JOC Article

Diastereoselective Protonation on Radical Anions of Electron-Deficient Alkenes via Photoinduced Electron Transfer

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Diastereoselective protonations in the photoinduced electron transfer (PET) reactions of 1,1-dicyanoethene derivatives (**1a**−**e**) by use of organosilicon compounds such as allyltrimethylsilane (**2**) and benzyltrimethylsilane (**5**) are described. Irradiation of an acetonitrile−acetic acid solution containing 4-*tert*-butylcyclohexylidenepropanedinitrile (**1a**) and an excess of **2** in the presence of phenanthrene (Phen) as a sensitizer afforded reduction and allylated products (**3a**, **4a**) in 63:37 and 57:43 ratios in a less regioselective manner. Photoreactions of 3,3,5-trimethylcyclohexylidenepropanedinitrile (**1b**), 2-methylcyclohexylidenepropanedinitrile (**1c**), bicyclo[2.2.1]-2-heptylidenepropanedinitrile (**1d**), and 1,7,7-trimethylbicyclo[2.2.1]-2-heptylidenepropanedinitrile (**1e**) with **2** showed higher diastereoselectivity via the PET process. Similar diastereoselectivities were obtained in the Phen-sensitized photoreaction of **1a**−**e** with **5**. When 2,4,6-trimethylpyridinium tosylate (**7**) was used as a proton source in place of acetic acid, the product ratios were substantially changed in several cases. From these results, steric and torsional effects have been postulated as important factors for the control of the diastereoselectivity in these PET reactions.

Introduction

The photochemistry of organosilicon compounds has been extensively investigated not only from synthetic and mechanistic perspectives but also in terms of their chemical and physical properties.[1] In the area of synthetic organic photochemistry, silyl substituents are developed as the direct protection of functional groups, their indirect protection by steric bulkiness, and the activation of organic molecules.[2] One most characteristic property of some organosilicon compounds such as allylic silanes is that they have lower oxidation potentials compared to those of the corresponding carbon compounds. Therefore, some selected organosilicon compounds can be used as excellent electron donors in PET reactions. For example, the photoallylation, benzylation, alkylation, and silylation of a variety of electron-deficient compounds such as iminium salts, cyanoaromatic compounds, cyanoalkenes, and carbonyl compounds by use of organosilicon compounds were developed.[3−13] In these photoreactions, radical anions or free radicals generated from the electron-deficient molecules and carbon radicals such as allylic radicals generated from radical cations of the organosilicon compounds were postulated as the reactive intermediates. Because of detailed studies of the syntheticand mechanistic aspects of these photoinduced carbon-functionalization reactions, many useful photoreactions have appeared in the past 2 decades, but the stereochemical control of PET reactions via radical ions has

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not been satisfactory, except for some intramolecular reactions.[14,15]

We have previously reported a highly stereoselective carbon functionalization of 2-substituted 1-dicyanomethylene-1,2,3,4-tetrahydronaphthalenes to give allylated and benzylated products having a quaternary carbon atom via the PET process.[5f] In this photoreaction, the bulkiness of substituents at the 2 position is critical for the stereoselectivity of the products, and the key step is the attack of the allyl radical to the free radical anions of 1-dicyanomethylene-1,2,3,4-tetrahydronaphthalenes.

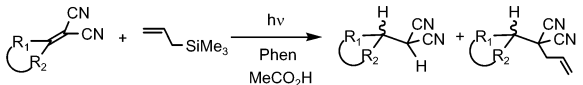
We have also reported the photoallylation of cyclohexylidenepropanedinitrile depending on the pK_a values of additives.[5g] However, there is no description of the stereochemical control in the photoallylation of cyclohexylidenepropanedinitrile.

We now report a novel diastereoselective protonation of alkylidenepropanedinitriles **1a**−**e** followed by allylation by the use of allyltrimethylsilane (**2**) via the PET process. We have succeeded in highly diasteroselective photoreduction and photoallylation depending on the proton source and the alkylidenepropanedinitriles. Plausible mechanisms for the regio- and diastereoselective photoreactions are also described.

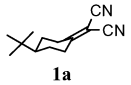
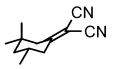
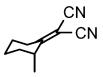
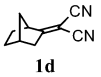
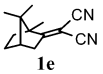
Results and Discussion

Photoallylation and Benzylation of Alkylidenepropanedinitriles in the Presence of Acetic Acid. Irradiation of an acetonitrile−acetic acid solution containing 4-*tert*-butylcyclohexylidenepropanedinitrile (**1a**) and an excess of **2** in the presence of phenanthrene (Phen) as a sensitizer with a 300 W high-pressure mercury lamp through a Pyrex filter (>280 nm light) afforded two kinds of products, reduction products **3a** and allylated products **4a** in ***cis***-**3a**:***trans***-**3a** = 63:37 and ***cis***-**4a**:***trans***-**4a** = 57:43 ratios in 15 and 51% yields, respectively (Scheme 1, reaction 1 and Table 1, run 1). The photoreactions of **1b**−**e** under the same reaction conditions also gave the corresponding reduction products **3b**−**e** and allylated products **4b**−**e** (Scheme 1, reactions 2−5 and Table 1, runs 2−5). Yields and product ratios are summarized in Table 1. Higher diastereoselectivity was observed in the cases of **1b**, **1d**, and **1e**. Similar photoreactions of **1a**−**e** with benzyltrimethylsilane (**5**) in the presence of Phen afforded the reduction and benzylated products **3a**−**e** and **6a**−**e** in almost the same ratios compared to the photoreaction of **1a**−**e** with **2** (Table 2). All of these products were isolated by column chromatography on silica gel and preparative HPLC. In these photoreactions, Phen was recovered almost quantitatively. The structures of these photoproducts were determined by their spectral properties, and some of them were determined by X-ray crystallographic analyses.

TABLE 1. Diastereoselective Photoreduction and Photoallylation of 1 in the Presence of 2 and Acetic Acid[a]



1 2 3 4

run	substrate	products	yields[b] / % (ratio)[c,d]	
1	 **1a**	**3a 4a**	15 (63 : 37)	51 (57 : 43)
2	 **1b**	**3b 4b**	19 (12 : 88)	44 (16 : 84)
3	 **1c**	**3c 4c**	11 (62 : 38)[e]	35 (63 : 37)
4	 **1d**	**3d 4d**	16 (82 : 18)[f]	46 (85 : 15)[f]
5	 **1e**	**3e 4e**	19 (78 : 22)[e,f]	45 (82 : 18)[f]

[a] Irradiation was carried out at room temperature for 8 h. [**1**] = 0.085 M, [**2**] = 0.255 M, [Phen] = 0.018 M, [$MeCO_2H$] = 0.170 M. [b] Isolated yields of two isomers. [c] Determined by GC−MS. [d] *cis*/*trans* ratio. [e] Determined by ^{1}H NMR. [f] *endo*/*exo* ratio.

Stereochemistry of Photoproducts 4, 5, and 6. The stereochemistry of some selected photoproducts has been determined by X-ray crystallographic analyses. Single crystals of ***trans***-**6a**, ***trans***-**6b**, ***cis***-**6c**, ***exo***-**6d**, and ***exo***-**6e** were obtained by slow evaporation of the methanol solutions. ORTEP drawings and crystallographic data are shown in Supporting Information. We decided the *cis*/*trans* and *endo*/*exo* ratios of products on the basis of the results, which are summarized in Table 2. The stereochemistry of the reduction products **3a**−**e** was determined by comparison with the authentic samples after conversion into the benzylated products **6**. Treatment of **3a**−**e** with NaH followed by the reaction with benzyl bromide in THF afforded **6a**−**e** in high yields. The stereochemistry of **4a**−**e** as shown in Table 1 was determined in a similar manner.

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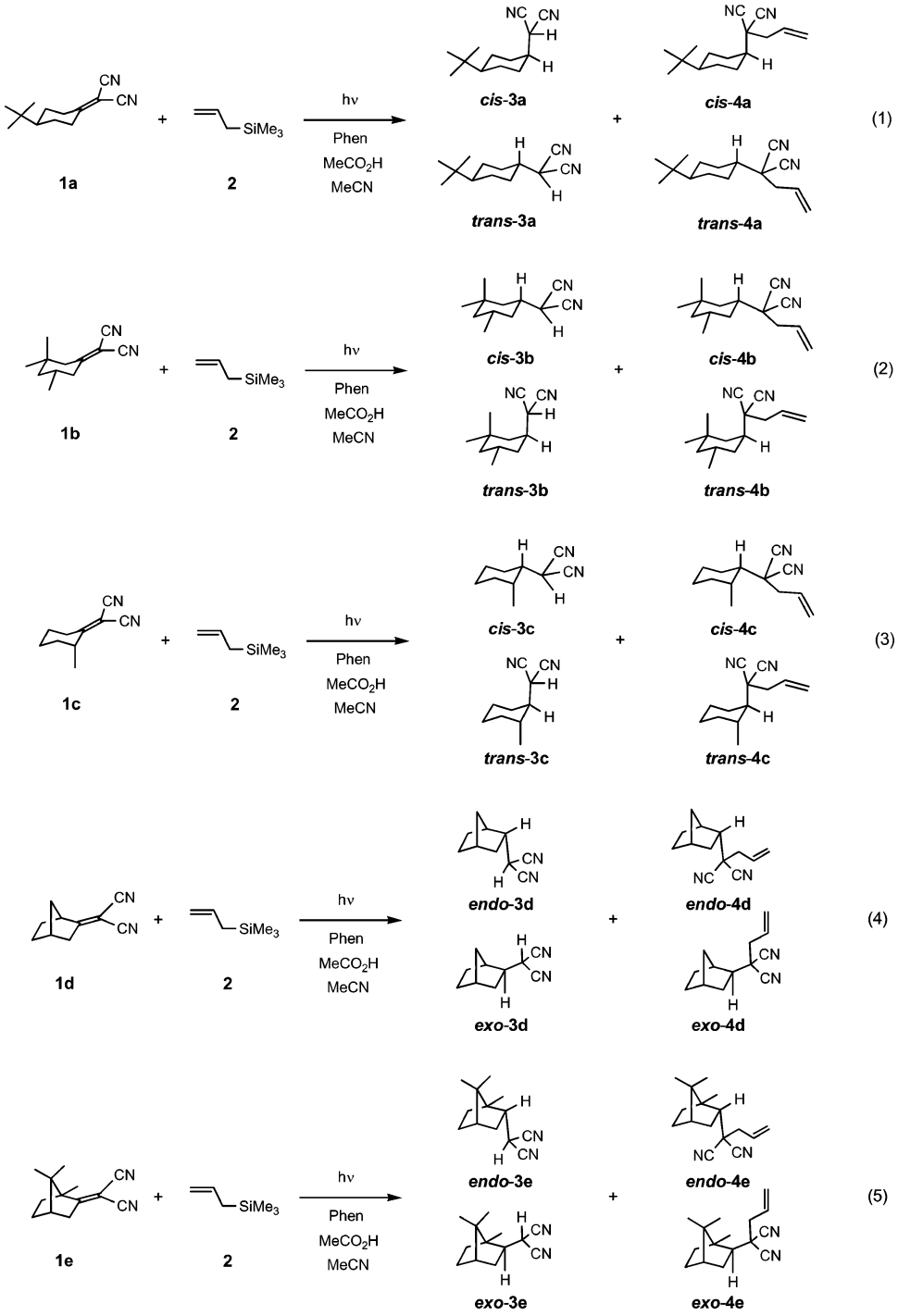
SCHEME 1



Photoallylation in the Presence of 2,4,6-Trimethylpyridinium Tosylate 7. 2,4,6-Trimethylpyridinium tosylate (**7**) can be used as an excellent proton source for diastereoselective photoallylation. The results of these photoreactions are summarized in Table 3.[16] Compared with the results in Tables 1 and 2, the diastereomeric ratios were substantially changed. In the cases of **1a** and **1b**, the photoallylation in the presence of **7** proceeded more stereoselectively (runs 1 and 2), but the photoreaction of **1c** afforded the reverse selectivity (run 3). In the photoreaction of **1e** (run 5), not only did the diastereoselectivity of **3e** and **4e** decrease from 78:22 to 60:40 and 82:18 to 60:40, respectively, but also the chemical yield of this photoreaction was decreased.

Mechanism. Recently, we have reported a simple mechanism for the photoallylation of alkylidenepropanedinitriles depending on pK_a values of additives.[5g] The photoreaction proceeded via the Phen-sensitized electron transfer (redox photosensitization) as shown in Scheme 2.[5,17] The primary step is generation of the radical cation

(16) The product ratios of these photoreactions were dependent on the pK_a values of the additives. Lower acidity of 2,4,6-trimethylpyridinium tosylate (**7**) compared with that of acetic acid increased the ratio of **3**/**4**. A pathway in which $\mathbf{1}^{-\bullet}$ abstracts allylic hydrogen of **1** may be included when **7** was used as a proton source. See ref 5g.

SCHEME 2

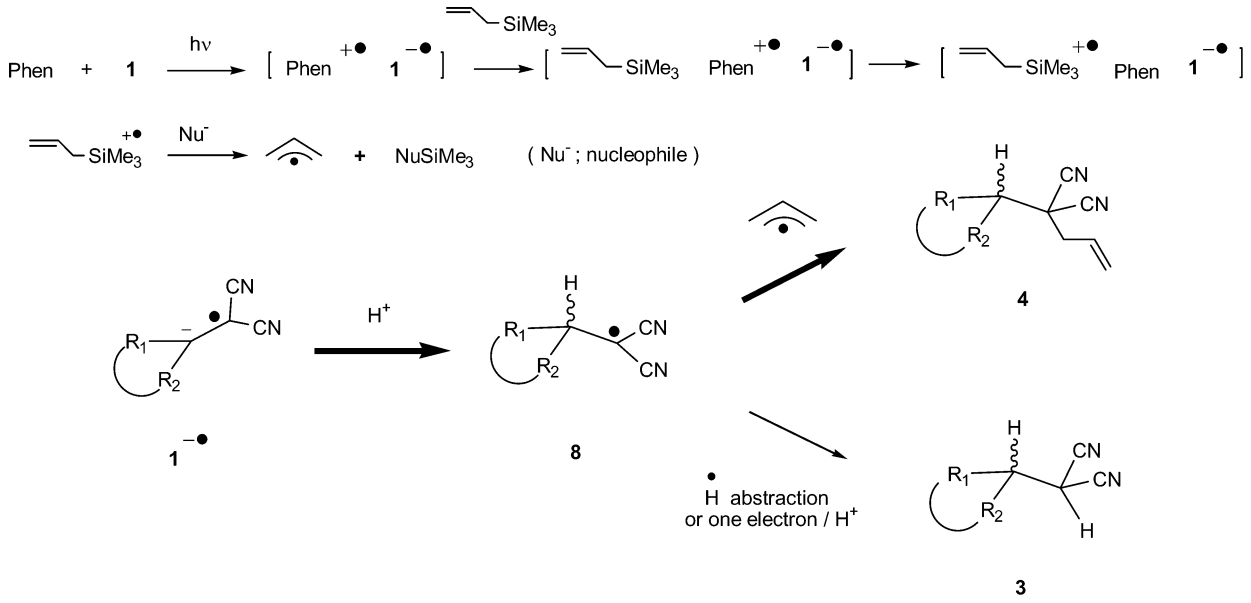
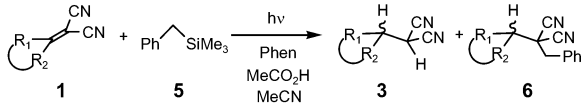
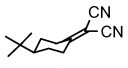
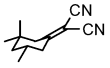
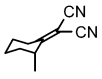
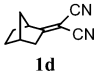
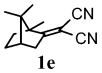


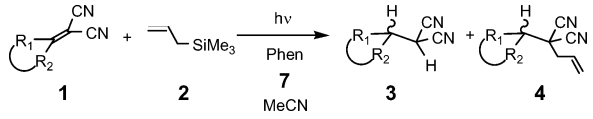
TABLE 2. Diastereoselective Photoreduction and Photobenzylation of 1 in the Presence of 5 and Acetic Acid[a]



run	substrate	products	yields[b] / % (ratio)[c,d]	
1	 **1a**	**3a 6a**	14 (58 : 42)	49 (55 : 45)
2	 **1b**	**3b 6b**	18 (12 : 88)	44 (18 : 82)
3	 **1c**	**3c 6c**	11 (62 : 38)[e]	35 (67 : 33)
4	 **1d**	**3d 6d**	16 (78 : 22)[f]	44 (83 : 17)[f]
5	 **1e**	**3e 6e**	19 (77 : 23)[e,f]	46 (85 : 15)[f]

[a] Irradiation was carried out at room temperature for 8 h. [**1**] = 0.085 M, [**5**] = 0.255 M, [Phen] = 0.018 M, [$MeCO_2H$] = 0.170 M. [b] Isolated yields of two isomers. [c] Determined by GC−MS. [d] *cis*/*trans* ratio. [e] Determined by ^{1}H NMR. [f] *endo*/*exo* ratio.

TABLE 3. Diastereoselective Photoallylation and Photoreduction of 1 in the Presence of 2 and 7[a]



run	substrate	products	yields[b]/% (ratios)[c,d]	
1	**1a**	**3a 4a**	55 (83:17)	22 (79:21)
2	**1b**	**3b 4b**	57 (5:95)	18 (5:95)
3	**1c**	**3c 4c**	58 (42:58)[e]	16 (40:60)
4	**1d**	**3d 4d**	58 (84:16)[f]	16 (86:14)[f]
5	**1e**	**3e 4e**	18 (60:40)[e,f]	3 (60:40)[f]

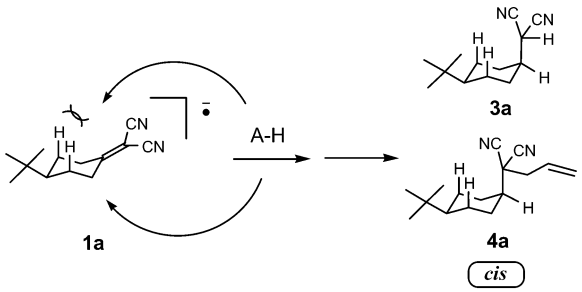
[a] Irradiation was carried out at room temperature for 8 h. [**1**] = 0.085 M, [**2**] = 0.255 M, [Phen] = 0.018 M, [**7**] = 0.170 M. [b] Isolated yields of two isomers. [c] Determined by GC−MS. [d] *cis*/*trans* ratio. [e] Determined by ^{1}H NMR. [f] *endo*/*exo* ratio.

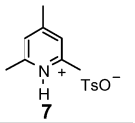
of Phen (Phen$^{+\bullet}$) and the radical anion of **1** (**1**$^{-\bullet}$) through a one-electron transfer from the excited singlet state of Phen (^{1}Phen*) to **1**. The secondary electron transfer from **2** to Phen$^{+\bullet}$ produces the radical cation of **2** (**2**$^{+\bullet}$), which gives the allyl radical via the nucleophile-assisted cleavage of the C−Si bond.[7] In the presence of a proton source, the protonation at the β position to the cyano group of **1**$^{-\bullet}$ predominantly takes place to generate the radical **8**.[16] This is evidently supported by the formation of **3**(d_1) and **4**(d_1) when acetic acid-d_1 is used as the proton source.[5g] Diastereoselectivity in the photoreaction should appear in this step; then the major pathway is the radical coupling of **8** with the allyl radical to give **4**. The minor pathway is the hydrogen abstraction of **8** or an electron transfer from **1**$^{-\bullet}$ to **8** followed by the protonation to give **3**.

The diastereoselectivity in the PET reactions of alkylidenepropanedinitriles summarized in Tables 1−3 can be reasonably explained by steric and torsional effects. The mechanisms of the protonation on the radical anions of cyclohexylidenepropanedinitriles and bicyclo[2.2.1]-heptylidenepropanedinitriles are shown in Schemes 3−7. In the case of **1a**, both the steric and torsional effects were not critical for the diastereoselective protonation of the radical anion of **1a** when acetic acid was used as the proton source. However, the use of sterically hindered proton source **7** resulted in higher diastereoselectivity as a result of the stereoselective equatorial attack of the

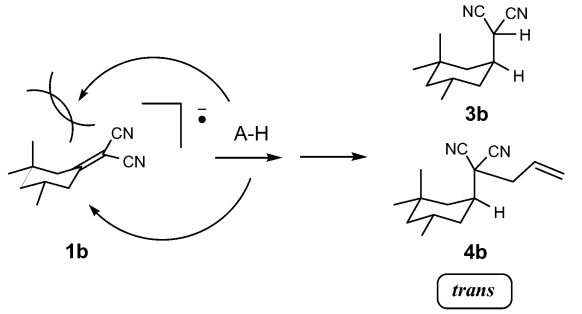
(17) (a) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265. (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

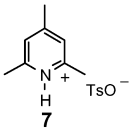
SCHEME 3



	cis / *trans* ratios	
product	$MeCO_2H$	 7
3a : reduction product	63 : 37	83 : 17
4a : allylated product	57 : 43	79 : 21

SCHEME 4



	cis / *trans* ratios	
product	$MeCO_2H$	 7
3b : reduction product	12 : 88	5 : 95
4b : allylated product	16 : 84	5 : 95

proton based on the steric repulsion between **7** and two axial hydrogens at the 3 and 5 positions. Consequently, the *cis*/*trans* ratios of **3a** and **4a** increased to 83:17 and 79:21, respectively (Scheme 3).

In the case of **1b** having an axial methyl group at the 3 position, the effect of the steric repulsion was much larger than that of **1a**, even if acetic acid was used. The higher diastereoselective photoreaction was achieved when **7** was used (Scheme 4).

A methyl group at the 2 position of cyclohexylidenepropanedinitrile in the case of **1c** plays a different role in the determination of the diastereomeric ratio in this photoreaction. When a small proton source was used, a torsional effect as shown in Scheme 5 predominantly controlled the stereochemistry of the photoproducts **3c**, **4c**, and **6c**. However, the torsional effect was not important when a larger proton source such as **7** was used.

The protonation on the radical anions of norbornyl derivatives **1d,e** is mainly controlled by torsional effects as shown in Schemes 6 and 7. High diastereoselectivity was achieved in both of the substrates in the presence of a small proton source. In the photoreaction of **1d**, the diastereomeric ratios in the presence of acetic acid were almost the same as those in the presence of **7**. However, the *exo* attack of the protons to the methylated norbornyl derivative **1e** was slightly suppressed because of steric repulsion between the methyl group and the proton source. This repulsion also caused the lowering of the yield.

Conclusion

The stereoselective photoallylation and benzylation of alkylidenepropanedinitriles (**1a**−**e**) effectively took place by use of **2** and **5** in the presence of Phen via the PET process. Highly diastereoselective protonation on the radical anions was achieved in some cases. The diastereomeric ratios of these photoreactions were changed depending on the proton source. In this type of PET reactions we have suggested that the diastereoselectivity can be controlled by two factors, the steric and torsinal effects.

Experimental Section

Preparation of 1a−**e.** A mixture of a corresponding ketone, malononitrile, and β-alanine in H_2O was refluxed for 8−12 h. The reaction was monitered by TLC. The cooled reaction mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in a vacuum. The organic residue was purified by column chromatography or Kugelrohr distillation. The product was recrystallized or redistillated before use for the photoreaction. Substrate **1e** was synthesized according to a literature procedure.[18]

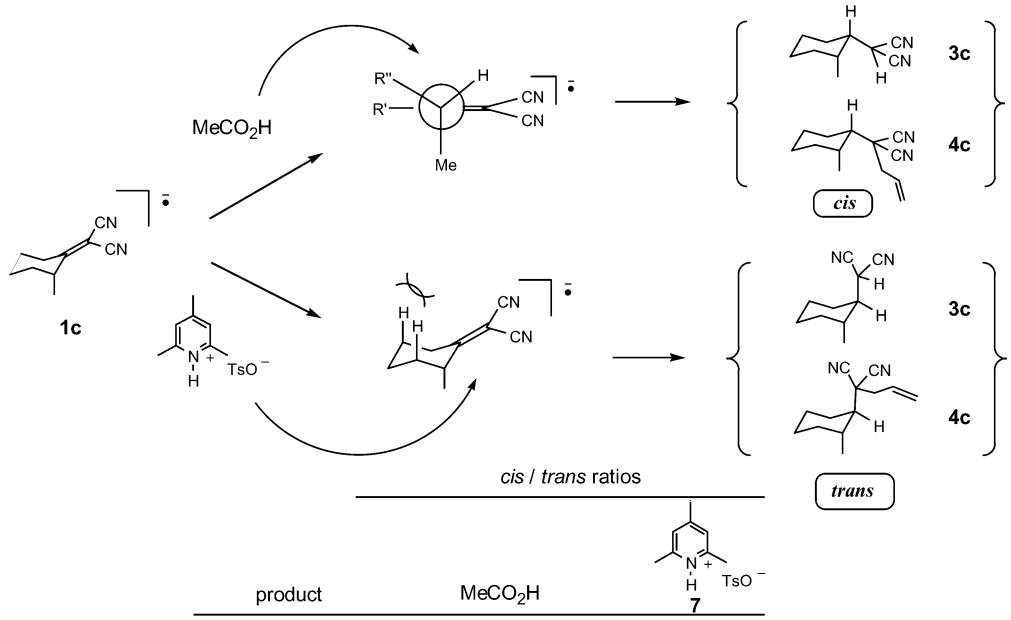
4-*tert*-Butylcyclohexylidenepropanedinitrile (1a).[19] This compound was prepared from 4-*tert*-butylcyclohexanone (8.00 g, 52 mmol), malononitrile (3.44 g, 52 mmol), β-alanine (0.01 g), and H_2O (10 mL) in a 82% yield (8.70 g) according to the general procedure: mp 87−88 °C; IR (KBr) 2955, 2228, 1592, 1479, 1465, 1437, 1424, 1393, 1366, 1177, 1152, 1091, 1016, 998, 928, 911, 825, 770, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 9H), 1.25−1.38 (m, 3H), 2.11−2.16 (m, 2H), 2.25−2.35 (m, 2H), 3.07−3.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 28.9, 32.7, 34.7, 46.9, 82.3, 111.6, 184.9; GC−MS (EI) m/z = 57, 79, 91, 104, 131, 145, 159, 187, 202 (M^+).

3,3,5-Trimethylcyclohexylidenepropanedinitrile (1b).[20] This compound was prepared from 3,3,5-trimethylcyclohexanone (3.50 g, 25 mmol), malononitrile (1.65 g, 25 mmol), β-alanine (0.01 g), and H_2O (5 mL) in a 72% yield (3.39 g) according to the general procedure: oil; IR (KBr) 2958, 28867, 2230, 1709, 1597, 1458, 1390, 1369, 1334, 1259, 1227, 1169, 1012, 979 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 3H), 1.06 (d, 3H, J = 6.0 Hz), 1.11 (s, 3H), 1.18 (d, 1H, J = 11.9 Hz), 1.54−1.59 (m, 1H), 1.77−1.88 (m, 2H), 2.080 (d, 1H, J = 13.0 Hz), 2.71−2.73 (m, 1H), 2.97−3.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 25.0, 31.2, 31.9, 36.8, 42.4, 47.1, 47.3, 83.2, 111.66, 111.73, 183.3; GC−MS (EI) m/z = 41, 55, 65, 77, 83, 91, 104, 119, 131, 145, 159, 173, 188 (M^+).

2-Methylcyclohexylidenepropanedinitrile (1c).[19] This compound was prepared from 2-methylcyclohexanone (5.05 g, 45 mmol), malononitrile (2.97 g, 45 mmol), β-alanine (0.01 g), and H_2O (5 mL) in a 73% yield (5.24 g) according to the general procedure: oil; IR (KBr) 2942, 2866, 2230, 1590, 1461, 1360, 1028, 982, 957 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (d,

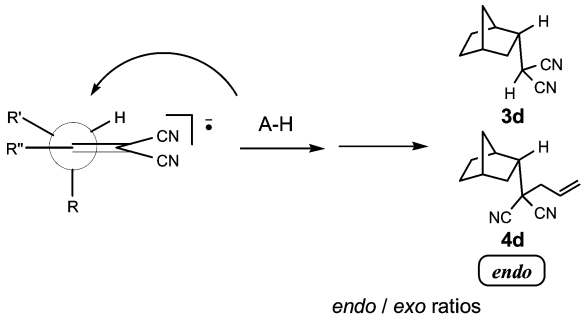
(18) Lalk, M.; Peseke, K.; Reinke, H. *J. Prakt. Chem.* **1999**, *341*, 552.
(19) Leitich, J.; Ritter-Thomas, U.; Heise, I.; Tsay, Y. H.; Rust, J. *J. Photochem. Photobiol. A* **2002**, *147*, 157 and references therein.
(20) Clarke, N. C.; Runciman, P. J. I.; Utley, J. H. P.; Landquist, J. K. *J. Chem. Soc., Perkin Trans. 2* **1987**, 435.

SCHEME 5



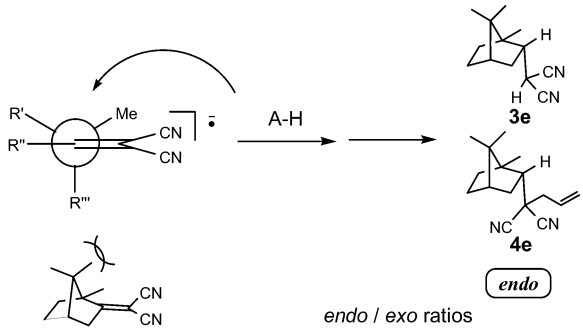
product	$MeCO_2H$	7
3c : reduction product	62 : 38	42 : 58
4c : allylated product	63 : 37	40 : 60

SCHEME 6



product	$MeCO_2H$	7
3d : reduction product	82 : 18	84 : 16
4d : allylated product	85 : 15	86 : 14

SCHEME 7



product	$MeCO_2H$	7
3e : reduction product	78 : 22	60 : 40
4e : allylated product	82 : 18	60 : 40

3H, J = 7.1 Hz), 1.38−1.83 (m, 5H), 2.03−2.11 (m, 1H), 2.39−2.50 (m, 1H), 2.87−2.95 (m, 1H), 3.27−3.30 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6, 19.5, 27.8, 30.6, 33.2, 36.9, 82.1, 111.4, 111.7, 189.1; GC−MS (EI) m/z = 41, 55, 69, 91, 105, 118, 132, 145, 159, 160 (M^+).

Bicyclo[2.2.1]hept-2-ylidenepropanedinitrile (1d).[19] This compound was prepared from bicyclo[2.2.1]heptan-2-one (3.30 g, 30 mmol), malononitrile (2.00 g, 30 mmol), β-alanine (0.01 g), and H_2O (5 mL) in a 75% yield (3.56 g) according to the general procedure: oil; IR (KBr) 2977, 2882, 2233, 1618, 1452, 1413, 1310, 1288, 1078, 960, 915, 844 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30−1.44 (m, 2H), 1.56−1.64 (m, 2H), 1.71−1.85 (m, 1H), 1.92−2.05 (m, 1H), 2.36−2.47 (m, 1H), 2.52−2.60 (m, 1H), 2.65−2.67 (m, 1H), 3.46 (br d, 1H J = 4.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.8, 27.8, 36.5, 39.8, 41.6, 47.5, 78.5, 111.6, 192.9; GC−MS (EI) m/z = 44, 67, 80, 92, 104, 119, 130, 143, 157, 158 (M^+).

Photoreaction of 1. An acetonitrile solution (8 mL) containing the proton source (1.36 mmol), the alkylidenepropanedinitriles **1** (0.68 mmol), and the organosilicon compound **2** or **5** (1.75 mmol) in the presence of phenanthrene (25 mg, 0.14 mmol) was irradiated at ambient temperature with a 300 W high-pressure mercury arc lamp in a merry-go-round apparatus through a Pyrex filter under argon atmosphere. The progress of the photoreaction was followed by estimating the amounts of **1** with GC. After 8 h (>90% consumption of **1**, except for the photoreaction of **1e** with **7**) the solvent was removed under reduced pressure, and the residue was analyzed by GC−MS and ^{1}H NMR. The photoproducts were isolated by column chromatography on silica gel and HPLC.

***cis*-3a:** mp 84−85 °C; IR (KBr) 2947, 2912, 2867, 2259, 1475, 1458, 1368, 1239, 1178 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 9H), 0.89−1.14 (m, 3H), 1.61−1.78 (m, 4H), 2.04−2.09 (m, 2H), 2.42−2.47 (m, 1H), 3.82 (d, 1H, J = 11.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 24.4, 27.3, 27.9, 35.7, 39.5, 47.5, 112.5; GC−MS (EI) m/z = 57, 81, 95, 123, 148, 189; HRMS (EI) calcd for $C_{13}H_{20}N_2$ (M^+) 204.1626, found 204.1629.

***trans*-3a:** mp 86−87 °C; IR (KBr) 2950, 2909, 2866, 2255, 1447, 1364, 1238, 1184 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 9H), 0.89−1.16 (m, 3H), 1.24−1.35 (m, 2H), 1.88−1.96

(m, 3H), 2.03−2.08 (m, 2H), 3.56 (d, 1H, J = 5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.4, 27.5, 29.3, 30.5, 32.4, 39.6, 47.0, 111.9; GC−MS (EI) m/z = 57, 81, 95, 123, 148, 189; HRMS (EI) calcd for $C_{13}H_{20}N_2$ (M^+) 204.1626, found 204.1623.

***cis*-4a:** oil; IR (KBr) 2245 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 9H), 1.15−1.25 (m, 1H), 1.56−1.70 (m, 4H), 1.72−1.93 (m, 4H), 1.97−2.06 (m, 1H), 2.70 (d, 2H, J = 7.1 Hz), 5.36−5.43 (m, 2H), 5.84−5.98(m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 25.8, 27.7, 33.0, 39.1, 40.2, 41.7, 43.9, 115.5, 122.7, 128.8; GC−MS (EI): m/z = 41, 57, 81, 97, 121, 148, 160, 178, 201, 229, 244 (M^+); HRMS (EI) calcd for $C_{16}H_{24}N_2$ (M^+) 244.1941, found 244.1939.

***trans*-4a:** IR (KBr) 2246 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 9H), 0.97−1.13 (m, 3H), 1.29−1.42 (m, 2H), 1.76 (tt, 1H, J = 3.5, 12.1 Hz), 1.92−2.01 (m, 2H), 2.05−2.17 (m, 2H), 2.68 (d, 2H, J = 7.1 Hz), 5.34−5.43 (m, 2H), 5.83−5.97(m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 27.5, 28.7, 32.4, 39.0, 43.0, 43.2, 47.2, 114.7, 122.6, 128.8; GC−MS (EI): m/z = 41, 57, 81, 97, 121, 148, 160, 178, 201, 229, 244 (M^+).

***cis*-6a:** oil; IR (KBr) 3033, 2954, 2246, 1604, 1458, 1365, 1240, 1178, 1086, 1031, 765, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 9H), 1.19−1.25 (m, 3H), 1.56−1.75 (m, 4H), 1.79−2.09 (m, 4H), 3.20 (s, 2H), 7.37−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 22.1, 25.8, 27.6, 32.9, 39.5, 41.5, 43.6, 115.4, 128.4, 128.7, 130.0, 132.2; GC−MS (EI) m/z = 57, 78, 91, 108, 130, 147, 161, 183, 196, 210, 238, 279, 294 (M^+); HRMS (EI) calcd for $C_{20}H_{26}N_2$ (M^+) 294.2096, found 294.2089.

***trans*-6a:** mp 121.5−122.5 °C; IR (KBr) 3029, 2962, 2941, 2862, 2251, 1478, 1451, 1365, 1258, 1236, 1086, 768, 707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 9H), 0.99−1.11 (m, 3H), 1.39−1.50 (m, 2H), 1.74−1.87 (m, 1H), 1.95−1.98 (m, 2H), 2.16−2.21 (m, 2H), 3.18 (s, 2H), 7.37−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 27.4, 28.9, 32.3, 40.5, 43.7, 45.0, 47.1, 114.6, 128.4, 128.7, 129.9, 132.3; GC−MS (EI) m/z = 57, 78, 91, 108, 130, 147, 161, 183, 196, 210, 238, 279, 294 (M^+); HRMS (EI) calcd for $C_{20}H_{26}N_2$ (M^+) 294.2096, found 294.2099.

***trans*-3b:** oil; IR (KBr) 2954, 2909, 2254, 1460, 1384, 1367, 1314, 1253, 1184, 1145, 999, 863 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (s, 3H), 1.01 (s, 3H), 1.04 (d, 3H, J = 7.1 Hz), 1.17 (dd, 1H, J = 6.4, 13.8 Hz), 1.34−1.45 (m, 2H), 1.51−1.66 (m, 3H), 1.81−2.01 (m, 1H), 2.31−2.42 (m, 1H), 3.69 (d, 1H, J = 7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 26.0, 28.8, 30.3, 31.0, 31.8, 33.7, 35.4, 41.4, 44.8, 112.1, 112.2; GC−MS (EI) m/z = 41, 55, 69, 83, 109, 119, 133, 148, 175, 189; HRMS (EI) calcd for $C_{12}H_{18}N_2$ (M^+) 190.1470, found 190.1472.

***trans*-4b:** oil; IR (KBr) 3087, 2954, 2929, 2247, 1645, 1461, 1384, 1367, 1295, 991, 934, 862, 732 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 3H), 1.01 (s, 3H), 1.05 (d, 3H, J = 7.3 Hz), 1.20−1.29 (m, 2H), 1.34−1.43 (m, 1H), 1.44−1.71 (m, 3H), 2.06−2.17 (m, 2H), 2.70 (d, 1H, J = 7.3 Hz), 5.37−5.45 (m, 2H), 5.83−5.97 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 27.0, 28.7, 31.1, 33.6, 33.8, 36.0, 39.0, 40.5, 43.1, 43.8, 114.7, 114.8, 122.7, 128.7; GC−MS (EI) m/z = 41, 55, 69, 83, 109, 123, 125, 148, 159, 173, 189, 215, 229, 230 (M^+); HRMS (EI) calcd for $C_{15}H_{22}N_2$ (M^+) 230.1783, found 230.1776.

***cis*-6b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.96 (d, 3H, J = 6.4 Hz), 1.02 (s, 3H), 1.22−1.28 (m, 2H), 1.41−1.46 (m, 1H), 1.72−2.78 (m, 2H), 2.02−2.10 (m, 2H), 3.19 (s, 2H), 7.37−7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 25.3, 27.8, 31.7, 32.9, 36.9, 40.4, 40.7, 40.5, 43.7, 47.3, 114.7, 128.5, 128.7, 130.0, 132.3; GC−MS (EI) m/z = 55, 69, 91, 109, 128, 148, 167, 265, 280 (M^+).

***trans*-6b:** mp 115−116 °C; IR (KBr) 3033, 2953, 2902, 2248, 1497, 1457, 1383, 1087, 766, 702, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.01 (s, 3H), 1.06 (d, 3H, J = 7.3 Hz), 1.231−1.55 (m, 3H), 1.57−1.68 (m, 1H), 1.72−1.80 (m, 2H), 2.09−2.20 (m, 2H), 3.20 (s, 2H), 7.38−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 27.0, 28.7, 31.1, 33.5, 33.9, 36.7, 40.5, 40.6, 43.7, 45.2, 114.6, 114.7, 128.5, 128.7, 130.0, 132.2; GC−MS (EI) m/z = 55, 69, 91, 109, 128, 148, 167, 265, 280 (M^+); HRMS (EI) calcd for $C_{19}H_{24}N_2$ (M^+) 280.1939, found 280.1936.

***cis*-3c:** oil; IR (KBr) 2936, 2862, 2253, 1716, 1469, 1448, 1388 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (d, 3H, J = 7.1 Hz), 1.25−1.62 (m, 5H), 1.66−1.73 (m, 1H), 1.84 (br d, 2H, J = 12.5 Hz), 2.14−2.22 (m, 1H), 2.26−2.32 (m, 1H), 3.45 (d, 1H, J = 10.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.0, 19.5, 24.8, 25.7, 27.3, 29.8, 32.7, 42.4, 111.9, 112.4; GC−MS (EI) m/z = 41, 55, 70, 81, 97, 108, 120, 134, 147, 161, 162 (M^+); HRMS (CI) calcd for $C_{10}H_{15}N_2$ (M+H) 163.1217, found 163.1226.

***trans*-3c:** oil; IR (KBr) 2930, 2859, 2253, 1717, 1465, 1448, 1385 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (d, 3H, J = 6.2 Hz), 1.03−1.19 (m, 1H), 1.25−1.68 (m, 5H), 1.72−1.91 (m, 3H), 2.05−2.11 (m, 1H), 3.99 (d, 1H, J = 3.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7, 25.6, 25.6, 26.8, 29.1, 34.6, 34.8, 45.8, 111.2, 112.5; GC−MS (EI) m/z = 41, 55, 69, 81, 97, 108, 120, 134, 147, 161, 162 (M^+).

***cis*-4c:** oil; IR (KBr) 3086, 2940, 2858, 2245, 1644, 1447, 1389, 1313, 1265, 1161, 991, 933, 860, 735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, 3H, J = 7.1 Hz), 1.20−1.40 (m, 1H), 1.42−1.57 (m, 3H), 1.59−1.78 (m, 3H), 1.87−1.97 (m, 2H), 2.30−2.38 (m, 1H), 2.64 (dd, 1H, J = 7.0, 13.9 Hz), 2.76 (dd, 1H, J = 7.0, 13.9 Hz), 5.29−5.70(m, 2H), 5.86−6.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 19.6, 22.9, 26.3, 30.5, 34.0, 40.3, 41.3, 46.0, 114.6, 115.3, 122.8, 128.9; GC−MS (EI) m/z = 41, 55, 69, 97, 120, 134, 145, 160, 173, 187, 202 (M^+); HRMS (CI) calcd for $C_{13}H_{19}N_2$ (M + H) 203.1549, found 203.1551.

***cis*-6c:** mp 120−121.5 °C; IR (KBr) 3031, 2943, 2902, 2866, 2245, 1453, 1388, 863, 777, 704, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, 3H, J = 7.1 Hz), 1.23−1.40 (m, 1H), 1.44−1.58 (m, 3H), 1.62−2.00 (m, 5H), 2.37−2.41 (m, 1H), 3.15 (d, 1H, J = 13.6 Hz), 3.26 (d, 1H, J = 13.6 Hz), 7.33−7.46 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 19.7, 23.0, 26.3, 30.8, 34.1, 42.0, 43.3, 46.5, 114.5, 115.3, 128.6, 128.8, 130.2, 132.3; GC−MS (EI) m/z = 41, 55, 65, 77, 91, 97, 115, 128, 140, 154, 167, 182, 196, 210, 224, 252 (M^+); HRMS (CI) calcd for $C_{17}H_{21}N_2$ (M + H) 253.1705, found 253.1709.

***endo*-3d:** IR (KBr) 2253 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (ddd, 1H, J = 2.1, 4.7, 10.9 Hz), 1.16−1.25 (m, 1H), 1.33−1.71 (m, 5H), 1.97−2.07 (m, 1H), 2.35 (br t, 1H, J = 4.2 Hz), 2.47−2.58 (m, 2H), 3.49 (d, 1H, J = 10.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 25.3, 29.5, 35.3, 37.1, 39.4, 39.5, 42.1, 112.2, 112.9; GC−MS (EI) m/z = 41, 67, 95, 106, 119, 132, 145, 159; HRMS (EI) calcd for $C_{10}H_{12}N_2$ (M^+) 160.1006, found 160.1000.

***endo*-4d:** oil; IR (KBr) 2245, 1643 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (dd, 1H, J = 5.6, 12.8 Hz), 1.41 (br s, 2H), 1.42−1.71 (m, 3H), 1.83−1.97 (m, 1H), 1.99−2.04 (m, 1H), 2.21−2.29 (m, 1H), 2.37 (br t, 1H, J = 4.4 Hz), 2.54 (br s, 1H), 2.56−2.72 (m, 2H), 5.35−5.43 (m, 2H), 5.84−5.98 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 28.8, 32.9, 37.3, 39.6, 40.4, 40.6, 42.5, 46.4, 114.9, 115.1, 122.7, 128.8; GC−MS (EI) m/z = 41, 67, 95, 107, 118, 132, 146, 159, 172, 185, 199, 200 (M^+); HRMS (EI) calcd for $C_{13}H_{16}N_2$ (M^+) 200.1317, found 200.1313.

***endo*-6d:** mp 118.5−119.5 °C; IR (KBr) 3035, 2966, 2914, 2873, 2244, 1457 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (dd, 1H, J = 5.5, 12.8 Hz), 1.41 (br s, 2H), 1.43−1.69 (m, 3H), 1.84−1.95 (m, 1H), 1.99−2.08 (m, 1H), 2.26−2.34 (m, 1H), 2.39 (br t, 1H, J = 4.0 Hz), 2.57 (br s 1H), 3.13 (d, 1H, J = 13.7 Hz), 3.19 (d, 1H, J = 13.6 Hz), 7.32−7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 28.8, 33.0, 37.4, 40.4, 40.9, 41.4, 44.1, 46.7, 115.0, 115.2, 128.6, 128.8, 130.1, 132.1; GC−MS (EI) m/z = 41, 51, 65, 71, 91, 115, 128, 140, 154, 180, 195, 222, 250 (M^+); HRMS (EI) calcd for $C_{17}H_{18}N_2$ (M^+) 250.1470, found 250.1464.

***exo*-6d:** mp 139.0−140.0 °C; IR (KBr) 3034, 2961, 2919, 2873, 2244, 1458 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19−1.29 (m, 3H), 1.59−1.66 (m, 3H), 1.69−1.77 (m, 1H), 1.87−1.95 (m, 2H), 2.43 (br s, 1H), 2.54 (br s, 1H), 3.14 (s, 2H), 7.34−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 31.3, 35.8, 35.9, 36.5, 39.7, 42.2, 43.6, 48.4, 115.0, 115.5, 128.5, 128.8, 130.1, 132.0; GC−MS (EI) m/z = 41, 51, 65, 77, 91, 115, 128, 140, 155, 168, 195, 250 (M^+); HRMS (EI) calcd for $C_{17}H_{18}N_2$ (M^+) 250.1470, found 250.1480.

***endo*-3e:** mp 77.5−78.5 °C; IR (KBr) 2251 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 3H), 0.92 (s, 3H), 1.02−1.11 (m, 1H), 1.05 (s, 3H), 1.14−1.25 (m, 1H), 1.35−1.44 (m, 1H), 1.50−1.61 (m, 1H), 1.73−1.89 (m, 2H), 2.17−2.35 (m, 1H), 2.38−2.47 (m, 1H), 3.60 (d, 1H, J = 9.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 18.4, 19.5, 24.5, 28.1, 28.6, 35.5, 44.1, 45.4, 48.8, 50.3, 113.0, 113.2; GC−MS (EI) m/z = 41, 55, 69, 81, 95, 110, 121, 137, 145, 159, 187, 202 (M^+); HRMS (EI) calcd for $C_{13}H_{18}N_2$ (M^+) 202.1470, found 202.1466.

***exo*-3e:** IR (KBr) 2255 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 3H), 0.88 (s, 3H), 1.07 (s, 3H), 1.19−1.31 (m, 2H), 1.62−1.70 (m, 1H), 1.75−1.84 (m, 4H), 2.17−2.26 (m, 1H), 3.67 (d, 1H, J = 11.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 20.1, 20.5, 26.3, 26.8, 35.5, 38.7, 44.5, 47.7, 48.10, 48.12, 112.2, 113.8; GC−MS (EI) m/z = 41, 55, 69, 81, 95, 110, 121, 137, 145, 159, 187, 202 (M^+).

***endo*-4e:** oil; IR (KBr) 2245 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 3H), 0.90 (s, 3H), 1.12 (s, 3H), 1.23−1.36 (m, 1H), 1.40−1.49 (m, 1H), 1.53−1.61 (m, 1H), 1.72−1.89 (m, 2H), 1.99−2.19 (m, 3H), 2.55−2.62 (m, 1H), 2.71−2.79 (m, 1H), 5.35−5.44 (m, 2H), 5.86−6.00 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 18.2, 19.1, 27.5, 29.0, 33.3, 38.7, 43.7, 43.9, 49.3, 49.6, 51.2, 115.3, 115.8, 122.9, 128.7; GC−MS (EI) m/z = 41, 55, 69, 81, 95, 110, 137, 159, 171, 199, 213, 227, 242 (M^+); HRMS (EI) calcd for $C_{16}H_{22}N_2$ (M^+) 242.1783, found 242.1787.

***endo*-6e:** mp 79.5−81 °C; IR (KBr) 2244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 3H), 0.91 (s, 3H), 1.10 (s, 3H), 1.41 (d, 1H, J = 7.9 Hz), 1.48−1.62 (m, 2H), 1.75−1.89 (m, 2H), 2.02−2.26 (m, 3H), 3.12 (d, 1H, J = 13.6 Hz), 3.26 (d, 1H, J = 13.6 Hz), 7.33−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 18.2, 19.1, 27.5, 29.0, 33.6, 40.4, 43.8, 45.3, 49.4, 49.8, 51.2, 115.3, 115.9, 128.6, 128.7, 130.3, 131.9; GC−MS (EI) m/z = 41, 55, 81, 91, 95, 110, 137, 155, 185, 250, 277, 292 (M^+); HRMS (EI) calcd for $C_{20}H_{24}N_2$ (M^+) 292.1939, found 292.1941.

***exo*-6e:** mp 94−95.5 °C; IR (KBr) 2243 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 3H), 1.14 (s, 3H), 1.22 (d, 1H, J = 8.4 Hz), 1.30 (s, 3H), 1.65−1.78 (m, 3H), 1.79−1.89 (m, 2H), 1.94−2.036 (m, 1H), 2.16 (t, 1H, J = 9.0 Hz), 3.07 (d, 1H, J = 13.5 Hz), 3.22 (d, 1H, J = 13.5 Hz), 7.30−7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 21.4, 22.0, 26.4, 34.8, 41.0, 41.5, 43.9, 44.6, 48.2, 49.6, 55.0, 115.8, 116.5, 128.59, 128.63, 130.5, 132.0; GC−MS (EI) m/z = 41, 55, 81, 91, 95, 110, 137, 155, 185, 250, 277, 292 (M^+); HRMS (EI) calcd for $C_{20}H_{24}N_2$ (M^+) 292.1939, found 292.1946.

X-ray Crystallographic Analysis. A single crystal was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation. A total of 44 oscillation images were collected. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The crystal structure was refined by full-matrix least-squares. All calculations were performed using the CrystalStructure[22,23] crystallographic software package. Crystal data and details of the data collection are provided in Supporting Information.

For ***trans*-6a**, a sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° steps, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 300.0 s/deg. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° steps, at χ = 45.0° and ϕ = 180.0°. The exposure rate was 300.0 s/deg. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.95 and −0.47 $e^-/Å^3$, respectively. The structure was solved by direct methods (SIR92)[24] and expanded using Fourier techniques.[21] The crystal structure was refined by full-matrix least-squares on F.

For ***trans*-6b**, a sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° steps, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 600.0 s/deg. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° steps, at χ = 45.0° and ϕ = 180.0°. The exposure rate was 600.0 s/deg. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.84 and −0.43 $e^-/Å^3$, respectively. The structure was solved by direct methods (SIR92)[24] and expanded using Fourier techniques.[21] The crystal structure was refined by full-matrix least-squares on F^2.

For ***cis*-6c**, a sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° steps, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 100.2 s/deg. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° steps, at χ = 45.0° and ϕ = 180.0°. The exposure rate was 100.2 s/deg. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.36 and −0.32 $e^-/Å^3$, respectively. The structure was solved by direct methods (SIR92)[24] and expanded using Fourier techniques.[21] The crystal structure was refined by full-matrix least-squares on F^2.

For ***exo*-6d**, a sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° steps, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 150.0 s/deg. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° steps, at χ = 45.0° and ϕ = 180.0°. The exposure rate was 150.0 s/deg. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.43 and −0.46 $e^-/Å^3$, respectively. The structure was solved by direct methods (SHELX97)[25] and expanded using Fourier techniques.[21] The crystal structure was refined by full-matrix least-squares on F^2.

For ***exo*-6e**, a sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° steps, at χ = 45.0° and ϕ = 0.0°. The exposure rate was 289.8 s/deg. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° steps, at χ = 45.0° and ϕ = 180.0°. The exposure rate was 289.8 s/deg. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.56 and −0.44 $e^-/Å^3$, respectively. The structure was solved by direct methods (SIR92)[24] and expanded using Fourier techniques.[21] The crystal structure was refined by full-matrix least-squares on F^2.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra for **1a**−**d** and the selected photoproducts and crystallographic data for ***cis*-3a**, ***trans*-6a**, ***trans*-6b**, ***cis*-6c**, ***exo*-6d**, and ***exo*-6e** in PDF and CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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