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THE PREPARATION AND REACTIONS OF 2-ACYL-3-PHENYLISOMENTHOPYRAZOLE†

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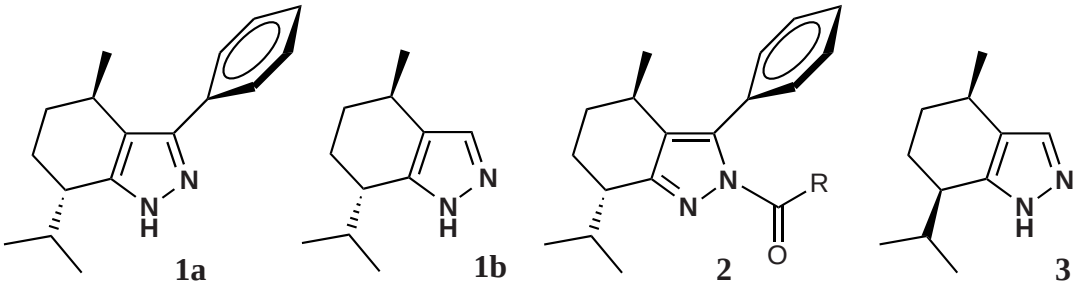
Abstract — 3-Phenylisomenthopyrazole (**4**) was useful as a chiral auxiliary, though the diastereomeric selectivity was lower than those of 3-phenyl-*l*-menthopyrazole (**1a**). In α-acylation and the Diels-Alder cycloaddition, the absolute configuration of the predominant products was different from that of the products using **1a**.

We have recently developed a method of preparation for 3-phenyl-*l*-menthopyrazole (**1a**) as a new chiral auxiliary,[1] which has a unique structure and properties that are relative to the conventional chiral auxiliaries.[2] The most important characteristics of this auxiliary are that the substrate bonds to a nitrogen atom of the heteroaromatic pyrazole ring in a chiral environment. That is, (4*R*)-methyl group of **1a** is located very closed to 3-phenyl group and their steric hindrance is relaxed by twisting the benzene ring, which overlaps one side of the terminal nitrogen atom.[1] These structural features cause the transmission of the chirality of (4*R*)-methyl group into terminal nitrogen atom through the torsional asymmetry of phenyl group, and cause the diastereofacial effect in the reactions on the substrate moiety. Moreover, a lone pair of electrons on the adjacent nitrogen plays a role of a Lewis base, and contributes to the N···Li-O chelation in the lithium enolate derived from 2-acyl-3-phenyl-*l*-menthopyrazoles (**2**). These chelations freeze the bond rotation of the acyl group to be fixed in a *syn* configuration. As a result, the chirality of the (4*R*)-methyl group of **2** causes a highly asymmetric induction on the α-position of acyl group in the reactions with alkyl halides,[3] diphenyl disulfide,[4] acyl chloride,[5] aldehydes,[6] and C=N compounds.[7] A similar chelation of N···Mg···O=C, which is observed in the mixture of *N*-acylpyrazoles and $MgBr_2 \cdot OEt_2$,[8] induces the asymmetric Michael addition of Grignard reagents,[9] Diels-Alder cycloaddition,[10] and 1,3-dipolar cycloaddition[11] on *N*-(α,β-unsaturated)acylpyrazoles.

The chiral environment of acyl substrate on *N*-acylpyrazole might be intensively affected by the conformational structure of 4-methyl group in the menthopyrazole analogues. Previous paper[12] reported the preparation of *l*-menthopyrazole ((*4R, 7S*)-4-methyl-7-isopropyl-4,5,6,7-tetrahydroindazole; **1b**), which

† This paper is dedicated to Professor Yuichi Kanaoka on the occasion of his 75th birthday for his brilliant achievement in the field of heterocyclic chemistry.

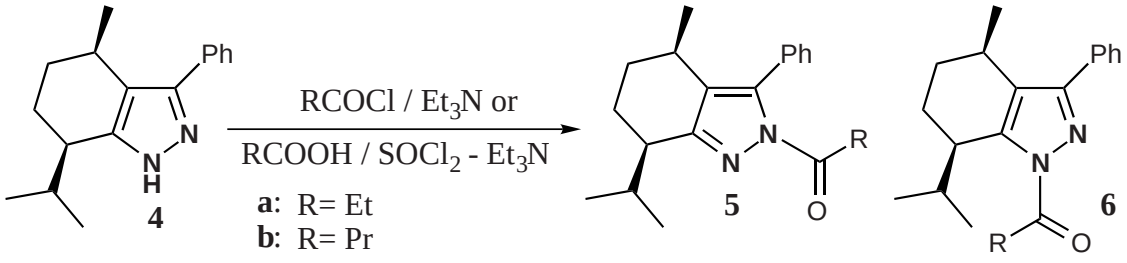
had the different stereo structure from (*4R*, *7R*)-4-methyl-7-isopropyl-4,5,6,7-tetrahydroindazole (isomenthopyrazole; **3**).[13] 3-Phenylisomenthopyrazole (**4**) was also prepared by 3 step reactions from (+)-isomenthol in over 70 % total yield. The reaction of **4** with (*S*)-α−methoxy-α-trifluoromethylphenylacetic acid (MTPA) by the action of thionyl chloride gave MTPA derivatives (**5f** and **6f**).[14] From their ^{1}H-NMR spectra, any diastereomer could not be detected and **4** was shown to be optically pure more than 95 % ee. Two substituent groups of **4** having cis conformation brought the labile cyclohexene structure, while the cyclohexene structure of **1b** was fixed in a half chair form. Therefor, the conformational difference of *4R*-methyl group in between 2-acyl-3-phenylisomenthopyrazoles (**5**) and **2** is much interested in the diastereoselective reactions on their acyl moiety. As the extension of the asymmetric syntheses using **1a**, we report here the preparation and the reactions of **5** comparing with those of **2**. Consequently, the mechanism of asymmetric selection should be more clarified related to the stereo chemistry of **1a**.



1a **1b** **2** **3**

When 3-phenylisomenthopyrazole (**4**) was treated with acyl chloride (method A),[15] 2-acyl-3-phenylisomenthopyrazole (**5**) and 1-acyl-3-phenylisomenthopyrazole (**6**) were obtained (Scheme 1). In some cases, **5** and **6** were prepared by the reaction of thionyl chloride towards the mixture of pyrazole and the corresponding carboxylic acid (method B). In both methods, **5** was predominantly formed in good total yield as summarized in Table 1. For the determination of the absolute configuration of the α-alkylation product described later, **4** was treated with (*S*)-2-methylbutanoic acid to afford (2'*S*)-*N*-(2'-methylbutanoyl)-3-phenylisomenthopyrazoles ((*S*)-**5e** and (*S*)-**6e**) by method B.

For the comparison of the asymmetric selectivity, the typical reactions of **5** were carried out modeling on those of **2**. As the examples of α-alkylation, 2-propanoyl- (**5b**) and 2-phenylacetyl-3-phenylisomenthopyrazole (**5c**) were treated with methyl iodide in the presence of LDA (Scheme 2). The asymmetric preference was coincided with that of **2** with comparably low de values summarized in Table 2.



4 **5** **6**

a: R= Et
b: R= Pr
c: R= Bn
d: R= CH=CH$_2$
e: R= (*S*)-CH(Me)-Et
f: R= (*S*)-C(OMe)(CF$_3$)-Ph

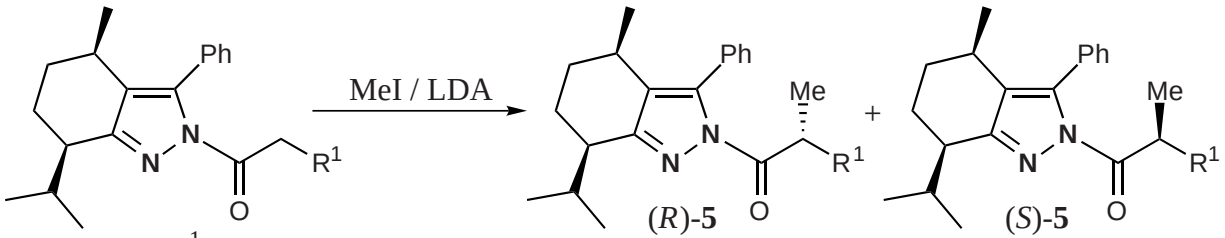
Scheme 1

Table 1. *N*-Acylation of 3-Phenylisomenthopyrazole (**4**)

Run	R	Method	Products	Yield	**5 : 6**
1	Et	A	**5a** / **6a**	75	72 : 28
2	Pr	A	**5b** / **6b**	89	76 : 24
3	Bn	A	**5c** / **6c**	48	76 : 24
4	$CH{=}CH_2$	A	**5d** / **6d**	68	55 : 45
5	(*S*)-CH(Me)-Et	B	**5e** / **6e**	48	70 : 30
6	(*S*)-C(OMe)(CF_3)-Ph	B	**5f** / **6f**	69	68 : 32

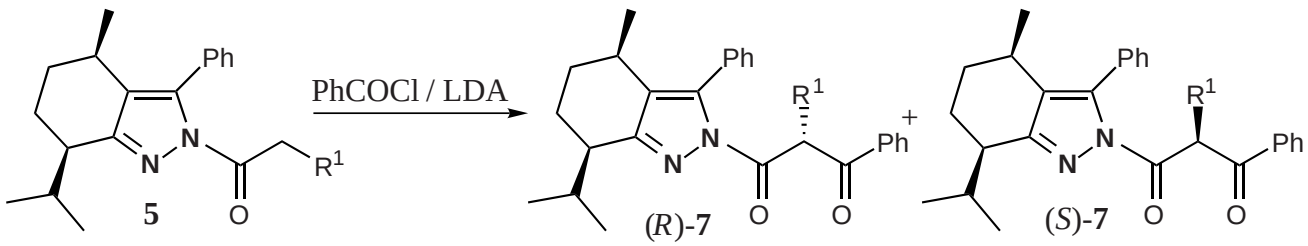
By the comparison with the authentic samples, the predominant products were found to be (*R*)-**5e** and (*2'R*)-2-(2'-phenyl)propanoyl-3-phenylisomenthopyrazole ((*R*)-**5g**), respectively.

Similarly, **5a** and **5b** gave 2-(2'-benzoyl)propanoyl- (**7a**) and 2-(2'-benzoyl)butanoyl-3-phenylisomenthopyrazole (**7b**) by α-acylation using benzoyl chloride in the presence of LDA (Scheme 3). In this reaction, the diastereomeric preferences were observed to be inverted from those of **2** by means of ^{1}H-NMR peaks attributable to 4-methyl group. The reaction profile of the Diels-Alder cycloaddition of **5d** with cyclopentadiene was similar to that of 2-acryloyl-3-phenyl-*l*-menthopyrazole (**2d**) in the total yield and the *endo / exo* product ratio (Scheme 4, Table 2). The products (**8**) were derived into methyl bicyclo-[2,2,1]hept-3-en-1-carboxylate by the treatment with sodium methoxide. When the enantiomer ratio of subsequent methyl ester was measured with GC using chiral stationary phase column, the stereo structure of



5b: R^1= Et
5c: R^1= Ph
5e: R^1= Et **5g**: R^1= Ph

Scheme 2

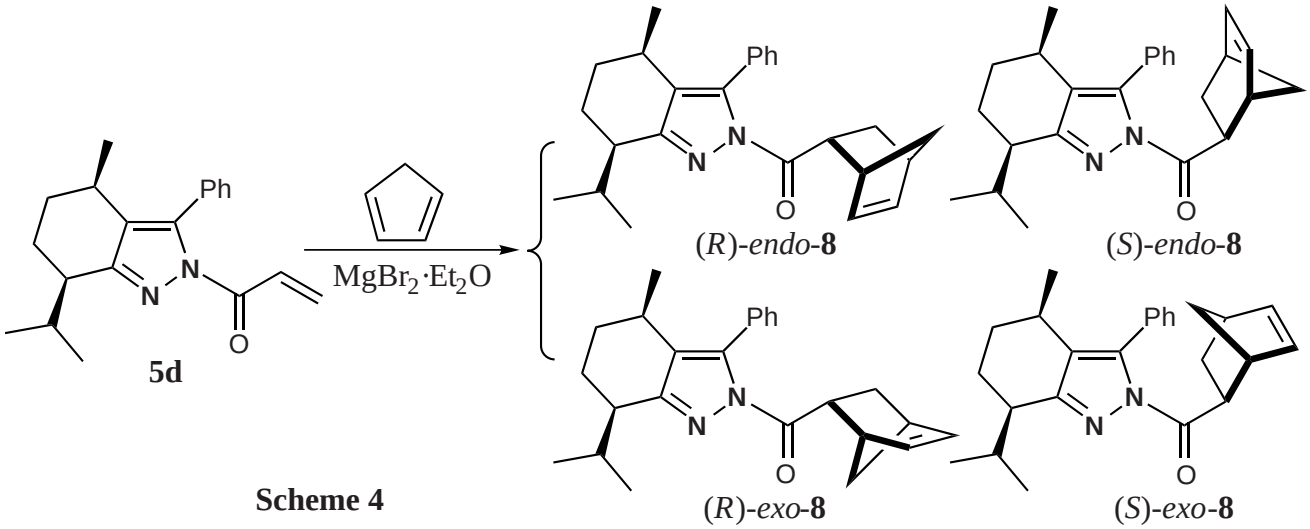


a: R^1= Me **b**: R^1= Et

Scheme 3

the predominant enantiomer was different from that of **2d**.

3-Phenylisomenthopyrazole (**4**) was concluded to be useful as a chiral auxiliary, though the diastereomeric selectivity was lower than those of 3-phenyl-*l*-menthopyrazole (**1a**). In α-acylation and the Diels-Alder cycloaddition, the absolute configuration of the predominant products was different from that of the products using **1a**.



Scheme 4

Table 2. Diastereoselectivity of
2-Acyl-3-phenylisomenthopyrazole (**5**) *vs* 2-Acyl-3-phenyl-*l*-menthopyrazole (**2**)

Run	Reaction	Condition	R	2-Acyl-3-phenyl-isomenthopyrazole (**5**)			2-Acyl-3-phenyl-*l*-menthopyrazole (**2**)	
					Yield (%)	De (%)	Yield (%)	De (%)
1	a-Alkylation	MeI / LDA	Pr	**5d**	28	49 (*R*)	77	60 (*R*)
2			Bn	**5g**	53	34 (*R*)	47	>95 (*R*)
3	a-Acylation	PhCOCl / LDA	Et	**7a**	88	84 (*R*)	96	80 (*S*)
4			Pr	**7b**	56	44 (*R*)	82	68 (*S*)
5	Diels-Alder	Cp[a] / $MgBr_2 \cdot Et_2O$	$CH=CH_2$	**8**	27	44 (*R*)[b]	98	84 (*S*)[b]
				endo : *exo* = 89 : 11			*endo* : *exo* = 96 : 4	

a: Cyclopentadiene was abbreviated to cp. b: De of *endo*-isomer.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a JEOL JNM-EX270 (270 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard. The enantiomer ratios were evaluated from the peak intensities of ^{1}H-NMR spectra. Optical rotations were observed using a JASCO DIP-370 digital polarimeter at 21℃. The evaluation of chemical and optical yields were also evaluated by the preparative HPLC on GL Sciences PU614 high performance liquid chromatograph using Inertsil PREP-

ODS column (ϕ 20 mm x 250 mm) eluting with methanol. Also the enantiomer ratios were evaluated by means of GC on SHIMADZU GC-14A gas chromatograph using Chromatopack Chirasil DEX-CB capillary column (ϕ 0.25 mm x 25 m). THF was dried over benzophenone ketyl radical, and toluene was distilled over calcium hydride.

Preparation of 3-phenyl*iso*menthopyrazole.

(3R,6R)-2-Benzoyl-3-methyl-6-isopropylcyclohexanone.

To the Et_2O solution (40 mL) of isomenthol (7.8 g, 50 mmol) in ice bath, sodium dichromate dihydrate (5.2g, 17mmol) in dilute sulfuric acid (25 mL, 7.2M) was added dropwise over 1 h. After stirring another 1 h at rt, the mixture was extracted with Et_2O. The combined organic layer was washed with saturated $NaHCO_3$ and saturated NaCl, and dried over anhydrous $MgSO_4$. After removal of a solvent, isomenthone (7.2 g, 47 mmol) was purified by Kugelrohr distillation. The subsequent isomenthone (1.5 g, 10 mmol) in THF (10 mL) was added to THF solution (10 mL) of LDA which was prepared *in situ* from diisopropylamine (1.6 mL) and butyllithium solution (7.5 mL, 1.59 M in hexane) at –5℃. After stirring for 15 min at –5℃, the mixture was treated with benzoyl chloride (1.6 g, 11 mmol) in THF (5 mL), and then warmed up to rt with stirring for 1.5 h. The mixture was quenched with dilute hydrochloric acid and extracted with Et_2O. The combined organic layer was washed with saturated NaCl, dried over anhydrous $MgSO_4$, and concentrated. The reaction residue was purified by recrystallization from methanol or hexane; yield 38 %; mp 108.5-109.5 ° C; ^{1}H-NMR ($CDCl_3$): δ 0.87 (3H, d, *J*=6.6 Hz), 0.94 (3H, d, *J*=6.6 Hz), 1.01 (3H, d, *J*=6.9 Hz), 1.54-1.65 (1H, m), 1.86-2.02 (3H, m), 2.10-2.22 (2H, m), 2.63-2.70 (1H, m), 4.17 (1H, d, *J*=7.6 Hz), 7.41-7.59 (3H, m), 7.88-7.93 (2H, m); ^{13}C-NMR ($CDCl_3$): δ 19.4 (CH_3), 20.4 (CH_3), 21.1 (CH_3), 26.2 (CH_2), 26.9 (CH_2), 28.0 (CH), 36.0 (CH), 56.8 (CH), 64.7 (CH), 128.4 (CH), 128.6 (CH), 133.2 (CH), 137.5 (C), 197.5 (C), 210.5 (C). *Anal.* Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.24; H, 8.55.

3-Phenylisomenthopyrazole (**4**).

The mixture of (3*R*,6*R*)-2-benzoyl-3-methyl-6-isopropylcyclohexanone (970 mg, 3.7 mmol), hydrazine monohydrate (2.8 g, 56 mmol) and hydrazine hydrochloride (400 mg, 5.9 mmol) in methanol (20 mL) was refluxed for 6 h. The reaction mixture was quenched with water and extracted with Et_2O. The organic layer was washed with aqueous $NaHCO_3$, and saturated NaCl, dried over anhydrous $MgSO_4$, and concentrated. The reaction residue was purified by recrystallization from aqueous methanol; mp 124-126℃ (from MeOH-H_2O); yield 89 %; $[\alpha]_D$ -10.8° (c 2.73, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.86 (3H, d, *J*=6.9 Hz), 1.05 (3H, d, *J*=6.9 Hz), 1.10 (3H, d, *J*=6.9 Hz), 1.67-1.73 (3H, m), 1.82-1.88 (1H, m), 2.26 (1H, oct, *J*=5.8 Hz), 2.71 (1H, dt, *J*=9.1, 4.6 Hz), 3.22 (1H, dq, *J*=12.7, 6.4 Hz), 7.31 (1H, d, *J*=7.4 Hz), 7.39 (2H, d, *J*=7.4 Hz), 7.68 (2H, d, *J*= 7.5 Hz); ^{13}C-NMR ($CDCl_3$): δ 17.8 (CH_3), 18.6 (CH_2), 20.4 (CH_3), 21.2 (CH_3), 25.8 (CH), 30.0 (CH), 30.3 (CH_2), 39.7 (CH), 119.2 (C), 126.7 (CH), 127.3 (CH), 128.5 (CH), 133.8 (C), 144.7 (C, broad), 145.3 (C, broad). *Anal.* Calcd for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 79.99; H, 8.72; N, 10.88.

General Acylation Methods of 3-Phenylisomenthopyrazole. 3-Phenylisomenthopyrazole (**4**) was acylated with the corresponding acid chloride by the presence of triethylamine in toluene according to

the formerly described method (method A).[15] Also the mixture of **4** and carboxylic acid in toluene was treated with thionyl chloride in the presence of triethylamine (method B). The product was purified by silica gel column chromatography with toluene-hexane mixture.

2-Propanoyl-3-phenylisomenthopyrazole (**5a**).

bp 150-160℃/ 9 mmHg; yield 54 %; $[\alpha]_D$: -53.8° (c 0.032, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.86 (3H, d, *J*=6.9 Hz), 0.97 (3H, d, *J*=6.9 Hz), 1.10 (3H, d, *J*=6.9 Hz), 1.16 (3H, t, *J*=7.3 Hz), 1.59-1.78 (4H, m), 2.37-2.45 (1H, m), 2.60-2.68 (1H, m), 2.78-2.85 (1H, m), 3.04-3.20 (2H, m), 7.27-7.32 (2H, m), 7.36-7.44 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 8.5 (CH_3), 18.5 (CH_3), 19.5 (CH_3), 20.3 (CH_3), 21.0 (CH_2), 24.8 (CH_2), 28.8 (CH), 29.8 (CH), 30.0 (CH), 41.0 (CH_2), 126.4 (C), 128.0 (CH), 128.0 (CH), 129.0 (C), 132.2 (C), 140.6 (C), 155.3 (C), 173.8 (C). *Anal.* Calcd for $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.02. Found: C, 77.46; H, 8.40; N, 9.03.

1-Propanoyl-3-phenylisomenthopyrazole (**6a**).

bp 150-160℃/ 9 mmHg; yield 21 %; $[\alpha]_D$: -24.2° (c 0.037, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.82 (3H, d, *J*=6.9 Hz), 1.00 (3H, d, *J*=6.9 Hz), 1.08 (3H, d, *J*=6.9 Hz), 1.25 (3H, t, *J*=7.6 Hz), 1.55-1.65 (1H, m), 1.68-1.88 (3H, m), 2.27-2.35 (1H, m), 3.04-3.12 (1H, m), 3.21 (2H, q, *J*=7.6 Hz), 3.44-3.47 (1H, m), 7.36-7.46 (3H, m), 7.68-7.74 (2H, m); ^{13}C-NMR ($CDCl_3$): δ 8.7 (CH_3), 18.8 (CH_3), 20.4 (CH_3), 20.5 (C), 21.2 (C), 26.4 (CH_2), 29.1 (CH), 29.1 (C), 30.2 (CH), 38.5 (CH_2), 124.8 (C), 127.7 (CH), 128.4 (CH), 128.4 (CH), 133.6 (C), 146.3 (C), 152.1 (C), 174.9 (C). *Anal.* Calcd for $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.02. Found: C, 77.43; H, 8.41; N, 9.05.

2-Butanoyl-3-phenylisomenthopyrazole (**5b**).

bp 140-150℃/ 10 mmHg; yield 76 %; $[\alpha]_D$: +35.0° (c 0.042, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.86 (3H, d, *J*=7.3 Hz), 0.97 (3H, d, *J*=6.6 Hz), 0.98 (3H, t, *J*=7.3 Hz), 1.10 (3H, d, *J*=6.9 Hz), 1.59-1.78 (6H, m), 2.38-2.46 (1H, m), 2.63-2.67 (1H, m), 2.78-2.84 (1H, m), 3.00-3.17 (2H, m), 7.27-7.31 (2H, m), 7.35-7.42 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 13.8 (CH_3), 17.9 (CH_3), 18.5 (CH_3), 19.4 (CH_3), 20.3 (CH_2), 21.0 (CH_2), 24.8 (CH_2), 29.8 (CH_2), 30.0 (CH), 37.1 (CH), 41.0 (CH), 126.5 (C), 128.0 (CH), 128.0 (C), 129.0 (CH), 132.2 (C), 140.5 (C), 155.3 (C), 173.0 (C). *Anal.* Calcd for $C_{21}H_{28}N_2O$: C, 77.74; H, 8.7; N, 8.63. Found: C, 77.90; H, 8.73; N, 8.66.

1-Butanoyl-3-phenylisomenthopyrazole (**6b**).

bp 140-150℃/ 10 mmHg; yield 13 %; $[\alpha]_D$: +45.0° (c 0.029, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.81 (3H, d, *J*=6.9 Hz), 1.00 (3H, d, *J*=6.9 Hz), 1.03 (3H, t, *J*=7.6 Hz), 1.08 (3H, d, *J*=6.9 Hz), 1.55-1.67 (1H, m), 1.69-1.86 (5H, m), 2.26-2.34 (1H, m), 3.05-3.25 (3H, m), 3.44-3.47 (1H, m), 7.37-7.47 (3H, m), 7.68-7.74 (2H, m); ^{13}C-NMR ($CDCl_3$): δ 13.7 (CH_3), 18.1 (CH_3), 18.8 (CH_3), 20.4 (CH_3), 20.6 (CH_2), 21.2 (C), 26.4 (C), 29.1 (CH_2), 30.3 (C), 37.5 (CH), 38.5 (C), 124.9 (C), 127.7 (C), 128.4 (CH), 128.4 (C), 133.7 (C), 146.3 (C), 152.1 (C), 174.2 (C). *Anal.* Calcd for $C_{21}H_{28}N_2O$: C, 77.74; H, 8.7; N, 8.63. Found: C, 77.82; H, 8.64; N, 8.73.

2-Phenylacetyl-3-phenylisomenthopyrazole (**5c**).

mp 105.5-106.5℃ (from aq. MeOH); yield 37 %; $[\alpha]_D$: +49.3° (c 0.046, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.84 (3H, d, *J*=6.9 Hz), 0.97 (3H, d, *J*=6.9 Hz), 1.12 (3H, d, *J*=6.9 Hz), 1.57-1.77 (4H, m), 2.44-2.51

(1H, m), 2.63-2.69 (1H, m), 2.79-2.85 (1H, m), 4.41 (2H, AB-q, *J*=14.8 Hz), 7.13-7.43 (10H, m); ^{13}C-NMR ($CDCl_3$): δ 18.5 (CH_3), 19.3 (CH_3), 20.3 (CH_3), 20.9 (CH_2), 24.8 (CH_2), 29.8 (CH), 29.9 (CH), 41.2 (CH), 42.0 (CH_2), 126.8 (C), 127.9 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 128.5 (C), 129.0 (CH), 129.9 (CH), 131.8 (C), 134.4 (C), 155.6 (C), 170.6 (C). *Anal.* Calcd for $C_{25}H_{28}N_2O$: C, 80.61; H, 7.58; N, 7.52. Found: C, 80.62; H, 7.64; N, 7.36.

1-Phenylacetyl-3-phenylisomenthopyrazole (**6 c**).

bp 180-190℃/ 7 mmHg; yield 11 %; $[\alpha]_D$: +49.7° (c 0.123, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.74 (3H, d, *J*=6.9 Hz), 0.93 (3H, d, *J*=6.9 Hz), 1.08 (3H, d, *J*=6.6 Hz), 1.52-1.85 (4H, m), 2.21-2.29 (1H, m), 3.08-3.11 (1H, m), 3.38-3.43 (1H, m), 4.51 (2H, AB-q, *J*=15.5 Hz), 7.26-7.49 (8H, m), 7.74-7.77 (2H, m); ^{13}C-NMR ($CDCl_3$): δ 18.6 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 21.0 (CH_2), 26.5 (CH_2), 29.1 (CH), 30.1 (CH), 38.5 (CH), 42.4 (CH_2), 125.4 (C), 127.0 (CH), 127.8 (CH), 128.3 (C), 128.5 (CH), 129.9 (CH), 133.5 (C), 134.4 (C), 146.7 (C), 171.8 (C). *Anal.* Calcd for $C_{25}H_{28}N_2O$: C, 80.61; H, 7.58; N, 7.52. Found: C, 80.48; H, 7.68; N, 7.51.

2-Acryloyl-3-phenylisomenthopyrazole (**5 d**).

Oil, yield 38 %; $[\alpha]_D$: -5.9° (c 0.034, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.87 (3H, d, *J*=6.9 Hz), 0.98 (3H, d, *J*=6.6 Hz), 1.11 (3H, d, *J*=6.6 Hz), 1.60-1.79 (4H, m), 2.41-2.49 (1H, m), 2.63-2.69 (1H, m), 2.84-2.88 (1H, m), 5.89 (1H, dd, *J*=10.6, 2.0 Hz), 6.51 (1H, dd, *J*=17.2, 1.7 Hz), 7.30-7.44 (5H, m), 7.62 (1H, dd, *J*=17.5, 10.6 Hz); ^{13}C-NMR ($CDCl_3$): δ 18.5 (CH_3), 19.3 (CH_3), 20.3 (CH_3), 20.9 (CH_2), 24.9 (CH_2), 29.8 (CH), 29.9 (CH), 41.1 (CH), 127.3 (C), 128.0 (CH), 128.3 (CH), 128.5 (CH), 128.5 (CH), 129.0 (CH), 131.3 (CH), 132.0 (C), 141.0 (C), 155.9 (C), 163.9 (C). *Anal.* Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.08. Found: C, 78.44; H, 7.92; N, 9.04.

1-Acryloyl-3-phenylisomenthopyrazole (**6 d**).

Oil, yield 30 %; $[\alpha]_D$: +6.4° (c 0.022, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.82 (3H, d, *J*=6.9 Hz), 1.02 (3H, d, *J*=6.9 Hz), 1.09 (3H, d, *J*=6.9 Hz), 1.54-1.93 (4H, m), 2.28-2.41 (1H, m), 3.07-3.15 (1H, m), 3.49-3.55 (1H, m), 5.95 (1H, dd, *J*=10.6, 2.0 Hz), 6.61 (1H, dd, *J*=17.2, 1.7 Hz), 7.32-7.47 (3H, m), 7.63-7.75 (2H, m), 7.71 (1H, dd, *J*=17.2, 10.6 Hz); ^{13}C-NMR ($CDCl_3$): δ 18.7 (CH_3), 20.4 (CH_3), 20.6 (CH_2), 21.0 (CH_3), 26.5 (CH_2), 29.2 (CH), 30.3 (CH), 38.6 (CH), 125.8 (C), 127.8 (CH), 128.5 (CH), 128.5 (CH), 128.9 (CH), 131.2 (CH), 133.5 (C), 146.8 (C), 152.5 (C), 165.0 (C). *Anal.* Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.08. Found: C, 77.69; H, 7.79; N, 8.72.

(S)-1-(α–Methoxy-α-trifluoromethylphenylacetyl)-3-phenylisomenthopyrazole (**5 f**).

Yield 22 %; ^{1}H-NMR ($CDCl_3$): δ 0.77 (3H, d, *J*=6.9 Hz), 0.99 (3H, d, *J*=6.6 Hz), 1.08 (3H, d, *J*=6.9 Hz), 1.51-1.63 (2H, m), 1.82-1.88 (2H, m), 2.42 (1H, oct, *J*=5.9 Hz), 3.03-3.17 (1H, m), 3.43-3.53 (1H, m), 3.54 (3H, s), 7.25-7.38 (8H, m), 7.56-7.60 (2H, m).

(S)-2-(α–Methoxy-α-trifluoromethylphenylacetyl)-3-phenylisomenthopyrazole (**6 f**).

Yield 47 %; ^{1}H-NMR ($CDCl_3$): δ 0.82 (3H, d, *J*=6.9 Hz), 0.89 (3H, d, *J*=6.9 Hz), 0.94 (3H, d, *J*=6.9 Hz), 1.51-1.62 (4H, m), 1.96-2.10 (1H, m), 2.22-2.29 (1H, m), 2.73-2.81 (1H, m), 3.66 (3H, s), 7.24-7.36 (6H, m), 7.40-7.47 (2H, m), 7.50-7.53 (2H, m).

General α-Methylation. To the solution of diisopropylamine (110 μL) in THF (3 mL), 0.5 mmol of butyllithium solution (1.6 M in hexane) was added under argon atmosphere at –5℃. After stirring for 30 min at –5℃, 2-acyl-3-phenylisomenthopyrazole (**5**, 0.28 mmol) in THF (1 mL) was added with the continuous stirring for 30 min. Methyl iodide (240 mg, 1.7 mmol) in THF (1 mL) was added at –5℃, and then the reaction mixture was warmed to rt with stirring for 6 h. The reaction mixture was quenched with acetic acid and the products were extracted with ether. The organic layer was washed with water, aqueous $NaHCO_3$, and aqueous saturated NaCl. After dried over anhydrous $MgSO_4$, the solvent was removed and the diastereomer ratio was revealed by GC and NMR of the residue. Then the residue was purified by preparative HPLC.

2-[(2R)-2-methylbutyryl]-3-phenylisomenthopyrazole ((*R*)-**5e**).

bp 160-170℃/ 9 mmHg; 6 %; $[\alpha]_D$: -22.3° (c 0.074, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.87 (3H, d, *J*=6.9 Hz), 0.90 (3H, t, *J*=7.6 Hz), 0.98 (3H, d, *J*=6.6 Hz), 1.10 (3H, d, *J*=6.9 Hz), 1.23 (3H, d, *J*=6.9 Hz), 1.42-1.83 (6H, m), 2.35-2.45 (1H, m), 2.61-2.69 (1H, m), 2.79-2.84 (1H, m), 3.79 (1H, sex, *J*=6.9 Hz), 7.25-7.32 (2H, m), 7.33-7.43 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 11.7 (CH_3), 17.2 (CH_3), 18.5 (CH_3), 19.6 (C), 20.2 (CH_3), 21.0 (CH_2), 24.8 (C), 26.3 (CH_2), 29.9 (C), 30.0 (CH), 39.8 (CH), 41.0 (CH), 126.5 (C), 127.9 (CH), 127.9 (CH), 128.9 (CH), 132.3 (C), 140.6 (C), 155.1 (C), 176.5 (C). *Anal.* Calcd for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 78.05; H, 8.88; N, 8.32.

2-[(2S)-2-methylbutyryl]-3-phenylisomenthopyrazole ((*S*)-**5e**).

bp 160-170℃/ 9 mmHg; yield 28 %; $[\alpha]_D$: -26.8° (c 0.030, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.85 (3H, d, *J*=6.9 Hz), 0.95 (3H, t, *J*=7.6 Hz), 0.98 (3H, d, *J*=6.6 Hz), 1.10 (3H, d, *J*=6.9 Hz), 1.19 (3H, d, *J*=6.9 Hz), 1.42-1.83 (6H, m), 2.35-2.45 (1H, m), 2.61-2.69 (1H, m), 2.79-2.84 (1H, m), 3.86 (1H, sex, *J*=6.9 Hz), 7.25-7.32 (2H, m), 7.33-7.43 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 11.7 (CH_3), 16.3 (CH_3), 18.5 (CH_3), 19.6 (C), 20.2 (CH_3), 21.0 (CH_2), 24.8 (C), 26.3 (CH_2), 27.3 (C), 30.0 (CH), 39.3 (CH), 41.0 (CH), 126.5 (C), 127.9 (CH), 127.9 (CH), 128.9 (CH), 132.3 (C), 140.6 (C), 155.1 (C), 176.5 (C). *Anal*. Calcd for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 78.39; H, 8.92; N, 8.43.

(2R)-2-(2-Phenylpropanoyl)-3-phenylisomenthopyrazole ((*R*)-**5g**).

Oil, yield 31 %; $[\alpha]_D$: +2.0° (c 0.050, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.87 (3H, d, *J*=7.3 Hz), 1.04 (3H, d, *J*=6.7 Hz), 1.13 (3H, d, *J*=6.9 Hz), 1.54 (3H, d, *J*=6.9 Hz), 1.57-1.73 (4H, m), 2.38-2.46 (1H, m), 2.56-2.60 (1H, m), 2.72-2.76 (1H, m), 5.24 (1H, q, *J*=6.9 Hz), 7.15-7.30 (5H, m), 7.35-7.41 (5H, m); ^{13}C-NMR ($CDCl_3$): δ 18.9 (CH_3), 19.1 (CH_3), 19.7 (CH_2), 20.2 (CH_3), 21.1 (CH_3), 24.7 (CH_2), 29.9 (CH), 30.1 (CH), 41.1 (CH), 43.9 (CH), 126.8 (CH), 127.0 (C), 127.9 (CH), 128.0 (CH), 128.2 (CH), 128.4 (CH), 129.0 (CH), 132.1 (C), 140.7 (C), 141.0 (C), 155.2 (C), 173.7 (C). *Anal.* Calcd for $C_{26}H_{30}N_2O$: C, 80.79; H, 7.82; N, 7.25. Found: C, 80.31; H, 7.92; N, 7.18.

(2S)-2-(2-Phenylpropanoyl)-3-phenylisomenthopyrazole ((*S*)-**5g**).

Oil, yield 22 %; $[\alpha]_D$: -2.9° (c 0.021, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.74 (3H, d, *J*=7.3 Hz), 0.84 (3H, d, *J*=6.6 Hz), 1.04 (3H, d, *J*=6.9 Hz), 1.48 (3H, d, *J*=6.9 Hz), 1.51-1.77 (4H, m), 2.39-2.47 (1H, m), 2.60-2.68 (1H, m), 2.80-2.86 (1H, m), 5.23 (1H, q, *J*=6.9 Hz), 7.16-7.44 (10H, m); ^{13}C-NMR ($CDCl_3$): δ 18.2 (CH_3), 18.3 (CH_3), 19.2 (CH_2), 20.1 (CH_3), 20.7 (CH_3), 24.8 (CH_2), 19.8 (CH), 41.1 (CH), 44.0

(CH), 126.6 (C), 126.8 (CH), 128.0 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH), 132.1 (C), 140.9 (C), 141.1 (C), 155.3 (C), 173.8 (C). *Anal.* Calcd for $C_{26}H_{30}N_2O$: C, 80.79; H, 7.82; N, 7.25. Found: C, 80.61; H, 7.84; N, 7.15.

General α-Benzoylation. To the solution of diisopropylamine (110 μL) in THF (3 mL), 0.5 mmol of butyllithium solution (300 μL, 1.6 M in hexane) was added under argon atmosphere at –5℃. After stirring for 30 min at –5℃, 2-acyl-3-phenylisomenthopyrazole (**5**, 0.28 mmol) in THF (1 mL) was added with the continuous stirring for 30 min. Benzoyl chloride (43 mg, 0.3 mmol) in THF (1 mL) was added at –5℃, and then the reaction mixture was warmed to rt with stirring for 6 h. The reaction mixture was quenched with acetic acid and the products were extracted with ether. The organic layer was washed with water and aqueous saturated NaCl. After dried over anhydrous $MgSO_4$, the solvent was removed. The residue was purified by silica gel column chromatography eluting with hexane–ethyl acetate mixture (v/v 10 : 1).

2-(2-Benzoylpropanoyl)-3-phenylisomenthopyrazole (**7a**).

mp 125-126℃ (from hexane); yield 65 %. *Anal*. Calcd for $C_{27}H_{30}N_2O_2$: C, 78.23; H, 7.29; N, 6.76. Found: C, 78.27; H, 7.69; N, 6.88.

(S)-Isomer: ^{1}H-NMR ($CDCl_3$): δ 0.77 (3H, d, *J*=6.9 Hz), 0.87 (3H, d, *J*=6.9 Hz), 0.87 (3H, d, *J*=6.9 Hz), 1.47 (3H, d, *J*=7.3 Hz), 1.52-1.72 (4H, m), 1.84-1.95 (1H, m), 2.33-2.42 (1H, m), 2.72-2.82 (1H, m), 5.49 (1H, q, *J*=7.3 Hz), 7.33-7.64 (8H, m), 8.00-8.04 (2H, m); ^{13}C-NMR ($CDCl_3$): δ 13.6 (CH_3), 18.3 (CH_3), 19.2 (CH_3), 20.0 (CH_2), 21.2 (CH_3), 24.7 (CH_2), 29.5 (CH), 29.8 (CH), 41.0 (CH), 48.5 (CH), 126.9 (C), 128.0 (CH), 128.5 (CH), 128.6 (CH), 128.9 (CH), 129.1 (CH), 131.3 (C), 132.9 (CH), 136.0 (C), 140.6 (C), 155.7 (C), 170.0 (C), 197.6 (C).

(R)-Isomer: ^{1}H-NMR ($CDCl_3$): δ 0.45 (3H, d, *J*=6.6 Hz), 0.74 (3H, d, *J*=7.3 Hz), 0.77 (3H, d, *J*=6.9 Hz), 1.46 (3H, d, *J*=7.3 Hz), 1.52-1.72 (4H, m), 1.81-1.86 (1H, m), 2.41-2.48 (1H, m), 2.83-2.88 (1H, m), 5.57 (1H, q, *J*=7.3 Hz), 7.33-7.64 (8H, m), 8.05-8.10 (2H, m); ^{13}C-NMR ($CDCl_3$): δ. 13.5 (CH_3), 17.6 (CH_3), 18.7 (CH_3), 19.8 (CH_2), 20.6 (CH_3), 24.7 (CH_2), 29.1 (CH), 29.8 (CH), 41.1 (CH), 48.0 (CH), 126.6 (C), 128.0 (CH), 128.2 (CH), 128.5 (CH), 128.9 (CH), 129.0 (CH), 131.3 (C), 133.1 (CH), 135.4 (C), 140.8 (C), 155.7 (C), 170.0 (C), 197.6 (C).

2-(2-Benzoylbutanoyl)-3-phenylisomenthopyrazole (**7b**).

Oil, yield 38 %. *Anal*. Calcd for $C_{28}H_{32}N_2O_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.53; H, 7.80; N, 6.62.

(S)-Isomer: ^{1}H-NMR ($CDCl_3$): δ 0.82 (3H, d, *J*=6.9 Hz), 0.88 (3H, d, *J*=7.3 Hz), 0.90 (3H, d, *J*=6.9 Hz), 1.00 (3H, t, *J*=7.3 Hz), 1.47-1.77 (4H, m), 1.82-1.97 (2H, m), 1.99-2.17 (1H, m), 2.44-2.52 (1H, m), 2.84-2.89 (1H, m), 5.42 (1H, d-d, *J*=7.6, 5.6 Hz), 7.26-7.62 (8H, m), 8.02-8.15 (2H, m); ^{13}C-NMR ($CDCl_3$): δ 12.6 (CH_3), 18.3 (CH_3), 19.1 (CH_3), 20.1 (CH_2), 21.2 (CH_3), 22.4 (CH_2), 24.8 (CH_2), 28.6 (CH), 29.5 (CH), 41.0 (CH), 55.2 (CH), 127.7 (C), 128.0 (CH), 128.5 (CH), 128.7 (CH), 128.9 (CH), 129.1 (CH), 131.8 (C), 132.9 (CH), 136.6 (C), 140.9 (C), 155.6 (C), 169.1 (C), 196.8 (C).

(R)-Isomer: ^{1}H-NMR ($CDCl_3$): δ 0.44 (3H, d, *J*=6.9 Hz), 0.76 (3H, d, *J*=7.3 Hz), 0.77 (3H, d, *J*=6.9 Hz), 1.00 (3H, t, *J*=7.3 Hz), 1.47-1.77 (4H, m), 1.82-1.97 (2H, m), 1.99-2.17 (1H, m), 2.44-2.52 (1H, m), 2.84-2.89 (1H, m), 5.50 (1H, d-d, *J*=8.6, 5.3 Hz), 7.26-7.62 (8H, m), 8.02-8.15 (2H, m); ^{13}C-

NMR ($CDCl_3$): δ 12.6 (CH_3), 17.5 (CH_3), 18.5 (C), 19.9 (CH_2), 20.6 (CH_3), 22.2 (CH_2), 24.7 (CH_2), 29.2 (CH), 29.8 (CH), 41.2 (CH), 54.8 (CH), 126.6 (C), 128.0 (CH), 128.2 (CH), 128.5 (CH), 128.9 (CH), 129.0 (CH), 131.3 (C), 133.1 (CH), 136.1 (C), 140.9 (C), 155.7 (C), 169.1 (C), 197.0 (C).

General Procedure for the Diels-Alder Reaction. A mixture of 2-acryloyl-3-phenylisomenthopyrazole (**5d**) (109 mg, 0.35 mmol) and $MgBr_2 \cdot OEt_2$ (91 mg, 0.35 mmol) in toluene (3 mL) was kept for 5 min at 32℃. Cyclopentadiene (100 μL) was added to the mixture and kept at 32 ℃ for another 3 h with stirring. The reaction mixture was quenched with water and extracted with ether. The organic layer was washed with 18 % hydrochloric acid, water, aqueous saturated $NaHCO_3$, and aqueous saturated NaCl, and dried over anhydrous $MgSO_4$. The solvent was removed. From the olefinic peak intensities in the ^{1}H NMR spectrum and/or the HPLC peaks, the diastereomer ratio was evaluated. The residue was then purified by preparative HPLC.

(2S)-endo-2-(Bicyclo[2,2,1]heptene-4'-carbonyl)-3-phenylisomenthopyrazole (*(S)-endo*-**8**)

Oil, yield 8 %; $[\alpha]_D$: -180.9° (c 0.039, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.84 (3H, d, *J*=6.9 Hz), 1.01 (3H, d, *J*=6.6 Hz), 1.13 (3H, d, *J*=6.9 Hz), 1.46 (2H, d, *J*=1.3 Hz), 1.49-1.92 (6H, m), 2.42-2.50 (1H, m), 2.63-2.70 (1H, m), 2.80-2.86 (1H, m), 2.92 (1H, s), 3.48 (1H, s), 4.13 (1H, dt, *J*=8.9, 4.3 Hz), 5.89 (1H, dd, *J*=5.6, 3.0 Hz), 6.21 (1H, dd, *J*=5.6, 3.0 Hz), 7.20-7.26 (2H, m), 7.32-7.40 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 18.5 (CH_3), 19.6 (CH_2), 20.3 (CH_3), 20.9 (CH_3), 24.8 (CH_2), 28.8 (CH_2), 29.8 (CH), 30.0 (CH_2), 41.0 (CH), 43.0 (CH), 43.9 (CH), 47.8 (CH_2), 50.4 (CH), 126.3 (C), 127.9 (CH), 128.0 (CH), 128.8 (CH), 131.2 (CH), 132.3 (C), 138.1 (CH), 140.7 (C), 155.0 (C), 173.6 (C). *Anal.* Calcd for $C_{25}H_{30}N_2O$: C, 80.17; H, 8.07; N, 7.48. Found: C, 79.71; H, 8.03; N, 7.58.

(2R)-endo-2-(Bicyclo[2,2,1]heptene-4'-carbonyl)-3-phenylisomenthopyrazole (*(R)-endo*-**8**)

Oil, yield 20 %; $[\alpha]_D$: 75.3° (c 0.046, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.85 (3H, d, *J*=6.9 Hz), 0.99 (3H, d, *J*=6.6 Hz), 1.11 (3H, d, *J*=6.9 Hz), 1.43 (3H, d, *J*=1.3 Hz), 1.46-1.79 (5H, m), 1.99-2.09 (1H, m), 2.39-2.47 (1H, m), 2.62-2.71 (1H, m), 2.90 (1H, s), 3.37 (1H, s), 4.06-4.13 (1H, m), 5.90 (1H, dd, *J*=5.6, 3.0 Hz), 6.14 (1H, dd, *J*=5.6, 3.0 Hz), 7.21-7.26 (2H, m), 7.32-7.39 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 18.6 (CH_3), 19.5 (CH_2), 20.2 (CH_3), 21.1 (CH_3), 24.8 (CH_2), 29.9 (CH_2), 30.1 (CH), 30.4 (CH_2), 41.1 (CH), 42.8 (CH), 44.3 (C), 47.0 (CH_2), 49.9 (CH), 126.1 (C), 127.9 (CH), 127.9 (CH), 128.9 (CH), 132.3 (C), 132.3 (CH), 137.4 (CH), 140.5 (C), 154.8 (C), 173.9 (C). *Anal.* Calcd for $C_{25}H_{30}N_2O$: C, 80.17; H, 8.07; N, 7.48. Found: C, 79.74; H, 7.94; N, 7.65.

exo-2-(Bicyclo[2,2,1]heptene-4'-carbonyl)-3-phenylisomenthopyrazole (*exo*-**8**)

Oil, yield 4 %.

(R)-Isomer: ^{1}H-NMR ($CDCl_3$): δ 0.87 (3H, d, *J*=6.9 Hz), 1.02 (3H, d, *J*=6.9 Hz), 1.10 (3H, d, *J*=6.6 Hz), 1.25-1.80 (7H, m), 1.92-2.03 (1H, m), 2.33-2.40 (1H, m), 2.59-2.68 (1H, m), 2.81-2.84 (1H, m), 2.90 (1H, s), 3.11 (1H, s), 3.46-3.53 (1H, m), 6.18-6.23 (2H, m), 7.25-7.31 (2H, m), 7.33-7.44 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 18.9 (CH_3), 19.9 (CH_2), 20.1 (CH_3), 21.1 (CH_3), 24.8 (CH), 29.9 (CH_2), 30.2 (CH), 30.6 (CH_2), 41.1 (CH), 41.9 (CH), 43.4 (CH), 46.0 (CH), 46.2 (CH_2), 126.3 (C), 128.0 (CH), 129.0 (CH), 129.0 (CH), 132.3 (C), 136.1 (CH), 138.2 (CH), 140.6 (C), 155.0 (C), 175.4 (C).

(S)-Isomer: ^{1}H-NMR ($CDCl_3$): δ 0.86 (3H, d, *J*=6.9 Hz), 0.97 (3H, d, *J*=6.9 Hz), 1.08 (3H, d, *J*=6.9 Hz), 1.25-1.80 (7H, m), 1.88-1.92 (1H, m), 2.33-2.40 (1H, m), 2.59-2.68 (1H, m), 2.81-2.84 (1H, m), 2.90 (1H, s), 3.07 (1H, s), 3.41-3.46 (1H, m), 6.18-6.23 (2H, m), 7.25-7.31 (2H, m), 7.33-7.44 (3H, m); ^{13}C-NMR ($CDCl_3$): δ 18.7 (CH_3), 19.7 (CH_2), 20.1 (CH_3), 21.1 (CH_3), 24.8 (CH), 29.9 (CH_2), 30.1 (CH), 32.0 (CH_2), 41.1 (CH), 41.9 (CH), 43.6 (CH), 46.7 (CH_2), 47.2 (CH), 126.4 (C), 128.0 (CH), 129.0 (CH), 129.0 (CH), 132.3 (C), 136.1 (CH), 138.1 (CH), 140.6 (C), 155.0 (C), 175.8 (C).

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