1,2-Ferrocenediylazaphosphinines 3: A New Class of Planar Chiral Ligands for Cu-Catalyzed Cyclopropanation[1]

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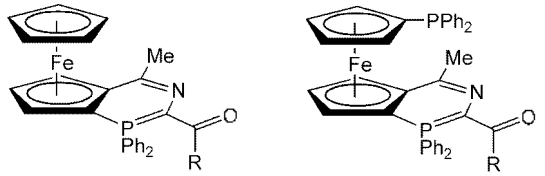
The synthesis and catalytic application of a new class of planar chiral ferrocenes, 1,2-ferrocenediylazaphosphinines (**1** and **2**) are described. They are powerful ligands for the copper(I)-catalyzed asymmetric cyclopropanation of a range of alkenes with diazo esters to exhibit an exceptionally high degree of diastereoselectivity (~100% de) in favor of *trans* isomers, regardless the structure of the olefins and the diazo compounds. Comparative studies between **1** and **2** reveal that the former works better in terms of diastereocontrol. In contrast, however, enantioselectivity is low with both **1** and **2** as a whole although, in certain cases with a proper combination of the olefin and the diazo ester, high optical yields (up to 100% ee) can be achieved. Other reaction parameters such as the reaction temperature and the structure of the ligand do exhibit some influence, although infinitesimal, on both chemical and optical yields.

Key Words : Ferrocenediylazaphosphinines, Asymmetric cyclopropanation, Copper-catalysis

Introduction

Asymmetric cyclopropanation of olefins with diazoacetates catalyzed by chiral transition metal complexes is well-established, and as such a great number of catalysts are now known.[2] Of a myriad of catalysts, copper complexes incorporating chiral diimines such as salicylaldimines,[3] semicorrins,[4] oxazolines,[5] bipyridines,[6] polypyrazoles,[7] porphyrins,[8] and related diimines[9] deserve a special attention as highly efficient catalysts. More recent examples of diimine ligands include C_2-symmetric planar chiral ferrocenes of the type (π-heterocycle)FeCp* developed by Fu.[10]

We have recently reported the synthesis of 1,2-ferrocenediylazaphosphinines (**1**, Chart 1) as a completely new family of planar chiral ferrocenes and shown that they are powerful ligands in a Cu-catalyzed cyclopropanation of styrene to achieve a complete diastereocontrol.[11] Encouraged by these findings and following our continuing effort in this field,[12] we decided to expand the scope of our investigation with **1** to establish their effectiveness as chiral ligands in the Cu(I)-catalyzed asymmetric cyclopropanation of even a wider range of olefin substrates (eq 1). In view of this line of investigation, the preparation of the closely related compound such as **2** (Chart 1) would be rationalized in that comparative studies would provide a suitable testing ground for determining the effectiveness of our ligand design. Here we report the preparation and the use of **1** and **2** as a new class of planar chiral ferrocene ligands in the Cu-catalyzed cyclopropanation of olefins with diazo esters.



1a: R = H
1b: R = Me
1c: R = Ph

2a: R = H
2b: R = Me
2c: R = Ph

Chart 1

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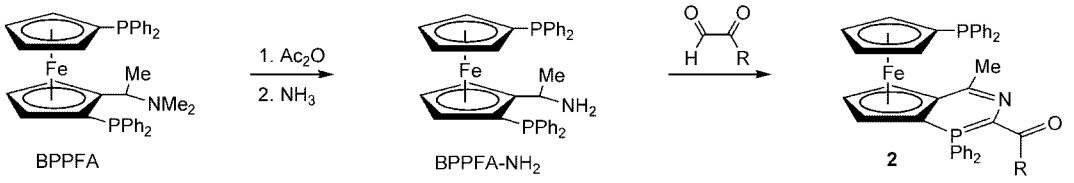
Results and Discussion

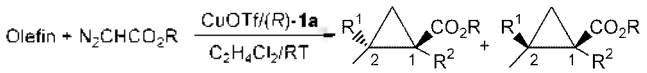
Synthesis and Characterization. 1,2-Ferocenediylazaphosphinines (**1**) were prepared according to the method described earlier by us,[11] and simple extension of the same method led to the formation of their phosphine analogues, 1'-diphenylphosphino-1,2-ferocenediylazaphosphinines (**2**). Thus, our synthesis of (*R*)- or (*S*)-**2** begins with (*S,R*)- or (*R,S*)-1-(α-aminoethyl)-1',2-bis(diphenylphosphino)ferrocene (BPPFA-NH_2, Scheme 1), which is available in two steps through acetoxylation followed by amination with liquid ammonia of well-known (*S,R*)- or (*R,S*)-1-(α-N,N-dimethylaminoethyl)-1',2-bis(diphenylphosphino)ferrocene (BPPFA), respectively.[13] Here the first *R* or *S* refers to the central chirality located on the asymmetric carbon atom and the second to the planar chirality due to the presence of two different substituents on the Cp ring.

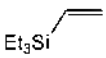
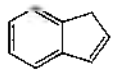
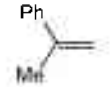
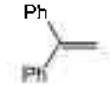
All these new compounds are stable indefinitely in the solid state, yet slowly undergo decomposition by air in solution. The ^{31}P NMR spectrum is the most revealing for structural confirmation of **2**. Thus in the case of **2a**, for example, two phosphorus signals arise at -5.57 and -18.50 ppm due to the ylidic phosphorus in the heterocyclic ring and the 1'-phosphine group, respectively. Their ^1H NMR patterns are also straightforward revealing the signals



Scheme 1

Table 1. Asymmetric Cyclopropanation of Olefins with (*R*)-**1a** as Ligand[a]

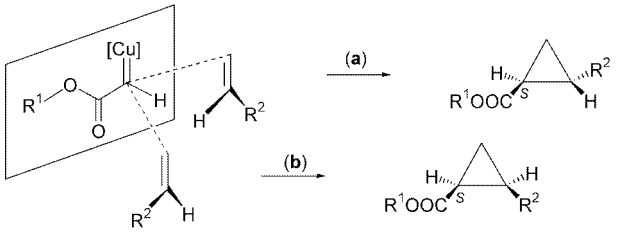


Entry	Olefin	R	Yield (%)	*trans*:*cis*	% ee (*trans*)
1		Et	99	100:0	63
2	R^1 = Ph; R^2 = H	^{t}Bu	91	90:10	11
3		BHT[b]	89	100:0	7
4		Et	87	99:1	18
5	R^1 = $SiEt_3$; R^2 = H	^{t}Bu	83	100:0	1
6		BHT	84	100:0	–
7		Et	88	94:6	23
8	R^1 = Ph; R^2 = Me	^{t}Bu	83	95:5	24
9		BHT	86	100:0	36
10		Et	92	98:2	2
11		^{t}Bu	93	94:6	3
12		BHT	88	100:0	10
13		Et	87	61:39	10
14		^{t}Bu	84	66:34	13
15	R^1 = Ph; R^2 = H	BHT	86	65:35	–
16		Et	88	–	85
17		^{t}Bu	87	–	90
18	R^1 = Ph; R^2 = H	BHT	85	–	42

[a]Detailed procedure provided in the experimental section. [b]BHT = 2,6-di-*t*-butyl-4-methylphenyl.

expected from their structures. Detailed NMR assignments for **2** were made possible by comparison with those of **1**. In addition, the high-resolution mass spectral data are in good agreement with the calculated values.

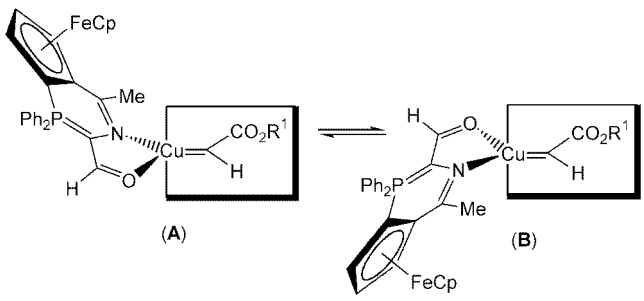
Catalysis. Table 1 shows the Cu(I)-catalyzed asymmetric cyclopropanation of various olefins employing (*R*)-**1a** as ligand. The most characteristic feature of the table is the achievement of an exceptionally high degree of diastereoselectivity (up to 100% de) in favor of *trans* isomers in most cases (entries 1-12). Thus, our ligand **1a** is far more excellent in diastereo-discrimination than the well-known C_2-symmetric diimines such as semicorrins,[4] bisoxazolines,[5] and bisazaferrocene.[10] The table also shows that the structure of the diazo ester has little impact on the diastereoselectivity established by **1a**. These observations are somewhat unusual



Scheme 2

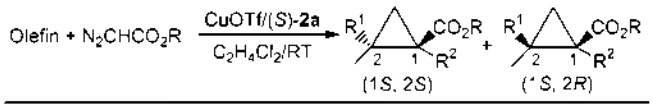
in the light of a general trend that increasing the steric demand of the diazo ester can lead to a significant improvement in diastereoselectivity as well as enantioselectivity when chiral C_2-symmetric diimines such as semicorrins, bisoxazolines, or bisazaferrocene are employed as ligands in Cu-catalyzed cyclopropanation.[2b] In fact, the origin of diastereoselectivity can be explained in terms of the ability of the hypothetical Cu-carbene intermediate to discriminate between two enantiotopic faces of the olefin. Namely, preferential attack of the olefin to the less hindered face of two diastereotopic faces of the M=C intermediate leads to the same absolute configuration (*S*) at the carboxyl-bearing carbon atom (Scheme 2). In our hands, near perfect diastereo-discrimination is established to take exclusively route (a), regardless the structure of the diazo ester as well as the olefin.

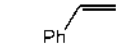
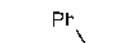
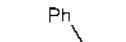
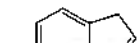
When it comes to enantioselectivity, however, the results are rather disappointing to give very low enantiomeric excesses (% ees) with all but one olefin 1,1'-diphenylethene (entries 16-17). Such low enantioselectivity may be explained in terms of the equilibrium between two diastereomeric Cu-carbene intermediates **A** and **B**, through which any enantio-discirmination experienced by the approaching olefin would be washed out (Scheme 3). In addition, the position of equilibrium is tilted toward neither direction since no steric congestion is conspicuous in either diastereomer. This line of argument may gain support from the well-documented fact that enantioselectivity is governed mostly



Scheme 3

Table 2. Asymmetric Cyclopropanation of Olefins with (*S*)-**2a** as Ligand

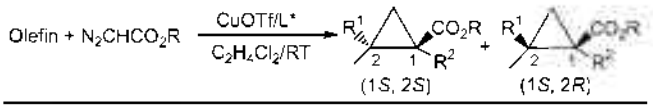


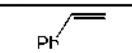
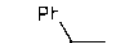
Entry	Olefin	R	Yield (%)	*trans*:*cis*	% ee (*trans*)
1		Et	97	80:20	3
2		^{t}Bu	95	79:21	18
3	R^1 = Ph; R^2 = H	BHT	92	100:0	24
4		Et	83	–	7
5		^{t}Bu	82	–	<1
6	R^1 = Ph; R^2 = H	BHT	70	–	100
7		Et	85	57:43	7
8		^{t}Bu	95	61:39	17
9	R^1 = Ph; R^2 = H	BHT	85	65:35	24
10		Et	93	75:25	8
11		^{t}Bu	90	85:15	5
12	R^1 = Ph; R^2 = Me	BHT	88	95:5	2
13		Et	96	81:19	4
14		^{t}Bu	93	87:13	7
15		BHT	89	100:0	1

by the interaction between the ester group (R^1) and the ligand substituents locating close to the reaction center in the Cu-carbene intermediate, thus for example, bulkier esters or ligand substituent(s) leading to higher % ees. This reasoning may partially account for the relatively high % ees achieved by 1,1'-diphenylethene (entries 16-17) since the presence of C_2-symmetry in this olefin can eliminate the possibility of the formation of additional isomers, thus providing the added bonus of an increase in the % ees. Here, an interesting structural features of **A** and **B** are the unusual coordination mode *via* η^2-N,O of the ligand **1a**, and proposed as such based on our parallel observations made with (η^2-N,O)M(CO)$_4$ (M=Mo, W), (η^2-N,O)MX(CO)$_3$ (M=Mn, Re), and [(C_3H_5)(η^2-N,O)Pd]BF_4.[14] It may be the bond-breaking and remaking of the Cu-oxygen bond that is involved in the equilibrium process.

The success with **1a** has prompted us to examine the related planar chiral ferrocene analogues such as **2** (Chart 1) as a potential source of chiral ligand. Our rationale was straightforward: the presence of softer, yet bulkier phosphine group in **2** near the reaction center by coordination probably in an η^2-P,N fashion to copper might lead to better enantiomeric excesses. Disappointingly, however, the results summarized in Table 2 are rather contrary to our initial expectation. The ligand **2a** works far less efficiently than **1a** both in diastereo- and enantio-control regardless the structure of the olefin and the diazo ester. Here again, one notable exception for high % ee is found from the reaction of 1,1'-diphenylethene implying the importance of the C_2-symmetric nature of the substrate (entry 6, Table 2). Other reaction parameters such as the reaction temperature and the structure of the ligand do exhibit some influence, although infinitestimal, on both chemical and optical yields as summarized in Table 3. Namely, the overall chemical yields increase with increase in the reaction temperature, while the trend is reversed in the case of % ees (entries 1-3 and 6-8). The effect of the ligand structure on enantioselectivity is as expected, thus % ees increasing with increase in the steric bulkiness: **2a** < **2b** < **2c**. The exact nature of coordination of **2** in connection with these trends has yet to be clarified.

Table 3. Asymmetric Cyclopropanation of Olefins with Ethyl Diazoacetate: Stereoselectivity as Functions of Ligand and Temperature



Entry	Olefin	L*	Temp. (°C)	Yield (%)	*trans*:*cis*	% ee (*trans*)
1		(*S*)-**2a**	-25	82	71:29	10
2		(*S*)-**2a**	RT	92	80:20	3
3	R^1 = Ph; R^2 = H	(*S*)-**2a**	50	95	73:27	2
4		(*S*)-**2b**	RT	92	75:25	5
5		(*S*)-**2c**	RT	95	73:27	12
6		(*S*)-**2a**	-25	83	59:41	10
7		(*S*)-**2a**	RT	85	57:43	7
8		(*S*)-**2a**	50	92	52:48	10
9	R^1 = Ph; R^2 = H	(*S*)-**2b**	RT	90	59:41	14
10		(*S*)-**2c**	RT	97	58:42	21

Conclusions

We have presented here the synthesis of a series of 1,2-ferrocenediylazaphosphines (**1** and **2**) as a new class of planar chiral ferrocenes. They have proved to be very efficient ligands for Cu(I)-catalyzed cyclopropanation of a range of olefins with various diazo esters to exhibit very high % des. In some cases, perfect diastereocontrol is achieved with **1a** as ligand. In contrast, % ees are rather low with both **1** and **2** although a few exceptions are found reaching up to 100% ee with a proper combination of the olefin and the diazo ester. Although infinitestimal, structural variation as well as other reaction parameters such as reaction temperature do show some influence not only on the chemical yield but also on the optical yield. Comparative studies reveal that **1** works better than **2** in both diastereo- and enantio-control for the reason unknown. Exact nature of catalytic properties of these new ligands awaits further investigation.

Experimental Section

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. ^{1}H 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. Coupling constants are in Hz. 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.

Materials. (*R*)-/(*S*)-**1**,[11] (*R,S*)-/(*S,R*)-BPPFA,[13] (*R,S*)-/(*S,R*)-BPPFA-NH_2.[11] Ethyl diazoacetate (EDA),[15] *tert*-butyl diazoacetate (^{t}Bu),[15] were prepared according to the literature methods. Olefins and 2,6-di-*t*-butyl-4-methylphenyl diazoacetate (BHT) were purchased from Aldrich and used as received.

Synthesis of (S)-2a. To a solution of (*R,S*)-BPPFA-NH_2 (0.500 g, 0.84 mmol) in MeOH (10 mL) was added an aqueous solution (40%) of glyoxal (0.17 mL, 1.00 mmol). The mixture was stirred for 5 h at room temperature, after which the solution was dried over anhydrous $MgSO_4$. Removal of any solids through filtration followed by concentration in vacuo gave the crude product which was purified by column chromatography on silica gel (eluent: Et_2O : MeOH, 9 : 1) to yield a dark orange solid (0.24 g, 45%). $[\alpha]_D^{27}$ = -1723 (c = 0.1 in $CHCl_3$). ^{31}P NMR ($CDCl_3$): -5.57 (s), -18.50 (s). ^{1}H NMR ($CDCl_3$): 9.54 (d, J_P = 25, 1H, CHO), 2.21 (s, 3H, CH_3), 4.33 (m), 4.50 (m), 4.73 (m) (ABC, 3H, C_5H_3), 4.10 (d, J_H = 21.3), 3.40 (d, J_H = 28.8) (A_2B_2, 4H, C_5H_4), 7.75-7.20 (m, 20H, PPh_2 and =PPh_2). IR (KBr): 1592 cm^{-1} (m), 1545 cm^{-1} (vs). HRMS (EI, *m/z*): Calcd for $C_{38}H_{31}NOP_2Fe$: 635.1230 (M^-). Found: 635.1230.

Synthesis of 2b. The title compound was prepared in the same manner as described above for **2a** by simply replacing glyoxal with methylglyoxal. Usual work-ups followed by recrystallization from a mixture of CH_2Cl_2 and methanol gave a yellow solid. Yield: 45%. $[\alpha]_D^{27}$ = -907 (c = 0.1, $CHCl_3$). ^{31}P NMR ($CDCl_3$): -8.53 (s), -18.31 (s). ^{1}H NMR ($CDCl_3$): 2.22 (s, 3H, -N=CCH_3), 2.38 (s, 3H, $COCH_3$), 3.22 (d, J = 54.2), 4.04 (d, J = 45.6) (AA'BB', 4H, C_5H_4), 4.27 (b), 4.41 (b), 4.69 (b) (ABC, 3H, C_5H_3), 7.20-7.79 (m, 20H, PPh_2 and =PPh_2). IR (KBr): 1577 cm^{-1} (vs), 1521 cm^{-1} (vs). HRMS (EI, *m/z*): Calcd for $C_{39}H_{33}NOP_2Fe$: 649.1388 (M^+). Found: 649.1379.

Synthesis of 2c. The title compound was prepared in the same manner as described above for **2a** by simply replacing glyoxal with phenylglyoxal. Yield: 50%. $[\alpha]_D^{25}$ = -2029 (c = 0.1, $CHCl_3$). ^{31}P NMR ($CDCl_3$): -10.98 (s), -18.35 (s). ^{1}H NMR ($CDCl_3$): 2.26 (s, 3H, CH_3), 3.22 (d, J = 59.2), 4.03 (d, J = 44.2) (AA'BB', 4H, C_5H_4), 4.29 (b), 4.41 (b), 4.71 (b) (ABC, 3H, C_5H_3), 7.22-8.29 (m, 25H, COPh and PPh_2). IR (KBr): 1581 cm^{-1} (vs), 1483 cm^{-1} (vs). HRMS (EI, *m/z*): Calcd for $C_{44}H_{35}NOP_2Fe$: 711.1544 (M^-). Found: 711.1546.

General procedure for asymmetric cyclopropanation. 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 at the desired temperature. 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 diastereomeric excess (% de) was determined by GC equipped with CBP-10 on a Shimadzu GC-17A. The enantiomeric excess (% ee) was determined by either GC equipped with AsTEC BPH or HPLC equipped with Chiralcel OJ, OD, or OD-H. The absolute configuration of enantiomer was determined by comparison of their specific rotation with reported one.

Reduction of cyclopropanecarboxylate esters. To a suspension of $LiAlH_4$ (3 molar excess) in diethyl ether (5 mL) was added a solution of cyclopropanecarboxylate ester in diethyl ether, and the mixture was heated under reflux for 5 h. After cooling, excess $LiAlH_4$ was destroyed with water and the precipitate that had formed was dissolved by addition of KOH pellets. The ethereal layer was extracted, dried over $MgSO_4$, and purified by column chromatography on silica gel (eluent: 30%, EtOAc/hexane).

Ethyl 2-phenylcyclopropane-1-carboxylate. This was obtained as the product from the reaction of styrene with EDA. Isolated yield: 95%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 20.130 min; t_R (*trans*), 21.960 min; oven temp., 100 °C; injection temp., 150 °C; initial time, 2 min; final temp., 270 °C; rate, 3 °C/min; detection temp., 270 °C; column pressure, 100 kPa. HPLC (Chiralcel OJ) conditions for enantiomeric separation: eluent, 2.0% isopropanol/hexane; flow rate, 1.0 mL/min; λ, 238 nm; t_R (*cis*), 8.903 min (1*R*, 2*S*) and 15.660 (1*S*, 2*R*); t_R (*trans*), 7.380 min (1*R*, 2*R*) and 14.425 min (1*S*, 2*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, 3H, CH_3), 1.25-1.35 (m, 2H, CH_2), 1.27 (t, J = 7.2, 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, 2H, *cis*-CH_2O), 4.15 (q, J = 7.1, 2H, *trans*-CH_2O), 7.08-7.30 (m, 5H, C_6H_5).

Ethyl 2-triethylsilylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of triethylvinylsilane with EDA. Isolated yield: 80%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 11.810 m. in; t_R (*trans*), 12.680 min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 2 °C/min; detection temp., 250 °C; column pressure, 100 kPa. GC (Chiraldex BPH) conditions for enantiomeric separation: t_R (*cis*), 20.130 min (1*R*, 2*S*) and 20.370 min (1*S*, 2*R*); t_R (*trans*), 20.690 min (1*R*, 2*R*) and 21.680 min (1*S*, 2*S*); oven temp., 70 °C; injection temp., 150 °C; initial time, 2 min; final temp., 180 °C; rate 2 °C/min; detection temp., 240 °C; column pressure, 100 kPa. MS: *m/z* (%): 228 (3, M^+), 199 (100), 171 (15), 73 (55), 55 (7). ^{1}H NMR ($CDCl_3$): 0.34-0.39

(m, 1H, CH), 0.46-0.54 (m, 6H, ($\underline{CH_2}CH_3)_3$), 0.73-0.79 (m, 1H, CH), 0.92-0.98 (m, 9H, ($CH_2\underline{CH_3})_3$), 1.17-1.34 (m, 1H, CH), 4.15 (q, J = 7.1, 2H, *cis*-CH_2O), 4.15 (q, J = 7.1, 2H, *trans*-CH_2O).

Ethyl 1-methyl-3-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of *trans*-β-methylstyrene with EDA. Isolated yield: 93%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 21.675 min; t_R (*trans*), 23.647 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanaol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*cis*), 19.038 min (1*R*, 2*S*) and 20.472 min (1*S*, 2*R*). t_R (*trans*), 29.437 min (1*R*, 2*R*) and 30.345 min (1*S*, 2*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, 3H, CH_3), 1.57 (t, J = 7.1, 3H, CH_3), 1.68 (d, J = 6.3, 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, 1H, CH), 2.73 (t, J = 5.7, 1H, CH), 4.16 (q, J = 7.1, 2H, CH_2O), 4.46 (q, J = 7.1, 2H, CH_2O), 7.35-7.58 (m, 5H, C_6H_5).

Ethyl 1,1a,6,6a-tetrahydrocyclopropa[a]indene-6a-carboxylate. A colorless oil obtained from the reaction of indene with EDA. Isolated yield: 96%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 25.532 min; t_R (*trans*), 28.102 min; oven temp., 70 °C; injection temp., 100 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanaol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*cis*), 22.410 min (1*R*, 2*S*) and 25.808 min (1*S*, 2*R*). t_R (*trans*), 34.375 min (1*R*, 2*R*) and 38.667 (1*S*, 2*S*). 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, 3H, CH_3), 1.22 (t, J = 7.05, 3H, CH_3), 1.95 (t, J = 8.1, 1H, CH), 2.19 (m, 1H, CH), 2.39 (m, 1H, CH), 2.94 (d, J = 6.3, 2H, CH_2), 3.18 (dd, J = 6.6, 1H, CH), 4.12 (q, J = 7.1, 2H, CH_2O), 3.80 (q, J = 7.1, 2H, CH_2O), 7.06-7.29 (m, 4H, C_6H_4).

Ethyl 2-methyl-2-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of a-methylstyrene with EDA. Isolated yields: 89-97%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 19.955 min; t_R (*trans*), 21.131 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. GC (Chiraldex BPH) conditions for enantiomeric separation: t_R (*cis*), 38.624 min (1*R*, 2*S*) and 38.892 (1*S*, 2*R*); t_R (*trans*), 41.413 min (1*R*, 2*R*) and 41.749 (1*S*, 2*S*); oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. MS: *m*/*z* (%): 204 (13, M^+), 175 (19), 159 (25), 147 (14), 131 (100), 130 (66), 115 (37), 91 (42), 77 (15), 65 (4), 51 (5). ^{1}H NMR ($CDCl_3$): 0.94 (t, J = 7.1, 3H, CH_3), 1.15 (dd, J = 7.8, 4.9, 1H, CH), 1.46 (s, 3H, CH_3), 1.78 (dd, J = 5.6 and 4.9, 1H, CH), 1.90 (dd, J = 7.8 and 5.6, 1H, CH), 3.81 and 3.85 (AB, J = 10.9 and 7.1, 2H, CH_2), 7.17-7.29 (m, 5H, C_6H_5).

Ethyl 2,2'-diphenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of 1,1'-diphenylethylene with EDA. Isolated yield: 83%. HPLC (Chiralcel OD-H) conditions for enantiomeric separation: eluent, 3.0% isopropanaol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R, 12.223 min (*R*) and 12.937 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, 3H, CH_3), 1.29-1.36 (m, 2H, CH_2), 1.31 (t, J = 7.2, 3H, CH_3), 2.17 (t, J = 5.4, 1H, CH), 3.86 (q, J = 7.1, 2H, *cis*-CH_2O), 4.17 (q, J = 7.1, 2H, *trans*-CH_2O), 7.11-7.35 (m, 10H, C_6H_5).

tert-Butyl 2-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of styrene with ^{t}Bu. Isolated yield: 95%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 22.402 min; t_R (*trans*), 24.224 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*cis*), 9.082 min (1*R*, 2*S*) and 9.465 (1*S*, 2*R*); t_R (*trans*), 7.995 min (1*R*, 2*R*) and 8.248 min (1*S*, 2*S*). MS: *m*/*z* (%): 218 (1, M^-), 145 (62), 117 (100), 91 (30), 57 (64). ^{1}H NMR ($CDCl_3$): *trans* isomer, 1.19-1.25 (m, 1H, CH), 1.46 (s, 9H, C_4H_9), 1.49-1.54 (m, 1H, CH), 1.80-1.85 (m, 1H, CH), 2.40-2.45 (m, 1H, CH), 7.07-7.28 (m, 5H, C_6H_5); *cis* isomer, 1.13 (s, 9H, C_4H_9), 1.26-1.31 (m, 1H, CH), 1.61-1.66 (m, 1H, CH), 1.94-2.00 (m, 1H, CH), 2.49-2.55 (m, 1H, CH), 7.07-7.28 (m, 5H, C_6H_5).

tert-Butyl 2-triethylsilylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of triethylvinylsilane with ^{t}Bu. Isolated yield: 64%. GC (CBP-10) conditions for diastereomeric separation: t_R (*trans*), 12.680 min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 240 °C; rate 2 °C/min; detection temp., 250 °C; column pressure, 100 kPa. GC (Chiraldex BPH) conditions for enantiomeric separation: t_R (*trans*), 21.370 min (1*R*, 2*R*) and 21.670 min (1*S*, 2*S*); oven temp., 70 °C; injection temp., 150 °C; initial time, 5 min; final temp., 180 °C; rate 2 °C/min; detection temp., 240 °C; column pressure, 100 kPa. MS: *m*/*z* (%): 256 (0.6, M^-), 200 (12), 171 (100), 127 (11), 75 (76), 53 (2). ^{1}H NMR ($CDCl_3$): 0.45-0.53 (m, 6H, ($\underline{CH_2}CH_3)_3$), 0.59-0.61 (m, 2H, CH_2), 0.68-0.71 (m, 1H, CH), 0.92-0.97 (t, J = 7.2, 9H, ($CH_2\underline{CH_3})_3$), 1.11-1.15 (m, 1H, CH), 1.44 (s, 9H, C_4H_9).

tert-Butyl 1-methyl-3-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of *trans*-β-methylstyrene with ^{t}Bu. Isolated yield: 90%. GC (CBP-10) conditions for diastereomeric separation after reduction: t_R (*cis*), 23.092 min; t_R (*trans*), 25.693 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column

pressure. 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*cis*), 19.548 min (1*R*, 2*S*) and 21.012 min (1*S*, 2*R*). t_R (*trans*), 29.060 min (1*R*, 2*R*) and 30.440 (1*S*, 2*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, 3H, CH_3), 1.57 (t, J = 7.1, 3H, CH_3), 1.68 (d, J = 6.3, 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, 1H, CH), 2.73 (t, J = 5.7, 1H, CH), 4.16 (q, J = 7.1, 2H, CH_2O), 4.46 (q, J = 7.1, 2H, CH_2O), 7.35-7.58 (m, 5H, C_6H_5).

tert-Butyl 1,1a,6,6a-tetrahydrocyclopropa[a]indene-6a-carboxylate. A colorless oil obtained from the reaction of indene with ^{t}Bu. Isolated yield: 93%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 27.117 min; t_R (*trans*), 29.802 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*cis*), 29.317 min (1*R*, 2*S*) and 31.755 min (1*S*, 2*R*). t_R (*trans*), 35.533 min (1*R*, 2*R*) and 39.937 min (1*S*, 2*S*). MS: *m*/*z* (%): 230 (1.8, M^+), 174 (49), 157 (18), 156 (4), 129 (100), 128 (42), 115 (6), 91 (4), 71 (4), 57 (24), 56 (7). ^{1}H NMR ($CDCl_3$): 1.13 (t, J = 5.4, 1H, CH), 1.46 (s, 9H, $C(CH_3)_3$), 2.36 (m, 1H, CH), 2.88 (m, 1H, CH), 3.03 (m, 1H, CH), 3.25 (dd, J = 6.3 and 6.3, 1H, CH), 7.11-7.35 (m, 4H, C_6H_4).

tert-Butyl 2-methyl-2-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of α-methylstyrene with ^{t}Bu. Isolated yield: 95%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 21.737 min; t_R (*trans*), 23.092 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. GC (Chiraldex BPH) conditions for enantiomeric separation: t_R (*cis*), 40.734 min (1*R*, 2*S*) and 40.751 min (1*S*, 2*R*).; t_R (*trans*), 43.377 min (1*R*, 2*R*) and 43.548 min (1*S*, 2*S*); oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.67; H, 8.68. ^{1}H NMR ($CDCl_3$) *trans* isomer: 1.13 (s, 3H, CCH_3), 1.35 (m, 2H, CH), 1.49 (s, 9H, $C(CH_3)_3$), 1.90 (m, 1H, CH), 7.18-7.31 (m, 5H, C_6H_5); ^{1}H NMR ($CDCl_3$) *cis* isomer: 1.07 (s, 1H, CH), 1.44 (s, 3H, CH_3), 1.51 (s, 9H, $C(CH_3)_3$), 1.70 (m, 1H, CH), 1.80 (m, 1H, CH), 7.18-7.31 (m, 5H, C_6H_5).

tert-Butyl 2,2-diphenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of 1,1'-diphenylethylene with ^{t}Bu. Isolated yield: 82%. HPLC (Chiralcel OD-H) conditions for enantiomeric separation: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R, 8.682 min (*R*) and 9.298 min (*S*). MS: *m*/*z* (%): 294 (0.4, M^-), 238 (96), 193 (100), 115 (82), 91 (25), 57 (41). ^{1}H NMR ($CDCl_3$): 1.11 (s, 9H, C_4H_9), 1.36-1.42 (m, 1H, CH), 1.99-2.02 (m, 1H, CH), 2.34-2.38 (m, 1H, CH), 7.04-7.29 (m, 10H, C_6H_5).

2,6-Di-t-butyl-4-methylphenyl 2-phenylcyclopropane-1-carboxylate. A colorless oil obtained fro the reaction of styrene with BHT. Isolated yield: 92%. GC (CBP-10) conditions for diastereomeric separation: t_R (*trans*), 40.998 min; oven temp., 100 °C; injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 240 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*trans*), 31.098 min (1*R*,2*R*) and 42.817 min (1*S*,2*S*). MS: *m*/*e* (%): 364 (3, M^+), 220 (4), 204 (5), 188 (2), 160 (2), 144 (100), 126 (21), 116 (18), 92 (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), 7.01 (s, 2H, Ar-H), 7.13-7.41 (m, 5H, C_6H_5).

2,6-Di-t-butyl-2-triethylsilylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of triethylvinylsilane with BHT. Isolated yield: 72%. GC (CBP-10) conditions for diastereomeric separation: t_R (*trans*), 55.562 min; oven temp., 150 °C; injection temp., 230 °C; initial time, 2 min; final temp., 255 °C; rate 3 °C/min; detection temp., 270 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R, 7.173 min (1*R*, 2*R*). MS: *m*/*z* (%): 402 (0.9, M^+), 387 (0.7), 373 (1), 220 (15), 205 (40), 183 (100), 161 (12), 145 (6), 127 (51), 115 (66), 87 (21), 69 (3), 57 (15). ^{1}H NMR (C_6D_6): 0.42 (q, J = 7.9, 6H, CH_2), 0.67-0.78 (m, 2H, CH_2), 0.93 (t, J = 7.9, 9H, CH_3), 1.45 (ddd, J = 2.8, 3.9, and 10.6, 1H, CH), 1.47 (s, 9H, $C(CH_3)_3$), 1.40-1.50 (m, 1H, CH), 1.51 (s, 9H, $C(CH_3)_3$), 2.19 (s, 3H, CH_3), 7.16 (m, 2H, Ar-H).

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 BHT. Isolated yield: 88%. GC (CBP-10) conditions for diastereomeric separation: t_R (*cis*), 41.902 min; t_R (*trans*), 43.014 min; oven temp., 100 °C; injection temp., 150 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 270 °C; column pressure, 100 kPa. HPLC (Chiralcel OD) conditions for enantiomeric separation after reduction: eluent, 2.0% isopropanol/hexane; flow rate, 1.0 mL/min; λ, 238 nm; t_R (*cis*), 26.478 min (1*R*, 2*S*) and 28.649 min (1*S*, 2*R*); t_R (*trans*), 31.173 min (1*R*, 2*R*) and 33.778 min (1*S*, 2*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, 1H, CH), 7.01 (s, 2H, Ar-H), 7.37-7.60 (m, 5H, C_6H_5).

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 BHT. Isolated yield: 89%. GC (CBP-10) conditions for diastereomeric separation: t_R (*trans*), 46.368 min; oven temp., 150 °C;

injection temp., 230 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 270 °C; column pressure, 100 kPa. HPLC (Chrial OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*trans*), 9.100 min (1*R*, 2*R*) and 9.480 min (1*S*, 2*S*). 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).

2,6-Di-t-butyl-4-methylphenyl 2-methyl-2-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of α-methylstyrene with BHT. Isolated yield: 85%. GC (Chiralcel BPH) conditions for diastereomeric separation: t_R (*cis*), 57.051 min; t_R (*trans*), 57.537 min; oven temp., 120 °C; injection temp., 240 °C; initial time, 2 min; final temp., 270 °C; rate 3 °C/min; detection temp., 270 °C; column pressure, 100 kPa. HPLC (Chiralcel OD-H) conditions for enantiomeric separation after reduction: eluent, 3.0% isopropanaol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R (*cis*), 6.717 min (1*R*, 2*S*) and 8.158 min (1*S*, 2*R*); t_R (*trans*), 6.718 min (1*R*, 2*R*) and 8.165 min (1*S*, 2*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, 1H, CH), 7.01 (s, 2H, Ar-H), 7.37-7.60 (m, 5H, C_6H_5).

2,6-Di-t-butyl-4-methylphenyl 2,2-phenylcyclopropane-1-carboxylate. A colorless oil obtained from the reaction of 1,1'-diphenylethylene with BHT. Isolated yield: 70%. HPLC (Chiralcel OD-H) conditions for enantiomeric separation: eluent, 3.0% isopropanaol/hexane; flow rate, 0.5 mL/min; λ, 254 nm; t_R, 7.173 min (1*R*, 2*R*). MS: *m*/*z* (%): 440 (5, M^+), 221 (100), 203 (16), 178 (12), 143 (12), 115 (27), 91 (11), 57 (5). ^{1}H NMR ($CDCl_3$): 1.25 (s, 9H, C(CH_3)$_3$), 1.33 (s, 9H, C(CH_3)$_3$), 1.76 (m, 1H, CH), 2.24 (s, 3H, CH_3), 2.27 (m, 1H, CH), 2.87 (m, 1H, CH), 7.01-7.44 (m, 12H, C_6H_5 and Ar-H).

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References

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