A Novel and Efficient Tandem Aldol Condensation–Diels–Alder Reaction Pathway for the Direct Synthesis of Dehydrodecaline Derivatives

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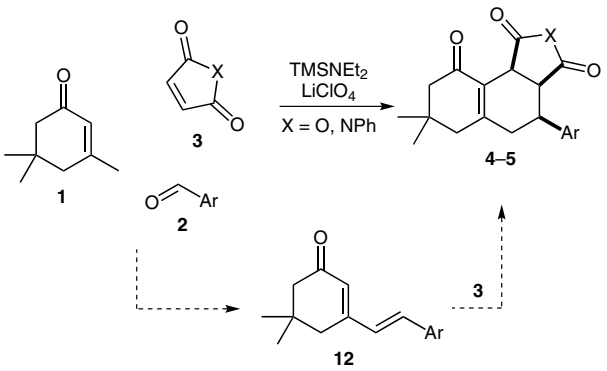
Abstract: An efficient direct synthesis of dehydrodecaline derivatives is reported via a tandem aldol condensation–Diels–Alder cycloaddition process under Lewis acidic conditions. Addition of dienophile moieties to conjugated dienes, formed in situ from the condensation of enone **1** with aldehydes, lead to high-yield stereoselective synthesis of the final *endo* products in relatively short time periods. Products precipitate upon concentration of the organic phase and are purified by recrystallization.

Key words: tandem reaction, aldol condensation, Diels–Alder reaction, *endo* addition, Lewis acid catalysis

Various condensation reactions of carbonyl compounds bearing acidic hydrogens[1] or active methylenes[2] with aldehydes or ketones are among the most important carbon–carbon bond formation reactions in synthetic organic chemistry because the resulting conjugated products are very useful intermediates to take part in other synthetic manipulations.[3] In situ engagement of these products in other organic transformations in a tandem fashion has become very popular in recent years due to the ability in constructing several carbon–carbon and carbon–heteroatom bonds in a one-pot process.[4] In particular, the incorporation of [4+2] Diels–Alder (DA) cycloadditions into tandem processes is very beneficial for rapid construction of complex target molecules and libraries of compounds.[5] This is due to the ability of the DA reaction itself to yield simultaneously two carbon–carbon bonds, a six-membered ring, and up to four stereogenic centers with predictable stereochemistry in a single-step process.[6]

In the course of our investigations on aldol condensation reactions,[7] we recently reported the synthesis of a series of styrylcyclohex-2-enone dienes,[8] as the products of the condensation of **1** with **2**, which were further explored for their DA reactivity.[9] In continuation, we were persuaded to combine the whole chemistry into a one-pot aldol condensation–DA process and examine the potential of this approach for direct construction of dehydrodecalins starting from isophorone, aldehydes, and dienophiles. Hereby, we would like to report the results of this strategy that leads to the synthesis of novel *endo* products obtained in one pot as opposed to step-by-step sequence of traditional reactions (Scheme 1).



Scheme 1

We first examined the conditions for the reaction of **1** with benzaldehyde and maleic anhydride (**3a**, X = O), as shown in Table 1.[10] TLC experiments showed that in the presence of $TMSNEt_2$ and $LiClO_4$ the intermediate diene formed efficiently by initial mixing of **1** and **2**.[11] Addition of the dienophile to this mixture led to sole formation of *endo* DA adduct **4a** (X = O) in 80% yield within 120 minutes (Table 1, entry 1). Successful use of other aldehydes showed the generality of the procedure. When 2-naphthaldehyde (Table 1, entry 2) or aldehydes with electron-rich (Table 1, entries 3 and 4), electron-deficient (Table 1, entries 5 and 6), or heterocyclic (Table 1, entries 7 and 8) aromatic rings were subjected to the conditions, single *endo* products **4b**–**h** were formed in high yields in all cases within relatively short time periods.

Molecular models generated by Chem3D program helped assign the stereochemistry of the products in which the newly formed π-bonds have rearranged to the more stable tetrasubstituted conjugate enone position (Figure 1). Analysis of the ^1H NMR spectrum of a typical product shows a 'medium' coupling constant of about 6 Hz for H-3a as a result of being coupled to H-4. This key coupling constant seems to be proportional to the *endo* structure. Conversely, the *exo* isomer is expected to show a 'large' $^3J_{H,H}$ coupling constant for the same proton. A support to this analogy is the observation made by Fields et al. for a closely related *exo* structure with $^3J_{H,H}$ of about 13 Hz for

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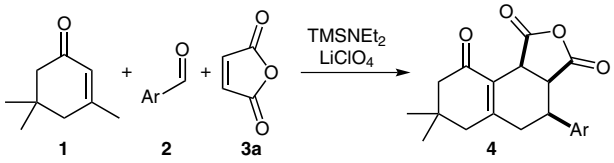
a similar proton.[12] In order to verify the proposed stereochemistry, a single crystal of **4h** was prepared and analyzed by X-ray crystallography.[13] The results are depicted in Figure 2 and clearly support the formation of *endo* stereoisomer as the sole DA product of the reaction.

Table 1 One-Pot Synthesis of **4**



Entry	Ar	Product	Time (min)	Yield (%)[a]
1	Ph	**4a**	120	80
2	2-naphthyl	**4b**	120	80
3	4-MeC_6H_4	**4c**	105	84
4	4-MeOC_6H_4	**4d**	75	86
5	4-ClC_6H_4	**4e**	90	78
6	3-BrC_6H_4	**4f**	150	72
7	1-furyl	**4g**	120	80
8	1-thienyl	**4h**	120	80

[a] Isolated yields.

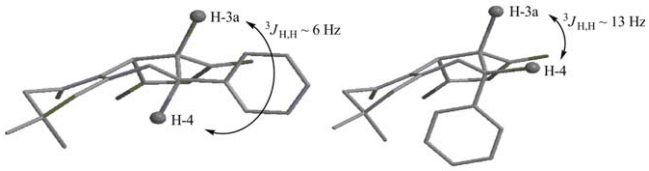


Figure 1 Diagnostic $^3J_{H,H}$ couplings in *exo* (left) and *endo* (right) diastereomers. For a better perception, only H-3a and H-4 are shown.

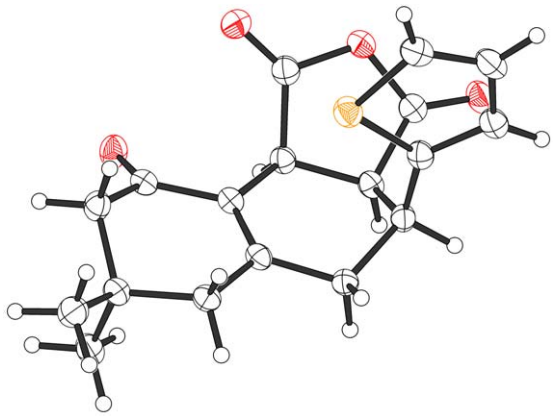
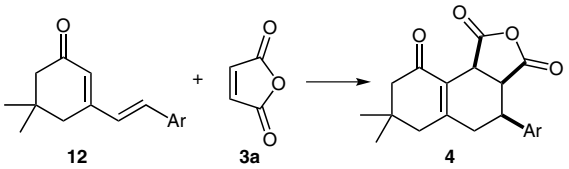


Figure 2 Crystal structure of **4h**. Displacement ellipsoids at 50% probability level.

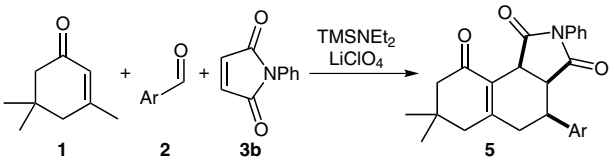
To get a grasp of the mechanism, reactions were stopped before the addition of the dienophile and after TLC showed the complete consumption of **1** and the aldehydes. Analysis of the reaction mixtures showed the presence of a single product **12** in each case. Products **12** were isolated and when subjected to react with **3a** under the same conditions, again high yields of **4a**–**h** were obtained within 60–90 minutes. Alternatively, in refluxing toluene high-yield formation of the same adducts was observed within 6–8 hours but along with *exo* isomers in ratios ranging from 8:1 to 10:1 for the major and minor isomers, respectively (Scheme 2).



Scheme 2

To show the generality of the method, we extended the procedure to the reactions of **1** with **3b** (X = NPh) and different aldehydes (Table 2). Experiments showed that under exactly the same conditions ($TMSNEt_2$ and $LiClO_4$) the intermediate dienes added efficiently to the dienophile to again solely produce *endo* DA adducts **5** in high yields within 60–120 minutes. In all cases, no formation of *exo* counterparts was detected under the Lewis acidic conditions, as also was previously noticed for stepwise synthesis of the same products.[9]

Table 2 One-Pot Synthesis of **5**



Entry	Ar	Product	Yield (%)[a]
1	Ph	**5a**	82
2	2-naphthyl	**5b**	82
3	4-MeC_6H_4	**5c**	86
4	4-MeOC_6H_4	**5d**	88
5	4-ClC_6H_4	**5e**	80
6	3-BrC_6H_4	**5f**	74
7	1-furyl	**5g**	82
8	1-thienyl	**5h**	82

[a] Isolated yields.

To further explore the scope of the method, we are currently studying the incorporation of singly activated dienophiles into the reaction. So far, the stepwise process has successfully been carried out. The process is regio- and stereoselective, and more attempts on the tandem version of the reaction are under way. Figure 3 shows the rep-

resentative products obtained from the reaction of three typical dienes **12** with methyl acrylate along with the X-ray depiction of one of the major *endo* adducts **6b**.[14]

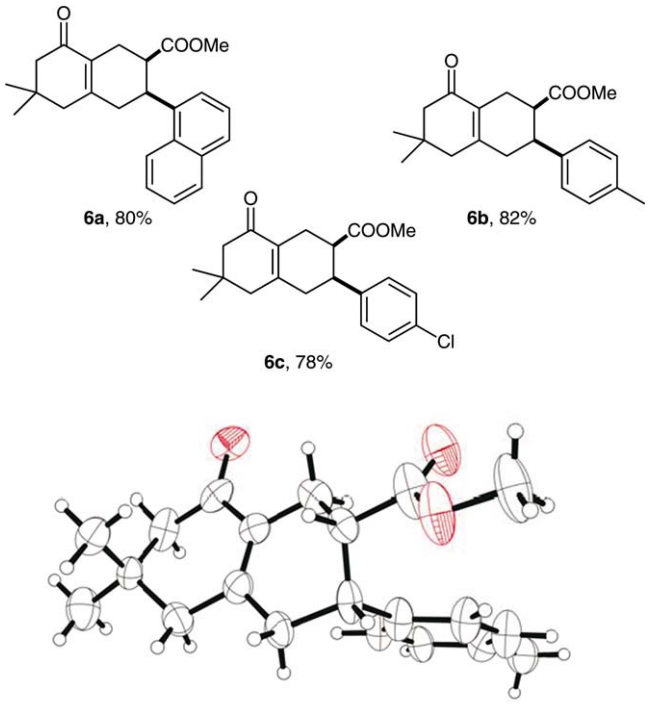


Figure 3 DA adducts of **12** with methyl acrylate (top) and crystal structure of **6b** with displacement ellipsoids at 50% probability level (bottom)

In conclusion, we have reported a convenient and efficient tandem protocol for the synthesis of dehydrodecaline derivatives. Products are prepared in high yields using a one-pot procedure without separation of the intermediate dienes. Reactions with highly substituted and hetero dienophiles are under study in our laboratory. Investigations to access milder reaction conditions are also in progress.

Melting points are uncorrected. FTIR spectra were recorded using KBr disks on a Shimadzu Prestige-21 spectrometer. NMR spectra were obtained on a FT-NMR Bruker Ultra Shield™ (500 MHz) as $CDCl_3$ solutions using TMS as internal standard reference. Elemental analyses were performed using a Thermo Finnigan Flash EA 1112 instrument. MS spectra were obtained on a Fisons 8000 Trio instrument at ionization potential of 70 eV. TLC experiments were carried out on precoated silica gel plates using PE–EtOAc (4:1) as the eluent. $TMSNEt_2$ was synthesized using known procedures.[15] All other chemicals and starting materials were purchased from commercial sources. Aldehydes were redistilled or recrystallized before being used. Products **4a**,**c**,**e**[16] and **5a**–**h**[8] are known and were identified by the comparison of their spectroscopic data with those available in the literature.

Typical Procedure for Tandem Reactions

A mixture of an aldehyde (2.0 mmol), enone **1** (276 mg, 2.0 mmol), *N*-(trimethylsilyl)diethylamine (416 μL, 2.2 mmol), and $LiClO_4$ (213 mg, 2 mmol) was stirred at r.t. under an inert atmosphere until TLC showed the consumption of the majority of the reactants. To this mixture was added maleic anhydride (196 mg, 1 mmol), and the stirring was continued while the course of the reaction was monitored by TLC experiments until all the reactants disappeared from the mixture. The mixture was diluted with Et_2O and washed with brine (2 × 10 mL). The organic phase was dried over Na_2SO_4, and the volatiles were removed under reduced pressure. Upon concentration, the mixture solidified, and the solid was recrystallized by means of EtOAc to obtain the final product.

(3a*S,4*S**,9b*S**)-7,7-Dimethyl-4-(naphthalen-2-yl)-4,5,7,8-tetrahydronaphtho[1,2-*c*]furan-1,3,9(3a*H*,6*H*,9b*H*)-trione (4b)**

Mp 143–145 °C. IR (KBr): 1863, 1780, 1728, 1654 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.94–7.84 (m, 3 H), 7.61–7.45 (m, 2 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.02 (s, 1 H), 4.82 (d, *J* = 9.0 Hz, 1 H), 3.98–3.88 (m, 2 H), 2.95 (dd, *J* = 11.0, 17.0 Hz, 1 H), 2.57–2.37 (m, 5 H), 1.12 (s, 3 H), 1.09 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.7, 169.6, 169.1, 159.7, 136.5, 133.8, 133.5, 130.8, 129.6, 128.5, 126.7, 125.8, 125.3, 125.1, 121.6, 50.8, 46.1, 44.4, 39.9, 35.5, 33.5, 33.1, 29.1, 27.3 ppm. MS (70 eV): *m/z* = 374 [M^+], 302, 246, 141, 128. Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 77.22; H, 6.11.

(3a*S,4*S**,9b*S**)-4-(4-Methoxyphenyl)-7,7-dimethyl-4,5,7,8-tetrahydronaphtho[2,1-*c*]furan-1,3,9(3a*H*,6*H*,9b*H*)-trione (4d)**

Mp 197–199 °C. IR (KBr): 1859, 1722, 1645 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 4.49 (d, *J* = 9.0 Hz, 1 H), 3.7 (s, 3 H), 3.61–3.56 (dd, *J* = 6.0, 9.0 Hz, 1 H), 3.39 (dd, *J* = 6.0, 12.0 Hz, 1 H), 2.63–2.26 (m, 6 H), 1.13 (s, 3 H), 1.06 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 177.3, 176.2, 158.6, 157.32, 132.5, 128.8, 128.4, 127.2, 114.2, 114.0, 55.2, 50.7, 47.2, 45.4, 44.0, 39.7, 33.6, 32.9, 29.1, 27.1 ppm. MS (70 eV): *m/z* = 354 [M^+], 282, 227, 108. Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.23; H, 6.33.

(3a*S,4*S**,9b*S**)-4-(3-Bromophenyl)-7,7-dimethyl-4,5,7,8-tetrahydronaphtho[1,2-*c*]furan-1,3,9(3a*H*,6*H*,9b*H*)-trione (4f)**

Mp 111–113 °C. IR (KBr): 1722, 1649 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 1 H), 7.36 (s, 1 H), 7.27–7.14 (m, 2 H), 4.60 (d, *J* = 9.0 Hz, 1 H), 3.70 (dd, *J* = 6.0, 9.0 Hz, 1 H), 3.30–3.24 (m, 1 H), 2.70–2.26 (m, 6 H), 1.08 (s, 3 H), 1.07 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.7, 170.1, 168.4, 157.9, 140.5, 130.9, 130.2, 126.4, 126.1, 125.0, 122.7, 50.8, 45.8, 45.4, 39.3, 38.2, 33.2, 32.8, 28.6, 27.6 ppm. MS (70 eV): *m/z* = 402 [M^+], 332, 277, 175. Anal. Calcd for $C_{20}H_{19}BrO_4$: C, 59.57; H, 4.75. Found: C, 59.63; H, 4.80.

(3a*S,4*S**,9b*S**)-4-(Furan-2-yl)-7,7-dimethyl-4,5,7,8-tetrahydronaphtho[1,2-*c*]furan-1,3,9(3a*H*,6*H*,9b*H*)-trione (4g)**

Mp 193–195 °C. IR (KBr): 1855, 1722, 1649 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 2.0 Hz, 1 H), 6.30 (dd, *J* = 2.0, 3.0 Hz, 1 H), 6.10 (d, *J* = 3.0 Hz, 1 H), 4.43 (d, *J* = 8.5 Hz, 1 H), 3.63 (dd, *J* = 5.5, 8.5 Hz, 1 H), 3.56 (dd, *J* = 5.5, 11.0 Hz, 1 H), 2.71–2.26 (m, 6 H), 1.11 (s, 3 H), 1.04 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.9, 170.3, 168.2, 156.0, 151.2, 141.6, 124.2, 110.6, 107.9, 50.9, 45.6, 43.8, 38.2, 33.2, 33.1, 32.2, 28.2, 28.0 ppm. MS (70 eV): *m/z* = 314 [M^+], 242, 186. Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.93; H, 6.01.

(3a*R,4*S**,9b*S**)-7,7-Dimethyl-4-(thiophen-2-yl)-4,5,7,8-tetrahydronaphtho[1,2-*c*]furan-1,3,9(3a*H*,6*H*,9b*H*)-trione (4h)**

Mp 191–193 °C. IR (KBr): 1724, 1645 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, *J* = 1.0, 5.0 Hz, 1 H), 6.95–6.88 (m, 2 H), 4.41 (d, *J* = 9.0 Hz, 1 H), 3.84 (dd, *J* = 5.5, 10.5 Hz, 1 H), 3.61 (dd, *J* = 5.5, 9.0 Hz, 1 H), 2.78–2.26 (m, 6 H), 1.15 (s, 3 H), 1.04 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.9, 170.5, 167.9, 155.8, 139.9, 127.1, 126.8, 126.7, 125.2, 51.0, 45.7, 45.6, 38.0, 35.9, 33.6, 33.3, 28.8, 27.6 ppm. MS (70 eV): *m/z* = 330 [M^+], 257, 202, 173. Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49. Found: C, 65.66; H, 5.70.

(2′*S,3′*R**)-Methyl 7′,7′-Dimethyl-5′-oxo-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1,2′-binaphthyl-3′-carboxylate (6a)**

Mp 89–91 °C. IR (KBr): 1732, 1654, 1444 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 1.5, 8.0 Hz,

1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.57–7.34 (m, 4 H), 4.10 (ddd, *J* = 4.5, 5.0, 9.0 Hz, 1 H), 3.34 (s, 3 H), 3.25 (ddd, *J* = 4.0, 4.5, 5.5 Hz, 1 H), 3.18 (dd, *J* = 9.5, 19.0 Hz, 1 H), 2.83–2.65 (m, 2 H), 2.54 (d, *J* = 5.0, 19.0 Hz, 1 H), 2.36 (s, 2 H), 2.31 (s, 2 H), 1.11 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7, 173.7, 154.5, 137.5, 133.9, 131.4, 129.2, 128.5, 127.6, 126.2, 125.5, 125.2, 123.6, 122.4, 51.4, 51.1, 45.3, 42.7, 34.9, 34.8, 33.3, 29.1, 27.4, 24.8 ppm. MS (70 eV): *m/z* 362 [M^+], 302, 246. Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23. Found: C, 79.68; H, 7.40.

(2*R,3*S**)-Methyl 6,6-Dimethyl-8-oxo-3-*p*-tolyl-1,2,3,4,5,6,7,8-octahydronaphthalene-2-carboxylate (6b)**

Mp 99–101 °C. IR (KBr): 1732, 1660, 1434 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 3.5 (s, 3 H), 3.46–3.42 (m, 1 H), 2.97–2.94 (m, 1 H), 2.74 (dd, *J* = 5.0, 18.5 Hz, 1 H), 2.66–2.62 (m, 2 H), 2.48 (dd, *J* = 4.5, 18.5 Hz, 1 H) 2.35 (s, 2 H), 2.33 (s, 3 H), 2.29 (s, 2 H), 1.11 (s, 3 H), 1.09 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.8, 174.2, 154.2, 139.1, 136.8, 129.6, 129.5, 127.8, 51.8, 51.7, 45.6, 44.1, 40.1, 36.8, 33.6, 29.0, 28.5, 22.7, 21.4 ppm. MS (70 eV): *m/z* = 326 [M^+], 295, 266, 251, 210. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.38; H, 7.92.

(2*R,3*S**)-Methyl 3-(4-Chlorophenyl)-6,6-dimethyl-8-oxo-1,2,3,4,5,6,7,8-octahydronaphthalene-2-carboxylate (6c)**

Mp 129–131 °C. IR (KBr): 1732, 1662, 1521 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 3.55 (s, 3 H), 3.43 (ddd, *J* = 4.0, 6.0, 10.0 Hz, 1 H), 2.95 (ddd, *J* = 3.5, 4.0, 5.5 Hz, 1 H), 2.67–2.59 (m, 3 H), 2.46–2.40 (m, 1 H), 2.32 (s, 2 H), 2.25 (s, 2 H), 1.07 (s, 3 H), 1.05 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 173.4, 153.2, 140.2, 132.7, 129.1, 128.8, 128.5, 51.4, 51.3, 45.1, 43.5, 39.4, 36.0, 33.2, 28.5, 28.0, 22.2 ppm. MS (70 eV): *m/z* = 346 [M^+], 286, 230, 165, 125. Anal. Calcd for $C_{20}H_{23}ClO_3$: C, 69.26; H, 6.68. Found: C, 69.42; H, 6.50.

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References and Notes

(1) (a) Larock, R. C. *Comprehensive Organic Transformations*, 2nd ed.; Wiley-VCH: New York, **1999**. (b) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 6th ed.; John Wiley and Sons: New York, **2007**.

(2) Gao, M.; Yang, Y.; Wu, Y.-D.; Deng, C.; Cao, L.-P.; Meng, X.-G.; Wu, A.-X. *Org. Lett.* **2010**, *12*, 1856.

(3) (a) Dubios, L.; Acher, F. C.; McCort-Tranchepain, I. *Synlett* **2012**, *23*, 791. (b) Sugiura, M.; Sato, N.; Sonoda, Y.; Kotani, S.; Nakajima, M. *Chem.–Asian J.* **2010**, *5*, 478. (c) Lee, K.-S.; Zhugralin, A. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7253. (d) Shen, Z.; Lu, X. *Tetrahedron* **2006**, *62*, 10896. (e) Bates, R. W.; Song, P. *Synthesis* **2010**, 2935. (f) Davies, S.; Smith, A. D.; Cowley, A. R. *Synlett* **2004**, 1957. (g) Liu, Y.; Hu, H.-Y.; Liu, Q.-J.; Hu, H.-W.; Xu, J. H. *Tetrahedron* **2007**, *63*, 2024.

(4) (a) Pellissier, H. *Adv. Synth. Catal.* **2012**, *354*, 237. (b) Oe, Y.; Uozumi, Y. *Synlett* **2011**, 787.

(5) (a) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137. (b) Parsons, P. J.; Penkett, C. S.; Shell, A. J. *Chem. Rev.* **1996**, *96*, 195. (c) Nandaluru, P. R.; Bodwel, G. J. *Org. Lett.* **2012**, *14*, 310. (d) Strübing, D.; Neumann, H.; Klaus, S.; Hübner, S.; Beller, M. *Tetrahedron* **2005**, *61*, 11333.

(6) (a) Fringuelli, F.; Taticchi, A. *The Diels–Alder Reacion: Selected Practical Methods*; John Wiley and Sons: Chichester, **2002**, 1–25. (b) Oppolzer, W. In *Comprehensive Organic Synthesis*, Vol. 5; Trost, B. M., Ed.; Pergamon Press: New York, **1991**. (c) Gioia, C.; Bernardi, L.; Ricci, A. *Synthesis* **2010**, 1612.

(7) (a) Mojtahedi, M. M.; Abaee, M. S.; Khakbaz, M.; Alishiri, T.; Samianifard, M.; Mesbah, A. W.; Harms, K. *Synthesis* **2011**, 3821. (b) Abaee, M. S.; Mojtahedi, M. M.; Pasha, G. F.; Akbarzadeh, E.; Shockravi, A.; Mesbah, A. W.; Massa, W. *Org. Lett.* **2011**, *13*, 5282. (c) Abaee, M. S.; Mojtahedi, M. M.; Hamidi, V.; Mesbah, A. W.; Massa, W. *Synthesis* **2008**, 2122. (d) Abaee, M. S.; Mojtahedi, M. M.; Zahedi, M. M.; Sharifi, R.; Khavasi, H. *Synthesis* **2007**, 3339. (e) Abaee, M. S.; Mojtahedi, M. M.; Forghani, S.; Ghandchi, N. M.; Forouzani, M.; Sharifi, R.; Chaharnazm, B. *J. Braz. Chem. Soc.* **2009**, *20*, 1895.

(8) Mojtahedi, M. M.; Abaee, M. S.; Zahedi, M. M.; Jalali, M. R.; Mesbah, A. W.; Massa, W.; Yaghoubi, R.; Forouzani, M. *Monatsh. Chem.* **2008**, *139*, 917.

(9) Abaee, M. S.; Mojtahedi, M. M.; Rezaei, M. T.; Khavasi, H. *Acta Chim. Slov.* **2011**, *58*, 605.

(10) As a result of a series of optimization reactions, the quoted conditions were selected. Under other sets of conditions, the yields of the desired intermediate dienes were low and reactions did not proceed efficiently.

(11) For a review on the use of $LiClO_4$ in catalysis of organic reactions, see: Bartoli, G.; Locatelli, M.; Melchiorre, P.; Sambri, L. *Eur. J. Org. Chem.* **2007**, 2037.

(12) Fields, E. K.; Dunlap, R. W.; Bruck, M.; Podias, A.; Hall, H. K. Jr. *J. Org. Chem.* **1989**, *54*, 2244.

(13) Crystallographic data for **4h** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-880918. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html].

(14) Crystallographic data for **6b** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-880919. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html].

(15) Colvin, E. W. *Silicon Reagents in Organic Synthesis (Best Synthetic Methods)*; Academic Press: London, **1988**, 87–89.

(16) El Barkaoui, Y.; Jorio, N.; Fkih-Tetouani, S.; El Louzi, A. *J. Soc. Chim. Tunisie* **1999**, *4*, 489.

