

Electronic Supporting Information

Regio- and Stereoselective Synthesis of 1,4-Dienes

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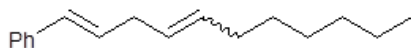
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Determination of Stereochemistry of the Z-Double Bonds Originated from Allenes.

The Z-stereochemistry of the double-bonds originated from allenes in the major isomers was determined based on the vicinal coupling constants of vinyl protons. For compounds **1b**, **1f**, **1g**, **1i**, and **1k**, their Z-geometry was determined on the basis of the *J* (Hz) values (**1b**: 11.5, **1f**: 8.7, **1g**: 12.7, **1i**: 8.6, **1k**: 8.6) directly obtained from their ¹H NMR spectra. In the case of the compounds **1c** and **1d**, the major isomers were isolated by TLC and their *J* (Ha-Hb) values were determined as 10.5 (**1c**) and 11.0 (**1d**) Hz by means of decoupling of allylic protons (–CHa=CHb–CH₂–NPh₂). The Z-configuration of **1e** was estimated by analogy with **1c** and **1d**. The vinylic protons of major isomers of **1h** and **1j** isolated by TLC appeared as overlapping multiplets. The vinyl protons Ha were assigned and the *J* (Ha-Hb) values were determined based on the results obtained by decoupling of Hx and Hy [–CH₂–CHa=CHb–CH₂–NPh₂] (**1h**, Ha: 5.59 ppm, *J* (Ha-Hb) = 10.9 Hz; **1j**, Ha: 5.57 ppm, *J* (Ha-Hb) = 10.9 Hz). The coupling constants are well consistent with their Z-stereochemistry.

Characterization Data

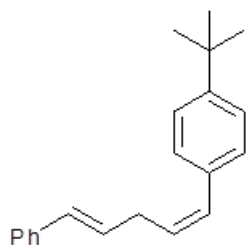
¹H and ¹³C NMR spectra were recorded in CDCl₃ and chemical shifts (δ) are quoted in parts per million from tetramethylsilane for ¹H NMR and from CDCl₃ for ¹³C NMR spectroscopy. IR absorptions are reported in cm⁻¹.



1a (dr = 54:46)

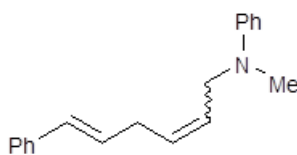
IR (neat) ν 3026, 2925, 2854, 1650, 1600, 1495, 1449, 1070, 963, 741, 691 cm⁻¹; ¹H NMR (300 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.22-1.42 (m, 8H), 2.02 (dt, *J* = 7.5, 6.0 Hz, 0.46H), 2.18 (dt, *J* = 6.9, 6.9 Hz, 0.54H), 2.90 (dd, *J* = 5.7, 5.7 Hz, 0.46H), 2.96 (dd, *J* = 6.6, 6.6 Hz, 0.54H), 5.42-5.55 (m, 2H), 6.19 (dt, *J* = 16.4, 6.4 Hz, 0.46H), 6.22 (dt, *J* = 16.4, 5.9 Hz, 0.54H), 6.37 (d, *J* = 16.0 Hz, 0.46H), 6.40 (d, *J* = 15.5 Hz, 0.56H), 7.16-7.37 (m, 5H); ¹³C NMR (75 MHz) δ 14.1, 22.6, 22.7, 27.2,

28.9, 29.0, 29.5, 29.6, 30.7, 31.7, 31.8, 32.6, 35.9, 125.9, 126.0, 126.5, 126.9, 127.5, 128.4, 129.1, 129.4, 129.9, 130.1, 131.4, 132.1, 137.8; HRMS (FAB) calcd for C₁₇H₂₃ [M-H]⁺: 227.1794; found: 227.1789.



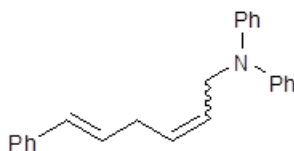
1b

IR (neat) ν 3024, 2962, 1650, 1600, 1495, 1462, 1362, 1269, 1202, 1109, 1017, 963, 841, 741, 692 cm⁻¹; ¹H NMR (300 MHz) δ 1.32 (s, 9H), 3.24 (dd, $J = 7.5, 6.2$ Hz, 2H), 5.74 (dt, $J = 11.5, 7.5$ Hz, 1H), 6.30 (dt, $J = 15.9, 6.1$ Hz, 1H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.53 (d, $J = 11.5$ Hz, 1H), 7.16-7.41 (m, 9H); ¹³C NMR (75 MHz) δ 31.3, 32.0, 34.5, 125.1, 126.0, 127.0, 128.4, 128.5, 128.6, 128.8, 130.0, 130.5, 134.4, 137.6, 149.7; HRMS (FAB) calcd for C₂₁H₂₄ [M]⁺: 276.1878; found: 276.1890.



1c (E:Z = 14:86)

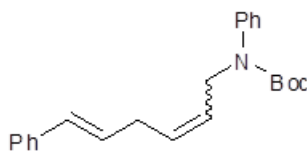
IR (neat) ν 3029, 1599, 1505, 1366, 1203, 1116, 1033, 965, 747, 690 cm⁻¹; ¹H NMR (300 MHz) δ 2.93 (s, 3H), 2.9-3.0 (m, 0.28H), 3.05 (dd, $J = 6.6, 6.4$ Hz, 1.72H), 3.90 (d, $J = 4.8$ Hz, 0.28H), 4.00 (d, $J = 5.9$ Hz, 1.72H), 5.47-5.77 (m, 2H), 6.14-6.28 (m, 1H), 6.36 (d, $J = 16.5$ Hz, 0.14H), 6.45 (d, $J = 15.9$ Hz, 0.86H), 6.66-6.84 (m, 3H), 7.14-7.42 (m, 7H); ¹³C NMR (75 MHz): the major isomer; δ 30.9, 38.1, 49.7, 113.1, 116.8, 126.0, 127.1, 127.4, 128.0, 128.5, 129.1, 129.3, 130.5, 137.5, 149.6; HRMS (FAB) calcd for C₁₉H₂₂N [M+H]⁺: 264.1747; found: 264.1765.



1d (E:Z = 13:87)

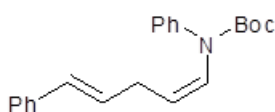
IR (neat) ν 3059, 3024, 2922, 1590, 1495, 1363, 1245, 1216, 1072, 966, 748, 692 cm⁻¹; ¹H NMR (500 MHz) 2.94 (dd, $J = 6.3, 6.3$ Hz, 0.26H), 3.00 (dd, $J = 6.9, 6.9$ Hz, 1.74H), 4.36 (d, $J = 6.3$ Hz, 0.26H), 4.43 (d, $J = 6.3$ Hz, 1.76H) 5.60-5.80 (m, 2H), 6.12 (dt, $J = 15.5, 6.6$ Hz, 0.87H), 6.18 (dt, $J = 16.0, 6.3$ Hz, 0.13H), 6.29 (d, $J = 16.0$ Hz, 0.13H), 6.35 (d, $J = 15.5$ Hz, 0.87H), 6.95 (t, $J = 7.60$

Hz, 2H), 7.00-7.10 (m, 4H), 7.18-7.36 (m, 9H); ^{13}C NMR (75 MHz): the major isomer; δ 31.0, 49.5, 116.2, 121.0, 121.4, 126.0, 127.0, 127.8, 127.9, 128.5, 129.0, 129.2, 130.5, 147.9; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$: 326.1903; found: 326.1903.



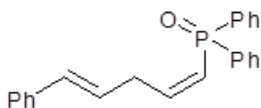
1e (E:Z = 25:75)

IR (neat) ν 3374, 3026, 2976, 2929, 1697, 1597, 1496, 1383, 1280, 1165, 966, 864, 746, 695 cm^{-1} ; ^1H NMR (300 MHz) δ 1.44 (s, 9H), 2.85 (dd, $J = 6.9, 6.7$ Hz, 1.5H), 2.91 (dd, $J = 4.8, 4.8$ Hz, 0.5H), 4.20 (d, $J = 4.2$ Hz, 0.5H), 4.32 (d, $J = 6.00$ Hz, 1.5H), 5.50-5.70 (m, 2H), 6.00 (dt, $J = 15.9, 6.5$ Hz, 0.75H), 6.15 (dt, $J = 15.9, 6.3$ Hz, 0.25H), 6.25 (d, $J = 15.9$ Hz, 0.75H), 6.32 (d, $J = 14.8$ Hz, 0.25H), 7.12-7.36 (m, 10H); ^{13}C NMR (75 MHz); δ 28.2, 28.3, 30.7, 35.4, 47.0, 52.1, 80.2, 80.3, 125.7, 126.0, 126.4, 126.6, 126.9, 127.0, 127.1, 128.0, 128.3, 128.4, 128.5, 128.6, 129.4, 130.4, 130.7, 137.5, 137.6, 142.6, 142.8, 154.5, 154.6; HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_2$ $[\text{M}-\text{H}]^+$: 348.1958; found: 348.1988.



1f

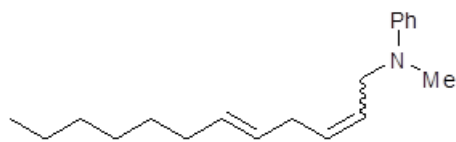
IR (neat) ν 3060, 3028, 2978, 2930, 1712, 1657, 1495, 1323, 1302, 1254, 1165, 740, 693 cm^{-1} ; ^1H NMR (300 MHz) δ 1.47 (s, 9H), 2.45 (dd, $J = 7.5, 6.5$ Hz, 2H), 5.00 (dt, $J = 8.7, 7.5$ Hz, 1H), 5.87 (dt, $J = 15.9, 6.5$ Hz, 1H), 6.10 (d, $J = 15.9$ Hz, 1H), 6.55 (d, $J = 8.7$ Hz, 1H), 7.14-7.39 (m, 10H); ^{13}C NMR (75 MHz) δ 28.2, 30.0, 81.3, 117.5, 125.8, 125.9, 126.7, 126.9, 127.5, 128.1, 128.4, 128.6, 130.3, 137.5, 141.9, 153.4; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_2$ $[\text{M}-\text{H}]^+$: 334.1802; found: 334.1809.



1g

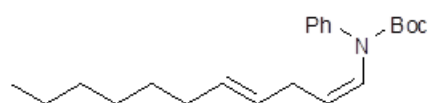
IR (neat) ν 3055, 3022, 2991, 2931, 1618, 1438, 1197, 1169, 1117, 1073, 963, 766, 730, 693, 588, 547 cm^{-1} ; ^1H NMR (300 MHz) δ 3.52 (m, 2H), 6.09 (dt, $J = 15.9, 6.7$ Hz, 1H), 6.20 (ddt, $J = 25.2, 12.7, 1.4$ Hz, 1H), 6.27 (dt, $J = 15.9, 1.3$ Hz, 1H), 6.74 (ddt, $J = 39.6, 12.7, 7.7$ Hz, 1H), 7.15-7.31 (m, 5H), 7.40-7.56 (m, 6H), 7.70-7.82 (m, 4H); ^{13}C NMR (75 MHz) δ 34.1 (d, $^3J_{\text{CP}} = 8.1$ Hz), 122.2 (d,

$^1J_{CP} = 100$ Hz), 126.0, 126.1 (d, $J_{CP} = 1.9$ Hz), 127.8 (d, $^1J_{CP} = 95.9$ Hz), 128.6 (d, $J_{CP} = 12.1$ Hz), 130.9, 131.0, 131.6 (d, $J_{CP} = 2.5$ Hz), 131.7, 133.5, 134.9, 137.36, 151.4; HRMS (FAB) calcd for $C_{23}H_{22}OP$ $[M+H]^+$: 345.1403; found: 345.1374.



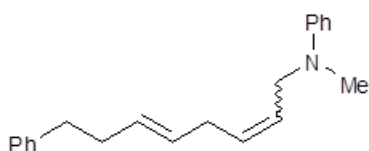
1h (E:Z = 16:84)

IR (neat) ν 3093, 3022, 2925, 1911, 1729, 1600, 1505, 1455, 1366, 1237, 1202, 1158, 1114, 1075, 1034, 994, 966, 926, 861, 747, 690, 433 cm^{-1} ; 1H NMR (300 MHz) δ 0.80-0.90 (m, 3H), 1.17-1.42 (m, 8H), 2.00 (dt, $J = 6.6, 6.6$ Hz, 2H), 2.71 (dd, $J = 5.9, 5.8$ Hz, 0.32H), 2.84 (dd, $J = 5.9, 5.8$ Hz, 1.68H), 2.90 (s, 2.52H), 2.91 (s, 0.48H), 3.88 (d, $J = 5.3$ Hz, 0.32H), 3.96 (d, $J = 6.4$ Hz, 1.68H), 5.30-5.67 (m, 4H), 6.68-6.80 (m, 3H), 7.18-7.29 (m, 2H); ^{13}C NMR (75 MHz): the major isomer; δ 14.1, 22.6, 28.8, 29.5, 30.6, 31.7, 32.6, 38.0, 49.6, 113.0, 116.6, 126.4, 127.4, 129.1, 130.5, 131.5, 149.7; HRMS (FAB) calcd for $C_{19}H_{28}N$ $[M-H]^+$: 270.2216; found: 270.2208.



1i

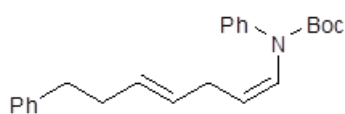
IR (neat) ν 3031, 2957, 2926, 2855, 1714, 1652, 1597, 1496, 1455, 1367, 1321, 1302, 1254, 1166 cm^{-1} ; 1H NMR (300 MHz) δ 0.87 (t, $J = 6.8$ Hz, 3H), 1.18-1.32 (m, 8H), 1.23 (s, 9H), 1.80-1.94 (m, 2H), 2.18-2.30 (m, 2H), 4.94 (dt, $J = 8.6, 7.3$ Hz, 1H), 5.11 (dt, $J = 15.4, 5.5$ Hz, 1H), 5.20 (dt, $J = 15.4, 5.7$ Hz, 1H), 6.43 (dt, $J = 8.6, 1.7$ Hz, 1H), 7.12-7.35 (m, 5H); ^{13}C NMR (75 MHz) δ 14.1, 22.6, 28.2, 28.8, 29.3, 29.7, 31.7, 32.5, 81.2, 119.5, 125.6, 126.6, 126.8, 127.3, 128.5, 131.3, 141.9, 153.5; HRMS (FAB) calcd for $C_{22}H_{32}NO_2$ $[M-H]^+$: 342.2428; found: 342.2411.



1j (E:Z = 18:82)

IR (neat) ν 3025, 2925, 1600, 1505, 1366, 1238, 1201, 1116, 1033, 969, 747, 691 cm^{-1} ; 1H NMR (300 MHz) δ 2.25-2.40 (m, 2H), 2.68 (m, 2H), 2.83 (dd, $J = 7.0, 6.1$ Hz, 2H), 2.88 (s, 2.46H), 2.89 (s, 0.54H), 3.85 (d, $J = 5.1$ Hz, 0.36H), 3.93 (d, $J = 6.1$ Hz, 1.64H), 5.38-5.64 (m, 4H), 6.64-6.78 (m, 3H), 7.12-7.34 (m, 7H); ^{13}C NMR (75 MHz): the major isomer; δ 30.6, 34.4, 36.0, 38.0, 49.6, 113.0,

116.6, 125.7, 126.5, 128.2, 128.4, 129.1, 130.2, 130.4, 142.0, 149.6; HRMS (FAB) calcd for $C_{21}H_{24}N$ $[M+H]^+$: 292.2059; found: 292.2385.



1k

IR (neat) ν 3028, 2977, 2929, 1712, 1652, 1597, 1495, 1454, 1335, 1164, 1070, 969, 858, 741, 696 cm^{-1} ; 1H NMR (300 MHz) δ 1.46 (s, 9H), 2.15-2.28 (m, 4H), 2.54-2.63 (m, 2H), 4.91 (dt, $J = 8.6, 7.3$ Hz, 1H), 5.15 (dt, $J = 15.2, 5.6$ Hz, 1H), 5.24 (dt, $J = 15.3, 5.8$ Hz, 1H), 6.44 (dt, $J = 8.6, 1.5$ Hz, 1H), 7.12-7.21 (m, 4H), 7.21-7.34 (m, 6H); ^{13}C NMR (75 MHz) δ 28.2, 29.7, 34.3, 35.8, 81.2, 119.1, 125.6, 125.7, 126.6, 127.5, 127.7, 128.2, 128.4, 128.5, 130.2, 141.9, 142.0, 153.5; HRMS (FAB) calcd for $C_{24}H_{28}NO_2$ $[M-H]^+$: 362.2115; found: 362.2138.

