Indium-Mediated Allylation of *N-tert*-Butylsulfinylaldimines with Dimethyl 2-[2-(Chloromethyl)allyl]malonate

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Abstract

The reaction of *N-tert*-butylsulfinylaldimines **5** with dimethyl 2-[2-(chloromethyl)allyl]-malonate (**10**), in the presence of indium metal and sodium iodide, at room temperature for 72 hours, led to the corresponding amino ester derivative **11**. The reaction preceeded in high yields and in a total stereoselective fashion, a single diastereoisomer being always isolated.

Keywords: *N-tert*-Butylsulfinylaldimines; Diastereoselective allylation; Indium; Amino esters.

Introduction

The addition of an allylic organometallic reagent to an imine represents an important process in synthetic organic chemistry because it is possible to perform the addition in a highly enantio- or diastereoselective manner. One, two or even more stereogenic centres can be generated in a single synthetic operation depending on the structure of the reactants, mainly of the allylic system.[1-5] In addition, the allylic moiety allows further possible transformations due to the presence of a double bond that can be manipulated synthetically. For the previously commented reasons, chiral homoallylic amines are valuable building blocks in organic synthesis. Nucleophilic addition to the less hindered face of the prostereogenic substrate takes always place in the allylation of chiral imines. This methodology is especially interesting when chiral imines with stereogenic centres located at the substituent bonded to the nitrogen are used (it could be a chiral auxiliary). These substrates are easily prepared from a carbonyl compound and an enantiopure chiral amine (access to both enantiomers would be highly desirable). Diastereoselective allylations of achiral imines are also possible by means of chiral allylating reagents. Through this strategy, chiral information could be located either on the allylic moiety or on the ligands bonded to the metal. In the last case, the ligands are not incorporated into the hydrocarbon back-bone of the resulting allylated product (Scheme 1).

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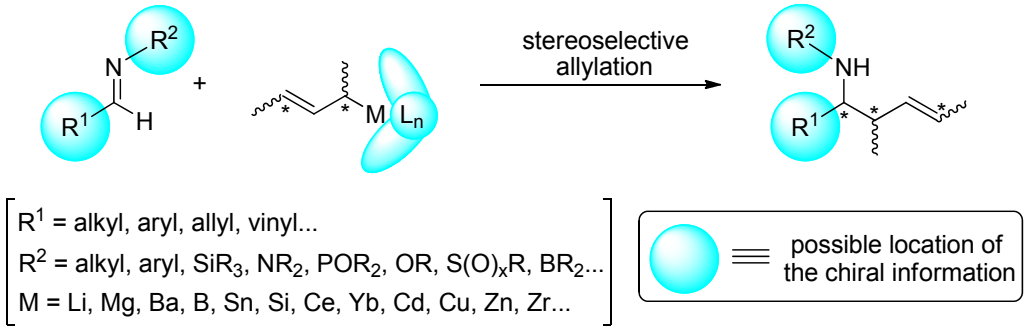


Scheme 1: Diastereoselective allylation of imines and imine derivatives

Typical examples of chiral imines **1**,[6] **2**,[7,8] **3**,[9] **4**[10] and **5**. Chiral allylating reagents **6**,[11] **7**,[12] **8**[13] and **9**[14] which have been efficiently used in diastereoselective allylation reactions are shown on Figure 1. It is worthy to be mentioned that *N-tert*-butanesulfinimines **5** have found high applicability in synthesis[15-20] due to the possibility of preparing their both enantiomers[21,22] and also because the chiral auxiliary can be easily removed under acidic conditions.[23] In addition, practical processes for recycling the *tert*-butylsulfinyl group upon deprotection of the resulting *N-tert*-butylsulfinylamines have been reported recently, making this chiral auxiliary of interest for large scale industrial processes.[24,25]

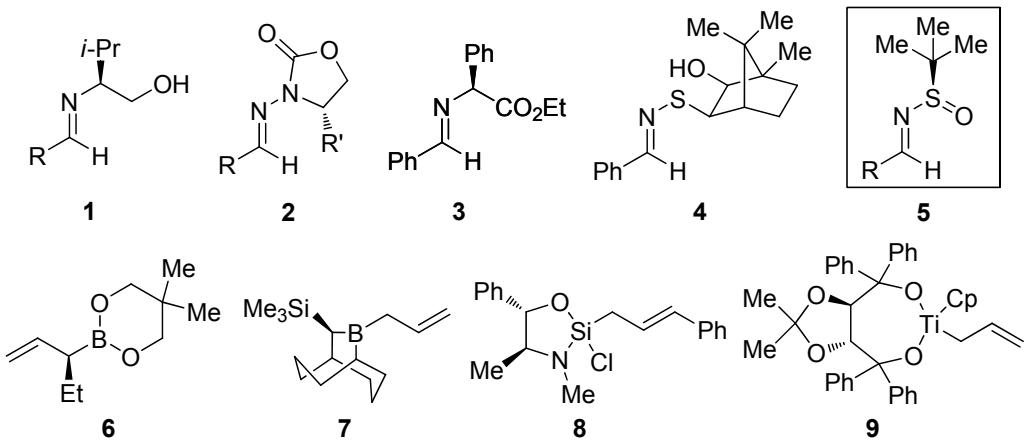


Figure 1

Continuing with our interest in indium mediated allylation of carbonyl compounds and *N-tert*-butylsulfinylaldimines **5** with allylic halides,[26-31] we report here the use of this metal for the stereoselective allylation of different *N-tert*-butylsulfinylaldimines **5** with dimethyl 2-[2-(chloromethyl)allyl]malonate (**10**).

Experimental

Materials and instruments

All chemicals were commercially available (Acros, Aldrich). TLC was performed on Merck silica gel 60 F_{254}, using aluminum plates and visualized with phosphomolybdic acid (PMA) stain. Chromatographic purification was performed by

flash chromatography using Merck silica gel 60 (0.040-0.063 mm) and hexane/EtOAc as eluent. IR spectra were measured (film) with a Nicolet Impact 510 P-FT Spectrometer. Melting points were recorded on an OptiMelt (Stanford Research Systems) apparatus and reported without corrections. NMR spectra were recorded with a Bruker AC-300 or a Bruker ADVANCE DRX-500 using $CDCl_3$ as the solvent and TMS as internal standard. LRMS (EI) were recorded on a Agilent 6890N.

(i) Preparation of dimethyl 2-[2-(chloromethyl)allyl]malonate (**10**).

To a solution of NaOMe (1.136 g, 20 mmol) in MeOH (50 mL) was added dropwise dimethyl malonate (2.693 g, 2.33 mL, 20 mmol) at 0 ºC. After stirring at the same temperature for 15 min, 3-chloro-2-(chloromethyl)prop-1-ene (2.551 g, 2.36 mL, 20 mmol) was also added. The resulting reaction mixture was stirred for 12 hours at 23 ºC. Then, MeOH was removed under vacuum and the resulting mixture was hydrolyzed with water (20 mL), extrated with EtOAc (3 × 20 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield pure compound **10** (1.215 g, 5.52 mmol, 28%). Physical and spectroscopic data for this compound follow: Colourless liquid; R_f 0.38 (hexane/EtOAc: 5/1); IR ν (film) 3002, 2956, 2847, 1739, 1437, 1341, 1232, 1154, 1028 cm^{-1}; ^{1}H-NMR: δ_H 2.81 (2H, d, *J* = 7.9 Hz, C*H*$_2$CH), 3.67 (1H, t, *J* = 7.9 Hz, C*H*CH_2), 3.75 (6H, s, 2×CH_3), 4.06 (2H, s, CH_2Cl), 5.01 (1H, s, C=C*H*H), 5.20 (1H, s, C=CH*H*); ^{13}C-NMR: δ_C 32.0, 47.7 (CH_2), 50.1 (CH), 52.7 (CH_3), 116.7 (CH_2), 141.4 (C), 169.1 (CO); LRMS (EI) *m/z* 185 (M^+-Cl, 100%), 157 (30), 153 (19), 129 (27), 125 (92), 67 (13), 65 (20), 59 (23).

(ii) Preparation of amino ester derivatives (**11**). *General procedure.*

A mixture of the corresponding aldimine **5** (0.5 mmol), dimethyl 2-[2-(chloromethyl)allyl]malonate (**10**, 0.337 g, 1.5 mmol), sodium iodide (0.153 g, 1 mmol) and indium powder (0.075 g, 0.65 mmol) was stirred for 72 h at 23 °C. Then, the resulting mixture was hydrolyzed with 1M HCl solution (10 mL), extrated with EtOAc (3 × 10 mL), dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield pure products **11**. Yields are given on Table 2. Physical and spectroscopic data follow.

*(6*S*,*R$_S$*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-4-methylenetetradecanoate* (**11a**): Colourless oil; R_f 0.38 (hexane/EtOAc: 1/1); IR ν (film) 3281, 2954, 2926, 2855, 1739, 1436, 1240, 1153, 1069 cm^{-1}; ^{1}H-NMR: δ_H 0.88 (3H, t, *J* = 5.4 Hz, C*H*$_3$CH$_2$), 1.19 [9H, s, $(CH_3)_3C$], 1.20-1.40 (12H, m, 6×CH_2), 1.48-1.53 (1H, m, CH_2), 2.22-2.38 (2H, m, C*H*$_2$CHNH), 2.63-2.67 (2H, m, C*H*$_2$CHCO), 3.23 (1H, d, *J* = 4.7 Hz, NH), 3.37-3.42 (1H, m, C*H*NH), 3.64 (1H, t, *J* = 8.0 Hz, CH_2C*H*CO), 3.73 (6H, s, 2×CH_3O), 4.92 (2H, br s, C=CH_2); ^{13}C-NMR: δ_C 13.9, 22.45 (CH_3), 25.05, 29.0, 29.3, 29.4, 31.6, 34.2, 35.0, 42.5 (CH_2), 50.1, 52.3 (CH), 53.05, 52.4 (CH_3), 55.5 (C), 114.6 (CH_2), 142.1 (C), 169.05, 169.1 (CO); LRMS (EI) *m/z* 266 [M^+-$(CH_3)_3SO$-HCO_2CH_3,

28%], 252 (18), 251 (100), 221 (11), 193 (10), 178 (14), 165 (12), 90 (16), 57 (13); $[\alpha]_D^{20}$ = -46 (c 1.29, CH_2Cl_2).

*(6*R,R_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-7-methyl-4-methyl-eneoctanoate* (**11b**): Colourless oil; R_f 0.32 (hexane/EtOAc: 1/1); IR ν (film) 3286, 2957, 1738, 1645, 1436, 1240, 1153, 1069, 900 cm^{-1};^{1}H-NMR: δ_H 0.89 (3H, d, *J* = 7.1 Hz, C*H*$_3$CH), 0.90 (3H, d, *J* = 8.1 Hz, C*H*$_3$CH), 1.21 [9H, s, $(CH_3)_3C$], 1.95-1.99 (1H, m, C*H*CH_3), 2.17 (1H, dd, *J* = 9.1, 14.1 Hz, C*H*HCHNH), 2.31 (1H, dd, *J* = 5.3, 14.1 Hz, CH*H*CHNH), 2.62-2.71 (2H, m, C*H*$_2$CHCO), 3.11 (1H, d, *J* = 4.1 Hz, NH), 3.29-3.33 (1H, m, C*H*NH), 3.64 (1H, t, *J* = 7.9 Hz, CH_2C*H*CO), 3.73 (6H, s, 2×CH_3O), 4.93 (1H, s, C=C*H*H), 4.94 (1H, s, C=CH*H*); ^{13}C-NMR: δ_C 17.4, 17.6, 22.7 (CH_3), 30.5 (CH), 34.1, 38.4 (CH_2), 50.3 (CH), 52.6, 52.65 (CH_3), 55.8 (CH), 56.5 (C), 61.0 (CH_2), 114.8 (CH_2), 142.4 (C), 169.2, 169.3 (CO); LRMS (EI) *m/z* 287 [M^+-(CH_3)-(CO_2CH_3), 12%], 272 (31), 187 (16), 142 (100), 119 (28), 100 (37), 59 (22); $[\alpha]_D^{20}$ = -54 (c 1.09, CH_2Cl_2).

*(6*S,R_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-4-methylene-8-phe-nyloctanoate* (**11c**): Colourless oil; R_f 0.29 (hexane/EtOAc: 1/1); IR ν (film) 3281, 3060, 3025, 2952, 2865, 1738, 1436, 1362, 1242, 1153, 1050, 901 cm^{-1}; ^{1}H-NMR:δ_H 1.23 [9H, s, $(CH_3)_3C$], 1.80-1.89 (2H, m, CH_2C*H*$_2$CHN), 2.36-2.39 (2H, m, C*H*$_2$CHNH), 2.60-2.77 (4H, m, PhC*H*$_2$, C*H*$_2$C=CH_2), 3.31 (1H, d, *J* = 5.2 Hz, NH), 3.44-3.50 (1H, m, C*H*NH), 3.64 (1H, t, *J* = 7.8 Hz, CH_2C*H*CO), 3.72 (3H, s, CH_3O), 3.73 (3H, s, CH_3O), 4.92 (2H, br s, C=CH_2), 7.16-7.21 (3H, m, ArH), 7.26-7.31 (2H, m, ArH); ^{13}C-NMR: δ_C 22.55 (CH_3), 31.5, 34.2, 36.8, 42.6 (CH_2), 55.0, 52.2 (CH), 52.5 (CH_3), 55.7 (C), 114.8 (CH_2), 125.8, 128.2 128.3 (CH), 141.5, 141.9 (C), 169.1 (CO); LRMS (EI) *m/z* 316 [M^+-$Ph(CH_2)_2$, 6%], 302 (16), 261 (10), 233 (41), 213 (19), 185 (84), 165 (15), 153 (22), 132 (14), 117 (17), 105 (16), 91 (100), 77 (22), 65 (18); $[\alpha]_D^{20}$ = -36 (c 1.27, CH_2Cl_2).

*(6*R,R_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-4-methylene-6-phe-nylhexanoate* (**11d**): Colourless oil; R_f 0.28 (hexane/EtOAc: 1/1); IR ν (film) 3278, 3090, 3025, 2954, 1739, 1645, 1436, 1372, 1242, 1153, 1048, 903 cm^{-1}; ^{1}H-NMR: δ_H 1.19 [9H, s, $(CH_3)_3C$], 2.40-2.50 (2H, m, C*H*$_2$CHNH), 2.63-2.68 (2H, m, C*H*$_2$C=CH_2), 3.62 (1H, t, *J* = 7.8 Hz, CH_2C*H*CO), 3.71 (1H, br s, NH), 3.72 (6H, s, 2×CH_3O), 4.53-4.58 (1H, m, C*H*NH), 4.97 (1H, s, C=C*H*H), 5.00 (1H, s, C=CH*H*), 7.26-7.31 (5H, m, ArH); ^{13}C-NMR: δ_C 22.4 (CH_3), 34.1, 45.6 (CH_2), 50.1 (CH), 52.55 (CH_3), 55.0 (CH), 55.5 (C), 115.42 (CH_2), 127.4, 127.65, 128.4 (CH), 141.55, 141.7 (C), 168.95, 169.0 (CO); LRMS (EI) *m/z* 217 [M^+-$(CH_3)_3$SONH-HCO_2CH_3, 100%], 189 (81), 161 (43), 133 (22), 105 (15), 103 (13), 80 (10), 66 (15); $[\alpha]_D^{20}$ = -76 (c 1.08, CH_2Cl_2).

*(6*R,S_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-4-methylenetetra-decanoate* (**11e**): Physical and spectroscopic data were found to be the same as that for **11a**; $[\alpha]_D^{20}$ = +49 (c 0.92, CH_2Cl_2).

*(6*S,S_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-7-methyl-4-methyl-eneoctanoate* (**11f**): Physical and spectroscopic data were found to be the same as that for **11b**; $[\alpha]_D^{20}$ = +67 (c 1.19, CH_2Cl_2).

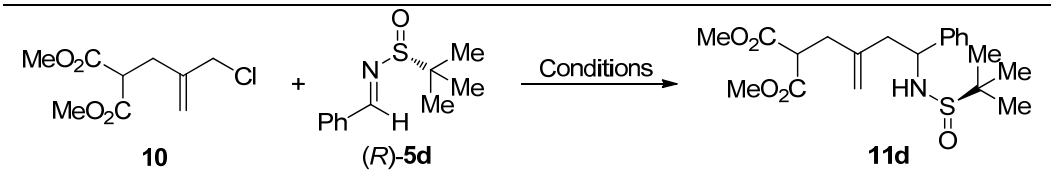
*(6*R,S_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-4-methylene-8-phenyloctanoate* (**11g**): Physical and spectroscopic data were found to be the same as that for **11c**; $[\alpha]_D^{20}$ = +36 (c 1.03, CH_2Cl_2).

*(6*S,S_S*)-Methyl* N-*(tert-butylsulfinyl)-6-amino-2-methoxycarbonyl-4-methylene-6-phenylhexanoate* (**11h**): Physical and spectroscopic data were found to be the same as that for **11d**; $[\alpha]_D^{20}$ = +62 (c 1.09, CH_2Cl_2).

Results and discussion

In order to know the best reaction conditions for the indium-promoted allylation of *N-tert*-butylsulfinyl aldimines **5** with dimethyl 2-[2-(chloromethyl)allyl]malonate [**10**, easily accessible from commercially available dimethyl malonate and 3-chloro-2-(chloromethyl)prop-1-ene], we took aldimine (*R*)-**5d**, derived from benzaldehyde and (*R*)-2-methyl-2-propanesulfinamide,[27] as the imine model. The reaction did not take place using 1.3 equivalents of indium and 1.5 equivalents of the allylic chloride **10** in THF at 60 ºC for 72 hours (Table 1, entry 1), which are the standard reaction conditions for the allylation of this type of imines with allyl bromide.[26] The allylation did not also took place at 100 ºC in a high pressure flask (Table 1, entry 2). A promising result was obtained when the reaction was performed in the absence of any solvent but using 3 equivalents of allylic chloride **10** at 23 ºC, allylated product **11d** being isolated in 12% yield after column chromatography (Table 1, entry 3). Under similar reaction conditions, we tried to improve the yield by adding 2 equivalents of potassium iodide, in order to facilitate the formation of the allylindium intermediate (chlorine-iodine exchange would lead to a more reactive allylic iodide), however, we obtained the expected product **11d** in just 8% yield (Table 1, entry 4). Fortunately, compound **11d** was isolated in 75% yield by simply switching from potassium to sodium iodide under almost identical reactions conditions (Table 1, entry 5). Finally, yield was not improved when the reaction was carried out in a saturated aqueous sodium bromide solution in the presence of 4 equivalents of indium and 2 equivalents of allylic chloride **10** at room temperature for 72 hours, compound **11d** being now isolated in 22% yield (Table 1, entry 6). Regarding the stereoselectivity of the process, surprisingly, a single diastereoisomer was observed by ^{1}H-NMR analysis of the crude reaction mixture in all cases.

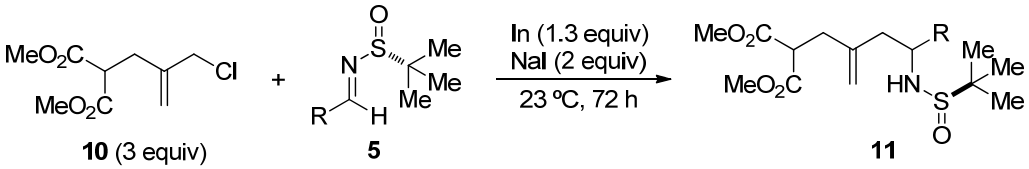
Table 1. Optimization of the reaction conditions.



Entry	Conditions[a]	**11d** (%)[b]
1	**10** (1.5 equiv), In (1.3 equiv), THF (3 mL), 60 ºC, 72 h	0
2	**10** (1.5 equiv), In (1.3 equiv), THF (3 mL), 100 ºC, 72 h	0
3	**10** (3 equiv), In (1.3 equiv), 23 ºC, 72 h	12
4	**10** (3 equiv), In (1.3 equiv), KI (2 equiv), 23 ºC, 12 h	8
5	**10** (3 equiv), In (1.3 equiv), NaI (2 equiv), 23 ºC, 72 h	75
6	**10** (3 equiv), In (4 equiv), saturated NaBr-H_2O (5 mL), 23 ºC, 72 h	22[c]

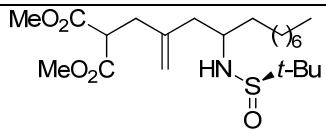
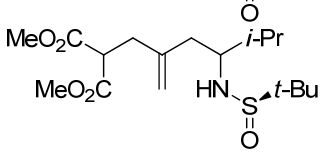
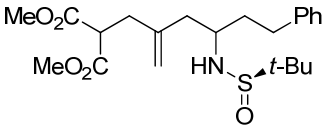
[a] All the reactions were carried out using 0.2 mmol of aldimine (*R*)-**5d**. [b] Isolated yield after column chromatography (silica gel, hexane/EtOAc) based on the starting aldimine (*R*)-**5d**. [c] Partial decomposition of the starting aldimine (*R*)-**5d** occurred.

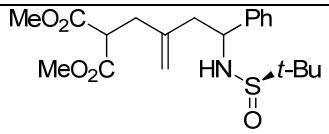
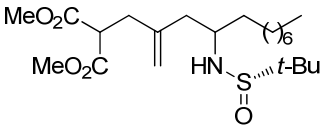
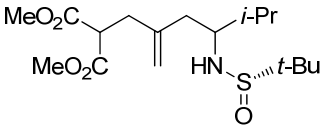
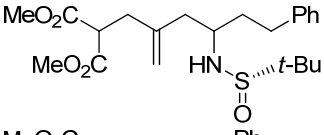
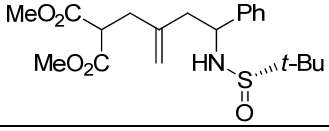
The reaction of dimethyl 2-[2-(chloromethyl)allyl]malonate (**10**) with different chiral *N*-sulfinyl aldimines **5** under the optimized conditions (Table 1, entry 5) led to compounds **11** in good yields (Scheme 2 and Table 2) and excellent diastereoselectivities (a single stereoisomer was always isolated). The highest yield was obtained with aldimine (*R*)-**5c** derived from 3-phenylpropanal (Table 2, entries 3 and 7). As it was expected, [α] values regarding the optical rotation of amino ester derivatives **11** showed opposite sign for each enantiomer (see Experimental part above).



Scheme 2

Table 2. Preparation of amino ester derivatives **11**.

	Aldimine **5**		Amino ester **11**[a]		
Entry	No.	R	No.	Structure	Yield (%)[b]
1	(*R*)-**5a**	$CH_3(CH_2)_7$	**11a**		87
2	(*R*)-**5b**	*i*-Pr	**11b**		87
3	(*R*)-**5c**	$Ph(CH_2)_2$	**11c**		90

	Aldimine **5**		Amino ester **11**[a]		
Entry	No.	R	No.	Structure	Yield (%)[b]
4	(*R*)-**5d**	Ph	**11d**		71
5	(*S*)-**5a**	$CH_3(CH_2)_7$	**11e**		77
6	(*S*)-**5b**	*i*-Pr	**11f**		75
7	(*S*)-**5c**	$Ph(CH_2)_2$	**11g**		82
8	(*S*)-**5d**	Ph	**11h**		72

[a] All products were >95% pure (GLC and/or 300 MHz ^{1}H RMN). [b] Isolated yield after column chromatography (silica gel, hexane/EtOAc) based on the starting aldimine **5**.

The configuration of the newly created stereogenic centre was not yet assigned. Two different models have been proposed in order to explain the stereochemical outcome of the addition of allylic nucleophiles, in our case, an allylindium sesquihalide intermediate of type **I** (Figure 2), to *N*-*tert*-butylsulfinyl aldimines: an open transition state **TSI**[19] (Figure 2) and a six-membered ring chelation control model **TSII**[26] (Figure 2). Opposite configurations are obtained depending on the operating mechanism. Based on our experience, we think that allylation of the imines takes place through a cyclic transition state of type **TSII** and the nucleophilic attack occurs to the *Si*-face of the imine unit for R_S-isomers (Table 2, entries 1-4) and to the *Re*-face in the case of S_S-derivatives (Table 2, entries 5-8).

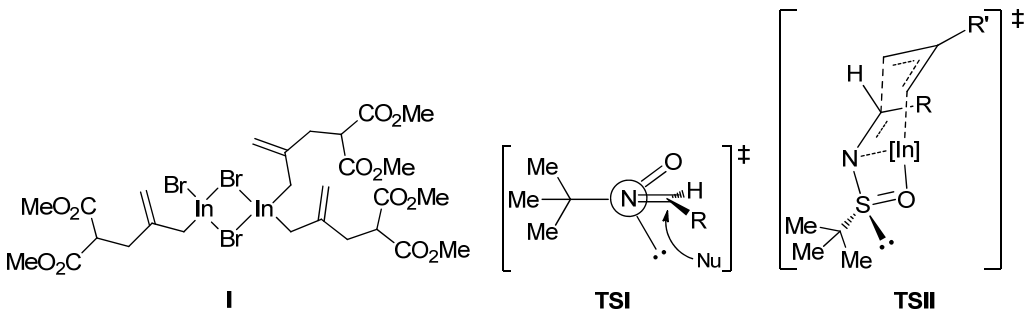
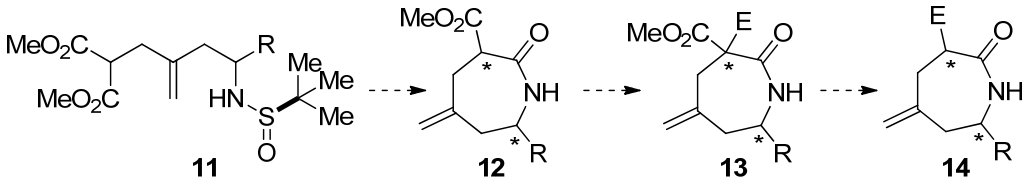


Figure 2

Enantiomerically pure amino ester derivatives **11** are of interest because they could be easily transformed into 3,7-disubstituted-5-methyleneazepan-2-ones **12**-**14** (Scheme 3). Work in this area is under progress and will be reported in the future in due course.



Scheme 3

Conclusions

We have reported herein that the indium-mediated allylation of *N*-*tert*-butylsulfinyl aldimines with dimethyl 2-[2-(chloromethyl)allyl]malonate in the presence of sodium iodide proceeded in high yields with an excellent diastereoselectivity. The resulting amino ester derivatives being potential precursors of interesting nitrogen-containing seven-membered heterocycles.

Acknowledgements

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