Supplementary Material (ESI) for Chemical Communications

Mild Lanthanide(III) Catalyzed Formation of 4,5-Diaminocyclopent-2-enones from 2-Furaldehyde and Secondary Amines: A Domino Condensation / Ring-opening / Electrocyclization Process

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Experimental Procedures

General Synthetic Methods

The following general experimental applies for all experiments described in this paper. Unless otherwise stated, all reactions were performed under nitrogen using flame-dried glassware. Reaction solvents were distilled under an inert atmosphere before use and transferred via syringe using standard techniques unless otherwise stated. CH_2Cl_2 and MeCN were distilled from CaH_2 under argon. All reagents, unless otherwise stated, were used as received (Aldrich, Fischer Scientific Ltd. or Lancaster).

IR spectra were obtained on a Perkin-Elmer Spectrum 1000, with samples loaded as films on NaCl plates. ^{1}H and ^{13}C NMR spectra were obtained on Varian Mercury 300 or Unity 400 or 500 spectrometers as solutions in $CDCl_3$. Chemical shifts are expressed in ppm values. Spectra were referenced to 7.26 ppm for $CDCl_3$ for proton chemical shifts, and 77.00 ppm for $CDCl_3$ for carbon chemical shifts. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplet; br, broad (this abbreviation is also used for designation of IR peaks); r, rotamer; *J*, coupling constant in Hz. Low resolution mass spectra (MS) were recorded on a Bell and Howell 21-490 spectrometer, high resolution mass spectra (HRMS) were recorded on an AEI MS3074 spectrometer. Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected.

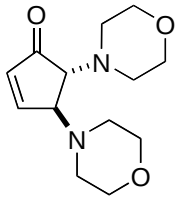
Flash column chromatography on silica gel (60Å, 230 - 400 mesh, obtained from Silicycle Inc.) was performed with distilled hexanes, or reagent grade solvents. Analytical thin-layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel plates

(Alugram SIL G/UV_{254} purchased from Rose Scientific Limited or Silicycle Inc.), visualized with a UV lamp (254 nm), iodine, ninhydrin, potassium permanganate, phosphomolybdic acid (Aldrich), or vanillin. References following the compound names indicate literature articles where ^{1}H and ^{13}C NMR data have previously been reported.

General Procedure for the Mild Lanthanide(III) Catalyzed Formation of *trans*-4,5-Diaminocyclopent-2-enones from 2-Furaldehyde and Secondary Amines

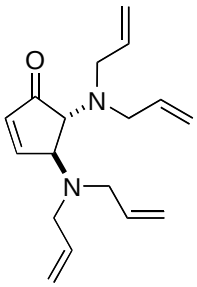
To a solution of 2-furaldehyde (0.500 mmol), secondary amine (1.00 mmol), and 4Å molecular sieves (0.10 g) in MeCN (6.0 mL) was added $Dy(OTf)_3$ (0.0500 mmol). The resulting reaction mixture was stirred for 16 hours at room temperature. H_2O (10 mL) was added and the mixture was filtered through Celite. The aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to obtain the crude product. The product was purified by silica gel column chromatography, eluting with CH_2Cl_2 and MeOH or hexanes and EtOAc.

***trans*-4,5-Dimorpholin-4-yl-cyclopent-2-enone** (**4a**)



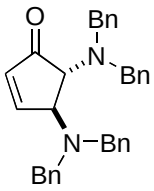
Isolated as a bright yellow crystalline solid (0.132 g, 99%): R_f = 0.52 (94:6 CH_2Cl_2:MeOH); mp = 91-94 °C; IR (thin film) ν 2955, 2851, 1705, 1590, 1451, 1292, 1256, 1114, 1070, 1005, 913, 864 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, dd, *J* = 6.0, 2.0 Hz), 6.22 (1H, dd, *J* = 6.0, 2.0 Hz), 3.79 (1H, ddd, *J* = 3.0, 2.0, 2.0 Hz), 3.71 (4H, t, *J* = 4.5 Hz), 3.67 (4H, t, *J* = 4.5 Hz), 3.28 (1H, d, *J* = 3.0 Hz), 2.84-2.79 (2H, m), 2.67-2.55 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 160.8, 135.6, 68.3, 67.5, 67.3, 66.9, 50.3, 50.1; MS (EI) *m/e* (rel intensity) 252 (100), 167 (34), 166 (70), 140 (72), 124 (41), 112 (39), 100 (29), 86 (49), 81 (23); HRMS (EI) calcd for $C_{13}H_{20}N_2O_3$ (M^+) 252.1474, found 252.1475.

***trans*-4,5-Bis-diallylaminocyclopent-2-enone** (**4b**)



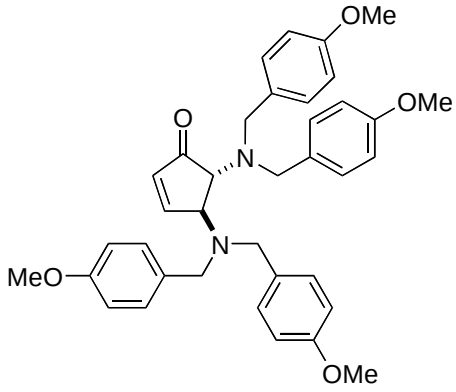
Isolated as a viscous, bright yellow oil (0.0721 g, 78%): R_f = 0.69 (93:5:2 hexanes:EtOAc:Et_3N); IR (thin film) ν 3076, 3008, 2977, 2908, 2824, 1710, 1638, 1417, 1352, 1150, 1109, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (1H, dd, *J* = 6.0, 2.0 Hz), 6.16 (1H, dd, *J* = 6.0, 2.0 Hz), 5.91-5.77 (4H, m), 5.26-5.10 (8H, m), 4.11 (1H, ddd, *J* = 3.0, 2.0, 2.0 Hz), 3.59 (1H, d, *J* = 3.0 Hz), 3.38-3.31 (2H, m), 3.23-3.10 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 162.6, 136.7, 136.3, 135.0, 117.6 (2 peaks), 65.2, 63.7, 54.6, 53.8; MS (EI) *m/e* (rel intensity) 272 (92), 231 (99), 176 (79), 149 (32), 136 (80), 134 (72), 122 (100), 110 (48), 96 (52), 68 (89); HRMS (EI) calcd for $C_{17}H_{24}N_2O$ (M^+) 272.1889, found 272.1880.

***trans*-4,5-Bis-dibenzylaminocyclopent-2-enone** (**4c**)



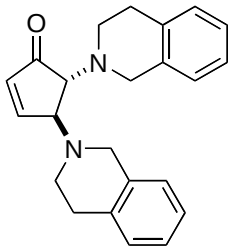
Isolated as a bright yellow, crystalline solid (0.134 g, 98%): R_f = 0.36 (90:10 hexanes:EtOAc); mp = 107-109 °C; IR (thin film) ν 3160, 3023, 2924, 2260, 1790, 1699, 1493, 1451, 1375, 1101, 903, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, *J* = 6.0, 2.0 Hz), 7.31-7.20 (20H, m), 6.20 (1H, dd, *J* = 6.0, 2.0 Hz), 4.08 (1H, ddd, *J* = 2.5, 2.0, 2.0 Hz), 3.86 (2H, d, *J* = 13.0 Hz), *3*.64 (1H, d, *J* = 2.5 Hz), *3*.57 (2H, d, *J* = 13.0 Hz), 3.43 (2H, d, *J* = 14.5 Hz), 3.39 (2H, d, *J* = 14.5 Hz); ^{13}C NMR (100 MHz, CDCl3) δ 208.6, 163.0, 139.3 (2 peaks), 135.5, 129.5, 128.6, 128.2 (2 peaks), 127.1 (2 peaks), 64.4, 63.3, 55.0, 54.6; MS (EI) *m/e* (rel intensity) 472 (52), 396 (28), 381 (68), 246 (21), 245 (92), 202 (10), 172 (11), 91 (100); HRMS (EI) *m/e* calcd for $C_{33}H_{32}N_2O$ (M^+) 472.2515, found 472.2505.

***trans*-4,5-Bis-[bis-(4-methoxybenzyl)amino]cyclopent-2-enone (4d)**



Isolated as a bright yellow, crystalline solid (0.151 g, 99%): R_f = 0.21 (80:20 hexanes:EtOAc); mp = 156-157 °C; IR (thin film) ν 2996, 2833, 1700, 1610, 1550, 1511, 1248, 1170, 1035, 821 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (1H, dd, *J* = 6.0, 2.0 Hz), 7.13 (4H, d, *J* = 8.5 Hz), 7.06 (4H, d, *J* = 8.5 Hz), 6.85-6.81 (8H, m), 6.17 (1H, dd, *J* = 6.0, 1.5 Hz), 3.98-3.97 (1H, m), 3.82 (6H, s), 3.81 (6H, s), 3.73 (2H, d, *J* = 13.0 Hz), 3.55 (1H, d, *J* = 2.5 Hz), 3.46 (2H, d, *J* = 13.0 Hz), 3.36 (2H, d, *J* = 13.5 Hz), 3.29 (2H, d, *J* = 13.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 162.9, 158.7 (2 peaks), 135.4, 131.6, 131.5, 130.6, 129.9, 113.6 (2 peaks), 64.7, 63.8, 55.5, 54.5, 54.2; MS (EI) *m/e* (rel intensity) 592(16), 472 (5), 471 (16), 122 (16), 121 (100), 91(5), 78 (6), 77 (7); HRMS (EI) *m/e* calcd for $C_{37}H_{40}N_2O_5(M^+)$ 592.2937, found 592.2912.

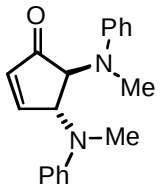
***trans*-4,5-Bis-(3,4-dihydro-*1H*-isoquinolin-2-yl)-cyclopent-2-enone (4e)**



Isolated as a viscous, bright yellow oil (0.158 g, 92%): R_f = 0.31 (70:30 hexanes:EtOAc); IR (thin film) ν 3069, 3015, 2924, 2809, 1703, 1581, 1497, 1448, 1269, 1131, 1101, 903 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (1H, dd, *J* = 6.0, 2.0 Hz), 7.16-7.00 (8H, m), 6.32 (1H, dd, *J* = 6.0, 2.0 Hz), 4.25-4.13 (2H, m), 3.95-3.90 (3H, m), 3.62 (1H, d, *J* = 3.0 Hz), 3.12-2.86 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 161.4, 135.4, 135.1, 134.5, 134.4, 134.2, 128.9, 126.6,

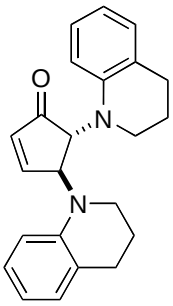
126.5, 126.4, 126.0, 125.8, 125.6, 67.9, 67.4, 53.0, 52.4, 47.5, 47.4, 30.3, 29.8; MS (EI) *m/e* (rel intensity) 344 (66), 213 (36), 186 (28), 170 (39), 132 (100), 117 (48), 104 (51), 91 (53), 78 (25); HRMS (EI) calcd for $C_{23}H_{24}N_2O$ (M^+) 344.1889, found 344.1884.

***trans*-4,5-Bis-(methylphenylamino)-cyclopent-2-enone** (**4f**) (Lewis, K. G.; Mulquiney, C. E. *Aust. J. Chem*. **1979**, *32*, 1079-1092.)



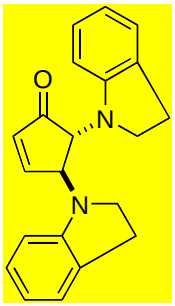
Isolated as a viscous, bright yellow oil (0.0821 g, 76%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (1H, dd, *J* = 6.5, 2.0 Hz), 7.19-7.12 (4H, m), 6.79-6.70 (4H, m), 6.57-6.54 (2H, m), 6.48 (1H, dd, *J* = 6.5, 2.0 Hz), 5.19-5.18 (1H, m), 4.32 (1H, d, *J* = 3.5 Hz), 2.85 (3H, s), 2.82 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 161.7, 149.2, 148.9, 143.7, 129.4, 129.3, 118.8, 118.3, 114.4, 113.9, 70.1, 62.8, 37.0, 34.0.

***trans*-4,5-Bis-(3,4-dihydro-2*H*-quinolin-1-yl)-cyclopent-2-enone** (**4g**)



Isolated as a viscous, bright yellow oil (0.163 g, 81%): R_f = 0.27 (80:20 hexanes:EtOAc); IR (thin film) ν 2962, 2901, 2855, 1749, 1459, 1371, 1238, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (1H, dd, *J* = 6.0, 2.0 Hz), 6.99-6.87 (4H, m), 6.65-6.50 (4H, m), 6.09 (1H, d, *J* = 8.0 Hz), 5.38 (1H, br s), 4.32 (1H, br s), 3.33-3.15 (4H, m), 2.82-2.66 (4H, m), 2.00-1.88 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 161.7, 144.4, 143.5, 134.4, 129.6 (2 peaks), 127.2, 126.9, 123.8, 123.6, 117.4, 117.2, 111.6, 110.9, 68.6, 60.1, 49.9, 45.6, 28.2 (2 peaks), 22.8, 22.6; MS (EI) *m/e* (rel intensity) 344 (40), 213 (22), 212 (100), 170 (11), 130 (11), 117 (9), 91 (10); HRMS (EI) calcd for $C_{23}H_{24}N_2O$ (M^+) 344.1889, found 344.1894.

***trans*-4,5-Bis-(2,3-dihydroindol-1-yl)-cyclopent-2-enone** (**4h**)

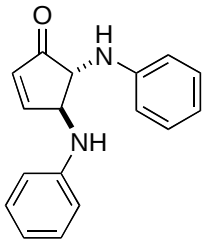


Isolated as a viscous, bright yellow oil (0.179 g, 99%): R_f = 0.25 (80:20 hexanes:EtOAc); IR (thin film) ν 3042, 2915, 2845, 1726, 1606, 1487, 1332, 1265, 1159, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (1H, dd, *J* = 6.0, 2.0 Hz), 7.08 (1H, d, *J* = 7.0 Hz), 7.05 (1H, d, *J* = 7.5 Hz), 6.96 (1H, dd, *J* = 7.5, 7.5 Hz), 6.91 (1H, dd, *J* = 7.5, 7.5 Hz), 6.67 (1H, dd, *J* = 7.5, 7.5 Hz), 6.63 (1H, dd, *J* = 7.5, 7.5 Hz), 6.49 (1H, dd, *J* = 6.0, 2.0 Hz), 6.35 (1H, d, *J* = 8.0 Hz), 6.07 (1H, d, *J* = 8.0 Hz), 5.01-4.99 (1H, m), 4.40 (1H, d, *J* = 3.5 Hz), 3.52 (1H, ddd, *J* = 7.5, 7.5, 7.5 Hz), 3.50 (1H, ddd, *J* = 8.0, 8.0, 8.0 Hz), 3.41 (1H, ddd, *J* = 8.0, 8.0, 8.0 Hz), 3.34 (1H, ddd, *J* = 8.0, 8.0, 8.0 Hz), 3.06-2.90 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 161.8, 145.0, 149.8, 135.3, 130.3, 130.1, 127.5, 127.3, 125.0, 124.9, 118.7, 118.3, 107.5, 106.7, 63.4, 58.7, 51.4, 49.8, 28.6, 28.5; MS (EI) *m/e* (rel intensity) 316 (26), 199 (18), 198 (100), 130 (12), 91 (10), 80 (9), 76 (9); HRMS (EI) calcd for $C_{21}H_{20}N_2O$ (M^+) 316.1576, found 316.1568.

General Procedure for the Mild Lanthanide(III) Catalyzed Formation of *trans*-4,5-Diaminocyclopent-2-enones from 2-Furaldehyde and Primary Anilines

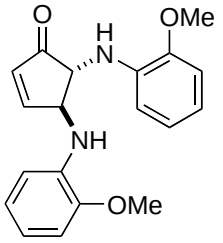
To a solution of 2-furaldehyde (0.500 mmol), primary aniline (1.00 mmol), and 4Å molecular sieves (0.10 g) in MeCN (6.0 mL) was added $Sc(OTf)_3$ (0.0500 mmol). The resulting reaction mixture was stirred for 48 hours at room temperature. H_2O (10 mL) was added and the mixture was filtered through Celite. The aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to obtain the crude product. The product was purified by silica gel column chromatography, eluting with CH_2Cl_2 and MeOH or hexanes and EtOAc.

***trans*-4,5-Bis-phenylaminocyclopent-2-enone** (**4i**) (Lewis, K. G.; Mulquiney, C. E. *Tetrahedron* **1977**, *33*, 463-475.)



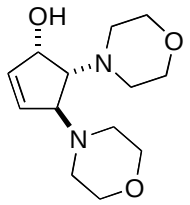
Isolated as a viscous, bright yellow oil (0.154, 78%): ^{1}H NMR (500 MHz, DMF-d_7) δ 7.76 (1H, dd, *J* = 6.0, 2.0 Hz), 7.15-7.06 (4H, m), 6.82-6.75 (4H, m), 6.64 (1H, tt, *J* = 7.5, 1.0 Hz), 6.60 (1H, tt, *J* = 7.5, 1.0 Hz), 6.40 (1H, dd, *J* = 6.0, 1.5 Hz), 6.26 (1H, d, *J* = 8.5 Hz), 6.03 (1H, d, *J* = 7.0 Hz), 4.75 (1H, dddd, *J* = 7.0, 3.5, 1.5, 1.5 Hz), 4.14 (1H, dd, *J* = 7.0, 3.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 162.3, 149.5, 149.0, 133.3, 130.2, 129.9, 118.0, 117.7, 114.1, 114.0, 66.1, 61.0.

***trans*-4,5-Bis-(2-methoxyphenylamino)cyclopent-2-enone** (**4j**)



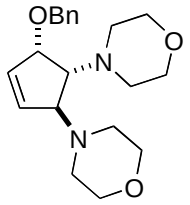
Isolated as a viscous, dark red oil (0.232, 52%): R_f = 0.24 (80:20 hexanes:EtOAc); IR (thin film) ν 3381, 3066, 2937, 2834, 1716, 1601, 1513, 1456, 1431, 1224, 1251, 1027, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (1H, dd, *J* = 6.0, 1.0 Hz), 6.83-6.69 (8H, m), 6.37 (1H, d, *J* = 6.0 Hz), 5.01 (1H, br s), 4.64-4.61 (2H, m), 3.89 (1H, br s), 3.86 (3H, s), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 161.2, 147.4 (2 peaks), 137.0, 136.1, 132.6, 121.5, 121.4, 118.3 (2 peaks), 111.9, 111.6, 110.1, 109.7, 66.2, 61.9, 55.7, 55.6; MS (EI) *m/e* (rel intensity) 324 (5), 203 (24), 202 (100), 186 (11), 123 (11), 108 (9), 80 (6), 77(9), 65 (9); HRMS (EI) *m/e* calcd for $C_{19}H_{20}N_2O_3$ (M^+) 324.1474, found 324.1480.

4,5-Dimorpholin-4-yl-cyclopent-2-enol



To a solution of **4a** (0.0500 g, 0.198 mmol) and $CeCl_3 \cdot 7H_2O$ (0.0900 g, 0.242 mmol) in MeOH (4.0 mL) was added $NaBH_4$ (0.0100 g, 0.264 mmol) at 0 °C. The resulting reaction mixture was stirred for 30 min at room temperature. The mixture was quenched by addition of sat'd $NaHCO_3$ (5 mL). The aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to obtain the crude product. The crude product was purified by silica gel column chromatography (eluting with CH_2Cl_2:MeOH 96:4) to give a pale yellow, crystalline solid (0.0478 g, 95%): R_f = 0.13 (96:4 CH_2Cl_2:MeOH); mp = 166-168 °C; IR (thin film) ν 3188, 2957, 2816, 2360, 1446, 1372, 1271, 1115, 1058, 886, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.12-6.06 (2H, m), 4.51 (1H, ddd, *J* = 6.0, 2.0, 2.0 Hz), 3.80-3.73 (5H, m), 3.68 (4H, t, *J* = 4.5 Hz), 2.83 (1H, dd, *J* = 6.0, 6.0 Hz), 2.75-2.44 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 132.6, 71.8, 70.4, 67.5, 67.3, 66.5, 52.4, 50.3; MS (EI) *m/e* (rel intensity) 254 (1), 238 (17), 237 (100), 168 (22), 100 (14), 86 (22), 84 (36), 51 (15); HRMS (EI) *m/e* calcd for $C_{13}H_{22}N_2O_3$ (M^+) 254.1630, found 254.1629.

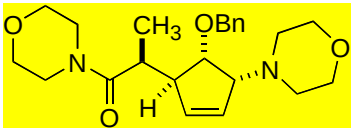
4,5-Dimorpholin-4-yl-cyclopent-2-enol (9)



To NaH (0.020 g, 1.57 mmol) in DMF (4.0 mL) was added a solution of 4,5-dimorpholin-4-yl-cyclopent-2-enol (0.200 g, 0.79 mmol) in DMF (4.0 mL) at 0 °C. The resulting reaction mixture was stirred for 30 min at 0 °C, and benzyl bromide (0.14 mL, 1.18 mmol) added. The reaction mixture was stirred and allowed to warm to room temperature overnight. The mixture was quenched by addition of aqueous NH_4Cl (5 mL), and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to obtain the crude product. The crude product was purified by

silica gel column chromatography to give **9** as a pale yellow oil (0.227 g, 84%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (5H, m), 6.12-6.03 (2H, m), 4.63-4.49 (3H, m), 3.92-3.88 (1H, m), 3.72 (4H, t, *J* = 4.5 Hz), 2.92 (1H, dd, *J* = 5.5, 5.5 Hz), 2.86-2.79 (2H, m), 2.64-2.48 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 133.8, 133.3, 128.3, 128.0, 127.6, 81.0, 71.3, 70.7, 67.4, 67.3, 65.7, 51.8, 50.1.

2-(5-Benzyloxy-4-morpholin-4-yl-cyclopent-2-enyl)-1-morpholin-4-yl-propan-1-one (**10**)



A round-bottom flask containing $TiCl_4$ (0.32 mL, 0.32 mmol) was charged with CH_2Cl_2 (10 mL), then treated with **9** (0.110 g, 0.319 mmol), followed by ^{i}PrNEt$_2$ (0.090 mL, 0.48 mmol). The solution was stirred for 5 min before a solution of propionyl chloride (0.38 mL, 1 M solution in CH_2Cl_2, 0.38 mmol) in CH_2Cl_2 was added dropwise over 1 min. The resulting dark red solution was stirred for 16 h. The reaction mixture was then diluted with Et_2O (10 mL) and washed with aqueous 1 N NaOH (5 mL). The aqueous layer was then extracted with ether, and the combined organic layers washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to obtain the crude product. The product was purified by silica gel column chromatography (eluting with CH_2Cl_2:MeOH 96:4) to give **10** as a clear, yellow oil as a single diasteromer (0.090 g, 72%): R_f = 0.35 (96:4 CH_2Cl_2:MeOH); IR (Thin Film) ν 2961, 2893, 2852, 1642, 1453, 1432, 1355, 1235, 1153, 1116, 1029, 911, 739, 700 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 7.45-7.32 (5H, m), 6.03 (1H, ddd, *J* = 6.0, 2.0, 2.0 Hz), 5.94 (1H, ddd, *J* = 6.5, 2.0, 2.0 Hz), 4.81 (1H, d, *J* = 11.5 Hz), 4.56 (1H, d, *J* = 11.5 Hz), 3.91 (1H, dd, *J* = 7.0, 5.5 Hz), 3.72 (1H, dddd, *J* = 7.0, 2.0, 2.0, 2.0 Hz), 3.67-3.50 (12H, m), 2.99-2.94 (1H, m), 2.82 (1H, dq, *J* = 6.5, 6.5 Hz), 2.73 (2H, dt, *J* = 11.0, 4.5 Hz), 2.61 (2H, dt, *J* = 11.5, 4.5 Hz), 1.02 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 138.9, 134.1, 129.0, 128.4 (2 peaks), 127.8, 81.4, 72.2, 69.4, 67.6, 67.5, 67.2, 67.0, 53.5, 52.0, 51.0, 46.3, 42.3, 36.1, 14.0; MS (ESI) *m/e* (rel intensity) 401 (100), 314 (30), 293 (29), 227 (6), 222 (8), 199 (2), 178 (5), 137 (22), 91 (11), 86 (2); HRMS (ESI) *m/e* calcd for $C_{23}H_{33}N_2O_4$ (MH^+) 401.2434, found 401.2421.

Ab initio Computational Study on Formation of 4,5-Diaminocyclopent-2-enones

Calculations were performed on an Apple Dual 1.4 GHz Power Mac using Spartan '02 Version 1.0.4e (Wavefunction Inc., Irvine, CA) (See: J. Kong, C.A. White, A.I. Krylov, C.D. Sherrill, R.D. Adamson, T.R. Furlani, M.S. Lee, A.M. Lee, S.R. Gwaltney, T.R. Adams, C. Ochsenfeld, A.T.B. Gilbert, G.S. Kedziora, V.A. Rassolov, D.R. Maurice, N. Nair, Y. Shao, N.A. Besley, P.E. Maslen, J.P. Dombroski, H. Daschel, W. Zhang, P.P. Korambath, J. Baker, E.F.C. Byrd, T. Van Voorhis, M. Oumi, S. Hirata, C.-P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B.G. Johnson, P.M.W. Gill, M. Head-Gordon, and J.A. Pople, *J. Computational Chem.* **2000**, *21*, 1532).

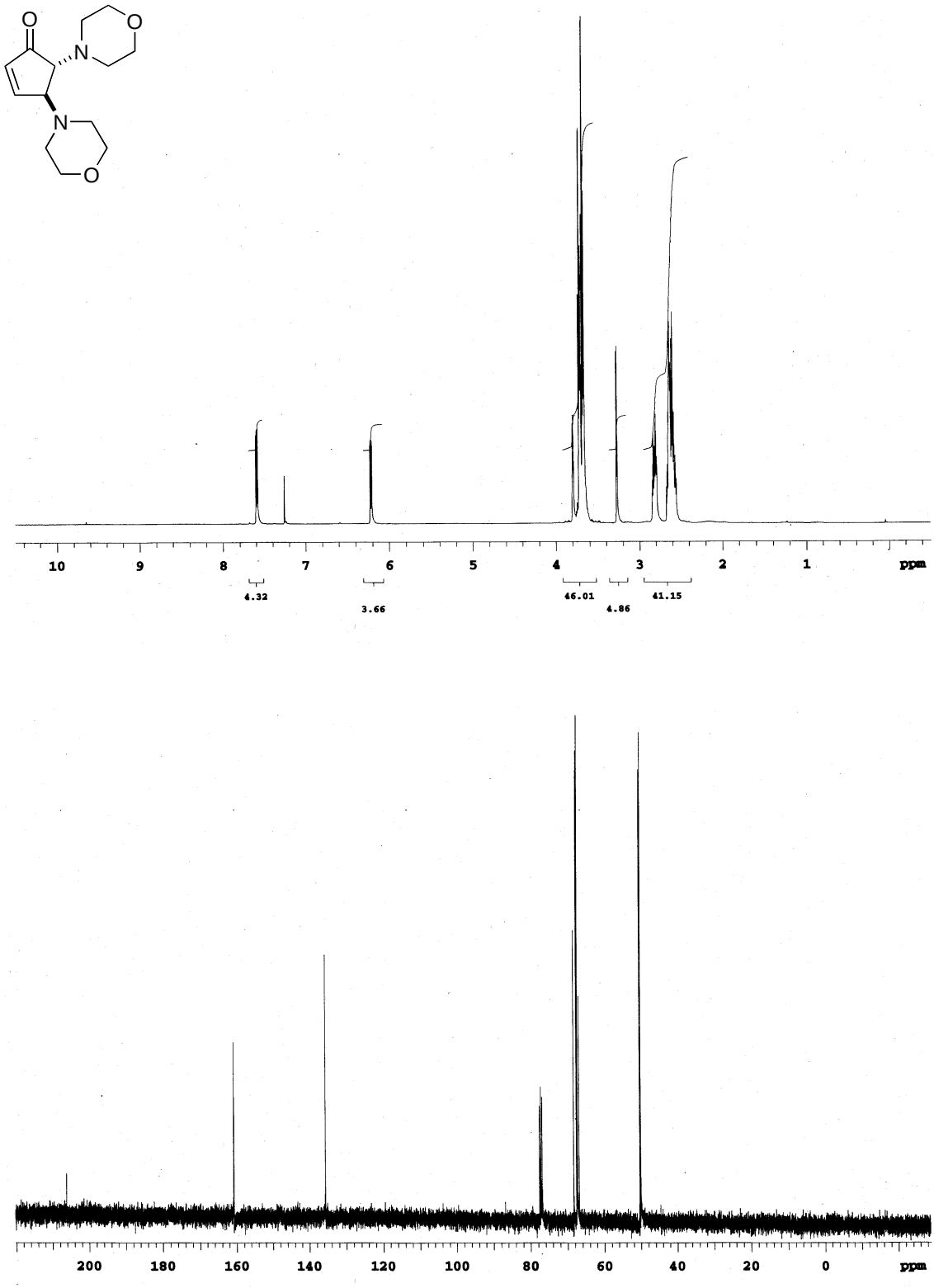
Exhaustive geometry optimizations, transition searches and single-point energies were conducted at the UHF/6-31G** level. Vibrational analysis was conducted at the UHF/6-31G** level, with single imaginary frequencies obtained for transition states. Zero-point energies (ZPVE's) were used unscaled. Relative energies are corrected for zero-point energies (kcal/mol), and are relative to the lowest energy structure cis-4,5-diaminocyclopent-2-enone. Only the lowest energy conrotatory π4a electrocyclization transition states are shown (two are possible, depending upon whether the motion occurs in a clockwise or counter-clockwise manner).

Table of Calculated Energy Minima and Transition States:

	Energy (kcal/mol)	**ZPVE (kcal/mol)**	**Energy + ZPVE (kcal/mol)**	**Relative Energy (kcal/mol)**	**Relative Energy (including ZPVE) (kcal/mol)**
Cis-4	-237040.62	90.24	-236950.38	0.00	**0.00**
Trans-4	-237039.20	89.73	-236949.47	1.42	**0.91**
8-*ZEZE*	-236995.06	88.01	-236907.05	45.56	**43.33**
8-*ZEZZ*	-236992.39	87.82	-236904.57	48.23	**45.81**
8-*ZZEE*	-237001.43	87.85	-236913.58	39.18	**36.80**
8-*ZZZE*	-237003.58	87.74	-236915.83	37.04	**34.55**
8-*ZZZZ*	-237007.83	87.96	-236919.87	32.79	**30.51**
Trans-TS	-236988.81	87.12	-236901.70	51.80	**48.68**
Cis-TS	-236978.55	87.28	-236891.27	62.07	**59.11**

^{1}H and ^{13}C NMR Spectra for all Compounds

4a


O
O
N
N
O
10
9
8
7
6
5
4
3
2
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ppm
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4.86
41.15
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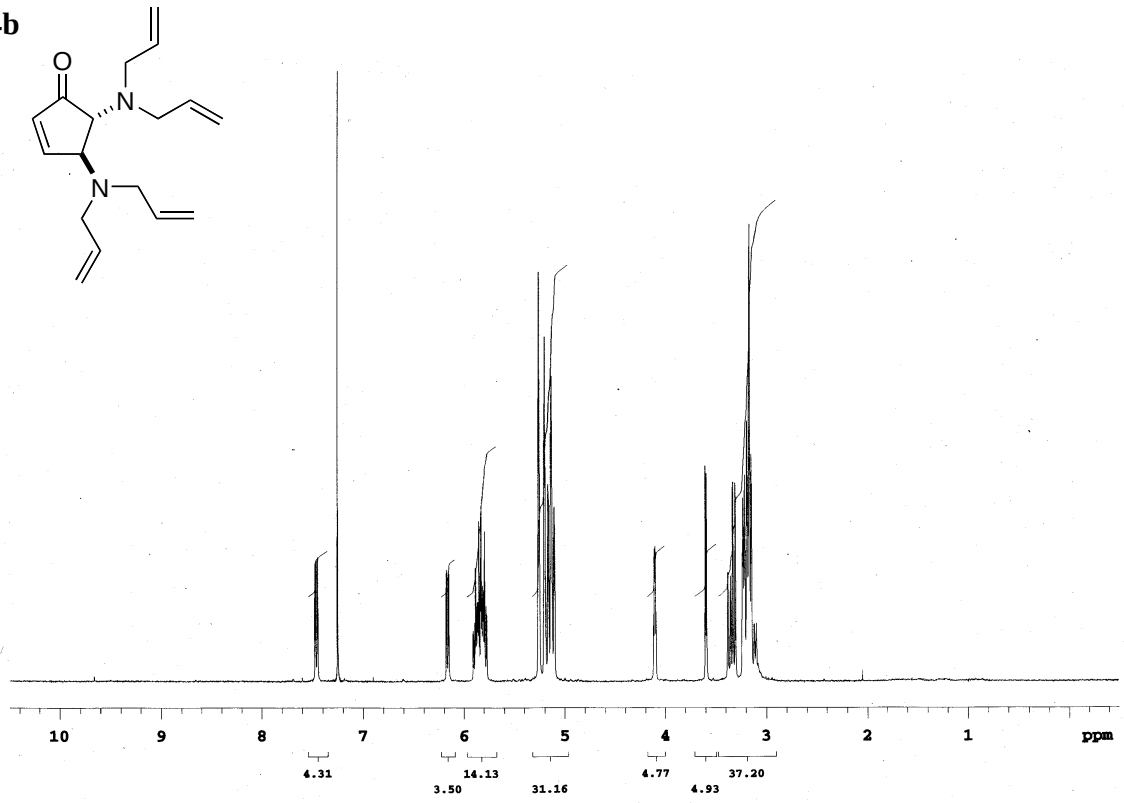
180
160
140
120
100
80
60
40
20
0
ppm

4b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N
N
10
9
8
7
6
5
4
3
2
1
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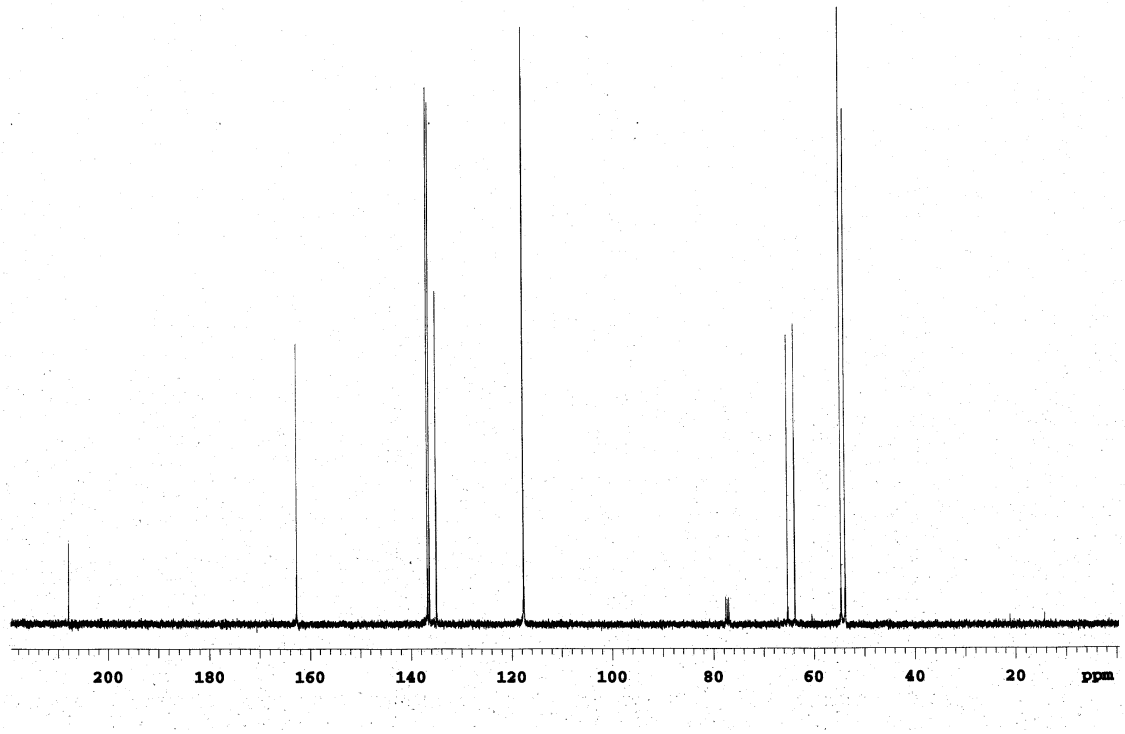
31.16
4.77
4.93
37.20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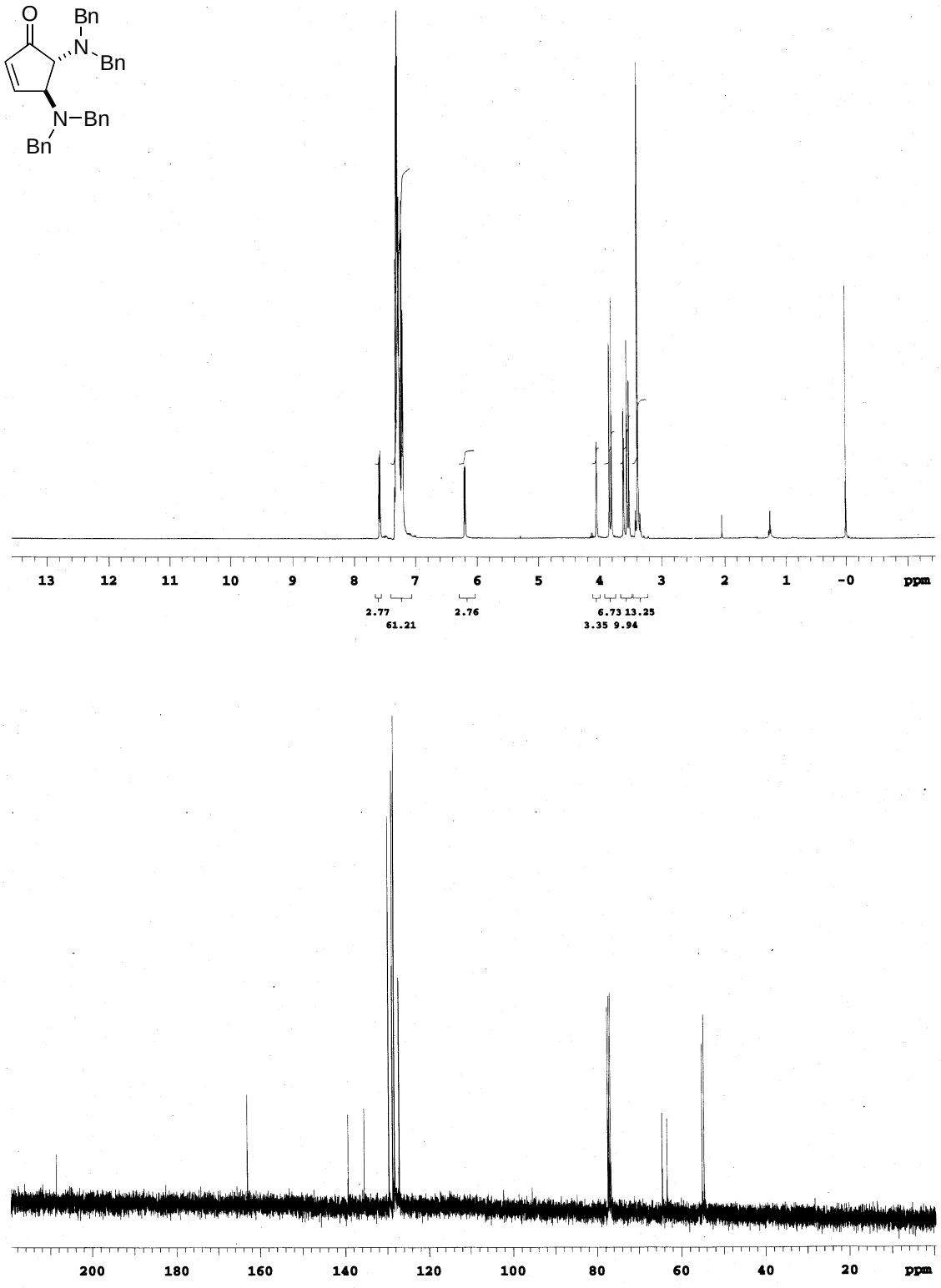
160
140
120
100
80
60
40
20
ppm

4c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Bn
N
Bn
N–Bn
Bn
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.77
61.21
2.76
6.73 13.25
3.35 9.94
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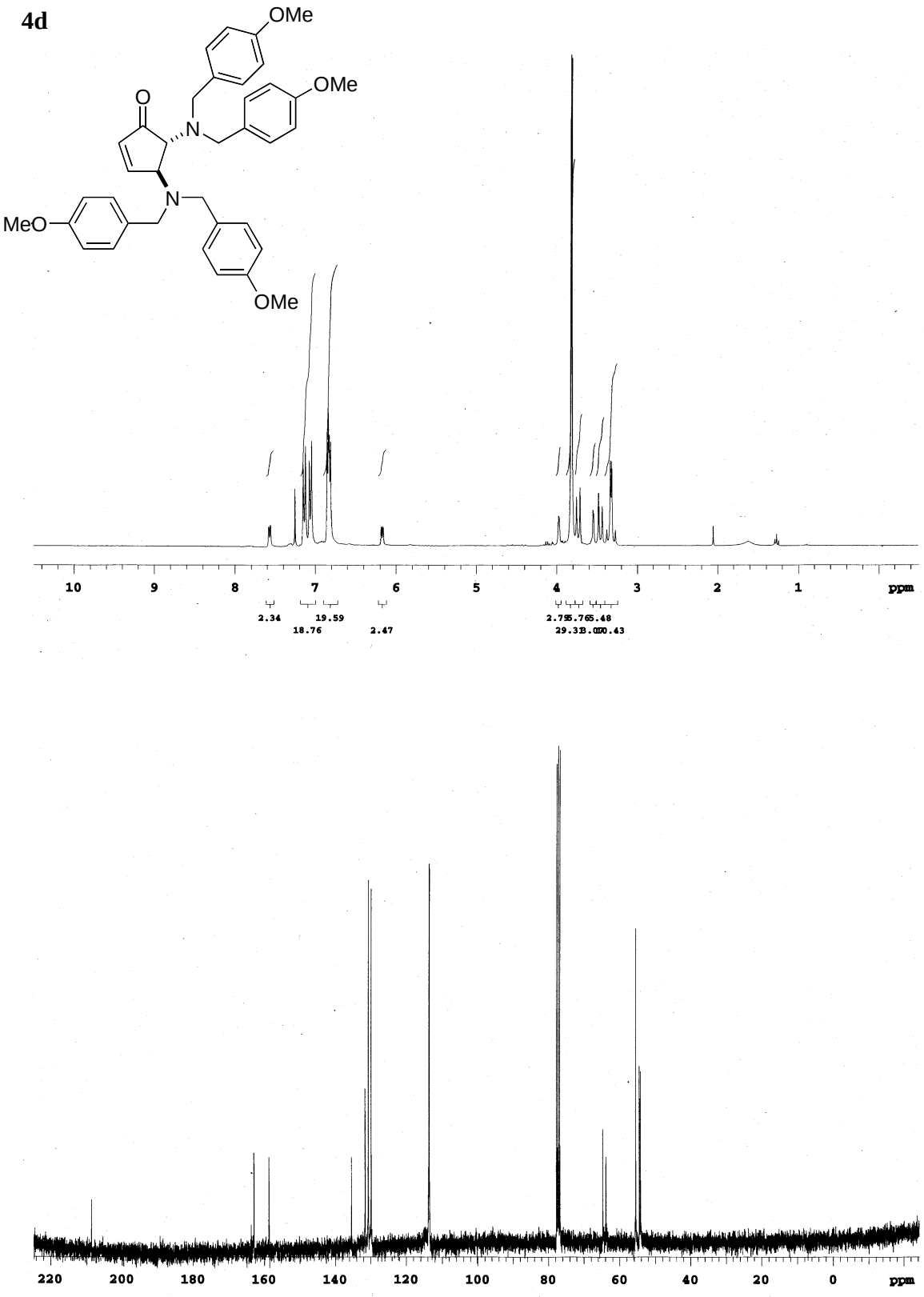
160
140
120
100
80
60
40
20
ppm

4d


OMe
OMe
O
N
N
MeO
OMe
10
9
8
7
6
5
4
3
2
1
ppm
2.34
19.59
18.76
2.47
2.75
5.76
5.48
29.31
3.00
0.43
220
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180
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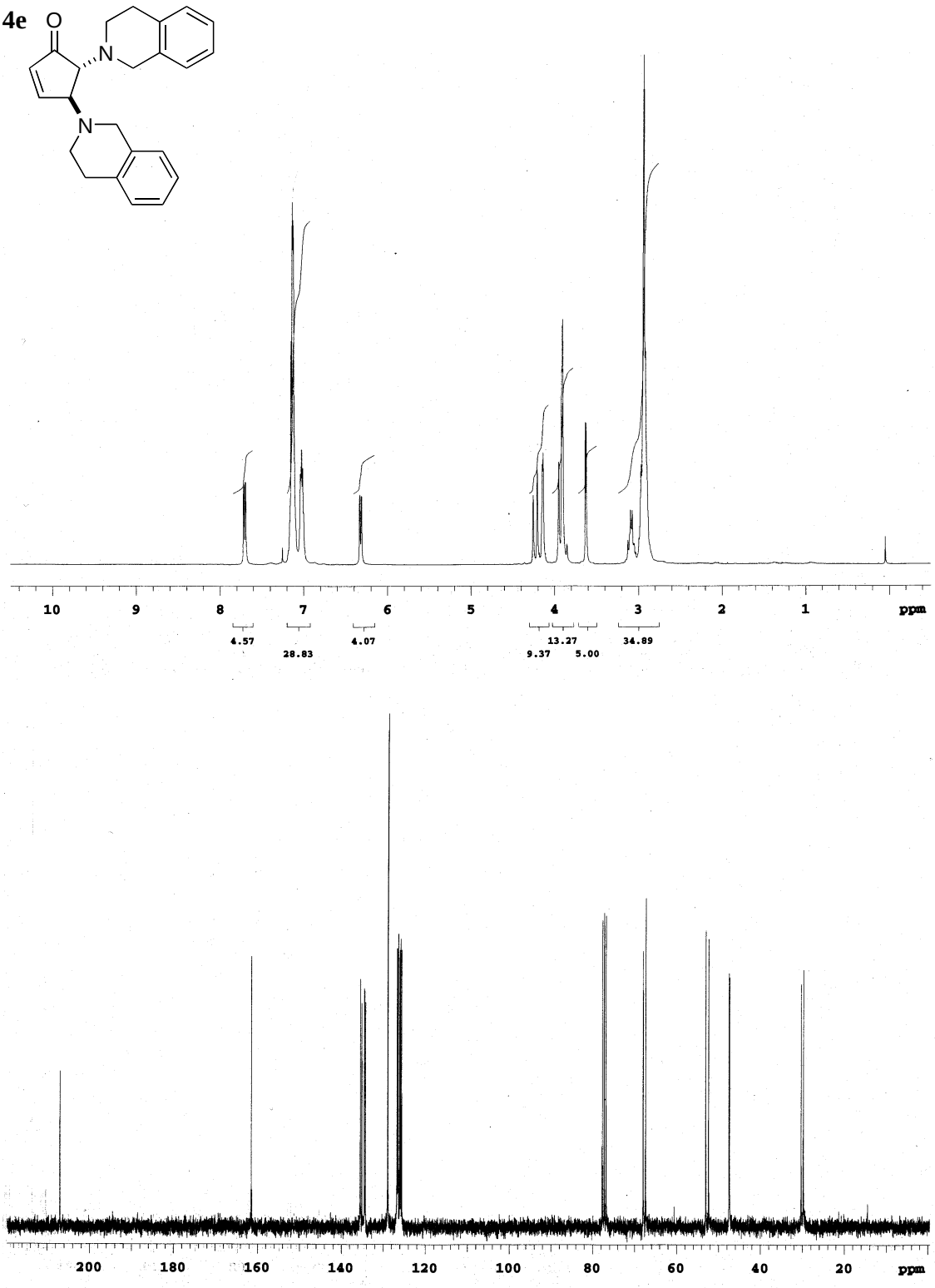
140
120
100
80
60
40
20
0
ppm

4e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N
N
10
9
8
7
6
5
4
3
2
1
ppm
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28.83
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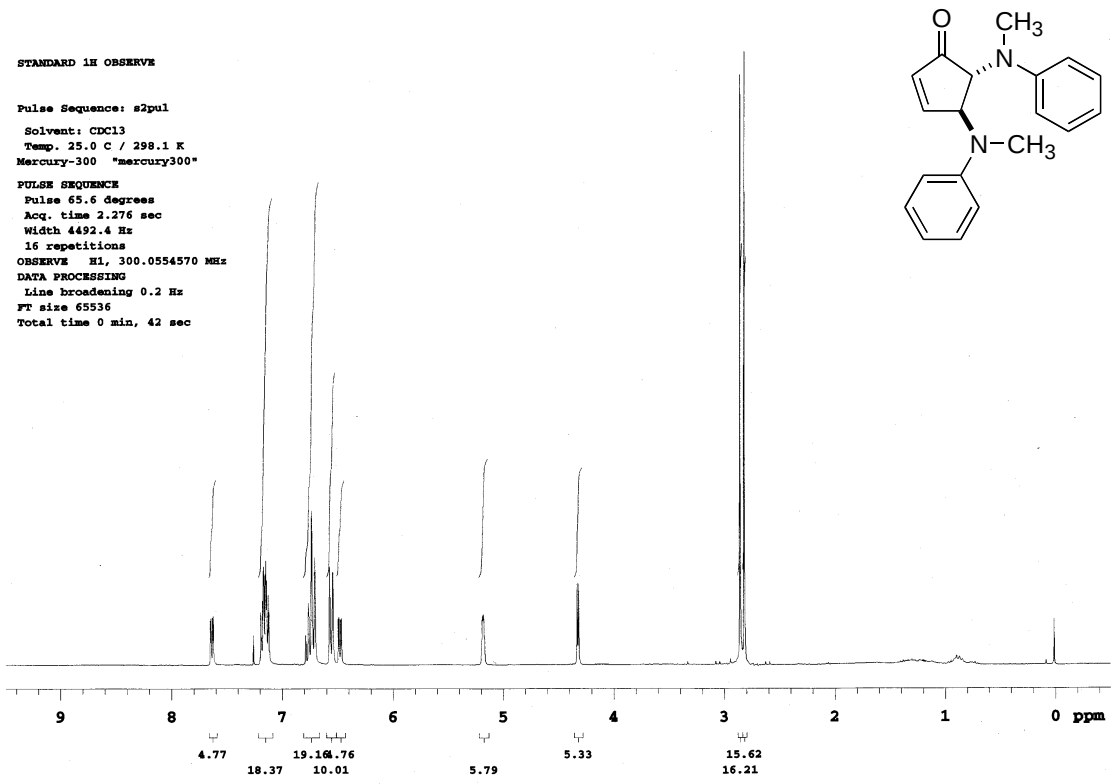
9.37
13.27
5.00
34.89
200
180
160
140
120
100
80
60
40
20
ppm

4f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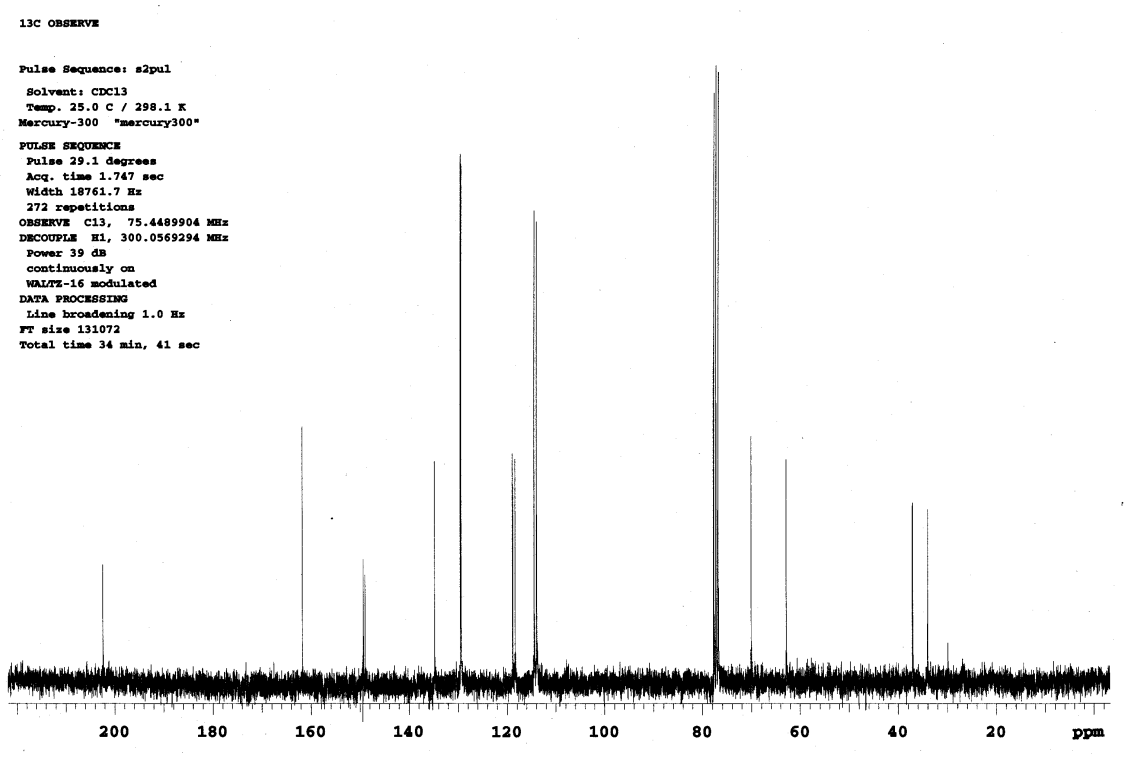
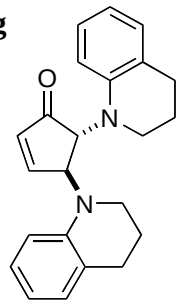
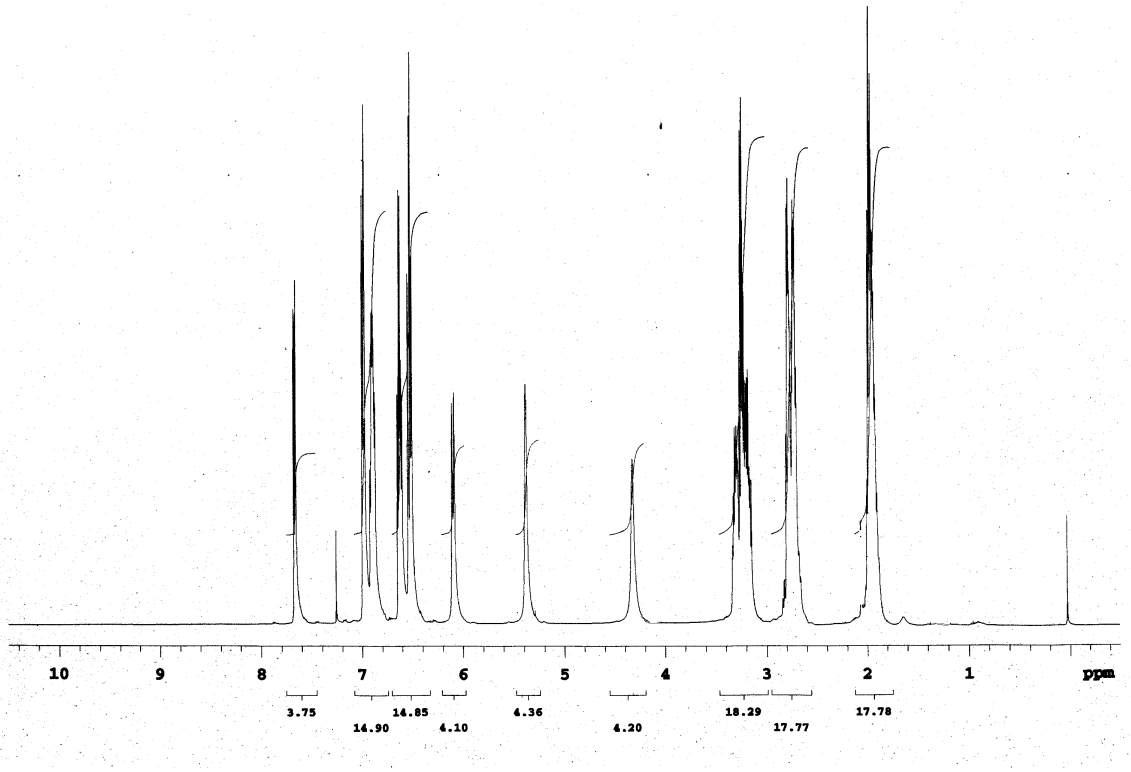
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"
PULSE SEQUENCE
Pulse 65.6 degrees
Acq. time 2.276 sec
Width 4492.4 Hz
16 repetitions
OBSERVE H1, 300.0554570 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 42 sec
O
CH3
N
N−CH3
9
8
7
6
5
4
3
2
1
0 ppm
4.77
18.37
19.16
4.76
10.01
5.79
5.33
15.62
16.21


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"
PULSE SEQUENCE
Pulse 29.1 degrees
Acq. time 1.747 sec
Width 18761.7 Hz
272 repetitions
OBSERVE C13, 75.4489904 MHz
DECOUPLE H1, 300.0569294 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 34 min, 41 sec
200
180
160
140
120
100
80
60
40
20
ppm

4g


O
N
N


10
9
8
7
6
5
4
3
2
1
ppm
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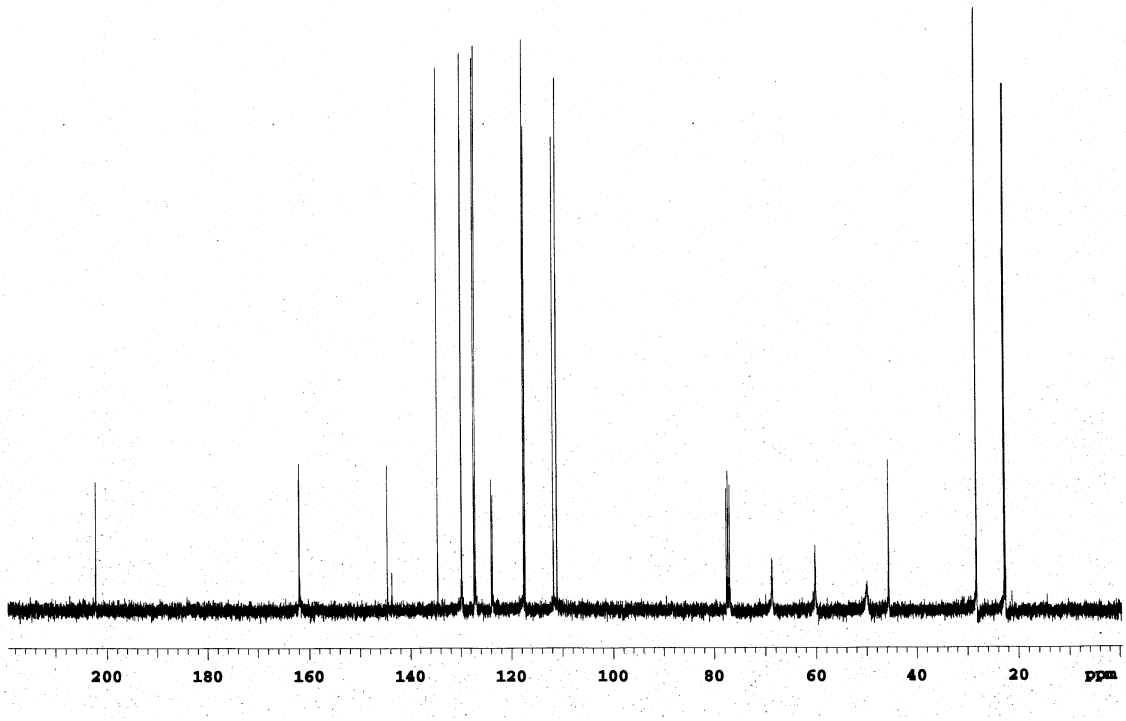
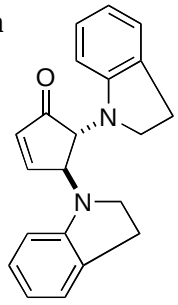
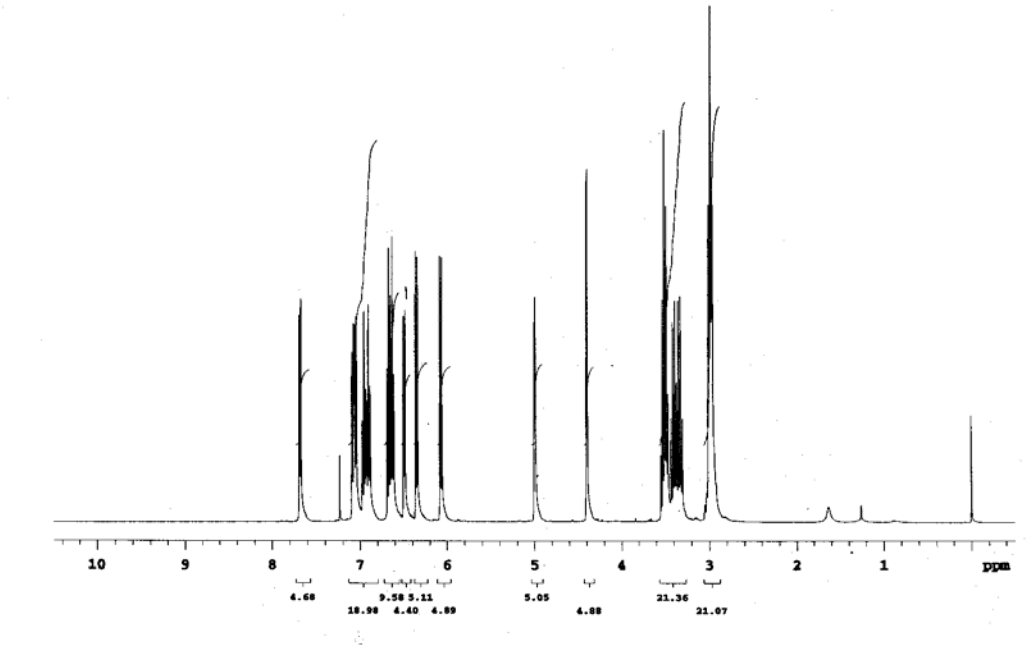
14.85
6.10
4.36
4.20
18.29
17.77
17.78


200
180
160
140
120
100
80
60
40
20
ppm

4h


O
N
N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9
8
7
6
5
4
3
2
1
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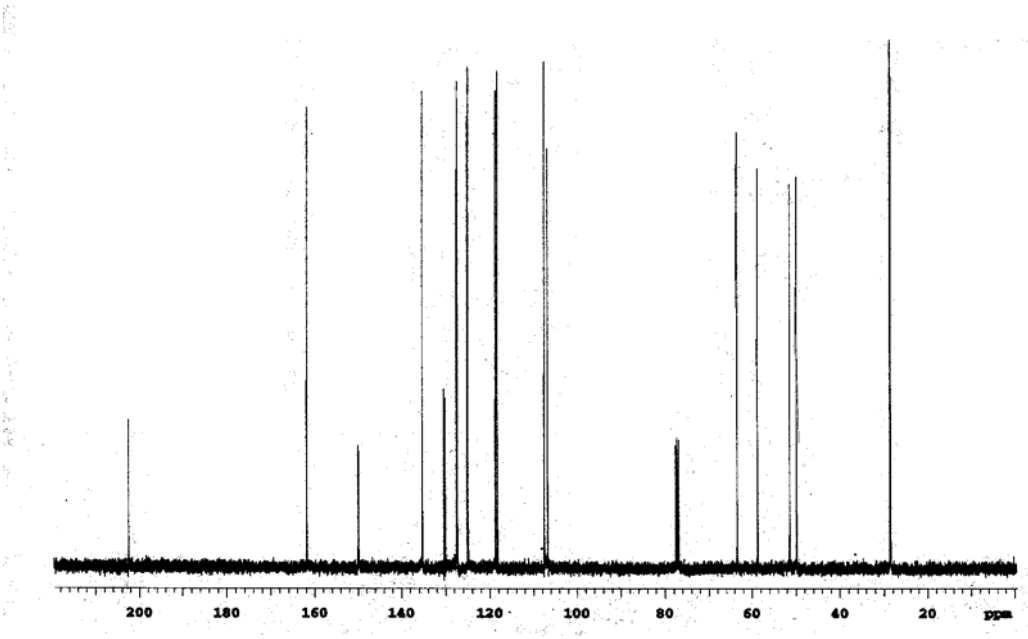
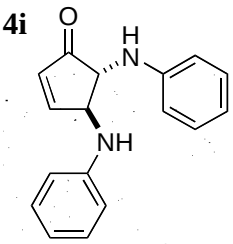
9.58
4.40
5.11
4.89
5.05
4.88
21.36
21.07


200
180
160
140
120
100
80
60
40
20
ppm

4i


O
H
N
NH

13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
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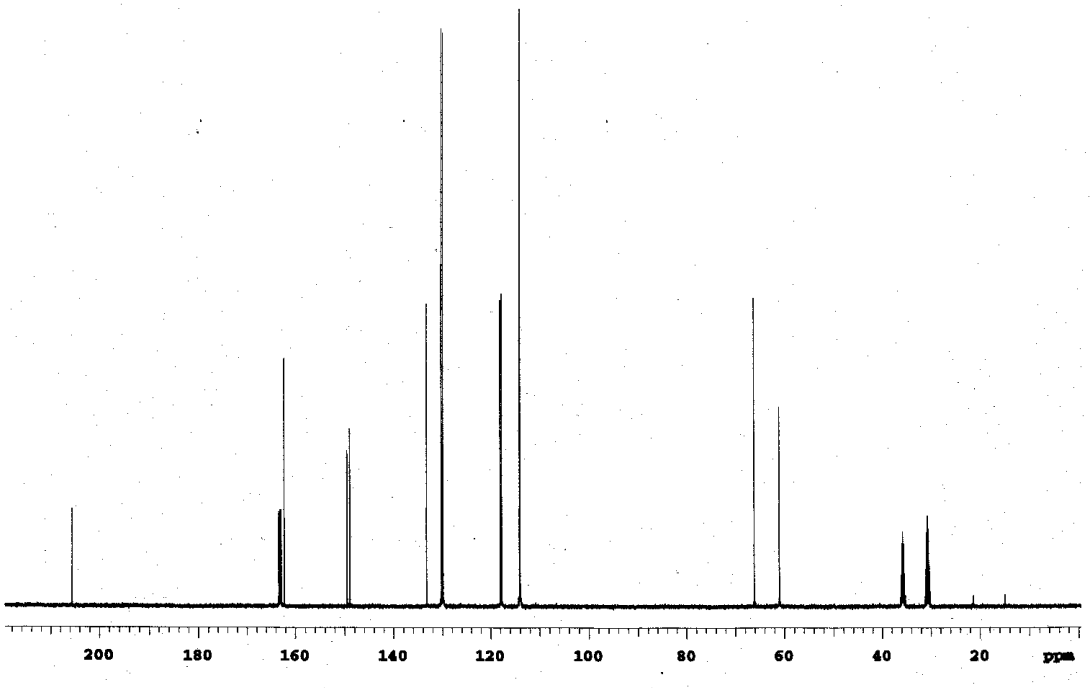
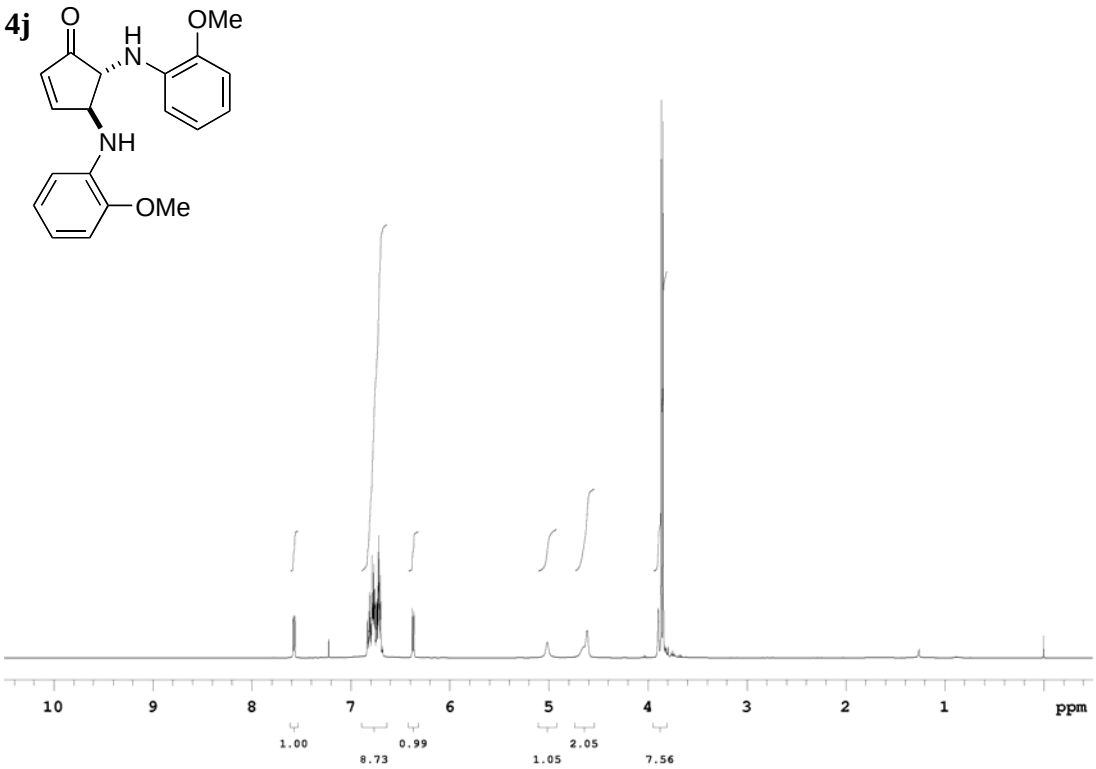
4.06
4.05
0.97
1.00
1.00
1.01
0.98
0.56


200
180
160
140
120
100
80
60
40
20
ppm

4j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H
N
OMe
NH
OMe
10
9
8
7
6
5
4
3
2
1
ppm
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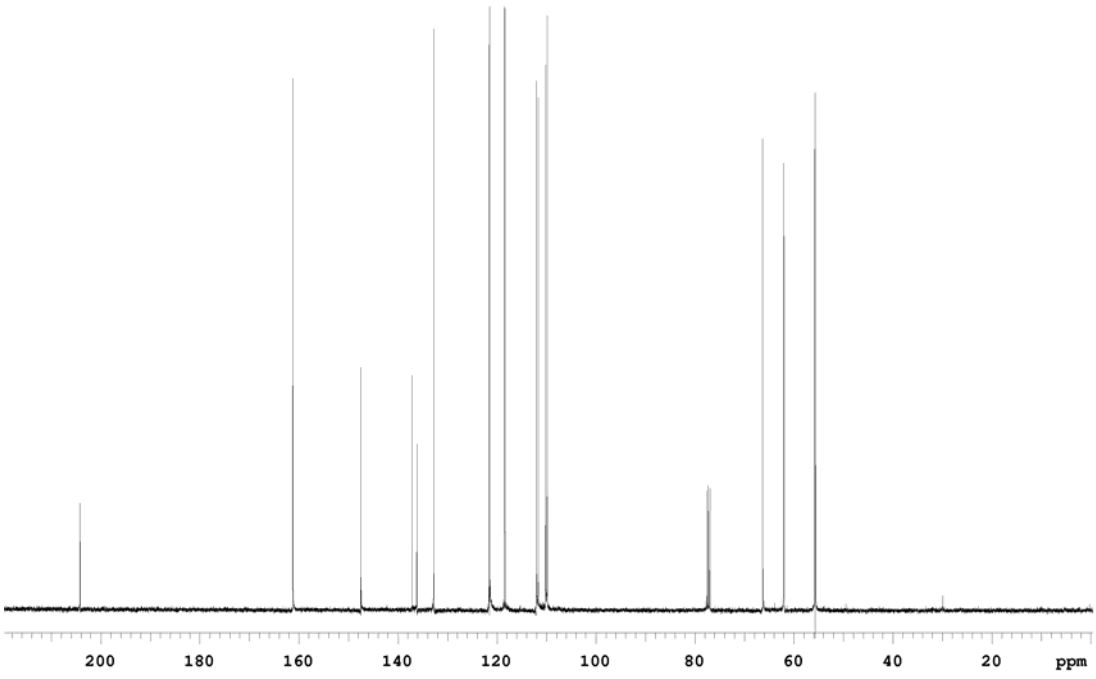
8.73
0.99
1.05
2.05
7.56


200
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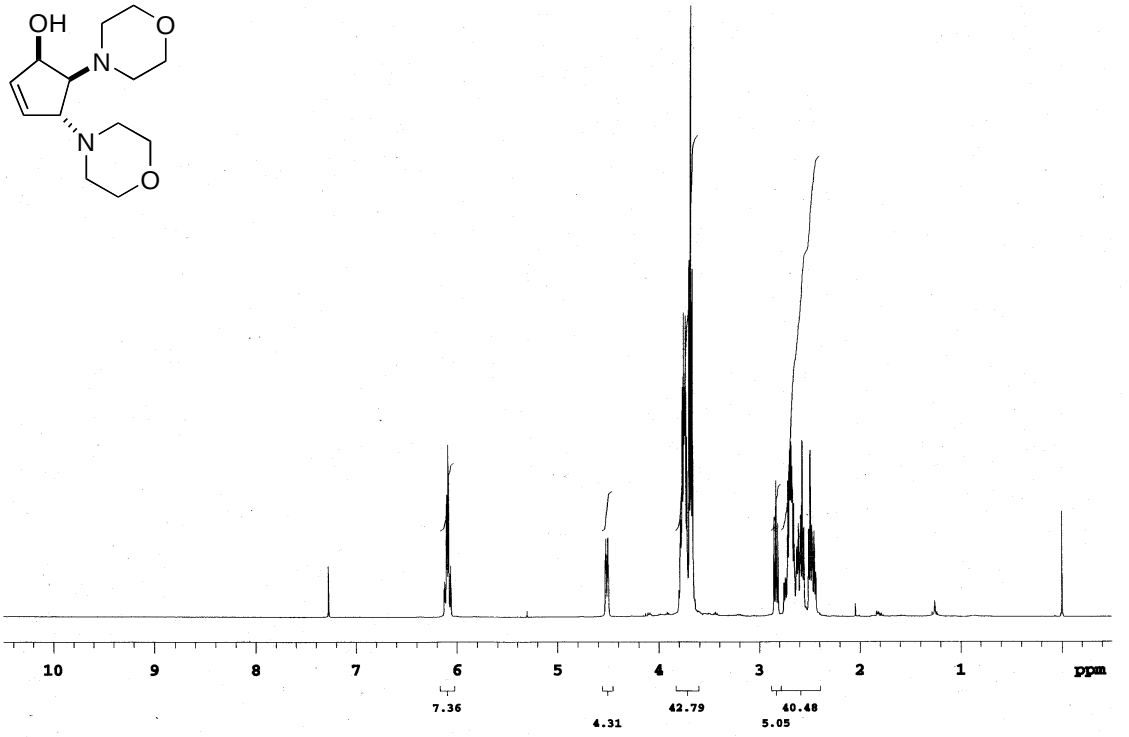
160
140
120
100
80
60
40
20
ppm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N
N
O
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9
8
7
6
5
4
3
2
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ppm
7.36
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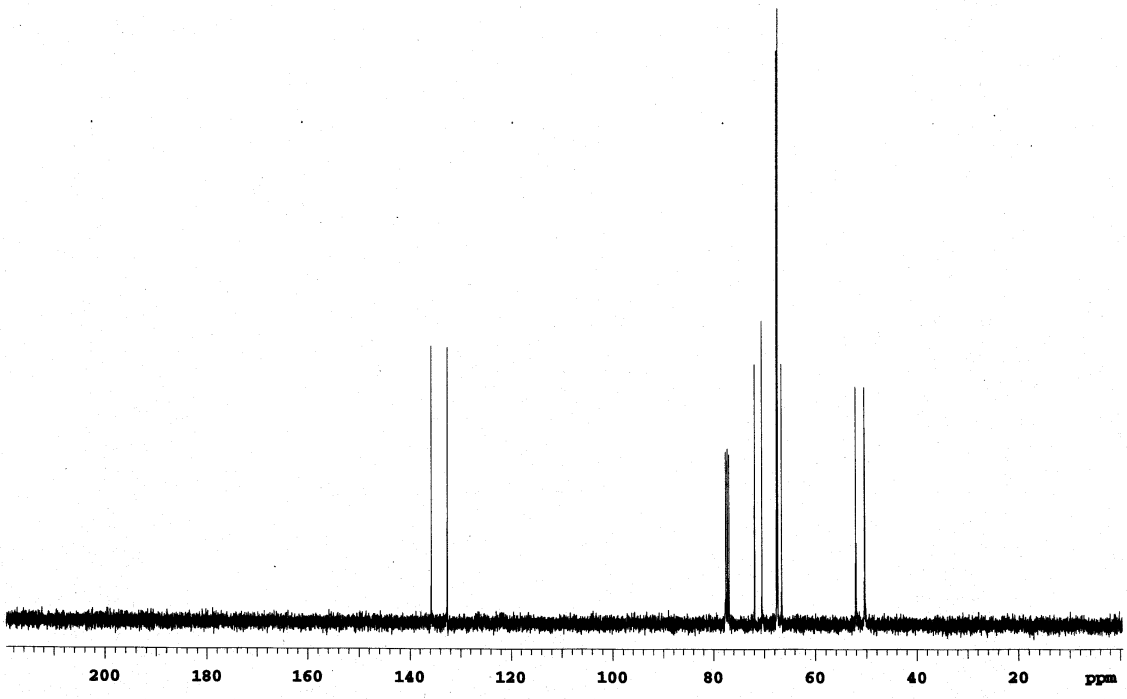
40.48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160
140
120
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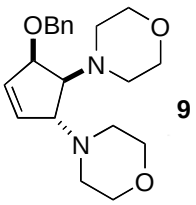
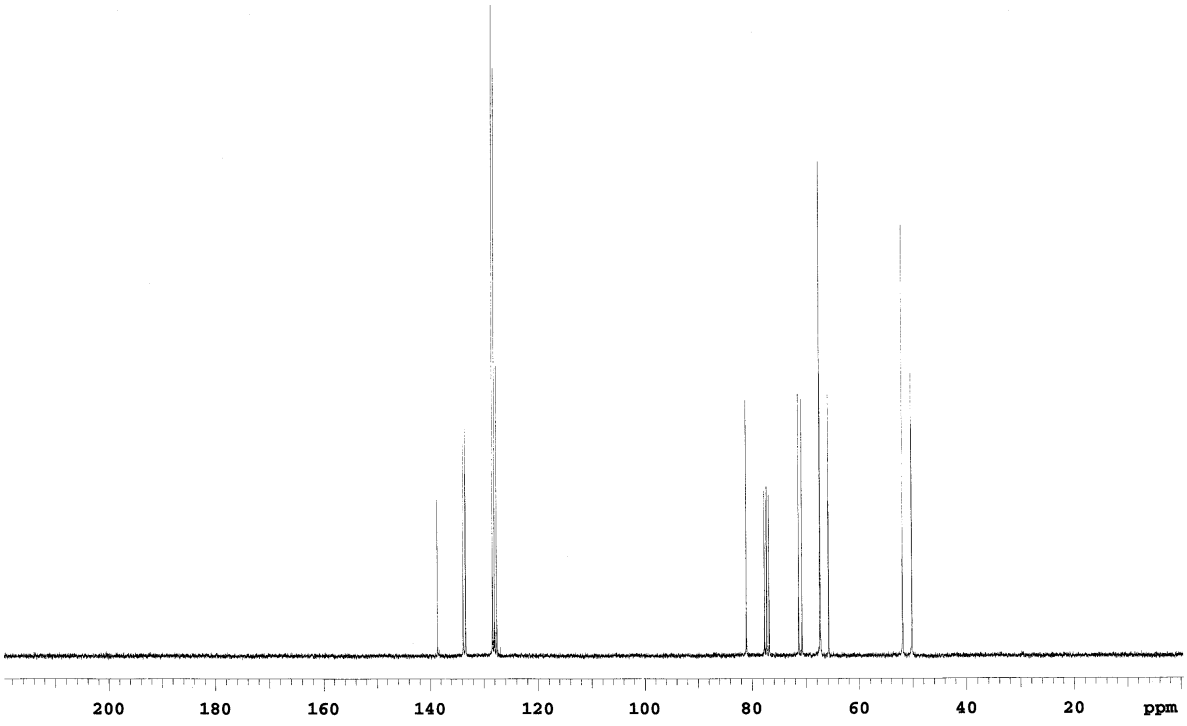
80
60
40
20
ppm



9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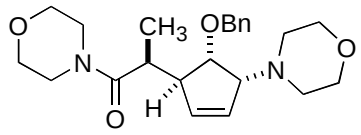
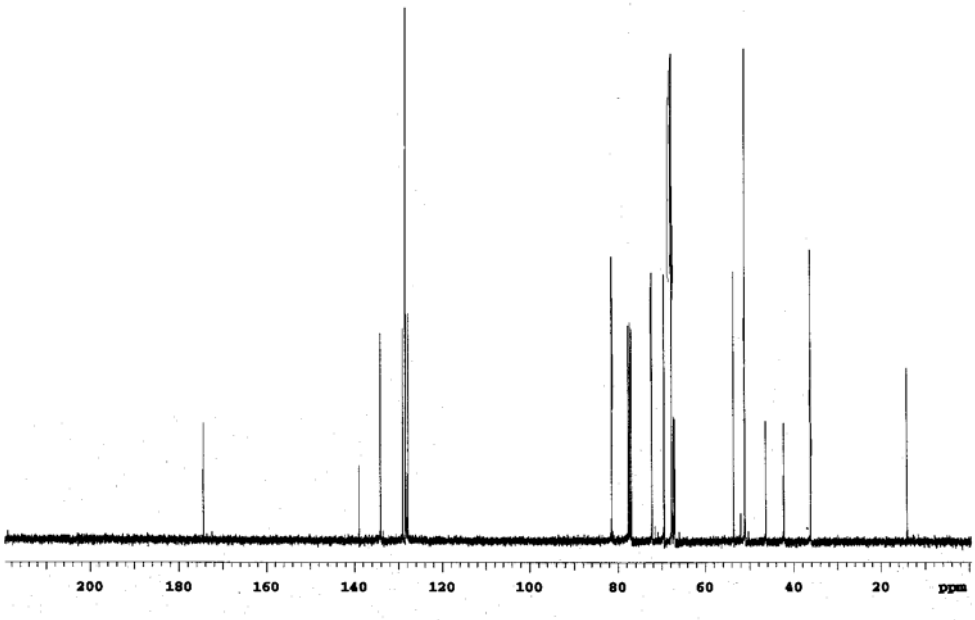
160
140
120
100
80
60
40
20
ppm

10


O
N
CH3
OBn
O
N
O
H

13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


200
180
160
140
120
100
80
60
40
20
ppm

X-Ray Structure and Crystal Data for 4d (determined by Dr. A. J. Lough)

(Thermal ellipsoids are shown at 30% probability):

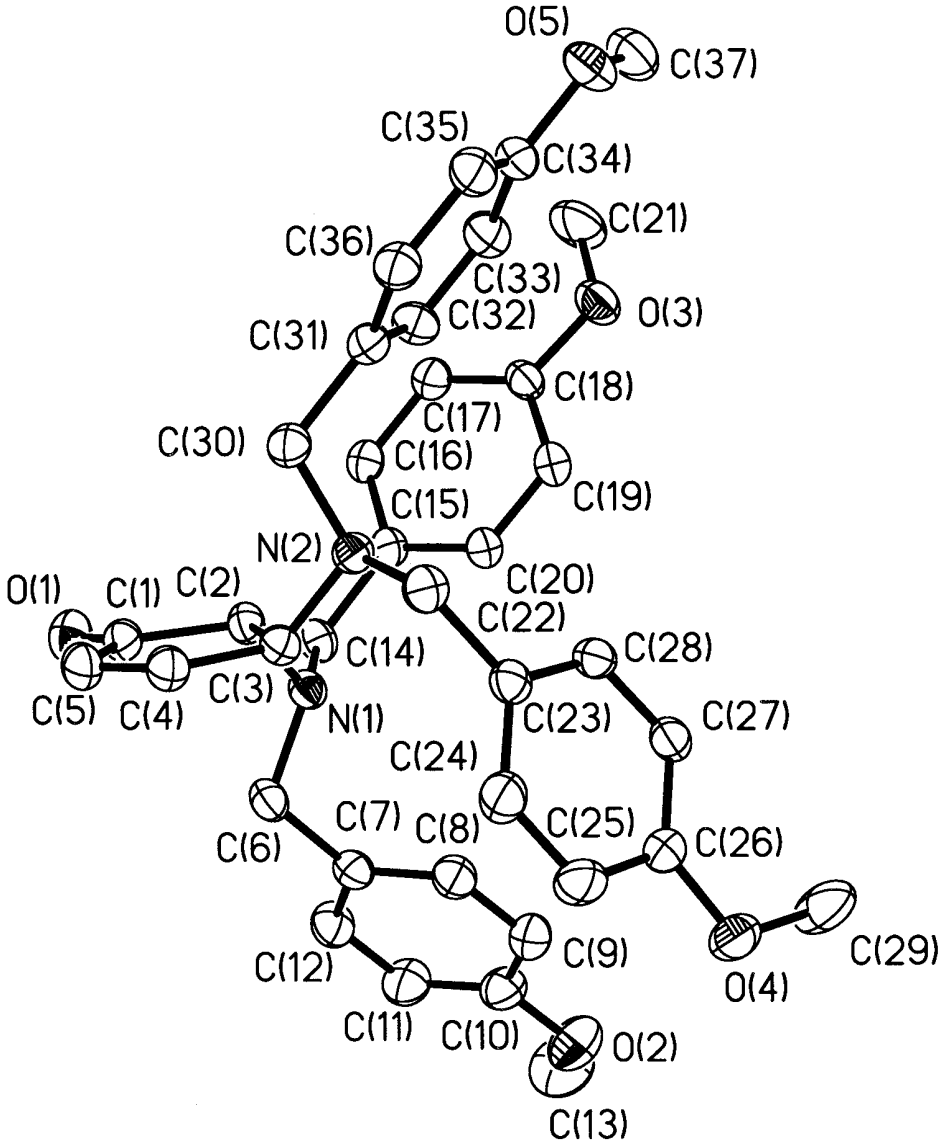


Table 1. Crystal data and structure refinement for **4d**.

Identification code	k01288	
Empirical formula	C37 H40 N2 O5	
Formula weight	592.71	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.3806(4) Å	α= 90°.
	b = 23.2130(10) Å	β= 94.869(2)°.
	c = 13.4673(6) Å	γ = 90°.
Volume	3233.4(2) $Å^3$	
Z	4	
Density (calculated)	1.218 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	1264	
Crystal size	0.30 x 0.30 x 0.12 mm^3	
Theta range for data collection	2.59 to 25.07°.	
Index ranges	0<=h<=12, 0<=k<=27, -16<=l<=15	
Reflections collected	22437	
Independent reflections	5707 [R(int) = 0.097]	
Completeness to theta = 25.07°	99.5 %	
Absorption correction	Semi-empirical from equivalent reflections	
Max. and min. transmission	0.9904 and 0.9762	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5707 / 2 / 410	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1485	
R indices (all data)	R1 = 0.1210, wR2 = 0.1773	
Extinction coefficient	0.0071(12)	
Largest diff. peak and hole	0.243 and -0.174 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5606(2)	2948(1)	5952(2)	64(1)
O(2)	3945(3)	440(1)	1185(2)	100(1)
O(3)	9214(2)	3911(1)	1120(2)	63(1)
O(4)	9160(2)	130(1)	2289(2)	69(1)
O(5)	13362(2)	4162(1)	3102(2)	67(1)
N(1)	6479(2)	2305(1)	4157(2)	41(1)
N(2)	9663(2)	2382(1)	4998(2)	41(1)
C(1)	6611(3)	2679(1)	5927(2)	46(1)
C(2)	7292(2)	2560(1)	4986(2)	41(1)
C(3)	8442(2)	2172(1)	5339(2)	40(1)
C(4)	8369(3)	2123(1)	6450(2)	48(1)
C(5)	7348(3)	2398(1)	6759(2)	54(1)
C(6)	5601(3)	1856(1)	4469(2)	47(1)
C(7)	5160(3)	1467(1)	3611(2)	45(1)
C(8)	6042(3)	1191(1)	3068(2)	53(1)
C(9)	5652(3)	846(1)	2261(2)	61(1)
C(10)	4343(3)	775(2)	1991(2)	63(1)
C(11)	3450(3)	1039(2)	2530(3)	66(1)
C(12)	3864(3)	1381(2)	3333(2)	58(1)
C(13*)	4768(8)	140(3)	580(6)	109(3)
C(13)	2690(5)	483(4)	697(6)	111(3)
C(14)	5801(2)	2731(1)	3499(2)	45(1)
C(15)	6726(2)	3063(1)	2905(2)	41(1)
C(16)	6586(3)	3651(1)	2743(2)	47(1)
C(17)	7395(3)	3954(1)	2155(2)	50(1)
C(18)	8353(3)	3661(1)	1713(2)	48(1)
C(19)	8520(3)	3077(1)	1874(2)	45(1)
C(20)	7716(2)	2782(1)	2463(2)	42(1)
C(21)	8988(4)	4493(2)	831(3)	95(1)
C(22)	10651(2)	1927(1)	4997(2)	47(1)

C(23)	10258(2)	1460(1)	4263(2)	44(1)
C(24)	9979(3)	907(1)	4576(2)	58(1)
C(25)	9607(3)	476(1)	3904(2)	64(1)
C(26)	9511(3)	589(1)	2896(2)	50(1)
C(27)	9749(3)	1139(1)	2558(2)	48(1)
C(28)	10117(3)	1563(1)	3251(2)	46(1)
C(29)	9187(5)	206(2)	1244(3)	101(2)
C(30)	10180(3)	2898(1)	5538(2)	46(1)
C(31)	11017(3)	3240(1)	4900(2)	45(1)
C(32)	10484(3)	3490(1)	4024(2)	52(1)
C(33)	11223(3)	3802(1)	3403(2)	55(1)
C(34)	12536(3)	3868(1)	3664(2)	53(1)
C(35)	13086(3)	3626(1)	4533(2)	55(1)
C(36)	12332(3)	3317(1)	5144(2)	50(1)
C(37)	12825(3)	4414(2)	2196(3)	75(1)

Table 3. Bond lengths [Å] and angles [°] for **4d**.

O(1)-C(1)	1.219(3)
O(2)-C(10)	1.370(4)
O(2)-C(13*)	1.412(2)
O(2)-C(13)	1.413(2)
O(3)-C(18)	1.376(3)
O(3)-C(21)	1.418(4)
O(4)-C(26)	1.373(3)
O(4)-C(29)	1.420(4)
O(5)-C(34)	1.373(3)
O(5)-C(37)	1.423(4)
N(1)-C(2)	1.466(3)
N(1)-C(14)	1.467(3)
N(1)-C(6)	1.469(3)
N(2)-C(3)	1.468(3)
N(2)-C(22)	1.473(3)
N(2)-C(30)	1.476(3)
C(1)-C(5)	1.457(4)
C(1)-C(2)	1.527(4)
C(2)-C(3)	1.538(4)
C(3)-C(4)	1.509(4)
C(4)-C(5)	1.334(4)
C(6)-C(7)	1.507(4)
C(7)-C(8)	1.377(4)
C(7)-C(12)	1.380(4)
C(8)-C(9)	1.384(4)
C(9)-C(10)	1.386(4)
C(10)-C(11)	1.370(5)
C(11)-C(12)	1.380(4)
C(13*)-C(13*)#1	1.796(11)
C(14)-C(15)	1.512(4)
C(15)-C(16)	1.388(4)
C(15)-C(20)	1.392(4)
C(16)-C(17)	1.393(4)

C(17)-C(18)	1.381(4)
C(18)-C(19)	1.382(4)
C(19)-C(20)	1.380(4)
C(22)-C(23)	1.500(4)
C(23)-C(28)	1.380(4)
C(23)-C(24)	1.389(4)
C(24)-C(25)	1.382(4)
C(25)-C(26)	1.379(4)
C(26)-C(27)	1.383(4)
C(27)-C(28)	1.388(4)
C(30)-C(31)	1.501(4)
C(31)-C(32)	1.386(4)
C(31)-C(36)	1.388(4)
C(32)-C(33)	1.387(4)
C(33)-C(34)	1.386(4)
C(34)-C(35)	1.378(4)
C(35)-C(36)	1.383(4)

C(10)-O(2)-C(13*)	125.4(5)
C(10)-O(2)-C(13)	122.1(4)
C(13*)-O(2)-C(13)	110.3(6)
C(18)-O(3)-C(21)	117.4(3)
C(26)-O(4)-C(29)	117.9(3)
C(34)-O(5)-C(37)	117.4(2)
C(2)-N(1)-C(14)	113.8(2)
C(2)-N(1)-C(6)	113.6(2)
C(14)-N(1)-C(6)	111.9(2)
C(3)-N(2)-C(22)	112.4(2)
C(3)-N(2)-C(30)	113.7(2)
C(22)-N(2)-C(30)	111.0(2)
O(1)-C(1)-C(5)	127.1(3)
O(1)-C(1)-C(2)	125.0(3)
C(5)-C(1)-C(2)	107.9(2)
N(1)-C(2)-C(1)	115.3(2)
N(1)-C(2)-C(3)	112.3(2)

C(1)-C(2)-C(3)	104.5(2)
N(2)-C(3)-C(4)	116.9(2)
N(2)-C(3)-C(2)	112.1(2)
C(4)-C(3)-C(2)	104.4(2)
C(5)-C(4)-C(3)	112.4(3)
C(4)-C(5)-C(1)	110.7(3)
N(1)-C(6)-C(7)	111.2(2)
C(8)-C(7)-C(12)	117.8(3)
C(8)-C(7)-C(6)	120.9(2)
C(12)-C(7)-C(6)	121.3(3)
C(7)-C(8)-C(9)	121.5(3)
C(8)-C(9)-C(10)	119.3(3)
C(11)-C(10)-O(2)	120.1(3)
C(11)-C(10)-C(9)	120.0(3)
O(2)-C(10)-C(9)	119.9(3)
C(10)-C(11)-C(12)	119.6(3)
C(7)-C(12)-C(11)	121.8(3)
O(2)-C(13*)-C(13*)#1	154.2(10)
N(1)-C(14)-C(15)	111.7(2)
C(16)-C(15)-C(20)	117.7(3)
C(16)-C(15)-C(14)	121.4(2)
C(20)-C(15)-C(14)	120.8(3)
C(15)-C(16)-C(17)	121.7(3)
C(18)-C(17)-C(16)	119.2(3)
O(3)-C(18)-C(17)	124.7(3)
O(3)-C(18)-C(19)	115.2(3)
C(17)-C(18)-C(19)	120.1(3)
C(20)-C(19)-C(18)	120.1(3)
C(19)-C(20)-C(15)	121.2(3)
N(2)-C(22)-C(23)	111.7(2)
C(28)-C(23)-C(24)	117.0(3)
C(28)-C(23)-C(22)	121.6(3)
C(24)-C(23)-C(22)	121.3(3)
C(25)-C(24)-C(23)	121.6(3)
C(26)-C(25)-C(24)	119.9(3)

O(4)-C(26)-C(25)	115.6(3)
O(4)-C(26)-C(27)	124.4(3)
C(25)-C(26)-C(27)	120.0(3)
C(26)-C(27)-C(28)	118.7(3)
C(23)-C(28)-C(27)	122.7(3)
N(2)-C(30)-C(31)	110.6(2)
C(32)-C(31)-C(36)	117.5(3)
C(32)-C(31)-C(30)	119.9(2)
C(36)-C(31)-C(30)	122.6(3)
C(31)-C(32)-C(33)	122.0(3)
C(34)-C(33)-C(32)	119.1(3)
O(5)-C(34)-C(35)	116.0(3)
O(5)-C(34)-C(33)	124.1(3)
C(35)-C(34)-C(33)	119.9(3)
C(34)-C(35)-C(36)	120.1(3)
C(35)-C(36)-C(31)	121.4(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	58(1)	72(2)	61(1)	-10(1)	11(1)	8(1)
O(2)	122(2)	88(2)	87(2)	-34(2)	3(2)	-17(2)
O(3)	66(1)	59(2)	66(1)	12(1)	24(1)	-3(1)
O(4)	107(2)	45(1)	57(1)	-5(1)	11(1)	-6(1)
O(5)	54(1)	73(2)	76(2)	9(1)	21(1)	-11(1)
N(1)	37(1)	49(2)	38(1)	0(1)	5(1)	-4(1)
N(2)	35(1)	42(1)	47(1)	-4(1)	5(1)	0(1)
C(1)	42(2)	50(2)	48(2)	-8(1)	10(1)	-4(1)
C(2)	36(1)	49(2)	38(2)	-4(1)	6(1)	-2(1)
C(3)	38(1)	42(2)	41(2)	0(1)	5(1)	-3(1)
C(4)	49(2)	52(2)	44(2)	-3(1)	6(1)	-4(2)
C(5)	61(2)	63(2)	38(2)	-4(2)	7(2)	-10(2)
C(6)	42(2)	59(2)	41(2)	1(1)	9(1)	-8(1)
C(7)	40(2)	48(2)	47(2)	2(1)	6(1)	-4(1)
C(8)	44(2)	58(2)	59(2)	-3(2)	6(2)	-4(2)
C(9)	62(2)	57(2)	67(2)	-9(2)	17(2)	1(2)
C(10)	74(2)	57(2)	57(2)	-8(2)	1(2)	-13(2)
C(11)	51(2)	72(2)	75(2)	-14(2)	-1(2)	-10(2)
C(12)	42(2)	70(2)	63(2)	-7(2)	8(2)	-4(2)
C(13*)	165(9)	82(6)	87(6)	-20(5)	57(6)	-11(6)
C(13)	92(6)	132(8)	100(6)	-30(6)	-37(5)	-26(6)
C(14)	38(2)	56(2)	42(2)	3(1)	5(1)	3(1)
C(15)	36(1)	47(2)	39(2)	1(1)	3(1)	2(1)
C(16)	47(2)	49(2)	47(2)	-5(1)	8(1)	6(1)
C(17)	52(2)	50(2)	49(2)	-1(2)	5(1)	3(2)
C(18)	47(2)	55(2)	42(2)	4(1)	10(1)	-7(2)
C(19)	43(2)	54(2)	41(2)	1(1)	9(1)	4(1)
C(20)	43(2)	46(2)	38(2)	1(1)	6(1)	1(1)
C(21)	111(3)	62(3)	120(3)	29(2)	48(3)	-6(2)
C(22)	39(2)	50(2)	52(2)	0(1)	4(1)	4(1)

C(23)	39(2)	44(2)	50(2)	2(1)	10(1)	5(1)
C(24)	79(2)	50(2)	47(2)	4(2)	10(2)	7(2)
C(25)	93(2)	42(2)	56(2)	7(2)	9(2)	0(2)
C(26)	59(2)	42(2)	52(2)	-3(1)	13(2)	1(1)
C(27)	47(2)	49(2)	49(2)	5(2)	14(1)	2(1)
C(28)	45(2)	39(2)	55(2)	3(1)	12(1)	-1(1)
C(29)	195(5)	56(3)	51(2)	-8(2)	10(3)	-15(3)
C(30)	40(2)	51(2)	47(2)	-7(1)	4(1)	-4(1)
C(31)	44(2)	44(2)	45(2)	-7(1)	5(1)	-4(1)
C(32)	40(2)	56(2)	58(2)	-1(2)	5(1)	-7(1)
C(33)	49(2)	57(2)	59(2)	3(2)	8(2)	-2(2)
C(34)	48(2)	50(2)	63(2)	-7(2)	20(2)	-6(2)
C(35)	38(2)	64(2)	61(2)	-8(2)	6(2)	-2(2)
C(36)	42(2)	54(2)	52(2)	-6(2)	1(1)	-1(1)
C(37)	77(2)	74(3)	77(2)	11(2)	28(2)	-7(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4d**.

	x	y	z	U(eq)
H(2A)	7642	2933	4752	49
H(3A)	8273	1781	5044	48
H(4A)	8980(30)	1867(12)	6950(20)	58
H(5A)	7132	2409	7430	64
H(6A)	4838	2040	4732	56
H(6B)	6048	1624	5011	56
H(8A)	6940	1239	3252	64
H(9A)	6275	659	1895	74
H(11A)	2552	986	2353	79
H(12A)	3239	1562	3705	69
H(13A)	4246	-70	59	163
H(13B)	5302	-132	990	163
H(13C)	5328	416	271	163
H(13D)	2597	208	144	166
H(13E)	2552	875	438	166
H(13F)	2049	398	1170	166
H(14A)	5332	3003	3904	54
H(14B)	5156	2531	3035	54
H(16A)	5921	3851	3041	57
H(17A)	7288	4357	2060	60
H(19A)	9191	2877	1580	55
H(20A)	7840	2381	2568	51
H(21A)	9664	4620	416	143
H(21B)	9000	4736	1427	143
H(21C)	8142	4524	452	143
H(22A)	10790	1758	5672	56
H(22B)	11478	2097	4827	56
H(24A)	10047	823	5269	70
H(25A)	9417	101	4137	76

H(27A)	9662	1224	1866	57
H(28A)	10279	1941	3018	55
H(29A)	8924	-153	902	152
H(29B)	10065	307	1092	152
H(29C)	8590	515	1018	152
H(30A)	10692	2778	6157	55
H(30B)	9454	3140	5725	55
H(32A)	9585	3445	3845	62
H(33A)	10835	3969	2806	66
H(35A)	13985	3672	4714	65
H(36A)	12722	3154	5743	60
H(37A)	13508	4611	1867	112
H(37B)	12157	4693	2341	112
H(37C)	12440	4112	1757	112