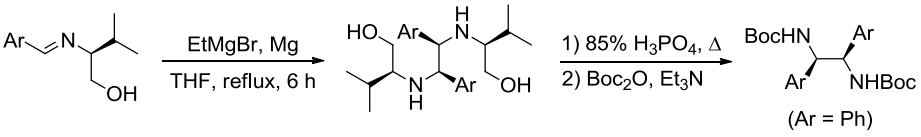
Graphical abstract



Diastereoselective imino-pinacol coupling of chiral imines promoted by Mg(0) and a Grignard reagent

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ABSTRACT

The reaction of chiral imines, derived from aromatic aldehydes and (*S*)-valinol, with a Grignard reagent in the presence of Mg(0) afforded imino-pinacol coupling products instead of alkylated amines, with a high level of diastereoselectivity. The chiral auxiliary in the product was successfully removed via dehydration followed by hydrolysis, and the corresponding (*R*,*R*)-ethylenediamine derivative was obtained as the *N*-Boc protected form.

Keywords:
Imino-pinacol coupling
Chiral 1,2-diamine
Grignard reagent
Magnesium

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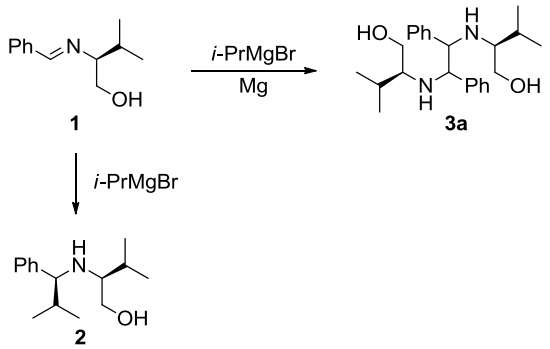
1. Introduction

Imino-pinacol coupling is a straightforward method for obtaining C_2 -symmetric 1,2-diamine derivatives. Several methods that use a variety of metals as reductants have been reported for the reductive homocoupling reaction.[1] Diastereoselective coupling of chiral imines is especially useful for synthesis of chiral 1,2-diamine derivatives; a valuable class of compounds used as ligands of chiral catalysts in asymmetric synthesis[2] and as medicinal products in pharmaceutical chemistry.[3] Although this diastereoselective coupling has been extensively examined in terms of the intramolecular reaction of chiral diimines[4] and the intermolecular reaction employing chiral imines[5] or chiral activators,[6] most studies use costly reducing agents, such as Sm and SmI_2, or a large excess of metals and acids.

Moreover, only a few studies have investigated the conversion of the products obtained from intermolecular reactions into free ethylenediamines by the removal of the chiral auxiliary.[5a, c, f]

Chiral imines have also been employed for the synthesis of chiral secondary amines.[7] Chiral aldimines derived from (*S*)-valinol can also be converted to chiral secondary amines with high diastereoselectivity via addition of Grignard or organolithium reagents. It has been reported that the reaction of aldimine **1**, prepared from benzaldehyde and (*S*)-valinol, with isopropyl magnesium bromide provides the corresponding secondary amine **2** in 61% yield and 86% diastereomeric excess (**Scheme 1**).[7c] When the same reaction was attempted in our laboratory, the desired chiral secondary amine was obtained in a similar manner. However, when the reaction was conducted in the presence of excess amounts of Mg(0), imino-pinacol coupling was predominant, giving the corresponding 1,2-diamine derivative as the major product. Although Mg(0) has been often employed in imino-pinacol coupling,[8] its use in diastereoselective coupling leading to chiral diamines is rare. Herein, we report a diastereoselective imino-pinacol coupling reaction promoted by a more practical method using Mg(0) and a Grignard reagent.



Scheme 1. Reaction of aldimine, derived from (*S*)-valinol, with a Grignard reagent in the presence or absence of Mg

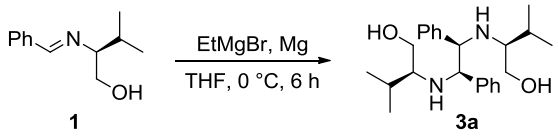
2. Results and discussion

To optimize the reaction conditions for the imino-pinacol coupling, the reaction of imine **1**,[9] using a commercially available solution of EtMgBr in THF, was attempted under several reaction conditions. This was accomplished by varying the amounts of Grignard reagent and Mg(0) and their proportions (**Table 1**). Initially, the reaction of **1** using equimolar amounts of EtMgBr and Mg(0) was conducted at 0 °C in THF. Consequently, the desired coupling products were obtained as a mixture of (*SRRS*)- and (*SRSS*)-diamines in a ratio of 92:8. The yield of the major isomer, (*SRRS*) adduct, was estimated to be 40% from the ^{1}H NMR spectrum (entry 1). The configuration of these products was determined by comparison with reported ^{1}H NMR spectral data[5e] of each diastereomer. Another possible

diastereomer, (*SSSS*)-diamine,[10] was not detected in the ^{1}H NMR spectrum of the crude product. To enhance the yield of the desired coupling product, an excess of EtMgBr and/or Mg(0) was added to the reaction mixture. The reaction with 1.5 equivalents of EtMgBr and 1.0 equivalent of Mg(0) was the most effective in affording the (*SRRS*)-diamine, resulting in a 74% yield without reducing the diastereomeric ratio (entry 2). The use of a larger excess of EtMgBr or Mg(0) did not improve the yield of the product (entries 3, 5). On the other hand, when the amount of Mg(0) was reduced to 0.5 equivalents, the coupling products were obtained in lower yield (entry 4). In addition, large excess amounts of EtMgBr and Mg(0) afforded diminished diastereoselectivity with only slightly enhanced yield (entry 6). The use of either a Grignard reagent or Mg(0) under similar reaction conditions afforded neither of the coupling products (entries 7, 8), indicating that both a Grignard reagent and Mg(0) are necessary for this coupling reaction.

Table 1

Imino-pinacol coupling of imine **1** using EtMgBr [a] and Mg(0)



1 **3a**

Entry	EtMgBr (equiv)	Mg (equiv)	Yield(%)[b]	dr[c]
1	1.0	1.0	40	92:8
2	1.5	1.0	74	94:6
3	3.0	1.0	75	91:9
4	1.5	0.5	55	93:7
5	1.5	3.0	78	95:5
6	3.0	3.0	83	91:9
7	-	1.0	- [d]	-
8	1.5	-	- [d]	-

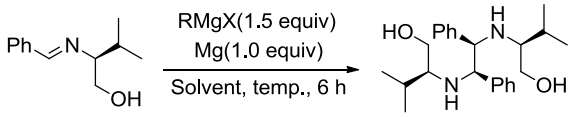
[a] Commercially available THF solution of the Grignard reagent was employed. [b] Yields of the major diastereomer, (*SRRS*)-diamine, estimated from the ^{1}H NMR spectrum. [c] Diastereomeric ratio (dr) of (*SRRS*):(*SRSS*) was determined by the ^{1}H NMR spectrum. [d] Coupling products were not obtained.

Furthermore, to examine the effect of the choice of Grignard reagent, reaction solvent, and temperature, similar reactions using **1** were attempted under a variety of reaction conditions (**Table 2**). Coupling products were also obtained when EtMgCl was used instead of bromide (entry 2); however, this was not the case when the iodides, EtMgI, or MeMgI were used (entries 3, 4). In the reactions using these iodides, only starting materials, i.e., imines, were recovered, and secondary amines that would be formed by Grignard reactions of the imines were not identified by ^{1}H NMR of the crude reaction products. The coupling reaction was also attempted using *i*-PrMgBr, but the diastereoselectivity and yields of the product were similar to the reaction with EtMgBr (entry 5).

Among the ethereal solvents pursued for this reaction, THF was preferred (entry 1 vs. entries 6, 7). Unexpectedly, toluene was also effective in generating the desired product in good yield and high diastereoselectivity (entry 8). While the reaction performed at a lower temperature resulted in a considerable reduction in yield, increasing the reaction temperature led to the formation of the product in the highest yield without loss of diastereoselectivity (entry 11).

Table 2

Imino-pinacol coupling of **1** under various reaction conditions [a]

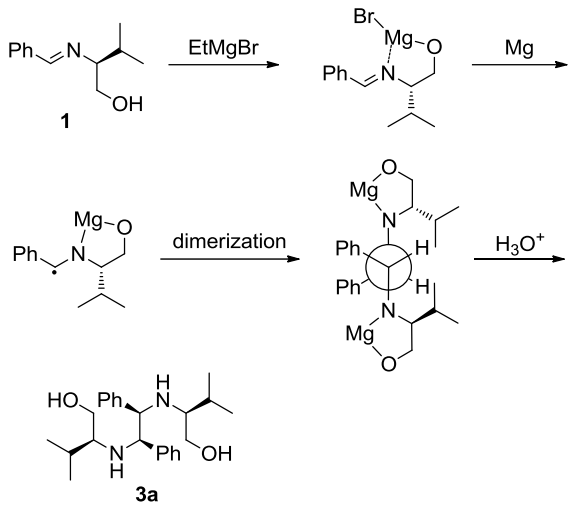


1 **3a**

Entry	R	X	Solvent	temp. (°C)	Yield [b] (%)	dr [c]
1	Et	Br	THF	0	74	94:6
2	Et	Cl	THF	0	63	93:7
3 [d]	Et	I	THF	0	- [e]	-
4 [f]	Me	I	THF	0	- [e]	-
5	*i*-Pr	Br	THF	0	74	91:9
6	Et	Br	Et_2O	0	43	95:5
7	Et	Br	DME	0	48	93:7
8	Et	Br	toluene	0	73	95:5
9	Et	Br	THF	-18	18	96:4
10	Et	Br	THF	rt	77	93:7
11	Et	Br	THF	reflux	80	94:6

[a] Commercially available THF solution of Grignard reagents was employed. [b] Yields of the major diastereomer, (*SRRS*)-diamine, estimated from the ^{1}H NMR spectrum. [c] Diastereomeric ratio (dr) was determined by the ^{1}H NMR spectrum. [d] Grignard reagent prepared *in situ*. [e] Coupling products were not obtained. [f] Commercially available solution of MeMgI in Et_2O was used.

Imino-pinacol coupling of **1** has been previously examined by Yanada et al. using the combination of $AlMe_3$, Sm, and a catalytic amount of I_2. The (*SRRS*)-diamine was successfully obtained as the major product, controlled by chelation of Lewis acidic Al.[5e] For the present dimerization by a Grignard reagent and Mg(0), Lewis acidic Mg^{2+} from the Grignard reagent was assumed to activate the imine through its chelation to the N and O atoms and promote the diastereoselective radical coupling illustrated in **Scheme 2**. For the transition state, approach from *Si* faces of the radicals would be favorable because of the steric hindrance of the isopropyl groups, which are fixed owing to the cyclic nature of the transition state, and the steric repulsion between the bulky constituents of the Mg–chelated aminoalcohol. Consequently, the (*SRRS*)-diamine would form as the major isomer.

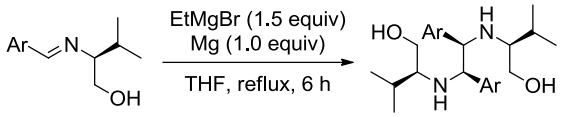


Scheme 2. Potential reaction mechanism for the formation of **3a**

2-Naphthalenylimine and other aromatic imines bearing a substituted benzene ring were applied to the coupling reactions under the optimized reaction conditions (**Table 3**). The reactions of 2-naphthalenylimine and *p*-*tert*-butylphenylimine provided the corresponding diamines in good yield with high diastereoselectivity, despite bulky substrates (entries 1, 2). Imines having electron-donating functional groups, for example, *p*-methyl, *p*-methoxy, and *p*-*N*,*N*-dimethylamino groups, could also tolerate this coupling reaction and were converted into their corresponding diamines in moderate yields (entries 3–5). The structures of all the major isomers were assumed to be (*SRRS*) from comparison of chemical shifts in ^{1}H NMR spectra with those of **3a**. All diamine derivatives, including **3a**, could be purified to afford a single diastereomer through column chromatography and recrystallization. The similar coupling reaction of an imine having a *p*-chlorophenyl group as an electron-withdrawing functional group was also attempted. However, complex reaction products were obtained and the desired diamine could not be isolated.

Table 3

Imino-pinacol coupling of various aryl imines[a]

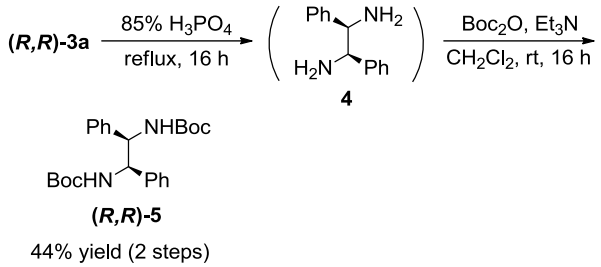


3b-f

Entry	Ar	Product	Yield(%)[b]	dr[c]
1	2-Naphthyl	3b	63	92:8
2	*p*-*t*BuC_6H_4	3c	63	93:7
3	*p*-MeC_6H_4	3d	48	91:9
4	*p*-MeOC_6H_4	3e	35	91:9
5	*p*-$Me_2NC_6H_4$	3f	44	87:13

[a] Commercially available THF solution of the Grignard reagent was employed. [b] Yields of the major diastereomer, (*SRRS*)-diamine, estimated from the ^{1}H NMR spectrum. [c] Diastereomeric ratio (dr) of (*SRRS*):(*SRSS*) was determined by the ^{1}H NMR spectrum.

Finally, conversion of the coupling product **(*R,R*)-3a** into 1,2-diphenylethylenediamine was attempted. In general, α-aminoalcohols can be converted to free amines through oxidative cleavage of the C–C bond adjacent to the NH and OH groups. Lin et al. have reported the conversion of a cyclic diamine, bearing the same chiral α-aminoalcohol moieties as **3a**, into the corresponding free diamine by oxidative cleavage using $NaIO_4$ and $MeNH_2$·HCl.[4h] These reaction conditions were used to synthesize the free ethylenediamine derivative from **3a**; however, the reaction led to a complex mixture of products, and the desired free ethylenediamine could not be isolated. It should be noted that acyclic diamines such as **3a** have relatively flexible conformations. Consequently, the oxidative cleavage of the C–C bond attached by two amino groups was expected to occur either competitively or preferentially. Therefore, another method for removing the chiral auxiliary needed to be applied. As a possible route to the free diamine, we assumed the dehydration of the α-aminoalcohols as a first step. This dehydration reaction produces enamines, which can be converted to their corresponding free amines through hydrolysis. Based on this proposed mechanism, dehydration of **(*R,R*)-3a** through the use of a wide variety of Brönsted acids, such as trifluoroacetic acid, trifluoromethanesulfonic acid, and sulfuric acid, was attempted. Unfortunately, most of these reactions did not proceed as expected. However, when a solution of **(*R,R*)-3a** in aqueous 85% H_3PO_4 was refluxed for 16 h, formation of the desired 1,2-ethylenediamine was demonstrated through the ^{1}H NMR spectrum of the crude product (**Scheme 3**). Because it was difficult to isolate the free diamine, the crude product was treated with Boc_2O in the presence of Et_3N, resulting in a 44% yield of the *N,N'*-diBoc-1,2-ethylenediamine derivative **5**, obtained in two steps from **3a**. The ^{1}H and ^{13}C NMR spectra of **5** were consistent with those previously reported for the enantiomer **(*S,S*)-5**.[11] In addition, specific rotation of the resulting product **5** has roughly the same magnitude as **(*S,S*)-5**, and we determined that **(*R,R*)-5** was provided without loss of stereochemistry under the applied reaction conditions.



Scheme 3. Synthesis of *N,N'*-diBoc-diamine, **(*R*,*R*)-5**, from **(*R*,*R*)-3a**

3. Conclusions

We demonstrated the diastereoselective imino-pinacol coupling of chiral (*S*)-valinol-derived imines promoted by inexpensive and commercially available Grignard reagents and Mg(0). The reactions proceeded to completion in the presence of 1.0 equivalent of Mg and a slight excess of a Grignard reagent to yield the corresponding coupling products with high diastereoselectivity in a ratio of 94:6. This protocol was especially effective for imines bearing a bulky substituent, such as 2-naphthalenyl and *p-tert*-butylphenyl, to afford the 1,2-diamine derivatives in acceptable yields. Other imines having heteroatom functional groups, such as MeO and Me_2N, were also applicable for this coupling reaction. The removal of the chiral auxiliary from the resulting imino-pinacol coupling products, which has been limited to a few examples, was also investigated. Although conversion of **3a** into the free 1,2-ethylenediamine derivative could not be accomplished by conventional oxidative cleavage, dehydration in aqueous 85% H_3PO_4 followed by hydrolysis enabled this transformation, and after treatment with Boc_2O the *N,N'*-diBoc-ethylenediamine could be isolated.

4. Experimental

4.1 General procedures

^1H NMR spectra were performed on a Bruker Avance 400 spectrometer. Proton chemical shifts are reported in parts per million (δ, ppm) relative to internal tetramethylsilane (TMS, δ 0.0 ppm). ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) with complete proton decoupling. Carbon chemical shifts are reported in parts per million (δ, ppm) relative to TMS with solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm). Infrared spectra were obtained on a Shimadzu IRTracer-100 FT-IR spectrometer. High-resolution mass spectra were obtained on a Bruker micrOTOF II LC-MS with an electrospray ionization source. The high-resolution mass spectra were performed using anhydrous CH_3CN as solvent. Specific rotation was measured on a Jasco DIP-370 digital polarimeter. Flash column chromatography was performed using Cica-Merck Silica Gel 60 N (40–50

μm). Coupling reactions were performed using dried glassware under a nitrogen atmosphere. Grignard reagents were purchased from Kanto Chemical Co., Inc. Magnesium (turnings) was purchased from Wako Pure Chemical Industries, LTD. The surface area of the magnesium was estimated to be 0.16 m^2/g from automated nitrogen gas sorption. All solvents were purified by conventional methods before use.

4.2 General procedure for imino-pinacol coupling

Magnesium (turnings, 0.0243 g, 1.0 mmol) was added to a two-neck round-bottom flask and stirred for 30 min under a nitrogen atmosphere. After THF (2 ml) and imine **1** (0.191 g, 1.0 mmol) were added to the flask, a 0.95 M solution of EtMgBr in THF (1.6 ml, 1.5 mmol) was slowly added to the mixture at 0 °C. As the Grignard reagent was added, the colorless reaction mixture changed to a yellow or brown solution and gas evolved. When the reaction mixture was refluxed after the addition of EtMgBr, the magnesium turnings gradually reduced in size, but they did not completely disappear. Precipitates such as magnesium salts were not observed. After reflux for 6 h, the reaction mixture was quenched with saturated aqueous NH_4Cl while cooling. The mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography using ethyl acetate/*n*-hexane (1/2 to 1/0) to give a mixture of (*S*,*R*,*R*,*S*)- and (*S*,*R*,*S*,*S*)-diamines as a white solid (0.155 g). The yield of the (*S*,*R*,*R*,*S*)-diamine was estimated from the ^1H NMR spectrum. The pure (*S*,*R*,*R*,*S*)-diamine could be obtained through recrystallization using ethyl acetate/*n*-hexane.

*4.2.1. (R,R)-1,2-Diphenyl-N,N'-bis((S)-1-(hydroxymethyl)-2-methylpropyl)-1,2-ethaenediamine (**3a**)*.[5e] mp 145 ℃; $[\alpha]_D^{28}$ -58.2 (c 1.04, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.12-7.16 (m, 4H), 7.03-7.09 (m, 6H), 3.93 (s, 2H), 3.76 (dd, *J*=3.6, 11.4 Hz, 2H), 3.69 (dd, *J*=7.4, 11.4 Hz, 2H), 2.48-2.53 (m, 2H), 1.57 (dsept, *J*=6.8, 6.8 Hz, a broad signal was superimposed, total 4H), 0.73 (d, *J*=6.8 Hz, 6H), 0.69 (d, *J*=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.1, 128.2, 127.1, 126.9, 69.0, 64.1, 63.9, 29.8, 19.2, 18.9; IR 3395, 3024, 2959, 2928, 2874, 1645, 1456, 1105, 1049, 700 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + H]^+$, calcd for $C_{24}H_{37}N_2O_2$ 385.2850, found 385.2859.

*4.2.2. (R,R)-1,2-Di-2-naphthalenyl-N,N'-bis((S)-1-(hydroxymethyl)-2-methylpropyl)-1,2-ethanediamine (**3b**)*. mp 177-178 ℃; $[\alpha]_D^{30}$ -47.7 (c 1.15, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.66 (m, 6H), 7.51 (brd, *J*=0.8 Hz, 2H), 7.25-7.37 (m, 6H), 4.25 (s, 2H), 3.85 (dd, *J*=3.5, 11.4 Hz, 2H), 3.74 (dd, *J*=7.4, 11.4 Hz, 2H), 2.55-2.60 (m, 2H), 1.58 (dsept, *J*=6.8, 6.8 Hz, 2H), 0.70 (d, *J*=6.8 Hz, 6H), 0.67 (d, *J*=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.3, 133.1, 132.5, 128.5, 127.7, 127.5, 126.4, 126.0, 125.6, 124.6, 69.0, 64.5, 64.0, 30.0, 19.2, 19.0; IR 3381, 3055, 2959, 2928,

2874, 1508, 1466, 1387, 1368, 1076, 1047, 820, 748 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + H]^+$, calcd for $C_{32}H_{41}N_2O_2$ 485.3163, found 485.3169.

*4.2.3. (R,R)-1,2-Bis(4-(1,1-dimethylethyl)phenyl)-N,N'-bis((S)-1-(hydroxymethyl)-2-methylpropyl)-1,2-ethanediamine (**3c**)*. mp 174-175 ℃; $[\alpha]_D^{29}$ -25.3 (c 1.01, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.10-7.13 (m, 4H), 6.91-6.94 (m, 4H), 3.87 (s, 2H), 3.73 (dd, *J*=3.2, 11.4 Hz, 2H), 3.66 (dd, *J*=7.1, 11.4 Hz, 2H), 2.47-2.51 (m, 2H), 1.58 (dsept, *J*=6.8, 6.8 Hz, 2H), 1.20 (s, 18H), 0.74 (d, *J*=6.8 Hz, 6H), 0.72 (d, *J*=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.5, 139.0, 126.6, 124.9, 68.6, 63.9, 63.7, 34.2, 31.1, 29.9, 19.2, 19.0; IR 3399, 3310, 2963, 2876, 1508, 1464, 1362, 1074, 1022, 822 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + H]^+$, calcd for $C_{32}H_{53}N_2O_2$ 497.4102, found 497.4106.

*4.2.4. (R,R)-1,2-Bis(4-methylphenyl)-N,N'-bis((S)-1-(hydroxymethyl)-2-methylpropyl)-1,2-ethanediamine (**3d**)*.[5e] mp 135-136 ℃; $[\alpha]_D^{28}$ -39.3 (c 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.91-6.96 (m, 8H), 3.89 (s, 2H), 3.74 (dd, *J*=3.6, 11.4 Hz, 2H), 3.67 (dd, *J*=7.4, 11.4 Hz, 2H), 2.48-2.52 (m, 2H), 2.21 (s, 6H), 1.56 (dsept, *J*=6.8, 6.8 Hz, 2H), 0.73 (d, *J*=6.8 Hz, 6H), 0.69 (d, *J*=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2, 136.3, 129.0, 126.9, 68.6, 64.3, 63.9, 29.9, 20.9, 19.2, 19.0; IR 3360, 3312, 2959, 2926, 2874, 1653, 1514, 1464, 1076, 816 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + H]^+$, calcd for $C_{26}H_{41}N_2O_2$ 413.3163, found 413.3171.

*4.2.5. (R,R)-1,2-Bis(4-methoxylphenyl)-N,N'-bis((S)-1-(hydroxymethyl)-2-methylpropyl)-1,2-ethanediamine (**3e**)*. mp 121-122 ℃; $[\alpha]_D^{29}$ -40.8 (c 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.93-6.95 (m, 4H), 6.66-6.69 (m, 4H), 3.86 (s, 2H), 3.75 (dd, *J*=3.6, 11.4 Hz, 2H), 3.68 (dd, *J*=7.4, 11.4 Hz), 3.71 (s) total 8H, 2.47-2.51 (m, 2H), 1.56 (dsept, *J*=6.8, 6.8 Hz, 2H), 0.73 (d, *J*=6.8 Hz, 6H), 0.69 (d, *J*=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.2, 134.4, 128.0, 113.6, 68.3, 64.1, 63.7, 54.9, 29.8, 19.2, 18.9; IR 3383, 3302, 2963, 2874, 1611, 1512, 1464, 1246, 1175, 1032, 824 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + H]^+$, calcd for $C_{26}H_{41}N_2O_4$ 445.3061, found 445.3070.

*4.2.6. (R,R)-1,2-Bis(4-N,N-dimethylaminophenyl)-N,N'-bis((S)-1-(hydroxymethyl)-2-methylpropyl)-1,2-ethanediamine (**3f**)*. mp 164-165 ℃; $[\alpha]_D^{28}$ 38.9 (c 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.11 (brd, 4H), 6.51 (brd, 4H), 2.83 (s, 12H), 2.64-2.68 (m, 2H), 1.75 (dsept, *J*=7.0, 7.0 Hz, 2H), 0.83 (d, *J*=7.0 Hz, 6H), 0.81 (d, *J*=7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.5, 128.4, 126.9, 112.3, 67.0, 63.1, 62.0, 40.2, 29.7, 19.2, 18.7; IR 3287, 2959, 2878, 1616, 1526, 1352, 1165, 1061, 818 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + H]^+$, calcd for $C_{28}H_{47}N_4O_2$ 471.3694, found 471.3690.

4.2 Synthesis of (*R,R*)-*N,N*'-diBoc-1,2-diphenyl-1,2-ethanediamine 5 from 3a

A solution of **3a** (0.385 g, 1.0 mmol) and 85% aqueous phosphoric acid (3 ml) was refluxed in a two-neck round-bottom flask for 16 h. After being cooled to rt and diluted with water, the solution was separated to aqueous and organic layers. The aqueous layer was washed with Et_2O and was made basic with 2 N aqueous NaOH. The resulting aqueous solution was extracted with Et_2O and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was subjected to the following protecting reaction without purification. The crude product (0.212 g, 1.0 mmol as a pure diamine), triethylamine (0.708 g, 7.0 mmol), Boc_2O (0.546 g, 2.5 mmol), and CH_2Cl_2 (7 ml) were added to a two-neck flask dried under vacuum. The mixture was stirred at rt for 16 h and subsequently poured into saturated aqueous NH_4Cl. The resulting mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography using ethyl acetate/*n*-hexane (1/5) and recrystallization with Et_2O to give **5** as a white solid (0.180 g, 44% from **3a**); mp 203 ℃; $[\alpha]_D^{28}$ -16.1 (c 1.00, $CHCl_3$,), $[\alpha]_D^{24}$ 15.0 (c 0.99, $CHCl_3$,) for reported (*S,S*)-**5**[11]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13-7.19 (m, 6H), 7.03-7.04 (m, 4H), 5.54 (brs, 2H), 4.86 (brs, 2H), 1.44 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 139.3, 128.4, 127.5, 127.4, 79.8, 60.7, 28.4; IR 3381, 2980, 2934, 1686, 1518, 1368, 1250, 1173, 700 (KBr, cm^{-1}); HRMS (ESI-TOF) *m/z* $[M + Na]^+$, calcd for $C_{24}H_{32}N_2O_4Na$ 435.2254, found 435.2259.

Acknowledgements

This work was supported by Shinshu University. We thank Dr. Yoshiyuki Hattori and Mr. Kento Sagisaka (Shinshu University) for the measurement of magnesium surface area.

References and notes

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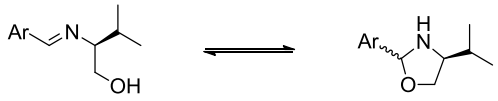
9. We determined from the ^{1}H NMR spectrum that (*S*)-valinol-derived imines exist as a mixture of imine and oxazolidine, its tautomer, (ca 6:4 to 9:1) in solution. In this manuscript, however, only the structure of imines was depicted in Schemes and Tables.



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Supplementary data

Copies of ^{1}H NMR and ^{13}C NMR spectra of products in this study are available. Supplementary data with this article can be found at http//.

Supporting information

Diastereoselective imino-pinacol coupling of chiral imines promoted by Mg(0) and a Grignard reagent

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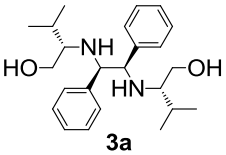

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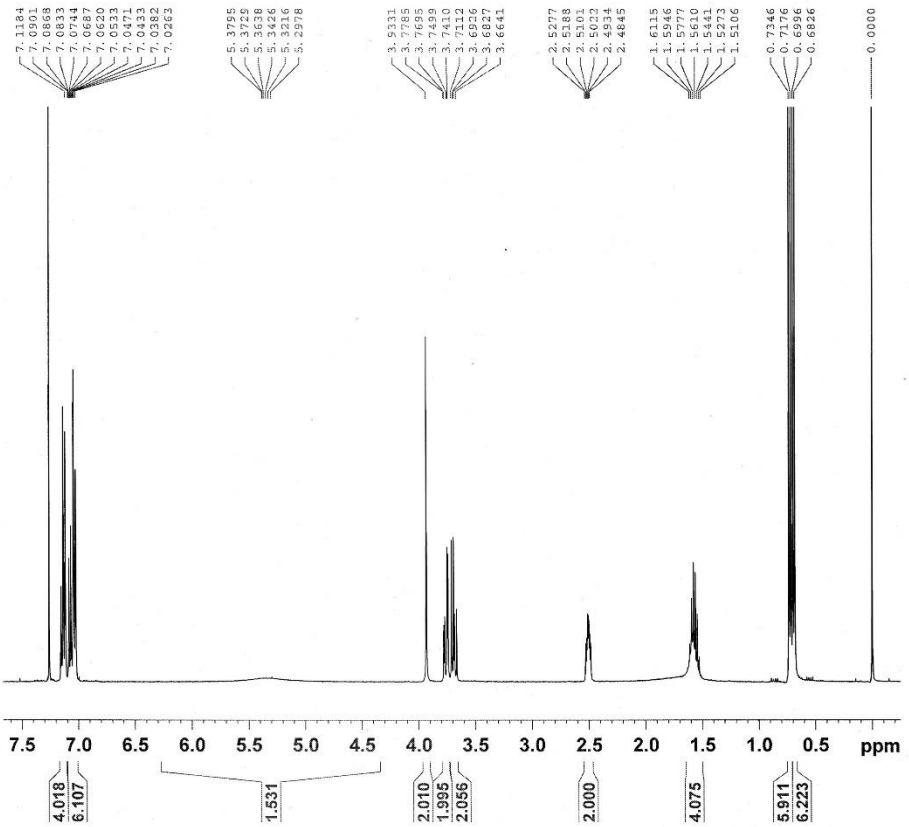

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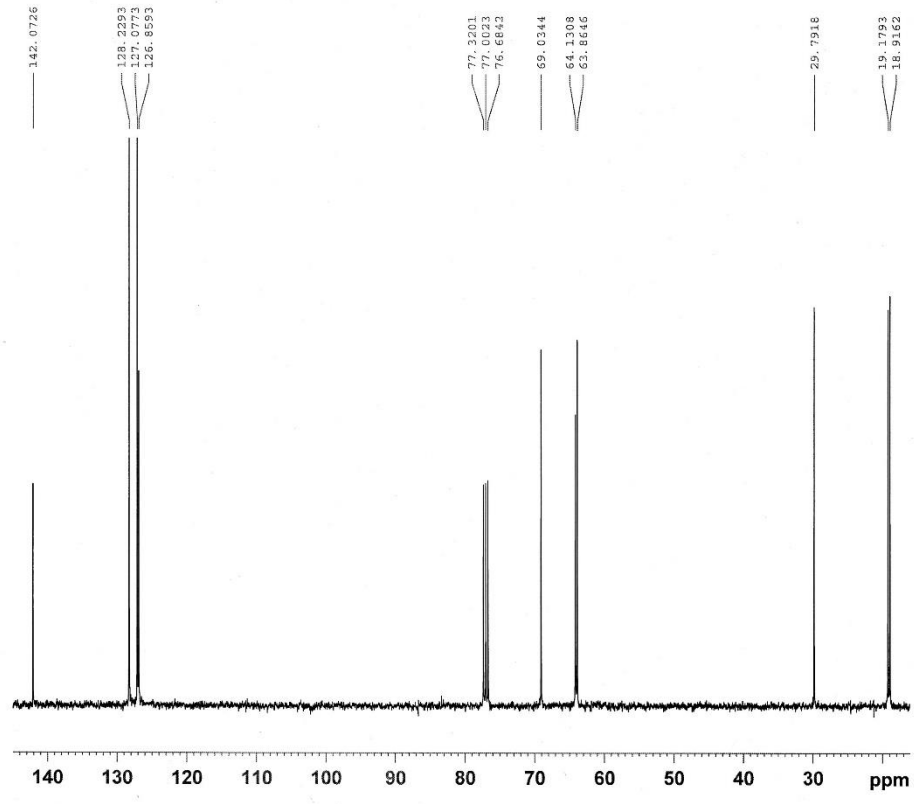

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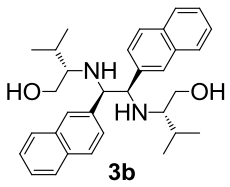

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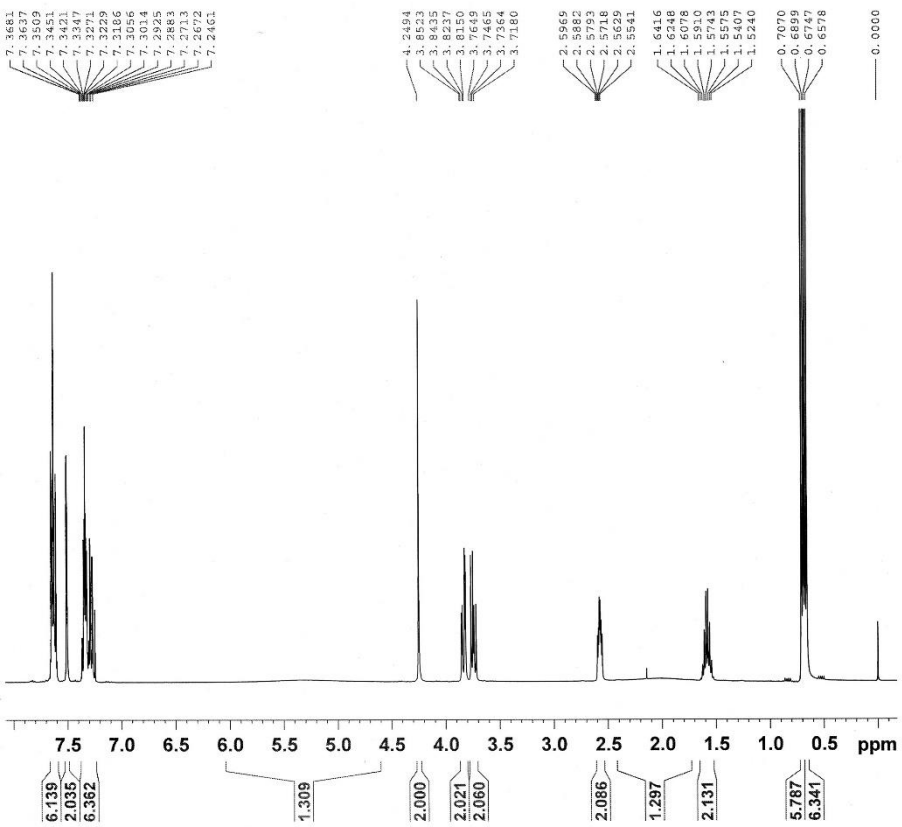

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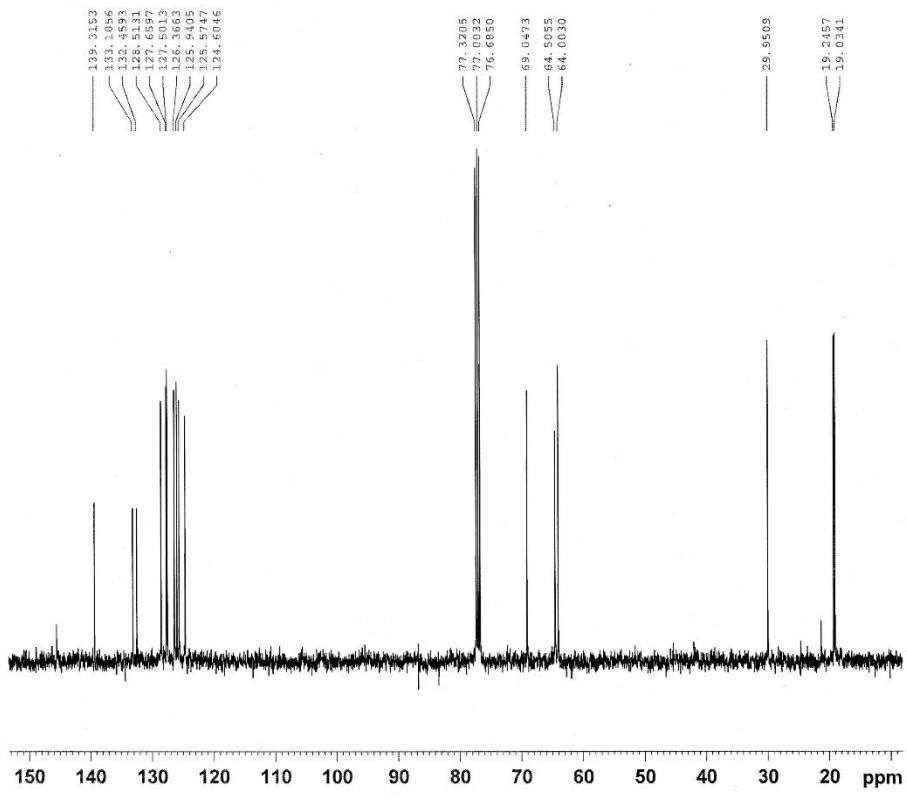

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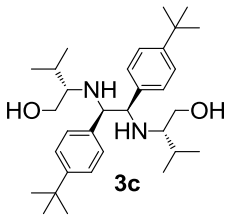

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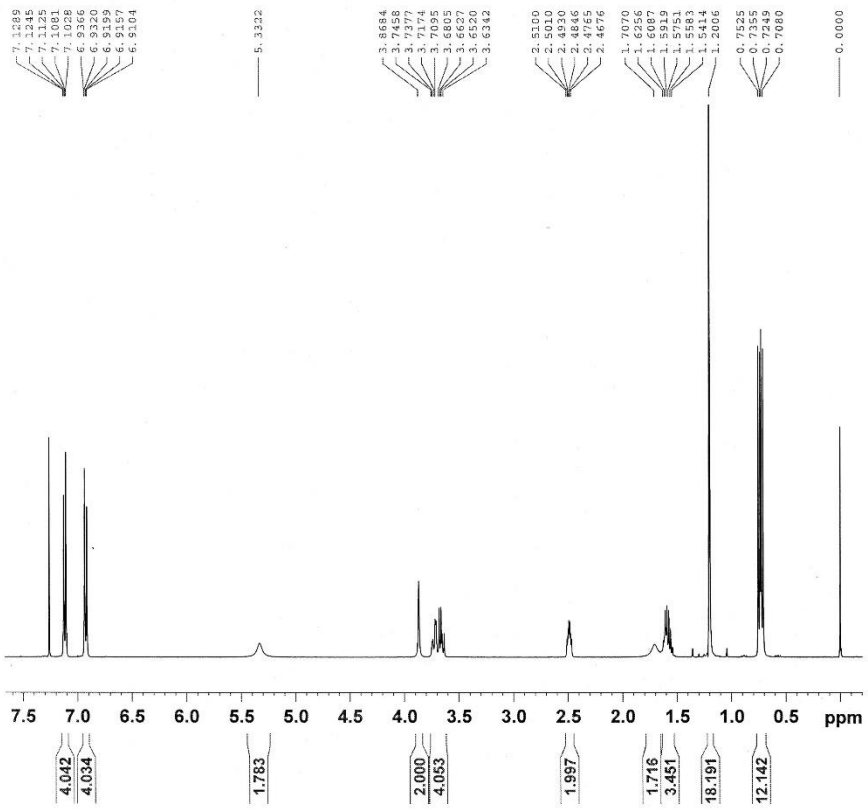

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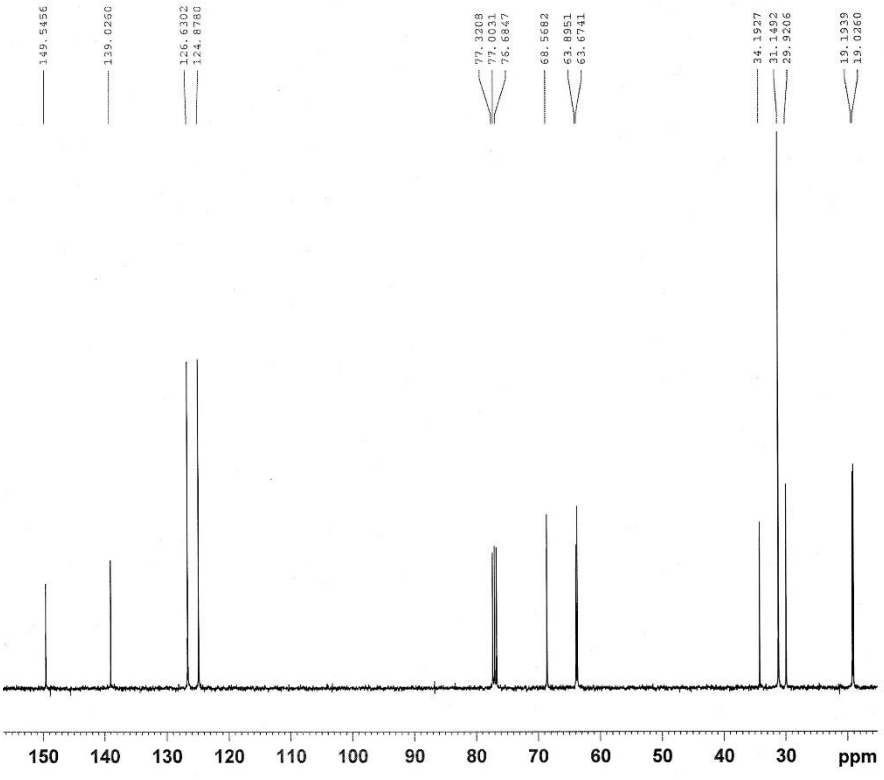

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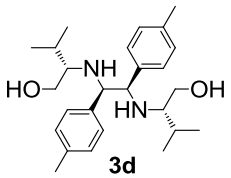

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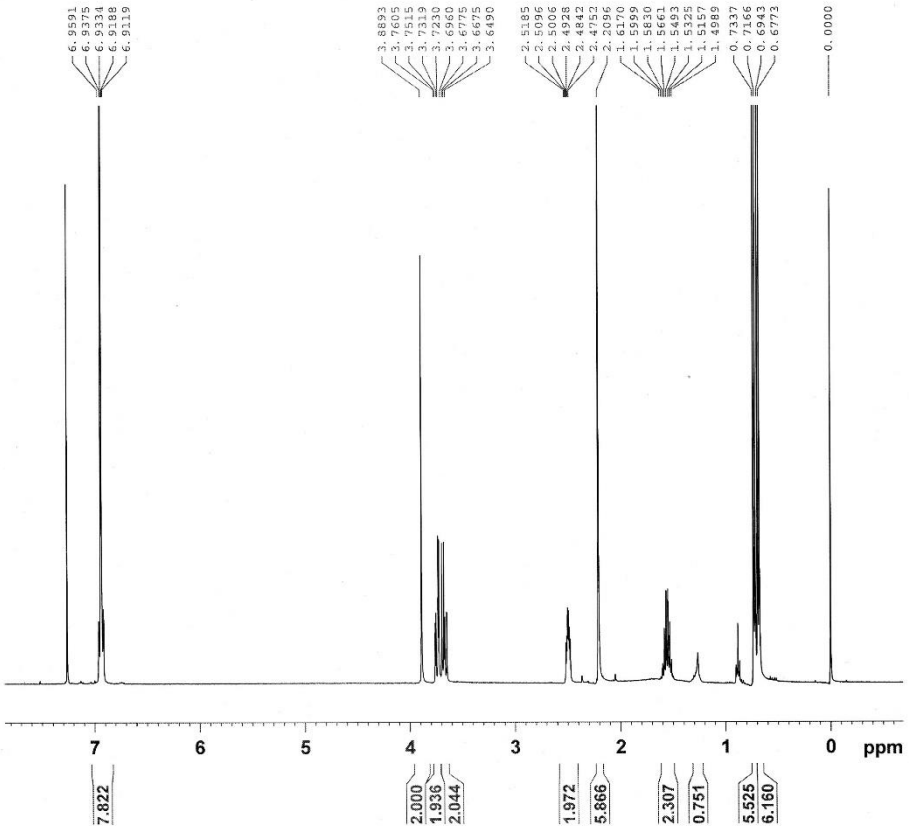

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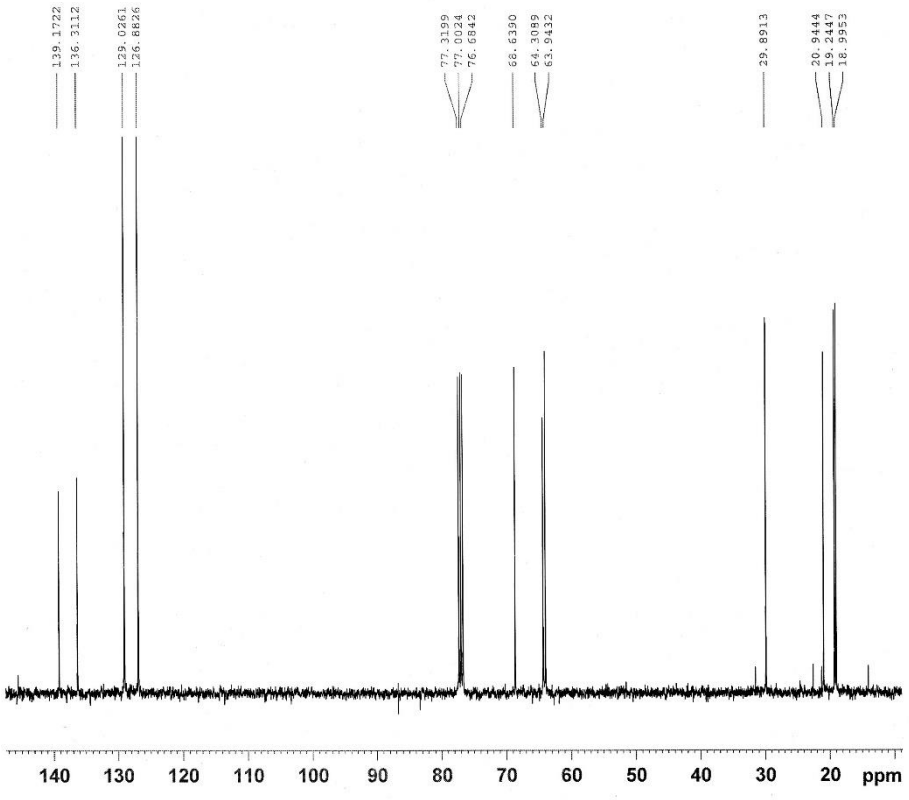

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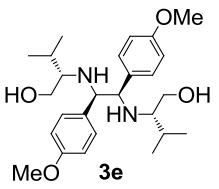

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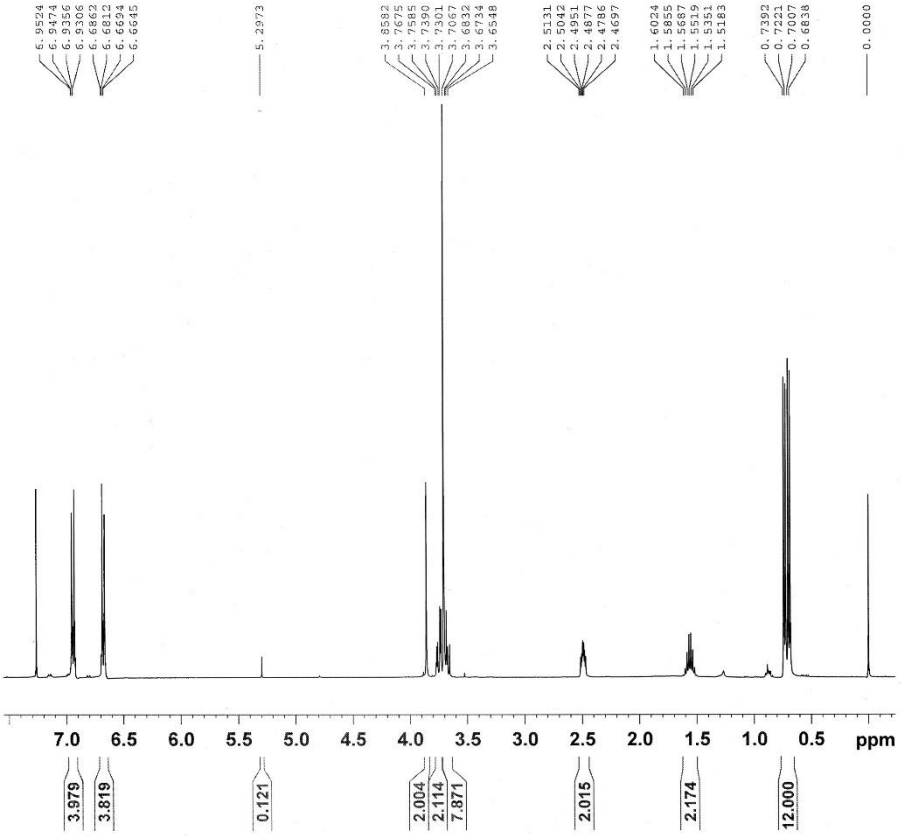

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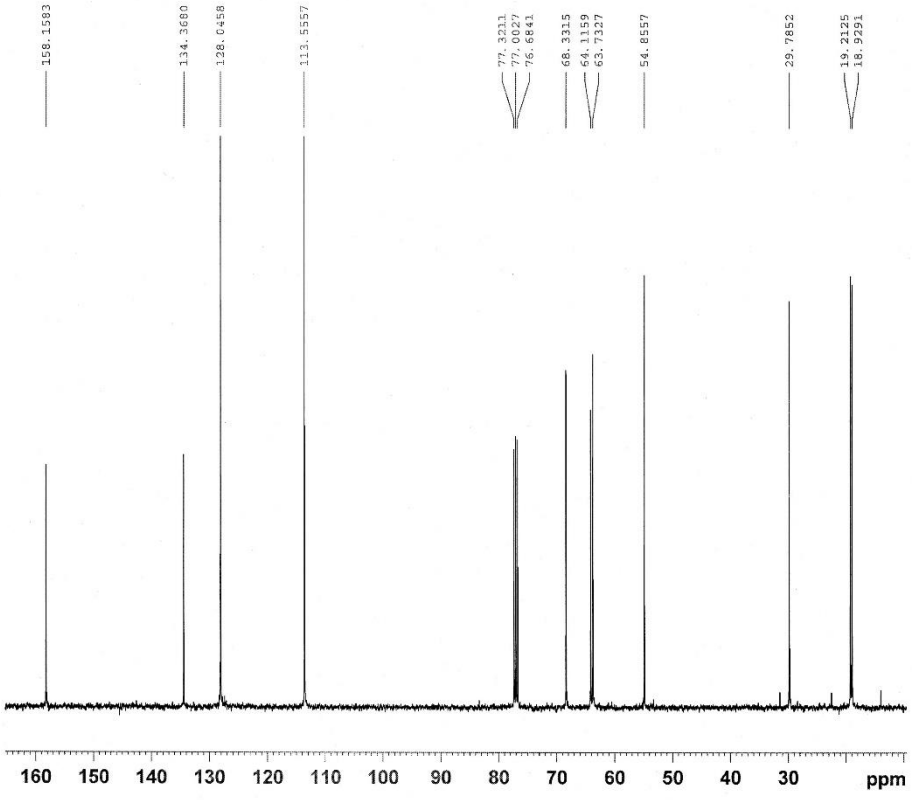
GB                      0
PC                   1.00
```



BRUKER

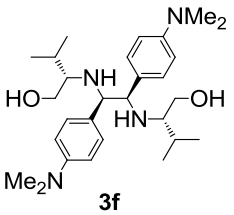
```
Current Data Parameters
NAME            Jul07-2014
EXPNO                  110
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140707
Time                 15.56
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             25125.629 Hz
FIDRES           0.383387 Hz
AQ               1.3042164 sec
RG                   8192
DW                19.900 usec
DE                 6.00 usec
TE                299.2 K
D1             3.00000000 sec
d11            0.03000000 sec
DELTA          2.90000010 sec
TD0                     1

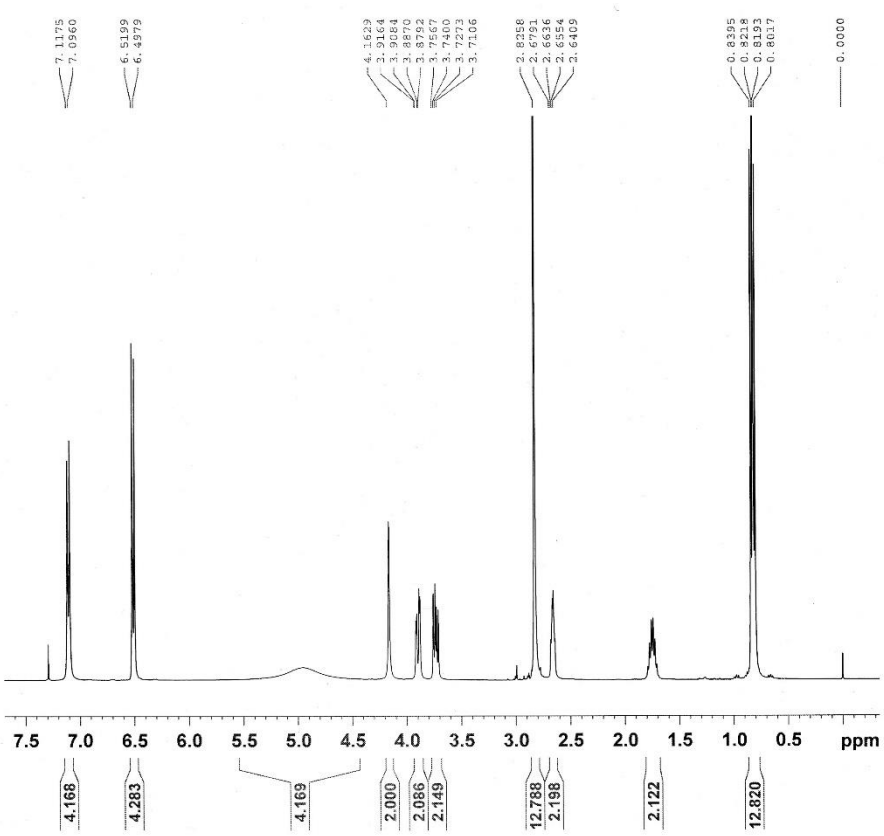
======== CHANNEL f1 ========
NUC1                  13C
P1                 15.00 usec
PL1                 7.50 dB
SFO1          100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 3.80 dB
PL12               23.00 dB
PL13               23.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127809 MHz
WDW                    EM
SSB                     0
LB                 2.00 Hz
GB                      0
PC                   1.40
```



3f



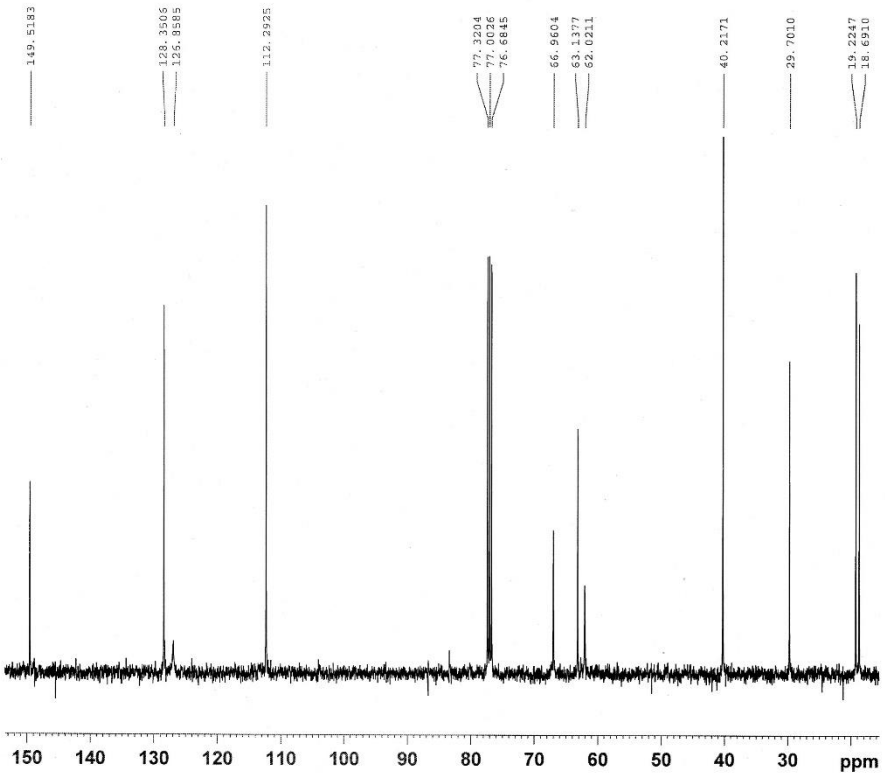
BRUKER

```
Current Data Parameters
NAME                  Jul09-2014
EXPNO                         20
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20140709
Time                        6.42
INSTRUM                    spect
PROBHD     5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                             8
DS                             2
SWH                     8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                          35.9
DW                        60.400 usec
DE                         6.00 usec
TE                        299.2 K
D1                   1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                         10.00 usec
PL1                         3.80 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1299965 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```



BRUKER

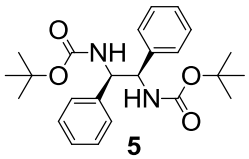
```
Current Data Parameters
NAME                  Jul07-2014
EXPNO                        100
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20140707
Time                       15.34
INSTRUM                    spect
PROBHD     5 mm QNP 1H/13
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                           128
DS                             4
SWH                    25125.629 Hz
FIDRES                 0.383387 Hz
AQ                     1.3042164 sec
RG                          8192
DW                        19.900 usec
DE                         6.00 usec
TE                        299.2 K
D1                   3.00000000 sec
d11                  0.03000000 sec
DELTA                2.90000010 sec
TD0                            1

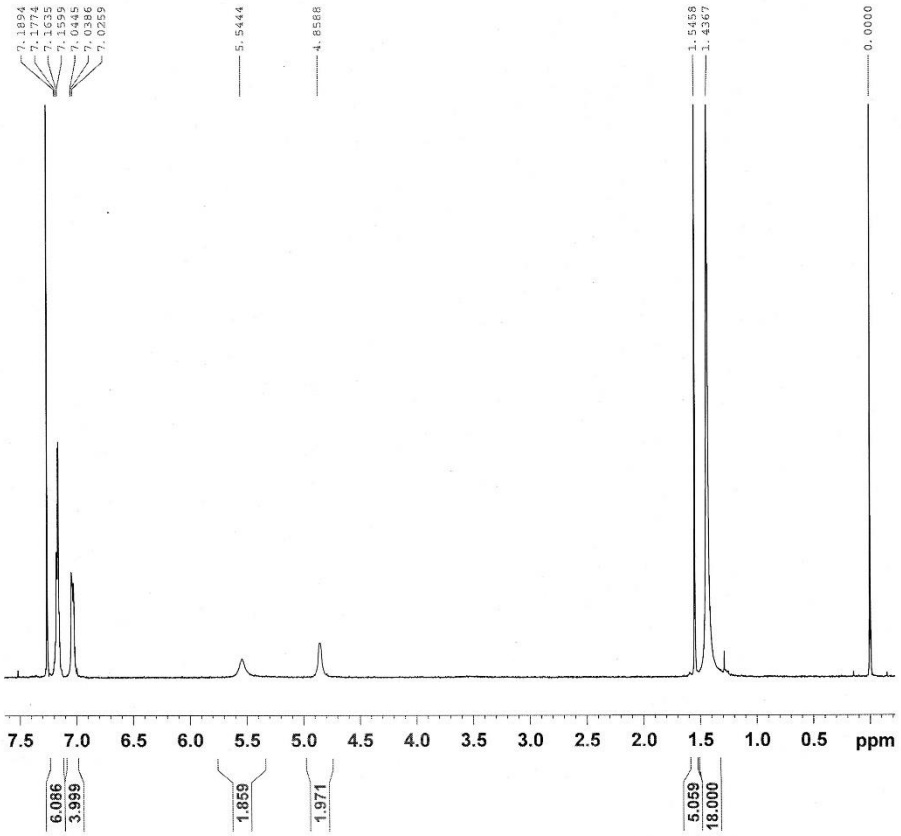
======== CHANNEL f1 ========
NUC1                         13C
P1                         15.00 usec
PL1                         7.50 dB
SFO1                100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                          1H
PCPD2                      80.00 usec
PL2                         3.80 dB
PL12                       23.00 dB
PL13                       23.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                  100.6127806 MHz
WDW                          EM
SSB                           0
LB                         2.00 Hz
GB                            0
PC                         1.40
```



5



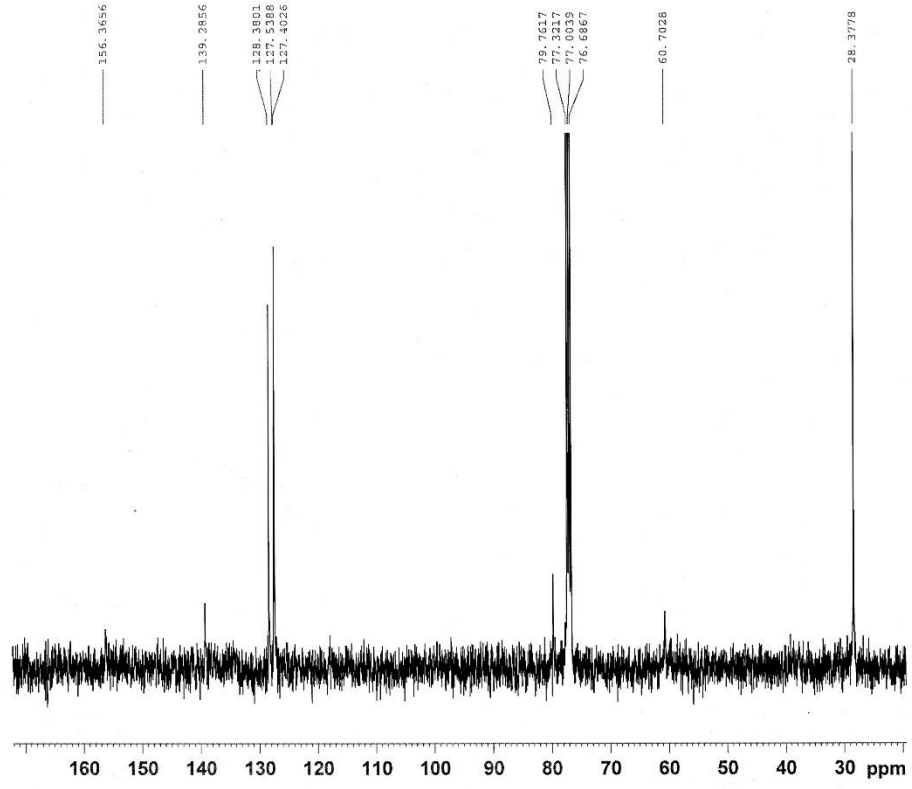
BRUKER

```
Current Data Parameters
NAME                  Jul07-2014
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20140707
Time                       14.18
INSTRUM                    spect
PROBHD     5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                             8
DS                             2
SWH                     8278.146 Hz
FIDRES                  0.126314 Hz
AQ                      3.9584243 sec
RG                         724.1
DW                        60.400 usec
DE                         6.00 usec
TE                        299.2 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                         10.00 usec
PL1                         3.80 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                         32768
SF                  400.1300096 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



BRUKER

```
Current Data Parameters
NAME                  Sep12-2014
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20140912
Time                        9.03
INSTRUM                    spect
PROBHD     5 mm QNP 1H/13
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          1024
DS                             4
SWH                    25125.629 Hz
FIDRES                  0.383387 Hz
AQ                      1.3042164 sec
RG                          8192
DW                        19.900 usec
DE                         6.00 usec
TE                        299.2 K
D1                    3.00000000 sec
d11                   0.03000000 sec
DELTA                 2.90000010 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          13C
P1                         15.00 usec
PL1                         7.50 dB
SFO1                100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                      80.00 usec
PL2                         3.80 dB
PL12                       23.00 dB
PL13                       23.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127703 MHz
WDW                           EM
SSB                            0
LB                          2.00 Hz
GB                             0
PC                          1.40
```