Supplementary Information for:

The Oxa-Di-Pi-Methane Photochemical Rearrangement of Quinuclidinones: a Novel Aza-variant. Synthesis of Pyrrolizidinones

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Analysis of COSY spectrum of photoproduct 2a:

The proton responsible for the peak at 4.22 ppm (d, $J = 4.8$ Hz) was coupled only to one proton at 3.06 ppm (dd, $J = 6.5, 4.9$ Hz), which in turn was coupled to only one other proton at 2.25 ppm. Of the protons $H_a - H_i$, only proton H_a was expected to be coupled to only one other proton, namely H_b . The chemical shift of 4.22 ppm was also reasonable for H_a (H on a cyclopropane ring and β to both a ketone and ester is at 1.48 ppm; add shift 2.5 ppm due to the α nitrogen, and calculated shift of H_a is 4.0 ppm). The multiplet at 3.06 ppm was therefore assigned to H_b , and was coupled to one other proton at 2.25 ppm. This other proton could be either H_c or H_d .

Figure 1 COSY spectrum of compound 2a.

In order to assist in the assignments, the tricyclic structure **2a** was submitted to molecular mechanics calculations to estimate the dihedral angles between the protons, and thus approximate the coupling constants using the Karplus equation (see **Table 1**). According to these calculations, H_b and H_c had a dihedral angle of approx. 13 deg., and thus an estimated coupling constant of 7.5 Hz, while H_b and H_d had a dihedral angle of approx. 110 deg. and an estimated coupling constant 1 Hz. The measured *J* value between signals at 3.06 and 2.25 ppm was 6.5 Hz, closely matching the calculated coupling constant between H_b and H_c. Therefore, H_c was assigned to the signal at 2.25 ppm. This multiplet (ddd) exhibited three coupling constants of 14.0, 7.0, 6.9 Hz. The large coupling of 14 Hz would be consistent with geminal coupling to proton H_d. The calculations predicted that in addition to H_b, H_c would couple to H_e with a dihedral angle of 32 deg., and an estimated coupling constant of 6 Hz. H_i was predicted to be nearly orthogonal to H_c, and thus have little or no coupling to H_c. From this data, H_d was assigned to the multiplet at 1.99 ppm, and H_e to the multiplet at 3.32 ppm. From the COSY spectrum, the multiplet at 1.99 ppm was further coupled to the multiplet at 2.79 ppm, which was assigned to H_i. The multiplet (dd) at 2.79 had two coupling constants of 12.3 and 6.2 Hz. The large coupling constant was geminal coupling with H_e. The other coupling constant was consistent with the calculation of the dihedral angle of 35 deg. between H_i and H_d. The protons H_g and H_h were coupled only to each other, and the exo proton H_g was assigned as the downfield doublet of doublets at 3.65 ppm.

The distances between the protons of the proposed structure were also calculated by molecular mechanics and are summarized in **Table 1**. The photoproduct was submitted to NOE experiments to verify the spatial relationships. The signals associated to H_a, H_b, H_c and H_e yielded meaningful data, and the NOE results are shown in **Table 1**. Results of the NOE experiments are in agreement with the proposed structure, where H_a, H_b, H_c and H_e are shown to be in a cis relationship.

Table 1 Comparison of calculated proton distances, dihedral angles and estimated *J* couplings, with empirical *J* couplings and NOE results.

Protons	Mechanics			Experimental	
	Distance (Å)	Angle(degrees)	<i>J</i> Coupling (Hz, est.)	<i>J</i> Coupling (Hz)	NOE effect
H _a - H _b	2.71	7.1	8	4.8	yes
H _b - H _c	2.47	13	7.5	6.5	yes
H _b - H _d	2.92	108	1	0	
H _c - H _d	1.81	109	10-20	14.0	yes
H _c - H _e	2.37	32	6	7.0	yes
H _c - H _i	2.77	87	< 1	0	
H _d - H _e	3.09	154	8	NA	
H _d - H _i	2.48	35	6	NA	
H _e - H _i	1.79	107	10-20	12.3	yes
H _g - H _h	1.8	108	10-20	18.0	yes

The ¹³C and HETCOR spectra in **Figures 2a** and **2b**, respectively, further verified the proposed structure **2a**. No carbon signals were detected in the alkene region of the spectrum, consistent with the lack of alkene protons. The only ketone carbonyl peak detected was at 207.6 ppm, consistent with the ketone in **2a**. The HETCOR data is summarized in **Table 2**.

Table 2 HETCOR data for compound **2a**.

Carbon	¹³ C ppm	Proton(s)	¹ H ppm
C-1	63.7	H _a	4.23
C-2	43.7	H _b	3.06
C-3	26.5	H _{c,d}	2.25, 1.99
C-4	64.3	H _{e,i}	3.32, 2.79
C-5	68.8	H _{g,h}	3.64, 2.84
C-6	53.1	H _j	3.75

Figure 2: (a) ^{13}C spectrum of compound 2a in $\text{CDCl}_3/\text{benzene-d}_6$. (b) HETCOR spectrum of compound 2a.

FULL EXPERIMENTAL PROCEDURES AND DATA

Preparation of 1a:

(1) 5,5-dimethoxy-1-azabicyclo[2.2.2]octane-3-carboxylic acid methyl ester (**3a**)⁵:

exo isomer: ¹H-NMR (CDCl₃): 3.61 (s, 3H, H's on C12), 3.36 (ddd, 1H, *J*=12.4, 5.3, 2.1 Hz, H on C3), 3.11 (s, 3H, H's on C9 or C10), 2.99 (s, 3H, H's on C10 or C9), 2.92-2.60 (m, 6H, H's on C2, C6, and C7), 2.44 (ddd, 1H, *J*=13.3, 6.2, 2.8 Hz, H on C4), 1.75 (dddd, 1H, *J*= 16.0, 11.2, 9.8, 2.8 Hz, H on C8), 1.42 (dddd, 1H, *J*= 15.9, 10.1, 6.5, 2.7 Hz, H on C8). ¹³C-NMR (CDCl₃): 174.2 (C11), 99.6 (C5), 58.8 (C6), 51.8 (C12), 48.8 (C10 or C9), 48.3 (C2), 47.7 (C9 or C10), 46.3 (C7), 39.7 (C3), 22.5 (C8). GC: Rt=18.3 min. MS: 229 (4), 214 (100), 198 (25), 166 (16), 139 (12), 96 (14), 55 (14). Spectral data are consistent with literature values.⁵

endo isomer: ¹H -NMR (CDCl₃): 3.65 (s, 3H, H's on C12), 3.36 (ddd, 1H, *J*=12.4, 5.3, 2.1 Hz, H on C3), 3.15 (s, 3H, H's on C9 or C10), 2.99 (s, 3H, H's on C10 or C9), 2.92-2.60 (m, 6H, H's on C2, C6, and C7), 2.44 (ddd, 1H, *J*=13.3, 6.2, 2.8 Hz, H on C4), 1.75 (dddd, 1H, *J*= 16.0, 11.2, 9.8, 2.8 Hz, H on C8), 1.42 (dddd, 1H, *J*= 15.9, 10.1, 6.5, 2.7 Hz, H on C8). ¹³C -NMR (CDCl₃): 174.2 (C11), 99.6 (C5), 58.2 (C6), 51.7 (C12), 48.6 (C10 or C9), 48.0 (C2), 47.7 (C9 or C10), 45.9 (C7), 37.2 (C3), 22.5 (C8). GC: Rt=18.5 min. MS: 229 (4), 214 (100), 198 (25), 166 (16), 139 (12), 96 (14), 55 (14). Spectral data are consistent with literature values.⁵

(2) 5,5-dimethoxy-3-phenylselenenyl-1-azabicyclo[2.2.2]octane-3-carboxylic acid methyl ester:

A 50 mL round-bottomed flask was charged with diisopropyl amine (0.722 g, 7.14 mmol) and THF (10 mL). The flask was cooled to 0°C as *n*-butyllithium (6.5 mL, 1.1 M in hexanes) was added. After stirring at 0° C for 45 min, ketal **3a** (0.692 g, 3.02 mmol) in THF (10 mL) was added by syringe pump over 90 min and allowed to stir at 0° C for 1 h. The flask was charged with phenylselenenyl chloride (0.675 g, 3.53 mmol) in THF (10 mL) and allowed to slowly warm to room temperature. After stirring at room temperature for 13 h the mixture was quenched with H₂O (40 mL). The layers were separated and the aqueous layer was washed with Et₂O (3 X 20 mL). The organic washes were combined, dried with MgSO₄, and the solvent was removed under reduced pressure to yield an orange oil (1.25 g). Column chromatography (1% NEt₃/Et₂O), yielded the selenide as a pale yellow oil as a single diastereomer (*R*_f=0.25, 1% NEt₃/Et₂O), (0.638 g, 1.66 mmol, 55%).

¹H-NMR (CDCl₃): 7.48 (d, 2H, *J*=6.8 Hz, H's on C14 and C18), 7.28-7.06 (m, 3H, H's on C15, C16, and C17), 3.76-3.41 (m, 1H, H on C4), 3.38 (s, 3H, H's on C12), 3.06 (s, 3H, H's on C9 or C10), 2.89 (s, 3H, H's on C10 or C9), 3.21-2.50 (m, 6H, H's on C2, C6, and C7), 2.21-2.05 (m, 1H, H on C8), 1.80-1.64 (m, 1H, H on C8).

^{13}C -NMR (CDCl_3): 173.8 (C11), 137.8 (C14 and C18), 129.1 (C15 and C17), 128.9 (C16), 128.0 (C13), 101.6 (C5), 57.8 (C6), 56.9 (C2), 51.9 (C3), 49.8 (C9, C10, or C12), 49.1 (C10, C12, or C9), 48.3 (C12, C9, or C10), 46.0 (C7), 36.2 (C4), 19.7 (C8). HRMS calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{Se}$: 382.074543, found: 382.076521.

GC: R_t =26.6 min. MS: 385 (6), 370 (25), 354 (12), 228 (100), 212 (15), 196 (17), 154 (62), 101 (11), 77 (19), 51 (14). IR (NaCl , cm^{-1}): 3055, 2959, 2873, 1728, 1639, 1438, 1260, 1120, 1038, 802, 736.

(3): 1-Aza-3-methoxycarbonylbicyclo-3-phenylselenylbicyclo[2.2.2]octan-5-one:

A 5 mL React Vial was charged with the methoxy-selenide (0.230 g, 0.634 mmol) and CH_2Cl_2 (0.9 mL). The flask was cooled to 0°C , and HClO_4 (0.48 mL, 70%) was slowly added. After stirring at 0°C for 30 min., the mixture was diluted with H_2O (0.5 mL) and CH_2Cl_2 (0.5 mL). Solid Na_2CO_3 was added until the mixture was basic (pH ~ 10). The layers were separated, and the aqueous layer was extracted with ether (3 x 1 mL). The combined organic extracts were dried with Na_2SO_4 , and concentrated to yield a brown oil (212.3 mg). Flash chromatography (1% $\text{Et}_3\text{N}/\text{Et}_2\text{O}$) yielded the keto-selenide as a pale yellow oil, R_t = 0.29 (5% $\text{Et}_3\text{N}/\text{Et}_2\text{O}$), (191.2 mg, 0.564 mmol, 89%).

^1H -NMR (CDCl_3): 7.55-7.52 (m, 2H, H's on C12 and C16), 7.45-7.27 (m, 3H, H's on C13, C14, C15), 3.84 (dd, 1H, J = 7.3, 2.2 Hz, H on C4), 3.50 (s, 3H, H's on C10), 3.30 - 2.74 (m, 7H, H's on C2, C6, C7, C8), 1.99 - 1.97 (m, 1H, H on C8). ^{13}C -NMR (CDCl_3): 214.8 (C5), 173.3 (C9), 137.4 (C12 and C16), 129.2 (C13 and C15), 129.2 (C14), 126.0 (C11), 61.8 (C6), 57.3 (C2), 52.5 (C3), 50.3 (C10), 46.4 (C4), 45.8 (7). HRMS calculated for $\text{C}_{15}\text{H}_{17}\text{NO}_3\text{Se}$: 339.0374, found: 339.0359; IR (NaCl , cm^{-1}): 3057, 2925, 1738, 1732, 1618, 690.

(4): 5-oxo-1-azabicyclo[2.2.2]oct-2-ene-3-carboxylic acid methyl ester (1a): The ketoselenide (see above, 60.2 mg, 0.178 mmol) was placed in a 1-mL React Vial, dissolved in glacial acetic acid (200 μL), and cooled to 0°C . Hydrogen peroxide (400 μL) was then added, and the reaction stirred for 30 min. The mixture was then diluted with water (400 μL), made basic with sat. aq. Na_2CO_3 , and extracted with ether (3 x 2 mL). The combined extracts were dried with Na_2SO_4 and evaporated to yield a clear oil (12.8 mg, 0.071 mmol, 39%). R_t = 0.49 (5% $\text{Et}_3\text{N}/\text{Et}_2\text{O}$).

^1H -NMR (CDCl_3): 7.54 (d, 1H, J =1.25 Hz, H on C2), 3.80 (s, 3H, H's on C10), 3.73 (m, 1H, H on C4), 3.20 (d, 1H, J =18.6 Hz, H on C6), 3.12 (d, 1H, J =20.5 Hz, H on C6), 3.07 (m, 1H, H on C7), 2.80 (m, 1H, H on C7), 2.17 (m, 1H, H on C8), 2.00 (m, 1H, H on C8). ^{13}C -NMR (CDCl_3): 213.6 (C5), 163.7 (C9), 154.4 (C2), 134.9 (C3), 58.1 (C6), 52.1 (C10), 47.7 (C7), 44.7 (C4), 26.3 (C8). HRMS calculated for $\text{C}_9\text{H}_{11}\text{NO}_3$: 181.0739, found: 181.0735. MS m/z (%): 181 (3), 153 (100), 150 (14), 94 (32), 93 (15), 66 (14), 59 (14).

Preparation of photoproduct 2a, 3-Oxo-1-azatricyclo[3.3.1.0^{4,6}]octane-4-carboxylic acid methyl ester:

The volatile photoprecursor **1a** (<5 mg, <0.0276 mmol) was dissolved in acetophenone and irradiated in a quartz tube at 350 nm for 15 h (a carousel reactor was utilized in this case). The solution was placed on a silica gel column, and eluted with ether until all the acetophenone had been eluted. The single product was then eluted with 1% Et₃N/Et₂O (1 mg, 0.005 mmol; R_f = 0.28, 5% Et₃N/Et₂O).

¹H-NMR (CDCl₃): 4.15 (d, 1H, *J*=4.8 Hz, H on C5), 3.75 (s, 3H, H's on C10), 3.64 (d, 1H, *J*=17.7 Hz, H on C2), 3.32 (m, 1H, β H on C8), 3.06 (dd, 1H, *J* = 6.5, 4.9 Hz, H on C6), 2.84 (d, 1H, *J* = 18.4 Hz, H on C2), 2.79 (dd, 1H, *J* = 12.3, 6.2 Hz, α H on C8), 2.25 (ddd, 1H, *J* = 14.0, 7.0, 6.9 Hz, β H on C7), 1.99, (m, 1H, α H on C7). ¹³C-NMR (CDCl₃): 207.6 (C3), 166.4 (C9), 68.4 (C2), 64.0 (C8), 63.2 (C5), 52.6 (C10), 48.1 (C4), 43.2 (C6), 26.3 (C7). HRMS calculated for C₉H₁₁NO₃: 181.0739, found: 181.0742. MS: 181 (76), 180 (21), 153 (40), 152 (16), 149 (43), 122 (100), 94 (50), 82 (97), 67 (34), 59 (28).

Preparation of 1b:**(1) 5,5-dimethoxy-1-azabicyclo[2.2.2]octane-3-carboxylic acid heptyl ester (3b):**

A 100 mL round-bottomed flask was charged with the ketal, **3a**, (1.50 g, 6.56 mmol), KCN (0.3583 g, 5.50 mmol), and heptanol (40 mL). After stirring at 130°C for 40 h, the solvent was removed under reduced pressure to yield an orange oil (2.22 g). The oil was diluted in H₂O (30 mL) and CH₂Cl₂ (30 mL). The layers were separated and the aqueous layer was washed with CH₂Cl₂ (4 X 30 mL). The organic washes were combined, dried with MgSO₄, and the solvent was removed under reduced pressure to yield a yellow oil (2.07 g). Column chromatography (1% NEt₃/2% MeOH/CH₂Cl₂), yielded **3b** as a pale yellow oil as a 1:1 mixture of diastereomers (R_f=0.33, 1% NEt₃/2% MeOH/CH₂Cl₂, 0.97 g, 3.10 mmol, 47%), (R_f=0.28, 1% NEt₃/2% MeOH/CH₂Cl₂, 0.93 g, 2.97 mmol, 45%).

exo isomer:

¹H -NMR (CDCl₃): 4.10 (t, 2H, *J*=5.9 Hz, H's on C12), 3.34 (dd, 1H, *J*=4.6, 2.9 Hz, H on C3), 3.19 (s, 6H, H's on C9 and C10), 3.02-2.62 (m, 6H, H's on C2, C6, and C7), 2.45 (dd, 1H, *J*=4.2, 2.9 Hz, H on C4), 1.65-1.56 (m, 3H, H's on C8 and C13), 1.34-1.22 (m, 8H, H's on C14, C15, C16, and C17), 0.85 (t, 3H, *J*=7.0 Hz, H's on C18). ¹³C - NMR (CDCl₃): 174.8 (C11), 100.9 (C5), 65.2 (C12), 59.3 (C2), 49.4 (C10), 48.8 (C6), 48.7 (C9), 46.8 (C7), 37.8 (C3), 32.0 (C4), 31.9 (C13), 29.5 (C14), 29.1 (C15), 26.4 (C16), 22.9 (C8), 18.3 (C17), 14.4 (C18). HRMS calculated for C₁₇H₃₁NO₄: 313.225309, found: 313.224571. GC: R_t=24.8 min. MS: 313 (2), 298 (100), 281 (15), 252 (12), 200 (28), 184 (9), 166 (10), 138 (26), 111 (13), 96 (14), 55 (13). IR (NaCl, cm⁻¹): 2933, 2857, 1723, 1466, 1362, 1312, 1190, 1122, 1035, 910, 732.

endo isomer:

¹H -NMR (CDCl₃): 4.08 (t, 2H, *J*=5.9 Hz, H's on C12), 3.19 (s, 6H, H's on C9 and C10), 3.11 (dd, 1H, *J*=18.2, 4.6 Hz, H on C3), 3.02-2.62 (m, 6H, H's on C2, C6, and C7), 2.43 (dd, 1H, *J*=4.2, 2.9 Hz, H on C4), 1.65-1.56 (m, 3H, H's on C8 and C13), 1.34-1.22 (m, 8H, H's on C14, C15, C16, and C17), 0.85 (t, 3H, *J*=7.0 Hz, H's on C18). ¹³C -

NMR (CDCl₃): 174.8 (C11), 100.9 (C5), 65.0 (C12), 58.7 (C2), 49.1 (C10), 48.7 (C6), 46.5 (C9), 46.8 (C7), 40.3 (C3), 32.1 (C4), 31.9 (C13), 29.5 (C14), 29.1 (C15), 26.3 (C16), 22.9 (C8), 18.3 (C17), 14.4 (C18). HRMS calculated for C₁₇H₃₁NO₄: 313.225309, found: 313.224571. GC: R_t=24.4 min. MS: 313 (2), 298 (100), 281 (15), 252 (12), 200 (28), 184 (9), 166 (10), 138 (26), 111 (13), 96 (14), 55 (13). IR (NaCl, cm⁻¹): 2933, 2857, 1723, 1466, 1362, 1312, 1190, 1122, 1035, 910, 732.

(2) 5,5-dimethoxy-3-phenylselenyl-1-azabicyclo[2.2.2]octane-3-carboxylic acid heptyl ester:

A 10 mL round-bottomed flask was charged with heptyl ester **3b** (0.449 g, 1.44 mmol) and THF (0.5 mL). The flask was cooled to -78 °C and LDA (4.0 mL, 0.5 M in THF/hexane) was added. The reaction mixture was stirred for 5 min. before warming to rt. After 15 min, the reaction mixture was recooled to -78 °C, and a solution of phenylselenenyl chloride (0.496 g, 2.50 mmol) in THF (0.5 mL) was quickly added via syringe. The reaction mixture was stirred at -78 °C for 2 h, and then added to water (2 mL). The layers were separated, and the aqueous layer extracted with ether (3x5 mL). The combined organic layers were dried with Na₂SO₄, and concentrated in vacuo to yield 0.783 g of a brown oil. Flash column chromatography (0.8% Et₃N/Et₂O) yielded a pale yellow oil (0.482 g, 1.03 mmol, 71%; R_f = 0.51 (5%Et₃N/Et₂O)).

¹H-NMR (CDCl₃): 7.54 (d, 2H, J=7.1 Hz, H's on C20 and C24), 7.38-7.24 (m, 3H, H's on C21, C22, and C23), 4.05-3.54 (m, 3H, H's on C4 and C12), 3.12 (s, 3H, H's on C9 or C10), 2.98 (s, 3H, H's on C10 or C9), 3.42-2.50 (m, 6H, H's on C2, C6, and C7), 2.31-2.14 (m, 1H, H on C8), 1.90-1.76 (m, 1H, H on C8), 1.42-1.34 (m, 2H, H's on C13), 1.28-1.14 (m, 8H, H's on C14, C15, C16, and C17), 0.85 (t, 3H, J=7.0 Hz, H's on C18). ¹³C-NMR (CDCl₃): 173.3 (C11), 137.2 (C20 and C24), 129.0 (C22), 128.7 (C21 and C23), 101.3 (C5), 64.6 (C12), 57.4 (C6), 56.2 (C2), 48.7 (C9 or C10), 47.6 (C3), 45.5 (C10 or C9), 35.4 (C4), 31.7 (C13), 28.8 (C14), 25.8 (C15), 22.5 (C16), 19.2 (C17), 14.0 (C18). HRMS calculated for C₂₃H₃₆NO₄Se: 465.178496, found: 465.177582. MS: 467 (1), 437 (7), 388 (8), 335 (7), 312 (28), 280 (53), 261 (100), 246 (39), 214 (22), 166 (49), 154 (81), 138 (31), 77 (63). IR (NaCl, cm⁻¹): 3054, 2968, 2872, 1723, 1639, 1466, 1382, 1206, 1124, 1070, 910, 732.

(3) 5-oxo-1-azabicyclo[2.2.2]oct-2-ene-3-carboxylic acid heptyl ester (1b**):**

A 25 mL round-bottomed flask was charged with the heptoxy-selenide (0.264 g, 0.56 mmol) and CH₂Cl₂ (7 mL). The flask was cooled to 0°C as HClO₄ (7 mL, 70%) was slowly added, the stirring mixture was then slowly warmed to room temperature. After stirring for 90 min at room temperature, the mixture was poured into 10% Na₂CO₃ (20 mL) and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 X 30 mL). The organic washes were combined, dried with MgSO₄, and the solvent was removed under reduced pressure to yield a black oil (0.32 g). Column chromatography (1% NEt₃/Et₂O) yielded **1b** as a pale yellow oil (0.137 g, 0.52 mmol, 93%; R_f=0.35, (1% NEt₃/Et₂O)).

¹H-NMR (CDCl₃): 7.51 (d, 1H, J=1.2 Hz, H on C2), 4.16 (t, 2H, J=6.5 Hz, H's on C10), 3.80-3.75 (m, 1H, H on C4), 3.29-2.95 (m, 3H, H's on C6, C7), 2.78 (dddd, 1H, J=14.2, 9.3, 5.1, 2.4 Hz, H on C8), 2.15 (dddd, 1H, J=14.1, 7.5, 5.2, 2.4 Hz, H on C8), 1.95 (ddd, 1H, J=18.1, 9.5, 4.4 Hz, H on C7), 1.66 (app pent, 2H, J=7.0 Hz, H's on C11), 1.42-1.16 (m, 8H, H's on C12, C13, C14, C15), 0.89-0.83 (t, 3H, J=6.5 Hz, H's on C16). ¹³C-NMR (CDCl₃): 209.0 (C5), 154.0 (C9), 137.4 (C2), 129.2 (C3), 65.4 (C6), 58.1 (C10), 47.7 (C7), 44.7 (C4), 31.7 (C11), 28.9 (C12), 28.5 (C13), 26.4 (C14), 25.9 (C15), 22.6 (C8), 14.0 (C16). HRMS calculated for C₁₅H₂₃NO₃:

265.167794, found: 265.167694. GC: Rt=23.8 min. MS: 266 (1), 237 (85), 208 (10), 194 (18), 150 (20), 140 (42), 122 (26), 95 (100), 67 (40), 55 (35). IR (NaCl, cm^{-1}): 2926, 1735, 1719, 1618, 1466, 1300, 1262, 1092, 910, 733. UV: λ_{max} =204 (log ϵ =3.24), 218 (log ϵ =3.40), 260 (log ϵ =2.68), 300 (log ϵ =2.20).

Preparation of photoproduct 2b, 3-Oxo-1-azatricyclo[3.3.1.0^{4,8}]octane-4-carboxylic acid heptyl ester: An 100 mL cone flask was charged with enone **1b** (0.168 g, 0.63 mmol), acetophenone (3 mL), and acetone (60 mL). The mixture was frozen under vacuum and then thawed under argon. This degassing process was repeated three times. The mixture was then irradiated with a Hanovia medium pressure 450 W lamp in an immersion photowell equipped with a quartz cooling jacket for 20 h. The solvent was removed under reduced pressure to yield an orange oil (0.19 g). Column chromatography (1% $\text{NEt}_3/\text{Et}_2\text{O}$) yielded **2b** as a pale yellow oil (R_f =0.24, 1% $\text{NEt}_3/\text{Et}_2\text{O}$), (0.117 g, 0.44 mmol, 70%) and enone **1b** (R_f =0.35, 1% $\text{NEt}_3/\text{Et}_2\text{O}$), (0.047 g, 0.18 mmol, 27%).

^1H -NMR (CDCl_3): 4.15 (d, 1H, J =4.8 Hz, H on C5), 4.09 (t, 2H, J =6.7 Hz, H's on C10), 3.60 (d, 1H, J =17.7 Hz, α or β H on C2), 3.29 (ddd, 1H, J =11.7, 11.7, 8.1 Hz, α H on C8), 3.00 (app. t, 1H, J =5.1 Hz, H on C6), 2.80 (d, 1H, J =17.7 Hz, α or β H on C2), 2.75 (dd, 1H, J =12.5, 6.3 Hz, β H on C8), 2.33-2.08 (m, 1H, β H on C7), 1.94 (m, 1H, α H on C7), 1.62 (m, 2H, H's on C11), 1.37-1.20 (m, 8H, H's on C12, C13, C14, and C15), 0.86 (t, 3H, J =6.4 Hz, H's on C16). ^{13}C -NMR (CDCl_3): 207.4 (C3), 165.9 (C9), 68.3 (C2), 65.7 (C8), 64.0 (C10), 63.0 (C5), 48.2 (C4), 42.7 (C6), 31.6 (C11), 28.8 (C12), 28.4 (C13), 26.1 (C7), 25.7 (C14), 22.5 (C15), 14.0 (C16). HRMS calculated for $\text{C}_{15}\text{H}_{23}\text{NO}_3$: 265.167794, found: 265.167000. GC: Rt=23.4 min. MS: 265 (21), 236 (25), 222 (15), 208 (8), 194 (13), 181 (14), 166 (34), 149 (28), 139 (60), 122 (54), 111 (15), 95 (75), 82 (100), 67 (36), 55 (44). IR (NaCl, cm^{-1}): 2928, 2856, 1744, 1716, 1458, 1354, 1256, 1235, 1142, 1041, 810. UV: λ_{max} =204 (log ϵ =3.20), 214 (log ϵ =3.40), 262 (log ϵ =2.74).

(5*S,6*R**)-3-hydroxy-6-methyl-1-azabicyclo[3.3.0]oct-3-ene-4-carboxylic acid heptyl ester (**5**):** A 25 mL round-bottomed flask was charged with CuI (0.030 g, 0.16 mmol) and Et_2O (7 mL) and cooled to 0° C. After stirring at 0° C for 15 min, MeLi (0.40 mL, 0.85 M) in Et_2O (3 mL) was added by syringe pump over a period of 60 min. After stirring at 0° C for 2 h, tricyclic amine **2b** (0.0207 g, 0.078 mmol) in Et_2O (5 mL) was added by syringe pump over a period of 60 min. After stirring at 0° C for 16 h the mixture was poured into 10% HCl (20 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL). The organic washes were combined, dried with MgSO_4 , and the solvent was removed under reduced pressure to yield an orange oil (0.028 g). Column chromatography (3% MeOH/ CH_2Cl_2) yielded **5** as a colorless oil (R_f =0.08, 3% MeOH/ CH_2Cl_2), (0.017 g, 0.060 mmol, 77%). NMR indicated a mixture of keto-enol forms.

^1H -NMR (CDCl_3): 5.62 (bs, H on O (enol form)), 4.15 (m, 1H, H on C5), 4.06 (t, 2H, J = 6.7 Hz, H's on C10), 3.65 (m, 2H, H's on C2), 3.18 (m, 1H, H C8), 2.83-2.67 (m, 1 H, H6), 2.62-2.52 (m, 1H, H8), 2.20 (m, 1H, H on C7), 2.05-1.91 (m, 1H, H on C7), 1.72-1.54 (m, 2H, H's on C11), 1.37 (d, 3H, J =6.8 Hz, H's on C17), 1.36-1.05 (m, 8H, H's on C12, C13, C14, and C15), 0.86 (m, 3H, H's on C16). ^{13}C -NMR (CDCl_3): 203.9 (C3, keto form), 194.0 (C3, enol form), 176.9 (C9, enol form), 170.6 (C9, keto form), 120.3 (C4, enol form), 77.2 (C2), 68.9 (C4, keto form), 68.3 (C8), 63.3 (C5), 53.0 (C10), 45.8 (C6), 31.7 (C11), 29.7 (C12), 28.8 (C13), 28.5 (C17), 26.2 (C7), 25.8 (C14), 22.5 (C15), 14.0 (C16). HRMS calculated for $\text{C}_{16}\text{H}_{27}\text{NO}_3$: 281.199094, found: 281.200165. GC: Rt=23.3 min. MS: 281 (2), 253 (13), 210 (8), 182 (5), 166 (10), 110 (100), 96 (27), 84 (22), 49 (40). IR (NaCl, cm^{-1}): 3366, 2926, 2855, 1734, 1718, 1654, 1458, 1263, 1078, 737.

3-hydroxy-1-azabicyclo[3.3.0]oct-3-ene-4-carboxylic acid heptyl ester (6): A 25 mL round-bottomed flask was charged with photoproduct **2b** (0.018 g, 0.068 mmol), Et₂O (3 mL) and HCl:Et₂O (5 mL, 1.0 M). The mixture was allowed to stir for 0.5 h, the solvent was removed via cannula and reduced pressure to yield the tricyclic amine salt (0.020 g). The salt was dissolved in ethanol (5 mL) and Pd/C (10%, 0.015 g) was added. The mixture was stirred under an atmosphere of H₂ for 16 h, filtered through celite, and concentrated under reduced pressure to yield an orange oil (0.021 g). Column chromatography (1% NEt₃/2% MeOH/CH₂Cl₂) yielded **6** as a pale yellow oil (R_f=0.41 1% NEt₃/3% MeOH/CH₂Cl₂), (0.015 g, 0.056 mmol, 82%).

¹H-NMR (CDCl₃): 5.62 (bs, H on O (enol form), 4.16 (m, 1H, H on C5), 4.05 (bt, 2H, *J*=6.8 Hz, H's on C10), 3.70-3.55 (m, 2H, H's on C2), 3.50-2.80 (m, 4H, H's on C6, C8), 2.05 (m, 1H, H on C7), 1.45 (m, 1H, H on C7), 1.46 (m, 2H, H's on C11), 1.26 (m, 8H, H's on C12, C13, C14, and C15), 0.86 (m, 3H, H's on C16). ¹³C-NMR (CDCl₃): 203.9 (C3, keto form), 194.0 (C3, enol form), 176.9 (C9, keto form), 170.6 (C9, enol form), 120.3 (C4, enol form), 77.2 (C2), 68.9 (C4, keto form), 68.3 (C8), 63.3 (C5), 53.0 (C10), 45.8 (C6), 31.7 (C11), 29.7 (C12), 28.8 (C13), 26.2 (C7), 25.8 (C14), 22.5 (C15), 14.0 (C16). HRMS calculated for C₁₅H₂₆NO₃: 268.191269 (M+H⁺), found: 268.190872. GC: Rt=24.7 min. MS: 267 (1), 264 (3), 239 (16), 219 (10), 196 (10), 152 (8), 141 (10), 96 (100), 84 (12), 71 (11), 55 (5). IR (NaCl, cm⁻¹): 3385, 2929, 2857, 1733, 1468, 1397, 1262, 1198, 909, 733.

5-Aza-2-ethoxycarbonylbicyclo[3.3.0]oct-2-ene-3-ol (7): A 50 mL round-bottomed flask was charged with hydrogenated photoproduct **6** (0.048 g, 0.18 mmol), KCN (0.010 g, 0.15 mmol) and freshly distilled ethanol (30 mL). The mixture was allowed to stir for 4 d at reflux, the solvent was removed under reduced pressure to yield a brown oil (0.050 g). The oil was dissolved in H₂O (20 mL) and organics were extracted with CH₂Cl₂ (4 X 20 mL) yield an orange oil (0.041 g). Column chromatography (1% NEt₃/2% MeOH/CH₂Cl₂) yielded **7** as a pale yellow oil (R_f=0.38 1% NEt₃/3% MeOH/CH₂Cl₂), (0.028 g, 0.14 mmol, 80%).

¹H-NMR (CDCl₃): 4.72 (bs, 1H, H on OH), 4.08 (t, 1H, *J*=7.1 Hz, H on C10), 4.03 (t, 1H, *J*=7.1 Hz, H on C10), 3.98 (m, 1H, H on C5), 3.39 (d, 1H, *J*=13.1 Hz, H on C2), 3.37 (d, 1H, *J*=13.1 Hz, H on C2), 2.34 (m, 2H, H's on C8), 2.20 (m, 1H, H on C6α or C6β), 1.63 (m, 2H, H's on C7), 1.52-1.39 (m, 1H, H on C6β or C6α), 1.13 (t, 3H, *J*=7.1 Hz, H's on C11). ¹³C-NMR (CDCl₃): 194.1 (C3), 170.5 (C9), 127.9 (C4), 59.9 (C2), 55.9 (C5 & C10), 41.8 (C8), 23.7 (C6), 20.5 (C7), 13.8 (C11). GC: Rt=24.6 min. MS: 196 (10), 177 (20), 149 (100), 121 (12), 105 (15), 93 (10), 76 (10). IR (NaCl, cm⁻¹): 3385, 2929, 2857, 1733, 1468, 1397, 1262, 1198, 909, 733.

125

145

266.23
259.80
252.90

393.12
380.87
369.53

511.83
504.98
497.99
490.92
484.06

660.50
658.22
650.58
647.47
645.13
641.70
638.52
636.43
601.87
597.60
592.72
588.09
583.58
574.46
569.84

551

165

185

257.61
251.19

401.78
394.53
382.11
378.01

492.49
485.66
478.98

683.75
676.07
669.37
662.03
655.08
646.30
645.14
638.32
597.60
591.06
584.96
578.46
572.52
566.02

205

77.427
77.002
76.579
68.340
65.691
63.957
62.966
48.212
42.671
31.639
28.827
28.425
26.145
25.703
22.536
14.018

165.852

207.374

The COSY NMR spectrum of the heptyl ester photoproduct 2b.

1025.71
1019.18
1012.65

1165.09

1231.53
1224.45
1217.34
1210.28
1194.54

1416.35

235

245

552