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Intramolecular Photocycloaddition of Unsaturated Isoquinuclidines. Synthesis of 2-Azatetracyclo[4.0.0.^{4,9}0^{7,10}]decanes and 3-Azatetracyclo[6.1.1.0.^{2,7}0^{5,9}]decanes

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2-Azabicyclo[2.2.2]oct-5-enes bearing an endo alkenyl substituent were synthesized by Diels−Alder addition of methyl vinyl ketone to a 1,6-dihydropyridine derived from methyl nicotinate. Although 1,5-dienes with this skeleton were unreactive under thermal conditions, they were photochemically reactive. Irradiation of these dienes through a Corex filter resulted in intramolecular [2 + 2] cycloaddition to give "parallel" and "crossed" photoadducts along with small amounts of a hexahydroisoquinoline. The latter is thought to represent leakage of a diradical intermediate responsible for the parallel photoadduct. The new 2-azatetracyclo[4.4.0.0.^{4,9}0^{7,10}]decane and 3-azatetracyclo[6.1.1.0.^{2,7}0^{5,9}]decane structures formed in the photochemical reactions are thermally stable.

Introduction

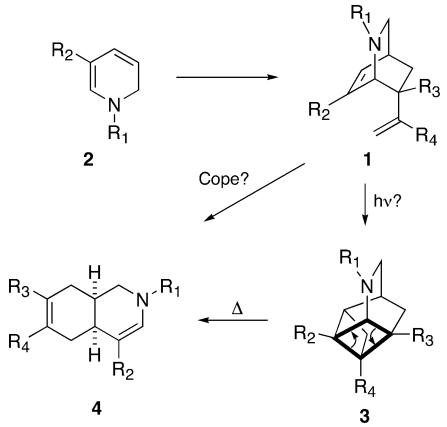
An interest in isoquinuclidines as precursors for the synthesis of certain *Gelsemium* alkaloids[1] led us to examine the thermal and photochemical behavior of a variety of substituted 2-azabicyclo[2.2.2]octenes with the general framework represented by **1** (Scheme 1). Structures such as **1** are readily prepared by Diels−Alder cycloaddition of an appropriate dienophile to a 1,6-dihydropyridine (**2**),[2,3] and it was expected that diene **1** would give rise to the [2 + 2] photoadduct **3** and perhaps to a hexahydroisoquinoline **4** by a subsequent thermal cycloreversion.

Alternatively, **1** could conceivably undergo a thermal (Cope) rearrangement leading to hexahydroisoquinoline **4**. Herein, we describe the preparation of several bicyclic dienes with the substitution pattern of **1** and we report on their photochemical reactions. The latter were found to lead to both "crossed" and "parallel" photoadducts, the proportion depending upon the nature of the substituents R_3 and R_4. The small quantity of **4** produced in this process was shown not to originate from **3**.

Results and Discussion

The isoquinuclidine **5** (Scheme 2) was prepared from methyl nicotinate following the method of Mariano[4] and was obtained in pure form by crystallization from a mixture which contained the exo- and endo-Diels−Alder adducts of methyl vinyl ketone with both 1,2- and 1,6-dihydronicotinates. The X-ray crystal structure of **5** proved unambiguously that it was the endo Diels−Alder adduct of methyl 1-methoxycarbonyl-1,6-dihydronicotinate. Deprotonation of **5** with lithium hexamethyldisilazide under kinetic conditions followed by treatment with chlorotrimethylsilane afforded a single silyl enol ether which was shown by NMR analysis to be **6**. Irradiation of **6** with a 450-W medium pressure mercury lamp through Pyrex glass resulted in recovery of the starting material, but when a Corex filter was used, a clean reaction occurred which was complete within 3 h. A single photoproduct was isolated which was shown to be the azatetracyclodecane **7** by cleavage of the silyl ether and conversion of the resulting alcohol **8** to its crystalline *p*-bromobenzoate **9**. X-ray crystallographic analysis of **9** established that **7** was the product of a "crossed" [2 + 2] photocycloaddition of **6**. Photoadduct **7** has the regiochemistry predicted by the Corey−de Mayo hypothesis,[5,6]

SCHEME 1



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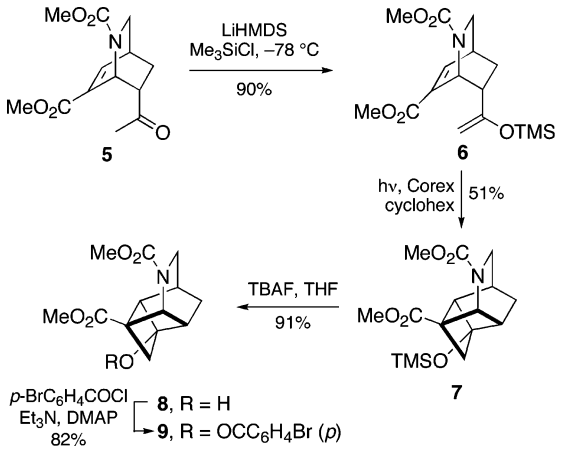
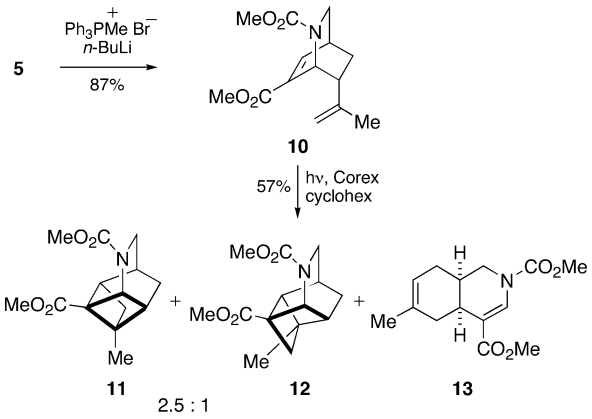
SCHEME 2



SCHEME 3

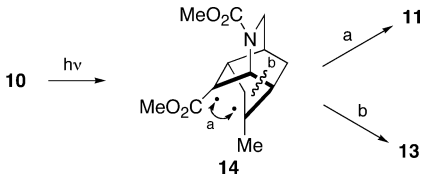


which postulates initial formation of an exciplex wherein electronic reorganization of the α,β-unsaturated ester places higher electron density at the β carbon.[7]

In contrast to its photochemical reactivity, 1,5-diene **6** was thermally stable, being recovered unchanged at temperatures as high as 250 °C. The thermal stability of **6** contrasts with the reactivity of carbocyclic analogues possessing this framework, since the latter are known to undergo Cope rearrangement to give hexahydronaphthalenes. More surprising is the fact that **7** and **8** were thermally stable, the strained cyclobutane in these structures remaining intact at temperatures as high as 200 °C.

Ketone **5** was also used as the source of diene **10**, which was obtained in high yield by a Wittig reaction with methylenetriphenylphosphorane. In contrast to the clean photochemical behavior of **6**, however, irradiation of **10** through a Corex filter gave a mixture of three products (Scheme 3), two of which were shown to be isomeric [2 + 2] cycloadducts in the ratio 2.5:1. The major isomer was identified as the "parallel" adduct **11**. A clear distinction between **11** and its "crossed" isomer **12** was made on the basis of a comparison of NMR signals due to protons attached to the cyclobutane ring in each case. Thus, **11** was found by COSY to have a vicinal $CH-CH_2$ connection

SCHEME 4



within the cyclobutane, whereas in **12** this relationship was absent. A minor product isolated from the photolysis of **10** was the cis-fused hexahydroisoquinoline **13**.

Although **13** is formally the Cope rearrangement product of **10**, there is no evidence to suggest that **13** is formed by this pathway since **10**, like **6**, is thermally stable at temperatures above 220 °C. Nor does **13** appear to be the result of thermal cycloreversion of the cyclobutane embedded within the framework of **11** because the latter is also quite stable toward heat. A possible explanation for the origin of **13** is suggested in Scheme 4, where the intervention of a photochemically generated diradical **14** could lead to either **11** by ring closure (path a) or to the minor product **13** by a fragmentation mechanism (path b). On the other hand, a mechanistic explanation for the different photochemical behavior of **6** and **10** is more difficult to formulate. The "rule of five" used to predict the regiochemical outcome of intramolecular photochemical cycloadditions[8,9] is obeyed by **6** but not by **10**, implying different excited-state pathways for these two substrates. In practice, the rule is known to be less reliable as the electron-donating ability of the substituent in the nonchromophic alkene decreases.[10−14]

Although 1,5-dienes **6** and **10** failed to undergo Cope rearrangement to a hexahydroisoquinoline, it seemed reasonable to postulate that incorporation of a hydroxyl function at C7 would overcome this problem by permitting a more favorable anionic oxy-Cope pathway[15−17] for the rearrangement. Accordingly, **10** was oxidized with selenium dioxide in a two-phase system consisting of 70% aqueous *tert*-butylhydroperoxide and dichloromethane[18] with the result that exo and endo tertiary alcohols **15** and **16** were produced in a 2:1 ratio, respectively (Scheme 5). By contrast, oxidation of **10** with selenium dioxide and *tert*-butyl hydroperoxide (5 M in nonane) in dichloromethane alone as the solvent gave a 1:1 mixture of diols **17** and **18**. The mixture of **15** and **16** was separated by column chromatography and **15** was converted to its trimethylsilyl ether **19** (Scheme 6). Neither **15**, as its

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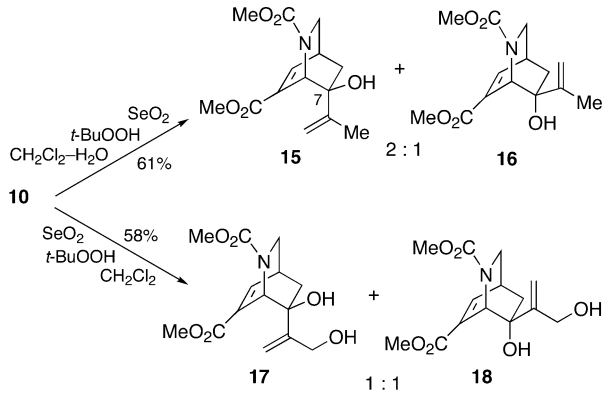
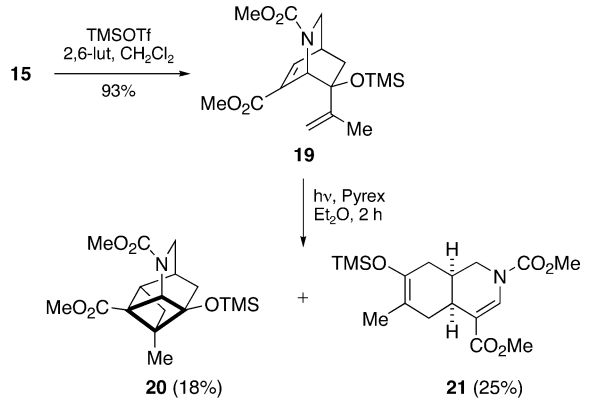
SCHEME 5



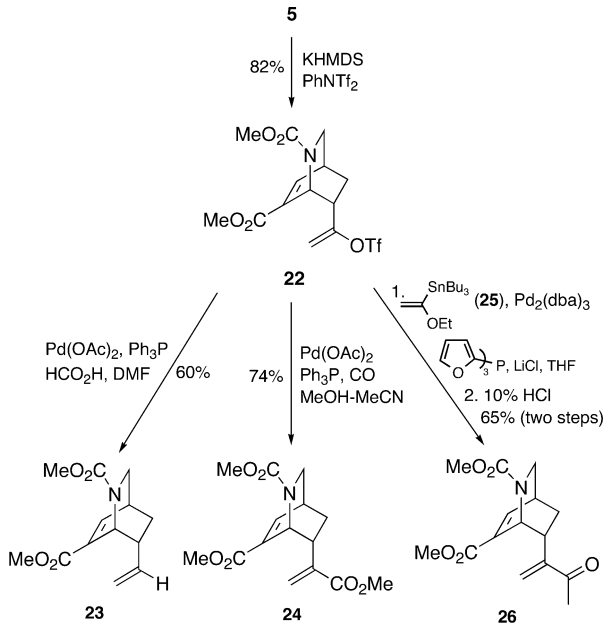
SCHEME 6



potassium alkoxide, nor **19** could be induced to undergo oxy-Cope rearrangement, but **19** proved to be quite reactive photochemically, and its irradiation in ether through Pyrex resulted in a rapid reaction which yielded principally two products. These were shown to be the parallel [2 + 2] adduct **20** and the hexahydroisoquinoline **21**, isolated in 18% and 25% yield, respectively. The photoproducts **20** and **21** can be explained by a pathway from **19** analogous to that shown in Scheme 4, where a diradical intermediate corresponding to **14** either closes to give **20** (path a) or undergoes fragmentation to give **21** (path b). We were unable to identify any other products from the photoreaction of **19**, but as with **11**, we were able to confirm that **20** is thermally stable and does not fragment to **21**.

In a further extension of our study of the photochemistry of unsaturated isoquinuclidines, ketone **5** was converted to enol triflate **22** (Scheme 7).[19] In addition to permitting synthesis of the vinyl- substituted isoquinuclidine **23** by reduction of the derived σ-palladium complex with formic acid,[20] **22** also provided access to the acrylate **24** via a palladium(II) mediated alkoxycarbonylation.[21] Furthermore, Stille coupling of **22** with the vinylstannane **25**[22] gave α,β-unsaturated ketone **26** after acidic hydrolysis. Each of these substrates was irradiated in cyclohexane with a 450-W medium-pressure mercury

SCHEME 7



SCHEME 8

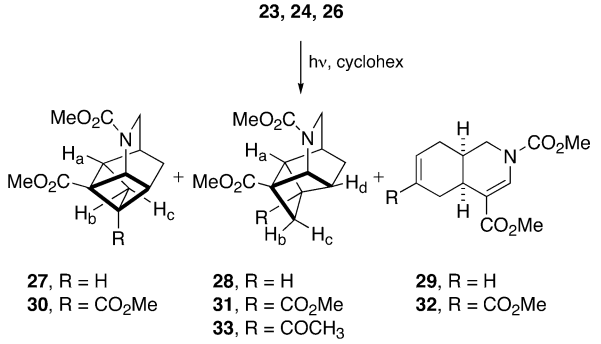


TABLE 1. Irradiation of Isoquinuclidines 23, 24, and 26

substrate	filter	reaction time (h)	products (% yield, ratio)
23	Corex	20	**27** + **28** (54, 1:1.5), **29** (3)
24	Corex	5	**30** + **31** (55, 1.1:1), **32** (3)
26	Pyrex	8	**33** (47)

lamp through either a Corex or a Pyrex filter (Scheme 8); the results are summarized in Table 1.

Substrates **23** and **24** gave a mixture of parallel (**27**, **30**) and crossed photoadducts (**28**, **31**), but **26** gave only the crossed adduct **33**. A clear distinction between the structures of parallel and crossed photoproducts could be made in every case on the basis of NOE experiments which correlated protons attached to the cyclobutanes embedded in these structures. For **27** and **30**, H_a was correlated with H_b and H_c, whereas **28**, **31**, and **33** displayed correlations between H_a and H_b and between H_c and H_d. The preponderance of crossed product **33** from **26** suggests that this photoreaction follows a pathway mechanistically different from that originating from **23** and **24**, but a more detailed rationale for this outcome must await the results of further photochemical studies on this system. In the case of **23** and **24**, a small quantity of hexahydroisoquinolines **29** and **32** accompanied the formation of [2 + 2] photoadducts, but none was detected in the product mixture from irradiation of **26**. To the

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extent that **29** and **32** may represent a small amount of "leakage" of a diradical analogous to **14** via path b in Scheme 4, the formation of **33** as the predominant photoadduct from **26** is consistent with the absence of a diradical intermediate and hence with the absence of any hexahydroisoquinoline.

In summary, substituted isoquinuclidines **6**, **10**, **19**, **23**, **24**, and **26** have been shown to react photochemically, giving parallel and crossed [2 + 2] photoadducts. The azatetracyclic products formed represent new ring systems which are surprisingly stable. The photoproducts can be explained in certain, though not all, cases by the intermediacy of a diradical.

Experimental Section

7-*endo*-Acetyl-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (5) and 7-*exo*-Acetyl-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester. To a suspension of methyl nicotinate (15.1 g, 0.11 mol) and sodium borohydride (4.2 g, 0.11 mol) in MeOH (250 mL) at −78 °C under argon was added a solution of methyl chloroformate (10.4 g, 0.11 mol) in Et_2O (10 mL). The mixture was stirred for 1.5 h at −78 °C, poured into ice−water (100 mL), and extracted with Et_2O (300 mL). The extract was washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give a yellow oil. The ^{1}H NMR showed this to be a 2.8:1.4:1 mixture of three products. To this mixture at room temperature under argon was added methyl vinyl ketone (22 mL, 0.26 mol), and the mixture was heated at 100 °C for 72 h. After removal of volatile materials, chromatography of the residue on silica (EtOAc−hexanes, 1:3 to 1:1) followed by recrystallization gave 7.34 g (21%) of **5**: mp 130−131°C; IR (neat) 1715, 1448, 1394, 1271, 1252, 1121, 1095 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54−1.75 (m, 1H), 1.76−1.92 (m, 1H), 2.14 (s, 1.5H), 2.16 (s, 1.5H), 2.82−3.01 (m, 2H), 3.10−3.19 (m, 1H), 3.22 (d, J = 10 Hz, 0.5H), 3.23 (d, J = 10 Hz, 0.5H), 3.60−3.68 (m, 6H), 5.48 (brs, 0.5H), 5.64 (brs, 0.5H), 7.26 (d, J = 7 Hz, 0.5H), 7.27 (d, J = 7 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 24.1, 28.9, 31.6, 31.9, 46.3, 46.7, 47.2, 47.3, 52.2, 52.6, 52.9, 53.1, 134.3, 134.4, 145.0, 155.4, 155.9, 163.9, 164.1, 206.0; MS (CI) m/z 268 $(M + H)^+$, 252, 236, 226, 197, 182, 161, 141, 123, 99, 84, 71; HRMS (CI) m/z 267.1101 (calcd for $C_{13}H_{17}O_5N$ 267.1107).

There was also obtained 1.47 g (4%) of the exo Diels−Alder adduct: mp 137−138 °C; IR (neat) 1716, 1448, 1392, 1242, 1120, 1093 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27−1.43 (m, 1H), 2.26−2.37 (m, 4H), 2.60−2.73 (m, 1H), 2.86−3.03 (m, 2H), 3.27−3.35 (m, 1H), 3.61 (s, 1.5H), 3.65 (s, 1.5H), 3.80 (s, 3H), 5.53 (brs, 0.5H), 5.71 (brs, 0.5H), 7.41 (d, J = 7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 29.0, 29.3, 31.6, 31.8, 46.4, 46.9, 47.7, 48.0, 52.4, 52.6, 53.0, 136.7, 137.2, 145.9, 146.0, 155.6, 156.4, 163.9, 206.4, 207.1; MS (CI) m/z 268 $(M + H)^+$, 252, 236, 209, 197, 182, 161, 151, 138, 99, 88; HRMS (CI) m/z 267.1100 (calcd for $C_{13}H_{17}O_5N$ 267.1107).

1,3-Dimethoxycarbonyl-8-trimethylsilyloxy-3-azatetracyclo[6.1.1.0^{2,7}.0^{5,9}]decane (7). To a solution of **5** (942 mg, 3.53 mmol) in THF (20 mL) at −78 °C was added a 1 M solution of lithium bis(trimethylsilyl)amide in THF (5.3 mL, 5.3 mmol), and the mixture was stirred for 1 h at −78 °C. A solution of chlorotrimethylsilane (770 mg, 7.06 mmol) was added, and the mixture was allowed to warm to room temperature during 1 h. Triethylamine (1.07 g, 10.6 mmol) was added at 0 °C, and the mixture was diluted with aqueous phosphate buffer (5 mL) and was extracted with ether. The extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes−Et_3N, 1:3:0.01) gave 1.08 g (90%) of **6** as an unstable, colorless oil. A solution of **6** (125 mg, 0.35 mmol) in cyclohexane (65 mL) was placed in a photoreaction vessel and was purged with argon for 1 h. The solution was irradiated with a 450-W medium-pressure mercury lamp using a Corex filter for 3 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica (EtOAc−hexanes, 1:3) to give 65 mg (51%) of **7** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.1−0.2 (m, 9H), 1.50−1.56 (m, 1H), 2.03−2.10 (m, 1H), 2.13−2.31 (m, 2H), 2.34 (dt, J = 2, 7 Hz, 0.5H), 2.37 (dt, J = 2, 7 Hz, 0.5H), 2.72 (dt, J = 2, 5 Hz, 0.5H), 2.76 (dt, J = 2, 5 Hz, 0.5H), 2.98 (brd, J = 11 Hz, 0.5H), 3.07 (brd, J = 11 Hz, 0.5H), 3.45 (d, J = 4 Hz, 0.5H), 3.47 (d, J = 4 Hz, 0.5H), 3.53 (d, J = 4 Hz, 0.5H), 3.55 (d, J = 4 Hz, 0.5H), 3.66 (s, 3H), 3.69 (s, 1.5H), 3.72 (s, 1.5H), 4.38 (dd, J = 2, 7 Hz, 0.5H), 4.53 (dd, J = 2, 7 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.1, 31.2, 34.6, 34.8, 40.7, 40.9, 46.5, 46.7, 47.5, 47.8, 48.15, 48.22, 52.3, 52.4, 52.9, 55.1, 55.4, 56.9, 57.1, 82.3, 157.4, 157.5, 172.5, 172.6.

1,3-Dimethoxycarbonyl-3-azatetracyclo[6.1.1.0^{2,7}.0^{5,9}]-decane-8-ol (8). To a solution of **7** (22 mg, 0.06 mmol) in THF (3 mL) at room temperature under argon was added a 1 M solution of TBAF in THF (0.09 mL, 0.09 mmmol). The mixture was stirred for 30 min at room temperature. The mixture was diluted with H_2O (0.5 mL) and was extracted with Et_2O (10 mL). The extract was washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:1) gave 16 mg (91%) of **8** as a colorless oil: IR (neat) 3395, 2956, 1733, 1702, 1675, 1456, 1402, 1340, 1285, 1252, 1196, 1112 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (m, 1H), 2.04−2.14 (m, 2H), 2.18−2.35 (m, 3H), 2.37−2.44 (m, 1H), 2.70 (dt, J = 2, 5 Hz, 0.5H), 2.74 (dt, J = 2, 5 Hz, 0.5H), 3.00 (d, J = 11 Hz, 0.5H), 3.08 (d, J = 11 Hz, 0.5H), 3.48 (dd, J = 4, 11 Hz, 0.5H), 3.56 (dd, J = 4, 11 Hz, 0.5H), 3.67 (s, 3H), 3.70 (s, 1.5H), 3.72 (s, 1.5H), 4.45 (dd, J = 2, 7 Hz, 0.5H), 4.59 (dd, J = 2, 7 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0, 31.1, 34.8, 35.0, 40.4, 40.6, 46.5, 46.6, 46.9, 47.1, 47.8, 52.4, 52.5, 52.9, 55.6, 56.0, 57.2, 57.3, 81.9, 157.3, 157.4, 172.1, 172.2; MS (CI) m/z 267 (M^+), 252, 235, 219, 208, 197, 182, 169, 152, 138, 126, 116, 102, 91; HRMS (CI) m/z 267.1108 (calcd for $C_{13}H_{17}O_5N$ 267.1107).

1,3-Dimethoxycarbonyl-8-oxo-3-azatetracyclo-[6.1.1.0^{2,7}.0^{5,9}]decanyl-*p*-bromobenzoate (9). To a solution of *p*-bromobenzoyl chloride (10 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) at room temperature under argon was added triethylamine (15 mg, 0.14 mmol), followed by a solution of **8** (6 mg, 0.02 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred for 1 h at room temperature, diluted with H_2O (0.5 mL), and extracted with CH_2Cl_2 (10 mL). The extract was washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:1) gave 7 mg (82%) of **9** as a colorless crystalline solid: mp 115−117 °C; IR (neat) 1728, 1704, 1449, 1399, 1288, 1270, 1254, 1199, 1105, 1086 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58−1.66 (m, 1H), 2.01−2.12 (m, 1H), 2.30−2.55 (m, 3H), 2.89−2.96 (m, 1H), 3.06 (d, J = 11 Hz, 0.5H), 3.15 (d, J = 11 Hz, 0.5H), 3.23−3.29 (m, 1H), 3.52 (dd, J = 4, 11 Hz, 0.5H), 3.61 (dd, J = 4, 11 Hz, 0.5H), 3.70 (s, 3H), 3.72 (s, 1.5H), 3.74 (s, 1.5H), 4.62 (dd, J = 2, 6 Hz, 0.5H), 4.71 (dd, J = 2, 7 Hz, 0.5H), 7.58 (d, J = 8 Hz, 2H), 7.86 (d, J = 8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0, 31.1, 34.5, 34.7, 38.7, 39.0, 45.45, 45.52, 46.3, 46.4, 52.5, 52.6, 53.0, 55.1, 55.3, 55.5, 84.6, 128.9, 129.2, 131.6 (2C), 132.2 (2C), 157.3, 157.5, 165.2, 171.7; MS (CI) m/z 449 (M − H), 420, 392, 372, 340, 312, 266, 249, 206, 183, 157, 131, 105; HRMS (CI) m/z 449.0475 (calcd for $C_{20}H_{20}O_6NBr$ 449.0474).

7-*endo*-Isopropenyl-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (10). To a suspension of dry methyltriphenylphosphonium bromide (467 mg, 1.31 mmol) in THF (10 mL) at 0 °C under argon was added dropwise *n*-BuLi (0.7 mL, 1.5 M in hexane, 1.05 mmol), and the mixture was stirred for 1.5 h at 0 °C. The yellow solution was recooled to −78 °C, and a solution of **5** (148 mg, 0.55 mmol) was added. The solution was stirred in THF (5 mL) at −78 °C

for 0.5 h and then was allowed to warm to room temperature during 1 h. The mixture was diluted with H_2O (5 mL) and was extracted with Et_2O (30 mL). The extract was washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:3) gave 127 mg (87%) of **10** as a colorless solid: R_f 0.21 (EtOAc−hexanes, 1:3); mp 59−61°C; IR (neat) 1717, 1449, 1393, 1276, 1251, 1120, 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) d 1.33−1.44 (m, 1H), 1.69−1.75 (m, 3H), 1.78−1.94 (m, 1H), 2.71−2.84 (m, 1H), 2.89−3.03 (m, 2H), 3.23−3.34 (m, 1H), 3.67 (s, 1.5H), 3.71 (s, 1.5H), 3.74 (s, 3H), 4.47−4.51 (m, 1H), 4.69−4.72 (m, 1H), 5.24−5.29 (m, 0.5H), 5.40−5.45 (m, 0.5H), 7.35−7.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 22.8, 22.9, 28.3, 32.1, 32.4, 45.4, 45.6, 46.1, 46.4, 48.6, 48.9, 52.2, 52.8, 53.1, 111.3, 135.4, 135.9, 144.1, 144.5, 145.6, 155.7, 155.9, 164.7; MS (CI) *m/z* 265 $(M)^+$, 234, 206, 197, 182, 166, 152, 138, 121, 119, 106, 86; HRMS (CI) *m/z* 265.1312 (calcd for $C_{14}H_{19}O_4N$ 265.1314).

2,10-Dimethoxycarbonyl-7-methyl-2-azatetracyclo-[4.4.0.0^{4,9}.0^{7,10}]decane (11), 1,3-Dimethoxycarbonyl-8-methyl-3-azatetracyclo[6.1.1.0^{2,7}.0^{5,9}]decane (12), and 6-Methyl-4a,5,8,8a-tetrahydro-1*H*-isoquinoline-2,4-dicarboxylic Acid Dimethyl Ester (13). A solution of **10** (186 mg, 0.72 mmol) in cyclohexane (65 mL) in a photoreaction vessel was purged with argon for 1 h and was irradiated with a 450-W medium-pressure mercury lamp using a Corex filter for 3 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica (EtOAc−hexanes, 1:5 to 1:3) to give 7 mg (4%) of **13** and 96 mg (53%) of **11** and **12** (2.5:1 mixture) as a colorless oil.

Data for **11**: IR (neat) 2952, 1702, 1449, 1401, 1341, 1289, 1235, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 1.5H), 1.12 (s, 1.5H), 1.58−1.64 (m, 1H), 1.98 (brd, J = 10 Hz, 1H), 2.22 (brd, J = 7 Hz, 1H), 2.25 (brd, J = 11 Hz, 1H), 2.28−2.37 (m, 1H), 2.43−2.52 (m, 1H), 2.57−2.63 (m, 1H), 3.06−3.14 (m, 1H), 3.60−3.65 (m, 1H), 3.68 (s, 1.5H), 3.69 (s, 1.5H), 3.71 (s, 3H), 4.68 (d, J = 8 Hz, 0.5H), 4.84 (d, J = 8 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 24.3, 24.4, 29.8, 33.7, 33.8, 35.9, 36.0, 42.7, 42.9, 44.5, 47.0, 47.2, 48.2, 52.0, 52.8, 56.0, 156.4, 171.7; MS (CI) *m/z* 265 $(M)^+$, 250, 234, 197, 183, 182, 169, 152, 138, 131, 106, 102, 91; HRMS (CI) *m/z* 265.1311 (calcd for $C_{14}H_{19}O_4N$ 265.1314).

Data for **12**: ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.51 (dd, J = 1.7, 12 Hz, 0.5H), 1.53 (dd, J = 1.5, 12 Hz, 0.5H), 1.70−1.75 (m, 2H), 1.86−1.93 (m, 1H), 2.11−2.21 (m, 1H), 2.23−2.32 (m, 1H), 2.50 (dt, J = 2, 5 Hz, 0.5H), 2.53 (dt, J = 2, 5 Hz, 0.5H), 3.00 (brd, J = 11 Hz, 0.5H), 3.10 (brd, J = 11 Hz, 0.5H), 3.44 (d, J = 4, 11 Hz, 0.5H), 3.53 (d, J = 4, 11 Hz, 0.5H), 3.67 (s, 3H), 3.72 (s, 1.5H), 3.73 (s, 1.5H), 4.49 (dd, J = 2, 6 Hz, 0.5H), 4.64 (dd, J = 2, 6 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 17.6, 31.3, 31.4, 34.9, 35.1, 38.2, 38.4, 46.9, 47.0, 47.8, 48.1, 51.2, 51.4, 52.2, 52.8, 53.9, 54.0, 55.0, 55.2, 57.0, 57.4, 156.4, 171.7.

Data for **13**: IR (neat) 1733, 1700, 1635, 1445, 1437, 1252, 1211 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.65−1.75 (m, 1H), 1.82−2.01 (m, 2H), 2.25−2.32 (m, 1H), 2.39−2.51 (m, 1H), 2.75−2.86 (m, 1H), 3.13−3.25 (m, 1H), 3.71−3.75 (m, 1H), 3.75 (s, 3H), 3.85 (s, 3H), 5.31 (brs, 1H), 7.91−8.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 28.0, 28.6, 29.6, 33.3, 43.9, 51.7, 54.1, 118.0, 130.8, 134.7, 168.0 (two carbonyl signals were too weak to observe); MS (CI) *m/z* 265 $(M)^+$, 234, 197, 182, 164, 152, 138, 101, 94; HRMS (CI) *m/z* 265.1316 (calcd for $C_{14}H_{19}O_4N$ 265.1314).

7-*exo*-Hydroxy-7-*endo*-isopropenyl-2-azabicyclo[2.2.2]-oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (15) and 7-*endo*-Hydroxy-7-*exo*-isopropenyl-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (16). To a solution of selenium dioxide (64 mg, 0.57 mmol) in CH_2Cl_2 (5 mL) at 0 °C under argon was added a solution of *tert*-butyl hydoperoxide (70%, 0.2 mL, 1.56 mmol), and the mixture was stirred for 30 min at 0 °C. A solution of **10** (152 mg, 0.57 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred for 18 h at room temperature and was concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:1 to MeOH−CH_2Cl_2, 1:15) gave 98 mg (61%) of **15** and **16** (2:1 mixture) as a colorless oil.

Data for **15**: IR (neat) 3434, 2955, 1717, 1455, 1397, 1251, 1236, 1128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (dd, J = 2.5, 13.9 Hz, 1H), 1.81 (s, 3H), 1.83−1.98 (m, 1H), 2.26−2.45 (m, 1H), 2.95−3.10 (m, 2H), 3.47 (dd, J = 1.8, 10.2 Hz, 1H), 3.71(s, 3H), 3.75 (s, 3H), 4.76 (brs, 1H), 4.82 (brs, 1H), 5.21 (brs, 0.5H), 5.36 (brs, 0.5H), 7.32 (d, J = 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 32.0, 36.7, 45.7, 46.2, 52.3, 53.2, 54.0, 54.5, 78.5, 78.9, 113.2, 136.6, 144.6, 147.7, 157.0, 157.9, 164.3; MS (CI) *m/z* 282 $(M + H)^+$, 264, 250, 197, 181, 166, 152, 138, 105, 88; HRMS (CI) *m/z* 281.1261 (calcd for $C_{14}H_{19}O_5N$ 281.1263).

Data for **16**: R_f 0.17 (EtOAc−hexanes, 1:1); IR (neat) 3450, 2951, 1717, 1451, 1394, 1274, 1253, 1126, 1091 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.43−1.52 (m, 1H), 1.63−1.74 (m, 1H), 1.90 (s, 1.5H), 1.92 (s, 1.5H), 2.10 (dd, J = 2.1, 14 Hz, 0.5H), 2.19 (dd, J = 2.2, 14 Hz, 0.5H), 2.92 (dt, J = 2.4, 10.3 Hz, 0.5H), 2.95 (dt, J = 2.4, 10.6 Hz, 0.5H), 2.99−3.08 (m, 1H), 3.16 (dd, J = 2.1, 10.2 Hz, 0.5H), 3.20 (dd, J = 2.0, 10.5 Hz, 0.5H), 3.64 (s, 1.5H), 3.68 (s, 1.5H), 3.79 (s, 1.5H), 3.80 (s, 1.5H), 4.93−4.98 (m, 1H), 5.04 (s, 0.5H), 5.15 (s, 0.5H), 5.23 (d, J = 1.2 Hz, 0.5H), 5.42 (d, J = 1.2 Hz, 0.5H), 7.40−7.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 19.5, 32.1, 32.3, 37.8, 37.9, 45.5, 45.7, 52.1, 52.4, 52.6, 53.0, 77.8, 78.2, 112.5, 112.9, 135.9, 136.6, 143.4, 144.0, 146.7, 146.8, 156.0, 156.2, 165.0, 165.1; MS (CI) *m/z* 282 $(M + H)^+$, 280, 264, 250, 219, 197, 177, 149, 88; HRMS (CI) *m/z* 282.1346 (calcd for $C_{14}H_{20}O_5N$ 282.1342).

7-*endo*-Isopropenyl-7-*exo*-trimethylsilyloxy-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (19). To a solution of trimethylsilyl trifluoromethanesulfonate (46 mg, 0.21 mmol) and 2,6-lutidine (30 mg, 0.28 mmol) in CH_2Cl_2 (3 mL) at 0 °C under argon was added a solution of **15** (39 mg, 0.14 mmol) in CH_2Cl_2 (1 mL), and the mixture was stirred for 1 h at room temperature. The mixture was diluted with saturated aqueous $NaHCO_3$ (1 mL) and was extracted with CH_2Cl_2 (10 mL). The extract was washed with H_2O and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:1) gave 46 mg (93%) of **19** as a colorless solid: IR (neat) 2956, 1712, 1440, 1394, 1284, 1251, 1070, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 4.5H), 0.09 (s, 4.5H), 1.63 (t, J = 3.2 Hz, 0.5H), 1.67 (t, J = 3.1 Hz, 0.5H), 1.80−1.83 (m, 3H), 2.01 (dt, J = 2.9, 13.6 Hz, 0.5H), 2.06 (dt, J = 3, 13.7 Hz, 0.5H), 2.94−2.99 (m, 1H), 3.01 (t, J = 2.6 Hz, 0.5H), 3.03 (t, J = 2.5 Hz, 0.5H), 3.41 (dd, J = 1.8, 10 Hz, 0.5H), 3.48 (dd, J = 1.9, 10.3 Hz, 0.5H), 3.69 (m, 1.5 Hz), 3.72 (m, 1.5H), 3.74 (m, 3H), 4.65 (s, 0.5H), 4.71 (s, 0.5H), 4.82−4.85 (m, 1H), 5.20 (d, J = 1.4 Hz, 0.5H), 5.39 (d, J = 1.4 Hz, 0.5H), 7.25−7.28 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7, 32.5, 32.7, 36.2, 36.9, 45.7, 46.3, 52.2, 52.7, 52.8, 54.3, 54.8, 81.0, 113.9, 114.2, 136.1, 137.0, 144.0, 144.5, 147.9, 148.0, 156.8, 157.1, 164.3, 164.4; MS (CI) *m/z* 353 (M^+), 337, 322, 264, 198, 196, 157, 138, 105, 88; HRMS (CI) *m/z* 353.1665 (calcd for $C_{17}H_{27}O_5NSi$ 353.1659).

2,10-Dimethoxycarbonyl-6-trimethylsilyloxy-7-methyl-2-azatetracyclo[4.4.0.0.^{4,9}0^{7,10}]decane (20) and 6-Methyl-7-trimethylsilyloxy-4a,5,8,8a-tetrahydro-1*H*-isoquinoline-2,4-dicarboxylic Acid Dimethyl Ester (21). A solution of **19** (29 mg, 0.08 mmol) in Et_2O (65 mL) in a photoreaction vessel was purged with argon for 1 h and was irradiated with a 450-W medium-pressure mercury lamp using a Pyrex filter for 3 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica (EtOAc−hexanes, 1:7) to give 5.2 mg (18%) of **20** and 7.3 mg (25%) of **21**, each as a colorless oil.

Data for **20**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (9H), 1.06 (3H), 1.61−1.68 (m, 2H), 1.99−2.04 (m, 1H), 2.21−2.57 (m, 3H), 2.92−3.03 (m, 1H), 3.71−3.82 (m, 7H), 4.62 (s, 0.5H), 4.79 (s, 0.5H).

Data for **21**: IR (neat) 1733, 1700, 1445, 1370, 1252, 1209, 871, 844 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 1.56 (s, 3H), 1.68−1.90 (m, 2H), 2.03−2.14 (m, 1H), 2.29−2.39 (m, 1H), 2.49−2.62 (m, 1H), 2.77−2.85 (m, 1H), 3.14−3.26 (m, 1H), 3.74 (s, 3H), 3.75−3.80 (m, 1H), 3.81 (s, 3H), 7.92−8,11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.1, 16.4, 29.6, 30.9, 32.7, 33.8, 43.9, 51.8, 54.1, 108.7, 134.7, 140.4, 167.9; MS (CI) *m/z* 353 $(M)^+$, 281, 250, 197, 152, 119, 91; HRMS (CI) *m/z* 353.1656 (calcd for $C_{17}H_{27}O_5SiN$ 353.1659).

7-*endo*-[(1-Trifluoromethanesulfonyloxy)-1-vinyl]-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (22). To a solution of **5** (1.23 g, 4.61 mmol) in THF (20 mL) at −78 °C was added a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (10.2 mL, 5.10 mmol), and the mixture was stirred for 1 h at −78 °C. A solution of *N*-phenyltrifluoromethanesulfonimide (1.97 g, 5.53 mmol) in THF (5 mL) was added, and the mixture was stirred for 1 h at −78 °C, diluted with saturated aqueous NH_4Cl (3 mL), and extracted with Et_2O (20 mL). The extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:2) gave 1.51 g (82%) of **22** as a colorless oil: IR (neat) 1720, 1450, 1417, 1395, 1250, 1212, 1131, 928 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64−1.71 (m, 1H), 1.82−1.92 (m, 1H), 2.52−2.64 (m, 1H), 3.02−3.13 (m, 2H), 3.33−3.42 (m, 1H), 3.71 (s, 1.5H), 3.74 (s, 1.5H), 3.84 (s, 3H), 5.24 (d, J = 4.1 Hz, 0.5H), 5.26 (d, J = 4.3 Hz, 0.5H), 5.32 (d, J = 4.3 Hz, 0.5H), 5.43 (d, J = 4.3 Hz, 0.5H), 5.43 (brs, 0.5H), 5.54 (brs, 0.5H), 7.42 (d, J = 6.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 31.5, 31.6, 43.5, 43.7, 47.5, 47.9, 52.5, 53.1, 105.3, 116.7, 120.9, 137.3, 138.0, 144.0, 144.3, 156.2, 156.7, 163.6; MS (CI) *m/z* 399 $(M)^+$, 368, 281, 266, 250, 218, 197, 182, 152, 138, 106, 86; HRMS (CI) *m/z* 400.0663 (calcd for $C_{14}H_{17}O_7NF_3S$ 400.0678).

7-*endo*-Vinyl-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (23). To a solution of **22** (190 mg, 0.48 mmol) in DMF (2 mL) at room temperature were added palladium acetate (2.1 mg, 0.01 mmol), triphenylphosphine (5 mg, 0.02 mmol), and Et_3N (144 mg, 1.43 mmol) at room temperature, and the mixture was stirred for 5 min. To the mixture was added dropwise formic acid (0.05 mL, 0.10 mmol), and the solution was heated at 60 °C for 1 h. The mixture was diluted with 10% HCl (0.15 mL) and extracted with Et_2O (20 mL). The extract was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:2) gave 72 mg (60%) of **23** as a colorless oil: IR (neat) 2953, 1716, 1449, 1393, 1351, 1276, 1252, 1224, 1191, 1120, 1090, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (ddd, J = 3, 4.5, 5.9 Hz, 0.5H), 1.22 (ddd, J = 3, 4.6, 5.9 Hz, 0.5H), 1.87−1.97 (m, 1H), 2.80−2.98 (m, 3H), 3.22−3.29 (m, 1H), 3.64−3.76 (m, 6H), 4.90 (d, J = 10.3 Hz, 1H), 4.96 (dd, J = 2.1, 17.3 Hz, 0.5H), 5.08 (brs, 0.5H), 5.24 (brs, 0.5H), 5.31 (ddd, J = 7, 10.3, 17.3 Hz, 0.5H), 5.36 (ddd, J = 6.6, 10.3, 17.3 Hz, 1H), 7.36 (d, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.08, 29.13, 31.9, 32.2, 42.7, 43.0, 46.1, 46.5, 49.6, 50.0, 52.2, 52.8, 52.9, 115.8, 115.9, 135.2, 135.8, 139.8, 144.6, 144.9, 155.6, 155.9, 164.5; MS (CI) *m/z* 251 $(M)^+$, 220, 197, 169, 152, 138, 119, 106, 86; HRMS (CI) *m/z* 251.1148 (calcd for $C_{13}H_{17}O_4N$ 251.1158).

7-*endo*-[(1-Methoxycarbonyl)-1-vinyl]-2-azabicyclo[2.2.2]-oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (24). To a solution of **22** (197 mg, 0.49 mmol) in CH_3CN (5 mL) at room temperature were added palladium acetate (11 mg, 0.05 mmol), triphenylphosphine (26 mg, 0.10 mmol), Et_3N (100 mg, 0.99 mmol), and MeOH (1 mL), and the mixture was kept for 1 h at room temperature under an atmosphere of carbon monoxide. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica (EtOAc−hexanes, 1:1) to give 113 mg (74%) of **24** as a colorless oil: IR (neat) 1716, 1630, 1449, 1394, 1352, 1276, 1192, 1093, 967, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19−1.33 (m, 1H), 2.02−2.17 (m, 1H), 2.95−3.04 (m, 2H), 3.30−3.44 (m, 2H), 3.65−3.81 (m, 9H), 5.27−5.46 (m, 2H), 6.08−6.15 (m, 1H), 7.38−7.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.4, 29.6, 32.0, 32.3, 39.6, 45.8, 46.3, 48.4, 48.9, 52.2, 52.4, 52.8, 53.1, 124.8, 125.1, 135.1, 135.7, 141.6, 141.8, 144.8, 144.9, 155.7, 164.5, 167.4; MS (CI) *m/z* 309 $(M)^+$, 277, 249, 246, 203, 197, 152, 138, 119, 86; HRMS (CI) *m/z* 309.1205 (calcd for $C_{15}H_{19}O_6N$ 309.1212).

7-*endo*-[(1-Acetyl)-1-vinyl]-2-azabicyclo[2.2.2]oct-5-ene-2,6-dicarboxylic Acid Dimethyl Ester (26). To a solution of **22** (187 mg, 0.47 mmol) in dry degassed THF (10 mL) at room temperature under argon were added tri(2-furyl)phosphine (11 mg, 0.05 mmol), palladium benzylideneacetone complex (22 mg, 0.02 mmol), and LiCl (99 mg, 2.35 mmol), and the mixture was stirred for 20 min at room temperature. A solution of (α-ethoxyvinyl)tributyltin (**25**, 185 mg, 0.51 mmol) in THF (2 mL) was added, and the mixture was heated at reflux for 3 h. After hydrolysis of the mixture with 10% HCl, it was extracted with Et_2O (15 mL), and the extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue on silica (EtOAc−hexanes, 1:1) gave 89 mg (65%) of **26** as a colorless oil: IR (neat) 1715, 1449, 1394, 1276, 1251, 1120, 1092 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09−1.28 (m, 1H), 2.10−2.18 (m, 1H), 2.30 (s, 3H), 2.91−3.03 (m, 2H), 3.29−3.37 (m, 1H), 3.43−3.53 (m, 1H), 3.65−3.75 (m, 6H), 5.13 (s, 0.5H), 5.32 (s, 0.5H), 5.51 (s, 0.5H), 5.57 (s, 0.5H), 5.94 (s, 0.5H), 5.96 (s, 0.5H), 7.40−7.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 29.4, 30.0, 32.1, 32.4, 38.0, 38.3, 45.7, 46.3, 48.3, 48.9, 52.3, 52.9, 53.1, 124.7, 125.3, 135.3, 135.8, 145.0, 150.0, 150.4, 155.7, 164.7, 199.5; MS (CI) *m/z* 293 $(M)^+$, 261, 230, 218, 197, 182, 175, 152, 138, 106, 92; HRMS (CI) *m/z* 293.1262 (calcd for $C_{15}H_{19}O_5N$ 293.1263).

2,7,10-Tris(methoxycarbonyl)-2-azatetracyclo-[4.4.0.0^{4,9}.0^{7,10}]decane (30), 1,3,8-Tris(methoxycarbonyl)-3-azatetracyclo[6.1.1.0^{2,7}.0^{5,9}]decane (31), and 4a,5,8,8a-tetrahydro-1*H*-isoquinoline-2,4,6-tricarboxylic Acid Trimethyl Ester(32). A solution of **24** (123 mg, 0.40 mmol) in cyclohexane (60 mL) in a photoreaction vessel was purged with argon for 1 h and was irradiated with a 450-W medium-pressure mercury lamp using a Corex filter for 5 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica (EtOAc−hexanes, 1:2) to give 4 mg (3%) of **32** and 68 mg (55%) of **30** and **31** (1.1:1) mixture as a colorless oil.

Data for **30**: IR (neat) 1728, 1704, 1450, 1401, 1286, 1258, 1236, 1125 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (d, J = 4.1 Hz, 0.5H), 1.78 (d, J = 3.7 Hz, 0.5H), 2.10 (d, J = 3 Hz, 0.5H), 2.13 (d, J = 3.1 Hz, 0.5H), 2.30−2.37 (m, 1H), 2.38−2.48 (m, 1H), 2.57−2.64 (m, 1H), 2.82 (dd, J = 4.9, 7.1 Hz, 0.5H), 2.84 (dd, J = 5, 7.3 Hz, 0.5H), 3.11−3.22 (m, 2H), 3.67−3.79 (m, 10H), 4.91 (d, J = 7.6 Hz, 0.5H), 5.06 (d, J = 7.6 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 24.2, 28.6, 29.5, 36.3, 36.4, 40.1, 40.4, 47.0, 47.6, 48.4, 48.6, 52.4, 52.5, 52.9, 58.4, 156.3, 156.5, 170.7, 172.2; MS (CI) *m/z* 309 $(M)^+$, 277, 250, 218, 198, 197, 182, 152, 138, 119, 103, 86; HRMS (CI) *m/z* 309.1216 (calcd for $C_{15}H_{19}O_6N$ 309.1212).

Data for **31**: IR (neat) 1731, 1704, 1450, 1399, 1256, 1203 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (d, J = 6.9 Hz, 0.5H), 1.62 (d, J = 6.8 Hz, 0.5H), 1.96 (d, J = 7.9 Hz, 0.5H), 2.00 (d, J = 7.9 Hz, 0.5H), 2.02 (ddd, J = 1.7, 3.4, 7.1 Hz, 0.5H), 2.05 (ddd, J = 1.6, 3.4, 7.1 Hz, 0.5H), 2.19 (d, J = 2.7 Hz, 0.5H), 2.21 (d, J = 2.9 Hz, 0.5H), 2.28−2.38 (m, 1H), 2.87 (ddd, J = 1.6, 3.4, 6.1 Hz, 0.5H), 2.90 (ddd, J = 1.6, 3.4, 6.1 Hz, 0.5H), 2.90 (ddd, J = 1.6, 3.4, 6.2 Hz, 0.5H), 3.06 (d, 11.3 Hz, 0.5H), 3.16 (d, 11.3 Hz, 0.5H), 3.16−3.18 (m, 0.5H), 3.20 (ddd, J = 1.9, 3.7, 5.3 Hz, 0.5H), 3.51 (dd, J = 3.9, 10.9 Hz, 0.5H), 3.60

(dd, J = 4.0, 10.3 Hz, 0.5H), 3.64−3.94 (m, 9H), 4.59 (dd, J = 1.9, 6.3 Hz, 0.5H), 4.74 (dd, J = 1.9, 6.3 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.37, 31.43, 35.5, 35.7, 35.9, 36.1, 46.4, 46.5, 52.25, 52.33, 52.4, 53.0, 53.55, 53.63, 55.6, 55.8, 56.06, 56.17, 56.24, 56.4, 157.4, 157.7, 171.8, 172.0, 172.2; MS (CI) m/z 310 $(M + H)^+$, 309, 278, 277, 250, 234, 218, 196, 190, 169, 152, 131, 126, 103, 86; HRMS (CI) m/z 309.1219 (calcd for $C_{15}H_{19}O_6N$ 309.1212).

Data for **32**: ^{1}H NMR (300 MHz, $CDCl_3$) d 1.81−1.91 (m, 1H), 2.12−2.30 (m, 2H), 2.64−2.73 (m, 1H), 2.81−2.93 (m, 2H), 3.05−3.18 (m, 1H), 3.65−3.91 (m, 10H), 6.96 (m, 1H), 8.01−8.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d 27.3, 28.3, 28.6, 29.1, 43.7, 51.9, 52.1, 54.2, 113.4, 127.4, 130.0, 135.0, 136.6, 158.7, 167.6.

2,10-Bis(methoxycarbonyl)-2-azatetracyclo[4.4.0.0^{4,9}.0^{7,10}]-decane (27), 1,3-Bis(methoxycarbonyl)-3-azatetracyclo-[6.1.1.0^{2,7}.0^{5,9}]decane (28), and 4a,5,8,8a-Tetrahydro-1*H*-isoquinoline-2,4-dicarboxylic Acid Dimethyl Ester (29). A solution of **23** (120 mg, 0.48 mmol) in cyclohexane (60 mL) in a photoreaction vessel was purged with argon for 1 h and was irradiated with a 450-W medium-pressure mercury lamp using a Corex filter for 20 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica (EtOAc−hexanes, 1:3) to give 3.6 mg (3%) of **29** and 65 mg (54%) of **27** and **28** (1:1.5 mixture) as a colorless oil.

Data for **27**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55−1.70 (m, 3H), 1.91 (d, J = 10.5 Hz, 1H), 2.22−2.30 (m, 1H), 2.49−2.74 (m, 2H), 2.85−2.92 (m, 1H), 3.07−3.15 (m, 1H), 3.59 (d, J = 4.3 Hz, 0.5H), 3.62 (d, J = 4.3 Hz, 0.5H), 3.66−3.71 (m, 6H), 4.64 (d, J = 7.6 Hz, 0.5H), 4.79 (d, J = 7.7 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 23.8, 27.6, 27.7, 30.4, 36.2, 36.4, 36.5, 37.9, 38.7, 47.7, 48.5, 48.7, 52.8, 55.1, 157.6, 157.8, 172.6.

Data for **28**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55−1.66 (m, 3H), 1.85−1.93 (m, 1H), 2.09−2.21 (m, 1H), 2.34−2.42 (m, 1H), 2.60−2.69 (m, 1H), 2.84−2.92 (m, 1H), 3.02 (brd, J = 11.2 Hz, 0.5H), 3.12 (brd, J = 10.8 Hz, 0.5H), 3.43 (dd, J = 3.9, 10.8 Hz, 0.5H), 3.52 (dd, J = 3.9, 11.2 Hz, 0.5H), 3.66−3.77 (m, 6H), 4.46 (dd, J = 1.9, 6.3 Hz, 0.5H), 4.60 (dd, J = 2.0, 6.4 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.46, 31.52, 33.0, 33.2, 37.6, 37.8, 43.5, 43.7, 44.9, 45.0, 46.7, 46.9, 52.1, 52.2, 52.4, 52.8, 52.9, 55.4, 55.7, 56.8, 56.9, 157.6, 157.8, 172.8, 173.2.

Data for **29**: ^{1}H NMR (300 MHz, $CDCl_3$) d 1.79−2.04 (m, 1H), 2.39−2.55 (m, 2H), 2.79−2.85 (m, 1H), 3.14−3.30 (m, 1H), 3.54−3.80 (m, 7H), 4.87−5.05 (m, 1H), 5.52−5.65 (m, 2H), 7.89−8.10 (m, 1H).

8-Acetyl-1,3-bis(methoxycarbonyl)-3-azatetracyclo-[6.1.1.0^{2,7}.0^{5,9}]decane (33). A solution of **26** (40 mg, 0.14 mmol) in cyclohexane (60 mL) in a photoreaction vessel was purged with argon for 1 h and was irradiated with a 450-W medium-pressure mercury lamp using a Pyrex filter for 8 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica (EtOAc−hexanes, 1:3 to 1:2) to give 19 mg (47%) of **33** as a colorless oil: IR (neat) 1731, 1699, 1449, 1399, 1253, 1197, 1124 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50−1.57 (m, 1H), 1.73−1.82 (m, 1H), 1.97−2.06 (m, 1H), 2.09−2.16 (m, 1H), 2.13 (s, 3H), 2.23−2.35 (m, 1H), 2.82−2.89 (m, 1H), 3.01−3.16 (m, 2H), 3.48 (dd, J = 4, 11 Hz, 0.5H), 3.57 (dd, J = 4, 11.3 Hz, 0.5H), 3.77−3.85 (m, 6H), 4.60 (dd, J = 2, 6.3 Hz, 0.5H), 4.75 (dd, J = 2, 6.3 Hz, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.3, 27.4, 31.3, 35.6, 35.7, 36.0, 36.2, 46.2, 46.3, 46.4, 46.6, 52.4, 52.5, 53.0, 53.2, 54.3, 54.4, 56.3, 56.7, 63.36, 63.43; MS (CI) m/z 293 $(M)^+$, 263, 261, 234, 218, 206, 190, 182, 158, 152, 138, 117, 103, 91; HRMS (CI) m/z 293.1258 (calcd for $C_{15}H_{19}O_5N$ 293.1263).

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Supporting Information Available: General experimental conditions; ^{1}H and ^{13}C NMR spectra for new compounds; X-ray crystallographic data for **5** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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