Chiral Silicon Lewis Acids Having Pentacoordinate Stereogenic Silicon Center : ^{29}Si NMR Studies and Application to Asymmetric Diels-Alder Reaction

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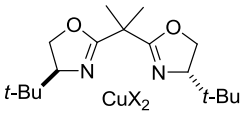
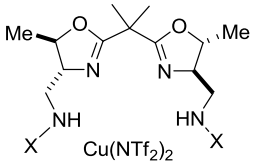
(1) Comparison with Evans, Sibi, Ellmann, and Ishihara's Chiral Catalysts

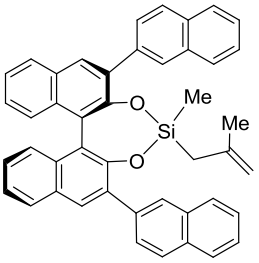
Chart S1. Representative catalysts exhibiting high enantioselectivities in Diels-Alder reaction between dienes and alkenoyloxazolidinones



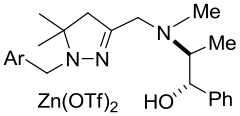
Evans 1[1]: X = SbF_6
Evans 2[1]: X = OTf



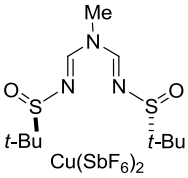
Ishihara 1[2]: X = Ms
Ishihara 2[2]: X = Tf



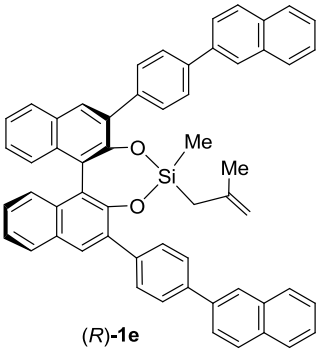
(*R*)-**1d**



Sibi 1[3]: Ar = Ph
Sibi 2[3]: Ar = 1-Naph

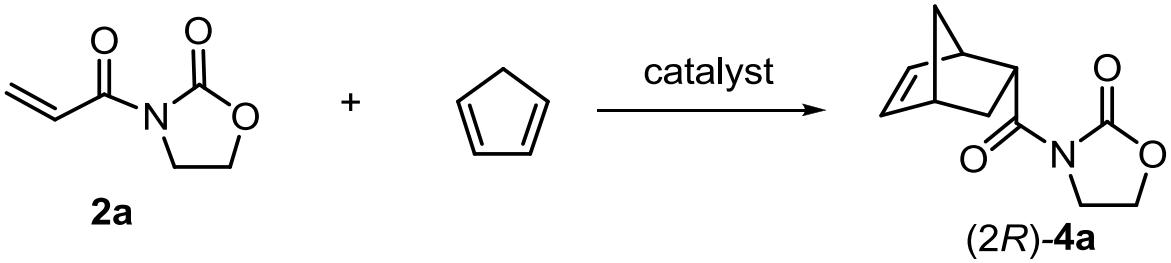


Ellman[4]



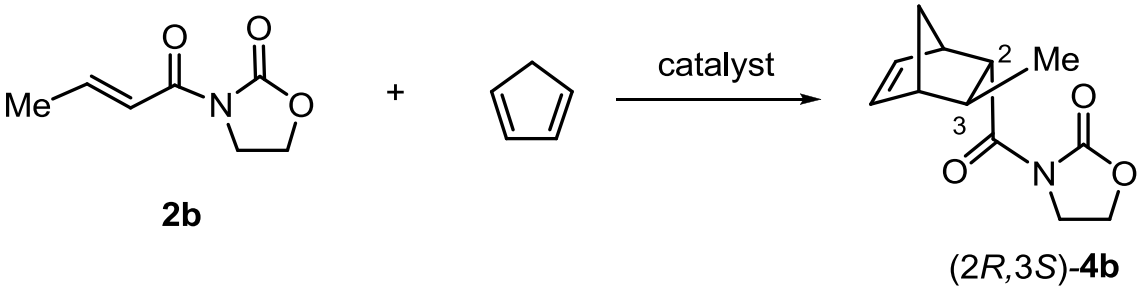
(*R*)-**1e**

Table S1.



catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	*endo*/*exo*	ee (%) (confign)
(*R*)-**1a**/$HNTf_2$ (2.5)	3.0	PhMe	-78 , 6	96	>97:3	92 (2*R*)
Ishihara 1 (1)	3.0	$EtNO_2$	-78 , 9	94	99:1	98 (2*R*)
Evans 1 (1)	10	CH_2Cl_2	-78 , 8	100	96:4	96 (2*S*)
Sibi 2 (13)	10	CH_2Cl_2	rt, —	83	3.8:1	96 (2*S*)
Ellmann (10)	5	CH_2Cl_2	-78 , 0.1	96	> 99:1	98 (2*S*)

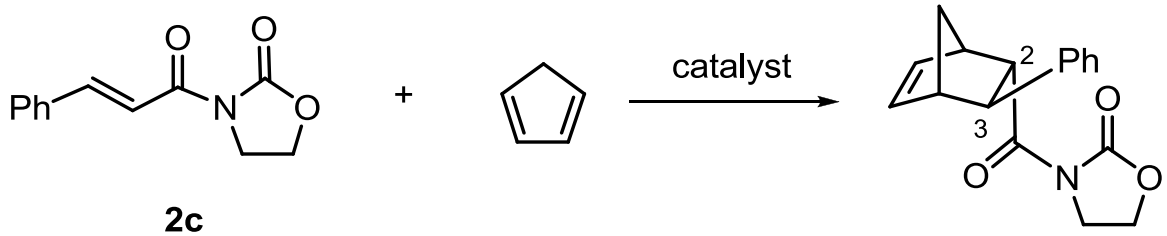
Table S2.



2b (2*R*,3*S*)-**4b**

catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	*endo*/*exo*	ee (%) (confign)
(*R*)-**1a**/$HNTf_2$ (2.5)	3.0	PhMe	-78 , 14	93	98:2	97 (2*R*,3*S*)
Ishihara 2 (5)	3.0	$EtNO_2$	-20 , 7	58	93:7	95 (2*R*,3*S*)
Evans 1 (10)	10	CH_2Cl_2	-15 , 20	99	85:15	99 (2*S*,3*R*)
Sibi 1 (13)		CH_2Cl_2	rt, —	82	94.4:5.6	97 (2*S*,3*R*)
Ellmann (10)	5	CH_2Cl_2	-40 , 8	76	98:2	97 (2*S*,3*R*)

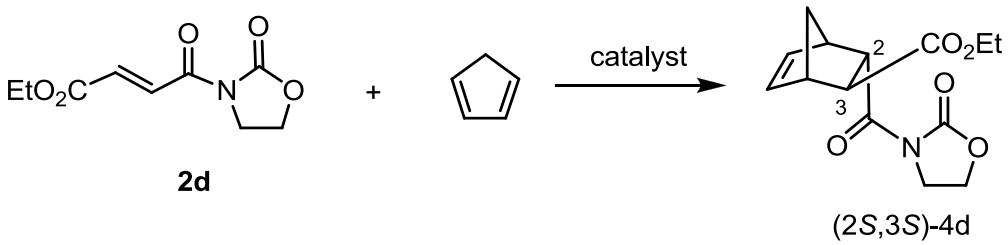
Table S3.



2c (2*S*,3*S*)-**4c**

catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	*endo*/*exo*	ee (%) (confign)
(*R*)-**1a**/$HNTf_2$ (2.5)	3.0	PhMe	-78 , 14	92	96:4	94 (2*S*,3*S*)
Ishihara	—	—	—	—	—	—
Evans 1 (10)	10	CH_2Cl_2	25 , 24	96	81:19	96 (2*R*,3*R*)
Sibi 2 (13)		CH_2Cl_2	rt, —	94	60:40	94 (2*R*,3*R*)
Ellmann (10)	5	CH_2Cl_2	0, 16	58	95:5	94 (2*R*,3*R*)

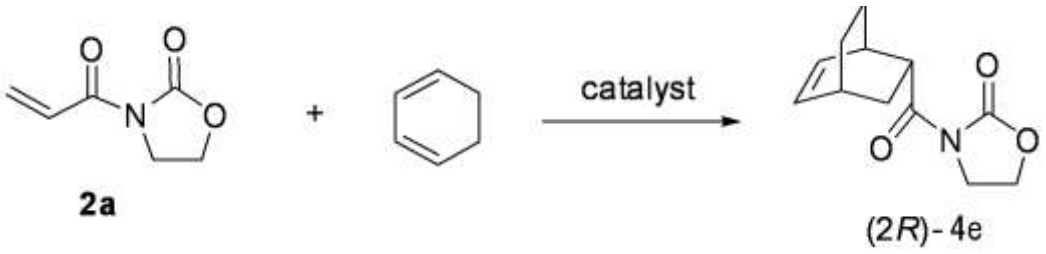
Table S4.



2d (2*S*,3*S*)-4d

catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	*endo*/*exo*	ee (%) (confign)
(*R*)-**1a**/$HNTf_2$ (2.5)	3.0	PhMe	-78 , 14	98	72:28	94 (2*S*,3*S*)
Ishihara 2 (5)	3.0	$EtNO_2$	-40, 21	99	89:11	89 (2*S*,3*S*)
Evans 2 (10)	10	CH_2Cl_2	-55, 20	92	94:6	95 (2*R*,3*R*)
Sibi 2 (13)		CH_2Cl_2	0,	90	57:43	96 (2*R*,3*R*)
Ellmann (10)	5	CH_2Cl_2	-78, 2	85	97:3	96 (2*R*,3*R*)

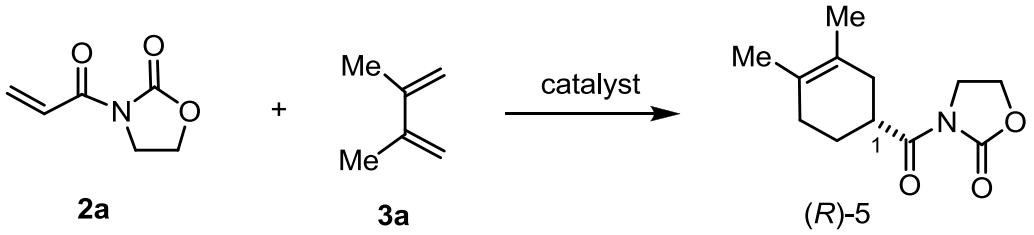
Table S5.



2a (2*R*)-4e

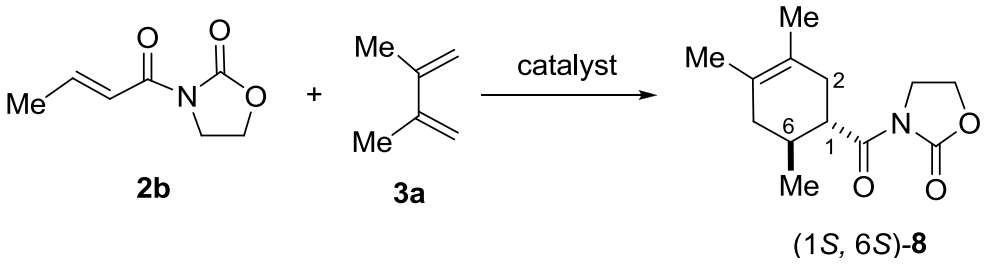
catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	*endo*/*exo*	ee (%) (confign)
(*R*)-**1a**/$HNTf_2$ (2.5)	3.0	PhMe	-78 , 14	85	98:2	88 (2*R*)
Ishihara 1 (5)	3.0	$MeNO_2$	0, 30	95	99:1	98 (2*R*)
Evans 1 (10)	10	CH_2Cl_2	25, 5	86	95:5	93 (2*S*)
Sibi 1 (13)		CH_2Cl_2	rt,	86	98:2	98 (2*S*)
Ellmann (10)	5	CH_2Cl_2	0, 16	50	98:2	90 (2*S*)

Table S6.



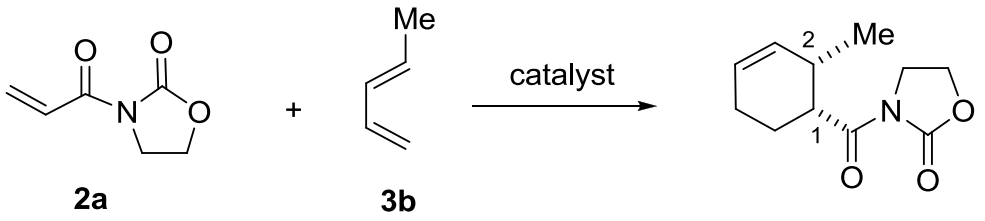
catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	ee (%) (confign)
(*R*)-**1d**/$HNTf_2$ (5)	3.0	PhMe	-78 , 14	85	75 (1*R*)
Ishihara 1 (5)	3.0	$MeNO_2$	-20, 52	83	95 (1*R*)
Evans 1 (10)	10	CH_2Cl_2	25, 24	83	95 (1*R*)
Sibi 1 (13)	—	CH_2Cl_2	0, —	67	90 (1*S*)
Ellmann (10)	—	CH_2Cl_2	0, 16	96	92 (1*S*)

Table S7.



catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	ee (%) (confign)
(*R*)-**1d**/$HNTf_2$ (5)	3.0	PhMe	-40, 24	78	81 (1*S*,6*S*)
Ishihara 1 and **2**	—	—	—	—	—
Evans 1 and **2**	—	—	—	—	—
Sibi 1 and **2**	—	—	—	—	—
Ellmann	—	—	—	—	—

Table S8.



2a + **3b** → (1*R*, 2*S*)-**6**

catalyst (mol%)	diene (equiv)	solvent	conditions (^{o}C, h)	yield (%)	isomer ratio	ee (%) (confign)
(*R*)-**1d**/$HNTf_2$ (5)	3.0	PhMe	-78 , 24	78[a]	84:16	88 (1*R*,2*S*)
Ishihara 1 (5)	3.0	$MeNO_2$	0, 72	92[b]	85:9:6	92 (1*R*,2*S*)
Evans 1 (10)	10	CH_2Cl_2	0, 72	92[b]	83:17	89 (1*S*,2*R*)
Sibi 1 (13)	—	—	—	—	—	—
Ellmann (10)	8	CH_2Cl_2	rt, 16	18[b]	2:1:0.4	41 (2*S*)

[a] Yield of compound **6**. [b] Total yield of stereo- and regioisomers.

(2) ^{29}Si NMR Studies of Silyl Triflimides

The catalytic activity of chiral allylsilanes/$HNTf_2$ catalyst systems can be correlated to the structure of the silyl triflimides. To shed light on the structure of the catalytically active species, ^{29}Si NMR studies were undertaken. All spectra were measured in CD_2Cl_2 or $CDCl_3$. The ^{29}Si NMR spectral data of silyl triflimides are summarized in Table S9. Silicon-29 chemical shifts of cationic pentacoordinate silicon compounds, whose structures have been unequivocally determined by spectral methods or X-ray crystallographic analysis, appear in a wide range from +6.9 to -120 ppm.[5] No clear trend can be seen for the ^{29}Si chemical shifts of these compounds; however, the weak coordination of donor atoms to pentacoordinate silicon tends to shift the ^{29}Si resonances to downfield.[5g] Chiral allylsilane (*R*)-**1a** exhibited ^{29}Si chemical shift at 9.35 ppm in CD_2Cl_2 solution at -50 ^{o}C (Figure S1) (Table S9, entry 1). When $HNTf_2$ (1 equiv) was added to the solution of (*R*)-**1a** in CD_2Cl_2 to form silyl triflimide, *substantial upfield shift of the ^{29}Si resonance* was observed (Figure, S2): (*R*)-**1a** derived silyl triflimide exhibited two peaks at -35.7 and -36.5 ppm at -50 ^{o}C (Table S9, entry 2), which are within the cationic pentacoordinate silicon region of the ^{29}Si

NMR spectrum.

The formation of tetracoordinate silyl triflimides by protodesilylation of the corresponding allylsilanes is usually attended by large downfield shift of δ^{29}Si (e.g., Me_3SiNTf: 54.3 ppm[6a]; $Me_3SiCH_2CH{=}CH_2$: 0.39 ppm[6f]). Therefore, observed substantial upfield shift is suggestive of the formation of pentacoordinate silyl triflimide. Furthermore, a general tendency for the δ^{29}Si of pentacoordinate silicon atoms to appear at higher field than tetracoordinate silicon atoms also supports the formation of pentacoordinate silyl triflimide from (*R*)-**1a**.[7] The appearance of two peaks at high field strongly implies that (*R*)-**1a** derived chiral silyl triflimide exists as a pair of diastereomers **A** and **B** due to the chiral pentacoordinate silicon atom (Figure S3). It should be noted that a silicon atom of a tetracoordinate silyl triflimides is achiral, exhibiting a single ^{29}Si signal. Actually silyl triflimide derived from (*R*)-**1e** exhibited a single ^{29}Si signal at 49.0 ppm (Figure S4) (Table S9, entry 3); thus (*R*)-**1e** derived silyl triflimide is apparently tetracoordinate (refer to next discussion).

The formation of silyl triflimides from (*R*)-**1e**/$HNTf_2$ was attended by a large downfield shift of the ^{29}Si resonance ($\Delta\delta^{29}$Si = +32 ppm) (Table S9, entries 3 and 4). Chiral allylsilane (*R*)-**1e** exhibited ^{29}Si chemical shift at 17.2 ppm in CD_2Cl_2 solution at -50 ^{o}C (Figure S5). Upon addition of $HNTf_2$ (1 equiv) to the solution of (*R*)-**1e** in CD_2Cl_2, the ^{29}Si signal was downfield-shifted to +49.0 ppm at -50 ^{o}C (Figure S4). ^{29}Si NMR spectra of tetracoordinate silyl triflimides having σSi-N bonds with $C_nSi_{3-n}Si\text{-}NTf_2$ coordination framework have the chemical sifts between +54 and +62 ppm (Table S9, entries 5-8).[6a,6b,6c] Thus, silyl triflimide derived from **1a** proved to be a tetracoordinate silyl triflimide by comparison with the ^{29}Si chemical shifts for a series of tetracoordinate silyl triflimides. It is noteworthy that ^{29}Si chemical shifts of tetracoordinate silyl triflimides are downfield-shifted by 50 to 60 ppm from the those of the corresponding silylamines $(C)_3Si\text{-}NR_2$ (R = Me, *n*-Bu) (Table S9, entries 9 and 10).[6d] Consequently, it is reasonable to conclude that in a series of tetracoordinate silyl triflimides having $\sigma Si\text{-}NTf_2$ bonds, a significant decrease in electron density of the silicon leads to the large downfield shifts of the δ^{29}Si, compared to $(C)_3Si\text{-}NR_2$ (R = alkyl)

Table S9. ^{29}Si Chemical shifts of chiral allylsilanes, silyl triflimides, and silylamines

entry	silicon compounds	^{29}Siδ (ppm)	reference
1 [a]	(*R*)-**1a**	9.35	***Figure S1***
2 [a]	(*R*)-**1a** / $HNTf_2$ (1 equiv)	-35.7, -36.5	***Figure S2***
3 [a]	(*R*)-**1e**/ $HNTf_2$ (1 equiv)	49.0	***Figure S4***
4 [a]	(*R*)-**1e**	17.2	***Figure S5***
5 [b]	Me_3SiNTf_2	54.3	6a
6 [b]	(*t*-Bu)Me_2SiNTf_2	55.5	6b
7 [a]	$Me_3SiMe_2SiNTf_2$	60.8	6b
8 [a]	$(Me_3Si)_3SiNTf_2$	62.2	6c
9 [b]	Me_3SiNMe_2	6.50	6d
10 [b]	$Me_3SiN(n\text{-}Bu)_2$	4.56	6d
11 [b]	$Me(i\text{-}PrO)_2SiNMe_2$	-34.6	6e
12 [b]	$Me(i\text{-}PrO)_2SiNEt_2$	-35.9	6e

[a] Measured in CD_2Cl_2. [b] Measured in $CDCl_3$.

Figure S1. ^{29}Si NMR spectra of allylsilane (*R*)-**1a** in CD_2Cl_2 at -50°C

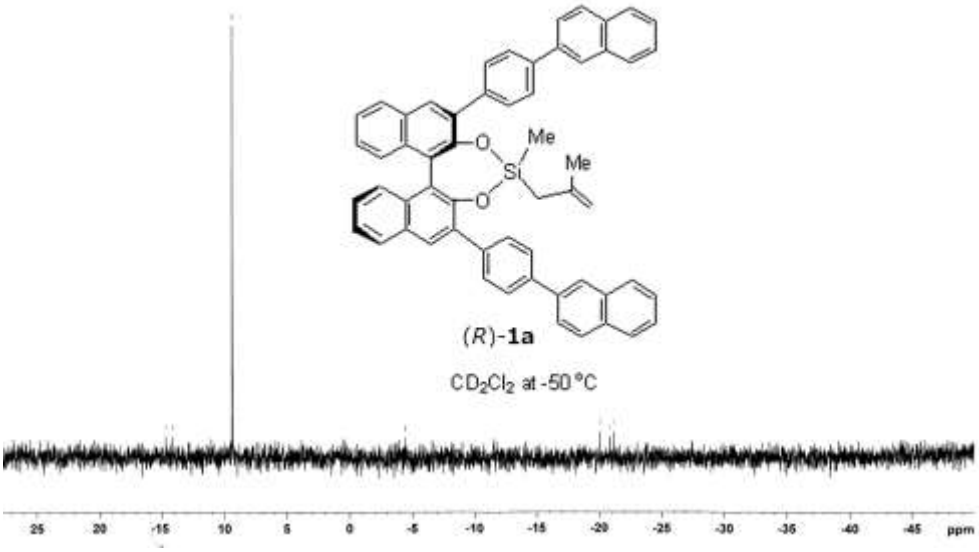


Figure S2. ^{29}Si NMR spectra of a mixture of allylsilane (*R*)-**1a** and $HNTf_2$ in CD_2Cl_2 at -50°C

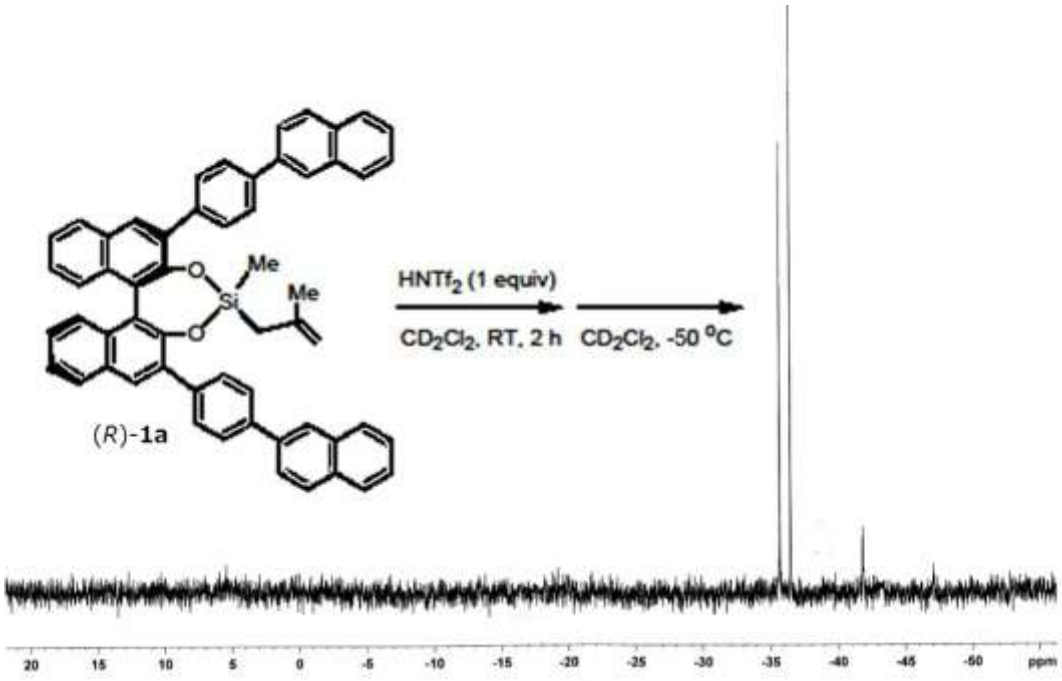
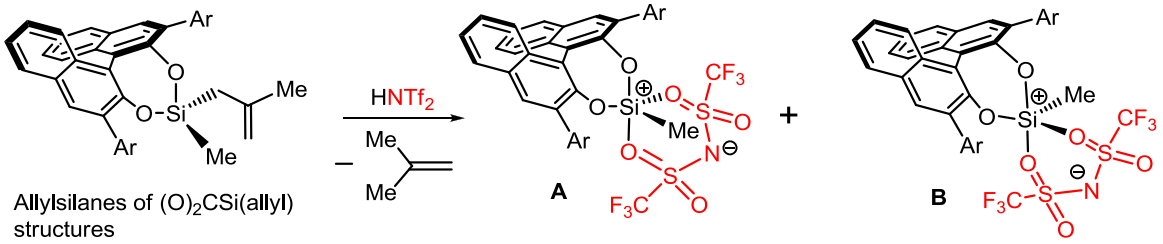


Figure S3.



Allylsilanes of $(O)_2CSi$(allyl) structures

Diastereomeric mixture of pentacoordinate silyl triflimides

Figure S4. ^{29}Si NMR spectra of a mixture of allylsilane (*R*)-**1e** and $HNTf_2$ in CD_2Cl_2 at -50°C

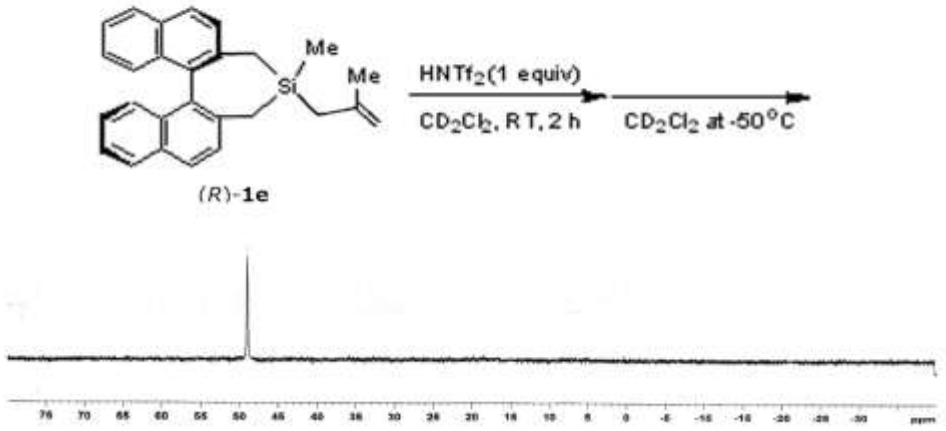


Figure S5. ^{29}Si NMR spectra of allylsilane (*R*)-**1e** in CD_2Cl_2 at -50°C

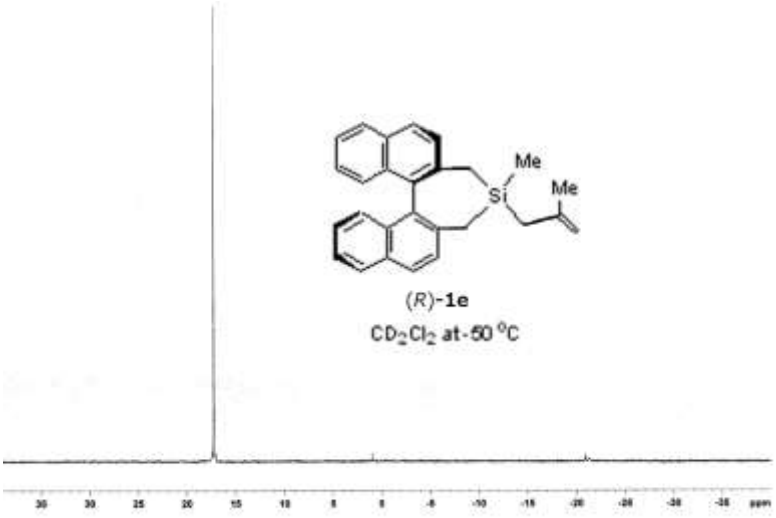
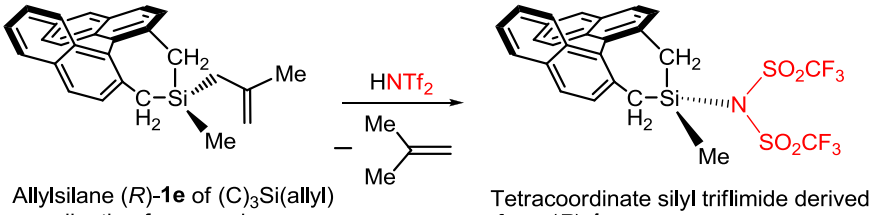


Figure S6



Allylsilane (*R*)-**1e** of $(C)_3Si$(allyl) coordination framework

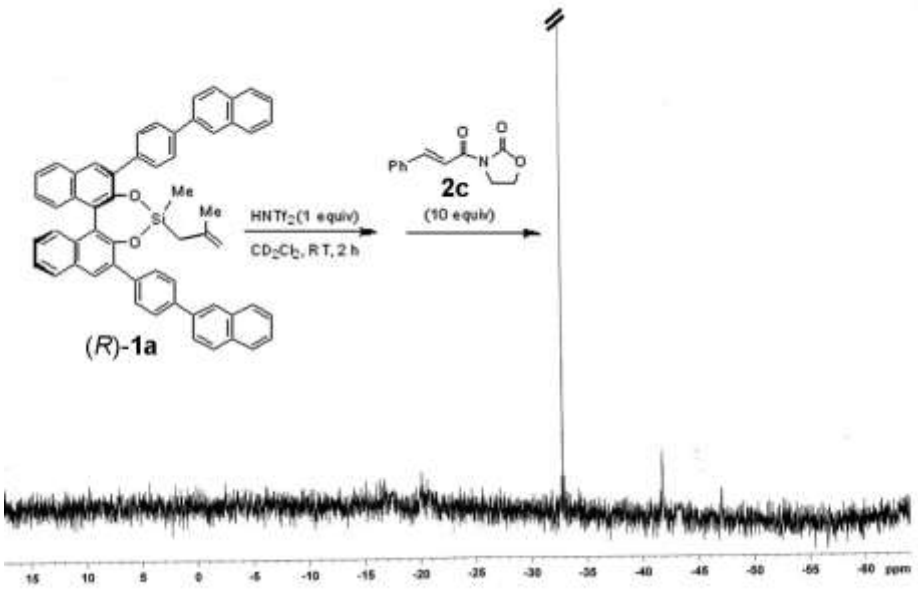
Tetracoordinate silyl triflimide derived from (*R*)-**1e**

On the other hand, further evidence in support of the pentacoordinate structure of silyl triflimide derived from (*R*)-**1a** is provided by comparison with the ^{29}Si chemical shifts of tetracoordinate silylamines having similar coordination frameworks, $(O)_2CSi\text{-}NR_2$ (R = alkyl). Silicon-29 chemical shifts are significantly influenced by the kind of coordinating donor atoms, namely, coordination framework. Interpretation of the shift of ^{29}Si resonances must be made, therefore, by comparison with the ^{29}Siδ of the compounds having similar coordination framework around the silicon. The ^{29}Si chemical shifts of tetracoordinate siylamines having $(O)_2CSi\text{-}NR_2$ (R = alkyl) framework appear between -34 to -36 ppm (Table S9, entries 11 and 12). We can reasonably predict that the ^{29}Si chemical shifts of hypothetical tetracoordinate silyl tiflimides, $(O)_2CSi\text{-}NTf_2$ must be significantly downfield-shifted from the those of $(O)_2CSi\text{-}NR_2$, due to the decrease in electron density of the silicon as discussed below. The observed ^{29}Si chemical shifts of **1e** derived silyl triflimide (-35.7 and -36.5 ppm, Table S9, entry 2) are not downfield-shifted compared to those of $(O)_2CSi\text{-}NR_2$ (R = Me, Et) (-34.5 and -35.9 ppm, Table S9, entries 11 and 12), strongly suggesting that (*R*)-**1a** derived silyl triflimide does not have tetracoordinate structure, but pentacoordinate structure. These observations lead to the conclusion that *protodesilylation of allylsilanes, $(C)_3Si\text{-}CH_2(Me)C{=}CH_2$ with $HNTf_2$ gives tetracoordinate silyl triflimides (Fig. S6), whereas protodesilylation of allylsilanes $(O)_2CSi\text{-}CH_2(Me)C{=}CH_2$ affords pentacoordinate silyl triflimides (Fig. S3).*

(3) Detailed Discussion of Diastereo- and Enantioselectivity of the Diels-Alder Reactions.

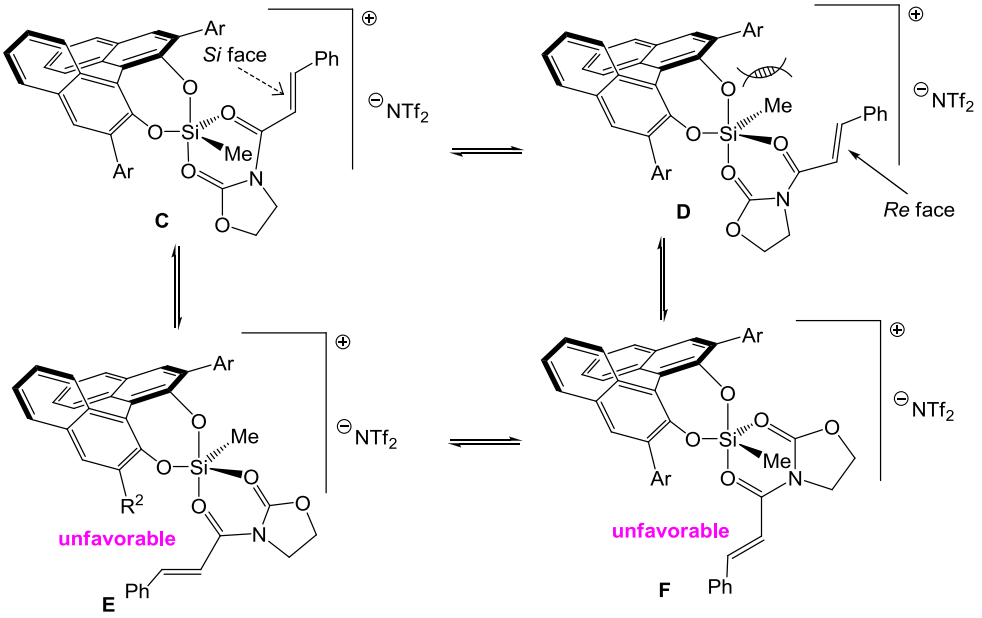
Addition of *N*-cinnamoyl oxazolidinone (10 equiv) to a solution of silyl triflimide derived from (*R*)-**1a** in CD_2Cl_2 resulted in appearance of a single ^{29}Si signal at -32.8 ppm (Fig. S7). The δ^{29}Si is within the cationic pentacoordinate silicon region of the ^{29}Si spectrum,[5] indicating the formation of a single pentacoordinate silicon-dienophile complex.

Figure S7. ^{29}Si NMR spectra of a mixture of allylsilane (*R*)-**1a**/$HNTf_2$ and *N*-cinnamoyloxazolidinone **2c** in CD_2Cl_2 at -50^{o}C



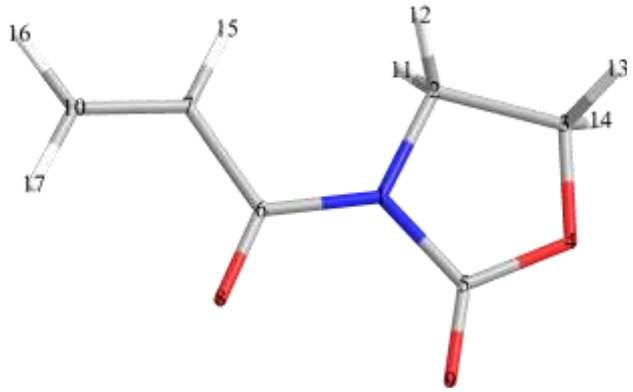
It seems reasonable to suppose that the *s-cis* configured *N*-cinnamoyl oxazolidinone is bound to the Lewis acidic silicon center in a bidentate fashion with the trigonal bipyramidal silicon geometry (Figure S8).[8]

Figure S8.



In general, electron-accepting atoms occupy the apical positions of pentacoordinate silicon compounds, due to the polarization of electron density from the central silicon to the atoms at apical position through 3c-4e hypervalent bonds.[9] Therefore, it is reasonable to postulate that the carbonyl oxygen atom of the dienophile bearing lower electron density would occupy the apical position of the *N*-alkenoyloxazolidinone-silicon complexes, while the carbonyl oxygen bearing higher electron density would occupy the equatorial position. DFT calculation of *s-cis* conformer of *N*-etenoyl oxazolidinone **2a** was carried out to reveal the electron density of two carbonyl oxygen atoms. Optimized geometry and Mulliken charges were obtained with the GAMESS package of program at the B3LYP/6-31G(d) level.[10] Mulliken charges and optimized structure are shown in Table S10.

Table S10. B3LYP/6-31G(d) optimized geometry and selected atom properties of *s-cis* *N*-ethenoyloxazolidinone (**2a**)



	Atom type	Mulliken charge	Muliken population
N(1)	N Amide	-0.551741	7.55174
C(5)	C Carbonyl	0.786671	5.21333
C(6)	C Carbonyl	0.591685	5.40832
O(8)	O Carbonyl	-0.450839	8.45084
O(9)	O Carbonyl	-0.428611	8.42861

Table S10 indicates that carbonyl oxygen of alkenoyl moiety O(9) has smaller Mulliken charge than that of carbonyl oxygen of oxazolidinone O(8). It therefore seems most likely that the carbonyl group of oxazolidinone moiety is bound to Si at the apical position and the

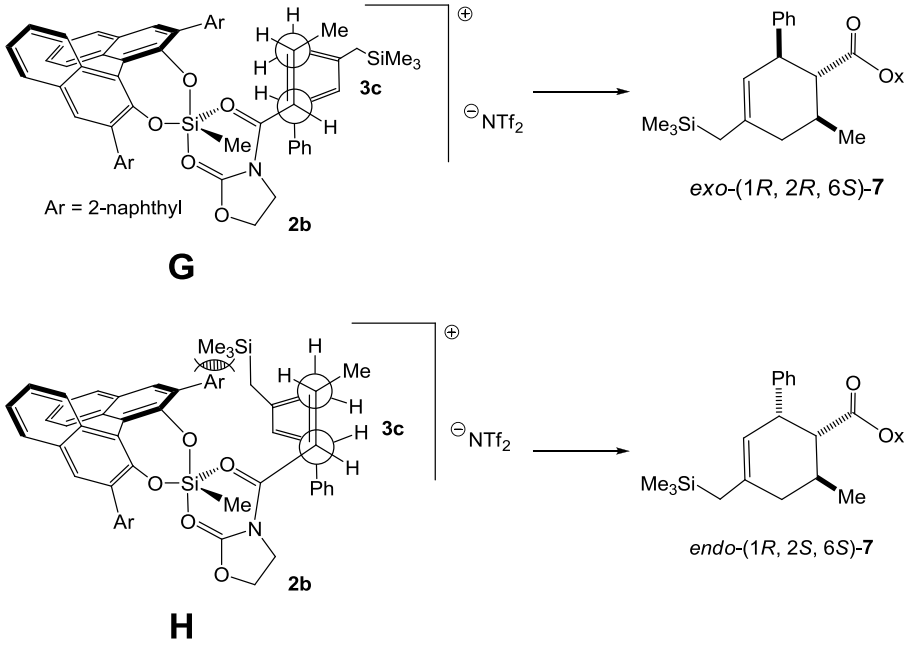
carbonyl group of alkenoyl moiety is bound at the equatorial position (Figure S8, **C** and **D**). The participation of dienophile-silicon complexes **E** and **F** in the Diels-Alder reaction can be ruled out, because these complexes seem to be less stable compared to complexes **C** and **D**. In complexes **E** and **F**, the carbonyl oxygens of alkenoyl moieties bearing higher electron density occupy the apical positions, destabilizing the dienophile-silicon complexes (Figure S8).

The observed sense of the asymmetric induction for the present Diels-Alder reaction catalyzed by chiral silyl triflimides derived from (*R*)-**1a**, (*R*)-**1b, (*R*)-1c**, and (*R*)-**1d** can be understood by considering the catalysis-dienophile complexes **C** or **D**. When Ar substituents at the 3,3'-positions are sterically demanding, (*e.g.*, (*R*)-**1a** and (*R*)-**1d**), complex **D** is destabilized due to the steric repulsion between the methyl on the silicon and the Ar substituents at the 3,3'-positions of (*R*)-BINOL. Therefore, equilibrium between **C** and **D** is shifted to the complex **C**. Thus, Diels-Alder reaction catalyzed by (*R*)-**1a** and (*R*)-**1d** derived silyl triflimides takes place through the complex **C**. Steric shielding of the *Re* face of the dienophile by the methyl on the silicon would favor the diene attack on the exposed *Si* face. The reversal of the enantioselectivity was observed, when (*R*)-**1b** and (*R*)-**1c** derived silyl triflimide are employed as a catalyst, affording the Diels-Alder adduct with opposite configuration via complex **D** (Ar = H). In complex **D**, where there is no steric repulsion between the methyl on the silicon and unsubtsiruted (*R*)-BINOL ligand, allows the approach of dienes from *Re* face, because *Si* face is shielded by methyl on the silicon. The proposed stereochemical models for the transition states assembly are completely consistent with the observed sense of asymmetric induction.

The *exo*/*endo* diastereoselectivity of the present Diels-Alder reaction depends greatly on the structure of 1,3-butadines. In the presence of 5 mol% of (*R*)-**1d** derived silyl triflimides catalyst, the reaction between 1-phenyl-3-(trimethylsilyl)methyl-1,3-butadiene (**3c**) and *N*-crotonoyl oxazolidinone **2b** afforded *exo*-Diels-Alder adduct **7** (*exo*/*endo* = 95/5, *exo* ee = 87%), whereas other reactions catalyzed by pentacoordinate silyl triflimides exclusively gave *endo* adducts with very high diastereoselectivity. This result implies that (trimethylsilyl)methyl group at the 3-position of diene **3c** is responsible for the inversion of the diastereoselectivity from *endo* to *exo*. As shown Scheme 1, diene **3c** approaches the exposed *Si* face of the dienophile **2b** binding to the catalyst so as to avoid the steric repulsion between (trimethylsilyl)methyl on the diene and naphthyl substituent of the catalyst, furnishing *exo*-**7** (**G**, Scheme 1). It is apparent that the approach of diene **3c** to

the opposite diastereoface of dienophile **2b** is blocked by the naphthyl group of **2b** (**H**, Scheme 1).

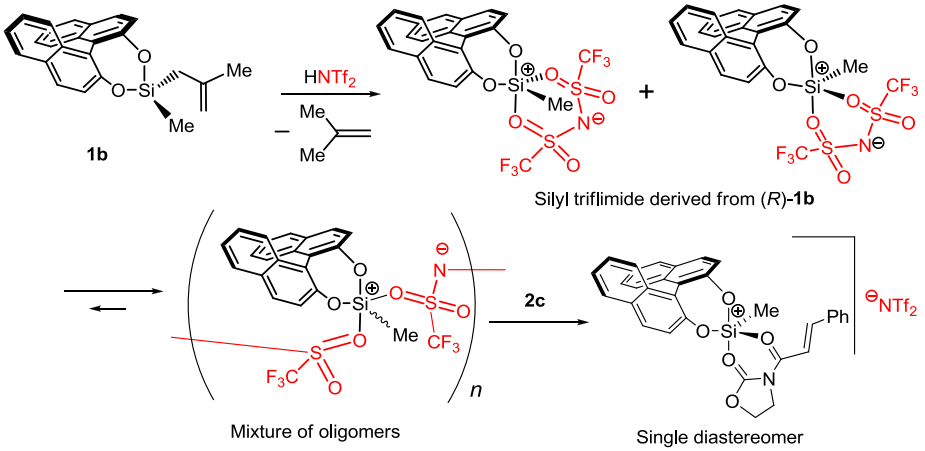
Scheme 1.



(4) Comparison of Catalytic Activities between Tetracoordinate Silyl Triflimide and Pentacoordinate Silyl Triflimide.

Based on the above discussion, it is clear that silyl triflimide derived from (*R*)-**1e**, whose coordination framework is $(C)_3Si\text{-}CH_2(Me)C{=}CH_2$, is tetracoordinate (Figure S6), whereas silyl triflimide derived from (*R*)-**1b** bearing (*R*)-BINOL ligand, $(O)_2CSi\text{-}CH_2(Me)C{=}CH_2$, is pentacoordinate, which would oligomerize to form many silicon species (Figure S9). Coordination of *N*-alkenoyl oxazolidinone **2c** to the mixture of oligomers gives a single **1b**-NTf_2-**2c** complex as indicate by ^{29}Si spectra (Figure 1 in the text).

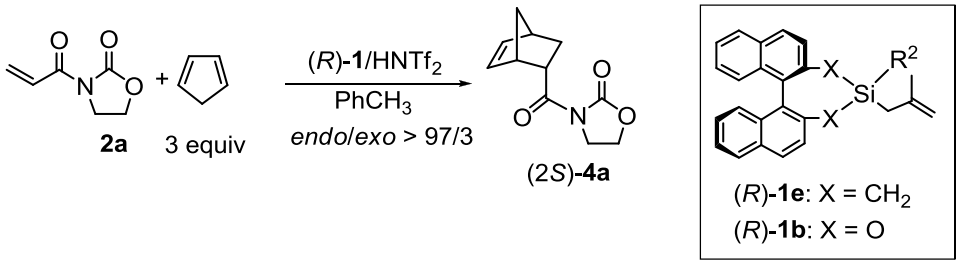
Figure S9.



We have found that *coordination number of the silicon atoms profoundly affects the catalytic activities of the silyl triflimides*. For comparison of the catalytic activities between pentacoordinate silyl triflimides and tetracoordinate one, we examined the Diels-Alder reaction of cyclopentadiene with *N*-ethenoyloxazolidinone (**2a**) catalyzed by silyl amides derived from (*R*)-**1e**/$HNTf_2$ and (*R*)-**1b**/$HNTf_2$ (Table S11). The reaction catalyzed by silyl triflimide derived from **1b** (5 mol%) afforded the corresponding adduct (2*S*)-**4a** in 85% yield with 69% ee at -78 ^oC (entry 1). NMR analysis of the reaction mixture indicated that the reaction was almost quantitative in less than 5 h. Under the same reaction conditions, the reaction catalyzed by (*R*)-**1e**/$HNTf_2$ (5 mol%) gave (2*S*)-**4a** in 27% yield with 57% ee, and dienophile **2a** was recovered in 58% (entry 2). To complete the

reaction by **1e** derived catalysis at -78 ^{o}C, higher catalyst loading (15 mol%) and longer reaction time (> 40 h) were needed (entry 3). The reaction at higher temperature (-20 ^{o}C) gave the good yield of (2*S*)-**4a** (88%), but enantioselectivity was very low (entry 4). These observations indicate that the catalytic activities of pentacoordinate silyl triflimides are much higher than that of tetracoordinate silyl triflimides. The higher catalytic activities of pentacoordinate silyl triflimides bearing BINOL ligands can be ascribed in part to the weak coordination of NTf_2 anion to the pentacoordinate silicon atoms.

Table S11.



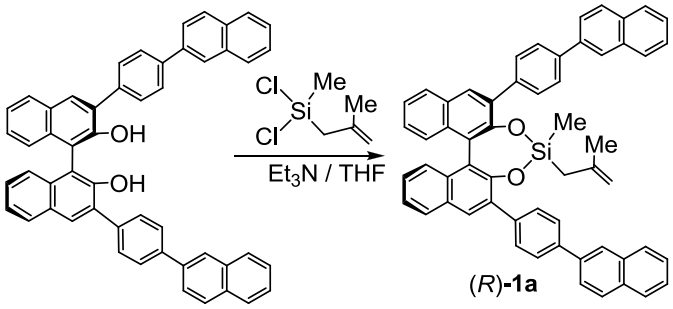
entry	catalyst	temperature (^{o}C)	reaction Time (h)	yield (%)	ee (%)
1	1**b**/$HNTf_2$ (5 mol %)	-78	6	85	69
2	1**e**/$HNTf_2$ (5 mol %)	-78	6	27	57
3	1**e**/$HNTf_2$ (15 mol %)	-78	48	86	56
4	1**e**/$HNTf_2$ (5 mol %)	-20	12	88	25

(5) Experimental Procedures and Spectral Data

General Methods. All Manipulations were carried out under nitrogen atmosphere using Schlenk tube technique. ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{29}SI (60 MHz) NMR spectra were recorded on a BRUKER-300 spectrometer. Chemical shifts are reported in parts per miliion (ppm) down field from TMS, using residual $CDCl_3$ (7.26 ppm) and CD_2Cl_2 (5.31 ppm) for ^{1}H NMR, $CDCl_3$ (77.0 ppm) and CD_2Cl_2 (53.62 ppm) for ^{13}C NMR as internal standards respectively, and Me_4Si (0 ppm) for ^{29}Si NMR. Infrared spectra were measured on a JASCO FT/IR-230 in Nujol mulls prepared under inert atmosphere. All the melting points were measured by using Yanagimoto micro melting point apparatus under inert

atmosphere and are uncorrected. Solvents were purified as follows: tetrahydrofuran, diethylether and hexane by distillation from benzophenone ketyl under nitrogen; dichloromethane by distillation from calcium hydride. Optical rotation was measured on RUDOLPH AUTOPOL IV digital polarimeter. Analytical HPLC was performed on a Shodex Model RI-72 instrument using Daicel CHIRALPACK AD-H (4.6 × 150 mm), and Daicel CHIRALPACK OJ-H (4.6 × 150 mm). High resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Facility of Osaka City University.

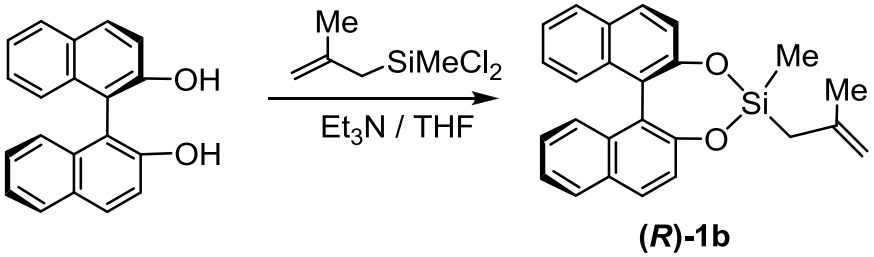
Preparation of Chiral Allylsilane (*R*)-1a.



To a solution of dichloro(2-methyl-2-propenyl)methylsilane (0.28 mL, 0.17 mmol) in THF (3 mL) was added a solution of (*R*)-3,3'-bis[4-(2-naphthyl)phenyl]-2,2'-dihydroxy-1,1'-binaphthyl (100 mg, 0.15 mmol) and triethylamine (0.061 mL, 0.44 mmol) in THF (3 mL). The solution was stirred at room temperature for 2 h. After removal of solvent under reduced pressure, the residue was extracted with dry ether (5 mL) for three times. Removal of the solvent gave **(*R*)-1a** as a colorless solid in 83% (98 mg, 0.12 mmol), which was recrystallized from toluene: mp 196-200 ^{o}C; $[\alpha]^{23}_{D}$ -271.6 (*c* 1.25, $CHCl_3$), IR (nujol) 3054, 2962, 1420, 1258, 811 cm^{-1}; ^{1}H NMR(300 Mz, CD_2Cl_2); δ –0.17 (s, 3H), 1.14 (d, *J* = 13.4 Hz), 1.43 (s, 3H), 1.45(d, *J* = 13.4 Hz, 1H), 4.21 (m, 1H), 4.42 (m, 1H), 7.26-7.33 (m, 4H), 7.44-7.55 (6H), 7.84-8.03 (m, 18H), 8.13-8.16 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, 24.6, 24.8, 111.1, 122.92, 123.16, 124.74, 124.78, 125.58, 125.80, 126.12, 126.22, 126.25, 126.48, 126.98, 127.09, 127.16, 127.8, 128.4, 128.46, 128.48, 128.62, 130.09, 130.26, 130.56, 130.68, 130.71, 132.80, 133.41, 133.85, 134.16, 134.25, 137.46, 132.65, 138.26, 130.90, 139.95, 140.02,

148.11, 148.21; ^{29}Si NMR (60 Mz, C_6D_6) δ 8.31; HRMS (FAB+) calcd for $C_{57}H_{42}O_2Si$: M^+ 786.2956, found 786.2955.

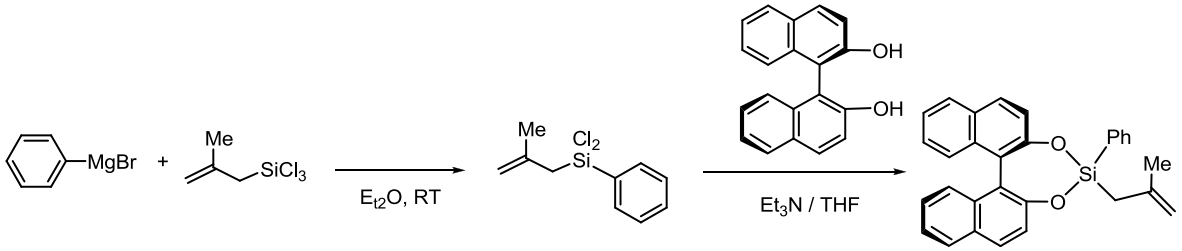
Preparation of Chiral Allylsilane (*R*)-1b.



(*R*)-1b

To a solution of dichloro(2-methyl-2-propenyl)silane (2.0 mL, 12.5 mmol) in THF (50 mL) was added a solution of triethylamine (4.35 mL, 31.2 mmol) and (*R*)-1,1'-bi(2-naphthol) (2.98 g, 10.4 mmol) in THF (50 mL). The solution was stirred at room temperature for 2 h, and then filtered to remove triethylammonium salt. After removal of the solvent, residue was extracted with dry pentane (30 mL) for three times. Removal of the solvent under reduced pressure gave **(*R*)-1b** as a colorless solid in 85% (3.38 g), which was recrystallized from hexane: mp 198 ^{o}C; $[\alpha]^{23}_{D}$ -342.3 (*c* 1.21, $CHCl_3$), IR (nujol) 3050, 2961, 1617, 987, 857 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 3H), 1.72-1.74 (m, 5H), 4.66 (m, 1H), 4.69 (m, 1H), 7.13-7.31 (m, 8H), 7.13-7.14 (m, 4H), 7.24-7.31 (m, 4H), 7.80-7.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.0, 25.2, 25.3, 111.6, 121.4, 121.6, 121.8, 121.9, 124.3, 126.0, 126.1 127.0, 127.1, 128.2, 130.1, 130.2, 130.4, 130.5, 133.6, 140.0, 150.3, 150.4 ; ^{29}Si NMR (60 Mz, $CDCl_3$) δ 7.51; HRMS (FAB+) calcd for $C_{25}H_{22}O_2Si$: M^+ 382.1389, found 382.1390.

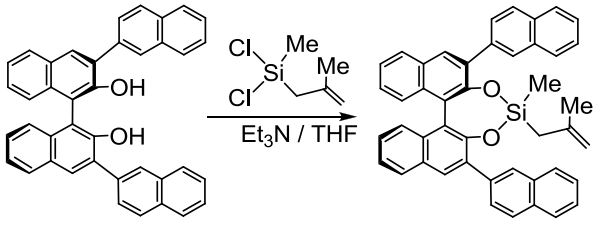
Preparation of Chiral Allylsilane (*R*)-1c.



(*R*)-1c

To a solution of PhMgBr (6.9 mmol) in Et_2O (13 mL) was added a solution of trichloro(2-methyl-2-propenyl)silane (1.1 mL, 6.9 mmol) in Et_2O (3 mL). The resulting solution was stirred for 4 h at room temperature. After removal of solvent under reduced pressure, the residue was extracted with dry hexane (10 mL) for three times. After removal of the solvent, crude product was subjected to bulb-to-bulb distillation (50-65 ^oC/20 mmHg) gave dichloro(2-methyl-2-propenyl)phenylsilane in 36% yield (0.52 mL). ^1H NMR (CD_2Cl_2); δ 1.75 (m, 3H), 2.37 (d, *J*=1.0Hz, 2H), 4.70 (m, 1H), 4.82 (m, 1H), 7.46-7.57 (m, 3H), 7.75-7.77 (m, 2H). To a solution of dichloro(2-methyl-2-propenyl)phenylsilane (1.0 mL, 4.8 mmol) in THF (50 mL) was added a solution of triethylamine (2.0 mL, 14.4 mmol) and (*R*)-1,1'- bi(2-naphthol) (1.4 g, 4.8 mmol) in THF (50 mL). The solution was stirred at room temperature for 2 h, and then filtered to remove triethylammonium salt. After removal of the solvent, residue was extracted with dry ether (30 mL) for three times. Removal of the solvent under reduced pressure gave **(*R*)-1c** as a colorless solid in 84% (1.79 g), which was recrystallized from toluene: mp 110-115 ^oC; $[\alpha]^{23}_D$ -170.6 (*c* 1.26, $CHCl_3$), IR (nujol) 3069, 2961, 1324, 964, 821 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$); δ 1.43-1.72 (m, 3H), 2.08 (s, 2H), 4.64 (s, 2H), 7.20-7.13 (m, 5H), 7.32 -7.51 (m, 11H), 7,64 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.81 (dd, *J* = 18.9, 8.4 Hz, 2H), 7.96 (dd, *J* = 19.3, 8.8 Hz, 2H) ; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 24.1, 25.29, 112.3, 121.4, 121.5, 122.15, 122.2, 124.3, 124.4, 126.0, 126.1, 127.1, 127.2, 128.0, 128.2, 130.1, 130.1, 130.4, 130.5, 130.5, 131.2, 133.5, 133.7, 134.4, 139.7, 150.34; ^{29}Si NMR (60 Mz, $CDCl_3$) δ -10.54; HRMS (FAB+) calcd for $C_{30}H_{24}O_2Si$: M^+ 444.1546, found 444.1538.

Preparation of Chiral Allylsilane (*R*)-1d

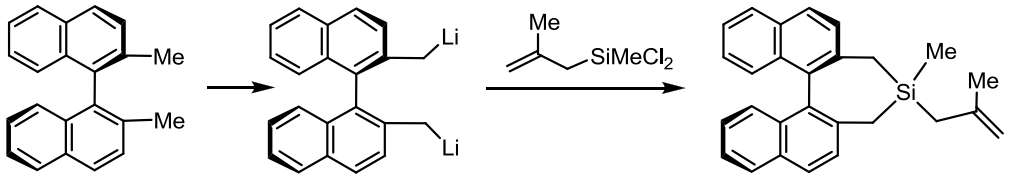


(*R*)-**1d**

To a solution of dichloro(2-methyl-2-propenyl)methylsilane (0.49 mL, 0.31

mmol) in THF (5 mL) was added a solution of triethylamine (0.12 mL, 0.84 mmol) and (*R*)-3,3'-bis(2-naphthyl)-2,2'-dihydroxy-1,1'-binaphthyl (150 mg, 0.28 mmol). The solution was stirred at room temperature for 2 h. After removal of solvent under reduced pressure, resulting residue was extracted with dry ether (5 mL) for three times. Removal of the solvent gave **(*R*)-1d** as a colorless solid in 97% (173 mg), which was recrystallized from toluene: mp 130-135 ^{o}C; $[\alpha]^{23}_{D}$ -302.4 (*c* 0.98, $CHCl_3$), IR (nujol) 3051, 2963, 1494, 1254, 1100, 798 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$); δ -0.33 (s, 3H), 0.92 (d, *J* = 14.3 Hz, 1H), 1.21 (s, 3H), 1.33 (d, *J* = 14.3 Hz, 1H), 4.00 (s, 1H), 4.20 (s, 1H), 7.25-7.40 (m, 3H), 7.40-7.55 (m, 6H), 7.79-7.94 (m, 9H), 7.99 (d, *J* = 8.10 Hz, 2H), 8.13-8.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.8, 24.5, 24.7, 110.9, 123.0, 123.2, 124.8, 124.9, 126.09, 126.15, 126.23, 126.27, 127.06, 127.14, 127.43, 127.51, 127.73, 128.33, 128.35, 128.41, 128.43, 128.48, 128.89, 128.99, 130.52, 130.57, 130.63, 130.70, 132.68, 133.40, 133.42, 133.50, 134.51, 134.54, 135.91, 136.18, 139.63, 148.18, 148.26; ^{29}Si NMR (60 Mz, C_6D_6) δ 8.17; HRMS (FAB+) calcd for $C_{45}H_{34}O_2Si$: M^+ 634.2328, found 634.2318.

Preparation of chiral allylsilane (*R*)-1e.



(*R*)-1e

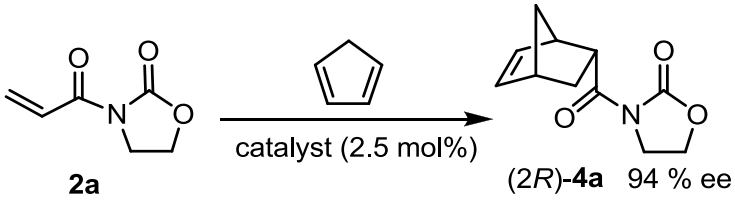
To a flame-dried flask under N_2 atmosphere, 5.6 mL of a 1.58 M *n*-BuLi (8.85 mmol) in hexane was charged, and hexane was removed under reduced pressure to give white solid. Dry Et_2O (20 mL) was added. To this solution, a solution of (*R*)-2,2'-dimethyl-1,1'-binaphthyl (1.0 g, 3.54 mmol) dissolved in Et_2O(10 mL) was added at 0 ^{o}C and stirred for 14 h at room temperature. Freshly distilled TMEDA (1.3 mL, 8.85 mmol) was added and resulting brown solution was allowed to stand for 12 h. After removal of the solvent under reduced pressure, the residue was washed by dry pentane (10 mL × 2). Dry THF (10 mL) was added and the solution was cooled to 0 ^{o}C. To the solution, dichloro(2-methyl-2-propenyl)silane (0.40 mL, 2.12 mmol) was added and stirred for 14 h.

After removal of the solvent, the crude product was purified by silica gel column chromatography using hexane to give pure (*R*)-**1e** as a white solid in 41% yield (0.536 g) : mp 118 ^{o}C; $[\alpha]^{23}_{D}$ -112.6 (*c* 1.00, $CHCl_3$), IR (KBr) 3042, 2926, 1649, 1511, 1253, 1160, 842 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ -0.038 (s, 3H), 1.48 (d, *J* = 13.5 Hz, 1H), 1.59 (d, *J* = 13.5 Hz, 1H), 1.63 (s, 3H), 1.78 (d, *J* = 13.2 Hz, 1H), 1.87 (s, 2H), 1.96 (d, *J* = 13.2 Hz, 1H), 4.48 (s, 1H), 4.58 (s, 1H), 7.06-7.16 (m, 4H), 7.27-7.37 (m, 4H), 7.76-7.83 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.0, 22.5, 23.1, 25.2, 25.4, 109.5, 124.4, 125.9, 126.5, 127.9, 128.2, 131.9, 132.5, 132.8, 136.7, 136.9, 142.7.; ^{29}Si NMR (60 Mz, CD_2Cl_2) δ 17.2; HRMS (FAB+) calcd for $C_{27}H_{26}Si$: M^+ 378.1804, found 378.1808.

Procedure for the Diels-Alder Reaction Catalyzed by Silyl Triflimides

Procedure for the Diels-Alder Reaction Catalyzed by Silyl Triflimides (Table 1, Entries 6-13)

3-[(1*R*,2*R*,4*R*)-Bicyclo[2.2.1]hept-5-enecarbo-nyl]oxazolidin-2-one (**3a**).[11] (Table 1, Entry 5)

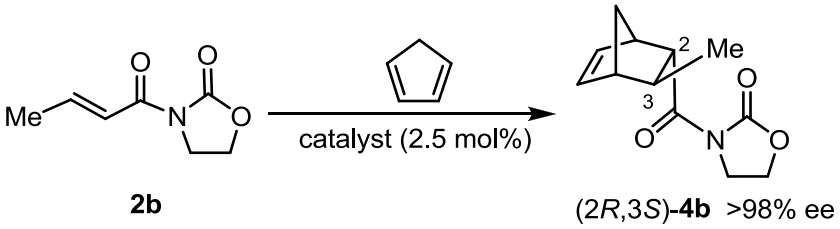


2a (2*R*)-**4a** 94 % ee

To a solution of allysilane (*R*)-**1a** (157 mg, 0.20 mmol) in toluene (10 mL) was added a solution of trifluoromethanesulphonimide ($HNTf_2$) (0.5 M in toluene, 0.4 mL, 0.20 mmol) at room tempereature. After stirring for 2 h at room temperature, the solution was cooled to -78 ^{o}C. A solution of 3-(2-propenoyl)oxazolidin-2-one (1.13 g, 8 mmol) in toluene (20 mL) was added dropwise at -78 ^{o}C, followed by addition of cyclopentadiene (2.0 mL, 1.59 g, 24 mmol). Stirring was continued for 6 h at -78 ^{o}C and at the end of reaction, triethylamine (1 mL) was added. Evaporation under reduced pressure afforded a brown oil which was purified by column chromatography on silica gel (EtOAc: hexane = 1 : 1) to yield 1.59 g of **4a** as a colorless solid (7.68 mmol, 96%). ^{1}H NMR analysis of the crude products indicated

endo/exo ratio was > 97/3. The enantiomeric excess (94% ee) was determined through chiral HPLC analysis (Daicel AS-H column; flow rate 0.5 mL/min; hexane:*i*-PrOH = 50 : 1; *endo* 2S t_R = 22.8 min, *endo* 2*R* t_R = 33.5 min). Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{25}_D$ +141.8 (*c* 1.0, $CHCl_3$); (lit.[11] $[\alpha]^{25}_D$ +145.4 (*c* 1.04, $CHCl_3$), 94% ee)

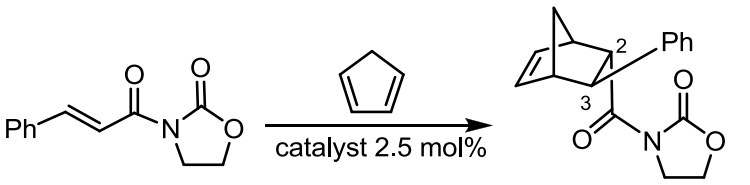
3-[(1*R*,2*R*,3*S*,4*S*)-3-Methylbicyclo[2.2.1]hept-5-enecarbonyl]oxazolidin-2-one (4b).[13]



2b (2*R*,3*S*)-**4b** >98% ee

^{1}H NMR analysis of the crude products indicated that the *endo*/*exo* ratio was 98/2. The enantiomeric excess of **4b** (>98% ee) was determined through chiral HPLC analysis (Daicel AD-H column; flow rate 0.5 mL/min; hexane:*i*-PrOH = 50 : 1; *endo* 2*R*,3*S* t_R = 53.2 min, *exo* major t_R = 48.5 min). Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{23}_D$ +167.1 (*c* 1.00, $CHCl_3$); (lit.[13] $[\alpha]^{25}_D$ -158.6 (*c* 1.02, $CHCl_3$), 93% ee).

3-[(1*R*,2*R*,3*S*,4*S*)-3-Phenylbicyclo[2.2.1]-hept-5-enecarbonyl]oxazolidin-2-one (4c).[12]

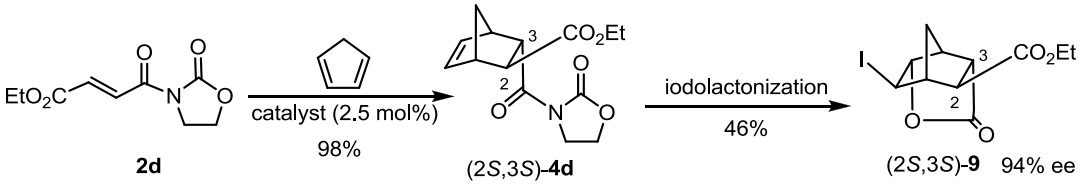


2c (2*S*,3*S*)-**4c** 94 % ee

To a solution of allysilane (*R*)-**1a** (95 mg, 0.12 mmol) in toluene (8 mL) was added a solution of trifluoromethanesulphonimide ($HNTf_2$) (0.5 M in toluene, 0.24 mL, 0.12 mmol) at room temperature. After stirring for 2 h at room temperature, the solution was cooled to -20 ^oC. A solution of 3-((*E*)-cinnamoyl)oxazolidin-2-one (1.0 g, 4.8 mmol) in CH_2Cl_2 (16 mL) was added dropwise at -20 ^oC, followed by addition of cyclopentadiene (1.2 mL, 14.4 mmol). Stirring was continued for 24 h at -20 ^oC and at the end of reaction, triethylamine (1 mL)

was added. Evaporation under reduced pressure afforded a brown solid which was purified by column chromatography on silica gel (EtOAc: hexane = 3 : 2) to yield 1.25 g of **4c** as a colorless solid (4.4 mmol, 92%). ^{1}H NMR analysis of the crude products indicated that the *endo*/*exo* ratio was 96/4. The enantiomeric excess of **4c** (94% ee) was determined through chiral HPLC analysis (Daicel AS-H column; flow rate 1.0 mL/min; hexane:*i*-PrOH = 25 : 1; *endo* 2*S*,3*S* t_R = 26.5 min, *endo* 2*R*,3*R* t_R = 35.3 min). Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{23}_D$ +165.6 (*c* 1.20, CCl_4); (lit.[12] $[\alpha]^{25}_D$ -143 (*c* 1.20, CCl_4), 81% ee).

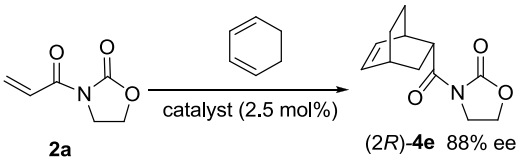
Ethyl [(1*S*,2*S*,3*S*,4*R*)-3-(2-oxazolidinone-3-carbonyl)bicyclo[2,2,1]hept-5-ene-2-carboxylate] (**4d**).[1a]



^{1}H NMR analysis of the crude products indicated that the *endo*/*exo* ratio was 72/28. The enantiomeric excess and the absolute configuration of *endo* **4d** (94% ee) were determined by conversion to iodolactone **9** according to literature procedure.[14] **9:** $[\alpha]^{23}_D$ -39.4 (*c* 1.95, $CHCl_3$); (lit.[15] $[\alpha]^{25}_D$ -39.2 (*c* 4.65, $CHCl_3$), (2*S*,3*S*)-**9** isomer, 94% ee).

1

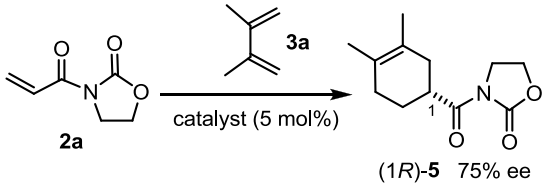
3-((1*R*,2*R*,4*R*)-Bicyclo[2.2.1]oct-5-enecarbonyl)oxazolidin-2-one (**4e**)[1b]



^{1}H NMR analysis of the crude products indicated that the *endo*/*exo* ratio was 98/2. The enantiomeric excess of **4e** (88% ee) was determined through chiral HPLC analysis (Daicel AD-H column; flow rate 1.0 mL/min; hexane:*i*-PrOH = 50 : 1; *endo* 2*R* t_R = 27.6 min, *endo* 2*S* t_R = 36.4 min). Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{23}_D$ +48.6 (*c* 1.00, CH_2Cl_2); (lit.[1b] $[\alpha]^{25}_D$ -51.6 (*c* 3.56, CH_2Cl_2),

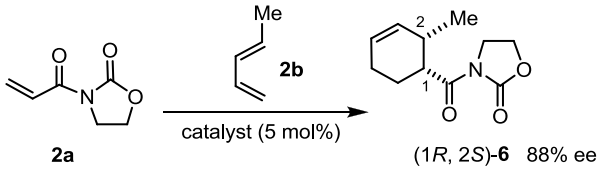
93% ee, 2*S*).

(*R*)-3-(3,4-Dimethylcyclohex-3-enecarbonyl)oxazolidin-2-one (**5**).[1b]



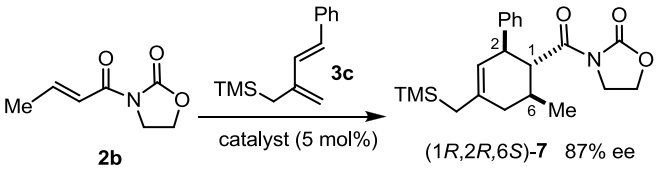
The enantiomeric excess of **5** (75% ee) was determined through chiral HPLC analysis (Daicel AD-H column; flow rate 1.0 mL/min; hexane:*i*-PrOH = 50 : 1; *S* t_R = 16.4 min, *R* t_R = 21.1 min). Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{23}_D$ +43.5 (*c* 1.00, CH_2Cl_2). (lit.[16] *S* isomer, 60% ee, $[\alpha]^{25}_D$ -35.7 (*c* 1.96, CH_2Cl_2)).

(1*R*,2*S*)-3-(2-Methylcyclohex-3-enecarbonyl)oxazolidin-2-one (6).[1a]



^{1}H NMR analysis of the crude products indicated that yield of compound **6** is 78% and no *trans*-isomer was formed. Recrystallization of the crude products from Et_2O/hexane gave enantiomerically pure **6** in 42% yield. The enantiomeric excess of **6** (88% ee: absolute configuration:1*R*,2*S*) purified by column chromatography (EtOAc : Hexane = 3 : 7) was determined through chiral HPLC analysis (Daicel AD-H column; flow rate 1.0 mL/min; hexane:*i*-PrOH = 50 : 1; 1*R*,2*S* t_R = 17.7 min, 1*S*,2*R* t_R = 13.2 min). Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{23}_D$ +201.3 (*c* 1.00, CH_2Cl_2). (lit.[1a] enantiomerically pure (1*S*, 2*R*)-**6**, $[\alpha]_D$ -230 (*c* 0.40, CH_2Cl_2)).

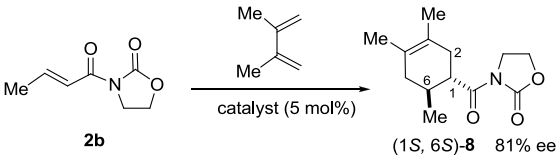
(1*R*,2*S*,6*S*)-3-[2-Phenyl-3-(trimethylsily)methyl-6-methyl-cyclohex-2-enecarbonyl]oxazolidin-2-one (7).



^{1}H NMR analysis of the crude products indicated that the *endo*/*exo* ratio was 5/95. The enantiomeric excess of **7** (88% ee: absolute configuration:1*R*,2*R*,6*S*), which was purified by column chromatography (Et_2O : Hexane = 3 : 7) was determined through chiral HPLC analysis (OJ-H column; flow rate 1.0 mL/min; hexane : EtOH = 97 : 3; *exo* (major), t_R = 19.8 min, *exo* (minor), t_R = 17.2 min,. Absolute configuration was determined in comparison with reported optical rotation: $[\alpha]^{23}_D$ -104.7 (*c* 0.01, CH_2Cl_2). (lit.[17] 1*S*,2*S*,6*R* isomer, 90% ee, $[\alpha]_D$ +110.4 (*c* 0.01, CH_2Cl_2).

Synthesis of racemic 3-(3,4,6-Trimethylcyclohex-3-enecarbonyl)oxazolidin-2-one (8) . To a suspension of $AlCl_3$ (120 mg, 0.90 mmol) in CH_2Cl_2 (5 mL) was added a solution of 3-(*trans*-crotonoyl)oxazolidin-2-one (93 mg, 0.60 mmol) in CH_2Cl_2 (5 mL) and 1,3-dimethyl-1,3-butadiene (0.34 mL, 3.0 mmol) at room temperature. After stirring for 24 h at room temperature, triethylamine (1 mL) was added. Evaporation under reduced pressure afforded a brown solid which was purified by column chromatography on silica gel (EtOAc: hexane = 3 : 7) to give 0.46 g of **8** as a colorless solid (32%). Spectral characteristics coincided with those of optically active **8**. Analysis by chiral HPLC (Daicel AD-H column; flow rate 1.0 mL/min; hexane : EtOH = 25 : 1) gave two peaks (t_R = 12.8 min and t_R = 18.7 min), which are assigned to (2*R*,6*R*)t_R and (2*S*,6*S*)t_R, respectively.

(1*S*,6*S*)-3-(3,4,6-Trimethylcyclohex-3-enecarbonyl) oxazolidin-2-one (8).



To a solution of allysilane (*R*)-**1d** (190 mg, 0.30 mmol) in toluene (10 mL) was added a solution of trifluoromethanesulphonimide ($HNTf_2$) (0.5 M in toluene, 0.60 mL, 0.30 mmol) at room temperature. After stirring for 2 h

at room temperature, the solution was cooled to -40 ^{o}C. A solution of 3-(*trans*-crotonoyl)oxazolidin-2-one (0.93 g, 6.0 mmol) in toluene (20 mL) was added at -40 ^{o}C, followed by slow addition of 1,3-dimethyl-1,3-butadiene (2.0 mL, 18 mmol) after 10 min. Stirring was continued for 24 h at -40 ^{o}C and at the end of reaction, triethylamine (1 mL) was added. Evaporation under reduced pressure afforded a brown solid which was purified by column chromatography on silica gel (EtOAc: hexane = 3 : 7) to yield 1.11 g of **8** as a colorless solid (4.68 mmol, 78%). mp 98-100 ^{o}C; $[\alpha]^{25}_{D}$ +98.6 (*c* 0.96, $CHCl_3$), IR (KBr) 2901, 1778, 1678, 1396, 1264 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.1 Hz, 3H), 1.53 (s, 6H), 1.73 (m, 1H), 1.87-2.02 (m, 2H), 2.05-2.15 (m, 2H), 3.62 (q, *J* = 6.1 Hz, 1H), 3.98 (t, *J* = 8.1 Hz, 3H), 4.34 (t, *J* = 8.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.7, 18.9, 19.4, 31.5, 35.5, 40.0, 42.9, 44.9, 61.9, 123.5, 125.2, 153.4, 177.0 ; HRMS(EI) calcd for $C_{13}H_{19}NO_3$ M^+ 237.1366, found 237.1368. The enantiomeric excess of **8** (81% ee) was determined through chiral HPLC analysis (Daicel AD-H column; flow rate 1.0 mL/min; hexane : EtOH = 25 : 1; (2*R*,6*R*)t_R = 12.7 min, (2*S*,6*S*)t_R = 17.7 min). Absolute configuration was assigned by analogy with Dieals-Alder adducts **5** and **6** provided under the same reaction conditions.

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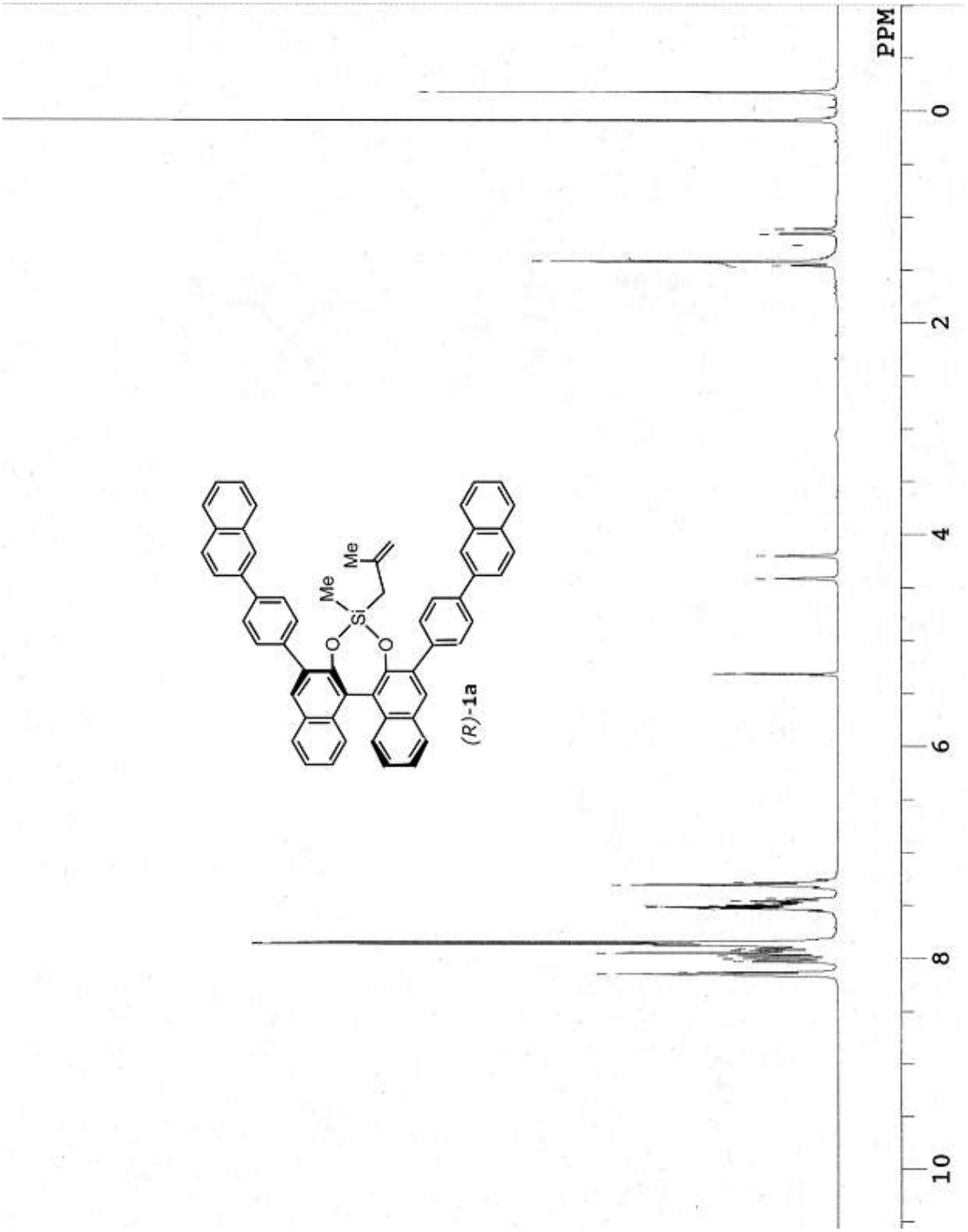
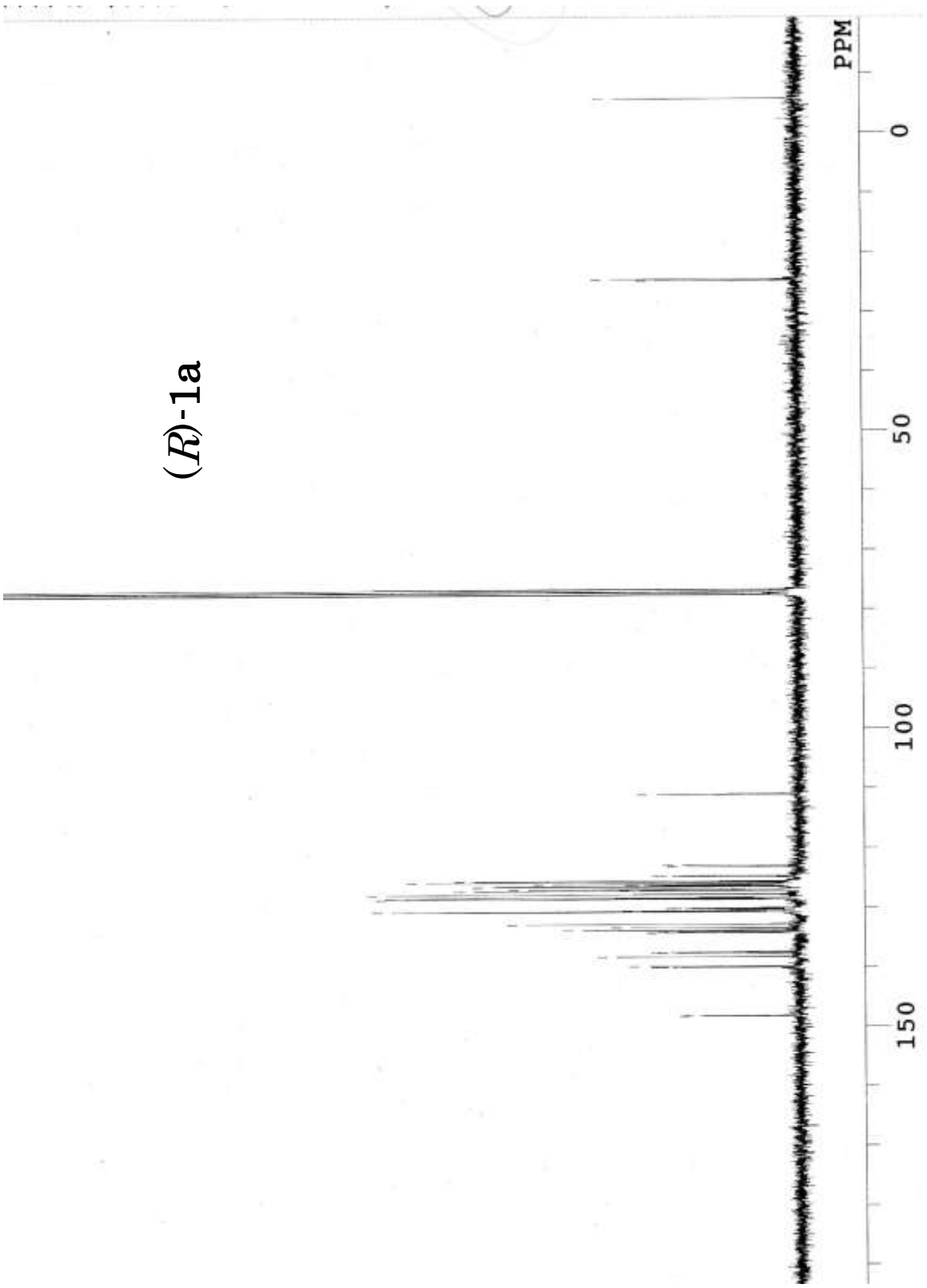
(7) ^{1}H, ^{13}C, and ^{29}Si NMR Spectra of New Compounds

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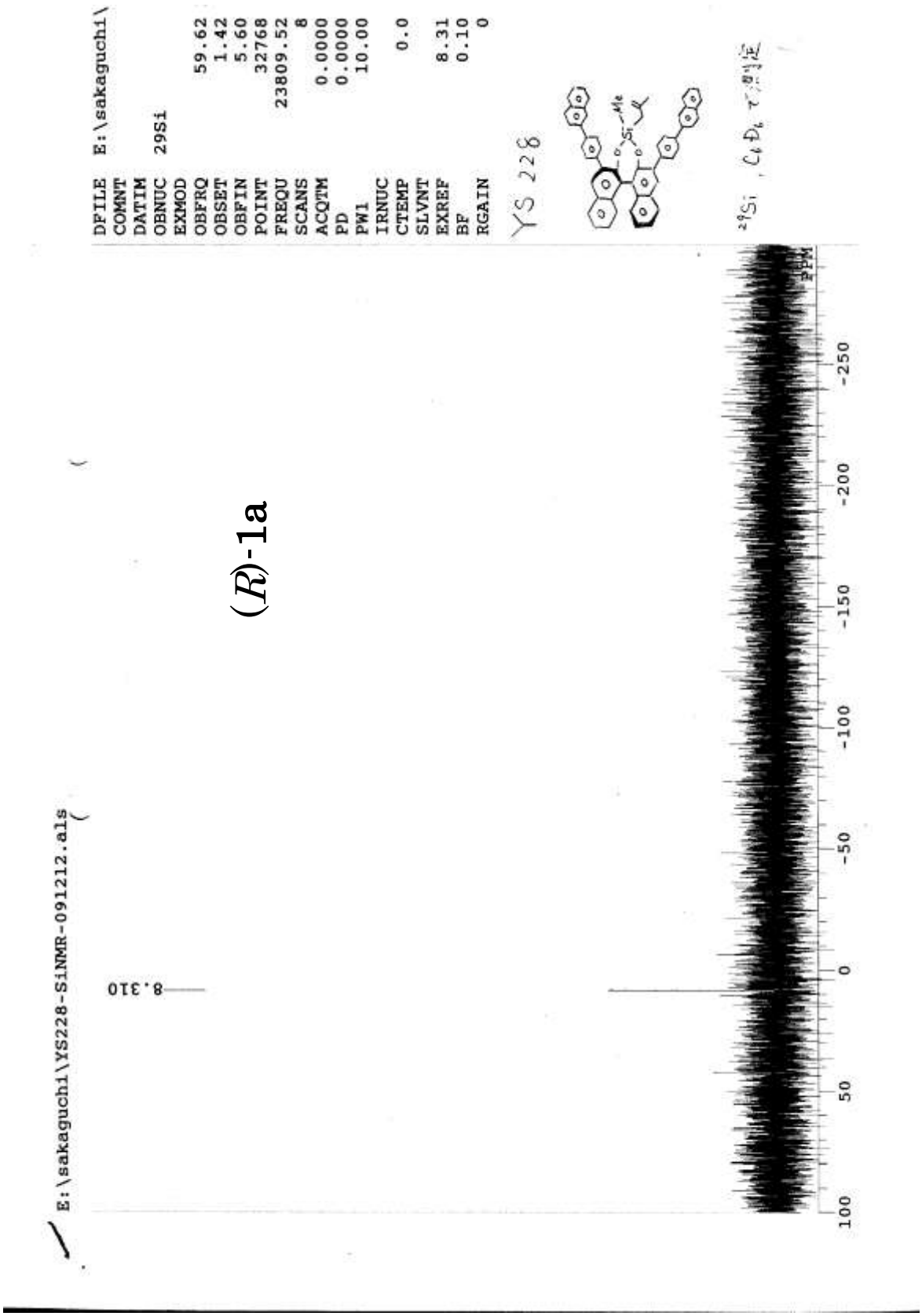
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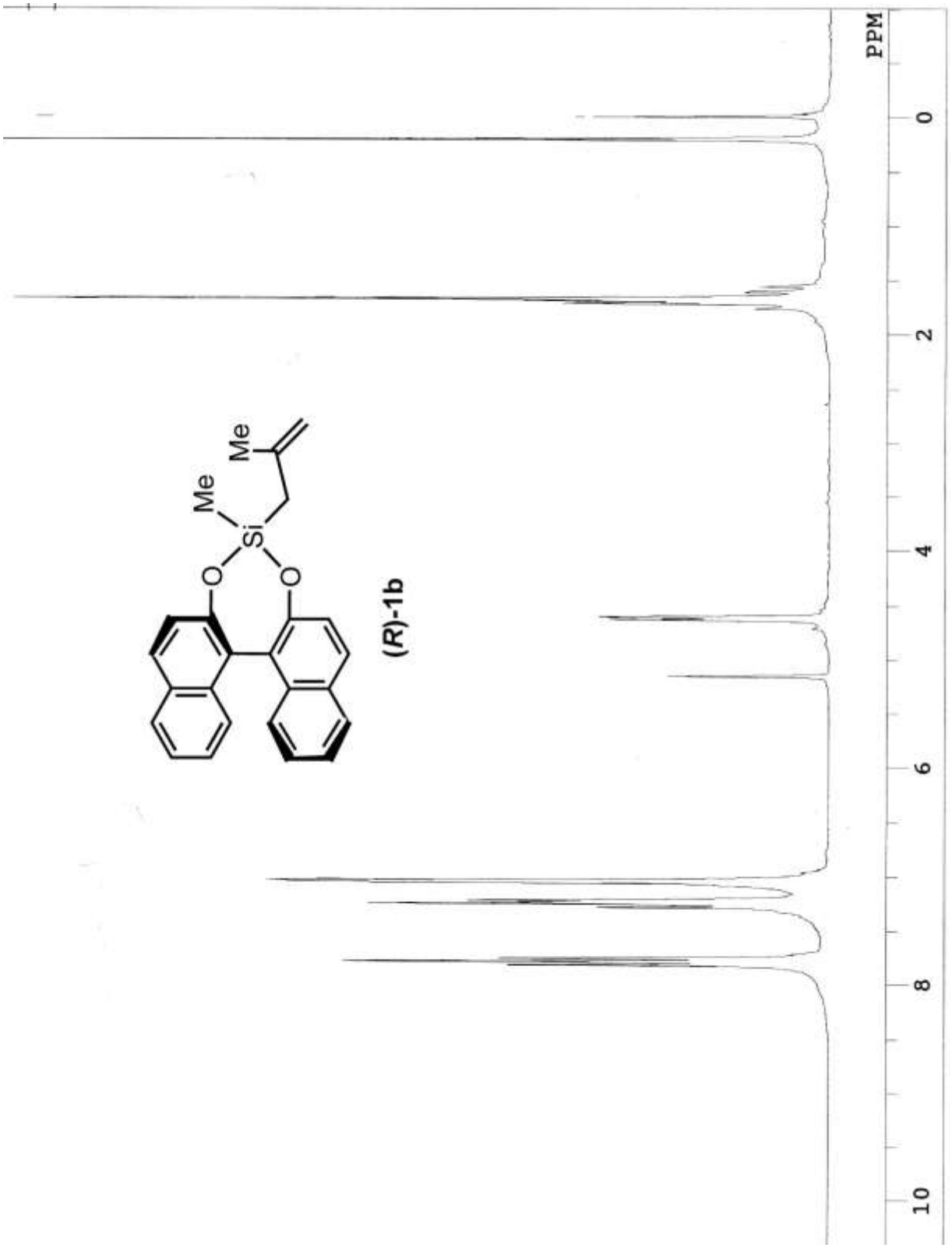
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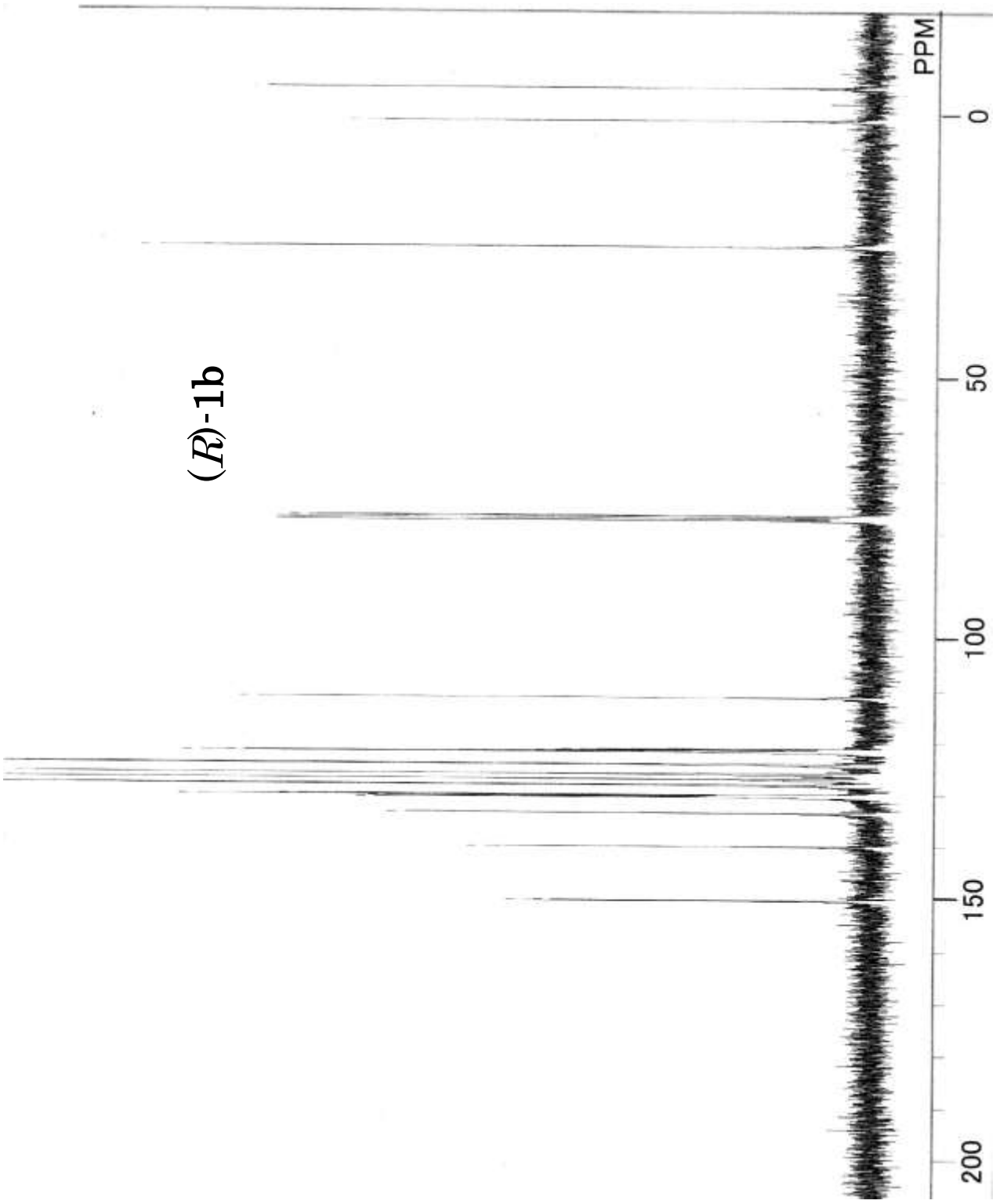
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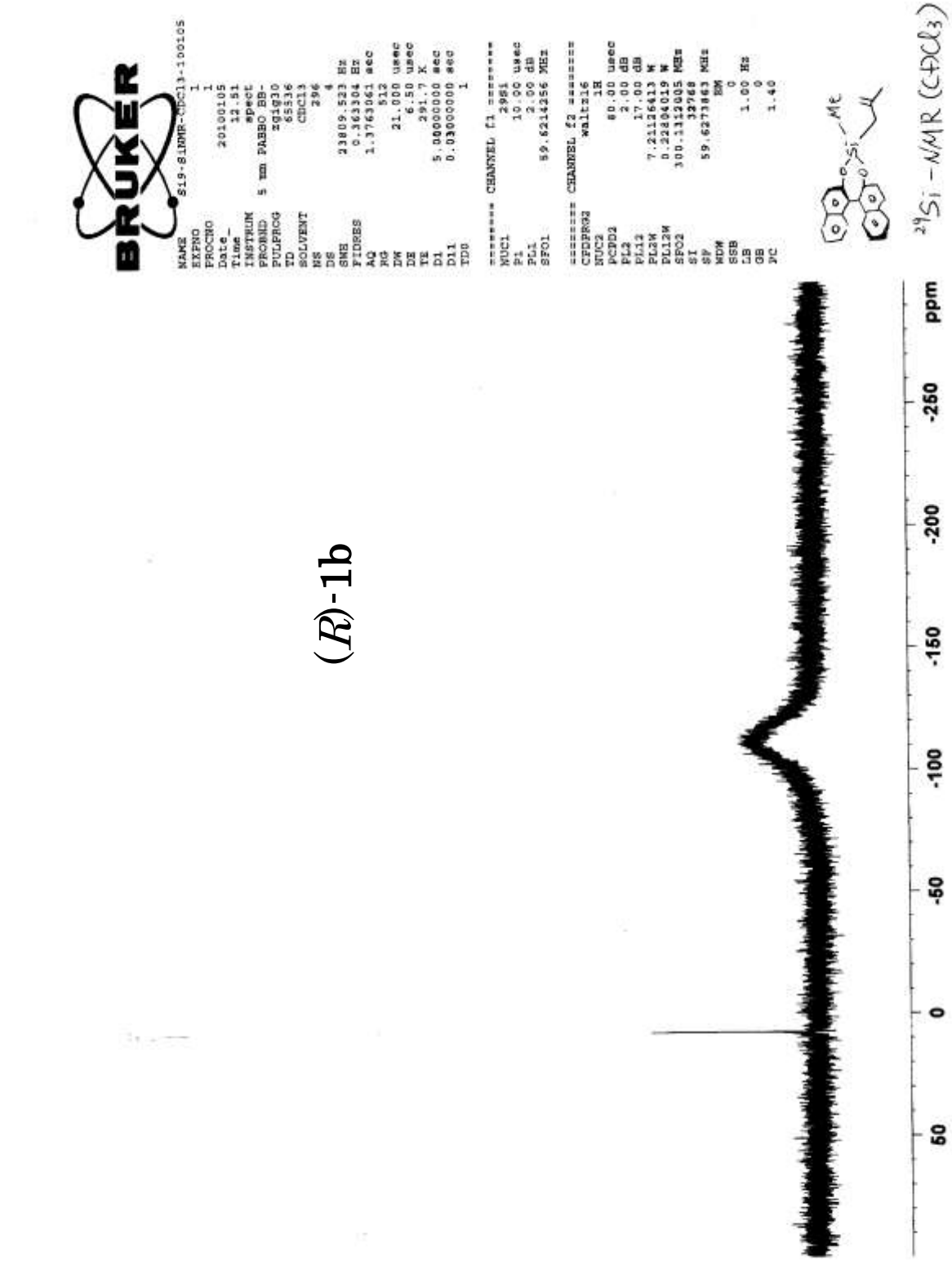
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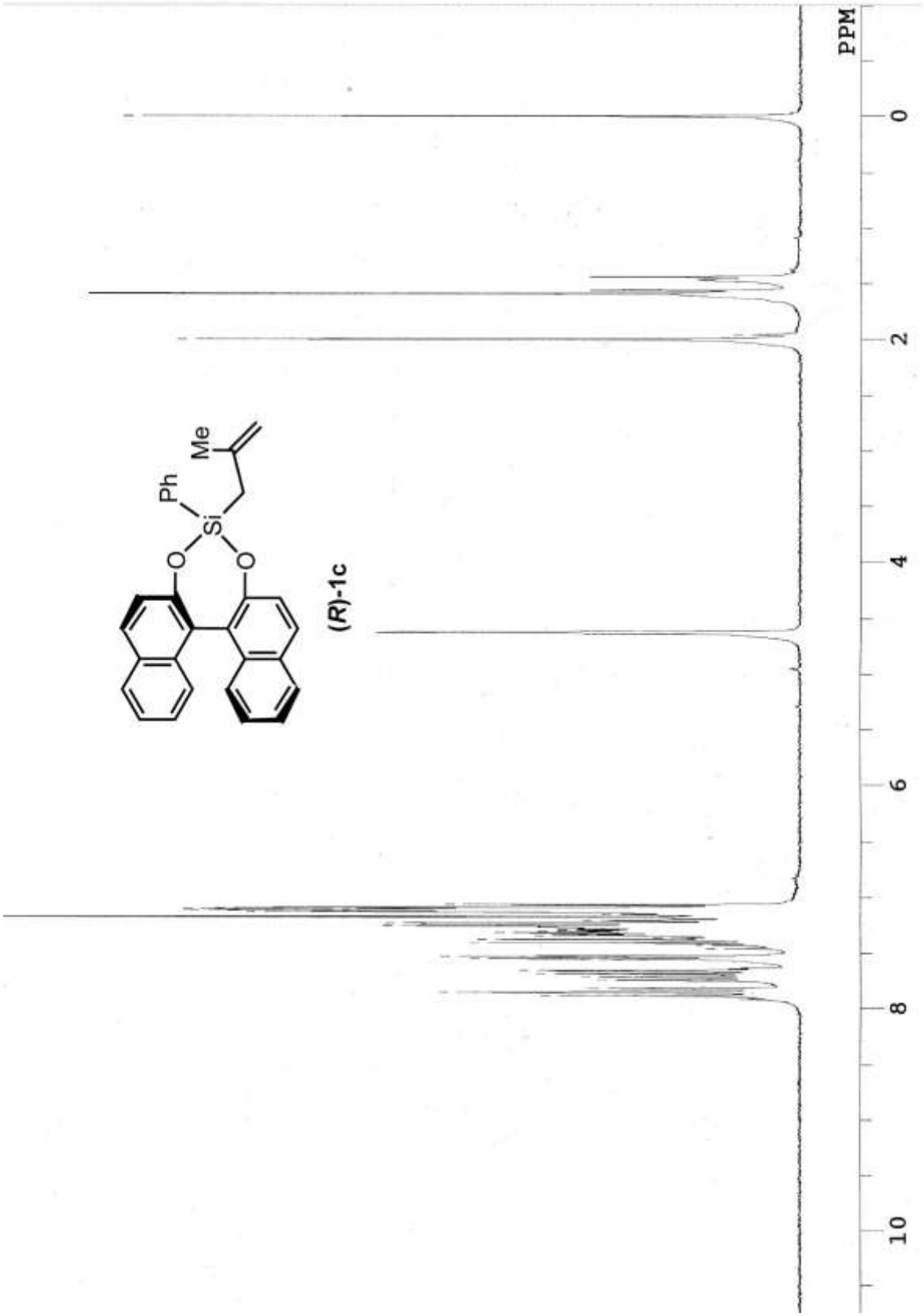
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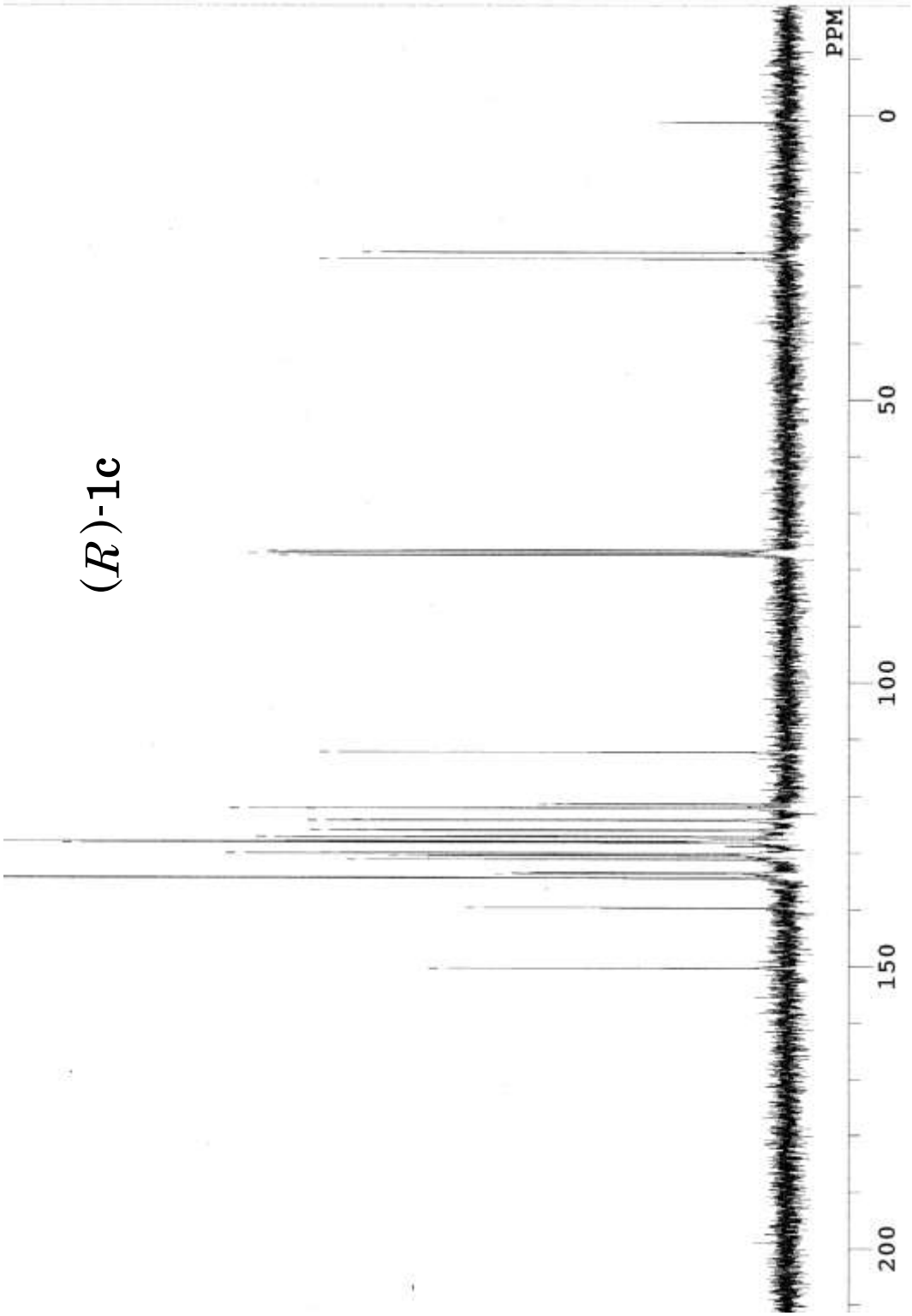
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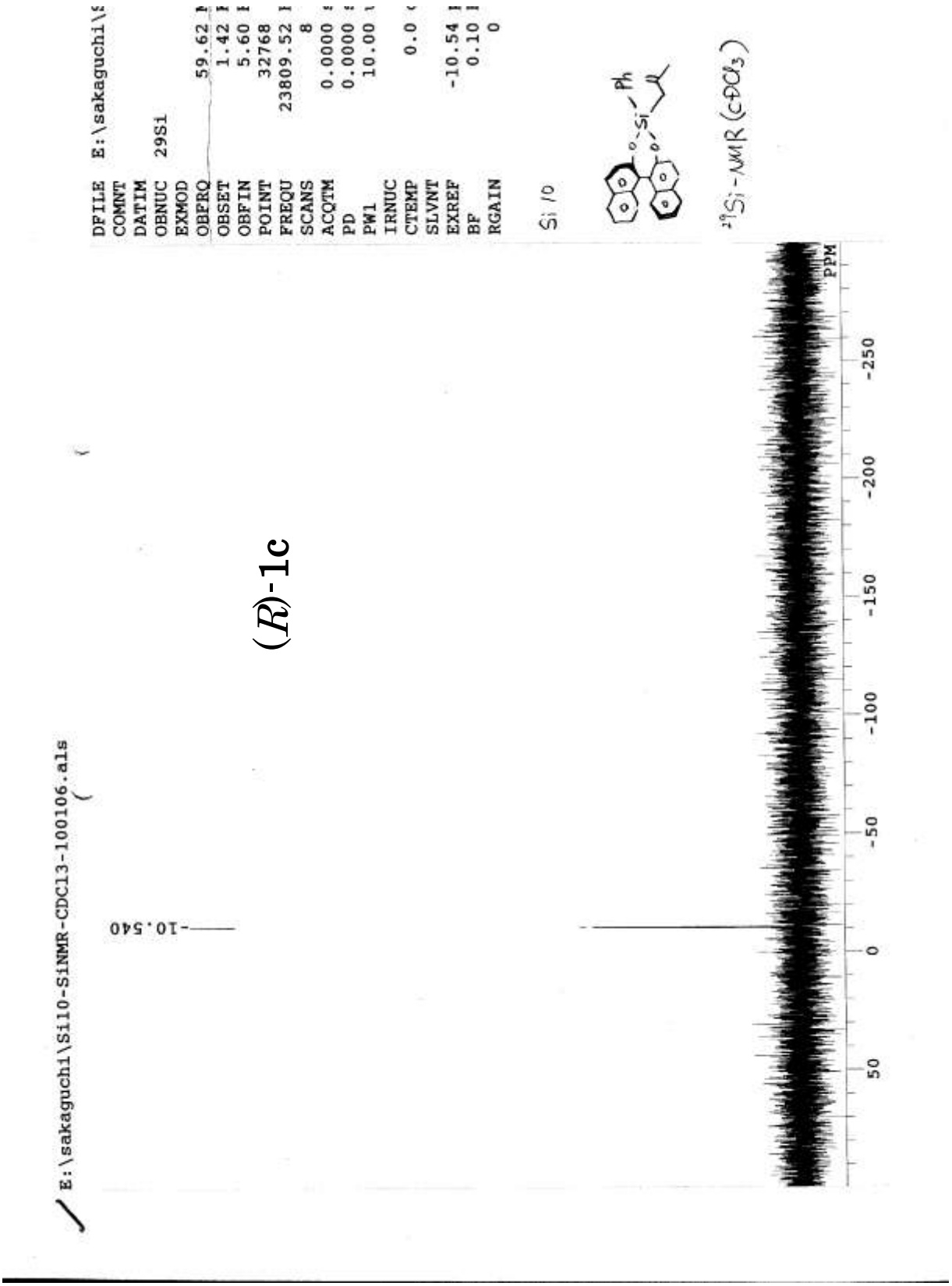
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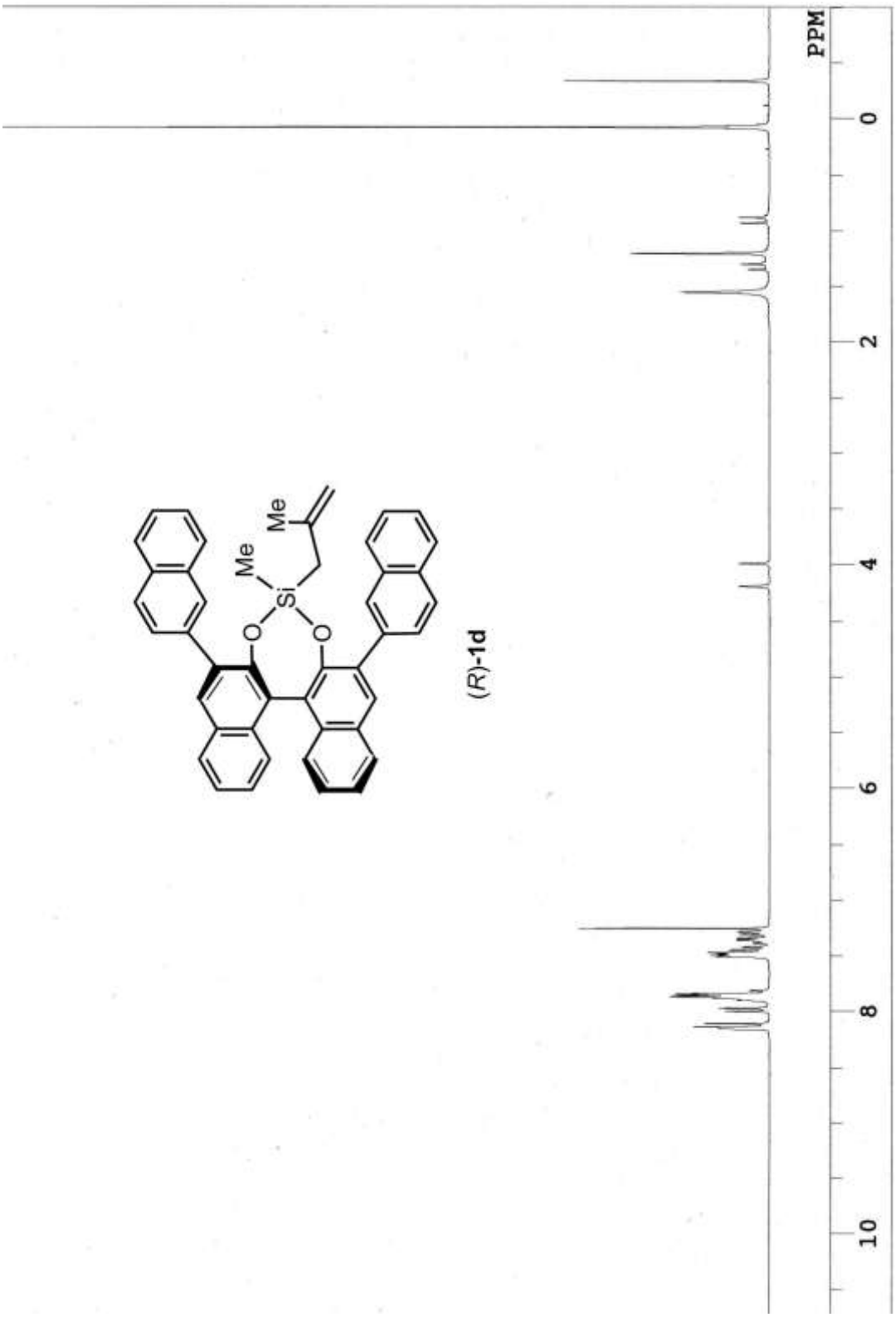
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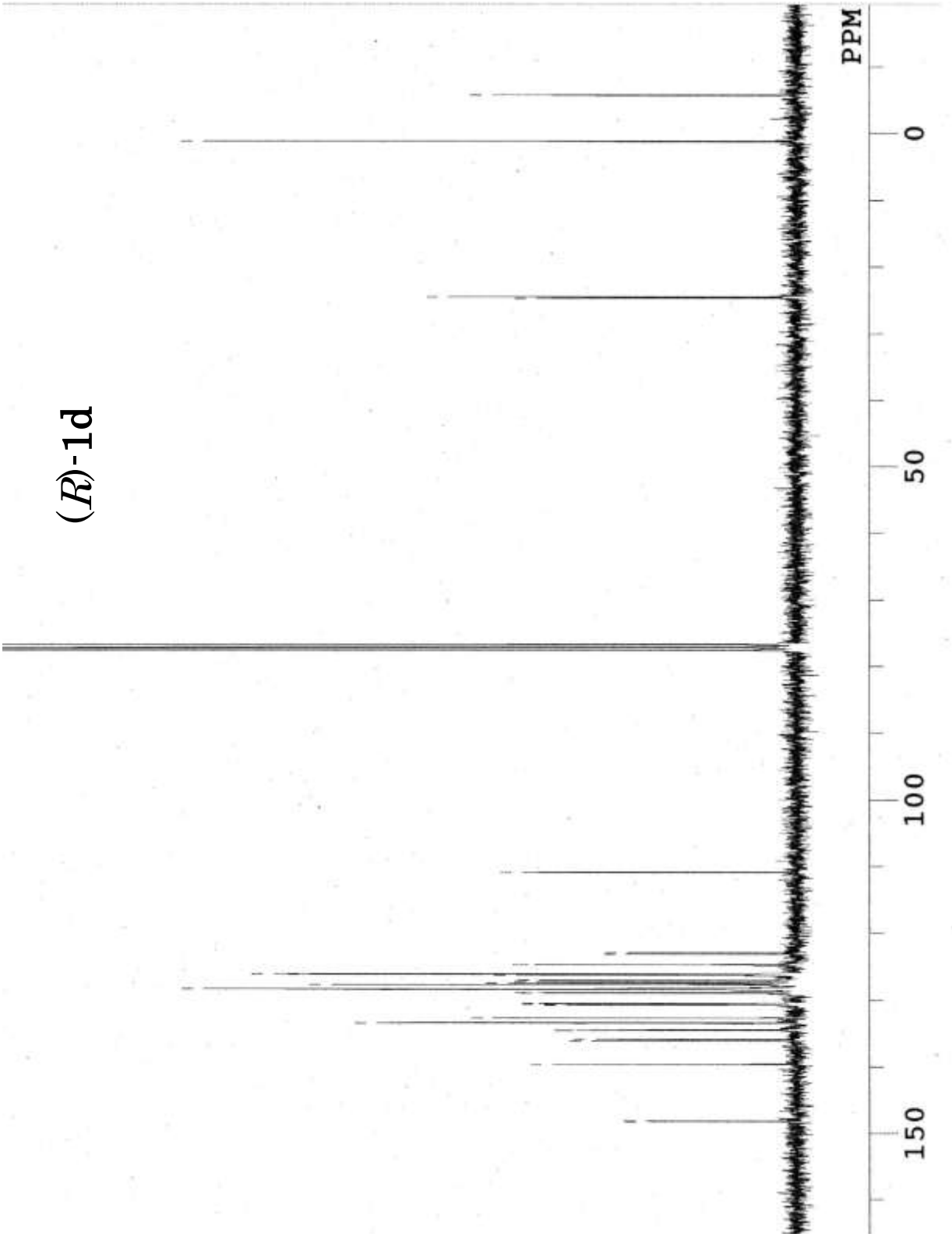
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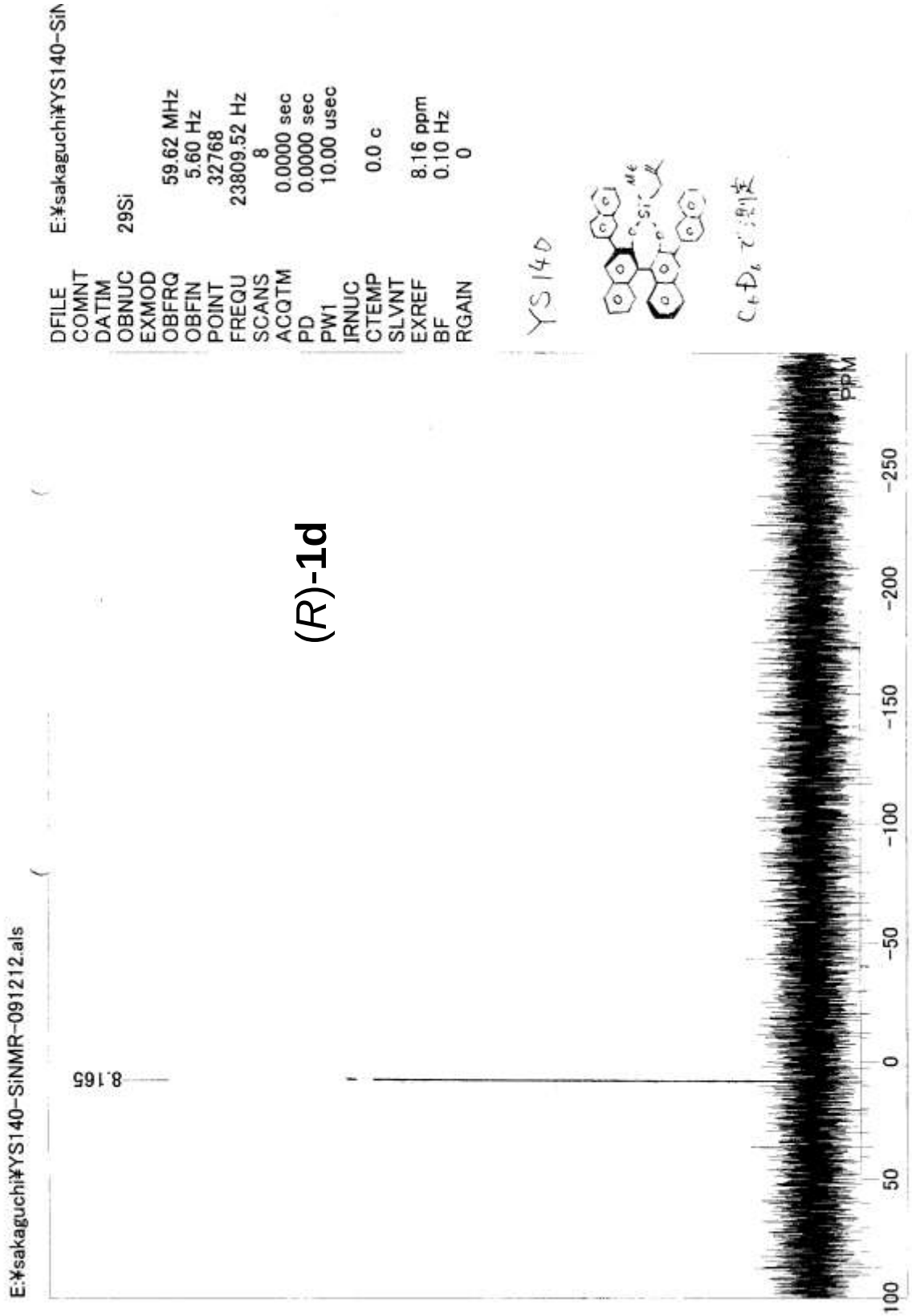
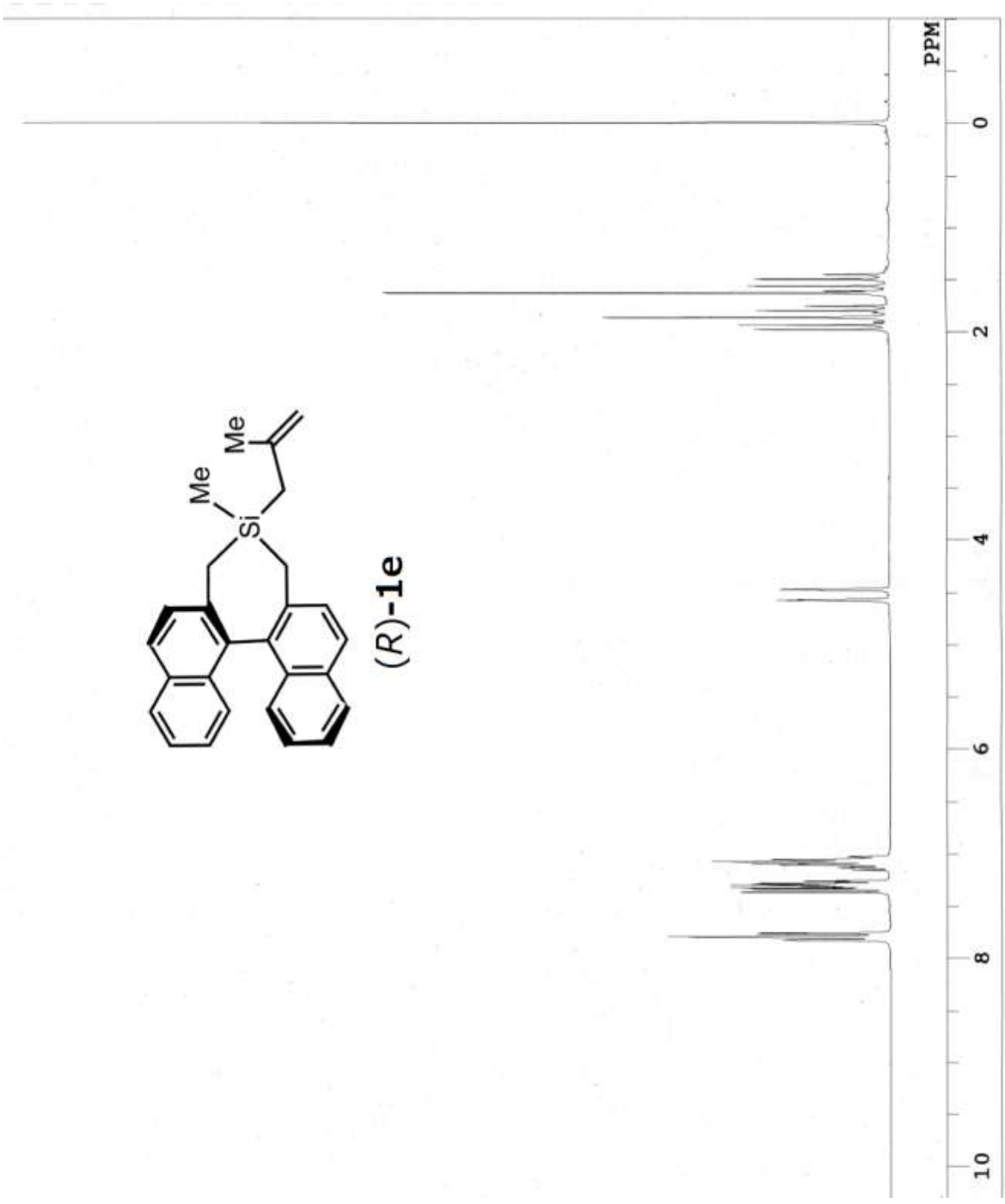
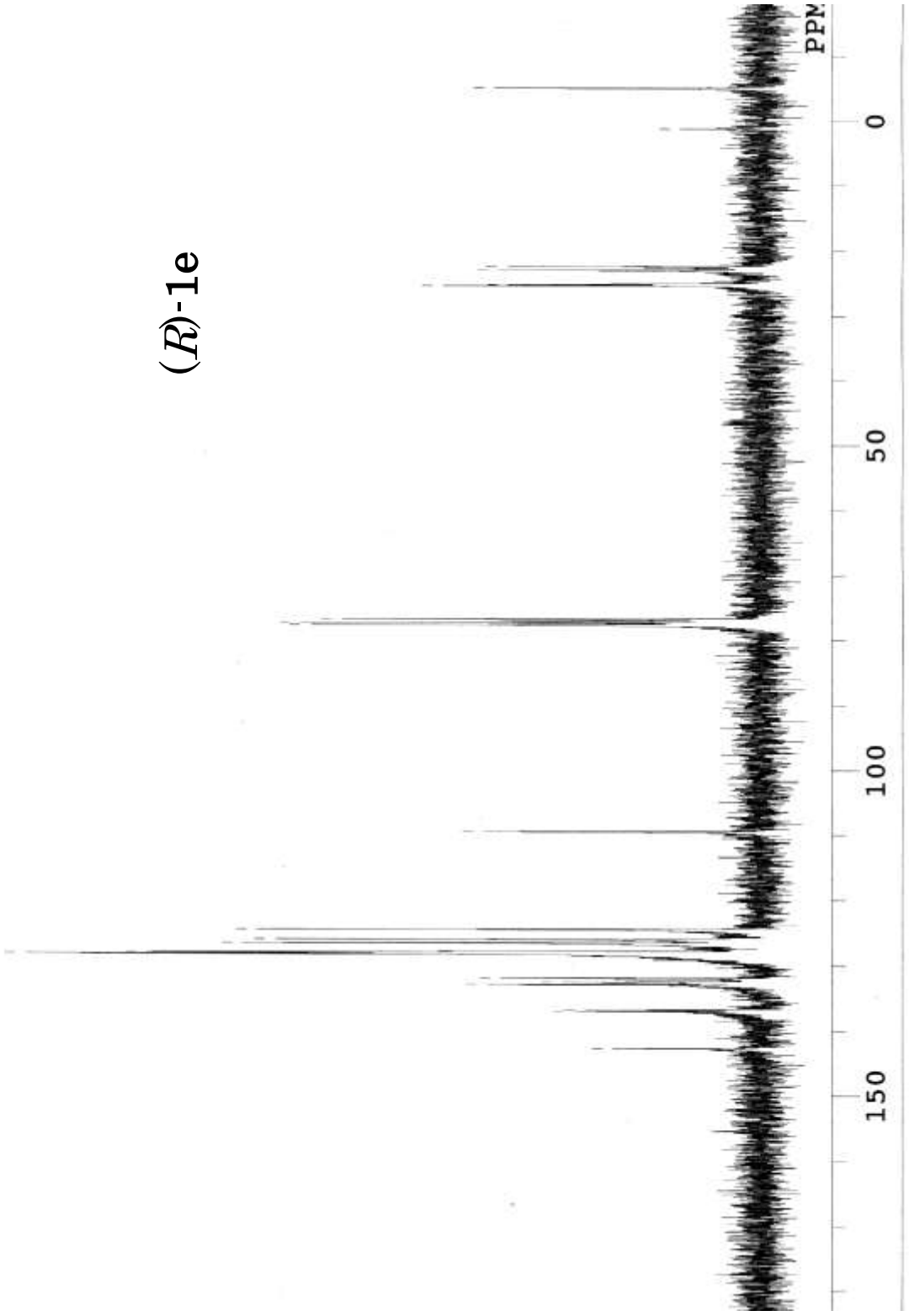
100
150

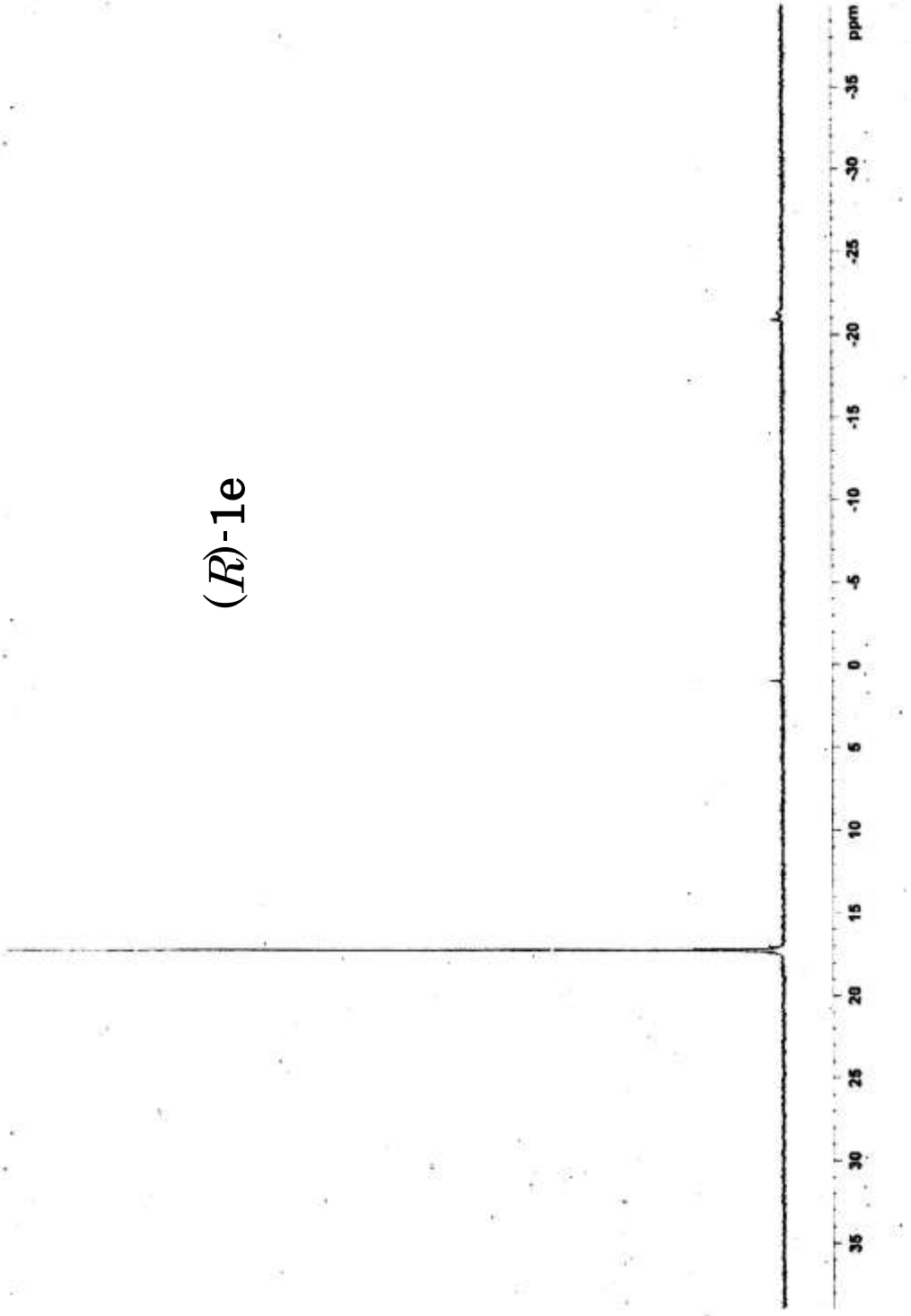


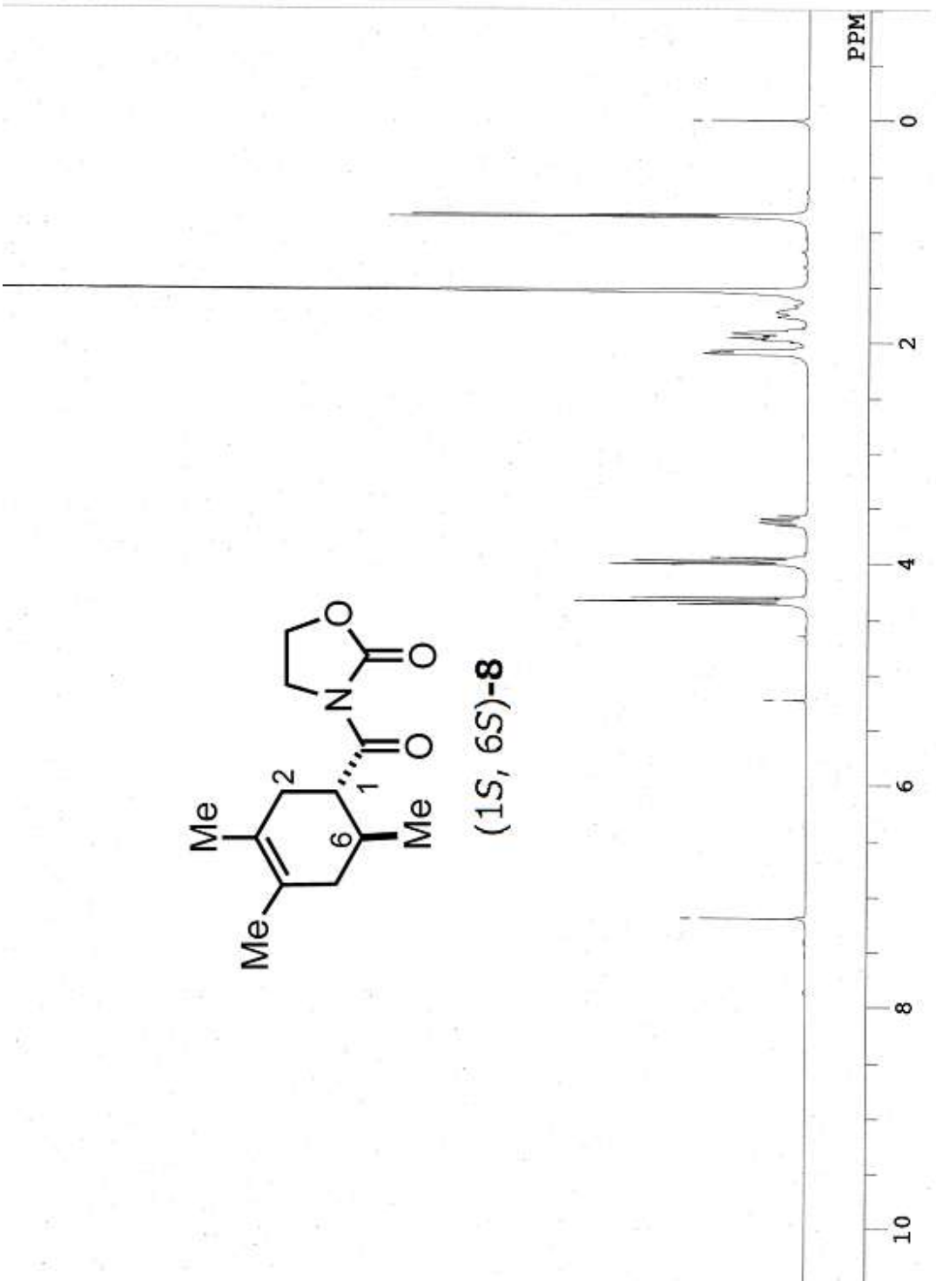
(*R*)-**1d**


Me
Me
Si
(R)-1e
PPM
0
2
4
6
8
10

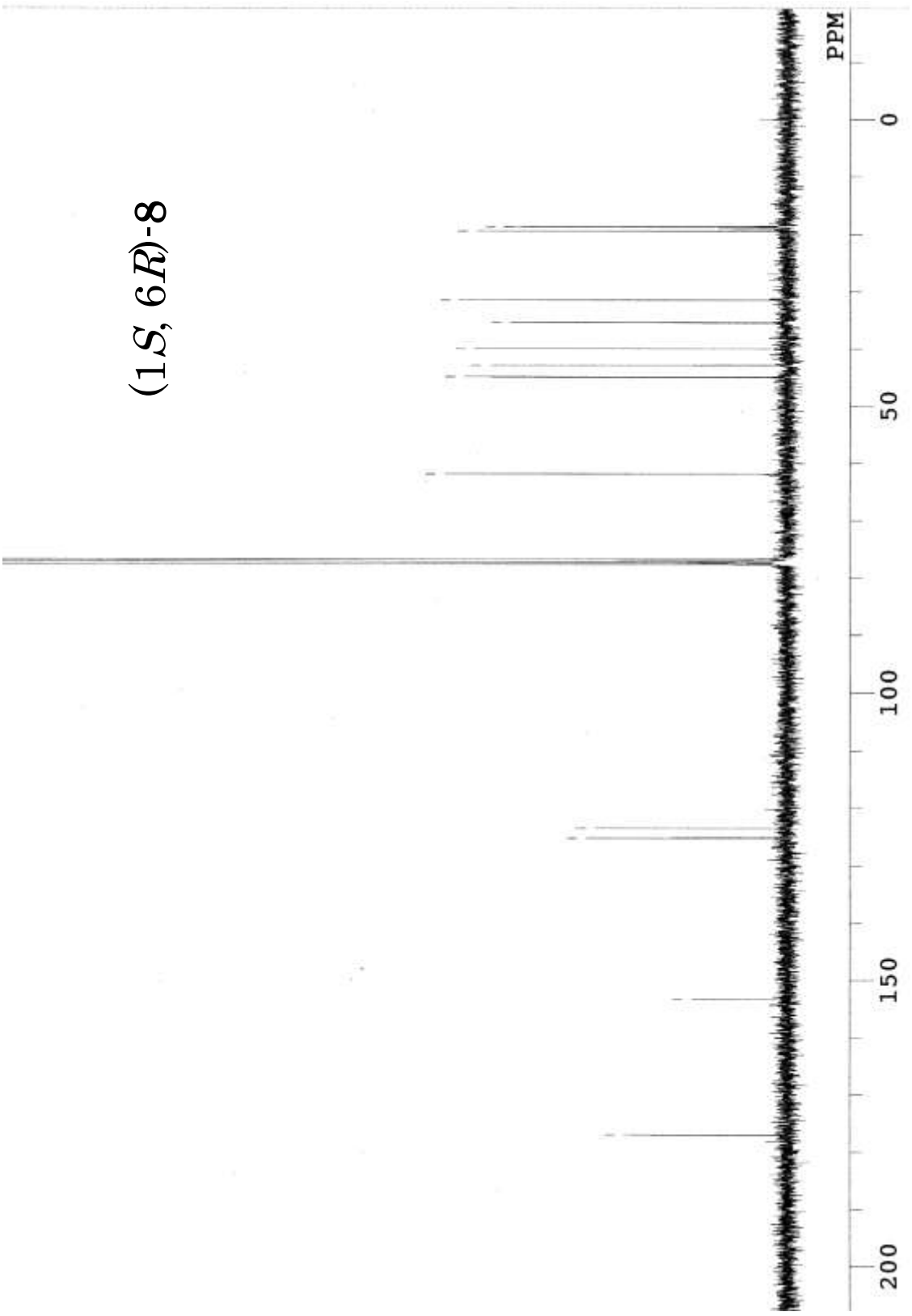

(R)-1e
PPM
0
50
100
150

(*R*)-1e



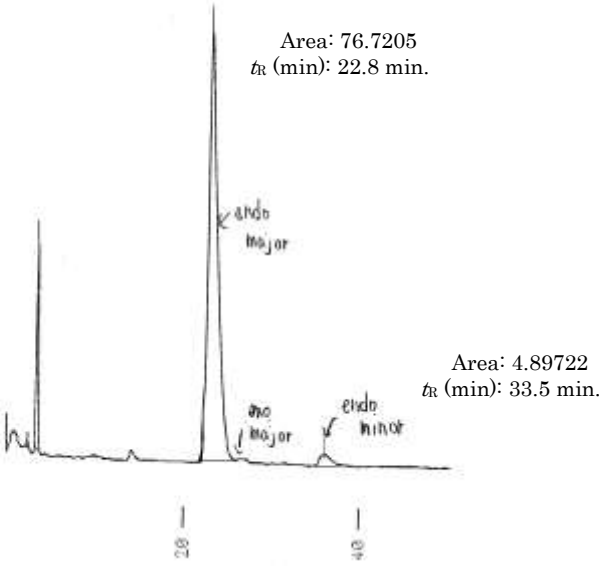


(1*S*, 6*S*)-**8**

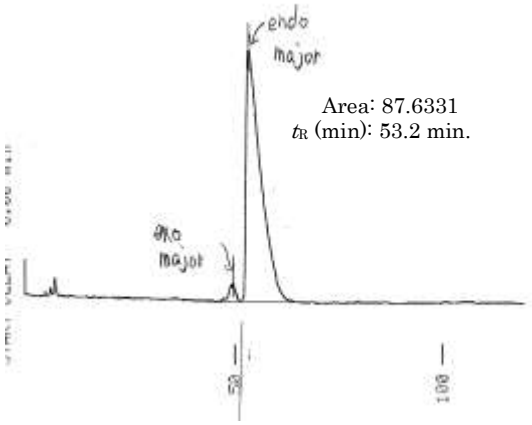

(1S, 6R)-8
PPM
0
50
100
150
200

(8) HPLC Analysis of Chiral Products

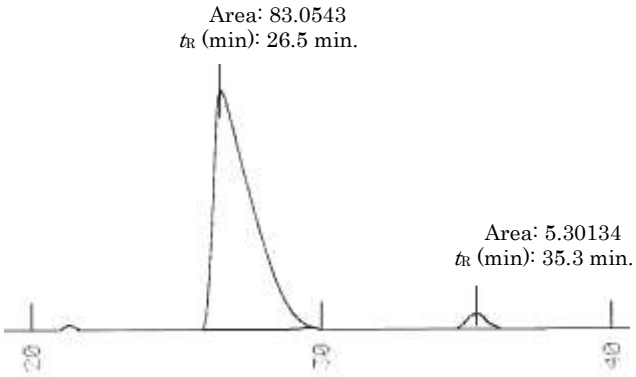
Compound **4a** (Table 1, entry 5)



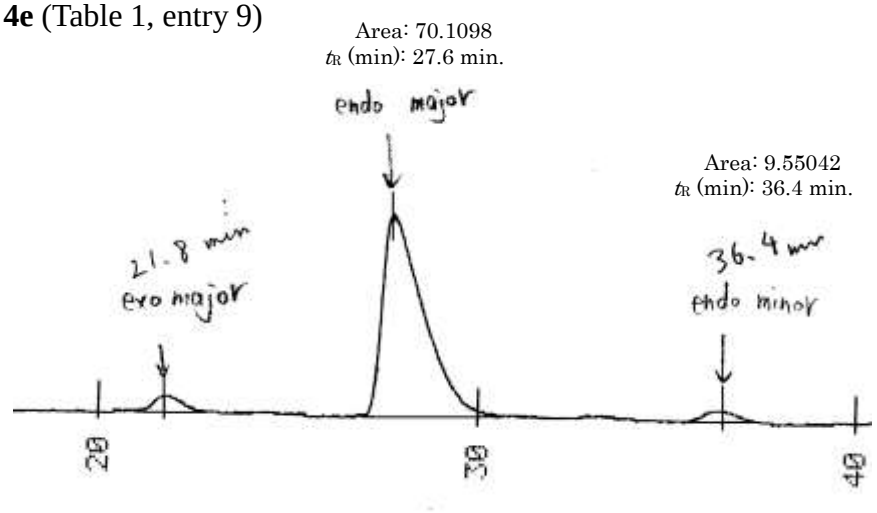
Compound **4b** (Table 1, entry 6)



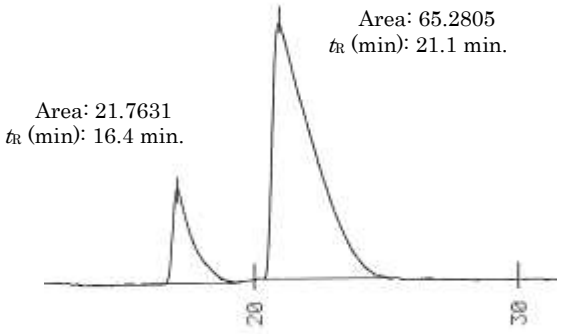
Compound **4c** (Table 1, entry 7)



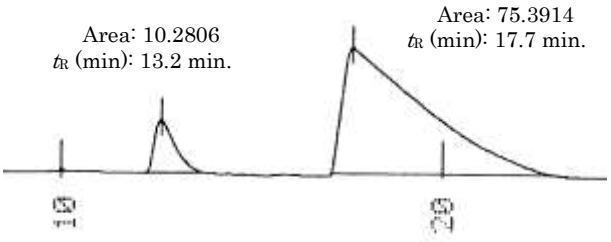
Compound **4e** (Table 1, entry 9)



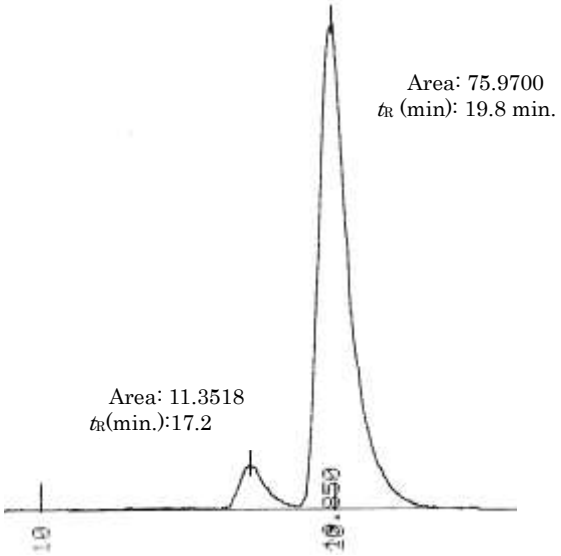
Compound **5** (Table 1, entry 10)



Compound **6** (Table 1, entry 11)



Compound **7** (Table 1, entry 12)



Compound 8 (Table 1, entry 13)