)	32(3)
Si1B	43(1)	46(1)	36(1)	18(1)	10(1)	9(1)
C21B	50(3)	97(13)	79(5)	60(10)	28(3)	24(5)
C22B	104(5)	69(7)	38(5)	6(5)	12(4)	-21(6)
C23B	41(3)	58(4)	43(3)	30(2)	3(2)	4(3)
C24B	65(3)	49(3)	69(7)	29(5)	8(6)	6(3)
C25B	51(4)	89(5)	70(5)	38(4)	-4(3)	25(4)
C26B	87(7)	78(11)	60(6)	42(8)	2(6)	13(7)
O3D	41(5)	96(5)	59(2)	57(2)	28(2)	32(3)
Si1D	43(1)	46(1)	36(1)	18(1)	10(1)	9(1)
C21D	50(3)	97(13)	79(5)	60(10)	28(3)	24(5)
C22D	65(3)	49(3)	69(7)	29(5)	8(6)	6(3)
C23D	41(3)	58(4)	43(3)	30(2)	3(2)	4(3)
C24D	104(5)	69(7)	38(5)	6(5)	12(4)	-21(6)
C25D	51(4)	89(5)	70(5)	38(4)	-4(3)	25(4)
C26D	87(7)	78(11)	60(6)	42(8)	2(6)	13(7)
C27B	38(2)	63(3)	66(3)	38(2)	21(2)	21(2)
S1A	46(1)	44(1)	57(1)	17(1)	12(1)	15(1)
O5A	76(2)	68(4)	72(2)	18(2)	28(2)	-2(2)
O6A	56(2)	34(2)	99(3)	-5(2)	-2(2)	13(2)
O7A	64(2)	54(2)	75(3)	16(2)	-4(2)	28(2)
C28A	83(5)	115(6)	63(3)	44(4)	14(3)	42(4)
F1A	166(4)	66(3)	86(3)	-29(2)	-37(3)	52(3)
F2A	112(3)	87(3)	101(3)	33(2)	-32(3)	33(2)
F3A	124(4)	112(3)	89(3)	54(2)	56(3)	31(3)
S1D	46(1)	44(1)	57(1)	17(1)	12(1)	15(1)
O5D	76(2)	68(4)	72(2)	18(2)	28(2)	-2(2)
O6D	56(2)	34(2)	99(3)	-5(2)	-2(2)	13(2)
O7D	64(2)	54(2)	75(3)	16(2)	-4(2)	28(2)
C28D	83(5)	115(6)	63(3)	44(4)	14(3)	42(4)
F1D	166(4)	66(3)	86(3)	-29(2)	-37(3)	52(3)

F2D	112(3)	87(3)	101(3)	33(2)	-32(3)	33(2)
F3D	124(4)	112(3)	89(3)	54(2)	56(3)	31(3)
S1B	29(1)	30(1)	51(1)	15(1)	6(1)	7(1)
O5B	50(2)	40(2)	83(2)	32(2)	12(2)	9(1)
O6B	34(1)	36(2)	75(2)	15(1)	-13(1)	4(1)
O7B	41(2)	57(2)	47(2)	16(1)	11(1)	15(1)
C28B	38(2)	45(2)	44(2)	15(2)	6(2)	11(2)
F1B	70(2)	67(2)	53(1)	18(1)	-12(1)	15(1)
F2B	78(2)	39(1)	69(2)	19(1)	-16(1)	-13(1)
F3B	68(2)	87(2)	71(2)	3(2)	33(1)	24(2)

Table 20. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 07123.

	x	y	z	U(eq)
H4AO	498	6125	2587	55
H2A	3435	8595	4313	32
H3A	543	8517	5118	33
H4A	-766	9843	4564	36
H5A	-1332	7648	4031	37
H5B	-1310	8414	3449	37
H6A	1533	7861	3224	35
H7A	573	6348	4784	39
H7B	-423	5772	4051	39
H8A	2438	4733	4569	44
H8B	550	4023	4377	44
H9A	2357	3173	3487	45
H9B	876	3884	3197	45
H10A	4116	4307	2411	45
H10B	5014	3720	2983	45
H11A	6437	5788	2683	51
H11B	6726	5584	3440	51
H12A	5416	7463	3769	41
H12B	4481	7259	3020	41
H14A	3020	7637	5477	38
H14B	4118	6826	4898	38
H15A	6129	8604	5037	50
H15B	4973	9524	5554	50
H18A	7035	8467	7178	96
H18B	9007	8515	7022	96
H18C	8286	7604	7478	96

H19A	9008	5426	5886	143
H19B	9479	5749	6693	143
H19C	10166	6729	6268	143
H20A	5829	5239	6170	141
H20B	5016	6543	6548	141
H20C	6135	5807	6983	141
H18D	9004	8312	6672	96
H18E	10159	7125	6437	96
H18F	9302	7366	7155	96
H19D	7098	4603	5836	143
H19E	8602	4871	6426	143
H19F	8948	5184	5711	143
H20D	5035	6436	6519	141
H20E	6189	7397	7142	141
H20F	6184	5857	7021	141
H21A	1625	9148	6617	88
H21B	1885	10506	7191	88
H21C	3440	9976	6749	88
H22A	-1380	10131	5977	73
H22B	-1131	11418	5715	73
H22C	-1094	11527	6518	73
H24A	2759	14148	5891	83
H24B	973	13281	5743	83
H24C	2559	12801	5308	83
H25A	5340	13221	6370	82
H25B	4914	11896	5781	82
H25C	5040	11871	6568	82
H26A	3011	14224	7092	116
H26B	2794	12928	7347	116
H26C	1176	13439	7024	116
H27A	1542	11142	4351	55
H27B	386	10556	3654	55
H27C	2132	9948	3778	55
H4BO	7452	13145	2551	75
H2B	7430	10675	316	42
H3B	9363	13048	274	55
H4B	6946	14135	517	54
H5C	8651	14109	1481	55
H5D	6706	14122	1679	55
H6B	6546	11840	1545	43
H7C	11224	12577	1058	48
H7D	10768	12908	1841	48

H8C	12447	10716	1139	47
H8D	13236	11866	1780	47
H9C	12351	9919	2107	46
H9D	11435	11152	2517	46
H10C	8907	8890	2460	49
H10D	10165	8069	1941	49
H11C	6844	7724	1683	65
H11D	8117	7474	1071	65
H12C	6806	9093	777	48
H12D	6275	9697	1546	48
H14C	9548	10549	-521	53
H14D	10979	11012	96	53
H15C	10600	9082	392	52
H15D	8858	8653	-82	52
H18G	13030	6223	-1191	117
H18H	13262	6410	-1941	117
H18I	11525	6736	-1579	117
H19G	15659	7703	-708	96
H19H	15875	9126	-828	96
H19I	15976	7871	-1455	96
H20G	11893	9044	-1727	119
H20H	13552	8606	-2122	119
H20I	13690	9874	-1488	119
H21D	11169	13198	-731	100
H21E	11125	12878	-1548	100
H21F	11096	11721	-1181	100
H22D	7737	10347	-1915	110
H22E	7764	11365	-2371	110
H22F	6136	11171	-1953	110
H24D	8054	16038	-732	87
H24E	9726	15267	-757	87
H24F	8304	15101	-241	87
H25D	5316	14937	-1209	99
H25E	5414	13968	-728	99
H25F	5065	13399	-1538	99
H26D	7538	15193	-1964	106
H26E	7319	13666	-2325	106
H26F	9157	14360	-2017	106
H21G	11590	13218	-676	100
H21H	11262	13675	-1359	100
H21I	10823	12187	-1365	100
H22G	8930	15342	64	87

H22H	7305	15371	-433	87
H22I	9181	15715	-642	87
H24G	6742	11293	-2472	110
H24H	7194	10968	-1760	110
H24I	8672	11510	-2155	110
H25G	4569	12596	-1882	99
H25H	5085	13930	-1309	99
H25I	5127	12572	-1116	99
H26G	7337	13426	-2599	106
H26H	8914	14091	-2067	106
H26I	7093	14663	-1979	106
H27D	4351	13177	765	75
H27E	5083	11780	564	75
H27F	4792	12548	-7	75

Table 21. Torsion angles [°] for 07123.

C21A-Si1A-O3A-C3A	82.0(3)	C22A-Si1A-O3A-C3A	-39.7(3)
C23A-Si1A-O3A-C3A	-160.1(2)	C13A-C1A-C2A-C3A	167.3(3)
C7A-C1A-C2A-C3A	-66.9(3)	C6A-C1A-C2A-C3A	54.7(3)
C13A-C1A-C2A-C14A	-67.5(3)	C7A-C1A-C2A-C14A	58.4(3)
C6A-C1A-C2A-C14A	180.0(2)	Si1A-O3A-C3A-C4A	95.8(3)
Si1A-O3A-C3A-C2A	-140.3(2)	C14A-C2A-C3A-O3A	57.9(3)
C1A-C2A-C3A-O3A	-177.5(2)	C14A-C2A-C3A-C4A	-179.8(3)
C1A-C2A-C3A-C4A	-55.2(3)	O3A-C3A-C4A-C5A	175.9(2)
C2A-C3A-C4A-C5A	54.9(3)	O3A-C3A-C4A-C27A	50.0(3)
C2A-C3A-C4A-C27A	-70.9(4)	C27A-C4A-C5A-C6A	67.2(3)
C3A-C4A-C5A-C6A	-58.8(3)	C4A-C5A-C6A-O4A	-177.0(3)
C4A-C5A-C6A-C1A	61.8(3)	C13A-C1A-C6A-O4A	65.4(3)
C2A-C1A-C6A-O4A	-178.0(2)	C7A-C1A-C6A-O4A	-53.9(3)
C13A-C1A-C6A-C5A	-174.3(3)	C2A-C1A-C6A-C5A	-57.7(3)
C7A-C1A-C6A-C5A	66.4(3)	C13A-C1A-C7A-C8A	11.4(4)
C2A-C1A-C7A-C8A	-113.5(3)	C6A-C1A-C7A-C8A	125.6(3)
C1A-C7A-C8A-C9A	-50.4(4)	C7A-C8A-C9A-N1A	59.6(4)
C8A-C9A-N1A-C13A	-32.4(4)	C8A-C9A-N1A-C10A	148.1(3)
C13A-N1A-C10A-C11A	20.0(4)	C9A-N1A-C10A-C11A	-160.5(3)
N1A-C10A-C11A-C12A	-25.5(4)	C10A-C11A-C12A-C13A	23.2(4)
C9A-N1A-C13A-C12A	175.4(3)	C10A-N1A-C13A-C12A	-5.0(4)
C9A-N1A-C13A-C1A	-8.2(5)	C10A-N1A-C13A-C1A	171.4(3)
C11A-C12A-C13A-N1A	-12.1(4)	C11A-C12A-C13A-C1A	171.6(3)
C2A-C1A-C13A-N1A	146.0(3)	C7A-C1A-C13A-N1A	19.2(4)

C6A-C1A-C13A-N1A	-98.6(3)	C2A-C1A-C13A-C12A	-38.2(4)
C7A-C1A-C13A-C12A	-165.0(3)	C6A-C1A-C13A-C12A	77.2(4)
C3A-C2A-C14A-C15A	-88.7(3)	C1A-C2A-C14A-C15A	145.8(3)
C16A-O1A-C15A-C14A	87.6(4)	C16D-O1A-C15A-C14A	71.6(11)
C2A-C14A-C15A-O1A	172.9(3)	C15A-O1A-C16A-O2A	5.4(8)
C16D-O1A-C16A-O2A	74(4)	C15A-O1A-C16A-C17A	-169.0(4)
C16D-O1A-C16A-C17A	-100(4)	O2A-C16A-C17A-C18A	137.6(7)
O1A-C16A-C17A-C18A	-48.2(8)	O2A-C16A-C17A-C19A	19.9(10)
O1A-C16A-C17A-C19A	-166.0(6)	O2A-C16A-C17A-C20A	-105.0(8)
O1A-C16A-C17A-C20A	69.1(7)	C16A-O1A-C16D-O2D	-104(5)
C15A-O1A-C16D-O2D	14(3)	C16A-O1A-C16D-C17D	66(4)
C15A-O1A-C16D-C17D	-175.6(12)	O2D-C16D-C17D-C18D	97(3)
O1A-C16D-C17D-C18D	-73(2)	O2D-C16D-C17D-C19D	-21(3)
O1A-C16D-C17D-C19D	169.0(18)	O2D-C16D-C17D-C20D	-139(3)
O1A-C16D-C17D-C20D	50(2)	O3A-Si1A-C23A-C24A	63.3(3)
C21A-Si1A-C23A-C24A	-179.3(3)	C22A-Si1A-C23A-C24A	-57.2(3)
O3A-Si1A-C23A-C26A	-176.8(3)	C21A-Si1A-C23A-C26A	-59.4(4)
C22A-Si1A-C23A-C26A	62.7(4)	O3A-Si1A-C23A-C25A	-55.9(3)
C21A-Si1A-C23A-C25A	61.5(3)	C22A-Si1A-C23A-C25A	-176.3(3)
C13B-C1B-C2B-C3B	163.2(3)	C7B-C1B-C2B-C3B	-70.1(4)
C6B-C1B-C2B-C3B	51.7(4)	C13B-C1B-C2B-C14B	-74.2(4)
C7B-C1B-C2B-C14B	52.5(4)	C6B-C1B-C2B-C14B	174.3(3)
C14B-C2B-C3B-O3D	52.6(15)	C1B-C2B-C3B-O3D	178.5(15)
C14B-C2B-C3B-O3B	59.9(9)	C1B-C2B-C3B-O3B	-174.2(8)
C14B-C2B-C3B-C4B	178.9(3)	C1B-C2B-C3B-C4B	-55.2(4)
O3D-C3B-C4B-C27B	58.6(9)	O3B-C3B-C4B-C27B	48.5(6)
C2B-C3B-C4B-C27B	-69.2(4)	O3D-C3B-C4B-C5B	-174.2(9)
O3B-C3B-C4B-C5B	175.6(5)	C2B-C3B-C4B-C5B	57.9(4)
C27B-C4B-C5B-C6B	66.2(4)	C3B-C4B-C5B-C6B	-60.7(4)
C4B-C5B-C6B-O4B	-178.1(3)	C4B-C5B-C6B-C1B	60.6(4)
C13B-C1B-C6B-O4B	69.1(4)	C7B-C1B-C6B-O4B	-50.5(4)
C2B-C1B-C6B-O4B	-175.2(3)	C13B-C1B-C6B-C5B	-170.6(3)
C7B-C1B-C6B-C5B	69.8(4)	C2B-C1B-C6B-C5B	-54.8(4)
C13B-C1B-C7B-C8B	20.0(4)	C2B-C1B-C7B-C8B	-105.0(3)
C6B-C1B-C7B-C8B	133.2(3)	C1B-C7B-C8B-C9B	-50.2(4)
C7B-C8B-C9B-N1B	52.5(4)	C8B-C9B-N1B-C13B	-27.7(5)
C8B-C9B-N1B-C10B	154.9(3)	C13B-N1B-C10B-C11B	16.3(4)
C9B-N1B-C10B-C11B	-166.1(3)	N1B-C10B-C11B-C12B	-24.5(4)
C10B-C11B-C12B-C13B	24.7(4)	C9B-N1B-C13B-C12B	-177.7(3)
C10B-N1B-C13B-C12B	-0.2(4)	C9B-N1B-C13B-C1B	-3.7(5)
C10B-N1B-C13B-C1B	173.8(3)	C11B-C12B-C13B-N1B	-16.0(4)
C11B-C12B-C13B-C1B	170.3(3)	C7B-C1B-C13B-N1B	8.0(4)

C2B-C1B-C13B-N1B	135.4(3)	C6B-C1B-C13B-N1B	-109.0(3)
C7B-C1B-C13B-C12B	-179.1(3)	C2B-C1B-C13B-C12B	-51.7(4)
C6B-C1B-C13B-C12B	63.9(4)	C3B-C2B-C14B-C15B	-166.6(3)
C1B-C2B-C14B-C15B	68.7(4)	C16B-O1B-C15B-C14B	81.2(4)
C2B-C14B-C15B-O1B	166.2(3)	C15B-O1B-C16B-O2B	4.7(5)
C15B-O1B-C16B-C17B	-173.8(3)	O2B-C16B-C17B-C19B	11.6(6)
O1B-C16B-C17B-C19B	-169.9(4)	O2B-C16B-C17B-C20B	-107.4(5)
O1B-C16B-C17B-C20B	71.1(5)	O2B-C16B-C17B-C18B	133.0(5)
O1B-C16B-C17B-C18B	-48.5(5)	O3D-C3B-O3B-Si1B	14(15)
C4B-C3B-O3B-Si1B	116(2)	C2B-C3B-O3B-Si1B	-122(2)
C3B-O3B-Si1B-C22B	159(2)	C3B-O3B-Si1B-C21B	37(3)
C3B-O3B-Si1B-C23B	-83(2)	O3B-Si1B-C23B-C25B	-51.0(7)
C22B-Si1B-C23B-C25B	65.6(7)	C21B-Si1B-C23B-C25B	-171.1(8)
O3B-Si1B-C23B-C24B	70.5(7)	C22B-Si1B-C23B-C24B	-172.9(6)
C21B-Si1B-C23B-C24B	-49.6(9)	O3B-Si1B-C23B-C26B	-170.6(8)
C22B-Si1B-C23B-C26B	-54.1(8)	C21B-Si1B-C23B-C26B	69.2(10)
O3B-C3B-O3D-Si1D	170(19)	C4B-C3B-O3D-Si1D	89(3)
C2B-C3B-O3D-Si1D	-144(2)	C3B-O3D-Si1D-C22D	-46(3)
C3B-O3D-Si1D-C21D	85(3)	C3B-O3D-Si1D-C23D	-164(3)
O3D-Si1D-C23D-C25D	58.8(17)	C22D-Si1D-C23D-C25D	-65.9(11)
C21D-Si1D-C23D-C25D	170.7(11)	O3D-Si1D-C23D-C24D	-61.1(19)
C22D-Si1D-C23D-C24D	174.3(12)	C21D-Si1D-C23D-C24D	50.8(14)
O3D-Si1D-C23D-C26D	-179(2)	C22D-Si1D-C23D-C26D	56.4(15)
C21D-Si1D-C23D-C26D	-67.0(16)	O5A-S1A-C28A-F3A	-176.4(5)
O7A-S1A-C28A-F3A	-52.5(6)	O6A-S1A-C28A-F3A	66.3(5)
O5A-S1A-C28A-F2A	60.1(6)	O7A-S1A-C28A-F2A	-176.0(5)
O6A-S1A-C28A-F2A	-57.2(6)	O5A-S1A-C28A-F1A	-57.8(5)
O7A-S1A-C28A-F1A	66.1(5)	O6A-S1A-C28A-F1A	-175.1(4)
O5D-S1D-C28D-F3D	160(3)	O7D-S1D-C28D-F3D	-39(3)
O6D-S1D-C28D-F3D	66(2)	O5D-S1D-C28D-F2D	47(3)
O7D-S1D-C28D-F2D	-152(3)	O6D-S1D-C28D-F2D	-47(2)
O5D-S1D-C28D-F1D	-83(3)	O7D-S1D-C28D-F1D	78(3)
O6D-S1D-C28D-F1D	-177(3)	O5B-S1B-C28B-F3B	-66.5(3)
O6B-S1B-C28B-F3B	55.8(3)	O7B-S1B-C28B-F3B	174.3(3)
O5B-S1B-C28B-F2B	174.5(3)	O6B-S1B-C28B-F2B	-63.2(3)
O7B-S1B-C28B-F2B	55.3(3)	O5B-S1B-C28B-F1B	54.4(3)
O6B-S1B-C28B-F1B	176.7(3)	O7B-S1B-C28B-F1B	-64.8(3)

Table 22. Hydrogen bonds for 07123 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O4A-H4AO...O5A	0.84	1.96	2.798(4)	178.6
O4A-H4AO...O5D	0.84	2.01	2.83(3)	167.0

Table 23. Lsq fit of molecule A and B.

ATOM	MODEL	DEVIATION
C1A	C1B	0.055
C2A	C2B	0.137
C3A	C3B	0.065
C4A	C4B	0.124
C5A	C5B	0.124
C6A	C6B	0.046
C7A	C7B	0.148
C8A	C8B	0.078
C9A	C9B	0.180
N1A	N1B	0.102
C10A	C10B	0.130
C11A	C11B	0.135
C12A	C12B	0.226
C13A	C13B	0.030

WEIGHTED R.M.S. DEVIATION = 0.1245 $\text{\AA}$

IDEALIZED CRYSTAL COORDINATES FOR MODEL ATOMS

Table 24. Lsq fit of molecule A and B.

NAME	SFAC	X	Y	Z	NEAREST ATOM	DEVIATION
O1B	4	0.59922	0.69063	0.56718	C16A	1.022
O2B	4	0.43208	0.51254	0.56863	C20A	2.113
O4B	4	-0.00706	0.63304	0.29338	O4A	0.107
C1B	1	0.18105	0.68334	0.39917	C1A	0.055
C2B	1	0.26155	0.80098	0.45849	C2A	0.137
C3B	1	0.12822	0.89485	0.48800	C3A	0.065
C4B	1	0.03413	0.94403	0.43311	C4A	0.124
C5B	1	-0.05211	0.82615	0.37845	C5A	0.124

C6B	1	0.07878	0.73716	0.34464	C6A	0.046
C7B	1	0.05990	0.58652	0.42361	C7A	0.148
C8B	1	0.13251	0.45921	0.42519	C8A	0.078
C9B	1	0.20636	0.39875	0.35741	C9A	0.180
N1B	3	0.32587	0.49350	0.34010	N1A	0.102
C10B	1	0.46480	0.45174	0.29500	C10A	0.130
C11B	1	0.58066	0.57582	0.30552	C11A	0.135
C12B	1	0.46102	0.68232	0.32869	C12A	0.226
C13B	1	0.32125	0.61837	0.35893	C13A	0.030
C14B	1	0.34939	0.76066	0.51828	C14A	0.295
C15B	1	0.51143	0.69315	0.50290	C14A	1.394
C16B	1	0.54106	0.59545	0.59570	C20A	1.242
C17B	1	0.63042	0.61302	0.66577	C20A	0.312
C18B	1	0.82408	0.63530	0.66197	C17A	0.870
C19B	1	0.58562	0.49227	0.69009	C20A	1.542
C20B	1	0.56513	0.73175	0.71419	C20A	1.625
O3B	4	0.22030	1.00480	0.53670	O3A	0.108
SI1B	6	0.20572	1.07372	0.62098	SI1A	0.507
C21B	1	0.15495	0.94476	0.66546	C21A	0.755
C22B	1	0.41217	1.16765	0.65408	C25A	1.142
C23B	1	0.03374	1.18742	0.63110	C22A	1.223
C24B	1	-0.14555	1.11385	0.61278	C22A	0.562
C25B	1	0.05647	1.28078	0.58653	C24A	1.399
C26B	1	0.03386	1.27112	0.70671	C26A	1.746
C27B	1	0.14660	1.03522	0.40404	C27A	0.260
