Calcd for $B_7C_9H_{15}$: C, 54.35; H, 7.60. Found: C, 54.54; H, 7.70.

Reaction of $Na^+C_2B_7H_{12}^-$ with $(CO)_5W\{=C(OCH_3)(C_6H_5)\}$. The general procedure as described above was employed by using 3 mmol of $Na^+C_2B_7H_{12}^-$, except that $(CO)_5W\{=C(OCH_3)(C_6H_5)\}$ (1.4 g, 3.2 mmol) was used instead of $(CO)_5Cr\{=C(OCH_3)(C_6H_5)\}$ and that the reaction was run until completion (12 h). The completion of the reaction was monitored by ^{11}B NMR spectroscopy. After *ca.* 2 h of further stirring, green brown reaction mixture was connected to a vacuum and the solvent was evaporated. The residue was dissolved in dry CH_2Cl_2, cooled to −78 ℃ and HCl/Et_2O (5.0 mmole, 1.7 equiv) was added. Cooling bath was removed, and the heterogeneous reaction mixture was stirred for 1 h at −10 ℃. The reaction mixture was quickly filtered through an activated pad of silica gel, and the solvent was removed under vacuum. The crude residue was purified by sublimation under 0.01 mmHg at room temperature gave **IIb** (0.31 g, 1.6 mmol, 52% yield).

Acknowledgment. This work was supported in part by the Basic Science Research Institute program, Ministry of Education (BSRI-94-3407) and the Korea-USA Cooperative Research Program, the Korea Science & Engineering Foundation. We thank for Dr. Larry G. Sneddon for help in obtaining NMR results and for useful discussions and suggestions.

References

1. (a) Jeon, H. J.; Ko, J. J.; Kim, S. J.; Shin, D. S.; Kang, S. O. *Bull. Kor. Chem. Soc.* **1992**, *13*, 220. (b) Jeon, H. J.; Ko, J. J.; Lee, G. B.; Kang, S. O. *Bull. Kor. Chem. Soc.* **1992**, *14*, 113.
2. (a) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580. (b) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445. (c) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Muller, J. *J. Organomet. Chem.* **1969**, *16*, p 29.
3. Kang, S. O.; L. G. Sneddon, In *Electron Deficient Boron and Carbon Clusters*; G. A. Olah, K. Wade, and R. E. Williams Eds.; John Wiley and Sons: New York, 1990; p 195.
4. Kang, S. O.; Furst, G. T.; Sneddon, L. G. *Inorg. Chem.* **1989**, *28*, 2339.
5. (a) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1665. (b) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1672. (c) Plumb, C. A.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1681.
6. (a) Su, K.; Barnum, B.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 2730. (b) Su, K.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1993**, *115*, 10004.
7. (a) Tebbe, F. N.; Garret, P. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1966**, *88*, 607. (b) Tebbe, F. N.; Garret, P. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 869.
8. Kang, S. O.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 3281.
9. Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*; 2nd ed.; Wiley: New York, 19 86.
10. Garrett, P. M.; George, T. A.; Hawthorne, M. F. *Inorg. Chem.* **1969**, *8*, 2008.
11. (a) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University Press: Delft, Holland, 1982. (b) Finster, D. C.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 400. (c) Venable, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

Resonance Raman Spectra of High-Valence Fluorooxoiron Tetrakis(pentafluorophenyl)porphyrin

Insook Rhee Paeng and Ki-Jung Paeng*†

Department of Chemistry, Seoul Woman's University, Seoul 139-774, Korea
†Department of Chemistry, Yonsei University, Wonju 222-701, Korea

Received June 7, 1995

The high valence oxoferryl porphyrins are often found in many heme containing enzymes as reaction intermediates in their respectable reaction cycles.[1~3] Given the diverse chemistry catalyzed by these various enzymes, the heme pocket modulation of the chemical reactivity of the $Fe^{IV}=O$ unit seems. Resonance Raman (RR) detection of the ν ($Fe^{IV}=O$) in various protein species and model compounds supports this notion.[4]

The tetrakis(pentafluorophenyl)porphyrin iron(III) chloride, Fe(TPFP)Cl, is one of the halogen substituted tetraphenylporphyrins (TPP) and have been frequently used as a mono oxygen transfer catalyst because of its high reactivity and its high resistence of the porphyrin ring to oxidative degradation. Fe(TPFP)Cl, which is known as the most electron deficient metalloporphyrin,[5] forms a very stable non-radical oxoferryl porphyrin through the reaction with oxidant such as *m*-chloroperoxybenzoic acid (mCPBA) at low temperature. That is contrast to a electron rich iron tetramesityl porphyrin chloride, Fe(TMP)Cl, which forms the π-cation radical oxoferryl porphyrin upon oxidation.[6] Thus, Fe(TFPF)Cl is an excellent target material to investigate the major role of porphyrin moeity in the active center of oxidation reaction. Goff *et al.*[7] reported that addition of mCPBA to Fe(TPP)F at −78 ℃ produces a fluorooxo iron(IV) porphyrin π-cation radical and binding of basic, "hard" axial ligand such as fluoride ion might stabilize the highly oxidized iron porphyrin species. The anion ligated oxoferryl porphyrins haven't had much attention. Especially, no vibrational data are available.

In this note, we report the RR spectra of oxoferryl iron porphyrin with fluoride ligand, O=Fe(TPFP)F in the presence or absence of hydrogen bonding, for the first time. We also obtained the RR spectra of O=Fe(TPFP)X (X= $OClO_3^-$, mCB^-). Finally, it is discussed the structure of this species and the magnitude of the trans ligand effect for those three anions in the O=Fe(TPFP)X.

*To whom correspondence should be addressed.

Table 1. Resonance Raman Frequencies of O=Fe(TPFP)X Species

Porphyrins	ν(Fe=O)	ν_4	ν_2
Fe(TPFP)*Cl		1366	1564
OFe(TPFP)	845(807)	1370	1569
OFe(TPFP)THF	841(−)	1370	1576
OFe(TPFP)DMF	835(−)	1370	1575
OFe(TPFP)Im	820(−)	1370	1375
OFe(TPFP)F	820(785)	1371	1579
OFe(TPFP)F·H_2O	811(780)	1369	1575
OFe(TPFP)(mCB)**	835(796)	1371	1579
OFe(TPFP)($OClO_3$)	838(799)	1371	1580

*Tetrakis(pentafluorophenyl)porphyrin. **m-chlorobenzoic acid

Experimental

Fe(TPFP)Cl and TBAF·$3H_2O$ were purchased from Aldrich chemical Co. and used without further purification. Oxygen labeled mCPBA[-$^{16}O^{16}O$-, -$^{18}O^{18}O$-, and scrambled (-$^{16}O^{16}O$- : -$^{16}O^{18}O$- : -$^{18}O^{18}O$-=1 : 2 : 1)] were prepared by the methods of Johnson[8] and Brown.[9] The reaction product was checked by O-O stretching vibration band in the Raman spectra. The solvent, methylene chloride, was purchased from Aldrich chemical Co. and dried by reflux over calcium hydride prior to use.

Low temperature Raman experiments were performed using a low temperature stirred dewar cell (LSC) with two mirror back scattering or cylinderical lens set up.[5] The sample solution was degassed by nitrogen gas for at least 30 min before use. The LSC was stirred by magnetic stirring bar rotated by externally mounted stirring rod. All reactants were introduced by syringe. The samples were kept at −78 ℃ by dry ice-acetone solution.

RR spectra were recorded on a Spex Model 1403 double monochromator coupled with a Hamamatsu R-928 photomultiplier and a Spex DM1B data station. Excitation at 406.7 nm was made with a Coherent Model Innova 100-K3 Kr^+ ion laser. The laser power on the sample was kept at 5-10 mW througout this work.

Results and Discussion

Previously, we[10] observed the RR spectra of the oxidation product of Fe(TPFP)Cl with mCPBA in methylene chloride solution at −78 ℃ and obtained $\nu(Fe^{IV}=O)$ at 845 cm^{-1}, which shifted to 807 cm^{-1} upon $^{16}O/^{18}O$ isotope substitution, for a five coordinate oxoferryl porphyrin, O=Fe(TPFP). The $\nu(Fe^{IV}=O)$ frequencies in Table 1 indicate that the influence of the trans ligand is large. $\nu(Fe^{IV}=O)$ is at 845 cm^{-1} in the absence of the trans ligand. And it is at 841 cm^{-1} for tetrahydrofuran(THF) and at 829 cm^{-1} for dimethylformamide (DMF) which are moderate neutral trans ligands. In the case of strong trans ligand such as imidazole (Im), it is shifted to 820 cm^{-1}.

Figure 1 shows the RR spectra (406.7 nm excitation) of Fe(TPFP)Cl solution which was dissolved together with TBAF·$3H_2O$ in dry methylene chloride solution and added mCPBA at −78 ℃. Trace A of Figure 1 obtained with ^{16}O labeled mCPBA and exhibits the typical band of Fe(TPFP) at 860 cm^{-1} and a new band at 811 cm^{-1}, which shifts to 780 cm^{-1} when ^{18}O labeled mCPBA is employed (Trace B). A similar experiment with an isotopically scrambed mCPBA gives two distinct Raman bands at 811 and 780 cm^{-1} with equal intensity (not shown). The fact that no new band is seen between these two bands rules out the possibility of assigning these bands to the ν(O-O) of the peroxo species, (TPFP)Fe-O-O-Fe(TPFP). The 811(780) cm^{-1} band cannot be attributed to the ν_5(Fe-O) of the μ-oxo dimer, (TPFP)Fe-O-Fe(TPFP) since it should show the ν_5(Fe-O) around 366 cm^{-1}.[11] Finally, these cannot be attributed to the dioxo species, Fe(TPFP)$(O)_2$ since their ν(O=Fe=O) frequencies should show three Raman bands when scrambled mCPBA is applied. The observed shift ($\Delta\nu$=31 cm^{-1}) is in good agreement with the calculated value ($\Delta\nu$=35 cm^{-1}) expected for a diatomic Fe-O vibrator. Thus, the bands at 811 and 780 cm^{-1} can be assigned to the ν (Fe=O) of ^{16}O=Fe(TPFP) F and its ^{18}O analogue, respectively. The structure of that will be discussed later in this note.

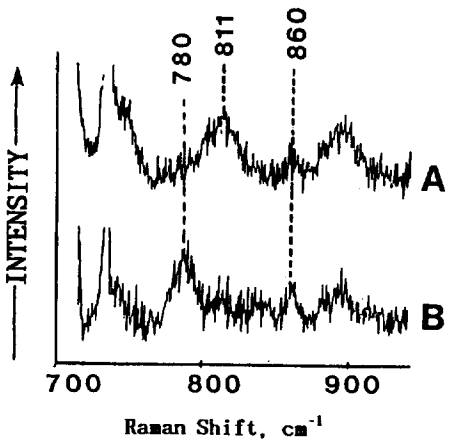


Figure 1. Resonance Raman spectra (406.7 nm excitation) of reaction product of Fe(TPFP)Cl with mCPBA in the presence of TBAF·$3H_2O$ in methylene chloride solution at −78 ℃. A: with -$^{16}O^{16}O$-mCPBA. B: with -$^{18}O^{18}O$-mCPBA.

The similar experiment were done with the dry condition by using TBAF anhydrous (TBAF·AH). When Fe(TPFP)Cl is dissolved together with TBAF·AH and ^{16}O labeled mCPBA in dry methylene chloride solution, a new band appears at 820 cm^{-1} which shifts to 785 cm^{-1} upon $^{16}O/^{18}O$ isotope substitution. As expected, only two ν(Fe=O) bands are observed at 820 cm^{-1} and 785 cm^{-1} when scrambled mCPBA is used (Figure 2A). The high frequency spectra (ν_4, oxidation and ν_2, spin state sensitive bands: Table 1) with and without water content were very similar.

Figure 2 shows a series of RR spectra of Fe(TPFP)Cl dissolved with TBAF·AH and added a different molar ratio(R) of scrambled mCPBA (R=[scrambled mCPBA]/[Fe(TPFP)Cl], Figure 2A; R=2, 2B; R=20 and 2C; R=50). The most significant features of these spectra are the frequency of ν (Fe=O) which depends on the molar ratio of the two compounds. On going from trace A to C, an oxygen sensitive ν (Fe=O) at 820 and 785 cm^{-1} disappear and those at 836 and 796 cm^{-1} are the marked strenthening. The former bands disappear completely and only the latter ones are left

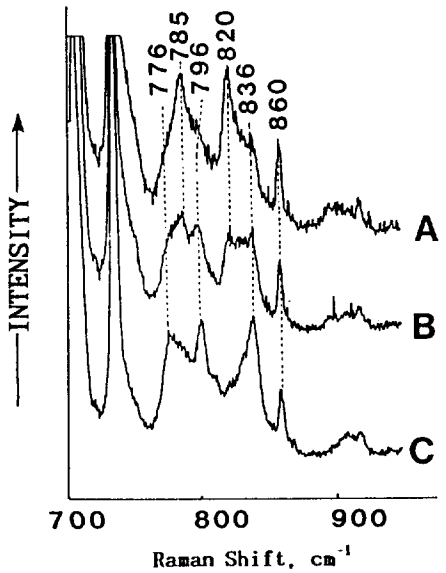


Figure 2. Resonance Raman spectra (406.7 nm excitation) of reaction product of Fe(TPFP)Cl with -$^{16}O^{18}O$-mCPBA in the presence of TBAF·AH in methylene chloride at −78 ℃. A: R=2, B: R=20 and C: R=50.

when the molar ratio(R) is 50 (Figure 2C).

Similar experiment with TBA·$OClO_3$ instead of TBAF gives ν(Fe=O) band of oxoferryl species at 838 cm^{-1} for ^{16}O labeled mCPBA (799 cm^{-1} for ^{18}O labeled mCPBA). All of the observed frequencies of ν (Fe=O) for O=Fe(TPFP)X are listed in Table 1. Finally, our RR studies shows that;

(1) In the ν(Fe=O) of OFe(TPFP)F system, the value of ν(Fe=^{16}O) obtained with TBAF·$3H_2O$ is 9 cm^{-1} low compared with that obtained with TBAF·AH. (The other conditions are the same). Thus, it provides a definitive evidence that the two different frequencies, at 811 cm^{-1} with TBAF·3 H_2O and at 820 cm^{-1} with TBAF·AH are interpreted in terms of the presence or absence of a hydrogen bond between the oxygen of oxo ligand and the hydrogen of water as reported on HRP II.[12]

(2) In the Fe^{IV}=O structure, it involves one σ[d_{z^2}(Fe)-p_z(O)] and an half of two π[d_{xz}(Fe)-p_x(O) and d_{yz}(Fe)-p_y(O)] bonds. Since the oxo ligand is both a strong σ donor and a moderate π donor, electron donation ligands to the Fe^{IV} ion could compete with this oxo ligand and tend to reduce electron donation from the oxo ligand to the Fe^{IV} ion and could weaken the Fe^{IV}=O bond due to the trans effect. In fact, for oxoferryl complexes, the ν(Fe=O) frequencies are the same when the trans ligand is F^- (820 cm^{-1}) and it is Im (820 cm^{-1}). This means, that the basic ligand, F^- is the similar σ donation ability to the iron compared with the strong ligand, Im. Also, the order of the ν(Fe=O) of O=Fe(TPFP)X (X=F^-, mCB^- and $OClO_3^-$) becomes 820 cm^{-1} (X=F^-)<836 cm^{-1} (X=mCB^-)<838 cm^{-1} (X=$OClO_3^-$) which reflects the reverse order of basic ligand; the larger the donation is, the lower the ν(Fe=O) frequency is.

(3) Previously, Grove *et al.*[13] inferred that the reaction product of mCPBA, that is, *m*-chlorobenzoic acid (mCBA) was coordinate to trans position of the oxo oxygen. In the presence of F^-, mCB^- would compete with F^- for coordinate at the axial position according to increasing molar ratio, R. Thus, the frequency upshift of the ν(Fe=O) at 820 (785) cm^{-1} to that at 836 (796) cm^{-1} is ascribed to the trans ligand exchange from F^- to mCB^-.

(4) The bands obtained with a coordinating netural ligand such as THF, DMF and Im has been shown to be the ν (Fe=O) of six coordinate non-radical oxoferryl porphyrin which involves a low spin (S=1) Fe atom with formal oxidation state IV. The likely structures of O=Fe(TPFP)X (X=F^-, mCB^- and $OClO_3^-$) species described here are proposed for two possibilities; ① the Fe^{IV}=O porphyrin π-cation radical, O=Fe^{IV} (TPFP)$^{\cdot+}$X ② the Fe^{V}=O neutral porphyrins, O =Fe^{V} (TPFP)X.

Goff *et al.*[7] suggested that Fe^{IV}=O π-cation radical porphyrin was generated when Fe(TPP)F was oxidized by mCPBA according to NMR spectroscopy. However, TPFP is highly acidic since the electron density on the porphyrin ring is reduced markedly due to strong electron withdrawing property of the fluorine atoms on the phenyl ring. In O_2 matrix studies,[6] only nonradical oxoferryl species was formed by Fe(TPFP) and it supported that this porphyrin core is too electron deficient to stabilize the π-cation radical species. In general, the high frequency region of RR spectra can be used to identify the characteristic features[14] associated with π-cation radical formation; the intensities of all the porphyrin modes due to π-cation radical (ν_2, ν_4, ν_3 and ν_{10}) decrease dramatically and these bands shift up or down according to A_{1u}, A_{2u} type π-cation radical. However, the high frequency spectra of RR spectra obtained in this note doesn't show these trends, but show the same pattern as neutral oxoferryl species. Thus, we could rule out the possibility of generation of π-cation radical porphyrin. Thus, the structure of this species is tentatively concluded to O=Fe^{V}(TPFP)X.

Aknowledgment. We thank Prof. J. R. Kincaid at Marquette university, milwakee, U.S.A. for his kind allowance to use his Raman system. This work was partially supported by Yonsei university research fund (1991).

References

1. Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187.
2. Nagai, A.; Chance, B. *Ann. Rev. Biochem.* **1986**, *55*, 137.
3. Frew, J. E.; Jones, P. *Advances in Inorganic and Bioinorganic Mechanism, Vol 3*; Academic Press: N.Y., 1984.
4. Kitagawa, T.; Mizutani, Y. *Coord. Chem. Rev.* **1994**, *135/136*, 685.
5. Kincaid, J. R.; Schnieder, A. J.; Paeng, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 735.
6. Proniewicz, L. M.; Paeng, I. R.; Nakamoto, K. *J. Am. Chem. Soc.* **1991**, *113*, 3294.
7. Hickman, D. L.; Nanthakumar, A.; Goff, H. M. *J. Am. Chem. Soc.* **1988**, *110*, 6384.
8. Johnson, R. A. *Tetrahedron Lett.* **1976**, *5*, 331.
9. Brown, G. *Organic Syntheses Collective, Vol. 1*; 1941.
10. Paeng, K. J.; Paeng, I. R. *Proc. Korea-U.S. Inorg. Chem. Conferences*; Seoul: 1993; p 81.
11. Burke, J. M.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 6077.
12. Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *Proc. Natl. Acad.*

Sci. U.S.A. **1986**, *83*, 2417.
13. Groves J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8443.
14. Macor, K. A.; Czernuszewicz, R. S.; Spiro, T. G. *Inorg. Chem.* **1990**, *29*, 1996.

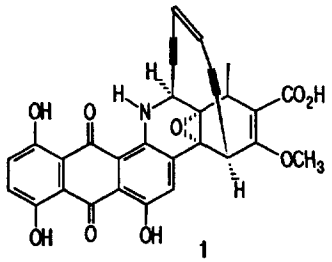
An Efficient One-Pot Synthesis of Cyclic Skeletons Related to Dynemicin A Models

Yong Pyo Hong*, Hoon Han Ryu, and Byung Soo Park

Department of Chemistry, Andong National University, Andong 760-749, Korea

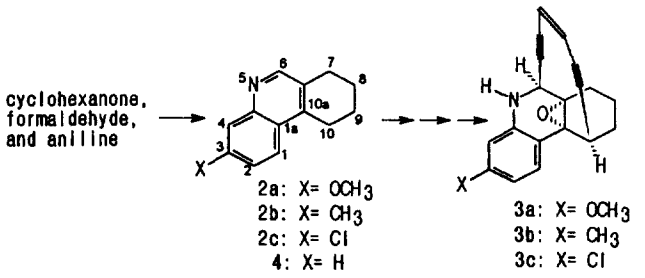
Received June 15, 1995

Dynemicin A (**1**) is a potent antitumor antibiotic isolated from the fermentation broth of *Micromonospora chersina*.[1] It has been confirmed that the anthraquinone moiety in **1** initiates the drug to activate *via* intercalation into minor groove of DNA and then, bioreduction of the quinone system.[2] The following internal epoxide ring opening triggers Bergman cycloaromatization[3] of the constrained 10-membered enediyne system to give benzenoid diradical resulting in DNA strand breakage. The suggestion that epoxide opening is a critical step of the drug activation has been supported by the results of molecular modeling and mechanistic studies.[4]

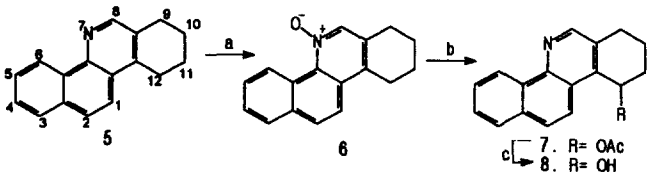


1

Even though many tricyclic dynemicin A models have been synthesized, most of the models have focused on the biological activity induced by substituent effect on enediyne system or DNA intercalator effect.[5] One can expect that a substituent on benzene ring can also affect epoxide ring opening electronically and then, biological activity of the models. Accordingly, it is thought that tricyclic models (*i.e.*, **3a-c**) with substituent at C3 position can provide a good information on activation and DNA cleavage of dynemicin A type drugs (Scheme 1). This note describes an efficient preparation method of tricyclic skeletons (*i.e.*, **2a-c**) which can be served as a precursor of new C3-substituted enediyne models. According to the recent reports,[6] tricyclic skeletons (e.g. **4**) have been prepared from ethyl 2-cyclohexanonecarboxylate and aniline. However, the use of expensive reagents, poor overall yield (<20%), moreover, complicate and time-consuming synthetic procedure enforced us to search another strategy for a large scale preparation of the requisite materials. For an efficient synthesis of substituted fused ring skeletons, pre-



Scheme 1. Formation of tricyclic compounds.



Reagents and conditions: (a) 1.2 equiv of mCPBA, CH_2Cl_2, 25 °C, 2 h, 80%; (b) Ac_2O, 100 °C, 30 min, 20%; (c) K_2CO_3 (catalytic), MeOH, 25 °C, 7 h, 92%.

Scheme 2. C10-functionalization of tetracyclic compound.

viously reported method[7] was a little modified as follows; Cyclohexanone and aqueous formaldehyde (0.95 eq) were stirred at room temperature in the presence of catalytic amount of soda lime until the solution became clear (2 h). After neutralized by acetic acid, substituted aniline (1.0 equiv) and its hydrochloride (0.5 equiv) were added to the solution. The solution mixture was diluted with ethanol and then, heated overnight at reflux temperature. After purification with column chromatography, the products were obtained in 30%, 29%, and 26% yields for **2a**, **2b**, and **2c**, respectively. Interestingly, the use of meta substituted anilines led to high yield formation of desired compounds compared with ortho and para substituted anilines.[8] This trend is consistent with previously reported suggestion[9] that an electron-donating substituent at C3 position can facilitate the formation of 1a-10a bond under acidic condition. The generation of tetracyclic skeleton **5** by using cyclohexanone, formaldehyde, and 1-aminonaphthalene was also accomplished in much better yield (20%) than conventional method (5%) utilizing ethyl 2-cyclohexanonecarboxylate and 1-aminonaphthalene. Further reactions with **5** were performed to prepare C12-functionalized compound **8** which is the requisite intermediate for the preparation of dynemicin A type tetracyclic enediyne models (Scheme 2).

The oxidation of **5** with m-chloroperoxybenzoic acid gave N-oxide **6** in high yield. The treatment of **6** with acetic anhydride furnished C8 and C12 acetoxylated products in competitive manner.[10] Unfortunately, the formation of unwanted C8-acetoxylated product surpassed the generation of C12-functionalized compound **7**. Finally, the acetate **7** was easily hydrolized to yield alcohol **8** under basic condition.

Further studies are underway for the generation of compounds **3a-c**.

Experimental Section

General Techniques. Melting points were recorded on