Tetrahedron 65 (2009) 748–751

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Efficient total syntheses of louisianins C and D

Ching-Yao Chang [a,*], Hui-Ming Liu [b], Ru-Ting Hsu [c]

[a] Department of Biotechnology, Asia University, Wufeng, Taichung 413, Taiwan, ROC
[b] Department of Safety, Health and Environmental Engineering, Hungkuang University, Shalu, Taichung 433, Taiwan, ROC
[c] Department of Nursing, Shu-Zen College of Medicine and Management, Lujhu, Kaohsiung 821, Taiwan, ROC

ARTICLE INFO

Article history:
Received 8 October 2008
Received in revised form 23 November 2008
Accepted 24 November 2008
Available online 27 November 2008

Keywords:
Louisianins A–D
Streptomyces sp. WK-4028
ortho-Lithiation
Cyclization–decarboxylation

ABSTRACT

An efficient synthetic route for the preparation of louisianins C and D was developed starting with the commercially available 4-cyanopyridine. Louisianins C and D were synthesized in seven steps and with overall yields 22% and 20%, respectively, following a novel cyclization–decarboxylation sequence involving 4-bromo-6,7-dihydrocyclopenta[*c*]pyridin-5-one as the key intermediate.

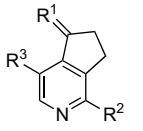
1. Introduction

Louisianins A–D were isolated from the cultured broth of *Streptomyces* sp. WK-4028.[1] Louisianin A inhibits the growth of SC 115 cells (IC_{50}=0.6 μg/mL) whereas louisianins C and D potently suppress tube formation by cultured vascular endothelial cells in vitro (Fig. 1).[1–3] To date, only limited reports have been published on the syntheses of louisianins C and D. In 2003, Kelly reported the synthesis of louisianin C via a symmetrical 3,5-diallyl-substituted pyridine (6 steps and 11% overall yield).[4] In 2006, Chang and co-workers successfully synthesized louisianin D with a fused bicyclic glutarimide as the key intermediate (10 steps and 18% overall yield).[5] Recently, Taylor and co-workers prepared both louisianins C and D starting with an unusual 1,2,4-triazine (8 steps, 16% overall yield for louisianin C; 9 steps, 13% overall yield for louisianin D).[6] The low overall yields obtained with the above-mentioned methods are quite unsatisfactory and leave considerable room for further improvements.

In our previous paper, we reported an efficient total synthesis of louisianin A via a cyclization–decarboxylation sequence to establish a fused cyclopentenone moiety.[7] The same strategy is applicable to the preparations of louisianins C and D that share a common skeleton with louisianin A. Herein, we disclose the syntheses of louisianins C and D and confirm the usefulness of the cyclization–decarboxylation sequence as a general route for the preparations of all members of the louisianin family.

2. Results and discussion

The complete synthetic sequence is shown in Scheme 1. *ortho*-Lithiation of cyanopyridine by treatment of 4-cyanopyridine (**1**) with lithium 2,2,6,6-tetramethylpiperidide (LTMP, 2 equiv) at −80 °C, followed by bromination led to 3-bromo-4-cyanopyridine (**2**) with a 64% yield.[8] The yield of **2** can be improved to 80% by performing the reaction at −95 °C. This result is better than the one previously reported by Rault. A second *ortho*-lithiation was achieved via the treatment of **2** with lithium diisopropylamide (LDA, 2 equiv) at −95 °C.[9] The reasoning behind this sequence was based on the increased acidity of H(5) of **2** resulting from the inductive effect of the bromine atom. Thus, 3-bromo-4-cyano-5-iodopyridine (**3**) was obtained in a 74% yield upon quenching of the resulting reaction mixture with iodine. The structure of compound **3** was confirmed via ^{1}H NMR spectroscopy with the appearance of two singlets at 8.98 ppm and 8.81 ppm, corresponding to H(2) and H(6), respectively.

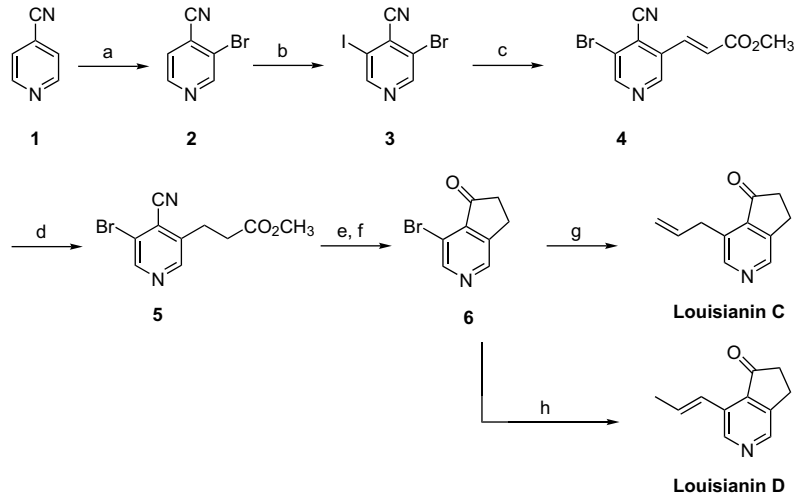


	R^1	R^2	R^3
A	O	OH	allyl
B	OH, H	OH	allyl
C	O	H	allyl
D	O	H	*trans*-1-propenyl

Figure 1. Structures of the members of the louisianin family.

* Corresponding author. Tel.: +886 4 23323456; fax: +886 4 23316699.
E-mail address: cychang@asia.edu.tw (C.-Y. Chang).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.11.075



Scheme 1. Reagents and conditions: (a) LTMP, THF, −95 °C, then CBr_4, 80%; (b) LDA, THF, −95 °C, then I_2, 74%; (c) methyl acrylate, $Pd(OAc)_2$, K_2CO_3, TBAB, CH_3CN, 90 °C, 92%; (d) H_2, PtO_2, MeOH, 64%; (e) *t*-BuOK, THF, 0 °C; (f) $HCl_{(aq)}$, CH_3OH, reflux, 71% over two steps; (g) allyltri-*n*-butyltin, $Pd(PPh_3)_4$, DMF, 85 °C, 90%; (h) allyltri-*n*-butyltin, $Pd(PPh_3)_4$, DBU, DMF, 85 °C, 82%.

The palladium-catalyzed coupling reaction of **3** with methyl acrylate according to the standard Heck procedure yielded a 1:1 mixture of (*E*)-methyl 3-(5′-bromo-4′-cyanopyridin-3′-yl)acrylate (**4**) and the deiodinated product **2**.[4,7] However, the regioselective product **4** could be obtained with a 92% yield using $Pd(OAc)_2$ in acetonitrile and in the presence of tetra-*n*-butylammonium bromide (TBAB).[10] The equal isotopic abundance of parent peaks at mass units 266 and 268 confirmed the persistence of a bromine atom. Subsequent hydrogenation with 10% Pd/C in methanol did not lead to the desired product, but rather gave the debrominated methyl 3-(4′-cyanopyridin-3′-yl)propanoate. The presence of two aromatic protons with a small coupling constant (ca. 5 Hz) indicated that they were located next to each other.[11,12] The target 3-(5′-bromo-4′-cyanopyridin-3′-yl)propanoate (**5**) was successfully obtained in a 64% yield using PtO_2 instead of 10% Pd/C as the catalyst.[13] In the ^1H NMR spectrum, the two aromatic protons resonate as singlets at 8.77 ppm and 8.63 ppm.

The key step of the synthesis was a cyclization–decarboxylation sequence that we had previously developed for the preparation of louisianin A. Thus, compound **5** was treated with potassium *tert*-butoxide at 0 °C to first generate an enolate that could then attack the cyano group to form a fused five-membered ring. Subsequent hydrolysis under acidic conditions induced a decarboxylation and gave 4-bromo-6,7-dihydrocyclopenta[*c*]pyridin-5-one (**6**) in a satisfactory yield (71%).[7] The infrared spectrum showed a strong absorption at 1724 cm^{-1} corresponding to the carbonyl group. The final Stille coupling with allyltri-*n*-butyltin in DMF and in the presence of $Pd(PPh_3)_4$ led to louisianin C in an excellent yield (90%).[7,14] The obtained spectral data are in agreement with those reported in the literature.[2,4,6]

As indicated in the literature,[3,6] louisianin C can be transformed into louisianin D by thermodynamic isomerization. Thus, the same procedure as the one described for the synthesis of louisianin C was followed for the synthesis of louisianin D but 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to the reaction mixture in order to induce the isomerization. Louisianin D was finally obtained in a remarkable yield of 82%. The large coupling constant (16.2 Hz) for the trans-located olefinic protons is consistent with the predicted structure. The spectroscopic data of the prepared louisianin D are identical to those previously reported.[2,5,6]

3. Conclusion

In summary, we report on a concise and expedient route for the total syntheses of louisianins C and D in overall yields of 22% and 20%, respectively. These yields are higher than the ones obtained with other published methods. The synthetic sequence is based on a previously developed cyclization–decarboxylation procedure to obtain the fused double ring structure in a common key intermediate. In this work we have thus developed a general and efficient route for the preparation of all members of the louisianin family.

4. Experimental

4.1. General

Starting materials were obtained from commercial suppliers and used without further purification unless otherwise stated. All reactions were performed in a flame-dried apparatus under an atmosphere of nitrogen at room temperature unless otherwise stated. THF was distilled from sodium/benzophenone under nitrogen. Flash chromatography was carried out using Merck silica gel 60, 70–230 mesh ASTM. Melting points are uncorrected. Infrared spectra were recorded on a Bruker FTIR Equinox 55. NMR spectra were recorded on a Varian Mercury 400 or on a Varian INOVA 600. The chemical shifts are reported as δ values in parts per million and relative to TMS (δ=0), which was used as an internal standard in $CDCl_3$ for the ^1H NMR spectra. The center peak of $CDCl_3$ (δ=77.0 ppm) was used as an internal standard in the ^{13}C NMR spectra. EI-mass spectra were collected using a Finnigan MAT 95XL Mass Spectrometer. Elemental analyses were collected using an Elementar vario III CHN-OS-RAPID Elemental Analyzer.

4.2. 3-Bromo-4-cyanopyridine (2)

A 1.6 M *n*-butyllithium solution (25 mL, 40 mmol) was added at −35 °C to a solution of 2,2,6,6-tetramethylpiperidine (6.9 mL, 40 mmol) in dry THF (150 mL). The LTMP solution was stirred at −35 °C for 15 min and then cooled to −95 °C. After 30 min of stirring at −95 °C, a solution of 4-cyanopyridine (2.08 g, 20 mmol) in THF (10 mL) was slowly added over a period of 20 min. A solution of

CBr_4 (8.00 g, 24 mmol) in THF (10 mL) was then added at −95 °C in one portion, and the resulting mixture was stirred for 10 s. The reaction mixture was quenched by addition of a saturated ammonium chloride solution (20 mL) and extracted with ethyl acetate (3×50 mL). The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to afford a brownish solid (4.23 g). The crude product was purified by flash column chromatography and eluted with hexane/EtOAc (10:1) to obtain **2** (2.93 g, 80%) as a white solid. Mp 97–98 °C; IR (KBr) 3077, 3013, 2238, 1573, 1470, 1403, 1280, 1218 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.72 (d, J=4.8 Hz, 1H), 7.56 (d, J=4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 148.5, 126.8, 123.2, 122.1, 114.8; MS (EI): m/z 182 (M^+); HRMS (EI) m/z calcd for $C_6H_3N_2Br$ 181.9480, found 181.9485. Anal. Calcd for $C_6H_3N_2Br$: C, 39.37; H, 1.64; N, 15.31. Found: C, 39.06; H, 1.36; N, 15.28.

4.3. 3-Bromo-4-cyano-5-iodopyridine (3)

A 1.6 M *n*-butyllithium solution (2.5 mL, 4 mmol) was added at −40 °C to a solution of diisopropylamine (0.56 mL, 4 mmol) in dry THF (50 mL). The LDA solution was stirred at −40 °C for 15 min and cooled to −95 °C. After 30 min of stirring at −95 °C, a solution of compound **2** (0.37 g, 2 mmol) in THF (3 mL) was slowly added over a period of 20 min. Subsequently, a solution of iodine (0.51 g, 2 mmol) in THF (3 mL) was added at −95 °C in one portion and the resulting mixture was stirred for 10 s. The reaction mixture was then quenched by addition of a saturated ammonium chloride solution (5 mL) at −95 °C and extracted with ethyl acetate (3×20 mL). The extracts were combined, washed with saturated sodium sulfite and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to afford a yellowish solid (0.63 g). The crude product was purified by flash column chromatography and eluted with hexane/EtOAc (30:1) to afford **3** (0.46 g, 74%) as a white solid. Mp 156–157 °C; IR (KBr) 2971, 2862, 2232, 1541, 1389, 1223, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.8, 130.1, 122.9, 116.0, 97.0; MS (EI): m/z 308 (M^+); HRMS (EI) m/z calcd for $C_6H_2N_2BrI$ 307.8446, found 307.8444. Anal. Calcd for $C_6H_2N_2BrI$: C, 23.32; H, 6.48; N, 9.07. Found: C, 23.71; H, 6.57; N, 9.37.

4.4. (*E*)-Methyl 3-(5′-bromo-4′-cyanopyridin-3′-yl)acrylate (4)

A solution of compound **3** (3.09 g, 10 mmol), methyl acrylate (2.7 mL, 30 mmol, 3 equiv), potassium carbonate (1.04 g, 7.5 mmol, 1.5 equiv), palladium(II) acetate (0.23 g, 10 mol %), and tetra-*n*-butylammonium bromide (3.22 g, 10 mmol, 1 equiv) in dry acetonitrile (100 mL) was flushed with nitrogen for 5 min. The reaction mixture was stirred at 90 °C for 29 h and monitored by thin-layer chromatography (TLC). The reaction mixture was then cooled to room temperature, filtered, and concentrated in vacuo to yield a dark brown solid. The crude solid was dissolved in water (30 mL) and extracted with ethyl acetate (3×50 mL). The organic phases were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to afford a brownish solid (5.92 g).The crude product was purified by flash column chromatography and eluted with hexane/EtOAc (3:1) to give **4** (2.46 g, 92%) as a white solid. Mp 144–145 °C; IR (KBr) 2955, 2238, 1712, 1642, 1447, 1326, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.88 (s, 1H), 7.86 (d, J=16 Hz, 1H), 7.75 (d, J=16 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3, 152.4, 146.6, 135.9, 133.4, 125.7, 123.1, 122.2, 113.5, 52.4; MS (EI): m/z 266 (M^+); HRMS (EI) m/z calcd for $C_{10}H_7N_2O_2Br$ 265.9691, found 265.9698. Anal. Calcd for $C_{10}H_7N_2O_2Br$: C, 44.96; H, 2.62; N, 10.49. Found: C, 45.00; H, 2.46; N, 10.21.

4.5. Methyl 3-(5′-bromo-4′-cyanopyridin-3′-yl)propanoate (5)

A solution of compound **4** (0.54 g, 2 mmol) and PtO_2 (23 mg, 5 mol %) in dry methanol (20 mL) was flushed three times with hydrogen gas and stirred under hydrogen atmosphere for 54 h. The solution was filtered and concentrated in vacuo to obtain a viscous liquid (0.56 g). The crude product was purified by flash column chromatography and eluted with hexane/EtOAc (3:1) to afford **5** (0.35 g, 64%) as a colorless solid. Mp 54–55 °C; IR (KBr) 3003, 2958, 2242, 1722, 1443, 1410, 1374 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.63 (s, 1H), 3.69 (s, 3H), 3.20 (d, J=7.4 Hz, 2H), 2.78 (d, J=7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 150.2, 149.1, 139.8, 123.2, 122.1, 113.8, 51.8, 33.5, 27.0; MS (EI): m/z 268 (M^+); HRMS (EI) m/z calcd for $C_{10}H_9N_2O_2Br$ 267.9847, found 267.9846 Anal. Calcd for $C_{10}H_9N_2O_2Br$: C, 44.62; H, 3.35; N, 10.41. Found: C, 45.00; H, 3.46; N, 10.35.

4.6. 4-Bromo-6,7-dihydrocyclopenta[*c*]pyridin-5-one (6)

Potassium *tert*-butoxide (0.34 g, 3.1 mmol, 2.4 equiv) was added at 0 °C and in one portion to a solution of compound **5** (0.35 g, 1.3 mmol) in dry THF (20 mL). The reaction mixture was stirred at 0 °C for 30 s, quenched by addition of acetic acid (1 mL) and water (5 mL), and extracted with ethyl acetate (3×20 mL). The combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to afford a greenish solid (0.34 g). The crude product was dissolved in methanol (40 mL) and concentrated hydrochloric acid (20 mL) was added at 0 °C. The acidic solution was heated to reflux for 16 h. Methanol was removed in vacuo and the dark brown residue was dissolved in ethyl acetate (50 mL). The mixture was basified with saturated sodium carbonate (20 mL) and extracted with ethyl acetate (3×30 mL). The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The brown crude product (0.38 g) was purified by flash chromatography and eluted with hexane/EtOAc (2:1) to give **6** (0.196 g, 71%) as a yellowish solid. Mp 87–88 °C; IR (KBr) 2933, 1724, 1579, 1550, 1407, 1267, 1141 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.73 (s, 1H), 3.20–3.17 (m, 2H), 2.82–2.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.4, 151.0, 150.2, 148.2, 140.2, 115.6, 36.7, 22.9; MS (EI): m/z 211 (M^+); HRMS (EI) m/z calcd for C_8H_6NOBr 210.9633, found 210.9640. Anal. Calcd for C_8H_6NOBr: C, 45.30; H, 2.83; N, 6.61. Found: C, 45.70; H, 3.02; N, 6.47.

4.7. Louisianin C

A solution of compound **6** (0.11 g, 0.5 mmol), allyltri-*n*-butyltin (0.17 mL, 0.55 mmol, 1.1 equiv), and tetrakis(triphenylphosphine) palladium (0.06 g, 10 mol %) in DMF (1 mL) was degassed by bubbling nitrogen for 5 min. The reaction mixture was heated to 85 °C for 1 h, cooled to room temperature, and filtered through a pad of silica gel to remove residual palladium. The pad was washed with ethyl acetate (3×10 mL) and the solution was concentrated in vacuo to give a yellowish liquid (0.16 g). Flash column chromatography with hexane/EtOAc (1:1) afforded louisianin C (78 mg, 90%) as a colorless liquid. IR (neat, KBr) 2925, 1720, 1638, 1587, 1419, 1253, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.47 (s, 1H), 6.04–5.94 (m, 1H), 5.12–5.06 (m, 2H), 3.81 (d, J=6.8 Hz, 2H), 3.18–3.15 (m, 2H), 2.74–2.71 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.3, 149.1, 148.2, 147.8, 139.7, 135.4, 133.0, 116.8, 36.5, 32.7, 23.2; MS (EI): m/z 173 (M^+); HRMS (EI) m/z calcd for $C_{11}H_{11}NO$ 173.0840, found 173.0848.

4.8. Louisianin D

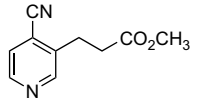
A solution of compound **6** (0.11 g, 0.5 mmol), allyltri-*n*-butyltin (0.17 mL, 0.55 mmol, 1.1 equiv), DBU (0.15 mL, 1 mmol, 2 equiv),

and tetrakis(triphenylphosphine) palladium (0.06 g, 10 mol %) in DMF (1 mL) was degassed by bubbling nitrogen for 5 min. The mixture was heated to 85 °C for 1 h, cooled to room temperature, and filtered through a pad of silica gel to remove residual palladium. The pad was washed with ethyl acetate (3×10 mL) and the solution was concentrated in vacuo to give a yellowish liquid (0.14 g). Purification by flash column chromatography with hexane/EtOAc (1:1) gave louisianin D (71 mg, 82%) as a white solid. Mp 165–166 °C; IR (KBr) 2932, 1714, 1641, 1576, 1456, 1293, 1196 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.67 (s, 1H), 7.41 (dd, J=1.6, 16.2 Hz, 1H), 6.60–6.51 (m, 1H), 3.14 (t, J=6.2 Hz, 2H), 2.73–2.70 (m, 2H), 1.98 (dd, J=1.6, 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.6, 147.6, 147.0, 145.0, 137.1, 132.4, 130.8, 123.7, 36.5, 23.0, 19.1; MS (EI): m/z 173 (M^+); HRMS (EI) m/z calcd for $C_{11}H_{11}NO$ 173.0840, found 173.0836.

Acknowledgements

Support from the National Science Council of the Republic of China is gratefully acknowledged. We thank the Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan, ROC for analyzing the NMR spectra and Prof. T. J. Chow for discussions and corrections.

References and notes

1. Komiyama, K.; Takamatsu, S.; Kim, Y.-P.; Matsumoto, A.; Takahashi, Y.; Hayashi, M.; Woodruff, H. B.; Ōmura, S. *J. Antibiot.* **1995**, *48*, 1086–1089.
2. Takamatsu, S.; Kim, Y.-P.; Hayashi, M.; Furuhata, K.; Takayanagi, H.; Komiyama, K.; Woodruff, H. B.; Ōmura, S. *J. Antibiot.* **1995**, *48*, 1090–1094.
3. Sunazuka, T.; Tian, Z.-M.; Harigaya, Y.; Takamatsu, S.; Hayashi, M.; Komiyama, K.; Ōmura, S. *J. Antibiot.* **1997**, *50*, 274–275.
4. Beierle, J. M.; Osimboni, E. B.; Metallinos, C.; Zhao, Y.; Kelly, T. R. *J. Org. Chem.* **2003**, *68*, 4970–4972.
5. Chen, H.-W.; Hsu, R.-T.; Chang, M.-Y.; Chang, N.-C. *Org. Lett.* **2006**, *8*, 3033–3035 and references cited therein.
6. Catozzi, N.; Wasnaire, P.; Taylor, R. J. K. *Tetrahedron Lett.* **2008**, *49*, 2865–2868.
7. Chang, C.-Y.; Liu, H.-M.; Chow, T. J. *J. Org. Chem.* **2006**, *71*, 6302–6304.
8. Cailly, T.; Fabis, F.; Lemaître, S.; Bouillon, A.; Rault, S. *Tetrahedron Lett.* **2005**, *46*, 135–137.
9. (a) Gribble, G. W.; Saulnier, M. G. *Tetrahedron Lett.* **1980**, *21*, 4137–4140; (b) Karig, G.; Spencer, J. A.; Gallagher, T. *Org. Lett.* **2001**, *3*, 835–838.
10. (a) Back, T. G.; Pandyra, A.; Wulff, J. E. *J. Org. Chem.* **2003**, *68*, 3299–3302; (b) Zhang, Z.; Zha, Z.; Gan, C.; Pan, C.; Zhou, Y.; Wang, Z.; Zhou, M.-M. *J. Org. Chem.* **2006**, *71*, 4339–4342.
11. 

3-(4'-cyanopyridin-3'-yl)propanoate

The compound was identified by ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.65 (d, J=5.2 Hz, 1H), 7.50 (d, J=5.2 Hz, 1H), 3.69 (s, 3H), 3.19 (t, J=7.6 Hz, 2H), 2.77 (t, J=7.6 Hz, 2H).
12. (a) Sone, T.; Umetsu, Y.; Sato, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 864–868; (b) Faucher, N.; Ambroise, Y.; Cintrat, J.-C.; Doris, E.; Pillon, F.; Rousseau, B. *J. Org. Chem.* **2002**, *67*, 932–934.
13. Nakazato, A.; Ohta, K.; Sekiguchi, Y.; Okuyama, S.; Chaki, S.; Kawashima, Y.; Hatayama, K. *J. Med. Chem.* **1999**, *42*, 1076–1087.
14. (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508–524; (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478–5486; (c) Markey, M. D.; Fu, Y.; Kelly, T. R. *Org. Lett.* **2007**, *9*, 3255–3257.