

Supplemental Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70eV. Unless otherwise noted, all reactions were performed in flame dried glassware under an atmosphere of dry argon. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate/hexane mixture as the eluent unless specified otherwise. All solids were recrystallized from ethyl acetate/hexane for analytical data.

2-Isopropenylhex-5-enoic Acid Ethyl Ester (6). To 100 mL (80 mmol) of a LDA solution (0.8 M/THF) was added 14 mL (80 mmol) of anhydrous hexamethylphosphoramide (HMPA) at -78 °C, followed by the dropwise addition of 8.6 g (67 mmol) of ethyl 3-methyl-2-butenate in 10 mL of THF. After stirring for 15 min, the mixture was treated with 10 g (74 mmol) of 4-bromo-1-butene at -78 °C. The resultant mixture was stirred at -78 °C for 1 h and was allowed to warm to rt. The mixture was quenched with a saturated NH₄Cl solution, diluted with water, and extracted with ether. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was distilled under vacuum to give 10 g (82%) of **6** as a colorless oil: bp 78-81 °C (5 mm) (lit¹ 85-87 °C (10 mm)); ¹H-NMR (CDCl₃, 400 MHz) δ 1.23 (t, 3H, J = 6.8 Hz), 1.64-1.67 (m, 1H), 1.73 (s, 3H), 1.87-1.92 (m, 1H), 1.98 (q, 2H, J = 6.8 Hz), 3.02 (t, 1H, J = 7.2 Hz), 4.12 (q, 2H, J = 6.8 Hz), 4.86-5.02 (m, 4H), and 5.73-5.80 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ 14.2, 20.1, 29.1, 31.4, 52.3, 60.4, 113.8, 115.2, 137.7, 142.3, and 173.5.

5-Bromomethyl-1-methylcyclopentene (8). To a degassed solution of 3.5 g (4.0 mmol) of bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride² in 3 L of dry CH₂Cl₂ at rt was added 3.0 g (16 mmol) of **6** under an argon atmosphere. The mixture was stirred at rt for 18 h and the solvent was removed under reduced pressure. The residue was distilled to give 1.6 g (63%) of ethyl 2-methyl-2-cyclopent-ene-1-carboxylate (**7**)³ as a colorless oil: IR (neat) 2954, 1730, 1445, 1161 cm⁻¹; ¹H-NMR (CDCl₃, 400

2

MHz) δ 1.25 (t, 3H, $J = 7.2$ Hz), 1.72 (s, 3H), 2.12-2.16 (m, 2H), 2.22-2.34 (m, 1H), 2.38-2.50 (m, 1H), 3.31 (m, 1H), 4.08-4.18 (m, 2H), and 5.49 (t, 1H, $J = 2.0$ Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 14.3, 15.2, 28.3, 31.6, 53.9, 60.3, 128.4, 137.6, and 175.0; Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 70.27; H, 9.23.

A solution containing 5.6 g (36 mmol) of ester **7** in 50 mL of dry ether at 0 °C was treated with 1.4 g (36 mmol) of lithium aluminum hydride portionwise. The mixture was stirred at 0 °C for 30 min and was then allowed to warm to rt and was stirred for an additional 30 min. The mixture was treated with a 2 N NaOH solution until gas evolution had ceased. The solution was washed with a saturated NH_4Cl solution and the organic layer was separated, washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. Purification of the residue by silica gel chromatography gave 3.7 g (91%) of (2-methyl-2-cyclopentenyl)methanol as a colorless oil: ^1H -NMR (CDCl_3 , 400 MHz) δ 1.37 (brs, 1H), 1.71 (s, 3H), 1.72-1.80 (m, 1H), 2.03 (m, 1H), 2.17-2.37 (m, 2H), 2.63 (brs, 1H), 3.62 (m, 2H), and 5.47 (brs, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 14.9, 27.2, 31.1, 50.7, 64.5, 127.6, and 139.2.

To a solution of 3.8 g (34 mmol) of the above alcohol in 50 mL of CH_2Cl_2 at 0 °C was added 5.2 mL (37 mmol) of triethylamine followed by 2.9 mL (37 mmol) of methanesulfonyl chloride. The mixture was stirred at 0 °C for 5 h and then water was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried over MgSO_4 and the solvent was removed under reduced pressure to give 6.4 g (98%) of 2-methyl-2-cyclopentenyl methanesulfonate which was used in the next step without further purification: ^1H -NMR (CDCl_3 , 400 MHz) δ 1.71 (s, 3H), 1.73 (m, 1H), 2.08 (m, 2H), 2.22 (m, 2H), 3.00 (s, 3H), 4.09 (dd, 1H, $J = 9.4$ and 6.8 Hz), 4.25 (dd, 1H, $J = 9.4$ and 4.8 Hz), and 5.46 (s, 1H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 14.9, 27.3, 30.6, 37.2, 47.7, 71.6, 128.2, and 137.8.

A solution containing 6.4 g (34 mmol) of the above mesylate in 70 mL of acetone was treated with 8.8 g (102 mmol) of lithium bromide. The mixture was heated at reflux for 6 h, cooled to rt, diluted with water, extracted with ether and the combined ethereal extracts were dried over MgSO_4 . Removal of the solvent under reduced pressure gave 4.6 g (78%) of 5-bromomethyl-1-methylcyclopentene (**8**) which was used in the next step without further purification: $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ 1.69 (s, 3H), 1.77 (m, 1H), 2.02-2.36 (m, 3H), 2.95 (brs, 1H), 3.35 (dd, 1H, $J = 10.0$ and 7.2 Hz), 3.55 (dd, 1H, $J = 10.0$ and 3.2 Hz), and 5.48 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 14.5, 29.2, 30.5, 38.0, 50.1, 127.8, and 139.5.

tert-Butyl N-[(2-Methyl-2-cyclopentyl)methyl]-N-(2-furyl) Carbamate (10). A mixture containing 1.1 g (6.3 mmol) of N-(furan-2-yl)carbamic acid tert-butyl ester (**9**),⁴ 0.9 g (22 mmol) of powdered sodium hydroxide, 1.7 g (13 mmol) of potassium carbonate, and 0.2 g (0.6 mmol) of tetrabutylammonium hydrogen sulfate in 60 mL of benzene was heated at reflux for 20 min and then 1.1 g (6.3 mmol) of bromide **8** was added dropwise to this mixture. The resulting mixture was maintained at reflux for an additional 2 h, quenched with water, and extracted with CH_2Cl_2 . The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give 1.4 g (79%) of carbamate **10** as a colorless oil: IR (neat) 2975, 1716, 1374, and 1168 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ 1.45 (s, 9H), 1.64 (m, 1H), 1.66 (s, 3H), 1.94 (m, 1H), 2.13 (m, 1H), 2.18 (m, 1H), 2.62 (brs, 1H), 3.41 (dd, 1H, $J = 13.6$ and 9.6 Hz), 3.73 (dd, 1H, $J = 13.6$ and 4.4 Hz), 5.37 (s, 1H), 6.00 (brs, 1H), 6.33 (dd, 1H, $J = 3.2$ and 2.0 Hz), and 7.18 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 14.1, 28.1, 28.4, 30.5, 47.7, 51.4, 80.9, 101.4, 110.8, 126.4, 126.5, 138.8, 140.6, and 148.6; Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.16; H, 8.47; N, 5.00.

7b-Methyl-5-oxo-2,2a,3,4,4a,5,6,7b-octahydro-1-aza-cyclopenta[cd]-indene-1-carboxylic Acid tert-Butyl Ester (13). A solution of 1.1 g (0.56 mmol) of furan **10** in

12 mL of toluene was heated in a sealed tube at 165 °C for 12 h under an argon atmosphere. After cooling to rt, the solution was concentrated under reduced pressure and the residue was purified by silica gel chromatography to give 0.82 g (78%) of keto-enamide **13** as a pale yellow solid: mp 117-118 °C; IR (neat) 2974, 1709, 1364, and 1155 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.21 (s, 3H), 1.33 (m, 1H), 1.46 (s, 9H), 1.84 (m, 2H), 1.97 (m, 1H), 2.22 (m, 1H), 2.55 (m, 1H), 2.76 (dd, 1H, J = 20.0 and 6.8 Hz), 3.06 (dd, 1H, J = 20.0 and 2.4 Hz), 3.48 (d, 1H, J = 11.2 Hz), 3.72 (dd, 1H, J = 11.2 and 5.6 Hz), and 5.65 (d, 1H, J = 5.6 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 21.2, 27.2, 27.7, 30.3, 36.1, 45.5, 52.2, 54.6, 57.0, 79.7, 95.9, 143.4, 151.7, and 210.2; Anal. Calcd for C₁₆H₂₃NO₃: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.40; H, 8.37; N, 5.04.

4-Isopropylfuran-2-carbaldehyde. To a suspension containing 200 g (1.5 mol) of aluminum chloride in 1.0 L of carbon disulfide was added 120 g (1.3 mol) of 2-furaldehyde. To the mixture was added dropwise 103 mL (1.3 mol) of isopropyl chloride, and the resulting solution was stirred at rt for 24 h. The dark mixture was carefully poured over 2 kg of ice and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, saturated NaHCO₃ solution, dried over Na₂SO₄, filtered through a pad of silica gel, and concentrated under reduced pressure. The residue was distilled under vacuum to give 27 g (20%) of 4-isopropyl-furan-2-carbaldehyde (**134**) as a yellow oil: bp 85-86 °C (10 mm) (lit.⁵ 101-103 °C (21 mm)); ¹H-NMR (CDCl₃, 300 MHz) δ 1.24 (d, 6H, J = 6.9 Hz), 2.85 (m, 1H), 7.17 (s, 1H), 7.47 (s, 1H), and 9.60 (s, 1H).

4-Isopropylfuran-2-carboxylic Acid (14). To a suspension containing 50 g (0.29 mol) of silver nitrate in 150 mL of 50% ethanol was added a solution of 18 g (0.13 mol) of the above aldehyde in 80 mL of ethanol, followed by the dropwise addition of 12 g (0.3 mol) of NaOH in 50 mL of water. During the addition, the internal temperature was maintained at 40-50 °C. The mixture was stirred at rt for 12 h and the resulting suspension was filtered through a pad of Celite. After removal of the ethanol under reduced pressure, the aqueous layer was washed with ether, acidified with 1 M HCl, and extracted with ether.

Removal of the solvent under reduced pressure afforded 19 g (95%) of 4-isopropylfuran-2-carboxylic acid (**14**) as a pale yellow solid: mp 75-76 °C (lit.⁶ mp 76-77 °C); ¹H-NMR (CDCl₃, 400 MHz) δ 1.23 (d, 6H, J = 6.9 Hz), 2.83 (m, 1H), 7.26 (s, 1H), 7.41 (s, 1H), and 10.03 (brs, 1H).

4-Isopropylfuran-2-ylcarbamic Acid tert-Butyl Ester (15). A solution containing 2.0 (13 mmol) of 4-isopropylfuran-2-carboxylic acid (**14**), 3.6 mL (26 mmol) of triethylamine, and 5.6 mL (26 mmol) of diphenylphosphoryl azide in 40 mL of tert-butyl alcohol was heated at reflux for 12 h. After cooling, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to give 2.4 g (83%) of carbamate **15** as a yellow oil: IR (KBr) 3281, 1702, 1547, and 1157 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.16 (d, 6H, J = 6.8 Hz), 1.50 (s, 9H), 2.71 (m, 1H), 6.00 (brs, 1H), 6.62 (brs, 1H), and 6.80 (t, 1H, J = 1.2 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 21.0, 22.8, 25.3, 28.2, 44.7, 130.4, 134.0, 145.3, and 151.7; Anal. Calcd for C₁₂H₁₉NO₃: C, 69.98; H, 8.50; N, 6.21. Found: C, 69.84; H, 8.25; N, 6.04.

N-[(2-Methyl-2-cyclopentyl)methyl]-N-(4-isopropylfuran-2-yl)carbamic Acid tert-Butyl Ester (1). A 2.3 g (10 mmol) sample of carbamate **15**, 3.3 g (10 mmol) of tetrabutylammonium bromide, and 2.1 g (12 mmol) of bromide **8** in 25 mL of CH₂Cl₂ at 0 °C was treated dropwise with 10 mL of a 50% NaOH solution. The mixture was heated at reflux for 14 h, cooled to rt, diluted with water, and the aqueous phase was extracted with CH₂Cl₂. The combined organic phase was washed with brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to give 2.3 g (71%) of **1** as a pale yellow oil: IR (neat) 3080, 2964, 1704, and 1545 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 0.88 (t, 1H, J = 2.8 Hz), 1.17 (d, 6H, J = 6.8 Hz), 1.26 (m, 6H), 1.46 (s, 9H), 1.67 (s, 3H), 2.68 (m, 1H, J = 6.8 Hz), 5.28 (s, 1H), 5.95 (brs, 1H), and 6.97 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ 14.9, 21.1, 22.8, 25.3, 27.3, 28.2, 28.3, 31.1, 44.7, 50.6, 127.6, 130.4, 134.0,

139.2, 145.3, and 151.7; Anal. Calcd for C₁₉H₂₉NO₃: C, 71.44; H, 9.15; N, 4.38.

Found: C, 71.28; H, 9.09; N, 4.30.

3-(tert-Butoxycarbonyl)-6-isopropyl-11-methyl-3-azatricyclo[6.2.1.0^{4,11}]-undec-

4-en-7-one (2). A 1.0 g (3.1 mmol) sample of carbamate **1** in 10 mL of toluene was heated in a sealed tube under an argon atmosphere at 165 °C for 15 h. After cooling to rt, the solution was concentrated under reduced pressure and the residue was purified by flash silica gel chromatography to give 0.74 g (74%) of **2** as a pale yellow oil which consisted of a 2:1-mixture of diastereomers that proved to be inseparable: IR (KBr) 2968, 1709, 1381, and 1154 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) major δ 0.77 (d, 3H, J = 6.8 Hz), 0.92 (d, 3H, J = 6.8 Hz), 1.22 (s, 3H), 1.42 (s, 9H), 1.70-1.90 (m, 3H), 2.16 (m, 2H), 2.50 (m, 2H), 2.83 (dd, 1H, J = 4.8 and 2.4 Hz) 3.43 (d, 1H, J = 11.2 Hz) 3.68 (dd, 1H, J = 11.2 and 6.0 Hz), and 5.59 (s, 1H); ¹H-NMR (CDCl₃, 400 MHz) minor δ 0.76 (d, 3H, J = 6.8 Hz), 0.91 (d, 3H, J = 6.8 Hz), 1.08 (s, 3H), 1.42 (s, 9H), 1.90-2.02 (m, 3H), 2.25 (m, 2H), 2.50 (m, 2H), 2.71 (t, 1H, J = 5.2 Hz), 3.40 (d, 1H, J = 11.2 Hz), 3.65 (dd, 1H, J = 11.2 and 6.0 Hz), and 5.70 (d, 1H, J = 4.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz) major δ 18.0, 20.1, 21.1, 26.7, 27.7, 30.1, 46.1, 50.0, 51.8, 56.5, 58.0, 79.7, 97.9, 142.5, 144.4, 151.7, and 210.1; ¹³C-NMR (CDCl₃, 100 MHz) minor δ 18.7, 20.1, 23.1, 26.1, 27.7, 28.3, 30.1, 46.1, 50.8, 51.7, 54.2, 79.5, 97.7, 100.8, 144.4, 151.7, and 211.5; Anal. Calcd for C₁₉H₂₉NO₃: C, 71.44; H, 9.15; N, 4.38. Found: C, 71.38; H, 9.18; N, 4.36.

7-Benzyloxy-3-(tert-butoxycarbonyl)-6-isopropyl-11-methyl-3-azatri-

cyclo[6.2.1.0^{4,11}]undecan-5-ol (16). To a solution containing 0.15 g (0.47 mmol) of keto-enamide **2** in 10 mL of methanol was added an aqueous solution containing 0.02 g (0.47 mmol) of sodium borohydride in 1 mL of water at 0 °C. The mixture was allowed to warm to rt and was maintained at that temperature for 1 h. The mixture was concentrated under reduced pressure, diluted with water, and extracted with ether. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure to give 0.14 g (93%) of crude 3-(tert-butoxycarbonyl)-6-isopropyl-11-

methyl-3-azatricyclo[6.2.1.0^{4,11}]undec-4-en-7-ol as a yellow oil, which was used in next step without further purification.

The above 2:1-mixture of alcohols was taken up into 5 mL of dry THF and the resulting solution was added dropwise to a stirred suspension containing 0.02 g (0.94 mmol) of sodium hydride in 5 mL of dry THF at 0 °C. After stirring for 15 min, 0.17 g (0.47 mmol) of tetrabutylammonium iodide and 0.1 g (0.6 mmol) of benzyl bromide were added to the yellow mixture. The resulting mixture was heated at reflux for 20 h, cooled to rt and quenched by the slow addition of water. The mixture was extracted with ether, and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to give 7-benzyloxy-3-(tert-butoxycarbonyl)-6-isopropyl-11-methyl-3-azatricyclo[6.2.1.0^{4,11}]undec-4-ene as a yellow oil that was used in the next step reaction without further purification.

The above oil was dissolved in 5 mL of dry THF and 0.5 mL (0.5 mmol) of a 1.0 M borane/THF solution was added at 0 °C under an argon atmosphere. The mixture was allowed to stir at rt for 4 h, cooled to 0 °C and then 0.9 mL of a 3.0 M NaOH aqueous solution was added dropwise to destroy the excess borane followed by 1 mL of a 30% hydrogen peroxide solution. The resulting mixture was stirred at 50 °C for 2 h, cooled to rt, diluted with water, extracted with ether, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give 0.08 g (50%) of the major diastereomer and 0.04 g (22%) of the minor stereoisomer as a pale yellow oils. The major stereoisomer **16a** exhibited the following spectral properties: IR (neat) 3402, 1666, 1403, 1365, and 1110 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 0.99 (d, 3H, J = 7.2 Hz), 1.07 (d, 3H, J = 7.2 Hz), 1.26 (s, 3H), 1.48 (s, 9H), 1.54-2.25 (m, 8H), 2.94 (dd, 1H, J = 10.8 and 7.2 Hz), 3.54-3.59 (m, 1H), 3.64 (d, 1H, J = 3.6 Hz), 3.84 (brs, 1H), 4.14-4.60 (m, 4H), and 7.23-7.34 (m, 5H); ¹³C-NMR (CDCl₃, 100 MHz) δ 19.4, 21.6, 27.3, 27.4, 28.2, 28.6, 28.7, 33.7, 49.0, 51.0, 51.6, 51.9, 52.2, 72.5, 73.4,

74.7, 79.7, 126.4, 127.1, 128.3, 139.2, and 156.1; HRMS Calcd for $C_{26}H_{39}NO_4+Li$: 436.3039. Found: 436.3020.

The minor stereoisomer **16b** exhibited the following spectral properties: IR (neat) 3400, 1666, 1403, 1365, and 1112 cm^{-1} ; 1H -NMR ($CDCl_3$, 400 MHz) δ 0.87 (d, 3H, $J = 6.4$ Hz), 1.00 (d, 3H, $J = 6.4$ Hz), 1.37 (s, 3H), 1.47 (s, 9H), 1.28-1.82 (m, 5H), 2.10-2.34 (m, 3H), 2.76 (dd, 1H, $J = 11.6$ and 8.8 Hz), 3.76-3.85 (m, 3H), 4.34 (d, 1H, $J = 11.6$ Hz), 4.40 (s, 2H), 4.71 (d, 1H, $J = 11.6$ Hz), and 7.27-7.34 (m, 5H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ 21.1, 21.2, 24.7, 28.0, 28.7, 31.1, 33.7, 41.3, 47.3, 48.0, 51.8, 52.4, 69.4, 70.2, 71.8, 79.2, 79.8, 127.9, 128.1, 128.7, 137.7, and 154.7; HRMS Calcd for $C_{26}H_{39}NO_4+Li$: 436.3039. Found: 436.3028.

3-(tert-Butoxycarbonyl)-6-isopropyl-11-methyl-3-azatricyclo[6.2.1.0^{4,11}]-undec-6-en-5-one (18). To a solution containing 0.06 g (0.14 mmol) of **16a** in 5 mL of dry CH_2Cl_2 was added 0.07 g (0.17 mmol) of Dess-Martin's periodinane⁷ and the mixture was stirred at rt for 4 h. To this solution was added 1 mL of a 3 M NaOH aqueous solution and the resulting mixture was stirred at rt for 1 h. The mixture was diluted with water and extracted with CH_2Cl_2 . The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure to give 7-benzyloxy-3-(tert-butoxycarbonyl)-6-isopropyl-11-methyl-3-azatricyclo[6.2.1.0^{4,11}]undecan-5-one (**17**) as a pale yellow oil which was used in the next step reaction without further purification: IR (neat) 1734, 1702, 1450, and 1397 cm^{-1} .

A mixture containing ketone **17** and 0.2 g of 5% palladium on charcoal in 5 mL of ethyl acetate was stirred under a hydrogen atmosphere overnight. The mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to give 7-hydroxy-3-(tert-butoxycarbonyl)-6-isopropyl-11-methyl-3-azatricyclo[6.2.1.0^{4,11}]undecan-5-one as a colorless oil which was used in the next step reaction without further purification: IR (neat) 3509, 1728, 1699, and 1371 cm^{-1} .

To a solution containing the above alcohol and 0.06 g (0.56 mmol) of triethylamine in 5 mL of dry CH₂Cl₂ was added 0.03 g (0.28 mmol) of methanesulfonyl chloride at 0 °C. The mixture was stirred at rt for 12 h and then heated at reflux for 2 h. The cooled mixture was diluted with water and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give 0.02 g (52%) of enone **18** as a colorless oil: IR (neat) 2961, 1703, 1391, 1365, and 1173 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.00 (d, 3H, J = 8.8 Hz), 1.05 (d, 3H, J = 8.8 Hz), 1.20-1.28 (m, 1H), 1.32 (s, 3H), 1.46 (s, 9H), 1.60 (s, 1H), 1.67-1.79 (m, 1H), 2.02-2.57 (m, 3H), 2.84 (p, 1H, J = 8.0 Hz), 2.99 (dd, 1H, J = 15.2 and 6.8 Hz), 3.71 (t, 1H, J = 9.6 Hz), 3.85 (brs, 1H), and 6.31 (dd, 1H, J = 6.8 and 2.0 Hz); ¹³C-NMR (CDCl₃, 75 MHz) δ 22.1, 27.9, 28.6, 29.4, 30.4, 35.2, 44.7, 49.6, 79.7, 140.5, 144.6, 155.3, and 198.0; HRMS Calcd for C₁₉H₂₉NO₃+Li: 326.2307. Found: 326.2304.

6-Isopropyl-3,11-dimethyl-3-azatricyclo[6.2.1.0^{4,11}]undec-6-en-5-one (3). To a solution containing 0.02 g (0.07 mmol) of enone **18** in 1 mL of dry CH₂Cl₂ was added 0.2 mL of trifluoroacetic acid (TFA). The mixture was stirred at rt for 2 h and the solvent was removed under reduced pressure. The residue was taken up into 1 mL of dry DMF and 0.2 g (1.4 mmol) of potassium carbonate and 0.1 g (0.7 mmol) of iodomethane were added. The resulting mixture was stirred at rt for 4 h, diluted with water, and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give 0.01 g (65%) of Kende's intermediate **38** as a colorless oil: IR (neat) 1669, 1368, 1260, and 1092 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 1.01 (d, 3H, J = 7.2 Hz), 1.06 (d, 3H, J = 7.2 Hz), 1.18 (s, 3H), 1.60-2.00 (m, 4H), 2.14 (s, 3H), 2.14-2.23 (m, 1H), 2.28 (s, 1H), 2.30-2.39 (m, 1H), 2.47 (t, 1H, J = 8.8 Hz), 2.76 (d, 1H, J = 8.8 Hz), 2.84-2.94 (m, 1H), and 6.46 (d, 1H, J = 4.8 Hz); ¹³C-NMR (CDCl₃, 100 MHz)

δ 21.3, 22.0, 26.4, 26.8, 33.8, 34.1, 41.3, 48.2, 50.2, 53.4, 64.6, 79.9, 141.0, 142.0, and 199.2; HRMS Calcd for C₁₅H₂₃NO: 233.1780. Found: 233.1788.

Experimental References

1. Yadav, V.; Fallis, A. G. *Can. J. Chem.* **1991**, *69*, 779.
2. Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.
3. Martin, S. F.; Li, W. *J. Org. Chem.* **1991**, *56*, 642.
4. Padwa, A.; Brodney, M. A.; Liu, B.; Satake, K.; Wu, T. *J. Org. Chem.* **1999**, *64*, 3595.
5. Gilman, H.; Calloway, N. O. *J. Am. Chem. Soc.* **1933**, *55*, 4197. Gilman, H.; Calloway, N. O. *J. Am. Chem. Soc.* **1935**, *57*, 906. Divald, S.; Chun, M. C.; Joullie, M. M. *J. Org. Chem.* **1976**, *41*, 2835.
6. Chadwick, D. J.; Chambers, J.; Hargraves, H. E.; Meakins, G. D.; Snowden, R. L. *J. Chem. Soc. Perkin 1* **1973**, 2327.
7. Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.
8. Kende, A. S.; Bentley, T. J.; Mader, R. A.; Ridge, D. *J. Am. Chem. Soc.* **1974**, *96*, 4332.