Electronic Supplementary Information

Ketones as Electrophiles in Two Component Baylis-Hillman Reaction: A Facile One-Pot Synthesis of Substituted Indolizines

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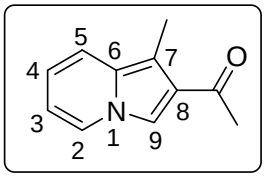
EXPERIMENTAL SECTION

General Remarks: Melting points were determined on MR-Vis+ visual melting point range apparatus from LABINDIA instruments private limited and were uncorrected. Infrared spectra were recorded on a JASCO FT-IR 5300 spectrophotometer and NICOLET 5700 FT-IR spectrometer. All the spectra were calibrated against polystyrene absorption at 1601 cm^{-1}. Solid samples were recorded as KBr wafers and liquid samples as thin film between NaCl plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker-AVANCE-400 spectrometer in deuterochloroform ($CDCl_3$) with tetramethylsilane (TMS, $\delta = 0$) as an internal standard for ^{1}H NMR and chloroform-*d* middle peak of the triplet ($\delta = 77.10$ ppm) as an internal standard for ^{13}C NMR. HRMS spectra were recorded on Bruker maXis ESI-TOF spectrometer. The X-ray diffraction measurements were carried out at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å).

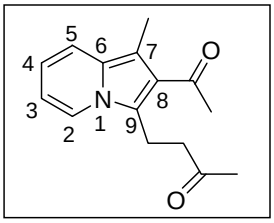
Representative procedure: Synthesis of 8-acetyl-1-aza-7-methylbicyclo[4.3.0]nona-2,4,6,8-tetraene (3a):

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (1.0 mmol, 0.222 g, 0.18 mL) was added at 0 °C to a stirring solution of 2-acetylpyridine (1.0 mmol, 0.121 g, 0.11 mL) and methyl vinyl ketone (2.0 mmol, 0.140 g, 0.16 mL) in acetonitrile (containing 1% H_2O, v/v) (2 mL). Reaction mixture was then heated under reflux for 12 h and allowed to come to room temperature (25–30 °C). The reaction mixture was diluted with dichloromethane (10 mL) and saturated aqueous K_2CO_3 solution (10 mL) was added. Organic layer was separated and aqueous layer was washed with dichloromethane (2 X 5 mL). Combined organic layer was dried over anhydrous sodium sulfate. Solvent was evaporated. Thus obtained crude [TLC (10% ethyl acetate in hexanes) showed three spots indicating that it is a mixture of three compounds] was purified by column chromatography (silica gel, 10% EtOAc in hexanes) to provide two products **3a** (0.107 g) in 62% and **4a** (0.049 g) in 20% yields as viscous liquids along with very small amounts of the strarting material (**1a**, 10 mg). Starting material elutes first. Afterwards the title compound **3a** (less polar) was collected follwed by the collection of the byproduct **4a** (more polar).



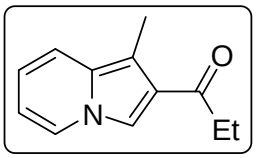
^{1}H NMR (400 MHz, $CDCl_3$) = δ 2.527 (s, 3H), 2.53 (s, 3H), 6.44–6.51 (m, 1H), 6.57–6.64 (m, 1H), 7.33 (d, 1H, J = 9.2 Hz), 7.71 (s, 1H), 7.77 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 10.15, 28.63, 109.87, 112.31, 115.93, 116.75, 118.78, 125.11, 125.93, 131.04, 195.78; IR (KBr) = ν 1659, 1484, 1435, 1220, 739 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{11}H_{11}NO$+Na $(M+Na)^+$: 196.0738; found: 196.0739.

8-Acetyl-1-aza-7-methyl-9-(3-oxobutyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (4a):



^{1}H NMR (400 MHz, $CDCl_3$) = δ 2.16 (s, 3H), 2.52 (s, 3H), 2.60 (s, 3H), 2.80 (t, 2H, J = 7.6 Hz), 3.36 (t, 2H, J = 7.6 Hz), 6.51–6.57 (m, 1H), 6.58–6.64 (m, 1H), 7.32–7.38 (m, 1H), 7.85 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 11.35, 19.13, 29.76, 31.80, 41.52, 107.74, 112.21, 115.87, 118.59, 121.67, 124.35, 126.40, 129.55, 197.62, 208.20; IR (neat) = ν 1709, 1648, 1495, 1418, 1237, 739 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{15}H_{17}NO_2$+H $(M+H)^+$: 244.1337; found: 244.1335.

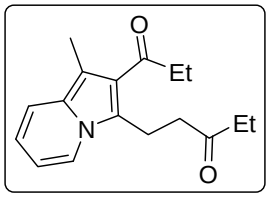
1-Aza-7-methyl-8-(1-oxopropyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (3b):



Reaction time :12 h; yield: 37%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, 3H, J = 7.2 Hz), 2.54 (s, 3H), 2.91 (q, 2H, J = 7.2 Hz), 6.44–6.51 (m, 1H), 6.56–6.64 (m, 1H), 7.33 (d, 1H, J = 9.2 Hz), 7.72 (s, 1H), 7.77 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.57,

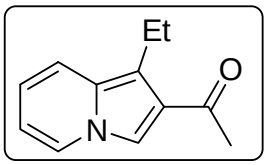
10.27, 33.85, 110.10, 112.33, 115.26, 116.70, 118.90, 125.19, 125.58, 131.11, 199.00; IR (KBr) = ν 1670, 1484, 1435, 1193, 739 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{12}H_{13}NO$ $(M)^+$: 187.0997; found: 187.0995.

1-Aza-7-methyl-9-(3-oxopentyl)-8-(1-oxopropyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (4b):



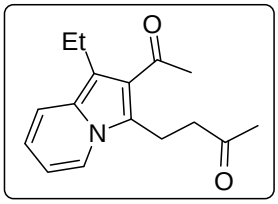
Yield: 13%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, 3H, J = 7.2 Hz), 1.22 (t, 3H, J = 7.2 Hz), 2.44 (q, 2H, J = 7.2 Hz), 2.52 (s, 3H), 2.79 (t, 2H, J = 7.6 Hz), 2.94 (q, 2H, J = 7.2 Hz), 3.35 (t, 2H, J = 7.6 Hz), 6.49–6.55 (m, 1H), 6.57–6.64 (m, 1H), 7.34 (d, 1H, J = 8.8 Hz), 7.86 (d, 1H, J = 7.2 Hz) ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.78, 8.28, 11.60, 19.48, 35.99, 36.69, 40.47, 107.29, 112.19, 115.95, 118.67, 121.87, 124.48, 126.52, 129.68, 201.03, 211.18; IR (neat) = ν 1714, 1654, 1489, 1451, 1215, 733 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{17}H_{21}NO_2$+Na $(M+Na)^+$: 294.1470; found: 294.1467.

8-Acetyl-1-aza-7-ethylbicyclo[4.3.0]nona-2,4,6,8-tetraene (3c):



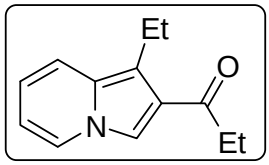
Reaction time: 12 h; yield : 57%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, 3H, J = 7.6 Hz), 2.53 (s, 3H), 3.02 (q, 2H, J = 7.6 Hz), 6.44–6.52 (m, 1H), 6.56–6.64 (m, 1H), 7.34 (d, 1H, J = 9.2 Hz), 7.70 (s, 1H), 7.77 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.79, 17.80, 28.58, 112.38, 116.29, 116.91, 117.04, 118.71, 125.17, 130.56, 195.43; IR (neat) = ν 1660, 1484, 1430, 1210, 745 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{12}H_{13}NO$+Na $(M+Na)^+$: 210.0889; found: 210.0892.

8-Acetyl-1-aza-7-ethyl-9-(3-oxobutyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (4c):



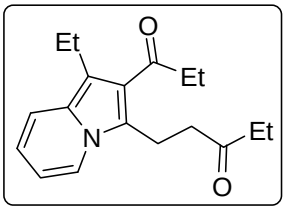
Reaction time : 12 h; yield: 23%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, 3H, J = 7.6 Hz), 2.17 (s, 3H), 2.62 (s, 3H), 2.80 (t, 2H, J = 7.6 Hz), 2.98 (q, 2H, J = 7.6 Hz), 3.32 (t, 2H, J = 7.6 Hz), 6.51–6.57 (m, 1H), 6.58–6.65 (m, 1H), 7.35 (d, 1H, J = 9.2 Hz), 7.83 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.76, 18.35, 19.25, 29.93, 31.28, 41.69, 112.40, 114.91, 116.09, 118.59, 121.84, 124.11, 125.93, 129.16, 198.06, 208.30; IR (neat): ν 1715, 1654, 1495, 1441, 1249, 745 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{16}H_{19}NO_2$+Na $(M+Na)^+$: 280.1313; found: 280.1315.

1-Aza-7-ethyl-8-(1-oxopropyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (3d):



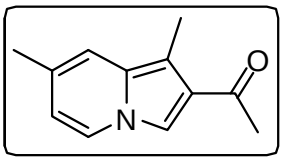
Reaction time: 12 h; yield : 23%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, 3H, J = 7.6 Hz), 1.22 (t, 3H, J = 7.6 Hz), 2.92 (q, 2H, J = 7.6 Hz), 3.03 (q, 2H, J = 7.6 Hz), 6.45–6.52 (m, 1H), 6.57–6.64 (m, 1H), 7.33-7.38 (m, 1H), 7.71 (s, 1H), 7.75–7.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.56, 15.86, 17.90, 33.71, 112.35, 115.52, 116.83, 117.20, 118.75, 124.73, 125.21, 130.55, 198.66; IR (KBr) = ν 1665, 1489, 1435, 1215, 755 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{13}H_{15}NO$+Na $(M+Na)^+$: 224.1051; found: 224.1065.

1-Aza-7-ethyl-9-(3-oxopentyl)-8-(1-oxopropyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (4d):



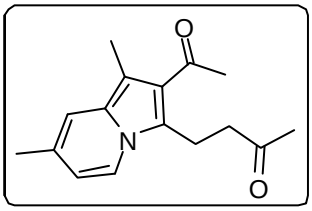
Reaction time: 12 h; yield: 14%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, 3H, J = 7.2 Hz), 1.22 (t, 3H, J = 7.2 Hz), 1.23 (t, 3H, J = 7.6 Hz), 2.44 (q, 2H, J = 7.2 Hz), 2.79 (t, 2H, J = 7.6 Hz), 2.91–3.01 (m, 4H), 3.31 (t, 2H, J = 7.6 Hz), 6.50–6.56 (m, 1H), 6.57–6.64 (m, 1H), 7.32–7.38 (m, 1H), 7.83 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.77, 8.49, 16.82, 18.49, 19.41, 36.00, 36.16, 40.46, 112.20, 114.38, 115.99, 118.52, 121.87, 124.18, 125.64, 129.14, 201.52, 211.01; IR (neat) = ν 1715, 1660, 1446, 1413, 1210, 742 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{18}H_{23}NO_2$+Na $(M+Na)^+$: 308.1626; found: 308.1627.

8-Acetyl-1-aza-4,7-dimethylbicyclo[4.3.0]nona-2,4,6,8-tetraene (3e):



Reaction time: 12 h; yield: 33%; black solid; m.p. 56–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) = δ 2.25 (s, 3H), 2.49 (s, 3H), 2.52 (s, 3H), 6.32 (dd, 1H, J = 1.2 & 6.8 Hz), 7.06 (s, 1H), 7.64 (s, 1H), 7.68 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 10.11, 21.13, 28.59, 108.08, 115.28, 115.42, 116.44, 124.63, 126.13, 126.83, 131.31, 195.93; IR (KBr) = ν 1654, 1484, 1419, 1232, 789 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}NO$+H $(M+H)^+$: 188.1075; found: 188.1072.

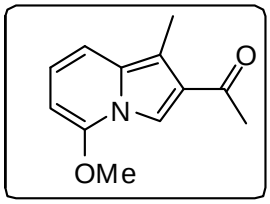
8-Acetyl-1-aza-4,7-dimethyl-9-(3-oxobutyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (4e):



Reaction time: 12 h; yield: 46%; greenish yellow solid; m.p. 91–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) = δ 2.15 (s, 3H), 2.26 (s, 3H), 2.48 (s, 3H), 2.58 (s, 3H), 2.79 (t, 2H, J = 7.6 Hz), 3.33 (t, 2H, J = 7.6 Hz), 6.38 (d, 1H, J = 7.6 Hz)*, 7.07 (s, 1H), 7.78 (d, 1H, J = 7.6 Hz); *unresolved dd. ^{13}C NMR (100 MHz, $CDCl_3$) = δ 11.43, 19.31, 21.00, 29.91, 31.89, 41.84, 105.94, 115.19, 116.37, 121.38, 124.45, 125.99, 129.82, 197.81, 208.54; IR (KBr) = ν 1715, 1649, 1495, 1463,

1419, 1243, 772 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{19}NO_2$+H $(M+H)^+$: 258.1494; found: 258.1498.

8-Acetyl-1-aza-2-methoxy-7-methylbicyclo[4.3.0]nona-2,4,6,8-tetraene (3f):



Reaction time: 12 h; yield: 59%; brownish green solid; m.p. 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) = δ 2.53 (s, 3H), 2.56 (s, 3H), 4.06 (s, 3H), 5.77 (d, 1H, J = 7.2 Hz), 6.65–6.71 (m, 1H), 7.02 (d, 1H, J = 9.2 Hz), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 10.41, 28.57, 55.98, 86.17, 109.68, 110.87, 111.80, 118.08, 126.04, 132.65, 148.84, 196.16; IR (KBr) = ν 1654, 1632, 1490, 1430, 1210, 739 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}NO_2$+H $(M+H)^+$: 204.1024; found: 204.1022.

Crystal data for **3f**: Empirical formula, $C_{12}H_{13}NO_2$; Formula weight, 203.23; crystal color, brown; habit, block; crystal dimensions, 0.24 x 0.16 x 0.14 mm^3 ; crystal system, orthorhombic; lattice type, primitive; lattice parameters, a = 14.886(4) Å, b = 8.048(2) Å, c = 17.590(4) Å, α = 90.00, β = 90.00, γ = 90.00; V = 2107.2(9) $Å^3$; space group, Pbca; Z = 8; D_{cald} = 1.281 g / cm^3; F_{000} = 864; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0635, wR^2 = 0.1466. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **3f** CCDC # 950620).

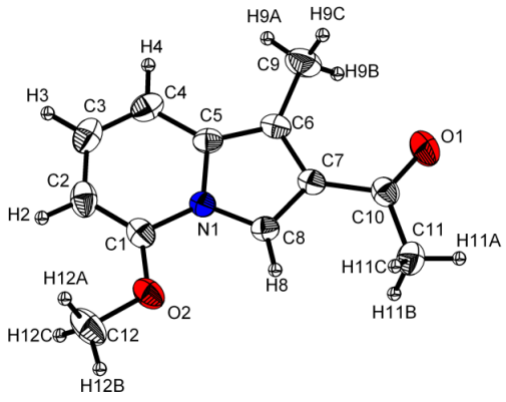
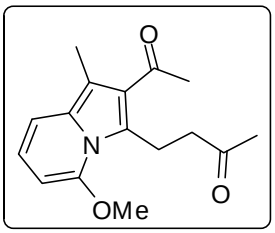


Figure 1. ORTEP diagram of compound **3f**

8-Acetyl-1-aza-2-methoxy-7-methyl-9-(3-oxobutyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (4f):



Reaction time :12 h; yield: 13%; yellow solid; m.p. 129–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) = δ 2.19 (s, 3H), 2.45 (s, 3H), 2.57 (s, 3H), 2.82 (t, 2H, J = 8.0 Hz), 3.59 (t, 2H, J = 8.0 Hz), 3.91 (s, 3H), 5.66 (d, 1H, J = 7.2 Hz), 6.53–6.61 (m, 1H), 6.95 (d, 1H, J = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 11.46, 22.51, 29.88, 32.25, 45.62, 56.01, 87.24, 107.09, 111.11, 117.12, 126.72, 127.01, 132.25, 151.94, 198.94, 208.68; IR (KBr) = ν 1704, 1649, 1621, 1473, 1424, 1232, 750 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{19}NO_3$+H $(M+H)^+$: 274.1443; found: 274.1445.

Crystal data for **4f**: Empirical formula, $C_{16}H_{19}NO_3$; Formula weight, 273.32; crystal color, yellow; habit, block; crystal dimensions, 0.23 x 0.20 x 0.18 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 4.9759(15) Å, b = 13.292(4) Å, c = 10.625(3) Å, α = 90.00, β = 90.818(5), γ = 90.00; V = 702.7(4) Å^3; space group, P2(1); Z = 2; D_{cald} = 1.292 g / cm^3; F_{000} = 292; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0462, wR^2 = 0.1238. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **4f** CCDC # 950621).

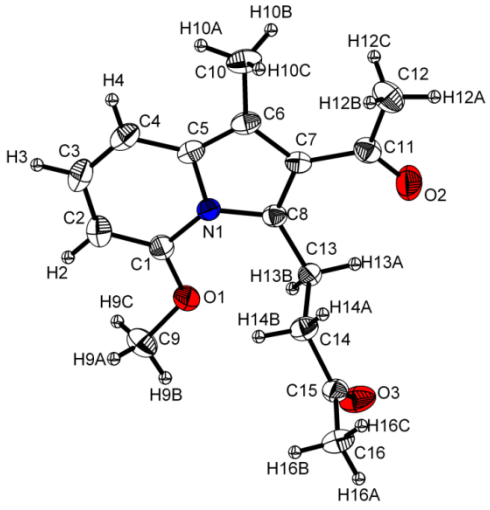
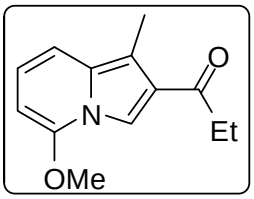


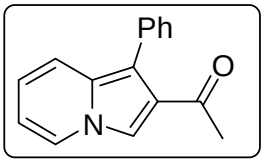
Figure 2. ORTEP diagram of compound **4f**

1-Aza-2-methoxy-7-methyl-8-(1-oxopropyl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (3g):



Reaction time: 12 h; yield: 41%; yellow solid; m.p. 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) = δ 1.23 (t, 3H, J = 7.2 Hz), 2.54 (s, 3H), 2.94 (q, 2H, J = 7.2 Hz), 4.05 (s, 3H), 5.76 (d, 1H, J = 6.8 Hz), 6.61–6.70 (m, 1H), 7.02 (d, 1H, J = 8.8 Hz), 7.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 8.66, 10.48, 33.70, 56.00, 86.15, 109.85, 110.92, 111.10, 117.97, 125.58, 132.63, 148.90, 199.34; IR (KBr) = ν 1671, 1638, 1484, 1463, 1282, 756 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{15}NO_2$+H $(M+H)^+$: 218.1181; found: 218.1176.

8-Acetyl-1-aza-7-phenylbicyclo[4.3.0]nona-2,4,6,8-tetraene (3h)[1]:



Reaction time : 12 h; yield: 49%; brown solid; m.p. 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 6.53–6.61 (m, 1H), 6.63–6.70 (m, 1H), 7.28–7.39 (m, 2H), 7.40–7.48 (m, 4H), 7.81 (s, 1H), 7.84–7.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.56, 113.00, 114.99, 116.14, 118.70, 119.42, 125.29, 126.60, 126.80, 128.19, 130.67, 131.49, 134.48, 195.90; IR (KBr) = ν 1660, 1484, 1424, 1205, 783 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{16}H_{13}NO$+H $(M+H)^+$: 236.1070; found: 236.1075.

Crystal data for **3h:** Empirical formula, $C_{16}H_{13}NO$; Formula weight, 235.27; crystal color, brown; habit, block; crystal dimensions, 0.80 x 0.40 x 0.20 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 9.286(2) Å, b = 11.358(3) Å, c = 11.827(3) Å, α = 90.00, β = 98.495(4), γ = 90.00; V = 1233.8(5) Å^3; space group, p2(1)/C; Z = 4; D_{cald} = 1.267 g / cm^3; F_{000} = 496; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0552, wR^2 = 0.1272. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **3h** CCDC # 950387).

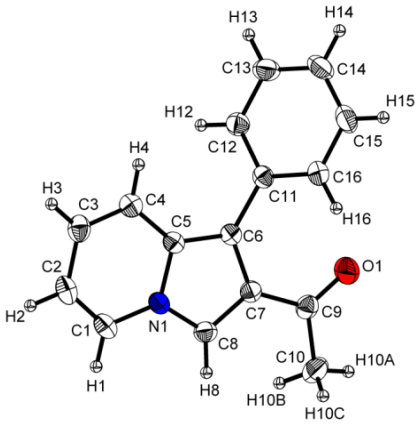
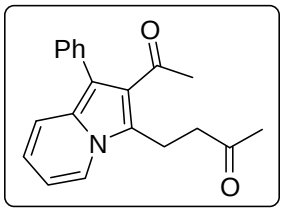


Figure 3. ORTEP diagram of compound **3h**

8-Acetyl-1-aza-9-(3-oxobutyl)-7-phenylbicyclo[4.3.0]nona-2,4,6,8-tetraene (4h):



Yield: 11%; colorless solid; m.p. 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.20 (s, 3H), 2.91 (t, 2H, J = 7.6 Hz), 3.35 (t, 2H, J = 7.6 Hz), 6.59–6.69 (m, 2H), 7.27–7.32 (m, 1H), 7.34–7.40 (m, 3H), 7.42–7.48 (m, 2H), 7.95 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.96, 29.89, 31.46, 42.02, 112.73, 114.74, 117.81, 119.18, 122.05, 125.01, 126.17, 126.85, 128.50, 129.76, 130.58, 135.22, 199.24, 208.15; IR (neat) = ν 1709, 1656, 1517, 1419, 1236, 763 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{20}H_{19}NO_2$+H $(M+H)^+$: 306.1494; found: 306.1489.

Crystal data for **4h**: Empirical formula, $C_{20}H_{19}NO_2$; Formula weight, 305.36; crystal color, colorless; habit, block; crystal dimensions, 0.60 x 0.40 x 0.20 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a = 9.1844(10) Å, b = 9.6681(11) Å, c = 10.4799(12) Å, α = 81.098(2), β = 65.775(2), γ = 79.753(2); V = 831.62(16) Å^3; space group, P-1; Z = 2; D_{cald} = 1.219 g / cm^3; F_{000} = 324; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0887, wR^2 = 0.1889. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **4h** CCDC # 950388).

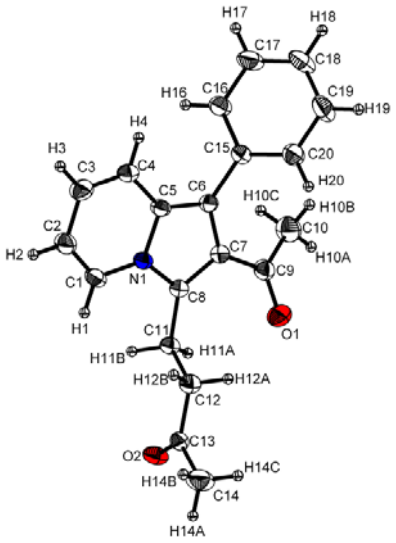
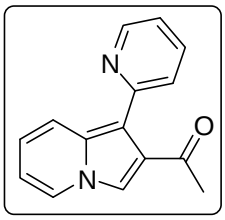


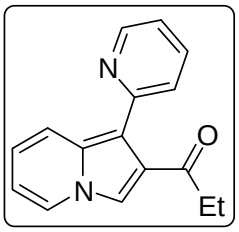
Figure 4. ORTEP diagram of compound **4h**

8-Acetyl-1-aza-7-(pyrid-2-yl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (3i):



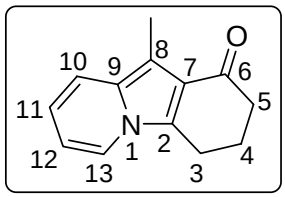
Reaction time: 12 h; yield: 31%; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 6.57–6.66 (m, 1H), 6.74–6.84 (m, 1H), 7.15–7.23 (m, 1H), 7.57 (d, 1H, J = 8.0 Hz), 7.68–7.78 (m, 2H), 7.80 (s, 1H), 7.89 (d, 1H, J = 6.8 Hz), 8.68 (d, 1H, J = 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.35, 113.20, 113.50, 117.05, 119.95, 120.15, 120.91, 125.36, 125.63, 126.37, 132.67, 135.64, 149.02, 153.96, 195.51; IR (neat) = ν 1665, 1473, 1413, 1200, 739 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{15}H_{12}N_2O$+H $(M+H)^+$: 237.1028; found: 237.1029.

1-Aza-8-(1-oxopropyl)-7-(pyrid-2-yl)bicyclo[4.3.0]nona-2,4,6,8-tetraene (3j):



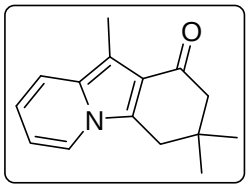
Reaction time :12 h; yield: 27%; yellow solid; m.p. 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, 3H, J = 7.2 Hz), 2.84 (q, 2H, J = 7.2 Hz), 6.58–6.65 (m, 1H), 6.76–6.82 (m, 1H), 7.15–7.22 (m, 1H), 7.53–7.60 (m, 1H), 7.68–7.76 (m, 2H), 7.79 (s, 1H), 7.89 (d, 1H, J = 7.2 Hz), 8.65–8.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.49, 34.58, 113.18, 113.55, 116.36, 120.02, 120.10, 120.93, 125.39, 125.65, 126.09, 132.66, 135.69, 149.07, 154.15, 198.81; IR (KBr) = ν 1665, 1484, 1413, 1194, 750 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{16}H_{14}N_2O$+H $(M+H)^+$: 251.1179; found: 251.1184.

1-Aza-8-methyl-6-oxotricyclo[7.4.0.0^{2,7}]trideca-2(7),8,10,12-tetraene (6a):



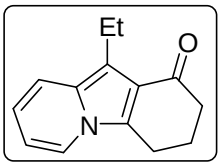
Reaction time: 12 h; yield: 60%; green solid; m.p. 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22–2.32 (m, 2H), 2.55 (s, 3H), 2.58–2.63 (m, 2H), 2.93 (t, 2H, J = 6.0 Hz), 6.47–6.53 (m, 1H), 6.54–6.62 (m, 1H), 7.30–7.36 (m, 1H), 7.56 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.63, 21.15, 23.53, 39.44, 107.75, 112.09, 116.03, 119.12, 121.00, 121.85, 129.96, 130.86, 197.23; IR (KBr) = ν 1654, 1435, 1402, 1232, 734 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{13}H_{13}NO$ $(M)^+$: 199.0997; found: 199.1031.

1-Aza-6-oxo-4,4,8-trimethyltricyclo[7.4.0.0^{2,7}]trideca-2(7),8,10,12-tetraene (6b):



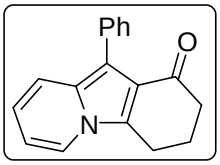
Reaction time: 12 h; yield: 31%; yellow solid; m.p. 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (s, 6H), 2.48 (s, 2H), 2.54 (s, 3H), 2.78 (s, 2H), 6.47–6.53 (m, 1H), 6.54–6.61 (m, 1H), 7.33 (d, 1H, J = 9.2 Hz), 7.54 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.58, 28.94, 35.31, 35.38, 53.57, 107.74, 112.09, 115.91, 119.24, 120.01, 121.79, 129.80, 130.36, 196.80; IR (KBr) = ν 1665, 1457, 1408, 1227, 734 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{15}H_{17}NO$ $(M)^+$: 227.1310; found: 227.1307.

1-Aza-8-ethyl-6-oxotricyclo[7.4.0.0^{2,7}]trideca-2(7),8,10,12-tetraene (6c):



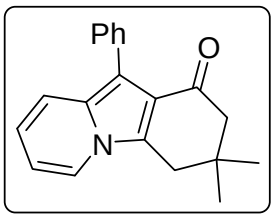
Reaction time:12 h; yield: 26%; brown solid; m.p. 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, 3H, J = 7.2 Hz), 2.23–2.33 (m, 2H), 2.61 (t, 2H, J = 6.8 Hz), 2.93 (t, 2H, J = 6.4 Hz), 3.02 (q, 2H, J = 7.2 Hz), 6.48–6.54 (m, 1H), 6.55–6.61 (m, 1H), 7.35 (d, 1H, J = 9.2 Hz), 7.56 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.93, 17.75, 21.25, 23.54, 39.57, 112.17, 115.02, 116.21, 119.11, 120.37, 121.93, 129.42, 131.10, 196.84; IR (KBr) = ν 1665, 1457, 1433, 1232, 734 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{14}H_{15}NO$ $(M)^+$: 213.1154; found: 213.1162.

1-Aza-6-oxo-8-phenyltricyclo[7.4.0.0^{2,7}]trideca-2(7),8,10,12-tetraene (6d):



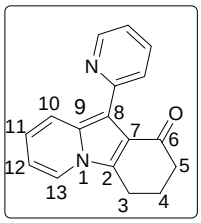
Reaction time: 12 h; yield: 35%; greenish yellow solid; m.p. 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22–2.36 (m, 2H), 2.55–2.67 (m, 2H), 2.96 (t, 2H, J = 6.0 Hz), 6.53–6.60 (m, 1H), 6.61–6.68 (m, 1H), 7.22–7.31 (m, 1H),7.35–7.43 (m, 2H), 7.46 (d, 1H, J = 8.8 Hz), 7.54 (d, 2H, J = 7.6 Hz), 7.62 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.38, 23.27, 39.75, 112.84, 112.99, 118.49, 119.76, 119.81, 122.08, 126.39, 127.84, 130.38, 130.47, 132.20, 133.80, 195.42; IR (KBr) = ν 1665, 1463, 1430, 1227, 767 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{18}H_{15}NO$ $(M)^+$: 261.1154; found: 261.1178.

1-Aza-4,4-dimethyl-6-oxo-8-phenyltricyclo[7.4.0.0^{2,7}]trideca-2(7),8,10,12-tetraene (6e):



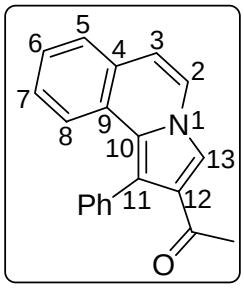
Reaction time: 12 h; yield: 10%; green solid; m.p. 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 6H), 2.53 (s, 2H), 2.87 (s, 2H), 6.57–6.63 (m, 1H), 6.64–6.72 (m, 1H), 7.27–7.33 (m, 1H), 7.37–7.45 (m, 2H), 7.50 (d, 1H, J = 9.2 Hz), 7.54–7.60 (m, 2H), 7.64 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.87, 35.20, 35.46, 53.87, 112.81, 112.91, 118.38, 118.73, 119.90, 122.00, 126.40, 127.89, 130.38, 130.77, 131.09, 133.70, 195.09; IR (KBr) = ν 1654, 1452, 1430, 1232, 745 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{20}H_{19}NO$ +Na $(M+Na)^+$: 312.1364; found: 312.1365.

1-Aza-6-oxo-8-(pyrid-2-yl)tricyclo[7.4.0.0^{2,7}]trideca-2(7),8,10,12-tetraene (6f):



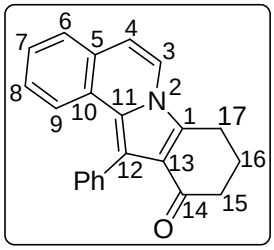
Reaction time: 12 h; yield: 59%; greenish yellow solid; m.p. 141–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30–2.40 (m, 2H), 2.68 (t, 2H, J = 6.0 Hz), 3.03 (t, 2H, J = 6.4 Hz), 6.64–6.72 (m, 1H), 6.78–6.85 (m, 1H), 7.10-7.17 (m, 1H), 7.67–7.75 (m, 2H), 7.87–7.95 (m, 1H), 8.04-8.11 (m, 1H), 8.61–8.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.43, 23.11, 39.86, 111.68, 113.35, 119.82, 120.02, 120.57, 121.36, 121.99, 125.94, 132.32, 132.83, 135.42, 148.56, 153.87, 195.55; IR (KBr) = ν 1665, 1473, 1424, 1232, 745 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{17}H_{14}N_2O$+H $(M+H)^+$: 263.1179; found: 263.1184.

12-Acetyl-1-aza-11-phenyltricyclo[8.3.0.0^{4,9}]trideca-2,4(9),5,7,10,12-hexaene (8):



Reaction time: 12 h; yield: 55%, pale yellow solid; m.p. 118–120 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (s, 3H), 6.81 (d, 1H, J = 7.2 Hz), 7.08–7.16 (m, 1H), 7.21–7.32 (m, 2H), 7.41–7.56 (m, 6H), 7.69 (d, 1H, J = 7.2 Hz), 7.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.51, 113.94, 118.62, 118.75, 122.85, 124.16, 126.18, 126.51, 126.85, 127.07, 127.25, 127.64, 127.75, 128.98, 130.70, 136.81, 195.29; IR (KBr) = ν 1671, 1473, 1430, 1221, 761 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{20}H_{15}NO$+Na $(M+Na)^+$: 308.1051; found: 308.1052.

2-Aza-14-oxo-12-phenyltetracyclo[11.4.0.0^{2,11},0^{5,10}]heptdeca-1(13),3,5(10),6,8,11-hexaene (9):



Reaction time: 12 h; yield : 45%; light pink solid; m.p. 249–251 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28–2.38 (m, 2H), 2.58 (t, 2H, J = 7.2 Hz), 3.05 (t, 2H, J = 6.4 Hz), 6.83 (d, 1H, J = 7.6 Hz), 7.08–7.18 (m, 1H), 7.23–7.31 (m, 1H), 7.38–7.53 (m, 7H), 7.56 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.36, 23.30, 39.32, 113.55, 116.74, 120.46, 120.80, 123.07, 125.74, 126.12, 127.20, 127.25, 127.48, 127.60, 128.49, 130.44, 134.38, 136.02, 194.63; IR (neat) = ν 1660, 1471, 1424, 1216, 765 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{22}H_{17}NO$+H $(M+H)^+$: 312.1388; found: 312.1391.

Crystal data for **9:** Empirical formula, $C_{22}H_{17}NO$; Formula weight, 311.37; crystal color, pink; habit, block; crystal dimensions, 0.20 x 0.18 x 0.16 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 10.5099(15) Å, b = 17.731(3) Å, c = 9.3383(13) Å, α = 90.00, β = 115.207(2), γ = 90.00; V = 1574.5(4) Å^3; space group, P2(1)/C; Z = 4; D_{cald} = 1.314 g / cm^3; F_{000} = 656; λ (Mo-Kα) = 0.71073 Å; R($I \geq 2\sigma_1$) = 0.0434, wR^2 = 0.1143. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **9** CCDC # 950389).

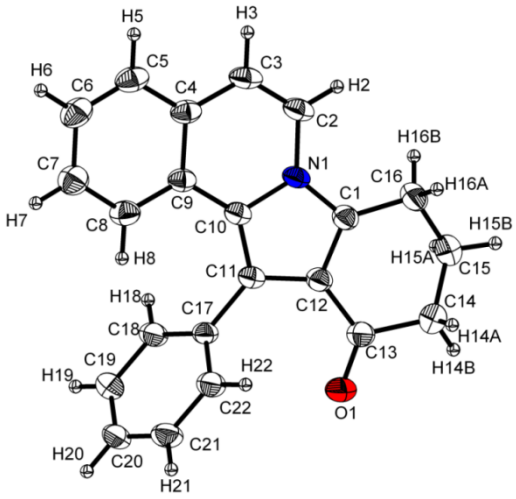


Figure 5. ORTEP diagram of compound **9**

Reference:

1. This compound is known in the literature and synthesized following a different procedure. However spectral data and melting point are not reported (see E. Pohjala, *Tetrahedron Lett.* 1972, **25**, 2585).