Supporting Information for

Catalytic Dicyanative [4+2] Cycloaddition Triggered by Cyanopalladation of Carbon-Carbon Triple Bonds Under Aerobic Conditions

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Experimental Section

General Remarks: All reactions were performed with dry solvents and reagents were purified by the usual methods. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merck silica gel plates (60F-254). Column chromatography was performed with silica gel (Fuji Silysia, PSQ-60B). IR spectra were recorded on a JASCO FT/IR-230 Fourier transform spectrophotometer. NMR spectra were recorded on spectrometers of JEOL-JMN-Alpha-400 and/or JEOL-JMN-ECP-600, operating at 400 and 600 MHz for ^1H NMR and 100 and 150 MHz for ^{13}C NMR with calibration using residual undeuterated solvent as an internal reference. Mass spectra was measured by JEOL JMS-AX 500 (for LR-MS) and JEOL JMS-HX 110 (for HR-MS), respectively.

Typical procedure for Pd-catalyzed dicyanative [4+2] cycloaddition of dienynes: To a solution of diyne (0.3 mmol) in propionitrile (3 mL) were added palladium cyanide (4.8 mg, 0.03 mmol, 10 mol%) and TMS-CN (0.1 mL, 0.75 mmol) at room temperature. The mixture was stirred for 3-24 h at 90 °C under oxygen atmosphere (1 atm). After monitoring the reaction by TLC, the following

direct column chromatography (hexane-AcOEt) gave the cycloadducts.

Colorless solid. ^1H NMR (600 MHz, CDCl_3) δ : 1.80-1.86 (m, 2H), 2.27-2.32 (m, 1H), 2.36 (m, 1H), 2.43 (s, 3H), 2.91 (dd, $J = 9.2, 12.0$ Hz, 1H), 3.02 (dd, $J = 9.6, 10.8$ Hz, 1H), 3.58-3.64 (m, 2H), 3.78 (dd, $J = 7.2, 9.2$ Hz, 1H), 6.87 (s, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 21.7, 28.4, 29.4, 37.6, 42.7, 49.5, 50.6, 109.7, 116.1, 117.7, 127.3, 130.2, 134.0, 144.2, 146.2; IR (ATR) ν : 2894, 2242, 2221, 1597, 1337, 1152, 1091, 1027, 810 cm^{-1} ; LRMS (EI) m/z : 327 (M^+), 257, 243, 229, 215, 210, 172 ($\text{M}^+ - \text{Ts}$), 55 (Ts), 141, 134, 115, 91, 84, 73, 59; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$, 327.1041 (M^+); found, 327.1041; mp. 157-158 $^\circ\text{C}$.

Colorless solid. ^1H NMR (600 MHz, CDCl_3) δ : 1.52-1.57 (m, 1H), 2.06 (ddd, $J = 5.2, 9.4, 13.8$ Hz, 1H), 2.38-2.44 (m, 1H), 2.46 (s, 3H), 2.80-2.86 (m, 1H), 2.99 (dd, $J = 8.0, 10.4$ Hz, 1H), 3.20 (dd, $J = 4.0, 10.8$ Hz, 1H), 3.41 (ddd, $J = 2.4, 5.2, 8.8$ Hz, 1H), 3.53 (dd, $J = 7.2, 10.8$ Hz, 1H), 3.65 (dd, $J = 8.4, 10.4$ Hz, 1H), 6.58 (dd, $J = 2.4, 4.4$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 21.7, 26.9, 27.4, 33.9, 37.8, 50.7, 51.9, 109.6, 115.7, 117.3, 127.5, 130.1, 132.5, 144.6, 146.0; IR (ATR) ν : 2936, 2247, 2222, 1333, 1159, 1094, 816 cm^{-1} ; LRMS (EI) m/z : 327 (M^+), 279, 197, 188, 172 ($\text{M}^+ - \text{Ts}$), 155 (Ts), 143, 139, 128, 115, 91, 77, 59; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$, 327.1041 (M^+); found, 327.1045; mp 152-153 $^\circ\text{C}$.

Colorless crystal. ^1H NMR (600 MHz, CDCl_3) δ : 1.73-1.79 (m, 1H), 1.87-1.95 (m, 1H), 2.05 (dd, $J = 1.2, 1.6$ Hz, 3H), 2.28-2.33 (m, 2H), 2.43 (s, 3H), 2.93 (dd, $J = 8.8, 11.2$ Hz, 1H), 3.05 (dd, $J = 10.0, 10.8$ Hz, 1H), 3.58-3.63 (m, 2H), 3.81 (dd, $J = 7.2, 8.8$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 20.5, 21.5, 28.1, 30.0, 37.7, 46.2, 48.9, 50.9, 103.2, 115.5, 118.2, 127.1, 130.0, 133.9, 144.0, 156.5; IR (ATR) ν : 2923, 2216, 1438, 1333, 1157, 1091, 811, 660 cm^{-1} ; LRMS (EI) m/z : 341 (M^+), 316 ($\text{M}^+ - \text{CN}$), 224,

198, 186 (M^+ -Ts), 161, 155 (Ts), 149, 139, 124, 118, 105, 91, 83, 77, 65, 59; HRMS (EI) calcd for $C_{18}H_{19}N_3O_2S$, 341.1198 (M^+); found, 341.1194; mp 190-191 °C.

Colorless crystal. 1H NMR (600 MHz, $CDCl_3$) δ : 1.25-1.30 (m, 1H), 2.01 (dt, J = 4.8, 13.6 Hz, 1H), 2.05 (d, J = 2.0 Hz, 3H), 2.28-2.34 (m, 1H), 2.46 (s, 3H), 2.74-2.80 (m, 1H), 2.89 (dd, J = 9.6, 10.0 Hz, 1H), 3.16 (dd, J = 2.0, 10.8 Hz, 1H), 3.40-3.46 (m, 1H), 3.55 (dd, J = 6.8, 10.8 Hz, 1H), 3.74 (dd, J = 8.8, 9.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ : 21.7, 22.7, 27.6, 29.1, 34.7, 42.7, 50.3, 52.9, 104.0, 115.3, 117.6, 127.5, 130.2, 132.7, 144.6, 155.3; IR (ATR) ν : 2954, 2251, 2217, 1331, 1159, 1087, 806, 665 cm^{-1} ; LRMS (EI) m/z : 341 (M^+), 316 (M^+ -CN), 224, 186 (M^+ -Ts), 184, 161, 155 (Ts), 149, 139, 132, 124, 118, 105, 91, 83, 77, 65, 59; HRMS (EI) calcd for $C_{18}H_{19}N_3O_2S$, 341.1198 (M^+); found, 341.1190; mp 168-169 °C.

Colorless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 1.89-1.97 (m, 1H), 2.02-2.13 (m, 1H), 2.40-2.44 (m, 1H), 2.45 (s, 3H), 2.63 (dd, J = 9.2, 11.6 Hz, 1H), 2.79-2.87 (m, 1H), 3.17 (dd, J = 10.0, 10.4 Hz, 1H), 3.61 (dd, J = 7.2, 9.2 Hz, 1H), 3.65 (dd, J = 7.2, 9.6 Hz, 1H), 3.77 (ddd, J = 1.2, 2.0, 6.8 Hz, 1H), 7.72-7.35 (m, 4H), 7.43-7.49 (m, 3H), 7.65 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 21.5, 28.1, 31.0, 38.0, 45.5, 50.0, 51.0, 103.7, 116.3, 118.2, 126.9, 127.0, 129.0, 130.0, 133.9, 134.9, 144.0, 158.0; IR (ATR) ν : 3065, 2887, 2217, 1596, 1443, 1320, 1145, 766, 658 cm^{-1} ; LRMS (EI) m/z : 403 (M^+), 378 (M^+ -Me), 248 (M^+ -Ts), 224, 205, 194, 184, 167, 155 (Ts), 149, 139, 128, 115, 105, 91, 77, 65; HRMS (EI) calcd for $C_{23}H_{21}N_3O_2S$, 403.1354 (M^+); found, 403.1361; mp. 194-195 °C.

Colorless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 1.43-1.53 (m, 1H), 2.14 (ddd, J = 4.8, 4.8, 13.6 Hz, 1H), 2.45-2.48 (m, 4H), 2.80 (dd, J = 9.2, 9.6 Hz, 1H), 3.23 (dd, J = 2.0, 10.8 Hz, 1H), 3.27-3.34 (m, 1H), 3.38 (dd, J = 8.8, 9.2 Hz, 1H), 3.57 (ddd, J = 2.0, 5.2, 11.6 Hz, 1H), 3.62 (dd, J = 6.8, 10.8 Hz, 1H), 7.27-7.31 (m, 2H), 7.36

(d, $J = 8.4$ Hz, 2H), 7.43-7.48 (m, 3H), 7.64 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 21.6, 27.5, 30.0, 34.8, 42.3, 50.3, 52.9, 104.7, 115.8, 117.4, 127.2, 127.4, 129.3, 130.0, 130.7, 132.8, 136.1, 144.4, 157.2; IR (ATR) ν : 3056, 2926, 2251, 2214, 1596, 1444, 1341, 1157, 1090, 714, 661 cm^{-1} ; LRMS (EI) m/z : 403 (M^+), 378 ($\text{M}^+ - \text{Me}$), 325, 248 ($\text{M}^+ - \text{Ts}$), 223, 219, 205, 194, 184, 167, 155 (Ts), 139, 121, 115, 105, 91, 77, 65; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$, 403.1354 (M^+); found, 403.1345; mp. 194-195 $^\circ\text{C}$.

Colorless solid. ^1H NMR (600 MHz, CDCl_3) δ : 2.10 (s, 3H), 2.34-2.44 (m, 1H), 2.46 (s, 3H), 2.52-2.57 (m, 1H), 2.84 (dd, $J = 10.0, 10.8$ Hz, 1H), 3.07-3.11 (m, 2H), 3.60 (dd, $J = 6.8, 10.0$ Hz, 1H), 3.68-3.69 (m, 1H), 3.87 (dd, $J = 7.2, 9.2$ Hz, 1H), 7.18-7.20 (m, 2H), 7.35-7.40 (m, 5H), 7.68 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 20.5, 21.7, 39.5, 40.9, 44.6, 48.1, 49.5, 50.6, 104.6, 115.5, 116.2, 127.2, 128.1, 129.0, 129.3, 130.2, 134.1, 136.0, 144.3, 156.0; IR (ATR) ν : 3030, 2902, 2212, 1594, 1333, 1160, 708, 661 cm^{-1} ; LRMS (EI) m/z : 417 (M^+), 262 ($\text{M}^+ - \text{Ts}$), 153, 91, 70, 58; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$, 417.1511 (M^+); found, 417.1513; mp. 237-238 $^\circ\text{C}$.

Colorless solid. ^1H NMR (600 MHz, CDCl_3) δ : 2.20-2.08 (m, 4H), 2.37-2.45 (m, 5H), 2.61-2.66 (m, 1H), 2.74 (ddd, $J = 6.3, 11.2, 17.6$ Hz, 1H), 2.81 (dd, $J = 9.6, 11.2$ Hz, 1H), 3.04 (dd, $J = 8.8, 11.2$ Hz, 1H), 3.32 (dd, $J = 7.2, 10.0$ Hz, 1H), 3.79 (dd, $J = 7.2, 9.2$ Hz, 1H), 7.08-7.09 (m, 2H), 7.26-7.33 (m, 5H), 7.66 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 19.9, 21.7, 37.6, 43.0, 45.7, 47.4, 50.0, 51.4, 108.2, 117.7, 126.8, 127.3, 127.6, 129.1, 129.9, 134.5, 141.4, 143.8, 150.8; IR (ATR) ν : 2925, 2206, 1330, 1159, 1087, 1039, 701, 663 cm^{-1} ; LRMS (EI) m/z : 392 (M^+), 391 ($\text{M}^+ - \text{H}$), 342, 275, 237 ($\text{M}^+ - \text{Ts}$), 224, 201, 184, 172, 155 (Ts), 115, 104, 91, 77, 58; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$, 392.1558 (M^+); found, 392.1540; mp. 205-206 $^\circ\text{C}$.

Colorless solid. ^1H NMR (600 MHz, CDCl_3) δ : 1.65-1.72 (m, 4H), 2.18 (d, $J = 1.4$ Hz, 3H), 2.31 (dd, $J = 10.1, 10.1$ Hz, 1H),

2.48 (s, 3H), 2.85 (dd, $J = 11.8, 12.1$ Hz, 1H), 2.98 (dd, $J = 6.1, 12.1$ Hz, 1H), 3.57 (dd, $J = 6.3, 11.8$ Hz, 1H), 3.58-3.61 (m, 1H), 3.60-3.67 (m, 1H), 7.02-7.03 (m, 2H), 7.34-7.38 (m, 3H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ : 21.3, 21.7, 24.0, 39.3, 40.7, 44.0, 50.7, 55.5, 59.0, 105.1, 115.7, 115.9, 127.3, 128.0, 128.9, 129.2, 130.3, 134.5, 135.9, 144.9, 156.2; IR (ATR) ν : 2987, 2922, 2215, 1596, 1333, 1159, 1085, 961, 820, 709, 662 cm^{-1} ; LRMS (EI) m/z : 431 (M^+), 416 ($\text{M}^+ - \text{Me}$), 346, 286, 276 ($\text{M}^+ - \text{Ts}$), 155, 117, 105, 91, 58; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_2\text{S}$, 431.1667 (M^+); found, 431.1663; mp. 252-253 $^\circ\text{C}$.

Colorless oil. ^1H NMR (400 MHz, CD_3OD) δ : 1.24-1.25 (m, 6H), 1.74-1.81 (m, 3H), 1.90 (t, $J = 8.8$ Hz, 1H), 2.12 (s, 3H), 2.20-2.21 (m, 1H), 2.36 (d, $J = 8.2$ Hz, 1H), 2.63 (dd, $J = 4.4, 8.8$ Hz, 1H), 2.78 (dd, $J = 4.4, 4.4$ Hz, 1H),

3.90 (d, $J = 4.4$ Hz, 1H), 4.14-4.22 (m, 4H); ^1H NMR (400 MHz, CDCl_3) δ : 1.24-1.39 (m, 6H), 1.72-1.81 (m, 2H), 1.89-1.91 (m, 2H), 2.13-2.15 (m, 4H), 2.36 (d, $J = 8.2$ Hz, 2H), 2.70 (ddd, $J = 4.4, 8.8, 16.7$ Hz, 2H), 3.61 (d, $J = 4.4$ Hz, 1H), 4.18-4.20 (m, 4H); ^{13}C NMR (100 MHz, CD_3OD): 14.1, 20.8, 30.5, 30.8, 36.0, 38.3, 38.9, 57.7, 57.8, 62.0, 102.4, 106.3, 118.3, 160.0, 171.5, 172.1; ^{13}C NMR (100 MHz, CDCl_3) δ : 13.0, 19.4, 29.5, 30.4, 35.5, 38.0, 39.0, 57.8, 60.2, 61.6, 102.2, 116.2, 119.3, 160.4, 171.9; IR (ATR) ν : 2985, 2215, 1726; LRMS (EI) m/z : 330 (M^+), 284, 229, 183, 156; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4$, 330.1579 (M^+); found, 330.1580.

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.19-1.22 (m, 6H), 1.61 (t, $J = 8.6$ Hz, 1H), 1.83-1.90 (m, 2H), 2.08-2.10 (m, 1H), 2.43 (d, $J = 8.8$ Hz, 1H), 2.47 (dd, $J = 4.4, 8.8$ Hz, 1H), 2.65-2.68 (m, 1H), 2.76 (dd, $J = 4.4, 8.8$ Hz, 1H), 3.76 (d, $J = 4.4$ Hz, 1H), 4.15-4.19 (m, 4H), 7.35-7.37 (m,

2H), 7.42-7.47 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.1, 30.4, 31.8, 37.3, 38.3, 39.1, 47.0, 57.5, 62.0, 103.3, 116.9, 118.9, 127.3, 128.9, 129.1, 130.1, 135.9, 161.4, 171.4, 172.2; IR (ATR) ν : 2981, 2160, 1725, 1178; LRMS (EI) m/z : 392 (M^+), 346, 318, 291, 272, 245, 218, 205; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_4$,

392.1737 (M^+); found, 392.1736.

Colorless oil. 1H NMR (600 MHz, CD_3OD) δ : 1.20-1.35 (m, 9H), 1.46-1.55 (m, 1H), 1.77 (t, $J = 12.9$ Hz, 1H), 1.85 (t, $J = 12.9$ Hz, 1H), 2.01-2.10 (m, 1H), 2.24-2.32 (m, 1H), 2.62 (dd, $J = 12.9, 6.6$ Hz, 1H), 2.72 (dd, $J = 12.9, 6.9$ Hz, 1H), 3.87-3.91 (m, 1H), 4.13-4.24 (m, 4H), 7.07 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ : 15.8, 13.1, 34.5, 36.1,

36.5, 36.7, 44.4, 44.8, 46.3, 61.57, 61.60, 109.1, 116.66, 116.69, 149.7, 171.8, 171.9; IR (ATR) ν : 2981, 2223, 1723, 1445, 1387, 1367, 1254 cm^{-1} ; LRMS (EI) m/z : 330 (M^+), 284 ($M^+ - EtOH$), 270, 256, 235, 131; HRMS (EI) calcd for $C_{18}H_{22}N_2O_4$, 330.1579 (M^+); found, 330.1579.

Colorless solid. 1H NMR (400 MHz, $CDCl_3$) δ : 1.05 (dd, $J = 11.6, 13.2$ Hz, 1H), 1.51 (dd, $J = 12.4, 12.8$ Hz, 1H), 1.84 (dd, $J = 6.0, 13.2$ Hz, 1H), 2.01 (dd, $J = 6.4, 12.8$ Hz, 1H), 2.04 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 2.33-2.49 (m, 2H), 3.04 (dd, $J = 5.6, 11.2$ Hz, 1H), 3.66-3.69 (m, 1H),

3.94 (s, 2H), 4.04 (s, 2H), 7.28-7.43 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ : 20.7, 20.9, 34.5, 35.8, 39.9, 41.4, 43.9, 46.6, 49.0, 67.7, 67.9, 103.5, 116.2, 116.9, 128.4, 129.0, 137.2, 159.9, 171.0; IR (ATR) ν : 2969, 2250, 2217, 1733, 1719, 1240, 1029, 914, 728, 704 cm^{-1} ; LRMS (EI) m/z : 406 (M^+), 379, 364, 346, 304, 286, 271, 259, 244, 195, 181, 169, 155, 142, 129, 117, 105, 91, 77; HRMS (EI) calcd for $C_{24}H_{26}N_2O_4$, 406.1892 (M^+); found, 406.1895; mp. 95-96 $^{\circ}C$.

White powder. 1H NMR (600 MHz, $CDCl_3$) δ : 1.17 (ddd, $J = 6.4, 13.0, 25.9$ Hz, 1H), 1.75-1.95 (m, 3H), 2.10 (dd, $J = 9.9, 10.4$ Hz, 1H), 2.18-2.26 (m, 2H), 2.28-2.35 (m, 1H), 2.41-2.44 (m, 4H), 2.74 (dd, $J = 9.7, 11.3$ Hz, 1H), 2.81 (ddd, $J = 4.7, 10.7, 16.2$ Hz, 1H), 3.62-3.72 (m, 3H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.4$

Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ : 19.6, 21.7, 27.2, 28.3, 29.0, 29.8, 36.4, 46.6, 51.9, 57.7, 101.8, 115.3, 118.4, 127.6, 130.0, 134.2, 144.1, 162.2; IR (ATR) ν : 2967, 2847, 2217, 1455, 1336, 1163, 1038, 666 cm^{-1} ; LRMS (EI) m/z : 367

(M⁺), 342, 275, 212 (M⁺-Ts), 201, 172, 155 (Ts), 149, 134, 104, 91, 77, 58; HRMS (EI) calcd for C₂₀H₂₁N₃O₂S, 367.1354 (M⁺); found, 367.1351; mp. 243-244 °C.

Colorless solid. ¹H NMR (600 MHz, CDCl₃) δ: 1.16 (ddd, *J* = 6.4, 13.0, 25.6 Hz, 1H), 1.36-1.42 (m, 1H), 1.65-1.74 (m, 1H), 1.79-1.85 (m, 1H), 1.94-2.10 (m, 3H), 2.14-2.18 (m, 1H), 2.21-2.28 (m, 1H), 2.38-2.44 (m, 5H), 2.60 (dd, *J* = 8.5, 10.7 Hz, 1H), 2.69 (ddd, *J* = 4.4, 11.6, 16.0 Hz, 1H), 3.55-3.61 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ: 19.8, 21.7, 23.4, 26.6, 27.7, 28.6, 38.8, 46.5, 52.8, 58.3, 105.7, 118.1, 127.6, 129.9, 134.0, 143.7, 156.6; IR (ATR) ν: 2920, 2847, 2210, 1596, 1336, 1159, 1028, 817, 664 cm⁻¹; LRMS (EI) *m/z*: 342 (M⁺), 341 (M⁺-H), 314, 275, 201, 187, 172, 155 (Ts), 104, 91, 83, 58; HRMS (EI) calcd for C₁₉H₂₂N₂O₂S, 342.1402 (M⁺); found, 342.1401; mp. 169-170 °C

Typical procedure for Pd-catalyzed intermolecular [4+2] cycloaddition using conjugated enynes with MA: To a solution of **3a** (106 mg, 1.0 mmol) and methyl acrylate (400 mg, 5.0 mmol) in propionitrile (1.0 mmol, 1 M) was added Pd(CN)₂ (16.0 mg, 0.1 mmol, 10 mol%) and the mixture was stirred for 24 h at 80 °C. The mixture was purified by direct flash column chromatography (hexane:AcOEt = 3:2) to give inseparable 1:1 diastereomers of **4a** (174.4 mg 60%) as a colorless oil.

The attempted reactions using following substrates: methyl methacrylate, methyl crotonate, ethyl acrylate, 2(5*H*)-furanone, allylbenzene, phenylpropyne, triethylvinylsilane instead of MA or an enyne derived from **3a** by Sonogashira coupling using PhI were all failed to give any trace of the corresponding cycloadducts.

¹H NMR (600 MHz, CDCl₃) δ: 1.10-1.19 (m, 1H X 0.5), 1.26-1.57 (m, 7H X 0.5), 1.74 (m, 2H X 0.5), 1.87-1.94 (m, 2H X 0.5), 1.95-2.01 (m, 2H X 0.5), 2.05-2.12 (m, 1H X 0.5), 2.22-2.29 (m, 1H X 0.5), 2.29-2.36 (m, 2H X 0.5), 2.55-2.61 (m, 1H X 0.5), 2.67-2.72 (m, 2H X 0.5), 2.90 (br d, *J* = 14.0

Hz, 1H X 0.5), 3.49-3.54 (m, 1H X 0.5), 3.60 (s, 3H X 0.5), 3.72 (s, 3H X 0.5), 3.75-3.78 (m, 1H X 0.5); ^{13}C NMR (150 MHz, CDCl_3) δ : 24.1, 25.1, 25.7, 26.7, 28.5, 28.9, 29.5, 30.5, 31.6, 33.7, 34.4, 35.9, 39.2, 40.4, 40.6, 41.2, 52.2, 52.8, 98.9, 99.6, 115.7, 116.2, 117.0, 118.3, 164.3, 164.8, 170.4, 171.9; IR (ATR) ν : 2938, 2215, 1732, 1437, 1236, 1202 cm^{-1} ; LRMS (EI) m/z : 244 (M^+), 217 ($\text{M}^+ - \text{HCN}$), 185, 158; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$, 244.1212 (M^+); found, 244.1202.

^1H NMR (600 MHz, CDCl_3) δ : 1.27-1.94 (m, 10H), 2.07-2.14 (m, 1H X 0.33), 2.27-2.33 (m, 1H X 0.67), 2.48-2.52 (m, 2H X 0.67), 2.53-2.62 (m, 1H X 0.67), 2.72-2.79 (m, 1H X 0.67+0.33), 2.82-2.87 (m, 1H X 0.33), 3.51-3.71 (m, 1H X 0.33), 3.75 (s, 3H X 0.33), 3.81 (s, 3H

X 0.67); ^{13}C NMR (150 MHz, CDCl_3) δ : 23.2, 24.5, 25.6, 27.4, 27.5, 28.0, 28.9, 29.5, 30.2, 30.6, 31.1, 31.8, 32.3, 34.7, 36.0, 39.8, 41.26, 41.33, 42.6, 52.4, 52.9, 101.4, 102.1, 115.9, 116.2, 116.9, 118.2, 165.6, 168.1, 170.3, 171.9; IR (ATR) ν : 2928, 2856, 2214, 1733, 1438, 1206 cm^{-1} ; LRMS (EI) m/z : 258 (M^+), 231 ($\text{M}^+ - \text{HCN}$), 199, 172; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$, 258.1368 (M^+); found, 258.1374.

^1H NMR (400 MHz, CDCl_3) δ : 0.97-1.10 (m, 1H X 0.5), 1.23-1.38 (m, 2H X 0.5), 1.40-1.60 (m, 5H X 0.5), 1.62-1.97 (m, 10H X 0.5), 1.98-2.19 (m, 2H X 0.5), 2.15-2.39 (m, 4H X 0.5), 2.44-2.60 (m, 4H X 0.5), 2.85-2.96 (m, 4H X 0.5), 3.56 (t, $J = 8.8$ Hz, 1H X 0.5),

3.75 (s, 3H X 0.5), 3.82 (s, 3H X 0.5), 3.82-3.85 (m, 1H X 0.5); ^{13}C NMR (100 MHz, CDCl_3) δ : 22.9, 24.0, 24.26, 24.29, 24.7, 25.0, 25.1, 25.8, 26.1, 26.3, 29.0, 30.5, 31.1, 31.7, 32.6, 35.9, 40.2, 40.4, 41.4, 42.9, 52.2, 52.7, 100.3, 101.8, 115.9, 116.27, 116.29, 118.2, 167.3, 170.2, 170.3, 171.8; IR (ATR) ν : 2928, 2214, 1732, 1437, 1201 cm^{-1} ; LRMS (EI) m/z : 272 (M^+), 245 ($\text{M}^+ - \text{HCN}$), 213, 186, 141, 119; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$, 272.1525 (M^+); found, 272.1522.

CCDC 746745 for *cis*-**2b** and 748867 for *trans*-**2b** contain the supplementary crystallographic data which can be available via free charge of www.ccdc.cam.ac.uk/conts/retrieving.html (from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CS21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

Preparation of Substrates for Dicyanative [4+2] Cycloaddition

(S1) (CAS-Reg# 54599-61-0): To the solution of (*E*)-ethyl 3-iodoacrylate (4.5 g, 20.0 mmol) in THF (40.0 mL) was added Et₃N (8.1 g, 80.0 mmol) and trimethylsilylacetylene (3.0 mL, 21.0 mmol) at 0 °C followed by Pd(PPh₃)₂Cl₂ (140.4 mg, 0.2 mmol) and CuI (38.1 mg, 0.2 mmol). The mixture was then warmed to room temperature and stirred for 9 h. The reaction was quenched by sat. NH₄Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 40:1-15:1) to afford **S1** as a colorless oil. Spectral data were identical to the literature data. (Trost, B. M. *et al. J. Am. Chem. Soc.* **2005**, 127, 17921.)

¹H NMR (400 MHz, CDCl₃) δ: 0.22 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 6.24 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H).

(S2) (CAS-Reg# 54599-61-0) Spectral data were identical to the literature data. (Trost, B. M. *et al. J. Am. Chem. Soc.* **2005**, 127, 17921.)

¹H NMR (400 MHz, CDCl₃) δ: 0.24 (s, 9H), 1.33 (t, *J* = 7.2 Hz, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.08 (d, *J* = 11.6 Hz, 1H), 6.16 (d, *J* = 11.6 Hz, 1H).

(S3) (CAS-Reg# 56053-90-8): To a solution of **S2** (850.0 mg, 4.3 mmol) in Et₂O (8.7 mL) was added a 0.97 M solution of DIBAL-H (10.7 mL, 10.4 mmol) in Et₂O at -78 °C and the mixture was stirred for 1 h at the same temperature. Then, the mixture was warmed to rt for over 4 h and quenched with MeOH and sat. Rochell salt at 0 °C. After being stirred for 1 h, the precipitate was filtrated through a Celite[®] pad and the organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 4:1-2:1) to afford **S3** (623.0 mg, 93%) as a colorless oil. Spectral data were identical to the literature data. (Feldman, K. S. *Tetrahedron Lett.* **1982**, 23, 3031.)

^1H NMR (400 MHz, CDCl_3) δ : 0.21 (s, 9H), 1.66 (t, $J = 5.2$ Hz, 1H), 4.43 (dd, $J = 5.2, 5.2$ Hz, 2H), 5.62 (d, $J = 11.6$ Hz, 1H), 6.12 (dt, $J = 5.2, 11.6$ Hz, 1H).

(S4): To a solution of *N*-allyl-4-methylbenzenesulfonamide (97.2 mg, 0.5 mmol) and PPh_3 (241.3 mg, 0.9 mmol) in THF (4.6 mL) was added **S3** (71.1 mg, 0.5 mmol) at rt. The mixture was stirred for 5 min at 0 °C and a 2.2 M solution of DEAD (0.4 mL, 0.8 mmol) in toluene was added. After being stirred for 1 h at rt, H_2O was added and the aqueous layer was extracted with AcOEt (10 mL x3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 6:1-3:1) to afford **S4** (102.1 mg, 64%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ : 0.16 (s, 9H), 2.44 (s, 3H), 3.76 (d, $J = 6.4$ Hz, 2H), 4.04 (dd, $J = 1.6, 6.8$ Hz, 2H), 5.15 (dd, $J = 1.6, 10.0$ Hz, 1H), 5.20 (dd, $J = 1.6, 16.8$ Hz, 1H), 5.59 (dt, $J = 1.6, 10.8$ Hz, 1H), 5.67 (ddt, $J = 6.4, 10.0, 16.8$ Hz, 1H), 5.79 (dt, $J = 6.8, 10.8$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : -0.3, 21.4, 46.0, 50.0, 100.2, 101.1, 112.8, 119.0, 127.1, 129.6, 132.3, 137.0, 138.4, 143.3; IR (ATR) ν : 2960, 2148, 1597, 1344, 1156, 1091, 974, 839, 659 cm^{-1} ; LRMS (EI) m/z : 347 (M^+), 332 ($\text{M}^+ - \text{Me}$), 282, 192 ($\text{M}^+ - \text{Ts}$), 176, 155 (Ts), 149, 139, 118, 109, 91, 83, 73, 68; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_2\text{SSi}$, 347.1375 (M^+); found, 347.1365.

(1d) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 2.44 (s, 3H), 3.13 (d, $J = 1.6$ Hz, 1H), 3.78 (d, $J = 6.4$ Hz, 2H), 4.04 (d, $J = 6.4$ Hz, 2H), 5.15 (dd, $J = 1.2, 10.4$ Hz, 1H), 5.20 (d, $J = 1.2, 17.2$ Hz, 1H), 5.56 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.66 (ddt, $J = 6.4, 10.4, 17.2$ Hz, 1H), 5.89 (dt, $J = 6.4, 10.8$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 21.4, 46.0, 50.3, 78.8, 83.6, 111.4, 119.2, 127.1, 129.6, 132.2, 136.8, 139.7, 143.3; IR (ATR) ν : 3272, 2923, 1729, 1597, 1440, 1339, 1154, 1090, 990, 929, 813, 659 cm^{-1} ; LRMS (EI) m/z : 275 (M^+), 274

(M⁺-H), 248 (M⁺-vinyl), 222, 210 (M⁺-CH₂CH=CHC≡CH), 196, 170, 155 (Ts), 139, 120 (M⁺-Ts), 105, 91, 77, 63; HRMS (EI) calcd for C₁₅H₁₇NO₂S, 275.0980 (M⁺); found, 275.0982.

(S5) (CAS-Reg. # 211060-30-9): To a solution of Pd(OAc)₂ (33.7 mg, 0.15 mmol) and TDMPP (66.4 mg, 0.15) in THF (5.0 mL) was added ethyl 2-butynoate (560.7 mg, 5.0 mmol) and trimethylsilyl acetylene (501.0 mg, 5.1 mmol) at 0 °C. The solution was stirred at rt for 3 h, then the solvent was evaporated. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 60:1-40:1) to afford **S5** (950.7 mg, 91%). Spectral data were identical to the literature data. (Carreira, E. M. *et al. Org. Lett.* **2005**, 7, 4249.)

¹H NMR (400 MHz, CDCl₃) δ: 0.21 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.28 (d, *J* = 1.2 Hz, 3H), 4.16 (q, *J* = 7.2 Hz, 2H), 6.10 (q, *J* = 1.2 Hz, 1H).

(S6) Orange oil. ¹H NMR (400 MHz, CDCl₃) δ: 0.20 (s, 9H), 1.31 (t, *J* = 6.8 Hz, 3H), 4.06 (q, *J* = 6.8 Hz, 2H), 6.33 (s, 1H), 7.33-7.36 (m, 3H), 7.40-7.44 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 0.0, 14.3, 60.7, 101.3, 105.3, 125.9, 128.1, 128.9, 129.2, 136.4, 138.1, 165.6; IR (ATR) ν: 2960, 2141, 1721, 1595, 1368, 1157, 1083, 1031, 838, 758, 694 cm⁻¹; LRMS (EI) *m/z*: 272 (M⁺), 257 (M⁺-Me), 243 (M⁺-Et), 229 (M⁺-CO₂), 213, 183, 169, 99, 84, 73, 59; HRMS (EI) calcd for C₁₆H₂₀O₂Si, 272.1233 (M⁺); found, 272.1238.

(S7) (CAS-Reg# 57514-97-1): Spectral data were identical to the literature data. (Trost, B. M. *et al. J. Am. Chem. Soc.* **2005**, 127, 17921.)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 0.21 (s, 9H), 1.39 (t, *J* = 5.6 Hz, 1H), 4.23 (dd, *J* = 4.8, 5.6 Hz, 2H), 5.80 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 4.8, 16.0 Hz, 1H).

(S8) (CAS-Reg. # 121635-27-6): Spectral data were identical to the literature data. (Roush, W. R.; Brown, B. B. *J. Am. Chem. Soc.* **1993**, 115, 2268.)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 0.19 (s, 9H), 1.25

(t, $J = 6.4$ Hz, 1H), 1.83 (d, $J = 1.2$ Hz, 3H), 4.22 (dd, $J = 6.4, 6.8$ Hz, 2H), 6.05 (tq, $J = 1.2, 6.8$ Hz, 1H).

(S9) Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.20 (s, 9H), 1.39 (t, $J = 6.0$ Hz, 1H), 4.30 (dd, $J = 6.0, 6.4$ Hz, 2H), 6.36 (t, $J = 6.4$ Hz, 1H), 7.29-7.39 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ : 0.0, 59.8, 94.1, 105.9, 125.8, 128.1, 128.3, 128.7,

136.4, 138.1; IR (ATR) ν : 3337, 2958, 2141, 1733, 1248, 1012, 836, 757, 697 cm^{-1} ; LRMS (EI) m/z : 230 (M^+), 215 ($\text{M}^+ - \text{Me}$), 197, 185, 157, 141, 115, 91, 84, 73, 59; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{OSi}$, 230.1127 (M^+); found, 230.1136.

(S10) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.18 (s, 9H), 2.43 (s, 3H), 3.79 (d, $J = 6.8$ Hz, 2H), 3.82 (d, $J = 6.4$ Hz, 2H), 5.12-5.17 (m, 2H), 5.53-5.63 (m, 2H), 5.93 (dt, $J = 6.4, 16.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J =$

8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 0.0, 21.7, 48.3, 49.9, 95.8, 102.5, 113.8, 119.6, 127.3, 129.8, 129.9, 132.5, 137.2, 138.6, 143.5; IR (ATR) ν : 2959, 2173, 2130, 1733, 1341, 1248, 1156, 1087, 839, 753, 657 cm^{-1} ; LRMS (EI) m/z : 347 (M^+), 332 ($\text{M}^+ - \text{Me}$), 282, 236, 222, 210, 192 ($\text{M}^+ - \text{Ts}$), 176, 155 (Ts), 149, 139, 118, 109, 91, 73, 68; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_2\text{SSi}$, 347.1375 (M^+); found, 347.1383.

(S11) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.17 (s, 9H), 1.75 (s, 3H), 2.43 (s, 3H), 3.78 (d, $J = 6.4$ Hz, 2H), 3.85 (d, $J = 7.2$ Hz, 2H), 5.14-5.18 (m, 2H), 5.59-5.69 (m, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H); ^{13}C

NMR (100 MHz, CDCl_3) δ : 0.0, 17.3, 21.5, 44.1, 49.9, 92.1, 107.0, 119.1, 121.8, 127.2, 129.7, 132.3, 132.7, 137.1, 143.3; IR (ATR) ν : 2959, 2143, 1340, 1156, 1091, 838, 754, 658 cm^{-1} ; LRMS (EI) m/z : 361 (M^+), 346 ($\text{M}^+ - \text{Me}$), 289, 282, 206 ($\text{M}^+ - \text{Ts}$), 190, 164, 155 (Ts), 149, 132, 97, 91, 73, 68; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{SSi}$, 361.1532 (M^+); found, 361.1526.

(S12) Orange oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.18 (s, 9H), 2.42 (s, 3H), 3.70 (d, $J = 6.8$ Hz, 2H), 3.92 (d, $J = 6.8$ Hz, 2H), 4.85 (dd, $J = 1.2, 16.8$ Hz, 1H), 4.93 (dd, $J = 1.2, 10.0$ Hz, 1H), 5.47 (ddt, $J = 6.8, 10.0, 16.8$ Hz, 1H), 6.00 (t, $J = 6.8$ Hz, 1H), 7.23-7.36 (m, 7H), 7.64 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 0.0, 21.6, 44.9, 50.2, 94.1, 105.5, 119.4, 127.1, 127.3, 128.1, 128.3, 128.7, 129.8, 132.2, 134.5, 136.1, 137.1, 143.4; IR (ATR) ν : 2957, 2143, 1733, 1327, 1248, 1154, 1089, 919, 841, 758, 661 cm^{-1} ; LRMS (EI) m/z : 423 (M^+), 408 ($\text{M}^+ - \text{Me}$), 268 ($\text{M}^+ - \text{Ts}$), 224, 194, 155 (Ts), 149, 140, 105, 91, 73, 68; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{SSi}$, 423.1688 (M^+); found, 423.1697.

(S13) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.17 (s, 9H), 1.73 (s, 3H), 2.44 (s, 3H), 3.89 (d, $J = 7.2$ Hz, 2H), 3.93 (d, $J = 6.4$ Hz, 2H), 5.70 (t, $J = 7.2$ Hz, 1H), 5.96 (dt, $J = 6.4, 15.6$ Hz, 1H), 6.43 (d, $J = 15.6$ Hz, 1H), 7.25-7.33 (m, 7H), 7.72 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 0.0, 17.4, 21.6, 44.3, 49.4, 92.3, 107.0, 122.0, 123.8, 126.5, 127.3, 128.0, 128.6, 129.8, 132.4, 134.2, 136.2, 137.2, 143.4; IR (ATR) ν : 3028, 2958, 2142, 1597, 1334, 1248, 1156, 1089, 838, 754, 732, 656 cm^{-1} ; LRMS (EI) m/z : 437 (M^+), 421 ($\text{M}^+ - \text{Me} - \text{H}$), 334, 298, 282 ($\text{M}^+ - \text{Ts}$), 256, 226, 208, 184, 155 (Ts), 144, 125, 117 ($\text{CH}_2\text{CH}=\text{CHPh}$), 105, 91, 73; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_2\text{SSi}$, 437.1845 (M^+); found, 437.1850.

(1a) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 2.44 (s, 3H), 2.88 (d, $J = 2.0$ Hz, 1H), 3.79 (d, $J = 6.4$ Hz, 2H), 3.84 (dd, $J = 1.6, 6.4$ Hz, 2H), 5.12-5.18 (m, 2H), 5.53-5.65 (m, 2H), 5.99 (dt, $J = 6.4, 15.6$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 21.4, 48.1, 49.8, 78.3, 80.9, 112.5, 119.3, 127.0, 129.7, 132.2, 136.8, 139.3, 143.4; IR (ATR) ν : 3275, 2922, 1597, 1336, 1154, 1089, 931, 813, 748, 658 cm^{-1} ; LRMS (EI) m/z : 275 (M^+), 222, 210, ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CHC}\equiv\text{CH}$), 196, 170, 155 (Ts), 139, 120 ($\text{M}^+ - \text{Ts}$), 105, 91, 77, 65; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$, 275.0980 (M^+); found, 275.0977.

(1b) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.77 (s, 3H), 2.43 (s, 3H), 2.81 (s, 1H), 3.78 (d, $J = 6.0$ Hz, 2H), 3.87 (d, $J = 6.8$ Hz, 2H), 5.14-5.19 (m, 2H), 5.59-5.72 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.1, 21.3, 43.9, 49.8, 75.4, 85.3, 118.9, 120.7, 127.0, 129.6, 132.5, 132.7, 136.9, 143.3; IR (ATR) ν : 3280, 2923, 1337, 1154, 1090, 988, 930, 908, 814, 744, 658 cm^{-1} ; LRMS (EI) m/z : 289 (M^+), 274 ($\text{M}^+ - \text{Me}$), 250, 224, 210, 184, 155 (Ts), 139, 134 ($\text{M}^+ - \text{Ts}$), 118, 107, 91, 79, 65; HRMS(EI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$, 289.1136 (M^+); found, 289.1130.

(1c) Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 2.43 (s, 3H), 2.97 (s, 1H), 3.70 (d, $J = 6.8$ Hz, 2H), 3.94 (d, $J = 6.8$ Hz, 2H), 4.88 (dd, $J = 1.2, 16.8$ Hz, 1H), 4.95 (dd, $J = 0.8, 10.0$ Hz, 1H), 5.49 (ddt, $J = 6.8, 10.0, 16.8$ Hz, 1H), 6.05 (t, $J = 6.8$ Hz, 1H), 7.24-7.37 (m, 7H), 7.63 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 21.3, 44.8, 50.1, 77.1, 84.0, 119.1, 125.8, 127.0, 128.1, 128.2, 128.4, 129.6, 132.0, 135.0, 135.6, 136.7, 143.3; IR (ATR) ν : 3280, 3058, 2922, 1492, 1443, 1339, 1154, 1090, 911, 814, 755, 658 cm^{-1} ; LRMS (EI) m/z : 315 (M^+), 286, 224, 196 ($\text{M}^+ - \text{Ts}$), 183, 167, 155 (Ts), 141, 128, 115, 105, 91, 68; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{S}$, 351.1293 (M^+); found, 351.1293.

(1e) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.74 (d, $J = 1.2$ Hz, 3H), 2.44 (s, 3H), 2.82 (s, 1H), 3.91-3.95 (m, 4H), 5.73 (tq, $J = 1.2, 6.8$ Hz, 1H), 5.96 (dt, $J = 6.8, 15.6$ Hz, 1H), 6.43 (d, $J = 15.6$ Hz, 1H), 7.23-7.33 (m, 7 H), 7.72 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.2, 21.4, 44.0, 49.3, 75.5, 85.3, 120.9, 123.5, 126.3, 127.1, 127.9, 128.5, 129.7, 132.7, 134.1, 135.9, 137.0, 143.4; IR (ATR) ν : 3278, 3028, 2923, 1336, 1154, 1089, 968, 910, 728 cm^{-1} ; LRMS (EI) m/z : 365 (M^+), 315, 299, 261, 225, 209 ($\text{M}^+ - \text{Ts} - \text{H}$), 184, 155 (Ts), 144, 132, 117, 106, 91, 77, 58; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$, 365.1449 (M^+); found, 365.1452.

(S14): To a solution of **S5** (841.0 mg, 4.0 mmol) in THF (8.0 mL) was added $\text{MeNH}(\text{OMe}) \cdot \text{HCl}$ (780.0 mg, 8.0 mmol) and the mixture was cooled to -10°C .

Then, a 2.0 M solution of *i*PrMgBr in THF (9.0 mL) was slowly added to the solution. After being stirred for 1 h at -10 °C, the reaction was quenched by sat. NH₄Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 4:1) to afford **S14** (739.0 mg, 82%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ: 0.22 (s, 9H), 2.26 (s, 3H),

3.22 (s, 3H), 3.70 (s, 3H), 6.56 (s, 1H); ¹³C NMR (100 MHz,

CDCl₃) δ: 0.0, 19.8, 32.3, 61.9, 97.5, 107.5, 123.4, 134.9,

166.9; IR (ATR) ν: 2960, 2140, 1647, 1605, 1367, 1249,

1176, 997, 837, 758 cm⁻¹; LRMS (EI) *m/z*: 225 (M⁺), 210

(M⁺-Me), 165, 144, 123, 107, 97, 83, 58; HRMS (EI) calcd for C₁₁H₁₉NO₂Si, 225.1185 (M⁺); found, 225.1189.

(S15): To a solution of **S14** (730.0 mg, 3.2 mmol) in THF (6.5 mL) was added a 1.09 M solution of MeLi in THF (3.3 mL) at -10 °C. After 1 h, additional MeLi (3.3 mL) was added. After being stirred for 30 min, the reaction was quenched by sat. NH₄Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was dissolved in MeOH (10.8 mL) and CeCl₃ · 7H₂O (1.8 g, 4.9 mmol) was added followed by NaBH₄ (134.8 mg, 3.6 mmol) at 0 °C. After being stirred for 45 min, the reaction was quenched by water and the aqueous layer was extracted with CH₂Cl₂ (10 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 4:1-3:1) to afford **S15** (380.5 mg, 64%, 2 steps) as an orange oil.

¹H NMR (400 MHz, CDCl₃) δ: 0.19 (s, 9H), 1.26 (d, *J* = 6.4 Hz,

3H), 1.39 (d, *J* = 4.0 Hz, 1H), 1.84 (d, *J* = 1.2 Hz, 3H),

4.55-4.63 (m, 1H), 5.90 (dq, *J* = 1.2, 8.4 Hz, 1H); ¹³C NMR

(100 MHz, CDCl₃) δ: 0.0, 17.4, 22.9, 64.5, 92.0, 107.5, 119.1,

141.6; IR (ATR) ν: 3365, 2963, 2143, 1372, 1248, 1056, 836,

757 cm⁻¹; LRMS (EI) *m/z*: 182 (M⁺), 181 (M⁺-H), 167 (M⁺-Me), 165, 154, 139, 125, 109, 97, 83, 75, 73, 58; HRMS (EI) calcd for C₁₀H₁₈OSi, 182.1127 (M⁺); found, 182.1132.

(**S16**) Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 0.16 (s, 9H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.77 (d, *J* = 1.2 Hz, 3H), 2.40 (s, 3H), 3.96 (d, *J* = 6.4 Hz, 2H), 4.80 (dq, *J* = 6.8, 8.8 Hz, 1H), 5.76 (dq, *J* = 1.2, 8.8 Hz, 1H), 6.11 (dt, *J* = 6.4,

16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 7.23-7.31 (m, 7H), 7.69 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 0.0, 17.5, 20.0, 21.5, 46.5, 51.3, 92.2, 107.2, 121.0, 126.5, 127.1, 127.3, 127.7, 128.6, 129.5, 132.3, 136.5, 136.9, 138.0, 143.1; IR (ATR) ν: 3028, 2960, 2142, 1597, 1337, 1248, 1152, 967, 839, 754 cm⁻¹; LRMS (EI) *m/z*: 451 (M⁺), 435, 312, 296 (M⁺-Ts), 270, 222, 213, 181, 165, 149, 117, 91, 73, 56; HRMS (EI) calcd for C₂₆H₃₃NO₂SSi, 451.2001 (M⁺); found, 451.2002.

(**1f**) Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 1.22 (d, *J* = 6.8 Hz, 3H), 1.78 (d, *J* = 1.2 Hz, 3H), 2.41 (s, 3H), 2.79 (s, 1H), 3.97 (d, *J* = 6.4 Hz, 2H), 4.82 (dq, *J* = 6.8, 8.8 Hz, 1H), 5.80 (dq, *J* = 1.2, 8.8 Hz, 1H), 6.11 (dt, *J* = 6.4, 16.0 Hz, 1H), 6.48 (d, *J* =

16.0 Hz, 1H), 7.24-7.27 (m, 3H), 7.31-7.32 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 17.4, 20.0, 21.4, 46.4, 51.1, 75.4, 85.6, 119.9, 126.3, 126.9, 127.2, 127.7, 128.5, 129.5, 132.3, 136.4, 137.2, 137.8, 143.1; IR (ATR) ν: 3279, 3026, 1597, 1447, 1331, 1152, 1086, 965, 885, 812, 748, 655 cm⁻¹; LRMS (EI) *m/z*: 379 (M⁺), 364 (M⁺-Me), 314, 286 (TsNCH₂CH=CHPh), 276, 240, 224 (M⁺-Ts), 208, 181, 167, 155 (Ts), 139, 130, 115, 105, 93, 77, 65, 56; HRMS (EI) calcd for C₂₃H₂₅NO₂S, 379.1606 (M⁺); found, 379.1595.

(**S17**) (CAS-Reg# 84214-06-2) To a solution of **S7** (914 mg, 5.0 mmol) in CH₂Cl₂ (50 mL), PPh₃ (2.2 g, 7.52 mmol) and NBS (1.3 g, 7.52 mmol) were added and the mixture was stirred for 6 h at room temperature. Then, the solvent was evaporated and the residue was purified by flash column chromatography (*n*-hexane only) to afford **S17** (978 mg, 91%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ : 0.16 (s, 9H), 3.97 (d, $J = 7.6$ Hz, 2H), 5.76 (d, $J = 15.6$ Hz, 1H), 6.29 (dt, $J = 7.6, 15.6$ Hz, 1H).

(S18) (CAS-Reg# 185946-23-0): Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.17 (s, 9H), 1.87 (s, 3H), 4.01 (d, $J = 8.0$ Hz, 2H), 6.13 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : -0.2, 16.9, 27.2, 94.6, 106.5, 123.9, 132.2.

(S19) (CAS-Reg# 337509-49-6): Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 0.21 (s, 9H), 4.06 (d, $J = 8.8$ Hz, 2H), 6.42 (t, $J = 8.8$ Hz, 1H), 7.33-7.47 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ : -0.3, 28.9, 96.3, 105.2, 126.3, 127.9, 128.0, 128.3, 128.3, 128.4, 128.5, 133.3.

(S20) To a solution of diethyl 2-cinnamylmalonate (700 mg, 2.5 mmol) in THF (8.4 mL) was added NaH (78.9 mg, 3.3 mmol) at 0 °C. After being stirred for 30 min, **S18** (596.6 mg, 2.6 mmol) was slowly added and the mixture was stirred for 1 h at room temperature. The reaction was quenched by NH_4Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in MeOH (6.1 mL) and K_2CO_3 (381.0 mg, 2.8 mmol) was added. The mixture was stirred at room temperature for 1 h. Then, H_2O was added and the aqueous layer was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 10:1) to afford **S20** (651.4 mg, 78%, 2 steps) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ : 1.21-1.28 (m, 6H), 1.80 (s, 3H), 2.73 (d, $J = 8.0$ Hz, 2H), 2.79 (d, $J = 8.0$ Hz, 2H), 4.17-4.25 (m, 4H), 5.83 (t, $J = 8.0$ Hz, 1H), 6.00 (dt, $J = 8.0, 16.0$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 7.21-7.30 (m, 5H);

^{13}C NMR (100 MHz, CDCl_3) δ : 14.1, 17.4, 31.6, 36.4, 57.4, 61.5, 74.5, 86.2,

120.3, 123.6, 126.2, 127.4, 128.5, 132.6, 134.2, 137.0, 170.6; IR (ATR) ν : 3281, 2980, 2934, 1721, 1598 cm^{-1} ; LRMS (EI) m/z : 354 (M^+), 280 ($\text{M}^+ - \text{CO}_2\text{Et}$), 229, 207, 173, 127, 117, 105, 91, 83, 77; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$, 354.1831 (M^+); found, 354.1831.

(1h) To a solution of diethyl 2-allylmalonate (165.5 mg, 0.8 mmol) in DMF (2.5 mL) was added NaH (21.6 mg, 0.9 mmol) at 0 °C and the mixture was stirred for 30 min.

Then, **S19** (218.0 mg, 0.8 mmol) was added and the mixture was stirred for 3 h at 0 °C. The reaction was quenched by water and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 20:1) to afford **1h** (177 mg, 69%) as a colorless oil.

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.26 (t, J = 7.2 Hz, 6H), 2.60 (d, J = 8.8 Hz, 2H), 2.84 (d, J = 8.8 Hz, 1H), 2.93 (s, 1H), 4.15-4.20 (m, 4H), 5.13-5.85 (m, 2H), 5.30-5.80 (m, 1H), 6.12 (t, J = 8.8 Hz, 1H), 7.27-7.35 (m, 3H), 7.56 (d, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.1, 34.3, 37.6, 57.5, 61.4, 80.4, 83.9, 119.4, 126.1, 127.9, 128.3, 132.2, 133.3, 137.4, 170.6; IR (ATR) ν : 3273, 2981, 1725, 1188; LRMS (EI) m/z : 340 (M^+), 299, 266, 253, 218, 193, 139, 115; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$ 340.1674; found, 340.1673.

(1i) Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.24 (t, J = 7.2 Hz, 6H), 1.65 (d, J = 7.2 Hz, 3H), 2.57 (d, J = 7.2 Hz, 2H), 2.78 (d, J = 7.2 Hz, 2H), 2.82 (s, 1H), 4.18 (q, J = 7.2

Hz, 4H), 5.24 (dt, J = 7.2, 14.8 Hz, 1H), 5.31-5.56 (m, 2H), 6.10 (dt, J = 7.2, 15.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.1, 18.0, 31.2, 35.8, 57.3, 61.3, 74.3, 86.3, 120.0, 124.3, 130.1, 132.8, 170.8; IR (ATR) ν : 3287, 2982, 1729; LRMS (EI) m/z : 278 (M^+), 204, 177, 131; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$ 278.1518; found, 278.1515.

(1g) To a solution of diethyl malonate (69.3 mg, 0.4 mmol) in DMF (1.4 mL) was added NaH (10.8 mg, 0.5 mmol) at 0 °C and the mixture was stirred for 30 min.

Then, **S18** (100.0 mg, 0.4 mmol) was added and the mixture was stirred for 2 h at room temperature. The reaction was quenched by sat. NH_4Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in DMF (1.3 mL) and NaH (9.9 mg, 0.4 mmol) was added at 0 °C. The mixture was stirred for 30 min at the same temperature and allyl bromide (52.1 mg, 0.4 mmol) was added and the mixture was stirred for 1.5 h at room temperature. The reaction was quenched by sat. NH_4Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 10:1) to afford **1g** (75.4 mg, 63%) as a colorless oil.

Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ : 1.24 (t, J = 7.2 Hz, 6H), 1.79 (s, 3H), 2.64 (d, J = 7.2 Hz, 2H), 2.68 (d, J = 7.6 Hz, 2H), 2.78 (s, 1H), 4.15-4.20 (m, 4H), 5.12-5.85 (m, 2H), 6.34-6.43 (m, 1H), 5.78 (t, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.0, 17.3, 31.2, 37.0, 57.1, 61.2, 61.4, 74.4, 86.1, 119.3, 120.3, 132.1, 132.4, 170.6; IR (ATR) ν : 3280, 2981, 1726, 1216, 1201; LRMS (EI) m/z : 279 ($\text{M}^+ + \text{H}$), 237, 191, 145, 131; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$ 278.1518; found, 278.1510.

(**S21**): To a solution of **S20** (620 mg, 1.8 mmol) in Et_2O (5.8 mL) was added LiAlH_4 (132.8 mg, 3.5 mmol) at 0 °C and the mixture was stirred for 1.5 h at rt. The reaction was quenched with MeOH, sat. Rochelle salt and the mixture was stirred for 1 h. The precipitate was filtrated through a Celite[®] pad and the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 2:1-1:1) to afford **S21** (443.8 mg, 94%) as a colorless oil.

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 1.84 (s, 3H), 2.06-2.08 (m, 2H), 2.19 (d, J = 8.4 Hz, 2H), 2.25 (d, J = 7.6 Hz, 2H), 2.82 8s, 1H), 3.65-3.67 (m, 4H), 6.05 (t, J = 8.4 Hz, 1H), 6.21 (dt, J = 7.6, 16.0 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 7.20-7.36 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.3, 30.2, 35.1, 43.4,

68.0, 74.1, 86.7, 119.4, 125.1, 126.0, 127.2, 128.5, 133.3, 134.3, 137.2; IR (ATR) ν : 3368, 3282, 2924, 2883, 1436, 1022, 968, 738, 692 cm^{-1} ; LRMS (EI) m/z : 270 (M^+), 255, 221, 181, 155, 143, 131, 117, 105, 91, 77, 58; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$, 270.1620 (M^+); found, 270.1612.

(1j) To a solution of **S21** (430.0 mg, 1.6 mmol) and DMAP (38.9 mg, 0.3 mmol) in CH_2Cl_2 (3.2 mL) was added Et_3N (965.4 mg, 9.5 mmol). The mixture was cooled to 0 °C and Ac_2O (487.1 mg, 4.8 mmol) was slowly added. After being stirred for 1.5 h at room temperature, the reaction was quenched by 1N HCl and the aqueous layer was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/ AcOEt = 6:1, 4:1) to afford **1j** (485.7 mg, 86%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ : 1.81 (s, 3H), 2.08 (s, 6H), 2.21 (d, J = 8.0 Hz, 2H), 2.28 (d, J = 7.6 Hz, 2H), 2.82 (s, 1H), 3.97-4.04 (m, 4H), 5.99 (t, J = 7.6 Hz, 1H), 6.13 (dt, J = 8.0, 15.6 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 7.21-7.26 (m, 1H), 7.29-7.34 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ : 17.2, 20.8, 30.8, 35.6, 41.3, 65.8, 74.4, 86.3, 120.0, 123.6, 126.0, 127.4, 128.5, 132.8, 134.1, 136.9, 170.7; IR (ATR) ν : 3281, 2950, 1735, 1364, 1221, 1033 cm^{-1} ; LRMS (EI) m/z : 354 (M^+), 312, 279, 250, 234, 219, 181, 167, 155, 143, 131, 117, 105, 91, 77, 58; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$, 354.1831 (M^+); found, 354.1842.

(S22) (CAS-Reg# 124267-25-0): To a solution of 3-iodocyclohex-2-enone (825.8 mg, 3.7 mmol) in THF (7.4 mL) was added Et_3N (1.5 g, 14.9 mmol) and trimethylsilylacetylene (401.7 mg, 4.1 mmol). Then, CuI (21.3 mg, 0.1 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (77.2 mg, 0.1 mmol) were added to the solution at 0 °C and the mixture was stirred for 30 min at room temperature. The reaction was quenched by sat. NH_4Cl aq. and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/ AcOEt = 20:1-10:1) to afford **S22** (653.3 mg, 91%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ: 0.23 (s, 9H), 1.99-2.05 (m, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 2.44 (dt, *J* = 1.6, 6.0 Hz, 2H), 6.21 (t, *J* = 1.6 Hz, 1H).

(S23) (CAS-Reg# 497838-27-4): To a solution of **S22** (671.0 mg, 3.5 mmol) and CeCl₃ · 7H₂O (2.0 g, 5.2 mmol) in MeOH (11.6 mL) was added NaBH₄ (145.3 mg, 3.8 mmol) at 0 °C and the mixture was stirred for 1 h at the same temperature. The reaction was quenched by water and the aqueous layer was extracted with CH₂Cl₂ (10 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 6:1) to afford **S23** (611.8 mg, 90 %) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ: 0.19 (s, 9H), 1.42 (d, *J* = 7.2 Hz, 1H), 1.56-1.64 (m, 2H), 1.71-1.79 (m, 1H), 1.83-1.91 (m, 1H), 2.07-2.19 (m, 2H), 4.22-4.27 (m, 1H), 6.15 (ddd, *J* = 1.6, 1.6, 3.2 Hz, 1H).

(S24) (CAS-Reg# 53247-05-5): To a solution of **S23** (636.9 mg, 3.2 mmol) in MeOH (16 mL) was added K₂CO₃ (679.4 mg, 4.9 mmol) and the mixture was stirred for 1 h at room temperature. Then, water was added and the aqueous layer was extracted with CH₂Cl₂ (10 mL x 5). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt = 4:1) to afford **S24** (345.3 mg, 88%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ: 1.47 (d, *J* = 6.8 Hz, 1H), 1.55-1.64 (m, 2H), 1.74-1.91 (m, 2H), 2.06-2.22 (m, 2H), 2.89 (s, 1H), 4.23-4.29 (m, 1H), 6.16-6.20 (m, 1H).

(1k) Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 1.51-1.59 (m, 2H), 1.76-1.90 (m, 2H), 2.08-2.10 (m, 2H), 2.43 (s, 3H), 2.86 (s, 1H), 3.61 (dd, *J* = 5.6, 16.4 Hz, 1H), 3.85 (dd, *J* = 5.6, 16.4 Hz, 1H), 4.52-4.58 (m, 1H), 5.12 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.11 (dd, *J* = 1.2, 17.2 Hz, 1H), 5.58-5.60 (m, 1H), 5.45 (dddd, *J* = 5.6, 5.6, 10.8, 17.2 Hz, 1H),

7.30 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 21.3, 21.4, 27.7, 28.5, 46.8, 55.2, 76.7, 83.6, 116.8, 124.6, 126.9, 129.6, 135.3, 135.9, 137.8, 143.1; IR (ATR) ν : 3272, 2930, 1329, 1154, 1089, 920, 813 cm^{-1} ; LRMS (EI) m/z : 315 (M^+), 224, 219, 160 ($\text{M}^+ - \text{Ts}$), 155 (Ts), 144, 131, 117, 105, 91, 83, 58; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}$, 315.1293 (M^+); found, 315.1294.

Preparation of substrates for intermolecular dicyanative [4+2] cycloaddition (Scheme 2): To a solution of ethynyltrimethylsilane (2.33 g, 23.8 mmol) in THF (23.0 mL) was added *n*-BuLi (12.0 mL, 23.8 mmol) at 0 °C and then the mixture was stirred for 10 min. After addition of a solution of cyclooctanone (2.5 g, 19.8 mmol) in THF (5.0 mL), the reaction mixture was stirred for 12 h at room temperature. The reaction was quenched with 1N HCl and the resulting organic layers were washed by brine, dried over Na_2SO_4 and the solvents were removed under *vacuo*. The residue was dissolved in MeOH (40 mL) and then K_2CO_3 (4.1 g, 29.7 mmol) was added. After the reaction was stirred for 1 h, inorganic salts were filtered and organic solvents were concentrated under reduced pressure. The resulting residue was dissolved in AcOEt and then the solution was washed with 1N HCl and brine, dried over Na_2SO_4 and concentrated under *vacuo* to give the desired *tert*-alcohol (3.08 g, quant). To a solution of the above alcohol (920 mg, 6.1 mmol) and NEt_3 (740 mg, 7.3 mmol) in CH_2Cl_2 (15 mL) was added MsCl (830 g, 7.3 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After being stirred for 19 h at room temperature, the reaction mixture was quenched with 1N HCl and the resulting mixture was extracted with CH_2Cl_2 (10 mL X 2), washed with brine, dried over Na_2SO_4 and concentrated under *vacuo*. The resulting residue was purified by flash column chromatography (hexane only) to give the desired enyne as a colorless liquid (264.0 mg, 32%).

^1H NMR (600 MHz, CDCl_3) δ : 1.47-1.58 (m, 6H), 1.59-1.67 (m, 2H), 2.14-2.22 (m, 2H), 2.28-2.35 (m, 2H), 2.77 (s, 1H), 6.18 (t, $J = 8.5$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ : 25.9, 26.4, 27.0, 28.4, 29.6, 29.9, 73.9, 86.4, 122.9, 139.4; IR (ATR) ν : 3307, 2924, 2850, 1467, 1446, 848 cm^{-1} ; LRMS (EI) m/z : 134 (M^+), 121, 106, 91, 84; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}$, 134.1096 (M^+); found, 134.1091.

¹H NMR (400 MHz, CDCl₃) δ: 1.48-1.63 (m, 4H), 1.60-1.71 (m, 2H), 2.14-2.37 (m, 2H), 2.33-2.40 (m, 2H), 2.85 (s, 1H), 6.39 (t, *J* = 6.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ: 26.5, 29.2, 32.1, 34.0, 74.3, 87.4, 125.9, 141.7; IR (ATR) ν: 3304, 2920, 2849, 1446, 852 cm⁻¹; LRMS (EI) *m/z*: 121 (M⁺+H), 88, 84, 58; HRMS (EI) calcd for C₉H₁₂, 120.0939 (M⁺); found, 120.0945.

Scheme S1

Scheme S2 ref. Trost, B. M. *et al. J. Am. Chem. Soc.* **1997**, *119*, 698-708.

Scheme S3

Scheme S4

Scheme S5

Scheme S6

*ref. Piers, E. *et al. Synth. Commun.* **1975**, *5*, 193-199.

JEOL

----- ACQUISITION PARAMETERS -----

File Name = GSSA(YK)-090217-1.3
 Author = JEOL LTD.
 Sample ID = GS
 Content = 435-07 exo-olefin
 Creation Date = 17-FEB-2009 09:50:26

Revision Date = 27-FEB-2009 10:21:51
 Spec Site = ECP600

Spec Type = DELTA_RMR
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 Spin_lock_attn = 13[dB]
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X : parts per Million : 1H

JEOL

----- ACQUISITION PARAMETERS -----

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 Sample ID = GS
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Revision Date = 27-FEB-2009 10:24:31
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 Irr_offset = 5.0[ppm]
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 X_angle = 45[deg]
 X_domain = 13C
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X : parts per Million : 13C

JEOL

ACQUISITION PARAMETERS

File Name: GSSA(YK)-090305.3
 Author: JEOL LTD.
 Sample ID: GS
 Content: 450-08
 Creation Date: 5-MAR-2009 11:43:53

Revision Date: 5-MAR-2009 11:48:03
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 Irr_pwidth: 55[us]
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JEOL

ACQUISITION PARAMETERS

File Name: GSSA(YK)-090305-2.2
 Author: JEOL LTD.
 Sample ID: GS
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Revision Date: 5-MAR-2009 12:39:46
 Spec Site: ECP600

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 Irr_freq: 600.17530548(MHz)
 Irr_noise: WAUGH
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 Irr_pwidth: 55[us]
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 Relaxation_delay: 1.5[s]
 Scans: 1000
 Solvent: CHLOROFORM-D
 Spin_get: 13[Hz]
 Spin_lock_90: 25[us]
 Spin_lock_attn: 13[dB]
 Temp_get: 25[deg]
 X90: 18.5[us]
 X_acq_duration: 1.736704[s]
 X_angle: 45[deg]
 X_domain: 13C
 X_freq: 150.9300327(MHz)
 X_offset: 110[ppm]
 X_points: 65536
 X_pscans: 4
 X_pulse: 9.25[us]
 X_resolution: 0.57581215(Hz)
 X_sweep: 37.73584906(KHz)
 Tri90: 10[us]
 Tri_noise: WALTZ
 Tri_pwidth: 1[us]
 Qua90: 10[us]
 Qua_noise: WAUGH
 Qua_pwidth: 1[us]

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509-LP-13C

X : parts per Million : 13C

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711-TM-13C

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23-20