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cis,cis-Spiro[4.4]nonane-1,6-diol: A New Chiral Auxiliary for the Asymmetric Diels-Alder Reaction

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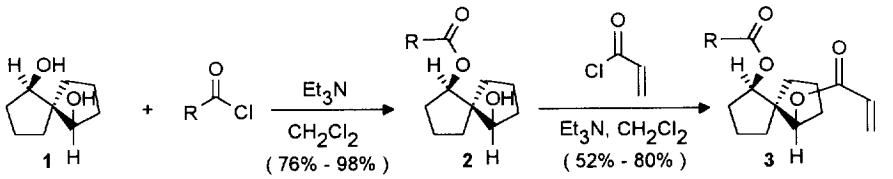
Abstract: The use of a mono-pivalate mono-acrylate bis-ester of (+)-1*S*,5*S*,6*S*-spiro[4.4]nonane-1,6-diol in an asymmetric Diels-Alder reaction with cyclopentadiene (2 equiv. BCl_3, -85°C, CH_2Cl_2) provided the expected *endo* bicyclo adduct in >97% de. Iodolactonization of the bicyclo adduct provided the (+)-lactone (**5**) with a 1*S*,4*S*,6*S*,8*R*,9*S* configuration (97% ee). The de's obtained from using various types and amounts of Lewis acids, and both chiral and racemic bis-esters in the Diels-Alder reaction with cyclopentadiene are also reported.

Exploration of chiral molecules as substrate bound chiral auxiliaries in organic transformations is an area which interests many research groups.[1] To our knowledge, the C_2-symmetric *cis,cis*-spiro[4.4]nonane-1,6-diol (**1**)[2] has not been used as a substrate bound chiral auxiliary[3,4] and thus we investigated its use as such in the Diels-Alder reaction. This paper describes our results in which a variety of groups were attached to diol **1** containing an acrylate dienophile and subjected to the Diels-Alder reaction with cyclopentadiene in the presence of a variety of Lewis acids. The best result was with the mono-pivalate mono-acrylate bis-ester of (+)-1*S*,5*S*,6*S*-spiro[4.4]nonane-1,6-diol (**1**), which underwent a Diels-Alder reaction with cyclopentadiene (2 equiv. BCl_3, -85°C, CH_2Cl_2) to produce the expected *endo* bicylco adduct in >97% de. Cleavage of the resulting adduct by iodolactonization yielded iodolactone **5** in 98% yield with an ee of 97%.

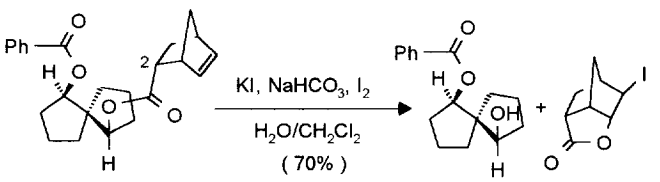


Scheme 1

To determine the optimum conditions for the Diels-Alder reaction we first used racemic diol **1** and then with these conditions we determined the absolute stereochemistry of the products by using optically pure **1**. The required starting bis-esters **3** were prepared by first desymmetrization of the C_2 symmetric diol **1** by esterification of one of the homotopic alcohols (Scheme 1). Treatment of **1** with the acid chloride of the corresponding blocking group (Et_3N, CH_2Cl_2) provided alcohol **2**, which after purification (column

chromatography), was subsequently, treated with acryloyl chloride (Et_3N, CH_2Cl_2) to provide bis-ester **3** in moderate to good yields. Bis-esters **3** were easily purified (column chromatography) and used in the Diels-Alder reaction with cyclopentadiene (Table 1).

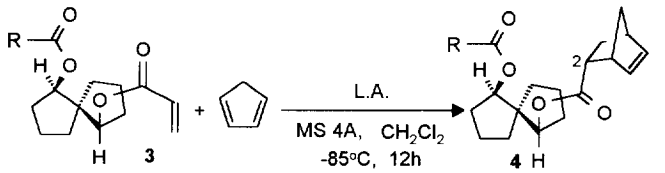
We first determined which Lewis acid would produce the best results in the Diels-Alder reaction by using the 2-naphthoate derivative of racemic diol **1** (entries 1-10, Table 1). Boron trichloride (2 equiv. of 1M in heptane) provided the highest de (75% at -85°C in CH_2Cl_2) of all the Lewis acids tried and HPLC indicated a 100% conversion to a mixture of products (*endo*:*exo*, 96:4). These optimized reaction conditions were used on substrates containing a variety of esters as blocking groups (Table 1, entries 10-13,15,16). Alteration of the 2-naphthyl group to the 1-naphthyl group made essentially no difference (entry 11). Changing the naphthyl group to a diphenylacetate resulted in a decrease in the de to 47% (entry 12). However, replacement of the 2-naphthoate ester with a smaller benzoate ester resulted in an increase in the de to 85% and a reduction in the formation of the *exo* adduct (hence higher stereoselectivity) while maintaining the high conversion (100%) to adduct (entry 13). The de could be increased to 88% by precooling a CH_2Cl_2 solution of cyclopentadiene to -85°C prior to its cannula addition to a mixture of the substrate and BCl_3 (entries 14-19). The addition of a *p*-nitro (entry 15) or *p*-methoxy (entry 16) group to the benzoate ring did not noticeably increase (or decrease) the de indicating that electronic interactions, such as π-stacking, may not be responsible for the high de's. Use of a diacrylate system (entry 18) in a double Diels-Alder reaction resulted in an de of 75%; however, the % ee of the resulting iodolactone **5** (Scheme 2) was 89% because of the distribution of absolute stereochemistry of the two bicycloadducts attached to the spiro-diol.[6] Finally, replacement of the benzoate ester with a pivalate ester (entry 19) resulted in a de of >97%. Subsequent workup and purification indicated that only one diastereomer was formed by NMR and HPLC; the other endo isomer, previously observed in a reaction with no Lewis Acid, was not detected.



4 **Scheme 2** **2** **(-)-5**

To determine the absolute stereochemistry of the adduct, (-)-1*R*,5*R*,6*R*-spiro[4.4]nonane-1,6-diol (**1**)[7] was used with the benzoate ester partner (entry 17). As expected a good yield of the *endo* adduct **4** was obtained with a de of 88%. The absolute configuration of the resulting bicyclo[2.2.1] system was determined by iodolactonization of product **4** to provide lactone **5** and recovered chiral auxiliary **2** (Scheme 2).[4f] The optical rotation of lactone **5** was $[\alpha]_D^{22.5}$ -102.7 (c 3.16, benzene) indicating the absolute stereochemistry at C-2 in the bicyclo[2.2.1] system of **4** was *R* with an ee of 89%.[8] Similar iodolactonizations (Scheme 2) on the

Table 1: Results for the Diels-Alder Reaction of 3.[5]



Entry	R	Equiv. of L.A.	L.A.	endo[a,b] (% yield)	% de[b] (% ee)	Product[b] (%)
1	2-Np	-	-	84	7	100[c]
2	2-Np	2	BF_3OEt_2	98	73	25
3	2-Np	1.1	$TiCl_4$	97	54	6
4	2-Np	3	$TiCl_4$	96	40	5
5	2-Np	1.1	$SnCl_4$	95	80	15
6	2-Np	3	$SnCl_4$	-	-20	14
7	2-Np	2	$SiCl_4$	-	54	8
8	2-Np	2.1	$SbCl_5$	94	53	74
9	2-Np	3	$AlMeCl_2$	97	59	100
10	2-Np	2	BCl_3	96	75	100
11	(*R*)-1-Np[f]	2	BCl_3	98	75[e]	100
12	Ph_2CH	2	BCl_3	97[d]	47[d]	100[d]
13	Ph	2	BCl_3	99	85	100
14	Ph	2	BCl_3	99	88[e]	100
15	p-NO_2Ph	2	BCl_3	98	84[e]	100
16	p-MeOPh	2	BCl_3	98	88[e]	100
17	(*R*)-Ph[f]	2	BCl_3	99	88[e](89)	100
18	(*S*)-H_2C=CH[f,g]	2	BCl_3	99	75[e](89)	100
19	(*S*)-Me_3C[f]	2	BCl_3	99	>97[e](97)	100

a) The remainder was the *exo* isomer. b) Refers to endo diastereomers, determined by HPLC using an ODS column with MeOH/H_2O (90:10), unless otherwise indicated. c) Cyclopentadiene was added to the reaction mixture at 8°C until the reaction was complete. d) ^1H NMR was used to determine the ratio. e) Cyclopentadiene was precooled in CH_2Cl_2 to -85°C and transfered to the reaction by cannula addition. f) The letter in brackets refers to the absolute configuration of the *cis,cis*-diol used (i.e. *R*=1*R*,5*R*,6*R*). g) Both acrylates undergo the Diels-Alder reaction.

diesters derived from the (+)-1*S*,5*S*,6*S*-diol **1** for entries 18 and 19 indicated that the configuration of the bicyclo[2.2.1]systems of **4** were *S* at C-2. The yield of iodolactone **5** from entry 18 and 19 was 97% (89% ee) and 98% (97% ee) respectively.[9]

In conclusion, we have obtained extremely high de's (and subsequently ee's of the cleaved bicyclo adduct) with the mono-benzoate mono-acrylate (88% de, 89% ee), diacrylate (75% de, 89% ee) and especially mono-pivalate mono-acrylate (>97% de, 97% ee) esters of *cis,cis*-spiro[4.4]nonane-1,6-diol (**1**) in the Diels-Alder reaction with cyclopentadiene. These results illustrate that spirodiol **1** is a very good chiral auxiliary for the Diels-Alder reaction. We plan to use other dienophiles and dienes in the asymmetric Diels-Alder reaction, investigate further other blocking groups and to alter the structure of diol **1** such that removal of the adduct can be done easily by a variety of procedures without cleaving the blocking group.

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Experimental Section

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ACE - 200 (^{1}H 200 MHz, ^{13}C 50 MHz) spectrometer. Unless otherwise stated, all NMR samples were obtained in $CDCl_3$ and the chemical shifts (ppm) are relative to the $C\underline{H}Cl_3$ peak as an internal reference (7.27 ppm for ^{1}H and 77.00 ppm for ^{13}C). Infrared (IR) spectra were recorded on a Mattson Model 4030 FT - IR spectrometer. Mass spectra (MS) were run on either a Varian CH5 or a VG 7070 instrument. Gas Chromatography Mass Spectrometry (GC/MS) analysis were performed on a Hewlett Packard 5890 Series II. High Resolution Mass Spectometry (HRMS) were recorded on a Kratos MS80. Microanalyses were performed by Ms. D. Fox, Department of Chemistry, University of Calgary. HPLC traces were obtained on an ICI LC using an Axxiom ODS C_{18} analytical column. All melting and boiling points are uncorrected.

Anhydrous THF was distilled from sodium benzophenone ketyl. Anhydrous benzene and methylene chloride were obtained by distillation from calcium hydride. All reactions were performed in oven dried glassware (120°C) under an atmosphere of nitrogen.

General procedure 1 for synthesis of Diester 3.

To diol **1** under N_2 was added CH_2Cl_2 (10 mL per mmol of **1**), Et_3N (2.2 equiv.) and RCOCl (1 equiv.). The reaction was stirred at rt and monitored by the loss of starting material by TLC (1:1 hexanes:ethyl acetate). The reation was worked up by addition of CH_2Cl_2, extracted with 5% HCl and 10% $NaHCO_3$ and subsequently dried over anhydrous $MgSO_4$. The product **2** was purified using a Chromatatron (5:1 hexanes:ethyl acetate). To the purified product under N_2 was added CH_2Cl_2 (15 mL per mmol of **2**), Et_3N (2 equiv.) and acryloyl chloride (2 equiv.). The reaction was stirred at rt and followed by loss of starting material by TLC (5:1 hexanes:ethyl acetate). The reaction was worked up by addition of CH_2Cl_2, extracted with both 5% HCl and 10% $NaHCO_3$ and subsequently dried over anhydrous $MgSO_4$. The product **3** was purified using a Chromatatron (loaded with $CHCl_3$ and then run using 9:1 hexanes:ethyl acetate).

***O*-Acryloyl-*O*-benzoyl-*cis,cis*-spiro[4.4]nonane-1,6-diol (3, R = Ph).**

General procedure 1 was used with (-)-1*R*,5*R*,6*R*-**1**. A colorless oil was obtained in 78% yield. IR (neat) 1721, 1277 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.5-2.1 (m, 14H), 4.05 (d, 1H, J=4.1 Hz), 5.33 (d,1H, J=3.8 Hz), 5.58 (dd, 1H, J=1.7, 10.2 Hz), 5.87(dd, 1H, J=10.2, 17.3 Hz), 6.11 (dd, 1H, J=1.7, 17.3 Hz), 7.37 (t, 2H, J=7.0 Hz), 7.45 - 7.52 (m, 1H), 7.90 (d, 2H, J=7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 20.9 (2C), 31.7 (2C), 33.6, 33.7, 58.1, 81.4, 81.8, 128.1, 128.4, 129.3, 130.5, 130.6, 132.6, 165.2, 165.7; MS *m/z*: 314 (0.6, M^+), 242 (19, M^+ - $HO_2CCH{=}CH_2$), 105 (100, PhCO+); Anal. calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. found: C, 72.07; H, 7.00. HRMS (EI) *m/z* calcd for $C_{19}H_{22}O_4$: 314.1518, found: 314.1549.

_O_-Diacryloyl-*cis,cis*-spiro[4.4]nonane-1,6-diol (3, R = CH=CH$_2$).

Only the second reaction in general procedure 1 was used with (+)-1*S*,5*S*,6*S*-diol **1**. A colorless oil was obtained in 51% yield. IR (neat) 1724, 1197 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.45-2.05 (m, 14H), 5.16 (d, 2H, J=3.9 Hz), 5.73 (dd, 2H, J=1.75, 10.3 Hz,), 5.99 (dd, 2H, J=10.3, 17.2 Hz), 6.27 (dd, 2H, J=1.8, 17.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 20.9 (2C), 31.6 (2C), 33.6 (2C), 58.0, 81.2 (2C), 128.6 (2C), 130.1 (2C), 165.3 (2C); MS *m/z*: 120 (51), 55 (100, H_2C=CHCO+); Anal. calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.84. found: C, 68.09; H, 7.63.

_O_-Acryloyl-_O_-pivaloyl-*cis,cis*-spiro[4.4]nonane-1,6-diol (3, R = CMe$_3$).

General procedure 1 was used with (+)-1*S*,5*S*,6*S*-**1**. A colorless solid was obtained in 70% yield. mp 36-37°C; IR (neat) 1728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.08 (s, 9H), 1.4-1.9 (m, 14H), 5.04 (d, 1H, J=3.9 Hz), 5.07 (d, 1H, J=3.7 Hz), 5.75 (dd, 1H, J=1.8, 10.3 Hz), 6.02 (dd, 1H, J=17.2, 10.3 Hz), 6.30 (dd, 1H, J=1.8, 17.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 20.8 (2C), 27.1 (3C), 31.5 (2C), 33.3, 33.4, 38.7, 57.9, 80.7, 81.8, 128.9, 130.3, 165.4, 177.4; MS *m/z*: 121 (63), 55 (100, H_2C=CHCO+); Anal. calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. found: C, 69.78; H, 8.79.

General Procedure 2 for the Diels-Alder Reaction Producing Diester 4.

To diester **3** (0.2mmol) under N_2 was added CH_2Cl_2 (4 mL) and 4Å MS (100 mg). The reaction was stirred and cooled to -85°C (ethyl acetate/N_2 bath). To the solution was added BCl_3 (2 equiv., 1.0 M in heptane) and was let stir at -85°C for 5 minutes. To this mixture was added, by cannula addition, precooled (-85°C) cyclopentadiene (3 equiv., freshly distilled) in CH_2Cl_2 (2 mL). The reaction was let stir for 0.5 h in the bath at -85°C before transfering it to a constant temperature bath at -85°C. The reaction mixture was stirred for 12 h and worked up by filtering it through silica gel. The crude product was purified using a Chromatatron (loaded with $CHCl_3$ and run with hexanes:ethyl acetate (9:1)). HPLC analysis was performed on the product using a ODS column with a typical mobile phase ratio of 90:10 (MeOH:H_2O).

_O_-Benzoyl-_O_-(5-norbornenyl-*endo*-2-carbonyl)-*cis,cis*-spiro[4.4]nonane-1,6-diol (4, R = Ph).

General procedure 2 was used on diester **3** (R = Ph) to provide compound **4** (R = Ph, entry 17 Table 1) as a colorless oil in 72% yield (88% de). Major diastereomer: IR (neat) 1729, 1715, 1276 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.31-1.12 (m, 3H), 2.07-1.52 (m, 13H), 2.77-2.67 (m, 2H), 2.92 (s, 1H), 5.08 (d, 1H, J= 3.6 Hz), 5.28 (d, 1H, J=3.5 Hz), 5.34 (dd, 1H, J=2.9, 5.7 Hz), 5.94 (dd, 1H, J=3.1, 5.7 Hz), 7.58-7.38 (m, 3H), 8.01-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 20.7, 20.8, 29.4, 31.7 (2C), 33.4, 33.5, 42.4, 43.3, 45.9, 49.7, 57.9, 81.1, 82.0, 128.3 (2C), 129.4 (2C), 130.7, 132.0, 132.7, 137.1, 165.8, 173.9; MS *m/z*: 380 (4, M$^+$), 243 (60,HO_2C-(C_7H_9)) 121 (100), 105 (98, PhCO+); HRMS (EI) *m/z* calcd for $C_{24}H_{28}O_4$: 380.1988, found: 380.2002.

Di(_O_-(5-norbornenyl-*endo*-2-carbonyl))-*cis,cis*-spiro[4.4]nonane-1,6-diol (4, R = C$_7$H$_9$).

General procedure 2 was used on diester **3** (R = CH=CH_2) to provide compound **4** (R = C_7H_9), entry 18 Table 1) as a colorless oil in 84% yield (~75% de). Major diastereomer: IR (neat) 1729 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.16-1.89 (m, 22H), 2.76-2.84 (m, 4H), 3.09 (br s, 2H), 4.88 (d, 2H, J=2.7 Hz), 5.83 (dd, 2H, J=2.8, 5.7 Hz), 6.09 (dd, 2H, J=3.0, 5.7 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 20.3 (2C), 29.3 (2C), 31.3 (2C), 32.7 (2C), 42.4 (2C), 43.7 (2C), 45.6 (2C), 49.5 (2C), 57.5, 80.7 (2C), 132.5 (2C), 137.2 (2C), 173.7 (2C); MS *m/z*: 396 (1.5, M$^+$), 259 (43, M$^+$ - O_2C-(C_7H_9)), 121 (100); HRMS (EI) *m/z* calcd for $C_{25}H_{32}O_4$: 396.2301, found: 396.2262.

_O_-Pivaloyl-_O_-(5-norbornenyl-*endo*-2-carbonyl)-*cis,cis*-spiro[4.4]nonane-1,6-diol (4, R = CMe$_3$).

General procedure 2 was used on diester **3** (R = CMe_3) to provide compound **4** (R = CMe_3, entry 19 Table 1) as a colorless solid (mp 74.8-76.5°C) in 77% yield (>97% de). IR (neat) 1728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 1.11 (s, 9H), 1.2-1.87 (m, 18H), 2.77-2.86 (m, 2H), 3.12 (br s, 1H), 4.93 (d, 1H, J= 3.1 Hz), 4.96 (d, 1H, J=3.5 Hz), 5.89 (dd, 1H, J=2.8, 5.7 Hz), 6.11 (dd, 1H, J=3.0, 5.7 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 20.4, 20.5, 27.0 (3C), 29.5, 31.3, 31.5, 33.0 (2C), 38.7, 42.4, 43.9, 45.6, 49.6, 57.8, 80.7, 80.9, 132.8, 137.2, 173.8, 177.4; MS *m/z*: 360 (9, M$^+$), 258 (7, M$^+$ - HO_2CCMe_3), 223.1 (51, M$^+$ - O_2C-(C_7H_9)), 121); HRMS (EI) *m/z* calcd for $C_{22}H_{32}O_4$: 360.2301, found: 360.2270.

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2. Nieman, J.A.; Parvez, M.; Keay, B.A. *Tetrahedron: Asymm.* **1993**, *4*, 1973. For proof of the absolute configuration of (-)-**1**, see: Nieman, J.A.; Keay, B.A.; Kubicki, M.; Yang, D.; Rauk, A., Tsankov, D.; Wieser, H. *J. Org. Chem.* **1995**, *60*, 1918. For the synthesis and resolution of a similar spirobiindane-1,1'-diol, see: Nieman, J.A.; Keay, B.A. *Tetrahedron: Asymm.* **1995**, *6*, 1575.
3. The use of spiro-diols as chiral auxiliaries has been limited to one report wherein *cis,cis*-spiro[4.4]nonane-1,6-diol (**1**) was used in conjunction with $LiAlH_4$ in the asymmetric reduction of aromatic ketones, see: Srivastava, N.; Mital, A.; Kumar, A. *J. Chem. Soc., Chem. Commun.* **1992**, 493. Attempts to repeat these results by both our and Seebach's groups have failed, see: Seebach, D.; Beck, A.K.; Dahinden, R.; Hoffmann, M.; Kuhnle, F.N.M. *Croatica Chemica Acta*, **1996**, *69*, 459.
4. For some examples of other diols which have been used as substrate bound chiral auxiliaries in the Diels-Alder reaction, see reference 1 and: (a) Oppolzer, W. *Angew Chem. Int. Ed. Engl.* **1984**, *23*, 876. (b) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (c) Gras, J.-L.; Pellissier, H. *Tetrahedron Lett.* **1991**, *32*, 7043. (d) Bezuldenhoudt, B.C.B.; Castle, G.H.; Geden, J.V.; Ley, S.V. *Tetrahedron Lett.* **1994**, *35*, 7451. (e) Maitra, U.; Mathivanan P. *J. Chem. Soc., Chem. Commun.* **1993**, 1469. (f) Mathivanan, P.; Maitra, U. *J. Org. Chem.* **1995**, *60*, 364.
5. The Lewis acid catalyzed procedure reported in reference 4(f) was used. An improved de was obtained using cannula addition of precooled cyclopentadiene in CH_2Cl_2. The isolated yield of **4** was low (48% for entry 17) when 25 equivalents of cyclopentadiene was used, due to polymer formation. The isolated yield of **4** was increased (89%, 72%, 84% and 77% for entries 11, 17, 18, and 19 respectively), with no loss of de, if only 3 equiv. of cyclopentadiene were used.
6. There are three diastereomers possible (assuming only the *endo* adduct is formed) from the Diels-Alder reaction with the bis-acrylate ester system, since two new asymmetric bicyclo adducts are formed per bisacrylate-diol. The absolute stereochemistry at C-2 of the bicylco adduct can have the following absolute configurations in the bisadduct-diol products: a) both *S*; b) one *S* and one *R*; and c) both *R*. Our analysis of the two diastereomers formed indicated that products a) and b) above were formed in a ratio of approximately 88:12 (~75% de). Iodolactonization of the two diastereomers provided iodolactones **5** in a ratio of 188:12 (1*S*,4*S*,6*S*,8*R*,9*S*:1*R*,4*R*,6*R*,8*S*,10*R*), which is consistent with the 89% ee observed.
7. There is confusion in the literature[10] with respect to the assignment of the absolute configuration to spiro-systems such as compound **1** (formally a (ab)C(ab) system). The spiro-carbon atom is treated as a chiral centre and not as an axis of chirality. Thus, the spiro centre in compound **1** (Scheme 1) has an *R* configuration. For further information, see: Cahn, R.S.; Ingol, C.; Prelog, V. *Angew. Chem. Int. Ed. Eng.* **1966**, *5*, 385.
8. The reported optical rotation of lactone **5** is $[\alpha]_D^{22}$ -116 (c 2.2, benzene).[11] Mathivanan and Maitra determined that the dextrorotory iodolactone **5** enantiomer corresponds to the 2*S* configuration of the bicyclo[2.2.1] system of the Diels-Alder adduct.[4f]
9. The actual results obtained were: $[\alpha]_D^{22.5}$ +102.7 (c 3.16, benzene) for entry 18 and $[\alpha]_D^{26}$ +112.4 (c 2.83, benzene) for entry 19.
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