Heteroatom Chemistry
Volume 25, Number 1, 2014

Iodine-Promoted Synthesis of 1-Alkyl-3-aroylindolizines from *N*-(Aroylmethyl) pyridinium Salts and Aliphatic Aldehydes

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Received 8 September 2013; revised 14 November 2013

ABSTRACT: *An effective and practical method has been developed for the diversity-oriented synthesis of 1-alkyl-3-aroylindolizines via the 1,3-dipolar cycloaddition of pyridinium ylides and aliphatic aldehydes in the presence of molecular iodine and a catalytic amount of MnO_2. The synthesis proceeds by tandem reactions involving [3+2] cycloaddition, dehydration of the cycloadduct, and dehydroaromatization. Molecular iodine served both as a catalyst and a dehydroaromatization reagent in the reaction.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem. 25:72–81, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21137

INTRODUCTION

The indolizine ring is a key structural unit for numerous natural products, synthetic pharmaceuticals, and a wide variety of biologically active compounds [1]. Indolizine derivatives have been a rich source of molecules with potential pharmaceutical applications [2]. Furthermore, substituted indolizines can also serve as versatile building blocks for the synthesis of novel classes of dyes, biological markers, and electroluminescent [3, 4]. Therefore, the development of efficient and convergent methods for rapid construction of indolizines has stimulated considerable interest.

Many substituted indolizines have been synthesized by various methods such as the Scholtz reaction, the Tschitschibabin reaction, 1,3-dipolar cycloadditions of pyridinium methylides with electron-deficient alkynes or alkenes, 1,5-dipolar cyclizations, and metal-catalyzed intramolecular cycloisomerizations of pyridines with specific C-2 functionalization [5–7]. The recently developed synthesis of indolizines using 1,3-dipolar cycloadditions of pyridinium ylide is especially noteworthy due to its simplicity, efficiency, and convenience [5i,8]. However, the 1,3-dipolar cycloadditions require the olefinic or acetylenic dipolarophiles to have one or two electron-withdrawing substituents, thus limiting its applicability. We report here the convenient synthesis of 1-alkyl-3-aroylindolizine analogues from the 1,3-dipolar cycloaddition of pyridinium ylide with aliphatic aldehydes.

More recently, molecular iodine has been used as a mild and efficient promoter for various

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Contract grant sponsor: National Natural Science Foundation of China
Contract grant number: NNSFC 21173181.
Contract grant sponsor: Priority Academic Program Development of Jiangsu Higher Education Institutions.
Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

organic transformations [9] through its usage from the stoichiometric level to a catalytic amount to afford the corresponding products in excellent yields with high selectivity. It has also been reported as a mild, cheap, and easily available oxidizing reagent for the fundamental organic reactions, and, moreover, owing to numerous advantages associated with this ecofriendly element and its solid form and is less toxic than molecular bromine or chlorine, iodine has been explored as a powerful catalyst for various organic transformations. We report here a convenient synthesis of 1-alkyl-3-aroylindolizine analogues by the more general 1,3-dipolar cycloaddition reactions of pyridinium ylide by using aliphatic aldehydes as the olefinic substrate. This strategy has overcome the inherent shortcomings of the 1,3-dipolar cycloadditions using conventional alkynes and alkenes in accessing the 1-alkyl indolizines by taking advantage of the novel dehydrogenation reaction of the primary cycloadducts under the action of the mild oxidant molecular iodine in the presence of catalyst manganese dioxide.

RESULTS AND DISCUSSION

A fraction of aldehyde molecules exist in the enol form, and the enol–aldehyde interconversion is catalyzed by acid or base. We thought to explore the reaction of the enol with pyridinium ylides (structure **1** in Scheme 1) in the synthesis of indolizine. The 1,3-dipolar cycloaddition of the ylide and enol (structure **2** in Scheme 1) will give the initial adduct **A**. Base-catalyzed elimination of water from adduct **A** will yield dihydroindolizine **B**, which is expected to undergo spontaneous aromatization to form indolizine **3**.

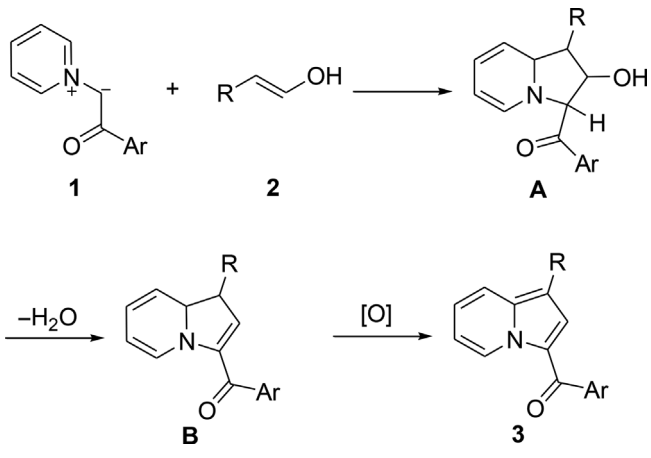
The reaction was then tested with 1-phenacyl pyridinium with butanal, and the results are presented in Table 1. When the reaction was carried out using pyridine as both a base and a solvent without any catalyst or promoter at 80°C for 40 h, the product was obtained but the yield was very low (entry 1). Considering that molecular iodine as a mild Lewis acid can promote the keto–enol tautomerism of aldyhydes and ketones [10], a catalytic amount of molecular iodine (0.1 equiv) was introduced into the reaction mixture. As a result, the yield was improved to 32% (entry 2).

Although dehydroaromatization of many heterocycles containing nitrogen can occur spontaneously in air, mild oxidants such as (Tetrakis-pyridinocobalt (II) dichromate, $Py_4Co(HCrO_4)_2$), MnO_2, and I_2 are used to facilitate the reaction. Therefore, the test reaction was carried out using 1 equiv of iodine as both a catalyst for the keto–enol tautomerism and a reagent for the aromatization of **B** to **3**. The yield was thus improved to a reasonable 49%, which was further increased to 52% upon addition of catalytic amount of MnO_2 (entries 3 and 4). In an effort to optimizing the reaction conditions, the reactions were tested in different temperature, time, base, and solvent, and the results are summarized in Table 1 (entries 5–10). The optimal reaction conditions were found to be 120°C and 40 h in pyridine with 1 equiv of iodine and 0.05 equiv of MnO_2, which gave a yield of 59%.

The side reaction in the present reaction is α-iodonation of aliphatic aldehydes in basic conditions. However, HI also partly reduces it to aldehyde together with molecular iodine. Some of α-iodoaldehyde may react further under the present conditions. Therefore, excess aldehyde was required.

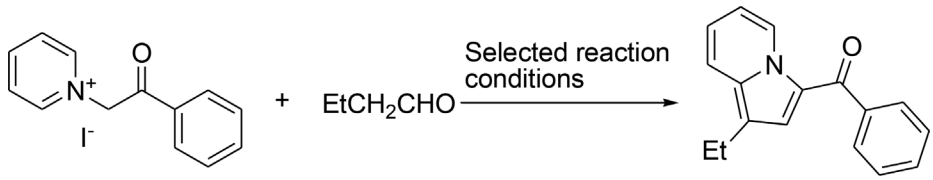
Yields for 1-alkyl-3-aroylindolizines were found to be good when the reactions were run with various pyridinium salts and aliphatic aldehyde (Table 2). It was found that C_4–C_{12} aliphatic aldehydes reacted equally well and different subsituted aryl groups (both electron donating and electron withdrawing) had no significant effect. Therefore, the reaction described proves to be a general and convenient method for the synthesis of the previously unknown 1-alkyl-3-aroylindolizines. The structure of (4-bromophenyl)(1-octylindolizin-3-yl)methanone (**3h**) was determined by X-ray crystallographic analysis (Fig. 1). Crystallographic data for **3h** have been deposited with the Cambridge Crystallographic Data Centre with the deposition number CCDC 933729. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

The title reaction is proposed to proceed by a mechanism as shown in Scheme 2.



SCHEME 1

TABLE 1 Optimization of Bases, Solvents, and Temperature in the Synthesis of **3j**



1b **2b** **3j**

Entry	*Selected Conditions*	*Yield (%)*
1	Pyridine/80°C/40 h	19
2	I_2 (0.1 equiv)/pyridine/80°C/40 h	32
3	I_2 (1 equiv)/pyridine/80°C/40 h	49
4	I_2 (1 equiv)/MnO_2(0.05 equiv)/pyridine/80°C/40 h	52
5	I_2 (1 equiv)/MnO_2(0.05 equiv)/pyridine/120°C/40 h	59
6	I_2 (1 equiv)/MnO_2(0.05 equiv)/K_2CO_2(1 equiv)/toluene/120°C/40 h	52
7	I_2 (1 equiv)/MnO_2(0.05 equiv)/DBU(1 equiv)/toluene/120°C/40 h	50
8	I_2 (1 equiv)/MnO_2(0.05 equiv)/piperidine(1 equiv)/toluene/120°C/40 h	54
9	I_2 (1 equiv)/MnO_2(0.05 equiv)/pyridine(1 equiv)/toluene/120°C/40 h	52
10	I_2 (1 equiv)/MnO_2(0.05 equiv)/pyridine/120°C/45 h	59

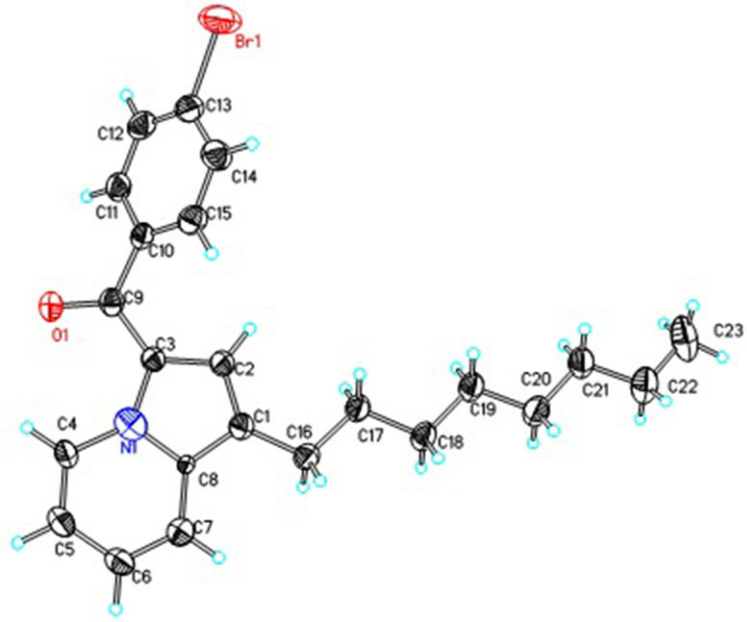


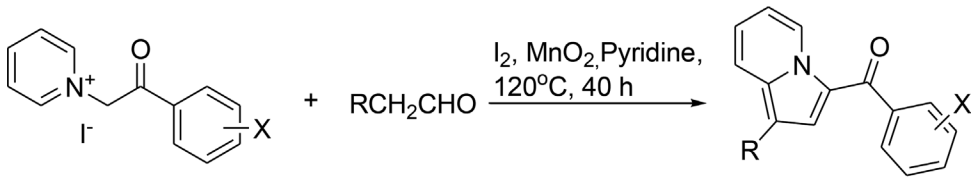
FIGURE 1 Molecular structure of indolizine **3h**.

First, molecular iodine is capable of binding with the carbonyl oxygen increasing the reactivities of parent carbonyl as it behaves as a mild Lewis acid [10], the keto–enol tautomerism of aliphatic aldehyde gave an intermediate enol in the presence of molecular iodine. Next, the N-ylide generated by deprotonation of the pyridinium salt with pyridine as a base took part in a 1,3-dipolar cycloaddition with enol to give the primary product **C**. Dehydration of **C** in the solvent formed the dihydroindolizine **D**. Further dehydroaromatization of **D** oxidized by molecular iodine led to the 1-alkyl-3-aroylindolizine **3j**.

CONCLUSIONS

In summary, 1-alkyl-3-aroylindolizines have been synthesized by the reaction of the pyridinium ylide with aliphatic aldehydes in the presence of molecular iodine and a catalytic amount of MnO_2. The reaction proceeds via tandem reactions involving

TABLE 2 Preparation of the 1-Alkyl-3-aroylindolizines



1a–f **2a–h** **3a–z**

Entry	*X*	*R*	*Product*	*Yield (%)*
1	*p*-Br	CH_3	**3a**	57
2	*p*-Br	C_2H_5	**3b**	56
3	*p*-Br	*n*-C_3H_7	**3c**	67
4	*p*-Br	*n*-C_4H_9	**3d**	71
5	*p*-Br	*n*-C_5H_{11}	**3e**	66
6	*p*-Br	*n*-C_6H_{13}	**3f**	60
7	*p*-Br	*n*-C_7H_{15}	**3g**	58
8	*p*-Br	*n*-C_8H_{17}	**3h**	59
9	H	CH_3	**3i**	58
10	H	C_2H_5	**3j**	59
11	H	*n*-C_3H_7	**3k**	75
12	H	*n*-C_4H_9	**3l**	72
13	H	*n*-C_5H_{11}	**3m**	64
14	H	*n*-C_6H_{13}	**3n**	66
15	H	*n*-C_7H_{15}	**3o**	57
16	H	*n*-C_8H_{17}	**3p**	58
17	*p*-CH_3O	CH_3	**3q**	51
18	*p*-CH_3O	C_2H_5	**3r**	50
19	*p*-CH_3O	*n*-C_3H_7	**3s**	53
20	*p*-CH_3O	*n*-C_4H_9	**3t**	65
21	*p*-CH_3O	*n*-C_5H_{11}	**3u**	54
22	*p*-CH_3O	*n*-C_6H_{13}	**3v**	53
23	*p*-CH_3O	*n*-C_7H_{15}	**3w**	64
24	*p*-CH_3O	*n*-C_8H_{17}	**3x**	67
25	*o*-CH_3	*n*-C_4H_9	**3y**	71
26	*o*-O_2N	*n*-C_4H_9	**3z**	72

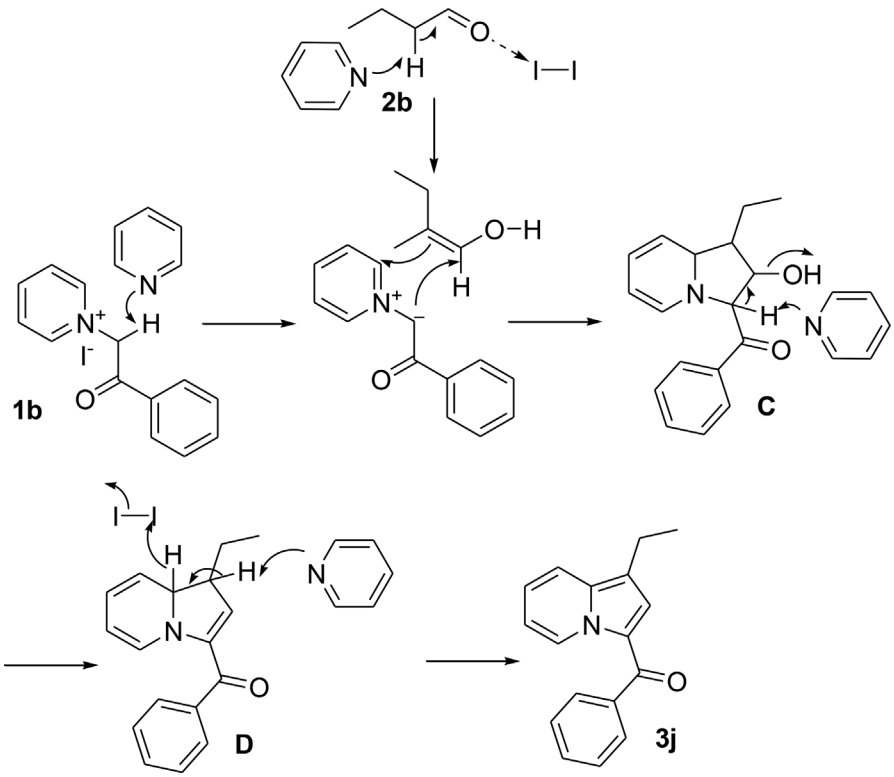
[3+2] cycloaddition, dehydration of the cycloadduct, and further dehydroaromatization of the dihydroindolizines. Molecular iodine served both as a catalyst and a dehydroaromatization reagent in the reaction. Pyridine was used both as a base reagent and a solvent in the reaction. The operational simplicity, ready availability of starting materials, and good yields make this reaction a potentially useful method in the diversity-oriented synthesis of indolizines.

EXPERIMENTAL

General

All melting points were determined in a SGW X-4B melting point apparatus and are uncorrected. IR spectra were recorded in a Nicolet FT-IR 5DX spectrometer. The ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded in a Bruker AV-600 spectrometer with TMS as an internal reference in $CDCl_3$ solutions. The *J* values are given in hertz. Only discrete or characteristic signals for the ^{1}H NMR are reported. The MS spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. The elemental analyses were performed in a Perkin–Elmer 240C instrument. Flash chromatography was performed on silica gel (230–400 mesh) eluting with an ethyl acetate–hexanes mixture. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

General Procedure for Preparation of 1-Alkyl-3-aroylindolizines **3a–z**. A mixture of 1-arylacyl pyridinium salt (4 mmol), aliphatic aldehyde (6 mmol), MnO_2 (18 mg, 0.2 mmol), and molecular iodine (1.02 g, 4 mmol) in pyridine (7 mL) was heated at 120°C for 40 h with magnetic stirring. The reaction course was monitored by TLC. After the reaction was completed, solid MnO_2 was filtered away, then



SCHEME 2 Tentative reaction mechanism.

the solvent was removed under reduced pressure, and the residue was dissolved with dichloromethane (20 mL). The resultant mixture was washed with 20% sodium thiosulfate solution (10 mL), water (10 mL), and brine (10 mL). The organic phase was dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was separated by flash chromatography on a silica gel column with petroleum ether (bp 60–90°C)/dichloromethane/ethyl acetate (16/4/1) as an eluent to give the products **3**.

*(4-Bromophenyl)(1-methylindolizin-3-yl)methanone (***3a***).* mp 125.5–126.3°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 6.9 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.13 (dd, J = 8.3 and 7.1 Hz, 1H), 6.84 (td, J = 6.8 and 1.0 Hz, 1H), 6.74 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.7, 139.1, 136.0, 130.3 (2C), 129.5 (2C), 124.1, 122.5, 121.8, 120.4, 119.8, 115.7, 112.8, 109.9, 10.5; IR (KBr, cm^{-1}): 2974, 1678, 1609, 1583, 1495, 1419, 1325, 874, 844, 762; MS(EI) (*m/z*): 312 [(M – 1)$^+$] (10%), 313 [M$^+$] (100%), 315 [(M + 2)$^+$] (35%); Anal. calcd. for $C_{16}H_{12}BrNO$: C, 61.17; H, 3.85; N, 4.46; Found: C, 61.02; H, 3.98; N, 4.20.

*(4-Bromophenyl)(1-ethylindolizin-3-yl)methanone (***3b***).* mp 131.2–132.9°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 7.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.14 (dd, J = 8.4 and 7.2 Hz, 1H), 6.83 (td, J = 6.8 and 1.1 Hz, 1H), 6.74 (s, 1H), 2.74 (q, J = 7.4 Hz, 2H), 1.32 (t, J = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.8, 139.2, 136.2, 130.3(2C), 129.5(2C), 126.6, 124.1, 122.6, 121.7, 119.9, 113.8, 112.8, 110.02, 18.0, 10.3; IR (KBr, cm^{-1}): 3057, 2964, 1678, 1632, 1589, 1555, 1490, 1292, 1239, 935, 873, 838, 762, 684; MS(EI) (*m/z*): 325 [(M – 2)$^+$] (75%), 326 [(M – 1)$^+$] (55%), 329 [(M + 2)$^+$] (100%); Anal. calcd. for $C_{17}H_{14}BrNO$: C, 62.21; H, 4.30; N, 4.27; Found: C, 62.01; H, 4.39; N, 4.22.

*(4-Bromophenyl)(1-propylindolizin-3-yl)methanone (***3c***).* mp 114.9–115.0°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 6.9 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.13 (dd, J = 8.4 and 7.2 Hz, 1H), 6.82 (td, J = 6.8 and 1.2 Hz, 1H), 6.74 (s, 1H), 2.71 (t, J = 7.6 Hz, 2H), 1.75–1.65 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.8, 139.2, 136.1, 130.3(2C), 129.5(2C),

125.0, 124.1, 122.5, 121.8, 119.9, 114.7, 112.7, 110.0, 26.7, 19.2, 12.9; IR (KBr, cm^{-1}): 2960, 2929, 2869, 1674, 1602, 1555, 1498, 1276, 1236, 876, 832, 763; MS(EI) (*m/z*): 341 [$(M)^+$] (72%), 342 [$(M + 1)^+$] (100%), 343 [$(M + 2)^+$] (35%); Anal. calcd. for $C_{18}H_{16}BrNO$: C, 63.17; H, 4.71; N, 4.09; Found: C, 63.02; H, 4.89; N, 4.12.

(4-Bromophenyl)(1-butylindolizin-3-yl)methanone (**3d**). mp 79.1–80.0°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.40 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.12 (dd, J = 8.4 and 7.2 Hz, 1H), 6.81 (td, J = 6.8 and 1.0 Hz, 1H), 6.72 (s, 1H), 2.72 (t, J = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.47–1.30 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.7, 139.2, 136.1, 130.3 (2C), 129.5 (2C), 125.2, 124.1, 122.5, 121.8, 119.9, 114.6, 112.7, 110.0, 28.0, 24.4, 21.5, 12.8; IR (KBr, cm^{-1}): 2952, 2927, 2868, 1638, 1603, 1555, 1497, 1298, 1251, 875, 832, 763, 684; MS(EI) (*m/z*): 356 [$(M + 1)^+$] (15%), 358 [$(M + 3)^+$] (100%); Anal. calcd. for $C_{19}H_{18}BrNO$: C, 64.06; H, 5.09; N, 3.93; Found: C, 63.89; H, 5.17; N, 3.69.

(4-Bromophenyl)(1-pentylindolizin-3-yl)methanone (**3e**). Mp 90.8–91.9°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.40 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.11 (dd, J = 8.4 and 7.0 Hz, 1H), 6.81 (td, J = 6.8 and 1.0 Hz, 1H), 6.72 (s, 1H), 2.71 (t, J = 7.6 Hz, 2H), 1.68-1.61 (m, 2H), 1.38-1.24 (m, 4H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.7, 139.2, 136.1, 130.3(2C), 129.5(2C), 125.2, 124.1, 122.5, 121.8, 119.9, 114.6, 112.7, 110.0, 30.6, 25.5, 24.7, 21.4, 12.9; IR (KBr, cm^{-1}): 2953, 2925, 2861, 1632, 1607, 1586, 1558, 1524, 1501, 1452, 1425, 1290, 1249, 1223, 878, 833, 762, 735, 686; MS(EI) (*m/z*): 369 [M^+] (46%), 370 [$(M + 1)^+$] (75%), 371 [$(M + 2)^+$] (100%), 373 [$(M + 4)^+$] (42%); Anal. calcd. for $C_{20}H_{20}BrNO$: C, 64.87; H, 5.44; N, 3.78; Found: C, 64.92; H, 5.32; N, 3.82.

(4-Bromophenyl)(1-hexylindolizin-3-yl)methanone (**3f**). mp 92.3–93.0°C (PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 6.9 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 8.4 and 7.2 Hz, 1H), 6.82 (td, J = 6.8 and 0.9 Hz, 1H), 6.73 (s, 1H), 2.72 (t, J = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.41–1.29 (m, 2H), 1.30–1.19 (m, 4H), 0.82 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.8, 139.2, 136.1, 130.2 (2C), 129.5 (2C), 125.2, 124.1, 122.5, 121.8, 119.9, 114.6, 112.7, 110.0, 30.5, 28.1, 25.8, 24.7, 21.5, 13.0; IR (KBr, cm^{-1}): 2921, 2858, 1634, 1608, 1551, 1524, 1498, 1448, 1421, 1244, 1218, 1153, 877, 833, 763; MS(EI) (*m/z*): 383 [$(M + 1)^+$] (100%), 384 [$(M + 1)^+$] (75%); Anal. calcd. for $C_{21}H_{22}BrNO$: C, 65.63; H, 5.77; N, 3.64; Found: C, 65.58; H, 5.68; N, 3.50.

(4-Bromophenyl)(1-heptylindolizin-3-yl)methanone (**3g**). mp 89.8–91.5°C (PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.40 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 8.4 and 7.2 Hz, 1H), 6.81 (td, J = 6.8 and 0.9 Hz, 1H), 6.72 (s, 1H), 2.72 (t, J = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.38–1.31 (m, 2H), 1.30–1.26 (m, 2H), 1.24–1.18 (m, 4H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.8, 139.2, 136.1, 130.3 (2C), 129.5 (2C), 125.2, 124.1, 122.5, 121.8, 119.9, 114.6, 112.7, 110.0, 30.7 , 28.4, 28.0, 25.8, 24.7, 21.6, 13.1; IR (KBr, cm^{-1}): 2924, 2852, 1632, 1602, 1562, 1523, 1496, 1250, 1237, 931, 872, 828, 763; MS(EI) (*m/z*): 398 [$(M + 1)^+$] (100%), 399 [$(M + 2)^+$] (72%); Anal. calcd. for $C_{22}H_{24}BrNO$: C, 66.33; H, 6.07; N, 3.52; Found: C, 66.10; H, 6.22; N, 3.30.

(4-Bromophenyl)(1-octylindolizin-3-yl)methanone (**3h**). mp 96.5–97.1°C (PE); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.40 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 8.3 and 7.2 Hz, 1H), 6.81 (td, J = 6.9 and 0.8 Hz, 1H), 6.72 (s, 1H), 2.71 (t, J = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.39–1.30 (m, 2H), 1.31–1.10 (m, 8H), 0.80 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 187.6, 139.2, 136.1, 130.3 (2C), 129.5 (2C), 125.2, 124.1, 122.5, 121.8, 119.9, 114.6, 112.7, 110.0, 30.8, 28.5, 28.3, 28.2, 25.8, 24.7, 21.6, 13.1; IR (KBr, cm^{-1}): 2923, 2854, 1601, 1557, 1498, 1424, 1295, 1253, 873, 830, 764; MS(EI) (*m/z*): 412 [$(M + 1)^+$] (55%), 413 [$(M + 2)^+$] (100%); Anal. calcd. for $C_{23}H_{26}BrNO$: C, 66.99; H, 6.36; N, 3.40; Found: C, 66.70; H, 6.46; N, 3.52.

(1-Methylindolizin-3-yl)(phenyl)methanone (**3i**). mp 93.0–94.1°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.50 (d, J = 8.6 Hz, 1H), 7.86 (d, J = 6.8 Hz, 1H), 7.74 (d, J = 7.8 Hz,, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 6.80 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 189.2, 140.4, 135.9, 129.5, 127.8 (2C), 127.0 (2C), 122.1, 121.7, 120.1, 119.9, 116.0, 112.6, 110.3, 10.4; IR (KBr, cm^{-1}): 2918, 1714, 1604, 1554, 1494, 1421, 1248, 932, 872, 747, 710; MS(EI) (*m/z*): 234 [$(M - 1)^+$] (100%), 237 [$(M + 2)^+$] (15%); Anal. calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95; Found: C, 81.49; H, 5.60; N, 5.72.

(1-Ethylindolizin-3-yl)(phenyl)methanone (**3j**). mp 65.0–66.7°C (PE/EA); ^{1}H NMR (600 MHz), δ (ppm): 8.42 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.12 (dd, J = 8.5 and 7.2 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 6.79 (s, 1H), 2.75 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 190.3, 141.5, 137.1, 130.6, 128.9 (2C), 128.1 (2C), 127.3, 123.3, 122.7, 121.0, 115.2, 113.6, 111.4, 19.0, 11.4; IR (KBr, cm^{-1}): 2969, 2935, 1608, 1497, 1291, 1238, 872, 796, 746; MS(EI) (*m/z*): 248 [$(M - 1)^+$] (24%), 250 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62; Found: C, 81.72; H, 6.26; N, 5.88.

Phenyl(1-propylindolizin-3-yl)methanone (**3k**). mp 79.0–80.0°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.49 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 6.9 Hz, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.18 (dd, J = 8.4 and 7.1 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 6.81 (s, 1H), 2.79 (t, J = 7.6 Hz, 2H), 1.84–1.75 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 189.2, 140.5, 135.9, 129.5, 127.9 (2C), 127.0 (2C), 124.8, 122.1, 121.7, 119.9, 115.0, 112.5, 110.4, 26.7, 19.2, 13.0; IR (KBr, cm^{-1}): 2951, 2924, 2867, 1630, 1600, 1570, 1546, 1495, 1421, 1374, 1309, 1276, 1233, 874, 831, 794, 751; MS(EI) (*m/z*): 263 [M^+] (100%), 264 [$(M + 1)^+$] (35%); Anal. calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32; Found: C, 82.02; H, 6.50; N, 5.60.

(1-Butylindolizin-3-yl)(phenyl)methanone (**3l**). mp 97.9–98.0°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.42 (d, J = 8.9 Hz, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.11 (dd, J = 8.2 and 6.9 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 6.79 (s, 1H), 2.73 (t, J = 7.6 Hz, 2H), 1.70–1.64 (m, 2H), 1.42–1.36 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 189.2, 140.5, 136.0, 129.5, 127.9 (2C), 127.1 (2C), 124.9, 122.1, 121.7, 120.0, 114.9, 112.5, 110.4, 28.0, 24.4, 21.5, 12.8; IR (KBr, cm^{-1}): 2919, 2859, 1677, 1601, 1538, 1495, 1416, 1296, 1237, 930, 869, 780; MS(EI) (*m/z*): 277 [M^+] (50%), 278 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05; Found: C, 82.04; H, 6.82; N, 5.01.

(1-Pentylindolizin-3-yl)(phenyl)methanone (**3m**). mp 74.0–75.1°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.42 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.76 (d, J = 6.6 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.11 (dd, J = 8.6 and 7.2 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 6.79 (s, 1H), 2.73 (t, J = 7.6 Hz, 2H), 1.71–1.63 (m, 2H), 1.37–1.29 (m, 4H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 190.3, 141.5, 137.0, 130.6, 128.9 (2C), 128.1 (2C), 126.0, 123.2, 122.7, 121.0, 115.9, 113.5, 111.4, 31.7, 26.6, 25.7, 22.4, 14.0; IR (KBr, cm^{-1}): 2925, 2860, 1602, 1572, 1548, 1526, 1496, 1444, 1293, 1248, 1222, 873, 790, 749; MS(EI) (*m/z*): 290 [$(M - 1)^+$] (100%), 291 [M^+] (23%), 292 [$(M + 1)^+$] (15%); Anal. calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81; Found: C, 82.32; H, 7.22; N, 4.78.

(1-Hexylindolizin-3-yl)(phenyl)methanone (**3n**). mp 83.5–84.9°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.49 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 6.9 Hz, 1H), 7.82 (d, J = 7.0 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.18 (dd, J = 8.5 and 7.0 Hz, 1H), 6.88 (t, J = 6.8 Hz, 1H), 6.86 (s, 1H), 2.80 (t, J = 7.6 Hz, 2H), 1.78–1.72 (m, 2H), 1.46-1.42 (m, 2H), 1.35–1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 189.2, 140.5, 136.0, 129.5, 127.9 (2C), 127.0 (2C), 125.0, 122.1, 121.7, 120.0, 114.9, 112.5, 110.4, 30.5, 28.1, 25.8, 24.7, 21.5, 13.0; IR (KBr, cm^{-1}): 2921, 2856, 1672, 1601, 1494, 1417, 1357, 1246, 1159, 871, 780, 743, 697; MS(EI) (*m/z*): 204 [$(M - 1)^+$] (100%), 205 [M^+] (14%), 306 [$(M + 1)^+$] (9%); Anal. calcd. for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59; Found: C, 82.43; H, 7.72; N, 4.66

(1-Heptylindolizin-3-yl)(phenyl)methanone (**3o**). mp 46.5–47.1°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 7.0 Hz, 1H), 7.74 (d, J = 7.0 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.08 (dd, J = 8.5 and 7.0 Hz, 1H), 6.78 (t, J = 6.8 Hz, 1H), 6.70 (s, 1H), 2.70 (t, J = 7.6 Hz, 2H), 1.69–1.62 (m, 2H), 1.35–1.30 (m, 2H), 1.29–1.24 (m, 2H), 1.23–1.18 (m, 4H), 0.81 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 190.2, 141.5, 137.0, 130.6, 128.9 (2C), 128.1 (2C), 126.0, 123.2, 122.7, 121.0, 115.9, 113.5, 111.4, 31.8, 29.5, 29.1, 26.9, 25.7, 22.6, 14.1; IR (KBr, cm^{-1}): 2917, 2852, 1694, 1600, 1563, 1495, 1418, 1294, 1242, 868, 755; MS(EI) (*m/z*): 318 [$(M - 1)^+$] (100%), 319 [M^+] (38%), 320 [$(M + 1)^+$] (15%); Anal. calcd. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38; Found: C, 82.88; H, 7.90; N, 4.32.

(1-Octylindolizin-3-yl)(phenyl)methanone (**3p**). mp 75.1–76.8°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*): 8.43 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 7.0 Hz, 1H), 7.74 (d, J = 7.0 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.09 (dd, J = 8.5 and 7.0 Hz, 1H), 6.78–6.70 (m, 2H), 2.71 (t, J = 7.2 Hz, 2H), 1.67–1.54 (m, 2H), 1.34–1.28 (m, 2H), 1.22–1.10 (m, 8H), 0.80 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 190.2,

141.5, 137.0, 130.6, 128.9(2C), 128.1(2C), 126.0, 123.1 122.7, 121.0, 115.9, 113.5, 111.4, 31.8, 29.5, 29.4, 29.2, 26.9, 25.8, 22.7; IR (KBr, cm^{-1}): 2917, 2849, 1688, 1600, 1562, 1494, 1418, 1374, 1297, 1239, 870, 754; MS(EI)(m/z): 332[$(M - 1)^+$] (31%), 333[M^+] (100%), 334 [$(M + 1)^+$] (38%); Anal. calcd. for $C_{22}H_{25}NO$: C, 82.84; H, 8.16; N, 4.20; Found: C, 82.67; H, 8.10; N, 4.29.

*(4-Methoxyphenyl)(1-methylindolizin-3-yl)methanone (***3q***)*. mp 128.3–129.1°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.39 (d, $J = 9.0$ Hz, 1H), 7.99 (d, $J = 9.0$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.09 (dd, $J = 6.6$ and 8.4 Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 2H), 6.82 (s, 1H), 6.80 (t, $J = 6.8$ Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 188.2, 160.7, 135.7, 132.9, 131.3, 130.1(2C), 121.7, 121.6, 119.9, 115.8, 112.7, 112.4, 112.2(2C), 54.40, 10.46; IR (KBr, cm^{-1}): 2980, 2903, 2841, 1685, 1601, 1499, 1247, 929, 877, 844; MS(EI) (*m/z*): 266 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28; Found: C, 76.88; H, 5.86; N, 5.02.

*(1-Ethylindolizin-3-yl)(4-methoxyphenyl)methanone (***3r***)*. mp 104.5–105.3°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.46 (d, $J = 8.7$ Hz, 1H), 7.90 (d, $J = 6.7$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.16 (dd, $J = 6.6$ and 8.4 Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 2H), 6.91 (s, 1H), 6.87 (t, $J = 6.5$ Hz, 1H), 3.89 (s, 3H), 2.83 (q, $J = 7.2$ Hz, 2H), 1.40 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 189.3, 161.8, 136.9, 134.0, 132.1, 131.1(2C), 128.3, 127.1, 122.7, 121.0, 114.9, 113.4(2C), 111.6, 55.4, 19.0, 11.4; IR (KBr, cm^{-1}): 2968, 2934, 2872, 2843, 1669, 1597, 1566, 1497, 1424, 1377, 1248, 1169, 943, 876, 842; MS(EI) (*m/z*): 278 [$(M - 1)^+$] (23%), 279 [M^+] (56%), 280 [$(M + 1)^+$] (100%), 281 [$(M + 2)^+$] (92%); Anal. calcd. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01; Found: C, 77.26; H, 6.10; N, 5.24.

*(4-Methoxyphenyl)(1-propylindolizin-3-yl)methanone (***3s***)*. mp 83.2–84.5°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.46 (d, $J = 8.7$ Hz, 1H), 7.91 (d, $J = 6.7$ Hz, 1H), 7.85 (d, $J = 8.3$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 2H), 6.90 (s, 1H), 6.85 (t, $J = 6.6$ Hz, 1H), 3.89 (s, 3H), 2.79 (t, $J = 7.4$ Hz, 2H), 1.85–1.75 (m, 2H), 1.05 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 189.3, 161.8, 136.9, 134.0, 131.1(2C), 125.5, 124.5, 122.7, 122.0, 121.0, 115.9, 113.3(2C), 111.6, 55.4, 27.8, 20.3, 14.1; IR (KBr, cm^{-1}): 32930, 2871, 2841, 1647, 1599, 1497, 1460, 1277, 1247, 902, 877, 847, 773; MS(EI) (*m/z*): 294 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77; Found: C, 77.63; H, 6.50; N, 4.88.

*(1-Butylindolizin-3-yl)(4-methoxyphenyl)methanone (***3t***)*. mp 75.1–76.8°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.38 (d, $J = 8.9$ Hz, 1H), 7.82 (d, $J = 6.9$ Hz, 1H), 7.77 (d, $J = 8.6$ Hz, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.81 (s, 1H), 6.76 (t, $J = 6.7$ Hz, 1H), 3.89 (s, 3H), 2.72 (q, $J = 7.2$ Hz, 2H), 1.69–1.62 (m, 2H), 1.42–1.34 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 188.2, 160.7, 135.8, 132.9, 130.0 (2C), 124.7, 121.8, 121.6, 119.9, 114.7, 112.4, 112.3 (2C), 110.5, 54.4, 27.9, 24.4, 21.5, 12.9; IR (KBr, cm^{-1}): 2931, 2870, 2838, 1677, 1604, 1497, 1461, 1249, 966, 902, 878, MS(EI) (*m/z*): 305 [$(M - 2)^+$] (92%), 307 [M^+] (100%); Anal. calcd. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56; Found: C, 78.02; H, 6.98; N, 4.50.

*(4-Methoxyphenyl)(1-pentylindolizin-3-yl)methanone (***3u***)*. mp 69.1–70.5°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.46 (d, $J = 8.9$ Hz, 1H), 7.91 (d, $J = 6.0$ Hz, 1H), 7.85 (d, $J = 7.2$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 2H), 6.89 (s, 1H), 6.86 (t, $J = 6.7$ Hz, 1H), 3.89 (s, 3H), 2.80 (d, $J = 7.2$ Hz, 2H), 1.79–1.74 (m, 2H), 1.45–1.35 (m, 4H), 0.92 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 189.3, 161.8, 136.8, 134.0, 131.1 (2C), 125.8, 122.7, 122.0, 121.0, 115.7, 113.3 (2C), 112.9, 111.5, 55.4, 31.7, 26.6, 25.7, 22.5, 14.0; IR (KBr, cm^{-1}): 2955, 2930, 2858, 1675, 1604, 1496, 1461, 1422, 1249, 1170, 966, 903, 878; MS(EI) (*m/z*): 321 [M^+] (24%), 322 [$(M + 1)^+$] (100%), 323 [$(M + 2)^+$] (65%); Anal. calcd. for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36; Found: C, 78.24; H, 7.20; N, 4.52.

*(1-Hexylindolizin-3-yl)(4-methoxyphenyl)methanone (***3v***)*. mp 58.4–59.6°C (PE/DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.38 (d, $J = 8.8$ Hz, 1H), 7.83 (d, $J = 6.7$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.81 (s, 1H), 6.78 (t, $J = 6.6$ Hz, 1H), 3.82 (s, 3H), 2.72 (t, $J = 7.2$ Hz, 2H), 1.73–1.61 (m, 2H), 1.40–1.35 (m, 2H), 1.29–1.24 (m, 4H), 0.83 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 188.2, 160.7, 135.8, 133.0, 130.0(2C), 124.7, 121.6, 121.5, 120.0, 114.7, 112.3 (2C), 112.0 110.5, 54.4, 30.6, 28.1, 25.9, 24.7, 21.6, 13.0; IR (KBr, cm^{-1}): 2925, 2858, 1670, 1599, 1497, 1278, 1242, 958, 934, 832, 797; MS(EI) (*m/z*): 334[$(M - 1)^+$] (45%), 335[M^+] (46%), 336 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18; Found: C, 78.68; H, 7.70; N, 4.29.

*(1-Heptylindolizin-3-yl)(4-methoxyphenyl)methanone (***3w***)*. mp 62.0–63.4°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*): 8.46 (d, $J = 8.8$ Hz, 1H), 7.91 (d, $J = 6.7$ Hz, 1H), 7.85 (d, $J = 8.6$ Hz, 2H),

7.15 (t, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 8.6$ Hz, 2H), 6.89 (s, 1H), 6.86 (t, $J = 6.8$ Hz, 1H), 3.89 (s, 3H), 2.72 (t, $J = 7.2$ Hz, 2H), 1.81–1.71 (m, 2H), 1.49–1.19 (m, 8H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 188.2, 160.7, 135.8, 132.9, 130.1 (2C), 124.7, 121.7, 121.6, 119.9, 114.7, 112.4, 112.2 (2C), 110.5, 54.4, 30.7, 28.4, 28.0, 25.9, 24.7, 21.6, 13.1; IR (KBr, cm^{-1}): 2925, 2854, 2830, 1648, 1598, 1497, 1465, 1249, 927, 876, 799; MS(EI) (*m/z*): 348 [$(M - 1)^+$] (58%), 349 [M^+] (30%), 350 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01; Found: C, 79.12; H, 7.88; N, 4.28.

*(4-Methoxyphenyl)(1-octylindolizin-3-yl)methanone (***3x***)*. mp 64.5–65.6°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.39 (d, $J = 8.9$ Hz, 1H), 7.83 (d, $J = 6.7$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.08 (t, $J = 7.2$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 2H), 6.82 (s, 1H), 6.79 (t, $J = 6.7$ Hz, 1H), 3.82 (s, 3H), 2.73 (t, $J = 7.5$ Hz, 2H), 1.75–1.63 (m, 2H), 1.40–1.31 (m, 2H), 1.30–1.25 (m, 2H), 1.25–1.16 (m, 6H), 0.81 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 188.2, 162.7, 140.6, 135.8, 134.0, 133.0, 132.2, 130.1 (2C), 124.7, 121.7, 121.6, 120.0, 114.7, 112.3 (2C), 54.4, 30.8, 28.5, 28.3, 28.2, 25.9, 24.7, 21.6; IR (KBr, cm^{-1}): 2954, 2913, 2852, 1651, 1608, 1545, 1497, 1288, 1247, 956, 924, 880, 770; MS(EI) (*m/z*): 362 [$(M - 1)^+$] (100%), 363 [M^+] (24%), 364 [$(M + 1)^+$] (25%), 365 [$(M + 2)^+$] (55%); Anal. calcd. for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85; Found: C, 79.38; H, 8.26; N, 3.68.

*(1-Butylindolizin-3-yl)(o-tolyl)methanone (***3y***)*. mp 64.0–65.0°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.39 (d, $J = 8.9$ Hz, 1H), 7.81 (d, $J = 6.9$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 7.9$ Hz, 2H), 7.06 (dd, $J = 8.1$, 7.5 Hz, 1H), 6.79 (s, 1H), 6.78 – 6.74 (m, 1H), 2.70 (t, $J = 7.7$ Hz, 2H), 2.35 (s, 3H), 1.71–1.60 (m, 2H), 1.43–1.31 (m, 2H), 0.88 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 189.0, 139.8, 137.6, 135.8, 128.0, 127.7, 124.7, 121.8, 121.6, 119.9, 114.8, 112.3, 110.5, 27.9, 24.3, 21.5, 20.4, 12.8; IR (KBr, cm^{-1}) ν: 2920, 1602, 1496, 1420, 1356, 1295, 1253, 1227, 1156, 876, 764; MS(EI) (*m/z*): 290.45 [$(M - 1)^+$] (100%); Anal. calcd. for $C_{20}H_{21}NO$:C, 82.44; H, 7.26; N, 4.81; Found: C, 82.62; H, 7.12; N, 4.90.

*(1-Butylindolizin-3-yl)(2-nitrophenyl)methanone (***3z***)*. mp 82.0–84.0°C (PE/EA); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.45 (d, $J = 8.9$ Hz, 1H), 8.25 (d, $J = 6.8$ Hz, 2H), 7.89 (d, $J = 6.9$ Hz, 1H), 7.85 (d, $J = 7.9$ Hz, 2H), 7.19 (dd, $J = 10.2$, 5.3 Hz, 1H), 6.88 (t, $J = 6.8$ Hz, 1H), 6.66 (s, 1H), 2.73 (t, $J = 7.7$ Hz, 2H), 1.71–1.59 (m, 2H), 1.45–1.30 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 186.4, 147.7, 146.0, 136.4, 128.5, 125.8, 123.4, 122.4, 122.0, 119.9, 114.4, 113.2, 109.7, 27.9, 24.3, 21.5, 12.8; IR (KBr, cm^{-1}) ν: 2934, 1737, 1525, 1497, 1425, 1348, 1232, 841, 745; MS(EI) (*m/z*): 323.59 [$(M + 1)^+$] (100%); Anal. calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69; Found: C, 70.88; H, 5.82; N, 8.78.

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