Supporting Information

A Direct Synthesis of the Phenanthroviridone Skeleton using a Highly Regioselective Nitroquinone Diels-Alder Reaction

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General Materials

All starting materials were purchased from Sigma-Aldrich, AK Scientific Institution and Oakwood Chemical; Solvents were all purchased from Sigma-Aldrich and Fisher Scientific, and used without further distillation. All reactions were monitored by thin layer chromatography (TLC) and ¹H NMR. All yields refer to separated yield after column chromatography unless indicated. TLC was obtained by silica plate using UV light as a visualizing agent or potassium permanganate solution with heat. All columns were performed with silica gel 60Å, particle size 40-63 µm. ¹H NMR and ¹³C NMR spectra were acquired in CDCl₃ or other deuterated solvents on a Varian MR-400 or Bruker Avance III 600 MHz spectrometer.

Experimental Procedure

General Procedure for additions to nitrohydroquinone 4.

Synthesis of 5a as an example.

2',4'-Dimethoxy-6-nitro-[1,1'-biphenyl]-2,5-dione (5a). To a 5 mL round bottom flask, 2-nitrohydroquinone **4** (47 mg, 0.3 mmol, 1.0 equiv.) and silver (I) oxide (139 mg, 0.6 mmol, 2.0 equiv.) in dry DCE, 1,3-dimethoxybenzene (62 mg, 0.45 mmol, 1.5 equiv.) was added. The reaction mixture was allowed to stir at ambient temperature without light overnight (the flask was fully covered by aluminum foil). After the reaction is finished (tracked by TLC), the crude mixture was loaded directly onto a silica column for chromatography. Using ethyl acetate/hexane (1:3) as eluent afforded the desired product **5a** as a highly colored solid (61 mg, 70% yield). ¹H NMR (400 MHz, Chloroform-d) δ 7.06 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 10.2 Hz, 1H), 6.92 (d, J = 10.3 Hz, 1H), 6.54 (d, J = 8.5 Hz, 1H), 6.49 (s, 1H), 3.84 (s, 3H), 3.73 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 184.64, 177.43, 163.98, 158.84, 137.54, 135.20, 134.82, 131.31, 109.12, 105.53, 99.27, 55.83, 55.76. HRMS (ESI-QTOF) calcd for C₁₄H₁₂NO₆ [M + H]⁺ 290.0660, found 290.0656.

General Procedure for ylide addition to nitrohydroquinone 4. Synthesis of 5m as an example.

4-Nitrobenzofuran-5-ol (5m). To a mixture of 2-nitrohydroquinone **4** (31mg, 0.2 mmol, 1.0 equiv.) and silver (I) oxide (51 mg, 0.22 mmol, 1.1 equiv.) in dry DCE, 2-(triphenyl-15-phosphaneylidene)acetaldehyde (91 mg, 0.3 mmol, 1.5 equiv.) was added. The suspension was sonicated for a short time, allowing for a better mixture, and was stirred without light overnight (covered by aluminum foil). The mixture was diluted with DCM, and filtered through a silica pad. Solvents were removed under vacuo and the crude material was loaded on a silica column. Elution with ethyl acetate/hexane (1:3) afforded the product **5m** as a yellow solid (23 mg with recovering 10 mg of **4**, 96% yield). ¹H NMR (400 MHz, Chloroform-d) δ 11.14 (s, 1H), 7.80 (d, J = 2.1 Hz, 1H), 7.73 (dd, J = 9.0, 0.9 Hz, 1H), 7.46 (dd, J = 2.1, 0.9 Hz, 1H), 7.06 (d, J = 9.0 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 154.25, 149.21,

149.05, 123.37, 121.52, 115.80, 108.17. HRMS (ESI-QTOF) calcd for $C_8H_5NO_4$ [M + e]⁻ 178.0146, found 178.0148.

2',4',6'-Trimethoxy-6-nitro-[1,1'-biphenyl]-2,5-dione (5b). ¹H NMR (400 MHz, Acetone-d6) δ 7.14 (d, J = 10.3 Hz, 1H), 7.09 (d, J = 10.3 Hz, 1H), 6.31 (s, 2H), 3.86 (s, 3H), 3.72 (s, 6H). ¹³C NMR (101 MHz, Acetone-d6) δ 185.42, 178.43, 165.23, 159.93, 138.50, 135.94, 134.62, 91.91, 56.38, 56.02. HRMS (ESI-QTOF) calcd for C₁₅H₁₃NO₇ [M + H]⁺ 320.0765, found 320.0764.

2',4',5'-Trimethoxy-6-nitro-[1,1'-biphenyl]-2,5-dione (5c). ¹H NMR (600 MHz, Acetone-d6) δ 7.13 (d, J = 10.3 Hz, 1H), 7.08 (d, J = 10.2 Hz, 1H), 6.82 (s, 1H), 6.80 (s, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H). ¹³C NMR (151 MHz, Acetone-d6) δ 185.31, 178.66, 154.14, 153.68, 144.22, 138.59, 135.81, 135.65, 115.11, 108.33, 98.84, 57.06, 56.85, 56.40. HRMS (ESI-QTOF) calcd for C₁₅H₁₃NO₇ [M + H]⁺ 320.0765, found 320.0764.

2-(1-Methylindolin-5-yl)-3-nitrocyclohexa-2,5-diene-1,4-dione (5d). ¹H NMR (400 MHz, Acetone-d6) δ 7.11 (dd, J = 8.4, 1.9 Hz, 1H), 7.07 – 6.90 (m, 3H), 6.50 (dd, J = 8.4, 1.4 Hz, 1H), 3.52 (d, J = 8.3 Hz, 2H), 2.98 (t, J = 8.4 Hz, 2H), 2.86 (s, 3H). ¹³C NMR (101 MHz, Acetone-d6) δ 186.04, 177.54, 156.02, 137.47, 134.98, 134.56, 131.44, 130.58, 128.77, 125.77, 125.51, 105.54, 54.57, 33.44, 27.39. HRMS (ESI-QTOF) calcd for C₁₅H₁₂N₂O₄ [M + H]⁺ 285.0870, found 285.0871.

2-(5-Methylfuran-2-yl)-3-nitrocyclohexa-2,5-diene-1,4-dione (5e). ¹H NMR (400 MHz, Chloroform-d) δ 7.67 (dd, J = 3.7, 1.4 Hz, 1H), δ 6.84 (d, J = 1.5 Hz, 2H)., 6.37 – 6.31 (m, 1H), 2.48 – 2.23 (m, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 184.54, 177.32, 161.39, 140.91, 136.97, 135.05, 127.53, 120.51, 112.25, 14.34. HRMS (APCI-QTOF) calcd for C₁₁H₇NO₅ [M + H]⁺ 234.0397, found 234.0392.

2-(5-Ethylfuran-2-yl)-3-nitrocyclohexa-2,5-diene-1,4-dione (5f). ¹H NMR (600 MHz, Acetone-d6) δ 7.65 (d, J = 3.7 Hz, 1H), 7.03 (d, J = 10.2 Hz, 1H), 6.99 (d, J = 10.2 Hz, 1H), 6.52 (d, J = 3.7 Hz, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). ¹³C NMR (151 MHz, Acetone-d6) δ 185.34, 178.64, 166.41, 141.85, 138.41, 135.57, 127.06, 127.05, 121.53, 111.31, 22.31, 12.09. HRMS (ESI-QTOF) calcd for C₁₂H₁₀NO₅ [M + H]⁺ 248.0560, found 248.0546.

2-(5-Methylthiophen-2-yl)-3-nitrocyclohexa-2,5-diene-1,4-dione (5g). ¹H NMR (400 MHz, Acetone-d6) δ 7.33 (d, J = 4.0 Hz, 1H), 7.13 (d, J = 10.2 Hz, 1H), 7.05 (d, J = 10.2 Hz, 1H), 7.00 (dd, J = 4.0, 1.0 Hz, 1H), 2.59 (s, 3H). ¹³C NMR (101 MHz, Acetone-d6) δ 186.19, 178.48, 154.21, 138.28, 135.49, 134.83, 128.42, 127.57, 125.25, 15.52. HRMS (ESI-QTOF) calcd for C₁₁H₇NO₄S [M - H]⁻ 248.0023, found 248.0018.

2-Nitro-3-(1H-pyrrol-2-yl)cyclohexa-2,5-diene-1,4-dione (5h). ¹H NMR (400 MHz, Acetone-d6) δ 11.43 (s, 1H), 7.46 (ddd, J = 3.5, 2.5, 1.3 Hz, 1H), 7.03 (d, J = 10.2 Hz, 1H), 6.97 (d, J = 10.2 Hz, 1H), 6.75 (ddd, J = 4.1, 2.7, 1.3 Hz, 1H), 6.42 (dt, J = 4.4, 2.4 Hz, 1H). ¹³C NMR (101 MHz, Acetone-d6) δ 189.04, 178.00, 138.19, 135.73, 130.46, 123.46, 119.80, 119.58, 113.57, 113.53. HRMS (ESI-QTOF) calcd for C₁₀H₇N₂O₄ [M + H]⁺ 219.0410, found 219.0398.

2-(2,5-Dimethyl-1H-pyrrol-3-yl)-3-nitrobenzene-1,4-diol (5i). ¹H NMR (400 MHz, Chloroform-d) δ 8.96 (s, 1H), 7.94 (s, 1H), 7.16 (d, J = 9.1 Hz, 1H), 7.02 (d, J = 9.1 Hz, 1H), 5.70 (dd, J = 2.8, 1.2 Hz, 1H), 5.56 (s, 1H), 2.26 (s, 3H), 2.03 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 148.01, 147.44, 135.68, 128.21, 125.20, 122.51, 118.68, 117.78, 109.11, 106.44, 13.20, 11.55. HRMS (ESI-QTOF) calcd for C₁₂H₁₂N₂O₄ [M + e]⁻ 247.0724, found 247.0721.

4'-(Dimethylamino)-6-nitro-[1,1'-biphenyl]-2,5-dione (5j). ¹H NMR (400 MHz, Acetone-d6) δ 7.25 (d, J = 9.1 Hz, 2H), 7.07 (d, J = 9.9 Hz, 1H), 7.01 (d, J = 10.1 Hz, 1H), 6.78 (d, J = 9.1 Hz, 2H), 3.06 (s, 6H). ¹³C NMR (101 MHz, Acetone-d6) δ 186.94, 178.57, 153.44, 148.06, 138.48, 135.58, 135.47, 132.47, 115.04, 112.45, 40.08. HRMS (ESI-QTOF) calcd for C₁₄H₁₂N₂O₄ [M + H]⁺ 273.0870, found 273.0867.

2-(1-Ethyl-1,2,3,4-tetrahydroquinolin-6-yl)-3-nitrocyclohexa-2,5-diene-1,4-dione (5k). ¹H NMR (400 MHz, Acetone-d6) δ 7.08 (dd, J = 8.8, 2.4 Hz, 1H), 7.05 (d, J = 10.0 Hz, 1H), 6.99 (d, J = 10.2 Hz, 1H), 6.96 (dd, J = 2.3, 1.3 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 3.49 – 3.38 (m, 4H), 2.70 (t, J = 6.3 Hz, 2H), 1.98 – 1.88 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Acetone-d6) δ 187.15, 178.37, 149.04, 147.38, 138.39, 135.57, 135.43, 131.94, 131.25, 123.07, 114.51, 110.95, 49.27, 45.97, 22.33, 11.46. HRMS (ESI-QTOF) calcd for C₁₇H₁₆N₂O₄ [M + H]⁺ 313.1183, found 313.1184.

2-Methyl-4-nitrobenzofuran-5-ol (5n). ¹H NMR (400 MHz, Chloroform-d) δ 11.08 (s, 1H), 7.59 (d, J = 8.9 Hz, 1H), 7.09 (s, 1H), 6.93 (d, J = 8.9 Hz, 1H), 2.51 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 161.02, 153.78, 148.66, 125.38, 120.54, 113.79, 104.70, 14.55. HRMS (ESI-QTOF) calcd for C₉H₆NO₄ [M - H]⁻ 193.0300, found 193.0288.

4-Nitro-2-phenylbenzofuran-5-ol (50). ¹H NMR (400 MHz, Chloroform-d) δ 11.18 (s, 1H), 7.95 – 7.87 (m, 2H), 7.77 – 7.69 (m, 2H), 7.49 (ddt, J = 8.2, 6.6, 1.2 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.02 (d, J = 9.0 Hz, 1H). 13C NMR (101 MHz, Chloroform-d) δ 160.64, 154.26, 148.83, 130.10, 129.37, 129.26, 129.24, 129.20, 125.78, 125.65, 125.51, 121.00, 115.01, 102.79. HRMS (ESI-QTOF) calcd for C₁₄H₈NO₄ [M - H]⁻ 254.0453, found 254.0460.

Tert-butyl((3,5-dimethoxybenzyl)oxy)dimethylsilane (6). To a solution of (3,5-dimethoxyphenyl)methanol (841 mg, 5.0 mmol, 1.0 equiv.) and imidazole (447 mg, 6.5 mmol, 1.3 equiv.) in 10 mL of dry DMF in ice bath, tert-butylchlorodimethylsilane (1130 mg, 7.5 mmol, 1.5 equiv.) was added in a single portion. The mixture was allowed to warm to room temperature, and stirred for 16 hours. The reaction was quenched with saturated NaHCO3 solution, extracted with ethyl acetate three times, and washed with brine. The organic phase was separated then dried over Na₂SO₄. After removal of the solvent under vacuo, the crude material was purified by flash column chromatography, affording the TBS ether 6 as a colorless oil (quantitative yield). ¹H NMR (400 MHz, Chloroform-d) δ 6.51 (dt, J = 1.6, 0.7 Hz, 2H), 6.35 (t, J = 2.3 Hz, 1H), 4.70 (s, 2H), 3.79 (s, 6H), 0.96 (s, 9H), 0.11 (s, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 160.77, 144.06, 103.71, 98.91, 64.84, 55.24, 25.93, 18.40, -5.27.

2'-(((Tert-butyldimethylsilyl)oxy)methyl)-4',6'-dimethoxy-6-nitro-[1,1'-biphenyl]-2,5-dione (7a) and

4'-(((tert-butyldimethylsilyl)oxy)methyl)-2',6'-dimethoxy-6-nitro-[1,1'-biphenyl]-2,5-dione (7b). Synthesized according to the general procedure of electron rich aromatics addition to nitroquinone on a 2 mmol scale. **7b** was isolated as a mixture of isomers in 4:1 ratio. ¹H NMR (600 MHz, Chloroform-d) δ 7.00 (d, J = 6.5 Hz, 1H), 6.98 (d, J = 6.4 Hz, 2H), 6.93 (d, J = 5.8 Hz, 2H), 6.92 (d, J = 5.8 Hz, 1H), 6.58 (d, J = 0.9 Hz, 1H), 6.52 (d, J = 2.2 Hz, 2H), 6.38 (d, J = 2.3 Hz, 2H), 4.74 (d, J = 0.9 Hz, 1H), 4.60 (d, J = 13.3 Hz, 2H), 4.52 (d, J = 13.4 Hz, 2H), 3.82 (s, 7H), 3.72 (s, 4H), 3.71 (s, 7H), 0.96 (s, 5H), 0.86 (s, 19H), 0.12 (s, 3H), 0.01 (s, 7H), 0.00 (s, 7H). ¹³C NMR (101 MHz, Chloroform-d) δ 184.54, 177.53, 162.63, 158.26, 157.94, 147.74, 142.68, 137.79, 137.66, 136.23, 134.86, 106.67, 104.24, 101.43, 97.48, 56.10, 56.01, 55.59, 26.13, 26.09, 18.76, -5.10, -5.22, -5.25. HRMS (ESI-QTOF) calcd for C₁₄H₈NO₄ [M + e]⁻ 433.1562, found 433.1569.

2-(2-(((Tert-butyldimethylsilyl)oxy)methyl)-4,6-dimethoxyphenyl)-5-hydroxy-3-n itronaphthalene-1,4-dione (9a).

Step 1: To a solution of a mixture of 7a and 7b (220 mg, 0.5 mmol, 1.0 equiv.) in 5 mL of DCM at room temperature, (buta-1,3-dien-1-yloxy)trimethylsilane (108 mg, 0.75 mmol, 1.5 equiv.) was added, and the solution was allowed to stir overnight. Solvents were removed under vacuo, and the crude adduct was taken in to the next step without further purification. The TMS ether 8a and 8b were not stable at room temperature, and OTMS group will eliminate to aromatize forming naphthohydroquinone. HRMS (ESI-QTOF) calcd for C₂₈H₄₁NO₈Si₂ [M + e]⁻ 574.2298, found 574.2293.

Step 2: To a solution of the TMS silyl ether **8a** and **8b** (crude from step 1) in 13.5 mL of THF, 1.5 mL of 0.5M HCl solution was added. The mixture was stirred at room temperature for about 2 hours (monitored by TLC analysis), and then ethyl acetate was added. The reaction was extracted by ethyl acetate three times, and washed with

water followed by brine. The organic phase was separated and was dried over Na₂SO₄. Removal of ethyl acetate under vacuo provided the crude alcohol, which was taken onto the next step immediately.

Step 3: To a suspension of PCC (1.0 gram, excess) and NaOAc (241mg, excess) in 25 mL of DCM at room temperature, a solution of alcohol **9** (crude from step 2) in another 25 mL of DCM was added dropwise. The mixture was allowed to stir for 3 hours then filtered through a silica pad. Solvent was removed under vacuo, and the crude material was loaded on a silica column. Elution with ethyl acetate/hexane (1:4) afforded the compound **9a** as a solid (76% yield over 3 steps). ¹H NMR (600 MHz, Chloroform-d) δ 11.44 (s, 1H), 7.72 (s, 1H), 7.40 – 7.33 (m, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.40 (d, J = 2.3 Hz, 1H), 4.64 (d, J = 13.4 Hz, 1H), 4.56 (d, J = 13.5 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 0.79 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 181.74, 180.74, 162.62, 162.09, 158.22, 151.38, 142.68, 139.55, 137.68, 131.87, 125.33, 120.90, 114.09, 107.15, 104.09, 97.52, 64.31, 56.14, 55.61, 26.00, 18.67, -5.39, -5.41. HRMS (ESI-QTOF) calcd for C₂₅H₃₀NO₈Si [M + e]⁻ 499.1668, found 499.1671.

3-Amino-2-(2-(((tert-butyldimethylsilyl)oxy)methyl)-4,6-dimethoxyphenyl)-5-hyd roxynaphthalene-1,4-dione (10). To a solution of nitroquinone 9a (151 mg, 0.3 mmol, 1.0 equiv.) with Pd/C (5 mg, catalytic) in 15 mL of methanol under Ar, hydrogen gas was sparged through the solution via a long needle for 10 minutes. The mixture was stirred under hydrogen atmosphere overnight at room temperature. After the reaction was finished (monitored by TLC), excess amount of activated MnO₂ powder was added, and the mixture was stirred for 20 minutes (similar yield can be achieved by stirring under air for 1-2 hours without addition of MnO₂). The suspension was filtered through a silica pad, and concentrated under vacuo. Purification by column chromatography afforded the product 10 as an orange solid (76% yield). ¹H NMR (400 MHz, Chloroform-d) δ 11.64 (s, 1H), 7.64 (dd, J = 7.5, 1.4) Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.16 (dd, J = 8.2, 1.4 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 4.96 (s, 2H), 4.53 – 4.40 (m, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 0.89 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 186.07, 180.90, 161.51, 161.48, 158.08, 146.12, 143.21, 137.39, 133.58, 122.41, 119.42, 114.48, 113.68, 110.18, 103.79, 97.97, 63.04, 56.06, 55.51, 26.09, 18.49, -5.13, -5.15. HRMS (ESI-QTOF) calcd for $C_{25}H_{31}NO_6Si [M + H]^+ 470.1993$, found 470.2004.

8-Hydroxy-1,3-dimethoxy-5H-dibenzo[c,g]chromene-7,12-dione (12). A suspension of TBS ether 11 (25 mg, 0.053 mmol, 1.0 equiv.) in 2 mL of 30% H₂SO₄ was heated under reflux for 2 hours. After the reaction is finished, the mixture was cooled to room temperature, then 20 mL of water was added. After extraction with ethyl acetate three times, the organic phase was washed with brine, dried over Na₂SO₄. Solvents were removed under vacuo, and the crude material was purified by flash column chromatography using ethyl acetate/hexane (2:1). The cyclization product was

obtained as a red solid (94% yield). ¹H NMR (400 MHz, Chloroform-d) δ 11.79 (s, 1H), 7.67 – 7.51 (m, 2H), 7.19 (d, J = 7.3 Hz, 1H), 6.49 (s, 1H), 6.34 (s, 1H), 5.10 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 183.95, 181.27, 163.27, 161.45, 157.90, 153.54, 136.59, 135.04, 133.77, 127.07, 123.53, 119.19, 114.18, 108.60, 102.41, 99.69, 70.87, 56.26, 55.83. HRMS (ESI-QTOF) calcd for C₁₉H₁₄O₆ [M + H]⁺ 339.0863, found 339.0854.

8-Hydroxy-1,3-dimethoxybenzo[b]phenanthridine-7,12-dione (11).

Step 1: To a solution of TBS ether **10** (15 mg, 0.03 mmol, 1.0 equiv.) in 1 mL of dry THF, a solution of 1M TBAF (0.06 mL, 0.06 mmol, 2.0 equiv.) in THF was added. The mixture was stirred at room temperature for 1 hour, and was quenched by addition of saturated NH₄Cl solution. After extraction with ethyl acetate three times, the organic phase was washed with brine, dried over Na₂SO₄. Solvent was removed under vacuo and the crude alcohol (as an orange solid) was taken into the next step without further purification.

Step 2: The orange solid from step 1 was dissolved in 3 mL of DCM at ambient temperature. Dess-Martin periodinane (excess amount) was added to the previous solution, and the mixture was stirred till the starting material **10** was fully reacted (MnO₂ will provide the same result in a much slower rate). Saturated NH₄Cl solution was added, and the resulted solution was extracted with ethyl acetate three times, and washed with brine. The separated organic phase was dried over Na₂SO₄. Solvents were removed under vacuo, and the product **11** was purified by flash column chromatography (3:1 of DCM/ethyl acetate) (>99% yield). ¹H NMR (400 MHz, Chloroform-d) δ 12.31 (s, 1H), 9.33 (s, 1H), 7.70 – 7.63 (m, 1H), 7.61 (dd, J = 7.4, 1.3 Hz, 1H), 7.28 (dd, J = 8.2, 1.2 Hz, 1H), 6.98 (d, J = 2.3 Hz, 1H), 6.91 (d, J = 2.3 Hz, 1H), 4.01 (s, 3H), 3.98 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 187.13, 184.93, 162.86, 162.16, 158.22, 155.91, 143.23, 136.94, 136.41, 133.85, 132.32, 123.49, 119.60, 118.63, 115.35, 105.82, 98.95, 56.56, 56.19. HRMS (ESI-QTOF) calcd for C₁₉H₁₃NO₅ [M + H]⁺ 336.0866, found 336.0867.

The following geometries were all calculated using B3LYP density functional theory and the 6-311G(d,p) basis set. All coordinates are presented in angstroms and all energies are given in the default atomic unit hartree.

Energy:	-1160.2583953	695 hartree	s
Element	X Y	<u>Z</u>	
С	-3.2835443 2.	.23889232	0.50640124
С	-2.136770251.	.29139113	0.57629502
С	-2.25142384-0	0.05164939	0.61996955
С	-3.63957024-0).63598669	0.45337951
С	-4.792779920.	.29766503	0.42053947
С	-4.628823281.	.62374818	0.42058441
Н	-5.76764965-0).17367916	0.36275601
Н	-5.456074712.	.32340121	0.37719876
С	-0.08918267 -1	1.04305136	-0.19620436
С	0.96086842 -1	1.95981991	-0.0786684
С	0.96179515 -2	2.84484982	1.00102568
С	-0.06064356-2	2.82382894	1.95625293
С	-1.09258235 -1	1.90321457	1.82738352
С	-1.13062382-0).99907017	0.74409181
0	-0.19888271-0	0.16510864	-1.22474444
Н	1.74517262 -1	1.98246026	-0.81779194
0	1.92731678 -3	3.77472925	1.21844912
Н	0.00125937 -3	3.51680613	2.78177071
0	-2.09440231 -1	1.75899673	2.72967291
0	-3.136519913.	.44264793	0.57541126
0	-3.80903816-1	1.82719374	0.29965159
Ν	-0.814733091	.95476043	0.6685856
0	-0.171825981.	.7872479	1.6920855
0	-0.485316812.	.63568377	-0.28671101
С	0.87980211 -0	0.01746426	-2.1422987
Н	0.58228832 0.	.78525013	-2.81394029
Η	1.80141973 0.	.26701811	-1.62498951
Н	1.04145586 -0).93490243	-2.71811843
С	3.02998352 -3	3.84677196	0.32163545
Η	3.59333825 -2	2.90774012	0.30669859
Н	2.70464277 -4	4.09791374	-0.69378918
Η	3.66691279 -4	4.64355135	0.70203793
С	-2.17583513 -2	2.67233372	3.81935048
Η	-1.29898036-2	2.5912087	4.46965599
Н	-3.06593871-2	2.38536191	4.37649918
Н	-2.28168941-3	3.70238423	3.46493244

5c:

5c_sym

Energy:	-1160.236510	0006 hartre	es
Element	t X	Y <u>Z</u>	
С	-0.04636000 -	-0.04604000	0.00000000
С	1.20883000 -	-0.54587001	0.00000000
С	1.41562998 -	-2.05717993	3 0.00000000
С	0.22959000 -	-2.93014979	0.00000000
С	-0.99797004 -	-2.40995002	2 0.00000000
С	-1.26196003 -	-0.94568002	2 0.00000000
0	2.53631020 -	-2.52091980	0.00000000
Н	0.42386001 -	-3.99688983	3 0.00000000
Н	-1.89651000 -	-3.01673985	5 0.00000000
0	-2.41202998-	-0.56716001	0.00000000
С	4.36093998	1.15812993	1.21609998
С	4.36093998	1.15812993	-1.21609998
С	4.96569967	1.46786010	0.00000000
С	2.48824000	0.20860000	0.00000000
С	3.11738014	0.52306002	1.20775998
С	3.11738014	0.52306002	-1.20775998
Н	4.86211967	1.43168008	2.13317990
Н	4.86211967	1.43168008	-2.13317990
Ν	-0.27298000	1.44222999	0.00000000
0	-1.42431998	1.83711004	0.00000000
0	0.71001005	2.16774011	0.00000000
0	6.17347002	2.12781000	0.00000000
С	7.34805012	1.30308998	0.00000000
Н	7.08743000	0.24179000	0.00000000
Н	7.94322014	1.52737999	0.88988000
Н	7.94322014	1.52737999	-0.88988000
0	2.42434001	0.16768999	2.32626987
0	2.42434001	0.16768999	-2.32626987
С	2.97390985	0.48896000	3.59967995
С	2.97390985	0.48896000	-3.59967995
Н	3.10043001	1.57029998	3.71422005
Н	3.10043001	1.57029998	-3.71422005
Н	2.25246000	0.12923001	4.33152008
Н	2.25246000	0.12923001	-4.33152008
Н	3.93389988 -	-0.01343000	3.75950980
Н	3.93389988 -	-0.01343000)-3.75950980

Butadiene Energy: -757.6441687110 hartree Element X Y Z

С	-0.047743743	-0.282693063	0.195972948
С	0.733528161	0.95533602 0.23	37736868
С	0.235427308	-1.384934865	-0.506898017
С	2.07164337 0.99	0.14	43220469
Н	-0.952256577	-0.280363173	0.802498505
Н	0.183409648	1.87769609 0.40	00084076
Н	-0.384801903	-2.270866866	-0.435473365
Н	1.087400395	-1.43535559 -1.1	77297156
Н	2.6501105280.07	7599126 0.07	70828492
0	2.868739522	2.085856685	0.155069797
Si	2.595013614	3.765195019	0.046210193
С	1.630677791	4.137004473	-1.528009884
С	1.632375322	4.352548163	1.556962159
С	4.369422087	4.475055234	0.008718957
С	4.316854692	6.009837901	-0.15366727
С	5.0950289114.12	24224569 1.32	25275121
С	5.155123345	3.865963615	-1.17191612
Н	3.774440049	6.493251407	0.665190436
Н	3.843348309	6.308614285	-1.094270525
Н	5.333513423	6.421475659	-0.15630928
Н	2.184544015	3.836807423	-2.421039116
Н	2.1132867384.03	33982647 2.48	35337123
Н	1.412070844	5.206222342	-1.60831756
Н	1.56325125 5.44	147282 1.57069	6436
Н	0.676741606	3.602929787	-1.535201942
Н	0.6118578333.96	50733755 1.50	50082304
Н	4.60233932 4.56	66623578 2.19	96519304
Н	4.699640799	4.108131258	-2.137132275
Н	6.123508864	4.506218073	1.304426135
Н	6.178477562	4.261689465	-1.186432282
Н	5.144355541	3.042837088	1.478462946
Н	5.217549869	2.777924147	-1.091327707

The following contains the orbital coefficients used in the frontier molecular orbital analysis:

HOMO coefficients on the diene carbons
--

Atom		Orbital	Coefficient
C1	S	-0.003	365
C1	S	-0.006	5026
C1	Х	0.004	073
C1	Y	-0.009	9042
C1	Ζ	0.127	934
C1	S	0.018	334

C1	Х	0.007129
C1	Y	-0.013972
C1	Ζ	0.197397
C1	S	0.01094
C1	Х	0.025043
C1	Y	-0.009371
C1	Ζ	0.182049
C1	XX	-0.002516
C1	YY	-0.001759
C1	ZZ	0.002452
C1	XY	0.00254
C1	XZ	-0.025132
C1	YZ	-0.00957
C4	S	-0.005993
C4	S	-0.009708
C4	Х	-0.075888
C4	Y	0.059254
C4	Ζ	-0.098976
C4	S	0.028575
C4	Х	-0.11045
C4	Y	0.083954
C4	Ζ	-0.145702
C4	S	0.023696
C4	Х	-0.137463
C4	Y	0.060502
C4	Ζ	-0.177041
C4	XX	0.001313
C4	YY	0.004652
C4	ZZ	-0.007914
C4	XY	-0.004595
C4	XZ	0.001037
C4	ΥZ	-0.004279

LUMO coefficients for dienophile carbons:

Atom		Orbital	Coefficient
C5	S	0.000	094
C5	S	0.000	267
C5	Х	0.005	188
C5	Y	-0.002	2707
C5	Ζ	-0.085	5181
C5	S	0.001	166
C5	Х	0.008	793
C5	Y	-0.004	4177

C5	Ζ	-0.132047
C5	S	-0.02159
C5	Х	0.012372
C5	Y	0.000939
C5	Ζ	-0.193001
C5	XX	0.002757

0.0908

0.1151

LUMO

0.0631

0.0628

(**5c**) C5

C6

НОМО

(diene)

C1

C4

C5	YY	-0.001108
C5	ZZ	-0.000267
C5	XY	0.000227
C5	XZ	-0.009009
C5	YZ	0.016723
C6	S	0.000178

C6	S	0.000311
C6	Х	-0.002252
C6	Y	0.003521
C6	Ζ	0.085368
C6	S	-0.001298
C6	Х	-0.002842
C6	Y	0.005415
C6	Ζ	0.132186
C6	S	0.007373
C6	Х	0.001442
C6	Y	-0.008492
C6	Ζ	0.193563
C6	XX	-0.000984
C6	YY	0.000103
C6	ZZ	0.000979
C6	XY	-0.001198
C6	XZ	0.012785
C6	YZ	0.014026

Frontier molecular orbital analysis values (V_{FMO}) for the HOMO of the diene and the LUMO of the dienophile. $V_{FMO} = \sum_i c_i^2$, for every orbital coefficient c_i on a specific carbon atom.



Figure S1: ¹H NMR spectrum of the product **5a**



Figure S2: ¹³C NMR spectrum of the product **5a**



Figure S3: ¹H NMR spectrum of the product **5b**



Figure S4: ¹³C NMR spectrum of the product **5b**



Figure S5: ¹H NMR spectrum of the product **5c**



Figure S6: $^{\scriptscriptstyle 13}\text{C}$ NMR spectrum of the product 5c



Figure S7: ¹H NMR spectrum of the product **5d**



Figure S8: ¹³C NMR spectrum of the product **5d**



Figure S9: ¹H NMR spectrum of the product **5e**



Figure S10: $^{\rm {\scriptscriptstyle 13}}{\rm C}$ NMR spectrum of the product ${\bf 5e}$



Figure S11: ¹H NMR spectrum of the product **5f**



Figure S12: ¹³C NMR spectrum of the product **5f**



Figure S13: ¹H NMR spectrum of the product **5g**



Figure S14: ¹³C NMR spectrum of the product **5g**

Figure S15: ¹H NMR spectrum of the product 5h









Figure S17: ¹H NMR spectrum of the product **5**i



Figure S18: $^{\scriptscriptstyle 13}\text{C}$ NMR spectrum of the product 5i



Figure S19: 1H NMR spectrum of the product 5j



Figure S20: $^{\scriptscriptstyle 13}\text{C}$ NMR spectrum of the product 5j



Figure S21: ¹H NMR spectrum of the product **5k**







Figure S23: ¹H NMR spectrum of the product **5**I



Figure S24: $^{\rm {\scriptscriptstyle 13}}{\rm C}$ NMR spectrum of the product ${\rm 5I}$



Figure S25: ¹H NMR spectrum of the product **5m**



Figure S26: $^{\scriptscriptstyle 13}\text{C}$ NMR spectrum of the product 5m







Figure S28: ¹³C NMR spectrum of the product **5n**



Figure S29: ¹H NMR spectrum of the product **50**



Figure S30: ¹³C NMR spectrum of the product **50**



Figure S31: ¹H NMR spectrum of the product **6**



Figure S32: ¹³C NMR spectrum of the product **6**



Figure S33: ¹H NMR spectrum of the product **7a+7b**



Figure S34: ¹³C NMR spectrum of the product **7a+7b**



Figure S35: ¹H NMR spectrum of the product **8a**



Figure S36: ¹H NMR spectrum of the product **9a**



Figure S37: ¹³C NMR spectrum of the product **9a**



Figure S38: ¹H NMR spectrum of the product **10**



Figure S39: ¹³C NMR spectrum of the product **10**



Figure S40: 1 H NMR spectrum of the product **12**



Figure S41: $^{\rm {\scriptscriptstyle 13}}{\rm C}$ NMR spectrum of the product 12



Figure S42: ¹H NMR spectrum of the product **11**



Figure S43: $^{\rm 13}{\rm C}$ NMR spectrum of the product ${\bf 11}$