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Photochemical Studies on 5-Methylbicyclo[1.1.1]pentane Derivatives: p-Orbital Overlap Controlled Enantioselectivity

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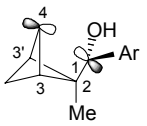
The first example of the p-orbital overlap controlled enantioselectivity of Norrish type II photocyclization reaction was described. Irradiation of 5-methyl bicyclo[1.1.1]pentanyl ketone with UV in the solid state as well as in the acetonitrile solution afforded the Norrish/Yang photocyclization compound as the sole product. Solid-state asymmetric photochemical studies using ionic chiral auxiliary technique led to the enantioselectivity as high as 60%. The results were rationalized by X-ray single crystal structure.

Keywords enantioselectivity, p-orbital overlap, solid state, Norrish type II photoreaction, ionic chiral auxiliary

Introduction

In the past several years, the approaches for the solid-state asymmetric synthesis had been well developed and successfully applied in a variety of photoreactions.[1] Among the methods reported, the solid-state ionic chiral auxiliary technique developed in Scheffer group has attracted widespread interest and attention.[2] In this procedure, the reactant is equipped with a carboxylic acid substituent to which an optically pure ammonium ion (the ionic chiral auxiliary) is attached by means of a salt bridge. Such salts are required to crystallize in chiral space groups, which provide the asymmetric environment responsible for chiral induction when the compounds are photolyzed in the solid state. A second requirement for the success of the solid-state ionic chiral auxiliary method of asymmetric synthesis is that the reactant must crystallize in a conformation favorable for reaction. For photochemical reactions involving intramolecular hydrogen atom abstraction, this requires a conformation in which the carbonyl oxygen is within approximately (2.7±0.2) Å of a γ-hydrogen atom.[3] In most cases, the differentia in the above distance between two γ-hydrogen atoms governs the high enantioselectivity in the solid-state photoreaction.[4] With our continuous studies on the photoreactions, we found that 5-methylbicylco[1.1.1]pentane **6** smoothly undergoes Norrish/Yang type II cyclization reaction under the irradiation with UV lamp, and speculated that, in this case, the enantioselectivity could also be controlled by the *p*-orbital overlap as only one γ-hydrogen atom existed in the structure. In this paper, we report what we have achieved in the asymmetric photochemical as well as the computational studies on 5-methyl bicyclo[1.1.1]pentane **6**.



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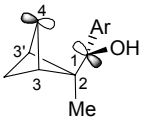

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Results and discussion

The synthesis of 5-methylbicylco[1.1.1]pentane **6** was started from cyclobutyl phenyl ketone **1** as shown in Scheme 1. According to the reported procedures,[5] compound **2** was synthesized from starting material **1** in several steps, which was then reacted with LDA/MeI, and sequentially reduced with $LiAlH_4$ in Et_2O to give the alcohol **3** in 54% yield (two steps). Alcohol **3** was oxidized by PCC in CH_2Cl_2 to afford the aldehyde **4**. Treatment of **4** with the Grignard reagent as used in previous work at −40 ℃ afforded the alcohol **5** in 48% yield (two steps from **3**), which was oxidized by PCC in CH_2Cl_2 to give the photoreactant **6** in 85% yield. Irradiation of compound **6** in acetonitrile through Pyrex using a 450 W medium-pressure mercury lamp led to the cyclobutanol compound **7** as a sole photoproduct in 91% yield via an intramolecular Norrish/Yang cyclization reaction. The formation of **7** was the conversion of achiral reactant to the chiral product, which is ideal for asymmetric photochemical studies.

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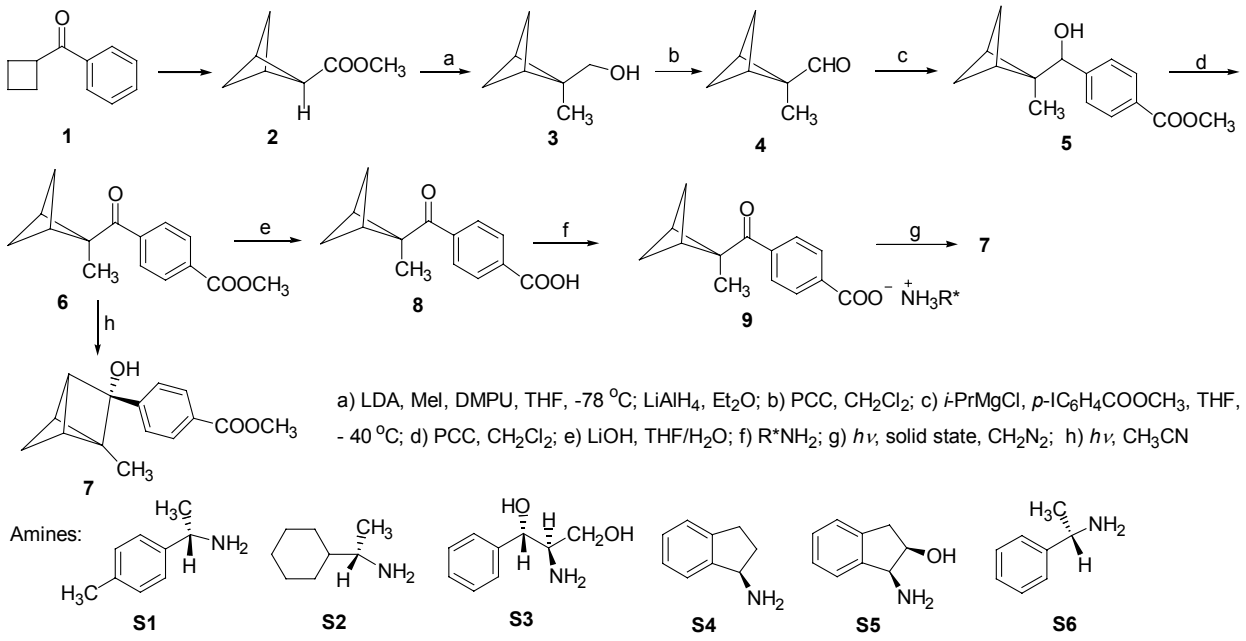
Scheme 1 Synthesis of ketone reactants and their photoproducts



Furthermore, Hyperchem MM3 (version 8.0.3) calculations showed that the C=O···H_γ distance is 2.60 Å, which is within the (2.72±0.2) Å range established for successful γ-hydrogen abstraction in the solid state. Therefore, 5-methylbicylco[1.1.1]pentane **6** hydrolyzed with LiOH in THF/H_2O to give carboxylic acid **8** in 97% yield, which was then treated with a variety of optically pure amines to form the corresponding ammonium carboxylate salts **9** (Scheme 1). Such salts are required to crystallize in chiral space groups, which provide the asymmetric environment responsible for chiral induction. Crystals of these salts (2—5 mg) were crushed between two Pyrex microscope slides, sealed in polyethylene bags under nitrogen, or suspended in 10 mL of hexane, and irradiated with a 450 W medium pressure mercury lamp.[6] Following photolysis, the photoproducts were treated with ethereal diazomethane, and the resulting methyl esters were analyzed by chiral HPLC to obtain the enantiomeric excess (*ee*) values and GC for the conversions. The results of the enantiomeric excess determinations are summarized in Table 1.

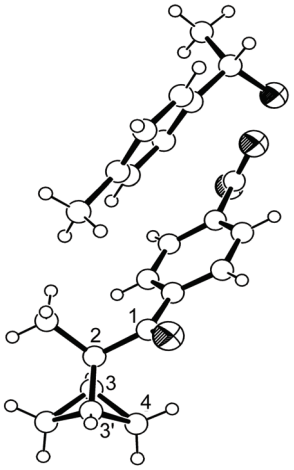
Unexpectedly, the photoreaction of salts **9** in the solid state became rather slow and longer reaction time had to be employed, which led to the crystals melted and the breakdown in order of the crystal lattice, resulting in low enantioselectivity. Therefore, as shown in Table 1, the enantiomeric excess values obtained for photoproduct **7** ranged from low to moderate. Before we begin to discuss the results observed in the solid state, there are several geometric parameters for Norrish/Yang photoreaction which should be introduced. The symbol *d* represents the distance between the carbonyl oxygen and the γ-hydrogen to be abstracted. Ideally these atoms should lie within 2.72 Å of each other, the sum of their van der Waals radii. The favorability of the cleavage reaction is gauged through the dihedral angles φ_1 and φ_4. The dihedral angle φ_1 represents the overlap between the p-orbital on C(1), the carbonyl carbon, with the C(2)—C(3) σ-bond that would be fragmented in a cleavage reaction. Dihedral angle φ_4 represents the

Table 1 Asymmetric studies on the irradiation of salts **9** in the solid state[a]

Entry	Amine	Method[b]	Conv.[c]/%	*ee*[d]/%	α[e]
1	**S1**	A	13	60	
2		B	38	53	−
3		B	50	23	−
4	**S2**	A	28	10	N.M.[f]
5		B	64	7	N.M.[f]
6		A	50	18	−
7		B	55	18	−
8	**S3**	A	36	18	−
9		B	55	12	−
10	**S4**	A	10	21	−
11		B	24	4	N.M.[f]
12	**S5**	A	28	21	+
13		B	32	20	+
14	**S6**	B	84	17	−

[a] Samples were irradiated through Pyrex using a 450-W Hanovia medium-pressure mercury lamp. [b] A: The sample was sandwiched between two microscope slides; B: the sample was suspended in hexane. [c] Conversion based on GC-MS. [d] *ee* analyzed on a Chiral AS column with *V*(hexane) : *V*(isopropanol)=99.5 : 0.5 as the eluting solvent. [e] Sign of rotation of major enantiomer at sodium D line. [f] Not measured.

overlap between the *p*-orbital on C(4) with the same C(2)—C(3) bond. For both cases an optimum value of 0° indicates maximum overlap and the ideal geometry for cleavage. Cyclization reaction is dependent on two factors. The symbol *D* is defined as the distance between the two reacting centres, C(1) and C(4), and should be less than 3.4 Å, the sum of the van der Waals radii for two carbon atoms. The second parameter of interest is β, the dihedral angle formed between the p-orbital on C(1) and the C(2)—C(4) vector. In the ideal situation this will be 0°, meaning that the *p*-orbital is pointed directly towards the *p*-orbital on the C(4) carbon, allowing for closure of the cyclobutane ring. As shown in Figure 1,[7] *d* and *D* are within the sum of the van der Waals radii. The values of β (6°), φ_1 (50°) and φ_4 (45°) suggested that the biradical from **6** has a better geometry for cyclization than cleavage. This prediction is in accordance with the results observed in the solid state, in which only the cyclization product **7** was obtained. Although the abstraction distance and other geometric parameters in this case are as good as or better than those of dozens of compounds known to react in the solid state,[8] the results of the solid-state photochemistry of salts **9** is puzzled, and intrigues us to do some theoretical calculations. MM2 (ChemBio3D 11.0) calculations showed that compound **7** has the higher strain energy than **6** with the difference in strain energy of 131.9 kJ/mol. This might be the reason for unfavorable formation of **7** in the solid state.



d/Å	*D*/Å	β/(°)	φ_1/(°)	φ_4/(°)
2.73	2.69	6	50	45

Figure 1 Solid-state conformation of 1-*p*-tolylethylammonium salt of keto acid **8**.

Experimental

General methods

Commercial spectral grade solvents were used for photochemical experiments unless otherwise stated. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer. Melting points were determined on a Fisher-Johns apparatus. High resolution mass spectra (HRMS) were recorded on a Kratos MS 50 instrument using electron impact (EI) ionization at 70 eV, or chemical ionization (CI) with the ionizing gas noted, or a Bruker Esquire LC mass spectrometer using electrospray ionization (ESI). ^{1}H NMR spectra were obtained at 400 MHz on Bruker AV-400 instrument. ^{13}C NMR spectra were recorded at 100 MHz.

Synthesis of alcohol 3 To the solution of DIAP (diisopropylamine, 2.2 mL, 15.7 mmol) in 60 mL of dried THF precooled at −78 ℃, *n*-BuLi (*n*-butyllithium 1.6 mol/L, 9.8 mL, 15.7 mmol) was added dropwise with stirring. After addition, the mixture was stirred for 1 h at this temperature. To this solution, 1.9 mL of *N*,*N*′-dimethylpropyleneurea (DMPU) was added, then 1.32 g of **2** dissolved in dried THF (10 mL) was added slowly. The mixture was stirred at −78 ℃ for 3 h and 3.25 mL of CH_3I was added with dropwise. The mixture was then left to stir overnight and warmed up to room temperature. After that, saturated ammonium chloride solution was added, and the solution was extracted with diethyl ether. The organic layer was washed with brine, and the solvent was removed *in vacuo* after being dried over $MgSO_4$. The residue was directly used in next steps without further purification.

The residue prepared by the above procedure was dissolved in anhydrous diethyl ether (50 mL) and added 780 mg (20.5 mmol) of $LiAlH_4$. The mixture was refluxed overnight. After that, water was added to destroy the excess $LiAlH_4$. The solution was extracted with diethyl ether twice and the combined organic layer was washed with saturated brine before it was dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography with petroleum ether and diethyl ether (V∶V=1∶1) as the eluting solvents to give 0.64 g of **3** as a colorless oil (54% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.82 (s, 2H), 2.41 (s, 2H), 2.38 (dd, J=10.9, 3.1 Hz, 1H), 2.33 (dd, J=10.9, 2.7 Hz, 1H), 1.65 (d, J=3.1 Hz, 1H), 1.62 (d, J=2.6 Hz, 1H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 65.2, 62.2, 45.2, 44.8, 38.1, 16.2; IR (neat) ν_{max}: 3334, 2921, 1473, 1286, 1009, 973, 677 cm^{-1}; MS (70 eV) *m/z* (%): 113 [M^++1], 97, 79 (100), 67, 53. HRMS (EI) calcd for $C_7H_{12}O$ 112.0888, found 112.0887.

Synthesis of alcohol 5 Alcohol **3** (1.76 g, 15.7 mmol) dissolved in 120 mL of methylene chloride was added pyridinium chlorochromate (PCC) (4.62 g, 0.02 mol) and Celite (10 g) ground homogeneously in a mortar. The mixture was stirred at room temperature overnight, filtered through a silica gel column and rinsed with diethyl ether. The solvent was then removed *in vacuo*, and the residue **4** was used for next step without purification (GC indicated a purity of approximately 98%).

To a solution of methyl *p*-iodobenzoate (6.18 g, 23.5 mmol) in 40 mL of anhydrous THF precooled to −40 ℃ was added dropwise isopropylmagnesium chloride

(2 mol/L, 11.8 mL). After addition, the mixture was stirred for 1 h at this temperature. To this solution, the aldehyde **4** dissolved in 10 mL of dry THF was added slowly. The solution was stirred at −40 ℃ for 4 h. Saturated ammonium chloride solution (30 mL) was added quickly and the solution was extracted with diethyl ether (50 mL×3), and the combined organic layer washed with saturated brine solution (30 mL×2). The solvent was removed *in vacuo* after being dried over magnesium sulfate, and the residue was purified by silica gel chromatography (20% petroleum ether/diethyl ether) to give alcohol **5** as a colorless oil (1.85 g, 48% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.97 (d, J=8.3 Hz, 2H), 7.37 (d, J=8.3 Hz, 2H), 5.62 (brs, 1H), 3.88 (s, 3H), 3.85 (s, 1H), 2.77 (dd, J=10.9, 3.8 Hz, 1H), 2.64 (d, J=18 Hz, 1H), 2.44 (d, J=18 Hz, 1H), 2.30 (dd, J=10.9, 3.0 Hz, 1H), 1.83 (d, J=3.8 Hz, 1H), 1.65 (d, J=3.0 Hz, 1H), 1.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.2, 148.8, 131.8, 128.3, 125.7, 71.5, 65.3, 52.0, 44.9, 44.5, 39.8, 38.7, 10.8; IR (neat) ν_{max}: 3606, 2953, 1722, 1702, 1610, 1283, 1018, 851, 774, 733 cm^{-1}; MS (70 eV) *m/z* (%): 247 [M^++1], 215, 205, 165, 151, 128, 105, 91, 77 (100), 59; HRMS (EI) calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1254.

Synthesis of ketone 6 To a solution of alcohol **5** (866 mg, 3.52 mmol) in 30 mL of anhydrous methylene chloride were added PCC (1.52 g, 7.0 mmol) and Celite (3 g). The mixture was stirred at room temperature overnight and diethyl ether (20 mL) was added. The solution was then filtered through a silica gel column and rinsed with diethyl ether. The solvent was removed *in vacuo* and the residue purified by column chromatography (10% petroleum ether/diethyl ether) to give ketone **6** as a colorless oil (730 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.08 (d, J=8.4 Hz, 2H), 7.96 (d, J=8.4 Hz, 2H), 3.91 (s, 3H), 2.95 (s, 2H), 2.36 (dd, J=10.3, 3.4 Hz, 1H), 1.78 (dd, J=10.3, 3.4 Hz, 1H), 1.70 (d, J=3.6 Hz, 1H), 1.68 (d, J=3.4 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 205.2, 166.2, 139.0, 133.5, 129.7, 128.6, 70.5, 52.4, 46.8, 42.5, 41.4, 15.7; IR (neat) ν_{max}: 2979, 2900, 1727, 1437, 1277, 1107, 975, 816, 733 cm^{-1}; MS (70 eV) *m/z* (%): 244 [M^+], 229, 213, 202, 185, 163 (100), 135, 104, 76, 53; HRMS (EI) calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1096.

Irradiation of ketone 6 in acetonitrile A solution of ketone **6** (100 mg, 0.41 mmol) in aceonitrile (80 mL) was purged with N_2 for 15 min and irradiated with 450 W medium mercury pressure lamp under N_2 for 24 h. After irradiation, the solvent was removed *in vacuo* and the residue purified by column chromatography (10% petroleum ether/diethyl ether) to give photoproduct **7** (91 mg, 91%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.96 (d, J=8.0 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 3.87 (s, 3H), 3.81 (s, 1H), 3.17 (d, J=17.1 Hz, 1H), 2.35 (d, J=17.1 Hz, 1H), 2.38 (s, 1H), 2.16 (d, J=5.6 Hz, 1H), 2.10 (d, J=5.6 Hz, 1H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.9, 145.2, 129.5, 129.1, 126.8, 86.0, 65.7, 54.5, 52.1, 42.3, 39.4, 35.9, 7.8; IR (neat) ν_{max}: 3606, 2953, 1718, 1437, 1281, 1108, 1074, 863, 777, 712 cm^{-1}; MS (70 eV) *m/z* (%): 244 [M^+], 226, 215, 195 (100), 163, 128, 103, 91, 59; HRMS (EI) calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1098.

Synthesis of keto-acid 8 To a solution of ketone **6** (730 mg, 3.00 mmol) in THF (20 mL) and H_2O (10 mL) was added LiOH (1.08 g, 45 mmol). The mixture was stirred at room temperature for 4 h and then diethyl ether (30 mL) was added. The organic layer was washed with water (20 mL×3) and the aqueous layers were combined and acidified with conc. HCl. The solution was then extracted with diethyl ether (40 mL×4) and the combined organic layer was washed with water (20 mL×3) and dried over $MgSO_4$. Removal of solvent *in vacuo* gave a white solid, which was recrystallized from methanol to afford keto-acid **8** as a colorless solid (667 mg, 97% yield), m.p. 137—138 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.18 (d, J=8.4 Hz, 2H), 8.02 (d, J=8.4 Hz, 2H, $CDCl_3$), 2.97 (s, 3H), 2.38 (dd, J=10.3, 3.3 Hz, 1H), 1.80 (dd, J=10.3, 3.5 Hz, 1H), 1.72 (d, J=3.5 Hz, 1H), 1.70 (d, J=3.5 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 205.3, 171.3, 139.7, 132.7, 130.4, 128.7, 70.5, 46.9, 42.5, 41.4, 15.7; IR (KBr) ν_{max}: 3328, 2966, 2552, 1689, 1431, 1234, 1199, 975, 872, 805, 737, 704 cm^{-1}; MS (ESI) *m/z*: 229.0 [M^+−1]. Anal. calcd for $C_{14}H_{14}O_3$: C 73.03, H 6.13; found C 73.03, H 6.26.

General procedure of synthesis of ammonium salts 9 To a solution of keto-acid **8** (80 mg, 0.35 mmol) in diethyl ether (5 mL) was added one equivalent of optically pure amine. Upon addition, a precipitate formed immediately. The resulting suspension was suction filtered to give the salt, which was then recrystallized from methanol.

(*S*)-(−)-*α*-Phenylethylamine salt Yield 99%. m.p. 145—147 ℃ (methanol); ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.89 (d, J=8.3 Hz, 2H), 7.83 (d, J=8.3 Hz, 2H), 7.34—7.26 (m, 5H), 4.32 (q, J=6.8 Hz, 1H), 3.19 (brs, 1H), 2.84 (s, 2H), 2.32 (dd, J=10.2, 3.3 Hz, 1H), 1.66 (dd, J=10.2, 3.2 Hz, 1H), 1.61 (d, J=3.2 Hz, 1H), 1.59 (d, J=3.3 Hz, 1H), 1.50 (d, J=6.8 Hz, 3H), 1.40 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 207.8, 173.9, 143.4, 140.1, 138.1, 130.4, 130.2, 130.0, 129.4, 127.6, 72.0, 52.3, 47.5, 43.2, 42.6, 20.9, 16.2; IR (KBr) ν_{max}: 3851, 2970, 1671, 1521, 1280, 975, 875, 820, 748, 693 cm^{-1}; MS (ESI) *m/z*: 352 [M^++1], 335, 253, 105. Anal. calcd for $C_{22}H_{25}NO_3$: C 75.19, H 7.17, N 3.99; found C 75.46, H 7.18, N 3.93.

(*R*)-(−)-1-Cyclohexyl ethylamonium salt m.p. 154—155 ℃ (methanol); ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.91 (d, J=8.4 Hz, 2H), 7.84 (d, J=8.4 Hz, 2H), 3.19 (brs, 1H), 2.97—2.95 (m, 1H), 2.84 (s, 2H), 2.33 (dd, J=10.2, 3.3 Hz, 1H), 1.67 (dd, J=10.2, 3.2 Hz, 1H), 1.61 (d, J=3.2 Hz, 1H), 1.59 (d, J=3.3 Hz, 1H), 1.70—1.56 (m, 5H), 1.40 (s, 3H), 1.17—1.15 (m, 2H), 1.13 (d, J=6.8 Hz, 3H), 1.06—1.05 (m, 1H), 0.96—0.93 (m, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 207.8, 174.0, 143.6, 138.1, 130.4, 129.4, 72.0, 53.4, 47.5, 43.2,

42.7, 42.6, 30.0, 28.8, 27.1, 27.0, 26.9, 16.2, 16.0; IR (KBr) ν_{max}: 3851, 2931, 1670, 1380, 1279, 977, 876, 819, 742 cm^{-1}; MS (ESI) *m/z*: 358 [M^++1], 291, 255, 195. Anal. calcd for $C_{22}H_{31}NO_3$: C 73.91, H 8.74, N 3.92; found C 74.20, H 8.79, N 3.80.

(*R*)-(−)-1-Amino-indan salt m.p. 167—169 ℃ (methanol); ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.89 (d, J=8.2 Hz, 2H), 7.83 (d, J=8.3 Hz, 2H), 7.36 (d, J=7.3 Hz, 1H), 7.21—7.15 (m, 3H), 4.66 (dd, J=7.6, 5.2 Hz, 1H), 3.19 (brs, 1H), 3.02—3.01 (m, 1H), 2.86—2.85 (m, 1H), 2.83 (s, 2H), 2.46—2.45 (m, 1H), 2.32 (dd, J=10.2, 3.3 Hz, 1H), 1.97—1.96 (m, 1H), 1.66 (dd, J=10.2, 3.2 Hz, 1H), 1.61 (d, J=3.2 Hz, 1H), 1.59 (d, J=3.3 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 207.8, 173.9, 145.4, 143.3, 140.1, 138.1, 130.6, 130.4, 129.4, 128.2, 126.3, 125.5, 72.0, 56.9, 47.5, 43.2, 42.6, 31.8, 31.0, 16.2; IR (KBr) ν_{max}: 3850, 2973, 2893, 2219, 1524, 1386, 977, 821, 755, 740, 711 cm^{-1}; MS (ESI) *m/z*: 364 [M^++1], 348, 285, 253, 231, 195, 181. Anal. calcd for $C_{23}H_{25}NO_3$: C 76.01, H 6.93, N 3.85; found C 75.94, H 6.95, N 3.79.

(1*S*,2*R*)-(−)-*cis*-1-Amino-2-indanol salt m.p. 155—157 ℃ (methanol); ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.90 (d, J=8.3 Hz, 2H), 7.83 (d, J=8.3 Hz, 2H), 7.36 (d, J=7.4 Hz, 1H), 7.23—7.16 (m, 3H), 4.61 (q, J=6.0 Hz, 1H), 4.46 (d, J=5.9 Hz, 1H), 3.19 (brs, 1H), 3.11 (dd, J=16.3, 6.4 Hz, 1H), 2.91 (dd, J=16.3, 5.1 Hz, 1H), 2.84 (s, 2H), 2.32 (dd, J=10.2, 3.4 Hz, 1H), 1.66 (dd, J=10.2, 3.3 Hz, 1H), 1.61 (d, J=3.3 Hz, 1H), 1.59 (d, J=3.4 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 207.8, 173.9, 143.2, 142.8, 138.2, 130.8, 130.4, 129.4, 128.4, 126.6, 126.2, 72.0, 71.9, 58.6, 47.5, 43.2, 42.6, 40.1, 16.2; IR (KBr) ν_{max}: 3851, 2983, 1667, 1587, 1375, 1279, 977, 808, 756, 741, 704 cm^{-1}; MS (ESI) *m/z*: 380 [M^++1], 337, 321, 299, 284, 253, 182, 150, 140. Anal. calcd for $C_{23}H_{25}NO_4$: C 72.80, H 6.64, N 3.69; found C 73.12, H 6.67, N 3.63.

(1*R*,2*R*)-(−)-2-Amino-1-phenyl-1,3-propanediol salt m.p. 161—163 ℃ (methanol); ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.91 (d, J=8.4 Hz, 2H), 7.84 (d, J=8.6 Hz, 2H), 7.32—7.21 (m, 5H), 4.64 (d, J=8.7 Hz, 1H), 3.44 (dd, J=11.7, 3.6 Hz, 1H), 3.31 (dd, J=11.7, 6.0 Hz, 1H), 3.20—3.19 (m, 1H), 3.17—3.16 (m, 1H), 2.84 (s, 2H), 2.33 (dd, J=10.3, 3.3 Hz, 1H), 1.67 (dd, J=10.3, 3.3 Hz, 1H), 1.61 (d, J=3.2 Hz, 1H), 1.59 (d, J=3.3 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 207.8, 173.9, 143.3, 142.1, 138.1, 130.4, 129.7, 129.5, 129.4, 127.9, 72.3, 72.0, 60.3, 60.0, 47.5, 43.2, 42.6, 16.2; IR (KBr) ν_{max}: 3851, 3240, 1672, 1581, 1396, 1280, 976, 822, 743, 700 cm^{-1}; MS (ESI) *m/z*: 398 [M^++1], 335, 190, 168, 150. Anal. calcd for $C_{23}H_{27}NO_5$: C 69.50, H 6.85, N 3.52; found C 69.80, H 6.89, N 3.57.

(*S*)-(−)-1-*p*-Tolylethylamine salt m.p. 172—174 ℃; ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.87 (d, J=8.5 Hz, 2H), 7.81 (d, J=8.5 Hz, 2H), 7.18 (d, J=8.0 Hz, 2H), 7.09 (d, J=8.0 Hz, 2H), 4.26—4.23 (m, 1H), 3.17 (brs, 1H), 2.81 (s, 3H), 2.30 (dd, J=10.2, 3.3 Hz, 1H), 2.19 (s, 3H), 1.64 (dd, J=10.2, 3.3 Hz, 1H), 1.58 (d, J=3.3 Hz, 1H), 1.56 (d, J=3.3 Hz, 1H), 1.46 (d, J=6.8 Hz, 3H), 1.38 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 207.8, 173.9, 143.4, 140.2, 138.1, 136.9, 130.8, 130.4, 129.4, 127.6, 72.0, 52.1, 47.5, 42.6, 43.2, 21.1, 20.8, 16.2; IR (KBr) ν_{max}: 3850, 2979, 2541, 1661, 1526, 1395, 1282, 975, 875, 811, 745, 718 cm^{-1}; MS (ESI) *m/z*: 366 [M^++1], 350, 307, 271, 195, 181, 136. Anal. calcd for $C_{23}H_{27}NO_3$: C 75.59, H 7.45, N 3.83; found C 75.55, H 7.41, N 3.69.

Conclusions

In summary, the photochemical behaviours of 5-methylbicylco[1.1.1]pentane **6** in the solid state and solution were described and discussed. As a first example, the p-orbital controlled enantioselectivies of Norrish/Yang photocylclization reaction was conducted by the asymmetric studies on **6** using ionic chiral auxiliary method in the solid state.

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[6] The reaction became faster when the sample was suspended in hexane. One disadvantage of this method is that the sample could be slightly soluble in the solvent, resulting in low enantioselectivities.

[7] Crystallographic data for the structures in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 773907. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac. uk).

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