Supporting Information

Oxidant triggered C₁-benzylation of isoquinoline by iodine-catalyzed cross-dehydrogenative-coupling with methylarenes

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I. General information

Unless stated otherwise, all commercially available compounds were used as provided without further purification. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). IR spectrum was characterized by PE-Spectrum One. Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for $^1$H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: $\delta$ 7.26 ppm). Chemical shifts for $^{13}$C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl$_3$: $\delta$ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

II. General experimental procedures

A general experimental procedure is described as following:

An oven-dried reaction vessel was charged with isoquinoline (1a) (0.4 mmol, 1 equiv), iodine (5.2 mg, 5 mol%), DTBP (Di-tert-butyl peroxide) in $p$-xylene (1 mL). The vessel was sealed and heated at 130°C for 12 h, then cool down to room temperature. The resulting mixture was transferred to silica gel column by eluting with hexanes and ethyl acetate (12:1) to give 1-(4-methylbenzyl)isoquinoline (3a).
### III. Detailed optimization

**Entry** | **Cat. (mol%)** | **[O] (3 equiv)** | **T (°C)** | **Yield (%)\(^a\)**
---|---|---|---|---
1 | I\(_2\) (5) | DTBP | 130 | 71 (< 2)
2 | I\(_2\) (5) | TBHP | 130 | 0 (72)
3 | I\(_2\) (5) | H\(_2\)O\(_2\) | 130 | 0
4 | I\(_2\) (5) | K\(_2\)S\(_2\)O\(_8\) | 130 | 0
5 | I\(_2\) (5) | BPO | 130 | 0
6 | Cul (10) | DTBP | 130 | 0
7 | KI (10) | DTBP | 130 | 50
8 | TBAI (10) | DTBP | 130 | 71
9 | NIS (10) | DTBP | 130 | 70
10 | I\(_2\) (0) | DTBP | 130 | trace
11 | I\(_2\) (2.5) | DTBP | 130 | 66
12 | I\(_2\) (10) | DTBP | 130 | 62
13 | I\(_2\) (5) | DTBP | 120 | 50
14 | I\(_2\) (5) | DTBP | 110 | 45
15 | I\(_2\) (5) | DTBP | 100 | < 2
16\(^b\) | I\(_2\) (5) | DTBP | 130 | 71
17\(^c\) | I\(_2\) (5) | DTBP | 130 | 71
16\(^d\) | I\(_2\) (5) | DTBP | 130 | 54

\(^a\) Conditions: **1a** (0.4 mmol, 1 equiv), catalyst (mol %), oxidant (3 equiv), in p-xylene (2a, 1 mL), reacted for 12 h under air atmosphere unless otherwise noted. Isolated yields of **3a**, the yield of **4a** was listed in parenthesis. \(^b\) p-xylene was dried by sodium. \(^c\) p-xylene was dried by sodium; H\(_2\)O (2 equiv) was added. \(^d\) Mixed solvent of p-xylene (10 equiv) and chlorobenzene (1 mL). TBHP = *tert*-Butyl hydroperoxide. BPO = Benzoyl peroxide. TBAI = Tetrabutylammonium iodide. NIS = Succinimidimide.
IV. Mechanistic experiments

To gain more insight into the reaction mechanism, control experiments were carried out as follows.

(a) A mixture of 1a (0.4 mmol, 1 equiv), iodine (5 mol%), DTBP (1.2 mmol, 3 equiv) and 1,1-Diphenylethylene (0.8 mmol, 2 equiv) in toluene (1 mL) was reacted at 130 °C for 12 h. Afterwards the resulting mixture was cooled to room temperature, transferred to silica gel column directly, and eluted with petroleum ether.

(b) A mixture of 1a (0.4 mmol, 1 equiv), iodine (5 mol%), DTBP (1.2 mmol, 3 equiv) in toluene (C7H8, 0.5 mL) and deuterated toluene (C7D8, 0.5 mL) was reacted at 130 °C for 6 h. Afterwards the resulting mixture was cooled to room temperature, transferred to silica gel column directly, eluted with petroleum ether and ethyl acetate (12:1). Then the ratio of product mixture was determined by 1H NMR.

(c) A mixture of 1a (0.4 mmol, 1 equiv), iodine (5 mol%), oxidant (1.2 mmol, 3 equiv) in toluene (C7H8, 1 mL) was reacted at 130 °C for 12 h. When TBHP was used as oxidant, benzyl iodide could be detected by GC-MS. While the oxidant switched to DTBP, no benzyl iodide can be detected. (See page S32)
V. Spectra data of products 3a-3s

(3a) 1-(4-methylbenzyl)isoquinoline

Yellow oil, (66.2 mg, 71%). $^1$$^1$$^1$H NMR (400 MHz, CDCl$_3$) δ 8.49 (d, J = 5.6 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.55 - 7.50 (m, 2H), 7.17 (d, J = 7.3 Hz, 2H), 7.05 (d, J = 7.4 Hz, 2H), 4.63 (s, 2H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.48, 142.11, 136.67, 136.49, 135.81, 129.88, 129.30, 128.59, 127.41, 127.28, 127.25, 125.94, 119.82, 41.76, 21.07.

(3b) 1-benzylisoquinoline

Yellow oil, (57.8 mg, 66%). $^1$$^1$$^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (d, J = 5.6 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.29 – 7.21 (m, 4H), 7.17 (t, J = 6.3 Hz, 1H), 4.68 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.26, 142.15, 139.58, 136.69, 129.93, 128.72, 128.61, 127.45, 127.32, 127.30, 126.36, 125.92, 119.90, 42.18.

(3c) 1-(3,5-dimethylbenzyl)isoquinoline

Yellow oil, (66.2 mg, 67%). $^1$$^1$$^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (d, J = 5.6 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.56 - 7.51 (m, 2H), 6.89 (s, 2H), 6.80 (s, 1H), 4.59 (s, 2H), 2.23 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.44, 142.06, 139.37, 138.02, 136.64, 129.86, 128.06, 127.36, 127.33, 127.23, 126.51, 125.98, 119.78, 41.99, 21.33.

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1 Reimann E, Höglmüller A. Archiv der Pharmazie 1985, 318, 487-495.
(3d) 1-(2-methylbenzyl)isoquinoline ¹

Yellow oil, (63.4 mg, 68%). $^1$H NMR (400 MHz, CDCl₃) δ 8.49 (d, $J$ = 5.6 Hz, 1H), 8.03 (d, $J$ = 8.4 Hz, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.65 (t, $J$ = 7.4 Hz, 1H), 7.57 (d, $J$ = 5.7 Hz, 1H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.21 (d, $J$ = 7.2 Hz, 1H), 7.12 (t, $J$ = 7.4 Hz, 1H), 7.01 (t, $J$ = 7.4 Hz, 1H), 6.78 (d, $J$ = 7.6 Hz, 1H), 4.64 (s, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 160.08, 142.19, 137.90, 136.42, 136.28, 130.18, 129.94, 128.95, 127.54, 127.44, 127.28, 126.40, 126.07, 125.69, 119.74, 39.38, 20.11.

(3e) 1-(3-methylbenzyl)isoquinoline ⁴

Yellow oil, (67 mg, 72%). $^1$H NMR (400 MHz, CDCl₃) δ 8.50 (d, $J$ = 5.6 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.0 Hz, 1H), 7.63 (t, $J$ = 7.4 Hz, 1H), 7.57 - 7.51 (2H), 7.16 - 7.06 (3H), 6.98 (d, $J$ = 6.8 Hz, 1H), 4.63 (s, 2H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 160.31, 142.04, 139.41, 138.15, 136.63, 129.89, 129.42, 128.45, 127.38, 127.28, 127.25, 127.12, 125.92, 125.72, 119.84, 42.04, 21.46.

(3f) 1-(4-methoxybenzyl)isoquinoline ⁵

White solid, (39.8 mg, 40%). $^1$H NMR (400 MHz, CDCl₃) δ 8.49 (d, $J$ = 5.6 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.0 Hz, 1H), 7.63 (t, $J$ = 7.4 Hz, 1H), 7.56 - 7.51 (2H), 7.19 (d, $J$ = 8.2 Hz, 2H), 6.79 (d, $J$ = 8.0 Hz, 2H), 4.61 (s, 2H), 3.74 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 160.58, 158.16, 142.05, 136.72, 131.65, 129.96, 129.67, 127.46, 127.30, 127.25, 125.95, 119.88, 114.07, 55.30, 41.23.

(3g) 1-(4-fluorobenzyl)isoquinoline ⁶

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white solid, (59.7 mg, 63%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.49 (d, \(J = 5.6\) Hz, 1H), 8.12 (d, \(J = 8.4\) Hz, 1H), 7.82 (d, \(J = 8.0\) Hz, 1H), 7.65 (t, \(J = 7.4\) Hz, 1H), 7.58 - 7.52 (m, 2H), 7.27 – 7.18 (m, 2H), 6.97 - 6.91 (m, 2H), 4.64 (s, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.35 (d, \(J = 280.5\) Hz), 160.32, 142.05, 136.66, 135.13 (d, \(J = 3.0\) Hz), 130.07 (d, \(J = 13.1\) Hz), 130.06, 127.50, 127.38, 127.13, 125.64, 120.00, 115.36 (d, \(J = 21.2\) Hz), 41.11.

(3h) 1-(4-chlorobenzyl)isoquinoline 7

Yellow oil, (72.8 mg, 72%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.49 (d, \(J = 5.6\) Hz, 1H), 8.09 (d, \(J = 8.4\) Hz, 1H), 7.83 (d, \(J = 8.2\) Hz, 1H), 7.65 (t, \(J = 7.5\) Hz, 1H), 7.58-7.52 (m, 2H), 7.21 (m, 4H), 4.63 (s, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.62, 142.03, 137.91, 136.64, 132.15, 130.04, 128.69, 127.51, 127.42, 127.10, 125.57, 120.06, 41.26.

(3i) 1-(4-bromobenzyl)isoquinoline 8

Yellow oil, (84.5 mg, 71%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.49 (d, \(J = 5.6\) Hz, 1H), 8.09 (d, \(J = 8.4\) Hz, 1H), 7.82 (d, \(J = 8.0\) Hz, 1H), 7.65 (t, \(J = 7.4\) Hz, 1H), 7.37 (d, \(J = 8.2\) Hz, 2H), 7.15 (d, \(J = 8.0\) Hz, 2H), 4.62 (s, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.49, 141.99, 138.40, 136.61, 131.61, 130.41, 130.03, 127.49, 127.42, 127.06, 125.53, 120.22, 120.06, 41.29.

(3j) 1-(4-iodobenzyl)isoquinoline 8

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Yellow oil, (88.5 mg, 62%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (d, $J$ = 5.6 Hz, 1H), 8.08 (d, $J$ = 8.5 Hz, 1H), 7.82 (d, $J$ = 8.0 Hz, 1H), 7.65 (t, $J$ = 7.4 Hz, 1H), 7.58 - 7.52 (m, 4H), 7.02 (d, $J$ = 8.0 Hz, 2H), 4.60 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.55, 142.16, 139.19, 137.66, 136.69, 130.82, 130.07, 127.57, 127.48, 127.16, 125.61, 120.10, 91.72, 41.56.

(3k) methyl 4-(isoquinolin-1-ylmethyl)benzoate

Yellow oil, (60.9 mg, 55%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J$ = 5.8 Hz, 1H), 8.08 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.83 (d, $J$ = 8.2 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.59 (d, $J$ = 6.0 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.33 (d, $J$ = 8.2 Hz, 2H), 4.72 (s, 2H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.11, 159.40, 144.93, 142.18, 136.73, 130.14, 130.00, 128.80, 128.40, 127.61, 127.54, 127.26, 125.64, 120.22, 52.14, 42.13.

(3l) 4-(isoquinolin-1-ylmethyl)benzonitrile

Yellow oil, (50.8 mg, 52%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J$ = 5.6 Hz, 1H), 8.05 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.70 - 7.66(m, 1H), 7.62 - 7.53 (m, 4H), 7.39 - 7.37 (m, 2H), 4.72 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.67, 145.02, 142.19, 136.72, 132.45, 130.28, 129.60, 127.73, 127.14, 125.27, 120.39, 119.05, 119.05, 110.37, 41.90.

(3m) 1-(2-bromobenzyl)isoquinoline

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Yellow oil, (71.3 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.51 (d, $J = 6.0$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.63 - 7.59 (m, 2H), 7.61 (t, $J = 6.8$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.14 – 7.03 (m, 2H), 6.89 (d, $J = 7.4$ Hz, 1H), 4.78 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.34, 142.05, 138.99, 136.48, 132.76, 130.52, 130.13, 128.04, 127.53, 127.51, 127.44, 127.36, 125.68, 124.56, 120.08, 41.72.

(3n) 6-methyl-1-(4-methylbenzyl)isoquinoline

white solid, (59.3 mg, 60%). M.p. 64.5-65.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, $J = 5.6$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.56 (s, 1H), 7.46 (d, $J = 5.4$ Hz, 1H), 7.34 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 4.60 (s, 2H), 2.50 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.17, 142.22, 140.21, 137.03, 136.64, 135.80, 129.53, 129.31, 128.58, 126.36, 125.82, 125.68, 119.43, 41.78, 21.94, 21.12. IR (KBr): v max(cm$^{-1}$): 3448, 3047, 2921, 1630, 1586, 775, 741. HRMS: calcd. for [M+Na]$^+$ C$_{18}$H$_{17}$NNa: 270.1253, found: 270.1240.

(3o) 6-(tert-butyl)-1-(4-methylbenzyl)isoquinoline

Yellow oil, (75.1 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 6.0$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 2.0$ Hz, 1H), 7.60 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.52 (d, $J = 5.6$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 7.9$ Hz, 2H), 4.60 (s, 2H), 2.27 (s, 3H), 1.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.95, 153.00, 142.15, 136.90, 136.64, 135.81, 129.32, 128.62, 126.29, 125.67, 122.44, 120.08, 41.75, 35.22, 31.10, 21.14. IR (KBr): v max(cm$^{-1}$): 3448, 2963, 2868, 1648, 1438, 1383, 824, 806. HRMS: calcd. for [M+Na]$^+$ C$_{21}$H$_{23}$NNa: 312.1723, found: 312.1718.
(3p) 1-(4-methylbenzyl)-4-phenylisoquinoline

white solid, (86.5 mg, 70%). M.p. 128.5-129.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (s, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.64 – 7.44 (m, 7H), 7.32 – 7.17 (m, 2H), 7.10 - 7.08 (m,2H), 4.68 (s, 2H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.73, 141.72, 137.24, 136.38, 135.76, 134.93, 132.34, 130.18, 129.91, 129.26, 128.53, 127.77, 127.01, 126.74, 126.04, 125.57, 41.72, 21.03. IR (KBr): $\nu_{\text{max}}$(cm$^{-1}$): 3421, 3025, 2975, 2921, 2360, 1511, 1384, 703. HRMS: calcd. for [M+H]$^+$ C$_{23}$H$_{20}$N: 310.1590, found: 310.1582.

(3q) 6-bromo-1-(4-methylbenzyl)isoquinoline

Yellow oil, (78.4 mg, 63%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.51 (d, $J = 5.8$ Hz, 1H), 8.09 – 7.87 (m, 2H), 7.58 (d, $J = 8.8$ Hz, 1H), 7.47 (d, $J = 5.6$ Hz, 1H), 7.14 - 7.12 (m, 2H), 7.07 - 7.05 (m, 2H), 4.60 (s, 2H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.74, 143.13, 137.84, 136.10, 136.07, 130.82, 129.53, 129.41, 128.50, 127.75, 125.64, 124.71, 118.87, 41.79, 21.12. IR (KBr): $\nu_{\text{max}}$(cm$^{-1}$): 3448, 3049, 3020, 2920, 2363, 2344, 1655, 1486, 880. HRMS: calcd. for [M+H]$^+$ C$_{17}$H$_{15}$BrN: 312.0382, found: 310.0374.

(3r) 5-bromo-1-(4-methylbenzyl)isoquinoline

Yellow oil, (62.2 mg, 50%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J = 6.0$ Hz, 1H), 8.13 (d, $J = 8.4$Hz, 1H), 7.95 – 7.86 (m, 2H), 7.38 – 7.34(m, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 4.64 (s,
2H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.91, 143.47, 136.16, 136.04, 135.82, 133.72, 129.40, 128.52, 128.38, 127.56, 125.74, 122.48, 118.76, 41.91, 21.12. IR (KBr): $\nu_{max}\text{(cm}^{-1})$: 3449, 2920, 2347, 1577, 1342, 744. HRMS: calcd. for [M+H]$^+$ C$_{17}$H$_{15}$BrN: 312.0382, found: 312.0369.

(3s) 4-bromo-1-(4-methylbenzyl)isoquinoline

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\text{\includegraphics{image.png}}
\]

white solid. (49.8 mg, 40%). M.p. 91.5-92.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.16 (m, 2H), 7.75 (ddd, $J = 8.3, 6.9, 1.2$ Hz, 1H), 7.59 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 7.9$ Hz, 2H), 4.59 (s, 2H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.15, 143.81, 136.11, 135.98, 135.31, 131.20, 129.43, 128.57, 128.52, 128.24, 126.84, 126.40, 118.58, 41.55, 21.13. IR (KBr): $\nu_{max}\text{(cm}^{-1})$: 3448, 1648, 1379, 760. HRMS: calcd. for [M+Na]$^+$ C$_{17}$H$_{14}$BrNNa: 334.0202, found: 334.0212.

prop-1-ene-1,1,3-triyltribenzene $^{10}$

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\text{\includegraphics{image.png}}
\]

Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.15 (m, 15H), 6.27 (t, $J = 7.6$ Hz, 1H), 3.47 (d, $J = 7.6$ Hz, 2H).

\[\text{\cite{ref}}\]

VI. Copies of $^1$H and $^{13}$C NMR spectra of products

(3a) 1-(4-methylbenzyl)isoquinoline
(3c) 1-(3,5-dimethylbenzyl)isoquinoline

\[ \text{\chem{N}} \]

\[
\begin{array}{c}
\text{1.05} \\
\text{1.06} \\
\text{1.02} \\
\text{1.04} \\
\text{1.06} \\
\text{1.05} \\
\text{2.05} \\
\text{2.06} \\
\text{3.54} \\
\text{1.95} \\
\end{array}
\]

\[
\begin{array}{c}
\text{3.59} \\
\text{1.92} \\
\text{1.47} \\
\text{2.32} \\
\end{array}
\]

\[
\begin{array}{c}
\text{2.32} \\
\text{3.59} \\
\end{array}
\]

\[
\begin{array}{c}
\text{1.92} \\
\text{1.47} \\
\end{array}
\]

\[
\text{S13}
\]
(3d) 1-(2-methylbenzyl)isoquinoline
(3e) 1-(3-methylbenzyl) isoquinoline
(3f) 1-(4-methoxybenzyl)isoquinoline
(3g) 1-(4-fluorobenzyl)isoquinoline
(3h) 1-(4-chlorobenzyl)isoquinoline

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\text{Chemical structure of (3h) 1-(4-chlorobenzyl)isoquinoline}
\]
(3i) 1-(4-bromobenzyl)isoquinoline

\[ \text{Chemical structure} \]

\[ \text{NMR Spectra} \]

\[ \text{Mass Spectra} \]

S19
(3j) 1-(4-iodobenzyl)isoquinoline

\[
\begin{align*}
&\text{H} & 8.49 & 7.91 & 7.72 & 7.37 & 7.05 \\
&\text{C} & 127.9 & 130.1 & 126.5 & 123.2 & 129.0
\end{align*}
\]
(3k) methyl 4-(isoquinolin-1-ylmethyl)benzoate
(3l) 4-(isoquinolin-1-ylmethyl)benzonitrile

\[
\text{[Chemical Structure Image]}
\]
(3m) 1-(2-bromobenzyl)isoquinoline
6-(tert-butyl)-1-(4-methylbenzyl)isoquinoline
(3p) 1-(4-methylbenzyl)-4-phenylisoquinoline
(3q) 6-bromo-1-(4-methylbenzyl)isoquinoline
(3r) 5-bromo-1-(4-methylbenzyl)isoquinoline
(3s) 4-bromo-1-(4-methylbenzyl)isoquinoline
prop-1-ene-1,1,3-triyltribenzene
**TBHP as the oxidant**

1a (0.4 mmol, 1 equiv), iodine (5 mol%), TBHP (1.2 mmol, 3 equiv) in toluene (C7H8, 1 mL) was reacted at 130 °C for 12 h. Benzyl iodide can be detected by GC-MS.

**DTBP as the oxidant**

1a (0.4 mmol, 1 equiv), iodine (5 mol%), DTBP (1.2 mmol, 3 equiv) in toluene (C7H8, 1 mL) was reacted at 130 °C for 12 h. Benzyl iodide can’t be detected by GC-MS.