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Tandem reactions catalyzed by lanthanide iodides. Part 2: Tandem iminoaldol–enolisation reactions

Richard Gil,† Marion Eternot, Marie-George Guillerez and Jacqueline Collin*

Laboratoire de Catalyse Moléculaire, UMR 8075, ICMMO, Université Paris-Sud, Bâtiment 420, 91405 Orsay, France

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Abstract—Samarium diiodide is a catalyst for the reaction of cyclic and acyclic *tert*-butyldimethylsilyl enoxysilanes with chelating imines. Reaction products are isolated as β-aminoenoxysilanes instead of β-aminoketones as previously observed with the corresponding trimethylsilyl enoxysilanes. Several mechanistic pathways are discussed.

1. Introduction

Reactions allowing the formation of carbon–carbon bonds from imines have been widely studied due to their important synthetic applications.[1] During recent years, Lewis acids catalyzed Mannich-type reactions have been developed. They involve either preformed or in situ prepared imines and silyl enolates to afford β-aminoesters or β-aminoketones, respectively. The initial work reported by Ojima described the reaction of imines with ketene silyl acetals promoted by $TiCl_4$ yielding β-aminoesters.[2] Later, a variety of efficient catalysts for iminoaldol type reactions involving ketene silyl acetals have been studied, such as metal halides, $TiBr_4$, TiI_4,[3] SmI_3,[4] trimethylsilyl triflate,[5] tris pentafluorophenyl borate,[6] or trityl or phosphonium salts.[7,8] The interest of ytterbium and scandium triflates as Lewis acids for a wide range of reactions has been demonstrated by Kobayashi.[9] These triflates catalyze Mannich-type reactions of preformed imines,[10] as well as three-component reactions involving aldehydes, amines and enoxysilanes or silyl ketene acetals,[11] since the preferential reactivity of aldimines over aldehydes in the presence of lanthanide triflates in catalytic amount has been demonstrated.[12] Mannich reactions can be performed in aqueous media using Lewis acids such as $Yb(OTf)_3$, $InCl_3$, $BF_3{\cdot}OEt_2$ or $Zn(BF_4)_2$,[13] or Brönsted acids such as HBF_4.[14]

In the course of our previous works, we have studied the catalytic activity of $SmI_2(THF)_2$ as a Lewis acid in a variety of reactions,[15] including Mukaiyama aldol and Michael reactions.[16] Samarium diiodide allows to isolate products as silyl ethers in the former case or enoxysilanes in the latter. This has allowed to carry out tandem Michael–aldol reactions through a one-pot procedure.[17] Besides, reaction of methyl trimethylsilyl dimethylketene acetal with bulky carbonyl compounds, ketones or aldehydes, catalyzed by samarium diiodide, led readily to enoxysilanes.[18] We examined next the reactivity of imines in cycloaddition or Mannich-type reactions catalyzed by samarium diiodide,[19] as well as in the second step of tandem Michael–iminoaldol reactions.[20] The influence of the nature of substrates in these tandem Michael–iminoaldol reactions is described in the preceding article,[20b] and we have found that the use of a ketene silyl acetal bearing a *tert*-butyldimethylsilyl group led to β-amino enoxysilanes instead of β-aminoketones as reaction products. The intermediate in these tandem reaction is a *tert*-butyldimethylsilyl enoxysilane as previously shown.[16] This led us to study iminoaldol reactions involving *tert*-dimethylsilyl enoxysilane and to evaluate these reactions as a new method of preparation of enoxysilanes.

2. Results and discussion

We have previously examined iminoaldol reactions catalyzed by samarium diiodide and found that glyoxylic and aromatic imines react with a ketene silyl acetal to give β-aminoesters and with cyclic or acyclic trimethylsilyl enoxysilanes to give β-aminoketones.[19] However, the presence of a coordinating group in aromatic imines was necessary to isolate reaction products in good yields.

The following work will thus be focused on iminoaldol reactions using chelating imines **1a** and **1b**. We first examined the reaction of cyclic *tert*-butyldimethylsilyl enoxysilanes **2** with glyoxylic imine **1a** in the presence of

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* Corresponding author. Tel.: +33-1-69154740; fax: +33-1-69154680; e-mail address: jacollin@icmo.u-psud.fr
† Université de Cergy Pontoise, 5 mail Gay-Lussac, Neuville sur Oise, 95031 Cergy-Pontoise cedex, France.

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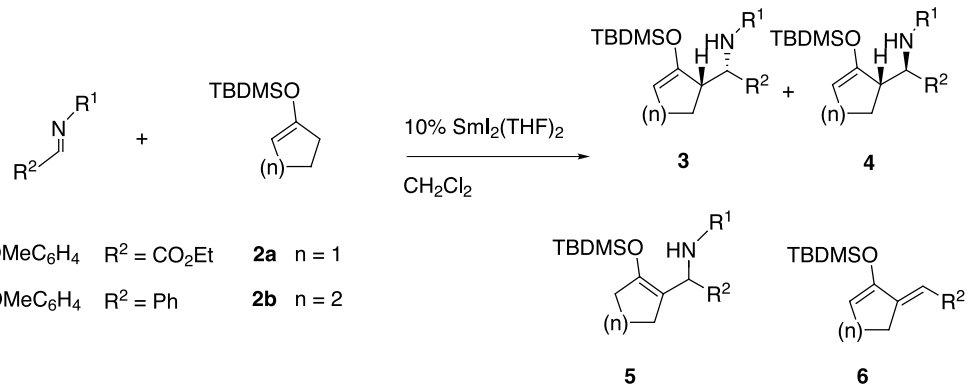


(1)

catalytic amounts of samarium diiodide, in methylene chloride. At room temperature, enoxysilane **2a** reacts with imine **1a** yielding a mixture of enoxysilanes **3aa**, **4aa**, **5aa** as reaction products, instead of the expected β-aminoketone (Table 1, entry 1). The regioisomers **3aa**+**4aa** (mixture of stereomers) and **5aa** were obtained in equal amounts in the crude product and could not be separated. For a longer reaction time, these enoxysilanes were converted into diene **6aa** which was then the sole compound in the crude product (entry 2). We studied the influence of the temperature on the selectivity of the reaction and observed only small effects on the regioselectivity and no effect on the ratio of stereomers **3aa/4aa** (entries 1, 3, 4). The six-membered ring enoxysilane **2b** reacted with the same imine **1a** at room temperature providing also the addition product as an enoxysilane. Surprisingly the reaction was regioselective, leading to sole isomer **5ab**. The reactions of chelating imine **1b** with enoxysilanes **2a** and **2b** were regioselective and led only to the mixture of diastereomers **3ba**+**4ba** for the five-membered ring enoxysilane (entries 6–8) and to the sole stereoisomer **3bb** for the six-membered ring enoxysilane (entry 9). A decrease in temperature for the reaction involving the five-membered ring enoxysilane had no effect on regioselectivity but resulted in a small increase in the diastereoselectivity of the reaction. Since stereoisomers **3** and **4** could not be separated, structure **3** was assigned to the major isomer by comparison with the tandem adducts of similar structure.[20b]

Formation of diene **6** from the reaction products took place readily either from the crude products or during the purification. This behavior is different from that of the tandem products obtained from Mukaiyama–Michael iminoaldol reactions. These were more stable towards decomposition and could be prepared without formation of by-product and easily purified. Total transformation into the corresponding diene **6**, from **3**, **4**, and **5** was observed during chromatography on silica gel and this degradation occurred also, but in a lesser extent, on alumina and explains the low yields in purificated products. The ratio in isomers **3**, **4** and **5** has thus been evaluated by integration of ^{1}H NMR spectra of crude products whenever possible.

In most cases, formation of enoxysilanes with the less substituted double bond is observed. In reactions involving imine **1b**, regioselectivity was similar to that observed in the case of tandem Michael–iminoaldol reactions, only stereoisomers **3** and **4** were formed in the absence of regioisomer **5**. Imine **1a** afforded the mixture of regioisomers for the five-membered enoxysilane **2a**, but led regioselectively to isomer **5** for the six-membered enoxysilane **2b**.

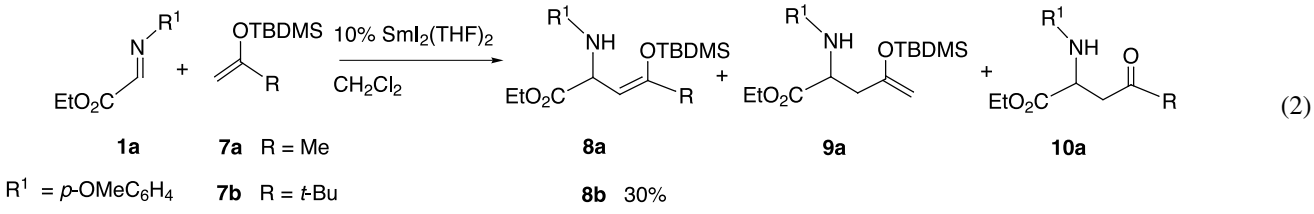
These iminoaldol reactions involving cyclic *tert*-butyldimethylsilyl enoxysilanes allow the preparation of new enoxysilanes substituted by an amino group and we have tried to extend these reactions to acyclic enoxysilanes. The glyoxylic imine **1a** reacted at room temperature or 0 °C with enoxysilane **7a** (Eq. 2) with total conversion after 12 h, providing iminoaldol products as a mixture of enoxysilanes **8a** and **9a** and β-aminoketone **10a**. Due to the complexity of NMR spectra, analysis of crude or purified products did not permit to evaluate the ratio of the different compounds. In

Table 1. Tandem iminoaldol–enolisation reactions catalyzed by samarium diiodide

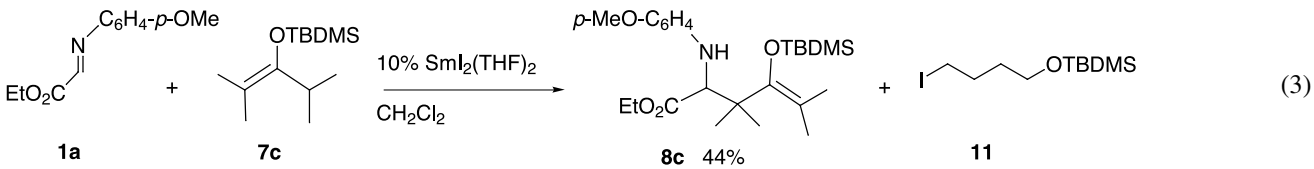
Entry	Imine	Enoxysilane	*T* (°C)	*t* (h)	**3**+**4**+**5** Yield[a,b] %	**3**+**4**/**5**[c]	**3**/**4**[c]	**6**[b]
1	**1a**	**2a**	20	2	88	48/52	50/50	5
2	**1a**	**2a**	20	18				100 (24)
3	**1a**	**2a**	0	18	80	54/46	50/50	7
4	**1a**	**2a**	−30	96	74 (40)	60/40	50/50	0
5	**1a**	**2b**	20	5	65 (25)	0/100		0
6	**1b**	**2a**	20	2	46 (14)	100/0	62/38	44
7	**1b**	**2a**	0	18	64 (19)	100/0	78/22	26
8	**1b**	**2a**	−40	18	57 (21)	100/0	85/15	45
9	**1b**	**2b**	12	72	(25)	100/0	100/0[d]	28[e]

[a] 10% $SmI_2(THF)_2$ in 8 mL CH_2Cl_2; ratio **1**/**2**: 1/1.
[b] Yield in crude product (isolated yield).
[c] Ratio measured by ^{1}H NMR on crude product.
[d] Only one isomer can be detected by ^{1}H and ^{13}C NMR after purification.
[e] Isolated yield.

order to prepare selectively a β-aminoenoxysilane, we tested substrates **7b** and **7c** (Eqs. 2 and 3) which could lead to a sole isomer after reaction. In both cases, we observed low rates and small conversions probably due to the bulkiness of substrates. 4-Iodo-*t*-butyldimethylsilyloxybutane **11** was obtained as a by-product. This compound resulted from the ring opening of the tetrahydrofuran coordinated to samarium, by *t*-butyldimethylsilyl iodide formed in situ. The opening of tetrahydrofuran has been already observed in iminoaldolisation reactions catalyzed by samarium diiodide,[21] and explains the deactivation of the catalyst.



(2)

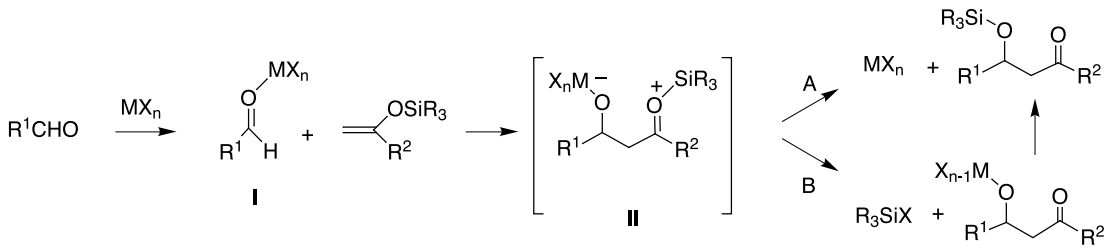


(3)

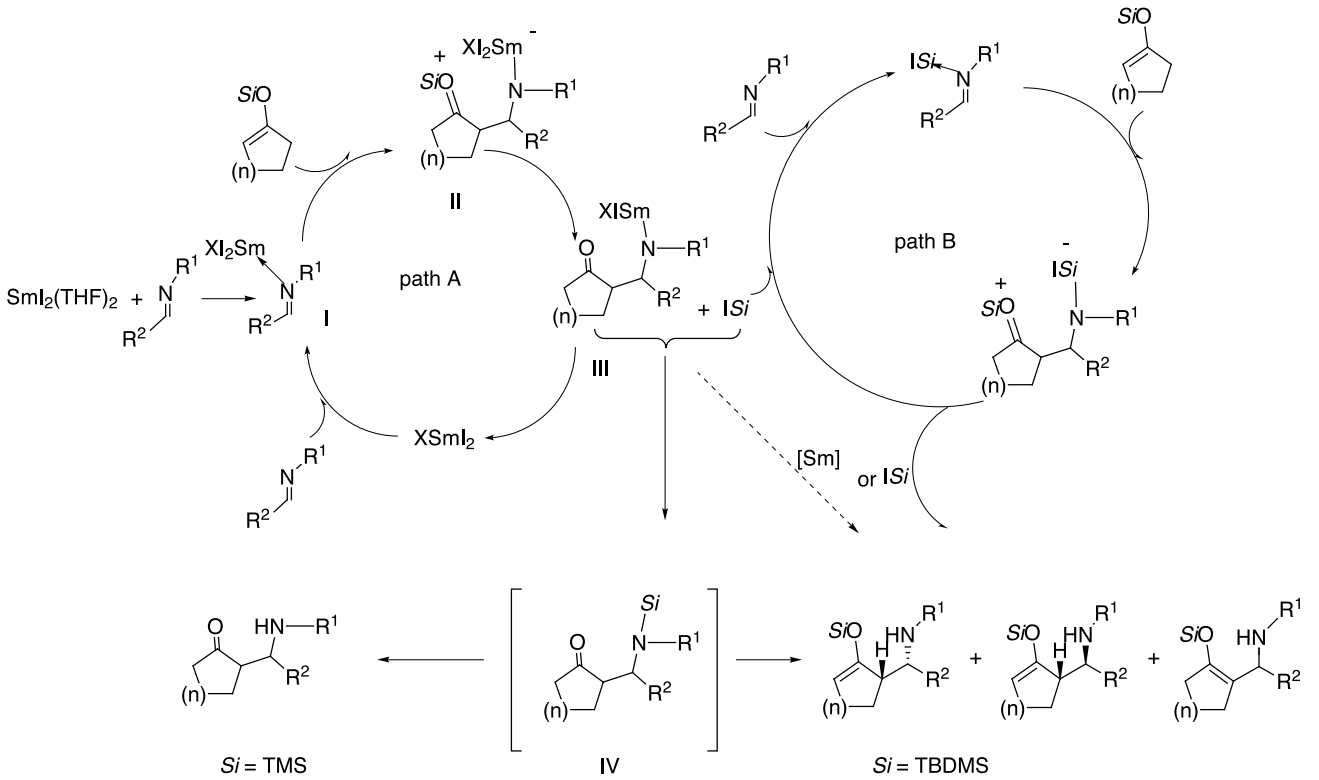
Reactions of the glyoxylic imine **1a** and chelating aromatic imine **1b** with *tert*-butyldimethylsilyl enoxysilanes catalyzed by samarium diiodide afforded Mannich-type products as was observed with trimethylsilyl enoxysilanes.[19] This reactivity differs from that of other Lewis acids such as $Yb(OTf)_3$, $InCl_3$, or $In(OTf)_3$ which catalyze cycloaddition reaction of *N*-phenylsubstituted imines and trimethylsilylenoxysilanes to give tetrahydroquinoline derivatives.[22]

2.1. Proposed mechanistic scheme for iminoaldolisation reaction

Several mechanisms have been proposed for Lewis acids catalyzed Mukaiyama aldol and Michael reactions, and the main different pathways proposed for the aldolisation reaction are depicted in Scheme 1.[23] In a first step the Lewis acid coordinates the carbonyl compound to form an intermediate I which reacts with the silyl derivative to afford the adduct II. The next step can be a concerted path A, or a non-concerted process B. The first one involves an intramolecular transfer of the silyl group, while, in the non-concerted process B, there is formation of an aldolate intermediate followed by intermolecular silylation reaction. In the latter process, the release of a silyl species R_3SiX allows a silicon-catalyzed competing process if the silylation of the aldolate is slow. In the course of our investigations concerning Mukaiyama aldol and Michael reactions catalyzed by lanthanide iodides, we had established, by performing crossover experiments, that intramolecular transfer of silicon does not occur.[16] We thus concluded that our aldolisation reactions should follow a process such as described in path B, in either a samarium-catalyzed, or a silicon-catalyzed process, or with both species as the actual catalysts. For iminoaldol reactions, a similar mechanism can be proposed, as depicted in Scheme 2. The first step is the coordination of the imine on a trivalent samarium species formed in situ. In all cases, reaction mixture turns from blue to yellow after the addition of the imine, indicating the trivalent state of samarium. Yet we have never detected reduction products such as amine or diamine and we have no information concerning the structure of the samarium species thus formed. The second step is the reaction of enoxysilane to form a samarium amide II, followed by liberation of silyl iodide and of the samarium amide III. Several reaction paths can then explain the formation of the reaction products. In presence of the silyl iodide the intermediate III can be transformed in a silylated β-aminoketone IV. This latter species either forms a β-aminoketone by cleavage of the nitrogen–silicon bond, or is transformed into enoxysilanes in the reactions involving *tert*-butyldimethylsilyl derivatives. The *tert*-butyldimethylsilyl enoxysilanes can alternatively be obtained directly from intermediates III by samarium catalyzed reactions, in a similar way to the transformation of ketones and aldehydes by reaction with ketene trimethylsilyl acetal catalyzed by samarium diiodide.[18] A silyl iodide-catalyzed process as indicated in path B can



Scheme 1.



Scheme 2.

alternatively occur, if the silylation of intermediate III is a slow step and explain the formation of the β-amino-enoxysilanes. In fact, silyl iodides prepared in situ can be used for the transformation of ketones in enoxysilanes.[24] However, we have obtained high enantiomeric excess for Mannich-type reactions of glyoxylic imines catalyzed by samarium iodo binaphtoxide, which indicates that in this latter case, catalysis by a samarium species was faster than with silyl iodide.[25] In the imino aldol reactions described above as well as in tandem Michael iminoaldol reactions,[20b] we have observed that the structures of reaction products are related to the silyl groups of the enoxysilanes or of the ketene silyl acetals for tandem reactions. Trimethylsilyl derivatives allow the isolation of ketones while *tert*-butyldimethylsilyl derivatives afford enoxysilanes. This may be explained by the transformation of β-amino trimethylsilylenoxysilanes in β-amino ketones during the treatment of reaction mixtures. However, in other samarium diiodide-catalyzed reactions, we have isolated trimethylsilyl enoxysilanes.[16,18] In iminoaldol reactions as well as in tandem Michael iminoaldol reactions, all our attempts to isolate trimethylsilyl substituted products, after filtration of samarium salts without hydrolysis of the reaction mixtures have been unsuccessful. If intermediates IV are formed after a silylation step, the difference of the nature of the products could be better explained by a difference in the strength of the nitrogen–silicon bond according to the nature of the silyl group. The weaker bond of trimethylsilyl group should be easily broken before the transfer of silicon on oxygen could occur.

In summary, we have shown that enoxysilanes substituted by a *tert*-butyldimethylsilyl group can be used in samarium diiodide catalyzed iminoaldol reactions as well as trimethylsilyl enoxysilanes. Thanks to the substitution of the silyl group, the nature of reaction products can be controlled, β-aminoketones are isolated with trimethylsilyl derivatives and β-aminoenoxysilanes with *tert*-butyldimethylsilyl derivatives. This confirms our previous results obtained for tandem Michael–iminoaldol reactions. Iminoaldol reactions using *tert*-butyldimethylsilyl enoxysilanes thus result in the functionalisation of the enoxysilanes by an amino group. This opens the route to new sequences of tandem reactions using samarium diiodide as a catalyst that we are currently investigating.

3. Experimental

3.1. General

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. CH_2Cl_2 was distilled from CaH_2 and degassed immediately prior to use. $SmI_2(THF)_2$ was prepared as previously described.[26] Enoxysilanes **2a**, **2b**, **7a**, **7b**, **7c** were prepared according to literature procedures.[24] Bruker AM 250 and AM 400 spectrometers, operating at 250 and 400 MHz for ^1H, 62.5 and 100.8 MHz for ^{13}C, were used for the NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane for spectra in $CDCl_3$. Infrared spectra were recorded as Nujol mulls using NaCl plates on a Perkin–Elmer 1000 FTIR spectrometer and are reported in cm^{-1}. HRMS were measured with a Perkin–Elmer Finnigan-Mat 955 spectrometer. Mass spectra (MS) (70 eV) data were determined on a Ribermag R-10 GC/MS. Flash chromatography were realized on

neutral alumina, using heptane/ethyl acetate mixtures as eluents.

3.2. Typical procedure for the synthesis of tandem products

In a Schlenk tube, a solution of SmI_2 in THF (0.1 M, 1 mL, 0.1 mmol) was carefully evaporated in vacuo to give $SmI_2(THF)_2$ as a blue powder, (alternatively $SmI_2(THF)_2$ (55 mg, 0.1 mmol) was weighed in a glovebox) and suspended in CH_2Cl_2 (4 mL). Then a solution of 1-*tert*-butyldimethylsilyloxycyclopentene **2a** (198 mg, 1 mmol) in CH_2Cl_2 (2 mL) was added, and the mixture was cooled at −30 °C. A solution of glyoxylic imine **1a** (207 mg, 1 mmol) in CH_2Cl_2 (2 mL) was cooled at the same temperature and rapidly added on the reaction mixture to give an orange solution. After one night stirring at the same temperature, reaction mixture was then hydrolyzed (10 mL H_2O) and extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on alumina (heptane/AcOEt: 85/15) to afford the mixture of **3aa**+**4aa**+**5aa** (162 mg, 40%).

3.2.1. [(2-*tert*-Butyldimethylsilyloxy-cyclopent-2-enyl]-(4-methoxyphenylamino)-acetic acid ethyl ester (mixture of diastereomers, *syn* 3aa+*anti* 4aa)+[(2-*tert*-butyldimethylsilyloxy-cyclopent-1-enyl]-(4-methoxy-phenylamino)-acetic acid ethyl ester (5aa): (*syn* 3aa+*anti* 4aa+5aa). ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): **3aa**+**4aa**+**5aa**: 6.76 (m, 2H), 6.60 (m, 2H), 4.96 (s, 0.4H, H, **5aa**), 4.70 (d, 0.6H, H_a, J=9 Hz, **3aa**+**4aa**), 4.20 (m, 2H), 4.10 (m, 0.6H, **3aa**+**4aa**), 3.75 (s, 3H), 3.20 (m, 0.6H, **3aa**+**4aa**), 2.40–1.80 (m, 4.8H), 1.3 (m, 3H), 0.99 (s, 3.6H, **5aa**), [0.94 (s, 2.7H,) 0.89 (s, 2.7H) **3aa**+**4aa**], 0.195 (s, 2.4H, **5aa**), [0.19 (s, 0.9 H), 0.18 (s, 0.9H), 0.17 (s, 0.9H), 0.11 (s, 0.9H), **3aa**+**4aa**]. ^{13}C NMR (62.5 MHz, $CDCl_3$, δ (ppm)): 172.95, 172.85, 172.36, 153.61, 152.42, 152.13, 151.84, 141.72, 141.55, 140.74, 116.04, 115.18, 114.94, 114.64, 112.89, 111.57, [103.42, 102.92, (**3aa**+**4aa**)], 61.09, 61.02, 60.79, 60.71, 59.45, 59.17, 55.71, 53.84 (**5aa**), 52.55, 48.02, 47.89, 47.74, 40.67, 33.60, 27.26, 27.16, 26.75, 25.70, 25.63, 24.52, 22.48, 20.21, 19.50, 18.10, 18.01, 14.20, −2.62, −2.96, −3.76, −4.02, −4.79, −4.95. FTIR (NaCl) (cm^{-1}): 3397, 1735, 1677, 1646. HRMS: calcd for $C_{22}H_{35}NO_4SiNa$ (M^++Na): 428.2229, found: 428.2233.

3.2.2. (2-*tert*-Butyldimethylsilyloxy-cyclopent-2-enyl-idene)-acetic acid ethyl ester, 6aa. ^{1}H NMR ($CDCl_3$, 250 MHz, δ (ppm)): 5.78 (s, 1H), 5.54 (s, 1H), 4.15 (q, 2H, J=6.8 Hz), 2.98 (m, 2H), 2.41 (m, 2H), 1.27 (t, 3H, J=6.8 Hz), 0.95 (s, 9H), 0.16 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.5 MHz, δ (ppm)): 206.50, 165.76, 147.38, 121.79, 75.68 61.00, 27.81, 25.63, 24.68, 18.07, 14.11, −3.00. GC-MS (EI) m/z (intensity): 283.1 (MH^+), 241.1 (100%). FTIR (NaCl) (cm^{-1}): 1713, 1644, 1521.

3.2.3. [(2-*tert*-Butyldimethylsilyloxy-cyclohex-1-enyl]-(4-methoxyphenylamino)-acetic acid ethyl ester, 5ab. ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 6.71 (d, 2H, J=12 Hz), 6.62 (d, 2H, J=12 Hz), 5.27 (s, 1H), 4.35 (s, 1H, NH), 4.18 (q, 2H, J=7.3 Hz), 3.71 (s, 3H), 2.09 (m, 2H), 1.98 (m, 2H), 1.75–1.40 (m, 4H), 1.23 (t, 3H, J=7.3 Hz), 1.01 (s, 9H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.5 MHz, δ (ppm)): 172.82, 151.87, 147.85, 140.70, 114.58, 110.77, 60.93, 55.66, 54.87, 30.31, 25.78, 23.06, 22.32, 22.20, 18.22, 14.20, −3.21, −3.81. FTIR (NaCl) (cm^{-1}): 3406, 1731, 1672, 1514. HRMS: calcd for $C_{23}H_{37}NO_4SiNa$ (M^++Na): 442.2387, found 442.2389.

3.2.4. [(2-*tert*-Butyldimethylsilyloxy-cyclopent-2-enyl)-phenyl-methyl]-(2-methoxy-phenyl)-amine (mixture of diastereomers, *syn* 3ba+*anti* 4ba). ^{1}H NMR ($CDCl_3$, 250 MHz, δ (ppm)) **3ba**+**4ba**: 7.35–7.10 (m, 5H), 6.70–6.47 (m, 3H), 6.14 (d, 0.15H, J=1.5 Hz, **4ba**), 6.11 (d, 0.85H, J=1.9 Hz, **3ba**), 4.63 (s, 0.85H, **3ba**), 4.54 (s, 0.15H, **4ba**), 4.45 (s, 1H), 3.78 (s, 0.45H, **4ba**), 3.72 (s, 2.55H, **3ba**), 3.05 (m, 0.85H, **3ba**), 2.90 (m, 0.15H, **4ba**), 2.11–1.62 (m, 4H), 0.87 (s, 1.35H, **4ba**), 0.78 (s, 7.65H, **3ba**), 0.12 (s, 0.45H, **4ba**), 0.08 (s, 2.55H, **3ba**), 0.01 (s, 0.45H, **4ba**), −0.03 (s, 2.55H, **3ba**). ^{13}C NMR ($CDCl_3$, 62.5 MHz, δ (ppm)): 128.17, 127.78, 126.93, 126.51, 121.09, 121.03, 116.41, 115.88, 111.92, 111.08, 109.09, 108.88, 104.42, 103.50, 58.96, 58.34, 52.17, 51.70, 55.36, 55.23, 31.90, 29.68, 25.73, 25.53, 24.26, 22.28, 17.99, −4.84, −5.65. FTIR (NaCl) (cm^{-1}): 3338, 1646. HRMS ($C_{25}H_{35}SiNO_2$-Na): calcd 432.2333, found 432.2335.

3.2.5. [(2-*tert*-Butyldimethylsilyloxy-cyclohex-2-enyl)-phenyl-methyl]-(2-methoxy-phenyl)-amine, *syn* 3bb. ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 7.20 (m, 5H), 6.71 (m 1H,), 6.55 (m, 2H), 6.14 (m, 1H), 5.02 (s, 1H), 4.81 (s, 1H), 4.77 (s, 1H), 3.85 (s, 3H), 2.66 (m, 1H), 2.20–2.00 (m, 2H), 1.70–1.50 (m, 2H), 1.30 (m, 2H), 0.79 (s, 9H), 0.16 (s, 3H), −0.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz, δ (ppm)): 150.05, 146.86, 142.64, 138.14, 128.21, 126.89, 126.42, 121.06, 116.00, 111.61, 109.06, 106.10, 57.59, 55.50, 46.21, 25.68, 24.20, 23.15, 21.93, 17.98, −5.30. FTIR (NaCl) (cm^{-1}): 3400, 1659. HRMS: calcd for $C_{26}H_{37}NO_2SiNa$ (M^++Na): calcd 446.2491, found 446.2491.

3.2.6. (6-Benzylidene-cyclohex-1-enyloxy)-*tert*-butyl-dimethyl-silane, 6bb. ^{1}H NMR ($CDCl_3$, 250 MHz, δ (ppm)): 7.17 (m, 5H), 6.76 (s, 1H), 5.13 (t, 1H, J=4.4 Hz), 2.55 (td, 2H, J=4.4 Hz, J=1.9 Hz), 2.12 (m, 2H), 1.55 (m, 2H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.5 MHz, δ (ppm)): 148.79, 137.94, 130.31, 129.28, 127.99, 126.16, 122.29, 110.15, 27.37, 25.96, 24.70, 23.08, 18.35, 1.02. MS (ESI POS): 339 (MK^+, 100%), 301 (MH^+).

Acknowledgements

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