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Supporting information for

Intramolecular Diels-Alder Cyclizations of *E*-1-Nitro-1,7,9-Decatrienes: Synthesis of the AB Ring System of Norzoanthamine

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Experimental Procedures:

(1*R*,3*S*,4*aR*,5*R*,7*Z*,8*aS*)-1-[2-(4-Methoxybenzyloxy)-ethyl]-3-methoxymethoxy-1,7-dimethyl-5-nitro-1,2,3,4,4*a*,5,6,8*a*-octahydronaphthalene (**18**) and (1*R*,3*S*,4*aS*,5*S*,7*Z*,8*aR*)-1-[2-(4-Methoxybenzyloxy)-ethyl]-3-methoxymethoxy-1,7-dimethyl-5-nitro-1,2,3,4,4*a*,5,6,8*a*-octahydronaphthalene (**19**) A solution of nitroalkene **17** (141 mg, 0.325 mmol) and benzene (3 mL) was heated to 80 °C for 18 h. The reaction was cooled to ambient temperature and concentrated *in vacuo* to a yellow oil. Purification by Flash chromatography (5 g SiO₂, 99:1 to 49:1 Et₂O/CH₂Cl₂) gave nitrodecalins **18** (11 mg, 8%) and **19** (118 mg, 84%) as clear oils.

Data for **18**: *R_f* 0.26 (49:1 CH₂Cl₂/Et₂O); [α]_D²² +17.8 (*c* 1.12, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.42 (br s, 1H), 4.50 (ABq, *J*_{AB} = 6.7 Hz, Δ *v*_{AB} = 20.1 Hz, 2H), 4.49 (m, 1H), 4.42 (ABq, *J*_{AB} = 11.5 Hz, Δ *v*_{AB} = 10.0 Hz, 2H), 3.90 (m, 1H), 3.80 (s, 3H), 3.59–3.45 (m, 2H), 3.27 (s, 3H), 2.66 (m, 1H), 2.45–2.36 (m, 2H), 2.14 (m, 1H), 1.89 (dt, *J* = 14.8, 2.4 Hz, 1H), 1.81–1.72 (m, 2H), 1.70 (s, 3H), 1.45 (m, 1H), 1.25 (td, *J* = 13.4, 2.9 Hz, 1H), 1.13 (dd, 14.8, 2.1 Hz, 1H), 1.01 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.1, 131.0, 130.8, 129.2, 121.4, 113.7, 94.7, 89.0, 72.6, 70.9, 67.4, 55.3, 55.2, 51.3, 39.8, 35.4, 35.1, 34.8, 33.2, 32.9, 27.7, 23.1; MS (CI/CH₄) *m/z*(relative intensity) 433(16), 371(16), 250(28), 201(12), 185(29), 177(10), 173(17), 171(13), 161(33), 157(28), 147(18), 138(31), 133(22), 122(58), 121(100), 120(17), 105(34), 95(23); HRMS *m/z* calcd for C₂₄H₃₅O₆N (M⁺) 433.2464, found 433.2467.

Data for **19**: *R_f* 0.17 (49:1 CH₂Cl₂/Et₂O); [α]_D²² +5.1 (*c* 1.21, CHCl₃); IR (neat) ν 2932, 2859, 1613, 1549, 1449, 1302, 1248, 1099, 1038, 916, 820, 756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.40 (br s, 1H), 4.61 (ABq, *J*_{AB} = 7.0 Hz, Δ *v*_{AB} = 3.4 Hz, 2H), 4.53 (m, 1H), 4.42 (s, 2H), 3.81 (s, 3H), 3.72–3.62 (m, 1H), 3.52 (t, *J* = 7.2 Hz, 2H), 3.32 (s, 3H), 2.70–2.59 (m, 1H), 2.45 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.02 (ddt, *J* = 12.1, 10.9, 2.8 Hz, 1H), 1.92–1.84 (m, 1H),

1.81–1.64 (m, 4H), 1.70 (s, 3H), 1.33 (t, $J = 12.2$ Hz, 1H), 1.06 (dt, $J = 11.7, 12.0$ Hz, 1H), 0.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.2, 131.5, 130.4, 129.2, 121.1, 113.8, 94.6, 88.8, 72.7, 71.2, 65.9, 55.3, 46.4, 46.6, 40.9, 40.3, 36.8, 36.4, 35.5, 34.8, 23.0, 20.1; **MS** (CI/CH_4) m/z (relative intensity) 433(2), 312(21), 202(11), 197(14), 161(26), 121(47), 120(100), 106(21), 91(21), 80(22), 78(22), 76(26); **HRMS** m/z calcd for $\text{C}_{24}\text{H}_{35}\text{NO}_6$ (M^+) 433.2464, found 433.2447; **Anal.** Calcd for $\text{C}_{24}\text{H}_{35}\text{NO}_6$: C, 66.49; H, 8.14; N, 3.23. Found: C, 66.29; H, 8.08; N, 3.12.

(Z,4aR,5R,7R,8aS)-5-[2-(4-Methoxybenzyloxy)-ethyl]-7-methoxymethoxy-3,5-dimethyl-4a,5,6,7,8,8a-hexahydro-4H-naphthalen-1-one (2) To a 0 °C solution of decalin **19** (30.0 mg, 0.0692 mmol) and THF (500 μL) was added potassium *tert*-butoxide (12.1 mg, 0.108 mmol) portionwise. The ice bath was removed, and the reaction stirred at ambient temperature 10 min. H_2O (20 μL) was added, and the reaction stirred for 5 min. Dimethyldioxirane (2.2 mL of a ~0.08M solution in acetone, 0.176 mmol) was added and the reaction stirred for 10 min. The mixture was diluted with saturated aqueous NH_4Cl (5 mL) and extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with H_2O (10 mL) and brine (10 mL), dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification by Flash chromatography (4 g SiO_2 , 3:1 to 2:1 Hex/ EtOAc) gave enone **2** (20.1 mg, 72%) along with unreacted nitroalkane **19** (3.8 mg, 83% of **2** based on recovered starting material): R_f 0.14 (2:1 Hex/ EtOAc); $[\alpha]_D^{22}$ -12.6 (c 1.13, CHCl_3); **IR** (neat) ν 2932, 2863, 1665, 1613, 1514, 1462, 1379, 1302, 1248, 1093, 1035, 916, 822 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 8.6$ Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 2H), 5.86 (s, 1H), 4.68 (ABq, $J_{\text{AB}} = 6.9$ Hz, $\Delta\nu_{\text{AB}} = 20.0$ Hz, 2H), 4.40 (s, 2H), 3.80 (s, 3H), 3.75–3.65 (m, 1H), 3.58–3.47 (m, 2H), 3.37 (s, 3H), 2.67–2.59 (m, 1H), 2.31 (dd, $J = 18.0, 4.3$ Hz, 1H), 2.17–2.05 (m, 2H), 1.89 (s, 3H), 1.74–1.63 (m, 4H), 1.30–1.22 (dd, $J = 11.8, 11.1$ Hz, 1H), 1.04 (dt, $J = 12.1, 12.6$ Hz, 1H), 0.95 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 200.2, 161.1, 159.2, 130.4, 129.2, 125.5, 113.8, 94.3, 72.8, 71.3, 65.9, 55.2, 55.2, 45.1, 43.8, 41.0, 36.6, 32.6, 31.6, 24.3, 20.7, 15.2; **MS** (CI/CH_4) m/z (relative intensity) 402(1), 357(30), 340(22), 221(444), 219(52), 218(33), 203(33), 201(23), 175(48), 173(24), 163(23), 161(24), 147(25), 136(49), 134(52), 121(100), 109(36), 91(30), 77(31); **HRMS** m/z calcd for $\text{C}_{24}\text{H}_{34}\text{O}_5$ (M^+) 402.2406, found 402.2396; **Anal.** Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_5$: C, 71.61; H, 8.51. Found: C, 71.05; H, 8.43.

^1H NMR spectral data:

5 β -nitro-1, 2, 3, 4, 4a α , 5, 6, 8a β -octahydronaphthalene (5a)

^1H NMR (400 MHz, CDCl_3): δ 5.58 (dddd, $J = 9.9, 7.3, 4.6, 2.7$ Hz, 1H), 5.47 (dd, $J = 9.9, 1.6$ Hz, 1H), 4.54 (dt, $J = 10.7$ Hz, 1H), 2.80–2.68 (m, 1H), 2.66–2.57 (m, 1H), 1.92–1.42 (m, 6H), 1.40–1.23 (m, 2H), 1.18–1.08 (m, 2H).

5 β -nitro-6 β -phenyl-1, 2, 3, 4, 4 α , 5, 6, 8 α -octahydronaphthalene (5c)

¹H NMR (400 MHz, CDCl₃): δ 7.33–7.29 (m, 3H), 7.16–7.13 (m, 2H), 5.76 (d, J = 9.9 Hz, 1H), 5.63 (ddd, J = 9.9, 4.6, 2.7 Hz, 1H), 4.83 (dd, J = 11.5, 6.7 Hz, 1H), 4.06 (m, 1H), 1.98–1.70 (m, 6H), 1.44–1.24 (m, 3H), 1.04–0.92 (m, 1H).

5 β -nitro-6 α -phenyl-1, 2, 3, 4, 4 α , 5, 6, 8 α -octahydronaphthalene (6c)

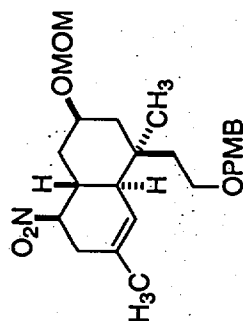
¹H NMR (400 MHz, CDCl₃): δ 7.33–7.29 (m, 3H), 7.16–7.13 (m, 2H), 5.87 (ddd, J = 9.9, 5.1, 2.7 Hz, 1H), 5.54 (dt, J = 9.9, 1.9 Hz, 1H), 4.86 (dd, J = 12.1, 9.9 Hz, 1H), 4.07 (ddd, J = 9.9, 5.1, 1.9 Hz, 1H), 2.56 (bd, J = 11.8 Hz, 1H), 2.43–2.34 (m, 1H), 1.90–1.76 (m, 2H), 1.64–1.46 (m, 2H), 1.46–1.13 (m, 4H).

3-Methyl-5 β -nitro-1, 2, 3, 4, 4 α , 5, 6, 8 α -octahydronaphthalene (5d)

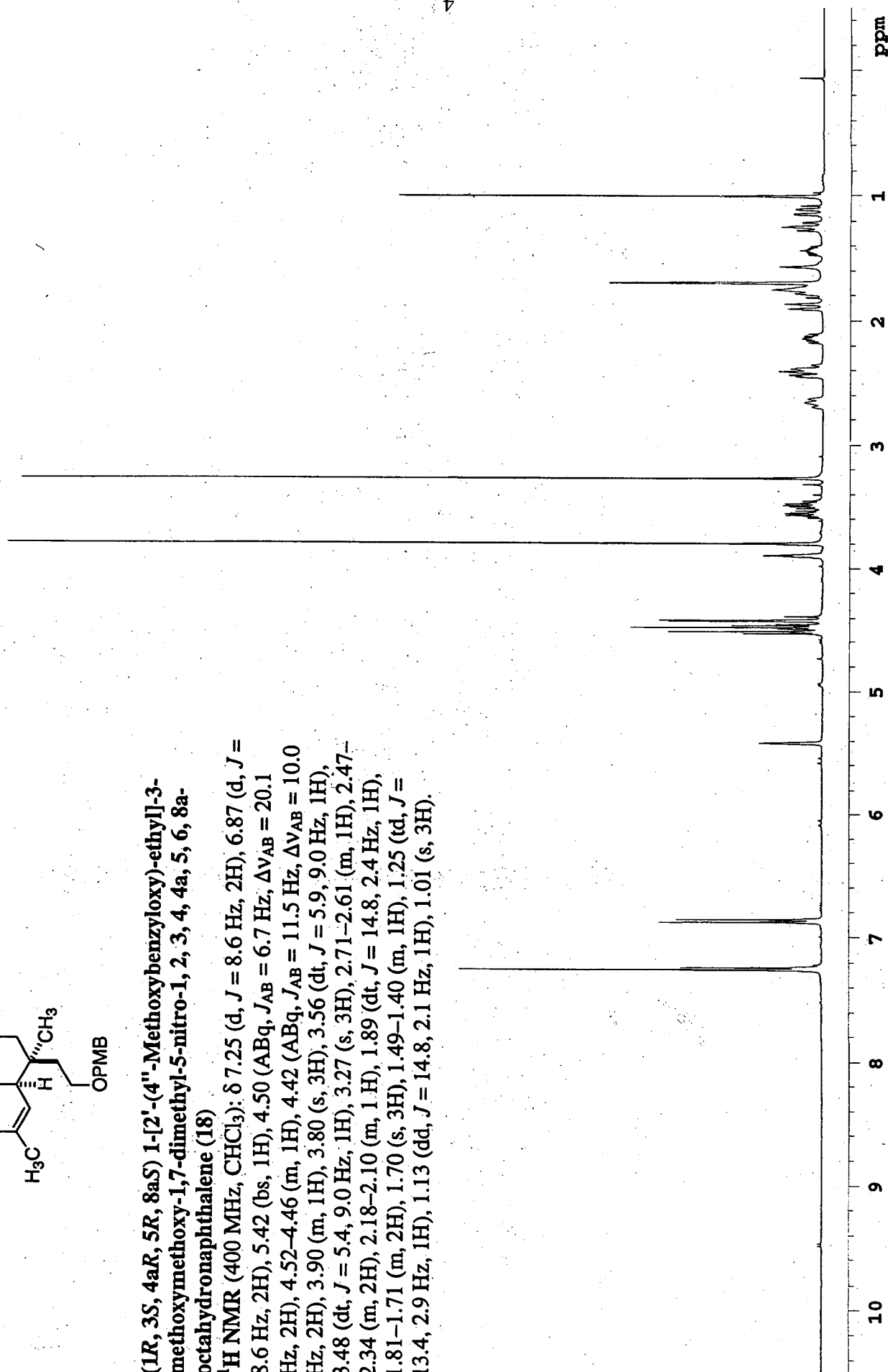
¹H NMR (400 MHz, CDCl₃): δ 5.58 (dddd, J = 9.7, 7.3, 4.7, 2.4 Hz, 1H), 5.50 (dd, J = 9.7, 1.1 Hz, 1H), 4.52 (dt, J = 10.7, 5.9 Hz, 1H), 2.77–2.69 (m, 1H), 2.65–2.58 (m, 1H), 1.86–1.74 (m, 4H), 1.64–1.35 (m, 2H), 1.22–1.11 (dtd, J = 12.9, 9.7, 3.5 Hz, 1H), 1.06–0.95 (m, 1H), 0.90 (d, J = 6.7 Hz, 3H), 0.82 (dt, J = 12.4, 11.5 Hz, 1H).

3-Methyl-5 β -nitro-1, 2, 3, 4, 4 α , 5, 6, 8 α -octahydronaphthalene (6d)

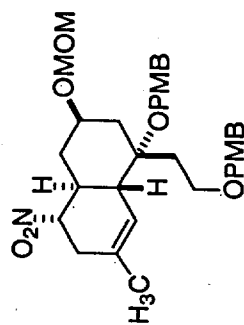
¹H NMR (400 MHz, CDCl₃): δ 5.63 (bd, J = 10.4 Hz, 1H), 5.46 (bd, J = 10.4 Hz, 1H), 4.51–4.45 (m, 1H), 2.85–2.73 (m, 1H), 2.56 (bd, J = 12.6 Hz, 1H), 2.39–2.25 (m, 2H), 1.91–1.67 (m, 1.5H), 1.61–1.35 (m, 3.5H), 1.00–0.80 (m, 2H), 0.89 (d, J = 6.3 Hz, 3H).



(1*R*, 3*S*, 4*aR*, 5*R*, 8*aS*) 1-[2'-(4''-Methoxybenzyloxy)-ethyl]-3-methoxymethoxy-1,7-dimethyl-5-nitro-1,2,3,4,4*a*,5,6,8*a*-octahydronaphthalene (**18**)
¹H NMR (400 MHz, CHCl₃): δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.42 (bs, 1H), 4.50 (ABq, *J*_{AB} = 6.7 Hz, Δ*v*_{AB} = 20.1 Hz, 2H), 4.52–4.46 (m, 1H), 4.42 (ABq, *J*_{AB} = 11.5 Hz, Δ*v*_{AB} = 10.0 Hz, 2H), 3.90 (m, 1H), 3.80 (s, 3H), 3.56 (dt, *J* = 5.9, 9.0 Hz, 1H), 3.48 (dt, *J* = 5.4, 9.0 Hz, 1H), 3.27 (s, 3H), 2.71–2.61 (m, 1H), 2.47–2.34 (m, 2H), 2.18–2.10 (m, 1H), 1.89 (dt, *J* = 14.8, 2.4 Hz, 1H), 1.81–1.71 (m, 2H), 1.70 (s, 3H), 1.49–1.40 (m, 1H), 1.25 (td, *J* = 13.4, 2.9 Hz, 1H), 1.13 (dd, *J* = 14.8, 2.1 Hz, 1H), 1.01 (s, 3H).

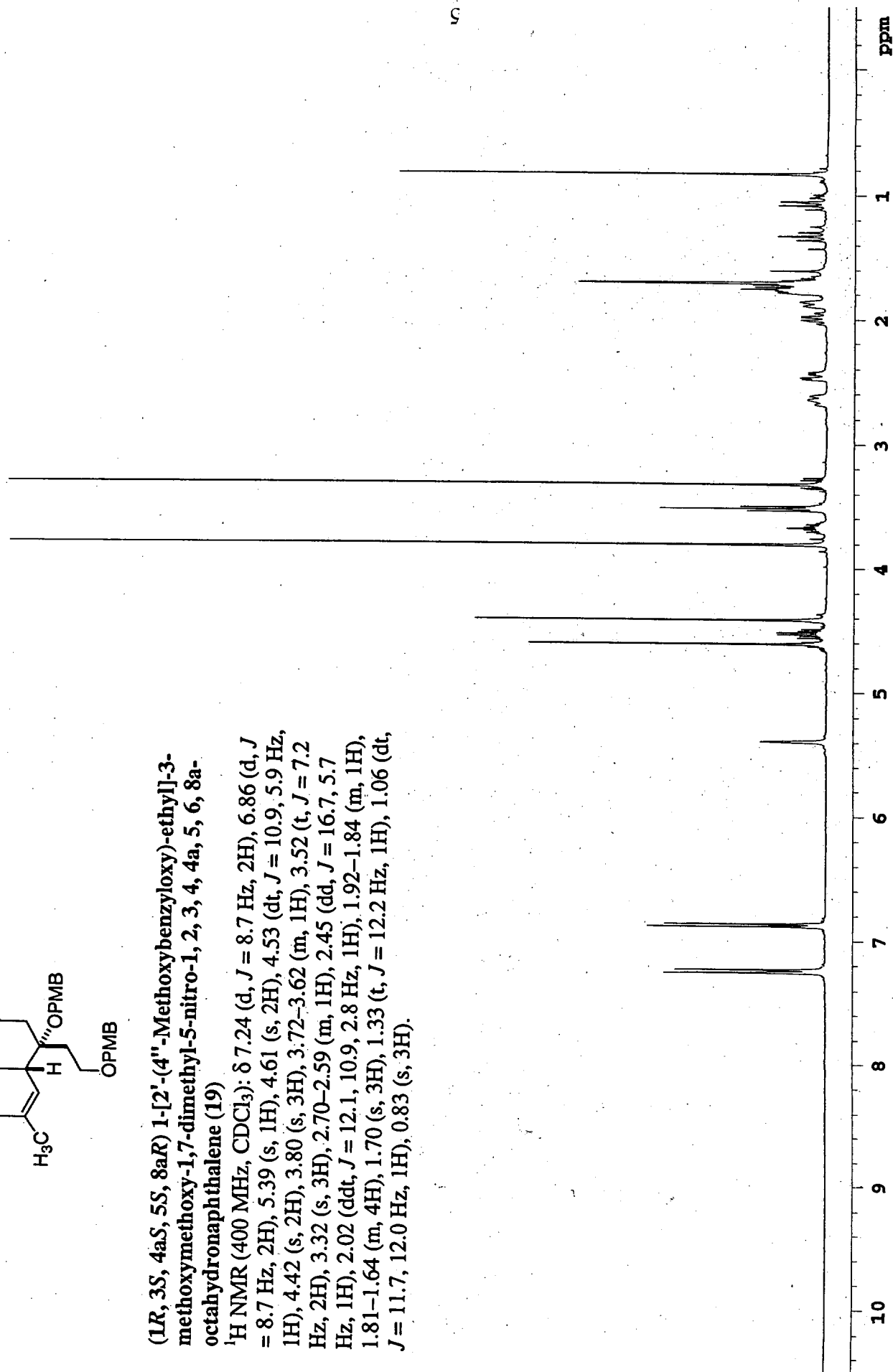


S

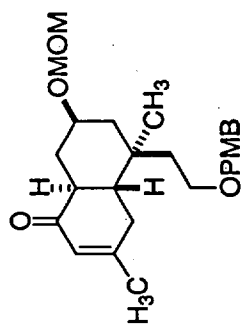


(1R, 3S, 4aS, 5S, 8aR) 1-[2'-(4''-Methoxybenzyloxy)-ethyl]-3-methoxymethoxy-1,7-dimethyl-5-nitro-1, 2, 3, 4, 4a, 5, 6, 8a-octahydronaphthalene (19)

¹H NMR (400 MHz, CDCl₃): δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.39 (s, 1H), 4.61 (s, 2H), 4.53 (dt, *J* = 10.9, 5.9 Hz, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.72–3.62 (m, 1H), 3.52 (t, *J* = 7.2 Hz, 2H), 3.32 (s, 3H), 2.70–2.59 (m, 1H), 2.45 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.02 (ddt, *J* = 12.1, 10.9, 2.8 Hz, 1H), 1.92–1.84 (m, 1H), 1.81–1.64 (m, 4H), 1.70 (s, 3H), 1.33 (t, *J* = 12.2 Hz, 1H), 1.06 (dt, *J* = 11.7, 12.0 Hz, 1H), 0.83 (s, 3H).



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(4aR, 5R, 7S, 8aS)-5-[2'-(4''-Methoxybenzyloxy)-ethyl]-7-methoxymethoxy-3,5-dimethyl-4a, 5, 6, 7 α , 8, 8a-hexahydro-4H-naphthalen-1-one (2)

^1H NMR (400 MHz, CDCl_3): δ 7.22 (d, J = 8.6 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 5.86 (s, 1H), 4.68 (ABq, J_{AB} = 6.9 Hz, $\Delta\nu_{\text{AB}}$ = 20.0 Hz, 2H), 4.40 (s, 2H), 3.80 (s, 3H), 3.75–3.65 (m, 1H), 3.58–3.47 (m, 2H), 3.37 (s, 3H), 2.67–2.59 (m, 1H), 2.31 (dd, J = 18.0, 4.3 Hz, 1H), 2.17–2.05 (m, 2H), 1.89 (s, 3H), 1.74–1.63 (m, 4H), 1.30–1.22 (dd, J = 11.8, 11.1 Hz, 1H), 1.04 (dt, J = 12.1, 12.6 Hz, 1H), 0.95 (s, 3H).

