Palladium-Catalyzed Nucleophilic Benzylic Substitutions of Benzylic Esters

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Supporting Information

General and Materials. NMR spectra were measured with Bruker AVANCE 400 (9.4 T magnet) spectrometer. Short column chromatograhies and medium-pressure liquid chromatographies (MPLC) were performed with silica gel 60 (230–400 mesh, Merck) and C.I.G. pre-packed column CPS-223L-1 (Kusano, Tokyo, Japan), respectively.

All reactions were carried out under nitrogen atmosphere. $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$[1] and benzylic methyl carbonates **3**[2] were prepared according to the literatures. *N*,*O*-Bis(trimethylsilyl)acetamide (BSA), 1,1'-bis(diphenylphosphino)ferrocene (DPPF), and bis(2-diphenylphosphinophenyl)ether were purchased from ACROS Organics, from TCI, and from STREM Chemicals, respectively, and were used without further purification. Other materials were purchased from commercial sources.

General Procedure of Optimization of Reaction Conditions (Table 1). Benzyl methyl carbonate (33 mg, 0.20 mmol), dimethyl malonate (53 mg, 0.30 mmol), tetradecane (20 mg, as an internal standard for GC analysis) were added to a solution of a palladium catalyst precursor (10 μmol), bisphosphine (11 μmol), and a base (0.30 mmol) in a solvent (1.0 ml) at room temperature. The solution was stirred at 80 ˚C, and the reaction was monitored by GC analysis with J&W capillary column DB-1 (0.53 mm $\phi \times$ 15 m, d_f 1.5 μm).

General Procedure of Palladium-Catalyzed Benzylic Alkylation. A benzylic ester **3** (1.0 mmol), a malonate (dimethyl malonate or **6**) (1.1 mmol), and BSA (224 mg, 1.1 mmol) were added to a solution of $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$ (3.4 mg, 10 μmol), DPPF (6.1 mg, 11 μmol), and KOAc (7.5 mg, 75 μmol) in THF (1.0 ml) at room temperature. The solution was stirred at 80 °C until the benzylic ester was consumed or until the reaction stopped. The mixture was evaporated under reduced pressure, and the residue was purified by a flash column chromatography on silica gel (EtOAc/hexane) or by MPLC (EtOAc/hexane) after passing through a short column on silica gel (EtOAc/hexane = 1/3–3/1) to give the corresponding benzylmalonate **4** or **7**.

Dimethyl Benzylmalonate (4a) (Scheme 1). The general procedure was followed with benzyl methyl carbonate (**3a**) (163 mg, 0.98 mmol) and dimethyl malonate (269 mg, 2.04 mmol). The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane) to give **4a** (153 mg, 70%) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.26 (d, J = 7.9 Hz, 2H), 3.68 (t, J = 7.9 Hz, 1H), 3.70 (s, 6H), 7.14–7.31 (m, 5H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 34.7, 52.5, 53.6, 126.8, 128.5, 128.7, 137.7, 169.2.

Dimethyl [(2-Methylphenyl)methyl]malonate (4b) (Scheme 1).[3] The general procedure was followed with methyl (2-methylphenyl)methyl carbonate (**3b**) (179 mg, 1.00 mmol) and dimethyl malonate (270 mg, 2.04 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **4b** (194 mg, 82%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.34 (s, 3H), 3.24 (d, J = 7.8 Hz, 2H), 3.68 (t, J = 7.7 Hz, 1H), 3.70 (s, 6H), 7.07–7.17 (m, 5H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 19.2, 32.0, 52.0, 52.5, 126.0, 126.9, 129.1, 130.4, 135.8, 136.2, 169.3.

Diethyl Benzylmethylmalonate (7a) (Table 2, entry 1).[4] The general procedure was followed with **3a** (165 mg, 0.99 mmol) and diethyl methylmalonate (**6a**) (260 mg, 1.49 mmol). The crude product was purified by by a flash column chromatography on silica gel (EtOAc/hexane) to give **7a** (161 mg, 61%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25 (t, J = 7.4 Hz, 6H), 1.33 (s,

3H), 3.23 (s, 2H), 4.19 (q, J = 7.4 Hz, 4H), 7.09–7.14 (m, 2H), 7.19–7.28 (m, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 19.7, 41.1, 54.8, 61.3, 126.9, 128.1, 130.2, 136.2, 172.0.

Diethyl Benzylphenylmalonate (7b) (Table 2, entry 2). The general procedure was followed with **3a** (166 mg, 1.0 mmol) and diethyl phenylmalonate (**6b**) (260 mg, 1.10 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7b** (309 mg, 95%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (t, J = 7.3 Hz, 6H), 3.61 (s, 2H), 4.20 (q, J = 7.3 Hz, 4H), 6.86–6.91 (m, 2H), 7.10–7.19 (m, 3H), 7.23–7.28 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 42.9, 61.6, 64.2, 126.7, 127.4, 127.76, 127.79, 128.3, 130.4, 136.1, 137.0, 170.1; IR (neat) 1736 cm^{-1}; Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.46; H, 6.77.

Diethyl (*N*-Acetylamino)benzylmalonate (7c) (Table 2, entry 3).[5] The general procedure was followed with **3a** (166 mg, 1.00 mmol) and diethyl (*N*-acetylamino)malonate (**6c**) (234 mg, 1.08 mmol). The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane) to give **7c** (273 mg, 89%): colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30 (t, J = 7.0 Hz, 6H), 2.03 (s, 3H), 3.65 (s, 2H), 4.21–4.33 (m, 4H), 6.53 (br s, 1H), 6.99–7.03 (m, 2H), 7.23–7.29 (m, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 23.0, 37.8, 62.6, 67.2, 127.2, 128.3, 129.9, 135.3, 167.5, 169.0.

Dimethyl Benzylmethoxymalonate (7d) (Table 2, entry 4).[6] The general procedure was followed with **3a** (166 mg, 1.00 mmol) and dimethyl methoxymalonate (**6d**) (181 mg, 1.12 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7d** (224 mg, 88%): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.37 (s, 2H), 3.47 (s, 3H), 3.74 (s, 6H), 7.16–7.29 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 39.0, 52.6, 54.0, 85.8, 127.1, 128.2, 130.0, 134.5, 168.6.

Diethyl (*N*-Acetylamino)[(2-methylphenyl)methyl]malonate (7e) (Table 2, entry 5).[7] The general procedure was followed with **3b** (180 mg, 1.00 mmol) and **6c** (240 mg, 1.10 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **7e** (271 mg, 84%): colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.28 (t, J = 7.1 Hz, 6H), 2.01 (s, 3H), 2.23 (s, 3H), 3.70 (s, 2H), 4.23 (dt, J = 10.8, 7.1 Hz, 2H), 4.29 (dt, J = 10.8, 7.1 Hz, 2H), 6.57 (br s, 1H), 6.94 (d, J = 7.6 Hz, 1H), 7.03–7.16 (m, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 19.3, 23.1, 34.7, 62.6, 67.0, 125.6, 127.1, 130.4, 130.6, 133.5, 137.6, 167.9, 169.2.

Dimethyl Methoxy[(2-methylphenyl)methyl]malonate (7f) (Table 2, entry 6). The general procedure was followed with **3b** (181 mg, 1.00 mmol) and **6d** (180 mg, 1.11 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7f** (247 mg, 92%): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H), 3.41 (s, 2H), 3.44 (s, 3H), 3.75 (s, 6H), 7.06–7.15 (m, 3H), 7.20–7.25 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.0, 35.6, 52.6, 54.2, 86.0, 125.7, 127.0, 129.7, 130.3, 133.2, 137.5, 168.9; IR (neat) 1745 cm^{-1}; Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.24; H, 6.82.

Diethyl [(4-Methoxyphenyl)methyl]phenylmalonate (7g) (Table 2, entry 7).[8] The general procedure was followed with (4-methoxyphenyl)methyl methyl carbonate (**3c**) (196 mg, 1.00 mmol) and **6b** (260 mg, 1.10 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7g** (334 mg, 94%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, J = 7.1 Hz, 6H), 3.54 (s, 2H), 3.75 (s, 3H), 4.20 (q, J = 7.1 Hz, 4H), 6.68 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 7.24–7.29 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 42.2, 55.1, 61.5, 64.4, 113.2, 127.3, 127.8, 128.0, 128.3, 131.4, 137.1, 158.4, 170.2.

Diethyl (*N*-Acetylamino)[(4-methoxyphenyl)methyl]malonate (7h) (Table 2, entry 8).[9] The general procedure was followed with **3c** (196 mg, 1.00 mmol) and **6c** (239 mg, 1.10 mmol). The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane) to give **7h** (338 mg, >99%): colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30 (t, J = 7.4 Hz, 6H), 2.03 (s, 3H), 3.59 (s, 2H), 3.78 (s, 3H), 4.21–4.33 (m, 4H), 6.53 (br s, 1H), 6.79 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9

Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 23.1, 37.0, 55.2, 62.6, 67.3, 113.7, 127.1, 130.8, 158.7, 167.6, 169.0.

Dimethyl Methoxy[(4-methoxyphenyl)methyl]malonate (7i) (Table 2, entry 9). The general procedure was followed with **3c** (197 mg, 1.00 mmol) and **6d** (177 mg, 1.09 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7i** (265 mg, 94%): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.30 (s, 2H), 3.46 (s, 3H), 3.75 (s, 6H), 3.77 (s, 3H), 6.80 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 38.4, 52.6, 54.0, 55.1, 85.9, 113.6, 126.5, 131.0, 158.7, 168.7; IR (neat) 1743 cm^{-1}; Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.49; H, 6.43.

Diethyl [(4-Methylphenyl)methyl]phenylmalonate (7j) (Table 2, entry 10). The general procedure was followed with methyl (4-methylphenyl)methyl carbonate (**3d**) (180 mg, 1.00 mmol) and **6b** (261 mg, 1.10 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7j** (333 mg, 98%): clorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, *J* = 7.2 Hz, 6H), 2.27 (s, 3H), 3.56 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 4H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 21.0, 42.5, 61.5, 64.2, 127.3, 127.8, 128.3, 128.5, 130.3, 132.8, 136.3, 137.0, 170.2; IR (neat) 1736 cm^{-1}; Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.09; H, 7.14.

Diethyl (*N*-Acetylamino)[(4-methylphenyl)methyl]malonate (7k) (Table 2, entry 11).[10] The general procedure was followed with **3d** (181 mg, 1.00 mmol) and **6c** (239 mg, 1.10 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **7k** (287 mg, 89%): colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30 (t, *J* = 7.2 Hz, 6H), 2.03 (s, 3H), 2.31 (s, 3H), 3.60 (s, 2H), 4.26 (dq, *J* = 10.5, 7.2 Hz, 2H), 4.28 (dq, *J* = 10.5, 7.2 Hz, 2H), 6.52 (br s, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 21.1, 23.0, 37.4, 62.6, 67.2, 129.0, 129.7, 132.0, 136.8, 167.6, 169.0.

Diethyl Phenyl[{4-(trifluoromethyl)phenyl}methyl]malonate (7l) (Table 2, entry 12). The general procedure was followed with methyl [4-(trifluoromethyl)phenyl]methyl methyl carbonate (**3e**) (235 mg, 1.00 mmol) and **6b** (262 mg, 1.11 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7l** (308 mg, 78%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (t, *J* = 7.0 Hz, 6H), 3.65 (s, 2H), 4.20 (q, *J* = 7.0 Hz, 4H), 7.01 (d, *J* = 8.1 Hz, 2H), 7.22–7.31 (m, 5H), 7.39 (d, *J* = 8.1 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.8, 42.6, 61.8, 64.1, 124.2 (q, *J* = 272 Hz), 124.6 (q, *J* = 4 Hz), 127.7, 128.0, 128.1, 129.0 (q, *J* = 33 Hz), 130.8, 136.6, 140.3, 169.9; IR (neat) 1736 cm^{-1}; Anal. Calcd for $C_{21}H_{21}O_4F_3$: C, 63.95; H, 5.37. Found: C, 64.02; H, 5.39.

Dimethyl Methoxy[{4-(trifluoromethyl)phenyl}methyl]malonate (7m) (Table 2, entry 13). The general procedure was followed with **3e** (235 mg, 1.00 mmol) and **6d** (177 mg, 1.09 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7i** (266 mg, 83%): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.41 (s, 2H), 3.48 (s, 3H), 3.76 (s, 6H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 39.2, 52.7, 54.3, 85.4, 124.1 (q, *J* = 272 Hz), 125.1 (q, *J* = 4 Hz), 129.4 (q, *J* = 32 Hz), 130.4, 138.8, 168.4; IR (neat) 1736 cm^{-1}; Anal. Calcd for $C_{14}H_{15}O_5F_3$: C, 52.50; H, 4.72. Found: C, 52.57; H, 4.74.

Diethyl [(4-Chlorophenyl)methyl]phenylmalonate (7n) (Table 2, entry 14). The general procedure was followed with (4-chlorophenyl)methyl methyl carbonate (**3f**) (200 mg, 1.00 mmol) and **6b** (259 mg, 1.09 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7n** (285 mg, 79%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, *J* = 7.1 Hz, 6H), 3.56 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 4H), 6.81 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.22–7.30 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 42.3, 61.7, 64.2, 127.5, 127.89, 127.93, 128.2, 131.8, 132.7, 134.6, 136.8, 170.0; IR (neat) 1735 cm^{-1}; Anal. Calcd for $C_{20}H_{21}O_4Cl$: C, 66.57; H, 5.87. Found: C, 66.50; H, 5.88.

Diethyl [{4-(Methoxycarbonyl)phenyl}methyl]phenylmalonate (7o) (Table 2, entry 15). The general procedure was followed with [4-(methoxycarbonyl)phenyl]methyl methyl carbonate (**3g**) (225 mg, 1.00 mmol) and **6b** (261 mg, 1.11 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/2) to give **7o** (331 mg, 86%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, *J* = 7.2 Hz, 6H), 3.64 (s, 2H), 3.88 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 4H), 6.95 (d, *J* = 8.6 Hz, 2H), 7.20–7.29 (m, 5H), 7.81 (d, *J* = 8.6 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 42.9, 52.0, 61.8, 64.1, 127.6, 128.0, 128.2, 128.6, 129.0, 130.5, 136.6, 141.6, 167.0, 169.9; IR (neat) 1724 cm^{-1}; Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.75; H, 6.26.

Diethyl Methyl[(1-naphthyl)methyl]malonate (7p) (Table 2, entry 16).[11] The general procedure was followed with methyl (1-naphthyl)methyl carbonate (**3h**) (219 mg, 1.01 mmol) and **6a** (190 mg, 1.09 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7p** (292 mg, 92%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, J = 7.3 Hz, 6H), 1.33 (s, 3H), 3.77 (s, 2H), 4.13 (dq, *J* = 10.5, 7.3 Hz, 2H), 4.16 (dq, J = 10.5, 7.3 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.42–7.50 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 13.9, 20.2, 36.1, 55.2, 61.3, 124.1, 125.1, 125.4, 125.7, 127.6, 128.2, 128.7, 132.8, 133.0, 133.8

Diethyl Methyl[(2-naphthyl)methyl]malonate (7q) (Table 2, entry 17). The general procedure was followed with methyl (2-naphthyl)methyl carbonate (**3i**) (217 mg, 1.00 mmol) and **6a** (192 mg, 1.10 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **7q** (290 mg, 92%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, *J* = 7.1 Hz, 6H), 1.38 (s, 3H), 3.40 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 4H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.40–7.48 (m, 2H), 7.60 (s, 1H), 7,74 (d, *J* = 8.4 Hz, 1H), 7.73–7.82 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 19.8, 41.2, 54.9, 61.4, 125.6, 125.9, 127.55, 127.58, 127.64, 128.4, 129.0, 132.4, 133.3, 133.8, 172.0; IR (neat) 1732 cm^{-1}; Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.22; H, 7.03.

General Procedure of Palladium-Catalyzed Benzylic Amination. A benzylic ester **3** (1.0 mmol) and an amine **8** (1.1 mmol) were added to a solution of [Pd(η^3-C_3H_5)(cod)]BF_4 (3.4 mg, 10 μmol), DPEphos (5.9 mg, 11 μmol) in DME (1.0 ml) at room temperature. The solution was stirred at 80 °C until the benzylic ester was consumed or until the reaction stopped. After cooling, the mixture was diluted with hexane, and was extracted with 1 *N* HCl aq. The combined aqueous layer was made basic with sat Na_2CO_3 aq, and was extracted with hexane. The combined organic layer was washed with brine, was dried with Na_2SO_4, and evaporated under reduced pressure. The residue passed through a short column on silica gel (EtOAc/hexane) to give the corresponding benzylamine **9**.

Benzyldibutylamine (9a).[12] The general procedure was followed with **3a** (167 mg, 1.00 mmol) and dibutylamine (**8a**) (143 mg, 1.10 mmol), giving **9a** (161 mg, 73%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.87 (t, *J* = 7.4 Hz, 6H), 1.28 (sextet, *J* = 7.4 Hz, 4H), 1.43 (quintet, *J* = 7.4 Hz, 4H), 2.37 (t, *J* = 7.4 Hz, 4H), 3.54 (s, 2H), 7.19–7.35 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 20.6, 29.2, 53.5, 58.6, 126.5, 128.0, 128.8, 140.4.

Dibutyl[(2-methylphenyl)methyl]amine (9b). The general procedure was followed with **3b** (180 mg, 1.00 mmol), **8a** (143 mg, 1.11 mmol), [Pd(η^3-C_3H_5)(cod)]BF_4 (6.9 mg, 20 μmol), DPEphos (11.9 mg, 22 μmol), giving **9b** (186 mg, 80%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.85 (t, *J* = 7.4 Hz, 6H), 1.27 (sextet, *J* = 7.4 Hz, 4H), 1.42 (quintet, *J* = 7.4 Hz, 4H), 2.34 (s, 3H), 2.38 (t, *J* = 7.2 Hz, 4H), 3.49 (s, 2H), 7.09–7.16 (m, 3H), 7.29–7.35 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 19.2, 20.6, 29.2, 53.7, 57.1, 125.4, 126.5, 129.5, 130.0, 137.1, 138.3; Anal. Calcd for $C_{16}H_{27}N$: C, 82.34; H, 11.66; N, 6.00. Found: C, 82.26; H, 11.58; N, 6.02.

Dibutyl[(4-methoxyphenyl)methyl]amine (9c). The general procedure was followed with **3c** (196 mg, 1.00 mmol), **8a** (144 mg, 1.11 mmol), [Pd(η^3-C_3H_5)(cod)]BF_4 (6.9 mg, 20 μmol), DPEphos (11.9 mg, 22 μmol), giving **9c** (223 mg, 90%): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.87 (t, *J* = 7.3 Hz, 6H), 1.29 (sextet, *J* = 7.3 Hz, 4H), 1.44 (quintet, *J* = 7.3 Hz, 4H), 2.39 (t, *J* = 7.3

Hz, 4H), 3.48 (s, 2H), 3.79 (s, 3H), 6.84 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 20.6, 29.2, 53.3, 55.2, 57.8, 113.4, 129.9, 132.2, 158.3; Anal. Calcd for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 76.89; H, 10.89; N, 5.57.

Dibutyl[{4-(trifluoromethyl)phenyl}methyl]amine (9d). The general procedure was followed with **3e** (234 mg, 1.00 mmol), **8a** (145 mg, 1.12 mmol), giving **9d** (252 mg, 88%): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.87 (t, J = 7.3 Hz, 6H), 1.29 (sextet, J = 7.3 Hz, 4H), 1.43 (quintet, J = 7.3 Hz, 4H), 2.39 (t, J = 7.3 Hz, 4H), 3.58 (s, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.1, 20.6, 29.3, 53.7, 58.3, 124.4 (q, J = 272 Hz), 125.0 (q, J = 3 Hz), 128.8, 128.9 (q, J = 32 Hz), 144.9; Anal. Calcd for $C_{16}H_{24}NF_3$: C, 66.87; H, 8.42; N, 4.87. Found: C, 66.87; H, 8.42; N, 4.87.

Methyl 4-(*N*,*N*-dibutylamino)benzoate (9e). The general procedure was followed with **3g** (224 mg, 1.00 mmol), **8a** (144 mg, 1.11 mmol), giving **9e** (266 mg, 96%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.87 (t, J = 7.3 Hz, 6H), 1.29 (sextet, J = 7.3 Hz, 4H), 1.45 (quintet, J = 7.3 Hz, 4H), 2.41 (t, J = 7.3 Hz, 4H), 3.60 (s, 2H), 3.91 (s, 3H), 7.42 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 20.5, 29.1, 52.0, 53.6, 58.4, 128.7, 129.40, 129.44, 130.2, 167.2; IR (neat) 1725 cm^{-1}; Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.78; H, 9.83; N, 5.09.

Dibutyl[(1-naphthyl)methyl]amine (9f). The general procedure was followed with **3h** (213 mg, 0.99 mmol) and **8a** (142 mg, 1.10 mmol), giving **9f** (246 mg, 93%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.83 (t, J = 7.3 Hz, 6H), 1.26 (sextet, J = 7.3 Hz, 4H), 1.48 (quintet, J = 7.3 Hz, 4H), 2.46 (t, J = 7.3 Hz, 4H), 3.96 (s, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.43–7.51 (m, 3H), 7.74 (d, J = 8.1 Hz, 1H), 7.81–7.84 (m, 1H), 8.31 (d, J = 7.9 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.0, 20.7, 29.0, 53,8, 57.4, 124.7, 125.2, 125.38, 125.40, 126.9, 127.4, 128.3, 132.5, 133.7, 136.0; Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10; N, 5.20. Found: C, 84.54; H, 10.16; N, 5.12.

4-[(1-Naphthyl)methyl]morpholine (9g).[13] The general procedure was followed with **3h** (216 mg, 1.00 mmol), morpholine (**8b**) (102 mg, 1.17 mmol), giving **9g** (223 mg, 98%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.51 (t, J = 4.5 Hz, 4H), 3.69 (t, J = 4.5 Hz, 4H), 3.90 (s, 2H), 7.37–7.44 (m, 2H), 7.46–7.55 (m, 2H), 7.78 (d, J = 7.5 Hz, 1H), 7.83–7.87 (m, 1H), 8.31 (d, J = 8.7 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 53.8, 61.6, 67.1, 124.8, 125.0, 125.6, 125.7, 127.5, 128.1, 128.4, 132.5, 133.6, 133.8.

***N*-[(1-Naphthyl)methyl]aniline (9h).**[14] The general procedure was followed with **3h** (216 mg, 1.00 mmol), aniline (**8c**) (102 mg, 1.10 mmol), giving **9h** (220 mg, 94%): pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.01 (br s, 1H), 4.74 (s, 2H), 6.70 (d, J = 7.3 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.49–7.56 (m, 3H), 7.81 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 9.1 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 46.4, 112.7, 117.6, 123.6, 125.5, 125.8, 126.0, 126.3, 128.2, 128.7, 129.3, 131.5, 133.9, 134.3, 148.2.

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