A facile synthesis of pyrrolo[2,3-*b*]quinolines *via* a Rh(I)-catalyzed carbodiimide-Pauson–Khand-type reaction†

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A new straightforward synthetic method for 2,3-dihydro-1*H*-pyrrolo[2,3-*b*]quinolin-2-ones *via* a $[RhCl(CO)_2]_2$–dppp catalyzed Pauson–Khand-type reaction of *N*-[2-(2-alkyn-1-yl)phenyl]carbodiimides is reported.

Introduction

The formal [2 + 2 + 1] cocyclization of an alkyne, an alkene and carbon monoxide by a transition metal reagent (Pauson–Khand (PK)-type reaction) has been frequently used as a convergent and atom-economical approach for the synthesis of the cyclopentenone framework.[1,2] The hetero-PK-type reaction using a heteroalkene counterpart, such as an aldehyde, ketone or imine, leading to γ-butyrolactones or γ-lactams, has also been developed.[3]

We have been focusing on functionalized heterocumulenes as substrates in various ring-forming reactions[4–7] and succeeded for the first time in the stoichiometric ($Mo(CO)_6$–DMSO)[5] and catalytic (Rh(I))[6] carbodiimide-Pauson–Khand (PK)-type reaction using **1** and **2** (Fig. 1), which allowed their facile transformation into pharmaceutically important 1*H*-pyrrolo[2,3-*b*]indol-2-ones and pyrrolo[2,3-*b*]pyrrolinones. Indeed, Mukai *et al.* reported the synthesis of (±)-physostigmine, (±)-flustramide B, and (±)-flustramines B and E by the $Co_2(CO)_8$-catalyzed PK reaction of *o*-alkynylphenylcarbodiimides **1**.[8] We further demonstrated the first C=S bond-involved PK cyclocarbonylation of *o*-alkynylphenyl isothiocyanates **3** as substrates to give thieno[2,3-*b*]indol-2-ones.[7]

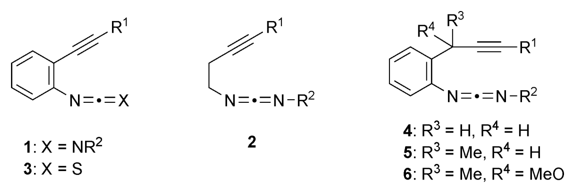
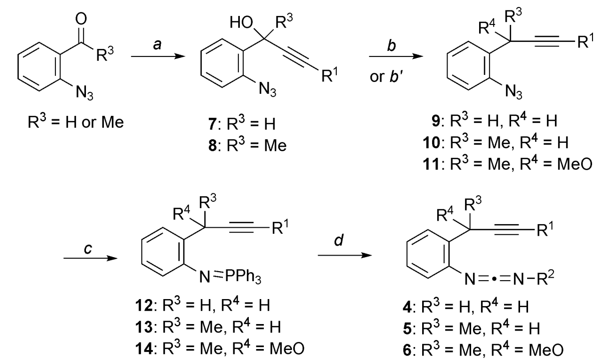


Fig. 1

The pyrrolo[2,3-*b*]quinoline core is often found in biologically active compounds such as blebbistatin (myosin II inhibitor)[9] and PGP-4008 (P-gp-specific MDR modulator).[10] Straightforward and efficient synthetic methods for such an important heterocyclic system are always desired. Hitherto-reported synthetic methods for pyrrolo[2,3-*b*]quinolines involved stepwise annulation strategies, *e.g.*, cyclization of preformed substituted aminoquinolines or 3-alkylidene-2-(phenylimino)-pyrrolidines.[11] In this context, we envisioned that the intramolecular PK-reaction of *N*-[2-(2-alkyn-1-yl)phenyl]carbodiimides **4–6** (Fig. 1) would enable a facile approach to the pyrrolo[2,3-*b*]quinoline framework. Herein, we wish to report the results.

Results and discussion

Carbodiimides **4–6** were prepared as outlined in Scheme 1: (a) addition of lithium acetylide to 2-azidobenzaldehyde or 1-(2-azidophenyl)ethanone, (b) hydrogenolysis with triethylsilane and trifluoroacetic acid, or (b′) *O*-methylation, (c) conversion to iminophosphorane (Staudinger reaction), and (d) aza-Wittig reaction with isocyanates.



Scheme 1 *Reagents and conditions*: (a) $R^1C{\equiv}CLi$, −78–0 °C, THF; (b) Et_3SiH, CF_3CO_2H, CH_2Cl_2, 0 °C; (b′) MeI, NaH; (c) PPh_3, CH_2Cl_2; (d) R^2NCO.

Initially, a brief screening of rhodium catalysts for the catalytic PK reaction was carried out using **4a** (Table 1).[12] The reaction in the presence of $[RhCl(CO)dppp]_2$,[13] prepared *in situ* from $[RhCl(CO)_2]_2$ (5 mol%) and 1,3-bis(diphenylphosphino)propane (dppp, 11 mol%) under an atmospheric pressure of carbon monoxide[13] in a gently refluxing toluene solution, provided pyrrolo[2,3-*b*]quinoline **15a**, a formal [1,3]-H migrated product of the PK product **16a**, in 26% yield along with unreacted **4a** (65%) (entry 1). When the reaction was carried out in refluxing xylene, **15a** was obtained in 41% yield along with recovered **4a** (47%) (entry 2). Increasing the amount of catalyst to 7 mol%

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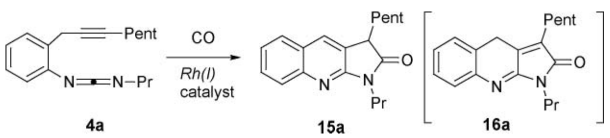
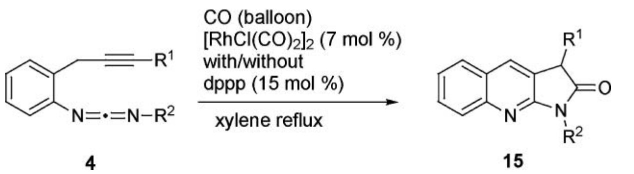
Table 1 Optimization of the Rh(I)-catalyzed Pauson–Khand reaction of alkynyl carbodiimide **4a**



Entry	Rh(I)-catalyst (mol%)	Solvent	Time/h	Yield (%) 15a	Yield (%) 4a (s.m.)
1	$[RhCl(CO)(dppp)]_2$ (5)	Toluene	4.0	26	65
2	$[RhCl(CO)(dppp)]_2$ (5)	Xylene	3.0	41	47
3	$[RhCl(CO)(dppp)]_2$ (7)	Xylene	2.5	80	—
4	$[RhCl(CO)_2]_2$ (5)	Xylene	2.5	66	—
5	$[RhCl(CO)_2]_2$ (7)	Xylene	2.0	72	—

Table 2 Rh(I)-catalyzed Pauson–Khand reactions of **4**

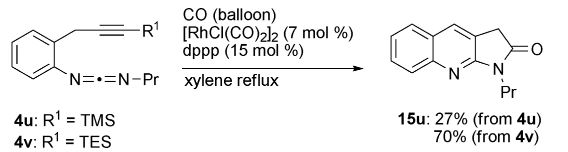


Entry	4	R[1]	R[2]	dppp	Time/h	15, Yield (%)[b]
1	**4a**	Pent	Pr	+[a]	2.5	**15a** (80)
2	**4b**	Pent	Bn	+[a]	1	**15b** (70)
3	**4c**	Pent	Cy	—	2	**15c** (75)
4	**4d**	Pent	Ph	+[a]	2	**15d** (33)
5	**4e**	Me	Pr	+[a]	7	**15e** (51)
6	**4f**	Me	Bn	—	2	**15f** (35)
7	**4g**	Me	Cy	—	6	**15g** (58)
8	**4h**	Me	Ph	+[a]	3	**15h** (41)
9	**4i**	*t*-Bu	Pr	—	0.5	**15i** (84)
10	**4j**	*t*-Bu	Bn	—	0.5	**15j** (85)
11	**4k**	*t*-Bu	Cy	—	0.5	**15k** (83)
12	**4l**	*t*-Bu	Ph	—	0.5	**15l** (84)
13	**4m**	Ph	Pr	+[a]	4	**15m** (63)
14	**4n**	Ph	Bn	+[a]	2	**15n** (71)
15	**4o**	Ph	Cy	+[a]	0.5	**15o** (66)
16	**4p**	Ph	Ph	+[a]	1.5	**15p** (70)
17	**4q**	TBS	Pr	—	1.5	**15q** (75)
18	**4r**	TBS	Bn	—	1	**15r** (58)
19	**4s**	TBS	Cy	—	3	**15s** (33)
20	**4t**	TBS	Ph	—	3	**15t** (52)

[a] dppp (15 mol%) was added. [b] Isolated yield.

substantially improved the yield of **15a** (80%), with substrate **4a** totally consumed (entry 3). The catalyst $[RhCl(CO)_2]_2$[14] was also found to be effective for the present reaction under these optimized reaction conditions (entry 5). The catalytic systems $[RhCl(CO)_2]_2$ (5 mol%) + Ph_3P (11 mol%) + $AgBF_4$ (11 mol%)[15] and $Ru_3(CO)_{12}$ (5 mol%)[16] turned out to be ineffective in this PK reaction of **4a**.

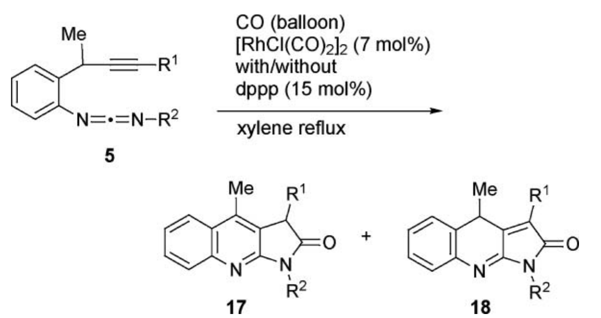
Under the optimized conditions (Table 1, entries 3 and 5), the catalytic PK reaction for a variety of alkynyl carbodiimides **4** was examined (Table 2). The reaction of alkyl alkynes **4a–l** (entries 1–12) proceeded smoothly and gave the corresponding products **15a–l** in moderate to high yields. The reaction rates and the yields of cycloadducts **15a–l** tend to increase with an increase in the steric bulk at the alkyne terminus: *t*-Bu (entries 9–12) > *n*-Pent (entries 1–4) > Me (entries 5–8). Phenylalkynyl carbodiimides **4m–p** (R^1 = Ph) are also good substrates for the Rh(I)-catalyzed PK reactions (entries 13–16). *t*-Butyldimethylsilylalkynyl carbodiimides **4q–t** (R^1 = TBS) were transformed to the corresponding pyrroloquinolines **15q–t** without elimination of the TBS group in moderate to good yields (entries 17–20), while both trimethylsilylalkyne carbodiimide **4u** (R^1 = TMS) and triethylsilylalkyne carbodiimide **4v** (R^1 = TES) were converted to the 3-unsubstituted pyrrolo[2,3-*b*]quinolin-2-one **15u** (27% and 70% yield, respectively) *via* elimination of the TMS or TES group under these conditions (Scheme 2).



Scheme 2 Synthesis of 3-unsubstituted-1*H*-pyrrolo[2,3-*b*]quinolin-2-(3*H*)-one.

Next, we examined the catalytic PK reactions of alkynyl carbodiimides **5a–h** bearing a methyl group on the benzylic position (Table 3). Carbodiimides **5a** and **5b** reacted more smoothly than the corresponding methylene-linked compounds **4e** and **4h** (Table 3, entries 1 and 2 *vs.* Table 2, entries 5 and 8), and the expected 4-methyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-ones **17a** and **17b** were obtained in 52 and 61% yields, respectively. Interestingly, when *t*-butyl alkynyl carbodiimides **5c** and **5d** were subjected to the reaction in the absence of dppp, dihydroquinolines **18a** (58%) and **18b** (75%) were obtained as major products along with a small amount of quinolines **17c** (8%) and **17d** (9%), respectively (entries 3 and 4). The reactions of phenylalkynyl carbodiimides **5e** and **5f** (R^1 = Ph) proceeded sluggishly to afford **17e** and **17f**, respectively, in 38% yields (entries 5 and 6). Meanwhile, TBS-alkynyl carbodiimides **5g** and **5h** were good substrates for the

Table 3 Rh(I)-catalyzed Pauson–Khand reactions of **5**

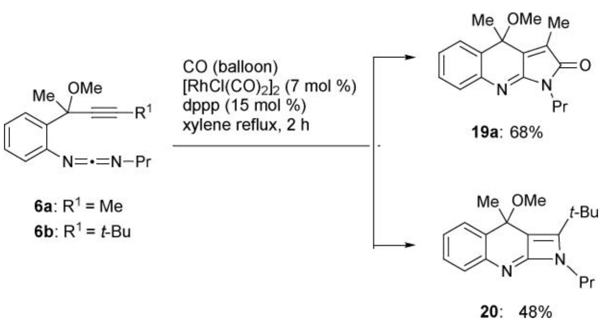


Entry	5	R[1]	R[2]	dppp	Time/h	Yield (%)[b] 17	Yield (%)[b] 18
1	**5a**	Me	Pr	+[a]	2	**17a** (52)	—
2	**5b**	Me	Ph	+[a]	1	**17b** (61)	—
3	**5c**	*t*-Bu	Pr	—	0.5	**17c** (8)	**18a** (58)
4	**5d**	*t*-Bu	Ph	—	1.5	**17d** (9)	**18b** (75)
5	**5e**	Ph	Pr	+[a]	4	**17e** (38)	—
6	**5f**	Ph	Ph	+[a]	2	**17f** (38)	—
7	**5g**	TBS	Pr	—	1	**17g** (75)	—
8	**5h**	TBS	Ph	—	1.5	**17h** (72)	—

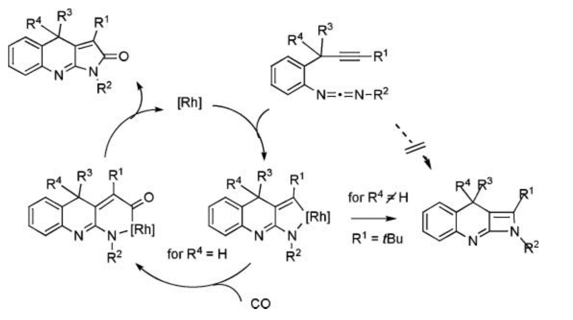
[a] dppp (15 mol%) was added. [b] Isolated yield.

PK reaction, and gave quinolines **17g** and **17h** in high yields, respectively (entries 7 and 8). Although **5g** and **5h** also contain a bulky TBS group on the alkyne terminus just like *t*-butylalkynyl carbodiimides **5c** and **5d**, dihydroquinolines **18** were not obtained, nor detected even at earlier stage of the reaction, in contrast to the reactions of **5c** and **5d** (entries 3 and 4).

Finally, alkynyl carbodiimides **6a,b**, which contain a benzylic quaternary carbon center (Scheme 3), were subjected to the catalytic PK reaction. The reaction of methylalkynyl carbodiimide **6a** was completed within 2 h to afford expected pyrroloquinoline **19a** in 68% yield. Meanwhile, the reaction of *t*-butylalkynyl carbodiimide **6b** yielded a cycloisomerized product, 2-*t*-butyl-3-methoxy-3-methyl-1-propyl-1,3-dihydro-azeto[2,3-*b*]quinoline (**20**) in 48% yield. No formation of **20** was observed in the absence of the Rh-catalyst in refluxing xylene. The formation of **20** instead of **19b** can be attributed to the difficulty of the CO-inserted metallacycle formation, due to steric reasons between the *t*-butyl group and the substituents (Me, MeO, Ar) on the quaternary carbon (Scheme 4).



Scheme 3 Rh(I)-catalyzed Pauson–Khand reactions of **6**.



Scheme 4 A plausible reaction pathway.

Conclusions

In summary, we have demonstrated for the first time $[RhCl(CO)_2]_2$ (7 mol%) + dppp (15 mol%)-catalyzed PK reactions of *N*-[2-(2-alkyn-1-yl)phenyl]carbodiimides for a new entry to synthetic methods of pyrrolo[2,3-*b*]quinolines.

Experimental

General information

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were recorded on a Horiba FT-710 model spectrophotometer. ^{1}H and ^{13}C NMR spectral data were obtained with a Bruker Avance-600, a JEOL JNM-EX 500, or a JEOL JNM-EX 300 instrument and chemical shifts are reported in ppm down field from tetramethylsilane (TMS) using an internal standard of TMS or $CDCl_3$. HRMS analysis were performed on a Bruker Daltonics microTOF. 2-Azidobenzaldehyde[17] and 1-(2-azidophenyl)-ethanone[18] were prepared according to the reported method.

Typical procedure for preparation of alcohols 7 and 8

1-(2-Azidophenyl)but-2-yn-1-ol (7b). *n*-Butyllithium/*n*-hexane solution (1.5 M, 27.8 mL, 44.0 mmol) was added to a solution of 1-bromo-1-propene (2.60 mL, 30.4 mmol) in THF (20 mL) at −78 °C. After stirring for 2 h, a solution of 2-azidobenzaldehyde (2.94 g, 20.0 mmol) in THF (10 mL) was added, and the mixture was stirred for a further 1 h. The mixture was quenched with saturated aqueous ammonium chloride and extracted with dichloromethane. The organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane = 1 : 4) to give the alcohol **7b** (3.72 g, 19.9 mmol, 99%) as a yellow solid. mp 50.0–51.5 °C. IR (KBr/cm^{-1}): 3301, 2291, 2129, 1581, 1303, 748. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.65 (dd, J = 1.7, 8.0 Hz, 1H), 7.36 (ddd, J = 1.5, 7.2, 7.8 Hz, 1H), 7.20–7.12 (m, 2H), 5.64–5.56 (m, 1H), 2.80–2.68 (br, 1H), 1.90 (d, J = 2.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 137.15 (C), 132.05 (C), 129.50 (CH), 128.22 (CH), 124.99 (CH), 118.16 (CH), 83.03 (C), 78.17 (C), 60.60 (CH), 3.70 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{10}H_9N_3NaO$, 210.0638; found, 210.0633. Anal calcd for $C_{10}H_9N_3O$: C 64.16, H 4.85, N 22.45, found: C 64.20, H 5.23, N 22.06.

2-(2-Azidophenyl)pent-3-yn-2-ol (8a). Yellow oil. IR (neat/cm^{-1}): 3055, 2129, 1473, 1265, 741. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.67(dd, J = 1.4, 7.8 Hz, 1H), 7.34 (ddd, J = 1.4, 7.7, 7.7 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.14 (ddd, J = 1.2, 7.6, 7.6 Hz, 1H), 3.82 (s, 1H), 1.90 (s, 3H), 1.86 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 136.58 (C), 135.67 (C), 128.96 (CH), 127.05 (CH), 124.91 (CH), 119.12 (CH), 82.21 (C), 80.83 (C), 69.14 (C), 30.44 (CH_3), 3.75 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{11}N_{11}N_3NaO$, 224.0794; found, 224.0789.

Typical procedure for preparation of 9 and 10

1-Azido-2-(but-2-ynyl)benzene (9b). Trifluoroacetic acid (0.22 mL, 3.0 mmol) was added to a mixture of alcohol **7b** (374 mg, 2.0 mmol) and triethylsilane (0.48 mL, 3.00 mmol) in dichloromethane (7 mL) at 0 °C. After stirring for 10 h at 0 °C, the mixture was quenched by addition of saturated aqueous sodium hydrogen carbonate. The mixture was extracted with dichloromethane, washed with brine, dried over anhydrous magnesium sulfate and evaporated. The residue was purified by silica gel column chromatography (hexane) to give alkynyl azide **9b** (142 mg, 0.83 mmol, 41%) as a yellow solid. mp 49.5–50.5 °C. IR (KBr/cm^{-1}): 2916, 2283, 2121, 1581, 1288, 748. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.51 (d, J = 7.3 Hz, 1H), 7.26 (dd, J = 7.3, 7.5 Hz, 1H), 7.20–7.04 (m, 2H), 3.44 (s, 2H), 1.84 (d, J = 1.5 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 137.45 (C), 129.57 (CH), 128.75 (C), 127.81 (CH), 124.75 (CH), 117.69 (CH), 78.14 (C), 75.79 (C), 20.49 (CH_2), 3.52 (CH_3). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_9N_3Na$, 194.0689; found, 194.0691.

1-Azido-2-(pent-3-yn-2-yl)benzene (10a). Yellow oil. IR (neat/cm^{-1}): 3054, 2121, 1265, 741. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.59 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.27 (ddd, *J* = 1.5, 7.7, 7.7 Hz, 1H), 7.14 (ddd, *J* = 1.2, 7.7, 7.7 Hz, 1H), 7.11 (dd, *J* = 1.2, 7.7 Hz, 1H), 3.99 (dq, *J* = 2.3, 2.4 Hz, 1H), 1.85 (d, *J* = 2.4 Hz, 3H), 1.37 (d, *J* = 7.1 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 136.57 (C), 135.23 (C), 128.40 (CH), 127.83 (CH), 125.02 (CH), 117.95 (CH), 81.58 (C), 77.25 (C), 26.62 (CH_3), 23.36 (CH), 3.60 (CH_3). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}N_3Na$, 208.0845; found, 208.0841.

Typical procedure for preparation of 11

1-Azido-2-(2-methoxypent-3-yn-2-yl)benzene (11a). A solution of azide alcohol **8a** (2.44 g, 12.1 mmol) in THF (5 mL) was added to a cold (–50 °C) stirred suspension of 60% NaH (726 mg, 18.1 mmol) in THF (15 mL). After stirring for 10 min, methyl iodide (1.1 mL, 18.1 mmol) was added. The mixture was allowed to warm to room temperature, stirred for a further 3 h then quenched with water. The resulting mixture was extracted with dichloromethane, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane = 1 : 4) to provide methyl ether **11a** as a yellow oil (2.30 g, 88%). IR (neat/cm^{-1}): 2931, 2121, 1481, 1296, 756. ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*): 7.80(dd, *J* = 1.5, 7.8 Hz, 1H), 7.34 (ddd, *J* = 1.6, 7.8, 7.8 Hz, 1H), 7.20 (dd, *J* = 1.1, 7.9 Hz, 1H), 7.13 (ddd, *J* = 1.0, 7.6, 7.6 Hz, 1H), 3.22 (s, 3H), 1.98 (s, 3H), 1.83 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, *δ*): 137.18 (C), 132.55 (C), 129.64 (CH), 129.13 (CH), 124.39 (CH), 119.58 (CH), 83.39 (C), 79.30 (C), 76.26 (C), 52.18 (CH_3), 29.11 (CH_3), 3.63 (CH_3). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}N_{13}N_3NaO$, 238.0951; found, 238.0949.

Typical procedure for preparation of iminophosphoranes 12–14

2-(But-2-ynyl)-*N*-(triphenylphosphonylidene)benzenamine (12b). Triphenylphosphine (228.7 mg, 0.82 mmol) was added to a solution of alkynyl azide **9b** (135.7 mg, 0.79 mmol) in dichloromethane (5 mL) at room temperature. After stirring for 10 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate–hexane = 1 : 4) to give iminophosphorane **12b** (318.8 mg, 0.78 mmol, 99%) as a yellow solid. mp 139.6–141.0 °C. IR (KBr/cm^{-1}): 3047, 1589, 1481, 1442, 1342, 1103, 748. ^{1}H-NMR (300 MHz, $CDCl_3$, *δ*): 7.84–7.68 (m, 6H), 7.55–7.35 (m, 10H), 6.78 (dd, *J* = 7.1, 7.1 Hz, 1H), 6.67 (dd, *J* = 7.1, 7.1 Hz, 1H), 6.49–6.38 (m, 1H), 3.85 (s, 2H), 1.83 (dd, *J* = 2.1, 2.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, *δ*): 148.54 (C), 132.49 (CH×6, d, *J* = 9.7 Hz), 131.63 (C×3, d, *J* = 100.0 Hz), 131.59 (C, d, *J* = 21.7 Hz), 131.50 (CH×3, d, *J* = 2.6 Hz), 128.49 (CH×6, d, *J* = 11.9 Hz), 127.92 (CH), 126.39 (CH), 120.36 (CH, d, *J* = 9.5 Hz), 117.23 (CH), 78.61 (C), 77.00 (C), 22.24 (CH_2), 3.67 (CH_3). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{25}NP$, 406.1719; found, 406.1718. Anal calcd for $C_{28}H_{24}NP$: C 82.94, H 5.97, N 3.45, found: C 82.56, H 6.05, N 3.43.

2-(Pent-3-yn-2-yl)-*N*-(triphenylphosphonylidene)benzenamine (13a). Yellow solid; mp 144.0–144.3 °C. IR (KBr/cm^{-1}): 3062, 2916, 1589, 1481, 1350, 1103, 694. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.80–7.67 (m, 6H), 7.55–7.47 (m, 4H), 7.45–7.35 (m, 6H), 6.79–6.72 (m, 1H), 6.70–6.64 (m, 1H), 6.45–6.37 (m, 1H), 4.81–4.69 (m, 1H), 1.85 (dd, *J* = 2.4, 2.4 Hz, 3H), 1.49 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 147.61 (C), 137.78 (C, d, *J* = 22.0 Hz), 132.48 (CH×6, d, *J* = 9.31 Hz), 131.63 (C×3, d, *J* = 99.3 Hz), 131.47 (CH×3, d, *J* = 2.6 Hz), 128.50 (CH×6, d, *J* = 12.2 Hz), 126.84 (CH), 126.36 (CH), 120.73 (CH, d, *J* = 10.1 Hz), 117.32 (CH), 84.26 (C), 75.87 (C), 27.42 (CH_3), 22.89 (CH), 3.70 (CH_3). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{29}H_{27}NP$, 420.1876; found, 420.1867.

2-(2-Methoxypent-3-yn-2-yl)-*N*-(triphenylphosphonylidene)-benzenamine (14a). Yellow solid; mp 140.9–141.3 °C. IR (KBr/cm^{-1}): 3055, 2977, 2931, 2245, 1913, 1581, 1473, 1342, 1111, 741. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.91–7.80 (m, 6H), 7.65–7.59 (m, 1H), 7.50–7.36 (m, 9H), 6.84–6.77 (m, 1H), 6.67–6.60 (m, 1H), 6.46–6.40 (m, 1H), 3.37 (s, 3H), 2.09 (s, 3H), 1.70 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 134.11 (C, d, J = 22.2), 132.57 (CH×6, d, *J* = 9.8 Hz), 132.00 (C, d, *J* = 9.8 Hz), 131.80 (C×3, d, *J* = 99.8 Hz), 131.28 (CH×3), 128.39 (CH×6, d, *J* = 11.9 Hz), 127.49 (CH), 127.47 (CH), 122.29 (CH, d, *J* = 11.6 Hz), 116.29 (CH), 81.72 (C), 80.46 (C), 77.07 (C), 51.80 (CH3), 27.56 (CH_3), 3.55 (CH_3). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{29}NOP$, 450.1981; found, 450.1986.

Typical procedure for preparation of carbodiimides 4–6

(2-But-2-ynyl)propylcarbodiimide (4e). Propyl isocyanate (0.16 mL, 1.66 mmol) was added to a solution of iminophosphorane **12b** (446.0 mg, 1.10 mmol) in dichloromethane (5 mL) at room temperature. After stirring for 10 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate–hexane = 1 : 4) to give carbodiimide **4e** (220.3 mg, 1.03 mmol, 94%) as a colorless oil. IR (neat/cm^{-1}): 2970, 2877, 2144, 1496, 1265, 1088, 740. ^{1}H-NMR (300 MHz, $CDCl_3$, *δ*): 7.49 (d, *J* = 7.4 Hz, 1H), 7.25–7.04 (m, 3H), 3.61–3.54 (m, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 1.84 (dd, *J* = 2.6, 2.6 Hz, 3H), 1.69 (tq, *J* = 7.1, 7.1 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, *δ*): 138.33 (C), 135.20 (C), 131.11 (C), 129.02 (CH), 127.38 (CH), 124.52 (CH), 123.54 (CH), 77.75 (C), 76.38 (C), 48.48 (CH_2), 24.65 (CH_2), 21.17 (CH_2), 11.37 (CH_3), 3.56 (CH_3). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{17}N_2$, 213.1386; found, 213.1385.

(2-(1-Methylbut-2-ynyl)phenyl)propylcarbodiimide (5a). Colorless oil. IR (neat/cm^{-1}): 2970, 2137, 1589, 1496, 1265, 741. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.56 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.20–7.08 (m, 3H), 4.20–4.14 (m, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 1.85 (d, *J* = 2.4 Hz, 3H), 1.71 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.39 (d, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (150 MHz, CDCl3, δ): 137.50 (C), 137.46 (C), 135.62 (C), 127.82 (CH), 127.36 (CH), 124.82 (CH), 123.84 (CH), 82.18 (C), 76.88 (C), 48.61 (CH_2), 27.09 (CH_3), 24.76 (CH_2), 23.50 (CH), 11.45 (CH_3), 3.64 (CH_3). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{18}N_2Na$, 249.1362; found, 249.1361.

Propyl-(2-(2-methoxypent-3-yn-2-yl))carbodiimide (6a). Colorless oil. IR (neat/cm^{-1}): 2970, 2939, 2144, 1496, 1095, 756. ^{1}H-NMR (600 MHz, $CDCl_3$, δ): 7.74 (d, *J* = 7.4 Hz, 1H), 7.24 (ddd, *J* = 1.5, 7.7, 7.7 Hz, 1H), 7.15 (dd, J = 1.3 7.8 Hz, 1H), 7.09 (ddd, *J* = 1.3, 7.4, 7.7 Hz, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 3.23 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.70 (tq, $J = 7.1, 7.3$ Hz, 2H), 1.01 (t, $J = 7.4$ Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$, δ): 138.07 (C), 134.33 (C), 134.30 (C), 128.97 (CH), 128.69 (CH), 125.61 (CH), 124.02 (CH), 82.93 (C), 79.77 (C), 76.61 (C), 52.13 (CH3), 48.50 (CH_2), 29.00 (CH_3), 24.74 (CH_2), 11.47 (CH_3), 3.72 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{16}H_{20}N_2NaO$, 279.1468; found, 279.1462.

Typical procedure for the catalytic Pauson–Khand reaction using $[Rh(CO)_2Cl]_2$-dppp to produce 15

3-Pentyl-1-propyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (15a) (Table 2, entry 1). 1,2-Bis(diphenylphosphino)propane (dppp) (28.4 mg, 0.069 mmol) was added to a stirred solution of $[Rh(CO)_2Cl]_2$ (12.5 mg, 0.032 mmol) in *p*-xylene (5 mL), and the mixture was degassed and charged with carbon monoxide. The resulting pale yellow suspension was heated at 130 °C, and a solution of carbodiimide **4a** (123.7 mg, 0.462 mmol) in *p*-xylene (1 mL) was added slowly. After heating at the same temperature for 2.5 h, the mixture was evaporated. The residue was purified by silica gel column chromatography (ethyl acetate–hexane = 1 : 10) to provide pyrroloquinoline **15a** (109.6 mg, 0.370 mmol, 80%) as a yellow oil. IR (neat/cm^{-1}): 2931, 2862, 1728, 1643, 1581, 1450, 1219, 1088, 756. ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*): 7.92 (d, $J = 8.3$ Hz, 1H), 7.81 (s, 1H), 7.73 (dd, $J = 0.9, 8.0$ Hz, 1H), 7.62 (ddd, $J = 1.4, 7.2, 8.4$ Hz, 1H), 7.40 (ddd, $J = 0.9, 7.4, 8.0$ Hz, 1H), 3.95–3.85 (m, 2H), 3.55 (ddd, $J = 1.1, 5.5, 6.7$ Hz, 1H), 2.09–2.01 (m, 1H), 1.99–1.91 (m, 1H), 1.84 (tq, $J = 7.4, 7.4$ Hz, 2H), 1.48–1.24 (m, 6H), 0.99 (t, $J = 7.5$ Hz, 3H), 0.86 (t, $J = 7.1$ Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, *δ*): 177.48 (C), 156.94 (C), 146.91 (C), 130.23 (CH), 129.19 (CH), 127.75 (CH×2), 125.95 (C), 124.63 (C), 124.34 (CH), 44.15 (CH), 40.88 (CH_2), 31.66 (CH_2), 30.58 (CH_2), 25.44 (CH_2), 22.35 (CH_2), 20.85 (CH_2), 13.93 (CH_3), 11.35 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{19}H_{24}N_2NaO$, 319.1781; found, 319.1775.

1-Benzyl-3-pentyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (15b). Yellow oil. IR (neat/cm^{-1}): 2931, 1720, 1643, 1442, 1219, 756. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.94 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.71 (dd, $J = 1.2, 7.9$ Hz, 1H), 7.62 (ddd, $J = 1.5, 7.0, 8.3$ Hz, 1H), 7.54 (d, $J = 7.3$ Hz, 2H), 7.39 (ddd, $J = 1.2, 7.0, 7.9$ Hz, 2H), 7.28 (dd, $J = 7.3, 7.3$ Hz, 1H), 7.22 (dd, $J = 7.3, 7.3$ Hz, 1H), 5.15–5.07 (m, 2H), 3.56 (t, $J = 6.0$ Hz, 1H), 2.10–1.90 (m, 2H), 1.42–1.21 (m, 6H), 0.82 (t, $J = 7.1$ Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 177.25 (C), 156.44 (C), 146.83 (C), 136.75 (C), 130.45 (CH), 129.23 (CH), 128.71 (CH×2), 128.41 (CH×2), 127.91 (CH), 127.74 (CH), 127.50 (CH), 126.12 (C), 124.52 (C), 124.44 (CH), 44.22 (CH), 42.73 (CH_2), 31.62 (CH_2), 30.62 (CH_2), 25.43 (CH_2), 22.32 (CH_2), 13.91 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{23}H_{24}N_2NaO$, 364.1781; found, 367.1791.

1-Cyclohexyl-3-pentyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (15c). Brownish solid; mp 67.8–69.0 °C. IR (KBr/cm^{-1}): 2931, 1720, 1635, 1581, 1435, 1219, 895, 748. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.92 (d, $J = 8.3$ Hz, 1H), 7.78 (s, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.61 (ddd, $J = 1.3, 7.2, 8.3$ Hz, 1H), 7.38 (ddd, $J = 0.8, 7.4, 7.4$ Hz, 1H), 4.48 (tt, $J = 3.8, 12.2$ Hz, 1H), 3.48 (t, $J = 5.6$ Hz, 1H), 2.61–2.49 (m, 2H), 2.06–1.84 (m, 4H), 1.76–1.69 (m, 2H), 1.51–1.22 (m, 10H), 0.85 (t, $J = 6.6$ Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 177.35 (C), 157.04 (C), 146.69 (C), 129.99 (CH), 129.03 (CH), 127.85 (CH), 127.59 (CH), 125.57 (C), 124.59 (C), 124.25 (CH), 51.98 (CH), 44.00 (CH), 31.64 (CH2), 30.65 (CH2), 28.83 (CH_2), 28.71 (CH_2), 26.01 (CH_2), 25.99 (CH_2), 25.29 (CH_2), 25.14 (CH_2), 22.32 (CH_2), 13.91 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{22}H_{28}N_2NaO$, 359.2094; found, 359.2097.

3-Pentyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (15d). Yellow solid; mp 103.4–106.3 °C. IR (KBr/cm^{-1}): 2924, 1736, 1581, 1427, 1219, 910, 748. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.91 (s, 1H), 7.87 (d, $J = 8.5$ Hz, 1H), 7.75 (d, $J = 7.9$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.40 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.54 (dd, $J = 7.7, 7.7$ Hz, 2H), 7.41 (dd, $J = 7.5, 7.5$ Hz, 2H), 3.73 (t, $J = 6.1$ Hz, 1H), 2.18–2.03 (m, 2H), 1.57–1.37 (m, 2H), 1.37–1.27 (m, 4H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 176.69 (C), 156.56 (C), 146.59 (C), 133.33 (C), 130.89 (CH), 129.29 (CH), 128.96 (CH×2), 128.16 (CH), 127.91 (CH), 127.58 (CH), 126.70 (CH×2), 126.22 (C), 124.74 (CH), 124.15 (C), 44.21 (CH), 31.65 (CH_2), 30.94 (CH_2), 25.42 (CH_2), 22.35 (CH_2), 13.94 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{22}H_{22}N_2NaO$, 353.1624; found, 353.1621.

3-Methyl-1-propyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (15e). Yellow solid; mp 105.0–105.8 °C. IR (KBr/cm^{-1}): 2939, 2360, 1712, 1635, 1442, 1373, 1219, 957, 756. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.92 (d, $J = 8.3$ Hz, 1H), 7.77 (s, 1H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.61 (ddd, $J = 1.4, 7.0, 8.3$ Hz, 1H), 7.38 (ddd, $J = 1.0, 7.5, 7.5$ Hz, 1H), 3.89 (t, $J = 7.3$ Hz, 2H), 3.53 (q, $J = 7.2$ Hz, 1H), 1.84 (tq, $J = 7.4, 7.4$ Hz, 2H), 1.54 (d, $J = 7.5$ Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 177.97 (C), 156.44 (C), 146.84 (C), 129.88 (CH), 129.10 (CH), 127.67 (CH), 127.61 (CH), 125.92 (C), 125.74 (C), 124.26 (CH), 40.76 (CH_2), 38.97 (CH), 20.76 (CH_2), 15.33 (CH_3), 11.24 (CH_3). HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{15}H_{17}N_2O$, 241.1335; found, 241.1343.

Typical procedure for the catalytic Pauson–Khand reaction using $[Rh(CO)_2Cl]_2$ to produce 17 and 18 (Table 3, Entry 3), and 19a and 20

A solution of $[Rh(CO)_2Cl]_2$ (14.0 mg, 0.036 mmol) in *p*-xylene (5 mL) was degassed, charged with carbon monoxide, and was heated to 130 °C. A solution of carbodiimide **5c** (138.4 mg, 0.516 mmol) in *p*-xylene (1 mL) was added, and the mixture was heated at the same temperature for 2.0 h. The mixture was evaporated, and the residue was purified by silica gel column chromatography (ethyl acetate–hexane = 1 : 10) to give pyrroloquinoline **17c** (13.1 mg, 0.041 mmol, 8% as a yellow oil) and **18a** (94.9 mg, 0.299 mmol, 58%).

3,4-Dimethyl-1-propyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (17a). Brown solid; mp 185.2–186.7 °C. IR (KBr/cm^{-1}): 3062, 2969, 1720, 1635, 1589, 1435, 1227, 748. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.91 (d, $J = 8.3$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.59 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.53 (dd, $J = 7.7, 7.7$ Hz, 2H), 7.46–7.38 (m, 2H), 3.76 (dt, $J = 7.4, 7.4$ Hz, 1H), 2.66 (s, 3H), 1.68 (d, $J = 7.4$ Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$, δ): 177.40 (C), 155.77 (C), 146.36 (C), 139.42 (C), 133.30 (C), 129.03 (CH), 128.93 (CH×2), 128.71 (CH), 127.86 (CH), 126.76 (CH×2), 126.48 (C), 124.53 (CH), 123.29 (CH), 122.98 (C), 39.14 (CH), 16.11 (CH_3), 14.67 (CH_3). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{19}H_{16}N_2NaO$, 311.1155; found, 311.1145.

3,4-Dimethyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (17b). Brown solid; mp 185.2–186.7 °C. IR (KBr/cm^{-1}): 3062, 2969, 1720, 1635, 1589, 1435, 1227, 748. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.91 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.59 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.53 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.46–7.38 (m, 2H), 3.76 (dt, *J* = 7.4, 7.4 Hz, 1H), 2.66 (s, 3H), 1.68 (d, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 177.40 (C), 155.77 (C), 146.36 (C), 139.42 (C), 133.30 (C), 129.03 (CH), 128.93 (CH×2), 128.71 (CH), 127.86 (CH), 126.76 (CH×2), 126.48 (C), 124.53 (CH), 123.29 (CH), 122.98 (C), 39.14 (CH), 16.11 (CH_3), 14.67 (CH_3). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{19}H_{16}N_2NaO$, 311.1155; found, 311.1145.

3-*tert*-Butyl-4-methyl-1-propyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (17c). Yellow oil. IR (KBr/cm^{-1}): 3070, 2962, 1720, 1628, 1466, 1358, 1288, 1219, 1103, 756. ^{1}H-NMR (600 MHz, $CDCl_3$, δ): 7.89 (d, *J* = 8.8 Hz, 2H), 7.62 (ddd, *J* = 1.4, 7.0, 8.3 Hz, 1H), 7.42 (ddd, *J* = 1.2, 6.9, 8.3 Hz, 1H), 3.90–3.84 (m, 1H), 3.81–3.74 (m, 1H), 3.33 (s, 1H), 2.60 (s, 3H), 1.88–1.74 (m, 2H), 1.08 (s, 9H), 1.01 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$, δ): 177.04 (C), 157.19 (C), 146.39 (C), 139.58 (C), 128.98 (CH), 128.00 (CH), 126.29 (C), 124.03 (CH), 123.82 (CH), 122.10 (C), 53.87 (CH), 40.58 (CH_2), 37.84 (C), 28.07 (CH_3×3), 21.00 (CH_2), 17.91 (CH_3), 11.61 (CH_3). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{19}H_{24}N_2NaO$, 319.1781; found, 319.1775.

3-*tert*-Butyl-4-methyl-1-propyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(4*H*)-one (18a). Yellow oil. IR (neat/cm^{-1}): 3062, 2962, 1712, 1635, 1450, 1365, 1088, 941, 764. ^{1}H-NMR (600 MHz, $CDCl_3$, δ): 7.42 (dd, *J* = 1.1, 7.8 Hz, 1H), 7.26 (ddd, *J* = 1.6, 7.5, 7.6 Hz, 1H), 7.18 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.13 (ddd, 1.2, 7.4, 7.4 Hz, 1H), 4.31 (q, *J* = 7.3 Hz, 1H), 3.75–3.65 (m, 2H), 1.73 (dtq, *J* = 1.2, 7.4, 7.4 Hz, 2H), 1.45 (s, 9H), 1.39 (d, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$, δ): 170.32 (C), 155.57 (C), 141.87 (C), 141.64 (C), 134.08 (C), 132.00 (C), 128.16 (CH), 127.87 (CH), 127.62 (CH), 125.91 (CH), 40.10 (CH_2), 34.51 (C), 33.11 (CH), 29.27 (CH_3×3), 28.16 (CH_3), 21.91 (CH_2), 11.36 (CH_3). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{19}H_{24}N_2NaO$, 319.1781; found, 319.1782.

3-*tert*-Butyl-4-methyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(3*H*)-one (17d). Yellow solid; mp 157.8–158.8 °C. IR (KBr/cm^{-1}): 3054, 2954, 1727, 1427, 1288, 1227, 1173, 918, 764. ^{1}H-NMR (600 MHz, $CDCl_3$, δ): 7.91 (dd, *J* = 1.0, 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.61–7.56 (m, 3H), 7.55–7.51 (m, 2H), 7.45–7.39 (m, 2H), 3.52 (s, 1H), 2.66 (s, 3H), 1.16 (s, 9H). ^{13}C-NMR (150 MHz, $CDCl_3$, δ): 176.17 (C), 156.84 (C), 146.03 (C), 140.40 (C), 133.27 (C), 129.05 (CH), 128.98 (CH×2), 128.46 (CH), 127.88 (CH), 126.90 (CH×2), 126.47 (C), 124.42 (CH), 123.66 (CH), 121.47 (C), 53.02 (CH), 38.57 (C), 27.95 (CH_3×3), 17.96 (CH_3). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{22}H_{22}N_2NaO$, 353.1624; found, 353.1634.

3-*tert*-Butyl-4-methyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(4*H*)-one (18b). Yellow oil. IR (neat/cm^{-1}): 3062, 2954, 1720, 1627, 1589, 1496, 1427, 1227, 918, 764. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.54 (d, *J* = 8.0 Hz, 2H), 7.48 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.27–7.19 (m, 2H), 7.16 (dd, *J* = 7.4, 7.4 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 1H), 1.51 (s, 9H), 1.47 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 169.23 (C), 155.01 (C), 141.47 (C), 141.37 (C), 134.96 (C), 133.07 (C), 131.92 (C), 128.67 (CH), 128.67 (CH×2), 127.68 (CH), 127.66 (CH), 127.07 (CH), 127.03 (CH×2), 126.40 (CH), 34.76 (C), 33.28 (CH), 29.31 (CH_3×3), 28.35 (CH_3). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{22}H_{22}N_2NaO$, 353.1624; found, 353.1624.

4-Methoxy-3,4-dimethyl-1-propyl-1*H*-pyrrolo[2,3-*b*]quinolin-2(4*H*)-one (19a). Yellow oil. IR (neat/cm^{-1}): 2970, 2931, 1720, 1635, 1442, 1103, 756. ^{1}H-NMR (600 MHz, $CDCl_3$, δ): 7.54 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.44 (dd, *J* = 1.1, 7.7 Hz, 1H), 7.33 (ddd, *J* = 1.4, 7.7, 7.7 Hz, 1H), 7.25 (ddd, *J* = 1.3, 7.5, 7.5 Hz, 1H), 3.76–3.67 (m, 2H), 2.94 (s, 3H), 2.22 (s, 3H), 1.76 (tq, *J* = 7.3, 7.5 Hz, 2H), 1.64 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$, δ): 170.74 (C), 156.46 (C), 143.75 (C), 135.83 (C), 133.31 (C), 131.33 (C), 129.04 (CH), 128.51 (CH), 126.75 (CH), 125.97 (CH), 74.40 (C), 52.47 (CH_3), 40.36 (CH_2), 31.01 (CH_3), 21.98 (CH_2), 11.32 (CH_3), 9.12 (CH_3). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{17}H_{20}N_2NaO_2$, 307.1417; found, 307.1415.

2-*tert*-Butyl-3-methoxy-3-methyl-1-propyl-1,3-dihydro-1,8-diaza-cyclobuta[*b*]naphthalene (20). Yellow oil. IR (neat/cm^{-1}): 2962, 1643, 1219, 1111, 756. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.70 (dd, *J* = 1.3, 8.0 Hz, 1H), 7.64 (dd, *J* = 1.2, 8.1 Hz, 1H), 7.45 (ddd, *J* = 1.5, 7.0, 8.2 Hz, 1H), 7.20 (ddd, *J* = 1.4, 7.0, 8.1 Hz, 1H), 3.45–3.25 (m, 2H), 3.21 (s, 3H), 2.40 (s, 3H), 1.95–1.78 (m, 2H), 1.13 (s, 9H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$, δ): 163.90 (C), 149.88 (C), 132.53 (C), 129.20 (C), 128.44 (CH), 126.28 (CH), 126.11 (C), 123.95 (CH), 121.63 (CH), 110.41 (C), 52.43 (CH_3), 45.12 (CH_2), 38.10 (C), 26.27 (CH_3×3), 22.62 (CH_2), 14.84 (CH_3), 11.84 (CH_3). HRMS-ESI (*m*/*z*): [M+H]$^+$ calcd for $C_{19}H_{27}N_2O$, 299.2118; found, 299.2104.

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