Supporting Information

Fast Assembly and High Throughput Screening of Structure and Antioxidant Relationship of Carotenoids

Dahye Kim, Gaosheng Shi, YunJi Kim, and Sangho Koo*

Department of Energy Science and Technology, Department of Chemistry, Myongji University, Myongji-Ro 116, Cheoin-Gu, Yongin, Gyeonggi-Do, 17058, Korea

*E-mail: sangkoo@mju.ac.kr

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1. Materials and Methods.

Materials: 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), 1,1-diphenyl-2-picryl-hydrazyl (DPPH), and potassium persulfate were purchased from Sigma–Aldrich, Inc. β-Carotene and Lycopene used for ABTS and DPPH assays were freshly prepared according to the literature procedure.

References
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Methods

ABTS assay: The ABTS cationic radical was prepared by treating ABTS diammonium salt (0.35 mL, 7.4 mM) with potassium persulfate (0.35 mL, 2.6 mM). The mixture was kept in the dark at room temperature for 12 h, and then diluted with methanol (about 1/5 of volume) until its absorbance value became 0.70±0.02 at 734 nm. Typically, carotenoid sample solutions in THF (20 μL, 1–1000 μg/mL) were added to 280 μL ABTS•+ solution in MeOH onto the 96 cells plate. Keeping them in the dark at room temperature for 60 min, the optical density (OD) of the mixture was measured at 734 nm by UV/Vis microplate spectrophotometer (Multiskan G0™ by Thermo Scientific Co.) and each carotenoid sample concentration was tested in fourfold analyses.

Scheme S-1. Preparation of ABTS cationic radical with K₂S₂O₈ (forward) and the radical scavenging by anti-oxidant (backward).
**DPPH assay:** DPPH is a stable free radical with UV absorption maximum at 517 nm. Because of the interference of carotenoids around at 510 nm the depletion of DPPH radical by carotenoid scavenging was measured at 580 nm. Typically, a $6.31 \times 10^{-2}$ mM stock solution of DPPH in methanol was freshly prepared. The sample solutions (20 μL, 1–1000 μg/mL) in THF were mixed with DPPH solution in methanol (280 μL, $6.31 \times 10^{-2}$ mM) onto the 96 cells plate. Keeping them in the dark at room temperature for 60 min, the optical density (OD) of the mixture was measured by UV/Vis microplate spectrophotometer (Multiskan GO™ by Thermo Scientific Co.) and each carotenoid sample concentration was tested in fourfold analyses.

![Scheme S-2. DPPH radical and the radical scavenging by anti-oxidant.](image)

**Hierarchical Clustering Analysis:** Hierarchical clustering analysis (HCA) is a common and well-established approach in unsupervised machine learning, in which clusters are formed sequentially according to their similarities. The most similar data sets are grouped first, and these groups are merged step-by-step into bigger groups according to their similarities until they become a single cluster, which comprises the whole data sets. Hierarchical clustering was performed with Euclidian distance as a similarity measure and Ward’s linkage. In the single linkage method, the distance (D) or similarity between two clusters A and B is defined as the minimum distance between a point in A and a point in B, where $d(y_i, y_j)$ is the Euclidean distance in (1).

$$D(A, B) = \min \{d(y_i, y_j); \text{for } y_i \text{ in A and } y_j \text{ in B}\} \quad (1)$$
At every phase, the two clusters with the smallest distance merged into a new cluster to calculate the distance among every pair of clusters, and then the procedure is repeated until all pairs of cluster go into one. The analyses were performed using the statistical software, Origin 8.0 (Origin Lab, USA), and IBM SPSS Statistics Desktop version 19.0 (Armonk, NY).

Table S-1. Proximity Matrix of Euclidean distance in Hierarchical Clustering Analysis of ABTS and DPPH assays for carotenoids 1a–1r (see Table 1, entries 1–18).

|          | 5    | 6    | 7    | 8    | 9    | 10   | 11   | 12   | 13   | 14   | 15   | 16   | 17   | 18   |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Proximity Matrix | 5    | 6    | 7    | 8    | 9    | 10   | 11   | 12   | 13   | 14   | 15   | 16   | 17   | 18   |
|          | S4   |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 1        | 1    | 0.00 | 0.56 | 0.41 | 0.80 | 0.83 | 0.63 | 0.94 | 0.72 | 1.03 | 0.64 | 1.40 | 1.13 | 1.30 | 1.54 |
| 2        | 2    | 0.56 | 0.00 | 0.22 | 0.90 | 0.16 | 0.85 | 0.42 | 0.24 | 0.52 | 0.36 | 0.86 | 0.63 | 0.91 | 1.02 |
| 3        | 3    | 0.41 | 0.22 | 0.00 | 0.48 | 0.26 | 0.57 | 0.34 | 0.66 | 0.45 | 1.38 | 0.75 | 1.44 | 2.58 | 2.05 |
| 4        | 4    | 0.80 | 0.49 | 0.00 | 0.16 | 0.12 | 0.32 | 0.20 | 0.14 | 0.60 | 0.35 | 0.53 | 0.76 | 2.14 | 1.73 |
| 5        | 5    | 0.83 | 0.18 | 0.00 | 0.16 | 0.26 | 0.00 | 0.06 | 0.37 | 0.18 | 0.75 | 0.47 | 0.80 | 2.17 | 2.17 |
| 6        | 6    | 0.63 | 0.19 | 0.00 | 0.16 | 0.26 | 0.00 | 0.06 | 0.37 | 0.18 | 0.75 | 0.47 | 0.80 | 2.17 | 2.17 |
| 7        | 7    | 0.72 | 0.24 | 0.13 | 0.26 | 0.11 | 0.22 | 0.17 | 0.14 | 0.31 | 0.57 | 1.02 | 1.53 | 1.86 | 3.96 |
| 8        | 8    | 0.32 | 0.28 | 0.33 | 0.37 | 0.16 | 0.06 | 0.22 | 0.37 | 0.14 | 0.31 | 0.57 | 1.02 | 1.53 | 1.86 |
| 9        | 9    | 0.43 | 0.14 | 0.06 | 0.22 | 0.22 | 0.22 | 0.17 | 0.14 | 0.31 | 0.57 | 1.02 | 1.53 | 1.86 | 3.96 |
| 10       | 10   | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 11       | 11   | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 12       | 12   | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 13       | 13   | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 14       | 14   | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 15       | 15   | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 16       | 16   | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 17       | 17   | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 18       | 18   | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

This is a dissimilarity matrix
Table S-2. Agglomeration Schedule in Hierarchical Clustering Analysis of ABTS and DPPH assays for carotenoids 1a–1r (see Table 1, entries 1–18).

| stage | cluster combined | coefficient | stage cluster first appears | next stage |
|-------|------------------|-------------|-----------------------------|------------|
|       | cluster 1 | cluster 2 | | cluster 1 | cluster 2 | |
| 1     | 5   | 17   | .033 | 0 | 0 | 6 |
| 2     | 1   | 9    | .074 | 0 | 0 | 7 |
| 3     | 4   | 10   | .128 | 0 | 0 | 11 |
| 4     | 6   | 12   | .199 | 0 | 0 | 6 |
| 5     | 3   | 8    | .290 | 0 | 0 | 8 |
| 6     | 5   | 6    | .388 | 1 | 4 | 11 |
| 7     | 1   | 16   | .508 | 2 | 0 | 12 |
| 8     | 3   | 11   | .665 | 5 | 0 | 10 |
| 9     | 2   | 19   | .851 | 0 | 0 | 13 |
| 10    | 3   | 18   | 1.063 | 8 | 0 | 16 |
| 11    | 4   | 5    | 1.297 | 3 | 6 | 15 |
| 12    | 1   | 13   | 1.599 | 7 | 0 | 15 |
| 13    | 2   | 7    | 2.027 | 9 | 0 | 17 |
| 14    | 14  | 15   | 2.529 | 0 | 0 | 17 |
| 15    | 1   | 4    | 3.294 | 12 | 11 | 16 |
| 16    | 1   | 3    | 4.578 | 15 | 10 | 18 |
| 17    | 2   | 14   | 6.575 | 13 | 14 | 18 |
| 18    | 1   | 2    | 13.573 | 16 | 17 | 0 |

**Explanation of the agglomeration procedure in Table S-2**

Stage 1, calculate the Euclidean distance between each pair (18 clusters). Then combine the two clusters that have the smallest Euclidean distance between them to form a new case. Now the whole cases are 17 clusters.

Stage 2, Then SPSS will recompute the distance measures between all single cases (17 clusters). The two cases (or clusters) with the smallest distance will be combined (repeat stage 1), yielding a new case. Now the whole cases become 16 clusters.

Stage 3, Repeat stage 1 and 2 until the last case. Now the whole cases become just only one big cluster.
Figure S-1. Dendrogram produced by Hierarchical Clustering Analysis of ABTS and DPPH assays for carotenoids 1a–1r (Table 1, entries 1–18). The clusters demonstrated the similarities in the structure of the aromatic rings and radical scavenging activity of the carotenoids (see Table 1).
2. Comparison of Antioxidant Activities

Table S-3. Comparison of antioxidant activities of the selected carotenoids 1a, 1d, 1j, 1n, and 1q with those of β-carotene and lycopene by EC$_{50}$ (mol/L) in ABTS and DPPH assays (Data for Figure 1)

| entry | carotenoid | R | ABTS  | DPPH  |
|-------|------------|---|-------|-------|
|       |            |   | EC$_{50}$ (mol/L) | EC$_{50}$ (mol/L) |
| 1     | β-Carotene |   | 0.06917±0.0004 | 0.7794±0.0005 |
| 2     | Lycopene   |   | 0.06608±0.0002 | 0.7277±0.0092 |
| 3     | a          |   | 0.05515±0.0005 | 0.4829±0.0013 |
| 4     | d          |   | 0.10350±0.0020 | 1.3172±0.0072 |
| 5     | j          |   | 0.14831±0.0020 | 2.0398±0.0124 |
| 6     | n          |   | 0.68709±0.0038 | 4.7315±0.0092 |
| 7     | q          |   | 0.68821±0.0049 | 4.7726±0.0387 |
3. Experimental Section

General experimental. $^1$H and $^{13}$C NMR spectra were respectively recorded on a 400 MHz and 100 MHz NMR spectrometer in CDCl$_3$ with tetramethylsilane as an internal reference unless noted otherwise. The column chromatography was performed by the method of Still with silica gel 60, 70-230 mesh ASTM using a gradient mixture of EtOAc/hexanes. Reactions were performed in a well-dried flask under argon atmosphere unless noted otherwise.

Diethyl 4-bromo-3-methylbut-2-enylphosphonate (7).

To a stirred mixture of isoprene (15 mL, 0.15 mol) in H$_2$O (60 mL) and was added N-bromosuccinimide (24.0 g, 0.135 mol) in a cold-water bath. The mixture was stirred at that temperature for 2 h, extracted with CH$_2$Cl$_2$, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give bromohydrin $A$ (21.66 g, 0.13 mol).

To a stirred solution of bromohydrin $A$ (21.66 g, 0.13 mol) in benzene (80 mL) and THF (10 mL) at 0 °C under argon atmosphere were added CuI (257 mg, 1.35 mmol) and then PBr$_3$ (5.1 mL, 52.17 mmol). The mixture was stirred at 0 °C for 2 h and filtered through a short pad of SiO$_2$ with a 2:1 mixture of hexane/Et$_2$O (200 mL). The filtrate was concentrated under reduced pressure to give a 4:1 $E/Z$ mixture of 1,4-dibromo-2-methylbut-2-ene ($6$) (21.49 g, 94.28 mmol) in 70% overall yield.

To a stirred solution of 1,4-dibromide $6$ (21.49 g, 94.28 mmol, 4:1 $E/Z$) in benzene (80 mL) was added triethyl phosphite (15.67 g, 94.28 mmol). The mixture was heated to reflux for 2 h under argon atmosphere and cooled to room temperature. The resulting mixture was diluted with EtOAc, washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated to give crude bromophosphonate (25.31 g), which was purified by SiO$_2$ flash column chromatography to give $7$ (16.56 g, 58.08 mmol, 4:1 $E/Z$) in 62% yield as clear oil. Data for (E)-$7$: R$_f$ = 0.28 (100% EtOAc); $^1$H-NMR $\delta$ = 1.32 (t, $J$ = 7.2 Hz, 6H), 1.82 (d, $J$ = 3.6 Hz, 3H), 2.60 (dd, $J$ = 22.4, 8.0 Hz, 2H), 3.99 (d, $J$ = 2.8 Hz, 2H), 4.03–4.20 (m, 4H), 5.66 (dt, $J_d$ = 7.6, $J_t$ = 7.2 Hz, 1H) ppm; $^{13}$C-NMR $\delta$ = 14.9, 16.4 (d, $J$
= 5.9 Hz), 26.9 (d, $J = 139.8$ Hz), 40.1 (d, $J = 2.3$ Hz), 61.9 (d, $J = 6.7$ Hz), 119.3 (d, $J = 11.1$ Hz), 136.4 (d, $J = 14.1$ Hz) ppm; IR (KBr) $\nu = 2995, 2930, 1745, 1446, 1373, 1237, 1176, 1028, 971, 876, 790, 737$ cm$^{-1}$; HRMS (CI$^+$) calcd for C$_{9}$H$_{19}$BrO$_{3}$P 285.0255, found 285.0255.

**Diethyl 4-(benzo[d]thiazol-2-ylthio)-3-methylbut-2-enylphosphonate (B).** To a stirred solution of bromo-phosphonate 7 (3.00 g, 10.52 mmol, 4:1 $E/Z$) in acetone (50 mL) were added 2-mercaptobenzothiazole (1.76 g, 10.52 mmol) and anhydrous K$_2$CO$_3$ (2.91 mmol, 21.04 mmol). The mixture was stirred vigorously at room temperature for 16.5 h, diluted with Et$_2$O, and washed with brine and H$_2$O. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated to give 3.65 g of bright yellow oily product, which was purified by SiO$_2$ flash column chromatography to give sulfide B (3.05 g, 8.21 mmol, 4:1 $E/Z$) in 78% yield as clear oil. Data for ($E$)-B: R$_f = 0.27$ (100% EtOAc); $^1$H NMR $\delta = 1.26$ (t, $J = 7.2$ Hz, 6H), 1.83 (d, $J = 3.6$ Hz, 3H), 2.60 (dd, $J = 22.4, 8.0$ Hz, 2H), 3.98–4.19 (m, 4H), 4.05 (d, $J = 2.4$ Hz, 2H), 5.64 (dt, $J_d = 7.6, J_t = 6.8$ Hz, 1H), 7.29 (dt, $J_d = 1.2, J_t = 8.0$ Hz, 1H), 7.41 (dt, $J_d = 1.2$ Hz, $J_t = 8.0$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H) ppm; $^{13}$C NMR $\delta = 15.4$ (d, $J = 2.2$ Hz), 16.2 (d, $J = 5.9$ Hz), 26.6 (d, $J = 139.0$ Hz), 42.1, 61.7 (d, $J = 6.7$ Hz), 118.5 (d, $J = 11.2$ Hz), 120.7, 121.3, 124.1, 125.8, 134.3 (d, $J = 14.1$ Hz), 152.9, 166.2 ppm; IR (KBr) $\nu = 2987, 2903, 1749, 1473, 1428, 1380, 1248, 1308, 1248, 1172, 1036, 1000, 956, 803, 767, 727, 675$ cm$^{-1}$; HRMS (CI$^+$) calcd for C$_{16}$H$_{23}$NO$_{3}$PS$_{2}$ 372.0857, found 372.0857.

**Diethyl 4-(benzo[d]thiazol-2-ylsulfonyl)-3-methylbut-2-enylphosphonate (8).** The mixture of Urea-H$_2$O$_2$ (4.30 g, 45.71 mmol) and phthalic anhydride (3.39 g, 22.86 mmol) in MeCN (40 mL) was stirred vigorously at room temperature for 2.5 h under argon atmosphere to give a clear solution of mono-perphthalic acid. To this solution was added a solution of sulfide B (2.83 g, 7.62 mmol) in CH$_2$Cl$_2$ (10 mL). The reaction mixture was stirred vigorously at room temperature for 1 d under argon atmosphere. The resulting white suspension was diluted with CH$_2$Cl$_2$, filtered to remove white solid, and the filtrate was concentrated. This process was
repeated once again to give the crude product (3.66 g) as light orange oil, which was purified by SiO2 flash column chromatography to give 8 (2.43 g, 6.03 mmol, 6:1 E/Z) in 79% yield as clear oil. Data for (E)-8: Rf = 0.24 (100% EtOAc); 1H NMR δ = 1.24 (t, J = 7.2 Hz, 6H), 1.92 (d, J = 4.4 Hz, 3H), 2.55 (dd, J = 22.4, 8.0 Hz, 2H), 3.93–4.05 (m, 4H), 4.24 (d, J = 2.0 Hz, 2H), 7.60 (dt, Jd = 1.2, Ji = 8.0 Hz, 1H), 7.54 (dt, Jd = 1.2, Ji = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H) ppm; 13C NMR δ = 16.3 (d, J = 5.9 Hz), 17.2 (d, J = 2.2 Hz), 27.1 (d, J = 139.1 Hz), 61.9 (d, J = 6.7 Hz), 63.9 (d, J = 3.0 Hz), 122.2, 125.4, 125.8 (d, J = 11.1 Hz), 126.6 (d, J = 14.9 Hz), 127.6, 128.0, 136.8, 152.6, 165.5 ppm; IR (KBr) ν = 2985, 2926, 1743, 1482, 1397, 1334, 1250, 1145, 1031, 972, 875, 807, 773, 740, 643 cm⁻¹; HRMS (Cl⁺) calcd for C₁₆H₂₃NO₅PS₂ 404.0755, found 404.0755.

(E)-Diethyl 3-methylbuta-1,3-dienylphosphonate (9). To a stirred solution of BT-sulfonyl phosphonate 8 (2.08 g, 5.16 mmol) in THF (30 mL) at -78 ºC under argon atmosphere was added 1 M THF solution of NaHMDS (5.4 mL, 5.4 mmol). The resulting red solution was stirred vigorously at -78 ºC for 20 min, β-cyclocitral (1.0 mL, 943 mg, 6.19 mmol) was added. The reaction mixture was stirred at -78 ºC for 1 h, warmed to and stirred at 0 ºC for 1.5 h, and quenched with 10% NH₄Cl solution. The mixture was extracted with Et₂O and washed with brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give orange-red oily product (2.73 g), which was purified by SiO2 flash column chromatography to give β-cyclocitral (100% recovery), 2-hydroxybenzothiazole (191 mg, 1.26 mmol) in 24% yield as off-white solid, and dienyl phosphonate 9 (253 mg, 1.24 mmol) in 24% yield as light orange oil. Data for 9: Rf = 0.39 (100% EtOAc); 1H NMR δ = 1.23 (t, J = 7.2 Hz, 6H), 1.77 (br s, 3H), 3.94–4.05 (m, 4H), 5.21 (br s, 1H), 5.23 (dd, J = 2.0, 1.2 Hz, 1H), 5.57 (dd, J = 18.0, 17.6 Hz, 1H), 7.07 (dd, J = 22.4, 17.6 Hz, 1H) ppm; 13C NMR δ = 16.3 (d, J =
2-(4-Bromo-3-methylbut-2-enylthio)benzo[d]thiazole (C) and 2,2’-(2-methylbut-2-ene-1,4-diyl)bis(sulfanediyl)dibenzo[d]thiazole (D). To a stirred solution of 1,4-dibromo-2-methylbut-2-ene (6) (21.34 g, 93.63 mmol, 4:1 E/Z) in acetone (100 mL) at 0 ºC were added 2-mercaptobenzothiazole (15.66 g, 93.63 mmol) and anhydrous K2CO3. The mixture was warmed to and stirred at room temperature overnight, diluted with Et2O, washed with brine and H2O, dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure to give orange oily product (28.39 g), which was purified by SiO2 flash column chromatography to give bromo-sulfide (17.27 g, 54.95 mmol, 4:1 E/Z) in 59% yield and disulfide (6.16 g, 15.38 mmol, 4:1 E/Z) in 16% yield as clear oils.

Data for (Z)-C: Rf = 0.57 (4:1 hexane:EtOAc); 1H NMR δ = 1.92 (s, 3H), 3.95 (s, 2H), 4.01 (d, J = 7.6 Hz, 2H), 5.86 (t, J = 7.6 Hz, 1H), 7.30 (dt, Jd = 1.2, Jt = 8.0 Hz, 1H), 7.42 (dt, Jd = 1.2, Jt = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H) ppm; 13C NMR δ = 15.1, 31.3, 39.8, 121.0, 121.5, 124.3, 124.3, 126.0, 135.4, 137.1, 153.1, 165.8 ppm; IR (KBr) ν = 3070, 2927, 1737, 1562, 1469, 1562, 1461, 1426, 1312, 1278, 1238, 1207, 1138, 1081, 993, 906, 849, 753, 731, 666 cm⁻¹; HRMS (Cl⁺) calcd for C12H13BrNS2 313.9673, found 313.9670.

Data for (E)-C: Rf = 0.54 (4:1 hexane:EtOAc); 1H NMR δ = 1.91 (s, 3H), 4.22 (d, J = 8.0 Hz, 2H), 4.23 (s, 2H), 5.65 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.39 (ddt, Jd = 3.2, 1.2, Jt = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H) ppm; 13C NMR δ = 22.9, 31.3, 34.7, 120.9, 121.5, 124.1, 124.3, 126.0, 135.2, 135.4, 153.2, 166.3 ppm; IR (KBr) ν = 3070, 2987, 1749, 1555, 1476, 1434, 1393, 1309, 1240, 1238, 1134, 1088, 994, 938, 860, 753, 731, 675 cm⁻¹; HRMS (Cl⁺) calcd for C12H13BrNS2 313.9673, found 313.9668.
Data for (E)-D: Rf = 0.50 (4:1 hexane:EtOAc); $^1$H NMR $\delta = 1.94$ (s, 3H), 3.99 (d, $J = 7.6$ Hz, 2H), 4.00 (s, 2H), 5.86 (t, $J = 7.6$ Hz, 1H), 7.25 (dt, $J_d = 1.2$, $J_t = 8.0$ Hz, 1H), 7.27 (dt, $J_d = 1.2$, $J_t = 8.0$ Hz, 1H), 7.37 (dt, $J_d = 1.2$, $J_t = 8.0$ Hz, 1H), 7.40 (dt, $J_d = 1.2$, $J_t = 8.0$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H) ppm; $^{13}$C NMR $\delta = 15.6$, 31.3, 42.2, 120.8, 120.9, 121.5, 121.5, 123.8, 124.2, 124.2, 126.0, 135.2, 135.3, 135.4, 135.4, 153.0, 153.1, 165.1, 165.1 ppm; IR (KBr) $\nu = 3074$, 2997, 2912, 1743, 1684, 1561, 1472, 1429, 1387, 1297, 1280, 1229, 1136, 1072, 996, 936, 906, 753, 728, 711, 673 cm$^{-1}$; HRMS (Cl$^+$) calcd for C$_{19}$H$_{17}$N$_2$S$_4$ 401.0275, found 401.0269.

(E)-2-(4-Bromo-3-methylbut-2-enylsulfonyl)benzo[d]thiazole (10). [Method 1] The mixture of Urea-H$_2$O$_2$ (11.93 g, 0.127 mol) and phthalic anhydride (9.39 g, 63.42 mmol) in MeCN (80 mL) was stirred vigorously at room temperature for 1.5 h under argon atmosphere to give a clear solution of mono-perphthalic acid. To this solution was added a solution of bromo-sulfide C (6.64 g, 21.14 mmol) in CH$_2$Cl$_2$ (10 mL). The reaction mixture was stirred vigorously at room temperature for 20 h under argon atmosphere. The resulting white suspension was diluted with CH$_2$Cl$_2$, filtered to remove white solid, and the filtrate was concentrated. This process was repeated once again to give the crude product (3.66 g) as orange-red oil, which was purified by SiO$_2$ flash column chromatography to give 10 (2.82 g, 8.16 mmol) in 39% yield as white solid. The pure E-isomer was obtained by trituration with Et$_2$O.

[Method 2] To a stirred suspension of bromo-sulfide C (10.60 g, 33.73 mmol) in MeOH (65 mL) were added Na$_2$WO$_4$·2H$_2$O (556 mg, 1.69 mmol) and 34.5% H$_2$O$_2$ solution (8.31 g, 84.33 mmol). The reaction mixture was stirred vigorously at room temperature for 11 h, and most of solvent was removed under reduced pressure. The crude product was diluted with CH$_2$Cl$_2$, washed with 1 M HCl, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated to sticky oily product (10.97 g), which was solidified under vacuum pump (10.70 g). The crude product was purified by trituration with Et$_2$O to give (E)-10 (3.44 g, 9.95 mmol) in 29% yield as light-yellow solid.
Data for (E)-10: Rf = 0.21 (4:1 hexane:EtOAc); 1H NMR δ = 1.71 (s, 3H), 3.87 (s, 2H), 4.27 (d, J = 8.0 Hz, 2H), 5.69 (t, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H) ppm; 13C NMR δ = 15.4, 38.2, 54.6, 114.4, 122.3, 125.4, 127.7, 128.1, 137.0, 143.5, 152.6, ppm; IR (KBr) ν = 2978, 2924, 1754, 1554, 1481, 1372, 1329, 1238, 1216, 1151, 1086, 1022, 909, 865, 765, 735, 700, 640, 618 cm⁻¹; HRMS (CI⁺) calcd for C₁₂H₁₃BrNO₂S₂ 347.9571, found 347.9575.

(E)-Diethyl 4-(benzo[d]thiazol-2-ylsulfonyl)-2-methylbut-2-enylphosphonate (5). The mixture of bromo-sulfone (E)-10 (3.45 g, 9.96 mmol) and triethyl phosphite (1.66 g, 9.96 mmol) in benzene (45 mL) was heated to reflux for 2 d under argon atmosphere. The mixture was diluted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give orange-yellow oil (4.26 g), which was purified by SiO₂ flash column chromatography (33%~70% Acetone/hexane) to give (E)-5 (1.20 g, 2.98 mmol) in 30% yield as light-yellow oil. Data for (E)-5: Rf = 0.25 (100% EtOAc); 0.32 (1:1 acetone/hexane); 1H NMR δ = 1.26 (t, J = 7.2 Hz, 6H), 1.78 (d, J = 2.8 Hz, 3H), 2.59 (d, J = 22.4 Hz, 2H), 4.04 (dq, Jd = 7.6, Jq = 7.2 Hz, 4H), 4.30 (dd, J = 7.6, 3.6 Hz, 2H), 5.45 (dt, Jd = 5.6, Ji = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H) ppm; 13C NMR δ = 16.3 (d, J = 6.0 Hz), 18.0 (d, J = 2.2 Hz), 37.1 (d, J = 136.9 Hz), 54.5 (d, J = 3.0 Hz), 61.9 (d, J = 6.7 Hz), 113.3 (d, J = 12.6 Hz), 122.3, 125.3, 127.6, 128.0, 136.9, 139.0 (d, J = 11.1 Hz), 152.6, 165.6 ppm; IR (KBr) ν = 3001, 2920, 1741, 1471, 1395, 1338, 1249, 1154, 1017, 969, 855, 770, 732, 690, 637 cm⁻¹; HRMS (CI⁺) calcd for C₁₆H₂₃NO₅PS₂ 404.0755, found 404.0759.

2-(4-Chloro-3-methylbut-2-enythio)benzo[d]thiazole (F). The mixture of isoprene (24.0 mL, 0.24 mol) and N-chlorosuccinimide (26.7 g, 0.20 mol) in H₂O (100 mL) and DMF (25 mL) was stirred vigorously at 40 °C for 2 d under argon atmosphere. The mixture was extracted with Et₂O, dried over anhydrous Na₂SO₄, filtered, and concentrated to give chlorohydrin E (18.8 g, 0.16 mol) in 78% yield as clear liquid. The crude product was pure enough not to be required for further
purification. Data for E: Rf = 0.44 (4:1 hexane:EtOAc); ¹H NMR δ = 1.38 (s, 3H), 2.17 (br s, 1H), 3.53 (A of ABq, J_AB = 10.8 Hz, 1H), 3.57 (B of ABq, J_AB = 10.8 Hz, 1H), 5.21 (dd, J = 10.7, 1.0 Hz, 1H), 5.38 (dd, J = 17.3, 1.0 Hz, 1H), 5.92 (dd, J = 17.3, 10.7 Hz, 1H) ppm; ¹³C NMR δ = 25.3, 54.0, 72.5, 114.7, 141.9 ppm.

To a stirred mixture of chlorohydrin E (13.87 g, 0.12 mol) in benzene (80 mL) and THF (10 mL) were added CuI (220 mg, 1.15 mmol) and PBr₃ (4.5 mL, 46.03 mmol) at 0 ºC under argon atmosphere. The mixture was stirred vigorously at that temperature for 2.5 h, filtered through a short pad of SiO₂ with a 3:1 mixed solution of Et₂O/hexane (120 mL). The filtrate was concentrated under reduced pressure to give 4-chloroallylic bromide 11 (19.50 g, 0.11 mol, 5:1 E/Z) in 92% yield as yellow liquid. Data for 11: Rf = 0.73 (4:1 hexane:EtOAc); ¹H NMR δ = 1.85 (s, 3H), 3.98 (dd, J = 8.3, 0.9 Hz, 2H), 4.03 (s, 2H), 5.87 (dt, J_t = 8.3, J_d = 0.9 Hz, 1H) ppm; ¹³C NMR δ = 14.1, 27.3, 50.6, 125.3, 137.8 ppm.

To a stirred mixture of 4-chloroallylic bromide 11 (19.49 g, 0.106 mol) and 2-mercaptobenzothiazole (16.15 g, 96.57 mmol) in acetone (100 mL) at 0 ºC was added anhydrous K₂CO₃ (20.02 g, 0.145 mol). The mixture was stirred vigorously under argon atmosphere at 0 ºC for 2 h, and slowly warmed to and stirred at room temperature for 11 h. The mixture was diluted with Et₂O, and washed with H₂O, 10% NaHCO₃ solution, and brine. The aqueous layer was extracted with Et₂O. The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give F (27.05 g, 0.100 mol) in 95% yield as yellow brown oil. The crude product was very pure and consisted of a 7:1 E/Z mixture according to the ¹H NMR spectrum. Data for (E)-F: Rf = 0.61 (4:1 hexane:EtOAc); ¹H NMR δ = 1.90 (s, 3H), 4.02 (s, 2H), 4.03 (d, J = 7.6 Hz, 2H), 5.82 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H) ppm; ¹³C NMR δ = 14.4, 30.9, 51.0, 120.8, 121.4, 123.7, 124.1, 125.9, 135.2, 136.7, 153.0, 165.8 ppm; IR (KBr) ν = 2989, 1473, 1436, 1321, 1275, 1243, 1078, 1004, 871, 765, 687, 724 cm⁻¹; HRMS (Cl⁺) calcd for C₁₂H₁₃ClNS₂ 270.0178, found 270.0180.
2-(4-Chloro-3-methylbut-2-enylsulfonyl)benzo[d]thiazole (12). [Method A] To a stirred solution of F (27.00 g, 0.100 mol) in MeOH (100 mL) and benzene (20 mL) under a cold-water bath were added Na₂WO₄·2H₂O (1.65 g, 5.00 mmol) and 34.5% H₂O₂ solution (24.64 g, 0.25 mol). The mixture was stirred vigorously overnight under argon atmosphere, and most of solvents was removed (not to dryness!). The crude mixture was diluted with CH₂Cl₂, washed with 1 M HCl and H₂O, dried over anhydrous Na₂SO₄, filtered, and concentrated to give ivory solid (28.26 g). The crude product was suspended in MeOH, filtered through a sintered glass funnel (to complete dryness) to give pure 12 (15.49 g, 51.32 mmol) in 51% yield as white solid. The product 12 was consisted of a 10:1 E/Z mixture according to the ¹H NMR spectrum.

[Method B] The mixture of Urea-H₂O₂ (44.35 g, 471.4 mmol) and phthalic anhydride (38.90 g, 235.7 mmol) in MeCN (150 mL) was stirred vigorously at room temperature for 1.5 h under argon atmosphere to give a clear solution of mono-perphthalic acid. To this solution was added a solution of chloro-sulfide F (21.20 g, 78.57 mmol) in CH₂Cl₂ (10 mL). The reaction mixture was stirred vigorously at room temperature for 12 h under argon atmosphere. The resulting white suspension was diluted with CH₂Cl₂, filtered to remove white solid. The filtrate was diluted with CH₂Cl₂, washed with H₂O, dried over anhydrous Na₂SO₄, filtered, and concentrated to give ivory solid. The crude product was suspended in MeOH, filtered through a sintered glass funnel (to complete dryness) to give (E)-12 (17.15 g, 56.82 mmol) in 72% yield as white solid.

Data for (E)-12: Rf = 0.22 (4:1 hexane:EtOAc); ¹H NMR δ = 1.70 (s, 3H), 3.95 (s, 2H), 4.29 (d, J = 7.6 Hz, 2H), 5.66 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H) ppm; ¹³C NMR δ = 14.0, 49.1, 53.4, 113.1, 121.4, 124.5, 126.8, 127.2, 136.1, 142.3, 151.7, 165.8 ppm; IR (KBr) ν = 2986, 2924, 1558, 1473, 1398, 1328, 1257, 1140, 1088, 1037, 910, 868, 765, 736, 689 cm⁻¹; HRMS (Cl⁺) calcd for C₁₂H₁₃ClNO₂S₂ 302.0076, found 302.0075.

Diethyl 4-(benzo[d]thiazol-2-ylsulfonyl)-2-methylbut-2-enylphosphonate (5).
**[Method 1]** The mixture of 12 (14.02 g, 47.06 mmol) and triethyl phosphite (8.1 mL, 47.06 mmol) in toluene (50 mL) was heated to gentle reflux for 4 d under argon atmosphere. Solvent was removed under reduced pressure to give dark brown oily crude product (18.55 g), which was purified by SiO$_2$ flash column chromatography (30%~100% acetone/hexane) to give (E)-5 (2.50 g, 6.20 mmol) in 13% yield as orange-yellow oil.

**[Method 2]** To a stirred solution of 12 (12.81 g, 42.44 mmol) in acetone (120 mL) was added NaI (9.54 g, 63.66 mmol). The mixture was stirred vigorously at room temperature for 8 h under argon atmosphere. The mixture was diluted with Et$_2$O, washed with H$_2$O and saturated Na$_2$S$_2$O$_3$ solution, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give yellow solid. The crude product was dissolved in toluene (100 mL) and triethyl phosphite (10.92 g, 63.66 mmol) was added. The mixture was then heated to reflux for 12 h under argon atmosphere. Most of solvent was removed under reduced pressure, and the crude product was purified by SiO$_2$ flash column chromatography (30%~100% hexane/acetone) to give 5 (12.95 g, 32.1 mmol, $E/Z = 4:1$) in 76% yield as yellow oil.

Data for (Z)-5: R$_f$ = 0.45 (1:1 acetone/hexane); $^1$H NMR $\delta$ = 1.31 (t, $J$ = 7.2 Hz, 6H), 1.91 (d, $J$ = 2.4 Hz, 3H), 2.65 (d, $J$ = 23.2 Hz, 2H), 4.04–4.15 (m, 4H), 4.37 (dd, $J$ = 8.0, 3.2 Hz, 2H), 5.49 (q, $J$ = 7.2 Hz, 1H), 7.60 (dt, $J_d$ = 1.2, $J_t$ = 7.6 Hz, 1H), 7.65 (dt, $J_d$ = 1.2, $J_t$ = 7.6 Hz, 1H), 8.02 (d, $J$ = 7.6 Hz, 1H), 8.22 (d, $J$ = 7.6 Hz, 1H) ppm; $^{13}$C NMR $\delta$ = 16.1 (d, $J$ = 5.9 Hz), 25.3 (d, $J$ = 2.2 Hz), 30.2 (d, $J$ = 135.4 Hz), 54.1 (d, $J$ = 3.0 Hz), 61.8 (d, $J$ = 7.4 Hz), 112.7 (d, $J$ = 11.9 Hz), 122.1, 125.0, 127.4, 127.8, 136.5, 138.2 (d, $J$ = 11.9 Hz), 152.2, 165.5 ppm.

**Tetraethyl (2E,4E,6E,8E,10E,12E,14E)-2,6,11,15-tetramethylhexadeca-2,4,6,8,10,12,14-heptaene-1,16-diylphosphonate (4).** To a stirred solution of (E)-5 (1.46 g, 3.62 mmol, 2.9 equiv.) and 2,7-dimethylocta-2,4,6-trienedial (2) (198 mg, 1.21 mmol, 1 equiv.) in THF (36 mL) at -78 °C under argon atmosphere was slowly added 1 M THF solution of NaHMDS (4.0 mL, 4.0 mmol, 3.1 equiv) for 15 min. The light-
yellow solution slowly turned to red upon addition. The mixture was stirred vigorously at -78 ºC for 1.5 h, and warmed to and stirred at room temperature for 3.5 h. The reaction mixture was quenched with 10% NH₄Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude red oil (1.52 g) was purified by SiO₂ flash column chromatography (30%~100% acetone/hexane) to give 4 (422 mg, 0.78 mmol, 6:1 all-E/Z mixture) in 64% yield as orange solid. Data for (E)-4: Rf = 0.19 (1:1 acetone/hexane); ¹H NMR δ = 1.31 (t, J = 7.2 Hz, 12H), 1.94 (s, 6H), 1.96 (d, J = 4.4 Hz, 6H), 2.65 (d, J = 23.2 Hz, 2H), 4.10 (dq, Jd = 7.2, Jq = 7.2 Hz, 8H), 6.05 (dd, J = 10.8, 5.6 Hz, 2H), 6.16–6.28 (m, 2H), 6.27 (dd, J = 15.2, 2.4 Hz, 2H), 6.46 (dd, J = 15.2, 10.8 Hz, 2H), 6.56–6.66 (m, 2H) ppm; ¹³C NMR δ = 12.7, 16.5 (d, J = 6.7 Hz), 18.2 (d, J = 3.0 Hz), 37.5 (d, J = 136.0 Hz), 61.9 (d, J = 6.7 Hz), 127.2 (d, J = 6.7 Hz), 128.5 (d, J = 14.2 Hz), 129.8, 130.2 (d, J = 14.1 Hz), 132.2, 136.0, 137.7 (d, J = 6.7 Hz) ppm; IR (KBr) 2995, 2915, 1734, 1679, 1456, 1385, 1251, 1166, 1023, 960, 847, 783, 733 cm⁻¹; HRMS (FAB⁺) calcd for C₂₈H₄₆O₆P₂ 540.2770, found 540.2769.

6,6’-((1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(1,2,3,4-tetramethoxy-5-methylbenzene) (1a). General procedure: To a stirred solution of bis(phosphonate) 4 (423 mg, 0.782 mmol) and 1,2,3,4-tetramethoxy-5-methylbenzaldehyde (940 mg, 3.91 mmol) in MeOH (30 mL) and toluene (30 mL) was added potassium methoxide (1.37 g, 19.55 mmol). The mixture was heated at 110 ºC for 12 h under argon atmosphere. Most of solvent was removed under reduced pressure. The crude mixture was diluted with Et₂O and washed with 10% NH₄Cl solution and H₂O. The aqueous layer was extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1a (134 mg, 0.187 mmol, all-E/9’-Z = 3:1) in 24% yield as dark red solid. Data for all-(E)-1a: Rf = 0.35 (4:1 hexane/EtOAc); ¹H NMR δ = 2.00 (s, 6H), 2.07 (s, 6H), 2.25 (s, 6H), 3.77 (s, 6H), 3.79 (s, 6H), 3.92 (s, 6H), 3.94 (s, 6H),
6.22–6.37 (m, 2H), 6.29 (d, J = 11.2 Hz, 2H), 6.41 (d, J = 15.2 Hz, 2H), 6.56 (d, J = 16.4 Hz, 2H), 6.60–6.72 (m, 2H), 6.69 (dd, J = 15.2, 11.2 Hz, 2H), 6.86 (d, J = 16.4 Hz, 2H) ppm; 13C NMR δ = 12.6, 12.8, 13.0, 60.5, 60.7, 61.2, 61.3, 121.5, 125.0, 125.1, 126.6, 130.2, 132.8, 132.9, 136.2, 136.6, 138.1, 138.6, 144.9, 145.7, 148.0, 148.1 ppm; UV (CH2Cl2, c = 2.39 × 10⁻⁵) λ (ε) = 452 (36,700), 474 (37,600) nm; IR (KBr) 2989, 2937, 2855, 2833, 1729, 1677, 1565, 1469, 1409, 1349, 1267, 1193, 1111, 1081, 1066, 1036, 1014, 969, 887, 753 cm⁻¹; HRMS (FAB) calcd for C44H56O8 712.3975, found 712.3967.

(((1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(3,5-dimethyl-4,1-phenylene))bis(methylsulfane) (1b). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (179 mg, 0.331 mmol) and 2,6-dimethyl-4-(methylthio)benzaldehyde (300 mg, 1.66 mmol) with potassium methoxide (580 mg, 8.27 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid products, which was purified by recrystallization from MeOH to give carotene 1b (56 mg, 0.094 mmol, all-E) in 29% yield as dark red solid. Data for all-(E)-1b: Rf = 0.66 (4:1 hexane/EtOAc); m.p.: 194 °C; 1H-NMR δ = 1.99 (s, 6H), 2.07 (s, 6H), 2.31 (s, 12H), 2.47 (s, 6H), 6.23 (d, J = 11.6 Hz, 2H), 6.23–6.33 (m, 2H), 6.37 (d, J = 16.4 Hz, 2H), 6.40 (d, J = 14.8 Hz, 2H), 6.54 (d, J = 16.4 Hz, 2H), 6.60–6.70 (m, 2H), 6.68 (dd, J = 14.8, 11.6 Hz, 2H), 6.96 (s, 4H) ppm; 13C-NMR δ = 12.4, 12.5, 15.6, 20.9, 124.5, 124.8, 125.8, 129.9, 132.1, 132.6, 134.1, 135.2, 135.5, 136.3, 136.4, 137.8, 138.5 ppm; UV (CH2Cl2, c = 3.35 × 10⁻⁵) λ (ε) = 472 (128,000) nm; IR (KBr) 3032, 2932, 1744, 1666, 1589, 1551, 1451, 1366, 1219, 964, 772 cm⁻¹; HRMS (FAB) calcd for C40H48S2 592.3197, found 592.3196.

2,2’-(((1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(1,3,5-trimethoxybenzene) (1c). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (157 mg, 0.29
mmol) and 2,4,6-trimethoxybenzaldehyde (285 mg, 1.45 mmol) with potassium methoxide (509 mg, 7.26 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1c (80.9 mg, 0.130 mmol, all-E/9'-Z = 2:1) in 45% yield as dark red solid. Data for all-(E)-1c: \( R_f = 0.55 \) (3:2 hexane/EtOAc); \(^1\)H NMR \( \delta = 1.99 \) (s, 6H), 2.05 (s, 6H), 3.83 (s, 6H), 3.86 (s, 12H), 6.15 (s, 4H), 6.21–6.31 (m, 2H), 6.28 (d, \( J = 11.2 \) Hz, 2H), 6.37 (d, \( J = 14.8 \) Hz, 2H), 6.58–6.68 (m, 2H), 6.70 (dd, \( J = 14.8, 11.2 \) Hz, 2H), 6.87 (d, \( J = 16.0 \) Hz, 2H), 7.28 (d, \( J = 16.0 \) Hz, 2H) ppm; \(^{13}\)C NMR \( \delta = 12.5, 12.8, 55.3, 55.7, 118.7, 120.2, 125.5, 129.9, 131.5, 132.1, 132.2, 135.2, 136.5, 136.8, 137.7, 159.2, 159.9 \) ppm; UV (CH\(_2\)Cl\(_2\), \( c = 1.20 \times 10^{-5} \)) \( \lambda (\varepsilon) = 495 \) (76,900) nm; IR (KBr) \( \nu = 2997, 2937, 2833, 1603, 1461, 1416, 1319, 1200, 1155, 1118, 1059, 1036, 969, 813, 753, 634 \) cm\(^{-1}\); HRMS (FAB) calcd for C\(_{40}\)H\(_{48}\)O\(_6\) 624.3451, found 624.3448.

Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (106 mg, 0.196 mmol) and 4-(diphenylamino)benzaldehyde (268 mg, 0.98 mmol) with potassium methoxide (344 mg, 4.9 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1d (67 mg, 0.086 mmol, all-E/9'-Z = 3:4) in 44% yield as dark red solid. Data for all-(E)-1d: \( R_f = 0.70 \) (4:1 hexane/EtOAc); \(^1\)H NMR \( \delta = 1.99 \) (s, 6H), 2.04 (s, 6H), 6.25–6.32 (m, 2H), 6.31 (d, \( J = 11.6 \) Hz, 2H), 6.40 (d, \( J = 15.2 \) Hz, 2H), 6.54 (d, \( J = 15.6 \) Hz, 2H), 6.62–6.69 (m, 2H), 6.68 (dd, \( J = 15.2, 11.6 \) Hz, 2H), 6.80 (d, \( J = 15.6 \) Hz, 2H), 7.00–7.34 (m, 28H) ppm; \(^{13}\)C NMR \( \delta = 12.8, 12.9, 122.9, 123.6, 124.4, 125.1, 126.0, 127.1, 129.2, 130.2, 132.0, 132.1, 132.5, 132.9, 135.8, 136.6, 137.8, 146.9, 147.5 ppm; UV (CH\(_2\)Cl\(_2\), \( c = 2.09 \times 10^{-5} \)) \( \lambda (\varepsilon) = 477 \) (40,200), 499 (44,000) nm; IR (KBr) \( \nu = 3034, 2922, 2855, 1737, 1588, 1491, 1327, 1282, 1178, 962, 895, 835, 753, 693 \) cm\(^{-1}\); HRMS (FAB) calcd for C\(_{58}\)H\(_{54}\)N\(_2\) 778.4287, found 778.4297.
4,4'-(1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diylbis(methoxybenzene) (1e).

Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (143 mg, 0.265 mmol) and p-anisaldehyde (180 mg, 1.32 mmol) with potassium methoxide (464 mg, 6.61 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1e (38.9 mg, 0.077 mmol, 9’-Z) in 29% yield as dark red solid. Data for 9’-(Z)-1e: Rf = 0.45 (4:1 hexane/EtOAc); 1H NMR δ = 1.99 (s, 3H), 2.02 (s, 3H), 2.04 (s, 6H), 3.82 (s, 3H), 3.83 (s, 3H), 6.13 (d, J = 11.2 Hz, 1H), 6.25–6.34 (m, 2H), 6.30 (d, J = 11.2 Hz, 1H), 6.33 (d, J = 14.8 Hz, 1H), 6.40 (d, J = 14.8 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 6.57 (d, J = 15.6 Hz, 1H), 6.60–6.72 (m, 2H), 6.67 (dd, J = 14.8, 11.2 Hz, 1H, calcd), 6.78 (d, J = 15.6 Hz, 1H), 6.80 (dd, J = 14.8, 11.2 Hz, 1H, calcd), 6.86 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 15.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H) ppm; 13C NMR δ = 12.8, 12.9, 12.9, 20.9, 55.3, 123.6, 123.7, 125.0, 127.0, 127.5, 127.5, 127.7, 128.7, 128.8, 130.0, 130.1, 130.6, 130.6, 131.1, 131.7, 132.2, 132.6, 132.8, 134.1, 135.7, 136.4, 136.5, 137.1, 137.7, 159.0, 159.2 ppm; UV (CH2Cl2, c = 5.65×10⁻⁵) λ (ε) = 483 (16,000), 515 (12,700) nm; IR (KBr) ν = 3019, 2915, 2840, 1737, 1595, 1506, 1461, 1439, 1327, 1305, 1252, 1170, 1111, 1029, 962, 857, 835, 813, 753, 663, 626, 544 cm⁻¹; HRMS (FAB) calcd for C36H40O2 504.3028, found 504.3029.

2,2'-(1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)difuran (1f).

Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (480 mg, 0.888 mmol) and 2-furaldehyde (427 mg, 4.44 mmol) with potassium methoxide (1.56 g, 22.2 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1f (152 mg, 0.36 mmol, all-E) in 40% yield as deep red solid. Data for all-(E)-1f: Rf = 0.78 (4:1 hexane/EtOAc); 1H NMR δ =
1.99 (s, 12H), 6.25–6.35 (m, 2H), 6.27 (d, J = 3.2 Hz, 2H), 6.33 (d, J = 11.6 Hz, 2H), 6.38 (d, J = 14.8 Hz, 2H), 6.40 (dd, J = 3.2, 1.6 Hz, 2H), 6.41 (d, J = 16.0 Hz, 2H), 6.61–6.70 (m, 2H), 6.66 (dd, J = 14.8, 11.6 Hz, 2H), 6.82 (d, J = 16.0 Hz, 2H), 7.36 (d, J = 1.6 Hz, 2H) ppm; 13C NMR δ = 12.6, 12.8, 108.0, 111.7, 115.3, 125.0, 130.3, 132.2, 133.1, 133.2, 135.1, 136.6, 138.2, 141.9, 153.9 ppm; UV (CH2Cl2, c = 1.18 × 10⁻⁵) λ (ε) = 460 (64,900), 487 (87,700), 522 (74,500) nm; IR (KBr) ν = 3146, 3116, 3027, 2982, 2919, 2855, 1733, 1718, 1703, 1674, 1655, 1603, 1551, 1480, 1439, 1390, 1379, 1252, 1219, 1152, 1073, 1014, 962, 928, 883, 753, 734 cm⁻¹; HRMS (FAB) calcd for C₃₀H₃₂O₂ 424.2402, found 424.2405.

(((1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(4,1-phenylene))bis(methylsulfane) (1g). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (605 mg, 1.12 mmol) and 4-(methylthio)benzaldehyde (852 mg, 5.6 mmol) with potassium methoxide (1.96 g, 27.98 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 ºC for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1g (251 mg, 0.468 mmol, 9'-Z) in 42% yield as dark red solid. Data for 9'-(Z)-1g: Rf = 0.60 (4:1 hexane/EtOAc); ¹H NMR δ = 1.99 (s, 3H), 2.03 (s, 3H), 2.04 (s, 6H), 2.49 (s, 3H), 2.50 (s, 3H), 6.16 (d, J = 11.6 Hz, 1H), 6.26–6.36 (m, 2H), 6.33 (d, J = 11.6 Hz, 1H), 6.35 (d, J = 14.8 Hz, 1H), 6.42 (d, J = 14.8, 1H), 6.53 (d, J = 14.8 Hz, 1H), 6.57 (d, J = 14.8 Hz, 1H), 6.60–6.70 (m, 2H), 6.67 (dd, J = 14.8, 11.6 Hz, 1H, calcd), 6.86 (d, J = 14.8 Hz, 1H), 6.88 (dd, J = 14.8, 11.6 Hz, 1H, calcd), 7.20 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 14.8 Hz, 1H, calcd), 7.40 (d, J = 8.0 Hz, 2H) ppm; ¹³C NMR (CDCl₃) δ = 12.8, 12.9, 12.9, 15.8, 15.8, 20.8, 123.5, 124.9, 125.0, 126.6, 126.7, 126.7, 126.8, 126.8, 126.8, 126.8, 126.9, 128.5, 130.2, 130.2, 130.3, 131.4, 132.9, 133.0, 133.1, 133.8, 134.7, 134.8, 135.5, 136.5, 136.5, 137.2, 137.5, 137.6, 138.2 ppm; IR (KBr) ν = 2975, 2932, 1750, 1442, 1383, 1231, 1064, 972, 902, 778 cm⁻¹; UV (CH₂Cl₂, c = 8.67×10⁻⁶) λ (ε) = 462 (53,000), 485 (60,000), 517 (45,000) nm; HRMS (FAB) calcd for C₃₆H₄₀S₂ 536.2571, found 536.2581.
4,4'-(1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(methylbenzene) (1h). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (228 mg, 0.422 mmol) and p-tolualdehyde (253 mg, 2.11 mmol) with potassium methoxide (740 mg, 10.6 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1h (129 mg, 0.274 mmol, 9'-Z) in 65% yield as dark red solid. Data for 9'-(Z)-1h: \( R_f = 0.75 \) (4:1 hexane/EtOAc); ^1H NMR \( \delta = 1.99 \) (s, 3H), 2.02 (s, 3H), 2.04 (s, 6H), 2.34 (s, 3H), 2.35 (s, 3H), 6.15 (d, \( J = 11.6 \) Hz, 1H), 6.24–6.34 (m, 2H), 6.32 (d, \( J = 11.6 \) Hz, 1H), 6.34 (d, \( J = 14.8 \) Hz, 1H), 6.41 (d, \( J = 14.8 \) Hz, 1H), 6.56 (d, \( J = 15.6 \) Hz, 1H), 6.60 (d, \( J = 15.6 \) Hz, 1H), 6.59–6.72 (m, 2H), 6.67 (dd, \( J = 14.8, 11.6 \) Hz, 1H), 6.86 (d, \( J = 16.0 \) Hz, 1H), 6.88 (dd, \( J = 14.8, 11.6 \) Hz, 1H), 7.08–7.20 (m, 4H), 7.30–7.40 (m, 4H), 7.39 (d, \( J = 16.0 \) Hz, 1H) ppm; ^13C NMR \( \delta = 12.8, 12.9, 20.9, 21.1, 21.3, 123.6, 124.6, 125.0, 126.4, 127.4, 129.1, 129.4, 129.4, 130.1, 130.2, 131.1, 132.7, 132.7, 132.9, 134.0, 135.0, 135.6, 136.4, 136.5, 137.0, 137.3, 137.4, 138.0 ppm; UV (CH2Cl2, c = 2.26 × 10^{-4}) \( \lambda (\varepsilon) = 455 \) (3,554), 481 (4,225), 514 (3,420) nm; IR (KBr) \( \nu = 3023, 2922, 2855, 1733, 1677, 1606, 1513, 1446, 1375, 1241, 1215, 1182, 1111, 1044, 965, 839, 805, 757 \) cm^{-1}; HRMS (FAB) calcd for C36H40 472.3130, found 472.3133.

5,5'-(1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(1,3-dimethylbenzene) (1i). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (176 mg, 0.325 mmol) and 3,5-dimethylbenzaldehyde (218 mg, 1.63 mmol) with potassium methoxide (570 mg, 8.13 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1i (81 mg, 0.162 mmol, all-E) in 50% yield as dark red solid. Data for all-(E)-1i: \( R_f = 0.80 \) (4:1 hexane/EtOAc); ^1H NMR \( \delta = 1.99 \) (s, 6H),
2.03 (s, 6H), 2.31 (s, 12H), 6.26–6.32 (m, 2H), 6.33 (d, \( J = 12.4 \) Hz, 2H), 6.41 (d, \( J = 14.8 \) Hz, 2H), 6.53 (d, \( J = 16.0 \) Hz, 2H), 6.62–6.69 (m, 2H), 6.68 (dd, \( J = 14.8, 12.4 \) Hz, 2H), 6.86 (s, 2H), 6.88 (d, \( J = 16.0 \) Hz, 2H), 7.06 (s, 4H) ppm; \(^{13}\)C NMR \( \delta = 12.8, 12.9, 21.3, 124.3, 124.3, 125.1, 127.7, 129.0, 130.3, 132.9, 133.0, 133.3, 135.7, 136.6, 137.7, 138.0 \) ppm; UV (CH\(_2\)Cl\(_2\), c = 1.08 \times 10^{-5}) \( \lambda (\varepsilon) = 455 \) (65,400), 481 (72,100) nm; IR (KBr) \( \nu = 3027, 2922, 2855, 1737, 1595, 1558, 1461, 1439, 1394, 1372, 1245, 1029, 1006, 962, 895, 849, 775, 686 \) cm\(^{-1}\); HRMS (FAB) calced for C\(_{38}\)H\(_{44}\) 500.3443, found 500.3434.

4,4'-(1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(bromobenzene) (1j). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (221 mg, 0.41 mmol) and 4-bromobenzaldehyde (378 mg, 2.04 mmol) with potassium methoxide (717 mg, 10.22 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1j (131 mg, 0.217 mmol, 9'-Z) in 53% yield as dark red solid. Data 9'-Z-1j: \( R_t = 0.73 \) (4:1 hexane/EtOAc); \(^1\)H NMR \( \delta = 1.99 \) (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 6.20 (d, \( J = 11.2 \) Hz, 1H), 6.26–6.34 (m, 2H), 6.35 (d, \( J = 11.2 \) Hz, 1H), 6.36 (d, \( J = 11.2 \) Hz, 1H), 6.43 (d, \( J = 14.8 \) Hz, 1H), 6.50 (d, \( J = 15.6 \) Hz, 1H), 6.53 (d, \( J = 15.6 \) Hz, 1H), 6.62–6.71 (m, 2H), 6.67 (dd, \( J = 14.8, 11.2 \) Hz, 1H), 6.86 (dd, \( J = 14.8, 11.2 \) Hz, 1H), 6.87 (d, \( J = 15.6 \) Hz, 1H), 7.29 (d, \( J = 8.4 \) Hz, 2H), 7.34 (d, \( J = 8.8 \) Hz, 2H), 7.41 (d, \( J = 15.6 \) Hz, 1H), 7.43 (d, \( J = 8.8 \) Hz, 2H), 7.46 (d, \( J = 8.4 \) Hz, 2H) ppm; \(^{13}\)C NMR \( \delta = 12.8, 12.8, 12.9, 20.8, 120.7, 121.1, 123.4, 124.9, 126.0, 126.1, 127.7, 127.7, 128.0, 128.0, 130.3, 130.4, 131.7, 131.7, 131.7, 131.7, 132.1, 133.1, 133.3, 133.7, 134.2, 136.5, 136.6, 136.7, 137.9, 138.6 ppm; UV (CH\(_2\)Cl\(_2\), c = 8.96 \times 10^{-6}) \( \lambda (\varepsilon) = 452 \) (79,600), 478 (104,800), 510 (86,000) nm; IR (KBr) \( \nu = 3027, 2922, 2855, 1729, 1707, 1588, 1483, 1401, 1245, 1215, 1178, 1103, 1073, 1006, 962, 820, 753, 663, 514 \) cm\(^{-1}\); HRMS (FAB) calced for C\(_{34}\)H\(_{34}\)Br\(_2\) 600.1027, found 600.1032.
2,2’-((1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)dithiophene (1k). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (91.5 mg, 0.169 mmol) and 2-thiophenecarboxaldehyde (94.9 mg, 0.846 mmol) with potassium methoxide (297 mg, 4.23 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1k (51 mg, 0.112 mmol, 9’-Z) in 66% yield as dark red solid. Data for 9’-(Z)-1k: Rf = 0.68 (4:1 hexane/EtOAc); 1H NMR δ = 1.99 (s, 3H), 2.01 (s, 3H), 2.02 (s, 6H), 6.14 (d, J = 11.6 Hz, 1H), 6.26–6.34 (m, 2H), 6.31 (d, J = 11.6 Hz, 1H), 6.34 (d, J = 14.8 Hz, 1H), 6.41 (d, J = 14.8 Hz, 1H), 6.60–6.70 (m, 2H), 6.64 (d, J = 15.6 Hz, 1H), 6.66 (dd, J = 14.8, 11.6 Hz, 1H, calcd), 6.70 (d, J = 16.0 Hz, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.84 (dd, J = 14.8, 11.6 Hz, 1H), 6.96–7.01 (m, 3H), 7.03 (d, J = 3.2 Hz, 1H), 7.14 (d, J = 4.8 Hz, 1H), 7.18 (d, J = 5.2 Hz, 1H), 7.24 (d, J = 15.6 Hz, 1H) ppm; 13C NMR (CDCl3) δ = 12.7, 12.8, 12.9, 20.7, 120.5, 122.1, 122.5, 123.6, 123.9, 124.3, 124.9, 125.4, 125.9, 127.6, 127.7, 130.2, 130.3, 131.4, 132.9, 133.0, 133.1, 133.4, 133.5, 135.0, 136.5, 136.5, 137.5, 138.3, 143.5, 143.7 ppm; IR (KBr) ν = 2922, 2855, 1737, 1461, 1372, 1245, 1163, 1021, 962, 850, 835, 805, 753, 693 cm⁻¹; UV (CH2Cl2, c = 8.45×10⁻⁵) λ (ε) = 464 (8,380), 489 (11,000), 522 (9,050) nm; HRMS (FAB) calcd for C30H32S2 456.1945, found 456.1945.

((1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)dibenzene (1l) and ((1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)dibenzene (1p). To a stirred solution of bis(phosphonate) 4 (155 mg, 0.287 mmol) and benzaldehyde (152 mg, 1.43 mmol) in MeOH (30 mL) and toluene (30 mL) was added potassium methoxide (503 mg, 7.18mmol). The mixture was stirred vigorously at 110 °C for 12 h under argon atmosphere. Most of solvent was removed under reduced pressure. The mixture was diluted with Et2O, washed with 10% NH4Cl solution and H2O, dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure to give the crude products as deep
red solid. The crude product was purified by recrystallization from MeOH to give carotene 11 (68 mg, 0.152 mmol, all-\(E/9'-Z = 1:20\)) in 53% yield as dark red solid. When the aqueous layer containing insoluble red solids was extracted with CH₂Cl₂ and purified by recrystallization from MeOH, pure all-(\(E\))-carotene 1p was obtained (less than 2% yield).

Data for 9\(^{\prime}\)-(Z)-11: \(R_f = 0.73\) (4:1 hexane/EtOAc); \(^1\)H NMR \(\delta = 2.00\) (s, 3H), 2.03 (s, 3H), 2.05 (s, 6H), 6.18 (d, \(J = 11.2\) Hz, 1H; H\(^{10}\)), 6.26–6.34 (m, 2H; H\(^{14}\)H\(^{14}\)), 6.35 (d, \(J = 11.2\) Hz, 1H; H\(^{10}\)), 6.35 (d, \(J = 14.8\) Hz, 1H; H\(^{12}\)), 6.42 (d, \(J = 14.8\) Hz, 1H; H\(^{12}\)), 6.58 (d, \(J = 15.6\) Hz, 1H; H\(^{7}\)), 6.62 (d, \(J = 15.6\) Hz, 1H; H\(^{7}\)), 6.62–6.70 (m, 2H; H\(^{15}\)H\(^{15}\)), 6.68 (dd, \(J = 14.8, 11.2\) Hz, 1H; H\(^{11}\)), 6.89 (dd, \(J = 14.8, 11.2\) Hz, 1H; H\(^{11}\)), 6.90 (d, \(J = 15.6\) Hz, 1H; H\(^{8}\)), 7.17–7.26 (m, 2H), 7.29–7.37 (m, 4H), 7.41–7.50 (m, 4H), 7.44 (d, \(J = 15.6\) Hz, 1H; H\(^{8}\)) ppm; \(^{13}\)C NMR \(\delta = 12.8, 12.9, 12.9, 20.9, 123.6, 125.0, 125.5, 126.3, 126.5, 127.1, 127.4, 127.5, 128.6, 128.7, 129.1, 130.2, 130.3, 131.6, 132.9, 133.1, 133.2, 133.6, 133.9, 135.5, 136.5, 136.5, 136.6, 137.5, 137.8, 138.3 ppm; UV (CH₂Cl₂, c = 9.64 × 10\(^{-4}\)) \(\lambda(\varepsilon) = 451\) (73,800), 476 (97,000), 508 (81,200) nm; IR (KBr) \(\nu = 3027, 2945, 2915, 1722, 1662, 1595, 1573, 1551, 1491, 1446, 1394, 1372, 1215, 1029, 962, 753, 693 cm\(^{-1}\)); HRMS (FAB) cale for C\(_{34}\)H\(_{36}\) 444.2817, found 444.2814.

Data for all-(\(E\))-1p: \(^1\)H NMR \(\delta = 2.00\) (s, 6H), 2.05 (s, 6H), 6.25–6.36 (m, 2H), 6.35 (d, \(J = 11.6\) Hz, 2H), 6.43 (d, \(J = 14.8\) Hz, 2H), 6.59 (d, \(J = 16.0\) Hz, 2H), 6.61–6.72 (m, 2H), 6.68 (dd, \(J = 14.8, 11.6\) Hz, 2H), 6.91 (d, \(J = 16.0\) Hz, 2H), 7.17–7.24 (m, 2H), 7.28–7.36 (m, 4H), 7.40–7.47 (m, 4H) ppm; \(^{13}\)C NMR \(\delta = 12.8, 12.9, 125.0, 126.3, 127.2, 127.4, 128.6, 130.3, 133.1, 133.2, 133.6, 135.5, 136.6, 137.8, 138.2 ppm; UV (CH₂Cl₂, c = 1.25 × 10\(^{-5}\)) \(\lambda(\varepsilon) = 454\) (52,000), 480 (73,700), 513 (65,600) nm; IR (KBr) \(\nu = 3027, 2945, 2915, 1722, 1662, 1595, 1573, 1551, 1491, 1446, 1334, 962, 745, 686 cm\(^{-1}\)); HRMS (FAB) cale for C\(_{34}\)H\(_{36}\) 444.2817, found 444.2816.
2,2'-(1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)bis(methylbenzene) (1m).

Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (154 mg, 0.284 mmol) and o-tolualdehyde (171 mg, 1.42 mmol) with potassium methoxide (499 mg, 7.12 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1m (57 mg, 0.121 mmol, all-1E/9'-Z = 2:1) in 43% yield as dark red solid. Data for all-(E)-1m: Rr = 0.73 (4:1 hexane/EtOAc); 1H NMR δ = 2.00 (s, 6H), 2.07 (s, 6H), 2.39 (s, 6H), 6.25–6.35 (m, 2H), 6.34 (d, J = 11.6 Hz, 2H), 6.42 (d, J = 14.8 Hz, 2H), 6.62–6.71 (m, 2H), 6.69 (dd, J = 14.8, 11.6 Hz, 2H), 6.78 (A of ABq, J = 16.0 Hz, 2H), 6.82 (B of ABq, J = 16.0 Hz, 2H), 7.10–7.21 (m, 6H), 7.53 (d, J = 8.0 Hz, 2H) ppm; 13C NMR δ = 12.8, 13.0, 19.9, 124.9, 125.0, 126.1, 127.1, 130.3, 130.4, 133.1, 133.1, 133.1, 134.8, 135.5, 135.8, 136.6, 136.6, 138.2 ppm; UV (CH2Cl2, c = 2.04 × 10^{-5}) λ (ε) = 456 (32,700), 480 (44,500), 511 (36,100) nm; IR (KBr) ν = 3019, 2922, 2855, 1722, 1670, 1595, 1565, 1483, 1454, 1439, 1379, 1260, 1215, 1029, 827, 805, 745, 663 cm^{-1}; HRMS (FAB) calcd for C36H40 472.3130, found 472.3130.

2,2'-(1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)dinaphthalene (1n). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (653 mg, 1.21 mmol) and 2-naphthaldehyde (943 mg, 6.04 mmol) with potassium methoxide (2.12 g, 30.2 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1n (258 mg, 0.474 mmol, 9'-Z) in 39% yield as dark red solid. Data for 9'-(Z)-1n: Rr = 0.68 (4:1 hexane/EtOAc); 1H-NMR (CDCl3) δ = 2.01 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 6.21 (d, J = 10.8 Hz, 1H), 6.28–6.35 (m, 2H), 6.38 (d, J = 14.4 Hz, 1H), 6.40 (d, J = 11.6 Hz, 1H), 6.45 (d, J = 14.8,
1H), 6.63–6.74 (m, 2H), 6.68 (dd, J = 14.4, 10.8 Hz, 1H, calcd), 6.76 (d, J = 15.6 Hz, 1H), 6.79 (d, J = 15.6 Hz, 1H), 6.95 (dd, J = 14.8, 11.6 Hz, 1H), 7.04 (d, J = 15.6 Hz, 1H), 7.39–7.49 (m, 4H), 7.57 (d, J = 15.6 Hz, 1H), 7.64–7.84 (m, 10H) ppm; 13C NMR δ = 12.8, 12.9, 13.0, 20.9, 123.6, 123.6, 125.0, 125.7, 125.8, 126.2, 126.3, 126.6, 127.5, 127.7, 127.7, 127.9, 128.0, 128.2, 128.3, 129.2, 129.3, 130.2, 130.4, 131.8, 132.6, 133.0, 133.4, 133.6, 133.8, 133.9, 134.0, 135.3, 135.4, 135.6, 136.6, 136.6, 137.7, 137.7, 138.4 ppm; IR (KBr) ν = 3053, 3023, 2922, 2855, 1737, 1625, 1595, 1439, 1368, 1241, 1047, 1025, 962, 895, 861, 816, 745, 619 cm⁻¹; UV (CH2Cl2, c = 7.59 × 10⁻⁵) λ (ε) = 458 (13,000), 484 (12,800), 517 (9,300) nm; HRMS (FAB) calcd for C₄₂H₄₀ 544.3130, found 544.3132.

3,3'-(1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diylbis(methylbenzene) (1o). Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (180 mg, 0.332 mmol) and m-tolualdehyde (199 mg, 1.66 mmol) with potassium methoxide (580 mg, 8.30 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 °C for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1o (66 mg, 0.14 mmol, all-E/9’-Z = 1:5) in 42% yield as dark red solid. Data for 9’-(Z)-1o: Rf = 0.75 (4:1 hexane/EtOAc); ¹H NMR δ = 1.99 (s, 3H), 2.03 (s, 3H), 2.04 (s, 6H), 2.35 (s, 3H), 2.38 (s, 3H), 6.16 (d, J = 11.2 Hz, 1H), 6.25–6.34 (m, 2H), 6.34 (d, J = 11.2 Hz, 1H), 6.35 (d, J = 15.2 Hz, 1H), 6.42 (d, J = 15.2 Hz, 1H), 6.56 (d, J = 15.6 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.63–6.72 (m, 2H), 6.69 (dd, J = 15.2, 11.2 Hz, 1H), 6.89 (dd, J = 15.2, 11.2 Hz, 1H), 6.89 (d, J = 15.6 Hz, 1H), 7.01–7.08 (m, 2H), 7.18–7.32 (m, 6H), 7.42 (d, J = 15.6 Hz, 1H) ppm; ¹³C NMR δ = 12.9, 13.3, 13.3, 21.4, 123.5, 123.7, 125.0, 125.3, 127.0, 127.4, 127.5, 128.0, 128.3, 128.5, 129.3, 130.1, 130.3, 131.4, 132.8, 133.0, 133.4, 133.9, 135.6, 136.5, 136.6, 137.7, 138.1 ppm; UV (CH2Cl2, c = 1.59 × 10⁻⁵) λ (ε) = 454 (42,800), 480 (57,800), 513 (48,900) nm; IR (KBr) ν = 3027, 2915, 2855, 1722, 1595, 1483, 1439, 1394, 1372, 1260, 1088, 1029, 962, 782, 752, 693 cm⁻¹; HRMS (FAB) calcd for C₃₆H₄₀ 472.3130, found 472.3127.
4,4’-((1E,3E,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-
nonaene-1,18-diyl)dibenzonitrile (1q).

Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (130 mg, 0.24 mmol) and 4-cyanobenzaldehyde (158 mg, 1.20 mmol) with potassium methoxide (422 mg, 6.01 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 ºC for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1q (32 mg, 0.0653 mmol, all-\(E\)/9’-\(Z\) = 3:2) in 27% yield as dark red solid. Data for all-\(E\)-1q: Rf = 0.25 (4:1 hexane/EtOAc); \(^1\)H NMR \(\delta = 2.00\) (s, 6H), 2.05 (s, 6H), 6.28–6.39 (m, 2H), 6.41 (d, \(J = 11.2\) Hz, 2H), 6.47 (d, \(J = 14.8\) Hz, 2H), 6.55 (d, \(J = 16.0\) Hz, 2H), 6.63–6.71 (m, 2H), 6.69 (d, \(J = 14.8\), 11.2 Hz, 2H), 6.99 (d, \(J = 16.0\) Hz, 2H), 7.48 (d, \(J = 8.4\) Hz, 4H), 7.58 (d, \(J = 8.4\) Hz, 4H) ppm; \(^{13}\)C NMR \(\delta = 12.8, 12.8, 109.8, 119.2, 124.8, 125.4, 126.6, 126.6, 126.8, 130.7, 132.4, 133.9, 135.6, 137.1, 139.7, 142.3\) ppm; UV (CH\(_2\)Cl\(_2\), c = \(3.03 \times 10^{-5}\)) \(\lambda (\varepsilon) = 474 \quad(24,400), 495 \quad(29,800), 527 \quad(23,200)\) nm; IR (KBr) \(\nu = 3012, 2922, 2855, 2221, 1737, 1670, 1595, 1551, 1498, 1439, 1394, 1372, 1305, 1170, 1006, 962, 857, 834, 812, 753, 663\) cm\(^{-1}\); HRMS (FAB) calcld for C\(_{36}H_{34}N_2\) 494.2722, found 494.2723.

4,4’-((1E,3Z,5E,7E,9E,11E,13E,15E,17E)-3,7,12,16-Tetramethyloctadeca-1,3,5,7,9,11,13,15,17-
nonaene-1,18-diyl)bis((trifluoromethyl)benzene) (1r).

Following the general procedure for 1a, the reaction of bis(phosphonate) 4 (153 mg, 0.283 mmol) and 4-(trifluoromethyl)benzaldehyde (246 mg, 1.41 mmol) with potassium methoxide (496 mg, 7.07 mmol) in MeOH (30 mL) and toluene (30 mL) at 110 ºC for 12 h produced the crude deep red solid product, which was purified by recrystallization from MeOH to give carotene 1r (38 mg, 0.0656 mmol, all-\(E\)/9’-\(Z\) = 1:3.6) in 23% yield as dark red solid. Data for 9’-(\(Z\))-1r: Rf = 0.60 (4:1 hexane/EtOAc); \(^1\)H NMR \(\delta = 2.00\) (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 6.23 (d, \(J = 12.0\) Hz, 1H), 6.26–6.35 (m, 2H), 6.38 (d, \(J = 14.8\) Hz, 1H), 6.39 (d, \(J = 12.0\) Hz, 1H), 6.45 (d, \(J = 14.8\) Hz, 1H), 6.58 (d, \(J = 15.6\) Hz, 1H), 6.61 (d, \(J = 15.6\) Hz, 1H), 6.62–6.73 (m, 2H), 6.68 (dd, \(J =
14.8, 12.0 Hz, 1H), 6.87 (dd, J = 14.8, 12.0 Hz, 1H), 6.96 (d, J = 16.0 Hz, 1H), 7.45–7.62 (m, 9H), ppm; 

$^{13}$C NMR $\delta = 12.8, 12.8, 12.9, 20.8, 122.9, 123.3, 124.8, 125.6, 125.6, 125.6, 125.7, 126.1, 126.3, 126.6, 127.5, 127.8, 130.4, 130.5, 133.0, 133.3, 133.3, 133.3, 133.6, 134.6, 134.7, 135.0, 135.9, 136.0, 136.5, 136.6, 138.4, 139.1, 141.3$ ppm; UV (CH$_2$Cl$_2$, c = $1.03 \times 10^{-5}$) $\lambda$ (e) = 458 (66,000), 483 (89,800), 516 (74,300) nm; IR (KBr) $\nu$ = 3034, 2922, 2855, 1610, 1565, 1416, 1319, 1163, 1111, 1066, 1014, 962, 865, 760, 596 cm$^{-1}$; HRMS (FAB) calcd for C$_{36}$H$_{34}$F$_6$ 580.2565, found 580.2570.
Sample Name: KDH-944-50-C
Data Collected on: Agilent-NMR.com-vnmr400
Archive directory: /home/vnmrl/vnmr4ays/data/1901-koo-2
Sample directory: KDH-944-50-C_01
FidFile: KDH-944-50-C_CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdc13
Data collected on: Jan 9 2019
Pulse Sequence: PROTON (s2pul)

Sample collected on: Jan 9 2019
Sample: SHK-1690-4
Sample ID: sh43_SHK-1690-4_koo+2_20131286_01
File: /home/walkups/vnmrsys/data/koo+2/SHK-1690-4_Proton_01.fid
Pulse Sequence: zgul
Solvent: dcl13
Ambient temperature
Sample #43, 25°C

File: SHK-1690-4.koo+2
Vnmrs-400

Relax. delay 3.94 s
Pulse 45.6 degrees
Acq. time 2.049 s
Width 63.9 Hz
8 repetitions

Observe H1 400.0340023 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT. size 65536
Total time 0 min, 31 sec

![Chemical Structure](image)
Sample: SHK-1700-4
Sample ID: s_43_SHK-1700-4_Koo-2_20131220_01
file: /home/walkup2/vnmrsys/data/koo-2/SHK-1700-4_Proton_01.fld

Pulse Sequence: szpul
Sovent: cca3
Ambient temperature
Sample #43, Operator: walkup2
File: SHK-1700-4_Koo-2_20131220_01

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6850.4 Hz
8 repetitions

DATA PROCESSING
Observe H1, 400.0340000 MHz
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 31 sec

---

1.10 1.00 2.19 4.07 3.31 6.25

---
Sample: SHK-1700-4C
Sample ID: s_4d_SHK-1700-4C_koo-2_20131223_01
File: /home/walkup2/vnmrcys/data/koo-2/SHK-1700-4C_Carbon_01.fid
Pulse Sequence: s2pul
Solvent: ccl3
Ambient temperature
Sample #44, Operator: walkup2
File: SHK-1700-4C_Carbon_01

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Window 24508.8 Hz
512 repetitions
OBSERVE C13, 100.5886343 MHz
DECOUPLE H1, 400.0360169 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 42 sec

![Chemical Structure](image-url)

- 160 140 120 100 80 60 40 20 ppm

S37
Sample: SHK-1709-1
File: exp
Pulse Sequence: s2pu1
Solvent: cdcl3
Ambient temperature
Operator: wakup2
VNMRS-400 4000MR

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.888 sec
Width 6630.6 Hz
9 repetitions

OBSERVE H1 400.0340119 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 5 min, 31 sec

\[
\text{Br} \quad \text{S} \quad \text{N} \quad (Z)\text{C}
\]

\[
\text{Br} \quad \text{S} \quad \text{S}
\]

pp
1.00 1.00
0.98 1.08
0.93
2.08
0.352.14
3.29
Sample: SHK-1709-2
file: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient Temperature
Operator: wakup2
VNMRS-400 "400MHz"

Relax, delay 1.000-0.00
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8030.6 Hz
8 repetitions
OBSEERVE H1, 400.00000134 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 31 sec

\[ \text{Br} \quad \text{N} \quad \text{S} \quad \text{(E)-C} \]
Sample: SHK-1769-2
File: exp
Pulse Sequence: s2pul
Solvent: cdc13
Ambient temperature
Operator: walkup3
VNMR=400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.389 sec
Width 245.68.8 Hz
256 repetitions
OBSERVE C13, 106.5866376 MHz
SUSPEND H2, 406.8308810 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec

(E)-C

Br-CH=N-S-S-CH-
Sample: SHK-1709-3
File: exp
Pulse Sequence: s2pu1
Solvent: cdcl3
Ambient temperature
Operator: walkup2
VNMRS-400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.200 sec
Width 24508.8 Hz
256 repetitions
OBSERVE C13, 100.5886372 MHz
DECouple H1, 400.0606169 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: SHK-1700-IR
File: exp
Pulse Sequence: 62pul
Solvent: cdc13
ambient temperature
Operator: walkup
VMRNS-400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 2.049 sec
Width 6650.6 Hz
8 repetitions
OBSERVE H1, 400.024600 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 55536
Total time 5 min, 31 sec

$\text{Br} \text{O}_2 \text{S} \text{N} 10$

[Chemical structure diagram]

\begin{align*}
\text{pD} & \approx 1.02 \\
& \approx 1.00 \\
& \approx 2.23 \\
& \approx 1.05 \\
& \approx 2.39 \\
& \approx 2.42 \\
& \approx 3.08
\end{align*}
Sample: SHK-1707-2R
File: exp
Pulse Sequence: s2pul
Solvent: ddc18
Ambient temperature
Operator: walkup2

VMRS-400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.280 sec
Width 24509.8 Hz
256 repetitions
Observe C13, 100.6888347 MHz
DECOUPLE H1, 400.8360169 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec

Br

-152.8650
-143.469
-137.862
-120.807
-125.722
-122.386
-114.379
77.338
77.606
54.594
30.248
15.369

10
Sample: SHK-1710-2-2
File: exp
Pulse Sequence: z2pu1
Solvent: cdc13
Ambient temperature
Operator: walkupz
VNMRS-400 "400MR"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.849 sec
Width 6890.6 Hz
6 repetitions
OBSERVE HI, 400.0339998 MHz
DATA PROCESSING
Line broadening 0.5 Hz
Fl size 50528
Total time 0 min, 31 sec

(E)-5

85
Sample: SHK-1710-2-2-c
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: wakup2
VTNRS-400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. line 1.380 sec
Width 24509.8 Hz
128 repetitions
OBSERVE C13, 100.55869272 MHz
DECORRELATE H1, 400.0366165 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 4 min, 56 sec
Sample: SHK-1728-1
File: /home/walkup2/vnmrsys/data/koo-2/SHK-1728-1_proton.fid

Pulse Sequence: s2pul
Solvent: dcl39
Ambient temperature
Operator: walkup2
File: SHK-1728-1_proton
VNMRS-400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 2.000 sec
Width 0.000 Hz
6 repetitions

OBSERVE H1, 400.0340098 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 31 sec

\[
\begin{array}{c}
\text{Cl} - \text{S\(\text{\rightleftharpoons}\)S} - \text{F}
\end{array}
\]
Sample: SHK-1728-1-C
Sample ID: s_37_SHK-1728-1-C_koo-2_20140207_01
File: /home/walkup2/ymer/sys/data/koo-2/SWK-1728-1-C_Carbon_01.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #37, Operator: walkup2
File: SHK-1728-1-C_Carbon_01

VNMRS-400 "400MHz"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 24.599.8 Hz
256 repetitions
Observe 1.0. 100.5886534 MHz
Decouple H1, 100.5866159 MHz
Power 42 db
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: SHK-1743-1-1
Sample ID: s40_SHK-1743-1-1_kdo-2_20140212_01
File: /home+Falk/KoP2/vnmrsys/data/kdo-2/SHK-1743-1-1_Protom_01.fid

Pulse Sequence: s2pul
Solvent: ddc13
Ambient temperature
Sample #:60, Operator: -
VNMRS-400 400MHz

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 2.044 sec
Width 6830.6 Hz
8 repetitions
DATA PROCESSING
Line broadening 0.5 Hz
RT size 8356
Total time 0 min, 31 sec

![Chemical Structure]

Sample: SHK-1743-1-1
Sample ID: s40_SHK-1743-1-1_kdo-2_20140212_01
File: /home+Falk/KoP2/vnmrsys/data/kdo-2/SHK-1743-1-1_Protom_01.fid

Pulse Sequence: s2pul
Solvent: ddc13
Ambient temperature
Sample #:60, Operator: -
VNMRS-400 400MHz

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 2.044 sec
Width 6830.6 Hz
8 repetitions
DATA PROCESSING
Line broadening 0.5 Hz
RT size 8356
Total time 0 min, 31 sec

![Chemical Structure]
Sample: SHK-1717-3R-1
File: exp
Pulse Sequence: s2pu1
Solvent: ddc13
Ambient temperature
Operator: walkup2
VNMRS-400 “400MR”

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.649 sec
Width 8836.6 Hz
8 repetitions
OBSERVE H1, 400.0300074 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 31 sec

[Chemical structure diagram]
Sample: SHK-1717-3R-c
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: walkup2
VNMRS-400 "400MR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions
OBSERVE C13, 100.5886329 MHz
DECOUPLE H1, 400.0369169 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample Name: KDH-683-ether-MeOH2-2
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsys/data/koo-2
Sample directory: KDH-683-ether-MeOH2-2_01
FidFile: KDH-683-ether-MeOH2-2_PROTON_01

Pulse Sequence: PROTON (s2pu1)
Solvent: cdcl3
Data collected on: Dec 8 2017

all-E:Z=3:1
Sample Name: KDH-683-ether-MeOH2-2-c
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrays/data/koc-2
Sample directory: KDH-683-ether-MeOH2-2-c_01
FidFile: KDH-683-ether-MeOH2-2-c_CARBON_01

Pulse Sequence: CARBON (a2p1)
Solvent: dcdl3
Data collected on: Dec 9 2017

1a
all-E:9-Z = 3:1

200 180 160 140 120 100 80 60 40 20 ppm
Sample: SHK-1962-1-2R
Sample ID: s_d1_SHK-1962-1-2R_koo-2_20160223_01
File: /home/WalkUp2/vnmrsys/data/koo-2/SHK-1962-1-2R_Proton_02.fid
Pulse Sequence: szpu!
Solvent: dcl3
Ambient temperature:
Sample ID: sample_1
Operator: walkup2
File: SHK-1962-1-2R_Proton_02
VNMRS=800 "400MHZ"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6030.6 Hz
3 repetitions
OBSR: 64, 400.03MHz WHz
URCA: PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 31 sec

![NMR Spectrum](image)

S58
Sample: SHK-1967-R
Sample ID: x_44_SHK-1967-R_koo-2_20160227_01
File: /home/wallup2/vnmrsys/data/koo-2/SHK-1967-R_Carbon_01.fid

Pulse Sequence: s2pol
Solvent: cdCl3
Ambient temperature
Sample #44, Operator wallup

VMRQ-400 -4.7.6.5.4.3.2.1

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.300 sec
Width 2250.0 Hz
256 repetitions
OBSERVE C13, 100.5666132 MHz
SOLVOL 31p, 148.0259999 MHz
Power 60 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample Name: EDB-782-NC-w2-C
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrays/data/1804-kco-2
Sample directory:
KDH-782-NC-w2-C_01
file: KDH-782-NC-w2-C_CAHON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 6 2018

all-E:9'-Z = 2:1
Sample Name: KDH-757-MC-W2
Data Collected on: Agilent-NMR.com-2018.04.03
Archive directory: /home/vmnmr/vnmrsys/data/KDH-757-MC-W2
Sample directory: KDH-757-MC-W2_01
FidFile: KDH-757-MC-W2_PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 9 2018

1d
all-E9'-Z = 3:4

0.27575.46 2.13 1.09 0.40
2.487.08 2.02 1.73 2.07
3.10
3.13
Sample Name: KDR-757-MC-W2-C
Data Collected on: Agilent-NMR.com
Archive directory: /home/vnmri/vnmrsys/data/1803-knu-2
Sample directory: KDR-757-MC-W2-C_01
File: KDR-757-MC-W2-C_CARBON_01

 Pulse Sequence: CARBON (s2pu1)
 Solvent: dcl3
 Data collected on: Mar 10 2018

Ph
Ph
Ph

all-E: Z = 3.4
Sample Name: KDH-755-MC-w
Data Collected on: Agilent-NMR.com-vnrrs6Q0
Archive directory: /home/vnarr/vnrrsys/data/koo-2
Sample directory: KDH-755-MC-w_01
FidFile: KDH-755-MC-w_PROTON_01

Pulse Sequence: PROTON (z2pul)
Solvent: cdc13
Data collected on: Feb 28 2018
Sample Name: KDH-733-MC-W-C
Data Collected on: Agilent-NMR.com=vmnrs400
Archive directory: /home/vmnrs/vmnrays/data/1802-kwo-2
Sample directory: KDH-733-MC-W-C_01
FidFile: KDH-733-MC-W-C_CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdc13
Data collected on: Feb 9 2018
Sample Name: KDK-786-MC-w
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmri/vnmrsys/data/1804-koo-2
Sample directory: KDK-786-MC-w_01
FidFile: KDK-786-MC-w_PROTON_01
Pulse Sequence: PROTON (a2p1)
Solvent: ccd13
Data collected on: Apr 11 2018

The diagram shows a spectrum with chemical shifts indicated by peaks at various ppm values, such as 0.83, 1.88, 4.94, and 3.24. The compound structure labeled as 1f is depicted.
Sample Name:
KDH-498-MC-w3
Data Collected on:
Agilent-NMR.com-vnmrs400
Archive directory:
/home/vnmrl/vnmrsys/data/kco-2
Sample directory:
KDH-498-MC-w3_01
FidFile: KDH-498-MC-w3_CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 27 2017

[Diagram of molecular structure]
Sample Name: KDM-510-0822
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsyss/data/koo-2
Sample directory: KDM-510-0822_01
FidFile: KDM-510-0822_PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 22 2017
Sample Name: KDH-510-MC-w-C
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsays/data/koo-2
Sample directory: KDH-510-MC-w-C_01
FidFile: KDH-510-MC-w-C_CARBON_01

pulse Sequence: CARBON (s2pul)
Solvent: cdc13
data collected on: May 1 2017
Sample Name: KDB-742-ether-w
Data Collected on: Agilent-NMR.com-wxsys400
Archive directory: /home/vmmrl/vnmrsys/data/2012-350-2
Sample directory: KDB-742-ether-w_01
FidFile: KDB-742-ether-w_PROTON_01

Pulse Sequence: PROTON (a2pul)
Solvent: cdcl3
Data collected on: Feb 22 2018
Sample Name: KDH-443-ether-w2-C
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsys/data/koo-2
Sample directory: KDH-443-ether-w2-C_01
FidFile: KDH-443-ether-w2-C_CARBON_01

Pulse Sequence: CARBON (a2pul)
Solvent: cdcl3
Data collected on: Mar 6 2017
Sample Name: KDH-660-MC-w2
Data Collected on:
Agilent-VNMRS.com-vnmrs400
Archive directory:
/home/vnmrl/vnmrsys/data/koo-2
Sample directory:
KDH-660-MC-w2_01
FidFile: KDH-660-MC-w2_PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cdc13
Data collected on: Nov 3 2017
Sample Name: KDH-660-MC-W2-C2
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmsl/vnmrs/data/koo-4
Sample directory: KDH-660-MC-W2-C2_01
Fidfile: KDH-660-MC-W2-C2_CARBON_01

Pulse Sequence: CARBON (s2ps1)
Solvent: cdc13
Data collected on: Nov 4 2017
Sample Name: KDH-669-MC-W
Data Collected on: Nov 18 2017
Archive directory: /home/vmr/VMRsys/data/kdh-2
Sample directory:
FidFile: KDH-669-MC-W_PROTON_01
Pulse Sequence: PROTON (e2pul)
Solvent: cdc13
Data collected on: Nov 18 2017

Chemical shifts and multiplicities:
- 3.52, 0.73, 5.60, 1.00, 1.84, 1.69
Sample Name: KDH-780-ether-M2
Data Collected on: Agilent-NMR.com-vnmrs300
archive directory: /home/vnmrl/vnmrs/data/1804-kob-2
Sample directory: KDH-780-ether-M2-C_01
iqFile: KDH-780-ether-M2-C_CARBON_01

Ise Sequence: CARBON (s2pu1)
Ievent: cdcl3
Ita collected on: Apr 1 2018
Sample Name: KDH-579-ether
Data Collected on: Agilent-NMR.com-vnmrs4D6
Archive directory: /home/vnmrl/vnmrsys/data/koo-2
Sample directory: KDH-579-ether_01
FidFile: KDH-579-ether_PROTON_01

Pulse Sequence: PROTON (e2pul)
Solvent: cdcl3
Data collected on: Jul 28 2017
Sample Name: KDH-579-MC-W-C
Data Collected on: Agilent-NMR.com-vnmr400
Archive directory: /home/vnmrl/vnmr.sys/data/koo-2
Sample directory: KDH-579-MC-W-C_01
FidFile: KDH-579-MC-W-C_CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: dclal3
Data collected on: Jul 24 2017
Sample Name: KDH-650-ether-w2
Data Collected on: Oct 11 2017

Instrument: Agilent-NMR.com

Archive directory: /home/vnmrl/vnmrsys/data/kpo-2
Sample directory: KDH-650-ether-w2_01
FidFile: KDH-650-ether-w2_PROTON_01

 Pulse Sequence: PROTON (z2pul)
Solvent: cdc13

Data collected on: Oct 11 2017

1H NMR (400 MHz, CDCl3) 
Chemical Shifts (δ ppm): 4.97, 3.13, 2.25, 1.74, 1.66, 1.12
26 sp² carbons
Sample Name: KDM-654-MC-w2
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmri/vnmrsys/data/koo-2
Sample directory: KDM-654-MC-w2_01
FidFile: KDM-654-MC-w2_PROTON_01

Pulse Sequence: PROTON (a2pul)
Solvent: cdc13
Data collected on: Oct 17 2017
Sample Name:
KDB-NaOEt-MC-w2-C
Data Collected on:
Agilent-NMR.com-vmr400
Archive directory:
/home/vmrl/vnmrsys/data/koo-2
Sample directory:
KDS NaOEt MC w2 C_01
FidFile: KDB-NaOEt-MC-w2-C_CARBON_01

Pulse Sequence: CARBON (n2pul)
Solvent: cdc13
Data collected on: Dec 28 2016

13 sp² carbons
**Calculation of all-\(E/9'-Z\) ratio**

Area (10'): \(9'-Z\) only
Area (12): \(9'-Z + E \times 2\)

E fraction = \(\frac{(\text{Area}(12) - \text{Area}(10'))}{2}\)

E.g. \(\frac{E}{Z} = 1:20\)
Sample Name: KDH-715-MC-w
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrs/vnmrsys/data/1801-zpc-2
Sample directory: KDH-715-MC-w_01
PdbFile: KDH-715-MC-w_PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 17 2018

all-E:9'-Z = 2:1
Sample Name: KDM-715-MC-W2-C
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsys/data/1801-koo-2
Sample directory: KDM-715-MC-W2-C_01
FidFile: KDM-715-MC-W2-C_CARBON_01

Pulse Sequence: CARBON (s2pu1)
Solvent: cdc13
Data collected on: Jan 20 2018

all-E:9'-Z = 2:1
Sample Name: KDH-494-MC-f
Data Collected on: Agilent
Archive directory: /home/vnar1/vnmrs/s/data/pco-2
Sample directory: KDH-494-MC-f.01
FigFile: KDH-494-MC-f_PROTON.01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 21 2017
Sample Name: KDH-752-MC-W-C
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmcl/vnmrsys/data/1802-koo-2
Sample directory: KDH-752-MC-W-C_01
FidFile: KDH-752-MC-W-C_CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdc13
Data collected on: Feb 27 2018
Pulse Sequence: PROTON (ezpul)
Solvent: cdcl3
Data collected on: Jan 19 2018

all-E:9'Z = 1:5
Sample Name: KDX-714-ether-W9-C_01
Data Collected on: Jan 21 2018

Use Sequence: CARBON (s2pul)
Solvent: cdc13

All-\(\text{E}:Z = 1:5\)
Sample Name: KDH-750-CN
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmr/vnmrsys/data/1806-kdp-2
Sample directory: KDH-750-CN_01
PfidFile: KDH-750-CN_PROTON_01

Pulse Sequence: PROTON (a2pul)
Solvent: cdcl3
Data collected on: Jun 7 2018

1q
all-E9'-Z = 3:2

14.59 4.97 7.50 5.45 42
11.00 1.72 5.18 481.00
37.72
Sample Name: KDH-750-CN
Data Collected on: Agilent-NMR.com-vnmrs400
archive directory: /home/vnmrl/vnmrsays/data/1806-koo-2
Sample directory: KDH-750-CN_02
fidFile: KDH-750-CN_CARBON_01

pulse Sequence: CARBON (a2pul)

 solvent: cdol3

1H collected on: Jun 5 2018

all-\(\pm\)-Z = 3:2

200 180 160 140 120 100 80 60 40 20 ppm
Sample Name: KDH-774-ether-w
Data Collected on: Agilent-NMR.com
Archive directory: /home/vnmrl/vnmrsys/data/1801-koo-Z
Sample directory:
FidFile: KDH-774-ether-w_01
Pulse Sequence: PROTON (s2pul)
Solvent: cdc13
Data collected on: Mar 27 2018
Sample Name: KDH-betacarotene-w
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vumrl/vnmrsys/data/1804-koo-2
Sample directory: KDH-betacarotene-w_01
FidFile: KDH-betacarotene-w_PROTON_01

Pulse Sequence: PROTON (z2pul)
Solvent: cdo13
Data collected on: Apr 6 2018

β-Carotene prepared for assays
Sample Name: KDB-854-R-w
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsays/data/1807-koo-2
Sample directory: KDB-854-R-w 01
FidFile: KDB-854-R-w_PROTON_01

Pulse Sequence: PROTON (z2pul)
Solvent: cdcl3
Data collected on: Jul 24 2018

Lycopene prepared for assays
Sample Name: KDH-854-R-w
Data Collected on: Agilent-NMR.com-vnmrs400
Archive directory: /home/vnmrl/vnmrsys/data/1807-koo-2
Sample directory: KDH-854-R-w_01
FidFile: KDH-854-R-w_PROTON_01

Pulse Sequence: PROTON (a2pul)
Solvent: cdcl3
Data collected on: Jul 24 2018

Lycopene prepared for assays

6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 ppm
2.07 1.11 1.08 3.04 1.00