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Trimethylsilyl bis(trifluoromethanesulfonyl)imide as a tolerant and environmentally benign Lewis acid catalyst of the Diels–Alder reaction

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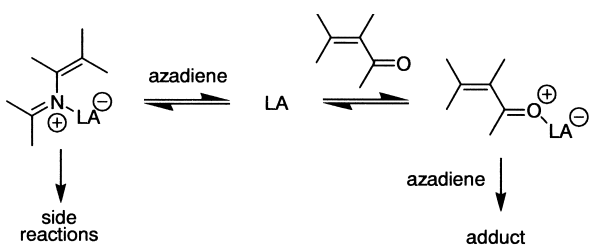
Abstract—*N*-trimethylsilyl bis(trifluoromethanesulfonyl)imide ($TMSNTf_2$) was readily prepared in situ by protodesilylation of trimethylsilane, allyl- or phenyltrimethylsilane with bis(trifluoromethylsulfonyl)imide. NMR studies showed that $TMSNTf_2$ was much more effective than TMSOTf in complexing the carbonyl group of *trans*-methylcrotonate. As a result, $TMSNTf_2$ was found to be superior to TMSOTf as a catalyst for the Diels–Alder reaction of α,β-unsaturated esters with a wide variety of dienes. In contrast to many metal derived Lewis acids, $TMSNTf_2$ was found tolerant of many sensitive functional groups present in the diene partner. © 2002 Elsevier Science Ltd. All rights reserved.

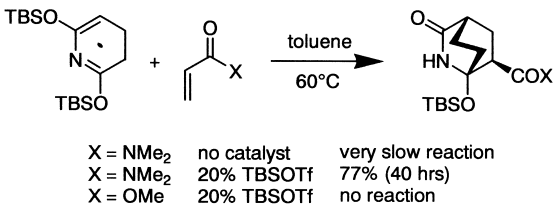
1. Introduction

Lewis acids are among the most useful catalysts of organic reactions.[1] They are often used to activate a carbonyl group of a reactant and consequently increase its electrophilicity. However, problems can be encountered when the reactants contain several functional groups which can act as Lewis bases. This can lead to the deactivation of the catalyst and, often, to undesired side reactions. We ran into this problem while studying Diels–Alder reactions of 1 and 2-azadienes which were found to decompose when exposed to several commonly used Lewis acids (Scheme 1).[2]

These studies also showed that trialkylsilyltriflates acted as efficient Lewis acid catalysts for the reaction of α,β-unsaturated amides with 2-azadienes (Scheme 2).[3]



Scheme 1.



Scheme 2.

No degradation of the sensitive 2-azadiene was observed under these conditions. However, trialkylsilyltriflates did not catalyze the reaction of methyl acrylate, a weaker Lewis base. A more powerful silylating agent was thus needed.[3]

In recent years, the interest of many research group for genuine silyl cations[4] has stimulated the search for highly electrophilic silylating agents. Table 1 shows some very electrophilic silylating agents along with their ^{29}Si chemical shift.

Table 1. ^{29}Si chemical shift of silylating agents

Entry	Silylating agent	$\delta\ ^{29}Si$	Reference
a	$Me_3SiCB_{11}F_{11}$	120	5
b	$Me_3SiB(C_6F_5)_4$	84.8	6
c	Me_3SiNTf_2	55.9	7
d	$Me_3SiN(SO_2F)_2$	44.9	8
e	Me_3SiOTf	43.5	9
f	Me_3SiClO_4	43.4	10
g	Me_3SiCl	32.5	10

Keywords: 2-azadienes; Diels–Alder reactions; amides.

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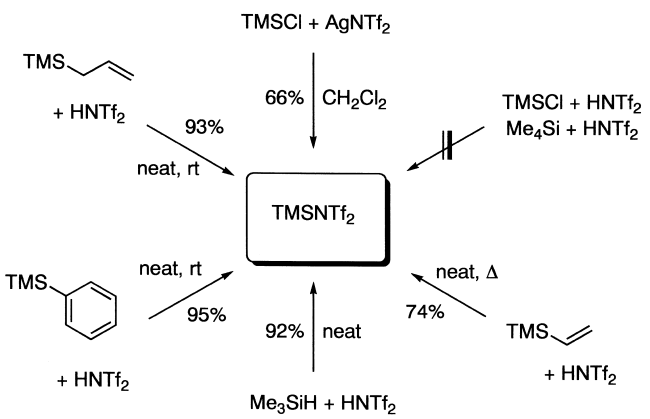
As a result of our previous experience with bis(trifluoromethylsulfonyl)imide salts which are stable and safe substitutes for the corresponding perchlorates,[11] we decided to study the corresponding silylated derivatives. The TMS derivative shows much lower ^{29}Si chemical shift than the TMS–carboranes and tetra(pentafluoro-phenyl)borate (entries a and b) but it is cheaper and easier to prepare. In 1997, we reported our preliminary results on the use of $TMSNTf_2$ as an efficient catalyst for the cycloaddition of methylacrylate to various dienes and for representative ene reactions.[12] Shortly after, the group of Mikami[13] reported that $TMSNTf_2$ was an effective catalyst for the Friedel–Crafts alkylation reaction and the group of Robertson[14] reported the use of $TMSNTf_2$ for the β-allylation of enones. More recently, we have described the first chiral silicon Lewis acid which led to significant facial selectivity in a model reaction.[15] Also Yamamoto's group recently demonstrated the efficiency of $TMSNTf_2$ as a catalyst for Mukayama–Aldol and Sakurai–Hosomi allylation reaction.[16] We now report the full detail of our study on the preparation, physical properties and catalytic efficiency of trimethylsilyl bis(trifluoromethansulfonyl)-imide.

2. Synthesis of $TMSNTf_2$

$TMSNTf_2$ had been first prepared by Foropoulos and Desmarteau by protodesilylation of trimethylsilane with $HNTf_2$ (Scheme 3).[17] This method requires the use of a closed vessel to avoid the loss of the volatile trimethylsilane.

$TMSNTf_2$ has also been prepared by metathesis of trimethylsilyl chloride with $AgN(SO_2CF_3)_2$ (Scheme 3).[7] This method required the use of an expensive and light sensitive reagent. Also it is not well adapted to an in situ preparation of $TMSNTf_2$ since it would involve a filtration under a strictly dry atmosphere. Scheme 3 shows the yields obtained by these methods after distillation of the crude products.

A more practical method involved the protodesilylation of allyltrimethylsilane. The reaction was fast at room temperature and yielded very pure $TMSNTf_2$ in essentially quantitative yields. It is particularly well suited for the in situ generation of $TMSNTf_2$. Phenyltrimethylsilane reacted equally well but vinyltrimethylsilane gave $TMSNTf_2$ contaminated by some impurities. A purification by distillation was needed.



Scheme 3.

Table 2. Comparative properties of HOTf and $HNTf_2$

HA/A$^-$	pK_a in acetic acid[20]	Donor number[21]
$HNTf_2$/$^-NTf_2$	7.8	5.4
HOTf/$^-$OTf	4.2	16.7

No reaction was observed with TMSCl or tetrametylsilane which had been previously shown to undergo protodesilylation in the presence of trifluoromethanesulfonic acid.[18] A protodesilylation reaction depends on both the strength of the acid which activates the substrate by protonation and the nucleophilicity of the conjugated base to displace the trimethylsilyl substituent.[19] As can be seen from Table 2, both pK_a and donor number should favor HOTf over $HNTf_2$.

3. Evaluation of the Lewis acidity of $TMSNTf_2$

To assess the Lewis acidity of $TMSNTf_2$, we have selected the much used[22] though sometimes debated[23] method of Childs et al. It involves the measurement of the variation of chemical shift of the proton at position 3 of an α,β-unsaturated carbonyl compound upon complexation with a Lewis acid.

A prerequisite for this study is the determination of the stoechiometry of the complex. We thus followed the change of the ^1H NMR spectrum of a solution of *trans*-methylcrotonate in $CDCl_3$ upon successive addition of small amounts of $TMSNTf_2$ (Fig. 1). This spectrometric titration showed an homogeneous chemical shift variation of all the protons up to a saturation level slightly above 1 equiv. of $TMSNTf_2$. This meant that the complex has a 1:1 stoechiometry.

Table 3 shows that $TMSNTf_2$ is very effective in complexing various types of carbonyl groups. In contrast, TMSOTf did not give any variation of the chemical shift. It is thus clear that $TMSNTf_2$ behaved as a much stronger Lewis acid than TMSOTf (Scheme 4). This was in line with the predictions based on the ^{29}Si chemical shifts of the two silylating agents. However it did not follow the order of Brönsted acidities which is HOTf>$HNTf_2$.[20] This was

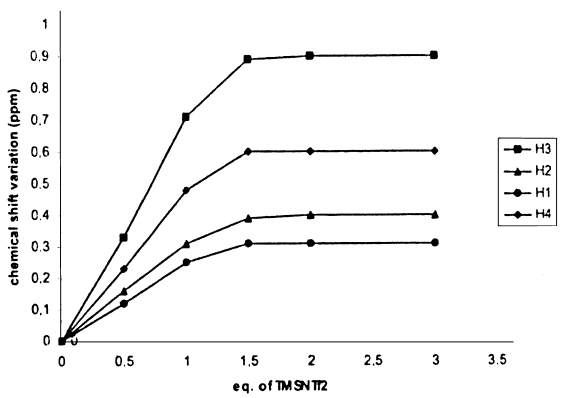
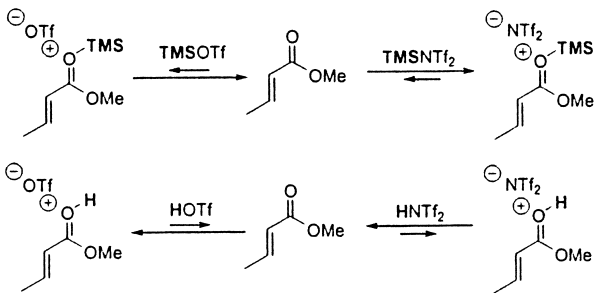


Figure 1. Spectrometric titration of *trans*-methylcrotonate with $TMSNTf_2$.

Table 3. Effect of Lewis and Brönsted acids on the chemical shifts of H^3 protons of α,β-unsaturated carbonyl compounds

LA/HA	$\Delta\delta$ H^3		
	Methylcrotonate	Crotonaldehyde	Cyclohexanone
$TMSNTf_2$	0.89	1.74	1.43
TMSOTf	~0	~0	~0
$HNTf_2$	0.11	0.46	0.2
HOTf	0.46	1.28	1.18



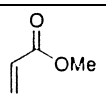
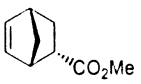
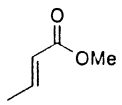
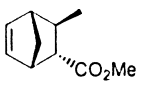
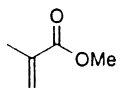
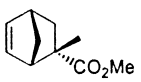
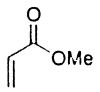
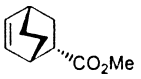
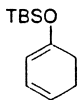
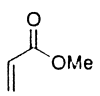
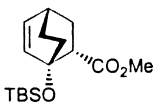
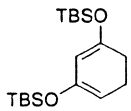
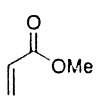
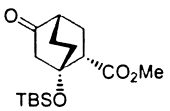
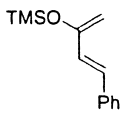
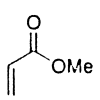
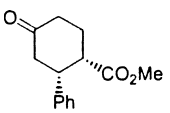
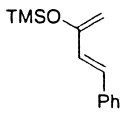
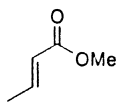
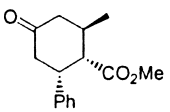
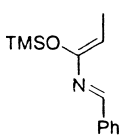
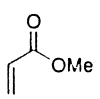
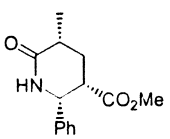
Scheme 4.

further illustrated by the variation of chemical shifts of protons at the position 3 of *trans*-methylcrotonate, *trans*-crotonaldehyde and cyclohexenone upon addition of 1.5 equiv. of HOTf or $HNTf_2$ (Table 3): the larger variations of chemical shift were observed with HOTf.

This surprising reversal of acidity sequence in going from the protic acid to the trimethylsilyl derivative could result from the size difference of the two anions. The bis(trifluoromethylsulfonyl)imide anion is much larger than the triflate anion. Therefore, the higher I-strain in $TMSNTf_2$ would thermodynamically favor the formation of the complex with a smaller ligand such as an ester group. This difference in I-strain does not exist in the protic acid.

Table 3 also showed that the chemical shift variations induced by $HNTf_2$ are one order of magnitude lower than those brought about by a similar amount of $TMSNTf_2$. This meant that a contamination of $TMSNTf_2$ by small amounts of $HNTf_2$ could only lead to a negligible underestimation of the Lewis acidity of $TMSNTf_2$.

Table 4. Diels–Alder reactions of α,β-unsaturated esters in toluene with 10 mol% silylating agent

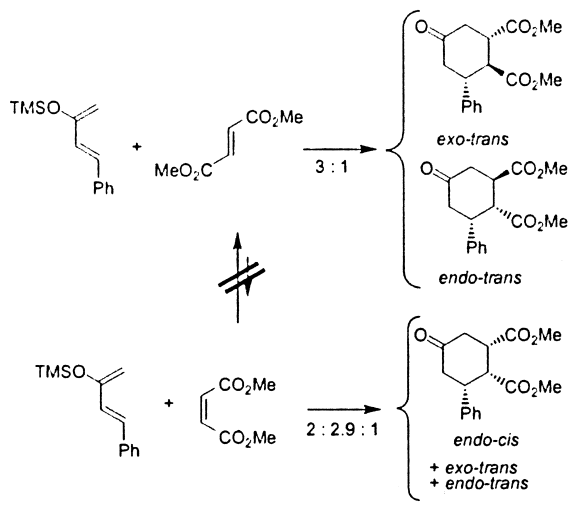
Entry	Diene	Dienophile	Conditions	Product (major)	Yield (%)	*Endo*/*exo*
a			0°C, 20 min, TMSOTf		<5	–
b			0°C, 20 min, $TMSNTf_2$		83	24:1
c			rt, TMSOTf		nr	–
d			rt, $TMSNTf_2$		Degradation	–
e			rt, $TMSNTf_2$+10 mol% $iPrNEt_2$		nr	–
f			rt, $TMSNTf_2$+10 mol% pyridine		nr	–
g			rt, $TMSNTf_2$+10 mol% collidine		nr	–
h			rt, $TMSNTf_2$+10 mol% BTBMP		94	11.5:1
i			rt, 15 min, $TMSNTf_2$		93	1.03:1
j			0°C, 1 h, TMSOTf		nr	–
k			0°C, 1 h, $TMSNTf_2$		92	49:1
l			0°C→rt, 1 h, TMSOTf		nr	–
m			0°C→rt, 1 h, $TMSNTf_2$		79	1.5:1
n			0°C→rt, 1 h, TMSOTf		nr	–
o			0°C→rt, 1 h, $TMSNTf_2$		76	24:1
p			−50°C→rt, 1 h, TMSOTf		nr	–
q			−50°C→rt, 1 h, $TMSNTf_2$		91	>99:1
r			−50°C→rt, 1 h, $TMSNTf_2$		79	9:1
s			0°C, 90 min, TMSOTf		<5	–
t			0°C, 90 min, $TMSNTf_2$		74	2:1

4. Diels–Alder reactions catalyzed by $TMSNTf_2$

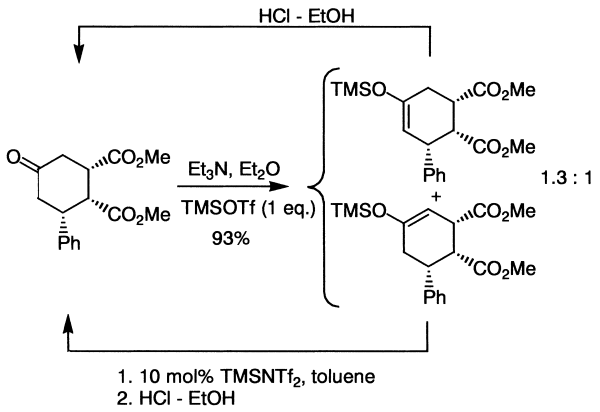
The difference in Lewis acidity between $TMSNTf_2$ and TMSOTf is dramatically illustrated by their effect on the rate of cycloaddition of dienes with α,β-unsaturated esters (Table 4).

TMSOTf was unable to catalyze the Diels–Alder reactions of methyl acrylate or *trans*-methylcrotonate whereas $TMSNTf_2$ always acted as an excellent Lewis acid catalyst. Another important conclusion of Table 4 is that $TMSNTf_2$ did not cause the degradation of the reactants even when very sensitive dienes like 2-azadienes were used. The reaction of methylcrotonate with cyclopentadiene is quite illustrative of this quality of the catalyst. We had observed degradation reactions in the presence of $TMSNTf_2$. It was believed that it was not due to $TMSNTf_2$ itself, but rather to traces of $HNTf_2$ contaminating the catalyst. The reaction of cyclopentadiene with methylcrotonate being slower than that of methylacrylate, degradation of the reactants (probably cyclopentadiene) by the residual acid could become more significant. Addition of various bases (entries e–g) did indeed suppress the degradation of the reactants but also deactivated the catalyst: no reaction was observed. Control experiments by ^1H NMR showed that the base was silylated by $TMSNTf_2$ under these conditions. The use of a very hindered base was anticipated to suppress the reaction with $TMSNTf_2$ while still allowing for a proton abstraction from $HNTf_2$. Rewardingly, it was found that, in the presence of 2,6-bis-*tert*-butyl-4-methylpyridine (BTBMP), no degradation occurred and the catalytic activity of $TMSNTf_2$ was restored (entry k). This observation led us to recommend the use of a small amount of BTBMP while running reactions in the presence of $TMSNTf_2$: this will suppress any reaction due to the presence of traces of $HNTf_2$ which are very difficult to avoid. A similar situation can be encountered with reactions catalyzed by TMSOTf: here also we recommend to add small amount of BTBMP to neutralize the residual HOTf.

We have also examined the stereochemistry of the catalyzed reaction (Scheme 5). The reaction of dimethylfumarate only



Scheme 5. Reaction conditions: 10 mol% $TMSNTf_2$, 10 mol% BTBMP, toluene, 0°C.



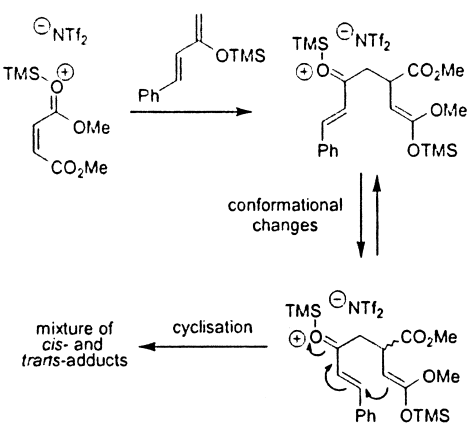
Scheme 6.

yielded *trans* adducts which were separated by preparative HPLC. The cycloaddition with dimethylmaleate gave three products, which were separated by HPLC. Control experiments showed that under the reaction conditions (1) no isomerization of dimethylmaleate to dimethylfumarate had occurred, (2) no isomerisation of the primary adducts was observed as shown in Scheme 6. The *endo-cis* adduct was silylated to give a mixture of enol ethers, which did not epimerize under the conditions used for the cycloaddition or upon treatment with HCl–EtOH.

The results described in Schemes 5 and 6 are of mechanistic significance. The formation of a mixture of *cis* and *trans*-adducts from dimethylmaleate suggest a two step mechanism for the cycloaddition reaction (Scheme 7).[24]

Reaction of the silylenol ether function of the diene on the activated form of dimethylmaleate would lead to an intermediate adduct which should undergo several conformationnal changes before undergoing the Mukaiyama-type cyclisation. These conformational changes of the intermediate adduct easily account for the formation of mixtures of *cis* and *trans*-adducts. However, conformational equilibrium has not been attained since we observed only *trans*-adducts from dimethylfumarate.

We believe that these results conclusively show that in situ generated $TMSNTf_2$ is an efficient Lewis acid catalyst for the Diels–Alder reaction of α,β-unsaturated esters with a wide variety of dienes, including some which have shown to



Scheme 7.

decompose in the presence of many conventional Lewis acids. They also show the superiority of $TMSNTf_2$ as a Lewis acid catalyst over TMSOTf. We are confident that this strong, non-metallic Lewis acid will find many applications as a tolerant and 'green' catalyst of reactions triggered by carbonyl groups.

5. Experimental

^1H NMR spectra were recorded in $CDCl_3$ on Varian Gemini-200, 300 or on Bruker DRX-500 spectrometers at 200, 300 or 500 MHz. ^{13}C NMR spectra were recorded at 50, 75 or 125 MHz. Chemical shifts are given in ppm relative to Me_4Si (0 ppm, ^1H) or $CDCl_3$ (77.0 ppm, ^{13}C). Mass spectra were recorded on a Finnigan MAT-TSQ 700 spectrometer. IR spectra were recorded on a BIO-RAD TFS 135 FT-IR spectrometer. All absorption values are expressed in wavenumbers (cm^{-1}). Melting point were obtained on a Büchi Melting Point B-545 or a Microthermal 8103 apparatus and are uncorrected. HPLC were run on Waters apparatus including a Waters 600 Controller and a Waters 486 detector fitted with a 6 μm silica column. TLC were run on silicagel $60F_{254}$. Column chromatographies were performed on silicagel 40 (230–400 μm, Merck). All solvents were distilled before use. $HN(SO_2CF_3)_2$ was graciously provided by Rhodia (Lyon, France) and was purified by distillation from 98% H_2SO_4. The various silanes were purchased from Aldrich and used without further purification. All reactions were run in flame dried glassware under strictly dry atmosphere of argon.

5.1. General procedure for the reaction of silanes with $HN(SO_2CF_3)_2$

In a one necked flask equipped with a condenser, the acid was introduced and covered with solvent. The silane was added at 0°C under stirring. Reaction was completed in the given conditions then the volatile compounds were evaporated under strictly dry vacuum. The residue was cannulated in a Kugelrohr distillation set and distillated under vacuum.

From allyltrimethylsilane. $HNTf_2$: 5 g (17.78 mmol, 1 equiv.), allyltrimethylsilane: 5.65 ml (4.06 g, 35.56 mmol, 2 equiv.); No solvent, reaction at 20°C until end of gas evolution; yield: 5.7 g (16.13 mmol, 91%).

From vinyltrimethylsilane. $HNTf_2$: 1.15 g (4.09 mmol, 1 equiv.), vinyltrimethylsilane: 3.15 ml (2.05 g, 20.45 mmol, 5 equiv.); no solvent, reaction at reflux for 18 h; yield: 1.06 g (3.01 mmol, 74%).

From phenyltrimethylsilane. $HNTf_2$: 98 mg (348 μmol, 1.2 equiv.), Me_3SiPh: 50 μl (43 mg, 290 μmol, 1 equiv.); $CDCl_3$: 0.6 ml, 1 h at 20°C; yield: >95% (determined by NMR).

RN: 82113-66-4; colourless liquid; bp: 115°C (2 Torr); ^1H NMR (200 MHz): 0.58 (s, 3H); ^{19}F NMR (282 MHz): −77.94 (s, CF_3); ^{13}C NMR (50 MHz): 0.29 (Me), 118.72 (q, J_{C-F}=320 Hz); ^{29}Si NMR (99 MHz): 54.3.

5.2. Complexation experiments

The experiments were performed under argon atmosphere in a 5 mm oven-dried NMR tube closed by a septum. The carbonyl compound (0.4 mmol) and 0.6 ml of $CDCl_3$ were syringed in and a ^1H spectrum was recorded at 0°C. The sample was cooled at −40°C and the Lewis or Brönsted acid were added to the mixture which was vortexed. The ^1H NMR spectra were recorded at 0°C.

5.3. General procedure for the catalyzed Diels–Alder reactions

A solution of the dienophile in toluene was placed in a two necked flask isolated from moisture with a silicagel trap. The solution was brought up to the selected temperature and 10 mol% of $TMSNTf_2$ followed by the diene were added to the solution of the dienophile. The reaction mixture was quenched by addition of 5 ml of a 1 M aqueous solution of $NaHCO_3$ and the resulting mixture was stirred for 1 h. The aqueous phase was extracted twice with 15 ml of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$. Removal of the solvent in vacuo left a residue which was purified by flash chromatography on silica gel.

5.3.1. Cycloaddition of methylacrylate with cyclopentadiene. Methylacrylate (200 μl, 191 mg, 2.22 mmol, 1 equiv.), cyclopentadiene (366 μl, 293 mg, 4.44 mmol, 2 equiv.), $TMSNTf_2$ (78 mg, 222 μmol, 0.1 equiv.), toluene (3 ml); 0°C, 20 min; cyclohexane/AcOEt 95:5; yield: 0.282 g (1.85 mmol, 83%); *endo*/*exo*: 96:4.

endo Cycloadduct; RN: 2903-75-5; ^1H NMR ($CDCl_3$, 300 MHz): 1.27 (1H, d, J=8.0 Hz), 1.36–1.45 (2H, m), 1.84–1.97 (1H, m), 2.85–2.99 (2H, m), 3.19 (1H, s large), 3.54 (3H, s), 5.93 (1H, dd, J=5.6, 2.9 Hz), 6.19 (1H, dd, J=5.6, 3.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 29.33, 42.56, 43.23, 45.68, 49.61, 51.29, 132.41, 137.65, 175.09.

5.3.2. Cycloaddition of methylcrotonate with cyclopentadiene. Methylcrotonate (200 μl, 188 mg, 1.88 mmol, 1 equiv.), cyclopentadiene (466 μl, 373 mg, 5.65 mmol, 3 equiv.), $TMSNTf_2$ (45 μl, 66 mg, 188 μmol, 0.1 equiv.), toluene (4 ml); rt, 15 min; petroleum ether/Et_2O 96:4; *endo*/*exo*: 92:8.

endo Cycloadduct; RN: 155325-46-5; ^1H NMR ($CDCl_3$, 500 MHz): 1.18 (3H, d, J=6.9 Hz), 1.43 (1H, dd, J=8.6, 1.9 Hz), 1.54 (1H, d, J=8.6 Hz), 1.82 (1H, ddq J=4.4, 6.9, 1.9 Hz), 2.37 (1H, dd, J=3.9, 4.4 Hz), 2.46 (1H, s large), 3.1 (1H, s large), 3.61 (3H, s), 5.98 (1H, dd, J=5.8, 3.2 Hz), 6.26 (1H, dd, J=5.8, 3.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 45.72, 52.24, 37.7, 48.65, 138.48, 133.12, 45.78, 20.74, 174.95, 51.19.

exo Cycloadduct; RN: 23217-30-3; ^1H NMR ($CDCl_3$, 500 MHz): 0.91 (3H, d, J=6.9 Hz), 1.44 (1H, dq, J=8.6, 1.7 Hz), 1.64 (1H, dd, J=5.2, 1.8 Hz), 1.67 (1H, d, J=8.6 Hz), 2.35 (1H, m), 2.7 (1H, s large), 2.94 (1H, s large), 3.69 (3H, s), 6.11 (1H, dd, J=5.8, 3.2 Hz), 6.2 (1H, dd, J=5.8, 3.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 47.19, 51.06, 38.94, 47.08, 135.14, 136.43, 47.97, 18.87, 176.52, 51.46.

5.3.3. Cycloaddition of methylmethacrylate with cyclopentadiene. Methylmetacrylate (200 μl, 187 mg, 1.86 mmol, 1 equiv.), cyclopentadiene (462 μl, 370 mg, 5.60 mmol, 3 equiv.), $TMSNTf_2$ (45 μl, 66 mg, 186 μmol, 0.1 equiv.), toluene (4 ml); rt, 15 min; petroleum ether/Et_2O 96:4; *endo*/*exo*: 57:43; yield: 0.289 g (1.74 mmol, 93%).

endo Cycloadduct; RN: 7167-29-5; ^1H NMR ($CDCl_3$, 500 MHz): 1.35–1.45 (2H, m), 1.49 (1H, d, J=8.6 Hz), 1.87 (3H, s), 1.87 (1H, dd, J=11.9, 2.6 Hz), 2.71 (1H, s large), 2.76 (1H, s large), 3.54 (3H, s), 5.95 (1H, dd, J=5.6, 2.9 Hz), 6.06 (1H, dd, J=5.6, 3.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 50.77, 49.72, 37.75, 42.35, 137.42, 135.05, 46.55, 26.11, 177.47, 51.07.

exo Cycloadduct; RN: 7167-28-4; ^1H NMR ($CDCl_3$, 500 MHz): 0.77 (1H, dd, J=11.9, 2.2 Hz), 1.02 (3H, s), 1.29 (1H, d, J=8.6 Hz), 1.36 (1H, dd, J=8.6, 2.2 Hz), 2.36 (1H, dd, J=11.9, 3.9 Hz), 2.74 (1H, s large), 2.95 (1H, s large), 3.62 (3H, s), 6.00 (1H, dd, J=5.6, 3.1 Hz), 6.14 (1H, dd, J=5.6, 3.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 50.22, 49.33, 37.48, 42.62, 138.38, 133.31, 48.82, 23.97, 178.84, 51.57.

5.3.4. Cycloaddition of methylacrylate with 1,3-cyclohexadiene. Methylacrylate (200 μl, 191 mg, 2.22 mmol, 1 equiv.), 1,3-cyclohexadiene (413 μl, 355 mg, 4.44 mmol, 2 equiv.), $TMSNTf_2$ (78 mg, 222 μmol, 0.1 equiv.), toluene (6 ml); 0°C, 60 min; cyclohexane/AcOEt 95:5; yield: 0.338 g (2.03 mmol, 92%); *endo*/*exo*: >95:5.

endo Cycloadduct; RN: 25578-17-0; ^1H NMR ($CDCl_3$, 500 MHz): 1.00–1.9 (6H, m), 2.34–3.00 (3H, m), 3.54 (3H, s), 5.59–6.40 (2H, m).

5.3.5. Cycloaddition of methylacrylate with 1-(*tert*-butyldimethylsilyloxy)cyclohexa-1,3-diene. Methylacrylate (100 μl, 95 mg, 1.11 mmol, 1 equiv.), 1-(*tert*-butyldimethylsilyloxy)cyclohexa-1,3-diene (303 mg, 1.44 mmol, 1.3 equiv.), $TMSNTf_2$ (39 mg, 111 μmol, 0.1 equiv.), toluene (3 ml); addition of reagents at 0°C then reaction at rt for 1 h; cyclohexane/AcOEt 96:4; yield: 0.257 g (0.23 mmol, 79%); *endo*/*exo*: 60:40.

endo Cycloadduct; ^1H NMR ($CDCl_3$, 500 MHz): 0.11 (6H, s), 0.87 (9H, s), 1.35–1.46 (2H, m), 1.5–1.51 (1H, m), 1.56–1.66 (2H, m), 1.87 (1H, ddd, J=12.5, 9.9, 2.8 Hz), 2.5–2.6 (1H, m), 2.74 (1H, dd, J=9.9, 5.9 Hz), 3.61 (3H, s), 6.16 (1H, d, J=8.6 Hz), 6.21 (1H, dd, J=8.6, 6.5 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 175.35, 136.35, 131.17, 76.40, 51.26, 49.93, 35.33, 33.22, 29.41, 25.78, 25.61, 17.98, −2.24, −2.44; IR (neat): 880, 1130, 1170, 1205, 1265, 1360, 1435, 1740, 2940, 2960; MS (EI, 70 eV): 73 (20%), 89 (14%), 151 (55%), 210 (46%), 239 (100%), 296 (5%); Elemental analysis calcd (%) for $C_{16}H_{28}O_3Si$: C 64.81, H 9.51; found: C 64.90, H 9.75.

exo Cycloadduct; ^1H NMR ($CDCl_3$, 200 MHz): 0.07 (3H, s), 0.12 (3H, s), 0.89 (9H, s), 1.2–1.8 (5H, m), 2.24 (1H, td, J=11.3, 3.5 Hz), 2.5–2.6 (2H, m), 3.66 (3H, s), 6.14 (1H, dd, J=8.7, 6.3 Hz), 6.26 (1H, d, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): 175.5, 139.31, 132.08, 77.19, 51.26, 49.11, 30.75, 29.52, 28.65, 26.13, 25.62, 18.4, −2.33, −2.56; IR (neat): 880, 1150, 1180, 1195, 1210, 1260, 1360, 1735, 2935s, 2955; MS (EI, 70 eV): 45 (59%), 55 (90%), 73 (100%), 75 (56%), 89 (30%), 151 (11%), 210 (5%), 239 (11%), 296 (1%); Elemental analysis calcd (%) for $C_{16}H_{28}O_3Si$: C 64.81, H 9.51; found: C 64.91, H 9.53.

5.3.6. Cycloaddition of methylacrylate with 1,3-bis(*tert*-butyldimethylsiloxy)cyclohexa-1,3-diene. 1,3-Bis(*tert*-butyldimethylsiloxy)cyclohexa-1,3-diene (450 mg, 1.32 mmol, 1.23 equiv.), methylacrylate (96 μl, 91 mg, 1.07 mmol, 1 equiv.), $TMSNTf_2$ (37 mg, 106 μmol, 0.1 equiv.), toluene (3 ml); addition of reagents at 0°C then reaction at rt for 1 h; cyclohexane/AcOEt 9:1; yield: 0.255 g (0.82 mmol, 76.5%); *endo*/*exo*: 96:4.

endo Cycloadduct; ^1H NMR ($CDCl_3$, 200 MHz): 0.07 (3H, s), 0.11 (3H, s), 0.83 (9H, s), 1.74–1.87 (4H, m), 1.98–2.05 (2H, m), 2.2–2.35 (1H, m), 2.23 (1H, d, J=19 Hz), 2.9 (1H, dd, J=9.2, 7.9 Hz), 3.22 (1H, d, J=18.6 Hz), 3.67 (3H, s); ^{13}C NMR ($CDCl_3$, 50 MHz): 211.75, 174.78, 74.31, 51.6, 47.76, 47.45, 41.35, 34.82, 27.43, 25.41, 22.25, 17.69, −2.21; IR (neat): 860, 1140, 1170, 1205, 1260, 1325, 1740, 2860, 2940, 2960; MS (EI, 70 eV, +Q1MS): 55 (43%), 75 (35%), 89 (30%), 195 (12%), 227 (26%), 255 (100%), 312 (1%); Elemental analysis calcd (%) for $C_{16}H_{28}O_4Si$: C 61.49, H 9.03; found: C 61.50, H 8.90.

exo Cycloadduct; ^1H NMR ($CDCl_3$, 200 MHz): 0.07 (3H, s), 0.11 (3H, s), 0.84 (9H, s), 1.57 (1H, tdd, J=11.9, 4.4, 2.1 Hz), 1.77 (1H, tm, J=13.0 Hz), 1.85–2.13 (3H, m), 2.27–2.54 (4H, m), 2.77 (1H, ddd, J=10.8, 6.4, 2.0 Hz), 3.69 (3H, s); ^{13}C NMR ($CDCl_3$, 50 MHz): 212.02, 174.71, 74.16, 53.3, 51.29, 48.27, 41.46, 28.03, 26.63, 25.39, 22.27, 17.77, −2.25; IR (neat): 870, 1135, 1170, 1205, 1260, 1335, 1370, 1735, 2860, 2940, 2960; MS (EI, 70 eV): 55 (16%), 75 (100%), 89 (30%), 227 (6%), 255 (16%), 312 (1%); Elemental analysis calcd (%) for $C_{16}H_{28}O_4Si$: C 61.49, H 9.03; found: C 61.60, H 9.00.

5.3.7. Cycloaddition of methylacrylate with 1-phenyl-3-(trimethylsilyloxy)buta-1,3-diene. 1-Phenyl-3-(trimethylsilyloxy)buta-1,3-diene (315 mg, 1.44 mmol, 1.3 equiv.), methylacrylate (100 μl, 95 mg, 1.11 mmol, 1 equiv.), $TMSNTf_2$ (39 mg, 111 μmol, 0.1 equiv.), toluene (3 ml); addition of reagents at −50°C then reaction at rt for 1 h; cyclohexane/AcOEt 8:2; yield: 0.232 g (1 mmol, 91%); *endo*/*exo*: >95:5 (single isomer observed).

endo Cycloadduct; RN: 136145-71-6; ^1H NMR ($CDCl_3$, 300 MHz): 2.1 (1H, dddd, J=14.1, 4.9, 5.5, 5.9 Hz), 2.24 (1H, dddd, J=14.1, 4.9, 5.5, 10.3 Hz), 2.4 (1H, ddd, J=15.5, 5.5, 5.5 Hz), 2.6 (1H, dd, J=14.6, 5.6 Hz), 2.8 (1H, ddd, J=15.5, 5.9, 10.3 Hz), 3.12 (1H, q, J=4.9 Hz), 3.27 (1H, dd, J=14.6, 10.4 Hz), 3.5 (1H, ddd, J=5.6, 10.4, 4.9 Hz), 3.55 (3H, s), 7.1–7.35 (5H, m); ^{13}C NMR ($CDCl_3$, 50 MHz): 26.14, 38, 43.36, 44.53, 45.08, 51.21, 127.08, 127.29, 128.38, 140.73, 173.23, 210.08.

5.3.8. Cycloaddition of methylcrotonate with 1-phenyl-3-(trimethylsilyloxy)buta-1,3-diene. 1-Phenyl-3-(trimethylsilyloxy)buta-1,3-diene: (315 mg, 1.44 mmol, 1.3 equiv.), methylcrotonate (117 μl, 111 mg, 1.11 mmol, 1 equiv.), $TMSNTf_2$ (39 mg, 111 μmol, 0.1 equiv.), toluene (3 ml); addition of reagents at −50°C then reaction at rt for 1 h;

cyclohexane/AcOEt 8:2; *endo*/*exo*: 9:1; yield: 0.215 g (0.87 mmol, 79%).

endo Cycloadduct; RN: 83194-78-9; ^{1}H NMR ($CDCl_3$, 500 MHz): 1.13 (3H, d, J=6.8 Hz), 2.17 (1H, dd, J=14.8, 6.8 Hz), 2.53 (1H, m, J=5.5, 6.8 Hz), 2.58 (1H, dd, J=14.6, 5.03 Hz), 2.85 (1H, t, J=5.5 Hz), 2.89 (1H, dd, J=14.8, 5.5 Hz), 3.2 (1H, dd, J=14.6, 9.86 Hz), 3.46 (3H, s), 3.61 (1H, ddd, J=5.03, 9.86, 5.5 Hz), 7.1–7.4 (5H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): 210.45, 43.02, 41.24, 52, 31.16, 45.32, 173.25, 51.09, 140.4, 127.31, 128.24, 126.96, 20.43.

5.3.9. Cycloaddition of methylacrylate with 1-phenyl-3-trimethylsilyloxy-2-azapenta-1,3-diene. 1-Phenyl-3-trimethylsilyloxy-2-azapenta-1,3-diene (310 mg, 1.33 mmol, 1.2 equiv.), methylacrylate: (100 μl, 95 mg, 1.11 mmol, 1 equiv.), $TMSNTf_2$ (39 mg, 111 μmol, 0.1 equiv.), toluene (3 ml); reaction at 0°C for 90 min; AcOEt/cyclohexane 75:25; yield: 0.205 g (0.83 mmol, 74%); *endo*/*exo*: 67:33.

endo Cycloadduct; ^{1}H NMR ($CDCl_3$, 200 MHz): 1.31 (3H, d, J=6.9 Hz), 1.76 (1H, q, J=13 Hz), 1.94 (1H, ddd, J=14.0, 6.9, 3.7 Hz), 2.4 (1H, hept, J=6.9, 12.3 Hz), 3.22 (1H, ddd, J=4.6, 3.7, 12.8 Hz), 3.56 (3H, s), 5.01 (1H, t, J=4.6 Hz), 6.54 (1H, s large), 7.1–7.35 (5H, m); ^{13}C NMR ($CDCl_3$, 50 MHz): 16.91, 25.89, 35.28, 44.69, 51.57, 57.11, 128.24, 128.29, 127.21, 138.42, 171.04, 174.72; IR (neat): 801, 1261, 1662, 1741, 2950, 3033, 3209; MS (EI, 70 eV): 55.1 (41%), 77 (34%), 106.1 (95%), 133.1 (21%), 161.1 (100%), 177 (97%), 188.2 (20%), 232.1 (4%), 247 (64%); HRMS (EI, 70 eV) calcd (%) for $C_{16}H_{28}O_4Si$ 247.1208; found 247.1213.

exo Cycloadduct; ^{1}H NMR ($CDCl_3$, 200 MHz): 1.21 (3H, d, J=7.2 Hz), 1.72 (1H, ddd, J=10.8, 5.6, 3.8 Hz), 2–2.4 (2H, m), 2.81 (1H, ddd, J=7.4, 4, 1.6 Hz), 3.62 (3H, s), 4.85 (1H, dd, J=1.5, 7.4 Hz), 6.51 (1H, s large), 7.2–7.4 (5H, m); ^{13}C NMR ($CDCl_3$, 75 MHz): 17.81, 29.68, 33.42, 44.68, 52.04, 58.3, 126.56, 128.3, 128.82, 140.58, 172.79, 175.24; IR (neat): 1193, 1355, 1455, 1661, 1734, 2954, 3063, 3219; MS (EI, 70 eV): 119 (4%), 161.1 (22%), 177.1 (100%), 188.2 (18%), 232.6 (1%), 247.3 (10%); HRMS (EI, 70 eV) calcd (%) for $C_{16}H_{28}O_4Si$ 247.1208; found 247.1204.

5.3.10. Cycloaddition of dimethylfumarate with 1-phenyl-3-(trimethylsilyloxy)buta-1,3-diene. Dimethylfumarate (200 mg, 1.39 mmol, 1 equiv.); 1-phenyl-3-(trimethylsilyloxy)buta-1,3-diene (393 mg, 1.80 mmol, 1.3 equiv.), 2,6-bis(*tert*-butyl)-4-methylpyridine: (28 mg, 138 μmol, 0.1 equiv.), $TMSNTf_2$ (33 μl, 49 mg, 138 μmol, 0.1 equiv.), toluene (4 ml); reaction at 0°C for 1 h; petroleum ether/AcOEt 75:25, HPLC separation of isomers: hexane/*i*PrOH 80:20, 25°C, 0.3 ml/min; yield: 0.293 g (1.01 mmol, 73%); *endo*/*exo*: 72:28.

exo-trans Cycloadduct; mp: 107.5°C; HPLC (6 μm silica column, eluent: hexane (90%)/*i*PrOH, flow: 0.5 ml/min, λ=254 nm): 17.373 min;^{1}H NMR (C_6D_6, 500 MHz): 2.53 (1H, dd, J=15.0, 13.8 Hz), 2.76 (1H, dd, J=15.0, 13.0 Hz), 2.8 (1H, ddd, J=15.0, 4.0, 1.8 Hz), 3.11 (1H, ddd, J=15.0, 4.4, 1.8 Hz), 3.33 (1H, ddd, J=11.1, 13.8, 4.0 Hz), 3.47 (1H, t, J=11.1 Hz), 3.5–3.55 (1H, m), 3.54 (3H, s), 7.3–7.7 (5H, m), 7.72 (3H, s); ^{13}C NMR (C_6D_6, 125 MHz): 204.55, 42.53, 46.02, 51.77, 46.66, 47.83, 173.42, 173.13, 51.87, 52.38, 141.84, 127.15 ($CDCl_3$), 128.8 ($CDCl_3$), 127.63 ($CDCl_3$); IR (neat): 702, 772, 1011, 1168, 1434, 1712, 1727, 2952, 3035; MS (EI, 70 eV): 59 (12%), 104.1 (14%), 129.1 (17%), 171.1 (100%), 230.1 (84%), 259.1 (28%), 290.2 (32%); HRMS (EI, 70 eV) calcd (%) for $C_{16}H_{18}O_5$ 290.1154; found 290.1160.

endo-trans Cycloadduct; mp: 90.5°C; HPLC (6 μm silica column, eluent: hexane (90%)/*i*PrOH, flow: 0.5 ml/min, λ=254 nm): 19.26 min; ^{1}H NMR ($CDCl_3$, 500 MHz): 2.6 (1H, dd, J=15.7, 9.3 Hz), 2.72 (1H, dd, J=15.7, 5.9 Hz), 2.9 (1H, dd, J=15.7, 5.3 Hz), 2.99 (1H, dd, J=15.7, 5.9 Hz), 3.24 (1H, ddd, J=8.6, 9.3, 5.3 Hz), 3.49 (1H, dd, J=5.1, 8.6 Hz), 3.54 (3H, s), 3.71 (3H, s), 3.79 (1H, q, J=5.9 Hz), 7.03–7.32 (5H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): 207.42, 43.57, 41.58, 47.33, 40.68, 40.82, 173.32, 172.03, 51.62, 52.31, 139.62, 127.44, 128.48, 127.38; IR (neat): 702, 908, 1018, 1164, 1276, 1435, 1738, 2953, 3003, 3030; HPLC-MS (APCI): 129.3 (16%), 143.2 (21%), 157.2 (24%), 171.2 (61%), 181.2 (35%), 199.1 (100%), 227.1 (22%), 231.1 (17%), 259.1 (45%), 290.9 (3%); HRMS (EI, 70 eV) calcd (%) for $C_{16}H_{18}O_5$ 290.1154; found 290.1169.

5.3.11. Cycloaddition of dimethylmaleate with 1-phenyl-3-(trimethylsilyloxy)buta-1,3-diene. Dimethylmaleate (200 μl, 230 mg, 1.60 mmol, 1 equiv.), 1-phenyl-3-(trimethylsilyloxy)buta-1,3-diene (453 mg, 2.08 mmol, 1.3 equiv.), 2,6-bis(*tert*-butyl)-4-methylpyridine (32 mg, 159 μmol, 0.1 equiv.), $TMSNTf_2$ (38 μl, 56 mg, 159 μmol, 0.1 equiv.), toluene (4 ml); reaction at 0°C for 1 h; petroleum ether/AcOEt 75:25; yield: 0.390 g (1.34 mmol, 84%); *endo-cis*/*exo-trans*/*endo-trans*: 34:17:49 (determined by HPLC).

endo-cis Cycloadduct; mp: 84.5°C; HPLC (6 μm silica column, eluent: hexane (90%)/*i*PrOH, flow: 0.5 ml/min, λ=254 nm): 16.27 min; ^{1}H NMR ($CDCl_3$, 500 MHz): 2.52 (1H, dd, J=14.4, 4.6 Hz), 2.68 (1H, dd, J=14.4, 4.6 Hz), 3.13 (1H, dt, J=13.7, 4.6 Hz), 3.28 (1H, dd, J=14.4, 13.7 Hz), 3.32 (1H, dt, J=13.7, 4.6 Hz), 3.4 (1H, dd, J=14.4, 13.7 Hz), 3.41 (1H, t, J=4.6 Hz), 3.43 (3H, s), 3.7 (3H, s), 7.1–7.4 (5H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): 208.17, 41.42, 44.01, 46.95, 44.46, 39.15, 171.78, 171.85, 51.29, 52.26, 139.79, 126.78, 128.53, 127.44; IR (neat): 700, 992, 1174, 1220, 1272, 1438, 1712, 1720, 1736, 2952, 3029, 3062; HPLC-MS (APCI): 129.3 (11%), 143.2 (22%), 157.2 (16%), 171.2 (56%), 181.3 (48%), 199.1 (100%), 227 (28%), 259.1 (20%); HRMS (EI, 70 eV) calcd (%) for $C_{16}H_{18}O_5$ 290.1154; found 290.1150.

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