

Gold-Catalyzed C-3-Alkylation of 7-Azaindoles Through Michael-Type Addition to α,β -Enones

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The Au^{III}-catalyzed reactions of 7-azaindole derivatives with α,β -enones are described. Factors that can direct the C-3-versus N-1-alkylation reaction on the 7-azaindole nucleus are explored. The Au^{III}-catalyzed reaction of 7-azaindole with β -unsubstituted α,β -enones afforded 1-substituted 7-azaindoles through an aza-Michael-type reaction. In contrast, 6-substituted 7-azaindoles underwent regioselective C-3-alkylation through a Na[AuCl₄] $\cdot$ 2H₂O-catalyzed conjugate addition-type reaction. Analogously, the

Na[AuCl₄] $\cdot$ 2H₂O-catalyzed reaction of 7-azaindole derivatives with β -aryl-substituted α,β -enones gave 3-substituted 7-azaindoles in moderate-to-satisfactory yields. Moreover, the Na[AuCl₄] $\cdot$ 2H₂O-catalyzed reaction of 1-substituted 7-azaindoles with α,β -enones allowed an easy entry to 1,3-disubstituted 7-azaindoles in moderate-to-high yields.

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Introduction

Azaindoles^[1] are an important component of many pharmaceuticals.^[2–6] Much interest in this heterocyclic moiety has arisen in recent pharmacological programs as it serves as a bioisoster of indole or purine.^[7–16] Applications in the preparation of bioactive molecules and in the syntheses of dopamine D-4 receptor ligands^[17] as well as of potent GnRH antagonists^[18] have been cited. The increased interest in this heterocyclic system has motivated considerable synthetic efforts towards functionalized azaindole derivatives. Substitution of the pyrrole ring can be effected either directly on the 7-azaindole core or, alternatively, by cyclization of a requisite pyridine precursor.^[19–34]

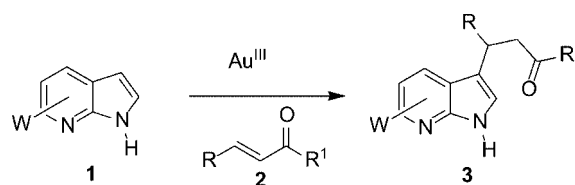
3-Substituted 7-azaindoles have been reported to possess a range of biological activities and have the potential to treat inflammation, asthma, anxiety, depression, sleeping disorders, Alzheimer's disease, migraine, and pain.^[2,4,35]

In an ongoing medicinal chemistry project,^[36] we have directed our efforts towards developing a synthetic methodology for the alkylation of the 3-position of 7-azaindoles **1** through a Michael-type addition reaction with α,β -enones **2**.

With the emergence of the concepts of “atom economy”^[37] and “green chemistry”,^[38] transition-metal-catalyzed C–H bond activation as well as the direct use of the unactivated C–H bond and subsequent C–C bond forma-

tion provide an alternative to traditional functional group organic chemistry. Catalytic elaboration at the C-3 position of indoles in particular has received considerable attention.^[39,40] The C-3-alkylation of indoles is a well-documented process^[41–43] that takes advantage of the electron-rich nature of this position, which can be viewed as possessing enamine-like character. In contrast, the electron-deficient nature of the pyridine moiety, which reduces the overall nucleophilicity of the 7-azaindole system, causes inertness of the 3-position of azaindoles when compared to that of indoles. As a consequence, documented examples of the direct functionalization of the 3-position of azaindoles are restricted to acylation,^[34] halogenation,^[44–46] the Mannich reaction,^[47] carbonylation,^[48] and condensation with an aldehyde.^[49]

The gold-catalyzed coupling process^[50–54] promises a new approach to the C-alkylation of the title heteroaromatics **1** through a gold-catalyzed conjugate addition-type reaction with α,β -enones **2** (Scheme 1). We have previously shown that Na[AuCl₄] $\cdot$ 2H₂O is a very efficient catalyst for the regioselective alkylation of the 3-position of 3-unsubstituted indoles through a conjugate addition-type reaction with α,β -enones.^[55] Activation of the C–H bonds followed



Scheme 1.

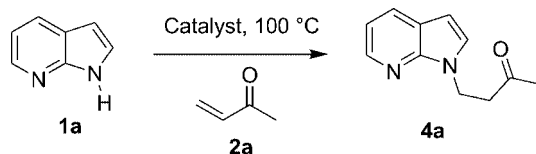
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by C–C bond formation points to the unique catalytic properties of gold derivatives.^[56–66]

Herein we report the results of our investigation.

Results and Discussion

Initially we explored the feasibility of the transformation. To the best of our knowledge only one example of erbium-metal-induced C–H activation of the azaindole system has previously been reported in the literature and this led to the unexpected formation of bis(1*H*-7-azaindol-3-yl)(2,4,5-triphenyl)methane from 7-azaindole and 1,2,4,5-tetramethylbenzene through a free-radical process.^[67] Furthermore, complexes formed between the azaindole nucleus and Lewis acids have also been reported to occur through coordination to the pyridine nitrogen atom which lowers the pK_a of the pyrrole N–H proton. A series of *N*-coordinated gold(III) complexes of pyridine derivatives have been synthesized and their reactivity evaluated.^[68–70] 7-Azaindole (**1a**) and methyl vinyl ketone (**2a**) were used as the model system. Under a variety of reaction conditions (Scheme 2, Table 1) the main product obtained was the aza-Michael derivative **4a**.



Scheme 2.

Table 1. Gold-catalyzed aza-Michael reaction of 7-azaindole (**1a**) with methyl vinyl ketone (**2a**).

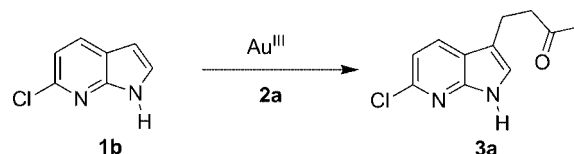
Entry	Catalyst	Time [h]	Reaction conditions ^[a]	Yield of 4a [%] ^[b]
1	Na[AuCl ₄] $\cdot$ 2H ₂ O	48	A	48 (28)
2	Na[AuCl ₄] $\cdot$ 2H ₂ O	88	B	54 (37)
3	AuBr ₃ , AgOTf	7	C	76 (22)
4	AuCl ₃ , AgOTf	7	C	44 (27)
5	–	24	D	– (98)

[a] Reactions were carried out at 100 °C using the following molar ratios: A = **1a**/**2a**/Na[AuCl₄] $\cdot$ 2H₂O = 1:2:0.05 in EtOH; B = **1a**/**2a**/Na[AuCl₄] $\cdot$ 2H₂O = 1:3:0.05 in EtOH; C = **1a**/**2a**/AuX₃/AgOTf = 1:3:0.05:0.10 in ClCH₂CH₂Cl; D = **1a**/**2a** = 1:1 in EtOH. [b] Figures in parentheses refer to the recovered starting 7-azaindole (**1a**).

The gold catalyst is clearly involved in the formation of **4a** as 98% of unreacted **1a** was recovered after 24 hours at 100 °C in the absence of the catalyst (Table 1, entry 5). AuBr₃ in combination with AgOTf gave the best yield of product **4a**. Both Au^{III} and Au^I catalysts have been reported to exhibit higher catalytic activity than conventional Lewis acids in the aza-Michael reactions of enones with carbamates.^[71,72] AgOTf alone did not catalyze the reaction under the same reaction conditions. Although the exact role of the silver salt is not clear, it may help to remove the halide ion from AuX₃ to generate more electrophilic Au^{III} species.^[53] AuX₃ alone gave low yields of **4a**. The conjugate addition of azaindoles to electron-deficient olefins to give *N*-1-alkylated derivatives has previously^[73] been reported to

occur under basic conditions and the formation of Michael adducts involved the *N*-alkylation of anionic 7-azaindoles obtained from **1** by the addition of a base such as K₂CO₃ in an aprotic solvent.

In contrast with the result of the gold-catalyzed reaction of **1a**, the 6-chloro-7-azaindole (**1b**) reacted with **2a** in the presence of a catalytic amount of a Au^{III} species to afford exclusively the C-3-alkylated derivative **3a** (Scheme 3).



Scheme 3.

When an equimolecular ratio of the azaindole derivative **1b** and the enone **2a** reacted in ethanol at 100 °C in the presence of Na[AuCl₄] $\cdot$ 2H₂O (5%), the C-3-alkylated derivative **3a** was isolated in 40% yield after 24 hours. The product **3a** was isolated in a better yield (68%) by increasing the **2a**/**1b** ratio (Table 2, entry 2). No side-products were observed and unreacted starting azaindole **1b** was recovered. These results encouraged us to investigate the factors that direct the C-3- versus *N*-1-alkylation reaction on the 7-azaindole nucleus. Some of the results of this study are summarized in Table 2.

The Au^{III}-catalyzed reaction of 4-chloro-7-azaindole (**1d**) with **2a** (Table 2, entry 5) afforded mainly the *N*-1-alkylation product **4b** (Scheme 4), but with the more hindered β -aryl-substituted α,β -enone **2c** only the C-3-alkylated derivative **3e** was formed albeit in low yield after a prolonged reaction time at 140 °C.

Very likely the presence of a bulky substituent at the β position of the α,β -enone moiety hampers the aza-Michael addition of the 7-azaindoles thereby favoring the formation of the C-3-alkylated derivative **3**. Indeed only C-3-alkylated products **3e–j** were observed to form when 7-azaindole (**1a**) was allowed to react in ethanol with β -aryl-substituted α,β -enones **2d–h** in the presence of a catalytic amount of Na[AuCl₄] $\cdot$ 2H₂O (5% mol). Of all the gold catalysts screened, only Na[AuCl₄] $\cdot$ 2H₂O was effective in forming the 3-alkyl-7-azaindole derivatives **3**. C-3-Alkylated products were not formed by using AuX₃/AgOTf as the catalytic system. Next we studied the effect of the reaction conditions on the Michael reaction in the synthesis of **3f**. The optimum conditions (140 °C and **1**/**2** ratio = 3) were applied to a variety of β -aryl-substituted α,β -enones. With more hindered α,β -enones, reaction times were prolonged and increasing the temperature from 100 to 140 °C resulted in an increase in the yields of the products **3**. Even if derivatives **3** were formed in moderate yields, the conversion of **1** to **3** was very high and as a consequence the unreacted starting 7-azaindoles **1** and the excess of α,β -enones **2** were recovered from the reaction mixture. A gold-catalyzed retro-Michael reaction^[74] at 140 °C can be ruled out on the basis that **3f** was recovered unchanged (60%) after heating for 24 hours at 140 °C in ethanol in the presence of Na[AuCl₄] $\cdot$ 2H₂O

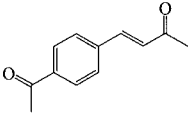
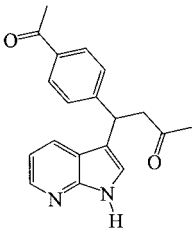
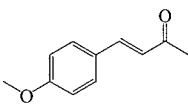
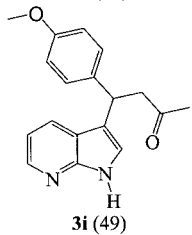
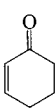
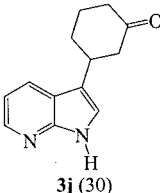
(5% mol). The rearrangement of N-1-substituted azaindoles **4** to 3-substituted azaindoles **3** was not observed, that is, **4c** was recovered unchanged (60%) after heating at 140 °C in ethanol for 24 hours in the presence of Na[AuCl₄]·2H₂O (5% mol). Heating at 140 °C triggered the decomposition of **3f** and **4c** to some extent. Longer reaction times

led to a worsening of the yield of the target derivative **3**, for example, when the reaction time for the formation of **3i** was increased from 24 to 40 hours the yield of **3i** decreased from 49 to 40% (Table 2, entries 13 and 14). The effect of steric factors on the reaction can be highlighted by considering the gold-catalyzed reaction of **1a** with the cyclic α,β -enone

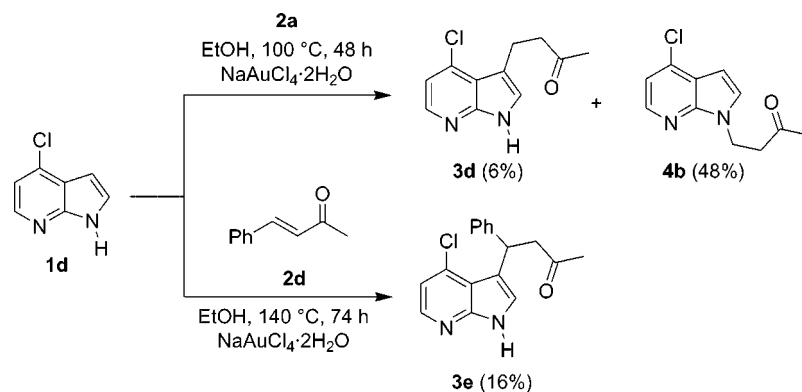
Table 2. Gold-catalyzed conjugate addition of 7-azaindole **1** to α,β -enones **2**.

Entry	Compound 1	Compound 2	<i>T</i> [°C]	Time [h]	[2]/[1] Ratio	Product 3 (% yield) ^[a]	% of Compound 1 recovered
1			100	24	1		53
2	1b	2a	100	24	2	3a (68)	25
3	1b		100	5	2		/
4			140	13	3		16
5		2a	100	48	2		38
6	1d		140	74	3		60
7		2d	100	24	1		28
8	1a	2d	140	48	1	3f (28)	43
9	1a	2d	140	48	2	3f (53)	38
10	1a	2d	140	48	3	3f (56)	40
11	1a		140	48	3		27

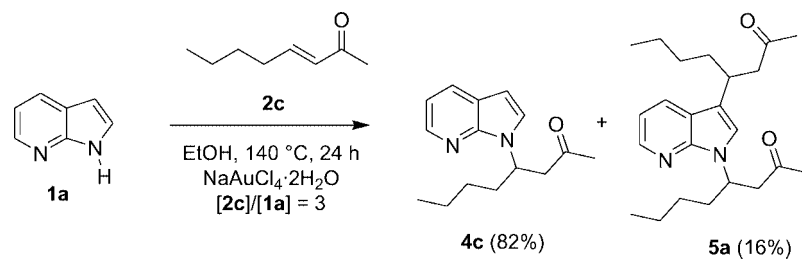
Table 2. (continued).

Entry	Compound 1	Compound 2	T [°C]	Time [h]	[2]/[1] Ratio	Product 3 (% yield) ^[a]	% of Compound 1 recovered
12	1a	 2f	140	48	3	 3b (51)	48
13	1a	 2g	140	24	3	 3i (49)	50
14	1a	2g	140	40	3	3i (40)	50
15	1a	 2h	140	60	3	 3j (30)	35

[a] Yields refer to single nonoptimized runs and are given for pure isolated products. [b] The aza-Michael derivative **4b** was isolated in 48% yield.

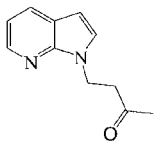
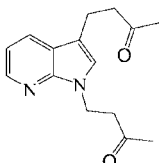
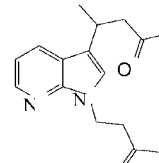
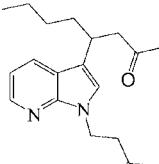
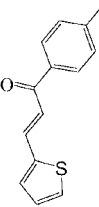
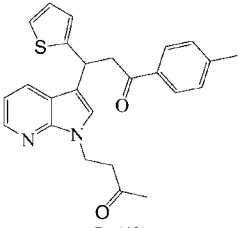
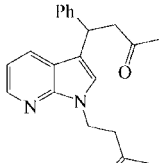
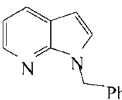
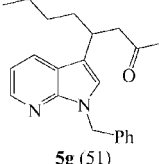
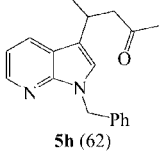
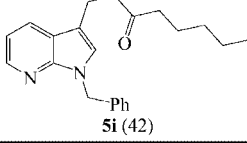


Scheme 4.

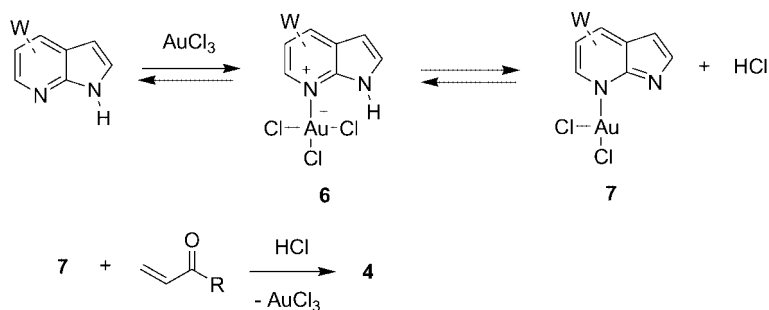


Scheme 5.

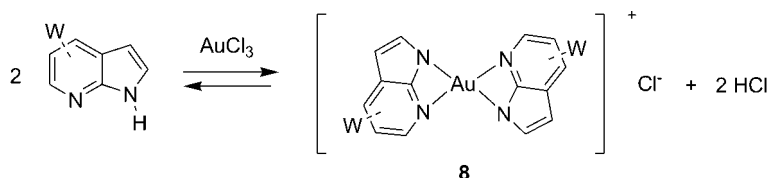
Table 3. Gold-catalyzed synthesis of 1,3-disubstituted 7-azaindoles.

Entry	Compound 4	Compound 2	<i>T</i> [°C]	Time [h]	[2]/[4] Ratio	Product 5 (% yield) ^[a]	% of Compound 4 recovered
1	 4a	2a	140	32	3	 5b (44)	/
2	4a	 2i	140	17	3	 5c (98)	/
3	4a	2c	140	22	3	 5d (73)	16
4	4a	 2j	140	21	3	 5e (40)	/
5	4a	2d	140	48	3	 5f (45)	/
6	 4d	2c	140	24	3	 5g (51)	42
7	4d	2i	140	48	3	 5h (62)	21
8	4d	2b	100	24	3	 5i (42)	18

[a] Yields refer to single nonoptimized runs and are given for pure isolated products.



Scheme 6.



Scheme 7.

2h and the less hindered β -alkyl- α,β -enone **2c**. Only the C-3-alkylated derivative **3j** (Table 2, entry 15) was isolated from the gold-catalyzed reaction of **1a** with **2h**. In contrast, the reaction of **1a** with **2c** gave a mixture of the N-1-alkylated derivative **4c** (82%) and the N-1,C-3-dialkyl derivative **5a** (16%). (Scheme 5).

The formation of **5a** suggested that compounds **4** might be used as starting materials for the synthesis of 1,3-disubstituted azaindole derivatives **5**. Indeed, the gold-catalyzed reaction of N-1-alkylated 7-azaindole derivatives **4a,d** with α,β -enones **2a–d,i,j** (Table 3) under the usual reaction conditions allowed the isolation of the derivatives **5b–i** in moderate-to-high yields. Note that this new gold-catalyzed reaction represents a versatile alternative method for the preparation of 1,3-disubstituted 7-azaindoles which are targets because of their pharmacological activities.^[18]

As a consequence of the results described above it appears that nitrogen versus oxygen coordination of the gold catalyst plays an important role in determining the reaction outcome. Au^{III} coordination to the nitrogen of the pyridine ring of the azaindole system can allow the formation of the complex^[75] **6** which readily deprotonates to give the complex **7**. The reaction of **7** with β -unsubstituted α,β -enones affords aza-Michael derivatives **4** (Scheme 6).

In the conjugate addition step, protons rather than metal ions very likely are the active catalysts. Accordingly the reaction of **1a** with **2a** in ethanol at 100 °C in the presence of a catalytic amount (0.15 mol) of the Brønsted acid *p*TsOH led to the formation of **4a** in 90% yield.

When a bulky substituent is present at the β position of the starting α,β -enone, its addition to the N-1-position of the 7-azaindole system is slowed down and the complex^[76] **8** may form under the reaction conditions (Scheme 7). The acid-catalyzed reaction of **8** with more hindered β -substituted α,β -enones affords the 3-substituted azaindoles **3** and regenerates the Au^{III} catalyst. According to the hypothesis that the conjugate addition of 7-azaindoles to hindered β -

substituted α,β -enones could be a Brønsted acid catalyzed process, the reaction of **1a** with **2d** in ethanol at 140 °C (48 h) in the presence of a catalytic amount (0.15 mol) of *p*TsOH gave **3f** in 48% yield. When the 6-position of the 7-azaindole nucleus is occupied, the Au^{III} coordination to the nitrogen of the pyridine ring of the azaindole system is hampered and the 3-substituted 7-azaindoles is formed.

Conclusions

In summary we have demonstrated that Au^{III}-catalyzed reactions of 7-azaindoles with α,β -enones can give 1- or 3-substituted 7-azaindole derivatives depending on the nature of the starting 7-azaindole and α,β -enone. The Na[AuCl₄] $\cdot$ 2H₂O-catalyzed reaction of 7-azaindole with β -unsubstituted α,β -enones afforded the N-1-substituted 7-azaindoles through an aza-Michael addition-type reaction. In contrast, 6-substituted 7-azaindoles underwent regioselective C-3-alkylation through a Na[AuCl₄] $\cdot$ 2H₂O-catalyzed conjugate addition-type reaction. Analogously, the Na[AuCl₄] $\cdot$ 2H₂O-catalyzed reaction of 7-azaindoles with β -aryl-substituted α,β -enones led in moderate-to-satisfactory yields to the regioselective formation of 3-substituted 7-azaindoles. Moreover, the gold-catalyzed reaction of 1-substituted 7-azaindole derivatives with α,β -enones allowed the preparation of 1,3-disubstituted 7-azaindoles in moderate-to-high yields.

Experimental Section

General Remarks: Temperatures are reported as the bath temperature. Solvents used in extraction and purification processes were distilled prior to use. Compounds were visualized on analytical thin-layer chromatograms (TLC) with UV light (254 nm). The products, after the usual work up, were purified by flash chromatography on silica gel (230–400 mesh), eluting with *n*-hexane/ethyl acetate mixtures. ¹H and ¹³C NMR spectra were recorded with a Bruker AC 200 E spectrometer. EI (70 eV) mass spectra

were recorded with a Varian Saturn 2100 T GC/MS instrument. IR spectra were recorded with a Perkin–Elmer 683 spectrometer. Only the most significant IR absorptions are given. All starting materials, catalysts, and solvents if not otherwise stated, are commercially available and were used as purchased without further purification. The 6-chloro-7-azaindole (**1b**),^[77] 6-(furan-2-yl)-7-azaindole (**1c**),^[32] 4-chloro-7-azaindole (**1d**),^[78] 1-benzyl-7-azaindole (**4d**),^[79] (*E*)-4-(4-acetylphenyl)but-3-en-2-one (**2f**), and (*E*)-4-(4-methoxyphenyl)but-3-en-2-one (**2g**)^[80] were prepared according to literature procedures.

Typical Experimental Procedure for Michael Addition of 7-Aza-indoles 1 to α,β -Enones 2: α,β -Enone **2** (2.52 mmol) and Na[AuCl₄]·2H₂O (0.042 mmol) were added to a screw-top vial (60 × 18 mm) with a solid-top cap charged with a solution of 7-azaindole **1** (0.850 mmol) in absolute ethanol (2 mL). The resulting mixture was then heated whilst stirring at 100 °C (for more reactive enones) or 140 °C. The reaction was monitored by TLC and GC–MS. After cooling, the mixture was filtered to remove the catalyst and the solvent concentrated under reduced pressure. The residue was directly purified by flash chromatography (silica gel, *n*-hexane/ethyl acetate) to give the product **3**.

4-(6-Chloro-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)butan-2-one (3a): Eluent for chromatography: *n*-hexane/ethyl acetate, 60:40 v/v. Yield: 0.128 g (68%). IR (neat): $\tilde{\nu}$ = 3160, 1710 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 2.16 (s, 3 H), 2.79–2.87 (m, 2 H), 2.98–3.05 (m, 2 H), 7.08 (d, *J* = 8.2 Hz, 1 H), 7.14 (s, 1 H), 7.89 (d, *J* = 8.2 Hz, 1 H), 10.49 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 19.1, 30.1, 43.9, 114.1, 115.2, 118.6, 122.4, 129.7, 144.1, 147.7, 207.9 ppm. MS (EI): *m/z* (%) = 223 (100) [M⁺], 179 (84). C₁₁H₁₁ClN₂O (222.67): calcd. C 59.33, H 4.98, N 12.58; found C 59.30, H 4.97, N 12.61.

1-(6-Chloro-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)octan-3-one (3b): Eluent for chromatography: *n*-hexane/ethyl acetate, 70:30 v/v. Yield: 0.142 g (60%). IR (KBr): $\tilde{\nu}$ = 3300, 1700 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 0.85 (t, *J* = 6.8 Hz, 3 H), 1.18–1.33 (m, 4 H), 1.51–1.59 (m, 2 H), 2.38 (t, *J* = 7.3 Hz, 2 H), 2.75–2.82 (m, 2 H), 2.97–3.04 (m, 2 H), 7.05 (d, *J* = 8.2 Hz, 1 H), 7.16 (s, 1 H), 7.86 (d, *J* = 8.2 Hz, 1 H), 11.50 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 13.9, 19.2, 22.5, 23.5, 31.4, 43.1, 113.9, 114.9, 118.8, 122.6, 129.8, 143.6, 147.8, 210.7 ppm. MS (EI): *m/z* (%) = 279 (100) [M⁺], 180 (91). C₁₅H₁₉ClN₂O (278.77): calcd. C 64.63, H 6.87, N 10.05; found C 64.57, H 6.84, N 10.00.

4-(6-Furan-2-yl-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)octan-2-one (3c): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.203 g (77%). IR (KBr): $\tilde{\nu}$ = 3350, 1720 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 0.78–0.95 (m, 3 H), 1.15–1.45 (m, 4 H), 1.48–1.69 (m, 2 H), 2.16 (s, 3 H), 2.80–2.83 (m, 2 H), 3.20–3.50 (m, 1 H), 6.25 (br. s, 1 H), 7.17–7.25 (m, 4 H), 7.21 (br. s, 1 H), 11.25 (br. s, 1 H) ppm. MS (EI): *m/z* (%) = 311 (50) [M + 1]⁺, 268 (100). C₁₉H₂₂N₂O₂ (310.39): calcd. C 73.52, H 7.14, N 9.03; found C 73.47, H 7.23, N 8.89.

4-(4-Chloro-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)butan-2-one (3d): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.011 g (6%). IR (KBr): $\tilde{\nu}$ = 3200, 1730 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 2.11 (s, 3 H), 2.84–2.91 (m, 2 H), 3.08–3.15 (m, 2 H), 7.08 (d, *J* = 5.1 Hz, 1 H), 7.34 (s, 1 H), 8.13 (d, *J* = 5.1 Hz, 1 H), 10.88 (br. s, 1 H) ppm. MS (EI): *m/z* (%) = 224 (100) [M + 1]⁺. C₁₁H₁₁ClN₂O (222.67): calcd. C 59.33, H 4.98, N 12.58; found C 59.37, H 4.88, N 12.47.

4-(4-Chloro-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)-4-phenylbutan-2-one (3e): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.041 g (16%). IR (KBr): $\tilde{\nu}$ = 3150, 1720 cm^{−1}. ¹H NMR

(200 MHz, [D₆]DMSO): δ = 2.08 (s, 3 H), 3.06–3.34 (m, 2 H), 5.16 (t, *J* = 7.7 Hz, 1 H), 7.05 (d, *J* = 5.1 Hz, 1 H), 7.12–7.27 (m, 5 H), 7.59 (s, 1 H), 8.09 (d, *J* = 5.1 Hz, 1 H), 11.94 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, [D₆]DMSO): δ = 30.0, 36.9, 50.1, 115.6, 115.9, 116.4, 124.4, 125.8, 127.7, 128.1, 134.2, 143.0, 144.9, 149.5, 206.5 ppm. MS (EI): *m/z* (%) = 299 (55) [M]⁺, 242 (100). C₁₇H₁₅ClN₂O (298.76): calcd. C 68.34, H 5.06, N 9.38; found C 68.46, H 5.19, N 9.30.

4-Phenyl-4-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)butan-2-one (3f): Eluent for chromatography: *n*-hexane/ethyl acetate, 60:40 v/v. Yield: 0.126 g (56%). IR (KBr): $\tilde{\nu}$ = 3140, 1720 cm^{−1}. ¹H NMR (200 MHz, [D₆]DMSO): δ = 2.22 (s, 3 H); 3.43 (dd, *J* = 17.5 and 7.5 Hz, 2 H), 4.87 (t, *J* = 7.5 Hz, 1 H), 7.08 (dd, *J* = 7.4 and 3.7 Hz, 1 H), 7.25–7.59 (m, 6 H), 7.94 (d, *J* = 7.4 Hz, 1 H), 8.25 (d, *J* = 7.3 Hz, 1 H), 11.67 (s, 1 H) ppm. ¹³C NMR (50.3 MHz, [D₆]DMSO): δ = 29.5, 37.2, 48.9, 114.1, 115.9, 118.6, 121.3, 125.5, 126.6, 127.2, 127.5, 140.9, 142.7, 148.0, 206.2 ppm. MS (EI): *m/z* (%) = 265 (55) [M + 1]⁺, 222 (42) 208 (100). C₁₇H₁₆N₂O (264.32): calcd. C 77.25, H 6.10, N 10.60; found C 77.22, H 6.03, N 10.53.

1,3-Diphenyl-3-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)propan-2-one (3g): Eluent for chromatography: *n*-hexane/ethyl acetate, 60:40 v/v. Yield: 0.152 g (55%). IR (KBr): $\tilde{\nu}$ = 3140, 1680 cm^{−1}. ¹H NMR (200 MHz, [D₆]DMSO): δ = 3.88–3.96 (m, 2 H); 4.92–5.06 (m, 1 H), 6.94–6.97 (m, 1 H), 7.10–7.14 (m, 1 H), 7.19–7.27 (m, 2 H), 7.43–7.60 (m, 6 H), 7.83 (d, *J* = 7.6 Hz, 1 H), 8.03 (d, *J* = 7.0 Hz, 2 H), 8.16 (br. s, 1 H), 11.49 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, [D₆]DMSO): δ = 37.6, 43.8, 114.7, 116.9, 118.6, 122.2, 125.8, 126.7, 126.9, 128.0, 128.6, 132.9, 136.7, 142.4, 144.8, 148.6, 198.1 ppm. MS (EI): *m/z* (%) = 328 (22) [M + 2]⁺, 224 (38), 210 (100). C₂₂H₁₈N₂O (326.39): calcd. C 80.96, H 5.56, N 8.58; found C 80.91, H 5.60, N 8.44.

4-(4-Acetylphenyl)-4-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)butan-2-one (3h): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.133 g (51%). IR (neat): $\tilde{\nu}$ = 3200, 1720 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 2.87 (s, 3 H); 2.94 (s, 3 H), 3.20–3.28 (m, 2 H), 4.78–4.89 (m, 1 H), 6.95 (dd, *J* = 7.8 and 4.3 Hz, 1 H), 7.23 (s, 1 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.65 (d, *J* = 7.8 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 2 H), 8.22 (d, *J* = 4.3 Hz, 1 H), 11.48 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 26.6, 30.5, 38.0, 49.4, 114.3, 115.4, 119.2, 122.2, 127.8, 127.9, 128.3, 135.6, 142.7, 149.5, 197.7, 206.5 ppm. MS (EI): *m/z* (%) = 306 (70) [M]⁺, 264 (61), 250 (100). C₁₉H₁₈N₂O₂ (306.36): calcd. C 74.49, H 5.92, N 9.14; found C 74.47, H 5.88, N 9.10.

4-(4-Methoxyphenyl)-4-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)butan-2-one (3i): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.122 g (49%). IR (KBr): $\tilde{\nu}$ = 3160, 1720, 760 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 2.06 (s, 3 H); 3.12–3.20 (m, 2 H), 3.73 (s, 3 H), 4.76 (t, *J* = 6.7 Hz, 1 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 6.95 (dd, *J* = 7.8 and 4.8 Hz, 1 H), 7.17 (d, *J* = 8.6 Hz, 2 H), 7.21 (s, 1 H), 7.65 (d, *J* = 7.8 Hz, 1 H), 8.25 (d, *J* = 4.8 Hz, 1 H), 11.72 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 30.6, 37.5, 50.1, 55.1, 113.8, 115.2, 117.3, 119.5, 122.0, 128.2, 128.6, 135.8, 142.2, 149.2, 158.1, 207.4 ppm. MS (EI): *m/z* (%) = 294(50) [M]⁺, 238 (100). C₁₈H₁₈N₂O₂ (294.35): calcd. C 73.45, H 6.16, N 9.52; found C 73.41, H 6.13, N 9.51.

3-(1*H*-Pyrrolo[2,3-*b*]pyridin-3-yl)cyclohexanone (3j): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.055 g (30%). IR (KBr): $\tilde{\nu}$ = 3140, 1710 cm^{−1}. ¹H NMR (200 MHz, CDCl₃): δ = 1.87–2.81 (m, 8 H), 3.36–3.43 (m, 1 H), 7.08 (dd, *J* = 7.9 and 4.8 Hz, 1 H), 7.19 (s, 1 H), 7.96 (d, *J* = 7.9 Hz, 1 H), 8.33 (d, *J* = 4.8 Hz, 1 H), 11.81 (br. s, 1 H) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 24.7, 31.6, 35.9, 41.4, 47.9, 115.0, 117.5, 119.0, 121.4,

127.6, 142.1, 148.9, 211.3 ppm. MS (EI): m/z (%) = 214 (100) $[M]^+$, 171 (52), 144 (58). $C_{13}H_{14}N_2O$ (214.26): calcd. C 72.87, H 6.59, N 13.07; found C 72.90, H 6.73, N 13.08.

4-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)butan-2-one (4a): Eluent for chromatography: *n*-hexane/ethyl acetate, 70:30 v/v. Yield: 0.068 g (54%). IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 3.02 (t, J = 6.4 Hz, 2 H), 4.53 (t, J = 6.4 Hz, 2 H), 6.38 (d, J = 3.5 Hz, 1 H), 7.03 (dd, J = 7.8 and 4.8 Hz, 1 H), 7.26 (d, J = 3.5 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 8.27 (d, J = 4.8 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.2, 39.3, 43.4, 99.3, 115.7, 120.4, 128.8, 129.1, 141.3, 142.4, 206.7 ppm. MS (EI): m/z (%) = 189 (100) $[M + 1]^+$, 145 (72), 118 (45). $C_{11}H_{12}N_2O$ (188.22): calcd. C 70.19, H 6.43, N 14.88; found C 70.24, H 6.49, N 14.75.

4-(4-Chloro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)butan-2-one (4b): Eluent for chromatography: *n*-hexane/ethyl acetate, 70:30 v/v. Yield: 0.091 g (48%). IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 3.10 (t, J = 6.7 Hz, 2 H), 4.54 (t, J = 6.7 Hz, 2 H), 6.56 (d, J = 3.2 Hz, 1 H), 7.15 (d, J = 5.1 Hz, 1 H), 7.59 (d, J = 3.2 Hz, 1 H), 8.19 (d, J = 5.1 Hz, 1 H) ppm. MS (EI): m/z (%) = 223 (59) $[M]^+$, 180 (100), 152 (44). $C_{11}H_{11}ClN_2O$ (222.67): calcd. C 59.33, H 6.98, N 12.58; found C 59.27, H 6.92, N 12.61.

4-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)octan-2-one (4c): Eluent for chromatography: *n*-hexane/ethyl acetate, 70:30 v/v. Yield: 0.170 g (82%). IR (KBr): $\tilde{\nu}$ = 1720, 890 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 0.78 (t, J = 7.2 Hz, 3 H), 0.89–1.30 (m, 4 H), 1.88–1.93 (m, 2 H), 2.03 (s, 3 H), 2.95–3.32 (m, 2 H), 4.95–5.10 (m, 1 H), 6.43 (d, J = 3.5 Hz, 1 H), 7.03 (dd, J = 7.8 and 4.7 Hz, 1 H), 7.22 (d, J = 3.5 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 8.29 (d, J = 4.7 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.8, 22.2, 28.3, 30.2, 34.4, 48.8, 52.1, 99.7, 115.7, 120.9, 126.6, 128.7, 142.5, 206.5 ppm. MS (EI): m/z (%) = 245 (100) $[M + 1]^+$, 145 (25), 119 (9). $C_{15}H_{20}N_2O$ (244.33): calcd. C 73.74, H 8.25, N 11.47; found C 73.81, H 8.40, N 11.35.

Typical Experimental Procedure for the Michael Addition of *N*-1-Substituted 7-Azaindoles 4 to α,β -Enone 2: α,β -Enone 2 (2.52 mmol) and $Na[AuCl_4] \cdot 2H_2O$ (0.042 mmol) were added to a screw-top vial (60 $\times$ 18 mm) with a solid-top cap charged with a solution of *N*-1-substituted 7-azaindoles 4 (0.850 mmol) in absolute ethanol (2 mL). The resulting mixture was heated whilst stirring at 140 or 100 $^{\circ}C$ (for more reactive enones). The reaction was monitored by TLC and GC-MS. After cooling, the mixture was filtered to remove the catalyst and the solvent concentrated under reduced pressure. The residue was directly purified by flash chromatography (silica gel, *n*-hexane/ethyl acetate) to give product 5.

4-[1-[1-(2-Oxopropyl)pentyl]-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl]octan-2-one (5a): Eluent for chromatography: *n*-hexane/ethyl acetate, 60:40 v/v. Yield: 0.050 g (16%). IR (neat): $\tilde{\nu}$ = 1730 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 0.77 (s, 3 H), 0.81 (s, 3 H), 1.10–1.85 (m, 10 H), 1.93 (s, 3 H), 2.03 (s, 3 H), 2.04–2.23 (m, 2 H), 3.02–3.07 (m, 2 H), 3.14–3.21 (m, 2 H), 3.25–3.42 (m, 1 H), 5.10–5.13 (m, 1 H), 6.99 (s, 1 H), 7.03 (d, J = 4.3 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 8.27 (d, J = 4.3 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.8, 13.9, 22.2, 22.5, 22.7, 27.4, 29.7, 30.1, 32.9, 34.2, 35.5, 50.3, 51.8, 51.9, 115.2, 119.2, 123.2, 123.4, 127.5, 128.7, 142.5, 206.3, 208.1 ppm. MS (EI): m/z (%) = 371 (100) $[M + 1]^+$, 313 (98). $C_{23}H_{34}N_2O_2$ (370.53): calcd. C 74.55, H 9.25, N 7.56; found C 74.43, H 9.20, N 7.48.

4-[3-(3-Oxobutyl)-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl]butan-2-one (5b): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.096 g (44%). IR (KBr): $\tilde{\nu}$ = 1730, 1710 cm^{-1} . 1H NMR

(200 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 2.16 (s, 3 H), 2.81–3.06 (m, 6 H), 4.48 (t, J = 6.4 Hz, 2 H), 7.01 (dd, J = 7.8 and 4.6 Hz, 2 H), 7.06 (s, 1 H), 7.84 (d, J = 7.8 Hz, 1 H), 8.27 (d, J = 4.6 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.8, 29.9, 38.8, 43.3, 43.6, 111.9, 114.8, 120.0, 125.8, 126.7, 142.3, 147.0, 206.5, 207.9 ppm. MS (EI): m/z (%) = 258 (84) $[M]^+$, 202 (100), 131 (66). $C_{15}H_{18}N_2O_2$ (258.32): calcd. C 69.74, H 7.02, N 10.84; found C 69.73, H 7.01, N 10.84.

4-[1-(3-Oxobutyl)-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl]pentan-2-one (5c): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.227 g (98%). IR (neat): $\tilde{\nu}$ = 1720 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 1.34 (d, J = 6.8 Hz, 3 H), 2.10 (s, 3 H), 2.12 (s, 3 H), 2.71–2.84 (m, 2 H), 3.03 (t, J = 6.4 Hz, 2 H), 3.40–3.70 (m, 1 H), 4.92 (t, J = 6.4 Hz, 2 H), 7.00–7.07 (m, 2 H), 7.90 (d, J = 7.9 Hz, 1 H), 8.28 (d, J = 4.7 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.3, 26.8, 30.2, 30.6, 39.2, 43.6, 51.3, 115.1, 118.1, 120.8, 121.6, 124.8, 127.4, 142.6, 206.7, 208.1 ppm. MS (EI): m/z (%) = 273 (62) $[M + 1]^+$, 272 (16) $[M]^+$, 216 (100). $C_{16}H_{20}N_2O_2$ (272.34): calcd. C 70.56, H 7.40, N 10.29; found C 70.55, H 7.43, N 10.34.

4-[1-(3-Oxobutyl)-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl]octan-2-one (5d): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.195 g (73%). IR (neat): $\tilde{\nu}$ = 1720, 1710 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.1 Hz, 3 H), 1.15–1.35 (m, 4 H), 1.68–1.99 (m, 1 H), 2.03 (s, 3 H), 2.10 (s, 3 H), 2.18–2.26 (m, 1 H), 2.47–2.81 (m, 2 H), 3.02 (t, J = 6.4 Hz, 2 H), 3.30–3.50 (m, 1 H), 4.49 (t, J = 6.4 Hz, 2 H), 6.99–7.06 (m, 2 H), 7.90 (d, J = 7.8 Hz, 1 H), 8.27 (d, J = 4.5 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.9, 22.6, 29.7, 30.3, 30.5, 32.6, 35.6, 39.2, 43.5, 50.2, 115.1, 116.3, 119.7, 125.7, 127.6, 142.6, 147.4, 206.7, 208.2 ppm. MS (EI): m/z (%) = 316 (100) $[M + 2]^+$, 315 (16) $[M + 1]^+$, 258 (25). $C_{19}H_{26}N_2O_2$ (314.42): calcd. C 72.58, H 8.33, N 8.91; found C 72.59, H 8.37, N 8.82.

4-[3-[3-Oxo-1-thiophen-2-yl-3-(*p*-tolyl)propyl]-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl]butan-2-one-5e: Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.141 g (40%). IR (neat): $\tilde{\nu}$ = 1720 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 2.39 (s, 3 H), 2.98–3.09 (m, 2 H), 3.75 (d, J = 7.0 Hz, 2 H), 4.46–4.58 (m, 3 H), 6.88 (s, 1 H), 6.99–7.29 (m, 6 H), 7.81–7.91 (m, 3 H), 8.25–8.31 (m, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 30.2, 33.4, 39.3, 43.5, 45.7, 99.3, 115.4, 115.7, 123.6, 124.2, 125.9, 126.6, 127.8, 128.2, 128.8, 129.1, 129.3, 142.6, 142.8, 144.0, 197.3, 206.6 ppm. MS (EI): m/z (%) = 416 (39) $[M]^+$, 298 (67), 284 (100). $C_{25}H_{24}N_2O_2S$ (416.54): calcd. C 72.09, H 5.81, N 6.73; found C 72.05, H 5.69, N 6.66.

4-[1-(3-Oxobutyl)-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl]-4-phenylbutan-2-one (5f): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.128 g (45%). IR (neat): $\tilde{\nu}$ = 1720 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 2.08 (s, 6 H), 3.01 (t, J = 6.4 Hz, 2 H), 3.14–3.22 (m, 2 H), 4.49 (t, J = 6.4 Hz, 2 H), 4.65–4.85 (m, 1 H), 6.90 (dd, J = 7.8 and 4.7 Hz, 1 H), 7.11–7.26 (m, 6 H), 7.61 (d, J = 7.8 Hz, 1 H), 8.23 (d, J = 4.7 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.2, 30.6, 38.1, 39.3, 43.5, 49.8, 115.3, 115.9, 125.6, 126.5, 127.6, 127.7, 127.9, 128.5, 142.8, 143.7, 206.7, 206.9 ppm. MS (EI): m/z (%) = 336 (100) $[M + 2]^+$, 278 (18). $C_{21}H_{22}N_2O_2$ (334.41): calcd. C 75.42, H 6.63, N 8.38; found C 75.48, H 6.41, N 8.33.

4-(1-Benzyl-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)octan-2-one (5g): Eluent for chromatography: *n*-hexane/ethyl acetate, 50:50 v/v. Yield: 0.145 g (51%). IR (neat): $\tilde{\nu}$ = 1720 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ = 0.80 (t, J = 6.9 Hz, 3 H), 1.14–1.29 (m, 4 H), 1.62–1.73 (m, 2 H), 1.97 (s, 3 H), 2.75–2.80 (m, 2 H), 3.37–3.43 (m, 1 H), 5.45 (s, 2 H), 6.95 (s, 1 H), 7.04 (dd, J = 7.8 and 4.7 Hz, 1 H),

7.11–7.29 (m, 5 H), 7.94 (d, $J = 7.8$ Hz, 1 H), 8.31 (d, $J = 4.7$ Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 13.9, 22.5, 29.7, 30.1, 32.7, 35.4, 47.4, 50.1, 115.3, 116.9, 119.2, 122.9, 124.6, 124.8, 127.4, 128.5, 137.9, 142.9, 147.9, 208.1$ ppm. MS (EI): m/z (%) = 335 (43) $[\text{M} + 1]^+$, 278 (100), 236 (27), 91 (47). $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}$ (334.45): calcd. C 79.07, H 7.84, N 8.38; found C 79.02, H 7.80, N 8.39.

4-(1-Benzyl-1H-pyrrolo[2,3-b]pyridin-3-yl)pentan-2-one (5h): Eluent for chromatography: *n*-hexane/ethyl acetate, 60:40 v/v. Yield: 0.154 g (62%). IR (neat): $\tilde{\nu} = 1710\text{ cm}^{-1}$. ^1H NMR (200 MHz, CDCl_3): $\delta = 1.32$ (d, $J = 6.9$ Hz, 3 H), 2.04 (s, 3 H), 2.67–2.82 (m, 2 H), 3.40–3.65 (m, 1 H), 5.43 (s, 2 H), 6.94 (s, 1 H), 7.03 (dd, $J = 7.8$ and 4.7 Hz, 1 H), 7.15–7.28 (m, 5 H), 7.93 (dd, $J = 7.8$ and 1.2 Hz, 1 H), 8.31 (dd, $J = 4.7$ and 1.2 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 21.3, 26.9, 30.5, 47.6, 51.3, 115.3, 118.8, 118.9, 123.6, 127.4, 128.6, 137.9, 143.1, 148.0, 208.0$ ppm. MS (EI): m/z (%) = 293 (43) $[\text{M} + 1]^+$, 236 (100), 91 (57). $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ (292.37): calcd. C 78.05, H 6.89, N 9.58; found C 78.07, H 6.90, N 9.56.

1-(1-Benzyl-1H-pyrrolo[2,3-b]pyridin-3-yl)nonan-3-one (5i): Eluent for chromatography: *n*-hexane/ethyl acetate, 60:40 v/v. Yield: 0.119 g (42%). IR (neat): $\tilde{\nu} = 1720\text{ cm}^{-1}$. ^1H NMR (200 MHz, CDCl_3): $\delta = 0.85$ (t, $J = 6.5$ Hz, 3 H), 1.16–1.28 (m, 4 H), 1.48–1.59 (m, 2 H), 2.34 (t, $J = 7.4$ Hz, 2 H), 2.75 (t, $J = 7.4$ Hz, 2 H), 2.99 (t, $J = 7.6$ Hz, 2 H), 5.43 (s, 2 H), 6.95 (s, 1 H), 7.05 (dd, $J = 7.8$ and 4.7 Hz, 1 H), 7.16–7.29 (m, 5 H), 7.88 (dd, $J = 7.8$ and 1.5 Hz, 1 H), 8.3 (dd, $J = 4.7$ and 1.5 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 13.9, 19.4, 22.4, 23.5, 29.7, 31.4, 43.1, 47.6, 113.2, 115.2, 119.9, 125.1, 127.0, 127.1, 127.5, 128.7, 137.9, 143.1, 147.9, 210.7$ ppm. MS (EI): m/z (%) = 334 (65) $[\text{M}]^+$, 281 (19), 221 (100), 91 (74). $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}$ (334.45): calcd. C 79.00, H 7.84, N 8.38; found C 78.98, H 8.35, N 8.43.

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