Supporting Information #1

Auto-Tandem Catalysis in the Synthesis of Substituted Quinolines from Aldimines and Electron-rich Olefins: Cascade Povarov-Hydrogen Transfer Reaction

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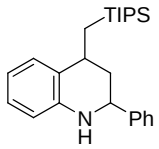
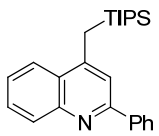
General Procedure: All non-aqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise noted. Solvents were dried and distilled according to standard protocols. Materials were obtained from commercial suppliers and used without further purification. Aldimines were prepared according to the procedure reported by Tashiro *et al*[S1] or azeotropic dehydration in toluene with Dean−Stark apparatus. Column chromatography was performed on silica gel 60 (230-400 mesh), and flash column chromatography was performed on silica gel 60 (spherical/40-100 μm). Preparative thin layer chromatography (PTLC) was performed on Silica Gel 60, 0.5 mm or 2.0 mm PTLC plates using indicated eluents. Reactions and chromatography fractions were analyzed employing pre-coated silica gel plate (Silica Gel 60 F_{254}). The ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane or $CDCl_3$ as internal standard.



(2*R,4*S**)- and (2*R**,4*R**)-4-(Triisopropylsilyl)methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans***- and *cis*-3ba as a 7 : 3 inseparable mixture).**

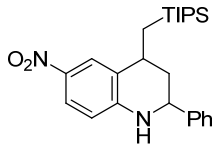
Colorless viscous oil. IR (neat) 2941, 2864, 1473, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ba**) δ 7.43-7.26 (m, 5H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.00 (dd, *J* = 7.9, 7.6 Hz, 1H), 6.67 (dd, *J* = 7.6, 7.3 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.55 (dd, *J* = 10.5, 3.7 Hz, 1H), 4.05 (bs, 1H), 3.15-3.09 (m, 1H), 2.00 (ddd, *J* = 13.2, 11.8, 5.1 Hz, 1H), 1.93 (dt, *J* = 13.2, 3.2 Hz, 1H), 1.20-0.98 (m, 23H), (for *cis*-**3ba**) δ 7.43-7.26 (m, 6H), 7.00 (dd, *J* = 7.9, 7.6 Hz, 1H), 6.73 (dd, *J* = 7.6, 7.3 Hz, 1H), 6.51 (d, *J* = 7.3 Hz, 1H), 4.41 (dd, *J* = 11.2, 2.7 Hz, 1H), 3.92 (bs, 1H), 3.29-3.20 (m, 1H), 2.28 (ddd, *J* = 12.7, 5.1, 2.7 Hz, 1H), 1.79 (ddd, *J* = 12.7, 12.2, 11.2 Hz, 1H), 1.54 (dd, *J* = 15.0, 2.4 Hz, 1H), 1.20-0.98 (m, 21H), 0.80 (dd, *J* = 15.0, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 144.8x2, 144.5, 143.5, 128.8, 128.7, 128.6, 128.5, 127.8, 127.6, 127.5, 127.0, 126.8x3, 126.6, 117.6, 117.2, 114.2, 114.0, 57.3, 52.1, 41.4, 37.7, 32.9, 31.8, 19.9, 19.0x2, 15.3, 11.8, 11.7; LRMS (EI) *m/z*

379 (M^+); Anal. calcd for $C_{25}H_{37}NSi$: C, 79.09; H, 9.82; N, 3.69. found: C, 78.78; H, 9.71; N, 3.64.



4-(Triisopropylsilyl)methyl-2-phenylquinoline (4ba).

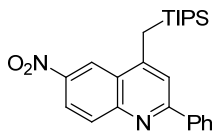
Colorless viscous oil. IR (neat) 2943, 2866, 1589, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 9.2, 6.0 Hz, 2H), 8.13 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.67 (s, 1H), 7.54-7.42 (m, 4H), 2.73 (s, 2H), 1.23-1.12 (m, 3H), 1.01 (d, *J* = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.4, 148.4, 140.0, 130.4, 129.2, 129.0, 128.7, 127.4, 126.8, 125.3, 123.9, 118.4, 18.6, 15.9, 11.5; LRMS (EI) *m/z* 375 (M^+); Anal. calcd for $C_{25}H_{33}NSi$: C, 79.94; H, 8.86; N, 3.73. found: C, 79.75; H, 8.73; N, 3.67.



(2*R,4*S**)- and (2*R**,4*R**)-4-(Triisopropylsilyl)methyl-6-nitro-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans***- and *cis*-3ca as a 7 : 3 inseparable mixture).**

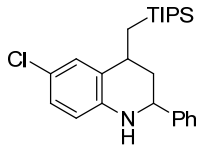
Pale yellow solids. IR (KBr) 3387, 2941, 2864, 1605, 1506, 1279 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ca**) 8.03 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.41-7.36 (m, 5H), 6.47 (d, *J* = 8.9 Hz, 1H), 4.89 (bs, 1H), 4.68 (dd, *J* = 8.7, 4.3 Hz, 1H), 3.16-3.08 (m, 1H), 2.04-1.94 (m, 2H), 1.18-0.99 (m, 23H), (for *cis*-**3ca**) δ 8.23 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 6.42 (d, *J* = 8.9 Hz, 1H), 4.77 (bs, 1H), 4.57 (dd, *J* = 11.1, 1.9 Hz, 1H), 3.22-3.13 (m, 1H), 2.32 (d, *J* = 13.2 Hz, 1H), 1.76 (ddd, *J* = 13.2, 12.2, 12.1, 1H), 1.53 (d, *J* = 14.5 Hz, 1H), 1.18-0.99 (m, 21H), 0.81 (dd, *J* = 14.5, 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 150.2, 149.1, 142.9, 142.6, 138.1, 137.8, 129.1, 128.9, 128.3, 128.1, 127.1, 126.6, 126.4, 125.0, 124.3, 124.1, 123.4, 112.6, 112.4, 57.5, 52.5, 39.7, 36.8, 32.7, 31.5, 19.0, 18.9, 18.4, 13.6, 11.9, 11.7; LRMS (EI) *m/z* 424 (M^+); Anal. calcd for $C_{25}H_{36}N_2O_2Si$: C, 70.71;

H, 8.54; N, 6.60. found: C, 70.52; H, 8.50; N, 6.51.



4-(Triisopropylsilyl)methyl-6-nitro-2-phenylquinoline (4ca)

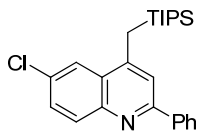
Pale yellow needles. mp 118-120 °C; IR (KBr) 2941, 2866, 1595, 1491, 1339 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 2.4 Hz, 1H), 8.45 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.22 (d, *J* = 9.2 Hz, 1H), 8.18-8.15 (m, 2H), 7.80 (s, 1H), 7.58-7.49 (m, 3H), 2.80 (s, 2H), 1.23-1.12 (m, 3H), 1.03 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.4, 151.0, 144.5, 138.4, 132.0, 130.2, 129.0, 127.7, 125.7, 122.7, 121.3, 119.7, 18.5, 16.9, 11.5; LRMS (EI) *m/z* 420 (M^+); Anal. calcd for $C_{25}H_{32}N_2O_2Si$: C, 71.39; H, 7.67; N, 6.66. found: C, 71.13; H, 7.68; N, 6.49.



(2*R,4*S**)- and (2*R**,4*R**)-6-Chloro-4-(triisopropylsilyl)methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans*- and *cis*-**3da** as a 4 : 1 inseparable mixture**).**

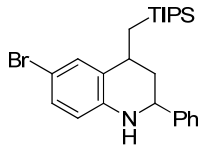
Colorless viscous oil. IR (neat) 2941, 2864, 1489, 1302, 881 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3da**) δ 7.40-7.22 (m, 6H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 4.53 (dd, *J* = 9.7, 4.3 Hz, 1H), 4.07 (bs, 1H), 3.05 (m, 1H), 2.01-1.89 (m, 2H), 1.23-0.92 (m, 23H), (for *cis*-**3da**) δ 7.40-7.22 (m, 8H), 6.43 (d, *J* = 8.5 Hz, 1H), 4.39 (dd, *J* = 11.3, 2.7 Hz, 1H), 3.95 (bs, 1H), 3.25-3.15 (m, 1H), 2.26 (ddd, *J* = 12.8, 5.1, 2.7 Hz, 1H), 1.75 (ddd, *J* = 12.8, 12.2, 11.3 Hz, 1H), 1.41 (dd, *J* = 15.0, 3.0 Hz, 1H), 1.23-0.92 (m, 21H), 0.79 (dd, *J* = 15.0, 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 144.4, 142.0, 129.9, 128.8, 128.7, 128.3, 127.6, 126.8, 126.7, 126.6, 126.5, 121.4, 115.2, 115.0, 57.3, 52.1, 40.8, 37.3, 33.1, 31.8, 19.5, 19.0, 18.9, 15.0, 11.9, 11.7; LRMS (EI) *m/z* 413 (M^+); Anal. calcd for $C_{25}H_{36}ClNSi\cdot 0.3H_2O$: C, 71.58; H, 8.79; N,

3.34. found: C, 71.50; H, 8.64; N, 3.26.



6-Chloro-4-(triisopropylsilyl)methyl-2-phenylquinoline (4da).

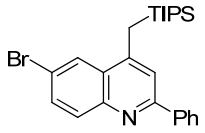
Colorless needles. mp 92-93 °C; IR (KBr) 2943, 2866, 1589, 1348, 881, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 2H), 8.07 (d, *J* = 8.7, Hz, 1H), 8.03 (d, *J* = 2.2 Hz, 1H), 7.67 (s, 1H), 7.62 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 2.67 (s, 2H), 1.22-1.10 (m, 3H), 1.02 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.8, 146.9, 139.6, 132.1, 131.2, 130.0, 129.3, 128.8, 127.5, 127.4, 123.2, 119.1, 18.6, 16.1, 11.5; LRMS (EI) *m/z* 409 (M^+); Anal. calcd for $C_{25}H_{32}ClNSi$: C, 73.22; H, 7.87; N, 3.42. found: C, 72.96; H, 7.86; N, 3.24.



(2*R,4*S**)- and (2*R**,4*R**)-6-Bromo-4-(triisopropylsilyl)methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans*- and *cis*-**3ea** as a 4 : 1 inseparable mixture**).**

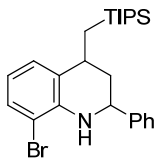
Colorless viscous oil. IR (neat) 2941, 2864, 1487, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ea**) δ 7.39-7.23 (m, 5H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.07 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.41 (d, *J* = 8.5 Hz, 1H), 4.54 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.09 (bs, 1H), 3.08-3.03 (m, 1H), 2.01-1.89 (m, 2H), 1.26-1.03 (m, 23H), (for *cis*-**3ea**) δ 7.39-7.23 (m, 5H), 7.16 (s, 1H), 7.07 (d, *J* = 9.4 Hz, 1H), 6.39 (d, *J* = 9.4 Hz, 1H), 4.39 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.97 (bs, 1H), 3.24-3.13 (m, 1H), 2.25 (m, 1H), 1.75 (ddd, *J* = 12.6, 12.2, 11.8 Hz, 1H), 1.40 (dd, *J* = 15.0, 3.1 Hz, 1H), 1.26-1.03 (m, 21H), 0.79 (dd, *J* = 15.0, 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 144.3, 144.0, 143.8, 142.5, 131.2, 130.4, 130.0, 129.5, 129.4, 128.8, 128.7, 127.8, 127.6, 126.7, 126.5, 115.6, 115.5, 109.2, 108.5, 57.3, 52.1, 40.7, 37.3, 33.1, 31.8, 19.5, 19.0x3, 18.9, 15.0, 11.9, 11.7; LRMS (EI) *m/z* 457, 459 (M^+,

M^++2); Anal. calcd for $C_{25}H_{36}BrNSi\cdot 0.6H_2O$: C, 63.97; H, 7.99; N, 2.98. found: C, 63.91; H, 7.64; N, 2.84.



6-Bromo-4-(triisopropylsilyl)methyl-2-phenylquinoline (4ea).

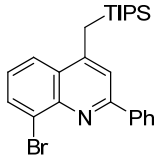
Colorless needles. mp 99-101 °C; IR (KBr) 2943, 2864, 1541, 1348, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 6.8 Hz, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.74 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.67 (s, 1H), 7.52 (dd, *J* = 7.6, 6.8 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 2.65 (s, 2H), 1.22-1.11 (m, 3H), 1.02 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 148.7, 147.1, 139.6, 132.5, 132.2, 129.3, 128.9, 128.1, 127.4, 126.6, 119.3, 119.1, 18.6, 16.2, 11.5; LRMS (EI) *m/z* 453, 455 (M^+, M^++2); Anal. calcd for $C_{25}H_{32}BrNSi$: C, 66.06; H, 7.10; N, 3.08. found: C, 66.01; H, 7.14; N, 2.98.



(2*R,4*S**)- and (2*R**,4*R**)-8-Bromo-4-(triisopropylsilyl)methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans*- and *cis*-**3fa** as a 3 : 2 inseparable mixture**).**

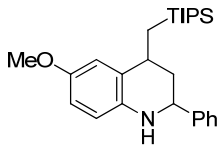
Colorless oil. IR (neat) 2939, 2864, 1464, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3fa**) δ 7.44-7.24 (m, 6H), 7.04 (d, *J* = 6.8 Hz, 1H), 6.53 (t, *J* = 7.7 Hz, 1H), 4.71 (bs, 1H), 4.63 (t, *J* = 7.0 Hz, Hz, 1H), 3.14-3.09 (m, 1H), 1.97-1.93 (m, 2H), 1.18-1.03 (m, 23H), (for *cis*-**3fa**) δ 7.44-7.24 (m, 7H), 6.58 (t, *J* = 7.7 Hz, 1H), 4.64 (bs, 1H), 4.49 (dd, *J* = 11.6, 3.0 Hz, 1H), 3.30-3.20 (m, 1H), 2.31-2.24 (m, 1H), 1.75 (ddd, *J* = 12.6, 12.2, 11.6 Hz, 1H), 1.48 (dd, *J* = 15.2, 3.1 Hz, 1H), 1.18-1.03 (m, 21H), 0.78 (dd, *J* = 15.2, 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 144.3, 144.0,

141.8, 140.5, 130.2, 130.0x2, 129.5, 128.8x2, 127.7x2, 126.6, 126.5, 125.8, 117.5, 117.3, 108.9, 108.6, 57.3, 52.3, 41.1, 37.6, 33.4, 32.4, 19.5, 19.0x3, ; LRMS (APCI) *m/z* 457, 459 (M^+, M^++2); Anal. calcd for $C_{25}H_{36}BrNSi$: C, 65.48; H, 7.91; N, 3.05. found: C, 65.48; H, 7.87; N, 2.95.



8-Bromo-4-(triisopropylsilyl)methyl-2-phenylquinoline (4fa)

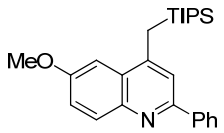
Colorless needles. mp 93-96 °C; IR (KBr) 2941, 2864, 1578, 1489, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.5 Hz, 2H), 8.02 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 8.0, 7.6 Hz, 1H), 2.71 (s, 2H), 1.22-1.08 (m, 3H), 1.01 (d, *J* = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 150.2, 145.4, 139.2, 133.0, 130.0, 128.8, 128.1, 127.5, 126.5, 125.5, 123.8, 118.6, 18.6, 16.3, 11.4; LRMS (EI) *m/z* 453, 455 (M^+, M^++2); Anal. calcd for $C_{25}H_{32}BrNSi$: C, 66.06; H, 7.10; N, 3.08. found: C, 66.15; H, 7.16; N, 3.04.



(2*R,4*S**)- and (2*R**,4*R**)-4-(Triisopropylsilyl)methyl-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline** (*trans*- and *cis*-**3ga** as a 9:1 inseparable mixture**).**

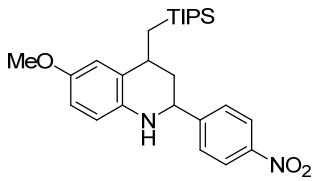
Colorless oil. IR (neat) 2939, 2864, 1502, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ga**) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.35 (dd, *J* = 7.7, 7.0 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 2.7 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.50 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.87 (bs, 1H), 3.76 (s, 3H), 3.12-3.07 (m, 1H), 2.01 (ddd, *J* = 13.0, 10.9, 5.0 Hz, 1H), 1.92 (dt, *J* = 13.0, 3.0 Hz, 1H), 1.25-0.92 (m, 23H), (for *cis*-**3ga**) δ 7.43-7.26 (m, 5H), 6.92-6.90 (m, 1H), 6.66-6.63 (m,

1H), 6.50-6.48 (m, 1H), 4.33 (dd, J = 11.1, 2.7 Hz, 1H), 3.29-3.20 (m, 1H), 2.37-2.33 (m, 1H), 1.83-1.74 (m, 1H), 1.25-0.92 (m, 23H); LRMS (EI) *m/z* 409 (M^+); HRMS calcd for $C_{26}H_{39}NOSi$: 409.2801 (M^+), found: 409.2786.



4-(Triisopropylsilyl)methyl-6-methoxy-2-phenylquinoline (4ga)

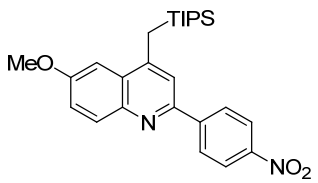
Colorless plates. mp 90-91 °C; IR (KBr) 2943, 2866, 1622, 1589, 1348, 1211, 1032, 881 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.2 Hz, 2H), 8.04 (d, J = 9.0 Hz, 1H), 7.64 (s, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 7.2 Hz, 1H), 7.35 (dd, J = 9.0, 3.0 Hz, 1H), 7.29 (d, J = 3.0 Hz, 1H), 3.96 (s, 3H), 2.66 (s, 2H), 1.23-1.14 (m, 3H), 1.02 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 154.2, 147.7, 144.5, 140.1, 132.0, 128.7, 127.6, 127.2, 121.5, 118.8, 116.9, 102.4, 55.5, 18.6, 16.0, 11.6; LRMS (EI) *m/z* 405 (M^+); Anal. calcd for $C_{26}H_{35}NOSi\cdot 0.1H_2O$: C, 76.64; H, 8.71; N, 3.44. found: C, 76.56; H, 8.63; N, 3.39.



(2*R,4*S**)- and (2*R**,4*R**)-4-(Triisopropylsilyl)methyl-2-(*p*-nitrophenyl)-6-methoxy-1,2,3,4-tetrahydroquinoline (***trans***- and *cis*-3ha** as a 4 : 1 inseparable mixture**).**

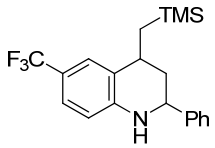
Orange solids. mp 119-121 °C; IR (KBr) 2941, 2866, 1502, 1348, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ha**) δ 8.21 (d, J =8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 2.8 Hz, 1H), 6.67 (dd, J = 8.8, 2.8 Hz, 1H), 6.55 (d, J = 8.8 Hz, 1H), 4.64 (dd, J = 10.0, 3.2 Hz, 1H), 3.90 (bs, 1H), 3.12-3.03 (m, 1H), 2.00 (ddd, J = 13.6, 10.0, 5.2 Hz, 1H), 1.92 (dt, J = 13.6, 3.2 Hz, 1H)1.20-0.97 (m, 23H), (for *cis*-**3ha**) δ 8.23 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 2.8 Hz, 1H),

6.69-6.64 (m, 1H), 6.54 (d, J = 8.8 Hz, 1H), 4.46 (dd, J = 11.6, 2.4 Hz, 1H), 3.84 (bs, 1H), 3.78 (s, 3H), 3.31-3.21 (m, 1H), 2.27 (ddd, J = 13.2, 5.6, 2.4 Hz, 1H), 1.70 (ddd, J = 13.2, 11.6, 11.2 Hz, 1H), 1.46 (dd, J = 15.6, 2.4 Hz, 1H), 1.20-0.97 (m, 21H), 0.79 (dd, J = 15.6, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 152.7, 152.6, 152.3, 152.1, 147.4, 147.3, 138.2, 136.9, 129.7, 129.5, 127.5, 127.4, 124.0, 123.9, 115.5, 115.3, 114.5, 113.7, 112.9, 112.1, 57.1, 55.8, 52.1, 41.9, 38.0, 33.2, 31.7, 19.8, 19.0, 18.9, 15.8, 11.8, 11.7; LRMS (EI) *m/z* 454 (M^+); Anal. calcd for $C_{26}H_{38}N_2O_3Si$: C, 68.68; H, 8.42; N, 6.16. found: C, 68.50; H, 8.34; N, 6.11.



4-(Triisopropylsilyl)methyl-2-(*p*-nitrophenyl)-6-methoxyquinoline (4ha).

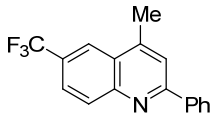
Yellow needles. mp 142-144 °C; IR (KBr) 2939, 2864, 1593, 1518, 1340, 1225, 854 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 9.0 Hz, 2H), 8.28 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 9.2 Hz, 1H), 7.67 (s, 1H), 7.40 (dd, J = 9.2, 2.4 Hz, 1H), 7.31 (d, J = 2.4 Hz, 1H), 3.97 (s, 3H), 2.69 (s, 2H), 1.24-1.13 (m, 3H), 1.03 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 151.3, 148.6, 148.0, 146.0, 144.5, 132.2, 128.1, 127.8, 124.0, 122.3, 118.6, 102.3, 55.5, 18.6, 16.3, 11.6; LRMS (EI) *m/z* 450 (M^+); Anal. calcd for $C_{26}H_{34}N_2O_3Si$: C, 69.30; H, 7.60; N, 6.22. found: C, 69.11; H, 7.64; N, 6.12.



(2*R,4*S**)- and (2*R**,4*R**)-6-trifluoromethyl-4-Trimethylsilylmethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans*- and *cis*-**3ab** as a 3 : 2 inseparable mixture**).**

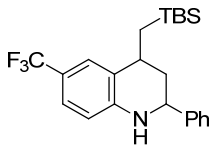
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ab**) δ 7.43-7.21 (m, 7H), 6.50 (d, J = 8.4 Hz, 1H), 4.47 (dd, J = 11.2, 2.4 Hz, 1H), 4.25 (bs, 1H), 3.19-3.11 (m, 1H), 2.21-2.17 (m, 1H), 1.75 (dd, J

= 12.0, 11.2 Hz, 1H), 1.36 (dd, J = 14.8, 3.6 Hz, 1H), 0.82 (dd, J = 14.8, 10.0 Hz, 1H), 0.05 (s, 9H), (for *cis*-**3ba**) δ 7.43-7.21 (m, 7H), 6.52 (d, J = 8.4 Hz, 1H), 4.58 (dd, J = 9.2, 4.8 Hz, 1H), 4.37 (bs, 1H), 3.00-2.94 (m, 1H), 1.98-1.94 (m, 2H), 1.04-0.99 (m, 2H), 0.07 (s, 9H); LRMS (APCI) m/z 364 ($M+H^+$); HRMS calcd for $C_{20}H_{24}F_3NSi$: 363.1630 (M^+), found: 363.1612.



6-Trifluoromethyl-4-methyl-2-phenylquinoline (7a).

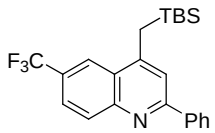
White solids. mp 98-100 °C; IR (KBr) 1605, 1472, 1310, 1153, 1124 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.26 (d, J = 8.8 Hz, 1H), 8.17 (dt, J = 7.2, 1.6 Hz, 2H), 7.88 (dd, J = 8.8, 1.6 Hz, 1H), 7.80 (s, 1H), 7.54 (ddt, J = 7.2, 6.8, 1.6 Hz, 1H), 7.49 (tt, J = 6.8, 1.6 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 149.3, 145.8, 139.1, 131.4, 129.8, 128.9, 127.6, 127.5 (q, $^2J_{(C,F)}$ = 32.0 Hz), 126.4, 125.0 (q, $^3J_{(C,F)}$ = 3.3 Hz), 124.3 (q, $^1J_{(C,F)}$ = 273.6 Hz), 121.6 (q, $^3J_{(C,F)}$ = 4.1 Hz), 120.7, 19.0; LRMS (EI) *m/z* 287 (M^+); Anal. calcd for $C_{17}H_{12}F_3NSi$: C, 71.07; H, 4.21; N, 4.88. found: C, 71.12; H, 4.41; N, 4.72.



(2*R,4*S**)- and (2*R**,4*R**)-4-(*tert*-Butyldimethylsilyl)methyl-6-trifluoromethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans***- and *cis*-3ac** as a 4 : 1 inseparable mixture**)**

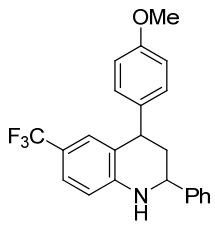
Colorless viscous oil. IR (neat) 2928, 1618, 1329, 1109 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ac**) δ 7.41-7.28 (m, 5H), 7.25-7.22 (m, 2H), 6.53 (d, J = 8.5 Hz, 1H), 4.58 (t, J = 6.0 Hz, 1H), 4.37 (bs, 1H), 2.99-2.94 (m, 1H), 1.98-1.95 (m, 2H), 1.05 (dt, J = 10.0, 5.2 Hz, 1H), 1.00 (dt, J = 10.0, 5.3 Hz, 1H), 0.87 (s. 9H), 0.07 (s, 3H), 0.01 (s, 3H), (for *cis*-**3ac**) δ 7.41-7.28 (m, 5H), 7.25-7.22 (m, 2H), 6.50 (d, J = 8.2 Hz, 1H), 4.47 (dd, J = 11.3, 3.0 Hz, 1H), 4.26 (bs, 1H), 3.22-3.11

(m, 1H), 2.20 (ddd, J = 13.5, 5.1, 3.0 Hz, 1H), 1.76 (ddd, J = 13.5, 12.3, 11.3 Hz, 1H), 1.36 (dd, J = 15.0, 3.9 Hz, 1H), 0.91 (s, 9H), 0.83-0.77 (m, 1H), 0.03 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 147.4, 146.0, 144.0, 143.7, 129.5 (q, $^1J_{(C,F)}$ = 269.5 Hz), 128.8x2, 127.9, 127.8, 127.8 (q, $^1J_{(C,F)}$ = 270.4 Hz), 127.4, 126.8, 126.6x2, 125.6 (q, $^3J_{(C,F)}$ = 3.3 Hz), 124.3 (q, $^3J_{(C,F)}$ = 4.1 Hz), 124.0 (q, $^3J_{(C,F)}$ = 4.1 Hz), 123.8 (q, $^3J_{(C,F)}$ = 3.3 Hz), 118.5 (q, $^2J_{(C,F)}$ = 32.8 Hz), 118.4 (q, $^2J_{(C,F)}$ = 32.8 Hz), 113.3, 113.1, 57.1, 52.0, 40.8, 37.1, 33.0, 26.5, 21.7, 17.3, 16.6, −4.3, −4.4, −5.4, −5.9; LRMS (APCI) *m/z* 406 (M^++1); Anal. calcd for $C_{23}H_{30}F_3NSi$: C, 68.11; H, 7.46; N, 3.45. found: C, 68.12; H, 7.48; N, 3.33.



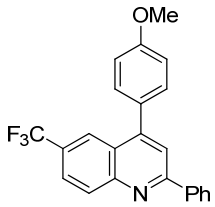
4-(*tert*-Butyldimethylsilyl)methyl-6-trifluoromethyl-2-phenylquinoline (4ac)

White solids. mp 74-76 °C; IR (KBr) 2931, 1591, 1470, 1313, 1121, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.1 Hz, 2H), 8.15 (d, J = 2.0 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.85 (dd, J = 8.8, 2.0 Hz, 1H), 7.62 (s, 1H), 7.54 (dd, J = 8.1, 6.8 Hz, 1H), 7.49 (t, J = 6.8 Hz, 1H), 2.70 (s, 2H), 1.04 (s, 9H), −0.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 150.1, 149.6, 139.3, 131.4, 129.6, 128.9, 127.6, 126.9, 126.2, 125.5, 124.8, 122.2, 119.2, 26.4, 19.9, 17.1, −6.0; LRMS (APCI) *m/z* 402 (M^++1); Anal. calcd for $C_{23}H_{26}F_3NSi$: C, 68.80; H, 6.53; N, 3.49. found: C, 68.81; H, 6.59; N, 3.41.



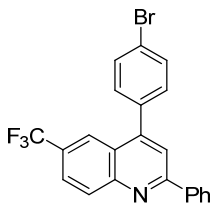
(2*R,4*S**)- and (2*R**,4*R**)-6-trifluoromethyl-4-(*p*-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (***trans***- and *cis*-3ad** as a 3 : 1 inseparable mixture**)**

Colorless viscous oil. IR (neat) 1616, 1513, 1327, 1253, 1107 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (for *trans*-**3ad**) δ 7.44-7.20 (m, 7H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 1H), 4.65 (dd, *J* = 11.0, 2.8 Hz, 1H), 4.36 (bs, 1H), 4.21 (dd, *J* = 12.2, 5.0 Hz, 1H), 3.81 (s, 3H), 2.31-2.24 (m, 1H), 2.23-2.11 (m, 1H), (for *cis*-**3ad**) δ 7.44-7.20 (m, 7H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 1H), 4.46 (bs, 1H), 4.33 (dd, *J* = 9.3, 4.2 Hz, 1H), 4.10 (t, *J* = 4.5 Hz, 1H), 3.80 (s, 3H), 2.23-2.11 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) (*trans* + *cis*) δ 158.5, 158.2, 147.8x2, 143.6, 143.2, 137.8, 135.8, 129.5, 129.4, 128.8, 128.7, 128.3-127.5 (m), 128.0, 127.7, 127.5x2, 127.5-120.5 (m), 126.6, 126.5, 124.8, 124.6, 124.4 (q, $^{3}J_{(C,F)}$ = 3.3 Hz), 123.9, 123.8, 121.8, 119.0, 118.8, 57.2, 55.5, 55.3, 52.0, 43.8, 41.4, 40.7, 38.6; LRMS (FAB) *m/z* 383 (M^+); HRMS (FAB) calcd for $C_{23}H_{20}F_3NO$: 383.1497 (M^+), found: 383.1512.



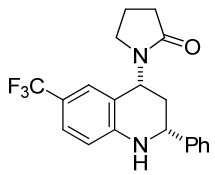
6-Trifluoromethyl-4-(*p*-methoxyphenyl)-2-phenylquinoline (4ad)

White solids. mp 127-128 °C; IR (KBr) 1607, 1592, 1467, 1314, 1165, 1110 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 8.25 (s, 1H), 8.21 (d, *J* = 7.0 Hz, 2H), 7.89 (s, 1H), 7.88 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.55 (t, *J* = 7.0 Hz, 3H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 158.8, 150.0, 149.9, 139.1, 131.3, 130.8, 129.9, 129.7, 129.0, 127.9 (q, $^{1}J_{(C,F)}$ = 272.3 Hz), 127.7, 125.1 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 125.0, 124.3 (q, $^{2}J_{(C,F)}$ = 32.4 Hz), 123.8 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 120.3, 114.5, 55.5; LRMS (FAB) *m/z* 380 (M^++1); HRMS (FAB) calcd for $C_{23}H_{17}F_3NO$: 380.1262 ($M+H^+$), found: 380.1264.



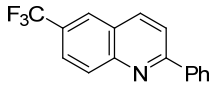
4-(*p*-Bromophenyl)-6-trifluoromethyl-2-phenylquinoline (4ae)

White solids. mp 148-149 °C; IR (KBr) 1597, 1466, 1314, 1162, 1108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 7.0 Hz, 2H), 8.13 (s, 1H), 7.91 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.88 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.56-7.48 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 149.9, 148.8, 138.8, 136.3, 132.2, 131.4, 131.0, 130.1, 129.0, 128.3 (q, $^{2}J_{(C,F)}$ = 32.4 Hz), 127.7, 125.4 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 124.6, 124.1 (q, $^{1}J_{(C,F)}$ = 272.3 Hz), 123.5, 123.3 (q, $^{3}J_{(C,F)}$ = 4.8 Hz), 120.2; LRMS (FAB) *m/z* 428 (M^+, M^++2); HRMS (FAB) calcd for $C_{22}H_{14}{}^{79}BrF_3N$: 428.0262 ($M+H^+$), found: 428.0275.



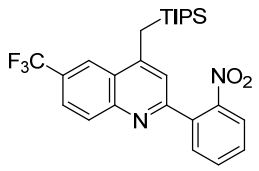
(2*R,4*R**)-6-Trifluoromethyl-4-(2-oxo-1-pyrrolidinyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (*cis*-3af).**

White solids. mp 208-209 °C; IR (KBr) 3301, 1659, 1620, 1317, 1103 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 4H), 7.35-7.31 (m, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.06 (s, 1H), 6.60 (d, *J* = 8.6 Hz, 1H), 5.70 (dd, *J* = 11.5, 6.3 Hz, 1H), 4.66 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.38 (s, 1H), 3.25-3.18 (m, 2H), 2.55 (ddd, *J* = 16.6, 8.6, 6.3 Hz, 1H), 2.45 (dt, *J* = 17.2, 8.6 Hz, 1H), 2.15-2.00 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 148.3, 142.2, 128.9, 128.3, 126.4, 125.5 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 124.7 (q, $^{1}J_{(C,F)}$ = 269.9 Hz), 123.7 (q, $^{3}J_{(C,F)}$ = 4.8 Hz), 119.6 (q, $^{2}J_{(C,F)}$ = 32.4 Hz), 118.4, 114.3, 56.1, 48.1, 42.2, 34.7, 31.2, 18.3; LRMS (FAB) *m/z* 361 (M^++1); HRMS calcd for $C_{20}H_{20}F_3N_2O$: 361.1528 ($M+H^+$), found: 361.1562.



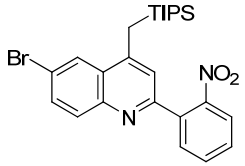
6-Trifluoromethyl-2-phenylquinoline (7b)

White solids. mp 120-122 °C; IR (KBr) 1307, 1119, 843, 763 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 9.2 Hz, 1H), 8.21-8.17 (m, 2H), 8.14 (s, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.89 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.57-7.48 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 149.3, 138.9, 137.5, 130.9, 130.9, 129.0, 128.0 (q, $^{2}J_{(C,F)}$ = 32.4 Hz), 127.7, 126.1, 125.4 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 125.3 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 124.1 (q, $^{1}J_{(C,F)}$ = 272.3 Hz), 120.1; LRMS (FAB) *m/z* 274 (M^{+}+1); HRMS calcd for $C_{16}H_{11}F_3N$: 274.0844 ($M+H^{+}$), found: 274.0893.



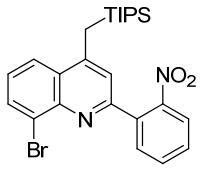
6-Trifluoromethyl-4-(triisopropylsilyl)methyl-2-(*o*-nitrophenyl)quinoline (4ia).

Pale yellow solids. mp 76-78 °C; IR (KBr) 2868, 1527, 1343, 1312, 1123 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.87 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 (td, *J* = 8.0, 1.6 Hz, 1H), 2.74 (s, 2H), 1.19-1.10 (m, 3H), 1.02 (d, *J* = 7.1 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 151.5, 149.2, 149.1, 135.8, 132.7, 131.6, 131.3, 129.6, 127.7 (q, $^{2}J_{(C,F)}$ = 32.4 Hz), 125.9, 125.2 (q, $^{3}J_{(C,F)}$ = 3.8 Hz), 124.6, 124.2 (q, $^{1}J_{(C,F)}$ = 272.3 Hz), 122.2 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 121.1, 18.4, 16.6, 11.4; LRMS (FAB) *m/z* 489 (M^{+}+1); HRMS (FAB) calcd for $C_{26}H_{32}F_3N_2O_2Si$: 489.2185 ($M+H^{+}$), found: 489.2187.



6-Bromo-4-(triisopropylsilyl)methyl-2-(*o*-nitrophenyl)quinoline (4ja).

White solids. mp 90-91 °C; IR (KBr) 2945, 1585, 1537, 1348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 2.4 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.76 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.70 (td, *J* = 8.0, 1.2 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (td, *J* = 8.0, 1.2 Hz, 1H), 7.30 (s, 1H), 2.65 (s, 2H), 1.21-1.10 (m, 3H), 1.01 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 149.4, 149.2, 146.6, 135.9, 132.9, 132.6, 132.1, 131.3, 129.3, 128.0, 126.6, 124.5, 120.7, 120.2, 18.5, 16.3, 11.4; LRMS (EI) *m/z* 498, 500 (M^+, M^++2); Anal. calcd for $C_{25}H_{31}BrN_2O_2Si$: C, 60.11; H, 6.26; N, 5.61. found: C, 59.96; H, 6.38; N, 5.61.

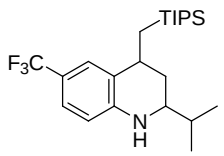


8-Bromo-4-(triisopropylsilyl)methyl-2-(*o*-nitrophenyl)quinoline (4ka).

Pale yellow solids. mp 150-152 °C; IR (KBr) 2945, 1583, 1535, 1366, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.56 (td, *J* = 8.0, 1.6 Hz, 1H), 7.40 (s, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 2.71 (s, 2H), 1.21-1.10 (m, 3H), 1.00 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 151.0, 149.9, 135.4, 133.4, 132.2, 131.4, 129.4, 128.0, 126.3, 126.2, 124.5, 123.8, 120.5, 18.5, 16.5, 11.4; LRMS (EI) *m/z* 498, 500 (M^+, M^++2); Anal. calcd for $C_{25}H_{31}BrN_2O_2Si$: C, 60.11; H, 6.26; N, 5.61. found: C, 59.90; H, 6.21; N, 5.51.

Procedure for three-component Tf_2NH-catalyzed cascade Povarov/Oxidation reaction.

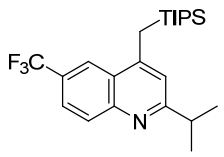
To a stirred solution of *p*-trifluoromethylaniline (**8**) (95.6 mg, 0.593 mmol) and isobutylaldehyde (**9**) (54 μL, 0.591 mmol) in 1,2-dichloromethane (0.9 mL) was added allyltriisopropylsilane **1a** (38.6 mg, 0.195 mmol), then Tf_2NH (0.4 M solution in toluene, 49 μL, 19.6 μmol, 10 mol%) at ambient temperature. The reaction mixture was stirred at 60 °C for 24 h, and then diluted with $CHCl_3$ and cooled to ambient temperature. The mixture was quenched with saturated aqueous solution of $NaHCO_3$, and the aqueous phase was extracted twice with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (2 : 3 $CHCl_3$-hexane with 0.5% NEt_3) to afford **3la** (59.1 mg, 60%, *trans*/*cis* = 50 : 50) as colorless oil.



(2*R,4*S**)- and (2*R**,4*R**)-6-Trifluoromethyl-2-isopropyl-4-(triisopropylsilyl)methyl-1,2,3,4-tetrahydroquinoline (***trans*- and *cis*-**3la** as a 3 : 2 inseparable mixture**).**

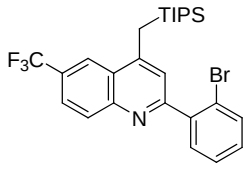
Colorless oil. IR (neat) 2960, 2866, 1618, 1327, 1109 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (for *trans*-**3la**) δ 7.19 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 4.10 (bs, 1H), 3.29 (dt, *J* = 11.6, 4.4 Hz, 1H), 3.14-3.07 (m, 1H), 1.78-1.66 (m, 2H), 1.60 (td, *J* = 12.0, 5.2 Hz, 1H), 1.20-0.88 (m, 29H), (for *cis*-**3la**) d 7.42 (s, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 4.02 (bs, 1H), 3.18 (ddd, *J* = 11.6, 5.2, 2.8 Hz, 1H), 3.02-2.94 (m, 1H), 2.10 (ddd, *J* = 12.4, 4.4, 2.8 Hz, 1H), 1.45 (dd, *J* = 14.8, 3.2 Hz, 1H), 1.34 (ddd, *J* = 14.8, 12.4, 11.6 Hz, 1H), 1.25 (dd, *J* = 3.6, 2.0 Hz, 1H), 1.20-0.88 (m, 27H), 0.77 (dd, *J* = 15.2, 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* + *cis*) δ 147.7, 146.3, 128.0, 127.4, 127.0-122.0 (m, $F_3\underline{C}$x2), 125.7 (q, $^3J_{(C,F)}$ = 4.1 Hz), 124.0 (q, $^3J_{(C,F)}$ = 4.1 Hz), 123.8 (q, $^3J_{(C,F)}$ = 4.1 Hz), 123.6 (q, $^3J_{(C,F)}$ = 4.1 Hz), 117.9 (q, $^2J_{(C,F)}$ = 32.0 Hz), 117.8 (q,

$^{2}J_{(C,F)}$ = 32.0 Hz), 113.0, 112.9, 57.6, 51.9, 33.9, 32.9, 32.8, 32.3, 31.6, 30.4, 19.6, 19.0x2, 18.9, 18.3x2, 17.9, 14.2, 11.9, 11.7; LRMS (EI) *m/z* 413 (M^+); Anal. calcd for $C_{23}H_{38}F_3NSi$: C, 66.78; H, 9.26; N, 3.39. found: C, 66.84; H, 9.04; N, 3.16.



6-Trifluoromethyl-2-isopropyl-4-(triisopropylsilyl)methylquinoline (4la).

To a stirred solution of *p*-trifluoromethylaniline (**8**) (40.6 mg, 0.25 mmol) and isobutylaldehyde (**9a**) (23 μL, 0.25 mmol) in 1,2-dichloroethane (0.2 mL) was added allyltriisopropylsilane (**2a**) (39.3 mg, 0.2 mmol), then Tf_2NH (0.4 M solution in toluene, 50 μL, 20 μmol, 10 mol%) at ambient temperature. The reaction mixture was stirred at 60 °C for 24 h, then cool to ambient temperature, followed by addition of DDQ (93.7 mg, 0.4 mmol) in one portion. The resulting brown mixture was stirred at ambient temperature for additional 10 min (exothermic), and then quenched with saturated aqueous solution of $NaHCO_3$. The aqueous phase was extracted twice with $CHCl_3$. Collected organic layers were washed with saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by silica gel flash column chromatography (3 : 1 $CHCl_3$-hexane with 0.5% NEt_3) to afford **4la** (42.0 mg, 52%) as colorless oil. IR (neat) 2962, 2868, 1593, 1313, 1165, 1126, 881 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.81 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.22 (s, 1H), 3.20 (sep, *J* = 7.2 Hz, 1H), 2.67 (s, 2H), 1.37 (d, *J* = 7.2 Hz, 6H), 1.16-1.05 (m, 3H), 0.99 (d, *J* = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 150.0, 149.2, 130.8, 126.5 (q, $^{2}J_{(C,F)}$ = 31.1 Hz), 125.6, 124.5 (q, $^{3}J_{(C,F)}$ = 3.3 Hz), 124.4 (q, $^{1}J_{(C,F)}$ = 272.0 Hz), 121.3 (q, $^{3}J_{(C,F)}$ = 4.9 Hz), 119.9, 37.3, 22.4, 18.4, 16.1, 11.5; LRMS (EI) *m/z* 409 (M^+); Anal. calcd for $C_{23}H_{34}F_3NSi$: C, 67.44; H, 8.37; N, 3.42. found: C, 67.29; H, 8.22; N, 3.18.



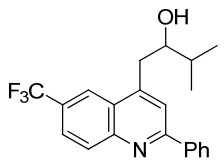
2-(*o*-Bromophenyl)-6-trifluoromethyl-4-(triisopropylsilyl)methylquinoline (4ma)

To a stirred solution of allyltrisopropylsilane (**1a**) (315 mg, 1.59 mmol), *p*-trifluoromethylaniline (**8**) (320 mg, 1.98 mmol) and *o*-bromobenzaldehyde (**9b**) (368 mg, 1.99 mmol) in 1,2-dichloroethane (3.2 mL) was added Tf_2NH (0.4 M solution in toluene, 400 μL, 0.16 mmol, 10 mol%). The reaction mixture was stirred at 60 °C for 9 h, and then cooled to ambient temperature, followed by addition of DDQ (741 mg, 3.26 mmol) in one portion. The resulting brown suspension was stirred at the same temperature for 10 min, and then filtered through a pad of celite. The precipitates was washed with $CHCl_3$, and the resulting filtrate was added saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted twice with $CHCl_3$. The collected organic layers were washed successively with sat. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture was purified with silica gel column chromatography (150 : 1 $CHCl_3$-AcOEt with 0.25% NEt_3) to afford **4ma** (710 mg, 86%) as white solids. mp 71-72 °C; IR (KBr) 2945, 1310, 1143, 1119 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.88 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.52 (s, 1H), 7.45 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.31 (dt, *J* = 8.0, 1.7 Hz, 1H), 2.74 (s, 2H), 1.22-1.13 (m, 3H), 1.00 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 150.2, 149.2, 141.6, 133.3, 131.5, 131.3, 130.1, 127.7, 127.5 (q, $^2J_{(C,F)}$ = 32.4 Hz), 125.8, 124.9 (q, $^3J_{(C,F)}$ = 3.6 Hz), 124.3 (q, $^1J_{(C,F)}$ = 272.3 Hz), 123.1, 122.2 (q, $^3J_{(C,F)}$ = 4.8 Hz), 121.7, 18.5, 16.4, 11.4; LRMS (FAB) *m/z* 522, 524 (M^++1, M^++3); HRMS calcd for $C_{26}H_{32}{}^{79}BrF_3NSi$: 522.1439 ($M+H^+$), found: 522.1462.

Protodesilylation of 4aa.

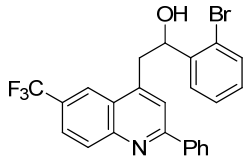
To a stirred solution of quinoline **4aa** (54.5 mg, 0.123 mmol), water (~10 μL) in THF (0.25 mL) was added *n*-tetrabutylammonium fluoride (TBAF, 1.0 M THF solution, 125 μL, 0.125 mmol) at ambient temperature. The reaction mixture was stirred at the same temperature until starting material

disappeared (monitoring by TLC, about 1 h), and then quenched with 10% aqueous solution of HCl. The water phase was basified with saturated aqueous solution of $NaHCO_3$, and then extracted twice with AcOEt. Collected organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by silica gel flash column chromatography (5 : 2 $CHCl_3$-hexane with 0.5% of NEt_3) to afford **7a** (34.6 mg, 98%) as white solids. Spectra data were described above.



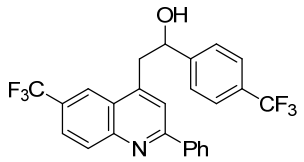
6-Trifluoromethyl-4-(2-hydroxy-3-methylbutyl)-2-phenylquinoline (10a).

To a stirred solution of **4aa** (31.9 mg, 0.072 mmol), isobutylaldehyde (**9a**) (20 μL, 0.22 mmol) in THF (0.2 mL) was added TBAF (1.0 M THF solution, 110 μL, 0.110 mmol) at ambient temperature. The reaction mixture was stirred at the same temperature for 12 h, and then quenched with 10% aqueous solution of HCl. The water phase was basified with saturated aqueous solution of $NaHCO_3$, and then extracted twice with EtOAc. Collected organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by PTLC (5 : 1 AcOEt-$CHCl_3$ with 0.5% of NEt_3) to afford **10a** (13.6 mg, 53%) as white solids. mp 142-143 °C; IR (KBr) 3314 (broad), 2961, 1603, 1474, 1312, 1124 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27-8.25 (m, 2H), 8.09 (dd, J = 8.0, 2.0 Hz, 2H), 7.87 (dd, J = 8.8, 1.6 Hz, 1H), 7.82 (s, 1H), 7.54-7.47 (m, 3H), 3.71 (bs, 1H), 3.40 (dd, J = 14.0, 2.0 Hz, 1H), 3.05 (dd, J = 14.0, 10.0 Hz, 1H), 2.03-1.99 (m, 1H), 1.93 (sep, J = 6.8 Hz, 1H), 1.12 (dd, J = 6.8, 2.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 149.4, 147.7, 138.4, 131.3, 130.0, 128.8, 127.6 (q, $^2J_{(C,F)}$ = 32.0 Hz), 127.5, 125.8, 125.0 (q, $^3J_{(C,F)}$ = 3.3 Hz), 124.2 (q, $^1J_{(C,F)}$ = 272.8 Hz), 121.5 (q, $^3J_{(C,F)}$ = 4.1 Hz), 121.2, 37.3, 34.3, 18.7, 17.7; LRMS (EI) *m/z* 359 (M^+); HRMS calcd for $C_{21}H_{20}ONF_3$: 359.1497 (M^+), found: 359.1477.



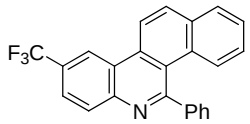
4-{2-(*o*-Bromophenyl)-2-hydroxyethyl}-6-trifluoromethyl-2-phenylquinoline (10b).

White solids. mp 220-222 °C; IR (KBr) 3243 (broad), 1315, 1170, 1121 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.56 (s, 1H), 8.26-8.22 (m, 3H), 8.05 (s, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.62-7.53 (m, 5H), 7.38 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 5.75 (d, J = 4.6 Hz, 1H), 5.29 (m, 1H), 3.58 (dd, J = 13.8, 4.0 Hz, 1H), 3.40 (dd, J = 13.8, 8.6 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.5, 148.9, 146.7, 143.7, 138.1, 132.1, 131.2, 130.0, 129.1, 128.9, 128.2, 127.8, 127.3, 125.9, 125.8 (q, $^{2}J_{(C,F)}$ = 31.2 Hz), 124.6 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 124.3 (q, $^{1}J_{(C,F)}$ = 272.3 Hz), 122.5 (q, $^{3}J_{(C,F)}$ = 4.8 Hz), 121.8, 120.9, 71.1; LRMS (FAB) *m/z* 472, 474 (M^{+}+1, M^{+}+3); HRMS calcd for $C_{24}H_{18}{}^{79}BrF_3NO$: 472.0524 ($M+H^{+}$), found: 472.0534.



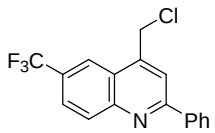
4-{2-(*p*-trifluoromethylphenyl)-2-hydroxyethyl}-6-Trifluoromethyl-2-phenylquinoline (10c).

White solids. mp 165-166 °C; IR (KBr) 3246 (broad), 1603, 1325, 1164, 1116 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 8.11 (s, 1H), 7.86-7.83 (m, 3H), 7.63 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.48-7.42 (m, 5H), 4.94-4.86 (m, 1H), 3.65 (s, 1H), 3.44 (dd, J = 13.7, 4.6 Hz, 1H), 3.38 (dd, J = 13.7, 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 149.2, 147.4, 145.6, 138.2, 131.2, 130.3 (q, $^{2}J_{(C,F)}$ = 32.4 Hz), 130.1, 128.9, 128.5 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 127.4, 126.0, 125.6, 125.6 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 125.3 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), {124.0 (q, $^{1}J_{(C,F)}$ = 272.3 Hz)}x2, 121.6, 121.4 (q, $^{3}J_{(C,F)}$ = 3.6 Hz), 73.3, 42.4; LRMS (FAB) *m/z* 462 (M^{+}+1); HRMS calcd for $C_{25}H_{18}F_6NO$: 462.1293 ($M+H^{+}$), found: 462.1315.



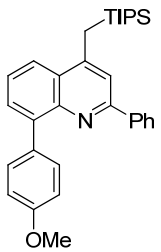
9-Trifluoromethyl-5-phenylbenzo[*i*]phenanthridine (11).

To a stirred solution of **10b** (94.7 mg, 0.20 mmol) in degassed benzene (20 mL, 0.01 M) were added AIBN (9.7 mg, 0.059 mmol) and tris(trimethylsilyl)silane (TTMSH; 125 μL, 0.41 mmol). The mixture was refluxed for 2 h, and then additional AIBN (9.7 mg, 0.059 mmol) and TTMSS (65 μL, 0.21 mmol) were added. After refluxed for 19 h, additional AIBN (13.3 mg, 0.081 mmol) was added. The mixture was refluxed for additional 27 h. The reaction mixture was cooled to ambient temperature and concentrated in vacuo. The resulting residue was dissolved in MeCN, washed four times with hexane, and concentrated in vacuo. The resulting amorphous solids were added THF (1.0 mL) and 2 N HCl (1.0 mL), and stirred vigorously at ambient temperature. After 12 h, the mixture was basified with 1 N NaOH and diluted with AcOEt and water. The aqueous layer was extracted twice with AcOEt. Collected organic layers were washed with brine, dried over $MgSO_4$, filtered, and concectrated in vacuo. The crude residue was purified by silica gel flash column chromatography (20 : 1 hexane-AcOEt with 0.5% NEt_3) to affod **11** (29.7 mg, 40%) as white solids. mp 204-205 °C; IR (KBr) 1322, 1294, 1113, 843 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.63 (d, J = 9.2 Hz, 1H), 8.34 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.97-7.93 (m, 2H), 7.79 (d, J = 9.2 Hz, 1H), 7.64-7.60 (m, 2H), 7.55-7.60 (m, 4H), 7.23 (td, J = 7.5, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 145.2, 144.0, 134.3, 133.4, 133.1, 130.8, 130.1, 129.1, 128.8x2, 128.6, 128.4 (q, $^2J_{(C,F)}$ = 32.4 Hz), 128.3, 126.9, 126.2, 124.9 (q, $^3J_{(C,F)}$ = 3.6 Hz), 124.4 (q, $^1J_{(C,F)}$ = 272.3 Hz), 123.0, 122.0, 120.5 (q, $^3J_{(C,F)}$ = 3.6 Hz), 119.4; LRMS (FAB) *m/z* 374 (M^++1); HRMS calcd for $C_{24}H_{15}F_3N$: 374.1157 ($M+H^+$). found: 374.1183.



6-Trifluoromethyl-4-chloromethyl-2-phenylquinoline (12).

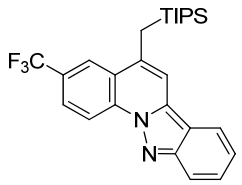
In a round-bottom flask, cesium fluoride (110 mg, 0.72 mmol) was dried using a heat gun under reduced pressure. To the resultant was added quinoline **4aa** (160 mg, 0.36 mmol), hexachloroethane (174 mg, 0.72 mmol), and anhydrous acetonitrile (3.0 mL). The suspension was refluxed for 24 h, and then quenched with water. After aqueous phase was extracted twice with AcOEt, the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (1 : 10 AcOEt-hexane) to afford **11a** (81.6 mg, 70%) as white solids. mp 104-106 °C; IR (KBr) 1604, 1312, 1178, 1122 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.33 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.4 Hz, 2H), 8.04 (s, 1H), 7.93 (dd, J = 8.8, 2.0 Hz, 1H), 7.59-7.50 (m, 3H), 5.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.6, 143.5, 138.3, 131.7, 130.1, 128.9, 128.4 (q, $^2J_{(C,F)}$ = 32.3 Hz), 127.6, 125.5 (q, $^3J_{(C,F)}$ = 3.3 Hz), 124.0, 124.0 (q, $^1J_{(C,F)}$ = 272.0 Hz), 121.0 (q, $^3J_{(C,F)}$ = 5.0 Hz), 120.0, 42.2; LRMS (EI) *m/z* 321 (M^+); Anal. calcd for $C_{17}H_{11}ClF_3N$: C, 63.46; H, 3.45; N, 4.35. found: C, 63.38; H, 3.54; N, 4.27.



4-(Triisopropylsilyl)methyl-8-(*p*-methoxyphenyl)-2-phenylquinoline (4na).

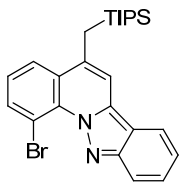
To a stirred solution of **4fa** (23.0 mg, 0.051 mmol) in toluene (0.3 mL) was added $Pd(PPh_3)_4$ (2.9 mg, 2.5 μmol, 5 mol%) and Na_2CO_3 (2 M aqueous solution, 40 μL, 0.080 mmol) at ambient temperature. The reaction mixture was stirred for 5 min, and then added a solution of 4-methoxyboronic acid (9.6 mg, 0.063 mmol) in ethanol (50 μL). After the resulting mixture was

refluxed for 8 h, the mixture was added water and extracted twice with AcOEt. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by PTLC (1 : 49 : 50 AcOEt-toluene-hexane) to afford **4na** (18.5 mg, 76%) as white solids. mp 77-79 °C; IR (KBr) 2941, 2865, 1590, 1508, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 2H), 8.04 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.75 (s, 1H), 7.72 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H), 2.75 (s, 2H), 1.25-1.14 (m, 3H), 1.04 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 154.6, 149.3, 145.9, 140.9, 139.8, 132.6, 132.4, 129.7, 129.0, 128.7, 127.4, 127.2, 125.1, 123.1, 117.5, 113.0, 55.4, 18.6, 16.3, 11.5; LRMS (FAB) *m/z* 481, 482 (M^+, M^++1); Anal. calcd for $C_{32}H_{39}NOSi$: C, 79.78; H, 8.16; N, 2.91. found: C, 79.41; H, 8.20; N, 2.81.



3-Trifluoromethyl-5-(triisopropylsilyl)methylindazolo[2,3-*a*]quinolone (13ia).

Yellow solids. mp 126-128 °C; IR (KBr) 2947, 1628, 1363, 1313, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.5 Hz, 1H), 8.41 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.82 (s, 1H), 7.56 (t, *J* = 8.5 Hz, 1H), 7.24 (t, *J* = 8.5 Hz, 1H), 2.71 (s, 2H), 1.25-1.13 (m, 3H), 1.04 (d, *J* = 7.2 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 135.5, 134.4, 132.9, 128.7, 127.4 (q, $^2J_{(C,F)}$ = 32.4 Hz), 125.3 (q, $^3J_{(C,F)}$ = 3.6 Hz), 124.7, 123.4 (q, $^3J_{(C,F)}$ = 3.6 Hz), 120.6, 120.0, 118.6, 116.5, 115.9, 114.8, 18.5, 15.7, 11.5; LRMS (FAB) *m/z* 457 (M^++1); HRMS calcd for $C_{26}H_{32}F_3N_2Si$: 457.2287 ($M+H^+$), found: 457.2267.



1-Bromo-5-(triisopropylsilyl)methylindazolo[2,3-*a*]quinolone (13ka).

Yellow solids. mp 157-159 °C; IR (KBr) 2939, 2861, 1630, 1539, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.72 (s, 1H), 7.51 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 2.58 (s, 2H), 1.15 (m, 3H), 1.00 (d, *J* = 6.9 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 136.8, 133.8, 133.5, 132.2, 128.2, 127.9, 125.2, 120.5, 119.4, 117.0, 114.8, 114.6, 111.1, 99.9, 18.6, 16.2, 11.5; LRMS (FAB) *m/z* 467, 469 (M^{+}+1, M^{+}+3); Anal. calcd for $C_{25}H_{31}BrN_2Si \cdot 0.3H_2O$: C, 63.49; H, 6.73; N, 5.92. found: C, 63.52; H, 6.57; N, 5.90.

Reference

S1. Simion, A.; Simion, C.; Kanda, T.; Nagashima, S.; Mitoma, Y.; Yamada, T.; Mimura, K.; Tashiro, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2071-2078.