Synthesis of Macrocycles via Cobalt-Mediated [2 + 2 + 2] Cycloadditions

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Supporting Information

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General Methods. All chemicals were reagent grade and used as purchased; $\text{CpCo}(\text{CO})_2$ was obtained from Strem Chemicals. Solvents were purchased as anhydrous from EM Science and Sigma-Aldrich. Chromatographic purification was performed using Silica gel 60 (230-400 mesh ASTM, EMD Chemicals). TLC was performed on fluorescent silica gel plates (Silica Gel 60 F₂₅₄, EMD Chemicals). ^1H NMR spectra were obtained at 300, 400, 500, and 600 MHz, and ^{13}C NMR spectra were acquired at 75, 100, 125, and 150 MHz, in CDCl_3 , with Me_4Si as an internal reference on Bruker-Biospin FT-NMR spectrometers. Exact mass spectra (HRMS) were obtained in FAB mode using a Micromass Autospec E high-resolution mass spectrometer. Low-resolution mass spectra were acquired in API-ES mode on the Agilent LC/MSD spectrometer.

Ref 50:

Table. Alkyne cyclotrimerization of dimethyl 2,2-di(prop-2-ynyl) malonate with 4-octyne^a

solvent	reaction atmosphere	% Yield		
		i	ii	iii
DME	CO	0	31	3
DME	Ar	0	34	7
1,4-dioxane	CO	27	15	3
1,4-dioxane	Ar	29	19	4

^a 15 mol % $\text{CpCo}(\text{CO})_2$, 0.005 M solvent, reflux, 24 h

Characterization Data for Ref 50:

5,6-Dipropylindan-2,2-dicarboxylic Acid Dimethyl Ester (i). ^1H NMR (CDCl_3 , 500 MHz): δ 6.97 (s, 2H), 3.74 (s, 6H), 3.54 (s, 4H), 2.53 (t, $J = 7.8$ Hz, 4H), 1.55-1.59 (m, 4H), 0.97 (t, $J = 7.3$ Hz, 6H).

Compound ii. ^1H NMR (CDCl_3 , 500 MHz): δ 7.08 (d, $J = 7.6$ Hz, 2H), 6.94 (m, 4H), 3.74 (s, 12H), 3.62 (s, 6H), 3.54 (s, 8H), 3.16 (s, 4H).

Characterization Data for Other Compounds:

3-Cyclopentyl-5,7-dihydro[2]pyrindine-6,6-dicarboxylic Acid Dimethyl Ester. ^1H NMR (CDCl_3 , 500 MHz): δ 8.36 (s, 1H), 7.05 (s, 1H), 3.76 (s, 6H), 3.59 (s, 2H), 3.56 (s, 2H), 3.10-3.17 (m, 1H), 2.05-2.07 (m, 2H), 1.67-1.83 (m, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 171.6, 164.2, 149.8, 144.7, 133.2, 117.4, 60.2, 53.1, 47.9, 40.3, 38.0, 33.6, 25.7. HRMS (FAB): Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4 + \text{H}^+$: 304.154883, Found: 304.154342.

3-Cyclohexyl-5,7-dihydro[2]pyrindine-6,6-dicarboxylic Acid Dimethyl Ester. ^1H NMR (CDCl_3 , 300 MHz): δ 8.35 (s, 1H), 7.02 (s, 1H), 3.76 (s, 6H), 3.58 (s, 2H), 3.57 (s, 2H), 2.61-2.70 (m, 1H), 1.25-1.93 (m, 10H). MS (API-ES, Positive Scan): 318.3 (MH^+).

3-(p-Tolyl)-5,6,7,8-tetrahydroisoquinoline. ^1H NMR (CDCl_3 , 300 MHz): δ 8.35 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.24 (d, J = 6.5 Hz, 1H), 2.77-2.79 (m, 4H), 2.39 (s, 3H), 1.81-1.86 (m, 4H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 154.4, 150.2, 146.6, 138.2, 136.9, 131.3, 129.3, 126.5, 120.3, 29.0, 26.0, 22.7, 22.5, 21.2.

1,2-Bis-(but-3-ynyloxymethyl)benzene (31). A suspension of benzene-1,2-diol (1.810g, 16.44 mmol) in acetone (55 mL) was added K_2CO_3 (5.468 g, 39.56 mmol, 2.41 mol equiv). After stirring the mixture at rt for 30 min, it was added with propargyl bromide (4.5 mL, 40.4 mmol, 2.46 mol equiv) and was stirred at 35 $^\circ\text{C}$ for 12 h. After cooling to rt, acetone was evaporated, and the residue was dissolved in EtOAc (150 mL). It was washed with brine (2 x 25 mL), dried (Na_2SO_4) and filtered. Concentration *in vacuo* and purification by flash chromatography (SiO_2 , hexane, 1:30 and then 1:15 EtOAc in hexanes) afforded 2.617g of compound **19** (85 %). ^1H NMR (CDCl_3 , 300 MHz): δ 7.06-7.09 (m, 2H), 6.97-7.00 (m, 2H), 4.77 (d, J = 2.4 Hz, 4H), 2.51 (t, J = 2.4 Hz, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 148.05, 122.58, 115.59, 79.03, 76.17, 57.31. HRMS (FAB): Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2$: 186.068080. Found: 186.068890. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2$: C, 77.40; H, 5.41. Found: C, 77.21; H, 5.39.

1,2-Bis-(prop-2-ynyloxymethyl)benzene (33). Compound **33** was prepared in 70% yield from 1,2-bis-bromomethyl-benzene and 4-trimethylsilanyl-but-3-yn-1-ol, in a similar manner as compound **3**. The silyl group was hydrolyzed under the reaction conditions. ^1H NMR (CDCl_3 , 300 MHz): δ 7.39-7.42 (m, 2H), 7.26-7.32 (m, 2H), 4.70 (s, 4H), 4.19 (d, J = 2.4 Hz, 4H), 2.48 (t, J = 2.3 Hz, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 136.2, 129.8, 128.6, 80.1, 75.0, 69.5, 57.7.

20-(p-Tolyl)-3,6,13,16-tetraoxa-19-azatricyclo[16.3.1.0^{7,12}]docosa-1(22),7(12),8,10,18,20-hexaene (9m). ^1H NMR (CDCl_3 , 500 MHz): δ 8.19 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.37 (s, 1H), 7.27 (obscured d, J = 8.2 Hz, 2H), 6.87-6.92 (m, 4H), 4.90 (s, 2H), 4.80 (s, 2H), 4.22-4.24 (m, 4H), 4.04 (m, 2H), 4.00 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 160.0, 156.7, 149.7, 148.7, 148.5, 138.8, 136.5, 129.4, 126.8, 120.9, 120.7, 116.31, 116.26, 111.9, 111.8, 73.3, 71.0, 69.6, 69.1, 67.7, 67.5, 21.3. MS (API-ES, Positive Scan): 392.1 (MH^+). HRMS (FAB): Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_4 + \text{H}^+$: 392.186184, Found: 392.186671.

20-(*p*-Tolyl)-3,6,13,16-tetraoxa-19-azatricyclo[16.2.2.0^{7,12}]docosa-1(21),7(12),8,10,18(22),19-hexaene (9p). ¹H NMR (CDCl₃, 500 MHz): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 6.71-6.85 (m, 4H), 4.93 (d, *J* = 13.2 Hz, 1H), 4.75 (d, *J* = 13.5 Hz, 1H), 4.53 (d, *J* = 13.4 Hz, 2H), 4.17 (dd, *J* = 9.4, 9.4 Hz, 1H), 4.11 (dd, *J* = 12.0, 3.3 Hz, 1H), 4.03 (dd, *J* = 10.4, 8.2 Hz, 1H), 3.78-3.83 (m, 2H), 3.73 (dd, *J* = 10.4, 3.0 Hz, 1H), 3.60 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.29 (dd, *J* = 11.3, 7.4 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 157.5, 157.0, 148.3, 148.2, 139.7, 138.1, 136.7, 130.4, 129.4, 128.9, 122.8, 120.6, 120.5, 112.0, 74.3, 68.8, 68.6, 68.4, 68.3, 68.0, 21.3. MS (API-ES, Positive Scan): 392.1 (MH⁺). HRMS (FAB): Calcd for C₂₄H₂₅NO₄ + H⁺: 392.186184, Found: 392.18187020.

22-(4-Bromophenyl)-6,15-dioxa-21-azatricyclo[18.3.1.0^{8,13}]tetracos-1(23),8,10,12,20(24),21-hexaene (21m). ¹H NMR (CDCl₃, 500 MHz): δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.35-7.37 (m, 2H), 7.31 (s, 1H), 7.25-7.27 (obscured m, 2H), 7.00 (s, 1H), 4.500 (s, 2H), 4.504 (s, 2H), 3.53 (t, *J* = 6.9 Hz, 4H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 6.6 Hz, 2H), 1.84-1.89 (m, 2H), 1.75-1.80 (m, 2H), 1.56-1.64 (obscured m, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 162.3, 156.5, 152.0, 139.2, 136.7, 132.0, 129.1, 128.0, 123.4, 122.4, 118.7, 70.9, 70.4, 37.8, 35.1, 28.1, 25.9. MS (API-ES, Positive Scan): 480.1 (MH⁺, 90), 482.2 (M + 2, 100). HRMS (FAB): Calcd for C₂₇H₃₀BrNO₂ + H⁺: 480.153816; Found: 480.151669.

22-(4-Bromophenyl)-6,15-dioxa-21-azatricyclo[18.2.2.0^{8,13}]tetracos-1(22),8,10,12,20,23-hexaene (21p). ¹H NMR (CDCl₃, 500 MHz): δ 7.44-7.47 (m, 3H), 7.38-7.40 (m, 1H), 7.27-7.31 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 4.29 (s, 2H), 4.23 (s, 2H), 3.29 (t, *J* = 7.0 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 2.88 (broad s, 2H), 2.75 (broad s, 2H), 1.89 (broad s, 2H), 1.46-1.52 (m, 2H), 1.42-1.46 (m, 2H), 1.16-1.22 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 159.6,

157.8, 140.2, 138.9, 137.0, 136.6, 132.1, 131.8, 131.2, 128.3, 128.0, 127.9, 127.7, 122.6, 122.5, 70.3, 70.0, 69.9, 69.8, 37.4, 31.6, 28.0, 27.3, 25.55, 25.47. HRMS (FAB): Calcd for $C_{27}H_{30}BrNO_2 + H^+$: 480.153816; Found: 480.152607.

22-Pyridin-4-yl-6,15-dioxa-21-azatricyclo[18.3.1.0^{8,13}]tetracos-1(23),8,10,12,20(24),21-hexaene (24m). 1H NMR ($CDCl_3$, 300 MHz): δ 8.71 (broad s, 2H), 7.90 (d, $J = 4.1$ Hz, 2H), 7.41 (s, 1H), 7.27-7.37 (m, 2H), 7.23-7.27 (m, 2H), 7.08 (s, 1H), 4.51 (s, 2H), 4.50 (s, 2H), 3.53 (t, $J = 6.8$ Hz, 4H), 2.91 (t, $J = 6.6$ Hz, 2H), 2.73 (t, $J = 6.6$ Hz, 2H), 1.77-1.90 (m, 4H), 1.53-1.75 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.1, 154.4, 152.0, 150.3, 146.9, 136.6, 136.5, 128.8, 128.7, 127.8, 127.7, 123.5, 121.3, 119.0, 70.29, 70.26, 70.20, 70.0, 37.3, 34.4, 27.7, 27.6, 26.2, 25.6. HRMS (FAB): Calcd for $C_{26}H_{30}N_2O_2 + H^+$: 403.238554. Found: 403.239995.

22-Pyridin-4-yl-6,15-dioxa-21-azatricyclo[18.2.2.0^{8,13}]tetracos-1(22),8,10,12,20,23-hexaene (24p). 1H NMR ($CDCl_3$, 300 MHz): δ 8.58 (broad s, 2H), 7.49 (obscured d, $J = 7.8$ Hz, 1H), 7.54-7.27 (m, 4H), 7.08 (d, $J = 7.8$ Hz, 1H), 4.28 (s, 2H), 4.22 (s, 2H), 3.30 (t, $J = 6.8$ Hz, 2H), 3.14 (t, $J = 6.6$ Hz, 2H), 2.88 (m, 2H), 2.78 (broad s, 2H), 1.92 (broad s, 2H), 1.49 (m, 5H), 1.19 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6, 155.9, 149.8, 148.5, 138.7, 136.6, 136.2, 132.1, 127.9, 127.6, 127.569, 127.4, 124.1, 122.8, 69.9, 69.6, 69.4, 69.1, 36.8, 31.0, 27.2, 27.0, 25.2, 25.1. HRMS (FAB): Calcd for $C_{26}H_{30}N_2O_2 + H^+$: 403.238554. Found: 403.240426.

22-Cyclohex-1-enyl-6,15-dioxa-21-azatricyclo[18.3.1.0^{8,13}]tetracos-1(23),8,10,12,20(24),21-hexaene (25m). 1H NMR ($CDCl_3$, 300 MHz): δ 7.38 (m, 2H), 7.26 (m, 2H), 6.95 (s, 1H), 6.86 (s, 1H), 6.71 (m, 1H), 4.49 (s, 2H), 4.48 (s, 2H), 3.51 (t, $J = 6.9$ Hz, 4H), 2.82 (t, $J = 6.5$ Hz, 2H), 2.62 (t, $J = 6.5$ Hz, 2H), 2.49 (broad s, 2H), 2.25 (broad s, 2H), 1.25-1.84 (m, 10H). HRMS (FAB): Calcd for $C_{27}H_{35}NO_2 + H^+$: 406.274605. Found: 406.273807.

22-Cyclohex-1-enyl-6,15-dioxa-21-azatricyclo[18.2.2.0^{8,13}]tetracos-1(22),8,10,12,20,23-hexaene (25p). ¹H NMR (CDCl₃, 300 MHz): δ 7.28 (m, 5H), 6.89 (d, J = 7.8 Hz, 1H), 5.68 (broad s, 1H), 4.23 (s, 4H), 3.21 (m, 4H), 2.85 (m, 2H), 2.78 (m, 2H), 2.30 (broad s, 2H), 2.18 (broad s, 2H), 1.85 (m, 2H), 1.70 (m, 6H), 1.40 (m, 4H). HRMS (FAB): Calcd for C₂₇H₃₅NO₂ + H⁺: 406.274605. Found: 406.272895.

22-Adamantan-1-yl-6,15-dioxa-21-azatricyclo[18.3.1.0^{8,13}]tetracos-1(23),8,10,12,20(24),21-hexaene (27). ¹H NMR (CDCl₃, 300 MHz): δ 7.28-7.36 (m, 2H), 7.23-7.26 (m, 2H), 6.84 (s, 1H), 6.80 (s, 1H), 4.47 (s, 2H), 4.46 (s, 2H), 3.44-3.52 (m, 4H), 2.79 (t, J = 6.6 Hz, 2H), 2.61 (t, J = 6.6 Hz, 2H), 2.08 (broad s, 3H), 1.97 (m, 5H), 1.75 (m, 9H), 1.58 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 168.7, 160.1, 150.5, 136.6, 128.6, 127.7, 120.1, 116.4, 70.2, 70.0, 42.0, 41.8, 38.7, 37.2, 36.7, 34.5, 28.9, 27.7, 27.6, 27.1, 26.2. HRMS (FAB): Calcd for C₃₁H₄₁NO₂ + H⁺: 460.321555. Found: 460.319823.

10-(*p*-Tolyl)-3,18-dioxa-9-azatricyclo[18.4.0.0^{8,13}]tetracos-1(24),8(13),9,11,20,22-hexaene (29o). ¹H NMR (CDCl₃, 500 MHz): δ 7.87 (d, J = 10 Hz, 2H), 7.41 (s, 2H), 7.32-7.37 (m, 2H), 7.24-7.27 (m, 4H), 4.60 (s, 2H), 4.58 (s, 2H), 3.60-3.64 (m, 4H), 2.86-2.89 (m, 2H), 2.64-2.67 (m, 2H), 2.38 (s, 3H), 1.93-1.96 (m, 2H), 1.72-1.81 (m, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 159.6, 154.4, 138.1, 137.7, 137.1, 136.9, 136.5, 133.3, 129.8, 129.7, 129.3, 128.0, 127.8, 126.6, 117.5, 70.6, 70.3, 69.8, 69.6, 34.6, 31.9, 29.3, 29.2, 27.8, 26.2, 21.2. HRMS (FAB) Calcd for C₂₈H₃₃NO₂ + H⁺: 416.258955. Found: 416.260303.

21-(*p*-Tolyl)-6,15-dioxa-24-azatricyclo[18.3.1.0^{8,13}]tetracos-1(23),8,10,12,20(24),21-hexaene (29m). ¹H NMR (CDCl₃, 500 MHz) δ 7.34-7.38 (m, 3H), 7.16-7.27 (m, 6H), 6.97 (d, *J* = 7.8 Hz, 1H), 4.58 (s, 2H), 4.56 (s, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.82 (m, 4H), 2.40 (s, 3H), 1.88-1.91 (m, 2H), 1.71-1.78 (m, 4H), 1.55-1.60 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 159.8, 158.1, 137.6, 137.3, 136.9, 136.8, 134.0, 129.1, 128.9, 128.7, 128.6, 127.6, 127.5, 120.0, 70.8, 70.7, 70.5, 70.4, 40.0, 34.3, 28.6, 28.3, 26.1, 25.6, 21.2. HRMS (FAB): Calcd for C₂₈H₃₃NO₂ + H⁺: 416.258955. Found: 416.258330.

10-(4-Methoxyphenyl)-3,18-dioxa-9-azatricyclo[18.4.0.0^{8,13}]tetracos-1(24),8(13),9,11,20,22-hexaene (30o). ¹H NMR (CD₃OD, 500 MHz): δ 7.82-7.85 (m, 2H), 7.50 (ABq, *J* = 8.0, 8.0 Hz, 2H), 7.34-7.37 (m, 2H), 7.26-7.29 (m, 2H), 6.98-7.01 (m, 2H), 4.61 (s, 2H), 4.60 (s, 2H), 3.83 (s, 3H), 3.63-3.66 (m, 4H), 2.84-2.87 (m, 2H), 2.67-2.70 (m, 2H), 1.83-1.88 (m, 2H), 1.72-1.81 (m, 6H). ¹³C NMR (CD₃OD, 125 Hz) δ 162.2, 161.2, 156.5, 140.2, 138.5, 138.4, 135.3, 133.9, 131.5, 131.4, 129.7, 129.5, 129.4, 119.6, 115.4, 71.9, 71.7, 71.2, 56.2, 35.5, 33.1, 30.8, 30.7, 29.6, 28.2. HRMS (FAB): Calcd for C₂₈H₃₃NO₃ + H⁺: 432.253869. Found: 432.252360.

Compound 30m is inseparable from **20m**.

17-(*p*-Tolyl)-4,13-dioxa-18-azatricyclo[14.3.1.0^{6,11}]eicosa-1(19),6,8,10,16(20),17-hexaene (32m). ¹H NMR (CDCl₃, 500 MHz): δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.59 (s, 1H), 7.36-7.40 (m, 3H), 7.31-7.33 (m, 2H), 7.27 (obscured d, *J* = 7.4 Hz, 2H), 4.37 (s, 2H), 4.35 (s, 2H), 3.90 (t, *J* = 5.2 Hz, 2H), 3.84 (t, *J* = 5.2 Hz, 2H), 3.14 (t, *J* = 4.5 Hz, 2H), 2.90 (t, *J* = 5.2 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, 125 Hz): δ 159.4, 156.8, 149.6, 138.5, 136.5, 131.0, 130.7, 129.4, 128.5, 127.8, 126.9, 124.0, 118.7, 71.6, 70.5, 38.9, 36.0, 21.3. MS (API-ES, Positive Scan): 360.0 (MH⁺).

18-(*p*-Tolyl)-4,13-dioxa-17-azatricyclo[14.2.2.0]^{6,11}eicosa-1(19),6,8,10,16(20),17-hexaene (32p). ¹H NMR (CDCl₃, 500 MHz): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.24 (obscured d, *J* = 7.8 Hz, 1H), 7.21-7.24 (obscured m, 2H), 7.19 (broad singlet, 1H), 7.18 (broad singlet, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 4.07 (ddd, *J* = 10.4, 4.5, 3.4 Hz, 1H), 3.95 (d, *J* = 12.1 Hz, 1H), 3.81 (obscured d, *J* = 11.7 Hz, 1H), 3.77-3.85 (obscured m, 1H), 3.60 (td, *J* = 4.5, 10.4 Hz, 1H), 3.44 (d, *J* = 11.6 Hz, 1H), 3.39 (d, *J* = 12.0 Hz, 1H), 3.30 (td, *J* = 3.9, 13.9 Hz, 1H), 3.17 (broad s, 1H), 3.14 (dt, *J* = 9.9, 3.6 Hz, 1H), 3.03 (ddd, *J* = 13.1, 10.7, 4.6 Hz, 1H), 2.73 (ddd, *J* = 14.1, 9.7, 4.7 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, 125 Hz): δ 158.8, 157.1, 139.8, 138.0, 137.6, 136.0, 135.3, 130.7, 129.3, 129.2, 127.9, 127.44, 127.42, 127.1, 122.9, 69.6, 39.3, 34.6, 21.3. MS (API-ES, Positive Scan): 360.0 (MH⁺).

20-Morpholin-4-yl-5,14-dioxa-19-azatricyclo[16.2.2.0]^{7,12}docosa-1(20),7,9,11,18,21-hexaene (37). ¹H NMR (CDCl₃, 500 MHz): δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.17-7.29 (m, 4H), 6.73 (d, *J* = 7.5 Hz, 1H), 3.80-3.96 (m, 6H), 3.73 (ddd, *J* = 11.0, 6.7, 2.7 Hz, 2H), 3.44-3.55 (m, 2H), 3.29-3.37 (m, 2H), 3.23 (ddd, *J* = 12.5, 6.6, 2.5 Hz, 2H), 2.97 (ddd, *J* = 13.9, 9.4, 4.2 Hz, 1H), 2.90 (ddd, *J* = 12.7, 6.5, 2.3 Hz, 2H), 2.87 (ddd, *J* = 11.0, 8.3, 3.6 Hz, 1H), 2.69 (ddd, *J* = 13.9, 9.4, 4.2 Hz, 1H), 2.50 (ddd, *J* = 14.3, 7.0, 4.3 Hz, 1H), 2.16-2.24 (m, 2H), 1.81-1.92 (m, 2H). ¹³C NMR (CDCl₃, 125 Hz): δ 160.8, 157.4, 139.3, 136.8, 136.1, 128.5, 127.7, 127.4, 127.2, 124.5, 117.9, 70.5, 69.8, 69.7, 69.4, 67.3, 50.7, 35.3, 28.8, 28.5, 28.1. MS (API-ES, Positive Scan): 383.0 (MH⁺).

20-Dimethylamino-5,14-dioxa-19-azatricyclo[16.2.2.0]^{7,12}docosa-1(20),7,9,11,18,21-hexaene-6,13-dione (38). ¹H NMR (CDCl₃, 500 MHz): δ 7.67-7.69 (m, 1H), 7.62-7.64 (m, 1H), 7.47-7.52 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 4.53 (ddd, *J* = 11.5, 8.1, 3.6 Hz, 1H), 4.21 (ddd, *J* = 11.2, 7.1, 3.8 Hz, 1H), 4.08 (ddd, *J* = 11.1, 7.0, 3.8 Hz, 1H), 4.03 (ddd, *J* = 11.5, 7.8, 3.8 Hz, 1H), 2.96-3.05 (m, 2H), 2.72-2.78 (m, 1H), 2.68 (s, 6H), 2.62 (td, *J* = 15.2, 6.2 Hz,

1H), 2.22-2.38 (m, 3H), 2.09-2.17 (m, 3H). ^{13}C NMR (CDCl_3 , 125 Hz): δ 167.5, 166.4, 161.5, 155.4, 139.1, 132.8, 131.5, 130.9, 130.4, 128.6, 128.5, 120.8, 116.3, 64.5, 63.2, 41.3, 34.3, 28.1, 25.5, 24.6. HRMS (FAB): Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4 + \text{H}^+$: 369.181433. Found: 369.181392.

20-Dibenzo[*b,f*]azepin-5-yl-3,6,13,16-tetraoxa-19-azatricyclo[16.3.1.07,12]docosa-1(21),7,9,11,18(22),19-hexaene (39m). ^1H NMR (CDCl_3 , 500 MHz): δ 7.58 (s, 1H), 7.43-7.50 (m, 4H), 7.38-7.39 (m, 2H), 7.30-7.33 (m, 2H), 6.80-6.88 (m, 6H), 5.80 (s, 1H), 4.45 (s, 2H), 4.43 (s, 2H), 4.13-4.15 (m, 4H), 3.90-3.92 (m, 2H), 3.86-3.87 (m, 2H). ^{13}C NMR (CDCl_3 , 125 Hz): δ 157.9, 157.8, 149.7, 148.8, 148.6, 142.6, 135.7, 130.6, 130.3, 129.7, 129.2, 126.7, 120.8, 120.6, 111.9, 111.8, 108.5, 101.9, 73.2, 71.3, 69.5, 69.0, 67.6, 67.5. MS (API-ES, Positive Scan): 492.9 (M^+). HRMS (FAB): Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_4 + \text{H}^+$: 493.212733. Found: 493.210880.

20-Dibenzo[*b,f*]azepin-5-yl-3,6,13,16-tetraoxa-19-azatricyclo[16.2.2.07,12]docosa-1(21),7(12),8,10,18(22),19-hexaene (39p). ^1H NMR (CDCl_3 , 500 MHz): δ 7.67 (d, $J = 7.6$ Hz, 1H), 7.60 (broad s, 2H), 7.26-7.29 (m, 2H), 7.20-7.22 (m, 2H), 7.14 (obscured d, $J = 7.3$ Hz, 1H), 7.12-7.15 (obscured m, 2H), 6.86 (s, 2H), 6.79-6.82 (m, 2H), 6.68-6.71 (m, 2H), 4.81 (d, $J = 13.1$ Hz, 1H), 4.31 (d, $J = 13.1$ Hz, 1H), 4.00 (obscured m, 1H), 3.98 (obscured d, $J = 13.7$ Hz, 1H), 3.91-3.93 (m, 2H), 3.73 (ddd, $J = 11.8, 4.9, 1.0$ Hz, 1H), 3.68 (obscured d, $J = 13.6$ Hz, 1H), 3.66-3.68 (m, 1H), 3.62 (ddd, $J = 10.4, 4.9, 1.0$ Hz, 1H), 3.56 (ddd, $J = 10.5, 3.5, 1.3$ Hz, 1H), 3.32 (ddd, $J = 11.9, 7.3, 1.1$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 Hz): δ 155.4, 155.0, 148.4, 146.3, 141.3, 135.2, 131.6, 128.9, 128.6, 128.3, 125.3, 121.4, 120.4, 120.3, 117.5, 111.9, 111.8, 73.9, 68.73, 68.68, 68.3, 68.15, 68.10. MS (API-ES, Positive Scan): 492.9 (M^+). HRMS (FAB): Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_4 + \text{H}^+$: 493.212733. Found: 493.210694.

17-Phenethyl-4,13-dioxo-17-azatricyclo[14.2.2.0]^{6,11}icosa-1(19),6,8,10,16(20)-pentaen-18-one (43p). ¹H NMR (CDCl₃, 500 MHz): δ 7.19-7.34 (m, 9H), 6.99 (d, J = 6.9 Hz, 1H), 5.92 (d, J = 7.0 Hz, 1H), 4.89 (ddd, J = 13.6, 9.4, 4.9 Hz, 1H), 4.20 (d, J = 11.3 Hz, 1H), 3.96 (d, J = 12.1 Hz, 1H), 3.84-3.91 (m, 4H), 3.78-3.82 (obscured m, 1H), 3.80 (obscured d, J = 11.2 Hz, 1H), 3.70 (d, J = 12.0 Hz, 1H), 3.63 (dt, J = 11.3, 3.2 Hz, 1H), 3.51 (ddd, J = 12.7, 9.2, 3.5 Hz, 1H), 3.22 (td, J = 13.2, 2.6 Hz, 1H), 3.10 (d, J = 13.6, 8.9, 4.9 Hz, 1H), 2.84-2.90 (m, 1H), 2.77 (td, J = 14.6, 4.1 Hz, 1H). ¹³C NMR (CDCl₃, 125 Hz): δ 163.1, 143.8, 138.4, 137.7, 135.6, 135.0, 129.0, 128.7, 128.6, 127.6, 127.5, 127.3, 126.9, 126.7, 109.5, 70.9, 70.7, 68.8, 67.5, 45.7, 35.6, 35.1, 33.4. MS (API-ES, Positive Scan): 390.0 (MH⁺).

11,12-Dipropyl-5,7,8,9,14,15,16,18-octahydro-6,17-dioxadibenzo[*a,h*]cyclotetradecene (57o). ¹H NMR (CDCl₃, 600 MHz): δ 7.29-7.30 (m, 2H), 7.22-7.24 (m, 2H), 6.87 (s, 2H), 4.57 (s, 4H), 3.65 (t, J = 5.3 Hz, 4H), 2.70 (t, J = 8.0 Hz, 4H), 2.45-2.48 (m, 4H), 1.84-1.88 (m, 4H), 1.51-1.55 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 138.5, 137.9, 137.2, 131.5, 130.9, 71.0, 70.5, 34.8, 31.9, 29.5, 24.7, 15.0. MS (MH⁺): MS (API-ES, Positive Scan): 381.1 (MH⁺).

19,20-Dipropyl-5,14-dioxatricyclo[16.2.2.0]^{7,12}docosa-1(21),7,9,11,18(22),19-hexaene (57p). ¹H NMR (CDCl₃, 600 MHz): δ 7.23-7.25 (m, 2H), 7.18-7.20 (m, 2H), 6.93 (s, 2H), 3.84 (AB q, J = 12.7, 4H), 3.46-3.51 (m, 4H), 2.91 (ddd, J = 11.7, 6.2, 3.6 Hz, 2H), 2.51-2.57 (m, 6H), 2.00-2.05 (m, 2H), 1.90-1.95 (m, 2H). MS (API-ES, Positive Scan): 381.1 (MH⁺). HRMS (FAB): Calcd for C₂₆H₃₆O₂ - H⁺: 379.263706. Found: 379.264777.

5,7,8,9,14,15,16,18-Octahydro-6,17-dioxadibenzo[*a,h*]cyclotetradecene-11,12-dicarboxylic Acid Dimethyl Ester (58o). ^1H NMR (CDCl_3 , 600 MHz): δ 7.53 (s, 2H), 7.36-7.37 (m, 2H), 7.31-7.33 (m, 2H), 4.62 (s, 4H), 3.89 (s, 6H), 3.68 (t, J = 5.4 Hz, 4H), 2.87 (t, J = 7.9 Hz, 4H), 1.92 (m, 4H). ^{13}C NMR (CDCl_3 , 150 MHz): δ 168.7, 145.0, 137.1, 131.5, 130.2, 129.1, 71.1, 69.7, 30.9, 29.3. MS (API-ES, Positive Scan): 413.0 (MH^+).

5,14-Dioxatricyclo[16.3.1.0^{7,12}]docosa-1(21),7(12),8,10,18(22),19-hexaene-19,20-dicarboxylic Acid Dimethyl Ester (58m). ^1H NMR (CDCl_3 , 600 MHz): δ 7.65 (d, J = 1.4 Hz, 1H), 7.37-7.40 (m, 2H), 7.34 (d, J = 1.3 Hz, 1H), 7.29-7.31 (m, 2H), 4.50 (s, 2H), 4.49 (s, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 3.39 (ddd, J = 6.0, 6.0, 6.0 Hz, 4H), 2.77-2.80 (m, 4H), 1.93-1.98 (m, 4H). ^{13}C NMR (CDCl_3 , 150 MHz): δ 170.3, 167.2, 142.4, 138.4, 136.7, 132.9, 129.8, 128.2, 128.4. MS (API-ES, Positive Scan): 412.9 (MH^+).

5-[3-(2-Hex-5-ynyloxymethyl-benzyloxy)propyl]benzene-1,2,3,4-tetracarboxylic Acid Tetramethyl Ester (59). ^1H NMR (CDCl_3 , 600 MHz): δ 7.99 (s, 1H), 7.38-7.40 (m, 2H), 7.29-7.30 (m, 2H), 4.574 (s, 2H), 4.568 (s, 2H), 3.92 (s, 4H), 3.89 (s, 4H), 3.86 (s, 4H), 3.85 (s, 4H), 3.58 (t, J = 6.0 Hz, 2H), 3.49 (t, J = 5.9 Hz, 2H), 2.83 (t, J = 7.7 Hz, 2H), 2.31 (dt, J = 6.7, 2.1 Hz, 2H), 1.90-1.93 (m, 3H), 1.81-1.84 (m, 2H).

3,18-Dioxatricyclo[18.4.0.0^{8,13}]tetracos-1(24),8(13),9,11,20,22-hexaene-10,11-dicarboxylic Acid Dimethyl Ester (60). ¹H NMR (CDCl₃, 500 MHz): δ 7.48 (s, 2H), 7.33-7.36 (m, 2H), 7.25-7.28 (m, 2H), 4.58 (s, 4H), 3.88 (s, 6H), 3.60 (t, *J* = 5.0 Hz, 4H), 2.67 (t, *J* = 7.7 Hz, 4H), 1.71-1.71 (m, 8H). ¹³C NMR (CDCl₃, 125 MHz): δ 168.3, 144.2, 136.6, 130.2, 129.8, 129.4, 128.0, 70.4, 69.5, 52.5, 32.4, 29.3, 27.9. MS (API-ES, Positive Scan): 441.0 (MH⁺).

5-[4-(2-Hex-5-ynyloxymethylbenzyloxy)butyl]benzene-1,2,3,4-tetracarboxylic Acid Tetramethyl Ester (61). ¹H NMR (CDCl₃, 500 MHz): δ 7.95 (s, 1H), 7.34-7.39 (m, 2H), 7.27-7.30 (m, 2H), 4.559 (s, 2H), 4.552 (s, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 3.862 (s, 3H), 3.859 (s, 3H), 3.48-3.50 (m, 4H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.21 (dt, *J* = 2.7, 7.1 Hz, 2H), 1.93 (t, *J* = 2.7 Hz, 1H), 1.58-1.75 (m, 8H). ¹³C NMR (CDCl₃, 125 MHz): δ 168.3, 167.7, 167.5, 165.8, 165.1, 142.5, 136.9, 136.6, 136.53, 136.51, 133.9, 133.2, 128.6, 128.5, 127.72, 127.69, 84.3, 70.5, 70.0, 69.9, 68.4, 53.1, 53.0, 52.8, 32.4, 29.5, 28.8, 27.8, 25.3, 18.2. MS (API-ES, Positive Scan): 605.1 (M + Na⁺).

6,7,9,14,16,17-Hexahydro-5,8,15,18-tetraoxadibenzo[*a,h*]cyclotetradecene-11,12-dicarboxylic Acid Dimethyl Ester (62). ¹H NMR (CDCl₃, 500 MHz): δ 7.79 (s, 2H), 6.87-6.92 (m, 4H), 4.96 (s, 4H), 4.22-4.23 (m, 4H), 4.01-4.03 (m, 4H), 3.89 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 168.0, 148.7, 140.2, 130.9, 128.2, 121.3, 113.3, 71.1, 69.8, 69.2, 52.5. MS (API-ES, Positive Scan): 417.0 (MH⁺). HRMS (FAB): Calcd for C₂₂H₂₄O₈: 416.147118, Found: 416.146990.

LRB 17681-74-6, CDCl₃, test = 298

Current Data Parameters
NAME: LRB 17681-74-6
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20080311
Time: 11:44
INSTRUM: spect
PROBHD: 5mmQNP1H
PULPROG: zgpg
TD: 32768
SOLVENT: CDCl₃
NS: 10
DS: 4
SWH: 12000 Hz
FIDRES: 0.00011 Hz
AQ: 0.180000 sec
RG: 327.680
DNY: 0.000000 sec
DE: 0.000000 sec
TE: 300.2 K
D1: 1.0000000 sec
=====

NAME: LRB 17681-74-6
EXPNO: 1
PROCNO: 1
F2 - Processing parameters
SI: 32768
SF: 600.1320100 MHz
WDW: EM
SSB: 0
LB: 0.300 Hz
GB: 0
PC: 1.00

Compound 58m: 600 MHz ¹H NMR

LRB 17631-74-7, CDCl₃, terset = 298

Compound 58o: HETCOR

Compound 58o: HMBC

Single-Crystal X-ray Analysis of 20-*p*-tolyl-5,14-dioxo-19-azatricyclo[16.3.1.0^{7,12}]docosa-1(21),7,9,11,18(22),19-hexaene (7m). Crystals of C₂₆H₂₉NO₂ (MW = 387.50 Da, colorless parallelepipeds), which had been recrystallized from chloroform are, at $-80 \pm 2^\circ\text{C}$, triclinic, space group P1 - C (No. 2) with $a = 5.359(1) \text{ \AA}$, $b = 9.927(1) \text{ \AA}$, $c = 20.085(2) \text{ \AA}$, $\alpha = 90.084(2)^\circ$, $\beta = 96.144(2)^\circ$, $\gamma = 94.173(2)^\circ$, $V = 1059.5(2) \text{ \AA}^3$ and $Z = 2$ molecules $\{d_{\text{calcd}} = 1.215 \text{ g cm}^{-3}$; $\mu_a(\text{MoK}) = 0.076 \text{ mm}^{-1}\}$. A full hemisphere of diffracted intensities (omega scan width of 0.29°) was measured using graphite-monochromated MoK α radiation on a Bruker SMART CCD Single Crystal Diffraction System. X-rays were provided by a normal-focus sealed x-ray tube operated at 50kV and 40mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 1739 reflections. A total of 6959 integrated reflection intensities having $2\theta(\text{MoK}) < 57.32^\circ$ were produced using the Bruker program SAINT. A total of 4893 of these were independent and gave $R_{\text{int}} = 0.033$. The Bruker SHELXTL-PC software package was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL-PC Version 5 software package. Final agreement factors at convergence are: $R_1(\text{unweighted, based on } F) = 0.045$ for 2479 independent reflections having $2\theta(\text{MoK}) < 57.32^\circ$ and $I > 2\sigma(I)$; $R_1(\text{unweighted, based on } F) = 0.113$ and $wR_2(\text{weighted, based on } F^2) = 0.100$ for all 4893 independent reflections having $2\theta(\text{MoK}) < 57.32^\circ$.

The structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Each hydrogen atom was located from a difference Fourier synthesis and refined as an independent isotropic atom.

Table 1. Atomic Coordinates for Nonhydrogen Atoms in Crystalline 20-(*p*-Tolyl)-5,14-dioxa-19-azatricyclo[16.3.1.0^{7,12}]docosa-1(21),7,9,11,18(22),19-hexaene, C₂₆H₂₉NO₂ (**7m**)^a

Atom Type ^b	Fractional Coordinates			Equivalent Isotropic Thermal Parameter, U, Å ² x 10 ³ ^c
	10 ⁴ x	10 ⁴ y	10 ⁴ z	
C ₁	2862(3)	3763(2)	1997(1)	36(1)
C ₂	2252(4)	3900(2)	1248(1)	42(1)
C ₃	-316(4)	3228(2)	975(1)	44(1)
C ₄	-768(3)	1803(2)	1213(1)	42(1)
O ₅	1141(2)	989(1)	1028(1)	41(1)
C ₆	1216(4)	-180(2)	1434(1)	46(1)
C ₇	3080(3)	-1121(2)	1230(1)	39(1)
C ₈	3704(4)	-1164(2)	580(1)	47(1)
C ₉	5403(4)	-2044(2)	395(1)	52(1)
C ₁₀	6479(4)	-2907(2)	856(1)	52(1)
C ₁₁	5859(4)	-2880(2)	1510(1)	49(1)
C ₁₂	4188(3)	-1988(2)	1706(1)	40(1)
C ₁₃	3607(4)	-1936(2)	2423(1)	48(1)
O ₁₄	5047(2)	-785(1)	2742(1)	44(1)
C ₁₅	3994(4)	-285(2)	3308(1)	45(1)
C ₁₆	5943(4)	693(2)	3683(1)	46(1)
C ₁₇	7003(4)	1815(2)	3248(1)	42(1)
C ₁₈	5109(3)	2747(2)	2951(1)	35(1)
N ₁₉	4046(3)	3540(1)	3379(1)	40(1)
C ₂₀	2421(3)	4440(2)	3121(1)	33(1)
C ₂₁	1832(3)	4564(2)	2442(1)	32(1)
C ₂₂	4497(3)	2839(2)	2266(1)	37(1)
C ₂₃	1379(3)	5327(2)	3605(1)	32(1)
C ₂₄	-759(3)	6000(2)	3428(1)	42(1)
C ₂₅	-1674(4)	6855(2)	3875(1)	43(1)
C ₂₆	-494(3)	7065(2)	4518(1)	36(1)
C ₂₇	1635(3)	6383(2)	4697(1)	43(1)
C ₂₈	2570(3)	5535(2)	4252(1)	41(1)
C ₂₉	-1523(5)	7966(2)	5008(1)	49(1)

- ^a The numbers in parentheses are the estimated standard deviations in the last significant digit.
^b Atoms are labeled in agreement with Figure 3.
^c This is one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Atomic Coordinates for Hydrogen Atoms in Crystalline **7m**^{a,b}

Atom Type ^c	10 ⁴ x	Fractional Coordinates 10 ⁴ y	10 ⁴ z	Isotropic Thermal Parameter, U, Å ² x 10 ³
H _{2a}	2280(30)	4876(17)	1118(8)	53(5)
H _{2b}	3590(30)	3469(14)	1020(7)	35(4)
H _{3a}	-1670(30)	3751(16)	1136(8)	55(5)
H _{3b}	-450(30)	3241(15)	475(9)	57(5)
H _{4a}	-2430(30)	1395(14)	1013(7)	36(4)
H _{4b}	-690(30)	1806(14)	1719(8)	37(4)
H _{6a}	1680(30)	132(17)	1954(9)	69(6)
H _{6b}	-470(30)	-686(17)	1388(8)	63(6)
H ₈	2910(30)	-569(16)	256(8)	55(5)
H ₉	5880(30)	-2056(18)	-75(10)	73(6)
H ₁₀	7700(30)	-3535(17)	709(8)	62(6)
H ₁₁	6540(30)	-3473(17)	1834(9)	57(6)
H _{13a}	1720(30)	-1814(15)	2479(8)	50(5)
H _{13b}	4130(30)	-2776(16)	2665(8)	55(5)
H _{15a}	3510(30)	-1075(16)	3595(8)	52(5)
H _{15b}	2480(30)	158(15)	3152(7)	37(5)
H _{16a}	7380(30)	170(15)	3885(7)	43(5)
H _{16b}	5180(30)	1087(15)	4068(8)	51(5)
H _{17a}	7790(30)	1385(14)	2891(7)	33(4)
H _{17b}	8360(30)	2363(16)	3539(9)	64(6)
H ₂₁	830(30)	5149(16)	2287(8)	47(5)
H ₂₂	5230(30)	2265(13)	1998(7)	28(4)
H ₂₄	-1680(30)	5864(14)	2987(8)	43(5)
H ₂₅	-3160(30)	7310(16)	3728(8)	51(5)
H ₂₇	2460(30)	6496(14)	5151(8)	44(5)
H ₂₈	4120(30)	5070(16)	4390(8)	49(5)
H _{29a}	-3040(40)	8331(18)	4835(9)	64(6)
H _{29b}	-340(40)	8770(20)	5146(10)	96(7)
H _{29c}	-1830(40)	7540(20)	5404(11)	95(8)

^a All hydrogen atoms were located from a difference Fourier map and refined as independent isotropic atoms.

^b The numbers in parentheses are the estimated standard deviations in the last significant digit.

^c Hydrogen atoms are labeled with the same numerical subscript(s) as the carbon atom to which they are covalently bonded; they also have an additional literal subscript (a, b or c) where necessary to distinguish between hydrogens bonded to the same carbon atom.

Table 3. Bond Lengths in Crystalline **7m**^a

Type ^b	Length, Å	Type ^b	Length, Å
C ₄ -O ₅	1.427(2)	C ₁ -C ₂₁	1.379(2)
O ₅ -C ₆	1.420(2)	C ₁ -C ₂₂	1.385(2)
C ₁₃ -O ₁₄	1.440(2)	C ₇ -C ₈	1.383(2)
O ₁₄ -C ₁₅	1.427(2)	C ₇ -C ₁₂	1.400(2)
		C ₈ -C ₉	1.384(2)
C ₁₈ -N ₁₉	1.361(2)	C ₉ -C ₁₀	1.373(3)
N ₁₉ -C ₂₀	1.357(2)	C ₁₀ -C ₁₁	1.389(3)
		C ₁₁ -C ₁₂	1.390(2)
C ₁ -C ₂	1.514(2)	C ₁₈ -C ₂₂	1.385(2)
C ₂ -C ₃	1.532(2)	C ₂₀ -C ₂₁	1.375(2)
C ₃ -C ₄	1.505(2)	C ₂₃ -C ₂₄	1.382(2)
C ₆ -C ₇	1.503(2)	C ₂₃ -C ₂₈	1.394(2)
C ₁₂ -C ₁₃	1.508(2)	C ₂₄ -C ₂₅	1.386(2)
C ₁₅ -C ₁₆	1.510(2)	C ₂₅ -C ₂₆	1.384(2)
C ₁₆ -C ₁₇	1.530(2)	C ₂₆ -C ₂₇	1.384(2)
C ₁₇ -C ₁₈	1.500(2)	C ₂₇ -C ₂₈	1.384(2)
C ₂₀ -C ₂₃	1.489(2)		
C ₂₆ -C ₂₉	1.502(2)	C ₁₅ -H _{15a}	1.01(2)
		C ₁₅ -H _{15b}	0.98(2)
C ₂ -H _{2a}	1.00(2)	C ₁₆ -H _{16a}	1.01(2)
C ₂ -H _{2b}	1.01(2)	C ₁₆ -H _{16b}	1.01(2)
C ₃ -H _{3a}	1.00(2)	C ₁₇ -H _{17a}	0.98(1)
C ₃ -H _{3b}	1.00(2)	C ₁₇ -H _{17b}	1.01(2)
C ₄ -H _{4a}	1.00(2)	C ₂₁ -H ₂₁	0.86(2)
C ₄ -H _{4b}	1.01(2)	C ₂₂ -H ₂₂	0.92(1)
C ₆ -H _{6a}	1.09(2)	C ₂₄ -H ₂₄	0.97(2)
C ₆ -H _{6b}	1.00(2)	C ₂₅ -H ₂₅	0.97(2)
C ₈ -H ₈	0.97(2)	C ₂₇ -H ₂₇	0.97(2)
C ₉ -H ₉	1.01(2)	C ₂₈ -H ₂₈	0.99(2)
C ₁₀ -H ₁₀	1.00(2)	C ₂₉ -H _{29a}	0.95(2)
C ₁₁ -H ₁₁	0.94(2)	C ₂₉ -H _{29b}	1.01(2)
C ₁₃ -H _{13a}	1.05(2)	C ₂₉ -H _{29c}	0.93(2)
C ₁₃ -H _{13b}	1.01(2)		

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.

^b Atoms are labeled in agreement with Figure 3.

Table 4. Bond Angles in Crystalline **7m**^a

Type ^b	Angle, (deg)	Type ^b	Angle, (deg)
C ₂₁ C ₁ C ₂	121.4(2)	N ₁₉ C ₁₈ C ₁₇	117.6(2)
C ₂₂ C ₁ C ₂	121.5(2)	C ₂₂ C ₁₈ C ₁₇	122.0(2)
C ₂₁ C ₁ C ₂₂	117.2(2)	N ₁₉ C ₁₈ C ₂₂	120.4(2)
C ₁ C ₂ C ₃	113.9(2)	C ₁₈ C ₁₇ C ₁₆	114.8(2)
C ₁ C ₂ H _{2a}	110.8(9)	C ₁₆ C ₁₇ H _{17a}	107.7(8)
C ₃ C ₂ H _{2a}	107.5(9)	C ₁₆ C ₁₇ H _{17b}	107.3(10)
C ₁ C ₂ H _{2b}	108.2(8)	C ₁₈ C ₁₇ H _{17a}	110.1(8)
C ₃ C ₂ H _{2b}	108.2(8)	C ₁₈ C ₁₇ H _{17b}	108.6(9)
H _{2a} C ₂ H _{2b}	108.0(12)	H _{17a} C ₁₇ H _{17b}	108.1(13)
C ₄ C ₃ C ₂	113.4(2)	C ₁₅ C ₁₆ C ₁₇	114.2(2)
C ₂ C ₃ H _{3a}	108.9(9)	C ₁₅ C ₁₆ H _{16a}	108.5(9)
C ₂ C ₃ H _{3b}	108.6(10)	C ₁₅ C ₁₆ H _{16b}	108.4(9)
C ₄ C ₃ H _{3a}	106.3(9)	C ₁₇ C ₁₆ H _{16a}	108.4(9)
C ₄ C ₃ H _{3b}	110.0(9)	C ₁₇ C ₁₆ H _{16b}	110.6(9)
H _{3a} C ₃ H _{3b}	109.6(13)	H _{16a} C ₁₆ H _{16b}	106.5(12)
O ₅ C ₄ C ₃	110.3(2)	O ₁₄ C ₁₃ C ₁₂	107.8(1)
O ₅ C ₄ H _{4a}	108.5(8)	O ₁₄ C ₁₃ H _{13a}	106.8(9)
O ₅ C ₄ H _{4b}	107.9(8)	O ₁₄ C ₁₃ H _{13b}	108.5(9)
C ₃ C ₄ H _{4a}	110.8(8)	C ₁₂ C ₁₃ H _{13a}	114.3(9)
C ₃ C ₄ H _{4b}	109.3(8)	C ₁₂ C ₁₃ H _{13b}	110.1(9)
H _{4a} C ₄ H _{4b}	110.0(12)	H _{13a} C ₁₃ H _{13b}	109.2(13)
C ₆ O ₅ C ₄	109.5(1)	C ₁₅ O ₁₄ C ₁₃	113.6(1)
O ₅ C ₆ C ₇	111.8(2)	O ₁₄ C ₁₅ C ₁₆	108.0(2)
O ₅ C ₆ H _{6a}	108.8(9)	O ₁₄ C ₁₅ H _{15a}	108.6(9)
O ₅ C ₆ H _{6b}	109.7(10)	O ₁₄ C ₁₅ H _{15b}	108.7(9)
C ₇ C ₆ H _{6a}	110.5(9)	C ₁₆ C ₁₅ H _{15a}	111.8(9)
C ₇ C ₆ H _{6b}	107.6(10)	C ₁₆ C ₁₅ H _{15b}	111.2(9)
H _{6a} C ₆ H _{6b}	108.4(13)	H _{15a} C ₁₅ H _{15b}	108.4(13)
C ₈ C ₇ C ₆	121.5(2)	C ₁₁ C ₁₂ C ₁₃	120.5(2)
C ₁₂ C ₇ C ₆	119.4(2)	C ₇ C ₁₂ C ₁₃	120.4(2)
C ₈ C ₇ C ₁₂	119.1(2)	C ₁₁ C ₁₂ C ₇	119.1(2)
C ₇ C ₈ C ₉	121.1(2)	C ₁₀ C ₁₁ C ₁₂	121.2(2)
C ₇ C ₈ H ₈	118.2(10)	C ₁₀ C ₁₁ H ₁₁	121.1(11)
C ₉ C ₈ H ₈	120.7(10)	C ₁₂ C ₁₁ H ₁₁	117.7(10)
C ₁₀ C ₉ C ₈	120.2(2)	C ₉ C ₁₀ C ₁₁	119.3(2)
C ₈ C ₉ H ₉	120.8(10)	C ₉ C ₁₀ H ₁₀	118.6(10)
C ₁₀ C ₉ H ₉	119.0(10)	C ₁₁ C ₁₀ H ₁₀	122.1(10)
C ₂₀ N ₁₉ C ₁₈	118.8(1)	C ₂₃ C ₂₄ H ₂₄	120.4(9)
N ₁₉ C ₂₀ C ₂₁	121.6(2)	C ₂₅ C ₂₄ H ₂₄	118.3(9)
N ₁₉ C ₂₀ C ₂₃	117.1(1)	C ₂₆ C ₂₅ C ₂₄	121.4(2)

C ₂₁ C ₂₀ C ₂₃	121.3(2)	C ₂₄ C ₂₅ H ₂₅	118.5(9)
C ₂₀ C ₂₁ C ₁	120.8(2)	C ₂₆ C ₂₅ H ₂₅	120.1(9)
C ₁ C ₂₁ H ₂₁	118.7(11)	C ₂₇ C ₂₆ C ₂₅	117.3(2)
C ₂₀ C ₂₁ H ₂₁	120.4(11)	C ₂₅ C ₂₆ C ₂₉	121.4(2)
C ₁₈ C ₂₂ C ₁	121.2(2)	C ₂₇ C ₂₆ C ₂₉	121.3(2)
C ₁ C ₂₂ H ₂₂	121.6(9)	C ₂₆ C ₂₇ C ₂₈	121.6(2)
C ₁₈ C ₂₂ H ₂₂	117.2(9)	C ₂₆ C ₂₇ H ₂₇	118.4(9)
C ₂₄ C ₂₃ C ₂₀	121.7(2)	C ₂₈ C ₂₇ H ₂₇	120.0(9)
C ₂₈ C ₂₃ C ₂₀	120.9(2)	C ₂₇ C ₂₈ C ₂₃	120.9(2)
C ₂₄ C ₂₃ C ₂₈	117.5(2)	C ₂₃ C ₂₈ H ₂₈	119.0(9)
C ₂₃ C ₂₄ C ₂₅	121.3(2)	C ₂₇ C ₂₈ H ₂₈	120.1(9)
C ₂₆ C ₂₉ H _{29a}	113.4(11)	H _{29a} C ₂₉ H _{29b}	104.8(15)
C ₂₆ C ₂₉ H _{29b}	112.6(12)	H _{29a} C ₂₉ H _{29c}	106.9(18)
C ₂₆ C ₂₉ H _{29c}	113.2(13)	H _{29b} C ₂₉ H _{29c}	105.2(18)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.
^b Atoms are labeled in agreement with Figure 3.

Table 5. Torsion Angles in Crystalline **7m**^a

Type ^b	Angle, (deg)	Type ^b	Angle, (deg)
C ₂₁ -C ₁ -C ₂ -C ₃	-78.2(2)	C ₂₂ -C ₁₈ -N ₁₉ -C ₂₀	-1.3(2)
C ₂₂ -C ₁ -C ₂ -C ₃	102.5(2)	C ₁₇ -C ₁₈ -N ₁₉ -C ₂₀	176.8(1)
C ₁ -C ₂ -C ₃ -C ₄	-48.8(2)	C ₁₈ -N ₁₉ -C ₂₀ -C ₂₁	0.0(2)
C ₂ -C ₃ -C ₄ -O ₅	-58.1(2)	C ₁₈ -N ₁₉ -C ₂₀ -C ₂₃	-177.6(1)
C ₃ -C ₄ -O ₅ -C ₆	160.5(2)	N ₁₉ -C ₂₀ -C ₂₁ -C ₁	0.7(2)
C ₄ -O ₅ -C ₆ -C ₇	176.2(1)	C ₂₃ -C ₂₀ -C ₂₁ -C ₁	178.2(1)
O ₅ -C ₆ -C ₇ -C ₈	-27.5(2)	C ₂₂ -C ₁ -C ₂₁ -C ₂₀	0.0(2)
O ₅ -C ₆ -C ₇ -C ₁₂	153.4(2)	C ₂ -C ₁ -C ₂₁ -C ₂₀	-179.3(2)
C ₁₂ -C ₇ -C ₈ -C ₉	-0.2(3)	N ₁₉ -C ₁₈ -C ₂₂ -C ₁	2.1(2)
C ₆ -C ₇ -C ₈ -C ₉	-179.3(2)	C ₁₇ -C ₁₈ -C ₂₂ -C ₁	-176.0(2)
C ₇ -C ₈ -C ₉ -C ₁₀	0.9(3)	C ₂₁ -C ₁ -C ₂₂ -C ₁₈	-1.4(2)
C ₈ -C ₉ -C ₁₀ -C ₁₁	-0.5(3)	C ₂ -C ₁ -C ₂₂ -C ₁₈	178.0(2)
C ₉ -C ₁₀ -C ₁₁ -C ₁₂	-0.6(3)	N ₁₉ -C ₂₀ -C ₂₃ -C ₂₄	-161.9(2)
C ₁₀ -C ₁₁ -C ₁₂ -C ₇	1.2(3)	C ₂₁ -C ₂₀ -C ₂₃ -C ₂₄	20.5(2)
C ₁₀ -C ₁₁ -C ₁₂ -C ₁₃	-177.8(2)	N ₁₉ -C ₂₀ -C ₂₃ -C ₂₈	19.7(2)
C ₈ -C ₇ -C ₁₂ -C ₁₁	-0.8(2)	C ₂₁ -C ₂₀ -C ₂₃ -C ₂₈	-157.9(2)
C ₆ -C ₇ -C ₁₂ -C ₁₁	178.3(2)	C ₂₈ -C ₂₃ -C ₂₄ -C ₂₅	0.5(2)
C ₈ -C ₇ -C ₁₂ -C ₁₃	178.2(2)	C ₂₀ -C ₂₃ -C ₂₄ -C ₂₅	-178.0(2)
C ₆ -C ₇ -C ₁₂ -C ₁₃	-2.7(2)	C ₂₃ -C ₂₄ -C ₂₅ -C ₂₆	-0.5(3)
C ₁₁ -C ₁₂ -C ₁₃ -O ₁₄	101.0(2)	C ₂₄ -C ₂₅ -C ₂₆ -C ₂₇	-0.1(3)
C ₇ -C ₁₂ -C ₁₃ -O ₁₄	-77.9(2)	C ₂₄ -C ₂₅ -C ₂₆ -C ₂₉	-178.5(2)
C ₁₂ -C ₁₃ -O ₁₄ -C ₁₅	156.0(2)	C ₂₅ -C ₂₆ -C ₂₇ -C ₂₈	0.6(3)
C ₁₃ -O ₁₄ -C ₁₅ -C ₁₆	167.4(2)	C ₂₉ -C ₂₆ -C ₂₇ -C ₂₈	179.0(2)
O ₁₄ -C ₁₅ -C ₁₆ -C ₁₇	53.2(2)	C ₂₆ -C ₂₇ -C ₂₈ -C ₂₃	-0.6(3)
C ₁₅ -C ₁₆ -C ₁₇ -C ₁₈	63.1(2)	C ₂₄ -C ₂₃ -C ₂₈ -C ₂₇	0.0(2)
C ₁₆ -C ₁₇ -C ₁₈ -N ₁₉	65.6(2)	C ₂₀ -C ₂₃ -C ₂₈ -C ₂₇	178.6(2)
C ₁₆ -C ₁₇ -C ₁₈ -C ₂₂	-116.4(2)		

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.
^b Atoms are labeled in agreement with Figure 3.

Single-Crystal X-ray Analysis of 6,7,9,14,16,17-hexahydro-5,8,15,18-tetraoxa-dibenzo[a,h]cyclotetradecene-11,12-dicarboxylic Acid Dimethyl Ester (62). Crystals of $C_{22}H_{24}O_8$ (MW = 416.41 Da, colorless thin plates), which had been recrystallized from chloroform, are, at $-80 \pm 2^\circ\text{C}$, orthorhombic, space group $Pbca - D$ (No. 61) with $a = 16.419(2) \text{ \AA}$, $b = 8.213(1) \text{ \AA}$, $c = 29.691(3) \text{ \AA}$, $V = 4003.7(8) \text{ \AA}^3$ and $Z = 8$ molecules $\{d_{\text{calcd}} = 1.382 \text{ gcm}^{-3}; \mu_a(\text{MoK}) = 0.105 \text{ mm}^{-1}\}$. A full hemisphere of diffracted intensities (1868 10-s frames with omega scan width of 0.30°) was measured using graphite-monochromated $\text{MoK}\alpha$ radiation on a Bruker SMART APEX CCD Single Crystal Diffraction System. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 35mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 3809 reflections. A total of 33343 integrated reflection intensities having $2\theta(\text{MoK}) < 55.00^\circ$ were produced using the Bruker program SAINT. A total of 4587 of these were independent and gave $R_{\text{int}} = 0.110$. The Bruker SHELXTL-PC software package was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL-PC Version 5 software package. Final agreement factors at convergence are: $R_1(\text{unweighted, based on } F) = 0.052$ for 2801 independent reflections having $2\theta(\text{MoK}) < 55.00^\circ$ and $I > 2\sigma(I)$; $R_1(\text{unweighted, based on } F) = 0.091$ and wR_2 (weighted, based on F^2) = 0.116 for all 4587 independent reflections having $2\theta(\text{MoK}) < 55.00^\circ$.

The structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The two methyl groups (C_{25} , C_{29} and their hydrogens) were included in the structural model as rigid groups (assuming idealized sp^3 -hybridization of the carbon atom and a C-H bond length of $0.98 \text{ \AA}$) which were allowed to rotate about their O-C bonds in least-squares refinement cycles. All additional hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 - or sp^3 -hybridization of the carbon atoms and C-H bond lengths of 0.95 - $0.99 \text{ \AA}$) "riding" on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at a value 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

Table 6. Atomic Coordinates for Nonhydrogen Atoms in Crystalline 6,7,9,14,16,17-Hexahydro-5,8,15,18-tetraoxadibenzo[a,h]cyclotetradecene-11,12-dicarboxylic Acid Dimethyl Ester, C₂₂H₂₄O₈ (**62**)^a

Atom Type ^b	Fractional Coordinates			Equivalent Isotropic Thermal Parameter, U, Å ² x 10 ³ ^c
	10 ⁴ x	10 ⁴ y	10 ⁴ z	
C ₁	4330(1)	-1218(3)	914(1)	44(1)
C ₂	3856(1)	-1916(2)	582(1)	47(1)
C ₃	3037(1)	-1614(3)	565(1)	48(1)
C ₄	2675(1)	-601(2)	883(1)	41(1)
O ₅	2853(1)	1096(2)	1549(1)	36(1)
C ₆	1998(1)	1064(2)	1641(1)	34(1)
C ₇	1883(1)	2039(2)	2061(1)	33(1)
O ₈	2275(1)	1205(1)	2424(1)	30(1)
C ₉	2530(1)	2272(2)	2774(1)	32(1)
C ₁₀	2686(1)	898(2)	3519(1)	30(1)
C ₁₁	3119(1)	33(2)	3843(1)	29(1)
C ₁₂	3930(1)	-364(2)	3758(1)	30(1)
C ₁₃	4280(1)	47(2)	3348(1)	30(1)
C ₁₄	4203(1)	1191(2)	2559(1)	32(1)
O ₁₅	4943(1)	314(2)	2515(1)	39(1)
C ₁₆	5414(1)	745(3)	2130(1)	39(1)
C ₁₇	5160(1)	-98(3)	1704(1)	41(1)
O ₁₈	4394(1)	577(2)	1570(1)	38(1)
C ₁₉	3144(1)	103(2)	1215(1)	33(1)
C ₂₀	3030(1)	1326(2)	3110(1)	28(1)
C ₂₁	3836(1)	856(2)	3016(1)	28(1)
C ₂₂	3984(1)	-197(2)	1229(1)	34(1)
C ₂₃	2737(1)	-399(2)	4281(1)	34(1)
O ₂₄	1954(1)	-752(2)	4231(1)	42(1)
C ₂₅	1493(1)	-1116(3)	4631(1)	48(1)
O ₂₆	3089(1)	-417(2)	4635(1)	61(1)
C ₂₇	4404(1)	-1395(2)	4083(1)	33(1)
O ₂₈	5052(1)	-622(2)	4244(1)	44(1)
C ₂₉	5541(1)	-1548(3)	4558(1)	51(1)
O ₃₀	4230(1)	-2765(2)	4173(1)	59(1)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.

^b Atoms are labeled in agreement with Figure 5.

^c This is one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7. Atomic Coordinates for Hydrogen Atoms in Crystalline **62**^a

Atom Type ^b	Fractional Coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
H ₁	4897	-1442	925
H ₂	4099	-2610	365
H ₃	2714	-2097	335
H ₄	2106	-396	872
H _{6a}	1809	-69	1686
H _{6b}	1689	1551	1389
H _{7a}	2123	3136	2024
H _{7b}	1295	2164	2126
H _{9a}	2048	2750	2925
H _{9b}	2859	3170	2646
H ₁₀	2138	1202	3580
H ₁₃	4833	-228	3292
H _{14a}	3818	854	2319
H _{14b}	4308	2372	2525
H _{16a}	5993	484	2190
H _{16b}	5375	1936	2083
H _{17a}	5572	77	1465
H _{17b}	5105	-1283	1756
H _{25a}	1026	-377	4652
H _{25b}	1841	-976	4897
H _{25c}	1299	-2244	4618
H _{29a}	5947	-832	4697
H _{29b}	5819	-2430	4397
H _{29c}	5190	-2010	4792

^a The two methyl groups (C₂₅, C₂₉ and their hydrogens) were included in the structural model as rigid groups (assuming idealized sp³- hybridization of the carbon atom and a C-H bond length of 0.98 Å) which were allowed to rotate about their O-C bonds in least-squares refinement cycles. All additional hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp²- or sp³-hybridization of the carbon atoms and C-H bond lengths of 0.95 -0.99 Å) "riding" on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at a value 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

^b Hydrogen atoms are labeled with the same numerical subscript(s) as the carbon atom to which they are covalently bonded; they also have an additional literal subscript (a, b or c) where necessary to distinguish between hydrogens bonded to the same carbon atom.

Table 8. Bond Lengths in Crystalline **62**^a

Type ^b	Length, Å	Type ^b	Length, Å
O ₅ -C ₁₉	1.369(2)	O ₁₈ -C ₂₂	1.371(2)
C ₂₃ -O ₂₄	1.327(2)	C ₂₇ -O ₂₈	1.328(2)
O ₅ -C ₆	1.429(2)	C ₁₇ -O ₁₈	1.431(2)
C ₇ -O ₈	1.428(2)	O ₁₅ -C ₁₆	1.427(2)
O ₈ -C ₉	1.422(2)	C ₁₄ -O ₁₅	1.418(2)
O ₂₄ -C ₂₅	1.441(2)	O ₂₈ -C ₂₉	1.448(2)
C ₂₃ -O ₂₆	1.200(2)	C ₂₇ -O ₃₀	1.191(2)
C ₁ -C ₂	1.380(3)	C ₃ -C ₄	1.392(3)
C ₁ -C ₂₂	1.378(3)	C ₄ -C ₁₉	1.378(3)
C ₂ -C ₃	1.368(3)	C ₁₁ -C ₁₂	1.395(2)
C ₁₉ -C ₂₂	1.402(3)	C ₂₀ -C ₂₁	1.406(2)
C ₁₂ -C ₁₃	1.387(3)	C ₁₀ -C ₁₁	1.392(2)
C ₁₃ -C ₂₁	1.396(2)	C ₁₀ -C ₂₀	1.385(2)
C ₆ -C ₇	1.494(2)	C ₁₆ -C ₁₇	1.501(3)
C ₉ -C ₂₀	1.507(2)	C ₁₄ -C ₂₁	1.510(2)
C ₁₁ -C ₂₃	1.488(3)	C ₁₂ -C ₂₇	1.502(2)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.
^b Atoms are labeled in agreement with Figure 5.

Table 9. Bond Angles in Crystalline **62**^a

Type ^b	Angle, (deg)	Type ^b	Angle, (deg)
C ₂ C ₃ C ₄	120.1(2)	C ₃ C ₂ C ₁	120.4(2)
C ₁₉ C ₄ C ₃	119.9(2)	C ₂₂ C ₁ C ₂	120.3(2)
C ₁₉ O ₅ C ₆	118.1(1)	C ₂₂ O ₁₈ C ₁₇	117.2(2)
C ₉ O ₈ C ₇	112.8(1)	C ₁₄ O ₁₅ C ₁₆	114.3(1)
O ₅ C ₆ C ₇	106.0(2)	O ₁₈ C ₁₇ C ₁₆	107.5(2)
O ₈ C ₇ C ₆	108.4(1)	O ₁₅ C ₁₆ C ₁₇	114.2(2)
O ₈ C ₉ C ₂₀	109.0(1)	O ₁₅ C ₁₄ C ₂₁	109.3(1)
C ₂₀ C ₁₀ C ₁₁	121.8(2)	C ₁₂ C ₁₃ C ₂₁	121.3(2)
C ₁₀ C ₁₁ C ₁₂	118.8(2)	C ₁₃ C ₁₂ C ₁₁	119.8(2)
C ₁₀ C ₁₁ C ₂₃	120.8(2)	C ₁₃ C ₁₂ C ₂₇	119.2(2)
C ₁₂ C ₁₁ C ₂₃	120.4(2)	C ₁₁ C ₁₂ C ₂₇	120.6(2)
O ₅ C ₁₉ C ₄	124.9(2)	O ₁₈ C ₂₂ C ₁	125.5(2)
O ₅ C ₁₉ C ₂₂	115.3(2)	O ₁₈ C ₂₂ C ₁₉	115.0(2)
C ₄ C ₁₉ C ₂₂	119.8(2)	C ₁ C ₂₂ C ₁₉	119.5(2)
C ₁₀ C ₂₀ C ₉	119.3(2)	C ₁₃ C ₂₁ C ₁₄	120.9(2)
C ₂₁ C ₂₀ C ₉	121.5(2)	C ₂₀ C ₂₁ C ₁₄	120.3(2)
C ₁₀ C ₂₀ C ₂₁	119.2(2)	C ₁₃ C ₂₁ C ₂₀	118.9(2)
O ₂₆ C ₂₃ O ₂₄	124.3(2)	O ₃₀ C ₂₇ O ₂₈	124.3(2)
O ₂₄ C ₂₃ C ₁₁	111.2(2)	O ₂₈ C ₂₇ C ₁₂	112.1(2)
O ₂₆ C ₂₃ C ₁₁	124.5(2)	O ₃₀ C ₂₇ C ₁₂	123.6(2)
C ₂₃ O ₂₄ C ₂₅	117.4(2)	C ₂₇ O ₂₈ C ₂₉	115.1(2)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.

^b Atoms are labeled in agreement with Figure 5.

Table 10. Torsion Angles in Crystalline **62**^a

Type ^b	Angle, (deg)	Type ^b	Angle, (deg)
C ₂₂ -C ₁ -C ₂ -C ₃	-0.6(3)	C ₁₂ -C ₁₃ -C ₂₁ -C ₁₄	-175.6(2)
C ₁ -C ₂ -C ₃ -C ₄	-0.1(3)	C ₁₀ -C ₂₀ -C ₂₁ -C ₁₃	-3.5(2)
C ₂ -C ₃ -C ₄ -C ₁₉	0.3(3)	C ₉ -C ₂₀ -C ₂₁ -C ₁₃	177.1(2)
C ₁₉ -O ₅ -C ₆ -C ₇	171.0(1)	C ₁₀ -C ₂₀ -C ₂₁ -C ₁₄	175.2(2)
O ₅ -C ₆ -C ₇ -O ₈	-65.7(2)	C ₉ -C ₂₀ -C ₂₁ -C ₁₄	-4.3(2)
C ₆ -C ₇ -O ₈ -C ₉	153.1(2)	O ₁₅ -C ₁₄ -C ₂₁ -C ₁₃	10.8(2)
C ₇ -O ₈ -C ₉ -C ₂₀	-172.6(1)	O ₁₅ -C ₁₄ -C ₂₁ -C ₂₀	-167.8(2)
C ₂₀ -C ₁₀ -C ₁₁ -C ₁₂	2.1(3)	C ₁₇ -O ₁₈ -C ₂₂ -C ₁	-21.4(3)
C ₂₀ -C ₁₀ -C ₁₁ -C ₂₃	179.5(2)	C ₁₇ -O ₁₈ -C ₂₂ -C ₁₉	158.1(2)
C ₁₀ -C ₁₁ -C ₁₂ -C ₁₃	-2.6(2)	C ₂ -C ₁ -C ₂₂ -O ₁₈	-179.3(2)
C ₂₃ -C ₁₁ -C ₁₂ -C ₁₃	-179.9(2)	C ₂ -C ₁ -C ₂₂ -C ₁₉	1.2(3)
C ₁₀ -C ₁₁ -C ₁₂ -C ₂₇	-175.7(2)	O ₅ -C ₁₉ -C ₂₂ -O ₁₈	-1.3(2)
C ₂₃ -C ₁₁ -C ₁₂ -C ₂₇	7.0(2)	C ₄ -C ₁₉ -C ₂₂ -O ₁₈	179.4(2)
C ₁₁ -C ₁₂ -C ₁₃ -C ₂₁	0.0(3)	O ₅ -C ₁₉ -C ₂₂ -C ₁	178.3(2)
C ₂₇ -C ₁₂ -C ₁₃ -C ₂₁	173.2(2)	C ₄ -C ₁₉ -C ₂₂ -C ₁	-1.1(3)
C ₂₁ -C ₁₄ -O ₁₅ -C ₁₆	-169.9(1)	C ₁₀ -C ₁₁ -C ₂₃ -O ₂₆	-143.5(2)
C ₁₄ -O ₁₅ -C ₁₆ -C ₁₇	-83.3(2)	C ₁₂ -C ₁₁ -C ₂₃ -O ₂₆	33.8(3)
O ₁₅ -C ₁₆ -C ₁₇ -O ₁₈	71.2(2)	C ₁₀ -C ₁₁ -C ₂₃ -O ₂₄	36.1(2)
C ₁₆ -C ₁₇ -O ₁₈ -C ₂₂	-169.7(1)	C ₁₂ -C ₁₁ -C ₂₃ -O ₂₄	-146.6(2)
C ₆ -O ₅ -C ₁₉ -C ₄	18.0(3)	O ₂₆ -C ₂₃ -O ₂₄ -C ₂₅	2.6(3)
C ₆ -O ₅ -C ₁₉ -C ₂₂	-161.3(2)	C ₁₁ -C ₂₃ -O ₂₄ -C ₂₅	-177.0(2)
C ₃ -C ₄ -C ₁₉ -O ₅	-179.0(2)	C ₁₃ -C ₁₂ -C ₂₇ -O ₃₀	-110.6(2)
C ₃ -C ₄ -C ₁₉ -C ₂₂	0.4(3)	C ₁₁ -C ₁₂ -C ₂₇ -O ₃₀	62.5(3)
C ₁₁ -C ₁₀ -C ₂₀ -C ₂₁	0.9(3)	C ₁₃ -C ₁₂ -C ₂₇ -O ₂₈	67.0(2)
C ₁₁ -C ₁₀ -C ₂₀ -C ₉	-179.6(2)	C ₁₁ -C ₁₂ -C ₂₇ -O ₂₈	-119.8(2)
O ₈ -C ₉ -C ₂₀ -C ₁₀	-104.4(2)	O ₃₀ -C ₂₇ -O ₂₈ -C ₂₉	-2.0(3)
O ₈ -C ₉ -C ₂₀ -C ₂₁	75.1(2)	C ₁₂ -C ₂₇ -O ₂₈ -C ₂₉	-179.6(2)
C ₁₂ -C ₁₃ -C ₂₁ -C ₂₀	3.0(2)		

^a The numbers in parentheses are the estimated standard deviations in the last significant digit.
^b Atoms are labeled in agreement with Figure 5.