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Synthesis of 2,6-disubstituted dihydropyrans via an efficient BiBr$_3$-initiated three component, one-pot cascade

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Abstract

The rapid synthesis of cis-2,6-disubstituted dihydropyrans is achieved in a three-component, one-pot cascade reaction. BiBr$_3$-mediated addition of ketene silyl acetals or silyl enol ethers to $\beta,\gamma$-unsaturated cis-4-trimethylsilyl-3-butenal provides a Mukaiyama aldol adduct containing a vinylsilane moiety tethered to a silyl ether. Addition of a second aldehyde initiates a domino sequence involving intermolecular addition followed by an intramolecular silyl-modified Sakurai (ISMS) reaction. Isolated yields of this one-pot reaction vary from 44 to 80% and all compounds were isolated as the cis-diastereomers (10 examples).

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1. Introduction

In efforts to reduce environmental impacts, increase atom economy as well as overall efficiency and convergence of experimental protocols, one-pot, multi-component reactions (MCRs) have become increasingly common in organic synthesis. Efforts toward a number of natural products have resulted in the development of several protocols in which formation of an initial adduct is required to provide the substrate for a subsequent reaction. The literature has alternatively referred to such processes as tandem, multi-component, cascade, or domino reactions, although the precise meaning of each adjective has not been entirely consistent.

As part of a program to further develop the uses of environmentally-benign$^{3,4}$ Bi(III) compounds in organic synthesis, we recently described$^5$ the BiBr$_3$-initiated intermolecular addition followed by intramolecular silyl-modified Sakurai reaction (ISMS)$^{6,7}$ toward 2,6-disubstituted dihydropyrans (DHPs) with cis-diastereoselectivity (Eq. 1). Similar DHPs were either present in, or could be used as intermediates toward syntheses of a number of biologically active natural products such as ambruticin$^1$, the phorboxazoles$^9$, leucascandrolide$^{10}$, kendomycin$^{11}$, neopeltolide$^{12}$, the clavisolides$^{13}$ and the diospongins$^{14}$. The prevalence of DHPs, and derivatives thereof, has led to a large number of concise and selective methods for their synthesis$^{15-18}$.

More specifically, the utility of a DHP moiety attached to the $\alpha$-position of a carbonyl compound$^{19}$ prompted us to further investigate a three-component, one-pot cascade reaction involving an initial Mukaiyama aldol reaction followed by an addition/ISMS sequence as shown in the retrosynthetic analysis below (Scheme 1).

Given how rapidly molecular complexity is increased in this short sequence, we examined the utility of several silane nucleophiles, and aldehydes (RCHO). Herein, we report further examples of this multi-component, one pot reaction and details of our optimization studies.

2. Results and discussion

In order to evaluate the feasibility of the first step of the three-component process, we prepared aldehyde, (Z)-2, in two, straightforward steps from commercially-available 4-trimethylsilyl-3-butyne-1-ol.$^{20}$

Scheme 1. Retrosynthetic analysis of 2,6-disubstituted DHPs.
Reduction under nickel catalyzed conditions (P-2)\textsuperscript{16k} was most convenient as it led to the best (Z):(E) ratios (\(\approx 95:5\)) with little or no over-reduction to the alkane. As expected, the resulting \(\beta,\gamma\)-unsaturated aldehyde, \(2\),\textsuperscript{4} is particularly sensitive, and Dess–Martin periodinane\textsuperscript{21} was the only oxidant that afforded the desired substrate in sufficient purity to study the three-component sequence. We chose to focus on using the (Z)-vinylsilane due to recent work by Meilert and Brimble\textsuperscript{22} as well Dobbs et al.\textsuperscript{23} showing that the cis-vinylsilane isomers efficiently participated in intramolecular reactions.

The initial Mukaiyama aldol\textsuperscript{14–26} between \(2\) and the commercially-available methyl trimethylsilyldimethyl-ketene acetal \(1\); \(R=\text{OMe}, R^1=R^2=\text{H}\) readily occurred at room temperature (Scheme 2) in the presence of 10 mol \% BiBr\textsubscript{3} in CH\textsubscript{2}Cl\textsubscript{2} (\(\approx 0.1\) M). Crude \textsuperscript{1}H NMR spectroscopic analyses and TLC indicated that the initial Mukaiyama aldol reaction cleanly affords the sensitive silylated aldol adduct, \(A\), which is an effective nucleophile for the second addition/silyl-Prins step (ISMS).\textsuperscript{5} Although the free alcohol corresponding to \(A\) could be isolated by column chromatography, in practice, we carried \(A\) onto the next step without isolation or purification. Mukaiyama aldol reactions involving Bi(III) are also efficient in CH\textsubscript{3}CN, but we chose CH\textsubscript{2}Cl\textsubscript{2} as the solvent since our previous studies indicated that the intermolecular addition and ISMS occurred more efficiently in this solvent versus CH\textsubscript{3}CN.\textsuperscript{3} Addition of a second aldehyde (\(R^2\)CHO) and 10 mol \% more BiBr\textsubscript{3} results in an intermolecular addition of \(A\) to the second aldoldehyde (\(R^2\)CHO) to afford the \(\varepsilon\)-oxocarbenium ion, \(B\). An intramolecular silyl-Prins reaction then affords \(3a\)–\(3j\) via the intermediate stabilized cation, \(C\).

When using 1.1–1.4 equiv of ketene acetal (Table 1, entries 1–4 and 11), the initial aldol reaction occurs very rapidly at temperatures down to \(-20\) °C in CH\textsubscript{2}Cl\textsubscript{2} or CH\textsubscript{3}CN. During optimization, we did find that the single most important variable for clean formation of the Mukaiyama adduct, \(A\), was the specific commercial samples of ketene silyl acetal. Although we examined individual samples by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy and found no significant impurities, some reactions required up to 1.4 equiv of the ketene silyl acetal nucleophile whereas another was effectively used with as little as 1.1 equivalents. This is most likely due to variations in trace water content and competing hydrolysis reactions during the Mukaiyama aldol step.

In all cases in which silyl enol ethers were used instead of the more nucleophilic ketene silyl acetal\textsuperscript{27} at the same concentration (entry 3 vs 5), the reaction was much slower at room temperature and did not proceed to completion unless the BiBr\textsubscript{3} was activated by sonication in the presence of NaI as reported by Le Roux et al.\textsuperscript{28} This presumably affords the more reactive BiI\textsubscript{3} salt in situ. We later found, however, that activation and sonication could be avoided, albeit less efficiently, if the aldol was conducted at \(-0.2\) M instead of \(-0.1\) M without NaI activation (entries 6 vs 7 and 8 vs 9).

In all cases where the hydrogens adjacent to the oxygen in the ring system could be sufficiently separated in the \textsuperscript{1}H NMR spectrum, qualitative \textsuperscript{1}H NOE spectra indicated that the cis-isomers\textsuperscript{49} of DHPs \(3a\)–\(3j\) were the only diastereomers observed in agreement with other silyl-Prins type cyclizations (Fig. 1)\textsuperscript{22,23}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Observed qualitative NOE enhancement.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Entry & \(R\) & \(R^1\) & \(R^2\) & Product & \(dr\) (cis/trans)\textsuperscript{a} & Yield\textsuperscript{b} (%) \\
\hline
1 & MeO– & –Me & PhCH\textsubscript{2}– & \(3a\) & >99:1 & 64 \\
2 & MeO– & –Me & i-Pr– & \(3b\) & >99:1 & 53 \\
3 & MeO– & –Me & n-C\textsubscript{6}H\textsubscript{11}– & \(3c\) & >99:1 & 64 \\
4 & MeO– & –Me & ortho-CHO\textsubscript{3}C\textsubscript{6}H\textsubscript{4}– & \(3d\) & >99:1 & 55 \\
5 & Ph– & –H & n-C\textsubscript{6}H\textsubscript{11}– & \(3e\) & >99:1 & 76\textsuperscript{c} \\
6 & Ph– & –H & 1-ethylpropyl– & \(3f\) & >19:1 & 66\textsuperscript{d} \\
7 & Ph– & –H & 1-ethylpropyl– & \(3f\) & >19:1 & 56\textsuperscript{d} \\
8 & tert-Bu– & –H & n-C\textsubscript{6}H\textsubscript{15}– & \(3g\) & >19:1 & 80\textsuperscript{d} \\
9 & tert-Bu– & –H & n-C\textsubscript{6}H\textsubscript{15}– & \(3g\) & >19:1 & 55\textsuperscript{d} \\
10 & tert-Bu– & –H & PhCH\textsubscript{2}CH\textsubscript{2}– & \(3h\) & >19:1 & 52\textsuperscript{d} \\
11 & MeO– & –Me & PhCH\textsubscript{2}CH\textsubscript{2}– & \(3i\) & >19:1 & 63 \\
12 & Ph– & –H & Ph– & \(3j\) & >19:1 & 44\textsuperscript{d} \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a} Diastereoselectivities were determined by \textsuperscript{1}H NMR or GC–MS analysis of crude reaction mixtures prior to chromatographic separation.
\textsuperscript{b} Yields are reported for pure, isolated cis-compounds characterized by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopy, IR spectrometry and HRMS or elemental analysis.
\textsuperscript{c} Initial Mukaiyama aldol carried out at \(-0.1\) M with added NaI and sonication.
\textsuperscript{d} Initial Mukaiyama aldol carried out at \(-0.2\) M with neither added NaI, nor sonication.
We were particularly interested in syntheses using $\beta, \beta$-unsubstituted enol ethers as nucleophiles since these resulting intermediates and products might be prone to aldol reactions or eliminations via putative enols or enolates. We were gratified to isolate several products with enolizable hydrogens $z$- to the carbonyl moiety; these were obtained in yields ranging from 52% to 80% (entries 5–10). The lowest yield was observed for product 3j (entry 12) even though both the initial Mukaiyama aldol and the subsequent addition/silyl-Prins reactions appeared clean by TLC analysis and $^1$H NMR spectroscopic evaluation of the crude product. This particular product appeared less stable than the other nine and prolonged reaction times led to complex mixtures while storage at room temperature also caused decomposition. This instability is likely due to the fact that the phenyl substituent ($R^2$) promotes ring opening under the reaction conditions via a benzylic cation.

Although we attempted cyclizations using (E)-vinylsilanes due to reports that the (E)-vinylsilanes provided trans,2,6-diastereomers, we found that in the two-component case analogous to that in Eq. 1, only trace quantities of cyclization products were afforded (GC–MS) using (E)-vinylsilanols. This result is consistent with the stereoelectronic stabilization of the developing cation by the axial trimethylsilyl moiety in intermediates $B$ and $C$ (Scheme 2) as described by Speckamp and Roush for DHPs as well as ketene silyl acetals and silyl enol ethers are effective nucleophiles afforded valuable 2,6-disubstituted dihydropyran products. Both $E$ and $Z$ isomers as a colorless oil: IR (neat) 717–728 (m, $\delta$H), 577–582 (m, 1H), 5.63 (dm, J = 10.3 Hz, 1H), 4.27 (br, 1H), 3.77 (dd, J = 11.0, 3.3 Hz, 1H), 3.55 (s, 3H), 2.38 (dd, J = 13.9, 8.1 Hz, 1H), 2.70 (dd, J = 13.9, 8.1 Hz, 1H), 2.06–2.15 (m, 1H), 1.77–1.85 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H); $^1$C NMR (APT) (100 MHz, CDCl$_3$) $\delta$ 177.2 (e), 138.7 (e), 129.72 (o), 129.69 (o), 128.0 (o), 126.1 (o), 125.0 (o), 78.4 (o), 76.5 (o), 52.0 (o), 46.6 (e), 42.1 (e), 25.4 (e), 21.3 (e), 20.4 (o). Anal. Calcd for C$_7$H$_2$O$_2$Si: C 74.42, H 8.08; found: C 74.53, H 8.30.

3.2. General procedure

3.2.1. Preparation of methyl cis-2-(6-benzyl-3,6-dihydro-2H-pyran-2-yl)-2,2-dimethyl propanoate (3a)

BiBr$_3$ (45 mg, 0.10 mmol, 0.10 equiv) was weighed into 25 mL round bottom flask and 10 mL CH$_2$Cl$_2$ was added via syringe. (Z)-4-(trimethylsilyl)but-3-enal (0.142 g, 1.00 mmol, 1.00 equiv) and methyl trimethylsilyl dimethylketene acetal (0.192 g, 1.10 mmol, 1.10 equiv) were added by syringe simultaneously. The mixture was stirred at room temperature until (Z)-4-(trimethylsilyl)but-3-enal, 2 was consumed by TLC (3 h). Additional BiBr$_3$ (45 mg, 0.010 mmol, 0.10 equiv) and phenylacetaldehyde (0.24 g, 2.00 mmol, 2.00 equiv) were added and the mixture was stirred for 12 h at rt. The solution was concentrated in vacuo, filtered through a small SiO$_2$ pipette column with CH$_2$Cl$_2$ as eluent and concentrated in vacuo again. The product was purified by column chromatography (9:1 petroleum ether:Et$_2$O. $R_f$ = 0.34) to provide 0.175 g (64%) of cis-isomer as a colorless oil: IR (neat) 3031 (s), 2982 (s), 2940 (s), 2879 (m), 1735 (s), 1451 (m), 1267 (s), 1140 (s), 1086 (s), 751 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17–7.28 (m, 5H), 5.77–5.82 (m, 1H), 5.63 (dm, J = 10.3 Hz, 1H), 4.27 (br, 1H), 3.77 (dd, J = 11.0, 3.3 Hz, 1H), 3.55 (s, 3H), 2.38 (dd, J = 13.9, 8.1 Hz, 1H), 2.70 (dd, J = 13.9, 8.1 Hz, 1H), 2.06–2.15 (m, 1H), 1.77–1.85 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H); $^1$C NMR (APT) (100 MHz, CDCl$_3$) $\delta$ 177.2 (e), 138.7 (e), 129.72 (o), 129.69 (o), 128.0 (o), 126.1 (o), 125.0 (o), 78.4 (o), 76.5 (o), 52.0 (o), 46.6 (e), 42.1 (e), 25.4 (e), 21.3 (e), 20.4 (o). Anal. Calcd for C$_7$H$_2$O$_2$Si: C 74.42, H 8.08; found: C 74.53, H 8.30.

3.2.2. Preparation of methyl cis-2-(6-(isopropyl-3,6-dihydro-2H-pyran-2-yl)-2,2-dimethyl propanoate (3b)

Using the general procedure, 3b was prepared from BiBr$_3$ (45 mg, 0.10 mmol, 0.10 equiv), (Z)-4-(trimethylsilyl)but-3-enal (0.142 g, 1.00 mmol, 1.00 equiv), methyl trimethylsilyl dimethylketene acetal (0.192 g, 1.10 mmol, 1.10 equiv), isobutyr aldehyde (0.182 mL, 2.00 mmol, 2.00 equiv), and BiBr$_3$ (45 mg, 0.10 mmol, 0.10 equiv) as a colorless oil: IR (neat) 2961 (s), 2931 (s), 2879 (m), 1735 (s), 1451 (m), 1267 (s), 1140 (s), 1086 (s), 751 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17–7.28 (m, 5H), 5.77–5.82 (m, 1H), 5.63 (dm, J = 10.3 Hz, 1H), 4.27 (br, 1H), 3.77 (dd, J = 11.0, 3.3 Hz, 1H), 3.55 (s, 3H), 2.38 (dd, J = 13.9, 8.1 Hz, 1H), 2.70 (dd, J = 13.9, 8.1 Hz, 1H), 2.06–2.15 (m, 1H), 1.77–1.85 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H); $^1$C NMR (APT) (100 MHz, CDCl$_3$) $\delta$ 177.2 (e), 138.7 (e), 129.72 (o), 129.69 (o), 128.0 (o), 126.1 (o), 125.0 (o), 78.4 (o), 76.5 (o), 52.0 (o), 46.6 (e), 42.1 (e), 25.4 (e), 21.3 (e), 20.4 (o). Anal. Calcd for C$_7$H$_2$O$_2$Si: C 74.42, H 8.08; found: C 74.53, H 8.30.

3.2.3. Preparation of methyl cis-2-(6-pentyl-3,6-dihydro-2H-pyran-2-yl)-2,2-dimethyl propanoate (3c)

This compound was prepared according to the general procedure described for 3a using BiBr$_3$ (45 mg, 0.10 mmol, 0.10 equiv), (Z)-4-(trimethylsilyl)but-3-enal (0.142 g, 1.00 mmol, 1.00 equiv), methyl trimethylsilyl dimethylketene acetal (0.192 g, 1.10 mmol, 1.10 equiv), hexanal (0.14 mL, 2.00 mmol, 2.00 equiv) and BiBr$_3$
(45 mg, 0.10 mmol, 0.10 equiv). The product was purified by column chromatography (9:1 petroleum ether:EtO₂, Rₖ=0.52) to provide 0.163 g (64%) of cis-isomer as a colorless oil: IR (neat) 3032 (m), 2929 (s), 2858 (s), 1708 (s), 1532 (s), 1284 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.98–8.01 (m, 1H), 7.56 (tt, J=7.3, 1.5 Hz, 1H), 7.44–7.48 (m, 1H), 7.28–7.32 (m, 1H), 4.09–4.14 (m, 2H), 4.04 (dd, J=15.6, 7.6 Hz, 1H), 1.29 (s, 6H), 0.82 (t, J=7.6 Hz, 3H); ¹³C NMR (APT) (100 MHz, CDCl₃) δ 128.0 (e), 127.8 (o), 124.7 (o), 124.0 (o), 123.8 (o), 123.4 (e), 123.1 (e), 121.9 (o), 121.7 (e), 121.3 (e), 120.6 (o), 128.6 (o), 128.4 (o), 0.10 mmol, 0.20 equiv) added and the mixture was stirred for 12 h. The solution was concentrated in vacuo, filtered through a small SiO₂ pipette column with CH₂Cl₂ as eluent and concentrated in vacuo again. The product was purified by column chromatography (9:1 petroleum ether:EtO₂, Rₖ=0.40) to provide 0.179 g (66%) of cis-isomer as a light yellow oil: IR (neat) 3032 (m), 2929 (s), 2858 (s), 1708 (s), 1532 (s), 1284 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.98–8.01 (m, 1H), 1.03 (t, J=7.6 Hz, 3H), 0.82 (t, J=7.6 Hz, 3H); ¹³C NMR (APT) (100 MHz, CDCl₃) δ 128.0 (e), 127.8 (o), 124.7 (o), 124.0 (o), 123.8 (o), 123.4 (e), 123.1 (e), 121.9 (o), 121.7 (e), 121.3 (e), 120.6 (o), 128.6 (o), 128.4 (o), 128.2 (o), 71.0 (o), 45.5 (e), 31.7 (e), 22.5 (e), 22.2 (e), 12.38 (o), 12.36 (o) Analy. Calcd for C₁₃H₂₂O₁ (328.39): C 69.22, H 9.50; found: C 69.78, H 11.31.

3.2.6. Preparation of cis-2-(6-(pentan-3-yl)-3,6-dihydro-2H-pyran-2-yl)-1-phenylethanone (3F)

BiBr₃ (45 mg, 0.10 mmol, 0.10 equiv) and NaI (50 mg, 0.15 mmol, 0.30 equiv) were weighed into 15 mL round bottom flask and 5 mL CH₂Cl₂ was added via syringe. After sonication for 1 h at rt, (Z)-4-(trimethylsilyl)but-3-ene-1-carbaldehyde (0.142 g, 1.00 mmol, 1.00 equiv) and 3-phenylpropionaldehyde (0.281 mL, 2.14 mmol, 2.00 equiv) were added and the mixture was stirred for 14 h. The solution was concentrated in vacuo, filtered through a small SiO₂ column with CH₂Cl₂ as eluent and concentrated in vacuo again. The product was purified by column chromatography (9:1 petroleum ether:EtO₂, Rₖ=0.43) to provide 0.225 g (80%) of cis-isomer as a colorless oil: IR (neat) 3032 (m), 2929 (s), 2858 (s), 1708 (s), 1532 (s), 1284 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.98–8.01 (m, 1H), 7.44–7.48 (m, 1H), 7.28–7.32 (m, 1H), 4.09–4.14 (m, 2H), 3.97 (dd, J=15.6, 7.6 Hz, 1H), 1.29 (s, 6H), 0.82 (t, J=7.6 Hz, 3H); ¹³C NMR (APT) (100 MHz, CDCl₃) δ 128.0 (e), 127.8 (o), 124.7 (o), 124.0 (o), 123.9 (e), 123.1 (e), 120.8 (o), 123.4 (e), 123.1 (e), 121.9 (o), 121.7 (e), 121.3 (e), 120.6 (o), 128.6 (o), 128.4 (o), 128.2 (o), 71.0 (o), 45.5 (e), 31.7 (e), 22.5 (e), 22.2 (e), 12.38 (o), 12.36 (o) Analy. Calcd for C₁₃H₂₂O₁ (328.39): C 79.77, H 11.50; found: C 79.81, H 11.31.
chromatography (95:5 to 9:1 petroleum ether:Et2O, Rf = 0.50 in 9:1 hexanes:EtOAc) to provide 0.158 g (52%) of the cis-isomer as a colorless oil: IR (neat) 3028 vs, 2980 vs, 2874 vs, 1728 vs; 1H NMR (400 MHz, CDCl3) δ 7.24–7.29 (m, 2H), 7.14–7.20 (m, 3H), 5.81 (ddd, δ = 9.9, 3.0, 2.8, 1.0 Hz), 5.74 (ddd, δ = 9.9, 7.3, 3.0 Hz), 1.79 (m, 2H) ppm, 2.33 ppm, 1.86 ppm, 2.19 ppm; 13C (100 MHz, CDCl3) δ 213.6 (e), 142.3 (e), 130.3 (o), 128.6 (o), 128.2 (o), 126.7 (o), 124.8 (o), 107.0 (o), 74.6 (e), 43.2 (e), 37.2 (e), 31.7 (e), 31.3 (e), 26.4 (o), Anal. Calc'd for C19H18O2Na (C28H24NaO2): C 79.66, H 9.18; found: C 79.64, H 9.18.

3.2.9. Preparation of methyl 2-methyl-2-(6-phenethyl-3,6-dihydro-2H-pyran-2-yl)propanoate (3f)

BiBr3 (58 mg, 0.13 mmol, 0.10 equiv) was weighed into 15 mL round bottom flask and 5.0 mL CH2Cl2 was added via syringe. After stirring the BiBr3 suspension for 5 min, 4,5-dihydro-2H-pyran-2-yl)methyl chloroformate (0.237 g, 1.23 mmol, 1.15 equiv) were dissolved in stirring the BiBr3 suspension for 5 min, (0.153 g, 1.07 mmol, 1.00 equiv) and 1-phenyl-1-trimethylsilylbut-3-enal, (0.295 g, 1.69 mmol, 1.33 equiv) were separately treated in vacuo again. The product was finally purified by column chromatography (95:5 to 9:1 petroleum ether:Et2O, Rf = 0.48 in 9:1 hexanes:EtOAc) to provide 0.158 g (52%) of the cis-3-isomer as a light yellow oil: IR (neat) 3343–3285; 1H NMR (400 MHz, CDCl3) δ 7.24–7.29 (m, 2H), 7.14–7.20 (m, 3H), 5.81 (ddd, δ = 9.9, 3.0, 2.8, 1.0 Hz), 5.74 (ddd, δ = 9.9, 7.3, 3.0 Hz), 1.79 (m, 2H) ppm, 2.33 ppm, 1.86 ppm, 2.19 ppm; 13C (100 MHz, CDCl3) δ 213.6 (e), 142.3 (e), 130.3 (o), 128.6 (o), 128.2 (o), 126.7 (o), 124.8 (o), 107.0 (o), 74.6 (e), 43.2 (e), 37.2 (e), 31.7 (e), 31.3 (e), 26.4 (o), Anal. Calc'd for C19H18O2Na (C28H24NaO2): C 79.66, H 9.18; found: C 79.64, H 9.18.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.083.


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In cases where Brønsted and Lewis acids are present, a number of interactions are possible, including Brønsted acid assisted Lewis acid catalysts [BLA], etc. See: Yahamoto, H.; Futatsugi, K. Angew. Chem., Int. Ed. 2005, 44, 1924–1942.


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