SUPPLEMENTAL DATA

(1) Synthesis of non-labeled derivative: Archazolid A (20 mg, 28 µmol), DMAP (7.1 mg, 58 µmol, 2.1 eq.) and EDC (11.1 mg, 58.0 µmol, 2.1 eq.) were exhibited under argon atmosphere. Then a solution of 4-(3-(trifluoromethyl)-*3H*-diazirin-3-yl)benzoic acid (9.5 mg, 41.4 µmol, 1.5 eq.) in CH_2Cl_2 (1 mL) was added and the resulting mixture was stirred for 18 h under light exclusion. The solvent was removed and the residue was purified by preparative TLC (EtOAc / hexanes = 1:2) to give the di-ester BD-archazolid (3.5 mg, 3.0 µmol, 11 %). 5 mg of archazolid A could be recovered. ^{1}H NMR (600 MHz, CD_3OD, BD-archazolid) δ = 0.97 (d, *J* = 7.0 Hz, 3 H), 1.01 (d, *J* = 7.0 Hz, 3 H), 1.02 (d, *J* = 7.0 Hz, 3 H), 1.07 (d, *J* = 7.0 Hz, 3 H), 1.12 (d, *J* = 7.0 Hz, 3 H), 1.35 (m, 1 H), 1.64 (s, 3 H), 1.65 (s, 3 H), 1.74 (m, 1H), 1.81 (m, 1 H), 1.84 (dd, *J* = 8.1 Hz, *J* = 4.7 Hz, 1 H), 1.89 (s, 3 H), 1.91 (s, 3 H), 1.95 (s, 3 H), 2.67 (m, 1 H), 2.75 (s, 3 H), 3.01 (d, *J* = 7.3 Hz, 1 H), 3.08 (dd, *J* = 13.6 Hz, *J* = 6.7 Hz, 1 H), 3.11 (s, 3 H), 3.23 (d, *J* = 9.2 Hz, 1 H), 5.25 (d, *J* = 9.9 Hz, 1 H), 5.31 (d, *J* = 9.5 Hz, 1 H), 5.53 (d, *J* = 12.5 Hz, 1 H), 5.54 (t, *J* = 9.9 Hz, 1 H), 5.80 (dd, *J* = 7.7, *J* = 3.7 Hz, 1 H), 5.89 (d, *J* = 8.1 Hz, 1 H), 5.90 (d, *J* = 8.1 Hz, 1 H), 6.00 (d, *J* = 5.1 Hz, 1 H), 6.03 (dd, *J* = 9.0 Hz, *J* = 4.6 Hz, 1 H), 6.09 (dd, *J* = 15.0 Hz, *J* = 10.6 Hz, 1 H), 6.61 (d, *J* = 15.7 Hz, 1 H), 6.84 (t, *J* = 7.0 Hz, 1 H), 7.17 (s, 1 H), 7.37 (d, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 8.07 (d, *J* = 8.4 Hz, 2 H), 8.11 (d, *J* = 8.44 Hz, 1 H); ^{13}C NMR (100 MHz, CD_3OD, BD-archazolid) δ = 12.4, 12.6, 17.0, 17.3, 18.0, 19.8, 22.3, 23.4, 24.3, 25.8, 27.5, 30.8, 39.8, 40.5, 42.6, 44.9, 46.0, 56.3, 73.3, 77.1, 77.5, 79.1, 88.5, 117.0, 125.5, 127.7, 127.7, 128.2, 129.3, 130.0, 131.1, 131.3, 132.0, 133.3, 133.3, 133.6, 134.7, 135.2, 135.7, 136.3, 141.2, 141.7, 156.0, 166.0, 166.2, 168.4, 174.0; HRMS: calculated for $C_{60}H_{68}F_6N_6O_9SNa$: 1185.4570, found: 1185.4752.

(2) Synthesis of labeled derivative: Archazolid A (20 mg, 28 µmol), DMAP (7.1 mg, 58 µmol, 2.1 eq.) and EDC (11.1 mg, 58.0 µmol, 2.1 eq.) were exhibited under argon atmosphere. Then a solution of ^{14}C labeled 4-(3-(trifluoromethyl)-*3H*-diazirin-3-yl)benzoic acid (9.5 mg, 41.4 µmol, 1.5 eq.) (Ref. 23) in CH_2Cl_2 (1 ml) was added and the resulting mixture was stirred for 18 h under light exclusion. The solvent was evaporated and the residue was purified by column chromatography on silica gel (EtOAc / hexanes = 1:2) to give 1.8 mg (1.5 µmol, 5 %) of the di-ester BD-archazolid. The spectroscopical data was identical to that for the non labeled compound. The only difference is, that the signal for the ^{14}C-Carbon atom is missing in the ^{13}C NMR Spektra (BD-archazolid: 166.0, 166.2).