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Chiral C_2-symmetric bisferrocenyldiamines as ligands for transition metal catalyzed asymmetric cyclopropanation and aziridination

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Abstract

A new series of chiral C_2-symmetric bisferrocenyldiimine **1** and bisferrocenyldiamines **2** and **3** proved to be efficient ligands for the copper(I)-catalyzed asymmetric cyclopropanation, cyclopropenation, and aziridination of alkenes and alkynes to give high diastereo- and enantioselectivity as well as high chemical yields. In some instances the enantiomeric excesses of cyclopropanated products are among the highest (>97% ee) ever reported. Comparative studies show that stereoselectivity depends highly on the steric variation both in the ligand and the substrate. Other transition metal complexes incorporating some of these ligands such as Ru(**3c**)Cl_2, [(NBD)Rh(**2**)]ClO_4, [Cu(**2**)$(MeCN)_2$]PF_6, and Pd(**2**)Cl_2 also demonstrated high enantioselectivity in cyclopropanation reactions.

1. Introduction

Catalytic C- and N-atom transfer to olefins leading to the formation of cyclopropanes and aziridines, respectively, have attracted much research interest due to their presence in numerous biomolecules.[1] Consequently, the last decade has seen development of a great number of catalysts capable of such transformation via cyclopropanation and aziridination of olefins.[2] Complexes of ruthenium,[3] rhodium,[4] palladium,[5] and copper[6–12] have been reported to be the most efficient with regard to both yields and diastereo- and enantioselectivities. In particular, copper catalysts deserve special attention in that soluble copper complexes incorporating chiral nitrogen-based ligands such as salicylaldimines,[6] semicorrins,[7] oxazolines,[8] bipyridines,[9] polypyrazoles,[10] porphyrins,[4e,11] and related diimines[12] have achieved asymmetric cyclopropanation and aziridination with moderate to high d.e. and e.e.

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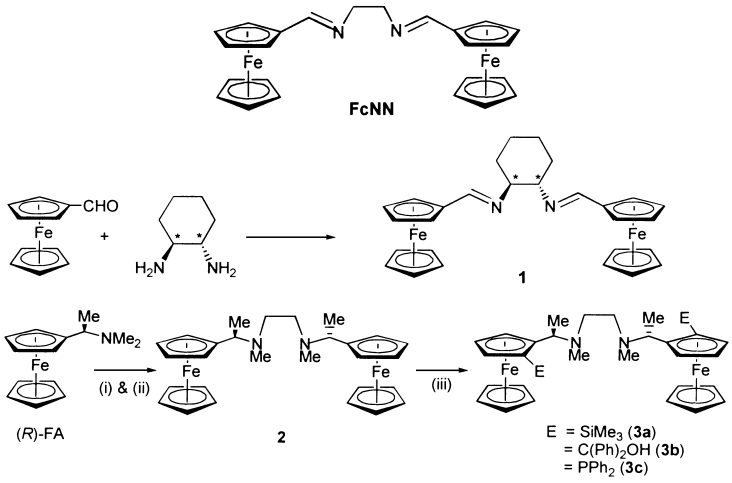
As part of our ongoing project on the design of new ferrocene-containing ligands and their applications to catalytic reactions and asymmetric catalysis, we have also recently demonstrated that ferrocene-based ligands such as FcNN (vide infra), **2**, and **3c** (Scheme 1) are efficient ligands for metal complexes in cyclopropanation and aziridination.[13,14] Prompted by these findings and the fact that the C_2-symmetrical amines and diamines have great potential in asymmetric synthesis,[15] we have attempted to add a new entry to the series of C_2-symmetric bisferrocenyldiamines as illustrated in Scheme 1. The motivation behind this effort is not only to test the general applicability of these ligands in asymmetric catalysis but investigate their relative capability in stereoselectivity of the reactions.



Scheme 1. (i) MeI; (ii) $MeNH(CH_2)_2NHMe$; (iii) 2 BuLi/$ClSiMe_3$ (**3a**); 2 BuLi/Ph_2CO/H_2O (**3b**); 2 BuLi/Ph_2PCl (**3c**)

In fact, a great variety of chiral ferrocenes such as aminophosphines, diphosphines, oxazolines, pyrazoles, hydroxyphosphines and hydroxyamines are now known.[16] Most of these ligands have been tested with great success in a number of asymmetric reactions such as hydrogenation, hydrosilylation, cross-coupling reactions, allylic substitution, aldol type condensation, cyclopropanation, and many others.[17] Our hope is that our new ligands would find as many successful applications as the above-mentioned ferrocene-based ligands.

2. Results and discussion

2.1. Synthesis

Scheme 1 shows the synthetic routes leading to the formation of bisferrocenyldiimine **1** and -diamines **2** and **3**. The resolution of *N*,*N*-dimethyl-1-ferrocenylethylamine (FA) with L-(+)-tartaric acid is achieved using the well-known Ugi's procedure from which both antipodes are obtained.[18] The preparation of **1** is readily achieved by simple condensation of ferrocenecarboxaldehyde with 1,2-(*R*,*R*)-diaminocyclohexane. The preparation of **2** and **3** is also quite straightforward simply by taking advantage of the fact that FA with a suitable leaving group such as trimethylammonium or acetate in the α-position undergoes nucleophilic substitution of S_N1-type with complete retention of configuration.[18a]

Thus, treatment of a twofold excess of (*R*)-*N*,*N*,*N*-trimethyl-1-ferrocenylethylammonium iodide with 1,2-bis(methylamino)ethane in the presence of anhydrous K_2CO_3 in acetonitrile resulted in **2**, as reported

in our earlier paper.[14] Lithiation with *n*-BuLi of **2** followed by electrophilic substitution with Me_3SiCl, $Ph_2C{=}O$, and $ClPPh_2$ resulted in the formation of **3a**, **3b**, and **3c**, respectively. Here the first (*R*) designates the carbon central configuration originated from (*R*)-FA and the second (*S*) designates the ferrocene planar configuration generated at the stereoselective lithiation.

The structural characterizations of the new compounds (**1**, **3a**, and **3b**) were performed by elemental analysis, NMR spectroscopy, and mass spectrometry. The ^1H NMR patterns are straightforward and reveal the signals expected from their structures. The presence of the electrophiles in **3** does not alter significantly the NMR patterns of the FA moiety. All these ligands form various transition metal complexes of the types Cu(L)OTf, $[Cu(L)(MeCN)_2]PF_6$, $Pd(L)Cl_2$, and $[(NBD)Rh(L)]ClO_4$ in a typical bidentate manner except for **3c** which behaves as a tetradentate upon complexation, i.e., Ru(**3c**)Cl_2.[14]

2.2. Catalysis

2.2.1. Asymmetric cyclopropanation

Table 1 shows that copper(I) complexes of the type Cu(L)(OTf) incorporating our new chiral C_2-symmetric bisferrocenyl ligands can catalyze the asymmetric cyclopropanation of some olefins to give the corresponding cyclopropanecarboxylates in a varying degree of *trans*:*cis* selectivity (90:10–62:38) and enantioselectivity (48–96% e.e. for the *trans* isomer) depending upon the steric and the eletronic properties of both substrates and ligands. For instance, an internal olefin such as indene showed the highest enantioselectivity (up to 96% e.e.) as well as the highest *trans*:*cis* diastereoselectivity (90:10).

When comparison was made among the ligands, the enantioselectivity also increased with the increase in the steric bulkiness of the α-substituent of the ferrocene moiety in the ligand. Thus, the enantioselectivity decreases approximately in the order **3c**∼**3b**>**3a**>**1**∼**2**.

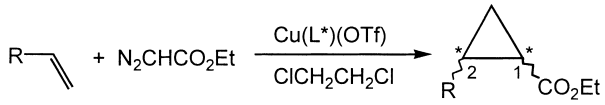
The steric effects on both enantio- and diastereoselectivity can be seen even more dramatically in Table 2 which shows that the sterically more crowded substrate 2,6-di-*t*-butyl-4-methylphenyl diazoacetate (BDA) gives even higher diastereo- and enantioselectivity than ethyl diazoacetate (EDA) although chemical yields drop a little with BDA. These same observations have already been made by others.[6d,e,19] In this connection, it is worth noting the extremely high *trans*-selectivity (98:2) and enantioselectivity (up to 97% e.e.) from the reaction of indene with BDA. These values are quite comparable to those obtained by others employing the well-known chiral oxazoline ligands incorporated in copper, rhodium, or ruthenium.[8]

These observations may be explained by the ability of the hypothetical Cu–carbene intermediate to discriminate between the two enantiotopic faces of the olefin as shown in Scheme 2. According to this Scheme, as the size of substituent (R^2) in the diazoactate increases, the olefin should approach the Cu–carbene in an *anti*-fashion (route a), leading to the formation of a *trans*-isomer.

This scheme may also explain the creation of absolute configuation of 1*S* in the cyclopropanated products from styrene and 1-hexene if these olefins are supposed to approach from the less hindered face of the Cu–carbene intermediate. We were unable to determine the absolute configuration of the product obtained from indene due to the lack of a suitable precedent.

The origin of enantioface discrimination may be explained in terms of the two diastereomeric Cu–carbene intermediates **A** and **B** that may be present in equilibrium with the conformer **A** being energetically more favored as illustrated in Scheme 3.[20] Under these circumstances, the olefin would predominantly approach the *si*-face of the Cu–carbene plane due to the congestion in the *re*-face. The *S* configuration of C_1 of the predominant enantiomer of the cyclopropanecarboxylates can be ascribed to this transition state geometry.

Table 1
Asymmetric cyclopropanation of some olefins with EDA by Cu(L*)(OTf)[a]



Olefin	Ligand	Yield(%)[b]	*Trans*:*Cis*[c]	% ee(*trans*/*cis*)[d]
Styrene	**1**	72	63:37	48/22
	2	86	63:37	87/23
	3a	61	66:34	83/79
	3b	65	69:31	93/68
	3c	62	66:34	93/71
1-Hexene	**1**	69	69:31	86/47
	2	79	70:30	71/51
	3a	62	78:22	70/82
	3b	58	62:38	87/82
	3c	58	77:23	85/86
Indene	**1**	55	73:27	78/76
	2	79	74:26	89/44
	3a	72	79:21	94/81
	3b	60	88:12	94/89
	3c	57	90:10	96/90

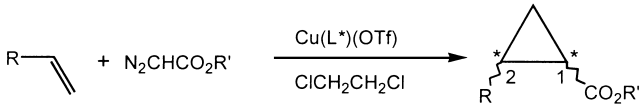
[a]Reaction conditions: [olefin] = 10 mmol; [diazoester] = 2.2 mmol; Addition rate = 2 mL/h.
[b]Isolated yield based on diazoester.
[c]Determined by GC and ^{1}H NMR analysis.
[d]Determined by chiral capillary GC (column, Astec B-DA, 30 m) with the corresponding methyl ester. Absolute configuration for the product: *trans* (1*S*,2*S*) / *cis* (1*S*,2*R*) for styrene; *trans* (1*S*,2*R*) / *cis* (1*S*,2*S*) for 1-hexene; unknown for indene. Absolute configuration was determined by measurement of specific rotation values and by chiroptical comparison with published values.[8]

Of course, it is possible that one of the diastereomeric diazoester complexes transforms stereospecifically to the less prefered isomer **B**. However, even in this case, the rotation of the Cu–carbene bond would convert **B** to the prefered structure **A**. Thus rotation could equilibrate two Cu–carbene conformers whose ratio is subject to their steric environments.

Encouraged by the high asymmetric induction with our copper catalysts and the fact that it is now well established that complexes of ruthenium, rhodium, and palladium have also been widely used as catalysts in the same reaction, we have carried out for comparative purposes the cyclopropanation of some olefins with EDA employing **2** as ligand in a series of complexes.

The results are summarized in Table 3 which demonstrates the highly efficient catalytic nature of our

Table 2
The steric effects of substrate on stereoselectivity[a]



Olefin	Ligand	R'[b]	Yield(%)[c]	*Trans*:*Cis*[d]	% ee(*trans/cis*)[e]
Styrene	**2**	A	86	63:37	87/23
		B	83	98:2	89/55
	3a	A	61	66:34	83/79
		B	58	97:3	92/66
1-Hexene	**2**	A	79	70:30	71/50
		B	78	92:8	83:84
	3a	A	62	78:22	70/82
		B	59	94:6	86/88
Indene	**2**	A	79	74:26	89/44
		B	71	93:7	97/80
	3a	A	72	79:21	94/81
		B	65	98:2	96/93

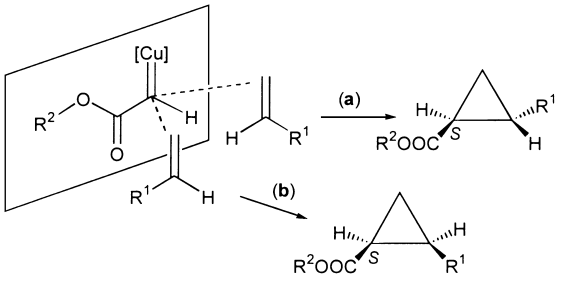
[a]Reaction conditions: [olefin] = 10 mmol; [diazoester] = 2.0 mmol; addition rate = 2 mL/h.

[b] A: R' = Et; B: R' = 2,6-di-*t*-Bu-4-methylphenyl.

[c]Isolated yield based on diazoester.

[d]Determined by GC and ^{1}H NMR analysis.

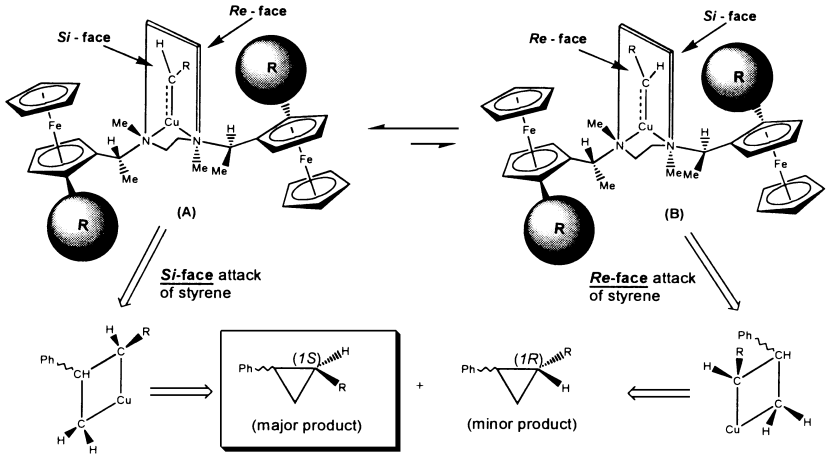
[e]Determined by chiral capillary GC (column, Astec B-DA, 30 m) with the corresponding methyl ester.



Scheme 2.

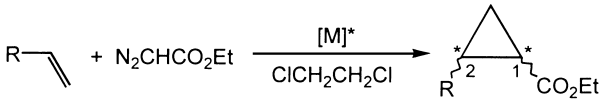
systems. Enantiomeric excesses obtained by complexes of metals other than copper are comparable to or even superior to those obtained by Cu(**2**)(OTf) in certain cases. In fact, to the best of our knowledge, this is the first time that the cationic rhodium complex of the type [Rh(**2**)(NBD)]ClO_4 has been used successfully as a catalyst in this reaction. These high enantiomeric excesses are also comparable to those obtained by others employing the same metals incorporating such ligands as oxazolines and so on.[7,8]

The catalytic carbene transfer process by copper(I) complexes incorporating our new bisferrocene ligands were further extended to the intramolecular cyclopropanation of methyl 2-diazo-3-oxo-7-



Scheme 3.

Table 3
The metal effects on the cyclopropanation[a]



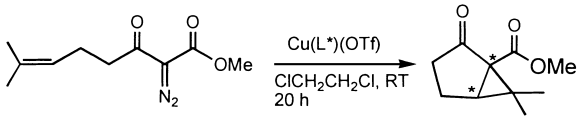
Olefin	Catalyst[b]	Yield(%)	*Trans*:*Cis*	% ee (*trans*/*cis*)
Styrene	Cu(**2**)(OTf)	86	63:37	87/43
	[Cu(**2**)]PF_6	69	67:33	83/48
	Ru(**2**)Cl_2	71	64:36	87/79
	[Rh(**2**)(NBD)]ClO_4	68	51:49	80/43
	Pd(**2**)Cl_2	75	68:32	94/18
1-Hexene	Cu(**2**)(OTf)	79	70:30	71/50
	[Cu(**2**)]PF_6	65	69:31	67/60
	Ru(**2**)Cl_2	73	70:30	72/74
	[Rh(**2**)(NBD)]ClO_4	40	46:54	48/30
	Pd(**2**)Cl_2	68	66:34	58/24
Indene	Cu(**2**)(OTf)	79	74:26	94/81
	[Cu(**2**)]PF_6	73	70:30	80/66
	Ru(**2**)Cl_2	65	72:28	89/75
	[Rh(**2**)(NBD)]ClO_4	58	51:49	78/69
	Pd(**2**)Cl_2	62	68:32	71/70

[a]Reaction conditions and the procedures for product separation and identification are the same as those listed in Table 1.

[b]Data with Ru(**2**)Cl_2 are taken from our previous report.[14]

methylocta-6-octenoate (MDOEA) and cyclopropenation of some alkynes as well. These results are shown in Tables 4 and 5, respectively.

Table 4
Intramolecular cyclopropanation of MDOEA by Cu(L*)(OTf)[a]



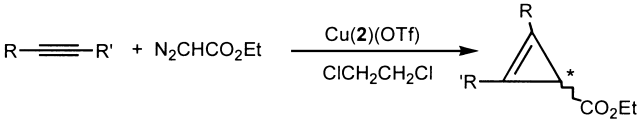
Ligand	Yield(%)[b]	% ee
2	71	55
3a	53	56
3b	54	73
3c	50	77

[a]Reaction conditions and the work-up procedure for product separation and identification the same as before.

[b]Isolated yields.

Here, too, common observations are that enantiomeric excesses depend significantly on the steric nature of both ligand and the substrate. Thus in the case of intramolecular cyclopropanation, for instance, the enantiomeric excesses reach the maximum with **3c** which would provide the most crowded environment around the central copper due to its coordination in a tetradentate manner. Enantiomeric excesses in both reactions are moderate as compared with those reported by others.

Table 5
Asymmetric cyclopropenation of alkynes with EDA by Cu(**2**)(OTf)[a]



R	R'	Yield(%)[b]	% ee
Ph	H	81	68
n-Bu	H	68	63
$BrCH_2$	H	60	64
Ph	$C(Me)_2OH$	69	70

[a]Reaction conditions and the work-up procedure for product separation and identification the same as before.

[b]Isolated yields.

2.2.2. *Asymmetric aziridination*

The catalytic capabilities of our Cu(**2**)(OTf) are not restricted to carbene transfer processes. Table 6 shows that alkenes and [(*p*-tolylsufonyl)imino]phenyliodinane, PhI=NTs, produce aziridines in relatively

Table 6
Asymmetric aziridination of olefins with PhI=NTs by Cu(**2**)(OTf)[a]

Olefin	Reaction time	Yield(%)[b]	% ee[c]
Styrene	1	88	74
trans-Stilbene	2.5	65	68
trans-β-Methylstyrene	2	75	69
1-Hexene	0.5	68	70

[a]Reaction conditions: [olefin] = 7.5 mmol; [PhI=NTs] = 0.73 mmol; [catalyst] = 0.08 mmol.

[b]Isolated yield based on PhI=NTs.

[C]Determined by a chiral GC column (Astec B-DA 30 m and B-PH 30 m).

high chemical and enantiomeric excesses when Cu(**2**)(OTf) is employed as catalyst. All reactions went to completion to achieve a 100% substrate conversion within 3 h at room temperature as checked by GC. The enantiomeric excesses are comparable to those obtained by other Cu(I)-catalysts employing the well-known nitrogen-based ligands.[8,10,12]

Here again, as is the case for the cyclopropanation of alkenes, a key intermediate in the catalytic cycle may be a Cu–carbene of the type (L)Cu=NTs as proposed by Jacobsen and co-workers for the (diimine)Cu-catalyzed asymmetric aziridination of alkenes.[12]

3. Conclusion

We have described the synthesis of new chiral C_2-symmetric bisferrocenyldiimines **1** and -diamines **2** and **3** and their metal complexes of the types $Ru(L)Cl_2$, $Pd(L)Cl_2$, $[Rh(NBD)(L)]ClO_4$, $[Cu(L)(MeCN)_2]PF_6$, and Cu(L)(OTf) (L=**1**, **2**, or **3**). All these complexes have proved to be very efficient catalysts in the asymmetric cyclopropantion and aziridination of some alkene and alkynes. In certain cases, the enantiomeric excesses reached were as high as 98% which are among the highest in the literature although asymmetric induction drops a little in the aziridination as compared with the cyclopropanation. Comparative studies show that steric variation both in the ligand and the substrate affects significantly not only diastereo- but also enantioselectivity of the reactions. The origins of these stereoselectivities were rationalized in terms of the metal–carbene intermediate.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of argon or nitrogen using Schlenk techniques. Solvents were purified by standard methods and were freshly distilled prior to use. All commercial reagents were used as received unless otherwise mentioned. Microanalyses were performed by the Center for Instrumental Analysis, Kyungpook National University. ^1H and ^{31}P NMR spectra were recorded on

a Varian Unity Plus spectrometer operating at 300 and 121.5 MHz, respectively. ^{1}H shifts are reported relative to internal TMS and ^{31}P shifts relative to 85% H_3PO_4. Melting points were measured using a Büchi 510 model and are uncorrected. Mass spectra were obtained by using a Micromass Quattro II GC8000 series model with electron energy of 20 or 70 eV. Optical rotations were measured on a Jasco DIP-360 digital polarimeter at ambient temperature. IR spectra were run on a Mattson FT-IR Galaxy 6030E spectrophotometer and Nicolet Magna-IR 550 spectrophotometer.

4.2. Materials

Ethyl diazoacetate (EDA),[21] 2,6-di-*t*-butyl-4-methylphenyl diazoacetate (BDA),[21] *N*-tosylimino-phenyliodinane (PhI=NTs),[22] iodosylbenzene (PhI=O),[23] methyl-2-diazo-3-oxo-7-methylocta-6-enoate (MDOEA),[24] [Ru(**3c**)]Cl_2, **2**, and **3c**[14] were prepared according to the literature methods.

4.3. Chiral C_2-symmetric bisferrocenyldiamines

4.3.1. (R,R)-N,N′-Cyclohexane-1,2-bis((ferrocenylmethylene)amine) **1**

A mixture of ferrocenecarboxaldehyde (2 g, 9.3 mmol), (*R,R*)-(−)-1,2-diaminocyclohexane (0.54 g, 4.7 mmol), and anhydrous $MgSO_4$ (0.5 g) in diethyl ether was stirred at room temperature for 20 h. The solid suspension was removed by filtration and the resulting orange solution evaporated to dryness and the residue recrystallized from toluene and ether to give orange crystals. Yield: 1.85 g, 78%. Mp: 137°C. $[\alpha]_D^{25}$=−45 (c=1.0, $CHCl_3$). Anal. calcd for $C_{28}H_{30}N_2Fe_2$: C, 66.27; H, 5.92; N, 4.73. Found: C, 65.98; H, 5.84; N, 4.93. ^{1}H NMR ($CDCl_3$): 1.46 (m, 4H, -CH_2), 1.72 (m, 4H, -CH_2), 3.27 (m, 2H, -CH), 4.14 (s, 10H, C_5H_5) and 4.38 (s), 4.60 (s) (8H, C_5H_4), 8.16 (s, 2H, HC=N).

4.3.2. N1,N2-Bis{(R)-1-[(S)-2-trimethylsilyl]-ferrocenylethyl}-N1,N2-dimethyl-1,2-ethanediamine **3a**

To a solution of **2** (1 g, 1.95 mmol) dissolved in THF (10 mL) in a Schlenk tube was added dropwise through a dropping-funnel 1.6 M *n*-BuLi (3.05 mL, 4.88 mmol) in hexane at −78°C. After stirring for 5 h as the tube gradually came to room temperature, it was chilled again at −78°C, to which was added dropwise a THF solution (5 mL) of chlorotrimethylsilane (0.62 mL, 4.88 mmol). The temperature was then raised gradually and the solution stirred for 10 h at room temperature. Following careful hydrolysis with aqueous sodium bicarbonate, the remaining reaction mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:CH_2Cl_2=95:5 (v/v)) and recrystallized from a mixture of CH_2Cl_2 and methanol (1:4, v/v) to give a yellow solid. Yield: 0.77 g, 60%. Mp: 104°C. $[\alpha]_D^{25}$=−280.6 (c=1.5, $CHCl_3$). Anal. calcd for $C_{34}H_{52}Fe_2N_2Si_2$: C, 62.19; H, 7.98; N, 4.26. Found: C, 62.30; H, 7.91; N, 4.11. ^{1}H NMR ($CDCl_3$): 0.25 (s, 18H, $Si(CH_3)_3$), 1.16 (d, *J*=6.9 Hz, 6H, CH_3), 1.86 (s, 6H, NCH_3), 2.31 (m) and 2.34 (m) (4H, CH_2), 3.82 (q, *J*=6.9 Hz, 2H, -CH), 4.01 (bs), 4.20 (bs), and 4.23 (bs) (ABC, 6H, C_5H_3), 4.05 (s, 10H, C_5H_5).

4.3.3. N1,N2-Bis{(R)-1-[(S)-2-diphenylhydroxymethyl)]-ferrocenylethyl}-N1,N2-dimethyl-1,2-ethane-diamine **3b**

The title compound was prepared in the same manner as described above for **3a** by simply replacing chlorotrimethylsilane with benzophenone. Usual work-ups followed by recrystallization from a mixture of CH_2Cl_2 and methanol gave a yellow solid. Yield: 1.0 g, 60%. Mp: 120°C. $[\alpha]_D^{25}$=−296 (c=1.5, $CHCl_3$). Anal. calcd for $C_{54}H_{56}Fe_2N_2O_2$: C, 73.97; H, 6.44; N, 3.19. Found: C, 73.64; H, 6.58; N, 3.08. ^{1}H NMR ($CDCl_3$): 1.06 (d, *J*=6.9 Hz, 6H, -CH_3), 1.52 (s, 6H, NCH_3), 1.62 (m) and 2.05 (m) (4H,

-CH_2), 3.84 (s, 10H, C_5H_5), 3.91 (bs), 4.11 (bs), and 4.18 (bs) (ABC, 6H, C_5H_3), 4.34 (q, J=6.9 Hz, 2H, -CH), 7.09–7.64 (m, 20H, C_6H_5), 8.16 (bs, 2H, -OH).

*4.4. General procedure for [Cu(L)]OTf (L=**1**–**3**)*

To a solution of $(CF_3SO_3Cu)_2 \cdot C_6H_6$ (0.17 g, 0.33 mmol) dissolved in 1,2-dichloroethane (10 mL) was added the bisferrocenyldiamine ligand (0.66 mmol). After stirring the reaction mixture for 3 h at ambient temperature, any solid impurities were removed by filtration. The filtrate was evaporated under reduced pressure to leave a crude product which was washed a few times with diethyl ether to remove excess ligand. An analytically pure product was obtained as a reddish-brown solid by recrystallization from a mixture of CH_2Cl_2 and diethyl. Caution! These compounds slowly decompose in the air and must be handled in a glove box.

*4.4.1. [Cu(**1**)]OTf*

Yield: 75%. Mp: 129°C. Anal. calcd for $C_{39}H_{30}Fe_2N_2CuF_3O_3S$: C, 64.64; H, 4.14; N, 3.87. Found: C, 64.57; H, 4.31; N, 3.74.

*4.4.2. [Cu(**2**)]OTf*

Yield: 80%. Mp: 121°C. Anal. calcd for $C_{29}H_{36}Fe_2N_2CuF_3O_3S$: C, 47.67; H, 4.93; N, 3.84; S, 4.38. Found: C, 47.39; H, 4.90; N, 3.78; S, 4.04.

*4.4.3. [Cu(**3a**)]OTf*

Yield: 70%. Mp: 112°C. Anal. calcd for $C_{35}H_{52}Fe_2N_2Si_2CuF_3O_3S$: C, 48.05; H, 5.95; N, 3.20; S, 3.66. Found: C, 48.17; H, 5.79; N, 3.15; S, 3.45.

*4.4.4. [Cu(**3b**)]OTf*

Yield: 70%. Mp: 123°C. Anal. calcd for $C_{55}H_{56}Fe_2N_2CuF_3O_5S$: C, 60.33; H, 5.12; N, 2.56; S, 2.93. Found: C, 60.06; H, 5.34; N, 2.48; S, 2.90.

*4.4.5. [Cu(**3c**)]OTf*

Yield: 60%. Mp: 199°C. Anal. calcd for $C_{53}H_{54}Fe_2N_2P_2CuF_3O_3S$: C, 57.92; H, 4.92; N, 2.55; S, 2.91. Found: C, 58.17; H, 4.88; N, 2.36; S, 2.97.

*4.5. [Cu(**2**)(MeCN)$_2$]PF$_6$*

To a suspension of $[Cu(MeCN)_4]PF_6$ (0.30 g, 0.81 mmol) in acetonitrile (5 mL) was added dropwise a solution of **2** (0.42 g, 0.82 mmol). After stirring the reaction mixture under reflux for 3 h, any solid suspension was removed by filtration and the filtrate dried under reduced pressure to leave a reddish-brown solid. This was washed several times with diethyl ether and redissolved in a mixture of acetonitrile and diethyl ether for crystallization. Yield: 0.49 g, 75%. Mp: 183°C. Anal. calcd for $C_{32}H_{42}Fe_2CuN_4PF_6$: C, 47.88; H, 5.24; N, 6.98. Found: C, 47.91; H, 5.19; N, 6.71.

*4.6. Pd(**2**)Cl$_2$*

To a solution of $Pd(MeCN)_2Cl_2$ (0.15 g, 0.58 mmol) in $CHCl_3$ (10 mL) in a Schlenk tube was added **2** (0.31 g, 0.6 mmol) dissolved in $CHCl_3$ (10 mL). The solution was further stirred for 3 h and the resulting

red solution was filtered to remove any solid impurities. The dark solid which was left after drying the filtrate under reduced pressure yielded dark red crystals by crystallization from a mixture of acetonitrile and diethyl ether. Yield: 0.32 g, 70%. Anal. calcd for $C_{35}H_{44}Fe_2N_2PdCl_2$: C, 48.76; H, 5.25; N, 4.06. Found: C, 48.54; H, 5.00; N, 3.85. ^{1}H NMR ($CDCl_3$): 1.33 (d, J=6.9 Hz, 6H, -CH_3), 1.62 (br d) and 2.94 (br d) (A_2X_2, J=8.7 Hz, 4H, -CH_2), 2.44 (s, 6H, -NCH_3), 4.16 (s, 10H, C_5H_5), 4.27 (bs) and 4.49 (bs) (A_2B_2, 8H, C_5H_4), 4.91 (q, J=6.9 Hz, 2H, -CH).

4.7. *[Rh(**2**)(NBD)]ClO_4*

A THF solution of $NaClO_4$ (0.05 g, 0.40 mmol) was added to an orange solution of $[Rh(NBD)Cl]_2$ (0.08 g, 0.16 mmol) in THF (10 mL). After stirring the solution for 1 h at ambient temperature, NaCl thus formed was removed by filtration, and the filtrate was heated under reflux for 1 h to be treated with a solution of **2** (0.33 mmol) in THF (10 mL). The resulting red solution was further stirred at ambient temperature for an additional 3 h after which time diethyl ether (5 mL) was added to complete precipitation of an orange solid. This was collected on Celite by filtration, washed with diethyl ether a few times, and then redissolved in CH_2Cl_2. Slow diffusion of hexane into this solution yielded the pure product as orange microcrystals. Yield: 0.19 g, 70%. Anal. calcd for $C_{35}H_{44}Fe_2N_2RhClO_4$: C, 52.11; H, 5.49; N, 3.47. Found: C, 52.25; H, 5.71; N, 3.30. ^{1}H NMR ($CDCl_3$): 1.43 (bs, 2H, -CH_2 of NBD), 1.58 (br d) and 2.65 (br d) (A_2X_2, J=9.6 Hz, 4H, -CH_2 of ethylenediamine), 2.32 (d, J=6.9 Hz, 6H, -CH_3), 2.42 (s, 6H, -NCH_3), 3.16 (q, J=6.9 Hz, 2H, -CH), 3.82 (bs, 2H, -CH of NBD), 4.08 (bs, 4H, vinylic groups of NBD), 4.15 (s, 10H, C_5H_5), 4.17 (bs, 8H, C_5H_4).

4.8. *General procedure for asymmetric cyclopropanation and cyclopropenation*

Catalyst (0.050 mmol) was dissolved in 10 mL of 1,2-dichloroethane, and 10 equiv. of the alkene (or alkyne) was added. Diazoester (2.5 mmol) was diluted in 10 mL of 1,2-dichloroethane and added slowly (15 h) with a syringe pump to the catalyst–olefin mixture, which was under reflux. After the addition was complete, the solvent and excess olefin were removed under vacuum. The oily residue was passed through a short silica gel column to remove catalyst using a 95:5 hexane:EtOAc mixture as an eluent. The GC conditions for the separation of *cis*- and *trans*-diastereomers are as follows: column OV 17 on a Shimadzu GC-14B series equipped with a split mode capillary system, Shimadzu CR-3A data processor, and a flame ionization detector; initial temp 70°C; final temp 230°C; initial time 2 min; final time 10 min; rate 3°C/min; injection temp 250°C; detector temp 250°C; flow rate 40 mL/min. GC conditions for enantiomers after hydrolysis followed by re-esterification of the reaction product to the corresponding methyl ester: chiral column Astect B-DA, G-TA, B-PH 30 m on a Shimadzu GC-17A; initial temp 120°C; final temp 200°C; initial time 2 min; final time 5 min; rate 5°C/min; oven temp 120°C (set) and 225°C (max); injection temp 230°C; detector temp 250°C; column pressure: 52 kPa, flow rate 0.44 mL/min; linear velocity 14.8 cm/s; split ratio −1.

4.8.1. *Ethyl 2-phenylcyclopropane-1-carboxylate*

This was obtained as the product from the reaction of styrene with EDA. Yield: 80%. t_R (in GC)=31.82 min (*cis*); 33.25 min (*trans*); 17.4 min (*S,R*); 18.6 min (*S,S*). MS: *m/z* (%): 190 (27, M^+), 162 (6), 144 (25), 133 (11), 117 (100), 116 (78), 106 (7), 91 (18), 65 (6), 52 (8). ^{1}H NMR ($CDCl_3$): 0.96 (t, J=7.35 Hz, 3H, -CH_3), 1.25–1.35 (m, 2H, -CH_2), 1.27 (t, J=7.2 Hz, 3H, -CH_3), 1.56–1.62 (m, 1H, *trans* CH), 1.68–1.74 (m, 1H, *cis* CH), 1.86–2.16 (m, 1H, -CH), 2.48–2.58 (m, 1H, -CH), 3.87 (q, J=7.1 Hz, 2H, *cis*-CH_2O), 4.15 (q, J=7.1 Hz, 2H, *trans*-CH_2O), 7.08–7.30 (m, 5H, C_6H_5).

4.8.2. Ethyl 2-butylcyclopropane-1-carboxylate

A colorless oil obtained from the reaction of 1-hexene with EDA. Yield: 75%. t_R (in GC)=15.50 min (*cis*); 17.21 min (*trans*); 4.78 min (*S,S*); 6.03 min (*S,R*). MS: *m/z* (%): 170 (0.3, M^+), 155 (0.6), 141 (2), 128 (10), 125 (18), 115 (3), 101 (31), 82 (30), 73 (60), 55 (100). ^{1}H NMR ($CDCl_3$): 0.66–0.69 (m, 2H, -CH_2), 0.85–0.94 (m, 9H, -$(CH_2)_3CH_3$), 0.95–1.02 (m, 2H, -CH_2), 1.23–1.37 (m, 1H, -CH), 1.26 (t, *J*=7.2 Hz, 3H, -CH_3), 1.41–1.56 (m, 1H, *trans*-CH), 1.62–1.69 (m, 1H, *cis*-CH), 4.12 (q, *J*=7.1 Hz, 2H, CH_2O).

4.8.3. Ethyl 1,1a,6,6a-tetrahydrocyclopropa[a]indene-6a-carboxylate

A colorless oil obtained from the reaction of indene with EDA. Yield: 75%. t_R (in GC)=36.76 min (*cis*); 38.88 min (*trans*); 20.0 min; 21.7 min. MS: *m/z* (%): 202 (11, M^+), 187 (0.1), 173 (11), 157 (8), 145 (5), 129 (100), 115 (9), 102 (5), 89 (2), 77 (7), 63 (6), 51 (5). ^{1}H NMR ($CDCl_3$): 0.90 (t, *J*=7.2 Hz, 3H, -CH_3), 1.22 (t, *J*=7.05 Hz, 3H, -CH_3), 1.95 (t, *J*=8.1 Hz, 1H, -CH), 2.19 (m, 1H, -CH), 2.39 (m, 1H, -CH), 2.94 (d, *J*=6.3 Hz, 2H, -CH_2), 3.18 (dd, *J*=6.6 Hz, 1H, -CH), 4.12 (q, *J*=7.1 Hz, 2H, CH_2O), 3.80 (q, *J*=7.1 Hz, 2H, CH_2O), 7.06–7.29 (m, 4H, C_6H_4).

4.8.4. Ethyl 1-methyl-2-phenylcyclopropane-1-carboxylate

A colorless oil obtained from the reaction of *trans*-β-methylstyrene with EDA. Yield: 65%. t_R (in GC)=32.1 min (*cis*); 34.1 min (*trans*); 17.8 min (*S,R*); 19.1 min (*S,S*). MS: *m/z* (%): 204 (12, M^+), 189 (1), 175 (1), 158 (13), 144 (3), 131 (100), 115 (29), 103 (5), 91 (44), 77 (12), 65 (8), 51 (10). ^{1}H NMR ($CDCl_3$): 1.28 (t, *J*=7.1 Hz, 3H, -CH_3), 1.57 (t, *J*=7.1 Hz, 3H, -CH_3), 1.68 (d, *J*=6.3 Hz, 3H, -CH_3), 1.98 (m, 1H, -CH), 2.14 (m, 1H, -CH), 2.32 (m, 1H, -CH), 2.38 (m, 1H, -CH), 2.62 (t, *J*=5.7 Hz, 1H, -CH), 2.73 (t, *J*=5.7 Hz, 1H, -CH), 4.16 (q, *J*=7.1 Hz, 2H, CH_2O), 4.46 (q, *J*=7.1 Hz, 2H, CH_2O), 7.35–7.58 (m, 5H, C_6H_5).

4.8.5. Ethyl 2,2′-diphenylcyclopropane-1-carboxylate

A colorless oil obtained from the reaction of 1,1′-diphenylethylene with EDA. Yield: 65%. t_R (in GC)=51.8 min; 34.5 min (*S*). MS: *m/z* (%): 266 (2, M^+), 237 (19), 221 (8), 192 (100), 178 (29), 165 (36), 152 (8), 115 (96), 105 (71), 91 (33), 77 (62), 51 (30). ^{1}H NMR ($CDCl_3$): 0.99 (t, *J*=7.4 Hz, 3H, -CH_3), 1.29–1.36 (m, 2H, -CH_2), 1.31 (t, *J*=7.2 Hz, 3H, -CH_3), 2.17 (t, *J*=5.4 Hz, 1H, -CH), 3.86 (q, *J*=7.1 Hz, 2H, *cis*-CH_2O), 4.17 (q, *J*=7.1 Hz, 2H, *trans*-CH_2O), 7.11–7.35 (m, 10H, C_6H_5).

4.8.6. 2,6-Di-t-butyl-4-methylphenyl 2-phenylcyclopropane-1-carboxylate

A colorless oil obtained from the reaction of styrene with BDA. Yield: 83%. t_R (in GC)=27.0 min (*cis*); 29.7 min (*trans*); 13.4 min (*S,R*); 15.9 min (*S,S*). MS: *m/e* (%): 364 (3, M^+), 220 (4), 204 (5), 188 (2), 160 (2), 144 (100), 126 (21), 116 (18), 90 (12), 77 (3), 57 (15), 41 (10). ^{1}H NMR ($CDCl_3$): 1.26–1.34 (m, 2H, -CH_2), 1.43 (s, 18H, -$C(CH_3)_3$), 1.53–1.64 (m, 1H, -CH), 1.85–2.21 (m, 1H, CH), 2.27 (s, 3H, -CH_3), 7.13–7.41 (m, 5H, C_6H_5).

4.8.7. 2,6-Di-t-butyl-4-methylphenyl 2-butylcyclopropane-1-carboxylate

A colorless oil obtained from the reaction of 1-hexene with BDA. Yield: 78%. t_R (in GC)=21.2 min (*cis*); 23.8 min (*trans*); 8.7 min (*S,S*); 10.8 min (*S,R*). MS: *m/z* (%): 344 (3, M^+), 220 (12), 205 (13), 190 (4), 177 (2), 162 (5), 149 (2), 125 (58), 97 (11), 82 (8), 55 (100), 41 (27). ^{1}H NMR ($CDCl_3$): 0.87–0.96 (m, 9H, -$(CH_2)_3CH_3$), 1.21–1.37 (m, 2H, -CH_2), 1.41 (s, 18H, -$C(CH_3)_3$), 1.47–1.61 (m, 1H, -CH), 1.81–2.20 (m, 1H, -CH), 2.24 (s, 3H, -CH_3), 6.97 (s, 2H, Ar-H), 7.10–7.38 (m, 5H, C_6H_5).

4.8.8. 2,6-Di-t-butyl-4-methylphenyl 1-methyl-2-phenylcyclopropane-1-carboxylate

A colorless oil obtained from the reaction of *trans*-β-methylstyrene with BDA. Yield: 51%. t_R (in GC)=28.5 min (*cis*); 30.8 min (*trans*); 15.1 min (*S*,*R*); 16.8 min (*S*,*S*). MS: *m/z* (%): 378 (1, M^+), 220 (10), 205 (12), 189 (4), 159 (100), 141 (11), 131 (20), 115 (10), 91 (16), 77 (6), 57 (19), 41 (7). ^{1}H NMR ($CDCl_3$): 1.47 (s, 18H, -C(CH_3)$_3$), 1.68 (d, *J*=6.3 Hz, 3H, -CH_3), 1.99–2.25 (m, 1H, -CH), 2.35 (s, 3H, -CH_3), 2.58–2.75 (m, 1H, -CH), 2.76 (t, *J*=5.7 Hz, 1H, -CH), 7.01 (s, 2H, Ar-H), 7.37–7.60 (m, 5H, C_6H_5).

4.8.9. 2,6-Di-t-butyl-4-methylphenyl 1,1a,6,6a-tetrahydrocyclopropa[a]indene-6a-carboxylate

A colorless oil obtained from the reaction of indene with BDA. Yield: 71%. t_R (in GC)=43.0 min (*cis*); 45.1 min (*trans*); 30.5 min; 31.4 min. MS: *m/z* (%): 376 (2, M^+), 364 (2), 292 (1), 257 (1), 220 (16), 205 (14), 157 (100), 144 (18), 129 (39), 116 (10), 77 (5), 57 (31). ^{1}H NMR ($CDCl_3$): 1.42 (s, 18H, -C(CH_3)$_3$), 1.95 (t, *J*=8.1 Hz, 1H, -CH), 2.23 (s, 3H, -CH_3), 2.25–2.39 (m, 1H, -CH), 2.58–2.75 (m, 1H, -CH), 2.76 (t, *J*=5.7 Hz, 1H, -CH), 7.01 (s, 2H, Ar-H), 7.37–7.60 (m, 5H, C_6H_5).

4.8.10. 1-Acetyl 6,6-dimethylbicyclo[3,1,0]hexane-2-one

A colorless oil obtained from the intramolecular cyclopropanation of MDOEA. Yield: 80%. t_R (in GC): 17.82 min; 19.25 min. ^{1}H NMR ($CDCl_3$): 0.93–1.47 (m, 2H, -CH_2), 1.71–1.78 (m, 1H, -CH), 1.79 (d, *J*=3.3 Hz, -CH_3), 1.99 (d, *J*=3.3 Hz, -CH_3), 2.35–2.44 (m, 2H, -CH_2), 3.21 (s, 3H, -OCH_3).

4.8.11. Ethyl 2-phenylcyclopropene-1-carboxylate

A colorless oil obtained from the reaction of phenylacetylene with EDA. Yield: 81%. MS: *m/z* (%): 188 (10, M^+), 159 (4), 143 (11), 126 (100), 114 (68), 104 (18), 98 (80), 81 (22), 71 (22), 55 (40). ^{1}H NMR ($CDCl_3$): 0.87 (d, *J*=6.9 Hz, 1H, -CH), 1.31 (t, *J*=7.2 Hz, 3H, -CH_3), 1.64 (d, *J*=6.9 Hz, 1H, -CH), 4.27 (q, *J*=7.1 Hz, 2H, CH_2O), 7.26–7.45 (m, 5H, C_6H_5).

4.8.12. Ethyl 2-butylcyclopropene-1-carboxylate

A colorless oil obtained from the reaction of 1-hexyne with EDA. Yield: 68%. MS: *m/z* (%): 168 (8, M^+), 139 (8), 127 (21), 125 (20), 123 (9), 97 (58), 95 (100), 81 (22), 67 (38), 53 (42), 41 (47). ^{1}H NMR ($CDCl_3$): 0.87–0.94 (m, 9H, -$(CH_2)_3CH_3$), 0.95 (d, *J*=6.9 Hz, 1H, -CH), 1.29 (t, *J*=7.2 Hz, 3H, -CH_3), 1.42 (d, *J*=6.9 Hz, 1H, -CH), 4.20 (q, *J*=7.1 Hz, 2H, CH_2O).

4.8.13. Ethyl 2-bromomethylcyclopropene-1-carboxylate

A colorless oil obtained from the reaction of propargyl bromide with EDA. Yield: 60%. MS: *m/z* (%): 205 (6, M^+), 193 (3), 177 (8), 152 (27), 135 (20), 115 (100), 105 (49), 88 (27), 63 (48), 52 (44). ^{1}H NMR ($CDCl_3$): 0.93 (d, *J*=6.9 Hz, 1H, -CH), 1.27 (t, *J*=7.2 Hz, 3H, -CH_3), 1.58 (d, *J*=6.9 Hz, 1H, -CH), 4.01 (s, 2H, -CH_2), 4.15 (q, *J*=7.1 Hz, 2H, CH_2O).

4.8.14. Ethyl 2-phenyl-3-(α-hydroxy-α-methyl)ethylcyclopropene-1-carboxylate

A colorless oil obtained from the reaction of 3,3′-dimethyl-1-phenylpropyn-3-ol with EDA. Yield: 69%. MS: *m/z* (%): 246 (4, M^+), 231 (53), 204 (2), 172 (5), 143 (100), 127 (62), 115 (19), 102 (9), 91 (5), 77 (11), 63 (5), 43 (8). ^{1}H NMR ($CDCl_3$): 1.47 (t, *J*=7.2 Hz, 3H, -CH_3), 1.81 (s, 6H, -CH_3), 4.42 (q, *J*=7.1 Hz, 2H, CH_2O), 4.50 (s, 1H, OH), 7.49–7.64 (m, 5H, C_6H_5).

4.9. General procedure for asymmetric aziridination

Complex Cu(**2**)OTf (19 mg, 0.03 mmol) was dissolved in acetonitrile (2 mL) in a Schlenk flask to which olefin (0.3 mmol) was added via syringe. The mixture was stirred for 15 min after which PhI=NTs (100 mg, 0.27 mmol) was then added portionwise over 30 min. After stirring for an additional 2 h at room temperature, the mixture was applied to a vacuum line to remove any volatiles. Column chromatography of the residue on silica gel (hexane:EtOAc=4:1 (v/v)) led to the isolation of the product.

4.9.1. N-*(*p-*Tolylsulfonyl)-2-phenylaziridine*

A white crystalline solid obtained from the reaction of styrene with PhI=NTs. Yield: 60 mg, 88%. Mass spectrum: *m/z* (relative intensity) 274 (2, M^+), 208 (0.2), 181 (0.3), 167 (0.3), 155 (1), 139 (2), 118 (100), 104 (2), 91 (99), 77 (4), 65 (19), 51 (6). ^{1}H NMR ($CDCl_3$): 2.39 (d, *J*=3.6 Hz, CH), 2.43 (s, Ar-CH3), 2.99 (d, *J*=6.9 Hz, CH), 3.77 (t, *J*=6 Hz, CHPh), 7.28 (m, Ar-H), 7.85 (d, *J*=8.7 Hz, Ar-H).

4.9.2. trans-N-*(*p-*Tolylsulfonyl)-2,3-diphenylaziridine*

A white crystalline solid obtained from the reaction of *trans*-stilbene with PhI=NTs. Yield: 65%. MS: *m/z* (%): 350 (9, M^+), 270 (1), 261 (2), 194 (100), 165 (15), 152 (8), 128 (0.9), 116 (10), 105 (11), 91 (23), 77 (10), 65 (13), 51 (7). ^{1}H NMR ($CDCl_3$): 2.38 (s, Ar-CH_3), 4.26 (s, -CH), 7.20 (d, *J*=8.7 Hz, Ar-H), 7.25–7.50 (m, Ar-H), 7.61 (d, *J*=8.7 Hz, Ar-H).

4.9.3. trans-N-*(*p-*Tolylsulfonyl)-2-phenyl-3-methylaziridine*

A white crystalline solid obtained from the reaction of *trans*-β-methylstyrene with PhI=NTs. Yield: 75%. Anal. calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.80; H, 5.84; N, 4.78. ^{1}H NMR ($CDCl_3$): 1.81 (d, *J*=6.0 Hz, -CH_3), 2.36 (s, Ar-CH_3), 2.92 (dq, *J*=6.0, 4.4 Hz, -$CHCH_3$), 3.76 (d, *J*=4.3 Hz, -CHPh), 7.14 (d, *J*=8.0 Hz, Ar-H), 7.20–7.25 (m, Ar-H), 7.80 (d, *J*=8.3 Hz, Ar-H).

4.9.4. N-*(*p-*Tolylsulfonyl)-2-*n*-butylaziridine*

A colorless oil obtained from the reaction of 1-hexene with PhI=NTs. Yield: 68%. Anal. calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.81; H, 7.60; N, 5.79. ^{1}H NMR ($CDCl_3$): 0.8 (t, 3H, *J*=7.0 Hz, -CH_3), 1.21–1.35 (m, 5H, aliphatic CH), 1.55 (m, 1H, aliphatic CH), 2.04 (d, 1H, *J*=4.6 Hz, -CH), 2.42 (s, 3H, Ar-CH_3), 2.64 (d, 1H, *J*=7.0 Hz, -CH), 2.70 (m, 1H, -CH), 7.31 (d, 2H, *J*=8.3 Hz, Ar-H), 7.83 (d, 2H, *J*=8.3 Hz, Ar-H).

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