Stereoselective synthesis of *trans*-2,6-diaryl-4-piperidones by using benzaldiminetricarbonylchromium derivatives

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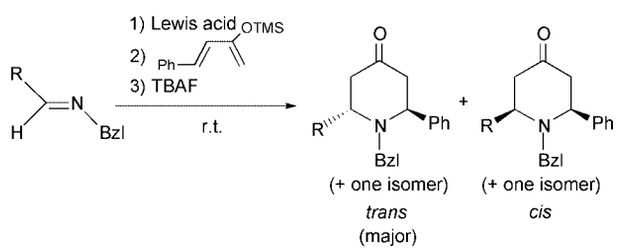
Stereoselective synthesis of *trans*-2,6-diaryl-4-piperidones has been carried out by cycloaddition of benzaldiminetricarbonylchromium derivatives **1** with 2-silyloxybuta-1,3-diene in the presence of trimethylsilyl triflate as a Lewis acid. The tricarbonylchromium moiety played an important role in increasing the stereoselectivities of the products.

Introduction

Aza-Diels–Alder reaction of aldimines with dienes is widely known as a powerful method for the construction of various piperidones or piperidine derivatives that are contained in numerous alkaloids.[1] Asymmetric cycloaddition with Brassard's diene or Danishefsky's diene using chiral auxiliaries,[2] chiral Lewis acids,[3] or chiral tricarbonylchromium complexes of substituted benzaldimines (benzylideneamines)[4] has received considerable attention and has been used to create a new chiral carbon center piperidones. Despite the great potential of the cycloaddition, reports on one-pot preparation of piperidones having more than two new chiral carbons are still rare.[5,6] Recently, Barluenga *et al.* have demonstrated that the cycloaddition of α-arylaldimines with 2-aminobuta-1,3-dienes gives 4-piperidones with two new chiral carbons at the 2- and 6-positions,[5d] but an unremovable *N*-aryl group is needed to obtain *trans*-piperidones.

In our previous work, we have described the synthesis of the *trans*-2,6-disubstituted-4-piperidones by a [4 + 2] type cycloaddition of *N*-benzylaldimines with 2-silyloxybuta-1,3-dienes in the presence of trimethylsilyl triflate, and the diastereoselectivities of the products were increased with an increase in the bulkiness of the α-substituent of the aldimine (Scheme 1).[6a]



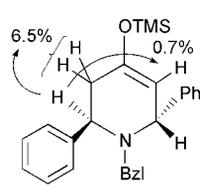
R = Pr, TMSOTf, 74 % de, 52 % yield
Pr^{i}, TMSOTf, 96 % de, 65 % yield
Ph, TMSOTf, 62 % de, 97 % yield
Ph, BF_3•Et_2O, 70 % de, 95 % yield

Scheme 1

With benzaldimine, however, high diastereoselectivities were not observed because of the moderate bulkiness of the aromatic ring at the α-position of the aldimine (up to 70% de, Scheme 1). To circumvent this problem, we envisioned that the use of benzaldimine derivatives attached to a tricarbonylchromium moiety[7] as a bulky substituent would be effective for the diastereocontrol, and the planar chiral tricarbonyl(1,2- or 1,3-disubstituted arene)chromium complexes[8] enhanced the enantioselectivities of the piperidones. To our knowledge, highly stereoselective and general synthesis of *trans*-2,6-diaryl-4-piperidones has not yet been reported.

Results and discussion

The chromium complexes **1** (Scheme 2) were prepared from tricarbonylchromium complexes of *o*- or *p*-substituted benzaldehydes according to the similar method described in the literature.[7b,9] The cycloaddition of the chromium complex **1a** with 2-silyloxybuta-1,3-diene was carried out in the presence of a Lewis acid. After work-up, a solution of the resulting crude cycloadducts **2a** and **3a** in dichloromethane was exposed to air and sunlight, and then treated with TBAF to remove the TMS group giving two diastereomers **6a** and **7a**. The diastereomeric ratio (*trans*:*cis*) was determined from the ^{1}H NMR spectrum of the crude products, and the diastereomers **6a** and **7a** were purified by flash column chromatography (*n*-hexane–CH_3COOEt = 2:1). The relative stereochemistry of the major diastereomer **4a**, which was separated as a pure diastereomer



4a

before deprotection of TMS group, was *trans* as found by DIFNOE experiments. Table 1 summarizes some of our results under a variety of reaction conditions involving different temperatures, solvents, and Lewis acids (TMSOTf, TIPSOTf, BF_3·Et_2O, $TiCl_4$, $ZnCl_2$, $EtAlCl_2$, Et_2AlCl, and $SnCl_4$).

The reaction of **1a** in the presence of trimethylsilyl triflate gave 80% de of the product (entry 1 in Table 1) which was a higher de compared to that with benzaldimine (62% de, Scheme 1). Though the reaction of benzaldimine in the presence of BF_3·Et_2O gave 70% de of the product (Scheme 1), small amounts of the cycloadducts were detected in the reaction of the chromium complex **1a** (entry 4 in Table 1). Titanium tetrachloride gave decomposed product even at −78 °C (entry 5) and catalytic amounts of TMSOTf (0.1 equiv.) lowered the diastereoselectivity (66% de, entry 6).

By using the optimized conditions (TMSOTf at room temperature), the reactions of **1b** and **1c** yielded the cycloadducts

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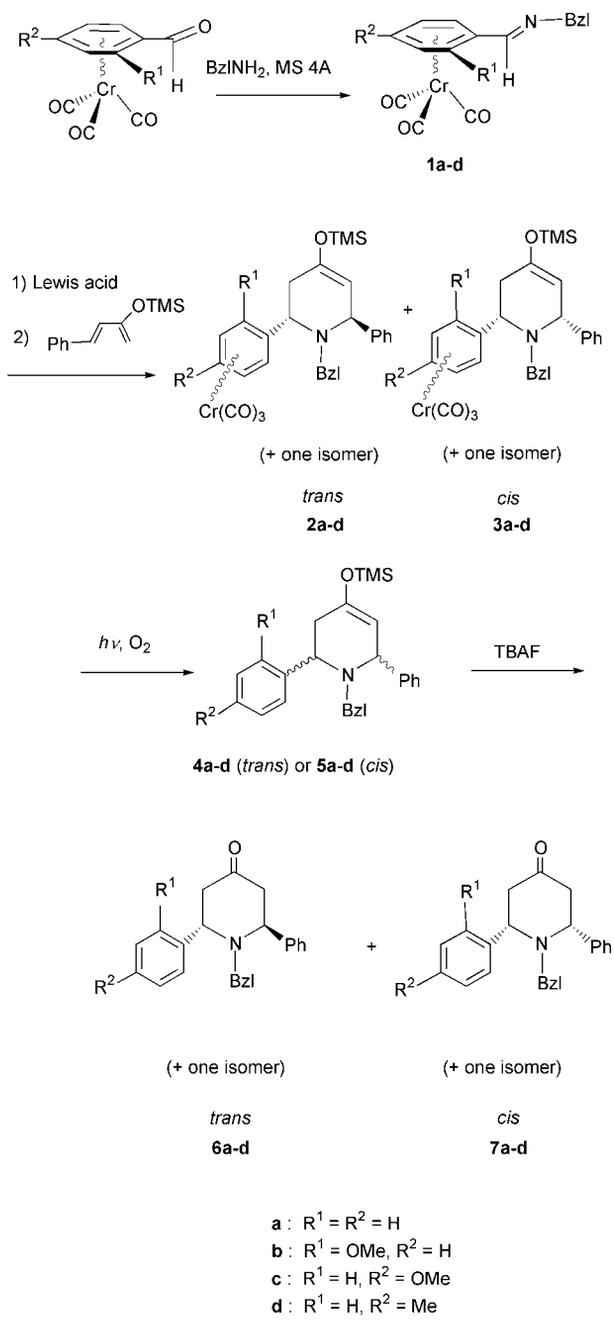
Table 1 Diastereoselectivities in the cycloaddition of benzaldiminetricarbonylchromium complexes **1** with 2-silyloxylbuta-1,3-diene[a]

Entry	Chromium complex	Lewis acid	Conditions	De (%)	Yield (%)[b]
1	**1a**	TMSOTf	rt, 3 h	80	84
2	**1a**	TMSOTf	0 °C, 12 h	76	70
3	**1a**	TMSOTf	40 °C, 1 h	80	66
4	**1a**	$BF_3{\cdot}Et_2O$	rt, 12 h	—[c]	<30
5	**1a**	$TiCl_4$	−78 °C, 30 min	70	30
6	**1a**	TMSOTf[d]	rt, 12 h	66	64
7	**1b**	TMSOTf	rt, 12 h	80	70
8	**1c**	TMSOTf	rt, 12 h	80[e]	78
9	**1d**	TMSOTf	rt, 12 h	>98[e]	90

[a] All cycloadditions were carried out with 2 equiv. of 2-silyloxybuta-1,3-diene in the presence of 1 equiv. of Lewis acid in dichloromethane. Desilylation was performed by using 1 equiv. of TBAF in THF. [b] Yields of isolated products after chromatography. [c] The de could not be determined. [d] 0.1 equiv. of TMSOTf. [e] The relative stereochemistry of the major diastereomer was not established.

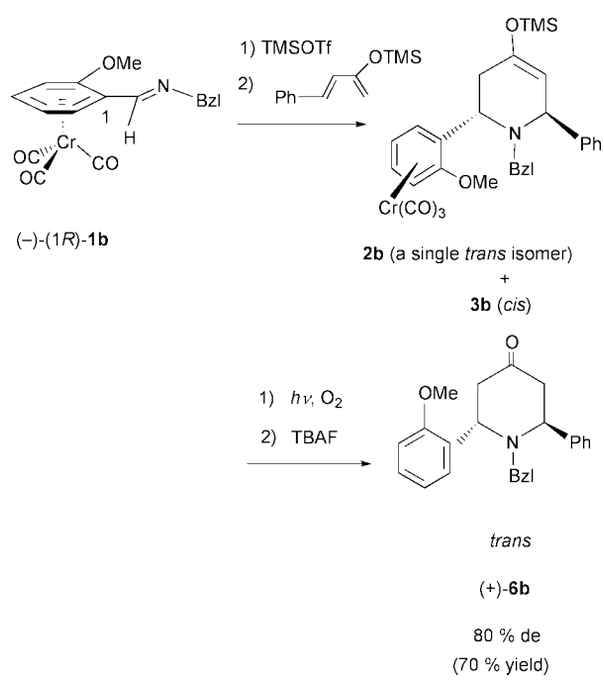


a : $R^1 = R^2 = H$
b : R^1 = OMe, R^2 = H
c : R^1 = H, R^2 = OMe
d : R^1 = H, R^2 = Me

Scheme 2

with high diastereocontrol (80% de, entries 7 and 8). No *cis* isomer was detected in the case of **1d** (>98% de, 90% yield, entry 9).

With these results in hand, the cycloaddition was carried out with (−)-(1*R*)-**1b** which was prepared from (−)-(1*R*)-*o*-anisaldehydetricarbonylchromium complex (Scheme 3).[10] The



Scheme 3

optical purity of the (−)-(1*R*)-*o*-anisaldehyde chromium complex was confirmed by using $Eu(hfc)_3$ in $CDCl_3$ according to the literature procedure,[11] and the enantiopure complex was converted to (−)-(1*R*)-**1b** ($[a]_D$ −62, *c* 0.19 in $CHCl_3$). After the cycloaddition, we tried to confirm the enantiopurity of *trans*-piperidone (+)-**6b** by using shift reagents or HPLC analysis, but were unsuccessful. However, the cycloaddition was completely facially diastereoselective because the ^1H NMR spectrum of the crude mixture of **2b** (*trans*) and **3b** (*cis*) showed that **2b** was a single *trans* isomer, indicating that the *trans*-piperidone (+)-**6b** should be the pure enantiomer ((+)-**6b**: $[a]_D$ +11, *c* 0.06 in $CHCl_3$. The absolute stereochemistry was not determined).

Whether the mechanism of the cycloaddition is stepwise or concerted is a matter of debate,[2b,c] but the stereochemical course of the reaction can be explained by the assumed transition state as depicted in Fig. 1. The formation of the *cis* isomer might be less favorable due to the steric interactions between the bulky aromatic ring of aldimines with a $Cr(CO)_3$ moiety and silyloxybutadiene, and the silyloxydiene might attack the opposite face of the tricarbonylchromium moiety to allow stereoselective reaction.

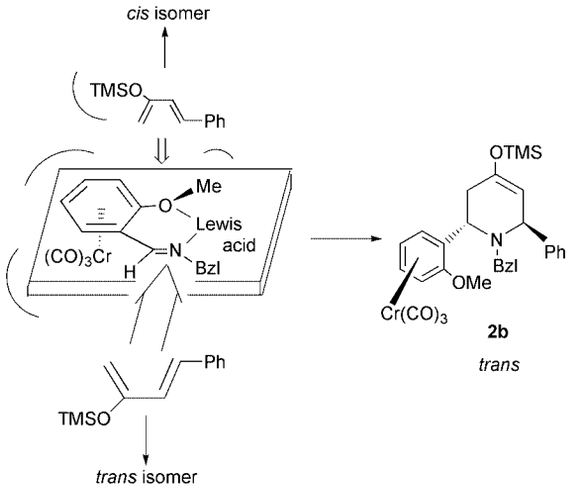


Fig. 1 Possible mechanism for the cycloaddition.

Experimental

All reactions were performed with oven-dried glassware under argon except for the irradiation procedure. Flash column chromatography was carried out with Merck silica gel 60 (0.063–0.200 mm) and silica gel 60N (spherical, neutral, Kanto Chemical Co.). All NMR spectra were recorded at 500 MHz (^{1}H and DIFNOE) or 125.7 MHz (^{13}C) on a Bruker DMX 500 instrument at room temperature using TMS as an internal standard. Chemical shifts δ are given in ppm relative to TMS, and *J*-values are given in Hz. Optical rotations were measured using a JASCO P-1020 polarimeter with a thermally jacketed cell at 20 °C (concentration *c* given as g mL^{-1}). High-resolution mass spectra were measured with a JEOL SX-102A spectrometer at the Instrument Center for Chemical Analysis, Hiroshima University. IR spectra were measured using a JASCO FT IR-230 spectrometer.

Preparation of benzaldiminetricarbonylchromium derivatives 1

To a stirred solution of benzaldehydetricarbonylchromium complex (3.1 mmol) and molecular sieves 4 Å (0.5 g) in dry diethyl ether (10 mL) was added 0.34 mL (3.1 mmol) of benzylamine under argon at room temperature. The reaction mixture was stirred at room temperature for 7 days in the dark, the molecular sieves were filtered off, and the solvent was evaporated. The crude product was recrystallised (dichloromethane–*n*-hexane 1 : 5) to give pure **1** as orange crystals (**1a**: 910 mg, 89% yield; **1b**: 894 mg, 80%; **1c**: 907 mg, 81%; **1d**: 751 mg, 70%). **1a**: δ_H (500 MHz; $CDCl_3$; Me_4Si) 4.71 (s, 2 H, CH_2), 5.27–5.36 (m, 3 H, ArCr), 5.78–5.79 (m, 2 H, ArCr), 7.18–7.35 (m, 5 H, Ph), 7.84 (s, 1 H, CH). **1b**: δ_H (500 MHz; $CDCl_3$; Me_4Si) 3.84 (s, 3 H, OMe), 4.78 (s, 2 H, CH_2), 4.97–4.98 (m, 1 H, ArCr), 5.08–5.09 (m, 1 H, ArCr), 5.67–5.68 (m, 1 H, ArCr), 6.50–6.51 (m, 1 H, ArCr), 7.26–7.34 (m, 5 H, Ph), 8.46 (s, 1 H, CH). **1c**: δ_H (500 MHz; $CDCl_3$; Me_4Si) 3.74 (s, 3 H, OMe), 4.72 (s, 2 H, CH_2), 5.17–5.18 (m, 2 H, ArCr), 6.06–6.07 (m, 2 H, ArCr), 7.28–7.34 (m, 5 H, Ph), 7.84 (s, 1 H, CH). **1d**: δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.24 (s, 3 H, Me), 4.75 (s, 2 H, CH_2), 5.18–5.19 (m, 2 H, ArCr), 5.93–5.94 (m, 2 H, ArCr), 7.26–7.36 (m, 5 H, Ph), 7.89 (s, 1 H, CH).

Typical procedure for cycloaddition of benzaldiminetricarbonylchromium derivatives 1 with 2-silyloxybuta-1,3-diene

To a stirred solution of the benzaldiminetricarbonylchromium complex (0.5 mmol) in dry dichloromethane (3 mL) was added 0.5 mmol of trimethylsilyl triflate and 1 mmol of 2-silyloxybuta-1,3-diene at room temperature. The reaction mixture was stirred at room temperature for 3–12 h, quenched with saturated aqueous $NaHCO_3$ (30 mL), and the mixture was extracted with dichloromethane (20 mL × 3). After the combined organic layers had been dried over $MgSO_4$, the solution was exposed to atmospheric oxygen and sunlight for 3 h with vigorous stirring. The solvent was evaporated, ether was added to the mixture, and the green precipitate was filtered off. The solvent was evaporated to give crude cycloadducts **4** and **5**. The crude mixture of **4** and **5** was dissolved in THF (5 mL), and TBAF in THF (0.5 mL, 1.0 M solution) was added to it at room temperature. The reaction mixture was stirred at room temperature for 1 h, quenched with H_2O (50 mL), and the mixture was extracted with dichloromethane (20 mL × 3). The combined organic phases were collected and dried ($MgSO_4$), and the solvent was evaporated. The crude products were purified by flash column chromatography (CH_3COOEt–*n*-hexane = 1 : 2) to give *trans*- and *cis*-2,6-diaryl-4-piperidones (**6a**+**7a**: 143 mg, 84% yield; **6b**+**7b**: 129 mg, 70%; **6c**+**7c**: 146 mg, 78%; **6d**: 159 mg, 90%). The diastereomers **6** and **7** were separated by flash column chromatography on neutral silica gel for further analysis (CH_3COOEt–*n*-hexane = 1 : 4).

The DIFNOE experiments on **4a** and **7b** were performed to determine the relative stereochemistry at the 2- and 6-positions of the piperidones, but in the case of **6c** (or **7c**) and **6d** (or **7d**), the ^{1}H NMR signals for the 2- and 6-positions of the piperidones were too close to determine the relative stereochemistries even when other solvents (C_6D_6, THF-d_8, or MeOH-d_4) were used. The NOE of **4a** might allow the relative stereochemistry of **6a** to be deduced because the *trans* : *cis* ratio of crude silyloxy compound (**4a**+**5a**) and that of crude piperidone (**6a**+**7a**) were the same, indicating that *trans*–*cis* isomerism did not occur under the desilylation procedure.

***trans*-*N*-Benzyl-2,6-diphenyl-4-piperidone 6a.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.85 (dd, 2 H, *J* 16.0, 7.0, CHCO), 2.91 (dd, 2 H, *J* 14.6, 5.1, CHCO), 3.37 (d, 1 H, *J* 14.2, CH_2Ph), 3.64 (d, 1 H, *J* 14.2, CH_2Ph), 4.29–4.31 (m, 2 H, CH), 7.08–7.43 (m, 15 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 43.4 (CH_2), 50.8 (CH_2), 58.7 (CH), 125.4, 127.5, 128.0, 128.4, 128.5, 128.8, 129.0, 130.5, 140.6, 143.3 (Ar), 209.4 (CO); ν(neat)/cm^{-1} 3061, 3028, 1714, 1495, 1450, 766, 698; HRFAB-MS: obsd *m*/*z* 342.1841. Calcd for $C_{24}H_{24}NO$: 342.1858 (M + H)$^+$.

***cis*-*N*-Benzyl-2,6-diphenyl-4-piperidone 7a.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.50 (dd, 2 H, *J* 15.3, 3.3, CHCO), 2.77 (dd, 2 H, *J* 14.1, 15.3, CHCO), 3.69 (s, 2 H, CH_2Ph), 3.95 (dd, 2 H, *J* 14.1, 3.3, CH), 6.84–7.53 (m, 15 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 50.6 (CH_2), 53.2 (CH_2), 64.6 (CH), 126.8, 127.5, 127.6, 128.0, 128.3, 128.8, 129.7, 129.8, 136.1, 143.1 (Ar), 207.3 (CO); ν(neat)/cm^{-1} 3062, 3028, 1722, 1493, 1454, 756, 700; HRFAB-MS: obsd *m*/*z* 342.1852. Calcd for $C_{24}H_{24}NO$: 342.1858 (M + H)$^+$.

***trans*-*N*-Benzyl-2-(2-methoxyphenyl)-6-phenyl-4-piperidone 6b.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.62–2.90 (m, 4 H, CHCO), 3.20 (d, 1 H, *J* 14.6, CH_2Ph), 3.63 (d, 1 H, *J* 14.6, CH_2Ph), 3.67 (s, 3 H, OMe), 4.27 (dd, 1 H, *J* 5.7, 5.4, CH), 4.59 (dd, 1 H, *J* 5.6, 5.4, CH), 7.11–7.49 (m, 14 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 44.8 (CH_2), 46.3 (CH_2), 51.9 (CH_2), 54.4 (CH), 54.6 (OCH_3), 60.3 (CH), 111.1, 120.3, 126.7, 127.2, 128.1, 128.2, 128.3, 128.4, 128.8, 129.0, 130.5, 134.4, 143.4, 157.6 (Ar), 208.6 (CO); ν(neat)/cm^{-1} 3061, 3028, 2960, 2837, 1713, 1493, 1450, 1255, 1028, 750, 694; HRFAB-MS: obsd *m*/*z* 372.1969. Calcd for $C_{25}H_{26}NO_2$: 372.1964 (M + H)$^+$.

***cis*-*N*-Benzyl-2-(2-methoxyphenyl)-6-phenyl-4-piperidone 7b.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.49–2.53 (m, 2 H, CHCO), 2.66 (dd, 1 H, *J* 13.5, 11.7, CHCO), 2.77 (dd, 1 H, *J* 13.6, 11.5, CHCO), 3.65 (d, 1 H, *J* 14.7, CH_2Ph), 3.71 (d, 1 H, *J* 14.7, CH_2Ph), 3.83 (s, 3 H, OMe), 3.95 (dd, 1 H, *J* 11.5, 3.3, CH), 4.48 (dd, 1 H, *J* 11.7, 3.5, CH), 7.03–7.59 (m, 14 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 43.6 (CH_2), 50.5 (CH_2), 53.3 (CH_2),

55.1 (OCH_3), 56.5 (CH), 64.2 (CH), 110.6, 121.1, 126.3, 126.7, 127.5, 128.0, 128.2, 128.4, 128.8, 129.6, 129.9, 130.9, 136.2, 143.5, 156.1 (Ar), 208.0 (CO); ν(neat)/cm^{-1} 3028, 2962, 2837, 1716, 1491, 1456, 1248, 1028, 758, 702; HRFAB-MS: obsd *m*/*z* 372.1978. Calcd for $C_{25}H_{26}NO_2$: 372.1964 $(M + H)^+$.

***trans*-*N*-Benzyl-2-(4-methoxyphenyl)-6-phenyl-4-piperidone 6c.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.79–2.87 (m, 4 H, CHCO), 3.36 (d, 1 H, *J* 14.0, CH_2Ph), 3.62 (d, 1 H, *J* 14.0, CH_2Ph), 3.79 (s, 3 H, OMe), 4.24–4.29 (m, 2 H, CH), 7.21–7.56 (m, 14 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 43.6 (CH_2), 50.7 (CH_2), 55.2 (OCH_3), 55.5 (CH_2), 58.7 (CH), 60.4 (CH), 113.8, 127.1, 127.5, 127.9, 128.2, 128.4, 128.5, 128.9, 129.1, 130.5, 132.4, 140.7, 143.4, 158.8 (Ar), 209.5 (CO); ν(neat)/cm^{-1} 3061, 3030, 2958, 2837, 1711, 1495, 1450, 1255, 1032, 746, 700; HRFAB-MS: obsd *m*/*z* 371.1866. Calcd for $C_{25}H_{25}NO_2$: 371.1885.

***cis*-*N*-Benzyl-2-(4-methoxyphenyl)-6-phenyl-4-piperidone 7c.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.39–2.43 (m, 2 H, CHCO), 2.60 (dd, 2 H, *J* 13.0, 12.0, CHCO), 3.58 (d, 1 H, *J* 15.0, CH_2Ph), 3.61 (d, 1 H, *J* 15.0, CH_2Ph), 3.75 (s, 3 H, OMe), 3.82 (dd, 1 H, *J* 11.2, 3.0, CH), 3.86 (dd, 1 H, *J* 12.0, 3.1, CH), 6.77–7.44 (m, 14 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 43.6 (CH_2), 50.7 (CH_2), 53.4 (CH_2), 55.3 (OCH_3), 58.7 (CH), 64.2 (CH), 114.1, 126.7, 127.1, 127.5, 127.9, 128.4, 128.5, 128.6, 128.8, 129.7, 135.1, 136.4, 143.1, 158.9 (Ar), 209.6 (CO); ν(neat)/cm^{-1} 3030, 2964, 2835, 1716, 1495, 1454, 1252, 1032, 760, 702; HRFAB-MS: obsd *m*/*z* 371.1880. Calcd for $C_{25}H_{25}NO_2$: 371.1885.

***trans*-*N*-Benzyl-2-(4-methylphenyl)-6-phenyl-4-piperidone 6d.** Colorless oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.20 (s, 3 H, CH_3), 2.68–2.80 (m, 4 H, CHCO), 3.24 (d, 1 H, *J* 14.0, CH_2Ph), 3.51 (d, 1 H, *J* 14.0, CH_2Ph), 4.15–4.17 (m, 2 H, CH), 7.04–7.28 (m, 14 H, ArH); δ_C (125.7 MHz; $CDCl_3$) 27.5 (CH_3), 31.5 (CH_2), 43.7 (CH_2), 50.8 (CH_2), 58.7 (CH), 60.3 (CH), 127.1, 127.4, 127.9, 128.2, 128.3, 128.4, 128.5, 128.9, 130.5, 134.4, 137.4, 140.6, 143.4 (Ar), 209.4 (CO); ν(neat)/cm^{-1} 3028, 1714, 1495, 1450, 748, 692; HRFAB-MS: obsd *m*/*z* 355.1918. Calcd for $C_{25}H_{25}NO$: 355.1936.

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