

Supporting Information for:

Metal-free Reductions of N-Heterocycles via Lewis Acid Catalyzed Hydrogenation

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General Considerations: All substituted quinolines were purchased from Sigma-Aldrich and used without further purification. $B(C_6F_5)_3$ purchased from Boulder Scientific and used without further purification. Toluene was dried using an Innovative Technologies drying column, degassed and stored over molecular sieves. H_2 was passed through a dririte column prior to use. $CDCl_3$ was distilled over CaH_2 .

General procedure for $B(C_6F_5)_3$ -catalyzed hydrogenations: A sealed 50 or 100 mL Schlenk bomb was charged with 100 mg of quinoline and the appropriate amount of $B(C_6F_5)_3$, dissolved in 5 mL of toluene. The bomb was subjected to 3 freeze-pump-thaw cycles and subsequently exposed to 1 atm of H_2 at 78 K (~4 atm). The reaction was carried out over times and temperatures shown in Table 1. Following the reaction, 5 mL of ethyl acetate was added to the solution and the mixture was run through a short plug of silica, volatiles were removed *in vacuo*.

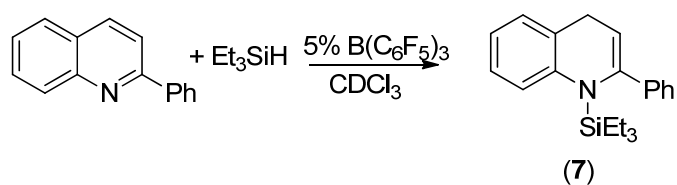
NMR data for compounds **1-4** and **6** matched that previously published: acridan (**1**);¹ 1,2,3,4-tetrahydro-2-phenylquinoline (**2**);² 1,2,3,4-tetrahydro-2-methylquinoline (**3**);²⁻⁴ 1,2,3,4-tetrahydro-8-methylquinoline (**4**);³ 1,2,3,4-tetrahydro-phenanthroline (**6**)⁵

1,10-phenanthroline- $B(C_6F_5)_3$ (**5**) – 1,10-phenanthroline (7 mg, 0.04 mmol) was added to $B(C_6F_5)_3$ (20 mg, 0.039 mmol) in 2 mL of CH_2Cl_2 . The solution was allowed to stir for 2 hours, pumped to dryness and washed with pentane (2x2mL). The resulting white solid was again pumped to dryness. X-Ray quality crystals were grown from a layered solution of $CDCl_3$ /pentane. Yield: 26 mg (96%). $C_{30}H_8BF_{15}N_2$: C, 52.06%; H, 1.16%; N, 4.05%. Found: C, 51.78%; H, 1.19%; N, 4.23%.

1H NMR ($CDCl_3$) δ : 7.77 (m, 2H), 7.84 (m, 1H), 8.09 (dd, $^3J_{H-H}=8$ Hz, $^4J_{H-H}=2$ Hz, 1H), 8.51 (d, $^3J_{H-H}=9$ Hz, 1H), 8.72 (d, $^3J_{H-H}=8$ Hz, 1H), 9.19 (q, $^3J_{H-H}=5$ Hz, 1H); ^{19}F NMR ($CDCl_3$) δ : -124.9 (br s, 1F, *o*- C_6F_5), -130.1 (br s, 1F, *o*- C_6F_5), -131.5 (br s, 1F, *o*- C_6F_5), -132.5 (br s, 1F, *o*- C_6F_5), -134.9 (br s, 1F, *o*- C_6F_5), -155.8 (br s, 1F, *p*- C_6F_5), -159.0 (br s, 1F, *p*- C_6F_5), -161.7 (br s, 1F, *p*- C_6F_5), -162.2 (br s, 1F, *m*- C_6F_5), -163.0 (br s, 1F, *m*- C_6F_5), -166.0 (br s, 1F, *m*- C_6F_5), -166.3 (br s, 1F, *m*- C_6F_5), -166.8 (br s, 1F, *m*- C_6F_5), -167.7 (br s, 1F, *m*- C_6F_5); ^{11}B NMR ($CDCl_3$) δ : -3.2;

^{13}C NMR (CDCl_3) (partial) δ : 123.2 (dm, $^1J_{\text{C-F}}=227$ Hz, CF), 125.9, 130.9 (dm, $^1J_{\text{C-F}}=296$ Hz, CF), 136.5, 146.0 (dm, $^1J_{\text{C-F}}=279$ Hz, CF), 153.2.

General procedure for hydrosilylation: a 20 mL vial was charged with acridine (or 2-phenylquinoline) and ~ 1.25 equivalents of Et_3SiH in CDCl_3 . $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mol %) was added and the solution was stirred. Hydrosilylation of 2-phenylquinoline reached 76% conversion after 4 hours and reached a maximum of 85% conversion to (**7**) after 48 hours.



(7) ^1H NMR (CDCl_3) δ : 0.80 (m, 15H, CH_2CH_3), 3.26 (d, $^3J_{\text{H-H}}=5$ Hz, 2H, CH_2), 5.33 (t, $^3J_{\text{H-H}}=5$ Hz, 2H alkenyl- CH), 6.95 (td, $^3J_{\text{H-H}}=6$ Hz, $^4J_{\text{H-H}}=2$ Hz, 1H), 7.01 (d, $^3J_{\text{H-H}}=7$ Hz, 1H), 7.09 (m, 2H), 7.24 (m, 3H), 7.45 (m, 3H), 8.14 (m, 1H). ^{29}Si NMR (CDCl_3) δ : 14.3.

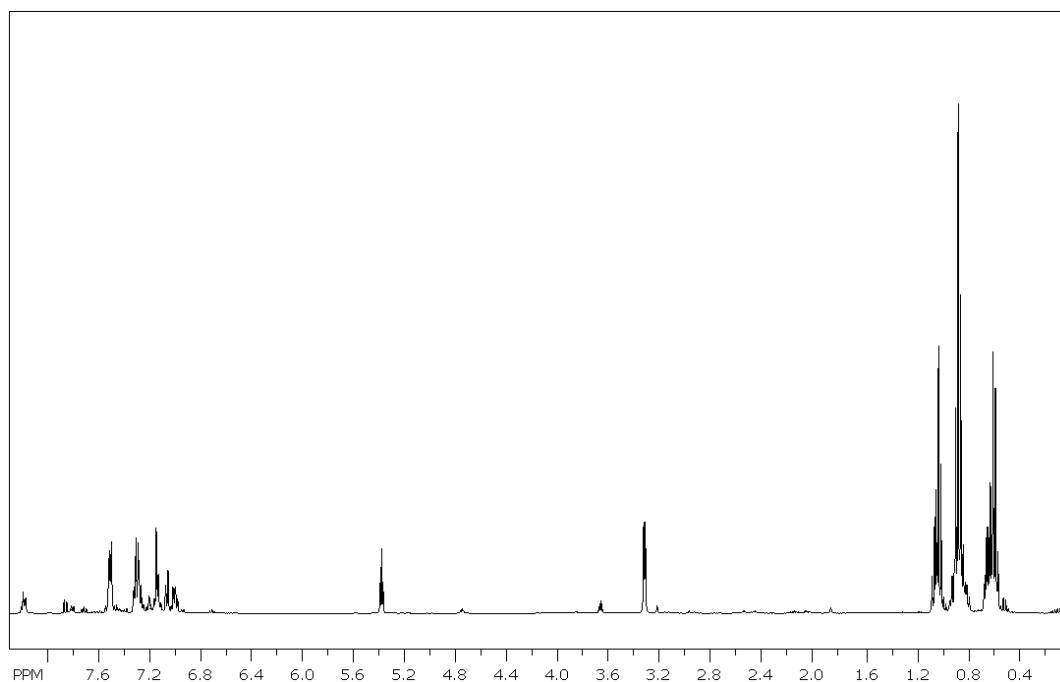


Figure 1: ^1H NMR of (8) in CDCl_3 after 48 hours at 25°C (Particularly characteristic of (7) are the resonance at 3.26 and 5.33 ppm, corresponding to the methylene and alkenyl protons, respectively).

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