Supporting Information

Reactivity Pattern of Dipropargyloxy Disulfides. Tandem Rearrangements and Cyclizations

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Experimental.

Dipropargyloxy disulfides.

3-{{(1-Ethylprop-2-ynyl)oxy|dithio|oxy}pent-1-yne (9b)
Was obtained as a yellow liquid with a strong smell of garlic, as a mixture of four diastereomers; yield: 72%.

$^1$H NMR (300 MHz, CDCl$_3$): δ 4.50 and 4.47 (td, $J = 6.3$, 2.1 Hz, 2H each), 4.46 (td, $J = 6.3$, 2.1 Hz, 2H for two isomers), 2.60, 2.59, 2.554, 2.548 (d, $J = 2.1$ Hz, 2H each), 1.94-1.77 (m, 4H for four isomers), 1.05, 1.04, 1.035 and 1.031 (t, $J = 6.7$ Hz, 6H each).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 81.6, 81.5, 81.41 and 81.39 (≡C– each), 76.5 (–CH–O for two isomers), 74.5 and 74.4 (–CH=–O each), 75.8, 75.6, 75.3 and 75.2 (HC≡ each), 29.0, 28.9, 28.9 and 28.7 (–CH$_2$– each), 9.4 and 9.4 (–CH$_3$ each), 9.2 (–CH$_3$ for two isomers).

IR (neat): 1093, 1331, 1462, 2118, 2247, 2950 cm$^{-1}$.

MS (CI/CH$_4$): m/z 231 (MH$^+$, 15%), 199 (M$^+$–“S”, 23%), 183 (M$^+$–“SO”, 38%).

HRMS (elemental composition): calc. (C$_{10}$H$_{15}$O$_2$S$_2$) 231.0513; found 231.0509.

3-{{(1-Pentylprop-2-ynyl)oxy|dithio|oxy}oct-1-yne (9c)
Was obtained as a yellow liquid, as a mixture of four diastereomers; yield 61%.

$^1$H NMR (300 MHz, CDCl$_3$): δ 4.54 and 4.51 (td, $J = 6.6$, 2.1 Hz, 2H each), 4.49 (td, $J = 6.6$, 2.1 Hz, 2H for two isomers), 2.59, 2.57, 2.55 and 2.54 (d, $J = 2.1$ Hz, 2H each), 1.86-1.76 (m, 4H for four isomers), 1.34-1.32 (m, 12H for four isomers), 0.90 (t, $J = 6.6$ Hz, 6H for four isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 81.6, 81.5, 81.41 and 81.39 (≡C– each), 76.5 (–CH–O for two isomers), 74.5 and 74.4 (–CH=–O each), 75.8, 75.6, 75.3 and 75.2 (HC≡ each), 29.0, 28.9, 28.9 and 28.7 (–CH$_2$– each), 9.4 and 9.4 (–CH$_3$ each), 9.2 (–CH$_3$ for two isomers).

IR (neat): 978, 1118, 1130, 1344, 1467, 2118, 2247, 2952 cm$^{-1}$.

MS (CI/CH$_4$): m/z 315 (MH$^+$, 15%), 199 (M$^+$–“S”, 23%), 183 (M$^+$–“SO”, 38%).

HRMS (elemental composition): calc. (C$_{16}$H$_{27}$O$_2$S$_2$) 315.1452; found 315.1463.

3-{{(1-Isopropylprop-2-ynyl)oxy|dithio|oxy}4-methylpent-1-yne (9d)
Was obtained as a yellow liquid with a strong smell of garlic, as a mixture of four diastereomers; yield: 87%.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.33, 4.31, 4.30 and 4.29 (dd, $J = 5.8, 2.1$ Hz, 2H each), 2.55, 2.56, 2.508 and 2.512 (d, $J = 2.1$ Hz, 2H each), 2.08-1.97 (m, 2H for four isomers), 1.03-0.97 (m, 12H for four isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 81.1, 81.1, 78.8 and 78.7 (=$C$–CH–O each), 80.53 (=$C$–for tree isomers) and 80.47 (=$C$–for one isomer), 76.5, 76.3, 75.9 and 75.8 (=$CH$ each), 33.4, 33.3, 33.2 and 33.0 (=$CH(CH_3)_2$ each), 18.4 ($\times 2$), 18.3 ($\times 2$), 17.8, 17.6, 17.3 and 17.2 ($–CH_3$ each).
IR (neat): 1130, 1467, 1947, 2967 cm$^{-1}$.

MS (CI/i-Bu): m/z 258 (M+, 41%), 129 (M$/^+$/2, 24%).
HRMS (elemental composition): calc. (C$_{12}$H$_{18}$O$_2$S$_2$) 258.0748; found 258.0726.

3-{$\{[\text{1-Isobutylprop-2-ynyl}]$oxy|dithio$|$oxy$\}$-5-methylhex-1-yne (9e)

Was obtained as a yellow liquid with a strong smell of garlic, as a mixture of four diastereomers; yield: 91%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.60-4.50 (m, 2H for four isomers), 2.59, 2.57, 2.545 and 2.539 (d, $J = 2.1$ Hz, 2H each), 1.89 (septet, $J = 6.9$ Hz, 2H for two isomers) and 1.88 (septet, $J = 6.9$ Hz, 2H for two isomers), AB system: 1.84-1.76 and 1.65-1.54 (m, 2H for four isomers), 0.99-0.91 (m, 12H for four isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 82.2 and 82.1 (=$C$– each), 82.0 (=$C$–for two isomers), 75.8, 75.6, 75.3 and 75.2 (=$CH$ each), 74.5 (=$CH$–O for two isomers), 72.2 and 72.1 (=$CH$–O each), 44.8 (=$CH_2$– for two isomers), 44.7 (=$CH_2$– for two isomers), 24.72 (=$CH(CH_3)_2$ for two isomers), 24.68 (=$CH(CH_3)_2$ for two isomers), 22.65, 22.56, 22.5 ($\times 2$), 22.45, 22.39 and 22.3 ($\times 2$) ($–CH_3$ each).
IR (neat): 1128, 1369, 1467, 2118, 2958 cm$^{-1}$.

MS (Cl/i-Bu): m/z 287 (MH$^+$, 10%), 286 (M$^+$, 9%), 238 (100%).
HRMS (elemental composition): calc. (C$_{14}$H$_{23}$O$_2$S$_2$) 287.1139; found 287.1144.

5,5-Dimethyl-3-{$\{[\text{1-neopentylprop-2-ynyl}]$oxy|dithio$|$oxy$\}$hex-1-yne (9f)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 89%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.67-4.55 (m, 2H for four isomers), 2.61, 2.57, 2.56 and 2.54 (d, $J = 2.1$ Hz, 2H each), 1.88-1.69 (m, 4H for four isomers), 1.00, 0.99, 0.98 ($\times 2$) (s, 18H each).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 83.4, 83.3, 83.1 ($\times 2$) (=$C$– each), 75.9, 75.6, 75.3 and 74.9 (=$CH$ each), 73.6, 73.4, 71.2 and 70.8 (=$CH$– each), 49.8, 49.7, 49.6 and 49.5 (=$CH_2$– each), 30.52, 30.50 and 30.4 ($\times 2$) (=$CH(CH_3)_3$ each), 30.03 and 30.00 ($\times 3$) (=$CH(CH_3)_3$ each).
IR (neat): 1367, 1475, 1947, 2252, 2959 cm$^{-1}$. 

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MS (CI/CH₄): m/z 315 (MH⁺, 36%), 283 (MH⁺-“S”, 100%), 157 (M⁺/2, 7%), 109 (M⁺/2-“SO”, 53%).
HRMS (elemental composition): calc. (C₁₆H₂₇O₂S₂) 315.1452; found 315.1441.

3-{1-[(1-Tetrahydrofuran-3-ylprop-2-ynyl)oxy]dithio}oxy|prop-2-ynyl|tetrahydrofuran (9g)
Was obtained as a yellow liquid, as a mixture of eight diastereomers; yield: 93%.

¹H NMR (300 MHz, CDCl₃): δ 4.50-4.44 and 4.43-4.38 (m, 1H for four isomers each), 3.92-3.82 (m, 2H for all the isomers), 3.80-3.70 (m, 2H for all the isomers), 2.67 (septet, J = 8.0 Hz, 1H for all the isomers), 2.67-2.64 and 2.61-2.60 (m, 1H for four isomers each), 2.12-2.01 (m, 1H for all the isomers), 1.94-1.78 (m, 1H for all the isomers).

¹³C NMR (75 MHz, CDCl₃): δ 80.5, 80.3, 80.2 and 80.1 (≡C– for two isomers each), 77.30, 77.26, 77.1, 77.0, 75.1, 74.9, 74.74 and 74.71 (–CH O each), 76.7, 76.6, 76.5, 76.3 (x2), 76.2, 76.0 and 75.9 (≡CH each), 70.1 (x2), 70.0, 69.8, 69.6, 69.5 and 69.4 (x2) (CH₂–CH₂O each), 68.0 (CH₂–CH₂–O for all the isomers), 44.5, 44.3 (x2), 44.2 (x4) and 44.1 (CH₂–CH–CH₂ each), 29.1 (x2), 29.0 (x2), 29.9, 28.8, 28.7 and 28.6 (C–CH₂–C each).

IR (neat): 1063, 2113, 2248, 2871, 3304 cm⁻¹.

MS (CI/i-Bu): m/z 315 (MH⁺, 15%), 314 (M⁺, 9.37%), 157 (M⁺/2, 9%), 109 (M⁺/2-“SO”, 98%).
HRMS (elemental composition): calc. (C₁₄H₁₉O₄S₂) 315.0725; found 315.0719.

3-{{[(1-Benzhydrylprop-2-ynyl)oxy]dithio}oxy}4,4-diphenylbut-1-yne (9h)
Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 91%.

¹H NMR (300 MHz, CDCl₃): δ 7.35-7.15 (m, 20H for four isomers), 5.21 (dd, J = 8.4, 2.1 Hz, 2H for the first isomer), 5.12 (dd, J = 7.8, 2.1 Hz, 2H for the second isomer), 5.04 (dd, J = 7.2, 2.1 Hz, 2H for the third isomer) and 4.80 (dd, J = 8.1, 2.1 Hz, 2H for the forth isomer), 4.378 (d, J = 8.4 Hz, 2H for the first isomer), 4.377 (d, J = 7.8 Hz, 2H for the second isomer), 4.31 (d, J = 7.2 Hz, 2H for the third isomer) and 4.22 (d, J = 8.1 Hz, 2H for the fourth isomer), 2.54 and 2.53 (d, J = 2.1 Hz, 2H each) and 2.44 (d, J = 2.1 Hz, 2H for two isomers).

¹³C NMR (75 MHz, CDCl₃): δ 140.3, 140.2, 140.1, 140.00, 139.96, 139.9, 139.8, 139.7, 129.1, 129.0, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 127.13, 127.08, 127.0 and 126.9 (Ar for all the isomers), 81.2, 80.9, 80.60 and 80.55 (≡C– each), 78.260, 78.2, 75.8 and 75.4 (–CH–O each), 78.261, 78.8, 77.5 and 77.4 (≡CH each), 56.45 and 56.40 (–CH– each) and 56.2 (–CH– for two isomers).

IR (neat): 923, 1096, 1388, 1491, 2253, 2368, 3305 cm⁻¹.

MS (Cl/CH₄): m/z 507 (MH⁺, 2%), 442 (M⁺-“SO₂”, 64%), 441 ((M–H)⁺-“SO₂”, 100%).
HRMS (elemental composition): calc. (C32H27O2S2) 507.1452; found 507.1456.

1-{(Pent-2-ynyloxy)dithio|oxy}pent-2-yne (10b)
Was obtained as a yellow liquid with a strong smell of garlic; yield: 85%.

1H NMR (300 MHz, CDCl3): AB system: δ 4.49 and 4.41 (dt, J = 14.7, 2.2 Hz, 2H), 2.25 (qt, J = 7.5, 2.2 Hz, 4H), 1.16 (t, J = 7.5 Hz, 6H).

13C NMR (75 MHz, CDCl3): δ 90.4 (C−), 74.3 (C−), 62.1 (−CH2−O), 13.6 (−CH3), 12.5 (−CH2−CH3).

IR (neat): 1001, 1144, 1358, 1454, 2235, 2979 cm⁻¹.

MS (Cl/CH4): m/z 231 (MH⁺, 9%), 183 (MH⁺−“SO”, 45%), 117 (100%).

HRMS (elemental composition): calc. (C10H15O2S2) 231.0513; found 231.0500.

2-Methyl-5-{{(4-methylpent-4-en-2-ynyl)oxy}dithio|oxy}pent-1-en-3-yne (10c)
Was obtained as a yellow liquid with a strong smell of garlic; yield: 98%.

1H NMR (300 MHz, CDCl3): δ 5.36-5.35 (m, 2H), 5.28 (quint, J = 1.8 Hz, 2H), ABq: 4.63 and 4.56 (d, J = 15.3 Hz, 2H), 1.90 (dd, J = 1.8, 1.2 Hz, 6H).

13C NMR (75 MHz, CDCl3): δ 126.0 (C−CH3), 123.1 (C−CH2), 89.2 (C−C−), 82.9 (C−C−), 62.1 (−CH2−), 23.2 (−CH3).

IR (neat): 1010, 1072, 1345, 1356, 1438, 1613, 2228, 2921 cm⁻¹.

MS (Cl/CH4): m/z 255 (MH⁺, 2%), 237 (36%), 145 (100%).

HRMS (elemental composition): calc. (C12H15O2S2) 255.0513; found 255.0510.

1-{{(4-(tert-Butyl-dimethyl-silanyloxy)-but-2-ynyl)oxy}dithio|oxy}-4-(tert-butyl-dimethyl-silanyloxy)-but-2-yne (10e)
Was obtained as a yellow liquid; yield: 92%.

1H NMR (300 MHz, CDCl3): AB system: δ 4.50 and 4.44 (dt, J = 15.3, 1.9 Hz, 2H), 4.34 (t, J = 1.9 Hz, 4H), 0.88 (s, 18H), 0.10 (s, 12H).

13C NMR (75 MHz, CDCl3): δ 87.0 (C−), 79.6 (C−), 61.62 (−CH2−OS), 51.8 (−CH2−OSi), 25.9 (−C(CH3)3), 18.3 (−C(CH3)3), -5.1 (−Si(CH3)3).

IR (neat): 837, 1092, 1256, 1362, 1471, 1939, 1969, 2250, 2930 cm⁻¹.

MS (Cl/CH4): m/z 463 (MH⁺, 2%), 431 (MH⁺−“S”, 12%), 373 (100%).

HRMS (elemental composition): calc. (C20H39O4Si2S2) 463.1828; found 463.1807.
1-(([(3-(Trimethylsilanyl)prop-2-ynyl)oxy]dithio)oxy)-3-(trimethylsilanyl)prop-2-yne (10f)
Was obtained as a yellow liquid; yield: 86%.

$^{1}H$ NMR (300 MHz, CDCl$_3$): ABq: δ 4.48 and 4.40 (d, $J = 15.6$ Hz, 2H), -0.17 (s, 18H).

$^{13}C$ NMR (75 MHz, CDCl$_3$): δ 99.9 (≡C–), 93.8 (≡C–), 62.2 (−CH$_2$−), -0.2 (−CH$_3$, d, $^{1}J (^{13}C$-Si) = 19.3 Hz)).

IR (neat): 845, 938, 1023, 1038, 1251, 1351, 1922, 2178, 2960 cm$^{-1}$.

MS (EI): $m/z$ 318 (M$,^+$, 79%), 147 (C$_5$H$_{15}$OSi$_2^+$, 100%).

HRMS (elemental composition): calc. (C$_{12}$H$_{22}$O$_2$Si$_2$S$_2$) 318.0600; found 318.0603.

1-(([(3-(tert-Butyl-dimethyl-silanyl)-prop-2-ynyl)oxy]dithio)oxy)-3-(tert-butyl-dimethyl-silanyl)-prop-2-yne (10g)
Was obtained as a yellow liquid; yield: 94%.

$^{1}H$ NMR (300 MHz, CDCl$_3$): ABq: δ 4.50 and 4.43 (d, $J_{gem} = 15.6$ Hz, 2H each), 0.94 (s, 18H), 0.12 (s, 12H).

$^{13}C$ NMR (75 MHz, CDCl$_3$): δ 100.6 (≡C–), 92.2 (≡C–), 62.1 (−CH$_2$−), 26.2 (−C(CH$_3$)$_3$), 16.6 (−C(CH$_3$)$_3$), -4.7 (Si(CH$_3$)$_2$).

IR (neat): 1023, 2178, 2930 cm$^{-1}$.

MS (CI/CH$_4$): $m/z$ 345 (M$^-$“C$_4$H$_9$, 3%), 147 (57%), 113 (100%).

HRMS (elemental composition): calc. (C$_{14}$H$_{25}$O$_2$Si$_2$S$_2$) 345.0835; found 345.0846.

1-(([(4,4-Dimethylpent-2-ynyl)oxy]dithio)oxy)-4,4-dimethylpent-2-yne (10h)
Was obtained as a yellow liquid; yield: 98%.

$^{1}H$ NMR (300 MHz, CDCl$_3$): ABq: δ 4.49 and 4.41 (d, $J = 15.0$ Hz, 2H), 1.23 (s, 18H), 0.12 (s, 12H).

$^{13}C$ NMR (75 MHz, CDCl$_3$): δ 97.3 (≡C–), 73.6 (≡C–), 62.3 (−CH$_2$−), 30.7 (−CH$_3$), 27.6 (−C(CH$_3$)$_3$).

IR (neat): 929, 1063, 1362, 1265, 1456, 2243, 2971, 3399 cm$^{-1}$.

MS (CI/CH$_4$): $m/z$ 287 (MH$^+$, 3%), 286 (M$^+$, 3%), 223 (93%), 143 (M$^+$/2, 90%), 127 (M$^+$/2−“O”, 100%).

HRMS (elemental composition): calc. (C$_{14}$H$_{23}$O$_2$S$_2$) 287.1139; found 287.1133.

1-[3-(([(3-Cyclohex-1-en-1-ylprop-2-ynyl)oxy]dithio)oxy)prop-1-ynyl]cyclohexene (11a)
Was obtained as a yellow liquid; yield: 98%.

$^{1}H$ NMR (300 MHz, CDCl$_3$): δ 6.18-6.15 (m, 2H), ABq: 4.62 and 4.55 (d, $J = 15.3$ Hz, 2H), 2.14-2.08 (m, 8H), 1.65-1.55 (m, 8H).
\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3\]: \delta 136.4 (\equiv \text{C} \equiv), 120.0 (\equiv \text{C} \equiv), 90.0 (\equiv \text{C} \equiv), 81.2 (\equiv \text{C} \equiv), 62.4 (\equiv \text{C} \equiv), 29.0 (\equiv \text{C} \equiv), 25.7 (\equiv \text{C} \equiv), 22.3 (\equiv \text{C} \equiv), 21.5 (\equiv \text{C} \equiv).\]

IR (neat): 937, 1000, 1136, 1344, 1436, 1630, 2221, 2247, 2936 cm\(^{-1}\).

MS (CI/CH\(_4\)): \(m/z\) 335 (MH\(^{+}\), 8%), 286 (M\(^{+}\)-“SO”, 79%), 238 (M\(^{+}\)-“S\(_2\)O\(_2\)”, 61%), 119 (M\(^{+}/2\)-“SO”, 100%).

HRMS (elemental composition): calc. (C\(_{18}\)H\(_{23}\)O\(_2\)S\(_2\)) 335.1139; found 335.1129.

1-(\{[(4-(Tetrahydro-2\(H\)-pyran-2-yloxy)but-2-ynyl)oxy]dithio\}oxy)-4-(tetrahydro-2\(H\)-pyran-2-yloxy)but-2-ynyl)oxy (11c)

Was obtained as a yellow liquid; yield: 98%.

\[ ^{1}H \text{ NMR (300 MHz, CDCl}_3\]: \delta 4.81 (t, \(J = 3.0\) Hz, 2H), AB system: 4.55 and 4.48 (dt, \(J = 15.3, 1.9\) Hz, 2H), AB system: 4.35 and 4.28 (dt, \(J = 15.6, 1.9\) Hz, 2H), 3.87-3.79 (m, 2H), 3.57-3.51 (m, 2H), 1.85-1.69 (m, 4H), 1.66-1.52 (m, 8H).

\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3\]: \delta 96.7 (O\(-\text{C} \equiv), 84.4 (\equiv \text{C} \equiv), 84.63 (\equiv \text{C} \equiv), 84.3, 83.0, 82.8 and 82.7 (\equiv \text{C} \equiv), 71.4 and 71.3 (\equiv \text{CH} \equiv \text{CH}_2 \equiv), 69.5 (\equiv \text{C} \equiv \text{CH}_3 \equiv), 62.0 (\equiv \text{CH}_2 \equiv \text{C} \equiv), 54.1 (\equiv \text{CH}_2 \equiv \text{O} \equiv), 30.2 (\equiv \text{CH}_2 \equiv \text{O} \equiv), 25.4 (\equiv \text{CH}_2 \equiv \text{O} \equiv), 22.5, 22.4, 22.3 and 22.2 (\equiv \text{CH}_3 \equiv), 19.0 (\equiv \text{CH}_2 \equiv \text{O} \equiv).

IR (neat): 937, 1000, 1136, 1344, 1436, 1630, 2221, 2247, 2936 cm\(^{-1}\).

MS (CI/i-Bu): \(m/z\) 403 (MH\(^{+}\), 8%), 354 (M\(^{+}\)-“SO”, 20%), 323 (M\(^{+}/2\)-“SO\(_2\)”, 10%).

HRMS (elemental composition): calc. (C\(_{18}\)H\(_{27}\)O\(_6\)S\(_2\)) 403.1249; found 403.1226.

1-({[(1-Methyl-4-(tetrahydro-2\(H\)-pyran-2-yloxy)but-2-ynyl)oxy]dithio\}oxy)-1-methyl-4-(tetrahydro-2\(H\)-pyran-2-yloxy)but-2-ynyl)oxy (11d)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 87%.

\[ ^{1}H \text{ NMR (300 MHz, CDCl}_3\]: \delta 4.82 (br s, 2H for four isomers), 4.70, 4.69, 4.66 and 4.65 (qt, \(J = 6.6, 1.5\) Hz, 2H each), AB system: 4.38-4.32 and 4.31-4.25 (m, 2H for four isomers), 3.88-3.80 (m, 2H for four isomers), 3.57-3.51 (m, 2H for four isomers), 1.90-1.70 (m, 4H for four isomers), 1.65-1.58 (m, 8H for four isomers), 1.54 and 1.52 (d, \(J = 6.6\) Hz, 6H each), 1.53 (d, \(J = 6.6\) Hz, 6H for two isomers).

\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3\]: \delta 96.7 (O\(-\text{C} \equiv), 84.4 (\equiv \text{C} \equiv), 84.63 (\equiv \text{C} \equiv), 84.3, 83.0, 82.8 and 82.7 (\equiv \text{C} \equiv), 71.4 and 71.3 (\equiv \text{CH} \equiv \text{CH}_2 \equiv), 69.5 (\equiv \text{C} \equiv \text{CH}_3 \equiv), 62.0 (\equiv \text{CH}_2 \equiv \text{C} \equiv), 54.1 (\equiv \text{CH}_2 \equiv \text{O} \equiv), 30.2 (\equiv \text{CH}_2 \equiv \text{O} \equiv), 25.4 (\equiv \text{CH}_2 \equiv \text{O} \equiv), 22.5, 22.4, 22.3 and 22.2 (\equiv \text{CH}_3 \equiv), 19.0 (\equiv \text{CH}_2 \equiv \text{O} \equiv).

IR (neat): 1023, 1120, 1336, 1442, 1964, 2249, 2948 cm\(^{-1}\).
MS (CI/CH₄): m/z 431 (MH⁺, 7%), 430 (M⁺, 11%), 347 (50%), 263 (M⁺/2+“SO”, 100%), 245 (60%).
HRMS (elemental composition): calc. (C₂₀H₃₁O₆S₂) 431.1562; found 431.1560.

[3-{{(1-Benzhydryl-3-phenylprop-2-ynyl)oxy}dithio}oxy}-4,4-diphenylbut-1-ynyl]benzene (11e)
Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 88%.

1H NMR (300 MHz, CDCl₃): δ 7.40-7.16 (m, 30H for four isomers), 5.45 (d, J = 8.1 Hz, 2H for the first isomer), 5.40 (d, J = 7.8 Hz, 2H for the second isomer), 5.29 (d, J = 7.2 Hz, 2H for the third isomer) and 5.15 (d, J = 7.5 Hz, 2H for the fourth isomer); 4.485 (d, J = 8.1 Hz, 2H for the first isomer), 4.484 (d, J = 7.8 Hz, 2H for the second isomer), 4.423 (d, J = 7.2 Hz, 2H for the third isomer) and 4.364 (d, J = 7.5 Hz, 2H for the fourth isomer).

13C NMR (75 MHz, CDCl₃): δ 140.6, 140.5, 140.45, 140.38, 140.2, 140.11, 140.08, 131.8, 131.7, 129.34, 129.28, 129.10, 129.07, 128.99, 128.96, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.0, 126.9, 122.5, 122.43, 122.37 and 122.3 (Ar for all the isomers); 90.1, 89.8, 89.5 and 89.4 (〓C– each); 86.9, 86.6, 86.4 and 86.3 (〓C– each); 78.94, 78.88, 77.0 and 76.5 (〓CH– each); 56.7, 56.65, 56.57 and 56.5 (〓CH– each).

IR (neat): 990, 1031, 1319, 1451, 1964, 2249, 3030, 3063 cm⁻¹.

MS (CI/i-Bu): m/z 659 (MH⁺, 3%), 329 (M⁺/2, 18%), 312 (100%).
HRMS (elemental composition): calc. (C₄₄H₃₅O₂S₂) 659.2078; found 659.2067.

1-Bromo-3-{{(3-bromoprop-2-ynyl)oxy}dithio}prop-1-ynyl)prop-1-ynyl (11f)
Was obtained as a yellow liquid; yield: 87%.

1H NMR (300 MHz, CDCl₃): ABq: δ 4.53 and 4.47 (d, J = 15.6 Hz, 2H).

13C NMR (75 MHz, CDCl₃): δ 75.1 (〓C–), 62.2 (〓CH₂–), 48.9 (〓C–Br).

IR (neat): 931, 1048, 1347, 1955, 2219, 2935 cm⁻¹.

MS (CI/i-Bu): m/z 331 (MH⁺, 1%), 197 (M⁺/2+“S”, 17%), 135 (Br–C≡C–CH₂OH⁺, 86), 134 (M⁺/2–“S”, 45%), 133 (100%).

HRMS (elemental composition): calc. (C₁₄H₁₂O₂S₂Br₂) 330.8098; found 330.8174.

{(4-{{(4-(Phenylsulfonyl)but-2-ynyl)oxy}dithio}oxy}but-2-ynyl)sulfonyl}benzene (11g)
Was obtained as a yellow-orange liquid; yield: 81%.

1H NMR (300 MHz, CDCl₃): δ 7.99-7.96 (m, 4H), 7.73-7.67 (m, 2H), 7.62-7.56 (m, 2H), AB system: 4.45 and 4.39 (dt, J = 15.6, 2.1 Hz, 2H), 4.06 (t, J = 2.1 Hz, 4H).
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 137.6, 134.4, 129.2 and 128.7 (Ar), 82.6 (==C--), 76.1 (==C--), 61.2 (==CH$_2$--), 48.6 (==CH$_2$--).

IR (neat): 1085, 1148, 1324, 1732, 1964, 2254, 2926 cm$^{-1}$.

MS (Cl/i-Bu): $m/z$ 483 (MH$^+$, 0.2%), 335 (100%).

HRMS (elemental composition): calc. (C$_{20}$H$_{19}$O$_6$S$_4$); 483.0065 found 483.0066.

[3-{(3-Phenyl-1-tert-butylprop-2-ynyl)oxy}dithio]oxy)-4,4-dimethylpent-1-ynyl]benzene (11h)

Was obtained as an orange liquid, as a mixture of four diastereomers; yield: 93%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.48-7.44 (m, 4H for all the isomers), 7.32-7.28 (m, 6H for all the isomers), 4.44, 4.42, 4.39 ($\times$2) (s, 2H each), 1.10, 1.09, 1.07 ($\times$2) (s, 18H each).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 132.0, 131.8, 128.6, 128.5, 128.4, 128.3, 122.82 (ipso), 122.76 (ipso), 122.7 (ipso) (Ar for all the isomers), 88.4, 88.2, 87.6, 87.5 (==C-- each), 86.6 ($\times$2), 86.3, 86.2 (==C-- each), 85.9, 85.7, 83.0, 82.7 (==CH--O each), 36.7, 36.6, 36.4, 36.3 (==C(CH$_3$)$_3$ each), 26.02, 25.95 ($\times$2), 25.9 (==C(CH$_3$)$_3$ each).

IR (neat): 1096, 1139, 1477, 2253, 2964 cm$^{-1}$.

MS (CI/CH$_4$): $m/z$ 438 (M$^+$, 6%), 105 (100%).

HRMS (elemental composition): calc. (C$_{26}$H$_{30}$O$_2$S$_2$) 438.1687; found 438.1639.

1-{(3-(tert-Butyl-diphenyl-silanyl)-prop-2-ynyl)oxy}dithio]oxy)-3-(tert-butyl-diphenyl-silanyl)-prop-2-yne (11i)

Was obtained as a yellow liquid; yield: 95%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.82-7.75 (m, 8H), 7.41-7.32 (m, 12H), 4.62 (s, 4H), 1.10 (s, 18H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 135.7, 132.8 (ipso), 129.8, 127.9 (Ar), 104.0 (==C--), 89.4 (==C--), 62.0 (==CH$_2$--), 27.2 (==C(CH$_3$)$_3$), 18.7 (==C(CH$_3$)$_3$).

IR (neat): 1021, 1111, 1429, 2180, 2930 cm$^{-1}$.

MS (Cl/CH$_4$): $m/z$ 593 (M$^+$--“C$_4$H$_9$”, 0.7%), 237 (100%), 199 (93%).

HRMS (elemental composition): calc. (C$_{34}$H$_{33}$O$_2$Si$_2$S$_2$) 593.1461; found 593.1453.

1-{3-[(3-(1-Naphthyl)prop-2-ynyl)oxy}dithio]oxy}prop-1-ynyl]naphthalene (11j)

Was obtained as a yellow liquid; yield: 95%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.32 (dm, $J$ = 8.0 Hz, 2H), 7.79 (dm, $J$ = 8.0 Hz, 4H), 7.66 (dd, $J$ = 7.0, 1.2 Hz, 2H), 7.56-7.44 (m, 4H), 7.35 (dd, $J$ = 8.0, 7.0 Hz, 2H), ABq: 4.90 and 4.84 (d, $J$ = 15.6 Hz, 2H each)
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 133.4 (C– ipso of naphthyl), 133.1 (C– ipso of naphthyl), 131.0, 129.4, 128.3, 127.0, 126.6, 126.1 and 125.2 (C– of naphthyl), 119.8 (C–C= ipso of naphthyl), 88.7 (C–), 86.4 (C–), 62.4 (–CH$_2$–O).

IR (neat): 1342, 2213, 3059 cm$^{-1}$.

MS (EI): m/z 426 (M$^+$, 0.1%), 181 (M$^+$/-“S”, 70%), 165 (M$^+$/-“SO”, 59%), 153 (M$^+$/-“SCO”, 100%).

HRMS (elemental composition): calc. (C$_{26}$H$_{18}$O$_2$S$_2$) 426.0748; found 426.0783.

4-{$[\{1-$(Ethynyl-2,2-dimethylbut-3-enyl)oxy$dithio$oxy]-3,3-dimethylhex-1-en-5-yne (12b)

Was obtained as a yellow-brown liquid, as a mixture of four diastereomers; yield: 93%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.90-5.73 (m, 2H for four isomers), 5.12-5.06 (m, 4H for four isomers), 4.24, 4.22, 4.20 and 4.18 (d, $J$ = 2.1 Hz, 2H each), 2.60, 2.57, 2.529 and 2.526 (d, $J$ = 2.1 Hz, 2H each), 2.17-2.13 (m, 4H for four isomers), 1.04-0.97 (m, 12H for four isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 134.2, 134.1 (×2) and 134.0 (C– each), 118.42, 118.37 (×2) and 118.2 (C$_2$ each), 83.7, 83.5, 80.9 and 80.3 (–CH–O each), 80.64, 80.59 and 80.3 (×2) (C– each), 77.0, 76.8, 76.2 and 76.1 (C–CH each), 43.0 (–CH$_2$– for four isomers), 39.1, 39.0 and 38.7 (×2) (–C(CH$_3$)$_2$ each), 23.2, 23.12, 23.08 and 23.0 (–CH$_3$ each), 22.83 (×2) and 22.75 (×2) (–CH$_3$ each).

IR (neat): 1130, 1367, 1469, 1639, 2118, 2965, 3302 cm$^{-1}$.

MS (CI/CH$_4$): m/z 339 (MH$^+$, 100%), 338 (M$^+$, 40%), 169 (M$^+$/-“O”, 36%), 121 (M$^+$/-“SO”, 25%).

HRMS (elemental composition): calc. (C$_{18}$H$_{27}$O$_2$S$_2$) 339.1452; found 339.1452.

5-Chloro-3-{$[\{1-$(2-chloro-1,1-dimethylethyl)prop-2-ylnyl$]oxy$dithio$oxy]-4,4-dimethylpent-1-ynyl (12c)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 88%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.55, 4.54, 4.51 and 4.48 (d, $J$ = 2.1 Hz, 2H each), 3.63-3.42 (m, 4H for four isomers), 2.64, 2.63, 2.58 and 2.57 (d, $J$ = 2.1 Hz, 2H each), 1.13-1.09 (m, 12H for four isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 80.60, 80.57, 77.9 and 77.8 (–CH–O each), 79.6, 79.5 (×2) and 79.4 (C– each), 77.6, 77.4, 76.9 and 76.6 (C–CH each), 52.03, 51.97 (×2) and 51.9 (–CH$_2$– each), 40.9, 40.8, 40.7 and 40.6 (–C(CH$_3$)$_2$ each), 23.4, 22.7, 21.9 (×2), 21.7, 21.0, 20.92 and 20.86 (–CH$_3$ (×2) each).

IR (neat): 1131, 1471, 2118, 2253, 2973, 3305 cm$^{-1}$.
MS (Cl/CH₄): m/z 354 (M⁺, 12%), 177 (M⁺/2, 11%), 129 (M⁺/2−“SO”, 34%), 93 (M⁺/2−“SOHCl”, 100%).

HRMS (elemental composition): calc. (C₁₄H₂₀O₂S₂Cl₂) 354.0282; found 354.0276.

5-Bromo-3-[(1-(2-bromo-1,1-dimethylethyl)prop-2-ynyl)oxy]dithio]oxy]-4,4-dimethylpent-1-yne (12d)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 85%.

¹H NMR (300 MHz, CDCl₃): δ 4.57, 4.54, 4.52 and 4.48 (d, J = 2.1 Hz, 2H each), 3.58-3.35 (m, 4H for four isomers), 2.65, 2.64, 2.59 and 2.58 (d, J = 2.1 Hz, 2H each), 1.18-1.11 (m, 12H for four isomers).

¹³C NMR (75 MHz, CDCl₃): δ 81.0, 80.9 and 78.3 (×2) (−CH−O each), 79.6, 79.4 (×2) and 79.3 (≡C− each), 77.6, 77.3, 76.8 and 76.5 (≡CH each), 42.4 and 42.2 (×3) (−CH₂− each), 40.0, 39.9, 39.8 and 39.7 (−C(CH₃)₂ each), 22.6 (×3) and 22.4 (−CH₃ each), 21.6 and 21.4 (×3) (−CH₃ each).

IR (neat): 1216, 2118, 2253, 2973, 3305 cm⁻¹.

MS (Cl/CH₄): m/z 442 (M⁺, 24%), 381 (100%).

HRMS (elemental composition): calc. (C₁₄H₂₀O₂S₂Br₂) 441.9271; found 441.9300.

3-[1-{[(1-Adamantan-3-ylprop-2-ynyl)oxy]dithio]oxy}prop-2-ynyl]adamantane (12e)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 84%.

¹H NMR (300 MHz, CDCl₃): δ 4.05, 4.03 and 4.02 (×2) (d, J = 2.1 Hz, 2H each), 2.60, 2.57, 2.524 and 2.518 (d, J = 2.1 Hz, 2H each), 2.01 (br s, 6H for all the isomers), 1.76-1.59 (m, 24H for all the isomers).

¹³C NMR (75 MHz, CDCl₃): δ 85.6, 85.4, 82.3 and 82.1 (−CH−O each), 80.3, 80.2 and 79.9 (×2) (≡C− each), 77.0, 76.7, 76.24 and 76.16 (≡CH each), 38.1, 38.05, 37.98 and 37.9 (−CH₂− each), 37.6 (×2) and 37.5 (×2) (−C−CHOH each), 37.0 (−CH₂− for all the isomers), 28.3 (C−CH−C for all the isomers).

IR (neat): 1130, 1451, 1943, 2248, 2907 cm⁻¹.

MS (Cl/i-Bu): m/z 442 (M⁺, 5%), 381 (100%).


4,4,4-Tribromo-3-[(1-(tribromomethyl)prop-2-ynyl)oxy]dithio]oxy]but-1-yne (12f)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 44%.

¹H NMR (300 MHz, CDCl₃): δ 5.17, 5.14, 5.11 and 5.09 (d, J = 2.1 Hz, 2H each), 2.97, 2.944, 2.936 and 2.93 (d, J = 2.1 Hz, 2H each).
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 86.7, 86.3, 85.0 and 84.9 (–CH–O each), 79.7, 79.5, 79.4 and 79.0 (≡C– each), 76.7 (≡CH for all isomers), 49.2 (–CBr$_3$ for all isomers).

IR (neat): 1022, 1069, 2127 cm$^{-1}$.

MS (CI/i-Bu): m/z 483 (C$_8$H$_5$O$_2$S$_8$I$^{37}$Br$_3$, 8%), 448 (C$_4$H$_4$OS$_2$Br, 4%).

HRMS (elemental composition): decomposed.

[1-{{[(1-Cyclohexylprop-2-ynyl)oxy]dithio}oxy}prop-2-ynyl]cyclohexane (12g)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 81%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.34-4.29 (m, 2H for four isomers), 2.60, 2.58 2.54 and 2.536 (d, $J$ = 2.1 Hz, 2H each), 1.87-1.69 (m, 12H for four isomers), 1.28-1.13 (m, 10H for four isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 80.98, 80.95, 80.83 and 80.79 (≡C– each), 80.60, 80.55, 78.24 and 78.16 (–CH–O each), 76.6, 76.4, 76.0 and 75.9 (≡CH each), 42.70, 42.68, 42.6 and 42.5 (–CH– each), 28.82, 28.78, 28.72, 28.69, 28.5, 28.3, 28.2, 28.1, 27.9, 27.8, 26.4, 26.3, 25.85, 25.80 and 25.76 (–CH$_2$– for four isomers).

IR (neat): 1095, 1167, 1330, 1379, 1450, 2253, 2855, 2932 cm$^{-1}$.

MS (CI/i-Bu): m/z 337 ((M–H)$^+$, 15%), 207 (100%).

HRMS (elemental composition): calc. (C$_{18}$H$_{25}$O$_2$S$_2$) 337.1296; found 337.1283.

[1-{{[(1-Phenylprop-2-ynyl)oxy]dithio}oxy}prop-2-ynyl]benzene (13a)

Was obtained as a yellow liquid, as a mixture of four diastereomers; yield: 41%. In this case the reaction was carried out at -15 $^\circ$C due to high reactivity of the ester.

From the crude mixture were established the following spectral data: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.60, 5.58, 5.53 and 5.50 (d, $J$ = 2.1 Hz, 2H each), 2.83, 2.80, 2.78 and 2.73 (d, $J$ = 2.1 Hz, 2H each).

Due to instability of this ester additional spectral data could not been measured.

Rearrangement of α-alkyl substituted dipropargyloxy disulfides.

(3S,5S,6S,Z)- and (3R,5S,6S,Z)-3-Ethyl-4-propylidene-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxides (18b/19b)

Were obtained as a mixture of two diastereomers 18b and 19b in the ratio of 2.0:1.0, respectively, as a yellow liquid, upon silica gel chromatography, using chloroform as eluent; total yield: 29%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.00 (td, $J$ = 7.2, 2.3 Hz, 1H (=CH–) for 18b) and 5.94 (td, $J$ = 7.2, 1.8 Hz, 1H (=CH–) for 19b), 5.50 (d, $J$ = 5.1 Hz, 1H (CH–C=) for 18b) and 5.42 (d, $J$ = 5.0 Hz, 1H (CH–C=) for 19b), 4.55 (d, $J$ = 5.1 Hz, 1H (CH–C=O) for 18b) and 4.53 (d, $J$ = 5.0 Hz, 1H
(1H (CH–Et) for 19b), 2.26-2.13 (m, 2H for both diastereomers), 1.06 (t, \(J = 7.2 \text{ Hz}, 3 \text{H for 18b}\)) and 1.056 (t, \(J = 7.2 \text{ Hz}, 3 \text{H for 19b}\)), 1.03 (t, \(J = 7.5 \text{ Hz}, 3 \text{H for 18b}\)) and 0.99 (t, \(J = 7.5 \text{ Hz}, 3 \text{H for 19b}\)).

\(^{13}\text{C NMR (75 MHz, CDCl}_3\)): \(\delta 201.7 \text{ (C=O for 18b) and 199.3 (C=O for 19b)}, 138.5 (=\text{CH–} \text{ for 19b) and 136.9 (=\text{CH–} \text{ for 18b)), 125.6 (=\text{C–} \text{ for 19b) and 124.8 (=\text{C–} \text{ for 18b), 68.9 (\text{CH–C}=O for 18b) and 67.3 (\text{CH–C}=O for 19b), 66.8 (\text{CH–C}=) \text{ for 18b) and 65.1 (\text{CH–C}=) \text{ for 19b), 53.3 (=\text{CH–Et for 19b) and 52.2 (=\text{CH–Et for 18b), 26.7 (=\text{CH–Et for 18b) and 21.5 (=\text{CH–Et for 18b), 21.3 (=\text{CH–} \text{ for 19b) and 18.2 (=\text{CH–} \text{ for 18b), 14.3 (=\text{CH3 for both diastereomers), 11.3 (=\text{CH3 for 18b) and 11.2 (=\text{CH3 for 19b).}}}} \text{ IR (neat): } 1108 (\text{S=O), 1711 (}\text{C=O} \text{ cm}^{-1}.\]

\(\text{MS (CI/CH}_4\): m/z 231 (MH+, 6%), 197 ((M-H)\text{+}“S”, 9%), 181 ((M-H)\text{+}“SO”, 100%).\]

\(\text{HRMS (elemental composition): calc. (C}_{10}\text{H}_{15}\text{O}_{2}\text{S}_{2}) 231.0513; found 231.0530.\]

**(3S,5S,6S,Z)- and (3R,5S,6S,Z)-4-Hexylidene-3-pentyl-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxides (18c/19c)**

Were obtained as a mixture of two diastereomers 18c and 19c in the ratio of 1.6:1.0, respectively, as a yellow liquid, upon silica gel chromatography, using n-hexane/chloroform (2:1) as eluent: total yield: 29%.

\(^{1}\text{H NMR (600 MHz, CDCl}_3\)): \(\delta 5.98 (\text{td, }J = 7.5, 2.3 \text{ Hz, 1H (=CH–) for 18c) and 5.93 (\text{td, }J = 7.5, 1.8 \text{ Hz, 1H (=CH–) for 19c), 5.49 (d, }J = 5.1 \text{ Hz, 1H (CH–C)=) for 18c) and 5.42 (d, }J = 5.0 \text{ Hz, 1H (CH–C)=) for 19c), 4.55 (d, }J = 5.1 \text{ Hz, 1H (CH–C)=O for 18c) and 4.52 (d, }J = 5.0 \text{ Hz, 1H (CH–C)=O for 19c), 4.04-4.00 (m, 1H (CH–Pentyl) for 18c) and 3.28 (tm, }J = 6.0 \text{ Hz, 1H (CH–Pentyl) for 19c), 2.18-2.09 (m, 2H for both diastereomers), 2.03-1.84 (m, 2H for both diastereomers), 1.49-1.30 (m, 12H for both diastereomers), 0.92-0.88 (m, 6H for both diastereomers).\]

\(^{13}\text{C NMR (50 MHz, CDCl}_3\)): \(\delta 201.6 (\text{C}=O for 18c) and 199.6 (\text{C}=O for 19c), 137.1 (=\text{CH–} \text{ for 19c) and 135.4 (=\text{CH–} \text{ for 18c), 128.7 (=\text{C–} \text{ for 19c) and 125.9 (=\text{C–} \text{ for 18c), 69.0 (\text{CH–C}=O for 18c) and 67.4 (\text{CH–C}=O for 19c), 67.0 (\text{CH–C}=) \text{ for 18c) and 65.3 (\text{CH–C}=) \text{ for 19c), 52.3 (=\text{CH–Pentyl for 19c) and 51.3 (=\text{CH–Pentyl for 18c), 34.1 (=\text{CH2–} \text{ for both diastereomers), 32.3 (=\text{CH2–} \text{ for both diastereomers), 31.7 (=\text{CH2–} \text{ for 19c), 31.4 (=\text{CH2–} \text{ for both diastereomers), 31.4 (=\text{CH2–} \text{ for 18c), 29.3 (=\text{CH2–} \text{ for both diastereomers), 28.1 (=\text{CH2–} \text{ for 18c), 27.9 (=\text{CH2–} \text{ for 19c), 26.6 (=\text{CH2–} \text{ for both diastereomers), 25.3 (=\text{CH2–} \text{ for both diastereomers), 22.4 (=\text{CH3 for both diastereomers), 14.0 (=\text{CH3 for both diastereomers).}}}} \text{- 13 -}


IR (neat): 1114 (S=O), 1713 (C=O) cm$^{-1}$.

MS (CI/CH$_4$): m/z 315 (MH$^+$, 34%), 282 (M$^+$-“S”, 36%), 280 (100%), 265 ((M-H)$^+$-“SO”, 28%).

HRMS (elemental composition): calc. (C$_{16}$H$_{27}$O$_2$S$_2$) 315.1452; found 315.1428.

(3S,5S,6S,Z)- and (3R,5S,6S,Z)-4-(3,3-Dimethylbutyldiene)-3-neopentyl-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxides (18f/19f)

Were obtained as a mixture of two diastereomers 18f and 19f in the ratio of 2.5:1.0, respectively, as a yellow liquid, upon silica gel chromatography, using n-hexane/ethyl acetate (8:1) as eluent; total yield: 32%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.14 (td, $J = 8.0$, 2.3 Hz, 1H (=CH$\equiv$) for 18f) and 6.04 (td, $J = 8.0$, 1.5 Hz, 1H (=CH$\equiv$) for 19f), 5.54 (d, $J = 5.1$ Hz, 1H (CH−C=) for 18f) and 5.41 (d, $J = 5.0$ Hz, 1H (CH−C=) for 19f), 4.62 (d, $J = 5.1$ Hz, 1H (CH−C=O) for 18f) and 4.54 (d, $J = 5.0$ Hz, 1H (CH−C=O) for 19f), 3.97-3.93 (m, 1H (CH−Neopentyl) for 18f) and 3.39-3.36 (m, 1H (CH−Neopentyl) for 19f), 2.10-1.97 (m, 2H for both diastereomers), 1.74-1.63 (m, 2H for both diastereomers), 1.02 (s, 3H for 19f) and 0.97 (s, 3H for 18f), 0.94 (s, 3H for 18f) and 0.93 (s, 3H for 19f).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 201.7 (C=O for 18f) and 200.4 (C=O for 19f), 134.0 (=C− for 18f), 133.0 (=C− for 19f) and 128.8 (=C− for 18f), 69.0 (CH−C=O for 18f) and 67.5 (CH−C= for 19f), 66.8 (CH−C= for 18f) and 65.4 (CH−C= for 19f), 50.2 (−CH−Neopentyl for 19f) and 48.6 (−CH−Neopentyl for 18f), 42.0 (−CH$_2$− for 18f) and 41.7 (−CH$_2$− for 19f), 36.8 (−CH$_2$− for both diastereomers), 31.7 (−C(CH$_3$)$_3$ for both diastereomers), 30.8 (−C(CH$_3$)$_3$ for both diastereomers), 29.6 (−C(CH$_3$)$_3$ for both diastereomers), 29.3 (−C(CH$_3$)$_3$ for both diastereomers).

IR (neat): 1102 (S=O), 1716 (C=O) cm$^{-1}$.

MS (CI/CH$_4$): m/z 314 (M$^+$, 22%), 282 (M$^+$-“S”, 7%), 266 (M$^+$-“SO”, 16%).

HRMS (elemental composition): calc. (C$_{16}$H$_{26}$O$_2$S$_2$) 314.1374; found 314.1376.

(3S,5S,6S,Z)- and (3R,5S,6S,Z)-3-Tetrahydrofuran-3-yl-4-(tetrahydrofuran-3-ylmethylene)-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxides (18g/19g)

Were obtained as a mixture of eight diastereomers (four 18g and four 19g) in the ratio of 1.2:1.0, respectively, as a yellow liquid, upon silica gel chromatography, using n-hexane/ethyl acetate (8:1→4:1→1:1→1:2) as eluent; total yield: 63%.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 6.00-5.80 (m, 1H (=CH−) for 18g+19g), 5.51-5.48 (m, 1H (CH−C=) for 18g) and 5.46-5.42 (m, 1H (CH−C=) for 19g), 4.56-4.53 (m, 1H (CH−C=O) for 18g+19g), 4.40-
4.37 (m, 1H for 18g), 4.30-4.24 (m, 1H for 19g), 4.05-3.63 (m, 8H for 18g+19g), 3.56-3.37 (m, 1H 18g+19g), 3.12-2.79 (m, 2H for 18g+19g), 2.29-2.08 (m, 1H for 18g+19g), 1.99-1.90 (m, 1H for 18g+19g), 1.81-1.68 (m, 1H for 18g+19g).

13C NMR (150 MHz, CDCl3): δ 200.3 (C=O for 18g) and 199.6 (C=O for 19g), 140.2, 140.1, 140.03, 139.98 (=CH− for 19g each) and 137.2, 137.1, 136.71, 136.69 (=CH− for 18g each), 126.0 (×2), 125.9, 125.8 (=C− for 19g each) and 125.6 (×2), 125.4 (×2) (=C− for 18g each), 73.2, 73.0, 72.9, 72.8, 72.0, 71.8 (=CH2−O for all the diastereomers 18g+19g), 70.0 (CH−C=O for 18g) and 68.45 (CH−C=O for 19g), 68.46 (CH−C= for 18g) and 65.6 (CH−C= for 19g), 68.4, 68.3, 68.1, 67.7, 67.5 (=CH2−O for all the isomers 18g+19g), 57.4, 57.3 (=CH−tetrahydropyranyl for 18g) and 56.8, 56.5, 56.4 (=CH−tetrahydropyranyl for 19g), 38.6, 38.5, 38.3, 38.2 (CH2−CH−CH2 for all the diastereomers 18g+19g), 34.2, 34.0, 33.8, 33.7, 33.5, 31.9, 30.9, 30.2, 29.7 (=CH2− for all the diastereomers 18g+19g).

IR (neat): 1110 (S=O), 1715 (C=O) cm−1.

MS (CI/CH4): m/z 315 (MH+, 19%), 281 ((M-H)+−“S”, 41%), 265 ((M-H)+−“SO”, 21%).

HRMS (elemental composition): calc. (C14H19O4S2) 315.0725; found 315.0718.

(3S,5S,6S,Z)- and (3R,5S,6S,Z)-3 -Benzhydryl-4-(2,2-diphenyl-ethylidene)-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxides (18h/19h)

Were obtained as a mixture of eight isomers (four 18h and four 19h) in the ratio of 1.0:2.75, respectively, as a yellow liquid, which converts to yellow solid in freezer, upon silica gel chromatography, using n-hexane/ethyl acetate (4:1) as eluent; total yield: 62%. The products are not stable at room temperature. For this reason mp could not been measured.

1H NMR (600 MHz, CDCl3): δ 7.36-7.10 (m, 16H of “Ar” groups for all 18h+19h isomers), 6.95-6.92 (m, 2H of “Ar” groups for 19h) and 6.83-6.80 (m, 2H of “Ar” groups for 18h), 6.68-6.64 (m, 2H of “Ar” groups for 18h) and 6.56-6.53 (m, 2H of “Ar” groups for 19h),  6.16 (d, J = 9.5 Hz, 1H (=CH−) for 18h) and 5.95 (d, J = 9.5 Hz, 1H (=CH−) for 19h), 5.36 (d, J = 5.0 Hz, 1H (S−CH−C=) for 18h) and 5.35 (d, J = 5.0 Hz, 1H (S−CH−C=) for 19h), 5.11 (d, J = 10.0 Hz, 1H (CH−CH−C=) for 19h) and 4.82 (d, J = 10.0 Hz, 1H (CH−CH−C=) for 18h), 4.69 (d, J = 9.5 Hz, 1H (Ph2CH−C=) for 19h) and 4.59 (d, J = 9.5 Hz, 1H (Ph2CH−C=) for 18h), 4.34 (d, J = 5.0 Hz, 1H (S−CH−C=) for 18h) and 4.29 (d, J = 5.0 Hz, 1H (S−CH−C=) for 19h), 4.27 (d, J = 10.0 Hz, 1H (CH−CH−C=) for all 18h+19h).

13C NMR (150 MHz, CDCl3): δ 198.2 (C=O for 18h) and 198.0 (C=O for 19h), 142.6 (=CH− for 19h) and 141.6 (=CH− for 18h), 143.0, 142.3, 141.7 and 140.8 (Cipso of “Ar” groups for all 18h+19h), 129.1, 129.0, 128.64 (×3), 128.56 and 128.2 (×2) (=CHorto+meta of “Ar” groups for all
Rearrangement of \( \gamma \)-alkyl substituted dipropargyloxy disulfides.

**Rearrangement of ester 8**: see Table 3. The products were isolated and separated using chloroform as eluent.

**Rearrangement of ester 10a**: see Table 3. The products were isolated and separated using n-hexane/chloroform (1:1→1:2→1:3→100% CHCl\(_3\)) as eluent.

3-Methyl-4-pent-3-ynyl-1,2-dithiete 1,1-dioxide (23a) and 4-methyl-3-pent-3-ynyl-1,2-dithiete 1,1-dioxide (24a)

\(^1\)H NMR (600 MHz, CDCl\(_3\)): see Scheme S1, Table S1.

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): see Scheme S1, Table S2.

IR (neat): 1113 (S=O), 1493, 1716 (C=O) cm\(^{-1}\).

MS (Cl/\(\text{CH}_4\)): \(m/z\) 507 (MH\(^+\), 2%), 473 (M-H\(^+\)-“S”, 3%), 167 (100%).

HRMS (elemental composition): calc. (C\(_{32}\)H\(_{27}\)O\(_2\)S\(_2\)) 507.1452; found 507.1411.

**Rearrangement of ester 10b**: see Table 3. The products were isolated and separated using chloroform as eluent.

(5S,6S)-1,5-Diethyl-4-methylene-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide (22b)

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 5.46 (t, \(J = 1.5\) Hz, 1H of =CH\(_2\) (cis to –CH\(_2\)=)), 5.33 (dd, \(J = 2.0\), 1.0 Hz, 1H of =CH\(_2\) (trans to –CH\(_2\)=)), AB system: 3.92 (dt, \(J_{gem} = 20.0\), \(J = 2.0\) Hz, 1H) and 3.46 (dt, \(J_{gem} = 20.0\), \(J = 1.0\) Hz, 1H), AB system: 2.40 and 2.31 (dq, \(J = 14.9\), 7.5 Hz, 1H each (CH\(_2\)-CH–C=)), AB system: 2.28 and 2.15 (dq, \(J = 14.9\), 7.5 Hz, 1H each (CH\(_2\)-CH–C=O)), 1.17 (t, \(J = 7.5\) Hz, 3H (CH\(_3\)-CH\(_2\)-CH–C=)), 1.07 (t, \(J = 7.5\) Hz, 3H (CH\(_3\)-CH\(_2\)-CH–C=O)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 199.2 (C=O), 136.9 (C=C–), 117.1 (C=CH\(_2\)), 79.3 (–C=C=O), 77.9 (–C=C=), 44.0 (–CH\(_2\)-C=O), 26.8 (–C=C–CH\(_2\)), 23.5 (O=C–C–CH\(_2\)), 10.3 (–CH\(_3\)), 10.0 (–CH\(_3\)).

IR (neat): 1104 (S=O), 1714 (C=O) cm\(^{-1}\).
MS (CI/CH₄): m/z 231 (MH⁺, 43%), 199 (MH⁺-“S”, 7%), 183 (MH⁺-“SO”, 34%), 151 (MH⁺-“S₂O”, 100%).
HRMS (elemental composition): calc. (C₁₀H₁₅O₂S₂) 231.0513; found 231.0551.

**Rearrangement of ester 10c**: see Table 3. The products were isolated and separated using n-hexane/chloroform (1:2→100% CHCl₃) as eluent.

**(5S,6S)-1,5-Diisopropenyl-4-methylene-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide (22c)**

¹H NMR (300 MHz, CDCl₃): δ 5.42 (t, J = 1.5 Hz, 1H of =CH₂ (cis to –CH₂–)), 5.32 (q, J = 1.5 Hz, 1H of isopropenyl), 5.29 (t, J = 1.8 Hz, 1H of =CH₂ (trans to –CH₂–)), 5.27 (q, J = 1.5 Hz, 1H of isopropenyl), 5.13 (q, J = 0.8 Hz, 1H of isopropenyl), 4.98 (q, J = 0.8 Hz, 1H of isopropenyl), AB system: 3.93 (dt, J₉ = 20.0, J = 2.0 Hz, 1H) and 3.61 (dt, J₉ = 20.0, J = 1.5 Hz, 1H), 1.95 (dd, J = 1.5, 0.8 Hz, 3H), 1.92 (dd, J = 1.5, 0.8 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 196.6 (C=O), 140.0 (=C–), 138.0 (=C–), 136.5 (=C–), 118.7 (=CH₂), 117.6 (=CH₂), 116.9 (=CH₂), 79.8 (=C=C=O), 77.9 (=C=C=), 43.4 (=CH₂–), 20.6 (=CH₃), 20.1 (=CH₃).

IR (neat): 1104 (S=O), 1643, 1716 (C=O) cm⁻¹.

MS (CI/CH₄): m/z 255 (MH⁺, 9%), 207 (MH⁺-“SO”, 52%).
HRMS (elemental composition): calc. (C₁₂H₁₅O₂S₂) 255.0513; found 255.0493.

**3-Isopropenyl-4-(5-methylhex-5-en-3-ynyl)-1,2-dithiete 1,1-dioxide (23c) and 4-isopropenyl-3-(5-methylhex-5-en-3-ynyl)-1,2-dithiete 1,1-dioxide (24c)**

¹H NMR (600 MHz, CDCl₃): see Scheme S1, Table S1.

¹³C NMR (75 MHz, CDCl₃): see Scheme S1, Table S2.

IR (neat): 1152, 1323, 1613, 2355, 2909 cm⁻¹.

MS (CI/CH₄): m/z 255 (MH⁺, 2%), 207 (MH⁺-“SO”, 10%), 190 (M⁺-“SO₂”, 49%), 175 (MH⁺-“S₂O”, 100%).
HRMS (elemental composition): calc. (C₁₂H₁₃O₂S₂) 255.0513; found 255.0471.

**Rearrangement of ester 10d**: see Table 3. The products were isolated and separated using chloroform as eluent.

**(5S,6S)-4-Methylene-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide (22d)**

¹H NMR (600 MHz, CDCl₃): δ 7.46-7.41 (m, 6H), 7.34-7.30 (m, 4H), 5.48 (t, J = 1.6 Hz, 1H of =CH₂ (cis to –CH₂–)), 4.84 (t, J = 1.8 Hz, 1H of =CH₂ (trans to –CH₂–)), AB system: 4.17 (dt, J₉ = 20.0, J = 1.8 Hz, 1H) and 3.85 (dt, J₉ = 20.0, J = 1.6 Hz, 1H).
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 196.6 (C=O), 139.6 (==C=), 136.5 (ipso), 131.6 (ipso), 129.4, 129.3, 129.0, 128.6, 128.3, 127.6, 127.3, 126.6 (Ar), 120.8 (==CH$_2$), 80.0 (==C==O), 77.4 (==C==), 44.0 (==CH$_2$).

IR (neat): 1104 (S=O), 1719 (C=O) cm$^{-1}$.

MS (Cl/CH$_4$): m/z 327 (MH$^+$, 50%), 279 (MH$^+-$“SO”, 44%), 278 (M$^+-$“SO”, 100%).

HRMS (elemental composition): calc. (C$_{18}$H$_{15}$O$_2$S$_2$) 327.0513; found 327.0497.

3-Phenyl-4-(4-phenylbut-3-ynyl)-1,2-dithiete 1,1-dioxide (23d) and 4-phenyl-3-(4-phenylbut-3-ynyl)-1,2-dithiete 1,1-dioxide (24d)

$^1$H NMR (600 MHz, CDCl$_3$): see Scheme S1, Table S1.

$^{13}$C NMR (75 MHz, CDCl$_3$): see Scheme S1, Table S2.

IR (neat): 1144, 1151, 1323, 2247 cm$^{-1}$.

MS (Cl/CH$_4$): m/z 327 (MH$^+$, 4.09%), 263 (MH$^+-$“SO$_2$”, 98%), 231 (100%).

HRMS (elemental composition): calc. (C$_{18}$H$_{15}$O$_2$S$_2$) 327.0513; found 327.0512.

Rearrangement of ester 10e: see Table 3. The products were isolated and separated using chloroform as eluent.

(5S,6S)-1,5-Di(tert-butyl-dimethyl-silanyloxymethyl)-4-methylene-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide (22e)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.40 (t, $J = 1.8$ Hz, 1H of $==CH_2$ (cis to $==CH_2$)), 5.33 (t, $J = 1.6$ Hz, 1H of $==CH_2$ (trans to $==CH_2$)), ABq ($==CH_2$–Si): 4.29 and 4.23 (d, $J_{gem} = 12.0$ Hz, 1H each), ABq ($==CH_2$–Si): 4.26 and 4.10 (d, $J_{gem} = 12.2$ Hz, 1H each), AB system ($==CH_2$–C=O): 3.90 (dt, $J_{gem} = 20.0$, $J = 2.1$ Hz, 1H) and 3.45 (dt, $J_{gem} = 20.0$, $J = 1.2$ Hz, 1H), 0.92 (s, 9H), 0.90 (s, 9H), 0.12 (s, 6H), 0.10 (s, 3H), 0.08 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 198.9 (C=O), 135.8 (==C–), 117.0 (==CH$_2$), 78.4 (==C–C=O), 77.9 (==C–C=), 63.0 (==CH$_2$–Si), 59.3 (==CH$_2$–Si), 44.0 (==CH$_2$–C=O), 25.9 ($\times 2$) (C(CH$_3$)$_3$), 18.4 (==C(CH$_3$)$_3$), 18.4 (==C(CH$_3$)$_3$), 5.29 (==Si(CH$_3$)$_2$), 5.32 (==Si(CH$_3$)$_2$).

IR (neat): 1114 (S=O), 1713 (C=O) cm$^{-1}$.

MS (Cl/i-Bu): m/z 463 (MH$^+$, 10%), 415 (MH$^+-$“SO”, 5%), 282 (100%).

HRMS (elemental composition): calc. (C$_{20}$H$_{39}$O$_4$Si$_2$S$_2$) 463.1828; found 463.1843.

3-(tert-Butyl-dimethyl-silanyloxymethyl)-4-[5-(tert-butyl-dimethyl-silanyloxymethyl)-pent-3-ynyl]-[1,2]dithiete 1,1-dioxide (23e) and 4-(tert-butyl-dimethyl-silanyloxymethyl)-3-[5-(tert-butyl-dimethyl-silanyloxymethyl)-pent-3-ynyl]-[1,2]dithiete 1,1-dioxide (24e)
\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): see Scheme S1, Table S1.
\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): see Scheme S1, Table S2.
IR (neat): 1083, 1136, 1256, 1323, 1611, 2239, 2955 cm\textsuperscript{-1}.
MS (Cl/i-Bu): \textit{m/z} 437 (100\%), 319 (95\%).
HRMS (elemental composition): MH\textsuperscript{+} not shown, compound decomposed.

**Rearrangement of ester 10f**: see Table 3. The product \textbf{23f} was isolated using n-hexane/chloroform (4:1 → 2:1 → 1:1 → 1:2 → 100\% CHCl\textsubscript{3}) as eluent.

**Rearrangement of ester 10g**: see Table 3. The products were isolated and separated using n-hexane/ethyl acetate (100:1) as eluent.

3-(tert-Butyl-dimethyl-silanyl)-4-[4-(tert-butyl-dimethyl-silanyl)-but-3-ynyl]-[1,2]dithiete 1,1-dioxide (23g) and 4-(tert-butyl-dimethyl-silanyl)-3-[4-(tert-butyl-dimethyl-silanyl)-but-3-ynyl]-[1,2]dithiete 1,1-dioxide (24g)
\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): see Scheme S1, Table S1.
\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): see Scheme S1, Table S2.
IR (neat): 1125, 1156, 1254, 1324, 2176, 2930 cm\textsuperscript{-1}.
MS (Cl/CH\textsubscript{4}): \textit{m/z} 403 (MH\textsuperscript{+}, 1\%), 402 (M\textsuperscript{+}, 2\%), 355 (MH\textsuperscript{+}--SO\textsuperscript{--}, 4\%), 339 (MH\textsuperscript{+}--SO\textsubscript{2}--\textsuperscript{--}, 2\%).
HRMS (elemental composition): calc. (C\textsubscript{18}H\textsubscript{35}O\textsubscript{2}Si\textsubscript{2}S\textsubscript{2}) 403.1617; found 403.1610.

**Rearrangement of ester 10h**: see Table 3. The product \textbf{23h} was isolated using n-hexane/chloroform (1:2 → 100\% CHCl\textsubscript{3}) as eluent.

(5S,6S)-1,5-Di-tert-butyl-4-methylene-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide (22h) could not be isolated from the crude mixture.
\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta 5.58\) (t, \(J = 1.5\) Hz, 1H of =CH\textsubscript{2} (cis to =CH\textsubscript{2}--)), \(5.48\) (t, \(J = 1.8\) Hz, 1H of =CH\textsubscript{2} (trans to =CH\textsubscript{2}--)), AB system: 3.91 (dt, \(J_{gem} = 19.8\), \(J = 1.8\) Hz, 1H) and 3.48 (dt, \(J_{gem} = 19.8\), \(J = 1.5\) Hz, 1H), 1.36 (s, 9H), 1.25 (s, 9H).
**Scheme S1.**

\[ \text{B} \]

\[ \text{C} \]

23a, 24a; \( R^3=R^3'=\text{CH}_3 \) (\( \alpha \))

23c, 24c; \( R^3=R^3'=\text{CH}_3 \) (\( \beta \))

23e, 24e; \( R^3=R^3'=\text{CH}_3 \) (\( \gamma \))

23g, 24g; \( R^3=R^3'=\text{CH}_3 \) (\( \delta \))

*\( \alpha^\prime, \beta^\prime, \gamma^\prime, \delta^\prime \) - correspond to \( R^3' \) groups

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**Table S1.** \(^1\text{H} \) NMR Chemical Shifts for 1,2-Dithiete 1,1-Dioxides.\(^a\)

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\( ^a \) NMR spectra were taken at 298 K in CDCl\(_3\) with TMS as internal reference and run at 600 (\( ^1\text{H} \)) MHz. Table S1 was unambiguously determined with the aid of two-dimensional techniques such as COSY, HMQC and HMBC.

\( \text{b ca. 2.4.} \)
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<sup>a</sup> NMR spectra were taken at 298 K in CDCl<sub>3</sub> with TMS as internal reference and run at 75 ('<sup>13</sup>C) MHz. Table S2 was unambiguously determined with the aid of two-dimensional techniques such as COSY, HMQC and HMBC.

<sup>b</sup>,<sup>d</sup> Values with the same superscript may be interchanged.

<sup>d</sup> ca. 1.78.

### Table S2. <sup>13</sup>C NMR Chemical Shifts for 1,2-Dithiete 1,1-Dioxides.<sup>a</sup>

Rearrangement of α-bulky substituted dipropargyloxy disulfides.

(3E,6E)-3,6-Bis-(3-chloro-2,2-dimethyl-propylidene)-2-oxa-5,7-dithia-bicyclo[2.2.1]heptane 5-oxides (34c/35c). See Table 4. The products were isolated and separated using n-hexane/ethyl acetate (100:1→200:5→95:5→8:1→4:1) as eluent.

#### The major isomer (34c)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 6.72 (s, 1H (CH−O)), 6.22 (s, 1H (=CH of “SO” side)), 5.77 (s, 1H (CH−SO)), 5.21 (s, 1H (=CH of “O” side)), ABq: 3.50 and 3.47 (d, J = 11.0 Hz, 1H each), ABq: 3.42 and 3.40 (d, J = 10.8 Hz, 1H each), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 152.4 (=C−SO), 143.3 (=C−O), 141.8 (=CH− of “SO” side), 114.2 (=CH− of “O” side), 82.0 (=CH−O), 69.5 (=CH−SO), 55.8 (=CH−2), 54.3 (=CH−2), 40.6 (=C(CH<sub>3</sub>)<sub>2</sub>), 36.9 (=C(CH<sub>3</sub>)<sub>2</sub>), 27.5 (=CH<sub>3</sub>), 26.7 (=CH<sub>3</sub>), 26.6 (=CH<sub>3</sub>), 26.3 (=CH<sub>3</sub>).

IR (neat): 1005, 1062 (S=O), 1466, 1672, 2969 cm<sup>-1</sup>.
MS (Cl/CH₄): \( m/z \) 354 (M⁺, 100%), 157 (60%).

HRMS (elemental composition): calc. (C₁₄H₂₀O₂S₂Cl₂) 354.0282; found 354.0283.

The minor isomer (35c)

\(^{1}\)H NMR (600 MHz, CDCl₃): \( \delta \) 6.57 (s, 1H (CH=O)), 5.88 (s, 1H (=CH of “SO” side)), 5.84 (s, 1H (CH=SO)), 5.51 (s, 1H (=CH of “O” side)), ABq: 3.48 and 3.45 (d, \( J = 11.0 \) Hz, 1H each), ABq: 3.47 and 3.44 (d, \( J = 10.8 \) Hz, 1H each), 1.35 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl₃): \( \delta \) 146.8 (=C=SO), 143.3 (=C=O), 137.2 (=C(H(CH₃)₂), 115.5 (=C(H(CH₃)₂), 83.0 (=C(H(CH₃)₂), 28.2 (=CH₃), 27.3 (=CH₃), 26.6 (=CH₃), 25.6 (=CH₃).

IR (neat): 1008, 1076 (S=O), 1467, 1672, 2970 cm⁻¹.

MS (CI/CH₄): \( m/z \) 354 (M⁺, 16%).

HRMS (elemental composition): calc. (C₁₄H₂₀O₂S₂Cl₂) 354.0282; found 354.0277.

(3E,6E)-3,6-Bis-(3-bromo-2,2-dimethyl-propylidene)-2-oxa-5,7-dithia-bicyclo[2.2.1]heptane 5-oxides (34d/35d). See Table 4. The products were isolated and separated using n-hexane/ethyl acetate (100:1 → 200:5 → 95:5 → 8:1 → 4:1 → 1:1) as eluent.

The major isomer (34d)

\(^{1}\)H NMR (600 MHz, CDCl₃): \( \delta \) 6.72 (t, \( J = 0.8 \) Hz, 1H (CH=O)), 6.22 (br s, 1H (=CH of “SO” side)), 5.77 (br s, 1H (CH=SO)), 5.22 (s, 1H (=CH of “O” side)), ABq: 3.41 and 3.37 (d, \( J = 10.3 \) Hz, 1H each), ABq: 3.36 and 3.32 (d, \( J = 10.0 \) Hz, 1H each), 1.405 (s, 3H), 1.395 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl₃): \( \delta \) 152.2 (=C=SO), 143.2 (=C=O), 142.1 (=C=O of “SO” side), 114.6 (=C=O of “O” side), 81.9 (=CH=O), 69.5 (=CH=SO), 46.1 (=CH₂=), 44.2 (=CH₂=), 40.0 (=C(CH₃)₂), 36.3 (=C(CH₃)₂), 28.3 (=CH₃), 27.5 (=CH₃), 27.4 (=CH₃), 27.1 (=CH₃).

IR (neat): 1004, 1062 (S=O), 1465, 1663, 2967 cm⁻¹.

MS (Cl/CH₄): \( m/z \) 442 (M⁺, 31%), 249 (30%).

HRMS (elemental composition): calc. (C₁₄H₂₀O₂S₂Br₂) 441.9271; found 441.9283.

The minor isomer (35d)

\(^{1}\)H NMR (600 MHz, CDCl₃): \( \delta \) 6.57 (br s, 1H (CH=O)), 5.87 (br s, 1H (=CH of “SO” side)), 5.84 (s, 1H (CH=SO)), 5.51 (s, 1H (=CH of “O” side)), ABq: 3.40 and 3.38 (d, \( J = 10.0 \) Hz, 1H each), ABq: 3.39 and 3.37 (d, \( J = 10.4 \) Hz, 1H each), 1.38 (s, 3H), 1.34 (s, 6H), 1.32 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl₃): \( \delta \) 146.7 (=C=SO), 143.3 (=C=O), 137.5 (=C=O of “SO” side), 115.7 (=C=O of “O” side), 82.9 (=CH=O), 64.2 (=CH=SO), 46.9 (=CH₂=), 44.6 (=CH₂=), 39.6 (=C(CH₃)₂), 36.4 (=C(CH₃)₂), 28.9 (=CH₃), 28.1 (=CH₃), 27.5 (=CH₃), 26.5 (=CH₃).
IR (neat): 1071 (S=O), 1466, 1672, 2967 cm$^{-1}$.
MS (Cl/CH$_4$): m/z 442 (M$^+$, 10%), 157 (100%).
HRMS (elemental composition): calc. (C$_{14}$H$_{20}$O$_2$S$_2$Br$_2$) 441.9271; found 441.9233.