Isoquinoline *N*-Oxide Synthesis under Pd-Catalysed C–H Activation/Annulation Processes

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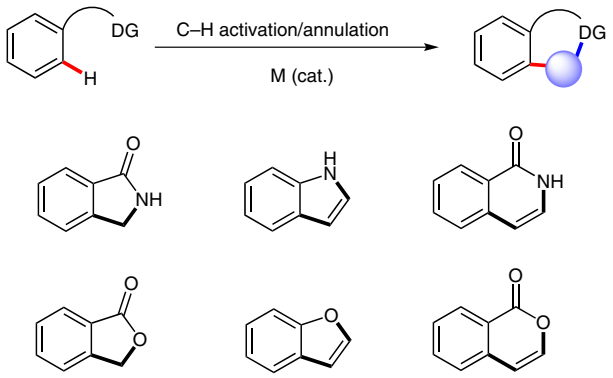
Abstract: An oxime directed C–H activation–annulation reaction for the selective synthesis of a range of isoquinoline *N*-oxides has been developed. Under palladium-catalyzed acid-assisted conditions, the reaction undergoes concerted metallation deprotonation followed by carbopalladation and transmetallation to give polysubstituted isoquinoline *N*-oxides in moderate to good yields.

Key words: oxime C–H activation–annulation, isoquinoline *N*-oxide, palladium catalysis

Ligand-associated transition-metal-catalysed C–H activation–annulation (CHAA) reaction has become one of the most efficient approaches for the construction of carbocycles and heterocycles.[1] In the last five years, a considerable number of well-established C–H activation–annulation approaches has been developed for the modular syntheses of useful ring systems. For instance, the syntheses of isoindolone,[2] indole,[3] isoquinolone,[4] isobenzofuranone,[5] benzofuran,[6] and isochromenone[7] can be achieved via bimolecular multihydrogen bonds (C–H, N–H, or O–H bond) activation (Scheme 1).



Scheme 1 CHAA reaction for the construction of useful heterocycle ring systems

Among the numerous metal-mediated CHAA reactions, oxime-directed[8] C–H activation–annulation reactions for the syntheses of isoquinolines have been established under rhodium- and ruthenium-catalysed conditions. The modular syntheses of isoquinoline developed by Cheng and Li utilising rhodium as the catalyst validated the construction of isoquinoline skeleton by the reaction of aryl oximes and alkyenes (Scheme 2, eq. 1).[9] Jeganmoban and Ackermann recently developed the similar transformation using a relatively less expensive ruthenium catalyst (Scheme 2, eq. 2).[10] With our ongoing research interests on the heterocycle ring construction under palladium-catalysed CHAA reaction, an oxime-directed isoquinoline *N*-oxide synthesis is developed. Different from rhodium and ruthenium catalyses, the palladium-catalysed reaction has shown excellent selectivity towards the isoquinoline *N*-oxide formation prior to the corresponding isoquinoline (Scheme 2, eq. 3).

To evaluate the reactivity and selectivity of the formation of isoquinoline *N*-oxide, oxime **1a** and commercially

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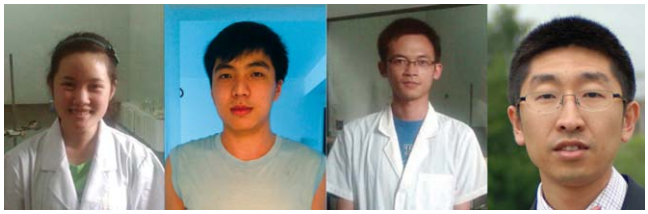
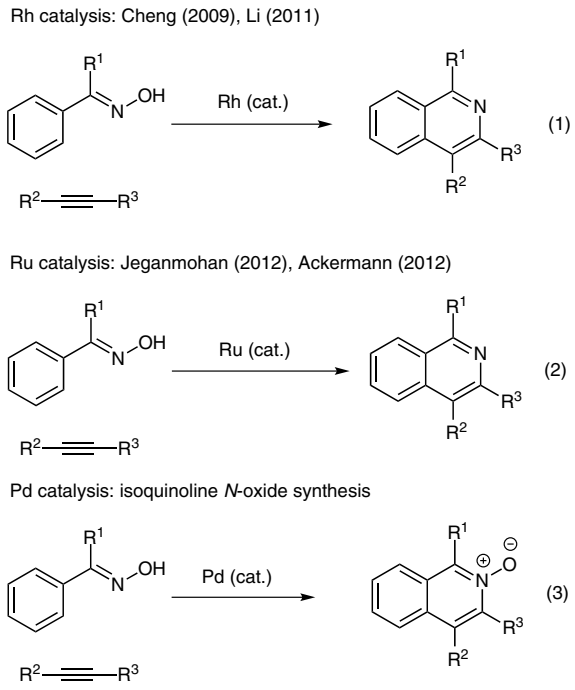


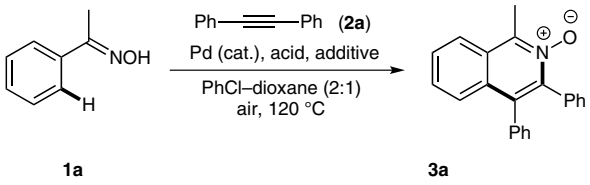
(From left to right) **Binyao Li** did her undergraduate studies at Tianjin Medical University from 2007–2011. She then moved to Tianjin University for her master degree under the supervision of Dr. Jianhui Huang, jointly supervised by Professor Kang Zhao at the School of Pharmaceutical Science and Technology. Her research project involves the development of new synthetic methodologies.
Pingxuan Jiao started his undergraduate studies in 2010, in the School of Pharmaceutical Science and Technology at Tianjin University. He is currently in his final year under the direction of Dr. Jianhui Huang working with the synthesis of useful heterocycles.
Hongban Zhong joined the School of Phamaceutical Science and Technology at Tianjin University in 2005. He then stayed in the same school for his postgraduate study where he obtained his master degree in 2012. After leaving the group he joined a pharmaceutical research centre in Zhejiang.
Jianhui Huang obtained a BSc Degree in 2000 at Hu'nan University, China, and his PhD with Professor Peter O'Brien at the University of York in 2006. He then spent three years as a postdoctoral research fellow with Professor Joseph Harrity at the University of Sheffield as well as with Dr. Simon Macdonald at GlaxoSmithKline, Stevenage before taking an associate professorship at Tianjin University in July, 2010. His research interests are broadly in the development and application of synthetic methods, particularly transition-metal-mediated direct C–H functionalization and the applications on active pharmaceutical ingredient synthesis.



Scheme 2 Oxime-directed CHAA reaction under rhodium-, ruthenium-, and palladium-catalysed conditions

available diphenylacetylene (**2a**) were employed for our initial studies. Mixed solvent PhCl–dioxane (2:1) demonstrated to be the optimal solvent system during our preliminary studies. When $Pd(OAc)_2$ was used without any additives, no product was detected, only trace amount of aryl ketone was isolated due to the hydrolysis of oxime **1a**. The introduction of 0.2 equivalents of trifluoroacetic acid (TFA) accelerated the hydrolysis processes and no oxime was detected after the reaction mixture was heated at 130 °C for four hours. Pleasingly, however, when 0.2 equivalents of strong Brønsted acid (PTSA) was used, our desired isoquinoline *N*-oxide **3a** was isolated in a useful 38% yield, interestingly, however, no corresponding isoquinoline was detected in the ^{1}H NMR spectrum from the crude reaction mixture. The acid screening was fruitful, when zinc halide salts (Lewis acid) were introduced instead of a strong Brønsted acid, the reaction yields were improved to 58% ($ZnCl_2$) and 74% ($ZnBr_2$), respectively. $Zn(OAc)_2$ and $Zn(OTf)_2$ are less efficient Lewis acids which provided the desired isoquinoline *N*-oxide in 22% and 41% yields. Copper and silver salts, however, failed to give any of our desired product instead only hydrolysis product was observed after the reaction mixture was heated at 120 °C for five hours (Table 1, entries 8–10). Pleasingly, when acetic acid (AcOH) or TFA were added as the additive, the yields have been improved to 78% and 89%, respectively. In addition other palladium sources are also proved to be active catalysts for this reaction, where $PdCl_2$ gave the corresponding product in 44% yield. $Pd(PPh_3)_2Cl_2$, however, due to the two phosphine ligands, failed to give any of our desired products while $Pd(TFA)_2$ provided isoquinoline *N*-oxide **3a** in a moderate 57% yield. We are pleased to find that $Pd_2(dba)_3$ as the low-valent palladium source is also a potentially useful catalyst for this transformation albeit with low yield (Table 1, entry 16). The role of $ZnBr_2$ as the additive is likely to be the halogen source for the soft ligand exchange for the generation of the more reactive palladium intermediate for both C–H activation and carbopalladation processes.[4c,11]

Table 1 Screening of Reaction Conditions[a]



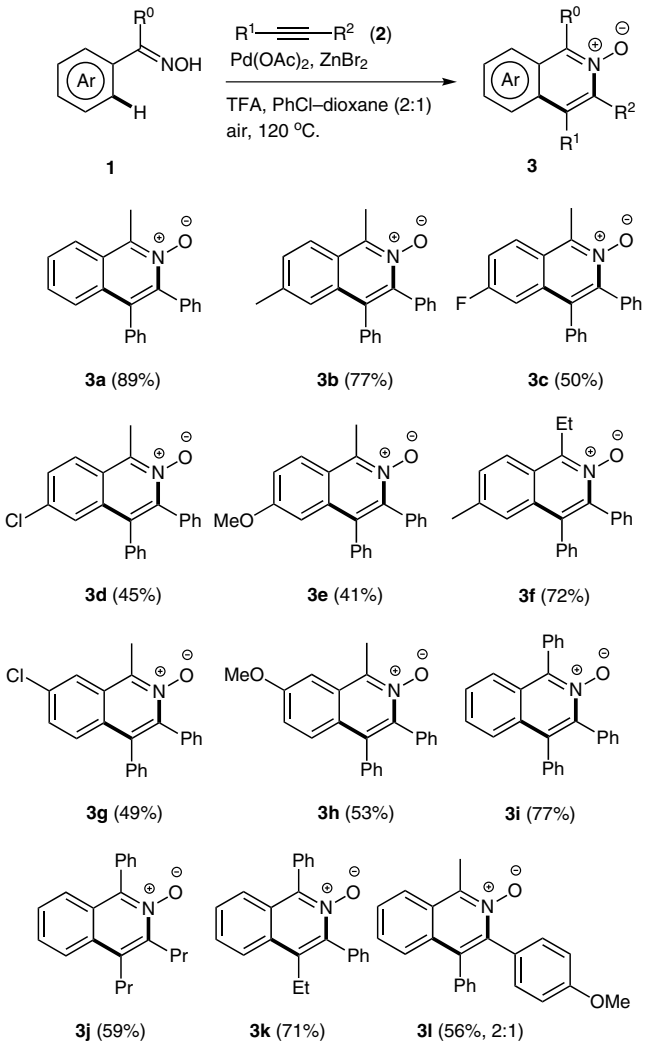
1a **3a**

Entry	Pd cat.	Acid	Additive	Yield (%)
1	$Pd(OAc)_2$	–	–	0
2	$Pd(OAc)_2$	TFA	–	0
3	$Pd(OAc)_2$	PTSA	–	38
4	$Pd(OAc)_2$	$ZnCl_2$	–	59
5	$Pd(OAc)_2$	$ZnBr_2$	–	74
6	$Pd(OAc)_2$	$Zn(OAc)_2$	–	22
7	$Pd(OAc)_2$	$Zn(OTf)_2$	–	41
8	$Pd(OAc)_2$	$CuCl_2$	–	0
9	$Pd(OAc)_2$	$CuBr_2$	–	0
10	$Pd(OAc)_2$	AgOTf	–	0
11	$Pd(OAc)_2$	$ZnBr_2$	AcOH	78
12	$Pd(OAc)_2$	$ZnBr_2$	TFA	89
13	$PdCl_2$	$ZnBr_2$	TFA	44
14	$Pd(PPh_3)_2Cl_2$	$ZnBr_2$	TFA	0
15	$Pd(TFA)_2$	$ZnBr_2$	TFA	57
16	$Pd_2(dba)_3$	$ZnBr_2$	TFA	31

[a] Reaction conditions: oxime **1a** (0.3 mmol), alkyne **2a** (0.45 mmol), $Pd(OAc)_2$ (10 mol%), $ZnBr_2$ (1.0 equiv), and TFA (0.2 equiv) at 120 °C in PhCl–dioxane (2:1; 1.5 mL, 0.2 M), 6–12 h.

With the optimal conditions in hand, we evaluated the scope and limitations of the reaction. When aryl oximes were utilised, a number of electron-rich and electron-deficient aryl oximes were evaluated, and the corresponding isoquinoline *N*-oxides were successfully prepared in moderate to good yields (Scheme 3). No isoquinolines were observed in most of the cases. Hydrolysis products and Beckmann rearrangement products were the major side products generated during the reaction as these reactions were carried out under Lewis acidic conditions. The reaction of *p*-methylbenzyl oxime underwent the CHAA reaction fluently to give our desired product in 77% yield. Aryl oximes bearing an electron-withdrawing group at the

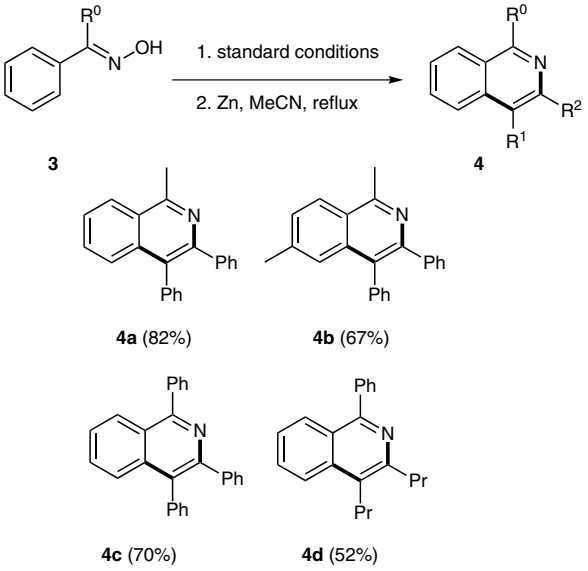
para position provided the corresponding products in moderate yields. As the side-reaction hydrolysis occurred during the reaction in the presence of acids resulting in the corresponding ketones. On the contrary, aryl oxime with electron-donating substituents at the *para* position gave similar moderate to good yields due to the Beckmann rearrangement reactions. *meta*-Substituted aryl oximes also provided our desired isoquinoline *N*-oxides **3g** and **3h** in useful 49% and 53% yields. Biaryl oximes are also tolerated in this transformation, multiaryl-substituted isoquinoline *N*-oxide **3i** was isolated in 77% yield. Reactions of aryl oxime with alkynes other than diphenyl acetylene were also successful, symmetrical dialkyl alkyne facilitated the corresponding product **3j** in 59% yield.



Scheme 3 Reaction scope. *Reagents and conditions*: oxime **1** (0.3 mmol), alkyne **2** (0.45 mmol), $Pd(OAc)_2$ (10 mol%), $ZnBr_2$ (1.0 equiv), and TFA (0.2 equiv) at 120 °C in PhCl–dioxane (2:1; 1.5 mL, 0.2 M), 6–12 h.

Reactions with unsymmetric alkynes were also feasible, however, the regioselectivity varies when different alkynes were utilised. When phenyl propyne was used, **3k** was isolated exclusively in a good 71% yield while the reaction of unsymmetric diaryl alkyne provide the product **3l** and **3l′** as a 2:1 mixture of regioisomers, which have been assigned via NOE studies. Similar to other CHAA reactions, the regioselectivity favours the carbopalladation onto the less hindered position of the alkynes.[2,3]

The isoquinoline *N*-oxides could be readily reduced onto the isoquinolines under Cheng's conditions.[12] The sequential synthesis of isoquinoline *N*-oxides followed by zinc reduction provided the corresponding isoquinolines **4a**–**e** in good overall yields (52–82%) from starting benzamides (Scheme 4). It is worth noting that no column chromatographic workup was needed between the two sequential steps.

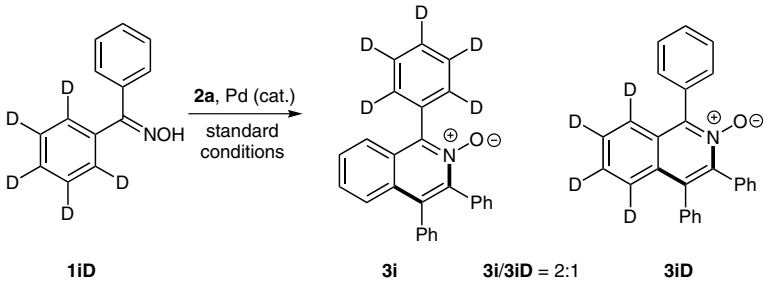


Scheme 4 Synthesis of isoquinoline from isoquinoline *N*-oxide. *Reagents and conditions*: 1) oxime **1** (0.3 mmol), alkyne **2** (0.45 mmol), $Pd(OAc)_2$ (10 mol%), $ZnBr_2$ (1.0 equiv), and TFA (0.2 equiv) at 120 °C in PhCl–dioxane (2:1; 1.5 mL, 0.2 M), 6–12 h; 2) Zn powder (5 equiv) in MeCN (1.5 mL), reflux, 5–10 h.

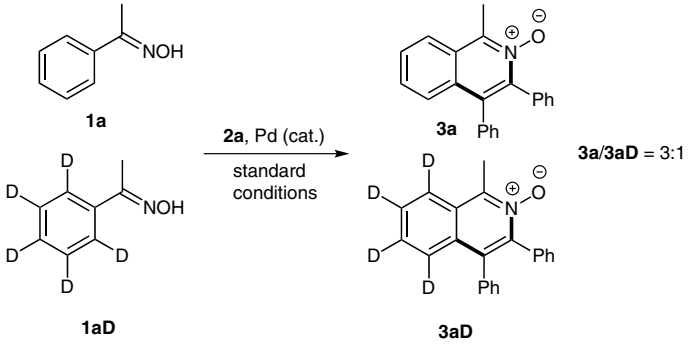
The kinetic isotope effect (KIE) studies have revealed that the C–H activation process is the turnover limiting step as we have observed 2:1 and 3:1 as the KIE values for both internal and external competition reactions. When aryl oxime **1iD** was treated with alkyne **2a** under our standard reaction conditions, a mixture of **3i** and **3iD** was isolated in a 2:1 ratio (Scheme 5; for experimental details see Supporting Information).

In addition, bimolecular competition between oxime **1a** and **1aD** provided a similar KIE value as shown in Scheme 6 (for experimental details see Supporting Information).

Similar to the reactions of isoquinoline and isoquinolone syntheses, the reaction is supposed to undergo oxime directed C–H activation via a CMD or/and Friedel–Crafts-type of processes to give palladacycle **6**. Active palladium intermediate **7** is formed after carbopalladation of the palladium species **6** with the addition onto the less hindered carbon of the unsymmetrical alkyne. Further transmetallation of nitrogen onto the palladium centre, the seven-



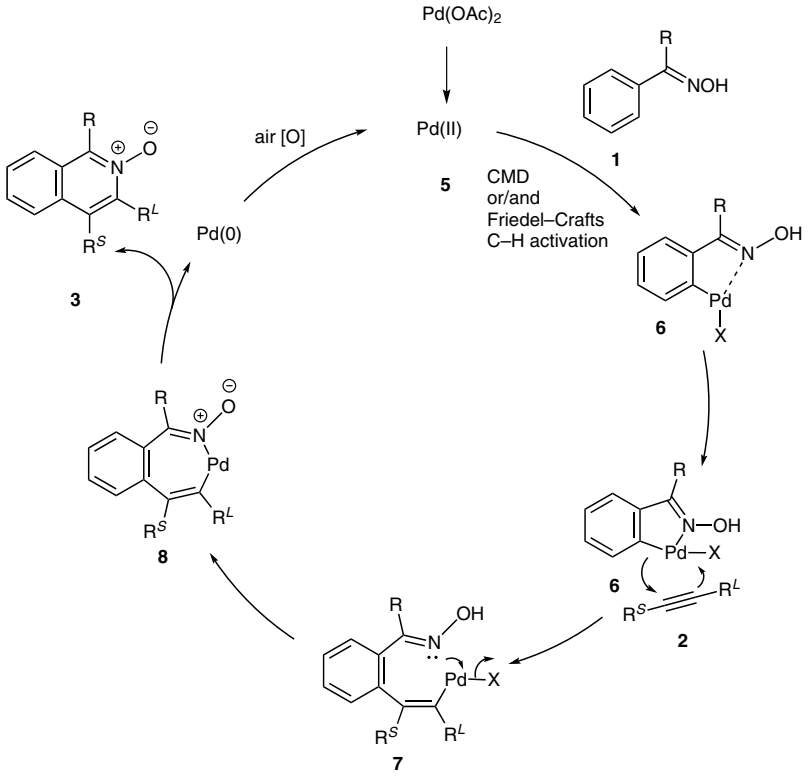
Scheme 5 Intramolecular KIE studies



Scheme 6 Intermolecular KIE studies

membered palladacycle **8** was then formed. The final reductive elimination could facilitate our desired isoquinoline *N*-oxide **3** after the releasing Pd(0) which can be reoxidised back to palladium(II) **5** to start the next catalytic cycle (Scheme 7).

In summary, we have demonstrated the selective formation of isoquinoline *N*-oxide under palladium-catalysed oxime-directed CHAA reaction. This methodology gives an insight of mild C–H activation under palladium catalysis which could be a potential direction for the sensitive functional group within C–H activation reactions.



Scheme 7 Plausible catalytic cycle

General Procedure

A solution of oxime (0.3 mmol), alkyne (0.45 mmol), $Pd(OAc)_2$ (10 mol%), $ZnBr_2$ (0.3 mmol), TFA (0.06 mmol) in PhCl–dioxane (2:1, 1.5 mL) was heated at 120 °C under air. The reaction was monitored by TLC. After the reaction was complete, the reaction mixture was cooled down to r.t. The mixture was washed with sat. aq $NaHCO_3$ (15 mL) to neutralise acid. The aqueous layers were extracted with EtOAc (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to provide the crude product. The crude product was purified by flash column chromatography on silica gel.

Selected Examples

1,6-Dimethyl-3,4-diphenylisoquinoline 2-Oxide (3b)

Following the general procedure, oxime **1b** (0.3 mmol, 45 mg), diphenylethyne (80 mg, 0.45 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), $ZnBr_2$ (63 mg, 0.3 mmol), and TFA (6.8 mg, 0.06 mmol) in PhCl–dioxane (2:1; 1.5 mL) was heated at 120 °C for 5 h to give the desired isoquinoline oxide **3b** (75 mg, 77%) as a pale yellow solid; mp 245–247 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.5 Hz, 1 H), 7.46 (d, *J* = 8.5 Hz, 1 H), 7.28–7.17 (m, 9 H), 7.12 (d, *J* = 6.7 Hz, 2 H), 2.98 (s, 3 H), 2.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.7, 145.4, 138.8, 135.4, 133.9, 133.3, 130.8, 130.7, 130.6, 129.5, 128.1, 127.9, 127.7, 127.6, 126.4, 125.8, 124.1, 21.9, 13.6. ESI-HRMS: *m/z* calcd for $C_{23}H_{19}NO$ [M + H]: 326.1545; found: 325.1546.

6-Chloro-1-methyl-3,4-diphenylisoquinoline 2-Oxide (3d)

Following the general procedure, oxime **1d** (0.3 mmol, 51 mg), diphenylethyne (80 mg, 0.45 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), $ZnBr_2$ (62.5 mg, 0.3 mmol), and TFA (6.84 mg, 0.06 mmol) in PhCl–dioxane (2:1, 1.5 mL) was heated at 120 °C for 8 h to give the desired isoquinoline oxide **3d** (47 mg, 45%) as a pale yellow solid; mp 206–208 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 9.0 Hz, 1 H), 7.56 (d, *J* = 9.0 Hz, 1 H), 7.42 (s, 1 H), 7.29–7.26 (m, 3 H), 7.24–7.18 (m, 5 H), 7.11 (d, *J* = 6.0 Hz, 2 H), 2.96 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.9, 144.9, 134.7, 134.3, 133.6, 132.8, 130.5, 130.4, 129.7, 129.5, 128.3, 128.1, 128.0, 127.8, 126.7, 125.7, 125.6, 13.7. ESI-HRMS: *m/z* calcd for $C_{22}H_{16}{}^{35}ClNO$ [M + H]: 346.0999; found: 346.1001.

1-Phenyl-3,4-dipropylisoquinoline 2-Oxide (3j)

Following the general procedure, oxime **1i** (0.3 mmol, 59 mg), dipropylacetylene (50 mg, 0.45 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), and $ZnBr_2$ (63 mg, 0.3 mmol) in PhCl–dioxane (2:1, 1.5 mL) was heated at 120 °C for 5 h to give the desired isoquinoline oxide **3j** (54 mg, 59%) as a pale yellow solid; mp 172–174 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.0 Hz, 1 H), 7.97 (t, *J* = 8.0 Hz, 1 H), 7.79–7.72 (m, 3 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 7.64–7.60 (m, 3 H), 3.47–3.36 (m, 2 H), 3.22–3.12 (m, 2 H), 1.89–1.888 (m, 2 H), 1.80–1.79 (m, 2 H), 1.22–1.17 (m, 3 H), 1.15–1.10 (m, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.0, 136.2, 135.7, 134.5, 130.8, 130.5, 130.3, 129.6, 128.6, 128.2, 127.1, 124.0, 100.0, 31.0, 30.9, 24.0, 22.1, 14.7, 14.4. ESI-HRMS: *m/z* calcd for $C_{21}H_{23}NO$ [M + H]: 306.1858; found: 306.1861.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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