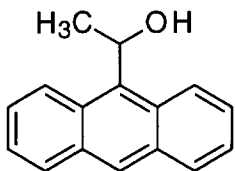


Experimental

General. Melting points were determined in capillaries and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian UNITY PLUS 400 (93.94 kG, ^1H 400 MHz, ^{13}C 100 MHz), and a Varian Gemini 300 (70.5 kG, ^1H 300 MHz, ^{13}C 75 MHz) as indicated in CDCl_3 (0.5 mL) or $\text{DMSO}-d_6$ (0.5 mL). The δ 7.24 resonance of residual CHCl_3 , and the center line of the $^{13}\text{CDCl}_3$ triplet (δ 77.0) were used as internal references for the ^1H and ^{13}C spectra, respectively, for spectra in CDCl_3 . For $\text{DMSO}-d_6$, the δ 2.49 resonance of residual $\text{DMSO}-d_5$, and the center line of the $^{13}\text{CD}_3\text{S}(\text{O})\text{CD}_3$ septet (δ 39.51) were used as internal references for the ^1H and ^{13}C spectra, respectively, for spectra in $\text{DMSO}-d_6$. All exchangeable proton resonances (OH) were identified by the addition of D_2O . Relative intensities of carbon resonances were determined by integration of spectra recorded under inverse gated decoupling ($D1 = 10$ s). Carbon chemical shifts are reported to a single decimal place with the exception of resolved resonances which can be distinguished numerically only to the second decimal position. Infrared spectra were recorded on a Perkin-Elmer 1800 spectrophotometer. Only diagnostic bands such as carbonyl and hydroxy bond stretching bands, are reported. Mass spectra were measured on a Finnigan MAT-90 spectrometer as indicated.

(S)-(+)-2,2,2-Trifluoro-1-(9-anthryl)ethanol (**2a**) and 9-anthraldehyde were purchased from Aldrich and used without further purification. 9-(1-methylpropyl)-Anthracene (**5**) was prepared according to literature procedures.¹ Anthracenes **1a - e** and **7** were stored at 4 °C under argon. All solvents were anhydrous, dried and distilled according to standard procedures prior to use.²



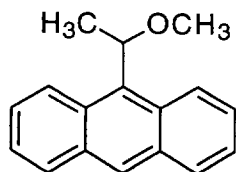
9-(1-Hydroxyethyl)anthracene (1a). To a solution of 9-anthraldehyde (1.031 g, 5.0 mmol) in anhydrous Et_2O (30 mL) was added dropwise with stirring CH_3Li (1.4 M in toluene, 4.28 mL, 6.0 mmol) at 0 °C. The mixture was stirred for 2 hr and then quenched by the addition of saturated NH_4Cl (5 mL). The layers were separated and the aqueous layer extracted with Et_2O (1 X 10 mL). The combined organic

(1) van de Griendt, F.; Cerfortain, H.; *J. Chem. Soc., Perkin Trans. 2*, **1980**, 19-22.

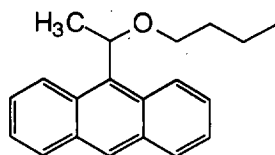
(2) Perrin, D. D.; Armarego, W.L.F.; Perrin, D.R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

extracts were dried over Na_2SO_4 , filtered, and then the solvent was removed in vacuo to afford crude **1a** (1.010 g, 91% yield) as pure yellow solid. Mp 121 - 122 °C; IR (KBr) ν_{max} 3359 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (br d, $J = 8.4$ Hz, 2H), 8.38 (s, 1H), 8.00 (dd, $J = 9.2, 1.6$ Hz, 2H) 7.50 - 7.42 (m, 4H), 6.48 (q, $J = 7.2$ Hz, 1H), 2.12 (br s, OH), 1.92 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 135.7, 131.7, 129.3 (2C), 128.8 (2C), 127.9, 125.5 (2C), 124.8 (4C), 67.3, 23.5; HRMS (EI, 70 eV) m/z 222.1047 ($[\text{M}]^+$, 2%), calcd for $\text{C}_{16}\text{H}_{14}\text{O}$ 222.1045. The product was stored at 4 °C and used without any further purification.

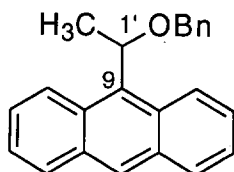
General procedure for the synthesis of anthracenes 1b, 1c, 1d, 2b and 7. A suspension of NaH (2 eq, 60% suspension in mineral oil) in anhydrous THF (5 mL), was prepared by repeated (X 2) washing to remove the mineral oil under argon using anhydrous THF, then adding fresh THF (5 mL). A THF solution (5 mL) of the respective anthryl carbinol (1 eq) was added dropwise with stirring using a canula at 0 °C, then the temperature allowed to rise to rt, followed by addition of the electrophile (CH_3I for **1b**, **2b** and **7**, $n\text{-BuBr}$ for **1c** and BnBr for **1d**; 5 eq). The mixture was stirred for 18 - 24 hr at rt (refluxed for **1d**), then quenched by addition of H_2O (5 mL). After adding ether (20 mL) the layers were separated and the organic layer extracted with H_2O (2 X 10 mL). The combined organic extracts were dried over Na_2SO_4 , filtered, and then the solvent was removed in vacuo to afford crude product. Flash chromatography on a silica gel column (CH_2Cl_2 :hexanes, 50:50) afforded pure products free of any unreacted starting alcohol.



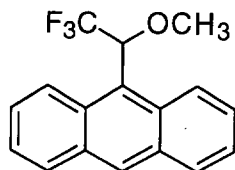
9-(1-Methoxyethyl)anthracene (1b). Prepared from **1a** (0.222 g, 1 mmol) according to the general procedure to afford **1b** (0.189 g, 80% yield) as a yellow solid. Mp 78 - 79 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (br s, 2H), 8.39 (s, 1H), 8.00 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.50 - 7.42 (m, 4H), 5.92 (q, $J = 6.8$ Hz, 1H), 3.20 (s, 3H), 1.85 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 133.3, 131.6 (2C), 129.5 (2C), 129.3 (2C), 127.8, 125.5 (2C), 124.7 (2C), 124.4 (br, 2C), 76.1, 56.5, 22.5; HRMS (EI, 70 eV) m/z 236.1216 ($[\text{M}]^+$, 53%), calcd for $\text{C}_{17}\text{H}_{16}\text{O}$ 236.1201.



9-(1-Butoxyethyl)anthracene (1c). Prepared from **1a** (0.222 g, 1 mmol) according to the general procedure to afford **1c** (0.112 g, 40% yield) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.70 (br s, 2H), 8.39 (s, 1H), 8.00 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.50 - 7.43 (m, 4H), 6.01 (q, $J = 6.8$ Hz, 1H), 3.33 (ddd, $J = 9.2, 6.6, 6.2$ Hz, 1H), 3.16 (ddd, $J = 9.2, 7.0, 6.6$ Hz, 1H), 1.85 (d, $J = 6.8$ Hz, 3H), 1.57 - 1.48 (m, 2H), 1.36 - 1.20 (m, 2H), 0.79 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 134.2, 131.6 (2C), 129.4 (2C), 129.2 (2C), 127.6, 125.3 (3C), 124.7 (3C), 74.3, 68.6, 32.1, 22.7, 19.4, 13.9; HRMS (EI, 70 eV) m/z 278.1681 ($[\text{M}]^+$, 96%), calcd for $\text{C}_{20}\text{H}_{22}\text{O}$ 278.1671.



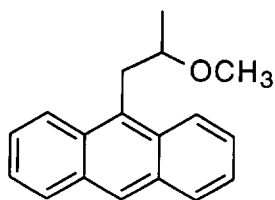
9-(1-Benzyloxyethyl)anthracene (1d). Prepared from **1a** (0.222 g, 1 mmol) according to the general procedure to afford **1d** (0.299 g, 96% yield) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1H), 8.03 - 8.00 (m, 2H), 7.48 - 7.44 (m, 4H), 7.30 - 7.19 (m, 6H), 6.10 (q, $J = 7.0$ Hz, 1H), 4.34 (d, $J_{\text{AB}} = 11.6$ Hz, 1H), 4.23 (d, $J = 11.6$ Hz, 1H), 1.88 (d, $J = 7.0$ Hz, 3H), the H1/H8 resonance was not observed at ambient temperature due to severe broadening caused by hindered rotation about the C9/C1' bond;³ ^{13}C NMR (75.5 MHz, CDCl_3) δ 138.5, 133.4, 131.6, 129.6 (2C), 129.3 (2C), 128.3 (3C), 128.04 (3C), 127.96, 127.5, 125.6 (3C), 124.8 (2C), 73.7, 70.7, 22.7; HRMS (EI, 70 eV) m/z 312.1500 ($[\text{M}]^+$, 27%), calcd for $\text{C}_{23}\text{H}_{20}\text{O}$ 312.1514.



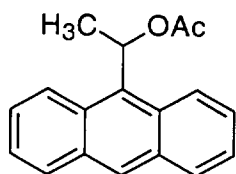
1-(9-Anthryl)-1-methoxy-2,2,2-trifluoroethane (2b). Prepared from **2a** (0.276 g, 1.0 mmol) according to the general procedure to afford **2b**

(3) (a) Jaime, C.; Virgili, C.; Claramunt, R. M.; Lopez, C.; Elguero, J. *J. Org. Chem.* **1991**, *56*, 6521-6523. (b) de Riggi, I.; Virgili, A.; de Moragas, M.; Jaime, C. *J. Org. Chem.* **1995**, *60*, 27-31.

(0.267 g, 92% yield) as a white solid. Mp 105 - 106 °C; $[\alpha]_D^{25} + 59^\circ$ (c 0.01, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.94 (d, *J* = 8.8 Hz, 1H), 8.54 (s, 1H), 8.18 (d, *J* = 9.2 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 8.8, 6.8 Hz, 1H), 7.53 - 7.40 (m, 3 H), 6.16 (q, ³*J*_{F,H} = 7.8 Hz, 1H), 3.38 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 132.0, 131.7, 131.0, 130.9, 130.7, 129.7, 128.9, 127.1, 126.6 (q, ³*J*_{F,C} = 3.1 Hz), 126.3, 125.2, 125.0 (q, *J*_{F,C} = 283.8 Hz), 124.7, 122.4, 121.9, 78.6 (q, ²*J*_{F,C} = 32.1 Hz), 58.0; HRMS (EI, 70 eV) *m/z* 290.0939 ([M]⁺, 59%), calcd for C₁₇H₁₃F₃O 290.0918.



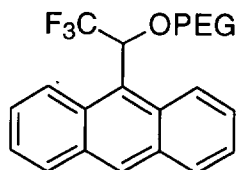
9-(2-Methoxypropyl)anthracene (7). Prepared from 9-(2-hydroxypropyl)anthracene.⁴ (0.545 g, 2.3 mmol) according to the general procedure to afford **7** (0.375 g, 65% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 8.32 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 8.8, 6.4 Hz, 2H), 7.45 (dd, *J* = 8.3, 6.4 Hz, 2H), 3.96 (dd, *J* = 13.7, 5.9 Hz, 1H), 3.85 (ddq, *J* = 7.3, 5.9, 5.9 Hz, 1H), 3.68 (dd, *J* = 13.7, 7.3 Hz, 1H), 3.33 (s, 3H), 1.15 (d, *J* = 5.9 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 131.6 (2C), 131.4, 130.4 (2C), 129.2 (2C), 126.3, 125.5 (2C), 124.9 (2C), 124.8 (2C), 78.4, 56.7, 34.6, 19.6; EIMS (70 eV) *m/z* 250 ([M]⁺, 89%), 192 ([M - C₃H₆O]⁺, 82%), 191 ([M - C₃H₇O]⁺, 97%), 59 (100%); HRMS (EI, 70 eV) *m/z* 250.1343 ([M]⁺, 50%), calcd for C₁₈H₁₈O 250.1358.



9-(1-Acetoxyethyl)anthracene (1e). To a solution of **1a** (0.435 g, 1.96 mmol) in anhydrous CH₂Cl₂ (5 mL) was added dropwise with stirring Et₃N (0.82 mL, 5.88 mmol) at 0 °C, followed by Ac₂O (0.20 mL, 2.15 mmol) and DMAP (0.024 g, 0.2 mmol). The mixture was stirred for 18 hr at rt and then quenched by addition of H₂O (2 mL). The layers were separated immediately and the organic layer extracted with H₂O (2 X 10 mL). The organic layer was dried over Na₂SO₄, filtered, and then the solvent removed in vacuo to afford crude product. Flash chromatography on silica gel

(4) Becker, H., -D.; Amin, K. A. *J. Org. Chem.* **1989**, *54*, 3182-3188.

(CH₂Cl₂/hexanes) afforded pure **1e** as a viscous yellow oil (0.352 g, 68% yield). IR (NaCl) ν_{\max} 1738 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.59 (br d, *J* = 8.4 Hz, 2H), 8.41 (s, 1H), 7.99 (dd, *J* = 8.1, 0.8 Hz, 2H), 7.51 (ddd, 8.4, 8.1, 1.2 Hz, 2H), 7.45 (ddd, 8.4, 8.1, 0.8 Hz), 7.40 (q, *J* = 7.0 Hz, 1H), 2.07 (s, 3H), 1.92 (d, *J* = 7.0 Hz, 3 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 170.3, 132.1, 131.5 (2C), 129.3 (2C), 128.9 (2C), 128.4, 125.8 (2C), 124.7 (2C), 124.5 (2C), 68.8, 21.5, 21.1; HRMS (EI, 70 eV) *m/z* 264.1147 ([M]⁺, 33%), calcd for C₁₈H₁₆O₂ 264.1150.



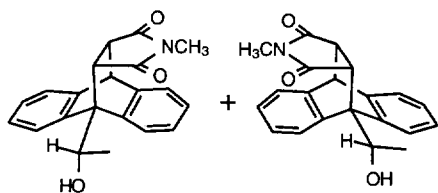
Compound 2c. A suspension of NaH (2 mmol, 0.080 g, 60% suspension in mineral oil) in anhydrous THF (5 mL) under argon, was prepared by repeated (X 2) washing to remove the mineral oil under argon using anhydrous THF, then adding fresh THF (5 mL). A THF solution (5 mL) of racemic **2a** (0.138 g, 0.5 mmol) also under argon, was added dropwise with stirring using a canula at 0 °C, then the temperature allowed to rise to rt, followed by addition of PEG₅₀₀₀OMs (0.500 g, 0.1 mmol). The mixture was stirred for 24 hr at rt, then the solvent was removed in vacuo to afford crude product which was repeatedly washed with *i*-PrOH (100 mL X 3) and ether (100 mL X 3) and filtered, until ¹H NMR showed no unreacted **2a**. The white solid thus obtained (0.420 g, ca. 52% bonded on PEG, based upon ¹H NMR integration of PEG-OCH₃ at 3.36) was dried under vacuum before further use. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (br d, *J* = 7.7 Hz, 2H), 7.95 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.69 - 7.63 (m, 2H), 7.53 - 7.49 (m, 3H), 5.50 (br s, 1H), 3.81 - 3.42 (PEG methylenes), 3.36 (s, PEG-OCH₃).

General procedure for thermal Diels-Alder cycloadditions of 1a - e and 2b with symmetric maleates. The respective anthracenes (1 eq) and dienophiles (1.2 eq) were refluxed in benzene (9 hr) or toluene (18 hr) as indicated in Table 1. For the cycloadditions indicated in Table 3, bromomaleic anhydride (1.1 eq) and citraconic anhydride (4 eq) were refluxed in toluene for 6-9 hr and 48 hr, respectively. After cooling to rt, the solvent was removed in vacuo to obtain crude products, which were analyzed by ¹H NMR for diastereoselectivity. The crude products were then dissolved in a minimum amount of CH₂Cl₂ and precipitated with hexanes to afford pure products.

General procedure for Lewis acid catalyzed Diels-Alder cycloadditions:

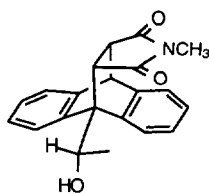
Cycloadditions of 1b and 1e. Anhydrous CH_2Cl_2 (3 - 4 mL) was added to a mixture of N, N'-dibenzylideneethylenediamine (0.275 mmol, 1.1 eq) and copper (II) triflate (0.25 mmol, 1.0 eq) in a dry conical flask equipped with a magnetic stirrer under argon. The green solution thus obtained was stirred at rt for 2 hr after which maleic anhydride (1.2 eq) and the respective anthracene (1.0 eq) were added sequentially. After 48 hr at rt, the reaction was quenched by adding H_2O (5 mL). Stirring was continued until the CH_2Cl_2 layer turned yellow and the H_2O layer turned blue, then CH_2Cl_2 (5 mL) was added and the layers were separated. The organic layer was extracted with H_2O (2 X 10 mL), then dried over Na_2SO_4 , filtered, and then the solvent was removed in vacuo to afford crude product, which was analyzed by ^1H NMR for diastereoselectivity. The crude products were then dissolved in a minimum amount of CH_2Cl_2 and precipitated with hexanes to afford pure products.

Cycloadditions of 2b. Anhydrous CH_2Cl_2 (3 - 4 mL) was added to a mixture of **2b** (1 eq) and NMM (1.5 eq) in a dry conical flask equipped with a magnetic stirrer under argon. The Lewis acid (1.1 eq) was added under the positive pressure of an argon filled balloon at 0 °C. The solution thus obtained was stirred at rt for 24 hr. The reaction was diluted with CH_2Cl_2 (5 mL) and quenched by adding H_2O (5 mL). The organic layer was extracted with H_2O (2 X 10 mL), then dried over Na_2SO_4 , filtered, and then the solvent removed in vacuo to afford crude product, which was analyzed by ^1H NMR for diastereoselectivity. Pure products were purified by flash chromatography on silica gel eluting with EtOAc/hexanes (1/4).

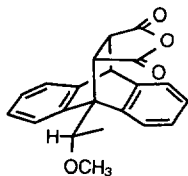


Cycloaddition of 1a and NMM. Prepared from **1a** (0.022 g, 0.1 mmol) according to the general procedure to afford **3a** (0.022 g, 66% yield) as 1:1.7 mixture of diastereomers, inseparable on by silica gel chromatography. Selected definitive ^1H NMR peaks used for determination of diastereoselectivity: Major diastereomer: ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 5.33 (br s, OH), 4.64 (d, $J = 3.3$ Hz, 1H), 3.26 (dd, $J = 8.4, 3.3$ Hz, 1H), 3.19 (d, $J = 8.4$ Hz, 1H), 2.32 (s, 3H), 1.81 (d, $J = 6.2$ Hz, 3H). Minor diastereomer: ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 5.47 (br s, OH), 4.67 (d, $J = 2.9$ Hz, 1H), 3.53 (d, $J = 8.4$ Hz, 1H), 3.12 (dd, $J = 8.4, 2.9$ Hz, 1H), 2.28 (s, 3H), 1.76 (d, $J = 5.9$ Hz, 3H). Mixture: EIMS (70 eV) m/z 333 ($[\text{M}]^+$, 38%), 223 ($[\text{retro D.A.} + 1]^+$, 46%), 222 ($[\text{retro D.A.}]^+$, 98%), 207 ($[\text{retro D.A.} - \text{CH}_3]^+$, 77%);

HRMS (EI, 70 eV) m/z 333.1392 ($[M]^+$, 92%), calcd for $C_{21}H_{19}NO_3$ 333.1365. The minor diastereomer **3a** was also obtained by debenzoylation of **3g**.

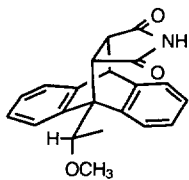


Cycloadduct 3a. To a solution of **3g** (0.085 g, 0.2 mmol) in anhydrous CH_2Cl_2 (10 mL) was added DDQ (0.227 g, 1.0 mmol) at rt. The mixture was stirred at rt for 12 hr, then quenched by the addition of H_2O (5 mL). The layers were separated and the organic layer extracted with H_2O (10 mL) and 10% $NaHCO_3$ (2 X 10 mL). The organic extract was dried over Na_2SO_4 , filtered, and then the solvent was removed in vacuo. Flash chromatography on silica gel (EtOAc/hexanes, 1/4) afforded pure **3a** as a pure white solid (0.043 g, 65% yield). Mp 229 - 231 °C; IR (KBr) ν_{max} 3549, 1767, 1693 cm^{-1} ; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.97 - 7.95 (m, 1H), 7.47 - 7.43 (m, 1H), 7.24 - 7.12 (m, 6H), 5.46 (bq, $J = 6.2$ Hz, 1H), 4.67 (d, $J = 3.0$ Hz, 1H), 3.53 (d, $J = 8.4$ Hz, 1H), 3.12 (dd, $J = 8.4, 3.0$, 1H), 2.28 (s, 3H), 1.76 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75.0 MHz, $DMSO-d_6$) δ 176.3, 175.7, 143.0, 139.6, 139.3, 138.9, 126.7, 126.2, 126.1, 125.7, 125.1, 124.6, 123.8, 123.5, 63.2, 53.7, 48.3, 46.6, 45.4, 23.7, 21.0; EIMS (70 eV) m/z 333 (8%), 223 ($[M]^+$, 28%), 222 ($[retro\ D.A.]^+$, 96%), 207 ($[retro\ D.A. - CH_3]^+$, 83%), 203 (29%), 202 (40%), 180 (22%), 179 (100%), 178 (87%), 176 (23%), 113 (64%), 85 (23%), 83 (39%), 43 (24%); HRMS (EI, 70 eV) m/z 333.1364 ($[M]^+$, 5%), calcd for $C_{21}H_{19}O_3N$ 333.1365.

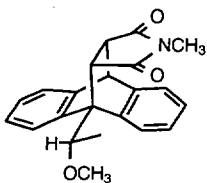


Cycloadduct 3b. Prepared from **1b** (0.047 g, 0.21 mmol) according to the general procedure to afford **3b** (0.062 g, 89% yield) as a white solid. Mp 242 - 243 °C; IR (KBr) ν_{max} 1850, 1828, 1776 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.83 (m, 1H), 7.38 - 7.34 (m, 2H), 7.23 - 7.17 (m, 5H), 4.98 (q, $J = 6.2$ Hz, 1H), 4.74 (d, $J = 3.3$ Hz, 1H), 3.92 (d, $J = 9.4$ Hz, 1H), 3.68 (s, 3H), 3.42 (dd, $J = 9.4, 3.3$ Hz, 1H), 1.87 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 170.5, 169.4, 141.9, 138.6, 138.4, 138.0, 127.5, 127.4, 127.0, 126.8, 126.3, 125.5, 124.0, 123.9, 73.5, 57.2, 54.6, 49.7, 48.3,

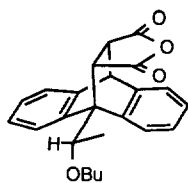
46.4, 16.7; EIMS (70 eV) m/z 334 ($[M]^+$, 2.7%), 236 ([retro D.A.] $^+$, 100%), 221 ([retro D.A - CH₃] $^+$, 93%); HRMS (EI, 70 eV) m/z 334.1224 ($[M]^+$, 1.5%), calcd for C₂₁H₁₈O₄ 334.1205.



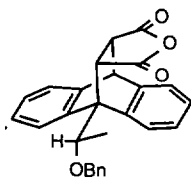
Cycloadduct 3c. Prepared from **1b** (0.047 g, 0.21 mmol) according to the general procedure to afford **3c** (0.062 g, 88% yield) as a white solid. Mp 270 - 272 °C; IR (KBr) ν_{\max} 1768, 1700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.86 - 7.84 (m, 1H), 7.36 - 7.34 (m, 1H), 7.33 - 7.30 (m, 1H), 7.18 - 7.13 (m, 5H), 5.06 (q, J = 6.2 Hz, 1H), 4.68 (d, J = 3.3 Hz, 1H), 3.68 (s, 3H), 3.65 (d, J = 8.8 Hz, 1H), 3.15 (dd, J = 8.8, 3.3 Hz, 1H), 1.85 (d, J = 6.2 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 176.4, 175.9, 142.4, 139.2, 138.9, 138.4, 126.91, 126.87, 126.76, 126.4, 125.9, 125.4, 123.9, 123.8, 73.7, 57.1, 54.6, 50.0, 48.1, 46.3, 16.8; CIMS (140 eV, NH₃) m/z 334 ($[M]^+$, 4%), 237 ([retro D.A. + 1] $^+$, 39%), 236 ([retro D.A.] $^+$, 94%), 235 ([retro D.A. - 1] $^+$, 93%), 222 (100%), 221 ([retro D.A. - CH₃] $^+$, 97%), 206 (32%), 205 (81%), 204 (20%), 178 (57%), 177 (21%); HRMS (CI, 140 eV, NH₃) m/z 334.1433 ($[M+H]^+$, 11%), calcd for C₂₁H₂₀NO₃ 334.1443.



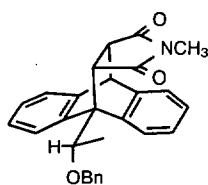
Cycloadduct 3d. Prepared from **1b** (0.047 g, 0.21 mmol) according to the general procedure to afford **3d** (0.067 g, 92% yield) as a white solid. Mp 243 - 244 °C; IR (KBr) ν_{\max} 1766, 1693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.87 - 7.85 (m, 1H), 7.37 - 7.34 (m, 1H), 7.28 - 7.26 (m, 1H), 7.17 - 7.12 (m, 5H), 5.10 (q, J = 6.3 Hz, 1H), 4.69 (d, J = 3.3 Hz, 1H), 3.70 (s, 3H), 3.59 (d, J = 8.6 Hz, 1H), 3.10 (dd, J = 8.6, 3.3 Hz, 1H), 2.44 (s, 3H), 1.84 (d, J = 6.3 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 176.8, 176.3, 142.4, 139.2, 138.8, 138.3, 126.8 (2C), 126.6, 126.3, 125.9, 125.1, 123.9, 123.5, 73.8, 57.1, 54.6, 48.8, 47.0, 46.4, 24.1, 16.7; EIMS (70 eV) m/z 347 ($[M]^+$, 8%), 332 ($[M - CH_3]^+$, 8%), 236 ([retro D.A.] $^+$, 99%), 221 ([retro D.A - CH₃] $^+$, 100%); HRMS (EI, 70 eV) m/z 347.1508 ($[M]^+$, 5%), calcd for C₂₂H₂₁NO₃ 347.1521.



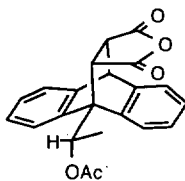
Cycloadduct 3e. Prepared from **1c** (0.072 g, 0.26 mmol) according to the general procedure to afford **3e** (0.068 g, 69% yield) as a white solid. Mp 242 - 243 °C; IR (KBr) ν_{\max} 1857, 1779 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 - 7.89 (m, 1H), 7.38 - 7.34 (m, 2H), 7.24 - 7.18 (m, 5H), 5.07 (q, $J = 6.2$ Hz, 1H), 4.74 (d, $J = 3.3$ Hz, 1H), 3.97 - 3.92 (m, 1H), 3.95 (d, $J = 9.2$ Hz, 1H), 3.73 (ddd, $J = 8.8, 6.2, 6.2$, 1H), 3.42 (dd, $J = 9.2, 3.3$ Hz, 1H), 1.85 (d, $J = 6.2$ Hz, 3H), 1.66 (tt, $J = 6.2, 6.2$, 2H), 1.46 (qt, $J = 7.3, 6.2$, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 170.6, 169.3, 141.9, 138.8, 138.4, 138.1, 127.5, 127.4, 127.3, 126.6, 126.2, 125.4, 123.94, 123.90, 71.8, 69.2, 54.7, 49.7, 48.3, 46.4, 32.4, 19.7, 17.3, 13.9; EIMS (70 eV) m/z 376 ($[\text{M}]^+$, 1%), 278 ([retro D.A.] $^+$, 89%), 277 (46%), 263 ([retro D.A - CH_3] $^+$, 75%), 221 (44%), 207 (50%), 206 (24%), 205 (70%), 204 (21%), 203 (30%), 202 (27%), 179 (33%), 178 (29%); HRMS (EI, 70 eV) m/z 376.1665 ($[\text{M}]^+$, 1%), calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4$ 376.1675.



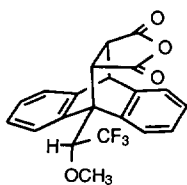
Cycloadduct 3f. Prepared from **1d** (0.63 g, 0.20 mmol) according to the general procedure to afford **3f** (0.057 g, 70% yield) as a white solid. Mp 260 - 261 °C; IR (KBr) ν_{\max} 1859, 1835, 1778 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.96 - 7.94 (m, 1H), 7.43 - 7.15 (m, 12H), 5.29 (q, $J = 6.4$ Hz, 1H), 5.01 (d, $J = 11.2$ Hz, 1H), 4.83 (d, $J = 11.2$ Hz, 1H), 4.74 (d, $J = 3.1$ Hz, 1H), 3.98 (d, $J = 9.3$ Hz, 1H), 3.41 (dd, $J = 9.3, 3.1$ Hz, 1H), 1.94 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 170.5, 169.5, 141.7, 138.7, 138.5, 138.4, 137.8, 128.4 (2C), 127.7 (2C), 127.6 (2C), 127.4, 127.1, 126.7, 126.3, 125.4, 124.0, 123.8, 72.5, 71.9, 54.6, 49.6, 48.3, 46.3, 17.5; EIMS (70 eV) m/z 410 ($[\text{M}]^+$, 5%), 312 ([retro D.A.] $^+$, 41%), 297 ([retro D.A - CH_3] $^+$, 8%), 205 ($[\text{C}_{15}\text{H}_{10}\text{O}]^+$, 100%), 91 (85%); HRMS (EI, 70 eV) m/z 410.1551 ($[\text{M}]^+$, 1%), calcd for $\text{C}_{27}\text{H}_{22}\text{O}_4$ 410.1518.



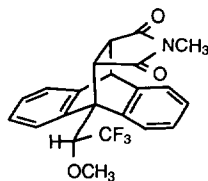
Cycloadduct 3g. Prepared from **1d** (0.156 g, 0.5 mmol) according to the general procedure to afford **3g** (0.165 g, 78% yield) as a white solid. Mp 226 - 228 °C; IR (KBr) ν_{\max} 1698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.98 - 7.96 (m, 1H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.37 - 7.24 (m, 5H), 7.19 - 7.13 (m, 5H), 5.39 (q, $J = 6.4$ Hz, 1H), 5.02 (d, $J_{\text{AB}} = 11.2$ Hz, 1H), 4.92 (d, $J_{\text{AB}} = 11.2$ Hz, 1H), 4.70 (d, $J = 3.4$ Hz, 1H), 3.66 (d, $J = 8.3$ Hz, 1H), 3.11 (dd, $J = 8.3, 3.4$ Hz, 1H), 2.45 (s, 3H), 1.91 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 176.9, 176.3, 142.3, 139.3, 139.2, 138.8, 138.2, 128.3 (2C), 127.6 (2C), 127.3, 127.1, 126.8, 126.7, 126.3, 125.9, 125.1, 123.8, 123.6, 72.9, 71.8, 54.8, 48.8, 47.1, 46.4, 24.1, 17.6; CIMS (140 eV) m/z 424 ($[\text{M} + 1]^+$, 98%), 312 ([retro D.A.] $^+$, 80%), 221 ([retro D.A. - C_7H_7] $^+$, 80%), 206 (100%), 205 (100%), 203 (83%), 178 (82%), 191 (81%), 91 (98%); HRMS (CI, 140 eV) m/z 424.1886 ($[\text{M} + 1]^+$, 2%), calcd for $\text{C}_{28}\text{H}_{25}\text{O}_3\text{N}$ 423.1834.



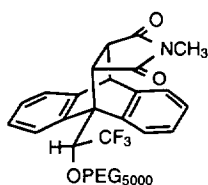
Cycloadduct 3h. Prepared from **1e** (0.066 g, 0.25 mmol) according to the general procedure for Lewis acid catalyzed Diels-Alder reaction to afford **3h** (0.047 g, 52% yield) as a white solid. Mp 245 - 250 °C (dec); IR (KBr) ν_{\max} 1780, 1730 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78 - 7.75 (m, 1H), 7.43 - 7.41 (m, 1H), 7.39 - 7.37 (m, 1H), 7.33 - 7.31 (m, 1H), 7.29 - 7.22 (m, 4H), 6.40 (q, $J = 6.4$ Hz, 1H), 4.78 (d, $J = 3.4$ Hz, 1H), 3.66 (d, $J = 9.3$ Hz, 1H), 3.47 (dd, $J = 9.3, 3.4$ Hz, 1H), 2.18 (s, 3H), 1.97 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 170.0, 169.6, 168.4, 141.8, 138.3, 138.2, 136.8, 128.0, 127.7, 127.1, 126.5, 126.1, 125.6, 124.4, 124.0, 68.5, 53.1, 49.7, 48.5, 46.1, 21.2, 18.9; EIMS (70 eV) m/z 362 ($[\text{M}]^+$, 13%), 265 (35%), 264 ([retro D.A.] $^+$, 100%), 222 ([retro D.A. - CH_2CO] $^+$, 24%), 211 (31%), 210 (77%), 209 (34%), 208 (87%), 207 (53%), 206 (25%), 205 (89%), 204 (88%), 203 (86%), 202 (72%), 194 (46%), 181 (22%), 180 (80%), 179 (31%), 178 (38%), 165 (24%), 152 (75%), 151 (36%), 85 (20%), 83 (31%), 76 (33%), 43 (89%); HRMS (EI, 70 eV) m/z 362.1189 ($[\text{M}]^+$, 2%), calcd for $\text{C}_{22}\text{H}_{18}\text{O}_5$ 362.1154.



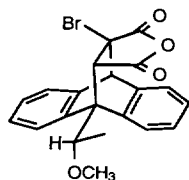
Cycloadduct 3i. Prepared from **2b** (0.029 g, 0.1 mmol) according to the general procedure to afford **3i** (0.029 g, 75% yield) as a white solid. Mp 244 - 245 °C; $[\alpha]_D^{25} - 33^\circ$ (c 0.018, CHCl_3); IR (KBr) ν_{max} 1771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 - 7.65 (m, 1H), 7.38 - 7.35 (m, 2H), 7.29 - 7.20 (m, 5H), 5.47 (q, $J_{\text{H,F}} = 8.5$ Hz, 1H), 4.79 (d, $J = 3.3$ Hz, 1H), 3.90 (d, $J = 9.5$ Hz, 1H), 3.88 (s, 3H), 3.43 (dd, $J = 9.5, 3.3$ Hz, 1H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 169.7, 169.6, 140.2, 137.5, 136.9, 136.8, 128.0, 127.7, 127.3, 126.8, 125.9 (q, $^1J_{\text{F,C}} = 288.5$ Hz), 125.4, 125.1 (q, $^4J_{\text{F,C}} = 4.0$ Hz), 123.9, 123.0 (q, $^4J_{\text{F,C}} = 3.3$ Hz), 80.6 (q, $^2J_{\text{F,C}} = 31.1$ Hz), 60.6, 52.8, 49.2, 48.7, 46.0; EIMS (70 eV) m/z 388 ($[\text{M}]^+$, 17%), 291 ([retro D.A. + 1] $^+$, 89%), 290 ([retro D.A.] $^+$, 94%), 259 (41%), 222 ([retro D.A. + 1 - CF_3] $^+$, 88%), 221 ([retro D.A. - CF_3] $^+$, 100%), 215 (35%), 207 (23%), 206 (84%), 205 (81%), 179 (20%), 178 (86%), 177 (51%), 176 (47%); HRMS (EI, 70 eV) m/z 388.0896 ($[\text{M}]^+$, 2%), calcd for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{O}_4$ 388.0922.



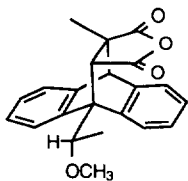
Cycloadduct 3j. Prepared from **2b** (0.029 g, 0.1 mmol) according to the general procedure to afford **3j** (0.030 g, 76% yield) as a white solid. Mp 242 - 243 °C; $[\alpha]_D^{25} - 45^\circ$ (c 0.012, CHCl_3); IR (KBr) ν_{max} 1767, 1694 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 - 7.66 (m, 1H), 7.37 - 7.34 (m, 1H), 7.28 - 7.16 (m, 6H), 5.62 (q, $J_{\text{H,F}} = 8.8$ Hz, 1H), 4.74 (d, $J = 3.3$ Hz, 1H), 3.89 (s, 3H), 3.56 (d, $J = 8.6$ Hz, 1H), 3.11 (dd, $J = 8.6, 3.3$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 176.3, 176.2, 140.9, 138.3, 137.4, 137.3, 127.2, 126.9 (2C), 126.4, 126.3 (q, $^1J_{\text{F,C}} = 288.6$ Hz), 125.1 (2C), 123.7, 122.7, 81.1 (q, $^2J_{\text{F,C}} = 30.6$ Hz), 60.4, 53.0, 47.9, 46.3, 24.2; EIMS (70 eV) m/z 401 ($[\text{M}]^+$, 10%), 291 ([retro D.A. + 1] $^+$, 77%), 290 ([retro D.A.] $^+$, 100%), 259 (19%), 222 ([retro D.A. + 1 - CF_3] $^+$, 76%), 221 ([retro D.A. - CF_3] $^+$, 97%), 206 (70%), 205 (70%), 203 (21%), 202 (29%), 178 (78%), 177 (34%), 176 (26%); HRMS (EI, 70 eV) m/z 401.1213 ($[\text{M}]^+$, 4%), calcd for $\text{C}_{22}\text{H}_{18}\text{F}_3\text{NO}_3$ 401.1239.



Compound 3k. Anthracene **2c** (0.080 g, ca. 0.016 mmol) and NMM (0.011 g, 0.096 mmol) were refluxed under argon in C_6H_6 (4 mL) for 24 hr. The solvent was evaporated in vacuo and the pink - white solid triturated with ether (50 mL) and filtered. The residue on top of the filter was washed by ether (5 X 10 mL). The residue thus obtained was washed with *i*-PrOH (2 X 5 mL), and dried in vacuo to afford **3k** (0.054 g, ca. 68% yield) as a pink - white solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.67 (m, 1H), 7.36 - 7.34 (m, 1H), 7.27 - 7.15 (m, 6H), 5.74 (q, $J_{HF} = 8.8$ Hz, 1H), 4.72 (d, $J = 3.1$ Hz, 1H), 4.22 (t, $J = 4.4$ Hz, PEG-2H), 3.83-3.42 (PEG - methylenes), 3.36 (s, PEG-OCH₃), 3.11 (dd, $J = 8.8, 3.1$ Hz, 1H), 2.43 (s, 3H).

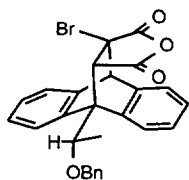


Cycloadduct 4a. Prepared from **1b** (0.236 g, 1 mmol) according to the general procedure to afford **4a** (0.338 g, 82% yield) as a white solid. Mp 230 - 231 °C (dec); IR (KBr) ν_{max} 1854, 1785 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.86 (m, 1H), 7.48 - 7.46 (m, 1H), 7.37 - 7.35 (m, 1H), 7.30 - 7.22 (m, 4H), 7.19 - 7.16 (m, 1H), 4.82 (q, $J = 6.6$ Hz, 1H), 4.79 (s, 1H), 3.98 (s, 1H), 3.66 (s, 3H), 1.85 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100.0 MHz, $CDCl_3$) δ 168.0, 166.4, 139.2, 137.22, 137.15, 136.8, 128.2, 128.1, 127.1, 126.9, 126.8, 126.7, 126.5, 124.0, 72.9, 59.2, 58.8, 57.0, 55.3, 53.3, 16.4; EIMS (70 eV) m/z 414 ($[M]^+$, 5%), 412 ($[M]^+$, 5%), 333 ($[M-Br]^+$, 99%), 236 ($[retro\ D.A.]^+$, 100%), 221 ($[retro\ D.A - CH_3]^+$, 99%); HRMS (EI, 70 eV) m/z 412.0343 ($[M]^+$, 2%), calcd for $C_{21}H_{17}^{79}BrO_4$ 412.0310.

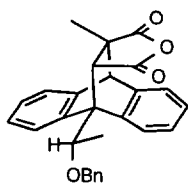


Cycloadduct 4b. Prepared from **1b** (0.118 g, 0.5 mmol) according to the general procedure to afford **4b** (0.146 g, 84% yield) as a white solid. Mp 230 - 232 °C; IR (KBr) ν_{max} 1845, 1777 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 7.0$ Hz, 1H), 7.36 (dd, $J = 6.6, 2.2$ Hz, 1H), 7.32 (dd, $J = 6.6, 2.5$ Hz, 1H), 7.22 - 7.16 (m, 5H), 4.90 (q, $J = 6.4$ Hz, 1H), 4.31 (s, 1H), 3.67 (s, 3H) 3.36 (s, 1H), 1.85 (d, $J = 6.4$ Hz,

3H), 1.14 (s, 3H); ^{13}C NMR (100.0 MHz, CDCl_3) δ 174.8, 169.1, 140.4, 139.6, 137.5, 137.4, 127.5, 127.3, 126.9, 126.5, 126.4, 126.2, 125.6, 123.8, 73.3, 57.1, 55.1, 54.6, 54.2, 52.1, 22.5, 16.5; EIMS (70 eV) m/z 348 ($[\text{M}]^+$, 19%), 236 ($[\text{retro D.A.}]^+$, 94%), 221 ($[\text{retro D.A.} - \text{CH}_3]^+$, 91%), 66 (100%); HRMS (EI, 70 eV) m/z 348.1354 ($[\text{M}]^+$, 1.4%), calcd for $\text{C}_{22}\text{H}_{20}\text{O}_4$ 348.1362.

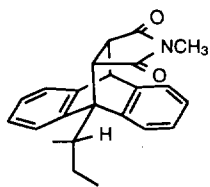


Cycloadduct 4c. Prepared from **1d** (0.493 g, 1.58 mmol) according to the general procedure to afford **4c** (0.616 g, 80% yield), as a white solid. Mp 245 - 246 °C (dec); IR (NaCl) ν_{max} 1854, 1782 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 5.8$, 2.6 Hz, 1H), 7.48 (dd, $J = 6.2$, 2.2 Hz, 1H), 7.49 - 7.20 (m, 11H), 5.12 (q, $J = 6.2$ Hz, 1H), 4.97 (d, $J_{\text{AB}} = 11.0$ Hz, 1H), 4.83 (d, $J_{\text{AB}} = 11.0$ Hz, 1H), 4.80 (s, 1H), 4.00 (s, 1H), 1.92 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 168.0, 166.5, 139.2, 138.4, 137.21, 137.16, 136.8, 128.4 (2C), 128.3, 128.2, 127.8 (2C), 127.7, 127.2, 127.1, 126.8, 126.7, 126.5, 124.1, 72.1, 71.9, 59.2, 58.9, 55.6, 53.3, 17.3; CIMS (140 eV, NH_3) m/z 490 ($[\text{M}]^+$, 4%), 488 ($[\text{M}]^+$, 3.5%), 312 ($[\text{retro D.A.}]^+$, 6%), 303 (93%), 275 (21%), 221 ($[\text{retro D.A.} - \text{Bn}]^+$, 11%), 206 (46%), 205 (100%), 202 (22%), 107 (68%), 91 (97%); HRMS (CI, 140 eV, NH_3) m/z 488.0634 ($[\text{M}]^+$, 2%), calcd for $\text{C}_{27}\text{H}_{21}^{79}\text{BrO}_4$ 488.0623.

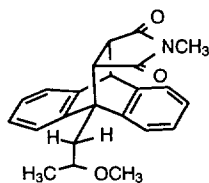


Cycloadduct 4d. Prepared from **1d** (0.162 g, 0.52 mmol) according to the general procedure to afford **4d** (0.190 g, 86% yield), as a white solid. Mp 205 - 206 °C; IR (KBr) ν_{max} 1845, 1775 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.94, (d, $J = 6.8$ Hz, 1H), 7.45 - 7.37 (m, 2H), 7.37 - 7.17 (m, 10H), 5.19 (q, $J = 6.4$ Hz, 1H), 4.98 (d, $J_{\text{AB}} = 11.1$ Hz, 1H), 4.84 (d, $J_{\text{AB}} = 11.1$ Hz, 1H), 4.31 (s, 1H), 3.39 (s, 1H), 1.91 (d, $J = 6.4$ Hz, 3H), 1.12 (s, 3H); ^{13}C NMR (100.0 MHz, CDCl_3) δ 174.7, 169.2, 140.4, 139.6, 138.8, 137.4 (2C), 128.4 (2C), 127.8 (2C), 127.5 (2C), 127.3, 127.1, 126.5, 126.4, 126.1, 125.6, 123.9, 72.4, 71.9, 55.2, 54.7, 54.3, 52.1, 22.6, 17.4; EIMS (70 eV) m/z 424 ($[\text{M}]^+$, 24%), 312 ($[\text{retro D.A.}]^+$, 77%), 297 ($[\text{retro D.A.} - \text{CH}_3]^+$, 15%), 221 ($[\text{retro}$

D.A - 91]⁺, 39%), 206 (100%), 205 (99%), 91 (90%); HRMS (EI, 70 eV) *m/z* 424.1676 ([M]⁺, 2%), calcd for C₂₈H₂₄O₄ 424.1674.

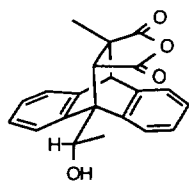


Cycloadduct 6. Prepared from **5** (0.024 g, 0.1 mmol) according to the general procedure to afford a 3:2 mixture of inseparable diastereomers **6** (0.023 g, 66% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 - 7.66 (m, 0.6H), 7.64 - 7.62 (m, 0.4H), 7.38 - 7.36 (m, 1H), 7.32 (d, *J* = 6.6 Hz, 0.4H), 7.25 - 7.09 (m, 5.6H), 4.68 (d, *J* = 3.1 Hz, 1H), 3.34 (d, *J* = 8.4 Hz, 0.4H), , 3.27 (d, *J* = 8.4 Hz, 0.6H), 3.25 (ddq, *J* = 7.3, 7.3, 7.0 Hz, 0.4H), 3.15 (dd, *J* = 7.3, 3.1 Hz, 0.6H), 3.14 (dd, *J* = 7.3, 3.1 Hz, 0.4H), 3.05 (ddq, *J* = 7.3, 7.3, 7.0 Hz, 0.6H), 2.433 (s, 1.8H), 2.427 (s, 1.2H), 2.35 (ddq, *J* = 12.8, 7.3, 7.0 Hz, 0.4H), 1.97 (ddq, *J* = 12.8, 7.3, 7.0 Hz, 1H), 1.85 (ddq, *J* = 12.8, 7.3, 7.0 Hz, 0.6H), 1.67 (d, *J* = 7.0 Hz, 1.8H), 1.52 (d, *J* = 7.0 Hz, 1.2H), 1.27 (t, *J* = 7.0 Hz, 3H); EIMS (70 eV) *m/z* 345 ([M]⁺, 1%), 235 ([retro D.A. + 1]⁺, 26%), 234 ([retro D.A.]⁺, 100%), 205 ([retro D.A - C₂H₅]⁺, 55%); HRMS (EI, 70 eV) *m/z* 345.1709 ([M]⁺, 2%), calcd for C₂₃H₂₃NO₂ 345.1729.

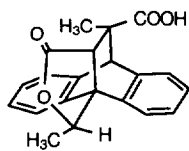


Cycloadduct 8. Prepared from **7** (0.125 g, 0.5 mmol) according to the general procedure for cycloaddition to afford **8** (0.114 g, 63% yield) as a 1.4:1.0 mixture of diastereomers which were separated on silica gel using EtOAc / hexanes (1 / 3). Major diastereomer: IR (KBr) ν_{\max} 1773, 1700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.35 (m, 1H), 7.28 - 7.02 (m, 7H), 4.66 (d, *J* = 2.9 Hz, 1H), 4.16 (br dq, *J* = 8.4, 6.2 Hz, 1H), 3.56 (d, *J* = 8.4 Hz, 1H), 3.40 (dd, *J* = 15.0, 8.4 Hz, 1H), 3.31 (s, 3H), 3.25 (dd, *J* = 8.4, 2.9 Hz, 1H), 2.61 (br d, *J* = 15.0 Hz, 1H), 2.48 (s, 3H), 1.56 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 177.1, 175.9, 143.6, 142.9, 142.5, 138.5, 126.8, 126.3, 126.2, 126.0, 124.8, 124.0, 123.7, 121.9, 74.6, 55.5, 47.8, 47.5, 46.3, 46.0, 34.6, 24.2, 20.1; EIMS (70 eV) *m/z* 361 ([M]⁺, 36%), 347 (27%), 346 (82%), 251 (70%), 235 (53%), 219 (21%), 218 (30%), 217 (49%), 215 (43%), 206 (22%), 205 (23%), 203 (55%), 202 (74%), 193 (26%), 192 (89%), 191 (97%), 190 (38%), 189 (79%), 178 (31%), 165 (31%), 112 (63%), 83 (28%), 59 (91%); (HRMS (EI, 70 eV) *m/z*

361.1665 ($[M]^+$, 3%), calcd for $C_{23}H_{23}NO_3$ 361.1678. Minor diastereomer: IR (KBr) ν_{\max} 1773, 1700 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J = 7.3$ Hz, 1H), 7.31 (dd, $J = 7.0, 1.5$ Hz, 1H), 7.25 - 7.04 (m, 6H), 4.68 (d, $J = 3.0$ Hz, 1H), 4.04 (ddq, $J = 6.6, 5.9, 4.0$ Hz, 1H), 3.33 (s, 3H), 3.31 (dd, $J = 8.4, 3.0$ Hz, 1H), 3.20 (d, $J = 8.4$ Hz, 1H), 3.06 (dd, $J = 14.6, 4.0$ Hz, 1H), 2.82 (dd, $J = 14.6, 6.6$ Hz, 1H), 2.49 (s, 3H), 1.56 (d, $J = 5.9$ Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 177.0, 176.4, 143.4, 142.5, 142.3, 138.9, 126.8, 126.5, 126.1, 126.0, 125.4, 124.9, 123.4, 122.1, 74.6, 55.8, 48.1, 48.0, 46.3, 45.9, 35.8, 24.2, 20.0; EIMS (70 eV) m/z 361 ($[M]^+$, 5%), 346 (62%), 251 ([retro D.A. + 1] $^+$, 77%), 250 ([retro D.A.] $^+$, 100%), 235 ([retro D.A. - CH_3] $^+$, 32%), 217 (23%), 192 (91%), 191 (93%), 83 (20%), 59.0 (97%); HRMS (EI, 70 eV) m/z 361.1694 ($[M]^+$, 1%), calcd for $C_{23}H_{23}NO_3$ 361.1678.

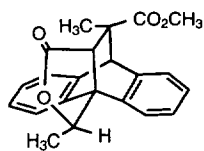


Compound 9. To a solution of **4d** (0.042 g, 0.1 mmol) in anhydrous CH_2Cl_2 (5 mL) was added DDQ (0.114 g, 0.5 mmol) at rt. The mixture was stirred at rt for 12 hr, then quenched by addition of H_2O (5 mL). The layers were separated and the organic layer extracted with H_2O (10 mL) and 10% $NaHCO_3$ (2 x 10 mL). The organic extract was dried over Na_2SO_4 , filtered, and then the solvent was removed in vacuo. The solid obtained was rapidly passed through a 2 inch SiO_2 plug to afford a white solid (0.023 g, 70% yield), which was used as such for the next step without further purification, since it was not stable to further silica gel chromatography. IR (KBr) ν_{\max} 3422, 1775 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.93 - 7.91 (m, 1H), 7.40 - 7.21 (m, 7H), 5.43 (q, $J = 6.4$ Hz, 1H), 4.32 (s, 1H), 3.30 (s, 1H), 1.94 (d, $J = 6.4$ Hz, 3H), 1.16 (s, 3H); EIMS (70 eV) m/z 334 ($[M]^+$, 18%), 245 (28%), 223 ([retro D.A. + 1] $^+$, 70%), 222 ([retro D.A.] $^+$, 100%), 208 ([retro D.A. + 1 - CH_3] $^+$, 24%), 207 ([retro D.A. - CH_3] $^+$, 88%), 205 (26%), 204 (23%), 203 (33%), 202 (41%), 180 (35%), 179 (95%), 178 (79%); HRMS (CI, 140 eV) m/z 334.1211 ($[M]^+$, 2%), calcd for $C_{21}H_{18}O_4$ 334.1205.

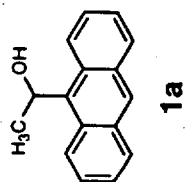


Compound 10. To a solution of **9** (0.022 g, 0.07 mmol) in anhydrous MeOH (4 mL) was added NaOMe (0.038 g, 0.7 mmol) at rt. The mixture was refluxed for

18 hr, then quenched by addition of H₂O (5 mL), followed by 0.5N HCl (5 mL). After adding 20 mL ether, the layers were separated and the organic layer extracted with H₂O (10 mL). The aqueous layer was then extracted with ether (2 x 5 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and then the solvent was removed in vacuo to obtain a white solid which was dissolved in minimum amount of CH₂Cl₂ and triturated with hexane to afford **10** (0.015 g, 65% yield). Mp 220 - 222 °C (dec); IR (KBr) ν_{\max} 3420, 1773 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.72 - 7.70 (m, 1H), 7.34 - 7.31 (m, 2H), 7.19 - 7.14 (m, 5H), 5.37 (q, *J* = 7.0 Hz, 1H), 4.43 (s, 1H), 3.42 (s, 1H), 2.22 (d, *J* = 7.0 Hz, 3H), 1.12 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 178.8, 171.8, 142.6, 141.4, 139.8, 135.6, 126.9, 126.8, 126.71, 126.67, 126.5, 125.8, 124.5, 119.7, 77.6, 55.8, 55.3, 55.1, 49.5, 20.7, 15.9; EIMS (70 eV) *m/z* 335 ([M+1]⁺, 64%), 334 ([M]⁺, 99%), 222 (37%), 221 (74%), 217 (23%), 216 (20%), 215 (61%), 207 (50%), 206 (58%), 205 (100%), 204 (98%), 203 (98%), 202 (90%), 191 (20%), 189 (30%), 179 (55%), 178 (74%), 177 (23%), 176 (33%), 113 (44%), 101 (27%), 44 (26%), 43 (52%), 41 (20%), 28 (30%); HRMS (EI, 70 eV) *m/z* 334.1194 ([M]⁺, 95%), calcd for C₂₁H₁₈O₄ 334.1205.



Compound 11. A solution of **10** (0.015 mg, 0.045 mmol) in anhydrous ether (2 mL) was treated with excess of freshly prepared CH₂N₂ at 0 °C. The mixture was allowed to slowly warm to rt and after 2 hr the solvent was removed in vacuo to afford **11** (0.016 g, 99% yield), as a nearly pure white solid. Mp 208 - 210 °C; IR (KBr) ν_{\max} 1780, 1730 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.72 - 7.70 (m, 1H), 7.34 - 7.30 (m, 1H), 7.28 - 7.26 (m, 1H), 7.20 - 7.14 (m, 5H), 5.34 (q, *J* = 6.8 Hz, 1H), 4.42 (s, 1H), 3.62 (s, 3H), 3.47 (s, 1H), 2.20 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 175.5, 171.9, 142.8, 141.4, 140.2, 135.8, 126.8, 126.62, 126.59 (2C), 126.5, 125.5, 124.4, 119.7, 77.5, 55.8, 55.4, 55.3, 52.7, 49.8, 20.7, 15.9; EIMS (70 eV) *m/z* 349 ([M+1]⁺, 21%), 348 ([M]⁺, 100%), 205 (71%), 204 (31%), 203 (24%), HRMS (70 eV) *m/z* 348.1360 ([M]⁺, 100%), calcd for C₂₂H₂₀O₄ 348.1361.



1.926
1.908

2.122

6.444
6.462
6.472
6.480
6.490
6.496

7.240
7.425
7.441
7.445

7.460
7.464
7.476
7.482
7.485
7.498
7.502

7.980
7.984
8.005

8.383
8.655
8.676

