Investigations toward a Unified Reaction Pathway of Thermal and TBSOTf-Mediated Oxidopyrylium-Alkene (5 + 2) Cycloadditions

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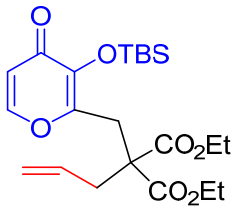
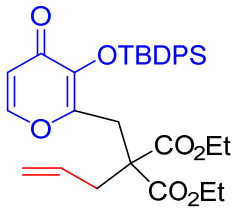
Supporting Information – Experimental

All reactions were performed under Ar atmosphere in oven-dried or flame-dried glassware. When heat was applied, an oil bath was utilized. All other commercially available anhydrous solvents and reagents were used as received. Sodium hydride (NaH) was a 60% dispersion in mineral oil. Thin layer chromatography was performed with glass or aluminum plates (silica gel F_{254}, Art 5715, 0.25 mm), visualized by fluorescence quenching under UV light, and stained with potassium permanganate. Flash column chromatography (FCC) was performed with silica gel 60A 40-63 μm (200-400 mesh). Mass spectral data was acquired using positive mode Electrospray Ionization (ESI+) and a high-resolution Time of Flight (TOF) mass spectrometer. ^{1}H NMR spectra were acquired at 400 or 500 MHz and $^{13}C\{^{1}H\}$ NMR spectra were acquired at 100 MHz or 125 MHz as noted. Chemical shifts are reported in ppm (δ) relative to the residual $CHCl_3$ (7.26) for ^{1}H NMR and the $CDCl_3$ shift (77.16 ppm) for $^{13}C\{^{1}H\}$ NMR. ^{1}H NMR coupling constants (*J*) are reported in Hertz (Hz), and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), td (triplet of doublets), ddt (doublet of doublet of triplets), dq (doublet of quartets), qq (quartet of quartets), ovlp (overlapping), br (broad), app (apparent). Based on intensity in the $^{13}C\{^{1}H\}$ spectra, both magnetic and chemical shift equivalent peaks are noted in parentheses. Selected examples of previously characterized compounds are included for ease of comparison with references included.



TBS-Pyrone Alkene 1a[1] **(Table 1, entry 1):** Prepared according to the procedure published by Mascareñas: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 5.5 Hz, 1H), 6.29 (d, *J* = 5.5 Hz, 1H), 5.74 (ddt, *J* = 16.9, 10.3, 7.4 Hz, 1H), 5.10-5.04 (m, 2H), 4.21 (ovlp q, *J* = 7.1 Hz, 4H), 3.45 (s, 2H), 2.62 (dt, *J* = 7.4, 1.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.98 (s, 9H), 0.27 (s, 6H); consistent with previously reported ^{1}H NMR spectrum.[1]



TBDPS-Pyrone Alkene 1b[2] **(Table 1, entry 2):** Prepared according to a similar procedure as published by Mascareñas.[1] To a solution of maltol (5.05 g, 39.9 mmol, 1.0 equiv.) in CH_2Cl_2 (100 mL) was added imidazole (4.87 g, 71.5 mmol, 1.8 equiv.) and TBDPSCl (11.5 mL, 44.2 mmol, 1.1 equiv.). The reaction was stirred 1.5 h at 23 °C, quenched with water (100 mL), stirred an additional 15 min, and then extracted with CH_2Cl_2 (100 mL). The combined organic extract was washed with sat. aq. NaCl (2 x 100 mL), dried with $MgSO_4$, filtered and concentrated. Purification by FCC (CH_2Cl_2 100% to CH_2Cl_2:EtOAc 90:10) delivered TBDPS-maltol (not shown) as a white

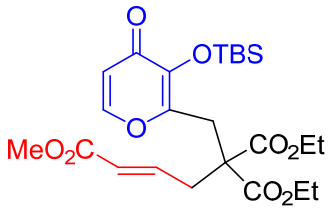
[1] Lopez, F.; Castedo, L.; Mascareñas, J. L. A Practical Route to Enantiopure, Highly Functionalized Seven-Membered Carbocycles and Tetrahydrofurans: Concise Synthesis of (+)-Nemorensic Acid. *Chem. Eur. J.* **2002**, *8*, 884-889.

[2] J. J. Bulandr, J. P. Grabowski, C. M. Law, J. L. Shaw, J. R. Goodell, T. A. Mitchell, Investigation of Transfer Group, Tether Proximity, and Alkene Substitution for Intramolecular Silyloxypyrone-Based (5 + 2) Cycloadditions. *J. Org. Chem.* **2019**, *84*, 10306-10320.

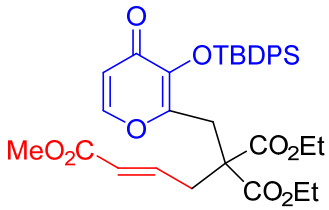
solid (15.96 g, 43.8 mmol, 99%). To a solution of TBDPS-maltol (15.96 g, 43.8 mmol) in benzene (220 mL) was added NBS (9.40 g, 52.8 mmol, 1.2 equiv.) and the solution was degassed for 10 min by bubbling Ar. AIBN (0.72 g, 4.40 mmol, 0.10 equiv.) was added and the reaction was degassed for an additional 2 min. The reaction was heated under an Ar atmosphere at 60 °C for 2 h, at which point the flask was cooled to room temperature and concentrated. Purification by FCC (CH_2Cl_2 100% to CH_2Cl_2:EtOAc 90:10) delivered TBDPS-maltol bromide **8** as a pale yellow solid (15.91 g, 35.9 mmol, 82%). To a suspension of NaH (1.45 g, 36.3 mmol, 2.0 equiv.) in THF (50 mL) was added diethyl malonate (5.5 mL, 36.3 mmol, 2.0 equiv.) slowly at –78 °C. Upon stirring for 5 min, the reaction was warmed to 23 °C by removal of the dry ice-acetone bath and stirred an additional 20 min. The reaction was cooled to –78 °C and TBDPS-maltol bromide (8.03 g, 18.1 mmol, 1.0 equiv.) in THF (15 mL) was added slowly over a period of 10 min. The reaction was stirred 2 h while slowly warming to ambient temperature, quenched slowly with sat. aq. NaCl (50 mL), and stirred 5 min. The solution was diluted with Et_2O (150 mL) and sat. aq. NaCl (50 mL) and separated. The combined aqueous layer was extracted with Et_2O (50 mL) and the resulting organic combined extract was washed with sat. aq. NaCl (50 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 60:40) delivered TBDPS-maltol diester as a white crystalline solid (5.03 g, 9.6 mmol, 53%): R_f = 0.40 (hexanes:EtOAc 60:40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.67 (m, 4H), 7.48 (d, *J* = 5.6 Hz, 1H), 7.38-7.31 (m, 6H), 6.06 (d, *J* = 5.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 4H), 3.83 (t, *J* = 7.7 Hz, 1H), 3.42 (d, *J* = 7.7 Hz, 2H) 1.26 (t, *J* = 7.2 Hz, 6H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.7, 168.2(2), 152.94, 152.92, 143.2, 134.7(4), 134.6(2), 129.4(2), 127.4(4), 115.6, 62.0(2), 49.1, 28.0, 27.2(3), 20.2, 14.2(2); mp 73–75 °C; ESI-HRMS calculated for $C_{29}H_{34}O_7SiNa$ $[M + Na]^+$ 545.1971, found 545.1954. To a solution of TBDPS-maltol diester (5.03 g, 9.6 mmol, 1.0 equiv.) in THF (100 mL) was added NaH

(461 mg, 11.5 mmol, 1.2 equiv.) at 23 °C and stirred ~30 min until the solution was almost clear indicative of enolate formation. Freshly purified over basic alumina, allyl bromide (3.3 mL, 38.4 mmol, 4.0 equiv.) was added slowly and the reaction was stirred 1.5 h. Upon quenching the reaction slowly with sat. aq. NH_4Cl (50 mL), the mixture was extracted with Et_2O (500 mL). The combined organic layer was washed with sat. aq. NH_4Cl (50 mL) and sat. aq. NaCl (50 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 60:40) delivered TBDPS-pyrone alkene **1b** as a white solid (4.97 g, 8.8 mmol, 92%): R_f = 0.67 (hexanes:EtOAc 60:40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.66 (m, 4H), 7.42 (d, *J* = 5.6 Hz, 1H), 7.38-7.31 (m, 6H), 6.05 (d, *J* = 5.6 Hz, 1H), 5.84-5.76 (m, 1H), 5.14-5.08 (m, 2H), 4.27-4.19 (m, 4H), 3.59 (s, 2H), 2.69 (app dt, *J* = 7.5, 1.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.07 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 172.6, 170.2(2), 152.84, 152.79, 143.9, 134.7(4), 134.6(2), 132.3, 129.4(2), 127.4(4), 119.7, 115.5, 61.8(2), 56.8, 37.8, 31.0, 27.2(3), 20.3, 14.2(2); mp 131–134 °C; ESI-HRMS calculated for $C_{32}H_{38}O_7SiNa$ $[M + Na]^+$ 585.2284, found 585.2259.

General Procedure A (cross-metathesis): A solution of silyloxypyrone in anhydrous CH_2Cl_2 was degassed for 10 min by bubbling Ar *by* balloon. Methyl acrylate (6-10 equiv.) and Grubbs-Hoveyda 2nd generation (GH2) catalyst (10 mol%) were added sequentially and the reaction degassed with Ar for an additional 10 min. Upon stirring at 23 °C for 24-32 h, the reaction was concentrated and purified by FCC to afford enoates that were previously characterized.[2]

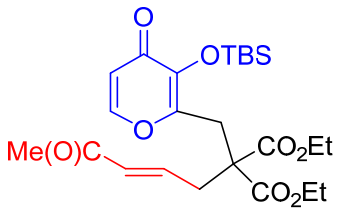


TBS-Pyrone Enoate[2] 1f (Table 1, entry 3): General procedure A was followed with **1a** (1.00 g, 2.28 mmol, 1.0 equiv.), CH_2Cl_2 (11.4 mL), methyl acrylate (2.1 mL, 22.8 mmol, 10 equiv.), and GH2 (142 mg, 0.23 mmol, 0.1 equiv.) for 24 h. Purification by FCC (hexanes:EtOAc 60:40) delivered enoate **1f** as a dark brown oil (688 mg, 1.39 mmol, 61%, dr >19:1): R_f = 0.35 (hexanes:EtOAc 60:40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 5.6 Hz, 1H), 6.83 (dt, *J* = 15.5, 7.7 Hz, 1H), 6.30 (d, *J* = 5.6 Hz, 1H), 5.82 (dt, *J* = 15.5, 1.3 Hz, 1H), 4.27-4.19 (m, 4H), 3.70 (s, 3H), 3.45 (s, 2H), 2.75 (dd, *J* = 7.7, 1.3 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 6H), 0.97 (s, 9H), 0.27 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.9, 169.7(2), 166.0, 152.9, 152.7, 144.3, 142.3, 125.2, 115.8, 62.1(2), 56.5, 51.5, 36.0, 31.1, 26.0(3), 18.9, 14.1(2), -3.6(2); ESI-HRMS calculated for $C_{24}H_{36}O_9SiNa$ $[M + Na]^+$ 519.2029, found 519.2024.

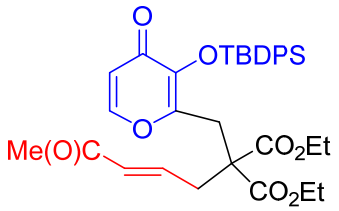


TBDPS-Pyrone Enoate[2] 1g (Table 1, entry 4): General procedure A was followed with **1b** (1.00 g, 1.78 mmol, 1.0 equiv.), CH_2Cl_2 (9.0 mL), methyl acrylate (1.6 mL, 17.8 mmol, 10 equiv.), and GH2 (111 mg, 0.18 mmol, 0.1 equiv.) for 24 h. Purification by FCC (hexanes:EtOAc 60:40) delivered enoate **1g** as a dark brown solid (1.01 g, 1.63 mmol, 92%, dr >19:1): R_f = 0.51 (hexanes:EtOAc 60:40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (m, 4H), 7.43 (d, *J* = 5.5 Hz, 1H), 7.39-7.31 (m, 6H), 6.91 (dt, *J* = 15.5, 7.7 Hz, 1H), 6.05 (d, *J* = 5.5 Hz, 1H), 5.86 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.30-4.19 (m, 4H), 3.64 (s, 3H), 3.58 (s, 2H), 2.82 (dd, *J* = 7.7, 1.4 Hz, 2H), 1.26 (t,

J = 7.2 Hz, 6H), 1.06 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 172.6, 169.7(2), 166.1, 152.8, 152.2, 144.1, 142.4, 134.8(4), 134.4(2), 129.4(2), 127.4(4), 125.3, 115.6, 62.2(2), 56.5, 51.6, 36.2, 31.4, 27.2(3), 20.3, 14.1(2); mp 103–106 °C; ESI-HRMS calculated for $C_{34}H_{40}O_9SiNa$ $[M + Na]^+$ 643.2339, found 643.2300.

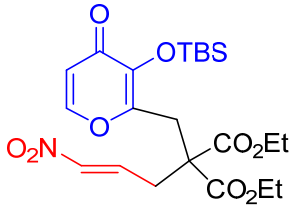


TBS-Pyrone enone 1k[3] (Table 1, entry 5): General procedure A was followed with **1a** (592 mg, 1.35 mmol, 1.0 equiv.), CH_2Cl_2 (15 mL), methyl vinyl ketone (553 µL, 6.76 mmol, 5.0 equiv.), and GH2 (85 mg, 0.135 mmol, 0.1 equiv.) for 24 h. Purification by FCC (CH_2Cl_2/Et_2O 95:5) delivered enone **1k** as a dark brown oil (393 mg, 0.818 mmol, 61%, dr >19:1): R_f = 0.07 (CH_2Cl_2/Et_2O 95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 5.6 Hz, 1H), 6.69 (dt, J = 15.9, 7.6 Hz, 1H), 6.31 (d, J = 5.6 Hz, 1H), 6.03 (dt, J = 15.9, 1.2 Hz, 1H), 4.22 (ovlp q, J = 7.1 Hz, 4H), 3.47 (s, 2H), 2.75 (dd, J = 7.6, 1.2 Hz, 2H), 2.20 (s, 3H), 1.26 (t, J = 7.1 Hz, 6H), 0.98 (s, 9H), 0.27 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 197.7, 173.9, 169.6(2), 152.9, 152.5, 144.3, 141.2, 134.7, 115.8, 62.1(2), 56.5, 36.4, 31.4, 26.9, 26.0(3), 18.8, 14.0(2), -3.7(2); ESI-HRMS calculated for $C_{24}H_{36}O_8SiNa$ $[M + Na]^+$ 503.2077, found 503.2063.



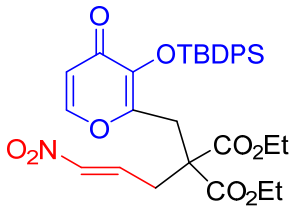
TBDPS-Pyrone enone 1l (Table 1, entry 6): General procedure A was followed with **1b** (1.30 g, 2.31 mmol, 1.0 equiv.), CH_2Cl_2 (15 mL), methyl vinyl ketone (1.2 mL, 14.82 mmol, 5.0 equiv.), and GH2 (186 mg, 0.300 mmol, 0.1 equiv.) for 24 h. Purification by FCC (CH_2Cl_2/Et_2O 95:5 to

85:15) delivered enone **1l** as a dark brown oil (812 mg, 1.34 mmol, 58%, dr >19:1): R_f = 0.12 (CH_2Cl_2/Et_2O 95:5); ^1H NMR (500 MHz, $CDCl_3$) δ 7.68-7.65 (m, 4H), 7.44 (d, *J* = 5.6 Hz, 1H), 7.40-7.31 (m, 6H), 6.74 (dt, *J* = 15.9, 7.5 Hz, 1H), 6.04 (d, *J* = 5.6 Hz, 1H), 6.04 (dt, *J* = 15.9, 1.3 Hz, 1H), 4.30-4.19 (m, 4H), 3.59 (s, 2H), 2.81 (dd, *J* = 7.5, 1.3 Hz, 2H), 2.15 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H), 1.07 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.8, 172.5, 169.6(2), 152.9, 152.0, 144.0, 141.3, 134.70, 134.69(4), 134.3(2), 129.4(2), 127.4(4), 115.5, 62.1(2), 56.5, 36.5, 31.8, 27.2(3), 26.8, 20.2, 14.1(2); ESI-HRMS calculated for $C_{34}H_{40}O_8SiNa$ $[M + Na]^+$ 627.2390, found 627.2373.



TBS-Pyrone Nitro-ene 1m (Table 1, entry 7): A solution of TBS-pyrone alkene **1a** (400 mg, 0.912 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was cooled to -78 ºC and ozone (30%) was bubbled into the reaction for 15 minutes. The reaction was degassed by exposure to oxygen for 15 minutes, followed by addition of PPh_3 (477 mg, 1.82 mmol, 2.0 equiv.). The resulting mixture was allowed to warm to room temperature with stirring over 15 minutes. The reaction mixture was concentrated and purified by FCC (hexanes:EtOAc 70:30) afforded TBS-pyrone aldehyde **S2** as a yellow oil (152 mg, 0.35 mmol, 38%): R_f = 0.18 (hexanes:EtOAc 70:30); ^1H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.52 (d, *J* = 5.6 Hz, 1H), 6.31 (d, *J* = 5.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 4H), 3.52 (s, 2H), 3.00 (s, 2H), 1.25 (t, *J* = 7.2 Hz, 6H), 0.96 (s, 9H), 1.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 174.1, 169.4(2), 153.0, 152.6, 144.6, 115.8, 62.4(2), 53.9, 46.2, 31.7, 26.1(3), 18.9, 14.0(2), -3.5(2); ESI-HRMS calculated for $[M + Na]^+$ 463.1764, found 463.1768. To a solution of aldehyde **S2** (500 mg, 1.13 mmol, 1.0 equiv.) in CH_3NO_2 (6 mL) at 23 °C was added Et_3N (50 µL, 0.34

mmol, 0.3 equiv.). The resulting mixture was stirred for 40 h, concentrated, and dissolved in CH_2Cl_2 (6 mL). Upon cooling to -78°C, triethylamine (700 µL, 4.97 mmol, 4.4 equiv.) was added followed by dropwise addition of MsCl (265 µL, 3.39 mmol, 3.0 equiv.). After stirring for 24 h, the resulting mixture was concentrated and purified by FCC (hexanes:EtOAc 90:10 to 70:30) to afford TBS-pyrone nitro-ene **1m** as a yellow oil (22 mg, 0.045 mmol, 4%): R_f = 0.56 (hexanes:EtOAc 50:50); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 5.6 Hz, 1H), 7.20 (dt, *J* = 8.1, 13.4 Hz, 1H), 6.91 (d, *J* = 13.4 Hz, 1H), 6.31 (d, *J* = 5.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 4H), 3.48 (s, 2H), 2.75 (dd, *J* = 1.1, 8.1 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 6H), 0.96 (s, 9H), 0.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 169.2(2), 153.0, 151.9, 144.6, 141.9, 136.6, 116.0, 62.5(2), 56.4, 32.1, 31.6, 26.1(3), 18.9, 14.1(2), -3.6(2); ESI-HRMS calculated for $[M + Na]^+$ 506.1822, found 506.1829.



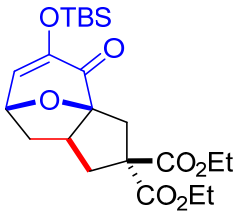
TBDPS-Pyrone Nitro-ene 1n (Table 1, entry 8): The TBDPS variant was isolated in better yield and allowed for characterization of the corresponding TBDPS-cycloadduct **2n** (*vide infra*); To a solution of TBDPS-pyrone aldehyde (*vide infra*) **12** (638 mg, 1.13 mmol, 1.0 equiv.) in CH_3NO_2 (6 mL) at 23 °C was added triethylamine (50 µL, 0.34 mmol, 0.3 equiv.). The resulting mixture was stirred for 40 hours, concentrated, and dissolved in CH_2Cl_2 (6 mL). Upon cooling to -78°C, triethylamine (700 µL, 4.97 mmol, 4.4 equiv.) was added followed by dropwise addition of MsCl (265 µL, 3.39 mmol, 3.0 equiv.). After stirring for 24 hours, the resulting mixture was concentrated and purified by FCC (hexanes:EtOAc 90:10 to 70:30) to afford TBDPS-pyrone nitro-ene **1n** as a yellow oil (98 mg, 0.16 mmol, 14%): R_f = 0.51 (hexanes:EtOAc 50:50); ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.73-7.68 (m, 4H), 7.47 (d, *J* = 5.6 Hz, 1H), 7.43-7.35 (m, 6H), 7.30 (dt, *J* = 8.1, 13.4 Hz, 1H), 6.92 (app. d, *J* = 13.4 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 4.29 (dq, *J* = 7.2, 8.8 Hz, 4H), 3.62 (s, 2H), 2.84 (dd, *J* = 1.1, 8.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 6H), 1.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 169.1(2), 152.9, 151.4, 144.2, 141.7, 136.7, 134.8(4), 134.1(2), 129.5(2), 127.5(4), 115.6, 62.4(2), 56.3, 32.3, 32.0, 27.2(3), 20.2, 14.1(2); ESI-HRMS calculated for $[M + Na]^+$ 630.2135, found 630.2139.

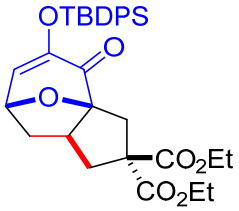
General Procedure B (Internal Standard (5 + 2) Cycloaddition): 0.05-0.10 mmol of pyrone was dissolved in toluene and heated to the appropriate temperature and time. Upon cooling to ambient temperature, the reaction was concentrated directly on vacuum pump. A solution of 1,3,5-trimethoxybenzene in $CDCl_3$ was added to the vial and the resulting solution transferred to an NMR tube with a Pasteur pipet. The NMR yield for both starting material and product was calculated upon comparison of diagnostic integrals and appropriate values were reported in Tables 1-2. Some compounds that were previously characterized in (J. J. Bulandr, J. P. Grabowski, C. M. Law, J. L. Shaw, J. R. Goodell, T. A. Mitchell, Investigation of Transfer Group, Tether Proximity, and Alkene Substitution for Intramolecular Silyloxypyrone-Based (5 + 2) Cycloadditions.[2] *J. Org. Chem.* 2019, *84*, 10306-10320) and (A. J. Youman, S. N. Rokey, J. P. Grabowski, W. Guo, Q. Sun, S. N. Angles, J. R. Goodell, D. J. Tantillo, T. A. Mitchell, Experimental and Theoretical Investigation of the Synchronicity of Ambident Silyloxypyrone-Based (5 + 2) Cycloadditions.[3] *J. Org. Chem.* 2023, *88*, 5972-5981) have been included in the supporting information for continuity and the cross-references included for each compound characterization.

[3] A. J. Youman, S. N. Rokey, J. P. Grabowski, W. Guo, Q. Sun, S. N. Angles, J. R. Goodell, D. J. Tantillo, T. A. Mitchell, Experimental and Theoretical Investigation of the Synchronicity of Ambident Silyloxypyrone-Based (5 + 2) Cycloadditions. *J. Org. Chem.* **2023**, *88*, 5972-5981.

General Procedure C (Isolated Yield for Selected (5 + 2) Cycloadditions): 0.2 to 1.0 mmol of terminal alkene was dissolved in toluene (0.1 M) and heated to the appropriate temperature for 24 hours (110 °C oil-bath temp. for terminal olefins and 60 °C oil-bath temp. for α,β-unsaturated carbonyls). Upon cooling to ambient temperature, the reaction was concentrated and purified by column chromatography.[2,3]

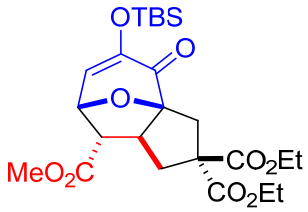


TBS-Cycloadduct 2a[1] (Table 1, entry 1): General Procedure C was followed with terminal olefin **1a** (219 mg, 0.5 mmol, 1.0 equiv.) and toluene (5 mL) at 110 °C. Purification by FCC (hexanes:EtOAc 80:20) delivered cycloadduct **2a** as a colorless oil (195 mg, 0.44 mmol, 89%, dr >19:1): R_f = 0.56 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (d, *J* = 5.0 Hz, 1H), 4.82 (dd, *J* = 5.3, 5.0 Hz, 1H), 4.26-4.12 (m, 4H), 3.14 (d, *J* = 14.7 Hz, 1H), 2.65-2.58 (m, 1H), 2.57 (app dd, *J* = 14.7, 1.2* Hz, 1H) *long-range coupling, 2.47 (app ddd, *J* = 13.4, 4.7, 1.2* Hz, 1H) *long-range coupling, 2.36 (dd, *J* = 13.4, 9.7 Hz, 1H), 2.18-2.09 (m, 2H), 1.25 (ovlp t, *J* = 7.1 Hz, 6H), 0.93 (s, 9H), 0.144 (s, 3H), 0.138 (s, 3H); consistent with previously reported ^{1}H NMR spectrum.[1]

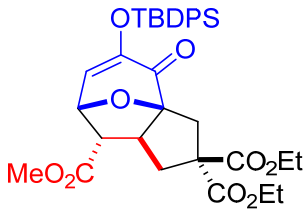


TBDPS-Cycloadduct 2b[2] (Table 1, entry 2): General Procedure C was followed with terminal olefin **1b** (281 mg, 0.5 mmol, 1.0 equiv.) and toluene (5 mL) at 110 °C. Purification by FCC (hexanes:EtOAc 80:20) delivered cycloadduct **2b** as a colorless oil (259 mg, 0.46 mmol, 92%, dr

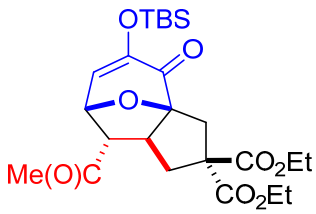
>19:1): R_f = 0.49 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.62 (m, 4H), 7.46-7.33 (m, 6H), 5.86 (d, *J* = 5.1, 1H), 4.58 (dd, *J* = 6.4, 5.1 Hz, 1H), 4.24-4.10 (m, 4H), 3.09 (d, *J* = 14.7 Hz, 1H), 2.52 (app dd, *J* = 14.7, 1.0* Hz, 1H) *long-range coupling, 2.36 (app ddd, *J* = 12.7, 4.0, 1.0* Hz, 1H) *long-range coupling, 2.25 (dd, *J* = 12.7, 9.7 Hz, 1H), 2.25-2.16 (m, 1H), 1.93 (ddd, *J* = 11.5, 6.4, 5.2 Hz, 1H), 1.64 (dd, *J* = 11.5, 8.6 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.4, 171.02, 170.96, 145.5, 135.7(2), 135.6(2), 132.6, 132.2, 130.17, 130.12, 129.0, 127.9(2), 127.8(2), 97.4, 75.4, 62.0, 61.8, 61.6, 43.4, 39.0, 37.7, 37.1, 26.6(3), 19.6, 14.1, 14.0; ESI-HRMS calculated for $C_{32}H_{38}O_7SiNa$ [M + Na]$^+$ 585.2287, found 585.2245.



TBS-Cycloadduct 2f[2] (Table 1, entry 3): General Procedure C was followed with enoate **1f** (248 mg, 0.5 mmol, 1.0 equiv.) and toluene (5 mL) at 60 °C. Purification by FCC (hexanes:EtOAc 70:30) delivered cycloadduct **2f** as a colorless oil (199 mg, 0.40 mmol, 80%, dr >19:1): R_f = 0.68 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 (d, *J* = 5.0 Hz, 1H), 4.94 (dd, *J* = 6.3, 5.0 Hz, 1H), 4.26-4.12 (m, 4H), 3.69 (s, 3H), 3.60 (dd, *J* = 6.3, 6.1 Hz, 1H), 3.12 (d, *J* = 14.8, 1H), 2.94 (ddd, *J* = 10.3, 6.1, 2.9 Hz, 1H), 2.67 (app ddd, *J* = 13.7, 2.9, 1.4* Hz, 1H) *long-range coupling, 2.53 (app dd, *J* = 14.8, 1.4* Hz, 1H) *long-range coupling, 2.31 (dd, *J* = 13.7, 10.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.3, 171.1, 171.0, 170.6, 146.9, 125.3, 97.7, 75.9, 61.9, 61.8, 61.6, 55.9, 52.2, 46.4, 37.8, 37.2, 25.6(3), 18.5, 14.1, 14.0, -4.7, -4.8; ESI-HRMS calculated for $C_{24}H_{36}O_9SiNa$ [M + Na]$^+$ 519.2026, found 519.2027.

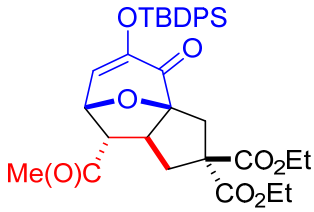


TBDPS-Cycloadduct 2g[2] (Table 1, entry 4): General Procedure C was followed with enoate **1g** (310 mg, 0.5 mmol, 1.0 equiv.) and toluene (5 mL) at 60 °C. Purification by FCC (hexanes:EtOAc 70:30) delivered cycloadduct **2g** as a colorless oil (262 mg, 0.42 mmol, 85%, dr >19:1): R_f = 0.61 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.60 (m, 4H), 7.44-7.35 (m, 6H), 5.81 (d, *J* = 5.0 Hz, 1H), 4.73 (dd, *J* = 6.3, 5.0 Hz, 1H), 4.25-4.10 (m, 4H), 3.47 (dd, *J* = 6.3, 6.2 Hz, 1H), 3.41 (s, 3H), 3.08 (d, *J* = 14.8 Hz, 1H), 2.82 (ddd, *J* = 10.2, 6.2, 2.7 Hz, 1H), 2.61 (app ddd, *J* = 13.7, 2.7, 1.4* Hz, 1H) *long-range coupling, 2.48 (app ddd, *J* = 14.8, 1.4* Hz, 1H) *long-range coupling, 2.24 (dd, *J* = 13.7, 10.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 191.3, 171.1, 170.6, 170.5, 146.3, 135.5(2), 135.4(2), 132.12, 132.07, 130.15, 130.08, 128.0(2), 127.9(2), 124.2, 97.5, 75.7, 61.9, 61.8, 61.6, 55.6, 52.0, 46.2, 37.7, 37.2, 26.5(3), 19.6, 14.1, 14.0; ESI-HRMS calculated for $C_{34}H_{40}O_9SiNa$ [M + Na]$^+$ 643.2339, found 643.2341.

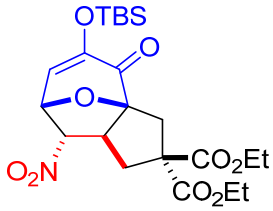


TBS-Cycloadduct 2k[3] (Table 1, entry 5): General Procedure C was followed with enone **1k** (90 mg, 0.2 mmol, 1.0 equiv.) and toluene (2 mL) at 60 °C. Purification by FCC (hexanes:EtOAc 70:30) delivered cycloadduct **2k** as a dark brown oil (61 mg, 0.136 mmol, 68%, dr >19:1): R_f = 0.45 (hexanes:EtOAc 70:30); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (d, *J* = 4.9 Hz, 1H), 4.95 (dd, *J* = 6.0, 4.9 Hz, 1H), 4.28-4.14 (m, 4H), 3.68 (dd, *J* = 6.4, 6.0 Hz, 1H), 3.12 (d, *J* = 14.8 Hz, 1H),

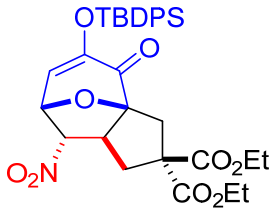
2.91 (ddd, J = 10.2, 6.4, 2.8 Hz, 1H), 2.66 (ddd, J = 13.7, 2.8, 1.3* Hz, 1H) *long-range coupling, 2.53 (dd, J = 14.8, 1.3* Hz, 1H) *long-range coupling, 2.30 (dd, J = 13.7, 10.2 Hz, 1H), 2.19 (s, 3H), 1.26 (ovlp t, J = 7.2 Hz, 6H), 0.92 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 204.1, 192.3, 171.2, 170.5, 146.7, 125.0, 97.7, 75.9, 64.9, 62.0, 61.9, 61.7, 45.4, 37.7, 37.2, 30.0, 25.6(3), 18.4, 14.1, 14.0, -4.71, -4.74; ESI-HRMS calculated for $C_{24}H_{36}O_8SiNa$ $[M + Na]^+$ 503.2077, found 503.2074.



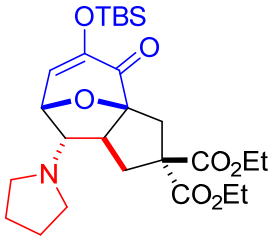
TBDPS-Cycloadduct 2l[3] (Table 1, entry 6): General Procedure C was followed with enone **1l** (100 mg, 0.2 mmol, 1.0 equiv.) and toluene (2 mL) at 60 °C. Purification by FCC (hexanes:EtOAc 70:30) delivered cycloadduct **2l** as a dark brown oil (63 mg, 0.136 mmol, 68%, dr >19:1): R_f = 0.41 (hexanes:EtOAc 70:30); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.59 (m, 4H), 7.46-7.34 (m, 6H), 5.85 (d, J = 5.0 Hz, 1H), 4.74 (dd, J = 6.0, 5.0 Hz, 1H), 4.25-4.11 (m, 4H), 3.49 (dd, J = 6.3, 6.0 Hz, 1H), 3.08 (d, J = 14.7 Hz, 1H), 2.68 (ddd, J = 10.2, 6.3, 2.7 Hz, 1H), 2.59 (ddd, J = 13.5, 2.7, 1.2* Hz, 1H) *long-range coupling, 2.48 (dd, J = 14.7, 1.2* Hz, 1H) *long-range coupling, 2.21 (dd, J = 13.5, 10.2 Hz, 1H), 1.88 (s, 3H), 1.23 (ovlp t, J = 7.1 Hz, 6H), 1.06 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 203.4, 191.3, 171.2, 170.5, 146.1, 135.49(2), 135.46(2), 132.10, 132.07, 130.1(2), 127.9(4), 124.4, 97.6, 75.6, 64.9, 61.9, 61.8, 61.6, 45.0, 37.6, 37.1, 29.5, 25.6(3), 19.6, 14.1, 14.0; ESI-HRMS calculated for $C_{34}H_{40}O_8SiNa$ $[M + Na]^+$ 627.2390, found 627.2388.



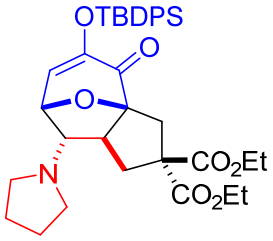
TBS-Cycloadduct 2m (Table 1, entry 7) could not be isolated pure, but NMR data was consistent with the TBDPS variant (*vide infra*) and ESI-HRMS calculated for $C_{22}H_{33}NO_9SiNa$ $[M + Na]^+$ 506.1822, found 506.1829.



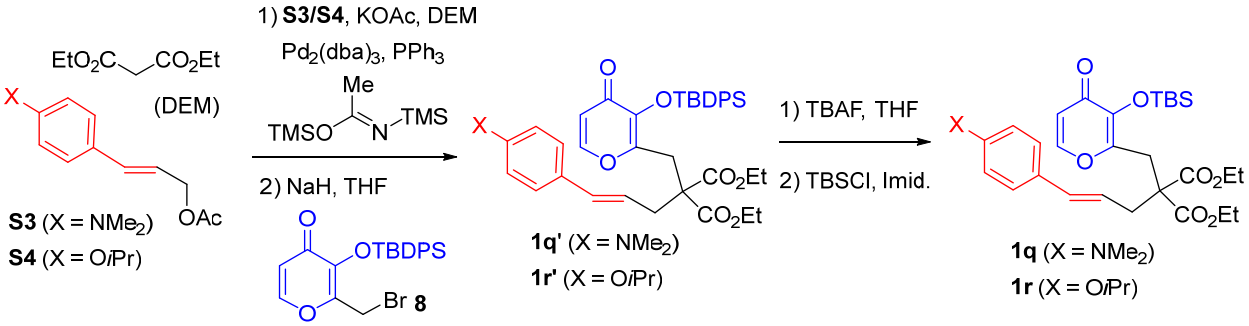
TBDPS-Cycloadduct 2n (Table 1, entry 8): A solution of TBDPS-pyrone nitro-ene **1n** (70 mg, 0.1 mmol, 1.0 equiv.) in toluene (2 mL) was heated to 80 °C and stirred for 20 hours. The resulting solution was concentrated and purified by FCC (hexanes:EtOAc 90:10 to 70:30) to afford TBDPS-cycloadduct **2n** as a yellow oil (61 mg, 0.087 mmol, 87%, dr >19:1): R_f = 0.54 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.59 (m, 4H), 7.46-7.37 (m, 6H), 5.81 (d, *J* = 5.0 Hz, 1H), 5.33 (dd, *J* = 5.5, 5.9 Hz, 1H), 4.92 (dd, *J* = 5.3, 5.9 Hz, 1H), 4.25-4.11 (m, 4H), 3.06 (d, *J* = 15.0 Hz, 1H), 3.01 (ddd, *J* = 2.3, 5.2, 10.4 Hz, 1H), 2.78 (dt, *J* = 2.0, 14.0 Hz, 1H), 2.44 (dd, *J* = 1.4, 15.0 Hz, 1H), 2.23 (dd, *J* = 10.4, 14.0 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 171.0, 169.9, 147.8, 135.5(2), 135.3(2), 131.8, 131.5, 130.4, 130.3, 128.05(2), 128.04(2), 121.5, 97.6, 91.0, 74.9, 62.16, 62.08, 61.2, 46.8, 37.1, 36.5, 26.5(3), 19.7, 14.1, 14.0; ESI-HRMS calculated for $[M + Na]^+$ 630.2135, found 630.2134.

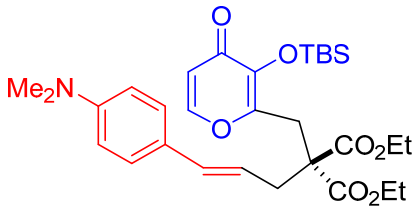


TBS-Cycloadduct 2o[3] (Scheme 3): To a solution of silyloxypyrone-aldehyde **5** (35 mg, 0.076 mmol, 1.0 equiv.) in $CDCl_3$ (760 µL) was added $MgSO_4$ (46 mg, 0.38 mmol, 5.0 equiv.) and a solution of pyrrolidine (13 µL, 0.15 mmol, 2.0 equiv.) in $CDCl_3$ (100 µL) delivered as 1/6th of a stock solution of 78 µL in 600 µL of $CDCl_3$. This mixture was stirred for 8 hours at 0 °C, concentrated, and quenched by subjecting to FCC (Et_2O 100%) and the further purified by FCC (CH_2Cl_2:Et_2O 90:10 to 80:20) which afforded unreacted aldehyde **5** as a yellow oil (10 mg, 0.021 mmol, 28%) and cycloadduct **2o** as a yellow oil (25 mg, 0.049 mmol, 64%, dr >19:1): R_f = 0.80 (CH_2Cl_2:Et_2O 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (d, *J* = 4.9 Hz, 1H), 4.67 (app t, *J* = 5.2 Hz, 1H), 4.25-4.11 (m, 4H), 3.08 (d, *J* = 14.8 Hz, 1H), 2.97 (app t, *J* = 5.2 Hz, 1H), 2.61 (dd, *J* = 13.0, 2.2 Hz, 1H), 2.53-2.40 (m, 6H), 2.33 (dd, *J* = 13.0, 10.1 Hz, 1H), 1.76-1.73 (m, 4H), 1.24 (ovlp t, *J* = 7.1 Hz, 6H), 0.93 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.9, 170.9(2), 146.6, 127.1, 97.3, 78.0, 76.4, 62.0, 61.9, 61.7, 54.0(2), 49.9, 37.9, 37.4, 25.8(3), 23.6(2), 18.6, 14.2, 14.1, -4.5, -4.7; ESI-HRMS calculated for $C_{26}H_{41}NO_7SiNa$ $[M + Na]^+$ 530.2550, found 530.2535.



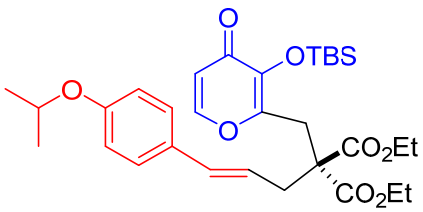
TBDPS-Cycloadduct 2p (Scheme 3): To a solution of silyloxypyrone-aldehyde **5′** (44 mg, 0.076 mmol, 1.0 equiv.) in $CDCl_3$ (760 µL) was added $MgSO_4$ (46 mg, 0.38 mmol, 5.0 equiv.) and a solution of pyrrolidine (13 µL, 0.15 mmol, 2.0 equiv.) in $CDCl_3$ (100 µL) delivered as 1/6th of a stock solution of 78 µL in 600 µL of $CDCl_3$. This mixture was stirred for 8 hours at 0 °C, concentrated, and quenched by subjecting to FCC (Et_2O 100%) and the further purified by FCC (CH_2Cl_2:Et_2O 90:10 to 80:20) which afforded unreacted aldehyde **5′** as a yellow oil (9 mg, 0.016 mmol, 20%) and cycloadduct **2p** as a yellow oil (23 mg, 0.036 mmol, 48%, dr >19:1): R_f = 0.85 (CH_2Cl_2:Et_2O 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.68 (m, 4H), 7.44-7.33 (m, 6H), 5.93 (d, *J* = 5.0 Hz, 1H), 4.47 (app t, *J* = 5.2 Hz, 1H), 4.24-4.10 (m, 4H), 3.05 (d, *J* = 14.8 Hz, 1H), 2.85 (m, 1H), 2.55 (m, 1H), 2.47 (d, *J* = 14.8 Hz, 1H), 2.38-2.20 (m, 6H), 1.68-1.57 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.1, 171.0, 170.9, 146.0, 135.6(4), 132.7, 132.6, 130.0, 129.9, 127.8(2), 127.7(2), 126.3, 97.3, 77.9, 76.1, 61.94, 61.87, 61.6, 53.7(2), 49.7, 37.9, 37.3, 26.7(3), 23.5(2), 19.7, 14.13, 14.08; ESI-HRMS calculated for $C_{36}H_{45}NO_7SiNa$ $[M + Na]^+$ 654.2863, found 654.2842.





TBS-Pyrone Styrene 1q[3] (Table 2, entry 1): To a solution of 4-dimethylamino styrenyl acetate **S3** (1.6 g, 7.30 mmol, 1.0 equiv.) in THF (50 mL, 0.15M) was added KOAc (72 mg, 0.73 mmol, 0.1 equiv.), bis(trimethylsilyl)acetamide (2.7 mL, 10.95 mmol, 1.5 equiv.), and diethyl malonate (990 µL, 6.57 mmol, 2.0 equiv.) and the solution was stirred until homogenous (~10 min). In a separate flask, the catalyst was prepared by dissolving triphenylphosphine (957 mg, 3.65 mmol, 0.5 equiv.) and $Pd_2(dba)_3$ (534 mg, 0.365 mmol, 0.05 equiv.) in THF (10 mL) and stirred for 5 min. This catalyst solution was added to the previously prepared mixture and sparged with Ar for 10 min and the resulting solution was heated to 70 °C and stirred for 4.5 h. The reaction was quenched slowly with H_2O (50 mL), extracted with Et_2O (3 x 75 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl, dried with Na_2SO_4, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 90:10) to afford the cinnamyl diester (not shown). To a solution of this cinnamyl diester (750 mg, 2.35 mmol, 1.0 equiv.) in THF (15 mL, 0.16M) was added NaH (188 mg, 4.70 mmol, 2.0 equiv.) and the solution was stirred for 15 min and then bromide **8** (1.25 g, 2.82 mmol, 1.2 equiv.) was added and stirred for an additional 1.5 h. The reaction was quenched slowly with H_2O (25 mL), extracted with Et_2O (3 x 50 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl (25 mL), dried with Na_2SO_4, filtered, and concentrated. Purification by consecutive FCC (CH_2Cl_2:Et_2O 95:5; hexanes:EtOAc 70:30) afforded TBDPS-pyrone styrene **1q′** as a brown oil (278 mg, 0.408 mmol, 17% 2-step yield). A solution of **1q′** (140 mg, 0.205 mmol, 1.0 equiv.) in THF (3 mL, 0.08M) was added TBAF (270 µL, 0.267 mmol, 1.2 equiv.) at 23 °C and stirred for 1 h. The reaction was

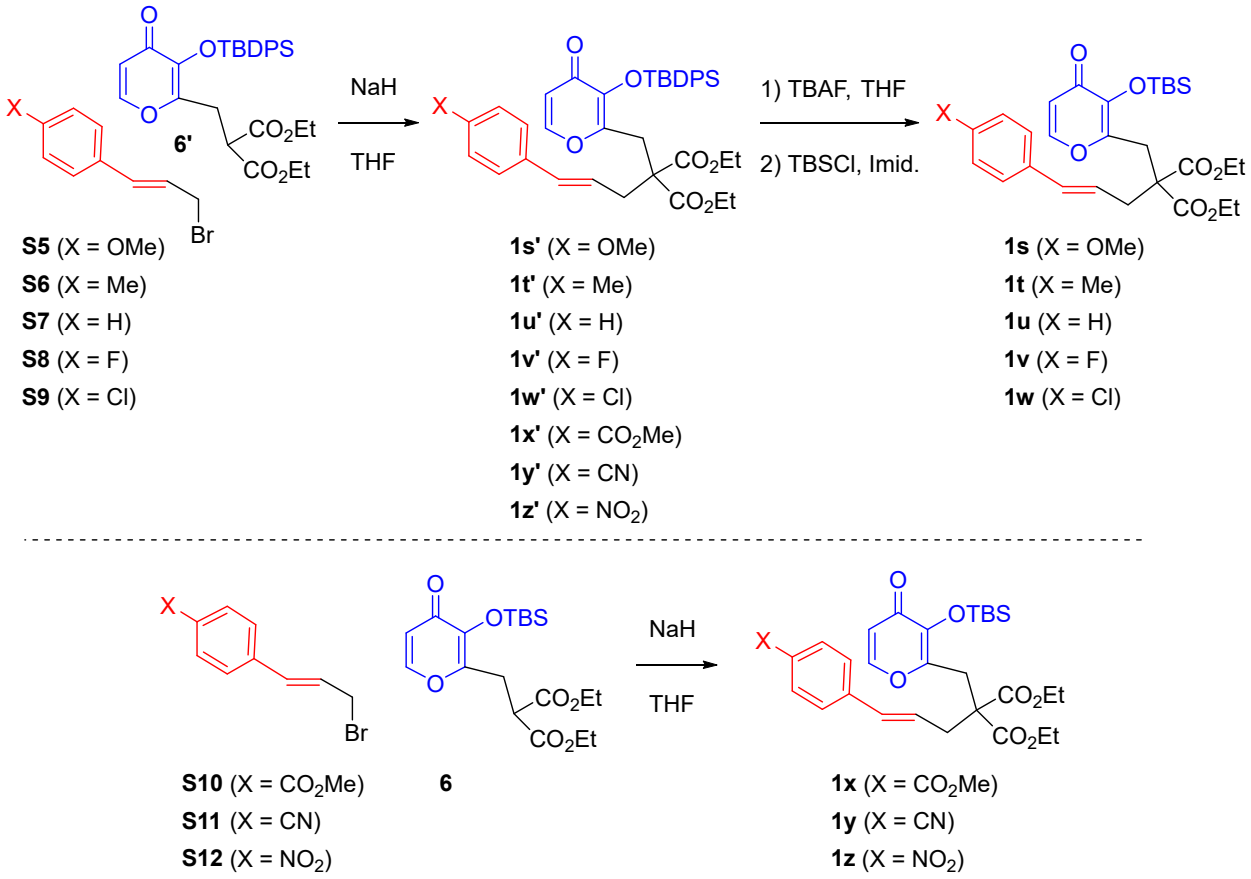
quenched slowly with sat. aq. NH_4Cl (5 mL), diluted with Et_2O (20 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl (5 mL), dried with $MgSO_4$, filtered, and concentrated. To a solution of crude enol in CH_2Cl_2 (3 mL) was added imidazole (45 mg, 0.656 mmol, 3.2 equiv.) and TBSCl (128 mg, 0.615 mmol, 3.0 equiv.) at 23 °C and stirred 24 h. The reaction was quenched slowly with H_2O (10 mL), diluted with CH_2Cl_2 (10 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl (10 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 70:30) to afford TBS-pyrone styrene **1q** as a brown oil (44 mg, 0.079 mmol, 39% 2-step yield): R_f = 0.33 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.6 Hz, 1H), 7.17 (app d, *J* = 8.8 Hz, 2H), 6.62 (app d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 5.6 Hz, 1H), 6.29 (app d, *J* = 15.5 Hz, 1H), 5.87 (dt, *J* = 15.5, 7.8 Hz, 1H), 4.25-4.15 (m, 4H), 3.49 (s, 2H), 2.94 (s, 6H), 2.75 (dd, *J* = 7.8, 1.0 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 6H), 0.95 (s, 9H), 0.25 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 174.1, 170.4(2), 153.8, 152.9, 150.2, 144.2, 134.6, 127.4(2), 125.8, 118.9, 115.8, 112.5(2), 61.8(2), 57.4, 40.7(2), 37.4, 31.0, 26.1(3), 18.9, 14.2(2), -3.5(2); ESI-HRMS calculated for $C_{30}H_{43}NO_7SiNa$ $[M + Na]^+$ 580.2706, found 580.2690.



TBS-Pyrone Styrene 1r[3] (Table 2, entry 2): To a solution of 4-isopropyl styrenyl acetate **S4** (1.5 g, 6.20 mmol, 1.0 equiv.) in THF (20 mL, 0.3M) was added KOAc (61 mg, 0.620 mmol, 0.1 equiv.), bis(trimethylsilyl)acetamide (2.3 mL, 9.30 mmol, 1.5 equiv.), and diethyl malonate (897 µL, 5.90 mmol, 1.0 equiv.) and the solution was stirred until homogenous (~10 min). In a separate flask, the catalyst was prepared by dissolving triphenylphosphine (813 mg, 3.10 mmol, 0.5 equiv.)

and $Pd_2(dba)_3$ (284 mg, 0.310 mmol, 0.05 equiv.) in THF (10 mL) and stirred for 5 min. This catalyst solution was added to the previously prepared mixture and sparged with Ar for 10 min and the resulting solution was heated to 70 °C and stirred for 3 h. The reaction was quenched slowly with H_2O (50 mL), extracted with Et_2O (3 x 50 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl (100 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 95:5) to afford the cinnamyl diester (not shown). To a solution of this cinnamyl diester (500 mg, 1.50 mmol, 1.0 equiv.) in THF (15 mL, 0.1M) was added NaH (120 mg, 3.00 mmol, 2.0 equiv.) and the solution was stirred for 15 min and then bromide **8** (798 mg, 1.78 mmol, 1.2 equiv.) was added and stirred for an additional 1.5 h. The reaction was quenched slowly with H_2O (20 mL), extracted with Et_2O (3 x 20 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl (75 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 80:20) afforded TBDPS-pyrone styrene **1r′** as a white foam (571 mg, 0.819 mmol, 20%, 2-step yield). To a solution of **1r′** (100 mg, 0.143 mmol, 1.0 equiv.) in THF (1.5 mL, 0.1M) was added TBAF (180 µL, 0.180 mmol, 1.3 equiv.) at 23 °C and stirred for 1 h. The reaction was quenched slowly with H_2O (5 mL), diluted with Et_2O (10 mL), and separated. The combined organic extracts were washed with sat. aq. NaCl (10 mL), dried with $MgSO_4$, filtered, and concentrated. To a solution of crude enol in CH_2Cl_2 (1.5 mL) was added imidazole (29 mg, 0.426 mmol, 3.0 equiv.) and TBSCl (63 mg, 0.418 mmol, 3.0 equiv.) at 23 °C and stirred 3 h. The reaction was quenched slowly with H_2O (2 mL) and extracted into CH_2Cl_2 (3 x 2 mL). The combined organic extracts were washed with sat. aq. NaCl (5 mL), dried with Na_2SO_4, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 80:20 to 70:30) afforded TBS-pyrone styrene **1r** as a clear oil (105 mg, 0.183 mmol, 50% 2-step yield): R_f = 0.46 (hexanes:EtOAc 60:40); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 5.5 Hz, 1H), 7.19 (app

d, J = 8.7 Hz, 2H), 6.78 (app d, J = 8.7 Hz, 2H), 6.30 (app d, J = 15.8 Hz, 1H), 6.30 (d, J = 5.5 Hz, 1H), 5.93 (dt, J = 15.8, 7.6 Hz, 1H), 4.52 (sept, J = 6.1 Hz, 1H), 4.25-4.17 (m, 4H), 3.49 (s, 2H), 2.75 (dd, J = 7.6, 1.0 Hz, 2H), 1.32 (d, J = 6.1 Hz, 6H), 1.24 (t, J = 7.1 Hz, 6H), 0.92 (s, 9H), 0.24 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.1, 170.3(2), 157.6, 153.6, 152.9, 144.2, 134.1, 129.7, 127.6(2), 121.0, 116.0(2), 115.8, 70.0, 61.8(2), 57.1, 37.2, 30.9, 26.1(3), 22.1(2), 18.9, 14.2(2), -3.6(2); ESI-HRMS calculated for $C_{31}H_{44}O_8SiNa$ $[M + Na]^+$ 595.2703, found 595.2675.



S5 (X = OMe)
S6 (X = Me)
S7 (X = H)
S8 (X = F)
S9 (X = Cl)

1s' (X = OMe)
1t' (X = Me)
1u' (X = H)
1v' (X = F)
1w' (X = Cl)
1x' (X = CO_2Me)
1y' (X = CN)
1z' (X = NO_2)

1s (X = OMe)
1t (X = Me)
1u (X = H)
1v (X = F)
1w (X = Cl)

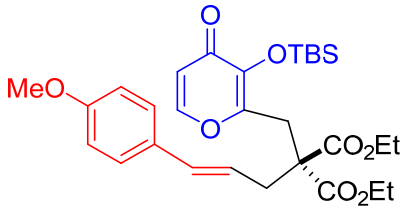
S10 (X = CO_2Me)
S11 (X = CN)
S12 (X = NO_2)

6

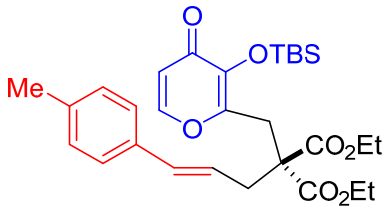
1x (X = CO_2Me)
1y (X = CN)
1z (X = NO_2)

General Procedure D for Synthesis of TBS-Pyrone Styrenes 1s-w:[3] To a solution of malonate **6′** in THF (0.1 M) was added NaH (2 equiv.) at 23 °C and stirred for 15 min. A solution of cinnamyl bromide **S5-9** (2-3 equiv.) in THF (0.1 M) was added and stirred for 1.5 h. The reaction was quenched slowly with sat. aq. NH_4Cl, diluted with Et_2O, and separated. The combined organic extracts were washed with sat. aq. NaCl, dried with $MgSO_4$, filtered, and concentrated. Purification

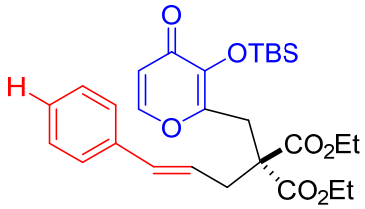
by FCC afforded TBDPS-pyrone styrenes **1s′-w′**. A solution of **1s′-w′** in THF (0.1M) was added TBAF (1.2 equiv.) at 23 °C and stirred for 1 h. The reaction was quenched slowly with sat. aq. NH_4Cl, diluted with Et_2O, and separated. The combined organic extracts were washed with sat. aq. NaCl, dried with $MgSO_4$, filtered, and concentrated. Purification by FCC afforded the corresponding enol. To a solution of enol in CH_2Cl_2 (0.1 M) was added imidazole (1.6 equiv.) and TBSCl (1.5 equiv.) at 23 °C and stirred for 1 h. The reaction was quenched slowly with sat. aq. NH_4Cl, diluted with CH_2Cl_2, and separated. The combined organic extracts were washed with sat. aq. NaCl, dried with $MgSO_4$, filtered, and concentrated to afford **TBS-Pyrone Styrenes 1s-w.**



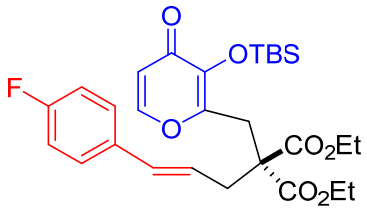
TBS-Pyrone Styrene 1s[3] (Table 2, entry 3): FCC (hexanes:EtOAc 80:20) afforded a colorless oil (263 mg, 0.485 mmol, 53% 2-step yield): R_f = 0.46 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.6 Hz, 1H), 7.22 (app d, *J* = 8.7 Hz, 2H), 6.80 (app d, *J* = 8.7 Hz, 2H), 6.31 (app d, *J* = 15.4 Hz, 1H), 6.30 (d, *J* = 5.6 Hz, 1H), 5.94 (dt, *J* = 15.4, 7.6 Hz, 1H), 4.24-4.18 (m, 4H), 3.80 (s, 3H), 3.50 (s, 2H), 2.75 (dd, *J* = 7.6, 1.1 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 6H), 0.93 (s, 9H), 0.25 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.1, 170.3(2), 159.3, 153.6, 152.9, 144.2, 134.0, 129.9, 127.6(2), 121.2, 115.8, 113.9(2), 61.8(2), 57.1, 55.4, 37.2, 31.0, 26.1(3), 18.9, 14.2(2), -3.6(2); ESI-HRMS calculated for $C_{29}H_{40}O_8SiNa$ $[M + Na]^+$ 567.2390, found 567.2387.



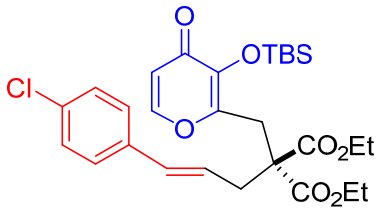
TBS-Pyrone Styrene 1t[3] (Table 2, entry 4): FCC (hexanes:EtOAc 70:30) afforded a colorless oil (317 mg, 0.168 mmol, 78% 2-step yield): R_f = 0.43 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.6 Hz, 1H), 7.18 (app d, *J* = 8.2 Hz, 2H), 7.07 (app d, *J* = 8.2 Hz, 2H), 6.34 (app d, *J* = 15.5 Hz, 1H), 6.30 (d, *J* = 5.6 Hz, 1H), 6.04 (dt, *J* = 15.5, 7.6 Hz, 1H), 4.24-4.17 (m, 4H), 3.50 (s, 2H), 2.76 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.32 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 6H), 0.94 (s, 9H), 0.25 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 170.2(2), 153.5, 152.8, 144.1, 137.2, 134.4, 134.2, 129.1(2), 126.3(2), 122.3, 115.7, 61.7(2), 57.1, 37.1, 30.9, 26.0(3), 21.2, 18.8, 14.1(2), -3.7(2); ESI-HRMS calculated for $C_{29}H_{40}O_7SiNa$ $[M + Na]^+$ 551.2441, found 551.2418.



TBS-Pyrone Styrene 1u[3] (Table 2, entry 5): Prepared previously as a colorless oil (1.50 g, 2.91 mmol, 87% yield) with the following spectral data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.6 Hz, 1H), 7.30-7.20 (m, 5H), 6.37 (dt, *J* = 15.7, 1.2 Hz, 1H), 6.31 (d, *J* = 5.6 Hz, 1H), 6.10 (dt, *J* = 15.7, 7.6 Hz, 1H), 4.22 (ovlp q, *J* = 7.1 Hz, 4H), 3.50 (s, 2H), 2.77 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.92 (s, 9H), 0.24 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.1, 170.3(2), 153.5, 152.9, 144.2, 137.0, 134.6, 128.5(2), 127.6, 126.4(2), 123.5, 115.8, 61.8(2), 57.1, 37.1, 31.0, 26.0(3), 18.9, 14.2(2), -3.6(2).



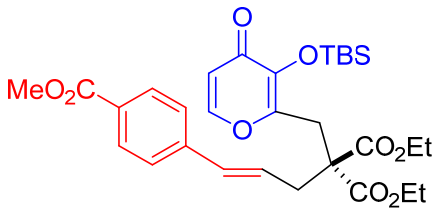
TBS-Pyrone Styrene 1v[3] (Table 2, entry 6): FCC (hexanes:EtOAc 70:30) afforded a colorless amorphous solid (296 mg, 0.536 mmol, 36% 2-step yield): R_f = 0.36 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.5 Hz, 1H), 7.24 (app dd, *J* = 8.8, 5.5 Hz, 2H), 6.95 (app t, *J* = 8.8 Hz, 2H), 6.31 (app d, *J* = 15.8 Hz, 1H), 6.30 (d, *J* = 5.5 Hz, 1H), 6.00 (dt, *J* = 15.8, 7.6 Hz, 1H), 4.24-4.19 (m, 4H), 3.50 (s, 2H), 2.75 (dd, *J* = 7.6, 1.0 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H), 0.92 (s, 9H), 0.24 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 170.2(2), 162.4 (d, *J* = 247.0 Hz), 153.4, 152.9, 144.2, 133.3, 133.2 (d, *J* = 3.6 Hz), 127.9(2) (d, *J* = 8.2 Hz), 123.3 (d, *J* = 2.7 Hz), 115.8, 115.4(2) (d, *J* = 20.9 Hz), 61.8(2), 57.0, 37.0, 31.0, 26.0(3), 18.9, 14.1(2), -3.6(2); ^{19}F NMR (470 MHz) -114.7 (tt, *J* = 8.6, 5.5 Hz); ESI-HRMS calculated for $C_{28}H_{37}FO_7SiNa$ $[M + Na]^+$ 555.2190, found 555.2171.



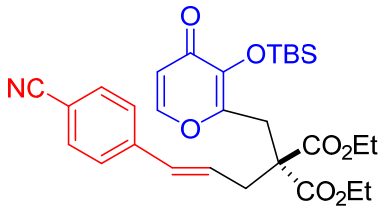
TBS-Pyrone Styrene 1w[3] (Table 2, entry 7): FCC (hexanes:EtOAc 70:30) afforded a yellow oil (238 mg, 0.131 mmol, 28% 2-step yield): R_f = 0.17 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.6 Hz, 1H), 7.24 (app d, *J* = 8.8 Hz, 2H), 7.20 (app d, *J* = 8.8 Hz, 2H), 6.31 (app d, *J* = 15.7 Hz, 1H), 6.30 (d, *J* = 5.6 Hz, 1H), 6.08 (dt, *J* = 15.7, 7.6 Hz, 1H), 4.22 (ovlp q, *J* = 7.1 Hz, 4H), 3.50 (s, 2H), 2.75 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.93 (s, 9H), 0.24 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 170.1(2), 153.3, 152.7, 144.2, 135.5,

133.2, 133.1, 128.6(2), 127.6(2), 124.4, 115.7, 61.8(2), 57.0, 37.0, 31.0, 26.0(3), 18.8, 14.1(2), -3.7(2); ESI-HRMS calculated for $C_{28}H_{37}ClO_7SiNa$ $[M + Na]^+$ 571.1895, found 571.1870.

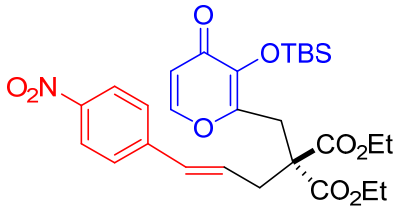
General Procedure E for Synthesis of TBS-Pyrone Styrenes 1x-z:[3] To a solution of malonate **6** in THF (0.1 M) was added NaH (2 equiv.) at 23 °C and stirred for 15 min. A solution of cinnamyl bromide **S10-12** (2-3 equiv.) in THF (0.1 M) was added and stirred for 1.5 h. The reaction was quenched slowly with sat. aq. NH_4Cl, diluted with Et_2O, and separated. The combined organic extracts were washed with sat. aq. NaCl, dried with $MgSO_4$, filtered, and concentrated. Purification by FCC afforded **TBS-Pyrone Styrenes 1x-z.**



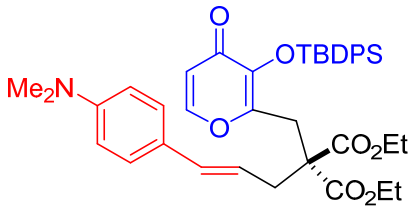
TBS-Pyrone Styrene 1x[3] **(Table 2, entry 8):** FCC (hexanes:EtOAc 70:30) afforded a yellow oil (483 mg, 0.843 mmol, 67%): R_f = 0.30 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (app d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.33 (app d, *J* = 8.4 Hz, 2H), 6.40 (app d, *J* = 15.7 Hz, 1H), 6.31 (d, *J* = 5.6 Hz, 1H), 6.23 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.81 (s, 3H), 3.51 (s, 2H), 2.78 (dd, *J* = 7.5, 1.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.82 (s, 9H), 0.24 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 170.1(2), 166.8, 153.2, 152.9, 144.2, 141.3, 133.6, 129.8(2), 129.0, 126.6, 126.2(2), 115.8, 61.8(2), 56.9, 52.0, 37.0, 31.0, 26.0(3), 18.8, 14.1(2), -3.7(2); ESI-HRMS calculated for $C_{30}H_{40}O_9SiNa$ $[M + Na]^+$ 595.2339, found 595.2334.



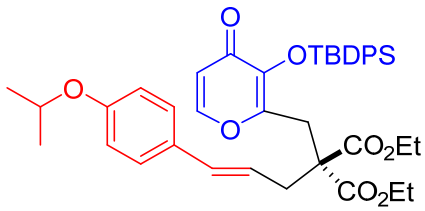
TBS-Pyrone Styrene 1y[3] (Table 2, entry 9): FCC (hexanes:EtOAc 70:30) afforded a yellow oil (141 mg, 0.261 mmol, 45%): R_f = 0.29 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (app d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 6.0 Hz, 1H), 7.35 (app d, *J* = 8.2 Hz, 2H), 6.36 (app d, *J* = 15.6 Hz, 1H), 6.31 (d, *J* = 6.0 Hz, 1H), 6.25 (dt, *J* = 15.6, 7.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 4H), 3.50 (s, 2H), 2.78 (dd, *J* = 7.4, 1.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.91 (s, 9H), 0.23 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 170.0(2), 153.1, 152.9, 144.2, 141.4, 132.9, 132.4(2), 128.1, 126.9(2), 119.0, 115.9, 110.9, 62.0(2), 56.8, 37.0, 31.1, 26.0(3), 18.8, 14.1(2), -3.7(2); ESI-HRMS calculated for $C_{29}H_{37}NO_7SiNa$ $[M + Na]^+$ 562.2237, found 562.2223.



TBS-Pyrone Styrene 1z[3] (Table 2, entry 10): FCC #1 (hexanes:EtOAc 80:20) and FCC #2 (CH_2Cl_2:acetone 98:2) afforded a pale yellow oil (237 mg, 0.423 mmol, 31%): R_f = 0.34 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (app d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 5.6 Hz, 1H), 7.41 (app d, *J* = 8.8 Hz, 2H), 6.42 (app d, *J* = 15.8 Hz, 1H), 6.32 (d, *J* = 5.6 Hz, 1H), 6.32 (dt, *J* = 15.8, 7.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 4H), 3.51 (s, 2H), 2.79 (dd, *J* = 7.5, 0.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 0.91 (s, 9H), 0.24 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 170.0(2), 153.05, 152.95, 147.1, 144.3, 143.3, 132.5, 129.2, 126.9(2), 124.0(2), 115.9, 62.0(2), 56.9, 37.1, 31.2, 26.0(3), 18.9, 14.2(2), -3.6(2); ESI-HRMS calculated for $C_{28}H_{37}NO_9SiNa$ $[M + Na]^+$ 582.2135, found 582.2130.

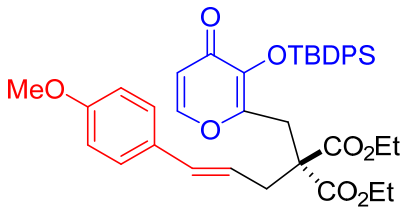


TBDPS-Pyrone Styrene 1q′ (Table 2, entry 1): FCC (CH_2Cl_2:Et_2O 95:5) afforded a brown oil (278 mg, 0.408 mmol, 17% 2-step yield): R_f = 0.25 (CH_2Cl_2:Et_2O 95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.66 (m, 4H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.38-7.29 (m, 6H), 7.16 (app d, *J* = 8.8 Hz, 2H), 6.58 (app d, *J* = 8.8 Hz, 2H), 6.31 (app d, *J* = 15.4 Hz, 1H), 6.05 (d, *J* = 5.5 Hz, 1H), 5.93 (dt, *J* = 15.4, 7.6 Hz, 1H), 4.26-4.18 (m, 4H), 3.63 (s, 2H), 2.92 (s, 6H), 2.82 (dd, *J* = 7.6, 1.0 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.6, 170.3(2), 153.1, 152.8, 150.1, 143.8, 134.8(2), 134.50(2), 134.48, 129.3(2), 127.4(4), 127.3(2), 125.6, 118.8, 115.4, 112.4(2), 61.7(2), 57.4, 40.5(2), 37.5, 31.2, 27.2(3), 20.3, 14.2(2); ESI-HRMS calculated for $C_{40}H_{47}NO_7SiNa$ $[M + Na]^+$ 704.3019, found 704.3005.

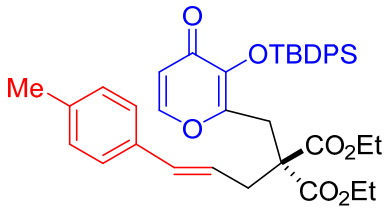


TBDPS-Pyrone Styrene 1r′ (Table 2, entry 2): FCC (hexanes:EtOAc 80:20 to 70:30) afforded a white foam (571 mg, 0.819 mmol, 20%, 2-step yield): R_f = 0.30 (hexanes:EtOAc 70:30); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.67 (m, 4H), 7.44 (d, *J* = 5.6 Hz, 1H), 7.37-7.29 (m, 6H), 7.17 (app d, *J* = 8.7 Hz, 2H), 6.73 (app d, *J* = 8.7 Hz, 2H), 6.33 (app d, *J* = 15.7 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 5.99 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.49 (sept, *J* = 6.1 Hz, 1H), 4.28-4.18 (m, 4H), 3.63 (s, 2H), 2.81 (dd, *J* = 7.5, 0.9 Hz, 2H), 1.30 (d, *J* = 6.1 Hz, 6H), 1.25 (t, *J* = 7.2 Hz, 6H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 170.3(2), 157.6, 153.0, 152.8, 143.9(2), 134.8(4), 134.5, 134.1, 129.6, 129.4(2), 127.6(2), 127.4(4), 121.1, 116.0(2), 115.5, 70.0, 61.8(2), 57.2, 37.3,

31.5, 27.2(3), 22.1(2), 20.3, 14.2(2); ESI-HRMS calculated for $C_{41}H_{48}O_8SiNa$ $[M + Na]^+$ 719.3016, found 719.2999.

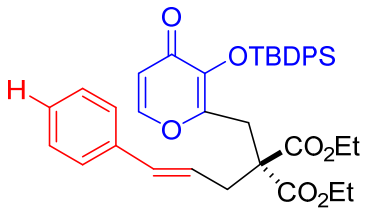


TBDPS-Pyrone Styrene 1s′ (Table 2, entry 3): FCC (hexanes:EtOAc 70:30) afforded a yellow oil (689 mg, 4.06 mmol, 65%): R_f = 0.23 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.66 (m, 4H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.38-7.29 (m, 6H), 7.19 (app d, *J* = 8.7 Hz, 2H), 6.75 (app d, *J* = 8.7 Hz, 2H), 6.34 (app d, *J* = 15.7 Hz, 1H), 6.06 (d, *J* = 5.5 Hz, 1H), 6.06 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.26-4.18 (m, 4H), 3.77 (s, 3H), 3.63 (s, 2H), 2.81 (dd, *J* = 7.5, 1.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.7, 170.3(2), 159.2, 153.0, 152.8, 143.9, 134.8(4), 134.5(2), 134.0, 129.8, 129.3(2), 127.6(2), 127.4(4), 121.2, 115.5, 113.9(2), 61.8(2), 57.2, 55.3, 37.3, 31.3, 27.2(3), 20.3, 14.2(2); ESI-HRMS calculated for $C_{39}H_{44}O_8SiNa$ $[M + Na]^+$ 691.2703, found 691.2704.

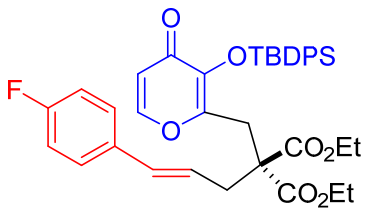


TBDPS-Pyrone Styrene 1t′ (Table 2, entry 4): FCC (hexanes:EtOAc 80:20) afforded a colorless oil (1.15 g, 1.76 mmol, 92%): R_f = 0.13 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.65 (m, 4H), 7.44 (d, *J* = 5.5 Hz, 1H), 7.38-7.29 (m, 6H), 7.16 (app d, *J* = 8.1 Hz, 2H), 7.02 (app d, *J* = 8.1 Hz, 2H), 6.37 (app d, *J* = 15.5 Hz, 1H), 6.10 (dt, *J* = 15.5, 7.5 Hz, 1H), 6.05 (d, *J* = 5.5 Hz, 1H), 4.28-4.18 (m, 4H), 3.63 (s, 2H), 2.82 (dd, *J* = 7.5, 1.1 Hz, 2H), 2.30 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 6H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.7, 170.3(2), 152.9, 152.8,

143.9, 137.3, 134.8(4), 134.5(3), 134.2, 129.4(2), 129.2(2), 127.4(4), 126.3(2), 122.5, 115.5, 61.8(2), 57.2, 37.4, 31.4, 27.2(3), 21.2, 20.3, 14.2(2); ESI-HRMS calculated for $C_{39}H_{44}O_7SiNa$ [M + Na]$^+$ 675.2754, found 675.2728.

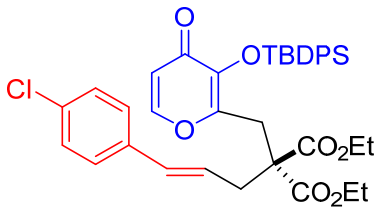


TBDPS-Pyrone Styrene 1u′ (Table 2, entry 5): Prepared previously as a white solid (1.50 g, 2.91 mmol, 87%) with the following spectral data:[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 4H), 7.45 (d, *J* = 5.6 Hz, 1H), 7.39-7.15 (m, 11H), 6.40 (app d, *J* = 15.7 Hz, 1H), 6.16 (dt, *J* = 15.7, 7.5 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 4.28-4.19 (m, 4H), 3.64 (s, 2H), 2.84 (dd, *J* = 7.5, 1.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 170.3(2), 152.9, 152.8, 144.0, 137.0, 134.9(4), 134.7, 134.6, 134.5, 129.4(2), 128.6(2), 127.6, 127.4(4), 126.4(2), 123.6, 115.5, 61.9(2), 57.2, 37.3, 31.4, 27.2(3), 20.3, 14.2(2).

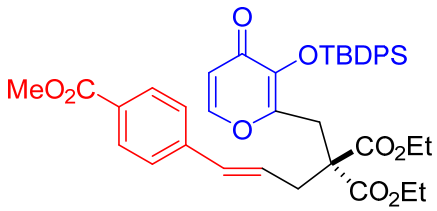


TBDPS-Pyrone Styrene 1v′ (Table 2, entry 6): FCC (hexanes:EtOAc 70:30) afforded a colorless oil (2.03 g, 3.10 mmol, 88%): R_f = 0.41 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.44 (d, *J* = 5.6 Hz, 1H), 7.37-7.30 (m, 6H), 7.21 (app dd, *J* = 8.7, 5.4 Hz, 2H), 6.89 (app t, *J* = 8.7 Hz, 2H), 6.35 (app d, *J* = 15.6 Hz, 1H), 6.07 (dt, *J* = 15.6, 7.6 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 4.26-4.19 (m, 4H), 3.64 (s, 2H), 2.81 (dd, *J* = 7.6, 1.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.6, 170.2(2), 162.3 (d, *J* = 247.0

Hz), 152.81, 152.79, 143.9, 134.8(4), 134.4(2), 133.3, 133.1 (d, J = 3.6 Hz), 129.4(2), 127.9(2) (d, J = 8.2 Hz), 127.4(4), 123.4 (d, J = 1.8 Hz), 115.5, 115.4(2) (d, J = 21.8 Hz), 61.8(2), 57.1, 37.1, 31.3, 27.2(3), 20.3, 14.1(2); ^{19}F NMR (470 MHz) -114.7 (tt, J = 8.7, 5.4 Hz); ESI-HRMS calculated for $C_{38}H_{42}FO_7Si$ $[M + H]^+$ 677.2684, found 677.2673.

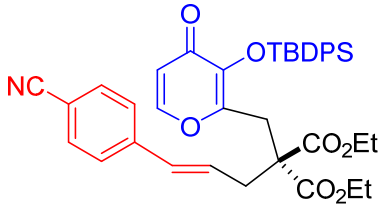


TBDPS-Pyrone Styrene 1w′ (Table 2, entry 7): FCC (hexanes:EtOAc 80:20 to 60:40) afforded a yellow foam (2.09 g, 3.10 mmol, 81%): R_f = 0.30 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.64 (m, 4H), 7.44 (d, J = 5.5 Hz, 1H), 7.38-7.28 (m, 6H), 7.17 (app s, 4H), 6.33 (app d, J = 15.5 Hz, 1H), 6.14 (dt, J = 15.5, 7.6 Hz, 1H), 6.06 (d, J = 5.5 Hz, 1H), 4.27-4.18 (m, 4H), 3.63 (s, 2H), 2.81 (dd, J = 7.6, 1.1 Hz, 2H), 1.25 (t, J = 7.2 Hz, 6H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.7, 170.2(2), 152.82, 152.75, 144.0, 135.4, 134.8(4), 134.4(2), 133.3, 133.2, 129.4(2), 128.7(2), 127.6(2), 127.4(4), 124.5, 115.5, 61.9(2), 57.1, 37.2, 31.4, 27.3(3), 20.3, 14.2(2); ESI-HRMS calculated for $C_{38}H_{42}ClO_7Si$ $[M + H]^+$ 673.2308, found 673.2361.

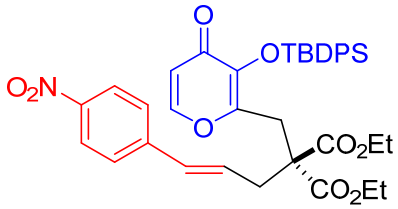


TBDPS-Pyrone Styrene 1x′ (Table 2, entry 8): FCC #1 (hexanes:EtOAc 70:30) and FCC #2 (CH_2Cl_2:EtOAc 97.5:2.5) afforded a yellow oil (379 mg, 0.55 mmol, 26%): R_f = 0.20 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (app d, J = 8.4 Hz, 2H), 7.68-7.66 (m, 4H), 7.44 (d, J = 5.5 Hz, 1H), 7.38-7.28 (m, 6H), 7.32 (app d, J = 8.4 Hz, 2H), 6.42 (app d, J

= 15.8 Hz, 1H), 6.29 (dt, *J* = 15.8, 7.4 Hz, 1H), 6.07 (d, *J* = 5.5 Hz, 1H), 4.29-4.19 (m, 4H), 3.90 (s, 3H), 3.64 (s, 2H), 2.85 (dd, *J* = 7.4, 0.9 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 172.6, 170.1(2), 166.8, 152.8, 152.6, 143.9, 141.3, 134.8(4), 134.3(2), 133.6, 129.9(2), 129.4(2), 129.0, 127.4(4), 126.7, 126.2(2), 115.5, 61.9(2), 57.0, 52.0, 37.2, 31.4, 27.2(3), 20.2, 14.1(2); ESI-HRMS calculated for $C_{40}H_{44}O_9SiNa$ $[M + Na]^+$ 719.2652, found 719.2640.



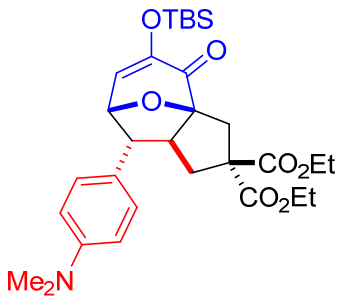
TBDPS-Pyrone Styrene 1y′ (Table 2, entry 9): FCC (hexanes:EtOAc 70:30 to 60:40) afforded a white foam (1.21 g, 1.83 mmol, 87%): R_f = 0.10 (hexanes:EtOAc 70:30); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 4H), 7.46 (app d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 5.6 Hz, 1H), 7.37-7.29 (m, 6H), 7.31 (app d, *J* = 8.2 Hz, 2H), 6.38 (app d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.8 Hz, 1H), 6.07 (d, *J* = 5.6 Hz, 1H), 4.27-4.21 (m, 4H), 3.64 (s, 2H), 2.83 (app d, *J* = 6.8 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 1.03 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 170.0(2), 152.9, 152.4, 143.9, 141.2, 134.7(4), 134.3(2), 132.8, 132.3(2), 129.4(2), 128.1, 127.4(4), 126.8(2), 118.9, 115.5, 110.7, 61.9(2), 56.9, 37.0, 31.3, 27.2(3), 20.2, 14.1(2); ESI-HRMS calculated for $C_{39}H_{41}NO_7SiNa$ $[M + Na]^+$ 686.2550, found 686.2535.



TBDPS-Pyrone Styrene 1z′ (Table 2, entry 10): FCC (hexanes:EtOAc 70:30) afforded an orange solid (1.16 g, 1.70 mmol, 89%): R_f = 0.24 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ

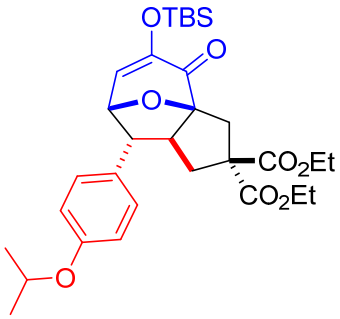
8.05 (app d, J = 8.8 Hz, 2H), 7.67-7.65 (m, 4H), 7.45 (d, J = 5.5 Hz, 1H), 7.37-7.30 (m, 6H), 7.34 (app d, J = 8.8 Hz, 2H), 6.43 (app d, J = 15.8 Hz, 1H), 6.36 (dt, J = 15.8, 7.0 Hz, 1H), 6.08 (d, J = 5.5 Hz, 1H), 4.28-4.22 (m, 4H), 3.65 (s, 2H), 2.85 (app d, J = 7.0 Hz, 2H), 1.26 (t, J = 7.1 Hz, 6H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 172.7, 170.0(2), 152.9, 152.5, 147.0, 144.1, 143.2, 134.9(4), 134.4(2), 132.5, 129.5(2), 129.3, 127.5(4), 126.9(2), 124.0(2), 115.6, 62.1(2), 57.0, 37.2, 31.5, 27.3(3), 20.3, 14.2(2); mp 124–125 °C; ESI-HRMS calculated for $C_{38}H_{41}NO_9SiNa$ $[M + Na]^+$ 706.2448, found 706.2433.

General Procedure F for (5 + 2) Cycloaddition (2q-z[3] and 2q′-2z′): To a 1-dram vial with a micro stir bar was added 0.05-0.10 mmol of pyrone and dissolved in 0.5-1.0 mL toluene. Upon stirring for the appropriate time and temperature and careful concentration on a vacuum pump to avoid external heating, a solution of 1,3,5-trimethoxybenzene in $CDCl_3$ was added and the resulting solution transferred to an NMR tube. The quantity of both starting material and product was calculated via comparison of diagnostic integrals and reported in the corresponding tables. Isolated yields were obtained by the following: A solution of silyloxypyrone (0.03-0.5 mmol) in toluene (0.1 M) was stirred for 2 d at 110 °C, concentrated, and purified by FCC to afford cycloadducts.

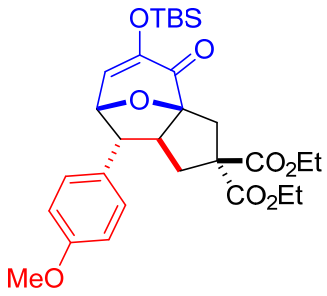


TBS-Cycloadduct 2q[3] (Table 2, entry 1): FCC (hexanes:EtOAc 80:20) afforded a colorless oil (8.5 mg, 0.015 mmol, 52%, dr >19:1): R_f = 0.67 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz,

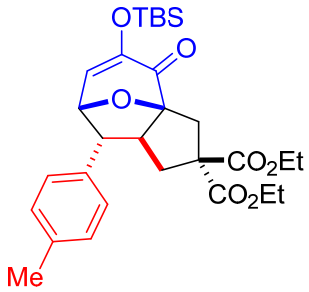
$CDCl_3$) δ 7.05 (app d, *J* = 8.9 Hz, 2H), 6.56 (app d, *J* = 8.9 Hz, 1H), 5.94 (d, *J* = 5.0 Hz, 1H), 4.80 (dd, *J* = 6.1, 5.0 Hz, 1H), 4.29-4.13 (m, 4H), 3.72 (dd, *J* = 6.5, 6.1 Hz, 1H), 3.17 (d, *J* = 14.7 Hz, 1H), 2.92 (s, 6H), 2.77 (ddd, *J* = 9.9, 6.5, 3.2 Hz, 1H), 2.67 (ddd, *J* = 13.6, 3.2, 1.1* Hz, 1H) *long-range coupling, 2.60 (dd, *J* = 14.7, 1.1* Hz, 1H) *long-range coupling, 2.31 (dd, *J* = 13.6, 9.9 Hz, 1H), 1.27 (ovlp t, *J* = 7.2 Hz, 6H), 0.92 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.9, 171.2, 171.0, 149.9, 146.4, 129.2(2), 127.0, 125.6, 112.7(2), 97.7, 79.7, 62.0, 61.9, 61.8, 55.7, 50.9, 40.7(2), 38.0, 37.4, 25.7(3), 18.5, 14.2(2), -4.4, -4.5; ESI-HRMS calculated for $C_{30}H_{43}NO_7SiNa$ $[M + Na]^+$ 580.2706, found 580.2704.



TBS-Cycloadduct 2r[3] (Table 2, entry 2): FCC (hexanes:EtOAc 90:10 to 80:20) afforded a colorless oil (34 mg, 0.0594 mmol, 61%, dr >19:1): R_f = 0.50 (hexanes:EtOAc 80:20); ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (app d, *J* = 8.6 Hz, 2H), 6.80 (app d, *J* = 8.6 Hz, 2H), 5.90 (d, *J* = 5.0 Hz, 1H), 4.83 (dd, *J* = 5.9, 5.0 Hz, 1H), 4.51 (sept, *J* = 6.1 Hz, 1H), 4.29-4.14 (m, 4H), 3.76 (dd, *J* = 6.7, 5.9 Hz, 1H), 3.17 (d, *J* = 14.7 Hz, 1H), 2.78 (ddd, *J* = 9.9, 6.7, 3.2 Hz, 1H), 2.68-2.64 (m, 1H), 2.61 (d, *J* = 14.7 Hz, 1H), 2.34 (dd, *J* = 13.5, 9.9 Hz, 1H), 1.32 (ovlp d, *J* = 6.1 Hz, 6H), 1.27 (ovlp t, *J* = 7.2 Hz, 6H), 0.91 (s, 9H), 0.12 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 192.8, 171.2, 171.0, 157.2, 146.5, 129.9, 129.4(2), 126.6, 116.0(2), 97.7, 79.6, 70.1, 62.1, 61.9, 61.8, 55.8, 50.7, 38.1, 37.4, 25.7(3), 22.2, 22.1, 18.5, 14.2, 14.1, -4.5, -4.6; ESI-HRMS calculated for $C_{31}H_{44}O_8SiNa$ $[M + Na]^+$ 595.2703, found 595.2691.

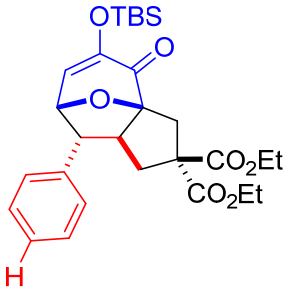


TBS-Cycloadduct 2s[3] (Table 2, entry 3): FCC (hexanes:EtOAc 85:15 to 70:30) afforded a colorless oil (41 mg, 0.08 mmol, 45%, dr >19:1): R_f = 0.76 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (app d, *J* = 8.6 Hz, 2H), 6.83 (app d, *J* = 8.6 Hz, 2H), 5.89 (d, *J* = 5.1 Hz, 1H), 4.83 (dd, *J* = 6.1, 5.1 Hz, 1H), 4.28-4.14 (m, 4H), 3.79 (s, 3H), 3.78 (dd, *J* = 6.6, 6.1 Hz, 1H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.78 (ddd, *J* = 9.9, 6.6, 3.3 Hz, 1H), 2.67 (ddd, *J* = 13.6, 3.3, 1.3* Hz, 1H) *long-range coupling, 2.61 (dd, *J* = 14.7, 1.3* Hz, 1H) *long-range coupling, 2.33 (dd, *J* = 13.6, 9.9 Hz, 1H), 1.27 (ovlp t, *J* = 7.1 Hz, 6H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.7, 171.2, 170.9, 158.9, 146.5, 130.1, 129.4(2), 126.5, 114.1(2), 97.7, 79.6, 62.1, 61.9, 61.8, 55.7, 55.4, 50.8, 38.0, 37.4, 25.7(3), 18.5, 14.13, 14.12, -4.5, -4.6; ESI-HRMS calculated for $C_{29}H_{40}O_8SiNa$ $[M + Na]^+$ 567.2390, found 567.2382.

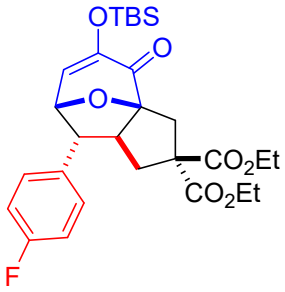


TBS-Cycloadduct 2t[3] (Table 2, entry 4): FCC (hexanes:EtOAc 95:5 to 80:20) afforded a colorless oil (51 mg, 0.096 mmol, 47%, dr >19:1): R_f = 0.56 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (app d, *J* = 8.4 Hz, 2H), 7.07 (app d, *J* = 8.4 Hz, 2H), 5.90 (d, *J* = 5.0 Hz, 1H), 4.85 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.30-4.14 (m, 4H), 3.79 (dd, *J* = 6.7, 6.0 Hz, 1H), 3.18 (d,

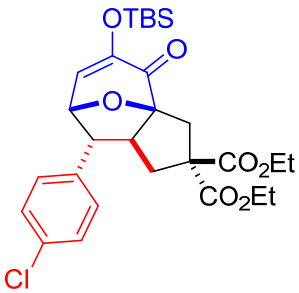
J = 14.7 Hz, 1H), 2.81 (ddd, J = 9.8, 6.7, 3.4 Hz, 1H), 2.67 (ddd, J = 13.6, 3.4, 1.1* Hz, 1H) *long-range coupling, 2.61 (dd, J = 14.7, 1.1* Hz, 1H) *long-range coupling, 2.33 (dd, J = 13.6, 9.8 Hz, 1H), 2.32 (s, 3H), 1.27 (ovlp t, J = 7.1 Hz, 6H), 0.91 (s, 9H), 0.125 (s, 3H) 0.122 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.7, 171.2, 170.9, 146.5, 136.9, 135.1, 129.3(2), 128.3(2), 126.5, 97.7, 79.6, 62.1, 61.9, 61.8, 56.1, 50.6, 38.0, 37.3, 26.7(3), 21.1, 18.5, 14.13, 14.12, -4.5, -4.6; ESI-HRMS calculated for $C_{29}H_{40}O_7SiNa$ $[M + Na]^+$ 551.2441, found 551.2414.



TBS-Cycloadduct 2u[3] (Table 2, entry 5): Prepared previously as a yellow oil (159 mg, 0.31 mmol, 62%) with the following spectral data:[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.18 (m, 5H), 5.88 (d, J = 5.1 Hz, 1H), 4.89 (dd, J = 6.2, 5.1 Hz, 1H), 4.30-4.14 (m, 4H), 3.85 (dd, J = 6.6, 6.2 Hz, 1H), 3.19 (d, J = 14.8 Hz, 1H), 2.85 (ddd, J = 9.9, 6.6, 3.5 Hz, 1H), 2.68 (ddd, J = 13.5, 3.5, 1.3* Hz, 1H) *long-range coupling, 2.62 (dd, J = 14.8, 1.3* Hz, 1H) *long-range coupling, 2.35 (dd, J = 13.5, 9.9 Hz, 1H), 1.27 (ovlp t, J = 7.2 Hz, 6H), 0.90 (s, 9H), 0.11 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 192.6, 171.1, 170.9, 146.4, 128.9, 128.6(2), 128.4(2), 127.2, 126.3, 97.8, 79.4, 62.0, 61.9, 61.7, 56.4, 50.3, 38.0, 37.3, 25.6(3), 18.4, 14.10, 14.09, -4.57, -4.64.

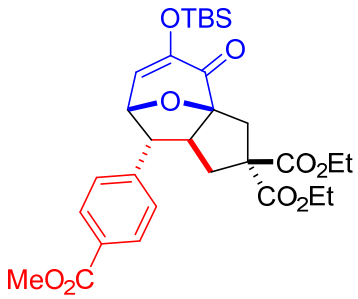


TBS-Cycloadduct 2v[3] (Table 2, entry 6): FCC (hexanes:EtOAc 80:20) afforded a colorless oil (59 mg, 0.111 mmol, 56%, dr >19:1): R_f = 0.70 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (app dd, *J* = 8.6, 5.3 Hz, 2H), 6.98 (app t, *J* = 8.6 Hz, 2H), 5.86 (d, *J* = 5.0 Hz, 1H), 4.86 (dd, *J* = 5.9, 5.0 Hz, 1H), 4.29-4.15 (m, 4H), 3.82 (dd, *J* = 6.7, 5.9 Hz, 1H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.78 (ddd, *J* = 9.9, 6.7, 3.3 Hz, 1H), 2.67 (ddd, *J* = 13.5, 3.3, 1.2* Hz, 1H) *long-range coupling, 2.61 (dd, *J* = 14.7, 1.2* Hz, 1H) *long-range coupling, 2.34 (dd, *J* = 13.5, 9.9 Hz, 1H), 1.27 (ovlp t, *J* = 7.2 Hz, 6H), 0.91 (s, 9H), 0.123 (s, 3H) 0.117 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.5, 171.1, 170.8, 162.1 (d, *J* = 246.2 Hz), 146.7, 133.9 (d, *J* = 2.9 Hz), 129.2(2) (d, *J* = 8.2 Hz), 126.0, 115.5(2) (d, *J* = 20.9 Hz), 97.8, 79.4, 62.05, 61.96, 61.8, 55.7, 50.7, 38.0, 37.3, 25.6(3), 18.5, 14.14, 14.12, -4.5, -4.6; ^{19}F NMR (470 MHz) -115.8 (tt, *J* = 8.6, 6.5 Hz); ESI-HRMS calculated for $C_{28}H_{37}FO_7SiNa$ $[M + Na]^+$ 555.2190, found 555.2188.

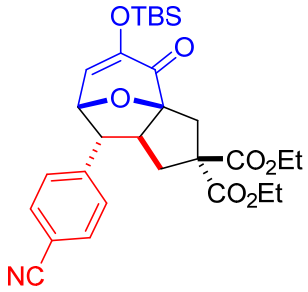


TBS-Cycloadduct 2w[3] (Table 2, entry 7): FCC (hexanes:EtOAc 90:10 to 60:40) afforded a colorless oil (41 mg, 0.07 mmol, 56%, dr >19:1): R_f = 0.63 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (app d, *J* = 8.4 Hz, 2H), 7.12 (app d, *J* = 8.4 Hz, 2H), 5.86 (d, *J* = 5.0 Hz,

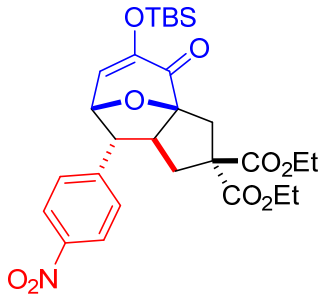
1H), 4.86 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.30-4.18 (m, 4H), 3.82 (dd, *J* = 6.4, 6.0 Hz, 1H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.78 (ddd, *J* = 9.9, 6.4, 3.4 Hz, 1H), 2.66 (ddd, *J* = 13.5, 3.4, 1.2* Hz, 1H) *long-range coupling, 2.61 (dd, *J* = 14.7, 1.2* Hz, 1H) *long-range coupling, 2.33 (dd, *J* = 13.5, 9.9 Hz, 1H), 1.27 (ovlp t, *J* = 7.1 Hz, 6H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.5, 171.1, 170.8, 146.7, 136.7, 133.2, 129.7(2), 128.8(2), 125.8, 97.8, 79.4, 62.04, 61.99, 61.8, 55.9, 50.6, 37.9, 37.3, 25.7(3), 18.5, 14.15, 14.13, -4.5, -4.6; ESI-HRMS calculated for $C_{28}H_{37}ClO_7SiNa$ $[M + Na]^+$ 571.1895, found 571.1870.



TBS-Cycloadduct 2x[3] (Table 2, entry 8): FCC (hexanes:EtOAc 90:10) afforded a colorless amorphous solid (26 mg, 0.045 mmol, 26%, dr >19:1): R_f = 0.62 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (app d, *J* = 8.4 Hz, 2H), 7.26 (app d, *J* = 8.4 Hz, 2H), 5.85 (d, *J* = 5.0 Hz, 1H), 4.92 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.29-4.14 (m, 4H), 3.92 (dd, *J* = 6.6, 6.0 Hz, 1H), 3.91 (s, 3H), 3.19 (d, *J* = 14.7 Hz, 1H), 2.86 (ddd, *J* = 9.9, 6.6, 3.3 Hz, 1H), 2.68 (ddd, *J* = 13.5, 3.3, 1.0* Hz, 1H) *long-range coupling, 2.62 (dd, *J* = 14.7, 1.0* Hz, 1H) *long-range coupling, 2.36 (dd, *J* = 13.5, 9.9 Hz, 1H), 1.27 (ovlp t, *J* = 7.1 Hz, 6H), 0.90 (s, 9H), 0.113 (s, 3H), 0.107 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 171.1, 170.8, 166.8, 146.8, 143.5, 129.9(2), 129.3, 128.4(2), 125.7, 97.9, 79.3, 62.04, 61.99, 61.90, 56.5, 52.2, 50.3, 37.9, 37.3, 25.6(3), 18.5, 14.14, 14.12, -4.5, -4.6; ESI-HRMS calculated for $C_{30}H_{40}O_9SiNa$ $[M + Na]^+$ 595.2339, found 595.2335.

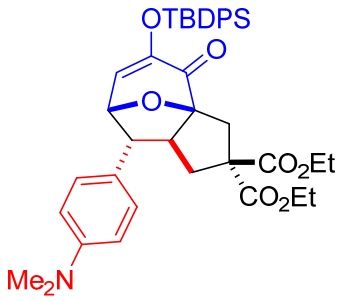


TBS-Cycloadduct 2y[3] (Table 2, entry 9): FCC (hexanes:EtOAc 70:30) afforded a colorless oil (71 mg, 0.131 mmol, 89%, dr >19:1): R_f = 0.60 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (app d, *J* = 8.4 Hz, 2H), 7.30 (app d, *J* = 8.4 Hz, 2H), 5.82 (d, *J* = 5.0 Hz, 1H), 4.91 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.29-4.15 (m, 4H), 3.92 (dd, *J* = 6.7, 6.0 Hz, 1H), 3.19 (d, *J* = 14.8 Hz, 1H), 2.82 (ddd, *J* = 9.9, 6.7, 3.5 Hz, 1H), 2.67 (ddd, *J* = 13.6, 3.5, 1.1* Hz, 1H) *long-range coupling, 2.62 (dd, *J* = 14.8, 1.1* Hz, 1H) *long-range coupling, 2.35 (dd, *J* = 13.6, 9.9 Hz, 1H), 1.27 (ovlp t, *J* = 7.2 Hz, 6H), 0.91 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.2, 171.1, 170.7, 147.0, 143.8, 132.5(2), 129.2(2), 125.0, 118.6, 111.4, 97.9, 79.2, 62.1, 62.0, 61.9, 56.5, 50.4, 37.9, 37.3, 25.6(3), 18.5, 14.15, 14.12, -4.5, -4.6; ESI-HRMS calculated for $C_{29}H_{37}NO_7SiNa$ $[M + Na]^+$ 562.2237, found 562.2234.

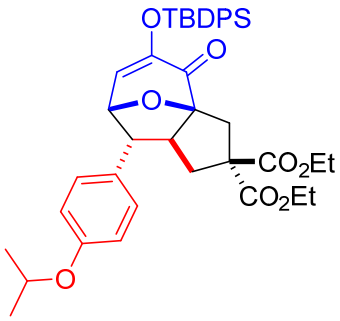


TBS-Cycloadduct 2z[3] (Table 2, entry 10): FCC (hexanes:EtOAc 85:15 to 70:30) afforded a colorless oil (84 mg, 0.16 mmol, 78%, dr >19:1): R_f = 0.72 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (app d, *J* = 8.7 Hz, 2H), 7.36 (app d, *J* = 8.7 Hz, 2H), 5.83 (d, *J* = 5.0 Hz, 1H), 4.94 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.30-4.15 (m, 4H), 3.98 (dd, *J* = 6.7, 6.0 Hz, 1H), 3.20 (d, *J* =

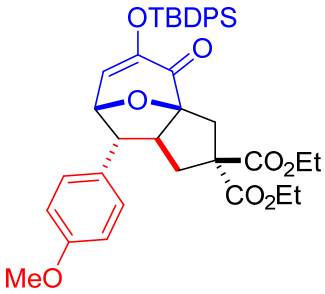
14.8 Hz, 1H), 2.85 (ddd, *J* = 10.0, 6.7, 3.2 Hz, 1H), 2.68 (ddd, *J* = 13.6, 3.2, 1.2* Hz, 1H) *long-range coupling, 2.63 (dd, *J* = 14.8, 1.2* Hz, 1H) *long-range coupling, 2.36 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.27 (ovlp t, *J* = 7.2 Hz, 6H), 0.90 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.2, 171.1, 170.6, 147.3, 147.0, 145.9, 129.3(2), 124.9, 123.8(2), 97.9, 79.2, 62.04, 61.99, 61.90, 56.3, 50.5, 37.8, 37.2, 25.6(3), 18.5, 14.11, 14.09, -4.5, -4.6; ESI-HRMS calculated for $C_{28}H_{37}NO_9SiNa$ $[M + Na]^+$ 582.2135, found 582.2125.



TBDPS-Cycloadduct 2q′ (Table 2, entry 1): FCC (hexanes:EtOAc 70:30) afforded a light brown foam (48 mg, 0.070 mmol, 48%, dr >19:1): R_f = 0.68 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.63 (m, 4H), 7.44-7.30 (m, 6H), 6.79 (app d, *J* = 8.6 Hz, 2H), 6.46 (app d, *J* = 8.6 Hz, 1H), 5.66 (d, *J* = 5.0 Hz, 1H), 4.59 (dd, *J* = 6.1, 5.0 Hz, 1H), 4.27-4.13 (m, 4H), 3.58 (dd, *J* = 6.9, 6.1 Hz, 1H), 3.16 (d, *J* = 14.7 Hz, 1H), 2.90 (s, 6H), 2.66 (ddd, *J* = 9.8, 6.9, 3.2 Hz, 1H), 2.61 (ddd, *J* = 13.5, 3.2, 1.1* Hz, 1H) *long-range coupling, 2.57 (dd, *J* = 14.7, 1.1* Hz, 1H) *long-range coupling, 2.26 (dd, *J* = 13.5, 9.8 Hz, 1H), 1.25 (ovlp t, *J* = 7.1 Hz, 6H), 1.06 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.1, 171.2, 171.0, 149.7, 145.8, 135.7(2), 135.5(2), 132.7, 132.3, 130.1, 130.0, 128.9(2), 127.9(4), 126.2, 125.3, 112.7(2), 97.5, 79.6, 62.0, 61.9, 61.7, 55.5, 50.8, 40.7(2), 37.9, 37.4, 26.6(3), 19.7, 14.12, 14.10; ESI-HRMS calculated for $C_{40}H_{47}NO_7SiNa$ $[M + Na]^+$ 704.3019, found 704.3016.

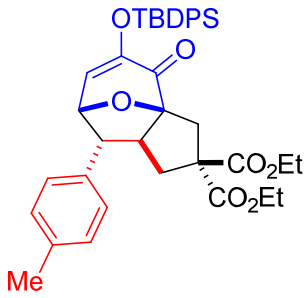


TBDPS-Cycloadduct 2r′ (Table 2, entry 2): FCC (hexanes:EtOAc 80:20) afforded a white foam (35 mg, 0.51 mmol, 51%, dr >19:1): R_f = 0.64 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.61 (m, 4H), 7.43-7.32 (m, 6H), 6.80 (app d, *J* = 8.6 Hz, 2H), 6.61 (app d, *J* = 8.6 Hz, 2H), 5.63 (d, *J* = 5.1 Hz, 1H), 4.62 (dd, *J* = 5.7, 5.1 Hz, 1H), 4.46 (sept, *J* = 6.1 Hz, 1H), 4.25-4.16 (m, 4H), 3.62 (dd, *J* = 7.1, 5.7 Hz, 1H), 3.17 (d, *J* = 14.9 Hz, 1H), 2.66 (ddd, *J* = 9.9, 7.1, 3.1 Hz, 1H), 2.61-2.56 (m, 2H), 2.28 (dd, *J* = 13.6, 9.9 Hz, 1H), 1.32 (ovlp d, *J* = 6.1, 6H), 1.27 (ovlp t, *J* = 7.2 Hz, 6H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.1, 171.2, 171.0, 157.0, 145.9, 135.7(2), 135.5(2), 132.6, 132.3, 130.2, 130.1, 129.5, 129.3(2), 127.9(4), 125.9, 115.8(2), 97.6, 79.5, 70.0, 62.1, 61.9, 61.8, 55.5, 50.6, 37.9, 37.4, 26.6(3), 22.2(2), 19.7, 14.2, 14.1; ESI-HRMS calculated for $C_{41}H_{48}O_8SiNa$ $[M + Na]^+$ 719.3016, found 719.3023.

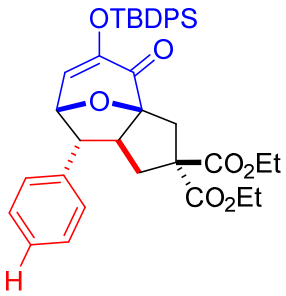


TBDPS-Cycloadduct 2s′ (Table 2, entry 3): FCC (hexanes:EtOAc 80:20) afforded a white solid (40 mg, 0.12 mmol, 59%, dr >19:1): R_f = 0.62 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.61 (m, 4H), 7.45-7.38 (m, 2H), 7.36-7.31 (m, 4H), 6.82 (app d, *J* = 8.6 Hz, 2H), 6.63 (app d, *J* = 8.6 Hz, 2H), 5.61 (d, *J* = 5.1 Hz, 1H), 4.62 (dd, *J* = 6.1, 5.1 Hz, 1H), 4.27-4.12

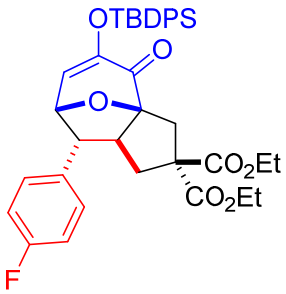
(m, 4H), 3.77 (s, 3H), 3.63 (dd, J = 6.9, 6.1 Hz, 1H), 3.17 (d, J = 14.9 Hz, 1H), 2.66 (ddd, J = 10.0, 6.9, 3.4 Hz, 1H), 2.60 (ddd, J = 13.7, 3.4, 1.3* Hz, 1H) *long-range coupling, 2.58 (dd, J = 14.9, 1.3* Hz, 1H) *long-range coupling, 2.28 (dd, J = 13.7, 10.0 Hz, 1H), 1.26 (ovlp t, J = 7.1 Hz, 6H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.0, 171.1, 170.9, 158.6, 145.9, 135.6(2), 135.5(2), 132.6, 132.2, 130.15, 130.14, 129.8, 129.2(2), 127.9(4), 125.7, 114.0(2), 97.6, 79.5, 62.1, 61.9, 61.7, 55.4, 55.3, 50.6, 37.9, 37.3, 26.6(3), 19.7, 14.13, 14.10; mp 101–102 °C; ESI-HRMS calculated for $C_{39}H_{44}O_8SiNa$ $[M + Na]^+$ 691.2703, found 691.2690.



TBDPS-Cycloadduct 2t′ (Table 2, entry 4): FCC (hexanes:EtOAc 85:15) afforded a white foam (75 mg, 0.12 mmol, 58%, dr >19:1): R_f = 0.40 (hexanes:EtOAc 85:15); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.58 (m, 4H), 7.44-7.36 (m, 2H), 7.35-7.29 (m, 4H), 6.93 (app d, J = 8.0 Hz, 2H), 6.81 (app d, J = 8.0 Hz, 2H), 5.61 (d, J = 5.1 Hz, 1H), 4.65 (dd, J = 5.9, 5.1 Hz, 1H), 4.26-4.18 (m, 4H), 3.66 (dd, J = 7.1, 5.9 Hz, 1H), 3.17 (d, J = 14.8 Hz, 1H), 2.74-2.67 (m, 1H), 2.63-2.55 (m, 2H), 2.29 (s, 3H), 2.28 (dd, J = 13.6, 9.7 Hz, 1H), 1.26 (ovlp t, J = 7.1 Hz, 6H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.0, 171.1, 170.9, 145.9, 136.6, 135.6(2), 135.4(2), 134.8, 132.6, 132.2, 130.12, 130.07, 129.2(2), 128.1(2), 127.87(2), 127.86(2), 125.8, 97.6, 79.5, 62.05, 61.9, 61.7, 55.9, 50.3, 37.9, 37.3, 26.6(3), 21.1, 19.7, 14.13, 14.12; ESI-HRMS calculated for $C_{39}H_{44}O_7SiNa$ $[M + Na]^+$ 675.2754, found 675.2735.

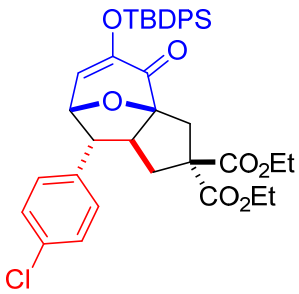


TBDPS-Cycloadduct 2u′ (Table 2, entry 5): Prepared previously as a white foam (271 mg, 0.43 mmol, 85%, dr >19:1) with the following spectral data:[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.61 (m, 4H), 7.45-7.30 (m, 8H), 7.19-7.12 (m, 3H), 5.63 (d, *J* = 5.2 Hz, 1H), 4.70 (dd, *J* = 6.2, 5.2 Hz, 1H), 4.28-4.18 (m, 4H), 3.72 (dd, *J* = 6.9, 6.2 Hz, 1H), 3.20 (d, *J* = 14.9 Hz, 1H), 2.76 (ddd, *J* = 9.9, 6.9, 3.3 Hz, 1H), 2.66-2.59 (m, 2H), 2.32 (dd, *J* = 13.8, 9.9 Hz, 1H), 1.28 (ovlp t, *J* = 7.1 Hz, 6H), 1.07 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0, 171.1, 170.9, 145.9, 137.8, 135.6(2), 135.4(2), 132.5, 132.2, 130.1(2), 128.6(2), 127.9(4), 127.0, 125.6, 97.6, 79.4, 62.0, 61.9, 61.7, 56.2, 50.3, 37.9, 37.3, 26.6(3), 19.6, 14.11, 14.09.

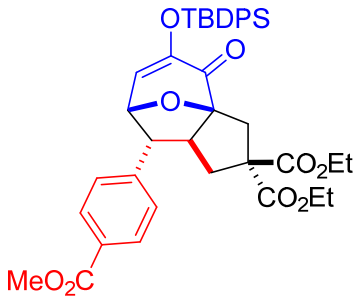


TBDPS-Cycloadduct 2v′ (Table 2, entry 6): FCC (hexanes:EtOAc 80:20) afforded a white solid (93 mg, 0.14 mmol, 71%, dr >19:1): R_f = 0.57 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.59 (m, 4H), 7.45-7.39 (m, 2H), 7.36-7.32 (m, 4H), 6.83 (app dd, *J* = 8.6, 5.4 Hz, 2H), 6.76 (app t, *J* = 8.6 Hz, 2H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.64 (dd, *J* = 6.1, 5.0 Hz, 1H), 4.27-4.15 (m, 4H), 3.67 (dd, *J* = 6.9, 6.1 Hz, 1H), 3.18 (d, *J* = 14.8 Hz, 1H), 2.65 (ddd, *J* = 9.7, 6.9, 3.3 Hz, 1H), 2.61-2.56 (m, 1H), 2.59 (d, *J* = 14.8, 1H), 2.29 (dd, *J* = 13.6, 9.7 Hz, 1H), 1.26 (ovlp t, *J*

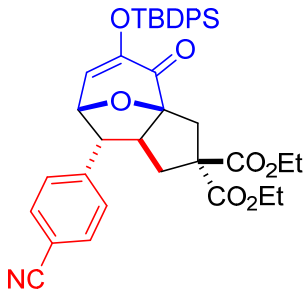
= 7.1 Hz, 6H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 191.9, 171.1, 170.8, 161.8 (d, *J* = 245.2 Hz), 146.1, 135.6(2), 135.4(2), 133.5 (d, *J* = 2.7 Hz), 132.4, 132.1, 130.24, 130.20, 129.6(2) (d, *J* = 7.6 Hz), 127.9(4), 125.1, 115.3(2) (d, *J* = 21.8 Hz), 97.6, 79.3, 62.0, 61.9, 61.7, 55.4, 50.5, 37.8, 37.3, 26.5(3), 19.6, 14.11, 14.08; ^{19}F NMR (470 MHz) -115.8 (tt, *J* = 8.6, 5.4 Hz); mp 35–39 °C; ESI-HRMS calculated for $C_{38}H_{41}FO_7SiNa$ $[M + Na]^+$ 679.2503, found 679.2499.



TBDPS-Cycloadduct 2w′ (Table 2, entry 7): FCC (hexanes:EtOAc 85:15) afforded a white foam (32 mg, 0.05 mmol, 24%, dr >19:1): R_f = 0.35 (hexanes:EtOAc 85:15); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.56 (m, 4H), 7.47-7.39 (m, 2H), 7.36-7.30 (m, 4H), 7.04 (app d, *J* = 8.4 Hz, 2H), 6.79 (app d, *J* = 8.4 Hz, 2H), 5.53 (d, *J* = 5.0 Hz, 1H), 4.67-4.64 (m, 1H), 4.21-4.16 (m, 4H), 3.69-3.65 (m, 1H), 3.18 (d, *J* = 14.9 Hz, 1H), 2.69-2.63 (m, 1H), 2.61-2.56 (m, 2H), 2.30 (dd, *J* = 13.7, 9.8 Hz, 1H), 1.26 (ovlp t, *J* = 7.1 Hz, 6H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 191.9, 171.1, 171.1, 170.9, 146.1, 136.4, 135.6(2), 135.4(2), 132.8, 132.3, 132.1, 130.31, 130.26, 129.4(4), 128.7(2), 128.0(4), 125.0, 97.7, 79.2, 62.1, 62.0, 61.8, 55.5, 50.2, 37.9, 37.3, 26.6(3), 19.6, 14.2, 14.1; ESI-HRMS calculated for $C_{38}H_{41}ClO_7SiNa$ $[M + Na]^+$ 695.2208, found 695.2175.

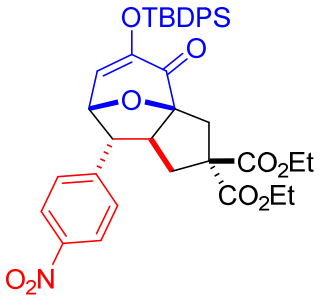


TBDPS-Cycloadduct 2x′ (Table 2, entry 8): FCC (hexanes:EtOAc 90:10 to 85:15) afforded a white solid (38 mg, 0.055 mmol, 47%, dr >19:1): R_f = 0.62 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (app d, *J* = 8.4 Hz, 2H), 7.63-7.55 (m, 4H), 7.42-7.28 (m, 6H), 6.95 (app d, *J* = 8.4 Hz, 2H), 5.54 (d, *J* = 5.0 Hz, 1H), 4.72 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.27-4.15 (m, 4H), 3.91 (s, 3H), 3.77 (dd, *J* = 6.7, 6.0 Hz, 1H), 3.19 (d, *J* = 14.8 Hz, 1H), 2.73 (ddd, *J* = 10.0, 6.7, 3.5 Hz, 1H), 2.63-2.58 (m, 1H), 2.59 (d, *J* = 13.6 Hz, 1H), 2.31 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.26 (ovlp t, *J* = 7.1 Hz, 6H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 171.1, 170.8, 168.8, 146.2, 143.2, 135.6(2), 135.4(2), 132.3, 132.0, 130.3, 130.2, 129.9(2), 128.9, 128.1(2), 127.9(4), 124.9, 97.8, 79.2, 62.1, 62.0, 61.8, 56.2, 52.2, 50.0, 37.9, 37.3, 26.5(3), 19.6, 14.14, 14.11; mp 43–49 °C; ESI-HRMS calculated for $C_{40}H_{44}O_9SiNa$ $[M + Na]^+$ 719.2652, found 719.2655.



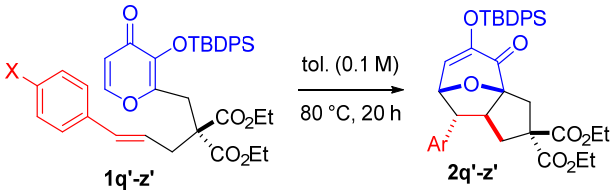
TBDPS-Cycloadduct 2y′ (Table 2, entry 9): FCC (hexanes:EtOAc 70:30) afforded a white solid (114 mg, 0.17 mmol, 86%, dr >19:1): R_f = 0.61 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.56 (m, 4H), 7.49-7.31 (m, 8H), 6.93 (app d, *J* = 8.1 Hz, 2H), 5.49 (d, *J* = 5.0 Hz, 1H), 4.70 (dd, *J* = 6.0, 5.0 Hz, 1H), 4.29-4.15 (m, 4H), 3.76 (dd, *J* = 6.8, 6.0 Hz, 1H), 3.20 (d, *J* =

15.0 Hz, 1H), 2.67 (ddd, J = 9.9, 6.8, 3.4 Hz, 1H), 2.62-2.56 (m, 2H), 2.30 (dd, J = 13.6, 9.9 Hz, 1H), 1.27 (ovlp t, J = 7.2 Hz, 6H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 191.5, 170.9, 170.5, 146.2, 143.3, 135.5(2), 135.3(2), 132.2(2), 132.0, 131.8, 130.3, 130.2, 128.8(2), 127.9(4), 124.1, 118.5, 110.8, 97.7, 78.9, 61.93, 61.91, 61.7, 56.0, 49.9, 37.6, 37.1, 26.3(3), 19.5, 14.02, 13.99; mp 41–47 °C; ESI-HRMS calculated for $C_{39}H_{41}NO_7SiNa$ $[M + Na]^+$ 686.2550, found 686.2548.



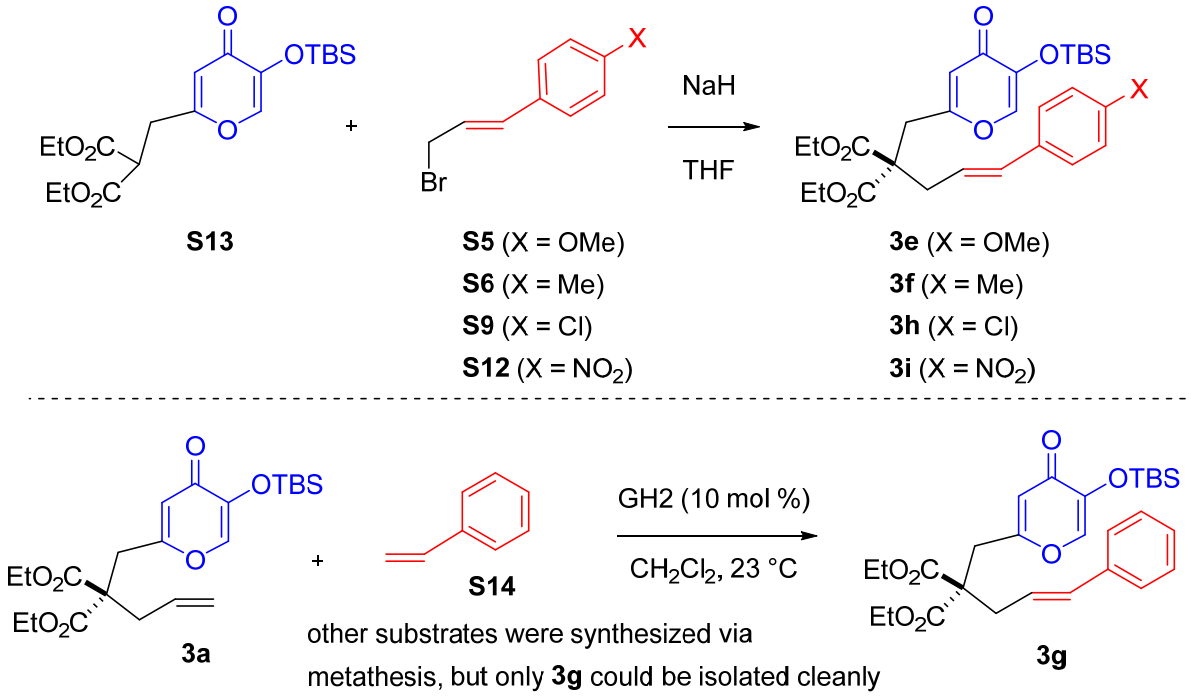
TBDPS-Cycloadduct 2z′ (Table 2, entry 10): FCC (hexanes:EtOAc 80:20) afforded a white solid (92 mg, 0.14 mmol, 68%, dr >19:1): R_f = 0.63 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (app d, J = 8.8 Hz, 2H), 7.63-7.57 (m, 4H), 7.44-7.40 (m, 2H), 7.37-7.31 (m, 4H), 6.98 (app d, J = 8.8 Hz, 2H), 5.49 (d, J = 5.0 Hz, 1H), 4.72 (dd, J = 6.1, 5.0 Hz, 1H), 4.27-4.17 (m, 4H), 3.81 (dd, J = 6.6, 6.1 Hz, 1H), 3.21 (d, J = 15.0 Hz, 1H), 2.71 (ddd, J = 9.9, 6.6, 2.9 Hz, 1H), 2.65-2.57 (m, 2H), 2.31 (dd, J = 13.6, 9.9 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 191.6, 171.1, 170.6, 146.9, 146.4, 145.5, 135.6(2), 135.4(2), 132.0, 131.8, 130.4, 130.3, 128.9(2), 128.0(4), 124.0, 123.7(2), 97.9, 79.1, 62.1, 62.0, 61.9, 56.0, 50.2, 37.7, 37.3, 26.5(3), 19.6, 14.2, 14.1; mp 55–58 °C; ESI-HRMS calculated for $C_{38}H_{41}NO_9SiNa$ $[M + Na]^+$ 706.2448, found 706.2433.

Table S1. Linear Free-Energy Relationship of TBDPS Styrenes

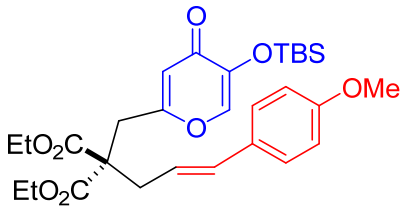


entry	X	% yield[a] (**2**)	σ_p	log (rate/rate
1	NMe_2	87 (**2q'**)	-0.83	0.271
2	O*i*Pr	65 (**2r'**)	-0.45	0.145
3	OMe	65 (**2s'**)	-0.27	0.146
4	Me	58 (**2t'**)	-0.17	0.097
5	H	47 (**2u'**)	0.00	0.000
6	F	46 (**2v'**)	0.06	-0.001
7	Cl	68 (**2w'**)	0.23	0.164
8	CO_2Me	77 (**2x'**)	0.39	0.221
9	CN	85 (**2y'**)	0.66	0.261
10	NO_2	94 (**2z'**)	0.78	0.306

[a] Determined by the average of two trials as measured by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

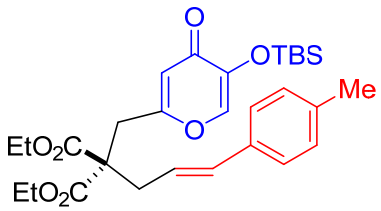


General Procedure G for Synthesis of TBS-Pyrone Styrenes 3: To a solution of malonate **S13** in THF (0.1 M) was added NaH (2 equiv.) at 23 °C and stirred for 15 min. A solution of cinnamyl bromide **S5,6,9,12** (2-3 equiv.) in THF (0.1 M) was added and stirred for 1.5 h. The reaction was quenched slowly with sat. aq. NH_4Cl, diluted with Et_2O, and separated. The combined organic extracts were washed with sat. aq. NaCl, dried with $MgSO_4$, filtered, and concentrated. Purification by FCC afforded **TBS-Pyrone Styrenes 3e,f,h,i.**

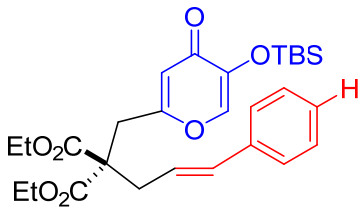


TBS-Pyrone Styrene 3e (Table 4, entry 1): FCC (hexanes:EtOAc 80:20) afforded a yellow oil (836 mg, 1.53 mmol, 66%): R_f = 0.50 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.24 (app d, J = 8.7 Hz, 2H), 6.83 (app d, J = 8.7 Hz, 2H), 6.38 (app d, J = 15.8 Hz, 1H), 6.22 (s, 1H), 5.85 (dt, J = 15.8, 7.5 Hz, 1H), 4.22 (ovlp q, J = 7.2 Hz, 4H), 3.80 (s, 3H), 3.16 (s,

2H), 2.76 (app d, J = 7.5 Hz, 2H), 1.25 (t, J = 7.2 Hz, 6H), 0.95 (s, 9H), 0.23 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 175.3, 169.8(2), 163.4, 159.4, 145.6, 144.0, 134.5, 129.7, 127.5(2), 120.6, 116.4, 114.1(2), 62.0(2), 57.3, 55.4, 36.5, 36.4, 25.8(3), 18.6, 14.2(2), -4.3(2); ESI-HRMS calculated for $C_{29}H_{40}O_8SiNa$ $[M + Na]^+$ 567.2390, found 567.2386.

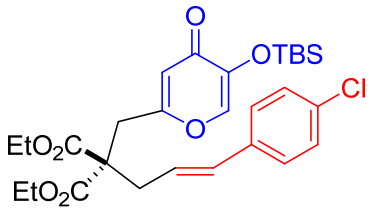


TBS-Pyrone Styrene 3f (Table 4, entry 2): FCC #1 (hexanes:EtOAc 80:20) and FCC #2 (CH_2Cl_2:acetone 100:1) afforded a yellow oil (725 mg, 1.37 mmol, 55%): R_f = 0.45 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.20 (app d, J = 7.9 Hz, 2H), 7.10 (app d, J = 7.9 Hz, 2H), 6.42 (app d, J = 15.5 Hz, 1H), 6.21 (s, 1H), 5.94 (dt, J = 15.5, 7.5 Hz, 1H), 4.22 (ovlp q, J = 7.2 Hz, 4H), 3.16 (s, 2H), 2.72 (dd, J = 7.5, 1.0 Hz, 2H), 2.33 (s, 3H), 1.25 (t, J = 7.2 Hz, 6H), 0.95 (s, 9H), 0.23 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 175.3, 169.8(2), 163.4, 145.6, 144.0, 137.6, 135.0, 134.1, 129.4(2), 126.3(2), 121.9, 116.4, 62.0(2), 57.3, 36.5, 36.4, 25.8(3), 21.3, 18.6, 14.2(2), -4.3(2); ESI-HRMS calculated for $C_{29}H_{40}O_7SiNa$ $[M + Na]^+$ 551.2441, found 551.2420.

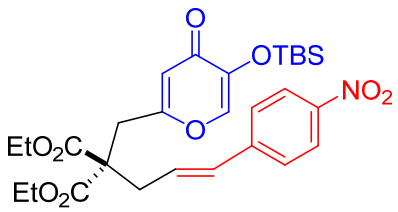


TBS-Pyrone Styrene 3g (Table 4, entry 3): This was synthesized according to General Procedure A but with styrene **S14** as the reacting partner; FCC (hexanes:EtOAc 80:20) afforded a yellow solid (239 mg, 0.46 mmol, 81%): R_f = 0.41 (hexanes:EtOAc 80:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.33-7.22 (m, 5H), 6.95 (dt, J = 15.7, 1.1 Hz, 1H), 6.22 (s, 1H), 6.00 (dt, J = 15.7,

7.6 Hz, 1H), 4.22 (ovlp q, J = 7.2 Hz, 4H), 3.17 (s, 2H), 2.78 (dd, J = 7.6, 1.1 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H), 0.95 (s, 9H), 0.23 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 175.2, 169.7(2), 163.3, 145.5, 144.0, 136.8, 135.1, 128.6(2), 127.7, 126.3(2), 122.9, 116.4, 62.0(2), 57.2, 36.5, 36.4, 25.7(3), 18.4, 14.2(2), -4.4(2); mp 99–102 °C; ESI-HRMS calculated for $C_{28}H_{39}O_7Si$ $[M + H]^+$ 515.2465, found 515.2457.

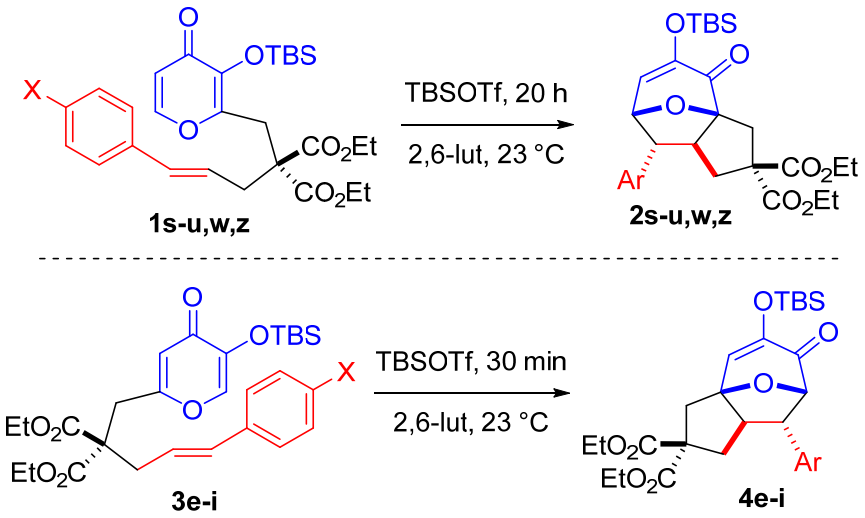


TBS-Pyrone Styrene 3h (Table 4, entry 4): FCC (hexanes:EtOAc 90:10) afforded a yellow oil (1.06 g, 1.93 mmol, 63%): R_f = 0.13 (hexanes:EtOAc 90:10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.28 (app d, J = 8.5 Hz, 2H), 7.23 (app d, J = 8.5 Hz, 2H), 6.39 (app d, J = 15.5 Hz, 1H), 6.21 (s, 1H), 5.94 (dt, J = 15.5, 7.5 Hz, 1H), 4.21 (ovlp q, J = 7.2 Hz, 4H), 3.16 (s, 2H), 2.76 (dd, J = 7.5, 1.1 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H), 0.95 (s, 9H), 0.23 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 175.2, 169.7(2), 163.2, 145.6, 144.0, 135.3, 133.8, 133.5, 128.8(2), 127.6(2), 123.8, 116.4, 62.1(2), 57.2, 36.6, 36.4, 25.7(3), 18.6, 14.2(2), -4.4(2); ESI-HRMS calculated for $C_{28}H_{37}ClO_7SiNa$ $[M + Na]^+$ 571.1895, found 571.1892.

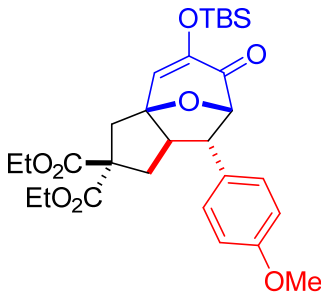


TBS-Pyrone Styrene 3i (Table 4, entry 5): FCC (hexanes:EtOAc 80:20) afforded an orange solid (644 mg, 1.15 mmol, 67%): R_f = 0.38 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (app d, J = 8.8 Hz, 2H), 7.57 (s, 1H), 7.44 (app d, J = 8.8 Hz, 2H), 6.51 (app d, J = 15.7 Hz, 1H), 6.24 (dt, J = 15.7, 7.5 Hz, 1H), 6.21 (s, 1H), 4.24 (ovlp q, J = 7.1 Hz, 4H), 3.17 (s, 2H), 2.82 (dd,

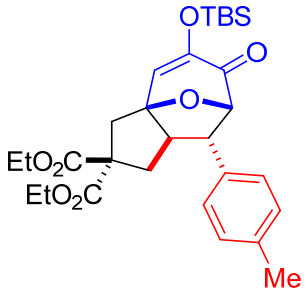
J = 7.5, 1.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 6H), 0.95 (s, 9H), 0.23 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 175.1, 169.5(2), 162.9, 147.1, 145.6, 144.0, 143.1, 132.9, 128.6, 126.9(2), 124.1(2), 116.4, 62.7(2), 57.0, 36.8, 36.6, 25.7(3), 18.6, 14.2(2), -4.4(2); mp 69–70 °C; ESI-HRMS calculated for $C_{28}H_{37}NO_9SiNa$ $[M + Na]^+$ 582.2135, found 582.2125.



General Procedure H for TBSOTf-mediated (5 + 2) Cycloadditions: To a solution of pyrone in DCM (0.05 M) was added TBSOTf (2.5 equiv.) and 2,6-lutidine (3.0 equiv.) at 23 °C and stirred for the appropriate time. Upon addition of water, separation, drying with Na_2SO_4, and concentration of the resulting organic solutions, 1,3,5-trimethoxybenzene in $CDCl_3$ was added to calculate the conversion according to ^{1}H NMR integrations. For the maltol derived substrates, the characterization was presented in the thermal-mediated series (*vide supra*) that were included from our previous report.[3] For the kojic acid derived substrates, separate reactions were carried to obtain full characterization of the cycloadducts.

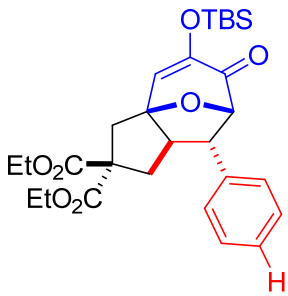


TBS-Cycloadduct 4e (Table 4, entry 1): FCC (hexanes:EtOAc 95:5) afforded a yellow oil (73 mg, 0.134 mmol, 67%, dr >19:1): R_f = 0.70 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (app d, *J* = 8.8 Hz, 2H), 6.78 (app d, *J* = 8.8 Hz, 2H), 6.54 (s, 1H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.29-4.13 (m, 4H), 3.78 (dd, *J* = 8.0, 4.7 Hz, 1H), 3.75 (s, 3H), 2.88 (ddd, *J* = 9.3, 6.3, 4.7 Hz, 1H), 2.68 (d, *J* = 14.4 Hz, 1H), 2.65 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.43 (dd, *J* = 13.5, 9.3 Hz, 1H), 1.27 (ovlp t, *J* = 7.1 Hz, 6H), 0.91 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 192.1, 171.7, 170.7, 158.8, 148.5, 130.3, 129.4(2), 128.3, 114.1(2), 92.2, 88.9, 62.4, 62.0, 61.8, 55.3, 54.9, 53.7, 42.8, 40.1, 25.7(3), 18.5, 14.1(2), -4.2, -4.4; ESI-HRMS calculated for $C_{29}H_{40}O_8SiNa$ $[M + Na]^+$ 567.2390, found 567.2365.

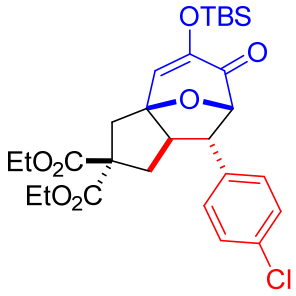


TBS-Cycloadduct 4f (Table 4, entry 2): FCC (hexanes:EtOAc 85:15) afforded a brown oil (69 mg, 0.13 mmol, 65%, dr >19:1): R_f = 0.54 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (app d, *J* = 8.0 Hz, 2H), 6.95 (app d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 4.70 (d, *J* = 8.0 Hz, 1H), 4.29-4.13 (m, 4H), 3.79 (dd, *J* = 8.0, 4.7 Hz, 1H), 2.91 (ddd, *J* = 9.4, 6.2, 4.7 Hz, 1H), 2.75 (d, *J* = 14.5 Hz, 1H), 2.68 (d, *J* = 14.5 Hz, 1H), 2.65 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.43 (dd, *J* = 13.5, 9.4

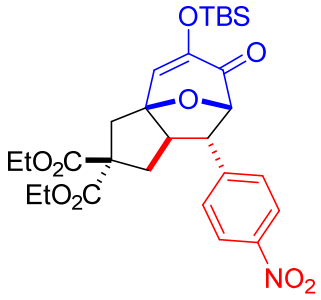
Hz, 1H), 2.28 (s, 3H), 1.26 (ovlp t, J = 7.1 Hz, 6H), 0.91 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.0, 171.7, 170.8, 148.5, 136.9, 133.2, 130.3, 129.4(2), 128.3(2), 92.3, 88.9, 62.4, 62.0, 61.8, 54.9, 54.1, 42.8, 40.1, 25.8(3), 21.1, 18.5, 14.1(2), -4.2, -4.4; ESI-HRMS calculated for $C_{29}H_{40}O_7SiNa$ $[M + Na]^+$ 551.2441, found 551.2443.



TBS-Cycloadduct 4g (Table 4, entry 3): FCC (hexanes:EtOAc 95:5) afforded a yellow oil (89 mg, 0.17 mmol, 87%, dr >19:1): R_f = 0.25 (hexanes:EtOAc 85:15); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.22 (m, 2H), 7.21-7.17 (m, 1H), 7.09-7.06 (m, 2H), 6.55 (s, 1H), 4.74 (d, J = 8.0 Hz, 1H), 4.29-4.14 (m, 4H), 3.84 (dd, J = 8.0, 4.8 Hz, 1H), 2.95 (ddd, J = 9.3, 6.2, 4.8 Hz, 1H), 2.77 (d, J = 14.5 Hz, 1H), 2.69 (d, J = 14.5 Hz, 1H), 2.67 (dd, J = 13.6, 6.2 Hz, 1H), 2.44 (dd, J = 13.5, 9.3 Hz, 1H), 1.27 (ovlp t, J = 7.1 Hz, 6H), 0.91 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 191.8, 171.7, 170.8, 148.6, 136.3, 130.2, 128.7(2), 128.4(2), 127.3, 92.4, 88.9, 62.4, 62.0, 61.8, 54.7, 54.5, 42.8, 40.2, 25.8(3), 18.5, 14.1(2), -4.3, -4.4; ESI-HRMS calculated for $C_{28}H_{38}O_7SiNa$ $[M + Na]^+$ 537.2284, found 537.2260.

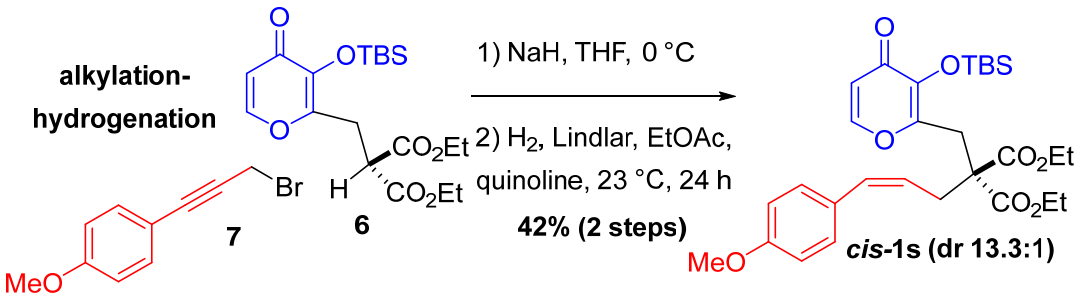


TBS-Cycloadduct 4h (Table 4, entry 4): FCC #1 (hexanes:EtOAc 95:5) and FCC #2 (CH_2Cl_2:acetone 100:1) afforded a colorless oil (55 mg, 0.10 mmol, 50%, dr >19:1): R_f = 0.23 (hexanes:EtOAc 85:15); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (app d, *J* = 8.5 Hz, 2H), 7.00 (app d, *J* = 8.5 Hz, 2H), 6.55 (s, 1H), 4.72 (d, *J* = 8.0 Hz, 1H), 4.29-4.14 (m, 4H), 3.80 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.90-2.85 (m, 1H), 2.77 (d, *J* = 14.7 Hz, 1H), 2.67 (d, *J* = 14.7 Hz, 1H), 2.65 (dd, *J* = 13.6, 6.1 Hz, 1H), 2.43 (dd, *J* = 13.6, 9.4 Hz, 1H), 1.27 (ovlp t, *J* = 7.0 Hz, 6H), 0.91 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 191.6, 171.4, 170.6, 148.5, 134.7, 133.1, 130.3, 129.6(2), 128.7(2), 92.3, 88.5, 62.2, 62.0, 61.7, 54.8, 53.7, 42.6, 39.9, 25.6(3), 18.4, 14.0(2), -4.4, -4.5; ESI-HRMS calculated for $C_{28}H_{37}ClO_7SiNa$ $[M + Na]^+$ 571.1895, found 571.1893.



TBS-Cycloadduct 4i (Table 4, entry 5): FCC (hexanes:EtOAc 85:15) afforded a yellow oil (68 mg, 0.12 mmol, 61%, dr >19:1): R_f = 0.36 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (app d, *J* = 8.6 Hz, 2H), 7.24 (app d, *J* = 8.6 Hz, 2H), 6.59 (s, 1H), 4.79 (d, *J* = 7.9 Hz, 1H), 4.30-4.15 (m, 4H), 3.95 (dd, *J* = 7.9, 5.0 Hz, 1H), 2.97-2.93 (m, 1H), 2.81 (d, *J* = 14.5 Hz, 1H), 2.69 (d, *J* = 14.5 Hz, 1H), 2.68 (dd, *J* = 13.6, 5.9 Hz, 1H), 2.45 (dd, *J* = 13.6, 9.6 Hz, 1H), 1.27

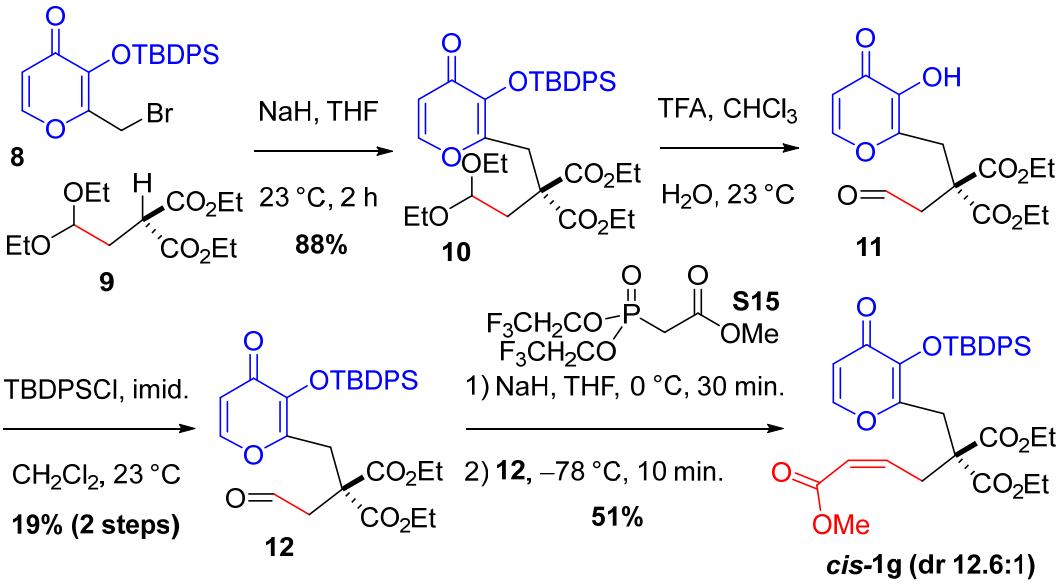
(ovlp t, J = 7.0 Hz, 6H), 0.91 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 191.3, 171.4, 170.7, 148.7, 147.2, 144.0, 130.7, 129.4(2), 123.9(2), 92.6, 88.5, 62.3, 62.2, 61.9, 54.9, 54.2, 42.7, 39.8, 25.7(3), 18.5, 14.1(2), -4.3, -4.4; ESI-HRMS calculated for $C_{28}H_{37}NO_9SiNa$ $[M + Na]^+$ 582.2135, found 582.2123.



TBS-*cis*-1s (Scheme 4): To a solution of malonate **6** (770 mg, 1.9 mmol, 1.0 equiv.) in THF (15 mL) was added NaH (155 mg, 3.9 mmol, 2.0 equiv.) at 0 °C. The reaction was stirred for 5 minutes and warmed to 23 °C for 20 minutes before cooling to 0 °C and adding propargyl bromide[4] **7** (878 mg, 3.9 mmol, 2.0 equiv.) as a solution in THF (2 mL). The reaction was warmed to 23 °C and stirred 1 h, quenched with H_2O (20 mL), and diluted with Et_2O (50 mL). The resulting phases were separated, and the aqueous phase was extracted with Et_2O (2 x 20 mL). The combined organic extract was washed with sat. aq. NaCl (100 mL), dried over $MgSO_4$, filtered and concentrated. Purification by FCC (100% CH_2Cl_2 to CH_2Cl_2:EtOAc 90:10) afforded TBS-pyrone alkyne **S15** as a yellow oil (745 mg, 1.37 mmol, 72%): R_f = 0.73 (CH_2Cl_2:EtOAc 90:10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 5.5 Hz, 1H), 7.28 (app d, J = 8.8 Hz, 2H), 6.79 (app d, J = 8.8 Hz, 2H), 6.29 (d, J = 5.5 Hz, 1H), 4.29-4.17 (m, 4H), 3.79 (s, 3H), 3.63 (s, 2H), 3.10 (s, 2H), 1.25 (t, J = 7.1 H, 6H), 0.93 (s, 9H), 0.25 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 173.9, 169.2(2), 159.4, 153.0, 152.8, 144.2, 133.0(2), 115.6, 115.2, 113.7(2), 83.6, 82.4, 61.9(2), 56.6, 55.1, 30.3, 25.9(3), 24.7,

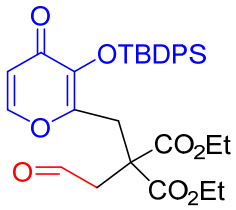
[4] Okitsu, T.; Sato, K.; Potewar, T. M.; Wada, A. *J. Org. Chem.* **2011**, *76*, 3438-3449.

18.7, 13.9(2), -3.7(2); ESI-HRMS calculated for $C_{29}H_{38}O_8SiNa$ $[M + Na]^+$ 565.2234, found 565.2244. To a solution of alkyne **S15** (500 mg, 0.92 mmol, 1.0 equiv.) in EtOAc (9.0 mL) was added quinoline (109 µL, 0.92 mmol, 1.0 equiv.) and Lindlar catalyst (500 mg). The reaction was stirred at 23 °C under an H_2 atmosphere for 24 h. The reaction was filtered over celite and concentrated. Purification by FCC (100% CH_2Cl_2 to CH_2Cl_2:EtOAc 95:5) afforded styrene TBS-*cis*-**1s** as a colorless oil (296 mg, 0.544 mmol, 59%, dr 13.3:1): R_f = 0.69 (CH_2Cl_2:EtOAc 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 5.6 Hz, 1H), 7.13 (app d, *J* = 8.7 Hz, 2H), 6.83 (app d, *J* = 8.7 Hz, 2H), 6.48 (app d, *J* = 11.7 Hz, 1H), 6.16 (d, *J* = 5.6 Hz, 1H), 5.47 (dd, *J* = 11.7, 7.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.80 (s, 3H), 3.44 (s, 2H), 2.96 (dd, *J* = 7.4, 1.7 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 6H), 0.98 (s, 9H), 0.26 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.8, 170.2(2), 158.5, 153.1, 152.6, 143.9, 132.2, 129.9(2), 129.4, 123.7, 115.4, 113.6(2), 61.7(2), 56.7, 55.2, 31.4, 30.2, 26.0(3), 18.8, 14.0(2), -3.6(2); ESI-HRMS calculated for $C_{29}H_{40}O_8SiNa$ $[M + Na]^+$ 567.2390, found 567.2387.



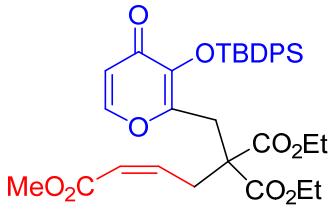
TBDPS-Pyrone Aldehyde 12 (Scheme 5): To a solution of malonate **9** (2.0 g, 7.24 mmol, 1.0 equiv.) in THF (40 mL) was added NaH (348 mg, 8.69 mmol, 1.2 equiv.) in THF (10 mL) at 23

°C. Upon stirring for 20 min, TBDPS-maltol bromide **8** (3.85 g, 8.69 mmol, 1.0 equiv.) in THF (10 mL) was added slowly over a period of 10 min. The reaction was stirred 2 h, quenched with H_2O (50 mL), and diluted with Et_2O (150 mL). The aqueous layer was extracted with Et_2O (50 mL), and the combined organic extract was washed with sat. aq. NaCl (50 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 85:15) afforded pyrone **10** as a colorless oil (4.09 g, 6.37 mmol, 88%). To a solution of pyrone **10** (4.09 g, 6.37 mmol, 1.0 equiv.) in $CHCl_3$ (30 mL) was added H_2O (15 mL) followed by TFA (12.3 mL) at 23 °C. The reaction was stirred 24 h, quenched slowly Na_2CO_3 (50 mL), separated and the combined aqueous layer was extracted with $CHCl_3$ (2 x 50 mL). The combined organic extract was washed with sat. aq. NaCl (50 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (hexanes:EtOAc 50:50) afforded pyrone **11** as a colorless oil (747 mg, 2.30 mmol, 36%). To a solution of enol **11** (747 mg, 2.30 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added imidazole (280 mg, 4.12 mmol, 1.1 equiv.) and TBDPSCl (660 µL, 2.51 mmol, 1.1 equiv.). The reaction was stirred 1 h at 23°C, quenched with H_2O (20 mL), stirred an additional 15 min, and then extracted with CH_2Cl_2 (30 mL). The combined organic extract was washed with sat. aq. NaCl (2 x 100 mL), dried with $MgSO_4$, filtered and concentrated. Purification by FCC (hexanes:EtOAc 70:30) delivered TBDPS-pyrone aldehyde **12** (688 mg, 1.22 mmol, 53%) as a white solid (see alternative procedure below).



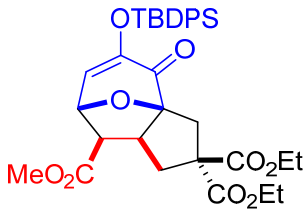
TBDPS-Pyrone Aldehyde 12[3] (alternative procedure illustrating the stability of the TBDPS as compared to the TBS variant S2): A solution of TBDPS-pyrone alkene **1b** (400 mg, 0.711 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was cooled to -78° C and ozone (30%) was bubbled into the

reaction for 12 minutes. The reaction was degassed by exposure to oxygen for 12 minutes, followed by addition of PPh_3 (373 mg, 1.42 mmol, 2.0 equiv.). The resulting mixture was allowed to warm to room temperature with stirring over 15 minutes, concentrated, and purified by FCC (hexanes:EtOAc 70:30) to afford TBDPS-pyrone aldehyde **12** as a white solid (399 mg, 0.70 mmol, 99%): R_f = 0.18 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.27 (t, *J* = 1.1 Hz, 1H), 7.67-7.65 (m, 4H), 7.42 (d, *J* = 5.6 Hz, 1H), 7.39-7.32 (m, 6H), 6.05 (d, *J* = 5.6 Hz, 1H), 4.31-4.21 (m, 4H), 3.67 (s, 3H), 3.06 (d, *J* = 1.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.06 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.0, 172.6, 169.4(2), 152.9, 151.9, 144.3, 134.7(4), 134.4(2), 129.4(2), 127.4(4), 115.5, 62.4(2), 53.9, 46.4, 31.8, 27.2(3), 20.2, 14.0(2); mp 84–86 °C; ESI-HRMS calculated for $C_{31}H_{36}O_8SiNa$ $[M + Na]^+$ 587.2077, found 587.2079.

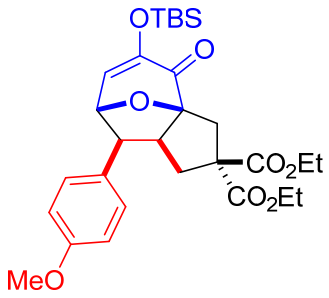


TBDPS-Pyrone Enoate *cis*-1g (Scheme 5): To a solution of NaH (67 mg, 1.68 mmol, 1.9 equiv.) in THF (6 mL) was added the Still-Gennari reagent **S16** (438 mg, 1.24 mmol, 1.4 equiv.) slowly at 0 °C and stirred 30 min. The solution was cooled to -78 °C and aldehyde **12** (500 mg, 0.886 mmol, 1.0 equiv.) in THF (6 mL) was added dropwise over 10 min. Upon stirring for 30 min, the reaction was quenched with sat. aq. NH_4Cl (5 mL), warmed to ambient temperature, and diluted with H_2O (20 mL). The aqueous layer was extracted with Et_2O (2 x 25 mL) and the combined organic extract was washed with sat. aq. NaCl (20 mL), dried with $MgSO_4$, filtered, and concentrated. Purification by FCC (CH_2Cl_2:Et_2O 97.5:2.5 to CH_2Cl_2:Et_2O 95:5) delivered TBDPS-pyrone enoate ***cis*-1g** as a colorless oil (281 mg, 0.45 mmol, 51%, dr 12.6:1): R_f = 0.22 (CH_2Cl_2:Et_2O 95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.65 (m, 4H), 7.42 (d, *J* = 5.5 Hz, 1H),

7.37-7.30 (m, 6H), 6.22 (dt, J = 11.6, 7.3 Hz, 1H), 6.04 (d, J = 5.5 Hz, 1H), 5.86 (dt, J = 11.6, 1.8 Hz, 1H), 4.24 (ovlp q, J = 7.2 Hz, 4H), 3.65 (s, 3H), 3.61 (s, 2H), 3.37 (dd, J = 7.3, 1.8 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H), 1.06 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 172.6, 170.1(2), 166.2, 152.8, 152.4, 143.9, 143.0, 134.9(4), 134.6(2), 129.4(2), 127.4(4), 122.5, 115.5, 62.1(2), 56.4, 51.3, 32.4, 31.5, 27.3(3), 20.3, 14.2(2); ESI-HRMS calculated for $C_{34}H_{40}O_9SiNa$ $[M + Na]^+$ 643.2339, found 643.2355.



TBDPS-Cycloadduct *cis*-2g (Scheme 6, eq. 1): General Procedure C was followed with TBDPS-pyrone enoate ***cis*-1g** (176 mg, 0.284 mmol, dr 12.6:1) and toluene (4 mL) at 60 °C. Purification by FCC (hexanes:EtOAc 90:10) afforded cycloadduct ***cis*-2g** as a colorless oil (130 mg, 0.21 mmol, 74%, dr 12.2:1): R_f = 0.26 (hexanes:EtOAc 80:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.60 (m, 4H), 7.46-7.35 (m, 6H), 5.91 (d, J = 5.4 Hz, 1H), 4.99 (d, J = 5.4 Hz, 1H), 4.30-4.08 (m, 4H), 3.67 (s, 3H), 3.18 (dd, J = 15.1, 1.2* Hz, 1H) *long-range coupling, 2.70 (ddd, J = 10.0, 9.6, 8.0 Hz, 1H), 2.55 (d, J = 9.6 Hz, 1H), 2.54 (d, J = 15.1 Hz, 1H), 2.53 (ddd, J = 13.0, 8.0, 1.2* Hz, 1H) *long-range coupling, 1.82 (dd, J = 13.0, 10.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.09 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 192.0, 171.4, 171.0, 170.2, 146.2, 135.63(2), 135.57(2), 132.3, 132.0, 130.4, 130.3, 128.1, 128.0(2), 127.9(2), 98.3, 77.3, 62.9, 62.0, 61.8, 52.2, 51.6, 47.3, 37.4, 36.7, 26.6(3), 19.6, 14.13, 14.08; ESI-HRMS calculated for $C_{34}H_{40}O_9SiNa$ $[M + Na]^+$ 643.2339, found 643.2336.



TBS-Cycloadduct *cis*-2s (Scheme 6, eq. 2): General Procedure C was followed with TBS-*cis*-**1s** (92 mg, 0.17 mmol, dr 13.3:1) at 110 °C and FCC (hexanes:EtOAc 90:10 to 85:15) afforded cycloadduct ***cis*-2s** as a colorless oil (54 mg, 0.10 mmol, 59%, dr 13.8:1): R_f = 0.66 (hexanes:EtOAc 70:30); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (app d, *J* = 8.7 Hz, 2H), 6.87 (app d, *J* = 8.7 Hz, 2H), 6.35 (d, *J* = 5.2 Hz, 1H), 5.00 (app d, *J* = 5.2 Hz, 1H), 4.27-4.14 (m, 3H), 4.01 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.80 (s, 3H), 3.45 (app d, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 14.8, 1.7* Hz, 1H) *long-range coupling, 3.09 (ddd, *J* = 10.9, 9.2, 8.2 Hz, 1H), 2.55 (d, *J* = 14.8 Hz, 1H), 2.11 (ddd, *J* = 13.2, 8.2, 1.7* Hz, 1H) *long-range coupling, 1.47 (dd, *J* = 13.2, 10.9 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.94 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.9, 171.1, 170.5, 158.5, 145.6, 132.3, 129.5(2), 128.0, 114.2(2), 97.9, 83.7, 64.2, 61.8, 61.6, 55.4, 49.8, 49.5, 37.9, 35.9, 25.7(3), 18.5, 14.1, 14.0, -4.5, -4.6; ESI-HRMS calculated for $C_{29}H_{40}O_8SiNa$ $[M + Na]^+$ 567.2390, found 567.2389.

Supporting Information – Theoretical Energy Diagrams

All computational structures are available in the ioChem-BD repository:
https://doi.org/10.19061/iochem-bd-6-585

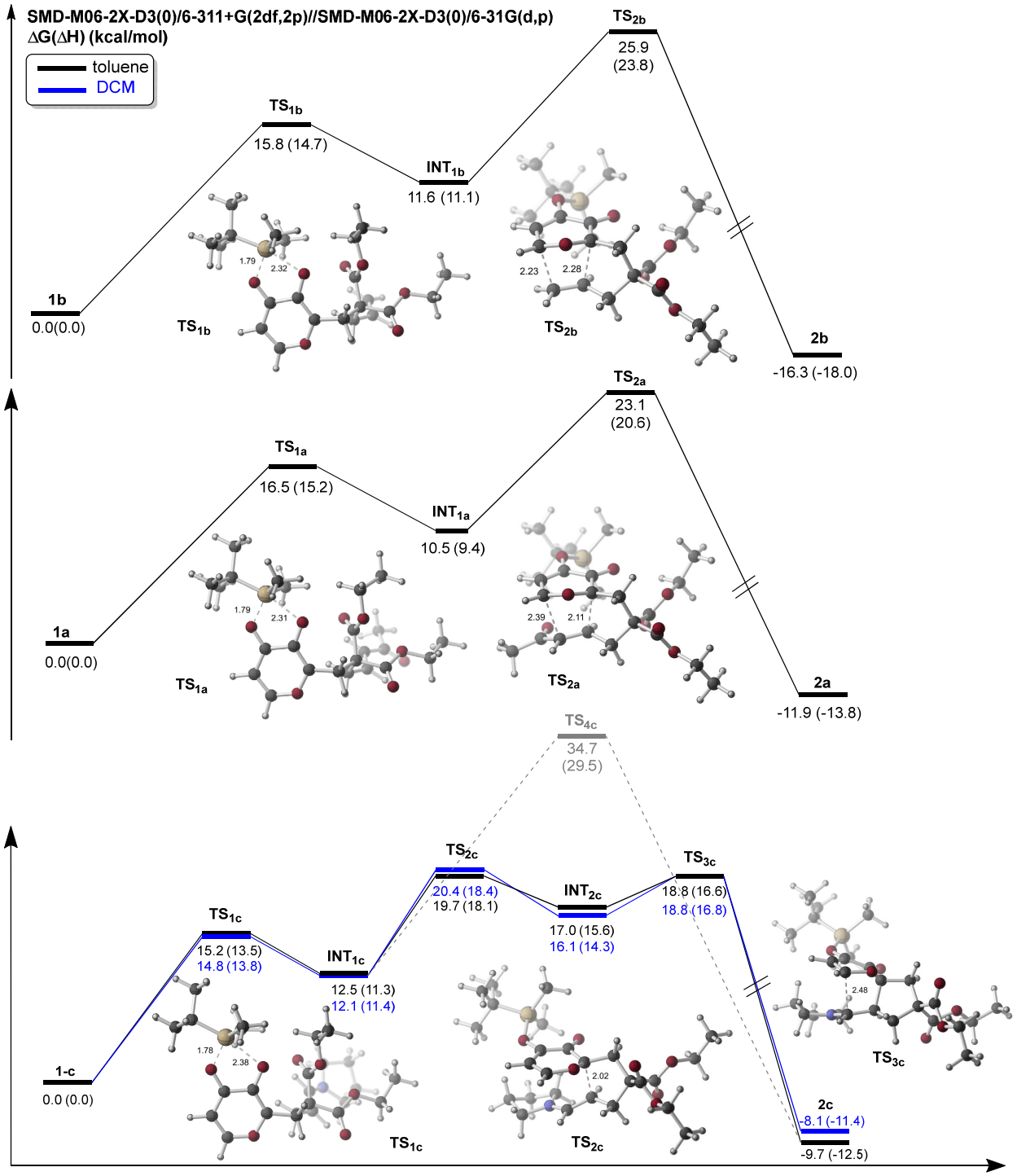


Figure S1.[3] Free Energy Profile of Reaction Pathway with CYLview images.[5] Relative Free Energies and Relative Enthalpy Energies Shown are for Stationary Points Optimized under SMD-M06-2x/6-311+G(d,p)//SMD-M06-2x/6-31G(d) Level of Theory.

[5] CYLview, 1.0b; Legault,C. Y., Universitéde Sherbrooke, **2009** (http://www.cylview.org).

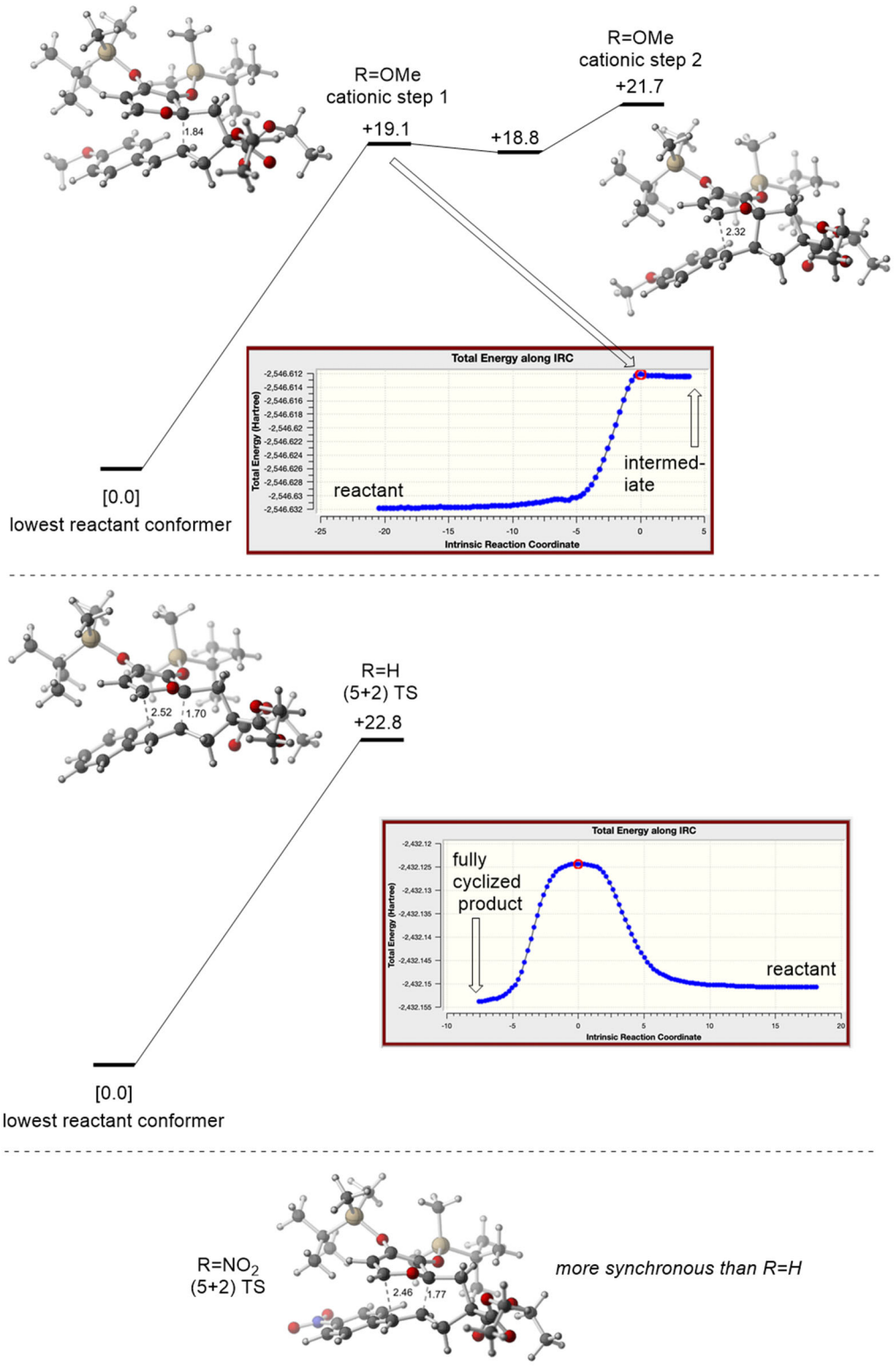


Figure S2. Free Energy Profile of Reaction Pathway with CYLview images.[5] Relative Free Energies and Relative Enthalpy Energies Shown are for Stationary Points Optimized under SMD-M06-2x/6-311+G(d,p)//SMD-M06-2x/6-31G(d) Level of Theory.