Supplemental Figure Legends

Supplemental 1. Reagents and conditions for the vinyl iodide **10/11**. **(A)** (a) cat. H_2SO_4/acetone, 3h; (b) $NaBH_4$/MeOH, 0 °C, 45 min; (c) $NAIO_4$, THF/H2O (1/1), 3h; (d) Ph_3PCHCO_2Et/cat. PhCOOH, CH_2Cl_2, reflux, 12 h; (e) $NaBH_4$, $NiCl_2$-$6H_2O$, MeOH, 0 °C, 1h; (f) DMSO, $(COCl)_2$, NEt_3, CH_2Cl_2, -78 °C, 1 h; (g) $ClPh_3PCH_2CHO$, NEt_2, PhH, reflux, 12 h; (h) CHI_3, $CrCl_2$, THF, 3 h; (i) TFA/H_2O/THF. Reagents and conditions for synthesis of Wittig terminal alkyne **14**. **(B)** (a) I_2, imidazole, PPh_3, CH_2Cl_2, 4 h; (b) PPh_3, MeCN, reflux, 12h**. (C)** Reagents and conditions for the acetaldehyde precursor **22** (a) cat. PTSA-H2O/DHP, 5 min; (b) 1-butyne, n-BuLi, BF_3-OEt_2, THF, 3 h; (c) TBDMS-Cl, Imidazole, DMF, 3 h; (d) $Ni(OAc)_2$-$4H_2O$, $NaBH_4$, $H_2NCH_2CH_2NH_2$, H_2, EtOH, 12 h; (e) $MgBr_2$, Et_2O, 4 h; (f) DMSO, $(COCl)_2$, NEt_3, CH_2Cl_2, 0.5 h; (g) $ClPh_3PCH_2CHO$, NEt_3, PhH, 12 h. **(D)** Reagents and conditions for the terminal alkyne building block **24** (a) NaHMDS, THF, -78°C, 3 h; (b) TBAF, THF, 40°C, 48 h. **(E)** Reagents and conditions for the final coupling **RvD4.** (a) $Pd[PPh_3]_4$, CuI, n-$BuNH_2$, PhH, 12 h; (b) Zn(Cu/Ag), MeOH (aq), 40°C, 12 h; (c) K_2CO_3, MeOH, 12 h.

Supplemental 2. 1D-^{1}H NMR spectroscopy was carried out in CD_3OD at 400 MHz. Figure subset shows the olefinic region and *J* coupling values for complete structural confirmation of synthetic RvD4 to be 4*S*,5*R*,17*S*-trihydroxydocosa- 6*E*,8*E*,10*Z*,13*Z*,15*E*-hexaenoic acid.

Supplemental 3. Conversion of RvD4 to its trans isomers. **(A**) RvD4 was treated in DME with 1M LiOH base and glutathione for 26hr. (**B**) Conversion of RvD4 was monitored by HPLC and characteristic UV-Vis absorption spectra to (**C**) 10*E* Resolvin D4 and (**D**) 10*E*, 13*E*, Resolvin D4.