DOI: 10.1002/ejoc.200700288

Stereoselective Synthesis of Pyrano[3,2-*c*]- and Furano[3,2-*c*]quinolines: Samarium Diiodide-Catalyzed One-Pot Aza-Diels–Alder Reactions

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Keywords: Catalysis / Diastereoselectivity / Cycloaddition / Samarium / Quinoline

Three-component aza-Diels–Alder reactions involving aromatic aldehydes, aromatic amines, and dihydropyran or dihydrofuran are effectively catalyzed by samarium diiodide to afford pyrano[3,2-*c*]- or furano[3,2-*c*]quinolines in good yields and with high stereoselectivities. Either the *cis* or the *trans* isomers can be obtained as the major products by conveniently controlling reaction conditions.

Introduction

The tetrahydroquinoline skeleton exists in many natural or synthetic biologically active materials, and its derivatives are widely applied in the pharmaceutical and biochemical fields.[1] Some of them, such as pyrano- and furanoquinolines, have attracted special attention as a result of their high degrees of structural diversity and wide spectra of biological actions.[2] The [4+2] cycloaddition reactions between *N*-arylimines (heterodienes) and dihydropyran or dihydrofuran (dienophiles) under Lewis acid catalysis conditions have long been recognized as one of the most convenient methods for the synthesis of quinolines of this type and have been explored for catalysts, scope, and applications.[3] However, most of the imines used as starting materials are unstable, which leads to difficulties in their isolation and purification. In this connection, much attention has been focused on three-component aza-Diels–Alder reactions involving aldehyde, amine, and either dihydropyran or dihydrofuran. A series of Lewis acids such as Ln(OTf)$_3$,[4] GdCl$_3$,[5] molecular iodine,[6] TMSCl,[7] SbCl$_3$,[8] and Selectfluor™[9] have been found to be effective catalysts for this purpose. Normally, the process affords the products as mixtures of *cis* and *trans* isomers, in which the *trans* isomer is the major one in most cases. It is noteworthy that the use of Lewis acids as catalysts in one-pot reactions to prepare the tetrahydroquinolines stereoselectively with particular preference for the *cis* isomers has met with limited success in the past. Kobayashi[4a] has reported the formation of furano[3,2-*c*]quinoline with 62% *cis* selectivity using (polyallyl)scandium trifylamide ditriflate as a catalyst. More recently, Yadav[9] has demonstrated the utility of Selectfluor™ as a catalyst to generate about 90% yields of *cis* pyrano- and furanoquinolines. Therefore, it is still necessary to develop new and efficient catalysts for stereoselective syntheses of tetrahydroquinolines to make better use of this one-pot synthesis methodology.

On the other hand, SmI_2 has served as a Lewis acid-type precatalyst and has been applied to a variety of reactions.[10] In our ongoing research into developing SmI_2 as a precatalyst in organic synthesis,[11] we investigated one-pot imino-Diels–Alder reactions of aldehydes and amines with dihydropyran or dihydrofuran in the presence of catalytic amount of SmI_2. It was found that SmI_2 was effective for this process and that the stereoselective synthesis of pyrano[3,2-*c*]- and furano[3,2-*c*]quinolines could conveniently be effected through control of the reaction conditions. We now wish to report on these results.

Results and Discussion

To select favorable reaction conditions, we first examined the model reaction with benzaldehyde, aniline, and 3,4-dihydro-2*H*-pyran (Scheme 1) in the presence of catalytic amount of SmI_2 (20 mol-%) in different solvents at room temperature. A strong influence of the solvent both on the yield and on the *cis*/*trans* ratio of the product was observed (Table 1). Tetrahydrofuran (Table 1, Entry 1) and acetonitrile (Table 1, Entry 2) were found to be the best solvents among those tested, which also included dimethoxyethane, diethyl ether, and toluene (Table 1, Entries 3–5). THF was finally chosen as the solvent in which to perform the reaction, owing to its superiority over CH_3CN in terms of nontoxicity.

To our surprise, a *cis* isomer was obtained as the major product when the reaction was carried out in the absence of solvent (Table 1, Entry 6). With regard to the reaction in THF or CH_3CN, it seems that in this SmI_2-catalyzed aza-

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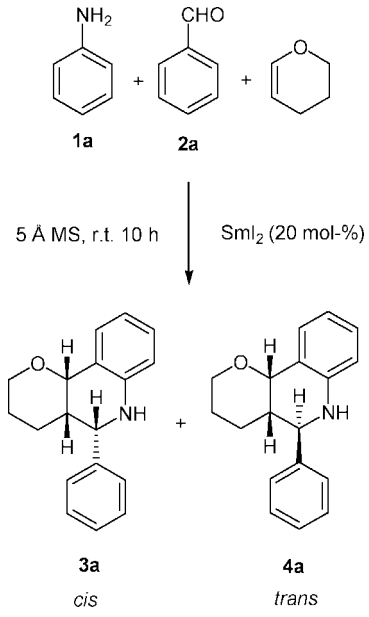


Scheme 1.

Table 1. SmI_2-catalyzed one-pot synthesis of pyrano[3,2-*c*]quinolines.[a]

Entry	Solvent	% isolated yield	**3a/4a**[b]
1	THF	90	28:72
2	CH_3CN	88	27:73
3	DME	70	40:60
4	Et_2O	46	42:58
5	toluene	15	–
6[c]	–	74	72:28

[a] Typical reaction conditions: benzaldehyde/aniline/dihydropyran = 1:1.1:1.4, 20 mol-% SmI_2 relative to aldehyde, room temperature, 10 h, 5-Å molecular sieves. [b] Determined by ^1H NMR spectroscopy. [c] The reaction time is 5 h.

Diels–Alder reaction there are some links between the ratio of the two isomers and the solvent conditions: the *trans* isomer was always the major product in organic solvents, while the *cis* isomer was the major one obtained under solvent-free conditions. Masaki[12] reported a one-pot imino-Diels–Alder reaction giving the *cis* isomer as the major cycloadduct with the polymer-supported dicyanoketene acetal (DCKA) as a π-acid catalyst, and to the best of our knowledge this was the unique "solvent-free" example of this procedure favoring a *cis* product. However, use of a large excess (11 equiv.) of the 3,4-dihydro-2*H*-pyran dienophile was necessary to ensure that the reaction would proceed smoothly under solvent-free conditions in that case, while similar results could be achieved here by using only 1.4 equiv. 3,4-dihydro-2*H*-pyran.

In addition, various conditions including temperature and substrate concentration were screened in order to address their influence on the stereoselectivity of the model reaction, and the results are presented in Table 2. It can be seen that increasing the reaction temperature led to an increase in the *trans* content of the product: when the reaction temperature was increased from –20 °C to 50 °C, the *trans* content increased from 74% to 96% for the reaction in 3 mL THF, from 64% to 84% for the reaction in 1 mL THF, and from 22% to 47% for the reaction without THF. Such a temperature dependence of stereoselectivity may be attributed to the difference in activation energy between the two reactions affording *cis* and *trans* isomers, respectively. In the meantime, decreasing the substrate concentration also resulted in an increase in the *trans* content, accompanied by a corresponding decrease in the *cis* content. For example, when the amount of THF was increased from 0 to 3 mL, the *trans* content increased dramatically, from 22% to 74% at –20 °C, 28% to 81% at room temperature, and 47% to 96% at 50 °C. It is obvious that the influence of the substrate concentration on the stereoselectivity is much stronger than that of the temperature. Generally speaking, a higher substrate concentration means a more rapid reaction rate. These results show that the *cis* adduct is favored at rapid reaction rates and lower temperatures, and the *trans* adduct at slower reaction rates and higher temperatures. Therefore, the *cis* isomer may be a kinetically controlled product and the *trans* isomer may be a thermodynamically controlled one, and so the reactions provide a new and efficient route for the controllable stereoselective synthesis of pyranoquinolines. If we wished to obtain the *trans* isomer as the major product, the reaction carried out at 50 °C and at a lower substrate concentration would give excellent yield and selectivity. If we wished to obtain the *cis* product as the major one, the right way would be to carry out the reaction at –20 °C under solvent-free conditions. Unfortunately, when the reaction was carried out at –40 °C in order to obtain a still higher *cis*/*trans* ratio, only a trace of the mixed product was detected even after 53 h.

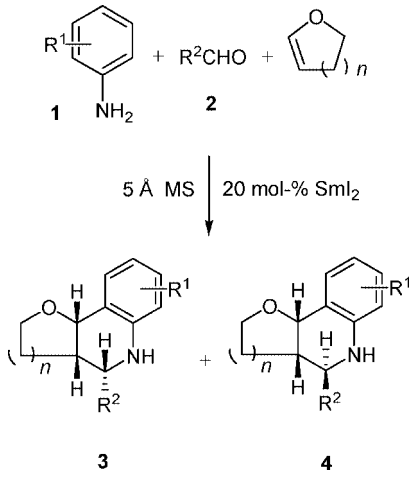
Table 2. SmI_2-catalyzed one-pot synthesis of pyrano[3,2-*c*]quinolines.[a]

Temp. (time)	**3a/4a**[b] (% overall yield)		
	Conditions A[c]	Conditions B[c]	Conditions C[c]
50 °C (5 h)	53:47 (73)	16:84 (91)	4:96 (93)
Room temp. (10 h)	72:28 (74)[d]	28:72 (90)	19:81 (82)
0 °C (24 h)	77:23 (70)	29:71 (89)	
–20 °C (48 h)	78:22 (53)	36:64 (88)	26:74 (86)

[a] Typical reaction conditions: benzaldehyde/aniline/dihydropyran = 1:1.1:1.4, 20 mol-% SmI_2 relative to aldehyde, 5-Å molecular sieves. [b] Determined by ^1H NMR spectroscopy. [c] Conditions A: solvent-free, conditions B: 1 mmol PhCHO/1 mL THF, conditions C: 1 mmol PhCHO/3 mL THF. [d] The reaction time is 5 h.

To assess the feasibility of this stereoselective methodology for the synthesis of pyrano- and furanoquinolines, reactions of structurally varied aromatic aldehydes and aromatic amines with dihydropyran and dihydrofuran (Scheme 2) in the presence of 20 mol-% SmI_2 were examined under different conditions; the results are summarized in Table 3 (Entries **a**–**o**). All the reactions proceeded smoothly except for that involving 2-furaldehyde and afforded the corresponding tetrahydroquinolines with moderate to high yields. The reactions in THF gave higher yields than those under solvent-free conditions. The reason for this may lie in poor mixing between the catalyst and the

substrates in the absence of solvent. The *trans* products were obtained almost quantitatively for all the substrates tested at 50 °C in THF, while the *cis* products were obtained with about 75% selectivity in all the reactions performed at 0 °C under solvent-free conditions. Electronic effects can be observed in the reactions of benzaldehyde and dihydropyran with different aromatic amines: the yields clearly increased when aromatic amines bearing electron-donating groups on the benzene ring were used, rather than those bearing electron-withdrawing groups. The method was equally effective for both electron-rich and electron-deficient aromatic aldehydes. 2-Furaldehyde gave a relatively lower yield at 50 °C in THF and complex byproducts were detected. The reason for this is not yet clear. Dihydrofuran exhibited behavior similar to that of dihydropyran.



Scheme 2.

Table 3. SmI_2-catalyzed one-pot synthesis of pyrano[3,2-*c*]- and furano[3,2-*c*]quinolines.[a]

Entry	R^1	R^2	*n*	**3/4** ratio[b] (% isolated yield) Conditions I[c]	Conditions II[c]
a	H	Ph	2	4:96 (93)	77:23 (70)
b	H	1-naphthyl	2	0:100 (89)	73:27 (76)
c	H	4-Me-C_6H_4	2	5:95 (93)	71:29 (73)
d	H	4-MeO-C_6H_4	2	4:96 (88)	73:27 (69)
e	H	4-Cl-C_6H_4	2	0:100 (94)	69:31 (63)
f	H	4-F-C_6H_4	2	9:91 (92)	77:23 (80)
g	H	4-CN-C_6H_4	2	10:90 (90)	79:21 (68)
h	4-Me	Ph	2	4:96 (93)	82:18[d] (70)
i	2-Me	Ph	2	0:100 (90)	74:36[d] (59)
j	4-MeO	Ph	2	2:98 (95)	75:25[d] (60)
k	4-F	Ph	2	11:89 (76)	79:21 (48)
l	4-Cl	Ph	2	9:91 (74)	83:17 (49)
m	H	2-furyl	2	3:97 (68)	–
n	H	Ph	1	4:96 (86)	76:24 (78)
o	H	4-Me-C_6H_4	1	6:94 (90)	79:21[d] (60)
p	H	cyclohexyl	2	19:81 (43)	66:34 (40)
q	H	cyclohexyl	1	24:76 (39)	85:15 (40)

[a] Typical reaction conditions: aldehyde/amine/dihydropyran or dihydrofuran = 1:1.1:1.4, 20 mol-% SmI_2 relative to aldehyde, 5-Å molecular sieves. [b] Determined by ^1H NMR spectroscopy. [c] Conditions I: 50 °C, 5 h, 1 mmol PhCHO/3 mL THF; conditions II: 0 °C, 24 h, solvent free. [d] Based on isolation by column chromatography.

However, the reaction encountered some difficulties when aliphatic aldehydes were used as substrates. Cinnamaldehyde and chain-saturated aldehyde such as isobutanal gave complicated products. The results may be due to the instabilities of imines formed in situ from aliphatic aldehydes and aniline. Fortunately, the pairs of diastereoisomers generated in the reactions with cyclohexanecarbaldehyde, aniline, and dihydropyran or dihydrofuran were separable as pure compounds, although the isolated yields were relatively lower (Table 3, Entries **p** and **q**). As was to be expected, the reactions produced the *trans* isomers as major products in THF and the *cis* ones under solvent-free conditions, exhibiting stereoselectivity analogous to that observed with the aromatic aldehydes.

Conclusions

In conclusion, we demonstrate here a novel and efficient methodology for the one-pot synthesis of pyrano- and furano[3,2-*c*]quinoline derivatives in the presence of catalytic amounts of SmI_2. In addition to the mild reaction conditions, the method offers the important advantage of controllable stereoselectivity. Either the *cis* or the *trans* isomers can be obtained as major products by changing the reaction conditions in a simple manner. Higher temperatures and lower substrate concentrations give more of the thermodynamically stable *trans* products, while lower temperatures and higher substrate concentrations result in fast formation of the kinetically favored *cis* products. Further application of this catalytic system and its accompanying stereoselectivity is in progress.

Experimental Section

General Remarks: All manipulations were conducted under dry Ar in flame-dried glassware. SmI_2 was synthesized by stirring a mixture of Sm metal and I_2 in THF at room temperature for several hours.[13] Liquid aldehydes, liquid amines, dihydropyran, and dihydrofuran were distilled from CaH_2 prior to use. THF was dried by heating at reflux for several hours over sodium and benzophenone and then distilled. Melting points were uncorrected. ^1H and ^{13}C NMR spectra were obtained on Varian INOVA-400 and System-300 spectrometers using tetramethylsilane (TMS) as an internal reference. Elemental analyses were determined on a Carlo–Erba EA1110-CHNS-O analyzer. HRMS data were obtained on a Micromass GCT instrument. The new compounds **3b**, **4b**, **3q**, **4q** were fully characterized by ^1H NMR, ^{13}C NMR, and HRMS.

Typical Experimental Procedure (Conditions A): A mixture of aniline (0.1 mL, 1.1 mmol), benzaldehyde (0.1 mL, 1.0 mmol), SmI_2 (0.2 mmol, 20 mol-%), and molecular sieves (5 Å, 125 mg) was stirred for 10 min at room temperature. 2,3-Dihydropyran (0.12 mL, 1.4 mmol) was then added and the mixture was allowed to stir at an appropriate temperature for a given time. Water was added to the residue, and the mixture was extracted with EtOAc. The combined organic layers were dried with anhydrous Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel [eluent: EtOAc/petroleum ether (60–90 °C) 1:30] to afford the pyrano[3,2-*c*]quinoline.

Typical Experimental Procedure (Conditions B): The reaction was performed in a manner similar to Method A in THF (1 mL). After completion of the reaction, THF was removed under reduced pressure. The resulting residue was treated as described in Conditions A.

Typical Experimental Procedure (Conditions C): The reaction was performed in a manner similar to Method A in THF (3 mL). After completion of the reaction, THF was removed under reduced pressure. The resulting residue was treated as described in Conditions A.

Spectroscopic Data for Selected Products

Quinoline 3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.37 (m, 5 H), 7.32 (t, J = 6.8 Hz, 1 H), 7.11 (t, J = 7.6 Hz, 1 H), 6.81 (t, J = 7.6 Hz, 1 H), 6.62 (d, J = 8.0 Hz, 1 H), 5.34 (d, J = 4.8 Hz, 1 H), 4.70 (s, 1 H), 3.61–3.41 (m, 2 H), 2.17 (d, J = 4.4 Hz, 1 H), 1.57–1.30 (m, 4 H) ppm.

Quinoline 4a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.31 (m, 5 H), 7.24 (t, J = 7.6 Hz, 1 H), 7.09 (t, J = 7.6 Hz, 1 H), 6.71 (t, J = 7.6 Hz, 1 H), 6.53 (d, J = 8.0 Hz, 1 H), 4.72 (d, J = 10.8 Hz, 1 H), 4.40 (d, J = 2.4 Hz, 1 H), 4.11 (m, 2 H), 3.73 (td, J = 2.0, 11.6 Hz, 1 H), 2.09 (m, 1 H), 1.85 (m, 1 H), 1.64 (m, 1 H), 1.47 (m, 1 H), 1.34 (m, 1 H) ppm.

Quinoline 3b: M.p. 161–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.78 (m, 4 H), 7.55–7.47 (m, 4 H), 7.13 (t, J = 7.5 Hz, 1 H), 6.83 (t, J = 7.5 Hz, 1 H), 6.66 (d, J = 8.1 Hz, 1 H), 5.48 (m, 2 H), 3.84 (s, 1 H), 3.59–3.40 (m, 2 H), 2.45 (t, J = 5.4 Hz, 1 H), 1.60–1.14 (m, 4 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 146.0, 136.5, 134.4, 130.9, 129.6, 128.6, 128.5, 128.3, 126.8, 126.2, 125.6, 124.2, 122.7, 120.7, 118.9, 115.2, 73.1, 61.1, 55.4, 37.0, 25.8, 19.0 ppm. HRMS: calcd. for $C_{22}H_{21}NO$ 315.1623; found 315.1627. $C_{22}H_{21}NO$ (315.41): calcd. C 83.78, H 6.71, N 4.44; found C 83.81, H 6.85, N 4.48.

Quinoline 4b: M.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35–7.42 (m, 7 H), 7.25 (d, J = 7.2 Hz, 1 H), 7.07 (t, J = 7.6 Hz, 1 H), 6.70 (t, J = 7.6 Hz, 1 H), 6.45 (d, J = 8.0 Hz, 1 H), 5.38 (d, J = 7.2 Hz, 1 H), 4.42 (d, J = 2.4 Hz, 1 H), 4.15 (br. s, 1 H), 4.02 (d, J = 10.8 Hz, 1 H), 3.65 (td, J = 2.0, 10.8 Hz, 1 H), 2.46 (m, 1 H), 1.77–1.26 (m, 4 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 145.1, 138.2, 134.5, 132.1, 131.1, 129.6, 129.4, 128.7, 126.5, 126.0, 125.9, 124.1, 120.7, 117.7, 114.4, 74.5, 67.9, 38.1, 27.3, 24.6, 23.0 ppm. HRMS: calcd. for $C_{22}H_{21}NO$ 315.1623; found 315.1619. $C_{22}H_{21}NO$ (315.41): calcd. C 83.78, H 6.71, N 4.44; found C 83.60, H 6.85, N 4.47.

Quinoline 3e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.8 Hz, 1 H), 7.36 (m, 3 H), 7.27 (d, J = 2.1 Hz, 1 H), 7.11 (t, J = 7.8 Hz, 1 H), 6.81 (t, J = 7.2 Hz, 1 H), 6.61 (d, J = 8.1 Hz, 1 H), 5.32 (d, J = 5.1 Hz, 1 H), 4.68 (s, 1 H), 3.83 (br. s, 1 H), 3.60 (d, J = 11.7 Hz, 1 H), 3.43 (t, J = 10.5 Hz, 1 H), 2.12 (m, 1 H), 1.59–1.26 (m, 4 H) ppm.

Quinoline 4e: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.33 (m, 4 H), 7.24–7.22 (m, 1 H), 7.12–7.08 (m, 1 H), 6.72 (t, J = 7.6 Hz, 1 H), 6.54 (d, J = 8.0 Hz, 1 H), 4.70 (d, J = 11.2 Hz, 1 H), 4.39 (d, J = 2.8 Hz, 1 H), 4.10 (m, 1 H), 4.04 (br. s, 1 H), 3.73 (td, J = 2.4, 11.6 Hz, 1 H), 2.05 (m, 1 H), 1.87–1.34 (m, 3 H), 1.26 (m, 1 H) ppm.

Quinoline 3j: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.26 (m, 5 H), 7.04 (d, J = 2.4 Hz, 1 H), 6.73 (dd, J = 2.7, 9.0 Hz, 1 H), 6.58 (d, J = 8.7 Hz, 1 H), 5.32 (d, J = 5.7 Hz, 1 H), 4.63 (s, 1 H), 3.79 (s, 3 H), 3.61 (m, 1 H), 3.43 (td, J = 2.1, 11.1 Hz, 1 H), 2.16 (m, 1 H), 1.58–1.25 (m, 4 H) ppm.

Quinoline 4j: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.38 (m, 5 H), 6.83–6.73 (m, 2 H), 6.51 (d, J = 8.4 Hz, 1 H), 4.68 (d, J = 10.4 Hz, 1 H), 4.39 (s, 1 H), 4.11 (m, 1 H), 3.77 (s, 3 H), 3.72 (m, 1 H), 2.16 (m, 1 H), 1.79 (m, 1 H), 1.65 (m, 1 H), 1.49 (m, 1 H), 1.34 (m, 1 H) ppm.

Quinoline 3q: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 7.6 Hz, 1 H), 7.03 (t, J = 7.6 Hz, 1 H), 6.74 (t, J = 7.6 Hz, 1 H), 6.51 (d, J = 8.4 Hz, 1 H), 5.11 (d, J = 8.0 Hz, 1 H), 3.80–3.76 (m, 1 H), 3.72–3.71 (m, 1 H), 3.11 (dd, J = 2.4, 9.2 Hz, 1 H), 2.77–2.70 (m, 1 H), 2.06–1.78 (m, 7 H), 1.45–1.37 (m, 1 H), 1.32–1.17 (m, 3 H), 1.04–0.95 (m, 2 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 145.0, 129.8, 128.1, 122.7, 118.5, 114.4, 75.9, 66.4, 57.4, 40.2, 30.0, 28.7, 26.2, 25.9, 23.8 ppm. HRMS: calcd. for $C_{17}H_{23}NO$ 257.1780; found 257.1770.

Quinoline 4q: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 7.6 Hz, 1 H), 7.07 (t, J = 7.6 Hz, 1 H), 6.71 (t, J = 7.6 Hz, 1 H), 6.58 (d, J = 8.4 Hz, 1 H), 4.60 (d, J = 6.0 Hz, 1 H), 3.96–3.90 (m, 1 H), 3.82–3.76 (m, 1 H), 2.71 (dd, J = 3.6, 9.6 Hz, 1 H), 2.42–2.34 (m, 1 H), 2.19–2.10 (m, 1 H), 1.94–1.13 (m, 12 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 145.4, 130.6, 128.6, 120.3, 117.8, 114.5, 75.5, 65.5, 57.0, 39.3, 38.2, 31.2, 29.2, 26.6, 26.4 ppm. HRMS: calcd. for $C_{17}H_{23}NO$ 257.1780; found 257.1785.

Acknowledgments

The authors thank the National Science Foundation of China (20572077, 20632040) and the State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial support.

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Received: April 1, 2007
Published Online: August 30, 2007

