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Article

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C(sp^3)–H Bond Arylations Catalyzed by Well-Defined [Ru(O$_2$CMes)$_2$(*p*-cymene)]

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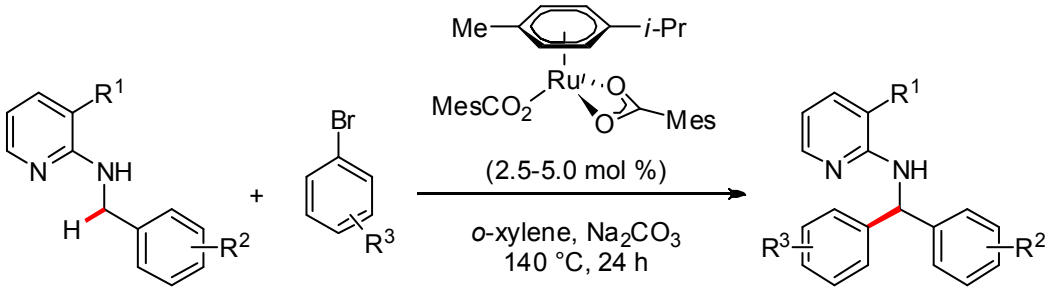


Abstract: The well-characterized ruthenium(II) biscarboxylate complex [Ru(O$_2$CMes)$_2$(*p*-cymene)] enabled versatile direct (hetero)arylations of C(sp^3)–H bonds with low (co-)catalyst loading and ample substrate scope. Detailed mechanistic studies provided strong support for a facile and reversible C(sp^3)–H bond metalation.

Introduction

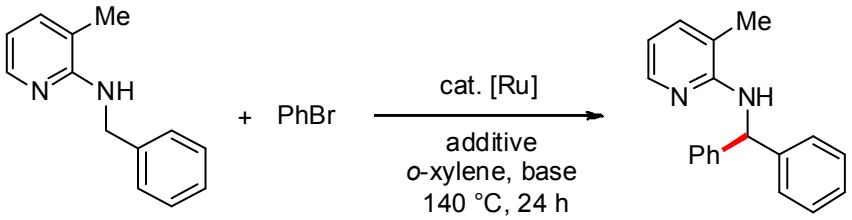
Catalyzed C–H bond functionalizations[1] are increasingly viable tools that avoid the use of prefunctionalized substrates, and thereby enable a streamlining of organic synthesis. In recent years, significant progress has particularly been made in step-economical ruthenium-catalyzed C(sp^2)–H bond functionalization.[2] Mechanistic insight into the importance of carboxylate assistance proved, hence, instrumental for the development of direct C(sp^2)–H bond arylations and alkylations,[3] as well as oxidative transformations.[4,5] On the contrary, ruthenium(II)-catalyzed functionalizations of C(sp^3)–H bonds[6] with organic electrophiles[7] have unfortunately thus far met with limited success. A notable very recent advance was, however, accomplished through direct arylations of benzyl amines with a catalytic system derived from the cocatalyst KOPiv, along with K_2CO_3 as the base.[8] Since the high loading of the additive KOPiv of 30 mol % represents a considerable practical limitation of this approach, and in order to gain insight into the catalysts working mode, we became interested in exploring the first use of well-defined ruthenium(II) biscarboxylate complexes, which were hitherto solely utilized for C(sp^2)–H bond functionalizations.[9] As a result, we report herein on a versatile well-defined ruthenium(II) catalysts for direct functionalizations of C(sp^3)–H bonds, and present detailed mechanistic insight into its mode of action.

Results and Discussion

At the outset of our studies, we tested the piano stool compounds [Ru(OPiv)$_2$(*p*-cymene)] (**4**)[10] and [Ru(O_2CMes)$_2$(*p*-cymene)] (**5**)[9] in the challenging direct arylation of substrate **1a** (Table 1). Notably, the catalyst **5** derived from the aryl-substituted carboxylate outperformed the pivalate-analogue **4**, which thereby allowed for a considerable reduction of the cocatalyst (entries 1, and 2) and the catalyst loading (entry 3). Among various solvents, the desired C–H bond functionalization occurred most efficiently in apolar organic solvent *ortho*-xylene, while H_2O[11] was not a suitable reaction medium (entries 2–5). As to the nature of the stoichiometric base, Na_2CO_3 proved to be superior as compared to the previously

employed bases K_2CO_3,[8] KOAc, or K_3PO_4 (entries 2, and 6–9). It is noteworthy that the C(sp^3)–H bond transformation did not occur in the absence of the ruthenium catalyst (entry 10).

Table 1. Optimization of C(sp^3)–H Bond Arylation[a]



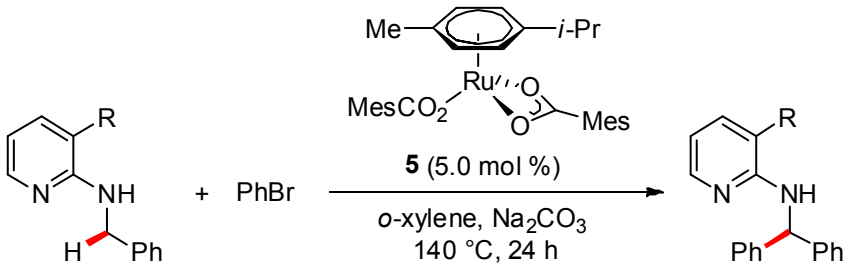
1a **2a** **3aa**

entry	catalyst	solvent	base	yield (%)
1	[Ru(OPiv)$_2$(*p*-cymene)] (**4**)	*o*-xylene	K_2CO_3	51
2	[Ru(O_2CMes)$_2$(*p*-cymene)] (**5**)	*o*-xylene	K_2CO_3	60
3	**5**	*o*-xylene	K_2CO_3	51[b]
4	**5**	DMF	K_2CO_3	---
5	**5**	H_2O	K_2CO_3	---
6	**5**	*o*-xylene	NaOAc	13
7	**5**	*o*-xylene	KOAc	17
8	**5**	*o*-xylene	K_3PO_4	46
9	**5**	***o*-xylene**	**Na_2CO_3**	**69**
10	---	*o*-xylene	Na_2CO_3	---

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), [Ru] (5.0 mol %), base (1.50 mmol), solvent (2.0 mL), 140 °C, 24 h; isolated yields. [b] **5** (2.5 mol %).

With optimized reaction conditions in hand, we next studied the effect exerted by the substitution pattern of the pyridine moiety in substrates **1** on the catalytic performance (Scheme 1). Thus, the pyridine **1b** being devoid of an additional substituent led unfortunately to unsatisfactory results. Among various 3-substituted pyridines, the substrate **1a** bearing a 3-methyl group was found to be optimal.

Scheme 1. Variation of the Pyridine Substitution Pattern

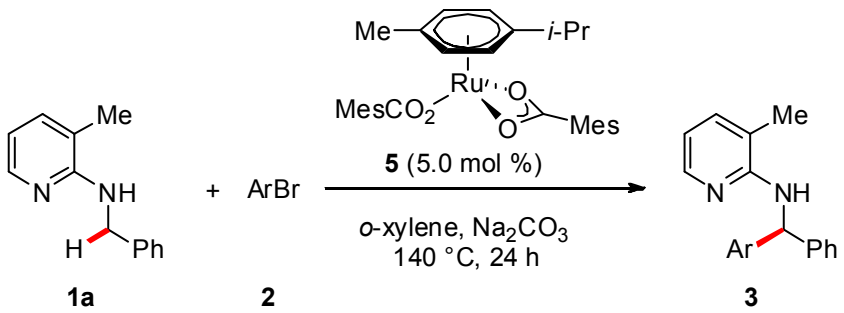


1 **2a**

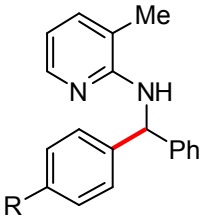
R = H (**3ba**): ---
R = OMe (**3ca**): < 8%
R = Ph (**3da**): 20%
R = CF_3 (**3ea**): 48%
R = Me (**3aa**): 69%

Subsequently, we evaluated the versatility of the C(sp^3)–H bond arylation, employing a set of representative (hetero)aryl bromides **2b**–**2k** as the electrophiles (Scheme 2). The well-defined biscarboxylate catalyst **5** proved to be broadly applicable, and its remarkable functional group tolerance allowed *inter alia* for the chemoselective conversion of substrates **2**, bearing a synthetically useful chloride for subsequent derivatization (**2e**) or a free (*NH*)-indole (**2k**).

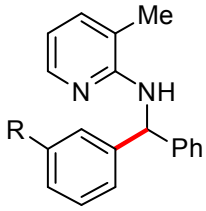
Scheme 2. Scope of C(sp^3)–H Bond Arylation with Bromides **2**



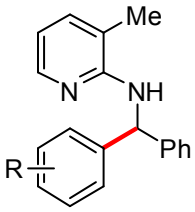
1a **2** **3**



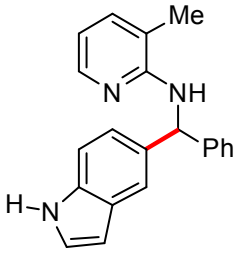
R = Me (**3ab**): 62%
R = OMe (**3ac**): 69%
R = *t*-Bu (**3ad**): 65%
R = Cl (**3ae**): 53% (150 °C)



R = Me (**3af**): 63%
R = OMe (**3ag**): 58%



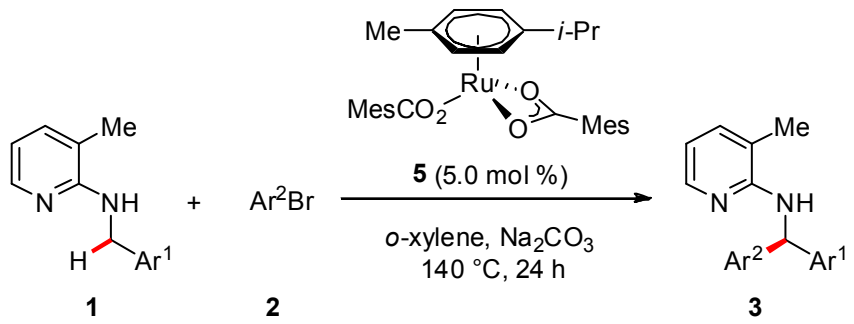
R = 3,5-Me_2 (**3ah**): 63%
R = 3,4-$(OMe)_2$ (**3ai**): 55%
R = 3,4,5-$(OMe)_3$ (**3aj**): 54%



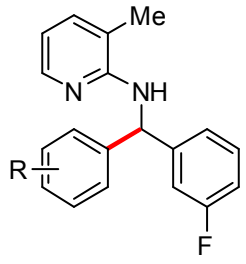
3ak: 65%

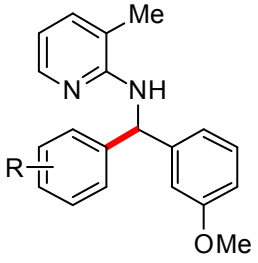
Likewise, a variety of benzyl amines **1f**–**1k** featuring substituents in *para*-, *meta*- or *ortho*-position proved to be viable substrates for the C(sp^3)–H bond arylation protocol (Scheme 3).

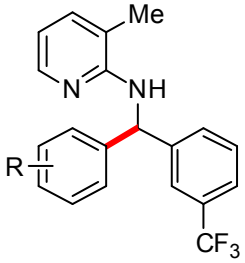
Scheme 3. C(sp^3)–H Bond Arylation with Amines **1**



1 **2** **3**



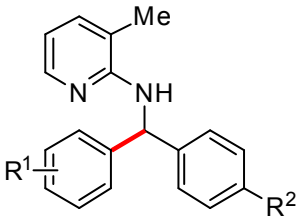


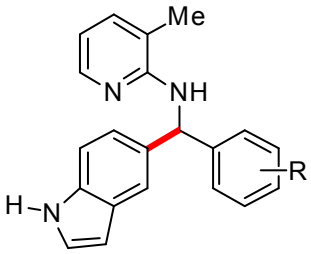


R = 4-OMe (**3fc**): 79%
R = 4-*t*-Bu (**3fd**): 80%
R = 3-OMe (**3fg**): 75%

R = 4-*t*-Bu (**3gd**): 71%
R = 3-OMe (**3gg**): 69%

R = 4-OMe (**3hc**): 52%
R = 4-*t*-Bu (**3hd**): 51%
R = 3-OMe (**3hg**): 67%





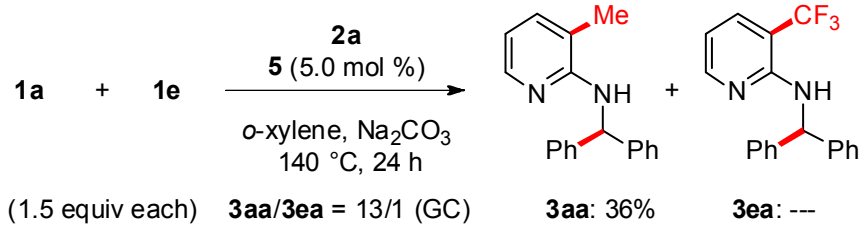
R^1 = 4-*t*-Bu, R^2 = F (**3id**): 64%
R^1 = 3-OMe, R^2 = F (**3ig**): 67%
R^1 = 4-*t*-Bu, R^2 = CF_3 (**3jd**): 61%
R^1 = 3-Me, R^2 = CF_3 (**3jf**): 59%

R = 3-F (**3fk**): 72%
R = 3-OMe (3**gk**): 60%
R = 3-CF_3 (**3hk**): 61%
R = 2-F (**3kk**): 51%

Mechanistic Studies. Given the remarkably high catalytic activity of complex **5**, we became intrigued by studying its mode of action. To this end, we performed intermolecular competition experiments with

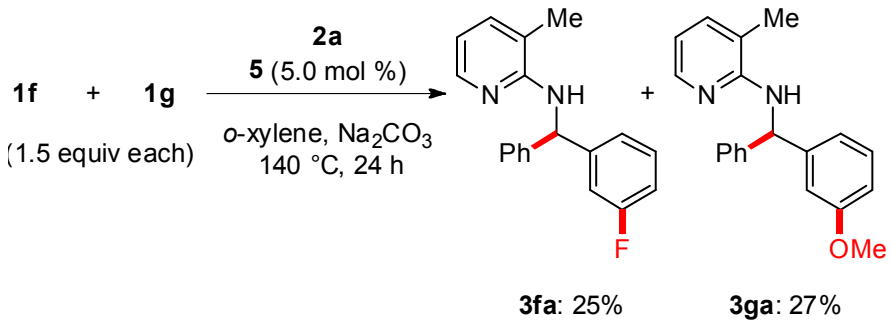
substrates **1a** and **1e**, which clearly highlighted the importance of the electron-donating abilities of the Lewis-basic directing group (Scheme 4).

Scheme 4. Competition Experiment with Substituted Pyridines



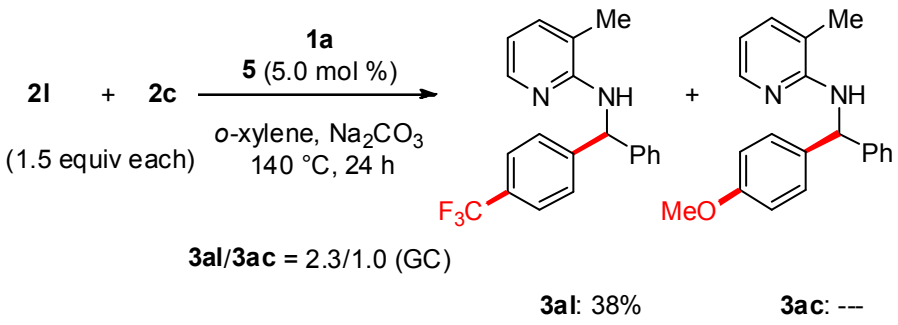
Conversely, the electronic nature of the substituents on the aromatic moiety of the benzyl amines **1** was found to be of minor importance for the efficacy of the catalyzed C(sp^3)–H bond functionalization (Scheme 5).

Scheme 5. Intermolecular Competition Experiments between Substituted Amines **1**



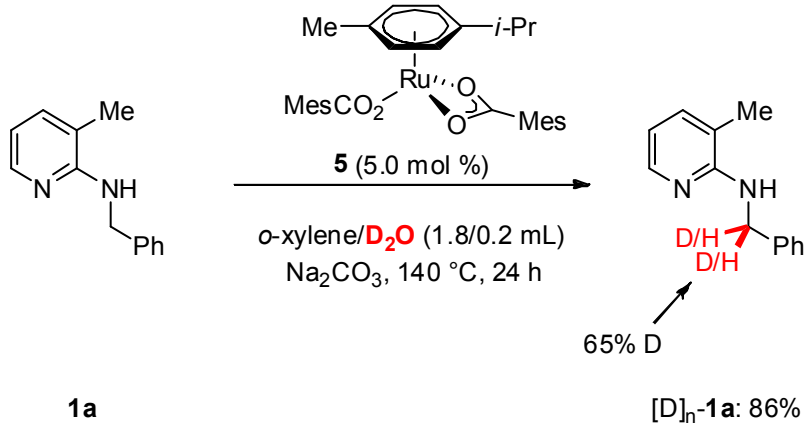
Intermolecular competition experiments with differently substituted organic electrophiles **2** revealed the more electron-deficient[12] aryl bromide **2k** to react preferentially (Scheme 6).

Scheme 6. Competition Experiment between Electrophiles **2c** and **2l**



Finally, we performed studies in the presence of D_2O, which unravelled a significant H/D exchange (Scheme 7), thereby providing strong support for a reversible C(sp^3)–H bond cleavage.

Scheme 7. H/D Exchange in the Presence of D_2O



Conclusions

In summary, we have reported on the unprecedented use of well-defined ruthenium(II) biscarboxylate complexes for C(sp^3)–H bond functionalizations. Particularly, the highly chemoselective complex [Ru(O_2CMes)$_2$(*p*-cymene)] (**5**) was found to be broadly applicable in direct arylations with aryl and even

heteroaryl bromides, which also allowed for the use of low loadings of the carboxylate (co)catalyst. Detailed mechanistic studies provided strong evidence for an initial, reversible (sp^3)–H bond activation.

Experimental Section

General remarks. Catalytic reactions were carried out under an inert atmosphere of nitrogen using predried glassware. Compounds **1a**–**1k**[8] were synthesized according to previously described methods. All other chemicals were used as received without further purification unless otherwise specified. *o*-Xylene was dried over sodium. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. NMR spectra were recorded in the solvent indicated; chemical shifts (δ) are given in ppm. High resolution mass spectrometry (HRMS): FTICR.

Representative Procedure for Ruthenium–Catalyzed C(sp^3)–H Bond Arylations: Synthesis of *N*-Benzhydryl-3-methylpyridin-2-amine (**3aa**): *N*-Benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol, 1.0 equiv), bromobenzene (**2a**) (118 mg, 0.75 mmol, 1.5 equiv), [Ru(O_2CMes)$_2$(*p*-cymene)] (**5**) (14 mg, 0.025 mmol, 5.0 mol %), Na_2CO_3 (159 mg, 1.50 mmol, 3.0 equiv) and *o*-xylene (2.0 mL) were stirred under an atmosphere of nitrogen at 140 °C for 24 h. At ambient temperature, the suspension was filtered through a short pad of Celite®, which was then washed with CH_2Cl_2 (50 mL). Evaporation of the solvent *in vacuo* and purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3aa** (95 mg, 69%) as a colorless solid (M.p. = 91–93 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 (dd, J = 5.2, 1.7 Hz, 1H), 7.39–7.21 (m, 11H), 6.59–6.48 (m, 2H), 4.67 (d, J = 7.0 Hz, 1H), 2.15 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.6 (C_q), 145.6 (CH), 143.5 (C_q), 136.9 (CH), 128.4 (CH), 127.5 (CH), 126.1 (CH), 116.3 (C_q), 113.1 (CH), 58.4 (CH), 17.0 (CH_3). IR (neat): 3438, 1595, 1485, 1465, 1057, 695 cm^{-1}. MS (EI) *m/z* (relative intensity): 274 ([M^+], 87), 182 (55), 167 (100), 165 (52), 98 (50), 43 (69). HR-MS (EI) *m/z* calcd for $C_{19}H_{18}N_2^+$ 274.1470, found 274.1462. The spectral data were in accordance with those reported in the literature.[7a]

***N*-Benzhydryl-3-phenylpyridin-2-amine (3da):** The representative procedure was followed using *N*-benzyl-3-phenylpyridin-2-amine (**1d**) (130 mg, 0.50 mmol) and bromobenzene (**2a**) (118 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3da** (34 mg, 20%) as a colorless solid. M.p. = 90–92 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.08 (dd, J = 5.1, 1.8 Hz, 1H), 7.48–7.16 (m, 16H), 6.65 (dd, J = 7.3, 5.0 Hz, 1H), 6.52 (d, J = 7.5 Hz, 1H), 5.20 (d, J = 7.5 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 154.4 (C_q), 147.2 (CH), 143.3 (C_q), 137.9 (C_q), 137.1 (CH), 129.2 (CH), 128.8 (CH), 128.4 (CH), 127.8 (CH), 127.4 (CH), 126.9 (CH), 122.2 (C_q), 113.2 (CH), 58.5 (CH). IR (neat): 3447, 3023, 1596, 1463, 1280, 767, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 336 ([M^+], 100), 335 (20), 182 (45), 167 (87), 165 (45). HR-MS (EI) *m/z* calcd for $C_{24}H_{20}N_2^+$ 336.1626, found 336.1629. The spectral data were in accordance with those reported in the literature.[7a]

***N*-Benzhydryl-3-(trifluoromethyl)pyridin-2-amine (3ea):** The representative procedure was followed using *N*-benzyl-3-(trifluoromethyl)pyridin-2-amine (**1e**) (126 mg, 0.50 mmol) and bromobenzene (**2a**) (118 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 50/1 → 40/1 → 30/1) yielded **3ea** (78 mg, 48%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.20 (ddd, J = 5.0, 1.9, 1.0 Hz, 1H), 7.67 (ddd, J = 7.6, 1.8, 0.8 Hz, 1H), 7.38–7.15 (m, 9H), 6.70–6.46 (m, 2H), 5.46 (d, J = 6.5 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 153.5 (C_q), 151.8 (CH), 142.6 (C_q), 134.9 (CH, J = 10.3 Hz), 128.6 (CH), 127.4 (CH), 127.2 (CH), 124.5 (C_q, J = 273.9 Hz), 111.9 (CH), 108.7 (C_q, J = 31.3 Hz), 58.4 (CH). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –63.7 (s). IR (neat): 3476, 1602, 1582, 1493, 1465, 1301, 1102, 1024, 697 cm^{-1}. MS (EI) *m/z* (relative intensity): 328 ([M^+], 90), 251 (25), 182 (45), 167 (100), 152 (35), 128 (30), 104 (20), 77 (15). HR-MS (EI) *m/z* calcd for $C_{19}H_{15}F_3N_2^+$ 328.1187, found 328.1176. The spectral data were in accordance with those reported in the literature.[7a]

3-Methyl-*N*-[phenyl(*p*-tolyl)methyl]pyridin-2-amine (3ab): The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-4-methylbenzene (**2b**) (128 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-

hexane/EtOAc 99/1 → 98/2) yielded **3ab** (90 mg, 62%) as a colorless solid. M.p. = 103–105 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 5.1, 1.7 Hz, 1H), 7.36–7.09 (m, 10H), 6.55–6.46 (m, 2H), 4.63 (d, J = 7.0 Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.7 (C_q), 145.6 (CH), 143.6 (C_q), 140.5 (C_q), 136.9 (CH), 136.6 (C_q), 129.2 (CH), 128.4 (CH), 127.5 (CH), 127.4 (CH), 126.9 (CH), 116.3 (C_q), 112.9 (CH), 58.2 (CH), 21.0 (CH_3), 17.1 (CH_3). IR (neat): 3446, 3024, 1597, 1464, 771, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 288 ([M^+], 75), 196 (33), 181 (100), 210 (35), 166 (38), 165 (40). HR-MS (EI) *m/z* calcd for $C_{20}H_{20}N_2^+$ 288.1626, found 288.1637. The spectral data were in accordance with those reported in the literature.[7a]

***N*-[(4-Methoxyphenyl)(phenyl)methyl]-3-methylpyridin-2-amine (3ac):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-4-methoxybenzene (**2c**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3ac** (105 mg, 69%) as a colorless solid. M.p. = 60–62 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 5.1, 1.7 Hz, 1H), 7.34–7.16 (m, 8H), 6.83 (dt, J = 8.7, 3.0 Hz, 2H), 6.50 (dd, J = 7.2, 5.1 Hz, 1H), 6.40(d, J = 7.0 Hz, 1H), 4.60 (d, J = 7.0 Hz, 1H), 3.76 (s, 3H), 2.12 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.6 (C_q), 155.7 (C_q), 145.6 (CH), 143.7 (C_q), 136.8 (CH), 135.7 (C_q), 128.7 (CH), 128.4 (CH), 127.4 (CH), 126.9 (CH), 116.2 (C_q), 113.8 (CH), 113.0 (CH), 57.8 (CH), 55.2 (CH_3), 17.1 (CH_3). IR (neat): 3026, 1596, 1508, 1482, 1243, 1172, 1029, 697 cm^{-1}. MS (EI) *m/z* (relative intensity): 304 ([M^+], 43), 198 (18), 197 (100), 153 (22). HR-MS (EI) *m/z* calcd $C_{20}H_{20}N_2O^+$ 304.1576, found 304.1570. The spectral data were in accordance with those reported in the literature.[7a]

***N*-[{4-(*tert*-Butyl)phenyl}(phenyl)methyl]-3-methylpyridin-2-amine (3ad):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-4-(*tert*-butyl)benzene (**2d**) (162 mg, 0.76 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3ad** (108 mg, 65%) as a colorless solid. M.p. = 121–123 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.36–7.19 (m, 10H), 6.50 (dd, J = 7.1, 4.8 Hz, 2H), 4.67 (d, J = 7.1 Hz, 1H), 2.13 (s, 3H), 1.29 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.7

(C_q) , 149.8 (C_q), 145.6 (CH), 143.6 (C_q), 140.4 (C_q), 136.8 (CH), 128.4 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 125.4 (CH), 116.3 (C_q), 112.9 (CH), 58.0 (CH), 34.4 (C_q), 31.3 (CH_3), 17.1 (CH_3). IR (neat): 3426, 2958, 1596, 1465, 785, 698 cm^{-1}. MS (EI) *m/z* (relative intensity): 330 ([M^+], 100), 238 (32), 223 (93), 193 (20). HR-MS (EI) *m/z* calcd $C_{23}H_{26}N_2^+$ 330.2096, found 330. 2100. The spectral data were in accordance with those reported in the literature.[7a]

***N*-[(4-Chlorophenyl)(phenyl)methyl]-3-methylpyridin-2-amine (3ae):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-4-chlorobenzene (**2e**) (143 mg, 0.75 mmol) at 150 °C. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3ae** (82 mg, 53%) as a colorless solid. M.p. = 116–118 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.36–7.21 (m, 10H), 6.53 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.46 (d, *J* = 6.7 Hz, 1H), 4.58 (d, *J* = 6.7 Hz, 1H), 2.12 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.5 (C_q), 145.6 (CH), 143.0 (C_q), 141.1 (C_q), 136.1 (CH), 132.6 (C_q), 128.8 (CH), 128.7 (CH), 128.5 (CH), 127.6 (CH), 127.3 (CH), 116.4 (C_q), 113.4 (CH), 58.0 (CH), 17.0 (CH_3). IR (neat): 3445, 2925, 1596, 1483, 1464, 1087, 755, 695 cm^{-1}. MS (EI) *m/z* (relative intensity): 308 ([M^+], 100), 216 (40), 201 (65), 166 (43), 165 (77). HR-MS (EI) *m/z* calcd for $C_{19}H_{17}ClN_2^+$ 308.1080, found 308.1076. The spectral data were in accordance with those reported in the literature.[7a]

3-Methyl-*N*-[phenyl(3-tolyl)methyl]pyridin-2-amine (3af): The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-3-methylbenzene (**2f**) (135 mg, 0.78 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3af** (91 mg, 63%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 5.2, 1.7 Hz, 1H), 7.39–7.02 (m, 10H), 6.56–6.48 (m, 2H), 4.65 (d, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 2.14 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.7 (C_q), 145.6 (CH), 143.5 (C_q), 143.4 (C_q), 138.1 (C_q), 136.8 (CH), 128.4 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 127.5 (CH), 126.9 (CH), 124.5 (CH), 116.2 (C_q), 112.9 (CH), 58.4 (CH), 21.5 (CH_3), 17.1 (CH_3). IR (neat): 3025, 1596, 1482, 1463, 1406, 773, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 288 ([M^+], 100), 287 (18), 196 (55),

181 (100), 165 (58). HR-MS (EI) *m/z* calcd for $C_{20}H_{20}N_2^+$ 288.1626, found 288.1619. The spectral data were in accordance with those reported in the literature.[7a]

***N*-[(3-Methoxyphenyl)(phenyl)methyl]-3-methylpyridin-2-amine (3ag):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-3-methoxybenzene (**2g**) (143 mg, 0.76 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3ag** (88 mg, 58%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.1, 1.9 Hz, 1H), 7.36–7.18 (m, 7H), 6.94–6.86 (m, 2H), 6.77 (ddd, J = 8.2, 2.5, 1.1 Hz, 1H), 6.60–6.45 (m, 2H), 4.64 (d, J = 6.9 Hz, 1H), 3.75 (s, 3H), 2.13 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.7 (C_q), 155.6 (C_q), 145.6 (CH), 145.1 (C_q), 143.3 (C_q), 136.9 (CH), 129.5 (CH), 128.5 (CH), 127.5 (CH), 127.0 (CH), 119.9 (CH), 116.3 (C_q), 113.5 (CH), 113.1 (CH), 112.0 (CH), 58.4 (CH), 55.1 (CH_3), 17.0 (CH_3). IR (neat): 2934, 1595, 1482, 1463, 1252, 1043, 773, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 304 ([M^+], 100), 303 (16), 212 (68), 197 (84). HR-MS (EI) *m/z* calcd for $C_{20}H_{20}N_2O^+$ 304.1576, found 304.1588. The spectral data were in accordance with those reported in the literature.[7c]

***N*-[(3,5-Dimethylphenyl)(phenyl)methyl]-3-methylpyridin-2-amine (3ah):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and bromo-3,5-dimethylbenzene (**2h**) (142 mg, 0.76 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3ah** (96 mg, 63%) as a colorless solid. M.p. = 117–119 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.34–7.18 (m, 6H), 6.92 (s, 2H), 6.87 (s, 1H), 6.50 (dd, J = 7.1, 5.1 Hz, 1H), 6.44 (d, J = 7.1, 1H), 4.63 (d, J = 7.1 Hz, 1H), 2.26 (s, 6H), 2.13 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.7 (C_q), 145.7 (CH), 143.6 (C_q), 143.4 (C_q), 137.9 (C_q), 136.8 (CH), 128.8 (CH), 128.4 (CH), 127.4 (CH), 126.8 (CH), 125.4 (CH), 116.2 (C_q), 112.9 (CH), 108.7 (C_q), 58.4 (CH), 21.4 (CH_3), 17.1 (CH_3). IR (neat): 3446, 2918, 1596, 1465, 1404, 755, 698 cm^{-1}. MS (EI) *m/z* (relative intensity): 302 ([M^+] 100), 301 (14), 210 (35), 195 (75), 165 (35). HR-MS (EI) *m/z* calcd for $C_{21}H_{22}N_2^+$ 302.1783, found 302. 1772.

***N*-[(3,4-Dimethoxyphenyl)(phenyl)methyl]-3-methylpyridin-2-amine (3ai):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and 4-bromo-1,2-dimethoxybenzene (**2i**) (173 mg, 0.79 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded **3ai** (91 mg, 55%) as a light brown solid. M.p.= 134–136 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 5.2, 1.8 Hz, 1H), 7.37–7.15 (m, 6H), 6.87–6.74 (m, 3H), 6.50 (dd, J = 7.0, 5.2 Hz, 1H), 6.44 (d, J = 7.0 Hz, 1H), 4.59 (d, J = 7.0 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.11 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.7 (C_q), 148.9 (C_q), 148.0 (C_q), 145.6 (CH), 143.5 (C_q), 136.9 (CH), 136.1 (C_q), 128.4 (CH), 127.4 (CH), 126.9 (CH), 119.5 (CH), 116.2 (C_q), 113.1 (CH), 111.2 (CH), 111.0 (CH), 58.1 (CH), 55.8 (CH_3), 55.8 (CH_3), 17.1 (CH_3). IR (neat): 3398, 3005, 2934, 1595, 1512, 1269, 1137, 1021, 701 cm^{-1}. MS (EI) *m/z* (relative intensity): 334 ([M^+], 52), 228(16), 227 (100). HR-MS (EI) *m/z* calcd for $C_{21}H_{22}N_2O_2^+$ 334.1681, found 334.1673.

3-Methyl-*N*-[(3,4,5-trimethoxyphenyl)(phenyl)methyl]pyridin-2-amine (3aj): The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and 5-bromo-1,2,3-trimethoxybenzene (**2j**) (185 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 95/5 → 90/10) yielded **3aj** (97 mg, 54%) as a violet solid. M.p. = 174–176 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.34–7.19 (m, 6H), 6.55–6.49 (m, 3H), 6.44 (d, J = 6.9 Hz, 1H), 4.60 (d, J = 6.9 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 6H), 2.13 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.6 (C_q), 153.1 (C_q), 145.5 (CH), 143.2 (C_q), 139.0 (C_q), 136.9 (CH), 136.8 (C_q), 128.4 (CH), 127.3 (CH), 126.9 (CH), 116.2 (C_q), 113.1 (CH), 104.7 (CH), 60.7 (CH_3), 58.5 (CH), 55.9 (CH_3), 16.9 (CH_3). IR (neat): 3399, 2970, 1589, 1487, 1460, 1157, 1008 cm^{-1}. MS (EI) *m/z* (relative intensity): 364 ([M^+], 58), 349 (15), 258 (15), 257 (100). HR-MS (EI) *m/z* calcd for $C_{22}H_{24}N_2O_3^+$ 364.1787, found 364.1783.

***N*-[(1*H*-Indol-5-yl)(phenyl)methyl]-3-methylpyridin-2-amine (3ak):** The representative procedure was followed using *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol) and 5-bromo-1*H*-indole (**2k**) (147 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-

pentane/EtOAc 5/1 → 2/1) yielded **3ak** (102 mg, 65%) as a colorless solid. M. p. = 148–149 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.57 (s_{br}, 1H), 7.98 (dd, J = 5.1, 1.7 Hz, 1H), 7.60–7.54 (m, 1H), 7.42–7.35 (m, 2H), 7.32–7.20 (m, 5H), 7.16–7.04 (m, 2H), 6.63 (d, J = 6.7 Hz, 1H), 6.52 (dd, J = 7.1, 5.1 Hz, 1H), 6.56–6.45 (m, 1H), 4.78 (d, J = 6.7 Hz, 1H), 2.15 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.8 (C_q), 145.5 (CH), 144.0 (C_q), 136.8 (CH), 135.0 (C_q), 134.9 (C_q), 128.2 (CH), 127.8 (C_q), 127.4 (CH), 126.6 (CH), 124.8 (CH), 122.1 (CH), 119.4 (CH), 116.3 (C_q), 112.8 (CH), 111.3 (CH), 102.4 (CH), 58.9 (CH), 17.1 (CH_3). IR (neat): 3641, 3024, 1599, 1467, 1427, 1277, 1107, 896, 799, 772, 723, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 313 ([M^+], 85), 221 (45), 207 (45), 206 (100), 204 (55), 179 (40), 178 (30), 92 (25), 65 (10). HR-MS (EI) *m/z* calcd for $C_{21}H_{19}N_3^+$ 313.1579, found 313.1574.

***N*-[(3-Fluorophenyl)(4-methoxyphenyl)methyl]-3-methylpyridin-2-amine (3fc):** The representative procedure was followed using *N*-(3-fluorobenzyl)-3-methylpyridin-2-amine (108 mg, 0.50 mmol) (**1f**) and 4-bromoanisole (**2c**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 10/1) yielded **3fc** (127 mg, 79%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (dd, J = 5.1, 1.7 Hz, 1H), 7.25–7.17 (m, 4H), 7.08 (dd, J = 7.7, 1.7 Hz, 1H), 7.01 (dt, J = 10.2, 2.1 Hz, 1H), 6.93–6.81 (m, 3H), 6.52 (dd, J = 7.1, 5.1 Hz, 1H), 6.42 (d, J = 6.7 Hz, 1H), 4.54 (d, J = 6.7 Hz, 1H), 3.77 (s, 3H), 2.12 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.0 (C_q, J = 245.5 Hz), 158.8 (C_q), 155.5 (C_q), 146.4 (C_q, J = 6.4 Hz), 145.6 (CH), 137.0 (CH), 135.2 (C_q), 129.8 (CH, J = 8.2 Hz), 128.8 (CH), 123.0 (CH, J = 2.8 Hz), 116.4 (C_q), 114.2 (CH, J = 22.0 Hz), 114.0 (CH), 113.6 (CH, J = 21.3 Hz), 113.3 (CH), 57.6 (CH), 55.3 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –113.3 (ddd, J = 10.1, 8.7, 5.9 Hz). IR (neat): 3450, 2932, 1597, 1509, 1482, 1463, 1245, 1175, 1031, 775 cm^{-1}. MS (EI) *m/z* (relative intensity): 322 ([M^+], 65), 230 (25), 215 (100), 183 (20), 171 (25), 92 (20), 65 (12). HR-MS (EI) *m/z* calcd for $C_{20}H_{19}FN_2O^+$ 322.1481, found 322.1471.

***N*-[(4-(*tert*-Butyl)phenyl)(3-fluorophenyl)methyl]-3-methylpyridin-2-amine (3fd):** The representative procedure was followed using *N*-(3-fluorobenzyl)-3-methylpyridin-2-amine (108 mg,

0.50 mmol) (**1f**) and bromo-4-(*tert*-butyl)benzene (**2d**) (160 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 30/1 → 20/1) yielded **3fd** (140 mg, 80%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, J = 5.1, 1.7 Hz, 1H), 7.35–7.28 (m, 2H), 7.25–7.15 (m, 4H), 7.10 (dd, J = 7.6, 1.7 Hz, 1H), 7.06–6.98 (m, 1H), 6.93–6.80 (dt, J = 8.5, 2.6 Hz, 1H), 6.50 (dd, J = 7.1, 5.1 Hz, 1H), 6.44 (d, J = 6.7 Hz, 1H), 4.60 (d, J = 6.7 Hz, 1H), 2.11 (s, 3H), 1.28 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.0 (C_q, J = 245.5 Hz), 155.5 (C_q), 150.2 (C_q), 146.4 (C_q, J = 6.6 Hz), 145.6 (CH), 139.9 (C_q), 136.9 (CH), 129.7 (CH, J = 8.2 Hz), 127.4 (CH), 125.6 (CH), 123.0 (CH, J = 2.7 Hz), 116.3 (C_q), 114.2 (CH, J = 21.9 Hz), 113.6 (CH, J = 21.3 Hz), 113.3 (CH), 57.8 (CH, J = 1.6 Hz), 34.5 (C_q), 31.3 (CH_3), 17.1 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –113.3 (ddd, J = 10.2, 8.7, 5.9 Hz). IR (neat): 2962, 1596, 1481, 1463, 1242, 776 cm^{-1}. MS (EI) *m/z* (relative intensity): 348 ([M^+], 100), 256 (50), 241 (95), 226 (28), 211 (25), 183 (18), 92 (20). HR-MS (EI) *m/z* calcd for $C_{23}H_{25}FN_2^+$ 348.2002, found 348.1999.

***N*-[(3-Fluorophenyl)(3-methoxyphenyl)methyl]-3-methylpyridin-2-amine (3fg):** The representative procedure was followed using *N*-(3-fluorobenzyl)-3-methylpyridin-2-amine (108 mg, 0.50 mmol) (**1f**) and 3-bromoanisole (**2g**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 30/1 → 20/1) yielded **3fg** (121 mg, 75%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (dd, J = 5.0, 1.6 Hz, 1H), 7.29–7.19 (m, 3H), 7.09 (ddt, J = 7.7, 1.8, 0.8 Hz, 1H), 7.05–6.98 (m, 1H), 6.91–6.84 (m, 3H), 6.79 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.52 (dd, J = 7.1, 5.0 Hz, 1H), 6.44 (d, J = 6.8 Hz, 1H), 4.59 (d, J = 6.8 Hz, 1H), 3.75 (s, 3H), 2.13 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.0 (C_q, J = 245.7 Hz), 159.8 (C_q), 155.4 (C_q), 146.1 (C_q, J = 6.6 Hz), 145.6 (CH), 144.6 (C_q), 137.0 (CH), 129.9 (CH, J = 8.2 Hz), 129.7 (CH), 123.1 (CH, J = 2.8 Hz), 120.0 (CH), 116.4 (C_q), 114.3 (CH, J = 22.0 Hz), 113.8 (CH, J = 21.3 Hz), 113.7 (CH), 113.4 (CH), 112.4 (CH), 58.1 (CH, J = 1.9 Hz), 55.2 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –113.2 (ddd, J = 10.3, 8.8, 5.9 Hz). IR (neat): 3450, 2937, 1595, 1481, 1463, 1244, 1043, 776 cm^{-1}. MS (EI) *m/z* (relative intensity):

322 ([M^+], 100), 230 (70), 215 (58), 183 (27), 171 (17), 107 (18), 92 (20). HR-MS (EI) *m/z* calcd for $C_{20}H_{19}FN_2O^+$ 322.1481, found 322.1482.

***N*-[{4-(*tert*-Butyl)phenyl}(3-methoxyphenyl)methyl]-3-methylpyridin-2-amine (3gd):** The representative procedure was followed using *N*-(3-methoxybenzyl)-3-methylpyridin-2-amine (**1g**) (114 mg, 0.50 mmol) and bromo-4-(*tert*-butyl)benzene (**2d**) (160 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1) yielded **3gd** (128 mg, 71%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.97 (dd, J = 5.1, 1.7 Hz, 1H), 7.32 (dt, J = 8.6, 2.1 Hz, 2H), 7.25–7.20 (m, 4H), 6.95–6.89 (m, 2H), 6.77 (ddd, J = 8.1, 2.5, 1.0 Hz, 1H), 6.53–6.45 (m, 2H), 4.66 (d, J = 7.2 Hz, 1H), 3.75 (s, 3H), 2.12 (s, 3H), 1.30 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 159.6 (C_q), 155.7 (C_q), 149.8 (C_q), 145.6 (CH), 145.3 (C_q), 140.3 (C_q), 136.8 (CH), 129.3 (CH), 127.2 (CH), 125.4 (CH), 119.8 (CH), 116.2 (C_q), 113.5 (CH), 113.0 (CH), 111.8 (CH), 58.0 (CH), 55.1 (CH_3), 34.4 (C_q), 31.3 (CH_3), 17.1 (CH_3). IR (neat): 3448, 2960, 1596, 1482, 1463, 1523, 1045, 775, 730 cm^{-1}. MS (EI) *m/z* (relative intensity): 360 ([M^+], 93), 268 (60), 253 (100), 238 (25), 223 (25), 197 (20), 165 (17), 92 (20). HR-MS (EI) *m/z* calcd for $C_{24}H_{28}N_2O^+$ 360.2202, found 360.2193.

***N*-[Bis(3-methoxyphenyl)methyl]-3-methylpyridin-2-amine (3gg):** The representative procedure was followed using *N*-(3-methoxybenzyl)-3-methylpyridin-2-amine (**1g**) (114 mg, 0.50 mmol) and 3-bromoanisole (**2g**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1 → 5/1) yielded **3gg** (115 mg, 69%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.97 (dd, J = 5.0, 1.6 Hz, 1H), 7.27–7.19 (m, 3H), 6.94–6.90 (m, 4H), 6.77 (ddd, J = 8.2, 2.5, 1.0 Hz, 2H), 6.51 (dd, J = 7.2, 5.1 Hz, 1H), 6.46 (d, J = 7.0 Hz, 1H), 4.64 (d, J = 7.0 Hz, 1H), 3.75 (s, 6H), 2.13 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.6 (C_q), 155.6 (C_q), 145.6 (CH), 145.0 (C_q), 136.9 (CH), 129.4 (CH), 119.8 (CH), 116.3 (C_q), 113.5 (CH), 113.1 (CH), 112.0 (CH), 58.3 (CH), 55.1 (CH_3), 17.0 (CH_3). IR (neat): 3411, 2998, 1593, 1463, 1431, 1248, 1162, 1033, 777, 694 cm^{-1}. MS (EI)

m/z (relative intensity): 334 ([M^+], 100), 242 (70), 227 (80), 212 (25), 196 (25), 92 (20). HR-MS (EI) *m/z* calcd for $C_{21}H_{22}N_2O_2^+$ 334.1681, found 334.1685.

***N*-[(4-Methoxyphenyl){3-(trifluoromethyl)phenyl}methyl]-3-methylpyridin-2-amine (3hc):** The representative procedure was followed using 3-methyl-*N*-[3-(trifluoromethyl)benzyl]pyridin-2-amine (133 mg, 0.50 mmol) (**1h**) and 4-bromoanisole (**2c**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 10/1 → 5/1) yielded **3hc** (97 mg, 52%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.2, 1.5 Hz, 1H), 7.62 (s, 1H), 7.56–7.36 (m, 3H), 7.28–7.18 (m, 3H), 6.91–6.84 (m, 2H), 6.55 (dd, J = 7.2, 5.2 Hz, 1H), 6.51 (d, J = 6.5 Hz, 1H), 4.60 (d, J = 6.5 Hz, 1H), 3.78 (s, 3H), 2.14 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.9 (C_q), 155.4 (C_q), 145.5 (CH), 144.7 (C_q), 137.0 (CH), 135.0 (C_q), 130.7 (CH), 130.5 (C_q, J = 31.1 Hz), 128.9 (CH), 128.7 (CH), 124.2 (C_q, J = 273.9 Hz), 124.0 (CH, J = 3.8 Hz), 123.6 (CH, J = 3.8 Hz), 116.4 (C_q), 114.1 (CH), 113.4 (CH), 57.8 (CH), 55.2 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.4 (s). IR (neat): 3449, 2935, 1597, 1464, 1325, 1247, 1117, 1070, 701 cm^{-1}. MS (EI) *m/z* (relative intensity): 372 ([M^+], 67), 266 (35), 265 (100), 153 (15), 92 (25). HR-MS (EI) *m/z* calcd for $C_{21}H_{19}F_3N_2O^+$ 372.1449, found 372.1447.

***N*-[{4-(*tert*-Butyl)phenyl}{3-(trifluoromethyl)phenyl}methyl]-3-methylpyridin-2-amine (3hd):** The representative procedure was followed using 3-methyl-*N*-[3-(trifluoromethyl)benzyl]pyridin-2-amine (**1h**) (133 mg, 0.50 mmol) and bromo-4-(*tert*-butyl)benzene (**2d**) (160 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1) yielded **3hd** (102 mg, 51%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (dd, J = 5.2, 1.6 Hz, 1H), 7.64 (s, 1H), 7.54–7.45 (m, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.37–7.31 (m, 2H), 7.26–7.16 (m, 3H), 6.53 (dd, J = 7.2, 5.1 Hz, 1H), 6.51 (d, J = 6.6 Hz, 1H), 4.63 (d, J = 6.6 Hz, 1H), 2.14 (s, 3H), 1.30 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.5 (C_q), 150.4 (C_q), 145.6 (CH), 144.6 (C_q), 139.7 (C_q), 137.0 (CH), 130.7 (CH), 130.6 (C_q, J = 29.7 Hz), 128.7 (CH), 127.4 (CH), 125.7 (CH), 124.2 (C_q, J = 272.3 Hz), 124.0 (CH,

J = 3.9 Hz), 123.6 (CH, J = 3.8 Hz), 116.4 (C_q), 113.4 (CH), 58.0 (CH), 34.5 (C_q), 31.3 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.4 (s). IR (neat): 3452, 2963, 1597, 1464, 1326, 1160, 1119, 989, 704 cm^{-1}. MS (EI) *m/z* (relative intensity): 398 ([M^+], 100), 306 (50), 291 (90), 276 (25), 261 (20), 107 (20), 92 (20). HR-MS (EI) *m/z* calcd for $C_{24}H_{25}F_3N_2^+$ 398.1970, found 398.1975.

***N*-[(3-Methoxyphenyl){3-(trifluoromethyl)phenyl}methyl]-3-methylpyridin-2-amine (3hg):** The representative procedure was followed using 3-methyl-*N*-[3-(trifluoromethyl)benzyl]pyridin-2-amine (**1h**) (133 mg, 0.50 mmol) and 3-bromoanisole (**2g**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 30/1 → 20/1 → 10/1) yielded **3hg** (125 mg, 67%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (dd, J = 5.0, 1.6 Hz, 1H), 7.60 (s, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.43–7.36 (m, 1H), 7.28–7.20 (m, 2H), 6.89–6.78 (m, 3H), 6.54 (dd, J = 7.2, 5.0 Hz, 1H), 6.51 (d, J = 6.6 Hz, 1H), 4.61 (d, J = 6.6 Hz, 1H), 3.76 (s, 3H), 2.14 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 159.9 (C_q), 155.4 (C_q), 145.6 (CH), 144.3 (C_q), 137.1 (CH), 131.1 (C_q, J = 33.1 Hz), 130.8 (C_q), 130.7 (CH, J = 1.1 Hz), 129.8 (CH), 128.8 (CH), 124.2 (C_q, J = 273.2 Hz), 124.1 (CH, J = 3.8 Hz), 123.8 (CH, J = 3.8 Hz), 120.0 (CH), 116.5 (C_q), 113.8 (CH), 113.5 (CH), 112.5 (CH), 58.3 (CH), 55.2 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.4 (s). IR (neat): 3450, 2938, 1596, 1464, 1326, 1160, 1117, 1072, 699 cm^{-1}. MS (EI) *m/z* (relative intensity): 372 ([M^+], 100), 280 (80), 265 (55), 152 (15), 107 (35), 92 (30). HR-MS (EI) *m/z* calcd for $C_{21}H_{19}F_3N_2O^+$ 372.1449, found 372.1447.

***N*-[{4-(*tert*-Butyl)phenyl}(4-fluorophenyl)methyl]-3-methylpyridin-2-amine (3id):** The representative procedure was followed using *N*-(4-fluorobenzyl)-3-methylpyridin-2-amine (**1i**) (108 mg, 0.5 mmol) and 1-bromo-4-(*tert*-butyl)benzene (**2d**) (160 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 10/1) yielded **3id** (112 mg, 64%) as a colorless solid. M. p. = 66–67 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 (dd, J = 5.1, 1.6 Hz, 1H), 7.38–7.27 (m, 4H), 7.26–7.20 (m, 3H), 7.04–6.94 (m, 2H), 6.53 (dd, J = 7.2, 5.1 Hz, 1H), 6.49 (d, J = 6.8 Hz, 1H), 4.64 (d, J = 6.8 Hz, 1H), 2.14 (s, 3H), 1.32 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 161.7 (C_q, J = 244.3 Hz), 155.6 (C_q), 150.0 (C_q), 145.6 (CH), 140.3 (C_q), 139.3 (C_q, J = 2.9 Hz), 136.9 (CH), 128.9 (CH,

J = 8.1 Hz), 127.3 (CH), 125.5 (CH), 116.3 (C_q), 115.1 (CH, J = 21.2 Hz), 113.1 (CH), 57.5 (CH), 34.4 (C_q), 31.3 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –116.3 (tt, J = 8.5, 5.2 Hz). IR (neat): 3429, 2962, 1597, 1488, 1467, 1224, 838, 785 cm^{-1}. MS (EI) *m/z* (relative intensity): 348 ([M^+], 75), 256 (25), 241 (100), 226 (20), 211 (20), 92 (10). HR-MS (ESI) *m/z* calcd for $[C_{23}H_{25}FN_2+H]^+$ 349.2075, found 349.2071.

***N*-[(4-Fluorophenyl)(3-methoxyphenyl)methyl]-3-methylpyridin-2-amine (3ig):** The representative procedure was followed using *N*-(4-fluorobenzyl)-3-methylpyridin-2-amine (**1i**) (108 mg, 0.5 mmol) and 3-bromoanisole (**2g**) (140 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 10/1) yielded **3ig** (108 mg, 67%) as a colorless solid. M. p. = 96–97 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 5.0, 1.7 Hz, 1H), 7.35–7.17 (m, 4H), 7.02–6.92 (m, 2H), 6.92–6.84 (m, 2H) 6.79 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.52 (dd, J = 7.1, 5.1 Hz, 1H), 6.45 (d, J = 6.9 Hz, 1H), 4.59 (d, J = 6.9 Hz, 1H), 3.75 (s, 3H), 2.13 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 161.8 (C_q, J = 245.0 Hz), 159.8 (C_q), 155.5 (C_q), 145.6 (CH), 145.0 (C_q), 139.1 (C_q, J = 3.1 Hz), 137.0 (CH), 129.6 (CH), 129.0 (CH, J = 8.0 Hz), 119.9 (CH), 116.3 (C_q), 115.2 (CH, J = 21.3 Hz), 113.6 (CH), 113.3 (CH), 112.2 (CH), 57.8 (CH), 55.1 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –(115.9–116.1) (m). IR (neat): 3443, 1598, 1479, 1464, 1279, 1213, 1046, 780 cm^{-1}. MS (EI) *m/z* (relative intensity): 322 ([M^+], 95), 230 (55), 215 (100), 183 (30), 171 (20), 92 (20), 43 (45). HR-MS (EI) *m/z* calcd for $C_{20}H_{19}FN_2O^+$ 322.1481, found 322.1477.

***N*-[{4-(*tert*-Butyl)phenyl}{4-(trifluoromethyl)phenyl}methyl]-3-methylpyridin-2-amine (3jd):** The representative procedure was followed using 3-methyl-*N*-[4-(trifluoromethyl)benzyl]pyridin-2-amine (**1j**) (133 mg, 0.5 mmol) and bromo-4-(*tert*-butyl)benzene (**2d**) (160 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1) yielded **3jd** (122 mg, 61%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 (dd, J = 5.2, 1.5 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.0, 2H), 7.35 (dd, J = 8.4, 2.0 Hz, 2H), 7.23–7.17 (m, 3H), 6.54 (dd, J = 7.2, 5.1 Hz, 1H), 6.49 (d, J = 6.4 Hz, 1H), 4.64 (d, J = 6.4 Hz, 1H), 2.14 (s, 3H), 1.30 (s, 9H). ^{13}C-NMR (125 MHz,

$CDCl_3$): δ = 155.5 (C_q), 150.5 (C_q), 147.7 (C_q), 145.6 (CH), 139.7 (C_q), 137.0 (CH), 128.9 (C_q, J = 32.2 Hz), 127.5 (CH), 127.5 (CH), 125.7 (CH), 125.3 (CH, J = 3.7 Hz), 124.3 (C_q, J = 278.2 Hz), 116.4 (C_q), 113.4 (CH), 58.1 (CH), 34.5 (C_q), 31.3 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.3 (s). IR (neat): 2923, 1596, 1464, 1406, 1321, 1159, 1106, 1064, 1016 cm^{-1}. MS (EI) *m/z* (relative intensity): 398 ([M^+], 100), 306 (60), 291 (85), 276 (40), 261 (35), 107 (30), 92 (30), 57 (20). HR-MS (EI) *m/z* calcd for $C_{24}H_{25}F_3N_2^+$ 398.1970, found 398.1978.

3-Methyl-*N*-[3-tolyl{4-(trifluoromethyl)phenyl}methyl]pyridin-2-amine (3jf): The representative procedure was followed using 3-methyl-*N*-[4-(trifluoromethyl)benzyl]pyridin-2-amine (**1j**) (133 mg, 0.5 mmol) and 3-bromotoluene (**2f**) (128 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1) yielded **3jf** (106 mg, 59%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J = 5.2, 1.8 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.31–7.18 (m, 2H), 7.14–7.05 (m, 3H), 6.55 (dd, J = 7.1, 5.2 Hz, 1H), 6.49 (d, J = 6.6 Hz, 1H), 4.62 (d, J = 6.6 Hz, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.4 (C_q), 147.6 (C_q), 145.6 (CH), 142.7 (C_q), 135.5 (C_q), 137.0 (CH), 128.9 (C_q, J = 32.5 Hz), 128.7 (CH), 128.5 (CH), 128.3 (CH), 127.6 (CH), 125.3 (CH, J = 3.7 Hz), 124.8 (CH), 124.3 (C_q, J = 278.3 Hz), 116.4 (C_q), 113.5 (CH), 58.5 (CH), 21.5 (CH_3), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.3 (s). IR (neat): 3025, 1597, 1405, 1321, 1101, 1016, 777, 702 cm^{-1}. MS (EI) *m/z* (relative intensity): 356 ([M^+], 100), 264 (75), 249 (60), 165 (30), 107 (25), 92 (20), 65 (15). HR-MS (EI) *m/z* calcd for $C_{21}H_{19}F_3N_2^+$ 356.1500, found 356.1498.

***N*-[(3-Fluorophenyl)(1*H*-indol-5-yl)methyl]-3-methylpyridin-2-amine (3fk):** The representative procedure was followed using *N*-(3-fluorobenzyl)-3-methylpyridin-2-amine (108 mg, 0.50 mmol) (**1f**) and 5-bromo-1*H*-indole (**2k**) (147 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 10/1 → 5/1) yielded **3fk** (119 mg, 72%) as a colorless solid. M. p. = 69–70 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.56–7.48 (m, 1H), 7.32–7.18 (m, 3H), 7.17–7.04 (m, 4H), 6.88 (dt, J = 8.3, 2.6 Hz, 1H), 6.60–6.44 (m, 3H), 4.69 (d, J = 6.4 Hz, 1H),

2.13 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.0 (C_q, J = 245.0 Hz), 155.6 (C_q), 147.0 (C_q, J = 6.4 Hz), 145.6 (CH), 136.9 (CH), 135.1 (C_q), 134.6 (C_q), 129.6 (CH, J = 8.1 Hz), 127.9 (C_q), 124.9 (CH), 123.0 (CH, J = 2.7 Hz), 122.2 (CH), 119.8 (CH), 116.4 (C_q), 114.1 (CH, J = 21.9 Hz), 113.4 (CH, J = 21.2 Hz), 113.1 (CH), 111.4 (CH), 102.7 (CH), 58.7 (CH, J = 1.5 Hz), 17.1 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –113.6 (ddd, J = 10.1, 8.6, 5.7 Hz). IR (neat): 3413, 1598, 1466, 1339, 1241, 1135, 749 cm^{-1}. MS (EI) *m/z* (relative intensity): 331 ([M^+], 55), 239 (25), 224 (100), 222 (25), 197 (10), 92 (10), 43 (15). HR-MS (EI) *m/z* calcd for $C_{21}H_{18}FN_3^+$ 331.1485, found 331.1479.

***N*-[(1*H*-Indol-5-yl)(3-methoxyphenyl)methyl]-3-methylpyridin-2-amine (3gk):** The representative procedure was followed using *N*-(3-methoxybenzyl)-3-methylpyridin-2-amine (**1g**) (114 mg, 0.50 mmol) and 5-bromo-1*H*-indole (**2k**) (147 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 5/1 → 2/1) yielded **3gk** (103 mg, 60%) as a colorless solid. M. p. = 70–71 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.49 (s_{br}, 1H), 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.55 (s, 1H), 7.27–7.19 (m, 3H), 7.14–7.08 (m, 2H), 6.99–6.92 (m, 2H), 6.75 (ddd, J = 8.2, 2.6, 1.0 Hz, 1H), 6.57 (d, J = 6.7 Hz, 1H), 6.54–6.43 (m, 2H), 4.73 (d, J = 6.7 Hz, 1H), 3.71 (s, 3H), 2.13 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 159.5 (C_q), 155.8 (C_q), 145.8 (C_q), 145.5 (CH), 136.8 (CH), 135.1 (C_q), 134.7 (C_q), 129.2 (CH), 127.8 (C_q), 124.7 (CH), 122.1 (CH), 119.8 (CH), 119.5 (CH), 116.3 (C_q), 113.3 (CH), 112.8 (CH), 111.8 (CH), 111.3 (CH), 102.5 (CH), 58.9 (CH), 55.1 (CH_3), 17.1 (CH_3). IR (neat): 3411, 1596, 1464, 1249, 1038, 747 cm^{-1}. MS (EI) *m/z* (relative intensity): 343 ([M^+], 65), 251 (25), 236 (100), 220 (15), 204 (15), 92 (15). HR-MS (EI) *m/z* calcd for $C_{22}H_{21}N_3O^+$ 343.1685, found 343.1690.

***N*-[(1*H*-Indol-5-yl){3-(trifluoromethyl)phenyl}methyl]-3-methylpyridin-2-amine (3hk):** The representative procedure was followed using 3-methyl-*N*-[3-(trifluoromethyl)benzyl]pyridin-2-amine (**1h**) (133 mg, 0.50 mmol) and 5-bromo-1*H*-indole (**2k**) (147 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 5/1 → 2/1) yielded **3hk** (116 mg, 61%) as a colorless solid. M. p. = 148–149 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.37 (s_{br}, 1H), 7.95 (dd, J = 5.0, 1.8 Hz, 1H), 7.64 (s, 1H), 7.58–7.42 (m, 3H), 7.40–7.22 (m, 3H), 7.16 (t, J = 2.8 Hz, 1H), 7.10 (dd, J = 8.4,

1.7 Hz, 1H), 6.59 (d, J = 6.3 Hz, 1H), 6.53 (dd, J = 7.2, 5.0 Hz, 1H), 6.51–6.48 (m, 1H), 4.69 (d, J = 6.3 Hz, 1H), 2.13 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.6 (C_q), 145.5 (CH), 145.2 (C_q), 137.0 (CH), 135.2 (C_q), 134.5 (C_q), 130.7 (CH), 130.4 (C_q, J = 29.6 Hz), 128.6 (CH), 128.0 (C_q), 124.9 (CH), 124.3 (C_q, J = 275.5 Hz), 124.0 (CH, J = 3.8 Hz), 123.5 (CH, J = 3.9 Hz), 122.2 (CH), 119.9 (CH), 116.5 (C_q), 113.3 (CH), 111.5 (CH), 102.7 (CH), 58.9 (CH), 17.1 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.3 (s). IR (neat): 3416, 1598, 1466, 1326, 1160, 1116, 1070, 951 cm^{-1}. MS (EI) *m/z* (relative intensity): 381 ([M^+], 55), 274 (100), 204 (25), 92 (10). HR-MS (EI) *m/z* calcd for $C_{22}H_{18}F_3N_3^+$ 381.1453, found 381.1464.

***N*-[(2-Fluorophenyl)(1*H*-indol-5-yl)methyl]-3-methylpyridin-2-amine (3kk):** The representative procedure was followed using *N*-(2-fluorobenzyl)-3-methylpyridin-2-amine (**1k**) (108 mg, 0.50 mmol) and 5-bromo-1*H*-indole (**2k**) (147 mg, 0.75 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 5/1 → 2/1) yielded **3kk** (85 mg, 51%) as a yellow solid. M. p. = 176–177 °C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 11.0 (s_{br}, 1H), 7.86 (d, J = 4.7 Hz, 1H), 7.65 (t, J = 6.8 Hz, 1H), 7.49–7.05 (m, 8H), 6.88 (d, J = 7.9 Hz, 1H), 6.52 (dd, J = 7.1, 4.8 Hz, 1H), 6.40 (s, 1H), 6.09 (d, J = 8.1 Hz, 1H), 2.22 (s, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 160.9 (C_q, J = 244.2 Hz), 156.5 (C_q), 145.6 (CH), 137.6 (CH), 135.9 (C_q), 133.7 (C_q), 132.5 (C_q, J = 14.2 Hz), 129.5 (CH, J = 4.2 Hz), 129.1 (CH, J = 8.0 Hz), 128.3 (C_q), 126.5 (CH), 125.0 (CH, J = 3.3 Hz), 122.1 (CH), 119.5 (CH), 117.8 (C_q), 115.8 (CH, J = 21.7 Hz), 113.3 (CH), 112.1 (CH), 101.9 (CH), 52.7 (CH, J = 3.3 Hz), 17.8 (CH_3). ^{19}F-NMR (282 MHz, DMSO-d_6): δ = –(101.2–127.2) (m). IR (neat): 3461, 3195, 1602, 1498, 1473, 1403, 1222, 1184, 757 cm^{-1}. MS (EI) *m/z* (relative intensity): 331 ([M^+], 50), 239 (15), 224 (100), 222 (20), 92 (10). HR-MS (EI) *m/z* calcd for $C_{21}H_{18}FN_3^+$ 331.1485, found 331.1482.

Intermolecular Competition Experiment between Substituted Pyridines 1a and 1e (Scheme 4). According to the representative procedure, *N*-benzyl-3-methylpyridin-2-amine (**1a**) (149 mg, 0.75 mmol), *N*-benzyl-3-(trifluoromethyl)pyridin-2-amine (**1e**) (189 mg, 0.75 mmol), bromobenzene (**2a**) (79 mg, 0.50 mmol), [Ru(O_2CMes)$_2$(*p*-cymene)] (**5**) (14 mg, 0.025 mmol, 5.0 mol %) and Na_2CO_3

(159 mg, 1.50 mmol) were reacted in *o*-xylene (2.0 mL) at 140 °C for 24 h. Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1) yielded **3aa** (50 mg, 36%). The ratio between **3aa** and **3ea** was found to be 13:1 as determined by GC-analysis.

Intermolecular Competition Experiment between Substituted Arenes 1f and 1g (Scheme 5). According to the representative procedure, *N*-(3-fluorobenzyl)-3-methylpyridin-2-amine (**1f**) (162 mg, 0.75 mmol), *N*-(3-methoxybenzyl)-3-methylpyridin-2-amine (**1g**) (171 mg, 0.75 mmol), bromobenzene (**2a**) (79 mg, 0.50 mmol), [$Ru(O_2CMes)_2$(*p*-cymene)] (**5**) (14 mg, 0.025 mmol, 5.0 mol %) and Na_2CO_3 (159 mg, 1.50 mmol) were reacted in *o*-xylene (2.0 mL) at 140 °C for 24 h. Purification by column chromatography on silica gel (*n*-pentane/EtOAc 30/1 → 20/1 → 10/1 → 5/1) yielded **3fa** (36 mg, 25%) and **3ga** (41 mg, 27%).

Intermolecular Competition Experiment between Electrophiles 2l and 2c (Scheme 6). According to the representative procedure, *N*-benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol), bromo-4-(trifluoromethyl)benzene (**2l**) (169 mg, 0.75 mmol), 4-bromoanisole (**2c**) (140 mg, 0.75 mmol), [$Ru(O_2CMes)_2$(*p*-cymene)] (**5**) (14 mg, 0.025 mmol, 5.0 mol %) and Na_2CO_3 (159 mg, 1.50 mmol) were reacted in *o*-xylene (2.0 mL) at 140 °C for 24 h. Purification by column chromatography on silica gel (*n*-pentane/EtOAc 20/1 → 10/1) yielded **3al** (65 mg, 38%) as a yellow oil. The ratio between **3al** and **3ac** was found to be 2.3:1.0 as determined by GC-analysis. **3al**: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.2, 1.6 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.44–7.25 (m, 6H), 6.70–6.49 (m, 2H), 4.64 (d, J = 6.5 Hz, 1H), 2.16 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.4 (C_q), 145.7 (C_q, J = 1.6 Hz), 145.5 (CH), 142.7 (C_q), 137.1 (CH), 129.1 (C_q, J = 32.2 Hz), 128.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 125.3 (CH, J = 3.7 Hz), 124.2 (C_q, J = 273.7 Hz), 116.4 (C_q), 113.5 (CH), 58.4 (CH), 17.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = –62.3 (s). IR (neat): 3451, 1597, 1465, 1321, 1161, 1106, 1065, 1016, 699 cm^{-1}. MS (EI) *m/z* (relative intensity): 342 ([M^+], 100), 250 (90), 235 (75), 215 (25), 165 (75), 107 (20), 92 (15). HR-MS (EI) *m/z* calcd for $C_{20}H_{17}F_3N_2^+$ 342.1344, found 342.1341. The spectral data were in accordance with those reported in the literature.[7a]

H/D Exchange in Substrate 1a in the Presence of D_2O (Scheme 7). *N*-Benzyl-3-methylpyridin-2-amine (**1a**) (99 mg, 0.50 mmol, 1.0 equiv), [Ru(O_2CMes)$_2$(*p*-cymene)] (**5**) (14 mg, 0.025 mmol, 5.0 mol %) and Na_2CO_3 (159 mg, 1.50 mmol, 3.0 equiv) were placed in a 25 mL sealed tube with a septum screw cap under an atmosphere of nitrogen. After adding *o*-xylene (1.8 mL) and D_2O (0.2 mL), the septum screw cap was removed and a teflon lined cap was fixed. The reaction mixture was stirred at 140 °C for 24 h. At ambient temperature, the suspension was filtered through a short pad of Celite®, which was then washed with CH_2Cl_2 (50 mL). Evaporation of the solvents *in vacuo* and purification by column chromatography on silica gel (*n*-hexane/EtOAc 99/1 → 98/2) yielded [D_n]-**1a** as a colorless oil (85 mg, 86%, 65%-D), as determined by ^{1}H-NMR. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.04 (dd, J = 5.1, 1.7 Hz, 1H), 7.43–7.19 (m, 6H), 6.55 (dd, J = 7.1, 5.1 Hz, 1H), 4.68 (d, J = 5.4 Hz, 2H), 4.35 (s_{br}, 1H), 2.07 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 156.6 (C_q), 145.4 (CH), 140.0 (C_q), 136.8 (CH), 128.5 (CH), 127.8 (CH), 127.1 (CH), 116.4 (C_q), 112.9 (CH), 45.8 (CH_2), 45.5 (CHD, J = 21.0 Hz), 17.0 (CH_3). IR (neat): 3447, 3027, 1597, 1490, 1466, 1381, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 200 (23), 199 (77), 198 (100), 197 (33), 108 (27), 107 (80), 106 (77), 93 (47), 92 (65), 91 (38), 65 (38). HR-MS (ESI) *m/z* calcd for $[C_{13}H_{12}D_2N_2+H]^+$ 201.1355, found 201.1355, *m/z* calcd for $[C_{13}H_{13}DN_2+H]^+$ 200.1293, found 200.1292, *m/z* calcd for $[C_{13}H_{14}N_2+H]^+$ 199.1230, found 199.1230.

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Associated Content

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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