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Nickel-Catalyzed Intramolecular Homoallylation of ω-Dienyl Aldehyde

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Supporting Information

General Procedure, Spectral data for **3**, **6a-c**, **7a-c**, **9a**, and **10** and ^{1}NMR spectra (400 MHz) of **3**, **7c**, **9a**, and **10**.

General Procedure (Table 1, runs 1 and 2): To a homogeneous solution of $Ni(acac)_2$ (25.7 mg, 0.1 mmol) and **4a** (196.2 mg, 1.0 mmol) in dry THF (5 ml) was added diethylzinc (2.4 ml, 1 M in hexane, run 1) or triethylborane (2.4 ml, 1 M in hexane, run 2). The mixture was stirred at room temperature for 15 min under N_2 and then poured onto an ice / 2 M HCl mixture. The mixture was extracted twice with EtOAc and the combined organic phase was washed with sat. $NaHCO_3$ and with brine and then was dried over $MgSO_4$ and concentrated *in vacuo*. The colorless residue was subjected to flash column chromatography over silica gel (hexane:ethyl acetate 8:1) to give *trans*-2-(*trans*-2-butenyl)-2-methoxycarbonylcyclopentanol (**6a**) in 72 % yield (142.8 mg) for run 1 and 67% yield for run 2.

(2*S*)-Hydroxy-(3*R*)-(2-propenyl)-1,7,7-trimethylbicyclo[2.2.1]heptane (**3**): IR (neat) 3390 (m), 1370 (m), 1280 (w), 1140 (w), 1030 (s), 970 (m), 790 (w), 750 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (s, 3 H), 0.89 (s, 3 H), 0.90 (s, 3 H), 1.16 (m, 1 H), 1.45 - 1.50 (m, 3 H), 1.59 (s, 1 H), 1.81 (dd, J = 13.9, 7.5 Hz, 1 H), 2.02 (m, 1 H), 2.25 -

2.33 (m, 2 H), 3.95 (dd, J = 9.2, 2.0 Hz, 1 H), 4.99 (dm, J = 10.3 Hz, 1 H), 5.08 (dq, J = 17.1, 1.8 Hz,1 H), 5.86 (ddt, J = 17.1, 10.3, 6.2 Hz, 1 H); HRMS calcd for $C_{13}H_{22}O$: 194.1671. Found *m/z* (relative intensity): 194.1646 (M^+, 44), 152 (24), 110 (24), 109 (24), 107 (22), 95 (100).

***trans*-2-(*trans*-2-Butenyl)-2-methoxycarbonylcyclopentanol (6a)**: IR (neat) 3447 (m), 2953 (s), 2853 (m), 1724 (s), 1437 (s), 1204 (s), 1076 (s), 968 (s), 669 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.55 – 1.76 (m, 4 H), 1.65 (br dd, J = 6.3, 1.1 Hz, 3 H), 1.95 – 2.08 (m, 2 H), 2.04 (br d J = 2.6 Hz, 1 H), 2.21 (br dd, J = 14.2, 7.2 Hz, 1 H), 2.52 (br dd, J = 14.2, 7.2 Hz, 1 H), 3.68 (s, 3 H), 4.33 (dt, J = 2.6, 3.7 Hz 1 H), 5.35 (dtq, J = 15.0, 7.2, 1.1 Hz, 1 H), 5.50 (ddq, J = 1.1, 15.0, 6.2, Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.0, 19.8, 31.1, 32.0, 35.0, 51.8, 57.4, 77.1, 126.9, 128.1, 177.0; HRMS calcd for $C_{11}H_{19}O_3$: 198.1256. Found *m/z* (relative intensity): 198.1277 (M^+, 100), 180 (43), 143 (45), 126 (64), 125 (78). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.74; H, 9.19.

***trans*-2-(Benzyloxymethyl)-2-(*trans*-2-butenyl)cyclopentanol (6b)**: IR (neat) 3447 (m), 3026 (m), 1452 (s), 1076 (s), 978 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.15 – 1.29 (m, 1 H), 1.46 – 1.76 (m, 4 H), 1.65 (dd, J = 6.0, 1.3 Hz, 3 H), 1.94 – 2.01 (m, 1 H), 1.98 (dd, J = 14.3, 7.2 Hz, 1 H), 2.39 (dd, J = 14.3, 7.2 Hz, 1 H), 3.13 (d, J = 8.4 Hz, 1 H), 3.47 (d, J = 8.4 Hz, 1 H), 4.05 (t, J = 7.7 Hz, 1 H), 4.47 (d, J = 12.1 Hz, 1 H), 4.51 (d, J = 12.1 Hz, 1 H), 5.40 (dtq, J = 15.0, 7.2, 1.3 Hz, 1 H), 5.49 (dq, J = 15.0, 6.0 Hz, 1 H), 7.28 – 7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.1, 19.6, 30.5, 31.6, 31.8, 48.3, 73.5, 76.5, 80.0, 127.6, 127.7, 128.4, 138.4; HRMS calcd for $C_{17}H_{24}O_2$: 260.1776. Found *m/z* (relative intensity): 260.1789, (M^+, 100), 259 (7), 242 (8), 169 (9), 136 (34), 121 (52). Anal. Calcd for $C_{11}H_{18}O_3$: C, 78.42; H, 9.29. Found: C, 78.55; H, 9.48.

***trans*-2-(Benzoxymethyl)-2-(*trans*-2-butenyl)cyclopentanol (6c):** IR (neat) 3445 (s), 1705 (s), 1653 (w), 1603 (m), 1026 (s), 940 (m), 710 (s) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz): δ 1.28 – 1.40 (m, 3 H), 1.46 – 1.65 (m, 3 H), 1.54 (br d, J = 5.9, 3 H), 1.76 – 1.84 (m, 1 H), 2.23 (dd, J = 14.2, 6.9 Hz, 1 H), 2.44 (dd, J = 14.2, 6.9 Hz, 1 H), 3.84 (t, J = 5.9 Hz, 1 H), 4.07 (d, J = 11.2 Hz, 1 H), 4.21 (d, J = 11.2 Hz, 1 H), 5.43 (dq, J = 15.0, 5.9 Hz, 1 H), 5.52 (dtq, J = 15.0, 6.9, 1.1 Hz, 1 H), 7.05 – 7.18 (m, 3 H), 8.17 – 8.23 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.1, 20.0, 31.2, 33.0, 33.8, 48.8, 68.7, 77.5, 127.2, 127.2, 128.1, 128.5, 129.6, 133.0, 166.7; HRMS calcd for $C_{17}H_{24}O_2$-OH: 257.1542. Found *m/z* (relative intensity): 257.1564, (M^+-OH, 1), 153 (6), 152 (58), 151 (2), 105 (100). Anal. Calcd for $C_{11}H_{18}O_3$: C, 74.42; H, 8.08. Found: C, 74.72; H, 8.31.

***trans*-2-(*trans*-2-Butenyl)-2-(methoxycarbonyl)cyclohexanol (7a):** IR (neat) 3506 (s), 3020 (m), 1728 (s), 1146 (s), 968 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.26 – 1.42 (m, 3 H), 1.64 (br dd, J = 6.2, 1.3 Hz, 3 H), 1.52 – 1.82 (m, 5 H), 2.26 (dd, J = 14.3, 7.1 Hz, 1 H), 2.50 (dd, J = 14.2, 7.1 Hz, 1 H), 2.98 (br s, 1 H), 3.69 (s, 3 H), 3.95 (dt, J = 8.4, 3.5, 1 H), 5.35 (dtq, J = 15.2, 1.3, 6.2 Hz, 1 H), 5.48 (ddq, J = 15.2, 6.2, 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.0, 21.3, 22.4, 29.4, 29.6, 34.3, 51.4, 51.6, 71.4, 126.3, 128.2, 177.2; HRMS calcd for $C_{11}H_{19}O_3$: 212.1412. Found *m/z* (relative intensity): 212.1443 (M^+, 60), 194 (48), 153 (11), 140 (21), 139 (5), 136 (11), 135 (100). Anal. Calcd for $C_{11}H_{18}O_3$: C, 67.89; H, 9.50. Found: C, 68.07; H, 9.50.

***trans, trans*-3-(Benzyloxymethyl)-2-(2-propenyl)cyclohexanol (7b)**: See reference 6.

***cis*-, and *trans*-2,3-Benzo-6-(*trans*-2-butenyl)cyclohexanol (*cis*- and *trans*-7c)**: IR (neat) 3350 (m), 1030 (s), 990 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.48 – 1.84 (m, 2 H, *cis* and *trans*), 1.63 (d, J = 7.2 Hz, 3 H, *trans*), 1.69 (d, J = 7.0 Hz, 1 H, *trans*), 1.71

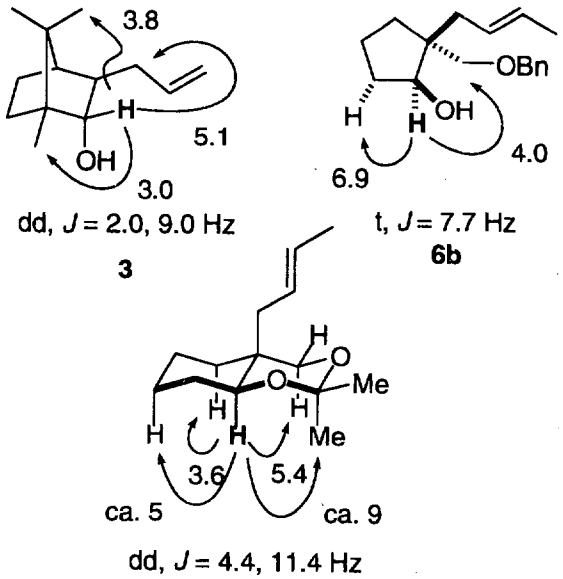
(d, J = 7.2 Hz, 3 H, *cis*), 1.97 – 2.15 (m, 2 H, *cis* and *trans*), 2.28 – 2.44 (m, 1 H, *cis* and *trans*), 2.73 – 2.91 (m, 2 H, *cis* and *trans*), 4.47 (q, J = 7.0 Hz, 1 H, *trans*), 4.64 (br s, 1 H, *cis*), 5.47 – 5.64 (m, 2 H, *cis* and *trans*), 7.07 – 7.24 (m, 3 H, *cis* and *trans*), 7.34 (dm, J = 7.2 Hz, 1 H, *cis*), 7.57 (dm, J = 7.2 Hz, 1 H, *trans*); HRMS calcd for $C_{14}H_{18}O$: 202.1358. Found *m/z* (relative intensity): 202.1373 (M+, 64), 184 (36), 159 (100).

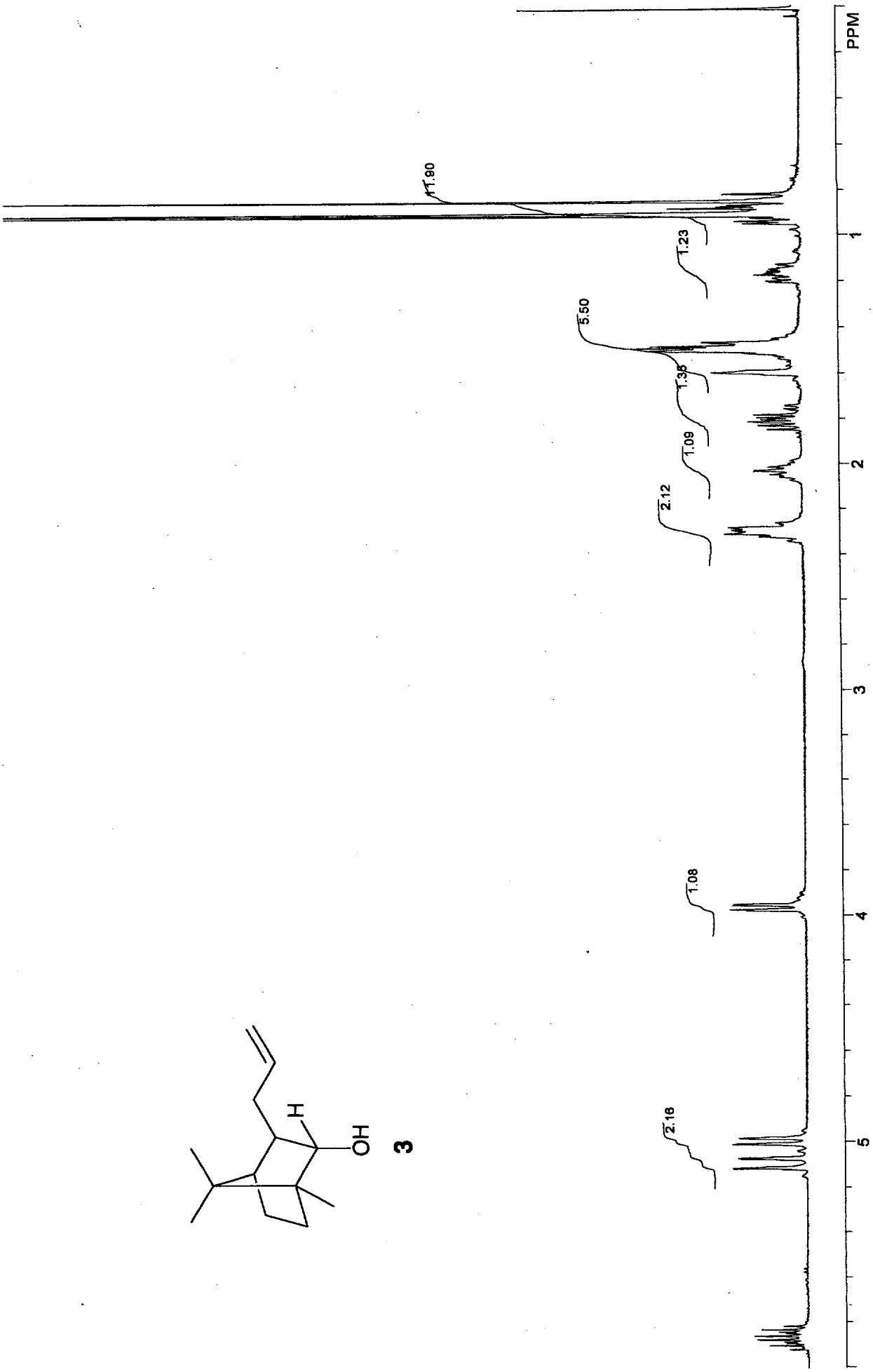
***cis*-, and *trans*-2,3-Benzo-6-(*trans*-1-butenyl)cyclohexanol** (*cis*- and ***trans*-9a**): IR (neat) 3370 (m), 1020 (s), 990 (m), 970 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.01 (t, J = 7.4 Hz, 3 H, *trans*), 1.02 (t, J = 7.4 Hz, 3 H, *cis*), 1.66 – 1.77 (m, 2 H, *cis* and *trans*), 1.79 – 1.86 (m, 1 H, *cis*), 1.92 – 2.02 (m, 1 H, *trans*), 2.05 – 2.14 (m, 2 H, *cis* and *trans*), 2.32 (dt, J = 3.0, 8.3 Hz, 1 H, *trans*), 2.55 (ddd, J = 3.7, 7.7, 14.5 Hz, 1 H, *cis*), 2.76 – 2.97 (m, 2 H, *cis* and *trans*), 4.48 (dd, J = 3.1, 8.3 Hz, 1 H, *trans*), 4.66 (dd, J = 3.7, 4.1 Hz, 1 H, *cis*), 5.43 (ddt, J = 8.3, 15.5, 1.4 Hz, 1 H, *trans*), 5.59 (ddm, J = 7.6, 15.5 Hz, 1 H, *cis*), 5.68 – 5.76 (m, 1 H, *cis* and *trans*), 7.08 – 7.25 (m, 3 H, *cis* and *trans*), 7.40 (d, J = 7.4 Hz, 1 H, *cis*), 7.58 (d, J = 7.4 Hz, 1 H, *trans*); HRMS calcd for $C_{14}H_{18}O$: 202.1358. Found *m/z* (relative intensity): 202.1329 (M+, 75), 184 (32), 159 (100).

***trans*-6-(*trans*-2-Butenyl)-3,3-dimethyl-2,4-dioxabicyclo[4.4]decane (10)**: IR (neat) 1363 (s), 1196 (s), 1096 (s), 1016 (m), 970 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.77 (m, 1 H), 1.42 (s, 3 H), 1.47 (s, 3 H), 1.68 (br dd, J = 6.2, 1.5 Hz, 3 H), 1.80 - 1.83 (m, 1 H), 2.17 (dd, J = 13.7, 7.5 Hz, 1 H), 2.60 (br dd, J = 13.7, 7.5 Hz, 1 H), 3.36 (dd, J = 11.4, 1.5 Hz, 1 H), 3.60 (d, J = 11.4 Hz, 1 H), 3.68 (dd, J = 4.4, 11.4 Hz, 1 H), 5.40 (m, 1 H, coalescing to dt, J = 15.0, 7.0 Hz by irradiation at 1.68), 5.55 (m, 1 H, coalescing to d, J = 15.0 Hz, by irradiation at 1.68); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.1, 19.8, 24.9, 26.1, 27.4, 28.5, 29.7, 30.0, 37.3, 68.7, 76.4, 99.3, 126.5, 128.1; HRMS calcd for $C_{14}H_{24}O_2$: 224.1776. Found *m/z* (relative intensity) 224.1774 (M^+, 27), 166 (100).

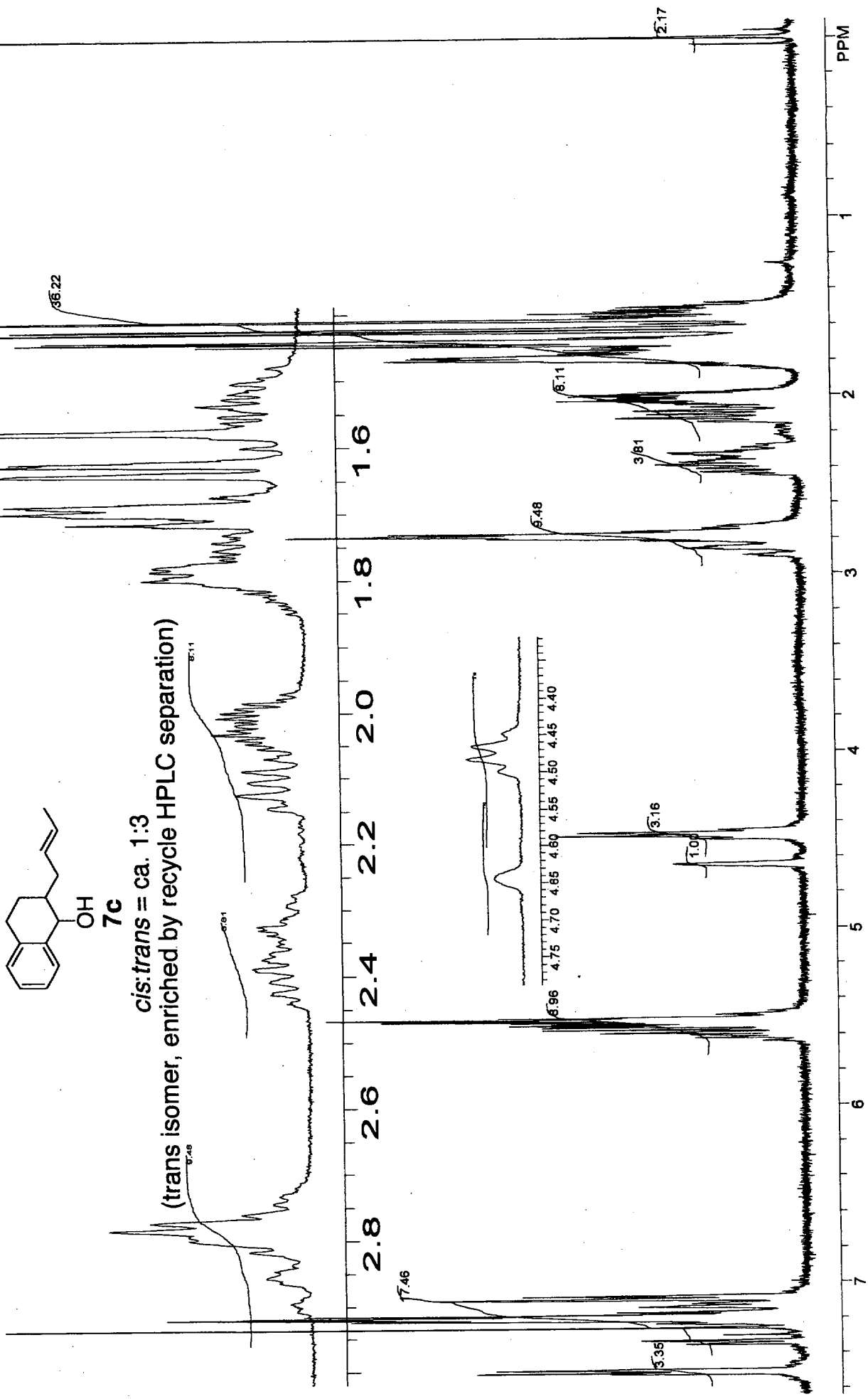
Structure Determination of 3, 6b, and 7a: Significant NOE's observed for one of the diastereotopic allylic methylene protons for **3** and also for one of the diastereotopic CH_2OBn methylene protons for **6b** are diagnostic for structure determination (Figure 1). For **6b**, the absence of NOE between the boldface proton and the allylic methylene protons further supports the structure. The structure of **7a** was determined as an acetonide derivative **10** ($LiAlH_4$/ether then cat. TsOH/2,2-dimethoxypropane). The *trans*-fused 2,4-dioxadecalin structure is apparent on the basis of the coupling pattern of the angular axial proton (boldface, dd, J = 4.4 and 11.4 Hz) and NOE increments for all the protons in a 1,3-diaxial relationship with this proton.

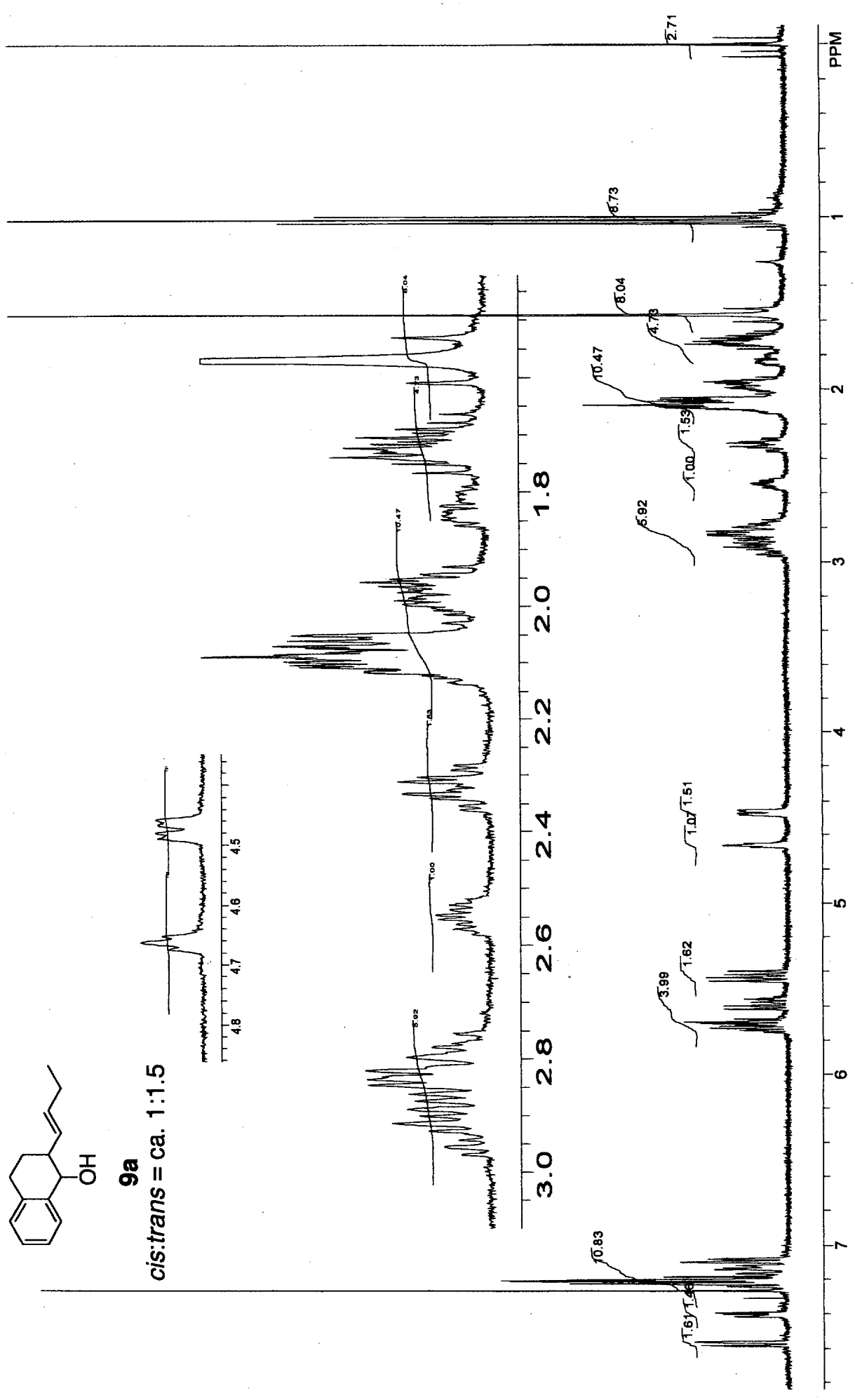
Figure 1. NOE data (% increment) and Coupling Patterns for the Boldface Proton.

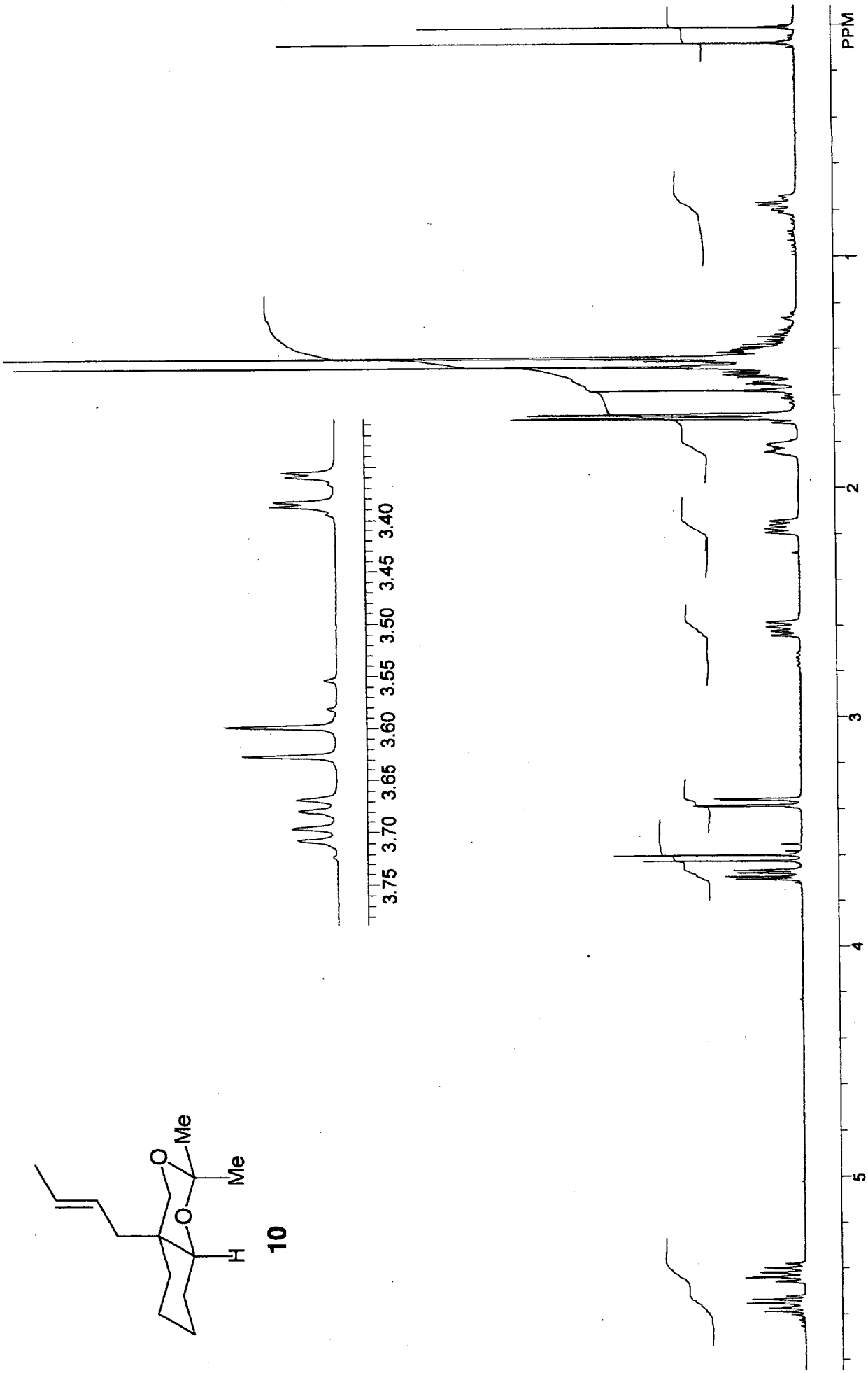




3




OH
9a
cis:trans = ca. 1:1.5
PPM



10