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SUPPLEMENTARY MATERIAL FOR:

A Combined Computational-Experimental Study of the Kinetics of Intramolecular Diels–Alder Reactions in a Series of 1,3,8-Nonatrienes

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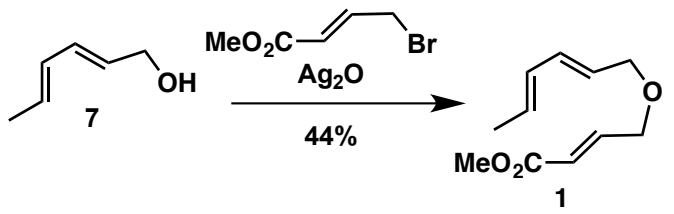
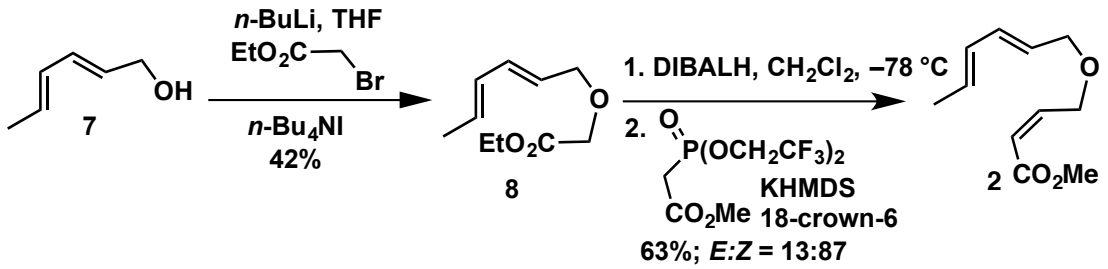
Methyl (*E*)-4-(((2*E*,4*E*)-hexa-2,4-dien-1-yl)oxy)but-2-enoate 1



This compound was prepared by a modification of a literature procedure.[1] Silver (I) oxide (2.78 g, 12 mmol) was stirred under reduced pressure for 2 h before (*E*)-methyl 4-bromobut-2-enoate (3.58 g, 20 mmol) and sorbyl alcohol **7** (6.87 g, 70 mmol) were added. The slurry was stirred under N_2 at room temperature for 90 h, diluted with CH_2Cl_2, filtered through celite and the volatile material was removed under reduced pressure. Flash column chromatography, eluting with 30–40° petrol/diethyl ether (4:1) gave the 1,3,8-nonatriene **1** as a colourless oil (1.71 g, 8.72 mmol, 44%). Colourless oil; R_f = 0.21; 40–60 petrol/diethyl ether (9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (1H, dtd, *J* = 15.6, 4.2, 0.9 Hz), 6.17 (1H, dd, *J* = 15.0, 10.5 Hz), 6.04 (1H, dtd, *J* = 15.6, 2.1, 0.9 Hz), 6.08 – 5.95 (1H, m), 5.68 (1H, dq, *J* = 15.0, 6.9 Hz), 5.56 (1H, dt, *J* = 15.3, 6.3 Hz), 4.08 (2H, dd, *J* = 4.2, 2.1 Hz), 3.98 (2H, d, *J* = 6.3 Hz), 3.69 (3H, s) 1.71 (3H, d, *J* = 6.6 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 144.8, 133.6, 130.7, 130.4, 125.9, 120.7, 71.1, 68.3, 51.6 and 18.1 ppm; IR (thin film) ν = 3020, 2951, 2850, 1725, 1663, 1436 cm^{-1}; MS (70 eV, EI): *m/z* (%): 196 (48) $[M]^+$, 161 (60), 136 (51), 97 (70), 55 (100); HRMS calc for $C_{11}H_{16}O_3$ $[M]^+$: 196.1099; found: 196.1098.

Methyl (*Z*)-4-(((2*E*,4*E*)-hexa-2,4-dien-1-yl)oxy)but-2-enoate 2



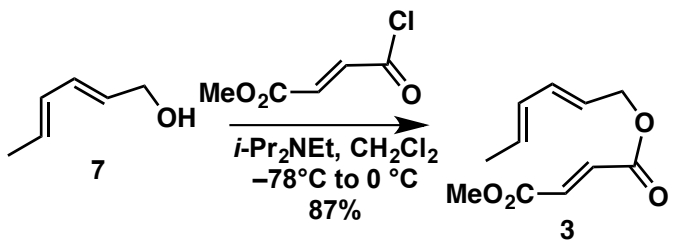
Compound **8** was prepared by a modification of a literature procedure.[2] A 1.6 M solution of *n*-butyllithium in hexanes (6.3 mL, 10 mmol) was added drop-wise to a stirred solution of sorbyl

alcohol (**7**) (0.98 g, 10 mmol) and tetrabutylammonium iodide (0.74 g, 2.0 mmol) in THF (40 mL) under N_2 at –78 °C. After 30 min, ethyl bromoacetate (5.55 mL, 50 mmol) was added drop-wise and the mixture was stirred for 4 h at –78 °C, then at room temperature for 16 h. The reaction mixture was partitioned between diethyl ether and water, the ethereal layer was washed three times with brine, dried over $MgSO_4$ and the volatile material was removed under reduced pressure. Flash column chromatography, eluting with 30–40° petrol/diethyl ether (9:1) gave the desired product **8** as a pale yellow oil (0.775 g, 4.21 mmol 42%): R_f = 0.50; 30–40 petrol/diethyl ether (9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (1H, dd, *J* = 14.1, 10.5 Hz), 6.04 (1H, ddq, *J* = 14.7, 10.5, 1.5 Hz), 5.70 (1H, dq, *J* = 14.7, 6.9 Hz), 5.59 (1H, dt, *J* = 14.7, 6.3 Hz), 4.19 (2H, q, *J* = 7.2 Hz), 4.08 (2H, d, *J* = 6.3 Hz), 4.03 (2H, s), 1.73 (3H, d, *J* = 6.9 Hz), 1.26 (3H, t, *J* = 7.2 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 134.5, 130.8, 130.7, 125.5, 71.9, 67.0, 60.9, 18.2 and 14.3 ppm; IR (thin film) ν = 2983, 1754, 1659, 1446 cm^{-1}; MS (70 eV, EI): *m/z* (%): 184 (78) $[M]^+$, 97 (93), 88 (37), 81 (100); HRMS calc for $C_{10}H_{16}O_3$ $[M]^+$: 184.1099; found: 184.1095.

The reduction of ester **8** to the corresponding aldehyde was performed by a modification of one literature procedure,[2] and the direct application of another.[3] A 1.0 M solution of DIBALH in CH_2Cl_2 (2.2 mL, 2.2 mmol) was added drop-wise to a stirred solution of ethyl 2-((2*E*,4*E*)-hexa-2,4-dienyloxy)acetate **8** (220 mg, 1.20 mmol) in CH_2Cl_2 (10 mL) under N_2 at –78 °C. After 90 min, methanol (100 μL, 2.42 mmol) was added and the mixture was stirred for a further 20 min at −78 °C. The flask was removed from the cooling bath, sat. aq. $KHSO_4$ (2.5 mL), water (2.5 mL), and a crystal of BHT were added and the biphasic mixture was stirred for another 10 min. The reaction mixture was added to water and extracted with CH_2Cl_2. The extracts were combined and washed with brine until the washings were neutral, dried over $MgSO_4$ and carefully reduced in volume under reduced pressure. The aldehyde was used in the next step without further purification. Following the procedure published by the Still group,[3] 18-crown-6 (1.80 g, 6.18 mmol), THF (10 mL) and bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl) phosphonate (0.28 mL, 1.32 mmol) were mixed under N_2 at –78 °C. A 0.5 M solution of potassium bis(trimethylsilyl) amide in toluene (2.60 mL, 1.30 mmol) was added drop-wise and 10 min later a solution of the crude aldehyde in THF (10 mL) was added over 10 min. The reaction was quenched after 40 min with the addition of sat. aq. NH_4Cl and the mixture was added to water and extracted with diethyl ether. The extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Flash column chromatography, eluting with 40–60° petrol/diethyl ether (9:1) allowed gave the Z-alkene **2** as a colourless oil. A small amount of the *E*-isomer **1** was also isolated (combined yield 0.147 g, 0.75 mmol, 63%, **2**:**1** = 87:13). Characterisation data for the *Z*-isomer **2**: colourless oil; R_f = 0.46; 40–60° petrol/diethyl ether (9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (1H, dt, *J* = 11.7, 4.8 Hz), 6.22 (1H,

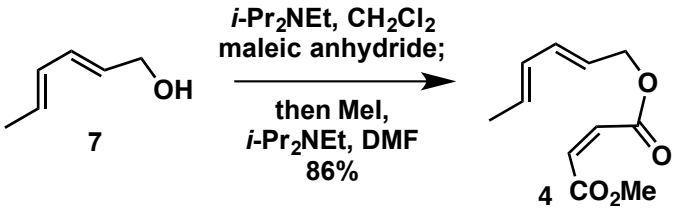
dd, J = 15.0, 10.5 Hz), 6.06 (1H, ddq, J = 14.7, 11.1, 1.5 Hz), 5.82 (1H, dt, J = 11.7, 2.4 Hz), 5.80–5.56 (2H, m), 4.57 (2H, dd, J = 5.0, 2.3 Hz), 4.02 (2H, d, J = 6.0 Hz), 3.71 (3H, s) 1.75 (3H, d, J = 7.2 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 148.9, 133.8, 130.9, 130.4, 126.3, 119.1, 71.3, 68.2, 51.5 and 18.2 ppm; IR (thin film) ν = 3021, 2952, 2851, 1721, 1655, 1438 cm^{-1}; MS (ES+): *m/z* (%): 219 (10) $[M+Na]^+$, 197(4) $[M+H]^+$; HRMS calc for $C_{11}H_{16}O_3$ $[M]^+$: 196.1099; found: 196.1102.

(2*E*,4*E*)-Hexa-2,4-dien-1-yl methyl fumarate 3



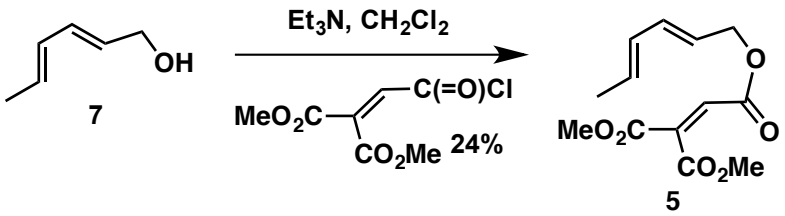
A solution of sorbyl alcohol **7** (8.4 g, 86 mmol) and diisopropylethylamine (16.6 g, 129 mmol) in CH_2Cl_2 (300 mL) was cooled to –78 °C. Methyl fumaroyl chloride (13.47g, 91 mmol) was added drop-wise over 20 min and the mixture was stirred at –78 °C for a further 20 min and then allowed to warm to 0 °C over 20 min. Aqueous HCl (1.0 M, 100 mL, 100 mmol) was added and the biphasic mixture was stirred at 0 °C for 10 min before being transferred to a separating funnel. The mixture was then diluted with diethyl ether and shaken carefully, and the lower, aqueous layer was discarded. The organic layer was washed twice with aqueous HCl (1.0 M), three times with saturated aqueous Na_2CO_3, once with water, once with brine, and then dried over $MgSO_4$. Removal of the solvents under reduced pressure at RT gave the title compound **3** as a white solid (15.68 g, 75 mmol, 87%) that gave analytical data matching previously reported values.[4] This compound can be taken up in *n*-pentane (20 mL/g) and recrystallised by slowly cooling from RT to –50°C. The recovery after five cycles was approximately 80%. This compound can be stored as a solid at −20 °C.

(2*E*,4*E*)-Hexa-2,4-dien-1-yl methyl maleate 4



A solution of sorbyl alcohol **7** (9.99 g, 102 mmol) and diisopropylethylamine (22.26 g, 172 mmol) in CH_2Cl_2 (200 mL) was cooled to 0 °C. Maleic anhydride (10.8 g 110 mmol) was added and the mixture was allowed to warm to RT over 1 hr. The reaction mixture was transferred to a separating funnel, diluted with diethyl ether, and washed four times with HCl (1.0 M) and once with a small quantity of water (10 mL). The organic layer was then dried over $MgSO_4$ and the solvents were quickly removed under reduced pressure at RT. The residue was taken up in DMF (40 mL) and cooled to 0 °C, and diisopropylethylamine (14.22 g, 110 mmol) was carefully added. Methyl iodide (28.39 g, 200 mmol) was added and the mixture was stirred at RT for 2 hr. The excess methyl iodide was removed under reduced pressure at RT. The reaction mixture was added to aqueous HCl (1.0 M, 200 mL), and the aqueous phase was washed four times with diethyl ether. The organic layers were pooled and washed four times with aqueous HCl (1.0 M) and twice with saturated aqueous $NaHCO_3$. The organic phase was then dried over $MgSO_4$ and the solvent was removed under reduced pressure at RT. The crude material was purified by flash column chromatography eluting with a gradient (30–40 petrol to 1% diethyl ether in 30–40 petrol) to give the title compound **4** as a colourless oil (18.47 g, 88 mmol, 86% over two steps) that gave analytical data matching previously reported values.[4] This compound can be taken up in *n*-pentane (50 mL/g) and recrystallised by slowly cooling from 0 °C to –78 °C. The recovery after three cycles was approximately 80%. This compound is best stored as a dilute solution in CH_2Cl_2 at –20 °C.

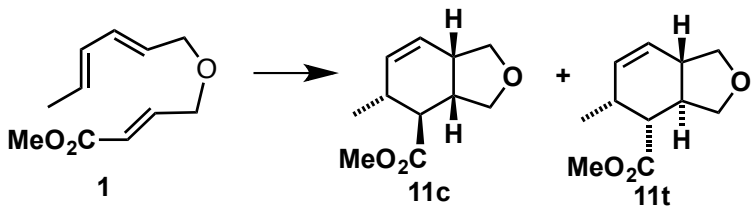
2-((2*E*,4*E*)-Hexa-2,4-dien-1-yl) 1,1-dimethyl ethene-1,1,2-tricarboxylate 5



1,1-Dimethyl 2-hydrogen ethylenetricarboxylic acid[5] was prepared from 2-*tert*-butyl 1,1-dimethyl ethylenetricarboxylate using the procedure of Snider.[6] Oxalyl chloride (76.4 mg, 0.602 mmol, 2.0 mol equiv) and DMF (0.4 mg, 6.02 μmol, 0.02 mol equiv) were added to a stirred solution of 1,1-dimethyl 2-hydrogen ethylenetricarboxylic acid[5] (56.6 mg, 0.301 mmol, 1.0 mol equiv) in benzene (0.5 mL) at RT under N_2. The solution was stirred for 20 min until the visible evolution of gas ceased. The mixture was concentrated under reduced pressure, diluted into CH_2Cl_2 (0.5 mL) and added to a solution of *trans,trans*-2,4-hexadienol-1-ol (29.5 mg, 0.301 mmol, 1.0 equiv) and triethylamine (45.6 mg, 0.451 mmol, 1.5 equiv) in pentanes (0.5 mL) stirred at 0 °C. The mixture was stirred for 10 min. Diethyl ether (10 mL) was added and the mixture was washed once with 2 M HCl then once with saturated brine, dried ($NaSO_4$), filtered and concentrated under reduced pressure. The crude material was subjected to column chromatography on silica (pentane/diethyl ether 70:30) to give triene **5** (19.0 mg, 0.0708 mmol, 24%) as a colourless oil. R_f = 0.42 (pentane/diethyl ether 70:30). ^{1}H NMR (300 MHz, C_6D_6): δ 6.87 (1H, s), 5.99 (1H, dd, *J* = 15.0, 10.4 Hz), 5.82 (1H, m), 5.44 (1H, dq, *J* = 15.0, 6.6 Hz), 5.35 (1H, ddd, *J* = 15.0, 6.7, 6.2 Hz), 4.37 (2H, d, *J* = 6.8 Hz), 3.59 (3H, s), 3.16 (3H, s), 1.49 (3H, d, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 164.6 (C), 163.4 (C), 162.8 (C), 139.4 (C), 135.9 (CH), 131.5 (CH), 130.9 (CH), 130.6 (CH), 123.2 (CH), 66.1 (CH_2), 52.6 (CH_3), 52.6 (CH_3), 18.1 (CH_3). IR (thin film): ν = 2955, 1798, 1735, 1635 cm^{-1}.

Intramolecular Diels–Alder (IMDA) reactions of 1,3,8-nonatrienes 1, 2, 3, 4 and 5

IMDA reaction of methyl (*E*)-4-(((2*E*,4*E*)-hexa-2,4-dien-1-yl)oxy)but-2-enoate 1



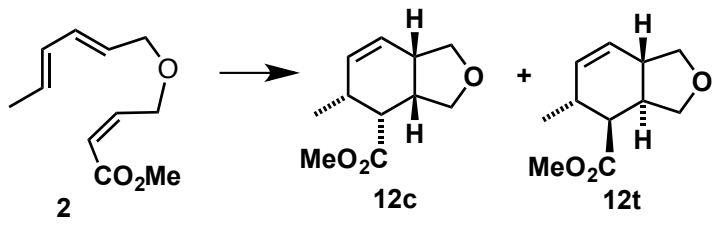
A stirred solution of (2*E*)-methyl 4-((2*E*,4*E*)-hexa-2,4-dienyloxy)but-2-enoate **1** (200 mg, 1.02 mmol) and a crystal of BHT in toluene (100 mL) was heated to reflux (110 °C) under N_2 for 20 h. The solvent was removed under reduced pressure and the crude material was subjected to flash

column chromatography, eluting with 30–40° petrol/diethyl ether (4:1), affording the diastereomeric IMDA adducts (131 mg, 0.67 mmol 66%, **11c**:**11t** = 27:73). The IMDA adducts were isolated in pure form by column chromatography.

Cycloadduct 11c: **methyl (3a*S**,4*S**,5*R**,7a*S**)-5-methyl-1,3,3a,4,5,7a-hexahydroisobenzo-furan-4-carboxylate:** colourless oil; R_f = 0.29; 30–40 petrol/diethyl ether (4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (1H, dt, *J* = 9.9, 2.7 Hz), 5.57 (1H, dt, *J* = 9.9, 1.8 Hz), 4.01 (1H, t, *J* = 8.4 Hz), 3.89 (1H, dd, *J* = 9.0, 5.7 Hz), 3.71 (3H, s), 3.67 (1H, dd, *J* = 9.3, 2.1 Hz), 3.35 (1H, dd, *J* = 9.6, 8.1 Hz), 2.88 – 2.51 (1H, m), 2.64 – 2.48 (1H, m), 2.50 – 2.32 (1H, m), 2.09 (1H, dd, *J* = 12.0, 10.8 Hz), 1.00 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 133.4, 124.4, 72.5, 72.4, 51.6, 49.4, 40.4, 39.3, 32.9 and 19.7 ppm; IR (thin film) ν = 3021, 2957, 2873, 1733, 1435 cm^{-1}; MS (70 eV, EI): *m/z* (%): 196 (7) [M]$^+$, 165 (26), 119 (51), 107 (100), 91 (94); HRMS calc for $C_{11}H_{16}O_3$ [M]$^+$: 196.1099; found: 196.1096.

Cycloadduct 11t: **methyl (3a*R**,4*R**,5*R**,7a*S**)-5-methyl-1,3,3a,4,5,7a-hexahydroisobenzo-furan-4-carboxylate**: colourless oil; R_f = 0.20; 30–40 petrol/diethyl ether (4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (1H, bd, *J* = 9.6 Hz), 5.61 (1H, dt, *J* = 9.9, 2.7 Hz), 4.27 (1H, t, *J* = 7.5 Hz), 4.04 (1H, t, *J* = 7.2 Hz), 3.69 (3H, s), 3.45 – 3.31 (2H, m), 2.92 – 2.76 (2H, m), 2.45 – 2.31 (1H, m), 2.13 (1H, qd, *J* = 11.1, 6.9 Hz), 0.94 (3H, d, *J* = 7.2 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 134.1, 123.5, 70.6, 70.4, 51.6, 47.0, 44.6, 40.0, 33.4 and 17.4 ppm; IR (thin film) ν = 3022, 2950, 2853, 1737, 1635, 1436 cm^{-1}; MS (70 eV, EI): *m/z* (%): 196 (4) [M]$^+$, 165 (13), 149 (15), 119 (48), 107 (100), 91 (83); HRMS calc for $C_{11}H_{16}O_3$ [M]$^+$: 196.1099; found: 196.1096.

IMDA reaction of methyl (*Z*)-4-(((2*E*,4*E*)-hexa-2,4-dien-1-yl)oxy)but-2-enoate 2



A stirred solution of (2*Z*)-methyl 4-((2*E*,4*E*)-hexa-2,4-dienyloxy)but-2-enoate **2** (80 mg, 0.41 mmol) in toluene (40 mL) was heated to reflux (110 °C) under N_2 for 6 h. The solvent was removed under reduced pressure and the crude material was subjected to flash column chromatography, eluting with 30–40° petrol/diethyl ether (4:1) to give a mixture of cycloadducts (75 mg, 0.38 mmol,

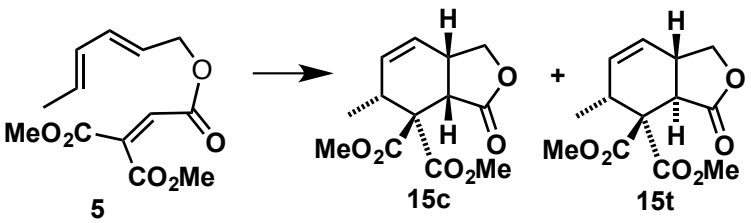
93%, **12c**:**12t** = 51:49. The diastereoisomeric IMDA adducts were separated by HPLC, eluting with 40–60° petrol/ethyl acetate (17:3).

Cycloadduct 12c: **methyl (3a*S***,4*R***,5*R***,7a*S***)-5-methyl-1,3,3a,4,5,7a-hexahydroisobenzo-furan-4-carboxylate:** colourless oil; t_R = 13.7 min, hexane-ethyl acetate (17:3); R_f = 0.51; 30–40 petrol/ethyl acetate (4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (1H, ddd, *J* = 13.2, 4.8, 1.8 Hz), 5.57 (1H, dm, *J* = 10.2 Hz), 4.06 – 3.90 (2H, m), 3.81 (1H, dd, *J* = 8.4, 6.3 Hz), 3.70 (3H, s), 3.66 (1H, dd, *J* = 8.1, 2.1 Hz), 3.04 (1H, dd, *J* = 6.0, 4.2 Hz) 2.86 – 2.74 (2H, m), 2.74 – 2.58 (1H, m), 1.05 (3H, d, *J* = 7.5 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 132.3, 127.1, 73.2, 70.6, 51.6, 44.1, 39.4, 38.0, 30.2 and 18.1 ppm; IR (thin film) ν = 3015, 2953, 2878, 1734, 1658, 1435 cm^{-1}; MS (70 eV, EI): *m/z* (%): 196 (19) $[M]^+$, 166 (39), 136 (19), 107 (100), 91 (72); HRMS calc for $C_{11}H_{16}O_3$ $[M]^+$: 196.1099; found: 196.1099.

Cycloadduct 12t: **methyl (3a*R***,4*S***,5*R***,7a*S***)-5-methyl-1,3,3a,4,5,7a-hexahydroisobenzo-furan-4-carboxylate:** colourless oil; t_R = 15.8 min, hexane-ethyl acetate (17:3); R_f = 0.51; 30–40 petrol/ethyl acetate (4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (1H, bd, *J* = 9.9 Hz), 5.62 (1H, dt, *J* = 9.9, 2.7 Hz), 4.06 (1H, t, *J* = 7.5 Hz), 3.96 (1H, t, *J* = 7.5 Hz), 3.66 (3H, s), 3.59 (1H, dd, *J* = 11.1, 7.5 Hz), 3.33 (1H, dd, *J* = 11.1, 7.2 Hz), 2.82 – 2.70 (1H, m), 2.71 (1H, d, *J* = 4.2 Hz), 2.58 – 2.43 (1H, m), 2.10 (1H, tdd, *J* = 11.4, 7.2, 4.2 Hz), 1.12 (3H, d, *J* = 7.5 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 133.4, 123.8, 70.7, 70.1, 51.6, 44.6, 40.9, 39.0, 33.4 and 21.8 ppm; IR (thin film) ν = 3021, 2956, 2872, 1734, 1636, 1436 cm^{-1}; MS (70 eV, EI): *m/z* (%): 196 (7) $[M]^+$, 166 (75), 119 (68), 107 (100), 91 (79); HRMS calc for $C_{11}H_{16}O_3$ $[M]^+$: 196.1099; found: 196.1099.

*The IMDA reactions of fumarate **3** and maleate **4** have been previously reported and cycloadducts **13c**, **13t**, **14c** and **14t** have been previously characterised.*

IMDA reaction of 2-((2*E*,4*E*)-hexa-2,4-dien-1-yl) 1,1-dimethyl ethene-1,1,2-tricarboxylate 5



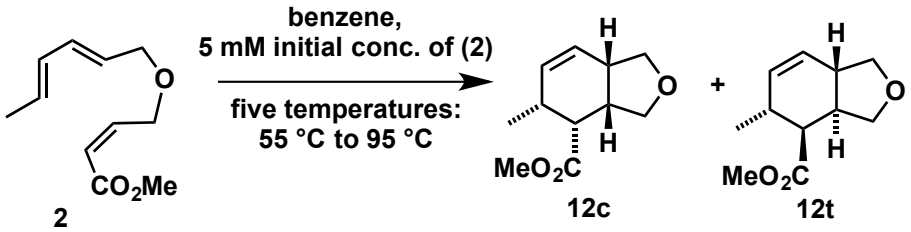
Triene **5** (19.0 mg, 0.0708 mmol, 1.0 mol equiv) and BHT (1.6 mg, 7.08 μmol, 0.1 equiv) in C_6D_6 (2 mL) was warmed to 25 °C for 20 h. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and the measured ratio of the *trans*-adduct **15t** and *cis*-adduct **15c**, **15t**:**15c** (95:5) was consistent with that obtained by GC analysis. The reaction mixture was concentrated under reduced pressure and the residue was recrystallised from hexanes/ethyl acetate 80:20 to give *trans*-adduct **15t** (15.2 mg, 0.0567 mmol, 80%) as colourless crystals. The supernatant was concentrated under reduced pressure and the residue (3.3 mg) was subjected to chromatography on silica (hexanes/ethyl acetate 60:40) to give a mixture of *trans*-adduct **15t** and *cis*-adduct **15c** (2.1 mg, 7.8 μmol, 11%; **15t**:**15c** = 44:56). For characterisation purposes, a portion of *trans*-adduct **15t** was epimerised (CH_2Cl_2, 1.1 mol equiv DBU, RT, 14 h) to give a quantitative yield of *cis*-adduct **15c**.

Cycloadduct 15*c*: dimethyl (3a*S,5*R**,7a*S**)-5-methyl-3-oxo-3,3a,5,7a-tetrahydroisobenzo-furan-4,4(1*H*)-dicarboxylate:** colourless crystalline solid, recrystallised from hexanes. R_f = 0.21 (hexanes/ethyl acetate 60:40). m.p. 94–95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.85 (1H, ddd, *J* = 10.1, 5.1, 2.4 Hz), 5.55 (1H, ddd, *J* = 9.9, 3.2, 1.5 Hz), 4.45 (1H, dd, *J* = 8.7, 8.0 Hz), 4.08 (1H, dd, *J* = 8.8, 3.9 Hz), 3.79 (3H, s), 3.75 (3H, s), 3.75 (1H, d, *J* = 9.3 Hz), 3.41 (1H, m), 3.08 (1H, m), 1.24 (3H, d, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 176.0 (C), 170.5 (C), 168.6 (C), 133.7 (CH), 124.9 (CH), 71.2 (CH_2), 57.9 (C), 53.5 (CH_3), 52.8 (CH_3), 52.8 (CH_3), 42.3 (CH), 35.4 (CH), 34.5 (CH), 17.8 (CH_3). IR (KBr): ν = 3047, 3005, 2971, 2927, 2852, 1765, 1751, 1733, 1656 cm^{-1}. EIMS (70 eV) *m/z* (%): 267 ([M–1]$^+$, 10), 237 ([M–CH_3O]$^+$, 10), 210 ([M–$C_2H_2O_2$]$^+$, 40), 112 ([M–$C_8H_{12}O_3$]$^+$, 100). HRMS: calcd for $C_{13}H_{16}O_6$ [M]$^+$: 268.0947; found: 268.0955.

Cycloadduct 15*t*: dimethyl (3a*R,5*R**,7a*S**)-5-methyl-3-oxo-3,3a,5,7a-tetrahydroisobenzo-furan-4,4(1*H*)-dicarboxylate:** colourless crystalline solid, recrystallised from hexanes/ethyl acetate 80:20. R_f = 0.17 (hexanes/ethyl acetate 60:40). m.p. 117–119 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 5.26 (1H, ddd, *J* = 9.8, 3.9, 2.5 Hz), 5.04 (1H, ddd, *J* = 9.8, 1.7, 1.7 Hz), 3.62 (1H, dd, *J* = 8.1, 6.9 Hz), 3.46 (1H, m), 3.38 (3H, s), 3.31 (3H, s), 2.98 (1H, dd, *J* = 11.2, 8.2 Hz), 2.50 (1H, d, *J* = 14.1 Hz), 2.34 (1H, m), 0.77 (3H, d, *J* = 7.5 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 170.9 (C), 169.4 (C), 168.4 (C), 134.8 (CH), 122.1 (CH), 68.8 (CH_2), 58.0 (C), 52.6 (CH_3), 52.2 (CH_3), 43.3 (CH), 38.3 (CH), 37.2 (CH), 18.1 (CH_3). IR (KBr): ν = 3008, 2969, 2955, 2921, 2902, 2866, 1799, 1752, 1729, 1640 cm^{-1}. EIMS (70 eV) *m/z* (%): 268 ([M]$^+$, 35), 237 ([M–CH_3O]$^+$, 30), 209 ([M–$C_2H_3O_2$]$^+$, 70), 177 ([M–$C_3H_7O_3$]$^+$, 100). HRMS: calcd for $C_{13}H_{16}O_6$ [M]$^+$: 268.0947; found: 268.0950.

Section 2: Experimental Rate Studies

The experimental method for the kinetic study of the IMDA reaction of Z-ether 2 is provided here as an example.



A solution of (2*Z*)-methyl 4-((2*E*,4*E*)-hexa-2,4-dienyloxy)but-2-enoate **5** (25 mg, 0.128 mmol), *t*-butyl benzene (5 mg, 0.037 mmol) and BHT (1 mg) in C_6D_6 (30 mL) was stirred under nitrogen for 30 mins. The solution was then sealed into 20 ampoules. These 20 ampoules were placed in an ethylene glycol-filled Lauda Ecoline 006 bath fitted with a Lauda E 300 thermostat and pump. The bath temperature was regulated to 55, 65, 75, 85 or 95 ±0.05 °C (328.15, 338.15, 348.15, 358.15 or 368.15 ±0.05 K). The ampoules were removed at regular intervals over two half-lives of reaction and cooled quickly by immersion in a CO_2/acetone bath. The ampoules were later brought to room temperature and opened, and the solutions were filtered and transferred to NMR tubes. Quantitative 300 MHz ^{1}H NMR spectra were obtained and the consumption of the triene **2** and production of the cycloadducts, **12c** and **12t**, were followed by the integrals of the resonances of the corresponding methyl groups relative to the resonance of the *t*-butyl group of the internal standard. The experimental rate constants and stereoselectivities are presented in Table S1.

Entry	Temperature (°C), (K)		k_{ob}(sec^{-1})	12c:12t	k(*cis*) (sec^{-1})	k(*trans*) (sec^{-1})
1	55	328.15	0.00122	0.935	0.000590	0.000631
2	65	338.15	0.00267	0.971	0.00132	0.00135
3	75	348.15	0.00565	1.020	0.00285	0.00279
4	85	358.15	0.01284	1.041	0.00654	0.00629
5	95	368.15	0.02659	1.075	0.0138	0.0128

Table S1. Observed rate constants, stereoselectivities, and partitioned rate constants obtained from kinetics study with 1,3,8-nonatriene **2**.

The observed rate constants were partitioned using the stereoselectivity data into rate constants for the cycloadditions producing the *cis* fused and *trans* fused IMDA adducts **12c** and **12t**. The partitioned rate constant data were used in the construction of Arrhenius plots from which the activation energies, E_a, and pre-exponential factors, A, of the cycloadditions giving the *cis* fused cycloadduct and the *trans* fused cycloadduct were calculated. The partitioned rate constant data were also used in the construction of Eyring plots, from which the enthalpies of activation $\Delta H^{\ddagger}$, entropies of activation $\Delta S^{\ddagger}$ and free energies of activation $\Delta G^{\ddagger}$ of the cycloadditions giving the *cis* fused cycloadduct **12c** and the *trans* fused cycloadduct **12t** were obtained.

Sample calculations of the enthalpy of activation, $\Delta H^{\ddagger}$, entropy of activation, $\Delta S^{\ddagger}$, and free energy of activation, $\Delta G^{\ddagger}$, for the cycloaddition of the Z-ether substrate 2 producing the cis-fused adduct are provided here as an example

An Eyring plot of ln (k/T) vs. 1/T gave a straight line described by the equation below,

$$y = mx + c$$

where

$$m = 9105.1$$

and

$$c = 14.55$$

The enthalpy of activation, $\Delta H^{\ddagger}$, for the cycloaddition producing adduct **12c** is calculated from the gradient, m, and the gas constant, R, as follows.

$$\Delta H^{\ddagger} = -m \times R$$
$$\Delta H^{\ddagger} = 9105.1 \times 8.314$$
$$\Delta H^{\ddagger} = 75.7\ kJ/mol$$

The entropy of activation, $\Delta S^{\ddagger}$, for the cycloaddition giving adduct **12c** is obtained from the y intercept, c, the gas constant, R, the Boltzmann constant, k_b, and the Planck constant, h, as follows.

$$\Delta S^{\ddagger} = R(c - \ln(k_b / h))$$
$$\Delta S^{\ddagger} = 8.314 \times (14.55 - \ln(1.381 \times 10^{-23} / 6.626 \times 10^{-34})$$
$$\Delta S^{\ddagger} = -76.6\, J/K/mol$$

The free energy of activation, $\Delta G^{\ddagger}$, for the cycloaddition giving adduct **12c** is calculated from $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and the absolute temperature, T, as follows.

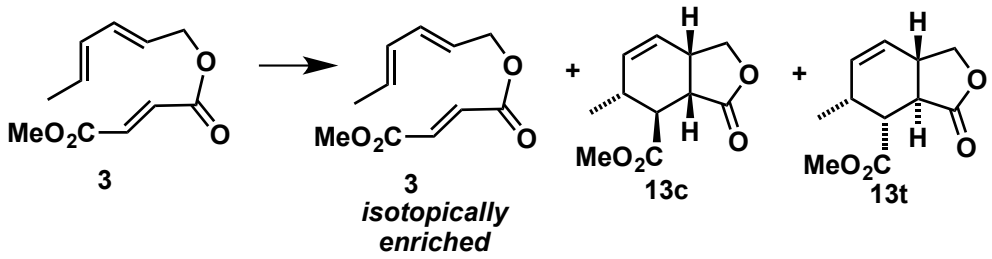
$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$
$$\Delta G^{\ddagger} = 75.7 - (348.15 \times -76.6)$$
$$\Delta G^{\ddagger} = 102.4\, kJ/mol\ at\ 75\,°C$$

Additional information on rate studies

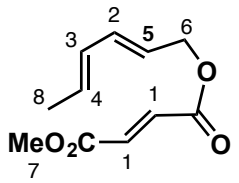
Reactant	*trans (t)*			*cis (c)*			Temperature (°C)	
	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	Exptl	Study range
E-ether **1**	0.8	1.3	1.3	0.9	1.3	1.4	90	70–110
Z-ether **2**	1.0	1.5	1.5	1.0	1.4	1.5	75	55–95
E-ester **3**	2.8	4.7	4.7	2.9	4.4	4.7	140	120–160
Z-ester **4**	1.5	2.8	2.5	1.7	3.5	3.0	90	70–110
Diester **5**	2.6	5.5	4.3	3.3	8.9	6.1	39	23–55

Table S2. Experimental uncertainties in activation enthalpies ($\Delta H^{\ddagger}$, kJ/mol), entropies ($\Delta S^{\ddagger}$, J/K/mol), and free energies ($\Delta G^{\ddagger}$, kJ/mol), reaction temperatures and experimental study ranges for IMDA reactions of trienes **1**–**5**.

Section 3. Experimental natural abundance kinetic isotope effect study with (2E,4E) hexadienyl methyl fumarate 3



A solution of BHT (220 mg 1.0 mmol) in chlorobenzene (5.4 L) was heated to reflux (130 °C) in a 10 L round bottom flask fitted with an overhead stirrer. A solution of >99.95% pure (2*E*,4*E*)-hexadienyl methyl fumarate **3** (10.193 g, 48.5 mmol) and benzophenone (1.9358 g, 10.6 mmol) in chlorobenzene (100 mL) was stirred under nitrogen for 30 min, before being poured into the 10 L round bottom flask. 400 minutes later, a coiled glass tube containing a stream of cold water was immersed in the contents of the flask, causing the internal temperature to drop to below +50 °C within approximately 5 min. The degree of completion of the reaction was then determined with high precision by a calibrated normal phase HPLC method using benzophenone as an internal standard. The degree of completion observed was 0.9614. The solvent was removed at RT under reduced pressure, leaving a mixture of cycloadducts containing small quantities of benzophenone and the 1,3,8-nonatriene. The unreacted 1,3,8-nonatriene was purified by two iterations of column chromatography eluting with hexane:ethyl acetate (20:1), giving 382 mg of triene **3**, a recovery of 97%. The recovered triene and a sample of the starting material for the isotopic fractionation reaction were taken up in $CHCl_3$ and transferred to NMR tubes. The quantitative 123 MHz ^{2}H NMR spectra of the two samples were integrated through a curve-fitting programme in the Bruker software, based on a Lorentzian lineshape. This gave NMR data suitable for the calculation of the ^{2}H KIEs and their associated uncertainties (Table S3).



Entry	Frequency	R_0 integral	R_{final} integral	R/R_0	F
1	6.86	350.323	358.380	1.0230	0.9614
2	6.29	222.654	223.389	1.0033	0.9614
3	6.07	247.850	220.884	0.8912	0.9614
4	5.78	271.593	235.091	0.8656	0.9614
5	**5.64**	**269.532**	**205.275**	**0.7616**	**0.9614**
6	4.69	334.855	341.318	1.0193	0.9614
7	3.80	526.953	526.953	1.0000	0.9614
8	1.77	586.403	559.722	0.9545	0.9614

Table S3. H NMR shifts and integrals for samples of 1,3,8-nonatriene (**3**), before and after a large scale isotopic fractionation event.

Using the data from entry 5, the KIE can be calculated in the following way:[7]

$$KIE_{calc} = \frac{\ln(1-F)}{\ln[(1-F)R/R_0]}$$

$$KIE_{calc} = \frac{\ln(0.0386)}{\ln[(0.0386)0.7616]}$$

$$KIE_{calc} = 0.92$$

Using conservative estimates of the uncertainties in the degree of completion, ΔF, and the ^{2}H NMR data, $\Delta R/R_0$, the uncertainty in the observed KIE for entry 5 can be calculated in the following way:[7]

$$\Delta KIE = \left[\frac{-\ln(R/R_0)}{(1-F)\ln^2[(1-F)R/R_0]}\Delta F\right] + \left[\frac{-\ln(1-F)}{(R/R_0)\ln^2[(1-F)R/R_0]}\Delta R/R_0\right]$$

$$\Delta KIE = \left[\frac{-\ln(0.7616)}{(0.0386)\ln^2[(0.0386)0.7616]}\times 0.001\right] + \left[\frac{-\ln(0.0386)}{(0.7616)\ln^2[(0.0386)0.7616]}\times 0.02\right]$$

$$\Delta KIE = 0.0009 + 0.0069 \approx 0.01$$

The experimental KIEs and their uncertainties for the other positions in triene **3** were calculated using the above equations.

References

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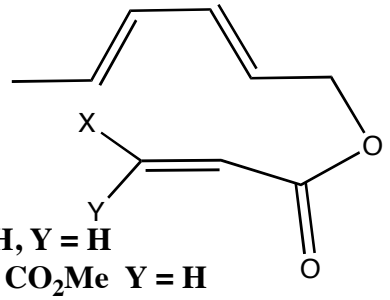
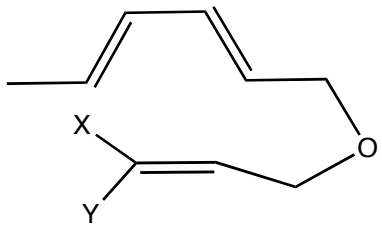
Section 4: Computational Section

Nomenclature for the molecules



acrylate X = H, Y = H
fumarate X = CO_2Me Y = H
maleate X = H Y = CO_2Me
9,9-diester X, Y = CO_2Me



9-

E-9-ester ether tether X = CO_2Me Y = H
Z-9-ether testher X = H Y = CO_2Me

1 Cartesian coordinates and energies of structures optimised in benzene using the CPCM solvation model

```
reactant_1_Me_acrylate
B3LYP/6-31G(d)[CPCM=BENZENE]
Eel = -500.58960360 au;  Energy(0K)) = -500.39897262 au
Enthalpy = -500.38554333 au;  Gibbs energy = -500.43952943 au
C     0.801902     -0.250670     0.622198
C     1.918213     -0.371426     -0.116192
C     -0.512781     -0.844335     0.239650
C     3.219705     0.158292     0.259799
C     4.329863     0.022596     -0.485980
C     5.682589     0.559231     -0.128249
O     -1.490629     0.230862     0.169887
C     -3.669371     1.031255     -0.069131
C     -2.770536     -0.150563     -0.031912
O     -3.117640     -1.310260     -0.164022
C     -4.982686     0.888686     -0.261792
H     0.831275     0.283141     1.571841
H     1.867949     -0.906485     -1.066035
H     -0.468177     -1.348760     -0.730816
H     -0.868718     -1.571302     0.978992
H     3.275670     0.695787     1.207598
```

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H     4.259985     -0.518800     -1.431074
H     6.424714     -0.248419     -0.064280
H     5.668335     1.086578     0.831286
H     6.048075     1.255209     -0.895862
H     -3.205618     2.003626     0.066926
H     -5.417963     -0.097719     -0.395258
H     -5.650759     1.743935     -0.290587
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##########################

CIS IMDA TS from 1_Me_acrylate B3LYP
B3LYP/6-31G(d)[CPCM=BENZENE]
Eel = -500.53509744 au; Energy(0K)) = -500.34352860 au
Enthalpy = -500.33229561 au; Gibbs energy = -500.37891450 au

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C     -0.451578     -1.324532     0.490133
C     0.274230     -1.456710     -0.686551
C     1.578015     -0.951012     -0.817020
C     2.227284     -0.253421     0.193174
C     3.575941     0.384305     -0.009433
C     -1.956847     -1.378514     0.497045
O     -2.482685     -0.190090     -0.154814
C     -1.651673     0.892378     -0.159419
C     -0.520120     0.842148     0.816901
C     0.698610     1.446637     0.555389
O     -1.877089     1.807423     -0.922308
H     0.055377     -1.424850     1.444451
H     -0.264146     -1.701391     -1.602080
H     2.006570     -0.915563     -1.818173
H     1.976863     -0.486126     1.224160
H     3.676474     1.308277     0.571192
H     3.753584     0.623306     -1.063332
H     4.379310     -0.288619     0.322532
H     -2.355272     -1.431964     1.515620
H     -2.362049     -2.215976     -0.079306
H     -0.815775     0.672847     1.850726
H     1.318713     1.792111     1.375179
H     0.865374     1.921605     -0.405309
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TRANS IMDA TS from 1_Me_acrylate B3LYP
B3LYP/6-31G(d)[CPCM=BENZENE]
Eel = -500.53408637 au; Energy(0K)) = -500.34246585 au
Enthalpy = -500.33126646 au; Gibbs energy = -500.37782137 au

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C     0.538001     -1.410633     0.623179
C     -0.581034     -0.602918     0.766640
C     -1.865556     -0.826779     0.031480
O     -2.568865     0.314178     -0.242979
C     -1.806354     1.544507     -0.135669
C     -0.364437     1.195500     -0.357133
C     0.747300     1.779126     0.231470
C     1.990848     1.123588     0.180548
C     2.183164     -0.103655     -0.441806
C     3.484968     -0.854710     -0.353571
O     -2.314747     -1.897969     -0.310309
H     0.553642     -2.176786     -0.146212
H     1.215398     -1.553137     1.455940
H     -0.707322     -0.060087     1.701170
H     -2.222770     2.204667     -0.904008
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H	-1.975912	2.000757	0.846885
H	-0.207357	0.640980	-1.280491
H	0.614610	2.576454	0.961400
H	2.779311	1.490845	0.837198
H	1.566231	-0.355478	-1.299162
H	3.322897	-1.938382	-0.332493
H	4.050451	-0.577867	0.542829
H	4.118306	-0.645799	-1.227576

##########################

9,9-Diester REACTANT B3LYP
B3lyp/6-31G(d)[CPCM=benzene]
Eel = -956.33647031 ; energy(0K) = -956.05967429
Enthalpy = -956.03548496 ; Gibbs energy = -956.11819968

M06-2X/6-31G(d)[CPCM=benzene]//B3lyp/6-31G(d)[CPCM=benzene]
Eel = -955.9325133 ; energy(0K) = -955.6557173
Enthalpy = -955.6315279 au; Gibbs energy = -955.7142427 au

H	3.620105	0.099352	-1.668990
C	3.589941	-0.340995	-0.672865
C	4.671072	-0.282720	0.123505
C	2.318779	-1.018080	-0.285706
C	5.937380	0.330910	-0.243532
H	4.617545	-0.726687	1.118958
C	7.009844	0.376299	0.565767
H	5.998359	0.776273	-1.237530
C	8.326300	1.003914	0.222168
H	6.934235	-0.074538	1.556818
H	8.581159	1.801729	0.933172
H	8.320119	1.433068	-0.785147
H	9.141049	0.268865	0.276689
H	2.045571	-1.820452	-0.980376
O	1.247918	-0.026145	-0.320525
H	2.368265	-1.444142	0.720854
C	-0.981120	0.611014	-0.154051
C	0.010070	-0.492718	-0.086774
O	-0.253224	-1.657988	0.150292
C	-2.294418	0.423448	0.039828
H	-0.613792	1.609772	-0.365775
C	-3.204476	1.611939	-0.054552
C	-2.911112	-0.903441	0.410211
O	-3.141476	-1.230464	1.552888
O	-3.214197	-1.619834	-0.678598
C	-3.797214	-2.914233	-0.423461
O	-2.834570	2.746975	-0.275621
O	-4.485358	1.252359	0.126703
C	-5.452868	2.318474	0.057399
H	-4.004998	-3.336643	-1.406033
H	-4.717559	-2.809897	0.155719
H	-3.088474	-3.540468	0.123418
H	-6.417903	1.844916	0.233026
H	-5.425637	2.789242	-0.928135
H	-5.243854	3.067520	0.824618

##########################

9,9_Diester TRANS TS B3LYP
B3lyp/6-31G(d)[CPCM=benzene]

Eel = -956.30339224 ; energy(0K) = -956.02563337
Enthalpy = -956.00347622 ; Gibbs energy = -956.07708003

M06-2X/6-31G(d)[CPCM=benzene]//B3lyp/6-31G(d)[CPCM=benzene]
Eel = -955.9087418 ; energy(0K) = -955.6309829
Enthalpy = -955.6088258 au; Gibbs energy = -955.6824296 au

C	-0.137997	0.414123	0.515799
C	-0.844667	-1.714161	-1.565927
C	-0.094129	-2.630915	-0.884473
C	1.237387	-2.409055	-0.440828
C	1.906616	-1.197560	-0.585126
C	1.166033	-0.019817	0.809343
C	3.341015	-1.011791	-0.167706
C	2.367008	0.913581	0.760491
O	3.503948	0.343402	0.303166
C	-0.291437	1.431596	-0.537112
C	-2.291797	-1.886854	-1.889644
O	0.560321	1.607869	-1.405588
O	2.361723	2.045315	1.176822
O	-1.418906	2.161771	-0.476600
C	-1.561944	3.161797	-1.499906
C	-1.207164	-0.219968	1.307291
O	-0.990149	-1.048477	2.184473
O	-2.461177	0.170927	0.983419
C	-3.506447	-0.413626	1.776849
H	-0.372174	-0.819032	-1.959910
H	-0.570267	-3.558607	-0.571933
H	1.688255	-3.178906	0.183754
H	1.609379	-0.536984	-1.397837
H	1.208718	-0.677134	1.677729
H	4.035228	-1.120775	-1.005659
H	3.633856	-1.704749	0.629598
H	-2.684734	-2.841093	-1.525737
H	-2.458736	-1.825545	-2.973575
H	-2.875749	-1.074035	-1.437138
H	-2.516200	3.647778	-1.296107
H	-1.570270	2.701477	-2.491494
H	-0.743957	3.884579	-1.447840
H	-3.368959	-0.172301	2.834025
H	-3.523223	-1.500400	1.658978
H	-4.432120	0.025175	1.403289

##########################

9,9_Diester CIS TS B3LYP
B3lyp/6-31G(d)[CPCM=benzene]
Eel = -956.29962641 ; energy(0K) = -956.02196709
Enthalpy = -955.99985027 ; Gibbs energy = -956.07325753

M06-2X/6-31G(d)[CPCM=benzene]//B3lyp/6-31G(d)[CPCM=benzene]
Eel = -955.9070062 ; energy(0K) = -955.6293469
Enthalpy = -955.6072301 au; Gibbs energy = -955.6806373 au

C	1.910691	-1.501222	0.075851
C	1.537985	-1.337795	1.410193
C	0.241955	-1.603245	1.925553
C	-0.828465	-1.967823	1.160961
C	-0.201478	0.370293	-0.604888
C	1.088955	-0.015837	-1.000472
C	2.291992	0.900053	-0.876392

```
O     2.286278     2.072577     -1.162547
O     3.441101     0.275408     -0.534558
C     3.321996     -1.153702     -0.347712
C     -2.225720     -2.087596     1.674272
C     -0.288339     1.234378     0.578595
O     0.681881     1.411384     1.311567
O     -1.485690     1.803517     0.817290
C     -1.542218     2.643680     1.981384
C     -1.307295     -0.181321     -1.412105
O     -1.135922     -1.003093     -2.307071
O     -2.534972     0.277543     -1.088849
C     -3.609922     -0.220715     -1.903550
H     1.412534     -2.280212     -0.495524
H     2.244022     -0.857399     2.083671
H     0.073981     -1.379746     2.977363
H     -0.680242     -2.236242     0.118556
H     1.094620     -0.562760     -1.944209
H     3.588888     -1.648503     -1.287058
H     4.065900     -1.412700     0.409074
H     -2.883507     -1.391693     1.135941
H     -2.623119     -3.095572     1.494419
H     -2.290792     -1.868435     2.744279
H     -1.333636     2.066712     2.886574
H     -0.818954     3.459553     1.904295
H     -2.559511     3.035225     2.005378
H     -3.687541     -1.307998     -1.822935
H     -3.455100     0.049227     -2.951241
H     -4.509765     0.256969     -1.515378

############################

9,9-Diester REACTANT CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -954.867659
Enthalpy(298K) = -954.844962;  Gibbs free energy(298K) = -954.922876
H     3.620533     0.069660     -1.670002
C     3.591329     -0.365332     -0.673900
C     4.666610     -0.293725     0.123009
C     2.324603     -1.046199     -0.287077
C     5.928342     0.327137     -0.242548
H     4.612293     -0.730784     1.119171
C     6.994468     0.388036     0.567920
H     5.989499     0.764937     -1.237634
C     8.305445     1.023947     0.225790
H     6.918150     -0.055530     1.559823
H     8.548282     1.826314     0.931747
H     8.300451     1.444642     -0.782155
H     9.123219     0.297119     0.290631
H     2.055527     -1.845221     -0.983381
O     1.250265     -0.054967     -0.319771
H     2.376591     -1.471122     0.717209
C     -0.971920     0.591534     -0.158773
C     0.011936     -0.518293     -0.093211
O     -0.253859     -1.677265     0.134825
C     -2.282430     0.420095     0.038436
H     -0.595923     1.584038     -0.374407
C     -3.179470     1.619253     -0.060377
C     -2.916607     -0.895432     0.416720
O     -3.132892     -1.219078     1.555920
```

```
O     -3.245877     -1.602746     -0.666853
C     -3.850963     -2.890080     -0.413761
O     -2.800191     2.742257     -0.288821
O     -4.459712     1.274399     0.129369
C     -5.425505     2.345247     0.062108
H     -4.076956     -3.299537     -1.394791
H     -4.760370     -2.771569     0.175616
H     -3.148349     -3.531387     0.118835
H     -6.387952     1.876833     0.248947
H     -5.405149     2.807928     -0.924921
H     -5.206745     3.095743     0.821935
```

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9,9_Diester TRANS TS CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -954.842721
Enthalpy(298K) = -954.821922; Gibbs free energy(298K) = -954.891389

```
C     -0.140426     0.406887     0.504115
C     -0.831159     -1.717822     -1.565893
C     -0.081104     -2.626505     -0.879699
C     1.246346     -2.397259     -0.438754
C     1.908776     -1.184882     -0.588057
C     1.165336     -0.018905     0.796080
C     3.341732     -0.994604     -0.175183
C     2.362055     0.921328     0.766136
O     3.498547     0.360487     0.302426
C     -0.299959     1.427973     -0.543383
C     -2.275537     -1.891328     -1.888598
O     0.550131     1.615580     -1.402359
O     2.350398     2.039243     1.198746
O     -1.431429     2.146093     -0.483464
C     -1.583684     3.158726     -1.496131
C     -1.202706     -0.228427     1.302620
O     -0.978665     -1.051319     2.175665
O     -2.456854     0.154970     0.985571
C     -3.502749     -0.422660     1.786945
H     -0.357919     -0.829047     -1.967680
H     -0.554365     -3.550078     -0.558790
H     1.701104     -3.160988     0.186698
H     1.609654     -0.532418     -1.403796
H     1.208986     -0.671583     1.665524
H     4.030517     -1.095248     -1.014980
H     3.638432     -1.686651     0.617864
H     -2.673925     -2.831532     -1.503263
H     -2.435906     -1.855325     -2.972260
H     -2.854697     -1.064792     -1.461720
H     -2.540620     3.630950     -1.287070
H     -1.586938     2.710879     -2.490893
H     -0.774295     3.886885     -1.433173
H     -3.356016     -0.181687     2.840506
H     -3.527437     -1.507074     1.669038
H     -4.425129     0.022145     1.420121
```

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9,9_Diester CIS TS CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -954.841023

Enthalpy(298K) = -954.820292; Gibbs free energy(298K) = -954.889489

C	1.921599	-1.487216	0.061340
C	1.554633	-1.344473	1.398026
C	0.266024	-1.622800	1.913582
C	-0.802120	-1.983235	1.148783
C	-0.206565	0.361074	-0.586585
C	1.087502	-0.009386	-0.983330
C	2.281075	0.920415	-0.870355
O	2.261063	2.086086	-1.153999
O	3.435183	0.304639	-0.535979
C	3.328254	-1.128647	-0.363068
C	-2.195633	-2.114383	1.660958
C	-0.303450	1.224330	0.596236
O	0.658329	1.403494	1.329637
O	-1.500375	1.789761	0.827561
C	-1.569665	2.644596	1.983227
C	-1.304177	-0.180799	-1.410611
O	-1.122948	-0.969464	-2.325233
O	-2.535004	0.249080	-1.074101
C	-3.609916	-0.228408	-1.904641
H	1.430300	-2.264469	-0.514022
H	2.259663	-0.869811	2.073037
H	0.100440	-1.412034	2.966040
H	-0.652414	-2.244055	0.106841
H	1.093657	-0.541662	-1.933235
H	3.592154	-1.609177	-1.307664
H	4.074028	-1.389859	0.386972
H	-2.857508	-1.428277	1.120435
H	-2.581097	-3.124360	1.481117
H	-2.263231	-1.894352	2.727745
H	-1.366990	2.079733	2.894515
H	-0.850246	3.460311	1.900883
H	-2.586212	3.031026	1.993457
H	-3.689108	-1.315039	-1.849639
H	-3.451213	0.066228	-2.942566
H	-4.507577	0.240626	-1.508369

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9,9-Diester REACTANT G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -955.100241
Enthalpy(298K) = -955.077531; Gibbs free energy(298K) = -955.155383

H	3.603126	0.126809	-1.644691
C	3.583211	-0.327002	-0.655852
C	4.669973	-0.281898	0.125946
C	2.314452	-1.004503	-0.267808
C	5.932150	0.331506	-0.242182
H	4.626105	-0.739670	1.114235
C	7.010748	0.363247	0.552310
H	5.982862	0.790297	-1.229227
C	8.323435	0.991099	0.204941
H	6.945329	-0.101015	1.536308
H	8.588254	1.775581	0.925221
H	8.308177	1.434720	-0.794504
H	9.135527	0.253800	0.241398
H	2.043632	-1.808492	-0.961255
O	1.245945	-0.017784	-0.302020
H	2.368264	-1.431773	0.737659

```
C     -0.980460     0.613775     -0.148272
C     0.010915     -0.487792     -0.082080
O     -0.250526     -1.649369     0.141435
C     -2.289037     0.424647     0.042638
H     -0.614916     1.612368     -0.357652
C     -3.203801     1.607270     -0.053329
C     -2.903661     -0.902092     0.407880
O     -3.127234     -1.237267     1.542669
O     -3.213830     -1.604875     -0.683943
C     -3.802135     -2.894567     -0.439419
O     -2.844700     2.738184     -0.275500
O     -4.477875     1.238082     0.131105
C     -5.451501     2.292703     0.061703
H     -4.025149     -3.306656     -1.422671
H     -4.714470     -2.792384     0.151997
H     -3.094531     -3.533913     0.093044
H     -6.414085     1.815807     0.239687
H     -5.430342     2.763750     -0.923554
H     -5.247750     3.046632     0.825186
```

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9,9_Diester TRANS TS   G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -955.072743
Enthalpy(298K) = -955.051962;  Gibbs free energy(298K) = -955.121267
C     -0.137302     0.403743     0.513632
C     -0.847976     -1.689106     -1.565882
C     -0.097953     -2.610664     -0.897584
C     1.232912     -2.397051     -0.460327
C     1.902651     -1.189088     -0.596313
C     1.164236     -0.030483     0.805490
C     3.335546     -1.006287     -0.178634
C     2.365542     0.902008     0.769713
O     3.498309     0.338533     0.306264
C     -0.286474     1.428170     -0.530574
C     -2.295885     -1.851945     -1.881305
O     0.569670     1.618547     -1.382857
O     2.358728     2.022417     1.197578
O     -1.417609     2.145746     -0.477374
C     -1.556886     3.150501     -1.490814
C     -1.205656     -0.230763     1.302946
O     -0.991690     -1.058759     2.172071
O     -2.455149     0.163875     0.981964
C     -3.498612     -0.416864     1.773582
H     -0.374505     -0.796418     -1.960767
H     -0.574648     -3.538360     -0.590591
H     1.686682     -3.172565     0.152710
H     1.603930     -0.517187     -1.397378
H     1.205184     -0.695460     1.666565
H     4.026414     -1.107871     -1.019923
H     3.628845     -1.711785     0.607024
H     -2.691989     -2.803777     -1.518522
H     -2.468329     -1.784580     -2.962804
H     -2.870523     -1.036867     -1.423726
H     -2.516173     3.629886     -1.297250
H     -1.549167     2.700281     -2.486646
H     -0.745127     3.878753     -1.425788
H     -3.358862     -0.179952     2.831108
```

```
H     -3.519341     -1.503228     1.656010
H     -4.425324     0.023234     1.405233
```

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9,9_Diester CIS TS G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -955.071126
Enthalpy(298K) = -955.050395; Gibbs free energy(298K) = -955.119543

```
C     1.909795     -1.492378     0.120405
C     1.539395     -1.291255     1.447236
C     0.246736     -1.536112     1.968853
C     -0.822906     -1.919275     1.218089
C     -0.202635     0.342661     -0.610258
C     1.087407     -0.051130     -0.992458
C     2.286884     0.871704     -0.901544
O     2.276249     2.029051     -1.219962
O     3.434002     0.262667     -0.540604
C     3.318807     -1.156073     -0.315243
C     -2.219151     -2.016957     1.732401
C     -0.290521     1.246059     0.541368
O     0.673751     1.445943     1.265998
O     -1.483497     1.823616     0.756475
C     -1.541675     2.701547     1.887202
C     -1.305161     -0.229722     -1.404068
O     -1.132954     -1.059569     -2.282005
O     -2.531303     0.224114     -1.082705
C     -3.602755     -0.290175     -1.885039
H     1.412154     -2.285585     -0.428209
H     2.248083     -0.797106     2.105830
H     0.079562     -1.281482     3.012266
H     -0.675493     -2.226162     0.187586
H     1.092511     -0.626481     -1.917805
H     3.584864     -1.679362     -1.238951
H     4.061223     -1.395964     0.448828
H     -2.872681     -1.339063     1.168822
H     -2.619262     -3.027828     1.585008
H     -2.284928     -1.761533     2.792963
H     -1.333581     2.158234     2.812642
H     -0.817340     3.513248     1.784858
H     -2.557462     3.096427     1.899407
H     -3.673040     -1.376606     -1.792148
H     -3.453261     -0.035038     -2.936875
H     -4.506649     0.184363     -1.503462
```

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E-9-estr-ether tether REACTANT B3LYP
B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.42214254 ;   energy(0K) = -654.16991169
Enthalpy = -654.15248928 ; Gibbs energy = -654.21666198

M06-2X/6-32G(d)[CPCM=benzene]//B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.1211772 ;   energy(0K) = -653.8689463
Enthalpy = -653.8515239 au; Gibbs energy = -653.9156966 au

```
C     -2.715309     0.652871     0.495275
C     -3.782153     0.331823     -0.255636
C     -1.541175     1.434000     -0.003286
C     -4.946651     -0.393266     0.229371
```

```
C     -6.012351     -0.701822     -0.529566
C     -7.221735     -1.450840     -0.057297
O     -0.348858     0.691302     0.251602
C     2.013718     0.612765     0.343217
C     0.824240     1.412767     -0.087708
C     3.104204     0.410439     -0.404205
C     4.258037     -0.353004     0.123864
O     4.339012     -0.850934     1.232099
O     5.240421     -0.435115     -0.802650
C     6.412953     -1.161614     -0.398566
H     -2.676950     0.356472     1.543477
H     -3.798830     0.630287     -1.305388
H     -1.642012     1.646868     -1.079881
H     -1.475273     2.407182     0.516974
H     -4.932778     -0.697483     1.277165
H     -6.015011     -0.390803     -1.575791
H     -8.134343     -0.852306     -0.184748
H     -7.139555     -1.726267     0.999388
H     -7.370933     -2.370591     -0.639585
H     1.976749     0.196913     1.348532
H     0.831803     2.386347     0.437445
H     0.861620     1.628367     -1.167827
H     3.187949     0.792292     -1.417934
H     6.157977     -2.196332     -0.154914
H     6.873329     -0.692142     0.474812
H     7.088994     -1.125551     -1.252913

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E-9-estr-ether tether TRANS IMDA TS B3LYP
B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.38352804 ;   energy(0K) = -654.12992551
Enthalpy = -654.11458060 ;  Gibbs energy = -654.17115592

 M06-2X/6-32G(d)[CPCM=benzene]//B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.0913475 ;   energy(0K) = -653.8377450
Enthalpy = -653.8224000 au;  Gibbs energy = -653.8789754 au
C     0.256303     -0.786372     -0.584824
C     0.663766     1.864291     -0.578806
C     -0.012981     2.095324     0.602374
C     -1.306086     1.615598     0.866449
C     -1.975887     0.778463     -0.039201
C     -1.017734     -0.898702     -0.000378
C     -3.360428     0.229625     0.215870
C     -2.170677     -1.589258     -0.708021
O     -3.406726     -1.157415     -0.153815
C     1.445750     -0.933566     0.238950
C     2.097835     2.236997     -0.796889
O     1.480658     -0.999588     1.461694
O     2.578301     -1.021717     -0.527012
C     3.794399     -1.223634     0.204879
H     0.383305     -0.821433     -1.662542
H     0.106378     1.600627     -1.471153
H     0.536640     2.548275     1.426210
H     -1.691154     1.704148     1.880976
H     -1.789322     0.976595     -1.093739
H     -0.992792     -1.104724     1.068881
H     -4.108423     0.776187     -0.375394
H     -3.636144     0.314301     1.274986
```

```
H     -2.126593     -2.672920     -0.553749
H     -2.123472     -1.397538     -1.792618
H     2.577908     2.561421     0.132054
H     2.180165     3.050867     -1.531318
H     2.662968     1.387266     -1.197367
H     3.751705     -2.153414     0.779388
H     3.981326     -0.393501     0.891835
H     4.584088     -1.279010     -0.545790
```

##########################

E-9-estr-ether tether CIS IMDA TS B3LYP
B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.38245623 ; energy(0K) = -654.12849661
Enthalpy = -654.11332339 ; Gibbs energy = -654.16949537

M06-2X/6-32G(d)[CPCM=benzene]//B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.0914580 ; energy(0K) = -653.8374984
Enthalpy = -653.8223252 au; Gibbs energy = -653.8784971 au

```
C     2.028980     0.521044     0.661249
C     1.832539     1.661421     -0.136280
C     0.595362     2.287744     -0.310063
C     -0.577343     1.843734     0.278913
C     -0.382181     -0.508048     -0.570980
C     0.847887     -0.950384     -0.056359
C     1.988290     -1.467893     -0.905037
O     3.166877     -1.486158     -0.113898
C     3.350637     -0.217154     0.539279
C     -1.912260     2.452752     -0.035259
C     -1.609969     -0.865898     0.136902
O     -1.691699     -1.224267     1.304659
O     -2.706852     -0.744660     -0.665184
C     -3.953607     -1.120805     -0.059327
H     1.525486     0.485806     1.625059
H     2.632445     1.945795     -0.819413
H     0.520612     3.057053     -1.077907
H     -0.525937     1.250271     1.185896
H     -0.480071     -0.204020     -1.607413
H     0.751213     -1.500956     0.879268
H     1.819111     -2.508297     -1.204884
H     2.105896     -0.860330     -1.817520
H     3.805162     -0.432555     1.511414
H     4.058707     0.388814     -0.045436
H     -2.662701     1.683806     -0.249067
H     -1.854694     3.121930     -0.900076
H     -2.283523     3.030883     0.822483
H     -4.165729     -0.499608     0.814971
H     -3.931360     -2.169851     0.248323
H     -4.711241     -0.967144     -0.828541
```

##########################

E-9-estr-ether tether REACTANT CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -653.303639
Enthalpy(298K) = -653.286047; Gibbs free energy(298K) = -653.350579

```
C     -2.713705     0.655164     0.493074
C     -3.779888     0.337752     -0.253686
C     -1.544328     1.441169     -0.001975
```

```
C     -4.938070     -0.396773     0.228414
C     -6.002748     -0.703221     -0.526219
C     -7.204748     -1.462807     -0.056928
O     -0.349228     0.696903     0.242851
C     2.011834     0.618923     0.341228
C     0.826467     1.419492     -0.089918
C     3.101043     0.415009     -0.400082
C     4.250695     -0.353932     0.128858
O     4.329691     -0.850659     1.230371
O     5.230238     -0.439342     -0.796870
C     6.405411     -1.171524     -0.401687
H     -2.668528     0.347929     1.535617
H     -3.801735     0.645007     -1.298631
H     -1.648488     1.659923     -1.074167
H     -1.478679     2.405189     0.529445
H     -4.918008     -0.710615     1.271123
H     -6.010967     -0.382260     -1.567151
H     -8.117925     -0.868256     -0.175562
H     -7.117013     -1.748014     0.993899
H     -7.349988     -2.374276     -0.648124
H     1.969900     0.200274     1.343130
H     0.833515     2.386250     0.442271
H     0.866482     1.636051     -1.166837
H     3.191067     0.795928     -1.411226
H     6.148723     -2.204429     -0.162365
H     6.869764     -0.706704     0.469220
H     7.074491     -1.132715     -1.257922

###########################

E-9-estr-ether tether TRANS IMDA TS  CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -653.275209
Enthalpy(298K) = -653.259632;  Gibbs free energy(298K) = -653.316849
C     0.255085     -0.773384     -0.585081
C     0.655210     1.853779     -0.585989
C     -0.001549     2.081636     0.604655
C     -1.287334     1.603297     0.884560
C     -1.971756     0.776265     -0.016679
C     -1.020209     -0.893618     -0.006622
C     -3.346861     0.223121     0.256075
C     -2.163865     -1.579729     -0.728853
O     -3.411515     -1.139952     -0.198327
C     1.439525     -0.928256     0.242044
C     2.084436     2.223981     -0.824128
O     1.467944     -0.999060     1.458925
O     2.574747     -1.011880     -0.515982
C     3.792726     -1.221272     0.215429
H     0.388184     -0.805793     -1.659574
H     0.083435     1.601632     -1.469800
H     0.561266     2.524879     1.421637
H     -1.656602     1.685726     1.902996
H     -1.803408     0.984105     -1.070083
H     -0.996179     -1.114554     1.057563
H     -4.112294     0.799093     -0.275938
H     -3.578996     0.247118     1.326347
H     -2.123687     -2.660120     -0.569548
H     -2.101702     -1.388622     -1.809587
H     2.587820     2.511982     0.101217
```

```
H     2.151172     3.061501     -1.529433
H     2.632698     1.388913     -1.268761
H     3.744477     -2.149800     0.786990
H     3.983042     -0.393955     0.901338
H     4.578912     -1.279889     -0.534755
```

##########################

E-9-estr-ether tether CIS IMDA TS CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -653.273866
Enthalpy(298K) = -653.258472; Gibbs free energy(298K) = -653.315198

```
C     2.022700     0.507989     0.669886
C     1.837257     1.649269     -0.126438
C     0.607853     2.280189     -0.306098
C     -0.568298     1.843276     0.276844
C     -0.385263     -0.495205     -0.565787
C     0.845963     -0.942777     -0.060848
C     1.976682     -1.454606     -0.922268
O     3.161552     -1.484173     -0.138973
C     3.340386     -0.234793     0.559243
C     -1.896033     2.459327     -0.042581
C     -1.609839     -0.862759     0.140921
O     -1.688792     -1.235834     1.297746
O     -2.707369     -0.730651     -0.654695
C     -3.957955     -1.118032     -0.058323
H     1.513670     0.474674     1.627997
H     2.643286     1.932409     -0.798970
H     0.541240     3.049227     -1.071667
H     -0.522771     1.253961     1.184265
H     -0.490470     -0.187418     -1.597952
H     0.750341     -1.504003     0.866064
H     1.801037     -2.488924     -1.229307
H     2.090320     -0.838429     -1.826255
H     3.763673     -0.483581     1.534314
H     4.066254     0.378238     0.010621
H     -2.656309     1.696864     -0.228742
H     -1.837314     3.104389     -0.922004
H     -2.249484     3.061169     0.803218
H     -4.176468     -0.505224     0.817655
H     -3.931396     -2.167143     0.240130
H     -4.709461     -0.962212     -0.829301
```

##########################

E-9-estr-ether tether REACTANT G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -653.480813
Enthalpy(298K) = -653.463192; Gibbs free energy(298K) = -653.527821

```
C     -2.709639     0.644436     0.496903
C     -3.777244     0.335469     -0.249996
C     -1.537960     1.431400     0.007670
C     -4.937731     -0.395867     0.224699
C     -6.003707     -0.692672     -0.530887
C     -7.209188     -1.448668     -0.067286
O     -0.348211     0.690995     0.253470
C     2.009456     0.606260     0.341175
C     0.821907     1.411472     -0.077744
C     3.102797     0.417441     -0.397614
```

```
C     4.250848     -0.356742     0.122911
O     4.324941     -0.875055     1.214739
O     5.235490     -0.419007     -0.797835
C     6.402203     -1.151984     -0.403349
H     -2.664846     0.330913     1.538437
H     -3.799627     0.651176     -1.293260
H     -1.640995     1.656498     -1.065834
H     -1.474811     2.399453     0.537425
H     -4.918536     -0.716088     1.266284
H     -6.011417     -0.365549     -1.570659
H     -8.121496     -0.849579     -0.183204
H     -7.123356     -1.740677     0.983235
H     -7.360282     -2.357211     -0.664204
H     1.965199     0.169010     1.335921
H     0.833321     2.379095     0.457956
H     0.859488     1.640955     -1.154591
H     3.198270     0.818382     -1.401200
H     6.147029     -2.190954     -0.180306
H     6.858063     -0.702899     0.482627
H     7.085787     -1.101268     -1.250508

############################

E-9-estr-ether tether TRANS IMDA TS  G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -653.450567
Enthalpy(298K) = -653.435027;  Gibbs free energy(298K) = -653.492014
C     0.256035     -0.778020     -0.584287
C     0.662311     1.852911     -0.578033
C     -0.009425     2.085334     0.602176
C     -1.298873     1.609965     0.869158
C     -1.971818     0.777921     -0.033711
C     -1.016231     -0.894392     -0.003537
C     -3.353444     0.227469     0.222188
C     -2.169062     -1.581224     -0.712260
O     -3.400879     -1.151919     -0.158433
C     1.442750     -0.928812     0.239958
C     2.094016     2.223598     -0.801746
O     1.475461     -0.998958     1.455844
O     2.572914     -1.013185     -0.523089
C     3.784283     -1.220366     0.207725
H     0.386339     -0.810562     -1.659878
H     0.102480     1.592986     -1.468140
H     0.542199     2.540128     1.421701
H     -1.684072     1.701215     1.881737
H     -1.786764     0.973349     -1.087434
H     -0.990291     -1.102990     1.063999
H     -4.102675     0.780454     -0.360791
H     -3.624003     0.306512     1.282802
H     -2.122769     -2.665016     -0.562048
H     -2.118775     -1.386700     -1.795859
H     2.578320     2.544927     0.124540
H     2.172925     3.037871     -1.534221
H     2.654879     1.375305     -1.207824
H     3.739039     -2.151175     0.779668
H     3.972252     -0.395311     0.899915
H     4.577701     -1.274800     -0.538526

############################
```

E-9-estr-ether tether CIS IMDA TS G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -653.449065
Enthalpy(298K) = -653.433690; Gibbs free energy(298K) = -653.490289

C	2.019872	0.516633	0.665616
C	1.824712	1.659283	-0.123784
C	0.590925	2.281378	-0.300760
C	-0.582955	1.834152	0.276420
C	-0.380902	-0.503756	-0.573190
C	0.848905	-0.943892	-0.063909
C	1.990317	-1.455455	-0.912640
O	3.164131	-1.475228	-0.123077
C	3.341927	-0.218607	0.545780
C	-1.914030	2.443316	-0.044427
C	-1.604177	-0.865216	0.137395
O	-1.680586	-1.232622	1.295526
O	-2.700911	-0.736559	-0.657735
C	-3.941160	-1.121608	-0.053314
H	1.511119	0.471572	1.624123
H	2.629262	1.951641	-0.795586
H	0.519202	3.056666	-1.060677
H	-0.538642	1.236538	1.179207
H	-0.484747	-0.195900	-1.606125
H	0.751455	-1.498053	0.868200
H	1.820569	-2.493680	-1.218221
H	2.104514	-0.843567	-1.822192
H	3.789108	-0.443483	1.518737
H	4.052065	0.397847	-0.024423
H	-2.658809	1.676234	-0.277822
H	-1.847351	3.124493	-0.897494
H	-2.297076	3.006220	0.816577
H	-4.151540	-0.513004	0.829748
H	-3.915856	-2.173239	0.243892
H	-4.704965	-0.962386	-0.814772

##########################

FUMARATE REACTANT B3LYP
B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.46942453 ; energy(0K) = -728.23529529
Enthalpy = -728.20491769 ; Gibbs energy = -728.31049672

M06-2X/6-31G(d)//B3LYP/6-31G(d)
Eel = -728.1490862 ; energy(0K) = -727.9149570
Enthalpy = -727.8845794 au; Gibbs energy = -727.9901584 au

C	-2.787314	0.478308	0.624906
C	-3.868118	0.299738	-0.153778
C	-1.597367	1.278389	0.213749
C	-5.058161	-0.437935	0.239749
C	-6.133171	-0.603766	-0.550232
C	-7.371041	-1.361356	-0.177238
O	-0.428852	0.406975	0.256584
C	1.862585	0.014704	0.109221
C	0.755608	1.003424	0.026785
O	0.890641	2.188611	-0.215650
C	3.132289	0.385606	-0.090451
C	4.238314	-0.602196	-0.008284
O	4.109384	-1.787169	0.234558

```
O     5.423990     -0.005599     -0.242499
C     6.574712     -0.868377     -0.189818
H     -2.758131     0.048199     1.625591
H     -3.875735     0.735633     -1.154225
H     -1.700433     1.679027     -0.799410
H     -1.407317     2.118711     0.891173
H     -5.056722     -0.876171     1.238798
H     -6.121255     -0.158760     -1.546702
H     -8.259267     -0.716538     -0.225315
H     -7.303355     -1.774952     0.834338
H     -7.552185     -2.190461     -0.874930
H     1.611026     -1.016658     0.335212
H     3.383226     1.416981     -0.317008
H     6.495520     -1.654971     -0.944519
H     6.662450     -1.326039     0.798749
H     7.430854     -0.225800     -0.393337
```

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FUMARATE TRANS IMDA TS B3LYP
B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.42320541 ; energy(0K) = -728.18846805
Enthalpy = -728.16061365 ; Gibbs energy = -728.25477824

M06-2X/6-31G(d)//B3LYP/6-31G(d)
Eel = -728.1111992 ; energy(0K) = -727.8764618
Enthalpy = -727.8486074 au; Gibbs energy = -727.9427720 au

```
C     0.257540     -0.782166     -0.435374
C     0.939407     1.813131     -0.832646
C     0.434384     2.250253     0.374173
C     -0.866071     1.966670     0.831343
C     -1.730145     1.154454     0.089902
C     -0.984250     -0.646946     0.194729
C     -3.104629     0.732549     0.536424
C     -2.244696     -1.250014     -0.384940
O     -3.370176     -0.552674     -0.075608
C     1.451562     -0.917742     0.388189
C     2.371227     1.977233     -1.237923
O     -2.309500     -2.263728     -1.037688
O     1.498383     -0.795042     1.605993
O     2.547892     -1.228734     -0.361478
C     3.758799     -1.433548     0.380788
H     0.332689     -0.992139     -1.496106
H     0.260189     1.505234     -1.620843
H     1.124175     2.711839     1.078610
H     -1.101876     2.182517     1.871738
H     -1.663482     1.242621     -0.993793
H     -0.944706     -0.736469     1.281430
H     -3.896188     1.399180     0.182535
H     -3.177063     0.639441     1.626117
H     2.983371     2.362073     -0.416131
H     2.456258     2.668915     -2.087797
H     2.795218     1.019675     -1.562488
H     3.640048     -2.252975     1.095031
H     4.041194     -0.527687     0.924359
H     4.518607     -1.684037     -0.360394
```

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FUMARATE CIS IMDA TS B3LYP
B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.42270451 ; energy(0K) = -728.18768407
Enthalpy = -728.15997660 ; Gibbs energy = -728.25354134

M06-2X/6-31G(d)//B3LYP/6-31G(d)
Eel = -728.1113849 ; energy(0K) = -727.8763645
Enthalpy = -727.8486570 au; Gibbs energy = -727.9422217 au

C	-1.730297	0.755869	0.965306
C	-1.664762	1.783984	0.015567
C	-0.455939	2.345369	-0.421347
C	0.784443	1.952503	0.043614
C	0.438702	-0.572693	-0.455765
C	-0.788881	-0.831127	0.157997
C	-2.006482	-1.210012	-0.640225
O	-2.005930	-1.777982	-1.707825
O	-3.179609	-0.868788	-0.042049
C	-3.017317	-0.022136	1.126706
C	2.070319	2.459382	-0.534500
C	1.663930	-0.875344	0.280153
O	1.733901	-1.096282	1.482956
O	2.755685	-0.872247	-0.530196
C	3.999720	-1.198057	0.111667
H	-1.065098	0.798240	1.823881
H	-2.553971	1.986723	-0.580515
H	-0.491832	3.012035	-1.281780
H	0.858394	1.446762	1.000914
H	0.506328	-0.404708	-1.523356
H	-0.719180	-1.340952	1.119756
H	-3.002597	-0.650379	2.023117
H	-3.908082	0.610732	1.153101
H	1.905969	3.012331	-1.464762
H	2.761504	1.633617	-0.739097
H	2.575843	3.125963	0.178498
H	3.956878	-2.201018	0.544393
H	4.228815	-0.478384	0.902057
H	4.754039	-1.154997	-0.674334

##########################

FUMARATE REACTANT CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -727.297558
Enthalpy(298K) = -727.279522; Gibbs free energy(298K) = -727.345676

C	-2.786581	0.498773	0.624260
C	-3.859994	0.303567	-0.154229
C	-1.601211	1.299679	0.209391
C	-5.044886	-0.438685	0.241365
C	-6.111828	-0.622968	-0.549128
C	-7.343495	-1.386494	-0.174351
O	-0.429526	0.428919	0.255836
C	1.856179	0.023448	0.110627
C	0.755297	1.018411	0.023183
O	0.894385	2.194929	-0.224331
C	3.124062	0.382759	-0.090750
C	4.224176	-0.611274	-0.004745
O	4.090874	-1.787806	0.242709
O	5.409654	-0.021689	-0.242478
C	6.564037	-0.883743	-0.189153

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H     -2.757300     0.079491     1.627141
H     -3.865755     0.727425     -1.157561
H     -1.705754     1.693113     -0.803784
H     -1.414732     2.139989     0.883927
H     -5.044653     -0.864579     1.243492
H     -6.098122     -0.189980     -1.548497
H     -8.233923     -0.750400     -0.235487
H     -7.278041     -1.787387     0.839564
H     -7.512131     -2.221828     -0.863528
H     1.596419     -1.002607     0.341561
H     3.382873     1.408889     -0.322393
H     6.484348     -1.670201     -0.940675
H     6.653220     -1.336652     0.798969
H     7.415902     -0.240935     -0.395433

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FUMARATE TRANS IMDA TSCBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -727.263434
Enthalpy(298K) = -727.247433;  Gibbs free energy(298K) = -727.305626
C     0.259695     -0.770506     -0.439045
C     0.931507     1.811987     -0.831292
C     0.434252     2.242772     0.378120
C     -0.860517     1.956700     0.838449
C     -1.726456     1.149980     0.096848
C     -0.983075     -0.641689     0.186530
C     -3.098054     0.728219     0.544457
C     -2.241527     -1.249568     -0.392064
O     -3.364573     -0.555091     -0.075314
C     1.448775     -0.913915     0.387900
C     2.359183     1.975169     -1.242720
O     -2.304627     -2.256441     -1.042515
O     1.490308     -0.801441     1.601084
O     2.547388     -1.216542     -0.357264
C     3.760083     -1.433499     0.383253
H     0.340925     -0.975251     -1.497819
H     0.248709     1.511853     -1.616324
H     1.126482     2.697419     1.081010
H     -1.092925     2.168667     1.877987
H     -1.662951     1.245318     -0.984206
H     -0.946416     -0.742672     1.270289
H     -3.886806     1.395735     0.194910
H     -3.166771     0.627336     1.631152
H     2.981035     2.326620     -0.417005
H     2.439942     2.692156     -2.068682
H     2.769361     1.027655     -1.603506
H     3.635706     -2.254096     1.091542
H     4.047864     -0.533369     0.929024
H     4.514684     -1.685147     -0.358914

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FUMARATE CIS IMDA TS CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -727.262901
Enthalpy(298K) = -727.246981;  Gibbs free energy(298K) = -727.304901
C     -1.728115     0.750793     0.962881
C     -1.664317     1.780515     0.016985
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C     -0.460335     2.345120     -0.416721
C     0.778940     1.955179     0.046589
C     0.439875     -0.560545     -0.453192
C     -0.788712     -0.819852     0.154435
C     -2.002196     -1.211502     -0.644130
O     -1.997499     -1.782419     -1.702198
O     -3.174166     -0.873521     -0.046036
C     -3.013591     -0.026165     1.124714
C     2.061751     2.465307     -0.528794
C     1.661802     -0.874803     0.281551
O     1.729879     -1.116672     1.474136
O     2.753714     -0.857397     -0.524485
C     4.001456     -1.199369     0.106731
H     -1.066616     0.794137     1.821191
H     -2.553034     1.985846     -0.574709
H     -0.498018     3.013804     -1.272581
H     0.852722     1.448750     1.001117
H     0.513728     -0.389585     -1.517543
H     -0.719063     -1.335326     1.110843
H     -2.997266     -0.654676     2.017753
H     -3.901546     0.605767     1.150471
H     1.898531     3.009272     -1.461257
H     2.758136     1.644761     -0.722204
H     2.556233     3.137910     0.182524
H     3.952575     -2.203811     0.529238
H     4.240408     -0.489473     0.900070
H     4.748440     -1.155366     -0.682545

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FUMARATE REACTANTG4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -727.482801
Enthalpy(298K) = -727.464751;  Gibbs free energy(298K) = -727.530866
C     -2.778845     0.462734     0.610823
C     -3.866202     0.299218     -0.154105
C     -1.592047     1.265647     0.202142
C     -5.051723     -0.440049     0.237321
C     -6.133663     -0.590262     -0.538817
C     -7.367391     -1.349741     -0.165359
O     -0.425841     0.399521     0.238880
C     1.861586     0.014265     0.100967
C     0.755151     1.001892     0.026921
O     0.888073     2.184589     -0.194050
C     3.129360     0.383875     -0.084212
C     4.234924     -0.602864     -0.010452
O     4.108306     -1.785121     0.212446
O     5.416826     -0.000050     -0.227764
C     6.566175     -0.858254     -0.181318
H     -2.737939     0.016009     1.602308
H     -3.884952     0.752035     -1.145501
H     -1.700436     1.672125     -0.807794
H     -1.404212     2.103988     0.882307
H     -5.038847     -0.894619     1.227561
H     -6.133048     -0.128907     -1.526325
H     -8.253181     -0.702383     -0.192584
H     -7.289068     -1.781021     0.836589
H     -7.559708     -2.163894     -0.875673
H     1.607232     -1.018592     0.309639
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H     3.383041     1.416755     -0.293523
H     6.494286     -1.635037     -0.946402
H     6.649658     -1.332514     0.799433
H     7.424312     -0.214226     -0.369588

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FUMARATE TRANS IMDA TSG4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -727.447186
Enthalpy(298K) = -727.431139;  Gibbs free energy(298K) = -727.489452
C     0.259147     -0.774316     -0.434864
C     0.936158     1.801601     -0.831401
C     0.433935     2.240025     0.372389
C     -0.862550     1.959528     0.830038
C     -1.727840     1.152367     0.091057
C     -0.981990     -0.643671     0.190918
C     -3.098348     0.726584     0.539936
C     -2.242246     -1.245855     -0.387759
O     -3.363626     -0.553854     -0.070003
C     1.450321     -0.912330     0.389713
C     2.365239     1.963828     -1.239823
O     -2.306381     -2.250643     -1.041934
O     1.494836     -0.794396     1.601389
O     2.544525     -1.218563     -0.358234
C     3.750916     -1.426629     0.383018
H     0.338576     -0.981626     -1.493993
H     0.256701     1.495016     -1.617864
H     1.123784     2.704299     1.072798
H     -1.099517     2.177457     1.868139
H     -1.663100     1.236908     -0.991686
H     -0.944354     -0.732602     1.276249
H     -3.889721     1.395174     0.190408
H     -3.165844     0.636931     1.629985
H     2.978417     2.350912     -0.421578
H     2.447728     2.651314     -2.091724
H     2.787116     1.006121     -1.562692
H     3.631469     -2.248092     1.094282
H     4.032738     -0.525020     0.933172
H     4.514721     -1.673934     -0.354583

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FUMARATE CIS IMDA TS G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -727.446534
Enthalpy(298K) = -727.430615;  Gibbs free energy(298K) = -727.488493
C     -1.721341     0.749758     0.968574
C     -1.655409     1.781249     0.027005
C     -0.450206     2.340355     -0.409212
C     0.788715     1.942187     0.045615
C     0.437644     -0.568443     -0.458398
C     -0.789951     -0.826038     0.149277
C     -2.009186     -1.199400     -0.646958
O     -2.012672     -1.757107     -1.712369
O     -3.175401     -0.861396     -0.042671
C     -3.007420     -0.027431     1.128243
C     2.071180     2.447947     -0.535730
C     1.659074     -0.876320     0.278544
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O     1.724863     -1.111966     1.471936
O     2.750121     -0.861447     -0.526746
C     3.988374     -1.196778     0.112580
H     -1.052651     0.780377     1.822599
H     -2.546821     1.994023     -0.559536
H     -0.487081     3.014413     -1.261972
H     0.867068     1.430514     0.997769
H     0.510494     -0.394508     -1.522956
H     -0.722043     -1.337602     1.108482
H     -2.990440     -0.659706     2.021374
H     -3.894169     0.609928     1.165345
H     1.902653     3.011217     -1.457485
H     2.755854     1.621526     -0.752919
H     2.585007     3.102546     0.180495
H     3.944255     -2.205307     0.531237
H     4.215347     -0.491468     0.915909
H     4.748393     -1.143139     -0.666785

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Maleate REACTANT B3LYP
B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.45973695 ;   energy(0K) = -728.22588524
Enthalpy = -728.20132856 ;  Gibbs energy = -728.28927906

M06-2X/6-31G(d)[CPCM=benzene]//B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.1410665 ;   energy(0K) = -727.9072148
Enthalpy = -727.8826581 au;  Gibbs energy = -727.9706086 au
C     2.447090     -0.366521     -0.518566
C     3.558263     -0.331907     0.236627
C     1.089567     -0.665237     0.023234
C     4.898491     -0.091779     -0.274699
C     6.001620     -0.068578     0.493234
C     7.394048     0.179619     -0.001726
O     0.219305     0.461525     -0.289466
C     -1.081414     0.301968     0.022173
O     -1.538571     -0.696654     0.548806
C     -1.859100     1.510566     -0.350679
C     -3.193774     1.564759     -0.280295
C     -4.090794     0.460534     0.195505
O     -4.673281     0.499550     1.259001
O     -4.231967     -0.506079     -0.721881
C     -5.058909     -1.618580     -0.326508
H     2.511769     -0.198431     -1.593247
H     3.471475     -0.499809     1.311428
H     0.649339     -1.559793     -0.432154
H     1.102354     -0.811348     1.107765
H     4.991477     0.078294     -1.348316
H     5.894104     -0.242153     1.565354
H     8.053299     -0.668406     0.229258
H     7.836945     1.058126     0.487336
H     7.415808     0.344307     -1.084026
H     -1.289292     2.375403     -0.675295
H     -3.707147     2.492673     -0.521701
H     -4.606708     -2.133964     0.524257
H     -5.097168     -2.274597     -1.195699
H     -6.060662     -1.276103     -0.056449

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Maleate TRANS ts B3lyp
B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.42176712 ; energy(0K) = -728.18689781
Enthalpy = -728.16469100 ; Gibbs energy = -728.24201840

M06-2X/6-31G(d)[CPCM=benzene]//B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.1098846 ; energy(0K) = -727.8750153
Enthalpy = -727.8528085 au; Gibbs energy = -727.9301359 au

C	0.401704	-0.299559	1.013716
C	1.225018	2.022862	-0.236314
C	0.120533	2.752523	0.135607
C	-1.209100	2.319606	-0.059071
C	-1.506053	1.041388	-0.534654
C	-0.989153	-0.182066	0.919321
C	-2.911507	0.527306	-0.680475
C	-1.878351	-1.302683	0.389361
O	-2.903855	-0.888523	-0.393080
C	1.150590	-1.056805	0.025644
C	2.630539	2.373240	0.140246
O	0.709998	-1.431830	-1.057323
O	-1.769993	-2.464340	0.694709
O	2.438398	-1.268820	0.407743
C	3.245901	-1.999433	-0.528571
H	0.932446	0.096388	1.869447
H	1.117587	1.244969	-0.984834
H	0.272851	3.647986	0.737259
H	-2.006694	2.907771	0.392447
H	-0.817738	0.583895	-1.244352
H	-1.466000	0.297357	1.775678
H	-3.292004	0.621202	-1.701789
H	-3.608138	1.025318	0.004233
H	2.669080	3.147103	0.913299
H	3.189167	2.732632	-0.736058
H	3.162158	1.484949	0.503273
H	4.227312	-2.088780	-0.061856
H	3.322501	-1.461836	-1.477846
H	2.820357	-2.989114	-0.714168

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Maleate CIS TS B3LYP
B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.41838202 ; energy(0K) = -728.18371764
Enthalpy = -728.16142886 ; Gibbs energy = -728.23922266

M06-2X/6-31G(d)[CPCM=benzene]//B3LYP/6-31G(d)[CPCM=benzene]
Eel = -728.1092643 ; energy(0K) = -727.8745999
Enthalpy = -727.8523111 au; Gibbs energy = -727.9301049 au

C	1.617261	1.428800	-0.014866
C	0.726691	1.602387	1.051794
C	-0.632099	1.911930	0.865751
C	-1.225430	2.009121	-0.372955
C	-0.343648	-0.355049	-1.144629
C	1.042569	-0.176671	-1.071528
C	1.952757	-1.135667	-0.319896
O	1.873661	-2.339503	-0.365359
O	2.973771	-0.541154	0.342949
C	3.009349	0.902395	0.251688

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C     -2.702822     2.154220     -0.574100
C     -1.061979     -0.987106     -0.049438
O     -0.592055     -1.203318     1.060816
O     -2.347228     -1.288779     -0.382496
C     -3.121409     -1.901560     0.658326
H     1.512558     2.098504     -0.864741
H     1.039916     1.289178     2.045708
H     -1.276430     1.894950     1.742863
H     -0.608296     2.166817     -1.251334
H     -0.879866     -0.145833     -2.061753
H     1.507407     0.122938     -2.013071
H     3.706710     1.178962     -0.546025
H     3.415158     1.246061     1.206456
H     -3.087158     1.371423     -1.239278
H     -2.940031     3.117984     -1.045370
H     -3.247482     2.088900     0.373039
H     -3.222555     -1.228983     1.515139
H     -2.653969     -2.831979     0.991938
H     -4.098611     -2.103684     0.218257

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Maleate REACTANT CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -727.291383
Enthalpy(298K) = -727.273331;  Gibbs free energy(298K) = -727.340729
C     2.459321     -0.380941     -0.545277
C     3.558197     -0.352677     0.221457
C     1.099845     -0.703315     -0.028321
C     4.900377     -0.083286     -0.265998
C     5.990988     -0.064543     0.513341
C     7.384395     0.214968     0.043345
O     0.227262     0.430296     -0.318476
C     -1.072607     0.270306     -0.012792
O     -1.532034     -0.731243     0.489713
C     -1.842220     1.489965     -0.364190
C     -3.170055     1.562133     -0.269374
C     -4.076245     0.475840     0.226643
O     -4.601957     0.508686     1.312037
O     -4.289886     -0.462960     -0.701112
C     -5.133115     -1.563452     -0.296891
H     2.534096     -0.183826     -1.612110
H     3.459941     -0.547977     1.288475
H     0.672142     -1.583574     -0.516682
H     1.102039     -0.879807     1.049201
H     5.003978     0.115010     -1.331676
H     5.872170     -0.266474     1.577074
H     8.049677     -0.628019     0.262473
H     7.806163     1.084336     0.560599
H     7.417806     0.407068     -1.031370
H     -1.266802     2.345377     -0.695904
H     -3.675417     2.493735     -0.503619
H     -4.660676     -2.110531     0.519463
H     -5.225492     -2.194140     -1.177261
H     -6.109993     -1.199390     0.022383

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Maleate CIS TS CBS-QB3
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CBS-QB3[CPCM=benzene]
Energy(0K) = -727.260924
Enthalpy(298K) = -727.244860; Gibbs free energy(298K) = -727.303334

C	1.637231	1.411153	-0.015581
C	0.752666	1.605106	1.050207
C	-0.598531	1.928952	0.864836
C	-1.190079	2.025460	-0.372595
C	-0.355604	-0.338624	-1.125321
C	1.032113	-0.180515	-1.057200
C	1.937461	-1.156866	-0.322930
O	1.844661	-2.352311	-0.379307
O	2.965784	-0.577351	0.338060
C	3.020950	0.867730	0.249744
C	-2.662266	2.194208	-0.574660
C	-1.081425	-0.975152	-0.038148
O	-0.621642	-1.201018	1.067240
O	-2.363425	-1.270496	-0.380259
C	-3.149555	-1.903263	0.643148
H	1.541471	2.076138	-0.867024
H	1.064359	1.298090	2.043945
H	-1.240579	1.924590	1.740904
H	-0.572319	2.176378	-1.248922
H	-0.888607	-0.128855	-2.041027
H	1.493388	0.109852	-2.000607
H	3.719037	1.133516	-0.547352
H	3.429041	1.203541	1.203076
H	-3.044579	1.471322	-1.301020
H	-2.882988	3.191398	-0.974376
H	-3.215523	2.065625	0.357499
H	-3.263190	-1.245198	1.506592
H	-2.682616	-2.835192	0.965368
H	-4.117677	-2.100928	0.188068

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Maleate TRANS ts CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -727.260864
Enthalpy(298K) = -727.244836; Gibbs free energy(298K) = -727.303126

C	0.404584	-0.294405	1.000719
C	1.218390	2.031913	-0.230407
C	0.110008	2.752626	0.137515
C	-1.212138	2.310867	-0.060220
C	-1.499489	1.032495	-0.537668
C	-0.985218	-0.177283	0.906827
C	-2.902020	0.518687	-0.693576
C	-1.879200	-1.304203	0.397010
O	-2.897017	-0.896319	-0.394946
C	1.152904	-1.055050	0.016888
C	2.618163	2.390408	0.150037
O	0.714310	-1.437288	-1.057204
O	-1.777639	-2.453157	0.724062
O	2.438933	-1.264793	0.399164
C	3.250544	-2.010891	-0.524912
H	0.935054	0.096605	1.855677
H	1.117436	1.255786	-0.978628
H	0.254044	3.648012	0.737112
H	-2.014442	2.893236	0.384935
H	-0.809404	0.584998	-1.248733

```
H     -1.458157     0.299311     1.764122
H     -3.269114     0.605221     -1.717388
H     -3.602528     1.018835     -0.018736
H     2.649489     3.159364     0.924368
H     3.171825     2.755747     -0.723823
H     3.155148     1.506576     0.507944
H     4.224225     -2.103180     -0.048946
H     3.339571     -1.482465     -1.475634
H     2.818989     -2.996568     -0.704155
```

##########################

```
Maleate REACTANT G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -727.477003
Enthalpy(298K) = -727.458955;  Gibbs free energy(298K) = -727.525730
C     2.446913     -0.339879     -0.524344
C     3.555369     -0.339379     0.227607
C     1.088872     -0.656431     0.001208
C     4.894013     -0.081449     -0.269283
C     5.994680     -0.093300     0.494884
C     7.385698     0.172550     0.012334
O     0.220011     0.471971     -0.284256
C     -1.080359     0.295323     0.001883
O     -1.537517     -0.718211     0.483613
C     -1.858076     1.510218     -0.342198
C     -3.186891     1.561475     -0.254773
C     -4.071935     0.450769     0.224318
O     -4.596632     0.450062     1.310652
O     -4.269165     -0.471286     -0.723364
C     -5.093256     -1.584548     -0.338039
H     2.511079     -0.126247     -1.589559
H     3.468642     -0.552920     1.293007
H     0.655011     -1.540445     -0.479647
H     1.098900     -0.834202     1.080666
H     4.986309     0.134329     -1.333409
H     5.887658     -0.312474     1.557212
H     8.042302     -0.684839     0.207761
H     7.830085     1.026287     0.539688
H     7.408183     0.383636     -1.060481
H     -1.289488     2.375650     -0.662320
H     -3.708640     2.486751     -0.482085
H     -4.613894     -2.142524     0.469524
H     -5.184549     -2.204900     -1.228799
H     -6.075343     -1.240491     -0.006301
```

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```
Maleate TRANS ts G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -727.445112
Enthalpy(298K) = -727.429107;  Gibbs free energy(298K) = -727.487204
C     0.398092     -0.293514     1.012389
C     1.237513     2.002255     -0.232987
C     0.140315     2.740439     0.130901
C     -1.188320     2.318668     -0.066231
C     -1.492793     1.044817     -0.538523
C     -0.989091     -0.170173     0.919740
C     -2.898510     0.537741     -0.686433
```

C	-1.884839	-1.287160	0.394213
O	-2.900359	-0.871596	-0.393143
C	1.138451	-1.057066	0.025238
C	2.643005	2.337819	0.148621
O	0.691234	-1.440111	-1.044979
O	-1.784752	-2.440984	0.706099
O	2.425243	-1.265714	0.398793
C	3.222551	-2.003823	-0.534233
H	0.934141	0.100136	1.863511
H	1.127055	1.225807	-0.980634
H	0.297930	3.636019	0.728374
H	-1.983506	2.914033	0.376333
H	-0.805319	0.575542	-1.239178
H	-1.465814	0.315451	1.770768
H	-3.272703	0.631895	-1.709761
H	-3.593812	1.047062	-0.009194
H	2.686470	3.106751	0.924445
H	3.206280	2.695285	-0.724022
H	3.164746	1.442941	0.506161
H	4.208717	-2.091758	-0.078244
H	3.291517	-1.477613	-1.490017
H	2.795116	-2.994334	-0.708883

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Maleate CIS TS G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -727.444546
Enthalpy(298K) = -727.428473; Gibbs free energy(298K) = -727.486911

C	1.616988	1.423394	-0.019030
C	0.729565	1.600864	1.045793
C	-0.625824	1.906166	0.862069
C	-1.222341	1.996069	-0.372399
C	-0.341996	-0.351128	-1.142091
C	1.041834	-0.176147	-1.068302
C	1.949979	-1.135632	-0.316275
O	1.867988	-2.332750	-0.358749
O	2.966164	-0.542090	0.346830
C	3.007075	0.895678	0.246777
C	-2.698937	2.134833	-0.568794
C	-1.061498	-0.981785	-0.048934
O	-0.594617	-1.201758	1.054927
O	-2.344525	-1.275392	-0.382084
C	-3.120380	-1.882563	0.655253
H	1.511702	2.086321	-0.871897
H	1.047763	1.299077	2.040100
H	-1.267054	1.896603	1.739814
H	-0.609980	2.153341	-1.252289
H	-0.878120	-0.141399	-2.056907
H	1.510033	0.122672	-2.006684
H	3.703459	1.168496	-0.552685
H	3.413159	1.247367	1.198172
H	-3.085077	1.336046	-1.211677
H	-2.939951	3.084826	-1.062337
H	-3.237110	2.091166	0.381876
H	-3.216344	-1.212207	1.513938
H	-2.659289	-2.815503	0.989559
H	-4.100052	-2.079387	0.219231

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###########################

Z-9-ester ether tether REACTANT B3LYP
B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.42143637 ;   energy(0K) = -654.16933580
Enthalpy = -654.14704849 ;  Gibbs energy = -654.22741942

 M06-2X/6-32G(d)[CPCM=benzene]//B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.1218565 ;   energy(0K) = -653.8697559
Enthalpy = -653.8474686 au;  Gibbs energy = -653.9278396 au
C     2.571578     -0.013947     0.685156
C     3.636032     -0.430332     -0.020747
C     1.193770     -0.580267     0.542275
C     4.987544     0.084982     0.138597
C     6.046586     -0.344752     -0.568918
C     7.447140     0.170335     -0.427335
O     0.279782     0.481329     0.280119
C     -1.929867     1.233525     -0.038613
C     -1.065517     0.035018     0.225189
C     -3.263147     1.258357     -0.189539
C     -4.101622     0.048541     -0.113239
O     -3.702335     -1.085902     0.098936
O     -5.405974     0.348224     -0.311898
C     -6.313075     -0.764998     -0.259094
H     2.686219     0.772350     1.431431
H     3.500542     -1.213228     -0.769102
H     1.160458     -1.327843     -0.267090
H     0.891276     -1.095707     1.472228
H     5.127818     0.869779     0.883702
H     5.893894     -1.131271     -1.310124
H     8.140728     -0.635680     -0.150501
H     7.514400     0.954164     0.334483
H     7.815909     0.583643     -1.376307
H     -1.382127     2.171513     -0.109190
H     -1.359128     -0.455845     1.168008
H     -1.201442     -0.723140     -0.562946
H     -3.776663     2.195515     -0.378572
H     -6.273491     -1.246825     0.721454
H     -6.063873     -1.500424     -1.028639
H     -7.302833     -0.344971     -0.438479

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Z-9-ester ether tether TRANS IMDA TS B3LYP
B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.38282613 ;   energy(0K) = -654.12885574
Enthalpy = -654.10892217 ;  Gibbs energy = -654.17971926

 M06-2X/6-32G(d)[CPCM=benzene]//B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.0909850 ;   energy(0K) = -653.8370146
Enthalpy = -653.8170810 au;  Gibbs energy = -653.8878781 au
C     0.406468     -0.336783     0.986881
C     0.739626     1.970808     -0.301257
C     -0.478022     2.514027     0.054488
C     -1.702814     1.844986     -0.114051
C     -1.764988     0.508088     -0.535474
C     -0.993451     -0.507221     0.933291
C     -3.080194     -0.235228     -0.669218
C     -1.707450     -1.765806     0.450299
```

```
O     -3.050309     -1.428579     0.126639
C     1.325784     -0.975935     0.064612
C     2.060633     2.582756     0.051277
O     1.038007     -1.508550     -1.005531
O     2.618987     -0.880062     0.496042
C     3.601182     -1.466369     -0.369297
H     0.847686     0.170409     1.835766
H     0.767910     1.190327     -1.054165
H     -0.481415     3.441988     0.625803
H     -2.597601     2.297654     0.311267
H     -1.007951     0.179458     -1.246203
H     -1.511780     -0.077592     1.790751
H     -3.257639     -0.500058     -1.722212
H     -3.926608     0.368014     -0.320983
H     -1.766799     -2.500779     1.260442
H     -1.176016     -2.211198     -0.398100
H     1.961083     3.362806     0.812958
H     2.532428     3.028147     -0.836679
H     2.752878     1.816552     0.420832
H     3.595071     -0.985019     -1.351369
H     3.414317     -2.535989     -0.499588
H     4.560315     -1.307139     0.124983
```

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Z-9-ester ether tether CIS IMDA TS B3LYP
B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.38161938 ; energy(0K) = -654.12755982
Enthalpy = -654.10776786 ; Gibbs energy = -654.17817901

M06-2X/6-32G(d)[CPCM=benzene]//B3LYP/6-32G(d)[CPCM=benzene]
Eel = -654.0928602 ; energy(0K) = -653.8388006
Enthalpy = -653.8190087 au; Gibbs energy = -653.8894198 au

```
C     -1.954120     0.964680     0.062857
C     -1.088243     1.334565     1.105910
C     0.201292     1.831017     0.893726
C     0.761149     1.950772     -0.367903
C     0.354857     -0.378761     -1.055686
C     -1.050881     -0.481607     -1.033930
C     -1.876422     -1.549391     -0.336956
O     -3.217894     -1.078229     -0.252842
C     -3.221343     0.198062     0.398290
C     2.196068     2.327004     -0.594194
C     1.211308     -0.960564     -0.029529
O     0.855177     -1.369526     1.068867
O     2.517780     -0.984217     -0.425538
C     3.439485     -1.522541     0.531211
H     -1.999943     1.621190     -0.803863
H     -1.342358     1.021171     2.117336
H     0.857317     1.927854     1.757381
H     0.104473     2.069730     -1.223627
H     0.844666     -0.094201     -1.979500
H     -1.506901     -0.216019     -1.988952
H     -1.921337     -2.461447     -0.942959
H     -1.460010     -1.793436     0.646329
H     -4.128222     0.711875     0.063494
H     -3.284964     0.056557     1.488681
H     2.791670     2.214145     0.317237
H     2.271213     3.373078     -0.924327
```

```
H     2.653120     1.710999     -1.376350
H     3.178053     -2.553483     0.786162
H     3.446277     -0.923875     1.446749
H     4.417544     -1.487779     0.049537
```

##########################

Z-9-ester ether tether REACTANT CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -653.303564
Enthalpy(298K) = -653.285997; Gibbs free energy(298K) = -653.351131

```
C     2.574770     -0.023287     0.683298
C     3.637907     -0.435937     -0.019743
C     1.200457     -0.592495     0.543473
C     4.985647     0.087061     0.134927
C     6.043968     -0.337834     -0.569529
C     7.440049     0.186158     -0.432741
O     0.283344     0.468114     0.280869
C     -1.926269     1.222893     -0.026873
C     -1.064899     0.025367     0.233642
C     -3.255176     1.253484     -0.180171
C     -4.100779     0.048591     -0.111677
O     -3.711876     -1.083091     0.096971
O     -5.399717     0.357120     -0.314844
C     -6.322576     -0.746843     -0.272142
H     2.685368     0.766614     1.423180
H     3.505496     -1.220862     -0.763463
H     1.168087     -1.337341     -0.264567
H     0.902812     -1.102325     1.474901
H     5.121760     0.875044     0.874410
H     5.894927     -1.127607     -1.304814
H     8.135878     -0.613549     -0.153889
H     7.503619     0.972595     0.322789
H     7.802748     0.594334     -1.383167
H     -1.374745     2.156572     -0.092285
H     -1.353661     -0.459208     1.178387
H     -1.206267     -0.731080     -0.551556
H     -3.763790     2.191148     -0.366109
H     -6.294033     -1.231282     0.704957
H     -6.077774     -1.479369     -1.042620
H     -7.303038     -0.313776     -0.454915
```

##########################

Z-9-ester ether tether CIS IMDA TS CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -653.274891
Enthalpy(298K) = -653.259605; Gibbs free energy(298K) = -653.315900

```
C     -1.966956     0.948323     0.049006
C     -1.115130     1.336696     1.095390
C     0.167789     1.841734     0.891257
C     0.736903     1.957994     -0.364702
C     0.361758     -0.364047     -1.039874
C     -1.042248     -0.485331     -1.018754
C     -1.850808     -1.564022     -0.322199
O     -3.200974     -1.113142     -0.250683
C     -3.229893     0.175562     0.379807
C     2.167389     2.348180     -0.579828
C     1.225807     -0.949020     -0.023265
```

```
O     0.879218     -1.367128     1.068000
O     2.528058     -0.966330     -0.426145
C     3.463306     -1.518350     0.513485
H     -2.013156     1.598176     -0.819570
H     -1.377168     1.033852     2.105419
H     0.813014     1.952377     1.758440
H     0.087805     2.068449     -1.224359
H     0.846252     -0.080624     -1.963687
H     -1.497090     -0.234964     -1.975714
H     -1.874371     -2.477089     -0.922729
H     -1.439951     -1.793511     0.664195
H     -4.133082     0.672870     0.020746
H     -3.307482     0.049602     1.468363
H     2.762127     2.217471     0.326422
H     2.231471     3.400919     -0.882216
H     2.626629     1.758573     -1.376969
H     3.202476     -2.549555     0.757650
H     3.482675     -0.930773     1.433192
H     4.431934     -1.479300     0.019505

###########################

Z-9-ester ether tether TRANS IMDA TS CBS-QB3
CBS-QB3[CPCM=benzene]
Energy(0K) = -653.273340
Enthalpy(298K) = -653.257877;  Gibbs free energy(298K) = -653.314750
C     0.408714     -0.320385     0.973924
C     0.724446     1.970762     -0.302061
C     -0.493779     2.509068     0.051997
C     -1.711186     1.835132     -0.113879
C     -1.766657     0.498431     -0.533859
C     -0.989844     -0.501139     0.923955
C     -3.078763     -0.246742     -0.665235
C     -1.692164     -1.770307     0.456277
O     -3.038027     -1.444836     0.127140
C     1.329844     -0.966862     0.060368
C     2.040766     2.587326     0.050062
O     1.045609     -1.517304     -0.994399
O     2.621299     -0.857479     0.487798
C     3.612019     -1.459509     -0.360867
H     0.848888     0.187369     1.819783
H     0.754158     1.194802     -1.056540
H     -0.501289     3.436588     0.619494
H     -2.607203     2.283107     0.307942
H     -1.013944     0.178018     -1.249527
H     -1.506506     -0.073745     1.780735
H     -3.260030     -0.510470     -1.714996
H     -3.921507     0.351017     -0.308027
H     -1.745856     -2.492374     1.274519
H     -1.160714     -2.219384     -0.386714
H     1.939180     3.359050     0.815952
H     2.502523     3.040052     -0.836335
H     2.737991     1.824398     0.408912
H     3.617392     -0.991136     -1.346710
H     3.421724     -2.527650     -0.477627
H     4.563773     -1.297335     0.140736

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```

Z-9-ester ether tether REACTANT G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -653.480475
Enthalpy(298K) = -653.462945; Gibbs free energy(298K) = -653.527696

C	2.566335	-0.013558	0.674705
C	3.631811	-0.430343	-0.020869
C	1.191048	-0.581083	0.532964
C	4.979229	0.086389	0.136832
C	6.039465	-0.344040	-0.560210
C	7.436366	0.174100	-0.418424
O	0.277595	0.475287	0.274244
C	-1.927826	1.229156	-0.038860
C	-1.063958	0.032598	0.220576
C	-3.256636	1.255060	-0.186818
C	-4.095029	0.047000	-0.111330
O	-3.699503	-1.082402	0.096113
O	-5.395638	0.349970	-0.305974
C	-6.302220	-0.758341	-0.253720
H	2.675307	0.778611	1.413611
H	3.501547	-1.219136	-0.762065
H	1.159564	-1.328665	-0.275911
H	0.891883	-1.099298	1.462312
H	5.113930	0.876590	0.875344
H	5.892227	-1.135924	-1.294654
H	8.129677	-0.627803	-0.133897
H	7.499478	0.963565	0.335939
H	7.807516	0.578144	-1.369040
H	-1.376409	2.163723	-0.108069
H	-1.358352	-0.461006	1.161247
H	-1.204282	-0.724478	-0.567292
H	-3.771961	2.190031	-0.372886
H	-6.262531	-1.243497	0.724839
H	-6.055793	-1.494839	-1.022677
H	-7.292932	-0.340480	-0.430939

##########################

Z-9-ester ether tether CIS IMDA TS G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -653.449928
Enthalpy(298K) = -653.434599; Gibbs free energy(298K) = -653.491044

C	-1.946076	0.965375	0.062978
C	-1.079893	1.335208	1.102151
C	0.207934	1.822602	0.889057
C	0.769281	1.936699	-0.369489
C	0.350360	-0.377022	-1.053753
C	-1.052838	-0.474969	-1.032081
C	-1.880890	-1.542367	-0.339101
O	-3.215676	-1.067785	-0.248479
C	-3.214662	0.204328	0.400370
C	2.204690	2.304585	-0.593273
C	1.204330	-0.959440	-0.028241
O	0.848409	-1.368607	1.062873
O	2.507385	-0.980651	-0.422146
C	3.426336	-1.517388	0.532097
H	-1.990456	1.617738	-0.804733
H	-1.338979	1.031532	2.113664
H	0.862287	1.924650	1.751473
H	0.116258	2.057420	-1.225809

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H     0.842494     -0.093337     -1.974444
H     -1.508818     -0.204993     -1.984524
H     -1.928304     -2.450185     -0.950367
H     -1.458748     -1.792707     0.639715
H     -4.119586     0.722734     0.068895
H     -3.274504     0.066525     1.491052
H     2.792781     2.207615     0.323365
H     2.284344     3.342630     -0.942781
H     2.665058     1.673769     -1.359801
H     3.167859     -2.549165     0.785218
H     3.429156     -0.923672     1.450432
H     4.406784     -1.479874     0.056371

###########################

Z-9-ester ether tether TRANS IMDA TS G4(MP2)
G4(MP2)[CPCM=benzene]
Energy(0K) = -653.448882
Enthalpy(298K) = -653.433464;  Gibbs free energy(298K) = -653.490066
C     0.402096     -0.330592     0.986973
C     0.752428     1.955108     -0.297933
C     -0.461125     2.506555     0.046601
C     -1.685458     1.846348     -0.124730
C     -1.753314     0.510686     -0.538489
C     -0.995657     -0.494048     0.936737
C     -3.069368     -0.227097     -0.676047
C     -1.717059     -1.751286     0.463263
O     -3.050883     -1.408874     0.128920
C     1.313898     -0.975915     0.064341
C     2.074151     2.556582     0.061190
O     1.020746     -1.514152     -0.993924
O     2.605820     -0.878049     0.486963
C     3.579359     -1.473196     -0.375515
H     0.850075     0.175127     1.830914
H     0.780383     1.174049     -1.048313
H     -0.461372     3.437332     0.610409
H     -2.580629     2.306618     0.287485
H     -0.993286     0.170144     -1.237949
H     -1.512086     -0.054251     1.788749
H     -3.238111     -0.499181     -1.728303
H     -3.914679     0.385278     -0.342639
H     -1.783985     -2.475571     1.281834
H     -1.180731     -2.208492     -0.375253
H     1.976534     3.335472     0.822407
H     2.552518     2.998644     -0.823391
H     2.758396     1.784866     0.430652
H     3.566545     -1.006101     -1.363930
H     3.391662     -2.543785     -0.493411
H     4.543594     -1.310406     0.106732

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2 Cartesian coordinates and energies of structures optimised in chlorobenzene using the PCM solvation model

Acrylate reactant

B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -500.59366141 au; Energy(0K)) = -500.40361601 au
Enthalpy = -500.39019015 au; Gibbs energy = -500.44414095 au

C	0.803956	-0.273251	0.638387
C	1.913507	-0.371210	-0.114408
C	3.217387	0.150540	0.265626
C	4.319183	0.038622	-0.496997
C	5.674628	0.567634	-0.137404
C	-0.511602	-0.858720	0.246896
O	-1.489591	0.221089	0.191958
C	-2.767238	-0.148722	-0.033919
C	-3.661031	1.036569	-0.055726
C	-4.972727	0.904122	-0.268223
O	-3.116709	-1.305632	-0.197187
H	0.840618	0.233056	1.604577
H	1.855408	-0.879683	-1.080257
H	3.281728	0.660203	1.229881
H	4.239760	-0.475341	-1.458243
H	6.419182	-0.239975	-0.104392
H	5.669284	1.067092	0.837278
H	6.031360	1.286185	-0.888470
H	-0.871120	-1.594600	0.976310
H	-0.468531	-1.347176	-0.732274
H	-3.194573	2.005588	0.108061
H	-5.636232	1.764233	-0.286347
H	-5.412860	-0.076751	-0.429679

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Acrylate CIS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -500.54046191 au; Energy(0K)) = -500.34943683 au
Enthalpy = -500.33820124 au; Gibbs energy = -500.38481980 au

C	-0.452169	-1.326679	0.491324
C	0.271719	-1.457208	-0.687070
C	1.575070	-0.949979	-0.818390
C	2.224815	-0.254785	0.193619
C	3.572982	0.383677	-0.011543
C	-1.956966	-1.379276	0.497521
O	-2.479727	-0.186169	-0.157402
C	-1.647216	0.892531	-0.157649
C	-0.519349	0.842960	0.818425
C	0.701522	1.444898	0.558713
O	-1.875514	1.808644	-0.923456
H	0.054438	-1.425017	1.447695
H	-0.267429	-1.703079	-1.603990
H	2.002035	-0.912675	-1.821836
H	1.977839	-0.492259	1.225818
H	3.676049	1.306241	0.571315
H	3.747745	0.625093	-1.065578
H	4.377272	-0.290469	0.316429
H	-2.358152	-1.427530	1.515516

H -2.365524 -2.214323 -0.080957
H -0.817857 0.668175 1.852425
H 1.321029 1.786830 1.381025
H 0.872039 1.922383 -0.400707

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Acrylate TRANS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -500.53919374 au; Energy(0K)) = -500.34807228 au
Enthalpy = -500.33686604 au; Gibbs energy = -500.38343958 au
C 0.542231 -1.410188 0.620129
C -0.578781 -0.605438 0.766717
C -1.861385 -0.826627 0.033621
O -2.567655 0.310363 -0.239073
C -1.805784 1.545975 -0.133560
C -0.365557 1.196998 -0.363001
C 0.744381 1.779517 0.229750
C 1.988622 1.124514 0.181079
C 2.181473 -0.101677 -0.443954
C 3.482288 -0.854428 -0.350449
O -2.315315 -1.898430 -0.311247
H 0.560798 -2.175355 -0.151003
H 1.220510 -1.551937 1.452870
H -0.704915 -0.059468 1.701370
H -2.230153 2.204634 -0.899697
H -1.972807 1.997561 0.851805
H -0.210750 0.642506 -1.288584
H 0.608904 2.576251 0.962289
H 2.774930 1.490909 0.843174
H 1.569210 -0.349816 -1.307599
H 3.319128 -1.938231 -0.335571
H 4.042220 -0.582118 0.550991
H 4.121750 -0.642277 -1.219482

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FUMARATE reactant
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -728.47486292 au; Energy(0K)) = -728.24148902 au
Enthalpy = -728.22359974 au; Gibbs energy = -728.28947912 au
C -2.787473 0.457238 0.632362
C -3.870623 0.296192 -0.147693
C -1.600265 1.265938 0.230664
C -5.062506 -0.443794 0.237137
C -6.139988 -0.587307 -0.554491
C -7.381884 -1.344145 -0.192750
O -0.425469 0.398841 0.267804
C 1.865279 0.010679 0.112027
C 0.755229 0.995848 0.029338
O 0.885344 2.181647 -0.220122
C 3.133504 0.384418 -0.093902

C	4.243210	-0.598640	-0.010144
O	4.122383	-1.783566	0.242591
O	5.424820	0.000924	-0.252904
C	6.582346	-0.853946	-0.198854
H	-2.756194	0.010438	1.627573
H	-3.879858	0.750340	-1.141922
H	-1.702508	1.674388	-0.780044
H	-1.413257	2.100450	0.917281
H	-5.059802	-0.901201	1.229295
H	-6.127644	-0.122224	-1.543464
H	-8.266257	-0.692665	-0.226091
H	-7.314624	-1.777817	0.810658
H	-7.570965	-2.158422	-0.906073
H	1.612571	-1.021330	0.345034
H	3.385584	1.416385	-0.327684
H	6.505115	-1.646168	-0.948250
H	6.677155	-1.303510	0.793086
H	7.433082	-0.206329	-0.410524

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FUMARATE TRANS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -728.43019574 au; Energy(0K)) = -728.19604379 au
Enthalpy = -728.18021858 au; Gibbs energy = -728.23797616 au

C	0.252974	-0.788667	-0.430398
C	0.950182	1.824151	-0.819753
C	0.434115	2.256633	0.383665
C	-0.871116	1.969298	0.826250
C	-1.728229	1.157428	0.075614
C	-0.988471	-0.644409	0.199526
C	-3.107315	0.745971	0.516318
C	-2.247840	-1.249116	-0.376861
O	-3.371790	-0.547185	-0.087597
C	1.447977	-0.929821	0.386212
C	2.385471	1.990677	-1.210691
O	-2.315084	-2.275579	-1.014427
O	1.502854	-0.827924	1.607344
O	2.543217	-1.226507	-0.372745
C	3.760392	-1.434699	0.357871
H	0.326856	-0.989322	-1.494920
H	0.278304	1.511205	-1.614257
H	1.114800	2.722043	1.097112
H	-1.120184	2.188353	1.865121
H	-1.652185	1.241481	-1.010020
H	-0.955887	-0.731147	1.288698
H	-3.895529	1.410167	0.148771
H	-3.188758	0.658885	1.606305
H	2.987435	2.388339	-0.387145
H	2.476410	2.672033	-2.068527
H	2.816425	1.030908	-1.520159
H	3.653054	-2.267826	1.058501

H 4.039172 -0.536327 0.915938
H 4.517660 -1.665911 -0.392530

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FUMARATE CIS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -728.42912646 au; Energy(0K)) = -728.19477336 au
Enthalpy = -728.17900210 au; Gibbs energy = -728.23659828 au
C -1.736133 0.770839 0.953591
C -1.658416 1.787756 -0.008048
C -0.444792 2.344942 -0.438268
C 0.789932 1.959813 0.047142
C 0.434149 -0.581857 -0.445406
C -0.794299 -0.829115 0.172651
C -2.008066 -1.218322 -0.624341
O -2.004140 -1.811643 -1.681238
O -3.183164 -0.862233 -0.047032
C -3.030321 0.005154 1.112000
C 2.081929 2.458607 -0.523762
C 1.661547 -0.880035 0.283982
O 1.741965 -1.103622 1.487279
O 2.749421 -0.874224 -0.532196
C 3.999311 -1.197274 0.100041
H -1.082131 0.820487 1.822499
H -2.542791 1.988373 -0.615701
H -0.473012 3.002731 -1.307836
H 0.853009 1.464527 1.011691
H 0.500444 -0.416485 -1.515328
H -0.733472 -1.332370 1.140468
H -3.031592 -0.611546 2.016912
H -3.918100 0.643690 1.113939
H 1.925824 3.014397 -1.453903
H 2.767410 1.627620 -0.727760
H 2.589813 3.119411 0.193187
H 3.965546 -2.204632 0.524175
H 4.228383 -0.483135 0.895720
H 4.748971 -1.142330 -0.690054

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MALEATE reactant
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -728.46528273 au; Energy(0K)) = -728.23213940 au
Enthalpy = -728.21430228 au; Gibbs energy = -728.28030793 au
C 2.459161 -0.388662 -0.558675
C 3.555693 -0.345781 0.218104
C 1.095955 -0.699805 -0.038898
C 4.902770 -0.091017 -0.268566
C 5.989279 -0.058176 0.522979
C 7.389056 0.204650 0.056496
O 0.226495 0.434718 -0.338133

C	-1.072425	0.281729	-0.021696
O	-1.535970	-0.721403	0.493929
C	-1.844467	1.499979	-0.372632
C	-3.176206	1.565696	-0.265613
C	-4.066012	0.467438	0.235380
O	-4.579253	0.482750	1.336152
O	-4.295635	-0.461628	-0.701633
C	-5.141266	-1.557593	-0.297101
H	2.541420	-0.217568	-1.633347
H	3.450932	-0.517793	1.292394
H	0.659873	-1.584114	-0.518768
H	1.095793	-0.865944	1.043290
H	5.014501	0.082132	-1.341448
H	5.861320	-0.234723	1.593882
H	8.052097	-0.637275	0.299774
H	7.813691	1.086608	0.555952
H	7.431413	0.371264	-1.025112
H	-1.274725	2.361208	-0.713710
H	-3.692541	2.497401	-0.499114
H	-4.661271	-2.120831	0.507125
H	-5.255215	-2.178840	-1.185388
H	-6.111621	-1.187772	0.043297

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MALEATE TRANS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -728.42785600 au; Energy(0K)) = -728.19360146 au
Enthalpy = -728.17775980 au; Gibbs energy = -728.23552345 au

C	0.397687	-0.308155	1.014454
C	1.218553	2.024359	-0.246415
C	0.118430	2.751149	0.143459
C	-1.212936	2.318838	-0.042903
C	-1.512890	1.045047	-0.529282
C	-0.993315	-0.190414	0.915173
C	-2.919456	0.534627	-0.670879
C	-1.879814	-1.304899	0.377265
O	-2.907109	-0.887770	-0.397799
C	1.153426	-1.062398	0.032177
C	2.627716	2.369198	0.120408
O	0.718955	-1.456732	-1.047822
O	-1.772767	-2.472694	0.669898
O	2.445428	-1.253259	0.415418
C	3.267987	-1.972043	-0.516866
H	0.924195	0.094267	1.871646
H	1.102849	1.251844	-1.000259
H	0.275435	3.643289	0.751506
H	-2.008348	2.904465	0.420066
H	-0.829686	0.597160	-1.250575
H	-1.475753	0.283468	1.774532
H	-3.308796	0.636646	-1.688745
H	-3.610977	1.022244	0.026843

H 2.674279 3.148333 0.887854
H 3.184284 2.718468 -0.761513
H 3.155559 1.480181 0.487958
H 4.253167 -2.032052 -0.052758
H 3.327900 -1.441998 -1.471838
H 2.867506 -2.974524 -0.691816

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MALEATE CIS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -728.42529641 au; Energy(0K)) = -728.19128133 au
Enthalpy = -728.17542311 au; Gibbs energy = -728.23326981 au
C 1.612484 1.433047 -0.022397
C 0.723891 1.607407 1.046396
C -0.637420 1.910353 0.863956
C -1.233712 2.005994 -0.373319
C -0.337446 -0.370467 -1.145160
C 1.047229 -0.181183 -1.068278
C 1.961919 -1.128810 -0.313847
O 1.894787 -2.336442 -0.354886
O 2.977789 -0.529452 0.347409
C 3.007150 0.917892 0.248892
C -2.712072 2.145845 -0.569389
C -1.057963 -0.999944 -0.052242
O -0.590834 -1.228517 1.058180
O -2.346963 -1.289810 -0.385989
C -3.133833 -1.882849 0.656136
H 1.504119 2.096356 -0.878966
H 1.042782 1.303733 2.043809
H -1.278423 1.895836 1.745630
H -0.619488 2.162008 -1.255765
H -0.872630 -0.158619 -2.064125
H 1.514803 0.118941 -2.011092
H 3.704678 1.189583 -0.550696
H 3.410279 1.266054 1.203758
H -3.095267 1.361696 -1.234035
H -2.953466 3.108728 -1.040999
H -3.254190 2.079350 0.379345
H -3.219745 -1.206049 1.511537
H -2.687307 -2.823045 0.992450
H -4.115745 -2.064521 0.216944

##############################

9.9-Diester reactant
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -956.34180681 au; Energy(0K)) = -956.06560046 au
Enthalpy = -956.04312747 au; Gibbs energy = -956.12026472 au
C 3.591808 -0.340431 -0.673505
C 4.674042 -0.281778 0.122237
C 5.939962 0.330633 -0.249316

C	7.013300	0.374154	0.559598
C	-2.291613	0.428141	0.047765
C	-0.977940	0.618795	-0.140983
C	0.012491	-0.486612	-0.074440
O	-0.255692	-1.651775	0.162489
O	1.249397	-0.023535	-0.309424
C	2.322765	-1.017729	-0.280951
C	8.330167	0.999612	0.212611
C	-2.905731	-0.902527	0.409009
O	-3.128602	-1.242591	1.550546
O	-3.217085	-1.606673	-0.683913
C	-3.803960	-2.902603	-0.441576
C	-3.208805	1.610327	-0.049781
O	-2.845642	2.748747	-0.269590
O	-4.486334	1.242111	0.126255
C	-5.465065	2.298496	0.048690
H	3.620378	0.097139	-1.672766
H	4.622307	-0.724937	1.120044
H	5.999128	0.775536	-1.245339
H	6.938309	-0.076701	1.552342
H	-0.606071	1.618658	-0.351010
H	2.375255	-1.443295	0.726281
H	2.043366	-1.818015	-0.976427
H	8.587547	1.798624	0.921780
H	9.144421	0.263686	0.267450
H	8.323022	1.426980	-0.795701
H	-3.096168	-3.535951	0.098778
H	-4.724198	-2.801238	0.138848
H	-4.013378	-3.314246	-1.428675
H	-5.435582	2.767664	-0.937867
H	-5.268921	3.050557	0.816833
H	-6.426286	1.814402	0.218388

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9.9-Diester CIS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -956.30599110 au; Energy(0K)) = -956.02898384 au
Enthalpy = -956.00842248 au; Gibbs energy = -956.07733091 au

C	1.912075	-1.506388	0.117498
C	1.531690	-1.305993	1.443352
C	0.230668	-1.548709	1.960661
C	-0.837228	-1.931881	1.202428
C	-0.192557	0.368027	-0.626126
C	1.099519	-0.025594	-1.003368
C	2.305337	0.881996	-0.879279
O	2.312520	2.051711	-1.187803
O	3.446502	0.261551	-0.514932
C	3.324423	-1.168771	-0.305432
C	-2.239526	-2.015540	1.709061
C	-0.292919	1.249094	0.544525
O	0.673821	1.456573	1.275125

O	-1.501520	1.795880	0.774421
C	-1.587468	2.630544	1.939826
C	-1.293360	-0.203573	-1.426041
O	-1.115084	-1.033499	-2.313794
O	-2.524257	0.245317	-1.106880
C	-3.597542	-0.277103	-1.908497
H	1.410831	-2.291648	-0.446494
H	2.238508	-0.813034	2.110808
H	0.060652	-1.290879	3.006123
H	-0.683255	-2.240077	0.171114
H	1.123434	-0.595226	-1.935289
H	3.594862	-1.675063	-1.238036
H	4.066587	-1.413329	0.458716
H	-2.876681	-1.310477	1.157270
H	-2.659336	-3.016507	1.540707
H	-2.305608	-1.779058	2.775537
H	-1.361888	2.058109	2.844091
H	-0.890950	3.470423	1.867310
H	-2.617147	2.989064	1.962743
H	-3.659732	-1.364680	-1.814983
H	-3.453486	-0.017555	-2.960723
H	-4.501318	0.193014	-1.519642

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9.9-Diester TRANS TS
B3LYP/6-31G()[PCM=chlorobenzene]
Eel = -956.30922351 au; Energy(0K)) = -956.03202890 au
Enthalpy = -956.01147455 au; Gibbs energy = -956.08022089 au

C	-0.126724	0.422639	0.531054
C	-0.862017	-1.698457	-1.570503
C	-0.123645	-2.620189	-0.883021
C	1.213822	-2.412222	-0.446841
C	1.896045	-1.210305	-0.602192
C	1.175932	-0.021120	0.812050
C	3.333270	-1.037149	-0.193968
C	2.384552	0.897064	0.748042
O	3.508862	0.321751	0.273396
C	-0.283476	1.444068	-0.516762
C	-2.313223	-1.848155	-1.886277
O	0.570051	1.633186	-1.382062
O	2.399518	2.028646	1.171673
O	-1.416116	2.165190	-0.454370
C	-1.577596	3.156909	-1.482744
C	-1.197598	-0.213144	1.318316
O	-0.981954	-1.028828	2.209615
O	-2.450845	0.156444	0.973191
C	-3.502040	-0.435059	1.753063
H	-0.376018	-0.814593	-1.975144
H	-0.610518	-3.540951	-0.560449
H	1.660279	-3.187322	0.178323
H	1.597899	-0.546594	-1.412345

H	1.231155	-0.681858	1.679323
H	4.023626	-1.150848	-1.035403
H	3.625422	-1.728201	0.605804
H	-2.720923	-2.792575	-1.512629
H	-2.484939	-1.791819	-2.969984
H	-2.878822	-1.021072	-1.435873
H	-2.543027	3.623103	-1.284058
H	-1.572631	2.692131	-2.472557
H	-0.775720	3.898338	-1.432216
H	-3.388144	-0.181193	2.810475
H	-3.500656	-1.523381	1.646188
H	-4.426930	-0.013553	1.357700

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