Supporting Information For:

**Synthesis of Substituted Quinolines Using the Dianion Addition of N-Boc-Anilines
and α -Tolylsulfonyl- α,β -unsaturated Ketones**

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2-(p-toluenesulfonyl)-4'-chloroacetophenone (2b). **2b** was prepared from 2-bromo-4'-chloroacetophenone (35.0 g, 150 mmol) and p-toluenesulfinic acid sodium hydrate (26.8 g, 150 mmol) in 86% yield as described above for **2a**. mp 138.0-139.0 °C; IR 3003, 1680, 1590, 1572 cm⁻¹; ¹H NMR (CDCl₃) 2.47 (s, 3H), 4.68 (s, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H); ¹³C NMR 21.6, 63.5, 128.4 (2C), 129.0 (2C), 129.8 (2C), 130.6 (2C), 134.0, 135.6, 140.8, 145.4, 187.0; Anal. Calcd for C₁₅H₁₆ClO₄S: C, 58.35; H 4.24; Cl, 11.48; S, 10.38; Found: C, 58.24; H, 4.38; Cl, 10.81; S, 10.26.

1-(p-toluenesulfonyl)-propan-2-one (2c). A mixture of chloroacetone (14.85 g, 160 mmol), p-toluenesulfinic acid sodium hydrate (28.6 g, 160 mmol) in ethanol (800 mL) was heated at reflux for 3 h. The mixture was stirred and cooled to room temperature and concentrated in vacuo. The resulting residue was diluted with EtOAc (400 mL), and the organic phase was washed with water (2 X 100 mL), brine (100 mL), and dried (MgSO₄). The solution was then concentrated in vacuo to give a solid. The solid was washed with hexane (100 mL), ether (2 X 50 mL) and dried to give 21.0 g (62%) of pure **2c**. mp 52.0-53.0 °C; IR 2990, 1715, 1597 cm⁻¹; ¹H NMR (CDCl₃) 2.40 (s, 3H), 2.46 (s, 3H), 4.14 (s, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H); ¹³C NMR 21.7, 31.4, 67.9, 128.2 (2C), 130.0 (2C), 135.7, 145.5, 196.0; Anal. Calcd for C₁₀H₁₂O₃S: C, 56.58; H 5.70; S, 15.11; Found: C, 56.57; H, 5.82; S, 15.05.

3-(4'-Chlorophenyl)-1-(4'-methoxyphenyl)-2-(p-toluenesulfonyl)-2-(E)-propen-1-one (3b). **3b** was prepared from **2a** (4.6 g, 15 mmol), 4-chlorobenzaldehyde (2.24 g, 16 mmol), piperidine (0.18 g, 2 mmol), acetic acid (0.42 g, 7 mmol) in toluene (40 mL) as described above for **3a** in 91% yield. mp 132.5-133.5 °C; IR 2984, 1651, 1597, 1572 cm⁻¹; ¹H NMR (CDCl₃)

2.44 (s, 3H), 3.83 (s, 3H), 6.84 (d, $J = 8.8$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.91 (s, 1H); ^{13}C NMR 21.6, 55.5, 114.1 (2C), 128.5, 128.6 (2C), 129.1 (2C), 129.7 (2C), 130.0, 131.2 (2C), 132.2 (2C), 136.4, 136.9, 138.6, 140.7, 144.7, 164.7, 190.0. Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{ClO}_4\text{S}$: C, 64.71; H, 4.49; Cl, 8.30; S, 7.51; Found: C, 64.42; H, 4.46; Cl, 8.25; S, 7.35.

1-(4'-Methoxyphenyl)-5-methyl-2-(p-toluenesulfonyl)-2-(E)-hexen-1-one (3c). **3c** was prepared from **2a** (4.6 g, 15 mmol), isovaleraldehyde (2.0 g, 22 mmol), piperidine (0.18 g, 2 mmol), acetic acid (0.36 g, 6 mmol) in toluene (40 mL) as described above for **3a** in 54% yield as an oil. IR 2957, 1658, 1597, 1571 cm^{-1} ; ^1H NMR (CDCl_3) 0.84 (d, $J = 6.7$ Hz, 6H), 1.78 (m, 1H), 1.92 (dd, $J = 7.0, 7.0$ Hz, 2H), 2.43 (s, 3H), 3.89 (s, 3H), 6.94 (d, $J = 8.8$ Hz, 2H), 7.17 (t, $J = 7.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.89 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR 21.5, 22.2, 28.0, 38.3, 55.5, 114.0 (2C), 128.2 (2C), 129.4, 129.6 (2C), 132.3 (2C), 136.9, 142.8, 144.38, 144.44, 164.6, 189.2. The *E*-conformation was assigned by 2D NOE experiment. Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4\text{S}$: C, 67.72; H 6.49; S, 8.61; Found: C, 67.59; H, 6.49; S, 8.67.

1-(4'-Chlorophenyl)-3-(4'-methylphenyl)-2-(p-toluenesulfonyl)-2-(E)-propen-1-one (3e). **3e** was prepared from **2b** (6.17 g, 20 mmol), p-tolualdehyde (2.7 g, 22 mmol), piperidine (0.36 g, 4 mmol), acetic acid (0.48 g, 8 mmol) in toluene (40 mL) as described above for **3a** in 85% yield. mp 103.0-105.0 $^{\circ}\text{C}$; IR 2934, 1657, 1597, 1572 cm^{-1} ; ^1H NMR (CDCl_3) 2.26 (s, 3H), 2.46 (s, 3H), 7.02 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 4H), 7.76 (d, $J = 8.7$ Hz, 2H), 7.82 (d, $J = 8.7$ Hz, 2H), 7.98 (s, 1H); ^{13}C NMR 21.3, 21.6, 128.4, 128.5 (2C), 129.1 (2C), 129.6 (2C), 129.7 (2C), 130.2 (2C), 131.1 (2C), 134.0, 136.7, 138.1, 140.8, 141.2, 141.9, 144.7, 191.3. Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{ClO}_3\text{S}$: C, 67.23; H 4.66; Cl, 8.63; S, 7.80; Found: C, 67.34; H, 4.87; Cl, 8.62; S, 7.97.

1-(4'-Methylphenyl)-2-(p-toluenesulfonyl)-1-(E)-buten-3-one (3f). **3f** was prepared from **2c** (4.24 g, 20 mmol), p-tolualdehyde (2.64 g, 22 mmol), piperidine (0.36 g, 4 mmol), and acetic acid (0.48 g, 8 mmol) in toluene (30 mL) at reflux for 1h as described above for **3a** in 78% yield. mp 88.0-90.0 °C; IR 2923, 1699, 1615, 1597 cm⁻¹; ¹H NMR (CDCl₃) 2.31 (s, 3H), 2.37 (s, 3H), 2.44 (s, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.80 (s, 1H); ¹³C NMR 21.5, 21.7, 31.9, 128.5 (2C), 128.8, 129.76, (2C), 129.79 (2C), 129.9 (2C), 136.8, 139.8, 141.2, 142.0, 144.7, 200.0. Anal. Calcd for C₁₈H₁₈O₃S: C, 68.76; H, 5.77; S, 10.20; Found: C, 69.07; H, 6.00; S, 10.15.

N-(tert-Butoxycarbonyl)-p-anisidine (4b). **4b** was prepared from of p-anisidine (7.4 g, 60 mmol) and di-*tert*-butyl dicarbonate (65 mL, 1.0 M in THF) in 89% yield as described above for **4a**. mp 95.0-96.0 °C; IR 3365, 2987, 1694, 1524 cm⁻¹; ¹H NMR (CDCl₃) 1.52 (s, 9H), 3.78 (s, 3H), 6.30 (br s, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H); ¹³C NMR 28.3 (3C), 55.4, 80.1, 114.1 (2C), 120.6 (2C), 131.4, 153.2, 155.6. Anal. Calcd for C₁₂H₁₇NO₃: C, 64.55; H 7.67; N, 6.27; Found: C, 64.54; H, 7.71; N, 6.28.

N-(tert-Butoxycarbonyl)-4-(trifluoromethyl)aniline (4c). To a solution of 4-(trifluoromethyl)aniline (8.05 g, 50 mmol) in 3.3 N NaOH (15 mL) was added di-*tert*-butyl dicarbonate (55 mL, 1.0 M in THF) slowly at room temperature. The mixture was stirred at room temperature for 1 day, then di-*tert*-butyl dicarbonate (20 mL, 1.0M in THF) was added, after 2 days, di-*tert*-butyl dicarbonate (30 mL, 1.0 M in THF) was added. The mixture was stirred at room temperature for additional 3 days and concentrated in vacuo. The residue was diluted with EtOAc (200 mL), and the organic phase was washed with water (60 mL), brine (2 X 60 mL), and dried (MgSO₄). The solution was then concentrated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc 6:1) to give 11.5 g (88%) of pure **4c** as a solid.

mp 121.0-122.0 °C; IR 3366, 2986, 1705, 1618, 1597, 1529, 1508 cm^{-1} ; ^1H NMR (CDCl_3) 1.52 (s, 9H), 6.60 (br s, 1H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.54 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR 28.3 (3C), 81.3, 117.9 (2C), 122.9 (CF_3), 124.6 (CCF_3), 125.0 (CCF_3), 125.5, (CF_3), 126.2 (2C), 141.5, 152.3; Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NO}_2$: C, 55.17; H, 5.40; F, 21.82; N, 5.36; Found: C, 55.26; H, 5.37; F, 21.45; N, 5.28.

6-Methoxy-2-(4'-methoxyphenyl)-4-(4'-methylphenyl)-quinoline (8b). **8b** was prepared from **4b** (446 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3a** (325 mg, 0.8 mmol) as described above for **8a** in 60% yield. mp 135.0-136.0 °C; IR 3015, 1620, 1593, 1516, 1497, 1238 cm^{-1} ; ^1H NMR (CDCl_3) 2.42 (s, 3H), 3.72 (s, 3H), 3.79 (s, 3H), 6.97 (d, $J = 9.0$ Hz, 2H), 7.16 (d, $J = 3.0$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.32 (dd, $J = 3.0, 9.0$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 8.67 (s, 1H), 8.08 (d, $J = 9.0$ Hz, 2H), 8.08 (d, $J = 9.0$ Hz, 1H); ^{13}C NMR 21.2, 55.1, 55.2, 103.7, 114.0 (2C), 118.9, 121.4, 126.3, 128.4 (2C), 129.1 (2C), 129.2 (2C), 131.2, 132.2, 135.7, 137.9, 144.7, 147.6, 154.0, 157.3, 160.4; MS(APCI) ($\text{M}+\text{H}$) $^+$ 356; Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.33; H, 6.14; N 3.74.

2-(4'-Methoxyphenyl)-4-(4'-methylphenyl)-6-trifluoromethyl-quinoline (8c). **8c** was prepared from **4c** (522 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3a** (325 mg, 0.8 mmol) as described above for **8a** in 55% yield. mp 138.0-139.0 °C; IR 3007, 1606, 1595, 1470, 1307 cm^{-1} ; ^1H NMR (CDCl_3) 2.45 (s, 3H), 3.83 (s, 3H), 7.00 (d, $J = 8.9$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.80 (br s, 1H), 7.83 (dd, $J = 1.5, 8.9$ Hz, 1H), 8.15 (d, $J = 8.9$ Hz, 2H), 8.20 (s, 1H), 8.24 (d, $J = 8.9$ Hz, 1H); ^{13}C NMR 21.2, 55.3, 114.2 (2C), 119.6, 122.8 (CF_3), 123.7, 124.6, 124.9, 125.6 (CF_3), 127.2 (CCF_3), 127.5 (CCF_3), 129.0 (2C), 129.3 (2C), 129.5 (2C), 130.9, 131.4, 134.5,

138.8, 149.8, 149.9, 158.2, 161.2; MS(APCI) (M+H)⁺ 394; Anal. Calcd for C₂₄H₁₈F₃NO: C, 73.27; H, 4.61; F, 14.49; N, 3.56. Found: C, 73.04; H, 4.80; F, 14.31; N, 3.49.

4-(4'-Chlorophenyl)-2-(4'-Methoxyphenyl)-6-methyl-quinoline (8d). **8d** was prepared from **4a** (518 mg, 2.5 mmol), t-BuLi (3.7 mL, 6.25 mmol, 1.7 M in pentane), CuCN (112 mg, 1.25 mmol), LiCl (53 mg, 1.25 mmol) and **3b** (426 mg, 1mmol) as described above for **8a** in 56% yield. mp 162.5-163.5 °C; IR 2952, 1604, 1584, 1518, 1253 cm⁻¹; ¹H NMR (CDCl₃) 2.44 (s, 3H), 3.84 (s, 3H), 7.01 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.51 (dd, *J* = 1.5, 9.0 Hz, 1H), 7.53 (br s, 1H), 7.65 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 2H); ¹³C NMR 21.7, 55.3, 114.2 (2C), 118.7, 124.0, 125.1, 128.68 (2C), 128.74 (2C), 129.7, 130.8 (2C), 131.7, 132.1, 134.4, 136.0, 137.1, 146.9, 147.3, 155.5, 160.7; MS(APCI) (M+H)⁺ 360; Ana. Calcd for C₂₃H₁₈ClNO: C, 76.77; H, 5.04; Cl, 9.85; N, 3.89. Found: C, 76.89; H, 5.38; Cl, 9.83; N 3.69.

6-Methoxy-4-(4'-chlorophenyl)-2-(4'-methoxyphenyl)-quinoline (8e).

8e was prepared from **4b** (446 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3b** (341 mg, 0.8 mmol) as described above for **8a** in 61% yield. mp 116.0-117.0 °C; IR 3007, 1620, 1598, 1515, 1490, 1238 cm⁻¹; ¹H NMR (CDCl₃) 3.71 (s, 3H), 3.78 (s, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 2.5 Hz, 1H), 7.30 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.60 (s, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 8.05 (d, *J* = 9.0 Hz, 2H); ¹³C NMR 55.1, 55.2, 103.2, 114.0 (2C), 118.8, 121.6, 125.8, 128.3 (2C), 128.7 (2C), 130.5 (2C), 131.3, 131.9, 134.2, 137.1, 144.6, 146.1, 153.8, 157.5, 160.4; MS(APCI) (M+H)⁺ 376; Anal. Calcd for C₂₃H₁₈ClNO₂: C, 73.50; H, 4.83; Cl, 9.43; N, 3.73. Found: C, 73.31; H, 5.11; Cl, 9.61; N, 3.63.

4-(4'-Chlorophenyl)-2-(4'-methoxyphenyl)-6-trifluoromethyl-quinoline (8f). **8f** was prepared from **4c** (522 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3b** (341 mg, 0.8 mmol) as described above for **8a** in 60% yield. mp 135.0-136.0 °C; IR 2966, 1598, 1467, 1315 cm⁻¹; ¹H NMR (CDCl₃) 3.84 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.76 (br s, 1H), 7.83 (dd, *J* = 1.5, 8.9 Hz, 1H), 8.08 (s, 1H), 8.14 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 1H); ¹³C NMR 55.3, 114.3 (2C), 119.6, 122.8 (CF₃), 123.1, 124.2, 125.2, 125.5 (CF₃), 127.5 (CCF₃), 127.9 (CCF₃), 129.0 (2C), 129.1 (2C), 130.7 (2C), 131.06, 131.09, 135.1, 135.9, 148.5, 149.8, 158.1, 161.4; MS(APCI) (M+H)⁺ 414; Ana. Calcd for C₂₃H₁₅ClF₃NO: C, 66.76; H, 3.65; Cl, 8.57; F, 13.77; N, 3.38. Found: C, 66.23; H, 3.97; Cl, 8.34; F, 13.99; N, 3.21.

2-(4'-Methoxyphenyl)-4-(2-methylpropyl)-6-methyl-quinoline (8g). **8g** was prepared from **4a** (518 mg, 2.5 mmol), t-BuLi (3.7 mL, 6.25 mmol, 1.7 M in pentane), CuCN (112 mg, 1.25 mmol), LiCl (53 mg, 1.25 mmol) and **3c** (372 mg, 1mmol) as described above for **8a** in 52% yield as a sticky oil. IR 2954, 1597, 1515, 1254 cm⁻¹; ¹H NMR (CDCl₃) 0.99 (d, *J* = 6.8, 6H), 2.10 (m, 1H), 2.52 (s, 3H), 2.90 (d, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.48 (dd, *J* = 1.5, 8.5 Hz, 1H), 7.55 (s, 1H), 7.70 (br s, 1H), 8.09 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 1H); ¹³C NMR 21.8, 22.6 (2C), 29.1, 41.7, 55.2, 114.1 (2C), 119.2, 122.5, 126.3, 128.8 (2C), 131.3, 131.6, 131.7, 135.5, 145.8, 148.2, 154.9, 160.7. HRMS: calcd for C₂₁H₂₄NO (M+H)⁺: 306.1858; found: 306.1850.

6-Methoxy-2-(4'-Methoxyphenyl)-4-(2-methylpropyl)-quinoline (8h). **8h** was prepared from **4b** (446 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3c** (298 mg, 0.8 mmol) as described above for **8a** in 58% yield as an oil. IR 2955, 1621, 1503, 1249 cm⁻¹; ¹H NMR (CDCl₃) 1.00 (d, *J* = 6.8 Hz,

6H), 2.10 (m, 1H), 2.87 (d, $J = 7.2$ Hz, 2H), 3.83 (s, 3H), 3.90 (s, 3H), 7.00 (d, $J = 8.9$ Hz, 2H), 7.20 (d, $J = 3.0$ Hz, 1H), 7.34 (dd, $J = 3.0, 8.5$ Hz, 1H), 7.55 (s, 1H), 8.07 (d, $J = 8.9$ Hz, 2H), 8.09 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR 22.8 (2C), 28.9, 41.9, 55.2, 55.3, 102.3, 114.1 (2C), 119.4, 121.1, 127.3, 128.6 (2C), 131.0, 131.8, 143.7, 147.1, 153.8, 157.2, 160.5; HRMS: calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 322.1807; found: 322.1803.

2-(4'-Methoxyphenyl)-4-(2-methylpropyl)-6-trifluoromethyl-quinoline (8i). **8i** was prepared from **4c** (522 mg, 2.0 mmol), *t*-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3c** (298 mg, 0.8 mmol) as described above for **8a** in 50% yield. mp 128.5-129.5 °C; IR 2964, 1599, 1472, 1305 cm^{-1} ; ^1H NMR (CDCl_3) 1.01 (d, $J = 6.7$ Hz, 6H), 2.09 (m, 1H), 2.95 (d, $J = 7.2$ Hz, 2H), 3.85 (s, 3H), 7.02 (d, $J = 8.9$ Hz, 2H), 7.68 (s, 1H), 7.82 (dd, $J = 1.5, 8.9$ Hz, 1H), 8.14 (d, $J = 8.9$ Hz, 2H), 8.20 (d, $J = 8.9$ Hz, 1H), 8.25 (s, 1H); ^{13}C NMR 22.7 (2C), 29.5, 41.6, 55.3, 114.2 (2C), 120.0, 121.5, 123.0 (CF_3), 124.6 125.6, 125.7 (CF_3), 126.9 (CCF_3), 127.2 (CCF_3), 129.0 (2C), 131.3, 131.6, 148.8, 149.7, 158.2, 161.2; MS(APCI) ($\text{M}+\text{H}$) $^+$ 360; Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{F}_3\text{NO}$: C, 70.18; H, 5.61; F, 15.86; N, 3.90. Found: C, 70.22; H, 5.71; F, 15.65; N, 3.88.

2-(4'-Methoxyphenyl)-4-methyl-6-methyl-quinoline (8j). **8j** was prepared from **4a** (414 mg, 2.0 mmol), *t*-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3d** (264 mg, 0.8 mmol) as described above for **8a** in 51% yield. mp 89.0-91.0 °C; IR 2923, 1594, 1548, 1516, 1348, 1256 cm^{-1} ; ^1H NMR (CDCl_3) 2.56 (s, 3H), 2.63 (s, 3H), 3.83 (s, 3H), 7.01 (d, $J = 8.9$ Hz, 2H), 7.52 (dd, $J = 3.0, 8.5$ Hz, 1H), 7.60 (br s, 1H), 7.69 (s, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 8.09 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR 18.9, 21.8, 55.3, 114.1 (2C), 119.2, 122.6, 126.9, 128.6 (2C), 129.7, 131.3, 132.4, 135.3, 143.8, 146.6, 155.7, 160.5;

MS(APCI) (M+H)⁺ 264; Anal. Calcd for C₁₈H₁₇NO: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.51; H, 6.54; N, 5.05.

2-(4'-Methoxyphenyl)-6-methoxy-4-methyl-quinoline (8k). **8k** was prepared from **4b** (446 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3d** (264 mg, 0.8 mmol) as described above for **8a** in 58% yield as an oil. IR 2932, 1620, 1599, 1502, 1239 cm⁻¹; ¹H NMR (CDCl₃) 2.63 (s, 3H), 3.83 (s, 3H), 3.90 (s, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 3.0 Hz, 1H), 7.33 (dd, *J* = 3.0, 8.8 Hz, 1H), 7.57 (br s, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 2H); ¹³C NMR 19.1, 55.2, 55.4, 101.9, 114.0 (2C), 119.4, 121.2, 127.7, 128.4 (2C), 131.3, 132.3, 143.1, 143.9, 154.3, 157.2, 160.4. HRMS: calcd for C₁₈H₁₈NO₂ (M+H)⁺: 280.1338; found: 280.1337.

2-(4'-Methoxyphenyl)-4-methyl-6-trifluoromethyl-quinoline (8l). **8l** was prepared from **4c** (522 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3d** (264 mg, 0.8 mmol) as described above for **8a** in 59% yield. mp 138.0-139.0 °C; IR 2975, 1605, 1476, 1319 cm⁻¹; ¹H NMR (CDCl₃) 2.77 (s, 3H), 3.89 (s, 3H), 7.04 (d, *J* = 8.9 Hz, 2H), 7.74 (br s, 1H), 7.85 (dd, *J* = 3.0, 8.8 Hz, 1H), 8.13 (d, *J* = 8.9 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.23 (s, 1H); ¹³C NMR 18.9, 55.4, 114.3 (2C), 120.2, 121.6, 122.5 (CF₃) 125.0, 126.05, 126.12 (CF₃) 127.0 (CCF₃), 127.4 (CCF₃), 129.0 (2C), 131.0, 131.5, 145.5, 149.2, 158.5, 161.2; MS(APCI) (M+H)⁺ 318; Anal. Calcd for C₁₈H₁₄F₃NO: C, 68.13; H, 4.45; F, 17.96; N, 4.41. Found: C, 67.79; H, 4.63; F, 18.29; N, 4.33.

2-(4'-Chlorophenyl)-4-(4'-methylphenyl)-6-methyl-quinoline (8m). **8m** was prepared from **4a** (414 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3e** (328 mg, 0.8 mmol) as described above for **8a** in 51% yield. mp 120.0-121.0 °C; IR 2915, 1589, 1544, 1492 cm⁻¹; ¹H NMR (CDCl₃) 2.44 (s, 3H), 2.46

(s, 3H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 2H), 7.52 (dd, $J = 2.0, 8.7$ Hz, 1H), 7.65 (br s, 1H), 7.67 (s, 1H), 8.09 (d, $J = 8.7$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR 21.3, 21.8, 118.8, 124.3, 125.8, 128.6 (2C), 128.9 (2C), 129.3 (2C), 129.4 (2C), 129.7, 131.8, 135.2, 135.5, 136.3, 138.1, 138.2, 147.3, 148.7, 154.5; MS(APCI) ($\text{M}+\text{H}$) $^{+}$ 344; Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{ClN}$: C, 80.34; H, 5.28; Cl, 10.31; N, 3.90. Found: C, 80.55; H, 5.51; Cl, 10.47; N, 3.93.

2-(4'-Chlorophenyl)-6-methoxy-4-(4'-methylphenyl)-quinoline (8n). **8n** was prepared from **4b** (446 mg, 2.0 mmol), *t*-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3e** (328 mg, 0.8 mmol) as described above for **8a** in 55% yield. mp 112.0-113.0 °C; IR 2959, 1622, 1492, 1224 cm^{-1} ; ^1H NMR (CDCl_3) 2.47 (s, 3H), 3.79 (s, 3H), 7.20 (d, $J = 2.7$ Hz, 1H), 7.34 (d, $J = 8.7$ Hz, 2H), 7.38 (dd, $J = 2.5, 8.5$ Hz, 1H), 7.46 (d, $J = 8.7$ Hz, 4H), 7.69 (s, 1H), 8.09 (d, $J = 8.7$ Hz, 2H), 8.11 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR 21.3, 55.4, 103.7, 119.1, 122.0, 126.8, 128.5 (2C), 128.9 (2C), 129.2 (2C), 129.4 (2C), 131.5, 135.0, 135.6, 138.2, 138.3, 144.8, 148.0, 153.2, 157.8; MS(APCI) ($\text{M}+\text{H}$) $^{+}$ 360; Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{ClNO}$: C, 76.77; H, 5.04; Cl, 9.85; N, 3.89. Found: C, 76.16; H, 5.18; Cl, 9.71; N, 3.82.

2-(4'-Chlorophenyl)-4-(4'-methylphenyl)-trifluoromethyl-quinoline (8o). **8o** was prepared from **4c** (522 mg, 2.0 mmol), *t*-BuLi (3.0 mL, 5.1 mmol, 1.7 M in pentane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3e** (328 mg, 0.8 mmol) as described above for **8a** in 50% yield. mp 147.0-148.0 °C; IR 2959, 1595, 1467, 1312, 1149 cm^{-1} ; ^1H NMR (CDCl_3) 2.48 (s, 3H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.81 (s, 1H), 7.87 (dd, $J = 2.2, 8.9$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 2H), 8.23 (s, 1H), 8.28 (d, $J = 8.9$ Hz, 1H); ^{13}C NMR 21.3, 119.8, 122.8 (CF_3), 123.8, 125.0, 125.3, 125.5 (CF_3), 128.0 (CCF_3), 128.3

(CCF₃), 128.9 (2C), 129.1 (2C), 129.3 (2C), 129.7 (2C), 131.0, 134.2, 136.3, 137.2, 139.1, 149.6, 150.6, 157.3. HRMS: calcd for C₂₃H₁₆ClF₃N (M+H)⁺: 398.0923; found: 398.0907.

2-Methyl-4-(4'-methylphenyl)-6-methyl-quinoline (8p). **8p** was prepared from **4a** (414 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol; 1.7 M in petane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3f** (251 mg, 0.8 mmol) as described above for **8a** except mesitylene was replaced with 1,2,3,5-tetramethyl benzene in 48% yield as a sticky oil. IR 2921, 1596, 1493, 1378 cm⁻¹; ¹H NMR (CDCl₃) 2.44 (s, 3H), 2.47 (s, 3H), 2.76 (s, 3H), 7.18 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.52 (dd, *J* = 2.0, 8.6 Hz, 1H), 7.63 (br s, 1H), 8.01 (d, *J* = 8.6 Hz, 1H); ¹³C NMR 21.3, 21.7, 24.9, 122.2, 124.5, 125.1, 127.0, 129.2 (2C), 129.4 (2C), 131.6, 135.5, 138.1, 143.4, 150.7, 155.2, 157.2. HRMS: calcd for C₁₈H₁₈N (M+H)⁺: 248.1439; found: 248.1441.

6-Methoxy-2-methyl-4-(4'-methylphenyl)-quinoline (8q). **8q** was prepared from **4b** (446 mg, 2.0 mmol), t-BuLi (3.0 mL, 5.1 mmol, 1.7 M in petane), CuCN (90 mg, 1.0 mmol), LiCl (43 mg, 1.0 mmol) and **3f** (251 mg, 0.8 mmol) as described above for **8a** except mesitylene was replaced with 1,2,3,5-tetramethyl benzene in 51% yield as a sticky oil. IR 2923, 1621, 1596, 1497 1225 cm⁻¹; ¹H NMR (CDCl₃) 2.43 (s, 3H), 2.70 (s, 3H), 3.73 (s, 3H), 7.14 (s, 1H), 7.18 (d, *J* = 3.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 3.0, 9.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 9.3 Hz, 1H); ¹³C NMR 21.1, 24.8, 55.2, 103.8, 121.2, 122.3, 125.8, 129.0 (2C), 129.2 (2C), 130.3, 135.4, 137.9, 144.3, 147.2, 155.7, 157.1; MS(APCI) (M+H)⁺ 264; Anal. Calcd for C₁₈H₁₇NO: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.29; H, 6.27; N, 5.52.

2-Methyl-4-(4'-methylphenyl)-6-trifluoromethyl-quinoline (8r). To **4c** (457 mg, 1.75 mmol) in THF (6 mL) at -30 °C was added t-BuLi (2.6 mL, 4.4 mmol, 1.7 M in petane) dropwise. The mixture was stirred at -20 °C for 2.5 h, then cooled to -50 °C. A solution of

CuCN (79 mg, 0.88 mmol) and LiCl (38 mg, 0.88 mmol) in THF (2 mL) was added to the above mixture. After 10 min., **3f** (220 mg, 0.7 mmol) in THF (2 mL) was added, followed by toluene (8 mL). The mixture was stirred from -50 °C to -10 °C for 1 h, and quenched with saturated aqueous ammonium chloride (5 mL). The reaction mixture was warmed to room temperature, and diluted with EtOAc (30 mL). The organic phase was separated, washed with water (10 mL), brine (2 X 10 mL), dried (Na₂SO₄), and concentrated in vacuo. Flash chromatography (hexane/EtOAc 3:1) of the residue gave 305 mg (76%) of the intermediate **5r** as diastereomers in 3:1(**a**:**b**) ratio: ¹H NMR (CDCl₃) 1.55 (s, 9H, **b**), 1.60 (s, 9H, **a**), 2.23 (s, 3H **a** and **b**), 2.25 (s, 3H, **b**), 2.32 (s, 3H, **a**), 2.33 (s, 3H, **a**), 2.40 (s, 3H, **b**), 4.86 (d, *J* = 11.8 Hz, 1H, **b**), 5.11 (d, *J* = 12.2 Hz, 1H, **a**), 5.15 (d, *J* = 12.2 Hz, 1H, **a**), 5.20 (d, *J* = 11.8 Hz, 1H, **b**), 6.82-7.79 (m, 12H, **a** and **b**); ¹³C NMR 20.92 (**a**), 20.97 (**b**), 21.4(**a**), 21.7 (**b**), 28.3 (3C, **b**), 28.4 (3C, **a**), 32.0 (**a**), 32.7 (**b**), 43.0 (**a**), 43.4 (**b**), 78.0 (**b**), 78.4 (**a**), 81.2 (**b**), 81.3 (**a**), 123.4 (**b**), 124.4 (**a**), 124.5 (**b**), 124.7 (**b**), 125.0 (**a**), 125.4 (**a**), 127.2 (2C, **a**), 127.5 (2C, **a**), 128.4 (2C, **b**), 128.7 (2C, **b**), 129.4 (2C, **b**), 129.5 (2C, **b**), 129.7 (2C, **a**), 130.1 (2C, **a**), 131.3 (**a**), 132.4 (**b**), 133.4 (**b**), 135.6 (**b**), 135.8 (**a**), 136.0 (**a**), 137.7 (**b**), 137.8 (**a**), 138.4 (**b**), 138.7 (**a**), 144.9 (**b**), 145.4 (**a**), 152.8 (**b**), 153.3 (**a**), 198.1 (**a**), 199.9 (**b**), 2 carbon (CCF₃, CF₃) were missing. HRMS calcd for C₃₀H₃₂F₃NO₅S (M+H)⁺: 576.2032; found: 576.2031. To the intermediate **5r** was added TFA (4 mL), the mixture was stirred at room temperature for 3 h. After removal of TFA, the residue was purified by flash chromatography (hexane/EtOAc 3:1) to give 223 mg (92%) of the intermediate **7r**: ¹H NMR (CDCl₃) 2.24 (s, 3H), 2.32 (s, 3H), 2.37 (s, 3H), 5.27 (s, 1H), 6.74 (s, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H); ¹³C NMR 18.9, 21.0, 21.4, 43.9, 109.5, 114.8, 124.3, 125.4, 126.1, 126.9 (2C), 127.2 (2C), 129.1 (2C), 129.3 (2C), 136.5, 138.2, 140.5, 142.8,

143.0, 145.2;), 2 carbon (CCF_3 , CF_3) were missing. MS(APCI) $(\text{M}+\text{H})^+$ 458. To the intermediate **7r** was added 1,2,3,5-tetramethyl benzene (8 mL), the mixture was heated at reflux overnight, and purified by flash chromatography (hexane/EtOAc 4:1) to give 126 mg (86%) of pure **8r** as a sticky oil. IR 3030, 2923, 1598, 1314 cm^{-1} ; ^1H NMR (CDCl_3) 2.48 (s, 3H), 2.80 (s, 3H), 7.31 (s, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.85 (dd, $J = 2.2, 8.8$ Hz, 1H), 8.18 (d, $J = 8.8$ Hz, 1H), 8.20 (s, 1H); ^{13}C NMR 21.3, 25.4, 122.4 (CF_3), 123.3, 123.7, 124.3, 125.0, 125.9 (CF_3), 126.9 (CCF_3), 127.3 (CCF_3), 127.7 (CCF_3), 128.1 (CCF_3), 129.3 (2C), 129.6 (2C), 130.0, 134.1, 138.9, 149.3, 149.6, 160.9. HRMS calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{N}$ $(\text{M}+\text{H})^+$: 302.1157; found: 302.1149.