Enhanced stereocontrol in Diels–Alder reactions of chiral dienols

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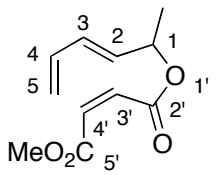
Contents

1. General Experimental Details

NMR spectra were recorded at 298K using a Varian Unity INOVA 500 MHz, Bruker DPX/DRX 400 MHz or a Varian Unity INOVA 300 MHz spectrometer. Residual protio-acetone (δ 2.04 ppm), -benzene (δ 7.15 ppm), -chloroform (δ 7.26 ppm), and -methanol (δ 3.31 ppm) were used as internal references for ^{1}H NMR spectra measured in these solvents. The ^{13}C NMR resonances of acetone (δ 29.8 ppm , 206.8 ppm), benzene (δ 128.1 ppm), chloroform (δ 77.1 ppm) and methanol (δ 49.0 ppm) were used as internal references for ^{13}C NMR spectra. Assignment of proton signals was assisted by ^{1}H–^{1}H COSY and NOESY experiments when necessary; assignment of carbon signals was assisted by DEPT experiments. IR spectra were recorded on a Perkin–Elmer 1600 F.T.I.R. or Perkin–Elmer Spectrum One spectrometer as neat films on NaCl plates for oils or as KBr pellets for solid products. Low resolution mass spectra were recorded on a Finnigan PolarisQ ion trap mass spectrometer using electron impact (EI) ionisation mode at 40 or 70 eV. High resolution mass spectra were recorded on a VG Autospec mass spectrometer operating at 70 eV. High resolution electrospray ionisation spectra were recorded on a Bruker BioApex FTICR with an Analytica ESI source, operating at 4.7 T. Microanalyses were performed at the Research School of Chemistry, Australian National University. Optical rotations were measured with an Optical Activity Polaar 2001or a Perkin Elmer 241 optical polarimeter. Melting points were measured on a Reichert melting point stage and are uncorrected. HPLC was performed using a Waters 510EF chromatograph pump and Waters U6K injector monitored by an Waters Lambda-Max 481 UV spectrophotometer at λ = 254 nm and an Erma ERC-7512 refractive index detector or a Waters 510EF chromatograph pump and Waters U6K injector monitored by an ISCO 226 UV spectrophotometer at λ = 254 nm and a Waters R403 refractive index detector. GC measurements were recorded on an Agilent 6850 gas chromatograph with a split/splitless capillary inlet and FID detector or GC measurements were recorded on a Hewlett Packard 5890A gas chromatograph with a split/splitless capillary inlet and FID detector. GC data was processed using Hewlett Packard ChemStation software. Analytical TLC was performed with Merck silica gel plates, precoated with silica gel 60 F254 (0.2 mm). Flash chromatography employed Merck Kiesegel 60 (230–400 mesh) silica gel. Reactions were conducted under a positive pressure of dry argon or nitrogen. Diethyl ether, toluene and THF were dried over sodium wire and distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Commercially available chemicals were purified by standard procedures or used as purchased.

2. Synthetic Procedures

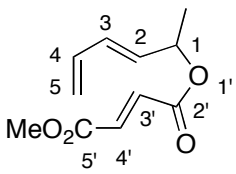
(±)-Methyl (1*S*,2*E*)-1-Methylpenta-2,4-dien-1-yl Maleate (18*Z*)



18*Z*

Triethylamine (1.707 g, 16.86 mmol, 1.6 equiv), maleic anhydride (2.326 g, 23.72 mmol, 2.25 equiv) and DMAP (128.8 mg, 1.054 mmol, 0.1 equiv) were added to a stirred solution of hexa-3,5-dien-2-ol (**28**)[1] (1.034 g, 10.54 mmol, 1.0 equiv) in dichloromethane (50 mL) at 0 °C. The mixture was stirred at this temperature for 10 min. The solution was allowed to warm to room temperature before being diluted with diethyl ether (200 mL). The mixture was washed with 2M HCl (100 mL), sat. aq. $NaHCO_3$ (100 mL), brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude material was diluted with toluene (5 mL) and cooled to -78 °C with stirring. An ethereal solution of diazomethane was added dropwise until TLC confirmed the reaction had gone to completion. Excess diazomethane was removed by bubbling N_2 gas through the solution. The solution was concentrated *in vacuo* and subjected to column chromatography on silica (hexanes/ethyl acetate 80:20) to give maleate **18*Z*** (1.257 g, 5.979 mmol, 57%) as a colourless oil. R_f = 0.45 (hexanes/ethyl acetate 80:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.32-6.19 (3H, m), 5.67 (1H, dd, *J* = 14.2, 6.7 Hz), 5.47 (1H, m), 5.22 (1H, m), 5.10 (1H, m), 3.73 (3H, s), 1.35 (3H, d, *J* = 6.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.6 (C), 164.3 (C), 135.9 (CH), 132.6 (CH), 132.0 (CH), 130.0 (CH), 129.4 (CH), 118.7 (CH_2), 71.7 (CH), 52.1 (CH_3), 19.9 (CH_3). IR (neat): ν = 2985, 2952 (C-H), 1728 (C=O), 1638 cm^{-1} (C=C). EIMS (70 eV) *m/z* (%): 210 ([M]$^+$, 5), 179 ([M-CH_3O]$^+$, 15), 164 ([M-CH_2O_2]$^+$, 60), 150 ([M-$C_2H_4O_2$]$^+$, 35), 105 ([M-$C_3H_5O_4$]$^+$, 100), 79 ([M-$C_5H_7O_4$]$^+$, 95). HRMS: calcd for $C_{11}H_{14}O_4$ [M]$^+$: 210.0892; found: 210.0890.

(±)-Methyl (1*S*,2*E*)-1-Methylpenta-2,4-dien-1-yl Fumarate (18*E*)

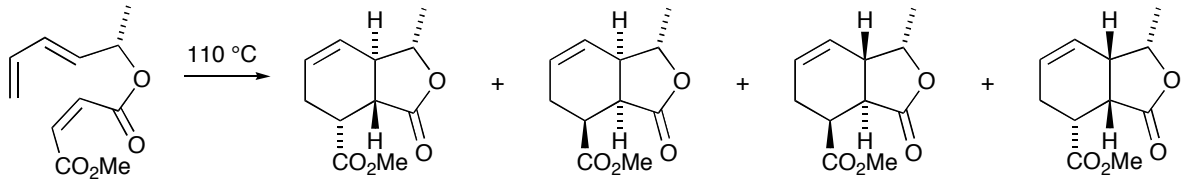


18*E*

A solution of DCC (2.862 g, 13.87 mmol, 1.13 equiv), DMAP (599.9 mg, 4.910 mmol, 0.4 equiv) and diethyl ether (30 mL) was added dropwise to a solution of hexa-3,5-dien-2-ol (**28**)[1] (1.205 g, 12.28 mmol, 1.0 equiv) and (*E*)-3-methoxycarbonylacrylic acid[2] (1.916 g, 14.73 mmol, 1.2 equiv) in diethyl ether (6mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 16 h. The mixture was filtered, washed with a cooled solution of 2M HCl (16 mL), sat. aq. $NaHCO_3$ (16 mL), brine (16 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was subjected to column chromatography on silica (hexanes/ethyl acetate 9:1) to give fumarate **18*E*** (1.620 g, 7.706 mmol, 63%) as a colourless oil. R_f = 0.39 (hexanes/ethyl acetate 90:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (2H, m), 6.34-6.21 (2H, m), 5.68 (1H, dd, *J* = 14.0, 6.3 Hz), 5.48 (1H, m), 5.28-5.19 (1H, m), 5.13 (1H, s), 3.79 (3H, s), 1.37 (3H, d, *J* = 6.5 Hz). ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 165.5 (C), 164.2 (C), 135.9 (CH), 134.2 (CH), 133.2 (CH), 132.8 (CH), 132.0 (CH), 118.9 (CH_2), 71.8 (CH), 52.3 (CH_3), 20.1 (CH_3). IR (neat): ν = 3087, 2983, 2954 (C-H), 1732 (C=O), 1644 cm^{-1} (C=C). EIMS (70 eV) *m/z* (%): 210 ($[M]^+$, 20), 113 ($[M-C_6H_9O]^+$, 100), 97 ($[M-C_5H_5O_3]^+$, 20). HRMS: calcd for $C_{11}H_{15}O_4$ $[M+H]^+$: 211.0970; found: 211.0974.

IMDA Reaction of Maleate 18*Z* in Toluene at 110 °C



A solution of maleate **18*Z*** (1.264 g, 6.012 mmol, 1.0 equiv) and BHT (132 mg, 0.601 mmol, 0.1 equiv) in toluene (600 mL) was stirred at 110 °C for 3 h. The reaction mixture was concentrated *in vacuo*, a portion of the residue dissolved in $CDCl_3$ and ^1H NMR analysis carried out. The residue contained *trans,lk*-IMDA adduct **23*Z***, *trans,ul*-IMDA adduct **25*Z***, *cis,lk*-IMDA adduct **24*Z***,[3] and *cis,ul*-IMDA adduct **26*Z*** (68:19:9:4, respectively). The residue was subjected to chromatography on silica (dichloromethane/diethyl ether 97:3) to give a mixture of the IMDA adducts [1.089 g, 5.181 mmol, 88%; *trans,lk*-IMDA adduct **23*Z***, *trans,ul*-IMDA adduct **25*Z***, *cis,lk*-IMDA adduct **24*Z***,[3] and *cis,ul*-IMDA adduct **26*Z*** (67:18:10:5)]. The mixture of IMDA adducts was separated by HPLC [Whatman Partisil column, eluting with hexanes/*iso*propanol 98:2, 13.5 mL min^{-1}] to give a mixture of *trans,lk*-IMDA adduct **23*Z*** and *trans,ul*-IMDA adduct **25*Z*** at t_R = 113.5 min, *cis,lk*-IMDA adduct **24*Z***,[3] at t_R = 116.0 min, and *cis,ul*-IMDA adduct **26*Z*** at t_R = 158.5 min. The mixture of *trans,lk*-IMDA adduct **25*Z*** and *trans,ul*-IMDA adduct **23*Z*** was separated by further HPLC [Alltech Altima C_{18} column, eluting with water/methanol 60:40, 11.25 mL min^{-1}] to give *trans,ul*-IMDA adduct **25*Z*** at t_R = 29.6 min and *trans,lk*-IMDA adduct **23*Z*** at t_R = 34.1 min.

(±)-Methyl (3*S*,3a*R*,7*R*,7a*S*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*trans,lk*-23*Z*): white crystalline solid after recrystallisation from hexanes/TBME 80:20. mp 87-89 °C. ^1H NMR (400 MHz, C_6D_6): δ = 5.33-5.26 (2H, m), 3.55 (1H, dq, *J* = 10.3, 6.0 Hz), 3.22 (3H, s), 3.01 (1H, dd, *J* = 8.1, 3.5 Hz), 2.74 (1H, m), 2.36 (1H, m), 1.95-1.86 (1H, m), 1.81 (1H, dd, *J* = 13.5, 3.7 Hz), 1.46 (3H, d, *J* = 6.1 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ =

172.9 (C), 172.2 (C), 128.3 (CH), 124.0 (CH), 78.9 (CH), 51.6 (CH_3), 45.4 (CH), 43.2 (CH), 35.8 (CH), 28.9 (CH_2), 18.2 (CH_3). IR (KBr): ν = 2956 (C-H), 1789, 1732 cm^{-1} (C=O). EIMS (70 eV): *m/z* (%) = 211 ($[M+1]^+$, 2), 210 ($[M]^+$, 2), 179 ($[M-CH_3O]^+$, 20), 164 ($[M-CH_2O_2]^+$, 85), 150 ($[M-C_2H_4O_2]^+$, 50), 105 ($[M-C_3H_5O_4]^+$, 100), 91 ($[M-C_4H_7O_4]^+$, 50), 79 ($[M-C_5H_7O_4]^+$, 75). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 63.09, H 6.78.

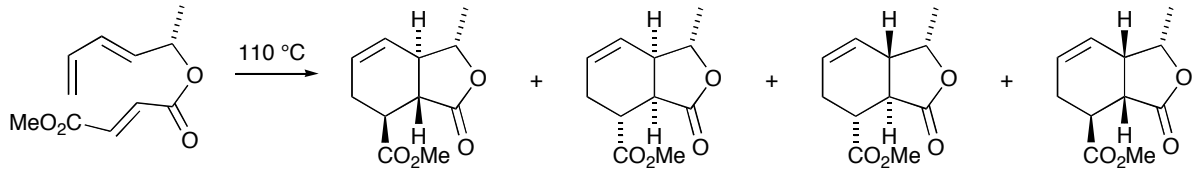
(±)-Methyl (3*S*,3a*R*,7*S*,7a*R*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*cis,lk*-**24*Z***):[3] white crystalline solid after recrystallisation from hexanes/ethyl acetate 60:40. mp 86-88 °C (lit. 153 °C after recrystallisation from water).[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (1H, m), 5.61 (1H, m), 4.36 (1H, dq, *J* = 6.5, 1.0 Hz), 3.75 (1H, s), 3.59 (1H, dd, *J* = 7.8, 4.2 Hz), 2.82 (1H, m), 2.75 (1H, ddd, *J* = 9.6, 6.9, 4.1 Hz), 2.38-2.25 (2H, m), 1.41 (3H, d, *J* = 6.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.7 (C), 172.8 (C), 128.4 (CH), 125.8 (CH), 80.6 (CH), 52.1 (CH_3), 42.2 (CH), 38.8 (CH), 36.7 (CH), 22.9 (CH_2), 20.2 (CH_3). IR (KBr): ν = 3028, 2979, 2947, 2907 (C-H), 1766, 1738 cm^{-1} (C=O). EIMS (70 eV): *m/z* (%) = 210 ($[M]^+$, 5), 178 ($[M-CH_4O]^+$, 10), 150 ($[M-C_2H_4O_2]^+$, 10), 138 ($[M-C_3H_4O_2]^+$, 20), 79 ($[M-C_5H_7O_4]^+$, 100). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 62.78, H 6.85.

(±)-Methyl (3*S*,3a*S*,7*S*,7a*R*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*trans,ul*-**25*Z***): white crystalline solid after recrystallisation from hexanes/ethyl acetate 50:50. mp 122-124 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 5.32-5.27 (1H, m), 5.23 (1H, m), 4.23 (1H, dq, *J* = 13.8, 6.9 Hz), 3.31-3.24 (1H, m), 3.24 (3H, s), 3.04 (1H, dd, *J* = 8.4, 3.9 Hz), 2.39 (1H, m), 2.02 (1H, dd, *J* = 14.1, 3.7 Hz), 1.91 (1H, m), 0.75 (3H, d, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ = 173.2 (C), 172.7 (C), 128.6 (CH), 124.7 (CH), 76.2 (CH), 51.6 (CH_3), 40.6 (CH), 38.1 (CH), 36.0 (CH), 29.0 (CH_2), 14.4 (CH_3). IR (KBr): ν = 2955 (C-H), 1776, 1737 cm^{-1} (C=O). EIMS (70 eV): *m/z* (%) = 210 ($[M]^+$, 5), 178 ($[M-CH_4O]^+$, 20), 150 ($[M-C_2H_4O_2]^+$, 30), 105 ($[M-C_3H_5O_4]^+$, 50), 79 ($[M-C_5H_7O_4]^+$, 100). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 62.93, H 6.93.

(±)-Methyl (3*S*,3a*S*,7*R*,7a*S*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*cis,ul*-**26*Z***)**:** white crystalline solid after recrystallisation from hexanes/ethyl acetate 70:30. mp 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (1H, m), 5.60 (1H, m), 4.66 (1H, m), 3.76 (3H, s), 3.63 (1H, dd, *J* = 7.3, 7.9 Hz), 3.09 (1H, m), 2.73 (1H, ddd, *J* = 10.8, 6.7, 3.9 Hz), 2.43-2.32 (2H, m), 1.38 (3H, d, *J* = 6.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.7 (C),

172.8 (C), 130.8 (CH), 121.9 (CH), 78.4 (CH), 52.2 (CH_3), 42.6 (CH), 40.8 (CH), 37.0 (CH), 22.9 (CH_2), 15.9 (CH_3). IR (KBr): ν = 2950 (C-H), 1766, 1732 cm^{-1} (C=O). EIMS (70 eV): *m/z* (%) = 210 ($[M]^+$, 15), 178 ($[M-CH_4O]^+$, 25), 150 ($[M-C_2H_4O_2]^+$, 35), 138 ($[M-C_3H_4O_2]^+$, 50), 79 ($[M-C_5H_7O_4]^+$, 100). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 62.69, H 6.71.

IMDA Reaction of Fumarate 18*E* in Toluene at 110 °C



A solution of fumarate **18*E*** (1.335 g, 6.350 mmol, 1.0 equiv) and BHT (139.9 mg, 0.635 mmol, 0.1 equiv) in toluene (635 mL) was stirred at 110 °C for 57 h. The reaction mixture was concentrated *in vacuo*, a portion of the residue dissolved in $CDCl_3$ and ^1H NMR analysis carried out. The residue contained *trans,lk*-IMDA adduct **23*E***, *trans,ul*-IMDA adduct **25*E***, *cis,lk*-IMDA adduct **24*E***, and *cis,ul*-IMDA adduct **26*E*** (56:16:12:16, respectively). The residue was subjected to chromatography on silica (dichloromethane) to give a mixture of the IMDA adducts [913.5 mg, 4.345 mmol, 71%; *trans,lk*-IMDA adduct **23*E***, *trans,ul*-IMDA adduct **25*E***, *cis,lk*-IMDA adduct **24*E***, and *cis,ul*-IMDA adduct **26*E*** (53:13:17:17)]. The mixture of IMDA adducts was separated by HPLC [Whatman Partisil column, eluting with hexanes/ethyl acetate 83:17, 13.5 mL min^{-1}] to give *cis,lk*-IMDA adduct **24*E*** at t_R = 58.2 min, *trans,lk*-IMDA adduct **23*E*** at t_R = 61.0 min, *cis,ul*-IMDA adduct **26*E*** at t_R = 66.8 min, and *trans,ul*-IMDA adduct **25*E*** at t_R = 74.2 min.

(±)-Methyl (3*S*,3a*R*,7*S*,7a*S*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*trans,lk*-**23*E***): white crystalline solid after recrystallisation from hexanes/dichloromethane 50:50. mp 135-137 °C. ^1H NMR (400 MHz, $CDCl_3/CD_3OD$ 75:25): δ = 5.86 (1H, m), 5.78 (1H, m), 4.28 (1H, dq, *J* = 10.4, 6.2 Hz), 3.75 (3H, s), 2.84 (1H, ddd, *J* = 11.4, 10.0 Hz), 2.74 (1H, dd, *J* = 13.0, 11.5 Hz), 2.56 (1H, m), 2.45 (1H, m), 2.36-2.25 (1H, m), 1.46 (3H, d, *J* = 6.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3/CD_3OD$ 75:25): δ = 175.7 (C), 175.3 (C), 129.5 (CH), 123.8 (CH), 81.1 (CH), 52.5 (CH_3), 47.9 (CH), 46.4 (CH), 40.4 (CH), 31.1 (CH_2), 18.4 (CH_3). IR (KBr): ν = 2975 (C-H), 1789, 1738 cm^{-1} (C=O). EIMS (70 eV): *m/z* (%) = 210 ($[M]^+$, 15), 178 ($[M-CH_4O]^+$, 30), 165 ($[M-CHO_2]^+$, 75), 151 ($[M-C_2H_3O_2]^+$, 90), 105 ($[M-C_3H_4O_2]^+$, 50),

79 ([M-$C_5H_7O_4$]$^+$, 100). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 63.04, H 6.89.

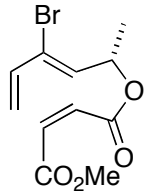
(±)-Methyl (3*R*,3a*S*,7*S*,7a*S*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*cis,lk*-24*E*): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.79 (1H, m), 5.61 (1H, m), 4.33 (1H, dq, *J* = 6.7, 2.4 Hz), 3.69 (3H, s), 3.32 (dd, *J* = 8.0, 4.3 Hz, 1H), 3.10 (ddd, *J* = 6.9, 3.7, 3.7 Hz, 1H), 2.81 (m, 1H), 2.44 (m, 1H), 2.23 (m, 1H), 1.40 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.7 (C), 173.7 (C), 127.2 (CH), 125.5 (CH), 81.0 (CH), 52.3 (CH_3), 39.9 (CH), 38.9 (CH), 36.7 (CH), 23.6 (CH_2), 20.4 (CH_3). IR (neat): ν = 3028, 2953, 2849 (C-H), 1767, 1731 (C=O), 1651 cm^{-1} (C=C). EIMS (70 eV): *m/z* (%) = 210 ([M]$^+$, 35), 179 ([M-CH_3O]$^+$, 25), 165 ([M-CHO_2]$^+$, 30), 151 ([M-$C_2H_3O_2$]$^+$, 30), 138 ([M-$C_3H_4O_2$]$^+$, 100), 107 ([M-$C_4H_7O_3$]$^+$, 45), 79 ([M-$C_5H_7O_4$]$^+$, 95). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 62.88, H 6.78.

(±)-Methyl (3*R*,3a*R*,7*S*,7a*S*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*trans,ul*-25*E*): white crystalline solid after recrystallisation from hexanes/ethyl acetate 70:30. mp 112-113 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 5.90 (1H, m), 5.79 (1H, m), 4.83 (1H, m), 3.69 (3H, s), 3.11 (1H, m), 2.85 (1H, ddd, *J* = 11.4, 10.2, 6.8 Hz), 2.74 (1H, dd, *J* = 13.5, 11.4 Hz), 2.55 (1H, m), 2.35-2.24 (1H, m), 1.28 (3H, d, *J* = 6.7 Hz). ^{13}C NMR (50 MHz, $(CD_3)_2CO$): δ = 174.7 (C), 174.5 (C), 129.7 (CH), 125.4 (CH), 78.1 (CH), 52.2 (CH_3), 42.9 (CH), 41.7 (CH), 40.8 (CH), 31.4 (CH_2), 14.8 (CH_3). IR (KBr): ν = 3044, 2993, 2977, 2952, 2916 (KBr), 1769, 1726 (C=O), 1633 cm^{-1} (C=C). EIMS (70 eV): *m/z* (%) = 210 ([M]$^+$, 20), 178 ([M-CH_4O]$^+$, 10), 165 ([M-CHO_2]$^+$, 35), 151 ([M-$C_2H_3O_2$]$^+$, 55), 79 ([M-$C_5H_7O_4$]$^+$, 100). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 62.97, H 6.78.

(±)-Methyl (3*S*,3a*S*,7*R*,7a*S*)-3-Methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (*cis,ul*-26*E*): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (1H, m), 5.54 (1H, m), 4.64 (1H, m), 3.65 (3H, s), 3.35 (1H, m), 3.16 (1H, m), 3.08 (1H, m), 2.46 (1H, m), 2.23 (1H, m), 1.32 (3H, d, *J* = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.8 (C), 173.6 (C), 129.2 (CH), 122.2 (CH), 78.5 (CH), 52.2 (CH_3), 41.9 (CH), 37.5 (CH), 36.5 (CH), 22.9 (CH_2), 15.9 (CH_3). IR (neat): ν = 3032, 2983, 2953, 2852 (C-H), 1767, 1732 cm^{-1} (C=O). EIMS (70 eV): *m/z* (%) = 211 ([M+1]$^+$, 5), 210 ([M]$^+$, 2), 179 ([M-CH_3O]$^+$, 10), 165 ([M-CHO_2]$^+$, 30), 151 ([M-

$C_2H_3O_2]^+$, 15), 79 ([M-$C_5H_7O_4]^+$, 100). Anal. calcd (%) for $C_{11}H_{14}O_4$ (210.1): C 62.85, H 6.71; found C 62.63, H 6.57

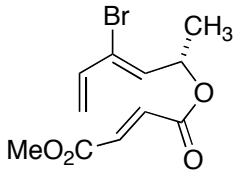
Methyl (1*S*,2*E*)-3-Bromo-1-methylpenta-2,4-dien-1-yl Maleate (27*Z*)



27*Z*

Triethylamine (52 μL, 0.37 mmol, 1.6 equiv), maleic anhydride (64 mg, 0.65 mmol, 2.8 equiv) and DMAP (3 mg, 0.03 mmol, 0.12 equiv) were added to a stirred solution of alcohol **29** (41 mg, 0.23 mmol, 1.0 equiv) in dichloromethane (2 mL) at 0 °C. The mixture was stirred at this temperature for 2.5 h. The solution was allowed to warm to room temperature before being diluted with diethyl ether (20 mL). The mixture was washed with 2M HCl (10 mL), sat. aq. $NaHCO_3$ (10 mL), brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The crude material was diluted with tetrahydrofuran (5 mL) and cooled to -78 °C with stirring. An ethereal solution of diazomethane was added dropwise until tlc confirmed the reaction had gone to completion. Excess diazomethane was removed by bubbling N_2 gas through the solution. The solution was concentrated *in vacuo* and subjected to column chromatography on silica (hexanes/ethyl acetate 90:10) to give maleate **27*Z*** (27 mg, 0.09 mmol, 40%) as a colourless oil. $[\alpha] = +37.4$ (c = 0.42, chloroform). ^{1}H NMR (300 MHz, C_6D_6): δ 6.03 (1H, dq, *J* = 7.7, 6.3 Hz), 5.90 (1H, ddd, *J* = 16.3, 10.3, 0.8 Hz), 5.79 (1H, dd, *J* = 7.7, 0.7 Hz), 5.68 (2H, d, *J* = 3.2 Hz), 5.58 (1H, dt, *J* = 16.3, 0.7 Hz), 4.94 (1H, d, *J* = 10.5 Hz), 3.31 (3H, s), 1.23 (3H, d, *J* = 6.5 Hz) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 164.9, 163.7, 134.9, 133.4, 129.9, 129.0, 126.2, 119.5, 71.4, 51.1, 18.8 ppm. IR (thin film): ν 2918, 1788, 1731 cm^{-1}. EIMS (70 eV) *m/z* (%): 290 (2), 288 (2), 175 (15), 113 (100). HRMS: calcd for $C_{11}H_{13}O_4{}^{79}$Br [M]$^+$: 287.9997; found: 288.0003.

Methyl (1*S*,2*E*)-3-Bromo-1-methylpenta-2,4-dien-1-yl Fumarate (27*E*)

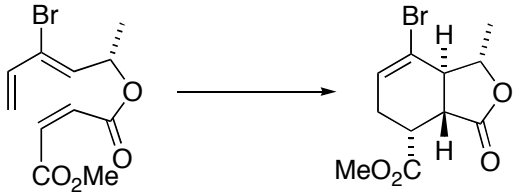


27*E*

To a stirred solution of alcohol **29** (54 mg, 0.31 mmol, 1.0 equiv) in diethyl ether (1.5 mL) at room temperature was added (*E*)-3-methoxycarbonylacrylic acid[2] (72 mg, 0.5 mmol, 1.8 equiv), DCC (127 mg, 0.61 mmol, 2.0 equiv) and DMAP (5.6 mg, 0.05 mmol, 0.15 equiv). Stirring was continued for 3 h. The reaction mixture was filtered through celite and concentrated *in vacuo*. The crude residue was subjected to column chromatography on silica (hexanes/ethyl acetate 9:1) to give fumarate **27*E*** (55.5 mg, 0.19 mmol, 63%) as a colourless oil. $[\alpha] = +94.0$ (c = 0.92, chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (2H, s), 6.29 (1H, dd, *J* = 16.3, 10.4 Hz), 6.03 (1H, d, *J* = 7.9 Hz), 5.88 (1H, dq, *J* = 6.6, 6.3 Hz), 5.68

(1H, d, J = 16.3 Hz), 5.32 (1H, d, 10.5 Hz), 3.80 (3H, s), 1.42 (3H, d, J = 6.4 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.5, 164.0, 134.9, 133.8, 133.6, 132.6, 126.8, 120.6, 72.0, 52.4, 19.5 ppm. IR (thin film): ν 2953, 2849, 1723, 1645 cm^{-1}. EIMS (70 eV) m/z (%): 290 (18), 288 (20), 209 (25), 159 (50), 113 (95), 85 (80), 79 (90), 59 (75), 53 (100). HRMS: calcd for $C_{11}H_{13}O_4{}^{79}Br$ $[M]^+$: 287.9997; found: 288.0003.

IMDA Reaction of Maleate 27*Z* in Toluene at 110 °C

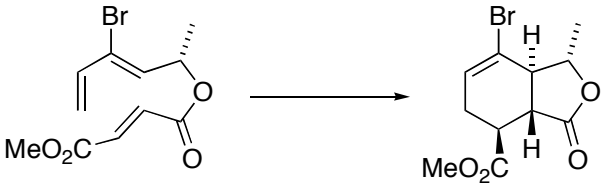


27*Z* *trans,lk*-**30*Z***

A solution of maleate **27*Z*** (12.2 mg, 42 μmol, 1.0 equiv) and BHT (1 mg, 4.5 μmol, 0.1 equiv) in toluene (4.2 mL) was stirred at 110 °C for 40 min. The reaction mixture was concentrated *in vacuo*. After column chromatography cycloadduct **30*Z*** (10.3 mg, 35 μmol, 83%) was obtained as a single isomer.

Methyl (3*S*,3a*R*,7*R*,7a*S*)-4-Bromo-3-methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzo furancarboxylate (30*Z*). White crystalline solid after recrystallistaion from hexane/dichloromethane. mp 86-88 °C $[\alpha] = -42.0$ (c = 0.82, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.05 (1H, m), 4.36 (1H, dq, J = 9.7, 5.9 Hz), 3.74 (3H, s), 3.35 (1H, dd, J = 8.3, 3.8 Hz), 3.11 (1H, m), 2.77 (1H, m), 2.71 (1H, dd, J = 13.2, 3.5 Hz), 2.58 (1H, ddt, J = 19.1, 8.0, 3.7 Hz), 1.69 (1H, d, J = 6.1 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 172.0, 130.0, 116.4, 79.8, 52.6, 47.3, 47.3, 35.0, 31.2, 19.9 ppm. IR (thin film): ν 2920, 1787, 1732 cm^{-1}. EIMS (70 eV) m/z (%): 290 (2), 244 (30), 228 (15), 105 (100), 77 (95). HRMS: calcd for $C_{11}H_{14}O_4{}^{81}Br$ $[M+H]^+$: 289.0075; found: 289.0082.

IMDA Reaction of Fumarate 27*E* in Toluene at 110 °C

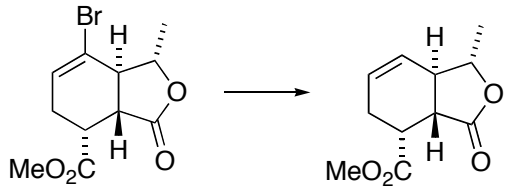


27*E* *trans,lk*-**30*E***

A solution of fumarate **27*E*** (14.6 mg, 50 μmol, 1.0 equiv) and BHT (1 mg, 4.5 μmol, 0.1 equiv) in toluene (5 mL) was stirred at 110 °C for 9 h 50 min. The reaction mixture was concentrated *in vacuo*. After column chromatography cycloadduct **30*E*** (10.4 mg, 36 μmol, 71%) was obtained as a single isomer.

Methyl (3*S*,3a*R*,7*S*,7a*S*)-4-Bromo-3-methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofuran carboxylate (30*E*) White crystalline solid after recrystallisation from hepatane/dichloromethane. mp 181-182 °C. [α] = + 88.7 (c = 0.94, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.09 (1H, q, *J* = 3.4 Hz), 4.41 (1H, dq, *J* = 10.0, 6.2 Hz), 3.78 (3H,s), 3.00 (1H, dd, *J* = 12.5, 11.7 Hz), 2.77 (1H, ddd, *J* = 11.7, 10.3, 7.0 Hz), 2.66 (1H, m), 2.53 (1H, dddd, *J* = 18.4, 6.8, 4.5, 2.7 Hz) 2.44 (1H, ddt, *J* = 18.4, 10.1, 3.7 Hz), 1.66 (3H, d, *J* = 6.2 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 172.0, 130.3, 115.6, 79.7, 52.5, 50.8, 47.6, 39.0, 32.7, 19.8 ppm. IR (thin film): ν 2990, 2937, 1779, 1743 cm^{-1}. EIMS (70 eV) *m/z* (%): 288 (20), 230 (25), 213 (60), 105 (98), 77 (100). HRMS: calcd for $C_{11}H_{14}O_4{}^{81}Br$ $[M+H]^+$: 289.0075; found: 289.0081.

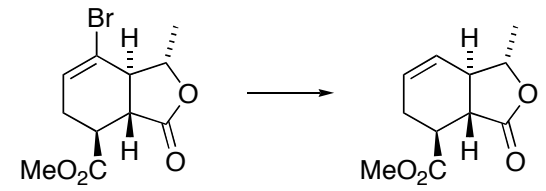
Reductive Debromination of Methyl (3*S*,3a*R*,7*R*,7a*S*)-4-Bromo-3-methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofurancarboxylate (30*Z*)



trans,lk-**30*Z*** *trans,lk*-**23*Z***

To a solution of cycloadduct **30*Z*** (10 mg, 30 μmol, 1.0 equiv) in toluene (500 μL) at room temperature was added tributyltin hydride (27 μL, 0.10 mmol, 2.9 equiv) and AIBN (1.0 mg, 6 μmol, 0.2 equiv) before warming to 80 °C for 3 h 50 min. The reaction mixture was then concentrated *in vacuo*. The crude product was passed through a short pad of silica (dichloromethane) to give **23*Z*** (3.8 mg, 18 mmol, 59%), spectroscopically identical to the major product obtained upon IMDA reaction of **18*Z***.

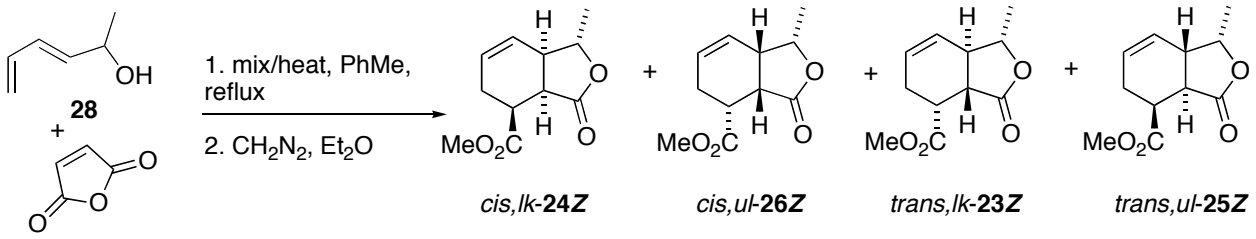
Reductive debromination of Methyl (3*S*,3a*R*,7*S*,7a*S*)-4-Bromo-3-methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofurancarboxylate (30*E*)



trans,lk-**30*E*** *trans,lk*-**23*E***

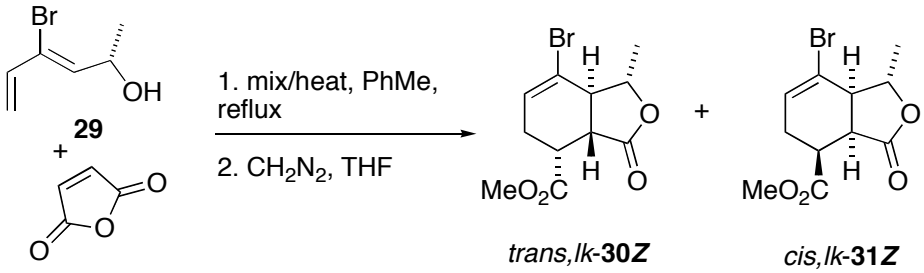
To a solution of cycloadduct **30*E*** (10 mg, 30 μmol, 1.0 equiv) in toluene (500 μL) at room temperature was added tributyltin hydride (27 μL, 0.10 mmol, 2.9 equiv) and AIBN (1.0 mg, 6 μmol, 0.2 equiv) before warming to 80 °C for 2 h 40 min. The reaction mixture was then concentrated *in vacuo*. The crude product was passed through a short pad of silica (dichloromethane) to give **23*E*** (3.8 mg, 18 mmol, 59%), spectroscopically identical to the major product obtained upon IMDA reaction of **18*E***.

"Mix and Heat" Procedure for Hexa-3,5-dien-2-ol (28)



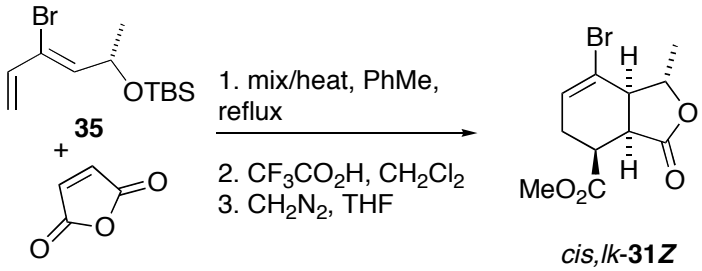
Maleic anhydride (156 mg, 1.59 mmol, 1.0 equiv) and BHT (35 mg, 0.16 mmol, 0.1 equiv) were added to a stirred solution of hexa-3,5-dien-2-ol **28** (156 mg, 1.59 mmol, 1.0 equiv) in toluene (3.2 mL) at RT. The reaction mixture was stirred at 110 °C for 2 h. After diazomethane treatment, ^{1}H NMR analysis of the crude product revealed four adducts ***23Z***, ***25Z***, ***24Z*** and ***26Z*** in a 9:2:56:33 ratio. The residue was subjected to chromatography on silica (dichloromethane/diethyl ether 97:3) to give a mixture of the four adducts (236 mg, 1.13 mmol, 71%; ***23Z***, ***25Z***, ***24Z*** and ***26Z*** = 10:1:57:32) eluting at R_f = 0.24. The product identities were determined by comparison of the GC and ^{1}H NMR spectra of the mixture to those of previously isolated and characterised compounds.

"Mix and Heat" Procedure for (*S*,*Z*)-4-bromohexa-3,5-dien-2-ol (29)



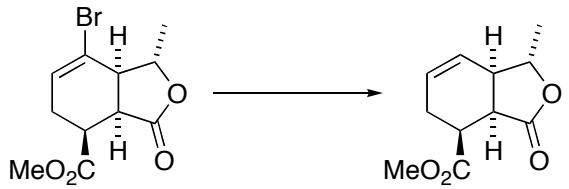
To a solution of **29**[4] (22 mg, 0.13 mmol, 1.0 equiv) in toluene (1mL) was added maleic anhydride (18 mg, 0.18 mmol, 1.5 equiv). The mixture was heated at reflux for 5 h 30 min then concentrated *in vacuo*. The crude material was diluted with tetrahydrofuran (5 mL) and cooled to -78 °C with stirring. An ethereal solution of diazomethane was added dropwise until tlc confirmed the reaction had gone to completion. Excess diazomethane was removed by bubbling N_2 gas through the solution. The solution was concentrated *in vacuo* and subjected to column chromatography on silica (hexanes/ethyl acetate 88:12) to give a mixture of ***30Z*** and ***31Z*** 13:87 (21mg, 0.08 mmol, 58%).

"Mix and Heat" Procedure for ((*S*,*Z*)-4-bromohexa-3,5-dien-2-yloxy)(*tert*-butyl) dimethyl silane (35)



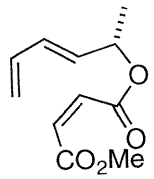
To a solution of **35**[4] (30 mg, 0.10 mmol, 1.0 equiv) in toluene (1 mL) was added maleic anhydride (11 mg, 0.11 mmol, 1.1 equiv). The mixture was heated at reflux for 74h then concentrated *in vacuo*. The crude material was dissolved in dichloromethane (2 mL) and trifluoroacetic acid (250 μL) was added the reaction mixture was stirred at RT for 18h then concentrated *in vacuo*. The crude material was diluted with tetrahydrofuran (5 mL) and cooled to -78 °C with stirring. An ethereal solution of diazomethane was added dropwise until tlc confirmed the reaction had gone to completion. Excess diazomethane was removed by bubbling N_2 gas through the solution. The solution was concentrated *in vacuo* and subjected to column chromatography on silica (hexanes/ethyl acetate 88:12) to give **31*Z*** (17 mg, 0.06 mmol, 58%). $[\alpha] = +64.6$ (c = 1.4, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.25 (1H, m), 4.84 (1H, q, J = 6.8 Hz), 3.80 (3H,s), 3.74 (1H, ddd, J = 8.3, 4.4, 1.0 Hz), 3.07 (1H, dd, J = 8.3, 1.5 Hz), 2.83 (1H, m), 2.50-2.35 (3H, m), 1.48 (3H, d, J = 6.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.7, 171.9, 131.2, 121.7, 79.6, 52.5, 49.6, 41.3, 36.3, 25.5, 20.6 ppm. IR (thin film): ν 2929, 1771, 1735 cm^{-1}. ESIMS (positive ion) *m*/*z* (%): 313 (90), 311 (95), 289 (100). HRMS: calcd for $C_{11}H_{13}O_4Br$ Na $[M+Na]^+$: 310.9895; found: 310.9897.

Reductive debromination of Methyl (3*S*,3a*R*,7*S*,7a*R*)- 4-Bromo-3-methyl-1-oxo-3,3a,6,7,7a-hexahydro-7-isobenzofurancarboxylate (31*Z*)

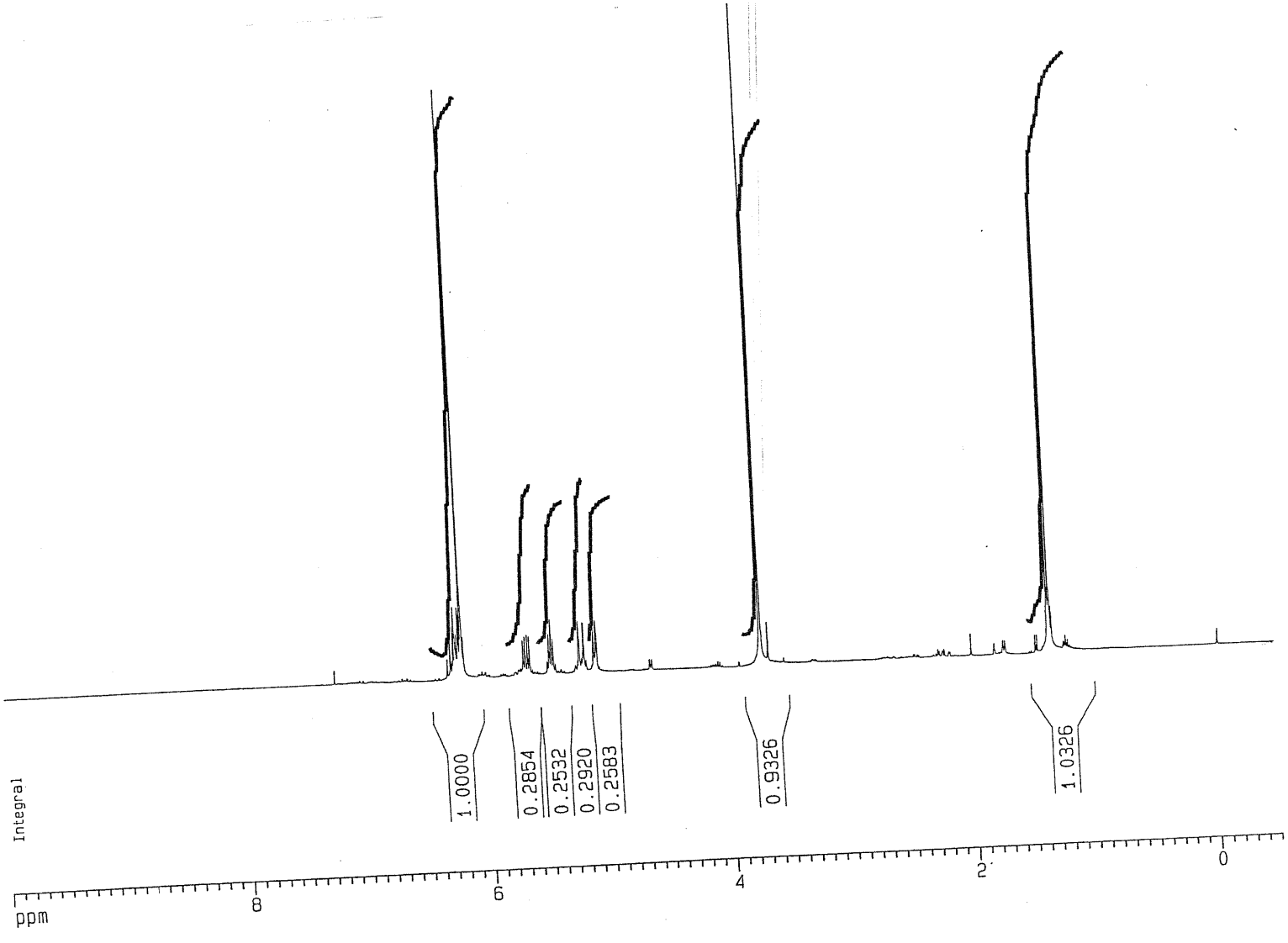


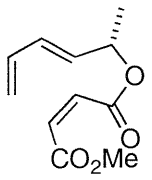
To a solution of cycloadduct **31*Z*** (5.5 mg, 19 μmol, 1.0 equiv) in toluene (500 μL) at room temperature was added tributyltin hydride (15 μL, 0.06 mmol, 2.9 equiv) and AIBN (1.0 mg, 6 μmol, 0.32 equiv) before warming to 80 °C for 3h. The reaction mixture was then concentrated *in vacuo*. The crude product was passed through a short pad of silica (dichloromethane) to give **24*Z*** (2.8 mg, 14 μmol, 72%).

3. ^{1}H and ^{13}C NMR spectra of all new compounds

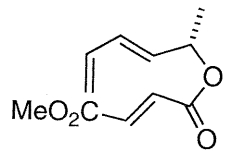


18*Z*
^{1}H NMR
$CDCl_3$
400 MHz

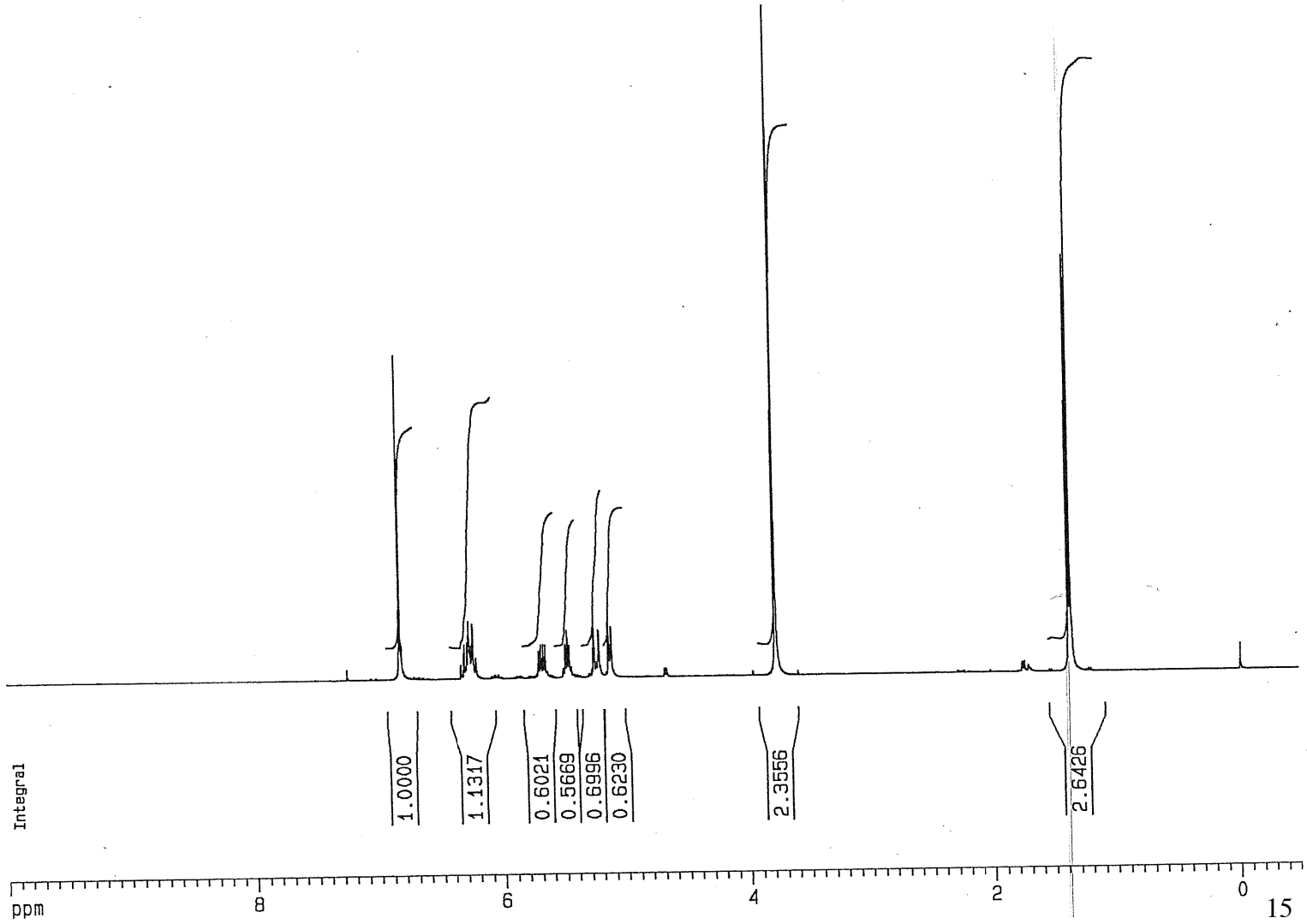


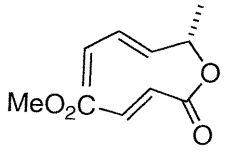


18*Z*
^{13}C NMR
$CDCl_3$
100 MHz

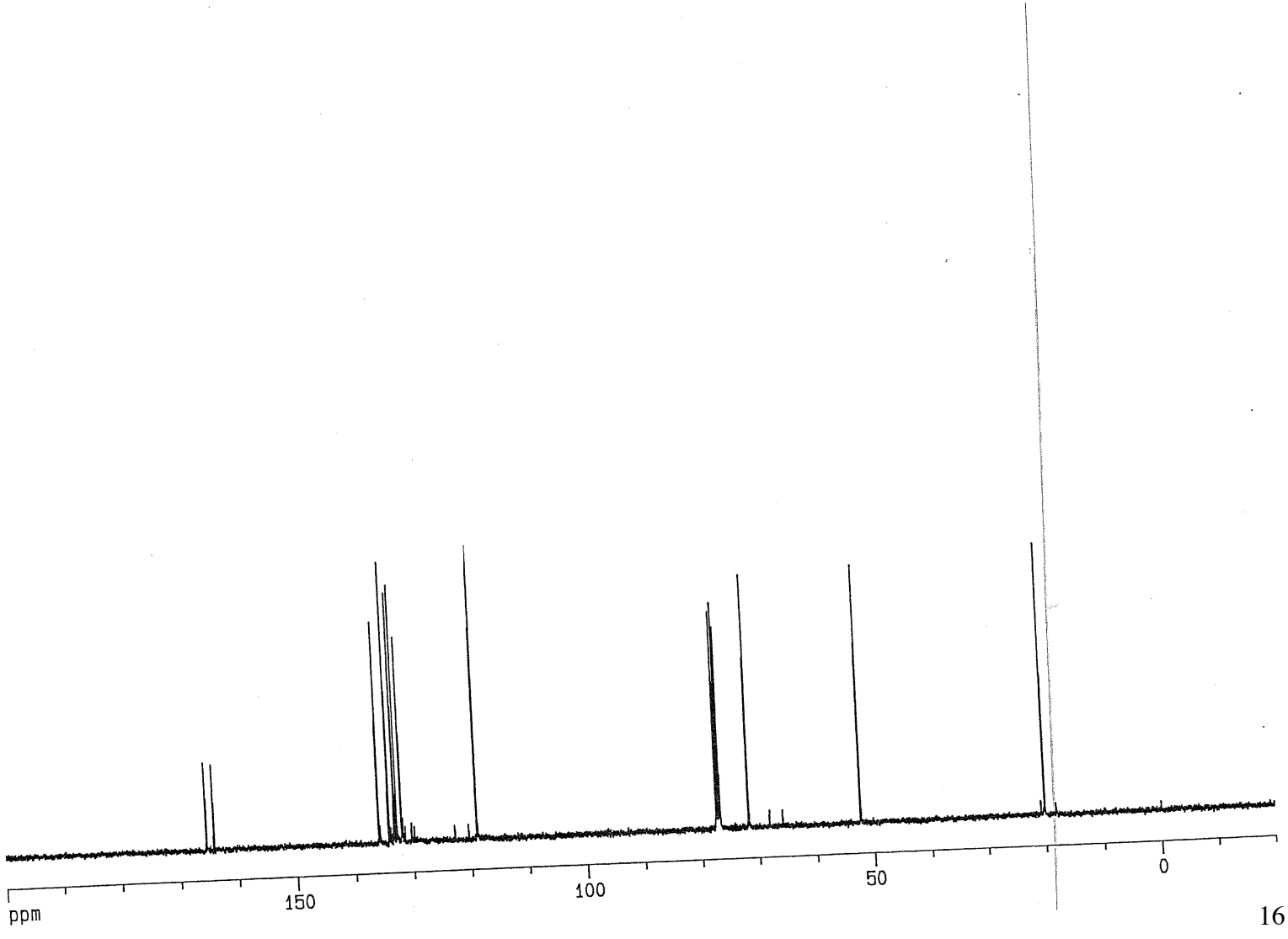


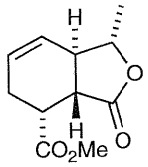
18*E*
^{1}H NMR
$CDCl_3$
400 MHz





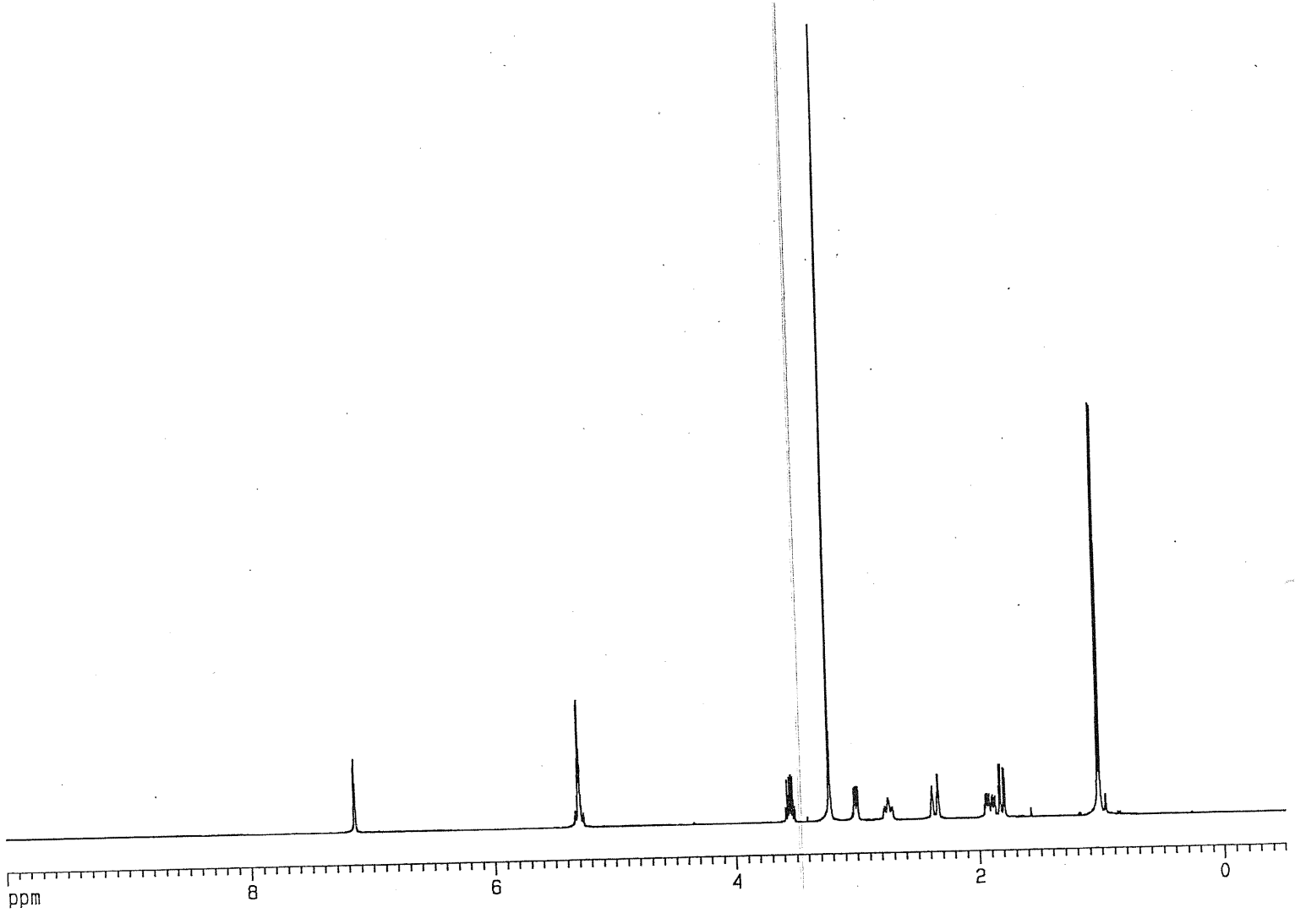
18E
^{13}C NMR
$CDCl_3$
125 MHz

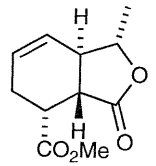




trans, Ik

23*Z*,
^{1}H NMR
C_6D_6
400 MHz





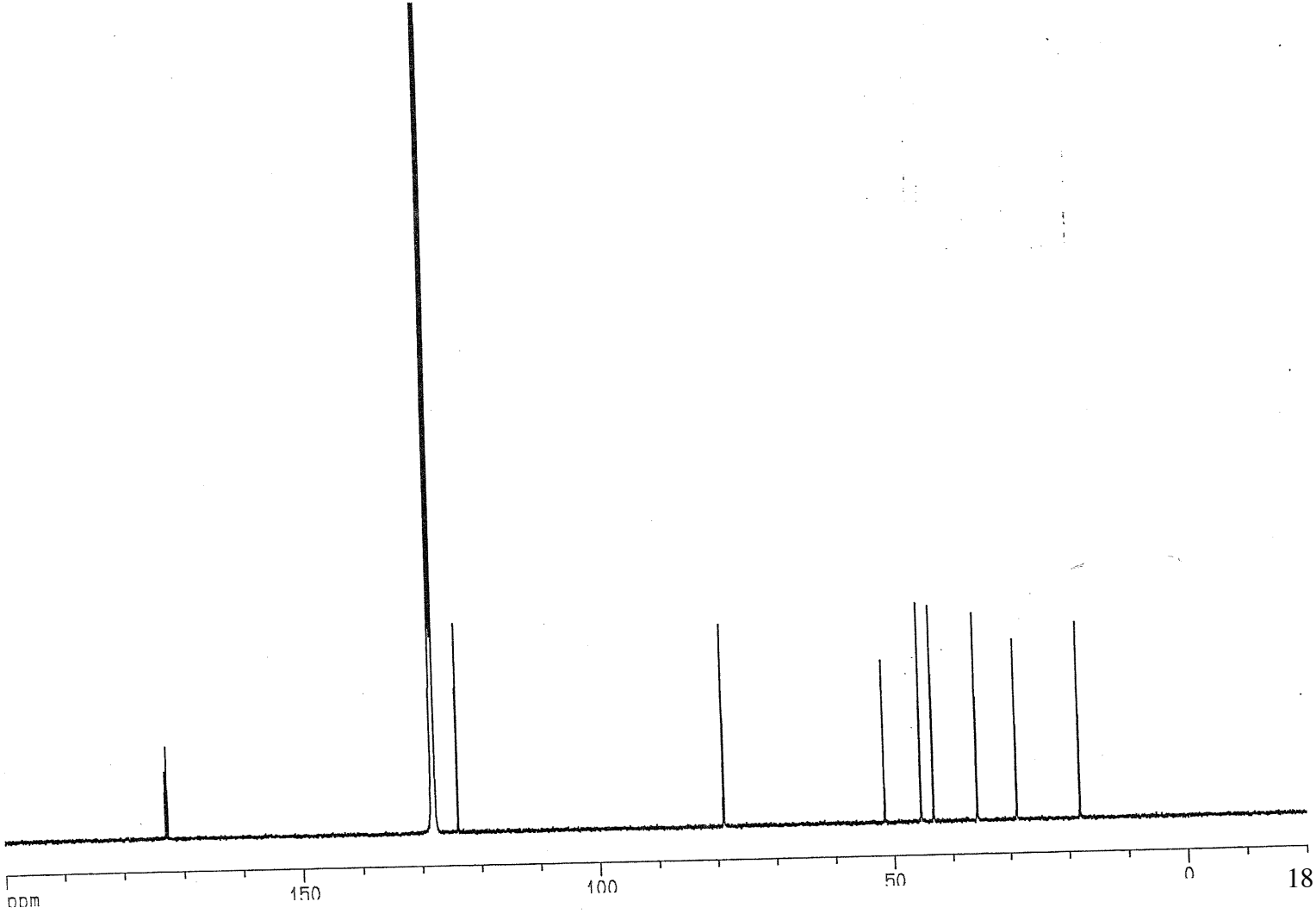
trans, Ik

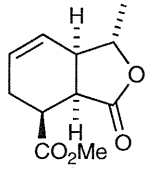
23*Z*

^{13}C NMR

C_6D_6

100 MHz





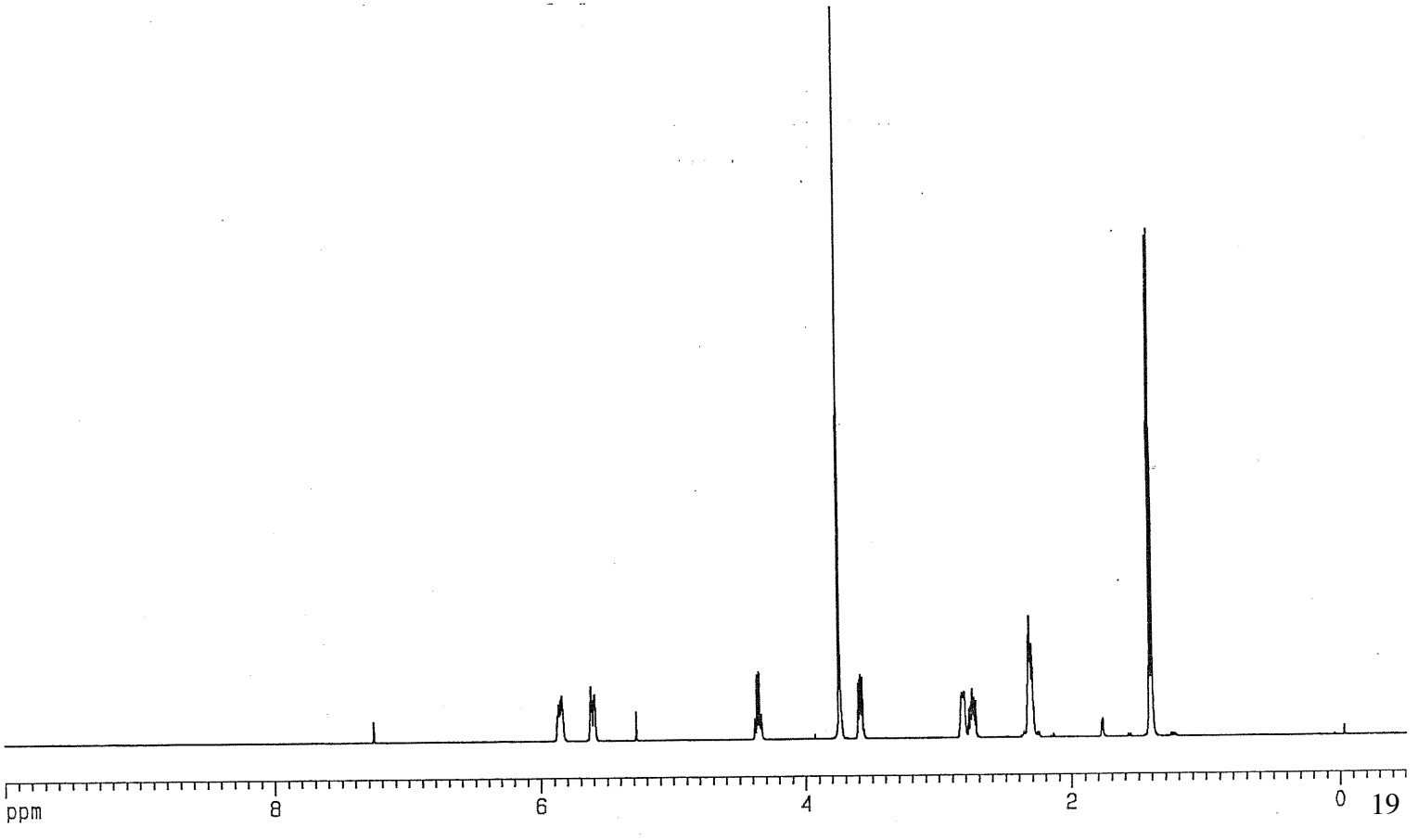
cis, Ik

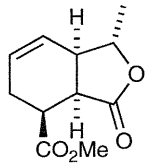
24*Z*

^{1}H NMR

$CDCl_3$

400 MHz

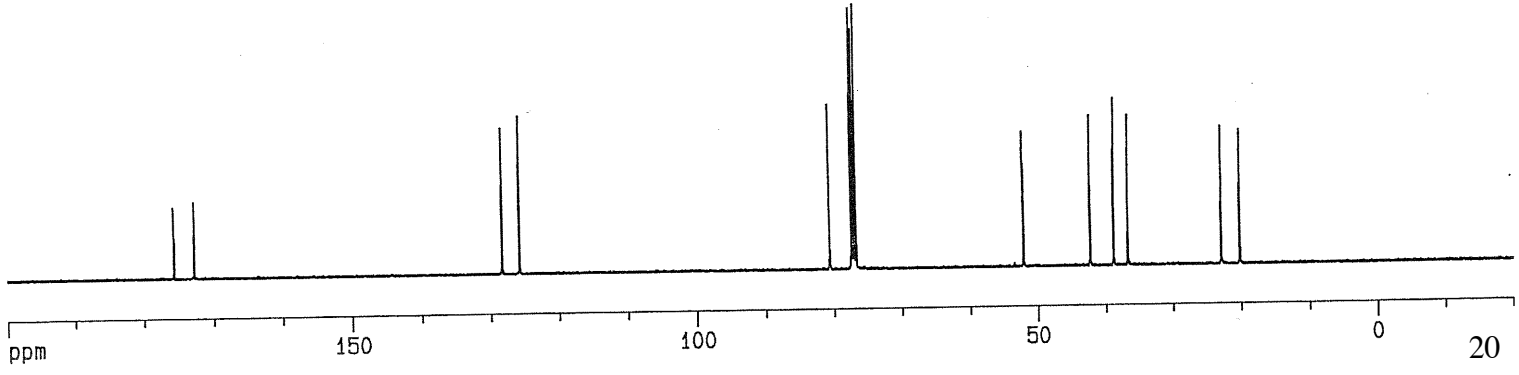


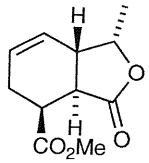


cis, Ik

24*Z*

^{13}C NMR
$CDCl_3$
100 MHz





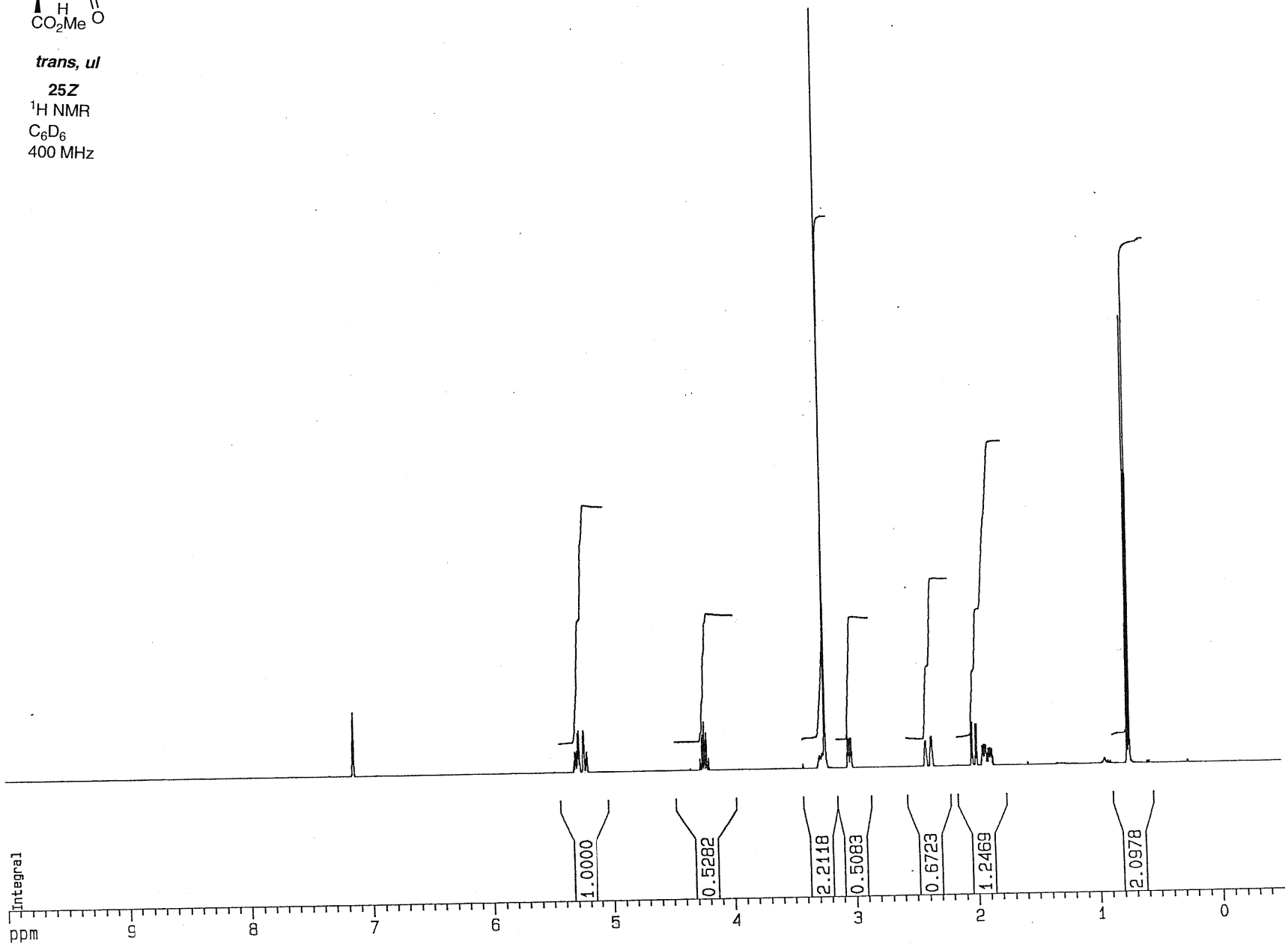
trans, ul

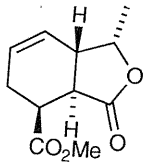
25*Z*

^{1}H NMR

C_6D_6

400 MHz





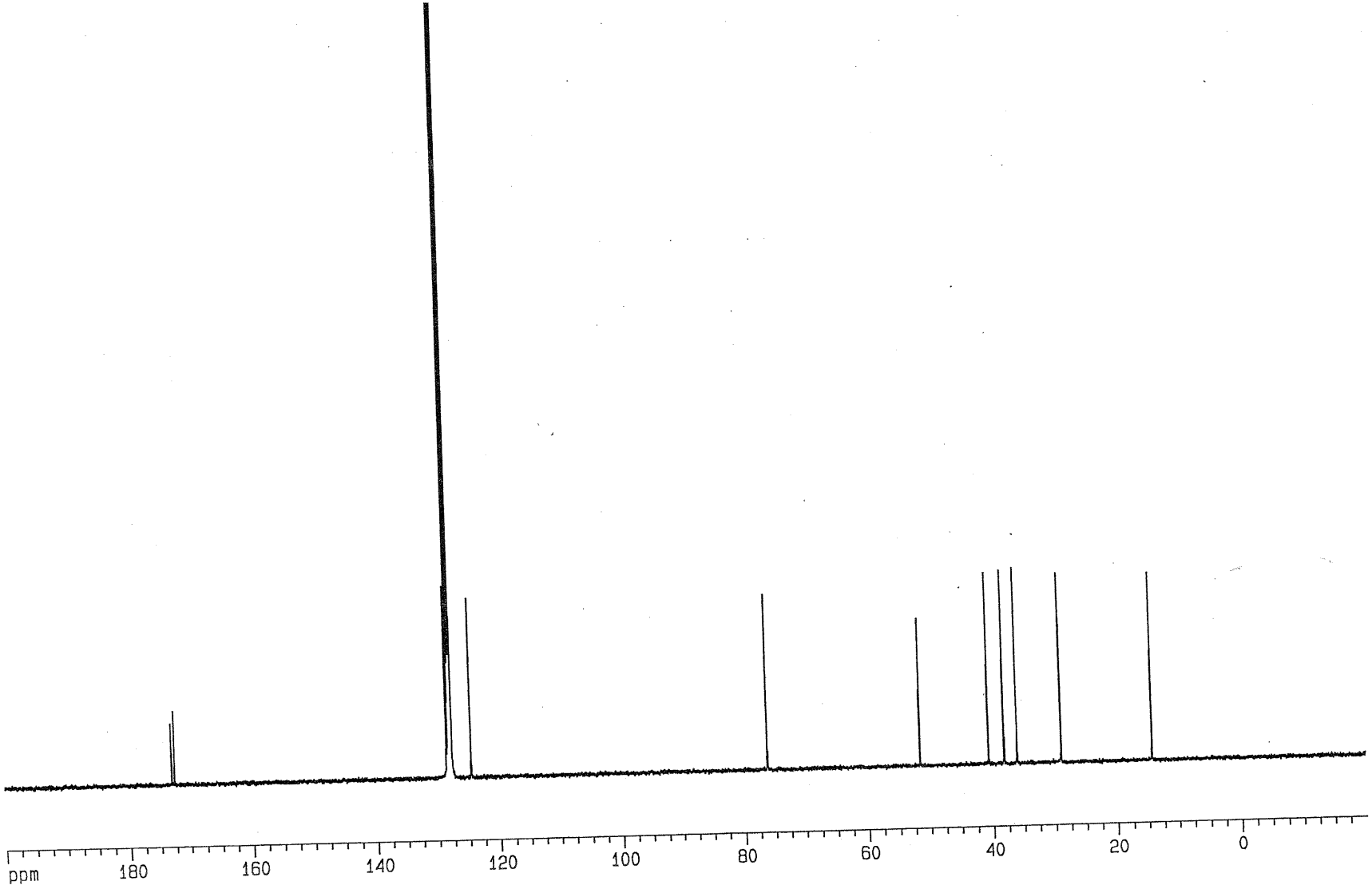
trans, ul

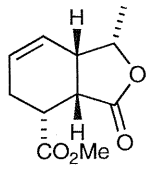
25Z

^{13}C NMR

C_6D_6

100 MHz





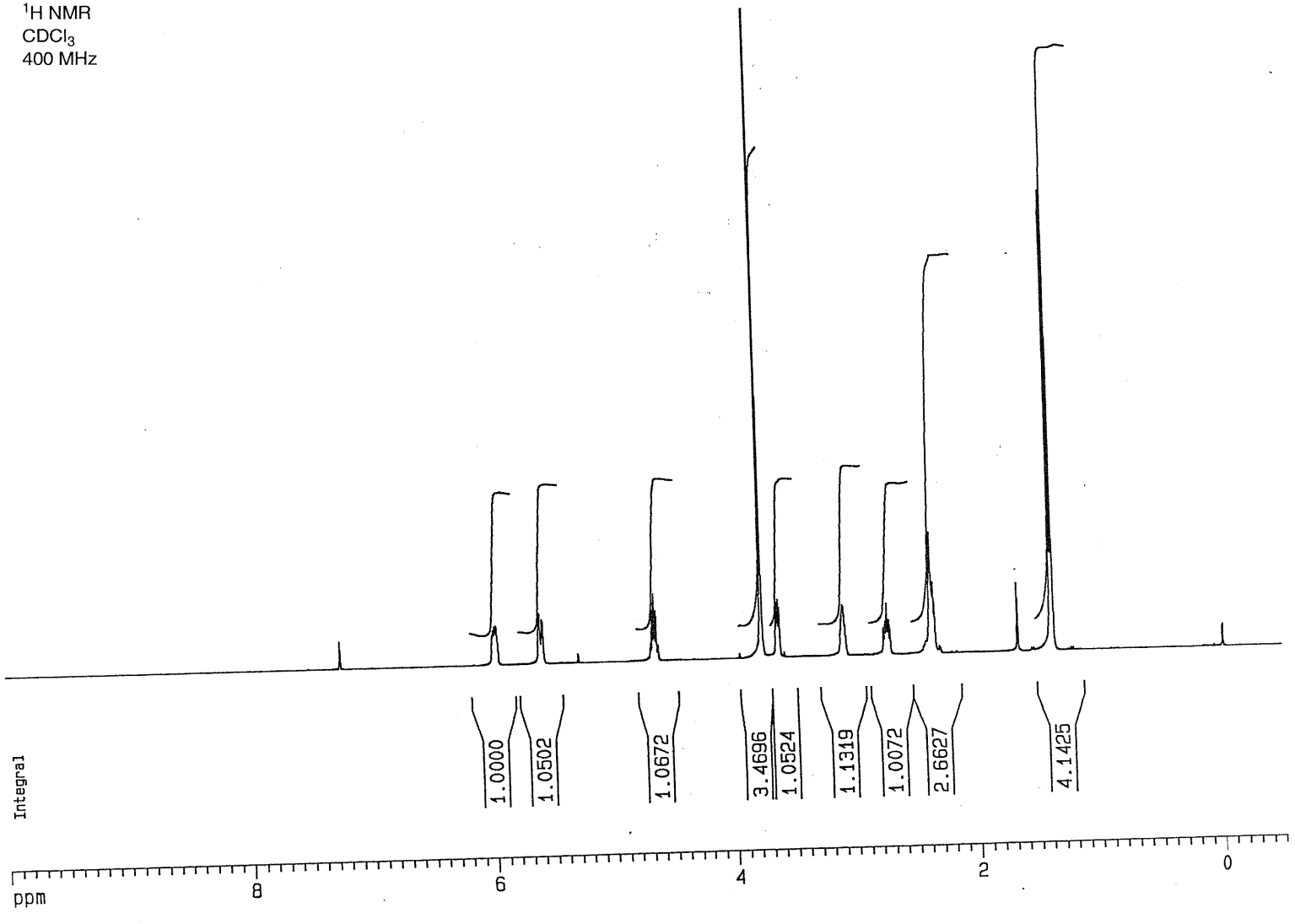
cis, ul

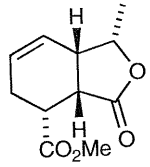
26*Z*

^{1}H NMR

$CDCl_3$

400 MHz





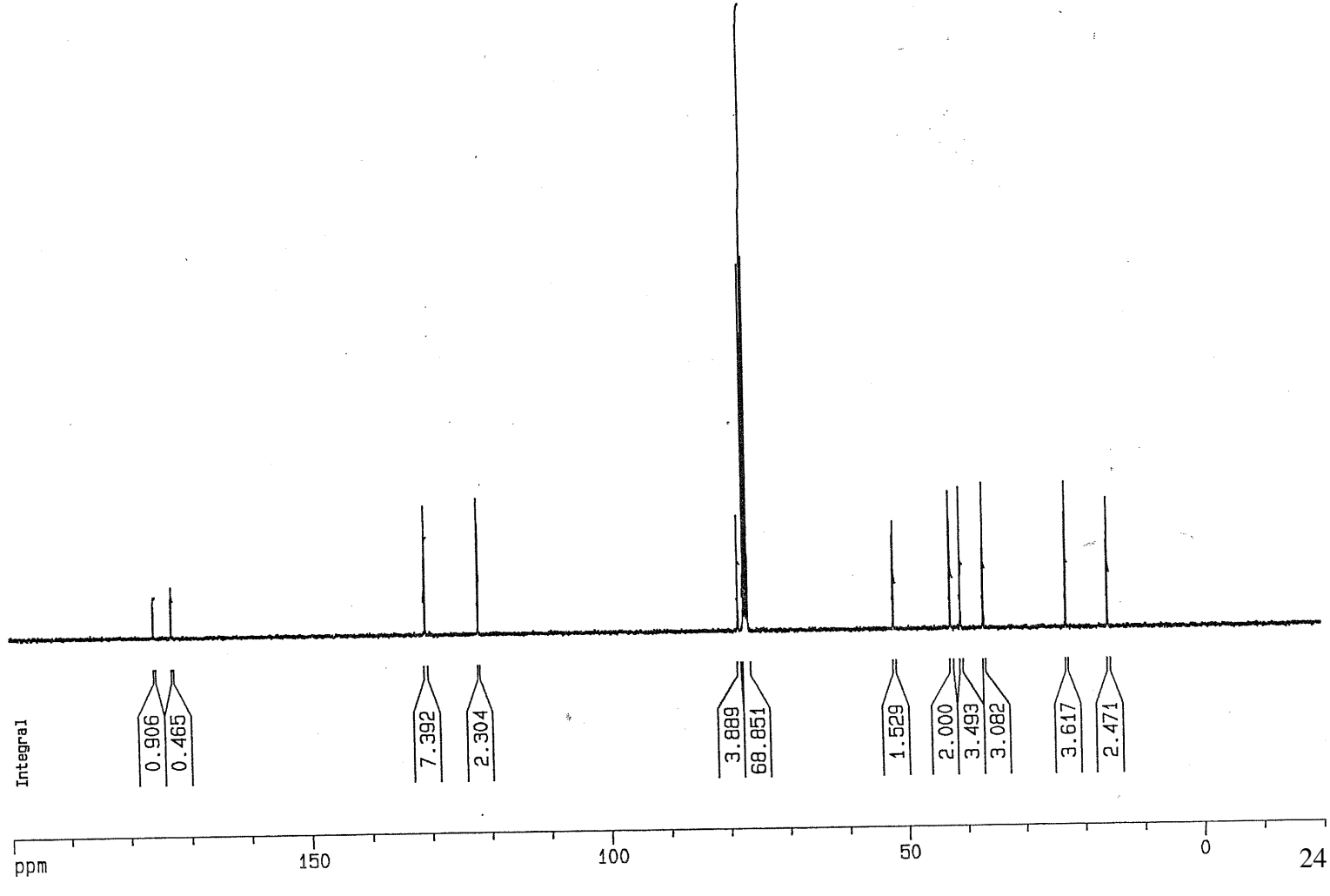
cis, ul

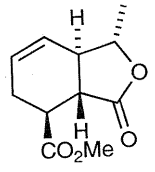
26*Z*

^{13}C NMR

$CDCl_3$

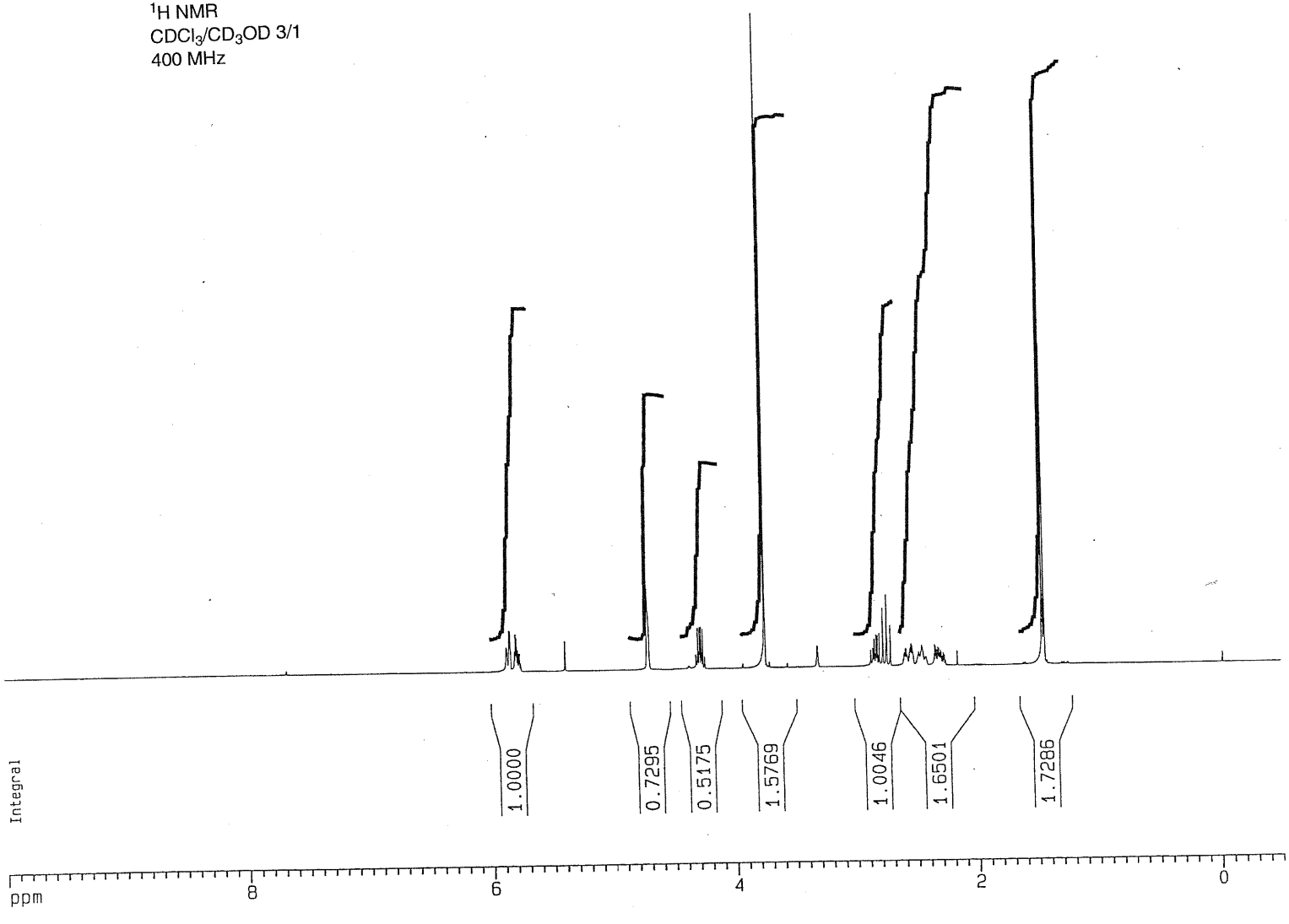
100 MHz

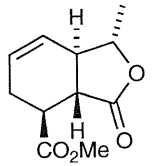




trans, Ik

23*E*
^{1}H NMR
$CDCl_3/CD_3OD$ 3/1
400 MHz





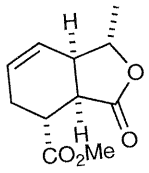
trans, Ik

23*E*

^{13}C NMR

$CDCl_3/CD_3OD$ 3/1

100 MHz



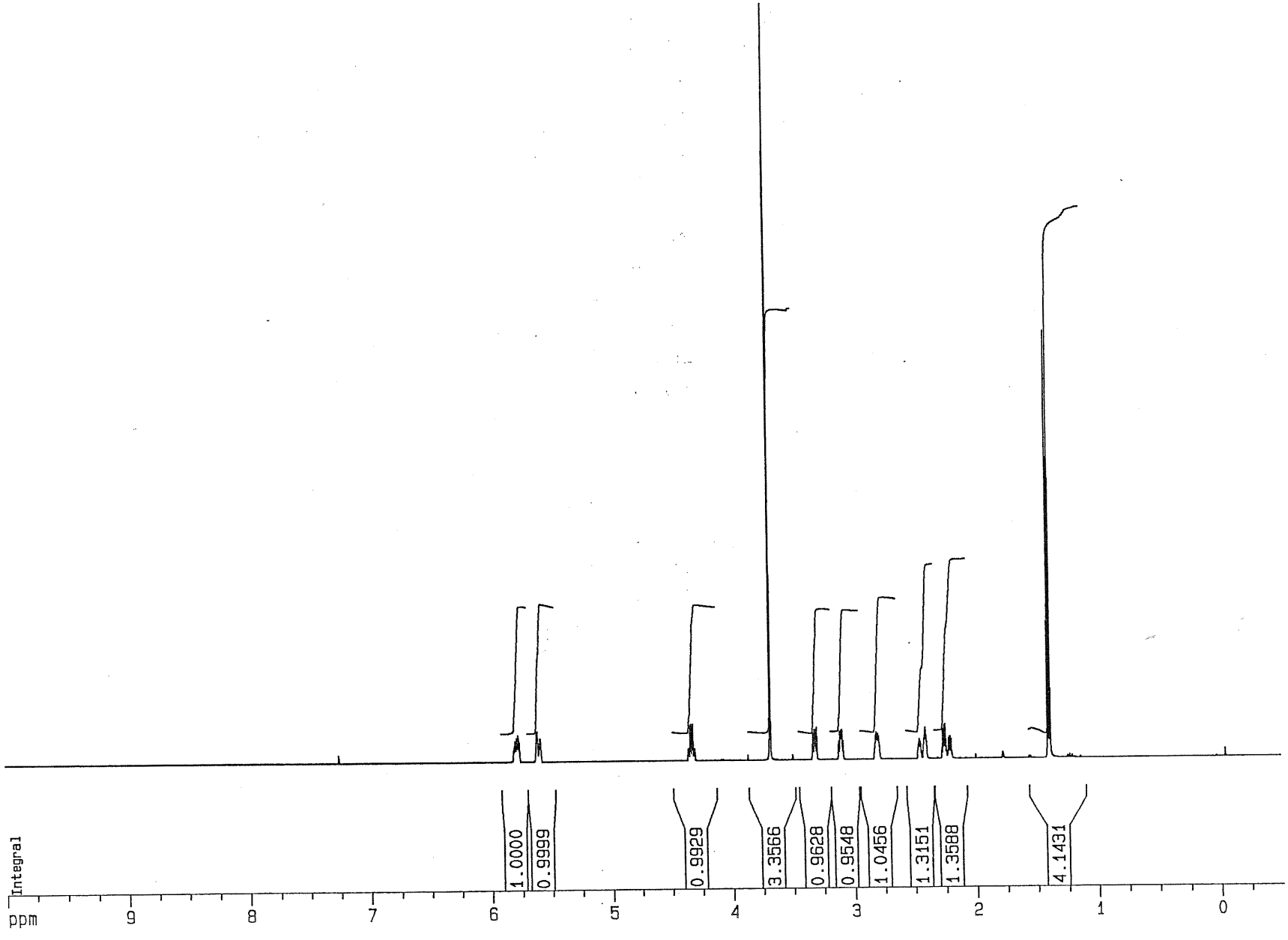
cis, Ik

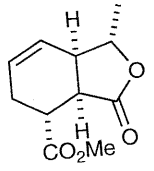
24*E*

^{1}H NMR

$CDCl_3$

400 MHz





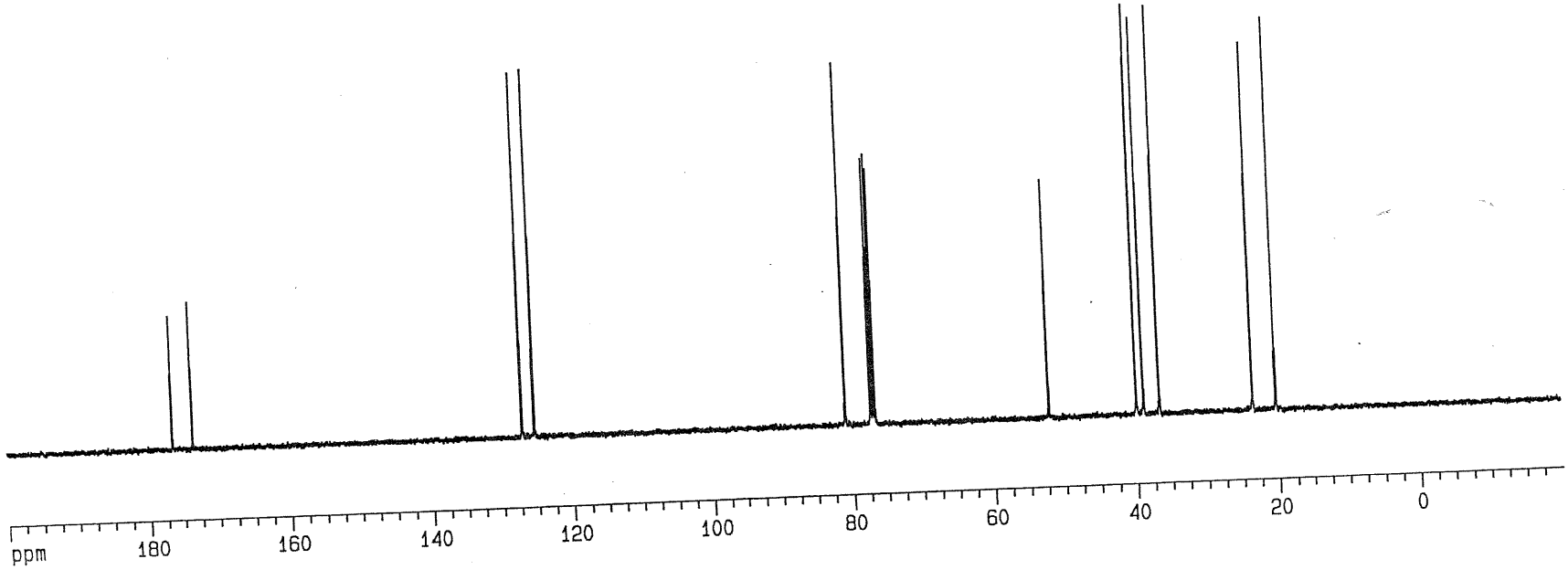
cis, lk

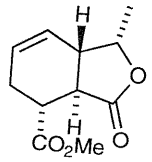
24*E*

^{13}C NMR

$CDCl_3$

100 MHz





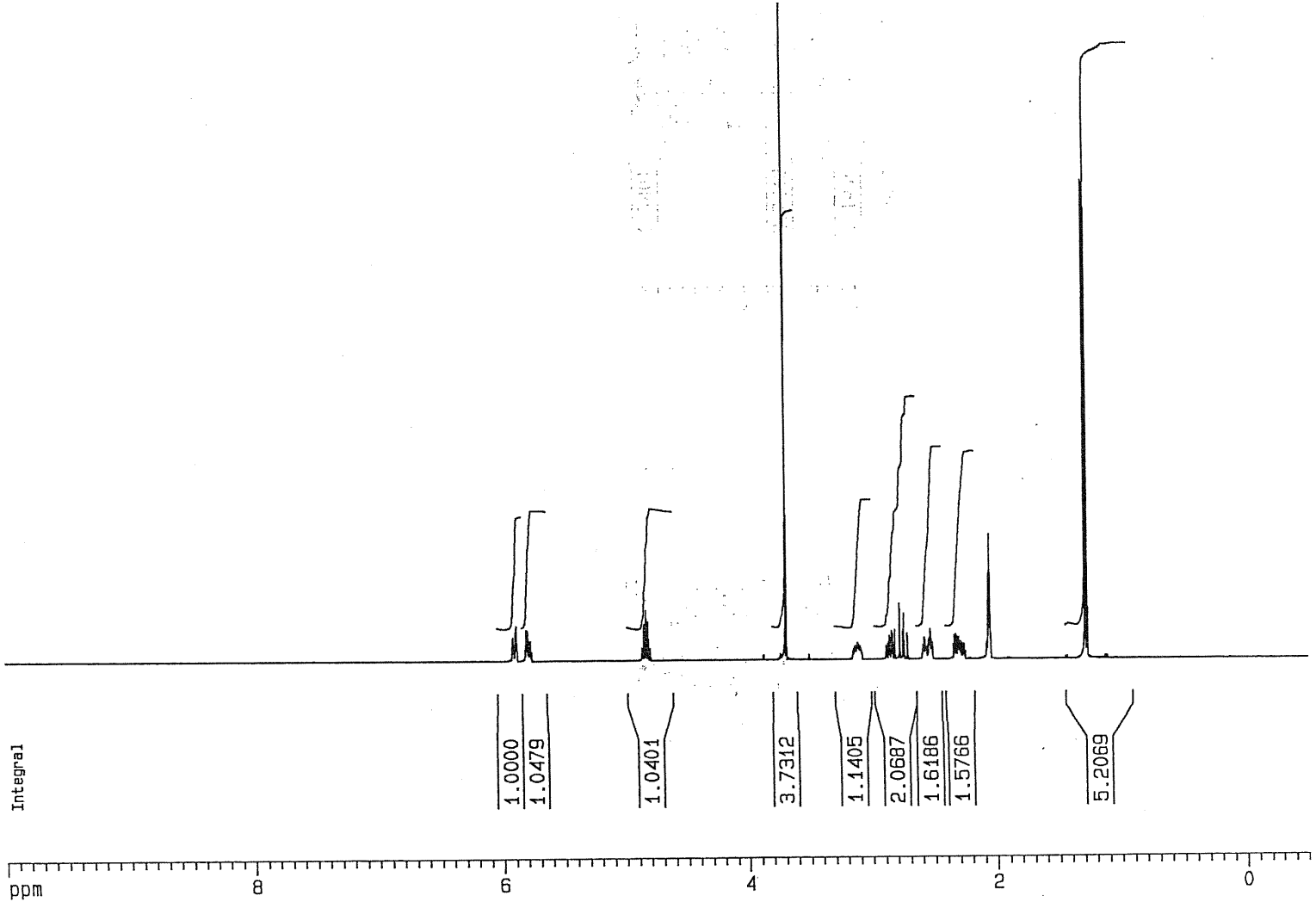
trans, ul

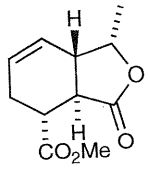
25*E*

^{1}H NMR

$(CD_3)_2CO$

400 MHz

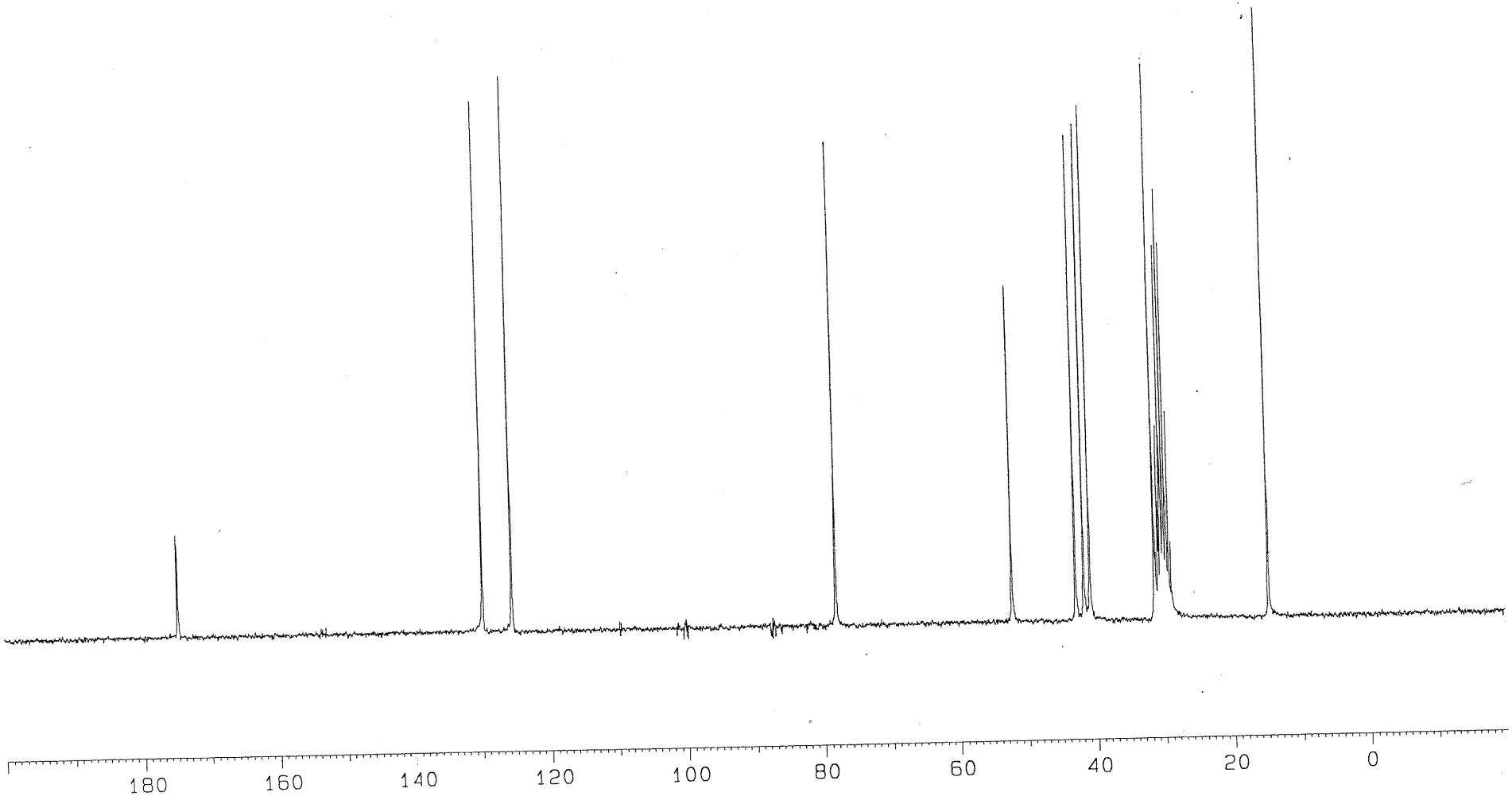


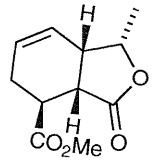


trans, ul

25*E*

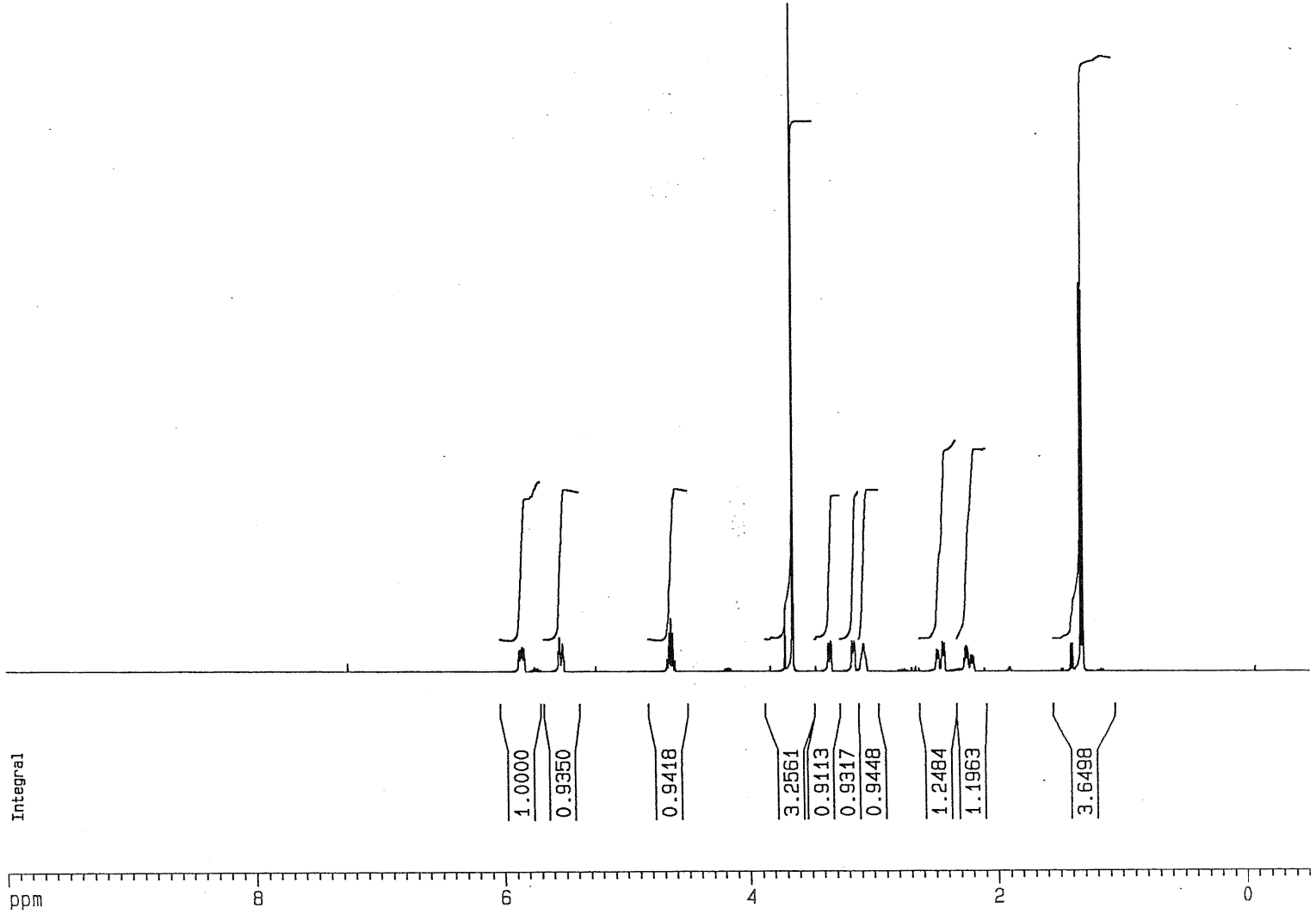
^{13}C NMR
$(CD_3)_2CO$
100 MHz

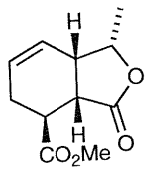




cis, ul

26E
^{1}H NMR
$CDCl_3$
400 MHz





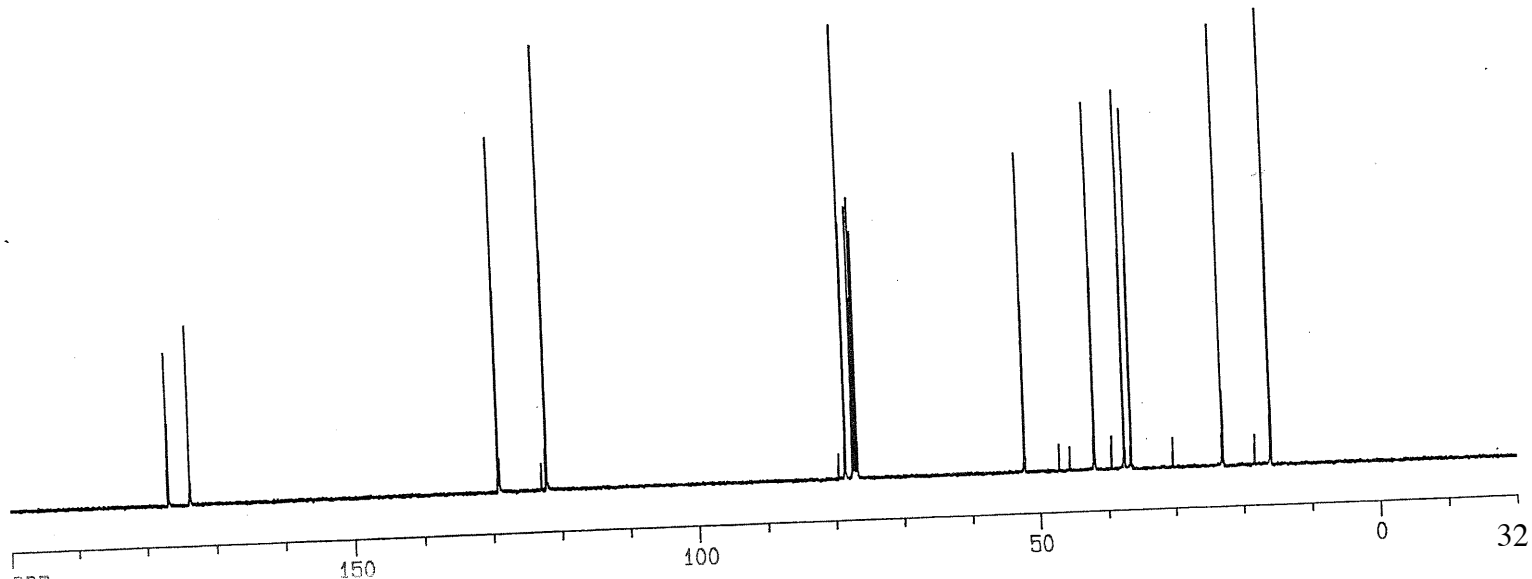
cis, ul

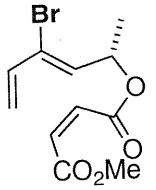
26*E*

^{13}C NMR

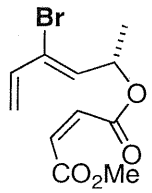
$CDCl_3$

100 MHz

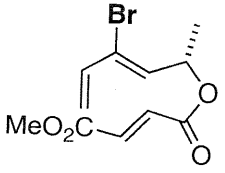




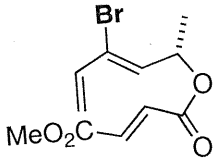
27*Z*
^{1}H NMR
C_6D_6
300 MHz



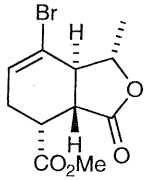
27*Z*
^{13}C NMR
C_6D_6
125 MHz



27*E*
^{1}H NMR
$CDCl_3$
300 MHz



27*E*
^{13}C NMR
$CDCl_3$
75 MHz



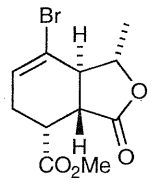
trans, Ik

30*Z*

^{1}H NMR

$CDCl_3$

500MHz



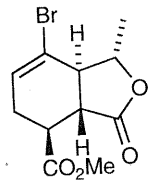
trans, Ik

30*Z*

^{13}C NMR

$CDCl_3$

125 MHz



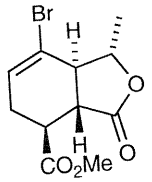
trans, Ik

30*E*

^{1}H NMR

$CDCl_3$

500MHz



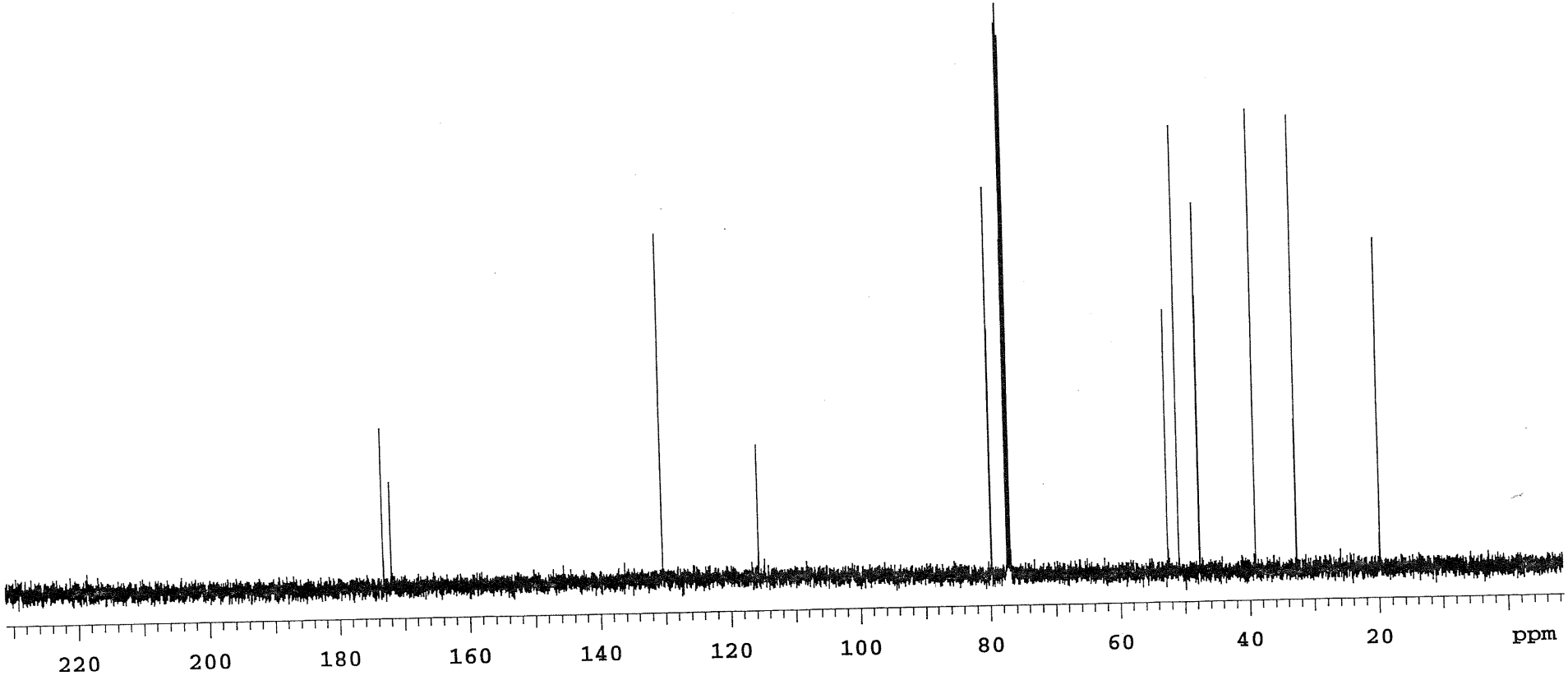
trans, Ik

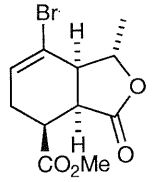
30*E*

^{13}C NMR

$CDCl_3$

125 MHz

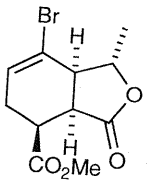




cis, Ik

31*Z*

^{1}H NMR
$CDCl_3$
500MHz



cis, Ik

31*Z*

^{13}C NMR
$CDCl_3$
125 MHz

4. Geometries of Fumarate Transition Structures

Figure S1. IMDA TSs from **18*E*** with destabilising interactions identified. Distances between interacting atoms, and forming bond lengths are given in Angstroms (Å).

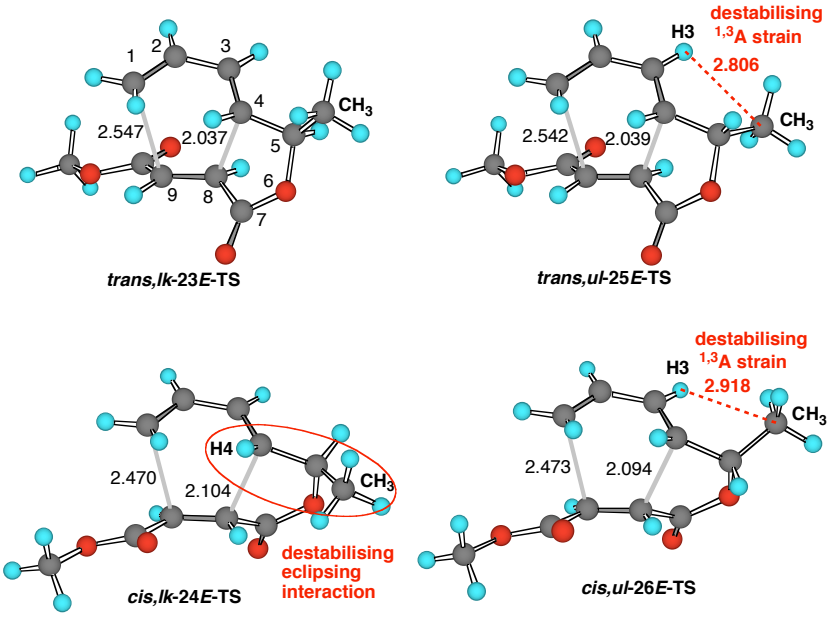
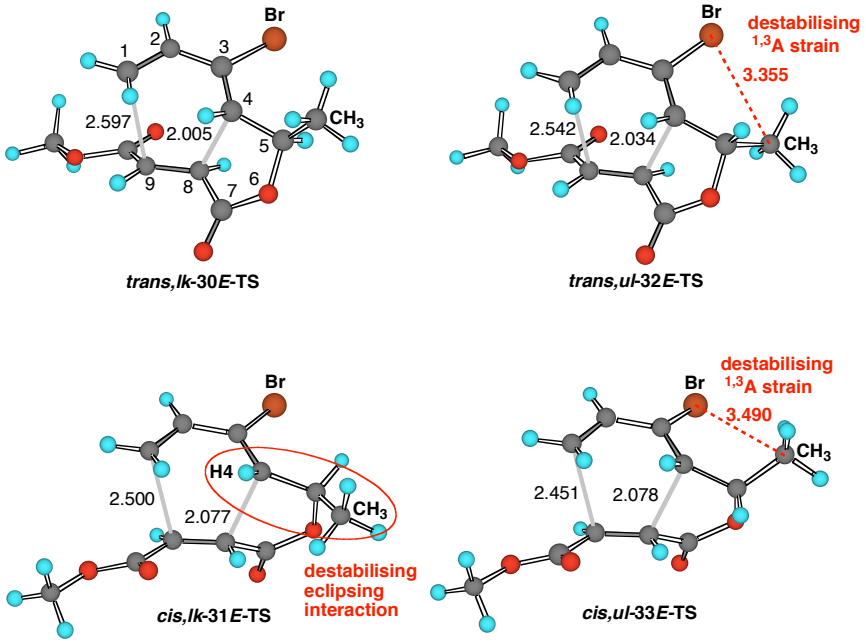


Figure S2. IMDA TSs from fumarate **27*E*** with destabilising interactions identified. Distances between interacting atoms, and forming bond lengths are given in Angstroms (Å).



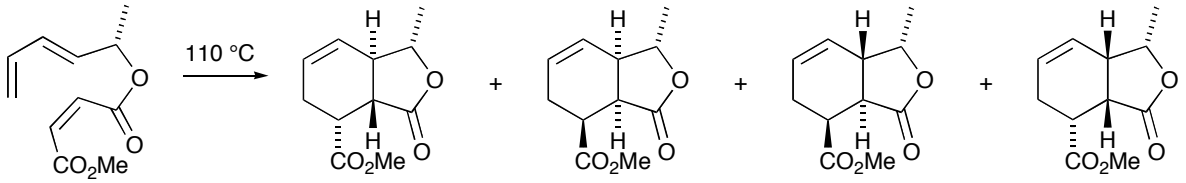
5. Computational Methods

Diels–Alder TSs were optimised using the B3LYP functional[5] and the 6-31+G(d) basis set.[6] Harmonic vibrational frequencies (at the same level of theory) were employed to characterize optimised geometries as either first order saddle structures (one negative Hessian eigenvalue) or minima (all frequencies real), and to provide Zero-Point Vibrational Energy (ZPVE; unscaled) corrections. ZPVE (0 K) corrected TS Boltzmann populations (383 K) were calculated from the electronic energies (ZPVE-corrected) using the electronic energies from optimized *cis,lk-*, *cis,ul-*, *trans,lk- and trans,ul-*IMDA TS isomers, and were used in place of enthalpies or free energies because they have been shown to give similar results.[4] The Gaussian 98[7] and 03[8] program packages were used throughout. Optimised geometries (in Cartesian coordinate form) and their energies are provided in the following section.

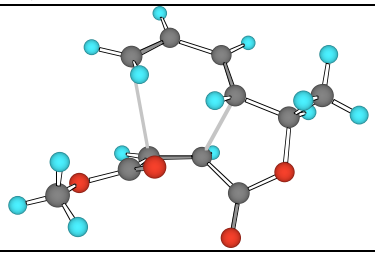
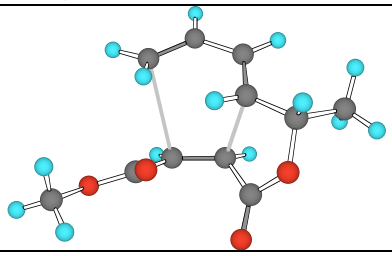
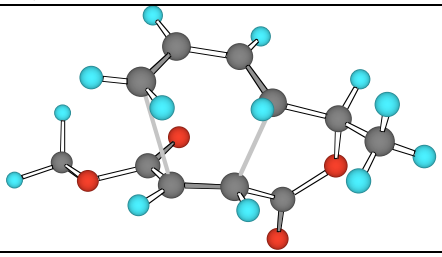
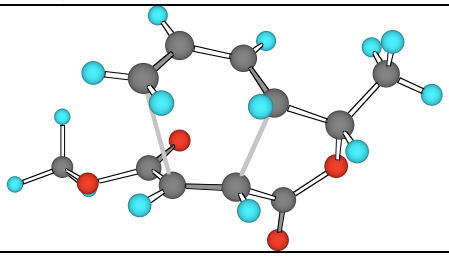
The B3LYP functional, in conjunction with either the 6-31G(d) or 6-31+G(d) basis sets, is known to give acceptable relative energies and geometries for a broad variety of Diels-Alder reactions.[9,10,11,12,13,14] Importantly, we have shown that the B3LYP/6-31+G(d) method correctly predicts *cis*/*trans* ratios for the IMDA reactions of several 9-substituted pentadienyl acrylates, often with an accuracy of 1 kJ/mol.[9] This level of theory is, therefore, adequate for this study. In this work we focus exclusively on the influence of electronic, strain and steric factors on *cis*/*trans* selectivities of IMDA reactions, without considering solvent effects; consequently, we have used *gas phase* DFT calculations. The excellent agreement found between gas phase B3LYP/6-31+G(d) predicted IMDA *cis*/*trans* ratios and the experimental ratios, obtained using toluene as solvent, suggests that weakly polar solvents – which are often used in IMDA reactions – have no significant influence on *cis*/*trans* selectivities.[9] A detailed computational and experimental study of solvent effects on IMDA stereoselectivity is currently underway in our laboratory.

6. Cartesian coordinates and energies of optimised TS geometries

(a) TSs for the IMDA reaction of 18*Z*:

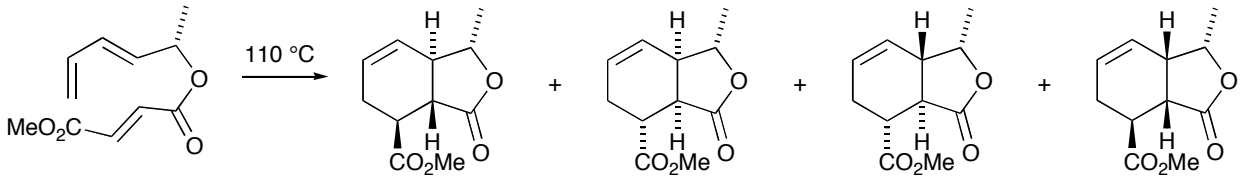


18*Z* ***trans, lk*-23*Z*** ***cis, lk*-24*Z*** ***trans, ul*-25*Z*** ***cis, ul*-26*Z***

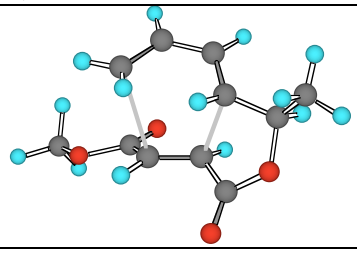
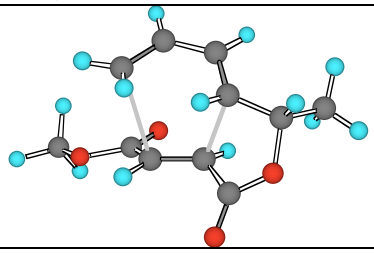
• *trans,lk*-**23*Z*-TS**	• *trans,ul*-**25*Z*-TS**
	
B3LYP/6-31G(d) (a.u.) -728.4126222 C 0 -1.023773 -0.817871 -0.986938 C 0 -1.483383 1.804916 -0.547592 C 0 -0.481644 2.291061 -1.347855 C 0 0.857529 1.846252 -1.271072 C 0 1.221649 0.787888 -0.441467 C 0 0.351089 -0.817825 -1.229340 C 0 2.618515 0.221100 -0.396561 C 0 1.313965 -1.761475 -0.509781 O 0 2.501694 -1.203674 -0.164261 C 0 -1.534012 -1.143021 0.343719 O 0 -0.876404 -1.075165 1.374435 O 0 1.106186 -2.933228 -0.335297 O 0 -2.843994 -1.486328 0.322006 C 0 -3.412003 -1.810028 1.599228 C 0 3.485077 0.790161 0.720917 H 0 -1.732285 -0.723083 -1.799088 H 0 -1.282608 1.343719 0.410477 H 0 -2.521088 2.056747 -0.746262 H 0 -0.748062 2.933228 -2.185837 H 0 1.551208 2.170776 -2.045944 H 0 0.689545 0.661743 0.501343 H 0 0.634247 -0.709534 -2.277252 H 0 3.117279 0.359695 -1.366119 H 0 -4.451843 -2.071045 1.399017 H 0 -3.355392 -0.953491 2.277267 H 0 -2.884628 -2.653732 2.052231 H 0 4.451828 0.277969 0.748138 H 0 3.656235 1.859009 0.556000 H 0 2.994293 0.656525 1.690140	B3LYP/6-31G(d) (a.u.) -728.4105105 C 0 -0.640259 -0.809875 -0.917419 C 0 -1.251480 1.754044 -0.639160 C 0 -0.052307 2.279526 -1.049683 C 0 1.195282 1.871811 -0.526321 C 0 1.282669 0.809662 0.371094 C 0 0.734436 -0.809875 -0.675018 C 0 2.573700 0.236862 0.911255 C 0 1.389145 -1.749008 0.335785 O 0 2.365082 -1.186600 1.092500 C 0 -1.572235 -1.165909 0.152771 O 0 -1.309875 -1.107971 1.346863 O 0 1.148682 -2.925200 0.415009 O 0 -2.788254 -1.524628 -0.322600 C 0 -3.754517 -1.878800 0.677536 C 0 3.827332 0.461823 0.073471 H 0 -1.026611 -0.717178 -1.923615 H 0 -1.376022 1.298477 0.334503 H 0 -2.167328 1.981262 -1.177124 H 0 -0.038757 2.925217 -1.926422 H 0 2.095703 2.235794 -1.016022 H 0 0.455963 0.664093 1.065155 H 0 1.357452 -0.700745 -1.562775 H 0 2.744598 0.614822 1.926422 H 0 -4.659256 -2.143707 0.129196 H 0 -3.944992 -1.035904 1.348114 H 0 -3.401855 -2.727554 1.269500 H 0 4.659241 -0.101532 0.505356 H 0 4.101059 1.522278 0.061264 H 0 3.688461 0.127579 -0.960541
• *cis,lk*-**24*Z*-TS**	• *cis,ul*-**26*Z*-TS**
	
B3LYP/6-31G(d) (a.u.): -728.4078469 C 0 1.172318 0.717911 0.915604	B3LYP/6-31G(d) (a.u.): -728.4069437 C 0 1.155624 0.531189 1.119354

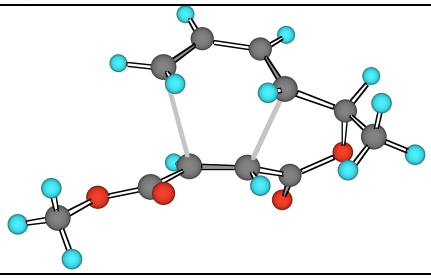
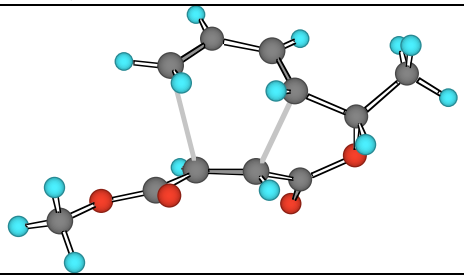
C 0 0.461670 1.700012 0.226761 C 0 -0.911896 1.926926 0.442108 C 0 -1.666016 1.157211 1.292633 C 0 -1.019653 -1.066956 0.208435 C 0 0.354065 -1.109039 0.446991 C 0 1.377502 -1.380020 -0.645874 O 0 1.263702 -2.244125 -1.476715 O 0 2.522507 -0.658676 -0.552048 C 0 2.580811 0.355881 0.484528 C 0 -1.519028 -0.647430 -1.101212 O 0 -0.855835 -0.042480 -1.928604 O 0 -2.823624 -0.974533 -1.282364 C 0 -3.374161 -0.590073 -2.548920 C 0 3.473969 -0.134460 1.618896 H 0 0.937302 0.570557 1.967514 H 0 0.915359 2.149353 -0.654037 H 0 -1.422592 2.597595 -0.244904 H 0 -1.226913 0.598206 2.109482 H 0 -2.747284 1.255798 1.320023 H 0 -1.719406 -1.511902 0.904785 H 0 0.638412 -1.613571 1.372070 H 0 3.052322 1.212021 -0.009705 H 0 -4.401200 -0.957535 -2.546646 H 0 -3.357925 0.497879 -2.664825 H 0 -2.807251 -1.039108 -3.368927 H 0 4.444809 -0.450867 1.227264 H 0 3.636307 0.667450 2.348038 H 0 3.021896 -0.986526 2.139938	C 0 0.499130 1.489349 0.346863 C 0 -0.873611 1.760696 0.512604 C 0 -1.671692 1.056473 1.379974 C 0 -1.045761 -1.237946 0.413284 C 0 0.329132 -1.279968 0.652039 C 0 1.351990 -1.555618 -0.442871 O 0 1.235443 -2.403015 -1.289154 O 0 2.499359 -0.832932 -0.336533 C 0 2.565155 0.064865 0.798813 C 0 -1.549088 -0.859344 -0.907730 O 0 -0.890549 -0.283371 -1.758774 O 0 -2.855164 -1.192230 -1.071533 C 0 -3.412155 -0.849594 -2.347000 C 0 3.574800 1.152359 0.454636 H 0 0.864151 0.453888 2.164368 H 0 0.975998 1.863983 -0.554749 H 0 -1.348969 2.402466 -0.225296 H 0 -1.273346 0.525848 2.235550 H 0 -2.750183 1.184814 1.369446 H 0 -1.745560 -1.657500 1.125275 H 0 0.614410 -1.774628 1.583176 H 0 2.944794 -0.516754 1.650100 H 0 -4.436905 -1.223175 -2.330185 H 0 -3.403931 0.234451 -2.496292 H 0 -2.845245 -1.319366 -3.155319 H 0 4.544556 0.701340 0.223511 H 0 3.250732 1.729340 -0.415802 H 0 3.697021 1.834579 1.302338

(b) TSs for the IMDA reaction of 18*E*:

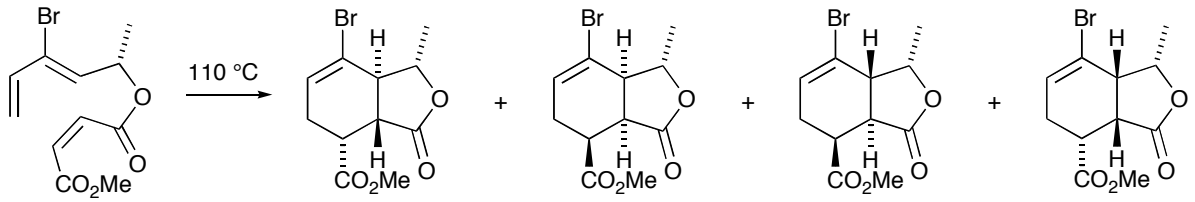


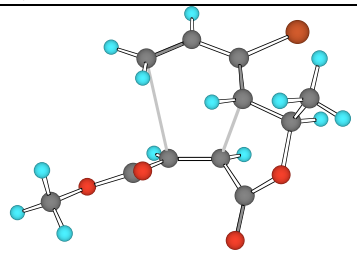
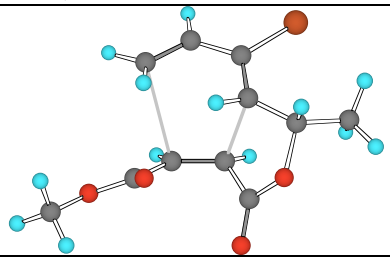
18*E* ***trans, lk*-23*E*** ***cis, lk*-24*E*** ***trans, ul*-25*E*** ***cis, ul*-26*E***

• *trans,lk*-**23*E*-TS**	• *trans,ul*-**25*E*-TS**
	
B3LYP/6-31G(d) (a.u.): -728.4148331 C1 -0.8395200212 -0.710657828 -0.5016493918 C2 -1.5521042058 1.7338846802 -0.4653332126 C3 -0.3046640326 2.2981152621 -0.606189805 C4 0.7797865186 1.9839130588 0.2390772945 C5 0.6267786742 1.0435702945 1.2522009163 C6 0.3202748008 -0.7139815652 0.2682829869 C7 1.7245036912 0.4685860104 2.1104246551 C8 0.4258710948 -1.4493248128 1.579216467 O9 1.3033142851 -0.8794709366 2.4563529972 C10 -0.7078876728 -0.6156099748 -1.9614764422 O11 0.3259895923 -0.364290773 -2.5590267739 O12 -0.1673287153 -2.457285299 1.8711609983	B3LYP/6-31G(d) (a.u.): -728.4129474 C1 -0.7117298233 -0.9496180635 -0.1015331944 C2 -2.1604317958 1.1343968972 -0.2466943096 C3 -1.1916425104 2.0138346968 -0.6733767409 C4 0.035119965 2.1960576681 -0.0004399981 C5 0.3288452463 1.4368734919 1.1273969552 C6 0.4806456881 -0.4764580573 0.43845711 C7 1.6367575645 1.3828383364 1.8832469543 C8 0.9927518623 -0.9114972993 1.7878047981 O9 1.7298582329 0.0379607185 2.4335442989 C10 -0.8093414558 -1.0787563082 -1.5615621389 O11 0.0039399095 -0.6444895422 -2.3611697248 O12 0.8182226169 -1.9950227834 2.2867399888

O13 -1.8894000829 -0.8545922831 -2.5877347619 C14 -1.8385223619 -0.8100654557 -4.0195139997 C15 1.9659909433 1.2094211904 3.4199995833 H16 -1.7878362236 -1.0375361611 -0.0907691252 H17 -1.9154371501 1.3556796212 0.4820159549 H18 -2.3095430252 1.8703274363 -1.2308693623 H19 -0.0849851589 2.8498557797 -1.5172510045 H20 1.7801808382 2.2726236176 -0.0787250605 H21 -0.3415023688 1.013619645 1.7512792824 H22 1.2496018576 -0.6816279072 -0.2995391984 H23 2.6598590427 0.4002022262 1.5385352922 H24 -2.8490764972 -1.0449663852 -4.3563987551 H25 -1.1261183296 -1.5444977384 -4.4053062086 H26 -1.5407482827 0.1836126466 -4.3674075418 H27 2.7024543505 0.6738553231 4.0268661381 H28 1.0372423748 1.2893497237 3.9941027559 H29 2.3422633664 2.2175113464 3.2172128442	O13 -1.9235024044 -1.7617460435 -1.9315800779 C14 -2.0754688676 -1.9580267901 -3.3433575377 C15 2.8960313563 1.7275848125 1.0979319531 H16 -1.4420650415 -1.4662775644 0.5105730947 H17 -2.2599325682 0.8375207166 0.7898908843 H18 -3.0125287367 0.9027289672 -0.8781361532 H19 -1.2830968171 2.4418861527 -1.6690043176 H20 0.8289710716 2.7311720591 -0.5159750884 H21 -0.5128060965 1.1903391372 1.7726578485 H22 1.2607969477 -0.2767049137 -0.2934393908 H23 1.5803358943 2.0249113057 2.7709652707 H24 -2.9919675659 -2.5375246844 -3.4619735206 H25 -1.2214647327 -2.5043094029 -3.7532509435 H26 -2.1598062035 -0.9985595033 -3.8624319309 H27 3.7764597043 1.5382643053 1.7185733786 H28 2.8945627719 2.7873866608 0.8203626895 H29 2.9851711554 1.1321716615 0.1836691929
• *cis,lk*-**24*E*-TS**	• *cis,ul*-**26*E*-TS**
	
B3LYP/6-31G(d) (a.u.): -728.4131212 C1 -0.5576915629 1.2732652236 1.2767235224 C2 -1.3262235522 1.9919992316 0.3644555238 C3 -0.8831172494 2.2889987716 -0.9373742926 C4 0.3442086444 1.8873819904 -1.4153526942 C5 0.1240002063 -0.5337815708 -0.9789702821 C6 -0.200061103 -0.5924689843 0.3710637956 C7 -1.5369198077 -1.0756829727 0.8539182704 O8 -2.2327221711 -1.8799088479 0.2826583616 O9 -1.9274214356 -0.552625788 2.0505496484 C10 -1.2152073571 0.6429937393 2.4901863285 C11 1.53141061 -0.7131385932 -1.3723924481 O12 2.4891938747 -0.6137396608 -0.6218935171 O13 1.6483359809 -0.9922455856 -2.6928234177 C14 2.9898529012 -1.1993033695 -3.1582657409 C15 -0.2633177838 0.3026837969 3.6302589502 H16 0.5138720453 1.4495118 1.3218372864 H17 -2.3906944972 2.1044395817 0.5693514287 H18 -1.6178975995 2.6730286752 -1.6422897339 H19 1.1870845351 1.713083991 -0.7576685917 H20 0.5883447503 2.0013511177 -2.4676704336 H21 -0.6370710272 -0.6700288787 -1.7373197474 H22 0.6328219052 -0.7956464825 1.0418965057 H23 -2.0136543179 1.2922975512 2.8667038134 H24 2.8999840931 -1.4090610214 -4.2246660583 H25 3.4521598337 -2.0436327203 -2.6396554952 H26 3.5997542592 -0.3068743136 -2.9918484655 H27 0.563124503 -0.3320297194 3.292914403 H28 -0.7996321303 -0.2267640055 4.4229155531 H29 0.16110998 1.2207999055 4.0520653369	B3LYP/6-31G(d) (a.u.): -728.4133542 C1 -1.0540564724 1.431044978 0.1714866709 C2 -0.353792774 2.0593805314 -0.8562898303 C3 1.0521157777 2.0576599629 -0.9159962181 C4 1.8367962247 1.4201128254 0.0197370549 C5 0.8323324205 -0.8334164444 -0.1449065811 C6 -0.526369123 -0.5892197117 0.019773505 C7 -1.5065772294 -0.7483248184 -1.1072744952 O8 -1.3788043094 -1.4943109346 -2.0471905487 O9 -2.614788391 0.0420552782 -0.9947075978 C10 -2.5226122289 1.0731796498 0.0293908981 C11 1.6134053821 -1.2652114338 1.0254830926 O12 1.2573898465 -1.1504941199 2.1878251397 O13 2.8042855967 -1.7996996323 0.6632668901 C14 3.6239743509 -2.2581718707 1.7482304176 C15 -3.4592986108 2.2008072097 -0.3844326854 H16 -0.6582710834 1.4870047037 1.1823594326 H17 -0.8885789653 2.3196903928 -1.7679999004 H18 1.5149683128 2.3936536715 -1.8418398599 H19 1.5020890065 1.2606752083 1.0373696246 H20 2.9048429845 1.308278355 -0.1435968878 H21 1.2479540917 -1.0073931461 -1.129556779 H22 -0.9228975336 -0.7865588777 1.015257143 H23 -2.8767786589 0.6396301074 0.9735285504 H24 4.5282975244 -2.6536417556 1.2844695214 H25 3.1112751254 -3.0396982163 2.3156055039 H26 3.8676830231 -1.4341450873 2.4248084236 H27 -4.4786701412 1.818997737 -0.4959530707 H28 -3.4604019064 2.9862909587 0.3785410689 H29 -3.1516800268 2.6397659478 -1.3377548106

(c) TSs for the IMDA reaction of 27Z:



• *trans,lk*-**30Z-TS**	• *trans,ul*-**32Z-TS**
	
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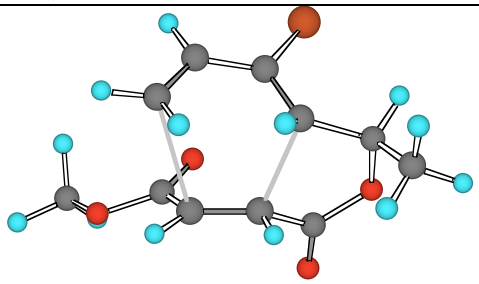
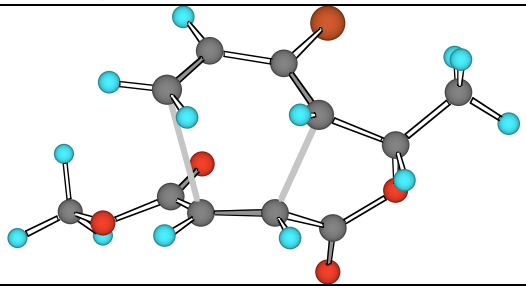
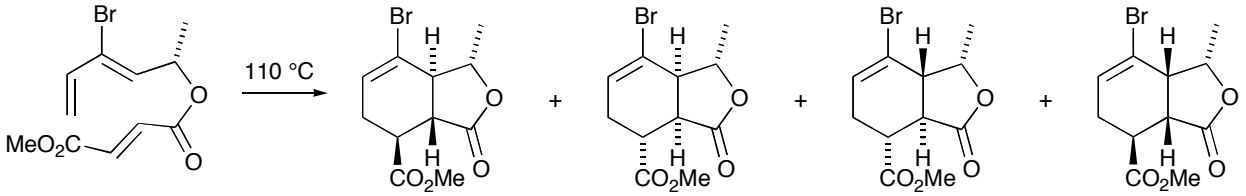
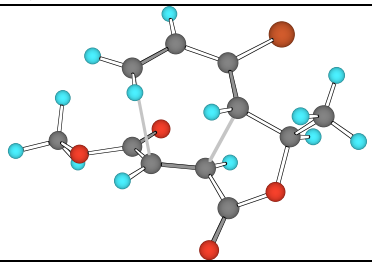
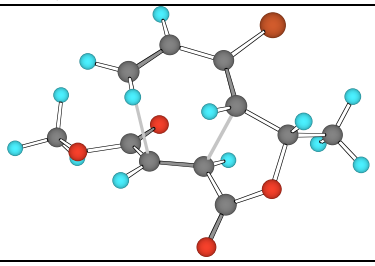
• *cis,lk*-**31Z-TS**	• *cis,ul*-**33Z-TS**
	
B3LYP/6-31+G(d) (a.u.): -3299.3409 C 0 1.245148 0.643707 1.129379 C 0 0.541214 1.628021 0.428177 C 0 -0.835556 1.850540 0.643463	B3LYP/6-31+G(d) (a.u.): -3299.335775 C 0 1.044617 0.549850 1.585052 C 0 0.394318 1.490662 0.777985 C 0 -0.987564 1.731049 0.928802

C 0 -1.585190 1.085007 1.501221 C 0 -0.935394 -1.171204 0.419952 C 0 0.441010 -1.171204 0.662643 C 0 1.490036 -1.451859 -0.403809 O 0 1.388809 -2.305511 -1.249298 O 0 2.641220 -0.749786 -0.258774 C 0 2.669754 0.248047 0.799011 C 0 3.454300 -0.285080 1.993027 Br 0 1.331604 2.539597 -1.040024 C 0 -1.472229 -0.801071 -0.891541 O 0 -0.865509 -0.151688 -1.728760 O 0 -2.746414 -1.237305 -1.061859 C 0 -3.345367 -0.925873 -2.331192 H 0 0.958496 0.547073 2.174469 H 0 -1.345078 2.529648 -0.033661 H 0 -1.153610 0.513214 2.312805 H 0 -2.664597 1.203949 1.531509 H 0 -1.614792 -1.622314 1.133423 H 0 0.722183 -1.657455 1.598862 H 0 3.207993 1.088608 0.353989 H 0 2.945480 -1.129669 2.472656 H 0 4.443481 -0.622894 1.670059 H 0 3.585632 0.507600 2.739258 H 0 -2.742752 -1.334290 -3.146835 H 0 -3.434219 0.157257 -2.457993 H 0 -4.331024 -1.391953 -2.307922	C 0 -1.780853 1.013809 1.793686 C 0 -1.152084 -1.260132 0.873672 C 0 0.226532 -1.260117 1.116745 C 0 1.286621 -1.544662 0.060303 O 0 1.187561 -2.362076 -0.819046 O 0 2.449936 -0.862473 0.255569 C 0 2.448151 -0.008514 1.428345 C 0 3.622116 0.957870 1.335800 Br 0 1.193054 2.246658 -0.773117 C 0 -1.700806 -0.976273 -0.457596 O 0 -1.121567 -0.359756 -1.335846 O 0 -2.962921 -1.460678 -0.591507 C 0 -3.579483 -1.240875 -1.871536 H 0 0.680084 0.538208 2.610275 H 0 -1.466675 2.362091 0.186188 H 0 -1.394714 0.503906 2.666855 H 0 -2.859344 1.142380 1.766907 H 0 -1.825500 -1.693436 1.603973 H 0 0.504822 -1.726166 2.065475 H 0 2.623688 -0.660767 2.295593 H 0 4.553146 0.386154 1.262253 H 0 3.543808 1.615250 0.470490 H 0 3.664000 1.570480 2.243774 H 0 -2.973511 -1.682846 -2.666855 H 0 -3.695984 -0.169815 -2.062317 H 0 -4.553131 -1.728485 -1.811111

(d) TSs for the IMDA reaction of 27*E*:



27*E* ***trans, lk*-30*E*** ***cis, lk*-31*E*** ***trans, ul*-32*E*** ***cis, ul*-33*E***

• *trans,lk*-**30*E*-TS**	• *trans,ul*-**32*E*-TS**
	
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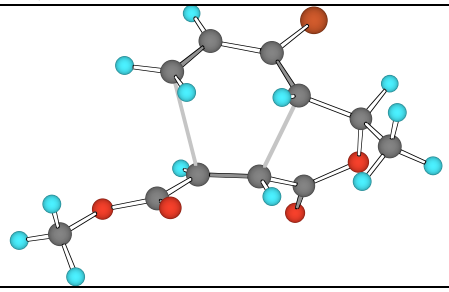
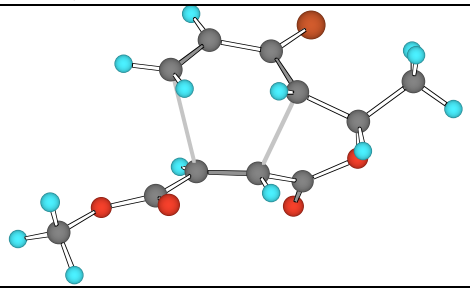
H 0 -1.314224 0.992294 1.792847 H 0 -2.380539 1.912247 0.619156 H 0 -0.453842 2.966644 -0.440063 H 0 0.622406 0.493546 2.119904 H 0 1.081314 -0.758072 -0.668259 H 0 3.174332 -0.120209 0.529037 H 0 4.312546 -0.233551 2.747772 H 0 2.853424 0.401093 3.541443 H 0 3.758728 1.420471 2.393570 H 0 -2.755005 -0.777649 -3.541443 H 0 -3.130798 0.858292 -2.943848 H 0 -4.312561 -0.472366 -2.699341	H 0 -1.389633 0.861496 2.416290 H 0 -2.521606 1.762207 1.292725 H 0 -0.683685 2.955856 0.243454 H 0 0.537979 0.483292 2.636856 H 0 1.015213 -0.744781 -0.137344 H 0 2.914429 0.233994 3.035202 H 0 4.360992 -0.870422 1.328781 H 0 4.145233 0.863556 1.021545 H 0 3.279877 -0.322784 0.029861 H 0 -2.791794 -0.701294 -3.035202 H 0 -3.196121 0.911377 -2.394135 H 0 -4.360992 -0.442429 -2.199265
• *cis,lk*-**31*E*-TS**	• *cis,ul*-**33*E*-TS**
	
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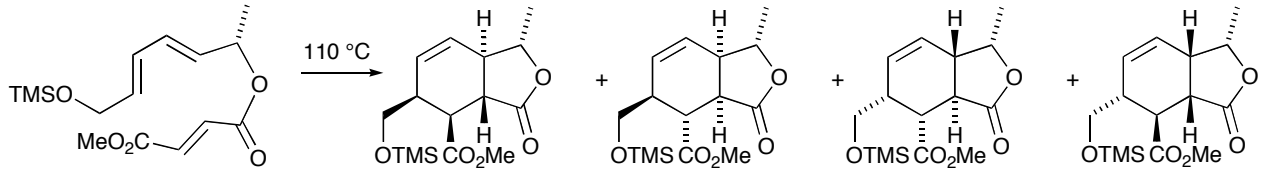
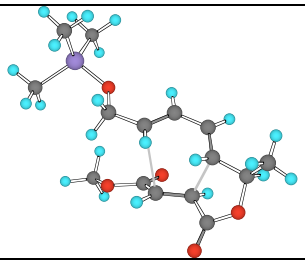
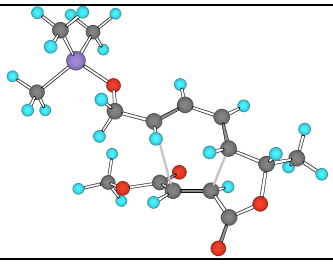
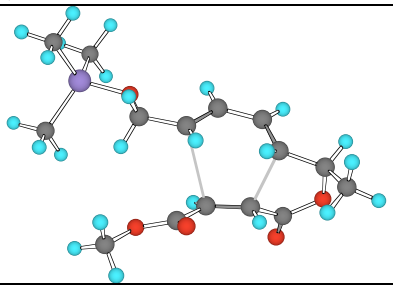
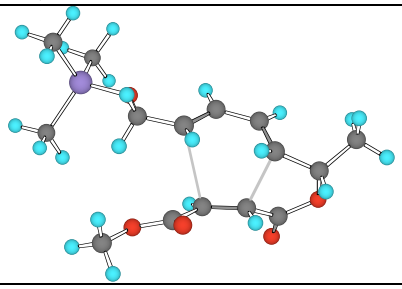
(e) TSs for the IMDA reaction of 34:



34 ***trans, lk*-36** ***cis, lk*-37** ***trans, ul*-38** ***cis, ul*-39**

• *trans,lk*-**36-TS**	• *trans,ul*-**38-TS**

	
B3LYP/6-31+G(d) (a.u.): -1251.32848 C 0 0.502029 -2.400055 0.150635 C 0 0.074142 0.160492 0.947037 C 0 1.225449 0.652893 0.372635 C 0 2.499496 0.088669 0.579605 C 0 2.665680 -1.060028 1.364822 C 0 1.881790 -2.521729 0.361313 C 0 3.986252 -1.757828 1.595825 C 0 2.464020 -3.544998 1.313416 O 0 3.655838 -3.155060 1.845474 C 0 0.030807 -2.044632 -1.182587 O 0 0.743942 -1.730484 -2.128128 O 0 1.982025 -4.617233 1.586517 O 0 -1.328339 -2.121628 -1.281021 C 0 -1.868851 -1.842087 -2.581894 C 0 4.779190 -1.257278 2.795517 C 0 -1.303070 0.672455 0.636215 O 0 -1.290573 1.609131 -0.420959 Si 0 -2.565842 2.633102 -0.835846 C 0 -1.920715 3.609512 -2.305740 C 0 -2.973190 3.769852 0.618088 C 0 -4.092041 1.619995 -1.297913 H 0 -0.216721 -2.766617 0.875458 H 0 0.114349 -0.482742 1.820007 H 0 1.115753 1.416489 -0.391953 H 0 3.310700 0.408615 -0.073013 H 0 2.012497 -1.142731 2.234985 H 0 2.477112 -2.420273 -0.548447 H 0 4.605194 -1.716324 0.689224 H 0 -2.947600 -1.971191 -2.481522 H 0 -1.467102 -2.540451 -3.321609 H 0 -1.626846 -0.819763 -2.885727 H 0 5.669022 -1.876800 2.947830 H 0 4.170776 -1.295120 3.705612 H 0 5.095840 -0.222107 2.627075 H 0 -1.711594 1.124084 1.558670 H 0 -1.952957 -0.180969 0.386703 H 0 -1.640656 2.942337 -3.129730 H 0 -1.032761 4.192551 -2.033157 H 0 -2.678497 4.308731 -2.681854 H 0 -2.091797 4.340805 0.935715 H 0 -3.345459 3.216171 1.489502 H 0 -3.752365 4.491104 0.338074 H 0 -4.446594 1.003403 -0.462006 H 0 -3.886810 0.950623 -2.142426 H 0 -4.921539 2.277420 -1.590485	B3LYP/6-31+G(d) (a.u.): -1251.325958 C 0 0.678970 -2.301270 0.382965 C 0 -0.002228 0.203354 1.137939 C 0 1.114868 0.798538 0.593887 C 0 2.431671 0.363602 0.843597 C 0 2.680679 -0.764542 1.636841 C 0 2.058624 -2.301224 0.626266 C 0 4.047058 -1.338867 1.958649 C 0 2.702011 -3.262589 1.603561 O 0 3.829010 -2.764679 2.182236 C 0 0.213623 -2.005722 -0.967224 O 0 0.920776 -1.639359 -1.898285 O 0 2.315918 -4.378021 1.856293 O 0 -1.129547 -2.207703 -1.099976 C 0 -1.657196 -1.996460 -2.418884 C 0 5.147003 -1.124435 0.926559 C 0 -1.411118 0.583466 0.781708 O 0 -1.452835 1.511047 -0.282822 Si 0 -2.803085 2.410156 -0.746353 C 0 -2.199615 3.444046 -2.194565 C 0 -3.368805 3.502747 0.688309 C 0 -4.209320 1.258408 -1.261459 H 0 -0.022705 -2.725830 1.092606 H 0 0.070435 -0.423279 2.020920 H 0 0.955994 1.545883 -0.178131 H 0 3.226334 0.772400 0.223465 H 0 1.995514 -0.906800 2.472763 H 0 2.658478 -2.161057 -0.273500 H 0 4.387543 -0.970505 2.933243 H 0 -2.722137 -2.221786 -2.344696 H 0 -1.173523 -2.665649 -3.136261 H 0 -1.500473 -0.960693 -2.732910 H 0 6.033997 -1.696930 1.214645 H 0 5.425018 -0.065262 0.882462 H 0 4.842377 -1.443420 -0.075790 H 0 -1.887711 1.000992 1.687363 H 0 -1.971252 -0.327927 0.520279 H 0 -1.827438 2.806854 -3.005753 H 0 -1.381409 4.108383 -1.891129 H 0 -3.005661 4.068695 -2.600327 H 0 -2.557190 4.153625 1.036789 H 0 -3.719955 2.916260 1.546875 H 0 -4.201004 4.148087 0.377304 H 0 -4.535690 0.611100 -0.437256 H 0 -3.910614 0.611511 -2.095337 H 0 -5.085037 1.835236 -1.587067
• *cis,lk*-**37-TS**	• *cis,ul*-**39-TS**
	
0 B3LYP/6-31+G(d) (a.u.): -1251.327191 C 0 3.128754 -0.082672 0.713058 C 0 2.609879 0.879623 -0.165482 C 0 1.251511 1.231628 -0.221100 C 0 0.288910 0.682144 0.600159	B3LYP/6-31+G(d) (a.u.): -1251.32724 C 0 2.286392 -0.246490 1.454056 C 0 1.812149 0.684464 0.517609 C 0 0.460785 1.054138 0.420654 C 0 -0.528183 0.547668 1.239532

C 0 0.877563 -1.791016 0.008804	C 0 0.032028 -1.946259 0.750702
C 0 2.254013 -1.833084 0.247818	C 0 1.409439 -1.988327 0.989900
C 0 3.250610 -2.102066 -0.849060	C 0 2.402634 -2.244690 -0.114410
O 0 3.040634 -2.746338 -1.849900	O 0 2.189133 -2.854553 -1.135315
O 0 4.481552 -1.576080 -0.605453	O 0 3.635239 -1.720000 0.141846
C 0 4.540939 -0.598541 0.482407	C 0 3.676041 -0.848785 1.313232
C 0 -0.026077 -2.248856 1.061249	C 0 -0.873962 -2.368210 1.815628
O 0 0.275345 -2.421356 2.237244	O 0 -0.572052 -2.512848 2.995255
O 0 -1.287048 -2.461197 0.592743	O 0 -2.138733 -2.577682 1.355469
C 0 -2.226624 -2.989212 1.544174	C 0 -3.083572 -3.063522 2.323929
C 0 5.214478 -1.207855 1.705750	C 0 4.832993 0.121567 1.119598
C 0 -1.177444 0.973114 0.453079	C 0 -1.987030 0.848800 1.044617
O 0 -1.456253 1.655243 -0.751526	O 0 -2.228149 1.482742 -0.193954
Si 0 -2.996078 2.070068 -1.304886	Si 0 -3.748947 1.878876 -0.809830
C 0 -2.686142 2.900665 -2.961380	C 0 -3.385742 2.640000 -2.488937
C 0 -3.814957 3.257614 -0.083862	C 0 -4.599426 3.117752 0.336166
C 0 -4.054031 0.517563 -1.498032	C 0 -4.806549 0.322600 -0.971725
H 0 2.755539 -0.106461 1.735077	H 0 1.876144 -0.215897 2.461411
H 0 3.238464 1.197174 -0.997910	H 0 2.452454 0.943619 -0.324081
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H 0 2.526855 -2.296890 1.196121	H 0 1.688965 -2.444458 1.941345
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H 0 4.608810 -2.003998 2.152618	H 0 5.769989 -0.431519 0.997650
H 0 6.185669 -1.630112 1.429886	H 0 4.922363 0.772461 1.996567
H 0 5.376785 -0.433792 2.465271	H 0 4.685318 0.746857 0.234222
H 0 -1.492371 1.579010 1.322296	H 0 -2.315170 1.494995 1.879318
H 0 -1.737030 0.026550 0.508911	H 0 -2.559311 -0.088165 1.126923
H 0 -2.186371 2.216263 -3.657486	H 0 -2.867783 1.926071 -3.140625
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H 0 -3.203003 4.155533 0.068726	H 0 -3.988586 4.019302 0.470642
H 0 -3.979248 2.794373 0.897537	H 0 -4.795197 2.695389 1.330231
H 0 -4.795410 3.583817 -0.455276	H 0 -5.566818 3.431396 -0.077942
H 0 -4.244568 0.023514 -0.536819	H 0 -5.025665 -0.133179 0.002228
H 0 -3.571808 -0.213455 -2.158554	H 0 -4.308426 -0.434784 -1.589355
H 0 -5.031006 0.766602 -1.933105	H 0 -5.769989 0.556641 -1.443756

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