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The search for tolerant Lewis acid catalysts. Part 2: Enantiopure cycloalkyldialkylsilyl triflimide catalysts

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Abstract—A series of 2-aryl- and arylmethyl-3-dialkylphenylsilyl cycloalkanones have been prepared and resolved. The pure enantiomers were reduced to the corresponding cycloalkane derivatives. These were used for the in situ generation of enantiopure cycloalkylsilyl triflimides by protodesilylation with bis(trifluoromethanesulfonyl)imide. The association of a bulky leaving group with a silicon atom carrying large substituents was again shown to favour the complexation of silicon with carbonyl groups: all these trialkylsilyl triflimides showed a high catalytic activity for Diels–Alder reactions. Enantiomeric excesses up to 59% were observed. This is the highest enantioselectivity ever observed for a Diels–Alder reaction catalysed by a silicon Lewis acid.

1. Introduction

In the course of our studies on enantioselective Diels–Alder reactions of activated azadienes,[1] we found that many metal-based chiral Lewis acid catalysts could not be used as a result of competitive bindings to the diene and the dienophile carbonyl group. In the case of 2-azadienes a solution was found, which uses the bidentate imide group and the Box copper(II) catalyst developed by Evans and Johnson.[2] However, this approach was totally unsuccessful for 1-azadiene cycloadditions.[3] Another solution for efficient catalysis of 2-azadienes cycloadditions was the use of a more basic activating group of the dienophilic double bond in conjunction with silyltriflates as Lewis acid catalysts: α,β-unsaturated amides were shown to react smoothly with 2-azadienes in the presence of TBDMSOTf.[4] However, silyltriflates were not acidic enough to activate the corresponding esters. In 1997, both our group and Mikami's group discovered that *N*-(trimethylsilyl)triflimide (Me_3SiNTf_2) was an extremely efficient carbonyl activator.[5,6] We observed an unexpected reversal of thermodynamic acidity on going from the Brönsted acids ($HOTf > HNTf_2$) to the TMS derivatives ($TMSOTf < TMSNTf_2$), which was assigned to the larger size of the triflimide group as compared to triflate.[5] Also our group demonstrated that increasing the size of the alkyl substituents on silicon resulted in a significant increase of Lewis acidity.[7] It was later shown by several groups that $TMSNTf_2$, often generated in situ, was an efficient catalyst for many carbon–carbon bond-forming reactions,[8] or, e.g., the acid-catalysed ring-opening polymerisation of cyclosiloxanes.[9]

Stimulated by these successful results, we decided to examine the possibility of generating chiral silyl triflimides, which could act as Lewis acids for the activation of carbonyl groups. The possibility of using an asymmetric silicon atom was rejected since these compounds are not readily accessible and steric course of substitution at silicon is complex. At the outcome of these studies, no such catalyst had been described. Examples of Diels–Alder reactions catalysed by an enantiopure silicon catalyst were described in 1998 but facial selectivities were very modest ($ee \leq 10\%$).[10] More recently Leighton et al. have reported the first examples of highly enantioselective carbon–carbon bond-forming reactions catalysed by silyl chlorides derived from enantiopure aminoalcohols.[11] At this point, however, the scope and limitations of this elegant approach have not yet been defined.

Our approach was inspired by the successful studies of chiral boron Lewis acid catalysts by Hawkins' group.[12] We first prepared several silylated triflimides derived from (−)-myrtenal and tested them as catalysts of the Diels–Alder reactions of methyl acrylate and methyl crotonate to cyclopentadiene (Scheme 1).[7] The best ee was ≈54%. We now wish to report the details of our studies of a variety of α-aryl- or arylmethyl-cycloalkylsilyl triflimides as catalysts for the asymmetric Diels–Alder reactions of α,β-unsaturated esters.

Keywords: Lewis acid; Enantioselective catalysis; Asymmetric Diels–Alder cycloadditions; Silylated triflimides.
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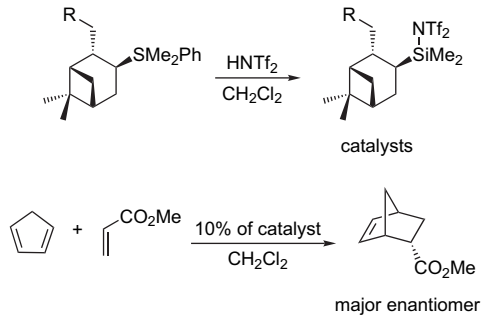
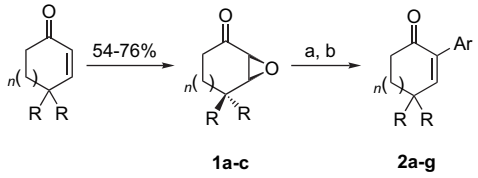


Scheme 1. Silylated triflimides derived from (−)-myrtenal. For R=OMe at −78 °C, yield=83%, ee=54%.

2. Synthesis of the enantiopure scaffolds

2.1. Synthesis of *trans*-2-aryl-3-dialkylphenylsilyl cycloalkanones

2,3-Epoxyketones are versatile building blocks in organic synthesis.[13] They have been shown to behave as versatile equivalents of α-ketovinyl cations.[14] Compounds **1a–c** were prepared by epoxidation of the cyclic enones with hydrogen peroxide under basic conditions following literature procedures[15] (Scheme 2).



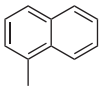
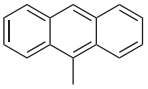
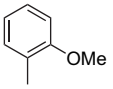
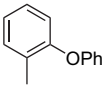
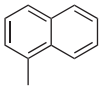
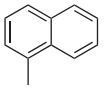
Scheme 2. *Reagents and conditions*: (a) LDA (1.1 equiv) in THF, −78 °C; (b) ArLi (2 equiv), −23 °C then PTSA (cat) in refluxing toluene.

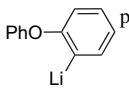
α-Aryl enones **2a–g** were prepared following Wender's general procedure[14d] (Scheme 2, Table 1). Prior formation of an enolate by treatment of **1a–c** with LDA was essential to ensure the chemo- and regioselective opening of the epoxide ring by the aryl lithium reagent.

The reaction of CuCN with dimethyl- or diethylphenylsilyllithium generated the corresponding cuprate reagents, which were reacted with enones **2a–g** according to Fleming's procedure (Scheme 3, Table 2).[18] The reactions were quenched by methanol at room temperature: these conditions only gave the *trans*-adduct **3a–h** as predicted on the basis of the early observations of the group of Seyden-Penne.[19] The trans-stereoselectivity was probably the result of a thermodynamically controlled protonation occurring at higher temperature and in more basic conditions.[19] Indeed, quench with a saturated NH_4Cl solution at 0 °C mainly gave mixtures of stereoisomers (*cis*-**4**>*trans*-**3**) except when n=0 and Ar=1-Np (only trans).

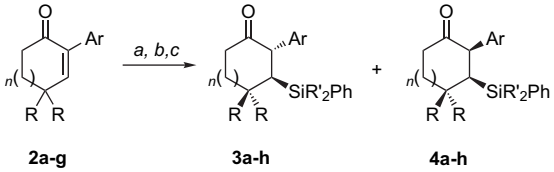
Figure 1 shows the typical ^1H and ^{13}C NMR patterns and assignments for a *cis*-adduct **4a**. The *cis*- and *trans*-isomers were distinguished by the values of coupling constants $J_{H_2-H_3}$, which varied from 5.1 to 5.7 Hz for the *cis*-isomers and from 11.1 to 13.0 Hz for the *trans*-isomers.[20] As shown later, the structure and configuration of **3f** was confirmed by X-ray diffraction analysis.

Table 1. α-Arylation of epoxyketones **1a–c**

	Ar	R	n	Yield, % (lit.)
2a		H	1	65 (64)
2b		H	1	54 (62)
2c		H	1	15
2d		H	1	34 (30)
2e		H	1	31[a]
2f		Me	1	46
2g		H	0	50[b]

[a]  prepared from Ph_2O.[16]

[b] Yields not mentioned in literature.[17]



Scheme 3. *Reagents and conditions*: (a) $PhMe_2SiCl$ or $PhEt_2SiCl$ (3 equiv), Li (9 equiv), THF; (b) addition of PhR'_2SiLi in suspension of CuCN (1.5 equiv), −30 °C then 0 °C; (c) **2a–g** (1 equiv), THF, −23 °C→rt then quench.

Table 2. Michael additions of phenyldialkylsilyl cuprate reagents to 2-arylcycloalkenones

Method of quenching[a]	n	R	R′	Ar	Yield,[b] %	
					3 (*trans*)	**4** (*cis*)
a	A	1	H	Me	Ph	3	70
a	B	1	H	Me	Ph	71	—
b	A	1	H	Me	1-Np	34	23
c	B	1	H	Me	9-An	20	—
c	A	1	H	Me	9-An	—	15
d	B	1	H	Me	2-PhOMe	67	—
e	B	1	H	Me	2-PhOPh	57	—
f	B	1	Me	Me	1-Np	50	—
g	A	0	H	Me	1-Np	73	—
h	B	1	H	Et	Ph	70	—

[a] A: aqueous NH_4Cl, 0 °C; B: MeOH, rt.

[b] Yields of isolated products.

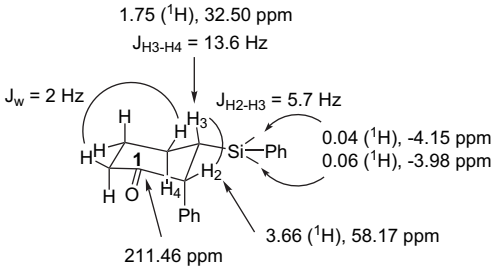


Figure 1. Typical ^{1}H and ^{13}C NMR patterns for a *cis* Michael adduct **4a**.

2.2. Synthesis of *trans*-2-arylmethyl-3-dimethylphenylsilyl-cyclohexanones 5

A series of *trans*-2-arylmethyl-3-silyl cycloalkanones **5a–c** were prepared by tandem reactions involving the 1,4-addition of silyl cuprate to cyclohexenone followed by reaction of the in situ generated enolates with arylmethyl bromides (Scheme 4, Table 3).[21] In all cases we obtained the pure *trans*-2-arylmethyl-3-silyl cycloalkanones **5** after column chromatography. In most cases, small amounts of diarylmethylated products **6** were also formed. However, we were not able to avoid the formation of **6** without significantly lowering the yield of **5**. In all cases the reactions were highly trans-stereoselective.

2.3. Resolution of the racemic cycloalkanones

Racemic ketones **3a–h** and **5a–c** were resolved by preparative HPLC. Chiralcell AD or OD-H columns gave excellent separation of these enantiomeric ketones. Enantiomers eluting first showed negative optical rotations while the isomers with longer retention times showed positive optical rotations. The absolute configurations of enantiomerically pure *trans*-cycloalkanone (−)-**3f** was shown to be (2*R*,3*S*) by X-ray diffraction analysis (Fig. 2) while (+)-**5a** and (+)-**5b** were shown to be the (2*S*,3*S*) configurations (Figs. 3 and 4).[22] The absolute configuration of other *trans*-cycloalkanones could be inferred from the above results: the enantiomeric ketones with positive optical rotations were assigned absolute configuration (2*S*,3*S*) and those with negative optical rotations were assigned configuration (2*R*,3*R*).

2.4. Synthesis of ENP 2-dialkylphenylsilyl-aryl (arylmethyl)-cycloalkanes

The carbonyl group of enantiomerically pure (ENP) cycloalkanones was reduced following the experimental protocol described by Kim et al.[23] The ketone was first converted into the corresponding tosylhydrazone. The crude tosylhydrazones showed two spots on TLC suggesting the presence of *syn* and *anti* isomers. Reduction of the crude hydrazone with $NaBH_3CN/ZnCl_2$ (2:1) yielded the corresponding cycloalkane (Scheme 5, Table 4).[23] Yields were moderate to good except for the reduction of the tosylhydrazone derived from ketone **3c**, which gave a complex mixture of products.

Table 3. Tandem 1,4-addition–alkylation of cyclohexenone and cyclopentenone

	Ar	*n*	Yields of **5**, %	Yields of **6**, %
a	Ph	1	85	9
b	2-Np	1	41	4
c	1-Np	1	39	7

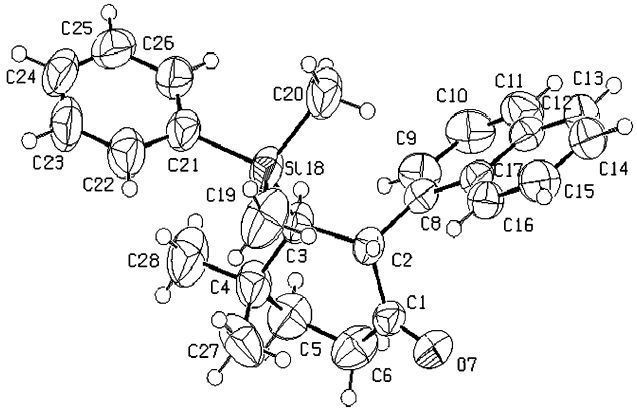


Figure 2. ORTEP drawing of compound (−)-**3f**.

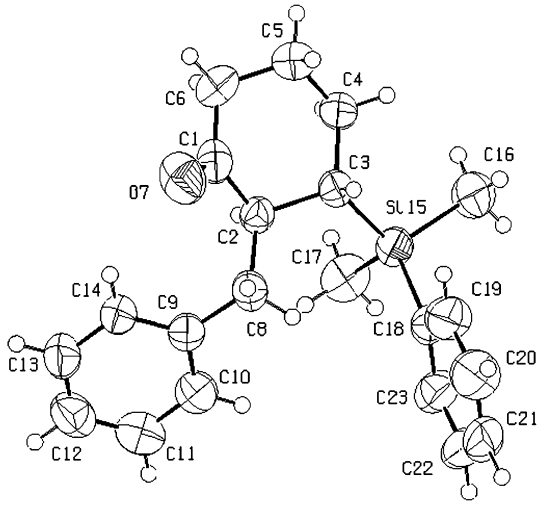
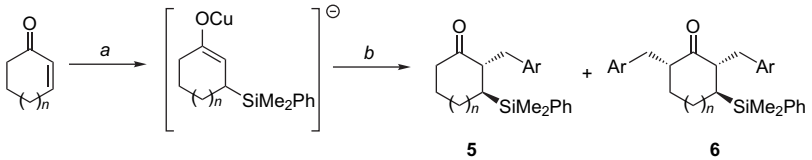


Figure 3. ORTEP drawing of compound (+)-**5a**.



Scheme 4. *Reagents and conditions*: (a) $PhMe_2SiLi$ (3 equiv), CuI (1.5 equiv), in THF/HMPA, −30 °C then addition of enone (1 equiv) at −78 °C→−23 °C; (b) arylmethyl bromide (2.8 equiv), −78 °C then aqueous NH_4Cl at 0 °C.

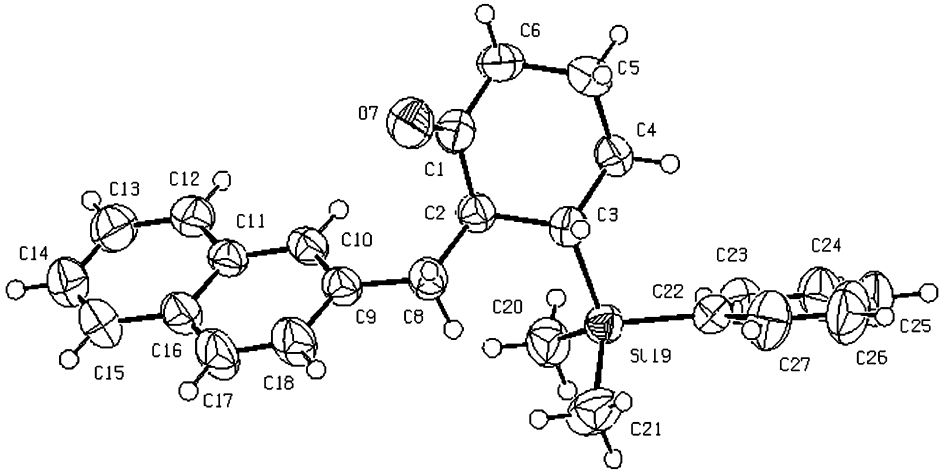
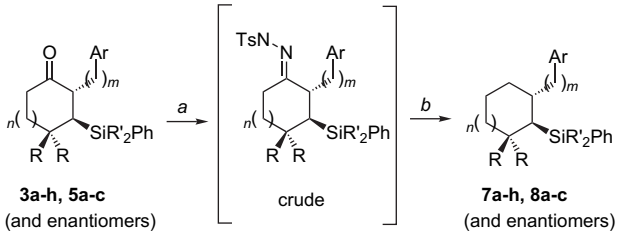
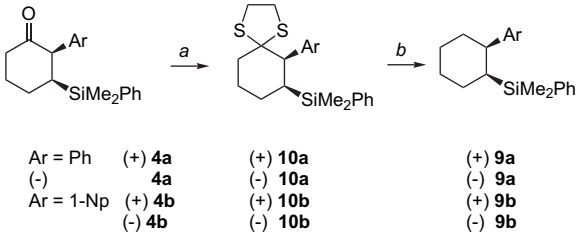


Figure 4. ORTEP drawing of compound (+)-**5b**.



Scheme 5. *Reagents and conditions*: (a) $TsNHNH_2$ (1.2 equiv), EtOH, 60 °C, 3–6 h; (b) $NaBH_3CN$ (5 equiv), $ZnCl_2$ (2.5 equiv), EtOH/MeOH (1:1), 60 °C, 3–10 h.



Scheme 6. *Reagents and conditions*: (a) ketone (1 equiv), ethanedithiol (1.2 equiv), $TiCl_4$ (0.3 equiv) in CH_2Cl_2, −40 °C→rt; (b) **10a** or **10b** (1 equiv), Ra–Ni (10 equiv) in CH_3OH, rt.

When applied to the *cis*-isomers **4a**, this method gave a mixture of *cis*- and *trans*-1,2-disubstituted cycloalkanes: epimerisation probably occurred during the formation of the tosylhydrazone. We then turned to an alternative reductive method involving the formation of a dithioketal followed by a desulfurisation reaction with Raney nickel (Scheme 6).[24,25]

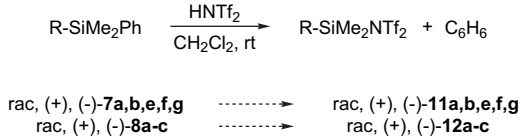
Table 4. Reduction of ENP 3-silylated cycloalkanones

Ketone	*n*	m	R	R′	Ar	Product	Yield,[a] %
(+)-**3a**	1	0	H	Me	Ph	(−)-**7a**	31
(−)-**3a**	1	0	H	Me	Ph	(+)-**7a**	44
(+)-**3b**	1	0	H	Me	1-Np	(+)-**7b**	45
(−)-**3b**	1	0	H	Me	1-Np	(−)-**7b**	39
(+)-**3c**	1	0	H	Me	9-An	Complex mixture	
(+)-**3d**	1	0	H	Me	2-PhOMe	(−)-**7d**	51
(−)-**3d**	1	0	H	Me	2-PhOMe	(+)-**7d**	57
(+)-**3e**	1	0	H	Me	2-PhOPh	(+)-**7e**	20
(−)-**3e**	1	0	H	Me	2-PhOPh	(−)-**7e**	25
(+)-**3f**	1	0	Me	Me	1-Np	(+)-**7f**	31
(−)-**3f**	1	0	Me	Me	1-Np	(−)-**7f**	27
(+)-**3g**	0	0	H	Me	1-Np	(+)-**7g**	32
(−)-**3g**	0	0	H	Me	1-Np	(−)-**7g**	32
(+)-**3h**	1	0	H	Et	Ph	(−)-**7h**	31
(−)-**3h**	1	0	H	Et	Ph	(+)-**7h**	35
(+)-**5a**	1	1	H	Me	Ph	(+)-**8a**	54
(−)-**5a**	1	1	H	Me	Ph	(−)-**8a**	85
(+)-**5b**	1	1	H	Me	2-Np	(+)-**8b**	34
(−)-**5b**	1	1	H	Me	2-Np	(−)-**8b**	38
(+)-**5c**	1	1	H	Me	1-Np	(+)-**8c**	31
(−)-**5c**	1	1	H	Me	1-Np	(−)-**8c**	33

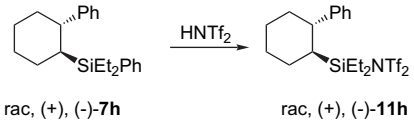
[a] Yields based on ketone for the two-step sequence.

3. Synthesis of the ENP silylated triflimides

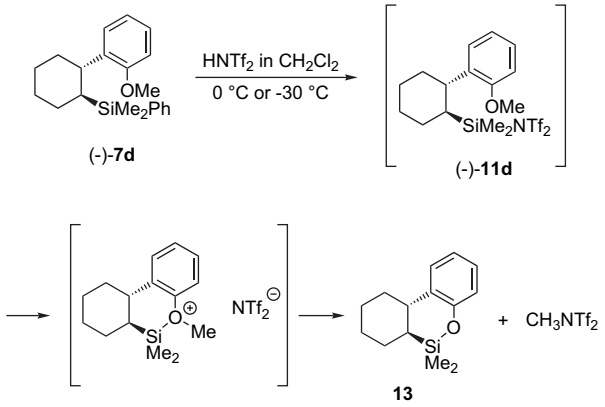
In an earlier paper in this series, we showed that $TMSNTf_2$ could be quantitatively generated by protodesilylation of the corresponding phenyltrimethylsilane.[18c,26] We have applied this method for the preparation of the new ENP catalysts (Scheme 7). The transformation of phenylsilanes into the corresponding silylated triflimides was monitored by ^1H NMR. The signals of the protons of the methyl groups connected to the silicon atom moved downfield (from 0.20 to 0.60 ppm) and a signal appeared at 7.36 ppm for the protons of benzene. When silicon carries two ethyl groups, the protodesilylation reaction became very slow at room temperature (~10% conversion after 3 h in CH_2Cl_2) but was quantitative at 80 °C in toluene (Scheme 8).



Scheme 7. General procedure for the generation of phenyldialkylsilyltriflimide catalysts.



Scheme 8. *Reagents and conditions*: CH_2Cl_2, rt, 3 h, yield=10% or toluene, 80 °C, 3 h, ~100%.



Scheme 9.

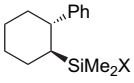
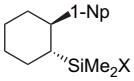
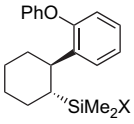
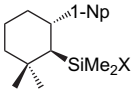
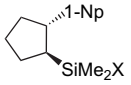
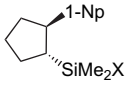
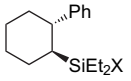
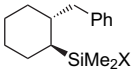
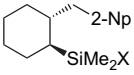
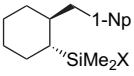
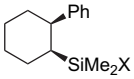
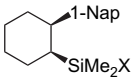
The protodesilylation of (−)-**3d** did not give the expected triflimide **11d** but a cyclic siloxane **13**, which probably resulted from an intramolecular silylation of the methoxy substituent followed by an irreversible demethylation reaction (Scheme 9).

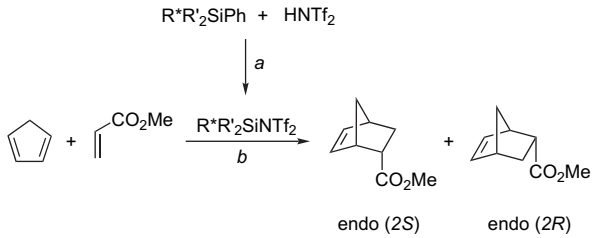
4. Evaluation of the ENP silylated triflimides as catalysts for the Diels–Alder reaction

We selected the cycloaddition of cyclopentadiene to methyl acrylate as model reaction. This should allow an easy comparison with the studies of Hawkins' group on related boron catalysts.[12]

The catalysts (10 mol %) were formed in the solvent (CH_2Cl_2 in most cases) of the Diels–Alder reaction (Scheme 10). Then 20 mol % 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) was added to neutralise any residual Brönsted $HNTf_2$. Methyl acrylate (1 equiv) and then cyclopentadiene (4 equiv) were added at −78 °C (or −100 °C) and the mixture was left at that temperature. The results are summarised in Table 5.

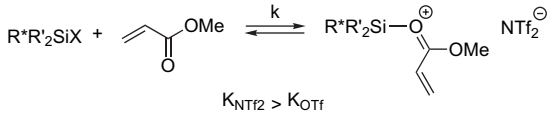
Table 5. ENP silylated triflimides as catalysts for the cycloaddition of methyl acrylate and cyclopentadiene

SM	Catalyst X=NTf_2	Conditions	Yield, %	*endo*/*exo*	ee, %	Product configuration
(−)-**7a**		−78 °C, CH_2Cl_2	95	32	47	2*R*
(−)-**7b**		−78 °C, CH_2Cl_2 −78 °C, toluene −100 °C, CH_2Cl_2	96 95 94	>100 >100 >100	50 44 59	2*R* 2*R* 2*R*
(−)-**7e**		−78 °C, CH_2Cl_2	80	19	35	2*S*
(+)-**7f**		−78 °C, CH_2Cl_2	95	49	40	2*S*
(+)-**7g**		−78 °C, CH_2Cl_2	95	99	49	2*S*
(−)-**7g**		−100 °C, CH_2Cl_2	95	32	56	2*R*
(−)-**7h**		−78 °C, toluene	99	99	36	2*R*
(−)-**8a**		−78 °C, CH_2Cl_2	95	99	0	—
(−)-**8b**		−78 °C, CH_2Cl_2	94	16	3	—
(−)-**8c**		−78 °C, CH_2Cl_2	95	49	7	2*S*
(−)-**9a**		−78 °C, CH_2Cl_2	80	7.4	42	2*S*
(+)-**9b**		−78 °C, CH_2Cl_2	90	49	45	2*S*



Scheme 10. *Reagents and conditions*: (a) 0.1 equiv of triflimides catalyst generated in situ at rt or 70–80 °C; (b) addition of methyl acrylate (1 equiv), cyclopentadiene (4 equiv), DTMB (0.2 equiv), −78 °C or −100 °C.

The first conclusions of these experiments were that these chiral silyl triflimides were *extremely active catalysts* for the Diels–Alder reaction. In most cases, reactions were almost quantitative in less than 2 h. This had already been demonstrated for the structurally more simple TMS and $TIPSNTf_2$, which have been shown to be much better catalysts than the corresponding triflates. This can be assigned to a relief of I-strain in going from the trialkylsilyltriflimide to the corresponding silylated carbonyl complex (Scheme 11).



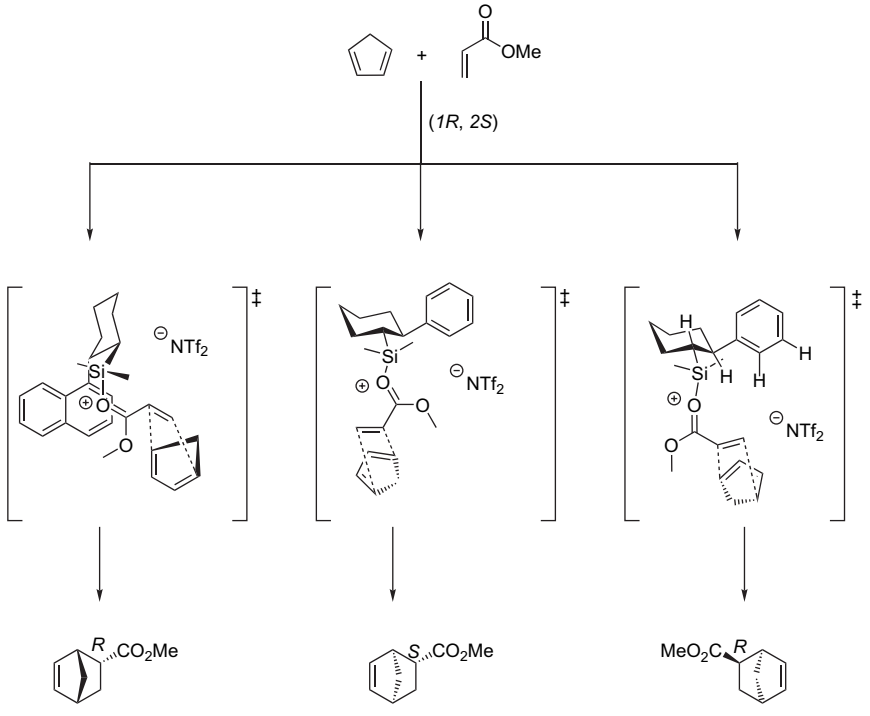
Scheme 11.

All reactions were highly *endo*-selective. Enantiomeric excesses were measured by GC (CHIRASIL-DEX CB column) for the *endo* isomers only. The best enantiomeric excesses was 59%, which is the highest enantioselectivity ever observed for a Diels–Alder reaction catalysed by a silicon Lewis acid. The selectivity was higher for catalysts having a 1-naphthyl group directly attached to the cycloalkane ring. Insertion of a methylene group allowing for more conformational mobility resulted in a significant decrease of facial selectivity. *cis*-Catalysts gave lower ee than the corresponding *trans*-catalysts. The presence of a phenoxy group on the phenyl substituent did not raise the selectivity in spite of a possible chelation of the oxygen with silicon.

An interesting observation was that catalyst derived from (−)-**7a** and (−)-**7b** led to the same enantiomer although they have opposite configurations. This suggested different transition state structures in going from the phenyl to the naphthyl-substituted catalysts. The selectivity observed with the 1-naphthyl-substituted catalyst can be rationalised on the basis of a an approach of the reactants similar to that of the corresponding boron-catalysed reaction (Scheme 12):[12a] (1) both naphthalene and silyl groups are equatorial, (2) silicon complexes the carbonyl group *anti* to the C–O ester bond, (3) the configuration of the enone unit is *s-trans*.[27] This approach is favoured by electrostatic and dipole-induced attractions between the complexed carbonyl group and the polarisable naphthalene substituent. Thus the naphthalene substituent blocks the α-face of the dienophile.

These attractive forces should be weaker when naphthyl (17.6 D) is replaced by the less polarisable phenyl group (10.4 D).[12b] Lower energy conformations of the methyl methacrylate/(−)-**11a** complex were calculated to be 0.477 kcal/mol apart (Fig. 5).[28]

In the most stable conformation **A** (Fig. 5), the silicon atom coordinates to the carbonyl group *syn* to the methoxy group of a *s-cis* enone. In this conformation, the reactive double



Scheme 12. Possible transition states for the catalysed cycloadditions.

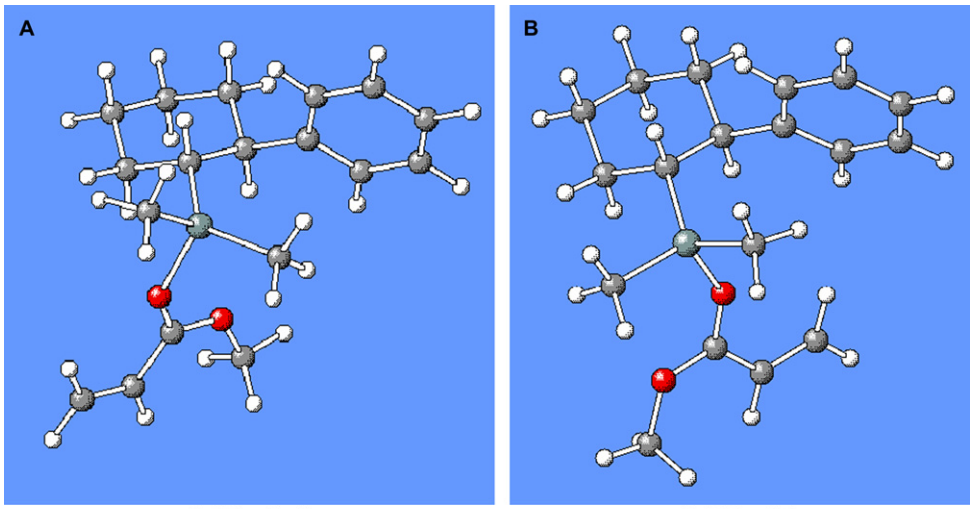


Figure 5. Low energy conformations of methyl acrylate/(−)-**11a** complex.

bond is far away from the aryl group. Conformation **B** is only 0.477 kcal higher than **A**. It differs from **A** by the conformation around the olefin–ester bond, which brings the reactive double bond closer to the aryl group. Therefore we have to consider two additional transition states **TS-2** and **TS-3** (Scheme 12) leading to adducts of opposite configurations. We are conscious that this analysis is still pretty rough but it should help the design of new catalysts of this class, which should have structural features favouring one TS over the others. The replacement of the cyclohexane ring by a decaline would be an interesting possibility.

5. Experimental

5.1. General

All reactions requiring anhydrous or inert conditions were carried out under an atmosphere of dried argon in flame-dried glassware. All solvents were dried by standard procedure and freshly distilled. Infrared spectra were recorded on a BIORAD FTS 135 FTIR. ^{1}H NMR spectra were recorded in $CDCl_3$ on Varian Gemini-200, 300 or on Bruker AM-500 spectrometers at 200, 300 or 500 MHz. ^{13}C NMR spectra were recorded at 50, 75 or 125 MHz. Chemical shifts (δ) are given in parts per million relative to Me_4Si (0, ^{1}H) or $CDCl_3$ (77.0, ^{13}C). Mass spectra were recorded on Varian MAT-44 or Finnigan MAT-TSQ 70 spectrometer. Melting points were obtained on a Büchi Melting Point B-545 and were uncorrected. Thin-layer chromatography (TLC) was run on precoated silica gel plates (Merck $60F_{254}$). Flash chromatography was carried out using flash silica gel 60 Merck (40–63 μm). Chiral GC analyses were performed on CE instrument HRGC-5300 equipped with a flame ionisation detector and Merck Hitachi integrators using CHIRASIL-DEX CB column.

5.2. Synthesis of 2-aryl-cycloalkenones 2

General procedure: 23.03 mL (15.96 g, 57.59 mmol) *n*-BuLi in 2.5 mol/L hexane was added at 0 °C to a solution of 8.07 mL (5.83 g, 57.59 mmol) diisopropylamine in 140 mL dry THF under argon. The mixture was stirred for 30 min and then cooled to −78 °C. Then, 5.87 g (52.35 mmol) 2,3-epoxycyclohexanone was added slowly. The mixture was stirred for another 30 min at this temperature.

To a solution of 14.56 mL (21.68 g, 104.7 mmol) 1-bromonaphthalene in 140 mL THF in a three-neck 500 mL flask, 123.18 mL (1.7 M, 81.30 g, 209.4 mmol) *t*-BuLi in pentane was added at −78 °C under argon. The reaction mixture was stirred for 1 h at −78 °C, then 10 min at 0 °C. The resulting mixture was then transformed to the above enolate solution through a cannula at −78 °C under the pressure of argon. After this transformation was completed, the mixture was stirred at −23 °C for 2 h and 50 mL saturated NH_4Cl was added at 0 °C. The mixture was extracted with 3×100 mL Et_2O. The organic layers were washed with 2×100 mL 3 N HCl, then 120 mL saturated $NaHCO_3$ solution. The collected organic phases were dried, filtered and evaporated in vacuum.

The above resulting crude product was placed into a 500 mL flask with a Dean–Stark to separate the water. Toluene (150 mL) and 10 mg *para*-toluenesulfonic acid (PTSA) were added. The mixture was heated under reflux for 2 h. After cooling, 80 mL saturated $NaHCO_3$ solution was added. The solution was extracted with 3×100 mL Et_2O and the organic layer was dried and filtered. The solvent was removed under reduced pressure. The residue was chromatographed with PE/AcOEt to give product **2b**.

5.2.1. 2-(1-Naphthyl)-cyclohexenone 2b. RN:108842-56-4; mp 107–108 °C; 54%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.22 (pent, 2H, 6.6 Hz), 2.61 (td, 2H, J=6.0, 4.5 Hz), 2.69 (t, 2H, J=6.4 Hz), 7.05 (t, 1H, J=4.5 Hz), 7.23 (dd, 1H, J=6.4, 1.6 Hz), 7.37–7.48 (m, 3H), 7.57–7.63 (m, 1H), 7.79–7.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 23.09, 26.43, 38.78, 125.20, 125.50, 125.60, 125.78, 126.99, 128.17, 128.28, 131.98, 133.46, 135.11, 140.49, 149.97, 198.03; IR (KBr): 780, 800, 1154, 1352, 1508, 1673, 2825, 2866, 2947, 3011, 3057 cm^{-1}; MS (EI, 70 eV) *m/z* (%): 152 (24), 165 (100), 178 (18), 194 (38), 222.1 (92).

5.2.2. 2-(9-Anthracyl)-cyclohexenone 2c. Mp 156 °C (decomposition); 15%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.38 (pent, 2H, J=6.8 Hz), 2.77 (td, 2H, J=6.8, 4.2 Hz), 2.82 (t, 2H, J=6.8 Hz), 7.08 (t, 1H, J=4.2 Hz), 7.42 (m, 4H), 7.79 (m, 2H), 8.00 (m, 2H), 8.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 23.36, 26.74, 38.92, 124.99 (2C), 125.54 (2C), 125.71 (2C), 127.13, 128.66 (2C), 130.24 (2C), 131.37 (2C), 131.46, 138.56, 152.02, 198.12; IR (KBr): 735, 859, 1155, 1364, 1597, 1675, 2861, 2949, 3052 cm^{-1}; MS (CI) m/z (%): 272.1 (24), 273.1 (100).

5.2.3. 2-(2-Phenoxy-phenyl)-cyclohexenone 2e. Mp 139–140 °C; 31%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.07 (pent, 2H, J=6.2 Hz), 2.41–2.54 (m, 4H), 6.81 (dd, 1H, J=8.1, 1.7 Hz), 6.89 (t, 1H, J=4.2 Hz), 6.99–7.36 (m, 7H), 7.86 (d, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.77, 26.15, 38.41, 117.83 (2C), 122.65 (2C), 128.43, 128.79 (2C), 130.98 (2C), 137.66, 148.44 (2C), 154.17 (2C), 197.18; IR (KBr): 754, 882, 1231, 1355, 1445, 1482, 1596, 1682, 2867, 2942, 3026, 3057 cm^{-1}; MS (CI) m/z (%): 153.9 (100), 171.1 (13), 237.0 (5), 265.9 (3).

5.2.4. 4,4-Dimethyl-2-(1-naphthyl)-cyclohexenone 2f. Mp 98–100 °C; 46%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.32 (s, 6H, 2Me), 2.09 (t, 2H, J=6.6 Hz), 2.73 (t, 2H, J=6.6 Hz), 6.74 (s, 1H), 7.23 (dd, 1H, J=7.0, 1.4 Hz), 7.41–7.49 (m, 3H), 7.57–7.62 (m, 1H), 7.80–7.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 27.98 (2C), 33.47, 35.02, 36.33, 125.11, 125.34, 125.53, 125.77, 127.06, 128.12, 128.29, 132.09, 133.54, 134.84, 137.36, 159.03, 197.55; IR (KBr): 788, 805, 1146, 1353, 1466, 1508, 1592, 1677, 2863, 2956, 3001, 3056 cm^{-1}; MS (CI) m/z (%): 94.9 (28), 140.9 (100), 251.0 (6).

5.3. Synthesis of *trans*-2-aryl-3-dialkylphenylsilyl cycloalkanones 3a–h

*General procedure (method **B**)*: 50 mL solution of $PhMe_2SiLi$ or $PhEt_2SiLi$ prepared from 6.4 mL (36.46 mmol) chlorodimethylphenylsilane or $PhEt_2SiCl$ and 0.63 g (91.15 mmol) lithium was added at −30 °C to a suspension of 1.63 g (18.23 mmol) CuCN (pre-dried) in 120 mL THF in a 500 mL three-neck flask under argon. The mixture was stirred for 1 h at 0 °C and cooled to −40 °C.

To the above mixture, was added slowly 10 mL solution of (1.57 g, 9.12 mmol) **2a** in THF through a syringe. The reaction mixture was stirred for 2.5 h at −23 °C and then for 2 h at 0 °C. The reaction mixture was warmed to room temperature in 1 h and 60 mL MeOH was added and the mixture was stirred for 15 min. Then, 70 mL H_2O was added. The mixture was filtered through 5–6 cm Celite and washed with CH_2Cl_2. The filtrate was extracted with 3×100 mL CH_2Cl_2. The combined organic layers were washed with brine, water, and dried over $MgSO_4$, and concentrated under the reduced pressure. The residue was chromatographed with PE/Et_2O to give 1.99 g *trans*-**3a** (71%).

5.3.1. *trans*-3-(Dimethylphenylsilyl)-2-phenyl-cyclohexanone 3a. Viscous oil; 71%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.132 (s, 3H, Me), −0.003 (s, 3H, Me), 1.70 (m, 1H), 1.77 (td, 1H, J=12.6, 3.2 Hz), 1.86 (m, 1H), 1.91 (m, 1H), 2.21 (m, 1H), 2.43 (td, J=13.1, 15.1, 5.6 Hz), 2.54 (dt, 1H, J=15.1, 3.2, 3.6 Hz), 3.42 (d, 1H, 12.6 Hz), 6.99–7.05 (m, 2H), 7.22–7.41 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 5.08, −3.10, 27.36, 29.92, 34.47, 42.12, 58.08, 127.01, 127.52 (2C), 127.96 (2C), 128.81, 129.67 (2C), 133.82 (2C), 137.42, 137.99, 210.84; IR (film): 814, 837, 1110, 1249, 1427, 1596, 1710, 2850, 2925, 3028, 3066 cm^{-1}; MS (EI, 70 eV) m/z (%): 137.0 (100), 211.0 (54), 308.1 (3); HRMS (CI) calculated for $C_{20}H_{24}OSi$: 308.1596, found: 308.1598. HPLC (Chiral AD column, hexane 98%/*i*-PrOH 2%, 0.5 mL/min): 5.86, 7.47 min. (2*R*,3*R*)-**3a**: $[\alpha]_D^{20}$ −87.8 (c 0.41, EtOH), (2*S*,3*S*)-**3a**: $[\alpha]_D^{20}$ +85 (c 0.4, EtOH).

5.3.2. *trans*-3-(Dimethylphenylsilyl)-2-(1-naphthyl)-cyclohexanone 3b. (Method **A**) viscous oil; 34% (work-up with saturated NH_4Cl solution at 0 °C). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: −026 (s, 3H, Me), −0.14 (s, 3H, Me), 1.77 (m, 1H), 1.94 (m, 1H, J=12.8, 3.6 Hz), 2.01 (m, 1H), 2.14 (td, 1H, J=12.5, 3.4 Hz), 2.24 (m, 1H), 2.5 (ddd, 1H, J=14, 12.8, 5.8 Hz), 2.62 (m, 1H), 4.14 (d, 1H, J=12.5 Hz), 7.18–7.45 (m, 9H), 7.68–7.75 (m, 2H), 7.79–7.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −4.63, −3.28, 27.82, 29.53, 33.64, 42.29, 55.3, 124.02, 125.03, 125.13, 125.55, 127.54 (2C), 127.95, 128.11, 128.83, 129.01, 131.97, 133.81 (2C), 134.09, 134.79, 137.39, 210.42; IR (film): 832, 1112, 1249, 1427, 1598 (C=C), 1709, 2856, 2931, 3046, 3067 cm^{-1}; MS (EI, 70 eV) m/z (%): 135.1 (10), 177.7 (10), 205.9 (56), 252 (40), 280 (56), 358.1 (100); HRMS (EI, 70 eV) calculated for $C_{24}H_{26}OSi$: 358.1752, found: 358.1763. HPLC (Chiral AD column, hexane 90%/*i*-PrOH 10%, 1 mL/min): 5.71, 6.81 min. (2*R*,3*R*)-**3b**: $[\alpha]_D^{20}$ −231 (c 0.2, toluene), (2*S*,3*S*)-**3b**: $[\alpha]_D^{20}$ +209 (c 0.2, toluene).

5.3.3. *trans*-2-(9-Anthracyl)-3-(dimethylphenylsilyl)-cyclohexanone 3c. Mp 110–112 °C; 20%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.65 (s, 3H, Me), −0.32 (s, 3H, Me), 1.90 (m, 1H), 2.12 (m, 1H), 2.18 (m, 1H, J=13.2, 3.4 Hz), 2.36 (m, 3H), 2.61 (ddd, 1H, J=12.7, 13.2, 3.0 Hz), 2.71 (ddd, 1H, J=13.2, 6.3, 15.3 Hz), 2.88 (m, 1H), 4.90 (d, J=12.7 Hz), 6.86 (dd, 2H, J=7.9, 1.3 Hz), 7.06 (t, 2H, J=7.4 Hz), 7.19 (m, 1H), 7.43 (m, 4H), 7.85 (m, 2H), 7.97 (m, 2H), 8.04 (m, 2H), 8.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −5.11, −4.44, 27.75, 28.01, 32.71, 41.97, 52.48, 123.53, 124.17 (2C), 124.39, 125.52, 126.92, 127.08 (2C), 127.67, 128.29, 129.29 (2C), 129.60, 130.46, 131.50, 131.61, 131.80, 133.02 (2C), 136.98, 209.66; IR (KBr): 730, 816, 835, 1112, 1158, 1249, 1426, 1446, 1558, 1612, 1704, 2852, 2923, 3048, 3067 cm^{-1}; MS (CI) m/z (%): 58.9 (74), 98.9 (100), 136.8 (14), 209.0 (61), 231.0 (31), 393.3 (4), 408.3 (15), 409.4 (9); HRMS (CI) calculated for $C_{28}H_{28}OSi$: 408.1909, found: 408.1904. HPLC (Chiral AD column, hexane 98%/*i*-PrOH 2%, 1 mL/min): 16.78, 28.58 min. (2*R*,3*R*)-**3c**: $[\alpha]_D^{20}$ −140 (c 0.5, $CHCl_3$), (2*S*,3*S*)-**3c**: $[\alpha]_D^{20}$ +142.6 (c 0.54, $CHCl_3$).

5.3.4. *trans*-2-(2-Methoxyphenyl)-3-(dimethylphenylsilyl)-cyclohexanone 3d. Viscous oil; 67%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.11 (s, 3H, Me), 0.08 (s, 3H, Me), 1.68 (qd, 1H, J=12.7, 3.5 Hz), 1.85 (m, 1H), 1.90 (m, 1H), 1.98 (td, 1H, J=12.9, 3.0 Hz), 2.18 (m, 1H), 2.44 (m, 1H, J=14.7, 12.7, 6.0 Hz), 2.57 (m, 1H), 3.76 (s, 3H, MeO), 3.82 (d, 1H, J=12.9 Hz), 6.82 (d, 1H, J=8.2 Hz), 6.90 (t, 1H, J=7.4 Hz), 7.00 (dd, 1H, J=7.4, 1.5 Hz), 7.22 (td, 1H,

J=8.2, 7.4, 1.3 Hz), 7.30–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −5.08, −0.11, 27.40, 29.05, 32.07, 41.93, 52.70, 54.91, 110.45, 120.07, 126.97, 127.31 (2C), 128.04, 128.50, 130.99, 133.65 (2C), 137.91, 156.93, 210.21; IR (film): 774, 827, 830, 1118, 1247, 1427, 1494, 1588, 1602, 1708, 2903, 2955, 3048, 3068 cm^{-1}; MS (CI) m/z (%): 58.9 (100), 135.1 (16), 261.0 (13), 323.1 (16), 338.1 (9), 339.2 (7); HRMS (CI) calculated for $C_{21}H_{26}O_2Si$: 338.1702, found: 338.1697. HPLC (Chiral AD column, hexane 99%/*i*-PrOH 1%, 1 mL/min): 10.83, 14.46 min. (2*R*,3*R*)-**3d**: $[\alpha]_D^{20}$ −84 (*c* 0.88, EtOH), (2*S*,3*S*)-**3d**: $[\alpha]_D^{20}$ +74 (*c* 0.59, EtOH).

5.3.5. *trans*-2-(2-Phenoxyphenyl)-3-(dimethylphenylsilyl)-cyclohexanone 3e. Viscous oil; 57%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.05 (s, 3H, Me), 0.21 (s, 3H, Me), 1.75 (m, 1H, J=13.3, 13.0 Hz), 1.85 (m, 1H), 1.91 (m, 1H), 2.10 (td, 1H, J=13.0, 2.9 Hz), 2.16 (m, 1H), 2.38 (td, 1H, J=13.1, 13.6, 5.5 Hz), 2.49 (ddd, J=13.6, 4.1, 3.1 Hz), 3.90 (d, 1H, J=13.0 Hz), 6.70 (d, 1H, J=7.8 Hz), 6.95 (m, 1H), 7.04 (m, 1H), 7.08 (m, 2H), 7.13 (m, 2H), 7.15 (m, 2H), 7.32 (m, 3H), 7.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −4.74, −2.80, 27.70, 29.22, 31.71, 41.92, 53.60, 117.3 (2C), 118.47, 121.60, 122.71, 127.55 (2C), 128.18, 128.30 (2C), 128.69, 129.38, 131.60, 133.70 (2C), 138.25, 155.32, 156.10, 209.22; IR (film): 770, 813, 833, 1112, 1246, 1427, 1453, 1488, 1599, 1710, 2854, 2925, 3046, 3075 cm^{-1}; MS (CI) m/z (%): 59.0 (100), 135.1 (8), 153.7 (28), 225 (19), 385.2 (5), 401.3 (5); HRMS (CI) calculated for $C_{26}H_{28}O_2Si$: 400.1859, found: 400.1918. HPLC (Chiral OD-H column, hexane 98%/*i*-PrOH 2%, 1 mL/min): 10.76, 13.66 min. (2*R*,3*R*)-**3e**: $[\alpha]_D^{20}$ −43 (*c* 2.0, EtOH), (2*S*,3*S*)-**3e**: $[\alpha]_D^{20}$ +45 (*c* 1.9, EtOH).

5.3.6. *trans*-3-(Dimethylphenylsilyl)-4,4-dimethyl-2-(1-naphthyl)-cyclohexanone 3f. Mp 93–95 °C, 50%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.11 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 1.12 (s, 3H, Me), 1.41 (s, 3H, Me), 1.86 (ddd, J=13.6, 3.8, 6.4 Hz), 2.19 (td, J=13.6, 11.7, 6.2 Hz), 2.45 (d, J=11.1 Hz), 2.62 (ddd, 1H, J=16.0, 3.8, 6.2 Hz), 2.69 (ddd, 1H, J=16.0, 6.4, 11.7 Hz), 4.50 (d, 1H, J=11.1 Hz), 7.12 (m, 2H), 7.16 (m, 2H), 7.18 (m, 1H), 7.29 (dd, 1H, J=8.0, 7.5 Hz), 7.36 (d, 1H, J=7.0 Hz), 7.46 (td, 1H, J=7.5, 1.0 Hz), 7.51 (td, 1H, J=6.9, 1.3 Hz), 7.69 (d, 1H, J=8.1 Hz), 7.81 (d, 1H, J=7.8 Hz), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −1.17, 0.00, 24.02, 32.02, 34.02, 36.60, 41.94, 43.24, 51.40, 123.99, 124.59, 124.92, 125.52, 127.13, (2C), 127.28, 127.83, 128.00, 128.75, 132.05, 133.10 (2C), 133.83, 134.83, 139.43, 211.27; IR (KBr): 775, 815, 831, 1110, 1250, 1426, 1511, 1597, 1708, 2864, 2952, 3044, 3066 cm^{-1}; MS (CI) m/z (%): 136.9 (69), 152.8 (26), 235.0 (100), 309.2 (40), 371.3 (16), 387.4 (10); HRMS (CI) calculated for $C_{26}H_{30}OSi$: 386.2066, found: 386.2070. HPLC (Chiral OD-H column, hexane 96%/*i*-PrOH 4%, 1 mL/min): 14.36, 17.82 min. (2*R*,3*S*)-**3f**: $[\alpha]_D^{20}$ −63 (*c* 0.87, $CHCl_3$), (2*S*,3*R*)-**3f**: $[\alpha]_D^{20}$ +61 (*c* 0.85, $CHCl_3$).

5.3.7. *trans*-3-(Dimethylphenylsilyl)-2-(1′-naphthyl)-cyclopentanone 3g. Viscous oil; 73%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.06 (s, 3H, Me), 0.09 (s, 3H, Me), 1.89 (m, 1H), 2.18 (m, 1H), 2.25 (m, 1H), 2.51 (m, 2H), 3.79 (d, 1H, J=12.7 Hz), 7.23 (d, 1H, J=7.0 Hz), 7.29 (dd, 2H, J=6.6, 5.5 Hz), 7.35 (d, 3H, J=7.0 Hz), 7.40 (t, 1H, J=6.6 Hz), 7.48 (m, 2H), 7.76 (d, 1H, J=8.0 Hz), 7.77 (m, 1H), 7.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −5.03, −4.39, 23.32, 31.65, 38.59, 54.84, 123.74, 125.04, 125.36, 125.76, 126.24, 127.58 (2C), 127.65, 128.89, 129.12, 131.89, 133.89 (2C), 134.05, 135.14, 136.14, 218.93; IR (film): 776, 838, 1250, 1427, 1596, 1737, 2852, 2924, 2956, 3046, 3050 cm^{-1}; MS (CI) m/z (%): 58.7 (100), 127.0 (16), 135.0 (14), 209.0 (75), 315.9 (3), 345.0 (3); HRMS (CI) calculated for $C_{23}H_{24}OSi$: 344.1596, found: 344.1596. HPLC (Chiral OD-H column, hexane 99%/*i*-PrOH 1%, 1 mL/min): 24.06, 31.77 min. (2*R*,3*R*)-**3g**: $[\alpha]_D^{20}$ −9.1 (*c* 0.55, EtOH), (2*S*,3*S*)-**3g**: $[\alpha]_D^{20}$ +13.6 (*c* 0.44, EtOH).

5.3.8. *trans*-3-(Diethylphenylsilyl)-2-phenyl-cyclohexanone 3h. Mp 44–46 °C; 70%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.095 (m, 1H), 0.28 (m, 1H), 0.64 (m, 2H), 0.60–0.87 (m, 6H), 1.71–2.04 (m, 4H), 2.18–2.52 (m, 3H), 3.31 (d, 1H, J=11.4 Hz), 6.93–6.98 (dd, 2H, J=7.6, 5.7 Hz), 7.25–7.36 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 1.38, 2.35, 7.10, 7.26, 27.46, 30.00, 32.05, 42.17, 58.74, 127.11, 127.59 (2C), 127.88 (2C), 128.97, 129.76 (2C), 134.71 (2C), 134.94, 138.18, 211.07; IR (KBr): 716, 763, 1006, 1108, 1160, 1236, 1427, 1455, 1601, 1711, 2873, 2954, 3027, 3066 cm^{-1}; MS (CI) m/z (%): 102.9 (8), 156.9 (100), 162.9 (19), 259.1 (30), 307.2 (31), 336.1 (55), 337.2 (15); HRMS (CI) calculated for $C_{22}H_{28}OSi$: 336.1909, found: 336.1910. HPLC (Chiral AD column, hexane 99%/*i*-PrOH 1%, 1 mL/min): 12.14, 14.97 min. (2*R*,3*R*)-**3h**: $[\alpha]_D^{20}$ −73 (*c* 1.0, EtOH), (2*S*,3*S*)-**3h**: $[\alpha]_D^{20}$ +69 (*c* 1.0, EtOH).

5.3.9. *cis*-3-(Dimethylphenylsilyl)-2-phenyl-cyclohexanone 4a. (*Method A*: work-up with saturated NH_4Cl solution at 0 °C), mp 79–80 °C (racemic, but each enantiomer is viscous oil); 70%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.036 (s, 3H), 0.059 (s, 3H), 1.75 (ddd, 1H, J=5.7, 13.6, 3.4 Hz), 1.81 (dq, 1H, J=13.0, 3.4, 3.7, 3.7 Hz), 1.85 (m, 1H), 2.16 (qd, 1H, J=13.0, 13.0, 13.6, 3.4 Hz), 2.31 (m, 1H), 2.37 (dt, 1H, J=15.0, 3.4, 3.7 Hz), 2.77 (td, 1H, J=15.0, 13.6, 6.1 Hz), 3.66 (d, 1H, J=5.7 Hz), 7.18–7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −4.15, −3.98, 22.28, 29.27, 32.50, 38.62, 58.17, 127.11, 127.58 (2C), 128.32 (2C), 128.89, 129.71 (2C), 133.66 (2C), 137.59, 138.26, 211.46; IR (KBr): 811, 833, 1112, 1248, 1427, 1598, 1706, 2862, 2951, 3024, 3067 cm^{-1}; MS (+CI) m/z (%): 74.9 (27), 134.9 (11), 148.9 (100), 211.0 (45), 293.0 (3), 308.1 (6, M^+), 309.5 (2, M^++1); Elemental analysis calculated for $C_{20}H_{24}OSi$: C 77.86%, H 7.84%; found: C 77.12%, H 7.69%. HPLC (chiral AD column, hexane 99.5%/*i*-PrOH 0.5%, 1 mL/min): 18.36, 26.57 min. $[\alpha]_D^{20}$ +16.3 (*c* 1.1, EtOH), $[\alpha]_D^{20}$ −15.9 (*c* 1.35, EtOH).

5.3.10. *cis*-3-(Dimethylphenylsilyl)-2-(1-naphthyl)-cyclohexanone 4b. (Method A), viscous oil, 23%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.034 (s, 3H), 0.17 (s, 3H), 1.89–2.17 (m, 3H), 2.23–2.44 (m, 3H), 2.78 (td, 1H, J=13.2, 13.2, 5.0 Hz), 4.57 (d, 1H, J=5.6 Hz), 7.17–7.51 (m, 8H), 7.72–7.84 (m, 3H), 8.16–8.21 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): −3.62, −3.18, 24.09, 30.53, 33.78, 38.06, 52.03, 124.21, 124.62, 125.59, 126.49, 126.99, 127.55 (2C),

127.99, 128.62, 128.90, 132.50, 133.68 (2C), 133.88, 134.53, 137.75, 212.07; IR (film): 791, 832, 1118, 1254, 1427, 1593, 1708, 2854, 2925, 2954, 3048, 3068 cm^{-1}; MS (+CI) *m/z* (%): 135.0 (17), 207.1 (100), 273 (40), 358.2 (30, M^+), 359.1 (10, M^++1); HRMS (CI) calculated for $C_{24}H_{26}OSi$: 358.1752, found: 358.1760. HPLC (chiral AS column, hexane 95%/*i*-PrOH 5%, 1 mL/min): 6.77, 14.16 min; $[\alpha]_D^{20}$ −7.8 (*c* 1.0, EtOH, Peak1), +8.2 (*c* 1.0, EtOH, Peak2).

5.4. Synthesis of *trans*-2-arylmethyl-3-dialkylphenylsilyl cycloalkanones 5a–c

General procedure: under argon, to a suspension of 17.56 g (92.21 mmol, 1.5 equiv) CuI in 120 mL dry THF and 40 mL hexamethylphosphoramide (HMPA) in a 500 mL three-neck flask, was added at −30 °C, 120 mL solution of dimethylphenylsilyllithium prepared from 31 mL (31.48 g, 184.41 mmol, 3 equiv) chlorodimethylphenylsilane and 3.84 g (553.23 mmol, 9 equiv) lithium. The mixture was stirred for 1 h at 0 °C and cooled down to −78 °C. Then 5.95 mL (5.91 g, 61.47 mmol, 1 equiv) 2-cyclohexene-1-one was slowly added through a syringe. The reaction mixture was warmed to −23 °C and continued to stir for 3 h and cooled down to −78 °C. Then, 21 mL (29.62 g, 127.73 mmol, 2.82 equiv) benzyl bromide was added dropwise. After being stirred for 5 h at −23 °C and 15 min at 0 °C, the reaction was stopped with 100 mL saturated NH_4Cl solution. The mixture was filtered through a pad of Celite and washed with CH_2Cl_2. The filtrate was extracted with 3×150 mL CH_2Cl_2, washed with brine and water. The collected extracts were dried, filtered and evaporated, the crude product was flash chromatographed to give 17.0 g **5a** (85% yield, R_f=0.31, EP/Et_2O=8/1) as a white solid.

5.4.1. *trans*-2-Benzyl-3-(dimethylphenylsilyl)-cyclohexanone 5a. Mp 55–58 °C; 85%. ^1H NMR ($CDCl_3$, 500 MHz, 42 °C) δ: 0.349 (s, 3H), 0.357 (s, 3H), 1.42 (td, 1H, *J*=8.6, 8.6, 3.8 Hz), 1.70 (m, 1H), 1.84 (m, 1H), 1.99 (m, 2H), 2.28 (m, 1H), 2.41 (m, 1H), 2.72 (m, 2H), 2.90 (dd, 1H, *J*=4.4, 14.8 Hz), 7.0 (dd, 2H, *J*=7.4, 1.4 Hz), 7.14 (m, 1H), 7.20 (m, 2H), 7.35 (m, 3H), 7.45 (dd, 2H, *J*=7.9, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, 42 °C) δ: −3.28, −2.93, 25.21, 28.70, 30.95, 36.42, 41.04, 53.56, 125.81, 128.03 (2C), 127.85 (2C), 128.91 (2C), 129.03, 133.66 (2C), 137.81, 140.02, 213.38; IR (KBr): 734, 773, 812, 832, 933, 1111, 1250, 1427, 1453, 1495, 1603, 1709, 2858, 2950, 3025, 3066 cm^{-1}; MS (CI) *m/z* (%): 135.0 (11), 171.0 (100), 245.1 (56), 307.1 (24), 322.1 (2), 323.2 (16); HRMS (CI) calculated for $C_{21}H_{26}OSi$: 322.1752, found: 322.1744. HPLC (Chiral OD-H column, hexane 99%/*i*-PrOH 1%, 1 mL/min): 12.69, 15.41 min. (2*R*,3*R*)-**5a**: $[\alpha]_D^{20}$ −79 (*c* 1.0, EtOH), (2*S*,3*S*)-**5a**: $[\alpha]_D^{20}$ +86 (*c* 1.0, EtOH).

5.4.2. *trans*-3-(Dimethylphenylsilyl)-2-(2-naphthylmethyl)-cyclohexanone 5b. Mp 92–93 °C; 41%. ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.36 (s, 3H), 0.37 (s, 3H), 1.44 (td, 1H, *J*=8.6, 8.6, 3.8 Hz), 1.73 (m, 1H), 1.86 (m, 1H), 2.02 (m, 2H), 2.29 (ddd, 1H, *J*=14.4, 9.7, 5.3 Hz), 2.41 (td, 1H, *J*=6.2, 6.2, 14.4 Hz), 2.80 (td, 1H, *J*=8.6, 8.4, 5.4 Hz), 2.84 (dd, 1H, *J*=5.4, 13.6 Hz), 3.03 (dd, 1H, *J*=8.4, 13.6 Hz), 7.12 (dd, 1H, *J*=8.4, 1.3 Hz), 7.32 (t, 2H, *J*=7.4 Hz), 7.36 (d, 1H, *J*=1.3 Hz), 7.39 (m, 1H), 7.41 (m, 1H), 7.43 (m, 1H), 7.45 (dd, 2H, *J*=7.9, 1.5 Hz), 7.66 (d, 1H, *J*=8.4 Hz), 7.69 (d, 1H, *J*=7.6 Hz), 7.76 (d, 1H, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −3.18, −2.74, 25.42, 29.00, 31.11, 36.23, 41.23, 53.68, 125.05, 125.60, 127.20, 127.39 (2C), 127.52, 127.55, 127.86 (2C), 129.07, 131.85, 133.24, 133.69 (2C), 137.59, 137.68, 213.64; IR (KBr): 735, 782, 817, 1039, 1114, 1251, 1427, 1505, 1601, 1634, 1693, 2854, 2910, 2949, 3023, 3063 cm^{-1}; MS (+CI) *m/z* (%): 135.0 (27), 141.0 (100), 295.0 (24), 373.4 (22, M^++1); HRMS (CI) calculated for $C_{25}H_{28}OSi$: 372.1909, found: 372.1894. HPLC (OD-H column, hexane 99%/*i*-PrOH 1%, 1 mL/min): 11.24, 13.37 min. (2*R*,3*R*)-**5b**: $[\alpha]_D^{20}$ −89 (*c* 1.0, EtOH), (2*S*,3*S*)-**5b**: $[\alpha]_D^{20}$ +67 (*c* 0.53, EtOH).

5.4.3. *trans*-3-(Dimethylphenylsilyl)-2-(1-naphthylmethyl)-cyclohexanone 5c. Viscous oil; 39%. ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.22 (s, 3H), 0.26 (s, 3H), 1.53 (q, 1H, *J*=6.2 Hz), 1.79 (m, 1H), 1.97 (m, 2H), 2.14 (m, 1H), 2.35 (dt, 1H, *J*=14.1, 6.0, 6.0 Hz), 2.54 (m, 1H), 3.00 (q, 1H, *J*=7.8, 7.4 Hz), 3.18 (dd, 1H, *J*=7.4, 14.0 Hz), 3.40 (dd, 1H, *J*=7.8, 14.0 Hz), 7.17 (d, 1H, *J*=7.0 Hz), 7.21 (m, 2H), 7.29 (m, 3H), 7.34 (dd, 1H, *J*=7.0, 8.2 Hz), 7.40 (m, 1H), 7.44 (m, 1H), 7.70 (d, 1H, *J*=8.2 Hz), 7.79 (d, 1H, *J*=8.3 Hz), 7.82 (dd, 1H, *J*=8.6, 1.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −3.58, −3.15, 23.72, 27.48, 29.78, 34.66, 40.12, 51.56, 123.57, 124.95, 125.27, 125.76, 126.57, 126.94, 127.68 (2C), 128.57, 128.87, 131.80, 133.46 (2C), 133.86, 135.08, 137.53, 213.53; IR (film): 732, 777, 810, 832, 1110, 1250, 1426, 1596, 1653, 1706, 2856, 2949, 3030, 3064 cm^{-1}; MS (+CI) *m/z* (%): 95 (22), 134.9 (44), 140.9 (60), 221.0 (100), 357.1 (12), 372.6 (42), 373.1 (44, M^++1); HRMS (CI) calculated for $C_{25}H_{28}OSi$: 372.1909, found: 372.1892. HPLC (OD-H column, Hexane 99%/*i*-PrOH 1%, 1 mL/min): 16.15, 18.02 min. (2*R*,3*R*)-**5c**: $[\alpha]_D^{20}$ −95.7 (*c* 0.6, EtOH), (2*S*,3*S*)-**5c**: $[\alpha]_D^{20}$ +97 (*c* 0.62, EtOH).

5.5. Synthesis of ENP *trans*-1-dialkylphenylsilyl-2-aryl-cycloalkanes 7a–h and *trans*-1-dialkylphenylsilyl-2-arylmethyl-cyclohexanones 8a–c

General procedure: to a 50 mL one-neck flask with a stirring bar and a condenser, were added 0.787 g (2.194 mmol, 1 equiv) (+) (2*S*,3*S*)-**3b**, 0.505 g (97%, 2.632 mmol, 1.2 equiv) *para*-toluenesulfonhydrazide in 15 mL EtOH. The solution was heated at 60 °C for 2 h (controlled by TLC) and cooled to room temperature. The solvent was removed under the reduced pressure to afford the corresponding tosylhydrazone, which was used for the next step without isolation.

To the solution of the obtained tosylhydrazone in 20 mL EtOH/MeOH (1:1), 0.726 g (10.97 mmol, 5 equiv) $NaBH_3(CN)$, 0.747 g (5.485 mmol, 2.5 equiv) $ZnCl_2$ were added. The mixture was heated at 60 °C for 3 h and cooled to room temperature. The mixture was filtered through 5–6 cm Celite and washed with CH_2Cl_2. After concentration, the residue was diluted with 5 mL CH_2Cl_2 and 5 mL saturated $NaHCO_3$ solution. The mixture was filtered through 5–6 cm Celite and washed with CH_2Cl_2. The filtrate was

extracted with 3×10 mL CH_2Cl_2 and the collected organic layers were dried over $MgSO_4$, filtered and evaporated. Flash chromatograph of the residue afforded 0.34 g (+) (1*S*,2*R*)-**9b** (45%, viscous oil, R_f=0.57/hexane).

5.5.1. *trans*-1-(Dimethylphenylsilyl)-2-phenyl-cyclohexane 7a. (1*R*,2*S*)-**7a**: 44%, viscous oil, $[\alpha]_D^{20}$ +33.3 (*c* 0.21, EtOH); (1*S*,2*R*)-**7a**: 31%, viscous oil, $[\alpha]_D^{20}$ −38.6 (*c* 0.44, EtOH).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.18 (s, 3H), 0.004 (s, 3H), 1.28 (m, 3H), 1.38 (m, 1H), 1.48 (m, 1H), 1.83 (m, 4H), 2.46 (td, 1H, *J*=8.2, 8.2, 11.0 Hz), 7.10–7.28 (m, 5H), 7.30–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −4.88, −2.96, 26.96, 27.43, 28.31, 31.11, 37.94, 46.69, 125.98, 127.27 (2C), 127.77 (2C), 128.06 (2C), 128.28, 133.84 (2C), 139.02, 147.47; IR (film): 775, 813, 834, 1111, 1248, 1427, 1445, 1491, 1600, 2849, 2922, 3025, 3066 cm^{-1}; MS (+CI) *m*/*z* (%): 134.8 (27), 136.1 (5), 216.9 (100), 279.0 (24), 294.2 (2), 295.6 (1); HRMS (CI) calculated for $C_{20}H_{26}Si$: 294.1803, found: 294.1794.

5.5.2. *trans*-1-(Dimethylphenylsilyl)-2-(1-naphthyl)-cyclohexanone 7b. (1*S*,2*R*)-**7b**: 45%, viscous oil, $[\alpha]_D^{20}$ +35.7 (*c* 0.7, EtOH); (1*R*,2*S*)-**7b**: 39%, viscous oil, $[\alpha]_D^{20}$ −32.8 (*c* 0.7, EtOH).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: −0.33 (s, 3H), 0.13 (s, 3H), 1.15–1.52 (m, 5H), 1.70–1.95 (m, 4H), 3.20–3.40 (br m, 1H), 7.02–7.16 (m, 3H), 7.17–7.20 (m, 2H), 7.22–7.32 (m, 2H), 7.40–7.50 (m, 2H), 7.64 (d, 1H, *J*=7.4 Hz), 7.80–7.88 (dd, 1H, *J*=5.8, 3.8 Hz), 8.00–8.01 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: −4.23, −2.89, 27.45, 27.75, 29.00, 30.82, 38.55, 39.39, 122.91, 124.84, 125.07, 125.37, 125.44, 126.24, 127.29 (2C), 128.29, 128.89, 130.93, 133.78 (2C), 134.00, 139.05, 143.60; IR (film): 776, 817, 834, 1112, 1248, 1427, 1444, 1511, 1596, 2848, 2924, 3046, 3067 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 83.8 (100), 135.1 (21), 208.1 (23), 267.2 (86), 271.1 (51), 329.1 (2), 344.2 (12).

5.5.3. *trans*-1-(Dimethylphenylsilyl)-2-(2-methoxyphenyl)-cyclohexane 7d. (1*R*,2*S*)-**7d**: 57%, viscous oil, $[\alpha]_D^{20}$ +20 (*c* 0.50, EtOH); (1*S*,2*R*)-**7d**: 51%, viscous oil, $[\alpha]_D^{20}$ −13.3 (*c* 1.2, EtOH).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: −0.195 (s, 3H), 0.032 (s, 3H), 1.25 (m, 2H), 1.38 (m, 2H), 1.49 (m, 1H), 1.76 (m, 4H), 3.01 (td, 1H, *J*=11.0, 11.0, 3.1 Hz), 3.77 (s, 3H), 6.76 (d, 1H, *J*=8.2 Hz), 6.82 (td, 1H, *J*=7.4, 7.4, 1.1 Hz), 7.09 (td, 1H, *J*=7.4, 7.4, 1.7 Hz), 7.12 (dd, 1H, *J*=7.4, 1.7 Hz), 7.25 (m, 3H), 7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −4.78, −3.25, 27.20, 27.66, 28.66, 30.00, 36.43, 38.68, 54.97, 110.49, 120.40, 126.60, 127.16 (2C), 128.06, 128.78, 133.74, 133.75 (2C), 139.67, 156.57; IR (film): 769, 815, 834, 1111, 1243, 1427, 1439, 1463, 1491, 1585, 1599, 2847, 2925, 3033, 3067 cm^{-1}; MS (+CI) *m*/*z* (%): 120.68 (64), 134.8 (22), 136.8 (14), 188.9 (79), 247.0 (100), 309.1 (41), 324.1 (13), 325.1 (7); HRMS (CI) calculated for $C_{21}H_{28}OSi$: 324.1909, found: 324.1905.

5.5.4. *trans*-1-(Dimethylphenylsilyl)-2-(2-phenoxyphenyl)-cyclohexane 7e. (1*S*,2*R*)-**7e**: 20%, viscous oil, $[\alpha]_D^{20}$ +25 (*c* 1.0, EtOH); (1*R*,2*S*)-**7e**: 25%, viscous oil, $[\alpha]_D^{20}$ −21 (*c* 1.0, EtOH).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: −0.13 (s, 3H), 0.18 (s, 3H), 0.99–1.70 (m, 6H), 1.72–2.0 (m, 3H), 3.0–3.2 (br m, 1H), 6.76 (d, 1H, *J*=7.9 Hz), 6.92–7.12 (m, 3H), 7.22–7.44 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: −4.77, −2.52, 27.10, 27.46, 28.62, 29.05, 33.68, 40.05, 118.5 (2C), 122.82, 126.81 (2C), 127.47 (2C), 127.69, 127.59, 128.38 (2C), 133.6, 133.83 (2C), 133.98, 140.1, 154.30, 156.09; IR (film): 769, 812, 834, 1064, 1112, 1227, 1246, 1426, 1443, 1482, 1596, 2847, 2922, 3020, 3066 cm^{-1}; MS (+CI) *m*/*z* (%): 135.1 (11), 169.2 (13), 271.1 (100), 309.5 (4), 371.3 (9), 387.7 (3, M^++1); HRMS (CI) calculated for $C_{26}H_{30}OSi$: 386.2066, found: 386.2096.

5.5.5. *trans*-1-(Dimethylphenylsilyl)-6,6-dimethyl-2-(1-naphthyl)-cyclohexane 7f. (1*R*,2*R*)-**7f**: 31%, viscous oil, $[\alpha]_D^{20}$ +69.9 (*c* 0.83, EtOH); (1*S*,2*S*)-**7f**, 27%, viscous oil, $[\alpha]_D^{20}$ −68.1 (*c* 0.83, EtOH).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.44 (s, 3H), 0.54 (s, 3H), 1.05 (s, 3H), 1.33 (s, 3H), 1.20–1.45 (m, 2H), 1.63–1.98 (m, 4H), 2.14–2.29 (m, 1H), 3.30–3.48 (m, 1H), 7.27–7.68 (m, 10H), 7.79–7.84 (dd, 1H, *J*=6.6, 1.6 Hz), 7.95 (d, 1H, *J*=6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 0.3, 0.86, 29.22, 30.32, 30.86, 32.44, 33.58, 35.81, 36.20, 38.26, 122.40, 123.19, 125.18, 125.57 (2C), 126.26, 127.74 (2C), 128.53, 128.95, 131.45, 133.79 (2C), 133.80, 141.10, 143.51; IR (film): 776, 813, 831, 1112, 1249, 1427, 1509, 1597, 2864, 2948, 3047, 3067 cm^{-1}; MS (+CI) *m*/*z* (%): 76.8 (17), 135.0 (16), 136.8 (19), 194.8 (100), 271.1 (47), 357.1 (4), 372.7 (2, M^+), 373.2 (3, M^++1); HRMS (CI) calculated for $C_{26}H_{32}Si$: 372.2273, found: 372.2265.

5.5.6. *trans*-1-(Dimethylphenylsilyl)-2-(1-naphthyl)-cyclopentane 7g. (1*S*,2*R*)-**7g**: 32%, viscous oil, $[\alpha]_D^{20}$ +15 (*c* 0.2, EtOH); (1*R*,2*S*)-**7g**: 32%, viscous oil, $[\alpha]_D^{20}$ −26 (*c* 0.39, EtOH).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.03 (s, 3H), 0.07 (s, 3H), 1.60 (m, 1H), 1.69 (m, 2H), 1.80 (m, 2H), 2.07 (m, 1H), 2.20 (m, 1H), 3.67 (td, 1H, *J*=8.6, 8.6, 10.2 Hz), 7.25 (m, 2H), 7.30 (m, 1H), 7.36 (m, 2H), 7.37 (m, 1H), 7.43 (m, 1H), 7.46 (m, 2H), 7.66 (dd, 1H, *J*=7.4, 1.6 Hz), 7.84 (m, 1H), 8.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −4.54, −3.56, 26.07, 28.95, 32.54, 37.86, 42.94, 123.37, 123.38, 125.01, 125.30 (2C), 126.03, 127.36 (2C), 128.56, 128.70, 131.85, 133.82 (3C), 138.38, 142.36; IR (film): 793, 830, 1060, 1118, 1245, 1427, 1591, 2865, 2955, 3049, 3068 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 56.8 (75), 135.0 (14), 151.0 (37), 193.0 (58), 271.0 (100), 330.1 (5, M^+); HRMS (EI) calculated for $C_{23}H_{26}Si$: 330.1804, found: 330.1797.

5.5.7. *trans*-1-(Diethylphenylsilyl)-2-phenyl-cyclohexane 7h. (1*R*,2*S*)-**7h**: 35%, viscous oil, $[\alpha]_D^{20}$ +56 (*c* 0.8, EtOH); (1*S*,2*R*)-**7h**: 31%, viscous oil, $[\alpha]_D^{20}$ −59 (*c* 0.8, EtOH).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.12 (m, 1H), 0.27 (m, 1H), 0.53 (q, 2H, *J*=7.6 Hz), 0.77 (t, 6H, *J*=7.7 Hz), 1.10–1.48 (m, 5H), 1.65–1.90 (m, 4H), 2.21–2.40 (m, 1H), 7.03–7.07 (dd, 2H, *J*=7.9, 2.1 Hz), 7.14–7.31 (m, 8H); ^{13}C NMR

($CDCl_3$, 50 MHz) δ: 1.76, 2.34, 7.28, 7.52, 26.97, 27.62, 28.48, 28.92, 38.28, 46.54, 126.06, 127.33 (2C), 127.87 (2C), 128.01 (2C), 128.41, 134.69 (2C), 136.68, 147.62; IR (film): 734, 757, 1007, 1057, 1107, 1235, 1427, 1444, 1490, 1600, 2873, 2919, 3025, 3067 cm^{-1}; MS (+CI) *m/z* (%): 163.0 (24), 164.3 (4), 245.1 (97), 293.2 (100), 323.3 (1, M^++1); HRMS (CI) calculated for $C_{22}H_{30}Si$: 322.2116, found: 322.2120.

5.5.8. *trans*-2-Benzyl-1-(dimethylphenylsilyl)-cyclohexane 8a. (1*S*,2*R*)-**8a**: 54%, viscous oil, $[\alpha]_D^{20}$ +11 (*c* 0.48, EtOH); (1*R*,2*S*)-**8a**: 85%, viscous oil, $[\alpha]_D{}^{20}$ −14.3 (*c* 0.42, EtOH).

^1H NMR ($CDCl_3$, 500 MHz) δ: 0.38 (s, 3H), 0.42 (s, 3H), 0.86 (td, 1H, *J*=11.5, 10.5, 3.1 Hz), 0.88 (m, 1H), 1.10 (qt, 1H, *J*=11.5, 3.3 Hz), 1.22 (qt, 1H, *J*=11.5, 3.1 Hz), 1.28 (qd, 1H, *J*=11.5, 3.1 Hz), 1.52 (dq, 1H, *J*=12.5, 3.6, 3.3 Hz), 1.55 (qt, 1H, *J*=10.5, 3.6 Hz), 1.62 (m, 1H), 1.69 (m, 1H), 1.81 (dq, 1H, *J*=11.5, 3.1 Hz), 2.00 (dd, 1H, *J*=13.4, 10.5 Hz), 2.94 (dd, 1H, *J*=13.4, 3.6 Hz), 6.94 (m, 2H), 7.14 (m, 1H), 7.21 (m, 2H), 7.37 (m, 3H), 7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −3.06, −2.24, 25.88, 27.69, 28.26, 30.80, 32.63, 40.85, 43.26, 125.37, 127.63 (2C), 127.86 (2C), 128.53, 128.90 (2C), 133.67 (2C), 139.81, 141.48; IR (film): 699, 733, 768, 831, 1051, 1063, 1114, 1251, 1427, 1588, 1603, 2850, 2927, 3024, 3067 cm^{-1}; MS (+CI) *m/z* (%): 135.0 (18), 217.0 (10), 231.0 (100), 293.1 (39), 307.1 (5), 309.2 (2, M^++1); HRMS (CI) calculated for $C_{21}H_{28}Si$: 308.1960, found: 308.1955.

5.5.9. *trans*-1-(Dimethylphenylsilyl)-2-(2-naphthylmethyl)-cyclohexane 8b. (1*S*,2*R*)-**8b**: 34%, viscous oil, $[\alpha]_D^{20}$ +33 (*c* 0.41, EtOH); (1*R*,2*S*)-**8b**: 38%, viscous oil, $[\alpha]_D^{20}$ −35 (*c* 0.4, EtOH).

^1H NMR ($CDCl_3$, 500 MHz) δ: ^{13}C NMR ($CDCl_3$, 125 MHz): −2.95, −2.14, 25.84, 27.69, 28.32, 30.85, 32.73, 40.82, 43.35, 124.83, 125.62, 127.05, 127.23, 127.33, 127.42, 127.62, 127.7 (2C), 128.61, 131.74, 133.31, 133.75 (2C), 139.01, 139.77; IR (film): 831, 1112, 1248, 1426, 1444, 1600, 2849, 2925, 3049 cm^{-1}; MS (+CI) *m/z* (%): 127.1 (23), 135.0 (13), 141.1 (24), 281.1 (100), 343.2 (16), 358.0 (4, M^+), 359.1 (2, M^++1); HRMS (CI) calculated for $C_{25}H_{30}Si$: 358.2117, found: 358.2112.

5.5.10. *trans*-1-(Dimethylphenylsilyl)-2-(1-naphthylmethyl)-cyclohexane 8c. (1*S*,2*R*)-**8c**: 31%, viscous oil, $[\alpha]_D^{20}$ +45 (*c* 0.75, EtOH); (1*R*,2*S*)-**8c**: 33%, viscous oil, $[\alpha]_D^{20}$ −44 (*c* 0.7, EtOH).

^1H NMR ($CDCl_3$, 500 MHz) δ: 0.44 (s, 3H), 0.48 (s, 3H), 0.93 (m, 2H), 1.07 (qt, 1H, *J*=12.3, 3.6 Hz), 1.26 (m, 2H), 1.42 (m, 1H), 1.59 (m, 1H), 1.69 (m, 1H), 1.84 (m, 1H), 1.93 (m, 1H), 2.51 (dd, 1H, *J*=11.3, 14.4 Hz), 3.37 (dd, 1H, *J*=14.4, 4.1 Hz), 7.13 (d, 1H, *J*=7.0 Hz), 7.29 (m, 1H), 7.34 (t, 1H, *J*=7.3 Hz), 7.42 (m, 4H), 7.47 (d, 1H, *J*=8.5 Hz), 7.65 (dd, 2H, *J*=7.3, 1.6 Hz), 7.67 (d, 1H, *J*=8.0 Hz), 7.80 (d, 1H, *J*=8.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): −2.35, −1.83, 25.75, 27.71, 28.26, 32.30, 32.89, 39.57, 40.37, 124.17, 125.01, 125.02, 125.27, 126.19, 127.07, 127.82 (2C), 128.37, 128.71, 132.08, 133.60, 133.85 (2C), 137.37, 139.57; IR (film): 767, 784, 809, 832, 1112, 1247, 1426, 1444, 1508, 1595, 2849, 2927, 3045, 3066 cm^{-1}; MS (+CI) *m/z* (%): 99.0 (100), 135.0 (10), 141.1 (11), 217.0 (5), 281.1 (12), 343.2 (4), 358.4 (1, M^+); HRMS (CI) calculated for $C_{25}H_{30}Si$: 358.2117, found: 358.2120.

5.6. Synthesis of ENP silyl dithioketals 10a,b

General procedure: to a 25 mL two-neck flask equipped with a tube of blue silica gel and stirring bar, were added 0.3 g (0.972 mmol, 1 equiv) (−)-**4a**, 0.101 mL (114 mg, 1.22 mmol, 1.25 equiv) 1,2-ethanedithiol and 8 mL dry CH_2Cl_2. The solution was cooled to −40 °C and 0.032 mL (55 mg, 0.29 mmol, 0.3 equiv) $TiCl_4$ was added under argon. The reaction mixture was warmed to room temperature and stirred for additional 5 h before the reaction was quenched with 3 mL saturated $NaHCO_3$ solution. The mixture was extracted three times with CH_2Cl_2. The organic phases were dried, filtered and evaporated in vacuum. Purification of the residue by flash chromatography (EP/Et_2O=30/1, R_f=0.33) gave 0.62 g (90%, yield) product (−)-**10a** as viscous oil.

5.6.1. Compound 10a. $[\alpha]_D^{20}$ +22.3 (*c* 1.0, EtOH), viscous oil, 88%; $[\alpha]_D^{20}$ –18 (*c* 1.0, EtOH), viscous oil, 90%.

^1H NMR ($CDCl_3$, 500 MHz) δ: −0.11 (s, 3H), −0.06 (s, 3H), 1.66 (m, 1H), 1.88 (m, 3H), 2.03 (m, 1H), 2.15 (m, 1H), 2.65 (m, 1H), 3.36 (d, 1H, *J*=3.1 Hz), 3.21–3.33 (m, 4H), 7.13–7.43 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: −5.05, −4.49, 20.40, 26.29, 30.25, 38.05, 38.48, 39.14, 55.55, 74.44, 126.92, 127.37 (2C), 127.54 (2C), 128.52, 130.69 (2C), 133.70 (2C), 138.10, 142.46; IR (film): 770, 812, 836, 1111, 1248, 1245, 1426, 1494, 1599, 2854, 2923, 3024, 3066 cm^{-1}; MS (+CI) *m/z* (%): 124.8 (100), 135.1 (10), 248.9 (48), 369.0 (13), 385.2 (16, M^++1); HRMS (CI) calculated for $C_{22}H_{28}S_2Si$: 384.1401, found: 384.1396.

5.6.2. Compound 10b. $[\alpha]_D^{20}$ +28 (*c* 0.8, EtOH), viscous oil, 47%; $[\alpha]_D^{20}$ −25 (c 0.8, EtOH), viscous oil, 50%.

^1H NMR ($CDCl_3$, 200 MHz) δ: −0.26 (s, 3H), −0.25 (s, 3H), 1.26–1.34 (m, 1H), 1.60–1.72 (m, 2H), 2.02–2.17 (m, 2H), 2.68–2.99 (m, 2H), 3.09–3.16 (m, 2H), 3.34–3.42 (m, 2H), 4.42 (d, 1H, *J*=3.2 Hz), 7.05 (dd, 1H, *J*=7.9, 1.5 Hz), 7.11–7.45 (m, 7H), 7.72–7.90 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: −4.26, −4.12, 20.88, 26.51, 30.43, 38.00, 38.63, 39.47, 45.87, 74.85, 124.48, 124.87, 124.94, 125.40, 126.69, 127.47 (2C), 127.80, 128.51, 128.71, 133.49, 133.65 (2C), 133.82, 138.18, 139.49; IR (film) in cm^{-1}: 779, 797, 834, 1117, 1255, 1427, 1488, 1597, 2859, 2928, 3049, 3067; MS (+CI) *m/z* (%): 58.9 (100), 74.9 (60), 135.0 (17), 136.8 (19), 207.1 (64), 299.2 (37), 419.2 (10), 434.2 (10, M^+), 435.3 (10, M^++1).

5.7. Synthesis of *cis*-2-arylmethyl-1-dialkylphenylsilyl cycloalkanones 9a,b

General procedure: to a solution of 0.45 g (1.17 mmol, 1.0 equiv) (−)-**10a** in 5 mL MeOH, an excess of Raney nickel was added (10-fold). The reaction mixture was stirred

at room temperature for 10 h (TLC check). The mixture was filtered through a pad of Celite and washed with CH_2Cl_2. The filtrate was extracted with 3×5 mL CH_2Cl_2. The organic layer was dried, filtered and concentrated. Flash chromatography of the residue (R_f=0.45, hexane) afforded 0.21 g (60%) product (−)-**9a** as viscous oil.

5.7.1. *cis*-1-(Dimethylphenylsilyl)-2-phenyl-cyclohexane 11a. (+)-**9a**: $[\alpha]_D^{20}$ +24 (*c* 1.0, EtOH), viscous oil, 58%; (−)-**9a**: $[\alpha]_D^{20}$ −25.6 (c 1.0, EtOH), viscous oil, 60%.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: −0.20 (s, 3H), 0.09 (s, 3H), 1.42–1.70 (m, 5H), 1.71–1.81 (m, 4H), 2.99–3.04 (m, 1H), 7.14–7.26 (m, 5H), 7.27–7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: −2.40, −1.87, 24.54, 25.85, 27.31, 30.94, 32.17, 43.83, 125.86, 127.39 (2C), 127.83 (2C), 128.18 (2C), 128.37, 133.80 (2C), 139.99, 146.41; IR (film) in: 814, 834, 1112, 1249, 1427, 1446, 1600, 2848, 2923, 3025, 3066 cm^{-1}, MS (+CI) *m*/*z* (%): 135.1 (4), 217.2 (30), 279.2 (100), 293.2 (28), 294.0 (24, 295.1 (8, M^++1); HRMS (CI) calculated for $C_{20}H_{26}Si$: 294.1803, found: 294.1796.

5.7.2. *cis*-1-(Dimethylphenylsilyl)-2-(1-naphthyl)-cyclohexane 9b. (+)-**9b**: $[\alpha]_D^{20}$ +30 (*c* 0.6, EtOH), viscous oil, 19%; (−)-**9b**: $[\alpha]_D^{20}$ −31 (*c* 0.5, EtOH), viscous oil, 20%.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: −0.41 (s, 3H), 0.12 (s, 3H), 1.40–1.70 (m, 4H), 1.71–2.10 (m, 5H), 3.70–3.80 (m, 1H), 7.11–7.26 (m, 4H), 7.34–7.53 (m, 5H), 7.63–7.68 (dd, 1H, *J*=6.0, 1.9 Hz), 7.78–7.80 (m, 1H), 8.04 (d, 1H, *J*=7.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: −4.10, −0.87, 25.48, 26.85, 28.00, 30.98, 32.27, 42.81, 122.92, 124.86, 125.00, 125.46, 125.84, 126.48, 127.48 (2C), 128.88, 128.98, 131.05, 133.86 (2C), 133.99, 139.04, 143.78; IR (film): 776, 817, 834, 1112, 1248, 1444, 1596, 2848, 2924, 3046, 3067 cm^{-1}; MS (+CI) *m*/*z* (%): 135.1 (3), 267.2 (86), 295.2 (14), 329.2 (72), 344.2 (100, M^+), 345.3 (28, M^++1); HRMS (CI) calculated for $C_{24}H_{28}Si$: 344.1960, found: 344.1954.

5.8. General procedure for in situ preparation of silylated triflimides and catalysed Diels–Alder reactions

To a 25 ml two-neck flask equipped with a tube of silica gel and a stirring bar, under argon were added 15 mol % ENP dialkylphenylsilyl-cycloalkane (1 equiv) and enough dry CH_2Cl_2 [solvent/diene=3:1 (v/v)]. A solution of bis-(trifluoromethanesulfonyl)imide (10 mol %) in CH_2Cl_2 was added at room temperature and the reaction continued for 2–3 h. 2,6-Di(*tert*-butyl)-4-methylpyridine (20 mol %, DTBMP, dissolved in CH_2Cl_2) was added and the mixture cooled to the temperature mentioned in the table. Methyl acrylate (1 equiv) was added and followed by cyclopentadiene (4 equiv) 15 min later. The reaction mixture was stirred for 1.5 h (checked by ^{1}H NMR) and quenched with 3 mL saturated $NaHCO_3$ aqueous solution. The mixture was extracted with 3×10 mL CH_2Cl_2, and the combined organic phases were dried, filtered and evaporated. The products were isolated by flash chromatography (yields, see Table 5). Enantiomeric excesses were determined by chiral GC. Conversions and ratio of *endo*/*exo* were measured by ^{1}H NMR on the crude product (*endo*/*exo* also by chiral GC).

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