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Supporting Information

Analytical Data

Reaction conditions are briefly summarized below and follow the procedure outlined in the text.

Entry 1

Conditions: Substrate (580 μ mol, 1 equiv), THF (6.0 mL), Ph_3P (1.16 mmol, 2.00 equiv), DEAD (1.16 mmol, 2.00 equiv), NBSH (1.74 mmol, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (2.0 hr), $23\text{ }^\circ\text{C}$ (2.0 hr).

Product: IR (neat, cm^{-1}) 3069 (m), 2964 (s), 2931 (s), 2871 (s), 2833 (s), 1682 (s), 1593 (s), 1470 (s); ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.62 (m, 2H, ArH), 7.49–7.42 (m, 2H, ArH), 6.93 (d, 1H, $J = 2.2$ Hz, ArH), 6.90 (d, 1H, $J = 8.8$ Hz, ArH), 6.65 (dd, 1H, $J = 2.5, 8.8$ Hz, ArH), 3.84 (s, 3H, ArOCH_3), 2.66 (q, 2H, $J = 7.5$ Hz, CH_2CH_3), 2.32 (s, 3H, $\text{CC}(\text{N})\text{CH}_3$), 1.22 (t, 3H, $J = 7.6$ Hz, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 155.9, 138.8, 134.4, 133.3, 131.1, 131.0, 129.0, 121.6, 115.0, 110.9, 101.5, 55.7, 17.2, 14.3, 13.0; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}_2$ [M^+] 327.1026, found 327.1014.

Entry 2

Conditions: Substrate (140 μ mol, 1 equiv), THF (1.5 mL), Ph_3P (280 μ mol, 2.00 equiv), DEAD (280 μ mol, 2.00 equiv), NBSH (420 μ mol, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (2.0 hr), $23\text{ }^\circ\text{C}$ (3.0 hr).

Product: IR (in CH_2Cl_2 , cm^{-1}) 2931 (s), 2866 (s), 1460 (w), 1378 (w), 1034 (w); ^1H NMR (400 MHz, CDCl_3) δ 3.61 (m, 1H, $\text{CH}_2\text{C}(\text{H})(\text{OH})\text{CH}_2$), 2.15–0.64 (m, 41H); ^{13}C NMR (100 MHz, CDCl_3) δ 71.9, 56.6, 56.4, 42.7, 42.1, 40.5, 40.2, 38.3, 36.5, 35.9, 35.6, 35.4, 34.6, 30.6, 28.3, 27.2, 26.5, 24.3, 23.4, 20.9, 19.2, 18.6, 14.6, 12.0; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{41}\text{O}$ [$\text{M}^+ - \text{H}$] 345.3157, found 345.3160.

Entry 3

Conditions: Substrate (2.00 mmol, 1 equiv), NMM (10 mL), Ph_3P (4.00 mmol, 2.00 equiv), DEAD (4.00 mmol, 2.00 equiv), NBSH (6.00 mmol, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (2.0 hr), $23\text{ }^\circ\text{C}$ (1.0 hr).

Product: IR (neat, cm^{-1}) 2930 (s), 2856 (s), 2594 (w), 2065 (w), 1607 (m), 1590 (s), 1515 (s), 1456 (s), 1416 (s), 1377 (m), 1335 (m), 1235 (s), 1191 (m), 1140 (s), 1085 (w), 1029 (s), 942 (w), 849 (m), 804 (s), 764 (s); ^1H NMR (400 MHz, CDCl_3) δ 6.81–6.67 (m, 3H, ArH), 3.86 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 2.55 (t, 2H, $J = 7.7$, ArCH_2CH_2), 1.58 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.34 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.92 (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 148.7, 147.0, 135.5, 120.1, 111.7, 111.2, 55.8, 55.7, 35.2, 33.8, 22.3, 13.9; HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$ [M^+] 194.1307, found 194.1303.

Entry 4

Conditions: Substrate (3.00 mmol, 1 equiv), NMM (13 mL), Ph_3P (6.00 mmol, 2.00 equiv), DEAD (6.00 mmol, 2.00 equiv), NBSH (9.00 mmol, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (2.0 hr), $23\text{ }^\circ\text{C}$ (1.5 hr).

Product: IR (neat, cm^{-1}) 3026 (w), 2985 (s), 2964 (s), 2916 (s), 2879 (s), 2837 (m), 1462 (w), 1434 (w), 1380 (w), 1364 (w), 1302 (w), 1265 (w), 1220 (w), 1204 (w), 960 (w), 886 (w), 803 (w); ^1H NMR (400 MHz, CDCl_3) δ 5.17–5.13 (m, 1H), 2.33 (dt, 1H, $J = 5.49, 8.41$ Hz), 2.28–2.12 (m, 2H), 2.09–2.03 (m, 1H), 2.01–1.84 (m, 3H), 1.26 (s, 3H), 1.12 (d, 1H, $J = 8.42$ Hz), 0.93 (t, 3H, $J = 7.32$ Hz), 0.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 114.5, 46.0, 41.1, 37.9, 31.7, 31.3, 29.7, 26.4, 21.2, 11.8; HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{18}$ [M^+] 150.1408, found 150.1402.

Entry 5

Conditions: Substrate (0.50 mmol, 1 equiv), NMM (3 mL), Ph_3P (1.60 mmol, 3.20 equiv), DEAD (1.50 mmol, 3.00 equiv), NBSH (1.50 mmol, 3.00 equiv), NPA (1.00 mmol, 2.00 equiv), -35°C (6.0 hr), 23°C (2.0 hr).

Product: IR (neat, cm^{-1}) 3027 (m), 2956 (s), 2926 (s), 2855 (s), 1604 (m), 1495 (m), 1454 (s), 1378 (m), 1030 (m), 746 (m), 697 (s); ^1H NMR (300 MHz, CDCl_3) δ 7.36–7.28 (m, 2H, ArH), 7.23–7.20 (m, 3H, ArH), 2.64 (t, 2H, $J = 7.8$ Hz, PhCH_2), 1.71–1.58 (m, 2H, $\text{PhCH}_2\text{CH}_2\text{CH}_2$), 1.42–1.23 (m, 8H, $\text{PhCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 0.92 (t, 3H, $J = 6.6$ Hz, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 142.9, 128.4, 128.2, 125.5, 36.0, 31.8, 31.5, 29.3, 29.2, 22.7, 14.1; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{20}$ [M^+] 176.1565, found 176.1565.

Entry 6

Conditions: Substrate (0.50 mmol, 1 equiv), NMM (3 mL), Ph_3P (1.60 mmol, 3.20 equiv), DEAD (1.50 mmol, 3.00 equiv), NBSH (1.50 mmol, 3.00 equiv), NPA (1.00 mmol, 2.00 equiv), -35°C (6.0 hr), 23°C (2.0 hr).

Product: IR (neat, cm^{-1}) 3030 (w), 2956 (s), 2931 (s), 2857 (s), 1496 (w), 1454 (m), 1361 (m), 1307 (w), 1204 (w), 1102 (s), 1028 (m), 734 (s), 697 (s), 611 (w); ^1H NMR (300 MHz, CDCl_3) δ 7.40–7.27 (m, 5H, ArH), 4.55 (s, 2H, PhCH_2), 3.51 (t, 2H, $J = 6.6$ Hz), 1.76–1.62 (m, 2H), 1.43–1.26 (m, 4H), 0.95 (t, $J = 6.9$ Hz, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 138.7, 128.3, 127.5, 127.4, 72.8, 70.5, 29.4, 28.3, 22.5, 14.0; HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{18}$ [M^+] 178.1358, found 178.1357.

Entry 7

Conditions: Substrate (1.00 mmol, 1 equiv), NMM (5.0 mL), Ph_3P (2.00 mmol, 2.00 equiv), DEAD (2.00 mmol, 2.00 equiv), isoprene (10.0 mmol, 10 equiv, diimide scavenger), NBSH (3.00 mmol, 3.00 equiv), -30°C (2.0 hr), 23°C (1.0 hr).

Product: IR (neat, cm^{-1}) 3064 (s), 3027 (s), 2926 (s), 2855 (s), 1943 (w), 1861 (w), 1824 (w), 1802 (w), 1737 (w), 1641 (s), 1604 (s), 1496 (s), 1454 (s), 1416 (m), 1334 (w), 1074 (w), 1030 (m), 995 (s), 912 (s), 746 (s); ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.35 (m, 2H, ArH), 7.35–7.26 (m, 3H, ArH), 5.97 (ddt, 1H, $J = 17, 10, 6.6$ Hz, CH_2CHCH_2), 5.16 (ddt, 1H, $J = 17, 1.9, 1.9$ Hz, CH_2CHCH_2), 5.11–5.06 (m, 1H, CH_2CHCH_2), 2.81 (t, 2H, $J = 7.3$ Hz, ArCH_2), 2.52–2.44 (m, 2H, $\text{CH}_2\text{CH}_2\text{CHCH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 141.8, 138.0, 128.4, 128.2, 125.8, 114.9, 35.5, 35.4; HRMS (FAB) calcd for $\text{C}_{10}\text{H}_{12}$ [M^+] 132.0938, found 132.0941.

Entry 8

Conditions: Substrate (1.00 mmol, 1 equiv), NMM (11 mL), Ph_3P (2.00 mmol, 2.00 equiv), DEAD (2.00 mmol, 2.00 equiv), NBSH (3.00 mmol, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (2.0 hr), added to refluxing toluene (88 mL) via cold cannula transfer.

Product: GC-LRMS calcd for C_6H_{12} [M^+] 84.09, found 84.15. Identity confirmed by co-injection with authentic samples purchased from Aldrich. Conditions for separation of product: Phenyl-methyl-silicone capillary column, oven temperature ($50\text{ }^\circ\text{C}$), detector temperature ($150\text{ }^\circ\text{C}$), injector temperature ($50\text{ }^\circ\text{C}$), Methylcyclohex-1-ene was used as an internal standard.

Entry 9

Conditions: Substrate ($370\text{ }\mu\text{mol}$, 1 equiv), THF (7.0 mL), Ph_3P ($740\text{ }\mu\text{mol}$, 2.00 equiv), DEAD ($740\text{ }\mu\text{mol}$, 2.00 equiv), NBSH (1.11 mmol, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (3.0 hr), $23\text{ }^\circ\text{C}$ (1.0 hr).

Product: IR (neat, cm^{-1}) 2935 (s, C-H), 2874 (m, C-H), 1650 (s, oxazoline), 1492, 1454, 1218, 983, 951, 757; ^1H NMR (400 MHz, CDCl_3) δ 7.19–7.03 (m, 4H, ArH), 4.22–4.11 (m, 2H, CH_2O), 3.87–3.74 (m, 2H, CH_2N), 2.69 (dd, 1H, $J = 16.8, 7.3\text{ Hz}$, ArCHH), 2.57 (dd, 1H, $J = 16.8, 10.6\text{ Hz}$, ArCHH), 2.44–2.35 (m, 1H, CH_2CHCH), 2.11–2.04 (m, 1H, CH_2CHCH), 1.86–1.70, 1.65–1.49, 1.32–1.19 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.59 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.8, 140.2, 136.5, 129.1, 129.0, 126.5, 125.9, 67.5, 54.8, 50.1, 44.0, 35.1, 32.4, 32.2, 31.1, 27.3, 22.3; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}$ [$\text{M}^+ + \text{H}$] 256.1701, found 256.1697.

Entry 10

Conditions: Substrate ($185\text{ }\mu\text{mol}$, 1 equiv), THF (3.0 mL), Ph_3P ($370\text{ }\mu\text{mol}$, 2.00 equiv), DEAD ($370\text{ }\mu\text{mol}$, 2.00 equiv), NBSH ($554\text{ }\mu\text{mol}$, 3.00 equiv), $-30\text{ }^\circ\text{C}$ (3.0 hr), $23\text{ }^\circ\text{C}$ (1.0 hr), additive, dimethyl sulfide (9.25 mmol, 50.0 equiv).

Product: IR (neat, cm^{-1}) 3333 (s, br, OH), 3060 (w, C-H), 2951 (s, C-H), 2875 (m, C-H), 1646 (s, oxazoline), 1482 (w), 1438 (m), 1378 (w), 1310 (w), 1194 (m), 1120 (s), 1063 (m), 986 (m), 954 (m), 744 (m), 722 (m), 542 (m); ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, 1H, $J = 7.3\text{ Hz}$, ArH), 7.29–7.18 (m, 3H, ArH), 4.65 (dd, 1H, $J = 9.0, 8.0\text{ Hz}$, CHOH), 4.12 (t, 2H, $J = 9.3\text{ Hz}$, CH_2O), 3.76 (t, 2H, $J = 9.3\text{ Hz}$, CH_2N), 3.41 (s, 1H, OH), 2.20–2.04 (m, 2H, CHCH), 1.97–1.54 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.66 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 140.7, 140.2, 127.5, 127.1, 127.0, 125.2, 71.3, 67.5, 54.7, 49.7, 46.5, 43.7, 30.8, 29.4, 28.4, 23.8; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_2$ [$\text{M}^+ + \text{H}$] 272.1650, found 272.1658.