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Syntheses of methylpyridine and methylpyridine *N*-oxide decorated benzoxazine and naphthoxazine platforms

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ABSTRACT

Simple, aqueous-based syntheses of methylpyridine and methylpyridine *N*-oxide decorated 3,4-dihydro-2*H*-naphthoxazine and 2,3-dihydro-1*H*-naphthoxazine monomers, as well as thermally promoted syntheses of 3,4-dihydro-2*H*-benzoxazine monomers and bisoxazine methylpyridine derivatives of substituted 1,5-, 2,6-, and 2,7-dihydroxynaphthalenes are described. The crystal structures of two derivatives are presented.

Benzoxazines and naphthoxazines, originally proposed by Holly and Cope[1] and subsequently elaborated upon by Burke and co-workers,[2] are obtained via Mannich-type condensation-cyclization reactions of phenols or naphthols with formaldehyde and primary amines in a 1:2:1 ratio. The scope of this chemistry is extensive, and the synthetic evolution has been reviewed by Synoradzki and co-workers[3] through 2005. The compounds display a host of interesting pharmacological properties that have been summarized by Nath and co-workers,[4] and Ishida and others have developed an intriguing family of robust phenolic resins that arise from thermally promoted ring opening of selected benzoxazine and naphthoxazine monomers.[5] In addition and pertinent to our own interests, Ishida has noted the formation of supramolecular benzoxazine monomers and oligomers that behave as ionophores toward alkali metal cations.[6] Laobuthee has extended this area by exploring the formation of alkali metal ion responsive supramolecular crown ethers containing ring opened benzoxazine fragments.[7] The ion extraction properties of several model 3,4-dihydro-3-(2′-hydroxyethylene)-6-alkyl-2*H*-benzoxazine monomers toward alkali metal cations and Ce(III) have also been recently reported, and it was proposed that these monomers complex Ce(III) through the ring ether O-atom.[8]

In our own program, we have explored the metal binding[9] and extraction properties[9q,r,10] of pyridine and pyridine *N*-oxide platforms decorated by methylphosphine oxide and alkyl amide donor groups. The favorable extraction properties of several of these reagents encouraged us to explore the formation of supramolecular structures and solid-phase supported materials that contain donor-decorated pyridine and pyridine *N*-oxide fragments. In this regard, although there has been some attention given to the synthesis of ring substituted benzoxazine and naphthoxazine monomers,[3,5] there have been few reports of examples that carry amide, phosphine oxide, pyridine, or pyridine *N*-oxide donor substituents suitable for coordination interactions with metal cations.[3,11] In order to eventually obtain multiply functionalized oligomers of interest in our separations program, we first sought to develop routes to simple, model monomers containing just the substituent-free pyridine and pyridine *N*-oxide platforms. Initially, the Burke methods[2] as well as a solvent-less procedure[12] were explored for the synthesis of the benzoxazine monomers, but these approaches produced inconsistent results. With several amines, phenols, and naphthols, varying yields of impure products were obtained. It became clear that for the target monomers, alternative procedures were required in order to improve the yield and purity of the products.

For the syntheses of the dihydronaphthoxazines **2a**, **2b**, and **3a**–**3c**, a modified one-pot, three-component procedure similar to that first reported by Mathew and Nath[4] and summarized in Scheme 1, was utilized. This aqueous-based method avoids the use of expensive, volatile organic solvents, and high reaction temperatures. In fact for **2a**, **2b**, and **3a**–**3c**, even modest reaction temperatures result in premature oxazine ring opening and the formation of undesirable intermediates and side products.

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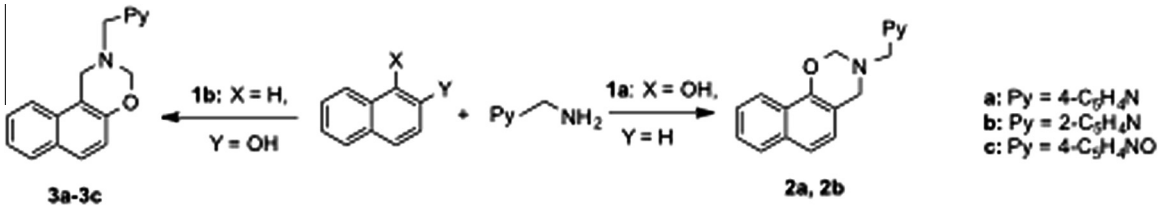


Scheme 1. Synthesis of dihydronaphthoxazines. Reagents and conditions: 2- or 4-aminomethylpyridine (1.0 equiv), H_2O, 37% formaldehyde solution (4.0 equiv), 0.5 h, rt then naphthol **1a** or **1b** (1.0 equiv), THF, rt, 14 h, 94%, **2a**; 83%, **2b**; 84%, **3a**; 4-aminomethylpyridine-*N*-oxide dihydrochloride (1.0 equiv), H_2O, saturated K_2CO_3, pH 7, 37% formaldehyde solution (2.0 equiv) then 2-naphthol (**1b**, 1.0 equiv), THF, 14 h, rt, 84%, **3c**.

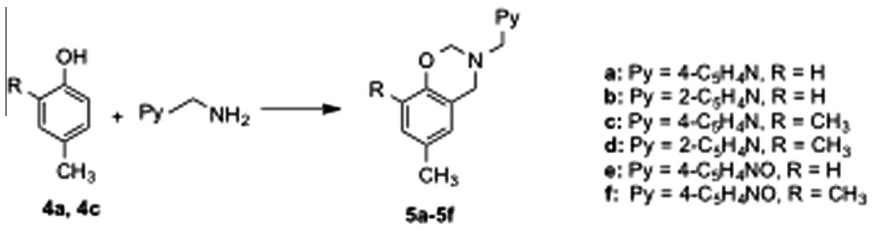
The appropriate naphthol (**1a** or **1b**) was added to a stirred aqueous solution containing 4-aminomethylpyridine or 2-aminomethylpyridine and fresh 37% aqueous formaldehyde solution. Because of the low solubility of the naphthols in this mixture, a small amount of tetrahydrofuran was added dropwise until a homogeneous solution was obtained. After one half hour, additional formaldehyde solution was added which improved the yield. Without the added THF, the reactions were slow and the yields were low. The solution was stirred overnight at room temperature and standard work-up afforded crude naphthoxazines, 3,4-dihydro-3-(4-pyridinylmethyl)-2*H*-naphth[2,1-*e*][1.3]oxazine (**2a**), 3,4-dihydro-3-(2-pyridinylmethyl)-2*H*-naphth[2,1-*e*][1.3]oxazine (**2b**), 2,3-dihydro-2-(4-pyridinylmethyl)-1*H*-naphth[2,1-*e*][1.3]oxazine (**3a**) and 2,3-dihydro-2-(2-pyridinylmethyl)-1*H*-naphth[2,1-*e*][1.3]oxazine (**3b**). Flash column chromatography using silica gel provided pure compounds in 82–94% yields. Compounds **3a** and **3b** have been previously reported in the literature but no spectral data were given.[11]

In a fashion similar to that described for **2a**, **2b**, **3a**, and **3b**, the pyridine *N*-oxide derivative, **3c**, was synthesized in 84% yield by reaction of 4-aminomethylpyridine-*N*-oxide dihydrochloride, naphthol (**1b**), and 37% formaldehyde solution in the presence of a saturated aqueous potassium carbonate solution. The 4-aminomethylpyridine-*N*-oxide dihydrochloride salt was synthesized from 4-pyridylacetamide[13] followed by oxidation and hydrolysis in hydrochloric acid.[14]

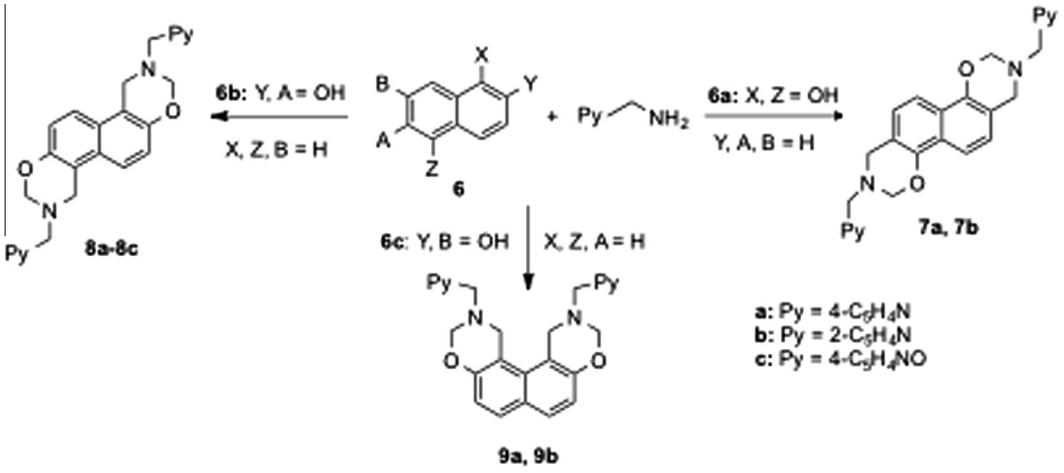
The synthesis of benzoxazines, **5a**–**5f**, from *p*-cresol (**4a**) and 2,3-dimethylphenol (**4c**), using similar reaction conditions, is described in Scheme 2. Phenol (**4a** or **4c**) was added to an aqueous solution containing 2-aminopyridine or 4-aminopyridine and fresh 37% aqueous formaldehyde. In these cases THF was not required to solubilize the reagents. However, the formation of benzoxazines did not occur readily at room temperature; therefore, the mixtures were heated at 80 °C for two to three hours. After standard work-up and chromatography, pure benzoxazines (**5a**–**5d**) were obtained in 56–67% yield. The *N*-oxides, **5e** and **5f**, were synthesized by combining 4-aminomethylpyridine *N*-oxide dihydrochloride, in sufficient aqueous potassium carbonate solution to reach pH 7, with 37% aqueous formaldehyde. After stirring for one half hour at room temperature the appropriate phenol (**4a** or **4c**) was added. The mixture was gently heated (80 °C), dissolved in dichloromethane, filtered, evaporated at room temperature, and chromatographed to afford **5e** and **5f** in 51% and 55% yields respectively.

The syntheses of bisnaphthoxazines, **7a**, **7b**, **8a**–**8c**, **9a**, and **9b** from dihydroxynaphthalenes, **6a**, **6b**, and **6c** are outlined in Scheme 3. In these cases, the best results were obtained without solvent. Pure, recrystallized dihydroxynaphthalenes were added to a solution containing 2-aminomethylpyridine or 4-aminomethylpyridine and 37% aqueous formaldehyde, and the mixture was heated (80 °C) for two to three hours using the method described by Talele.[15] The resulting solid was dissolved in dichloromethane, filtered, and allowed to evaporate at room temperature. Pure bisnaphthoxazines, **7a**, **7b**, **8a**, **8b**, **9a**, and **9b** were obtained in 53–84% yield after recrystallization. Attempts to improve the yields by using toluene as the solvent and heating the reaction mixture at gentle reflux resulted in impure products.[16] The *N*-oxide, compound **8c**, was synthesized using a procedure similar to that used for the synthesis of compounds **5e** and **5f**. After heating the mixture containing 4-aminomethylpyridine N-oxide dihydrochloride, 37% aqueous formaldehyde and 2,6-dihydroxynaphthalene (**6b**) and cooling, the resulting solid was dissolved in dichloromethane, dried, and filtered. Evaporation at room temperature afforded **8c** in 51% yield after recrystallization.

The structures of the naphthoxazines (**2a**, **2b**, **3a**–**3c**), benzoxazines (**5a**–**5f**), and bisnaphthoxazines (**7a**, **7b**, **8a**–**8c**, **9a**, **9b**) monomers were verified by proton and carbon NMR spectral data as well as infrared data,[6,16–18] which are presented in the Supplementary information. The proton NMR spectra for the compounds contain three singlets between 4.00 and 5.00 ppm, characteristic of the methylene units in the oxazine ring[5] and the methylene unit for the pyridine ring. In the carbon NMR spectra the methylene resonances appear at approximately 50 and 80 ppm for the oxazine ring and at 55 ppm for the pyridine ring. The proton NMR spectra also display a downfield resonance that can be assigned to the proton(s) *ortho* to the nitrogen atom in the pyridine ring.[11,17] The protons *ortho* to the nitrogen atom in pyridine *N*-oxides (**3c**, **5e**, **5f**, **8c**) are shifted upfield compared to the pyridine analogs. This upfield shift also occurs for the *ortho* carbon resonances. Assignments were made using DEPT, COSY, HMQC, and HMBC spectral data in addition to routine proton and carbon NMR spectra. The infrared



Scheme 2. Synthesis of dihydronaphthoxazines. Reagents and conditions: 2- or 4-aminomethylpyridine (1.0 equiv), H_2O, 37% formaldehyde solution (2.0 equiv), 0.5 h, rt then phenol **4a** or **4c** (1.0 equiv), 80 °C, 2–3 h, 67%, **5a**; 55%, **5b**; 61%, **5d**; 4-aminomethylpyridine-*N*-oxide dihydrochloride (1.0 equiv), H_2O, saturated k_2CO_3, pH 7, 37% formaldehyde solution (2.0 equiv), 0.5 h, then naphthol **4a** or **4b** (1.0 equiv), 80 °C, 2–3 h, 51%, **5e**; 55% **5f**.



Scheme 3. Synthesis of bisdihydronaphthoxazines. Reagents and conditions: 2- or 4-aminomethylpyridine (2.0 equiv), 37% formaldehyde solution (4.0 equiv), 0.5 h, rt then dihydroxynaphthalene **6a**, **6b** or **6c** (1.0 equiv), 80 °C, 2–3 h, 69%, **7a**; 53%, **7b**; 83%, **8a**; 76%, **8b**; 84%, **9a**; 59%, **9b**; 4-aminomethylpyridine-*N*-oxide dihydrochloride (2.0 equiv), H_2O, saturated k_2CO_3, pH 7, 37% formaldehyde solution (4.0 equiv), 0.5 h, rt then dihydroxynaphthalene (**4b**, 1.0 equiv), 80 °C, 3 h, 51%, **8c**.

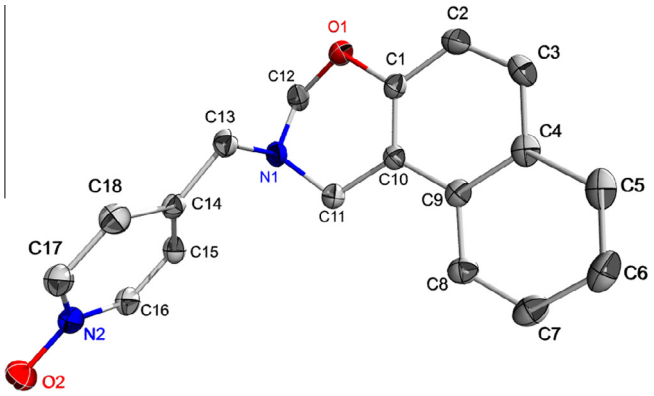


Figure 1. ORTEP view of **3c** with atom labeling scheme (50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å): O1–C1 1.379(2), O1–C12 1.455(2), N1–C11 1.471(2), N1–C12 1.425(2), N1–C13 1.464(2), N2–O2 1.315(2), N2–C16 1.356(3), N2–C17 1.363(3).

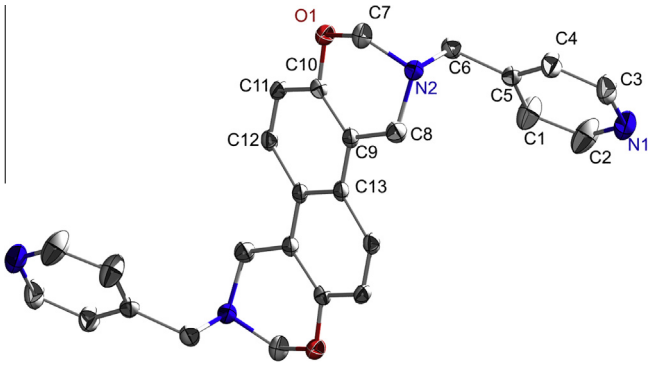


Figure 2. ORTEP view of **8a** with atom labeling scheme (50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å): O1–C10 1.376(3), O1–C7 1.449(3), N1–C3 1.325(3), N1–C2 1.328(3), N2–C7 1.425(3), N2–C8 1.474(3), N2–C6 1.475(3).

spectra for the compounds display the characteristic infrared absorptions at 1030–1040 cm^{-1} for the C–O–C symmetric stretch, 1226–1237 cm^{-1} for the Ar–O–C asymmetric stretch, and 930–945 cm^{-1} for the oxazine ring.[4,18] An additional N–O stretch at 1220 cm^{-1} was observed for compounds **3c**, **5e**, **5f**, and **8c**. Further verification of the structures of compounds **3c** and **8a** is provided by single crystal X-ray diffraction analysis and views of the molecules are shown in Figures 1 and 2. The bisnaphthoxazines exhibit considerable symmetry as evidenced by the number of resonances seen in the proton and carbon NMR spectra. In the IR spectra an additional absorption at 942–966 cm^{-1} assigned to the C–H out of plane deformation of disubstituted naphthalenes was observed.[19]

In conclusion, efficient syntheses have been developed for model methylpyridine and methylpyridine *N*-oxide decorated naphthoxazine, benzoxazine, and bisnaphthoxazine monomers. The development of this chemistry will permit studies of the metal ion coordination chemistry for ring-opened analogs which, in turn, will guide the assembly of the benzoxazine and naphthoxazine monomers and oligomers decorated with more complicated metal chelating ligands such as described in our earlier work.[9]

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Supplementary data

Supplementary data (experimental procedures, spectroscopic and HRMS data and copies of ^{1}H, ^{13}C NMR, IR) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.129. Crystallographic data (excluding structure factors) for the structures in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-959251 (**8a**) and -959252 (**3c**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

References and notes

1. Holly, F. W.; Cope, A. C. *J. Am. Chem. Soc.* **1944**, *66*, 1875–1879.

2. (a) Burke, W. J. *J. Am. Chem. Soc.* **1949**, *71*, 609–612; (b) Burke, W. J.; Weatherbee, C. *J. Am. Chem. Soc.* **1950**, *72*, 4691–4694; (c) Burke, W. J.; Smith, R. P.; Weatherbee, C. *J. Am. Chem. Soc.* **1952**, *74*, 602–605; (d) Burke, W. J.; Kolbezen, M. J.; Stephens, C. W. *J. Am. Chem. Soc.* **1952**, *74*, 3601–3605; (e) Burke, W. J.; Murdock, K. C.; Ec, G. *J. Am. Chem. Soc.* **1954**, *76*, 1677–1679; (f) Burke, W. J.; Glennie, E. L. M.; Weatherbee, C. *J. Org. Chem.* **1964**, *29*, 909–912; (g) Burke, W. J.; Nasutavicus, W. A.; Weatherbee, C. *J. Org. Chem.* **1964**, *29*, 407–410; (h) Burke, W. J.; Bishop, J. L.; Glennie, E. L. M.; Bauer, W. N., Jr. *J. Org. Chem.* **1965**, *30*, 3423–3427.
3. Bujnowski, K.; Adamczyk, A.; Synoradzki, L. *Org. Prep. Proced. Int.* **2007**, *39*, 417–446.
4. (a) Mathew, B. P.; Nath, M. *J. Heterocycl. Chem.* **2009**, *46*, 1003–1006; (b) Mathew, B. P.; Kumar, A.; Sharma, S.; Shukla, P. K.; Nath, M. *Eur. J. Med. Chem.* **2010**, *45*, 1502–1507.
5. *Handbook Of Benzoxazine Resins*; Ishida, H., Agag, T., Eds.; Elsevier: Amsterdam, 2011. and references therein; (b) Baqar, M.; Agag, T.; Huang, R.; Maia, J.; Qutubuddin, S.; Ishida, H. *Macromolecules* **2012**, *45*, 8119–8125. and references therein.
6. (a) Chirachanchai, S.; Laobuthee, A.; Phontamrag, S.; Siripattanasarakit, W.; Ishida, H. *J. Appl. Polym. Sci.* **2000**, *77*, 2561–2568; (b) Laobuthee, A.; Chirachanchai, S.; Ishida, H.; Tashiro, K. *J. Am. Chem. Soc.* **2001**, *123*, 9947–9955; (c) Laobuthee, A.; Ishida, H.; Chirachanchai, S. *J. Inclusion Phenom. Macrocyclic Chem.* **2003**, *47*, 179–185.
7. (a) Chirachanchai, S.; Phongtamrug, S.; Laobuthee, A. *Chem. Lett.* **2003**, *32*, 432–433; (b) Rungsimanon, T.; Laobuthee, A.; Miyata, M.; Chirachanchai, S. *J. Inclusion Phenom. Macrocyclic Chem.* **2008**, *62*, 333–338; (c) Chirachanchai, S.; Laobuthee, A.; Phongtamrug, S. *J. Heterocycl. Chem.* **2009**, *46*, 714–721; (d) Chirachanchai, S.; Rungsimanon, T.; Phongtamrug, S.; Miyata, M.; Laobuthee, A. *Tetrahedron* **2009**, *65*, 5855–5861; (e) Kaewvilai, A.; Rungsimanon, T.; Koonsaeng, N.; Chirachanchai, S.; Laobuthee, A. *Asian J. Chem.* **2010**, *22*, 7628–7640.
8. Kaewvilai, A.; Rujitanapanich, S.; Wattanathana, W.; Veranitisagul, C.; Suramitr, S.; Koonsaeng, N.; Laobuthee, A. *Molecules* **2012**, *17*, 511–526.
9. (a) McCabe, D. J.; Russell, A. A.; Karthikeyan, S.; Paine, R. T.; Ryan, R. R. *Inorg. Chem.* **1987**, *26*, 1230–1235; (b) Conary, G. S.; Russell, A. A.; Paine, R. T.; Ryan, R. R. *Inorg. Chem.* **1988**, *27*, 3242–3245; (c) Russell, A. A.; Meline, R. L.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1995**, *231*, 1–5; (d) Rapko, B. M.; Duesler, E. N.; Smith, P. H.; Paine, R. T.; Ryan, R. R. *Inorg. Chem.* **1993**, *32*, 2164–2174; (e) Engelhardt, U.; Rapko, B. M.; Duesler, E. N.; Frutos, D.; Paine, R. T. *Polyhedron* **1995**, *14*, 2361–2369; (f) Bond, E. M.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Polyhedron* **2000**, *19*, 2135–2140; (g) Bond, E. M.; Duesler, E. N.; Paine, R. T.; Neu, M. P.; Matonic, J. H.; Scott, B. L. *Inorg. Chem.* **2000**, *39*, 4152–4155; (h) Gan, X.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **2001**, *40*, 4420–4427; (i) Paine, R. T.; Bond, E. M.; Parveen, S.; Donhart, N.; Duesler, E. N.; Nöth, H. *Inorg. Chem.* **2002**, *41*, 444–448; (j) Matonic, J. H.; Neu, M. P.; Enriquez, A. E.; Paine, R. T.; Scott, B. L. *J. Chem. Soc. Dalton Trans.* **2002**, 2328–2332; (k) Gan, X.; Paine, R. T.; Duesler, E. N.; Nöth, H. *J. Chem. Soc. Dalton* **2003**, 153–159; (l) Gan, X.; Rapko, B. M.; Duesler, E. N.; Binyamin, I.; Paine, R. T.; Hay, B. P. *Polyhedron* **2005**, *24*, 469–474; (m) Pailloux, S.; Shirima, C. E.; Ray, A. D.; Duesler, E. N.; Paine, R. T.; Klaehn, J. R.; McIlwain, M. E.; Hay, B. P. *Inorg. Chem.* **2009**, *48*, 3104–3113; (n) Pailloux, S.; Binyamin, I.; Deck, L. M.; Hay, B. P.; Zakharov, L. N.; Kassel, W. S.; Rheingold, A. L.; Paine, R. T. *Polyhedron* **2009**, 3979–3984; (o) Pailloux, S.; Shirima, C. E.; Duesler, E. N.; Smith, K. A.; Paine, R. T. *Polyhedron* **2011**, *30*, 2746–2757; (p) Rosario-Amorin, D.; Duesler, E. N.; Paine, R. T.; Hay, B. P.; Reilley, S.; Scott, B. L.; Gaunt, A. *J. Inorg. Chem.* **2012**, *51*, 6667–6681; (q) Rosario-Amorin, D.; Ouizem, S.; Dickie, D. A.; Wen, Y.; Paine, R. T.; Gao, J.; Grey, J. K.; de Bettencourt-Dias, A.; Hay, B. P.; Delmau, L. H. *Inorg. Chem.* **2013**, *52*, 3063–3083; (r) Pailloux, S.; Rosario-Amorin, D.; Chakravarty, M.; Camus, J. M.; Smith, K. A.; Duesler, E. N.; Dickie, D. A.; Paine, R. T.; Klausmeyer, K. K.; Padron, D. A.; Hay, B. P.; Delmau, L. H. *Z. Anorg. Allg. Chem.* **2013**, *639*, 1101–1116.
10. (a) Blaha, S. L.; McCabe, D. J.; Paine, R. T.; Thomas, K. W. *Radiochim. Acta* **1989**, *46*, 123–125; (b) Blaha, S. L.; Caudel, L. J.; Conary, G. C.; Paine, R. T. *Radiochim. Acta* **1989**, *48*, 59–64; (c) Bond, E. M.; Englehardt, U.; Deere, T. P.; Rapko, B. M.; Paine, R. T.; FitzPatrick, J. R. *Solvent Extr. Ion Exch.* **1997**, *15*, 381–400; (d) Bond, E. M.; Englehardt, U.; Deere, T. P.; Rapko, B. M.; Paine, R. T.; FitzPatrick, J. R. *Solvent Extr. Ion Exch.* **1998**, *16*, 967–983; (e) Nash, K. L.; Lavallette, C.; Borkowski, M.; Paine, R. T.; Gan, X. *Inorg. Chem.* **2002**, *41*, 5849–5858; (f) Sulakova, J.; Paine, R. T.; Chakravarty, M.; Nash, K. L. *Sep. Sci. Tech.* **2012**, *47*, 2015–2023.
11. (a) Kuehne, M. E.; Konopka, E. A. *J. Med. Pharm. Chem.* **1962**, *5*, 257–280; (b) Demir, K. D.; Tasdelen, M. A.; Uyar, T.; Kawaguchi, A. W.; Sudo, A.; Endo, T.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4213–4220; (c) Sponton, M.; Larrechi, M. S.; Ronda, J. C.; Galia, M.; Cadiz, V. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7162–7172; (d) Lin, L. K.; Wu, C. S.; Su, W. C.; Liu, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 3523–3530.
12. (a) Brunovska, Z.; Liu, J. P.; Ishida, H. *Macromol. Chem. Phys.* **1999**, *200*, 1745–1752; (b) Inoue, S.; Kim, R.; Hoshino, Y.; Honda, K. *Chem. Commun.* **2006**, 1974–1976.
13. Plater, M. J.; Barnes, P.; McDonald, L. K.; Wallace, S.; Archer, N.; Gelbrich, T.; Horton, P. N.; Hursthouse, M. B. *Org. Biomol. Chem.* **2009**, *7*, 1633–1641.
14. Gribble, A. D.; Ife, R. J. *Eur. Pat. Appl.* **1986**, EP 194746 A2 19860917.
15. Talele, H. R.; Bedeka, A. V. *Org. Biomol. Chem.* **2012**, *10*, 8579–8582.
16. (a) Dunkers, J.; Ishida, H. *Spectrochim. Acta, Part A* **1995**, *51*, 1061–1074; (b) Dunkers, J.; Ishida, H. *Spectrochim. Acta, Part A* **1995**, *51*, 855–867; (c) Chutayothin, P.; Ishida, H. *Macromolecules* **2010**, *43*, 4562–4572; (d) Liu, J.; Agag, T.; Ishida, H. *Polymer* **2010**, *51*, 5688–5694; (e) Ishida, H.; Sanders, D. P. *Polymer* **2001**, *42*, 3115–3125; (f) Neuvonen, K.; Pihlaja, K. *Magn. Reson. Chem.* **1990**, *28*, 239–245; (g) Neuvonen, K.; Pihlaja, K. *J. Chem. Soc. Perk. 2* **1988**, 461; (h) Andreu, R.; Reina, J. A.; Ronda, J. C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3353–3366.
17. (a) Kitching, W.; Bullpitt, M.; Gartshore, D.; Adcock, W.; Khor, T. C.; Doddrell, D.; Rae, I. D. *J. Magn. Reson.* **1976**, *22*, 279–289; (b) Howie, J. K.; Bosserman, P.; Sawyer, D. T. *Inorg. Chem.* **1980**, *19*, 2293–2296.
18. Kerton, F. M.; Holloway, S.; Power, A.; Soper, R. G.; Sheridan, K.; Lynam, J. M.; Whitwood, A. C.; Willans, C. E. *Can. J. Chem.* **2008**, *86*, 435–442.
19. (a) Uyar, T.; Koyuncu, Z.; Ishida, H.; Hacaloglu, J. *Polym. Degrad. Stab.* **2008**, *93*, 2096–2103; (b) Uyar, T.; Hacaloglu, J.; Ishida, H. *J. Appl. Polym. Sci.* **2013**, *127*, 3114–3123.