Macrocycle Ring Expansion by Double Stevens Rearrangement

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SUPPORTING INFORMATION

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General Experimental

Reactions were conducted under argon atmosphere unless otherwise noted. Benzene was distilled from CaH_2 immediately prior to use. Xylene (mixture of isomers) was distilled from CaH_2 and stored over 4 Å molecular sieves. GC mass spectra were obtained on a benchtop HP gc/mass spectrometer. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ or acetone-d_6 at the indicated frequency. ^{1}H NMR spectra were referenced at 0 ppm on the TMS signal and ^{13}C NMR spectra were referenced at 77.0 ppm for $CDCl_3$. Spectra in acetone-d_6 were referenced at the residual acetone signal which was at 2.04 ppm and 206.0 ppm for ^{1}H and ^{13}C NMR, respectively. Ethyl diazomalonate,[1] 1,3-bis(methoxy)-2-imidazolidinone,[2] 1,3-bis(methoxy)-2-benzimidazolidinone[3] and dithiols were synthesized by literature methods.

[1] Regitz, M.; Liedhegener, A., *Chem. Berichte* **1966,** *99*, 3128-4.
[2] Petersen, H.; Reuther, W. *Liebigs Ann.* **1972***, 766,* 58.
[3] Zinner, H.; Spangenberg, B. *Liebigs Ann.* **1958***, 91,* 1432.

4, 11-Dithiabenzimidazolophane 2A

A 1 L 2-necked rb flask equipped with a reflux condensor, magnetic stir bar and an addition funnel was charged with 12 g (36 mmol) of 3,10-dithia-benzimidazolophane **1A**,[4] 790 mg (1.8 mmol) of $Rh_2(OAc)_4$ and 350 mL xylenes and brought to reflux under an argon atmosphere. The addition funnel was loaded with 14 g (76 mmol) of diethyl-diazomalonate in 50 mL xylenes and this was added over a period of 1.5 h to the h. After addition was complete, refluxing was continued for another 2h at which time TLC indicated full consumption of starting materials. Solvents were removed *in vacuo* and the crude mass was loaded onto a silica gel column. The product was eluted with 25%/25%/50% v/v/v ethyl acetate-chloroform-hexanes to give 12 g **2A** (51%) as a white solid. Crystals of **2A** were obtained by slow evaporation from CH_2Cl_2 and diethyl ether, mp 160°C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) 7.22 – 7.18 (m, 6H), 6.06 (br s, 2H), 4.85 (br d, *J* = 76 Hz, 4H), 4.44 – 4.30 (m, 8H), 3.72 (d, *J* = 15.5 Hz, 2H), 3.01 (br d, *J* = 15 Hz, 2H), 1.39 – 1.34 (m, 12H). ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) 169.4, 167.5, 151.6, 132.63, 129.2 (broad signal), 128.9 121.6 (CH), 108.2 (CH), 63.0 (CH2), 62.9 (CH2), 42.7, 39.2 (broad signal), 14.0 (CH3), 13.9 (CH3). FT-IR (thin film, cm^{-1}) 2982, 2936, 1725, 1619, 1517, 1494, 1424, 1388, 1367, 1245, 1201, 1157, 1095, 1027, 860, 816. High resolution MS (EI, *m/z*): anal calcd for $C_{31}H_{36}N_2S_2O_9$: 644.1862; found: 644.1817, error: 7 ppm. Elemental analysis, calculated: C, 57.8; H, 5.6; N, 4.3%; found: C, 57.7; H, 5.6; N, 4.3%.

Crystals of **2A** were subjected to x-ray analysis. See attached cif file.

4, 11-Dithiabenzimidazolophane 2B

A 50 mL Schlenk flask equipped with a coldfinger condenser, magnetic stir bar and a rubber septum was charged with 70 mg (0.2 mmol) dithiabenzimidazolophane **1B**,[4] 2.2 mg (0.005 mmol) of $Rh_2(OAc)_4$ and 2 mL xylenes and brought to reflux under an argon atmosphere. Diethyl diazomalonate (112 mg, 0.6 mmol) was dissolved in 2 mL xylenes and this solution was added over a period of 1.5 h to the reaction mixture. After addition was complete, reflux was continued for another 2 h at which point TLC indicated full consumption of starting materials. Solvents were removed *in vacuo* and the crude mass was loaded onto a silica gel column (1 cm x 4 cm). The product was eluted with 1:3 ethyl acetate:hexanes to give 78 mg of a colorless oil which yielded 56 mg **2B** (42%) as a white solid upon trituration with diethyl ether from a dichloromethane solution, mp 179-180°C. Analytical TLC (20% ethyl acetate/hexanes) R_f 0.25. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm) δ 7.18 – 7.15 (m, 2H), 7.10 – 7.06 (m, 2H), 6.94 – 6.94 (br m, 2H), 6.74 (br s, 1H), 5.00 (br d, *J* = 15.5 Hz, 2H), 4.82 (br s, 1H), 4.69 (d, *J* = 15.5 Hz, 1H), 4.46 – 4.27 (m, 8H), 3.59 (br d, *J* = 14 Hz, 1H), 3.49 – 3.45 (m, 2H), 3.11 (br d, *J* = 17 Hz, 1H), 2.35 (s, 3H), 1.38 – 1.33 (m, 12H), 1.26 – 1.19 (m, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) 169.4, 169.1, 168.3, 168.2, 135.1, 133.5, 131.9, 130.8, 130.0, 128.9, 128.5, 121.4(3), 121.4(0), 108.4, 108.1, 62.8, 62.7, 41.8, 35.7, 34.9, 31.5, 22.6, 20.2, 17.6, 14.1, 14.0, 13.9(2), 13.9(1), 13.8. FT-IR (thin film, cm^{-1}) 2977, 2934, 1728, 1618,

[4] Ellis, K. K.; Wilke, B.; Zhang, Y.; Diver, S. T. *Org. Lett.* **2000**, *2*, 3785-3788.

1489, 1426, 1387, 1242, 1156, 1097, 1027, 858, 753. High resolution MS (EI, *m/z*): anal calcd for $C_{33}H_{40}N_2S_2O_9$: 672.2177; found: 673.2248 ($M+H^+$), error: 1.6 ppm.

[3.3] Benzimidazolophane 3A

Dithiacyclophane **2A** (4.5 g, 7 mmol) was dissolved in 200 mL $(EtO)_3P$ by heating to 60 °C for about 10 min and was then transferred to an immersion well reactor, equipped with a medium pressure Hg lamp (Hanovia) in a pyrex water-jacketed cold finger. The solution was sparged with argon during UV irradiation. Irradiation was conducted for 2 h at which time, TLC showed full conversion of the starting material. The solvent was removed *in vacuo* in a fume hood and the residue was rinsed with ice cold diethyl ether yielding 1.89 g (46%) of **3A** as a white solid. This was rinsed several times with more diethyl ether and observed to be pure by NMR. Crystals were grown by slow evaporation from CH_2Cl_2 and diethyl ether, mp 141-143 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.23 (s, 2H), 7.01-6.93 (m, 4H), 6.44 (s, 2H), 4.82 (d, *J* =15 Hz, 2H), 4.44-4.31 (m, 8H), 4.13 (d, *J* = 15 Hz, 2H), 3.48 (d, *J* = 15 Hz, 2H), 3.36 (d, *J* = 15 Hz, 2H), 1.39-1.32 (m, 12H). ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ 171.9, 170.3, 152.5, 133.4 (CH), 130.1 (CH), 129.5, 127.6, 120.9 (CH), 108.2 (CH), 62.4 (CH_2), 62.2 (CH_2), 57.5, 43.1 (CH_2), 38.4 (CH_2), 13.9 (CH_3), 13.8 (CH_3). FT-IR (thin film, cm^{-1}) 2978, 2359, 1731, 1495, 1440, 1365, 1300, 1236, 1114, 1095, 1081, 860, 772. High resolution MS (EI, *m/z*): anal calcd for $C_{31}H_{36}N_2O_9$: 580.2445; found: 580.2420; error: 4.3 ppm. Elemental analysis, calculated: C, 64.1; H, 6.3; N, 4.8%; found, C, 63.9; H, 6.3; N, 4.8%.

Crystals of **3A** were subjected to x-ray analysis. See attached cif file.

[3.3] Benzimidazolophane 3B

Dithiacyclophane **2B** (50 mg, 0.07 mmol) was dissolved in 5 mL $(EtO)_3P$ by heating to 60 °C for about 10 min and was then transferred to a quartz photolysis tube with a constant sparge of argon. A medium pressure Hg lamp (Hanovia) in a pyrex water-jacketed cold finger was employed for side-on photolysis. Irradiation was conducted for 3 h, at which time full conversion of starting material was observed (TLC). The solvent was removed *in vacuo* in a fume hood and the residue was rinsed with cold diethyl ether yielding 14 mg (31%) of **3B** as a white solid, mp 130 -131 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) 7.08 – 7.06 (m, 1H), 6.98 – 6.94 (m, 2H), 6.89 (s, 1H), 6.86 – 6.84 (m, 1H), 6.75 (s, 1H), 5.12 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 4.60 – 4.53 (m, 1H), 4.54 – 4.23 (m, 8H), 4.14 – 4.06 (m, 2H), 3.85 (d, *J* = 15.5, 1H), 3.61 (d, *J* = 16.5, 1H), 3.22 – 3.12 (m, 2H), 2.35 (s, 3H), 1.44 – 1.31 (m, 12H), 1.27 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) 172.5, 171.9, 171.2, 170.4, 153.4, 135.5, 132.9, 132.4, 131.1, 130.2, 129.7, 129.4, 120.9, 120.8, 108.6, 108.2, 62.6, 62.4(3), 62.4(0), 62.2, 58.0, 57.8, 43.9, 42.2, 32.9, 32.5, 20.3, 17.7, 14.0(4), 14.0(1), 13.9. FT-IR (thin film, cm^{-1}) 2979, 2363, 2341, 1729, 1493, 1446, 1366, 1236, 1091, 1029, 859. High resolution MS (EI, *m/z*): anal calcd for $C_{33}H_{40}N_2O_9$: 608.2735; found: 631.2623 ($M+Na^+$); error: 0.5 ppm.

3,9-Dithiaimidazolidinophane 7A

A 500 mL rb flask equipped with a magnetic stirbar and rubber septum was charged with 150 mL methanol and 15 drops of H_2SO_4 and stirred at room temperature under an argon atmosphere. Two gas tight syringes (5 mL) with teflon-tipped plungers were individually loaded with solutions of 348 mg of 1,3-bis(methoxy)-2-imidazolidinone (2 mmol) and 340 mg of 1,3-benzenedimethanethiol (2 mmol) each in methanol (5 mL total volume), which were added over a period of 6 h via syringe pump. After the addition was complete, TLC indicated complete consumption of reactants. The contents were diluted with 100 mL of $CHCl_3$ and transferred into a 500 mL separatory funnel and washed with $NaHCO_3$ (2 x 100 mL portions), dried (K_2CO_3) and evaporated (rotary evaporator) to give a crude white solid. This was dissolved in a minimum of $CHCl_3$, evaporated onto 2 g flash-grade silica gel *in vacuo* (rotary evaporator), then loaded onto a silica gel column (4 cm x 15 cm) and eluted with 20 % ethyl acetate-hexanes to give 377 mg **7A** (67 %) as a white solid. Crystals of **7A** were obtained by slow evaporation from CH_2Cl_2, mp 159-161 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.34 – 7.30 (m, 1H), 7.23 – 7.22 (m, 2H), 7.15 (s, 1H), 5.44 (d, *J* = 15, 2H), 3.77 (d, *J* = 15 Hz, 2H), 3.75 – 3.66 (m, 4H), 2.80 – 2.78 (m, 2H), 2.67 – 2.64 (m, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ 157.5, 139.6, 129.1(CH), 128.0 (CH), 126.9 (CH), 47.9 (CH_2), 38.4 (CH_2), 37.1 (CH_2). COSY analysis showed coupling between protons with δ 7.23 – 7.22 and 3.75 – 3.66; 5.44 and 3.75 – 3.66. FT-IR (thin film, cm^{-1}) 1690, 1486, 1439, 1249, 1224, 715. High resolution MS (EI, *m/z*): anal calcd for $C_{13}H_{16}N_2S_2O$: 280.0701; found: 280.0699, error: 1.0 ppm.

3,9-Dithiaimidazolidinophane 7B

A 500 mL rb flask equipped with a magnetic stir bar and rubber septum was charged with 150 mL methanol and 15 drops of H_2SO_4 and stirred at room temperature under an argon atmosphere. A gas tight syringe (10 mL) with teflon-tipped plunger was loaded with a solution of 348 mg of 1,3-bis(methoxy)-2-imidazolidinone **6** (2 mmol) and 396 mg of 1,3 benzenedimethanethiol **5B** (2 mmol) in methylene chloride (10 mL total volume). This solution was added over a period of 6 h via syringe pump. After the addition was complete, TLC indicated complete consumption of reactants. The contents were diluted with 100 mL of $CHCl_3$ and transferred to a 500 mL separatory funnel and washed with $NaHCO_3$ (2 x 100 mL portions), dried (K_2CO_3), and concentrated (rotary evaporator) to give a crude white solid. This was dissolved in a minimum of $CHCl_3$, evaporated onto 2 g flash-grade silica gel in *vacuo* (rotary evaporator), then loaded onto a silica gel column (4 cm x 15 cm) and eluted with 20 % ethyl acetate-hexanes to give 290 mg **7B** (47%) as a white solid. Crystals of **7B** were obtained by slow evaporation from CH_2Cl_2, mp 234 – 236 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.26 (s, 1H), 7.03 (s, 1H), 6.94 (s, 1H), 5.51 (d, *J* = 12 Hz, 2H), 3.82 – 3.75 (m, 4H), 3.66 (d, *J* = 14.5 Hz, 2H), 2.82 – 2.69 (m, 4H), 2.31 (s, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ 157.8, 134.9, 134.3, 132.5 (CH), 129.2 (CH), 48.0 (CH_2), 38.4 (CH_2), 35.8 (CH_2), 18.6 (CH_3). COSY analysis indicates coupling between signals at δ 7.03 and 3.82 – 3.75; 7.03 and 2.31; 6.94 and 3.66; 6.94 and 2.31; 5.51 and 3.82 – 3.75; 5.51 and 3.66; 3.82 – 3.75 and 2.31. FT-IR

(thin film, cm^{-1}) 1686, 1488, 1435, 1247, 1227, 906. High resolution MS (EI, m/z): anal calcd for $C_{15}H_{20}N_2S_2O$: 308.1007; found: 308.1012, error: 1.4 ppm.

3,9-Dithia-benzimidazolophane 8A

Into an argon-flushed 50 mL rb flask equipped with magnetic stirbar and rubber septum was placed 44 mg 1,3-bis(methoxymethyl)-2-benzimidazolidinone (0.2 mmol), 34 mg 1,4-benzenedimethanethiol (0.2 mmol) in 10 mL CH_2Cl_2 at room temperature to which 0.1 mL BF_3-OEt_2 (0.113 g, 0.8 mmol) was added dropwise via syringe. The reactants were stirred for 4 h at room temperature at which time the reaction was complete (TLC). The reaction contents were poured into a separatory funnel containing 50 mL $NaHCO_3$, partitioned, and the aqueous layer was extracted three times with 20 mL portions of CH_2Cl_2. The pooled organics were dried (K_2CO_3) and concentrated to give 84 mg of a white foam which was purified by flash chromatography (1 cm x 12 cm) 1:4 ethyl acetates-hexanes (100 mL) then gradient elution to 1:1 ethyl acetate-hexanes) to afford 53 mg **8A** as a white solid (83 %). Crystallization from CH_2Cl_2 gave white crystals, mp 173 – 174 °C. Analytical TLC: (1:3 ethyl acetate-hexanes) R_f 0.45. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.08 (s, 1H), 6.86 (s, 4H), 6.72 (br d, *J* = 7.8 Hz, 2H), 6.60 – 6.54 (m, 1H), 5.75 (d, *J* = 14.4 Hz, 2H), 4.40 (d, *J* = 14.4 Hz, 2H), 3.77 – 3.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 153.6, 137.8, 128.0, 127.0, 126.7, 121.0, 109.8, 44.4, 37.2. FT-IR (thin film, cm^{-1}) 3060, 2916, 1703, 1611, 1492, 1422, 1393, 1291, 1159, 1034, 890. High resolution MS (EI, *m/z*): anal calcd for $C_{17}H_{16}N_2S_2O$: 328.0699; found: 328.0699; error: 0 ppm.

3,9-Dithia-benzimidazolophane 8B

Into an argon-flushed 50 mL rb flask equipped with magnetic stirbar and rubber septum was placed 44 mg (0.2 mmol) 1,3-bis(methoxymethyl)-2-benzimidazolidinone, 34 mg (0.2 mmol) 1,3 – bismercaptomethyl – 4, 6-dimethylbenzene[5] in 10 mL CH_2Cl_2 at room temperature to which 0.1 mL BF_3OEt_2 (0.113 g, 0.8 mmol) was added dropwise via syringe. The reactants were stirred for 4 h at room temperature at which time the reaction was complete (TLC). The reaction contents were poured into a separatory funnel containing 50 mL $NaHCO_3$, partitioned, and the aqueous layer was extracted three times with 20 mL portions of CH_2Cl_2. The pooled organics were dried (K_2CO_3) and concentrated to give a white foam which was purified by flash chromatography (1 cm x 12 cm, 1:4 ethyl acetate-hexanes (100 mL) then gradient elution to 1:1 ethyl acetate-hexanes) to afford 20 mg **8B** as a white solid (29 %). Crystallization from CH_2Cl_2 gave white crystals, mp 206 – 208 °C. Analytical TLC: (1:3 ethyl acetate-hexanes) R_f 0.45. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.00 – 6.97 (m, 3H), 6.90 – 6.88 (m, 2H), 6.33 (s, 1H), 5.91 (d, *J* = 14.5 Hz, 2H), 4.49 (d, *J* = 14.5 Hz, 2H), 3.80 (d, *J* = 15 Hz, 2H), 3.72 (d, *J* = 15 Hz, 2H), 2.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 153.7, 134.7, 132.6 (CH), 131.6, 128.0 (CH), 127.1, 120.8 (CH), 109.9, 44.3 (CH_2), 36.0 (CH_2), 18.3 (CH_3). FT-IR (thin film, cm^{-1}) 1701, 1559, 1492, 1425, 1394, 1286, 1034. High resolution MS (EI,

[5] Gerisch, M.; Krumper, J. R.; Bergman, R. G.; Tilley, T. D. *Organometallics* **2003**, *22*, 47-58.

m/z): anal calcd for $C_{19}H_{20}N_2S_2O$: 356.10126; found: 356.1012; error: 0.3 ppm.

[2.2] Benzimidazolophane 9A

Into an immersion well reactor was dissolved 1.3g crude **8A** in 200 mL of 2:3 v/v benzene-$P(OEt)_3$ which was equipped with a medium pressure Hg lamp (Hanovia) contained in a pyrex water-jacketed cold finger. The solution was continuously sparged with a stream of argon and was irradiated for 5 h. The solvents were removed *in vacuo* (high vacuum) and the crude was purified by flash chromatography (2.5 cm x 12 cm, 1:4 ethyl acetate-hexanes) affording 250 mg (25%) of **9A**. Crystals of **9A** were obtained by slow evaporation of CH_2Cl_2, mp 148 – 149 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.33 – 7.10 (m, 7H), 5.20 (s, 1H), 4.04 – 3.85 (m, 4H), 2.85 – 2.66 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 158.2, 138.5, 131.7, 131.4, 129.9, 126.6, 121.8, 109.9, 45.7, 33.8. FT-IR (thin film, cm^{-1}) 2942, 2360, 1718, 1486, 1439, 1372, 1345, 1298, 1142, 1013, 786, 749, 719. High resolution MS (E/I, *m/z*): anal calcd for $C_{17}H_{16}N_2O$: 264.1257; found: 264.1261; error: 1.6 ppm.

Crystals of **9A** were subjected to x-ray analysis. See attached cif file.

[2.2] Benzimidazolophane 9B

Into an immersion well reactor was dissolved 1.5 g **8B** in 250 mL of 2:3 v/v benzene-$P(OEt)_3$ which was equipped with a medium pressure Hg lamp (Hanovia) contained in a pyrex water-jacketed cold finger. The solution was continuously sparged with a stream of argon and was irradiated for 3 h. The volatiles were removed *in vacuo* (high vacuum) and the crude product was purified by flash chromatography (2.5 cm x 12 cm, 1:4 ethyl acetate-hexanes) affording 134 mg (11%) of **9B**. Crystals of **9B** were obtained by slow evaporation of CH_2Cl_2, mp 177 – 179 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.17 – 7.14 (m, 2H), 7.11 – 7.09 (m, 2H), 6.96 (s, 1H), 5.00 (s, 1H), 3.96 – 3.93 (m, 2H), 3.87 – 3.81 (m, 2H), 2.86 (d, J = 13.5 Hz, 2H), 2.58 – 2.52 (m, 2H), 2.306 (s, 6H). ^{13}C NMR (75.5MHz, $CDCl_3$, ppm) δ 158.3, 134.2, 134.0, 132.4 (CH), 132.2 (CH), 131.5, 121.6 (CH), 109.9 (CH), 44.4 (CH_2), 30.2 (CH_2), 18.4 (CH_3). FT-IR (thin film, cm^{-1}) 2940, 2868, 1719, 1487, 1446, 1374, 1341, 1152, 1013, 748. High resolution MS (E/I, m/z): anal calcd for $C_{19}H_{20}N_2O$: 292.1570; found: 292.1575; error: 1.7 ppm.

STANDARD PROTON PARAMETERS

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File: elliscyclophane
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Line broadening 0.7 Hz
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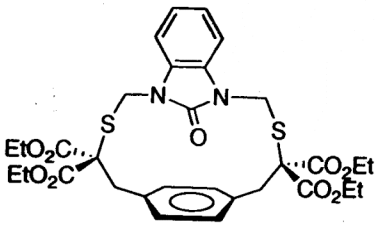
Total time 1 min, 18 sec



2A

KKE1180revC13ag 7/4/02

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INOVA-500 "nmrdata.chem.buffalo.edu"

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DECOUPLE H1, 499.9008902 MHz
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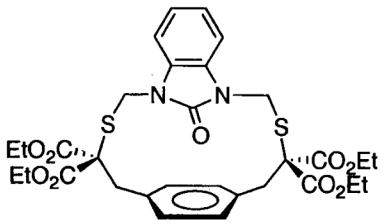
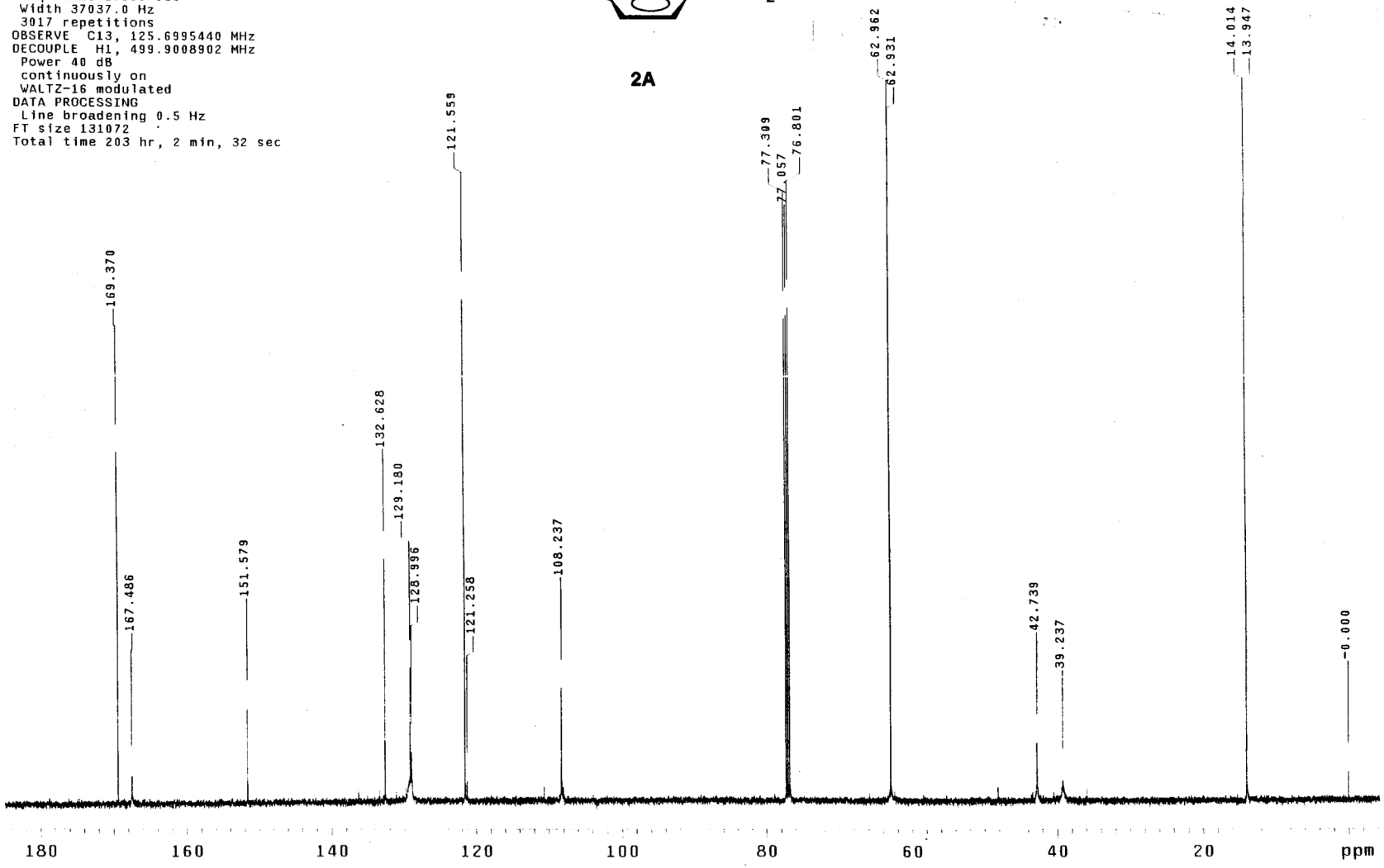
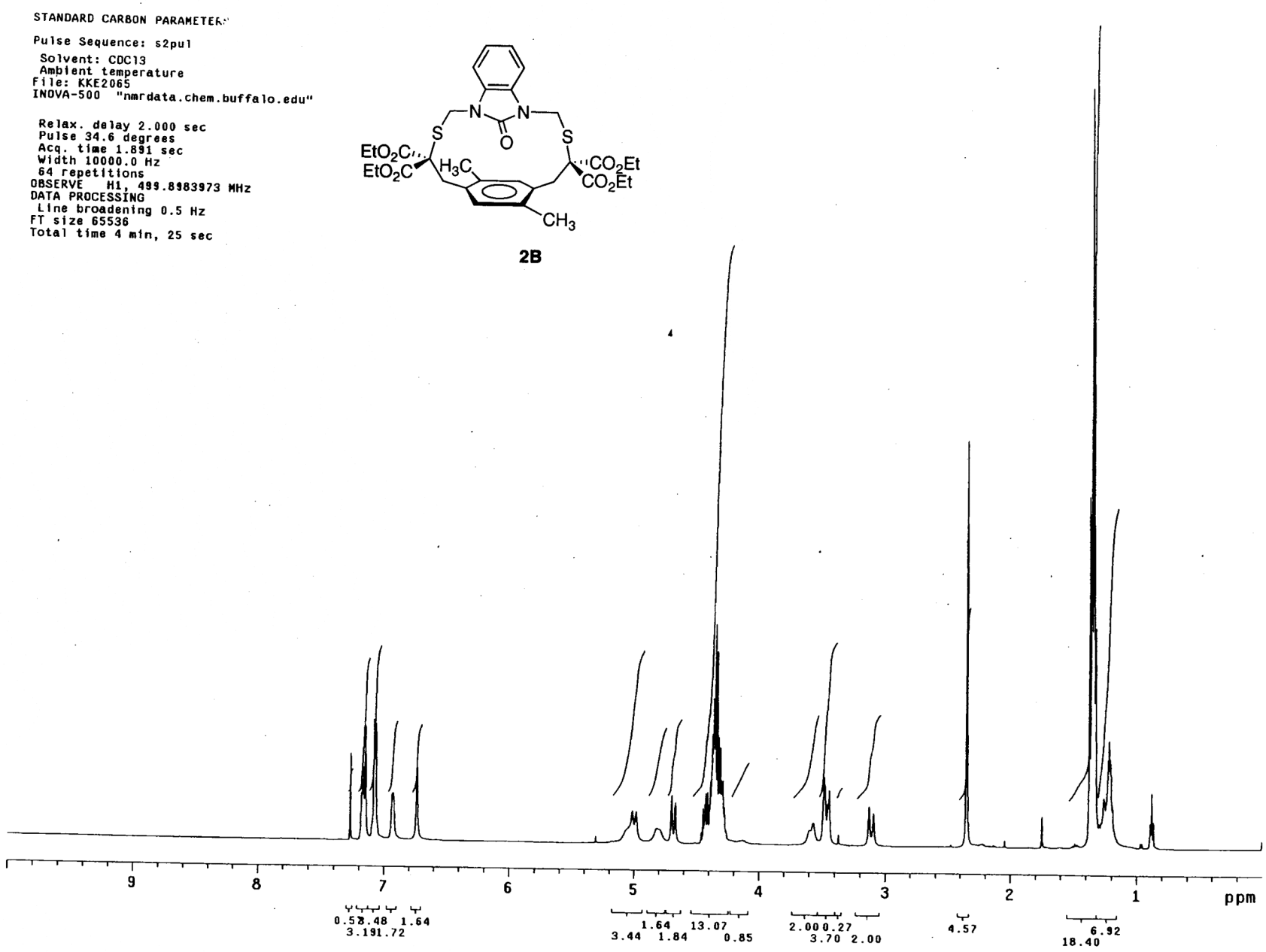


2A

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Ambient temperature
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DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 4 min, 25 sec
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EtO2C
H3C
CO2Et
CO2Et
CH3
2B
9
8
7
6
5
4
3
2
1
ppm
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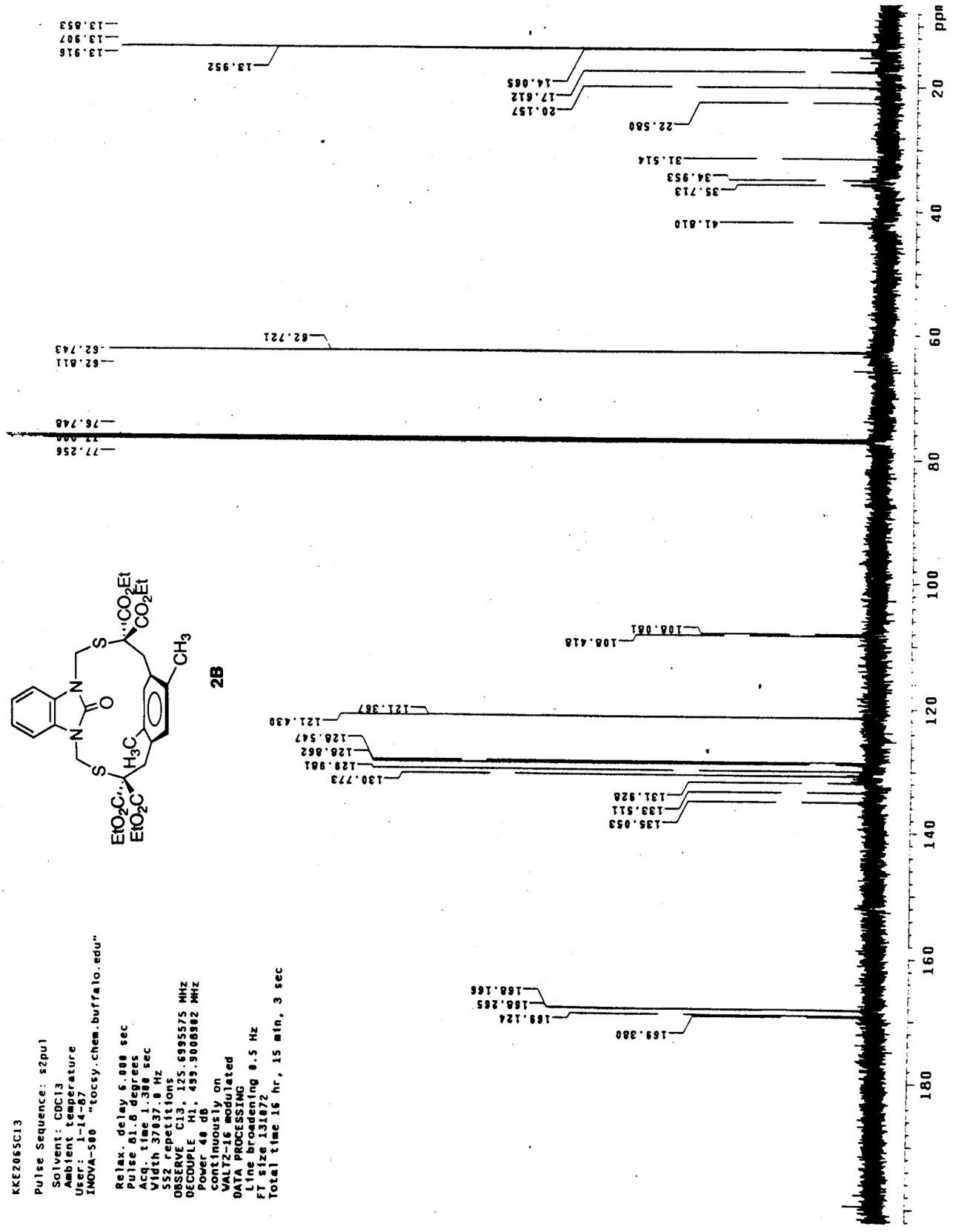
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Solvent: CDCl3
Ambient temperature
User: 1-14-87
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Pulse 81.8 degrees
Acq. time 1.300 sec
Width 37037.0 Hz
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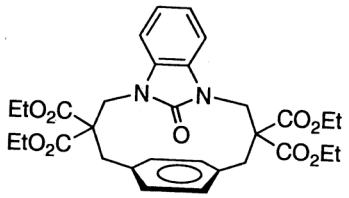
OBSERVE C13, 125.6995575 MHz
DECOUPLE H1, 499.9008982 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 16 hr, 15 min, 3 sec
2B
13.916
13.907
13.853
13.952
14.065
17.612
20.157
22.560
31.514
34.953
35.713
41.810
62.721
62.811
62.743
76.748
77.256
108.061
108.418
121.367
121.430
128.547
128.862
129.861
130.773
131.926
133.511
135.053
168.166
168.265
169.124
169.380
ppm

KKE3.3ins

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
40 repetitions
OBSERVE H1, 499.8984008 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 2 min, 51 sec

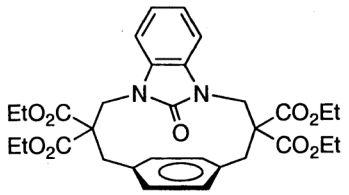


3A

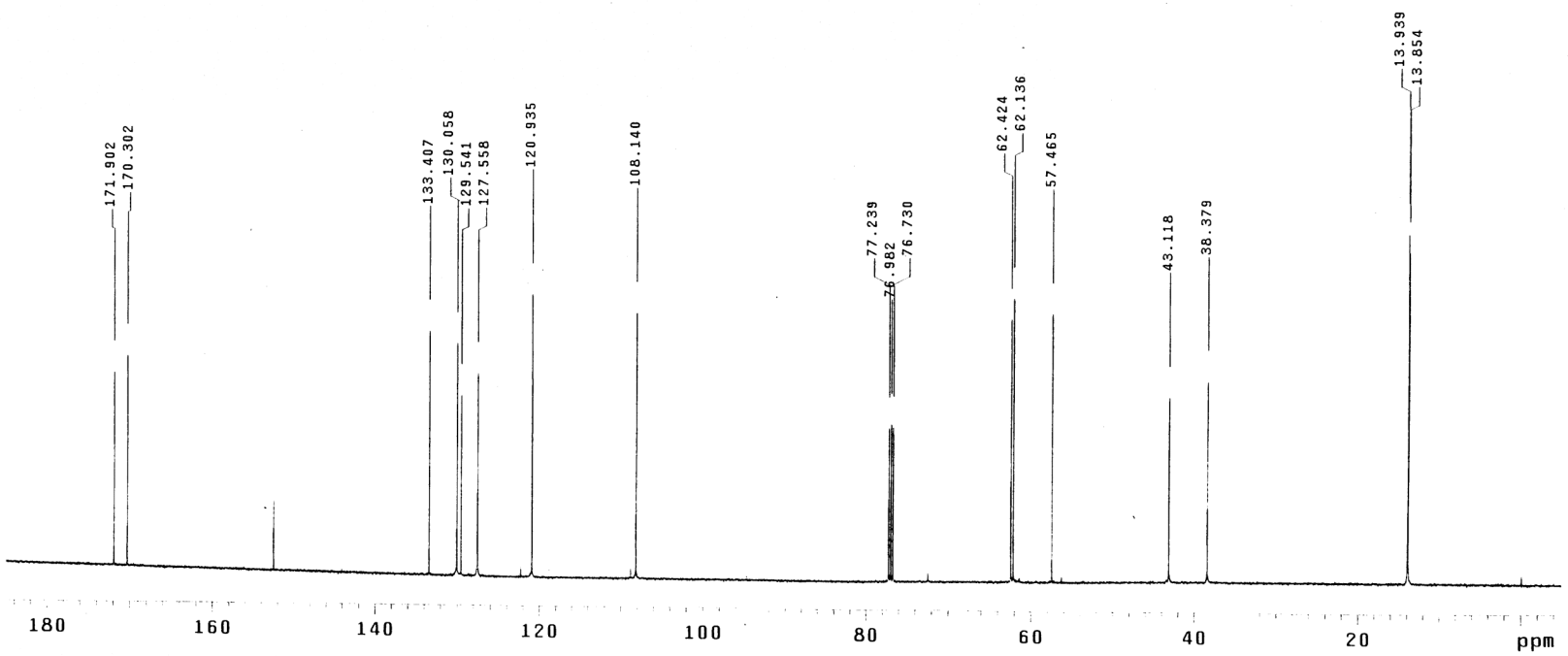
KKE1200

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
User: 1-14-87
INOVA-500 "tocsy.chem.buffalo.edu"

 Relax. delay 6.000 sec
 Pulse 117.4 degrees
 Acq. time 1.300 sec
 Width 37037.0 Hz
 848 repetitions
OBSERVE C13, 125.6995597 MHz
DECOUPLE H1, 499.9008902 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 162 hr, 26 min, 7 sec



3A

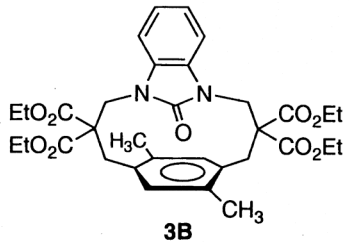


KKE202

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
64 repetitions
OBSERVE H1, 499.8984009 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 4 min, 25 sec

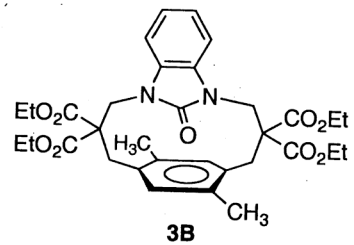


3B

2072c13wodeciss

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
User: 1-14-87
INOVA-500 "tocsy.chem.buffalo.edu"

 Relax. delay 6.000 sec
 Pulse 81.8 degrees
 Acq. time 1.300 sec
 Width 37037.0 Hz
 1680 repetitions
OBSERVE C13, 125.6995518 MHz
DECOUPLE H1, 499.9008902 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 162 hr, 26 min, 7 sec

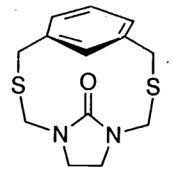


3B

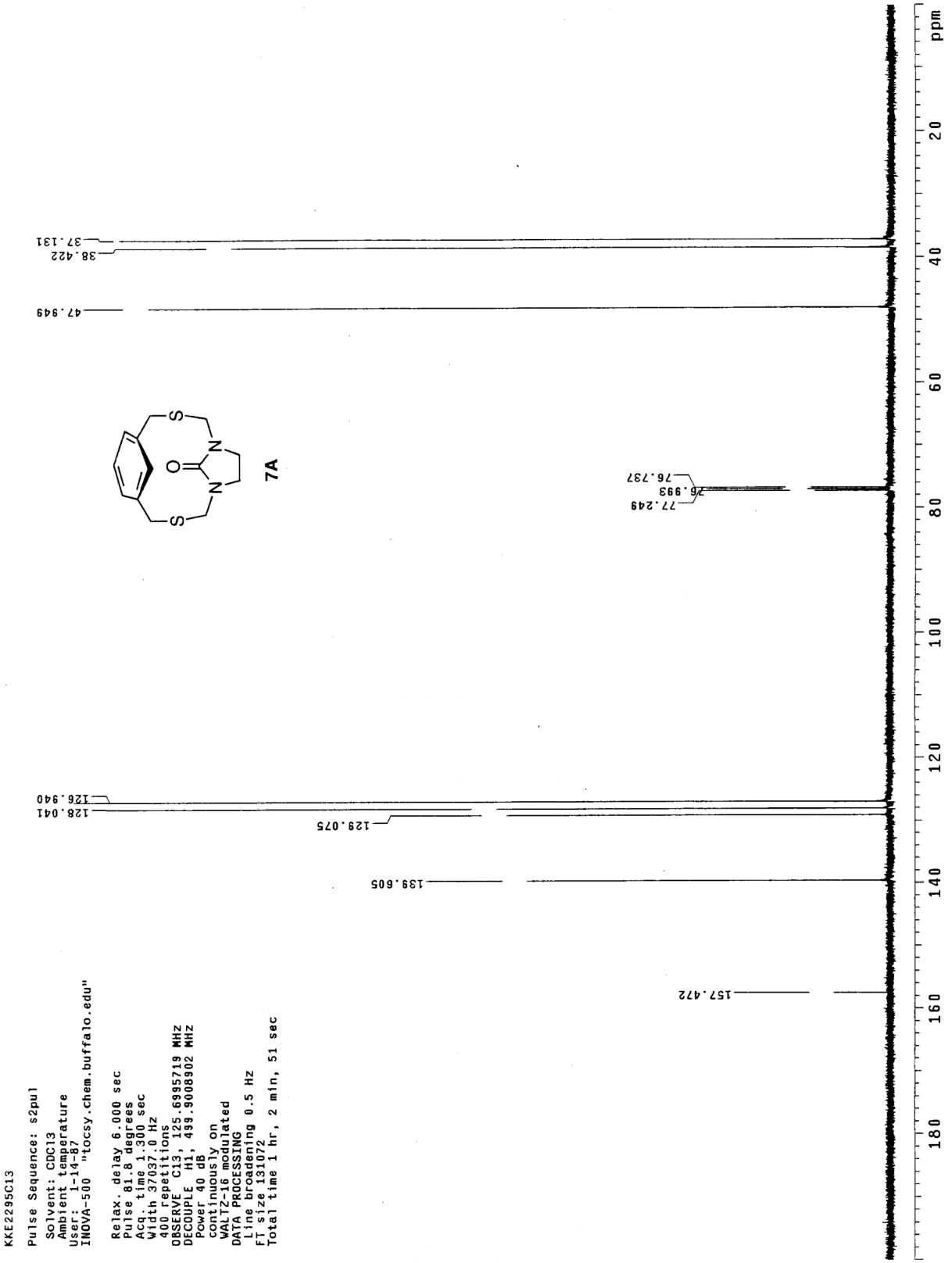
KKE2295

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
64 repetitions
OBSERVE H1, 499.8983866 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 4 min, 25 sec



7A

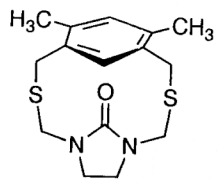

KKE2295C13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 6.000 sec
Pulse 81.8 degrees
Acq. time 1.300 sec
Width 37037.0 Hz
400 repetitions
OBSERVE C13, 125.6995719 MHz
DECOUPLE H1, 499.9008902 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 2 min, 51 sec
7A
157.472
139.605
129.075
128.041
126.940
77.249
76.993
76.737
47.949
38.422
37.131
ppm

KKE3032

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 29.1 degrees
Acq. time 1.499 sec
Width 12001.2 Hz
64 repetitions
OBSERVE H1, 399.9389037 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 3 min, 58 sec

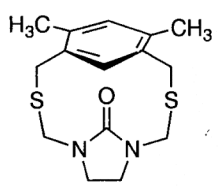


7B

KKE3032C13

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
5648 repetitions
OBSERVE C13, 75.4536607 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 155 hr, 16 min, 13 sec

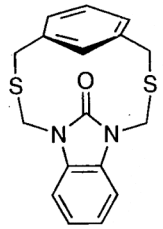


7B

KKE2275

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: KKE2275
INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.0739628 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 4 min, 32 sec

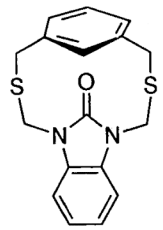


8A

KKE2275C13

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: KKE2275C13
INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
160 repetitions
OBSERVE C13, 75.4536640 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 55 min, 2 sec

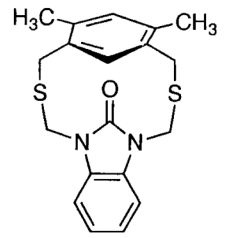


8A

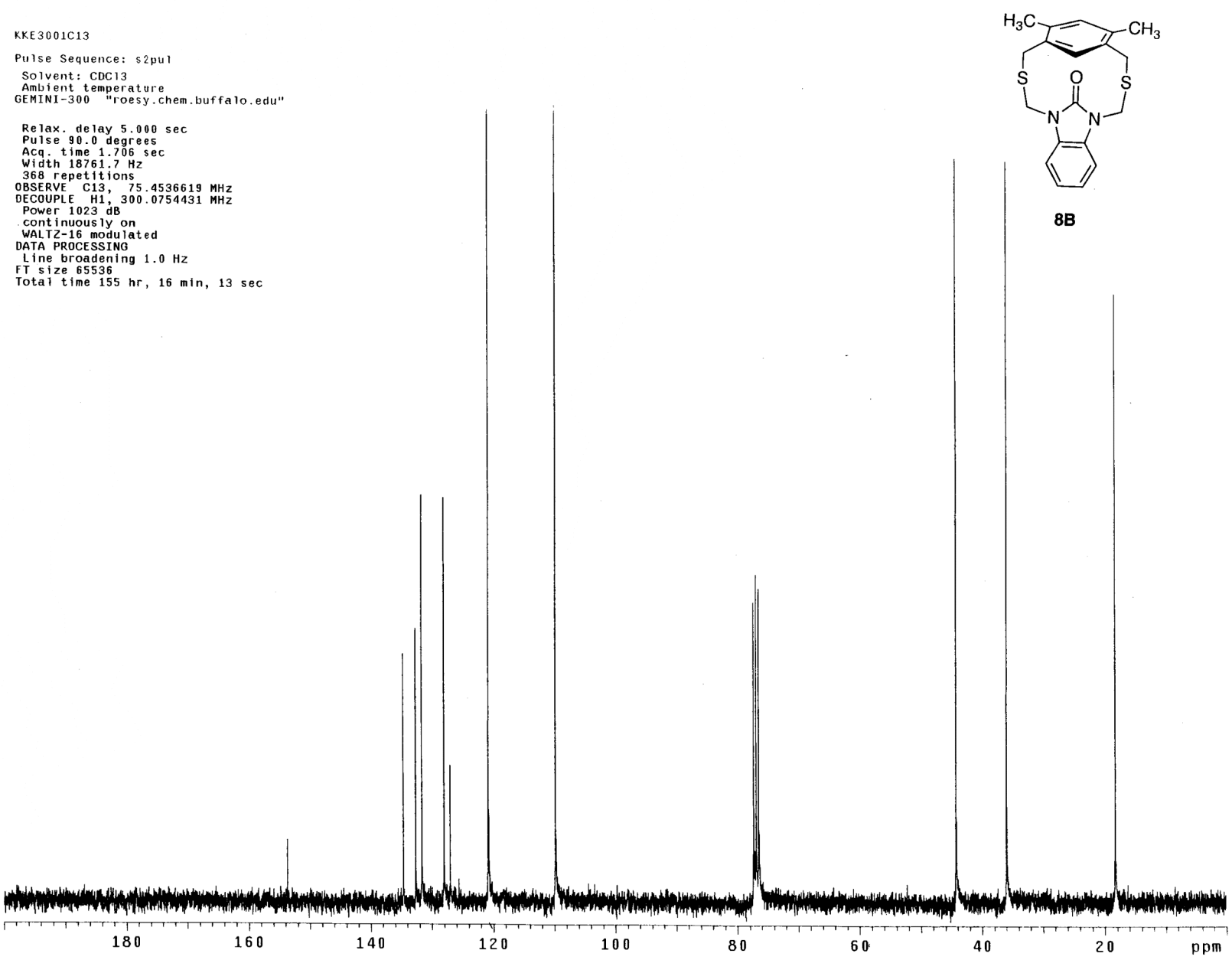
KKE3001

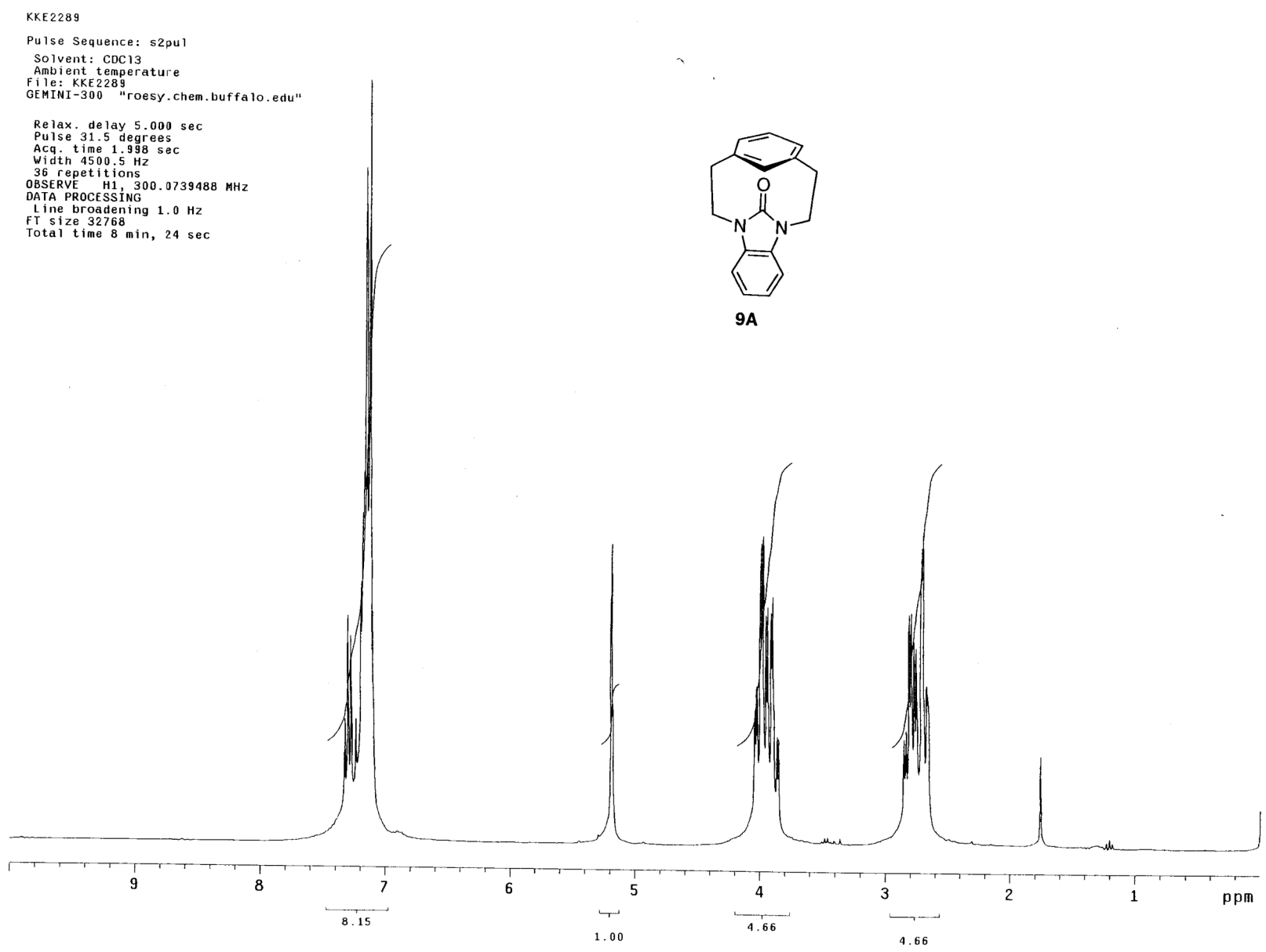
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
64 repetitions
OBSERVE H1, 499.8984065 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 4 min, 25 sec



8B

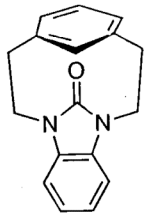

KKE3001C13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
368 repetitions
OBSERVE C13, 75.4536619 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 155 hr, 16 min, 13 sec
H3C
CH3
S
O
S
N
N
8B
180
160
140
120
100
80
60
40
20
ppm


KKE2289
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: KKE2289
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
36 repetitions
OBSERVE H1, 300.0739488 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 24 sec
O
N
N
9A
9
8
7
6
5
4
3
2
1
ppm
8.15
1.00
4.66
4.66

KKE2289C13

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
640 repetitions
OBSERVE C13, 75.4536664 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 12 hr, 25 min, 57 sec

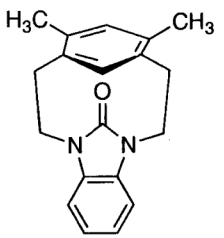


9A

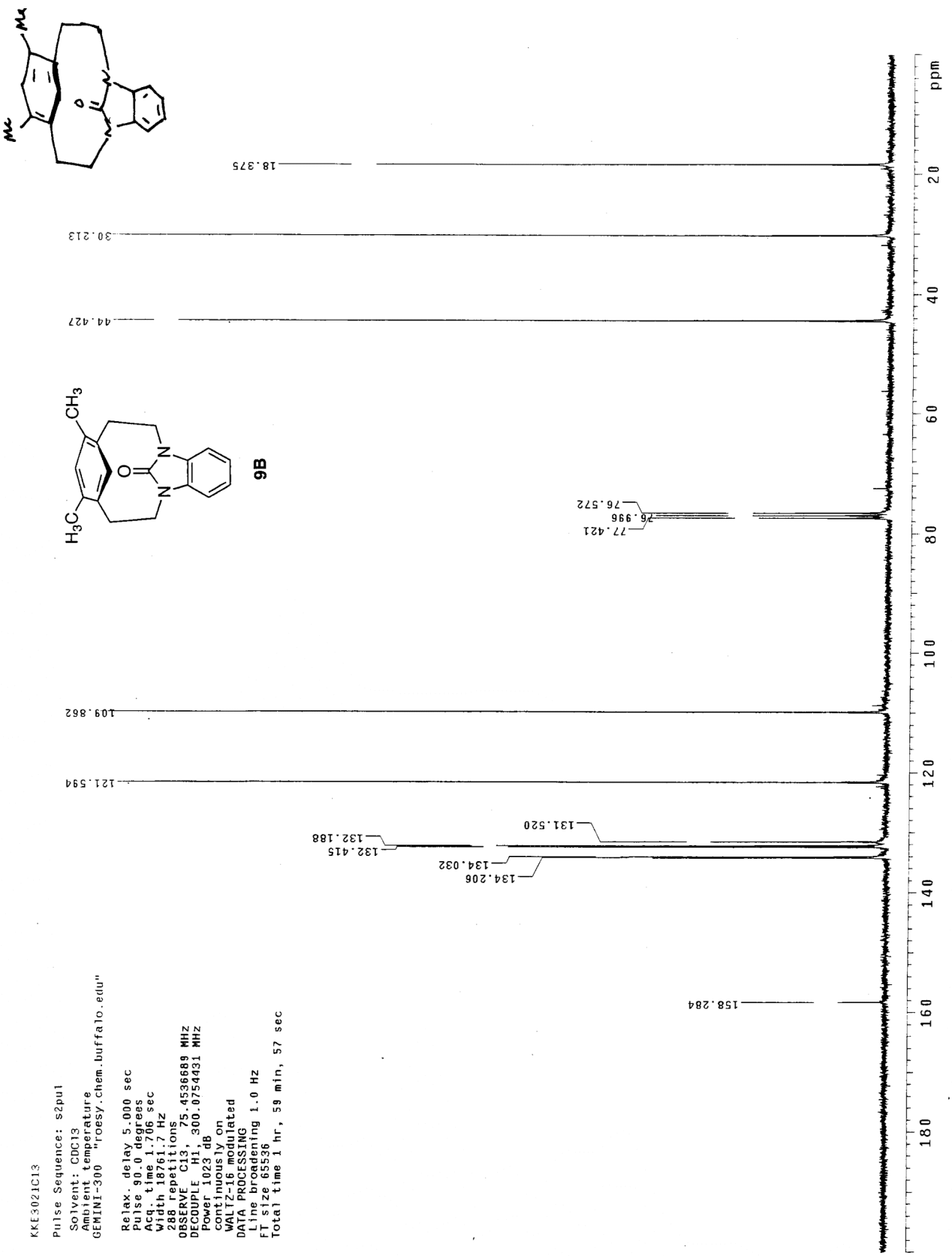
KKE3021

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 499.8984245 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec



9B


KKE3021C13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
288 repetitions
OBSERVE C13, 75.4536689 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 59 min, 57 sec
18.375
30.213
44.427
76.572
76.996
77.421
109.862
121.594
131.520
132.188
132.415
134.032
134.206
158.284
ppm
9B