**Electronic Supplementary Information**

# Dirhodium(II)-Catalyzed *ortho* C−H Amination of Sterically Congested *N,N*-Dialkylanilines

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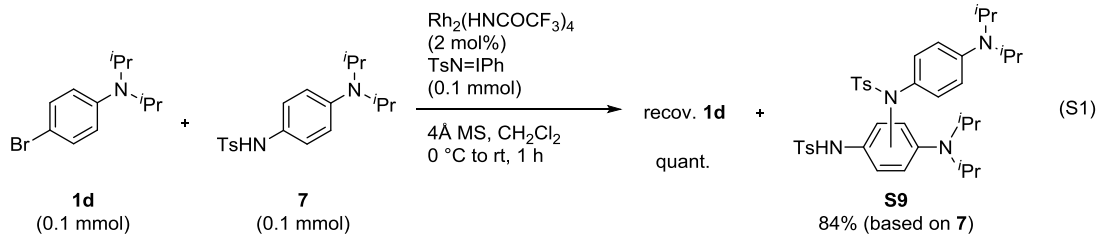
## Experimental Section

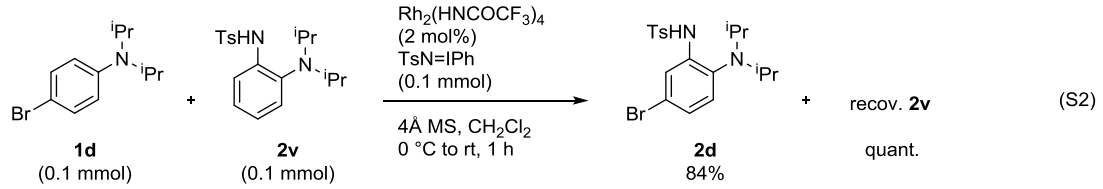
**General.** All melting points were measured on a Yanagimoto micro melting point apparatus. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer and absorbance bands are reported in wavenumber ($cm^{-1}$). $^{1}H$ NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) spectrometer or a JEOL JNM-ECA 400 (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane at $\delta_H$ 0.00, $CDCl_3$ at $\delta_H$ 7.26, $CD_3OD$ at $\delta_H$ 3.34, $CD_3CN$ at $\delta_H$ 1.96). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. $^{13}C$ NMR spectra were recorded on a JEOL JNM-ECA 400 (100 MHz) spectrometer. Chemical shifts are reported relative to internal standard ($CDCl_3$ at δ 77.00, $CD_3CN$ at δ 1.79 and 118.26). Mass spectra were recorded on a JEOL JMS 700 instrument with a direct inlet system. Column chromatography was carried out on Kanto silica gel 60 N (40–50 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 $F_{254}$ plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. All non-aqueous reactions were carried out in flame-dried glassware under Ar atmosphere unless otherwise noted. Reagents and solvents were used without purification. 4Å MS (powder) from nacalai tesque was used after drying. Dirhodium(II) complex catalysts, $Rh_2(esp)_2$ and $Rh_2(HNCOCF_3)_4$, were prepared according to literatures,[1,2] while $Rh_2(esp)_2$ is commercially available. Iminoiodinanes were prepared according to a literature.[3] *N*,*N*-Diisopropylanilines **1g** and **1w−z** were prepared from corresponding primary anilines by reductive amination with 2-methoxypropene in high yields (>90%).[4] Other *N*,*N*-diisopropylanilines **1e**, **1f**, **1h**, **1i**, and **1u** were synthesized from **1d**[5] via Pd-catalyzed coupling with organometallic reagents ($^{n}$BuMgBr for **1e**, phenylboronic acid for **1f**) or halogen-lithium exchange with $^{n}$BuLi followed by treatment with electrophiles ($RO_2CCl$ for **1h** and **1i**, estrone 3-methyl ether for **1u**).

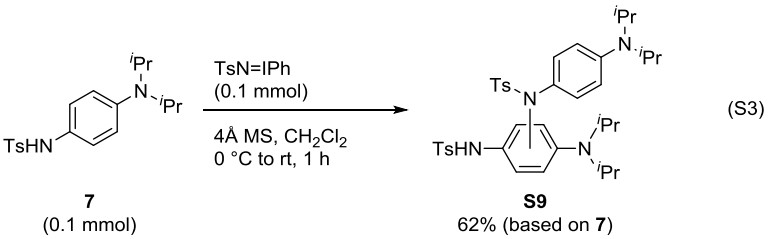
## 1. Competition experiments between C−H amination products and 1d

In order to investigate the over-oxidation of *para* amination product **7** formed under the C−H amination conditions, a series of competition experiments was performed. A competition experiment between **7** and **1d** under C−H amination conditions led to dimerization of **7**, while a quantitative amount of **1d** was recovered [eqn (S1)]. Therefore, over-oxidation of **7** proceeded much faster than C−H amination. The formation **S9** was also observed undrer the conditions using TsN=IPh in the absence of the dirhodium(II) catalyst [eqn (S3)]. Conversely, no detectable degradation of *ortho* amination product **2v** was observed in the competition experiment with **1d** under the same conditions [eqn (S2)]. These results indicate that a bulky amino group with two secondary alkyl groups prevents over-oxidation of ortho amination products **2**.

**Scheme S1.**

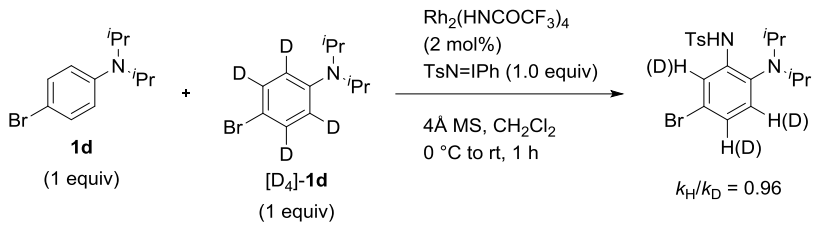


## 2. KIE experiment between 1d and [D4]-1d

**Scheme S2.**

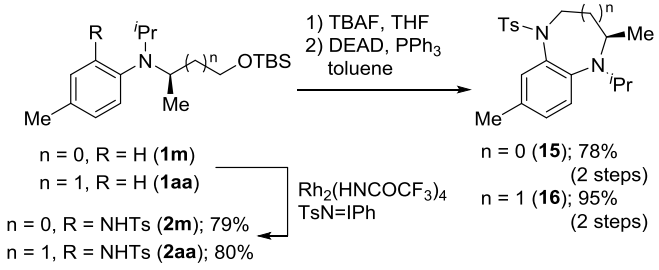



[D4]-**1d** was synthesized from commercially available aniline-$d_7$ by reductive amination with 2-methoxypropene[4] followed by treatment with NBS in DMF.[5]

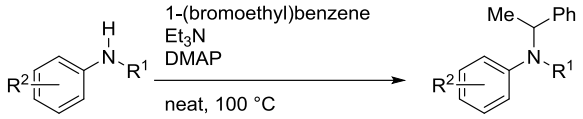
TsN=IPh (37.3 mg, 0.10 mmol) was added to a stirred mixture of **1d** (25.6 mg, 0.10 mmol), [D4]-**1d** (26.0 mg, 0.10 mmol), $Rh_2(HNCOCF_3)_4$ (1.3 mg, 0.002 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt) to give a mixture of **2d** and [D4]-**2d** (33.6 mg) with recovery of a mixture of starting materials (32.5 mg). The $k_H/k_D$ value was determined to be 0.96 by $^1$H NMR analysis of the mixture of products (**2d**:[D4]-**2d** = 49:51). Ratio of the recovered starting materials **1d** and [D4]-**1d** was also determined to be 51:49.

## 3. Synthesis of chiral tetrahydroquinoxaline 15 and 1,5-benzodiazepine 16

**Scheme S3.**

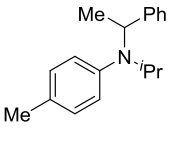


## 4. General procedure for the preparation of *N*-alkyl-*N*-(1-phenylethyl)anilines




A reaction vessel was equipped with a stirring bar and charged with *N*-alkylaniline (2.0 mmol), (1-bromoethyl)benzene (0.68 mL, 5.0 mmol), $Et_3N$ (2.0 mL) and DMAP (24.4 mg, 0.20 mmol) before sealing with glass stopper. After heating at 100 °C for 12 h, formed precipitate was suspended in AcOEt, and resulting suspension was filtered through a plug of Celite with AcOEt. The filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel) to give *N*-alkyl-*N*-(1-phenylethyl)aniline in 16−75% yield.

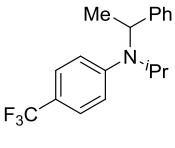
### *N*-Isopropyl-*N*-(1-phenylethyl)-*p*-toluidine (1j)




**1j**

Colorless oil; IR (KBr) *v* 2969, 1515, 1452, 1373, 1262, 1178, 1109, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.07 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.09 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 2.25 (s, 3H, ArC*H*$_3$), 3.67 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.66 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 6.79 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.98 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.21 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.31 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.42 (d, *J* = 7.6 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 19.6 ($CH_3$), 20.4 ($CH_3$), 20.9 ($CH_3$), 48.7 (CH), 55.3 (CH), 122.0 (CH), 126.3 (CH), 127.0 (CH), 128.2 (CH), 128.8 (CH), 129.1 (C), 144.2 (C), 145.5 (C); HRMS (FAB) calcd for $C_{18}H_{23}N$ $[M]^+$ 253.1830, found 253.1829.

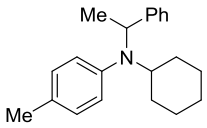
### *N*-Isopropyl-*N*-(1-phenylethyl)-4-trifluoromethylaniline (1k)




**1k**

Colorless oil; IR (KBr) *v* 2975, 1613, 1524, 1326, 1108, 825, 703 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.25 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.30 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.66 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 4.12 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.93 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 6.70 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.22−7.25 (m, 1H, Ar*H*), 7.31−7.37 (m, 6H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 18.0 ($CH_3$), 19.9 ($CH_3$), 20.9 ($CH_3$), 48.8 (CH), 52.7 (CH), 115.0 (CH), 117.8 (q, *J* = 31 Hz, C), 125.1 (q, *J* = 268 Hz, $CF_3$), 125.7 (q, *J* = 3.8 Hz, CH), 126.5 (CH), 126.6 (CH), 128.5 (CH), 143.1 (C), 149.6 (C); HRMS (FAB) calcd for $C_{18}H_{21}F_3N$ $[M+H]^+$ 308.1621, found 308.1632.

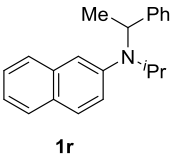
***N*-Cyclohexyl-*N*-(1-phenylethyl)-*p*-toluidine (1l)**



1l

Colorless oil; IR (KBr) *v* 2930, 1510, 1450, 1236, 1161, 1111, 699 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.99−1.06 (m, 1H, $^c$Hex), 1.15−1.34 (m, 4H, $^c$Hex), 1.45 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 1.57 (d, *J* = 12.8 Hz, 1H, $^c$Hex), 1.71−1.77 (m, 2H, $^c$Hex), 1.90−1.93 (m, 2H, $^c$Hex), 2.23 (s, 3H, ArC*H*$_3$), 3.30 (t, *J* = 11.2 Hz, 1H, $^c$Hex), 4.72 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 6.72 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.94 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.20 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.30 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.41 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 20.1 ($CH_3$), 20.4 ($CH_3$), 26.0 ($CH_2$), 26.2 ($CH_2$), 26.3 ($CH_2$), 30.9 ($CH_2$), 31.2 ($CH_2$), 54.8 (CH), 58.2 (CH), 121.2 (CH), 126.2 (CH), 126.9 (CH), 128.2 (CH), 128.5 (C), 128.7 (CH), 144.6 (C), 145.5 (C); HRMS (FAB) calcd for $C_{21}H_{27}N$ $[M]^+$ 293.2143, found 293.2140.

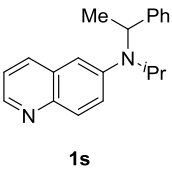
***N*-Isopropyl-*N*-(1-phenylethyl)naphthalen-2-amine (1p)**



1r

Colorless oil; IR (KBr) *v* 3056, 2970, 1626, 1597, 1507, 1373, 1276, 1234, 1185, 827, 743, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.20 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.26 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.57 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 4.00 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.87 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 7.05 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar*H*), 7.15 (s, 1H, Ar*H*), 7.15−7.25 (m, 2H, Ar*H*), 7.32−7.36 (m, 3H, Ar*H*), 7.46 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.55 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.61 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.66 (d, *J* = 8.0 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 19.7 ($CH_3$), 20.5 ($CH_3$), 49.0 (CH), 54.2 (CH), 113.7 (CH), 113.8 (CH), 122.1 (CH), 122.6 (CH), 125.8 (CH), 126.4 (CH), 126.8 (CH), 127.3 (CH), 127.4 (CH), 127.8 (C), 128.3 (CH), 134.5 (C), 144.9 (C), 145.1 (C); HRMS (FAB) calcd for $C_{21}H_{24}N$ $[M+H]^+$ 290.1903, found 290.1909.

***N*-Isopropyl-*N*-(1-phenylethyl)quinolin-6-amine (1q)**

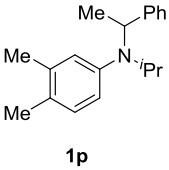


1s

Colorless oil; IR (KBr) *v* 2971, 1616, 1588, 1504, 1374, 1256 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.25 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.32 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.64 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)Ph), 4.10 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 4.93 (q, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)Ph), 6.98 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.20−7.26 (m, 3H, Ar*H*), 7.34 (t, *J* = 7.2 Hz, 2H, Ar*H*), 7.44 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.79 (d, *J* = 9.6 Hz, 1H, Ar*H*), 7.88 (d, *J* = 8.0 Hz, 1H, Ar*H*) 8.61 (d, *J* = 3.2 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 19.0 ($CH_3$), 20.2 ($CH_3$), 20.9 ($CH_3$), 49.1 (CH), 53.5 (CH), 77.2 (CH), 110.6 (CH), 121.0 (CH), 124.1 (CH), 126.5 (CH), 126.7 (CH), 128.4 (CH), 128.8 (CH), 129.4 (CH), 129.4 (C), 134.1 (CH), 142.9 (C), 144.0 (C), 145.6 (C), 146.7 (CH);

HRMS (FAB) calcd for $C_{20}H_{23}N$ $[M+H]^+$ 291.1856, found 291.1861.

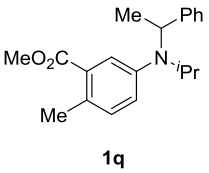
**_N_-Isopropyl-_N_-(1-phenylethyl)-3,4-dimethylaniline (1r)**



**1p**

Colorless oil; IR (KBr) *v* 2968, 1613, 1508, 1452, 1372, 1265, 1181, 1108, 765, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.10 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 2.16 (s, 3H, ArC*H*$_3$), 2.18 (s, 3H, ArC*H*$_3$), 3.66 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.66 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 6.63 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.72 (s, 1H, Ar*H*), 6.92 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.20 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.30 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.42 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 18.8 ($CH_3$), 19.5 ($CH_3$), 20.2 ($CH_3$), 20.4 ($CH_3$), 21.0 ($CH_3$), 48.7 (CH), 55.3 (CH), 119.6 (CH), 123.3 (CH), 126.3 (CH), 127.0 (CH), 127.8 (C), 128.2 (CH), 129.2 (CH), 136.1 (C), 144.6 (C), 145.6 (C); HRMS (FAB) calcd for $C_{19}H_{26}N$ $[M+H]^+$ 268.2060, found 268.2068.

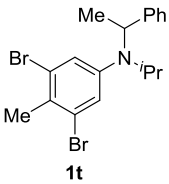
**_N_-Isopropyl-_N_-(1-phenylethyl)-3-methoxycarbonyl-4-methylaniline (1s)**



**1q**

Colorless oil; IR (KBr) *v* 2970, 1722, 1610, 1508, 1435, 1254, 1075, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.13 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.43 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 2.47 (s, 3H, ArC*H*$_3$), 3.73 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.85 (s, 3H, $CO_2C$*H*$_3$), 4.71 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 6.86 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar*H*), 6.99 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.22 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.31 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.40 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.48 (d, *J* = 2.8 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 19.7 ($CH_3$), 20.0 ($CH_3$), 20.8 ($CH_3$), 48.8 (CH), 51.7 ($CH_3$), 55.0 (CH), 122.8 (CH), 125.5 (CH), 126.4 (CH), 126.9 (CH), 128.3 (CH), 129.3 (C), 130.8 (C), 131.4 (CH), 144.5 (C), 144.8 (C), 168.5 (C=O); HRMS (FAB) calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$ 312.1958, found 312.1968.

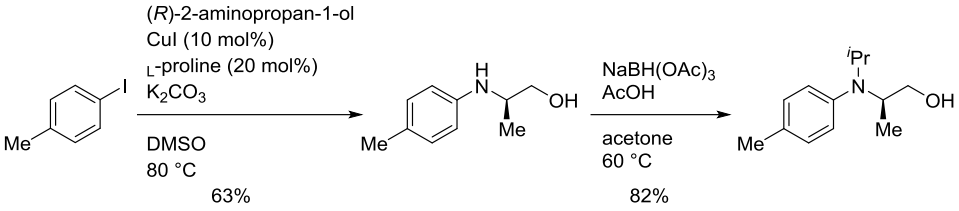
**_N_-Isopropyl-_N_-(1-phenylethyl)-3,5-dibromo-4-methylaniline (1t)**



**1t**

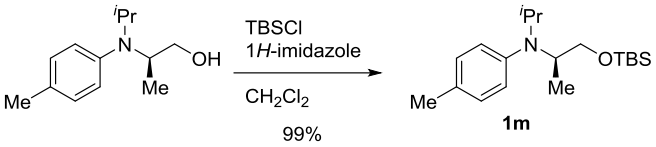
Colorless solid; mp 85−86 °C; IR (KBr) *v* 2971, 1594, 1482, 1261, 1180, 1037, 733 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.13 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.19 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.52(d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)Ph), 2.43 (s, 3H, ArC*H*$_3$), 3.77 (septet, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.73 (q, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)Ph), 6.95 (s, 2H, Ar*H*), 7.22−7.25 (m, 1H, Ar*H*), 7.30−7.35 (m, 4H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 18.8 ($CH_3$), 20.4 ($CH_3$), 22.5 ($CH_3$), 48.9 (CH), 54.2 (CH), 121.8 (CH), 121.9 (CH), 124.7 (C), 126.1 (C), 126.7 (CH), 128.4 (CH), 143.4 (C), 146.5 (C); HRMS (FAB) calcd for $C_{18}H_{21}Br_2N$ $[M]^+$ 409.0041, found 409.0037.

**5. Procedure for the preparation of (*R*)-*N*-isopropyl-*N*-(1-oxypropan-2-yl)-*p*-toluidines**

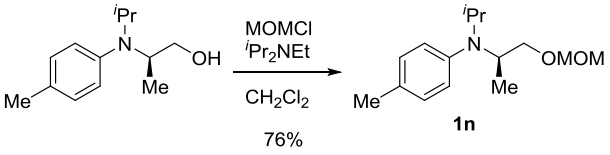



A mixture of 4-iodotoluene (2.18 g, 10 mmol), (*R*)-2-aminopropan-1-ol (1.16 mL, 15 mmol), CuI (191 mg, 1.0 mmol, 10 mol%), L-proline (230 mg, 2.0 mmol, 20 mol%), and $K_2CO_3$ (2.76 g, 20 mmol) in DMSO (6.0 mL) was heated to 80 °C under Ar atmosphere. After stirring for 12 h at the same temperature, the reaction was quenched with saturated aqueous $NH_4Cl$, and the mixture was extracted with AcOEt. The combined organic extracts were successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 3:2 *n*-hexane/AcOEt) to give (*R*)-*N*-(1-hydroxypropan-2-yl)-*p*-toluidine[6] (1.04 g, 63%) as a colorless oil: $[\alpha]_D^{23}$ = −36.0 (*c* 1.33, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): δ 1.17 (d, *J* = 6.3 Hz, 3H, CH(C*H*$_3$)CH$_2$), 2.24 (s, 3H, ArC*H*$_3$), 3.48 (dd, *J* = 10.5, 6.3 Hz, 1H, CHCH*H*O), 3.59 (ddq, *J* = 6.3, 6.3, 4.8 Hz, 1H, C*H*(CH$_3$)CH$_2$), 3.71 (dd, *J* = 10.5, 4.2 Hz, 1H, CHCH*H*O), 6.60 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.99 (d, *J* = 8.4 Hz, 2H, Ar*H*).

To a solution of (*R*)-*N*-(1-hydroxypropan-2-yl)-*p*-toluidine (330 mg, 2.0 mmol) and AcOH (0.34 mL, 6.0 mmol) in acetone (10 mL) was added $NaBH(OAc)_3$ (1.27 g, 6.0 mmol) at room temperature under Ar atmosphere and the mixture was heated to 60 °C. After stirring for 12 h at the same temperature, the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The combined organic extracts were successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt) to give (*R*)-*N*-isopropyl-*N*-(1-hydroxypropan-2-yl)-*p*-toluidine (340 mg, 82%) as a colorless oil: $[\alpha]_D^{24}$ = −167.3 (*c* 1.01, $CHCl_3$); IR (KBr) *v* 3366, 2969, 1616, 1514, 1184, 1042 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)CH$_2$), 1.12 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 2.30 (s, 3H, ArC*H*$_3$), 3.28 (dd, *J* = 10.4, 9.2 Hz, 1H, CH*H*O), 3.44 (dd, *J* = 10.4, 5.2 Hz, 1H, C*H*HO), 3.51−3.55 (m, 1H, C*H*(CH$_3$)CH$_2$), 3.59 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 6.94 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.06 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.6 ($CH_3$), 20.7 ($CH_3$), 21.3 ($CH_3$), 23.3 ($CH_3$), 49.4 (CH), 54.7 (CH), 64.2 ($CH_2$), 125.5 (CH), 129.1 (CH), 132.5 (C), 144.0 (C); HRMS (FAB) calcd for $C_{13}H_{22}NO$ $[M+H]^+$ 208.1696, found 208.1708.

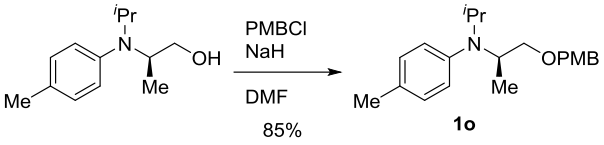



To a solution of (*R*)-*N*-isopropyl-*N*-(1-hydroxypropan-2-yl)-*p*-toluidine (311 mg, 1.5 mmol) and 1*H*-imidazole (153 mg, 2.3 mmol) in $CH_2Cl_2$ (5.0 mL) was added TBSCl (339 mg, 2.3 mmol) at 0 ºC under Ar atmosphere. After stirring at room temperature for 1 h, the reaction was quenched with water, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **1m** (478 mg, 99%) as a colorless oil: $[\alpha]_D^{24}$ = −27.1 (*c* 1.01, $CHCl_3$); IR (KBr) *v* 2928, 1515, 1253, 1088, 836 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.00 (s, 6H, Si(C*H*$_3$)$_2$), 0.87 (s, 9H, Si$^t$Bu) 1.11−1.17 (m, 9H, CH(C*H*$_3$)$_2$ and CH(C*H*$_3$)CH$_2$), 2.23 (s, 3H, ArC*H*$_3$), 3.54 − 3.57 (m, 2H, C*H*$_2$OSi), 3.68 − 3.76 (m, 2H, C*H*(CH$_3$)$_2$ and C*H*(CH$_3$)CH$_2$), 6.78 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.97 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ −5.4 ($CH_3$), 16.3 ($CH_3$), 18.2 (C), 20.4 ($CH_3$), 21.0 ($CH_3$), 21.9 ($CH_3$), 25.9 ($CH_3$), 48.9 (CH), 54.0 (CH), 66.7 ($CH_2$), 120.4 (CH), 128.1 (C), 128.9 (CH), 145.5 (C); HRMS (FAB) calcd for $C_{19}H_{36}NOSi$ $[M+H]^+$ 322.2561, found 322.2565.



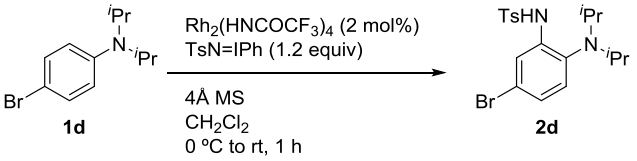

To a solution of (*R*)-*N*-isopropyl-*N*-(1-hydroxypropan-2-yl)-*p*-toluidine (160 mg, 0.77 mmol) and $^i$Pr$_2$NEt (0.20 mL, 1.2 mmol) in $CH_2Cl_2$ (10 mL) was added MOMCl (71 μL, 0.93 mmol) at room temperature under Ar atmosphere. After stirring for 12 h, the reaction was quenched with water, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **1n** (147 mg, 76%) as a colorless oil: $[\alpha]_D^{24}$ = −48.2 (*c* 1.06, $CHCl_3$); IR (KBr) *v* 2969, 1616, 1515, 1109, 1045, 920, 808 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.17 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)CH$_2$), 2.26 (s, 3H, ArC*H*$_3$), 3.34 (s, 3H, OC*H*$_3$), 3.49 (t, *J* = 8.0 Hz, 1H, CH(CH$_3$)CH*H*), 3.62−3.76 (m, 3H, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)C*H*H), 4.60 (s, 2H, OC*H*$_2$OCH$_3$), 6.82 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.01 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 16.6 ($CH_3$), 20.4 ($CH_3$), 21.0 ($CH_3$), 21.9 ($CH_3$), 48.9 (CH), 52.0 (CH), 55.2 ($CH_3$), 71.8 ($CH_2$), 96.6 ($CH_2$), 121.2 (CH), 129.0 (CH), 129.0 (C), 145.2 (C); HRMS (FAB) calcd for $C_{15}H_{26}NO_2$ $[M+H]^+$ 252.1958, found

252.1960.




To a solution of (*R*)-*N*-isopropyl-*N*-(1-hydroxypropan-2-yl)-*p*-toluidine (175 mg, 0.84 mmol) in DMF (1.7 mL) was added NaH (60%, 50.4 mg, 1.3 mmol) at 0 ºC under Ar atmosphere. After stirring at room temperature for 30 min, PMBCl (0.17 mL, 1.3 mmol) was added at 0 ºC. After stirring at room temperature for 4 h, the reaction was quenched with water, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **1o** (234 mg, 85%) as a colorless oil: $[\alpha]_D^{24}$ = −38.7 (*c* 1.05, $CHCl_3$); IR (KBr) *v* 2969, 1613, 1513, 1247, 1095, 1036, 808 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.15 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)CH$_2$), 2.26 (s, 3H, ArC*H*$_3$), 3.42 (t, *J* = 8.4 Hz, 1H, CH(CH$_3$)CH*H*), 3.55 (dd, *J* = 8.4, 4.8 Hz, 1H, CH(CH$_3$)C*H*H), 3.69−3.76 (m, 2H, C*H*(CH$_3$)$_2$ and C*H*(CH$_3$)CH$_2$), 3.80 (s, 3H, ArOC*H*$_3$), 4.41 (s, 2H, OC*H*$_2$OAr), 6.80 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.86 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.99 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.23 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 16.8 ($CH_3$), 20.4 ($CH_3$), 21.0 ($CH_3$), 21.8 ($CH_3$), 48.8 (CH), 51.9 (CH), 55.2 ($CH_3$), 72.7 ($CH_2$), 74.1 ($CH_2$), 113.7 (CH), 120.9 (CH), 128.6 (C), 129.0 (CH), 129.1 (CH), 130.6 (C), 145.3 (C), 159.0 (C); HRMS (FAB) calcd for $C_{21}H_{30}NO_2$ $[M+H]^+$ 328.2271, found 328.2274.

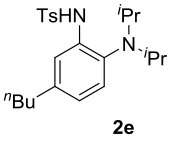
## 6. Typical procedure for Rh(II)-catalyzed *ortho* C−H amination of *N*,*N*-dialkylanilines: Preparation of *N*,*N*-diisopropyl-4-bromo-2-(tosylamido)aniline (2d)




TsN=IPh (44.7 mg, 0.12 mmol) was added to a stirred mixture of *N*,*N*-diisopropyl-4-bromoaniline (**1d**) (25.6 mg, 0.10 mmol), $Rh_2(HNCOCF_3)_4$ (1.3 mg, 0.002 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt) to give 1,2-diaminobenzene **2d** (35.3 mg, 83%) as a colorless solid: mp 151−153 °C; IR (KBr) *v* 3194, 2971, 1485, 1382, 1165, 913,

745 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.85 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.36 (s, 3H, ArC*H*$_3$), 3.35 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.94 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar*H*), 7.24 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.76 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.78 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.54 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 50 °C): δ 20.4 ($CH_3$), 21.4 ($CH_3$), 50.1 (CH), 118.6 (CH), 120.0 (C), 125.4 (CH), 127.2 (CH), 129.6 (CH), 129.8 (CH), 134.0 (C), 137.1 (C), 139.4 (C), 144.0 (C); HRMS (FAB) calcd for $C_{19}H_{26}BrN_2O_2S$ $[M+H]^+$ 425.0893, found 425.0891.

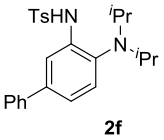
***N*,*N*-Diisopropyl-4-butyl-2-(tosylamido)aniline (2e)**



**2e**

Yield 87%; purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt); colorless solid; mp 97−98 °C; IR (KBr) *ν* 3208, 2967, 1501, 1381, 905 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.84 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 0.92 (t, *J* = 7.6 Hz, 3H, (CH$_2$)$_3$C*H*$_3$), 1.32 (sextet, *J* = 7.6 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 1.58 (quintet, *J* = 7.6 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), 2.34 (s, 3H, ArC*H*$_3$), 2.55 (t, *J* = 7.6 Hz, 2H, ArC*H*$_2$CH$_2$), 3.34 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.72 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.96 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.18 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.42 (s, 1H, Ar*H*), 7.78 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.54 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 13.9 ($CH_3$), 20.6 ($CH_3$), 21.3 ($CH_3$), 22.3 ($CH_2$), 33.3 ($CH_2$), 35.5 ($CH_2$), 50.1 (CH), 115.6 (CH), 122.4 (C), 127.3 (CH), 128.1 (CH), 129.3 (CH), 132.5 (CH), 137.6 (C), 137.7 (C), 141.3 (C), 143.5 (C); HRMS (FAB) calcd for $C_{23}H_{35}N_2O_2S$ $[M+H]^+$ 403.2414, found 403.2422.

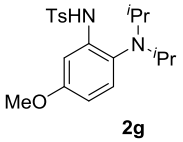
***N*,*N*-Diisopropyl-4-phenyl-2-(tosylamido)aniline (2f)**



**2f**

Yield 87%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless amorphous; IR (KBr) *ν* 3200, 2971, 1484, 1380, 1162, 942, 752 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.90 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 2.33 (s, 3H, ArC*H*$_3$), 3.40 (septet, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 7.13 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.31 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.41 (t, *J* = 8.0 Hz, 2H, Ar*H*), 7.56 (dd, *J* = 8.0, 2.0 Hz, 2H, Ar*H*), 7.82 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.85 (d, *J* = 2.0 Hz, 1H, Ar*H*), 8.61 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.6 ($CH_3$), 21.3 ($CH_3$), 50.2 (CH), 114.1 (CH), 120.9 (CH), 127.0 (CH), 127.3 (CH), 127.4 (CH), 128.6 (CH), 128.7 (CH), 129.5 (CH), 134.3 (C), 137.6 (C), 138.3 (C), 139.4 (C), 140.6 (C), 143.6 (C); HRMS (FAB) calcd for $C_{25}H_{31}N_2O_2S$ $[M+H]^+$ 423.2101, found 423.2098.

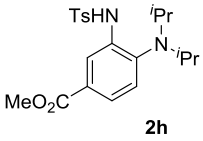
***N*,*N*-Diisopropyl-4-methoxy-2-(tosylamido)aniline (2g)**



**2g**

Yield 92%; purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); colorless solid; mp 130−132 °C; IR (KBr) *v* 2971, 1505, 1381, 1159, 1091 $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$, 70 ºC): δ 0.86 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.36 (s, 3H, ArC*H*$_3$), 3.38 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 3.76 (s, 3H, OC*H*$_3$), 6.53 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar*H*), 7.09 (m, 2H, Ar*H*), 7.32 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.80 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.60 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CD_3CN$, 70 ºC): δ 20.8 ($CH_3$), 21.2 ($CH_3$), 50.9 (CH), 55.9 ($CH_3$), 102.1 (CH), 108.5 (CH), 128.0 (CH), 128.7 (C), 130.4 (CH), 130.5 (CH), 138.1 (C), 139.6 (C), 145.2 (C), 158.8 (C); HRMS (FAB) calcd for $C_{20}H_{29}N_2O_3S$ $[M+H]^+$ 377.1893, found 377.1908.

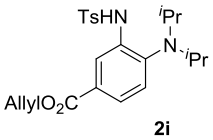
***N*,*N*-Diisopropyl-4-methoxycarbonyl-2-(tosylamido)aniline (2h)**



**2h**

Yield 78%; purified by column chromatography (silica gel, 6:1 to 4:1 *n*-hexane/AcOEt); colorless solid; mp 157−159 °C; IR (KBr) *v* 3209, 2974, 1720, 1383, 1245, 1164, 913, 746 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.85 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.36 (s, 3H, ArC*H*$_3$), 3.40 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 3.92 (s, 3H, $CO_2Me$), 7.17 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.23 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.63 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.81 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.26 (s, 1H, Ar*H*), 8.66 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 20.2 ($CH_3$), 21.5 ($CH_3$), 50.0 (CH), 52.2 ($CH_3$), 116.2 (CH), 123.6 (CH), 127.2 (CH), 128.2 (CH), 128.2 (C), 129.6 (CH), 136.6 (C), 138.0 (C), 139.7 (C), 143.9 (C), 166.5 (C=O); HRMS (FAB) calcd for $C_{21}H_{29}N_2O_4S$ $[M+H]^+$ 405.1843, found 405.1856.

***N*,*N*-Diisopropyl-4-allyloxycarbonyl-2-(tosylamido)aniline (2i)**

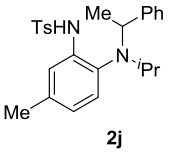


**2i**

Yield 72%; purified by column chromatography (silica gel, 8:1 to 6:1 *n*-hexane/AcOEt); colorless oil; IR (KBr) *v* 3207, 2973, 1720, 1382, 1239, 1165, 944, 749 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.89 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.35 (s, 3H, ArC*H*$_3$), 3.41 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 4.81 (d, *J* = 5.6 Hz, 2H, C*H*$_2$CH=CHH), 5.29 (d, *J* = 10.4 Hz, 1H, CH$_2$CH=C*H*H), 5.41 (d, *J* = 17.2 Hz, 1H, CH$_2$CH=CH*H*), 6.03 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H, CH$_2$C*H*=CHH), 7.16 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.64 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.82 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.23 (d, *J* = 2.0 Hz, 1H, Ar*H*), 8.57 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.5 ($CH_3$), 21.4 ($CH_3$), 50.3 (CH), 65.5 ($CH_2$), 116.6 (CH), 118.0 ($CH_2$), 123.5 (CH), 127.4 (CH), 128.4 (CH), 128.5 (C), 129.6 (CH), 132.3 (CH), 137.2 (C), 138.3 (C), 139.9 (C), 143.9 (C), 165.6 (C=O); HRMS (FAB)

calcd for $C_{23}H_{31}N_2O_4S$ $[M+H]^+$ 431.1999, found 431.2014.

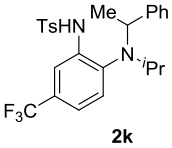
**_N_-Isopropyl-_N_-(1-phenylethyl)-2-(tosylamido)-_p_-toluidine (2j)**



**2j**

Yield 78%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless oil; IR (KBr) *v* 3222, 2971, 1504, 1379, 1235, 1168, 1090, 910, 704 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.70 (d, *J* = 6.4 Hz, 3H, $CH(CH_3)_2$), 0.80 (brs, 3H, $CH(CH_3)Ph$), 0.90 (d, *J* = 6.4 Hz, 3H, $CH(CH_3)_2$), 2.30 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 3.13 (septet, *J* = 6.4 Hz, 1H, $CH(CH_3)_2$), 4.21 (q, *J* = 6.4 Hz, 1H, $CH(CH_3)Ph$), 6.76 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.00 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.24−7.40 (m, 6H, Ar*H*), 7.80 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.64 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.8 ($CH_3$), 21.3 ($CH_3$), 21.4 ($CH_3$), 21.8 ($CH_3$), 50.4 (CH), 60.4 (CH), 116.5 (CH), 123.1 (CH), 127.2 (CH), 127.3 (CH), 128.5 (CH), 128.7 (CH), 129.5 (CH), 129.5 (CH), 131.1 (C), 136.6 (C), 137.8 (C), 138.0 (C), 143.6 (C), 144.7 (C); HRMS (FAB) calcd for $C_{25}H_{31}N_2O_2S$ $[M+H]^+$ 423.2101, found 423.2113.

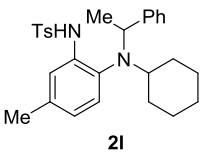
**_N_-Isopropyl-_N_-(1-phenylethyl)-2-(tosylamido)-4-trifluoromethylaniline (2k)**



**2k**

Yield 59%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless oil; IR (KBr) *v* 3232, 2973, 1598, 1507, 1384, 1167, 947, 701 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 50 °C): δ 0.72 (d, *J* = 6.4 Hz, 3H, $CH(CH_3)_2$), 0.83 (d, *J* = 6.4 Hz, 3H, $CH(CH_3)Ph$), 0.92 (d, *J* = 6.4 Hz, 3H, $CH(CH_3)_2$), 2.34 (s, 3H, $ArCH_3$), 3.20 (septet, *J* = 6.4 Hz, 1H, $CH(CH_3)_2$), 4.26 (q, *J* = 6.4 Hz, 1H, $CH(CH_3)Ph$), 7.22−7.37 (m, 9H, Ar*H*), 7.80 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.87 (s, 1H, Ar*H*), 8.73 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 50 °C): δ 17.3 ($CH_3$), 20.6 ($CH_3$), 21.4 ($CH_3$), 21.6 ($CH_3$), 50.7 (CH), 60.3 (CH), 112.8 (q, *J* = 3.8 Hz, CH), 118.9 (q, *J* = 3.8 Hz, CH), 123.8 (q, *J* = 270 Hz, $CF_3$), 127.2 (CH), 127.3 (CH), 127.6 (CH), 128.9 (CH), 129.0 (q, *J* = 32 Hz, C), 129.3 (CH), 129.7 (CH), 136.9 (C), 137.3 (C), 138.9 (C), 143.7 (C), 144.2 (C); HRMS (FAB) calcd for $C_{25}H_{28}F_3N_2O_2S$ $[M+H]^+$ 477.1818, found 477.1819.

**_N_-Cyclohexyl-_N_-(1-phenylethyl)-2-(tosylamido)-_p_-toluidine (2l)**

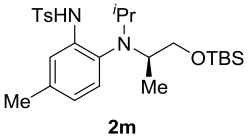


**2l**

Yield 68%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless oil; IR (KBr) *v* 3220, 2930, 1504, 1370, 1167, 1090, 911, 734 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.65 (ddd, *J* = 24.4, 12.4, 3.6 Hz, 1H, $^c$Hex), 0.83−0.99 (m, 7H, $CH(CH_3)Ph$ and $^c$Hex), 1.38−1.47 (m, 2H, $^c$Hex), 1.58−1.60 (m, 2H, $^c$Hex), 1.95−1.98 (m, 1H, $^c$Hex), 2.30 (s, 3H,

ArC$H_3$), 2.33 (s, 3H, ArC$H_3$), 2.64-2.70 (m, 1H, $^c$Hex), 4.29 (q, *J* = 6.4 Hz, 1H, C*H*($CH_3$)Ph), 6.74 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.98 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.19 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.24−7.32 (m, 5H, Ar*H*), 7.40 (s, 1H, Ar*H*), 7.78 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.63 (brs, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$, 60 °C): δ 14.0 ($CH_3$), 21.3 ($CH_2$), 21.4 ($CH_2$), 21.6 ($CH_3$), 25.7 ($CH_2$), 25.8 ($CH_2$), 26.0 ($CH_2$), 31.6 ($CH_3$), 59.6 (CH), 59.7 (CH), 116.4 (CH), 123.0 (CH), 127.2 (CH), 127.3 (CH), 127.3 (CH), 128.6 (CH), 128.9 (CH), 129.5 (CH), 131.8 (C), 136.5 (C), 137.8 (C), 137.9 (C), 143.5 (C); HRMS (FAB) calcd for $C_{28}H_{35}N_2O_2S$ $[M+H]^+$ 463.2414, found 463.2417.

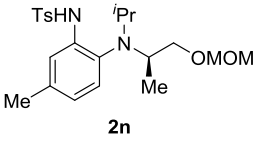
**(*R*)-*N*-Isopropyl-*N*-[1-(*tert*-butyldimethylsilyloxy)propan-2-yl]-2-(tosylamido)-*p*-toluidine (2m)**



**2m**

TsN=IPh (1.5 equiv) was used. Yield 79%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless oil; $[\alpha]_D^{24}$ = −36.8 (*c* 0.62, $CHCl_3$); IR (KBr) *v* 3202, 2928, 1505, 1384, 1169, 1091, 835 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.06 (s, 6H, SiC$H_3$), 0.84−0.88 (m, 18H, CH(C$H_3$)$_2$, CH(C$H_3$)$CH_2$ and Si$^t$Bu), 2.27 (s, 3H, ArC$H_3$), 2.35 (s, 3H, ArC$H_3$), 3.24−3.29 (m, 3H, C*H*($CH_3$)$_2$, CH($CH_3$)C$H_2$), 3.41−3.45 (m, 1H, C*H*($CH_3$)$CH_2$), 6.71 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.99 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.38 (s, 1H, Ar*H*), 7.78 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.59 (brs, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$, 60 °C): δ −5.31 ($CH_3$), −5.28 ($CH_3$), 15.7 ($CH_3$), 18.4 (C), 21.2 ($CH_3$), 21.4 ($CH_3$), 21.4 ($CH_3$), 26.1 ($CH_3$), 51.2 (CH), 56.6 (CH), 65.9 ($CH_2$), 117.0 (CH), 123.0 (CH), 127.2 (CH), 129.4 (CH), 129.6 (CH), 131.9 (C), 136.5 (C), 138.0 (C), 138.2 (C), 143.3 (C); HRMS (FAB) calcd for $C_{26}H_{43}N_2O_3SSi$ $[M+H]^+$ 491.2758, found 491.2765.

**(*R*)-*N*-Isopropyl-*N*-[1-(methoxymethoxy)propan-2-yl]-2-(tosylamido)-*p*-toluidine (2n)**

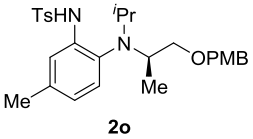


**2n**

TsN=IPh (1.5 equiv) was used. Yield 77%; purified by column chromatography (silica gel, 8:1 to 6:1 *n*-hexane/AcOEt); colorless oil; $[\alpha]_D^{24}$ = −26.6 (*c* 0.52, $CHCl_3$); IR (KBr) *v* 3163, 2970, 1506, 1384, 1159, 1043, 814 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.86 (d, *J* = 6.0 Hz, 3H, CH(C$H_3$)$CH_2$), 0.94 (d, *J* = 6.4 Hz, 6H, CH(C$H_3$)$_2$), 2.23 (s, 3H, ArC$H_3$), 2.34 (s, 3H, ArC$H_3$), 3.33−3.40 (m, 7H, C*H*($CH_3$)$_2$, C*H*($CH_3$)C$H_2$, OC$H_3$), 4.68 (d, *J* = 6.4 Hz, 1H, OC*H*$HOCH_3$), 4.72 (d, *J* = 6.4 Hz, 1H, OCH*H*$OCH_3$), 6.70 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 6.98 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.38 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.79 (d, *J* = 8.0 Hz, 2H, Ar*H*), 9.03 (brs, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$, 60 °C): δ 15.4 ($CH_3$), 21.3 ($CH_3$), 21.4 ($CH_3$), 21.9 ($CH_3$), 55.5 ($CH_3$), 69.6 ($CH_2$), 96.8 ($CH_2$), 116.9

(CH), 122.9 (CH), 127.3 (CH), 129.4 (CH), 129.9 (CH), 131.8 (C), 136.6 (C), 138.0 (C), 138.3 (C), 143.3 (C) (Two of *C*H−N were not found); HRMS (FAB) calcd for $C_{22}H_{33}N_2O_4S$ $[M+H]^+$ 421.2156, found 421.2159.

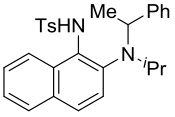
**(*R*)-*N*-Isopropyl-*N*-[1-(*p*-methoxybenzyloxy)propan-2-yl]-2-(tosylamido)-*p*-toluidine (2o)**



**2o**

Yield 76%; purified by column chromatography (silica gel, 8:1 to 6:1 *n*-hexane/AcOEt); colorless oil; $[\alpha]_D^{24}$ = −30.2 (*c* 0.84, $CHCl_3$); IR (KBr) *v* 3134, 2969, 1510, 1380, 1246, 1159, 1091, 814, 706 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.81−0.91 (m, 9H, CH(C*H*$_3$)$_2$ and CH(C*H*$_3$)CH$_2$), 2.27 (s, 3H, ArC*H*$_3$), 2.33 (s, 3H, ArC*H*$_3$), 3.12−3.25 (m, 4H, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)C*H*$_2$), 3.79 (s, 3H, OC*H*$_3$), 4.46 (d, *J* = 12.0 Hz, 1H, OC*H*HOAr), 4.56 (d, *J* = 12.0 Hz, 1H, OCH*H*OAr), 6.68 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.87 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.95 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.17 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.28 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.41 (s, 1H, Ar*H*), 7.78 (d, *J* = 8.0 Hz, 2H, Ar*H*), 9.10 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 15.5 (CH$_3$), 21.3 (CH$_3$), 21.4 (CH$_3$), 21.9 (CH$_3$), 55.3 (CH$_3$), 71.9 (CH$_2$), 72.7 (CH$_2$), 113.9 (CH), 117.0 (CH), 122.9 (CH), 127.3 (CH), 129.3 (CH), 129.6 (CH), 130.0 (CH), 130.5 (C), 132.1 (C), 136.5 (C), 138.0 (C), 138.4 (C), 143.2 (C), 159.4 (C) (Two of *C*H−N were not found); HRMS (FAB) calcd for $C_{28}H_{37}N_2O_4S$ $[M+H]^+$ 497.2469, found 497.2473.

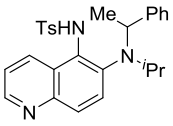
***N*-Isopropyl-*N*-(1-phenylethyl)-1-(tosylamido)naphthalen-2-amine (2p)**



**2p**

Yield 86%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless amorphous; IR (KBr) *v* 2972, 1596, 1493, 1454, 1379, 1301, 1153, 1092, 911, 812, 734 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 50 °C): δ 0.87 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 0.98 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)Ph), 1.11 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 2.45 (s, 3H, ArC*H*$_3$), 3.31 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 4.46 (q, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)Ph), 7.23 (t, *J* = 6.8 Hz, 1H, Ar*H*), 7.27 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.31−7.42 (m, 6H, Ar*H*), 7.47 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.63 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.76 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.89 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.96 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 50 °C): δ 17.5 (CH$_3$), 21.4 (CH$_3$), 21.5 (CH$_3$), 21.9 (CH$_3$), 51.3 (CH), 60.2 (CH), 124.7 (CH), 125.3 (CH), 125.8 (CH), 126.1 (CH), 126.2 (CH), 127.3 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 127.9 (C), 128.7 (CH), 129.5 (CH), 132.8 (C), 135.0 (C), 135.4 (C), 139.3 (C), 143.6 (C), 144.8 (C); HRMS (FAB) calcd for $C_{28}H_{31}N_2O_2S$ $[M+H]^+$ 459.2101, found 459.2102.

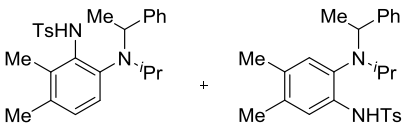
***N*-Isopropyl-*N*-(1-phenylethyl)-5-(tosylamido)quinolin-6-amine (2q)**




**2q**

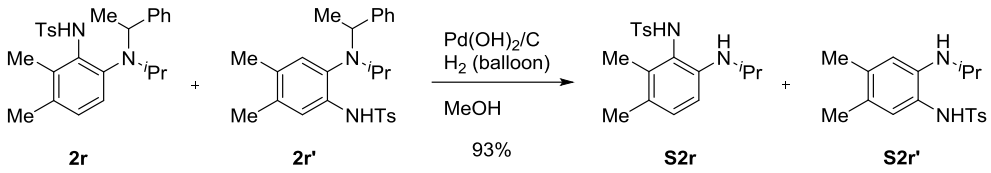
Yield 79%; purified by column chromatography (silica gel, 2:1 to 3:2 *n*-hexane/AcOEt); colorless amorphous; IR (KBr) *v* 2972, 1590, 1564, 1494, 1378, 1300, 1157, 1091, 908, 813, 763 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.89 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 0.95 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)Ph), 1.06 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 2.43 (s, 3H, ArC*H*$_3$), 3.31 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 4.45 (q, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)Ph), 7.20 (dd, *J* = 8.0, 4.0 Hz, 1H, Ar*H*), 7.27−7.32 (m, 5H, Ar*H*), 7.36 (t, *J* = 7.2 Hz, 2H, Ar*H*), 7.61 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.79 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.91 (d, *J* = 9.6 Hz, 1H, Ar*H*), 8.27 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.79 (brs, 1H, N*H*), 8.83 (dd, *J* = 4.0, 1.6 Hz, 1H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 17.9 ($CH_3$), 21.3 ($CH_3$), 21.4 ($CH_3$), 21.5 ($CH_3$), 51.4 (CH), 60.0 (CH), 120.1 (CH), 123.3 (C), 126.1 (CH), 127.3 (CH), 127.4 (CH), 127.6 (CH), 128.7 (CH), 129.7 (CH), 129.7 (CH), 134.5 (CH), 134.9 (C), 135.4 (C), 138.7 (C), 144.0 (C), 144.3 (C), 147.2 (C), 150.2 (CH); HRMS (FAB) calcd for $C_{27}H_{30}N_3O_2S$ $[M+H]^+$ 460.2053, found 460.2057.

***N*-Isopropyl-*N*-(1-phenylethyl)-3,4-dimethyl-2-(tosylamido)aniline (2r) and *N*-isopropyl-*N*-(1-phenylethyl)-4,5-dimethyl-2-(tosylamido)aniline (2r')**



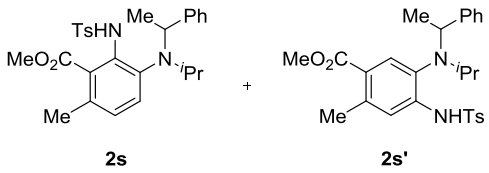

**2r** **2r'**

Yield 83% (**2r**:**2r'** = 70:30); purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless amorphous; IR (KBr) *v* 1971, 1493, 1323, 1154, 1092, 702 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, ): δ 0.68 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$ for **2r'**), 0.77 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)Ph for **2r'**), 0.85 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$ for **2r**), 0.90 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$ for **2r'**), 0.97 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)Ph for **2r**), 1.15 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$ for **2r**), 1.96 (s, 3H, ArC*H*$_3$ for **2r**), 2.15 (s, 3H, ArC*H*$_3$ for **2r'**), 2.21 (s, 3H, ArC*H*$_3$ for **2r'**), 2.22 (s, 3H, ArC*H*$_3$ for **2r**), 2.32 (s, 3H, ArC*H*$_3$ for **2r'**), 2.44 (s, 3H, ArC*H*$_3$ for **2r**), 3.11 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$ for **2r'**), 3.23 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$ for **2r**), 4.20 (d, *J* = 6.4 Hz, 1H, CH(C*H*$_3$)Ph for **2r'**), 4.33 (d, *J* = 6.4 Hz, 1H, CH(C*H*$_3$)Ph for **2r**), 6.86 (s, 1H, Ar*H* for **2r'**), 6.93 (d, *J* = 8.0 Hz, 1H, Ar*H* for **2r**), 7.03 (d, *J* = 8.0 Hz, 1H, Ar*H* for **2r**), 7.18 (d, *J* = 8.0 Hz, 2H, Ar*H* for **2r'**), 7.23−7.37 (m, 5H, Ar*H* for **2r** and 6H, Ar*H* for **2r'**), 7.45 (d, *J* = 8.0 Hz, 2H, Ar*H* for **2r**), 7.80 (d, *J* = 8.0 Hz, 2H, Ar*H* for **2r'**), 7.89 (d, *J* = 8.0 Hz, 2H, Ar*H* for **2r**), 8.49 (brs, 1H, N*H* for **2r'**), 8.91 (brs, 1H, N*H* for **2r**); HRMS (FAB) calcd for $C_{26}H_{33}N_2O_2S$ $[M+H]^+$ 437.2257, found 437.2261.




The structures of **2r** and **2r'** were assigned after removal of their 1-phenylethyl groups. A solution of **2r** and **2r'** (70:30, 53.8 mg) in MeOH (1.0 mL) was stirred with 20% $Pd(OH)_2/C$ (27 mg) under 1 atm of $H_2$ at room temperature for 6 h. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt) to give a mixture of **S2r** and **S2r'** (65:35, 38.1 mg, 93%) as a colorless oil: IR (KBr) *v* 3271, 2966, 1607, 1513, 1325, 1159, 1092, 916, 813 $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3OD$): δ 0.91 (d, *J* = 6.4 Hz, 6H, $CH(CH_3)_2$ for **S2r**), 0.97 (d, *J* = 6.4 Hz, 6H, $CH(CH_3)_2$ for **S2r'**), 1.65 (s, 3H, $ArCH_3$ for **S2r**), 1.83 (s, 3H, $ArCH_3$ for **S2r'**), 1.94 (s, 3H, $ArCH_3$ for **S2r**), 2.03 (s, 3H, $ArCH_3$ for **S2r'**), 2.30 (s, 3H, $ArCH_3$ for **S2r'**), 2.32 (s, 3H, $ArCH_3$ for **S2r**), 3.33 (septet, *J* = 6.4 Hz, 1H, $CH(CH_3)_2$ for **S2r**), 3.39 (septet, *J* = 6.4 Hz, 1H, $CH(CH_3)_2$ for **S2r'**), 6.20 (s, 1H, Ar*H* for **S2r'**), 6.32 (d, *J* = 8.0 Hz, 1H, Ar*H* for **S2r**), 6.36 (s, 1H, Ar*H* for **S2r'**), 6.79 (d, *J* = 8.0 Hz, 1H, Ar*H* for **S2r**), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H* for **S2r'**), 7.22 (d, *J* = 8.0 Hz, 2H, Ar*H* for **S2r**), 7.46 (d, *J* = 8.0 Hz, 2H, Ar*H* for **S2r'**), 7.50 (d, *J* = 8.0 Hz, 2H, Ar*H* for **S2r**); HRMS (FAB) calcd for $C_{18}H_{25}N_2O_2S$ $[M+H]^+$ 333.1631, found 333.1643.

**_N_-Isopropyl-_N_-(1-phenylethyl)-4-methyl-3-methoxycarbonyl-2-(tosylamido)aniline (2s) and _N_-isopropyl-_N_-(1-phenylethyl)-4-methyl-5-methoxycarbonyl-2-(tosylamido)aniline (2s')**

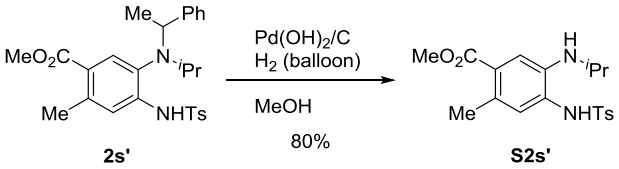



TsN=IPh (2.0 equiv) was used. Yield 78% (**2s**:**2s'** = 5:>95); **2s** and **2s'** were separable by column chromatography (silica gel, 6:1 to 4:1 *n*-hexane/AcOEt).

**2s**; colorless oil; $^1H$ NMR (300 MHz, $CDCl_3$): δ 0.76 (d, *J* = 6.6 Hz, 3H, $CH(CH_3)_2$), 0.78 (d, *J* = 6.6 Hz, 3H, $CH(CH_3)_2$), 0.88 (d, *J* = 6.6 Hz, 3H, $CH(CH_3)Ph$), 2.36 (s, 3H, $ArCH_3$), 2.39 (s, 3H, $ArCH_3$), 3.11 (septet, *J* = 6.6 Hz, 1H, $CH(CH_3)_2$), 3.67 (s, 3H, $CO_2CH_3$), 4.22 (q, *J* = 6.6 Hz, 1H, $CH(CH_3)Ph$), 6.96 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.15 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.23−7.36 (m, 7H, Ar*H*), 7.81 (d, *J* = 8.1 Hz, 2H, Ar*H*), 9.10 (brs, 1H, N*H*).

**2s'**; colorless amorphous; IR (KBr) *v* 3235, 2972, 1719, 1562, 1453, 1305, 1255, 1169, 1090, 894, 702 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60°C): δ 0.72 (d, *J* = 6.4 Hz, 3H, $CH(CH_3)_2$), 0.85−0.94 (m, 6H, $CH(CH_3)_2$ and $CH(CH_3)Ph$), 2.35 (s, 3H, $ArCH_3$), 2.56 (s, 3H, $ArCH_3$),

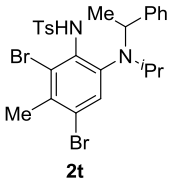
3.18 (septet, $J$ = 6.4 Hz, 1H, C*H*($CH_3$)$_2$), 3.85 (s, 3H, $CO_2CH_3$), 4.27 (q, $J$ = 6.4 Hz, 1H, C*H*($CH_3$)Ph), 7.22 (d, $J$ = 8.0 Hz, 2H, Ar*H*), 7.26−7.34 (m, 5H, Ar*H*), 7.41 (s, 1H, Ar*H*), 7.73 (s, 1H, Ar*H*), 7.80 (d, $J$ = 8.0 Hz, 2H, Ar*H*), 8.75 (brs, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.7 ($CH_3$), 21.4 ($CH_3$), 21.7 ($CH_3$), 22.0 ($CH_3$), 50.5 (CH), 51.6 (CH), 60.3 ($CH_3$), 118.0 (CH), 123.3 (CH), 127.2 (CH), 127.2 (C), 127.5 (CH), 128.8 (CH), 129.7 (CH), 131.0 (C), 131.4 (CH), 137.4 (C), 139.9 (C), 141.5 (C), 144.0 (C), 144.2 (C), 167.4 (C=O); HRMS (FAB) calcd for $C_{27}H_{33}N_2O_4S$ $[M+H]^+$ 481.2156, found 481.2158.




The structure of isolated **2s'** was assigned after removal of the 1-phenylethyl group. The reaction was carried out according to the procedure for hydrogenolysis of **2r** and **2r'**.

**S2s'**; yield 80%; purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt); colorless oil: IR (KBr) $\nu$ 3245, 2967, 1721, 1518, 1437, 1335, 1248, 1157, 909 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, $J$ = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 2.32 (s, 3H, ArC*H*$_3$), 2.41 (s, 3H, ArC*H*$_3$), 3.47 (septet, $J$ = 6.4 Hz, 1H, C*H*($CH_3$)$_2$), 3.85 (s, 3H, $CO_2CH_3$), 6.71 (s, 1H, Ar*H*), 7.23 (s, 1H, Ar*H*), 7.26 (d, $J$ = 8.0 Hz, 2H, Ar*H*), 7.65 (d, $J$ = 8.0 Hz, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 20.7 ($CH_3$), 21.5 ($CH_3$), 22.5 ($CH_3$), 44.9 (CH), 51.8 ($CH_3$), 116.9 (CH), 126.5 (C), 127.4 (CH), 128.4 (C), 128.9 (CH), 129.7 (CH), 129.9 (C), 136.1 (C), 140.1 (C), 144.1 (C), 167.9 (C=O); HRMS (FAB) calcd for $C_{19}H_{25}N_2O_4S$ $[M+H]^+$ 377.1530, found 377.1537.

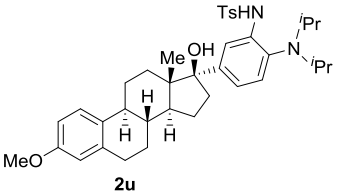
### *N*-Isopropyl-*N*-(1-phenylethyl)-3,5-dibromo-4-methyl-2-(tosylamido)aniline (2t)




TsN=IPh (1.5 equiv) was used. Yield 59%; purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); colorless amorphous; IR (KBr) $\nu$ 3149, 2971, 1446, 1323, 1155, 1091, 900, 811, 735 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 0.88 (d, $J$ = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.01 (d, $J$ = 6.4 Hz, 3H, CH(C*H*$_3$)Ph), 1.25 (d, $J$ = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 2.45 (s, 3H, ArC*H*$_3$), 2.56 (s, 3H, ArC*H*$_3$), 3.25 (septet, $J$ = 6.4 Hz, 1H, C*H*($CH_3$)$_2$), 4.36 (q, $J$ = 6.4 Hz, 1H, C*H*($CH_3$)Ph), 7.28−7.33 (m, 3H, Ar*H*), 7.39 (t, $J$ = 8.0 Hz, 2H, Ar*H*), 7.40−7.52 (m, 3H, Ar*H*), 7.92 (d, $J$ = 8.0 Hz, 2H, Ar*H*), 8.75 (brs, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 16.7 ($CH_3$), 21.1 ($CH_3$), 21.6 ($CH_3$), 21.8 ($CH_3$), 24.7 ($CH_3$), 50.8 (CH), 60.8 (CH), 119.5 (C), 119.7 (C), 127.0 (CH), 127.5 (CH), 127.6 (CH), 128.8 (CH), 128.9 (CH), 131.7 (CH), 137.1 (C), 138.5 (C), 139.4

(C), 139.8 (C), 143.1 (C), 143.8 (C); HRMS (FAB) calcd for $C_{25}H_{29}Br_2N_2O_2S$ $[M+H]^+$ 579.0311, found 579.0312.

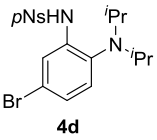
**3-*O*-Methyl-17-[4-(diisopropylamino)-3-(tosylamido)phenyl]estradiol (2u)**



**2u**

Yield 83%; purified by column chromatography (silica gel, 3:1 *n*-hexane/AcOEt); colorless solid; mp 100−103 °C, $[\alpha]_D^{26}$ = +24.8 (*c* 0.70, $CHCl_3$); IR (KBr) *v* 3543, 3199, 2931, 1499, 1379, 1237, 1162, 911, 813, 732 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.53 (dt, *J* = 12.8, 4.0 Hz, 1H, C16-*H*), 0.87−0.90 (m, 12H, CH(C*H*$_3$)$_2$), 1.06 (s, 3H, C18-*H*), 1.27−1.64 (m, 7H), 1.81−1.91 (m, 3H), 2.06−2.14 (m, 2H), 2.32 (s, 3H, ArC*H*$_3$), 2.32 −2.39 (m, 1H), 2.79−2.86 (m, 2H), 3.38 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 3.74 (s, 3H, OC*H*$_3$), 6.59 (d, *J* = 2.0 Hz, 1H, Ar*H*), 6.65 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.01−7.09 (m, 3H, Ar*H*), 7.19 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.53 (s, 1H, Ar*H*), 7.80 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.52 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 14.8 ($CH_3$), 20.7 ($CH_3$), 21.4 ($CH_3$), 24.0 ($CH_2$), 26.4 ($CH_2$), 27.5 ($CH_2$), 29.8 ($CH_2$), 33.9 ($CH_2$), 38.8 ($CH_2$), 39.7 (CH), 43.6 (CH), 47.3 (C), 48.5 (CH), 50.1 (CH), 55.2 ($CH_3$), 86.0 (C), 111.6 (CH), 114.0 (CH), 114.9 (CH), 121.4 (CH), 126.0 (CH), 127.1 (CH), 127.3 (CH), 129.5 (CH), 132.7 (C), 133.7 (C), 137.1 (C), 138.0 (C), 138.0 (C), 143.5 (C), 144.5 (C), 157.7 (C); HRMS (FAB) calcd for $C_{38}H_{51}N_2O_4S$ $[M+H]^+$ 631.3564, found 631.3570.

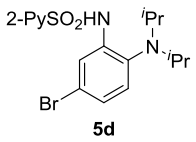
***N*,*N*-Diisopropyl-4-bromo-2-(*p*-nosylamido)aniline (4d)**



**4d**

*p*NsN=IPh (1.5 equiv) was used instead of TsN=IPh under otherwise identical conditions to the typical procedure. Yield 93%; purified by column chromatography (silica gel, 3:1 to 2:1 *n*-hexane/AcOEt); yellow solid; mp 143−145 °C; IR (KBr) *v* 3180, 2972, 1530, 1484, 1348, 1171, 1090, 939, 854, 736 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.85 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$) 3.37 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.99 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.12 (dd, *J* = 8.0, 2.4 Hz, 1H, Ar*H*), 7.77 (d, *J* = 2.4 Hz, 1H, Ar*H*), 8.09 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.30 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.78 (s, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.4 ($CH_3$), 50.2 (CH), 118.6 (CH), 120.3 (C), 124.3 (CH), 126.3 (CH), 128.3 (CH), 130.1 (CH), 134.2 (C), 138.5 (C), 145.7 (C), 150.6 (C); HRMS (FAB) calcd for $C_{18}H_{23}BrN_3O_4S$ $[M+H]^+$ 456.0587, found 456.0596.

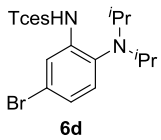
***N*,*N*-Diisopropyl-4-bromo-2-(2ryridinesulfonylamido)aniline (5d)**



**5d**

2rySO$_2$N=IPh was used instead of TsN=IPh under otherwise identical conditions to the typical procedure. Yield 70%; purified by column chromatography (silica gel, 3:1 to 2:1 *n*-hexane/AcOEt); colorless solid; mp 108−110 °C; IR (KBr) *v* 3194, 2972, 1585, 1485, 1382, 1177, 940, 869, 736 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.93 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 3.40 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.96 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.42 (dd, *J* = 8.0, 4.8 Hz, 1H, Ar*H*), 7.83 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.87 (dt, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 8.07 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.61 (d, *J* = 4.8 Hz, 1H, Ar*H*), 8.83 (brs, 1H, N*H*); $^{13}$C NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.5 ($CH_3$), 50.2 (CH), 118.8 (CH), 120.0 (C), 122.5 (CH), 125.5 (CH), 126.9 (CH), 129.8 (CH), 134.2 (C), 137.8 (CH), 139.3 (C), 150.1 (CH), 157.0 (C); HRMS (FAB) calcd for $C_{17}H_{23}BrN_3O_2S$ $[M+H]^+$ 412.0689, found 412.0702.

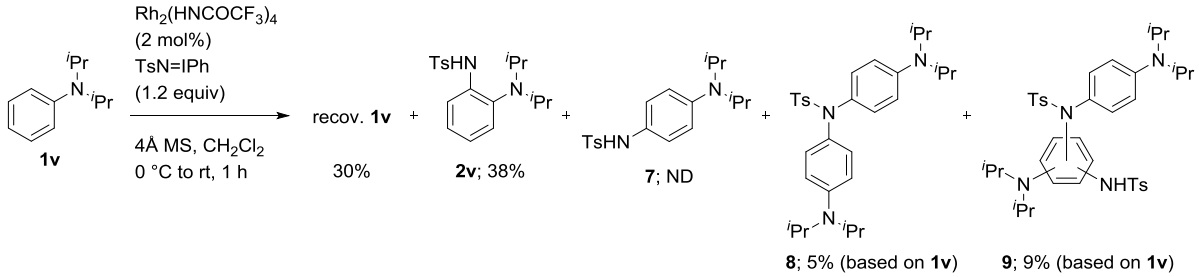
***N*,*N*-Diisopropyl-4-bromo-2-(trichloroethoxysulfonylamido)aniline (6d)**



**6d**

TcesN=IPh was used instead of TsN=IPh under otherwise identical conditions to the typical procedure. Yield 79%; purified by column chromatography (silica gel, 2:1 to 3:2 *n*-hexane/AcOEt); colorless oil; IR (KBr) *v* 3566, 2978, 1597, 1480, 1395, 1147, 992, 843, 726 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, 60 °C): δ 1.02 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 3.48 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 4.66 (s, 2H, OC*H*$_2$CCl$_3$), 7.06 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.18 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar*H*), 7.72 (d, *J* = 2.0 Hz, 1H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.5 ($CH_3$), 50.6 (CH), 78.8 ($CH_2$), 93.2 (C), 119.9 (CH), 120.5 (C), 126.4 (CH), 129.4 (CH), 133.8 (C), 138.6 (C); HRMS (FAB) calcd for $C_{14}H_{21}BrCl_3N_2O_3S$ $[M+H]^+$ 480.9516, found 480.9524.

**7. Rh(II)-catalyzed C(sp$^2$)−H amination of *N*,*N*-diisopropylaniline (1v)**




TsN=IPh (134 mg, 0.36 mmol) was added to a stirred mixture of *N*,*N*-diisopropylaniline (**1v**) (53.2 mg, 0.30 mmol), $Rh_2(HNCOCF_3)_4$ (3.9 mg, 0.006 mmol, 2 mol %) and 4Å MS (powder, 120 mg) in $CH_2Cl_2$ (3.0 mL) at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite,

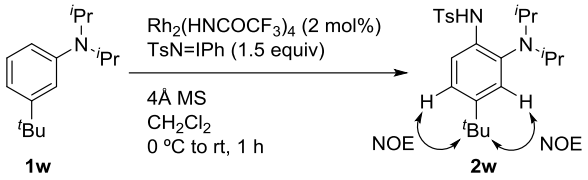
and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 6:1 to 4:1 *n*-hexane/AcOEt) to give **2v** (39.9 mg, 38%), **8** (3.6 mg, 5%), and **9** (8.9 mg, 9%).

**2v**; colorless solid; mp 100−102 °C; IR (KBr) *v* 3205, 2971, 1597, 1490, 1382, 1165, 1091, 934, 913, 754 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.87 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.34 (s, 3H, ArC*H*$_3$), 3.37 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.91 (dt, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.08−7.11 (m, 2H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.56 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.78 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.61 (s, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.5 ($CH_3$), 21.3 ($CH_3$), 50.1 (CH), 115.6 (CH), 122.3 (CH), 126.5 (CH), 127.2 (CH), 128.5 (CH), 129.5 (CH), 135.1 (C), 137.7 (C), 138.1 (C), 143.5 (C); HRMS (FAB) calcd for $C_{19}H_{27}N_2O_2S$ $[M+H]^+$ 347.1788, found 347.1784.

**8**; colorless amorphous; IR (KBr) *v* 2969, 1603, 1509, 1350, 1290, 1163, 814 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.20 (d, *J* = 6.4 Hz, 24H, CH(C*H*$_3$)$_2$), 2.44 (s, 3H, ArC*H*$_3$), 3.76 (septet, *J* = 6.4 Hz, 4H, C*H*(CH$_3$)$_2$), 6.71 (d, *J* = 9.2 Hz, 4H, Ar*H*), 7.04 (d, *J* = 9.2 Hz, 4H, Ar*H*), 7.25 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.59 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 21.2 ($CH_3$), 21.6 ($CH_3$), 47.4 (CH), 117.3 (CH), 127.9 (CH), 128.8 (CH), 129.2 (CH), 131.2 (C), 138.2 (C), 142.7 (C), 147.2 (C); HRMS (FAB) calcd for $C_{31}H_{44}N_3O_2S$ $[M+H]^+$ 522.3149, found 522.3157.

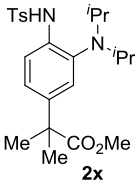
**9**; colorless amorphous; IR (KBr) *v* 3198, 2971, 1602, 1512, 1352, 1166, 1090, 1011, 911, 813 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.79 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.25 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.30 (s, 3H, ArC*H*$_3$), 2.42 (s, 3H, ArC*H*$_3$), 3.28 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 3.81 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.76 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.89 (dd, *J* = 8.0, 2.8 Hz, 1H, Ar*H*), 6.95 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.01 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.10 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.24 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.62−7.65 (m, 5H, Ar*H*), 8.42 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 20.5 ($CH_3$), 21.4 ($CH_3$), 21.5 ($CH_3$), 47.7 (CH), 50.1 (CH), 113.9 (CH), 117.4 (CH), 121.0 (CH), 127.4 (CH), 128.1 (CH), 128.6 (CH), 129.4 (CH), 129.8 (CH), 130.2 (CH), 133.9 (C), 137.0 (C), 137.9 (C), 138.2 (C), 140.8 (C), 142.0 (C), 143.2 (C), 143.5 (C), 148.0 (C); HRMS (FAB) calcd for $C_{38}H_{51}N_4O_4S_2$ $[M+H]^+$ 691.3346, found 691.3361.

**8. Typical procedure for Rh(II)-catalyzed *ortho* C−H amination of *papa*-unsubstituted *N*,*N*-dialkylanilines: Preparation of *N*,*N*-diisopropyl-5-*tert*-butyl-2-(tosylamido)aniline (2w)**



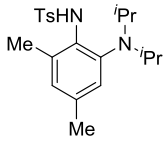

TsN=IPh (56.0 mg, 0.15 mmol) was added to a stirred mixture of *N*,*N*-diisopropyl-3-*tert*-butylaniline (**1w**) (23.3 mg, 0.10 mmol), $Rh_2(HNCOCF_3)_4$ (1.3 mg, 0.002 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt) to give 1,2-diaminobenzene **2w** (26.9 mg, 67%) as a colorless oil: IR (KBr) *ν* 3215, 2965, 1499, 1365, 1166, 1091, 889, 813 $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3CN$, 60 °C): δ 0.77 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (s, 9H, $^t$Bu), 2.26 (s, 3H, ArC*H*$_3$), 3.34 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 7.08 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar*H*), 7.11 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.21 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.33 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.70 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.42 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CD_3CN$, 60 °C): δ 20.8 ($CH_3$), 21.1 ($CH_3$), 31.3 ($CH_3$), 34.5 (C), 50.6 (CH), 115.3 (CH), 123.6 (CH), 126.8 (CH), 127.8 (CH), 130.3 (CH), 135.5 (C), 136.0 (C), 138.2 (C), 145.0 (C), 146.3 (C); HRMS (FAB) calcd for $C_{23}H_{35}N_2O_2S$ $[M+H]^+$ 403.2414, found 403.2426.

***N*,*N*-Diisopropyl-5-[2-(methoxycarbonyl)propan-2-yl]-2-(tosylamido)aniline (2x)**




Yield 59%; purified by column chromatography (silica gel, 4:1 *n*-hexane/AcOEt); colorless solid; mp 104−106 °C; IR (KBr) *ν* 3212, 2972, 1731, 1499, 1382, 1254, 1165 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.86 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.50 (s, 6H, ArC(C*H*$_3$)$_2$), 2.36 (s, 3H, ArC*H*$_3$), 3.37 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 3.60 (s, 3H, $CO_2CH_3$), 7.06−7.09 (m, 2H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.45 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.79 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.47 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 20.6 ($CH_3$), 21.4 ($CH_3$), 26.4 ($CH_3$), 46.1 (C), 50.2 (CH), 51.9 ($CH_3$), 115.1 (CH), 123.4 (CH), 126.6 (CH), 127.2 (CH), 129.5 (CH), 134.7 (C), 136.5 (C), 137.9 (C), 138.8 (C), 143.6 (C), 177.0 (C=O); HRMS (FAB) calcd for $C_{24}H_{35}N_2O_4S$ $[M+H]^+$ 447.2312, found 447.2317.

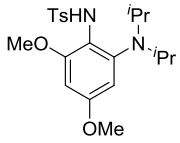
***N*,*N*-Diisopropyl-3,5-dimethyl-2-(tosylamido)aniline (2y)**



**2y**

Yield 97%; purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt); colorless oil; IR (KBr) *v* 2970, 1474, 1322, 1154, 1093, 922, 812 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.03 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.97 (s, 3H, ArC*H*$_3$), 2.25 (s, 3H, ArC*H*$_3$), 2.43 (s, 3H, ArC*H*$_3$), 3.45 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 6.78 (d, *J* = 1.6 Hz, 1H, Ar*H*), 6.87 (d, *J* = 1.6 Hz, 1H, Ar*H*), 7.30 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.88 (d, *J* = 8.0 Hz, 2H, Ar*H*), 9.00 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 20.6 ($CH_3$), 21.0 ($CH_3$), 21.3 ($CH_3$), 21.5 ($CH_3$), 50.0 (CH), 126.0 (CH), 126.7 (CH), 129.2 (CH), 129.6 (C), 129.7 (CH), 133.0 (C), 135.6 (C), 138.7 (C), 140.0 (C), 142.8 (C); HRMS (FAB) calcd for $C_{21}H_{31}N_2O_2S$ $[M+H]^+$ 375.2101, found 375.2102.

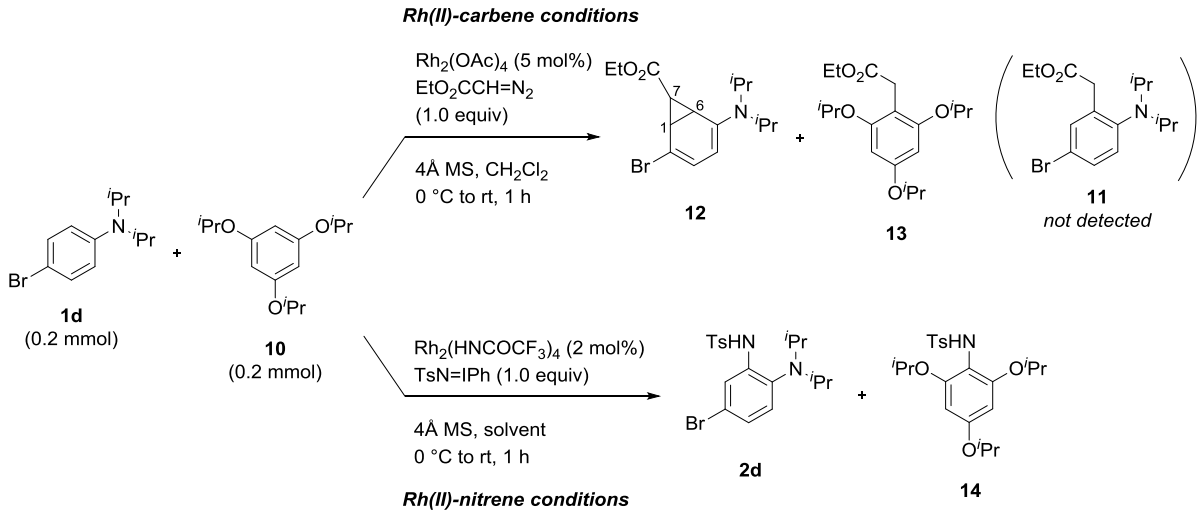
***N*,*N*-Diisopropyl-3,5-dimethyl-2-(tosylamido)aniline (2z)**



**2y**

Yield 65%; purified by prep. TLC (silica gel, 10:1 *n*-hexane/AcOEt); beige solid: mp 115−117 °C; IR (KBr) *v* 3180, 2968, 1598, 1487, 1329, 1151, 915 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.06 (d, *J* = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 2.43 (s, 3H, ArC*H*$_3$), 3.39 (s, 3H, OC*H*$_3$), 3.49 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 3.74 (s, 3H, OC*H*$_3$), 6.30 (d, *J* = 2.4 Hz, 1H, Ar*H*), 6.41 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.31 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.88 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.19 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 20.6 ($CH_3$), 21.5 ($CH_3$), 50.0 (CH), 54.6 ($CH_3$), 55.4 ($CH_3$), 97.1 (CH), 105.4 (CH), 122.7 (C), 126.8 (CH), 128.7 (CH), 139.5 (C), 140.4 (C), 142.3 (C), 151.7 (C), 156.2 (C); HRMS (FAB) calcd for $C_{21}H_{30}N_2O_4S$ $[M]^+$ 406.1926, found 406.1926.

## 9. Competition experiments between *N*,*N*-diisopropyl-4-bromoaniline (1d) and 1,3,5-triisopropylbenzene (10)



**Rh(II)-carbene conditions:** To a stirred mixture of **1d** (51.2 mg, 0.20 mmol), **10** (50.4 mg, 0.20 mmol), $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol, 5 mol %) and 4Å MS (powder, 40 mg) in $CH_2Cl_2$ (1.0 mL) was added a solution of ethyl diazoacetate in $CH_2Cl_2$ (0.1 M, 1.0 mL, 0.10 mmol) dropwise at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 10:1 to 6:1 *n*-hexane/AcOEt) to give cyclopropane **12** (5.5 mg, 16%) and C−H insertion product **13** (6.4 mg, 19%) with recovery of a mixture of starting materials (40.1 mg, **1d**:**10** = 51:49).

**12**; yellow amorphous; IR (KBr) *v* 2975, 1685, 1529, 1490, 1252, 1215, 1044, 911, 750 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.25−1.38 (m, 16H, CH(C*H*$_3$)$_2$, C7-*H* and $CO_2CH_2CH_3$), 3.72 (septet, *J* = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$), 4.10−4.26 (m, 3H, C1-*H* and $CO_2CH_2CH_3$), 5.06 (ddd, *J* = 8.0, 8.0, 1.2 Hz, 1H, C6-*H*), 6.06 (dd, *J* = 11.2, 1.2 Hz, 1H, C4-*H*), 7.07 (d, *J* = 11.2 Hz, 1H, C3-*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 14.5 ($CH_3$), 22.3 ($CH_3$), 36.7 (CH), 53.5 (CH), 59.8 ($CH_2$), 104.4 (CH), 111.7 (CH), 116.5 (CH), 123.1 (CH), 131.7 (CH), 144.9 (C), 167.2 (C=O); HRMS (FAB) calcd for $C_{16}H_{24}BrNO_2$ $[M]^+$ 341.0990, found 341.0992.

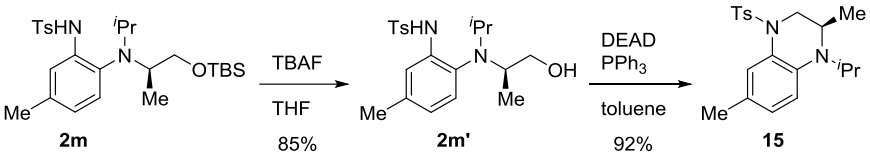
**13**; colorless oil; IR (KBr) *v* 2976, 1740, 1607, 1117, 1034, 815 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.2 Hz, 3H, $OCH_2CH_3$), 1.29 (d, *J* = 6.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.33 (d, *J* = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 3.56 (s, 2H, Ar$CH_2CO_2$), 4.12 (q, *J* = 7.2 Hz, 2H, $OCH_2CH_3$), 4.46 (septet, *J* = 6.0 Hz, 3H, C*H*(CH$_3$)$_2$), 6.09 (s, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 14.3 ($CH_3$), 22.1 ($CH_3$), 22.1 ($CH_3$), 29.1 ($CH_2$), 60.1 ($CH_2$), 69.9 (CH), 70.5 (CH), 94.7 (CH), 106.9 (C), 157.3 (C), 158.1 (C), 172.8 (C=O); HRMS (FAB) calcd for $C_{19}H_{31}O_5$ $[M+H]^+$ 339.2166, found 339.2167.

**Rh(II)-nitrene conditions:** TsN=IPh (37.3 mg, 0.10 mmol) was added to a stirred mixture of **1d** (51.2 mg, 0.20 mmol), **10** (50.4 mg, 0.20 mmol), $Rh_2(HNCOCF_3)_4$ (1.3 mg, 0.002 mmol, 2 mol %) and 4Å MS (powder, 40 mg) in indicated solvent (1.0 mL) at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 4:1 to 1:1 *n*-hexane/AcOEt) to give **2d** and **14** with recovery of a mixture of starting materials.

**14**; light yellow oil; IR (KBr) *v* 3282, 2977, 1596, 1496, 1329, 1117, 811 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.14 (d, *J* = 6.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.32 (d, *J* = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 2.39 (s, 3H, Ar*CH*$_3$), 4.38 (septet, *J* = 6.0 Hz, 2H, C*H*(CH$_3$)$_2$), 4.45 (septet, *J* = 6.0 Hz, 1H, C*H*(CH$_3$)$_2$), 6.00 (s, 2H, Ar*H*), 7.21 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.71 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 21.4 ($CH_3$), 21.7 ($CH_3$), 22.1 ($CH_3$), 70.1 (CH), 70.6 (CH),

94.4 (CH), 108.6 (C), 127.5 (CH), 128.9 (CH), 138.6 (C), 142.6 (C), 154.9 (C), 157.7 (C); HRMS (FAB) calcd for $C_{22}H_{31}NO_5S$ $[M]^+$ 421.5520, found 421.1930.

**10. Procedure for the synthesis of tetrahydroquinoxaline 15**

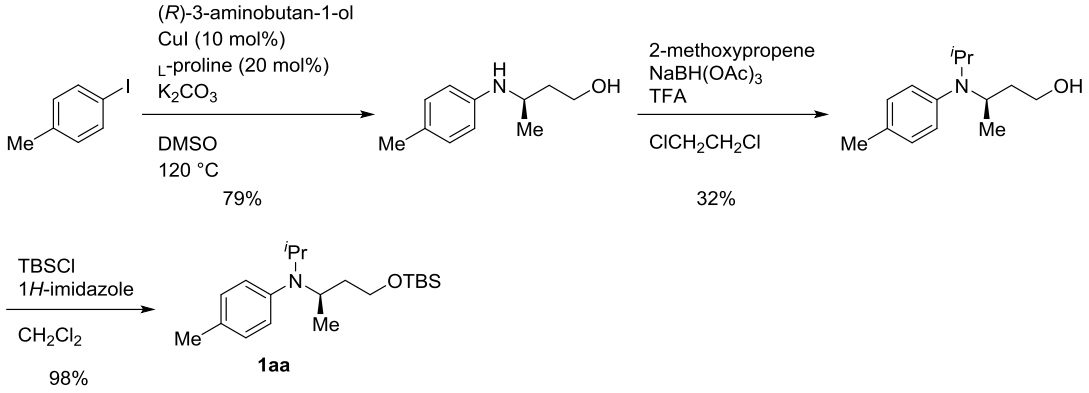



To a solution of **2m** (147 mg, 0.30 mmol) in THF (3.0 mL) was added a solution of TBAF in THF (1.0 M, 0.45 mL, 0.45 mmol) at room temperature under Ar atmosphere. After stirring for 1 h, water was added and the mixture was extracted with AcOEt. The combined organic extracts were successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 1:1 *n*-hexane/AcOEt) to give **2m'** (95.8 mg, 85%) as a colorless oil: $[\alpha]_D^{20}$ = −44.8 (*c* 1.03, $CHCl_3$); IR (KBr) *v* 3520, 3142, 2969, 1506, 1383, 1327, 1157, 1091, 814 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.85 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 0.94 (d, *J* = 4.8 Hz, 3H, CH(C*H*$_3$)CH$_2$), 0.98 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 2.27 (s, 3H, ArC*H*$_3$), 2.36 (s, 3H, ArC*H*$_3$), 3.30−3.38 (m, 4H, C*H*(CH$_3$)$_2$ and C*H*(CH$_3$)C*H*$_2$O), 6.71 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.98 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.37 (s, 1H, Ar*H*), 7.83 (d, *J* = 8.0 Hz, 2H, Ar*H*), 9.00 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 14.9 ($CH_3$), 21.4 ($CH_3$), 21.4 ($CH_3$), 21.5 ($CH_3$), 50.5 (CH), 56.7 (CH), 64.9 ($CH_2$), 116.9 (CH), 123.0 (CH), 127.3 (CH), 129.4 (CH), 129.9 (CH), 131.7 (C), 136.7 (C), 137.9 (C), 138.4 (C), 143.4 (C); HRMS (FAB) calcd for $C_{20}H_{29}N_2O_3S$ $[M+H]^+$ 377.1893, found 377.1903.

To a solution of **2m'** (37.5 mg, 0.10 mmol) and $PPh_3$ (39.3 mg, 0.15 mmol) in toluene (1.0 mL) was added a solution of DEAD in toluene (2.2 M, 68 μL, 0.15 mmol) dropwise at room temperature under Ar atmosphere. After stirring for 6 h, the whole mixture was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 6:1 *n*-hexane/AcOEt) to give **15** (33.2 mg, 92%) as a colorless oil: $[\alpha]_D^{20}$ = −42.9 (*c* 0.68, $CHCl_3$); IR (KBr) *v* 2971, 1508, 1341, 1160, 1090, 810 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.00 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.10 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.13 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)CH$_2$), 2.20 (s, 3H, ArC*H*$_3$), 2.39 (s, 3H, ArC*H*$_3$), 3.50 (dd, *J* = 12.8, 4.4 Hz, 1H, CH(CH$_3$)CH*H*O), 3.53−3.57 (m, 1H, C*H*(CH$_3$)CHHO) 3.74 (septet, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 3.89 (dd, *J* = 12.8, 5.2 Hz, 1H, CH(CH$_3$)C*H*HO), 6.64 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.79 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 7.23−7.25 (m, 3H, Ar*H*), 7.64 (d, *J*

= 8.0 Hz, 2H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 19.6 ($CH_3$), 19.9 ($CH_3$), 20.8 ($CH_3$), 21.4 ($CH_3$), 46.3 (CH), 49.6 (CH), 50.7 ($CH_2$), 114.0 (CH), 122.7 (CH), 123.0 (CH), 124.2 (C), 125.2 (C), 126.9 (CH), 127.1 (CH), 129.4 (CH), 129.7 (CH), 135.5 (C), 138.0 (C), 143.3 (C); HRMS (FAB) calcd for $C_{20}H_{26}N_2O_2S$ $[M]^+$ 358.1715, found 358.1720.

**11. Procedure for the synthesis of 1,5-benzodiazepine 16.**

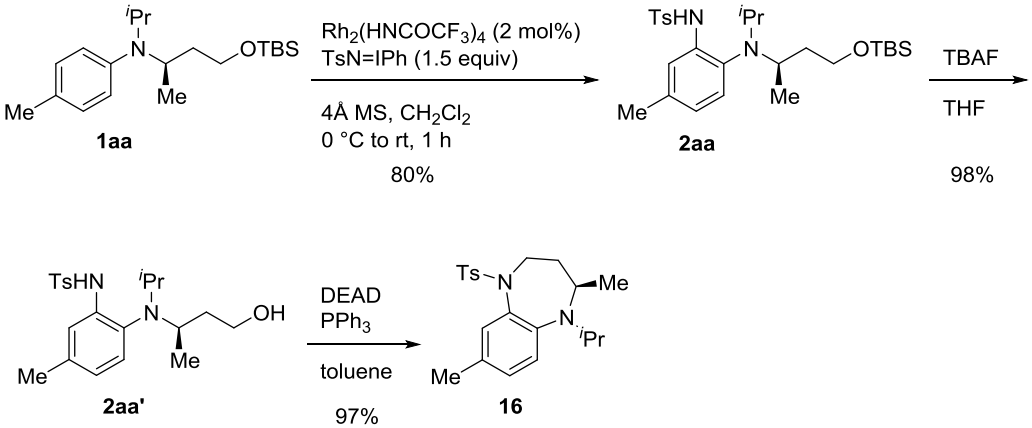



The mixture of 4-iodotoluene (2.04 g, 9.4 mmol), (*R*)-3-aminobutan-1-ol (1.00 g, 11 mmol), CuI (179 mg, 0.94 mmol, 10 mol%), L-proline (215 mg, 1.9 mmol, 20 mol%), and $K_2CO_3$ (2.58 g, 19 mmol) in DMSO (5.6 mL) was heated to 120 °C under Ar atmosphere. After stirring for 12 h at the same temperature, the reaction was quenched with saturated aqueous $NH_4Cl$, and the mixture was extracted with AcOEt. The combined organic extracts were successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 1:1 *n*-hexane/AcOEt) to give (*R*)-*N*-(4-hydroxybutan-2-yl)-*p*-toluidine[7] (1.30 g, 79%) as a colorless oil: $[\alpha]_D^{23}$ = −84.5 (*c* 1.03, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 1.19 (d, *J* = 6.0 Hz, 3H, CH(C*H*$_3$)CH$_2$), 1.72−1.78 (m, 2H, CHC*H*$_2$CH$_2$), 2.24 (s, 3H, Ar*H*), 2.93 (brs, 1H, O*H*), 3.64 (sextet, *J* = 6.3 Hz, 1H, C*H*(CH$_3$)CH$_2$), 3.82 (t, *J* = 6.0 Hz, 2H, CH$_2$C*H*$_2$O), 6.59 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.99 (d, *J* = 8.4 Hz, 2H, Ar*H*).

To a solution of (*R*)-*N*-(4-hydroxybutan-2-yl)-*p*-toluidine (538 mg, 3.0 mmol), 2-methoxypropene (0.42 mL, 4.5 mmol), and TFA (0.23 mL, 3.0 mmol) in 1,2-dichloroethane (9.0 mL) was added $NaBH(OAc)_3$ (954 mg, 4.5 mmol) at room temperature under Ar atmosphere. After stirring for 12 h, the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The combined organic extracts were successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 2:1 *n*-hexane/AcOEt) to give (*R*)-*N*-isopropyl-*N*-(4-hydroxybutan-2-yl)-*p*-toluidine (215 mg, 32%) as a colorless oil: $[\alpha]_D^{23}$ = −102.7 (*c* 1.02, $CHCl_3$); IR (KBr) *v* 3323, 2967, 1616,

1515, 1286, 1181, 1053, 807 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.12 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)CH$_2$), 1.13 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.14 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 1.58 (ddd, *J* = 14.4, 10.0, 4.4 Hz, 1H, CHCH*H*CH$_2$), 1.81 (ddd, *J* = 14.4, 8.0, 5.2 Hz, 1H, CHC*H*HCH$_2$), 2.29 (s, 3H, ArC*H*$_3$), 3.61−3.92 (m, 4H, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)CH$_2$C*H*$_2$O), 6.98 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.05 (d, *J* = 8.4 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 18.5 (CH$_3$), 20.6 (CH$_3$), 21.1 (CH$_3$), 22.3 (CH$_3$), 36.4 (CH$_2$), 48.9 (CH), 52.6 (CH), 62.1 (CH$_2$), 124.6 (CH), 128.9 (CH), 131.5 (C), 144.3 (C); HRMS (FAB) calcd for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1852, found 222.1865.

To a solution of (*R*)-*N*-isopropyl-*N*-(4-hydroxypropan-2-yl)-*p*-toluidine (177 mg, 0.80 mmol) and 1*H*-imidazole (81.7 mg, 1.2 mmol) in $CH_2Cl_2$ (4.0 mL) was added TBSCl (181 mg, 1.2 mmol) at room temperature under Ar atmosphere. After stirring for 1 h, the reaction was quenched with water, and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 10:1 *n*-hexane/AcOEt) to give **1aa** (264 mg, 98%) as a colorless oil: $[\alpha]_D^{23}$ = −16.7 (*c* 1.03, $CHCl_3$); IR (KBr) *v* 2957, 1617, 1516, 1255, 1098, 835 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 3H, SiC*H*$_3$), 0.03 (s, 3H, SiC*H*$_3$), 0.89 (s, 9H, Si$^t$Bu), 1.18−1.20 (m, 9H, CH(C*H*$_3$)CH$_2$ and CH(C*H*$_3$)$_2$), 1.65 (ddt, *J* = 14.0, 8.0, 6.0 Hz, 1H, CHCH*H*CH$_2$), 1.89 (dt, *J* = 14.0, 6.0 Hz, 1H, CHC*H*HCH$_2$), 2.25 (s, 3H, ArC*H*$_3$), 3.57−3.74 (m, 4H, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)CH$_2$C*H*$_2$O), 6.81 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.98 (d, *J* = 8.4 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ −5.41 (CH$_3$), −5.36 (CH$_3$), 18.3 (C), 19.2 (CH$_3$), 20.4 (CH$_3$), 21.6 (CH$_3$), 21.7 (CH$_3$), 25.9 (CH$_3$), 38.7 (CH$_2$), 48.3 (CH), 48.7 (CH), 60.9 (CH$_2$), 119.6 (CH), 127.4 (CH), 129.0 (C), 145.9 (C); HRMS (FAB) calcd for $C_{20}H_{38}NOSi$ $[M+H]^+$ 336.2717, found 336.2722.




TsN=IPh (224 mg, 0.60 mmol) was added to a stirred mixture of **1aa** (134 mg, 0.40 mmol), $Rh_2(HNCOCF_3)_4$ (5.2 mg, 0.008 mmol, 2 mol %) and 4Å MS (powder, 160 mg) in

$CH_2Cl_2$ (4.0 mL) at 0 °C under Ar atmosphere. After stirring at room temperature for 1 h, the whole mixture was filtered through a pad of Celite, and the filtrate was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 8:1 *n*-hexane/AcOEt) to give diaminobenzene **2aa** (161 mg, 80%) as a colorless oil: $[\alpha]_D^{23}$ = +3.75 (*c* 0.99, $CHCl_3$); IR (KBr) *ν* 3210, 2956, 1504, 1382, 1169, 1092, 835 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.02 (s, 3H, SiC*H*$_3$), 0.03 (s, 3H, SiC*H*$_3$), 0.86−0.89 (m, 18H, Si$^t$Bu, CH(C*H*$_3$)$CH_2$ and CH(C*H*$_3$)$_2$), 1.09 (ddd, *J* = 18.0, 9.6, 4.8 Hz, 1H, CHCH*H*$CH_2$), 1.73−1.81 (m, 1H, CHC*H*$HCH_2$), 2.28 (s, 3H, ArC*H*$_3$), 2.35 (s, 3H, ArC*H*$_3$), 3.32 (septet, *J* = 6.4 Hz, 1H, C*H*$(CH_3)_2$), 3.40 (ddq, *J* = 16.0, 6.4, 3.2 Hz, 1H, C*H*$(CH_3)CH_2$), 3.48 (ddd, *J* = 10.4, 8.4, 4.8 Hz, 1H, $CH_2$CH*H*O), 3.56 (ddd, *J* = 10.4, 6.0, 4.8 Hz, 1H, $CH_2$C*H*HO), 6.71 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.96 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.20 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.39 (s, 1H, Ar*H*), 7.79 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.51 (brs, 1H, N*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ −5.4 ($CH_3$), −5.3 ($CH_3$), 17.5 ($CH_3$), 18.3 (C), 21.0 ($CH_3$), 21.4 ($CH_3$), 21.4 ($CH_3$), 26.0 ($CH_3$), 36.9 ($CH_2$), 50.4 (CH), 51.7 (CH), 60.6 ($CH_2$), 116.2 (CH), 123.1 (CH), 127.3 (CH), 128.4 (CH), 128.5 (C), 129.5 (CH), 132.5 (C), 136.4 (C), 137.8 (C), 143.5 (C); HRMS (FAB) calcd for $C_{27}H_{45}N_2O_3SSi$ $[M+H]^+$ 505.2915, found 505.2927.

To a solution of **2aa** (126 mg, 0.25 mmol) in THF (2.5 mL) was added a solution of TBAF in THF (1.0 M, 0.38 mL, 0.38 mmol) at room temperature under Ar atmosphere. After stirring for 1 h, the reaction was quenched with water, and the mixture was extracted with AcOEt. The combined organic extracts were successively washed with brine, and dried over anhydrous $Na_2SO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 3:2 *n*-hexane/AcOEt) to give **2aa'** (95.2 mg, 98%) as a colorless oil: $[\alpha]_D^{23}$ = −12.7 (*c* 0.42, $CHCl_3$); IR (KBr) *ν* 3212, 2970, 1504, 1370, 1167, 1090, 967, 814 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.85 (d, *J* = 6.4 H, 3H, CH(C*H*$_3$)$_2$), 0.90 (d, *J* = 6.4 H, 3H, CH(C*H*$_3$)$_2$), 0.94 (d, *J* = 6.4 H, 3H, CH(C*H*$_3$)$CH_2$), 1.25 (ddd, *J* = 19.6, 9.6, 5.6 Hz, 1H, CHCH*H*$CH_2$), 1.68−1.76 (m, 1H, CHC*H*$HCH_2$), 2.28 (s, 3H, ArC*H*$_3$), 2.35 (s, 3H, ArC*H*$_3$), 3.36 (m, 2H, C*H*$(CH_3)_2$ and C*H*$(CH_3)CH_2$), 3.54−3.60 (m, 1H, $CH_2$CH*H*O), 3.56 (dt, *J* = 12.0, 6.0 Hz, 1H, $CH_2$C*H*HO), 5.03 (brs, 1H, O*H*), 6.72 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.98 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.21 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.39 (s, 1H, Ar*H*), 7.79 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 17.8 ($CH_3$), 21.0 ($CH_3$), 21.4 ($CH_3$), 21.4 ($CH_3$), 37.0 ($CH_2$), 50.0 (CH), 52.3 (CH), 60.5 ($CH_2$), 116.4 (CH), 123.1 (CH), 127.2 (CH), 128.7 (CH), 129.5 (CH), 132.3 (C), 136.5 (C), 137.8 (C), 137.8 (C), 143.5 (C); HRMS (FAB) calcd for $C_{21}H_{31}N_2O_3S$ $[M+H]^+$ 391.2050, found 391.2064.

To a solution of **2aa'** (52.7 mg, 0.14 mmol) and $PPh_3$ (53.1 mg, 0.20 mmol) in toluene (5.4 mL) was added a solution of DEAD in toluene (2.2 M, 92 μL, 0.20 mmol)

dropwise at room temperature under Ar atmosphere. After stirring for 6 h, the whole mixture was evaporated in vacuo to furnish the crude product, which was purified by column chromatography (silica gel, 6:1 *n*-hexane/AcOEt) to give **16** (48.8 mg, 97%) as a colorless solid: mp 120−121 °C; $[\alpha]_D^{24}$ = −177.8 (*c* 1.03, $CHCl_3$); IR (KBr) *v* 2967, 1504, 1343, 1160, 1091, 981, 812 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C): δ 0.54 (d, *J* = 6.4 H, 3H, $CH(CH_3)_2$), 0.74 (d, *J* = 6.4 H, 3H, $CH(CH_3)CH_2$), 1.04 (d, *J* = 6.4 H, 3H, $CH(CH_3)_2$), 1.26 (dddd, *J* = 14.4, 7.6, 7.6, 2.0 Hz, 1H, $CHCHHCH_2$), 1.86 (dddd, *J* = 14.4, 9.2, 5.2, 2.8 Hz, 1H, $CHCHHCH_2$), 2.29 (s, 3H, $ArCH_3$), 2.36 (s, 3H, $ArCH_3$), 3.32 (septet, *J* = 6.4 Hz, 1H, $CH(CH_3)_2$) 3.37 (dd, *J* = 12.0, 6.4 Hz, 1H, $CH(CH_3)CH_2$), 3.44 (ddd, *J* = 12.0, 9.2, 2.0 Hz, 1H, $CH_2CHHN$), 4.00 (ddd, *J* = 12.0, 8.0, 2.8 Hz, 1H, $CH_2CHHN$), 6.84 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.97 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.16 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.28 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.55 (d, *J* = 8.0 Hz, 2H, Ar*H*); $^{13}C$ NMR (100 MHz, $CDCl_3$, 60 °C): δ 15.1 ($CH_3$), 20.6 ($CH_3$), 20.9 ($CH_3$), 21.3 ($CH_3$), 21.9 ($CH_3$), 34.0 ($CH_2$), 45.0 ($CH_2$), 48.2 (CH), 49.2 (CH), 124.3 (CH), 127.6 (CH), 128.2 (CH), 129.1 (CH), 131.1 (CH), 132.3 (C), 133.7 (C), 138.6 (C), 141.6 (C), 142.5 (C); HRMS (FAB) calcd for $C_{21}H_{29}N_2O_2S$ $[M+H]^+$ 373.1944, found 373.1951.

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