(Supporting Information)

Synthesis of Nitrogen Heterocycles by Intramolecular Michael Type of Amination via Reduction of Imines with Di-*n*-butyliodotin Hydride (*n*-Bu_2SnIH)

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Experimental Section

Analysis. IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All the ^1H and ^{13}C spectra were recorded with a JEOL JNM-GSX-270 (270 and 67 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303 or a Shimadzu GCMS-QP2000A spectrometer. Column chromatography was performed by using Fuji Davison silica gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel.

Materials. Di-*n*-butyltin dihydride (*n*-Bu_2SnH_2) was prepared by the reduction of di-*n*-butyltin dichloride (*n*-Bu_2SnCl_2) with $LiAlH_4$. Di-*n*-butyltin diiodide (*n*-Bu_2SnI_2) was prepared according to described methods (Jones, W. J.; Evans, D. P.; Gulwell, T.; Griffith, D. C. *J. Chem. Soc.*, **1935**, 39). Di-*n*-butyliodotin hydride (*n*-Bu_2SnIH) was synthesized by the redistribution between *n*-Bu_2SnI_2 and *n*-Bu_2SnH_2. THF was freshly distilled from sodium benzophenone ketyl. All reactions were carried out under dry nitrogen.

Representative preparation of bifunctional substrates 5 and 10a. Starting substrate **5** was prepared by the treatment of *o*-phtalaldehyde with the corresponding Wittig reagent. In a dry 300 mL round bottomed flask, triphenylphosphine (26.0 g, 100 mmol) and phenacyl chloride (15.5 g, 100 mmol) were stirred in $CHCl_3$ (150 mL) at room temperature for 3 h. The reaction mixture was poured into 500 mL of ether, and the precipitate was filtered. The obtained salt was dissolved in 10% aqueous Na_2CO_3 (600 mL) solution, and further stirred at rt for 20 h. The ylide was precipitated, which was isolated by filtration and purified by recrystallization from benzene to afford **5** (24.0 g, yield 63%).

To a 300 mL round bottomed flask containing *o*-phtalaldehyde (3.4 g, 25 mmol) in CH_2Cl_2 (50 mL) was added the ylide (10.4 g, 25 mmol) in 50 mL CH_2Cl_2 dropwise at rt for 30 min, and the mixture was stirred at rt for 16 h. Removal of the solvent followed by silica-gel column chromatography (eluent: hexane/EtOAc= 3/1) gave **5** as a yellowish oil (5.2 g, 88% based on ylide). IR (neat) 1660, 1690 cm^{-1}: ^1H NMR ($CDCl_3$) *d* 7.34-8.60 (m, 11H), 10.31 (s, 1H); ^{13}C NMR ($CDCl_3$) d127.1, 128.0, 128.2, 128.5, 128.6, 128.63, 129.9, 132.9, 133.8, 134.1,

137.6, 141.1, 190.4, 191.6.

Compound **10a** was prepared by a similar method from glutaraldehyde with the 1 equiv of the corresponding Wittig reagent. For example, spectral data of **10a** was as follows. IR (neat) 1670, 1724 cm^{-1}: ^1H NMR ($CDCl_3$) *d* 1.85-1.88 (m, 2H), 2.35-2.38 (m, 2H), 2.52 (t, 2H, *J*= 7.3 Hz), 6.88-7.95 (m, 7H), 9.78 (s, 1H); ^{13}C NMR ($CDCl_3$) d20.4, 31.7, 42.9, 128.4, 128.5, 132.7, 137.7, 148.0, 190.4, 201.6.

Representative preparation of nitrogen heterocycle 8a. The reaction to form **8a** is provided as a representative procedure. To a dry argon-filled 10 mL round bottomed flask containing di-*n*-butyltin dihydride (*n*-Bu_2SnH_2, 0.118 g, 0.5 mmol) in THF (1mL) was added di-*n*-butyltin diiodide (*n*-Bu_2SnI_2, 0.243 g, 0.5 mmol) at rt. After stirring at rt for 10 min, di-*n*-butyliodotin hydride (*n*-Bu_2SnIH, 1 mmol) is formed *in situ,* which was confirmed by the change of IR absorption band (v(Sn-H)) from 1837 cm^{-1} to 1846 cm^{-1} (ref. 5a). To the resulting solution were added substrate **5a** (0.236 g, 1 mmol) and aniline **6** (0.091 g, 1 mmol). After the mixture was stirred at 0°C for 2 h, MeOH (2 mL) was added, and volatiles were removed under reduced pressure. The residue was chromatographed on silica-gel column chromatography (FL100DX (Fuji silysia)), eluted with hexane/EtOAc (3/1) to give **8a** (0.20 g, 64%).

Spectral data of for **8a** was as follows. IR(neat) 1675, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.29 (dd, 1H, *J*= 8.8 and 17.6 Hz), 3.66 (dd, 1H, *J*= 2.0 and 17.6 Hz), 4.58 (d, 1H, *J*= 13.2 Hz), 4.76 (dd, 1H, *J*= 2.9 and 13.2 Hz), 5.81-5.86 (m, 1H), 6.71-8.22 (m, 14H); ^{13}C NMR ($CDCl_3$) δ43.0, 53.7, 59.2, 112.2, 116.4, 122.4, 123.1, 127.4, 127.5, 128.1, 128.5, 129.6, 133.2, 136.9, 137.0, 142.3, 145.5, 199.2(d); HRMS calcd for $C_{22}H_{19}ON$ 313.1468: Found 313.1491.

Spectral data of for **8b** was as follows. IR(neat) 1675, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H), 3.28 (dd, 1H, *J*= 8.8 and 17.6 Hz), 3.66 (dd, 1H, *J*= 2.0 and 17.6 Hz), 4.56 (d, 1H, *J*= 13.2 Hz), 4.76 (dd, 1H, *J*= 2.4 and 13.2 Hz), 5.75-5.80 (m, 1H), 6.65-7.89 (m, 13H); ^{13}C NMR ($CDCl_3$) δ20.3, 43.0, 53.9, 59.3, 112.3, 122.4, 123.1, 125.5, 127.3, 127.4, 128.5, 128.8, 130.1, 130.9, 133.2, 136.6, 137.1, 142.4, 143.4, 199.4(d); HRMS calcd for $C_{23}H_{21}ON$ 327.1623: Found 327.1608.

Spectral data of for **8c** was as follows. IR(neat) 1675, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.29 (dd, 1H, *J*= 8.8 and 17.6 Hz), 3.62 (dd, 1H, *J*= 2.0 and 17.6 Hz), 3.768 (s, 3H), 4.53 (d, 1H, *J*= 13.2 Hz), 4.76 (dd, 1H, *J*= 2.5 and 13.2 Hz), 5.77 (d, 1H, *J*= 9.3 Hz), 6.69-7.92 (m, 13H); ^{13}C NMR ($CDCl_3$) δ43.1, 54.3, 55.9, 59.7, 113.1, 115.4, 122,3, 123.1, 127.3, 127.4, 128.1, 129.7, 133.2, 137.1, 137.2, 140.3, 142.5, 151.4, 199.4(d); HRMS calcd for $C_{23}H_{21}O_2N$ 343.1572 Found 343.1579.

Spectral data of for **8d** was as follows.IR(neat) 1675, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30 (dd, 1H, *J*= 8.8 and 17.6 Hz), 3.57 (dd, 1H, *J*= 2.4 and 17.6 Hz), 4.53 (d, 1H, *J*= 13.2 Hz), 4.73 (dd, 1H, *J*= 2.9 and 13.2 Hz), 5.76-5.81 (m, 1H), 6.69-7.93 (m, 13H); ^{13}C NMR ($CDCl_3$) δ42.8, 53.9, 59.4, 113.2, 121.3, 122.4, 123.0, 127.5, 127.6, 128.1, 128.6, 129.3, 133.3, 136.6, 136.9, 142.0, 144.1, 198.0(d); HRMS calcd for $C_{22}H_{18}ONCl$ 347.1077: Found 347.1082.

Spectral data of for **12a** was as follows. IR(neat) 1727, 1677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62-1.91 (m, 6H), 2.93 (dd, 1H, *J*= 2.4 and 16.2 Hz), 3.32 (dd, 1H, *J*= 9.8 and 16.2 Hz), 2.92-3.01 (m, 1H), 3.31-3.40 (m, 1H) 4.51-4.59 (m, 1H), 6.95-7.93 (m, 10H). ^{13}C NMR ($CDCl_3$) δ19.5, 25.5, 28.6, 35.3, 44.5, 52.7, 117.0, 119.4, 127.9, 128.6, 129.1, 133.3, 137.0, 150.4, 199.5; HRMS calcd for $C_{19}H_{21}ON$ 279.1623: Found 279.1620.

Spectral data of for **12b** was as follows. IR(neat) 1727, 1677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60-1.96 (m, 6H), 2.24 (s, 3H), 2.93 (dd, 1H, *J*= 2.9 and 16.2 Hz), 3.23 (dd, 1H, *J*= 9.8 and 16.2 Hz), 2.89-2.98 (m, 1H), 3.19-3.28 (m, 1H), 4.41-4.43 (m, 1H), 6.87-7.82 (m, 9H); ^{13}C NMR ($CDCl_3$) δ19.5, 20.3, 25.7, 28.9, 36.1, 45.6, 53.4, 117.9, 127.9, 128.4, 129.1, 129.6, 132.8, 137.0, 148.3, 199.5; HRMS calcd for $C_{20}H_{23}ON$ 293.1780: Found 293.1775.

Spectral data of for **12c** was as follows. IR(neat) 1727, 1677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61-1.94 (m, 6H), 2.89 (dd, 1H, *J*= 3.4 and 16.1 Hz), 3.29 (dd, 1H, *J*= 9.8 and 16.1 Hz), 2.89-2.98 (m, 1H), 3.27-3.35 (m, 1H) 4.47-4.55 (m, 1H), 6.84-7.84 (m, 9H); ^{13}C NMR ($CDCl_3$) δ19.0, 25.4, 28.6, 35.9, 44.4, 52.7, 118.1, 127.9, 128.5, 129.0, 130.8, 133.1, 137.0, 149.0, 199.2; HRMS calcd for $C_{19}H_{20}ONCl$ 313.1233: Found 313.1235

Spectral data of for **12d** was as follows. IR(neat) 1712, 1673 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54-1.88 (m, 6H), 2.07 (s, 3H), 2.42 (dd, 1H, *J*= 3.4 and 16.6 Hz), 3.23 (dd, 1H, *J*= 9.8 and 16.6 Hz), 2.79-2.88 (m, 1H), 3.24-3.32 (m, 1H) 4.28-4.36 (m, 1H), 6.84 (d, 2H, *J*= 9.3 Hz), 7.18 (d, 2H, *J*= 9.3 Hz); ^{13}C NMR ($CDCl_3$) δ19.2, 25.4, 28.8, 30.7, 41.5, 44.7, 52.0, 118.1, 124.2, 129.1, 149.1, 192.2; HRMS calcd for $C_{14}H_{18}ONCl$ 251.1077: Found 251.1076.