Electronic Supplementary Information

A new method for the generation of indole-2,3-quinodimethanes and 2-(*N*-acylamino)-1,3-dienes. Intramolecular Heck/Diels-Alder cascade starting from acyclic α-phosphono enecarbamates

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General remarks

All reactions were performed using oven-dried glasswares under an atmosphere of argon. Anhydrous THF was purchased from Kanto Chemicals Inc. and distilled from Na/benzophenone immediately prior to use. Anhydrous DMF was purchased from Kanto Chemicals, Co. Inc. and used as received. Anhydrous 1,4-dioxane was purchased from Wako Pure Chemical Industries, Ltd. and used as received. CH_3CN and toluene were distilled from CaH_2 under an atmosphere of argon. HMPA was distilled from CaH_2 under reduced pressure. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure (D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121) and stored under argon at −20 °C. All other chemicals were purchased at the highest commercial grade and used as received. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} pre-coated glass plates (0.25 mm-thickness). Flash column chromatography was carried out using Fuji Silysia silica gel BW-300 (200-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA-500 or INOVA-600 spectrometer. Chemical shift values are reported in δ (ppm) downfield from tetramethylsilane with reference to internal residual solvent [^1H NMR $CHCl_3$ (7.24); C_6HD_5 (7.15); ^{13}C NMR $CDCl_3$ (77.0); C_6D_6 (128.0)]. Coupling constants (*J*) are reported in hertz (Hz). Multiplicities of signals are designated as follows: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. FAB mass spectra were measured on a JEOL JMS-700 spectrometer and ESI-TOF mass spectra were recorded on a Bruker microTOFfocus spectrometer.

Representative experimental procedure

The synthesis of compound **9a,b** is representative. To a solution of imide **8** (117.5 mg, 0.4502 mmol) in THF (8 mL) were added HMPA (0.23 mL, 1.32 mmol) and $(PhO)_2P(O)Cl$ (0.28 mL, 1.35 mmol). The resultant mixture was cooled to −78 °C and treated with KHMDS (0.5 M solution in toluene, 1.80 mL, 0.90 mmol). After being stirred at −78 °C for 0.5 h, the reaction was quenched with 3% NH_4OH and diluted with diethyl ether. The resultant mixture was allowed to warm to room temperature over 20 min and extracted with EtOAc. The organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude α-phosphono enecarbamate thus obtained was used immediately without further purification.

To a solution of the above crude material in DMF (8 mL) were added K_2CO_3 (124.4 mg, 0.900 mmol), $Pd(PPh_3)_4$ (52.0 mg, 0.045 mmol), and methyl acrylate (0.400 mL, 4.44 mmol). The resultant

mixture was heated at 80 °C for 2 h. After cooling to room temperature, the resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (silica gel, 5% EtOAc/hexanes) gave *ca.* 2:1 mixture of **9a,b** (111.6 mg, 75%) as a pale yellow oil.

Spectroscopic data for newly synthesized compounds

Compound **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.26—7.19 (m, 2H), 3.99 (dd, *J* = 17, 2.0 Hz, 1H), 3.39—3.31 (m, 2H), 3.28 (dd, *J* = 17.0, 2.0 Hz, 1H), 3.20 (dd, *J* = 17.0, 7.5 Hz, 1H), 2.92 (m, 1H), 2.89 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 179.5, 150.2, 136.0, 132.9, 128.2, 124.1, 122.7, 117.7, 115.5, 114.3, 84.2, 39.7, 38.7, 28.3, 25.2, 23.3, 20.3; HRMS (FAB) calcd for $C_{20}H_{22}N_2O_4Na$ [$(M+Na)^+$] 377.1477, found 377.1483.

Compound **22**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.5 Hz, 1H), 7.13 (dd, *J* = 8.5, 8.5 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.50 (m, 1H), 3.43 (m, 1H), 3.12—3.00 (m, 3H), 2.92 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 174.7, 153.6, 150.4, 137.3, 130.7, 124.5, 108.6, 103.4, 83.8, 55.2, 52.1, 52.0, 42.2, 41.7, 28.2 (× 2), 26.2; HRMS (ESI) calcd for $C_{22}H_{27}NO_7Na$ [$(M+Na)^+$] 440.1685, found 440.1661.

Compound **23**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.53 (dd, *J* = 17.5, 5.0 Hz, 1H), 3.18—3.04 (m, 4H), 2.75 (m, 1H), 1.64 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 174.5, 155.9, 150.3, 133.4, 130.5, 129.5, 116.3, 114.1, 112.3, 100.6, 83.7, 55.6, 52.2, 52.1, 42.4, 41.2, 28.24, 28.16, 24.0; HRMS (ESI) calcd for $C_{22}H_{27}NO_7Na$ [$(M+Na)^+$] 440.1685, found 440.1682.

Compound **24**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.50 (dd, *J* = 17.5, 5.0 Hz, 1H), 3.17—3.03 (m, 4H), 2.74 (m, 1H), 1.65 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 174.6, 157.5, 150.4, 136.9, 131.1, 122.5, 118.0, 114.2, 111.4, 100.4, 83.7, 55.6, 52.13, 52.11, 42.5, 41.2, 28.22, 28.19, 23.8; HRMS (ESI) calcd for $C_{22}H_{27}NO_7Na$ [$(M+Na)^+$] 440.1685, found 440.1667.

Compound **25**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.50 (dd, *J* = 17.5, 4.5 Hz, 1H), 3.19—3.07 (m, 3H), 3.03 (dd, *J* = 16.0, 5.0 Hz, 1H), 2.75 (m, 1H), 1.64 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 174.3, 150.0, 134.3, 134.1, 129.8, 128.3, 124.0, 117.3, 116.5, 113.7, 84.3, 52.20, 52.17, 42.2, 41.0, 28.2, 27.9, 23.4; HRMS (ESI) calcd for $C_{21}H_{24}{}^{35}ClNO_6Na$ [$(M+Na)^+$] 444.1190, found 444.1182; calcd for $C_{21}H_{24}{}^{37}ClNO_6Na$ [$(M+Na)^+$] 446.1160; found 446.1162.

Compound **26**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.50 (dd, *J* = 14.5, 4.0 Hz, 1H), 3.18-3.03 (m, 4H), 2.75 (m, 1H), 1.65 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 174.4, 149.9, 136.3, 133.3, 129.8, 127.1, 123.1, 118.2, 115.9, 114.0, 84.5, 52.20, 52.17, 42.2, 41.0, 28.1, 27.9, 23.5; HRMS (ESI) calcd for $C_{21}H_{24}{}^{35}ClNO_6Na$ [$(M+Na)^+$] 444.1190, found 444.1173; calcd for $C_{21}H_{24}{}^{37}ClNO_6Na$ [$(M+Na)^+$] 446.1160, found

446.1150.

Compound **27** (*ca.* 12:1 mixture of inseparable diastereomers, data for the major diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.27—7.22 (m, 3H), 7.16—7.13 (m, 3H), 6.89 (dd, *J* = 8.0, 7.5 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 9.5 Hz, 1H), 3.65 (s, 3H), 3.63 (m, 1H), 3.51 (s, 3H), 3.34—3.24 (m, 2H), 3.07 (m, 1H), 1.67 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 173.6, 150.4, 141.2, 136.2, 133.7, 128.5, 128.3, 128.0, 127.2, 123.6, 122.4, 119.7, 117.0, 115.2, 84.1, 52.1, 51.9, 51.7, 44.0, 43.2, 28.3, 28.2; HRMS (FAB) calcd for $C_{27}H_{29}O_6NNa$ [$(M+Na)^+$] 486.1893, found 486.1900.

Compound **28** (*ca.* 1:1 mixture of inseparable diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.0 Hz, 0.5H), 8.08 (d, *J* = 7.0 Hz, 0.5H), 7.51 (d, *J* = 7.5 Hz, 0.5H), 7.41 (d, *J* = 6.5 Hz, 0.5H), 7.35—7.18 (m, 2H), 3.76 (s, 3H), 3.75 (s, 1.5H), 3.72 (s, 1.5H), 3.64—3.47 (m, 2H), 3.31—3.20 (m, 1H), 3.13—3.05 (m, 1H), 2.94 (m, 0.5H), 2.74 (m, 0.5H), 1.654 (s, 4.5H), 1.646 (s, 4.5H), 1.45 (d, *J* = 5.5 Hz, 1.5H), 1.15 (d, *J* = 5.5 Hz, 1.5H); HRMS (FAB) calcd for $C_{22}H_{27}NO_6Na$ [$(M+Na)^+$] 424.1736, found 424.1744.

Compounds **34a,b** (*ca.* 1:1 mixture of inseparable diastereomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.39 (s, 2H), 4.12 (br, 1H), 3.76 (s, 3H), 3.68—3.64 (m, 6H), 3.41 (br, 1H), 3.00—2.79 (m, 2H), 2.71—2.58 (m, 1.5H), 2.49 (m, 0.5H), 2.31 (m, 1H), 2.15 (m, 1H), 1.93 (m, 1H), 1.69—1.41 (m, 13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0 (× 0.5), 174.7 (× 0.5), 174.6 (× 0.5), 174.5 (× 0.5), 159.0, 152.4, 130.5, 129.14 (× 2), 129.13, 113.7, 80.0, 72.49 (× 0.5), 72.47 (× 0.5), 70.0, 58.30 (× 0.5), 58.27 (× 0.5), 55.2, 51.93 (× 0.5), 51.90 (× 0.5), 51.90 (× 0.5), 51.88 (× 0.5), 42.1 (× 0.5), 41.6 (× 0.5), 41.5 (× 0.5), 40.9 (× 0.5), 36.3, 31.7, 28.36 (× 0.5), 28.34 (× 0.5), 28.27 (× 0.5), 27.5 (× 0.5), 26.8 (× 0.5), 26.6 (× 0.5), 24.8 (× 0.5), 24.7 (× 0.5); HRMS (FAB) calcd for $C_{28}H_{39}NO_8Na$ [$(M+Na)^+$] 540.2573, found 540.2578.

Compound **35**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 2H), 4.17 (br, 1H), 3.77 (s, 3H), 3.752 (s, 3H), 3.748 (s, 3H), 3.45—3.30 (m, 3H), 3.00—2.97 (m, 2H), 2.69 (m, 1H), 1.98 (m, 1H), 1.68 (m, 1H), 1.62—1.50 (m, 4H), 1.44 (s, 9H); HRMS (ESI) calcd for $C_{28}H_{37}NO_8Na$ [$(M + Na)^+$] 538.2417, found 538.2423.

Compound **36**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.35—4.00 (brm, 10H), 3.68 (s, 3H), 3.38—3.29 (brm, 2H), 2.62 (brm, 1H), 1.96 (brm, 1H), 1.64 (brm, 1H), 1.56—1.40 (brm, 3H), 1.35 (s, 9H), 1.15 (brm, 6H); HRMS (FAB) calcd for $C_{28}H_{42}N_3O_8$ [$(M+H)^+$] 548.2972, found 548.2975.

Compounds **38a,b** (*ca.* 1:1 mixture of inseparable diastereomers): ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (d. *J* = 7.5 Hz, 1H), 7.21—7.15 (m, 3H), 7.07 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.89 (br, 1H), 4.50—4.43 (m, 2H), 3.92—3.76 (m, 1H), 3.41 (s, 1.5H), 3.37—3.27 (m, 5.5H), 3.17 (s, 1.5H), 3.14 (s, 1.5H), 3.14—3.02 (m, 2H), 2.99—2.91 (m, 1H), 2.56 (br, 0.5H), 2.52 (dd, *J* = 13.5, 11.5 Hz, 0.5H), 2.44 (m, 0.5H), 2.37 (dd, *J* = 13.5, 11.5 Hz, 0.5H), 2.28 (m, 0.5H), 2.20 (m, 0.5H), 2.14—1.98 (m, 1.5H), 1.90 (m, 0.5H), 1.79 (m,

1H), 1.22 (s, 4.5H), 1.19 (s, 4.5H); ^{13}C NMR (125 MHz, C_6D_6) δ 174.7 (× 0.5), 174.6 (× 0.5), 174.2 (× 0.5), 174.0 (× 0.5), 152.5, 140.3, 139.6, 129.7, 128.5, 128.4, 126.3 (× 0.5), 126.2 (× 0.5), 116.3, 96.25 (× 0.5), 96.22 (× 0.5), 79.9, 73.23 (× 0.5), 73.17 (× 0.5), 57.8, 55.35 (× 0.5), 55.31 (× 0.5), 51.6 (× 0.5), 51.54 (× 0.5), 51.50 (× 0.5), 51.48 (× 0.5), 43.2 (× 0.5), 41.61 (× 0.5), 41.58 (× 0.5), 40.8 (× 0.5), 33.0 (× 0.5), 32.9 (× 0.5), 32.7 (× 0.5), 32.0 (× 0.5), 31.3 (× 0.5), 30.7 (× 0.5), 30.3 (× 0.5), 29.4 (× 0.5), 27.97 (× 0.5), 27.96 (× 0.5); HRMS (ESI) calcd for $C_{27}H_{37}NO_8Na$ $[(M+Na)^+]$ 526.2417, found 526.2417.

Compound **39**: ^{1}H NMR (600 MHz, C_6D_6) δ 7.18—7.13 (m, 4H), 7.04 (m, 1H), 4.94 (br, 1H), 4.55 (br, 1H), 4.48 (d, J = 9.5 Hz, 1H), 4.45 (d, J = 9.5 Hz, 1H), 3.75 (br, 1H), 3.47 (s, 3H), 3.39 (s, 3H), 3.16 (s, 3H), 3.14 (m, 1H), 2.92 (m, 1H), 2.85—2.70 (m, 2H), 2.41 (dd, J = 11.5, 10.5 Hz, 1H), 1.94 (dd, J = 14.5, 5.0 Hz, 1H), 1.74 (dd, J = 14.5, 8.5 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6) δ 168.1, 167.4, 153.1, 139.6, 135.0, 129.7, 128.4, 126.3, 125.2, 96.3, 80.3, 73.2, 57.5, 55.4, 51.8, 51.7, 32.4, 32.2, 32.1, 30.9, 27.9; HRMS (ESI) calcd for $C_{27}H_{35}NO_8Na$ $[(M+Na)^+]$ 524.2260, found 524.2265.