Diastereoselective metal-catalyzed [4+2+2] carbocyclization reactions utilizing a rhodium(I) *N*-heterocyclic carbene (NHC) complex: the first example of a rhodium(I)-NHC-catalyzed [m+n+o] carbocyclization

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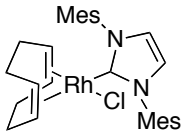
Representative Experimental Procedures and Supplemental Data



RhCl(IMes)(COD). Silver oxide (231 mg, 1.0 mmol) was added to a stirred solution of 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride (685 mg, 2.0 mmol) in dichloromethane (15 mL) at room temperature and allowed to stir for an additional 2 hours. The resulting suspension was filtered through a small plug of celite® into a solution of $[Rh(COD)Cl]_2$ (490 mg, 1.0 mmol) and dichloromethane (5 mL). The yellow solution was stirred at room temperature for *ca*. 18 hours and the solvent was concentrated *in vacuo* to afford a crude solid. Purification by flash chromatography (10-50% gradient elution with ether/pentane) afforded Rh(IMes)(COD)Cl (938 mg, 86%) as orange-yellow crystals.

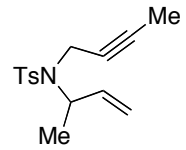
MP 212-214 °C (Uncorrected)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 2H), 6.99 (s, 2H), 6.93 (s, 2H), 4.50 (s, 2H), 3.27 (s, 2H), 2.38 (s, 6H), 2.37 (s, 6H), 2.09 (s, 6H), 1.89-1.78 (m, 4H), 1.58-1.52 (m, 4H).

^{13}C NMR (100 MHz, C_6D_6) δ 183.69 (d, $^1J_{RhC}$ = 51.9 Hz, e), 138.77 (e), 137.70 (e), 136.38 (e) 134.46 (e), 129.81 (o), 128.23 (o), 123.63 (o), 96.21 (d, $^1J_{RhC}$ = 7.6 Hz, o), 67.93 (d, $^1J_{RhC}$ = 14.5 Hz, o), 32.83 (e), 28.50 (e), 21.25 (o), 19.92 (o), 18.24 (o).

IR (neat) 3116 (w), 3084 (w), 2911 (m), 2874 (m), 2829 (w), 1483 (s), 1317 (s), 1261 (s), 848 (s), 738 (s), 708 (vs) cm^{-1}.

HRMS (FAB, M^+) calcd for $C_{29}H_{36}ClN_2Rh$ 550.1620, found 550.1624.



1a

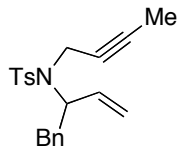
***N*-But-2-yn-1-yl-4-methyl-*N*-(1-methylprop-2-en-1-yl)benzene sulfonamide 1a.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.83 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 2H), 5.71-5.62 (m, 1H), 4.91 (d, *J* = 16.5 Hz, 1H), 4.88 (d, *J* = 10.4 Hz, 1H), 4.63-4.60 (m, 1H), 4.10-4.05 (m, 1H), 3.79-3.73 (m, 1H), 1.97 (s, 3H), 1.33 (t, *J* = 2.3 Hz, 3H), 1.08 (dd, *J* = 7.0, 2.4 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.60 (e), 139.22 (e), 138.22 (o), 129.34 (o), 127.92 (o) 116.40 (e), 80.09 (e), 76.09 (e), 55.05 (o), 33.09 (e), 21.15 (o), 17.20 (o), 3.14 (o).

IR (neat) 3087 (w), 3066 (w), 2981 (m), 2921 (m), 2230 (w), 1640 (w), 1598 (m), 1336 (vs), 1157 (vs), 1095 (vs) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{15}H_{19}NO_2S$ 277.1136, found 277.1115.



1b

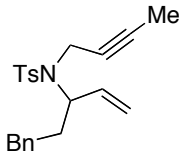
***N*-(1-benzylprop-2-en-1-yl)-*N*-but-2-yn-1-yl-4-methylbenzene sulfonamide 1b.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.09-7.01 (m, 5H), 6.72 (d, *J* = 7.9 Hz, 2H), 5.74 (ddd, *J* = 17.1, 10.3, 6.3 Hz, 1H), 4.95-4.84 (m, 3H), 4.15 (dd, A of ABX, J_{AB} = 18.3 Hz, J_{AX} = 2.4 Hz, 1H), 3.87 (dd, B of ABX, J_{AB} = 18.2 Hz, J_{BX} = 2.4 Hz, 1H), 3.05 (dd, A of ABX, J_{AB} = 13.6 Hz, J_{AX} = 6.2 Hz, 1H), 2.84 (dd, B of ABX, J_{AB} = 13.6 Hz, J_{BX} = 9.0 Hz, 1H), 1.86 (s, 3H), 1.31 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.58 (e), 139.16 (e), 138.47 (e), 135.48 (o), 129.65 (o), 129.23 (o), 128.61 (o), 126.59 (o), 118.13 (e), 80.48 (e), 75.86 (e), 61.86 (o), 39.64 (e), 34.06 (e), 21.09 (o), 3.12 (o).

IR (neat) 3086 (w), 3064 (w), 3028 (w), 2921 (w), 2856 (w), 1598 (w), 1496 (w), 1455 (w), 1337 (m), 1160 (vs), 1094 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{21}H_{23}NO_2S$ 353.1449, found 353.1442.



1c

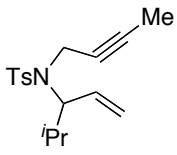
***N*-But-2-yn-1-yl-4-methyl-*N*-[1-(2-phenylethyl)prop-2-en-1-yl] benzenesulfonamide 1c.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (d, J = 8.2 Hz, 2H), 7.15-7.13 (m, 2H), 7.07-7.05 (m, 3H), 6.76 (d, J = 7.9 Hz, 2H), 5.59 (ddd, J = 17.3, 10.6, 5.8 Hz, 1H), 4.88 (dt, J = 17.3, 1.3 Hz, 1H), 4.85 (dt, J = 10.5, 1.2 Hz, 1H), 4.57-4.51 (m, 1H), 4.12 (dd, A of ABX, J_{AB} = 18.3 Hz, J_{AX} = 2.3 Hz, 1H), 3.79 (dd, B of ABX, J_{AB} = 18.3 Hz, J_{BX} = 2.4 Hz, 1H), 2.76 (ddd, A of ABMX, J_{AB} = 15.0 Hz, J_{AX} = 10.6 Hz, J_{AM} = 5.5 Hz, 1H), 2.52 (ddd, B of ABMX, J_{AB} = 15.0 Hz, J_{BX} = 10.9 Hz, J_{BM} = 5.4 Hz, 1H), 2.00-1.90 (m, 1H), 1.87 (s, 3H), 1.80-1.71 (m, 1H), 1.32 (t, J = 2.4 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.65 (e), 142.11 (e), 139.28 (e), 136.45 (o), 129.30 (o), 128.73 (o), 128.61 (o), 127.97 (o), 126.14 (o), 117.44 (e), 79.95 (e), 76.01 (e), 59.90 (o), 33.88 (e), 33.33 (e), 32.98 (e), 21.09 (o), 3.15 (o).

IR (neat) 3085 (w), 3063 (w), 3027 (w), 2921 (w), 2859 (w), 1599 (w), 1496 (w), 1455 (w), 1338 (s), 1160 (vs), 1094 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{22}H_{25}NO_2S$ 367.1606, found 367.1605.



1d

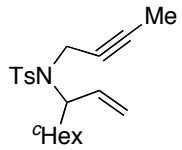
***N*-But-2-yn-1-yl-*N*-(1-isopropylprop-2-en-1-yl)-4-methylbenzene sulfonamide 1d.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.80 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 7.9 Hz, 2H), 5.63 (ddd, J = 17.1, 10.4, 9.2 Hz, 1H), 4.85 (d, J = 16.5 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.02 (t, J = 9.8 Hz, 1H), 4.00-3.85 (m, 2H), 1.93 (s, 3H), 1.81-1.75 (m, 1H), 1.33 (t, J = 2.2 Hz, 3H), 1.05 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.53 (e), 139.25 (e), 135.20 (o), 129.12 (o), 128.15 (o), 118.52 (e), 80.24 (e), 75.60 (e), 67.85 (o), 33.88 (e), 30.07 (o), 21.12 (o), 20.46 (o), 20.32 (o), 3.09 (o).

IR (neat) 3077 (w), 2963 (m), 2923 (m), 2874 (w), 1599 (w), 1337 (s), 1159 (s), 1092 (s) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{17}H_{23}NO_2S$ 305.1449, found 305.1432.



1e

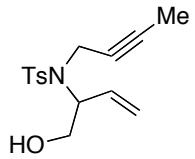
***N*-But-2-yn-1-yl-*N*-(1-cyclohexylprop-2-en-1-yl)-4-methylbenzene sulfonamide 1e.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.84 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 8.2 Hz, 2H), 5.61 (dt, J = 18.1, 9.1 Hz, 1H), 4.90 (d, J = 15.8 Hz, 1H), 4.85 (d, J = 11.5 Hz, 1H), 4.18 (t, J = 9.5 Hz, 1H), 3.95 (dq, A of ABX, J_{AB} = 18.4 Hz, J_{AX} = 2.4 Hz, 1H), 3.85 (dq, B of ABX, J_{AB} = 18.2 Hz, J_{BX} = 2.4 Hz, 1H), 2.15-2.14 (m, 1H), 1.88 (s, 3H), 1.72-1.47 (m, 5H), 1.33 (t, J = 2.4 Hz, 3H), 1.15-1.08 (m, 4H), 0.78-0.69 (m, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.36 (e), 139.48 (e), 135.01 (o), 129.07 (o), 128.17 (o), 118.53 (e), 80.07 (e), 75.70 (e), 66.72 (o), 39.13 (o), 33.84 (e), 30.91 (e), 30.72 (e), 26.66 (e), 26.41 (e), 26.32 (e), 21.09 (o), 3.09 (o).

IR (neat) 3076 (w), 2923 (s), 2852 (s), 1599 (w), 1450 (m), 1337 (s), 1156 (s), 1094 (m), 1040 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{20}H_{27}NO_2S$ 345.1762, found 345.1749.



1f

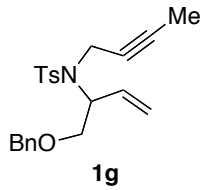
***N*-But-2-yn-1-yl-*N*-[1-(hydroxymethyl)prop-2-en-1-yl]-4-methyl benzenesulfonamide 1f.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.83 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.2 Hz, 2H), 5.56 (ddd, J = 16.8, 10.7, 5.5 Hz, 1H), 4.99 (d, J = 17.4 Hz, 1H), 4.92 (d, J = 10.7 Hz, 1H), 4.66 (dd, J = 13.7, 5.8 Hz, 1H), 4.20 (dd, A of ABX, J_{AB} = 18.3 Hz, J_{AX} = 2.4 Hz, 1H), 3.80 (dd, B of ABX, J_{AB} = 18.3 Hz, J_{BX} = 2.1 Hz, 1H), 3.75-3.72 (m, 1H), 3.69-3.63 (m, 1H), 2.57 (bs, 1H), 1.95 (s, 3H), 1.30 (t, J = 2.3 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 143.11 (e), 138.69 (e), 133.17 (o), 129.43 (o), 128.02 (o), 118.69 (e), 80.74 (e), 75.62 (e), 62.74 (e), 62.00 (o), 33.70 (e), 21.15 (o), 2.97 (o).

IR (neat) 3538 (bs), 2922 (w), 2882 (w), 1598 (w), 1428 (w), 1333 (m), 1159 (s), 1094 (s), 1054 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{15}H_{19}NO_3S$ 293.1086, found 293.1086.



1g

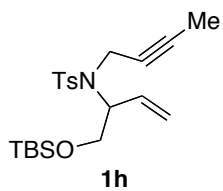
***N*-{1-[(Benzyloxy)methyl]prop-2-en-1-yl}-*N*-but-2-yn-1-yl-4-methylbenzenesulfonamide 1g.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.86 (d, J = 8.1 Hz, 2H), 7.15-7.06 (m, 5H), 6.73 (d, J = 8.1 Hz, 2H), 5.81 (ddd, J = 16.8, 10.4, 5.5 Hz, 1H), 5.12 (d, J = 17.4 Hz, 1H), 5.00 (d, J = 10.6 Hz, 1H), 4.86 (q, J = 6.1 Hz, 1H), 4.24 (dq, A of ABX, J_{AB} = 18.0 Hz, J_{AX} = 2.0 Hz, 1H), 4.18 (d, A of AB, J_{AB} = 11.2 Hz, 1H), 4.15 (d, B of AB, J_{AB} = 11.9 Hz, 1H), 4.02 (dq, B of ABX, J_{AB} = 18.0 Hz, J_{BX} = 2.4 Hz, 1H), 3.61 (dd, A of ABX, J_{AB} = 9.9 Hz, J_{AX} = 6.0 Hz, 1H), 3.53 (dd, B of ABX, J_{AB} = 9.9 Hz, J_{BX} = 6.2 Hz, 1H), 1.88 (s, 3H), 1.28 (t, J = 2.4Hz, 3H)

^{13}C NMR (100 MHz, C_6D_6) δ 142.41 (e), 139.33 (e), 138.61 (e), 134.27 (o), 129.13 (o), 128.46 (o), 128.11 (o), 127.64 (o), 118.31 (e), 80.01 (e), 75.87 (e), 73.02 (e), 71.09 (e), 59.50 (o), 34.53 (e), 21.09 (o), 3.09 (o).

IR (neat) 3064 (m), 3030 (m), 2920 (m), 2861 (m), 1641 (m), 1598 (m), 1496 (m), 1455 (m), 1336 (s), 1159 (vs), 1094 (s).

HRMS (CI, M+H^+) calcd for $C_{22}H_{26}NO_3S$ 384.1633, found 384.1635.



1h

***N*-[1-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)prop-2-en-1-yl]-*N*-but-2-yn-1-yl-4-methylbenzenesulfonamide 1h.**

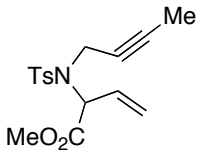
^{1}H NMR (400 MHz, C_6D_6) δ 7.85 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 8.2 Hz, 2H), 5.88 (ddd, J = 17.0, 10.6, 6.1 Hz, 1H), 5.13 (dt, J =

17.4, 1.5 Hz, 1H), 5.02 (dt, J = 10.6, 1.4 Hz, 1H), 4.65 (q, J = 6.3 Hz, 1H), 4.26 (dq, A of ABX, J_{AB} = 18.0, J_{AX} = 2.3 Hz, 1H), 4.05 (dd, B of ABX, J_{AB} = 18.0, J_{BX} = 2.3 Hz, 1H), 3.90 (dd, A of ABX, J_{AB} = 10.3 Hz, J_{AX} = 6.7 Hz, 1H), 3.86 (dd, B of ABX, J_{AB} = 10.3, J_{BX} = 6.0 Hz, 1H), 1.89 (s, 3H), 1.32 (t, J = 2.3 Hz, 3H), 0.90 (s, 9H), 0.01 (s, 6H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.55 (e), 139.39 (e), 134.26 (o), 129.29 (o), 118.72 (e), 80.18 (e), 76.09 (e), 64.90 (e), 61.65 (o), 34.92 (e), 26.04 (o), 21.11 (o), 18.44 (e), 3.16 (o), -5.37 (o).

IR (neat) 2955 (m), 2929 (m), 2885 (m), 2857 (m), 1598 (w), 1495 (w), 1472 (m), 1338 (s), 1161 (vs), 1094 (s) cm^{-1}.

HRMS (ESI, M+Na$^+$) calcd for $C_{21}H_{33}NNaO_3SSi$ 430.1848, found 430.1850.



1i

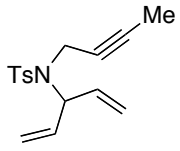
Methyl 2-{but-2-yn-1-yl[(4-methylphenyl)sulfonyl]amino}but-3-enoate 1i.

^{1}H NMR (400 MHz, C_6D_6) δ 7.84 (d, J = 8.2 Hz, 2H), 6.73 (d, J = 8.2 Hz, 2H), 6.07 (ddd, J = 16.8, 10.4, 6.1 Hz, 1H), 5.28 (d, J = 6.1 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 5.04 (d, J = 10.4 Hz, 1H), 4.29 (dq, A of ABX, J_{AB} = 18.0 Hz, J_{AX} = 2.4 Hz, 1H), 4.13 (dq, B of ABX, J_{AB} = 18.0 Hz, J_{BX} = 2.4 Hz, 1H), 3.19 (s, 3H), 1.85 (s, 3H), 1.26 (t, J = 2.4 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 170.00 (e), 142.97 (e), 138.25 (e), 131.53 (o), 129.27 (o), 128.17 (o), 120.10 (e), 80.92 (e), 74.71 (e), 61.95 (o), 51.76 (o), 35.93 (e), 21.08 (o), 3.11 (o).

IR (neat) 3030 (w), 2954 (m), 2922 (m), 1746 (vs), 1598 (w), 1436 (m), 1349 (s), 1162 (s), 1093 (s) cm^{-1}.

HRMS (EI, M$^+$) calcd for $C_{16}H_{19}NO_4S$ 321.1035, found 321.1021.



1j

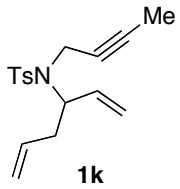
***N*-But-2-yn-1-yl-4-methyl-*N*-(1-vinylprop-2-en-1-yl)benzenesulfonamide 1j.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.86 (d, *J* = 8.3 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 5.79 (2ddd, *J* = 17.1, 10.3, 5.9 Hz, 2H), 5.17-5.14 (m, 1H), 5.02 (2dt, *J* = 17.3, 1.2 Hz, 2H), 4.94 (2dt, *J* = 10.5, 1.2 Hz, 2H), 4.00 (q, *J* = 2.3 Hz, 2H), 1.88 (s, 3H), 1.27 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.59 (e), 139.36 (e), 135.42 (o), 129.17 (o), 118.30 (e), 80.49 (e), 75.78 (e), 62.44 (o), 34.39 (e), 21.15 (o), 3.15 (o).

IR (neat) 2922 (s), 2852 (m), 1598 (w), 1337 (m), 1160 (vs), 1093 (s) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{16}H_{19}NO_2S$ 289.1136, found 289.1127.



1k

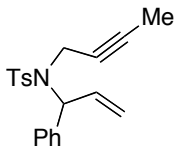
***N*-But-2-yn-1-yl-4-methyl-*N*-(1-vinylbut-3-en-1-yl)benzenesulfonamide 1k.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.78 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 5.70-5.60 (m, 2H), 4.96-4.92 (m, 2H), 4.91-4.88 (m, 2H), 4.53-4.51 (m, 1H), 4.03 (dt, A of ABX, J_{AB} = 18.3 Hz, J_{AX} = 2.1 Hz, 1H), 3.84 (dt, B of ABX, J_{AB} = 18.3 Hz, J_{BX} = 2.1 Hz, 1H), 2.36 (dt, A of ABX, J_{AB} = 14.3 Hz, J_{AX} = 7.6 Hz, 1H), 2.26 (dt, B of ABX, J_{AB} = 14.3 Hz, J_{BX} = 7.3 Hz, 1H), 1.97 (s, 3H), 1.34 (t, *J* = 2.1 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.86 (e), 139.12 (e), 135.99 (o), 135.10 (o), 129.29 (o), 127.97 (o), 117.58 (e), 117.20 (e), 80.35 (e), 75.71 (e), 59.95 (o), 36.85 (e), 33.51 (e), 21.15 (o), 3.12 (o).

IR (neat) 3078 (m), 2980 (s), 2921 (m), 2856 (m), 1642 (w), 1598 (w), 1441 (w), 1338 (m), 1160 (vs), 1093 (s) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{17}H_{21}NO_2S$ 303.1293, found 303.1254.



1l

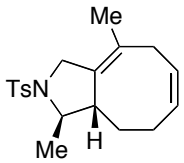
***N*-But-2-yn-1-yl-4-methyl-*N*-(1-phenylprop-2-en-1-yl)benzene sulfonamide 1l.**

^{1}H NMR (400 MHz, C_6D_6) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.10-7.00 (m, 3H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.11 (ddd, *J* = 17.4, 10.7, 7.9 Hz, 1H), 5.80 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 17.1 Hz, 1H), 4.13 (dq, A of ABX, J_{AB} = 18.2 Hz, J_{AX} = 4.8 Hz, 1H), 3.74 (dq, B of ABX, J_{AB} = 18.2 Hz, J_{BX} = 4.6 Hz, 1H), 1.89 (s, 3H), 1.21 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.57 (e), 139.25 (e), 139.00 (e), 134.76 (o), 129.06 (o), 128.65 (o), 128.47 (o), 128.35 (o), 118.80 (e), 80.61 (e), 75.42 (e), 63.98 (o), 34.64 (e), 24.113 (o), 3.05 (o).

IR (neat) 3026 (m), 2929 (m), 2855 (m), 1651 (w), 1599 (m), 1495 (m), 1455 (m), 1344 (s), 1161 (vs), 1095 (s) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{20}H_{22}O_2NS$ 340.1371, found 340.1371.



2a

(6*Z*,9*E*)-3,9-Dimethyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5, 8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2a.

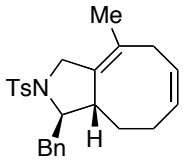
Representative Procedure for Intermolecular Rhodium(I)-Catalyzed [4+2+2] Carbocyclization: Silver triflate (13.0 mg, 0.05 mmol) was added to RhCl(IMes)(COD) (14.0 mg, 0.025 mmol) in anhydrous toluene (5.0 mL) under an atmosphere of nitrogen in a sealed tube. The catalyst was allowed stir in the dark for *ca.* 15 minutes. Enyne **1a** (69.0 mg, 0.25 mmol) was then added to the catalyst under a stream of nitrogen. The sealed tube was evacuated and refilled with 1,3-butadiene three times. The sealed tube was then heated in a 110 ºC oil bath overnight. The resulting mixture was purified by flash chromatography (eluting with 5-10% ethyl acetate/hexanes) furnishing **2a** (62 mg, 75%) as a clear thick oil.

^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (d, J = 7.9 Hz, 2H), 6.79 (d, J = 8.2 Hz, 2H), 5.52 (ddd, J = 11.5, 7.2, 4.8 Hz, 1H), 5.29-5.23 (m, 1H), 4.08 (d, A of AB, J_{AB} = 13.7 Hz, 1H), 3.86 (dd, B of ABX, J_{AB} = 14.0 Hz, J_{BX} = 1.2 Hz, 1H), 3.68 (dq, J = 6.4, 1.2 Hz, 1H), 2.70-2.63 (m, 2H), 2.18 (dd, B of ABX, J_{AB} = 17.6 Hz, J_{BX} = 3.9 Hz, 1H), 1.99 (dt, A of ABX, J_{AB} = 13.6 Hz, J_{AX} = 4.2 Hz, 1H), 1.88 (s, 3H), 1.71 (ddd, B of ABMX, J_{AB} = 13.0 Hz, J_{BX} = 9.8 Hz, J_{BM} = 6.4 Hz 1H), 1.28 (s, 3H), 1.23 (d, J = 6.5 Hz, 3H), 1.17-1.09 (m, 1H), 0.80-0.71 (m, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.62 (e), 137.34 (e), 130.78 (e), 130.32 (o), 129.94 (e), 129.55 (o), 129.00 (o), 127.73 (o), 63.18 (o), 50.42 (e), 48.92 (o), 35.91 (e), 29.35 (e), 25.36 (e), 21.86 (o), 21.07 (o) 20.83 (o).

IR (neat) 3017 (w), 2929 (m), 2865 (m), 1710 (w), 1652 (w), 1598 (w), 1495 (w), 1455 (m), 1377 (m), 1341 (vs), 1305 (m), 1289 (m), 1163 (vs), 1095 (s), 1050 (m), 1018 (m), 756 (m), 666 (vs), 549 (s) cm^{-1}.

HRMS (EI, M^+) calcd. For $C_{19}H_{25}NO_2S$ 331.1606, found 331.1590.



2b

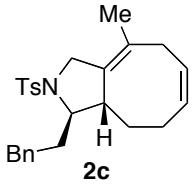
(6*Z*,9*E*)-3-Benzyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2b.

^{1}H NMR (400 MHz, C_6D_6) δ 7.82 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 7.3 Hz, 2H), 7.10 (t, J = 7.5 Hz, 2H), 7.03-7.01 (m, 1H), 6.79 (d, J = 8.2 Hz, 2H), 5.46 (ddd, J = 11.3, 6.7, 4.8 Hz, 1H), 5.16-5.09 (m, 1H), 4.02 (dd, J = 8.9, 3.7 Hz, 1H), 3.98 (d, A of AB, J_{AB} = 14.0 Hz, 1H), 3.88-3.83 (m, 1H), 3.15 (dd, A of ABX, J_{AB} = 13.1 Hz, J_{AX} = 3.7 Hz, 1H), 3.00 (dd, J = 11.8, 4.5 Hz, 1H), 2.83 (dd, B of ABX, J_{AB} = 13.1 Hz, J_{BX} = 8.5 Hz, 1H), 2.67 (dd, A of ABX, J_{AB} = 18.5 Hz, J_{AX} = 6.6 Hz, 1H), 2.19 (dd, B of ABX, J_{AB} = 18.3 Hz, J_{BX} = 2.1 Hz, 1H), 1.99-1.89 (m, 1H), 1.87 (s, 3H), 1.58-1.51 (m, 1H), 1.22 (s, 3H), 0.95 (tt, A of ABX, J_{AB} = 12.4 Hz, J_{AX} = 4.2 Hz, 1H), 0.63 (tt, B of ABX, J_{AB} = 12.5 Hz, J_{BX} = 4.7 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.71 (e), 138.68 (e), 137.43 (e), 130.82 (e), 130.14 (o), 129.91 (o), 129.59 (o), 129.18 (e), 128.53 (o), 128.49 (o), 127.67 (o), 126.57 (o), 68.55 (o), 50.71 (e), 44.80 (o), 42.75 (e), 36.37 (e), 29.15 (e), 24.85 (e), 21.06 (o), 20.84 (o).

IR (neat) 3062 (w), 3025 (w), 2928 (m), 2854 (w), 1731 (w), 1654 (w), 1598 (w), 1494 (m), 1454 (m), 1343 (vs), 1161 (vs), 1096 (s), 1056 (m), 1017 (w), 751 (s), 668 (s), 547 (s) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{25}H_{30}NO_2S$ 408.1992, found 408.1982.



2c

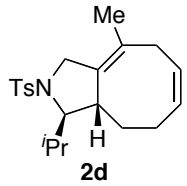
(6*Z*,9*E*)-9-Methyl-2-[(4-methylphenyl)sulfonyl]-3-(2-phenylethyl)-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2c.

^{1}H NMR (400 MHz, C_6D_6) δ 7.79 (d, J = 8.2 Hz, 2H), 7.17-7.05 (m, 5H), 6.76 (d, J = 8.1 Hz, 2H), 5.52 (ddd, J = 11.4, 7.2, 4.7 Hz, 1H), 5.25 (q, J = 9.0 Hz, 1H), 4.10 (d, A of AB, J_{AB} = 14.1 Hz, 1H), 3.95 (dd, B of ABX, J_{AB} = 14.2 Hz, J_{BX} = 1.1 Hz, 1H), 3.72 (dd, J = 7.3, 5.1 Hz, 1H), 2.87 (dd, J = 11.8, 3.7 Hz, 1H), 2.76-2.63 (m, 3H), 2.23-2.09 (m, 2H), 2.05-1.96 (m, 1H), 1.91-1.82 (m, 1H), 1.86 (s, 3H), 1.73-1.65 (m, 1H), 1.28 (s, 3H), 1.09 (tt, A of ABX, J_{AB} = 12.3 Hz, J_{AX} = 4.0 Hz, 1H), 0.63 (tt, B of ABX, J_{AB} = 12.5 Hz, J_{BX} = 4.7 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.82 (e), 142.08 (e), 137.17 (e), 131.24 (e), 130.51 (o), 129.70 (o), 129.63 (o), 128.84 (o), 128.81 (o), 128.67 (o), 127.78 (e), 126.11 (o), 67.22 (o), 50.96 (e), 46.29 (o), 38.22 (e), 36.19 (e), 32.59 (e), 29.58 (e), 25.30 (e), 21.11 (o), 20.92 (o).

IR (neat) 3062 (w), 3024 (m), 2927 (m), 2856 (m), 1652 (w), 1599 (w), 1496 (m), 1454 (m), 1343 (s), 1305 (m), 1290 (w), 1161 (vs), 1095 (m), 1050 (m), 1017 (w), 753 (m), 668 (s), 548 (m) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{26}H_{32}NO_2S$ 422.2148, found 422.2138.



2d

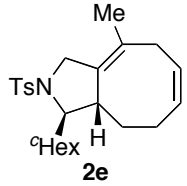
(6*Z*,9*E*)-3-Isopropyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2d.

^{1}H NMR (400 MHz, C_6D_6) δ 7.84 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 7.9 Hz, 2H), 5.51 (ddd, J = 11.3, 7.0, 4.6 Hz, 1H), 5.24 (q, J = 9.0 Hz, 1H), 4.11 (d, A of AB, J_{AB} = 14.3 Hz, 1H), 3.99 (d, B of AB, J_{AB} = 14.0 Hz, 1H), 3.65 (d, J = 4.6 Hz, 1H), 2.98 (dd, J = 11.6, 4.0 Hz, 1H), 2.68 (dd, A of ABX, J_{AB} = 18.2 Hz, J_{AX} = 6.6 Hz, 1H), 2.30-2.19 (m, 2H), 2.08-1.97 (m, 1H), 1.86 (s, 3H), 1.70-1.64 (m, 1H), 1.28 (s, 3H), 1.08 (tt, A of ABX, J_{AB} = 12.4 Hz, J_{AX} = 4.2 Hz, 1H), 0.92 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H), 0.63 (tt, B of ABX, J_{AB} = 12.7 Hz, J_{BX} = 4.4 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.70 (e), 137.12 (e), 132.23 (e), 130.44 (o), 129.55 (o), 128.61 (o), 128.08 (e), 127.85 (o), 73.08 (o), 51.89 (e), 41.88 (o), 36.24 (e), 34.16 (o), 30.34 (e), 25.08 (e), 21.07 (o), 20.89 (o), 19.49 (o), 17.22 (o).

IR (neat) 3017 (w), 2960 (m), 2929 (m), 2871 (m), 1653 (w), 1599 (w), 1494 (w), 1463 (m), 1388 (w), 1344 (s), 1305 (m), 1290 (m), 1162 (vs), 1094 (m), 1051 (m), 1017 (m), 669 (s) cm^{-1}.

HRMS (CI, M+H$^+$) calcd for $C_{21}H_{30}NO_2S$ 360.1992, found 360.2007.



2e

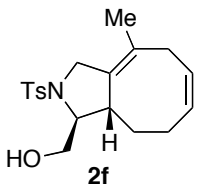
(6*Z*,9*E*)-3-Cyclohexyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2e.

^{1}H NMR (400 MHz, C_6D_6) δ 7.86 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 7.9 Hz, 2H), 5.53 (ddd, J = 11.3, 6.9, 4.8 Hz, 1H), 5.31-5.24 (m, 1H), 4.09 (d, A of AB, J_{AB} = 14.0 Hz, 1H), 4.05-4.01 (m, 1H), 3.67 (d, J = 4.9 Hz, 1H), 3.05 (dd, J = 11.8, 3.9 Hz, 1H), 2.71 (dd, A of ABX, J_{AB} = 18.0 Hz, J_{AX} = 6.7 Hz, 1H), 2.22 (d, B of AB, J_{AB} = 18.0 Hz, 1H), 2.10-2.00 (m, 1H), 1.95-1.89 (m, 1H), 1.86 (s, 3H), 1.79-1.56 (m, 6H), 1.29 (s, 3H), 1.26-0.95 (m, 6H), 0.65 (tt, B of ABX, J_{AB} = 12.5 Hz, J_{BX} = 4.8 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.64 (e), 137.40 (e), 132.43 (e), 130.46 (o), 129.53 (o), 129.79 (o), 128.12 (e), 127.86 (o), 72.89 (o), 51.91 (e), 44.34 (o), 42.86 (o), 36.27 (e), 30.44 (e), 30.19 (e), 28.36 (e), 26.83 (e), 26.66 (e), 26.52 (e), 25.22 (e), 21.06 (o), 20.90 (o).

IR (neat) 3018 (w), 2926 (vs), 2853 (s), 1654 (w), 1598 (w), 1494 (w), 1449 (m), 1342 (m), 1304 (m), 1289 (m), 1161(vs), 1094 (m), 1052 (m), 1017 (w), 756 (m), 670 (m), 546 (m) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{24}H_{34}NO_2S$ 400.2305, found 400.2314.



2f

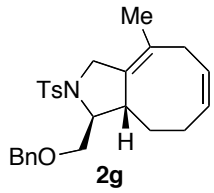
{(3a*E*,6*Z*)-4-Methyl-2-[(4-methylphenyl)sulfonyl]-2,3,5,8,9,9a-hexahydro-1*H*-cycloocta[*c*]pyrrol-1-yl}methanol 2f.

^{1}H NMR (400 MHz, C_6D_6) δ 7.78 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 8.1 Hz, 2H), 5.50 (ddd, J = 11.5, 7.3, 4.9 Hz, 1H), 5.21 (q, J = 8.9 Hz, 1H), 4.14 (d, A of AB, J_{AB} = 14.0 Hz, 1H), 3.83 (d, B of AB, J_{AB} = 14.0 Hz, 1H), 3.74 (dd, J = 12.5, 8.2 Hz, 1H), 3.56-3.55 (m, 2H), 2.99 (d, J = 9.4 Hz, 1H), 2.68 (dd, A of ABX, J_{AB} = 17.4 Hz, J_{AX} = 7.3 Hz, 1H), 2.50 (bs, 1H), 2.11 (dd, B of ABX, J_{AB} = 17.0 Hz, J_{BX} = 4.3 Hz, 1H), 1.96-1.86 (m, 1H), 1.85 (s, 3H), 1.73-1.65 (m, 1H), 1.26 (s, 3H), 1.07 (tt, A of ABX, J_{AB} = 11.0 Hz, J_{AX} = 3.8 Hz, 1H), 0.46 (ddt, B of ABMX, J_{AB} = 11.5 Hz, J_{BX} = 5.9 Hz, J_{BM} = 4.0 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 143.20 (e), 135.83 (e), 130.72 (o), 130.37 (e), 130.11 (e), 129.71 (o), 128.74 (o), 127.92 (o), 69.12 (o), 65.61 (e), 51.62 (e), 44.05 (o), 35.83 (e), 29.63 (e), 25.40 (e), 21.08 (o), 20.80 (o).

IR (neat) 3512 (bs), 3017 (m), 2930 (m), 2855 (m), 1598 (w), 1494 (w), 1453 (m), 1400 (w), 1380 (w), 1340 (s), 1306 (m), 1290 (m), 1216 (w), 1161 (vs), 1095 (s), 1054 (m), 1017 (m), 756 (m), 668 (s), 547 (m) cm^{-1}.

HRMS (EI, $M-OCH_3^+$) calcd for $C_{18}H_{22}NO_2S$ 316.1371, found 316.1374.



2g

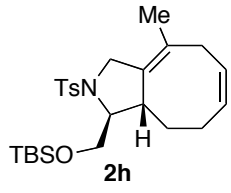
(6*Z*,9*E*)-3-[(Benzyloxy)methyl]-9-methyl-2-[(4-methylphenyl) sulfonyl]-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2g.

^{1}H NMR (400 MHz, C_6D_6) δ 7.80 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.3 Hz, 2H), 7.16-7.13 (m, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 8.2 Hz, 2H), 5.53 (ddd, J = 11.3, 7.0, 4.6 Hz, 1H), 5.24 (q, J = 9.1 Hz, 1H), 4.33 (d, A of AB, J_{AB} = 12.2 Hz, 1H), 4.26 (d, B of AB, J_{AB} = 12.2 Hz, 1H), 4.12 (d, A of AB, J_{AB} = 13.7 Hz, 1H), 3.94-3.88 (m, 2H), 3.83 (dd, J= 9.1, 4.2 Hz, 1H), 3.42 (t, J = 8.7 Hz, 1H), 3.33 (dd, J = 11.8, 3.9 Hz, 1H), 2.73 (dd, A of ABX, J_{AB} = 17.7 Hz, J_{AX} = 7.0 Hz, 1H), 2.19 (dd, B of ABX, J_{AB} = 17.9 Hz, J_{BX} = 3.6 Hz, 1H), 2.00 (ddd, A of ABMX, J_{AB} = 13.3 Hz, J_{AX} = 11.3 Hz, J_{AM} = 4.0 Hz, 1H), 1.84 (s, 3H), 1.75-1.68 (m, 1H), 1.26 (s, 3H), 1.20 (tt, A of ABX, J_{AB} = 12.2 Hz, J_{AX} = 4.0 Hz, 1H), 0.62 (tt, B of ABX, J_{AB} = 12.5 Hz, J_{AX} = 4.8 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.81 (e), 139.06 (e), 136.80 (e), 130.92 (e), 130.49 (o), 129.63 (e), 129.58 (o), 128.75 (o), 128.48 (o), 128.29 (o), 127.70 (o), 127.61 (o), 73.24 (e), 73.18 (e), 66.60 (o), 51.17 (e), 44.23 (o), 36.16 (e), 29.56 (e), 25.35 (e), 21.08 (o), 20.86 (o).

IR (neat) 3063 (w), 3026 (w), 2928 (m), 2857 (m), 1723 (w), 1652 (w), 1598 (w), 1454 (m), 1400 (w), 1345 (vs), 1306 (m), 1163 (vs), 1096 (s), 739 (m), 667 (s), 547 (m) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{26}H_{32}NO_3S$ 438.2097, found 438.2093.



2h

(6*Z*,9*E*)-3-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)-9-methyl -2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1*H*-cyclo octa[*c*]pyrrole 2h.

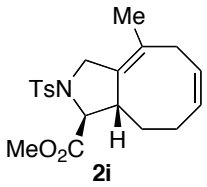
^{1}H NMR (400 MHz, C_6D_6) δ 7.80 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 7.9 Hz, 2H), 5.55 (ddd, J = 11.3, 7.2, 4.5 Hz, 1H), 5.29-5.22 (m, 1H), 4.16 (d, A of AB, J_{AB} = 13.7 Hz, 1H), 4.00 (dd, J = 9.8, 3.7 Hz, 1H), 3.89 (dd, B of ABX, J_{AB} = 13.7 Hz,

J_{BX} = 1.2 Hz 1H), 3.76 (dd, A of ABX, J_{AB} = 7.9 Hz, J_{AX} = 3.4 Hz, 1H), 3.61 (dd, B of ABX, J_{AB} = 9.8 Hz, J_{BX} = 8.3 Hz, 1H), 3.34 (dd, J = 11.9, 3.7 Hz, 1H), 2.77 (dd, A of ABX, J_{AB} = 18.3 Hz, J_{AX} = 7.0 Hz, 1H), 2.24 (d, B of AB, J_{AB} = 18.0 Hz, 1H), 2.09-1.88 (m, 1H), 1.86 (s, 3H), 1.74 (ddt, J = 11.9, 7.8, 4.2 Hz, 1H), 1.30 (s, 3H), 1.21(tt, A of ABX, J_{AB} = 12.2 Hz, J_{AX} = 3.8 Hz, 1H) , 0.93 (s, 9H), 0.61 (tt, B of ABX, J_{AB} = 12.5 Hz, J_{BX} = 4.7 Hz, 1H), 0.06 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.79 (e), 136.79 (e), 131.08 (e), 130.45 (o), 129.60 (o), 129.20 (e), 128.78 (o), 127.78 (e), 68.46 (o), 66.32 (e), 51.58 (e), 43.47 (o), 36.23 (e), 29.76 (e), 25.98 (o), 25.33 (e), 21.07 (o), 20.93 (o), 18.32 (e), -5.22 (o), -5.41 (o).

IR (neat) 3018 (m), 2929 (vs), 2857 (s), 1920 (w), 1718 (w), 1655 (w), 1599 (m), 1494 (w), 1463 (m), 1384 (m), 1346 (s) 1255 (s), 1215 (w), 1163 (vs), 1096 (vs), 1017 (m), 1006 (m) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{25}H_{40}NO_3SSi$ 462.2493, found 462.2493.



2i

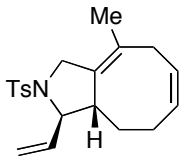
Methyl (3a*E*,6*Z*)-4-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,5,8, 9,9a-hexahydro-1*H*-cycloocta[*c*]pyrrole-1-carboxylate 2i.

^{1}H NMR (400 MHz, C_6D_6) δ 7.87 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 5.46 (ddd, J = 11.5, 7.6, 4.6 Hz, 1H), 5.26-5.19 (m, 1H), 4.54 (d, J = 0.9 Hz, 1H), 4.25 (d, A of AB, J_{AB} = 12.8 Hz, 1H), 4.12 (d, B of AB, J_{AB} = 13.1 Hz, 1H), 3.43-3.37 (m, 1H), 3.18 (s, 3H), 2.53 (dd, A of ABX, J_{AB} = 18.3 Hz, J_{AX} = 7.3 Hz, 1H), 2.18 (d, B of AB, J_{AB} = 18.0 Hz, 1H), 2.07-1.97 (m, 1H), 1.87 (s, 3H), 1.76-1.69 (m, 1H), 1.39 (tt, A of ABX, J_{AB} = 12.2 Hz, J_{AX} = 4.1 Hz, 1H), 1.31-1.15 (m, 1H), 1.18 (s, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 172.07 (e), 142.92 (e), 137.40 (e), 130.21 (e), 129.82 (o), 129.55 (o), 129.18 (o), 67.78 (o), 51.64 (o), 51.26 (e), 45.91 (o), 35.87 (e), 30.34 (e), 25.16 (e), 21.06 (o), 20.97 (o).

IR (neat) 3021 (w), 2932 (w), 2857 (w), 1743 (s), 1598 (w), 1495 (w), 1437 (m), 1347 (vs), 1306 (w), 1289 (m), 1207 (m), 1163 (vs), 1096 (s), 1070 (m), 1018 (w), 755 (m), 670 (s), 549 (m) cm^{-1}.

HRMS (CI, $M+H^+$) calcd for $C_{20}H_{26}NO_4S$ 376.1577, found 376.1584.



2j

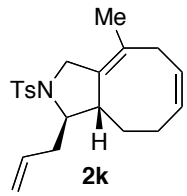
(6*Z*,9*E*)-9-Methyl-2-[(4-methylphenyl)sulfonyl]-3-vinyl-2,3,3a,4,5, 8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2j.

^{1}H NMR (400 MHz, C_6D_6) δ 7.83 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 5.70 (ddd, J = 17.1, 10.3, 7.0 Hz, 1H), 5.51 (ddd, J = 11.5, 7.3, 4.9 Hz, 1H), 5.31-5.24 (m, 1H), 5.21 (dt, J = 17.1, 1.2 Hz, 1H), 4.95 (dt, J = 10.4, 1.1 Hz, 1H), 4.05-4.01 (m, 2H), 3.96-3.92 (m, 1H), 2.86 (d, J = 10.4 Hz, 1H), 2.64 (dd, A of ABX, J_{AB} = 17.1 Hz, J_{AX} = 7.3 Hz, 1H), 2.16 (dd, B of ABX, J_{AB} = 17.4, J_{BX} = 4.3 Hz, 1H), 2.01 (dd, A of ABMX, J_{AB} = 18.6 Hz, J_{AX} = 13.7 Hz, J_{AM} = 4.0 Hz, 1H), 1.88 (s, 3H), 1.81-1.73 (m, 1H), 1.32-1.27 (m, 1H), 1.26 (s, 3H), 1.05-0.97 (m, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.71 (e), 138.21 (o), 136.99 (e), 130.52 (e), 130.05 (o), 129.93 (e), 129.44 (o), 129.30 (o), 128.12 (o), 115.17 (e), 69.58 (o), 50.97 (e), 47.85 (o), 35.67 (e), 29.09 (e), 25.42 (e), 21.09 (o), 20.87 (o).

IR (neat) 3015 (w), 2027 (m), 2856 (w), 1645 (w), 1598 (w), 1494 (w), 1452 (w), 1345 (vs), 1163 (vs), 1095 (s), 1058 (m), 1017 (m), 669 (s) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{20}H_{25}NO_2S$ 343.1606, found 343.1600.



2k

(6*Z*,9*E*)-3-Allyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5, 8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2k.

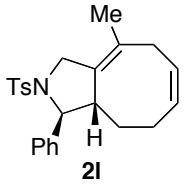
^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 5.78 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H), 5.50 (ddd, J = 11.3, 7.0, 4.6 Hz, 1H), 5.28-5.21 (m, 1H), 5.00 (dd, J = 17.1, 1.5 Hz, 1H), 4.97 (d, J = 10.4 Hz,

1H), 4.06 (d, A of AB, J_{AB}= 13.7 Hz, 1H), 3.90 (dd, B of ABX, J_{AB} = 14.0 Hz, J_{BX} = 1.2 Hz, 1H), 3.77 (dd, *J*= 8.2, 4.0 Hz, 1H), 2.95 (dd, *J*= 11.6, 4.0 Hz, 1H), 2.71 (dd, A of ABX, J_{AB}= 18.0 Hz, J_{AX}= 6.7 Hz, 1H), 2.58-2.52 (m, 1H), 2.34 (dt, *J* = 13.7, 7.4 Hz, 1H), 2.21 (dd, B of ABX, J_{AB}= 17.9 Hz, J_{BX}= 3.6 Hz, 1H), 2.06-1.92 (m, 1H), 1.90 (s, 3H), 1.73-1.67 (m, 1H), 1.30 (s, 3H), 1.17-1.09 (m, 1H), 0.69 (tt, B of ABX, J_{AB}= 12.5 Hz, J_{BX}= 4.5 Hz, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.77 (e), 137.32 (e), 134.92 (o), 131.02 (e), 130.38 (o), 129.59 (o), 129.50 (e), 128.68 (o), 127.71 (o), 117.51 (e), 66.99 (o), 50.89 (e), 45.34 (o), 41.01 (e), 36.23 (e), 29.53 (e), 25.13 (e), 21.09 (o), 20.91 (o).

IR (neat) 3074 (w), 3015 (w), 2926 (m), 2853 (m), 1640 (w), 1599 (w), 1494 (w), 1441 (w), 1345 (vs), 1163 (vs), 1096 (s), 1054 (m), 1017 (m), 668 (s), 547 (s) cm^{-1}.

HRMS (CI, $M+H^+$) calcd. for $C_{21}H_{28}NO_2S$ 358.1841, found 358.1838.



2l

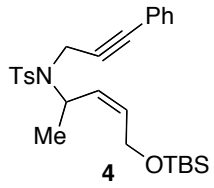
(6*Z*,9*E*)-9-Methyl-2-[(4-methylphenyl)sulfonyl]-3-phenyl-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 2l.

^{1}H NMR (400 MHz, C_6D_6) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.08-7.00 (m, 3H), 6.69 (d, *J* = 7.9 Hz, 2H), 5.38 (ddd, *J* = 11.4, 7.1, 4.8 Hz, 1H), 5.26-5.20 (m, 1H), 4.85 (s, 1H), 4.20 (s, 2H), 3.15 (dd, *J* = 11.4, 3.6 Hz, 1H), 2.50 (dd, A of ABX, J_{AB} = 18.1 Hz, J_{AX} = 6.8 Hz, 1H), 2.13-2.03 (m, 2H), 1.84 (s, 3H), 1.77-1.71 (m, 1H), 1.44 (tt, A of ABX, J_{AB} = 12.3 Hz, J_{AX} = 4.1 Hz, 1H), 1.28 (s, 3H), 1.20-1.12 (m, 1H).

^{13}C NMR (100 MHz, C_6D_6) δ 143.60(e), 142.47(e), 137.23(e), 130.84 (e), 130.16 (o), 129.91 (e), 129.31 (o), 128.82 (o), 128.67 (o), 127.36 (o), 126.79 (o), 70.80 (o), 51.57 (e), 50.59 (o), 35.93 (e), 30.14 (e), 25.19 (e), 21.05 (o), 21.02 (o).

IR (neat) 3063 (w), 3026 (w), 2929 (m), 2855 (m), 1650 (w), 1599 (w), 1495 (w), 1455 (m), 1400 (w), 1344 (vs), 1306 (m), 1290 (m), 1163 (vs), 1095 (s), 1071 (m), 1031 (m), 1017 (m), 756 (vs), 670 (vs) cm^{-1}.

HRMS (EI, M^+) calcd. for $C_{24}H_{27}NO_2S$ 393.1762, found 393.1753.



4

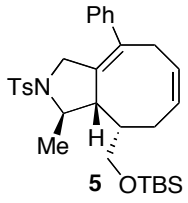
***N*-((2*Z*)-4-{[*tert*-Butyl(dimethyl)silyl]oxy}-1-methylbut-2-en-1-yl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide 4.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.28-7.17 (m, 7H), 5.59-5.52 (m, 2H), 4.85 (dq, J = 10.6, 7.0 Hz, 1H), 4.32 (s, 2H), 4.29-4.24 (m, 1H), 4.15-4.10 (m, 1H), 2.33 (s, 3H), 1.29 (d, J = 6.8 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.22 (e), 138.12 (e), 133.03 (o), 131.51 (o), 129.45 (o), 128.80 (o), 128.48 (o), 128.33 (o), 127.82 (o), 122.69 (e), 85.44 (e), 84.59 (e), 59.51 (e), 51.03 (o), 33.63 (e), 26.03 (o), 21.58 (o). 20.34 (o), 18.41 (e), -5.12 (o)

IR (neat) 3025 (m), 2955 (s), 2929 (s), 2857 (s), 1599 (m), 1491 (m), 1349 (vs), 1165 (vs), 1092 (vs), 838 (vs), 660 (s) cm^{-1}.

HRMS (CI, M^+) calcd for $C_{27}H_{37}NO_3SSi$ 483.2263, found 483.2273.



5

(6*Z*,9*Z*)-4-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)-3-methyl-2-[(4-methylphenyl)sulfonyl]-9-phenyl-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole 5.

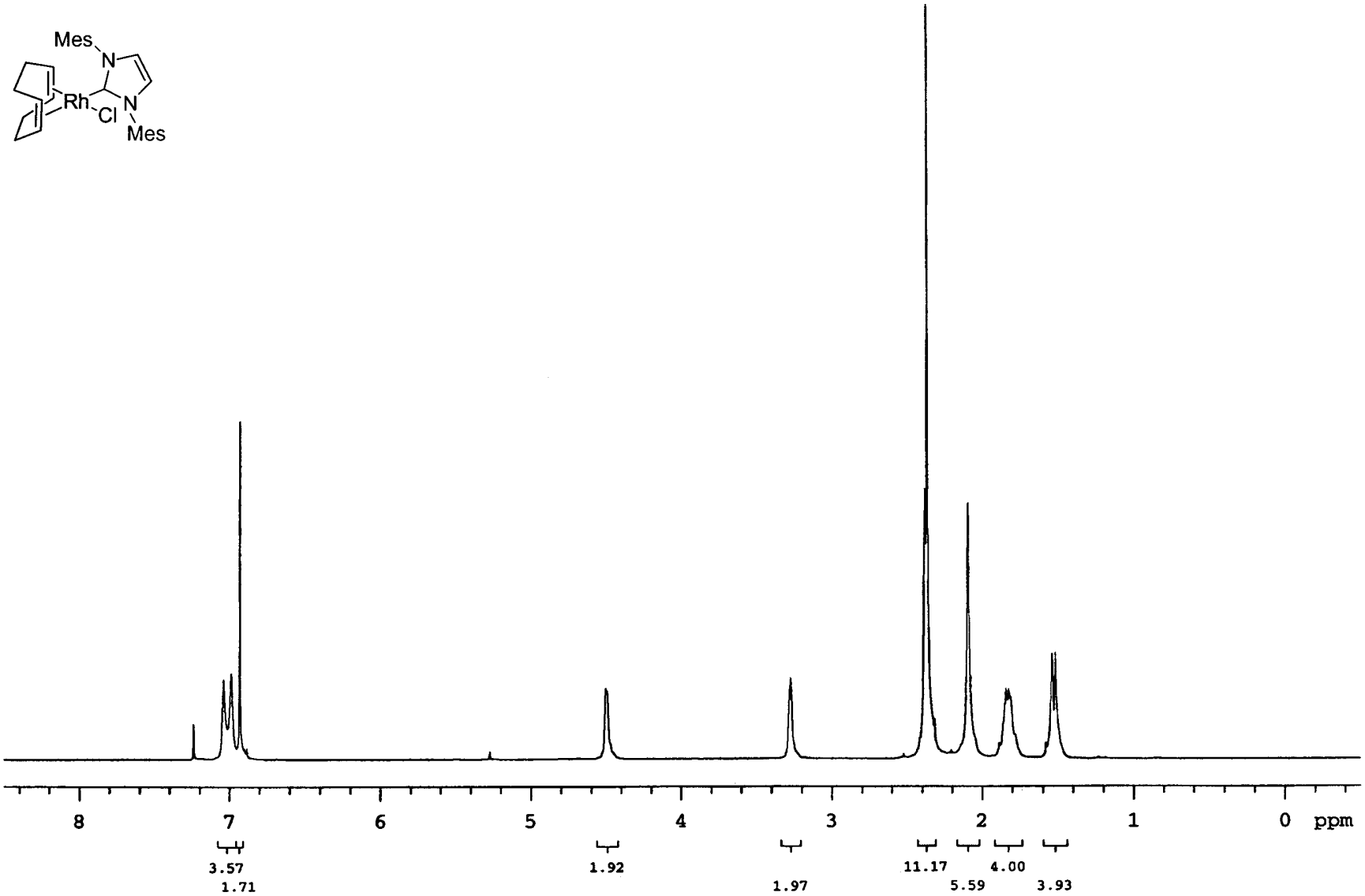
^{1}H NMR (400 MHz, C_6D_6) δ 7.62 (d, J = 7.9 Hz, 2H), 7.07 (t, J = 7.3 Hz, 2H), 7.02-6.95 (m, 3H), 6.67 (d, J = 7.9 Hz, 2H), 5.80-5.74 (m, 1H), 5.68-5.62 (m, 1H), 4.02 (d, A of AB, J_{AB} = 13.7 Hz, 1H), 3.94 (d, B of AB, J_{AB} = 13.7 Hz, 1H), 3.73 (dq, J = 9.8, 3.8 Hz, 1H), 3.66 (dd, J = 9.5, 4.0 Hz, 1H), 3.54 (t, J = 10.4 Hz, 1H), 3.18 (dd, A of ABX, J_{AB} = 13.6 Hz, J_{AX} = 9.1 Hz, 1H), 2.99 (bs, 1H), 2.67-2.56 (m, 2H), 2.42

(dd, B of ABX, J_{AB} = 14.0 Hz, J_{BX} = 6.3 Hz, 1H), 1.97-1.93 (m, 1H), 1.86 (s, 3H), 1.28 (d, J = 6.1 Hz, 3H), 0.99 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (100 MHz, C_6D_6) δ 142.77 (e), 138.16 (e), 136.14 (e), 132.04 (o), 131.60 (e), 129.69 (o), 128.93 (o), 128.41 (e), 128.35 (o), 127.96 (o), 127.54 (o), 127.40 (o), 62.43 (o), 61.81 (e), 53.24 (e), 42.91 (o), 35.79 (e), 30.43 (e), 26.16 (o), 21.85 (o), 21.18 (o), 18.44 (e), -5.15 (o), -5.35 (o).

IR (Neat): 3024 (s), 2929 (s), 2858 (s), 1752 (m), 1647 (w), 1599 (s), 1494 (s), 1462 (s), 1347 (vs), 1254 (s), 1163 (vs), 1094 (s), 838 (vs), 758 (vs), 593 (s) cm^{-1}.

HRMS (FAB, $M+H^+$): calcd for $C_{31}H_{44}NO_3SSi$ 538.2811, found 538.2819.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Rh
Cl
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1.97
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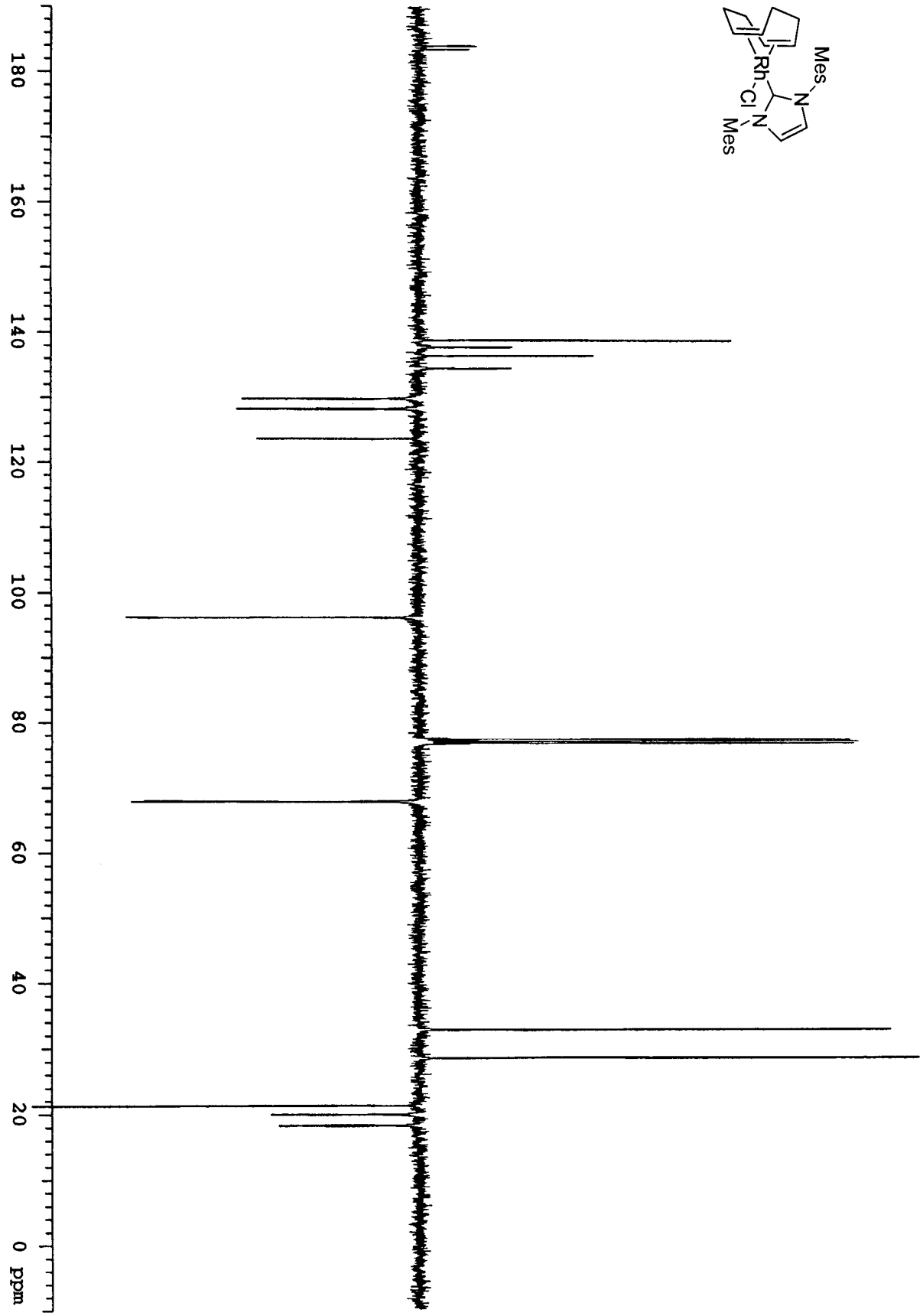
4.00
3.93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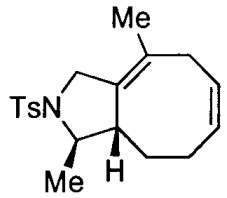
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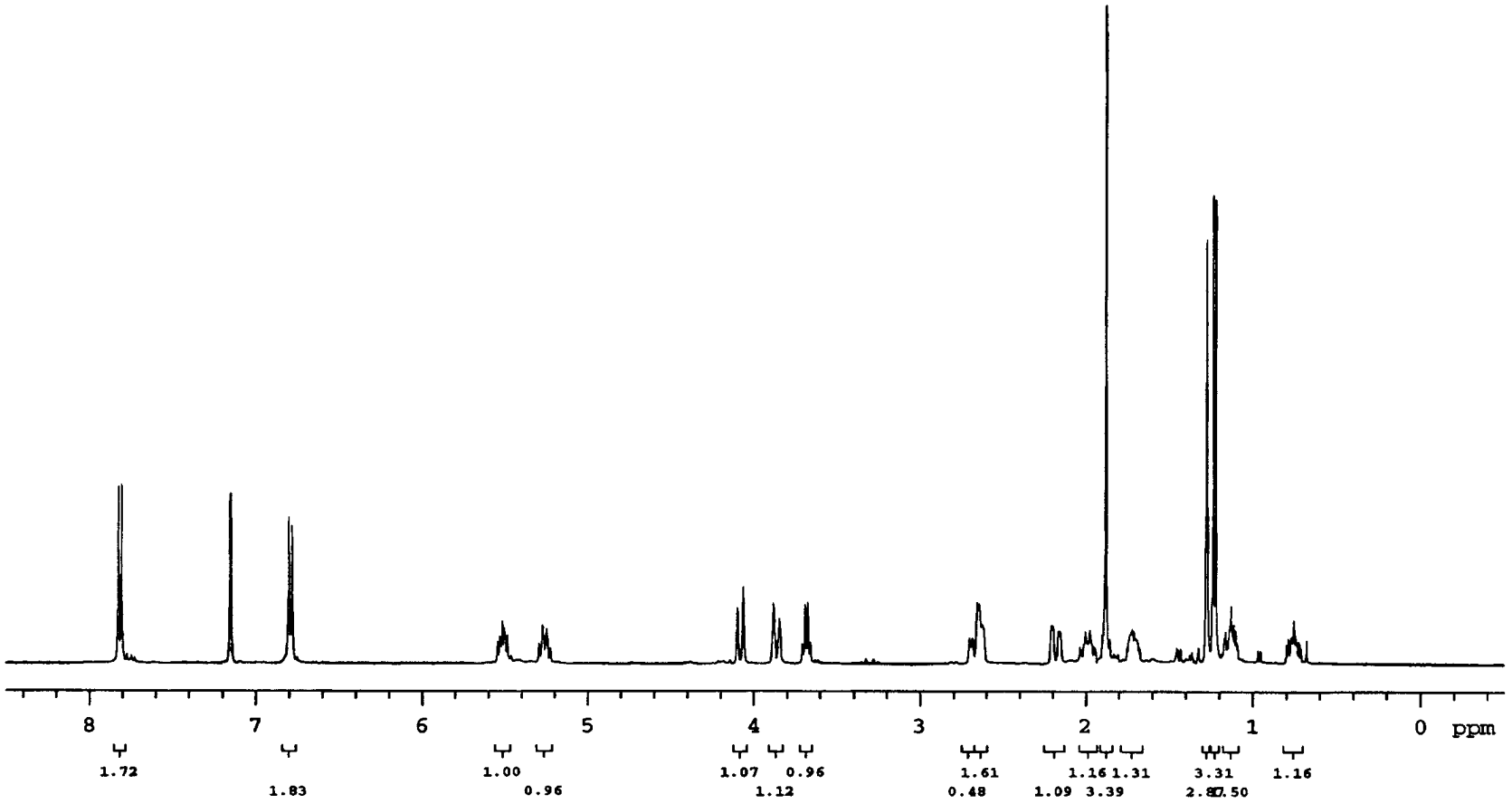
H

2a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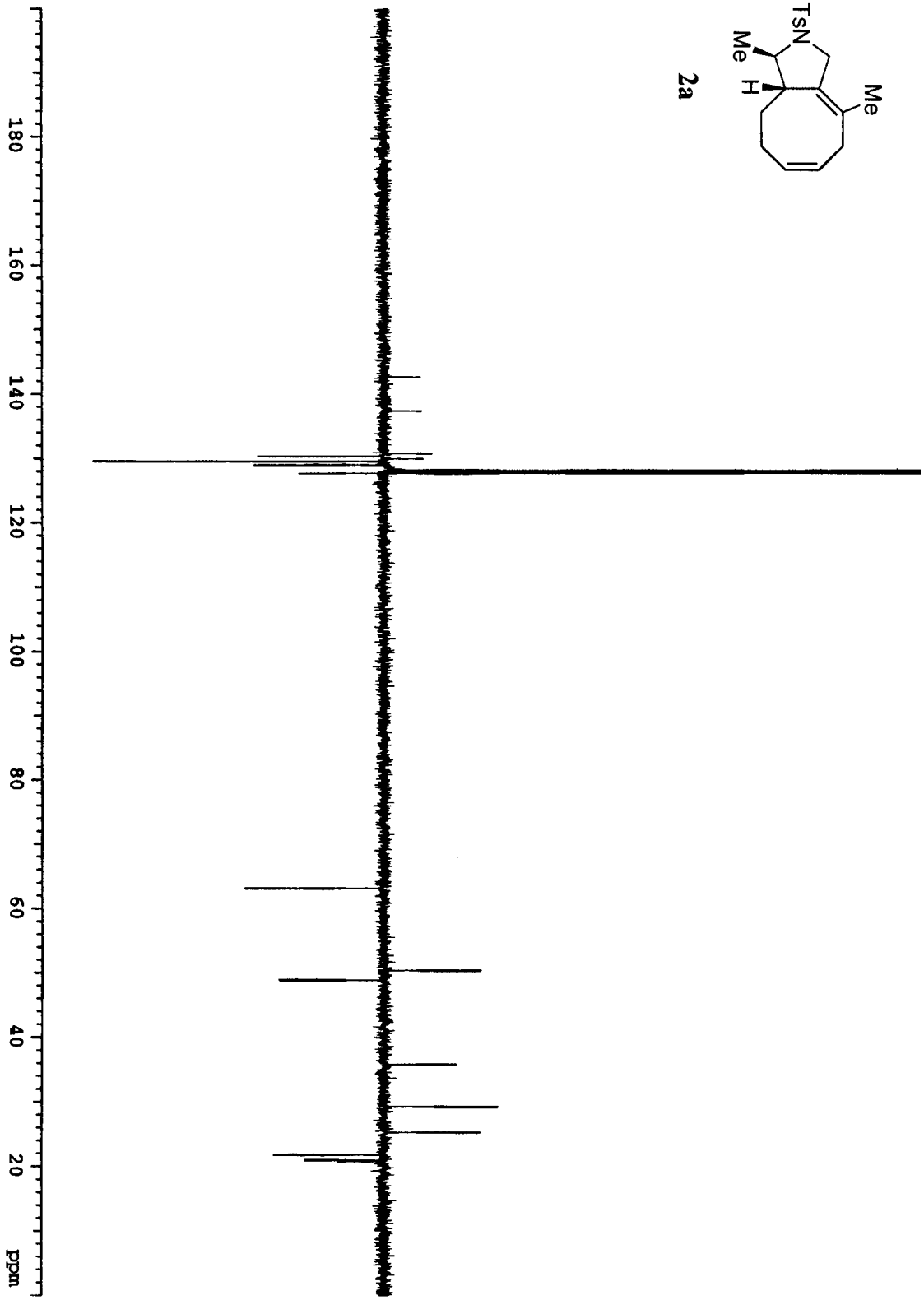
1.16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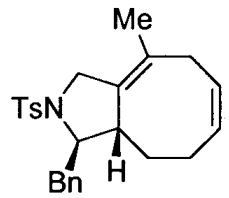
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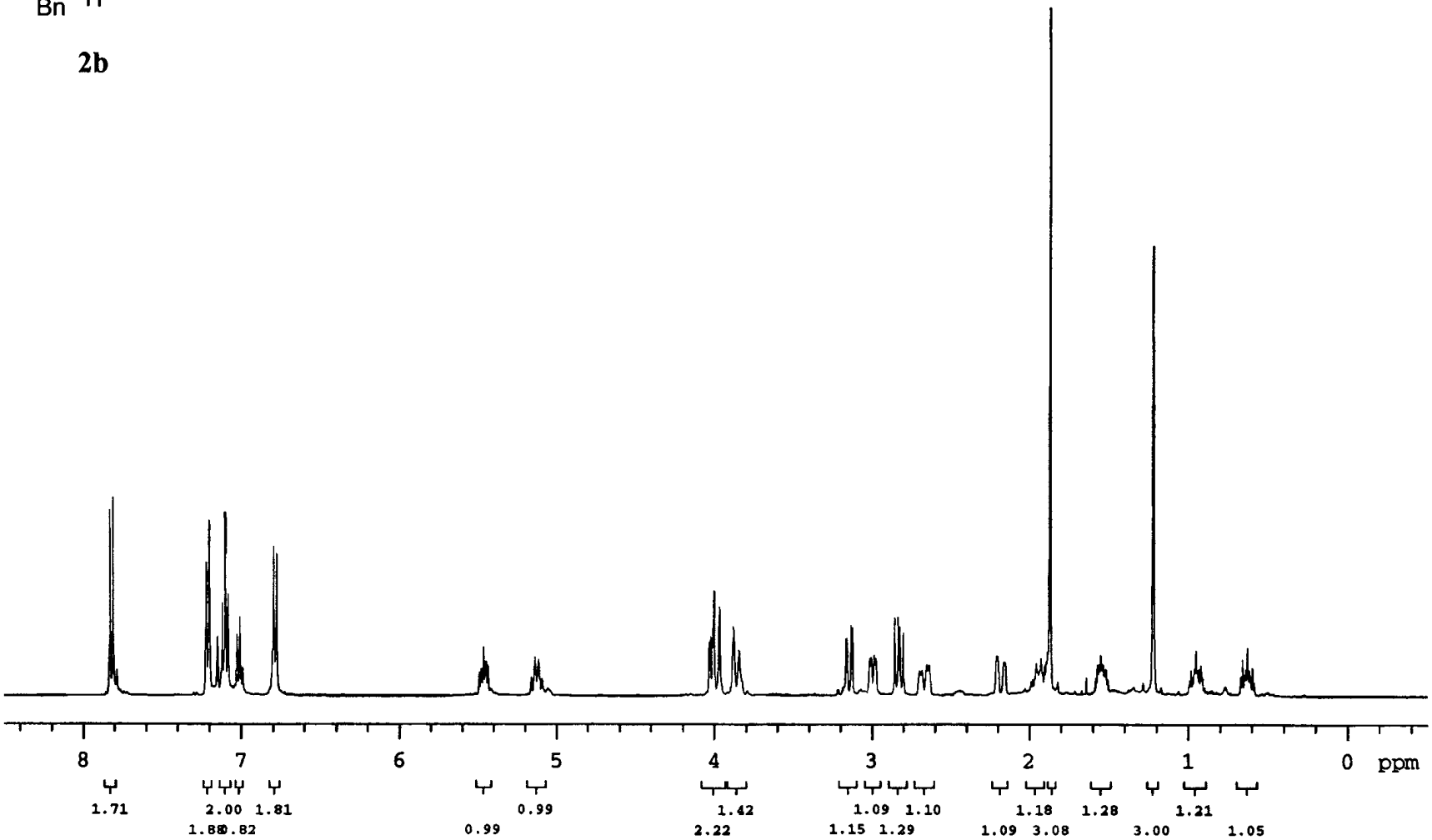
TsN
Bn
H

2b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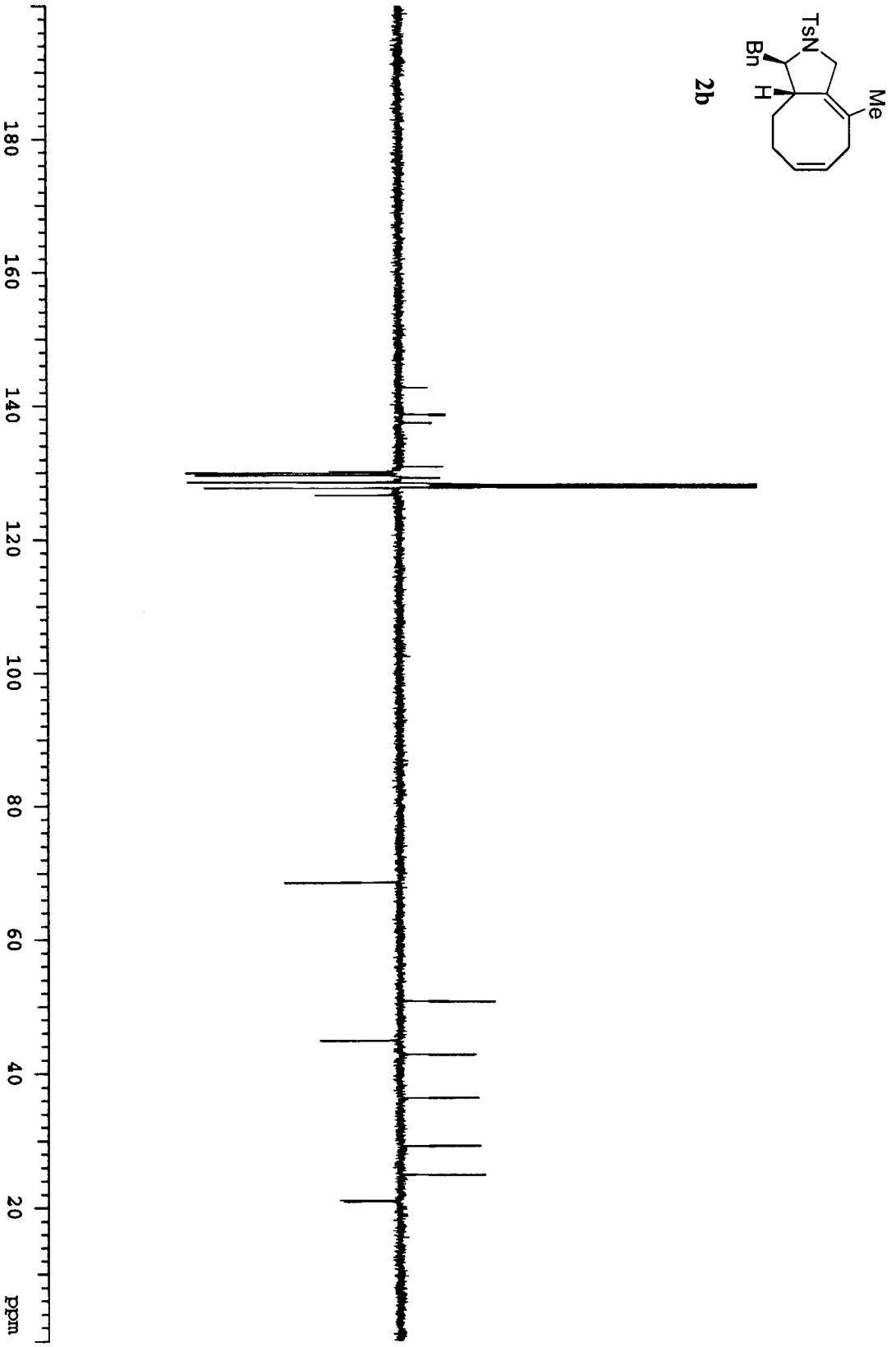
1.05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Bn
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Me
2b
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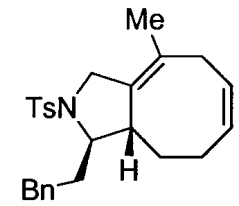
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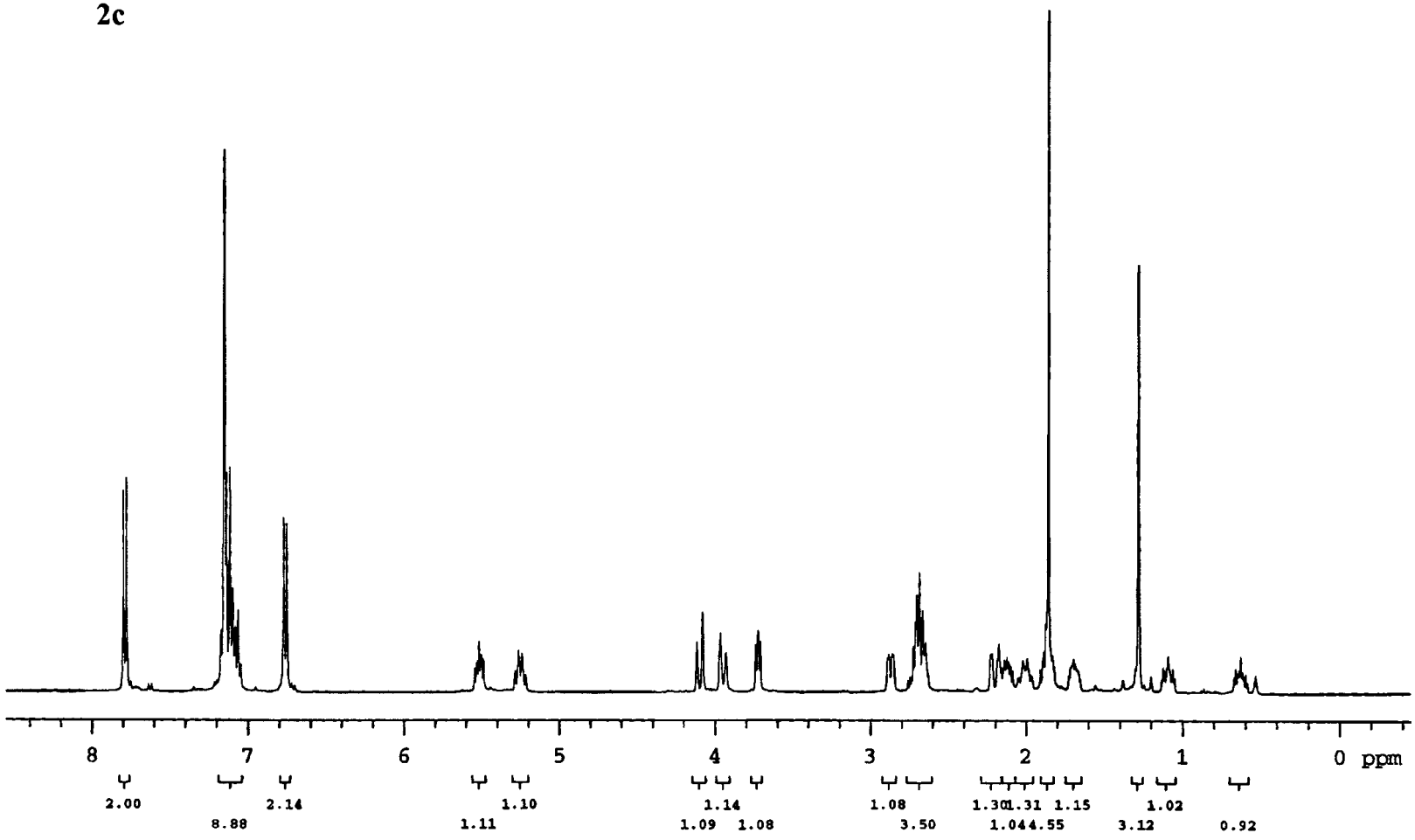
TsN
H
Bn

2c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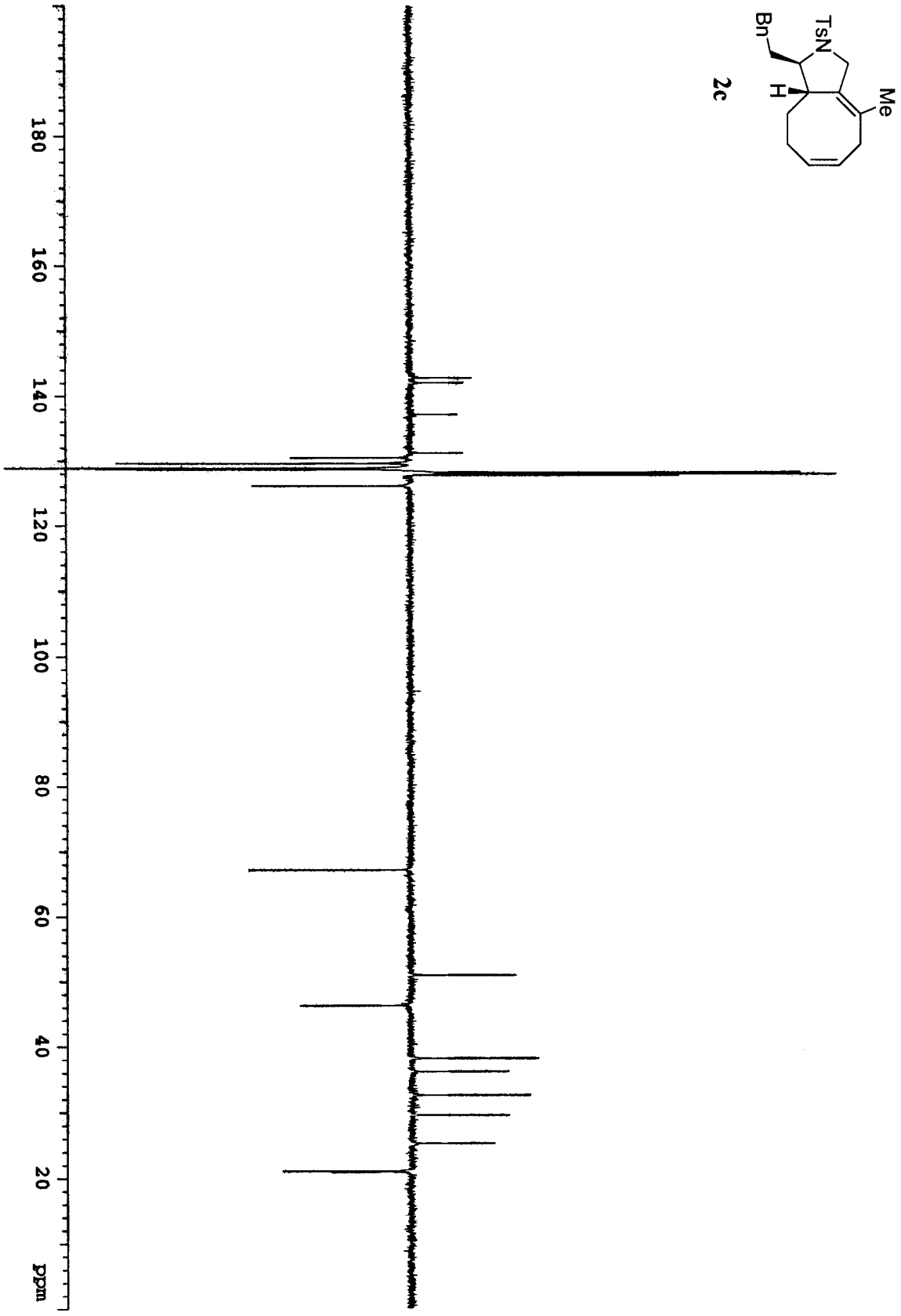
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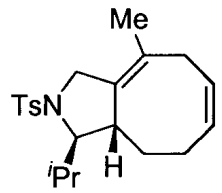
ppm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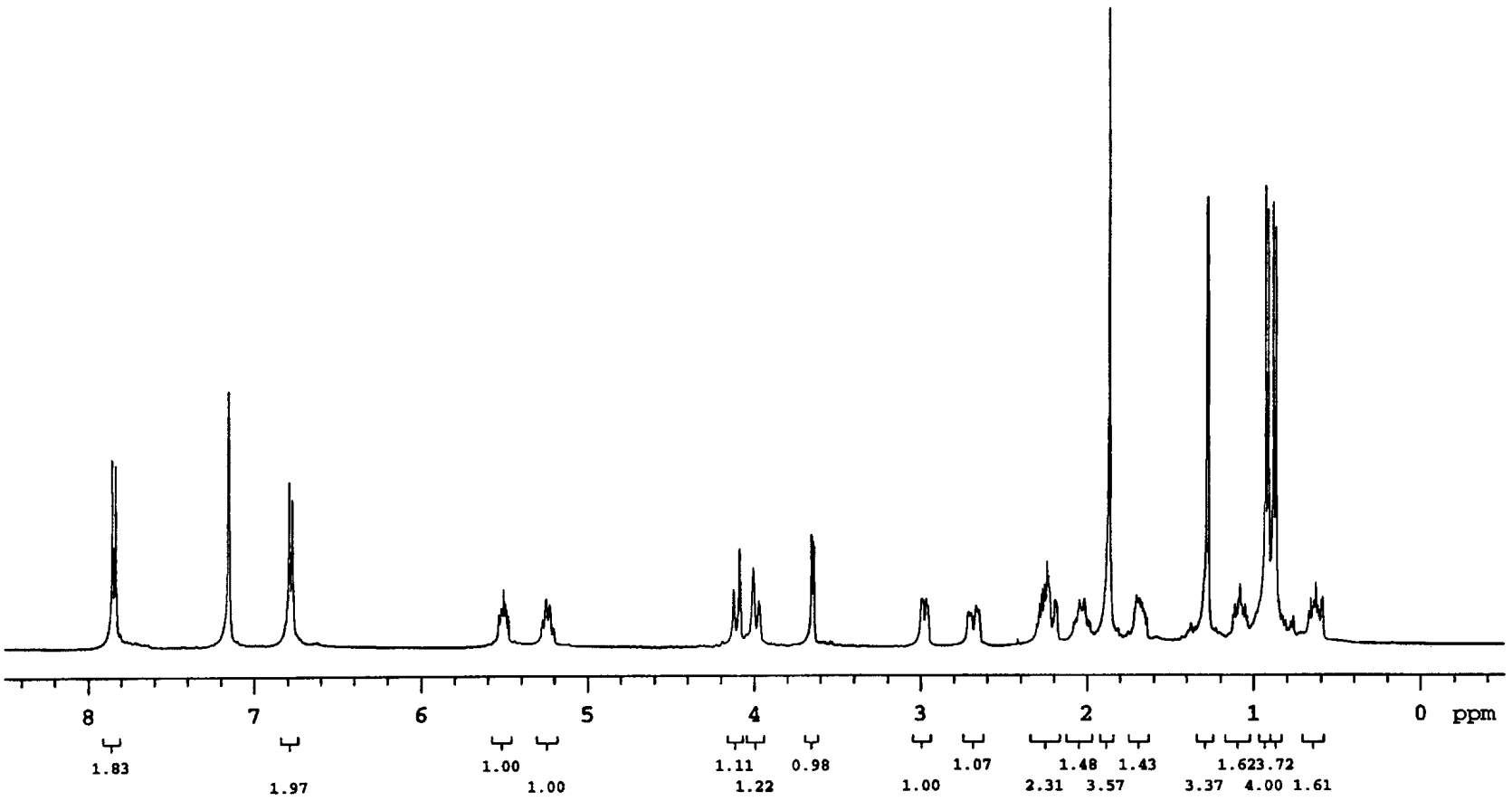
H

2d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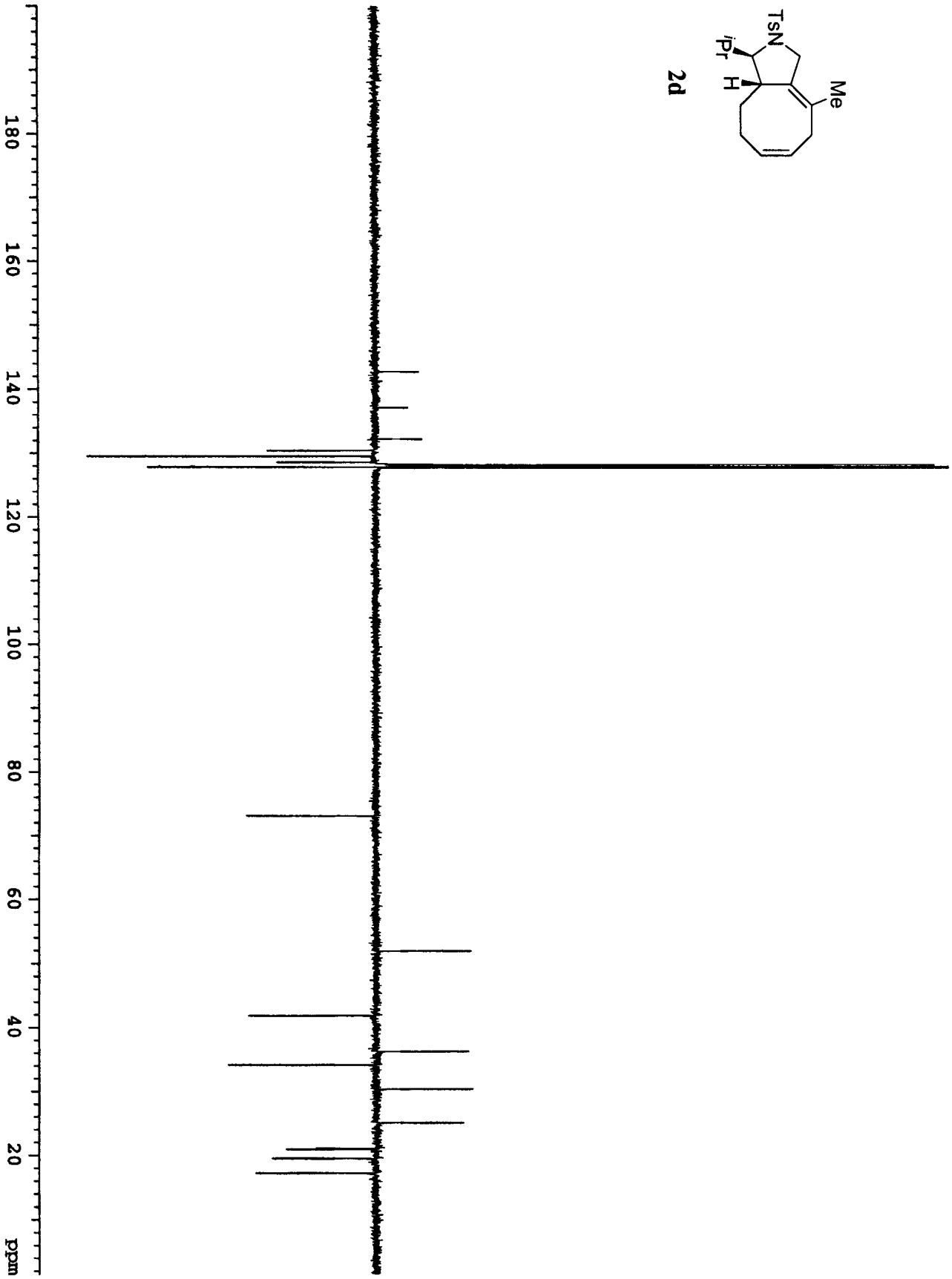
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Me
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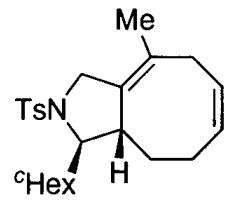
ppm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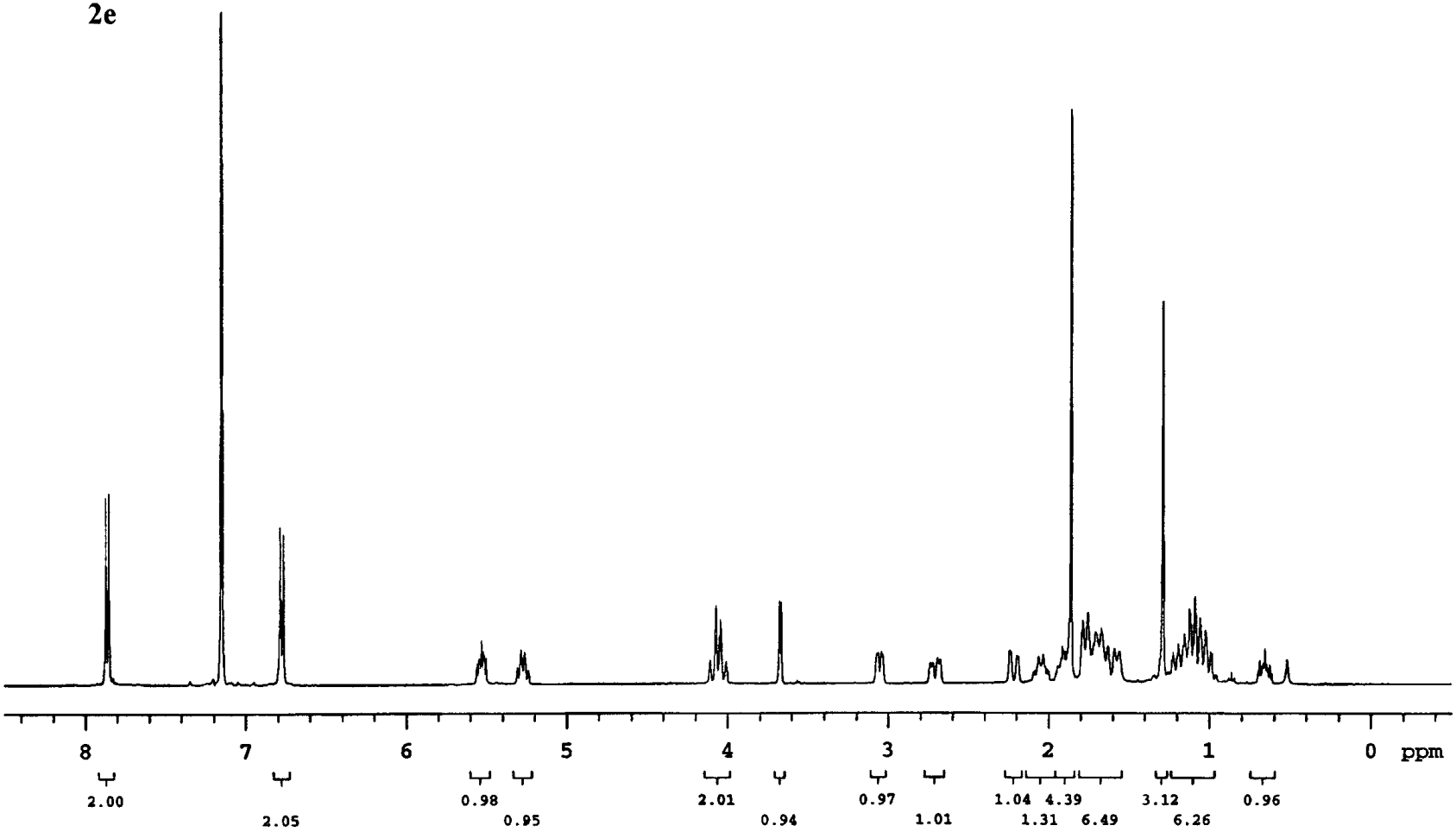
TsN
cHex
H

2e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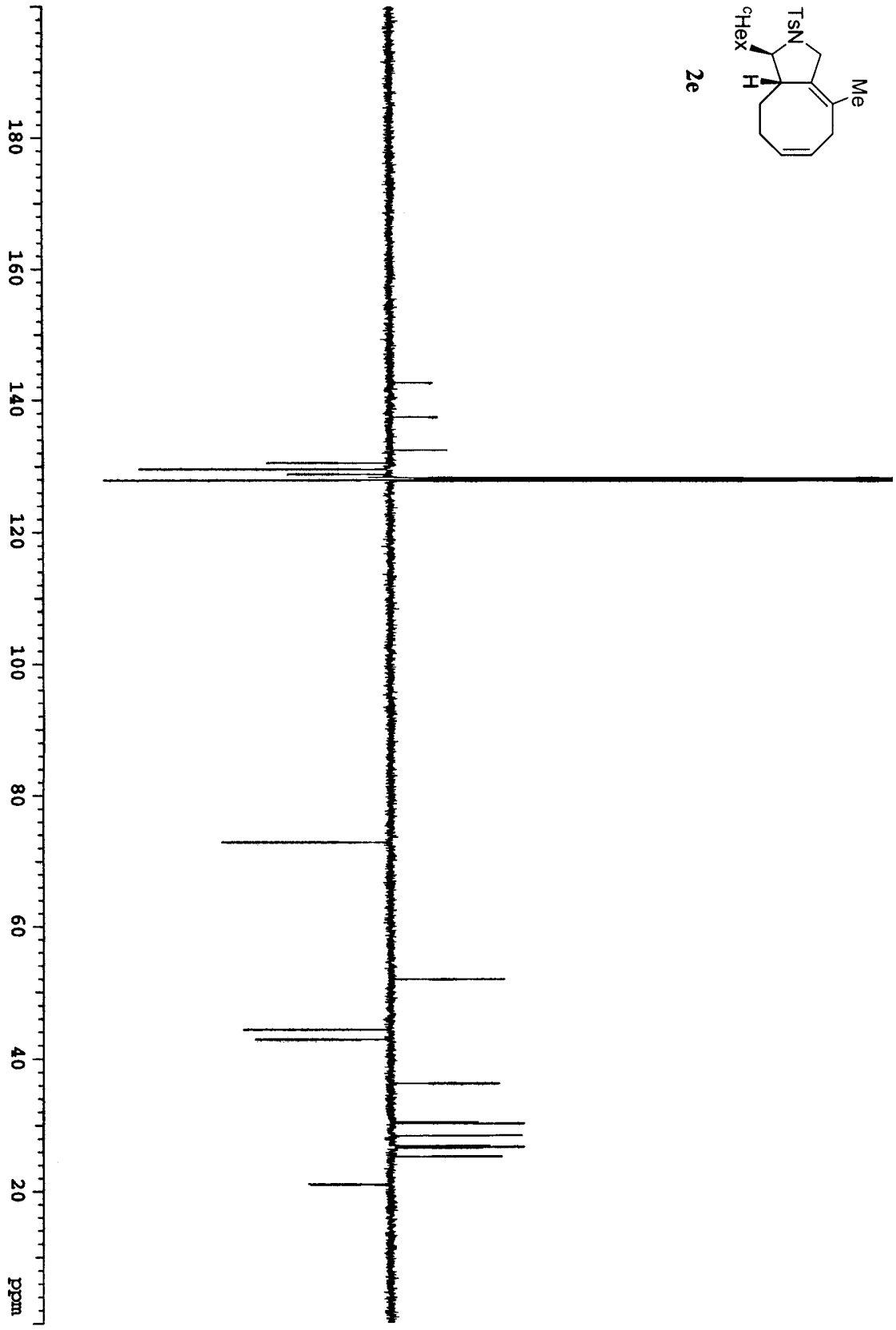
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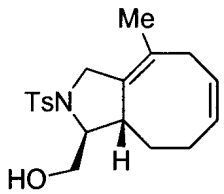
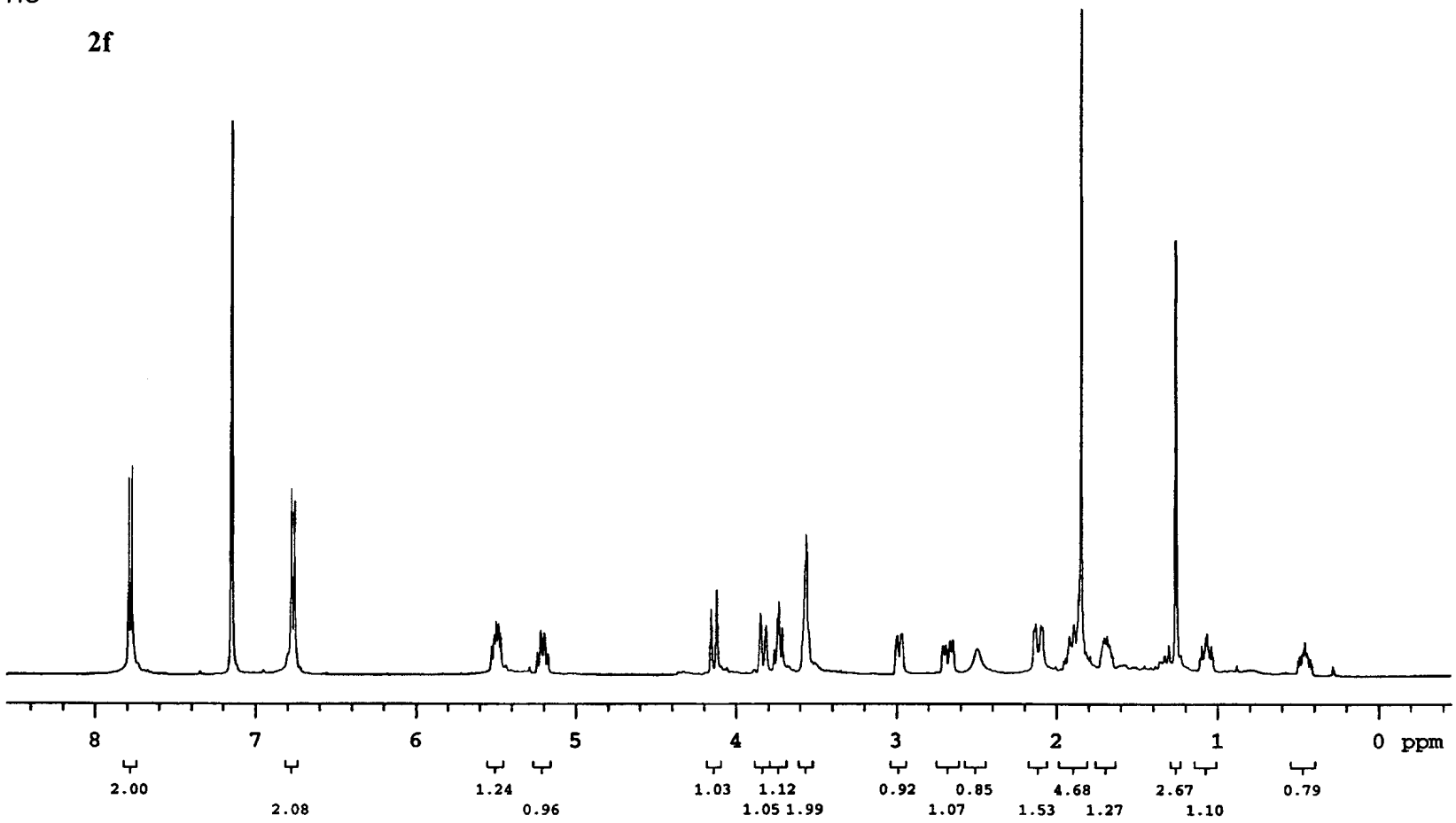

Me
TsN
H
HO

2f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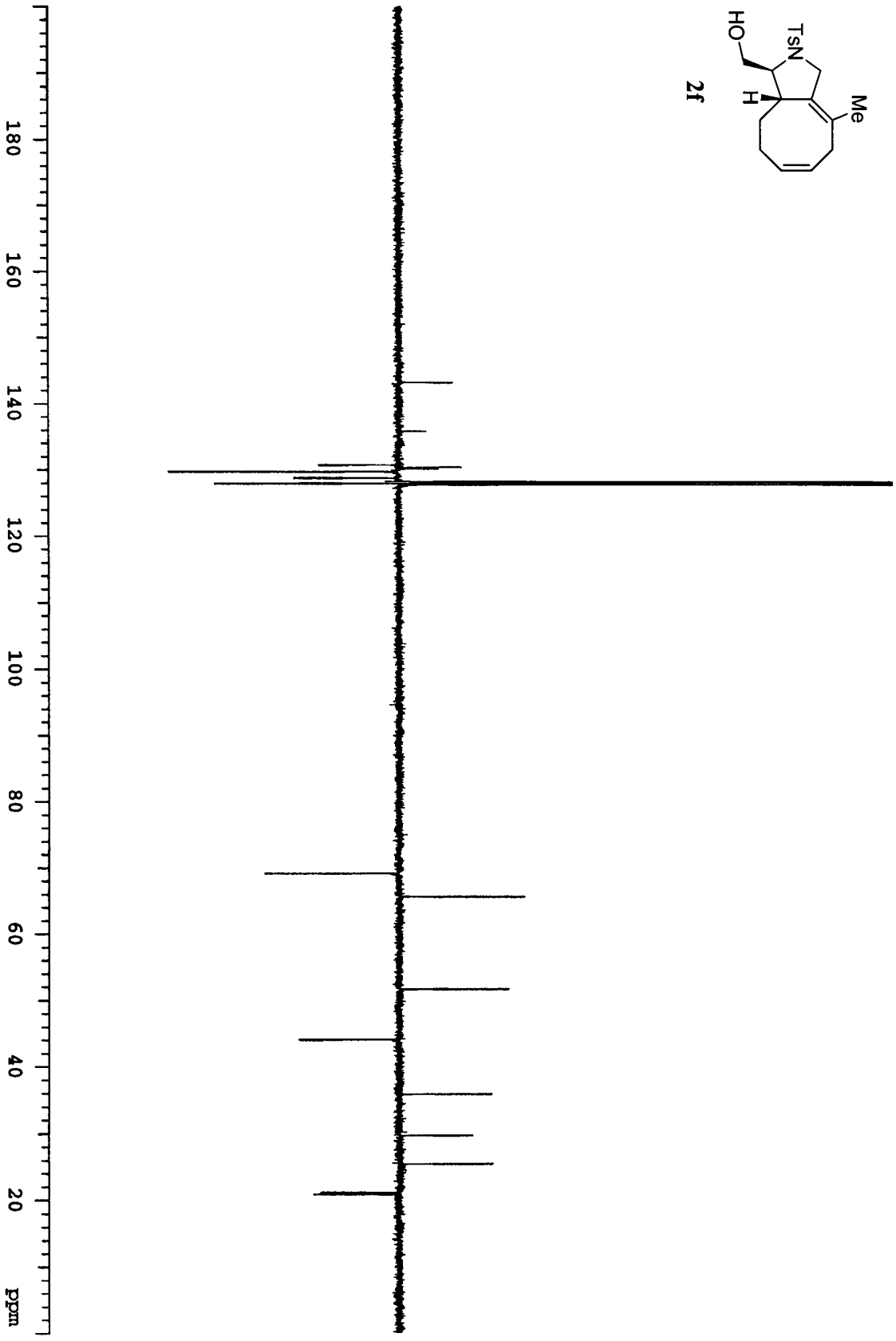
2.08
1.24
0.96
1.03
1.12
1.05
1.99
0.92
0.85
1.07
1.53
4.68
1.27
2.67
1.10
0.79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TsN
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2f
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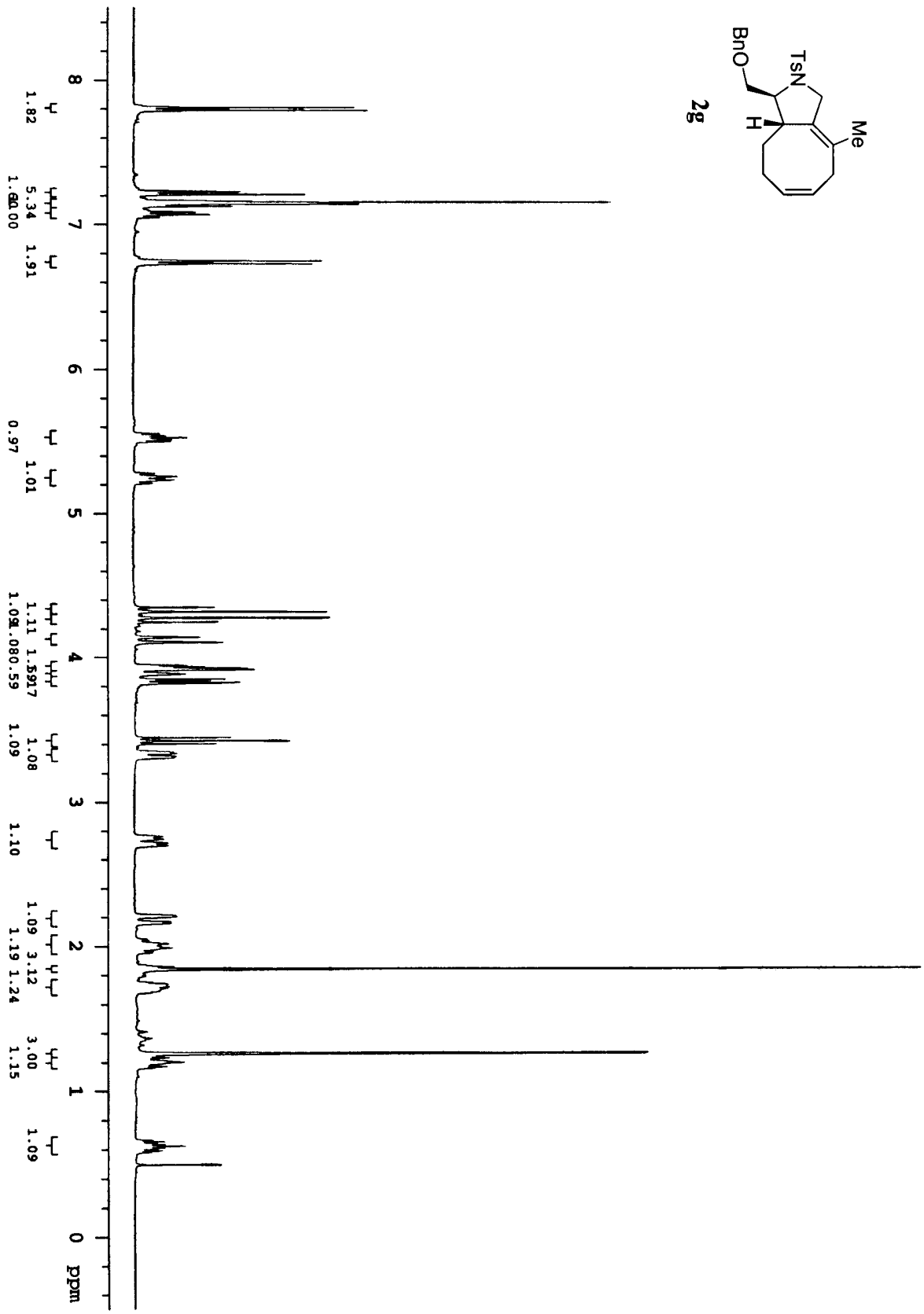
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H
Me
2g
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6
5
4
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2
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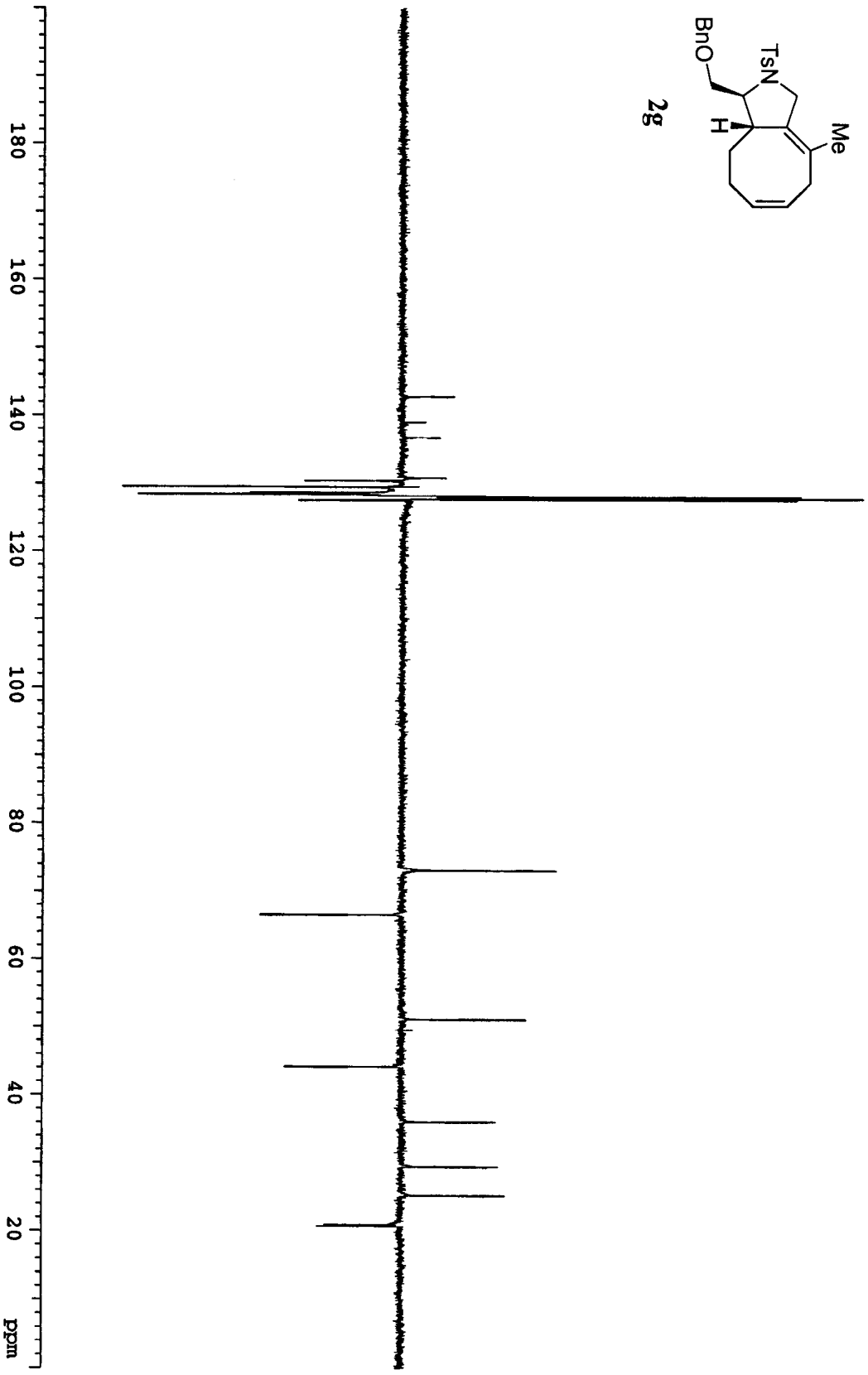
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H
Me
2g
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100
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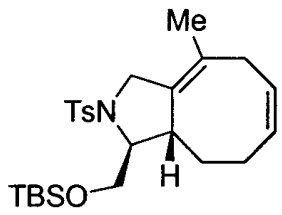
20
ppm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TBSO

2h

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0.91
1.03
1.14
1.05
1.04
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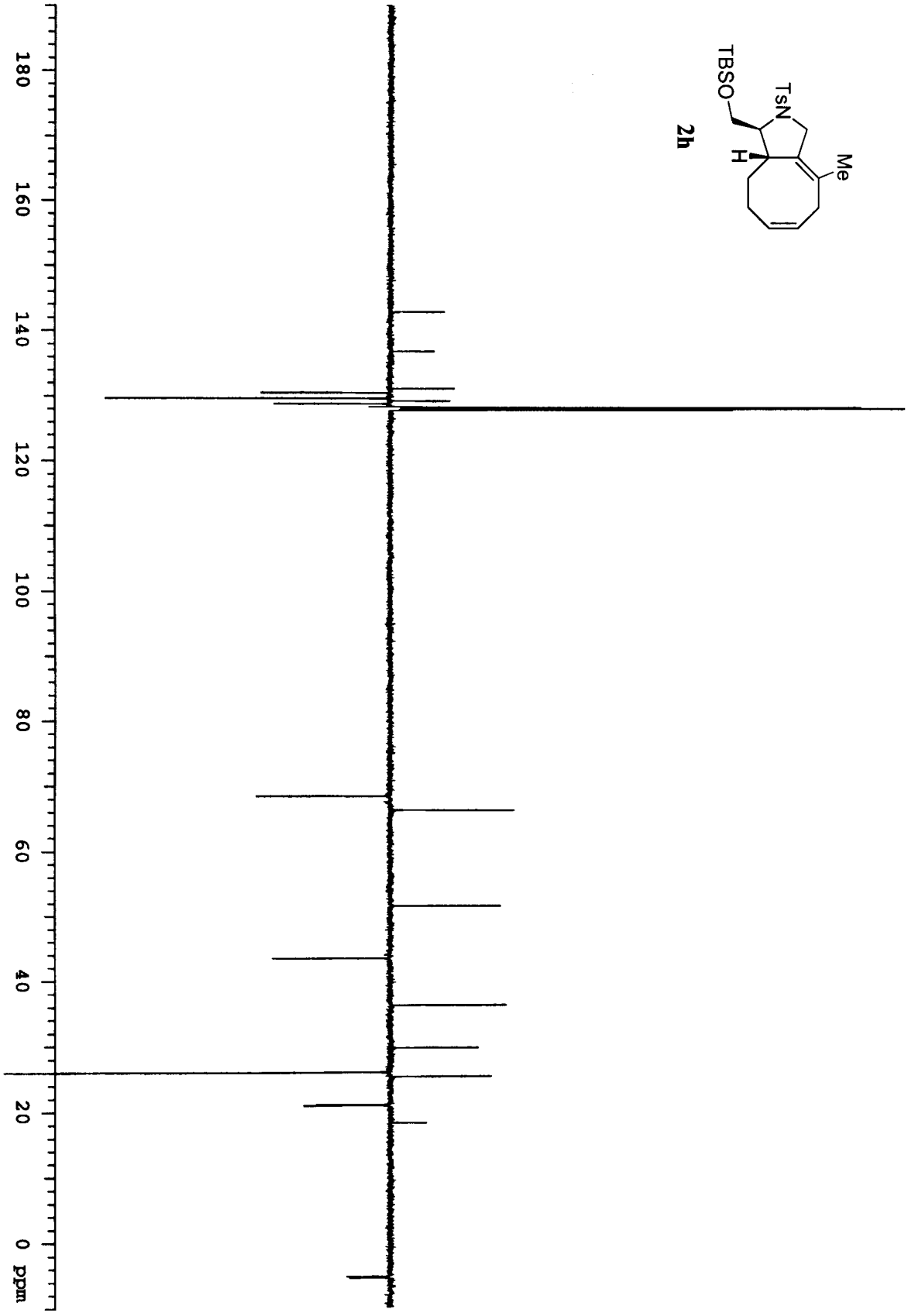
4.68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H
Me
2h
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160
140
120
100
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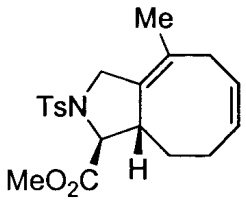
60
40
20
0 ppm


Me
TsN
MeO2C
H

2i

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7
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5
4
3
2
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1.19
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1.59
1.68
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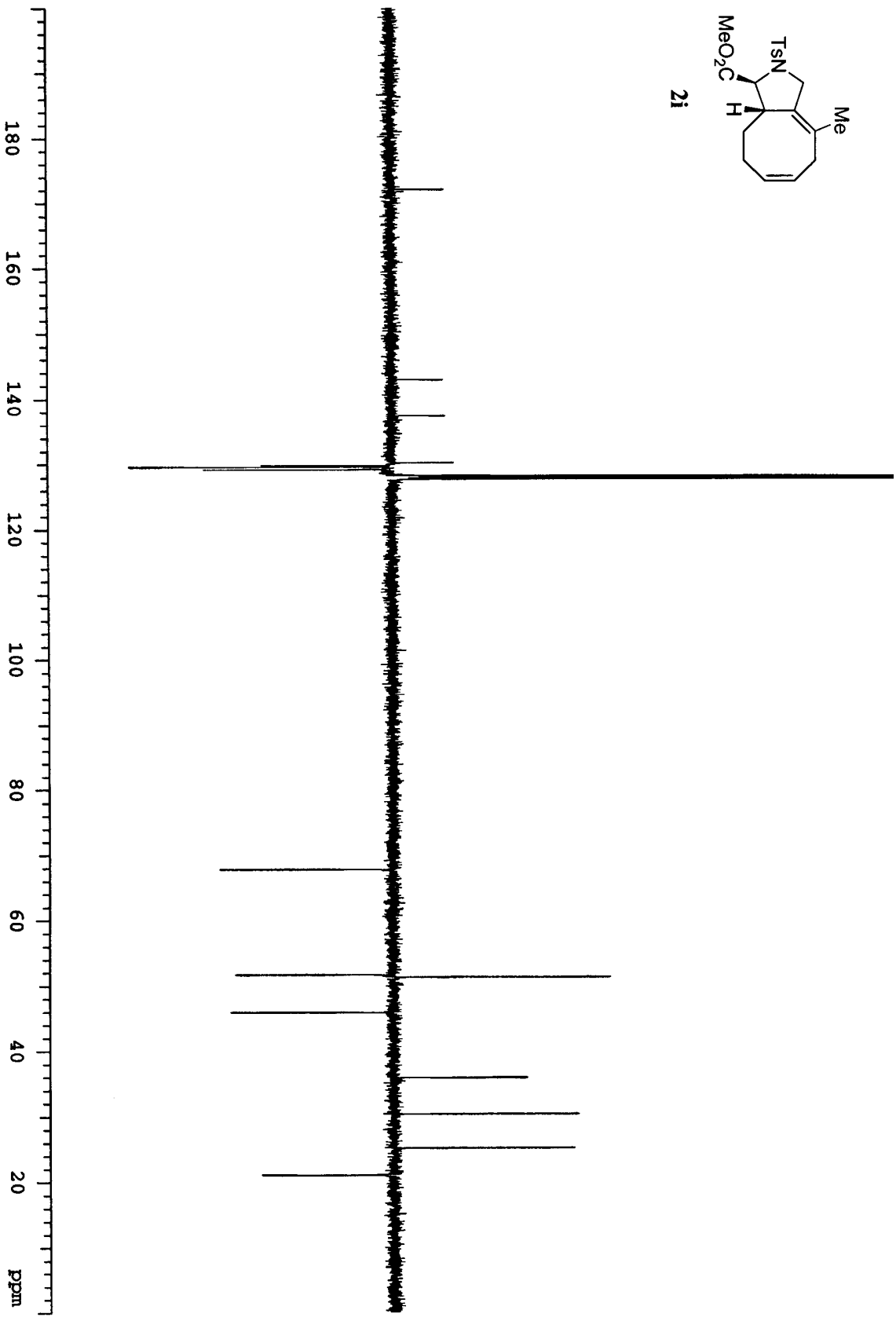
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MeO2C
H
Me
2i
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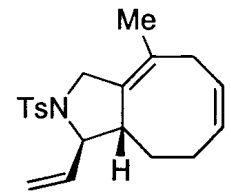
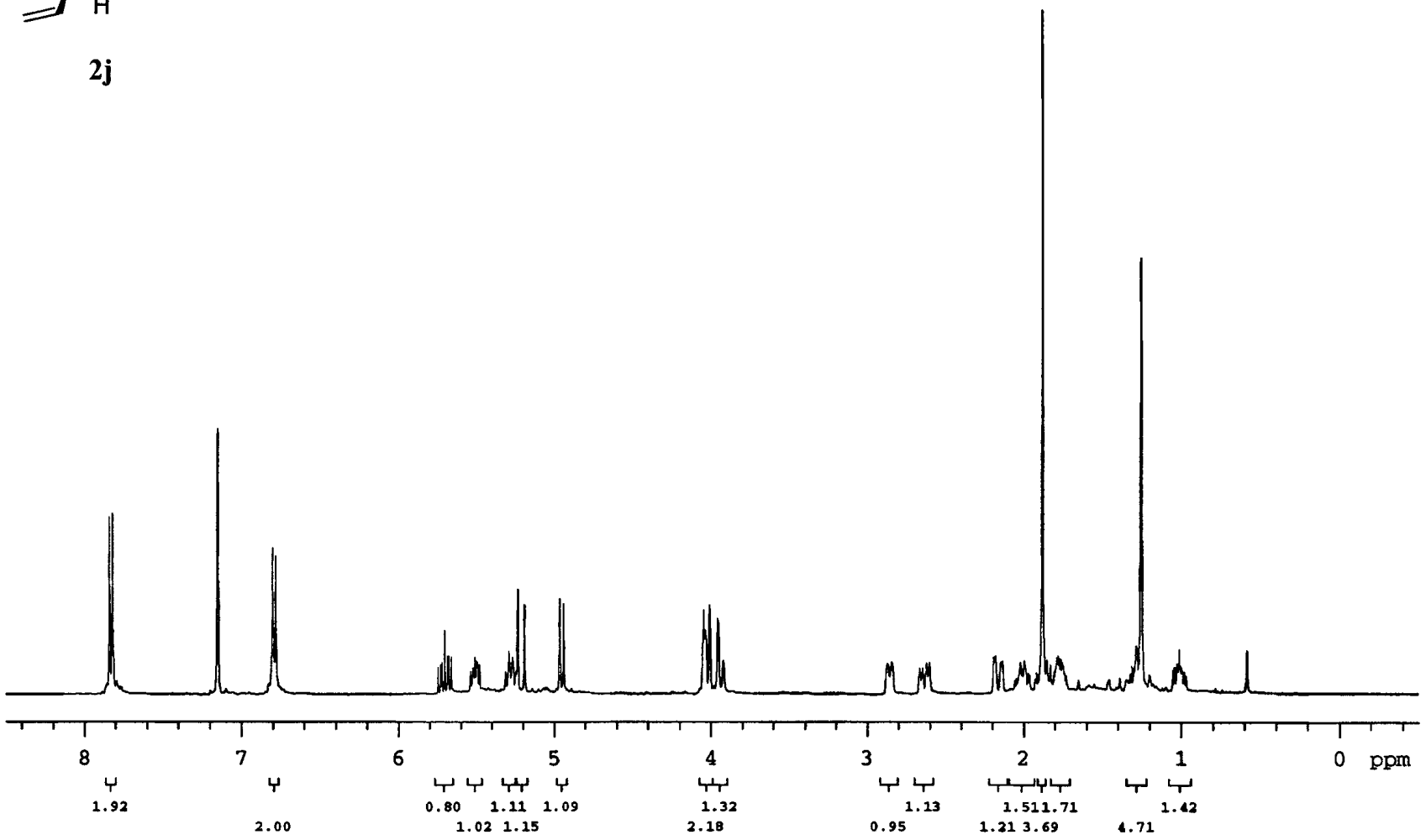
120
100
80
60
40
20
ppm


Me
TsN
H

2j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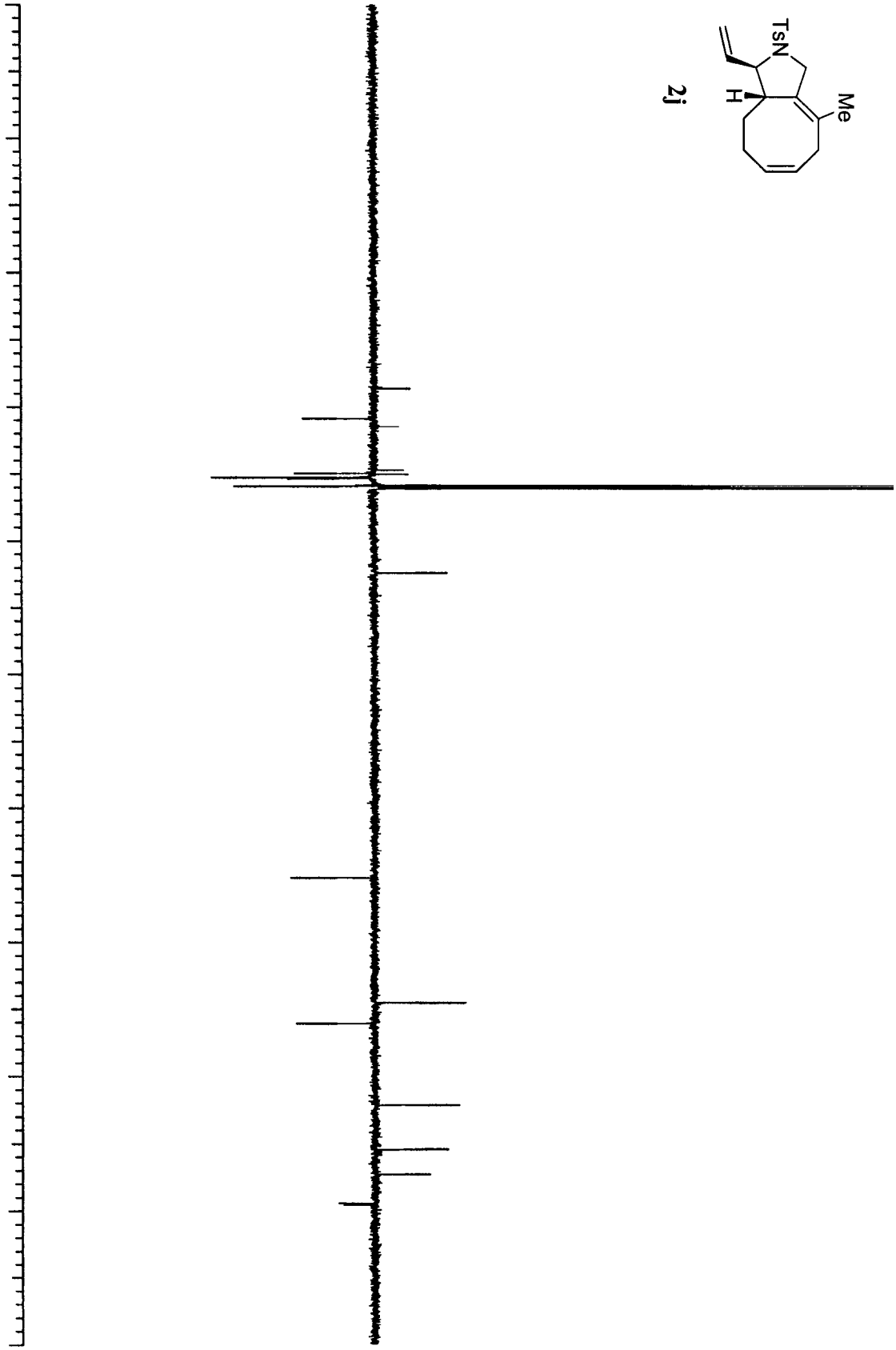
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2j
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80
60
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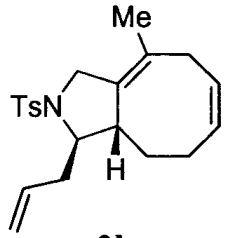
ppm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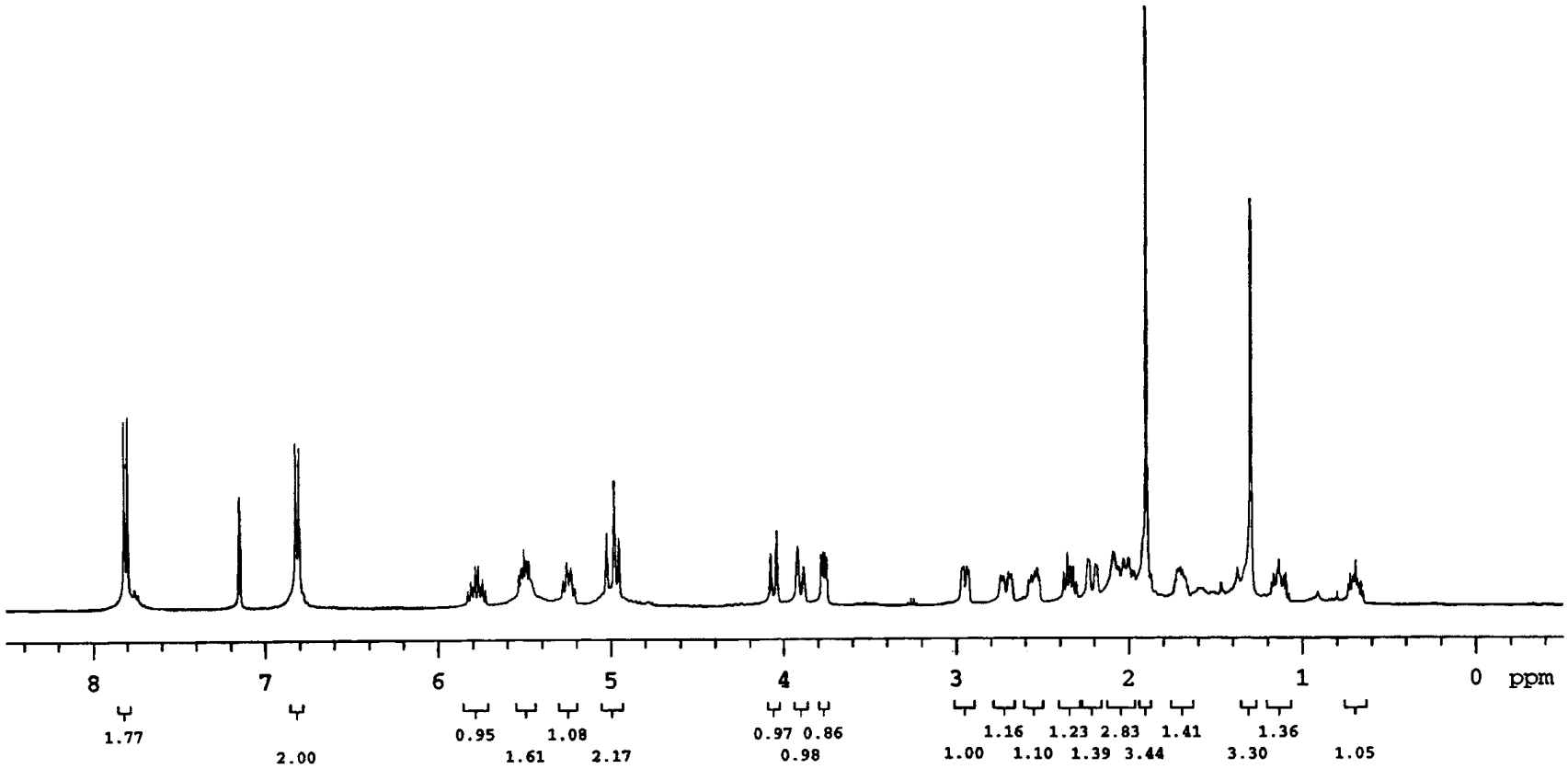
TsN
H

2k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0.86
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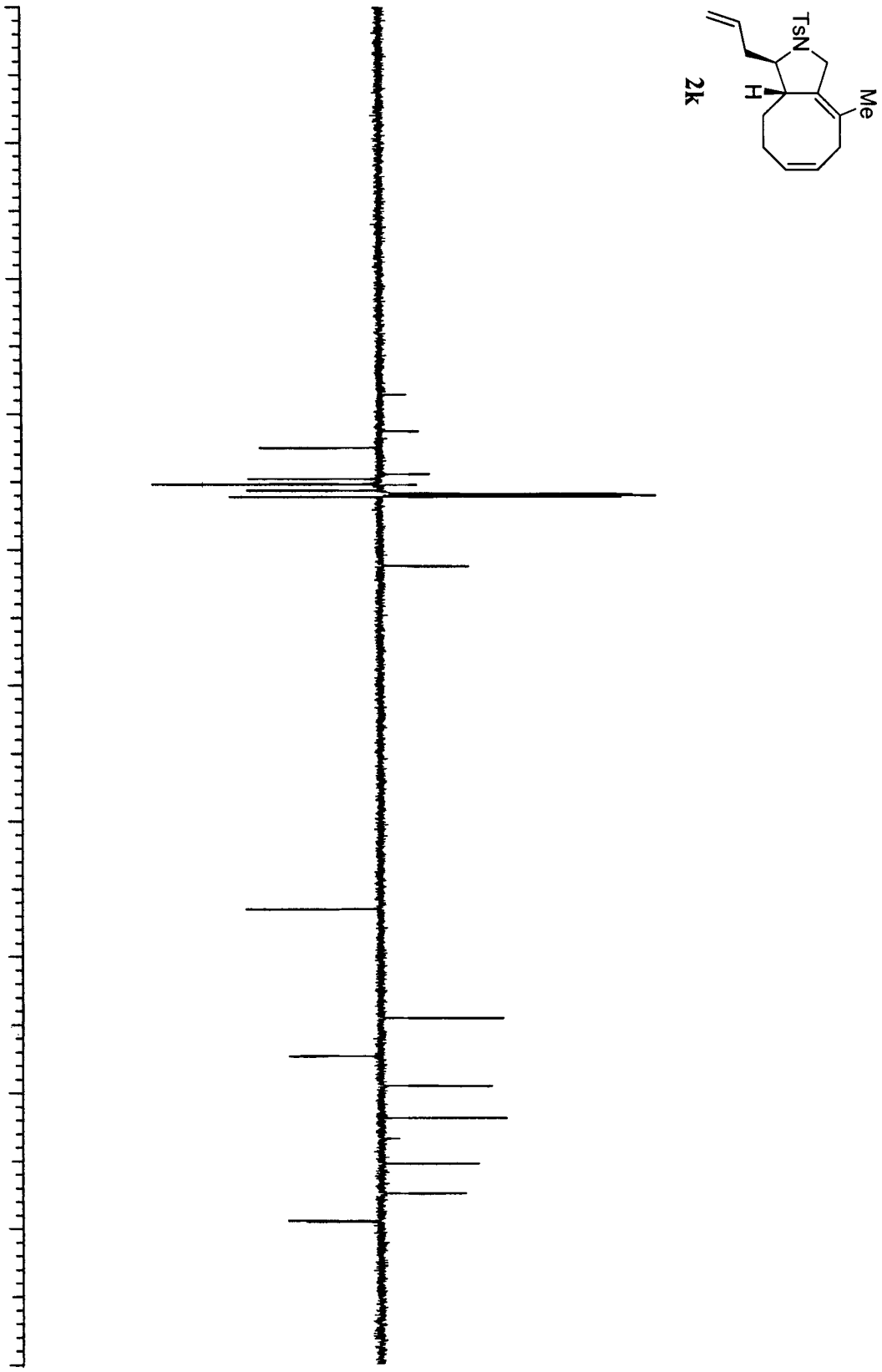
3.30
1.36
1.05


TsN
H
Me
2k
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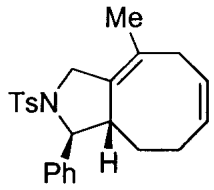
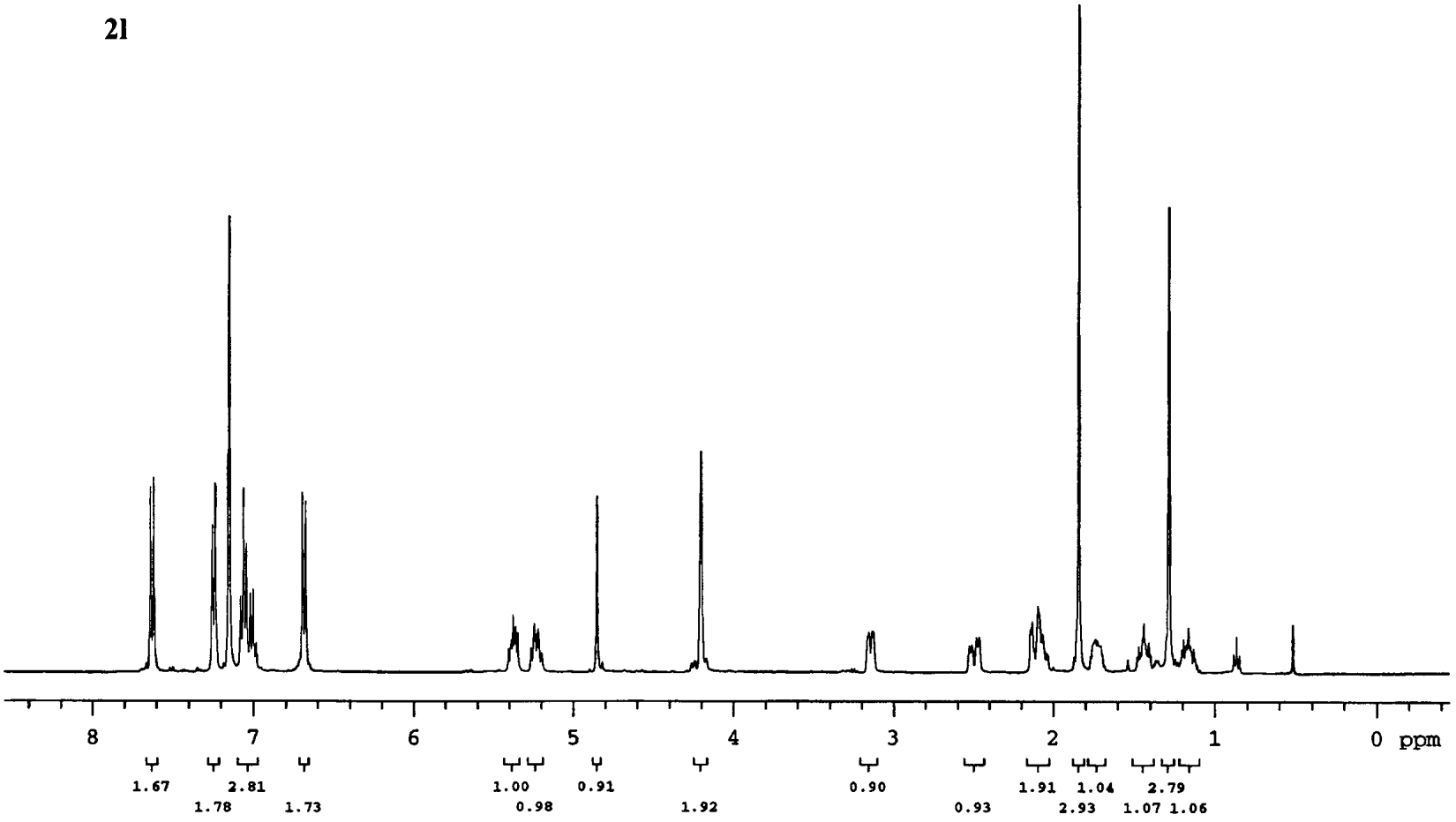
160
140
120
100
80
60
40
20
ppm


Me
TsN
Ph
H

21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7
6
5
4
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2
1
0 ppm
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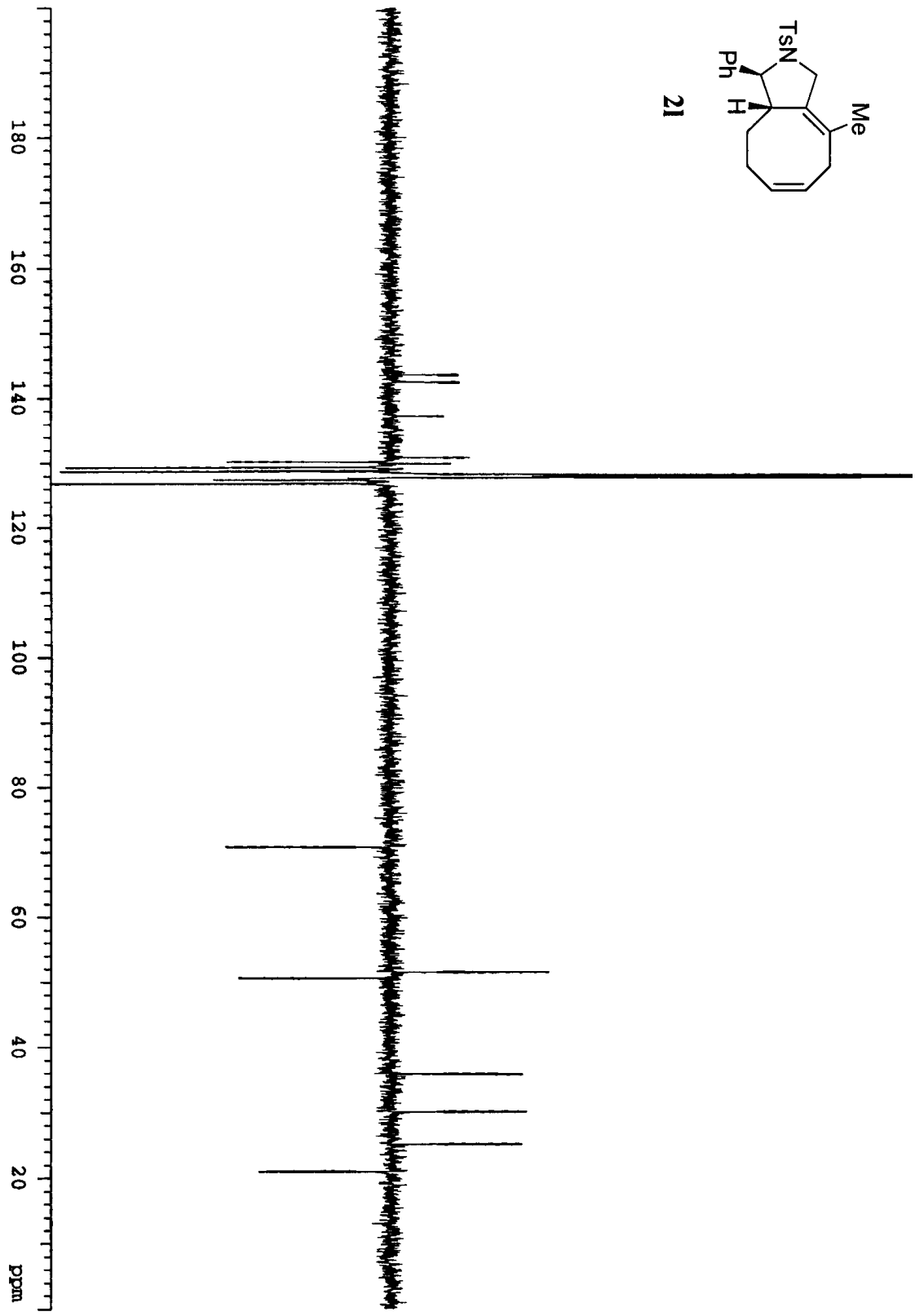
0.91
1.92
0.90
0.93
1.91
1.04
2.93
2.79
1.07
1.06


TsN
Ph
H
Me
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160
140
120
100
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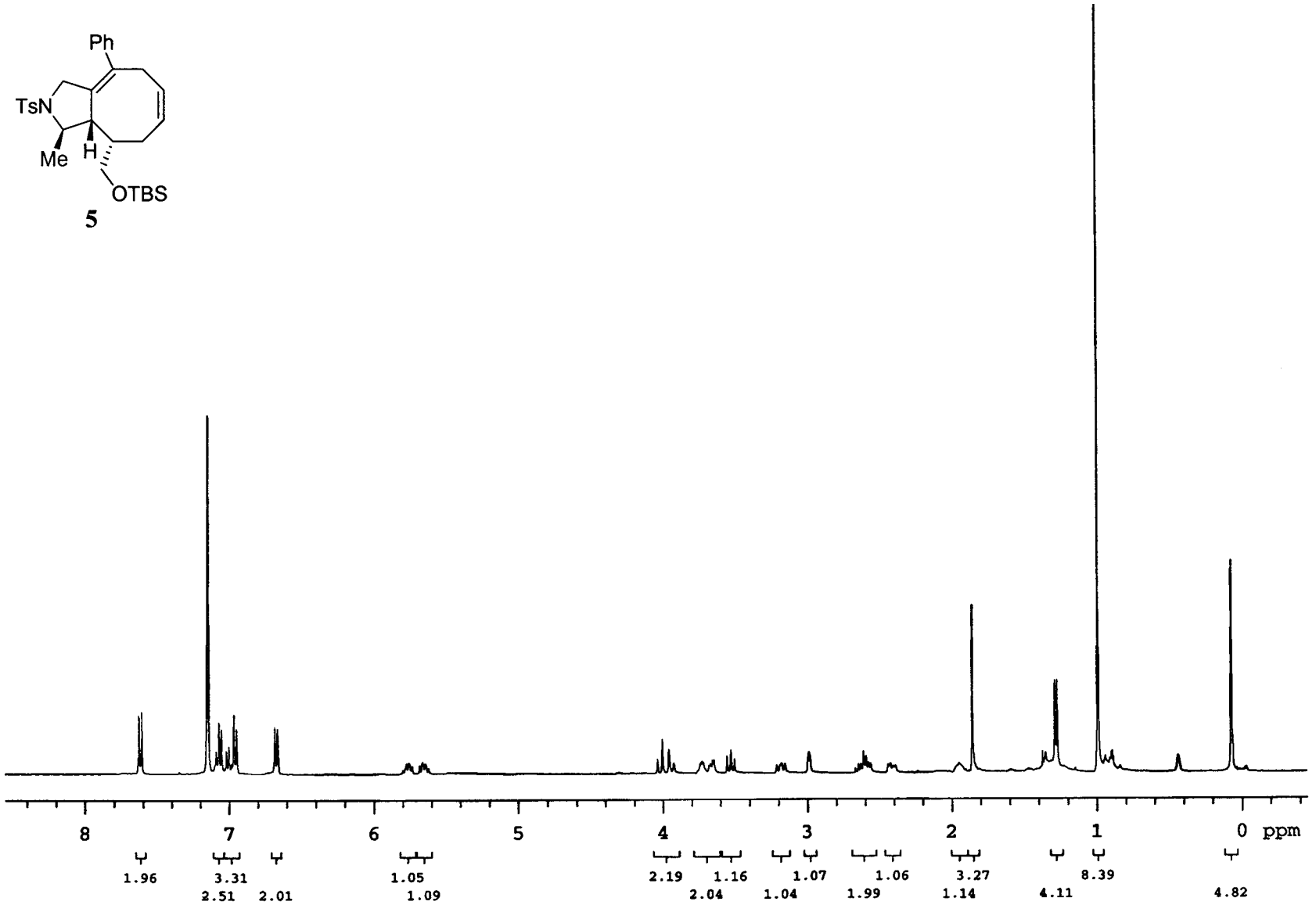
60
40
20
ppm


Ph
TsN
Me
H
OTBS
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8
7
6
5
4
3
2
1
0 ppm
1.96
3.31
2.51
2.01
1.05
1.09
2.19
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2.04
1.07
1.04
1.06
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1.14
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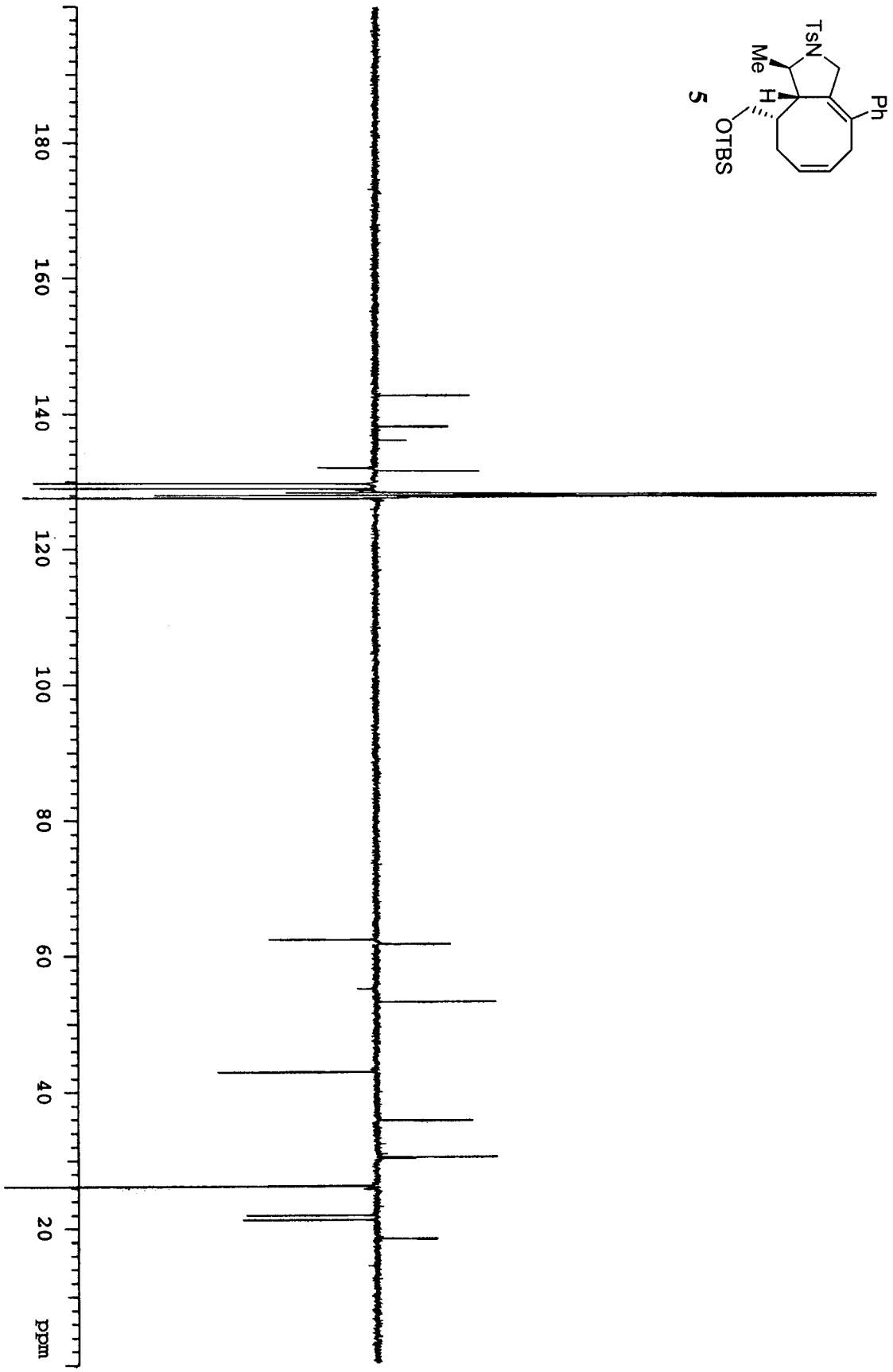
4.82

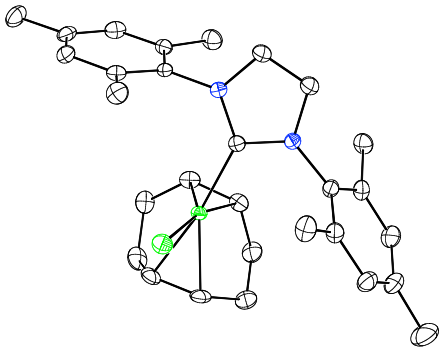

TsN
Me
H
Ph
OTBS
5
180
160
140
120
100
80
60
40
20
ppm

Indiana University Molecular Structure Center

Report 03094: $C_{29}H_{36}ClN_2Rh$

Maren Pink
May 8, 2003

Empirical Formula	C29 H36 Cl N2 Rh
Molecular Weight	550.96
Instrument	IUMSC SMART6000
Crystal color	yellow
Crystal size	0.20 × 0.11 × 0.10 mm^3
Crystal System	Tetragonal
Space Group	$I4_1/a$
Cell Dimensions (113 K)	
a =	32.464(2) Å
b =	32.464 Å
c =	9.9286(7) Å
α =	90°
β =	90°
χ =	90°
Volume	10463.7(10) $Å^3$
Z (Molecules/Cell)	16
Calculated Density	1.399 Mg/m^3
Absorption Coefficient	0.774 mm^{-1}
Final Residuals	
R1, observed data	0.0276
wR2, all data	0.0690



The sample was submitted by Erich Baum (research group of Prof. P. A. Evans, Department of Chemistry, Indiana University). A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 339 reflections. The data collection was carried out using Mo Ka radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 5.09 cm. A randomly oriented region of reciprocal space was surveyed to the extent of a quadrant. Two major sections of frames were collected with 0.30º steps in w at two different f settings and a detector position of –43° in 2q. An additional set of 80 frames was collected in order to model decay. Data to a resolution of 0.71 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 7032 strong reflections from the actual data collection after integration.The intensity data were corrected for absorption.

The structure was found as proposed. C-H…X hydrogen bonds were observed.

Complete data are available at
http://bl-chem-iumsc110.chem.indiana.edu/recipnet/showsample.jsp?sampleId=59057656

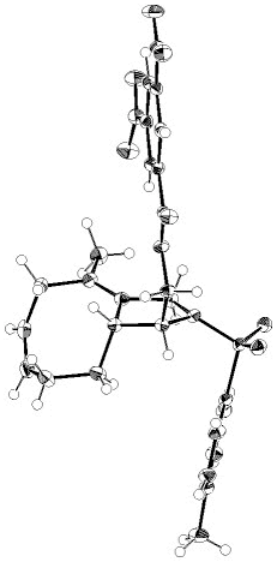
Indiana University Molecular Structure Center

Report 03220: $C_{26}H_27N_3O_8S$; CH_2Cl_2; 3,5-Dinitrobenzoate of **2f**

John C. Huffman
October 23, 2003

```
Empirical Formula:        C27H29Cl2N3O8S
Color of Crystal:            pale yellow
Crystal System:               Monoclinic
Space Group:                     P2(1)/n
Cell Dimensions (at 118(2) K; 990 data)
        a =                   11.1295(9)
        b =                   10.5003(9)
        c =                   24.1594(18)
    alpha =                   90
     beta =                   94.137(2)
    gamma =                   90

Z (Molecules/cell):                    4
Volume:                       2816.0(4)
Calculated Density:               1.478
Molecular Weight:                626.49
Linear Absorption Coefficient:    0.360
Final residuals are:
    R(F) (observed data)      =   0.0465
    Rw(F2) (refinement data) =   0.1423
```



The sample was submitted by Aleem Fazal from the research group of Prof. P. A. Evans, Department of Chemistry, Indiana University. The crystals occur as pale yellow layered prisms that cleaved easily. A fragment of one of the plates of approximate dimensions 0.30 × 0.30 × 0.25 mm onto the tip of a 0.15 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 118(2) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 30 frames. The data collection was carried out using graphite monochromated Mo Kα radiation with a frame time of 2 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Six sections of 606 frames were collected with 0.30º steps in ω at different ϕ settings with the detector set at –43° in 2θ. Final cell constants were calculated from the xyz centroids of 990 strong reflections from the actual data collection after integration (SAINT).

Complete data are available at
http://bl-chem-iumsc110.chem.indiana.edu/recipnet/showsample.jsp?sampleId=59057303&sampleHistoryId=-1

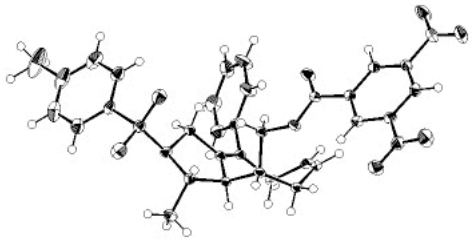
Indiana University Molecular Structure Center

Report 03228: $C_{32}H_{31}N_3O_8S$; 3,5-Dinitrobenzoate of **5**

John C. Huffman
October 31, 2003

```
Empirical Formula:           C32H31N3O8S
Color of Crystal:              colorless
Crystal System:               Monoclinic
Space Group:                     P2(1)/c
Cell Dimensions (at 110(2) K; 911 data)
         a =                  13.3244(14)
         b =                   7.2183(8)
         c =                 30.905(3)
     alpha =                 90
      beta =                100.270(3)
     gamma =                 90

Z (Molecules/cell):                    4
Volume:                         2924.8(5)
Calculated Density:                1.403
Molecular Weight:                 617.66
Linear Absorption Coefficient:     0.169
Final residuals are:
     R(F) (observed data)      =  0.0405
     Rw(F2) (refinement data) =  0.1045
```



The sample was submitted by Aleem Fazal from the research group of Prof. P. A. Evans, Department of Chemistry, Indiana University. The crystals occur as elongated transparent prisms plates that tend to grow in clumps. A well-formed typical sample was cleaved to form a fragment of dimensions 0.25 × 0.14 × 0.10 mm onto the tip of a 0.1 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 11(02) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 30 frames. The data collection was carried out using graphite monochromated Mo Kα radiation with a frame time of 15 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Four sections of 606 frames were collected with 0.30º steps in ω at different ϕ settings with the detector set at –43° in 2θ. Final cell constants were calculated from the xyz centroids of 911 strong reflections from the actual data collection after integration (SAINT).

Complete data are available at
http://bl-chem-iumsc110.chem.indiana.edu/recipnet/jamm.jsp?sampleId=59057557&sampleHistoryId=-1