Supporting Information for
Copper-Mediated, Palladium-Catalyzed Coupling of Thiol Esters with Aliphatic
Organoboron Reagents.

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General Experimental Methods

All reactions were performed under an atmosphere of dry N₂ or Ar in oven-dried glassware unless otherwise noted. THF, DMA, DMF, 1,4-Dioxane, toluene, benzene and CH₂Cl₂ were dried over 4Å molecular sieves and titrated for water content prior to use with a Fisher Coulomatic K-F titrater. Et₃N was dried over KOH pellets. Hexanes, ethyl acetate (EtOAc), and diethyl ether (Et₂O) were obtained from EM Science and used as purchased. 'Brine' refers to a saturated aqueous solution of NaCl. Unless otherwise specified, solutions of NH₃·H₂O, HCl, NaOH, NaHCO₃, Na₂CO₃ and K₂CO₃ refer to aqueous solutions. Purification by flash chromatography was performed by the method of Still¹ using Whatman 60Å 230-400 mesh SiO₂ with compressed air as a source of positive pressure. Analytical thin-layer chromatography (TLC) was carried out using Merck Kieselgel 60F₂₅₄ plates with visualization by UV, phosphomolybdic acid, or iodine stain.

Melting points were obtained in open capillary tubes. ¹H NMR spectra were internally referenced to CDCl₃ (7.26 ppm); ¹³C NMR spectra were internally referenced to CDCl₃ (77.23 ppm). Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), hex (hextet), hept (heptet), m (multiplet), exch (exchangeable), app (apparent); coupling constants, *J*, are reported (Hz). Infrared (IR) peaks are reported (cm⁻¹) with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak 20-40%), and br (broad). GC/MS analysis was carried out on a bonded 5% diphenylsiloxane capillary column (30 m, 0.25 mm id, 0.25 μm df).

Starting Materials

Thiophene-2-carboxylic acid, copper(I) oxide, benzoyl chloride, *p*-tolylthiol, *p*-chlorophenylthiol, benzoic acid, 4-(dimethylamino)pyridine (DMAP), 1,3-dicyclohexylcarbodiimide (DCC), morpholine, chloroacetyl chloride, thiobenzoic acid, adamantoyl chloride, lauroyl chloride, 0.5 M 9-BBN in THF, 1-undecene, 4-vinyl anisole, 4-chlorostyrene, α-methylstyrene, 4-vinyl-1-cyclohexene, 4-methyl-1,3-pentadiene, 1-nonen-4-yne, 5-hexen-2-one, acrolein dimethyl acetal, allyl chloride, (R)-alpine-borane, Pd(PPh₃)₄ and Cs₂CO₃ were all obtained from Aldrich and used without further purification. Styrene

and cyclohexene were purchased from Aldrich and distilled before use. *n*-Butylboronic acid was obtained from Frontier Scientific, Inc. Cu(I) 2-thiophenecarboxylate (CuTC) was prepared following a literature procedure.²

***S*-(4-Methylphenyl) thiobenzoate, 1a.**³ *p*-Tolylthiol (2.48 g, 20.0 mmol) was dissolved in aqueous 0.1 M NaOH solution (200 mL). The solution was protected under argon and cooled to 0 °C. Then, benzoyl chloride (2.32 mL, 20.0 mmol) was added dropwise. A white precipitate was observed immediately and the solution was stirred at room temperature overnight. The white precipitate was filtered, washed with water, and air-dried to obtain the crude product as an off-white solid. The crude product was refluxed in hexanes for 2 h. After filtration of the refluxed solution, the filtrate was left for crystallization to give the product as a white solid in 65% yield (2.96 g). TLC (hexanes:Et₂O = 1:1, *R*_f = 0.71); Mp 64-65 °C (ethyl ether; lit. {65 °C}³); ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 9 Hz, 2H), 7.35-7.55 (m, 5H), 7.18 (d, *J* = 9 Hz, 2H), 2.34 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 190.8, 140.0, 136.9, 135.2, 133.8, 130.3, 128.9, 127.7, 123.9, 21.6; IR (neat, cm⁻¹): 2918 (w), 1668 (s), 1594 (m), 1490 (m), 1447 (m).

***S*-(4-Chlorophenyl) thiobenzoate, 1b.**² Benzoic acid (2.442 g, 20.0 mmol), *p*-chlorophenylthiol (3.471 g, 24.0 mmol) and DMAP (0.244 g, 2.0 mmol) were dissolved in CH₂Cl₂ (60 mL) in a round-bottomed flask and the solution was cooled to 0 °C. DCC (4.952 g, 24.0 mmol) was dissolved in CH₂Cl₂ (40 mL) and then slowly added into the flask via a dropping funnel. The solution was stirred under the protection of argon overnight. After filtration, the filtrate was washed with H₂O, saturated NaHCO₃, brine and then filtered through a pad of silica. The solvent was evaporated and the residue was dissolved in hexanes for crystallization to give the product 3.38 g (68%) as a white solid. Mp 70-71 °C (hexane, lit. {57-59 °C}²); ¹H NMR (300 MHz, CDCl₃) δ 8.0-8.15 (m, 2H), 7.2-7.7 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 189.8, 136.5, 136.2, 134.1, 129.7, 129.0, 127.7, 126.0; IR (neat, cm⁻¹): 3057 (w), 1675 (s), 1594 (m), 1475 (m), 1447 (m), 1204 (s).

S-(4-Acetyl morpholyl) thiobenzoate, 1c.⁴ Morpholine (3.05 mL, 35 mmol) and Et₃N (5.11 mL, 36.4 mmol) were added to THF (60 mL) and the solution was cooled to -78 °C. The solution was purged with argon and chloroacetyl chloride (2.79 mL, 35 mmol) was added dropwise via syringe. A white precipitate was observed. The suspension was stirred overnight and slowly allowed to reach room temperature. After filtering the solid, the solvent was evaporated. The residue was extracted with Et₂O and washed with water and sat. NaHCO₃. The aqueous layer was back extracted with CH₂Cl₂. All the organic layers were combined and washed with water, brine, and dried over MgSO₄. Evaporation of the solvent gave an oily yellow residue in 4.40 g. THF (50 mL) was added to the oily residue, followed by thiobenzoic acid (4.12 g, 27 mmol). The solution was degassed and stirred at room temperature. Et₃N (4.12 mL, 29 mmol) was added via syringe. The suspension was stirred overnight. After filtration of the precipitate, CH₂Cl₂ (20 mL) was added to the filtrate and quenched with water (20 mL), 10% HCl (10 mL), sat. NaHCO₃ (10 mL), and brine successively. All the aqueous layers were combined and extracted with CH₂Cl₂ (20 mL) again. The organic layers were combined and dried over MgSO₄. Evaporation of solvent gave a solid yellow residue. Recrystallization from CH₂Cl₂/Et₂O gave 5.31 g of the product as colorless crystals (57%). Mp 127-128 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.97 (m, 2H), 7.59 (m, 1H), 7.46 (m, 2H), 4.00 (s, 2H), 3.59-3.72 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 190.8, 166.6, 136.3, 134.0, 128.9, 127.6, 66.9, 66.8, 46.8, 42.8, 31.5; IR (neat, cm⁻¹): 2964 (m), 1660 (s), 1640 (s), 1621 (s), 1451 (s); HRMS(FAB+) Calcd for C₁₃H₁₅O₃NSLi (M+Li⁺): 272.0933. Found: 272.0943.

S-Adamantoyl-p-mercaptotoluene, 2.⁵ Following a literature procedure,⁵ adamantoyl chloride (4.95 g, 0.025 mol), *p*-tolylthiol (3.10 g, 0.025 mol) and triethylamine (2.78 g, 0.028 mol) were reacted in THF (50 mL). The product was obtained as a white solid in 5.58 g (78%). Mp 111-112 °C (ether/hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 7.27-7.19 (m, 4H), 2.37 (s, 3H), 2.09 (br s, 3H), 1.99 (d, *J* = 2.7 Hz, 6H), 1.75 (d, *J* = 2.4 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 204.6, 139.2, 136.9, 129.9, 48.9, 39.2, 36.4, 28.2, 21.3; IR (neat, cm⁻¹): 1691.

S-Lauroyl-p-mercaptotoluene, 3.⁵ Following a literature procedure,⁵ lauroyl chloride (10.9 g, 0.05 mol) and *p*-tolylthiol (6.2 g, 0.05 mol) were dissolved in hexanes (100 mL) and the mixture was cooled to 0 °C. Triethylamine (5.56 g, 0.055 mol) was added dropwise to the stirred reaction mixture. After stirring at room temperature overnight, the white precipitate was filtered. The filtrate was dried over MgSO₄ and evaporated to give 14.9 g of the product as colorless oil (98%). ¹H NMR (CDCl₃, 400MHz): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.70 (q, *J* = 8.0 Hz, 2H), 1.26 (br s, 16H), 0.88 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 198.2, 139.5, 134.4, 129.9, 124.4, 43.6, 31.9, 29.6, 29.4, 29.3, 29.2, 28.9, 25.6, 22.7, 21.3, 14.1. IR (neat, cm⁻¹): 1710 (s).

Thiol Ester - B-Alkyl-9-BBN Coupling Products

Dodecanophenone, 4a.⁶ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), (130 mg, 0.40 mmol) Cs₂CO₃, Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-undecyl-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was purified by silica gel chromatography (hexanes/ Et₂O, 1:1) to give the product dodecanophenone (86 mg, 83%) as an off-white solid. TLC R_f = 0.79 (hexanes: Et₂O = 1:1); Mp 44-45 °C (ethyl ether, lit. {43-45 °C (EtOAc/hexane)}⁶); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (m, 2H), 7.44-7.57 (m, 3H), 2.96 (t, *J* = 7.2 Hz, 3H), 1.73 (p, *J* = 7.2 Hz, 2H), 1.21-1.38 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 137.3, 133.1, 128.8, 128.3, 38.9, 32.1, 29.8, 29.7, 29.6, 29.6, 24.6, 22.9, 14.3; IR (neat, cm⁻¹): 3057 (w), 2918 (s), 2853 (s), 1687 (s).

1,3-Diphenylpropan-1-one, 4b.⁷ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-2-phenylethyl-9-BBN (0.96 mL, 0.48 mmol) in THF (0.50 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (69 mg, 82%). TLC R_f = 0.54 (hexanes Et₂O = 2:1); Mp 70-71 °C (ethyl ether, lit. {70-72 °C}⁷); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.97 (m, 2H), 7.44-7.58 (m, 3H), 7.19-7.33 (m, 5H), 3.31 (t, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100

MHz, CDCl₃) δ 199.4, 141.5, 137.0, 133.3, 128.8, 128.7, 128.6, 128.2, 126.3, 40.7, 30.3; IR (neat, cm⁻¹): 3065 (w), 1683 (s).

3-(*p*-Chlorophenyl)-1-phenyl-1-propanone, 4c.⁸ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-(4-chlorophenyl)ethyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (74 mg, 76%); TLC R_f = 0.24 (hexanes:EtOAc = 9:1); Mp 58-59 °C (diethyl ether, lit. {56.5-58 °C}⁸); ¹H NMR (400 MHz, CDCl₃) δ 7.88-8.04 (m, 2H), 7.45-7.59 (m, 3H), 7.19-7.28 (m, 4H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 139.9, 136.9, 133.4, 132.0, 130.0, 128.8, 128.7, 128.2, 40.3, 29.5; IR (neat, cm⁻¹): 2930 (w), 1668 (s).

3-(*p*-Methoxyphenyl)-1-phenyl-1-propanone, 4d.⁹ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-(4-methoxyphenyl)ethyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (75 mg, 78%). TLC R_f = 0.61 (hexanes: Et₂O = 1:1); Mp 60-61 °C (ethyl ether, lit. {62-63 °C (pentane)}⁹); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.97 (m, 2H), 7.44-7.57 (m, 3H), 7.16-7.18 (m, 2H), 6.83-6.85 (m, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 158.2, 137.1, 133.5, 133.2, 129.6, 128.8, 128.2, 114.1, 55.5, 40.9, 29.5; IR (neat, cm⁻¹): 3003 (w), 2961 (w), 1679 (s).

3-Cyclohexenyl-1-phenyl-1-propanone, 4e.¹⁰ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-(cyclohex-3-enyl)-ethyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as colorless oil (55 mg, 64%). TLC R_f = 0.57 (hexanes Et₂O = 1:1); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.98 (m, 2H), 7.44-7.58 (m, 3H), 5.63-5.69 (m, 2H), 3.01(t, *J* = 7.4 Hz, 2H), 2.05-2.17 (m, 3H), 1.61-1.81 (m, 6H), 1.23-1.33 (m, 1H); ¹³C NMR

(100 MHz, CDCl₃) δ 200.8, 137.2, 133.1, 128.8, 128.2, 127.3, 126.4, 36.3, 33.5, 31.9, 31.1, 28.9, 25.4; IR (neat, cm⁻¹): 3022 (w), 2914 (s), 1683 (s).

5-Methyl-1-phenylhex-4-en-1-one, 4f.¹¹ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(4-methyl-3-pentenyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as colorless oil (39 mg, 52%). TLC R_f = 0.66 (hexanes:Et₂O = 1:2); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.97 (m, 2H), 7.43-7.57 (m, 3H), 5.16-5.19 (m, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.6 Hz, 2H), 1.69 (s, 3H), 1.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.2, 137.2, 133.1, 132.9, 128.7, 128.2, 123.1, 38.9, 25.8, 13.1, 17.8; IR (neat, cm⁻¹): 2968 (w), 1687 (s).

1-Phenyl-dec-5-yn-1-one, 4g.¹² *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(non-4-ynyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as colorless oil (77 mg, 85%). TLC R_f = 0.78 (hexanes:Et₂O = 1:2); ¹H NMR (400 MHz, CDCl₃) δ 7.97-8.00 (m, 2H), 7.44-7.58 (m, 3H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.26-2.31 (m, 2H), 2.12-2.17 (m, 2H), 1.92 (pent, *J* = 7.2 Hz, 2H), 1.36-1.48 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.2, 137.2, 133.2, 128.8, 128.3, 81.5, 79.4, 37.5, 31.3, 23.7, 22.2, 18.6, 18.5, 13.9; IR (neat, cm⁻¹): 2957 (s), 2934 (s), 1687 (s).

1-Phenyl-heptane-1,6-dione, 4h.¹³ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-hexanonyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (38 mg, 47%). TLC R_f = 0.34 (hexanes:Et₂O = 1:2); Mp 43-44 °C (ethyl ether, lit. {42-43 °C}¹³); ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.96 (m, 2H), 7.44-7.57 (m, 3H), 2.99 (t, *J* = 7.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 1.63-1.76 (m, 4H); ¹³C

NMR (100 MHz, CDCl₃) δ 209.0, 200.2, 137.1, 133.2, 128.8, 128.2, 43.7, 38.5, 30.1, 23.8, 23.6; IR (neat, cm⁻¹): 2945 (m), 1706 (s), 1675 (s).

4,4'-Dimethoxy-1-phenylbutanone, 4i.¹⁴ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(3,3-dimethoxypropyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as colorless oil (40 mg, 48%). TLC R_f = 0.47 (hexanes:Et₂O = 1:2); ¹H NMR (300 MHz, CDCl₃) δ 7.96-7.99 (m, 2H), 7.43-7.58 (m, 3H), 4.48 (t, *J* = 7.4 Hz, 1H), 3.35 (s, 6H), 3.06 (t, *J* = 9.6 Hz, 2H), 2.03-2.10 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 137.1, 133.2, 128.8, 128.2, 104.1, 53.5, 33.4, 27.1; IR (neat, cm⁻¹): 2926 (m), 1722 (m), 1683 (s), 1598 (m).

4-Chlorobutyrophenone, 4j.¹⁵ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(3-chloropropyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as colorless oil (15 mg, 21%). TLC R_f = 0.57 (hexanes:Et₂O = 1:2); ¹H NMR (400 MHz, CDCl₃) δ 7.96-7.98 (m, 2H), 7.44-7.58 (m, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.22 (pent, *J* = 6.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 136.8, 133.3, 128.8, 128.1, 44.8, 35.4, 26.9; IR (neat, cm⁻¹): 2964 (w), 1687 (s).

3-Phenylbutyrophenone, 4k.¹⁶ *S*-(4-Acetyl morpholyl) thiobenzoate **1c** (106 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-phenylpropyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (50 mg, 56%). TLC R_f = 0.55 (hexanes:Et₂O = 1:1); Mp 71-72 °C (ethyl ether, lit. {70.5-71 °C (methanol)})¹⁶; ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.94 (m, 2H), 7.43-7.57 (m, 3H), 7.18-7.33 (m, 5H), 3.51 (hex, *J* = 7.2 Hz, 1H), 3.16-3.33 (m, 2H), 1.34 (d, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.3, 146.8, 137.4, 133.2, 128.8, 128.7, 128.3, 127.1, 126.5, 47.2, 35.8, 22.1; IR (neat, cm⁻¹): 2964 (w), 1683 (s).

1-Adamantanyl-1-dodecanone, 4l.¹⁷ *S*-Adamantoyl-*p*-mercaptotoluene (115 mg, **0.40 mmol**), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-undecyl-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (66 mg, 52%). TLC R_f = 0.54 (hexanes:EtOAc = 9:1); Mp 26 °C (ethyl ether, lit. {27 °C}¹⁷); ¹H NMR (400 MHz, CDCl₃) δ 2.41 (t, *J* = 7.4 Hz, 2H), 2.02 (s, 3H), 1.65-1.78 (m, 12H), 1.50 (pent, *J* = 7.0 Hz, 2H), 1.20-1.29 (m, 16H), 0.86 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 216.1, 46.5, 38.4, 36.8, 36.1, 32.1, 29.8, 29.7, 29.6, 29.5, 28.1, 23.9, 22.9, 14.3; IR (neat, cm⁻¹) 2922 (s), 2853 (s), 1702 (s).

1-Adamantan-3-(*p*-methoxyphenyl)-1-propanone, 4m. *S*-Adamantoyl-*p*-mercaptotoluene (115 mg, **0.40 mmol**), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-(4-methoxyphenyl)ethyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (75 mg, 63%). TLC R_f = 0.28 (hexanes:EtOAc = 9:1); Mp 35.5-37.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.70-2.82 (m, 4H), 2.02 (s, 3H), 1.65-1.77 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 215.0, 158.0, 133.9, 129.4, 113.9, 55.4, 46.4, 38.4, 38.3, 36.7, 29.1, 28.1; IR (neat, cm⁻¹) 2907 (s), 2853 (s), 1690 (s), 1613 (m), 1513 (s); Anal. Calcd for C₂₀H₂₆O₂ (MW 298.42): C, 80.50; H, 8.78. Found: C, 80.45; H, 8.76.

12-Tricosanone, 4n.¹⁸ *S*-Lauroyl-*p*-mercaptotoluene (123 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-undecyl-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (122 mg, 90%). TLC R_f = 0.40 (hexanes:EtOAc = 9:1); Mp 69-70 °C (ethyl ether, lit. {67 °C}¹⁸); ¹H NMR (400 MHz, CDCl₃) δ 2.38 (t, *J* = 7.4 Hz, 4H), 1.50-1.60 (m, 4H), 1.20-1.30 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 212.0, 43.0, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 24.1, 22.9, 14.3; IR (neat, cm⁻¹) 2918 (s), 2849 (s), 1702 (s).

1-Dodecyl-3-(*p*-methoxyphenyl)-1-propanone, 4o. *S*-Lauroyl-*p*-mercaptotoluene (123 mg, 0.40 mmol), CuTC (91 mg, 0.48 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and *B*-(2-(4-methoxyphenyl)ethyl)-9-BBN (0.96 mL, 0.48 mmol) in THF (0.5 mmol/mL) were reacted in THF (4 mL) at 45 °C for 16 h. The product was isolated as a white solid (70 mg, 55%). TLC R_f = 0.42 (hexanes:EtOAc = 9:1); Mp 53.0-54.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.08-7.11 (m, 2H), 6.80-6.83 (m, 2H), 3.78 (s, 3H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.50-1.58 (m, 2H), 1.20-1.31 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.8, 158.1, 133.4, 129.4, 114.0, 55.4, 44.7, 43.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 24.0, 22.9, 14.3; IR (neat, cm⁻¹) 2957 (m), 2918 (s), 2853 (s), 1702 (s), 1517 (m), 1471 (m); Anal. Calcd for C₂₁H₃₄O₂ (MW 318.26): C, 79.19; H, 10.76. Found: C, 78.96; H, 10.87.

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