Investigation of intramolecular [2+2] photocycloadditions : using new cycloaddition/fragmentation strategies toward medium ring-containing natural products

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INVESTIGATION OF INTRAMOLECULAR [2+2] PHOTOCYCLOADDITIONS: USING NEW CYCLOADDITION/FRAGMENTATION STRATEGIES TOWARD MEDIUM RING-CONTAINING NATURAL PRODUCTS

A dissertation by

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STEPHANIE M. NG

Thesis Advisor: Marc L. Snapper

ABSTRACT

Intramolecular [2+2] photocycloadditions have been studied: (i) Previous studies in our group have demonstrated that there is a regiochemical dependence of intramolecular [2+2] photocycloadditions on the solvent employed. In order to understand the generality of hydrogen bonding effects of photochemical reactions of β-hydroxyl enones, we examined the photochemical outcome of enones with both acyclic and cyclic olefin tethers. (ii) An application of an intramolecular [2+2] photocycloaddition/ fragmentation strategy to form 5-8-5 ring systems has been demonstrated toward the synthesis of the natural product cycloaraneosene.

Acknowledgements

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The Snapper group has been a fun and interesting place to work, and I will remember each character that I have met over the last five years. In the last six months the Snapper group has had to go from being a fun and interesting environment with everyone having their own space to a fun and interesting environment with everyone not having any space. As stressful as it is to move and adjust to a new lab, especially with such strong individual personalities, I believe that the Snapper group has done so with a great sense of humor and perspective. As for the daily toil of lab work, I could not have survived the many long days, nights, and weekends without coffee, walks across, and lunch room conversations. I also could not have survived my time in Merkert without dear friends, past and present, as well as Snapper and non-Snapper group members. There are far too many people to list personally, but I have to give a special thanks to Jason Rodrigo and Krista Granger.

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Chapter 1

The Role of Hydrogen Bonding in [2+2] Photocycloadditions

I.1 Introduction

The [2+2] photocycloaddition is a powerful carbon-carbon bond-forming strategy that provides rapid access to four-membered rings, making this approach widely used in the synthesis of polycyclic natural products.[1] Much effort has been made in understanding the factors that control the selectivity of this cycloaddition.[2] For example, there are steric and electronic considerations that influence the outcome of the reaction and can be rationalized from a mechanistic point of view, such as their effect on transition states.[3] Other studies, however, have focused on factors such as pre-association of the reacting partners or non-bonding interactions that can control the

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[1] For reviews on the application of [2+2] in organic synthesis, see: (a) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052-1103. (b) DeKeukeleire, D.; He, S. L. *Chem. Rev.* **1993**, *93*, 359-380. (c) Lee-Ruff, E.; Mladenova, G. *Chem. Rev.* **2003**, *103*, 1449-1483.

[2] For some examples of efforts to control [2+2] photocycloadditions, see: (a) Fleck, M.; Yang, C.; Wada, T.; Inoue, Y.; Bach, T. *Chem. Commun.* **2007**, 822-824. (b) Chen, C.; Chang, V.; Cai, X.; Duesler, E.; Mariano, P. S. *J. Am. Chem. Soc.* **2001**, *123*, 6433-6434. (c) Langer, K.; Mattay, J. *J. Org. Chem.* **1995**, *60*, 7256-7266. Also, DFT calculations have been made to further understand enone-alkene cycloadditions, see: (a) Wilsey, S.; Gonazlez, L.; Robb, M. A.; Houk, K. N. *J. Am. Chem. Soc.* **2000**, *122*, 5866-5876. (b) De Proft, F.; Fias, S.; Van Alsenoy, C.; Geerlings, P. *J. Phys. Chem. A.* **2005**, *109*, 6335-6343. (c) Garcia-Exposito, E.; Bearpark, M. J.; Ortuno, R. M.; Robb, M. A.; Branchadell, V. *J. Org. Chem.* **2002**, *67*, 6070-6077.

[3] For example, studies have shown that the outcome of some photoreactions are reflected in the molecular geometry prior to intersystem crossing processes, constituting a "memory effect". These studies focus on the lifetime of biradicals to explain the outcome of the reaction. See: Griesbeck, A. G.; Mauder, H.; Stadtmuller, S. *Acc. Chem. Res.* **1994**, *27*, 70-75. Also, structural effects on triplet biradical lifetimes have been studied: Caldwel, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629-630.

photocycloaddition. These often overcome stereoelectronic biases of a system and are examples of directed photocycloadditions.

Directed [2+2] photocycloadditions involve the organization of the two reacting partners prior to the onset of the reaction, either through covalent bonding, Lewis acid or base interactions, or hydrogen bonding involving the polar functional groups on the substrates, to dictate the course of the reaction.[4] In particular, hydrogen bonding can be advantageous in photoinduced reactions because these interactions are formed independent of photoexcitation and have been shown to affect both the regio- and stereoselectivity of the cycloaddition.[5]

This chapter is intended to serve as a review on the role of hydrogen bonding in [2+2] photocycloadditions. Specifically, the Paterno-Büchi reaction (Scheme I.1, eq. 1) and the inter- and intramolecular [2+2] photocycloaddition of alkenes (eq. 2 and eq. 3) will be covered. Additionally, only processes where both reacting partners are involved in the hydrogen bond will be included.[6] Focus will be placed on the selectivity induced by the directing functionality, and, where applicable, the interaction of the hydrogen bond in the proposed transition states.

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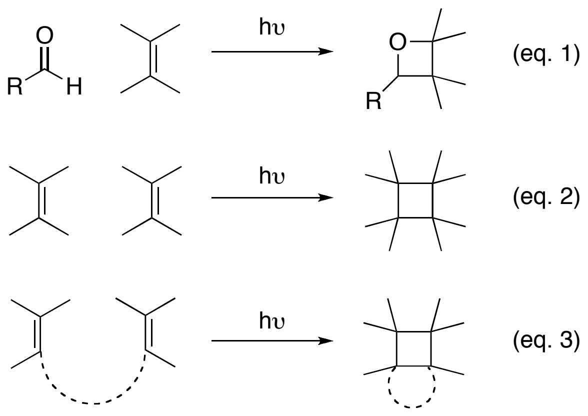
[4] For a review on directed reactions, see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307-1370.

[5] For some examples of hydrogen bond influence on photochemical cycloadditions, see: (a) Zhu, M.; Qiu, Z.; Hiel, G. P.; Sieburth, S. McN. *J. Org. Chem.* **2002**, *67*, 3487-3493. (b) Sieburth, S. M.; McGee, Jr. K. F. *Org. Lett.* **1999**, *1*, 1775-1777. (c) Rigby, J. H.; Mateo, M. E. *J. Am. Chem. Soc.* **1997**, *119*, 12655-12656.

[6] That is, neither solid-state dimerizations nor host-guest interactions, although important topics, will be discussed.

Scheme I.1. The Paterno-Buchi, Inter-, and Intramolecular [2+2] Photocycloaddition



I.2 General Overview of the [2+2] Photocycloaddition Mechanism

In order to facilitate an understanding of the factors that influence the [2+2] photocycloaddition, a brief review of the mechanism[7] must be presented. The Woodward-Hoffmann rules[8] are used to explain the reactivity for concerted reactions. Whether certain cycloadditions are allowed can often be described with the help of frontier orbital theory, as shown by Fukui.[9] If we consider the cycloaddition between two ethylene molecules, the highest occupied molecular orbital (HOMO) of one molecule must interact with the lowest unoccupied molecular orbital (LUMO) of another. Thermally, the cycloaddition would not occur because the frontier orbitals have an antibonding interaction where one of the new bonds needs to be formed (Scheme I.2, a).

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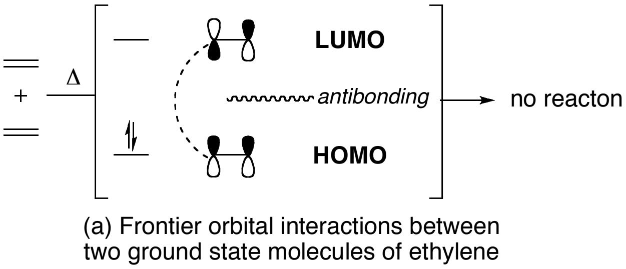
[7] For a more detailed discussion of the mechanism that is beyond the scope of this review, see Fleming, Ian. Frontier Orbitals and Organic Chemical Reactions. Chichester: John Wiley & Sons, 1976.

[8] Woodward, R. B.; Hoffmann, R. *Angew. Chem. Int. Ed.* **1969**, *8*, 781- 853.

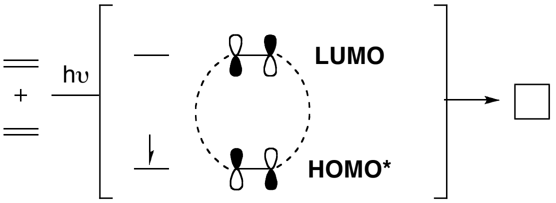
[9] Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57-64.

The photoexcitation of one molecule of ethylene promotes an electron from its HOMO into its LUMO, now making it the highest occupied molecular orbital (HOMO*). The HOMO* can now interact with the LUMO of another molecule in the ground state; the frontier orbitals now have a bonding interaction (Scheme I.2, b). This theory explains why the [2+2] cycloaddition occurs photochemically.

Scheme I.2. Thermal vs. Photochemical [2+2] Cycloadditions.



(a) Frontier orbital interactions between two ground state molecules of ethylene



(b) Frontier orbital interactions between a photochemically excited molecule and a ground state molecule of ethylene

Further mechanistic examination[10] is presented in Scheme I.3, which provides a simplified overview of the [2+2] photocycloaddition mechanism. The proposed mechanism can be applied to the formation of both oxetanes and cyclobutanes.

Oxetane formation results from the [2+2] cycloaddition of a carbonyl compound and an alkene, commonly known as the Paterno-Büchi reaction.[11] This excitation of the

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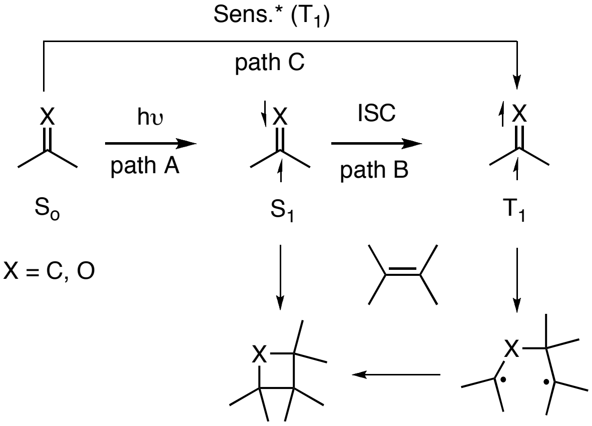
[10] Bach, T. *Synthesis* **1998**, 683-703, and references therein.

chromophore, the carbonyl, leads to the n-π^* absorption which produces the corresponding singlet state (S_1). The addition of an olefin can then occur from the S_1 state (Scheme I.3, path A), but the Paterno-Büchi reaction, in general, occurs from the carbonyl triplet state (T_1),[12] a result of intersystem crossing (ISC). The triplet state carbonyl can then add to an olefin (Scheme I.3, path B). It is fairly well accepted that the reaction proceeds with intermediate 1,4-biradicals[13] that combine to give the desired oxetane.

Scheme I.3. Proposed Mechanism of [2+2] Photocycloadditions.



The [2+2] cycloaddition of two olefins also proceeds with a similar mechanism. The excitation of an alkene leads to the lowest excited singlet state (S_1), which can

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[11] (a) Paterno, E.; Chieffi, G. *Gazz. Chim. Ital.* **1909**, *39*, 341. (b) Büchi, G.; Inman, C. G.; Lipinsky, E. S. *J. Am. Chem. Soc.* **1954**, *76*, 4327-4331.

[12] For a more detailed discussion on the Paterno-Büchi reaction, see: Horspool, W. M.; Song, P-S., eds. CRC Handbook of Organic Photochemistry and Photobiology. Boca Raton: CRC Press, 1995, chapters 43-45.

[13] (a) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255-6257. (b) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 3819-3822.

directly lead to cyclobutane formation (Scheme I.3, path A). Simple alkenes undergo concerted dimerization via the S_1 states.[14] Aryl substituted alkenes can also react by this π–π* excitation singlet pathway.[15]

For enones involved in the [2+2] photocycloaddition, the S_1 state is a result of the n-π* excitation. The excitation is followed by intersystem crossing, leading to the T_1 state, and cyclobutanes are formed through 1,4-biradical intermediates (Scheme I.3, path B).[16]

It is also possible to excite an alkene to its triplet state without ISC through a sensitized reaction (Scheme I.3, path C). A sensitizer may be used in a photochemical reaction to transfer its triplet energy to the participating alkene (S_o directly to T_1), which can then undergo cyclobutane formation.

The mechanism is often applied toward understanding the effect of substituents, solvent properties, concentration, and temperature on the stereoselectivity of photoinduced reactions.[17] With a general understanding of the [2+2] mechanism, the following sections will discuss the effect of hydrogen bonding in the cycloaddition.

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[14] Arnold, D. R.; Abraitys, V. Y. *Chem. Comm.* **1967**, 1053-1054.

[15] Peters, K. S.; Li, B.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 11119-11122.

[16] For a more detailed discussion on enone alkene mechanisms, see: Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 3-22 and references therein.

[17] For a detailed analysis from a spin multiplicity point of view, see: Griesbeck, A. G. *Synlett* **2003**, *4*, 451-472. Also, see ref. 3.

I.3 Directed Paterno-Büchi Reactions

As a general rule, the regioselective outcome for the Paterno-Büchi reaction is determined by the formation of the most stable biradical upon addition of the carbonyl to the olefin. Both the conformational preference and closure of the 1,4-biradical species account for the diastereoselective outcome of the cycloaddition.[12] Facial diastereoselective Paterno-Büchi reactions are often substrate or auxiliary induced.[10] Bach and coworkers have also demonstrated the unique ability of a chiral host[18] to promote facial selectivity in the [2+2] cycloaddition of an aromatic aldehyde and an enamide induced by hydrogen bonding.[19] Hydroxyl-assisted or directed Paterno-Büchi reactions, however, employ the features of allylic alcohols to induce selectivity.

The hydroxyl-directing property of chiral allylic alcohols has been utilized in photooxygenation reactions, not only in the ene[20] and [4+2] cycloaddition,[21] but also in the [2+2] cycloaddition of singlet oxygen.[22] The hydroxyl group of the chiral allylic alcohol is conformationally fixed by 1,3-allylic strain and directs the addition of singlet oxygen to the alkene through hydrogen bonding. Thus, the formation of the resulting dioxetane is diastereoselective due to both conformational strain and hydrogen bonding. The ability for singlet oxygen to add across an olefin in a diastereoselective manner led to

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[18] Host guest interactions induced by hydrogen bonding will not be discussed in this review. For selected examples, see: (a) Selig, P.; Bach, T. *J. Org. Chem.* **2006**, *71*, 5662-5673. (b) Bach, T.; Bergmann, H. Grosch, B.; Harms, K. *J. Am. Chem. Soc.* **2002**, *124*, 7982-7990.

[19] (a) Bach, T.; Bergmann, H.; Harms, K. *J. Am. Chem. Soc.* **1999**, *121*, 10650-10651. (b) Bach, T. *Synlett* **2000**, *12*, 1699-1707.

[20] For example, see Adam, W.; Nestler, B. *J. Am. Chem. Soc.* **1992**, *114*, 6549-6550.

[21] For example, see Adam, W.; Prein, M. *Acc. Chem. Res.*, **1996**, *29*, 275-283.

[22] Adam, W.; Saha-Moller, C. R.; Schambony, S. B. *J. Am. Chem. Soc.* **1999**, *121*, 1834-1838.

the exploration of other possible directed [2+2] photocycloadditions, namely the addition of benzophenone to allylic alcohols.

In 2000, Stegmann and coworkers[23] reported the hydroxyl-directed regio-and diastereoselective Paterno-Büchi reaction of benzophenone and chiral allylic alcohol **I.1** (Table I.1). The [2+2] photocycloaddition of benzophenone to allylic alcohols **I.1** afforded regioisomers **I.2** and **I.3**. These reactions were performed at 10 ^{o}C in deuterated benzene, irradiated, and the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy. A diastereomeric *threo* and *erythro* mixture of the major regioisomer **I.2**, was observed. Increasing the steric encumbrance of the R substituent improved the diastereomeric ratio (entries 1-3), and for the large *tert*-butyl group, the *threo*-diastereomer was exclusively formed (entry 4). Protection of the directing functionality as the silyl ether (entry 6) significantly decreased both the diastereoselectivity and the regioselectivity. This trend was also observed when the reaction was run in the presence of deuterated methanol (entry 5).

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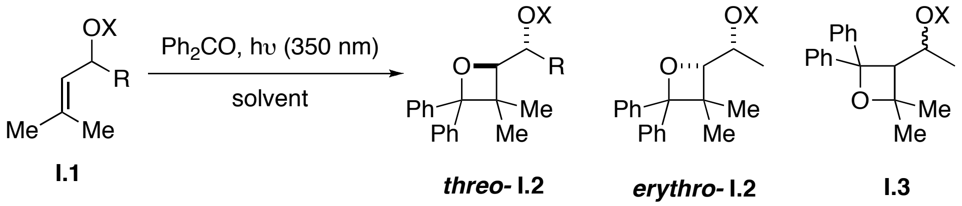
[23] Adam, W.; Peters, K.; Peters, E. M.; Stegmann, V. R. *J. Am. Chem. Soc.* **2000**, *122*, 2958-2959.

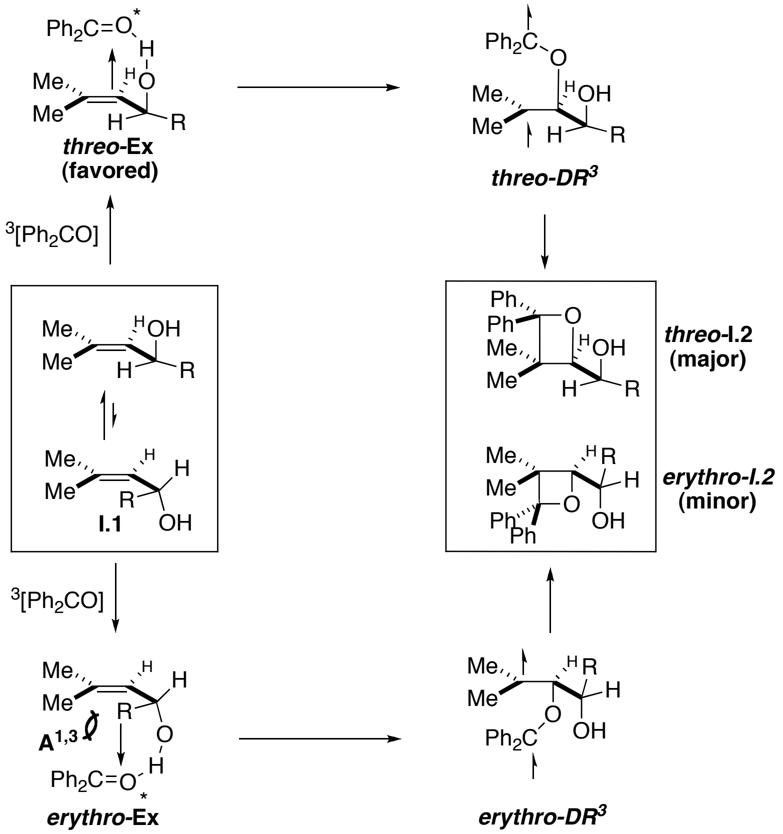
Table I.1. Photocycloaddition of Benzophenone to Allylic Alcohols.



entry	X	R	solvent	diastereo (*threo:erythro*)	regio (**I.2**:**I.3**)
1	H	Me	C_6D_6	90:10	>95:5
2	H	Et	C_6D_6	97:7	>95:5
3	H	*i*Pr	C_6D_6	95:5	>95:5
4	H	*t*Bu	C_6D_6	>95:5	>95:5
5	H	Me	C_6D_6/D_3COD (1:1)	69:31	95:5
6	SiMe$_2$*t*Bu	Me	C_6D_6	52:48	83:17

The regioselective and facial preference for these [2+2] photocycloadditions can be explained as shown in Scheme I.4. The 1,3-allylic strain between the R group and the *cis*-methyl group aligns the hydroxyl functionality such that the regioselective *threo* attack of the triplet-excited benzophenone is favored through hydrogen bonding. The favored ***threo*-EX** converts to the triplet diradical ***threo*-DR^3**, which then cyclizes to the major oxetane photoproduct ***threo*-I.2**. This model explains the increasing diastereoselective trend with the increasing size of the R group on the allylic alcohol, as well as the observed decreasing selectivities when using protic solvents or protecting the allylic alcohol. In turn, both the regio- and diastereoselective outcome of this Paterno-Büchi reaction is enhanced by hydrogen bonding and allylic strain, compared to the non-hydrogen bonding cases.

Scheme I.4. Facial Selectivity of the Paterno-Buchi Reaction.



The same group also reported further studies on this reaction using aldehydes and unsymmetrical ketones with allylic alcohols.[24] Hydrogen bonding was again used as an explanation for the regio- and stereoselective enhancement of the photocycloaddition.

Griesbeck and coworkers[25] also examined the role of hydrogen bonding in the Paterno-Büchi reaction of other allylic alcohols by comparing prenol and its O-protected substrate, prenyl acetate (Table I.2). Interestingly, the regioselectivity for the photocycloaddition with both **I.4** or **I.5** and an aldehyde was high and demonstrated that

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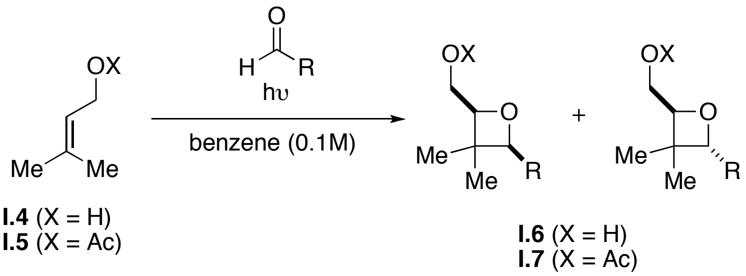
[24] Adam, W.; Stegmann, V. R. *Synthesis* **2001**, *8*, 1203-1214.

[25] Griesbeck, A. G., Bondock, S. *J. Am. Chem. Soc.* **2001**, *123*, 6191-6192.

hydrogen bonding was not responsible for controlling product regiochemistry. The diastereoselectivity of the reaction was moderate with aliphatic aldehydes (entries 1-3) and high for benzaldehyde (entry 4). Comparison of *cis/trans*-**I.6** and *cis/trans* **I.7** for each aldehyde, however, showed that the *cis/trans*-selectivity for prenol was only slightly higher than prenyl acetate. Based on concentration and competition experiments, the authors were able to rationalize that the diastereoselectivity for the [2+2] cycloaddition of prenol and prenyl acetate with an aldehyde was a result of the intersystem crossing geometries at the triplet biradical stage and not hydrogen bonding. A hydroxyl group directing effect, however, was still postulated to be responsible for the selectivities observed with substrates with allylic strain.

Table I.2. Photocycloaddition of Aldehyde to Prenol and Prenyl Acetate.



I.4 (X = H)
I.5 (X = Ac)

I.6 (X = H)
I.7 (X = Ac)

entry	R	*cis/trans*- **I.6**	*cis/trans*-**I.7**
1	Me	81:19	77:23
2	Et	86:14	81:19
3	*t*Bu	83:17	80:20
4	Ph	>97:3	93:7

From these investigations, there is a delicate synergy between hydrogen bonding and substrate conformation, or in this case, allylic strain, that is responsible for the selectivity observed in the Paterno-Büchi reaction.

I.4 Directed Intermolecular [2+2] Photocycloadditions

The regio- and diastereoselectivity is not straightforward to predict in the [2+2] photocycloaddition of olefins. For example, mixtures of head to head (HH) and head to tail (HT) complexes, or regioisomers, are often found in the reaction. Additionally, there can be mixtures of *exo* and *endo* products, or diastereomers, which result from differentiating the facial preference of the two reacting olefins. One way to control these mixtures may be to rigidify the reacting π-systems by using cyclic enones.[26] Alternatively, dimerization of olefins can occur in the solid state via hydrogen bonding to a linker molecule. Resorcinol, for example, can preorganize two polyenes for [2+2] photoaddition through two O-H-N hydrogen-bonding interactions to construct ladderanes in the solid state[27] (eq. 4). The selectivity of these types of solid-state reactions is, however, due to the conformation of the rigid crystal structure.[28] Selectivity can also be

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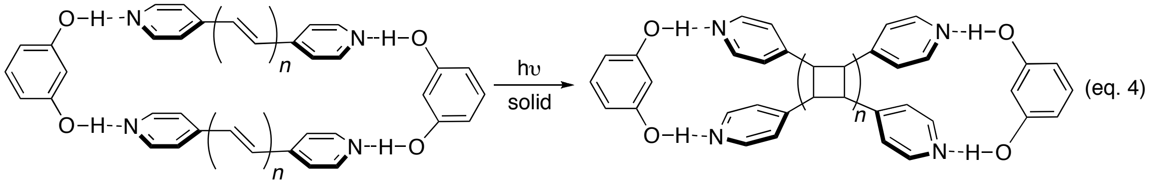
[26] Horspool, W. M.; Song, P-S., eds. CRC Handbook of Organic Photochemistry and Photobiology. Boca Raton: CRC Press, 1995, chapters 52-53.

[27] For an interesting paper on the synthesis of ladderanes using this method, see: Gao, X.; Frixcic, T.; Macgillivray, L. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 232-236.

[28] There are also reported solid-state photochemical reactions that occur without the help of a template or linker. For more on solid-state [2+2], see: (a) Ito, Y. *Synthesis* **1998**, 1-32. (b) Friscic, T.; MacGillivray, L. R. *Chem. Comm.* **2005**, 5748-5750. (c) Natarajan, A.; Mague, J. T.; Venkatesan, K.; Ramamurthy, V. *Org. Lett.* **2005**, *7*, 1895-1898. (d) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480-486. and references therein.

governed through substrate-induced [2+2] cycloadditions,[29] but few of these are directed. Thus, controlling the intermolecular [2+2] photocycloaddition of alkenes has been a challenging goal.



Hydrogen bonds have been used to control the stereoselective outcome of a [2+2] photocycloaddition between alkenes and naphthalene rings. In 1980, Faggiani and coworkers[30] reported that the cycloaddition of 4-methyl-1-napthonitrile **I.8** with tetramethylethylene **I.9** (Scheme I.5, eq. 5) afforded cycloadduct **I.10** as the single regioisomeric product. Mizuno and coworkers[31] examined the photocycloaddition of other 4-substituted 1-cyanonaphthalenes (**I.11**) and 1-substituted 3-methyl-2-butenes (**I.12**) (Scheme I.5, eq. 6), which regioselectively yielded two stereoisomers, ***endo*- I.13** and ***exo*- I.13**. The attractive interaction, namely a hydrogen bond, was predicted to direct the facial preference to give the *endo*-isomer over the *exo*-isomer.

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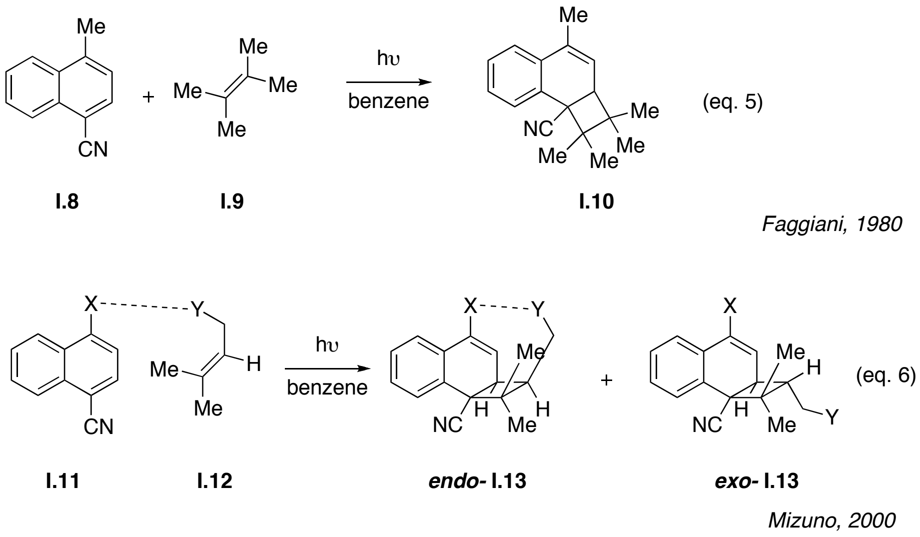
[29] See ref. 1 and 10 and references therein.

[30] McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1980**, *102*, 7782-7784.

[31] Mizuno, K.; Yokoyama, A. *Org. Lett.* **2000**, *2*, 3457-3459.

Scheme I.5. Intermolecular [2+2] Photocycloaddition of Alkenes to Naphthalene



I.8 **I.9** **I.10**

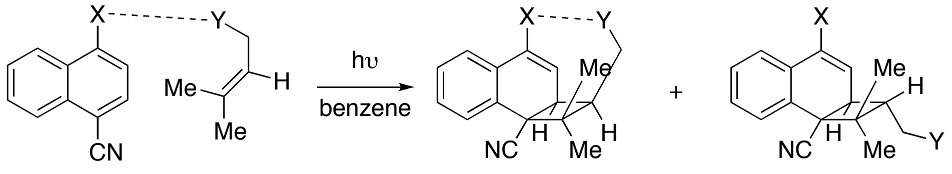
Faggiani, 1980

I.11 **I.12** ***endo-* I.13** ***exo-* I.13**

Mizuno, 2000

The substituent effect of the cycloaddition was initially screened using benzene as the solvent. In cases where X and Y were able to form a hydrogen bond, the *endo*-isomers were preferentially favored over the *exo*-isomers (Table I.3, entries 3-5). No preference for *endo/exo* selectivity was observed when hydrogen bonding was not possible (entries 1, 2, and 6). These reactions were carried out at room temperature for 20-21 hours.

Table I.3. Substituent Screen of Intermolecular [2+2] Photocycloaddition.



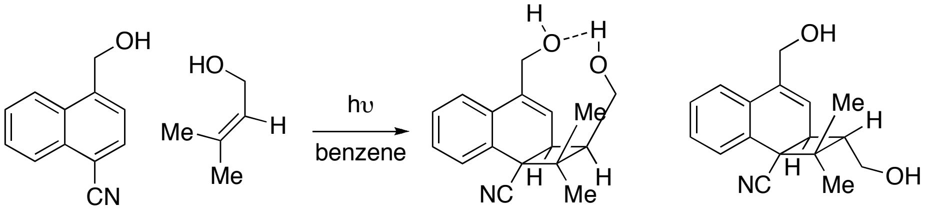
I.11 **I.12** ***endo-* I.13** ***exo-* I.13**

entry	X	Y	Yield	***endo-/exo-I.13***	RSM
1	H	OH	41	0.72	24
2	CH_3	OH	22	0.84	45
3	CH_2OH	OH	42	3.3	18
4	CH_2OCH_3	OH	47	2.4	33
5	CH_2OH	OCH_3	22	1.7	62
6	CH_2OCH_3	OCH_3	18	0.95	40

All reactions carried out at room temperature for 20-21 hours.

These cycloadditions were also examined using other solvents, including dichloromethane, acetonitrile, and methanol (Table I.4). The use of polar solvents decreased the *endo/exo* selectivity (entries 5 and 6), and employing MeOH as the solvent resulted in no selectivity (entry 7). The use of a protic solvent would disrupt the hydrogen bond between the two reacting partners. Lowering the temperature from room temperature to -20 ^{o}C and -60 ^{o}C in dichloromethane also improved the yield and selectivity (entries 3 and 4).

Table I.4. Solvent and Temperature Screen of Intermolecular [2+2] Photocycloadditions.

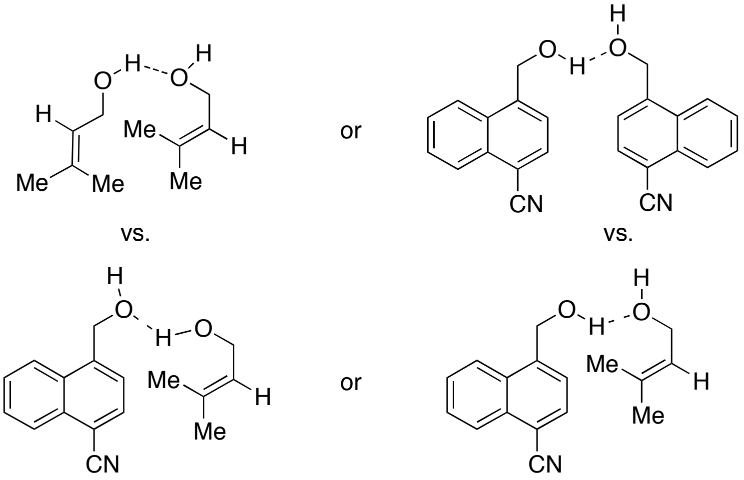


I.11 **I.12** ***endo-* I.13** ***exo-* I.13**

entry	solvent	temperature	yield	***endo-/exo-I.13***	RSM
1	benzene	RT	42	3.3	18
2	CH_2Cl_2	RT	33	3.4	10
3	CH_2Cl_2	-20 °C	28	6.6	trace
4	CH_2Cl_2	-60 °C	73	13	trace
5	CH_3CN	RT	39	1.6	10
6	MeOH: CH_3CN 5:95	RT	32	1.7	20
7	MeOH	RT	28	1.0	17

The authors conducted low-temperature ^{1}H-NMR studies to explain the increasing selectivity with decreasing temperatures. They found that at lower temperatures, there was less formation of dimeric **I.11** or **I.12** and a higher concentration of a **I.11-I.12** combination (Figure I.1). At room temperature, there seemed to be a competing dimeric species that would affect product formation.

Figure I.1. Dimeric **I.11** or **I.12** vs. **I.11-I.12** Combination.



In a recent paper by Sadlej and coworkers,[32] the intramolecular hydrogen bond energies for 3-aminopropenal and 3-aminopropenthial were found to be roughly 5-7 kcal/mol according to their estimation scheme. The authors concluded that in terms of energies, inter- and intramolecular hydrogen bonds are fairly similar. That is, there is only a slight energy difference between the intramolecular hydrogen bond of 3-aminopropenal (dictating a *s-cis* conformer) and the intermolecular hydrogen bond of two molecules of 3-aminopropenal (dictating a dimeric arrangement) (Figure I.2). While Sadlej's substrates are different than the ones that have been presented here, perhaps these findings offer a rationale as to why hydrogen bonding cannot always be used to achieve perfect selectivity; there can be some competition with the intermolecular interactions to form dimeric species. This is in accord with what Mizuno and coworkers observed with their low temperature studies and unwanted dimeric species formation.

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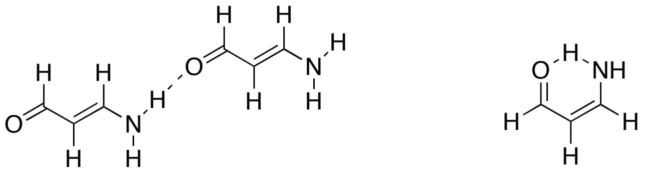
[32] Jablonski, M.; Kaczmarek, A.; Sadlej, A. J. *J. Phys. Chem. A.* **2006**, *110*, 10890-10898.

Figure I.2. Inter- vs. Intramolecular Hydrogen Bond of 3-aminopropenal.



It would be interesting to see what kind of selectivities would be achieved if unsymmetrical olefins were used in Mizuno's intermolecular [2+2] photocycloaddition studies. Nevertheless, with this data, the authors concluded that the formation of the hydrogen bond in the ground state, which preorganizes the two interacting olefins, was responsible for the observed selectivity.

I.5 Directed Intramolecular 2+2 Photocycloadditions

The presence of a tether dictates a greater control over the outcome of a [2+2] photocycloaddition, particularly regarding regioselectivity.[33] Additionally, substituents on the tether have been shown to induce selectivity by invoking some sort of conformational bias.[34] Thus, it would be interesting to explore whether or not a hydroxyl substituent would overcome this natural conformational bias and induce a directed selectivity.

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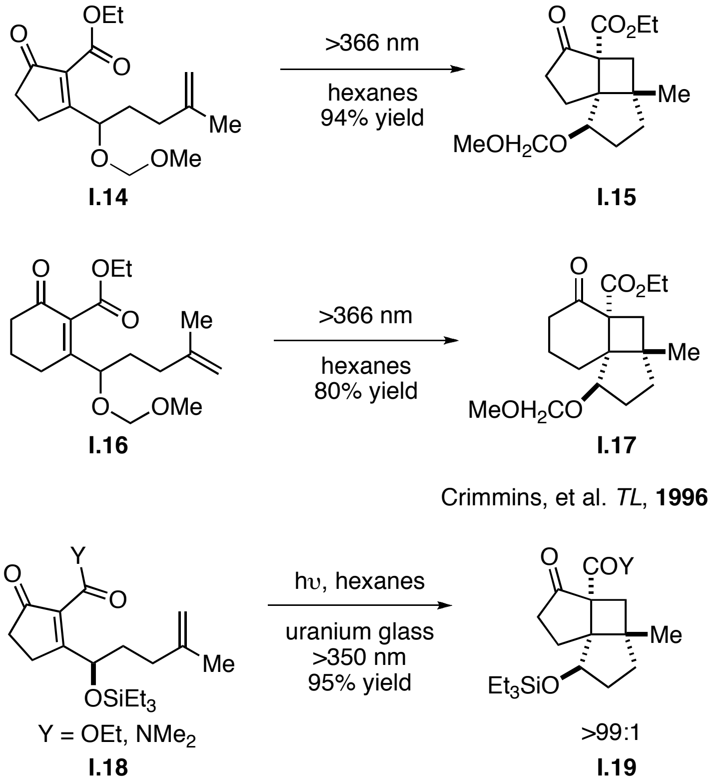
[33] Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453-1473.

[34] For one example, see: Adam, J. M.; Ghosez, L.; Houk, K. H. *Angew. Chem. Int. Ed.* **1999**, *38*, 2728-2729.

It has been shown by Crimmins and coworkers[35] that substrates **I.14**, **I.16**, and **I.18** typically undergo intramolecular photocycloadditions in excellent yield (Scheme I.6). This mode of cycloaddition also results in high diastereoselectivity of the resulting cycloadduct. For example, irradiation of ester **I.18** produced a single cycloadduct **I.19** in hexanes, as well as other solvents including dichloromethane, THF, acetonitrile, and methanol without change in diastereoselectivity.

Scheme I.6. The normal mode of cycloaddition for **I.14**, **I.16**, **I.18**.



Crimmins, et al. *TL*, **1996**, *37*, 6519-6522.

Crimmins, et al. *JACS*, **1997**, *119*, 10237-10238.

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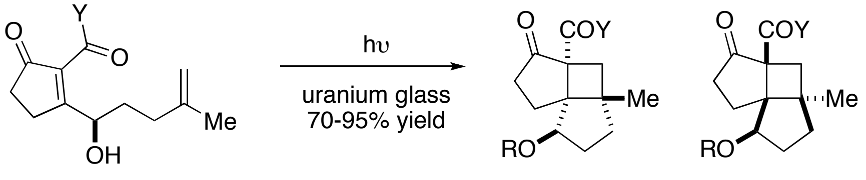
[35] (a) Crimmins, M. T.; Huang, S.; Guise-Zawacki, L. E. *Tet. Lett.* **1996**, *37*, 6519-6522. (b) Crimmins, M. T.; Choy, A. L. *J. Am. Chem. Soc.* **1997**, *199*, 10237-10238.

In 1997, Crimmins and coworkers[37b] reported their ability to reverse the normal diastereoselectivity of this intramolecular [2+2] enone-olefin photocycloaddition by taking advantage of an intramolecular hydrogen bond (Table I.5). Removal of the silyl group from ester **I.18** under acidic conditions (*p*-TSA, 4:1 THF: H_2O) afforded free alcohol **I.20** in 90% yield, and a pronounced solvent effect on the diastereoselectivity of the reaction was observed in the cycloaddition. Using MeOH as a solvent (entry 5) resulted in a 5:1 ratio of **I.21A:I.21B**, while in acetonitrile (entry 4), **I.21A** was preferred in a 3.3:1 ratio. In aprotic solvents such as hexanes (entry 3), the reaction was non-selective, with a 1.1:1 ratio of **I.21A** to **I.21B**. An amide substrate, which would be a better electron donor for hydrogen bonding, was also examined under these reaction conditions to see if this would improve the selectivity for the abnormal diastereomer. Irradiation of the protected silyl ether amide (entry 2) gave high diastereoselectivity and no solvent effect was observed. Using aprotic solvents such as hexanes and dichloromethane (entry 6 and 7) gave a better selectivity for the abnormal diastereomer **I.21B**. Using a protic solvent such as MeOH (entry 8) disrupted the intramolecular hydrogen bond and gave the normal, expected cycloadduct. From these experiments, the presence or absence of an intramolecular hydrogen bond and the diastereoselective outcome of the reaction correlated well.

Table I.5. Crimmins' Solvent Effects on Intramolecular [2+2] Photocycloadditions.

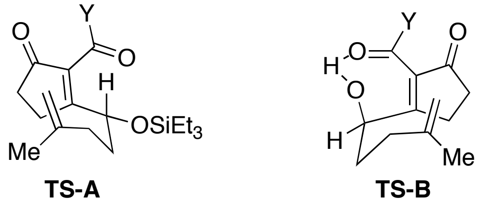


I.20 **1.21A** **1.21B**

entry	Y	R	solvent	**A:B**
1	OEt	$SiEt_3$	hexanes	>99:1
2	NMe_2	$SiEt_3$	hexanes	>99:1
3	OEt	H	hexanes	1.1:1
4	OEt	H	CH_3CN	3.3:1
5	OEt	H	MeOH	5:1
6	NMe_2	H	hexanes	1:4
7	NMe_2	H	CH_2Cl_2	1:3
8	NMe_2	H	MeOH	1.5:1

The authors proposed two possible conformations of the starting enone (Figure I.3). **TS-A** not only accurately predicted the normal cycloadduct, but was also calculated to be the lowest energy conformation of the starting material. This also resulted in placing the secondary substituent *cis* to the substituent on the internal carbon of the alkene. Thus, the absence of an intramolecular hydrogen bond should give the product dictated by **TS-A**. **TS-B** orients the hydroxyl group in an axial position to undergo an intramolecular hydrogen bond, giving the so-called abnormal cycloadduct.

Figure I.3. Proposed Transition States Crimmins' Intramolecular Photocycloaddition.



TS-A **TS-B**

Arnett and coworkers[36] have measured hydrogen bond enthalpies for the intermolecular hydrogen bond between *p*-fluorophenol and hydrogen bond acceptors, such as amides and esters. Based on their calculations, the hydroxyl-amide hydrogen bond is roughly 2.3-2.7 kcal/mol stronger than a hydroxyl-ester hydrogen bond. Thus, an amide moiety, compared to an ester moiety, should dictate a more selective directed photocycloaddition. The dimethyl amide provided a 4:1 selectivity for the reversed product (Table I.4, entry 7) in hexanes, while the ethyl ester provided a 1:1.1 selectivity (entry 3) in hexanes. A more selective reaction for the amide might have been expected based on the predictions made by the difference in hydrogen bond strengths, but there are many other factors to consider. Crimmins[37b] proposed that the steric bulk of an amide may somehow destabilize the hydrogen-bonded form for the amide or that the nature of an intramolecular hydrogen bond does not allow the ideal geometry for hydrogen bonding.

Crimmins applied these solvent effects in his approach toward Ginkgolide B.[37] Unfortunately, the hydrogen-bond controlled cycloadditions only afforded modest selectivities, leading the authors to seek a more highly selective and efficient cycloaddition that did not involve an intramolecular hydrogen bond. Nevertheless, the methodology demonstrated the hydrogen bonding ability to affect the outcome of [2+2] photocycloaditions. Further exploration of this methodology could be the use of a chelating metal or a Lewis acid in breaking up the interacting intramolecular hydrogen

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[36] Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875-3891.

[37] Crimmins, M. T.; Pace, J. M.; Nantermet, P. G.; Kim-Meade, A. S.; Thomas, J. B.; Watterson, S. H.; Wagman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 8453-8463.

bond. Additionally, changing the hydroxyl substituent to influence the electron donating/accepting properties of the system could enhance the selectivities.

I.6 Conclusion

The utility of a hydrogen bond in the [2+2] photocycloaddition has been demonstrated in the literature. In some examples, this favorable interaction has helped enhance the natural selectivity of the reacting system; other studies have shown that the hydrogen bond can even overcome the natural bias of the two olefinic partners. However, the reactions are often influenced by additional factors, such as allylic strain or the subtle stereoelectronics of the system. Given these observations, are we any closer to using hydrogen bonding as a predictive tool for the outcome of [2+2] photocycloadditions? For example, can the energies of conformational minima or various hydrogen bonds[38] be calculated and applied toward the analysis of the reaction? One has to ask, however, if energy differences are sufficient for predicting the outcome, or if other considerations need to be factored into the analysis.

Even without achieving perfect selectivity, hydrogen bonding certainly plays a role in dictating the outcome of a [2+2] photocycloaddition. The research presented here offers ample foundation for further questioning and probing into the role of hydrogen bonding in photoinduced cycloadditions, particularly in the limited examples of intramolecular [2+2] photocycloadditions. Can we look at new substrates and observe a

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[38] For a recent paper on calculations of hydrogen bond strength, see: Oliveira, B. G.; Pereira, F. S.; deAraujo, R. C. M. U.; Ramons, M. N. *Chem. Phys. Lett.* **2006**, *427*, 181-184.

similar directed effect in the photocycloaddition due to an intramolecular hydrogen bond? Where do sterics, for example, come into play? Further investigations of intramolecular hydrogen bonding in photocycloadditions will be examined in Chapter II.

Chapter 2

Solvent-Controlled Intramolecular [2+2] Photocycloadditions of α-Substituted Enones

II.1 Introduction

Previous studies in our group have shown that there is a regiochemical dependence on protic versus aprotic solvents in the photochemical reaction of 2'-hydroxyl enones.[1] Photocycloaddition of enone **II.1** afforded two products, a "head to head" cycloaddition product **II.2** and a "head to tail" product **II.3** (Scheme II.1). Irradiation of **II.1** in protic media, such as acetone/water, led to a preference of the straight "head to head" cycloadduct in a 7:1 ratio. Alternatively, when the photocycloaddition was carried out in dichloromethane, the crossed "head to tail" cycloadduct was favored by a 10:1 ratio.

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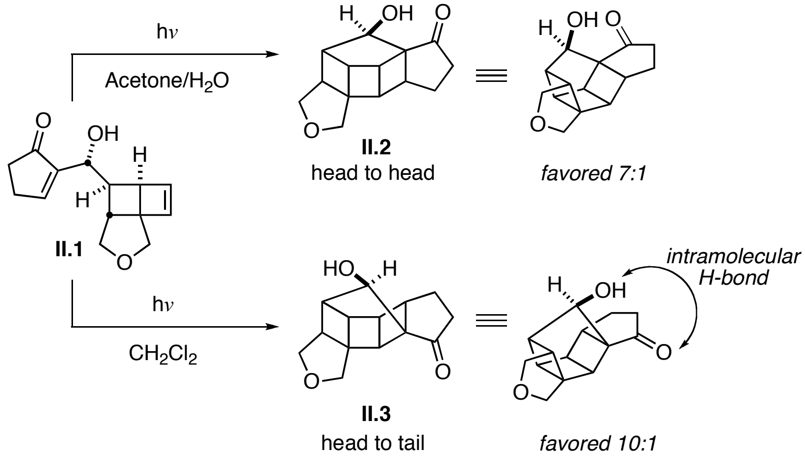
[1] Bader, S. J.; Snapper, M. L. *J. Am. Chem. Soc.* **2005**, *127*, 1201-1205.

Scheme II.1. Solvent-Dependent Regioselective Intramolecular [2+2] Photocycloadditions.



It was hypothesized that the intramolecular hydrogen bond between the carbonyl and the β-hydroxyl group was governing the regioselective outcome of this cycloaddition. In aprotic media, the intramolecular hydrogen bond held the enone in a conformation that gave predominantly the crossed cycloadduct **II.3**. Disruption of this intramolecular interaction, or competition with a protic solvent, relaxed the conformation of the enone, allowing for the straight product **II.2** as the major cycloadduct.

As shown in chapter I, hydrogen bonds play an important role in dictating the outcome of [2+2] photocycloadditions. Given these observations and our past interest in inter- and intramolecular [2+2] photocycloadditions of functionalized cyclobutenes,[2] we turned our attention toward directed intramolecular enone-alkene cycloadditions.[3] Specifically, we sought to explore the role of 2'-functionalization, since the role of 2'-

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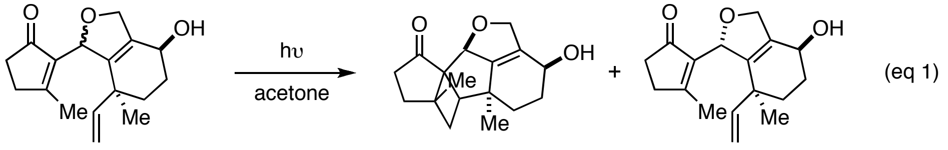
[2] (a) Randall, M. L.; Lo, P. C.-K.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1999**, *121*, 4534-4545. (b) Lo, P. C.-K.; Snapper, M. L. *Org. Lett.* **2001**, *3*, 2819-2821.

[3] For mechanistic insight into enone-alkene cycloadditions, see: Schuster, D.I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 3-22. For a review on synthetic applications of intramolecular enone-olefin photocycloadditions, see: Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453-1473.

substituents in these enone-olefin intramolecular [2+2] photocycloadditions is unclear. For example, in an approach to the guanacastepenes, Sorensen observed a highly diastereoselective intramolecular [2+2] photocycloaddition of a 2’-substituted system (eq 1).[4] Only one diastereomer was a competent substrate in the [2+2] photocycloaddition. However, although Sorensen’s substrate contained oxygenation in the 2’ position, it was incapable of forming an intramolecular hydrogen bond. Thus, we were interested in examining the generality of solvent effects on intramolecular [2+2] photocycloadditions of 2’-hydroxyl enones and determining if a directed effect could be observed.



II.2 Diastereoselective Solvent-Controlled [2+2] Photocycloadditions

Enones with 2’-hydroxyl-containing acyclic tethered olefins were synthesized in order to observe the role of hydrogen bonding in intramolecular [2+2] photocycloadditions. The simplified system of **II.4** would act as a mimic for **II.1** and allow us to observe the role that steric effects and hydrogen bonding play in [2+2] photocycloadditions (Figure II.1).

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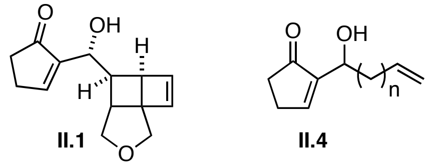
[4] Shipe, W. D.; Sorensen, E. J. *Org. Lett.* **2002**, *4*, 2063-2066.

Figure II.1. Substrates for the Intramolcular [2+2] Photocycloaddition.



These simplified substrates were prepared in a straightforward manner starting with known vinyl bromides **II.5** and **II.11**[5] (Scheme II.2). Lithium-halogen exchange of **II.5** or **II.11** occurred at -78 °C followed by addition of 4-pentenal and acidic workup to afford enone **II.6** and **II.12**, respectively, in a 60-80% yield. Enone **II.6** was transformed to methyl ether **II.7** using conditions reported by Trost.[6] This substrate would allow us to examine the photocycloaddition in a system without the opportunity for an intramolecular hydrogen bond.

In a similar fashion, enones with an additional methylene in the tether were also synthesized. The addition of Weinreb amide **II.8** to the respective vinyllithium species afforded products **II.9** and **II.13**. Luche reduction[7] followed by acidic workup provided enones **II.10** and **II.14** in high yields.

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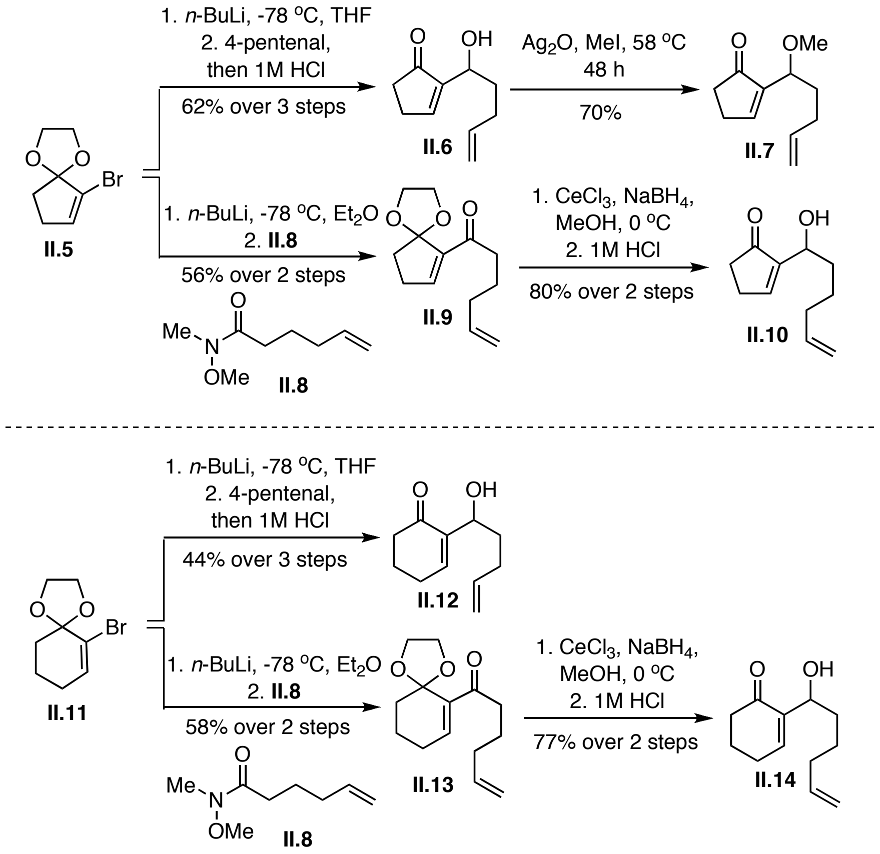
[5] (a) Kowalski, C.; Weber, A.; Fields, K. *J. Org. Chem.* **1982**, *47*, 5088-5093. (b) House, H.; McDaniel, W. *J. Org. Chem.* **1977**, *42*, 2155-2160.

[6] Trost, B.; Yang, H.; Probst, G. D. *J. Am. Chem. Soc.* **2004**, *126*, 48-49.

[7] Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454-5459.

Scheme II.2. Synthesis of 2'-Hydroxy Enones.



Similar structures have been examined under photochemical conditions. Agosta and coworkers[8] observed a regiochemical control in the cycloaddition of enones with acyclic tethered olefins (Table II.1). These enones responded to substitution on the internal carbon of the tethered olefin with a crossed closure, yielding a mixture of the head-to-head cycloadduct to the head-to-tail cycloadduct (entries 2 and 3). Interestingly, enones with no substitution (entry 1) or enones with substitution on the terminal olefin (entry 4) only afforded the straight closure cycloadduct. Becker was able to report similar

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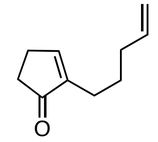
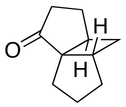
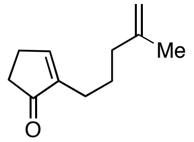
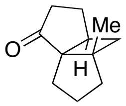
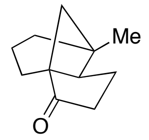
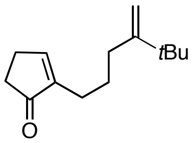
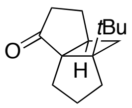
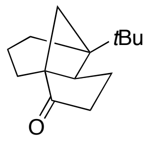
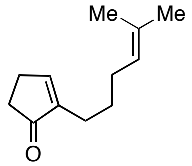
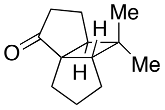
[8] Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 3385-3394.

findings on six-membered enones.[9] We hoped that our oxygenated substrates would respond to a hydrogen bonding interaction in order to dictate the outcome of the photocycloaddition.

Table II.1. Photocycloaddition of tetered cyclopentenones change.

entry	dienone	straight closure	crossed closure	ratio of straight/crossed
(1)				only
(2)				73/27
(3)				80/20
(4)				only

With our functionalized 2'-hydroxyl enones in hand, we examined the photocycloaddition of these systems in a variety of solvents. Enone **II.6** was irradiated with a 450 W medium-pressure lamp through Pyrex filters in various solvents to yield mixtures of **II.15a** and **II.15b** (Table II.2). These two isolated products were not regioisomeric as originally observed in the cyclobutene system, but rather diastereomeric, a result of the facial preference of the interacting π-systems. The ratio of cycloadducts as

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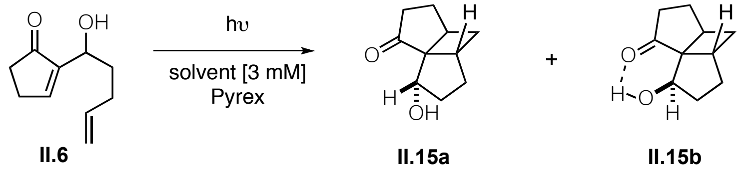
[9] (a) Becker, D.; Haddad, N.; Sahali, Y. *Tet. Lett.* **1989**, *30*, 4429-4432. (b) Becker, D.; Haddad, N. *Tet. Lett.* **1986**, *27*, 6393-6396.

shown in Table II.2 suggested that an intramolecular hydrogen bond between the hydroxyl group and the enone carbonyl was influencing the facial selectivity. Resubjection of either cycloadduct to photochemical conditions did not lead to formation of the other cycloadduct, an observation indicating that the products were not equilibrating under the photolysis conditions.

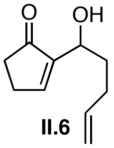
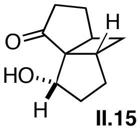
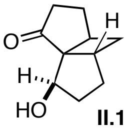
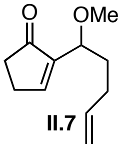
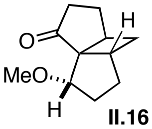
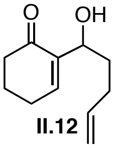
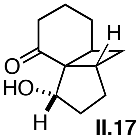
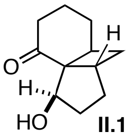
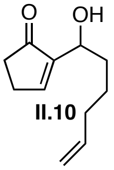
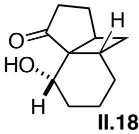
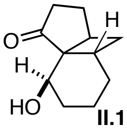
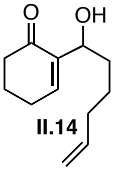
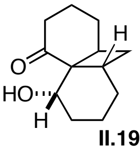
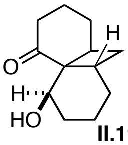
Table II.2. Solvent Screen of **II.6**.



entry	solvent	**a:b**	yield (%)
1	acetone/ 10% H_2O	>20:1	60
2	methanol	>20:1	65
3	acetonitrile	5:3	77
4	diethyl ether	2:1	90
5	dichloromethane	1:4	64
6	pentane	1:2	63
7	cyclohexane	1:3	42

The screen indicated that the solvent was playing a role in controlling the intramolecular photocycloaddition. In an aprotic solvent such as methylene chloride, the intramolecular hydrogen bond between the β-hydroxyl group and the carbonyl group fixed the enone and pendent olefin to provide a particular facial selectivity between these two reactive π-systems, giving cycloadduct **II.15b**. In a protic solvent such as methanol or acetone/water mixture, disruption of the intramolecular hydrogen bond with the solvent afforded the opposite facial selectivity between the enone and the tethered olefin. This orientation led to diastereomer **II.15a**. As shown in Table II.3, photocycloaddition of methyl ether **II.7** led to only one cycloadduct **II.16** regardless of the solvent employed. The stereochemistry of **II.16** is similar to that of adduct **II.15a**, where the intramolecular hydrogen bond is not present.

Table II.3. Solvent-Dependent Photocycloadditions.[a]

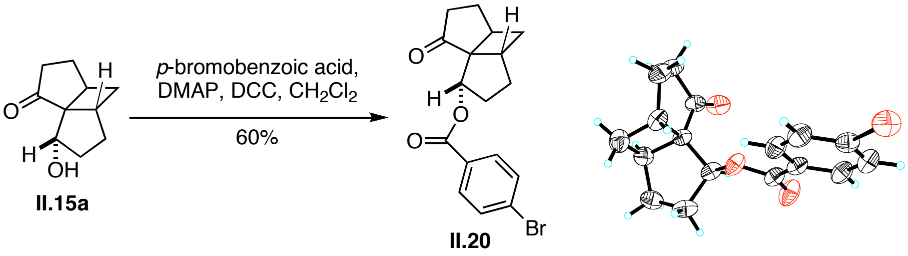
entry	enone	products	solvent/yield/ratio
(1)	 **II.6**	 **II.15a**  **II.15b**	CH_2Cl_2 64% **a:b** 1:4 acetone/H_2O 60% **a:b** > 20:1
(2)	 **II.7**	 **II.16**	CH_2Cl_2 89% (81% conv.) MeOH 60% (87% conv.)
(3)	 **II.12**	 **II.17a**  **II.17b**	CH_2Cl_2 72% **a:b** 1:4 acetone/H_2O 74% **a:b** 6:1
(4)	 **II.10**	 **II.18a**  **II.18b**	CH_2Cl_2 47% **a:b** < 1:20 acetone/H_2O 38% **a:b** > 20:1
(5)	 **II.14**	 **II.19a**  **II.19b**	CH_2Cl_2 21% **a:b** 1:10 acetone/H_2O 40% **a:b** 16:1

[a] All reactions: hυ, Pyrex filter, 3 mM in solvent.

Entries 3-5 of Table II.3 explore the scope of the solvent-controlled photocycloadditions with 2’-hydroxyl-containing substrates with larger cyclic enones and longer tethered olefins. In all cases, the two reacting π-systems interacted in a head-to-head fashion; facial selectivity was dictated by the presence or absence of an intramolecular hydrogen bond. Cyclohexenone **II.12**, for example, reacted in a similar manner as cyclopenteneone **II.6** (entry 3). Extending the tether by an additional methylene afforded the cycloadducts as shown in entries 4 and 5. In these examples, the solvent-dependent facial control improved in protic and aprotic solvents, but the overall efficiency suffered. While other minor products were observed, none of these side products were identified or proven to be head-to-tail regioisomers in this series of photocycloadditions.

The structures of the cycloadducts were determined through correlation studies. Treatment of **II.15a** with *p*-bromobenzoic acid gave a crystalline compound that confirmed the relative stereochemistry for diastereomer **II.15a** and verified the head-to-head connectivity (Scheme II.3).

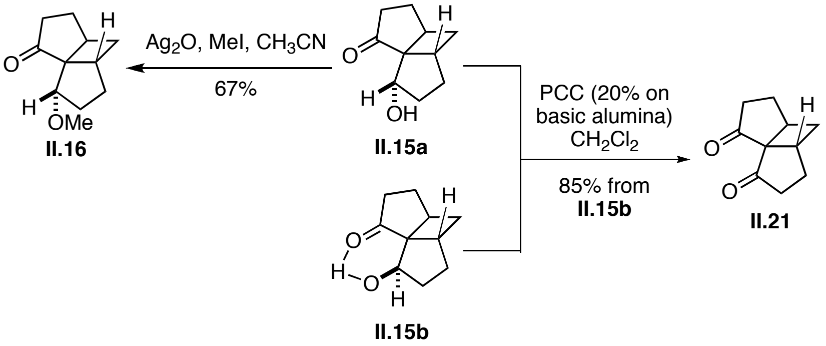
Scheme II.3. Derivitization of **II.15a** to **II.21**.



ORTEP of **II.20**

Cycloadducts **II.15a** and **II.15b** were proven to be diastereomers through oxidation of both secondary alcohols to the same diketone **II.21** (Scheme II.4). The structure of methyl ether **II.16** was proven through methylation of cycloadduct **II.15a**.

Scheme II.4. Oxidation of **II.15a** and **II.15b** and Methylation of **II.15a**.



The structures and stereochemistry of photoadducts **II.17**, **II.18**, and **II.19** were confirmed in a related fashion. Cycloadducts **II.17a**, **II.17b**, **II.18a**, and **II.18b** were all transformed to diketone **II.22** with PCC on basic alumina (Scheme II.5). Derivitization of **II.17a** led to bromobenzoate **II.23**. X-ray analysis of crystalline **II.23** confirmed the relative stereochemistry of the cycloadducts.[10]

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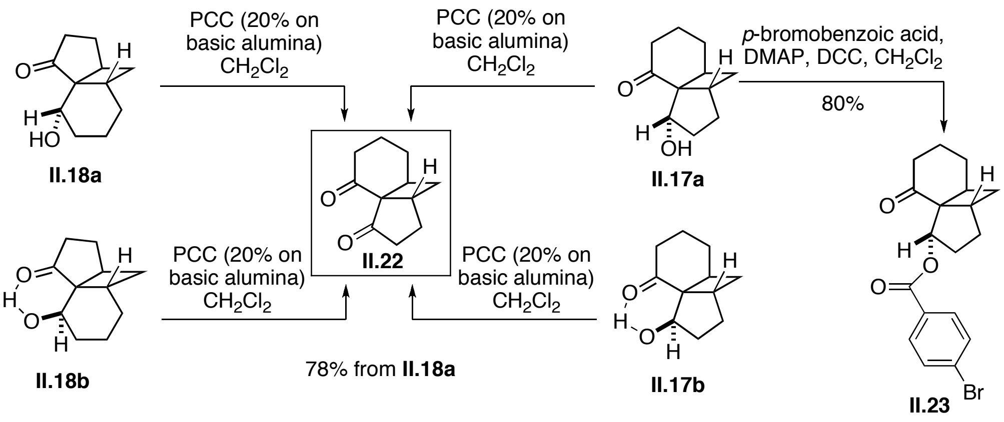
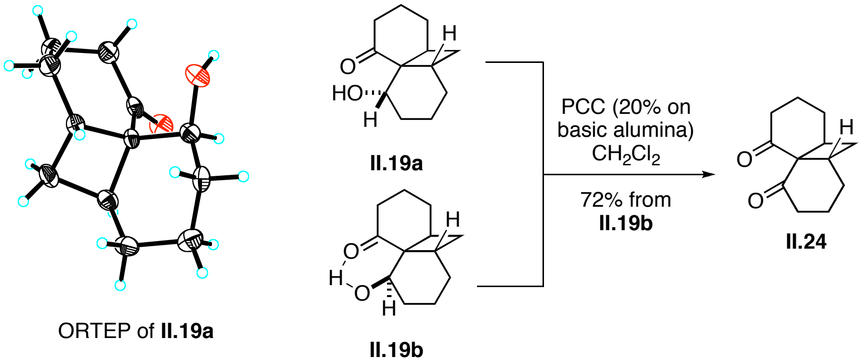
[10] See experimental section for X-ray information.

Scheme II.5. Oxidation of Photocycloadducts of **II.17** and **II.18**.



Similarly, the diastereomeric relationship between adducts **II.19a** and **II.19b** were demonstrated through oxidation to diketone **II.24** (Scheme II.6). X-ray quality crystals of cycloadduct **II.19a** allowed for structural confirmation.

Scheme II.6. Structural Confirmation of **II.19a** and **II.9b**.



II.3 Regioselective Solvent-Controlled [2+2] Photocycloadditions

The diastereoselective cycloadditions of enones with acyclic tethered olefins differ from the regioselective cycloadditions observed with enone **II.1**, most likely due to the structural constraints imposed by the polycyclic ring system of **II.1**. That is, in **II.1**, only one face of the attacking olefin is available to the excited enone. For substrates with acyclic tethered olefin, both reacting π-systems have facial availability to afford diastereomeric cycloadducts; perhaps in substrates with limited olefin accessibility, the photochemical outcome may change. The generality of solvent-controlled photocycloadditions was probed with substrates that had limited olefin accessibility.

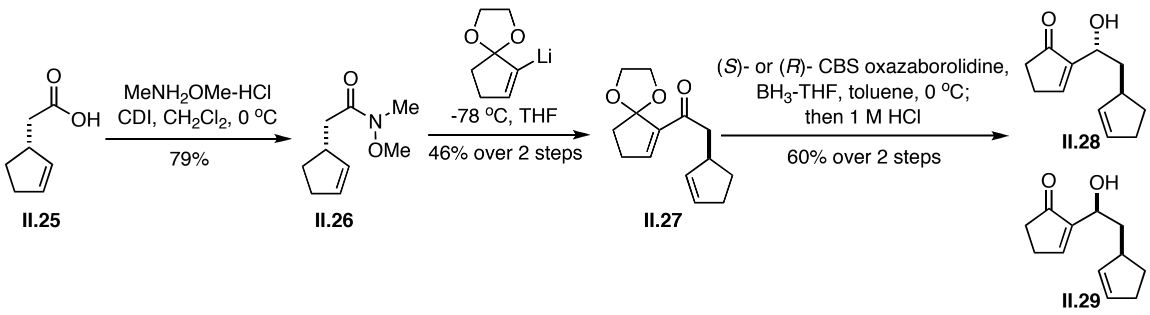
In order to test our hypothesis, enones **II.28** and **II.29** were prepared for study in intramolecular [2+2] photocycloadditions in protic and aprotic solvents (Scheme II.7). Enones **II.28** and **II.29** were generated starting with enantioenriched acid **II.25**.[11] Acid **II.25** was converted to Weinreb amide **II.26** employing Scheffer's protocol.[12] Addition of the vinyl lithium reagent derived from cyclopentene **II.5** to amide **II.26** yielded substrate **II.27** in 46% yield. CBS reductions using each antipode of the catalyst, followed by mild hydrolysis, produced the diastereomeric enones **II.28** and **II.29**.

---

[11] (a) Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258-1267. (b) He, F.; Bo, Y.; Altom, J. D.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 6771-6772. (c) Trost, B.; Van Vranken, D.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327-9343.

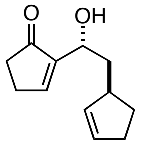
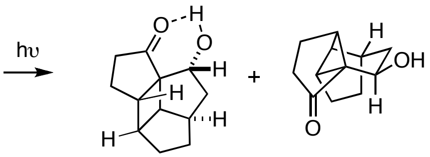
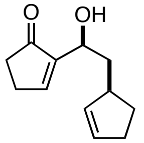
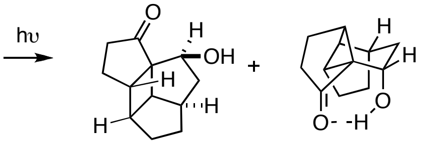
[12] Chong, K.; Scheffer, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 4040-4041.

Scheme II.7. Synthesis of Sterically Hindered Enones.



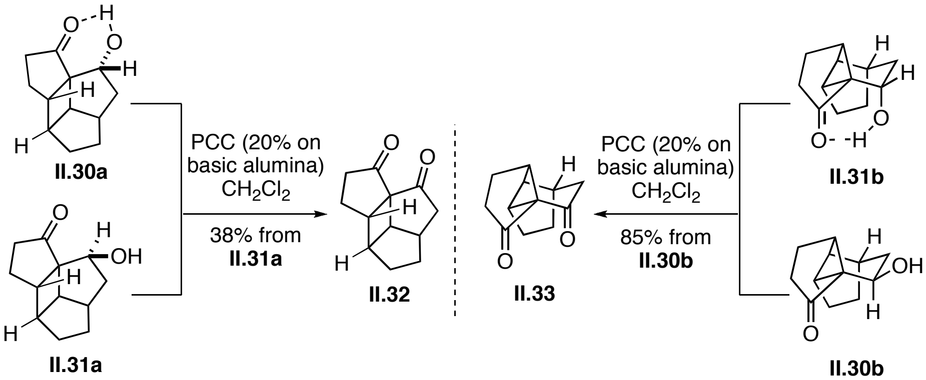
Enone **II.28** underwent an intramolecular photochemical cycloaddition in methylene chloride to give the head-to-head cycloadduct **II.30a** as the major product, albeit in low yield (Table II.4). Using acetone/water as the solvent, however, disrupted the intramolecular hydrogen bond in **II.28**, forcing the cycloaddition to go in a head-to-tail fashion to provide compound **II.30b** as the major isolable product. Likewise, when diastereomer **II.29** was subjected to the same set of reaction conditions, a similar but less pronounced selectivity trend was observed. Irradiation of enone **II.29** in a protic medium afforded mainly the head-to-head cycloadduct **II.31a**, while switching the solvent to dichloromethane generated more of the head-to-tail regioisomer **II.31b**, but still in a minor amount compared to **II.31a** (entry 2). For this series of photocycloadditions, the limited olefin accessibility, along with the absence or presence of an intramolecular hydrogen bond, played an important role in dictating the regioselective outcome of these intramolecular [2+2] photocycloadditions.

Table II.4. [2+2] Photocycloadditions of **II.28** and **II.29**.

entry	enone	cycloadduct	solvent	yield/ratio
(1)	 **II.28**	 **II.30a** **II.30b**	CH_2Cl_2 acetone/H_2O	25% **a/b** (3:1) 25% **a/b** (<1:20)
(2)	 **II.29**	 **II.31a** **II.31b**	CH_2Cl_2 acetone/H_2O	60% **a/b** (2:1) 64% **a/b** (>20:1)

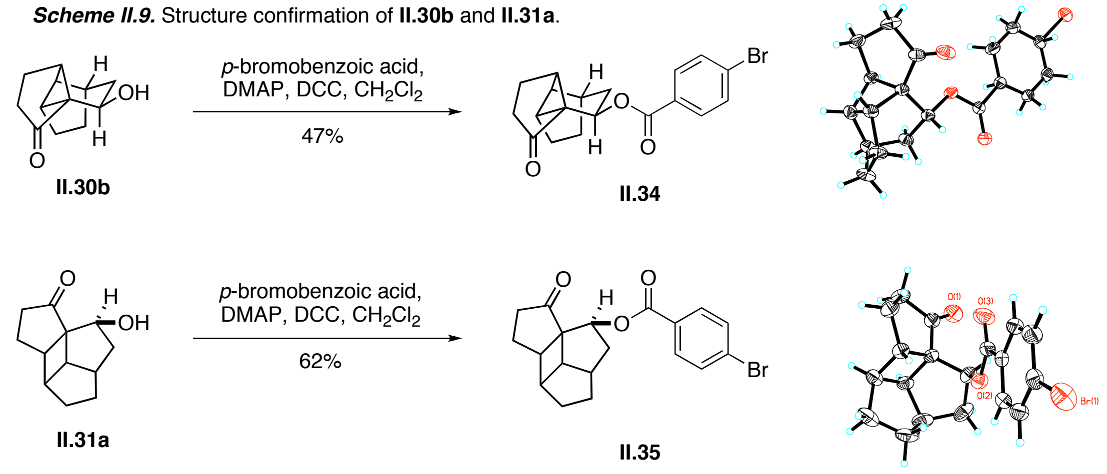
As with the previous substrates, the diastereomeric relationship of cycloadducts **II.30** and **II.31** was proven through oxidation to diketones **II.32** and **II.33** (Scheme II.8).

Scheme II.8. Oxidation of Cycloadducts **II.30** and **II.31**.



The structure of cycloadducts **II.30b** and **II.31a** was affirmed through derivitization to **II.34** and **II.35**, respectively (Scheme II.9).

Scheme II.9. Structure confirmation of **II.30b** and **II.31a**.



II.4 Conclusion

We have been able to demonstrate that hydrogen bonding plays a role in the intramolecular [2+2] photocycloadditions of β-hydroxyenones. An intramolecular hydrogen bond between the 2’-hydroxyl group and the carbonyl can govern the facial selectivity between the two interacting π-systems under photochemical conditions. Changing the tether to a conformationally restricted olefin limits one π-system, affording complimentary regioselective cycloadditions in protic and aprotic solvents.

II.5. Experimental Section

Starting materials and reagents were purchased from commercial suppliers and used without further purification except the following: triethylamine and pentane were distilled from CaH_2 under anhydrous nitrogen atm; tetrahydrofuran, benzene, diethyl ether, and dichloromethane were dried on alumina columns using a solvent dispensing system;[1] pentane, hexanes, and diethyl ether used in chromatography were distilled prior to use. All reactions were conducted in oven- (135 °C) and flame-dried glassware under an inert atm of dry nitrogen. *n*-BuLi was titrated using menthol and N-phenylnapthylamine in diethyl ether.

Infrared (**FTIR**) spectra were recorded on a Nicolet 210 FT-Infrared spectrophotometer or a Nicolet Avatar 360 spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). Proton nuclear magnetic resonance spectra (**^{1}H NMR**) were recorded on either a Varian Gemini-400 instrument (400 MHz), or a Varian Gemini-500 instrument (500 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent reference as the internal standard ($CHCl_3$: δ 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), coupling constants (Hz), and integration. **^{13}C NMR** spectra were recorded on either a Varian Gemini-400 instrument (100 MHz), or a Varian Gemini-500 instrument (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ

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[1] Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J *Organometallics* **1996**, *15*, 1518-1520.

77.23 ppm). Elemental analyses (**Anal.**) were performed by Robertson Microlit Laboratories, Inc. Madison, NJ and are reported in percent abundance. High resolution mass spectral analyses (**HRMS**) were performed by Mass Spectrometry Facility, Boston College.

X-ray data were collected using a Bruker SMART APEX CCD (charge coupled device) based diffactometer with Mo (λ=0.71073 Å) radiation equipped with an LT-3 low-temperature apparatus operating at 183 K. A stable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 s, such that a hemisphere was collected. A total of 1305 frames were collected with a maximum resolution of 0.75 Å. Cell parameters were retrieved using SMART[2] software and refined using SAINT on all observed reflections. The structures are solved by the direct method using the SHELXS-97[3] program and refined by least squares method on F^2, SHELXTL-97,[4] incorporated in SHELXTL-PC V 5.10.[5] The crystals used for the diffraction studies showed no decomposition during data collection. The drawing was displayed at 35 % ellipsoids.

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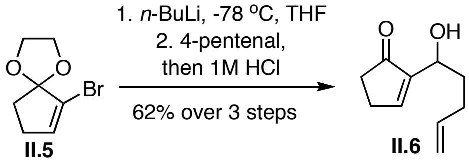
[2] SMART V 5.050 (NT) *Software for the CCD Detector System;* Bruker Analytical X-ray Systems, Madison, WI (1998).

[3] Sheldrick, G.M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany, 1990.

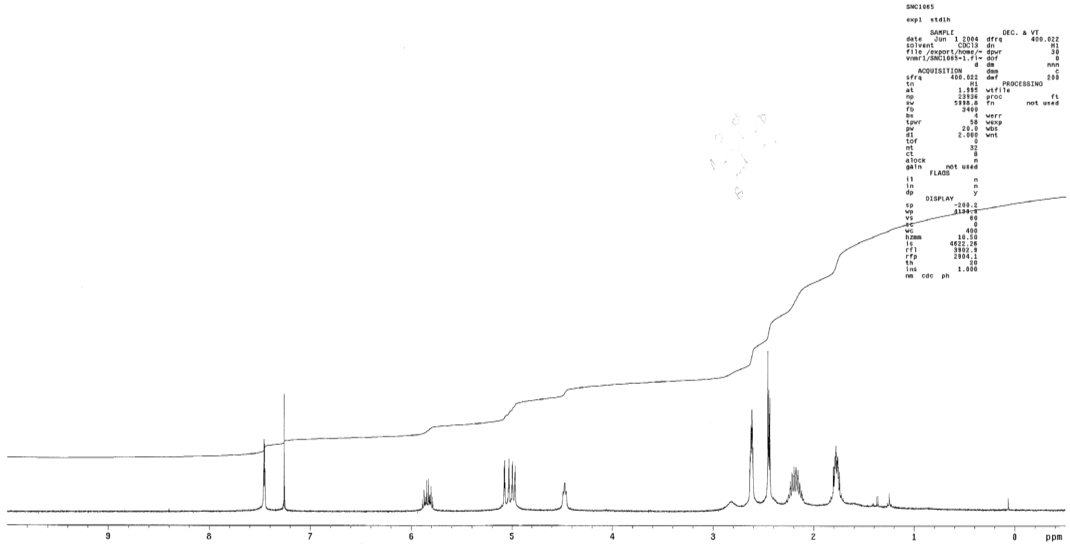
[4] Sheldrick, G.M. SHELXS-97, *Program for the Refinement of Crystal Structure*, University of Gottingen, Germany, 1997.

[5] SHELXTL 5.10 (PC-Version), *Program Library for Structure Solution and Molecular Graphics;* Bruker Analytical X-ray Systems, Madison, WI (1998).



A solution of **II.5** (200 mg, 0.99 mmol) in THF (1.95 mL) under N_2 in a flame dried round bottom flask was cooled to -78 °C and treated with *n*-BuLi (0.99 mmol, 1.8 M) in hexanes. After 1 h, pent-4-enal (81.9 mg, 0.99 mmol) was added dropwise at -78 °C. The mixture was allowed to stir at -78 °C for 1 h, after which it was allowed to warm to room temperature. The reaction was quenched with HCl (1M, 2 mL) and stirred for 30 min to fully deprotect the ketal. The aqueous layer was extracted with Et_2O (2 x 5 mL) and the combined organic layers were washed with brine (5 mL) and dried with $MgSO_4$. The solution was filtered and evaporated *in vacuo*. Product was purified by silica gel chromatography (pentane:Et_2O 4:1) to give compound **II.6** (100 mg, 62 % yield) as a pale yellow oil.

2-(1-hydroxypent-4-enyl)cyclopent-2-enone (II.6): R_f 0.24 (pentane:Et_2O 4:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.45 (td, 1H, J = 2.4, 1.0 Hz), 5.83 (ddt, 1H, J = 16.8, 10.4, 6.8 Hz), 5.02 (m, 2H), 4.47 (t, 1H, J = 6.0 Hz), 2.82 (br s, 1H, O-H) 2.62 (m, 2H), 2.45 (m, 2H), 2.18 (m, 2H), 1.78 (m, 2H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 209.9, 157.9, 147.6, 138.1, 115.2, 67.5, 35.4, 35.0, 29.8, 26.8. **IR** (NaCl, thin film) 3468 (br), 2974 (m), 2922 (s), 2858 (m), 1703 (s) cm^{-1}. **HRMS** (M + Na) $C_{10}H_{14}O_2Na$ Calcd: 189.0891. Found: 189.0897.



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SNC1065

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vnmr1/SNC1065=1.fi~ dof                0
                  d  dm              nnn
   ACQUISITION       dmm               c
sfrq        400.022  dmf             200
tn               H1       PROCESSING
at            1.995  wtfile
np            23936  proc             ft
sw           5998.8  fn         not used
fb             3400
bs                4  werr
tpwr             58  wexp
pw             20.0  wbs
d1            2.000  wnt
tof               0
nt               32
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
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wp           4199.8
vs               60
sc                0
wc              400
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rfp          2904.1
th               20
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nm  cdc  ph
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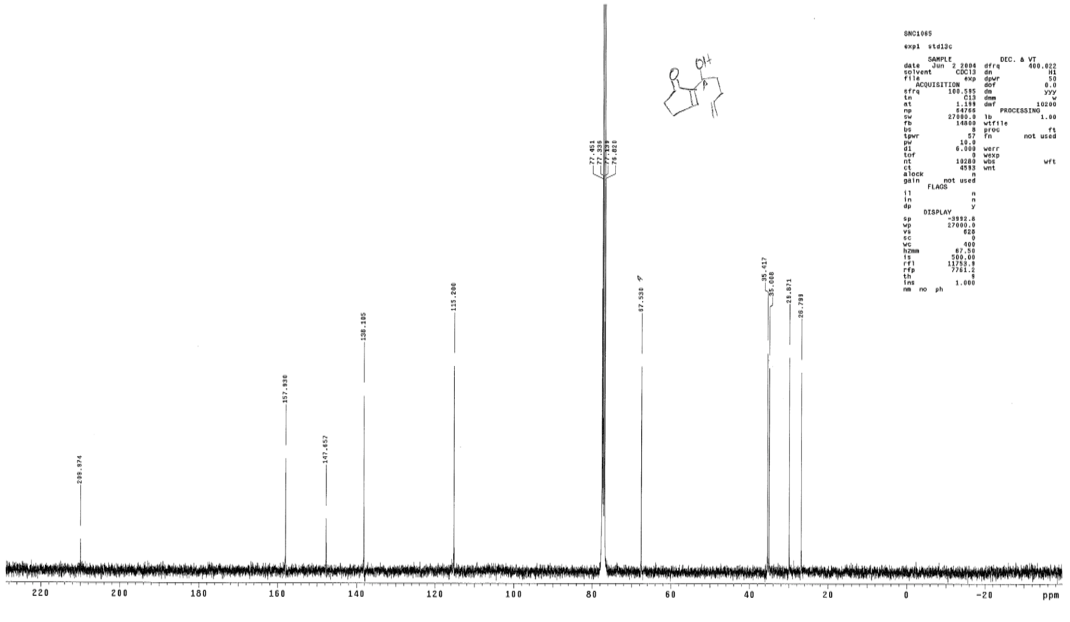

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SNC1065

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tn              C13  dmm               w
at            1.199  dmf           10200
np            64766       PROCESSING
sw          27000.0  lb             1.00
fb            14800  wtfile
bs                8  proc             ft
tpwr             57  fn         not used
pw             10.0
d1            6.000  werr
tof               0  wexp
nt            10280  wbs             wft
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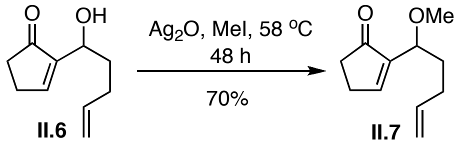
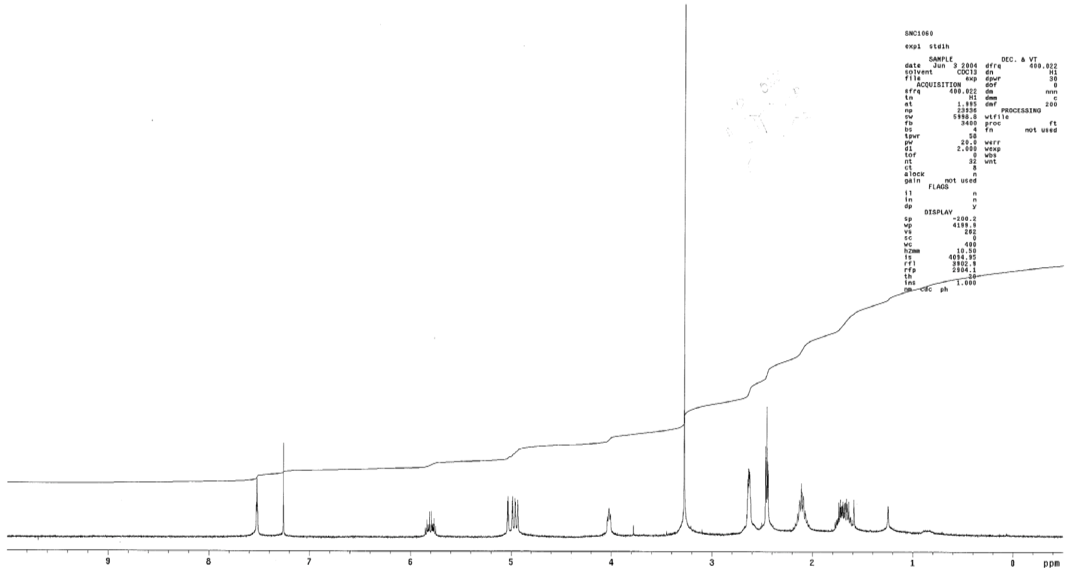


MeI (0.19 mL, 3.0 mmol) and Ag$_2$O (76.7 mg, 0.33 mmol) were added to a solution of enone **II.6** (50.0 mg, 0.30 mmol) in acetonitrile (0.50 mL) in a dry heavy walled reaction tube. The reaction was purged with nitrogen and sealed with a Teflon screw cap. The reaction was allowed to stir at 58 °C for 2 d, then allowed to cool to room temperature and diluted with diethyl ether (2 mL). The solution was filtered through celite. The solvent was removed *in vacuo*. Product was purified by silica gel chromatography (pentane:Et$_2$O 3:2) to give compound **II.7** (32.2 mg, 70 % yield, 85% conversion) as a pale yellow oil.

2-(1-methoxypent-4-enyl)cyclopent-2-enone (II.7): R$_f$ 0.43 (pentane:Et$_2$O 3:2); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 7.52 (td, 1H, J = 2.4, 1.2 Hz), 5.80 (ddt, 1H, J = 16.8, 10.0, 6.4 Hz), 4.97 (m, 2H), 4.02 (m, 1H), 3.27 (s, 3H), 2.63 (m, 2H), 2.45 (m, 2H), 2.10 (m, 2H), 1.68 (m, 2H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 208.5, 158.7, 146.6, 138.1, 114.8, 75.5, 57.3, 35.5, 34.0, 29.6, 26.8. **IR** (NaCl, thin film) 2977 (m), 2926 (m), 1701 (s), 1106 (m) cm^{-1}. **HRMS** (M + Na) $C_{11}H_{16}O_2Na$ Calcd: 203.1048. Found: 203.1050.


SNC1060
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ct 8
alock n
gain not used
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il n
in n
dp y
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vs 262
sc 0
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hzmm 10.50
is 4094.95
rfl 3902.9
rfp 2904.1
th 20
ins 1.000
nm cdc ph
DEC. & VT
dfrq 400.022
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dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
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werr
wexp
wbs
wnt
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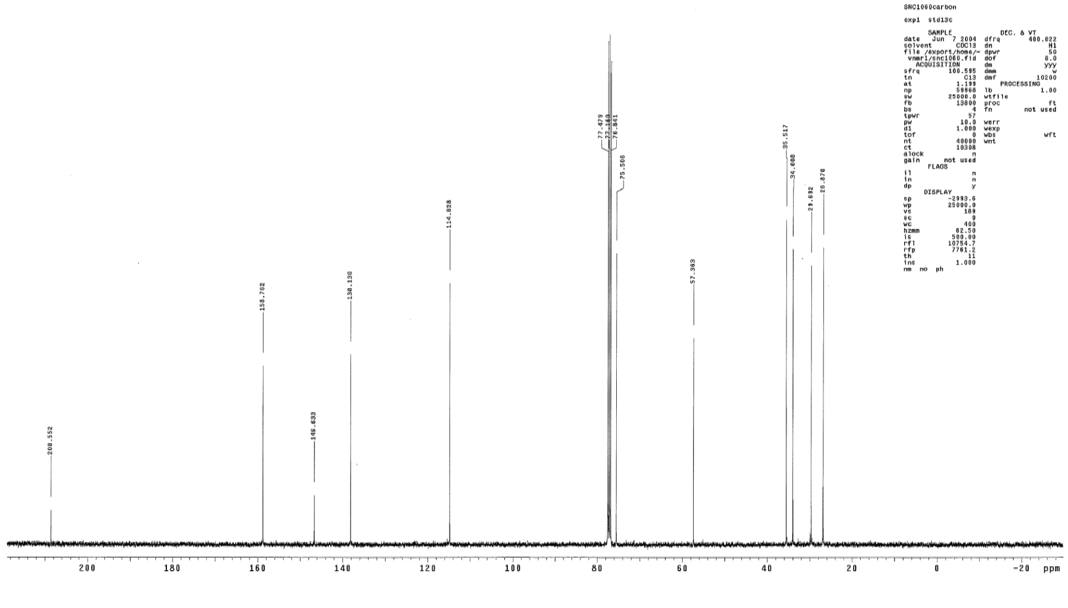
8
7
6
5
4
3
2
1
0
ppm


SNC1060carbon
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date Jun 7 2004
solvent CDCl3
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tn C13
at 1.199
np 59968
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fb 13800
bs 4
tpwr 57
pw 10.0
d1 1.000
tof 0
nt 40000
ct 10308
alock n
gain not used
FLAGS
il n
in n
dp y
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wp 25000.0
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sc 0
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is 500.00
rfl 10754.7
rfp 7761.2
th 11
ins 1.000
nm no ph
DEC. & VT
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dmm w
dmf 10200
PROCESSING
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wtfile
proc ft
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wexp
wbs wft
wnt
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75.506
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20
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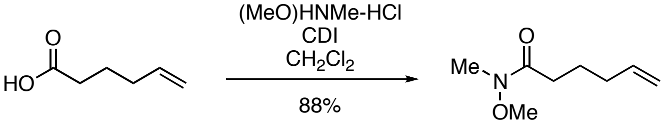
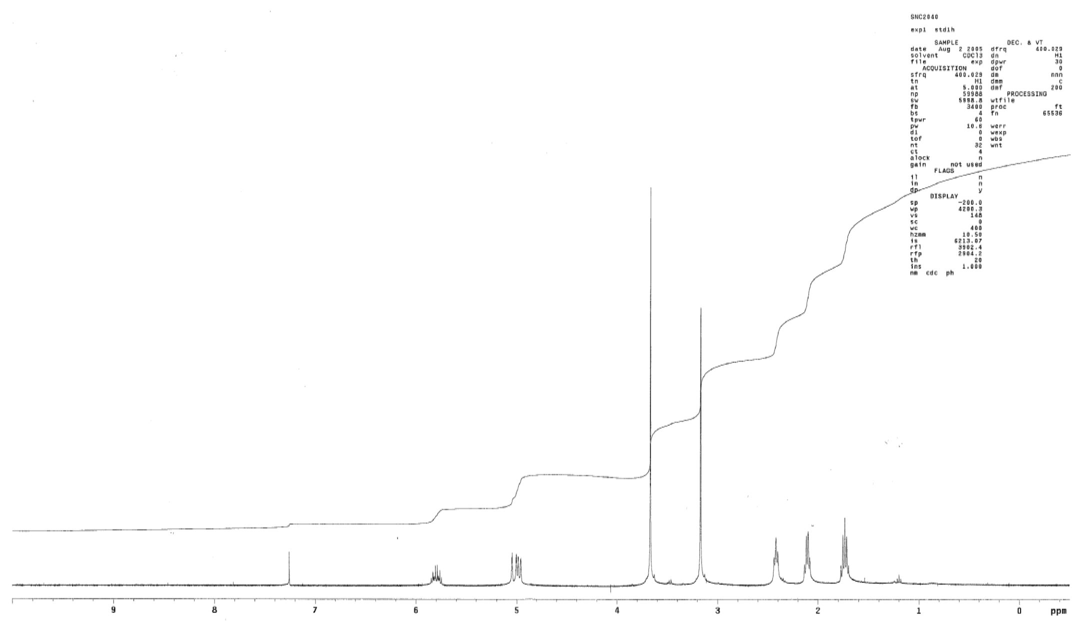
ppm



II.8

A solution of 5-hexenoic acid (500 mg, 4.37 mmol) in CH_2Cl_2 (21.9 mL) was cooled to 0 °C in a flame dried flask. 1,1'-Carbonyl diimidazole (850 mg, 5.24 mmol) was added to the reaction mixture at this temperature. After stirring for 30 min, N,O-dimethyl hydroxylamine hydrochloride (1.06 g, 10.9 mmol) was added and the reaction was warmed to room temperature. After 4 h (judged complete by TLC), the salts were filtered through a cotton plug and the filtrate was washed with aqueous HCl (25 mL, 1 M) and brine (25 mL). The organic layer was dried with $MgSO_4$ and concentrated to obtain a clear oil (605 mg, 88 % yield). The product was taken on to the next step without further purification.

Weinreb amide (II.8): R_f 0.30 (pentane:Et_2O 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 5.79 (ddt, 1H, J = 16.4, 10.0, 6.0 Hz), 4.98 (m, 2H), 3.65 (s, 3H), 3.17 (s, 3H), 2.40 (t, 1H, J = 8.0 Hz), 2.32 (t, 1H, J = 8.0 Hz), 2.08 (q, 2H, J = 7.0 Hz), 1.71 (p, 2H, J = 7.6 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 174.4, 138.1, 115.1, 61.4, 33.5, 32.5, 31.4, 23.9. **IR** (NaCl, thin film) 3075 (w), 2949 (m), 2895 (w), 1732 (m), 1666 (s), 1460 (m), 1385 (m) cm^{-1}. **HRMS** (M + H) $C_8H_{16}NO_2$ Calcd: 158.1181. Found: 158.1180.



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SNC2040

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tn              H1  dmm              c
at           5.000  dmf            200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc            ft
bs               4  fn           65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs
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alock            n
gain      not used
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in               n
dp               y
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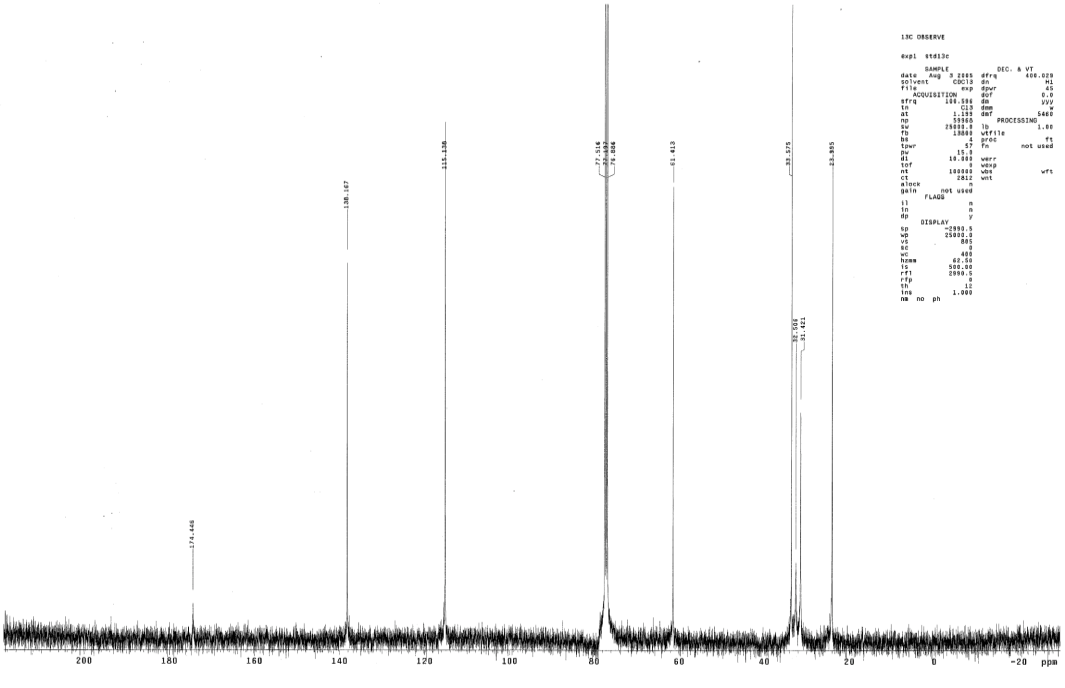

```
13C OBSERVE

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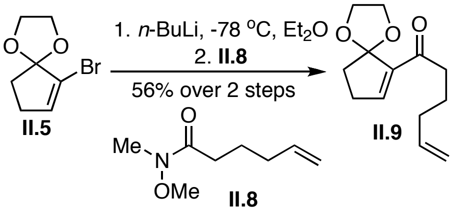
sfrq       100.596  dm             yyy
tn             C13  dmm              w
at           1.199  dmf           5460
np           59968       PROCESSING
sw         25000.0  lb            1.00
fb           13800  wtfile
bs               4  proc            ft
tpwr            57  fn        not used
pw            15.0
d1          10.000  werr
tof              0  wexp
nt          100000  wbs            wft
ct            2812  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp         -2990.5
wp         25000.0
vs             805
sc               0
wc             400
hzmm         62.50
is          500.00
rfl         2990.5
rfp              0
th              12
ins          1.000
nm  no  ph
```



A solution of **II.5** (100 mg, 0.49 mmol) in dry Et_2O (0.98 mL) was cooled to -78 °C under N_2. Freshly titrated *n*-BuLi (0.49 mmol, 2.0 M) in hexanes was added dropwise and the reaction mixture was allowed to stir at -78 °C for 1 h. Weinreb amide **II.8** (77 mg, 0.49 mmol) was added dropwise and the mixture was allowed to stir for 1.5 h, at which time it was warmed to room temperature and quenched with water (2 mL). The ethereal layer was washed with saturated KH_2PO_4 (5 mL) and brine (5 mL). The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified on silica gel (pentane:Et_2O 4:1) to give product **II.9** (61 mg, 56 % yield) as a pale yellow oil.

1-(1,4-dioxaspiro[4.4]non-6-en-6-yl)hex-5-en-1-one (II.9): R_f 0.42 (pentane:Et_2O 3:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.01 (t, 1H, J = 2.8 Hz), 5.77 (ddt, 1H, J = 16.8, 10, 6.4 Hz), 4.99 (m, 2H), 4.21 (m, 2H), 3.96 (m, 2H), 2.66 (t, 2H, J = 7.2 Hz), 2.47 (td, 2H, J = 6.4, 2.8 Hz), 2.14 (t, 2H, J = 6.8 Hz), 2.07 (dd, 2H, J = 14.4, 7.2 Hz), 1.71 (tt, 2H, J = 14.8, 7.6 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 197.6, 149.2, 143.4, 138.4, 118.7, 115.3, 66.0, 39.4, 37.2, 33.3, 28.2, 23.0. **IR** (NaCl, thin film) 3019 (m), 2924 (s), 2838 (w), 1679 (s), 924 (m), 775 (m) cm^{-1}. **HRMS** (M + H) $C_{13}H_{19}O_3$ Calcd: 223.1334. Found: 223.1330.

```
SNC2042

exp1  stdlh

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sfrq       400.029   dm             nnn
tn              H1   dmm              c
at           5.000   dmf            200
np           59988       PROCESSING
sw          5998.8   wtfile
fb            3400   proc            ft
bs               4   fn           65536
tpwr            60
pw            10.6   werr
d1               0   wexp
tof              0   wbs
nt              32   wnt
ct              16
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs              38
sc               0
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rfl         3902.4
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
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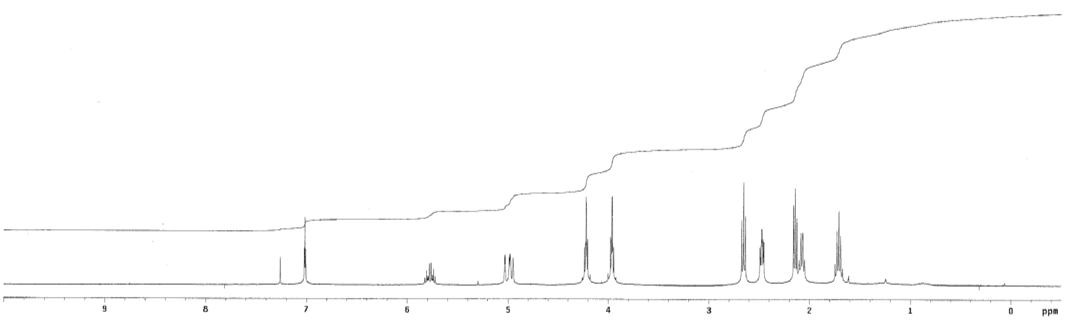

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vnmr1/SNC2042carbo~  dof              0
             n.fid   dm               y
   ACQUISITION       dmm              w
sfrq       125.684   dmf          12346
tn             C13   dseq
at           0.999   dres           1.0
np           60288   homo             n
sw         30165.9   temp          28.0
fb           17000         DEC2
bs               4   dfrq2            0
tpwr            61   dn2
pw             5.0   dpwr2            1
d1           6.000   dof2             0
tof         1759.4   dm2              n
nt           10000   dmm2             c
ct             400   dmf2         10000
alock            n   dseq2
gain            50   dres2          1.0
      FLAGS          homo2            n
il               n       PROCESSING
in               n   lb            1.00
dp               y   wtfile
hs              nn   proc            ft
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sp         -1383.5   math             f
wp         30165.9
vs            2384   werr
sc               0   wexp
wc             380   wbs            wft
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rfp              0
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ai    ph
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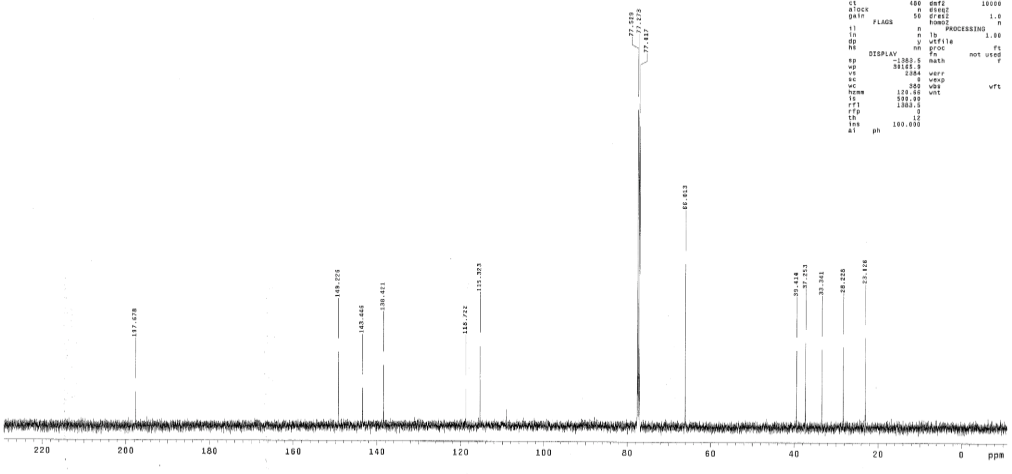
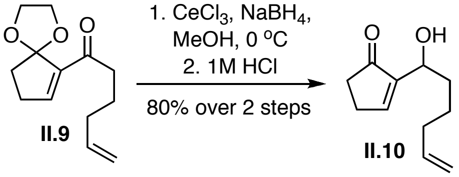
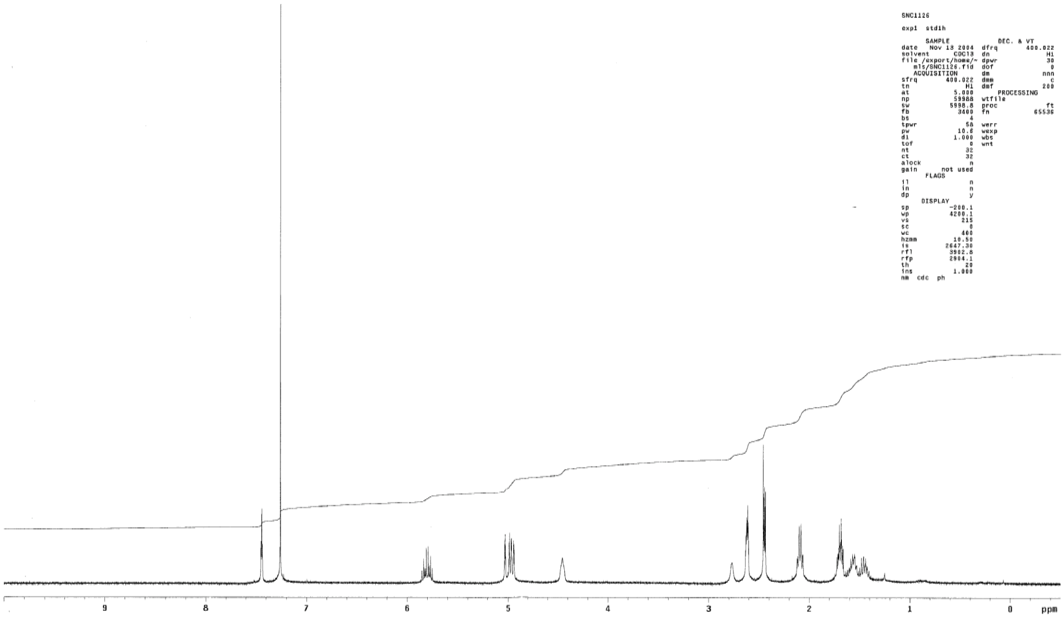




To a solution of compound **II.9** (81.5 mg, 0.367 mmol) and methanol (3.67 mL) cooled to 0 °C was added $CeCl_3{\bullet}7H_2O$ (164 mg, 0.44 mmol) and allowed to stir at 0 °C for 5 min. $NaBH_4$ (27.7 mg, 0.734 mmol) was added and allowed to stir at 0 °C for 30 min. The reaction was quenched with aqueous HCl (2 mL, 1 M) and warmed to room temperature. The reaction was allowed to stir for another 30 min at room temperature and diluted with Et_2O (6 mL) after the deprotection was deemed complete by TLC analysis. The organic layer was washed with brine (5 mL) and dried with $MgSO_4$. Product was purified through a short silica gel plug (3 cm) to give enone **II.10** (53 mg, 80 % yield) as a clear oil.

2-(1-hydroxyhex-5-enyl)cyclopent-2-enone (II.10): R_f 0.17 (pentane:Et_2O 3:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.45 (td, 1H, J = 2.8, 1.2 Hz), 5.80 (ddt, 1H, J = 16.8, 10.0, 6.8 Hz), 4.98 (m, 2H), 4.45 (m, 1H), 2.78 (br s, 1H, O-H) 2.61 (m, 2H), 2.45 (m, 2H), 2.10 (m, 2H), 1.68 (m, 2H), 1.57 (m, 1H), 1.46 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 210.2, 158.2, 148.1, 138.9, 115.2, 68.2, 35.9, 35.8, 34.1, 27.2, 25.4. **IR** (NaCl, thin film) 3463 (br), 2947 (m), 2862 (m), 1693 (s), 1638 (m), 1439 (m), 1000 (m) cm^{-1}. **HRMS** (M + Na) $C_{11}H_{16}O_2Na$ Calcd: 203.1048. Found: 203.1044.



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SNC1126

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   mls/SNC1126.fid  dof              0
   ACQUISITION      dm             nnn
sfrq       400.022  dmm              c
tn              H1  dmf            200
at           5.000      PROCESSING
np           59988  wtfile
sw          5998.8  proc            ft
fb            3400  fn           65536
bs               4
tpwr            58  werr
pw            10.6  wexp
d1           1.000  wbs
tof              0  wnt
nt              32
ct              32
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.1
wp          4200.1
vs             215
sc               0
wc             400
hzmm         10.50
is         2647.30
rfl         3902.8
rfp         2904.1
th              20
ins          1.000
nm  cdc  ph
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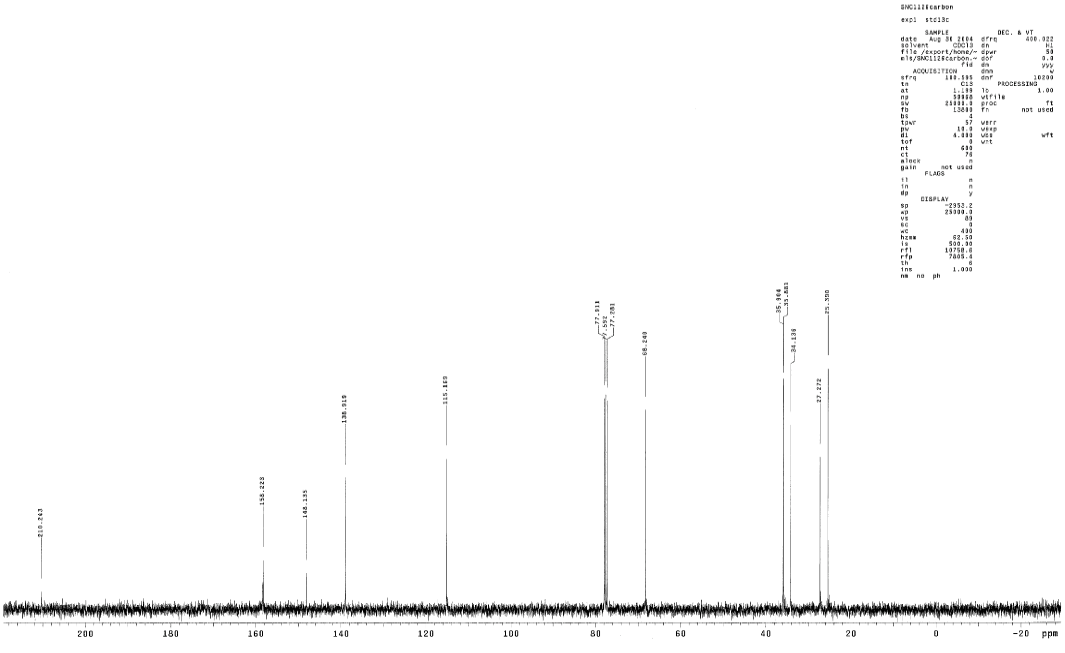

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SNC1126carbon

exp1  std13c

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               fid  dm             yyy
   ACQUISITION      dmm              w
sfrq       100.595  dmf          10200
tn             C13      PROCESSING
at           1.199  lb            1.00
np           59968  wtfile
sw         25000.0  proc            ft
fb           13800  fn        not used
bs               4
tpwr            57  werr
pw            10.0  wexp
d1           4.000  wbs            wft
tof              0  wnt
nt             600
ct              76
alock            n
gain      not used
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in               n
dp               y
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wp         25000.0
vs              89
sc               0
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hzmm         62.50
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rfp         7805.4
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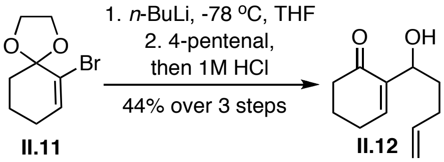
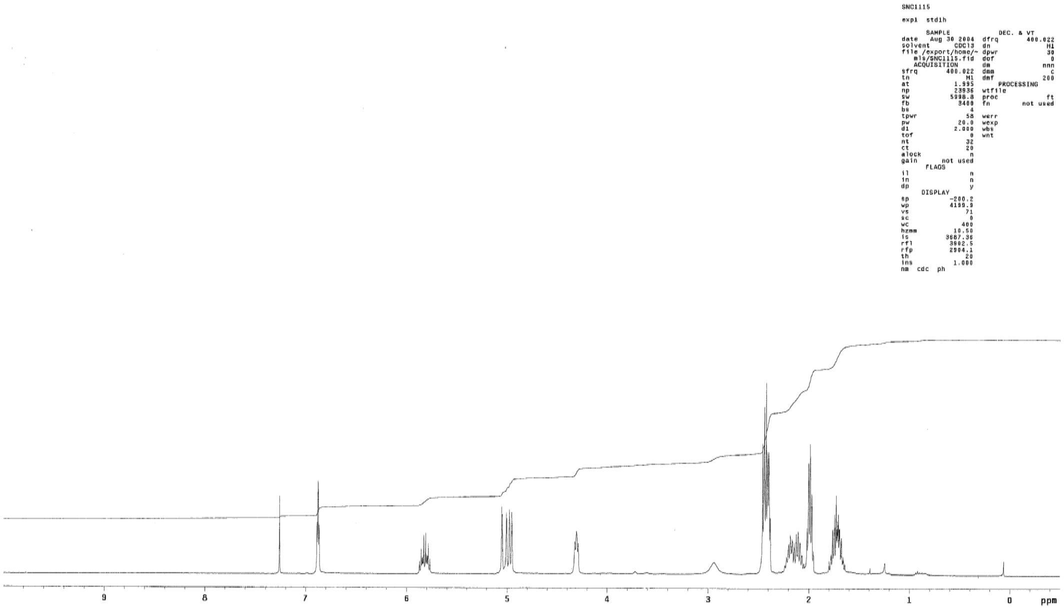


II.11 **II.12**

A solution of **II.11** (100 mg, 0.46 mmol) in Et_2O (0.913 mL) under N_2 in a flame dried round bottom flask was cooled to -78 °C and treated with *n*-BuLi (0.25 mL, 1.8 M) in hexanes. After 1 h, pent-4-enal (38.3 mg, 0.46 mmol) was added dropwise at -78 °C. The mixture was allowed to stir at -78 °C for 1 hr, after which it was allowed to warm to room temperature. The reaction was quenched with aqueous HCl (2 mL, 1 M) and stirred for 30 min to fully deprotect the ketal. The aqueous layer was extracted with Et_2O (2 x 5 mL) and the combined organic layers were washed with brine (5 mL) and dried with $MgSO_4$. The solution was filtered and evaporated *in vacuo*. Product was purified by silica gel chromatography (pentane:Et_2O 3:2) to give compound **II.12** (35.9 mg, 44 % yield) as a pale yellow oil.

2-(1-hydroxypent-4-enyl)cyclohex-2-enone (II.12): R_f 0.19 (pentane:Et_2O 3:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 6.87 (t, 1H, J = 4.4 Hz), 5.81 (ddt, 1H, J = 16.8, 9.6, 6.4 Hz), 4.99 (m, 2H), 4.30 (t, 1H, J = 6.4 Hz), 2.93 (br s, 1H, O-H) 2.42 (m, 4H), 2.13 (m, 2H), 1.98 (m, 2H), 1.72 (m, 2H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 200.8, 146.3, 141.1, 138.6, 115.3, 71.7, 39.3, 35.9, 30.8, 26.3, 23.2. **IR** (NaCl, thin film) 3441 (br), 2951 (s), 2869 (s), 1659 (s), 1429 (m), 1382 (m), 1172 (m), 915 (m) cm^{-1}. **HRMS** (M + Na) $C_{11}H_{16}O_2Na$ Calcd: 203.1048 Found: 203.1049.



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SNC1115

exp1  std1h

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sfrq       400.022  dmm               c
tn              H1  dmf             200
at           1.995      PROCESSING
np           23936  wtfile
sw          5998.8  proc             ft
fb            3400  fn         not used
bs               4
tpwr            58  werr
pw            20.0  wexp
d1           2.000  wbs
tof              0  wnt
nt              32
ct              20
alock            n
gain      not used
      FLAGS
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in               n
dp               y
     DISPLAY
sp          -200.2
wp          4199.9
vs              71
sc               0
wc             400
hzmm         10.50
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rfl         3902.5
rfp         2904.1
th              20
ins          1.000
nm  cdc  ph
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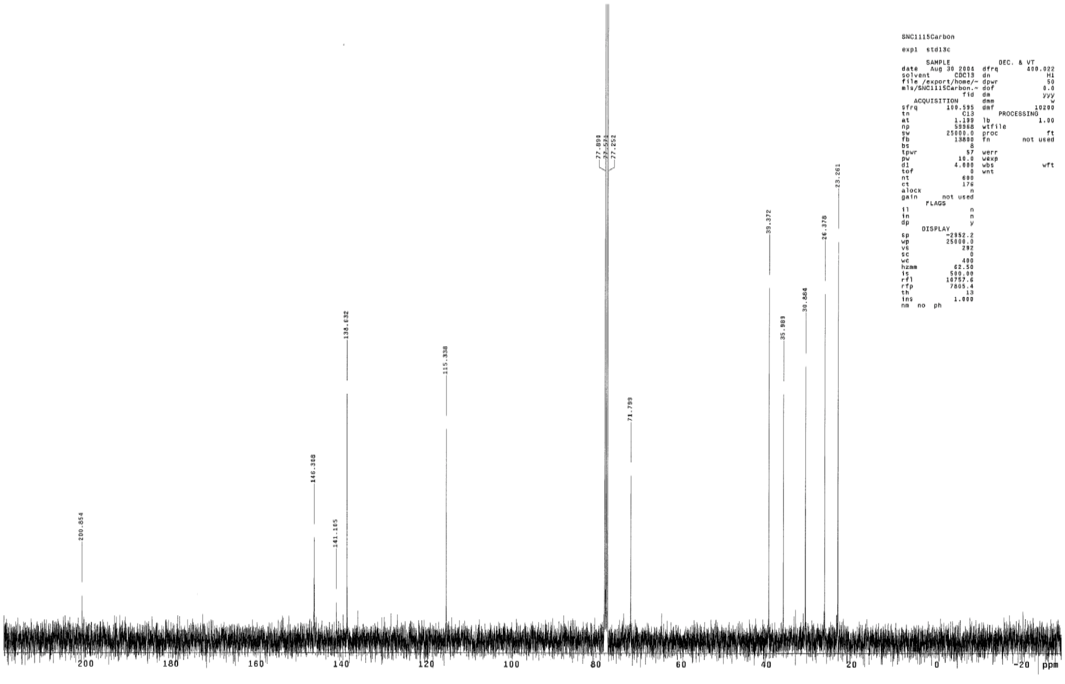

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SNC1115Carbon

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mls/SNC1115Carbon.~ dof             0.0
               fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       100.595  dmf           10200
tn             C13      PROCESSING
at           1.199  lb             1.00
np           59968  wtfile
sw         25000.0  proc             ft
fb           13800  fn         not used
bs               8
tpwr            57  werr
pw            10.0  wexp
d1           4.000  wbs             wft
tof              0  wnt
nt             600
ct             176
alock            n
gain      not used
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il               n
in               n
dp               y
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wp         25000.0
vs             292
sc               0
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rfl        10757.6
rfp         7805.4
th              13
ins          1.000
nm  no  ph
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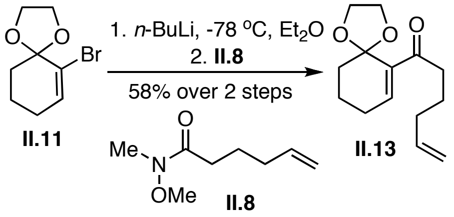
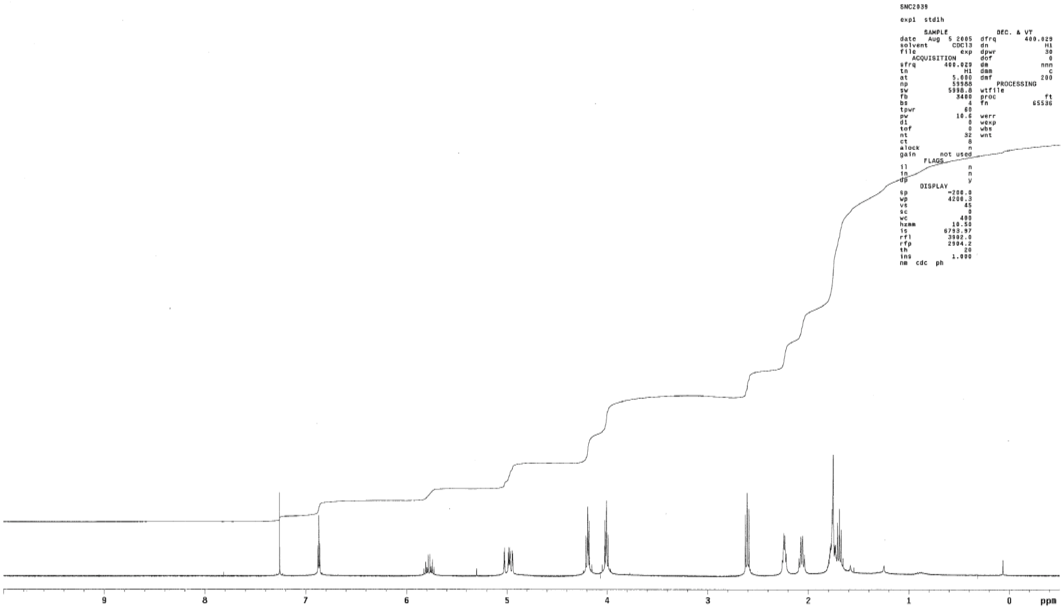


A solution of **II.11** (100 mg, 0.456 mmol) in dry diethyl ether (0.913 mL) was cooled to -78 °C under N_2. Freshly titrated *n*-BuLi (0.456 mmol, 2.0 M) in hexanes was added dropwise and the reaction mixture was allowed to stir at -78 °C for 1 h. Weinreb amide **II.8** (71.6 mg, 0.456 mmol) was added dropwise and the mixture was allowed to stir for 1.5 h, at which time it was warmed to room temperature and quenched with water (2 mL). The ethereal layer was washed with saturated KH_2PO_4 (5 mL) and brine (5 mL). The organic layer was dried with $MgSO_4$ and concentrated. Product was purified on silica gel (pentane: Et_2O 4:1) to give product **II.13** (63.2 mg, 58 % yield) as a pale yellow oil.

1-(1,4-dioxaspiro[4.5]dec-6-en-6-yl)hex-5-en-1-one (II.13): R_f 0.29 (pentane:Et_2O 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.87 (t, 1H, *J* = 3.6 Hz), 5.77 (ddt, 1H, *J* = 17.2, 10.4, 6.8 Hz), 4.98 (m, 2H), 4.19 (m, 2H), 4.00 (m, 2H), 2.60 (t, 2H, *J* = 7.6 Hz), 2.23 (dd, 2H, *J* = 9.2, 5.2 Hz), 2.06 (dd, 2H, *J* = 14.4, 7.2 Hz), 1.72 (m, 6H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 201.1, 143.3, 139.7, 138.5, 115.2, 106.6, 65.3, 39.4, 34.5, 33.4, 26.0, 23.2, 19.9. **IR** (NaCl, thin film) 2950 (s), 2892 (m), 1685 (s), 1631 (w), 1188 (m) cm^{-1}. **HRMS** (M + H) $C_{14}H_{21}O_3$ Calcd: 237.1491. Found: 237.1481.



```
SNC2039

exp1  std1h

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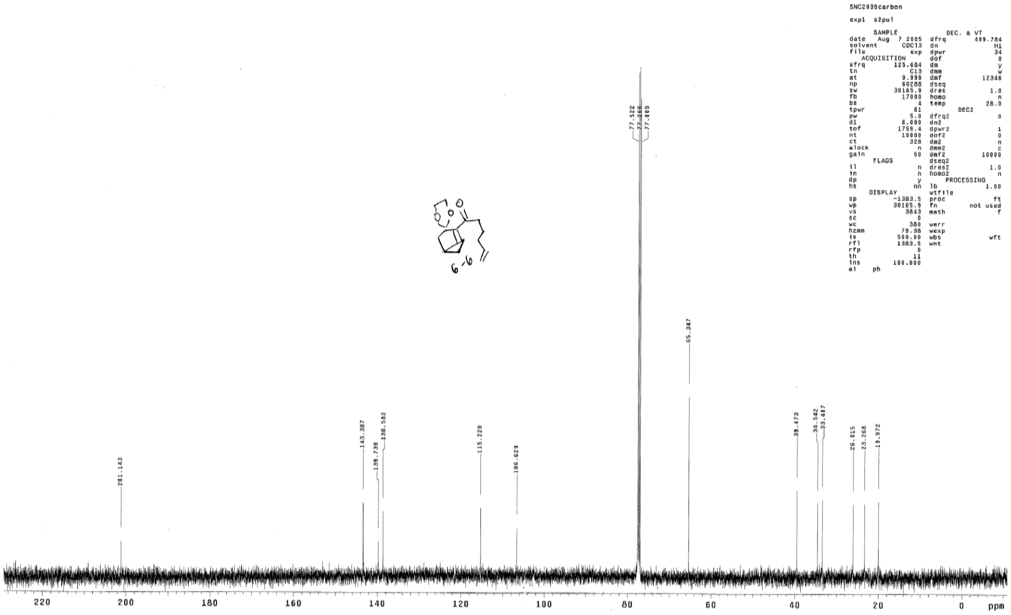
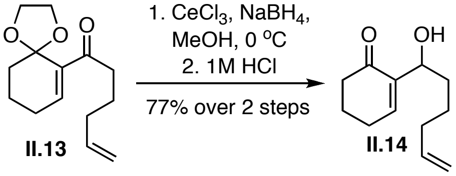
   ACQUISITION      dof               0
sfrq       400.029  dm              nnn
tn              H1  dmm               c
at           5.000  dmf             200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn            65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs
nt              32  wnt
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs              45
sc               0
wc             400
hzmm         10.50
is         6793.97
rfl         3802.0
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
```



```
SNC2039carbon

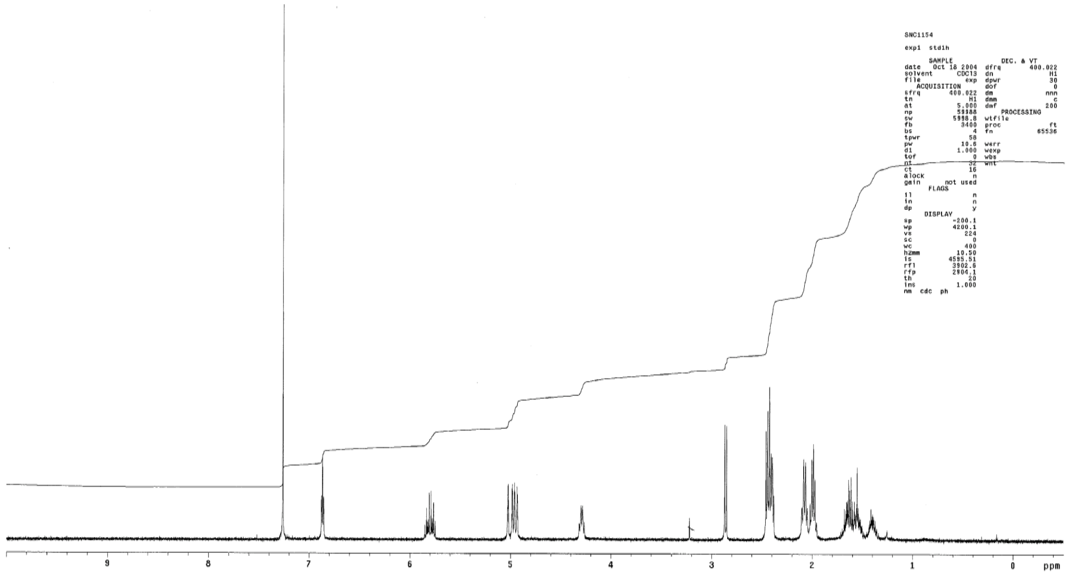
exp1  s2pul

      SAMPLE            DEC. & VT
date   Aug  7 2005  dfrq        499.784
solvent      CDCl3  dn               H1
file           exp  dpwr             34
   ACQUISITION      dof               0
sfrq       125.684  dm                y
tn             C13  dmm               w
at           0.999  dmf           12346
np           60288  dseq
sw         30165.9  dres            1.0
fb           17000  homo              n
bs               4  temp           28.0
tpwr            61        DEC2
pw             5.0  dfrq2             0
d1           6.000  dn2
tof         1759.4  dpwr2             1
nt           10000  dof2              0
ct             328  dm2               n
alock            n  dmm2              c
gain            50  dmf2          10000
      FLAGS         dseq2
il               n  dres2           1.0
in               n  homo2             n
dp               y       PROCESSING
hs              nn  lb             1.00
     DISPLAY        wtfile
sp         -1383.5  proc             ft
wp         30165.9  fn         not used
vs            3843  math              f
sc               0
wc             380  werr
hzmm         79.38  wexp
is          500.00  wbs             wft
rfl         1383.5  wnt
rfp              0
th              11
ins        100.000
ai    ph
```



To a solution of compound **II.13** (110.5 mg, 0.468 mmol) and methanol (4.68 mL) cooled to 0 °C was added $CeCl_3•7H_2O$ (164 mg, 0.44 mmol) and allowed to stir at 0 °C for 5 min. $NaBH_4$ (35.4 mg, 0.93 mmol) was added and allowed to stir at 0 °C for 30 min. The reaction was quenched with 1 M HCl (2 mL) and warmed to room temperature. The reaction was allowed to stir for another 30 min at room temperature and diluted with Et_2O (6 mL) after the deprotection was deemed complete by TLC analysis. The organic layer was washed with brine (5 mL) and dried with $MgSO_4$. Product was purified through a short silica gel plug (3 cm) to give enone **11.14** (70 mg, 77 % yield) as a clear oil.

2-(1-hydroxyhex-5-enyl)cyclohex-2-enone (11.14): **R_f** 0.22 (pentane:Et_2O 3:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 6.86 (t, 1H, J = 4 Hz), 5.80 (ddt, 1H, J = 16.8, 10.0, 6.4 Hz), 4.96 (m, 2H), 4.28 (dd, 1H, J = 13.2, 7.6 Hz), 2.86 (br s, 1H, O-H) 2.41 (m, 4H), 2.07 (dd, 2H, J = 14.4, 7.6 Hz), 1.99 (dd, 2H, J = 12.8, 6.0 Hz), 1.37- 1.68 (m, 4H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 200.8, 146.1, 141.2, 139.0, 115.0, 72.0, 39.3, 36.3, 34.1, 26.3, 25.9, 23.2. **IR** (NaCl, thin film) 3438 (br), 2927 (m), 2865 (w), 1667 (s), 1382 (m), 1172 (m), 911 (m) cm^{-1}. **HRMS** (M + Na) $C_{12}H_{18}O_2Na$ Calcd: 217.1204. Found: 217.1204.



```
SNC1154

exp1  std1h

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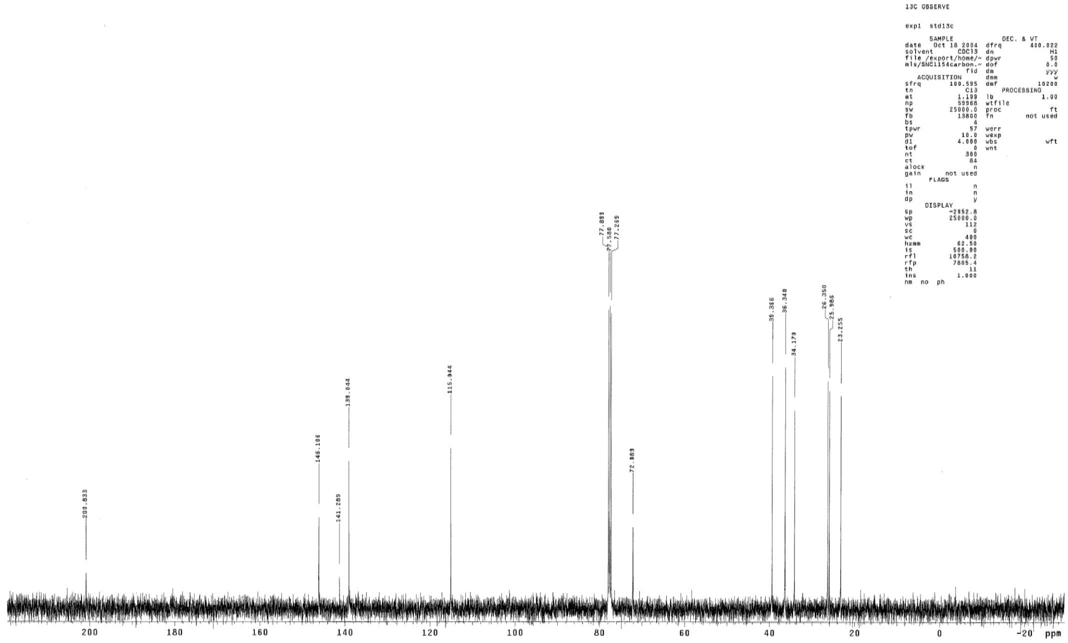
date   Oct 18 2004  dfrq        400.022
solvent      CDCl3  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       400.022  dm              nnn
tn              H1  dmm               c
at           5.000  dmf             200
np           59988      PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn            65536
tpwr            58
pw            10.6  werr
d1           1.000  wexp
tof              0  wbs
nt              32  wnt
ct              16
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp          -200.1
wp          4200.1
vs             224
sc               0
wc             400
hzmm         10.50
is         4595.51
rfl         3902.6
rfp         2904.1
th              20
ins          1.000
nm  cdc  ph
```



```
13C OBSERVE

exp1  std13c

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solvent      CDCl3  dn               H1
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mls/SNC1154carbon.~ dof             0.0
               fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       100.595  dmf           10200
tn             C13      PROCESSING
at           1.199  lb             1.00
np           59968  wtfile
sw         25000.0  proc             ft
fb           13800  fn         not used
bs               4
tpwr            57  werr
pw            10.0  wexp
d1           4.000  wbs             wft
tof              0  wnt
nt             300
ct              84
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp         -2952.8
wp         25000.0
vs             112
sc               0
wc             400
hzmm         62.50
is          500.00
rfl        10758.2
rfp         7805.4
th              11
ins          1.000
nm  no  ph
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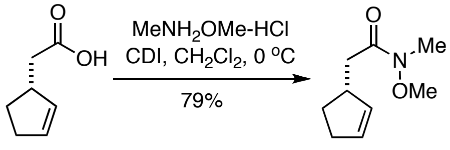
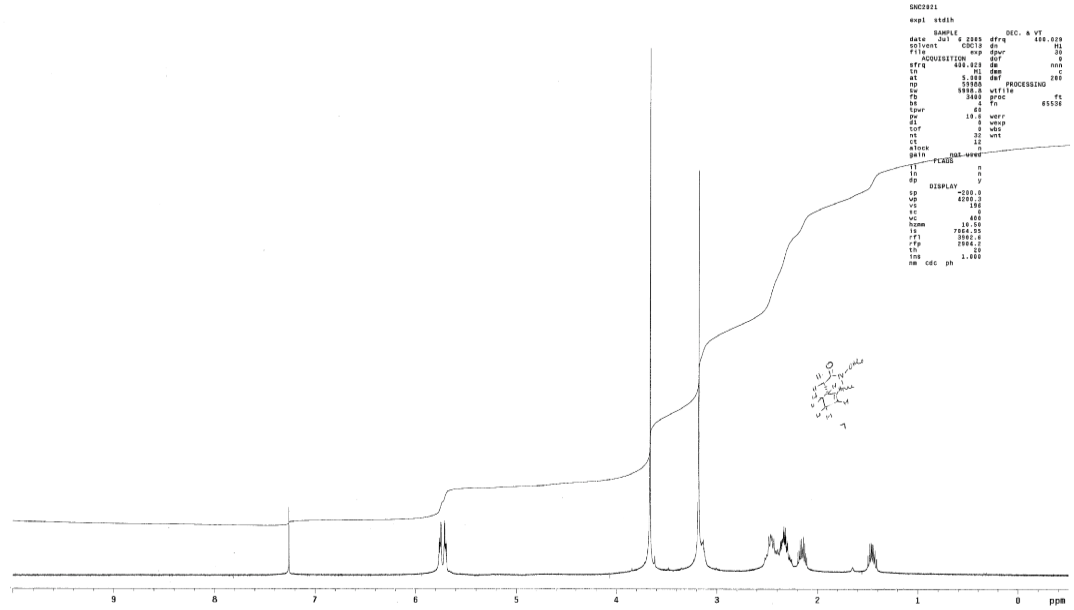


II.25 **II.26**

A solution of **II.25** (224 mg, 1.78 mmol) in CH_2Cl_2 (8.9 mL) was cooled to 0 °C in a flame dried flask. 1,1'-Carbonyl diimidazole (347 mg, 2.14 mmol) was added to the reaction mixture at this temperature. After stirring for 30 min, N,O-dimethyl hydroxylamine hydrochloride (429 mg, 4.45 mmol) was added and warmed to room temperature. After 4 h (judged complete by TLC), the salts were filtered through a cotton plug and the filtrate was washed with aqueous HCl (10 mL, 1 M) and brine (10 mL). The organic layer was dried with $MgSO_4$ and concentrated to obtain a clear oil (237 mg, 79 % yield). The product was taken on to the next step without further purification.

(R)-2-(cyclopent-2-enyl)-N-methoxy-N-methylacetamide (II.26): **R_f** 0.16 (pentane:Et_2O 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 5.72 (m, 2H), 3.67 (s, 1H), 3.66 (s, 3H), 3.18 (s, 3H), 2.30-2.50 (m, 5H), 2.15 (m, 1H), 1.45 (ddt, 1H, J = 12.8, 9.2, 6.4 Hz). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 173.8, 134.3, 130.8, 61.1, 41.7, 38.0, 32.2, 31.9, 30.0. **IR** (NaCl, thin film) 3048 (w), 2958 (m), 2895 (w), 1728 (w), 1665 (s), 1461 (w), 1384 (m) cm^{-1}. **HRMS** (M + H) $C_9H_{16}NO_2$ Calcd: 170.1181. Found: 170.1173. **$[\alpha]^{20}_D$** -98 (c = 1.00, CH_2Cl_2).



```
SNC2021

exp1  std1h

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date   Jul  6 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             30
    ACQUISITION     dof               0
sfrq       400.029  dm              nnn
tn              H1  dmm               c
at           5.000  dmf             200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn            65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs
nt              32  wnt
ct              12
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp          -200.0
wp          4200.3
vs             196
sc               0
wc             400
hzmm         10.50
is         7064.95
rfl         3902.6
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
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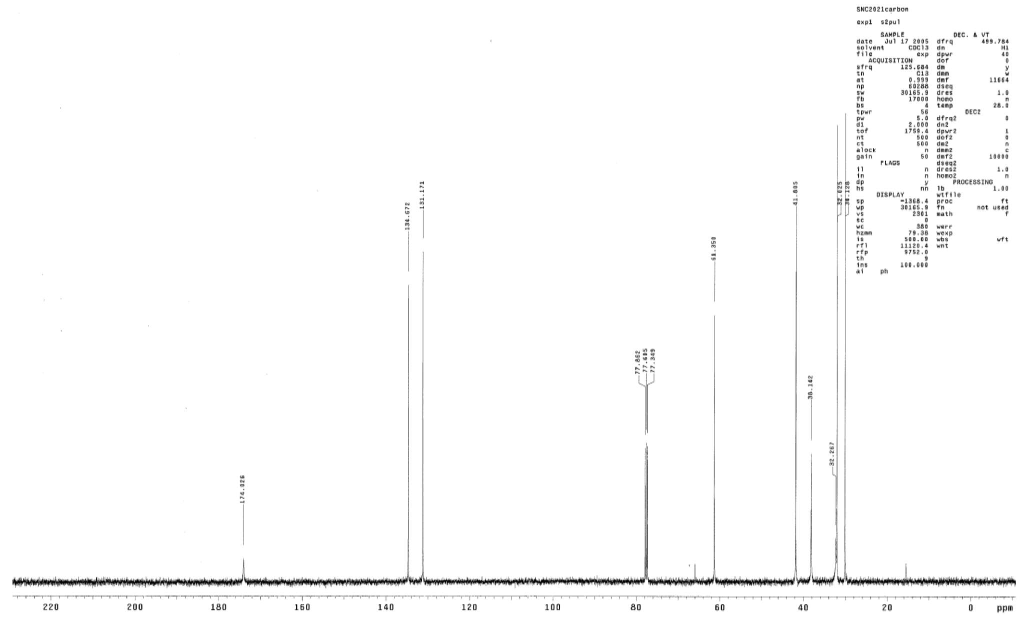

```
SNC2021carbon

exp1  s2pul

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date   Jul 17 2005  dfrq        499.784
solvent      CDCl3  dn               H1
file           exp  dpwr             40
    ACQUISITION     dof               0
sfrq       125.684  dm                y
tn             C13  dmm               w
at           0.999  dmf           11664
np           60288  dseq
sw         30165.9  dres            1.0
fb           17000  homo              n
bs               4  temp           28.0
tpwr            56          DEC2
pw             5.0  dfrq2             0
d1           2.000  dn2
tof         1759.4  dpwr2             1
nt             500  dof2              0
ct             500  dm2               n
alock            n  dmm2              c
gain            50  dmf2          10000
       FLAGS        dseq2
il               n  dres2           1.0
in               n  homo2             n
dp               y       PROCESSING
hs              nn  lb             1.00
      DISPLAY       wtfile
sp         -1368.4  proc             ft
wp         30165.9  fn         not used
vs            2301  math              f
sc               0
wc             380  werr
hzmm         79.38  wexp
is          500.00  wbs             wft
rfl        11120.4  wnt
rfp         9752.0
th               9
ins        100.000
ai    ph
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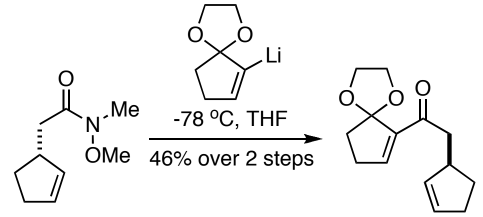

II.26 **II.27**

A solution of **II.5** (200 mg, 0.98 mmol) in dry Et_2O (1.95 mL) was cooled to -78 °C under N_2. Freshly titrated *n*-BuLi (0.98 mmol, 1.8 M) in hexanes was added dropwise and the reaction mixture was allowed to stir at -78 °C for 1 h. Weinreb amide **II.26** (149 mg, 0.88 mmol) was added dropwise and the mixture was allowed to stir for 1.5 h, at which time it was warmed to room temperature and quenched with water (2 mL). The ethereal layer was washed with saturated KH_2PO_4 (5 mL) and brine (5 mL). The organic layer was dried with $MgSO_4$ and concentrated. Product was purified on silica gel (pentane: Et_2O 3:1) to give product **II.27** (104 mg, 46 % yield) as a pale yellow oil.

(R)-2-(cyclopent-2-enyl)-1-(1,4-dioxaspiro[4.4]non-6-en-6-yl)ethanone (II.27): R_f 0.32 (pentane:Et_2O 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.00 (t, 1H, J = 2.4 Hz), 5.73 (m, 1H), 5.66 (m, 1H), 4.23 (td, 2H, J = 6.0, 3.6 Hz), 3.96 (td, 2H, J = 5.6, 3.2 Hz), 3.13 (m, 1H), 2.74 (dd, 1H, J = 16.8, 6.4 Hz), 2.64 (dd, 1H, J = 16.4, 7.6 Hz), 2.47 (m, 2H), 2.30 (m, 2H), 2.14 (m, 3H), 1.39 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 197.5, 149.5, 144.0, 134.9, 131.5, 119.0, 66.3, 46.8, 41.6, 37.6, 32.3, 30.5, 28.5. **IR** (NaCl, thin film) 3049 (w), 3026 (w), 2954 (s), 2890 (m), 1678 (s), 1617 (s), 1368 (m), 1293 (m), 1211 (m) cm^{-1}. **HRMS** (M + H) $C_{14}H_{19}O_3$ Calcd: 235.1341. Found: 235.1334. **$[\alpha]^{20}_D$** -55 (c = 1.0, CH_2Cl_2).

```
SNC1288

exp1  std1h

      SAMPLE              DEC. & VT
date   Jul  7 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             30
   mls/SNC1288.fid  dof               0
   ACQUISITION      dm              nnn
sfrq       400.029  dmm               c
tn              H1  dmf             200
at           5.000      PROCESSING
np           59988  wtfile
sw          5998.8  proc             ft
fb            3400  fn            65536
bs               4
tpwr            60  werr
pw            10.6  wexp
d1               0  wbs
tof              0  wnt
nt              32
ct              20
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs              41
sc               0
wc             400
hzmm         10.50
is          500.00
rfl         3901.7
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
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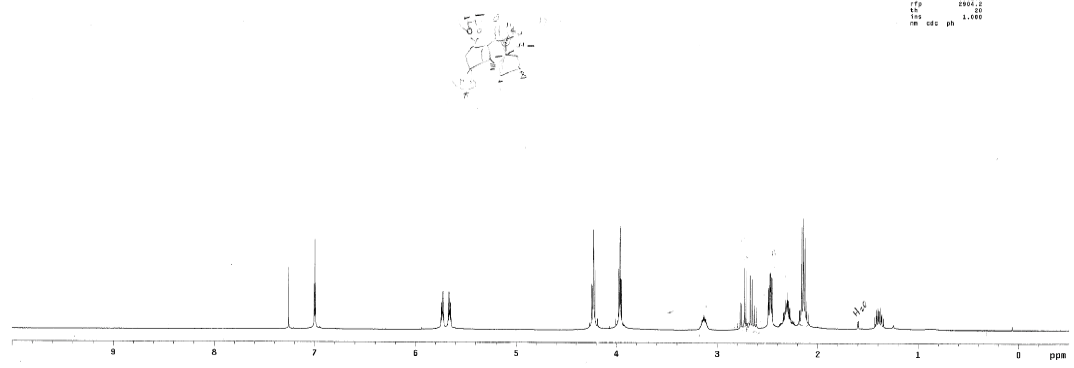

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13C OBSERVE

exp1  std13c

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mls/SNC1301carbon.~ dof             0.0
               fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       100.596  dmf            5460
tn             C13      PROCESSING
at           1.199  lb             1.00
np           67184  wtfile
sw         28000.0  proc             ft
fb           15400  fn         not used
bs               4
tpwr            57  werr
pw            15.0  wexp
d1           2.000  wbs             wft
tof              0  wnt
nt          100000
ct            8908
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
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sp         -4448.3
wp         28000.0
vs             385
sc               0
wc             400
hzmm         70.00
is          500.00
rfl        12253.8
rfp         7805.5
th              10
ins          1.000
nm  no  ph
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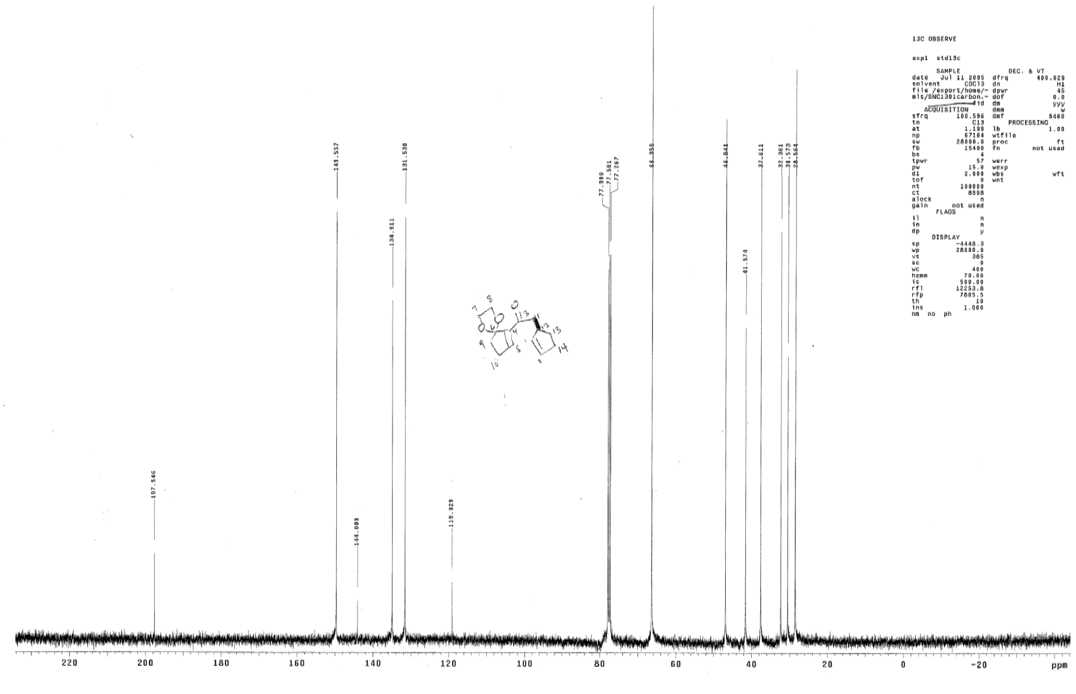
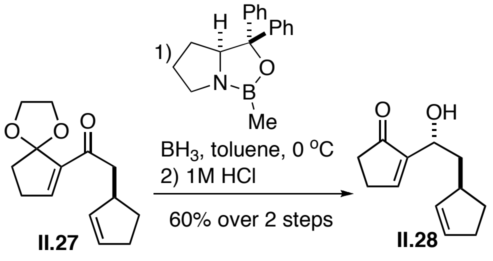
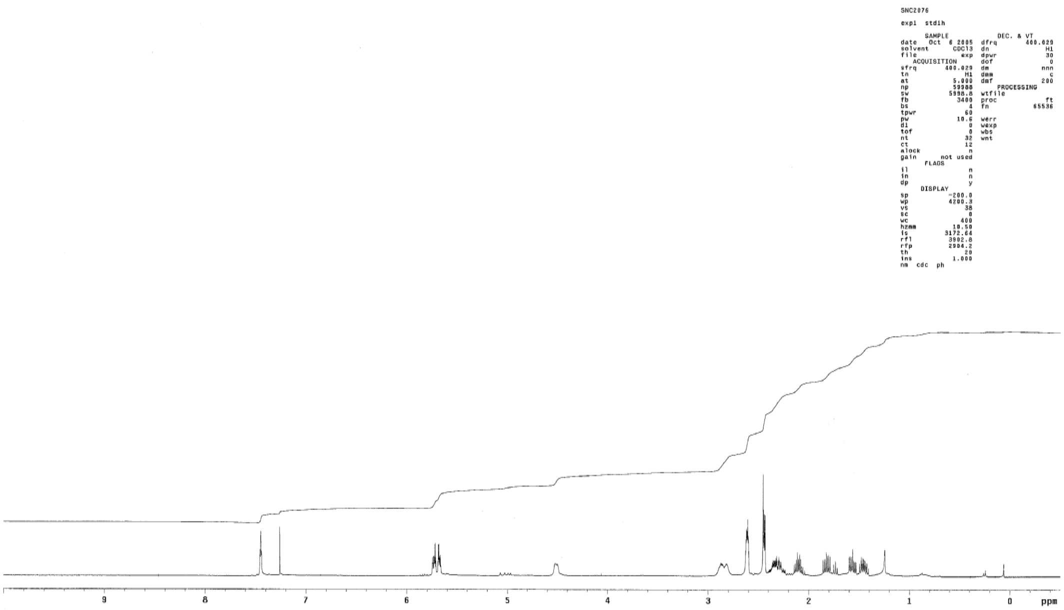




To a flame dried Schlenk flask purged with N_2 was added **II.27** (38.5 mg, 0.165 mmol) in toluene (0.825 mL). (S)-Methyl-3,3 diphenyl-1H,3H pyrrolo [1,2-c][1,3,2] oxazaborole (0.082 mmol, 1 M in toluene) was added dropwise and the flask was cooled to 0 °C in an ice bath. A solution of $BH_3 \cdot THF$ (0.165 mmol, 1 M THF) was added dropwise and stirred for 15 min at 0 °C and then quenched with MeOH (1 mL). The reaction mixture was allowed to stir for 15 min, then warmed to room temperature and allowed to stir for another 15 min before opening the flask to air. Aqueous HCl (2 mL, 1M) was added and the reaction mixture was allowed to stir for 1h. The reaction mixture was then diluted with diethyl ether (10 mL) and washed with brine (5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified on silica gel (pentane:Et_2O 1:1) to give **II.28** (18.9 mg, 60 % yield) as a pale yellow oil.

2-((R)-2-((R)-cyclopent-2-enyl)-1-hydroxyethyl)cyclopent-2-enone (II.28): R_f 0.28 (pentane:Et_2O 2:3); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.44 (td, 1H, J = 2.4, 0.8 Hz), 5.73 (m, 1H), 5.67 (m, 1H), 4.52 (m, 1H), 2.85 (m, 2H), 2.61 (m, 2H), 2.44 (m, 2H), 2.31 (m, 1H), 2.10 (dtd, 1H, J = 12.8, 8.0, 4.4 Hz), 1.82 (m, 1H), 1.56 (ddd, 1H, J = 13.2, 9.2, 4.0 Hz), 1.45 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 210.2, 157.8, 148.3, 135.2, 130.8, 67.0, 42.3, 42.2, 35.4, 35.0, 29.9, 26.8. **IR** (NaCl, thin film) 3430 (br), 2947 (m), 1689 (s), 1340 (m), 1089 (w) cm^{-1}. **HRMS** (M + H) $C_{12}H_{17}O_2$ Calcd: 193.1229. Found: 193.1234.



```
SNC2076

expl  stdih

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solvent       CDCl3   dn               H1
file            exp   dpwr             30
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sfrq        400.029   dm              nnn
tn               H1   dmm               c
at            5.000   dmf             200
np            59988       PROCESSING
sw           5998.8   wtfile
fb             3400   proc             ft
bs                4   fn            65536
tpwr             60
pw             10.6   werr
d1                0   wexp
tof               0   wbs
nt               32   wnt
ct               12
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -200.0
wp           4200.3
vs               38
sc                0
wc              400
hzmm          10.50
is          3172.64
rfl          3902.8
rfp          2904.2
th               20
ins           1.000
nm  cdc  ph
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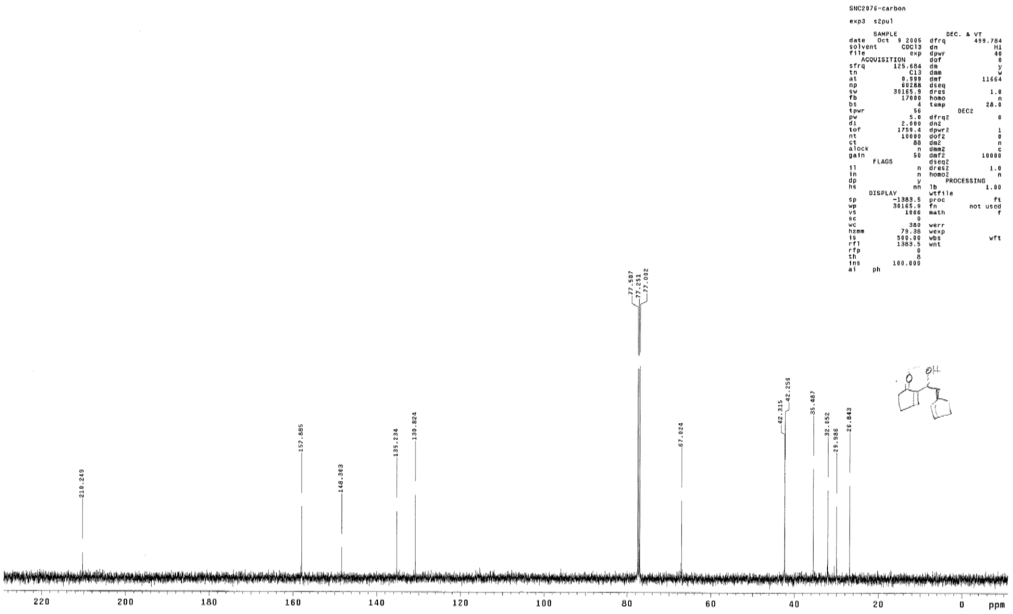

```
SNC2076-carbon

exp3  s2pul

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date   Oct  9 2005   dfrq          499.784
solvent       CDCl3  dn                 H1
file            exp  dpwr               40
   ACQUISITION       dof                 0
sfrq        125.684  dm                  y
tn              C13  dmm                 w
at            0.999  dmf             11664
np            60288  dseq
sw          30165.9  dres              1.0
fb            17000  homo                n
bs                4  temp             28.0
tpwr             56         DEC2
pw              5.0  dfrq2               0
d1            2.000  dn2
tof          1759.4  dpwr2               1
nt            10000  dof2                0
ct               88  dm2                 n
alock             n  dmm2                c
gain             50  dmf2            10000
      FLAGS          dseq2
il                n  dres2             1.0
in                n  homo2               n
dp                y      PROCESSING
hs               nn  lb               1.00
     DISPLAY         wtfile
sp          -1383.5  proc               ft
wp          30165.9  fn           not used
vs             1066  math                f
sc                0
wc              380  werr
hzmm          79.38  wexp
is           500.00  wbs               wft
rfl          1383.5  wnt
rfp               0
th                8
ins         100.000
ai    ph
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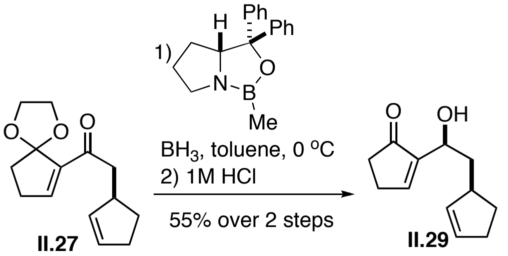
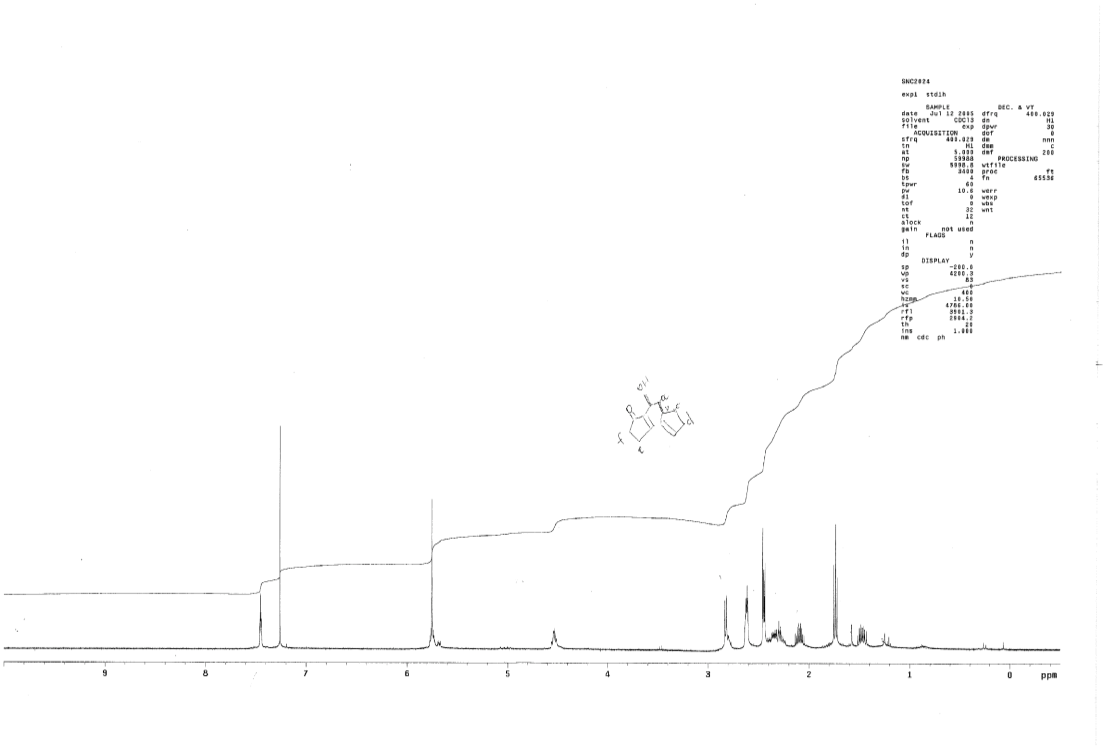


To a flame dried Schlenk flask purged with N_2 was added **II.27** (46.3 mg, 0.20 mmol) in toluene (0.99 mL). (R)-Methyl-3,3 diphenyl-1H,3H-pyrrolo[1,2-c][1,3,2]-oxazaborole (0.082 mmol, 1 M in toluene) was added dropwise and the flask was cooled to 0 °C in an ice bath. A solution of $BH_3 \cdot THF$ (0.20 mmol, 1 M THF) was added dropwise and stirred for 15 min at 0 °C and then quenched with MeOH (1 mL). The reaction mixture was allowed to stir for 15 min, then warmed to room temperature and allowed to stir for another 15 min before opening the flask to air. Aqueous HCl (3 mL, 1 M) was added and the reaction mixture was allowed to stir for 1 h. The reaction mixture was then diluted with diethyl ether (10 mL) and washed with brine (5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. Crude product was purified on silica gel (pentane:Et_2O 1:1) to give **II.29** (20.7 mg, 55 % yield) as a pale yellow oil.

2-((S)-2-((R)-cyclopent-2-enyl)-1-hydroxyethyl)cyclopent-2-enone (II.29): R_f 0.28 (pentane:Et_2O 2:3); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.45 (td, 1H, J = 2.4, 0.8 Hz), 5.72 (m, 2H), 4.53 (dd, 1H, J = 12.4, 6.0 Hz), 2.82 (m, 1H), 2.61 (m, 2H), 2.44 (m, 2H), 2.32 (m, 2H), 2.09 (dtd, 1H, J = 12.8, 8.4, 4.4 Hz), 1.74 (t, 2H, J = 6.8 Hz), 1.46 (ddt, 1H, J = 12.8, 9.2, 6.8 Hz). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 210.3, 158.1, 147.9, 134.5, 131.2, 67.2, 42.28, 42.23, 35.4, 32.2, 30.5, 26.8. **IR** (NaCl, thin film) 3425 (br), 2948 (m), 2858 (m), 1689 (s), 1439 (m), 1338 (m), 1253 (m) cm^{-1}. **HRMS** (M + H) $C_{12}H_{17}O_2$ Calcd: 193.1229. Found: 193.1227.



```
SNC2024

exp1  std1h

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date   Jul 12 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             30
    ACQUISITION     dof               0
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tn              H1  dmm               c
at           5.000  dmf             200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn            65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs
nt              32  wnt
ct              12
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
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wp          4200.3
vs              83
sc               0
wc             400
hzmm         10.50
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rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
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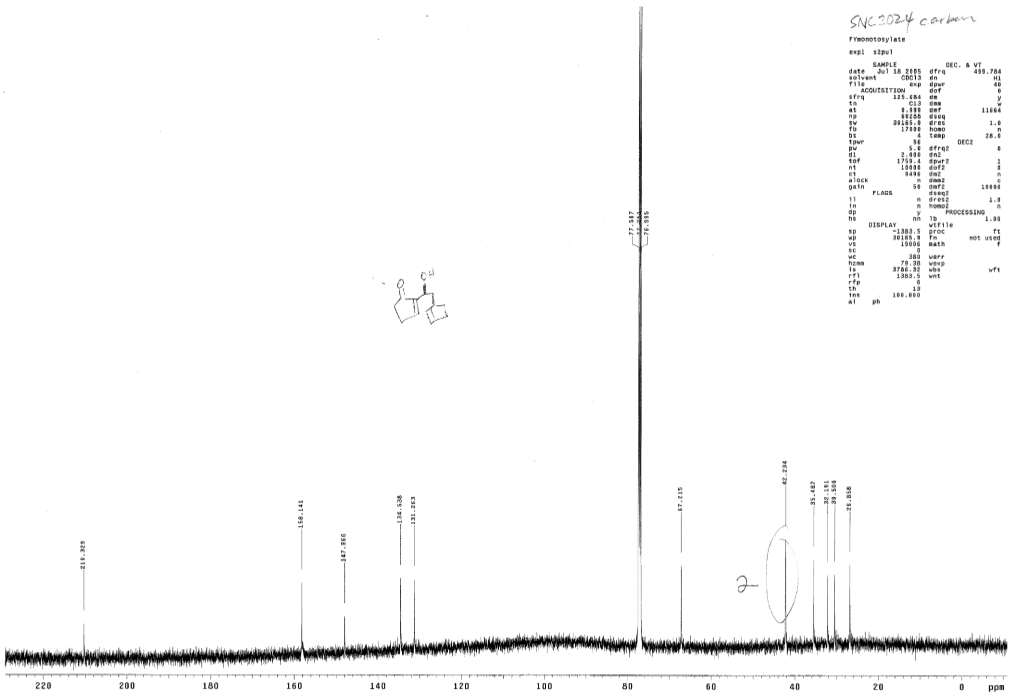

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FYmonotosylate

exp1  s2pul

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file           exp   dpwr              40
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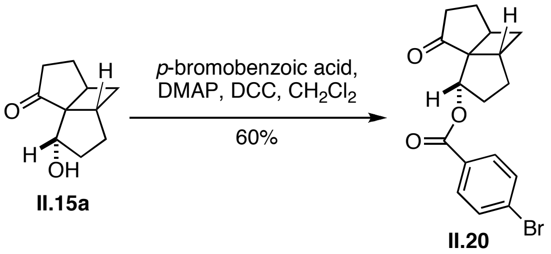
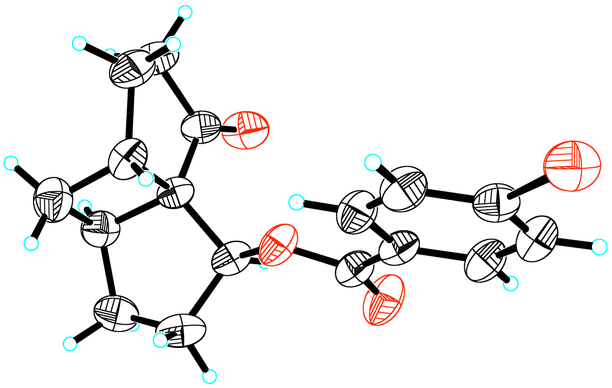
sfrq       125.684   dm                 y
tn             C13   dmm                w
at           0.999   dmf            11664
np           60288   dseq
sw         30165.9   dres             1.0
fb           17000   homo               n
bs               4   temp            28.0
tpwr            56          DEC2
pw             5.0   dfrq2              0
d1           2.000   dn2
tof         1759.4   dpwr2              1
nt           10000   dof2               0
ct            9496   dm2                n
alock            n   dmm2               c
gain            50   dmf2           10000
       FLAGS         dseq2
il               n   dres2            1.0
in               n   homo2              n
dp               y        PROCESSING
hs              nn   lb              1.00
      DISPLAY        wtfile
sp         -1383.5   proc              ft
wp         30165.9   fn          not used
vs           19006   math               f
sc               0
wc             380   werr
hzmm         79.38   wexp
is         3786.32   wbs              wft
rfl         1383.5   wnt
rfp              0
th              13
ins        100.000
ai     ph
```

(A) Representative procedure for the derivatization of the [2+2] photocycloadducts: To a solution of cycloadduct (1 equiv) in CH_2Cl_2 (0.1 M) cooled to 0 °C was added 4-bromo-benzoic acid (1.1 equiv), 4-dimethylaminopyridine (DMAP, 0.5 equiv), and *N*,*N'*-dicyclohexylcarbodiimide (DCC, 1.1 equiv). The reaction was slowly warmed to room temperature. After the reaction was deemed complete by TLC analysis, the mixture was diluted with CH_2Cl_2 and dried with $MgSO_4$. The solution was filtered and concentrated. The reaction was concentrated *in vacuo*, and purified on silica gel. The product was recrystallized in the appropriate conditions.

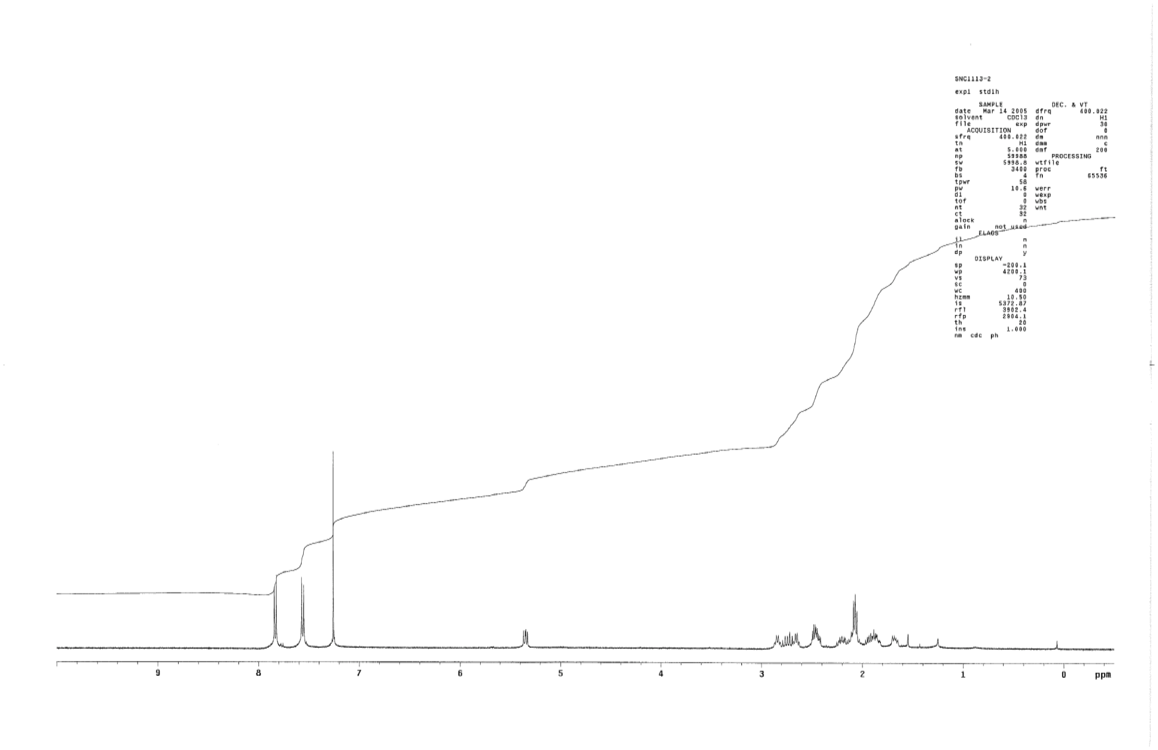


*See representative procedure (A) for the derivatization of photocycloadduct **II.15a**.* A solution of cycloadduct **II.15a** (10.7 mg, 0.06 mmol) was converted in 2.5 h, and the resulting residue was purified on silica gel (pentane:Et_2O 3:1). The product was recrystallized in pentane to give colorless crystals (13.4 mg, 60 %).

Bromo-benzoate (II.20): R_f 0.23 (pentane:Et_2O 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.83 (d, 2H, J = 8.4 Hz), 7.56 (d, 2H, J = 8.4 Hz), 5.34 (dd, 1H, J = 6.8, 9.2 Hz), 2.6-2.8 (m, 3H), 2.4 (m, 2H), 2.0-2.2 (m, 4H), 1.8 (m, 2H), 1.7 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 219.8, 165.6, 132.1, 131.4, 129.4, 128.5, 78.1, 60.9, 41.4, 38.2, 32.4, 32.1, 30.6, 30.3, 28.3. **IR** (NaCl, thin film) 2949 (m), 2863 (w), 1728 (s), 1589 (m), 1271 (s) cm^{-1}. **HRMS** (M + H) $C_{17}H_{18}O_3Br$ Calcd: 349.0439. Found: 349.0439. **mp** 74-78 ^{o}C.



ORTEP of **II.20**



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SNC1113-2

expl  stdlh

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tn              H1  dmm              c
at           5.000  dmf            200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc            ft
bs               4  fn           65536
tpwr            58
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nm  cdc  ph
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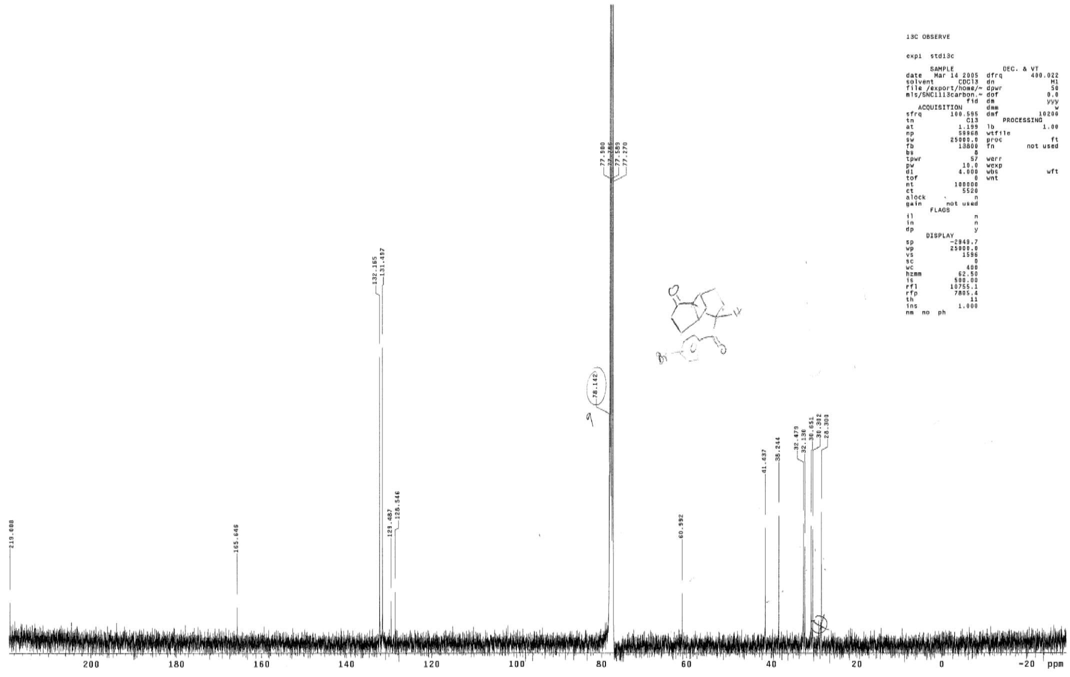

```
13C OBSERVE


expi  stdi3c

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file /export/home/~ dpwr             50
mls/SNC1113carbon.~ dof             0.0
               fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       100.595  dmf           10200
tn             C13      PROCESSING
at           1.199  lb             1.00
np           59968  wtfile
sw         25000.0  proc             ft
fb           13800  fn         not used
bs               8
tpwr            57  werr
pw            10.0  wexp
d1           4.000  wbs             wft
tof              0  wnt
nt          100000
ct            5520
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
      DISPLAY
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wp         25000.0
vs            1596
sc               0
wc             400
hzmm         62.50
is          500.00
rfl        10755.1
rfp         7805.4
th              11
ins          1.000
nm  no  ph
```

Table 1. Crystal data and structure refinement for **II.20**.

Identification code	sn01	
Empirical formula	C17 H17 Br O3	
Formula weight	349.22	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.6324(5) Å	a= 80.465(2)°.
	b = 7.3864(9) Å	b= 80.050(2)°.
	c = 16.3004(14) Å	g = 74.974(2)°.
Volume	753.49(13) Å^3	
Z	2	
Density (calculated)	1.539 Mg/m^3	
Absorption coefficient	2.735 mm^{-1}	
F(000)	356	
Crystal size	0.30 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.28 to 28.27°.	
Index ranges	-8<=h<=4, -9<=k<=9, -21<=l<=20	
Reflections collected	5657	
Independent reflections	3700 [R(int) = 0.0157]	
Completeness to theta = 28.27°	98.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3700 / 0 / 190	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1051	
R indices (all data)	R1 = 0.0438, wR2 = 0.1082	
Largest diff. peak and hole	1.005 and -0.224 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for sn01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-1629(1)	2961(1)	11886(1)	54(1)
O(1)	4141(2)	2064(2)	8073(1)	44(1)
C(1)	423(3)	2771(3)	10913(1)	40(1)
O(3)	4911(3)	5781(2)	6266(1)	58(1)
C(3)	1381(3)	2129(3)	9495(1)	43(1)
C(12)	4035(3)	2746(3)	6588(1)	36(1)
C(13)	3691(3)	4813(3)	6276(1)	42(1)
C(7)	4945(3)	2364(3)	8726(1)	40(1)
C(16)	1855(3)	2245(3)	6682(1)	43(1)
C(4)	3349(3)	2483(3)	9488(1)	37(1)
O(2)	6705(3)	2543(3)	8690(1)	60(1)
C(2)	-74(3)	2256(3)	10212(2)	46(1)
C(5)	3801(3)	2989(3)	10207(1)	45(1)
C(11)	4876(4)	1460(3)	5863(1)	45(1)
C(8)	5440(3)	1933(3)	7269(1)	41(1)
C(6)	2342(4)	3158(3)	10923(1)	47(1)
C(9)	6400(4)	-131(4)	7119(2)	54(1)
C(10)	6750(4)	-55(4)	6168(2)	53(1)
C(17)	2725(4)	915(4)	6001(2)	55(1)
C(14)	1597(4)	5439(4)	5939(2)	55(1)
C(15)	292(4)	4107(4)	6442(2)	53(1)

Table 3. Bond lengths [Å] and angles [°] for sn01.

Br(1)-C(1)	1.902(2)
O(1)-C(7)	1.342(2)
O(1)-C(8)	1.442(3)
C(1)-C(6)	1.378(3)
C(1)-C(2)	1.379(3)
O(3)-C(13)	1.207(3)
C(3)-C(2)	1.381(3)
C(3)-C(4)	1.394(3)
C(12)-C(13)	1.498(3)
C(12)-C(8)	1.519(3)
C(12)-C(16)	1.560(3)
C(12)-C(11)	1.575(3)
C(13)-C(14)	1.514(3)
C(7)-O(2)	1.199(3)
C(7)-C(4)	1.485(3)
C(16)-C(15)	1.530(3)
C(16)-C(17)	1.541(4)
C(4)-C(5)	1.388(3)
C(5)-C(6)	1.381(3)
C(11)-C(10)	1.533(3)
C(11)-C(17)	1.551(3)
C(8)-C(9)	1.535(3)
C(9)-C(10)	1.522(4)
C(14)-C(15)	1.523(4)
C(7)-O(1)-C(8)	119.33(16)
C(6)-C(1)-C(2)	121.9(2)
C(6)-C(1)-Br(1)	119.80(17)
C(2)-C(1)-Br(1)	118.34(16)
C(2)-C(3)-C(4)	120.1(2)
C(13)-C(12)-C(8)	118.46(18)
C(13)-C(12)-C(16)	106.72(16)

C(8)-C(12)-C(16)	119.24(17)
C(13)-C(12)-C(11)	112.94(17)
C(8)-C(12)-C(11)	106.47(16)
C(16)-C(12)-C(11)	89.38(16)
O(3)-C(13)-C(12)	125.81(19)
O(3)-C(13)-C(14)	126.4(2)
C(12)-C(13)-C(14)	107.72(18)
O(2)-C(7)-O(1)	124.2(2)
O(2)-C(7)-C(4)	124.92(19)
O(1)-C(7)-C(4)	110.85(16)
C(15)-C(16)-C(17)	117.2(2)
C(15)-C(16)-C(12)	105.64(17)
C(17)-C(16)-C(12)	90.22(17)
C(5)-C(4)-C(3)	118.9(2)
C(5)-C(4)-C(7)	119.65(17)
C(3)-C(4)-C(7)	121.40(18)
C(1)-C(2)-C(3)	119.42(19)
C(6)-C(5)-C(4)	121.46(19)
C(10)-C(11)-C(17)	116.9(2)
C(10)-C(11)-C(12)	105.29(18)
C(17)-C(11)-C(12)	89.30(17)
O(1)-C(8)-C(12)	108.19(16)
O(1)-C(8)-C(9)	111.57(18)
C(12)-C(8)-C(9)	104.82(18)
C(1)-C(6)-C(5)	118.2(2)
C(10)-C(9)-C(8)	104.08(18)
C(9)-C(10)-C(11)	105.25(19)
C(16)-C(17)-C(11)	90.99(17)
C(13)-C(14)-C(15)	104.71(19)
C(14)-C(15)-C(16)	106.40(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sn01. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	50(1)	56(1)	47(1)	4(1)	2(1)	-11(1)
O(1)	35(1)	63(1)	36(1)	0(1)	-8(1)	-17(1)
C(1)	39(1)	36(1)	41(1)	5(1)	-4(1)	-8(1)
O(3)	49(1)	46(1)	80(1)	9(1)	-11(1)	-20(1)
C(3)	35(1)	53(1)	46(1)	-5(1)	-9(1)	-16(1)
C(12)	32(1)	38(1)	36(1)	2(1)	-5(1)	-7(1)
C(13)	37(1)	40(1)	43(1)	3(1)	-4(1)	-8(1)
C(7)	36(1)	45(1)	42(1)	1(1)	-12(1)	-12(1)
C(16)	40(1)	54(1)	38(1)	2(1)	-7(1)	-19(1)
C(4)	32(1)	39(1)	41(1)	4(1)	-11(1)	-10(1)
O(2)	38(1)	100(2)	51(1)	-11(1)	-8(1)	-27(1)
C(2)	34(1)	55(1)	53(1)	-4(1)	-8(1)	-16(1)
C(5)	37(1)	57(1)	45(1)	1(1)	-12(1)	-19(1)
C(11)	46(1)	47(1)	40(1)	-3(1)	-3(1)	-8(1)
C(8)	33(1)	48(1)	38(1)	5(1)	-7(1)	-10(1)
C(6)	49(1)	55(1)	40(1)	1(1)	-13(1)	-18(1)
C(9)	45(1)	49(1)	54(1)	11(1)	-6(1)	-1(1)
C(10)	46(1)	47(1)	58(1)	-5(1)	1(1)	-4(1)
C(17)	54(1)	60(1)	58(1)	-12(1)	-9(1)	-19(1)
C(14)	42(1)	54(1)	63(2)	9(1)	-16(1)	-4(1)
C(15)	34(1)	64(1)	57(1)	-3(1)	-9(1)	-7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sn01.

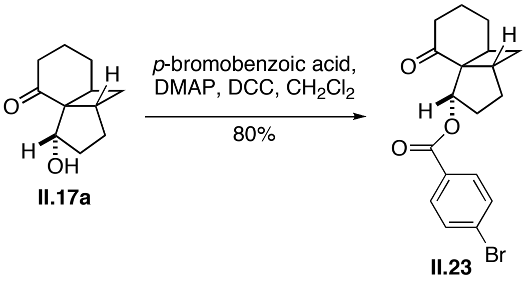
	x	y	z	U(eq)
H(3)	1040	1799	9005	51
H(16)	1434	1583	7247	52
H(2)	-1406	1991	10222	56
H(5)	5143	3224	10207	54
H(11)	5211	2168	5299	54
H(8)	6570	2633	7217	49
H(6)	2653	3530	11408	56
H(9A)	7748	-627	7352	65
H(9B)	5420	-939	7379	65
H(10A)	6784	-1295	6002	64
H(10B)	8095	293	5927	64
H(17A)	1974	1290	5502	66
H(17B)	2815	-433	6217	66
H(14A)	1786	5324	5332	66
H(14B)	910	6766	6024	66
H(15A)	-708	3904	6100	63
H(15B)	-519	4641	6952	63

Table 6. Torsion angles [°] for sn01.

C(8)-C(12)-C(13)-O(3)	28.3(3)
C(16)-C(12)-C(13)-O(3)	166.3(2)
C(11)-C(12)-C(13)-O(3)	-97.1(3)
C(8)-C(12)-C(13)-C(14)	-154.3(2)
C(16)-C(12)-C(13)-C(14)	-16.4(2)
C(11)-C(12)-C(13)-C(14)	80.2(2)
C(8)-O(1)-C(7)-O(2)	0.3(3)
C(8)-O(1)-C(7)-C(4)	179.05(17)
C(13)-C(12)-C(16)-C(15)	-2.0(2)
C(8)-C(12)-C(16)-C(15)	135.6(2)
C(11)-C(12)-C(16)-C(15)	-115.81(18)
C(13)-C(12)-C(16)-C(17)	116.36(19)
C(8)-C(12)-C(16)-C(17)	-106.0(2)
C(11)-C(12)-C(16)-C(17)	2.55(17)
C(2)-C(3)-C(4)-C(5)	-0.9(3)
C(2)-C(3)-C(4)-C(7)	-179.8(2)
O(2)-C(7)-C(4)-C(5)	5.6(3)
O(1)-C(7)-C(4)-C(5)	-173.16(19)
O(2)-C(7)-C(4)-C(3)	-175.5(2)
O(1)-C(7)-C(4)-C(3)	5.7(3)
C(6)-C(1)-C(2)-C(3)	-0.3(3)
Br(1)-C(1)-C(2)-C(3)	179.29(18)
C(4)-C(3)-C(2)-C(1)	1.2(3)
C(3)-C(4)-C(5)-C(6)	-0.4(3)
C(7)-C(4)-C(5)-C(6)	178.5(2)
C(13)-C(12)-C(11)-C(10)	131.77(19)
C(8)-C(12)-C(11)-C(10)	0.1(2)
C(16)-C(12)-C(11)-C(10)	-120.30(18)
C(13)-C(12)-C(11)-C(17)	-110.46(19)
C(8)-C(12)-C(11)-C(17)	117.88(18)
C(16)-C(12)-C(11)-C(17)	-2.53(17)
C(7)-O(1)-C(8)-C(12)	-146.75(18)

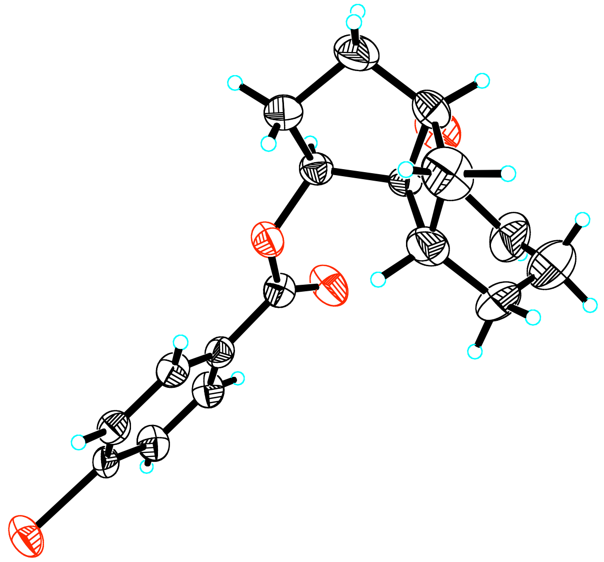
C(7)-O(1)-C(8)-C(9)	98.5(2)
C(13)-C(12)-C(8)-O(1)	90.1(2)
C(16)-C(12)-C(8)-O(1)	-42.6(3)
C(11)-C(12)-C(8)-O(1)	-141.42(17)
C(13)-C(12)-C(8)-C(9)	-150.77(19)
C(16)-C(12)-C(8)-C(9)	76.5(2)
C(11)-C(12)-C(8)-C(9)	-22.3(2)
C(2)-C(1)-C(6)-C(5)	-1.0(3)
Br(1)-C(1)-C(6)-C(5)	179.44(17)
C(4)-C(5)-C(6)-C(1)	1.3(3)
O(1)-C(8)-C(9)-C(10)	153.25(18)
C(12)-C(8)-C(9)-C(10)	36.4(2)
C(8)-C(9)-C(10)-C(11)	-36.4(2)
C(17)-C(11)-C(10)-C(9)	-74.8(3)
C(12)-C(11)-C(10)-C(9)	22.3(2)
C(15)-C(16)-C(17)-C(11)	105.2(2)
C(12)-C(16)-C(17)-C(11)	-2.59(17)
C(10)-C(11)-C(17)-C(16)	109.4(2)
C(12)-C(11)-C(17)-C(16)	2.56(17)
O(3)-C(13)-C(14)-C(15)	-154.2(3)
C(12)-C(13)-C(14)-C(15)	28.4(3)
C(13)-C(14)-C(15)-C(16)	-29.4(3)
C(17)-C(16)-C(15)-C(14)	-79.1(3)
C(12)-C(16)-C(15)-C(14)	19.4(3)

Symmetry transformations used to generate equivalent atoms:

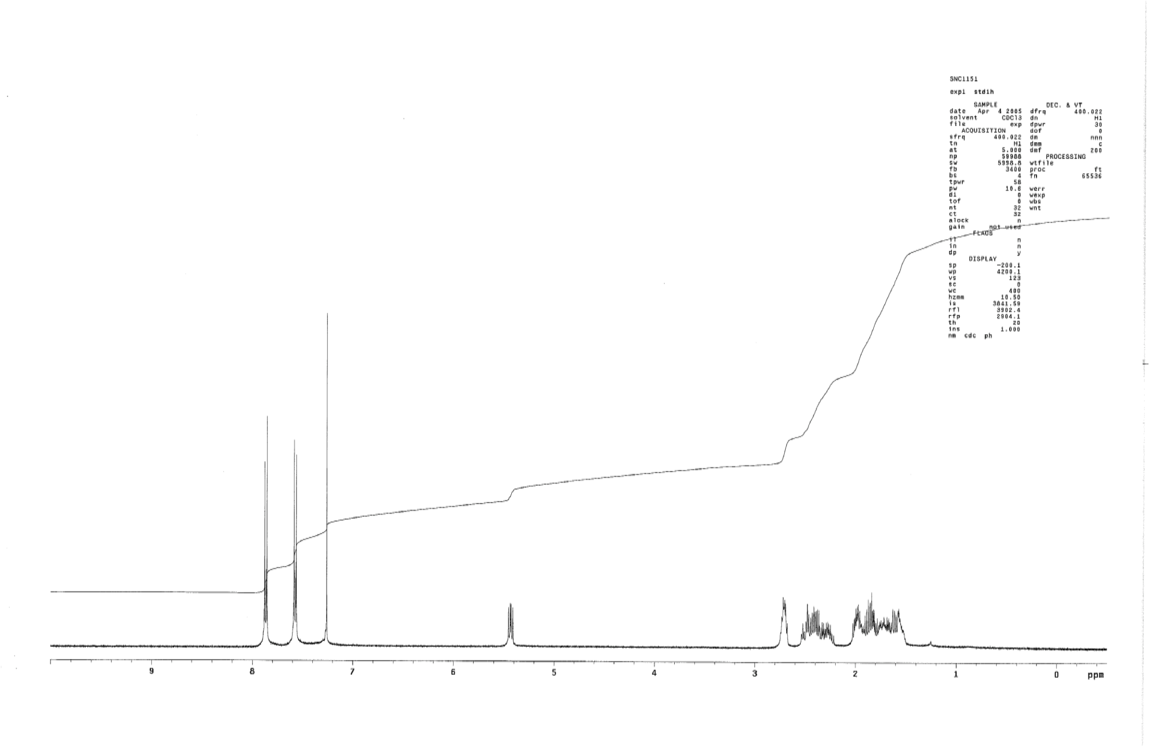


*See representative procedure (A) for the derivatization of photocycloadduct **II.23**.* A solution of cycloadduct **II.17a** (21.3 mg, 0.12 mmol) was converted in 4.5 h, and the resulting residue was purified on silica gel (pentane:Et_2O 4:1). The product was recrystallized in pentane and Et_2O to give colorless crystals (34.3 mg, 80 % yield).

Bromo-benzoate (II.23): R_f 0.41 (pentane:Et_2O 3:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.86 (d, 2H), 7.57 (d, 2H), 5.43 (dd, 1H, J = 10.4, 6.8 Hz), 2.71 (m, 2H), 2.26-2.52 (m, 4H), 1.55-2.02 (m, 8H), 1.80 (m, 2H), 1.70 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 214.0, 165.8, 132.2, 131.5, 129.4, 128.6, 81.2, 58.1, 43.4, 40.4, 31.0, 29.6, 29.5, 28.7, 20.0. **IR** (NaCl, thin film) 2953 (m), 2864 (m), 1719 (s), 1694 (m) cm^{-1}. **HRMS** (M + H) $C_{18}H_{20}O_3Br$ Calcd: 363.0596. Found: 363.0594. **mp** 107-110 °C.



ORTEP of **II.23**



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SNC1151

expl  stdih

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solvent       CDCl3   dn              H1
file            exp   dpwr            30
    ACQUISITION       dof              0
sfrq        400.022   dm             nnn
tn               H1   dmm              c
at            5.000   dmf            200
np            59988       PROCESSING
sw           5998.8   wtfile
fb             3400   proc            ft
bs                4   fn           65536
tpwr             58
pw             10.6   werr
d1                0   wexp
tof               0   wbs
nt               32   wnt
ct               32
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -200.1
wp           4200.1
vs              123
sc                0
wc              400
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is          3841.59
rfl          3902.4
rfp          2904.1
th               20
ins           1.000
nm  cdc  ph
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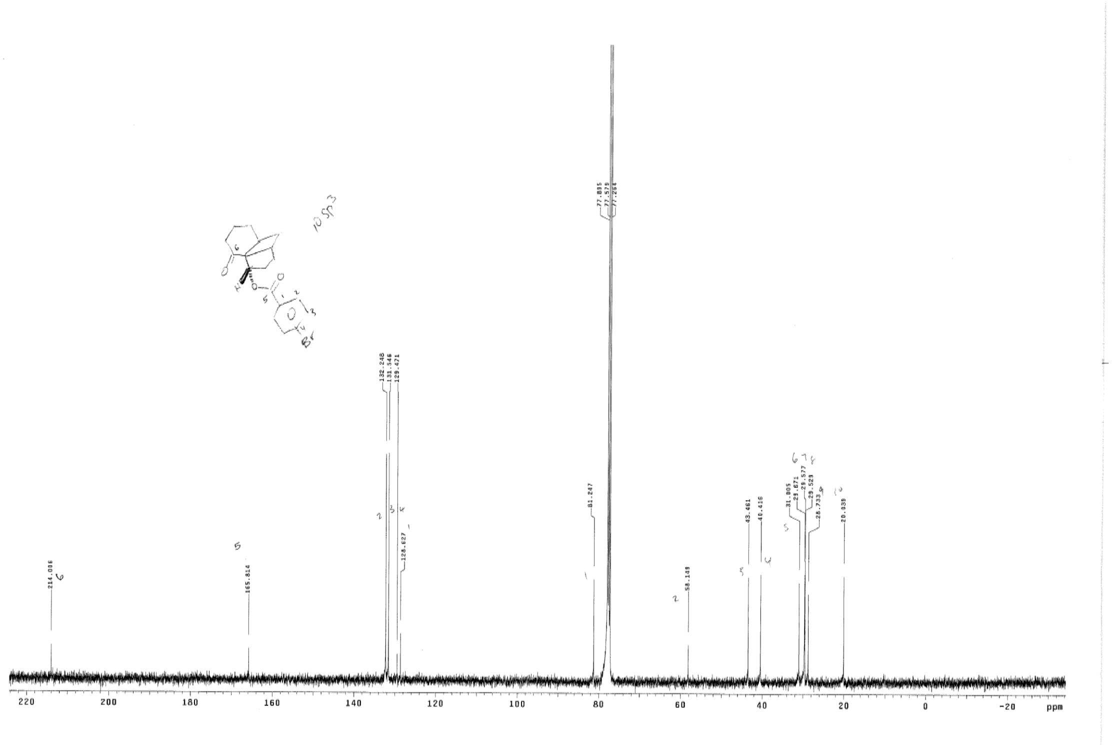
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6
H
O
O
5
1
2
3
4
Br
214.006
6
165.814
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131.546
129.471
128.627
2
3
4
1
81.247
1
77.895
77.579
77.264
58.149
2
43.461
3
40.416
4
31.805
29.671
29.577
29.529
28.733
5
6
7
8
9
20.039
10
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

Table 1. Crystal data and structure refinement for **II.23**.

Identification code	mls104	
Empirical formula	C18 H19 Br O3	
Formula weight	363.24	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 22.515(6) Å	a= 90°.
	b = 11.347(3) Å	b= 106.377(5)°.
	c = 12.840(3) Å	g = 90°.
Volume	3147.4(14) Å^3	
Z	8	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	2.622 mm^{-1}	
F(000)	1488	
Crystal size	0.14 x 0.08 x 0.08 mm^3	
Theta range for data collection	0.94 to 28.30°.	
Index ranges	-29<=h<=30, -12<=k<=15, -17<=l<=14	
Reflections collected	22604	
Independent reflections	7794 [R(int) = 0.0295]	
Completeness to theta = 28.30°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7794 / 0 / 397	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2sigma(I)]	R1 = 0.0683, wR2 = 0.1623	
R indices (all data)	R1 = 0.0927, wR2 = 0.1725	
Largest diff. peak and hole	0.934 and -0.714 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for mls104. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	3518(1)	2593(1)	4736(1)	47(1)
O(1A)	5437(2)	1867(3)	9757(3)	36(1)
C(3)	6435(2)	2265(4)	11218(3)	28(1)
C(4)	4078(2)	2708(4)	6150(4)	32(1)
O(4)	5440(2)	3839(3)	9834(3)	49(1)
C(6)	4847(2)	1837(4)	7604(4)	32(1)
C(7)	4872(2)	2858(4)	8211(4)	30(1)
C(8)	4497(2)	3818(4)	7773(4)	36(1)
O(5)	6238(2)	3607(4)	12490(3)	57(1)
C(10)	5771(2)	1782(4)	10902(4)	33(1)
C(11)	4098(2)	3751(4)	6740(4)	37(1)
C(12)	5280(2)	2942(4)	9353(4)	32(1)
C(13)	4447(2)	1765(4)	6562(4)	33(1)
C(14)	6483(2)	3462(5)	11765(4)	43(1)
C(15)	6821(2)	1316(5)	11997(4)	39(1)
C(16)	5821(3)	462(5)	11153(5)	47(1)
C(17)	6366(3)	410(5)	12197(5)	50(1)
C(18)	6804(3)	2035(6)	10386(4)	51(1)
C(19)	6854(4)	4396(6)	11461(6)	71(2)
C(20)	7370(5)	3930(11)	11126(9)	135(5)
C(21)	7193(4)	3069(9)	10209(6)	92(3)
Br(2)	11432(1)	7494(1)	1133(1)	50(1)
O(2A)	9517(2)	6806(3)	4260(3)	37(1)
C(24)	10102(2)	7807(4)	3300(4)	31(1)
C(25)	8525(2)	7075(4)	4773(4)	35(1)
C(26)	10091(2)	6809(4)	2669(4)	34(1)
O(3)	9574(2)	8784(3)	4438(3)	49(1)
C(28)	9697(2)	7891(4)	4055(4)	34(1)

C(29)	10884(2)	7650(4)	2015(4)	35(1)
C(30)	9208(2)	6716(4)	5103(4)	33(1)
C(31)	10498(2)	8736(4)	3269(4)	37(1)
O(1)	8615(2)	8625(4)	6031(4)	66(1)
C(33)	10895(2)	8656(4)	2617(5)	40(1)
C(34)	10482(2)	6726(4)	2013(4)	37(1)
C(35)	8206(2)	6129(4)	5317(4)	37(1)
C(36)	7840(3)	5680(5)	4200(5)	48(1)
C(37)	8424(3)	8327(5)	5076(5)	46(1)
C(38)	8719(2)	5323(5)	5982(5)	45(1)
C(39)	9227(2)	5411(5)	5408(5)	42(1)
C(40)	8136(2)	6603(5)	3640(4)	45(1)
C(47)	7968(4)	8700(8)	3082(7)	88(3)
C(48)	8084(4)	9156(6)	4204(7)	74(2)
C(45)	7139(3)	1027(6)	11122(5)	61(2)
C(46)	7690(3)	7509(8)	2955(6)	82(3)

Table 3. Bond lengths [Å] and angles [°] for mls104.

Br(1)-C(4)	1.901(4)
O(1A)-C(12)	1.334(6)
O(1A)-C(10)	1.454(5)
C(3)-C(14)	1.520(7)
C(3)-C(10)	1.534(6)
C(3)-C(18)	1.550(7)
C(3)-C(15)	1.557(6)
C(4)-C(13)	1.366(6)
C(4)-C(11)	1.399(7)
O(4)-C(12)	1.192(6)
C(6)-C(13)	1.388(7)
C(6)-C(7)	1.388(7)
C(7)-C(8)	1.396(6)
C(7)-C(12)	1.498(6)
C(8)-C(11)	1.379(7)
O(5)-C(14)	1.218(7)
C(10)-C(16)	1.530(7)
C(14)-C(19)	1.469(8)
C(15)-C(17)	1.525(8)
C(15)-C(45)	1.529(8)
C(16)-C(17)	1.542(7)
C(18)-C(21)	1.520(10)
C(18)-C(45)	1.539(9)
C(19)-C(20)	1.449(14)
C(20)-C(21)	1.495(14)
Br(2)-C(29)	1.903(5)
O(2A)-C(28)	1.345(6)
O(2A)-C(30)	1.446(5)
C(24)-C(26)	1.387(7)
C(24)-C(31)	1.390(6)
C(24)-C(28)	1.510(7)
C(25)-C(37)	1.507(7)

C(25)-C(30)	1.531(6)
C(25)-C(35)	1.562(7)
C(25)-C(40)	1.566(7)
C(26)-C(34)	1.384(7)
O(3)-C(28)	1.192(6)
C(29)-C(33)	1.376(7)
C(29)-C(34)	1.385(7)
C(30)-C(39)	1.529(7)
C(31)-C(33)	1.389(7)
O(1)-C(37)	1.227(7)
C(35)-C(36)	1.525(7)
C(35)-C(38)	1.532(7)
C(36)-C(40)	1.525(8)
C(37)-C(48)	1.497(9)
C(38)-C(39)	1.529(7)
C(40)-C(46)	1.529(9)
C(47)-C(46)	1.480(12)
C(47)-C(48)	1.483(12)

C(12)-O(1A)-C(10)	117.3(4)
C(14)-C(3)-C(10)	112.2(4)
C(14)-C(3)-C(18)	119.2(4)
C(10)-C(3)-C(18)	115.4(4)
C(14)-C(3)-C(15)	111.5(4)
C(10)-C(3)-C(15)	104.4(4)
C(18)-C(3)-C(15)	90.8(4)
C(13)-C(4)-C(11)	122.0(4)
C(13)-C(4)-Br(1)	118.9(4)
C(11)-C(4)-Br(1)	119.1(3)
C(13)-C(6)-C(7)	120.2(4)
C(6)-C(7)-C(8)	120.0(4)
C(6)-C(7)-C(12)	121.3(4)
C(8)-C(7)-C(12)	118.6(4)
C(11)-C(8)-C(7)	120.0(4)

O(1A)-C(10)-C(16)	105.3(4)
O(1A)-C(10)-C(3)	115.6(4)
C(16)-C(10)-C(3)	106.6(4)
C(8)-C(11)-C(4)	118.7(4)
O(4)-C(12)-O(1A)	124.8(4)
O(4)-C(12)-C(7)	125.0(4)
O(1A)-C(12)-C(7)	110.1(4)
C(4)-C(13)-C(6)	119.0(4)
O(5)-C(14)-C(19)	121.3(6)
O(5)-C(14)-C(3)	119.0(5)
C(19)-C(14)-C(3)	119.6(5)
C(17)-C(15)-C(45)	117.1(5)
C(17)-C(15)-C(3)	107.1(4)
C(45)-C(15)-C(3)	88.3(4)
C(10)-C(16)-C(17)	102.3(4)
C(15)-C(17)-C(16)	103.6(4)
C(21)-C(18)-C(45)	117.5(6)
C(21)-C(18)-C(3)	114.7(6)
C(45)-C(18)-C(3)	88.2(4)
C(20)-C(19)-C(14)	112.3(7)
C(19)-C(20)-C(21)	114.5(8)
C(20)-C(21)-C(18)	115.0(6)
C(28)-O(2A)-C(30)	116.5(4)
C(26)-C(24)-C(31)	120.6(4)
C(26)-C(24)-C(28)	120.8(4)
C(31)-C(24)-C(28)	118.6(4)
C(37)-C(25)-C(30)	113.1(4)
C(37)-C(25)-C(35)	114.2(4)
C(30)-C(25)-C(35)	104.3(4)
C(37)-C(25)-C(40)	118.5(4)
C(30)-C(25)-C(40)	115.0(4)
C(35)-C(25)-C(40)	88.4(4)
C(34)-C(26)-C(24)	120.1(4)
O(3)-C(28)-O(2A)	125.4(5)

O(3)-C(28)-C(24)	124.8(4)
O(2A)-C(28)-C(24)	109.7(4)
C(33)-C(29)-C(34)	122.5(5)
C(33)-C(29)-Br(2)	120.0(4)
C(34)-C(29)-Br(2)	117.5(4)
O(2A)-C(30)-C(25)	115.5(4)
O(2A)-C(30)-C(39)	106.0(4)
C(25)-C(30)-C(39)	106.4(4)
C(24)-C(31)-C(33)	119.7(5)
C(29)-C(33)-C(31)	118.7(5)
C(26)-C(34)-C(29)	118.4(5)
C(36)-C(35)-C(38)	116.6(5)
C(36)-C(35)-C(25)	90.2(4)
C(38)-C(35)-C(25)	106.8(4)
C(35)-C(36)-C(40)	91.3(4)
O(1)-C(37)-C(48)	122.3(6)
O(1)-C(37)-C(25)	118.9(5)
C(48)-C(37)-C(25)	118.8(5)
C(39)-C(38)-C(35)	104.0(4)
C(38)-C(39)-C(30)	102.4(4)
C(36)-C(40)-C(46)	115.5(5)
C(36)-C(40)-C(25)	90.1(4)
C(46)-C(40)-C(25)	114.1(5)
C(46)-C(47)-C(48)	112.2(7)
C(47)-C(48)-C(37)	114.8(6)
C(15)-C(45)-C(18)	92.3(4)
C(47)-C(46)-C(40)	111.2(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for mls104. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	51(1)	40(1)	38(1)	-2(1)	-8(1)	1(1)
O(1A)	37(2)	31(2)	33(2)	-1(1)	2(1)	-1(1)
C(3)	30(2)	30(2)	26(2)	2(2)	10(2)	3(2)
C(4)	26(2)	36(2)	30(2)	4(2)	1(2)	-7(2)
O(4)	57(2)	35(2)	44(2)	-3(2)	-4(2)	5(2)
C(6)	28(2)	28(2)	40(3)	6(2)	8(2)	4(2)
C(7)	25(2)	31(2)	34(2)	4(2)	8(2)	-1(2)
C(8)	35(3)	27(2)	42(3)	-1(2)	8(2)	2(2)
O(5)	70(3)	51(2)	47(2)	-16(2)	12(2)	11(2)
C(10)	30(2)	38(3)	32(2)	4(2)	8(2)	4(2)
C(11)	33(2)	31(2)	41(3)	2(2)	4(2)	5(2)
C(12)	29(2)	30(2)	38(2)	1(2)	9(2)	4(2)
C(13)	35(2)	28(2)	36(2)	1(2)	11(2)	-1(2)
C(14)	43(3)	34(3)	42(3)	6(2)	-2(2)	3(2)
C(15)	35(3)	43(3)	36(3)	0(2)	4(2)	9(2)
C(16)	48(3)	45(3)	42(3)	13(2)	4(2)	-7(2)
C(17)	58(3)	46(3)	40(3)	12(2)	4(3)	4(3)
C(18)	41(3)	80(4)	34(3)	-4(3)	16(2)	3(3)
C(19)	72(5)	41(3)	91(5)	7(3)	11(4)	-22(3)
C(20)	133(10)	149(10)	104(8)	47(7)	3(7)	-93(9)
C(21)	57(4)	163(9)	61(4)	27(5)	28(4)	-35(5)
Br(2)	50(1)	48(1)	64(1)	5(1)	35(1)	3(1)
O(2A)	39(2)	37(2)	39(2)	3(1)	17(2)	-3(2)
C(24)	25(2)	34(2)	32(2)	7(2)	4(2)	1(2)
C(25)	34(2)	43(3)	26(2)	0(2)	7(2)	1(2)
C(26)	32(2)	32(2)	36(2)	8(2)	7(2)	-4(2)
O(3)	59(2)	38(2)	55(2)	-4(2)	26(2)	-5(2)
C(28)	33(2)	30(2)	36(2)	6(2)	5(2)	-5(2)
C(29)	31(2)	40(3)	37(2)	11(2)	12(2)	4(2)

C(30)	31(2)	39(3)	29(2)	4(2)	9(2)	-5(2)
C(31)	35(3)	31(2)	46(3)	4(2)	12(2)	1(2)
O(1)	82(3)	56(3)	70(3)	-30(2)	36(3)	-15(2)
C(33)	35(3)	32(3)	58(3)	10(2)	20(2)	1(2)
C(34)	40(3)	34(2)	33(2)	8(2)	8(2)	4(2)
C(35)	31(2)	40(3)	42(3)	4(2)	13(2)	1(2)
C(36)	40(3)	46(3)	54(3)	-5(3)	6(2)	-3(2)
C(37)	48(3)	38(3)	58(3)	0(2)	26(3)	-5(2)
C(38)	38(3)	51(3)	48(3)	19(2)	15(2)	-1(2)
C(39)	35(3)	42(3)	48(3)	15(2)	11(2)	2(2)
C(40)	41(3)	60(3)	29(2)	-6(2)	2(2)	6(2)
C(47)	101(6)	95(6)	69(5)	42(5)	24(5)	34(5)
C(48)	86(5)	43(4)	105(6)	27(4)	46(5)	19(3)
C(45)	46(3)	76(4)	65(4)	-4(3)	21(3)	27(3)
C(46)	61(4)	116(7)	48(4)	36(4)	-17(3)	-23(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3})
for mls104.

	x	y	z	U(eq)
H(6)	5103	1185	7903	39
H(8)	4517	4518	8187	43
H(10)	5529	2177	11346	40
H(11)	3841	4400	6434	44
H(13)	4431	1071	6142	39
H(15)	7106	1649	12677	47
H(16A)	5913	10	10558	57
H(16B)	5435	156	11280	57
H(17A)	6229	622	12842	60
H(17B)	6553	-386	12304	60
H(18)	6531	1729	9683	61
H(19)	6765	5213	11482	85
H(20A)	7660	3539	11757	162
H(20B)	7594	4595	10909	162
H(21A)	7576	2758	10076	110
H(21B)	6961	3494	9546	110
H(26)	9814	6183	2688	41
H(30)	9439	7187	5749	39
H(31)	10498	9423	3692	45
H(33)	11168	9285	2588	48
H(34)	10475	6051	1572	44
H(35)	7940	6473	5746	45
H(36A)	7387	5776	4052	58
H(36B)	7945	4860	4055	58
H(38A)	8871	5600	6743	54
H(38B)	8570	4502	5979	54
H(39A)	9135	4903	4756	50

H(39B)	9636	5190	5900	50
H(40)	8403	6235	3227	54
H(47)	8062	9124	2510	106
H(48A)	7681	9351	4330	89
H(48B)	8324	9896	4268	89
H(45A)	7032	237	10797	73
H(45B)	7594	1130	11370	73
H(46A)	7582	7274	2182	98
H(46B)	7304	7523	3180	98

Table 6. Torsion angles [°] for mls104.

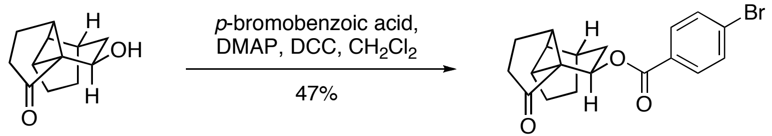
C(13)-C(6)-C(7)-C(8)	-0.2(7)
C(13)-C(6)-C(7)-C(12)	177.6(4)
C(6)-C(7)-C(8)-C(11)	0.5(7)
C(12)-C(7)-C(8)-C(11)	-177.4(4)
C(12)-O(1A)-C(10)-C(16)	173.9(4)
C(12)-O(1A)-C(10)-C(3)	-68.7(5)
C(14)-C(3)-C(10)-O(1A)	103.4(5)
C(18)-C(3)-C(10)-O(1A)	-37.6(6)
C(15)-C(3)-C(10)-O(1A)	-135.6(4)
C(14)-C(3)-C(10)-C(16)	-139.9(4)
C(18)-C(3)-C(10)-C(16)	79.1(5)
C(15)-C(3)-C(10)-C(16)	-18.9(5)
C(7)-C(8)-C(11)-C(4)	0.0(7)
C(13)-C(4)-C(11)-C(8)	-0.8(7)
Br(1)-C(4)-C(11)-C(8)	178.7(4)
C(10)-O(1A)-C(12)-O(4)	6.8(7)
C(10)-O(1A)-C(12)-C(7)	-172.8(4)
C(6)-C(7)-C(12)-O(4)	161.6(5)
C(8)-C(7)-C(12)-O(4)	-20.6(7)
C(6)-C(7)-C(12)-O(1A)	-18.8(6)
C(8)-C(7)-C(12)-O(1A)	159.0(4)
C(11)-C(4)-C(13)-C(6)	1.0(7)
Br(1)-C(4)-C(13)-C(6)	-178.5(3)
C(7)-C(6)-C(13)-C(4)	-0.5(7)
C(10)-C(3)-C(14)-O(5)	47.3(6)
C(18)-C(3)-C(14)-O(5)	-173.3(5)
C(15)-C(3)-C(14)-O(5)	-69.6(6)
C(10)-C(3)-C(14)-C(19)	-136.6(5)
C(18)-C(3)-C(14)-C(19)	2.8(7)
C(15)-C(3)-C(14)-C(19)	106.6(6)
C(14)-C(3)-C(15)-C(17)	115.4(5)
C(10)-C(3)-C(15)-C(17)	-6.1(5)

C(18)-C(3)-C(15)-C(17)	-122.6(5)
C(14)-C(3)-C(15)-C(45)	-126.7(5)
C(10)-C(3)-C(15)-C(45)	111.8(4)
C(18)-C(3)-C(15)-C(45)	-4.7(5)
O(1A)-C(10)-C(16)-C(17)	159.7(4)
C(3)-C(10)-C(16)-C(17)	36.3(5)
C(45)-C(15)-C(17)-C(16)	-68.6(6)
C(3)-C(15)-C(17)-C(16)	28.3(6)
C(10)-C(16)-C(17)-C(15)	-39.4(6)
C(14)-C(3)-C(18)-C(21)	0.5(7)
C(10)-C(3)-C(18)-C(21)	138.7(5)
C(15)-C(3)-C(18)-C(21)	-114.8(6)
C(14)-C(3)-C(18)-C(45)	120.1(5)
C(10)-C(3)-C(18)-C(45)	-101.7(5)
C(15)-C(3)-C(18)-C(45)	4.7(4)
O(5)-C(14)-C(19)-C(20)	145.6(7)
C(3)-C(14)-C(19)-C(20)	-30.5(9)
C(14)-C(19)-C(20)-C(21)	56.5(10)
C(19)-C(20)-C(21)-C(18)	-54.1(12)
C(45)-C(18)-C(21)-C(20)	-77.8(10)
C(3)-C(18)-C(21)-C(20)	23.6(11)
C(31)-C(24)-C(26)-C(34)	0.9(7)
C(28)-C(24)-C(26)-C(34)	-177.4(4)
C(30)-O(2A)-C(28)-O(3)	-7.2(7)
C(30)-O(2A)-C(28)-C(24)	170.5(4)
C(26)-C(24)-C(28)-O(3)	-162.7(5)
C(31)-C(24)-C(28)-O(3)	19.0(7)
C(26)-C(24)-C(28)-O(2A)	19.5(6)
C(31)-C(24)-C(28)-O(2A)	-158.8(4)
C(28)-O(2A)-C(30)-C(25)	78.9(5)
C(28)-O(2A)-C(30)-C(39)	-163.5(4)
C(37)-C(25)-C(30)-O(2A)	-96.7(5)
C(35)-C(25)-C(30)-O(2A)	138.6(4)
C(40)-C(25)-C(30)-O(2A)	43.7(6)

C(37)-C(25)-C(30)-C(39)	146.0(4)
C(35)-C(25)-C(30)-C(39)	21.3(5)
C(40)-C(25)-C(30)-C(39)	-73.7(5)
C(26)-C(24)-C(31)-C(33)	-1.2(7)
C(28)-C(24)-C(31)-C(33)	177.1(4)
C(34)-C(29)-C(33)-C(31)	1.7(8)
Br(2)-C(29)-C(33)-C(31)	-178.8(4)
C(24)-C(31)-C(33)-C(29)	0.0(7)
C(24)-C(26)-C(34)-C(29)	0.7(7)
C(33)-C(29)-C(34)-C(26)	-2.0(7)
Br(2)-C(29)-C(34)-C(26)	178.5(3)
C(37)-C(25)-C(35)-C(36)	121.4(5)
C(30)-C(25)-C(35)-C(36)	-114.6(4)
C(40)-C(25)-C(35)-C(36)	0.7(4)
C(37)-C(25)-C(35)-C(38)	-120.6(5)
C(30)-C(25)-C(35)-C(38)	3.3(5)
C(40)-C(25)-C(35)-C(38)	118.7(4)
C(38)-C(35)-C(36)-C(40)	-109.7(5)
C(25)-C(35)-C(36)-C(40)	-0.8(4)
C(30)-C(25)-C(37)-O(1)	-57.5(6)
C(35)-C(25)-C(37)-O(1)	61.6(7)
C(40)-C(25)-C(37)-O(1)	163.7(5)
C(30)-C(25)-C(37)-C(48)	123.8(6)
C(35)-C(25)-C(37)-C(48)	-117.2(6)
C(40)-C(25)-C(37)-C(48)	-15.1(7)
C(36)-C(35)-C(38)-C(39)	72.5(6)
C(25)-C(35)-C(38)-C(39)	-26.5(6)
C(35)-C(38)-C(39)-C(30)	39.1(5)
O(2A)-C(30)-C(39)-C(38)	-161.3(4)
C(25)-C(30)-C(39)-C(38)	-37.8(5)
C(35)-C(36)-C(40)-C(46)	-116.2(6)
C(35)-C(36)-C(40)-C(25)	0.8(4)
C(37)-C(25)-C(40)-C(36)	-117.6(5)
C(30)-C(25)-C(40)-C(36)	104.3(5)

C(35)-C(25)-C(40)-C(36)	-0.7(4)
C(37)-C(25)-C(40)-C(46)	0.5(7)
C(30)-C(25)-C(40)-C(46)	-137.6(5)
C(35)-C(25)-C(40)-C(46)	117.4(5)
C(46)-C(47)-C(48)-C(37)	50.1(9)
O(1)-C(37)-C(48)-C(47)	171.6(7)
C(25)-C(37)-C(48)-C(47)	-9.7(9)
C(17)-C(15)-C(45)-C(18)	113.1(5)
C(3)-C(15)-C(45)-C(18)	4.8(5)
C(21)-C(18)-C(45)-C(15)	112.2(6)
C(3)-C(18)-C(45)-C(15)	-4.8(5)
C(48)-C(47)-C(46)-C(40)	-64.8(9)
C(36)-C(40)-C(46)-C(47)	140.3(6)
C(25)-C(40)-C(46)-C(47)	37.9(9)

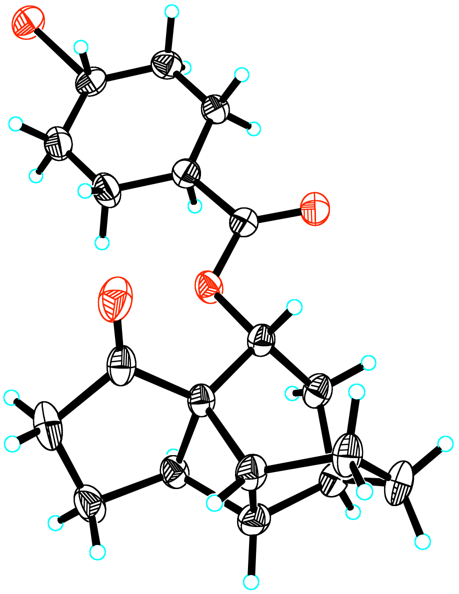
Symmetry transformations used to generate equivalent atoms:



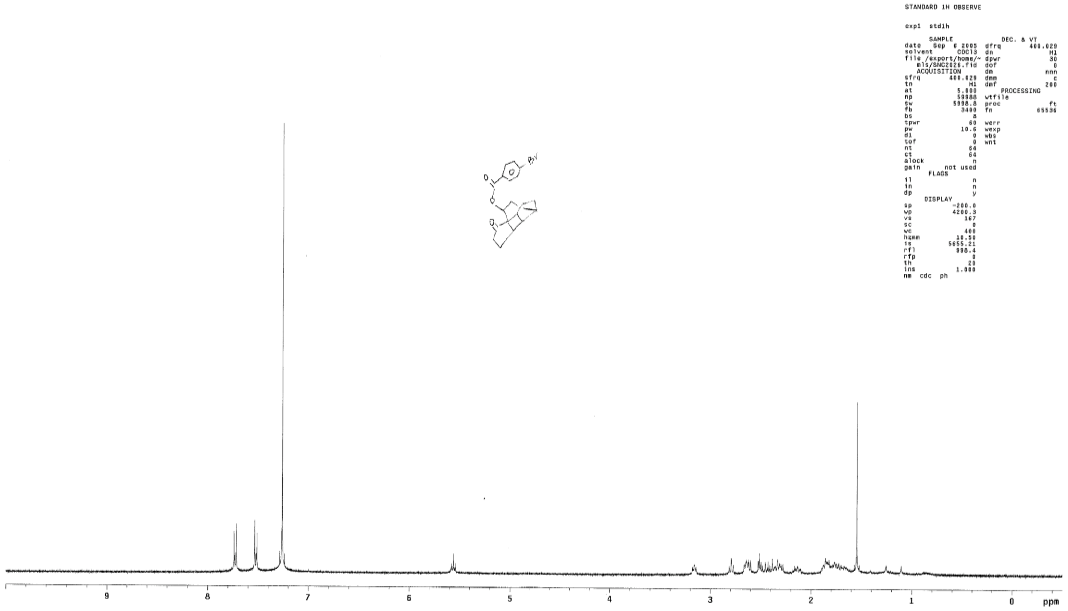
II.30b **II.34**

See representative procedure (A) for the derivatization of photocycloadduct ***II.34***. A solution of cycloadduct **II.30b** (2.5 mg, 0.01 mmol) was converted in 15 h, and the resulting residue was purified on silica gel (pentane:Et_2O 3:1). The product was recrystallized in Et_2O/pentane at -20 °C to give colorless crystals (2.3 mg, 47% yield).

Bromo-benzoate (II.34): R_f 0.75 (pentane:Et_2O 2:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.27 (d, 2H), 7.52 (d, 2H), 5.56 (t, 1H, J = 7.6 Hz), 3.15 (m, 1H), 2.79 (t, 1H, J = 8.0 Hz), 2.61 (m, 2H), 2.28-2.52 (m, 4H), 2.15 (m, 1H), 1.67-1.87 (m, 6H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) ***partial*** δ 165.4, 131.8, 131.2, 71.3, 61.0, 47.9, 47.1, 42.0, 39.5, 36.6, 35.3, 34.6, 23.7, 23.1. **IR** (NaCl, thin film) 3024 (w), 2923 (s), 1720 (s), 1271 (s), 1115 (m) cm^{-1}. **HRMS** (EI) $C_{19}H_{19}BrO_3$ Calcd: 374.0517. Found: 374.0514.



ORTEP of **II.34**



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STANDARD 1H OBSERVE

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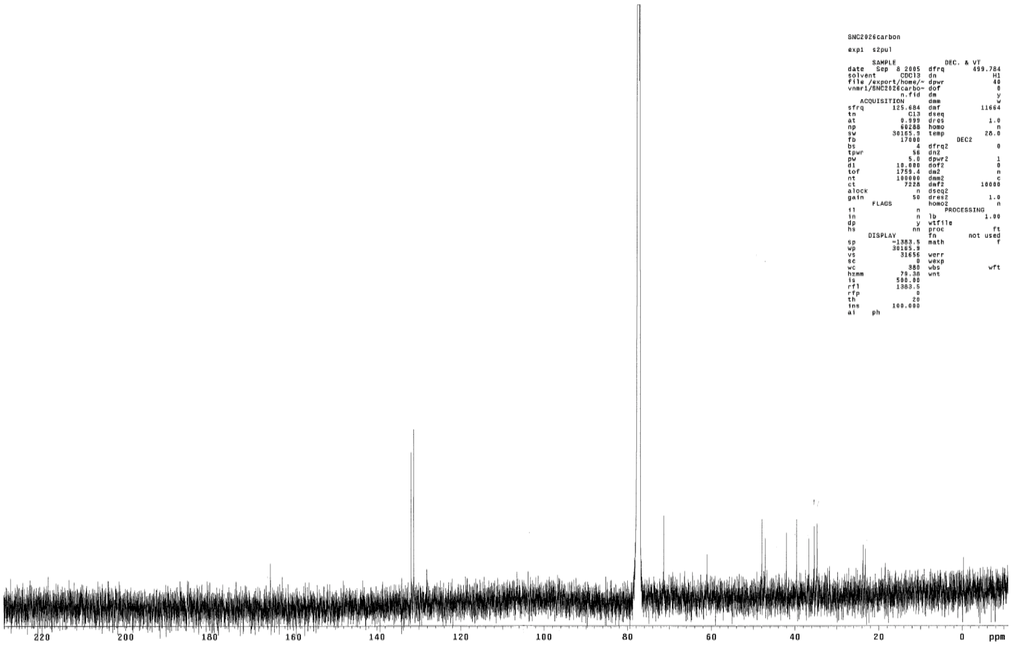
date   Sep  6 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             30
   mls/SNC2026.fid  dof               0
   ACQUISITION      dm              nnn
sfrq       400.029  dmm               c
tn              H1  dmf             200
at           5.000        PROCESSING
np           59988  wtfile
sw          5998.8  proc             ft
fb            3400  fn            65536
bs               8
tpwr            60  werr
pw            10.6  wexp
d1               0  wbs
tof              0  wnt
nt              64
ct              64
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs             167
sc               0
wc             400
hzmm         10.50
is         5655.21
rfl          998.4
rfp              0
th              20
ins          1.000
nm  cdc  ph
```



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SNC2026carbon

exp1  s2pul

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solvent      CDCl3  dn               H1
file /export/home/~ dpwr             40
vnmr1/SNC2026carbo~ dof               0
             n.fid  dm                y
   ACQUISITION      dmm               w
sfrq       125.684  dmf           11664
tn             C13  dseq
at           0.999  dres            1.0
np           60288  homo              n
sw         30165.9  temp           28.0
fb           17000         DEC2
bs               4  dfrq2             0
tpwr            56  dn2
pw             5.0  dpwr2             1
d1          10.000  dof2              0
tof         1759.4  dm2               n
nt          100000  dmm2              c
ct            7228  dmf2          10000
alock            n  dseq2
gain            50  dres2           1.0
      FLAGS         homo2             n
il               n       PROCESSING
in               n  lb             1.00
dp               y  wtfile
hs              nn  proc             ft
     DISPLAY        fn         not used
sp         -1383.5  math              f
wp         30165.9
vs           31656  werr
sc               0  wexp
wc             380  wbs             wft
hzmm         79.38  wnt
is          500.00
rfl         1383.5
rfp              0
th              20
ins        100.000
ai    ph
```

Table 1. Crystal data and structure refinement for **II.34**.

Identification code	testsn06	
Empirical formula	C19 H19 Br O3	
Formula weight	375.25	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.403(2) Å	a= 90°.
	b = 14.050(4) Å	b= 97.826(4)°.
	c = 8.221(2) Å	g = 90°.
Volume	847.2(4) Å^3	
Z	2	
Density (calculated)	1.471 Mg/m^3	
Absorption coefficient	2.438 mm^{-1}	
F(000)	384	
Crystal size	0.10 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.50 to 28.28°.	
Index ranges	-9<=h<=8, -18<=k<=18, -7<=l<=10	
Reflections collected	6104	
Independent reflections	3899 [R(int) = 0.0237]	
Completeness to theta = 28.28°	99.7 %	
Absorption correction	EMPIRACAL	
Max. and min. transmission	1.0000 and 0.7926	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3899 / 1 / 208	
Goodness-of-fit on F^2	0.720	
Final R indices [I>2sigma(I)]	R1 = 0.0243, wR2 = 0.0665	
R indices (all data)	R1 = 0.0255, wR2 = 0.0672	
Absolute structure parameter	0.003(6)	
Largest diff. peak and hole	0.553 and -0.241 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for testsn06. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(4)	1691(2)	11999(1)	8876(2)	38(1)
C(27)	-1874(3)	11482(1)	10852(2)	27(1)
C(26)	452(2)	10191(1)	10523(2)	24(1)
C(24)	-2284(3)	10501(2)	13177(3)	38(1)
C(25)	-1166(3)	11835(2)	7064(2)	40(1)
C(17)	-839(3)	9470(1)	11172(2)	30(1)
C(18)	-2612(3)	9924(1)	11573(2)	30(1)
C(19)	-2983(3)	11412(2)	7403(2)	35(1)
C(20)	-1345(3)	11426(1)	12706(2)	34(1)
C(21)	-3302(3)	10701(1)	10291(2)	30(1)
C(22)	-2480(2)	10614(1)	8683(2)	26(1)
C(15)	-670(2)	10977(1)	9660(2)	23(1)
C(14)	194(3)	11656(1)	8582(2)	28(1)
Br(1)	7077(1)	7785(1)	4386(1)	38(1)
C(1)	6170(2)	7871(2)	7623(2)	29(1)
C(3)	2764(3)	9166(1)	9792(2)	26(1)
O(1)	3135(2)	8916(1)	11216(2)	34(1)
O(2)	1408(2)	9763(1)	9272(2)	27(1)
C(7)	5728(2)	8209(1)	6042(2)	29(1)
C(8)	3755(2)	8835(1)	8444(2)	26(1)
C(9)	5179(2)	8192(1)	8829(2)	27(1)
C(11)	3332(3)	9160(1)	6836(2)	32(1)
C(12)	4313(3)	8842(2)	5624(2)	36(1)

Table 3. Bond lengths [Å] and angles [°] for testsn06.

O(4)-C(14)	1.202(3)
C(27)-C(20)	1.523(3)
C(27)-C(21)	1.549(3)
C(27)-C(15)	1.581(2)
C(27)-H(27)	1.0000
C(26)-O(2)	1.456(2)
C(26)-C(15)	1.500(2)
C(26)-C(17)	1.538(2)
C(26)-H(26)	1.0000
C(24)-C(18)	1.539(3)
C(24)-C(20)	1.548(3)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(14)	1.514(3)
C(25)-C(19)	1.531(3)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(17)-C(18)	1.534(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(21)	1.555(3)
C(18)-H(18)	1.0000
C(19)-C(22)	1.548(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.534(3)
C(21)-H(21)	1.0000
C(22)-C(15)	1.552(2)
C(22)-H(22)	1.0000
C(15)-C(14)	1.504(3)

Br(1)-C(7)	1.8918(18)
C(1)-C(9)	1.387(3)
C(1)-C(7)	1.380(3)
C(1)-H(1)	0.9500
C(3)-O(1)	1.217(3)
C(3)-O(2)	1.333(2)
C(3)-C(8)	1.485(3)
C(7)-C(12)	1.381(3)
C(8)-C(9)	1.392(2)
C(8)-C(11)	1.393(2)
C(9)-H(9)	0.9500
C(11)-C(12)	1.385(3)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500

C(20)-C(27)-C(21)	109.49(16)
C(20)-C(27)-C(15)	120.47(16)
C(21)-C(27)-C(15)	85.24(13)
C(20)-C(27)-H(27)	112.8
C(21)-C(27)-H(27)	112.8
C(15)-C(27)-H(27)	112.8
O(2)-C(26)-C(15)	105.15(14)
O(2)-C(26)-C(17)	110.95(14)
C(15)-C(26)-C(17)	108.57(14)
O(2)-C(26)-H(26)	110.7
C(15)-C(26)-H(26)	110.7
C(17)-C(26)-H(26)	110.7
C(18)-C(24)-C(20)	104.56(16)
C(18)-C(24)-H(24A)	110.8
C(20)-C(24)-H(24A)	110.8
C(18)-C(24)-H(24B)	110.8
C(20)-C(24)-H(24B)	110.8
H(24A)-C(24)-H(24B)	108.9
C(14)-C(25)-C(19)	106.71(16)

C(14)-C(25)-H(25A)	110.4
C(19)-C(25)-H(25A)	110.4
C(14)-C(25)-H(25B)	110.4
C(19)-C(25)-H(25B)	110.4
H(25A)-C(25)-H(25B)	108.6
C(18)-C(17)-C(26)	113.00(15)
C(18)-C(17)-H(17A)	109.0
C(26)-C(17)-H(17A)	109.0
C(18)-C(17)-H(17B)	109.0
C(26)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
C(17)-C(18)-C(24)	111.31(16)
C(17)-C(18)-C(21)	111.00(15)
C(24)-C(18)-C(21)	102.13(15)
C(17)-C(18)-H(18)	110.7
C(24)-C(18)-H(18)	110.7
C(21)-C(18)-H(18)	110.7
C(22)-C(19)-C(25)	105.60(16)
C(22)-C(19)-H(19A)	110.6
C(25)-C(19)-H(19A)	110.6
C(22)-C(19)-H(19B)	110.6
C(25)-C(19)-H(19B)	110.6
H(19A)-C(19)-H(19B)	108.8
C(27)-C(20)-C(24)	103.31(16)
C(27)-C(20)-H(20A)	111.1
C(24)-C(20)-H(20A)	111.1
C(27)-C(20)-H(20B)	111.1
C(24)-C(20)-H(20B)	111.1
H(20A)-C(20)-H(20B)	109.1
C(22)-C(21)-C(27)	88.79(14)
C(22)-C(21)-C(18)	113.27(15)
C(27)-C(21)-C(18)	98.48(14)
C(22)-C(21)-H(21)	117.1
C(27)-C(21)-H(21)	117.1

C(18)-C(21)-H(21)	117.1
C(21)-C(22)-C(19)	116.13(16)
C(21)-C(22)-C(15)	86.75(13)
C(19)-C(22)-C(15)	102.99(15)
C(21)-C(22)-H(22)	115.6
C(19)-C(22)-H(22)	115.6
C(15)-C(22)-H(22)	115.6
C(26)-C(15)-C(14)	119.56(15)
C(26)-C(15)-C(22)	112.74(14)
C(14)-C(15)-C(22)	108.06(14)
C(26)-C(15)-C(27)	111.10(14)
C(14)-C(15)-C(27)	113.68(14)
C(22)-C(15)-C(27)	87.04(13)
O(4)-C(14)-C(25)	126.17(18)
O(4)-C(14)-C(15)	126.17(16)
C(25)-C(14)-C(15)	107.66(16)
C(9)-C(1)-C(7)	118.74(17)
C(9)-C(1)-H(1)	120.6
C(7)-C(1)-H(1)	120.6
O(1)-C(3)-O(2)	123.43(18)
O(1)-C(3)-C(8)	123.90(18)
O(2)-C(3)-C(8)	112.66(15)
C(3)-O(2)-C(26)	116.82(14)
C(12)-C(7)-C(1)	122.05(17)
C(12)-C(7)-Br(1)	118.70(15)
C(1)-C(7)-Br(1)	119.25(14)
C(9)-C(8)-C(11)	119.63(17)
C(9)-C(8)-C(3)	118.01(16)
C(11)-C(8)-C(3)	122.35(16)
C(1)-C(9)-C(8)	120.40(17)
C(1)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(12)-C(11)-C(8)	120.31(17)
C(12)-C(11)-H(11)	119.8

C(8)-C(11)-H(11)	119.8
C(11)-C(12)-C(7)	118.86(18)
C(11)-C(12)-H(12)	120.6
C(7)-C(12)-H(12)	120.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for testsn06. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(4)	41(1)	40(1)	34(1)	3(1)	7(1)	-14(1)
C(27)	31(1)	24(1)	26(1)	-4(1)	7(1)	4(1)
C(26)	26(1)	24(1)	23(1)	-1(1)	5(1)	1(1)
C(24)	49(1)	42(1)	26(1)	-3(1)	14(1)	-5(1)
C(25)	53(1)	39(1)	25(1)	6(1)	-2(1)	-7(1)
C(17)	33(1)	26(1)	32(1)	4(1)	9(1)	-1(1)
C(18)	29(1)	33(1)	28(1)	-2(1)	10(1)	-5(1)
C(19)	38(1)	41(1)	24(1)	1(1)	-1(1)	8(1)
C(20)	44(1)	34(1)	24(1)	-6(1)	7(1)	-1(1)
C(21)	24(1)	35(1)	31(1)	-5(1)	7(1)	1(1)
C(22)	25(1)	28(1)	25(1)	-4(1)	2(1)	0(1)
C(15)	25(1)	21(1)	22(1)	-3(1)	3(1)	0(1)
C(14)	38(1)	24(1)	23(1)	-2(1)	8(1)	0(1)
Br(1)	37(1)	45(1)	35(1)	-4(1)	13(1)	6(1)
C(1)	26(1)	28(1)	33(1)	-2(1)	5(1)	4(1)
C(3)	22(1)	27(1)	29(1)	0(1)	7(1)	-1(1)
O(1)	32(1)	45(1)	26(1)	7(1)	6(1)	9(1)
O(2)	28(1)	31(1)	23(1)	-1(1)	5(1)	5(1)
C(7)	27(1)	31(1)	32(1)	-5(1)	9(1)	-1(1)
C(8)	26(1)	25(1)	27(1)	1(1)	6(1)	1(1)
C(9)	26(1)	28(1)	27(1)	3(1)	4(1)	1(1)
C(11)	33(1)	34(1)	28(1)	6(1)	5(1)	11(1)
C(12)	38(1)	42(1)	29(1)	7(1)	8(1)	8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for testsn06.

	x	y	z	U(eq)
H(27)	-2284	12132	10470	32
H(26)	1338	10451	11443	29
H(24A)	-1488	10146	14036	46
H(24B)	-3452	10645	13586	46
H(25A)	-757	11526	6095	47
H(25B)	-1295	12527	6848	47
H(17A)	-1144	8966	10339	36
H(17B)	-202	9166	12175	36
H(18)	-3569	9428	11634	35
H(19A)	-3742	11904	7845	42
H(19B)	-3667	11148	6384	42
H(20A)	-1800	11986	13258	41
H(20B)	-5	11385	13000	41
H(21)	-4617	10885	10205	36
H(22)	-2442	9955	8227	31
H(1)	7136	7428	7880	35
H(9)	5475	7971	9926	32
H(11)	2366	9602	6570	38
H(12)	4019	9055	4523	43

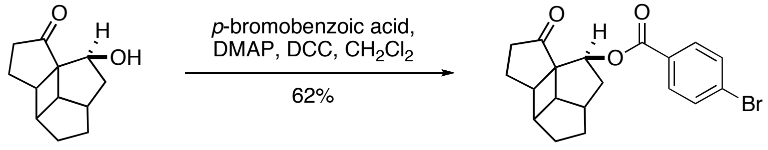
Table 6. Torsion angles [°] for testsn06.

O(2)-C(26)-C(17)-C(18)	-144.07(15)
C(15)-C(26)-C(17)-C(18)	-29.0(2)
C(26)-C(17)-C(18)-C(24)	-74.9(2)
C(26)-C(17)-C(18)-C(21)	38.2(2)
C(20)-C(24)-C(18)-C(17)	75.7(2)
C(20)-C(24)-C(18)-C(21)	-42.8(2)
C(14)-C(25)-C(19)-C(22)	-25.9(2)
C(21)-C(27)-C(20)-C(24)	8.0(2)
C(15)-C(27)-C(20)-C(24)	-88.1(2)
C(18)-C(24)-C(20)-C(27)	21.3(2)
C(20)-C(27)-C(21)-C(22)	-146.62(15)
C(15)-C(27)-C(21)-C(22)	-25.93(13)
C(20)-C(27)-C(21)-C(18)	-33.26(18)
C(15)-C(27)-C(21)-C(18)	87.43(14)
C(17)-C(18)-C(21)-C(22)	18.9(2)
C(24)-C(18)-C(21)-C(22)	137.63(17)
C(17)-C(18)-C(21)-C(27)	-73.43(17)
C(24)-C(18)-C(21)-C(27)	45.29(17)
C(27)-C(21)-C(22)-C(19)	-76.49(18)
C(18)-C(21)-C(22)-C(19)	-175.19(15)
C(27)-C(21)-C(22)-C(15)	26.40(13)
C(18)-C(21)-C(22)-C(15)	-72.31(17)
C(25)-C(19)-C(22)-C(21)	122.83(18)
C(25)-C(19)-C(22)-C(15)	30.06(19)
O(2)-C(26)-C(15)-C(14)	-47.29(18)
C(17)-C(26)-C(15)-C(14)	-166.09(15)
O(2)-C(26)-C(15)-C(22)	81.34(18)
C(17)-C(26)-C(15)-C(22)	-37.5(2)
O(2)-C(26)-C(15)-C(27)	177.18(13)
C(17)-C(26)-C(15)-C(27)	58.37(18)
C(21)-C(22)-C(15)-C(26)	85.80(16)
C(19)-C(22)-C(15)-C(26)	-158.12(15)

C(21)-C(22)-C(15)-C(14)	-139.83(14)
C(19)-C(22)-C(15)-C(14)	-23.74(19)
C(21)-C(22)-C(15)-C(27)	-25.86(13)
C(19)-C(22)-C(15)-C(27)	90.22(15)
C(20)-C(27)-C(15)-C(26)	22.2(2)
C(21)-C(27)-C(15)-C(26)	-87.62(15)
C(20)-C(27)-C(15)-C(14)	-116.07(18)
C(21)-C(27)-C(15)-C(14)	134.08(15)
C(20)-C(27)-C(15)-C(22)	135.49(18)
C(21)-C(27)-C(15)-C(22)	25.65(13)
C(19)-C(25)-C(14)-O(4)	-168.7(2)
C(19)-C(25)-C(14)-C(15)	10.9(2)
C(26)-C(15)-C(14)-O(4)	-41.3(3)
C(22)-C(15)-C(14)-O(4)	-172.03(19)
C(27)-C(15)-C(14)-O(4)	93.2(2)
C(26)-C(15)-C(14)-C(25)	139.03(16)
C(22)-C(15)-C(14)-C(25)	8.3(2)
C(27)-C(15)-C(14)-C(25)	-86.49(18)
O(1)-C(3)-O(2)-C(26)	5.6(3)
C(8)-C(3)-O(2)-C(26)	-174.89(14)
C(15)-C(26)-O(2)-C(3)	167.45(14)
C(17)-C(26)-O(2)-C(3)	-75.36(19)
C(9)-C(1)-C(7)-C(12)	-1.1(3)
C(9)-C(1)-C(7)-Br(1)	179.60(14)
O(1)-C(3)-C(8)-C(9)	0.8(3)
O(2)-C(3)-C(8)-C(9)	-178.71(16)
O(1)-C(3)-C(8)-C(11)	-177.79(19)
O(2)-C(3)-C(8)-C(11)	2.7(3)
C(7)-C(1)-C(9)-C(8)	0.6(3)
C(11)-C(8)-C(9)-C(1)	-0.3(3)
C(3)-C(8)-C(9)-C(1)	-178.95(17)
C(9)-C(8)-C(11)-C(12)	0.4(3)
C(3)-C(8)-C(11)-C(12)	179.01(19)
C(8)-C(11)-C(12)-C(7)	-0.8(3)

C(1)-C(7)-C(12)-C(11)	1.2(3)
Br(1)-C(7)-C(12)-C(11)	-179.48(16)

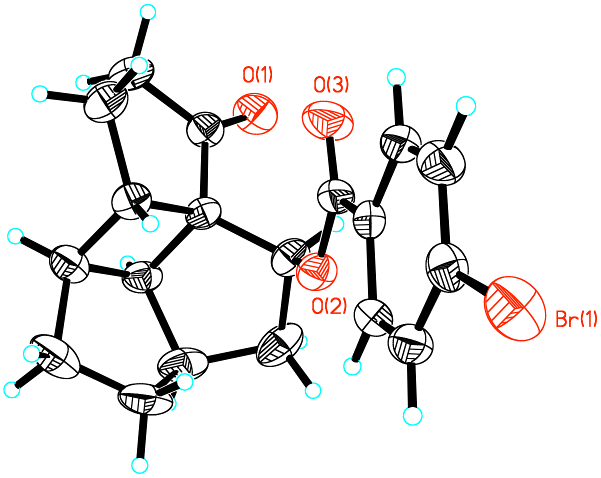
Symmetry transformations used to generate equivalent atoms:



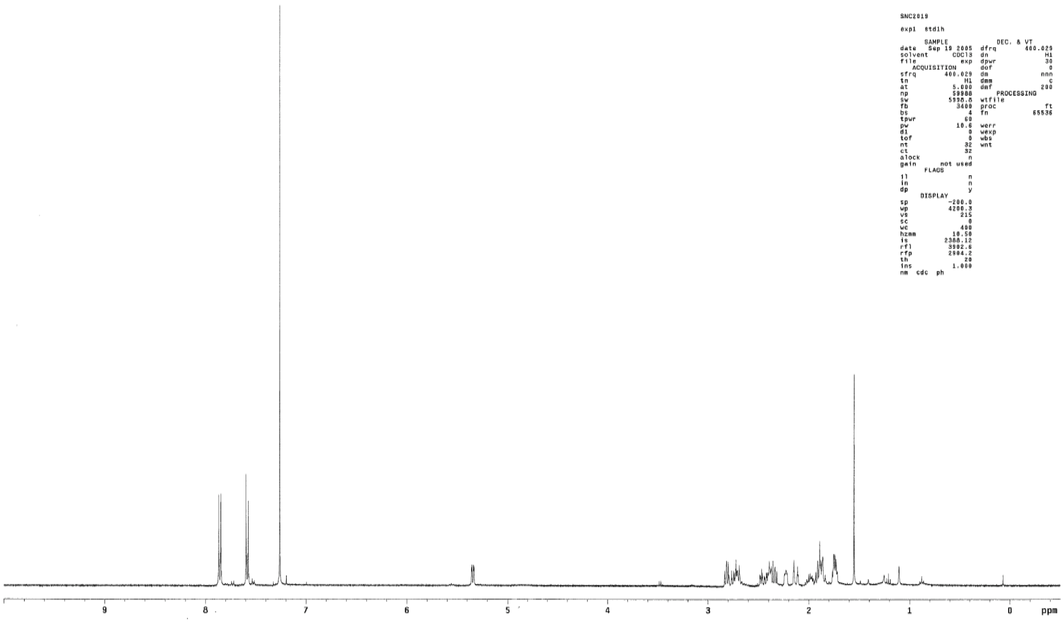
II.31a **II.35**

See representative procedure (A) for the derivatization of photocycloadduct ***II.35***. A solution of cycloadduct **II.31a** (4.6 mg, 0.02 mmol) was converted in 15 h, and the resulting residue was purified on silica gel (pentane:Et_2O 3:1). The product was recrystallized in Et_2O and pentane at -20 °C to give colorless crystals (5.6 mg, 62 % yield).

Bromo-benzoate (II.35): $\mathbf{R_f}$ 0.37 (pentane:Et_2O 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.85 (d, 2H, J = 8.8 Hz), 7.58 (d, 2H, J = 8.8 Hz), 5.34 (dd, 1H, J = 7.6, 1.6 Hz), 2.80 (m, 1H), 2.71 (m, 2H), 2.31-2.48 (m, 3H), 2.22 (m, 1H), 2.13 (m 1H), 1.83-2.00 (m, 4H), 1.74 (m, 2H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 218.9, 165.7, 132.0, 131.2, 129.2, 128.3, 81.4, 59.3, 52.8, 44.9, 40.1, 40.0, 39.7, 36.7, 34.8, 31.9, 27.2. **IR** (NaCl, thin film) 3025 (m), 2881 (w), 1730 (s), 1703 (s), 1274 (m), 1116 (m) cm^{-1}. **HRMS** (EI) $C_{19}H_{19}BrO_3$ Calcd: 374.0517. Found: 374.0514.



ORTEP of **II.35**



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file           exp  dpwr             30
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sfrq       400.029  dm              nnn
tn              H1  dmm               c
at           5.000  dmf             200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn            65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs
nt              32  wnt
ct              32
alock            n
gain      not used
     FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs             215
sc               0
wc             400
hzmm         10.50
is         2388.12
rfl         3902.6
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
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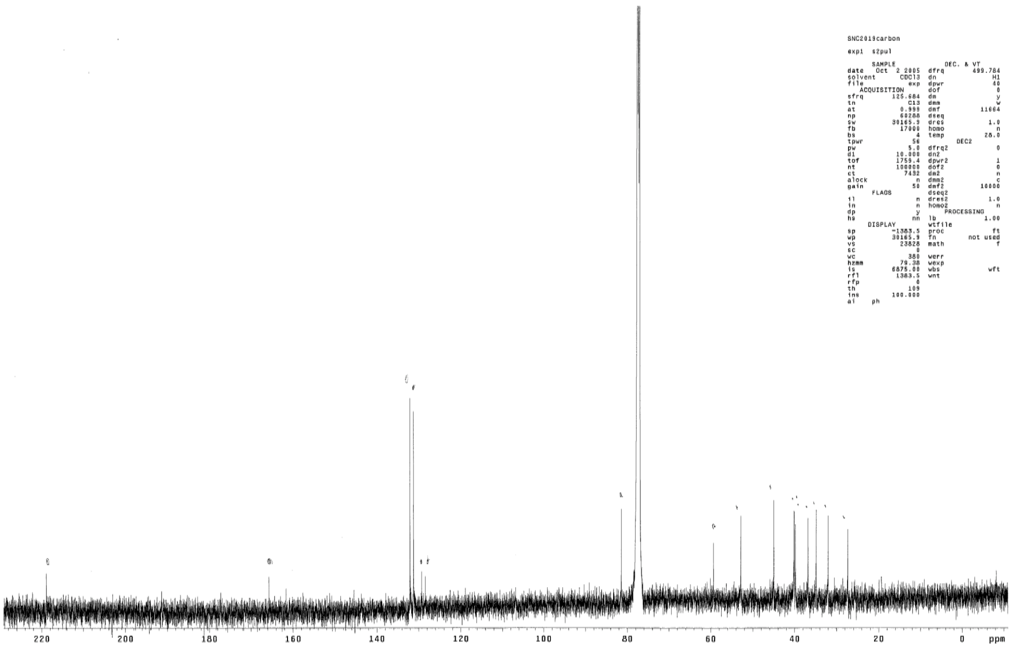

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SNC2019carbon

exp1  s2pul

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solvent       CDCl3   dn               H1
file            exp   dpwr             40
   ACQUISITION        dof               0
sfrq        125.684   dm                y
tn              C13   dmm               w
at            0.999   dmf           11664
np            60288   dseq
sw          30165.9   dres            1.0
fb            17000   homo              n
bs                4   temp           28.0
tpwr             56          DEC2
pw              5.0   dfrq2             0
d1           10.000   dn2
tof          1759.4   dpwr2             1
nt           100000   dof2              0
ct             7432   dm2               n
alock             n   dmm2              c
gain             50   dmf2          10000
       FLAGS          dseq2
il                n   dres2           1.0
in                n   homo2             n
dp                y       PROCESSING
hs               nn   lb             1.00
      DISPLAY         wtfile
sp          -1383.5   proc             ft
wp          30165.9   fn         not used
vs            23828   math              f
sc                0
wc              380   werr
hzmm          79.38   wexp
is          6875.00   wbs             wft
rfl          1383.5   wnt
rfp               0
th              109
ins         100.000
ai    ph
```

Table 1. Crystal data and structure refinement for **II.35**.

Identification code	sn09t1	
Empirical formula	C19 H19 Br O3	
Formula weight	375.25	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.6996(13) Å	a= 88.000(3)°.
	b = 14.279(3) Å	b= 77.060(2)°.
	c = 15.933(3) Å	g = 76.470(3)°.
Volume	1659.6(5) Å^3	
Z	4	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	2.489 mm^{-1}	
F(000)	768	
Crystal size mm^3	0.20	x 0.18 x 0.16
Theta range for data collection	1.31 to 28.43°.	
Index ranges	-9<=h<=10, -8<=k<=19, -21<=l<=21	
Reflections collected	12412	
Independent reflections	9906 [R(int) = 0.0182]	
Completeness to theta = 28.43°	98.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.4061	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9906 / 3 / 829	
Goodness-of-fit on F^2	0.964	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0873	
R indices (all data)	R1 = 0.0500, wR2 = 0.0912	
Absolute structure parameter	0.012(5)	
Largest diff. peak and hole	1.044 and -0.415 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for sn09t1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	4874(1)	5733(1)	1385(1)	50(1)
O(1)	14934(4)	9587(2)	-645(2)	46(1)
O(2)	9996(3)	8834(2)	-400(2)	35(1)
O(3)	12013(4)	8010(2)	325(2)	49(1)
C(8)	8272(6)	6257(3)	1283(2)	39(1)
C(10)	6178(5)	7280(3)	537(2)	33(1)
C(11)	7452(5)	7825(3)	237(2)	31(1)
C(12)	11656(4)	10049(3)	-150(2)	28(1)
C(15)	10564(5)	8145(3)	131(3)	34(1)
C(18)	9535(5)	6807(3)	994(3)	35(1)
C(22)	9146(5)	7585(3)	465(2)	30(1)
C(25)	10474(5)	10254(3)	790(2)	32(1)
C(27)	6606(5)	6500(3)	1038(2)	34(1)
C(28)	7795(6)	11621(4)	513(4)	52(1)
C(30)	11274(5)	9411(3)	-795(2)	34(1)
C(35)	13614(5)	9871(3)	-64(2)	33(1)
C(36)	13674(5)	10142(4)	829(3)	42(1)
C(37)	10911(5)	11120(3)	-364(3)	34(1)
C(38)	11831(5)	10043(4)	1381(3)	41(1)
C(39)	10387(7)	10100(4)	-1412(3)	47(1)
C(41)	7713(5)	11069(3)	-252(3)	49(1)
C(43)	9803(5)	11326(3)	583(3)	37(1)
C(44)	9532(6)	11063(3)	-913(3)	45(1)
Br(2)	13545(1)	3471(1)	10473(1)	52(1)
O(4)	6100(3)	5720(2)	8863(2)	40(1)
O(5)	2812(4)	7317(3)	8017(2)	52(1)
O(6)	8041(3)	6672(2)	8400(2)	31(1)
C(48)	7578(5)	5904(3)	8804(2)	30(1)

C(49)	10736(5)	5570(3)	9099(2)	32(1)
C(50)	9081(5)	5307(3)	9169(2)	30(1)
C(51)	11739(5)	4216(3)	9926(2)	35(1)
C(52)	12093(5)	5013(3)	9484(2)	34(1)
C(53)	6607(5)	7350(3)	8094(2)	32(1)
C(54)	4020(6)	5961(4)	7018(3)	49(1)
C(55)	8782(5)	4486(3)	9617(3)	35(1)
C(56)	6042(5)	6923(3)	7353(2)	32(1)
C(57)	10114(5)	3929(3)	9997(3)	39(1)
C(58)	7943(6)	8026(3)	6740(3)	46(1)
C(59)	7219(5)	5998(3)	6835(2)	34(1)
C(60)	4094(5)	6803(3)	7538(3)	40(1)
C(61)	9782(6)	7296(4)	6441(3)	53(1)
C(62)	6525(6)	7517(4)	6538(3)	45(1)
C(63)	7373(6)	8208(3)	7701(3)	44(1)
C(64)	7582(6)	6590(4)	6017(3)	51(1)
C(65)	5966(6)	5318(3)	6855(3)	44(1)
C(89)	9548(7)	6708(5)	5723(3)	64(1)
Br(3)	10752(1)	5828(1)	3284(1)	65(1)
O(10)	3844(4)	3544(2)	4932(2)	45(1)
O(11)	6183(3)	2630(2)	5422(2)	34(1)
O(12)	1157(4)	2004(3)	5809(2)	58(1)
C(67)	8531(5)	3763(3)	4722(2)	35(1)
C(68)	9095(6)	5101(3)	3868(3)	40(1)
C(70)	5406(5)	3383(3)	5003(2)	32(1)
C(71)	5046(5)	1953(3)	5756(2)	32(1)
C(72)	9728(5)	4321(3)	4339(3)	39(1)
C(73)	272(6)	3383(4)	6782(3)	51(1)
C(74)	3413(5)	2416(3)	6476(2)	31(1)
C(75)	6711(5)	4001(3)	4635(2)	32(1)
C(76)	6110(5)	4801(3)	4178(3)	40(1)
C(77)	6198(6)	1115(3)	6168(3)	45(1)
C(78)	3627(6)	1848(3)	7308(3)	45(1)
C(79)	7289(6)	5360(3)	3784(3)	43(1)

C(80)	1489(6)	4026(3)	6929(3)	45(1)
C(81)	3323(5)	3350(3)	6968(2)	35(1)
C(82)	5688(6)	1337(3)	7127(3)	46(1)
C(83)	1548(5)	2524(3)	6274(3)	41(1)
C(84)	5180(8)	2690(5)	8106(3)	63(1)
C(85)	6601(6)	2062(4)	7420(3)	51(1)
C(86)	3408(6)	2784(4)	7799(3)	46(1)
Br(4)	-3305(1)	3464(1)	2216(1)	73(1)
O(7)	7583(4)	-443(3)	4562(2)	49(1)
O(8)	2228(3)	329(2)	4292(2)	32(1)
O(9)	4236(4)	1229(2)	3749(2)	43(1)
C(4)	-494(5)	1448(3)	3649(2)	33(1)
C(5)	-1835(6)	1974(3)	3270(3)	41(1)
C(6)	3624(5)	-302(3)	4668(2)	33(1)
C(7)	2732(5)	1069(3)	3850(3)	34(1)
C(13)	2164(6)	-1895(4)	3894(3)	45(1)
C(17)	1237(5)	1641(3)	3463(3)	34(1)
C(19)	5219(5)	-850(3)	3976(2)	29(1)
C(20)	1601(6)	2371(3)	2907(3)	43(1)
C(21)	-1454(6)	2700(3)	2718(3)	45(1)
C(23)	5098(5)	-933(3)	3022(2)	31(1)
C(24)	7067(5)	-649(3)	3952(3)	36(1)
C(26)	5265(5)	-2033(3)	3105(3)	36(1)
C(29)	8192(5)	-798(4)	3036(3)	43(1)
C(31)	3526(6)	-2352(4)	3083(3)	48(1)
C(32)	6778(5)	-624(3)	2467(2)	38(1)
C(33)	3295(5)	-1946(3)	4581(3)	41(1)
C(34)	5251(5)	-1940(3)	4072(2)	34(1)
C(40)	251(7)	2908(3)	2534(3)	45(1)
C(42)	2746(5)	-1073(3)	5167(3)	40(1)

Table 3. Bond lengths [Å] and angles [°] for sn09t1.

Br(1)-C(27)	1.896(4)
O(1)-C(35)	1.210(4)
O(2)-C(15)	1.335(5)
O(2)-C(30)	1.453(5)
O(3)-C(15)	1.194(4)
C(8)-C(18)	1.380(6)
C(8)-C(27)	1.387(6)
C(8)-H(8)	0.9500
C(10)-C(27)	1.368(6)
C(10)-C(11)	1.384(6)
C(10)-H(10)	0.9500
C(11)-C(22)	1.394(5)
C(11)-H(11)	0.9500
C(12)-C(35)	1.505(5)
C(12)-C(30)	1.517(5)
C(12)-C(37)	1.557(5)
C(12)-C(25)	1.566(5)
C(15)-C(22)	1.494(6)
C(18)-C(22)	1.388(6)
C(18)-H(18)	0.9500
C(25)-C(38)	1.530(5)
C(25)-C(43)	1.546(6)
C(25)-H(25)	1.0000
C(28)-C(41)	1.496(7)
C(28)-C(43)	1.532(5)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(30)-C(39)	1.522(6)
C(30)-H(30)	1.0000
C(35)-C(36)	1.502(5)
C(36)-C(38)	1.527(6)
C(36)-H(36A)	0.9900

C(36)-H(36B)	0.9900
C(37)-C(44)	1.536(5)
C(37)-C(43)	1.558(6)
C(37)-H(37)	1.0000
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(39)-C(44)	1.542(7)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(41)-C(44)	1.552(6)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(43)-H(43)	1.0000
C(44)-H(44)	1.0000
Br(2)-C(51)	1.901(4)
O(4)-C(48)	1.209(4)
O(5)-C(60)	1.207(5)
O(6)-C(48)	1.334(5)
O(6)-C(53)	1.450(5)
C(48)-C(50)	1.486(6)
C(49)-C(50)	1.391(5)
C(49)-C(52)	1.401(6)
C(49)-H(49)	0.9500
C(50)-C(55)	1.390(6)
C(51)-C(52)	1.368(6)
C(51)-C(57)	1.385(6)
C(52)-H(52)	0.9500
C(53)-C(63)	1.536(6)
C(53)-C(56)	1.536(5)
C(53)-H(53)	1.0000
C(54)-C(60)	1.504(6)
C(54)-C(65)	1.534(6)
C(54)-H(54A)	0.9900
C(54)-H(54B)	0.9900

C(55)-C(57)	1.384(6)
C(55)-H(55)	0.9500
C(56)-C(60)	1.511(5)
C(56)-C(62)	1.549(6)
C(56)-C(59)	1.557(5)
C(57)-H(57)	0.9500
C(58)-C(63)	1.509(6)
C(58)-C(61)	1.536(7)
C(58)-C(62)	1.539(6)
C(58)-H(58)	1.0000
C(59)-C(65)	1.516(6)
C(59)-C(64)	1.537(6)
C(59)-H(59)	1.0000
C(61)-C(89)	1.508(8)
C(61)-H(61A)	0.9900
C(61)-H(61B)	0.9900
C(62)-C(64)	1.541(7)
C(62)-H(62)	1.0000
C(63)-H(63A)	0.9900
C(63)-H(63B)	0.9900
C(64)-C(89)	1.528(7)
C(64)-H(64)	1.0000
C(65)-H(65A)	0.9900
C(65)-H(65B)	0.9900
C(89)-H(89A)	0.9900
C(89)-H(89B)	0.9900
Br(3)-C(68)	1.895(4)
O(10)-C(70)	1.201(4)
O(11)-C(70)	1.336(5)
O(11)-C(71)	1.462(5)
O(12)-C(83)	1.198(5)
C(67)-C(72)	1.383(6)
C(67)-C(75)	1.400(5)
C(67)-H(67)	0.9500

C(68)-C(72)	1.376(7)
C(68)-C(79)	1.388(6)
C(70)-C(75)	1.500(6)
C(71)-C(74)	1.534(5)
C(71)-C(77)	1.536(6)
C(71)-H(71)	1.0000
C(72)-H(72)	0.9500
C(73)-C(83)	1.508(6)
C(73)-C(80)	1.514(7)
C(73)-H(73A)	0.9900
C(73)-H(73B)	0.9900
C(74)-C(83)	1.513(5)
C(74)-C(81)	1.550(5)
C(74)-C(78)	1.550(6)
C(75)-C(76)	1.376(6)
C(76)-C(79)	1.379(6)
C(76)-H(76)	0.9500
C(77)-C(82)	1.515(6)
C(77)-H(77A)	0.9900
C(77)-H(77B)	0.9900
C(78)-C(86)	1.528(7)
C(78)-C(82)	1.550(6)
C(78)-H(78)	1.0000
C(79)-H(79)	0.9500
C(80)-C(81)	1.525(6)
C(80)-H(80A)	0.9900
C(80)-H(80B)	0.9900
C(81)-C(86)	1.532(6)
C(81)-H(81)	1.0000
C(82)-C(85)	1.519(7)
C(82)-H(82)	1.0000
C(84)-C(85)	1.506(7)
C(84)-C(86)	1.526(7)
C(84)-H(84A)	0.9900

C(84)-H(84B)	0.9900
C(85)-H(85A)	0.9900
C(85)-H(85B)	0.9900
C(86)-H(86)	1.0000
Br(4)-C(21)	1.894(4)
O(7)-C(24)	1.199(5)
O(8)-C(7)	1.335(5)
O(8)-C(6)	1.457(5)
O(9)-C(7)	1.207(5)
C(4)-C(5)	1.371(6)
C(4)-C(17)	1.389(5)
C(4)-H(4)	0.9500
C(5)-C(21)	1.377(7)
C(5)-H(5)	0.9500
C(6)-C(19)	1.530(5)
C(6)-C(42)	1.531(6)
C(6)-H(6)	1.0000
C(7)-C(17)	1.489(6)
C(13)-C(31)	1.525(6)
C(13)-C(33)	1.534(6)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(17)-C(20)	1.382(6)
C(19)-C(24)	1.508(5)
C(19)-C(23)	1.554(5)
C(19)-C(34)	1.554(5)
C(20)-C(40)	1.377(6)
C(20)-H(20)	0.9500
C(21)-C(40)	1.378(7)
C(23)-C(32)	1.541(5)
C(23)-C(26)	1.550(6)
C(23)-H(23)	1.0000
C(24)-C(29)	1.514(6)
C(26)-C(31)	1.520(6)

C(26)-C(34)	1.549(5)
C(26)-H(26)	1.0000
C(29)-C(32)	1.540(6)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(42)	1.505(6)
C(33)-C(34)	1.544(5)
C(33)-H(33)	1.0000
C(34)-H(34)	1.0000
C(40)-H(40)	0.9500
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(15)-O(2)-C(30)	117.2(3)
C(18)-C(8)-C(27)	118.7(4)
C(18)-C(8)-H(8)	120.6
C(27)-C(8)-H(8)	120.6
C(27)-C(10)-C(11)	119.7(3)
C(27)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	120.1
C(10)-C(11)-C(22)	119.7(4)
C(10)-C(11)-H(11)	120.2
C(22)-C(11)-H(11)	120.2
C(35)-C(12)-C(30)	116.2(3)
C(35)-C(12)-C(37)	111.3(3)
C(30)-C(12)-C(37)	108.4(3)
C(35)-C(12)-C(25)	105.2(3)
C(30)-C(12)-C(25)	123.5(3)
C(37)-C(12)-C(25)	88.9(3)
O(3)-C(15)-O(2)	123.8(4)

O(3)-C(15)-C(22)	124.6(4)
O(2)-C(15)-C(22)	111.5(3)
C(8)-C(18)-C(22)	120.5(3)
C(8)-C(18)-H(18)	119.7
C(22)-C(18)-H(18)	119.7
C(18)-C(22)-C(11)	119.7(4)
C(18)-C(22)-C(15)	119.5(3)
C(11)-C(22)-C(15)	120.7(4)
C(38)-C(25)-C(43)	115.9(3)
C(38)-C(25)-C(12)	105.9(3)
C(43)-C(25)-C(12)	90.8(3)
C(38)-C(25)-H(25)	113.9
C(43)-C(25)-H(25)	113.9
C(12)-C(25)-H(25)	113.9
C(10)-C(27)-C(8)	121.6(4)
C(10)-C(27)-Br(1)	118.4(3)
C(8)-C(27)-Br(1)	120.0(3)
C(41)-C(28)-C(43)	104.9(4)
C(41)-C(28)-H(28A)	110.8
C(43)-C(28)-H(28A)	110.8
C(41)-C(28)-H(28B)	110.8
C(43)-C(28)-H(28B)	110.8
H(28A)-C(28)-H(28B)	108.9
O(2)-C(30)-C(12)	112.8(3)
O(2)-C(30)-C(39)	108.0(3)
C(12)-C(30)-C(39)	105.4(3)
O(2)-C(30)-H(30)	110.2
C(12)-C(30)-H(30)	110.2
C(39)-C(30)-H(30)	110.2
O(1)-C(35)-C(36)	125.6(3)
O(1)-C(35)-C(12)	124.4(3)
C(36)-C(35)-C(12)	109.9(3)
C(35)-C(36)-C(38)	104.2(3)
C(35)-C(36)-H(36A)	110.9

C(38)-C(36)-H(36A)	110.9
C(35)-C(36)-H(36B)	110.9
C(38)-C(36)-H(36B)	110.9
H(36A)-C(36)-H(36B)	108.9
C(44)-C(37)-C(12)	103.6(3)
C(44)-C(37)-C(43)	107.0(3)
C(12)-C(37)-C(43)	90.7(3)
C(44)-C(37)-H(37)	117.3
C(12)-C(37)-H(37)	117.3
C(43)-C(37)-H(37)	117.3
C(36)-C(38)-C(25)	106.3(3)
C(36)-C(38)-H(38A)	110.5
C(25)-C(38)-H(38A)	110.5
C(36)-C(38)-H(38B)	110.5
C(25)-C(38)-H(38B)	110.5
H(38A)-C(38)-H(38B)	108.7
C(30)-C(39)-C(44)	106.1(3)
C(30)-C(39)-H(39A)	110.5
C(44)-C(39)-H(39A)	110.5
C(30)-C(39)-H(39B)	110.5
C(44)-C(39)-H(39B)	110.5
H(39A)-C(39)-H(39B)	108.7
C(28)-C(41)-C(44)	105.1(3)
C(28)-C(41)-H(41A)	110.7
C(44)-C(41)-H(41A)	110.7
C(28)-C(41)-H(41B)	110.7
C(44)-C(41)-H(41B)	110.7
H(41A)-C(41)-H(41B)	108.8
C(28)-C(43)-C(25)	114.8(3)
C(28)-C(43)-C(37)	104.7(3)
C(25)-C(43)-C(37)	89.6(3)
C(28)-C(43)-H(43)	114.9
C(25)-C(43)-H(43)	114.9
C(37)-C(43)-H(43)	114.9

C(37)-C(44)-C(39)	103.2(3)
C(37)-C(44)-C(41)	104.9(4)
C(39)-C(44)-C(41)	113.8(4)
C(37)-C(44)-H(44)	111.5
C(39)-C(44)-H(44)	111.5
C(41)-C(44)-H(44)	111.5
C(48)-O(6)-C(53)	116.4(3)
O(4)-C(48)-O(6)	123.4(4)
O(4)-C(48)-C(50)	124.4(4)
O(6)-C(48)-C(50)	112.2(3)
C(50)-C(49)-C(52)	120.2(4)
C(50)-C(49)-H(49)	119.9
C(52)-C(49)-H(49)	119.9
C(55)-C(50)-C(49)	119.7(4)
C(55)-C(50)-C(48)	118.5(3)
C(49)-C(50)-C(48)	121.7(4)
C(52)-C(51)-C(57)	122.9(4)
C(52)-C(51)-Br(2)	118.7(3)
C(57)-C(51)-Br(2)	118.4(3)
C(51)-C(52)-C(49)	118.3(4)
C(51)-C(52)-H(52)	120.9
C(49)-C(52)-H(52)	120.9
O(6)-C(53)-C(63)	108.4(3)
O(6)-C(53)-C(56)	112.0(3)
C(63)-C(53)-C(56)	104.9(3)
O(6)-C(53)-H(53)	110.5
C(63)-C(53)-H(53)	110.5
C(56)-C(53)-H(53)	110.5
C(60)-C(54)-C(65)	104.8(3)
C(60)-C(54)-H(54A)	110.8
C(65)-C(54)-H(54A)	110.8
C(60)-C(54)-H(54B)	110.8
C(65)-C(54)-H(54B)	110.8
H(54A)-C(54)-H(54B)	108.9

C(57)-C(55)-C(50)	120.6(4)
C(57)-C(55)-H(55)	119.7
C(50)-C(55)-H(55)	119.7
C(60)-C(56)-C(53)	115.7(3)
C(60)-C(56)-C(62)	113.2(3)
C(53)-C(56)-C(62)	108.0(3)
C(60)-C(56)-C(59)	105.4(3)
C(53)-C(56)-C(59)	123.0(3)
C(62)-C(56)-C(59)	88.7(3)
C(55)-C(57)-C(51)	118.4(4)
C(55)-C(57)-H(57)	120.8
C(51)-C(57)-H(57)	120.8
C(63)-C(58)-C(61)	114.3(4)
C(63)-C(58)-C(62)	104.4(3)
C(61)-C(58)-C(62)	104.0(4)
C(63)-C(58)-H(58)	111.2
C(61)-C(58)-H(58)	111.2
C(62)-C(58)-H(58)	111.2
C(65)-C(59)-C(64)	117.0(3)
C(65)-C(59)-C(56)	106.9(3)
C(64)-C(59)-C(56)	90.6(3)
C(65)-C(59)-H(59)	113.4
C(64)-C(59)-H(59)	113.4
C(56)-C(59)-H(59)	113.4
O(5)-C(60)-C(54)	126.1(4)
O(5)-C(60)-C(56)	125.0(4)
C(54)-C(60)-C(56)	108.9(3)
C(89)-C(61)-C(58)	106.1(4)
C(89)-C(61)-H(61A)	110.5
C(58)-C(61)-H(61A)	110.5
C(89)-C(61)-H(61B)	110.5
C(58)-C(61)-H(61B)	110.5
H(61A)-C(61)-H(61B)	108.7
C(58)-C(62)-C(64)	107.7(4)

C(58)-C(62)-C(56)	103.9(3)
C(64)-C(62)-C(56)	90.8(3)
C(58)-C(62)-H(62)	117.0
C(64)-C(62)-H(62)	117.0
C(56)-C(62)-H(62)	117.0
C(58)-C(63)-C(53)	106.7(4)
C(58)-C(63)-H(63A)	110.4
C(53)-C(63)-H(63A)	110.4
C(58)-C(63)-H(63B)	110.4
C(53)-C(63)-H(63B)	110.4
H(63A)-C(63)-H(63B)	108.6
C(89)-C(64)-C(59)	115.0(4)
C(89)-C(64)-C(62)	105.1(4)
C(59)-C(64)-C(62)	89.7(3)
C(89)-C(64)-H(64)	114.7
C(59)-C(64)-H(64)	114.7
C(62)-C(64)-H(64)	114.7
C(59)-C(65)-C(54)	105.5(4)
C(59)-C(65)-H(65A)	110.6
C(54)-C(65)-H(65A)	110.6
C(59)-C(65)-H(65B)	110.6
C(54)-C(65)-H(65B)	110.6
H(65A)-C(65)-H(65B)	108.8
C(61)-C(89)-C(64)	103.7(4)
C(61)-C(89)-H(89A)	111.0
C(64)-C(89)-H(89A)	111.0
C(61)-C(89)-H(89B)	111.0
C(64)-C(89)-H(89B)	111.0
H(89A)-C(89)-H(89B)	109.0
C(70)-O(11)-C(71)	115.9(3)
C(72)-C(67)-C(75)	120.2(4)
C(72)-C(67)-H(67)	119.9
C(75)-C(67)-H(67)	119.9
C(72)-C(68)-C(79)	122.3(4)

C(72)-C(68)-Br(3)	119.1(3)
C(79)-C(68)-Br(3)	118.6(4)
O(10)-C(70)-O(11)	123.8(4)
O(10)-C(70)-C(75)	124.0(4)
O(11)-C(70)-C(75)	112.1(3)
O(11)-C(71)-C(74)	111.5(3)
O(11)-C(71)-C(77)	108.3(3)
C(74)-C(71)-C(77)	106.1(3)
O(11)-C(71)-H(71)	110.3
C(74)-C(71)-H(71)	110.3
C(77)-C(71)-H(71)	110.3
C(68)-C(72)-C(67)	118.6(4)
C(68)-C(72)-H(72)	120.7
C(67)-C(72)-H(72)	120.7
C(83)-C(73)-C(80)	105.4(3)
C(83)-C(73)-H(73A)	110.7
C(80)-C(73)-H(73A)	110.7
C(83)-C(73)-H(73B)	110.7
C(80)-C(73)-H(73B)	110.7
H(73A)-C(73)-H(73B)	108.8
C(83)-C(74)-C(71)	115.3(3)
C(83)-C(74)-C(81)	106.2(3)
C(71)-C(74)-C(81)	123.1(3)
C(83)-C(74)-C(78)	113.4(3)
C(71)-C(74)-C(78)	107.4(3)
C(81)-C(74)-C(78)	88.6(3)
C(76)-C(75)-C(67)	119.7(4)
C(76)-C(75)-C(70)	118.9(3)
C(67)-C(75)-C(70)	121.4(4)
C(75)-C(76)-C(79)	121.0(4)
C(75)-C(76)-H(76)	119.5
C(79)-C(76)-H(76)	119.5
C(82)-C(77)-C(71)	106.0(3)
C(82)-C(77)-H(77A)	110.5

C(71)-C(77)-H(77A)	110.5
C(82)-C(77)-H(77B)	110.5
C(71)-C(77)-H(77B)	110.5
H(77A)-C(77)-H(77B)	108.7
C(86)-C(78)-C(74)	90.6(3)
C(86)-C(78)-C(82)	106.9(4)
C(74)-C(78)-C(82)	103.8(3)
C(86)-C(78)-H(78)	117.2
C(74)-C(78)-H(78)	117.2
C(82)-C(78)-H(78)	117.2
C(76)-C(79)-C(68)	118.3(4)
C(76)-C(79)-H(79)	120.8
C(68)-C(79)-H(79)	120.8
C(73)-C(80)-C(81)	105.7(4)
C(73)-C(80)-H(80A)	110.6
C(81)-C(80)-H(80A)	110.6
C(73)-C(80)-H(80B)	110.6
C(81)-C(80)-H(80B)	110.6
H(80A)-C(80)-H(80B)	108.7
C(80)-C(81)-C(86)	116.6(4)
C(80)-C(81)-C(74)	106.2(3)
C(86)-C(81)-C(74)	90.4(3)
C(80)-C(81)-H(81)	113.7
C(86)-C(81)-H(81)	113.7
C(74)-C(81)-H(81)	113.7
C(77)-C(82)-C(85)	115.3(4)
C(77)-C(82)-C(78)	104.4(3)
C(85)-C(82)-C(78)	104.5(4)
C(77)-C(82)-H(82)	110.7
C(85)-C(82)-H(82)	110.7
C(78)-C(82)-H(82)	110.7
O(12)-C(83)-C(73)	126.5(4)
O(12)-C(83)-C(74)	125.8(4)
C(73)-C(83)-C(74)	107.7(3)

C(85)-C(84)-C(86)	103.4(4)
C(85)-C(84)-H(84A)	111.1
C(86)-C(84)-H(84A)	111.1
C(85)-C(84)-H(84B)	111.1
C(86)-C(84)-H(84B)	111.1
H(84A)-C(84)-H(84B)	109.1
C(84)-C(85)-C(82)	106.9(4)
C(84)-C(85)-H(85A)	110.3
C(82)-C(85)-H(85A)	110.3
C(84)-C(85)-H(85B)	110.3
C(82)-C(85)-H(85B)	110.3
H(85A)-C(85)-H(85B)	108.6
C(84)-C(86)-C(78)	106.1(4)
C(84)-C(86)-C(81)	114.7(4)
C(78)-C(86)-C(81)	90.1(3)
C(84)-C(86)-H(86)	114.4
C(78)-C(86)-H(86)	114.4
C(81)-C(86)-H(86)	114.4
C(7)-O(8)-C(6)	115.8(3)
C(5)-C(4)-C(17)	119.8(4)
C(5)-C(4)-H(4)	120.1
C(17)-C(4)-H(4)	120.1
C(4)-C(5)-C(21)	119.3(4)
C(4)-C(5)-H(5)	120.3
C(21)-C(5)-H(5)	120.3
O(8)-C(6)-C(19)	111.7(3)
O(8)-C(6)-C(42)	107.2(3)
C(19)-C(6)-C(42)	105.7(3)
O(8)-C(6)-H(6)	110.7
C(19)-C(6)-H(6)	110.7
C(42)-C(6)-H(6)	110.7
O(9)-C(7)-O(8)	124.1(4)
O(9)-C(7)-C(17)	124.4(4)
O(8)-C(7)-C(17)	111.4(3)

C(31)-C(13)-C(33)	105.4(3)
C(31)-C(13)-H(13A)	110.7
C(33)-C(13)-H(13A)	110.7
C(31)-C(13)-H(13B)	110.7
C(33)-C(13)-H(13B)	110.7
H(13A)-C(13)-H(13B)	108.8
C(20)-C(17)-C(4)	120.1(4)
C(20)-C(17)-C(7)	118.8(4)
C(4)-C(17)-C(7)	121.1(4)
C(24)-C(19)-C(6)	116.1(3)
C(24)-C(19)-C(23)	106.1(3)
C(6)-C(19)-C(23)	122.8(3)
C(24)-C(19)-C(34)	112.2(3)
C(6)-C(19)-C(34)	107.6(3)
C(23)-C(19)-C(34)	88.7(3)
C(40)-C(20)-C(17)	120.1(4)
C(40)-C(20)-H(20)	119.9
C(17)-C(20)-H(20)	119.9
C(5)-C(21)-C(40)	121.6(4)
C(5)-C(21)-Br(4)	120.2(4)
C(40)-C(21)-Br(4)	118.2(3)
C(32)-C(23)-C(26)	115.9(3)
C(32)-C(23)-C(19)	106.6(3)
C(26)-C(23)-C(19)	90.9(3)
C(32)-C(23)-H(23)	113.7
C(26)-C(23)-H(23)	113.7
C(19)-C(23)-H(23)	113.7
O(7)-C(24)-C(19)	125.6(4)
O(7)-C(24)-C(29)	125.8(4)
C(19)-C(24)-C(29)	108.6(3)
C(31)-C(26)-C(34)	105.4(3)
C(31)-C(26)-C(23)	114.5(3)
C(34)-C(26)-C(23)	89.1(3)
C(31)-C(26)-H(26)	114.9

C(34)-C(26)-H(26)	114.9
C(23)-C(26)-H(26)	114.9
C(24)-C(29)-C(32)	105.1(3)
C(24)-C(29)-H(29A)	110.7
C(32)-C(29)-H(29A)	110.7
C(24)-C(29)-H(29B)	110.7
C(32)-C(29)-H(29B)	110.7
H(29A)-C(29)-H(29B)	108.8
C(26)-C(31)-C(13)	104.2(3)
C(26)-C(31)-H(31A)	110.9
C(13)-C(31)-H(31A)	110.9
C(26)-C(31)-H(31B)	110.9
C(13)-C(31)-H(31B)	110.9
H(31A)-C(31)-H(31B)	108.9
C(29)-C(32)-C(23)	104.7(3)
C(29)-C(32)-H(32A)	110.8
C(23)-C(32)-H(32A)	110.8
C(29)-C(32)-H(32B)	110.8
C(23)-C(32)-H(32B)	110.8
H(32A)-C(32)-H(32B)	108.9
C(42)-C(33)-C(13)	114.2(4)
C(42)-C(33)-C(34)	104.7(3)
C(13)-C(33)-C(34)	105.0(3)
C(42)-C(33)-H(33)	110.9
C(13)-C(33)-H(33)	110.9
C(34)-C(33)-H(33)	110.9
C(33)-C(34)-C(26)	107.0(3)
C(33)-C(34)-C(19)	103.5(3)
C(26)-C(34)-C(19)	91.0(3)
C(33)-C(34)-H(34)	117.2
C(26)-C(34)-H(34)	117.2
C(19)-C(34)-H(34)	117.2
C(20)-C(40)-C(21)	118.9(4)
C(20)-C(40)-H(40)	120.5

C(21)-C(40)-H(40)	120.5
C(33)-C(42)-C(6)	106.4(3)
C(33)-C(42)-H(42A)	110.5
C(6)-C(42)-H(42A)	110.5
C(33)-C(42)-H(42B)	110.5
C(6)-C(42)-H(42B)	110.5
H(42A)-C(42)-H(42B)	108.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sn09t1. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	46(1)	41(1)	60(1)	10(1)	-1(1)	-15(1)
O(1)	27(1)	57(2)	51(2)	-2(2)	-2(1)	-9(1)
O(2)	31(1)	34(2)	43(2)	3(1)	-12(1)	-13(1)
O(3)	34(1)	44(2)	73(2)	6(2)	-22(1)	-8(1)
C(8)	47(2)	37(2)	26(2)	5(2)	-8(2)	-1(2)
C(10)	29(2)	33(2)	38(2)	2(2)	-9(2)	-5(2)
C(11)	31(2)	26(2)	35(2)	0(2)	-10(2)	-2(2)
C(12)	27(2)	31(2)	26(2)	3(2)	-8(1)	-10(2)
C(15)	30(2)	29(2)	46(2)	-4(2)	-17(2)	-4(2)
C(18)	31(2)	36(2)	37(2)	-6(2)	-13(2)	1(2)
C(22)	31(2)	26(2)	32(2)	-8(2)	-9(2)	-2(2)
C(25)	29(2)	36(2)	31(2)	3(2)	-6(1)	-11(2)
C(27)	36(2)	30(2)	31(2)	-2(2)	-2(2)	-6(2)
C(28)	33(2)	36(3)	83(4)	4(2)	-10(2)	0(2)
C(30)	32(2)	41(2)	32(2)	1(2)	-6(2)	-16(2)
C(35)	26(2)	34(2)	38(2)	1(2)	-7(2)	-10(2)
C(36)	36(2)	54(3)	42(2)	4(2)	-19(2)	-13(2)
C(37)	34(2)	32(2)	43(2)	8(2)	-18(2)	-12(2)
C(38)	45(2)	49(3)	31(2)	4(2)	-10(2)	-15(2)
C(39)	64(3)	56(3)	34(2)	12(2)	-21(2)	-34(2)
C(41)	31(2)	47(3)	74(3)	15(2)	-26(2)	-8(2)
C(43)	30(2)	31(2)	47(2)	2(2)	-8(2)	-5(2)
C(44)	52(2)	42(3)	54(3)	23(2)	-30(2)	-20(2)
Br(2)	41(1)	56(1)	55(1)	10(1)	-16(1)	-1(1)
O(4)	29(1)	51(2)	46(2)	12(1)	-10(1)	-19(1)
O(5)	27(1)	51(2)	71(2)	-14(2)	-2(1)	-1(1)
O(6)	30(1)	38(2)	29(1)	4(1)	-9(1)	-15(1)
C(48)	32(2)	36(2)	24(2)	-2(2)	-4(2)	-12(2)
C(49)	34(2)	33(2)	29(2)	-2(2)	-1(2)	-11(2)

C(50)	29(2)	38(2)	23(2)	-2(2)	-2(1)	-11(2)
C(51)	30(2)	39(2)	30(2)	1(2)	-6(2)	1(2)
C(52)	26(2)	40(2)	34(2)	-4(2)	-4(2)	-5(2)
C(53)	31(2)	29(2)	32(2)	-1(2)	-4(2)	-5(2)
C(54)	36(2)	58(3)	55(3)	-15(2)	-11(2)	-13(2)
C(55)	34(2)	38(2)	35(2)	0(2)	-3(2)	-14(2)
C(56)	29(2)	34(2)	33(2)	3(2)	-8(1)	-5(2)
C(57)	43(2)	37(2)	38(2)	6(2)	-7(2)	-14(2)
C(58)	45(2)	41(3)	52(3)	22(2)	-12(2)	-12(2)
C(59)	31(2)	40(2)	30(2)	-4(2)	-7(2)	-4(2)
C(60)	33(2)	42(2)	45(2)	-2(2)	-13(2)	-7(2)
C(61)	39(2)	64(3)	52(3)	15(2)	1(2)	-17(2)
C(62)	44(2)	46(3)	43(2)	18(2)	-15(2)	-6(2)
C(63)	45(2)	35(2)	51(3)	8(2)	-10(2)	-13(2)
C(64)	53(2)	68(3)	33(2)	2(2)	-11(2)	-17(2)
C(65)	43(2)	42(3)	46(2)	-10(2)	-9(2)	-9(2)
C(89)	61(3)	74(4)	44(3)	7(3)	14(2)	-15(3)
Br(3)	74(1)	76(1)	60(1)	16(1)	-16(1)	-49(1)
O(10)	33(1)	58(2)	49(2)	14(2)	-16(1)	-13(1)
O(11)	30(1)	38(2)	30(1)	6(1)	-5(1)	-7(1)
O(12)	48(2)	62(2)	73(2)	-14(2)	-20(2)	-23(2)
C(67)	36(2)	40(2)	29(2)	-1(2)	-8(2)	-10(2)
C(68)	46(2)	47(3)	34(2)	-9(2)	-6(2)	-24(2)
C(70)	32(2)	41(2)	25(2)	-4(2)	-5(1)	-9(2)
C(71)	35(2)	32(2)	30(2)	-3(2)	-8(2)	-10(2)
C(72)	35(2)	47(3)	36(2)	-7(2)	-8(2)	-12(2)
C(73)	35(2)	63(3)	55(3)	-12(2)	-10(2)	-9(2)
C(74)	33(2)	31(2)	32(2)	2(2)	-8(2)	-13(2)
C(75)	33(2)	40(2)	22(2)	0(2)	-6(1)	-7(2)
C(76)	37(2)	43(2)	39(2)	0(2)	-10(2)	-7(2)
C(77)	51(2)	33(2)	49(2)	2(2)	-15(2)	-4(2)
C(78)	51(2)	46(3)	37(2)	13(2)	-6(2)	-16(2)
C(79)	56(2)	33(2)	40(2)	6(2)	-16(2)	-10(2)
C(80)	44(2)	46(3)	40(2)	-9(2)	-6(2)	-4(2)

C(81)	40(2)	39(2)	28(2)	-3(2)	-7(2)	-14(2)
C(82)	54(3)	39(2)	45(2)	14(2)	-17(2)	-9(2)
C(83)	37(2)	43(2)	47(2)	-3(2)	-11(2)	-18(2)
C(84)	84(4)	69(4)	43(3)	0(2)	-37(3)	-11(3)
C(85)	58(3)	57(3)	46(2)	7(2)	-29(2)	-13(2)
C(86)	54(2)	57(3)	27(2)	3(2)	-8(2)	-12(2)
Br(4)	88(1)	69(1)	50(1)	-1(1)	-33(1)	22(1)
O(7)	39(2)	67(2)	47(2)	-11(2)	-16(1)	-12(2)
O(8)	26(1)	31(2)	38(1)	2(1)	-6(1)	-6(1)
O(9)	32(1)	42(2)	55(2)	2(1)	-9(1)	-12(1)
C(4)	35(2)	32(2)	29(2)	-1(2)	-5(2)	-3(2)
C(5)	36(2)	44(3)	38(2)	-6(2)	-8(2)	0(2)
C(6)	31(2)	39(2)	28(2)	-3(2)	-7(2)	-4(2)
C(7)	37(2)	29(2)	35(2)	-6(2)	-4(2)	-9(2)
C(13)	36(2)	48(3)	58(3)	11(2)	-13(2)	-24(2)
C(17)	39(2)	26(2)	32(2)	-6(2)	0(2)	-5(2)
C(19)	29(2)	32(2)	27(2)	1(2)	-8(1)	-6(2)
C(20)	47(2)	39(2)	38(2)	0(2)	1(2)	-9(2)
C(21)	54(2)	40(3)	33(2)	-5(2)	-14(2)	8(2)
C(23)	34(2)	32(2)	26(2)	2(2)	-5(1)	-7(2)
C(24)	32(2)	36(2)	41(2)	-1(2)	-9(2)	-7(2)
C(26)	36(2)	31(2)	41(2)	-6(2)	-9(2)	-6(2)
C(29)	31(2)	60(3)	38(2)	-5(2)	0(2)	-16(2)
C(31)	57(3)	42(3)	53(3)	-2(2)	-16(2)	-22(2)
C(32)	37(2)	43(2)	31(2)	-1(2)	-2(2)	-12(2)
C(33)	35(2)	40(2)	42(2)	13(2)	-1(2)	-10(2)
C(34)	33(2)	30(2)	37(2)	7(2)	-9(2)	-4(2)
C(40)	69(3)	30(2)	33(2)	5(2)	-10(2)	-6(2)
C(42)	32(2)	55(3)	30(2)	11(2)	-2(2)	-8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sn09t1.

	x	y	z	U(eq)
H(8)	8540	5722	1642	46
H(10)	5010	7448	396	40
H(11)	7174	8359	-122	37
H(18)	10679	6652	1159	42
H(25)	9475	9898	941	38
H(28A)	6980	11450	1040	63
H(28B)	7424	12324	426	63
H(30)	12445	8987	-1115	41
H(36A)	13817	10811	852	50
H(36B)	14699	9702	1025	50
H(37)	11833	11510	-591	41
H(38A)	11430	10508	1872	49
H(38B)	11923	9384	1609	49
H(39A)	9432	9847	-1593	56
H(39B)	11315	10186	-1932	56
H(41A)	6646	11387	-491	58
H(41B)	7616	10403	-93	58
H(43)	10201	11791	911	44
H(44)	9391	11618	-1312	54
H(49)	10947	6128	8790	39
H(52)	13230	5185	9438	41
H(53)	5519	7574	8577	38
H(54A)	3678	6178	6467	58
H(54B)	3119	5611	7341	58
H(55)	7654	4304	9661	42
H(57)	9919	3365	10300	46
H(58)	7925	8643	6421	55
H(59)	8352	5702	7045	41

H(61A)	10779	7634	6230	63
H(61B)	10083	6877	6921	63
H(62)	5477	7927	6323	53
H(63A)	6425	8816	7837	52
H(63B)	8438	8256	7933	52
H(64)	7027	6435	5544	61
H(65A)	6088	4847	7321	52
H(65B)	6264	4962	6299	52
H(89A)	10433	6075	5655	77
H(89B)	9715	7051	5171	77
H(67)	8945	3217	5044	41
H(71)	4608	1708	5280	38
H(72)	10962	4168	4400	47
H(73A)	-395	3180	7338	62
H(73B)	-631	3724	6454	62
H(76)	4866	4972	4134	48
H(77A)	5916	498	6049	54
H(77B)	7522	1069	5938	54
H(78)	2728	1445	7534	53
H(79)	6876	5908	3464	51
H(80A)	954	4398	7476	53
H(80B)	1645	4482	6451	53
H(81)	4399	3640	6752	41
H(82)	5889	731	7462	55
H(84A)	5458	3328	8146	75
H(84B)	5103	2383	8675	75
H(85A)	7662	1727	7656	61
H(85B)	7037	2457	6930	61
H(86)	2268	2957	8263	56
H(4)	-748	953	4038	40
H(5)	-3016	1839	3386	49
H(6)	4074	71	5060	39
H(13A)	1193	-2255	4075	54
H(13B)	1585	-1218	3792	54

H(20)	2785	2502	2782	52
H(23)	3905	-570	2900	38
H(26)	6415	-2442	2752	44
H(29A)	8967	-1462	2948	52
H(29B)	8990	-336	2902	52
H(31A)	3739	-3063	3094	58
H(31B)	3077	-2118	2560	58
H(32A)	7261	-1017	1929	45
H(32B)	6457	64	2316	45
H(33)	3288	-2548	4921	49
H(34)	6294	-2358	4285	41
H(40)	489	3415	2155	55
H(42A)	3192	-1227	5704	48
H(42B)	1396	-843	5320	48

Table 6. Torsion angles [°] for sn09t1.

C(27)-C(10)-C(11)-C(22)	-1.4(6)
C(30)-O(2)-C(15)-O(3)	3.4(6)
C(30)-O(2)-C(15)-C(22)	-177.9(3)
C(27)-C(8)-C(18)-C(22)	-0.4(6)
C(8)-C(18)-C(22)-C(11)	1.3(5)
C(8)-C(18)-C(22)-C(15)	-177.5(4)
C(10)-C(11)-C(22)-C(18)	-0.4(5)
C(10)-C(11)-C(22)-C(15)	178.4(3)
O(3)-C(15)-C(22)-C(18)	-4.4(6)
O(2)-C(15)-C(22)-C(18)	176.8(3)
O(3)-C(15)-C(22)-C(11)	176.8(4)
O(2)-C(15)-C(22)-C(11)	-2.0(5)
C(35)-C(12)-C(25)-C(38)	-7.7(4)
C(30)-C(12)-C(25)-C(38)	129.1(4)
C(37)-C(12)-C(25)-C(38)	-119.4(3)
C(35)-C(12)-C(25)-C(43)	109.6(3)
C(30)-C(12)-C(25)-C(43)	-113.6(4)
C(37)-C(12)-C(25)-C(43)	-2.2(3)
C(11)-C(10)-C(27)-C(8)	2.4(6)
C(11)-C(10)-C(27)-Br(1)	-176.7(3)
C(18)-C(8)-C(27)-C(10)	-1.5(6)
C(18)-C(8)-C(27)-Br(1)	177.6(3)
C(15)-O(2)-C(30)-C(12)	-67.5(4)
C(15)-O(2)-C(30)-C(39)	176.5(3)
C(35)-C(12)-C(30)-O(2)	118.8(4)
C(37)-C(12)-C(30)-O(2)	-115.1(3)
C(25)-C(12)-C(30)-O(2)	-13.8(5)
C(35)-C(12)-C(30)-C(39)	-123.6(4)
C(37)-C(12)-C(30)-C(39)	2.5(4)
C(25)-C(12)-C(30)-C(39)	103.8(4)
C(30)-C(12)-C(35)-O(1)	31.2(6)
C(37)-C(12)-C(35)-O(1)	-93.4(5)

C(25)-C(12)-C(35)-O(1)	171.7(4)
C(30)-C(12)-C(35)-C(36)	-151.5(4)
C(37)-C(12)-C(35)-C(36)	83.9(4)
C(25)-C(12)-C(35)-C(36)	-11.0(4)
O(1)-C(35)-C(36)-C(38)	-157.5(4)
C(12)-C(35)-C(36)-C(38)	25.2(5)
C(35)-C(12)-C(37)-C(44)	148.6(3)
C(30)-C(12)-C(37)-C(44)	19.7(4)
C(25)-C(12)-C(37)-C(44)	-105.5(3)
C(35)-C(12)-C(37)-C(43)	-103.8(3)
C(30)-C(12)-C(37)-C(43)	127.3(3)
C(25)-C(12)-C(37)-C(43)	2.2(3)
C(35)-C(36)-C(38)-C(25)	-29.5(5)
C(43)-C(25)-C(38)-C(36)	-75.8(4)
C(12)-C(25)-C(38)-C(36)	23.1(5)
O(2)-C(30)-C(39)-C(44)	96.9(4)
C(12)-C(30)-C(39)-C(44)	-23.9(4)
C(43)-C(28)-C(41)-C(44)	-37.7(5)
C(41)-C(28)-C(43)-C(25)	-65.0(5)
C(41)-C(28)-C(43)-C(37)	31.5(5)
C(38)-C(25)-C(43)-C(28)	-143.6(4)
C(12)-C(25)-C(43)-C(28)	108.2(4)
C(38)-C(25)-C(43)-C(37)	110.3(3)
C(12)-C(25)-C(43)-C(37)	2.2(3)
C(44)-C(37)-C(43)-C(28)	-13.3(4)
C(12)-C(37)-C(43)-C(28)	-117.7(3)
C(44)-C(37)-C(43)-C(25)	102.2(3)
C(12)-C(37)-C(43)-C(25)	-2.2(3)
C(12)-C(37)-C(44)-C(39)	-33.6(4)
C(43)-C(37)-C(44)-C(39)	-128.5(4)
C(12)-C(37)-C(44)-C(41)	85.8(4)
C(43)-C(37)-C(44)-C(41)	-9.1(4)
C(30)-C(39)-C(44)-C(37)	36.3(4)
C(30)-C(39)-C(44)-C(41)	-76.7(4)

C(28)-C(41)-C(44)-C(37)	28.9(5)
C(28)-C(41)-C(44)-C(39)	141.0(4)
C(53)-O(6)-C(48)-O(4)	5.8(5)
C(53)-O(6)-C(48)-C(50)	-174.2(3)
C(52)-C(49)-C(50)-C(55)	-0.5(5)
C(52)-C(49)-C(50)-C(48)	177.2(3)
O(4)-C(48)-C(50)-C(55)	-0.6(6)
O(6)-C(48)-C(50)-C(55)	179.4(3)
O(4)-C(48)-C(50)-C(49)	-178.4(4)
O(6)-C(48)-C(50)-C(49)	1.7(5)
C(57)-C(51)-C(52)-C(49)	1.0(6)
Br(2)-C(51)-C(52)-C(49)	-178.5(3)
C(50)-C(49)-C(52)-C(51)	-0.2(6)
C(48)-O(6)-C(53)-C(63)	176.5(3)
C(48)-O(6)-C(53)-C(56)	-68.2(4)
C(49)-C(50)-C(55)-C(57)	0.4(6)
C(48)-C(50)-C(55)-C(57)	-177.4(3)
O(6)-C(53)-C(56)-C(60)	115.9(4)
C(63)-C(53)-C(56)-C(60)	-126.7(4)
O(6)-C(53)-C(56)-C(62)	-116.1(3)
C(63)-C(53)-C(56)-C(62)	1.3(4)
O(6)-C(53)-C(56)-C(59)	-15.6(5)
C(63)-C(53)-C(56)-C(59)	101.8(4)
C(50)-C(55)-C(57)-C(51)	0.4(6)
C(52)-C(51)-C(57)-C(55)	-1.2(6)
Br(2)-C(51)-C(57)-C(55)	178.4(3)
C(60)-C(56)-C(59)-C(65)	-8.2(4)
C(53)-C(56)-C(59)-C(65)	127.4(4)
C(62)-C(56)-C(59)-C(65)	-121.9(3)
C(60)-C(56)-C(59)-C(64)	110.3(3)
C(53)-C(56)-C(59)-C(64)	-114.1(4)
C(62)-C(56)-C(59)-C(64)	-3.4(3)
C(65)-C(54)-C(60)-O(5)	-156.0(5)
C(65)-C(54)-C(60)-C(56)	25.3(5)

C(53)-C(56)-C(60)-O(5)	31.1(6)
C(62)-C(56)-C(60)-O(5)	-94.2(5)
C(59)-C(56)-C(60)-O(5)	170.5(4)
C(53)-C(56)-C(60)-C(54)	-150.1(4)
C(62)-C(56)-C(60)-C(54)	84.5(5)
C(59)-C(56)-C(60)-C(54)	-10.8(5)
C(63)-C(58)-C(61)-C(89)	141.4(4)
C(62)-C(58)-C(61)-C(89)	28.2(5)
C(63)-C(58)-C(62)-C(64)	-128.2(4)
C(61)-C(58)-C(62)-C(64)	-8.1(4)
C(63)-C(58)-C(62)-C(56)	-32.9(4)
C(61)-C(58)-C(62)-C(56)	87.3(4)
C(60)-C(56)-C(62)-C(58)	148.8(4)
C(53)-C(56)-C(62)-C(58)	19.4(4)
C(59)-C(56)-C(62)-C(58)	-105.0(3)
C(60)-C(56)-C(62)-C(64)	-102.8(4)
C(53)-C(56)-C(62)-C(64)	127.8(3)
C(59)-C(56)-C(62)-C(64)	3.4(3)
C(61)-C(58)-C(63)-C(53)	-78.2(5)
C(62)-C(58)-C(63)-C(53)	34.7(4)
O(6)-C(53)-C(63)-C(58)	97.6(4)
C(56)-C(53)-C(63)-C(58)	-22.2(4)
C(65)-C(59)-C(64)-C(89)	-140.7(4)
C(56)-C(59)-C(64)-C(89)	110.0(4)
C(65)-C(59)-C(64)-C(62)	112.7(4)
C(56)-C(59)-C(64)-C(62)	3.4(3)
C(58)-C(62)-C(64)-C(89)	-14.5(5)
C(56)-C(62)-C(64)-C(89)	-119.4(4)
C(58)-C(62)-C(64)-C(59)	101.4(3)
C(56)-C(62)-C(64)-C(59)	-3.4(3)
C(64)-C(59)-C(65)-C(54)	-76.1(5)
C(56)-C(59)-C(65)-C(54)	23.5(4)
C(60)-C(54)-C(65)-C(59)	-29.9(5)
C(58)-C(61)-C(89)-C(64)	-37.6(5)

C(59)-C(64)-C(89)-C(61)	-65.2(6)
C(62)-C(64)-C(89)-C(61)	31.7(5)
C(71)-O(11)-C(70)-O(10)	3.8(5)
C(71)-O(11)-C(70)-C(75)	-176.3(3)
C(70)-O(11)-C(71)-C(74)	-66.8(4)
C(70)-O(11)-C(71)-C(77)	176.8(3)
C(79)-C(68)-C(72)-C(67)	1.7(6)
Br(3)-C(68)-C(72)-C(67)	-176.3(3)
C(75)-C(67)-C(72)-C(68)	-0.7(6)
O(11)-C(71)-C(74)-C(83)	115.1(4)
C(77)-C(71)-C(74)-C(83)	-127.1(4)
O(11)-C(71)-C(74)-C(81)	-17.4(5)
C(77)-C(71)-C(74)-C(81)	100.3(4)
O(11)-C(71)-C(74)-C(78)	-117.4(3)
C(77)-C(71)-C(74)-C(78)	0.3(4)
C(72)-C(67)-C(75)-C(76)	-1.0(6)
C(72)-C(67)-C(75)-C(70)	176.8(3)
O(10)-C(70)-C(75)-C(76)	-0.6(6)
O(11)-C(70)-C(75)-C(76)	179.5(3)
O(10)-C(70)-C(75)-C(67)	-178.5(4)
O(11)-C(70)-C(75)-C(67)	1.6(5)
C(67)-C(75)-C(76)-C(79)	1.8(6)
C(70)-C(75)-C(76)-C(79)	-176.1(4)
O(11)-C(71)-C(77)-C(82)	98.3(4)
C(74)-C(71)-C(77)-C(82)	-21.5(4)
C(83)-C(74)-C(78)-C(86)	-103.6(4)
C(71)-C(74)-C(78)-C(86)	127.9(3)
C(81)-C(74)-C(78)-C(86)	3.5(3)
C(83)-C(74)-C(78)-C(82)	148.8(4)
C(71)-C(74)-C(78)-C(82)	20.3(4)
C(81)-C(74)-C(78)-C(82)	-104.1(4)
C(75)-C(76)-C(79)-C(68)	-0.8(6)
C(72)-C(68)-C(79)-C(76)	-1.0(6)
Br(3)-C(68)-C(79)-C(76)	177.0(3)

C(83)-C(73)-C(80)-C(81)	-30.4(5)
C(73)-C(80)-C(81)-C(86)	-75.6(4)
C(73)-C(80)-C(81)-C(74)	23.3(4)
C(83)-C(74)-C(81)-C(80)	-7.4(4)
C(71)-C(74)-C(81)-C(80)	128.7(4)
C(78)-C(74)-C(81)-C(80)	-121.4(3)
C(83)-C(74)-C(81)-C(86)	110.5(3)
C(71)-C(74)-C(81)-C(86)	-113.4(4)
C(78)-C(74)-C(81)-C(86)	-3.5(3)
C(71)-C(77)-C(82)-C(85)	-79.6(4)
C(71)-C(77)-C(82)-C(78)	34.4(4)
C(86)-C(78)-C(82)-C(77)	-128.5(4)
C(74)-C(78)-C(82)-C(77)	-33.5(4)
C(86)-C(78)-C(82)-C(85)	-7.0(4)
C(74)-C(78)-C(82)-C(85)	88.0(4)
C(80)-C(73)-C(83)-O(12)	-155.6(5)
C(80)-C(73)-C(83)-C(74)	26.0(5)
C(71)-C(74)-C(83)-O(12)	30.2(6)
C(81)-C(74)-C(83)-O(12)	170.2(4)
C(78)-C(74)-C(83)-O(12)	-94.1(5)
C(71)-C(74)-C(83)-C(73)	-151.4(4)
C(81)-C(74)-C(83)-C(73)	-11.4(5)
C(78)-C(74)-C(83)-C(73)	84.3(5)
C(86)-C(84)-C(85)-C(82)	-35.8(5)
C(77)-C(82)-C(85)-C(84)	140.6(4)
C(78)-C(82)-C(85)-C(84)	26.6(5)
C(85)-C(84)-C(86)-C(78)	30.7(5)
C(85)-C(84)-C(86)-C(81)	-67.0(6)
C(74)-C(78)-C(86)-C(84)	-119.4(4)
C(82)-C(78)-C(86)-C(84)	-14.7(5)
C(74)-C(78)-C(86)-C(81)	-3.5(3)
C(82)-C(78)-C(86)-C(81)	101.1(4)
C(80)-C(81)-C(86)-C(84)	-140.3(4)
C(74)-C(81)-C(86)-C(84)	111.4(4)

C(80)-C(81)-C(86)-C(78)	111.9(4)
C(74)-C(81)-C(86)-C(78)	3.5(3)
C(17)-C(4)-C(5)-C(21)	-1.1(6)
C(7)-O(8)-C(6)-C(19)	-66.6(4)
C(7)-O(8)-C(6)-C(42)	178.0(3)
C(6)-O(8)-C(7)-O(9)	0.4(5)
C(6)-O(8)-C(7)-C(17)	177.5(3)
C(5)-C(4)-C(17)-C(20)	1.0(6)
C(5)-C(4)-C(17)-C(7)	-178.7(3)
O(9)-C(7)-C(17)-C(20)	4.1(6)
O(8)-C(7)-C(17)-C(20)	-173.0(3)
O(9)-C(7)-C(17)-C(4)	-176.2(4)
O(8)-C(7)-C(17)-C(4)	6.7(5)
O(8)-C(6)-C(19)-C(24)	117.6(4)
C(42)-C(6)-C(19)-C(24)	-126.1(4)
O(8)-C(6)-C(19)-C(23)	-15.6(5)
C(42)-C(6)-C(19)-C(23)	100.7(4)
O(8)-C(6)-C(19)-C(34)	-115.8(3)
C(42)-C(6)-C(19)-C(34)	0.5(4)
C(4)-C(17)-C(20)-C(40)	-0.2(6)
C(7)-C(17)-C(20)-C(40)	179.6(4)
C(4)-C(5)-C(21)-C(40)	0.4(6)
C(4)-C(5)-C(21)-Br(4)	-178.0(3)
C(24)-C(19)-C(23)-C(32)	-8.3(4)
C(6)-C(19)-C(23)-C(32)	128.8(4)
C(34)-C(19)-C(23)-C(32)	-121.0(3)
C(24)-C(19)-C(23)-C(26)	109.1(3)
C(6)-C(19)-C(23)-C(26)	-113.8(4)
C(34)-C(19)-C(23)-C(26)	-3.6(3)
C(6)-C(19)-C(24)-O(7)	31.6(6)
C(23)-C(19)-C(24)-O(7)	172.0(4)
C(34)-C(19)-C(24)-O(7)	-92.7(5)
C(6)-C(19)-C(24)-C(29)	-151.2(4)
C(23)-C(19)-C(24)-C(29)	-10.8(4)

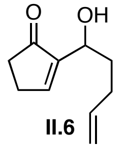
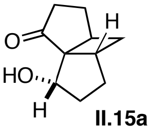
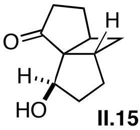
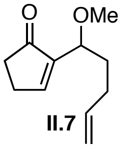
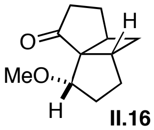
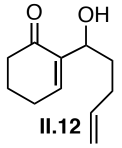
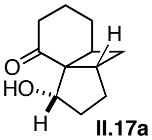
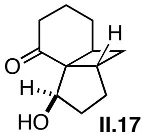
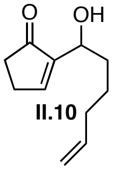
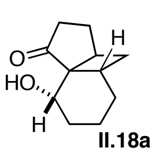
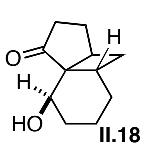
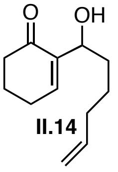
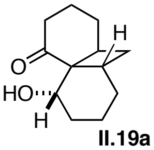
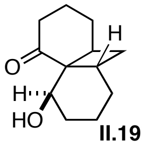
C(34)-C(19)-C(24)-C(29)	84.5(4)
C(32)-C(23)-C(26)-C(31)	-140.7(4)
C(19)-C(23)-C(26)-C(31)	110.3(3)
C(32)-C(23)-C(26)-C(34)	112.7(3)
C(19)-C(23)-C(26)-C(34)	3.6(3)
O(7)-C(24)-C(29)-C(32)	-157.1(5)
C(19)-C(24)-C(29)-C(32)	25.8(5)
C(34)-C(26)-C(31)-C(13)	31.4(4)
C(23)-C(26)-C(31)-C(13)	-64.9(5)
C(33)-C(13)-C(31)-C(26)	-36.8(5)
C(24)-C(29)-C(32)-C(23)	-30.2(5)
C(26)-C(23)-C(32)-C(29)	-75.7(4)
C(19)-C(23)-C(32)-C(29)	23.7(4)
C(31)-C(13)-C(33)-C(42)	141.5(4)
C(31)-C(13)-C(33)-C(34)	27.4(5)
C(42)-C(33)-C(34)-C(26)	-128.5(3)
C(13)-C(33)-C(34)-C(26)	-7.9(4)
C(42)-C(33)-C(34)-C(19)	-33.3(4)
C(13)-C(33)-C(34)-C(19)	87.3(4)
C(31)-C(26)-C(34)-C(33)	-14.5(4)
C(23)-C(26)-C(34)-C(33)	100.7(3)
C(31)-C(26)-C(34)-C(19)	-118.9(3)
C(23)-C(26)-C(34)-C(19)	-3.6(3)
C(24)-C(19)-C(34)-C(33)	148.9(3)
C(6)-C(19)-C(34)-C(33)	20.0(4)
C(23)-C(19)-C(34)-C(33)	-104.1(3)
C(24)-C(19)-C(34)-C(26)	-103.3(3)
C(6)-C(19)-C(34)-C(26)	127.8(3)
C(23)-C(19)-C(34)-C(26)	3.6(3)
C(17)-C(20)-C(40)-C(21)	-0.5(6)
C(5)-C(21)-C(40)-C(20)	0.4(6)
Br(4)-C(21)-C(40)-C(20)	178.8(3)
C(13)-C(33)-C(42)-C(6)	-79.7(4)
C(34)-C(33)-C(42)-C(6)	34.5(4)

O(8)-C(6)-C(42)-C(33)	97.7(4)
C(19)-C(6)-C(42)-C(33)	-21.7(4)

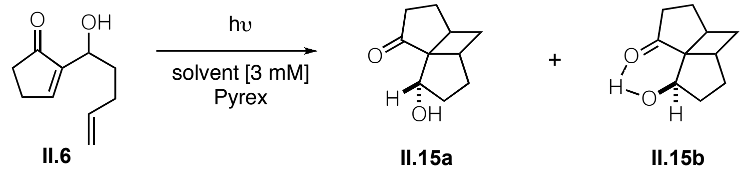
Symmetry transformations used to generate equivalent atoms:

(B) Representative procedure for the intramolecular [2+2] photocycloaddition: To a thick walled flame-dried reaction tube was added the α,β-unsaturated ketone (1 equiv) and solvent (3.7 mM). The solution was degassed by bubbling N_2 through the solution for 15 min and irradiated with a 450 W Hanovia mercury lamp with a barrier of Pyrex until deemed finished by TLC analysis. The reaction was concentrated *in vacuo*, and purified through silica gel flash chromatography.

Table II.3. Solvent-Dependent Photocycloadditions.[a]

entry	enone	products	solvent/yield/ratio
(1)	 **II.6**	 **II.15a**  **II.15b**	CH_2Cl_2 64% **a:b** 1:4 acetone/H_2O 60% **a:b** > 20:1
(2)	 **II.7**	 **II.16**	CH_2Cl_2 89% (81% conv.) MeOH 60% (87% conv.)
(3)	 **II.12**	 **II.17a**  **II.17b**	CH_2Cl_2 72% **a:b** 1:4 acetone/H_2O 74% **a:b** 6:1
(4)	 **II.10**	 **II.18a**  **II.18b**	CH_2Cl_2 47% **a:b** < 1:20 acetone/H_2O 38% **a:b** > 20:1
(5)	 **II.14**	 **II.19a**  **II.19b**	CH_2Cl_2 21% **a:b** 1:10 acetone/H_2O 40% **a:b** 16:1

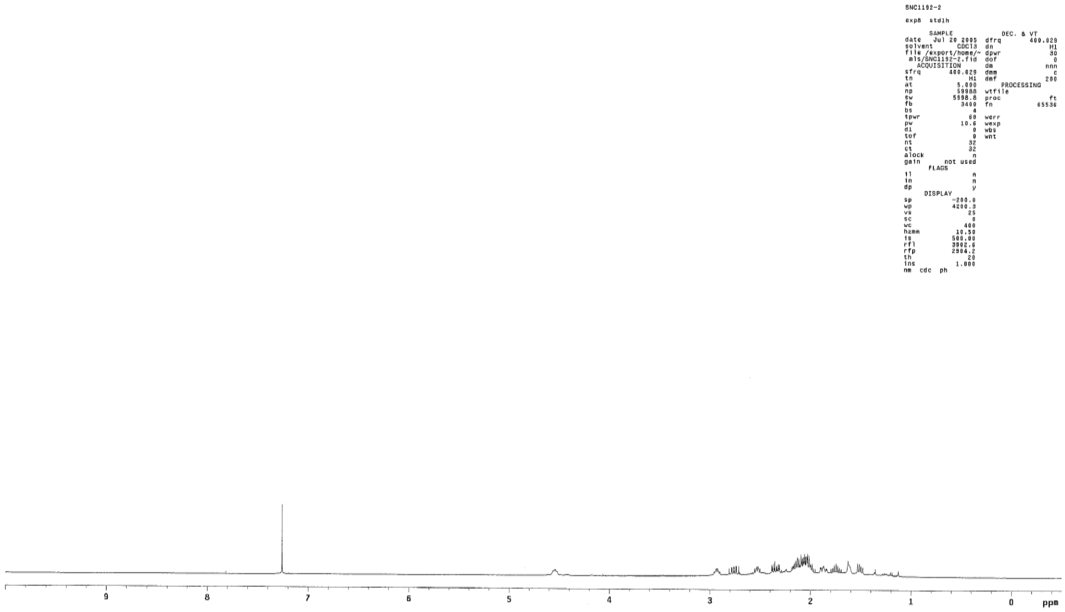
[a] All reactions: hυ, Pyrex filter, 3 mM in solvent.



*See general procedure (B) for intramolecular [2+2] photocycloaddtion of enone **II.6**.*

Enone **II.6** (10 mg, 0.060 mmol) was dissolved in the appropriate solvent. The residue was purified on silica gel (pentane:Et_2O 4:1) to give compounds **II.15a** and **II.15b**.

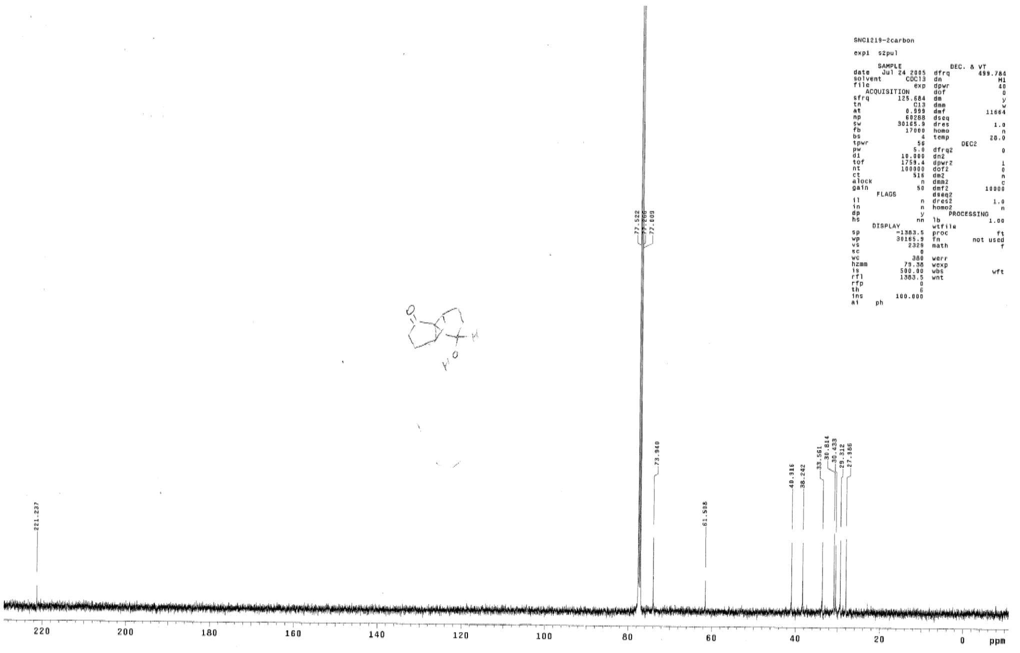
Photocycloadduct (II.15a): colorless oil. **R_f** 0.34 (pentane:Et_2O 4:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 4.54 (m, 1H), 2.92 (dd, 1H, J = 13.2, 7.6 Hz), 2.76 (ddd, 1H, J = 18, 11.6, 9.6 Hz), 2.52 (dd, 1H, J = 13.2, 8.0 Hz), 2.34 (ddd, 1H, J = 17.6, 12.4, 9.2 Hz), 1.98-2.16 (m, 5 H), 1.87 (m, 1H), 1.75 (m, 1H), 1.50 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 221.2, 73.9, 61.5, 40.9, 38.2, 35.5, 33.5, 30.8, 30.4, 29.3, 27.9. **IR** (NaCl, thin film) 3411 (br), 2953 (s), 2866 (m), 1723 (s), 1409 (w), 1300 (w) cm^{-1}. **HRMS** (M + H) $C_{10}H_{15}O_2$ Calcd: 167.1072. Found: 167.1066.



```
SNC1192-2

exp8  std1h

      SAMPLE              DEC. & VT
date   Jul 20 2005  dfrq       400.029
solvent      CDCl3  dn              H1
file /export/home/~ dpwr            30
 mls/SNC1192-2.fid  dof              0
   ACQUISITION      dm             nnn
sfrq       400.029  dmm              c
tn              H1  dmf            200
at           5.000      PROCESSING
np           59988  wtfile
sw          5998.8  proc            ft
fb            3400  fn           65536
bs               4
tpwr            60  werr
pw            10.6  wexp
d1               0  wbs
tof              0  wnt
nt              32
ct              32
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs              25
sc               0
wc             400
hzmm         10.50
is          500.00
rfl         3902.6
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
```

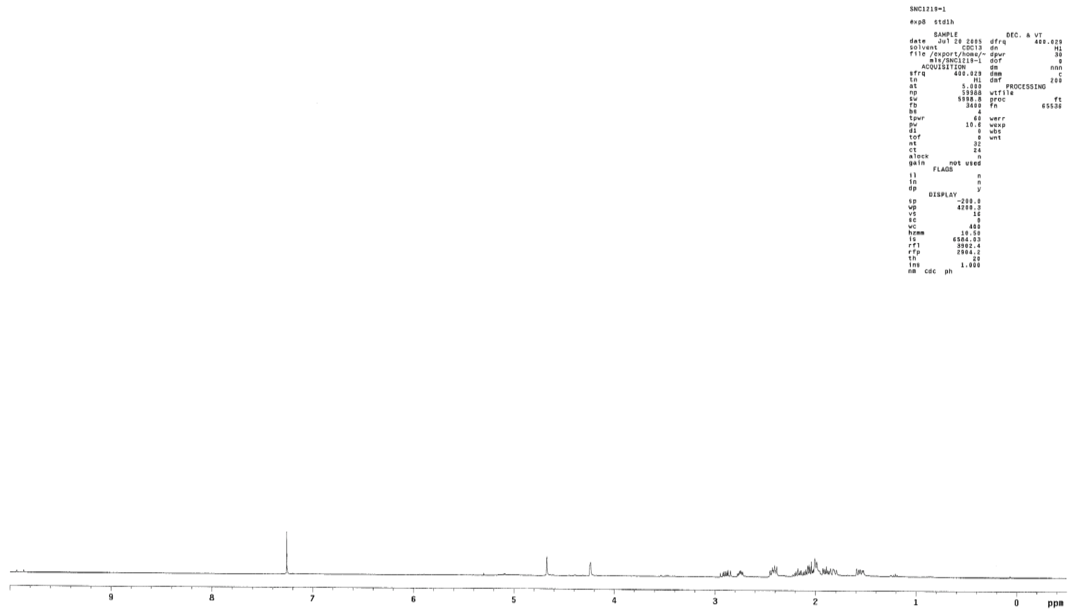


```
SNC1219-2carbon

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jul 24 2005  dfrq       499.784
solvent      CDCl3  dn              H1
file           exp  dpwr            40
   ACQUISITION      dof              0
sfrq       125.684  dm               y
tn             C13  dmm              w
at           0.999  dmf          11664
np           60288  dseq
sw         30165.9  dres           1.0
fb           17000  homo             n
bs               4  temp          28.0
tpwr            56         DEC2
pw             5.0  dfrq2            0
d1          10.000  dn2
tof         1759.4  dpwr2            1
nt          100000  dof2             0
ct             516  dm2              n
alock            n  dmm2             c
gain            50  dmf2         10000
      FLAGS         dseq2
il               n  dres2          1.0
in               n  homo2            n
dp               y      PROCESSING
hs              nn  lb            1.00
     DISPLAY        wtfile
sp         -1383.5  proc            ft
wp         30165.9  fn        not used
vs            2329  math             f
sc               0
wc             380  werr
hzmm         79.38  wexp
is          500.00  wbs            wft
rfl         1383.5  wnt
rfp              0
th               6
ins        100.000
ai    ph
```

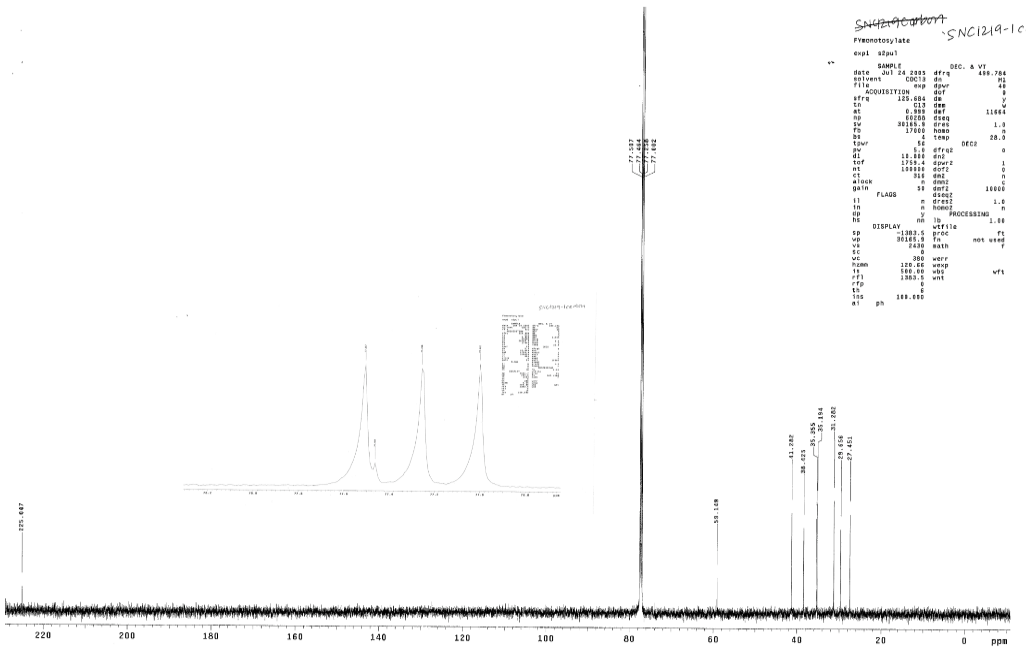
Photocycloadduct (II.15b): colorless oil. **R$_f$** 0.42 (pentane:Et$_2$O 1:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 4.67 (m, 1H), 4.23 (m, 1H), 2.89 (ddd, 1H, J = 18, 12.8, 9.6 Hz), 2.75 (td, 1H, J = 8.4, 4.4 Hz), 2.41 (m, 2H), 1.79-2.17 (m, 7 H), 1.55 (m, 1H). **^{13}C-NMR** (CDCl$_3$, 125 MHz) δ 225.0, 77.4, 59.1, 41.2, 38.4, 35.5, 35.1, 31.2, 29.6, 27.5. **IR** (NaCl, thin film) 3455 (br), 2920 (s), 1705 (s), 1402 (w), 1006 (w) cm^{-1}. **HRMS** (M + Na) C$_{10}$H$_{14}$O$_2$Na Calcd: 189.0891. Found: 189.0889.



```
SNC1219-1

exp8  std1h

      SAMPLE              DEC. & VT
date   Jul 20 2005   dfrq        400.029
solvent       CDCl3   dn              H1
file /export/home/~  dpwr             30
     mls/SNC1219-1   dof               0
   ACQUISITION       dm              nnn
sfrq        400.029  dmm               c
tn               H1  dmf             200
at            5.000       PROCESSING
np            59988  wtfile
sw           5998.8  proc             ft
fb             3400  fn            65536
bs                4
tpwr             60  werr
pw             10.6  wexp
d1                0  wbs
tof               0  wnt
nt               32
ct               24
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -200.0
wp           4200.3
vs               16
sc                0
wc              400
hzmm          10.50
is          6584.03
rfl          3902.4
rfp          2904.2
th               20
ins           1.000
nm  cdc  ph
```

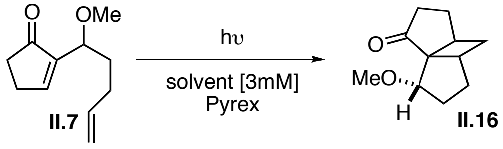


~~SNC1219carbon~~ 'SNC1219-1carbon'

```
FYmonotosylate

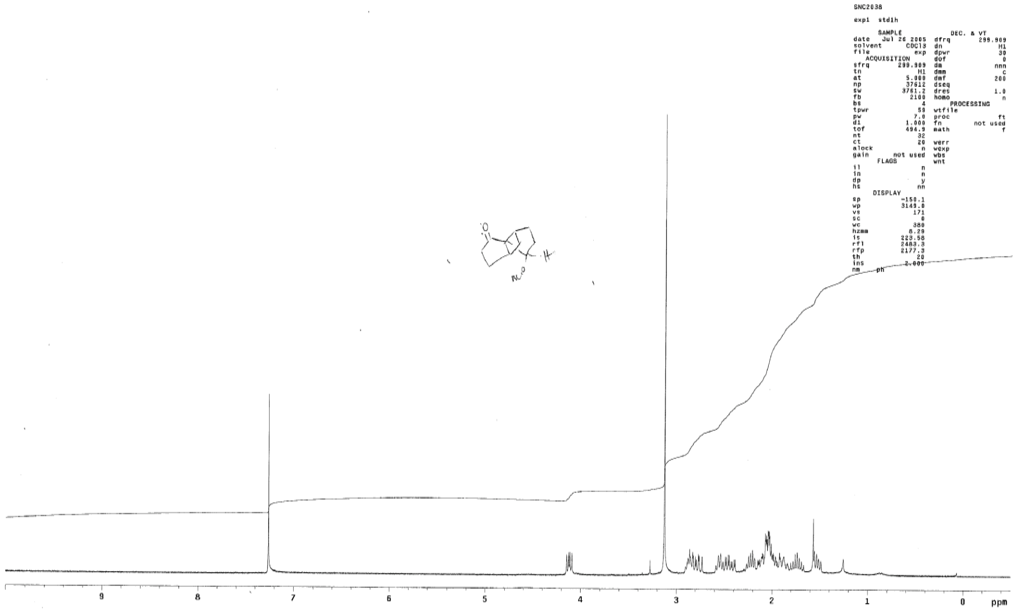
expl  s2pul

       SAMPLE               DEC. & VT
date   Jul 24 2005  dfrq       499.784
solvent      CDCl3  dn              H1
file           exp  dpwr            40
   ACQUISITION      dof              0
sfrq       125.684  dm               y
tn             C13  dmm              w
at           0.999  dmf          11664
np           60288  dseq
sw         30165.9  dres           1.0
fb           17000  homo             n
bs               4  temp          28.0
tpwr            56         DEC2
pw             5.0  dfrq2            0
d1          10.000  dn2
tof         1759.4  dpwr2            1
nt          100000  dof2             0
ct             316  dm2              n
alock            n  dmm2             c
gain            50  dmf2         10000
      FLAGS         dseq2
il               n  dres2          1.0
in               n  homo2            n
dp               y      PROCESSING
hs              nn  lb            1.00
     DISPLAY        wtfile
sp         -1383.5  proc            ft
wp         30165.9  fn        not used
vs            2430  math             f
sc               0
wc             380  werr
hzmm        120.66  wexp
is          500.00  wbs            wft
rfl         1383.5  wnt
rfp              0
th               6
ins        100.000
ai    ph
```



*See representative procedure (B) for intramolecular [2+2] photocycloaddtion of enone **II.7**.* The residue was purified on silica gel (pentane:Et_2O 5:1) to give compound **II.16** as a colorless oil.

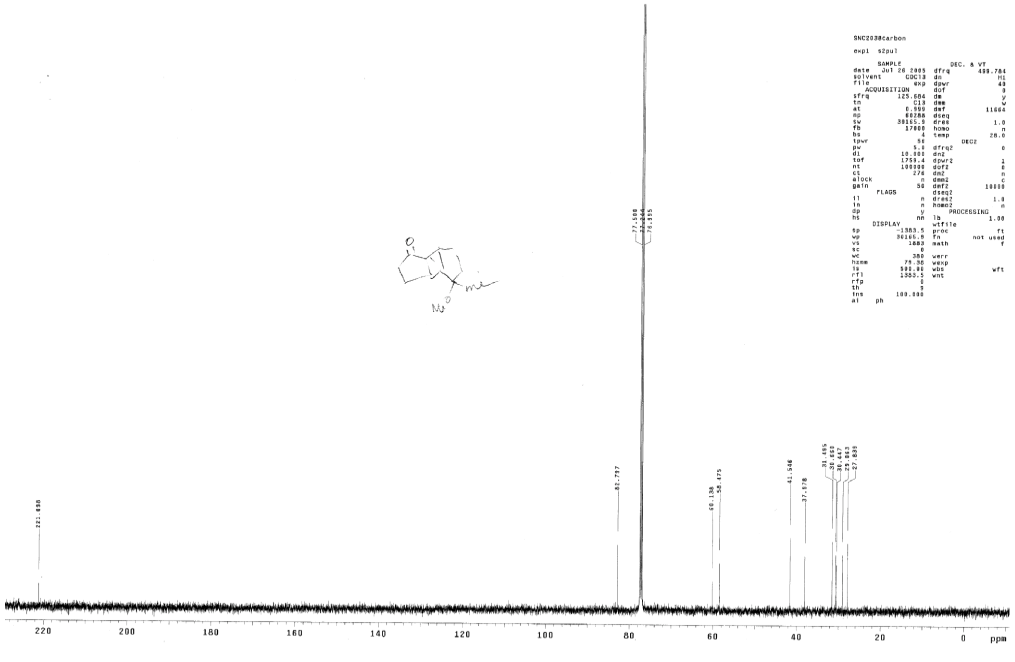
Photocycloadduct (II.16): R_f 0.58 (pentane:Et_2O 3:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 4.11 (dd, 1H, J = 10.8, 6.4 Hz), 3.12 (s, 3H), 2.74-2.88 (m, 2H), 2.54 (dd, 1H, J = 14.0, 8.0 Hz), 2.43 (ddd, 1H, J = 12.4, 9.2, 2.8 Hz), 2.21 (m, 1H), 1.84-2.15 (m, 5 H), 1.73 (tt, 1H, J = 13.6, 7.6 Hz), 1.51 (dd 1H, J = 13.6, 8.0 Hz). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 221.0, 82.7, 60.1, 58.4, 41.5, 37.9, 31.4, 30.6, 30.4, 29.0, 27.8. **IR** (NaCl, thin film) 2955 (m), 2867 (w), 1726 (s), 1115 (m), 750 (w) cm^{-1}. **HRMS** (EI) $C_{11}H_{16}O_2$ Calcd: 180.1150. Found: 180.1149.



```
SNC2038

exp1  std1h

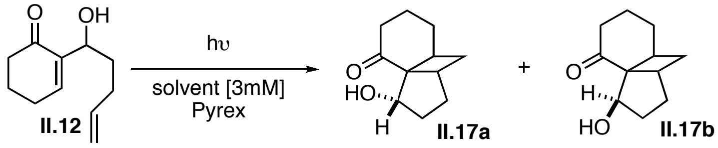
      SAMPLE              DEC. & VT
date   Jul 26 2005  dfrq        299.909
solvent      CDCl3  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       299.909  dm              nnn
tn              H1  dmm               c
at           5.000  dmf             200
np           37612  dseq
sw          3761.2  dres            1.0
fb            2100  homo              n
bs               4      PROCESSING
tpwr            59  wtfile
pw             7.0  proc             ft
d1           1.000  fn         not used
tof          494.9  math              f
nt              32
ct              20  werr
alock            n  wexp
gain      not used  wbs
      FLAGS         wnt
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -150.1
wp          3149.8
vs             171
sc               0
wc             380
hzmm          8.29
is          223.58
rfl         2483.3
rfp         2177.3
th              20
ins          2.000
nm    ph
```



```
SNC2038carbon

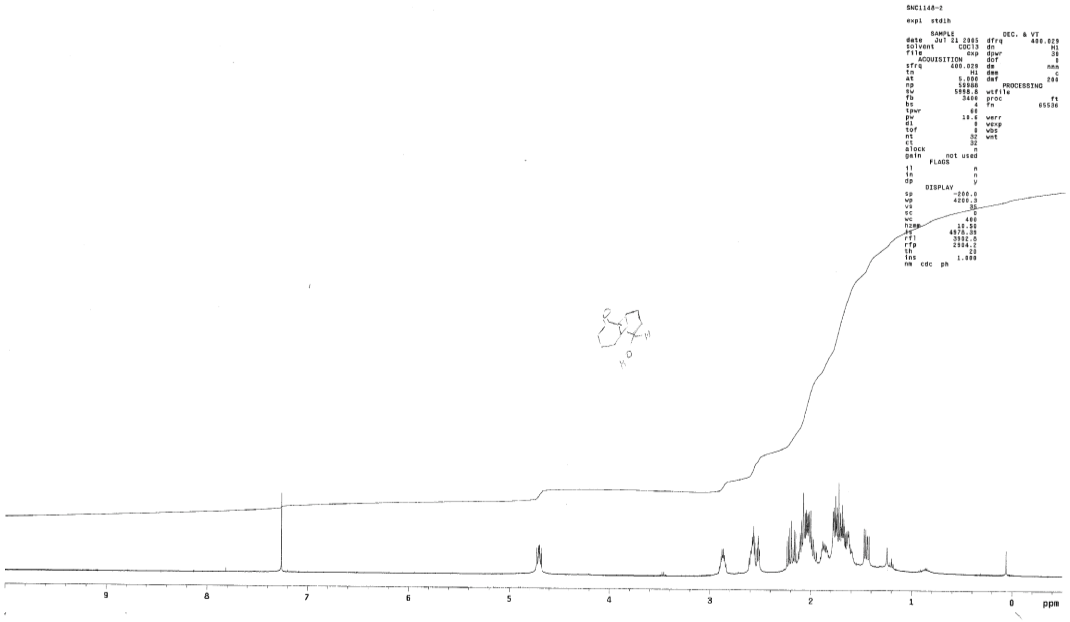
exp1  s2pul

      SAMPLE              DEC. & VT
date   Jul 26 2005  dfrq        499.784
solvent      CDCl3  dn               H1
file           exp  dpwr             40
   ACQUISITION      dof               0
sfrq       125.684  dm                y
tn             C13  dmm               w
at           0.999  dmf           11664
np           60288  dseq
sw         30165.9  dres            1.0
fb           17000  homo              n
bs               4  temp           28.0
tpwr            56          DEC2
pw             5.0  dfrq2             0
d1          10.000  dn2
tof         1759.4  dpwr2             1
nt          100000  dof2              0
ct             276  dm2               n
alock            n  dmm2              c
gain            50  dmf2          10000
      FLAGS         dseq2
il               n  dres2           1.0
in               n  homo2             n
dp               y      PROCESSING
hs              nn  lb             1.00
     DISPLAY        wtfile
sp         -1383.5  proc             ft
wp         30165.9  fn         not used
vs            1883  math              f
sc               0
wc             380  werr
hzmm         79.38  wexp
is          500.00  wbs             wft
rfl         1383.5  wnt
rfp              0
th               9
ins        100.000
ai    ph
```



*See representative procedure (B) for intramolecular [2+2] photocycloaddtion of enone **II.12**.* The residue was purified on silica gel (pentane:Et_2O 2:1) to give compounds **II.17a** and **II.17b**.

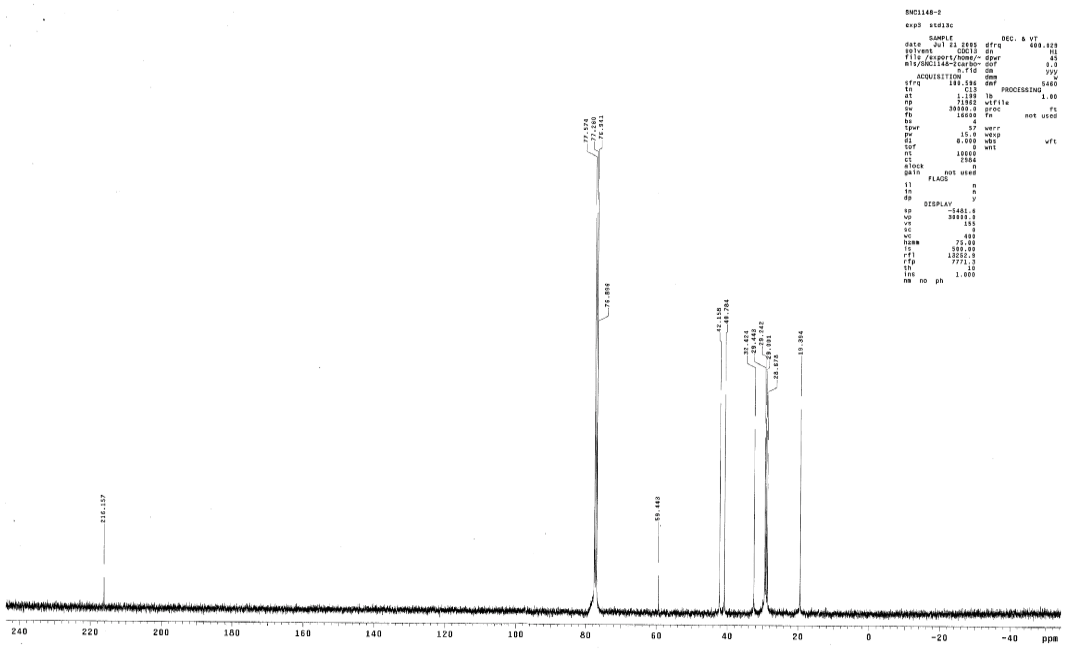
Photocycloadduct (II.17a): colorless oil. **R_f** 0.38 (pentane:Et_2O 1:4); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 4.69 (dd, 1H, J = 10.8, 6.8 Hz), 2.87 (m, 1H), 2.55 (m, 2H), 2.18 (m, 2H), 2.04 (m, 3H), 1.86 (m, 2H), 1.59-1.78 (m, 4H) 1.44 (dd, 1H, J = 13.2, 6.8 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 216.1, 76.8, 59.4, 42.1, 40.7, 32.4, 29.4, 29.3, 29.0, 28.6, 19.3. **IR** (NaCl, thin film) 3410 (br), 3038 (m), 2949 (s), 1679 (s), 1074 (m) cm^{-1}. **HRMS** (M + Na) $C_{11}H_{16}O_2Na$ Calcd: 203.1048. Found: 203.1044.



```
SNC1148-2

exp1  stdlh

      SAMPLE               DEC. & VT
date   Jul 21 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       400.029  dm              nnn
tn              H1  dmm               c
at           5.000  dmf             200
np           59988        PROCESSING
sw          5998.8  wtfile
fb            3400  proc             ft
bs               4  fn            65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs
nt              32  wnt
ct              32
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs              35
sc               0
wc             400
hzmm         10.50
is         4978.39
rfl         3902.8
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
```

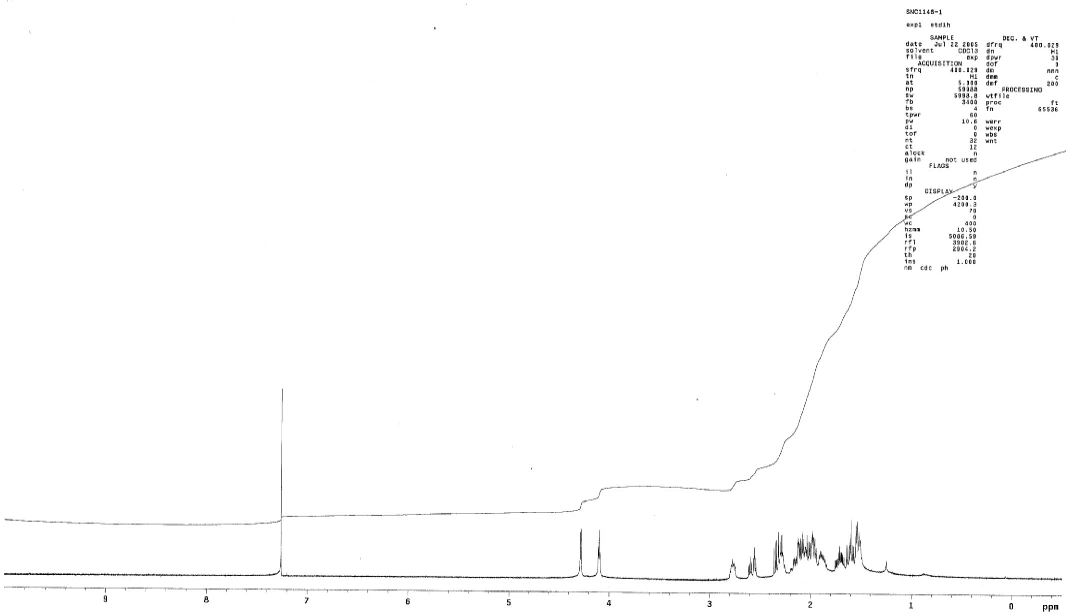


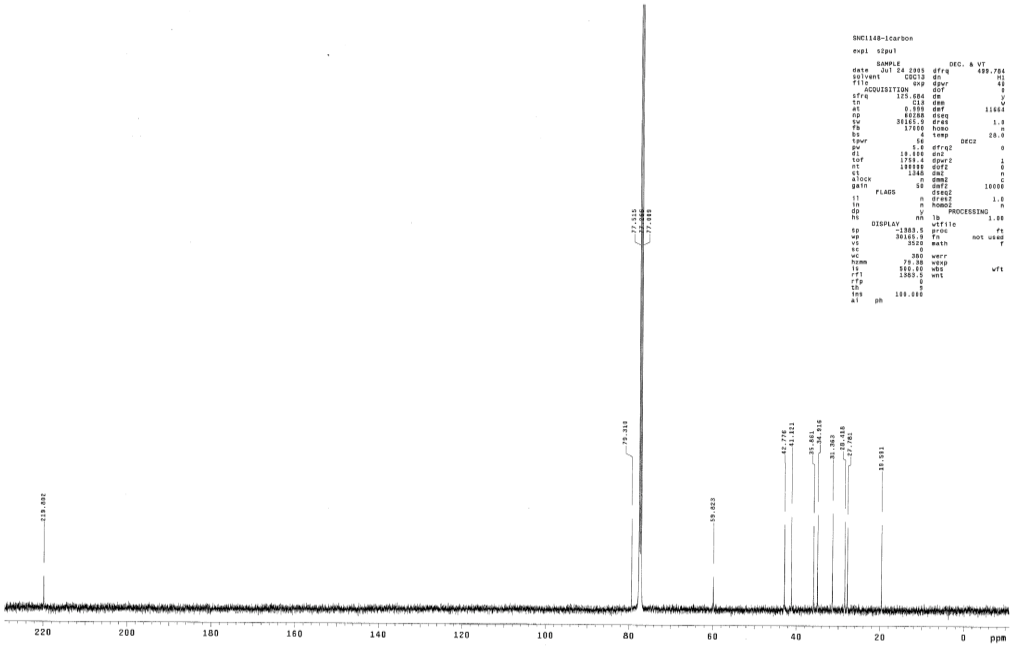
```
SNC1148-2

exp3  std13c

      SAMPLE               DEC. & VT
date   Jul 21 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             45
mls/SNC1148-2carbo~ dof             0.0
             n.fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       100.596  dmf            5460
tn             C13        PROCESSING
at           1.199  lb             1.00
np           71962  wtfile
sw         30000.0  proc             ft
fb           16600  fn         not used
bs               4
tpwr            57  werr
pw            15.0  wexp
d1           8.000  wbs             wft
tof              0  wnt
nt           10000
ct            2984
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp         -5481.6
wp         30000.0
vs             155
sc               0
wc             400
hzmm         75.00
is          500.00
rfl        13252.9
rfp         7771.3
th              10
ins          1.000
nm  no  ph
```

Photocycloadduct (II.17b): colorless oil. **R$_f$** 0.48 (pentane:Et$_2$O 1:4); **^{1}H- NMR** (CDCl$_3$, 400 MHz) δ 4.28 (d, 1H, *J* = 3.2 Hz OH), 4.09 (m, 1H), 2.77 (m, 1H), 2.57 (m, 1H), 2.31 (m, 2H), 1.84-2.17 (m, 7H), 1.50-1.75 (m, 3H). **^{13}C-NMR** (CDCl$_3$, 125 MHz) δ 219.8, 79.3, 59.8, 42.7, 41.1, 35.8, 34.9, 31.3, 28.4, 27.7, 19.6. **IR** (NaCl, thin film) 3433 (br), 2951 (s), 2866 (m), 1694 (s), 1268 (w), 1010 (m) cm^{-1}. **HRMS** (M + Na) $C_{11}H_{16}O_2Na$ Calcd: 203.1048. Found: 203.1039.

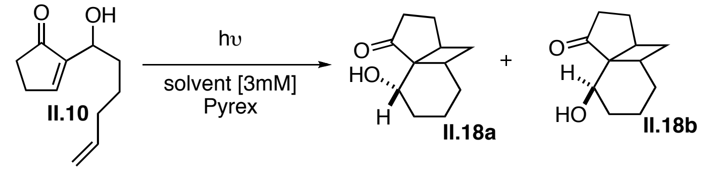




```
SNC1148-1carbon

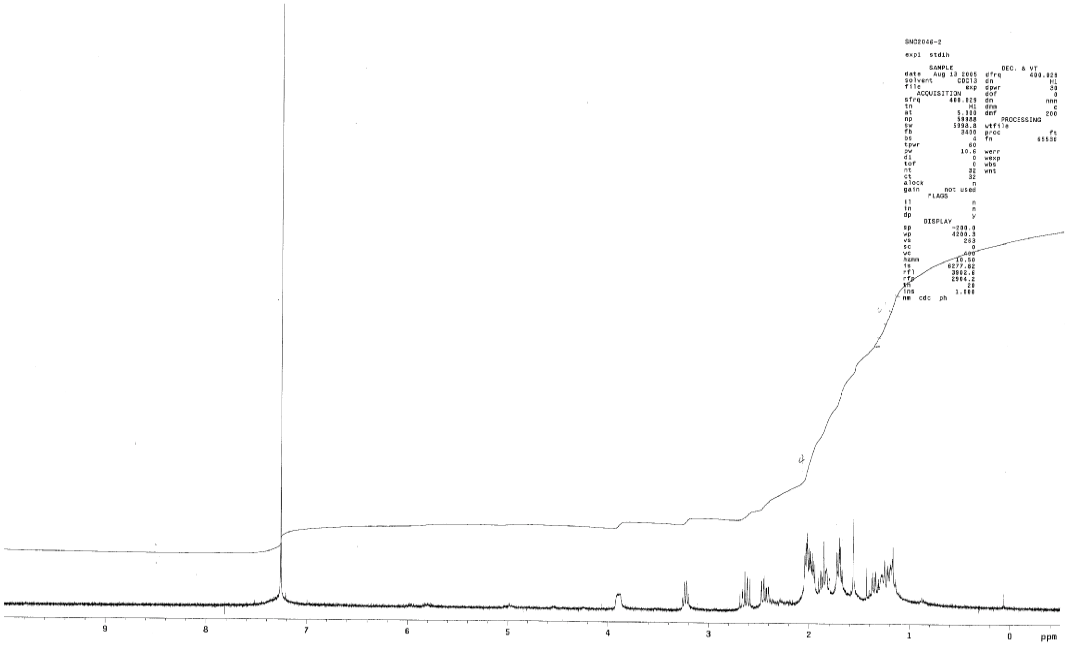
exp1  s2pul

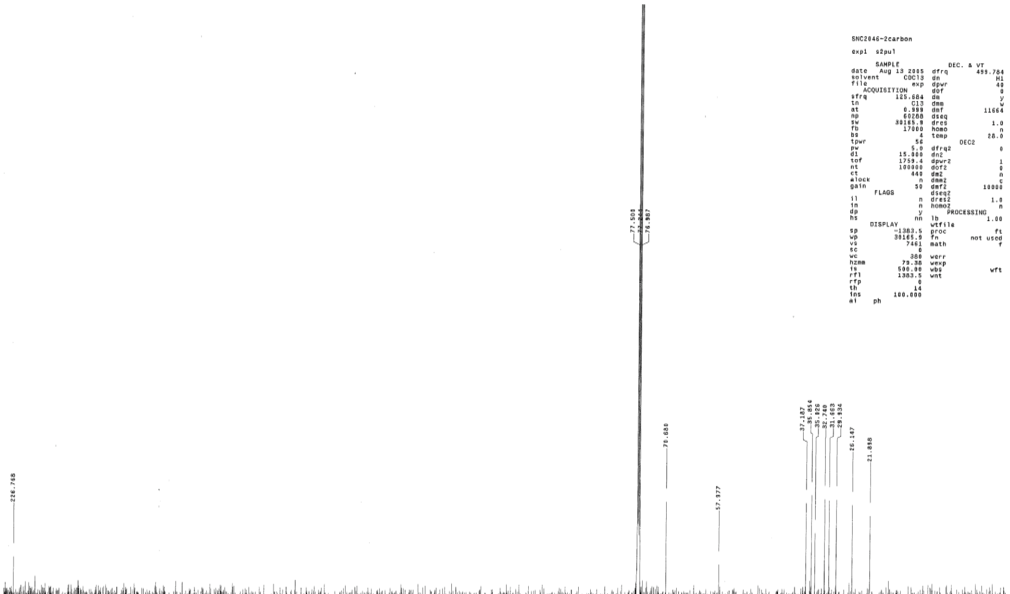
       SAMPLE              DEC. & VT
date   Jul 24 2005   dfrq       499.784
solvent      CDCl3   dn              H1
file           exp   dpwr            40
    ACQUISITION      dof              0
sfrq       125.684   dm               y
tn             C13   dmm              w
at           0.999   dmf          11664
np           60288   dseq
sw         30165.9   dres           1.0
fb           17000   homo             n
bs               4   temp          28.0
tpwr            56          DEC2
pw             5.0   dfrq2            0
d1          10.000   dn2
tof         1759.4   dpwr2            1
nt          100000   dof2             0
ct            1348   dm2              n
alock            n   dmm2             c
gain            50   dmf2         10000
       FLAGS         dseq2
il               n   dres2          1.0
in               n   homo2            n
dp               y      PROCESSING
hs              nn   lb            1.00
      DISPLAY        wtfile
sp         -1383.5   proc            ft
wp         30165.9   fn        not used
vs            3520   math             f
sc               0
wc             380   werr
hzmm         79.38   wexp
is          500.00   wbs            wft
rfl         1383.5   wnt
rfp              0
th               9
ins        100.000
ai    ph
```



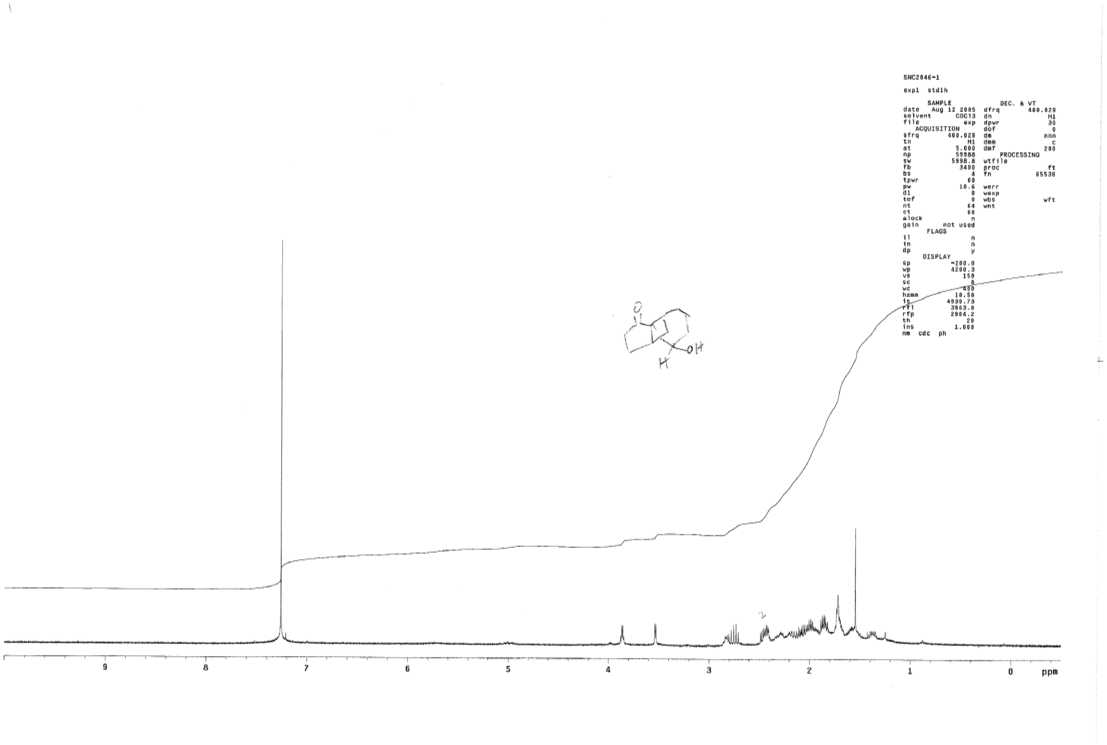
*See representative procedure (B) for intramolecular [2+2] photocycloaddtion of enone **II.10***. Benzophenone (0.075 equiv.) was added to the reaction mixture pre-irradiation. Product was purified on silica gel (pentane:Et$_2$O 4:1) to give compound **18a** and **18b**.

Photocycloadduct (18a): colorless oil. **R$_f$** 0.23 (pentane:Et$_2$O 1:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 3.88 (m, 1H), 3.22 (dd, 1H, J = 14.0, 6.8 Hz), 2.63 (ddd, 1H, J = 19.6, 10.8, 9.2 Hz), 2.43 (ddd, 1H, J = 11.6, 10.0, 2.0 Hz), 2.00 (m, 4H), 1.85 (m, 2H), 1.69 (m, 2H), 1.13-1.39 (m, 4H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 226.7, 70.6, 57.9, 37.1, 35.8, 35.0, 32.7, 31.6, 29.9, 26.1, 21.8. **IR** (NaCl, thin film) 3420 (br), 3039 (s), 3015(s), 2923 (m), 1720 (s), 1059 (w), 595 (m) cm^{-1}. **HRMS** (EI) $C_{11}H_{16}O_2$ Calcd: 180.1150. Found: 180.1148.


SNC2046-2
exp1 stdlh
date Aug 13 2005
solvent CDCl3
9
8
7
6
5
4
3
2
1
0
ppm


SNC2046-2carbon
exp1 s2pul
date Aug 13 2005
solvent CDCl3
226.768
77.508
77.244
76.987
70.680
57.977
37.187
35.856
35.026
32.740
31.663
29.834
26.147
21.898
220
200
180
160
140
120
100
80
60
40
20
0
ppm

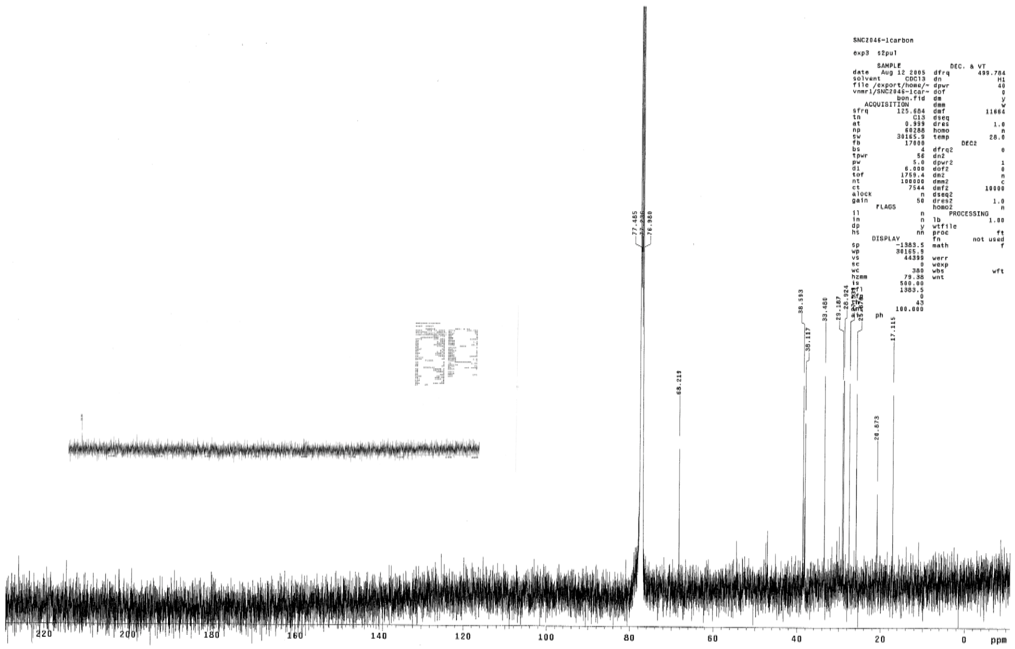
Photocycloadduct (18b): colorless oil. **R$_f$** 0.33 (pentane:Et$_2$O 1:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 3.86 (dd, 1H, J = 8.4, 4.4 Hz), 3.53 (d, 1H, J = 4.0 Hz), 2.70-2.86 (m, 2H), 1.59-2.49 (m, 11H), 1.38 (m, 1H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 226.0, 68.2, 38.6, 38.1, 33.4, 29.1, 28.9, 27.5, 25.8, 20.8, 17.1. **IR** (NaCl, thin film) 3466 (br), 3041 (m), 2952 (m), 1726 (s), 1406 (w), 775 (m) cm^{-1}. **HRMS** C$_{11}$H$_{16}$O$_2$ (EI) Calcd: 180.1150. Found: 180.1149.



```
SNC2046-1

exp1  std1h

      SAMPLE             DEC. & VT
date   Aug 12 2005   dfrq       400.029
solvent      CDCl3   dn              H1
file           exp   dpwr            30
   ACQUISITION       dof              0
sfrq       400.029   dm             nnn
tn              H1   dmm              c
at           5.000   dmf            200
np           59988       PROCESSING
sw          5998.8   wtfile
fb            3400   proc            ft
bs               4   fn           65536
tpwr            60
pw            10.6   werr
d1               0   wexp
tof              0   wbs            wft
nt              64   wnt
ct              60
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp          -200.0
wp          4200.3
vs             150
sc               0
wc             400
hzmm         10.50
is         4930.73
rfl         3903.0
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
```



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SNC2046-1carbon

exp3  s2pul

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date   Aug 12 2005   dfrq        499.784
solvent      CDCl3   dn               H1
file /export/home/~  dpwr             40
vnmr1/SNC2046-1car~  dof               0
           bon.fid   dm                y
   ACQUISITION       dmm               w
sfrq       125.684   dmf           11664
tn             C13   dseq
at           0.999   dres            1.0
np           60288   homo              n
sw         30165.9   temp           28.0
fb           17000           DEC2
bs               4   dfrq2             0
tpwr            56   dn2
pw             5.0   dpwr2             1
d1           6.000   dof2              0
tof         1759.4   dm2               n
nt          100000   dmm2              c
ct            7544   dmf2          10000
alock            n   dseq2
gain            50   dres2           1.0
      FLAGS          homo2             n
il               n       PROCESSING
in               n   lb             1.00
dp               y   wtfile
hs              nn   proc             ft
     DISPLAY         fn         not used
sp         -1383.5   math              f
wp         30165.9
vs           44399   werr
sc               0   wexp
wc             380   wbs             wft
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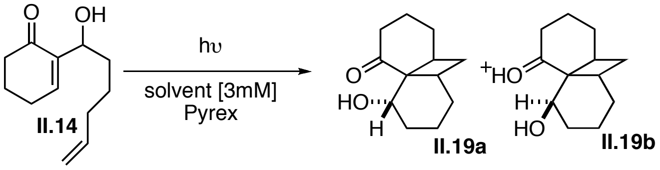
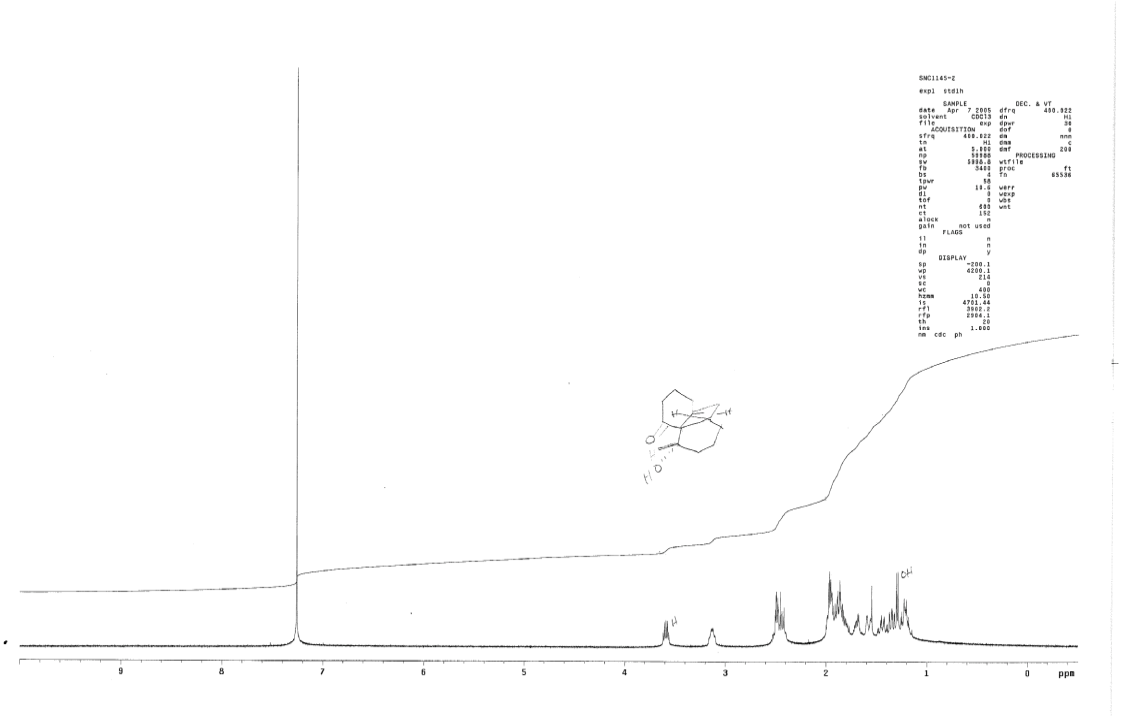
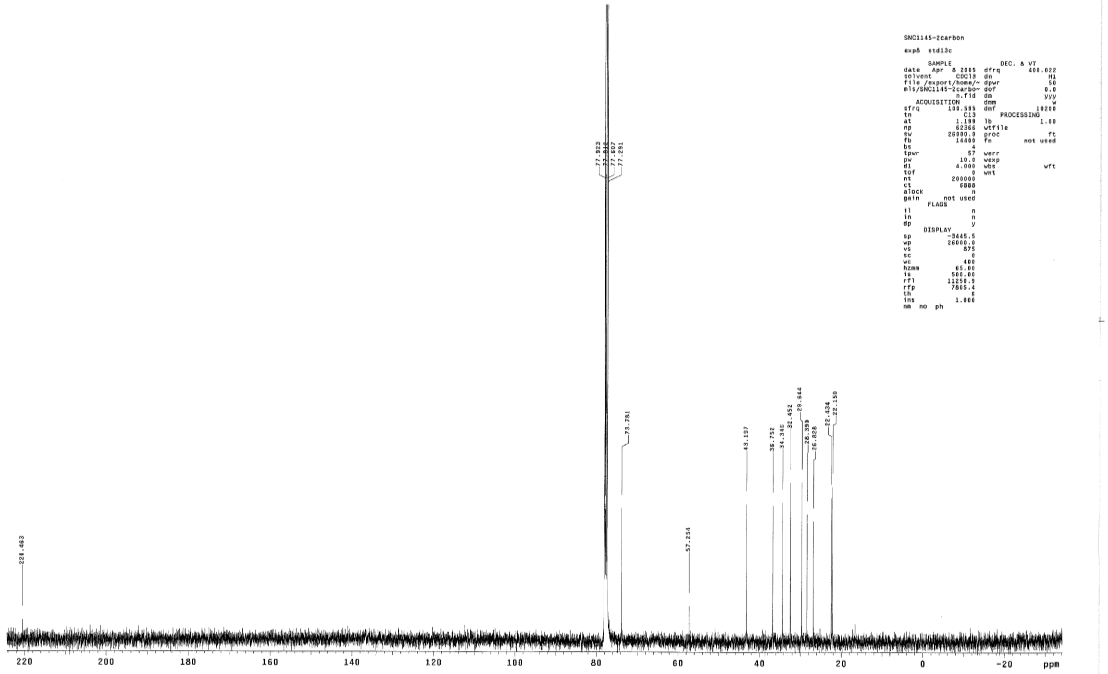
rfl         1383.5
rfp              0
th              43
ins        100.000
ai    ph
```



See representative procedure (B) for intramolecular [2+2] photocycloaddtion of ***II.14***. Enone **II.14** (10 mg, 0.051 mmol) was dissolved in solvent. The residue was purified on silica gel (pentane:Et$_2$O 2:1) to give **II.19a** and **II.19b**.

Photocycloadduct (II.19a): colorless crystals. **R$_f$** 0.42 (pentane:Et$_2$O 1:2); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 3.58 (td, 1H, J = 11.2, 5.6 Hz), 3.12 (m, 1H), 2.46 (m, 4H), 1.20-1.98 (m, 12H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 220.4, 73.8, 57.2, 43.2, 36.7, 34.3, 32.4, 29.6, 28.4, 26.8, 22.4, 22.2. **IR** (NaCl, thin film) 3435 (br), 2952 (s), 2866 (m), 1692 (s) cm^{-1}. **HRMS** (M + H) C$_{12}$H$_{19}$O$_2$ Calcd: 195.1385. Found: 195.1380.





```
SNC1145-2carbon

exp8  std13c

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solvent      CDCl3  dn              H1
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mls/SNC1145-2carbo~ dof            0.0
             n.fid  dm             yyy
   ACQUISITION      dmm              w
sfrq       100.595  dmf          10200
tn             C13        PROCESSING
at           1.199  lb            1.00
np           62366  wtfile
sw         26000.0  proc            ft
fb           14400  fn        not used
bs               4
tpwr            57  werr
pw            10.0  wexp
d1           4.000  wbs            wft
tof              0  wnt
nt          200000
ct            6888
alock            n
gain      not used
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in               n
dp               y
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sp         -3445.5
wp         26000.0
vs             875
sc               0
wc             400
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is          500.00
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rfp         7805.4
th               6
ins          1.000
nm  no  ph
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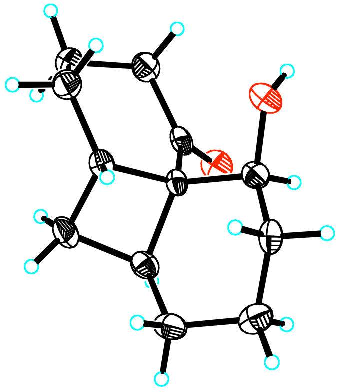


ORTEP of **II.19a**

Table 1. Crystal data and structure refinement for **II.19a**.

Identification code	sn02t	
Empirical formula	C12 H18 O2	
Formula weight	194.26	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.606(3) Å	a= 90°.
	b = 8.357(2) Å	b= 97.840(5)°.
	c = 12.604(4) Å	g = 90°.
Volume	1002.4(5) Å^3	
Z	4	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	424	
Crystal size	0.08 x 0.08 x 0.04 mm^3	
Theta range for data collection	2.14 to 24.99°.	
Index ranges	-11<=h<=7, -9<=k<=9, -14<=l<=14	
Reflections collected	4913	
Independent reflections	1623 [R(int) = 0.0377]	
Completeness to theta = 24.99°	92.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1623 / 0 / 199	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1193	
R indices (all data)	R1 = 0.0562, wR2 = 0.1245	
Largest diff. peak and hole	0.283 and -0.182 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for sn02t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5329(1)	463(2)	1430(1)	30(1)
O(2)	2078(2)	-305(2)	-478(1)	28(1)
C(1)	4265(2)	1229(2)	1132(2)	22(1)
C(2)	4322(2)	2726(3)	483(2)	28(1)
C(3)	3353(2)	4051(3)	778(2)	29(1)
C(4)	1850(2)	3455(3)	713(2)	26(1)
C(5)	1749(2)	1977(2)	1389(2)	21(1)
C(6)	2244(2)	2071(3)	2611(2)	27(1)
C(7)	2813(2)	352(2)	2573(2)	24(1)
C(8)	1756(2)	-914(3)	2823(2)	28(1)
C(9)	1738(2)	-2374(3)	2110(2)	29(1)
C(10)	1353(2)	-1883(3)	948(2)	25(1)
C(11)	2490(2)	-830(2)	599(2)	21(1)
C(12)	2842(2)	605(2)	1343(1)	19(1)

Table 3. Bond lengths [Å] and angles [°] for sn02t.

O(1)-C(1)	1.220(2)
O(2)-C(11)	1.429(2)
O(2)-H(1)	0.89(3)
C(1)-C(2)	1.500(3)
C(1)-C(12)	1.520(3)
C(2)-C(3)	1.525(3)
C(2)-H(3)	1.02(2)
C(2)-H(2)	0.96(2)
C(3)-C(4)	1.519(3)
C(3)-H(4)	0.96(2)
C(3)-H(5)	0.98(2)
C(4)-C(5)	1.511(3)
C(4)-H(7)	0.99(2)
C(4)-H(6)	0.98(2)
C(5)-C(6)	1.552(3)
C(5)-C(12)	1.561(3)
C(5)-H(8)	0.991(18)
C(6)-C(7)	1.540(3)
C(6)-H(9)	1.00(2)
C(6)-H(10)	1.00(2)
C(7)-C(8)	1.529(3)
C(7)-C(12)	1.569(3)
C(7)-H(11)	0.97(2)
C(8)-C(9)	1.514(3)
C(8)-H(12)	0.97(2)
C(8)-H(13)	0.97(2)
C(9)-C(10)	1.517(3)
C(9)-H(15)	0.99(2)
C(9)-H(14)	0.98(2)
C(10)-C(11)	1.514(3)
C(10)-H(17)	1.00(2)
C(10)-H(16)	0.99(2)

C(11)-C(12)	1.532(3)
C(11)-H(18)	0.989(19)

C(11)-O(2)-H(1)	105.2(18)
O(1)-C(1)-C(2)	120.98(17)
O(1)-C(1)-C(12)	120.08(18)
C(2)-C(1)-C(12)	118.79(16)
C(1)-C(2)-C(3)	113.84(17)
C(1)-C(2)-H(3)	107.4(12)
C(3)-C(2)-H(3)	112.8(13)
C(1)-C(2)-H(2)	106.6(14)
C(3)-C(2)-H(2)	107.3(13)
H(3)-C(2)-H(2)	108.6(17)
C(4)-C(3)-C(2)	110.85(18)
C(4)-C(3)-H(4)	109.1(13)
C(2)-C(3)-H(4)	110.5(13)
C(4)-C(3)-H(5)	110.6(12)
C(2)-C(3)-H(5)	110.8(12)
H(4)-C(3)-H(5)	104.8(18)
C(5)-C(4)-C(3)	111.79(17)
C(5)-C(4)-H(7)	110.1(13)
C(3)-C(4)-H(7)	108.9(13)
C(5)-C(4)-H(6)	111.0(13)
C(3)-C(4)-H(6)	108.7(12)
H(7)-C(4)-H(6)	106.2(18)
C(4)-C(5)-C(6)	118.93(17)
C(4)-C(5)-C(12)	118.96(15)
C(6)-C(5)-C(12)	87.55(14)
C(4)-C(5)-H(8)	110.2(10)
C(6)-C(5)-H(8)	108.9(10)
C(12)-C(5)-H(8)	110.3(11)
C(7)-C(6)-C(5)	89.05(15)
C(7)-C(6)-H(9)	111.6(12)
C(5)-C(6)-H(9)	110.5(12)

C(7)-C(6)-H(10)	116.4(13)
C(5)-C(6)-H(10)	117.5(12)
H(9)-C(6)-H(10)	110.3(17)
C(8)-C(7)-C(6)	112.98(17)
C(8)-C(7)-C(12)	113.53(16)
C(6)-C(7)-C(12)	87.70(14)
C(8)-C(7)-H(11)	110.8(12)
C(6)-C(7)-H(11)	116.3(12)
C(12)-C(7)-H(11)	113.8(12)
C(9)-C(8)-C(7)	112.92(17)
C(9)-C(8)-H(12)	107.4(12)
C(7)-C(8)-H(12)	111.0(13)
C(9)-C(8)-H(13)	110.6(14)
C(7)-C(8)-H(13)	109.0(13)
H(12)-C(8)-H(13)	105.8(17)
C(8)-C(9)-C(10)	109.68(18)
C(8)-C(9)-H(15)	109.4(12)
C(10)-C(9)-H(15)	110.5(12)
C(8)-C(9)-H(14)	110.8(13)
C(10)-C(9)-H(14)	109.4(13)
H(15)-C(9)-H(14)	107.0(18)
C(11)-C(10)-C(9)	110.36(16)
C(11)-C(10)-H(17)	107.2(12)
C(9)-C(10)-H(17)	111.9(12)
C(11)-C(10)-H(16)	109.0(12)
C(9)-C(10)-H(16)	110.0(12)
H(17)-C(10)-H(16)	108.2(16)
O(2)-C(11)-C(10)	109.72(15)
O(2)-C(11)-C(12)	110.50(16)
C(10)-C(11)-C(12)	112.62(16)
O(2)-C(11)-H(18)	109.1(11)
C(10)-C(11)-H(18)	108.9(11)
C(12)-C(11)-H(18)	106.0(11)
C(1)-C(12)-C(11)	106.88(15)

C(1)-C(12)-C(5)	112.35(16)
C(11)-C(12)-C(5)	120.26(15)
C(1)-C(12)-C(7)	110.90(14)
C(11)-C(12)-C(7)	117.87(16)
C(5)-C(12)-C(7)	87.68(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for sn02t. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	39(1)	31(1)	4(1)	5(1)	2(1)
O(2)	29(1)	35(1)	20(1)	-2(1)	5(1)	-1(1)
C(1)	23(1)	27(1)	17(1)	-7(1)	4(1)	-3(1)
C(2)	30(1)	28(1)	28(1)	0(1)	10(1)	-7(1)
C(3)	37(1)	22(1)	30(1)	2(1)	8(1)	-4(1)
C(4)	30(1)	21(1)	26(1)	1(1)	5(1)	1(1)
C(5)	20(1)	23(1)	20(1)	-3(1)	5(1)	-2(1)
C(6)	33(1)	29(1)	22(1)	-6(1)	10(1)	-3(1)
C(7)	25(1)	28(1)	19(1)	2(1)	4(1)	0(1)
C(8)	31(1)	32(1)	24(1)	8(1)	9(1)	0(1)
C(9)	29(1)	25(1)	35(1)	8(1)	8(1)	-2(1)
C(10)	26(1)	19(1)	30(1)	-3(1)	5(1)	-1(1)
C(11)	21(1)	22(1)	21(1)	0(1)	4(1)	2(1)
C(12)	21(1)	21(1)	17(1)	0(1)	4(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)
for sn02t.

	x	y	z	U(eq)
H(1)	2850(30)	-380(30)	-790(20)	61(9)
H(3)	5340(20)	3070(30)	549(17)	31(5)
H(2)	4010(20)	2440(30)	-252(19)	35(6)
H(4)	3380(20)	4950(30)	306(18)	31(6)
H(5)	3680(20)	4480(20)	1498(18)	23(5)
H(7)	1260(20)	4320(30)	951(19)	39(6)
H(6)	1490(20)	3250(30)	-41(19)	31(6)
H(8)	781(19)	1540(20)	1269(14)	12(4)
H(9)	3020(20)	2870(30)	2769(16)	26(5)
H(10)	1510(20)	2250(30)	3089(18)	34(6)
H(11)	3730(20)	150(20)	2978(16)	26(5)
H(12)	810(20)	-480(30)	2737(16)	27(5)
H(13)	1970(20)	-1220(30)	3570(20)	40(6)
H(15)	2670(20)	-2890(30)	2219(16)	28(5)
H(14)	1060(20)	-3170(30)	2297(18)	35(6)
H(17)	1250(20)	-2830(30)	458(17)	31(6)
H(16)	460(20)	-1290(30)	857(16)	24(5)
H(18)	3370(20)	-1460(20)	631(15)	19(5)

Table 6. Torsion angles [°] for sn02t.

O(1)-C(1)-C(2)-C(3)	-141.14(19)
C(12)-C(1)-C(2)-C(3)	43.5(2)
C(1)-C(2)-C(3)-C(4)	-54.8(2)
C(2)-C(3)-C(4)-C(5)	54.8(2)
C(3)-C(4)-C(5)-C(6)	59.7(2)
C(3)-C(4)-C(5)-C(12)	-44.8(2)
C(4)-C(5)-C(6)-C(7)	-143.39(17)
C(12)-C(5)-C(6)-C(7)	-21.37(14)
C(5)-C(6)-C(7)-C(8)	-93.38(17)
C(5)-C(6)-C(7)-C(12)	21.26(13)
C(6)-C(7)-C(8)-C(9)	139.28(18)
C(12)-C(7)-C(8)-C(9)	41.4(2)
C(7)-C(8)-C(9)-C(10)	-59.8(2)
C(8)-C(9)-C(10)-C(11)	65.7(2)
C(9)-C(10)-C(11)-O(2)	-176.79(16)
C(9)-C(10)-C(11)-C(12)	-53.3(2)
O(1)-C(1)-C(12)-C(11)	-71.6(2)
C(2)-C(1)-C(12)-C(11)	103.85(19)
O(1)-C(1)-C(12)-C(5)	154.47(17)
C(2)-C(1)-C(12)-C(5)	-30.1(2)
O(1)-C(1)-C(12)-C(7)	58.1(2)
C(2)-C(1)-C(12)-C(7)	-126.44(18)
O(2)-C(11)-C(12)-C(1)	-74.90(18)
C(10)-C(11)-C(12)-C(1)	162.01(16)
O(2)-C(11)-C(12)-C(5)	54.7(2)
C(10)-C(11)-C(12)-C(5)	-68.4(2)
O(2)-C(11)-C(12)-C(7)	159.49(15)
C(10)-C(11)-C(12)-C(7)	36.4(2)
C(4)-C(5)-C(12)-C(1)	31.3(2)
C(6)-C(5)-C(12)-C(1)	-90.70(17)
C(4)-C(5)-C(12)-C(11)	-95.8(2)
C(6)-C(5)-C(12)-C(11)	142.18(17)

C(4)-C(5)-C(12)-C(7)	142.96(17)
C(6)-C(5)-C(12)-C(7)	20.98(14)
C(8)-C(7)-C(12)-C(1)	-153.94(17)
C(6)-C(7)-C(12)-C(1)	91.94(17)
C(8)-C(7)-C(12)-C(11)	-30.3(2)
C(6)-C(7)-C(12)-C(11)	-144.44(16)
C(8)-C(7)-C(12)-C(5)	92.98(18)
C(6)-C(7)-C(12)-C(5)	-21.14(14)

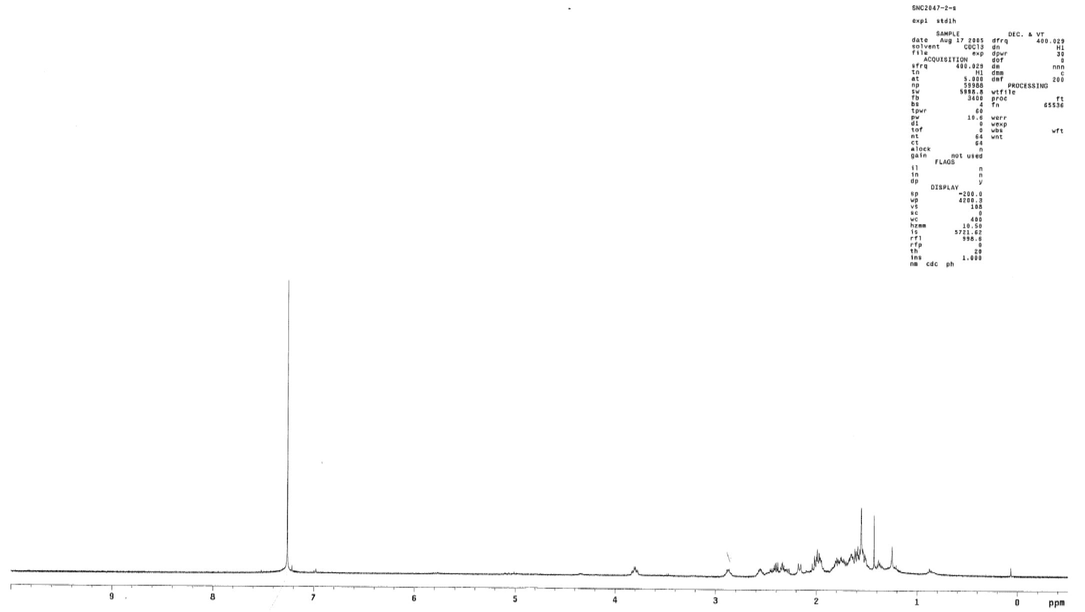
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for sn02t [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(1)...O(1)#1	0.89(3)	2.02(3)	2.913(2)	176(3)

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

Photocycloadduct (II.19b): colorless oil. **R$_f$** 0.48 (pentane:Et$_2$O 1:4); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 3.79 (td, 1H, J = 9.6, 4.4 Hz), 2.86 (m, 1H), 2.27-2.55 (m, 3H), 2.16 (m, 1H), 1.97 (m, 4H), 1.51-1.82 (m, 6H), 1.38 (m, 2H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 215.9, 74.5, 54.7, 40.1, 39.1, 36.8, 32.0, 27.9, 27.5, 26.0, 22.7, 20.2. **IR** (NaCl, thin film) 3434 (br), 2949 (s), 2863 (m), 1693 (s) cm^{-1}. **HRMS** (M + Na) C$_{12}$H$_{18}$O$_2$Na Calcd: 217.1204. Found: 217.1199.



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SNC2047-2-s

exp1  std1h

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file           exp   dpwr             30
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sfrq       400.029   dm              nnn
tn              H1   dmm               c
at           5.000   dmf             200
np           59988        PROCESSING
sw          5998.8   wtfile
fb            3400   proc             ft
bs               4   fn            65536
tpwr            60
pw            10.6   werr
d1               0   wexp
tof              0   wbs             wft
nt              64   wnt
ct              64
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
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sp          -200.0
wp          4200.3
vs             108
sc               0
wc             400
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rfl          998.6
rfp              0
th              20
ins          1.000
nm  cdc  ph
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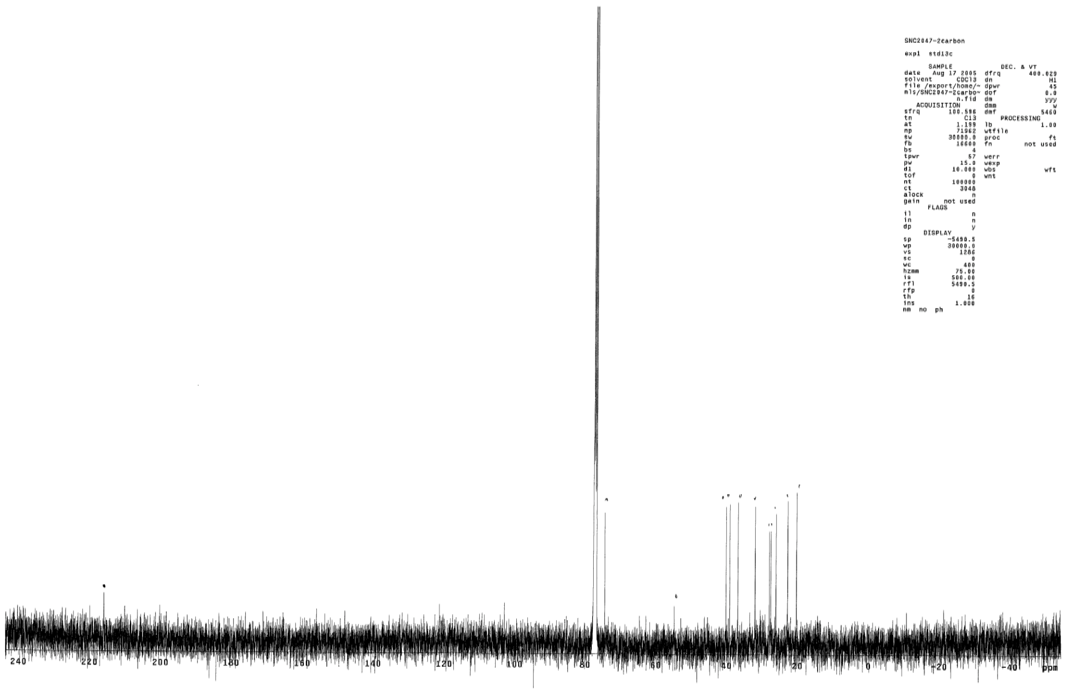

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SNC2047-2carbon

exp1  std13c

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solvent       CDCl3  dn               H1
file /export/home/~  dpwr              45
mls/SNC2047-2carbo~  dof              0.0
              n.fid  dm               yyy
   ACQUISITION       dmm                w
sfrq        100.596  dmf             5460
tn              C13       PROCESSING
at            1.199  lb              1.00
np            71962  wtfile
sw          30000.0  proc              ft
fb            16600  fn          not used
bs                4
tpwr             57  werr
pw             15.0  wexp
d1           10.000  wbs              wft
tof               0  wnt
nt           100000
ct             3048
alock             n
gain       not used
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in                n
dp                y
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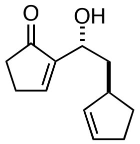
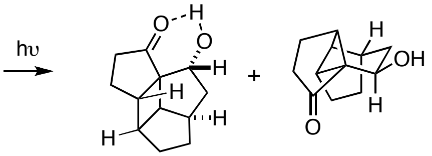
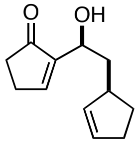
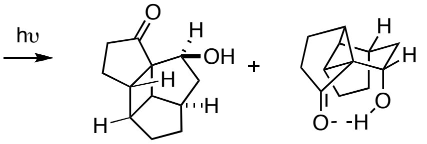
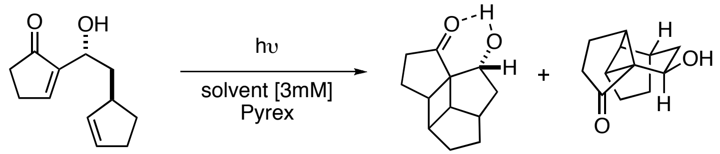
sp          -5490.5
wp          30000.0
vs             1286
sc                0
wc              400
hzmm          75.00
is           500.00
rfl          5490.5
rfp               0
th               16
ins           1.000
nm  no  ph
```

Table II.4. [2+2] Photocycloadditions of **II.28** and **II.29**.

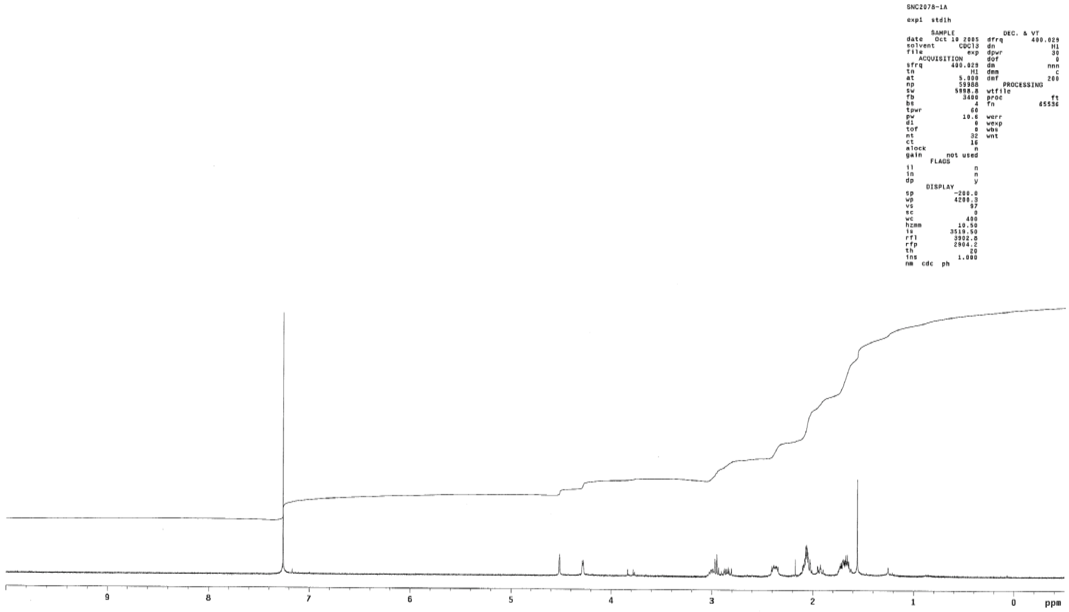
entry	enone	cycloadduct	solvent	yield/ratio
(1)	 **II.28**	 **II.30a** **II.30b**	CH_2Cl_2 acetone/H_2O	25% **a/b** (3:1) 25% **a/b** (<1:20)
(2)	 **II.29**	 **II.31a** **II.31b**	CH_2Cl_2 acetone/H_2O	60% **a/b** (2:1) 64% **a/b** (>20:1)



II.28 **II.30a** **II.30b**

*See representative procedure (B) for intramolecular [2+2] photocycloaddtion of enone **II.28***. Product was purified on silica gel (pentane:Et_2O 1:2) to give compound **II.30a** and **II.30b**.

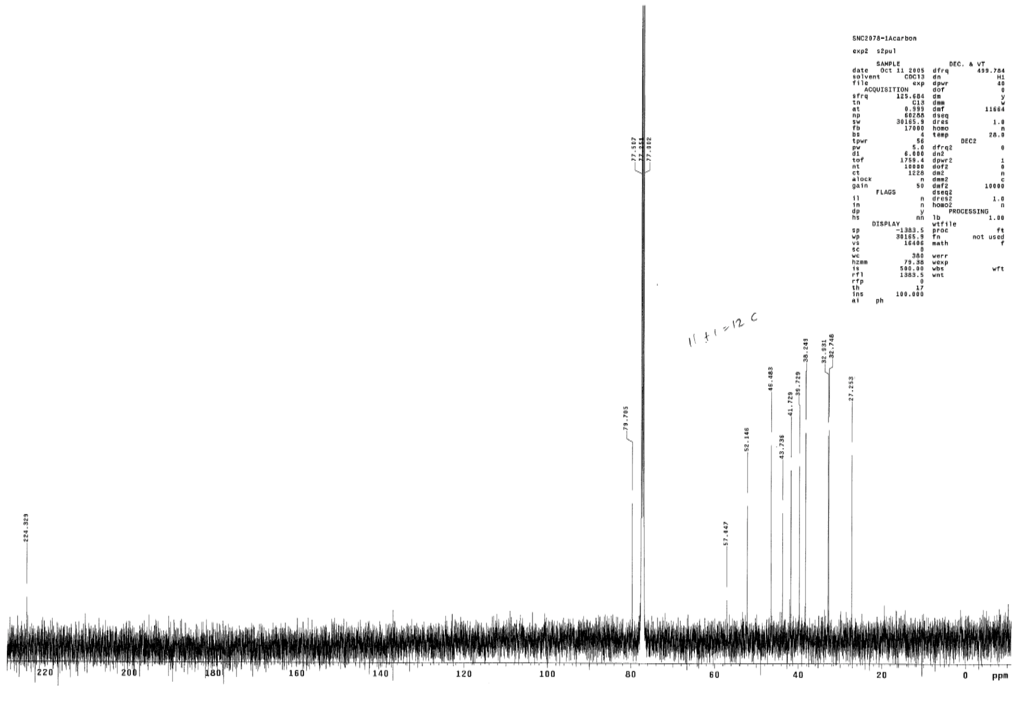
Photocycloadduct (II.30a): colorless oil. **R$_f$** 0.70 (pentane:Et_2O 1:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 4.51 (m, 1H), 4.28 (d, 1H J = 3.6 Hz), 2.80-3.02 (m, 4H), 2.37 (m, 2H), 2.06 (m, 3H), 1.92 (m, 1H), 1.67 (m, 4H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 224.3, 79.7, 57.0, 52.1, 46.4, 43.7, 41.7, 39.7, 38.2, 32.9, 32.7, 27.2. **IR** (NaCl, thin film) 3477 (br), 3027 (m), 2949 (s), 2862 (m), 1707 (s), 793 (w) cm^{-1}. **HRMS** (EI) $C_{12}H_{16}O_2$ Calcd: 192.1150. Found: 192.1148.



```
SNC2078-1A

exp1  std1h

      SAMPLE            DEC. & VT
date   Oct 10 2005  dfrq       400.029
solvent       CDCl3  dn              H1
file            exp  dpwr            30
   ACQUISITION       dof              0
sfrq        400.029  dm             nnn
tn               H1  dmm              c
at            5.000  dmf            200
np            59988       PROCESSING
sw           5998.8  wtfile
fb             3400  proc            ft
bs                4  fn           65536
tpwr             60
pw             10.6  werr
d1                0  wexp
tof               0  wbs
nt               32  wnt
ct               16
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
      DISPLAY
sp           -200.0
wp           4200.3
vs               97
sc                0
wc              400
hzmm          10.50
is          3519.50
rfl          3902.8
rfp          2904.2
th               20
ins           1.000
nm  cdc  ph
```



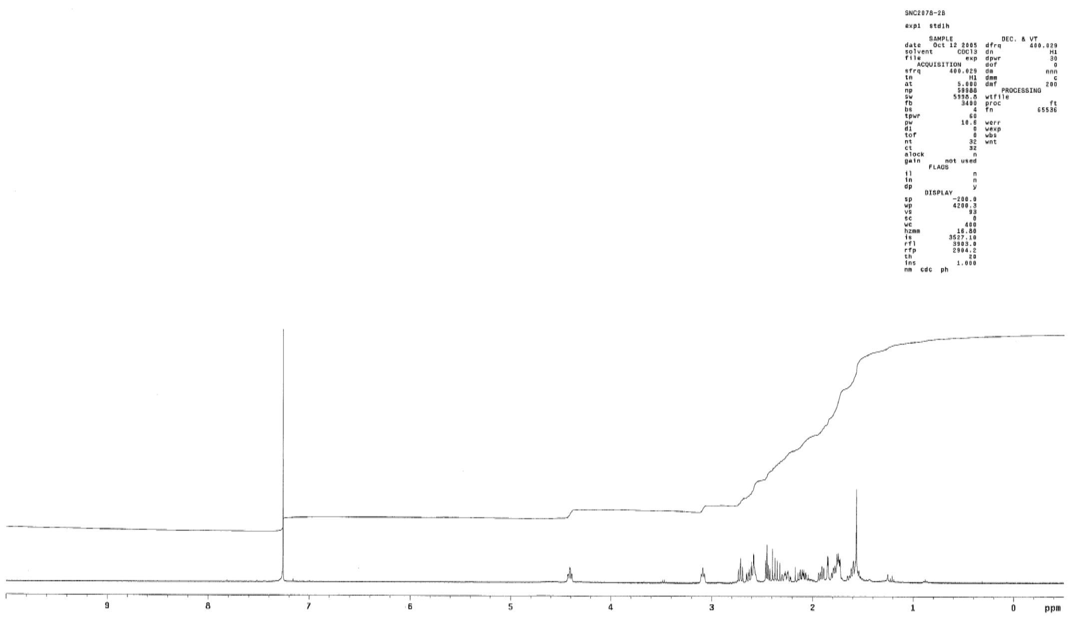
```
SNC2078-1Acarbon

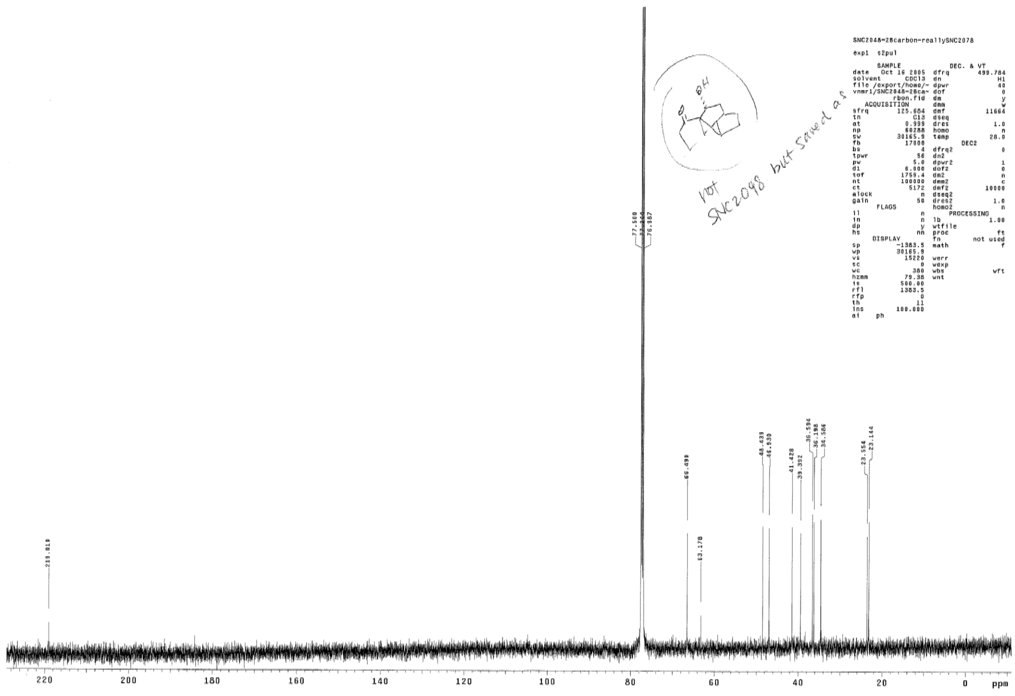
exp2  s2pul

      SAMPLE            DEC. & VT
date   Oct 11 2005  dfrq       499.784
solvent       CDCl3  dn              H1
file            exp  dpwr            40
   ACQUISITION       dof              0
sfrq        125.684  dm               y
tn              C13  dmm              w
at            0.999  dmf          11664
np            60288  dseq
sw          30165.9  dres           1.0
fb            17000  homo             n
bs                4  temp          28.0
tpwr             56         DEC2
pw              5.0  dfrq2            0
d1            6.000  dn2
tof          1759.4  dpwr2            1
nt            10000  dof2             0
ct             1228  dm2              n
alock             n  dmm2             c
gain             50  dmf2         10000
       FLAGS         dseq2
il                n  dres2          1.0
in                n  homo2            n
dp                y       PROCESSING
hs               nn  lb            1.00
      DISPLAY        wtfile
sp          -1383.5  proc            ft
wp          30165.9  fn        not used
vs            16406  math             f
sc                0
wc              380  werr
hzmm          79.38  wexp
is           500.00  wbs            wft
rfl          1383.5  wnt
rfp               0
th               17
ins         100.000
ai    ph
```

11 + 1 = 12 C

Photocycloadduct (II.30b): colorless oil. **R$_f$** 0.24 (pentane:Et$_2$O 1:2); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 4.40 (td, 1H, J = 8.0, 2.8 Hz), 3.08 (t, 1H, J = 6.0 Hz), 2.71 (t, 1H, J = 8.0 Hz), 2.61 (m, 2H), 2.24-2.46 (m, 4H), 2.10 (m, 1H), 1.72-1.94 (m, 4H), 1.59 (m, 2H). **^{13}C-NMR** (CDCl$_3$, 125 MHz) δ 219.0, 66.4, 63.1, 48.4, 46.9, 41.4, 39.3, 36.6, 36.2, 34.5, 23.5, 23.1. **IR** (NaCl, thin film) 3413 (br), 2950 (s), 1724 (s), 1044 (m), 756 (w) cm^{-1}. **HRMS** (EI) C$_{12}$H$_{16}$O$_2$ Calcd: 192.1150. Found: 192.1148.



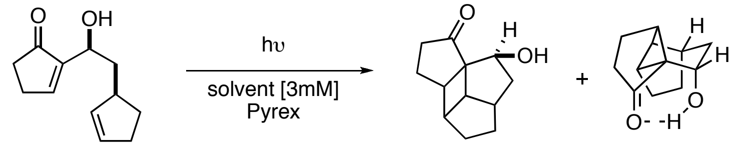


not SNC2098 but saved as

```
SNC2048=28carbon-reallySNC2078

expl  s2pul

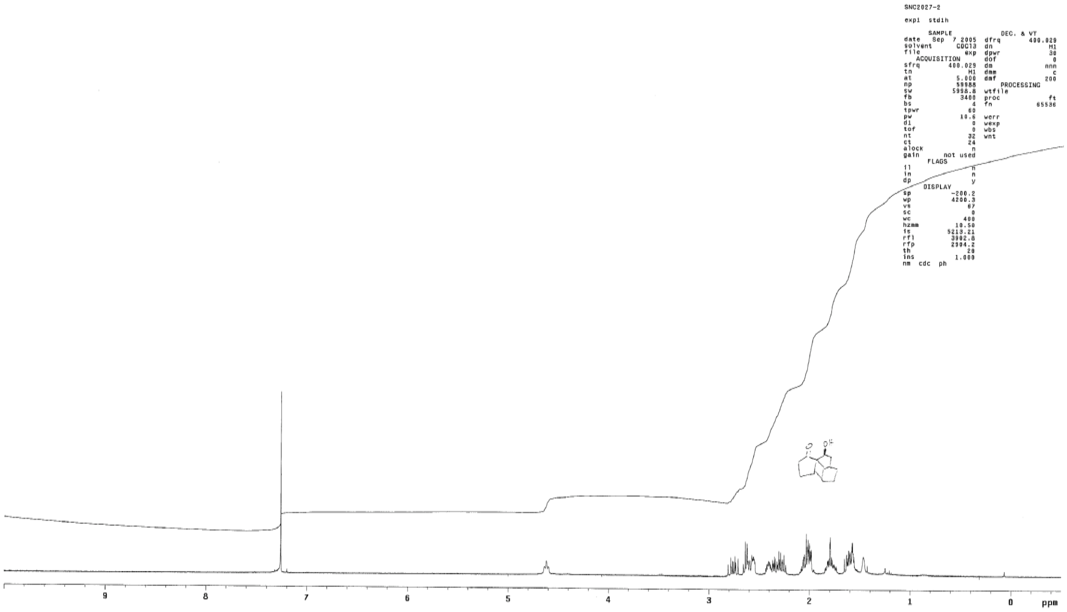
      SAMPLE              DEC. & VT
date   Oct 16 2005   dfrq         499.784
solvent       CDCl3  dn                H1
file /export/home/~  dpwr              40
vnmr1/SNC2048=28ca~  dof                0
           rbon.fid  dm                 y
   ACQUISITION       dmm                w
sfrq        125.684  dmf            11664
tn              C13  dseq
at            0.999  dres             1.0
np            60288  homo               n
sw          30165.9  temp            28.0
fb            17000           DEC2
bs                4  dfrq2              0
tpwr             56  dn2
pw              5.0  dpwr2              1
d1            6.000  dof2               0
tof          1759.4  dm2                n
nt           100000  dmm2               c
ct             5172  dmf2           10000
alock             n  dseq2
gain             50  dres2            1.0
      FLAGS          homo2              n
il                n       PROCESSING
in                n  lb              1.00
dp                y  wtfile
hs               nn  proc              ft
     DISPLAY         fn          not used
sp          -1383.5  math               f
wp          30165.9
vs            15220  werr
sc                0  wexp
wc              380  wbs              wft
hzmm          79.38  wnt
is           500.00
rfl          1383.5
rfp               0
th               11
ins         100.000
ai    ph
```



II.29 **II.31a** **II.31b**

*See representative procedure (B) for intramolecular [2+2] photocycloaddtion of enone **II.29**.* Product was purified on silica gel (pentane:Et_2O 2:1) to give compound **II.31a** and **II.31b**.

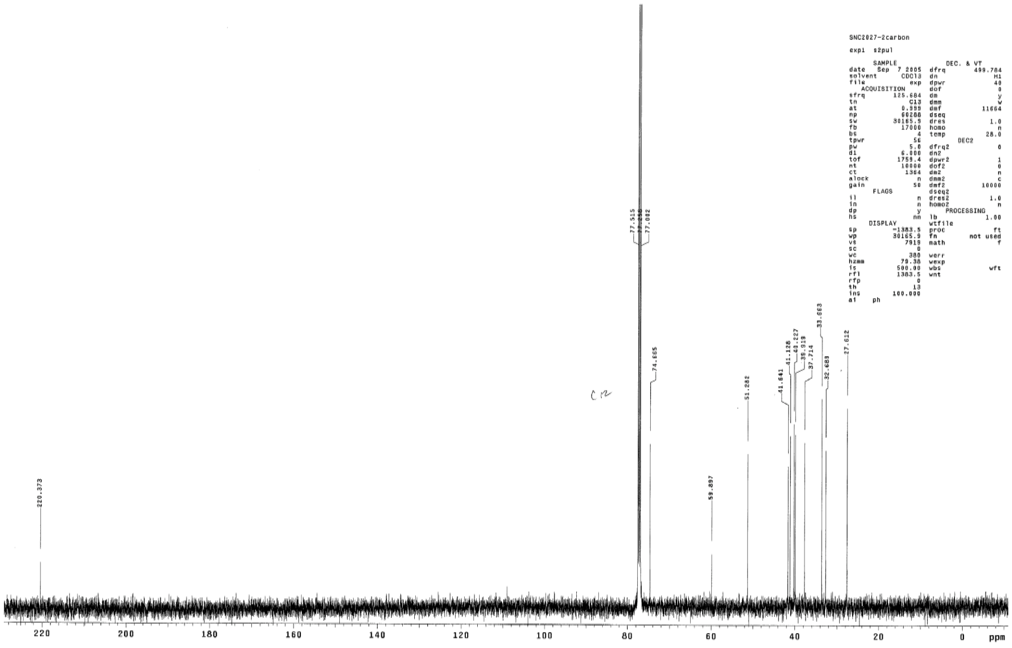
Photocycloadduct (II.31a): colorless oil. **R_f** 0.32 (pentane:Et_2O 2:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 4.62 (t, 1H, J = 7.2 Hz), 2.76 (m, 1H), 2.60 (m, 3H), 2.23-2.43 (m, 3H), 2.02 (m, 3H), 1.79 (m, 2H), 1.60 (m, 2H), 1.47 (br s, 1H, OH). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 220.3, 74.6, 59.8, 51.2, 41.6, 41.1, 40.2, 39.9, 37.3, 33.6, 32.6, 27.6. **IR** (NaCl, thin film) 3420 (br), 2950 (s), 2866 (m), 1724 (s), 1159 (w), 1076 (s) cm^{-1}. **HRMS** (EI) $C_{12}H_{16}O_2$ Calcd: 192.1150. Found: 192.1148.



```
SNC2027-2

exp1  std1h

      SAMPLE              DEC. & VT
date   Sep  7 2005   dfrq        400.029
solvent       CDCl3   dn               H1
file            exp   dpwr             30
   ACQUISITION        dof               0
sfrq        400.029   dm              nnn
tn               H1   dmm               c
at            5.000   dmf             200
np            59988        PROCESSING
sw           5998.8   wtfile
fb             3400   proc             ft
bs                4   fn            65536
tpwr             60
pw             10.6   werr
d1                0   wexp
tof               0   wbs
nt               32   wnt
ct               24
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -200.2
wp           4200.3
vs               67
sc                0
wc              400
hzmm          10.50
is          5213.21
rfl          3902.8
rfp          2904.2
th               20
ins           1.000
nm  cdc  ph
```

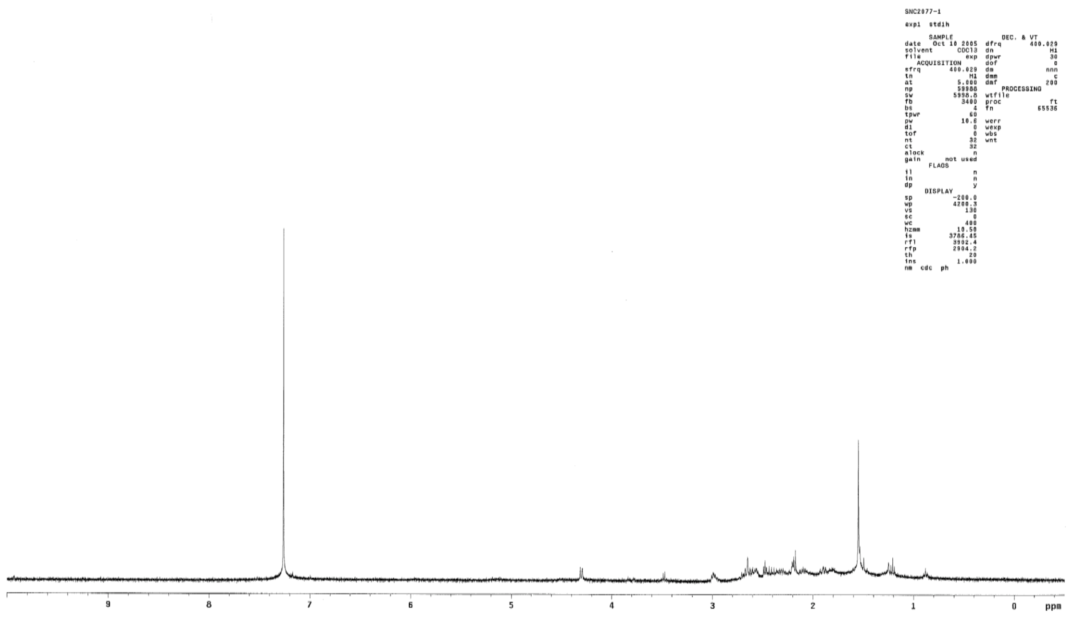


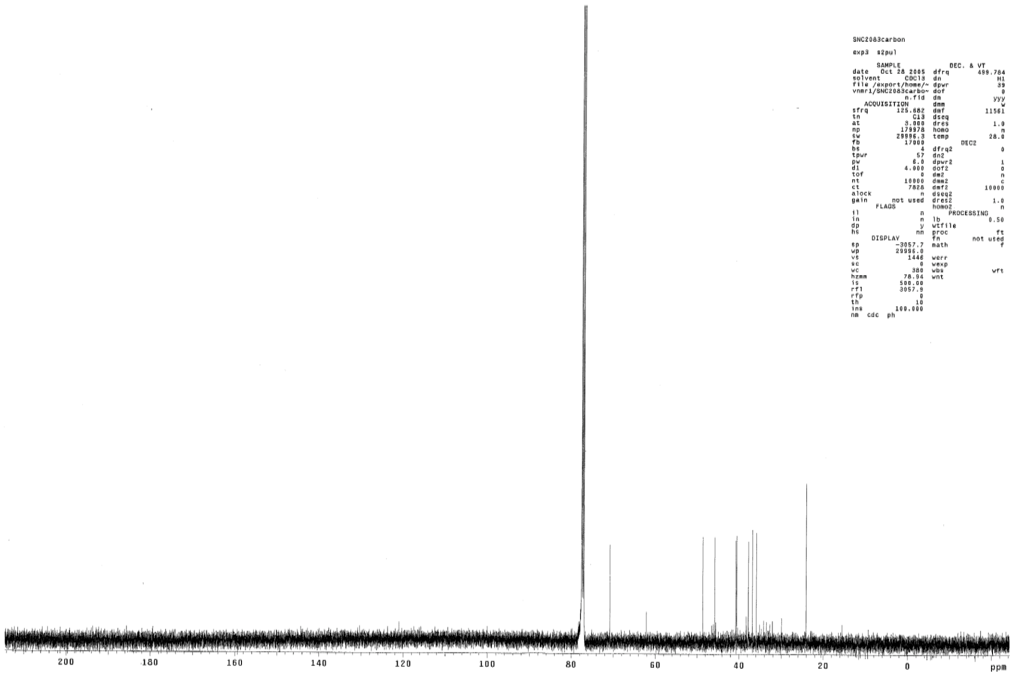
```
SNC2027-2carbon

exp1  s2pul

      SAMPLE              DEC. & VT
date   Sep  7 2005   dfrq        499.784
solvent       CDCl3   dn               H1
file            exp   dpwr             40
   ACQUISITION        dof               0
sfrq        125.684   dm                y
tn              C13   dmm               w
at            0.999   dmf           11664
np            60288   dseq
sw          30165.9   dres            1.0
fb            17000   homo              n
bs                4   temp           28.0
tpwr             56           DEC2
pw              5.0   dfrq2             0
d1            6.000   dn2
tof          1759.4   dpwr2             1
nt            10000   dof2              0
ct             1364   dm2               n
alock             n   dmm2              c
gain             50   dmf2          10000
      FLAGS           dseq2
il                n   dres2           1.0
in                n   homo2             n
dp                y        PROCESSING
hs               nn   lb             1.00
     DISPLAY          wtfile
sp          -1383.5   proc             ft
wp          30165.9   fn         not used
vs             7919   math              f
sc                0
wc              380   werr
hzmm          79.38   wexp
is           500.00   wbs             wft
rfl          1383.5   wnt
rfp               0
th               13
ins         100.000
ai    ph
```

Photocycloadduct (II.31b): colorless oil. **R$_f$** 0.47 (pentane:Et$_2$O 1:2); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 4.30 (d, 1H, J = 8.8 Hz), 2.98 (m, 1H), 2.65 (m, 4H), 2.02-2.48 (m, 7H), 1.86 (m, 3H). **^{13}C-NMR** (CDCl$_3$, 125 MHz) δ 70.7, 62.0, 48.5, 45.7, 40.7, 40.5, 38.2, 37.7, 36.8, 35.9, 24.0. **IR** (NaCl, thin film) 3464 (br), 3025 (s), 2948 (s), 2863 (w), 1712 (s), 1008 (w), 753 (m) cm^{-1}. **HRMS** (EI) C$_{12}$H$_{16}$O$_2$ Calcd: 192.1150. Found: 192.1144.



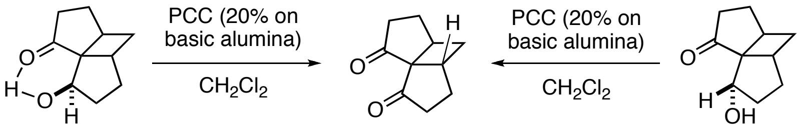


```
SNC2083carbon

exp3  s2pul

      SAMPLE               DEC. & VT
date   Oct 28 2005  dfrq        499.784
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             39
vnmr1/SNC2083carbo~ dof               0
             n.fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       125.682  dmf           11561
tn             C13  dseq
at           3.000  dres            1.0
np          179978  homo              n
sw         29996.3  temp           28.0
fb           17000          DEC2
bs               4  dfrq2             0
tpwr            57  dn2
pw             6.0  dpwr2             1
d1           4.000  dof2              0
tof              0  dm2               n
nt           10000  dmm2              c
ct            7828  dmf2          10000
alock            n  dseq2
gain      not used  dres2           1.0
      FLAGS         homo2             n
il               n      PROCESSING
in               n  lb             0.50
dp               y  wtfile
hs              nn  proc             ft
     DISPLAY        fn         not used
sp         -3057.7  math              f
wp         29996.0
vs            1446  werr
sc               0  wexp
wc             380  wbs             wft
hzmm         78.94  wnt
is          500.00
rfl         3057.9
rfp              0
th              10
ins        100.000
nm  cdc  ph
```

(C) Representative procedure for the oxidation of photocycloadducts: To a stirred solution of the photocycloadduct (1.0 equiv) in methylene chloride (0.1-0.01 mM) was added pyridinium chlorochromate (PCC 20% on basic alumina) (2.0 equiv). The reaction was stirred at room temperature until the reaction was deemed finished by TLC analysis. The reaction mixture was filtered through a plug (1.5 cm) of celite and the filtrate was washed with a solution of saturated $CuSO_4$ (2 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by a Kugelrohr distillation.

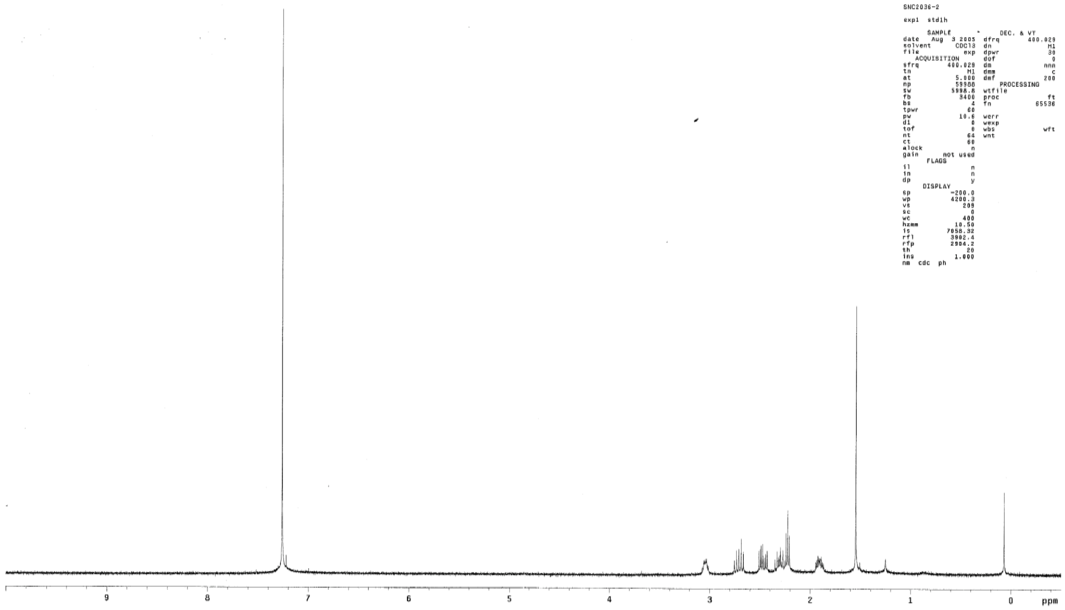


II.15b **II.21** **II.15a**

85% from **II.15b**

*See representative procedure (C) for the oxidation of photocycloadducts **II.15a** and **II.15b**.* The reaction mixture was stirred for 48 h until complete. Product was purified by bulb-to-bulb distillation to give compound **II.21** (85 % yield from **II.15b**) as a clear oil.

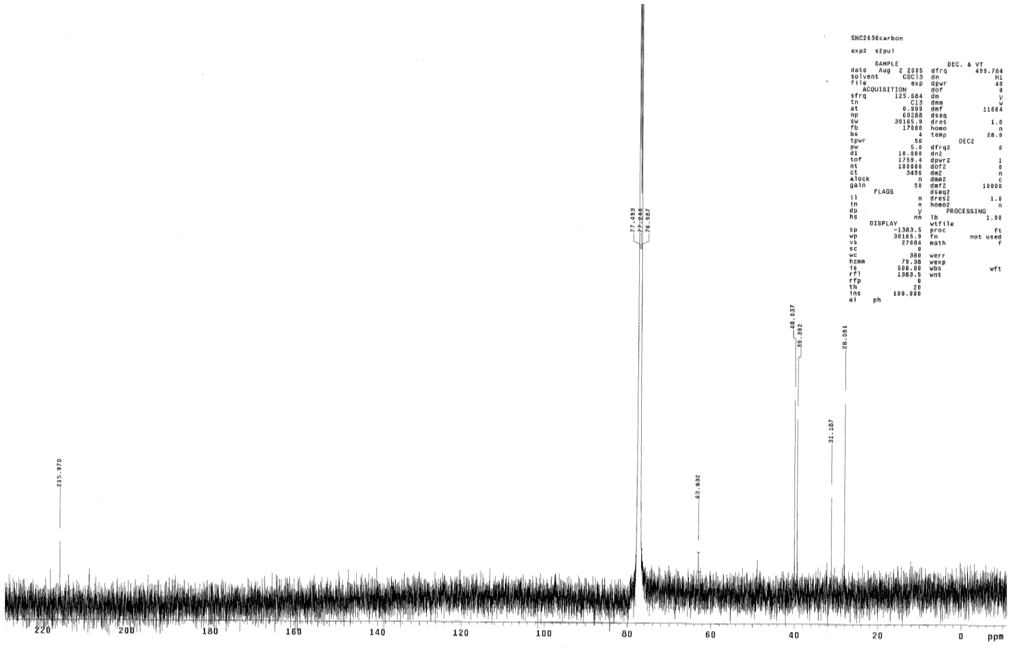
Diketone (II.21): R$_f$ 0.63 (pentane:Et_2O 1:4); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 3.03 (m, 2H), 2.71 (m, 2H), 2.46 (m, 2H), 2.30 (m, 2H), 2.22 (t, 2H, J = 6.4 Hz), 1.91 (m, 2H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 215.9, 63.0, 40.0, 39.3, 31.1, 28.0. **IR** (NaCl, thin film) 2925 (s), 2854 (m), 1741 (s), 1712 (s), 1293 (w), 1159 (w) cm^{-1}. **HRMS** (M + Na) $C_{10}H_{12}O_2Na$ Calcd: 187.0735. Found: 187.0721.



```
SNC2036-2

exp1  std1h

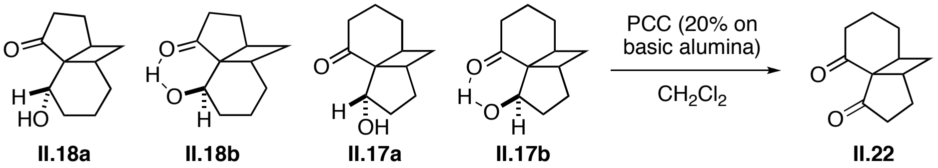
      SAMPLE          -      DEC. & VT
date   Aug  3 2005  dfrq       400.029
solvent      CDCl3  dn              H1
file           exp  dpwr            30
    ACQUISITION     dof              0
sfrq       400.029  dm             nnn
tn              H1  dmm              c
at           5.000  dmf            200
np           59988       PROCESSING
sw          5998.8  wtfile
fb            3400  proc            ft
bs               4  fn           65536
tpwr            60
pw            10.6  werr
d1               0  wexp
tof              0  wbs            wft
nt              64  wnt
ct              60
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -200.0
wp          4200.3
vs             209
sc               0
wc             400
hzmm         10.50
is         7058.32
rfl         3902.4
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
```



```
SNC2036carbon

exp2  s2pul

      SAMPLE               DEC. & VT
date   Aug  2 2005  dfrq       499.784
solvent      CDCl3  dn              H1
file           exp  dpwr            40
    ACQUISITION     dof              0
sfrq       125.684  dm               y
tn             C13  dmm              w
at           0.999  dmf          11664
np           60288  dseq
sw         30165.9  dres           1.0
fb           17000  homo             n
bs               4  temp          28.0
tpwr            56         DEC2
pw             5.0  dfrq2            0
d1          10.000  dn2
tof         1759.4  dpwr2            1
nt          100000  dof2             0
ct            3496  dm2              n
alock            n  dmm2             c
gain            50  dmf2         10000
      FLAGS         dseq2
il               n  dres2          1.0
in               n  homo2            n
dp               y        PROCESSING
hs              nn  lb            1.00
     DISPLAY        wtfile
sp         -1383.5  proc            ft
wp         30165.9  fn        not used
vs           27084  math             f
sc               0
wc             380  werr
hzmm         79.38  wexp
is          500.00  wbs            wft
rfl         1383.5  wnt
rfp              0
th              20
ins        100.000
ai    ph
```



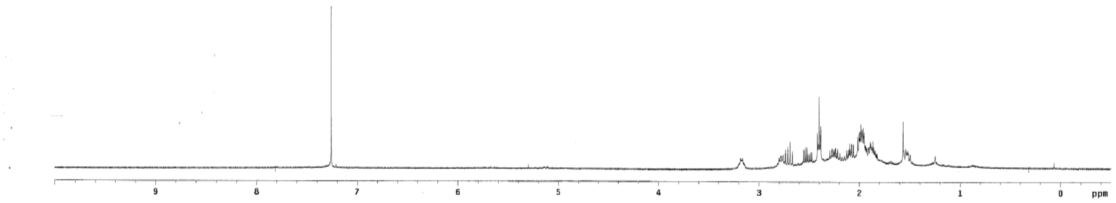
*See representative procedure (C) for the oxidation of photocycloadducts **II.17a, II.17b, II.18a**, and **II.18b**.* The reaction mixture was stirred for 20 h until complete. Product was purified by bulb-to-bulb distillation to give compound **II.22** (78 % yield from **II.18a**) as a clear oil.

Diketone (II.22): R_f 0.40 (pentane:Et_2O 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 3.16 (m, 1H), 2.71 (m, 1H), 2.70 (dd, 1H, J = 18.4, 9.2 Hz), 2.54 (dd, 1H, J = 10, 5.2 Hz), 2.49 (dd, 1H, J = 9.6, 5.2 Hz), 2.40 (m, 2H), 2.25 (m, 1H), 2.09 (m, 1H), 1.82-2.01 (m, 4H), 1.52 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 216.7, 210.7, 63.6, 40.7, 40.2, 39.1, 37.8, 30.3, 29.1, 27.1, 21.1. IR (NaCl, thin film) 3027 (m), 2933 (s), 1735 (s), 1690 (s), 1149 (w), 753 (w) cm^{-1}. **HRMS** (EI) $C_{11}H_{14}O_2$ Calcd: 178.0993. Found: 178.0989.

```
SNC2049

exp1  std1h

       SAMPLE                DEC. & VT
date   Aug 16 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             30
   mls/SNC2049.fid  dof               0
   ACQUISITION      dm              nnn
sfrq       400.029  dmm               c
tn              H1  dmf             200
at           5.000       PROCESSING
np           59988  wtfile
sw          5998.8  proc             ft
fb            3400  fn            65536
bs               4
tpwr            60  werr
pw            10.6  wexp
d1               0  wbs
tof              0  wnt
nt              32
ct              16
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
      DISPLAY
sp          -200.0
wp          4200.3
vs              60
sc               0
wc             400
hzmm         10.50
is          500.00
rfl         3902.6
rfp         2904.2
th              20
ins          1.000
nm  cdc  ph
```



```
SNC2048carbon

exp1  std13c

       SAMPLE                DEC. & VT
date   Aug 22 2005  dfrq        400.029
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             45
mls/SNC2048carbon.~ dof             0.0
               fid  dm              yyy
   ACQUISITION      dmm               w
sfrq       100.596  dmf            5460
tn             C13       PROCESSING
at           1.199  lb             1.00
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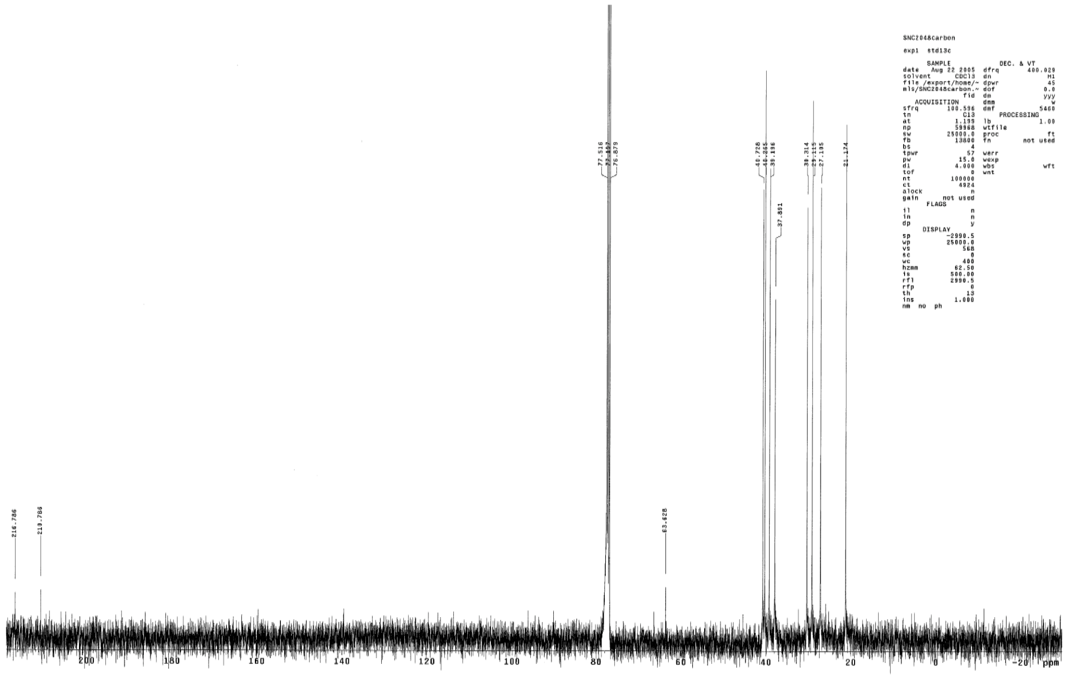
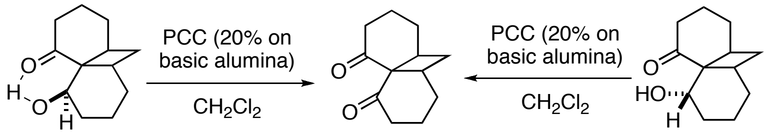
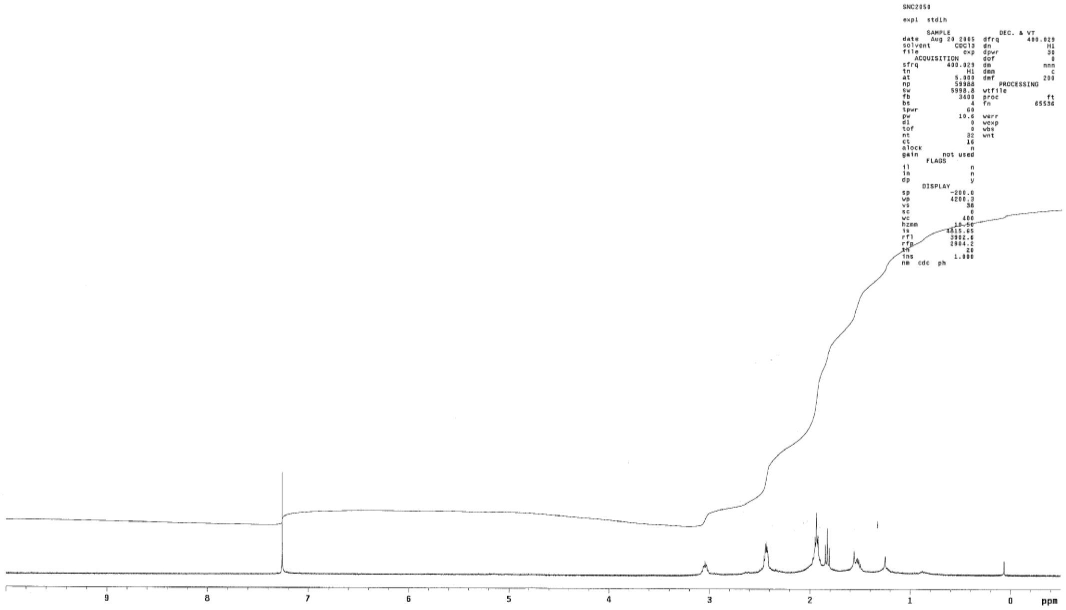




II.19b **II.24** **II.19a**

See representative procedure (C) for the oxidation of photocycloadducts ***II.19a*** *and* ***II.19b****.* The reaction mixture was stirred for 48 h until complete. Product was purified by bulb-to-bulb distillation to give compound **II.24** (72 % yield from **II.19b**) as a clear oil.

Diketone (II.24): R$_f$ 0.48 (pentane:Et$_2$O 1:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 3.04 (m, 1H), 2.43 (m, 2H), 1.93 (m, 2H), 1.83 (t, 2H, J = 7.6 Hz), 1.52 (m, 1H). **^{13}C-NMR** (CDCl$_3$, 125 MHz) δ 211.2, 63.5, 40.2, 39.4, 28.2, 27.5, 21.7. **IR** (NaCl, thin film) 2923 (s), 2870 (m), 1738 (m), 1712 (m), 1260 (w), 1100 (w) cm^{-1}. **HRMS** (EI) $C_{12}H_{16}O_2$ Calcd: 192.1153. Found: 192.1150.



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tpwr            60
pw            10.6  werr
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tof              0  wbs
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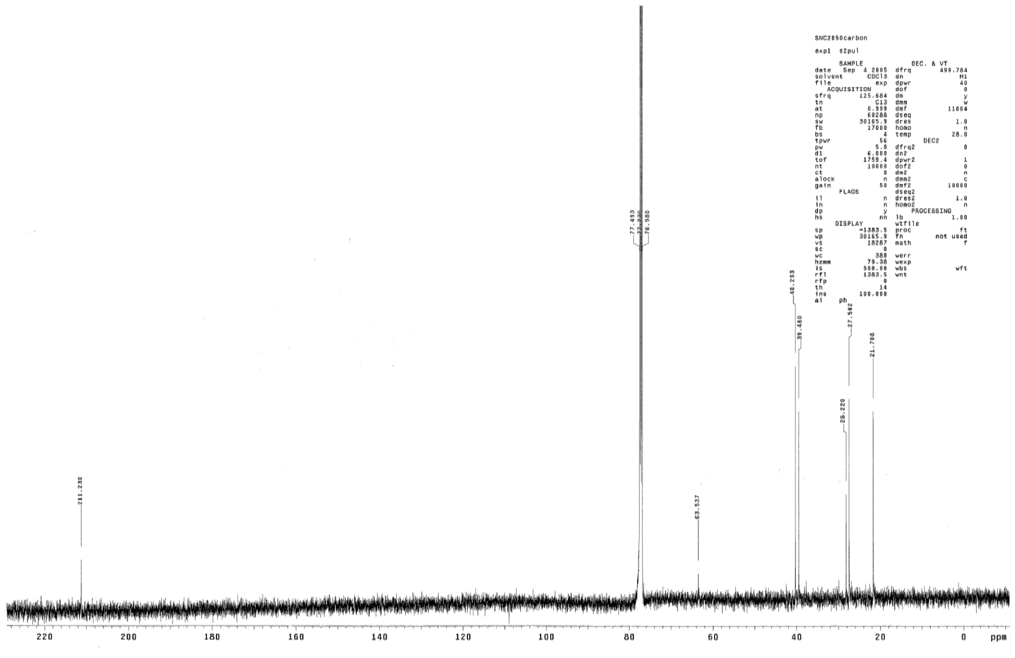

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SNC2050carbon

expl  s2pul

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dp               y      PROCESSING
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wc             380  werr
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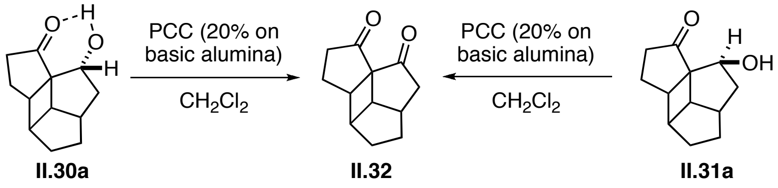
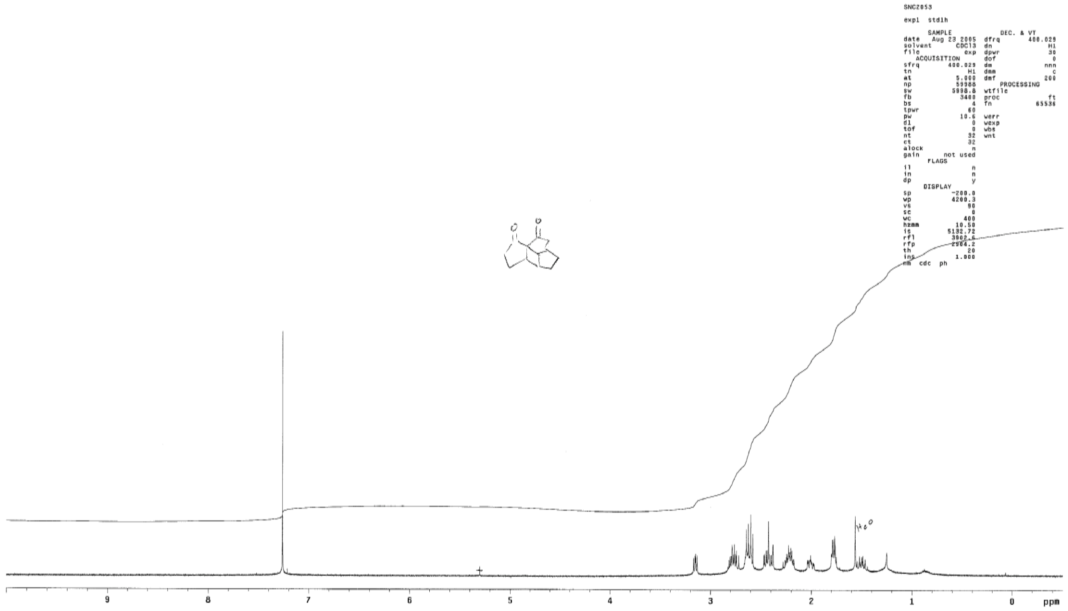
rfp              0
th              14
ins        100.000
ai    ph
```



Diketone head to head II.32. *See representative procedure (C) for the oxidation of photocycloadducts **II.30a** and **II.31a**.* The reaction mixture was stirred for 13 h until complete. Product was purified by bulb-to-bulb distillation to give the desired product (38 % yield from **II.31a**) as a clear oil.

Diketone head to head (II.32): $\mathbf{R_f}$ 0.48 (pentane:Et_2O 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 3.15 (dd, 1H, *J*= 6.0, 8.0 Hz), 2.77 (m, 2H), 2.60 (m, 4H), 2.42 (m, 2H), 2.22 (m, 2H), 2.00 (m, 1H), 1.77 (m, 1H), 1.50 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 216.4, 215.8, 60.2, 49.9, 49.2, 44.9, 42.5, 38.4, 37.2, 33.4, 32.7, 27.5. **IR** (NaCl, thin film) 3027 (m), 2921 (s), 1745 (m), 1711 (m), 1288 (w), 1159 (w) cm^{-1}. **HRMS** (EI) $C_{12}H_{14}O_2$ Calcd: 190.0993. Found: 190.0998.



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at           5.000   dmf             200
np           59988       PROCESSING
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fb            3400   proc             ft
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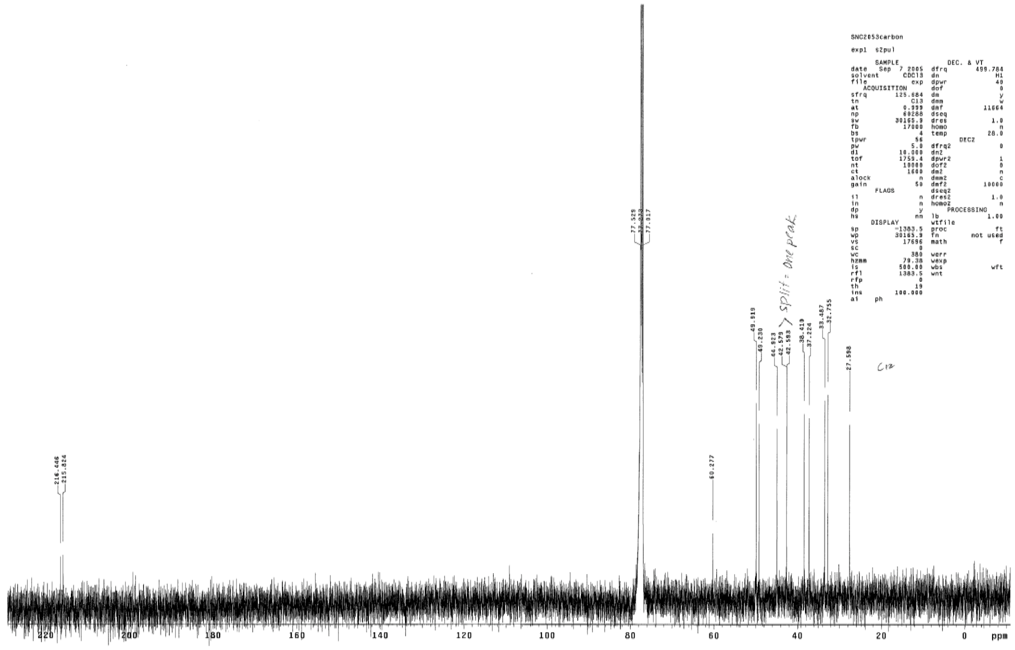

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SNC2053carbon

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tn             C13   dmm               w
at           0.999   dmf           11664
np           60288   dseq
sw         30165.9   dres            1.0
fb           17000   homo              n
bs               4   temp           28.0
tpwr            56          DEC2
pw             5.0   dfrq2             0
d1          10.000   dn2
tof         1759.4   dpwr2             1
nt           10000   dof2              0
ct            1600   dm2               n
alock            n   dmm2              c
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in               n   homo2             n
dp               y       PROCESSING
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sc               0
wc             380   werr
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ai    ph
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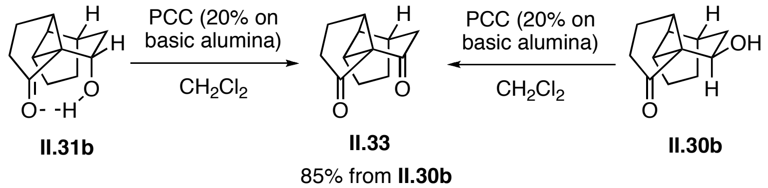
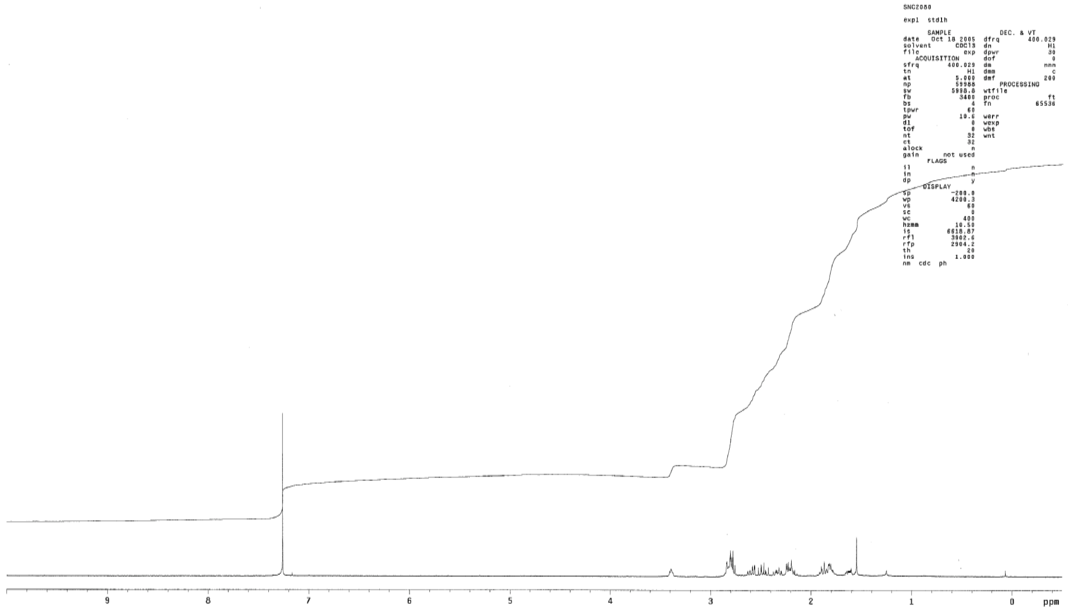


See representative procedure (C) for the oxidation of photocycloadducts ***II.31b*** *and* ***II.30b***. The reaction mixture was stirred for 20 h until complete. Product was purified by bulb-to-bulb distillation to give the desired product (85 % yield from **II.30b**) as a clear oil.

Diketone head to tail (II.33): R_f 0.21 (pentane:Et_2O 1:2); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 3.39 (m, 1H), 2.79 (m, 4H), 2.59 (ddd, 1H, J = 18.8, 8.8, 2.0 Hz), 2.46 (m, 1H), 2.32 (m, 1H), 2.20 (m, 2H), 1.85 (m, 3H), 1.62 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 210.4, 206.2, 69.5, 49.6, 47.6, 44.0, 41.9, 38.7, 38.5, 37.5, 25.9 23.7. **IR** (NaCl, thin film) 3041(s), 2958 (s), 2873 (m), 1746 (s), 1644(s), 1252 (w) cm^{-1}. **HRMS** (EI) $C_{12}H_{14}O_2$ Calcd: 190.0993. Found: 190.0993.



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fb            3400   proc             ft
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tpwr            60
pw            10.6   werr
d1               0   wexp
tof              0   wbs
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ct              32
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gain      not used
      FLAGS
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in               n
dp               y
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nm  cdc  ph
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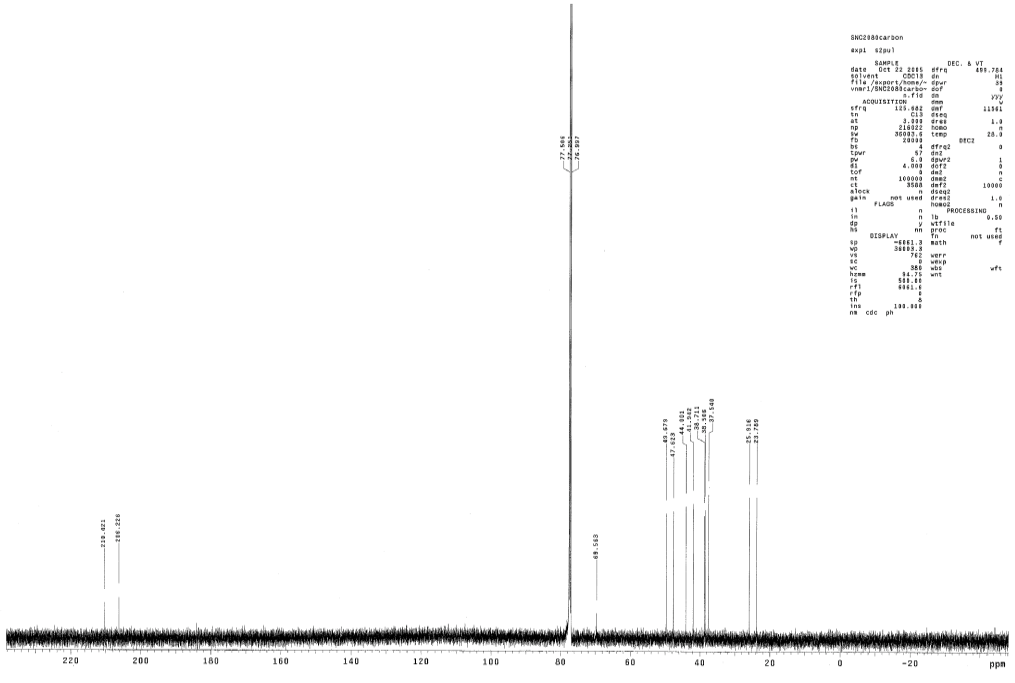

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tn             C13   dseq
at           3.000   dres            1.0
np          216022   homo              n
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tpwr            57   dn2
pw             6.0   dpwr2             1
d1           4.000   dof2              0
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th               8
ins        100.000
nm  cdc  ph
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Chapter 3

Using a [2+2] Photocycloaddition/Fragmentation Strategy Toward the Synthesis of Cycloaraneosene

III.1 Introduction

Previous studies in our group have demonstrated an efficient construction of 5-8-5 ring systems utilizing functionalized cyclobutenes in a [2+2] photocycloaddition/thermal fragmentation strategy.[1] As shown in equations 1 and 2, both 2- and 3-substituted cyclopentenones underwent intermolecular [2+2] photocycloadditions with functionalized cyclobutenes to give photocycloadducts placing the R_2 substitutent at the C10 position; fragmentation of these cycloadducts yielded a 5-8-5 ring system.[2]

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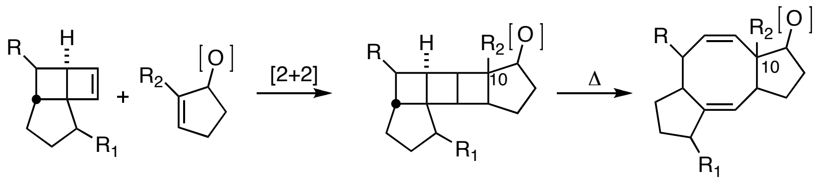
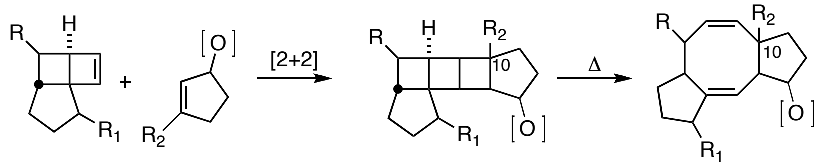
[1] For a review on [2+2] photocycloaddition/fragmentation strategies in organic synthesis, see: Winkler, J. D.; Bowen, C. M.; Liotta, F. *Chem. Rev.* **1995**, *95*, 2003-2020.

[2] Randall, M. L.; Lo, P. C.-K.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1999**, *121*, 4534-4535.

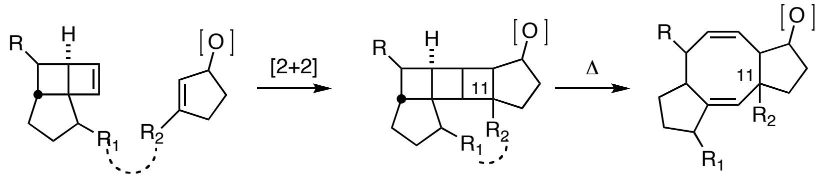


(eq 1)



(eq 2)

The inherent steric preference observed in the intermolecular photocycloaddition can be reversed if the [2+2] is carried out intramolecularly.[3] As shown in equation 3, the R_1 substitutent of the functionalized cyclobutene can serve to tether a reacting partner in the cycloaddition. Thus, the regioselectivity of the intramolecular [2+2] photocycloaddition of the tethered substrate is dictated by the temporary tether; thermal fragmentation of the resulting cycloadduct opens to a 5-8-5 ring system with the R_2 substituent now in the C11 position.



(eq 3)

Most of the natural products containing 5-8-5 ring systems belong to two structural families, fusicoccane and ophiobolane (Figure III.1).[4] Our thermolysis product

---

[3] Lo, P. C.-K.; Snapper, M. L. *Org. Lett.* **2001**, *3*, 2819-2821.

[4] (a) Petasis , N. A.; Patane, M. A. *Tetahedron*, **1992**, *48*, 5757-5821. (b) Cordell, G. A. *Phytochemistry*, **1974**, *13*, 2343-2364.

from the intramolecular photocycloaddition/fragmentation strategy shares the 5-8-5 ring structures and functionality at the C3, C7, C11, and C14 positions with these families.

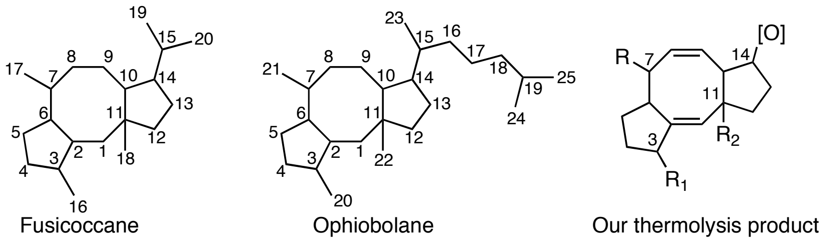


Figure III.1. Two Structural Familes with 5-8-5 Ring Systems.

This methodology provides a versatile core structure and can be applied to the synthesis of the cyclooctanoid natural products shown in Figure III.2.

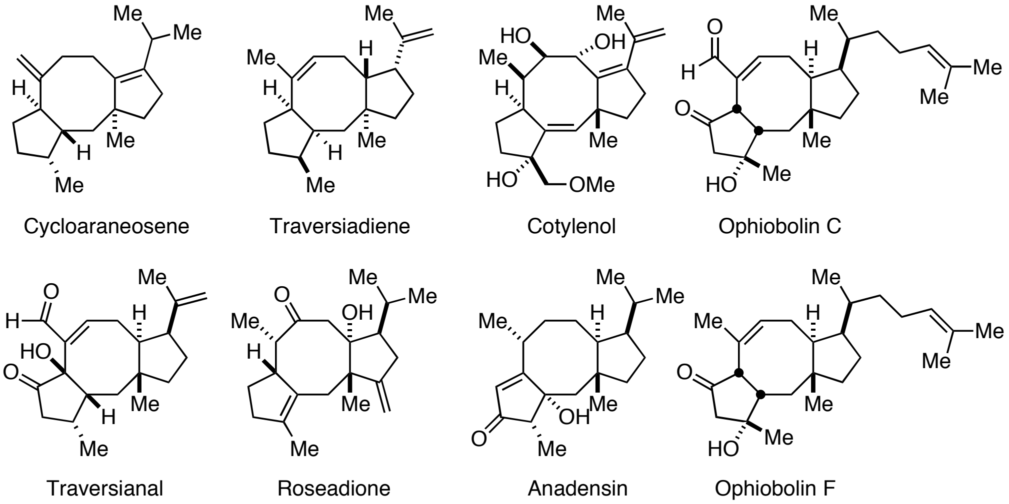


Figure III.2. Natural Products with 5-8-5 Ring Systems.

III.2 Background

III.2.1 Intramolecular [2+2] Photocycloaddition/Thermal Fragmentation Strategy

As mentioned previously, our intermolecular photocycloadditions afford strained cycloadducts that, upon thermolysis, expand to a cyclooctanoid system. Except for the additional tether and the location of the ring junction substituent, the intramolecular photoadducts are structurally similar to the intermolecular analogs. Interestingly, the C3 configuration plays an important role in dictating the outcome of the cycloaddition, giving complementary inter- and intramolecular [2+2] photocycloadditions of functionalized cyclobutanes[5] (Figure III.3.). For the intramolecular [2+2] photocycloaddition, the nature of the tether places the R_1 and R_2 substituent *syn* to one another.

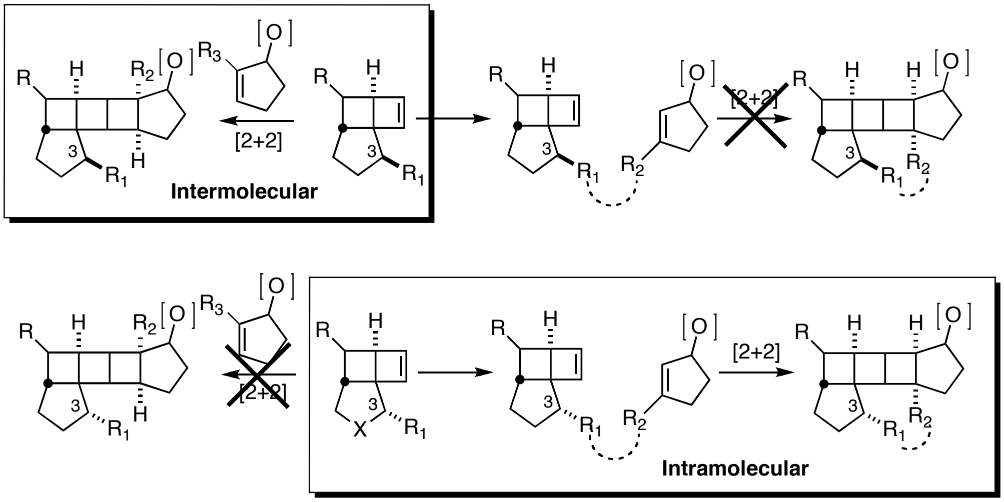


Figure III.3. Complementary Inter- vs Intramolecular [2+2] Photocycloaddition of Functionalized Cyclobutenes.

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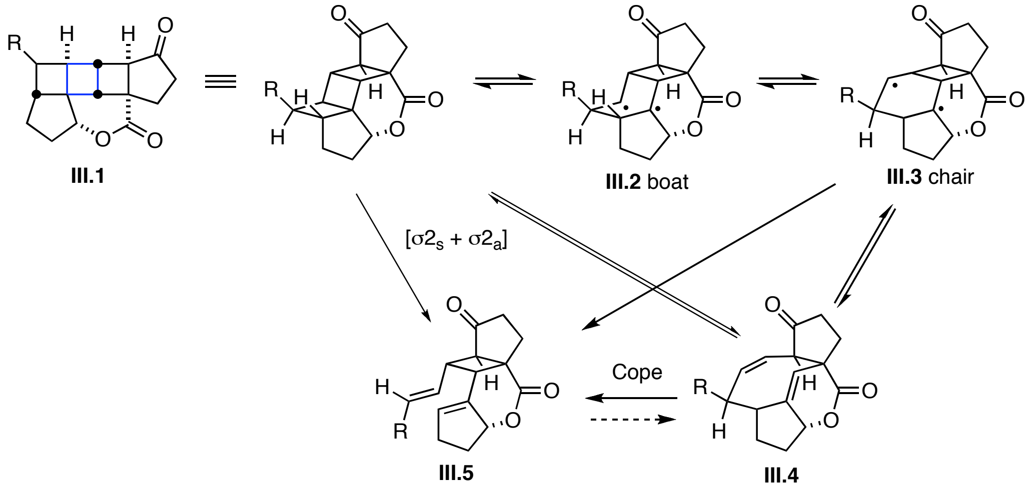
[5] For a more detailed discussion, see Lo, Priscilla Ph.D. Thesis, Boston College, **2002**. Also, see refs. 2 and 3.

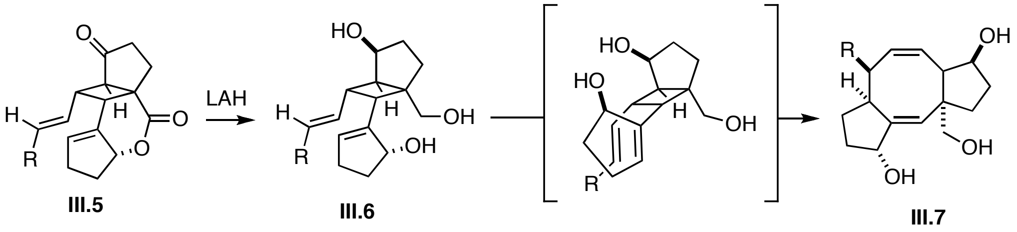
Our choice of an ester tether in the photocycloaddition resulted in cycloadduct **III.1** (Scheme III.1). Thermolysis of intramolecular cycloadduct **III.1** led to the isolated dialkenylcyclobutane **III.5** instead of the expected *cis,trans*-cycloocta-1,5-diene **III.4**. From our mechanistic rationale, thermolysis of **III.1** at 235 °C in benzene led to *cis,trans*-cycloocta-1,5-diene **III.4** either through a stepwise biradical or a concerted [$\sigma 2_s + \sigma 2_a$] mechanism. The transient species **III.4** was then transformed to the thermodynamically more stable product **III.5** through a Cope rearrangement.

Scheme III.1. Thermal Fragmentation of Photocycloadduct **III.1**.



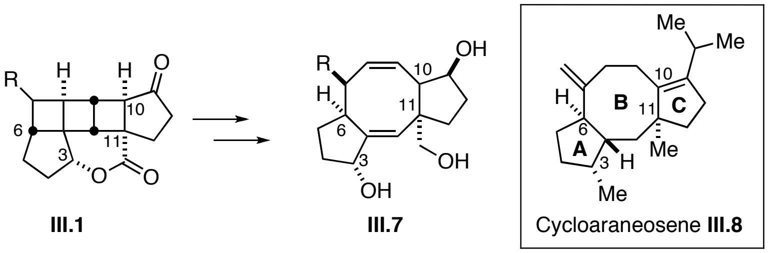
Dialkenylcyclobutane **III.5** is believed to be unavailable for further transformations (i.e. rearrangements to the cyclooctanoid system) due to the geometric restrictions imposed by the lactone. Fortunately, when the lactone tether was removed with lithium aluminum hydride, triol **III.6** underwent bond rotation and Cope rearrangement, affording the corresponding 5-8-5 ring system **III.7** (Scheme III.2).

Scheme III.2. Tether Removal and Cope Rearrangement.



Several points about this proposed mechanism should be noted. Inversion of the stereochemistry at C6 in photoadduct **III.1** occurs during formation of the 5-8-5 ring system (Scheme III.3). Additionally, the lactone tether affords a 5-8-5 ring system with substituents at C3 and C11 *syn* to each other after hydrolysis to the alcohols. Cycloaraneosene **III.8**, a natural product in the fusicoccane family, also contains methyl substituents *syn* to each other at the C3 and C11 sites, as well as the corresponding stereochemistry at C6. Based on these features, we decided to test and highlight our methodology on the synthesis of cycloaraneosene.

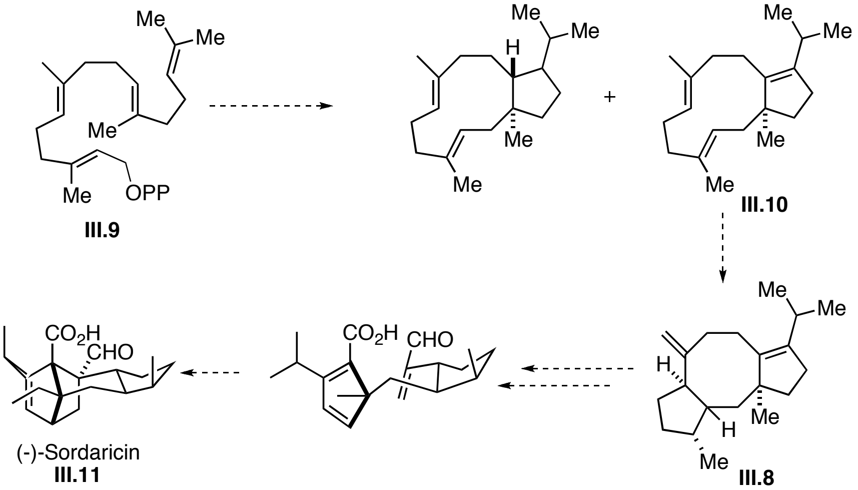
Scheme III.3. Thermolysis Product and Cycloaraneosene.



III.2.2 Cycloaraneosene

Cycloaraneosene was isolated from the mold *Sordaria araneosa* in 1975;[6] the constitutional formula for cycloaraneosene was proposed on the basis of degradation studies and spectroscopy. The molecular structure was later corroborated though extensive 2D-NMR studies.[7] This diterpenoid natural product obeys the biogenetic isoprene rule and is most likely derived from the bicyclic precursor **III.10** though an acid-catalyzed cyclization (Scheme III.4). It was also suggested that cycloaraneosene is a key biogenetic precursor of other oxygenated metabolites, such as (-)-sordaricin **III.11**, [8] which is a member of a class of potent antifungal compounds.[9]

Scheme III.4. Proposed Biosynthesis of Cycloaraneosene.



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[6] Borschberg, H.-J., Ph.D. Thesis, Eidgenössischen Technischen Hochschule Zürich, No. 5578, 1975.

[7] Jenny, L., Ph. D. Thesis, Eidgenössischen Technischen Hochschule Zürich, No. 10920, 1994.

[8] Jenny, L.; Borschberg, H.-J. *Helv. Chim. Acta*. **1975**, *78*, 715-731.

[9] For a total synthesis of Sordaricin, see: Mander, L.N.; Thomson, R. J *Org. Lett.* **2003**, *5*, 1321-1324.

The structure was also proven by means of one previous total synthesis by Takeshita and coworkers in 1986.[10] Their approach involved constructing the eight membered ring in the last stages after functional group manipulations. We envisioned that our cycloaddition/thermal fragmentation strategy would allow for a novel more rapid approach to the natural product.

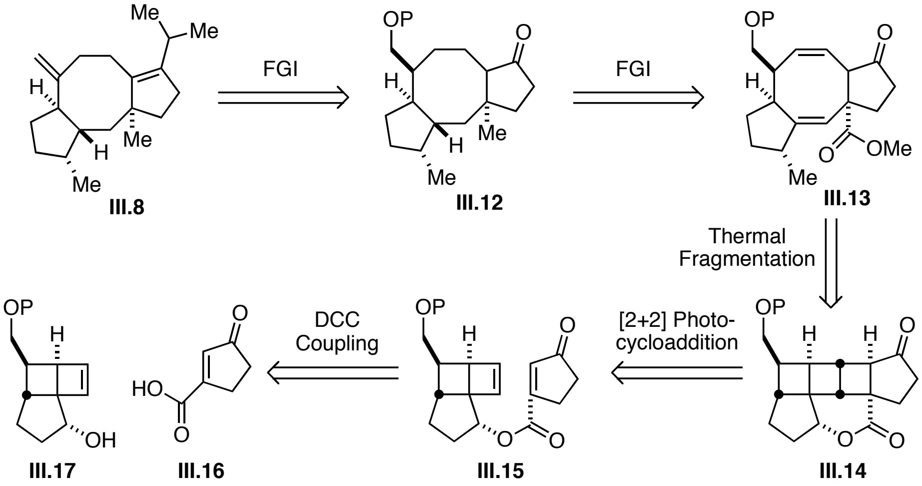
III.2.3 Retrosynthetic Analysis of Cycloaraneosene

Key features of cycloaraneosene include the *syn* methyl groups, the *exo* olefin, the *trans* AB ring fusion, and the isopropyl group of the C ring. In our proposed synthesis, our cycloadditon/fragmentation strategy will provide the 5-8-5 core structure (Scheme III.5). Functional group interconversions (FGI) will be carried out after the synthesis of **III.13**. Cycloadduct **III.14** will stem from photoprecursor **III.15**, which can easily be obtained from the coupling of cyclobutene **III.17** and acid **III.16**.

---

[10] (a) Kato, N.; Tanaka, S.; Takeshita, H. *Chem. Lett.* **1986**, 1989-1992. (b) Kato, N.; Wu, X.; Tanaka, S.; Takeshita, H. *Chem. Lett.* **1989**, 91-94.

Scheme III.5. Retrosynthetic Analysis of Cycloaraneosene.



III.3 Studies Toward the Synthesis of Cycloaraneosene

III.3.1 Iron-Stabilized Cyclobutadiene Strategy Toward Cyclobutenes

As mentioned previously, both our cycloaddition/thermal fragmentation studies and our approach to cycloaraneosene required the synthesis of a functionalized cyclobutene, which can be readily accessed from iron-stabilized cyclobutadienes.[11] The synthesis of cycloaraneosene began with iron-stabilized cyclobutadiene **III.18** (Scheme III.6).[12] CAN oxidation of **III.18** liberated cyclobutadiene, which underwent [4+2] cycloaddition immediately with the tethered olefin to give a 3.3:1 β:α mixture of

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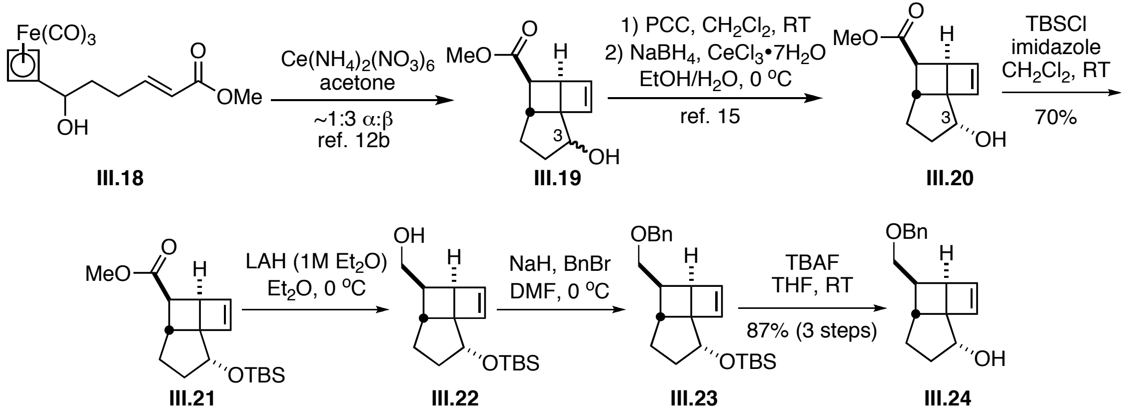
[11] Agar, J.; Kaplan, F.; Roberts, B. W. *J. Org. Chem.* **1974,** *39,* 3451-3452. Also, for synthetic efforts from this strategy, see: (a) Limanto, J.; Snapper, M. L. *J. Am. Chem. Soc.* **2000**, *122*, 8071-8072. (b) Bader, Scott J. Ph.D. Thesis. Boston College, **2005**. Also, see ref. 12.

[12] For the synthesis of **III.18**, see: Williams, M. J.; Deak, H. L.; Snapper, M. L. *J. Am. Chem. Soc.* **2007**, *129*, 486-487.

diastereomeric cyclobutenes **III.19**.[13] Oxidation of this mixture **III.19** with PCC immediately followed by reduction with sodium borohydride afforded cyclobutene **III.20** with the desired α configuration at C3, with hydride delivery occurring from the less hindered face of the rigid strained ring system. Protection of the secondary alcohol with TBSCl afforded **III.21** in 70% yield. Cyclobutene **III.21** was then reduced with lithium aluminum hydride, and the resulting primary alcohol **III.22** was benzylated with NaH and BnBr and subsequently treated with TBAF to afford cyclobutene **III.24** in high yields over three steps, requiring only one silica gel chromatography for purification after the deprotection.

Scheme III.6. Iron-Stabilitzed Synthesis of Cyclobutene **III.24**.



III.3.2 Intramolecular [2+2] Photocycloaddition

Cyclobutene **III.24** can now be used in our cycloaddition/thermal fragmentation strategy to form the cycloaraneosene core. Photoprecursor **III.25** was generated by DCC-

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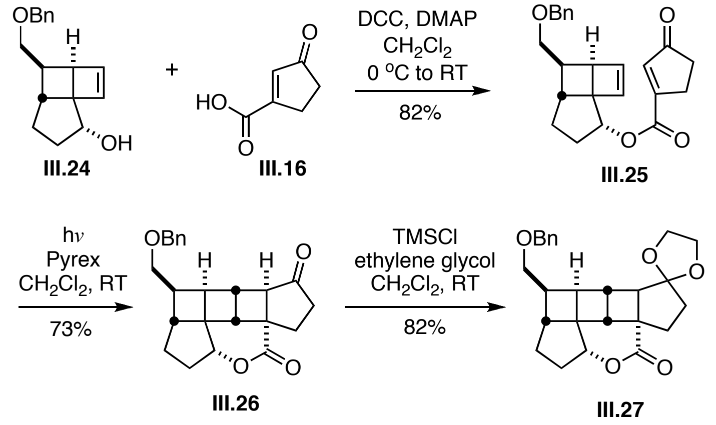
[13] (a) Tallarico, J. A.; Randall, M. L; Snapper, M. L. *J. Am. Chem. Soc.* **1996**, *118*, 9196-9197. (b) Snapper, M. L.; Tallarico, J. A.; Randall, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 1478-1479. (c) Limanto, J.; Tallarico, J. A.; Porter, J. R.; Khuong, K. S.; Houk, K. N.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 14748-14758.

mediated esterification of **III.24** with known acid **III.16**[14] (Scheme III.7). Irradiation of **III.25** furnished [2+2] cycloadduct **III.26**. Ketone protection of cycloadduct **III.26** with TMSCl and ethylene glycol afforded **III.27** in 82% yield.[15]

Scheme III.7. Synthesis of Photoprecursor and Intramolecular [2+2] Photocycloaddition.



III.3.3 Thermal Fragmentation Into the 5-8-5 Framework

Photoadduct **III.26** was previously shown to undergo thermal fragmentation at 235 °C in benzene (Scheme III.8) to give the resulting divinyl cyclobutane **III.28** in 89% yield.[16] Copper-mediated S_N2'-nucleophilic substitution of **III.28** followed by methylation of the resulting carboxylic acid gave methyl ester **III.29**. Subsequent [3,3] sigmatropic rearrangement of **III.29** gave access to the desired 5-8-5 **III.30** with a methyl group installed at C3 with the correct α stereochemistry. At this point, the core of cycloaraneosene was established, but several functional group manipulations were still

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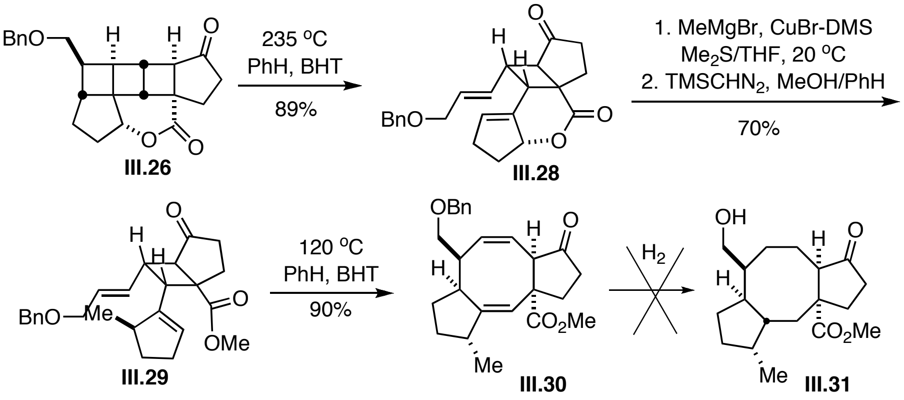
[14] (a) Mori, K. *Tetahedron*, **1978**, *34*, 915-920. (b) Herzog, H.; Koch, H.; Scharf, H.-D.; Runsink, J. *Tetahedron*, **1986**, *42*, 3547-3558.

[15] Chan, T. H.; Brook, M. A.; Chaly, T. *Synthesis*, **1983**, 203-205.

[16] Lo, Priscilla Ph.D. Thesis, Boston College, **2002**.

required. Attempts to hydrogenate cyclooctadiene **III.30** were futile and did not provide ketone **III.31** with the correct *trans*-fused relationship of the AB ring junction.[17]

Scheme III.8. Thermolysis of **III.26** into the 5-8-5 Core.[a]



[a] Work done by Dr. Priscilla Lo

The synthetic challenge of forming the *trans*-fused AB ring junction necessitated a closer look at the 5-8-5 ring. Figure III.4 shows both *trans* **III.32** and *cis* **III.33**. Based on RB3LYP-6-31G* calculations,[18] the *trans* compound is more stable than the *cis* compound by ΔH = 1.86 kcal/mol which is ~20:1 product ratio. Thus, while the copper mediated methylation of **III.28** was an elegant way to install the C16 methyl group, in order to access the proper ring junction stereochemistry, we decided to slightly modify our synthetic route. If the isopropyl group in the C ring is established first, we should be able to use the oxygenation at C3 to install the desired *trans* ring junction stereochemistry. The C16 methyl group could then be introduced at a later stage through an olefination/hydrogenation strategy.

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[17] For more details on hydrogenation, see ref. 16.

[18] Calculations done in collaboration with Dr. Dong Yun Shin.

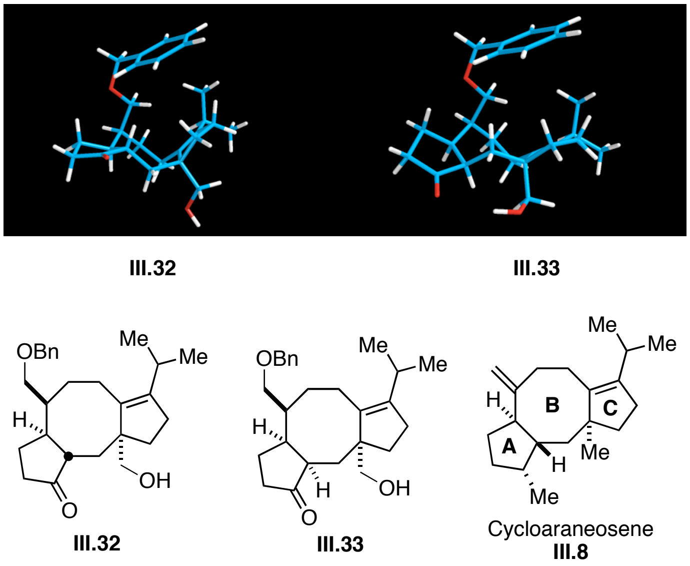

Figure III.4. *Trans* vs. *cis* AB ring junction.

Ketal **III.27** was also subjected to thermal fragmentation at 235 °C in benzene to afford divinyl cyclobutane **III.34** (Scheme III.9). Lactone clevage with LAH yielded diol **III.35**, which was then heated to 140 °C in benzene to give diol **III.36**. With the 5-8-5 ring framework of cycloaraneosene established, including installation of the isopropyl group of the C ring, deoxygenation, and elimination of a primary alcohol became our new goals toward accessing our target.[19]

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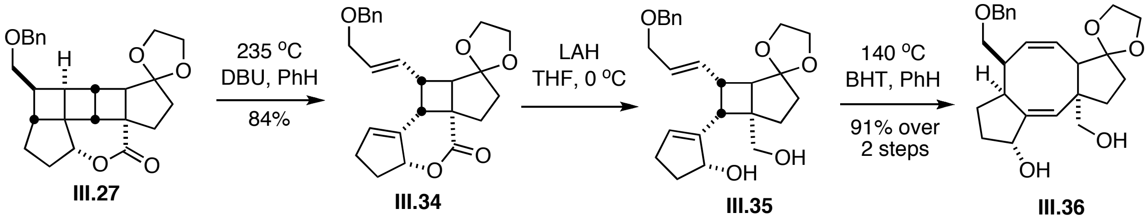
[19] In collaboration with Dr. Dong Yun Shin.

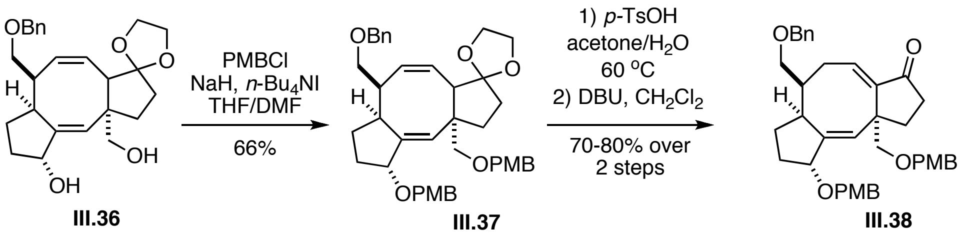
Scheme III.9. Thermolysis of **III.27** into the 5-8-5 Core.



III.3.4 Functional Group Manipulation of the Cyclooctanoid System

Protection of diol **III.36** was achieved by subjecting the diol to NaH, PMBCl, and *n*-Bu_4NI to furnish bis PMB ether **III.37**[20] (Scheme III.10). The ketal protecting group was then removed using carbon tetrabromide and triphenyl phosphine,[21] and basic alumina in dichloromethane isomerized the olefin into conjugation to form enone **III.38**. These conditions, however, proceeded with low yields, long reaction times, and undesired side products. Alternatively, treatment of **III.37** with *p*-TSOH in acetone/H_2O at 60 °C for one hour followed by isomerization of the olefin with DBU furnished enone **III.38** in high yields over 2 steps.

Scheme III.10. Removal of the Ketal and isomerization of an Olefin.



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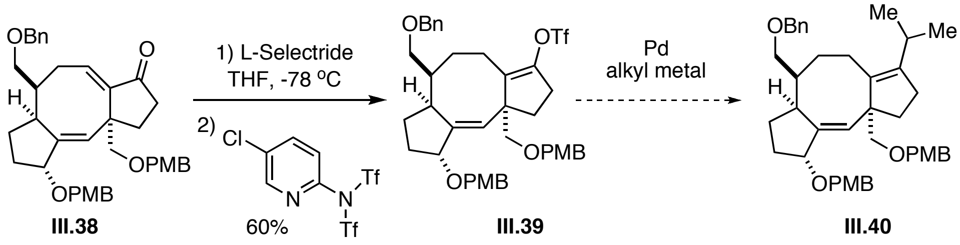
[20] Mootoo, D. R.; Fraser-Reid, B. *Tetahedron*, **1990**, *46*, 185-200.
[21] Johnstone, C.; Kerr, W. J.; Scott, J. S. *Chem. Comm.* **1996**, 341-342.

Enone **III.38** then underwent a 1,4-reduction with L-Selectride, and the resulting enolate was trapped with Comins' reagent[22] to give triflate **III.39**[23] (Scheme III.11). Palladium-mediated coupling of vinyl triflate **III.39** with an isopropyl organometallic reagent[24] should deliver the isopropyl group on the C ring of the natural product.

Scheme III.11. Formation of Vinyl Triflate **III.39** and Installation of the Isopropyl Group.



Unfortunately, the cross-coupling of secondary alkyl reagents is complicated by the competing formation of *n*-alkyl and reduction side products. In 1984, Kumada and coworkers reported the use of dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium-(II), or $PdCl_2dppf$, as an effective catalyst for the cross coupling of secondary alkyl grignard reagents with organic halides.[25] The authors reasoned that with a larger bite angle[26] of the bidentate phosphine ligand on palladium, reductive elimination should occur faster than the undesired σ-π interconversion, giving a more selective reaction (Scheme III.12).

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[22] Comins, D. L.; Dehghani, A. *Tet. Lett.* **1992**, *33*, 6299-6302.

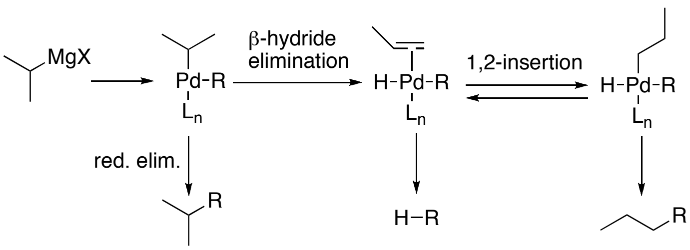
[23] Smith, A. B. III; Kurti, L.; Davulcu, A. H. *Org. Lett.* **2006**, *8*, 2167-2170.

[24] Busacca, C. A.; Eriksson, M. C.; Fiaschi, R. *Tet. Lett.* **1999**, *40*, 3101-3104.

[25] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158-163.

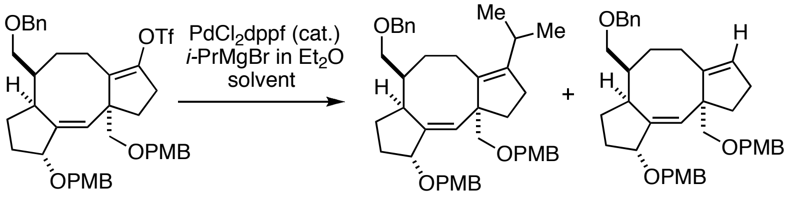
[26] Dppf has been reported to have a bite angle of 99.07°. For comparison, dppp and dppe is reported to have a bite angle of 90.6 ° and 85.8 °, respectively. Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432-2439.

Scheme III.12. Side Reactions of the Kumada Coupling.



Busacca and coworkers were able to cross couple vinyl triflates with *i*-PrMgCl in the presence of $PdCl_2$dppf in toluene to obtain >20:1 of *i*-Pr:*n*-Pr product and less than 5% of reduced material[24] Given these results, vinyl triflate **III.39** was subjected to Kumada coupling with $PdCl_2$dppf and isopropyl grignard reagent; the reaction, however, gave not only the desired product **III.40**, but also a significant amount of reduced product **III.41**, a result of unwanted β-hydride elimination (Scheme III.13).

Scheme III.13. Installation of the Isopropyl Group.



III.39 **III.40** **III.41**

Many reaction conditions were examined in attempt to improve the ratio of **III.40** to **III.41** (Table III.1). Isopropyl magnesium chloride, bromide, and iodide were screened (entries 3, 5, and 6) and showed poor selectivity, as well as using benzene as the solvent (entry 2). Cooling the reaction to 0 ^{o}C gave no conversion (entry 4). Addition of excess dppf ligand (entry 1) or other additives known to inhibit β-hydride elimination[27] such as LiCl, LiBr, or LiOH (entries 7, 8, or 9) did not improve selectivity, and the reaction became inconsistent, inefficient, and sluggish. Low conversion was also observed when nickel catalysts were employed[28] (entries 10 and 11). Using THF as the solvent resulted in low conversion (entry 12), but switching the solvent to diethyl ether gave a 3:1 ratio of **III.40**:**III.41** (entry 13). Solvents often act as weak ligands, and it is possible that the coordination of diethyl ether to palladium slows σ-π interconversion by filling an open coordination site on the metal. Thus, reductive elimination occurs faster than β-hydride elimination. THF will bind more tightly to palladium than Et_2O,[29] possibly shutting down the catalyst as observed by our inhibited reactivity. Treatment of **III.39** with 25% $PdCl_2$dppf and excess *i*PrMgBr in Et_2O gave the desired product in thirty minutes at room temperature in high yields.

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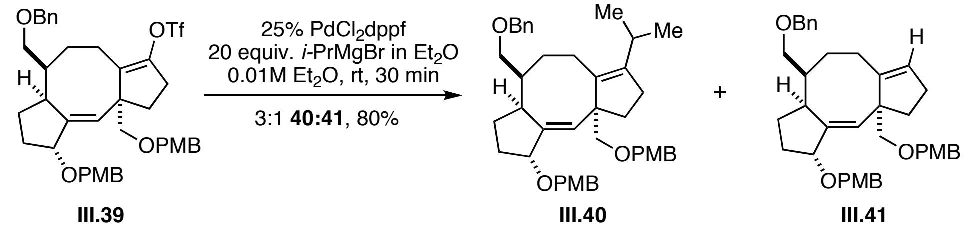
[27] Wang, Z.; Lu, X. *J. Org. Chem.* **1996**, *61*, 2254-2255.

[28] Tamao, K.; Kiso, Y.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9268-9269.

[29] Since the pK_a measures the tendency for a ligand to bind to a proton, there is some correlation with the σ-donor power of a ligand, or the ability for the ligand to bind to the metal. Sterics also play a role in the binding ability of a ligand. See: Crabtree, R. H. The Organometallic Chemistry of the Transition Metals 2001: John Wiley & Sons, Inc. pg 109 and refs. therein.

Table III.1. Kumada Coupling Screen.



entry	solvent	catalyst	additives	grignard	temp	40:41
1	Toluene	20% PdCl$_2$dppf	10% dppf	iPrMgCl	RT	2:1, low conversion
2	Benzene	25% PdCl$_2$dppf	-	iPrMgCl	RT	1: 0.8
3	Toluene	25% PdCl$_2$dppf	-	iPrMgCl	RT	1.3:1
4	Toluene	25% PdCl$_2$dppf	-	iPrMgBr	0 °C	NR
5	Toluene	25% PdCl$_2$dppf	-	iPrMgBr	RT	3:1, inconsistent
6	Toluene	25% PdCl$_2$dppf	-	iPrMgI	RT	sluggish
7	Toluene	25% PdCl$_2$dppf	LiCl	iPrMgBr	RT	1:1
8	Toluene	25% PdCl$_2$dppf	LiBr	iPrMgBr	RT	inconsistent, sluggish
9	Toluene	25% PdCl$_2$dppf	LiOH	iPrMgBr	RT	
10	Toluene	25% NiCl$_2$dppp	-	iPrMgBr	RT	Very low conversion
11	Toluene	25% NiCl$_2$dppe	-	iPrMgBr	RT	
12	THF	25% PdCl$_2$dppf	-	iPrMgBr	RT	
13	Et$_2$O	25% PdCl$_2$dppf	-	iPrMgBr	RT	3:1

With the synthetically useful ratio of 3:1 **III.40**:**III.41**, we could continue on with the synthesis of cycloaraneosene. A one-pot deprotection/ allylic oxidation[30] of **III.40** with DDQ in benzene/water furnished enone **III.42** in moderate yields (Scheme III.14). Based on our calculations, conjugate reduction of enone **III.42** should afford the thermodynamically favored *trans* relationship of the AB ring junction.

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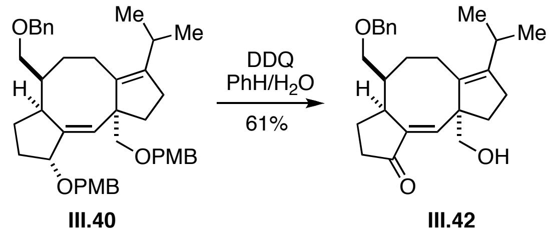
[30] Burstein, S. H.; Ringold, H. J. *J. Am. Chem. Soc.* **1964**, *86*, 4952-4958.

Scheme III.14. One-pot Deprotection/ Allylic Oxidation.



Conjugate reduction of **III.42** with L-Selectride[31] or Stryker's reagent[32] gave only a mixture of starting material and unidentified products. Radical-mediated conjugate reduction of α,β-unsaturated ketones has also been achieved using organotin reagents.[33] Treatment of enone **III.42** with tributyltin hydride and either *t*-butyl peroxide or AIBN as a radical initiator in refluxing toluene gave a mixture of two products (Scheme III.15). Addition of DBU to this crude mixture afforded a single product that, based on our calculations, should be the desired *trans* ring junction. Since deoxygenation at the C18 position on the 5-8-5 ring was also necessary, a one pot Barton-McCombie[34]/conjugate reduction using the same tin conditions was attempted, but did not give ketone **III.44**.[35] Barton has also observed difficulty in reducing primary alcohols under these conditions.[36] Given the struggles and inconsistency of the reduction/deoxygenation under these reaction conditions, which also required a large excess of toxic tin reagent, other reactions were considered and explored.

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[31] Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194-2200.

[32] Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M. *J. Am. Chem. Soc.* **1988**, *110,* 291-293.

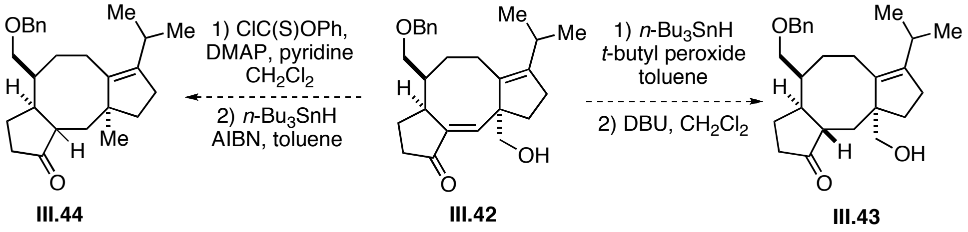
[33] (a) Pereyre, M.; Colin, G.; Valade, J. *Tet. Lett.* **1967**, *48*, 4805-4808. (b) Johnson, C. R.; Chen, Y.-F. *J. Org. Chem.* **1991**, *56*, 3352-3357. (c) Hays, D. S.; Scholl, M.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 6751-6752.

[34] Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tet. Lett.* **1990**, *31*, 3991-3994.

[35] The simple deoxygenated enone was also not observed.

[36] Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc. Perkin I*, **1975**, 1574-1585.

Scheme III.15. Reduction and deoxygenation of enone **III.42**.



Myers and coworkers were able to report a single step process for the reductive deoxygenation of unhindered primary alcohols.[37] The method involves the subjection of an alcohol with *o*-nitrobenzenesulfonylhydrazine[38] (NBSH) followed by in situ elimination of *o*-nitrobenzene-sulfinic acid. Although this chemistry provides valuable methodology for the deoxygenation of unhindered alcohols by avoiding toxic tin reagents and reducing a two-step process to one, the authors believe that the reaction is a free-radical process. After examination of some possible conformations of **III.42** (Figure III.5), we were concerned with both the steric environment at C18 and our previously unsuccessful attempts at deoxygenation with other radical-based methods, and examined alternative methods.

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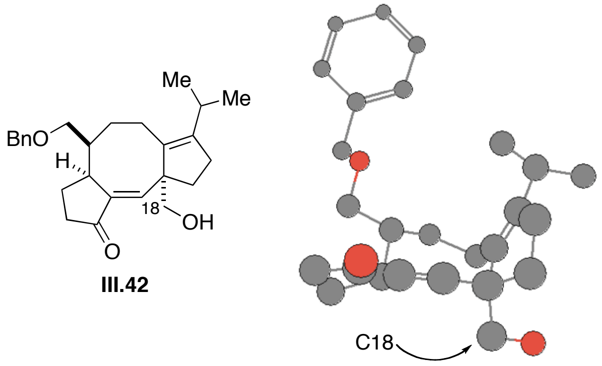
[37] Myers, A. G.; Movassaghi, M.; Zheng, B. *J. Am. Chem. Soc.* **1997**, *119,* 8572-8573.

[38] Myers, A. G.; Zheng, B; Movassaghi, M. *J. Org. Chem.* **1997**, *62,* 7507-7507.



III.42

Figure III.5. Three Dimensional Representation of a Possible Conformation of **III.42**.

We then turned to more traditional methods of deoxygenation, namely reducing sulfonate ester derivatives with LAH or other hydride sources.[39] Interestingly, Danishefsky was able to cleave a C-*O*-mesyl group under dissolving metal conditions in his synthesis of the toxin equisetin.[40] Both removal of the benzyl protecting group and conjugate reduction of the enone[41] should also occur under metal ammonia conditions. Thus, mesylation of primary alcohol **III.42** proceeded smoothly with MsCl and triethylamine at 0 °C to give **III.45** in 82% yield (Scheme III.16). With **III.45** in hand, a one-pot triple-transformation was attempted with lithium metal and condensed ammonia. Enone reduction under these conditions should give the thermodynamically favored *trans* AB ring junction. Unfortunately, the reaction did not yield any desired product based on mass spectrometry.

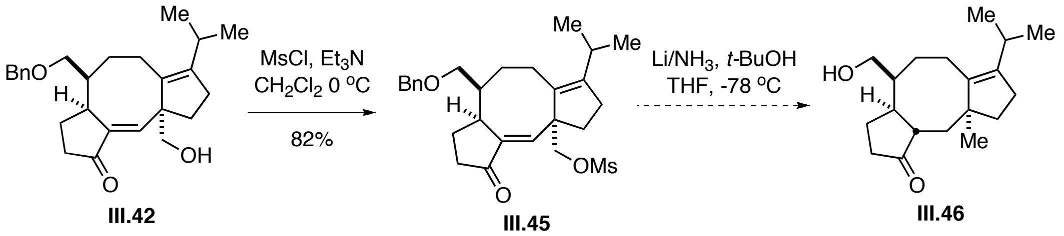
---

[39] (a) Porco, J. A.; Lei, X. *J. Am. Chem. Soc.* **2006**, *128,* 14790-14791. (b) Thomas, S. Huynh, T.; Enriquez-Rios, V.; Singaram, B. *Org. Lett.* **2001**, *3*, 3915-3918.

[40] Turos, E.; Audia, J. E.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111,* 8231-8236.

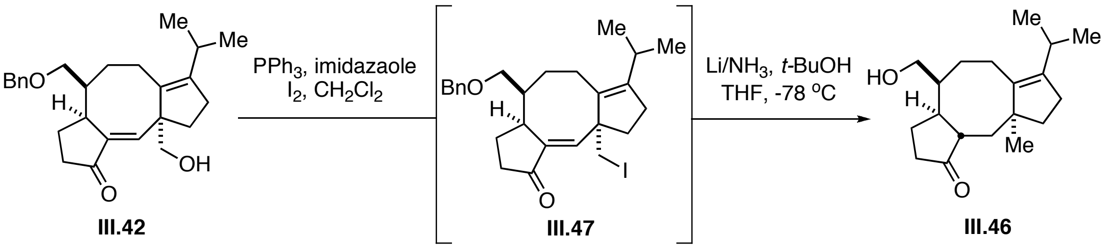
[41] Dutcher, J. S.; Macmillan, J. G.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41,* 2663-2669.

Scheme III.16. Mesylation of **III.42** and Metal-Ammonia Reduction.



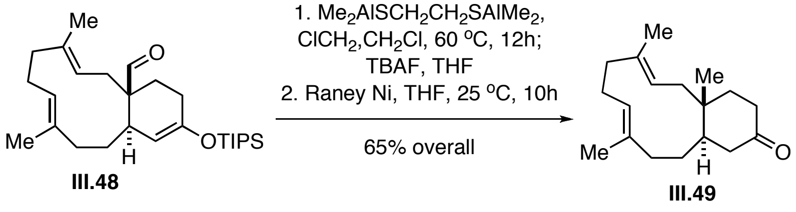
The primary alcohol of **III.42** was instead converted to primary iodide **III.47** (Scheme III.17). Iodination of **III.42** with iodine, triphenylphosphine, and imidazole furnished unstable iodide **III.47**, which was subsequently treated with lithium metal and liquid ammonia at -78 °C. Iodide **III.47** underwent deprotection, reduction, and deoxygenation all in one-pot to give compound **III.46**, characterized by the appropriate mass data and IR stretches. Unfortunately, with the unstable nature of **III.47** and insufficient NMR characterization of **III.46**, we sought alternative routes to deoxygenation.

Scheme III.17. Iodination of **III.42** and Metal-Ammonia Reduction.



Snyder and Corey[42] recently reported total syntheses of several dolabellane-type marine natural products (Scheme III.18). The targeted natural products had a 5-11 ring system, a similar framework to cycloaraneosene except for an internal carbon-carbon bond. Deoxygenation was also required at a neopentyl ring junction and was accomplished in two steps that depended on dithiolane formation of **III.48**. After silyl ether cleavage, the dithiolane was treated with deactivated Raney Ni to afford **III.49** in 65% overall yield. Other protocols such as arylsulfonylhydrzaone reduction, Wolff-Kishner reduction, and Barton-McCombie deoxygenation failed to convert **III.48** to **III.49**. Because cycloaraneosene is structurally similar to this system, this procedure could be employed if the primary alcohol at C18 is oxidized to the corresponding aldehyde.

Scheme III.18. Deoxygenation of **III.48**.



The primary alcohol of enone **III.42** was oxidized with Dess-Martin periodinate to the corresponding aldehyde, which was immediately treated with 1,3 propanedithiol and $BF_3 \cdot OEt_2$ at 0 °C (Scheme III.19). The reaction was quenched immediately with an aqueous solution of sodium bicarbonate, affording dithiane **III.50**. After the dithiane product was treated through a plug of basic alumina, the crude was immediately treated

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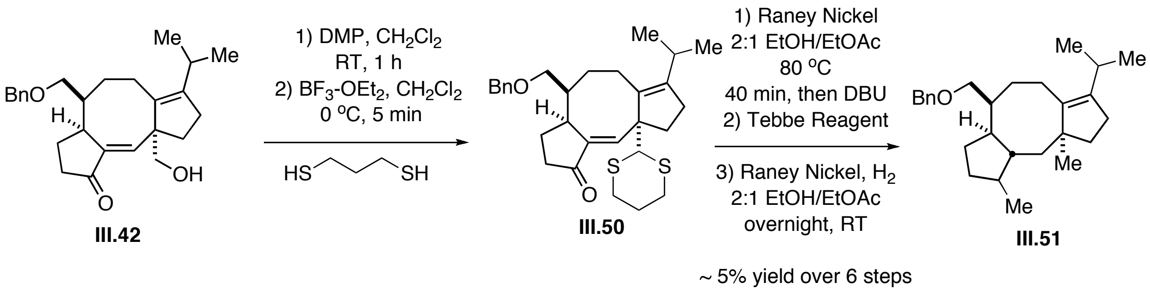
[42] Snyder, S. A.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128,* 740-742.

with Raney Nickel 2800 in a mixture of ethanol/ ethyl acetate at 80 °C to undergo both dithiane reduction and enone reduction,[43] giving a mixture of diastereomers. Treatment of that mixture with DBU afforded ketone that has tentatively been assigned to have a *trans* relationship in the AB ring. The ketone was immediately olefinated under Tebbe[44] conditions. Other olefination attempts with either Wittig or Petasis conditions did not yield desired product. The resulting olefin was subsequently reduced under an atmosphere of H_2 in the presence of Raney Nickel 2800, yielding **III.51** in an unoptimized yield of 5% over 6 steps.[45] The stereochemistry of the resulting methyl group has yet to be defined.

Scheme III.19. Deoxygenation and Enone Reduction.



III.42 **III.50** **III.51**

With only two transformations away from accessing our target cycloaraneosene, we noted that the final step, which required an elimination of the primary alcohol to form an exocyclic olefin, had been previously reported[10b] (Scheme III.20). Thus, synthesis of

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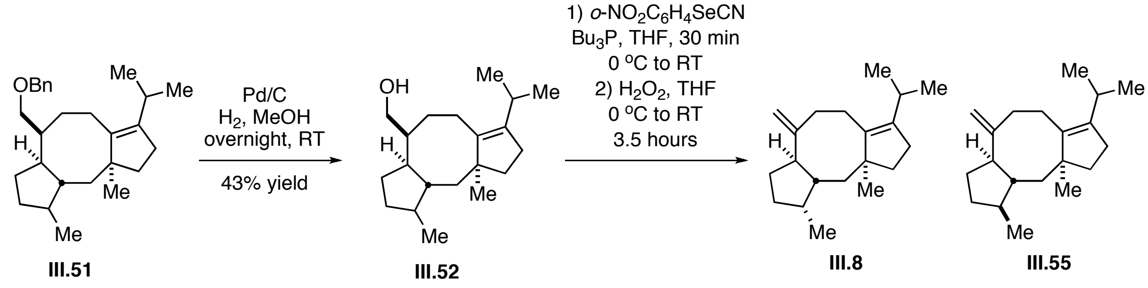
[43] Reduction of the dithiane occurred first, followed by enone reduction. In the event of dithiane reduction and only partial enone reduction, the mixture could be pushed to completion by resubjecting the mixture to Raney Nickel and an atmosphere of hydrogen at room temperature for 45 minutes to yield a mixture of diastereomeric ketones.

[44] Tebbe reagent prepared by Andrew Leyhane.

[45] Intermediates along the way were characterized by ^{1}H NMR and mass spectrometry.

primary alcohol **III.52** would be a formal synthesis of our natural product. Unfortunately, deprotection of the primary alcohol did not occur efficiently under Raney Nickel conditions, nor with 10% Pd on carbon with H_2 when ethanol was used as a solvent. However, removal of the benzyl protecting group with 10% Pd on carbon with H_2 in methanol yielded primary alcohol **III.52**, completing what would be a formal synthesis of our target. However, although the ultimate step has been reported, there was no spectral data on **III.52** provided, nor an experimental procedure published. Fortunately, the two-step Grieco elimination[46] of primary alcohol **III.52** proceeded smoothly; preliminary data[47] points to the synthesis of a mixture of our target cycloaraneosene **III.8** as well as what is to believed to be *epi*-cycloaraneosene **III.55** at C16. With such a small amount of product, perhaps comparison with an authentic sample or derivatization of **III.52** could help further confirm the structure of our compounds. Future investigations also include exploring a more selective hydrogenation toward the synthesis of **III.51**.

Scheme III.20. End Route to Cycloaraneosene.



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[46] (a) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485-1486. (b) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947-949.

[47] Less than 0.5 mg of the product was synthesized, requiring an overnight ^{1}H NMR. Chemical shifts in the reported proton spectra match the synthesized material.

III.4 Conclusion

Our [2+2] photocycloadditions/thermal fragmentation strategy allows us to access medium-ring frameworks in a unique and rapid fashion. We have gained a great deal of knowledge from our synthetic efforts, but there is still much to learn about 5-8-5 ring systems. While we can rapidly access our core framework, the synthesis has shown us that as synthetic chemists we are not without limitations. Often times, a planned synthetic strategy is not as straightforward as it appears. Nevertheless, we have been able to demonstrate the synthetic utility of iron-stabilized cyclobutadiene and functionalized cyclobutenes as building blocks toward medium ring natural products.

III.5 Experimental Section

Starting materials and reagents were purchased from commercial suppliers and used without further purification except the following: triethylamine and pentane were distilled from CaH_2 under anhydrous nitrogen atm; tetrahydrofuran, benzene, diethyl ether, and dichloromethane were dried on alumina columns using a solvent dispensing system;[1] pentane, hexanes, and diethyl ether used in chromatography were distilled prior to use. All reactions were conducted in oven-(135 °C) and flame-dried glassware under an inert atm of dry nitrogen. *n*-BuLi was titrated using menthol and N-phenylnapthylamine in diethyl ether.

Infrared (**FTIR**) spectra were recorded on a Nicolet 210 FT-Infrared spectrophotometer or a Nicolet Avatar 360 spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). Proton nuclear magnetic resonance spectra (**^{1}H NMR**) were recorded on either a Varian Gemini-400 instrument (400 MHz), or a Varian Gemini-500 instrument (500 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent reference as the internal standard ($CHCl_3$: δ 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), coupling constants (Hz), and integration. **^{13}C NMR** spectra were recorded on either a Varian Gemini-400 instrument (100 MHz), or a Varian Gemini-500 instrument (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ

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[1] Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J *Organometallics* **1996**, *15*, 1518-1520.

77.23 ppm). Elemental analyses (**Anal.**) were performed by Robertson Microlit Laboratories, Inc. Madison, NJ and are reported in percent abundance. High resolution mass spectral analyses (**HRMS**) were performed by Mass Spectrometry Facility, Boston College.

X-ray data were collected using a Bruker SMART APEX CCD (charge coupled device) based diffactometer with Mo (λ=0.71073 Å) radiation equipped with an LT-3 low-temperature apparatus operating at 183 K. A stable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 s, such that a hemisphere was collected. A total of 1305 frames were collected with a maximum resolution of 0.75 Å. Cell parameters were retrieved using SMART[2] software and refined using SAINT on all observed reflections. The structures are solved by the direct method using the SHELXS-97[3] program and refined by least squares method on F^2, SHELXTL-97,[4] incorporated in SHELXTL-PC V 5.10.[5] The crystals used for the diffraction studies showed no decomposition during data collection. The drawing was displayed at 35 % ellipsoids.

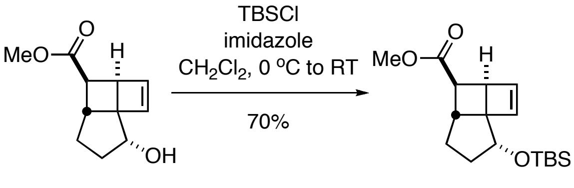
---

[2] SMART V 5.050 (NT) *Software for the CCD Detector System;* Bruker Analytical X-ray Systems, Madison, WI (1998).

[3] Sheldrick, G.M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany, 1990.

[4] Sheldrick, G.M. SHELXS-97, *Program for the Refinement of Crystal Structure*, University of Gottingen, Germany, 1997.

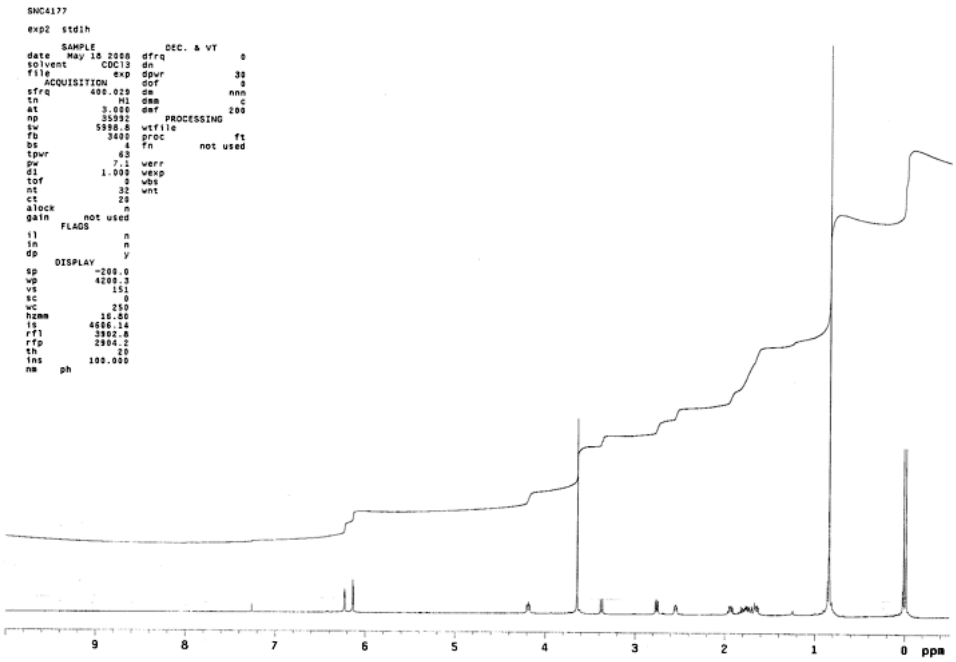
[5] SHELXTL 5.10 (PC-Version), *Program Library for Structure Solution and Molecular Graphics;* Bruker Analytical X-ray Systems, Madison, WI (1998).



III.20 **III.21**

Imidazole (748 mg, 11.0 mmol) and TBSCl (826 mg, 5.5 mmol) were added to a solution of cyclobutene **III.20** (712 mg, 3.7 mmol) in dichloromethane (7.3 mL) in a round bottom flask at 0 °C. The reaction was warmed to room temperature and allowed to stir for 20 h, or until complete by TLC. The cloudy solution was then diluted with H_2O (10 mL). The aqueous layer was washed with CH_2Cl_2 (2 x 10 ml) and the organic layers were collected and dried with $MgSO_4$. The solvent was removed *in vacuo*. Product was purified by silica gel chromatography (hexanes:EtOAc 95:5) to give compound **III.21** (797.1 mg, 70 % yield) as a pale yellow oil.

Cyclobutene methyl ester (III.21): R_f 0.56 (hexanes:EtOAc 9:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 6.27 (dd, 1H, J = 2.8, 1.6 Hz), 6.13 (d, 1H, J = 2.8 Hz), 4.19 (dd, 1H, J = 8.8, 6.0 Hz), 3.64 (s, 3H), 3.37 (d, 1H, J = 8.4 Hz), 2.75 (dd, 1H, J = 8.4, 4.8 Hz), 2.54 (dd, 1H, J = 7.2, 4.8 Hz), 1.89-1.96 (m, 1H), 1.62-1.85 (m, 3H), 0.84 (s, 9H), 0.01 (s, 3H), -0.02 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 174.2, 140.1, 136.8, 73.2, 61.4, 51.5, 42.3, 41.0, 40.7, 33.6, 27.3, 26.0, 18.4, -4.5, -4.6. **IR** (NaCl, thin film) 2953 (s), 2929 (s), 2856 (m), 1737 (s), 1246 (s), 1118 (s), 861 (m), 739 (w) cm^{-1}. **HRMS** (M + H) $C_{17}H_{29}O_3Si$ Calcd: 309.1886. Found: 309.1883.



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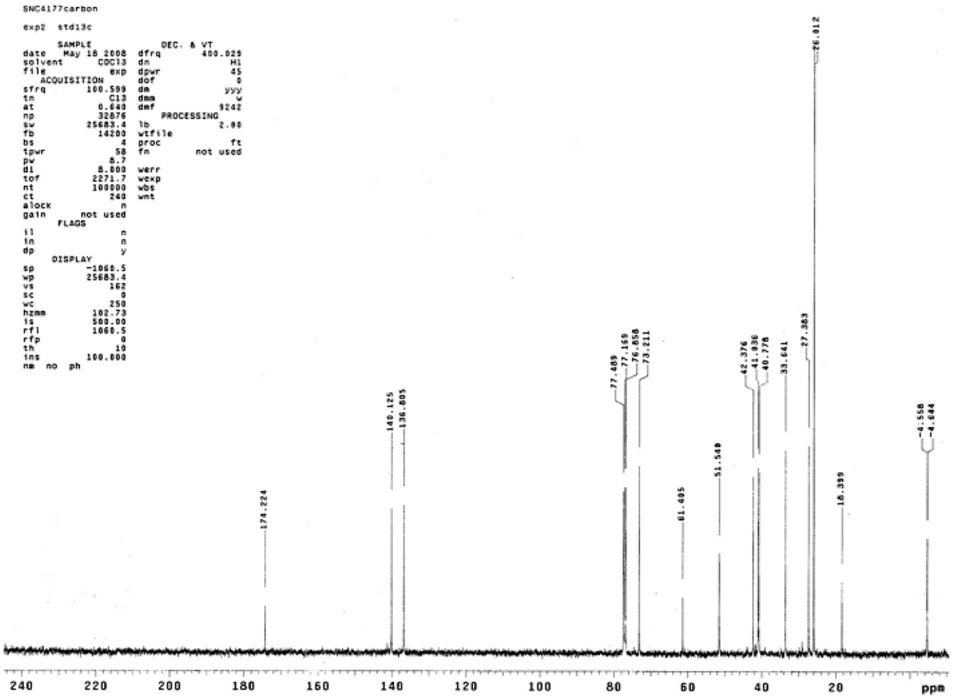

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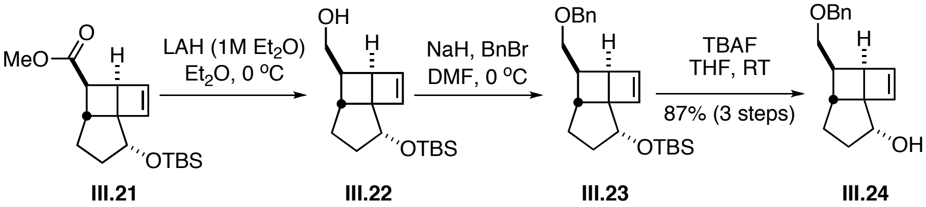
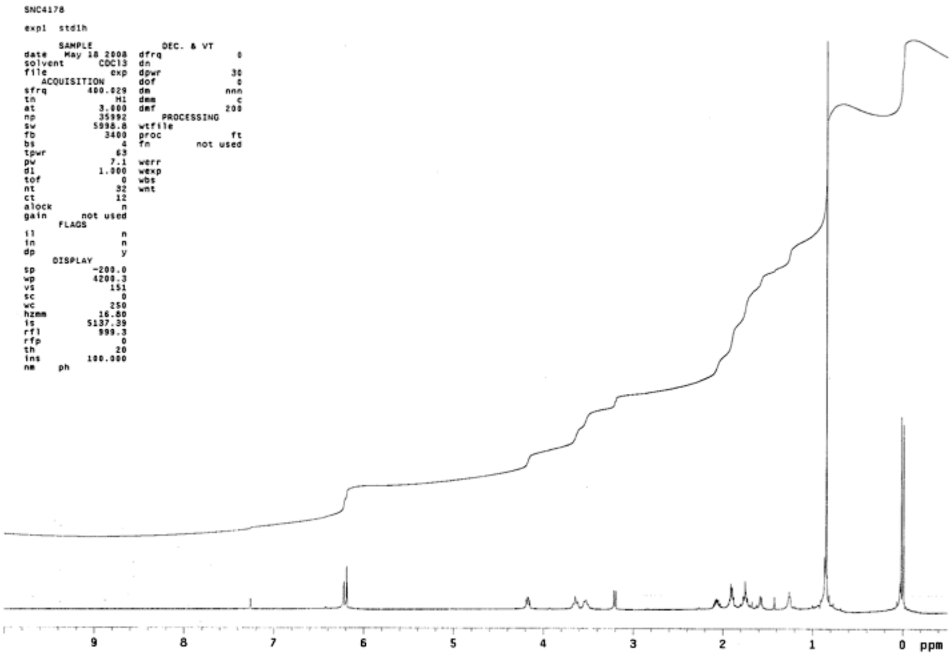


III.21 **III.22** **III.23** **III.24**

To a solution of **III.21** (1.32 g, 4.27 mmol) in Et_2O (25 mL) at 0 °C was added a solution of $LiAlH_4$ (1M Et_2O, 5.6 mL, 5.55 mmol) dropwise. The reaction mixture was stirred at this temperature for 10 minutes at which time it was judged complete by TLC analysis. The reaction was cautiously quenched at 0 °C with saturated aqueous Na_2SO_4 (0.5 mL). The thick suspension was then diluted with Et_2O and $MgSO_4$ was added to form a slurry, which was then filtered through silica gel in a fritted funnel. The filtrate was concentrated *in vacuo* to give alcohol **III.22** (1.16 g, 4.14 mmol) in 96% crude yield. The crude product was used in the next step without purification.

Cyclobutene alcohol (III.22): R_f 0.29 (hexanes:EtOAc 2:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 6.22 (m, 1H), 6.19 (d, 1H, J = 2.0 Hz), 4.17 (dd, 1H, J = 9.2, 6.4 Hz), 3.64 (m, 1H), 3.53 (m, 1H), 3.20 (d, 1H, J = 7.6 Hz), 2.06 (m, 1H), 1.90 (m, 2H), 1.75 (m, 2H), 1.58 (m, 1H), 0.84 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 140.4, 136.6, 73.5, 64.7, 61.0, 41.4, 40.4, 38.7, 33.7, 27.7, 26.0, 18.4, -4.5, -4.6. **IR** (NaCl, thin film) 3327 (br), 2953 (s), 2857 (s), 1462 (w), 1255 (m), 1118 (s), 861 (m), 752 (w) cm^{-1}. **HRMS** (M + H) $C_{16}H_{29}O_2Si$ Calcd: 281.1937. Found: 281.1940.



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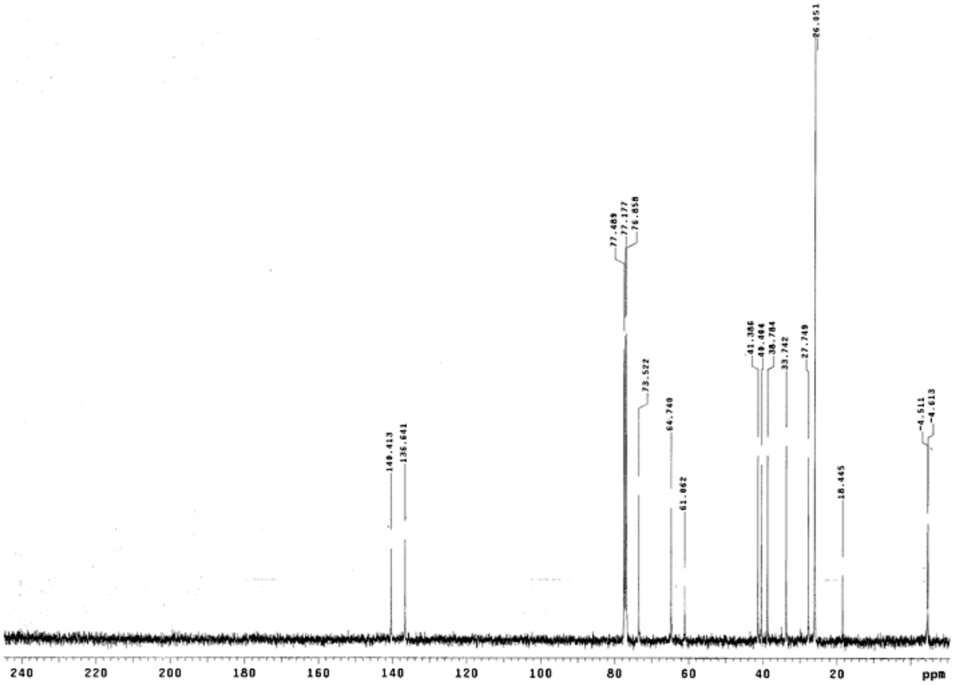
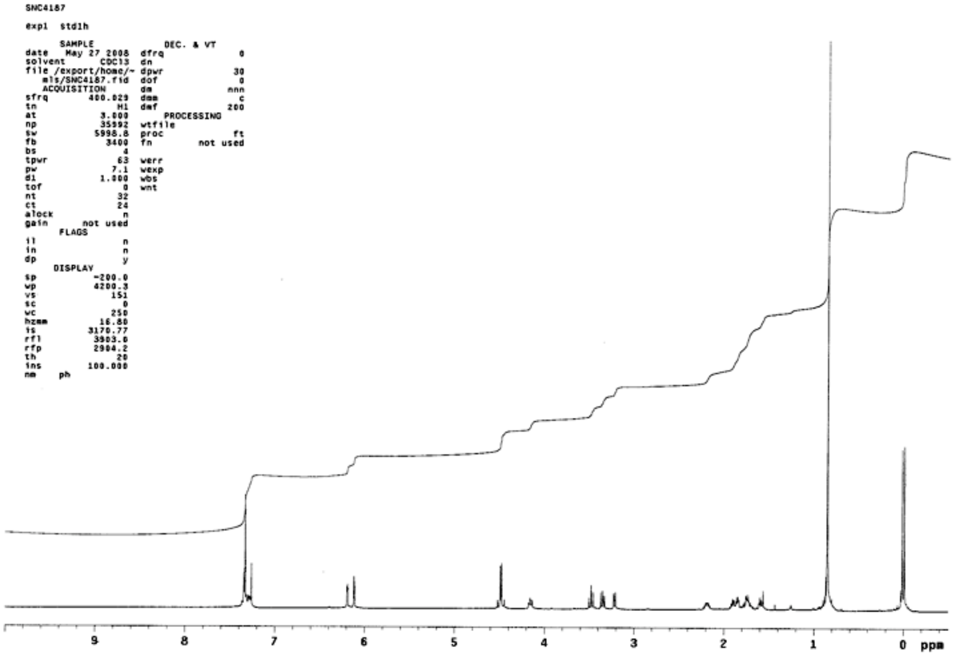


To a suspension of NaH (297 mg, 12.4 mmol) in DMF (5 mL), a solution of **III.22** (1.16 g, 4.14 mmol) in DMF (5 mL) was added slowly at 0 ^{o}C. The yellow foamy reaction was allowed to warm to room temperature and stirred for 1 hour, at which time it was cooled to 0 ^{o}C again and BnBr (0.64 mL, 5.38 mmol) was added. The thick foamy yellow solution was allowed to warm to room temperature and stirred for 3 hours. The reaction was judged complete by TLC and quenched cautiously at 0 ^{o}C with a saturated aqueous solution of NH_4Cl (2 mL). The solution was diluted with water (15 mL) and extracted with hexane (2 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to afford benzylated cyclobutene **III.23** (1.47 g, 3.97 mmol) in 96% crude yield. The crude product was used in the next step without purification.

Benzylated cyclobutene (III.23): R_f 0.71 (hexanes:EtOAc 4:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.26-7.34 (m, 5H), 6.19 (dd, 1H, J = 2.4, 1.2 Hz), 6.11 (d, 1H, J = 2.4 Hz), 4.48 (dd, 2H, J = 17.2, 12.0 Hz), 4.15 (dd, 1H, J = 8.8, 6.4 Hz), 3.48 (t, 1H, J = 9.2 Hz), 3.35 (dd, 1H, J = 9.6, 6.8 Hz), 3.21 (d, 1H, J = 7.6 Hz), 2.18 (td, 1H, J = 8.0, 4.8 Hz), 1.81-1.91 (m, 2H), 1.69-1.78 (m, 2H), 1.59 (t, 1H, J = 5.2 Hz), 0.84 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 140.1, 138.8, 137.0, 128.4, 127.7, 127.5, 73.5, 72.9, 72.1, 61.1, 40.8, 39.3, 38.9, 33.7, 27.7, 26.0, 18.4, -4.5, -4.6. **IR** (NaCl, thin film) 3027 (w), 2929 (s), 2855 (s), 2360 (w), 1362 (w), 1255 (m), 1117 (s), 835 (s), 688 (w) cm^{-1}. **HRMS** (M + H) $C_{23}H_{35}O_2Si$ Calcd: 371.2406. Found: 371.2418.



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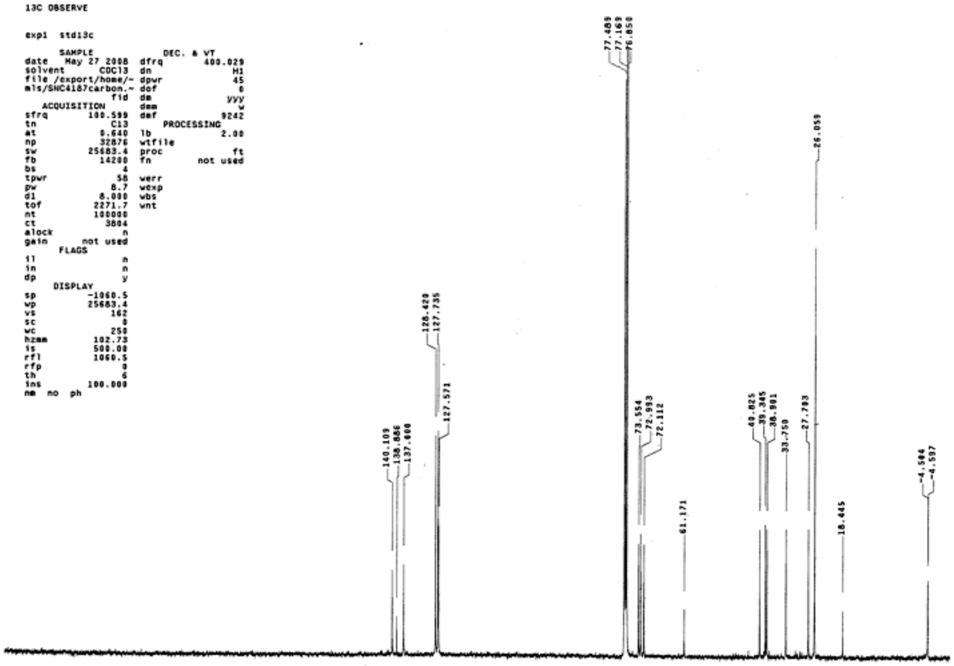

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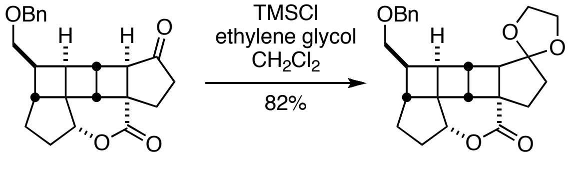
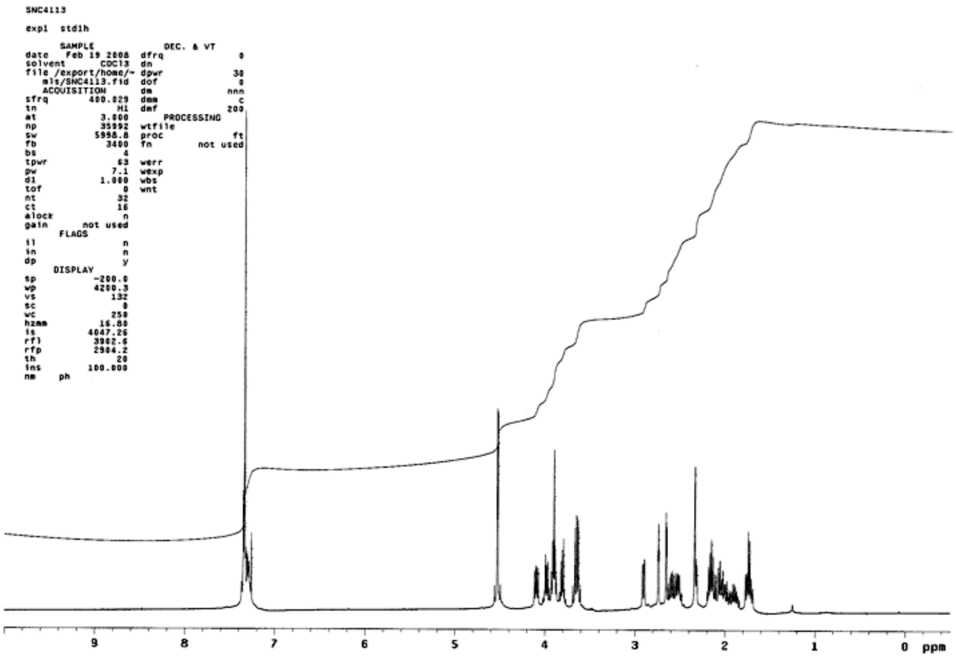
To a solution of **III.23** (1.47 g, 3.97 mmol) in THF (40 mL) at 0 ^{o}C was added tetrabutylammonium fluoride hydrate (3.10 g, 11.9 mmol) and stirred at room temperature for 23 hours or until judged complete by TLC. The reaction mixture was diluted with water (20 mL) and then extracted with EtOAc (3 x 30 mL). The organic layers were combined and dried over $MgSO_4$ and concentrated *in vacuo*. The concentrate was purified by silica gel chromatography (3:1 hexanes/EtOAc to 3:1 EtOAc/hexane) to give **III.24** (887 mg, 3.46 mmol) in 87% yield.



III.26 **III.27**

To a stirring solution of **III.26** (432 mg, 1.19 mmol) in dichloromethane (11.9 mL) was added ethylene glycol (0.26 mL, 4.75 mmol) and chlorotrimethylsilane (0.68 mL, 5.35 mmol). The solution was allowed to stir at room temperature for 20 hours. The reaction mixture was then diluted with water (10 mL) and extracted with dichloromethane (10 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo.* The concentrate was purified by silica gel chromatography (2:1 EtOAc/hexanes) to give **III.27** (399 mg, 0.98 mmol) as a sticky yellow oil in 82% yield.

Cycloadduct (III.27): R_f 0.37 (hexanes:EtOAc 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.33 (m, 5H), 4.53 (dd, 2H, J = 14.4, 12.0 Hz), 4.09 (dd, 1H, J = 10.4, 6.0 Hz), 3.98 (m, 1H), 3.90 (m, 2H), 3.80 (m, 1H), 3.64 (dq, 2H, J = 16.0, 9.6 Hz), 2.90 (d, 1H, J = 7.6 Hz), 2.74 (t, 1H, J = 2.4 Hz), 2.65 (d, 1H, J = 2.8 Hz), 2.48-2.63 (m, 2H), 2.32 (m, 2H), 1.85-2.19 (m, 5H), 1.73 (td, 2H, 2.90 J = 11.6, 6.0 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 174.3, 138.4, 128.5, 127.8, 127.7, 116.9, 80.3, 73.3, 70.8, 65.2, 64.4, 59.6, 48.9, 47.9, 42.1, 41.1, 40.5, 38.7, 34.3, 33.4, 30.8, 29.4, 29.2. **IR** (NaCl, thin film) 3060 (m), 3027 (s), 2933 (m), 2851 (w), 1720 (s), 1084 (m), 754 (s), 699 (m) cm^{-1}. **HRMS** (M + Na) $C_{25}H_{28}O_5Na$ Calcd: 431.1834. Found: 431.1829.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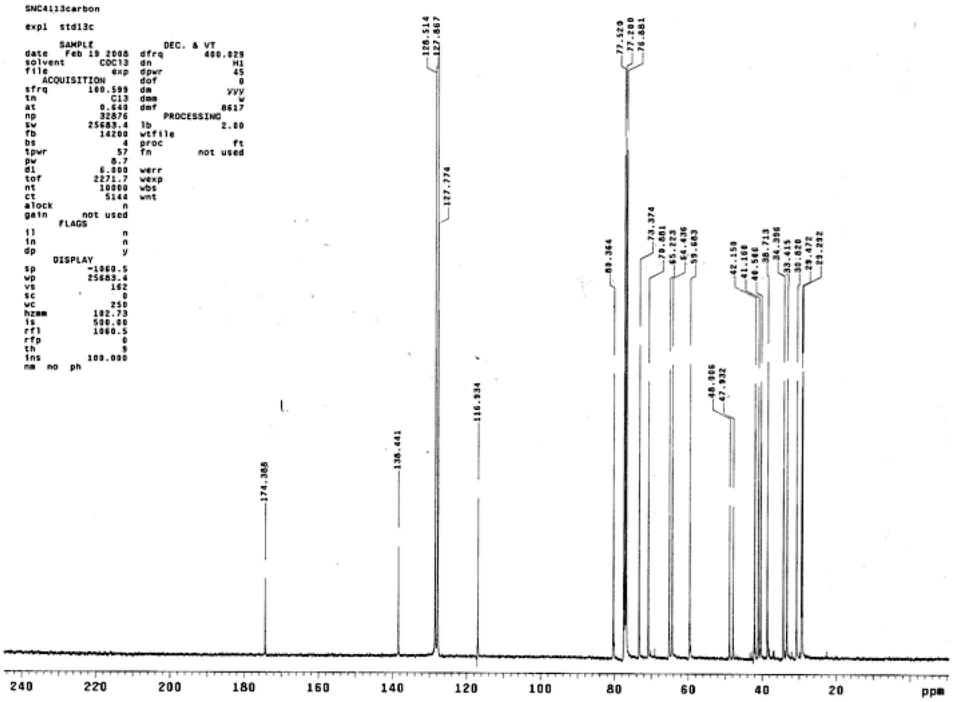
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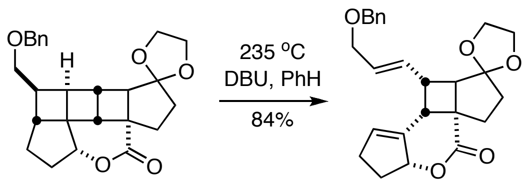
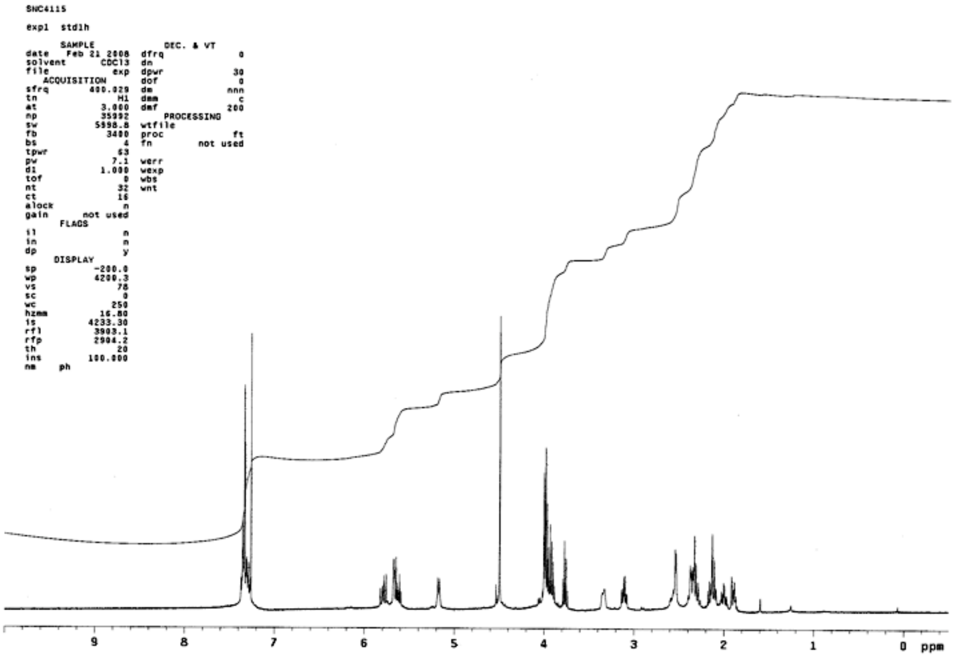


III.27 **III.34**

A heavy-walled reaction tube was charged with **III.27** (140 mg, 0.34 mmol), DBU (0.05 mL, 0.34 mmol), and benzene (34 mL). The solution was purged with N_2 for 15 min. and sealed with a PTFE screw cap. The reaction was heated to 235 °C in a silicone oil bath for 2.5-4 hours, or until the starting material was not observed by TLC. The resulting solution was cooled to room temperature and concentrated *in vacuo*. The concentrate was purified by silica gel chromatography (3:1 hexanes/EtOAc to 2:1 hexanes/EtOAc) to afford **III.34** (118 mg, 0.29 mmol) in 84% yield.

Divinyl cyclobutane (III.34): R_f 0.47 (hexane:EtOAc 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-2.37 (m, 5H), 5.78 (m, 1H), 5.95-5.67 (m, 2H), 5.17 (d, 1H, J = 7.2 Hz), 4.49 (s, 2H), 3.88-4.01 (m, 5H), 3.76 (dd, 1H, J = 12.4, 6.0 Hz), 3.32 (m, 1H), 3.11 (td, 1H, J = 9.6, 4.4 Hz), 2.54 (m, 2H), 2.33 (m, 3H), 2.13 (m, 2H), 2.00 (td, 1H, J = 9.2, 4.4 Hz), 1.89 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 176.6, 138.4, 135.0, 133.7, 130.0, 128.5, 127.9, 127.7, 127.5, 117.1, 86.3, 72.2, 70.5, 65.2, 64.5, 54.9, 47.7, 39.5, 37.7, 34.6, 34.3, 31.5, 29.4. **IR** (NaCl, thin film) 3026 (s), 2931 (s), 2854 (w), 1725 (s), 1325 (w), 1113 (m), 1036 (m), 754 (m) cm^{-1}. **HRMS** (M + Na) $C_{25}H_{28}O_5Na$ Calcd: 431.1834. Found: 431.1849.



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SNC4115

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tn              H1  dmm              c
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np           35992       PROCESSING
sw          5998.8  wtfile
fb            3400  proc            ft
bs               4  fn        not used
tpwr            63
pw             7.1  werr
d1           1.000  wexp
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in               n
dp               y
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th              20
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nm    ph
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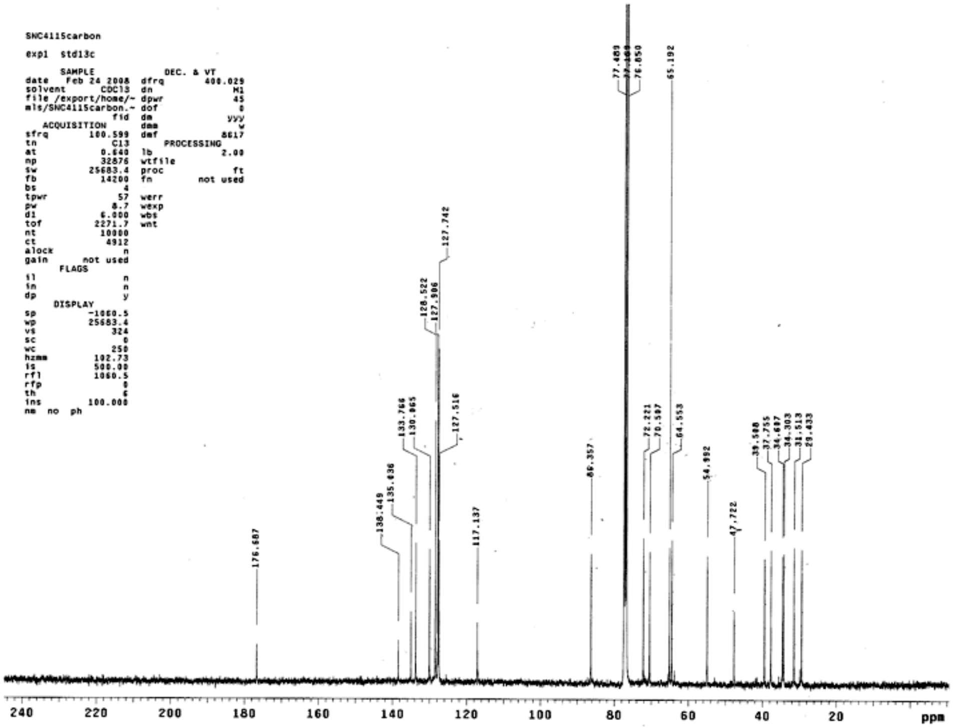

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SNC4115carbon

exp1  std13c

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               fid  dm             yyy
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sfrq       100.599  dmf           8617
tn             C13       PROCESSING
at           0.640  lb            2.00
np           32876  wtfile
sw         25683.4  proc            ft
fb           14200  fn        not used
bs               4
tpwr            57  werr
pw             8.7  wexp
d1           6.000  wbs
tof         2271.7  wnt
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dp               y
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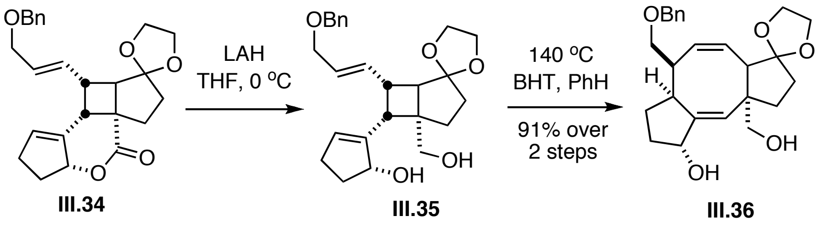
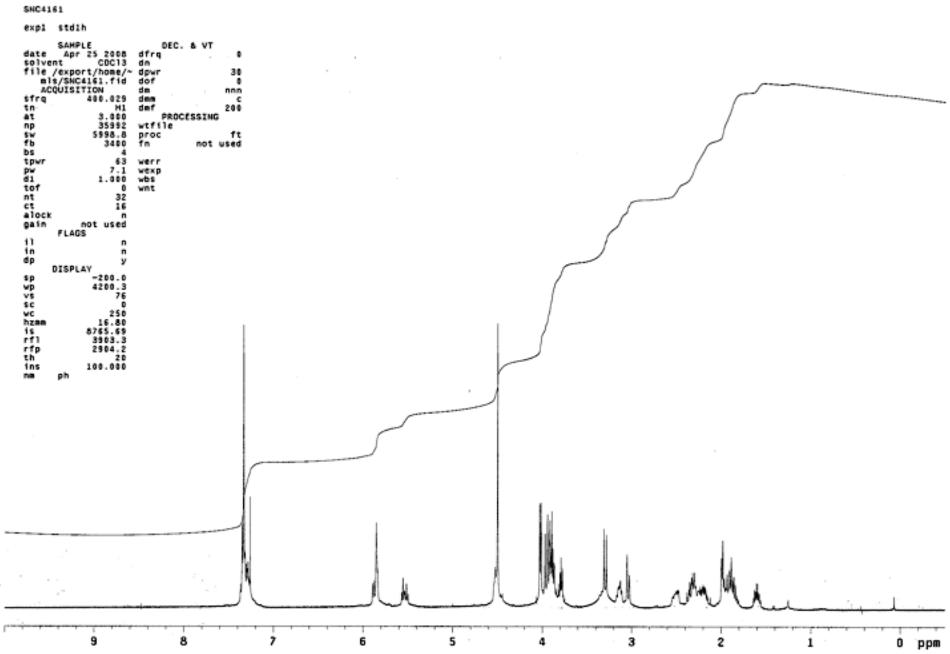


To a stirring solution of **III.34** (119 mg, 0.29 mmol) in THF (2.9 mL) was added a solution of LAH (1M Et_2O, 0.88 mL, 0.88 mmol) at 0 °C and was allowed to stir at this temperature. After 30 minutes the reaction was judged complete by TLC and slowly quenched with a solution of aqueous Na_2SO_4 (0.5 mL). The thick suspension was then warmed to room temperature, diluted with EtOAc, and $MgSO_4$ was added to form a slurry, which was then filtered through silica gel in a fritted funnel. The filtrate was concentrated *in vacuo* to give alcohol **III.35** and the crude product was immediately taken on to the next step.

Dialkenyl cyclobutane diol (III.35): R_f 0.32 (hexane:EtOAc 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.34 (m, 5H), 5.86 (m, 2H), 5.53 (dtd, 1H, J = 15.6, 6, 1.6 Hz), 4.52 (m, 1H), 4.50 (s, 2H), 4.02 (d, 2H, J = 6 Hz), 3.86-3.96 (m, 4H), 3.78 (m, 1H), 3.29 (d, 1H, J = 10.4 Hz), 3.13 (m, 1H), 3.03 (d, 1H, J = 10.0 Hz), 2.49 (m, 1H), 2.12-2.38 (m, 3H), 1.80-2.00 (m, 4H), 1.60 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 142.6, 138.6, 135.3, 131.4, 128.5, 127.8, 127.7, 126.1, 118.3, 82.1, 72.1, 70.9, 65.7, 65.1, 64.2, 50.3, 49.2, 42.4, 36.8, 34.5, 33.8, 33.2, 31.3. **IR** (NaCl, thin film) 3317 (br), 2953 (s), 2873 (s), 1311 (w), 1114 (s), 1065 (s), 1013 (s), 915 (m), 696 (m) cm^{-1}. **HRMS** (M + Na) $C_{25}H_{32}O_5Na$ Calcd: 435.2147. Found: 435.2158.



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SNC4161

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sfrq       400.029  dmm               c
tn              H1  dmf             200
at           3.000      PROCESSING
np           35992  wtfile
sw          5998.8  proc             ft
fb            3400  fn         not used
bs               4
tpwr            63  werr
pw             7.1  wexp
d1           1.000  wbs
tof              0  wnt
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dp               y
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nm     ph
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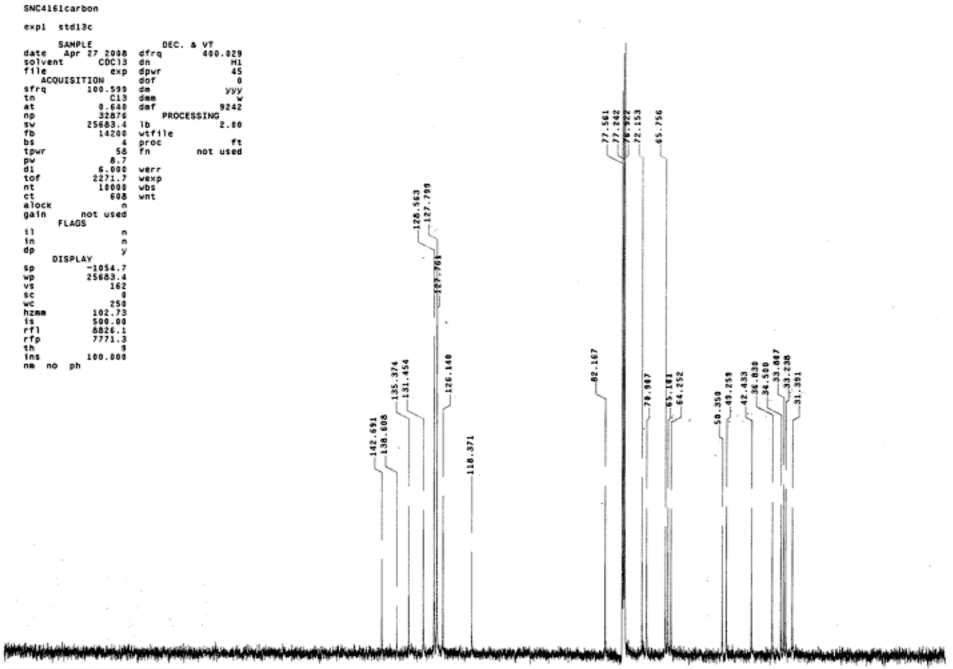

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SNC4161carbon

exp1  std13c

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np           32876      PROCESSING
sw         25683.4  lb             2.00
fb           14200  wtfile
bs               4  proc             ft
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d1           6.000  werr
tof         2271.7  wexp
nt           10000  wbs
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alock            n
gain      not used
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dp               y
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rfp         7771.3
th               9
ins        100.000
nm  no  ph
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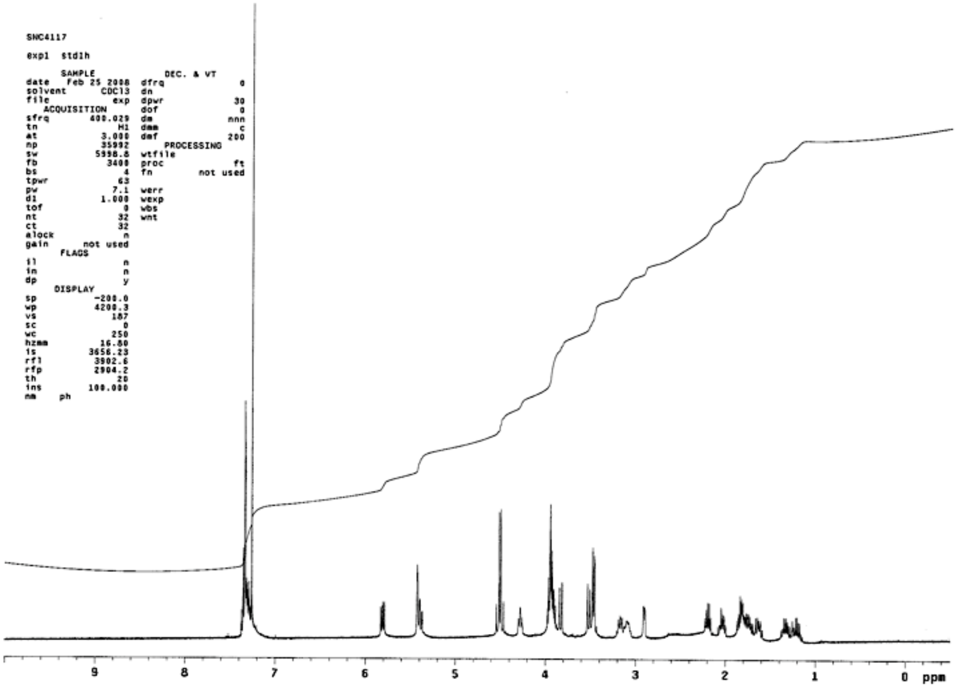
A heavy-walled reaction tube was charged with crude **III.35**, BHT (70.6 mg, 0.32 mmol), and benzene (37 mL). The solution was purged with N_2 for 15 min. and sealed with a PTFE screw cap. The reaction was heated to 140 ^oC in a silicone oil bath for 4.5 hours, or until the starting material was not observed by TLC. The resulting solution was cooled to room temperature and concentrated *in vacuo*. The concentrate was purified by silica gel chromatography (2:1 hexanes/acetone to 1:2 hexanes/acetone) to afford **III.36** (110 mg, 0.27 mmol) in 91% yield.

Cyclooctadiene diol (III.36): **R_f** 0.10 (hexanes:EtOAc 1:5); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.35 (m, 5H), 5.80 (dd, 1H, J = 10.4, 6.4 Hz), 5.36-5.42 (m, 2H), 4.50 (dd, 2H, J = 19.2, 12.0 Hz), 4.28 (t, 1H, J = 7.2 Hz), 3.89-3.98 (m, 4H), 3.83 (d, 1H, J = 10.4 Hz), 3.52 (d, 1H, J = 10.4 Hz), 3.46 (m, 2H), 3.07-3.20 (m, 2H), 2.90 (m, 1H), 2.18 (quintet, 1H, J = 6.4 Hz), 2.03 (m, 1H), 1.59-1.87 (m, 4H), 1.28-1.38 (m, 1H), 1.20 (dtd, 1H, J = 23.6, 12.0, 6.4 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.5, 138.4, 130.5, 130.3, 129.2, 128.4, 127.8, 127.7, 127.4, 118.0, 77.7, 73.3, 71.8, 68.0, 65.1, 64.4, 51.9, 51.6, 44.0, 39.6, 35.9, 33.6, 24.7. **IR** (NaCl, thin film) 3354 (br), 2957 (s), 2869 (s), 1460 (w), 1314 (w), 1090 (m), 1037 (m), 735 (s) cm^{-1}. **HRMS** (M + Na) $C_{25}H_{32}O_5Na$ Calcd: 435.2147. Found: 435.2163.



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SNC4117

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at            3.000   dmf             200
np            35992        PROCESSING
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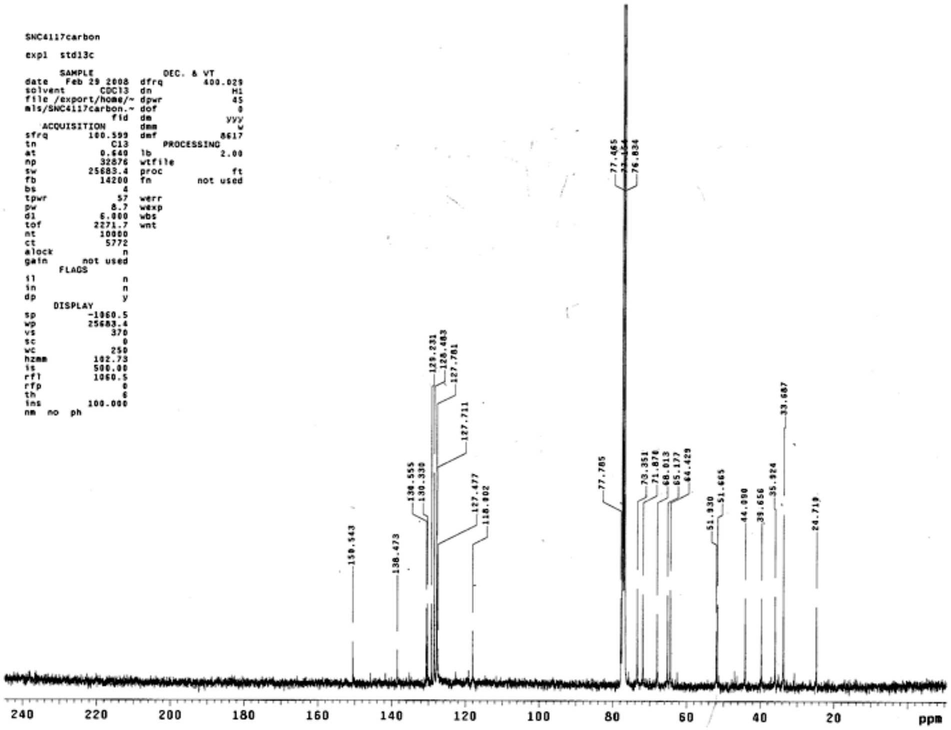

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SNC4117carbon

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sw          25083.4   proc            ft
fb            14200   fn        not used
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tpwr             57   werr
pw              8.7   wexp
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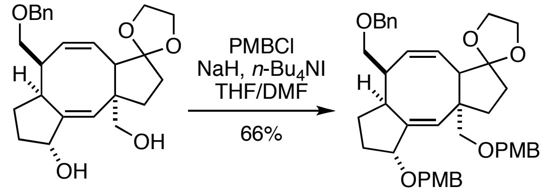
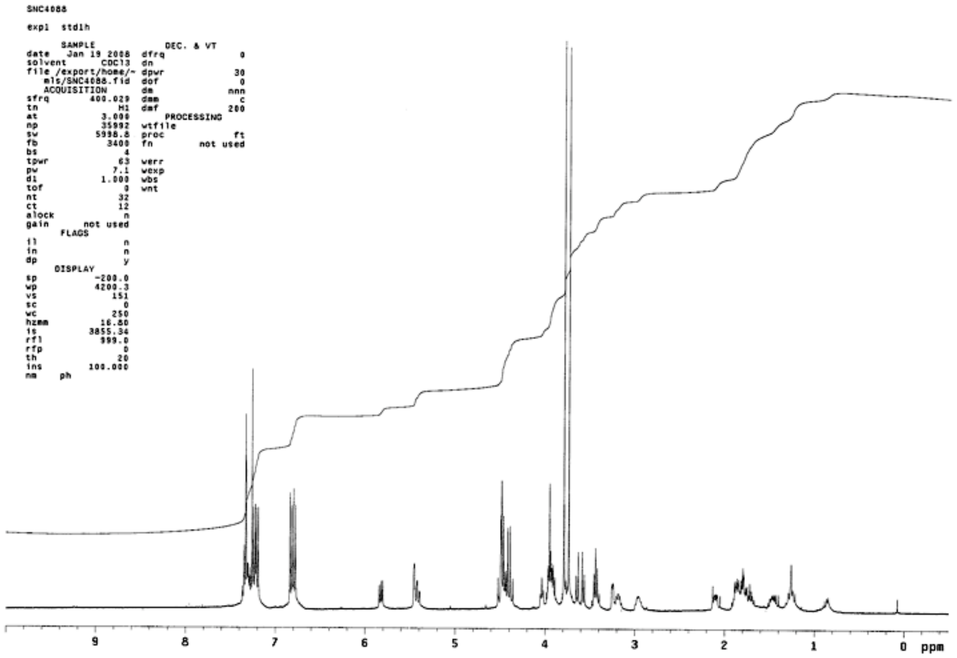


III.36 **III.37**

A suspension of NaH (85.2 mg, 3.55 mmol) in DMF/THF (1.1 mL / 1 mL) was added to a flame dried round bottom flask and cooled to 0 °C. A solution of **III.36** (183 mg, 0.44 mmol) in THF (2.3 mL) was added, along with tetrabutylammonium iodide (57.9 mg, 0.22 mmol). The reaction was allowed to warm to room temperature and stirred for 30 minutes. The yellow solution was then cooled to 0 °C again and PMBCl (0.24 mL, 1.77 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred at this temperature for 2 days. The reaction mixture was then quenched slowly at 0 °C with saturated aqueous NH_4Cl (0.5 mL). The solution was diluted with water (2 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo.* The product was purified by silica gel chromatography (9:1 hexanes/EtOAc to 4:1 hexane/EtOAc to 1:1 hexanes/EtOAc) to afford **III.37** (191 mg, 0.29 mmol) in 66% yield as a yellow oil.

Cyclooctadiene diol (III.37): R_f 0.64 (hexane:EtOAc 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.34 (m, 5H), 7.21 (dd, 4H, J = 13.6, 8.4 Hz), 6.80 (ddd, 4H, J = 16.0, 8.8, 2.0 Hz), 5.82 (dd, 1H, J = 10.4, 5.6 Hz), 5.39-5.45 (m, 2H), 4.36-4.52 (m, 6H), 4.13 (t, 1H, J = 6.0 Hz), 3.89-3.98 (m, 4H), 3.79 (s, 3H), 3.73 (s, 3H), 3.50 (dd, 2H, J = 27.2, 9.2 Hz), 3.39-3.47 (m, 2H), 3.16-3.25 (m, 2H), 2.96 (m, 1H), 2.10 (m, 1H), 1.67-1.89 (m, 5H), 1.45 (m, 1H), 1.26 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.0, 145.4, 131.7, 130.2, 129.6, 129.4, 129.1, 128.4, 127.7, 127.6, 118.7, 113.8, 85.3, 76.7, 73.1, 72.3, 69.2, 65.0, 64.6, 55.4, 50.7, 50.3, 43.6, 39.4, 38.4, 34.1, 30.2, 24.8. **IR** (NaCl, thin film) 2952 (s), 2864 (s), 1612 (m), 1512 (s), 1248 (s), 1093 (m), 1033 (w), 827 (m), 581 (w) cm^{-1}. **HRMS** (M + Na) $C_{41}H_{48}O_7Na$ Calcd: 675.3298. Found: 675.3285.



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at           3.000        PROCESSING
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sw          5998.8   proc            ft
fb            3400   fn        not used
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tpwr            63   werr
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dp               y
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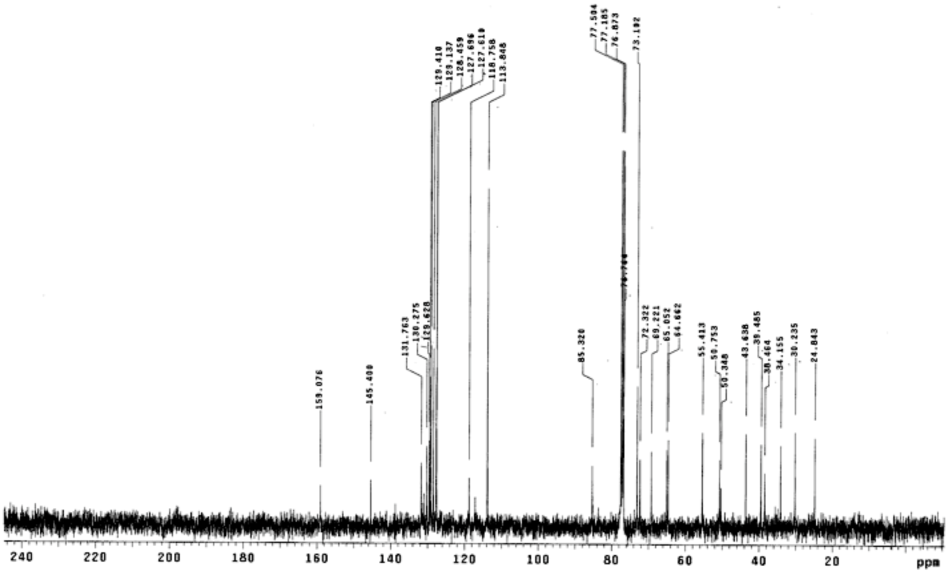
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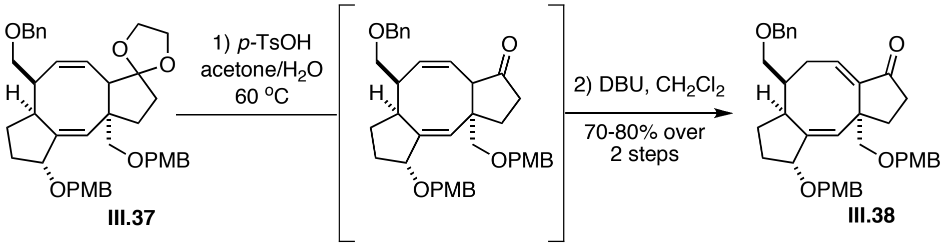


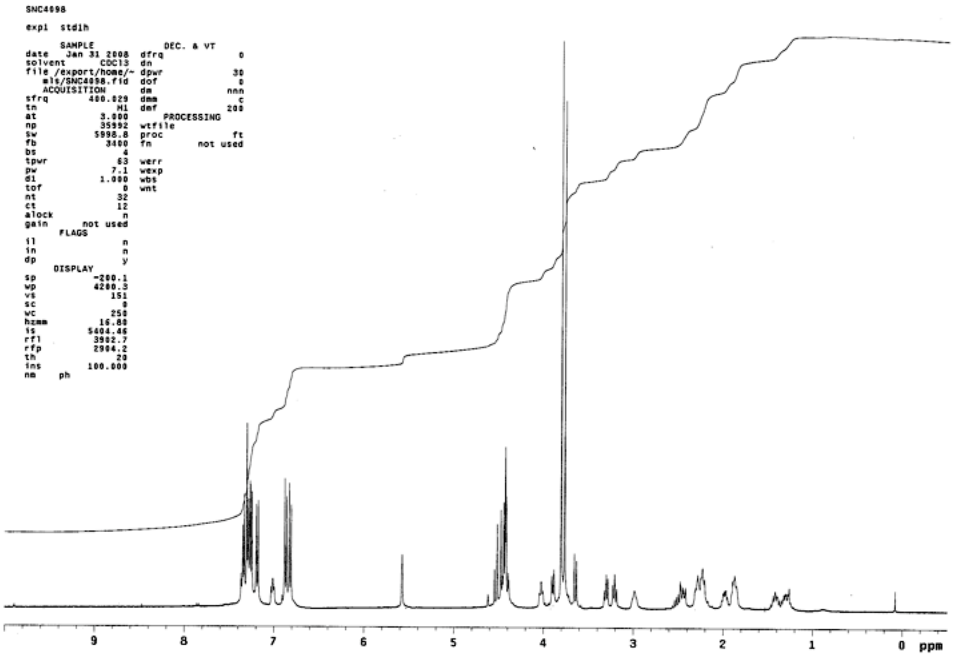
A solution of **III.37** (236 mg, 0.36 mmol) in acetone/H_2O (10:1, 7.2 mL) was degassed for five minutes. *p*-TsOH (68.8 mg, 0.36 mmol) was added and the reaction was fitted with a condenser and heated to 60 °C in a silicone oil bath under N_2. The reaction was allowed to stir for 1 hour, at which time it was cooled to room temperature and quenched with a saturated aqueous solution of $NaHCO_3$ (2 mL). The solution was extracted with EtOAc (2 x 10 mL) and the organic layers were collected, dried over $MgSO_4$, and concentrated *in vacuo*. Since the product decomposed gradually upon standing, it was subjected to the subsequent reaction without purification.

Ketone: ^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.34 (m, 5H), 7.20 (dd, 4H, J = 11.6, 8.8 Hz), 6.83 (dd, 4H, J = 13.6, 8.4 Hz), 5.59 (dd, 1H, J = 10.0, 5.2 Hz), 5.51 (td, 1H, J = 8.8, 2.0 Hz), 5.40 (s, 1H), 4.40-4.52 (m, 6H), 3.99 (t, 1H, J = 6.4 Hz), 3.79 (s, 3H), 3.75 (s, 3H), 3.65 (d, 2H, J = 9.2 Hz), 3.44 (m, 2H), 3.15 (m, 1H), 3.05 (m, 1H), 2.50-2.60 (m, 1H), 2.25 (m, 3H), 1.81-1.93 (m, 4H), 1.48 (m, 1H).

To the crude ketone dissolved in dichloromethane (5.8 mL) was added DBU (0.10 mL, 0.72 mmol). The yellow solution was allowed to stir at room temperature for 2 hours, at which time it was judged complete by TLC analysis. The reaction was concentrated *in vacuo* and the product was purified by silica gel chromatography (4:1

hexanes/EtOAc to 3:1 hexanes/EtOAc) to give **III.38** (159 mg, 0.26 mmol) in 72% yield over 2 steps as a glassy oil.

Enone (III.38): R$_f$ 0.26 (hexanes:EtOAc 2:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 7.24-7.37 (m, 7H), 7.18 (d, 2H, J = 8.4 Hz), 7.01 (t, 1H, J = 7.2 Hz), 6.85 (dd, 4H, J = 19.6, 8.4 Hz), 5.58 (s, 1H), 4.38-4.61 (m, 6H), 4.02 (t, 1H, J = 6.8 Hz), 3.89 (d, 1H, J = 9.2 Hz), 3.80 (s, 3H), 3.76 (s, 3H), 3.64 (d, 1H, J = 9.2 Hz), 3.30 (t, 1H, J = 8.8 Hz), 3.20 (t, 1H, J = 8.0 Hz), 2.98 (m, 1H), 2.41-2.53 (m, 2H), 2.17-2.30 (m, 4H), 1.95 (m, 1H), 1.87 (m, 2H), 1.26-1.46 (m, 2H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 207.1, 159.3, 146.1, 142.5, 138.6, 138.5, 131.0, 130.5, 129.4, 129.3, 128.5, 128.2, 127.7, 114.0, 113.0, 83.8, 73.3, 73.1, 71.9, 70.4, 55.5, 48.8, 42.8, 40.8, 36.2, 36.1, 30.2, 28.0, 25.7. **IR** (NaCl, thin film) 2953 (s), 2862 (s), 1716 (s), 1513 (s), 1454 (m), 1301 (w), 1248 (s), 820 (m) cm^{-1}. **HRMS** (M + Na) $C_{39}H_{44}O_6Na$ Calcd: 631.3036. Found: 631.3050.



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tn              H1  dmf           200
at           3.000      PROCESSING
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sw          5998.8  proc           ft
fb            3400  fn       not used
bs               4
tpwr            63  werr
pw             7.1  wexp
d1           1.000  wbs
tof              0  wnt
nt              32
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alock            n
gain      not used
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in               n
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nm    ph
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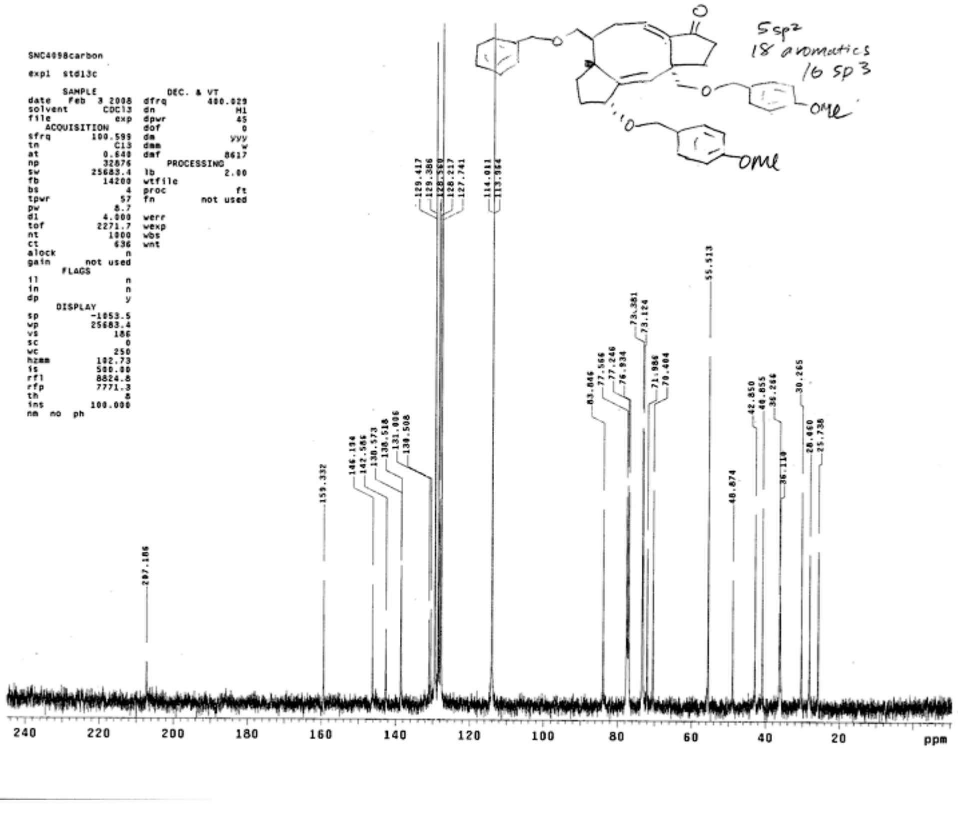

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SNC4098carbon

expl  std13c

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at            0.640 dmf          8617
np            32876     PROCESSING
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fb            14200 wtfile
bs                4 proc           ft
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pw              8.7
d1            4.000 werr
tof          2271.7 wexp
nt             1000 wbs
ct              636 wnt
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gain       not used
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dp                y
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nm  no  ph
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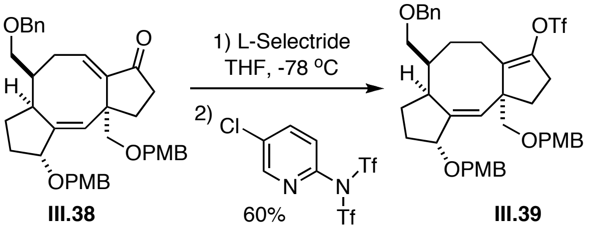
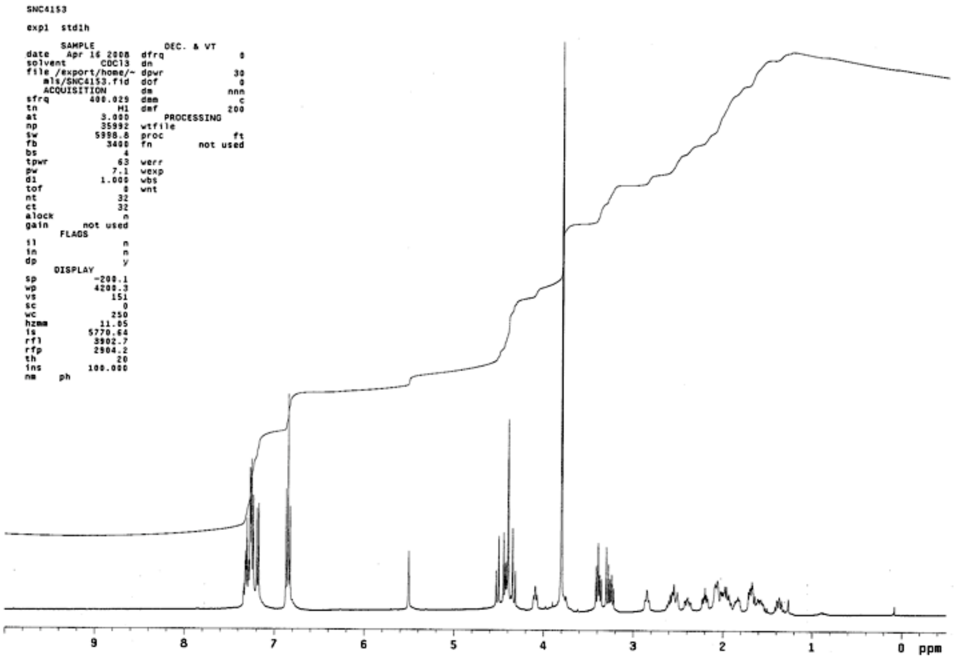
5sp2
18 aromatics
16 sp3



A solution of **III.38** (70.1 mg, 0.11 mmol) in THF (1.1 mL) was cooled to -78 ^{o}C and L-Selectride (1M THF, 0.23 mL, 0.23 mmol) was added dropwise. The yellow solution was allowed to stir at this temperature for 10 minutes, at which time a solution of Comin's reagent (90.5 mg, 0.23 mmol) in THF (0.77 mL) was added dropwise. The reaction mixture was allowed to stir at -78 ^{o}C for 30 min and judged complete by TLC analysis. The reaction was quenched with saturated aqueous NH_4Cl (0.5 mL) and allowed to warm to room temperature. The solution was diluted with water (2 mL) and extracted with EtOAc (2 x 5 mL). The organic layers were combined and washed with 10% NaOH (1 x 5 mL) and dried over $MgSO_4$. The product was purified by silica gel chromatography (4:1 hexanes/EtOAc) to give **III.39** (51.8 mg, 0.07 mmol) in 60% yield.

Triflate (III.39): R_f 0.70 (hexanes:EtOAc 2:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.23-7.32 (m, 7H), 7.18 (d, 2H, J = 8.4 Hz), 6.84 (t, 4H, J = 8.4 Hz), 5.50 (t, 1H, J = 2.4 Hz), 4.31-4.52 (m, 6H), 4.09 (dd, 1H, J = 8.8, 6.8 Hz), 3.80 (s, 3H), 3.79 (s, 3H), 3.37 (m, 2H), 3.25 (m, 2H), 2.85 (t, 1H, J = 8.8 Hz), 2.50-2.62 (m, 2H), 2.39 (ddd, 1H, J = 14, 9.6, 3.6 Hz), 2.19 (tt, 1H, J = 9.2, 4.0 Hz) 1.90-2.08 (m, 4H), 1.83 (m, 1H), 1.54-1.71 (m, 3H), 1.36 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.1, 144.6, 141.5, 138.5, 134.6, 131.0, 130.6, 129.2, 129.0, 128.4, 127.8, 127.6, 127.3, 113.9, 113.8, 83.7, 74.8, 73.4, 73.0, 72.7, 70.6, 55.4, 52.9, 41.5, 39.9, 34.4, 30.3, 29.0, 28.9, 28.4, 21.1. **IR** (NaCl, thin film) 2960 (w), 2860 (w), 1611 (m), 1512 (m), 1301 (s), 1089 (s), 1028 (s), 796 (s), 609 (w) cm^{-1}. **HRMS** (M + Na) $C_{40}H_{45}O_8F_3SNa$ Calcd: 765.2685. Found: 765.2699.



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SNC4153

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tn              H1  dmf             200
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np           35992  wtfile
sw          5998.8  proc             ft
fb            3400  fn         not used
bs               4
tpwr            63  werr
pw             7.1  wexp
d1           1.000  wbs
tof              0  wnt
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in               n
dp               y
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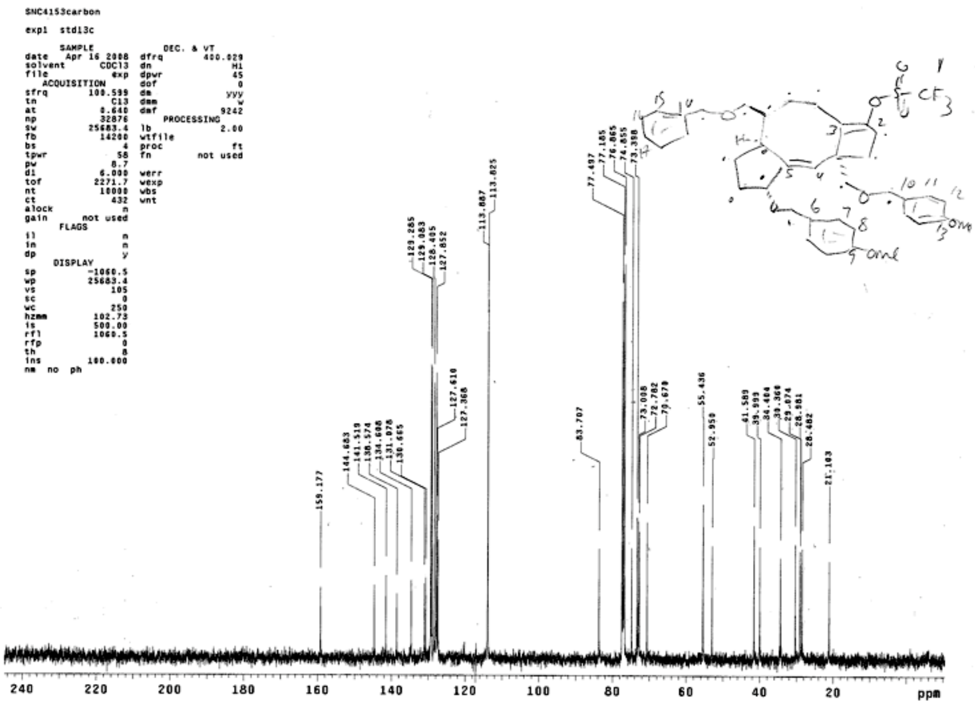

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SNC4153carbon

exp1  std13c

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sfrq       100.599   dm             yyy
tn             C13   dmm              w
at           0.640   dmf           9242
np           32876        PROCESSING
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bs               4   proc            ft
tpwr            58   fn        not used
pw             8.7
d1           6.000   werr
tof         2271.7   wexp
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alock            n
gain      not used
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in               n
dp               y
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nm  no  ph
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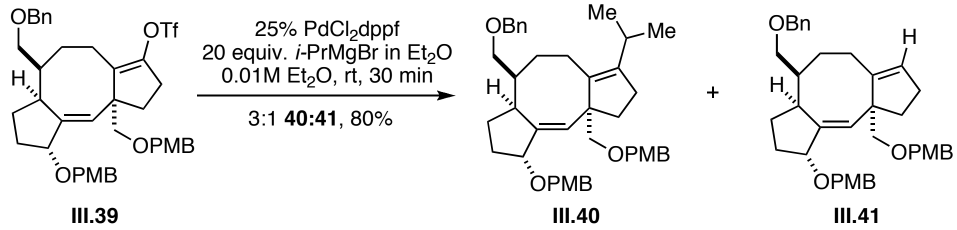
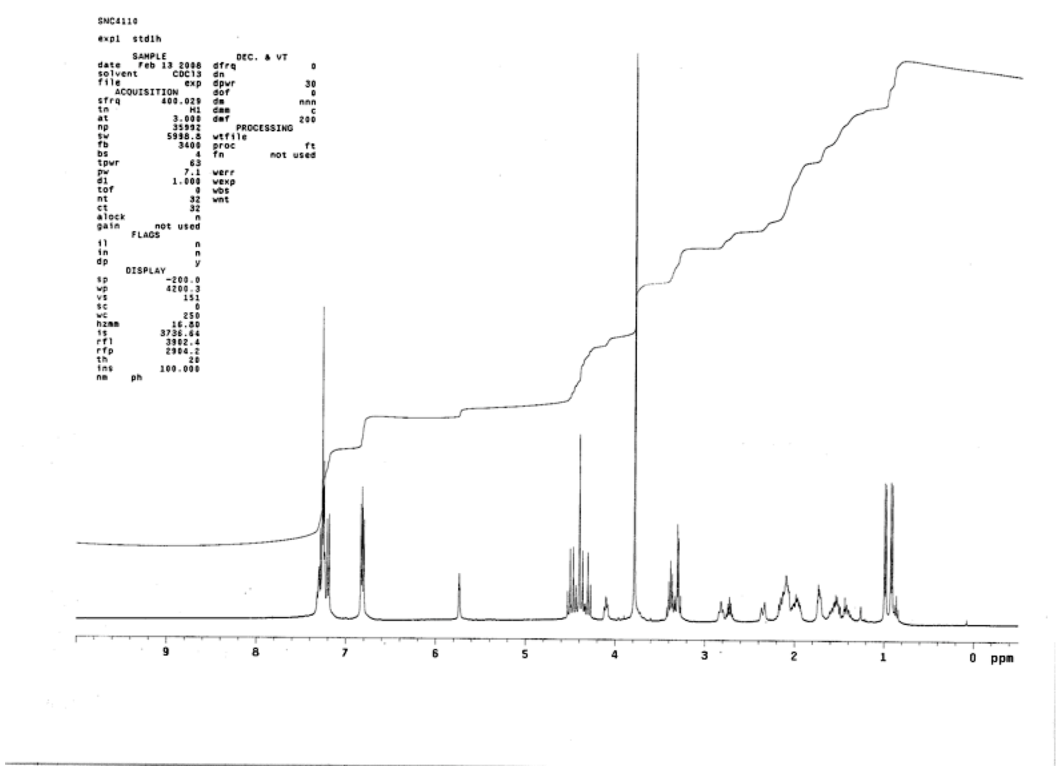


To a solution of **III.39** (40.0 mg, 0.05 mmol) in Et_2O (5.4 mL) was added [1,1'-Bis(diphenylphosphino)-ferrocene]dichloropalladium(II) complex with dichloromethane (1:1) (10.9 mg, 0.01 mmol) and the suspension was allowed to stir at room temperature for 10 minutes. Isopropyl magnesium bromide (2.1M Et_2O, 0.51 mL, 1.07 mmol) was added slowly to the pink cloudy solution. The reaction turned from pink to light yellow. The reaction was allowed to stir at this temperature for 30 minutes, at which time it was judged complete by TLC. The reaction was quenched slowly with saturated aqueous NH_4Cl (1 mL) and the solution was diluted with water (2 mL). The solution was the extracted with Et_2O (2 x 5 mL) and the organic layers were combined, washed with brine (5 mL), and dried over $MgSO_4$. The crude ^{1}H-NMR analysis showed a 3:1 ratio of **40:41**. The products were purified by silica gel chromatography (9:1 hexanes/EtOAc) to give a combined yield of 80%.

Cyclooctanoid (III.40): R_f 0.58 (hexanes:EtOAc 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.30 (m, 7H), 7.19 (d, 2H, J = 8.8 Hz) 6.81 (dd, 4H, J = 8.4, 5.4 Hz), 5.73 (t, 1H, J = 2.0 Hz), 4.27-4.53 (m, 6H), 4.10 (dd, 1H, J = 10.4, 6.4 Hz), 3.79 (s, 3H), 3.78 (s, 3H), 3.38 (m, 2H), 3.30 (dd, 2H, J = 14.0, 8.8 Hz), 2.81 (t, 1H, J = 8.4 Hz), 2.72 (quintet, 1H, J = 6.8 Hz), 2.35 (m, 1H), 1.92-2.17 (m, 6H), 1.73 (m, 2H), 1.39-1.60 (m, 4H), 0.98 (d, 3H, J = 6.8 Hz), 0.91 (d, 3H, J = 6.8 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.0, 158.9, 144.3, 138.8, 137.5, 135.1, 131.5, 131.4, 129.9, 129.2, 128.9, 128.7, 128.3, 127.7, 127.4, 113.8, 113.6, 85.2, 76.6, 73.2, 73.0, 69.8, 58.1, 55.4, 41.7, 40.5, 35.4, 31.0, 30.6, 30.5, 29.9, 27.4, 27.2, 22.5, 21.2, 21.1. **IR** (NaCl, thin film) 2954 (m), 2863 (m), 1612 (w), 1513 (s), 1247 (s), 1094 (m), 820 (w), 697 (w) cm^{-1}. **HRMS** (M + Na) $C_{42}H_{52}O_5Na$ Calcd: 659.3712. Found: 659.3690.



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SNC4110

expl  stdlh

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tn               H1   dmm                c
at            3.000   dmf              200
np            35992         PROCESSING
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ins         100.000
nm     ph
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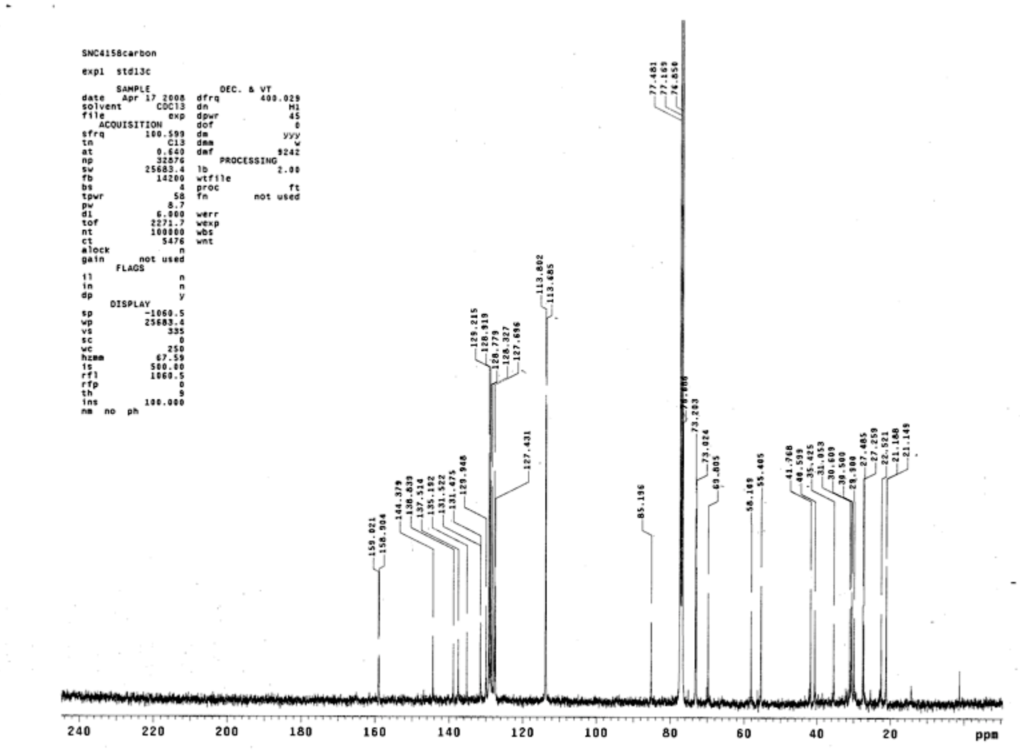
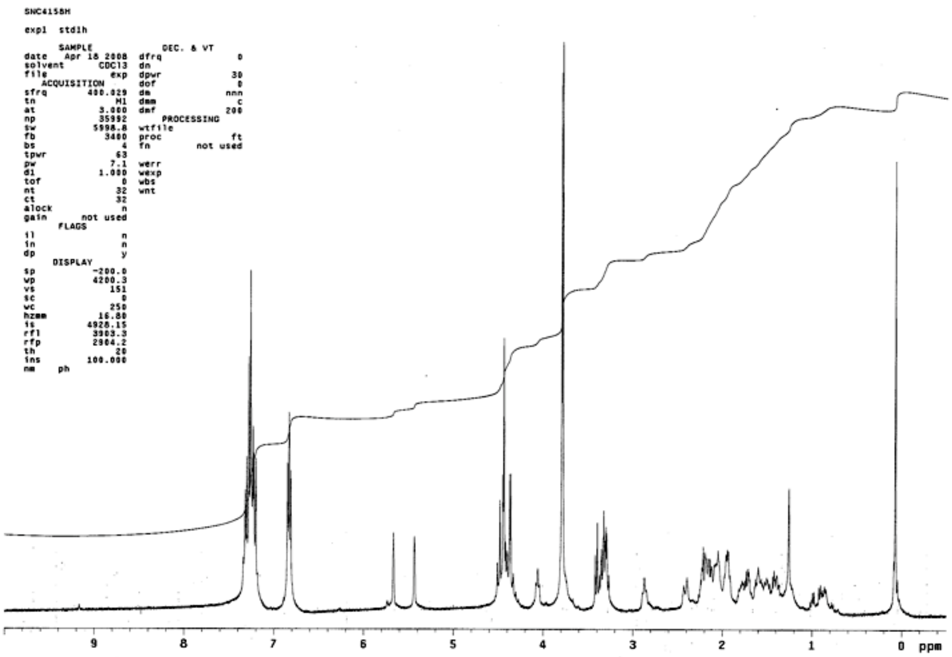


Cyclooctanoid (III.41): **R$_f$** 0.55 (hexanes:EtOAc 3:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 7.20-7.32 (m, 9H), 6.83 (dd, 4H, J = 8.4, 6.4 Hz), 5.67 (s, 1H), 5.43 (s, 1H), 4.33-4.51 (m, 6H), 4.06 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.27-3.41 (m, 4H), 2.87 (m, 1H), 2.40 (m, 1H), 1.93-2.24 (m, 6H), 1.70-1.78 (m, 2H), 1.36-1.78 (m, 4H). **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 159.1, 146.9, 140.4, 139.0, 131.4, 131.2, 129.4, 129.3, 129.2, 128.5, 128.1, 127.8, 127.6, 113.9, 113.8, 84.4, 75.2, 73.4, 73.3, 73.1, 70.2, 56.4, 55.5, 42.2, 39.7, 38.6, 31.1, 30.5, 29.5, 29.3, 25.5. **IR** (NaCl, thin film) 2931 (w), 2851 (w), 1512 (s), 1453 (w), 1245 (s), 1091 (m), 820 (w) cm^{-1}. **HRMS** (M + Na) $C_{39}H_{46}O_5Na$ Calcd: 617.3243. Found: 617.3226.



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SNC4158H

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tn              H1   dmm             c
at           3.000   dmf           200
np           35992         PROCESSING
sw          5998.8   wtfile
fb            3400   proc           ft
bs               4   fn       not used
tpwr            63
pw             7.1   werr
d1           1.000   wexp
tof              0   wbs
nt              32   wnt
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gain      not used
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in               n
dp               y
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nm    ph
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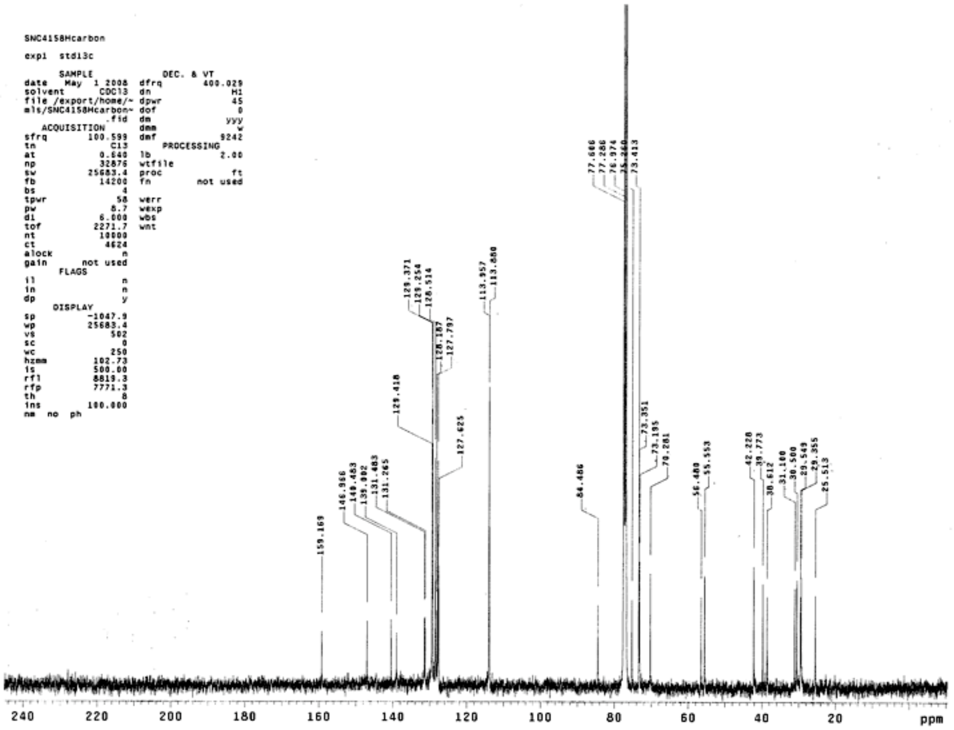

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SNC4158Hcarbon

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mls/SNC4158Hcarbon~  dof             0
              .fid   dm            yyy
   ACQUISITION       dmm             w
sfrq       100.599   dmf          9242
tn             C13         PROCESSING
at           0.640   lb           2.00
np           32876   wtfile
sw         25683.4   proc           ft
fb           14200   fn       not used
bs               4
tpwr            58   werr
pw             8.7   wexp
d1           6.000   wbs
tof         2271.7   wnt
nt           10000
ct            4624
alock            n
gain      not used
      FLAGS
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in               n
dp               y
     DISPLAY
sp         -1047.9
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nm  no  ph
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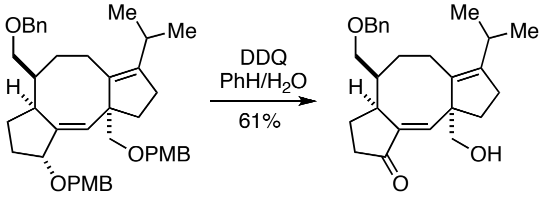

III.40 **III.42**

To a solution of **III.40** (17.3 mg, 0.03 mmol) in benzene/H_2O (10:1, 0.9 mL) was added DDQ (24.7 mg, 0.11 mmol). The reaction was allowed to stir at room temperature for 15 hours, at which time it was judged complete by TLC analysis. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (0.5 mL) and diluted with water (1 mL). The solution was extracted with EtOAc (3 x 2 mL) and the organic layers were combined and dried over $MgSO_4$. The product was purified by silica gel chromatography (4:1 hexanes/EtOAc to 2:1 hexanes/EtOAc) to afford **III.42** (6.5 mg, 0.02 mmol) in 61% yield.

Enone (III.42): R_f 0.39 (hexanes:EtOAc 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.19-7.30 (m, 5H), 6.64 (d, 1H, J = 2.8 Hz), 4.37 (d, 1H, J = 11.6 Hz), 4.25 (d, 1H, J = 11.6 Hz), 3.46 (s, 2H), 3.30 (m, 2H), 3.12 (t, 1H, J = 8.4 Hz), 2.76 (quintet, 1H, J = 7.2 Hz), 2.34-2.47 (m, 2H), 1.83-2.26 (m, 9H), 1.58-1.71 (m, 2H), 0.99 (d, 3H, J = 6.8 Hz), 0.96 (d, 3H, J = 6.4 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 208.0, 147.2, 140.9, 138.2, 135.2, 133.1, 128.4, 127.9, 127.7, 73.4, 72.0, 68.2, 59.6, 42.5, 40.6, 36.9, 34.1, 30.5, 27.7, 27.5, 27.1, 21.8, 21.7, 21.0. **IR** (NaCl, thin film) 2926 (m), 1705 (s), 1624 (s), 1453 (m), 1203 (m), 1071 (s), 913 (w), 699 (w) cm^{-1}. **HRMS** (M + Na) $C_{26}H_{34}O_3Na$ Calcd: 417.2406. Found: 417.2390.

```
SNC4160

exp1  std1h

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tn              H1   dmm              c
at           3.000   dmf            200
np           35992        PROCESSING
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fb            3400   proc            ft
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in               n
dp               y
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nm    ph
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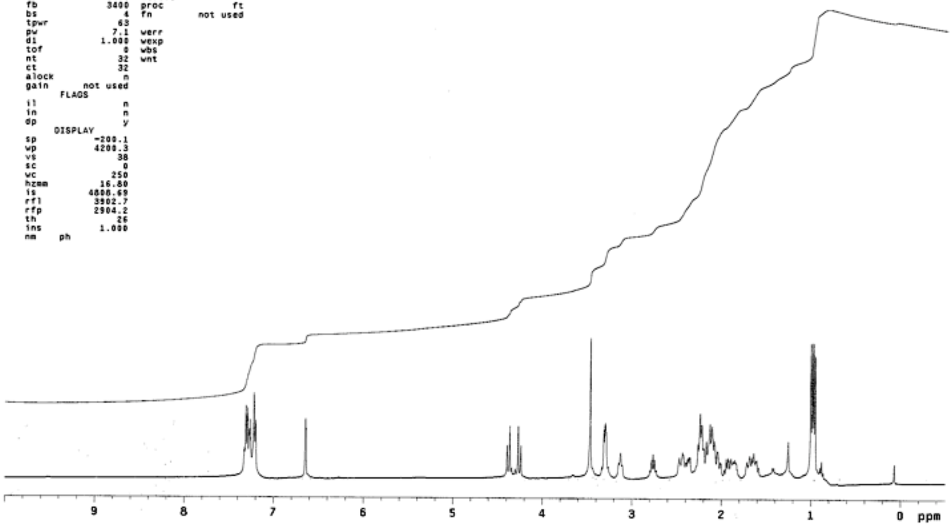

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SNC4160carbon

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at           0.640   dmf           9242
np           32876        PROCESSING
sw         25683.4   lb            2.00
fb           14200   wtfile
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d1           6.000   werr
tof         2271.7   wexp
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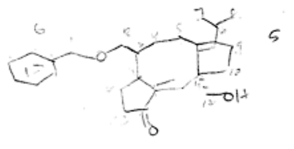
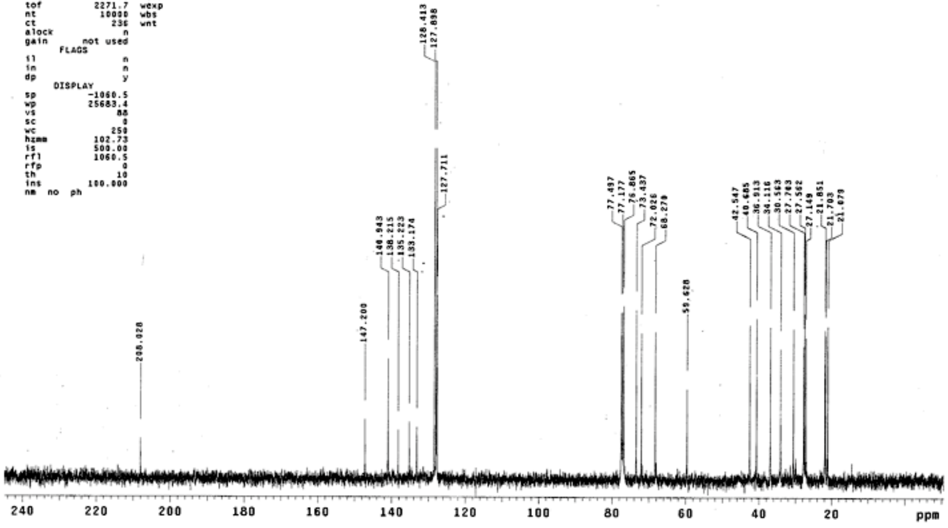
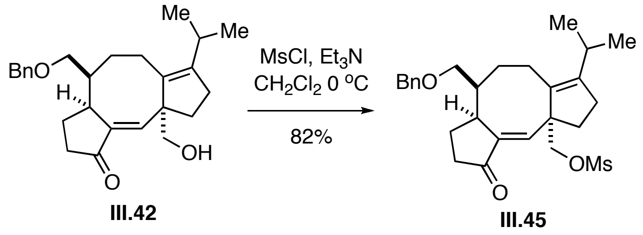
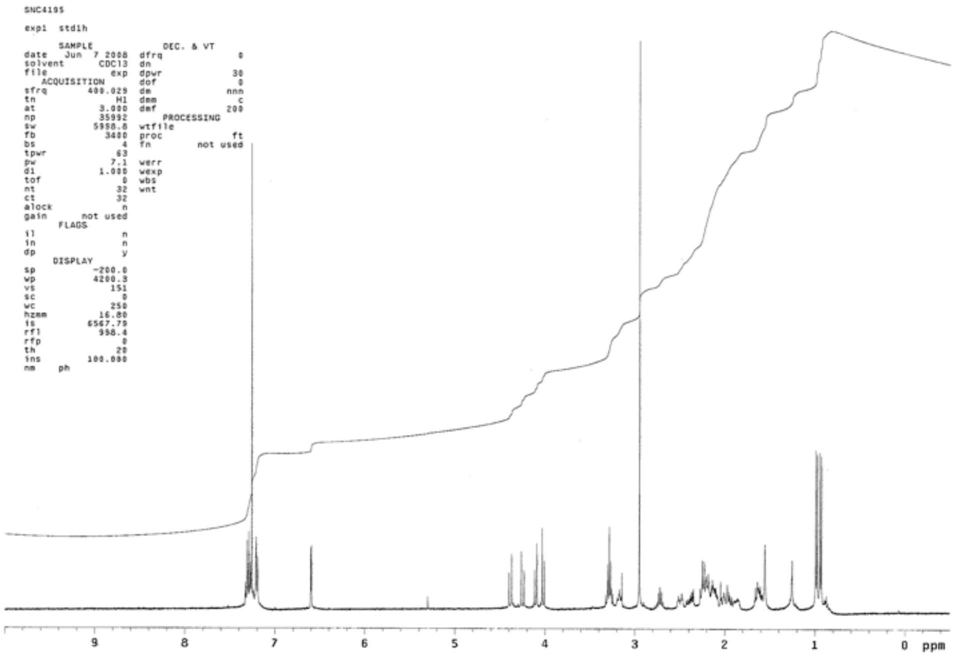






A solution of **III.42** (5.0 mg, 0.01 mmol) in dichloromethane (0.25 mL) was cooled to 0 °C and MsCl (2.18 mg, 0.02 mmol) and triethylamine (2.9 μl, 0.02mmol) were added at this temperature. The reaction was allowed to stir for 1 hour, at which time it was judged complete by TLC analysis. The reaction was quenched at 0 °C with water (0.5 mL). The solution was extracted with dichloromethane (2 x 1 mL) and the organic layers were combined and dried over $MgSO_4$. The product was purified by silica gel chromatography (3:1 hexanes/EtOAc to 1:1 hexanes/EtOAc) to afford **III.45** (4.9 mg, 0.01 mmol) in 82% yield.

Enone (III.45): **R_f** 0.50 (hexanes:EtOAc 1:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.19-7.32 (m, 5H), 6.59 (d, 1H, J = 2.8 Hz), 4.38 (d, 1H, J = 12.0 Hz), 4.25 (d, 1H, J = 12.0 Hz), 4.10 (d, 1H, J = 9.6 Hz), 4.02 (d, 1H, J = 9.6 Hz), 3.28 (m, 2H), 3.17 (m, 1H), 2.94 (s, 3H), 2.71 (quintet, 1H, J = 6.4 Hz), 2.49 (m, 1H), 2.39 (m, 1H), 1.85-2.27 (m, 9H), 1.58-1.65 (m, 2H), 0.98 (d, 3H, J = 6.8 Hz), 0.94 (d, 3H, J = 6.8 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 207.8, 147.4, 138.4, 138.1, 136.5, 132.5, 128.4, 127.9, 127.7, 73.4, 72.9, 71.9, 56.8, 42.6, 40.6, 37.6, 36.7, 34.3, 30.4, 27.5, 27.2, 26.8, 22.0, 21.2, 21.0. **IR** (NaCl, thin film) 2957 (s), 2868 (m), 1720 (s), 1632 (m), 1460 (w), 1356 (s), 1175 (s), 951 (m), 830 (w) cm^{-1}. **HRMS** (M + Na) $C_{27}H_{36}O_5NaS$ Calcd: 495.2181. Found: 495.2190.



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SNC4195

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fb             3400   proc          ft
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dp                y
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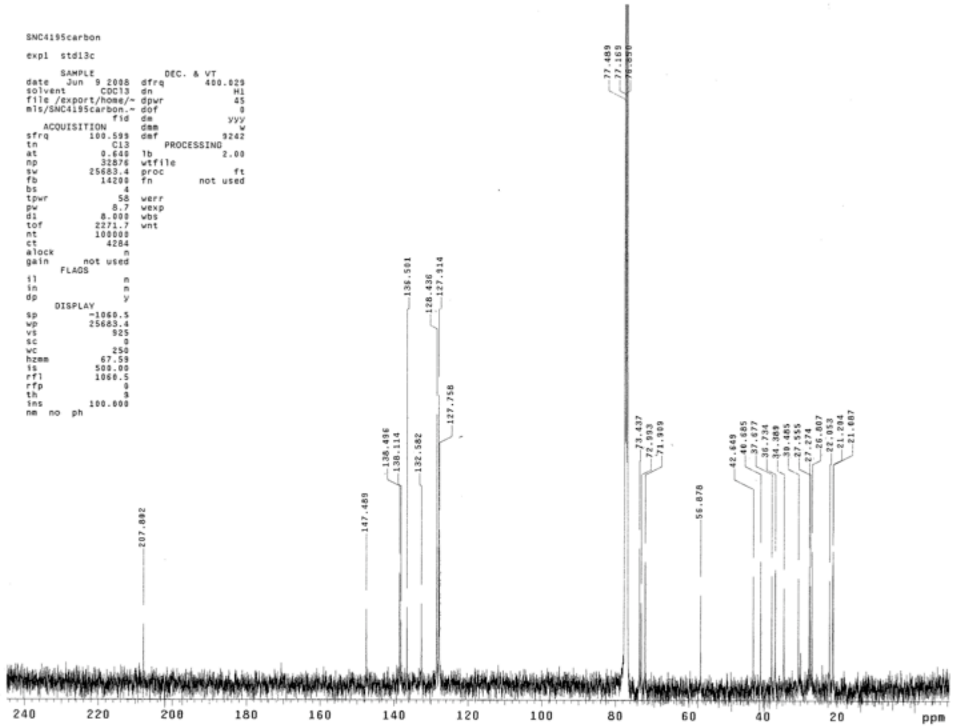

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SNC4195carbon

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                fid   dm           yyy
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sfrq        100.599   dmf         9242
tn              C13        PROCESSING
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np            32876   wtfile
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fb            14200   fn      not used
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tpwr             58   werr
pw              8.7   wexp
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tof          2271.7   wnt
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nm  no  ph
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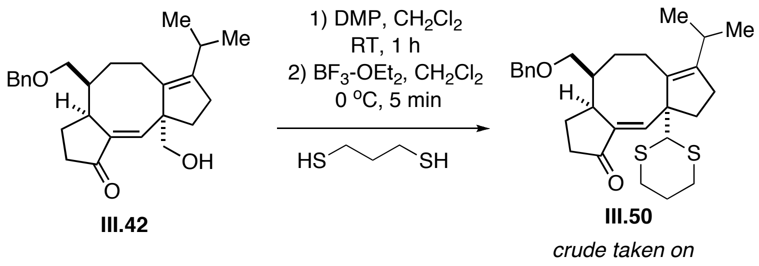
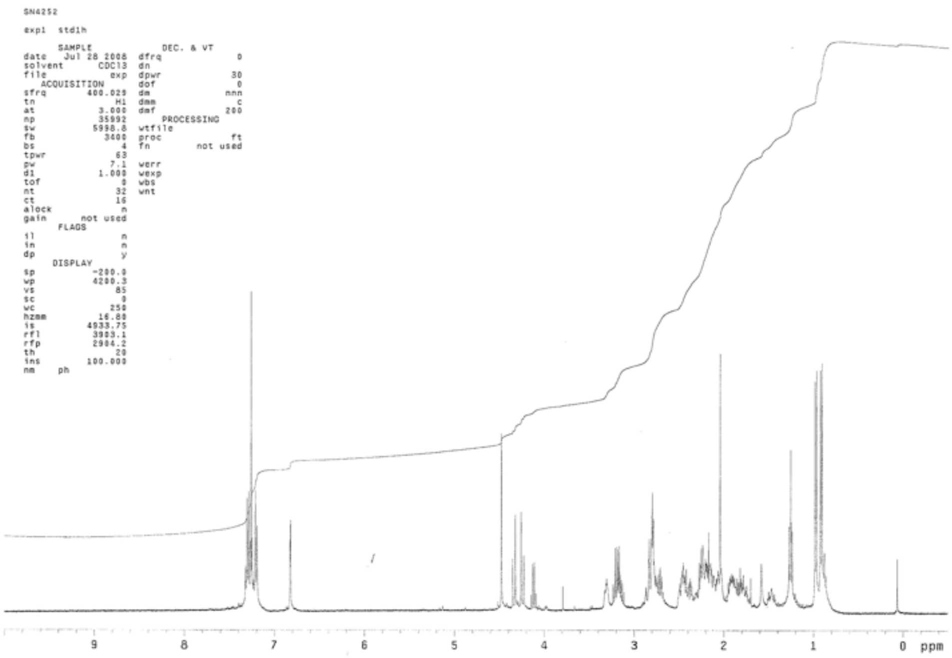


To a solution of enone **III.42** (30.0 mg, 0.07 mmol) in dichloromethane (0.76 mL) was added Dess-Martin periodinate. The reaction was allowed to stir at room temperature for 1 hour, at which time it was judged complete by TLC analysis. The reaction was quenched at room temperature with an aqueous solution of 1:1 $NaHCO_3$:$Na_2S_2O_3$ (0.5 mL). The solution was extracted with dichloromethane (3 x 1 mL) and the organic layers were combined and dried over $MgSO_4$. The crude product was then dissolved in dichloromethane (0.76 mL) and cooled to 0 ^oC. Excess 1,3-propanedithiol was added (9.87 mg, 0.09 mmol), followed by addition of excess $BF_3{\cdot}OEt_2$ (12.9 mg, 0.09 mmol). The reaction turned orange and was immediately judged complete by TLC analysis and quenched at 0 ^oC with a saturated aqueous solution of $NaHCO_3$ (0.5 mL) and warmed to room temperature. The solution was extracted with dichloromethane (1 mL) and washed with an aqueous solution of 10% NaOH (1 mL). The organic layers were separated and dried with $MgSO_4$, filtered, and the crude residue was run through a basic alumina plug (3:1 hexanes/EtOAc). Dithiane **III.50** (24.4 mg) was taken on immediately.

Dithiane (III.50): **R_f** 0.24 (hexanes:EtOAc 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.19-7.30 (m, 5H), 6.82 (d, 1H, J = 2.4 Hz), 4.47 (s, 1H), 4.34 (d, 1H, J = 12.0 Hz), 4.24 (d, 1H, J = 12.0 Hz), 3.30 (m, 1H), 3.11-3.23 (m, 2H), 2.69-2.86 (m, 5H), 2.35-2.48 (m, 3H), 2.02-2.35 (m, 7H), 1.74-1.95 (m, 4H), 1.46 (m, 1H), 0.98 (d, 3H, *J* = 6.8 Hz), 0.91 (d, 3H, *J* = 7.2 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 208.0, 147.3, 143.4, 138.1, 135.9, 133.4, 128.3, 128.0, 127.7, 73.4, 72.5, 60.8, 59.1, 43.9, 39.7, 36.4, 36.0, 31.7, 31.5, 30.4, 28.2, 27.6, 26.9, 26.3, 22.7, 21.1, 20.8.



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SN4252

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dp               y
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nm     ph
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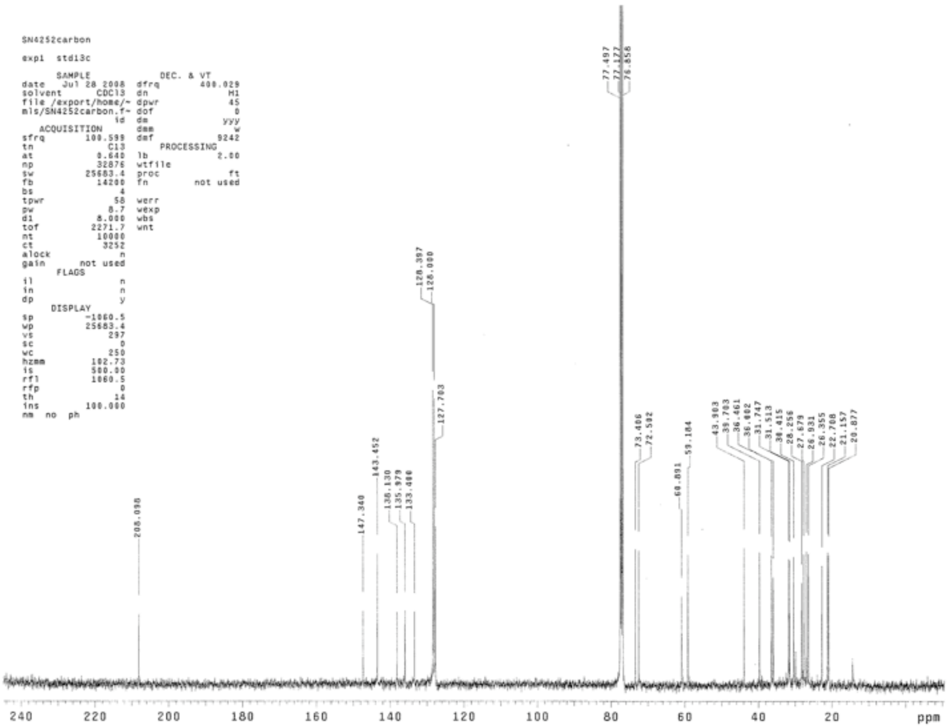

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SN4252carbon

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sfrq       100.599   dmf           9242
tn             C13        PROCESSING
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sw         25683.4   proc            ft
fb           14200   fn        not used
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tpwr            58   werr
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gain      not used
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dp               y
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nm  no  ph
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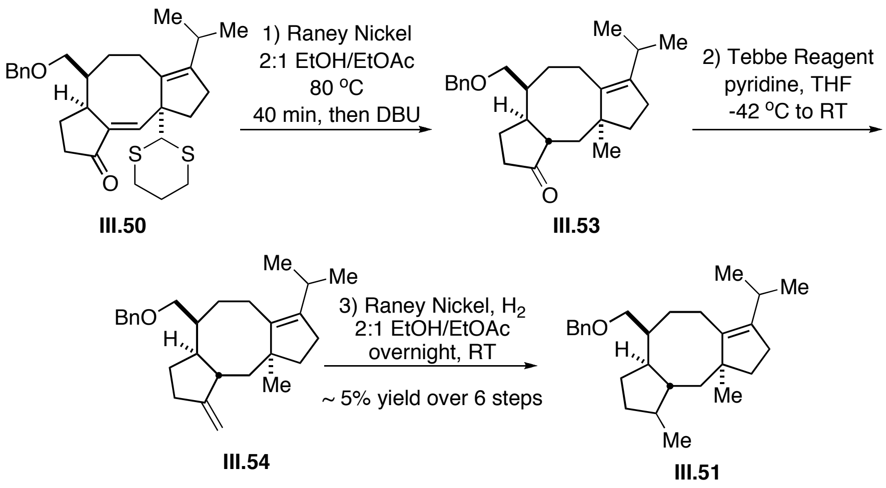
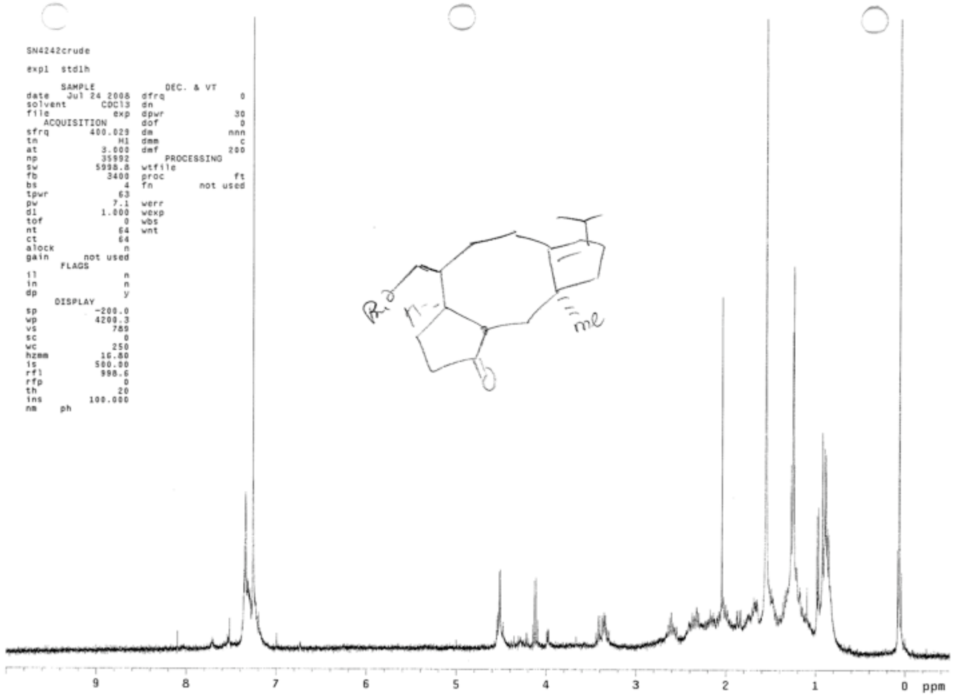


III.50 **III.53** **III.54** **III.51**

Note: This procedure was optimized at 12 mgs of dithiane **III.50**. Two cm^3 of Raney Nickel 2800 (measured from a 1 cm^3 spoon) were added to a round bottom flask fitted with a stir bar and washed with acetone (1 x 1 mL) and then with ethanol (1 x 1mL). Ethanol (10 mL) was added to the nickel and the slurry was stirred under an atmosphere of nitrogen. A solution of dithiane **III.50** (12.0 mg, 0.025 mmol) in ethyl acetate (5 mL) was added to the nickel/ethanol slurry. The reaction was then fitted with a reflux condenser and submerged in a pre-heated 80 ^{o}C bath and allowed to stir for 40 minutes. The reaction was judged complete by TLC analysis and cooled to room temperature. The gray solution was filtered through celite with several washes of ethyl acetate and the filtrate was concentrated and purified silica gel chromatography (4:1 hexanes/EtOAc). The resulting crude oil was diluted with dichloromethane (1 mL) and treated with several drops of DBU, at which time was concentrated and run through a plug of silica gel to yield ketone **III.53** (3.7 mg, 0.009 mmol) and was immediately taken on to the next step.

Ketone (III.53): **R$_f$** 0.67 (hexanes:EtOAc 3:1); **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 7.26-7.35 (m, 5H), 4.47-4.55 (m, 2H), 3.29-3.44 (m, 2H), 2.54-2.62 (m, 2H), 1.15-2.37 (m, 17H), 0.98 (d, 3H, *J* = 7.2 Hz), 0.93 (s, 3H), 0.89 (d, 3H, *J* = 6.8 Hz). **HRMS DART** (M+H) $C_{26}H_{37}O_2$ Calcd: 381.2795. Found: 381.2789. **IR** (NaCl, thin film) 2956 (s), 2869 (2), 1726 (s), 1462 (m), 1262 (s), 1075 (s), 800 (m) cm^{-1}.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SN4242crude

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ins        100.000
nm     ph
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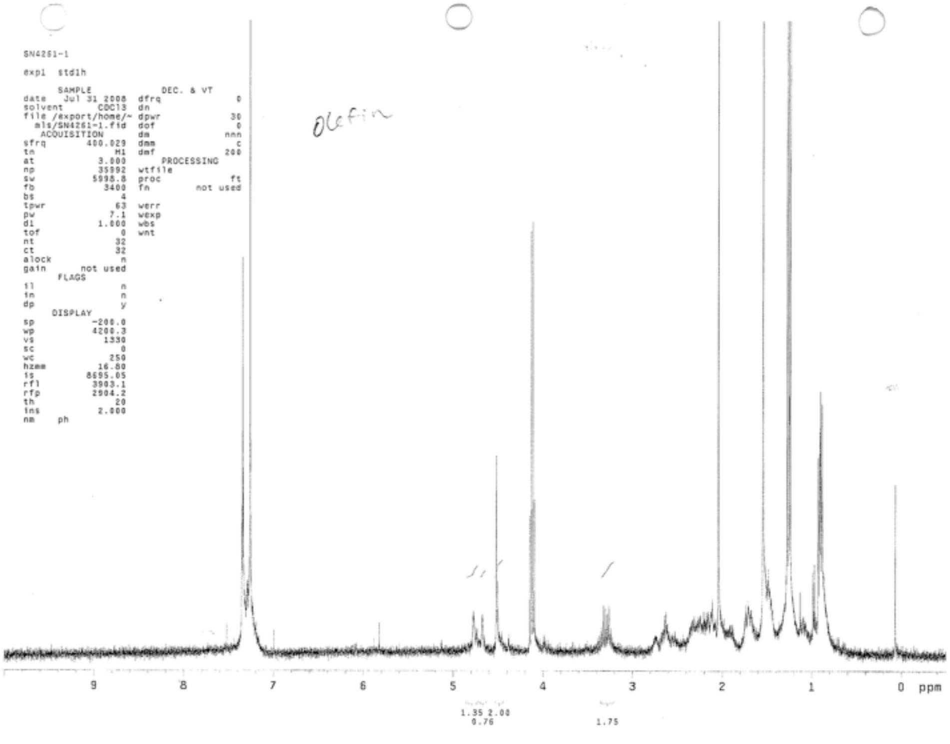
To a solution of ketone **III.53** (2.3 mg, 0.006 mmol) in THF (0.06mL) was added pyridine (1.43 mg, 0.018 mmol) and cooled to -42 °C in a dry ice/ acetonitrile bath. Tebbe reagent (0.29 M in toluene, 0.042 mL, 0.012 mmol), which was previously titrated with acetophenone, was added to the reaction flask. The reaction flask was allowed to stir for 30 min at this temperature and then warmed to room temperature, at which time was judged complete by TLC analysis. The reaction was cooled again to -42 °C and carefully quenched with an aqueous solution of 10% NaOH (0.1 mL). The solution was then diluted with hexanes (1 mL) and filtered through a plug of celite. The crude product was run through a plug of silica gel (9:1 hexanes/EtOAc) to afford **III.54** (1.5 mg, 0.004 mmol) and immediately taken on to the next step.

Olefin (III.54): $\mathbf{R_f}$ 0.89 (hexanes:EtOAc 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.35 (m, 5H), 4.77 (m, 1H), 4.67 (m, 1H), 4.51 (m, 2H), 3.26-3.34 (m, 2H), 2.52-2.64 (m, 3H), 1.89-2.43 (m, 8H), 1.68-1.74 (m, 3H), 1.48 (m, 5H), 0.98 (d, 3H, J = 7.2 Hz), 0.93 (s, 3H), 0.89 (d, 3H, J = 6.8 Hz). **HRMS DART** (M+H) $C_{27}H_{39}O_2$ Calcd: 379.3000. Found: 379.2989.



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SN4261-1

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sw           5998.8  proc            ft
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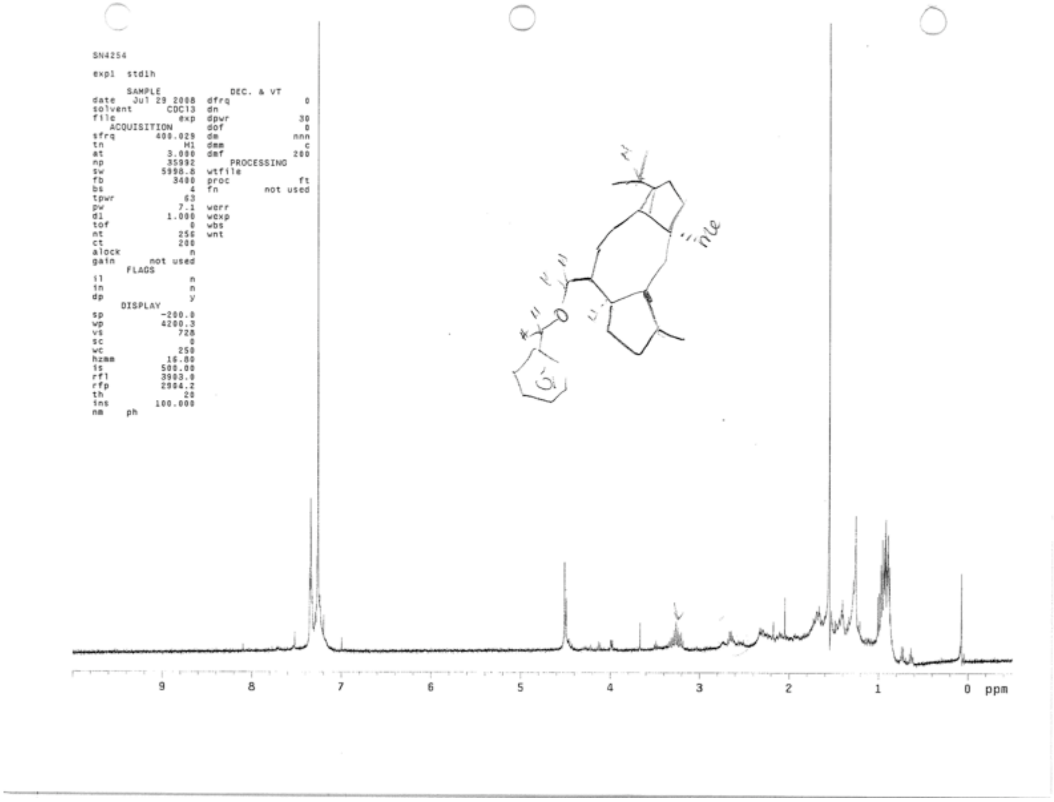
nm     ph
```

One cm^3 of Raney Nickel 2800 (measured from a 1 cm^3 spoon) was added to a round bottom flask fitted with a stir bar and washed with acetone (1 x 1 mL) and then with ethanol (1 x 1mL). Ethanol (0.27 mL) was added to the nickel and the slurry was stirred under an atmosphere of nitrogen. A solution of olefin **III.54** (3.1 mg, 0.008 mmol) in ethyl acetate (0.13 mL) was added to the nickel/ethanol slurry. The reaction was then stirred under an atmosphere of H_2 with a balloon for 15 hours. The slurry was then filtered though celite with several washes of ethyl acetate and concentrated. The product was purified by silica gel chromatography (pentane to 9:1 pentane/EtOAc) to give **III.51** (1.5 mg, 0.003 mmol) in an unoptimized 5% yield over 6 steps.

Cyclooctanoid (III.51): R_f 0.89 (hexanes:EtOAc 3:1); **^{1}H-NMR *partial*** ($CDCl_3$, 400 MHz) δ 7.32-7.35 (m, 5H), 4.50 (m, 2H), 3.20-3.29 (m, 2H), 2.64 (m, 3H). **^{13}C-NMR *partial*** ($CDCl_3$, 100 MHz) δ 142.8, 138.9, 128.5, 128.4, 127.8, 127.7. **HRMS DART** (M+H) $C_{27}H_{41}O_1$ Calcd: 381.3157. Found: 381.3134. **HRMS DART** (M-OH) $C_{20}H_{33}$ Calcd: 273.2582. Found: 273.2578.



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SN4254

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tof              0  wbs
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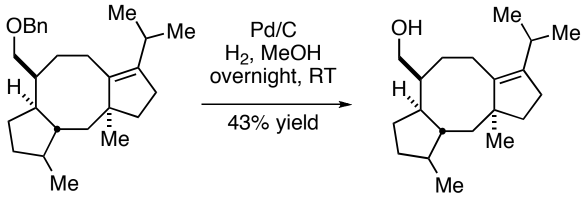
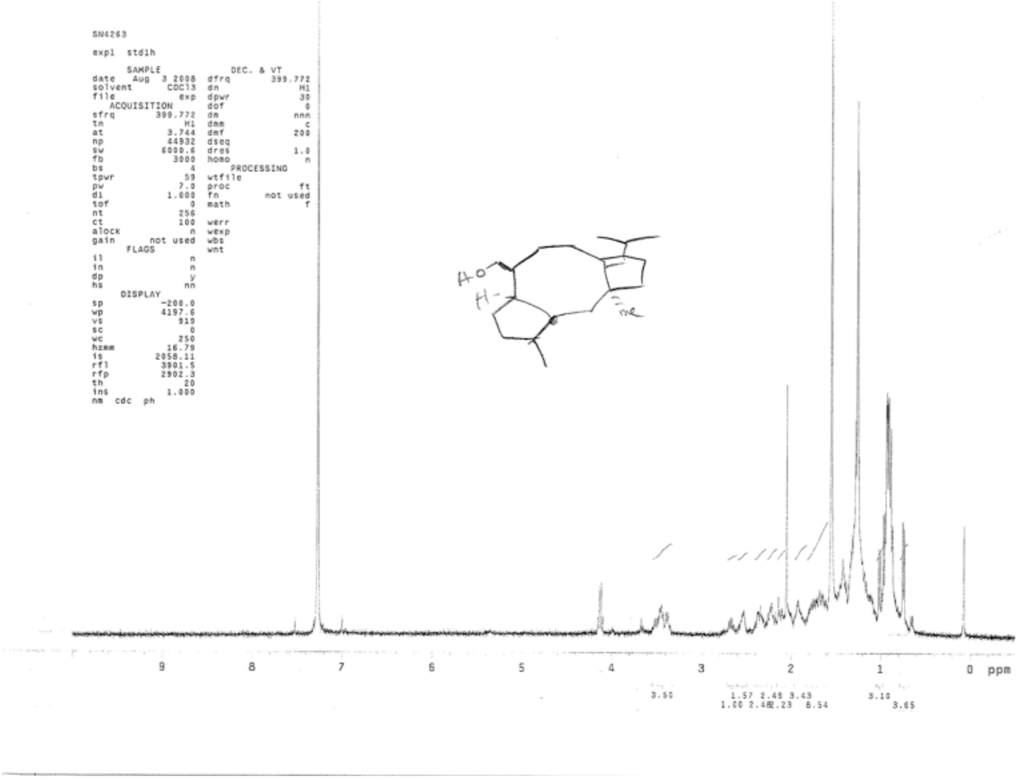


III.51 **III.52**

To a solution of **III.51** (1.5 mg, 0.003 mmol) in MeOH (0.1 mL) was added a spatula tip of 10% Pd on carbon (excess). The reaction was stirred under an atmosphere of H_2 with a balloon for 20 hours or until judged complete by TLC analysis. The slurry was filtered through celite with several washes of EtOAc and concentrated. The product was purified by silica gel chromatography (9:1 pentane/EtOAc) to yield desired alcohol **III.52** (0.4 mg, 0.001 mmol) in a 43% yield.

Alcohol (III.52): R_f 0.45 (hexanes: EtOAc 3:1); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 3.36-3.51 (m, 2H), 2.67 (m, 1H), 2.52 (m, 2H), 1.15-2.36 (m, 8H), 1.01 (d, 3H, J = 6.8 Hz), 0.95 (d, 3H, J = 6.4 Hz), 0.93 (s, 3H), 0.74 (d, 3H, J = 6.8 Hz). **HRMS DART** (M+H) $C_{20}H_{25}O$ Calcd: 291.2687. Found: 291.2673. **HRMS DART** (M-OH) $C_{20}H_{33}$ Calcd: 273.2582. Found: 273.2570.



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SN4263

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nm  cdc  ph
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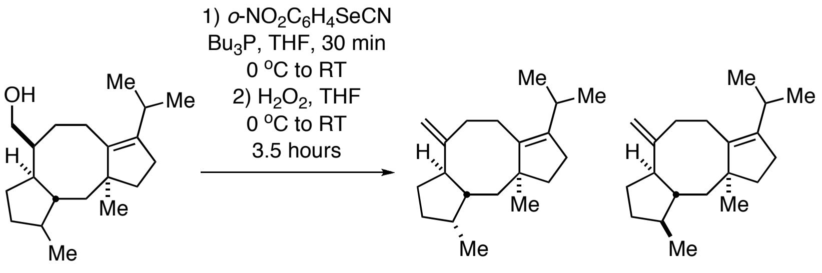

III.52 **III.8** **III.55**

To a solution of **III.52** (0.4 mg, 0.001 mmol) in THF (0.069 mL) was added 2-nitrophenyl selenocyanate (2.95 mg, 0.013 mmol). The reaction was cooled to 0 °C and tributyl phosphine (3.85 μL, 0.015 mmol) was added, turning the solution dark red. The reaction was allowed to warm to room temperature, at which time the reaction turned orange. The reaction was allowed to stir for 30 min, at which time was judged complete by TLC analysis. The solution was immediately purified by silica gel chromatography (9:1 pentane:EtOAc) to give an oil. The oil was diluted with THF (0.03 mL) and cooled to 0 °C. Hydrogen peroxide (30% in water, 5 μL) was added and the bright yellow reaction was allowed to stir at room temperature. After 3.5 hours, the pale yellow solution was judged complete by TLC analysis and the solution was purified by silica gel chromatography (pentane) to collect a mixture of **III.8** and **III.55**.