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Lithium Bis[(1*R*,5*R*)-3-aza-3-benzyl-1,5-diphenylpentan-1,5-diolato]-Aluminium – A New Heterobimetallic Catalyst for Michael Addition Reactions

G. Manickam and G. Sundararajan*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, INDIA.

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Abstract: The C_2-symmetric amino diol, (1*R*,5*R*)-3-aza-3-benzyl-1,5-diphenyl pentan-1, 5-diol, **1** [(*R*,*R*)-**1**] reacts with $LiAlH_4$ to give the heterobimetallic complex **2** of the composition [(1_2-Al)Li]. Complex **2** was characterised by ^{1}H-, ^{13}C-, ^{27}Al- and ^{7}Li-NMR spectral data. Also, **2** when used in catalytic amounts accelerates Michael addition of malonates and thiophenol to α,β-unsaturated compounds like aldehydes, ketones, cyano and nitro compounds with high yield. Asymmetric induction in the Michael adducts has also been observed when a enantiomerically pure catalyst **2** was employed.

INTRODUCTION

In recent years, acceleration of asymmetric Michael addition reactions by chiral metal catalysts has been recognised as an efficient method for enantioselective carbon-carbon and carbon-heteroatom bond formation.[1] In particular, use of enantiomerically pure C_2-symmetric binaphthol to form heterobimetallic complexes and their role in enhancing the rate of certain organic reactions has been explored by Shibasaki and co-workers.[2] In a series of reports these authors discussed the ability of such heterobimetallic complexes of BINOL-aluminium (or lanthanide)-alkali metals in bringing about highly enantioselective Michael addition reactions.[3] Recently, a catalytic enantioselective Michael addition of α-nitroesters to α,β-unsaturated ketones using 10 mol % of heterobimetallic catalyst Al-Li-BINOL with an enantiomeric excess of 80 % in the adducts was reported.[4]

Earlier we described the use of a chiral titanium(IV) alkoxide complex derived from the C_2-symmetric amino diol, (1*R*,5*R*)-3-aza-3-benzyl-1,5-diphenyl pentan-1, 5-diol, **1** [(*R*,*R*)-**1**] in the acceleration of asymmetric Diels-Alder and ene reactions that proceeded with good yield and moderate enanatioselectivity.[5] Also, in a prior report, we had outlined the synthesis of lithium-aluminium heterobimetallic complex, **2** [1_2-Al-Li], derived from **1** that effectively catalyses asymmetric Michael addition reactions with high enantioselectivities (up to 94% ee).[6] In this paper we elaborate on the synthesis and characterisation of the

* Corresponding author. Email: gsundar@acer.iitm.ernet.in

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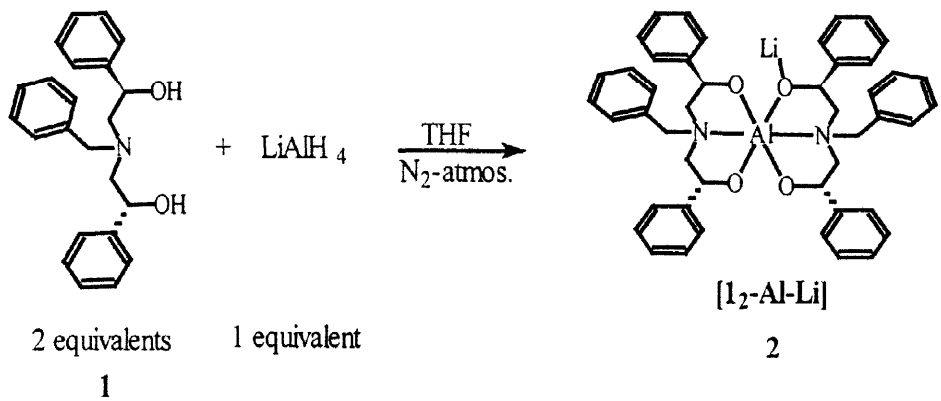
heterobimetallic catalyst **2**, the effect of substitution on the nitrogen atom of the C_2-symmetric ligand and the Michael addition of malonic esters and thiophenols to a variety of α,β-unsaturated compounds like aldehydes, cyano and nitro compounds.

RESULTS AND DISCUSSION

The heterobimetallic complex **2** was obtained readily by reacting **1** (2 equivalents) with $LiAlH_4$ (1 equivalent) in THF with accompanying evolution of hydrogen (Eq.1). Removal of solvent yielded a semi-solid, which eluded crystallisation and hence further characterisation by single crystal X-ray diffraction. However, gasimetric analysis indicated two moles of hydrogen are generated per mole of amino diol. From the infrared spectrum, it was clear that there were no free hydroxyl groups belonging to unreacted amino-diol. Based on these observations, we inferred the formation of a heterobimetallate of formula, [$\mathbf{1}_2$-Al-Li] (Eq.1) which is similar to the structure proposed for $LiAlH_4$-BINOL complexes.[7] The formation of the heterobimetallic complex **2** was further supported by ^{1}H-, ^{13}C-, ^{27}Al-, and ^{7}Li-NMR spectral data as well as by Inductively Coupled Plasma (ICP) analysis.



Eq.1

The ^{1}H-NMR spectrum of complex **2** clearly indicated the absence of free hydroxyl groups and complete conversion of **1** into alkoxide. The ^{27}Al-NMR spectrum of complex **2** showed a new broad singlet at δ = 60.04 ppm (Fig. 1(a)) suggesting the removal of all the four hydrides in $LiAlH_4$. To compare and contrast, the ^{27}Al-NMR spectrum for free $LiAlH_4$ gave a quintet at δ = 98.43 ppm, due to the coupling of hydrogen with aluminium Fig. 1(b). In the ^{7}Li-NMR spectra a single signal at δ = +1.12 ppm was seen while the ^{7}Li-NMR spectrum of free $LiAlH_4$ has a signal at a higher field *viz.* δ = - 0.25 ppm. This could be taken as an indication for the different environments for the lithium atom in the complex and in the hydride. Moreover, an ICP-AES analysis gave aluminium and lithium metal contents in **2** that are close to the expected values (*vide experimental*).

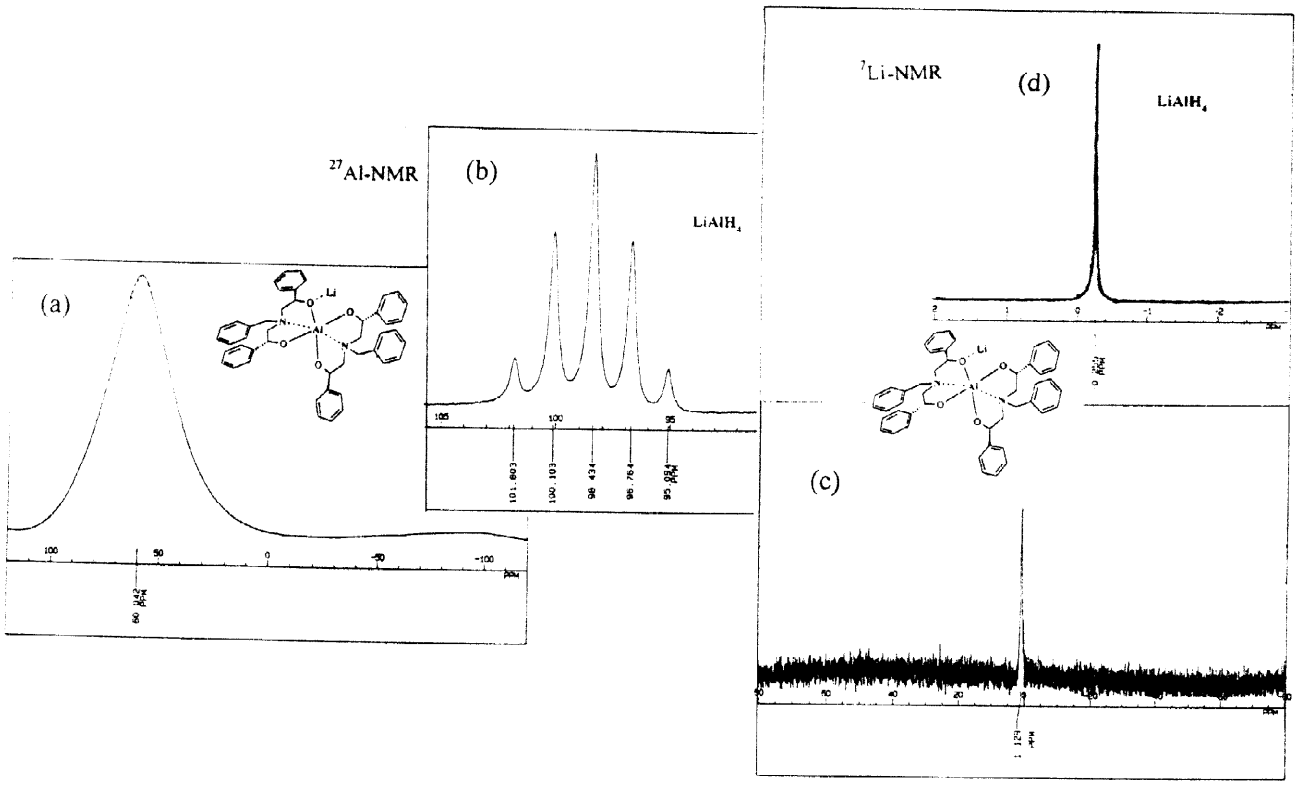
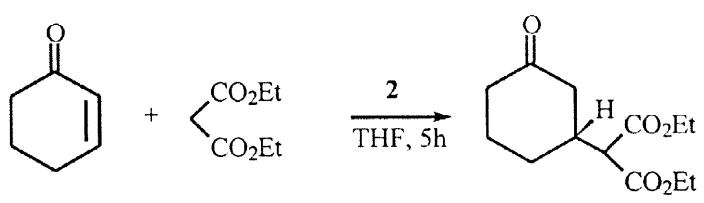


Fig. 1: (a) ^{27}Al-NMR spectrum of **2**, (b) ^{27}Al-NMR spectrum of $LiAlH_4$, (c) ^{7}Li-NMR spectrum of **2**, (d) ^{7}Li-NMR spectrum of $LiAlH_4$

Asymmetric Michael addition of malonates and thiolphenols to cyclic/acyclic ketones with a high level of enantioselectivity using the heterobimetallic catalyst **2** was previously reported by us (Eq.2).[6] It has been suggested in the literature that the observed enantioselectivity in the Michael adduct depended not only on the nature of the catalyst used, but also on the nature of the substituents on the ligand. To examine this suggestion, we chose to study the effect of different substitutents on the nitrogen atom of the C_2-symmetric ligand **1**. The ligands so synthesised were reacted with $LiAlH_4$ to yield the corresponding heterobimetallic complexes which were in turn tested for the relative efficiency in affecting asymmetric induction in Michael addition of malonates to 2-cyclohexenone. The results are summarised in Table 1.



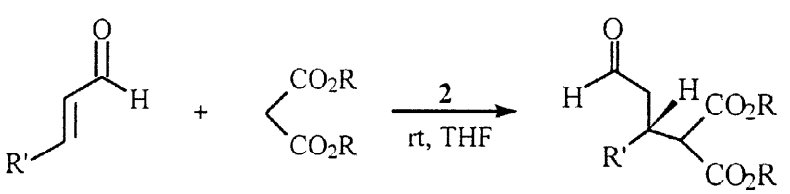
3 **4** **5** Eq.2

It can be seen from Table 1 that the enantiomeric excess of the Michael adduct decreased as the bulkiness of the ligand decreased, even though the absolute yields of the adducts did not show much deviation. For comparison, we also prepared the heterobimetallic complex of TADDOL (2 equivalents) [(4*R*,5*R*)-4,5-bis(biphenyl-hydroxy-methyl)-2,2-dimethyl-dioxolane] and $LiAlH_4$ (1 equivalent) in THF. This complex also promoted Michael addition reaction of diethyl malonate to cyclohexenone. Though the isolated yields were lower (60%) than those obtained with the heterobimetallic catalyst **2** (87%) for the same reaction time of 5h, the observed enantiomeric excess was higher.

Table 1: Ligand (substituent) effect on asymmetric Michael addition of 2-cyclohexen-1-one with diethyl malonate

Ligand	Time (h)	% Yield	% ee
1; R = Bn	5	87	80
1; R = Cy	„	87	83
1; R = ^{i}Pr	„	81	72
TADDOL	„	60	87

The high enantioselectivity obtained for the Michael adducts *via* 1,4-addition of malonic esters to cyclic enones in the presence of heterobimetallic catalysts **2**, encouraged us to study the utilisation of such catalysts in the Michael addition of malonic esters to α,β-unsaturated aldehydes. The reactions performed included crotonaldehyde and cinnamaldehyde as acceptors, and diethyl-, di(*tert*-butyl)- and dibenzyl malonates as donors in the presence of 20 mol % heterobimetallic catalyst as a promoter (Scheme 1). The results obtained are listed in Table 2.



6 R′ = Me
7 R′ = Ph

4 R = Et
8 R = ^{t}Bu
9 R = Bn

10 R′ = Me, R = Et
11 R′ = Me, R = ^{t}Bu
12 R′ = Me, R = Bn
13 R′ = Ph, R = Et
14 R′ = Ph, R = ^{t}Bu
15 R′ = Ph, R = Bn

Scheme 1: Asymmetric Michael addition of malonates to α,β-unsaturated aldehydes in the presence of heterobimetallic catalyst **2**

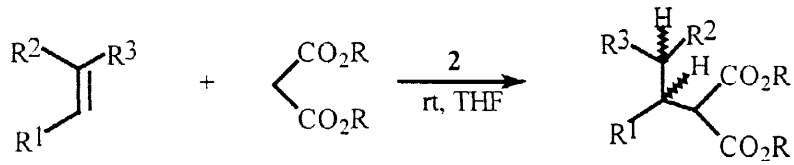
Table 2: Asymmetric Michael addition of malonates to α,β-unsaturated aldehydes in the presence of **2**

Compd	Aldehyde (R')	Malonate (R)	Time (h)	Yield (%)	$[\alpha]_D^{26}$
10	Me	Et	3	87	+ 1.4 [a]
11	Me	'Bu	3	93	+ 4.0 [a]
12	Me	Bn	3	95	+ 1.2 [a]
13	Ph	Et	5	85	+ 3.1 [a]
14	Ph	'Bu	5	82	+ 1.4 [a]
15	Ph	Bn	7	60	+2.1 [a]

[a] Solvent CCl_4 and concentration 2.35-2.65

The results shown in Table 2 indicate that the yield of Michael adducts depended not only on the nature of the ester group of the malonate, but also on the group attached to the aldehyde. Thus sterically less crowded aldehydes like crotonaldehyde gave higher yields with bulkier malonic esters than the sterically more crowded cinnamaldehyde. Reaction of dibenzyl ester with cinnamaldehyde gave a low yield with a long reaction time. Our attempts to evaluate quantitatively the enantiomeric excesses of the adducts by analysing with chiral columns on HPLC or with chiral shift reagents in NMR spectra did not give useful information. As the optical rotation values for the enantiomerically pure compounds are not available in the literature we were unable to calculate the optical purity and so the observed optical rotation data are included.

The Michael addition reaction of diethyl malonate to nitro styrene and other α,β-unsaturated compounds were also performed to demonstrate the versatility and efficiency of **2** with substrates other than the α,β-unsaturated ketones and aldehydes (Scheme 2). The results are listed in Table 3.



16 R^1=Ph, R^2=Me, R^3=NO_2 **4**

17 R^1=Ph, R^2=CN, R^3=CO_2Et

18 R^1=Ph, R^2=H, R^3=COCH=CHPh

19 R^1=Ph, R^2=Me, R^3=NO_2, R=Et

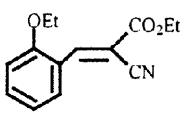
20 R^1=Ph, R^2=CN, R^3=CO_2Et, R=Et

21 R^1=Ph, R^2=H, R^3=COCH=CHPh, R=Et

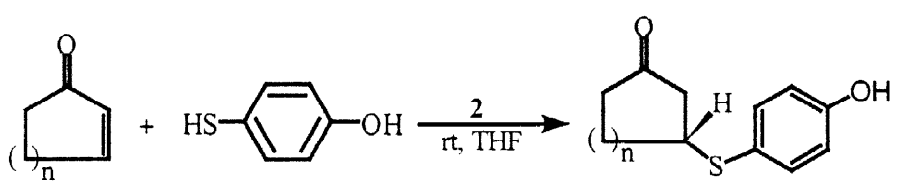
Scheme 2: Michael addition of diethyl malonate to other α,β-unsaturated compounds

Accordingly, Michael addition of diethyl malonate to compounds **16** and **17** gave diastereoisomers **19** and **20** in the ratio 2:1 and 7:3 respectively as estimated from the relative intensities of the methyl protons in the ^{1}H-NMR spectrum. From Table 3 it is also clear that the time taken for the formation of Michael adducts is shorter and the yields are higher. The lower yield for adducts **22** and **23** (Table 3) could probably be attributed to the steric crowding of the starting materials.

Table 3: Michael addition of malonates to other α,β-unsaturated compounds in the presence of heterobimetallic catalyst **2**

Compd	R^1	R^2	R^3	Malonate (R)	Time (h)	Yield (%)
19	Ph	Me	NO_2	Et	3	88
20	Ph	CN	CO_2Et	Et	6	79
21	Ph	H	OCCH=CHPh	Et	6	80
22	2-Cyclohexen-1-one			$NC-CH_2-CO_2Et$	10	65
23				Et	10	45

References to the application of heterobimetallic complexes for the asymmetric Michael addition of thiols to α,β-unsaturated carbonyl compounds are rare in the literature. Hence we employed **2** as a promoter in the addition of thiols to cyclic enones. To our surprise the reactions proceeded with ease and completed within 60 seconds at 0°C (Scheme 3). The results are summarised in Table 4. The time required for the conversion to products was less compared to other similar addition reactions of thiols to α,β-unsaturated ketones previously described by Hodge (24 to 240h).[8]



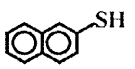
24 n = 1 **25** **26** n = 1, R = OH

3 n = 2 **27** n = 2, R = OH

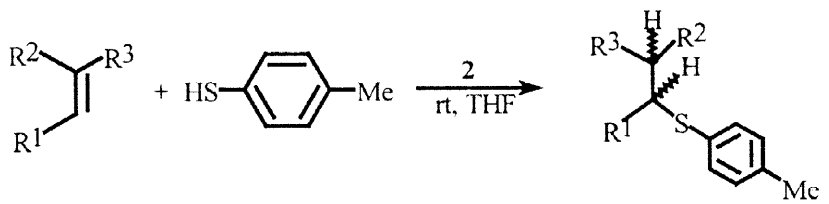
Scheme 3: Asymmetric Michael addition of thiophenols to cyclic ketones

It is clear that the heterobimetallic catalyst **2** is highly efficient towards promoting thiol addition, when compared to malonate addition reactions. A point to note here would be that the Michael addition of *p*-hydroxy thiophenol to cyclic enones, chemoselectively gave 1,4-S-addition product and *no 1,4-O-addition products*. The addition of thioacetic acid and β-thionaphthol to 2-cyclohexenone also gave higher yields in short reaction times.

Table 4: Michael addition of thiophenols to cyclic ketones in the presence of **2**

Compd	Enone	Thiol	Time (Sec)	Yield (%)
26	n = 1	**25**	60	96
27	n = 2	**25**	60	94
28	n = 2	CH_3COSH	90	92
29	n = 2		90	89

Michael addition of *p*-methylthiophenol to other α,β-unsaturated compounds was also studied in the presence of the heterobimetallic catalyst **2** with acceptors other than the carbonyl compound (Scheme 4).



6 R^1=Me, R^2=H, R^3=CHO
7 R^1=Ph, R^2=H, R^3=CHO
16 R^1=Ph, R^2=Me, R^3=NO_2

30 R^1=Me, R^2=H, R^3=CHO
31 R^1=Ph, R^2=H, R^3=CHO
32 R^1=Ph, R^2=Me, R^3=NO_2

Scheme 4: Michael addition of *p*-methylthiophenol to other α,β-unsaturatedcompounds

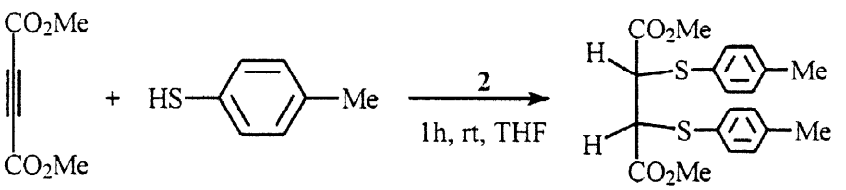
Thus, the addition of *p*-methylthiophenol to nitrostyrene and substituted nitrostyrene resulted in higher yield > 90 % with shorter reaction time. An interesting point to note here is that the addition of *p*-methylthiophenol to aldehydes gave a lower yield, because of the competing thioacetalisation. At room temperature the formation of thioacetal product was higher compared to Michael adduct. This problem could be overcome by reducing the temperature to 0 °C. Below this temperature the reaction yielded Michael adduct as a major product (> 85 %).

Table 5: Asymmetric Michael addition of *p*-methylthiophenol to other α,β-unsaturated compounds in the presence of **2**

Compd. No.	R^1	R^2	R^3	Time (Sec)	Yield (%)
30	Me	H	CHO	60	73[a]
31	Ph	H	CHO	60	72[a]
32	Ph	Me	NO_2	3h	90

[a] at 0 °C the yield is >85 %

Another interesting observation was made in the addition of *p*-methylthiophenol to dimethylacetylene dicarboxylate, where the double Michael addition product was obtained (Eq. 3) (yield, 95%). A careful analysis of the ^1H and ^{13}C-NMR spectra indicated the formation of the *meso* diastereomer.



Eq.3

33 **34**

In conclusion, we have demonstrated that the heterombimetallic complex **2** is an efficient promoter for Michael addition reactions and we have uncovered many interesting details. The structure of **2** was inferred from various spectral and analytical data. Addition of malonates to α,β-unstaurated ketones, aldehydes, cyanao and nitro compounds proceeds with good yield with reduced reaction times when performed in the prsence of **2**. Wherever determined, the enantiomeric excesses of the Michael adducts were comparable to or better than those obtained in other reported procedures. The title complex is also capable of promoting thiol addition to cyclic enones in good yield in an extremely short reaction time. We are currently investigating the various aspects of this heterobimetallic complex such as the ability to promote Michael addition with other substrates and for increasing asymmetric induction.

EXPERIMENTAL SECTION

Infrared spectra were obtained on a Shimadzu IT-470 spectrometer. ^1H-NMR spectra were recorded on a Jeol GSX-400 FT instrument. For routine analysis a Hitachi R-600 (60 MHz) FT-NMR instrument was used. $CDCl_3$ was used as the solvent with tetramethylsilane as the internal standard unless otherwise stated. The ^1H-NMR spectral data are given with the multiplicities denoted as s-singlet, d-doublet, t-triplet, q-quartet, m-

multiplet and bs-broad singlet within parentheses. The ^{13}C-NMR spectra were recorded on a JEOL GSX-400 instrument operating at 100.5 MHz and the spectroscopic data are given with multiplicities observed in the off-resonance spectra within parentheses. ^{27}Al- and ^{7}Li-NMR were also recorded on the JEOL GSX-400 operating at 104.17 and 155.37 MHz respectively with THF as the solvent. One molar solution of aluminium nitrate and lithium chloride in D_2O was used as external standards to measure ^{27}Al and ^{7}Li-NMR spectra respectively. Chemical shift values are reported in parts per million and coupling constants in Hertz.

Mass spectra, both EI (70 eV) and HRMS, were recorded on a Finnigan MAT 8230 spectrometer. HRMS were recorded using peak matching technique with perfluorokerosene (PFK) as the reference (resolution >5000). Optical rotations were measured with a JASCO DIP-370 Digital Polarimeter (with 10 or 100-mm cell). The concentration (g per 100 ml) and solvent used are given in the parenthesis. HPLC analysis was performed using Waters (510 HPLC pump) with Waters 486 tunable absorbance detector at fixed wavelength of 254 nm. The 9:1 mixture of hexane:isopropanol was used as solvent for elution at the flow rate of 1 ml/min. ICP-AES analyses were performed using ARL 3410 (ICP with mini torch) instrument and the spectral range was 189-800 nm (flame temperature 11,000 K). All reactions were performed under dry nitrogen atmosphere.

2-Cyclopenten-1-one,[9] 2-cyclohexe-1-one,[9] β-nitrostyrene,[10] benzalacetophenone,[11] benzalacetone,[12] dimethyl acetylene dicarboxylate[13] and malonic esters[14] were synthesised according to the literature reported procedure. $LiAlH_4$, thiophenols and benzylamine were purchased from E-Merck and used as received. Anhydrous THF was obtained by distillation over sodium-benzophenone ketyl. All transfers were performed in a glove bag filled with dry nitrogen or using dry syringes. Schlenck techniques were employed wherever necessary.

***Preparation of the Heterobimetallic Complex* 2**

Enantiomerically pure amino diol **1** (183mg, 0.53mmol) in dry THF (2ml) was added to a cooled solution of $LiAlH_4$ (10mg, 0.268mmol) in dry THF (1ml). The mixture was then stirred for 30 min at 0 °C. For ^{27}Al, ^{7}Li, ^{1}H and ^{13}C-NMR spectral data, the complex was generated in a NMR tube and the NMR spectra were recorded at room temperature using aluminium nitrate, lithium chloride and TMS as references respectively. For a blank, 10mg of $LiAlH_4$ was taken in 1.5 ml THF to record ^{27}Al and ^{7}Li NMR.
^{1}H-NMR: δ 2.53-2.66 (m, 4H), 3.42 (d_{AB}, 1H, J=13.7 Hz), 3.75 (d_{AB}, 1H, J=13.7 Hz), 4.54 (d, 2H, J=8.5 Hz), 7.25-7.61 (m, 15H); ^{13}C-NMR: δ 59.68 (t), 62.44 (t), 70.73 (d), 77.33 (d), 125.94 (d), 127.32 (d), 127.44 (d), 128.30 (d), 128.44 (d), 129.17 (d), 138.19 (s), 142.36 (s); ^{27}Al-NMR (104 MHz, THF): For $LiAlH_4$ δ = 98.43 ppm (quintet, due to coupling of aluminium with 4H), for heterobimetallic complex δ = 60.04 ppm (bs);
^{7}Li-NMR (155 MHz, THF): For $LiAlH_4$ δ = -0.255 ppm (s), for heterobimetallic complex δ = +1.12 ppm (s)

Gasimetric and ICP-analysis

Enantiomerically pure amino diol **2** (183mg, 0.53 mmol) in dry THF (4ml) was added to a cooled solution of $LiAlH_4$ (10mg, 0.26 mmol) in dry THF. The evolved hydrogen gas was measured by the usual displacement technique. The volume of gas evolved was 23.60 ml (calculated gas volume = 23.74 ml). The

mixture was stirred for 30 minutes at 0 °C and the reaction mixture was filtered through Celite using Schelenck apparatus. After removal of the solvent, the complex was obtained as a semi-solid. From this 44 mg of the complex was weighed and made upto 10 ml using 1:1 mixture of water and concentrated nitric acid. The aqueous solution was filtered through Whatmann 40 filter paper and this solution was used for ICP analysis (Model: ARL 3410 ICP-AES with Mini Torch, spectral range: 189 to 800 nm, Flame temperature: 11, 000 K, RF generator: 27.12 MHz, 750 Watts output). The observed values are Al = 165.24 ppm, Li = 44.02 (calculated values Al =164.01, Li = 43.00).

General procedure for Michael addition reaction of malonates to aldehydes

Enantiomerically pure amino diol, **1** (201mg, 0.58mmol) in dry THF (4ml) was added to a cooled solution of $LiAlH_4$ (11mg, 0.29mmol) in dry THF (1ml). The mixture was stirred for 30 min at 0 °C, then the aldehydes **6** or **7** (1.45 mmol) in dry THF (2ml) and malonates **4**, **8** or **9** (1.45 mmol) in dry THF (2ml) were added. The mixture was warmed to room temperature and stirred for 3 to 7 h. After completion of the reaction, the mixture was quenched with 1N HCl (0.5ml) and extracted with ethyl acetate (50 ml). The organic phase was washed successively with saturated aq. $NaHCO_3$ (2 x 10 ml), brine (2 x 20 ml) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a syrupy mass, which on flash column chromatographic separation on silica gel using EtOAc:hexane (1:20) as eluent gave the pure products **10-15**.

***3-[Bis(ethoxy carbonyl)methyl]butanal* 10** : Colourless liquid; Yield 87 %; IR (CCl_4, cm^{-1}) 2976, 2816, 2704, 1754, 1725, 1440, 1372, 1174, 1033; ^{1}H-NMR: δ 0.99 (d, 3H, J=6.7 Hz), 1.10 (t, 3H, J=6.7 Hz), 1.28 (t, 3H, J=6.7 Hz) 2.31-2.39 (m, 1H), 2.58-2.60 (m, 1H), 2.83-2.91 (m, 1H), 3.51 (d, 1H, J=6.7 Hz), 3.92 (q, 2H, J=6.7 Hz), 4.18(q, 2H, J=6.7 Hz), 9.72 (bs, 1H); ^{13}C-NMR: 13.82 (q), 14.22 (q), 16.89 (q), 28.02 (d), 48.21 (t), 56.21 (d), 60.98 (t), 61.24 (t), 167.40 (s), 168.23 (s), 201.01 (d);); Mass (70 eV, EI) m/z 230 (M^+), 202, 185, 160 (base peak), 70; HRMS for $C_{11}H_{18}O_5$: Calculated 230.1154, found: 230.1203; $[\alpha]_D^{26}$ = +1.4 (c = 2.63, CCl_4).

***3-[Bis(tert-butoxy carbonyl)methyl]butanal* 11** : Oil; Yield 93 %; IR (CCl_4, cm^{-1}) 2976, 2928, 2800, 2720, 1744, 1721, 1369, 1308, 1136; ^{1}H-NMR: δ 1.10 (d, 3H, J=7.1 Hz), 1.21 (s, 9H), 1.43 (s, 9H), 2.31-2.39 (m, 1H), 2.58-2.89 (m, 2H), 3.54 (d, 1H, J=6.8 Hz), 9.61 (t, 1H, J=1.45 Hz); ^{13}C-NMR: 18.01 (q), 27.31 (q), 27.89 (q), 28.32 (d), 47.83 (t), 55.98 (d), 81.98 (s), 82.10 (s), 167.50 (s), 168.01 (s), 199.83 (d); Mass (70 eV, EI) m/z 286 (M^+), 258, 216 (base peak), 185.70; HRMS for $C_{15}H_{26}O_5$: Calculated: 286.1780, Found: 286.2138; $[\alpha]_D^{26}$ = +4.0 (c = 2.38, CCl_4).

***3-[Bis(benzyloxy carbonyl)methyl]butanal* 12** : Viscous oil; Yield 95 %; IR (CCl_4, cm^{-1}) 2976, 2816, 2704, 1754, 1725, 1459, 1446, 1299, 1033; ^{1}H-NMR: δ 1.02 (d, 3H, J=6.8 Hz), 2.33-2.40 (m, 1H), 2.54-2.59 (m, 1H), 2.84-2.87 (m, 1H), 3.48 (d, 1H, J=7.3 Hz), 5.12 (s, 4H), 7.28-7.34 (m, 10H), 9.63 (s, 1H); ^{13}C-NMR: 17.85 (q), 27.85 (d), 47.75 (t), 56.17 (d), 68.03 (t), 128.16 (d), 128.33 (d), 128.47 (d), 135.06 (s), 167.95 (s), 200.77 (d);

Mass (70 eV, EI)m/z 355 $(M+1)^+$, 284, 139, 108(base peak), 91; HRMS for $C_{21}H_{22}O_5$: Calculated: 354.1467, Found: 354.1298; $[\alpha]_D^{26}$ = +1.2 (c = 2.65, CCl_4).

***3-[Phenyl-bis(ethoxy carbonyl)methyl]propanal* 13 :** Oil; Yield 85 %; IR (neat, cm^{-1}) 2976, 2928, 2720, 1747, 1718, 1443, 1363, 1027, 860, 764, 697; ^{1}H-NMR: δ 0.99 (t, 3H, J=7.3 Hz), 1.26 (t, 3H, J=7.3 Hz), 2.88-2.92 (m, 2H), 3.71 (d, 1H, J=9.8 Hz), 3.94 (q, 2H, J=7.3 Hz), 3.98-4.02 (m, 1H), 4.20 (q, 2H, J=7.3 Hz), 7.21-7.30 (m, 5H), 9.59 (t, 1H, J=1.5 Hz); ^{13}C-NMR: 13.72 (q), 14.01 (q), 39.52 (d), 47.43 (t), 57.51 (d), 61.44 (t), 61.81 (t), 127.49, 128.12, 128.69, 139.80 (s), 167.45 (s), 168.02 (s), 200.13 (d); Mass (70 eV, EI) m/z 292 (M+), 264, 201, 160(base peak), 133, 105, 91, 77; HRMS for $C_{16}H_{20}O_5$: Calculated : 292.1311, Found: 292.1321; $[\alpha]_D^{26}$ =+ 3.1 (c = 2.58, CCl_4).

***3-[Phenyl-bis(tert-butoxy carbonyl)methyl]propanal* 14 :** Oil; Yield 82 %; IR (neat, cm^{-1}) 2976, 2928, 2832, 2720, 1744, 1718, 1683, 1472, 1360, 851, 745, 700; ^{1}H-NMR: 1.19 (s, 9H), 1.46 (s, 9H), 2.69-2.89 (m, 2H), 3.53 (d, 1H, J=10.3 Hz), 3.90 (dt, 1H, J=4.3 and 10.2 Hz), 7.21-7.56 (m, 5H), 9.59 (dd, 1H, J=1.5 and 2.45 Hz); ^{13}C-NMR: 27.42 (q), 27.82 (q), 38.87 (t), 40.95 (d), 58.77 (d), 82.01 (s), 82.15 (s), 127.15 (d), 128.26 (d), 128.39 (d), 139.92 (s), 166.71 (s), 167.41 (s), 177.10 (s), 200.10 (d); Mass (770 eV, EI) m/z 348 (M+), 292, 264, 236, 208, 173, 133, 104(base peak), 91, 77; HRMS for $C_{20}H_{28}O_5$: Calculated : 348.1937, Found: 348.1897; $[\alpha]_D^{26}$ =+ 1.4 (c = 2.35, CCl_4).

***3-[Phenyl-bis(benzyloxy carbonyl)methyl]propanal* 15 :** Resin; Yield 60 %; IR (neat, cm^{-1}) 2928, 2848, 2720, 1750, 1718, 1491, 1145, 1011, 700; ^{1}H-NMR: 2.75-2.86 (m, 2H), 3.81-3.93 (m, 1H), 4.87 (dd, 1H, J=3.4 and 8.3 Hz), 5.13 (s, 4H), 7.20-7.35 (m, 15H), 9.52 (bs, 1H); ^{13}C-NMR: 37.88 (s), 39.42 (d), 41.03 (d), 47.14 (t), 57.37 (d), 57.08 (d), 65.24 (s), 67.12 (t), 67.35 (t), 126.95, 127.19, 127.41, 127.59, 128.00, 128.19, 128.21, 128.38, 128.42, 128.51, 128.97, 130.06, 134.86, 134.92, 134.95, 139.38, 139.51, 175.78 (s), 199.96 (d); Mass (70 eV, EI) m/z 416 (M+), 388, 284 (base peak), 132, 91, 77; HRMS for $C_{26}H_{24}O_5$: Calculated: 416.1624, Found: 416.1537; $[\alpha]_D^{26}$ =+ 2.1 (c = 1.82, CCl_4).

General procedure for Michael addition reaction of malonates to α,β-unsaturated compound

Enantiomerically pure amino diol, **1** (219mg, 0.63mmol) in dry THF (4ml) was added to a cooled solution of $LiAlH_4$ (12mg, 0.32mmol) in dry THF (1ml). The mixture was stirred for 30 min at 0 °C, then the corresponding α,β-unsaturated compound (0.63 mmol) in dry THF (2ml) and malonates (0.63 mmol) in dry THF (2ml) were added. The mixture was warmed to room temperature and stirred for 3 to 10h. After completion of the reaction, the mixture was quenched with 1N HCl (0.5ml) and extracted with ethyl acetate (50 ml). The organic phase was washed successively with saturated aq. $NaHCO_3$ (2 x 10 ml), brine (2 x 20 ml) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a syrupy mass, which on

flash column chromatographic separation on silica gel using EtOAc:hexane (1:9) as eluent gave the pure products (**19-23**).

2-[Phenyl-1,1'-bis(ethoxycarbonyl)methyl]-3-metyl nitroethane **19** : Viscous oil; Yield 88 %; Diastereomeric ratio: 2:1; IR (CCl_4, cm^{-1}) 3056, 2832, 1440, 1385, 1325, 979, 871, 700; ^{1}H-NMR: Major: 0.91 (t, 3H, J=6.8 Hz), 1.30 (t, 3H, J=6.8 Hz), 1.43 (d, 3H, J=6.8 Hz), 3.79 (dd, 1H, J=4.4 and 10.7 Hz), 3.86-3.97 (m, 2H), 4.15-4.31 (m, 3H), 5.16 (m, 1H), 7.10-7.31 (m, 5H); Minor: 0.99 (t, 3H, J=6.8 Hz), 1.24 (t, 3H, J=7.3 Hz), 1.35 (d, 3H, J=6.8), 1.43 (d, 3H, J=6.8 Hz), 3.79 (dd, 1H, 4.4 and 10.8 Hz), 3.86-3.97 (m, 2H), 4.15-4.31 (m, 3H), 5.06-5.09 (m, 1H), 7.10-7.31 (m, 5H); ^{13}C-NMR: Major: 13.51 (q), 13.93 (q), 16.83 (q), 48.56 (d), 54.40 (d), 62.03 (t), 83.03, 128.24, 128.38, 128.46, 128.58, 129.00, 129.14, 133.97(s), 134.65, 167.16 (s), 167.92 (s); Minor: 13.55 (q), 13.82 (q), 15.83 (q), 48.27 (d), 54.03 (d), 61.58 (t), 84.10, 128.24, 128.38, 128.46, 128.58, 129.00, 129.14, 133.97 (s), 134.65, 166.45 (s), 167.19 (s); Mass (70 eV, EI) m/z 323 (M+), 276, 231, 203(base peak), 185, 157, 129; HRMS for $C_{16}H_{21}NO_6$: Calculated: 323.1369; Found: 323.1384.

2-[Phenyl-1,1'-bis(ethoxycarbonyl)methyl]-3-ethoxycarbonyl cyanoethane **20** : Resin; Yield 79 %; Diastereomeric ratio: 7:3; IR (neat, cm^{-1}) 3046, 2972, 2228, 1731, 1443, 1366, 1289, 1088, 1014, 700; ^{1}H-NMR: Major: 0.91 (t, 3H, J=6.8 Hz), 1.06 (t, 3H, J=7.3 Hz), 1.31 (t, 3H, J=7.3 Hz), 3.88 (q, 2H, J=3.2 Hz), 3.93-4.32 (m, 1H), 4.03 (dd, 1H, J=1.9 and 6.8 Hz), 4.28 (d, 1H, J=6.8 Hz), 4.51 (d, 1H, J=3.4 Hz), 7.29-7.37 (m, 5H); Minor: 0.96 (t, 3H, J=6.8 Hz), 1.00 (t, 3H, J=7.3 Hz), 1.28 (t, 3H, J=7.3 Hz), 3.88 (q, 2H, J=3.2 Hz), 3.93-4.32 (m, 1H), 4.03 (dd, 1H, J=1.9 and 6.8 Hz), 4.28 (d, 1H, J=6.8 Hz), 4.51 (d, 1H, J=3.4 Hz), 7.29-7.37 (m, 5H); ^{13}C-NMR: Major: 13.50 (q), 13.67 (q), 13.90 (q), 41.93, 43.92, 44.80, 54.49, 55.23, 61.64, 62.32, 62.70, 115.04 (s), 127.94, 128.32, 128.62, 134.69 (s), 164.28 (s), 166.46 (s), 167.53 (s); Minor: 13.53 (q), 13.72 (q), 13.85 (q), 41.84, 43.90, 44.80, 54.00, 61.23, 61.61, 62.14, 62.87, 115.12 (s), 128.53, 128.76, 129.33, 135.68 (s), 164.73 (s), 166.53 (s), 167.63 (s); Mass (70 eV, EI) m/z 361 (M+), 288 (base peak), 270, 241, 160, 131, 103, 91, 77; HRMS for $C_{19}H_{23}NO_6$: Calculated: 361.1526, Found: 361.1542.

2-[Phenyl-1,1'-bis(ethoxycarbonyl)methyl]-3-cinnamoyl ethane **21** : Oil; Yield 80 %; IR (neat, cm^{-1}) 3072, 2976, 1747, 1731, 1689, 1613, 1171, 1024, 694; ^{1}H-NMR: 0.93 (t, 3H, J=7.3 Hz), 1.18 (t, 3H, J=7.3 Hz), 3.07 (m, 2H), 3.72 (d, 1H, J=9.8 Hz), 3.87 (q, 2H, J=7.1 Hz), 4.02 (dt, 1H, J=4.9 and 9.3 Hz), 4.14 (m, 2H), 6.56(d, J=16.1 Hz), 7.03-7.44 (m, 10H); ^{13}C-NMR: 13.72 (q), 13.98 (q), 40.98 (t), 44.82 (t), 57.46, 61.32, 61.64, 61.83, 125.34, 125.45, 125.91, 126.56, 127.17, 128.20, 128.27, 128.87, 134.39, 134.77, 140.28, 142.77, 142.91, 143.36, 168.27 (s), 167.68 (s), 197.46 (s); Mass (70 eV, EI) m/z 394 (M^+), 287, 241, 173, 160, 131, 107, 77, 51; HRMS for $C_{24}H_{26}O_5$: Calculated: 394.1780, Found: 394.1738.

***3-[(Cyano-1'-ethoxycarbonyl)methyl]cyclohexanone* 22** : Oil; Yield 65 %; Diaseteromeric ratio: 1.2:1; IR (CCl_4, cm^{-1}) 3046, 2829, 2231, 1758, 1723, 1385, 1125, 979, 871, 700; ^{1}H-NMR: 1.33 (t, 3H, J=6.8 Hz), 1.66-1.79 (m, 2H), 1.95-2.10 (m, 1H), 2.15-2.37 (m, 1H), 2.40-2.51 (m, 5H), 3.60 (d, 1H, J=6.2 Hz), 4.23-4.25 (m, 2H); ^{13}C-NMR: 13.87 (q), 24.04 (t), 27.38 (t), 29.11 (t), 38.53 (d), 40.39 (t), 43.62, 62.97 (t), 114.58 (s), 164.52 (s), 207.92 (s); Mass (70 eV, EI) m/z 209 (M^+), 164, 106, 85, 60; HRMS for $C_{11}H_{15}NO_3$: Calculated: 209.10519; Found: 209.10238

***2-[ortho-Ethoxyphenyl-1,1-bis(ethoxycarbonyl)metyl]-3-methyl nitroethane* 23** : Viscous oil; Yield 45 %; Diastereomeric ratio: 3.2:1; IR (CCl_4, cm^{-1}) 2976, 1747, 1734, 1382, 1289, 1033, 740; ^{1}H-NMR: 0.89 (t, 3H, J=6.8 Hz), 1.31 (t, 3H, J=6.8 Hz), 1.41 (d, 3H, J=6.8 Hz), 1.45 (t, 3H, J=6.8 Hz), 3.85 (q, 2H, J=6.8 Hz), 4.02 (q, 2H, J=6.8 Hz), 4.25-4.30 (m, 4H), 5.22-5.26 (m, 1H), 6.81-7.23 (m, 4H); ^{13}C-NMR: 13.47 (q), 13.94 (q), 14.61 (q), 16.61 (q), 53.26 (d), 61.29 (t), 61.85 (t), 63.63 (t), 82.95 (d), 111.39 (d), 120.23 (d), 122.69 (s), 129.34 (d), 157.01 (s), 167.31 (s), 168.38 (s); Mass (70 eV, EI) m/z 367 (M+), 275, 247, 201(base peak), 173, 105, 91; HRMS for $C_{18}H_{25}NO_7$: Calculated: 367.1631; Found: 367.1604.

General procedure for Michael addition reaction of thio phenols to cyclic enones

Enantiomerically pure amino diol, **1** (183mg, 0.53mmol) in dry THF (4ml) was added to a cooled solution of $LiAlH_4$ (10mg, 0.26mmol) in dry THF (1ml). The mixture was stirred for 30 min at 0 °C, then the enone (1.04mmol) in dry THF (2ml) and the corresponding thiophenol (0.91mmol) in dry THF (2ml) were added. The mixture was stirred for 60 sec at 0 °C, then quenched with 1N HCl (0.5ml) and extracted with ethyl acetate (50 ml). The organic phase was washed successively with saturated aq. $NaHCO_3$ (2 x 10 ml), brine (2 x 20 ml) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a syrupy mass, which on flash column chromatographic separation on silica gel using acetone:hexane (1:30) as eluent gave the pure products (**26-34**).

***(R)-3-(4-Hydroxy-phenylthio)cyclopentanone* 26** : White crystalline solid, m.pt 102-104 °C; Yield 96 %; IR (KBr, cm^{-1}) 3216(broad), 2944, 1722, 1600, 1584, 1494, 1437, 1273, 1165, 838, 825; ^{1}H-NMR: 1.97-2.18 (m, 1H), 2.21-2.32 (m, 3H), 2.44-2.58 (m, 2H), 3.7 (q, 1H, J=6.8 Hz), 6.81 (d, 2H, J=6.8 Hz), 7.33 (d, 2H, J=6.8 Hz); ^{13}C-NMR: 29.07 (t), 36.91 (t), 44.69 (d), 45.26 (t), 116.30 (d), 123.22 (s), 136.06 (d), 156.60 (s), 219.20 (s); Mass (70 eV, EI) m/z 208 (M+), 126 (base peak), 97, 83, 69; HRMS for $C_{11}H_{12}SO_2$: Calculated: 208.0557; Found: 208.0534; $[\alpha]_D^{27}$ = - 0.96 (c = 0.5, $CHCl_3$).

***(R)-3-(4-Hydroxy-phenylthio)cyclohexanone* 27** : White crystalline solid, m.pt 118-120 °C; Yield 96 %; IR (neat, cm^{-1}) 3216, 2944, 1693, 1600, 1590, 1443, 1273, 838, 694; ^{1}H-NMR: 1.68-1.72 (m, 2H), 2.12-2.15 (m, 2H), 2.31-2.39 (m, 3H), 2.65 (dd, 1H, J=4.4 and 8.3 Hz), 3.25 (m, 1H), 6.38 (bs, 1H), 6.75 (d, 2H, J=6.8 Hz);

7.35 (d, 2H, J=6.8 Hz); ^{13}C-NMR: 23.98 (t), 31.04 (t), 40.86 (t), 47.04 (d), 47.68 (t), 116.21 (d), 122.36 (s), 136.78 (d), 156.68 (s), 210.96 (s); Mass (70 eV, EI) m/z 222 (M^+, base peak), 126, 97, 69, 55; HRMS for $C_{12}H_{14}SO_2$: Calculated: 222.0714; Found: 222.0692; $[\alpha]_D^{27}$ = -1.73 (c=0.82, $CHCl_3$).

***3-(Acetylthio)cycohexanone* 28 :** Oil; Yield 89 %; IR (CCl_4, cm^{-1}) 1710, 1680, 1025, 957; ^{1}H-NMR: 1.65-1.72 (m, 2H), 1.91-2.06 (m, 2H), 2.19 (s, 3H), 2.14-2.35 (m, 3H), 2.55-2.60 (m, 1H), 3.69-3.72 (m, 1H); ^{13}C-NMR: 24.05 (t), 30.43, 30.70 (q), 40.49 (t), 41.33 (d), 46.87 (t), 194.15 (s), 207.72 (s); Mass (70 eV, EI) m/z 172 (M^+), 129, 94 (base peak), 72; HRMS for $C_8H_{12}SO_2$: Calculated: 172.0558; Found: 172.0731; $[\alpha]_D^{27}$ = -1.4 (c=1.16, $CHCl_3$).

***3-(β-Naphthylthio)cyclohexanone* 29 :** Resin; Yield 92 %; IR (CCl_4, cm^{-1}) 3056, 2944, 1715, 1497, 1446, 1318, 1222, 816, 749; ^{1}H-NMR: 1.70-1.81 (m, 2H), 2.11-2.16 (m, 2H), 2.29-2.44 (m, 3H), 2.69-2.74 (m, 1H), 3.49-3.56 (m, 1H), 7.45-7.90 (m, 7H); ^{13}C-NMR: 23.95 (t), 31.21 (t), 40.81 (t), 46.00 (d), 47.69 (t), 126.39 (d), 126.57 (d), 127.41 (d), 127.63 (d), 128.59 (d), 130.15 (d), 130.29 (s), 132.10 (d), 132.48 (s), 133.53 (s), 208.69 (s); Mass (70 eV, EI) m/z 256 (M^+), 160 (base peak), 128, 96; HRMS for $C_{16}H_{16}SO$: Calculated: 256.0968; Found: 256.1003; $[\alpha]_D^{27}$ = -4.2 (c=1.03, $CHCl_3$).

***3-(4-Methyl-phenylthio)butanal* 30 :** Colourless Liquid; Yield 73 %; IR (neat, cm^{-1}) 3156, 2844, 2758, 1715, 1446, 1318, 1222, 816, 749; ^{1}H-NMR: 1.32 (d, 3H, J=6.8 Hz), 2.33 (s, 3H), 2.51-2.68 (m, 2H), 3.58-3.63 (m, 1H), 7.01 (d, 2H, J=6.8 Hz), 7.35 (d, 2H, J=6.8 Hz) 9.72 (t, 1H, J=1.5 Hz); ^{13}C-NMR: 21.02 (q), 21.05 (q), 37.87 (d), 49.45 (t), 129.55 (s), 129.73 (d), 133.63 (d), 137.91 (s), 200.56 (d); Mass (70 eV, EI) m/z 194 (M^+), 124 (base peak), 91; HRMS for $C_{11}H_{14}SO$: Calculated: 194.0765; Found: 194.0587; $[\alpha]_D^{27}$ = -2.5 (c=0.98, $CHCl_3$).

***3-Phenyl(4-methyl-phenylthio)propanal* 31 :** Oil; Yield 72 %; IR (neat, cm^{-1}) 3024, 2912, 2816, 2720, 1728, 1686, 1484, 1174, 694; ^{1}H-NMR: 2.28 (s, 3H), 2.55-2.70 (m, 1H), 4.55-4.68 (m, 1H), 7.20-7.55 (m, 10H), 9.46 (bs, 1H); ^{13}C-NMR: 21.06 (q), 43.01 (d), 49.48 (t), 127.61, 128.91, 129.07, 129.59, 130.00, 132.19, 134.10, 197.37 (d); Mass (70 eV, EI) m/z 256 (M^+), 228, 132, 124 (base peak), 91, 77 ; HRMS for $C_{16}H_{16}SO$: Calculated: 256.0922; Found: 256.1120; $[\alpha]_D^{27}$ = -3.2 (c=1.23, $CHCl_3$).

***1-Methyl-2-(phenyl, 4-methyl-phenylthio)nitroethane* 32 :** Isomer I: Resin; Yield 90 % (isomer I & II); IR (neat, cm^{-1}) 2980, 1455, 1408, 1361, 1130, 700; ^{1}H-NMR : 1.39 (d, 3H, J=6.8 Hz), 2.30 (s, 3H), 4.50 (d, 1H, J=9.3 Hz), 4.88-4.95 (m, 1H), 7.01-7.28 (m, 9H); ^{13}C-NMR: 17.44 (q), 21.17 (q), 56.95 (d), 86.28 (d), 127.94, 128.22, 128.37, 128.72, 129.81 (d), 134.45 (d), 136.63 (s), 138.87 (s); Mass (70 eV, EI) m/z 287 (M^+), 163, 117 (base peak), 91, 77, 65, 51; Isomer II: White crystalline solid, IR (neat, cm^{-1}) 2978, 1488, 1410, 1359, 1120, 691; ^{1}H-NMR : 1.81 (d, 3H, J=6.8 Hz), 2.28 (s, 3H), 4.49 (d, 1H, J=9.3 Hz), 4.92-4.97 (m, 1H), 7.00-7.25 (m, 9H); ^{13}C-NMR: 18.12 (q), 21.80 (q), 57.46 (d), 86.74 (d), 127.89, 128.04, 128.30, 128.49, 129.76 (d),

134.12 (d), 137.58 (s), 138.72 (s); Mass (70 eV, EI) m/z 287 (M^+), 163, 117 (base peak), 91, 77, 65, 51; HRMS for $C_{16}H_{17}NO_2S$: Calculated: 287.0980; Found: 287.1025; $[\alpha]_D^{27}$ = +13.7 (c=1.05, $CHCl_3$).

***α,α'-Di[(4-methylphenylthio)methyl]succinate* 34 :** White solid, m.pt 134 °C; Yield 95 %; IR (KBr, cm^{-1}) 3152, 2944, 1728, 1488, 1437, 1299, 1005, 813; ^{1}H-NMR: 2.32 (s, 3H), 3.72 (s, 3H), 3.84(s, 1H), 7.21 (ABq, 4H, J=7.8 Hz); ^{13}C-NMR: 21.21 (q), 51.71 (q), 52.34 (d), 127.64 (s), 129.82 (d), 134.81 (d), 139.33 (s), 169. 50 (s); Mass (70 eV, EI) m/z 390 (M^+), 267, 208, 131, 123 (base peak), 91, 77; HRMS for $C_{20}H_{22}O_4S_2$: Calculated: 390.09581; Found: 390.10326; $[\alpha]_D^{27}$ = 0.00 (c=1.24, $CHCl_3$).

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