Supporting Information

Synthesis of Spiro[2.5]octa-4,7-dien-6-one with Consecutive Quarternary Centers via 1,6-Conjugate Addition Induced Dearomatization of para-Quinone Methides

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1. General Information

Reagents and Solvents: All solvents were purified and dried according to standard methods. PE refers to petroleum ether (b.p. 60 - 90 °C) and EA refers to ethyl acetate. Malontes 2a, 2b, 2h were commercially available, 2g was synthesized according reported procedure.[1]

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressur and conducted by eluting with PE/EA listed as volume/volume ratios.

Data collection: $^1$H and $^{13}$C NMR spectra were collected on BRUKER AV - 300 (300 MHz) spectrometer using CDCl$_3$ as solvent. Chemical shifts of $^1$H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard (CDCl$_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of $^{13}$C NMR were reported in ppm with the solvent as the internal standard (CDCl$_3$: δ = 77.0 ppm). Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer. Absorptions are reported in reciprocal centimeters. High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.
2. Preparation of Bromomalonates\cite{2,3}

\[ \text{ROOC}^\text{COOR} \xrightarrow{\text{DBU, CBr}_4, \text{THF}, -78^\circ\text{C}-\text{r.t.}} \text{ROOC}^\text{COOR} \cdot \text{Br} \]

\(2\text{c, 2d, 2e, 2f, 2h, 2i, 2j}\)

Malonates (1 equiv) was dissolved in THF at 0 °C and then DBU (1 equiv) was added. The solution was stirred for 1h at room temperature before cooled to -78°C. After that, CBr\(_4\) (1 equiv) was added. The mixture was stirred until completed (detected by TLC). After quenching with NH\(_4\)Cl, the phases were separated and diluted with CH\(_2\)Cl\(_2\). The aqueous layer was washed twice with CH\(_2\)Cl\(_2\), and combined organic layers were washed with brine. Then the organic layer was dried over anhydrous sodium sulfate and concentrated under vacum. The crude product was purified by flash chromatography (PE/EA = 100:1 – 20:1) to obtain the pure product as colorless oil.
3. Preparation of p-QMs

1a-1n was synthesized according to the following procedure\(^4\):

\[
\begin{array}{c}
\text{t-Bu} \quad \text{OH} \quad \text{t-Bu} \quad + \quad \text{RCHO} \quad \xrightarrow{\text{Tol, reflux}} \quad \text{O} \quad \text{t-Bu} \quad \text{t-Bu}
\end{array}
\]

1a - 1n

In a Dean-Stark apparatus, a solution of phenols (1 equiv) and the corresponding aldehydes (1 equiv) in toluene was heated to reflux. Piperidine (2 equiv) was added dropwise within 1 h. The reaction mixture was continued to reflux for 3 hrs. After cooling just below the boiling point of the reaction mixture, acetic anhydride (2 equiv) was added and stirring was continued for 15 min. Then the reaction mixture was poured into water and extracted with CH\(_2\)Cl\(_2\). The combined organic phase was dried over anhydrous Na\(_2\)SO\(_4\), and solvents were removed under reduced pressure. The crude products were purified by flash column chromatography and further recrystallized from n-hexane, affording the desired p-QMs 1a-1n.

1o and 1p were synthesized according to the following procedure\(^5\):

\[
\begin{array}{c}
\text{t-Bu} \quad \text{OH} \quad \text{t-Bu} \quad + \quad \text{NaOH, Na}_4\text{Fe(CN)}_6\cdot\text{10H}_2\text{O, n-hexane} \quad \xrightarrow{\text{N}_2\text{S}_2\text{O}_8, n\text{-hexane}} \quad \text{O} \quad \text{t-Bu} \quad \text{t-Bu}
\end{array}
\]

1o \( R^1=\text{Me}, R^2=\text{H} \)

1p \( R^1=\text{Me}, R^2=\text{Et} \)

NaOH (2.1 equiv), Na\(_4\)Fe(CN)\(_6\) \( \cdot \) 10H\(_2\)O (0.4 equiv) were dissolved in water, and a solution of substituted 2,6-di-tert-butylphenol (1 equiv) in n-hexane was added. Under Ar atmosphere, a solution of Na\(_2\)S\(_2\)O\(_8\) (1.05 equiv) in water was slowly added. The mixture was stirred for 4 hrs, and then poured into separated funnel. Organic phase was separated and dried over anhydrous Na\(_2\)SO\(_4\). The solvents were removed under reduced pressure and recrystallized from n-hexane to obtain the pure products 1o and 1p.

1q and 1r were synthesized according to the following procedure\(^6\):

\[
\begin{array}{c}
\text{R} \quad \text{OH} \quad \text{R} \\
\text{S1} \quad \xrightarrow{\text{AlCl}_3, \text{PhCOCl} \quad \text{Tol, 0\text{oC}-r.t.}} \quad \text{OH} \quad \text{R} \\
\text{S2} \quad \xrightarrow{\text{H}_2/\text{Pd}-\text{C} \quad \text{EtOH}} \quad \xrightarrow{\text{K}_3\text{Fe(CN)}_6} \quad \text{O} \\
\text{1q, R=Me} \quad \text{1r, R=n-Pr}
\end{array}
\]

Phenols (1 equiv) were dissolved in toluene, and benzoyl chloride (1.8 equiv) was added dropwise. Then, aluminium chloride (0.4 equiv) was slowly added and the mixture was stirred at
room temperature for 7 hrs. After completion, solvents were evaporated and directly subjected to flash chromatography to obtain the pure product S1.

Palladium (10% by weight on carbon powder) (5% equiv) was added in one portion to a solution of S1 (1.0 equiv) in ethanol under an atmosphere of H₂ (balloon). The reaction mixture was stirred vigorously for 3 hrs at 23 °C and then filtered through a pad of celite. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography to afford S2.

Potassium ferricyanide (4 equiv) and potassium hydroxide (4.2 equiv) in water was added in one portion to a solution of S2 (1 equiv) in hexane under an Ar atmosphere. The reaction mixture was stirred vigorously for 1 h at 23 °C. The aqueous layer was separated and extracted with hexanes. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography to afford 1q and 1r.

1s was synthesized according to the following procedure[^4n.7]:

In a Deal-Stark apparatus, 3,5-dibromo-4-hydroxybenzaldehyde (8.9 mmol, 2.5 g) and PTSA (0.45 mmol, 86 mg) were dissolved in toluene (30 mL) under Ar atmosphere and heated to reflux. To the stirred solution was added glycol (18 mmol, 1 mL). After stirred overnight, K₂CO₃ (1.8 mmol, 250 mg) was added and stirring was continued for 1 h. Then, the mixture was filtered and the solvents were removed under reduced pressued. The residue was purified by chromatography to obtain the pure product S3.

A mixture of S3 (1.9 g, 5.86 mmol), HMDS (2.46 mL, 11.72 mmol) in anhydrous THF (15 mL) was refluxed for 5 hrs. Solvents were then removed under reduced pressure to obtain the crude intermediate (2.47 g). Then the intermediate was dissolved in THF (17 mL), and cooled to -78 °C. To the stirred solution was slowly added 1.6M n-BuLi (5.86 mmol, 3.7 mL). After 1h, the reaction was moved to room temperature and stirring was continued for 2hrs. After quenching with saturated NH₄Cl, the mixture was extracted with EtOAc, washed with brine, and dried over anhydrous sodium sulfate. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography to afford 1s.
chromatography to afford product S4.

A mixture of S4 (4.92 mmol, 1.56 g), TMSCl (7.38 mmol, 0.9 mL), Et₃N (7.38 mmol, 1.0 mL) in THF (15 mL) was stirred for 1 h and then cooled to -78 °C. 1.6M n-BuLi (4.92 mmol, 3.1 mL) was slowly added and the mixture was continued to stir overnight. After quenching with saturated NH₄Cl, the mixture was extracted with EtOAc, washed with brine, and dried over anhydrous sodium sulfate. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography to afford product S5.

S5 (3.5 mmol, 1.1 g) was dissolved in acetone, and PTSA (0.35 mmol, 67 mg) was added. The mixture was stirred for 1 h and diluted with EtOAc and H₂O. The mixture was extracted with EtOAc, washed with brine, and dried over anhydrous sodium sulfate. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography to afford product S6 (710 mg, 75% yield).

S6 (2.7 mmol, 710 mg) was dissolved in anhydrous THF (15 mL) at 0°C under Ar atmosphere. Then PhMgBr (1M in THF, 11mmol) was slowly added. Then the reaction mixture was refluxed for 30 min and quenched with saturated NH₄Cl. After extraction with EtOAc, the mixture was washed with brine, and dried over anhydrous sodium sulfate. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The residue was purified by silica gel flash column chromatography to afford product S7.

A mixture of S7 (2.9 mmol, 1 g), Et₃N (6.4 mmol, 0.9 mL) in dry CH₂Cl₂ (30mL) was slowly added CH₂SO₂Cl (3.2 mmol, 0.3 mL) at 0°C. The mixture was then warmed to room temperature and stirred for 1hr. The mixture was diluted with CH₂Cl₂ and water, then the mixture was extracted with CH₂Cl₂, washed with brine, and dried over anhydrous sodium sulfate. The mixture was filtrated and concentrated by rotary evaporation. The crude product 1s was used directly without further purification.

1t was synthesized according to the following procedure[46]:

S8 was synthesized in the same manner as S1 described before.

Treatment of S8 (1 equiv) in THF with LiAlH₄ (1.5 equiv) was performed under Ar at 0°C. The mixture was slowly warmed to room temperature and stirred overnight. After quenching with 1N HCl, the mixture was extracted with EtOAc, and washed with brine. The combined organic phase was dried over anhydrous Na₂SO₄, and the filtrate was concentrated under reduced pressure. The residue obtained was purified by flash column chromatography on silica gel to afford the pure product 1t.
4. Procedures for ring-open reactions

4a: In a 10 mL test tube was added 3aa (0.05 mmol, 22.6 mg), In(OTf)$_3$ (0.01 mmol, 5.6 mg) and 0.1 mL CH$_2$Cl$_2$. The mixture was stirred at room temperature for 30 min until the color turned red. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE / EA = 20 : 1) on silica gel to afford 4a as a colorless solid in quantitative yield.

White solid, m.p. 58 – 59 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 7.17 (s, 2H), 5.22 (s, 1H), 4.51 (s, 1H), 4.26 – 4.15 (m, 4H), 1.43 (s, 18H), 1.27 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 168.7, 153.8, 135.8, 126.0, 123.4, 61.6, 57.9, 34.3, 30.3, 14.1 ppm. IR(KBr): $\tilde{v} =$ 3608, 1949, 1753, 1722, 1629, 1436, 1218, 1151, 1036 cm$^{-1}$. HRMS (ESI): $m/z$ calculated for [C$_2$H$_3$O$_3$]+: 365.2323; found: 365.2322.

4b: In a 25 mL round bottom was added 3aa (0.05 mmol, 22.6 mg), AlCl$_3$ (0.25 mmol, 34 mg) and 5 mL CH$_2$Cl$_2$ under Ar atmosphere. The mixture was stirred at room temperature for 1 h, and water was added to quench the reaction. Then the mixture was diluted with CH$_2$Cl$_2$ and washed with water. The combined organic phase was washed with brine. Then solvents were removed under reduced pressure and the residue was purified by flash column chromatography (PE / EA = 20 : 1) on silica gel to afford 4b as a colorless solid (16mg, 65% yield).

White solid, m.p. 153 - 155 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 7.15 – 7.12 (m, 1H), 7.06 – 7.01 (m, 2H), 6.92 (s, 2H), 6.83 – 6.81 (m, 2H), 5.95 (s, 1H), 5.23 (s, 1H), 4.46 – 4.30 (m, 2H), 4.23 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.32 (s, 18H), 1.22 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 169.2, 167.8, 153.7, 137.0, 134.3, 130.0, 128.0, 127.6, 126.8, 122.6, 69.6, 65.0, 62.1, 62.0, 34.2, 30.2, 14.1, 14.0 ppm. IR(KBr): $\tilde{v} =$ 3610, 1865, 1762, 1731, 1630,
5. General procedure for the synthesis of spiro-compounds

a) General procedure

In a 10 mL test tube was sequentially added p-QMs 1 (0.1 mmol, 1 equiv), Cs₂CO₃ (0.2 mmol, 2 equiv), 2 (0.15 mmol, 1.5 equiv) and CH₂Cl₂ (0.5 mL). Then, the tube was sealed and stirred overnight. After the reaction was completed (detected by TLC), solvent was directly removed under reduced pressure and the crude mixture was purified by flash column chromatography on silica gel to afford the pure product.

b) Characterization of the products

Diethyl 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3aa)

Light yellow solid, m.p. 155 - 156°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.38 - 7.31 (m, 3H), 7.26 - 7.24 (m, 2H), 6.79 (d, J = 2.8, 1H), 6.31 (d, J = 2.8, 1H), 4.39 – 4.28 (m, 2H), 4.20 (q, J = 7.1, 2H), 3.95 (s, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.28 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H), 1.23 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 185.8, 167.3, 165.2, 150.3, 148.3, 137.3, 136.4, 132.2, 129.9, 128.3, 127.9, 126.5, 62.0, 50.2, 41.9, 37.9, 35.5, 35.2, 29.3, 29.3, 14.2, 14.0 ppm. IR(KBr): ν = 3009, 2957, 2867, 1734, 1648, 1621, 1239, 744, 701 cm⁻¹. HRMS (ESI): m/z calculated for [C₂₉H₂₂O₂⁺]: 453.2636; found: 453.2635.

Diethyl 5,7-di-tert-butyl-6-oxo-2-(p-tolyl)spiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ba)

White solid, m.p. 147 - 148°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.07 (m, 4H), 6.74 (d, J = 2.8, 1H), 6.23 (d, J = 2.8 Hz, 1H), 4.27 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.85 (s, 1H), 2.30 (t, J = 7.1 Hz, 3H), 1.23 - 1.20 (m, 12H), 1.17 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 185.9, 167.4, 165.2, 150.2, 148.2, 137.6, 137.4, 136.6, 129.7, 129.1, 128.9, 62.4, 61.9, 50.2, 41.8, 37.9, 35.5, 35.2, 29.3, 29.2, 14.2, 14.0 ppm. IR(KBr): ν = 2985, 2955, 2861, 1748, 1727, 1649, 1245 cm⁻¹. HRMS (ESI): m/z calculated for [C₂₀H₁₈O₂⁺]: 467.2792; found: 467.2788.

Diethyl 5,7-di-tert-butyl-2-(4-methoxyphenyl)-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ca)

White solid, m.p. 148 - 149°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.12 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.71 (d, J = 2.7 Hz, 1H), 6.25 (d, J = 2.7 Hz, 1H), 4.33 - 4.22 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.85 (s, 1H), 3.78 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.25 - 1.23 (m, 11H), 1.20 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 185.9, 167.3, 165.1, 159.0, 150.1, 148.2, 137.4, 136.6, 131.0, 124.0, 113.6, 62.4, 61.9, 55.2, 50.3, 41.4, 38.0, 35.5, 35.2, 29.3, 29.2, 14.2, 14.0 ppm. IR(KBr): ν = 2991, 2958, 2861, 1736, 1647, 1621, 1518, 1255, 1085,
Diethyl 5,7-di-tert-butyl-6-oxo-2-(4-(trifluoromethyl)phenyl)spiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3da)

Light yellow solid, m.p. 135 - 136°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.57 (d, J = 8.2, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 2.7 Hz, 1H), 6.26 (d, J = 2.7 Hz, 1H), 4.39 - 4.25 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.87 (s, 1H), 1.33 (t, J = 7.1 Hz, 3H), 1.24 - 1.22 (m, 12H), 1.95 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 185.6, 167.0, 164.9, 150.6, 149.0, 136.7, 136.4, 135.2, 130.3, 129.9, 125.7, 125.2 (q, J/C₆ = 3.6 Hz), 62.7, 62.2, 49.7, 41.2, 37.7, 35.5, 35.2, 29.3, 29.3, 14.1, 13.9 ppm. IR(KBr): ʋ = 2997, 2956, 2861, 1741, 1729, 1652, 1326, 1121, 1066 cm⁻¹. HRMS (ESI): m/z calculated for [C₂₀H₃₈O₆S⁺H⁺]: 521.2509; found: 521.2508.

Diethyl 5,7-di-tert-butyl-2-(4-chlorophenyl)-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ea)

White solid, m.p. 150 - 151°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.30 (d, J = 8.3, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 2.7 Hz, 1H), 6.28 (d, J = 2.7 Hz, 1H), 4.39-4.25 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.85 (s, 1H), 1.32 (t, J = 7.1 Hz, 3H), 1.27 - 1.25 (m, 12H), 1.21 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 185.7, 167.1, 164.9, 150.4, 148.7, 136.9, 135.7, 133.8, 131.3, 130.7, 128.5, 62.6, 62.1, 49.9, 41.1, 37.8, 35.5, 35.2, 29.3, 29.2, 14.1, 14.0 ppm. IR(KBr): ʋ = 2958, 2861, 1734, 1648, 1621, 1399, 1246, 995 cm⁻¹. HRMS (ESI): m/z calculated for [C₂₃H₃₆ClO₅S⁺H⁺]: 487.2246; found: 487.2248.

Diethyl 5,7-di-tert-butyl-2-(3-chlorophenyl)-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3fa)

White solid, m.p. 142 - 143°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.27 - 7.24 (m, 3H), 7.10 - 7.19 (m, 1H), 6.67 (d, J = 2.8 Hz, 1H), 6.24 (d, J = 2.8 Hz, 1H), 4.36 - 4.25 (m, 2H), 4.22 - 4.13 (qd, J = 7.1, 2.5 Hz, 2H), 3.85 (s, 1H), 1.32 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.24 (s, 9H), 1.21 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 185.7, 167.0, 164.8, 150.5, 148.7, 136.7, 135.7, 134.2, 134.1, 130.2, 129.5, 128.2, 128.1, 62.6, 62.2, 49.8, 41.0, 37.6, 35.5, 35.2, 29.3, 29.2, 14.2, 14.1 ppm. IR(KBr): ʋ = 2985, 2958, 2861, 1730, 1649, 1631, 1267, 1243, 933, 682 cm⁻¹. HRMS (ESI): m/z calculated for [C₂₃H₃₆ClO₅S⁺H⁺]: 487.2246; found: 487.2241.

Diethyl 5,7-di-tert-butyl-2-(2-chlorophenyl)-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ga)

White solid, m.p. 108 - 109°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.38 (d, J = 7.5, 1H), 7.27 - 7.16 (m, 3H), 6.69 (d, J = 2.7 Hz, 1H), 6.28 (d, J = 2.7 Hz, 1H), 4.40 - 4.24 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.79 (s, 1H), 1.33 (t, J = 7.1 Hz, 3H), 1.24 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H), 1.17 (s,
9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 185.7, 167.1, 165.3, 150.5, 149.0, 137.3, 136.1, 135.1, 130.9, 130.5, 129.6, 129.2, 126.3, 62.4, 62.1, 49.1, 41.5, 38.6, 35.5, 35.2, 29.3, 29.1, 14.2, 13.8 ppm. IR(KBr): $\tilde{\nu} =$ 3003, 2961, 2861, 1733, 1649, 1620, 1257, 1240, 760 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{28}$H$_{36}$O$_6$+H]$^+$: 487.2246; found: 487.2245.

**Diethyl 2-(2-bromophenyl)-5,7-di-tert-butyl-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ha)**

![Diagram of 3ha](image)

White solid, m.p. 126 - 127°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 7.58 (d, $J =$ 7.7 Hz, 1H), 7.26 - 7.14 (m, 3H), 6.65 (d, $J =$ 2.7 Hz, 1H), 6.32 (d, $J =$ 2.7 Hz, 1H), 4.38 - 4.26 (m, 2H), 4.20 (q, $J =$ 7.1 Hz, 2H), 3.79 (s, 1H), 1.33 (t, $J =$ 7.1 Hz, 3H), 1.26-1.21 (m, 12H). 1.16 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 185.7, 167.0, 165.3, 150.7, 149.0, 137.3, 135.1, 133.0, 132.7, 130.5, 129.4, 126.9, 126.3, 62.5, 62.2, 49.3, 43.6, 38.9, 35.4, 35.2, 29.3, 29.1, 14.2, 13.9 ppm. IR(KBr): $\tilde{\nu} =$ 2985, 2961, 2867, 1753, 1731, 1654, 1624, 1242, 751 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{28}$H$_{38}$BrO$_6$+H]$^+$: 531.1741; found: 531.1739.

**Diethyl 2-[[1,1'-biphenyl]-4-yl]-5,7-di-tert-butyl-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ia)**

![Diagram of 3ia](image)

White solid, m.p. 147 - 148°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 7.60 - 7.53 (m, 4H), 7.46 - 7.25 (m, 5H), 6.80 (d, $J =$ 2.8 Hz, 1H), 6.31 (d, $J =$ 2.8 Hz, 1H), 4.37 - 4.16 (m, 4H), 3.94 (s, 1H), 1.33 (t, $J =$ 7.2 Hz, 3H), 1.27 - 1.25 (m, 12H), 1.23 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 185.9, 167.3, 165.2, 150.4, 148.5, 140.7, 140.3, 137.2, 136.3, 131.3, 130.3, 128.8, 127.5, 127.0, 126.9, 62.6, 62.1, 50.2, 41.7, 38.0, 35.5, 35.2, 29.4, 29.3, 14.2, 14.0 ppm. IR(KBr): $\tilde{\nu} =$ 2962, 2867, 1729, 1647, 1637, 1618, 1253, 1089 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{32}$H$_{41}$O$_5$+H]$^+$: 529.2949; found: 529.2943.

**Diethyl 2-(2-bromo-5-methoxyphenyl)-5,7-di-tert-butyl-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ja)**

![Diagram of 3ja](image)

White solid, m.p. 131 - 132°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta =$ 7.45 (d, $J =$ 8.8 Hz, 1H), 6.83 (d, $J =$ 2.2 Hz, 1H), 6.72 (dd, $J =$ 8.6, 2.7 Hz, 1H), 6.61 (d, $J =$ 2.7 Hz, 1H), 6.29 (d, $J =$ 2.7 Hz, 1H), 4.39 - 4.13 (m, 4H), 3.75 (s, 1H), 3.74 (s, 3H), 1.32 (t, $J =$ 7.1 Hz, 3H), 1.24 (t, $J =$ 7.1 Hz, 3H), 1.23 (s, 9H), 1.16 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 185.8, 167.0, 165.3, 158.5, 150.7, 149.0, 137.2, 135.1, 133.6, 133.5, 133.4, 116.8, 114.7, 62.5, 62.2, 55.4, 49.3, 43.6, 38.8, 35.4, 35.2, 29.4, 29.1, 14.2, 13.9 ppm. IR(KBr): $\tilde{\nu} =$ 3001, 2959, 2855, 1735, 1654, 1624, 1245, 1165 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{29}$H$_{38}$BrO$_6$+H]$^+$: 561.1846; found: 561.1847.

510
(E)-diethyl 5,7-di-tert-butyl-6-oxo-2-(2-styrylphenyl)spiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ka)

White solid, m.p. 137 - 138°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.71 (d, $J$ = 7.8 Hz, 1H), 7.38 - 7.20 (m, 8H), 7.11 (d, $J$ = 16.2 Hz, 1H), 6.97 (d, $J$ = 16.2 Hz, 1H), 6.87 (d, $J$ = 2.8 Hz, 1H), 6.22 (d, $J$ = 2.8 Hz, 1H), 4.44 - 4.25 (m, 2H), 4.18 - 3.96 (m, 2H), 3.94 (s, 1H), 1.33 (t, $J$ = 7.1 Hz, 3H), 1.27 - 1.20 (m, 12H), 1.09 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 185.8, 167.6, 165.3, 151.0, 148.7, 137.8, 137.6, 137.0, 135.9, 130.5, 129.9, 128.6, 128.3, 127.8, 127.1, 126.6, 125.2, 125.1, 62.5, 62.2, 50.5, 41.7, 38.7, 35.5, 35.2, 29.4, 29.1, 14.2, 13.6 ppm. IR(KBr): $\tilde{\nu}$ = 2985, 2960, 2867, 1731, 1660, 1630, 1246, 1092, 759, 699 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{38}$H$_{43}$O$_3$]+: 555.3105; found: 555.3106.

Diethyl 5,7-di-tert-butyl-6-oxo-2-(2-(phenylethynyl)phenyl)spiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3la)

Brown solid, m.p. 120 - 121°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.58 - 7.55 (m, 1H), 7.46 - 7.43 (m, 2H), 7.31 - 7.26 (m, 5H), 7.18 (d, $J$ = 6.4 Hz, 1H), 6.86 (d, $J$ = 2.7 Hz, 1H), 6.28 (d, $J$ = 2.7 Hz, 1H), 4.32 - 4.07 (m, 4H), 4.14 (s, 1H), 1.26 (t, $J$ = 7.1 Hz, 3H), 1.18 (s, 9H), 1.17 (s, 9H), 1.09 (t, $J$ = 7.1 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 185.9, 167.3, 165.5, 150.4, 148.6, 137.9, 135.7, 134.4, 132.7, 131.7, 129.5, 128.4, 128.2, 127.8, 125.0, 123.0, 94.6, 87.1, 62.3, 62.0, 49.6, 42.4, 38.9, 35.5, 35.1, 29.7, 29.2, 14.2, 13.7 ppm. IR(KBr): $\tilde{\nu}$ = 3050, 2958, 2861, 1744, 1729, 1650, 1244, 756, 691 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{38}$H$_{41}$O$_3$]+: 553.2949; found: 553.2943.

Diethyl 5,7-di-tert-butyl-2-(naphthalen-1-yl)-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ma)

White solid, m.p. 128 - 129°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.86 - 7.78 (m, 3H), 7.49 - 7.36 (m, 5H), 6.78 (d, $J$ = 2.7 Hz, 1H), 6.34 (d, $J$ = 2.7 Hz, 1H), 4.74 - 4.26 (m, 2H), 4.18 (s, 1H), 4.10 - 3.95 (m, 2H), 1.38 (t, $J$ = 7.1 Hz, 3H), 1.32 (s, 9H), 1.09 - 1.03 (m, 12H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 185.7, 167.5, 165.3, 151.0, 148.4, 137.4, 136.4, 133.6, 132.8, 128.9, 128.6, 127.2, 126.3, 126.0, 124.7, 124.2, 62.6, 62.0, 50.1, 41.1, 38.4, 35.3, 29.4, 28.9, 14.3, 13.7 ppm. IR(KBr): $\tilde{\nu}$ = 2985, 2861, 1732, 1647, 1618, 1265, 1245, 1231, 771 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{32}$H$_{36}$O$_5$]+: 503.2792; found: 503.2797.
Diethyl 5,7-di-tert-butyl-6-oxo-2-(thiophen-2-yl)spiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3na)

White solid, m.p. 149 - 150°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 7.26 - 7.25 (m, 2H), 6.96 - 6.94 (m, 1H), 6.84 (d, $J$ = 2.9 Hz, 1H), 6.31 (d, $J$ = 2.9 Hz, 1H), 4.37 - 4.13 (m, 4H), 3.92 (s, 1H), 1.31 (t, $J$ = 7.1 Hz, 3H), 1.26 (t, $J$ = 7.1 Hz, 3H), 1.23 (s, 9H), 1.22 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 185.7, 166.7, 164.7, 150.5, 148.8, 136.2, 135.7, 134.3, 128.5, 126.7, 126.0, 63.0, 62.2, 50.9, 38.6, 37.1, 35.5, 35.2, 29.3, 29.2, 14.2, 13.9 ppm. IR(KBr): $\tilde{\nu}$ = 3002, 2955, 2867, 1749, 1729, 1450, 1621, 1257, 1243, 1230, 1088 cm$^{-1}$. HRMS (ESI): $m/z$ calculated for [C$_{26}$H$_{35}$O$_5$S$^+$]$: 459.2200$; found: 459.2198.

Diethyl 5,7-di-tert-butyl-2-methyl-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3oa)

White solid, m.p. 93 - 94°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 6.67 (d, $J$ = 2.7 Hz, 1H), 6.33 (d, $J$ = 2.7 Hz, 1H), 4.28 - 4.13 (m, 4H), 2.63 (q, $J$ = 6.7 Hz, 1H), 1.38 (d, $J$ = 6.7 Hz, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H), 1.28 - 1.23 (m, 12H), 1.19 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 185.7, 167.4, 165.6, 149.9, 149.5, 137.9, 134.7, 62.3, 61.9, 49.9, 37.8, 35.5, 35.1, 33.8, 29.3, 29.2, 14.1, 10.3 ppm. IR(KBr): $\tilde{\nu}$ = 2955, 2914, 2862, 1731, 1646, 1256, 1238, 919 cm$^{-1}$. HRMS (ESI): $m/z$ calculated for [C$_{26}$H$_{35}$O$_5$S$^+$]$: 391.2479$; found: 391.2475.

Diethyl 5,7-di-tert-butyl-2-ethyl-2-methyl-6-oxospiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3pa)

White solid, m.p. 90 - 91°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 6.83 (d, $J$ = 3.0 Hz, 1H), 6.73 (d, $J$ = 3.0 Hz, 1H), 4.22 (q, $J$ = 7.1 Hz, 4H), 1.90 (m, 2H), 1.51 (s, 3H), 1.30 - 1.24 (m, 24H), 0.95 (t, $J$ = 7.3 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 185.2, 166.4, 166.3, 149.3, 149.1, 136.7, 61.9, 61.8, 54.4, 44.7, 39.7, 35.5, 35.4, 30.3, 29.4, 29.3, 26.8, 16.8, 14.1, 10.5 ppm. IR(KBr): $\tilde{\nu}$ = 3003, 2961, 2873, 1736, 1647, 1620, 1459, 1387, 1094, 1023 cm$^{-1}$. HRMS (ESI): $m/z$ calculated for [C$_{26}$H$_{36}$O$_5$S$^+$]$: 419.2794$; found: 419.2794.

Diethyl 5,7-dimethyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3qa)

White solid, m.p. 87 - 88°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 7.31 - 7.29 (m, 3H), 7.22 - 7.20 (m, 2H), 6.81 (d, $J$ = 1.3 Hz, 1H), 6.41 (d, $J$ = 1.3 Hz, 1H), 4.37 - 4.27 (m, 2H), 4.25 - 4.16 (m, 2H), 3.93 (s, 1H), 1.96 (dd, $J$ = 3.7, 1.0, 2H), 1.29 (t, $J$ = 7.1 Hz, 3H), 1.26 (t, $J$ = 7.1 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 186.6, 167.1, 165.0, 140.8, 139.5, 138.3, 136.9, 132.1, 129.8, 128.4, 128.0, 62.6, 62.2, 50.1, 41.9, 38.1, 16.8, 16.4, 14.0, 13.9 ppm. IR(KBr): $\tilde{\nu}$ = 2982, 2920, 1732, 1660, 1633, 1370, 1243, 1092, 748, 700 cm$^{-1}$. HRMS (ESI): $m/z$ calculated for [C$_{22}$H$_{23}$O$_5$S$^+$]$: 369.1697$; found: 369.1699.
Diethyl 5,7-diisopropyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ra)

White solid, m.p. 76 - 77°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 7.31 - 7.28 (m, 3H), 7.21 - 7.19 (m, 2H), 6.73 (d, J = 3.0, 1H), 6.27 (d, J = 3.0 Hz, 1H), 4.36 - 4.23 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.96 (s, 1H), 3.11 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.09 - 0.99 (m, 12H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 184.6, 167.2, 165.1, 148.5, 146.6, 137.3, 136.6, 132.2, 129.9, 128.3, 127.9, 62.6, 62.1, 50.4, 42.1, 38.0, 26.8, 26.7, 22.0, 21.9, 21.8, 21.7, 14.1, 14.0 ppm. IR(KBr): $\tilde{\nu}$ = 2979, 2956, 2867, 1749, 1725, 1655, 1627, 1251, 702 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{26}$H$_{35}$O$_{5}$+H]$^+$: 425.2323; found: 425.2321.

Diethyl 6-oxo-2-phenyl-5,7-bis(trimethylsilyl)spiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3sa)

White solid, m.p. 150 - 151°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 7.27 - 7.24 (m, 3H), 7.19 - 7.07 (m, 2H), 7.07 (d, J = 3.1 Hz, 1H), 6.60 (d, J = 3.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.14 (qd, J = 7.1, 2.0 Hz, 2H), 3.93 (s, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 190.1, 165.4, 163.3, 150.8, 149.9, 143.5, 141.5, 130.3, 128.2, 126.8, 126.5, 61.1, 60.7, 49.7, 41.2, 37.1, 12.6, 12.4, 12.3 ppm. IR(KBr): $\tilde{\nu}$ = 2985, 2961, 1734, 1615, 1599, 1244, 860, 838. HRMS (ESI): m/z calculated for [C$_{26}$H$_{35}$O$_{5}$Si$_2$+H]$^+$: 485.2171; found: 485.2171.

Diethyl 4'-oxo-3-phenyl-4'H-spiro[cyclopropane-1,1'-naphthalene]-2,2-dicarboxylate (3ta)

White solid, m.p. 163 - 164°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 8.31-8.28 (m, 1H), 7.54 - 7.71 (m, 9H), 6.63 (d, J = 10.6 Hz, 1H), 4.44 (s, 1H), 4.22 - 4.15 (m, 2H), 4.15 - 3.78 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 184.8, 165.8, 164.9, 145.6, 138.5, 133.8, 132.1, 131.7, 129.6, 129.1, 128.7, 128.0, 127.7, 127.5, 122.8, 62.4, 62.1, 54.2, 40.9, 37.6, 13.9, 13.5 ppm. IR(KBr): $\tilde{\nu}$ = 2991, 2949, 1741, 1727, 1658, 1624, 1217, 1187, 844, 762, 703. HRMS (ESI): m/z calculated for [C$_{26}$H$_{27}$O$_{5}$+H]$^+$: 391.1540; found: 391.1539.

Dimethyl 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ab)

White solid, m.p. 158 - 159°C. $^1$H NMR (300 MHz, CDCl$_3$) δ = 7.34 - 7.28 (m, 3H), 7.20 - 7.17 (m, 2H), 6.72 (d, J = 3.0, 1H), 6.26 (d, J = 3.0 Hz, 1H), 3.92 (s, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 1.23 (s, 9H), 1.19 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 185.7, 167.7, 165.5, 150.5, 148.5, 137.1, 136.1, 132.1, 129.8, 128.3, 127.9, 53.3, 52.8, 49.8, 42.1, 37.9, 35.5, 35.2, 29.3, 29.2 ppm. IR(KBr): $\tilde{\nu}$ = 2991, 2955, 2855, 1732, 1735, 1650, 1622, 1437, 1250, 1088, 702 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{26}$H$_{33}$O$_{5}$+H]$^+$: 425.2323; found: 425.2322.
Diisopropyl 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ac)

White solid, m.p. 180 - 181°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.30 - 7.27 (m, 3H), 7.24 – 7.21 (m, 2H), 6.80 (d, $J$ = 2.9 Hz, 1H), 6.26 (d, $J$ = 2.9 Hz, 1H), 5.16 (m, 1H), 5.03 (m, $J$ = 6.3 Hz, 1H), 3.90 (s, 1H), 1.32 – 1.20 (m, 30H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 186.0, 166.9, 164.6, 150.2, 148.1, 137.4, 136.7, 132.4, 129.9, 128.2, 127.8, 70.5, 69.9, 50.6, 41.7, 37.8, 35.5, 35.2, 29.3, 29.3, 21.9, 21.7, 21.6, 21.5 ppm. IR(KBr): $\tilde{\nu}$ = 2956, 2861, 1726, 1647, 1620, 1256, 1109, 1084, 930, 745, 701. HRMS (ESI): m/z calculated for [C$_{30}$H$_{41}$O$_3$+H]$^+$: 481.2949; found: 481.2947.

Di-tert-butyl 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ad)

Yellow solid, m.p. 157 - 158°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.28 - 7.26 (m, 5H), 6.73 (d, $J$ = 2.7 Hz, 1H), 6.33 (d, $J$ = 2.7 Hz, 1H), 3.81 (s, 1H), 1.53 (s, 9H), 1.43 (s, 9H), 1.26 (s, 9H), 1.21 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 186.2, 166.4, 163.8, 149.9, 147.6, 137.6, 137.4, 132.7, 130.1, 128.0, 127.7, 83.0, 82.8, 52.3, 41.4, 37.7, 35.4, 35.2, 29.4, 29.3, 28.0, 27.9 ppm. IR(KBr): $\tilde{\nu}$ = 3000, 2957, 2867, 1723, 1648, 1618, 1371, 1303, 699, 507, 463 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{32}$H$_{44}$NaO$_3$Na]$^+$: 531.3081; found: 531.3080.

Dibenzyl 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ae)

White solid, m.p. 147 - 148°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.31 - 7.14 (m, 15H), 6.74 (d, $J$ = 2.8 Hz, 1H), 6.21 (d, $J$ = 2.8 Hz, 1H), 5.19 (s, 2H), 5.05 (dd, $J$ = 28.5, 12 Hz, 2H), 3.93 (s, 1H), 1.17 (s, 9H), 1.14 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 185.7, 167.2, 165.0, 150.4, 148.5, 137.0, 136.1, 134.9, 134.6, 132.1, 129.9, 128.8, 128.7, 128.6, 128.6, 128.3, 127.9, 68.3, 67.9, 50.1, 42.1, 38.3, 35.5, 35.1, 29.3, 29.2 ppm. IR(KBr): $\tilde{\nu}$ = 2955, 2920, 1730, 1648, 1618, 1369, 1170, 699 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{38}$H$_{46}$NaO$_3$Na]$^+$: 599.2768; found: 599.2765.

Diallyl 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3af)

White solid. m.p. 118 - 119°C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.31 – 7.28 (m, 3H), 7.27 – 7.20 (m, 2H), 6.75 (d, $J$ = 2.9 Hz, 1H), 6.28 (d, $J$ = 2.9 Hz, 1H), 5.93 – 5.82 (m, 2H), 5.40 – 5.22 (m, 4H), 4.75 – 4.72 (m, 2H), 4.60 – 4.58 (m, 2H), 3.94 (s, 1H), 1.25 (s, 9H), 1.20 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 185.8, 167.0, 164.8, 150.4, 148.5, 137.1, 136.1, 132.1, 131.2, 131.1, 129.9, 128.3, 128.0, 119.6, 119.5, 67.1, 66.7, 49.9, 42.1, 38.1, 35.5, 35.2, 29.3, 29.2 ppm. IR(KBr): $\tilde{\nu}$ = 2944 1736, 1647, 1620, 1231, 1171, 963, 916, 700 cm$^{-1}$. HRMS (ESI): m/z calculated for [C$_{36}$H$_{48}$O$_3$+H]$^+$: 477.2636; found: 477.2625.
5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarbonitrile (3ag)

Yellow solid, m.p. 165 - 166°C. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = 7.52 - 7.49 \) (m, 3H), 7.38 – 7.34 (m, 2H), 6.42 (d, \( J = 3.0 \) Hz, 1H), 6.12 (d, \( J = 3.0 \) Hz, 1H), 3.82 (s, 1H), 1.38 (s, 9H), 1.24 (s, 9H) ppm. \( ^13C \) NMR (75 MHz, CDCl\(_3\)) \( \delta = 184.4, 153.7, 153.5, 134.1, 131.1, 129.7, 129.6, 129.3, 128.3, 113.2, 111.1, 44.1, 40.5, 35.9, 35.7, 29.2, 29.1, 20.2 ppm.

IR(KBr): \( \tilde{\nu} = 2956, 2919, 2865, 2239, 1659, 1625, 1448, 1381, 913, 696 \) cm\(^{-1}\). HRMS (ESI): m/z calculated for [C\(_{24}\)H\(_{27}\)N\(_2\)O\(_3\)]\(^+\): 359.2118; found: 359.2109.

1,1’-(5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-diyl)diethanone (3ah)

White solid. m.p. 129 - 130°C. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = 7.29 - 7.24 \) (m, 3H), 7.00 (m, 2H), 6.69 (d, \( J = 3.1 \) Hz, 1H), 5.92 (d, \( J = 3.1 \) Hz, 1H), 4.35 (d, \( J = 1.0 \) Hz, 1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.27 (s, 9H), 0.86 (s, 9H) ppm. \( ^13C \) NMR (75 MHz, CDCl\(_3\)) \( \delta = 194.6, 185.2, 167.7, 146.3, 146.0, 137.4, 136.8, 128.4, 127.4, 114.4, 84.5, 58.5, 34.3, 34.0, 29.2, 28.9, 28.3, 14.8 ppm. IR(KBr): \( \tilde{\nu} = 2958, 2914, 1673, 1650, 1600, 1365, 1275, 1261, 931, 750 \) cm\(^{-1}\). HRMS (ESI): m/z calculated for [C\(_{26}\)H\(_{32}\)O\(_3\)]\(^+\): 393.2419; found: 393.2424.

Di(but-3-en-1-yl) 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3ai)

White solid. m.p. 83 - 84°C. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = 7.29 - 7.28 \) (m, 3H), 7.24 – 7.17 (m, 2H), 6.73 (d, \( J = 3.0 \) Hz, 1H), 6.25 (d, \( J = 3.0 \) Hz, 1H), 5.76 - 5.68 (m, 2H), 5.15 - 5.04 (m, 4H), 4.33 – 4.20 (m, 2H), 4.17 – 4.08 (m, 2H), 3.89 (s, 1H), 2.45 – 2.31 (m, 4H), 1.23 (s, 9H), 1.19 (s, 9H) ppm. \( ^13C \) NMR (75 MHz, CDCl\(_3\)) \( \delta = 185.8, 167.2, 165.1, 150.4, 148.4, 137.2, 136.2, 133.4, 133.2, 132.1, 129.9, 128.3, 127.9, 117.7, 117.6, 115.6, 65.6, 65.2, 50.1, 42.1, 38.0, 35.5, 35.2, 32.8, 32.6, 29.3, 29.3 ppm. IR(KBr): \( \tilde{\nu} = 2954, 1759, 1733, 1648, 1628, 1230, 1247, 1188, 930, 704 \) cm\(^{-1}\). HRMS (ESI): m/z calculated for [C\(_{30}\)H\(_{36}\)O\(_5\)]\(^+\): 505.2949; found: 505.2941.

Bis(cyclopropylmethyl) 5,7-di-tert-butyl-6-oxo-2-phenylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3aj)

White solid. m.p. 158 - 159°C. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = 7.30 - 7.27 \) (m, 5H), 6.80 (s, 1H), 6.30 (s, 1H), 4.09 (d, \( J = 7.1 \) Hz, 2H), 4.03 - 3.91 (m, 3H), 1.26 (s, 9H), 1.22 (s, 9H), 1.10 (m, 2H), 0.62 - 0.55 (m, 4H), 0.34 - 0.33 (m, 2H), 0.25 (m, 2H) ppm. \( ^13C \) NMR (75 MHz, CDCl\(_3\)) \( \delta = 185.9, 167.5, 165.4, 150.3, 148.3, 137.4, 136.6, 132.3, 129.9, 128.3, 127.9, 71.4, 71.0, 50.3, 41.9, 38.0, 35.5, 35.2, 29.3, 29.3, 9.7, 9.6, 3.6, 3.5, 3.4 ppm. IR(KBr): \( \tilde{\nu} = 2953, 1734, 1619, 1230, 1255, 1238, 1171, 958, 706 \) cm\(^{-1}\). HRMS (ESI): m/z calculated for C\(_{32}\)H\(_{40}\)O\(_5\): 505.2949; found: 505.2941 [M+H]\(^+\).
6. References


7. $^1$H and $^{13}$C NMR Spectra of Title Compounds
NAME  SK10526-4
EXPER  2
PROCNO  1
DEV-L  20150526
TIME  6.11
INSTRUM  spectru
RUNNO  3 mm TROG 10C
POLYPH  4000
H  200
SOLVENT  CDCl3
NS  16
DS
SM  7211.339 Hz
FIDRES  0.222019 Hz
AQ  2.2719666 usec
SM  69.333 usec
DS  7.00 usec
TE  300.0 K
D1  1.00000000 usec
d0  1
-- CHANNEL F1 --------
NEX1  1
F1  19.25 usec
F1  -1.00 dB
FWHM  2.366050117 Hz
RF1  300.1301145656 Hz
RF2  300.130091561 Hz
RF3  0
SR  0.00 Hz
DB  0
PC  0.00
3sa
NAME
EXPER
PROCNO
DATE
TIME
INSTRUM
PROBno
EVLPERS
IC
SOVLENT
NS
DS
SNH
FID RES
AQ
RG
DM
DE
TE
D1
D11
TD0

----------- CHANNEL f1 -----------
NUC1
P1
P1L1
F1
F01

----------- CHANNEL f2 -----------
CPDPROG
NUC2
PCPB2
P12
P1L2
P2W
F2
F02
S1
SF
ME
SSB
LB
GB
PC