

Supporting Information

Value of Zeolites In Asymmetric Induction During Photocyclization of Pyridones, Cyclohexadienones and Naphthalenones

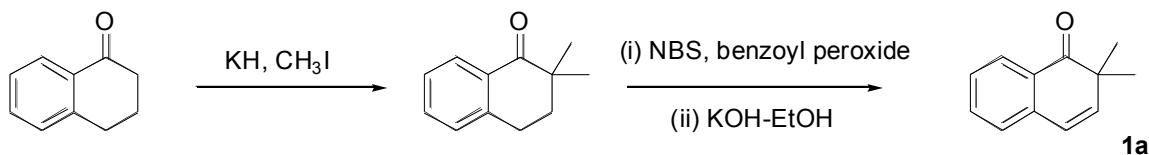
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Synthesis of 2,2-dimethyl-1,2-dihydro-naphthalenone (1a)

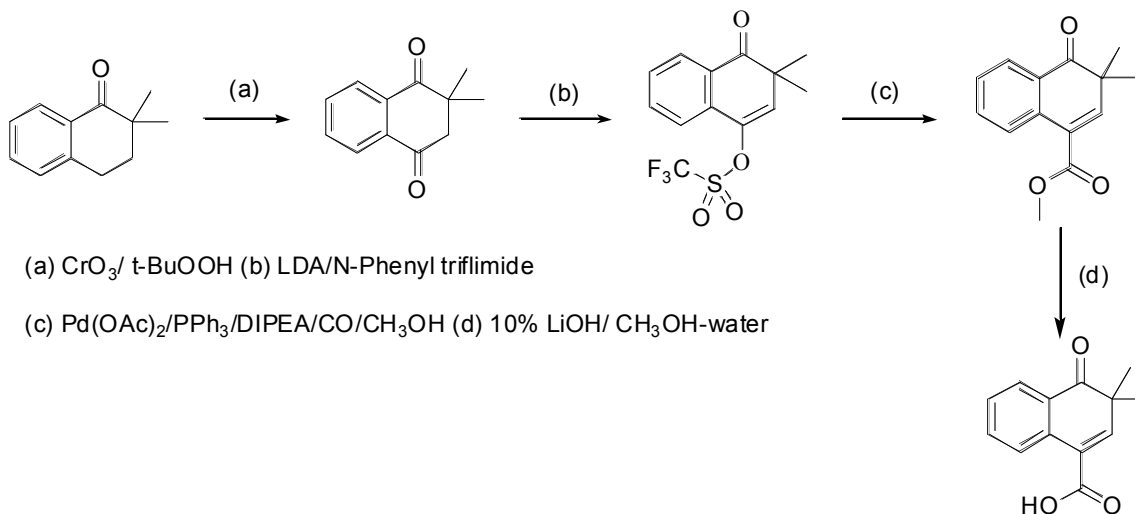


Scheme S1: Synthesis of 2,2 dimethyl-1,2-dihydro-naphthalenone

Step 1: Synthesis of 2,2-dimethyl- α -tetralone (DMT): To a cold (0°C) suspension of KH in mineral oil 3g (75mmol) and methyl iodide 19g (134mmol) in dry (distilled) THF (200ml) under a dry atmosphere of nitrogen gas, was added α -tetralone 5g (34.2mmol) in THF (200ml) over 0.5hr. The solution was allowed to warm up to room temperature after the initial rapid evolution of hydrogen had ceased and was stirred for 32hrs. The reaction was then carefully quenched by adding aqueous ammonium chloride followed by extraction with diethyl ether (three 100ml portions). The organic layer was washed with water and brine and dried over magnesium sulfate and concentrated in vacuo. Fractional vacuum distillation yielded product as a straw colored liquid. (5.42g, 91%).

Step 2: Synthesis of 2,2-dimethyl-1,2-dihydro-naphthalenone: A mixture of 1.51g (0.0087mol) of the preceding ketone, 1.96g (0.011mol) of N-bromosuccinimide, 5.8ml of carbon tetrachloride, and 0.02g of benzoyl peroxide was refluxed in an atmosphere of nitrogen for 12hrs. The cooled mixture was filtered to remove precipitated succinimide and evaporated to remove solvent. The residue was refluxed with 15ml of 20% ethanolic potassium hydroxide for 12hrs and the solvent again evaporated. This residue was treated with water and extracted with ether. Fractional vacuum distillation yielded product as a colorless liquid. (0.9g, 60%).

Synthesis of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid



Scheme S2: Synthesis of 2,2 dimethyl-1,2-dihydronaphthalenone-4-carboxylic acid.

Synthesis of 2,2-dimethyl-1,2-dihydronaphthalenone-4-carboxylic acid

Step 1: Oxidation of dimethyltetralone to 2,2-dimethyl-1,4-naphthoquinone: In a 250 ml round bottom flask, 5.5g of dimethyltetralone, 50ml of dichloromethane and 9ml of water were taken. 20ml of *t*-butylhydroperoxide (*t*-BuOOH) and 0.3g of chromic oxide (CrO_3) were added to this solution and the reaction mixture was stirred vigorously for 4 days. The hydroperoxide and the chromic oxide were replenished by adding 0.25g of CrO_3 and 20ml of *t*-BuOOH. The reaction was quenched with dilute aqueous sodium thiosulphate solution filtered and passed through celite. The dione was extracted using ether, washed with water, brine and dried with anhydrous sodium sulfate. The solvent was evaporated and the dione was purified as a pale yellow solid using column chromatography (silica column, 30% dichloromethane in hexane).

Step 2: Preparation of the vinyl triflate: To a cold (-78°C) solution of LDA (10.8mmol, formed from the reaction between diisopropylamine (1.7ml, 11.8mmol) and *n*-BuLi (10.8mmol) taken in a round bottomed flask under a dry atmosphere of nitrogen was added the above-prepared dione (1.85g, 9.84mmol) in THF (10ml) over 5 minutes.

The enolate was allowed to form in the cold for 1.5 hours. Solid N-Phenyl triflimide (4.04g, 11.3 mmol) was added in one portion. The suspension was allowed to warm to room temperature and was stirred for 2 hours. Workup with 5% aqueous sodium bicarbonate was followed by extraction into ether, water and brine washes, MgSO₄ drying and solvent removal under vacuum. Flash chromatography (silica gel, 15% ether in petroleum ether) furnished the vinyl triflate as a viscous oil (75% pure by GC). Further purification was not attempted – this product was carried through to the next reaction.

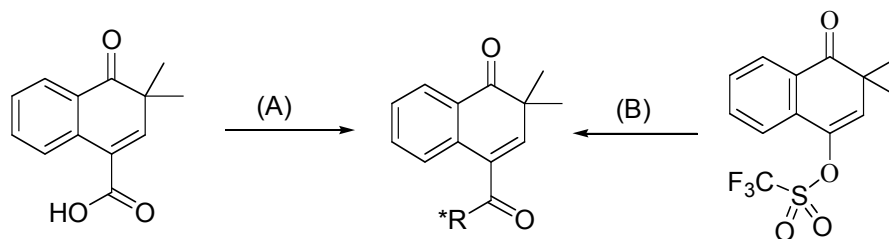
Step 3: Methoxy carbonylation of the vinyl triflate: To a solution of Pd(OAc)₂ (176mg, 0.8mmol), triphenylphosphine (444mg, 1.7mmol), diisopropylethylamine (Huning's base, 4.5ml, 26mmol) and methanol (20mL) in dry DMF(50ml) under a dry nitrogen atmosphere, was added the vinyl triflate isolated from the previous reaction. A stream of CO was bubbled through the solution for 9 hours. Standard workup with ether and water gave a black oil after the removal of solvent. Flash chromatography (silica gel, 12% ether in petroleum ether) gave the product as a pale yellow liquid (1.33g , 60% over two steps).

Step 4: Hydrolysis of ester to acid: The ester obtained in the above step was stirred with 10% LiOH solution in methanol water mixture for 8-12 hours. Methanol was removed under vacuum and added cold water to this mixture and acidified with dilute hydrochloric acid to precipitate the acid. The acid was filtered, dried and subsequently used for the amidation step.

Synthesis of chiral amides and esters of 2,2-dimethyl-1,2-dihydronaphthalenone-4-carboxylic acid (Scheme S3)

The above acid was stirred with 1 equivalent of chiral amine/alcohol along with 1 equivalent of EDC and catalytic amount of DMAP in dichloromethane to obtain the desired chiral amide or ester. In yet another route, the triflate obtained after the step III was stirred with atleast two equivalents of chiral alcohol or amine in the presence of 1 equivalent of DIPEA, catalytic amount of Pd(OAc)₂-PPh₃ in DMF(for esters) or dichloromethane (for amide) purged with carbon monoxide gas. A positive pressure of CO was maintained throughout the reaction. DIPEA was avoided during the synthesis of

amides as the free amines by themselves act as base. All the chiral compounds were purified by column chromatography (silica gel). A 25% ethylacetate in hexane mixture and 12% ethyl ether in hexane was used as eluent for amide and ester systems respectively.



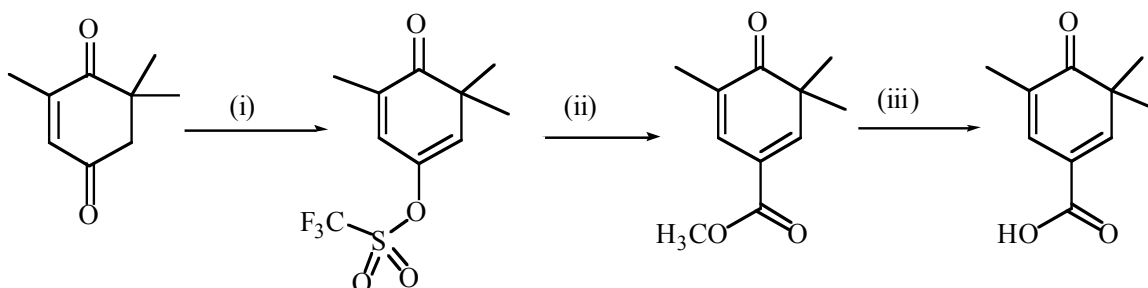
(A) EDC/DMAP/ amine or alcohol

(B) $Pd(OAc)_2/PPh_3/DIPEA/CO/alcohol$

(or) $Pd(OAc)_2/PPh_3/CO/Amine$

Scheme S3: Synthesis of chiral amides and esters.

Synthesis of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid



(i). LDA/N-Phenyl triflimide

(ii). Pd(OAc)₂/PPh₃/DIPEA/CO/CH₃OH

(iii). LiOH/CH₃OH:H₂O

Scheme S4: Synthesis of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5diene carboxylic acid.

Step 1 Synthesis of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-triflate: In a clean dry 100ml 3 necked round-bottomed flask 20ml of LDA was taken at -78°C and stirred for 5 minutes under nitrogen. 5g of 4-oxoisophorone was dissolved in 20ml of dry THF and this solution was added in drops using a dropping funnel onto the cooled LDA over a period of 5 minutes. The enolate was allowed to form over a period of 2 hrs and 10.0g of solid N-phenyl triflimide was added in one portion to the above enolate and the suspension was stirred continuously and warmed to room temperature. Stirring was continued for additional 12hrs. The reaction mixture was quenched with saturated ammonium chloride solution and extracted with ether. The ether extract was washed thrice with water, 5% sodium bicarbonate solution and dried using anhydrous sodium sulfate. The solvent was removed under suction and the crude triflate was purified by column chromatography (silica gel, 15% ether in hexane). The triflate was obtained as a yellow liquid. (85% yield).

¹H-NMR (CDCl₃, 400MHz): δ 6.6-6.8 (s,1H), 6-6.13 (s, 1H), 1.83-1.95 (s, 3H), 1.17-1.28 (s, 6H).

Mass Spectral data: m/e (relative intensity): 284 (M^+ 7), 205 (1), 177 (0.5), 153 (6), 151 (87), 123 (11), 107 (7), 95 (100), 84 (40), 67 (27), 55 (38), 40 (24).

Step 2 Methoxy carbonylation of the vinyl triflate: To a solution of Pd(OAc)₂ (176mg, 0.8mmol), triphenylphosphine (444mg, 1.7mmol), diisopropylethylamine (Huning's base, 4.5ml, 26mmol) and methanol (20mL) in dry DMF(50ml) under a dry nitrogen atmosphere, was added 2g of the vinyl triflate isolated from the previous reaction. A stream of CO was bubbled through the solution for 20 mins and stirred with a CO balloon for 12 hours. Standard workup with ether and water gave black oil after the removal of solvent. Flash chromatography (silica gel, 12% ether in petroleum ether) gave the product as a pale yellow liquid (1.33g).

¹H-NMR (CDCl₃, 400MHz): δ 7.2-7.4 (d, 1H), 6.4-6.65 (d, 1H), 3.66-3.91 (s, 3H), 1.8-2.1 (d, 3H), 1.25-1.35(s,6H).

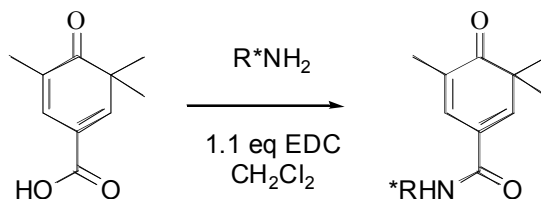
Mass Spectral data: m/e (relative intensity): 194 (M^+ ,95), 179 (17), 162 (20), 151 (68), 135 (48), 134 (75), 124 (23), 107 (78), 91 (100), 79 (28), 77 (26), 65 (30), 52 (16), 43 (28), 39 (33).

Step 3: Hydrolysis of ester to acid: The ester obtained in the above step was stirred with 10% LiOH solution in methanol water mixture for 8-12 hours. Methanol was removed under vacuum and added cold water to this mixture and acidified with dilute hydrochloric acid to precipitate the acid. The acid was filtered, dried and subsequently used for the amidation step.

Chiral esters of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid

All the chiral esters were made using the same experimental protocol mentioned for the methyl ester except for the fact the methanol used in the reaction is replaced by the desired chiral alcohol which was taken in 2 equivalents as compared to the triflate as against 40 equivalents of methanol used in the methyl ester and the reaction mixture was stirred for 18 hrs.

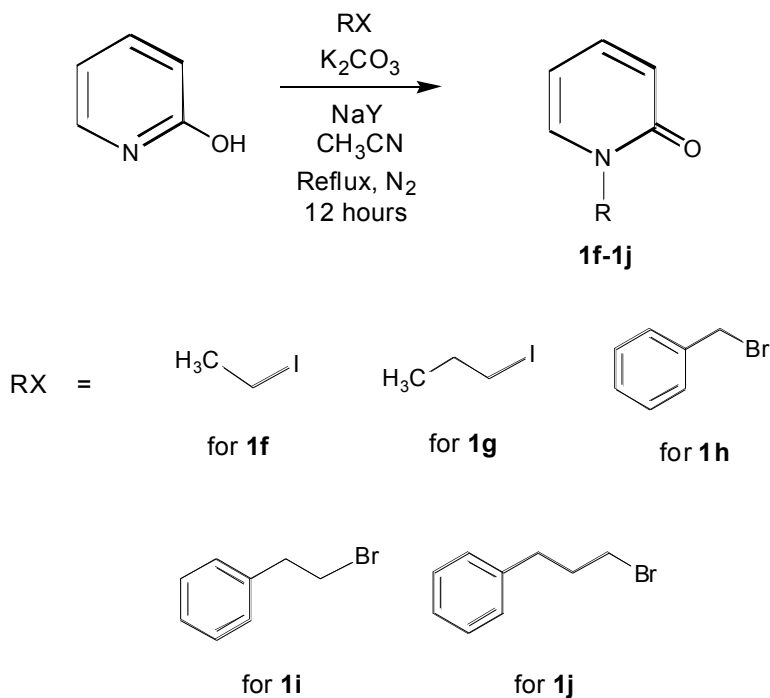
Chiral amides 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid



Scheme S5: Synthesis of chiral amides of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid.

Syntheses of substrates 1f-1j

Substrates **1f-1j** were synthesized according to reaction outlined in **Scheme S6**. To 500 mg of 2-hydroxy pyridine, 2 equivalents of potassium carbonate and 300 mg of NaY zeolite was added in acetonitrile. The mixture was then refluxed for 30 mins under nitrogen and this was followed by the addition of corresponding iodide (3 equivalents). The reflux was continued for 12 h under nitrogen. The compounds were purified by column chromatography (silica gel) using 50% ethyl acetate:hexanes solvent systems for substrates **1g-1j** and 2% methanol/chloroform solvent mixture for substrate **1f**. The product was characterized by 1H , ^{13}C NMR spectroscopy.



Scheme S6: Synthesis of pyridones (**1f-1j**)

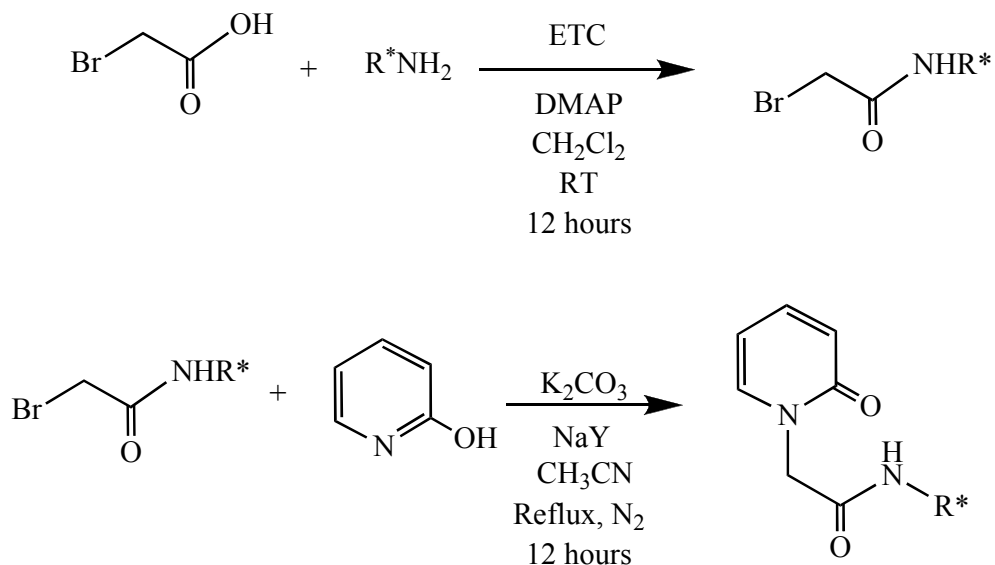
The above acid was stirred with 1 equivalent of chiral amine, 1.1 equivalent of EDC in dichloromethane to obtain the desired chiral amide. Chiral amides were purified by column chromatography with 25% ethyl acetate in hexane.

Syntheses of substrates **6e**, **6g**, **6i-6m** and **6o-6q**

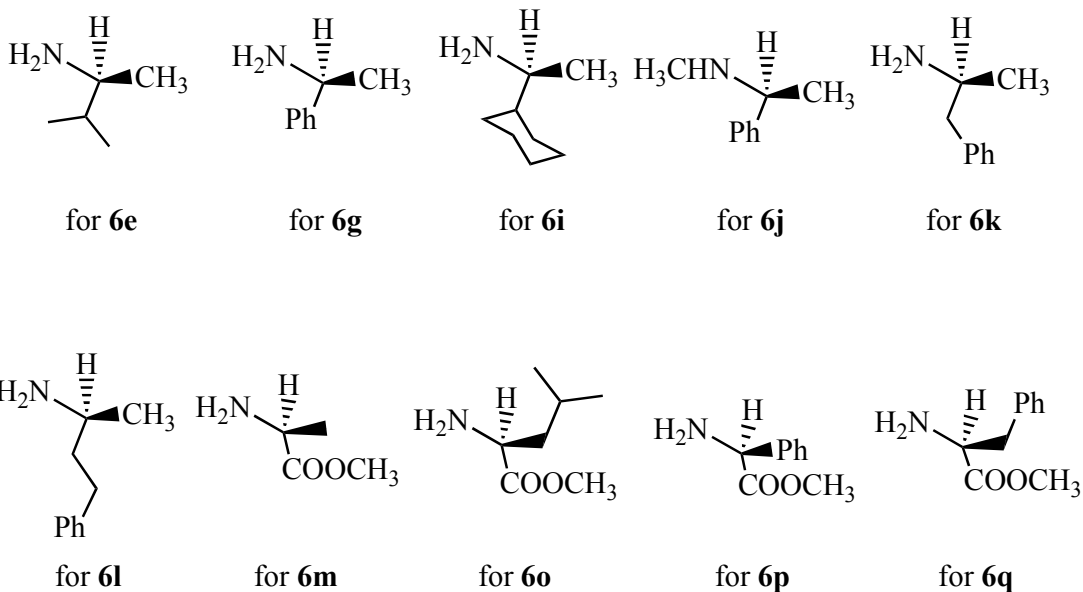
The substrates were synthesized by the procedure outlined in **Scheme S7**. The synthesis involved two steps.

Step 1: The first step involved the coupling of enantiomeric pure amine or amino acids to bromo acetic acid by using ETC(1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide)/DMAP (4-dimethylaminopyridine). The synthetic procedure involved for the synthesis is as follows. To 1 equivalent of bromo acetic acid (250 mg), 1.1 equivalent of pure amine or amino acid is added in dichloromethane followed by addition of catalytic amount of DMAP. The solution was allowed to stir for 30 mins. This was followed by the addition of ETC (1 equivalent) and the stirring was continued for 8 hours at room temperature. The reaction was monitored by TLC. The

solution was then washed with 5x10 ml of deionized water and dried over sodium sulfate. The solution was then concentrated and purified by column chromatography (silica gel) using 50% ethyl acetate:hexanes solvent mixture. The resulting compound was used for the next step.



R*NH₂ =



Scheme S7: Syntheses of substrates (**6e**, **6g**, **6i-6m** and **6o-6q**)

Amide derived from Bromo acetic acid and S-(-)-1-phenylethylamine (g)

^1H NMR (CDCl_3 , 400 MHz) δ 1.4-1.5 (m, 3H), 3.6-3.7 (m, 2H), 5.0-5.1 (m, 1H), 6.9-7.0 (d, $J=7.6$ Hz, 1H), 7.2-7.4 (m, 5H).

Amide derived from Bromo acetic acid and D-(+)-amphetamine.sulfate salt (k)

^1H NMR (CDCl_3 , 400 MHz) δ 1.1-1.2 (m, 3H), 2.7-2.9 (m, 2H), 3.6-3.85 (m, 2H), 4.2-4.3 (m, 1H), 6.1-6.2 (d, $J=7.2$ Hz, 1H), 7.2-7.4 (m, 5H).

Amide derived from Bromo acetic acid and S-(+)-1-Methyl-3-phenyl propyl amine (l)

^1H NMR (CDCl_3 , 400 MHz) δ 1.15-1.2 (m, 3H), 1.7-1.8 (m, 2H), 2.6-2.7 (m, 2H), 3.6-3.7 (m, 2H), 3.95-4.0 (m, 1H), 6.1-6.2 (d, $J=7.7$ Hz, 1H), 7.1-7.4 (m, 5H).

Amide derived from Bromo acetic acid and S-(-)-Cyclohexyl ethyl amine (i)

^1H NMR (CDCl_3 , 400 MHz) δ 1.1-1.9 (m, 14 H), 3.6-3.7 (m, 2H), 3.75-3.8 (m, 1H), 6.1-6.2 (d, $J=7.6$ Hz, 1H).

Amide derived from Bromo acetic acid and S-N-Methyl-1-phenyl ethyl amine (j)

Due to the restriction rotation of N-Me-CO group, the CH_3 , N- CH_3 and the CH protons appeared as set of two signals in the ^1H NMR spectrum.

^1H NMR (CDCl_3 , 400 MHz) δ 1.4-1.5; 1.6-1.65 (d, 3H), 2.6-2.7 (s, 3H), 3.7-3.9 (m, 2H), 5.9-6.0; 5.05-5.1 (q, $J=7.2$ Hz, 1H), 7.2-7.4 (m, 5H).

Amide derived from Bromo acetic acid and S-(+)-2-Methyl-3-butyl amine (e)

¹H NMR (CDCl₃, 400 MHz) δ 0.7-0.8 (m, 6H), 1.05-1.1 (d, J=7.2 Hz, 3H), 1.65-1.75 (m, 1H), 3.7-3.9 (m, 3H), 6.3-6.4 (d, J=7.2 Hz, 1H).

Amide derived from Bromo acetic acid and S-(+)-2-Phenylglycinemethylester.HCl (p)

¹H NMR (CDCl₃, 400 MHz) δ 3.7 (s, 3H), 3.67-3.75 (m, 2H), 5.45-5.5 (d, J=7.2 Hz, 1H), 7.3-7.4 (m, 5H), 7.6-7.65 (d, J=7.6 Hz, 2H).

Amide derived from Bromo acetic acid and L-Phenyl alanine methyl ester.HCl (q)

¹H NMR (CDCl₃, 400 MHz) δ 3.0-3.2 (m, 2H), 3.7 (s, 3H), 3.6-3.75 (m, 2H), 4.8-4.9 (m, 1H), 6.8-6.9 (d, J=7.2 Hz, 1H), 7.1-7.3 (m, 5H).

Amide derived from Bromo acetic acid and (L)-Alanine methyl ester.HCl (m)

¹H NMR (CDCl₃, 400 MHz) δ 1.4 (m, 3H), 3.7 (s, 3H), 3.6-3.8 (m, 2H), 4.5-4.6 (m, 1H), 6.9-7.0 (d, J=7.2 Hz, 1H).

Amide derived from Bromo acetic acid and (L)-Leucine methyl ester.HCl (o)

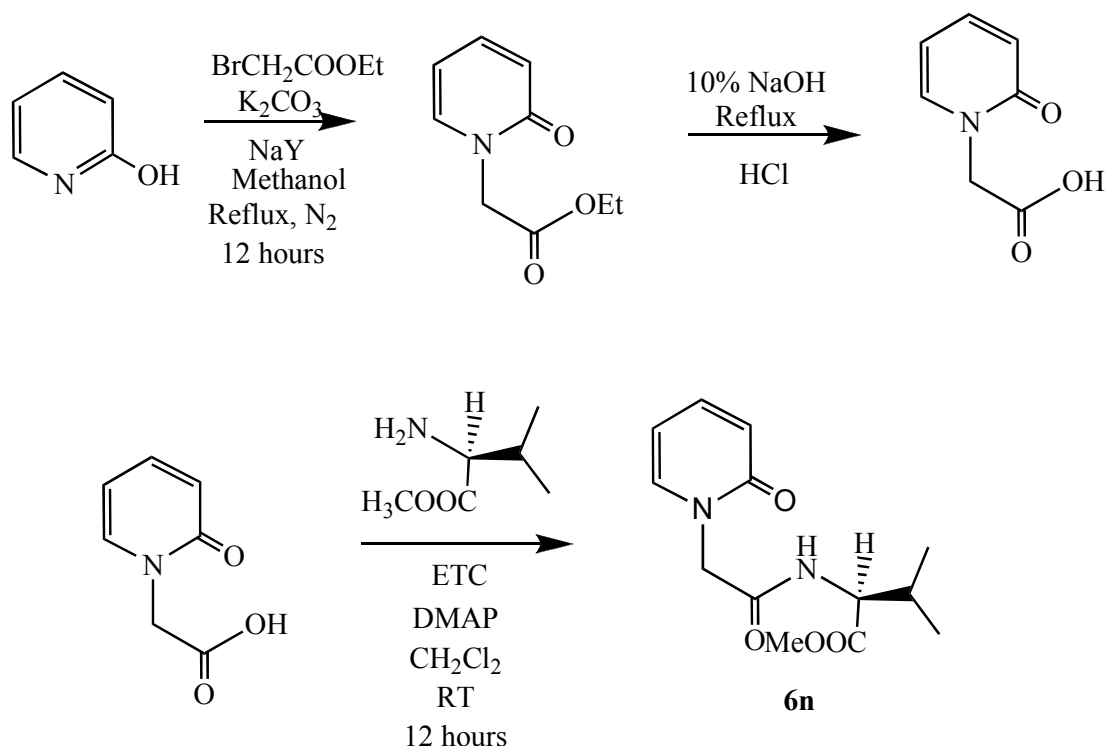
¹H NMR (CDCl₃, 400 MHz) δ 0.85-0.95 (d, J=7.6 Hz 6H), 1.5-1.7 (m, 3H), 3.65 (s, 3H), 3.7-3.9 (m, 2H), 4.52-4.6 (m, 1H), 6.9-6.94 (d, J=7.2 Hz, 1H).

Step 2: To 150 mg of 2-hydroxy pyridine, 2 equivalents of potassium carbonate and 300 mg of NaY zeolite was added in acetonitrile. The mixture was then refluxed for 30 mins under nitrogen. This was followed by the addition of the compound obtained

from Step 1. The reflux was continued for 12 hours under nitrogen. The compounds were purified by column chromatography (silica gel) using 2-3% methanol:ethyl acetate solvent mixture. The product was characterized by ^1H and ^{13}C NMR spectroscopy.

Synthesis of substrate **6n**

The substrate **6n** was synthesized according to **Scheme S8**. The first step involved the syntheses of N-pyridoneacetic acid by hydrolysis of N-pyridone acetic acid methyl ester followed by coupling of (L)-Valine methyl ester.HCl to it by using ETC (1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide) and DMAP (4-dimethyl amino pyridine).



Scheme S8: Synthesis of substrate **6n**

Step 1: The N-pyridone acetic acid ethyl ester was synthesized by refluxing hydroxy pyridine, ethyl bromo acetate and potassium carbonate in methanol. To a solution of hydroxy pyridine in methanol, potassium carbonate was added (1 eq)

followed by the addition of 300 mg of NaY and ethyl bromo acetate (2 eq). The solution was refluxed for 12 hours under nitrogen. The product (N-pyridone acetic acid methyl ester) was purified by column chromatography (silica gel) by using 25% ethyl acetate:hexanes. The product was characterized by ^1H and ^{13}C NMR spectroscopy. The product (N-pyridone acetic acid methyl ester) was refluxed with 10% sodium hydroxide in methanol/water for 12 hours followed by acidification using conc. HCl. The N-pyridone acetic acid obtained was used for further reaction. This hydrolysis reaction worked only once and could not be repeated for obtaining the hydrolyzed product (N-pyridone acetic acid) and hence the procedure outlined in **step2** was used to couple enantiomeric pure amines and amino acids to pyridones.

Characterization Methyl ester of N-Pyridone acetic acid

^1H NMR (CDCl_3 , 400 MHz) δ 3.75 (s, 3H), 4.5 (s, 2H), 6.1-6.15 (m, 2H), 6.45-6.5 (m, 1H), 7.2-7.35 (m, 2H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 51.5, 53.5, 106.3, 120.8, 138.3, 140.4, 162.5, 167.9.

Characterization N-Pyridone acetic acid

^1H NMR (CD_3OD , 400 MHz) δ 4.7 (s, 2H), 6.4-6.45 (m, 1H), 6.5-6.6 (m, 1H), 7.55-7.65 (m, 2H).

^{13}C NMR (CD_3OD , 100 MHz) δ 50.5, 107.1, 119.3, 139.3, 141.5, 163.6, 169.6.

Step 2: To 500 mg of the N-pyridone acetic acid, 1.1 eq of L-valine methyl ester hydro chloride, 1 eq ETC (1-[3-(dimethylamino)propyl]-3-ethylcarbodiimidemethiodide) and catalytic amount of DMAP (4-dimethyl amino pyridine) was added in dichloromethane and the solution was stirred for 12 hours. The solution was then washed with 5x10 ml of deionized water and dried over sodium sulfate. The solution was then concentrated and purified by column chromatography (silica gel) using 2% methanol/ ethyl acetate solvent mixture and characterized by ^1H and ^{13}C NMR spectroscopy.

Characterization of reactants

2,2-dimethyl-1,2-dihydro-naphthalenone (1a)

¹H-NMR (CDCl₃, 400MHz): δ 1.25-1.31 (s, 6H, Me), 6.07-6.12 (d, J = 9.6Hz, 1H), 6.47-6.50 (d, J = 9.6Hz, 1H), 7.22-7.26 (d, J= 7.6 Hz, 1H), 7.30-7.36 (t, J = 7.6Hz, 1H), 7.51-7.56 (t, J = 7.6 Hz, 1H), 8.02-8.06 (d, J = 7.6Hz, 1H).

Mass Spectral data: m/e (relative intensity): 172 (M⁺ 89), 157 (61), 143 (12.4), 141 (7), 129 (100), 115 (20), 102 (14.4), 91 (3), 89 (7), 77 (16.7), 63 (15.5), 51 (15.5), 39 (14).

Methyl ester of 2,2-dimethyl-1, 2-dihydronaphthalenone-4-carboxylic acid (1b)

¹H NMR (CDCl₃, 400MHz): δ 1.28 (s, 6H, Me), 3.85 (s, 3H), 7.00 (s, 1H), 7.38(m,1H), 7.57 (m, 1H), 8.09 (m, 2H).

Mass Spectral data: m/e (relative intensity): 230 (M⁺, 84), 215(9, 199 (22), 198 (30), 187 (100), 171 (77), 170(36), 159(8), 145 (33), 143 (37), 128(63), 115(48), 102(15), 91(10), 77(18), 63(15), 51(19), 39(19).

Methyl ester of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid (1c)

¹H-NMR (CDCl₃, 400MHz): δ 7.2-7.4 (d, J=7.2 Hz, 1H), 6.4-6.65 (d, J=7.2 Hz, 1H), 3.66-3.91 (s, 3H), 1.8-2.1 (d, J=7.6 Hz, 3H), 1.25-1.35(s, 6H).

Mass Spectral data: m/e (relative intensity): 194 (M⁺,95), 179 (17), 162 (20), 151 (68), 135 (48), 134 (75), 124 (23), 107 (78), 91 (100), 79 (28), 77 (26), 65 (30), 52 (16), 43 (28), 39 (33).

3,4,6,6-tetramethyl cyclohexa 2,4-diene-1-none (1d)

¹H-NMR (CDCl₃, 400MHz): δ 5.97 (s, 1H), 5.9 (s, 1H), 2.05 (s, 3H), 1.93 (s, 3H), 1.15 (s, 6H).

¹³C-NMR: 205.6, 144, 128, 123.6, 105, 46.3, 25.54, 25.53, 20.93, 18.8.

Mass Spectral data: m/e (relative intensity): 150 (M⁺, 35), 135 (20), 122 (16), 108 (44), 107 (100), 91 (48), 79 (28), 77 (20), 65 (15), 53 (16), 41(28), 39 (38), 27 (23).

N-Ethyl pyridone (1f)

^1H NMR (CDCl_3 , 400 MHz) δ 6.8-7.0 (m, 2H), 6.0-6.2 (m, 1H), 5.6-5.7 (m, 1H), 3.4-3.5 (q, 2H, $J=7.2$ Hz), 0.7-0.8 (t, 3H, $J=7.2$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 162.5, 139.5, 137.1, 121.2, 106.4, 45.0, 14.9.

N-Propyl pyridone (1g)

^1H NMR (CDCl_3 , 400 MHz) δ 7.1-7.2 (m, 2H), 6.3-6.36 (m, 1H), 5.95-6.0 (m, 1H), 3.68-3.73 (t, 2H, $J=7.2$ Hz), 1.54-1.62 (m, 2H), 0.74-0.77 (t, 3H, $J=7.2$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 162.6, 139.4, 137.8, 120.9, 105.9, 51.4, 22.5, 11.1,

N-Benzyl pyridone (1h)

^1H NMR (CDCl_3 , 400 MHz) δ 7.0-7.2 (m, 7H), 5.9-6.0 (m, 1H), 6.36-6.41 (m, 1H), 4.9 (s, 2H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 162.7, 139.8, 137.7, 136.6, 128.9, 128.5, 128, 120.9, 106.5, 51.9.

GC-MS (EI) spectral data m/e (relative intensity) 185 (M^+ , 62), 91 (100), 79 (25), 65 (26), 51 (14).

N-Ethyl phenyl pyridone (1i)

^1H NMR (CDCl_3 , 400 MHz) δ 6.8-7.3 (m, 7H), 6.46-6.5 (m, 1H), 5.8-5.9 (m, 1H), 4.02-4.05 (t, 2H, $J=8$ Hz), 2.94-2.97 (t, 2H, $J=7.2$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 163.0, 140.0, 138.2, 138.15, 129.2, 128.8, 126.9, 121.0, 106.8, 35.2, 52.5.

N-Propyl phenyl pyridone (1j)

^1H NMR (CDCl_3 , 400 MHz) δ 7.0-7.2 (m, 7H), 6.4-6.45 (m, 1H), 6.0-6.03 (m, 1H), 3.8-3.84 (t, 2H, $J=7.2$ Hz), 2.45-2.54 (t, 2H, $J=7.2$ Hz), 1.9-2.0 (m, 2H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 162.8, 141.0, 139.6, 137.8, 128.6, 128.5, 126.3, 121.1, 106.2, 49.6, 32.9, 30.6.

S- (-)-2-methyl-1-butylester of 2,2-dimethyl-1, 2-dihydronaphthalenone-4-carboxylic acid (2a)

¹H-NMR (CDCl₃, 400MHz): δ 0.94-1.03 (m, 6H), 1.21-1.33 (m, 1H), 1.34-1.37 (s, 6H), 1.45-1.57 (m, 1H), 1.81-1.91 (m 1H), 4.07-4.23 (m, 2H), 7-7.02 (s, 1H), 7.39-7.45 (t, J=7.6 Hz, 1H), 7.6-7.66 (m, 1H), 8.07-.8.18 (m, 2H).

Mass Spectral data: m/e (relative intensity): 286 (M⁺ 18.8), 216 (100), 198 (42.5), 171 (57.5), 170 (30), 143 (21.2), 128 (47.5), 115 (22.5), 91 (5), 77 (8.8), 55 (11.2), 43 (65).

(+)Menthyl ester of 2,2-dimethyl-1, 2-dihydronaphthalenone-4-carboxylic acid (2b)

¹H-NMR (CDCl₃, 400MHz): δ 0.82-0.9 (d, J=7.2 Hz, 3H), 0.91-1.0 (q, J=7.2 Hz, 7H), 1.09-1.21 (m, 2H), 1.34-1.37 (s, 6H), 1.5-1.64 (m, 2H), 1.7-1.8 (m, 2H), 1.89-1.98 (m, 1H), 2.1-2.18 (m, 1H), 4.92-5.0 (m, 1H), 6.93-6.95 (s, 1H), 7.4-7.45 (m, 1H), 7.61-7.67 (m, 1H), 8.09-8.16 (m, 2H).

Mass Spectral data: m/e (relative intensity): 354 (M⁺,5), 217 (17), 216 (100), 198 (20), 188 (13), 171 (22), 143 (10), 128 (23), 95 (25), 81 (27), 67 (20), 55 (25), 41 (27).

R-(+)-Fenchyl ester of 2,2-dimethyl-1, 2-dihydronaphthalenone-4-carboxylic acid (2c)

¹H-NMR (CDCl₃, 400MHz): δ 0.8-1.0 (m, 6H), 1.0-1.1 (s, 3H), 1.13-1.17 (s, 2H), 1.2-1.23 (s, 2H), 1.34-1.37 (s, 6H), 1.4-1.64 (m, 2H), 1.7-1.8 (m, 1H), 4.6 (s, 1H), 7.0-7.08 (s, 1H), 7.4-7.45 (t, J=7.6 Hz, 1H), 7.61-7.67 (t, J=7.6 Hz, 1H), 8.08-8.13 (d, J=7.2 Hz 1H), 8.15-8.2 (d, J=7.2 Hz, 1H).

Mass Spectral data: m/e (relative intensity): 352 (M⁺, 2), 216 (70), 199 (24), 171 (20.4), 143 (15), 137 (62), 128 (48), 115 (15.1), 95 (24), 81 (100), 67 (18), 55 (17), 41 (30).

(R)-(+)-Bornylamide of 2,2-dimethyl-1, 2-dihydronaphthalenone carboxylic acid (2d)

¹H-NMR (CDCl₃, 400MHz): δ 0.8-2.0 (m), 4.42-4.55 (m, 1H), 5.8-5.9 (s,1H), 6.36-6.39 (s, 1H), 7.2-7.31 (t, J = 8.8 Hz, 1H), 7.6-7.76 (m, 2H), 8.1-8.17 (d, J = 8.8 Hz, 1H).

Mass Spectral data: m/e (relative intensity): 351 (M^+ 78.8), 323 (14), 215 (84), 199 (48), 188 (50), 187 (53), 172 (100), 171 (33), 143 (33), 128 (67.5), 115 (21.5), 95 (53), 81 (63), 67 (37), 55 (33), 44 (61), 41 (63).

(S)-(+)-(3-methyl-2-butyl)amide of 2,2-dimethyl-1, 2-dihydronaphthalenone-4-carboxylic acid (2e)

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 0.94-0.98 (q, $J=7.6$ Hz, 6H), 1.16-1.21 (q, $J=7.2$ Hz, 6H), 1.29-1.32 (d, $J=7.2$ Hz, 3H), 1.72-1.85 (m, 1H), 4.0-4.1 (m, 1H), 5.86-5.92 (d, 1H, $J=10\text{Hz}$), 6.26-6.28 (s, 1H), 7.36-7.41 (d(t), 1H), 7.56-7.66 (m, 2H), 8.04-8.07 (d, $J=7.2$ Hz, 1H).

Mass Spectral data: m/e (relative intensity): 285 (M^+ , 70), 257 (7.4), 242 (43.5), 215 (409.4), 214 (100), 200 (35), 199 (90), 186 (28.2), 172 (40), 171 (35.3), 143 (35), 128 (87.5), 115 (26), 102 (11.8), 91 (7), 71 (13) 55 (13), 43 (84) .

(S)-1-Phenylethylamide of 2,2-dimethyl-1,2-dihydronaphthalenone-4-carboxylic acid (2g)

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 1.3-1.34 (d, 6H, $J = 2$ Hz), 1.61-1.66 (d, $J = 7.2$ Hz, 3H), 5.3-5.4 (q, $J = 10$ Hz, 1H), 6.16-6.25 (d, $J = 10$ Hz, 1H, -NH), 6.3-6.35 (s, 1H), 7.3-7.45 (m, 6H), 7.6-7.67 (m, 2H), 8.07-8.17 (d, $J = 8.8$ Hz, 1H).

$^{13}\text{C-NMR}$: 22 (2C), 26, 45, 49, 126, 126.5(2C), 127.5, 127.7, 128.6, 128.7, 129 (2C), 131.6, 134.6, 134.8, 140.5, 142.7, 168, 203.

Mass Spectral data: m/e (relative intensity): 319 (M^+ , 33), 276 (10), 215 (23), 207 (10), 187 (44), 172 (23), 143 (20), 128 (44), 105 (100), 77 (28), 51 (10), 42 (13).

(R)-Cyclohexylethylamide of 2,2-dimethyl-1, 2-dihydronaphthalenone-4-carboxylic acid (2i)

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 1.34-1.4 (m, 8H), 1.16-1.21 (q, $J=7.2$ Hz, 6H), 1.59-1.32 (m, 1H), 1.92-1.95 (m, 1H), 4.0-4.1 (m, 1H), 5.86-5.92 (d, 1H), 6.26-6.28 (s, 1H), 7.36-7.41 (d(t), 1H), 7.56-7.66 (m, 2H), 8.04-8.07 (d, $J=7.2$ Hz, 1H).

Mass Spectral data: m/e (relative intensity): 325 (M^+ 73), 297 (6), 282 (1.5), 242 (45.5), 215 (67), 214 (77), 199 (100), 187 (12), 172 (59), 143 (38), 128 (88), 115 (26), 102 (11), 83 (10), 69 (23), 55 (50), 41 (44).

S(-) N-methyl -1-phenyl ethylamide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2j)

^1H NMR (CDCl_3 , 400MHz): δ 1.2-1.6 (d, $J=7.2$ Hz, 9H), 2.8 & 2.6 (s, 3H), 5.08-5.18 (q, $J=7.2$ Hz, 1H), 6.05-6.25 (s, 1H), 7.10-7.64 (m, 8H), 8.07-8.10 (m, 1H).

Mass Spectral data: m/e (relative intensity): 333 (M^+ , 39), 304 (3), 290 (7), 229 (21), 200 (35), 172 (35), 143 (18), 128 (32), 105 (100), 77 (20).

Alanine methyl ester amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2m)

Mass Spectral data: m/e (relative intensity): 301 (M^+ , 67), 269 (33), 241 (89), 214 (65), 199 (50), 186 (54), 172 (66), 143 (47), 128 (100), 115 (43), 102 (27), 69 (5), 55 (5).

L-valine methyl ester amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2n)

^1H NMR (CDCl_3 , 400MHz): δ 0.95-0.97 (d, $J=7.2$ Hz, 3H), 1.02-1.04 (d, $J=7.2$ Hz, 3H), 1.32 (s, 3H), 1.33 (s, 3H), 2.25-2.30 (m, 1H), 3.78 (s, 3H), 4.74-4.78 (dd, $J=14$ Hz, 1H), 6.34-6.36 (d, $J=8$ Hz, 1H), 6.39 (s, 1H), 7.38-7.42 (m, 1H), 7.57-7.66 (m, 2H), 8.07-8.09 (dd, $J=14$ Hz, 1H).

Mass Spectral data: m/e (relative intensity): 329 (M^+ , 30), 214 (25), 199 (30), 172 (25), 143 (40), 128 (100), 115 (40), 101 (20), 69 (45), 55 (80).

L-leusine methyl ester amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2o)

^1H NMR (CDCl_3 , 400MHz): δ 0.964-0.971 (d, 3H, $J=6.0$ Hz), 0.998-1.013 (d, 3H, $J=6.0$ Hz), 1.314 (s, 3H), 1.319 (s, 3H), 1.61-1.68 (m, 3H), 3.77 (s, 3H), 4.78-4.82 (dt, 1H, $J=8.4$ Hz), 6.249-6.270 (d, 1H, $J=8.4$ Hz), 6.39 (s, 1H), 7.37-7.42 (m, 1H), 7.57-7.66 (m, 2H), 8.05-8.07 (dd, 1H).

D-phenyl glycine methyl ester amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2p)

^1H NMR (CDCl_3 , 400MHz): δ 1.302 (s, 3H), 1.307 (s, 3H), 3.77 (s, 3H), 5.75-5.73 (d, 1H, $J=7.2$ Hz), 6.41 (s, 1H), 6.39 (s, 1H), 6.87-6.85 (d, 1H, $J=7.2$ Hz), 7.34-7.44 (m, 6H), 7.54-7.64 (m, 2H), 8.05-8.07 (dd, $J=14$ Hz, 1H).

Mass Spectral data: m/e (relative intensity): 363 (M^+ , 45), 331 (7), 304 (25), 276 (43), 214 (32), 199 (20), 186 (18), 172 (100), 157 (16), 143 (36), 128 (65), 106 (30), 91 (21), 77 (27).

L-phenyl alanine methyl ester amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2q)

^1H NMR (CDCl_3 , 400MHz): δ 1.24 (s, 3H), 1.26 (s, 3H), 3.10-3.35 (ddd, 2H), 3.79 (s, 3H), 5.05-5.10 (m, 1H), 6.20 (s, 1H), 6.32-6.34 (d, $J=7.2$ Hz, 1H), 7.13-7.54 (m, 8H), 8.02-8.04 (dd, $J=14$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3): δ 202.2, 172.2, 167.7, 141.5, 135.9, 134.6, 134.5, 129.5, 128.9, 128.6, 127.8, 127.5, 126.2, 60.6, 53.3, 52.8, 44.8, 38, 25.7 (d).

Mass Spectral data: m/e (relative intensity): 377 (M^+ , 64), 345 (5), 317 (22), 286 (43), 258 (50), 226 (32), 214 (25), 198 (55), 172 (55), 143 (39), 128 (100), 104 (35), 91 (50), 65 (15).

(-)- Norephedrine amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2s)

^1H NMR (CDCl_3 , 400MHz): δ 1.053-1.07 (d, 3H, $J=6.8$ Hz), 1.205 (s, 3H), 1.209 (s, 3H), 4.39-4.44 (m, 1H), 4.86-4.87 (d, $J=7.2$ Hz, 1H), 6.116-6.137 (d, $J=7.2$ Hz, 1H), 6.19 (s, 1H), 7.26-7.34 (m, 6H), 7.48-7.54 (m, 2H), 7.967-7.988 (dd, $J=13$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3): δ 202.4, 168.7, 140.9, 134.7, 134.6, 131.5, 128.8, 128.5, 128, 127.8, 126.5, 126.2 60.6, 51.3, 44.8, 25.7 (d) 14.9.

(-) Pseudoephedrine amide of 3,4-dihydro-3,3-dimethyl-4-oxonaphthalene-1-carboxylic acid (2t)

¹H NMR (CDCl₃, 400MHz): δ 1.22 (s, 3H), 1.23 (m, 6H), 2.77 (s, 3H), 3.77 (s, 3H), 4.00-4.07 (m, 1H), 4.44-4.54 (m, 1H), 6.19 (s, 1H), 7.10-7.42 (m, 8H), 8.05-8.07 (dd, J=14 Hz, 1H).

(S)-(methoxy-2-propyl)amide of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid (4a)

¹H-NMR (CDCl₃, 400MHz): δ 7-7.23 (s,1H), 6.4-6.6 (s, 1H), 5.6-5.8(d, J=8 Hz, 1H), 3.8-4.1(m, 1H), 3.5-3.7 (d, J=7.2 Hz, 2H), 3.1-3.3 (d, J=7.2 Hz, 3H), 1.83-1.90 (s, 3H), 1.3-1.43 (s, 6H), 1.1-1.23 (s, 3H).

Mass Spectral data: m/e (relative intensity): 251 (36 M⁺), 236 (7), 219 (26), 204 (17), 191 (6), 178 (100), 163 (94), 150 (13.5), 135 (97), 119 (13), 107 (63), 91 (51.5), 65 (19), 45 (31), 41 (26).

(S)-(+)-(3-methyl-2-butyl)amide of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid (4e)

¹H-NMR (CDCl₃, 400MHz): δ 7-7.23 (s,1H), 6.4-6.6 (s, 1H), 5.6-5.8(d, J=7.2 Hz, 1H), 3.8-4.0(m,1H), 1.83-1.90 (s, 3H), 1.6-1.8 (m,1H), 1.03-1.23 (s,6H), 0.9-1.0 (d, J=7.2 Hz 3H), 0.7-1.0 (d, 6H).

¹³C-NMR (CDCl₃): 204.8, 165.8, 145.5, 136, 133.7, 128.2, 50.7, 46.3, 33.3, 25.7, 18.8, 17.7, 15.8.

Mass Spectral data: m/e (relative intensity): 249(28 M⁺), 234 (5.5), 221 (10), 206 (13), 178 (100), 163 (65), 136 (22), 135 (57), 107 (41), 91 (31.5), 77 (9), 65 (10), 43 (26), 41 (15).

(S)-(methoxy-2-propyl)amide of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid (4f)

¹H-NMR (CDCl₃, 400MHz): δ 7-7.23 (s,1H), 6.4-6.6 (s, 1H), 5.6-5.8(d,1H, J=7.6 Hz), 3.8-4.1(m,1H), 3.5-3.7 (d, J=7.2 Hz, 2H), 3.1-3.3 (d, J=7.2 Hz, 3H), 1.83-1.90 (s, 3H), 1.3-1.43 (s,6H), 1.1-1.23 (s,3H).

Mass Spectral data: m/e (relative intensity): 251 (36 M⁺), 236 (7), 219 (26), 204 (17), 191 (6), 178 (100), 163 (94), 150 (13.5), 135 (97), 119 (13), 107 (63), 91 (51.5), 65 (19), 45 (31), 41 (26).

(S)-(-)-1-Phenylethyl amide of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid (4g)

¹H-NMR (CDCl₃, 400MHz): δ 7.28-7.42 (m, 5H), 6.6-6.8 (s, 1H), 6-6.18 (s, 1H), 5.2-5.4 (q, J=7.6 Hz, 1H), 1.83-1.95 (s, 3H), 1.45-1.65 (d, J=7.2 Hz, 3H), 1.17-1.28 (s, 6H).

Mass Spectral data: m/e (relative intensity): 283 (21 M⁺), 268 (95), 255 (7), 240 (6), 214 (2), 179 (12), 164 (9), 151 (44), 136 (16), 105 (100), 91 (915), 77 (16), 51 (5), 41 (5).

S-(-)-1-Phenylpropyl amide of 2,6,6-trimethyl-cyclohexa-2,4-diene-1-one-4-carboxylic acid (4h)

¹H-NMR (CDCl₃, 400MHz): δ 7.25-7.4 (m, 5H), 6.61-6.82 (s, 1H), 6-6.2 (s, 1H), 5.2-5.4 (q, J=7.2 Hz, 1H), 1.83-1.95 (s, 3H), 1.66-1.8 (m, 2H), 1.45-1.65 (d, 3H), 1.17-1.28 (s, 6H).

Mass Spectral data: m/e (relative intensity): 297 (53 M⁺), 282 (3), 268 (11), 240 (37.5), 228 (3), 212 (1.5), 179 (12.5), 163 (922), 151 (36), 135 (26.5), 107 (28), 91 (100), 77 (12.5), 51 (6), 41 (17).

S(-) -N-methyl phenyl ethylamide of amide of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid (4j)

¹H NMR (CDCl₃, 400MHz): δ 1.21 (s, 6H), 1.566-1.588 (d, J=7.6 Hz, 3H), 1.90-1.91 (d, J=7.2 Hz 3H), 2.7 (s, 3H), 6.24-6.25 (m, 1H), 6.92-6.93 (m, 1H), 7.28-7.38 (m, 6H).

L-valine methyl ester amide of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid (4n)

¹H NMR (CDCl₃, 400MHz): δ 0.93-0.97 (dd, 6H), 1.23-1.24 (d, J=7.2 Hz, 6H), 1.917 (s, 3H), 2.18-2.23 (m, 1H), 3.76 (s, 3H), 4.63-4.67 (dd, 1H), 6.38-6.40 (d, J=7.2 Hz, 1H), 6.70 (m, 1H), 7.22 (m, 1H).

L-leusine methyl ester amide of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid (4o)

¹H NMR (CDCl₃, 400MHz): δ 0.91-0.94 (dd, 6H), 1.205-1.209 (d, J=7.2 Hz, 6H) 1.87-1.88 (d, J=7.2 Hz, 3H), 1.917 (s, 3H), 2.18-2.23 (m, 1H), 3.76 (s, 3H), 4.68-4.70 (dd, J=14 Hz, 1H), 6.43-6.45 (d, J=7.6 Hz, 1H), 6.701-6.708 (m, 1H), 7.20-7.22 (m, 1H).

Mass Spectral data: m/e (relative intensity): 307 (M⁺, 100), 292 (10), 279 (16), 264 (5), 251 (32), 232 (12), 219 (45), 204 (45), 191 (32), 179 (35), 162 (90), 150 (15), 134 (80), 119 (15), 107 (65), 91 (60), 65 (15), 55 (15).

L-Phenyl alanine methyl ester amide of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid (4q)

¹H NMR (CDCl₃, 400MHz): δ 1.21 (s, 6H), 1.90-1.91 (d, 3H), 3.0-3.2 (m, 2H), 3.70 (s, 3H), 4.80-5.00 (m, 1H), 6.10-6.15 (d, J=7.2 Hz, 1H), 6.92-6.93 (m, 1H), 7.28-7.38 (m, 6H).

Mass Spectral data: m/e (relative intensity): 340 (M⁺, 100), 325 (7), 312 (12), 280 (24), 252 (7), 222 (48), 190 (10), 179 (29), 162 (68), 151 (20), 135 (51), 107 (52), 91 (72), 65 (15), 77 (12).

N-methyl phenyl alanine methyl ester amide of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid (4r)

¹H NMR (CDCl₃, 400MHz): δ 1.05-1.20 (d, J=7.2 Hz, 6H, 2 signals), 1.70-1.85 (s, 3H, 2 signals), 2.8-3.0 (s, 3H, 2 signals), 3.00-3.20 (m, 2H), 3.80 (s, 3H, 2 signals), 4.73 & 5.30 (m, 1H), 5.60 & 5.80 (s, 1H, 2 signals), 6.15 & 6.45 (s, 1H, 2 signals), 7.00-7.38 (m, 6H).

Mass Spectral data: m/e (relative intensity): 355 (M⁺, 50), 340 (5), 312 (5), 296 (12), 264 (6), 236 (18), 193 (10), 163 (100), 135 (86), 135 (51), 107 (90), 91 (99), 65 (25).

(-) Norephedrine amide of 3,3,5-Trimethyl-4-oxo-cyclohexa-1,5-diene carboxylic acid (4s)

¹H NMR (CDCl₃, 400MHz): δ 1.31-1.32 (d, J=7.6 Hz, 9H), 2.084-2.089 (d, J=7.2 Hz, 3H), 4.55-4.60 (m, 1H), 5.09-5.10 (d, J=7.6 Hz, 1H), 6.23-6.25 (d, 1H), 6.77-6.78 (m, 1H), 7.4-7.52 (m, 6H).

Amide derived from N-Pyridone derivative and S-(+)-2-Methyl-3-butyl amine (7e)

¹H NMR (CDCl₃, 400 MHz) δ 0.7-0.8 (m, 6H), 0.9-1.0 (d, 3H, J=7 Hz), 1.5-1.6 (m, 1H), 4.4-4.6 (dd, 2H, J=14 Hz), 3.7-3.8 (m, 1H), 6.5-6.6 (m, 1H), 6.15-6.2 (m, 1H), 6.9-7.0 (d, 1H, J=8 Hz), 7.3-7.45 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz) δ 17.5, 18.4, 18.6, 33.0, 50.5, 54.1, 107.1, 120.7, 138.5, 140.8, 163.0, 166.7.

Amide derived from N-Pyridone derivative and S-(-)-1-phenyl ethyl amine (7g)

¹H NMR (CDCl₃, 400 MHz) δ 1.34-1.36 (d, 3H, J=7 Hz), 4.3-4.7 (dd, 2H, J=14 Hz), 4.95-5.1 (q, 1H, J=7 Hz), 6.16-6.20 (m, 1H), 6.48-6.50 (m, 1H), 7.1-7.35 (m, 7H), 8.09-8.10 (d, J=7.6 Hz).

¹³C NMR (CDCl₃, 100 MHz) δ 22.4, 49.4, 54.0, 107.1, 120.8, 126.1, 127.4, 128.8, 138.5, 140.8, 143.2, 163.1, 166.4.

GC-MS (EI) spectral data m/e (relative intensity) 256 (M⁺, 20), 161 (80), 136 (62), 109 (100), 96 (62), 81 (50), 53 (26).

Amide derived from N-Pyridone derivative and S-(-)-Cyclohexylethylamine (7i)

¹H NMR (CDCl₃, 400 MHz) δ 0.8-1.7 (m, 11H), 0.96-0.99 (d, 3H, J=7 Hz), 3.65-3.8 (m, 1H), 4.48-4.6 (2H, dd, J=14 Hz), 6.3-6.4 (m, 1H), 6.5-6.6 (m, 1H), 7.0-7.1 (d, 1H, J=8Hz), 7.3-7.5 (2H, m).

^{13}C NMR (CDCl_3 , 100 MHz) δ 17.8, 26.5, 28.8, 29.2, 43.0, 49.6, 53.9, 107, 120.7, 138.6, 140.7, 163, 166.6.

Amide derived from N-Pyridone derivative and S-N-Methyl-1-phenyl ethyl amine (7j)

Due to the restriction rotation of N-Me-CO group, the CH_3 , N- CH_3 and the CH protons appeared as set of two signals in the ^1H NMR spectrum.

^1H NMR (CDCl_3 , 400 MHz) δ 1.47-1.49;1.61-1.65 (d, 3H), 2.7-2.8 (s, 3H), 4.7-5.0 (dd, $J=14$ Hz, 2H), 5.95-6.0;5.35-5.38 (q, $J=7.2$ Hz, 1H) , 6.19-6.21 (m, 1H), 6.45-6.6 (m, 1H), 7.2-7.5 (m, 5H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 15.7, 29.2, 49.8, 51.5, 106.15, 120.8, 126.7, 127.7, 128.7, 138.9, 140.0, 140.3, 163.1, 166.4.

GC-MS (EI) spectral data m/e (relative intensity) 222 (M^+ , 5), 179 (15), 136 (100), 108 (30), 80 (25), 53 (15).

Amide derived from N-Pyridone derivative and D-(+)-amphetamine.sulfate salt (7k)

^1H NMR (CDCl_3 , 400 MHz) δ 1.07-1.10 (d, 3H, $J=6.4$ Hz), 2.6-2.85 (m, 2H), 4.1-4.2 (m, 1H), 4.3-4.6 (dd, 2H, $J=14$ Hz), 6.18-6.24 (m, 1H), 6.58-6.60 (m, 1H), 6.9-7.0 (d, 1H, $J=6.8$ Hz), 7.0-7.4 (m, 7H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 20.2, 42.6, 46.8, 54.1, 107.1, 120.9, 126.4, 128.4, 129.4, 138.1, 138.3, 140.7, 163.0, 166.6

GC-MS (EI) spectral data m/e (relative intensity) 270 (M^+ , 6), 179 (22), 136 (100), 108 (33), 80 (22), 53 (10)

Amide derived from N-Pyridone derivative and S-(+)-1-Methyl-3-phenyl propyl amine (7l)

^1H NMR (CDCl_3 , 400 MHz) δ 1.0-1.1 (d, 3H, $J=6$ Hz), 1.6-1.8 (m, 2H), 2.4-2.6 (m, 2H), 3.8-3.9 (m, 1H), 4.4-4.6 (dd, 2H, $J=14$ Hz), 6.1-6.2 (m, 1H), 6.5-6.6 (m, 1H), 6.9-7.0 (d, 1H, $J=8$ Hz), 7.0-7.4 (m, 7H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 21, 32.5, 38.6, 45.6, 54.2, 107.2, 120.8, 126.0, 128.6, 138.5, 140.8, 141.8, 163.1, 166.7.

GC-MS (EI) spectral data m/e (relative intensity) 284 (M^+ , 20), 180 (20), 136 (100), 109 (36), 96 (90), 80 (30), 53 (16).

Amide derived from N-Pyridone derivative and L-Alanine methyl ester.HCl (7m)

^1H NMR (CDCl_3 , 400 MHz) δ 1.34-1.36 (d, 3H, $J=7.2$ Hz), 3.65-3.7 (s, 3H), 4.44-4.5 (q, 1H, $J=7.6$ Hz), 4.53-4.66 (dd, 2H, $J=14.4$ Hz), 6.21-6.24 (m, 1H), 6.57-6.60 (m, 1H), 7.36-7.39 (m, 2H), 7.54-7.55 (d, 1H, $J=6.8$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 18.0, 48.5., 52.6, 53.3, 107.1, 120.9, 138.5, 140.8, 163.0, 167, 173.1.

Amide derived from N-Pyridone derivative and L-Valine methyl ester.HCl (7n)

^1H NMR (CDCl_3 , 400 MHz) δ 0.81-0.84 (m, 6H), 2.0-2.2 (m, 1H), 3.63 (s, 3H), 4.38-4.42 (m, 1H), 4.45-4.8 (dd, 2H, $J=14$ Hz), 6.6-6.65 (m, 1H), 7.25-7.4 (m, 2H), 7.5-7.7 (d, 1H, $J=6.8$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 17.8, 19.1, 31.0, 52.3, 53.4, 57.7, 107.0, 120.8, 138.6, 140.8, 163.0, 167.5, 172.0.

Amide derived from N-Pyridone derivative and L-Leucine methyl ester.HCl (7o)

^1H NMR (CDCl_3 , 400 MHz) δ 0.8-0.9 (m, 6H), 1.5-1.7 (m, 3H), 3.62-3.65 (s, 3H), 4.44-4.48 (m, 1H), 4.55-4.65 (dd, 2H, $J=14$ Hz), 6.19-6.25 (m, 1H), 6.5-6.6 (m, 1H), 7.3-7.4 (m, 2H), 7.5-7.56 (d, 1H, $J=8$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 21.9, 22.9, 24.9, 41.1, 51.2, 52.4, 53.1, 107.0, 120.7, 138.6, 140.8, 163.0, 167.3, 173.1.

GC-MS (EI) spectral data m/e (relative intensity) 224 (M^+ , 22), 136 (100), 109 (36), 80 (18), 53 (13).

Amide derived from N-Pyridone derivative and S-(+)-2-Phenyl glycine methyl ester .HCl (7p)

^1H NMR (CDCl_3 , 400 MHz) δ 3.63 (s, 3H), 4.56-4.66 (dd, 2H, $J=14.4$ Hz), 5.45-5.48 (d, 1H, $J=7.2$ Hz), 6.18-6.22 (m, 1H), 6.57-6.59 (m, 1H), 7.1-7.45 (m, 7H), 7.45-7.5 (d, 1H, $J=6.8$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 53.0, 53.1, 57.0, 107, 120.8, 127.5, 128.7, 129.1, 135.9, 138.6, 140.7, 163, 166.9, 170.9.

Amide derived from N-Pyridone derivative and L-Phenyl alanine methyl ester.HCl (7q)

^1H NMR (CDCl_3 , 400 MHz) δ 2.95-3.15 (m, 2H), 3.6 (s, 3H), 4.63-4.64 (dd, 2H, $J=14.4$ Hz), 4.73-4.78 (m, 1H), 6.18-6.22 (m, 1H), 6.57-6.59 (m, 1H), 7.1-7.45 (m, 7H), 7.45-7.5 (d, 1H, $J=6.8$ Hz).

^{13}C NMR (CDCl_3 , 100 MHz) δ 37.9, 52.5, 53.2, 53.7, 106.5, 120.9, 127.1, 128.6, 129.0, 136.0, 138.4, 140.6, 162.5, 167.1, 171.6.

Characterization of photoproducts

Photoproduct of 1a

^1H -NMR (CDCl_3 , 400MHz): δ 7.8-7.9 (d, $J = 7.6$ Hz, 1H), 7.5-7.6 (d, $J = 7.6$ Hz, 1H), 7.5-7.6 (t, $J = 7.6$ Hz, 1H), 7.2-7.4 (d, $J = 7.6$ Hz, 1H), 2.2 (s, 1H), 2.105(s, 1H), 1.24 (s, 6H).

Mass Spectral data for the photoproducts: m/e (relative intensity): 172 (M^+ 86), 157 (54), 143 (10), 141 (6), 129 (100), 128 (66), 115 (20), 102 (20), 91 (3), 89 (7), 77 (20), 63 (17.5), 51 (17.5), 39 (18).

Photoproduct of 1b

^1H -NMR (CDCl_3 , 400MHz): δ 7.90-7.915 (d, $J = 7.6$ Hz, 1H), 7.59-7.63 (d, $J = 7.6$ Hz, 1H), 7.53-7.58 (t, $J = 7.6$ Hz, 1H), 7.23-7.4 (d, $J = 7.6$ Hz, 1H), 3.825 (s,3H), 2.805(s, 1H), 1.54 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 200.3, 170, 148, 134, 128, 127.5, 123.8, 53.4, 51.7, 46, 45.7, 24, 17.8.

Mass Spectral data for the photoproducts(enantiomers were not resolved in the GC): m/e (relative intensity): 230 (M^+ , 60), 202 (25), 198 (30), 188 (20), 187 (100), 171 (70), 170 (33), 169 (38), 158 (18), 143 (30), 141 (28), 128 (63), 115 (60), 102 (27),.

Photoproduct 3a

^1H -NMR (CDCl_3 , 400MHz): δ 0.8-2.04 (m, 14H), 2.2-2.45(2 signals, m, 1H, methane CH), 2.78-2.8 (2 sets of signals, s, 1H), 4.0-4.25 (2 sets of signals, m, 2H), 7.15-7.2 (2

signals, m, 1H), 7.57-7.58 (2 signals, t, J = 2 Hz, 1H), 7.88- 7.92 (2 signals, m, 1H), 7.98-8.05 (2 signals, d, 7.6Hz, 1H).

Mass Spectral data for both the diastereomeric photoproducts of (S)- (-)-2-methyl butyl ester have similar fragmentation patterns:

Mass Spectral data: m/e (relative intensity): 286 (M^+ 8.8), 216 (100), 199 (20), 198 (42.5), 188 (33), 171 (57.5), 170 (30), 143 (21.2), 128 (47.5), 115 (22.5), 91 (5), 77 (8.8), 55 (11.2), 43 (65).

Photoproduct 3b

Mass spectra for photoproducts of (-)-menthyl ester: (Both diastereomers have similar fragmentation patterns):

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 0.8-2.14 (m, 14H), 2.758 and 2.777 (2 signals, s, 1H, cyclopropyl), 4.8-4.9 (2 sets of signals, m, 1H), 7.31-7.37 (2 signals, t, J = 7.2 Hz, 2H), 7.5- 7.68 (2 signals, m, 1 H), 7.84-7.92 (2 signals, d, J=7.6Hz, 1H).

Mass Spectral data: m/e (relative intensity): 354 (M^+ ,1), 217 (17), 216 (100), 198 (17), 188 (13), 172 (22), 171 (19), 143 (10), 128 (23), 115 (3), 95 (2), 83 (25), 69 (10), 55 (17), 41 (10).

Mass spectra for photoproducts of (+)-menthyl ester: (Both diastereomers have similar patterns):

Mass Spectral data: m/e (relative intensity): 354 (M^+ ,1), 217 (15), 216 (100), 198 (19), 188 (12), 171 (25), 143 (12), 128 (23), 115 (2), 95 (2), 83 (24), 69 (13), 55 (17), 41 (10).

Photoproduct 3c

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 0.7-0.8 (2 signals, s, 3H), 0.83-0.88 (d, J = 5.2Hz, 3H), 1.0-1.14 (m, 6H), 1.18-1.24 (2 signals, s, 2H), 1.39-1.43 (d, J= 4 Hz, 3H), 1.43-1.84 (m, 5H), 2.75-2.81 (2 signals, s, 1H), 4.46-4.54 (2 signals, s, 1H), 7.31-7.37 (t, J = 7.2 Hz, 1H), 7.5-7.58 (t, J = 7.6 Hz, 1H), 7.58- 7.64 (d, J = 7.6 Hz, 1 H), 7.86-7.96 (m, 1H).

^{13}C NMR (CDCl_3 , 100MHz): δ : 198, 169.5, 159.2, 158.8, 138, 135, 134.2, 128.6, 127.9, 124, 93, 92, 51.4, 51.2, 48.6, 48.2, 46, 45.8, 45.4, 42.6, 42.2, 39.2, 30, 27.8, 27.6, 27.3, 26.4, 24.5, 22, 21.8, 21.5, 21, 17.

Mass Spectral data: m/e (relative intensity): 352 (M^+ , 16), 216 (22), 199 (24), 172 (45), 143 (6), 137 (40), 128 (10), 115 (5), 95 (10), 81 (100), 69 (10), 55 (5), 41 (10).

Photoproduct 3d

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 0.75-1.85 (m, 22H), 2.49-2.51 (2 signals, d, 1H), 4.22-4.54 (2 signals, m, 1H), 5.65-5.87 (2 signals each d, $J = 6$ Hz, 1H), 7.31-7.37 (2 sets of signals each t, $J = 7.6$ Hz, 1H), 7.5-7.58 (t, $J = 7.6$ Hz, 1H), 7.7- 7.81 (2 signals each d, $J = 7.6$ Hz, 1 H), 8.05- 8.10 (2 signals, s, 1H).

Mass Spectra of photoproducts of bornyl amide (from solution irradiation): both diastereomers have same fragmentation pattern

Mass Spectral data: m/e (relative intensity): 351 (M^+ 26.8), 323 (6), 215 (27), 198 (8), 188 (42), 187 (23), 172 (100), 143 (13), 128 (37), 115 (8), 95 (27), 81 (46), 67 (17), 55 (15), 44 (20), 41 (40).

Photoproduct 3e

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 0.7-2.2 (m, 17H), 2.45-2.5 (2 signals, s, 1H), 3.7-4.0 (2 signals, s, 1H), 7.32-7.37 (t, $J = 7.2$ Hz, 1H), 7.5-7.58 (t, $J = 7.6$ Hz, 1H), 7.6- 7.64 (d, $J = 7.6$ Hz, 1 H), 7.72-7.77 (t, 1H).

Mass Spectra of photoproducts of (S)-(+)-(3-methyl-2-butyl)amide (from solution irradiation): both diastereomers have same fragmentation pattern.

Mass Spectral data: m/e (relative intensity): 285 (M^+ , 41), 257 (7.4), 242 (23.5), 215 (29.4), 214 (100), 199 (26), 186 (28.2), 172 (40), 171 (35.3), 143 (35), 128 (67.5), 115 (26), 102 (11.8), 91 (7), 71 (13) 55 (13), 44 (84) .

Photoproduct 3j

Mass Spectral data: m/e (relative intensity): 333 (M^+ , 7), 172 (82), 134 (7), 105 (100), 77 (10).

Photoproduct 3m

^1H NMR (CDCl_3 , 400MHz): δ 1.14-1.16 & 1.27-1.29 (d, $J=7$ Hz, 3H), 1.70 (s, 6H), 2.1 & 2.2 (s, 1H), 3.58 & 3.70 (s, 3H), 4.4-4.5 (m, 1H), 5.54 & 5.60 (d, $J=7.5$ Hz, 1H), 7.40-7.46 (m, 2H), 7.54-7.60 (m, 1H), 8.14-8.18 (m, 1H).

Mass Spectral data: m/e (relative intensity): 301 (M^+ , 14), 188 (81), 172 (100), 157 (22), 128 (32), 115 (30), 102 (20), 55 (28).

Photoproduct 3n

^1H NMR (CDCl_3 , 400MHz): δ 0.80-0.93 (m, 9H), 1.30-1.32 (d, 3H), 2.10-2.20 (m, 1H), 2.54 & 2.57 (s, 1H), 3.66 & 3.71 (s, 3H), 4.57-4.62 (dd, 1H), 6.24-6.26 & 6.34-6.36 (d, 1H), 7.26-7.32 (m, 1H), 7.46-7.50 (m, 1H), 7.55-7.58 (m, 1H), 7.65-7.73 (d, 1H).

Photoproduct 3o

^1H NMR (CDCl_3 , 400MHz): δ 0.80-0.93 (m, 9H), 1.30-1.32 (d, 3H), 1.50-1.60 (m, 1H), 2.54 & 2.57 (s, 1H), 3.66 & 3.71 (s, 3H), 4.60-4.64 (m, 1H), 6.26-6.28 & 6.36-6.38 (d, $J=7.5$ Hz, 1H), 7.26-7.32 (m, 1H), 7.46-7.50 (m, 1H), 7.55-7.58 (m, 1H), 7.65-7.73 (d, $J=7.8$ Hz, 1H).

Mass Spectral data: m/e (relative intensity): 343 (M^+ , 2), 172 (100), 157 (19), 128 (15).

Photoproduct 3p

^1H NMR (CDCl_3 , 400MHz): δ 0.85 (s, 3H), 1.24 (s, 3H), 2.58 & 2.62 (s, 1H), 3.70 & 3.73 (s, 3H), 5.61-5.63 (d, $J=7$ Hz, 1H), 6.72-6.74 & 6.87-6.89 (d, $J=6.8$ Hz, 1H), 7.26-7.36 (m, 5H), 7.48-7.62 (m, 3H), 7.68-7.74 (m, 1H).

Mass Spectral data: m/e (relative intensity): 363 (M^+ , 10), 304 (3), 172 (100), 157 (9), 128 (18), 106 (7), 77 (5).

Photoproduct 3q

^1H NMR (CDCl_3 , 400MHz): δ 1.20 (s, 3H), 1.61 & 1.67 (s, 3H), 2.82 & 2.84 (s, 1H), 2.71-2.77 & 3.10-3.15 (m, 1H), 3.71 & 3.56 (s, 3H), 4.65-4.79 (m, 1H), 6.20 & 6.30 (d, 1H), 7.10-7.30 (m, 3H), 7.35-7.58 (m, 6H).

Mass Spectral data: m/e (relative intensity): 377 (M^+ , 8), 215 (4), 172 (100), 157 (10), 128 (20), 91 (10).

Photoproduct 3s

^1H NMR (CDCl_3 , 400MHz): δ 0.84-0.85 (d, 3H), 1.025-1.046 & 1.128-1.145 (d, 3H), 1.278-1.291 (m, 3H), 2.489-2.492 (s, 2 signals, 1H), 4.32-4.40 (m, 1H), 4.84-4.87 (dd, $J=10$ Hz, 1H), 6.10 & 6.18 (d, 1H), 7.20-7.40 (m, 5H), 7.46-7.60 (m, 3H), 7.70-7.80 (m, 1H).

Photoproduct of 1c

^1H -NMR (CDCl_3 , 400MHz): δ 5.2 (s, 1H), 3.7 (s, 3H), 2.3 (s, 3H), 1.64 (s, 1H), 1.17-1.25 (s, 6H).

Mass Spectral data: m/e (relative intensity): 194 (M^+ , 35), 179 (12), 162 (18), 151 (68), 135 (48), 134 (75), 124 (27), 107 (100), 103 (18).

Photoproduct of 1d

IR (neat): 1692 (carbonyl), 1383, 1453, 2935 and 2982cm^{-1} (CH).

^1H - NMR (400MHz, CDCl_3): δ 5.45 (q, 1H, $J = 1.5$ Hz), 1.96 (d, 3H, $J = 1.5$ Hz), 1.51 (s, 3H), 1.49(s, 1H) 1.24 (s, 3H), 1.14 (s, 3H).

UV(λ_{max} (MeOH)) : 228, 260 and 320nm (ϵ 5950, 3080, 500).

Mass Spectral data of the photoproducts in an achiral GC (enantiomers are not resolved):

Mass Spectral data: m/e (relative intensity): 150 (M^+ , 53), 135 (100), 107 (4), 105 (10), 91 (18), 79 (10), 77 (10), 65 (7.5), 53 (8.6), 41(10), 39 (15).

Photoproduct 5a

^1H -NMR (CDCl_3 , 400MHz): δ 0.8-2.04 (m, 14H), 2.2-2.45(2 signals, m, 1H), 2.78-2.8 (2 sets of signals, s, 1H), 4.0-4.25 (2 sets of signals, m, 2H), 7.15-7.2 (2 signals, m, 1H), 7.57-7.58 (2 signals, t, $J = 2$ Hz, 1H), 7.88- 7.92 (2 signals, m, 1H), 7.98-8.05 (2 signals, d, $J= 7.6\text{Hz}$, 1H).

Mass Spectral data for both the diastereomeric photoproducts of (S)- (-)-2-methyl butyl ester have similar fragmentation patterns:

Mass Spectral data: m/e (relative intensity): 286 (M^+ 8.8), 216 (100), 199 (20), 198 (42.5), 188 (33), 171 (57.5), 170 (30), 143 (21.2), 128 (47.5), 115 (22.5), 91 (5), 77 (8.8), 55 (11.2), 43 (65).

Photoproduct 5e

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 5.88-5.95 (2 signals, d, $J=2\text{Hz}$, 1H), 3.8-4.0 (2 sets of signals, m, 1H), 0.9-2.4 (20H).

Mass Spectral data: m/e (relative intensity): 249(M^+), 234 (5.5), 221 (13), 206 (15), 178 (95), 163 (63), 151 (20), 136 (32), 135 (67), 120 (13), 107 (100), 103 (17).

Photoproduct 5f

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 5.9-6 (2 signals, d, $J= 2.4\text{Hz}$, 1H), 4.05-4.25 (2 sets of signals, m, 1H), 3.4-3.5 (2 signals, d, 2H, $J=4\text{ Hz}$), 3.24-3.3 (2 signals, s, 3H), 2.0-2.04 (2signals,s, 3H) 0.9-1.4 (10H).

Mass Spectral data: m/e (relative intensity): 251 (M^+ 52), 236 (2), 219 (24), 204 (18), 179 (18), 178 (192), 163 (84), 150 (16.5), 135 (87), 119 (11), 107 (100), 103 (18.2).

Photoproduct 5g

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 7.2-7.42 (m, 5H), 5.9-6.1 (2 signals, s,1H), 5.0-5.2 (2 sets of signals, m,1H), 1.83-1.95 (2 signals, s, 3H), 1.45-1.65 (2 signals, d, 3.6 Hz, 3H), 1.17-1.28 (2 signalss, 6H).

Mass spectral data of the diastereomeric products (both diastereomers have same fragmentation pattern):

Mass Spectral data: m/e (relative intensity): 283 (M^+ 2), 136 (100), 105 (75), 77 (10), 65 (3.3), 41 (4.3).

Photoproduct 5h

$^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ 6.9-7.4 (2 sets of signals, m, 5H), 5.8-6.0 (2 signals, s,1H), 4.7-5.1 (2 sets of signals, m, 1H), 1.83-2.4 (2 signals, m, 5H), 0.8-1.35 (2 signals, m, 10H).

Photoproducts 5n

Mass Spectral data: m/e (relative intensity): 293 (M^+ , 7), 178 (5), 136 (100), 121 (6), 91 (5).

Photoproduct 5o

Mass Spectral data: m/e (relative intensity): 307 (M^+ , 5), 152 (5), 136 (100), 121 (5), 91 (5).

Photoproduct 5q

Mass Spectral data: m/e (relative intensity): 340 (M^+ , 5), 136 (100), 121 (8), 91 (15).

Photoproducts 5r

Mass Spectral data: m/e (relative intensity): 355 (M^+ , 15), 296 (5), 264 (5), 220 (100), 192 (82), 160 (96), 135 (50), 121 (24), 107 (22), 91 (72), 65 (15).

Photoproduct of 1e

^1H NMR (CDCl_3 , 400 MHz) δ 3.4 (s, 3H), 4.2-4.25 (m, 1H), 4.3 -4.35 (m, 1H), 6.55-6.7 (m, 2H).

Photoproduct of 1f

^1H NMR (CDCl_3 , 400 MHz) δ 1.13 (t, $J=7.6$ Hz, 3H), 3.13-3.3 (m, 2H), 4.11-4.13 (m, 1H), 4.32-4.34 (m, 1H), 6.6-6.65 (m, 2H).

Photoproduct of 1g

^1H NMR (CDCl_3 , 400 MHz) δ 0.77- 0.8 (t, $J=7.6$ Hz, 3H), 1.5-1.6 (m, 2H), 3.1-3.3 (m, 2H), 4.15-4.18 (m, 1H), 4.32-4.36 (m, 1H), 6.6-6.65 (m, 2H).

Photoproduct of 1h

^1H NMR (CDCl_3 , 400 MHz) δ 4.17-4.2 (m, 1H), 4.3-4.41 (m, 1H), 6.2 (m, 1H), 6.55 (m, 1H), 7.1-7.3 (m, 5H).

Photoproduct of 1i

¹H NMR (CDCl₃, 400 MHz) δ 2.94-2.97 (m, 2H), 3.95-4.15 (m, 1H), 4.3-4.45 (m, 1H), 6.15-6.2 (m, 1H), 6.6-6.7 (m, 1H), 7.0-7.2 (m, 5H).

Photoproduct of 1j

¹H NMR (CDCl₃, 400 MHz) δ 1.7-1.9 (m, 2H), 2.35-2.55 (m, 2H), 3.6-3.8 (m, 3H), 3.85-4.0 (m, 1H), 4.15-4.35 (m, 1H), 6.15-6.2 (m, 1H), 6.55-6.7 (m, 1H), 7.0-7.3 (m, 5H).

Photoproducts 7e

¹H NMR (CDCl₃, 400 MHz) δ 0.75-0.85 (m, 6H), 1.0-1.05 (m, 3H), 1.5-1.65 (m, 1H), 3.58-3.62 (m, 1H), 3.7-3.8 (m, 1H), 3.85-3.95 (m, 1H), 4.16-4.21 (m, 1H), 4.4-4.6 (m, 1H), 6.54-6.58 (m, 2H).

GC-MS (EI) spectral data m/e (relative intensity) 222 (M⁺, 0.02), 179 (15), 136 (100), 108 (30), 80 (25), 53 (15).

Photoproducts 7g

¹H NMR (CDCl₃, 400 MHz) δ 1.3-1.45 (m, 3H), 3.59-3.7 (m, 1H), 3.9-4.01 (m, 1H), 4.2-4.4 (m, 2H), 5.0-5.1 (m, 1H), 6.48-6.58 (m, 5H).

Photoproducts 7i

¹H NMR (CDCl₃, 400 MHz) δ 1.0-2.0 (m, 14H), 3.78-3.82 (m, 1H), 3.6-3.68 (m, 1H), 3.9-3.98 (m, 1H), 4.2-4.25 (m, 1H), 4.42-4.48 (m, 1H), 5.9-6.0 (m, 1H), 6.57-6.60 (m, 2H).

Photoproducts 7j

¹H NMR (CDCl₃, 400 MHz) δ 1.4-1.6 (two sets, m, 3H), 2.6-2.7 (two sets, s, 3H), 3.7-3.8 (m, 1H), 4.1-4.25 (m, 1H), 4.20-4.22 (m, 1H), 4.69-4.71 (m, 1H), 5.0-5.1;5.9-6.0 (m, 1H), 6.55-6.65 (m, 2H), 7.25-7.35 (m, 5H).

Photoproducts 7k

¹H NMR (CDCl₃, 400 MHz) δ 1.0-1.1 (m, 3H), 2.65-2.9 (m, 2H), 3.42-3.58 (m, 1H), 3.9-4.0 (m, 1H), 4.15-4.25 (m, 1H), 4.1-4.2 (m, 1H), 4.35-4.38 (m, 1H), 5.8-6.0 (m, 1H), 6.45-6.6 (m, 2H), 7.10-7.13 (m, 5H).

GC-MS (EI) spectral data m/e (relative intensity) 270 (M⁺, 0.02), 179 (20), 136 (100), 108 (25), 80 (18), 53 (10).

Photoproducts 7l

¹H NMR (CDCl₃, 400 MHz) δ 1.1-1.2 (m, 3H), 1.6-1.8 (m, 2H), 2.45-2.55 (m, 2H), 3.5 (m, 1H), 3.85-3.95 (m, 1H), 3.92-4.0 (m, 1H), 4.35-4.45 (m, 1H), 4.15-4.2 (m, 1H), 5.9-6.0 (m, 1H), 6.5-6.6 (m, 2H), 7.05-7.25 (m, 5H).

GC-MS (EI) spectral data m/e (relative intensity) 284 (M⁺, 20), 180 (20), 136 (100), 109 (36), 96 (85), 91 (36), 80 (30), 53 (16).

Photoproducts 7m

¹H NMR (CDCl₃, 400 MHz) δ 1.35 (d, 3H), 3.45-3.65 (m, 1H), 3.7 (s, 3H), 3.95-4.05 (m, 1H), 4.2-4.45 (m, 2H), 4.5-4.6 (m, 1H).

Photoproducts 7n

¹H NMR (CDCl₃, 400 MHz) δ 0.9-1.0 (m, 6H), 2.1-2.2 (m, 1H), 3.5-3.7 (m, 1H), 3.7 (s, 3H), 4.0-4.15 (m, 1H), 4.25-4.3 (m, 1H), 4.48-4.55 (m, 1H), 4.58-4.6 (m, 1H), 6.45-6.5 (d, 1H), 6.55-6.65 (m, 2H).

Photoproducts 7o

¹H NMR (CDCl₃, 400 MHz) δ 0.8-0.9 (m, 6H), 1.5-1.7 (m, 3H), 3.47-3.65 (m, 1H), 3.67-3.68 (s, 2H), 3.9-4.0 (m, 1H), 4.2-4.25 (m, 1H), 4.4-4.5 (m, 1H), 4.51-4.6 (m, 1H), 6.3-6.4 (m, 1H), 6.54-6.59 (m, 2H).

Photoproducts 7p

¹H NMR (CDCl₃, 400 MHz) δ 3.7 (s, 3H), 3.6-3.7 (m, 1H), 4.0-4.1 (m, 1H), 4.25-4.5 (m, 2H), 5.5-5.6 (m, 1H), 6.45-6.65 (m, 2H), 7.05-7.15 (m, 1H), 7.2-7.4 (m, 5H).

Photoproducts 7q

^1H NMR (CDCl_3 , 400 MHz) δ 3.0-3.2 (m, 2H), 3.5-3.6 (m, 1H), 3.8 (s, 3H), 4.0-4.1 (m, 1H), 4.15-4.35 (m, 2H), 4.8-4.9 (m, 1H), 6.38-6.4 ; 6.46-6.49 (d, 1H), 6.4-6.6 (m, 2H), 7.0-7.3 (m, 5H).

Table S1: Analysis conditions for photoproducts of **1e-1j**.

Susbtrate	GC/HPLC column	Condition	Retention time (minutes)
Photoproducts of 1e	GC – Chiral column Beta dex 350	Starting temp : 50°C Initial time : 1 min Ramp : 5°C/min Final temp: 60°C Hold time: 40 min Final ramp: 20°C/min Final temp: 200°C Final time:10 min	Enantiomer A : 7.9 Enantiomer B : 10.5
		Starting temp : 50°C Initial time : 1 min Ramp : 2°C/min Final temp: 120°C Hold time: 0 min Final ramp: 10°C/min Final temp: 200°C Final time:10 min	Enantiomer A : 22.7 Enantiomer B : 24.6
1f	GC – Chiral column Beta dex 350	Starting temp : 50°C Initial time : 1 min Ramp : 5°C/min Final temp: 60°C Hold time : 40 min Final ramp: 20°C/min Final temp : 200°C Final time : 10 min	Enantiomer A : 22.7 Enantiomer B : 24.6
1g	GC – Chiral column Beta dex 350	Starting temp : 50°C Initial time : 1 min Ramp : 5°C/min Final temp: 60°C Hold time : 40 min Final ramp: 20°C/min Final temp : 200°C Final time : 10 min	Enantiomer A : 22.7 Enantiomer B : 24.6
1h	HPLC, Chiralcel OD	Hex:Iproh = 96:4 Flow : 0.4 ml/min Abs. Wav. : 254 nm	Enantiomer A : 54.5 Enantiomer B : 59.4

1i	HPLC, Chiralcel OD	Hex:Iproh = 98:2 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Enantiomer A : 73 Enantiomer B : 79
1j	HPLC, Chiralcel OB	Hex:Iproh = 90:10 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Enantiomer A : 58 Enantiomer B : 68

- (a) After elution of the photoproduct, in the HPLC Hex:iPrOH ratio was changed to 60:40 to get the starting material.
- (b) Column dimensions of Chiralcel OD and OB (length=250 mm, internal diameter = 4.6 mm).
- (c) Column dimension of Beta dex 350 (length=30m, internal diameter = 0.25 mm, film thickness = 0.25 μ m).

Table S2: Analysis conditions for photoproducts of **6e**, **6g**, **6i-6q**.^a

Susbtrate	HPLC column	Condition	Retention time (minutes)
7e	Chiralpak AD	Hex:Iproh = 95:5 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 24.9 Diastereomer B : 28.8
7g	Chiralcel OB	Hex:Iproh = 96:4 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 64 Diastereomer B : 73.2
7i	Chiralpak AD	Hex:Iproh = 96:4 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 45.8 Diastereomer B : 59.4
7j	Chiralpak ADRH	Hex:Iproh = 90:10 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 29.1 Diastereomer B : 43.5
7k	Chiralpak ADRH	Hex:Iproh = 95:5 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 31.4 Diastereomer B : 37.5
7l	Chiralpak ADRH	Hex:Iproh = 96:4 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 47 Diastereomer B : 59
7m	Chiralpak ADRH	Hex:Iproh = 93:7 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 36.2 Diastereomer B : 47.2

7n	Chiralpak ADRH	Hex:Iproh = 96:4 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 44.7 Diastereomer B : 55.6
7o	Chiralpak ADRH	Hex:Iproh = 97:3 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 44.1 Diastereomer B : 57.4
7p	Chiralpak ADRH	Hex:Iproh = 96:4 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 75.8 Diastereomer B : 82.6
7q	Chiralpak ADRH	Hex:Iproh = 93:7 Flow : 0.5 ml/min Abs. Wav. : 254 nm	Diastereomer A : 33.1 Diastereomer B : 47.1

- (a) After elution of the photoproduct, in the HPLC Hex: iPrOH ratio was changed to 60:40 to get the starting material.
- (b) Column dimensions of Chiralpak AD and OB (length=250 mm, internal diameter = 4.6 mm).
- (c) Column dimensions of Chiralpak ADRH (length=150 mm, internal diameter = 4.6 mm).

Analysis conditions for photoproducts of 4a-4r and 2b-2t

4a: HPLC column-chiralcel OD, mobile phase: 99:1 hexane to isopropanol; flow rate=0.2 ml/min; abs. wav. = 280 nm , retention time of diastereomers: 52 and 57.5 min.

4g: Temperature program: Initial temperature: 100⁰ C; 5 min, rate : 5⁰ /min, final tempature 270⁰ C; final time: 5 min; retention time of diastereomers: 27.3 and 27.7 min.

4n: GC column HP-5 (Column dimension: length=30 mm, internal diameter = 0.25 mm, film thickness = 0.25 µm); Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final tempature 1: 225⁰ C; final time 1: 15 min; rate 2: 20⁰ /min, final

temperature 2: 270⁰ C; final time 2: 20 min; retention time of diastereomers: 27.4 and 27.7 min.

4o: GC column HP-5; Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 150⁰ C; final time 1: 40 min; rate 2: 20⁰ /min, final temperature 2: 270⁰ C; final time 2: 20 min; retention time of diastereomers: 37.3 and 40.3 min.

4s: GC column HP-5; Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 160⁰ C; final time 1: 40 min; rate 2: 20⁰ /min, final temperature 2: 270⁰ C; final time 2: 20 min; retention time of diastereomers: 29.3 and 29.8 min.

4j: GC column HP-5; Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 220⁰ C; final time 1: 40 min; rate 2: 20⁰ /min, final temperature 2: 270⁰ C; final time 2: 20 min; retention time of diastereomers: 30.1 and 30.6 min.

4q: HPLC column-chiralpak AD, mobile phase: 75:25 hexane to isopropanol; flow rate=0.5 ml/min; retention time of diastereomers: 30.3 and 37.2 min.

4r: HPLC column-chiralcel OD, mobile phase: 90:10 hexane to isopropanol; flow rate=0.5 ml/min; retention time of diastereomers: 46.5 and 105 min.

2b: GC column SE-30 (Column dimension: length=30 mm, internal diameter = 0.25 mm, film thickness = 0.25 μm) Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 230⁰ C; final time 1: 20 min; rate 2: 10⁰ /min, final temperature 2: 270⁰ C; final time 2: 10 min; retention time of diastereomers: 33.4 and 35.9 min.

2c: GC column SE-30 Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 230⁰ C; final time 1: 15 min; rate 2: 10⁰ /min, final temperature 2: 270⁰ C; final time 2: 10 min; retention time of diastereomers: 35.5 and 36.8 min.

2d: GC column SE-30 Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 230⁰ C; final time 1: 15 min; rate 2: 10⁰ /min, final temperature 2: 270⁰ C; final time 2: 10 min; retention time of diastereomers: 29.6 and 30.8 min.

2e: GC column SE-30 Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 210⁰ C; final time 1: 15 min; rate 2: 10⁰ /min, final temperature 2: 270⁰ C; final time 2: 10 min; retention time of diastereomers: 31.5 and 33.4 min.

2g: GC column SE-30 Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 220⁰ C; final time 1: 15 min; rate 2: 10⁰ /min, final temperature 2: 270⁰ C; final time 2: 10 min; retention time of diastereomers: 27.2 and 28.5 min.

2i: GC column SE-30 Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 220⁰ C; final time 1: 15 min; rate 2: 10⁰ /min, final temperature 2: 270⁰ C; final time 2: 10 min; retention time of diastereomers: 29.2 and 30.4 min.

2j: HPLC column-chiralpak AD, mobile phase: 93:07 hexane to isopropanol; flow rate=0.5 ml/min; retention time of diastereomers: 49.8 and 68 min.

2m: HPLC column-chiralcel OD, mobile phase: 83:17 hexane to isopropanol; flow rate=0.4 ml/min; retention time of diastereomers: 39.7 and 50.5 min.

2n: GC column HP-5

Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 200⁰ C; final time 1: 20 min; rate 2: 20⁰ /min, final temperature 2: 270⁰ C; final time 2: 20 min; retention time of diastereomers: 29.3 and 29.8 min.

2o: GC column HP-5

Temperature program: Initial temperature: 100⁰ C; 1 min, rate 1: 5⁰ /min, final temperature 1: 210⁰ C; final time 1: 25 min; rate 2: 20⁰ /min, final temperature 2: 270⁰ C; final time 2: 20 min; retention time of diastereomers: 29.4 and 29.9 min.

2p: HPLC column-chiralpak AD, mobile phase: 90:10 hexane to isopropanol; flow rate=0.5 ml/min; retention time of diastereomers: 30 and 48 min.

2q: HPLC column-chiralcel OD, mobile phase: 95:05 hexane to isopropanol; flow rate=0.6 ml/min; retention time of diastereomers: 45 and 55 min.

2s: HPLC column-chiralpak AD-RH, mobile phase: 93:07 hexane to isopropanol; flow rate=0.6 ml/min; retention time of diastereomers: 28.5 and 46 min.

2t: HPLC column-chiralcel OD, mobile phase: 90:10 hexane to isopropanol; flow rate=0.5 ml/min; retention time of diastereomers: 47 and 53 min.