Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for "Excited State Properties of β-Carotene Analogs Incorporating a Lactone Ring"

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1. NMR data of BL-7 and 8

3-[(1'*E*)-2'',6'',6''-Trimethylcyclohex-1''-ylethene-1'-yl]-2-*tert*-buthyldimethylsilylfuran (4). To a suspension of silylfuran-Wittig reagent **3** (1.64 g, 10.79 mmol) in diethyl ether (54.0 mL) was added dropwise *n*-butyllithium (1.6M in hexane, 10.1 mL, 16.1 mmol) at 0 ^{o}C. After the mixture was stirred for 10 min at 0 ^{o}C, a solution of cyclocotral in diethyl ether (5.5 mL) was added at the same temperature. After being stirred for 40 min at room temperature, the resulting mixture was poured into water, and extracted with diethyl ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (only hexane) afforded iodide **4** (1.86 g, 52%) as a colorless oil: IR (neat, cm^{-1}) 2927, 2857, 1546, 1470, 1389, 1250, 1090; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, *J* = 1.8 Hz, 1H), 6.61 (d, *J* = 1.8 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 2.03 (t, *J* = 5.9 Hz, 2H), 1.73 (s, 3H), 1.63 (m, 2H), 1.47 (m, 2H), 1.05 (s, 6H), 0.91 (s, 9H), 0.30 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 138.1, 136.0, 129.4, 127.5, 124.3, 107.5, 40.0, 34.5, 33.3, 29.2, 26.7, 22.0, 19.6, 17.9, -5.2.

5-Hydroxy-[(1'*E*)-2'',6'',6''-trimethylcyclohex-1''-ylethene-1'-yl]-2(5H)-furanone (5). A solution of silylfuran **4** (1.78 g, 5.38 mmol) and tetraphenyl porphine (1.5 mg) in dichloromethane (53.8 mL) was irradiated with halogen-tungsten lamp under oxygen atmosphere for 30 min at -78 ^{o}C. After the mixture was allowed to warm to room temperature, the solvents were removed *in vacuo*. Purification by silica gel column chromatography (from 1% to 10% ethyl acetate in hexane) afforded butenolide **5** (1.10 g, 91%) as a yellow oil: IR (neat, cm^{-1}) 3398, 2929, 2865, 1765, 1456, 1091; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7 .32 (d, *J* = 16 .5 Hz, 1 H), 6. 88 (s, 1 H), 6. 12 (bs, 1 H), 6. 10 (d, *J* = 16 .9 Hz, 1 H), 2. 03 (t, *J* = 5. 8 Hz, 2 H), 1. 73 (s, 3 H), 1. 61 (m, 2 H), 1. 47 (m, 2 H), 1. 04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.1, 139.9, 137.7, 137.6, 133.4, 132.6, 120.3, 96.4, 39.9, 34.5, 33.5, 29.2, 22.0, 19.4; ESI-HRMS m/z calcd for $C_{15}H_{20}O_3Na$ $(M+Na)^+$ 271.1310, found 271.1315.

(3*Z*,5*E*)-1,1-Dibromo-6-(2',6',6'-trimethylcyclohex-1'-yl)-4-allyloxycarbonylhexa-1,3,5-triene (6). To a solution of the butenolide **5** (1.34 g, 5.40 mmol) in DMSO (54.0 mL) was added diisopropylethylamine (2.83 mL, 16.2 mmol) at room temperature. After the resulting mixture was stirred for 15 min at the same temperature, allyl bromide (2.81 mL, 32.4 mmol) was added dropwise. After being stirred for 30 min at room temperature, the resulting mixture was poured into water, and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford crude ester aldehyde, which was used in the next reaction without further purification.

To a solution of carbon tetrabromide (3.58g, 10.8 mmol) in dichloromethane (81.0 mL) of the obtained ester aldehyde at -20 °C was added dropwise the solution of triphenylphosphine (5.66 g, 21.6 mmol) in dichloromethane (7.0 mL). After the resulting mixture was stirred for 20 min at the same temperature, a solution of crude aldehyde and triethylamine (1.52 mL, 10.8 mmol) in dichloromethane (7.0 mL) was added at -60 °C. After the resulting mixture was stirred for 20 min at the same temperature, the precipitate was filtered in hexane through a pad of Celite, and the filtrate was concentrated *in vacuo*. Purification by silica gel column chromatography (from only hexane to 5% ethyl acetate in hexane) afforded dibromide **6** (1.84 g, 77%) as a yellow oil: IR (neat, cm^{-1}) 2927, 2863, 1717, 1611, 1539, 1455, 1213, 1148, 963; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, *J* = 11.5 Hz, 1H), 6.46 (d, *J* = 16.1 Hz, 1H), 6.36 (d, *J* = 11.4 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 5.99 (m, 1H), 5.39 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.30 (dd, *J* = 10.5, 0.9 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 2H), 2.01 (t, *J* = 6.4 Hz, 2H), 1.72 (s, 3H), 1.61 (m, 2H), 1.45 (m, 2H), 1.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0, 137.7, 135.4, 133.9, 133.4, 131.9, 131.8, 130.2, 129.1, 119.6, 96.9, 66.1, 39.9, 34.5, 33.5, 29.2, 22.1, 19.5.

((3*Z*,5*E*)-6-(2,6,6-trimethylcyclohexene)-4-allyloxycarbonylhexa-3,5-dien-1-yne (7). To a solution of dibromide **6** (113 mg, 0.25 mmol) in THF (2.5 mL) was dropwise sodium hexamethyldisilazide (1.0M in THF, 0.76 mL, 0.76 mmol) at 100 °C. After the reaction mixture was stirred for 10 min at the same temperature, ethylmagnesium bromide (1.0 M in THF, 0.76 mL, 0.76 mmol) was added dropwise at the same temperature. After the mixture was stirred 20 min, the reaction mixture was poured into water and MeOH, and then extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from only hexane to 30% ethyl acetate in hexane) afforded acetylene **7** (56 mg, 78%) as a yellow oil: IR (neat, cm^{-1}) 2959, 2930, 2095, 1732, 1161; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.40 (d, *J* = 15.6 Hz, 1H), 6.08 (d, *J* = 16.1 Hz, 1H), 5.99 (m, 1 H), 5.74 (d, *J* = 2.2 Hz, 1H), 5.41 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.27 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.79 (d, *J* = 7.3 Hz, 2H), 3.35 (d, *J* = 2.8 Hz, 1H), 2.01 (t, *J* = 5.8 Hz, 2H), 1.70 (s, 3H), 1.60 (m, 2H), 1.45 (m, 2H), 1.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 145.3, 137.3, 134.1, 132.1, 132.0, 128.9, 119.3, 110.3, 86.3, 80.8, 66.1, 39.9, 34.5, 33.4, 29.2, 22.0, 19.4; ESI-HRMS m/z calcd for $C_{19}H_{24}ONa$ $(M+Na)^+$ 307.1674, found 307.1673.

(2*E*,4*E*)-5-(2',6',6'-trimethylcyclohexene)-3-methylpenta-2,4-diene-1-ol (8). To a solution of ethyl diethyl phosphono acetate (5.15 mL, 26.0 mmol) in THF (20 mL) was added sodium hydride (1.04, 26.0 mmol) at 0 °C. After the mixture was stirred for 10 min at 0 °C, a solution of the β-ionone (1.0 mg, 5.2 mmol) obtained above in THF (5.0 mL) was added at 0 °C. After being stirred for 20 h at 50 °C, the resulting mixture was poured into water, and extracted with

ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from hexane on1y to 1% ethy1 acetate in hexane) afforded the desired ester (1.30 g, 95%) as a colorless oil (*E*/ *Z* = 7/ 1). *E* isomer: IR (neat, cm^{-1}) 2929, 2865, 1709, 1606, 1232; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.55 (d, *J* = 16.1 Hz, l H), 6.08 (d, *J* = 16.0 Hz, l H), 5.74 (s, l H), 4.17 (q, *J* = 6.9 Hz, 2 H), 2 .33 (s, 3 H), 2. 02 (t, *J* = 6. 4 Hz, 2 H), 1.69 (s, 3 H), 1.61 (m, 2 H), 1.45 (m, 2 H), 1.28 (t, *J* = 7.3 Hz, 3 H), 1.01 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.6, 153.1, 137.5, 136.5, 133.9, 131.4, 118.4, 59.9, 39.8, 34.5, 33.4, 29.2, 21.9, 19.4, 14.7, 14.0; ESI-HRMS m/z calcd for $C_{17}H_{26}O_2Na$ $(M+Na)^+$ 285.1830, found 285.1830.

To a solution of the resulting ester (1.3 g, 4.95 mmol) in dichloromethane (24.8 mL) was added dropwise diisobutylaluminium hydride (1.0 M in toluene, 14.9 mL, 14.9 mmol) at 0 °C. After the reaction mixture was stirred for 10 min at the same temperature, aqueous potassium sodium (+)-tartrate tetrahydrate solution was added, and then resulting mixture was extracted with ethyl acetate. The organic 1ayers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (from 1% to 20% ethy1 acetate in hexane) afforded alcohol **8** (1.03 g, 94%) as a colorless oil. *E*-isomer: IR (neat, cm^{-1}) 3370, 2926, 2864, 1455; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.12 (d, *J* = 16.5 Hz, l H), 6.02 (d, *J* = 16.1 Hz, l H), 5.61 (t, *J* = 6.8 Hz, l H), 4.29 (d, *J* = 6.8 Hz, 2 H), 1.99 (t, *J* = 7.0 Hz, 2 H), 1.84 (s, 3 H), 1.68 (s, 3 H), 1.60 (m, 2 H), 1.45 (m, 2 H), 0.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.9, 137.3, 137.2, 129.2, 128.7, 127.4, 59.7, 39.8, 34.5, 33.2, 29.1, 29.0, 21.9, 19.5, 12.7.

6-(2,6,6-trimethylcyclohexene)-1-iodo-4-methylhexa-l,3,5-triene (9). A mixture of alcohol **8** (312 mg, 1.42 mmol) and manganese dioxide (4.21 g) in THF (7 mL) was stirred at 70 °C for 15 h. The precipitate was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo* to afford crude aldehyde, which was used in the next reaction without further purification.

To a suspension of prepared $CH_2IP^+Ph_3I^-$ (917 mg, 1.73 mmo1) in THF (6.0 mL) was added dropwise lithium bis(trimethylsilyl)amide (1.0 M in THF, 1.73 mL, 1.73 mmol) at 0 °C. After the mixture was stirred for 5 min at 0 °C, a solution of the aldehyde in THF (0.90 mL) was added. After being stirred for 10 min at room temperature, the resulting mixture was poured into water, and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (hexane only) afforded iodide **9** (225 mg, 57%) as a yellow oil as a mixture of isomers.

Butenolide compound 1. To a solution of alkyne **7** (26 mg, 0.096 mmol) and iodide **10** (27 mg,

0.101 mmol) in triethylamine (0.96 mL) was added tetrakis(triphenylphosphine)palladium (11 mg, 0.0096 mmol) and cuprous iodide (1 mg, 0.0096 mmol) at room temperature. The reaction mixture was stirred at room temperature until **7** was completely consumed by monitoring with TLC (*ca*. 30 min), and formic acid (0.01 mL, 0.288 mmol) was added dropwise. After being stirred for 24 h, the resulting mixture was poured into a saturated aqueous NH_4Cl solution, and then extracted with ethyl acetate. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography afforded **1** (19 mg, 50%): IR (neat, cm^{-1}) 2926, 2361, 1763, 1688, 1458, 1048, 970; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.30 (d, *J* = 16.5 Hz, 1H), 7.04 (s, 1H), 6.63 (d, *J* = 12.3 Hz, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 6.26 (d, *J* = 16.9 Hz, 1H), 6.22 (d, *J* = 16.5 Hz, 1H), 6.19 (d, *J* = 12.4 Hz, 1H), 2.05 (m, 4H), 2.01 (s, 3H), 1.77 (s, 3H), 1.74 (s, 3H), 1.67 (m, 4H), 1.48 (m, 4H), 1.07 (s, 6H), 1.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 148.5, 141.7, 138.0, 137.9, 137.5, 135.8, 132.7, 132.2, 131.5, 130.4, 128.0, 123.8, 121.8, 110.8, 40.1, 34.6, 34.5, 29.4, 29.3, 22.2, 19.5, 19.4, 13.1; ESI-HRMS m/z calcd for $C_{30}H_{40}O_2Na_1$ $(M+Na)^+$ 455.2926, found 455.2915.

Butenolide compound 2. To a solution of alkyne **7** (9.2 mg, 0.032 mmol) and iodide **9** (12.3 mg, 0.036 mmol) in triethylamine (0.26 mL) was added tetrakis(triphenylphosphine)palladium (3.6 mg, 0.0032 mmol) and cuprous iodide (0.6 mg, 0.0032 mmol) at room temperature. The reaction mixture was stirred at room temperature until **7** was completely consumed by monitoring with TLC (ca. 15 min), and formic acid (0.03 mL) was added dropwise. After being stirred for 5h, the resulting mixture was poured into a saturated aqueous NH_4Cl solution, and then extracted with ethyl acetate. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography afforded **2** (8.0 mg, 54%). The partial separation by preparative HPLC [column: Develosil CN-UG (10 x 250 mm); mobile phase: *n*-hexane; flow rate: 2.0 mL/ min.; UV detect: 435 nm; retention time: (all-*trans*-isomer) 12 min] in the dark afforded the desired **2** as a red powder: IR (neat, cm^{-1}) 2927, 2360, 1760, 1684, 1461, 1048; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, *J* = 15.6 Hz, l H), 7.01 (s, l H), 6.83 (dd, *J* = 15.1, 11.3 Hz, l H), 6.75 (dd, *J* = 14.7, 9.6 Hz, l H), 6.29 (d, *J* = 15.5 Hz, l H), 6.21 (d, *J* = 16.5 Hz, l H), 6.20 (d, *J* = 11.9 Hz, l H), 6.16 (d, *J* = 16.5 Hz, l H), 5.90 (d, *J* = 11.0 Hz, l H), 2.05 (t, *J* = 7.8 Hz, 2 H), 2.03 (t, *J* = 7.8 Hz, 2 H), 1.76 (s, 3 H), 1.73 (s, 3 H), 1.61 (m, 4 H), 1.47 (m, 4 H), 1.06 (s, 6 H), 1.03 (s, 6 H); ESI-HRMS m/z calcd for $C_{32}H_{42}O_2Na$ $(M+Na)^+$ 481.3082, found 481.3070.

1. Additional ultrafast spectroscopic data of BL-7 and 8

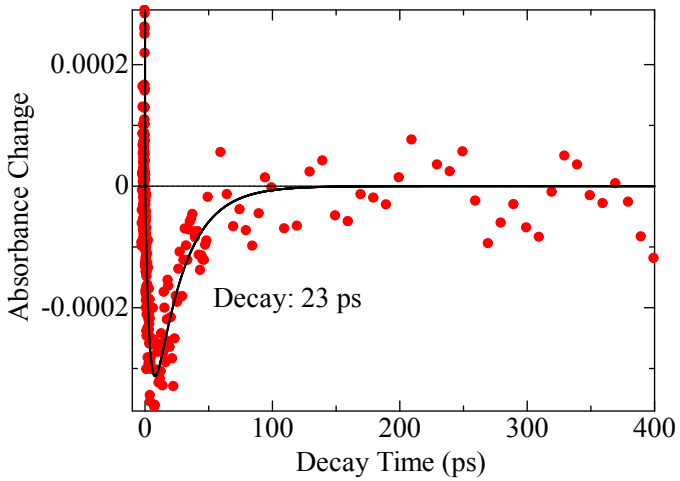

Figure S1: Kinetic trace of the stimulated emission of BL-7 in methanol probed at 750 nm.

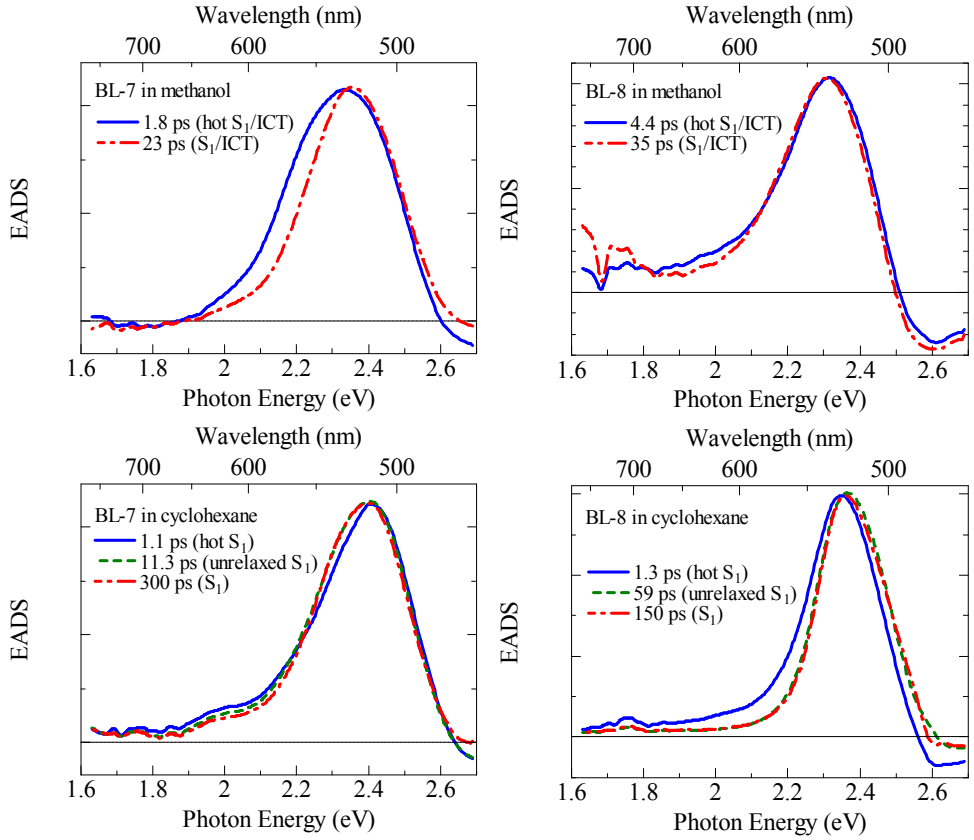

Figure S2: Normalized EADS of each sample.