SUPPORTING INFORMATION

Cyclization Reactions through DDQ-Mediated Oxidations of Vinyl Oxazolidinones

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Experimental

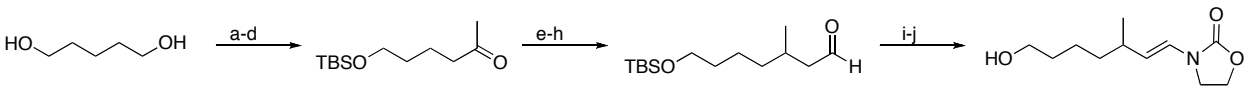
General Experimental:

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 spectrometer at 300 MHz and 75 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23. Data are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; dt = doublet of triplets; br = broad. High resolution and low resolution mass spectra were recorded on a VG 7070 spectrometer. Infrared (IR) spectra were collected on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as a thin film on a NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the CH_2Cl_2. Methylene chloride was distilled under N_2 from CaH_2. 1,2–dichloroethane was dried over 4 Å molecular sieves. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether, pentane and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. All reactions were performed in oven or flame-dried glassware under a positive pressure of N_2 with magnetic stirring unless otherwise noted.

General procedure for the synthesis of *trans*-vinyl oxazolidinones:[1]
An ~0.1 M solution of oxazolidinone (1.05 eq), aldehyde (1.0 eq), and pyridinium *p*-toluenesulfonate (0.1 equiv) in benzene was heated at reflux with azeotropic removal of water overnight. Upon disappearance of the starting material monitored via TLC, the solution was concentrated *in vacuo*. Further purification was performed using silica gel flash column chromatography (hexane/EtOAc) to afford the pure *trans*-vinyl oxazolidinone as a colorless oil.

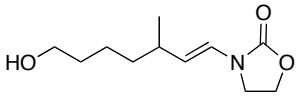
General procedure for enol acetate preparation:[2]
A mixture of Na_2CO_3 (15 mol%), $[(p\text{-cymene})RuCl_2]_2$ (0.04 eq), tri(2-furyl)phosphine (0.08 eq), acetic acid (2.0 eq), and 1-decyne (0.5 eq) in toluene was heated to and stirred for 1 h. Another portion of acetic acid (2.0 eq) and the alkyne substrate (1.0 eq) were dissolved in toluene and added to the mixture (~0.15 M final substrate concentration). The reaction was stirred at 80 °C overnight. Then crude mixture was concentrated on a rotary evaporator and purified by chromatography to give the desired enol acetate product.

General procedure for the cyclization reactions: The substrate (1 eq), 2,6-dichloropyridine (2 eq), and 4 Å molecular sieves (2 mass eq) were dissolved in anhydrous 1,2-dichloroethane to give an ~0.1 M solution. The mixture was stirred at room temperature for 15 minutes, followed by addition of $LiClO_4$ (0.2 eq). After 5 min DDQ (1.5 eq) was added. The reaction was monitored by TLC at room temperature unless specified and, upon starting material consumption, was quenched by 5% aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 three times, and combined organic layers were dried over $MgSO_4$. The filtrate was concentrated and purified by flash chromatography to give the desired product.



Reagents and conditions
a) NaH, TBSCl, THF, 58%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 89%. c) MeMgBr, Et_2O, 65%. d) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 91%. e) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF. f) DIBAL-H, PhMe, 89%, two steps. g) H_2, 10% Pd/C, THF. h) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 84%, two steps. i) 2-Oxazolidinone, PPTS, C_6H_6, 73%. j) Bu_4NF, THF, 97%.

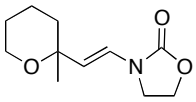
Scheme 1. Synthesis of substrate **1**.[3]



(*E*)-3-(7-hydroxy-3-methylhept-1-enyl)oxazolidin-2-one (1)
^1H NMR (300 MHz, $CDCl_3$) δ 6.62 (d, J = 14.3 Hz, 1H), 4.68 (dd, J = 8.2, 14.3 Hz, 1H), 4.46-4.41 (m, 2H), 3.71-3.62 (m, 4H), 2.26-2.14 (m, 1H), 1.58-1.52 (m, 2H), 1.37-1.30 (m, 4H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 155.7, 123.0, 117.4, 63.1, 62.3, 42.8, 37.5, 34.8, 33.0, 23.8, 21.6; IR

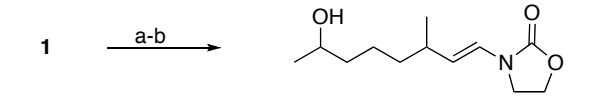
[1] Ko, C.; Hsung, R. P.; Al-Rashid, Z. F.; Feltenberger, J. B.; Lu, T.; Yang, J.; Wei, Y.; Zificsak, C. A. *Org. Lett.* **2007**, *9*, 4459.
[2] Goossen, L. J.; Paetzold, J.; Koley, D. *Chem. Commun*. **2003**, 706.
[3] Alcohol oxidation: Parikh, J.P.; Doering, W.E. *J. Am. Chem. Soc.* **1967**, *89*, 5505.

(neat) 3377, 2925, 2854, 1740, 1667, 1421, 1233, 1034 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{19}NO_3$ (M^+) 213.1365, found 213.1357.



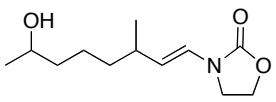
(*E*)-3-(2-(2-methyltetrahydro-2H-pyran-2-yl)vinyl)oxazolidin-2-one (3)

The general cyclization reaction procedure was followed: **2** (42 mg, 0.20 mmol), and 4 Å molecular sieves (80 mg) were dissolved in 1,2-dichloroethane (2.0 mL) at 0 °C, followed by DDQ (67 mg, 0.30 mmol). The reaction was stirred at 0 °C for 20 minutes and then quenched by Et_3N. The crude mixture was passed through a silica gel pad with EtOAc. After concentration, it was purified by flash chromatography (40% hexane in EtOAc) to give the desired product (41 mg, 98%). ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (d, J = 14.8 Hz, 1H), 4.83 (d, J = 14.9 Hz, 1H), 4.49-4.44 (m, 2H), 3.75-3.62 (m, 4H), 1.80-1.74 (m, 1H), 1.68-1.47 (m, 5H), 1.30 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 155.7, 124.8, 116.5, 73.2, 62.8, 62.4, 42.7, 35.2, 29.1, 26.0, 20.1; IR (neat) 2929, 1748, 1665, 1415, 1222, 1081, 1041 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{17}NO_3Na$ $(M+Na)^+$ 234.1106, found 234.1103.



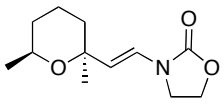
Reagents and conditions
a) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 86%. b) MeMgBr, Et_2O, 70%.

Scheme 2. Synthesis of substrate **4**.



(*E*)-3-(7-hydroxy-3-methyloct-1-enyl)oxazolidin-2-one (4)

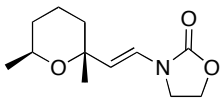
^1H NMR (300 MHz, $CDCl_3$) δ 6.57 (d, J = 14.3 Hz, 1H), 4.67 (m, 1H), 4.39 (t, J = 7.3 Hz, 2H), 3.77-3.71 (m, 1H), 3.65 (t, J = 8.2 Hz, 2H), 2.19-2.10 (m, 1H), 1.84 (s, 1H), 1.37-1.22 (m, 6H), 1.14 (d, J = 6.1 Hz, 3H), 0.98 (d, J = 6.7 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 155.7, 122.8, 117.4, 68.0, 67.9, 62.3, 42.7, 39.4, 39.3, 37.6, 37.5, 34.7, 34.6, 23.7, 23.6, 23.6, 23.5, 21.5, 21.4; IR (neat) 3437, 2961, 2926, 2857, 1741, 1668, 1457, 1420, 1233, 1083 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{21}NO_3$ (M^+) 227.1521, found 227.1514.



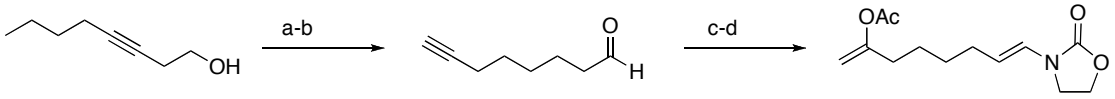
3-((*E*)-2-(2,6-dimethyltetrahydro-2H-pyran-2-yl)vinyl)oxazolidin-2-one (5)

The general cyclization reaction procedure was followed: **4** (17 mg, 0.075 mmol) and 4 Å molecular sieves (30 mg) were dissolved in anhydrous toluene (0.7 mL) at –30 °C, followed by DDQ (25 mg, 0.11 mmol). The reaction was stirred at –30 °C for 7 h and then quenched by Et_3N. The crude mixture was passed through a silica gel pad with EtOAc. After concentration the mixture was purified by flash chromatography (40% EtOAc in hexane) to give the desired products (dr = 2.8:1, totally 14 mg, 84%). ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, J = 14.6 Hz, 1H), 4.98 (d, J = 14.6 Hz, 1H), 4.45-4.40 (m, 2H), 3.80-3.70 (m, 3H), 1.73-1.61 (m, 3H), 1.57-1.49 (m, 3H), 1.35 (s, 3H), 1.14 (d, J = 6.1 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 155.8, 123.2, 120.2, 73.0, 66.8, 62.4, 42.7, 35.6, 33.5, 22.9, 21.3, 20.1; IR (neat) 2971, 2931, 2867, 1752, 1668, 1483, 1415, 1227, 1085, 1030 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{19}NO_3$ (M^+)

225.1365, found 225.1358.

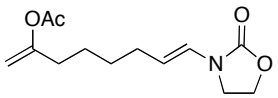


3-((*E*)-2-(2,6-dimethyltetrahydro-2H-pyran-2-yl)vinyl)oxazolidin-2-one
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (d, *J* = 15.0 Hz, 1H), 4.79 (d, *J* = 15.0 Hz, 1H), 4.49-4.44 (m, 2H), 3.76-3.70 (m, 2H), 3.69-3.58 (m, 1H), 1.84-1.79 (m, 1H), 1.67-1.59 (m, 3H), 1.57-1.45 (m, 2H), 1.29 (s, 3H), 1.13 (d, *J* = 6.2 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 155.4, 124.8, 115.8, 73.8, 67.7, 62.1, 42.6, 34.2, 33.2, 32.5, 22.4, 20.4; IR (neat) 2970, 2931, 1761, 1665, 1483, 1416, 1276, 1228, 1081, 1051, 755 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{19}NO_3$ (M^+) 225.1365, found 225.1361.

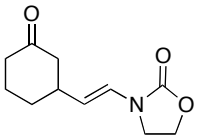


Reagents and conditions
a) Ethylene diamine, NaH, 60 °C, 85%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 86%. c) 2-Oxazolidinone, PPTs, benzene, reflux, 58%. d) HOAc, Na_2CO_3, $[(p\text{-cymene})RuCl_2]_2$, $(Fur)_3P$, PhMe, 80 °C, 86%.

Scheme 3. The preparation of substrate **6**.[4]

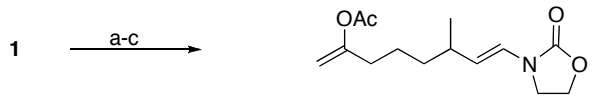


(*E*)-8-(2-Oxooxazolidin-3-yl)octa-1,7-dien-2-yl acetate (6)
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (d, *J* = 14.1 Hz, 1H), 4.79 (dt, *J* = 7.2, 14.4 Hz, 1H), 4.73 (s, 2H), 4.46-4.41 (m, 2H), 3.72-3.66 (m, 2H), 2.21 (t, *J* = 6.6 Hz, 2H), 2.15 (s, 3H), 2.09 (dd, *J* = 6.3, 13.2 Hz, 2H), 1.54-1.38 (m, 4H); ^{13}C (75 MHz, $CDCl_3$) δ 169.2, 156.2, 155.5, 124.1, 110.8, 101.3, 62.2, 42.6, 33.1, 29.6, 29.3, 25.8, 21.1; IR (neat) 2922, 2854, 1747, 1667, 1481, 1413, 1369, 1195, 1073, 1018, 943 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{19}NO_4$ (M^+) 253.1314, found 253.1313.



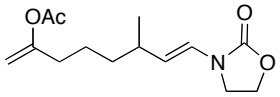
(*E*)-3-(2-(3-Oxocyclohexyl)vinyl)oxazolidin-2-one (7)
The general cyclization reaction procedure was followed: **6** (33 mg, 0.13 mmol), 2,6-dichloropyridine (38 mg, 0.26 mmol), and 4 Å molecular sieves (60 mg) were dissolved in 1,2-dichloroethane (1.4 mL) at 0 °C, followed by $LiClO_4$ (4 mg, 0.04 mmol) and DDQ (58 mg, 0.26 mmol). The reaction was stirred at 0 °C for 1 h and then quenched by 5% aqueous $NaHCO_3$. The crude mixture was extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (30% hexane in EtOAc) to give the desired product (21 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (d, *J* = 14.4 Hz, 1H), 4.76 (dd, *J* = 7.2, 14.3 Hz, 1H), 4.47-4.42 (m, 2H), 3.71-3.66 (m, 2H), 2.62-2.53 (m, 1H), 2.51-2.37 (m, 2H), 2.33-2.15 (m, 2H), 2.13-1.93 (m, 2H), 1.77-1.65 (m, 1H), 1.60-1.48 (m, 1H); ^{13}C (75 MHz, $CDCl_3$) δ 210.6, 155.6, 124.0, 113.9, 62.3, 48.5, 42.7, 41.3, 39.7, 32.2, 25.0; IR (neat) 2929, 2852, 1752, 1709, 1669, 1482, 1418, 1230, 1080, 1018, 948, 756 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{15}NO_3Na$ $(M+Na)^+$ 232.0950, found 232.0954.

[4] Alkyne isomerization: Denmark, S. E.; Yang, S. *J. Am. Chem. Soc.* **2002**, *124*, 2102.

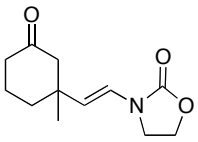


Reagents and conditions
a) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 85%. b) $(MeO)_2P(O)C(N_2)C(O)CH_3$, K_2CO_3, MeOH, 99%. c) HOAc, [(*p*-cymene)$RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 76%.

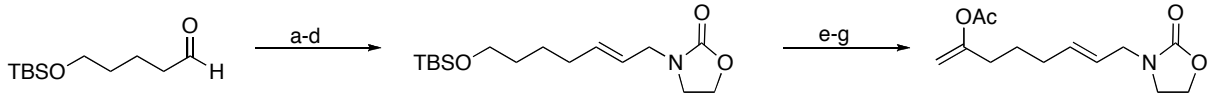
Scheme 4. Synthesis of substrate **8**.[5]



(*E*)-6-Methyl-8-(2-oxooxazolidin-3-yl)octa-1,7-dien-2-yl acetate (8)
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (d, *J* = 14.4 Hz, 1H), 4.70 (s, 2H), 4.66 (dd, *J* = 8.3, 14.4 Hz, 1H), 4.45-4.39 (m, 2H), 3.70-3.64 (m, 2H), 2.22-2.14 (m, 3H), 2.12 (s, 3H), 1.49-1.22 (m, 4H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C(75 MHz, $CDCl_3$) δ 169.3, 156.4, 155.6, 123.1, 117.1, 101.4, 62.3, 42.8, 36.9, 34.6, 33.5, 24.3, 21.5, 21.2; IR (neat) 2928, 2867, 1755, 1668, 1483, 1418, 1371, 1227, 1080, 1035, 949, 756 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{21}NO_4$ (M^+) 267.1471, found 267.1472.



(*E*)-3-(2-(1-Methyl-3-oxocyclohexyl)vinyl)oxazolidin-2-one (9)
The general cyclization reaction procedure was followed: **8** (50 mg, 0.19 mmol), 2,6-dichloropyridine (55 mg, 0.37 mmol) and 4 Å molecular sieves (100 mg) were dissolved in 1,2-dichloroethane (1.9 mL), followed by $LiClO_4$ (4 mg, 0.04 mmol) and DDQ (64 mg, 0.28 mmol). The reaction was stirred at room temperature for 30 minutes, quenched by 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (40% hexane in EtOAc) to give the desired product (31 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, *J* = 14.7 Hz, 1H), 4.76 (d, *J* = 14.7 Hz, 1H), 4.46-4.41 (m, 2H), 3.69-3.64 (m, 2H), 2.39-2.22 (m, 4H), 1.95-1.86 (m, 2H), 1.83-1.65 (m, 2H), 1.13 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 211.0, 155.6, 123.2, 118.7, 62.3, 53.8, 42.7, 41.0, 40.1, 37.4, 27.7, 22.4; IR (neat) 2955, 1751, 1710, 1665, 1415, 1227, 1084, 953, 756 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{17}NO_3$ (M^+) 223.1208, found 223.1211.



Reagents and conditions
a) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, 70%. b) DIBAL-H, PhMe, 81%. c) MsCl, Et_3N, LiBr, CH_2Cl_2, THF. d) 2-Oxazolidinone, KO^{t}Bu, 18-C-6, THF, 75%, two steps. e) Bu_4NF, THF, then SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 94%, two steps. f) $(MeO)_2P(O)C(N_2)C(O)CH_3$, K_2CO_3, MeOH, 99%. g) HOAc, [(*p*-cymene)$RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 89%.

Scheme 5. Synthesis of substrate **10**.[6]

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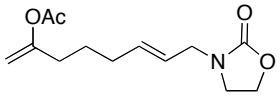
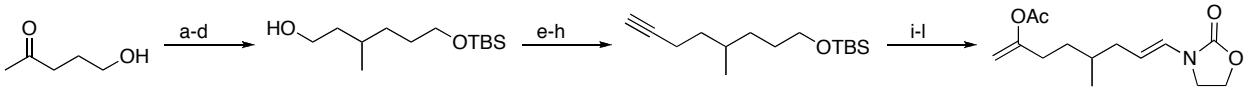
[5] Alkyne formation: (a) Muller, S.; Liepold, B.; Roth, G.; Bestmann, H. J. *Synlett* **1996**, 521. (b) Roth, G.; Liepold, B.; Muller, S.; Bestmann, H. J. *Synthesis* **2004**, 59.



(*E*)-8-(2-oxooxazolidin-3-yl)octa-1,6-dien-2-yl acetate (10)

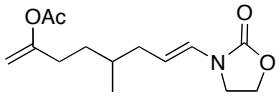
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72-5.62 (m, 1H), 5.48-5.38 (m, 1H), 4.74-4.73 (m, 2H), 4.36-4.30 (m, 2H), 3.83 (dd, *J* = 0.96, 6.7 Hz, 2H), 3.53-3.49 (M, 2H), 2.22 (t, *J* = 7.6 Hz, 2H), 2.15 (s, 3H), 2.13-2.07 (m, 2H), 1.62-1.52 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 169.2, 158.3, 156.0, 134.8, 124.4, 101.6, 61.9, 46.3, 44.1, 32.7, 31.4, 25.8, 21.1; IR (neat) 2929, 1750, 1667, 1486, 1428, 1370, 1200, 1036, 973 cm^{-1}; HRMS(EI) calcd for $C_{13}H_{19}NO_4$ (M^+) 253.1314, found 253.1310.



Reagents and conditions

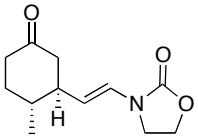
a) TBSCl, imidazole, DMF, 99%. b) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, 92%. c) DIBAL-H, CH_2Cl_2, 81%. d) H_2, 10% Pd/C, THF. e) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 84%, two steps. f) $Ph_3P^+CH_2OMeCl^-$, NaHMDS, THF. g) $Hg(OAc)_2$, THF, H_2O, then KI, 99%, two steps. h) $(MeO)_2P(O)C(N_2)C(O)CH_3$, K_2CO_3, MeOH, 80%. i) Bu_4NF, THF. j) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 98%, two steps. k) 2-Oxazolidinone, PPTs, C_6H_6, 35%. l) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 73%.

Scheme 6. Synthesis of substrate **11**.[7]



(*E*)-5-Methyl-8-(2-oxooxazolidin-3-yl)octa-1,7-dien-2-yl acetate (11)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, *J* = 14.3 Hz, 1H), 4.81-4.71 (m, 3H), 4.47-4.42 (m, 2H), 3.73-3.67 (m, 2H), 2.27-2.16 (m, 2H), 2.15 (s, 3H), 2.13-2.04 (m, 1H), 1.97-1.88 (m, 1H), 1.58-1.46 (m, 2H), 1.33-1.24 (m, 1H), 0.89 (d, *J* = 6.5 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 169.4, 156.7, 155.6, 125.1, 109.3, 101.4, 62.3, 42.8, 37.3, 33.2, 33.1, 31.2, 21.3, 19.4; IR (neat) 2955, 2920, 1749, 1668, 1483, 1415, 1371, 1217, 1081, 1039, 947, 756 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{21}NO_4$ (M^+) 267.1471, found 267.1466.



***trans*-3-((*E*)-2-(2-Methyl-5-oxocyclohexyl)vinyl)oxazolidin-2-one (12)**

The general cyclization reaction procedure was followed: **11** (36 mg, 0.13 mmol), 2,6-dichloropyridine (39.8 mg, 0.27 mmol) and 4 Å molecular sieves (70 mg) were dissolved in 1,2-dichloroethane (1.4 mL), followed by $LiClO_4$ (4 mg, 0.04 mmol) and DDQ (61 mg, 0.27 mmol). The reaction was stirred at –15 °C for 1.5 h, quenched by 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (30% hexane in EtOAc) to give the desired products. (23 mg, 77%, dr = 7.3:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (d, *J* = 14.3 Hz, 1H), 4.63 (dd, *J* = 9.0, 14.3 Hz, 1H), 4.46-4.42 (m, 2H), 3.69 (t, *J* = 8.2 Hz, 2H), 2.38-2.31 (m, 3H), 2.23 (dd, *J* = 12.5, 13.8 Hz, 1H), 2.11-2.02 (m, 2H), 1.66-1.57 (m, 1H), 1.46-1.38 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 210.5, 155.5, 124.9, 113.5, 62.3, 48.1, 46.9, 42.7, 41.2, 36.6, 34.1, 19.6; IR (neat) 2956, 2925, 1755, 1711, 1669, 1419, 1231, 1077, 948, 756

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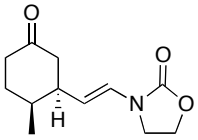
[6] Oxazolidinone alkylation: Martínez, M. M.; Hoppe, D. *Eur. J. Org. Chem.* **2005**, 1427.

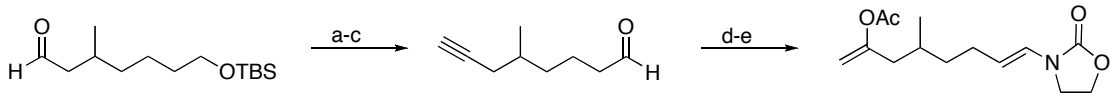
[7] Enol ether hydrolysis: Ansell, M. F.; Caton, M. P. L.; Stuttle, K. A. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1069.

cm^{-1}; HRMS (EI) calcd for $C_{12}H_{17}NO_3$ (M^+) 223.1208, found 223.1211.



***cis*-3-((*E*)-2-(2-Methyl-5-oxocyclohexyl)vinyl)oxazolidin-2-one**

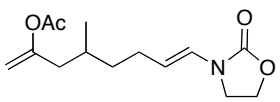
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (d, *J* = 14.2 Hz, 1H), 4.62 (dd, *J* = 9.4, 14.2 Hz, 1H), 4.45 (t, *J* = 8.1 Hz, 2H), 3.73-3.64 (m, 2H), 2.77-2.73 (m, 1H), 2.58 (dd, *J* = 5.2, 13.8 Hz, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 2.33 (dd, *J* = 5.7, 13.9 Hz, 1H), 2.17-2.10 (m, 1H), 1.90-1.85 (m, 1H), 1.70-1.62 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 211.2, 155.5, 125.9, 109.0, 62.4, 46.7, 43.8, 42.8, 40.0, 34.1, 30.7, 17.2; IR (neat) 2955, 2924, 1756, 1709, 1669, 1419, 1076, 947, 756 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{17}NO_3$ (M^+) 223.1208, found 223.1210.



Reagents and conditions

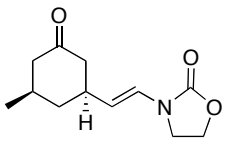
a) $(MeO)_2P(O)C(N_2)C(O)CH_3$, K_2CO_3, MeOH, 99%. b) Bu_4NF, THF. c) SO_3•Py, DMSO, Et_3N, CH_2Cl_2.
d) 2-Oxazolidinone, PPTS, C_6H_6, 54%, three steps. e) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 90%.

Scheme 7. Synthesis of substrate **13**.



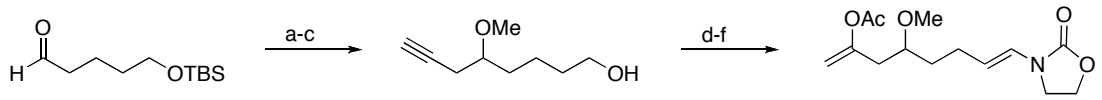
(*E*)-4-Methyl-8-(2-oxooxazolidin-3-yl)octa-1,7-dien-2-yl acetate (13)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (d, *J* = 14.4 Hz, 1H), 4.90-4.72 (m, 3H), 4.46-4.41 (m, 2H), 3.71-3.66 (m, 2H), 2.28-2.00 (m, 4H), 2.14 (s, 3H), 1.68-1.43 (m, 2H), 1.28-1.18 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 169.2, 155.6, 155.2, 124.2, 111.2, 102.9, 62.3, 42.8, 41.3, 37.0, 30.1, 27.5, 21.3, 19.5; IR (neat) 2921, 1750, 1668, 1415, 1371, 1180, 1022, 755 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{21}NO_4Na$ $(M+Na)^+$ 290.1368, found 290.1344.



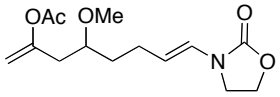
3-((*E*)-2-(3-Methyl-5-oxocyclohexyl)vinyl)oxazolidin-2-one (14)

The general cyclization reaction procedure was followed: **13** (38 mg, 0.14 mmol), 2,6-dichloropyridine (42 mg, 0.28 mmol) and 4 Å molecular sieves (70 mg) were dissolved in 1,2-dichloroethane (1.5 mL), followed by $LiClO_4$ (4 mg, 0.04 mmol) and DDQ (86 mg, 0.38 mmol). The reaction was stirred at room temperature for 1 h, quenched by 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (30% hexane in EtOAc) to give starting material (3 mg) and the desired product (22 mg, 69%, 75% based on starting material recovery). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (d, *J* = 14.4 Hz, 1H), 4.76 (dd, *J* = 7.2, 14.4 Hz, 1H), 4.47-4.42 (m, 2H), 3.71-3.66 (m, 2H), 2.55-2.32 (m, 3H), 2.14-1.81 (m, 4H), 1.30-1.18 (m, 1H), 1.05 (d, *J* = 6.0 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 210.2, 155.6, 123.9, 114.2, 62.3, 49.5, 47.8, 42.7, 41.2, 38.8, 33.0, 22.5; IR (neat) 2954, 2924, 1753, 1712, 1669, 1482, 1254, 1228, 1077, 946, 756 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{17}NO_3Na$ $(M+Na)^+$ 246.1106, found 246.1084.

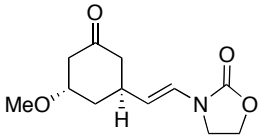


Reagents and conditions
a) Propargyl bromide, Zn, ICH_2CH_2I, THF, 87%. b) NaH, MeI, THF. c) Bu_4NF, THF, 74%, two steps. d) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 75%. e) 2-Oxazolidinone, PPTS, C_6H_6, 31%. f) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 74%.

Scheme 8. Synthesis of substrate **15**.[8]

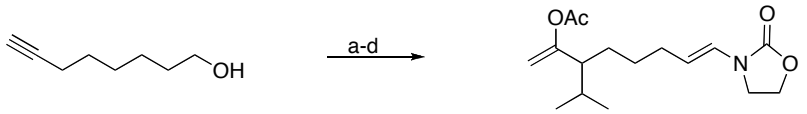


(*E*)-4-Methoxy-8-(2-oxooxazolidin-3-yl)octa-1,7-dien-2-yl acetate (15) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (d, *J* = 14.3 Hz, 1H), 4.85-4.76 (m, 3H), 4.46-4.39 (m, 2H), 3.72-3.66 (m, 2H), 3.36-3.29 (m, 1H), 3.34 (s, 3H), 2.48 (dd, *J* = 6.2, 14.9 Hz, 1H), 2.37 (dd, *J* = 5.9, 14.9 Hz, 1H), 2.27-2.08 (m, 2H), 2.15 (s, 3H), 1.64-1.57 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 169.3, 155.6, 153.5, 124.4, 110.8, 104.0, 77.9, 62.3, 57.0, 42.8, 37.9, 34.2, 25.8, 21.3; IR (neat) 2928, 1752, 1701, 1670, 1482, 1416, 1370, 1220, 1084, 1038, 947, 757 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{21}NO_5Na$ $(M+Na)^+$ 306.1317, found 306.1314.



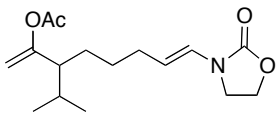
3-((*E*)-2-(3-Methoxy-5-oxocyclohexyl)vinyl)oxazolidin-2-one (16) The general cyclization reaction procedure was followed: **15** (29 mg, 0.10 mmol), 2,6-dichloropyridine (30 mg, 0.20 mmol) and 4 Å molecular sieves (60 mg) were dissolved in 1,2-dichloroethane (1.1 mL), followed by $LiClO_4$ (3 mg, 0.03 mmol) and DDQ (63 mg, 0.28 mmol). The reaction was stirred at 0 °C for 1.5 h, quenched by 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (20% hexane in EtOAc) to give starting material (5 mg) and the desired product (15 mg, 61%, 74% based on starting material recovery). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (d, *J* = 14.4 Hz, 1H), 4.77 (dd, *J* = 7.4, 14.4 Hz, 1H), 4.49-4.43 (m, 2H), 3.92-3.89 (m, 1H), 3.72-3.67 (m, 2H), 3.32 (s, 3H), 2.97-2.88 (m, 1H), 2.66 (ddt, *J* = 2.1, 4.0, 14.6 Hz, 1H), 2.50 (ddt, *J* = 2.0, 4.2, 14.1 Hz, 1H), 2.43 (dd, *J* = 3.5, 14.6 Hz, 1H), 2.21-2.13 (m, 2H), 1.65 (ddd, *J* = 2.2, 11.9, 13.9 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ 208.3, 155.6, 124.2, 113.7, 76.6, 62.4, 56.2, 48.2, 45.6, 42.7, 35.8, 33.6; IR (neat) 2922, 2852, 1750, 1712, 1668, 1417, 1216, 1075, 1032, 944, 756 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{17}NO_4Na$ $(M+Na)^+$ 262.1055, found 262.1038.

[8] Propargylzinc addition: Lee, A. S.-Y.; Chu, S.-F.; Chang, Y. T.; Wang, S.-H. *Tetrahedron Lett.* **2004**, *45*, 1551.



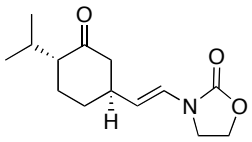
Reagents and conditions
a) ^{n}BuLi, ^{i}PrI, THF, 25%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 99%. c) 2-Oxazolidinone, PPTS, C_6H_6, 51%. d) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 53%.

Scheme 9. Synthesis of substrate **17**.[9]



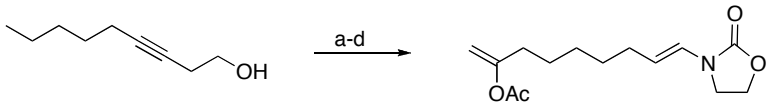
(*E*)-3-Isopropyl-8-(2-oxooxazolidin-3-yl)octa-1,7-dien-2-yl acetate (17)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, *J* = 14.1 Hz, 1H), 4.87-4.71 (m, 3H), 4.46-4.44 (m, 2H), 3.71-3.66 (m, 2H), 2.13 (s, 3H), 2.12-1.98 (m, 2H), 1.91-1.82 (m, 1H), 1.72-1.61 (m, 1H), 1.52-1.24 (m, 4H), 0.92 (d, *J* = 6.6 Hz, 3H), 0,91 (d, *J* = 6.6 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 168.9, 156.1, 155.4, 123.9, 111.2, 102.5, 62.1, 51.2, 42.6, 29.9, 29.9, 28.4, 28.0, 21.4, 20.4, 20.2; IR (neat) 2931, 1756, 1670, 1483, 1416, 1197, 1076, 1036, 946, 756 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{25}NO_4$ (M^+) 295.1784, found 295.1772.



3-((*E*)-2-(4-Isopropyl-3-oxocyclohexyl)vinyl)oxazolidin-2-one (18)

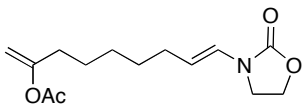
The general cyclization reaction procedure was followed: **17** (35 mg, 0.12 mmol), 2,6-dichloropyridine (35 mg, 0.24 mmol) and 4 Å molecular sieves (70 mg) were dissolved in 1,2-dichloroethane (1.2 mL), followed by $LiClO_4$ (4 mg, 0.04 mmol) and DDQ (46 mg, 0.20 mmol). The reaction was stirred at –10 °C for 45 minutes, quenched by 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (50% EtOAc in hexane) to give the desired product. (24 mg, 79%, dr = 9:1) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.69 (d, *J* = 14.4 Hz, 1H), 4.76 (dd, *J* = 7.1, 14.3 Hz, 1H), 4.47-4.42 (m, 2H), 3.72-3.65 (m, 2H), 2.55-2.38 (m, 2H), 2.21-1.95 (m, 4H), 1.80-1.70 (m, 1H), 1.57-1.36 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 211.2, 155.6, 123.8, 114.3, 62.3, 56.2, 49.3, 42.7, 40.9, 32.7, 27.6, 26.2, 21.4, 18.9; IR (neat) 2956, 2870, 1748, 1703, 1666, 1481, 1414, 1205, 1079, 1034, 943, 754 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{21}NO_3$ (M^+) 251.1521, found 251.1509.



Reagents and conditions
a) NaH, $H_2NCH_2CH_2NH_2$, 60 °C, 99%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 93%. c) 2-Oxazolidinone, PPTS, C_6H_6, 73%. d) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 76%.

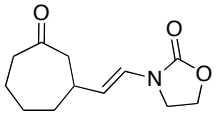
Scheme 10. Synthesis of substrate **19**.

[9] Alkyne dianion alkylation: (a) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, *61*, 5440. (b) Liang, K.; Chandrasekharam, M.; Li, C.; Liu, R. *J. Org. Chem.* **1998**, *63*, 7289.



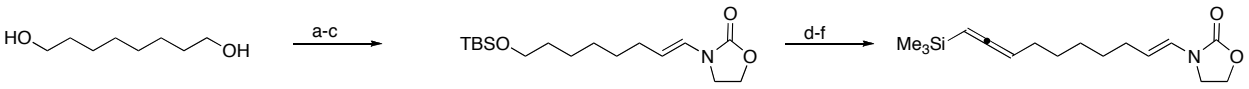
(*E*)-9-(2-Oxooxazolidin-3-yl)nona-1,8-dien-2-yl acetate (19)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.58 (d, J = 14.3 Hz, 1H), 4.76 (dt, J = 7.1, 14.2 Hz, 1H), 4.68-4.67 (m, 2H), 4.41-4.36 (m, 2H), 3.68-3.62 (m, 2H), 2.16 (t, J = 7.1 Hz, 2H), 2.10 (s, 3H), 2.07-1.99 (m, 2H), 1.47-1.19 (m, 6H); ^{13}C (75 MHz, $CDCl_3$) δ 169.3, 156.4, 155.5, 123.9, 111.1, 101.3, 62.2, 42.7, 33.2, 29.8, 29.7, 28.3, 26.2, 21.1; IR (neat) 2926, 2855, 1749, 1669, 1483, 1415, 1370, 1223, 1077, 945, 756 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{21}NO_4$ (M^+) 267.1471, found 267.1470.



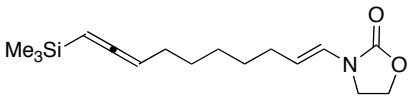
(*E*)-3-(2-(3-Oxocycloheptyl)vinyl)oxazolidin-2-one (20)

The general cyclization reaction procedure was followed: **19** (58 mg, 0.22 mmol), 2,6-dichloropyridine (64 mg, 0.43 mmol) and 4 Å molecular sieves (120 mg) were dissolved in 1,2-dichloroethane (2.0 mL), followed by $LiClO_4$ (7 mg, 0.07 mmol) and DDQ (74 mg, 0.33 mmol). The reaction was stirred at 10 °C for 30 minutes, quenched by 5% $NaHCO_3$ (aq), extracted with CH_2Cl_2 (3x). After concentration, it was purified by flash chromatography (40% hexane in EtOAc) to give the desired product. (14 mg, 30%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (d, J = 14.3 Hz, 1H), 4.77 (dd, J = 7.2, 14.4 Hz, 1H), 4.47-4.42 (m, 2H), 3.70-3.65 (m, 2H), 2.08-2.49 (m, 4H), 1.97-1.88 (m, 3H), 1.71-1.58 (m, 2H), 1.53-1.46 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 213.3, 155.7, 123.6, 115.2, 62.3, 50.5, 44.2, 42.7, 37.9, 37.1, 28.3, 24.2; IR (neat) 2922, 2852, 1748, 1694, 1666, 1415, 1221, 1032 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{17}NO_3$ (M^+) 223.1208, found 223.1204.



Reagents and conditions
a) NaH, TBSCl, THF, 61%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 93%. c) 2-Oxazolidinone, PPTS, C_6H_6, 72%. d) Bu_4NF, THF, then SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 87%, two steps. e) Me_3SiCCH, ^{n}BuLi, THF, 88%. f) *o*-$NO_2PhSO_2NHNH_2$, Ph_3P, DIAD, THF, 69%.

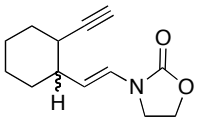
Scheme 11. Synthesis of substrate **21**.[10]



(*E*)-3-(10-(Trimethylsilyl)deca-1,8,9-trienyl)oxazolidin-2-one (21)

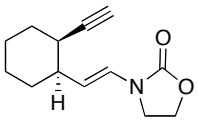
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (d, J = 14.3 Hz, 1H), 4.89-4.72 (m, 3H), 4.45-4.39 (m, 2H), 3.71-3.65 (m, 2H), 2.07-2.02 (m, 2H), 1.97-1.91 (m, 2H), 1.43-1.25 (m, 6H), 0.08 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) δ 210.1, 155.6, 124.0, 111.5, 83.5, 82.7, 62.3, 42.8, 30.1, 29.9, 29.7, 28.7, 27.9, -0.7; IR (neat) 2926, 2853, 1936, 1761, 1670, 1415, 1246, 1077, 840 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{27}NO_2Si$ (M^+) 293.1811, found 293.1809.

[10] Allene formation: Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492.



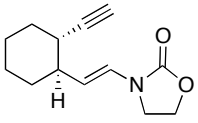
3-((*E*)-2-(2-Ethynylcyclohexyl)vinyl)oxazolidin-2-one (22)

The general cyclization reaction procedure was followed: **21** (90 mg, 0.31 mmol) and 2,6-Cl_2Py (90.8 mg, 0.61 mmol) were dissolved in 1,2-dichloroethane (3.0 mL), followed by $LiClO_4$ (6 mg, 0.06 mmol) and DDQ (104 mg, 0.46 mmol). The reaction was stirred at 0 °C for 30 minutes, quenched by 5% aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (3x). After concentration, 4 mL THF was added followed by TBAF (1.8 mL, 1.8 mmol). After 1 h at 0 °C, the reaction was quenched by addition of H_2O, and extracted with EtOAc (3x). The organic phase was dried over $MgSO_4$, and concentrated. It was purified by flash chromatography (40% hexane in EtOAc) to give the products (42 mg, 63%, dr = 1:1).



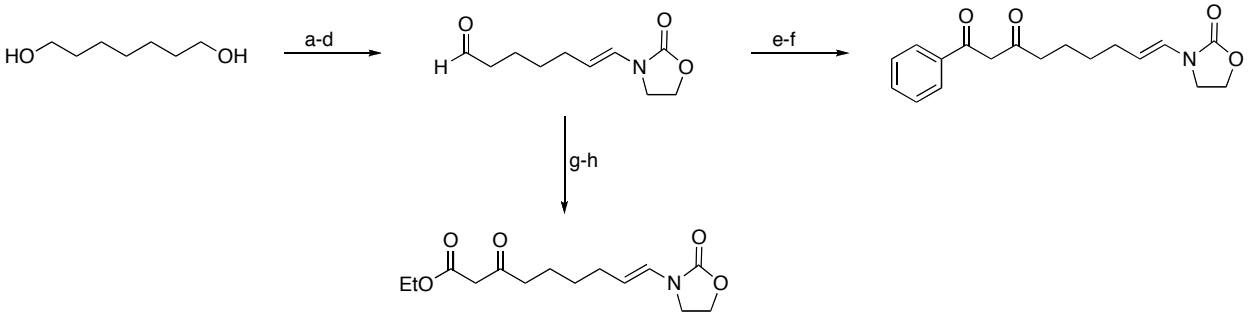
***cis*-3-((*E*)-2-(2-Ethynylcyclohexyl)vinyl)oxazolidin-2-one**

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (d, *J* = 14.4 Hz, 1H), 4.93 (dd, *J* = 8.4, 14.4 Hz, 1H), 4.46-4.41 (m, 2H), 3.75-3.70 (m, 2H), 2.73-2.71 (m, 1H), 2.21-2.16 (m, 1H), 2.08 (d, *J* = 2.4 Hz, 1H), 1.87-1.82 (m, 1H), 1.76-1.64 (m, 1H), 1.63-1.47 (m, 4H), 1.46-1.21 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 155.7, 123.9, 114.7, 85.5, 71.2, 62.3, 42.8, 41.4, 34.0, 31.1, 29.1, 25.6, 21.5; IR (neat) 3288, 2928, 2855, 1753, 1668, 1417, 1244, 1070, 944 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{17}NO_2$ (M^+) 219.1259, found 219.1256.



***trans*-3-((*E*)-2-(2-ethynylcyclohexyl)vinyl)oxazolidin-2-one**

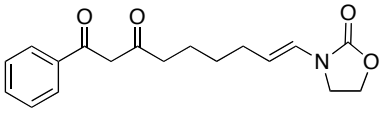
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (d, *J* = 14.4 Hz, 1H), 4.87 (dd, *J* = 6.9, 14.5 Hz, 1H), 4.44 (t, *J* = 7.8 Hz, 2H), 3.72 (t, *J* = 8.5 Hz, 2H), 2.07 (d, *J* = 1.6 Hz, 1H), 2.06-2.00 (m, 2H), 1.84-1.72 (m, 3H), 1.54-1.37 (m, 2H), 1.32-1.091 (m, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 155.7, 124.2, 114.7, 87.8, 71.2, 69.6, 62.3, 43.5, 42.8, 36.3, 33.2, 32.7, 25.6; IR (neat) 3286, 2927, 2855, 1752, 1669, 1558, 1540, 1417, 1244, 1070, 944 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{17}NO_2$ (M^+) 219.1259, found 219.1255.



Reagents and conditions

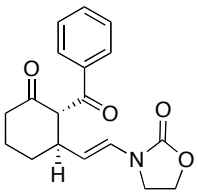
a) NaH, TBSCl, THF, 60%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 91%. c) 2-Oxazolidinone, PPTS, C_6H_6, 61%. d) Bu_4NF, THF, then SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 88%, two steps. e) Acetophenone, LDA, THF, –78°C, 90%. f) Dess-Martin periodinane, $NaHCO_3$, THF, 82%. g) EtOAc, LDA, THF, –78 °C, 92%. g) Dess-Martin periodinane, $NaHCO_3$, THF, 88%.

Scheme 12. Syntheses of substrates **23** and **25**.



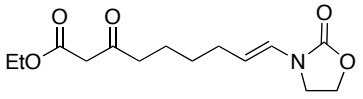
(*E*)-9-(2-Oxooxazolidin-3-yl)-1-phenylnon-8-ene-1,3-dione (23)

^{1}H NMR (300 MHz, $CDCl_3$) δ 16.19 (s, 1H), 7.90-7.88 (m, 2H), 7.53-7.44 (m, 3H), 6.67 (d, *J* = 14.3 Hz, 1H), 6.18 (s, 1H), 4.80 (dt, *J* = 7.1, 14.3 Hz, 1H), 4.45-4.40 (m, 2H), 3.68 (t, *J* = 8.3 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.16-2.09 (m, 2H), 1.74-1.66 (m, 2H), 1.53-1.45 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 196.9, 183.6, 155.6, 135.2, 132.5, 128.8, 127.2, 124.5, 110.8, 96.4, 62.3, 42.8, 39.2, 29.8, 29.7, 25.3; IR (neat) 2921, 2852, 1751, 1670, 1599, 1573, 1481, 1414, 1233, 1073, 942, 755 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{21}NO_4$ (M^+) 315.1471, found 315.1464.



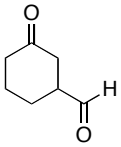
3-((*E*)-2-(2-Benzoyl-3-oxocyclohexyl)vinyl)oxazolidin-2-one (24)

The general cyclization reaction procedure was followed: **23** (70 mg, 0.22 mmol) and 4 Å molecular sieves (140 mg) were dissolved in 1,2-dichloroethane (3.0 mL), followed by $LiClO_4$ (5 mg, 0.05 mmol) and DDQ (65 mg, 0.29 mmol). The reaction was stirred at –15 °C for 1.5 h, quenched by 5% $NaHCO_3$ (aq), and filtered through a short silica gel pad with EtOAc. After concentration, it was purified by flash chromatography (30% hexane in EtOAc) to give the desired product (52 mg, 75%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.60-7.40 (m, 3H), 6.74 (d, *J* = 14.4 Hz, 1H), 4.74 (dd, *J* = 7.6, 14.4 Hz, 1H), 4.40-4.35 (m, 2H), 4.24 (d, *J* = 9.8 Hz, 1H), 3.54 (dt, *J* = 2.1, 7.5 Hz, 2H), 3.30-3.21 (m, 1H), 2.63-2.42 (m, 2H), 2.18-2.11 (m, 2H), 1.94-1.72 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 207.5, 197.2, 155.5, 137.6, 133.5, 128.9, 128.6, 125.4, 111.9, 64.7, 62.3, 42.6, 41.9, 41.7, 30.6, 24.7; IR (neat) 2921, 2851, 1751, 1708, 1671, 1447, 1417, 1234, 1077, 946, 757 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{19}NO_4$ (M^+) 313.1314, found 313.1304.



(*E*)-Ethyl 3-oxo-9-(2-oxooxazolidin-3-yl)non-8-enoate (25)

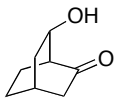
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (d, *J* = 14.3 Hz, 1H), 4.79 (dt, *J* = 7.1, 14.3 Hz, 1H), 4.44 (t, *J* = 7.7 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.69 (t, *J* = 8.4 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.09 (q, *J* = 7.0 Hz, 2H), 1.67-1.57 (m, 4H), 1.45-1.35 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 202.9, 167.5, 155.6, 124.5, 110.7, 62.3, 61.6, 49.6, 42.9, 42.8, 29.7, 29.6, 22.9, 14.3; IR (neat) 2929, 1743, 1714, 1670, 1482, 1415, 1307, 1236, 1072, 1030, 944, 755 cm^{-1}.



3-oxocyclohexanecarbaldehyde (29)

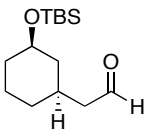
A solution of **7** (30 mg, 0.14 mmol) in 4 mL DCM at -78 °C was treated with ozone gas until the solution changed from colorless to blue. After that, 1 mL Me_2S was added, and the mixture was warmed to room temperature and stirred overnight. After concentration the mixture was purified by flash chromatography (30% EtOAc in hexane) to give the desired product. (17 mg, 96%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (s, 1H), 2.87-2.77 (m, 1H), 2.59-2.27 (m, 4H), 2.21-2.07 (m, 2H), 1.84-1.71 (m, 2H); ^{13}C (75 MHz,

$CDCl_3$) δ 209.1, 201.1, 50.4, 41.4, 40.5, 24.8, 24.7; IR (neat) 2949, 2870, 1715, 1225 cm^{-1}; HRMS (EI) calcd for $C_7H_{10}O_2$ (M^+) 126.0681, found 126.0683.



6-hydroxybicyclo[2.2.2]octan-2-one (30)

To a solution of **7** (20 mg, 0.095 mmol) in 2 mL THF was added 1 mL 2 M HCl at room temperature. After stirring at room temperature for overnight, the mixture was concentrated and purified by flash chromatography (40% hexane in EtOAc) to give the desired product. (11 mg, 81%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24 (ddd, J = 3.4, 3.4, 8.7 Hz, 1H), 2.61 (s, 1H), 2.45 (dd, J = 3.4, 6.4 Hz, 1H), 2.34 (dt, J = 1.9, 18.0 Hz, 1H), 2.27-2.09 (m, 4H), 1.86-1.63 (m, 2H), 1.62-1.45 (m, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 216.2, 69.2, 50.9, 44.6, 36.2, 27.9, 23.8, 20.1. These data are consistent with reported literature values.[11]



2-(3-(*tert*-butyldimethylsilyloxy)cyclohexyl)acetaldehyde (31)

To a solution of **7** (50 mg, 0.24 mmol) in MeOH (2 mL) at –10 °C was added $NaBH_4$ (5 mg, 0.1 mmol) in one portion. After stirring at that temperature for 10 minutes, reaction was quenched with H_2O. After concentration, it was purified by flash chromatography (10% hexane in EtOAc) to give the desired alcohol (47 mg, 93%, dr = 5:1). To a solution of this alcohol (20 mg, 0.095 mmol) in THF (2 mL) was added 0.6 mL 2 M HCl at room temperature. After stirring at room temperature overnight, the mixture was quenched with saturated $NaHCO_3$ (aq), and extracted with Et_2O (4x). After concentration, it was purified by flash chromatography (10% hexane in Et_2O) to give the desired aldehyde (13 mg, 97%). To the aldehyde (12 mg, 0.084 mmol) in CH_2Cl_2 (1.5 mL) was added imidazole (7 mg, 0.1 mmol) and DMAP (1 mg, 8 μmol) at room temperature. After stirring for 2.5 h, the mixture was concentrated and purified by flash chromatography (5% Et_2O in hexane) to give the desired product (17 mg, 77%, dr = 5:1). *cis*-Isomer (major): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, J = 2.1 Hz, 1H), 3.64-3.54 (m, 1H), 2.35 (dd, J = 2.0, 6.6 Hz, 2H), 2.01-1.85 (m, 3H), 1.79-1.72 (m, 1H), 1.69-1.62 (m, 1H), 1.33-1.02 (m, 4H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) δ 202.5, 71.1, 51.1, 42.9, 35.9, 32.2, 31.5, 26.1, 24.1, 18.4, -4.4, -4.4; IR (neat) 2929, 2856, 1727, 1253, 1107, 1063, 835 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{29}O_2Si$ (M+H) 257.1937, found 257.1936. trans-Isomer (minor) ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (t, J = 2.4 Hz, 1H), 4.04 (m, 1H), 2.48-2.35 (m, 1H), 2.27-2.23 (m, 2H), 1.84-1.57 (m, 4H), 1.50-0.99 (m, 4H), 0.90 (s, 9H), 0.04 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) δ 203.2, 66.9, 51.1, 40.6, 33.5, 32.82, 27.1, 26.1, 20.1, -4.6, -4.7; IR (neat) 2930, 2856, 1724, 1253, 1107, 1063, 835 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{29}O_2Si$ (M+H) 257.1937, found 257.1939. These data are consistent with reported literature values.[12]

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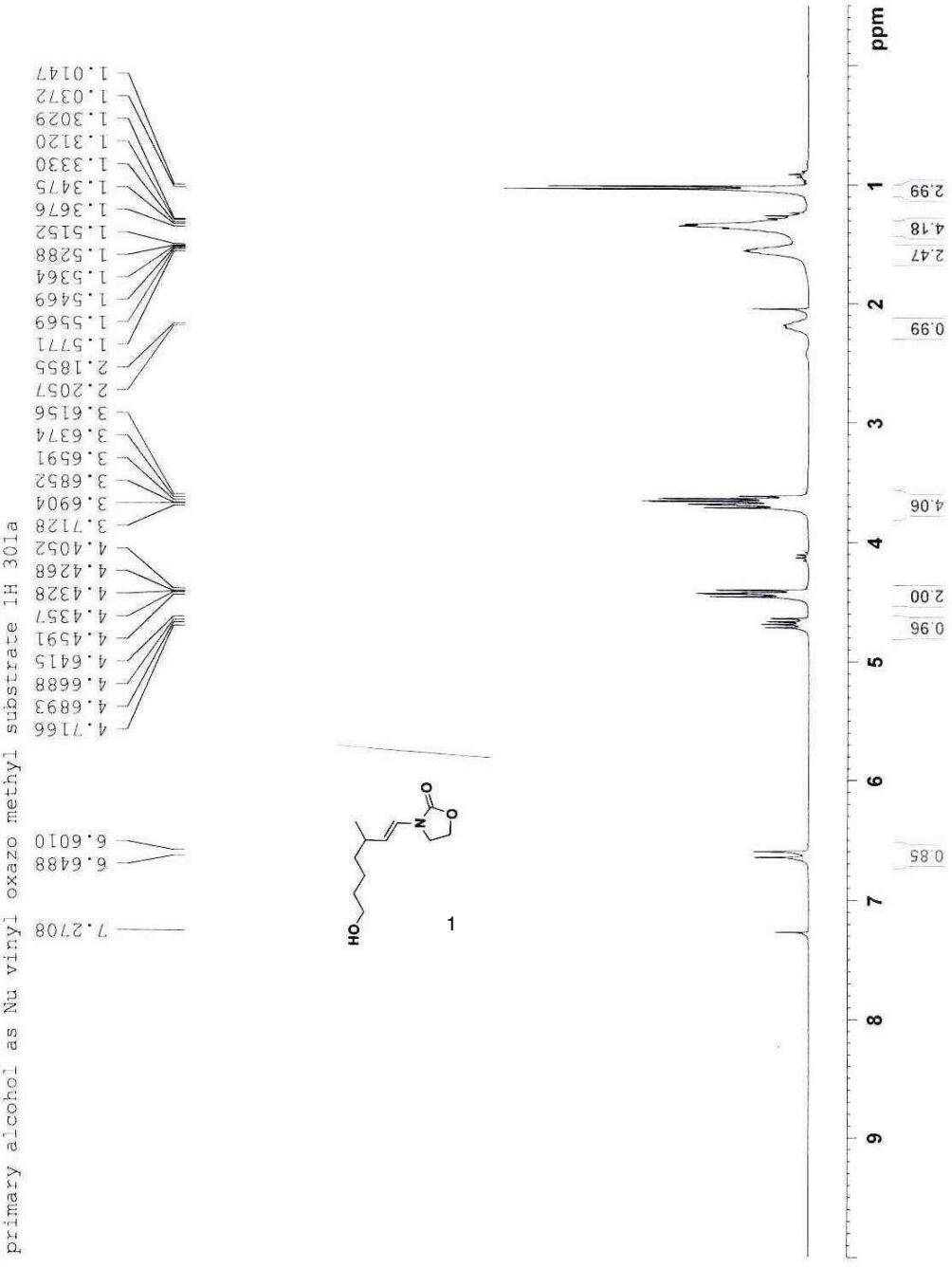
[11] Tzvetkov, N. T.; Schmoldt, P.; Neumann, B.; Stammler, H. G.; Mattay, J. *Tetrahedron: Asymmetry* **2006**, *17*, 993.

[12] Ren, L.; Crudden, C. M. *J. Org. Chem.* **2002**, *67*, 1746.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4.6688
4.6415
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4.4357
4.4328
4.4268
4.4052
3.7128
3.6904
3.6852
3.6591
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3.6156
2.2057
2.1855
1.5771
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1.3029
1.0372
1.0147
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O
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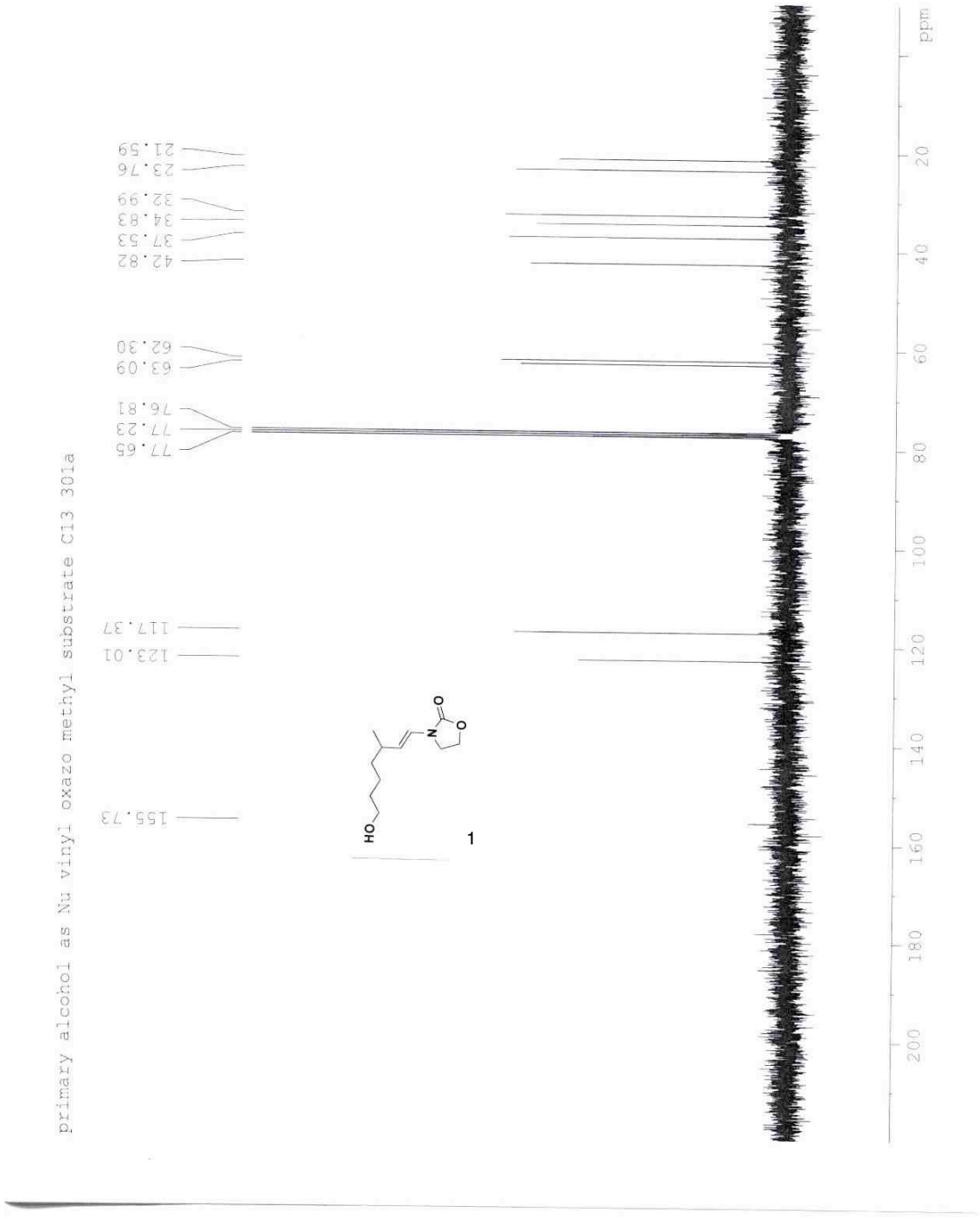
0.85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63.09
62.30
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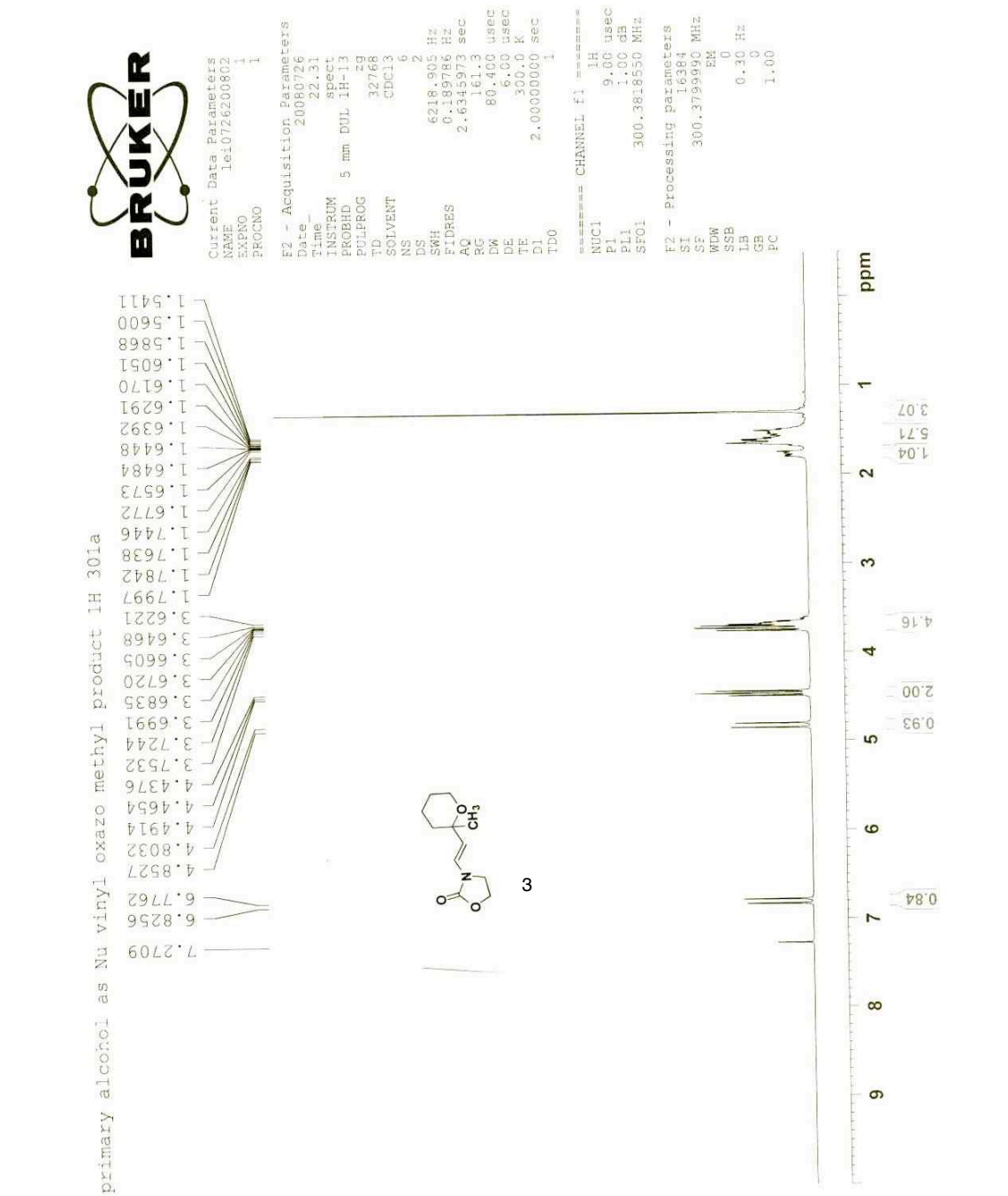
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PROCNO 1
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Date_ 20080726
Time 22.31
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TD 32768
SOLVENT CDCl3
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FIDRES 0.189786 Hz
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DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
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PL1 1.00 dB
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F2 - Processing parameters
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SF 300.3799990 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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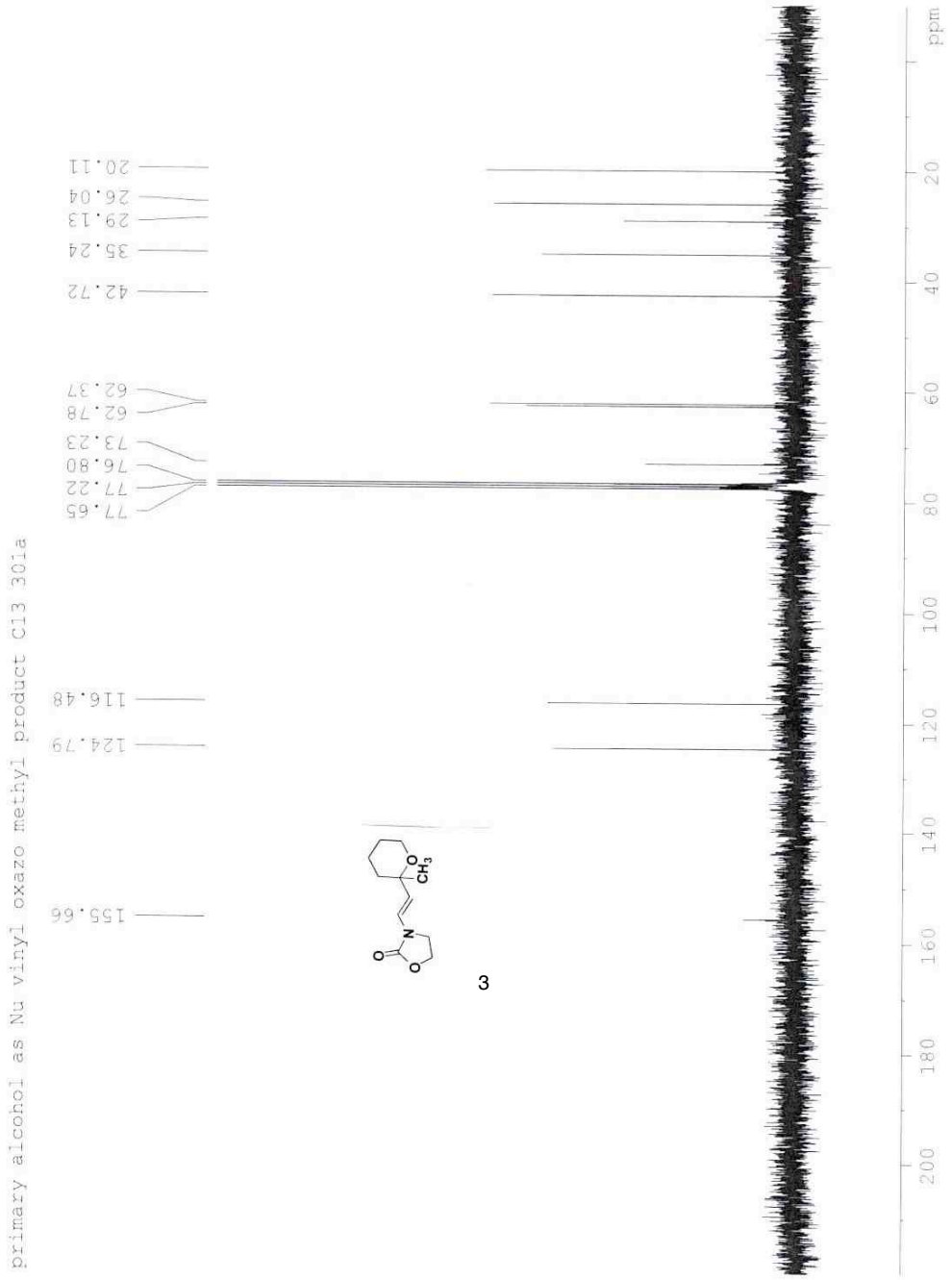
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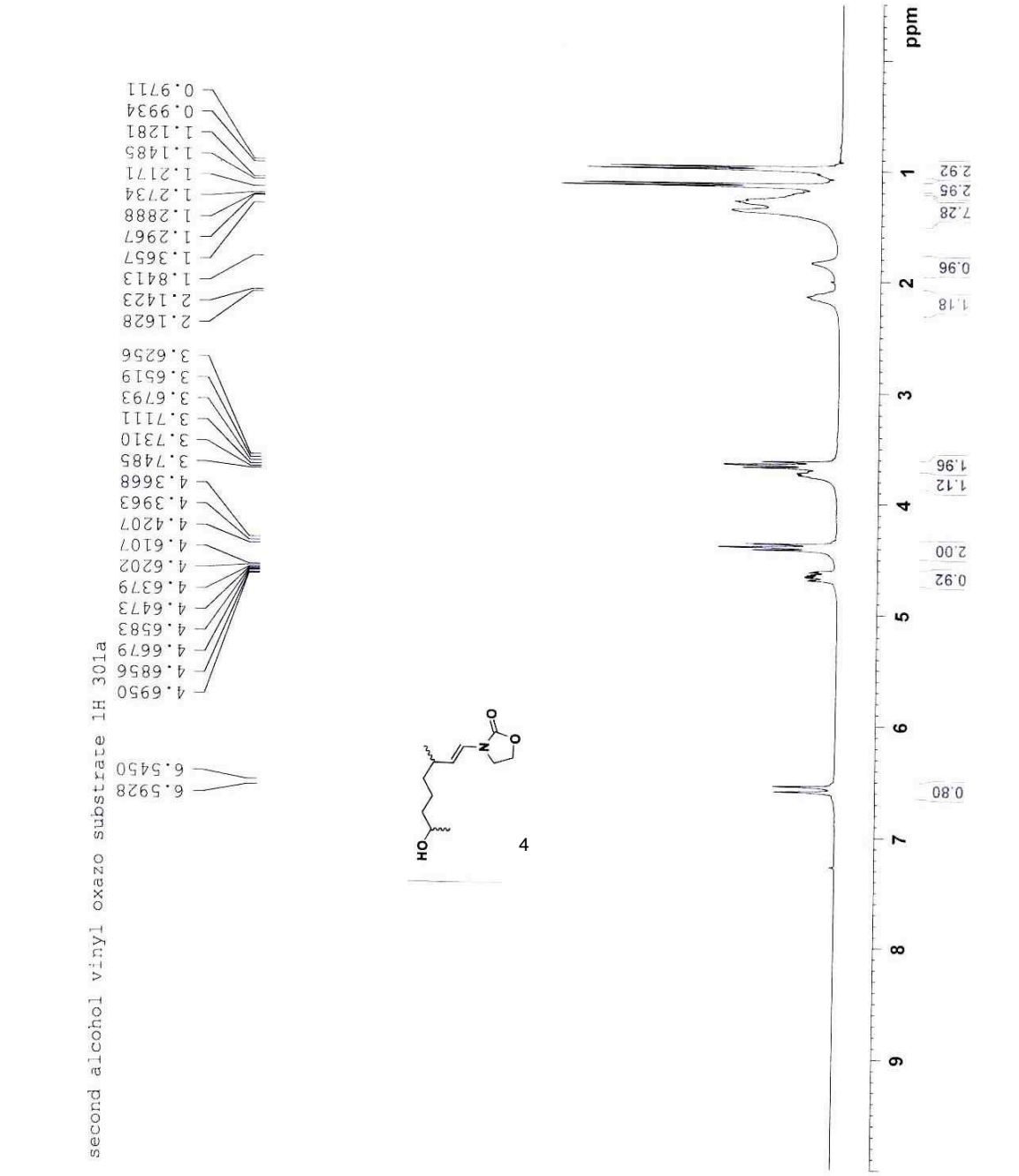
3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3.6793
3.6519
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2.95
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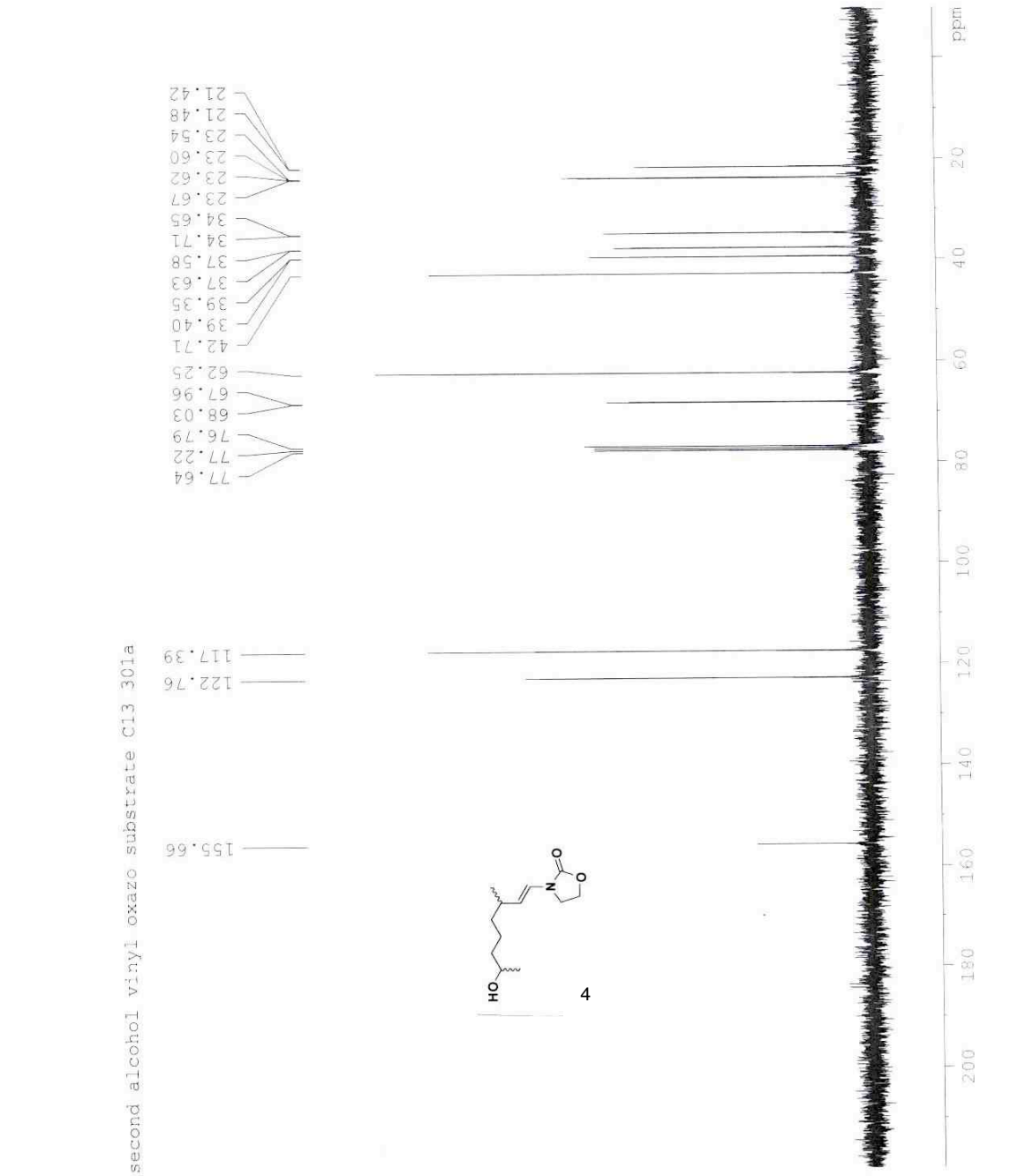
1.18


second alcohol vinyl oxazo substrate C13 301a
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77.64
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76.79
68.03
67.96
62.25
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39.35
37.63
37.58
34.71
34.65
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23.54
21.48
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ppm
20
40
60
80
100
120
140
160
180
200
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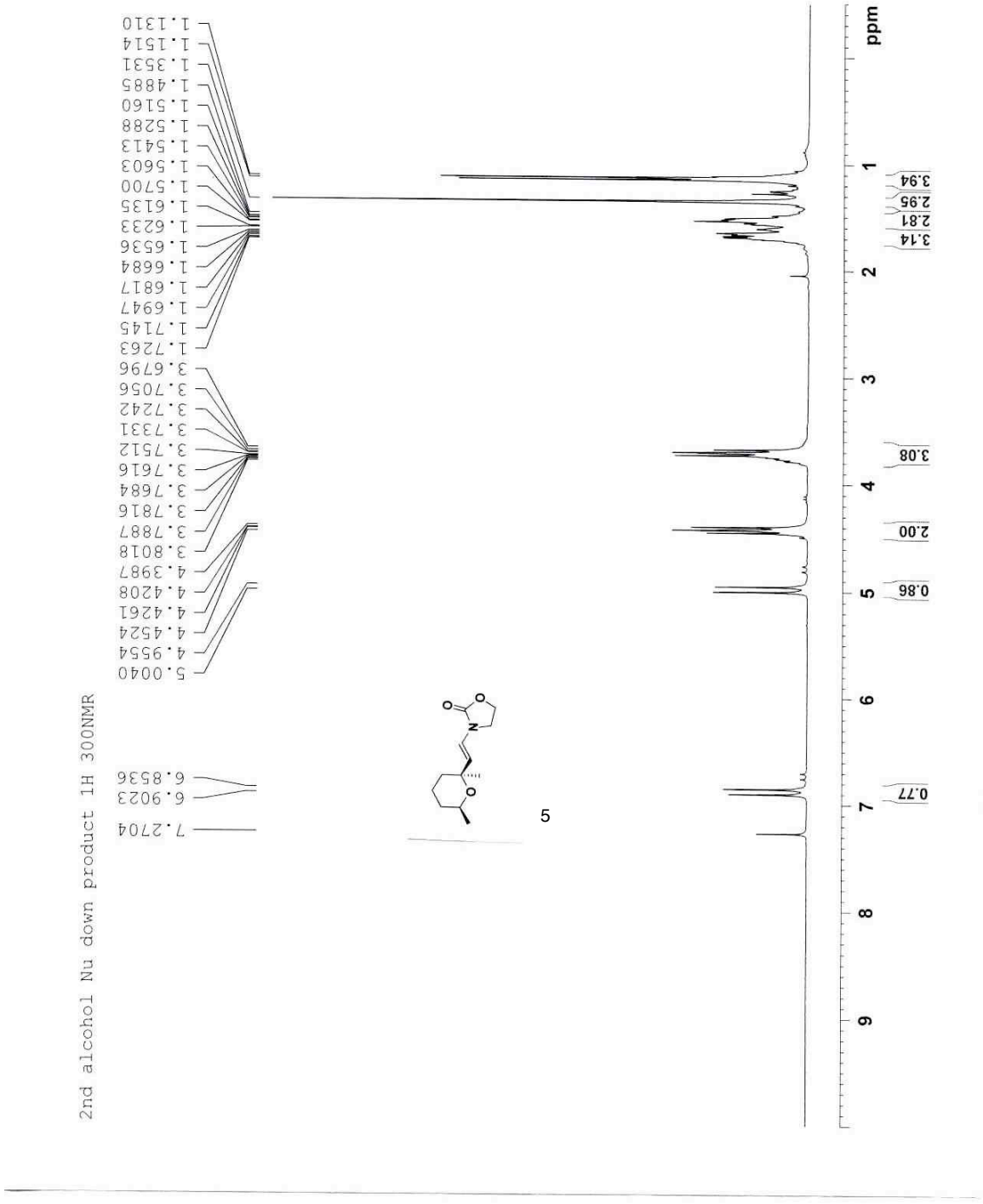
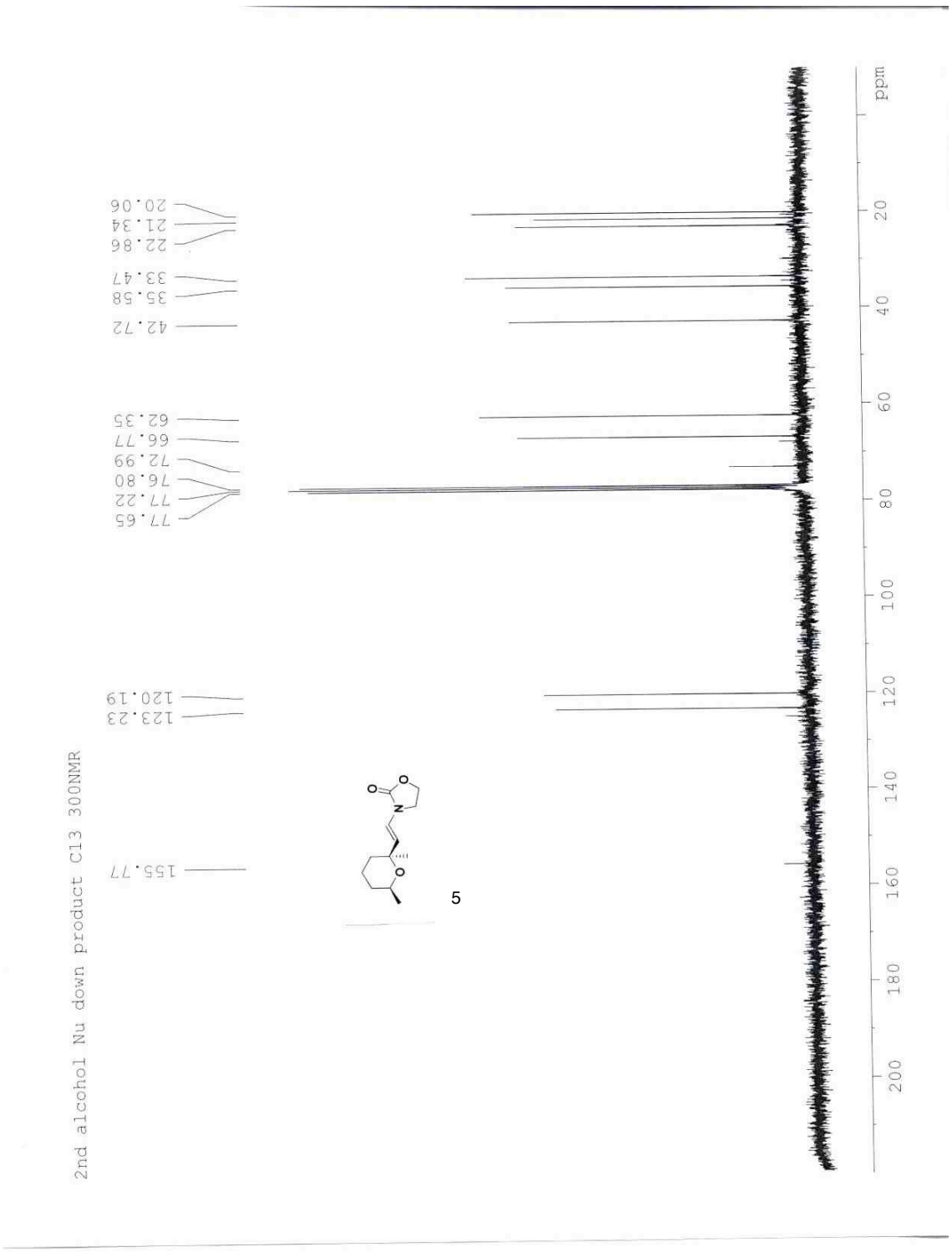
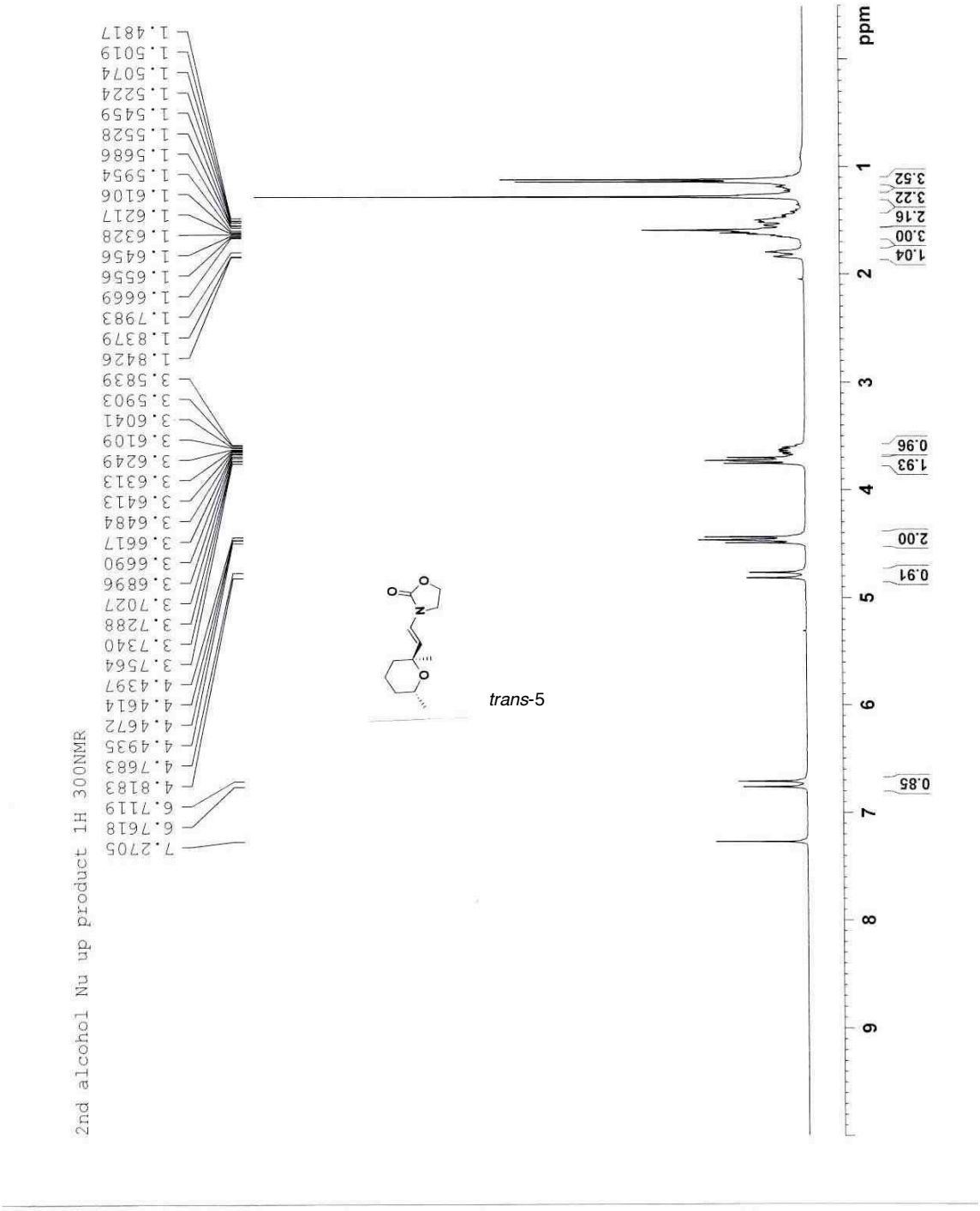
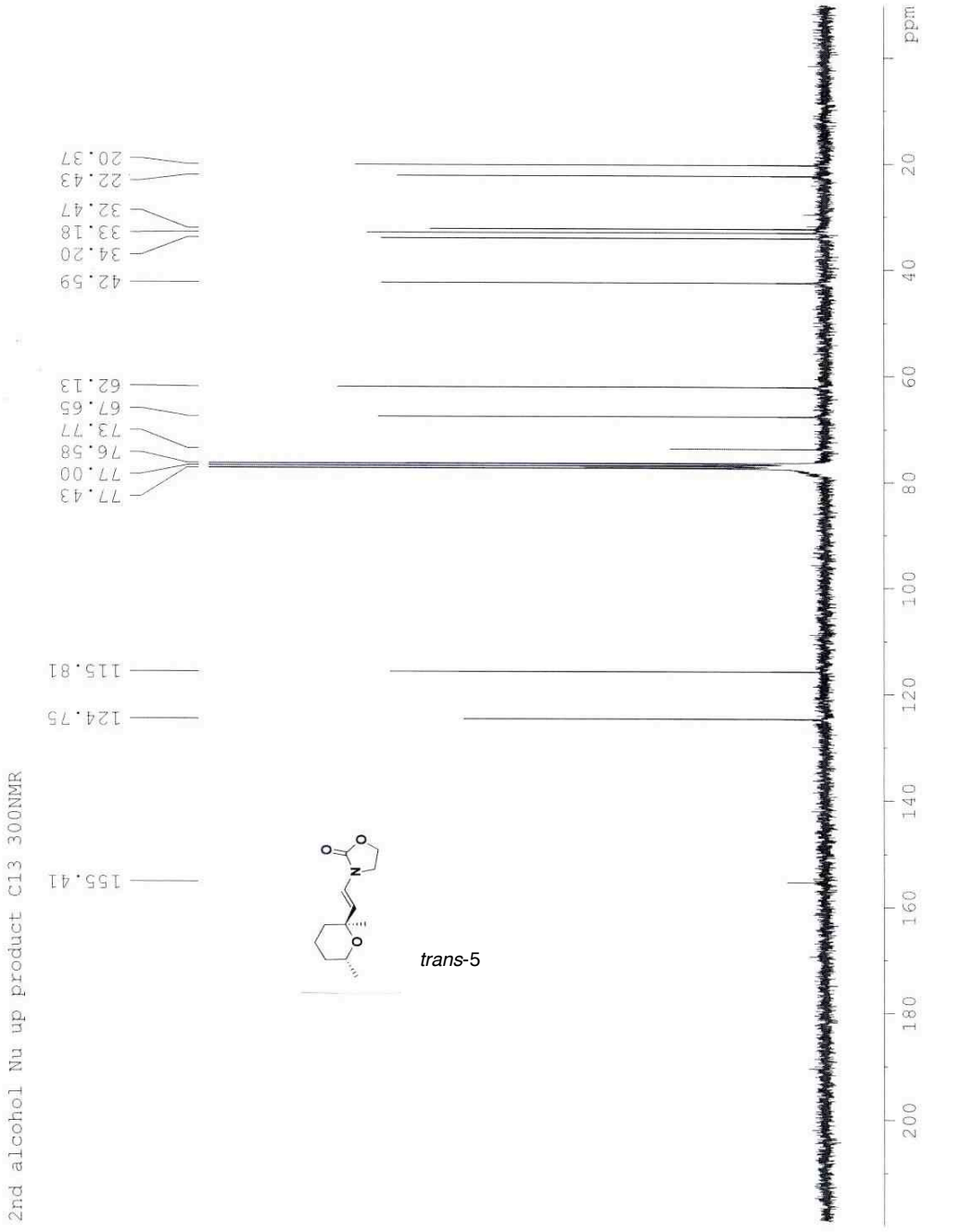
O
N
O
4


2nd alcohol Nu down product 1H 300NMR
7.2704
6.9023
6.8536
5.0040
4.9554
4.4524
4.4261
4.4208
4.3987
3.8018
3.7887
3.7816
3.7684
3.7616
3.7512
3.7331
3.7242
3.7056
3.6796
1.7263
1.7145
1.6947
1.6817
1.6684
1.6536
1.6233
1.6135
1.5700
1.5603
1.5413
1.5288
1.5160
1.4885
1.3531
1.1514
1.1310
ppm
3.94
2.95
2.81
3.14
3.08
2.00
0.86
0.77

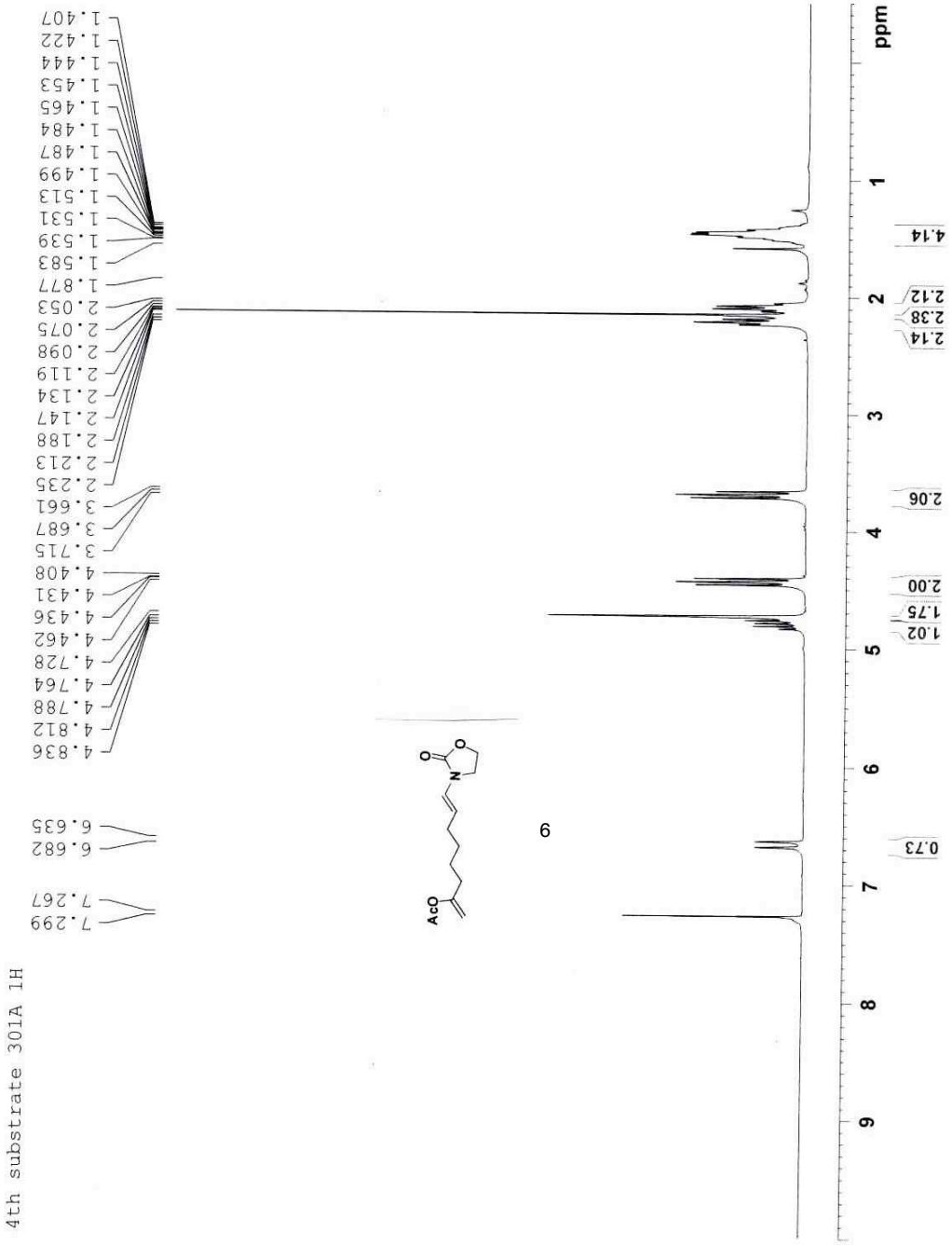
5

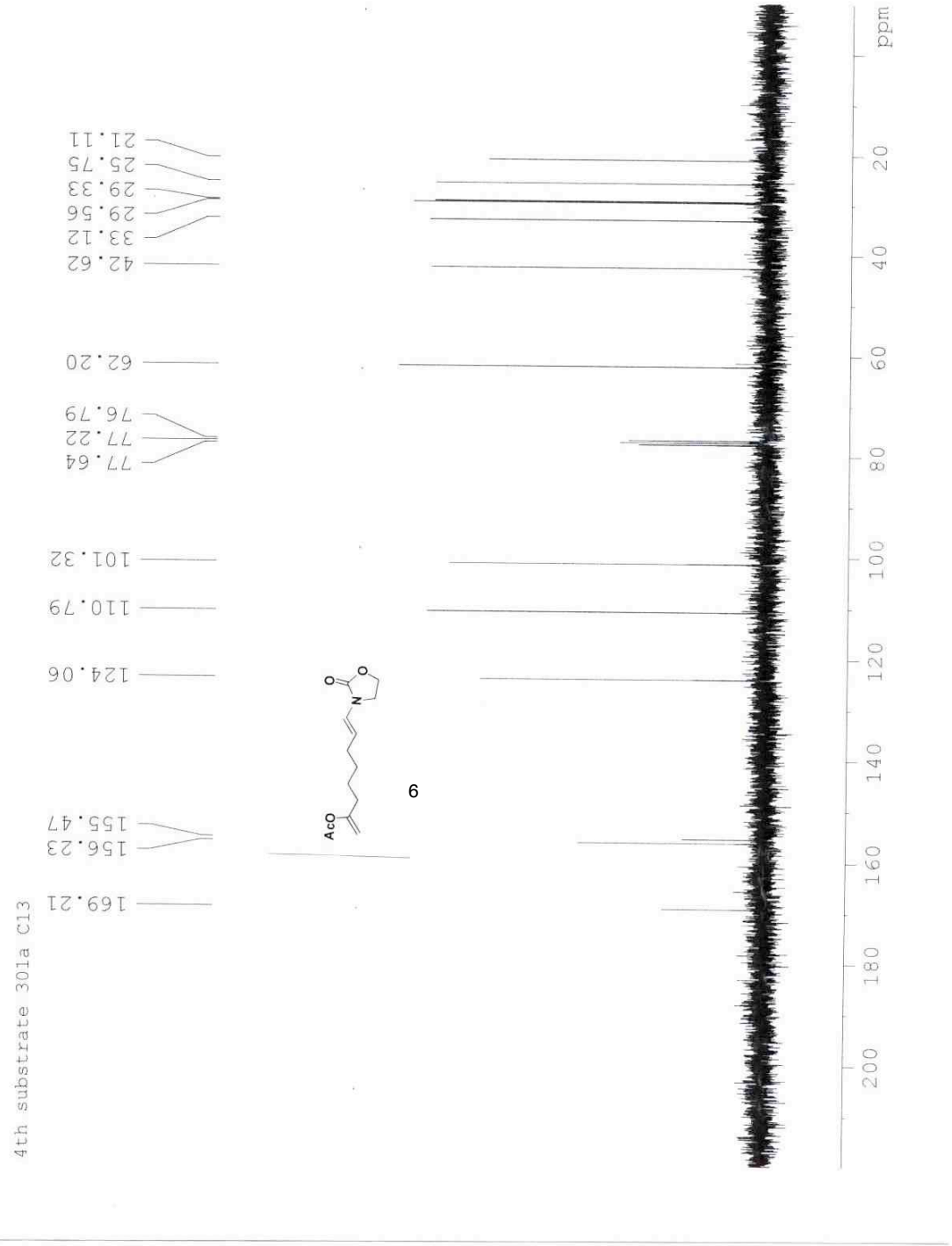

2nd alcohol Nu down product C13 300NMR
155.77
123.23
120.19
77.65
77.22
76.80
72.99
66.77
62.35
42.72
35.58
33.47
22.86
21.34
20.06
ppm
20
40
60
80
100
120
140
160
180
200
5

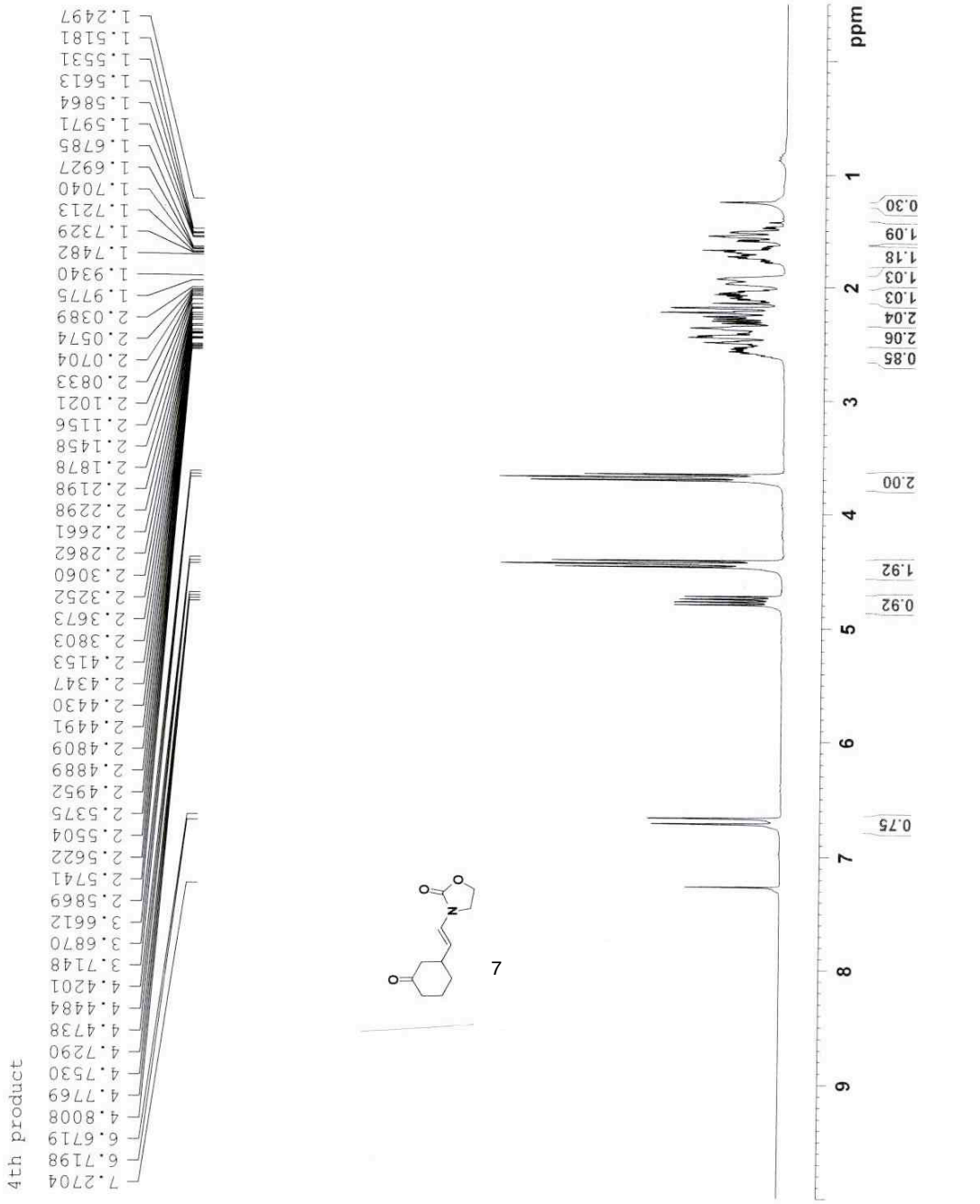

2nd alcohol Nu up product 1H 300NMR
7.2705
6.7618
6.7119
4.8183
4.7683
4.4935
4.4672
4.4614
4.4397
3.7564
3.7340
3.7288
3.7027
3.6896
3.6690
3.6617
3.6484
3.6413
3.6313
3.6249
3.6109
3.6041
3.5903
3.5839
1.8426
1.8379
1.7983
1.6669
1.6556
1.6456
1.6328
1.6217
1.6106
1.5954
1.5686
1.5528
1.5459
1.5224
1.5074
1.5019
1.4817
ppm
1
2
3
4
5
6
7
8
9
3.52
3.22
2.16
3.00
1.04
0.96
1.93
2.00
0.91
0.85
trans-5


2nd alcohol Nu up product C13 300NMR
155.41
124.75
115.81
77.43
77.00
76.58
73.77
67.65
62.13
42.59
34.20
33.18
32.47
22.43
20.37
ppm
20
40
60
80
100
120
140
160
180
200

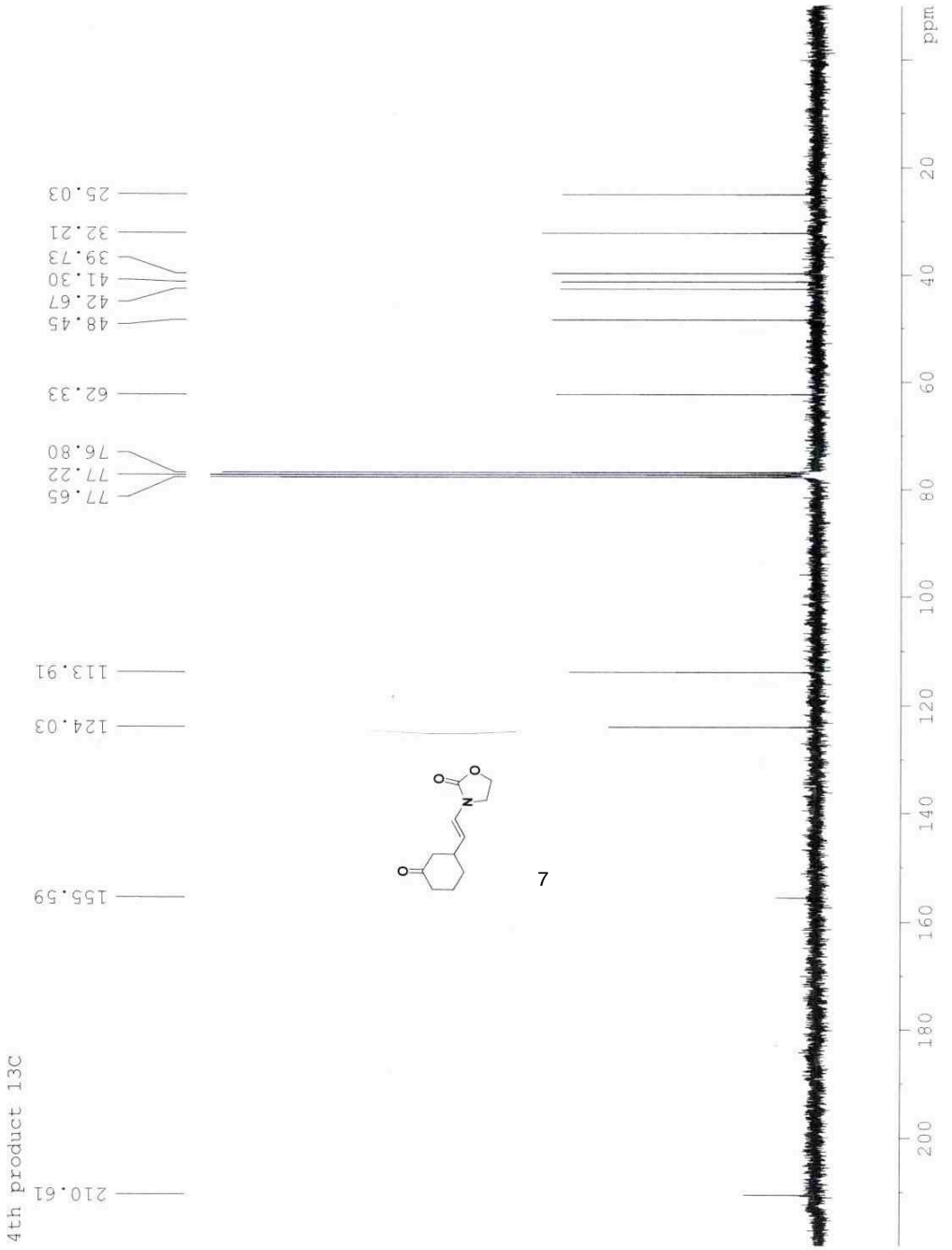
trans-5

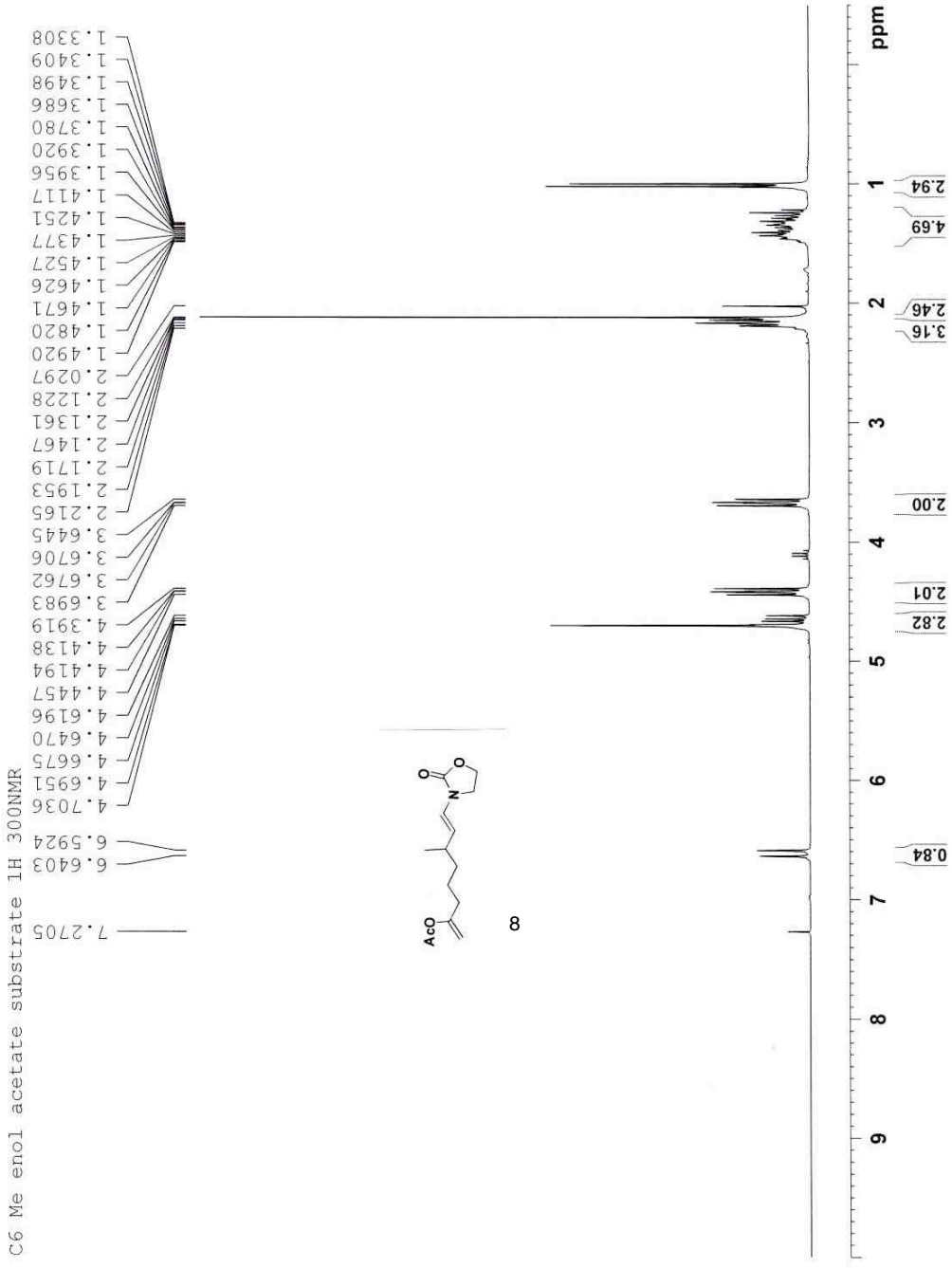

4th substrate 301A 1H
7.299
7.267
6.682
6.635
4.836
4.812
4.788
4.764
4.728
4.462
4.436
4.431
4.408
3.715
3.687
3.661
2.235
2.213
2.188
2.147
2.134
2.119
2.098
2.075
2.053
1.877
1.583
1.539
1.531
1.513
1.499
1.487
1.484
1.465
1.453
1.444
1.422
1.407
AcO
6
ppm
4.14
2.12
2.38
2.14
2.06
2.00
1.75
1.02
0.73

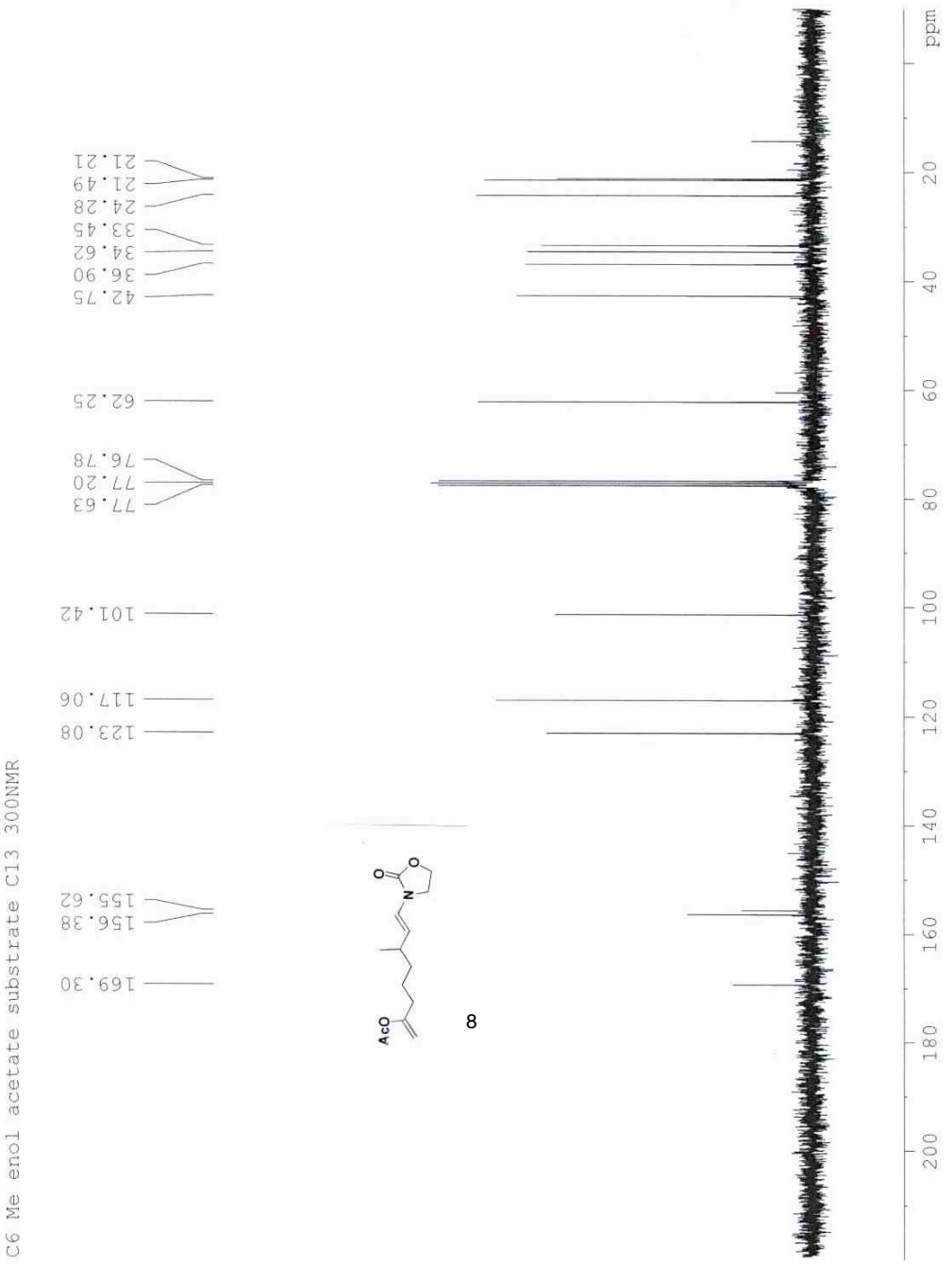

4th substrate 301a C13
169.21
156.23
155.47
124.06
110.79
101.32
77.64
77.22
76.79
62.20
42.62
33.12
29.56
29.33
25.75
21.11
AcO
6
ppm
200
180
160
140
120
100
80
60
40
20

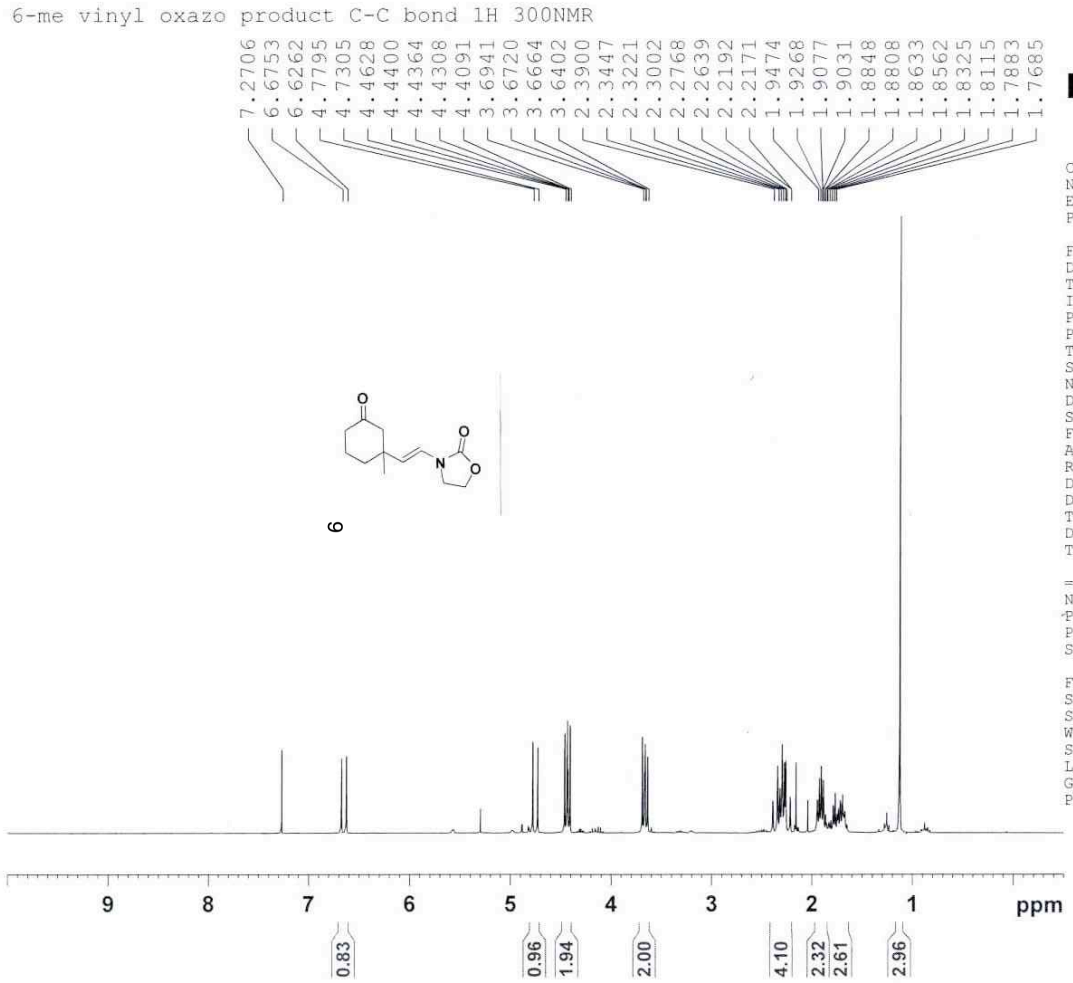

4th product
7.2704
6.7198
6.6719
4.8008
4.7769
4.7530
4.7290
4.4738
4.4484
4.4201
3.7148
3.6870
3.6612
2.5869
2.5741
2.5622
2.5504
2.5375
2.4952
2.4889
2.4809
2.4491
2.4430
2.4347
2.4153
2.3803
2.3673
2.3252
2.3060
2.2862
2.2661
2.2298
2.2198
2.1878
2.1458
2.1156
2.1021
2.0833
2.0704
2.0574
2.0389
1.9775
1.9340
1.7482
1.7329
1.7213
1.7040
1.6927
1.6785
1.5971
1.5864
1.5613
1.5531
1.5181
1.2497
ppm
0.30
1.09
1.18
1.03
1.03
2.04
2.06
0.85
2.00
1.92
0.92
0.75

7


4th product 13C
210.61
155.59
124.03
113.91
77.65
77.22
76.80
62.33
48.45
42.67
41.30
39.73
32.21
25.03
ppm
20
40
60
80
100
120
140
160
180
200
O
O
N
O
7


C6 Me enol acetate substrate 1H 300NMR
7.2705
6.6403
6.5924
4.7036
4.6951
4.6675
4.6470
4.6196
4.4457
4.4194
4.4138
4.3919
3.6983
3.6762
3.6706
3.6445
2.2165
2.1953
2.1719
2.1467
2.1361
2.1228
2.0297
1.4920
1.4820
1.4671
1.4626
1.4527
1.4377
1.4251
1.4117
1.3956
1.3920
1.3780
1.3686
1.3498
1.3409
1.3308
AcO
O
N
O
8
ppm
0.84
2.82
2.01
2.00
3.16
2.46
4.69
2.94


C6 Me enol acetate substrate C13 300NMR
169.30
156.38
155.62
123.08
117.06
101.42
77.63
77.20
76.78
62.25
42.75
36.90
34.62
33.45
24.28
21.49
21.21
AcO
8
ppm
20
40
60
80
100
120
140
160
180
200



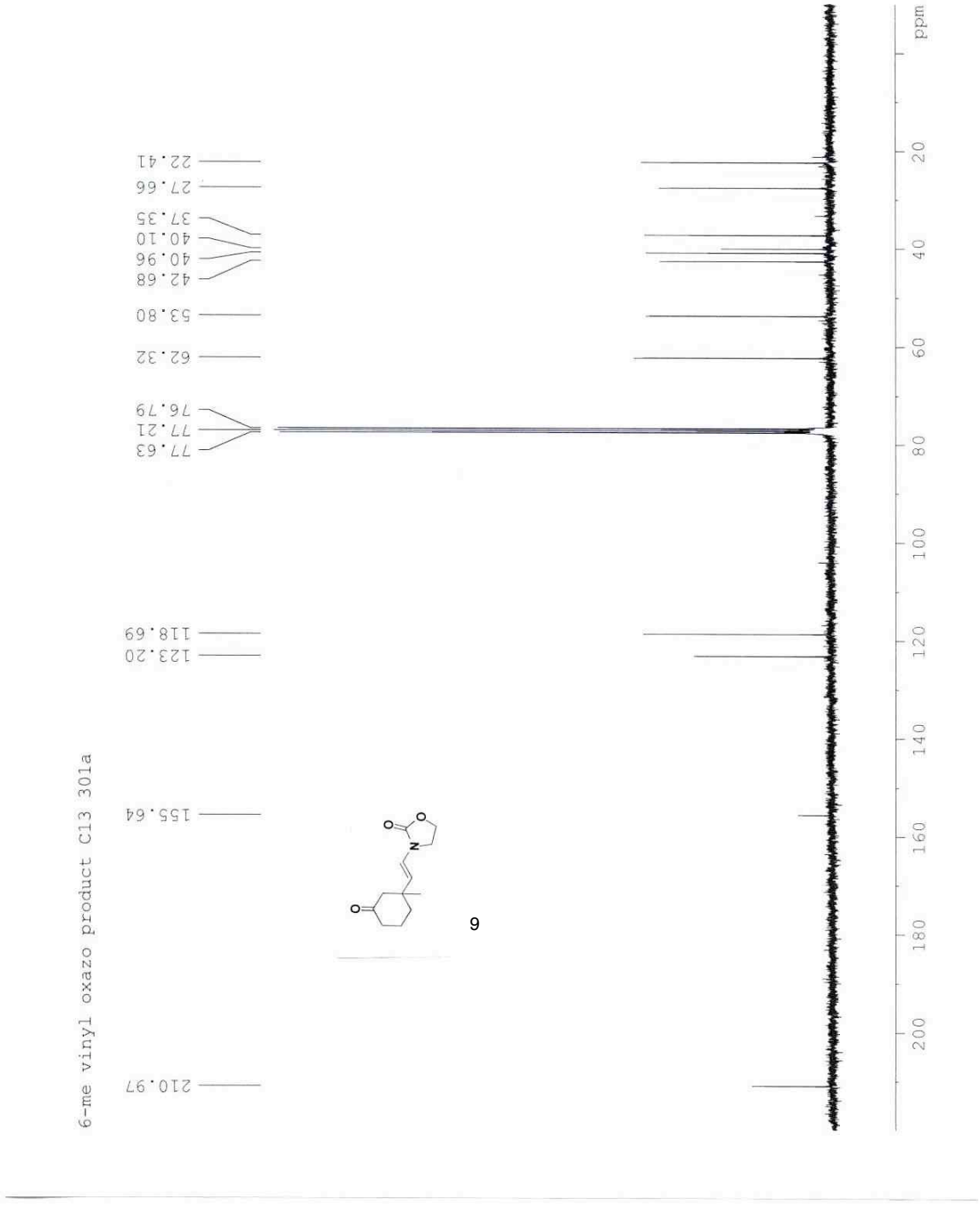
BRUKER

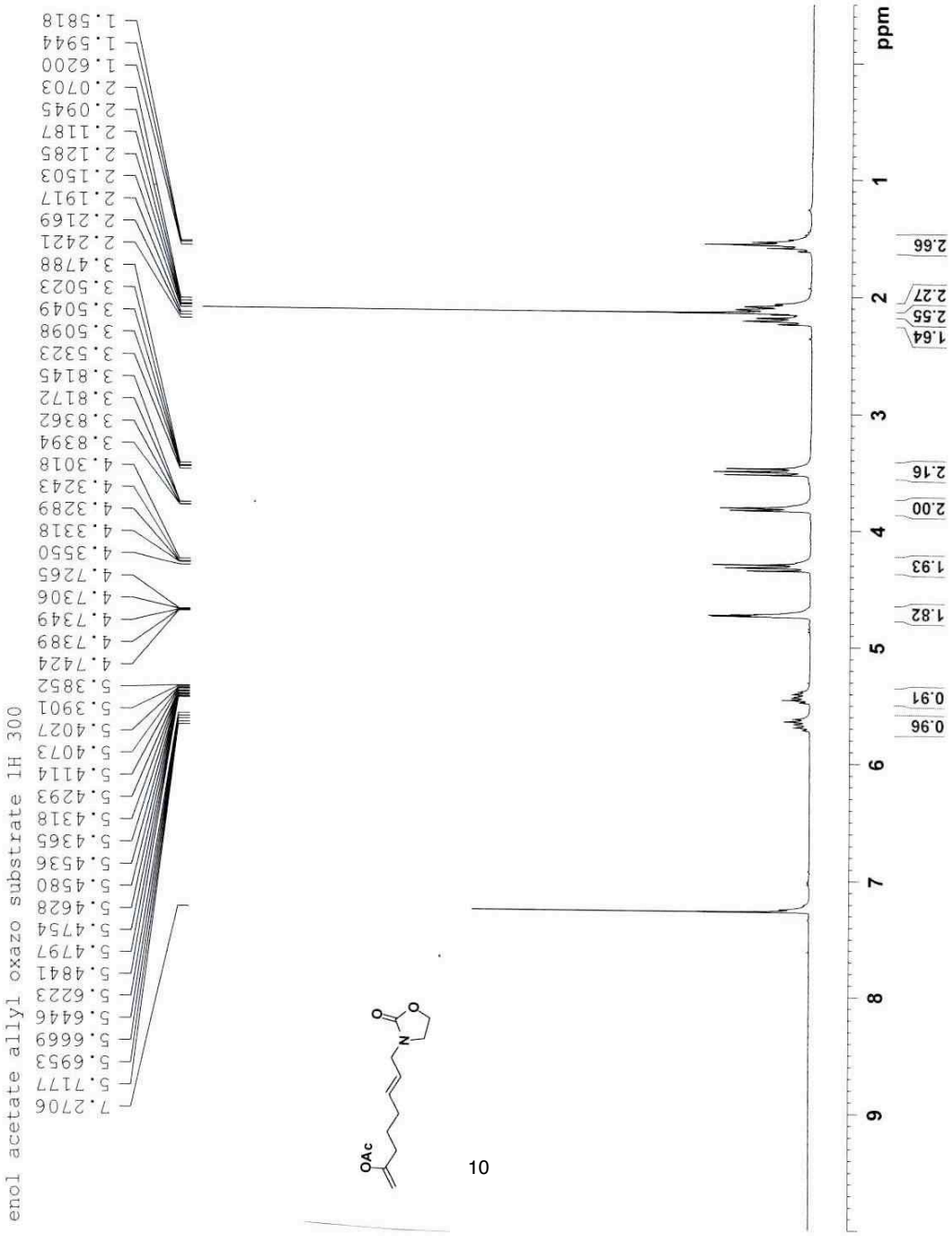
Current Data Parameters
NAME lei0829200803
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080829
Time 18.24
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz

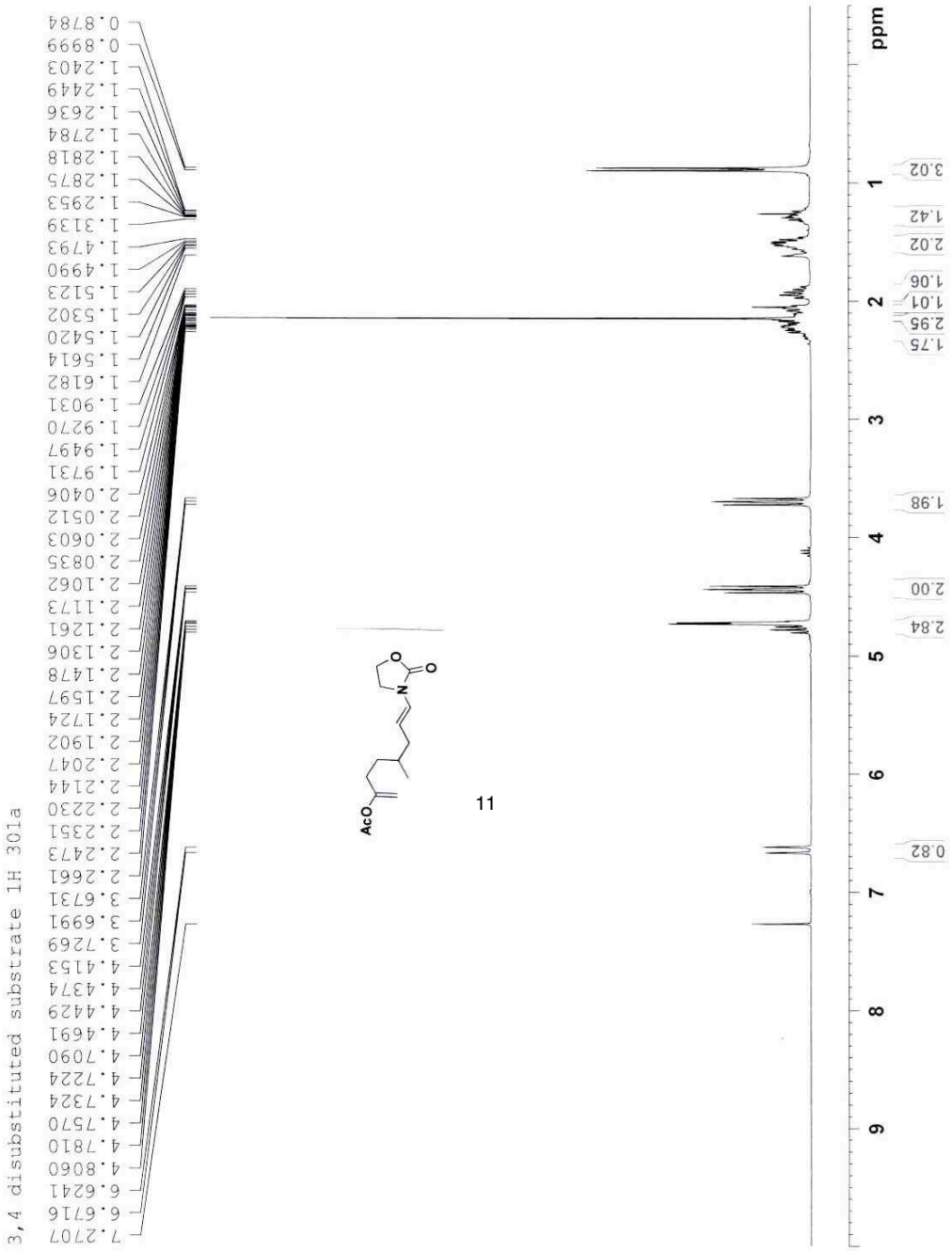
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

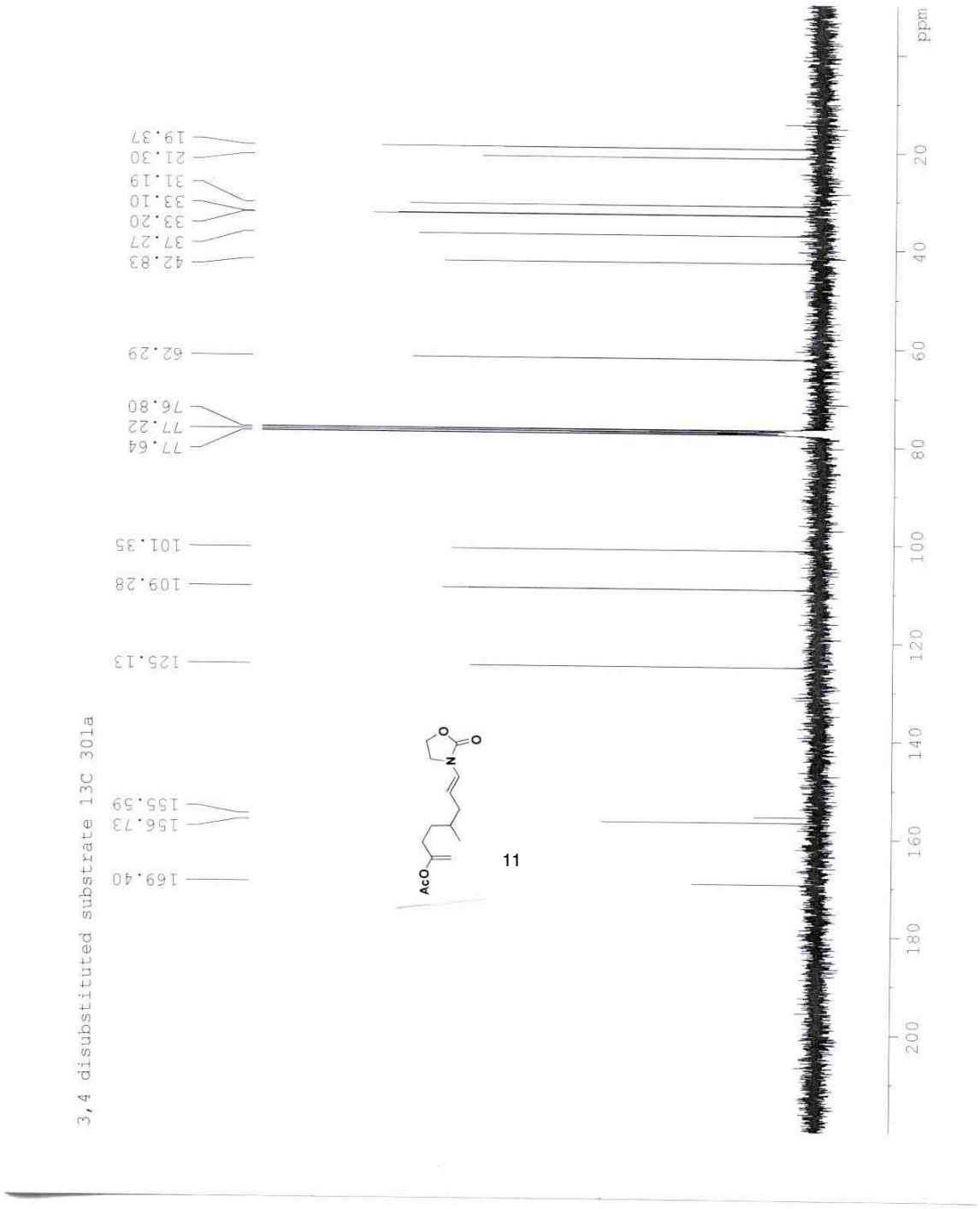

6-me vinyl oxazo product C13 301a
210.97
155.64
123.20
118.69
77.63
77.21
76.79
62.32
53.80
42.68
40.96
40.10
37.35
27.66
22.41
ppm
20
40
60
80
100
120
140
160
180
200
O
O
N
O
9

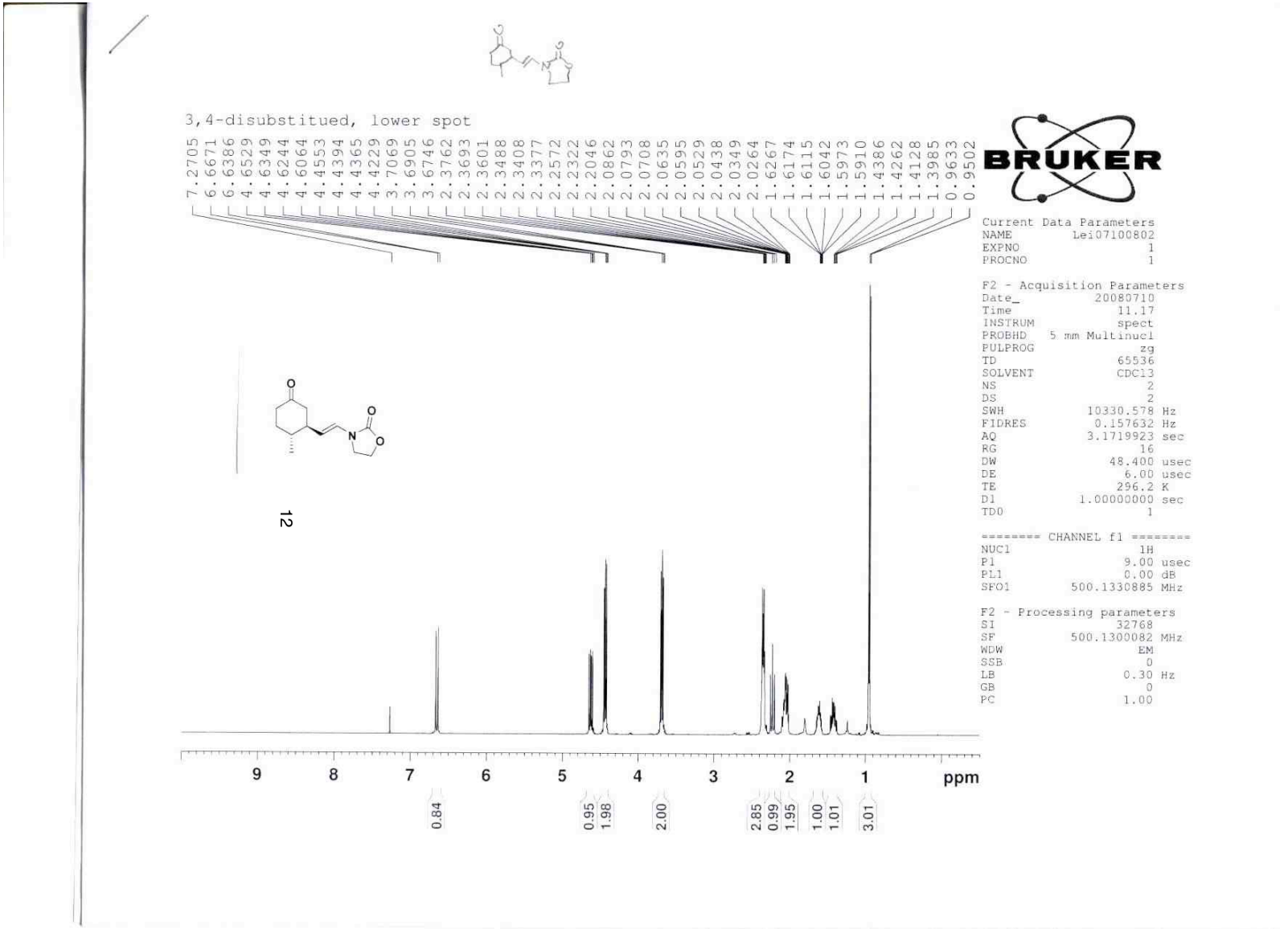

enol acetate allyl oxazo substrate 1H 300
7.2706
5.7177
5.6953
5.6669
5.6446
5.6223
5.4841
5.4797
5.4754
5.4628
5.4580
5.4536
5.4365
5.4318
5.4293
5.4114
5.4073
5.4027
5.3901
5.3852
4.7424
4.7389
4.7349
4.7306
4.7265
4.3550
4.3318
4.3289
4.3243
4.3018
3.8394
3.8362
3.8172
3.8145
3.5323
3.5098
3.5049
3.5023
3.4788
2.2421
2.2169
2.1917
2.1503
2.1285
2.1187
2.0945
2.0703
1.6200
1.5944
1.5818
OAc
ppm
1
2
3
4
5
6
7
8
9
2.66
2.27
2.55
1.64
2.16
2.00
1.93
1.82
0.91
0.96

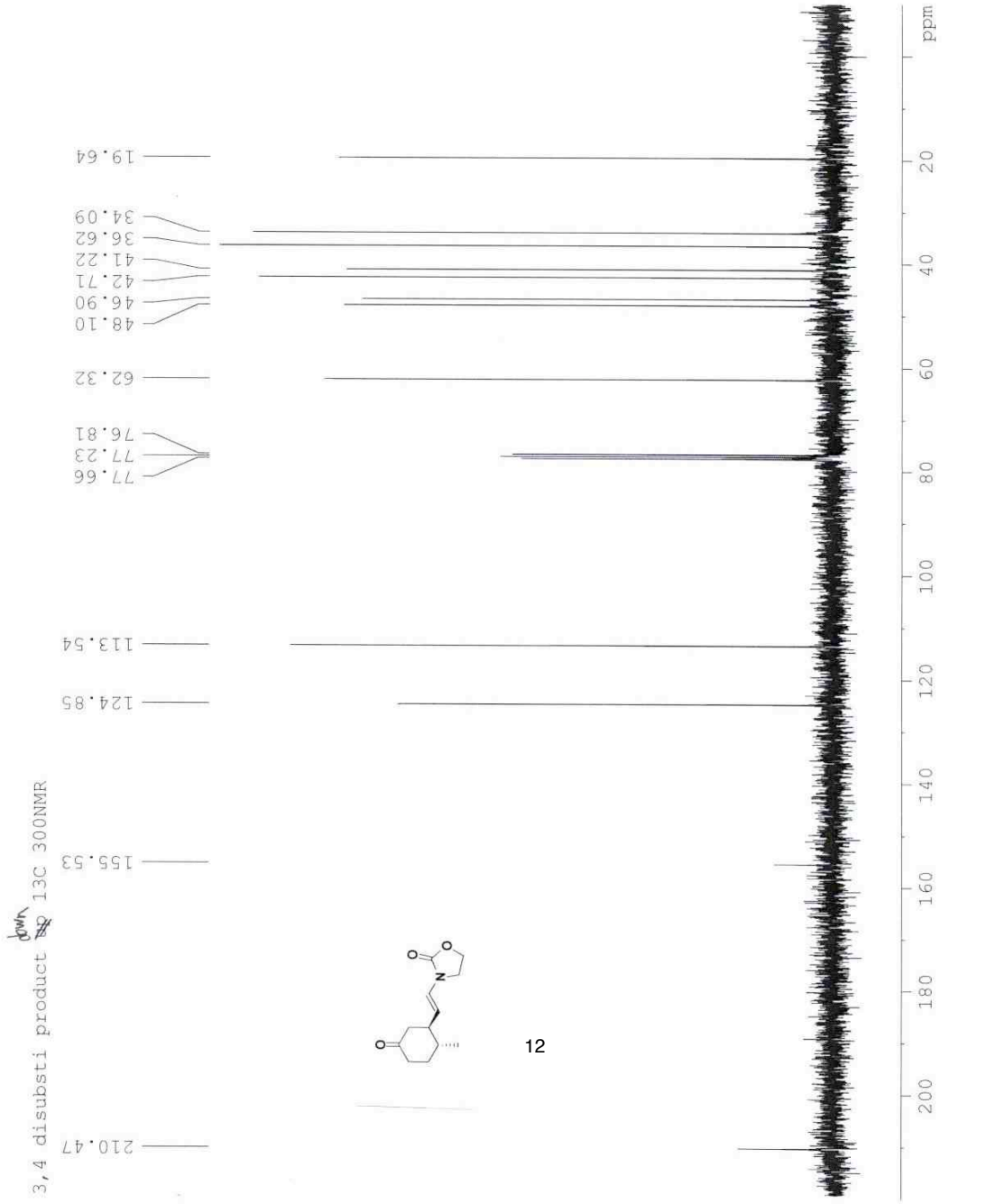
10

enol acetate allyl oxazo substrate 13C 301b
169.22
158.30
155.99
134.83
124.36
101.55
77.66
77.23
76.81
61.85
46.29
44.10
32.71
31.37
25.77
21.13
OAc
O
N
O
10
200
180
160
140
120
100
80
60
40
20
ppm

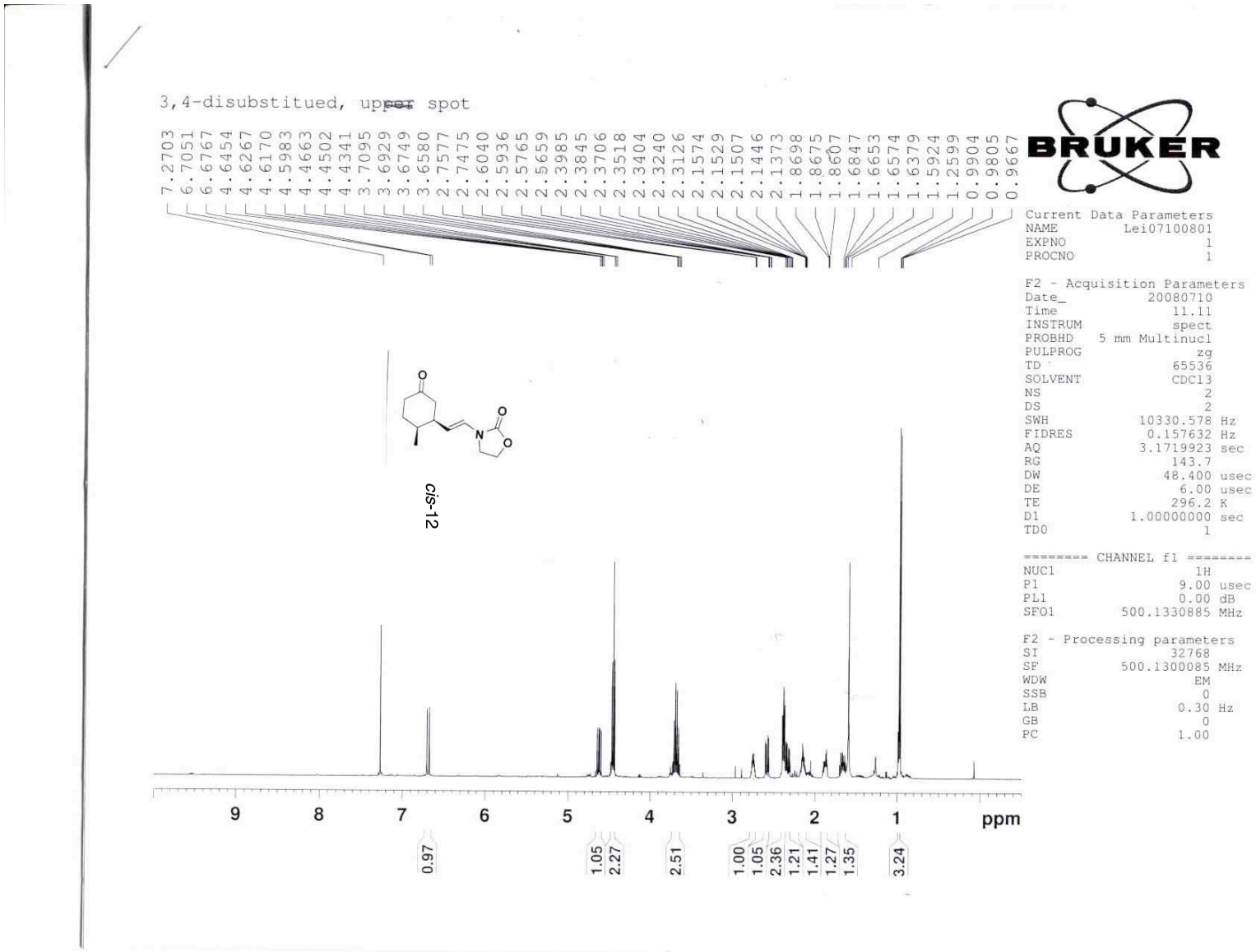

3,4 disubstituted substrate 1H 301a
ppm
AcO
11

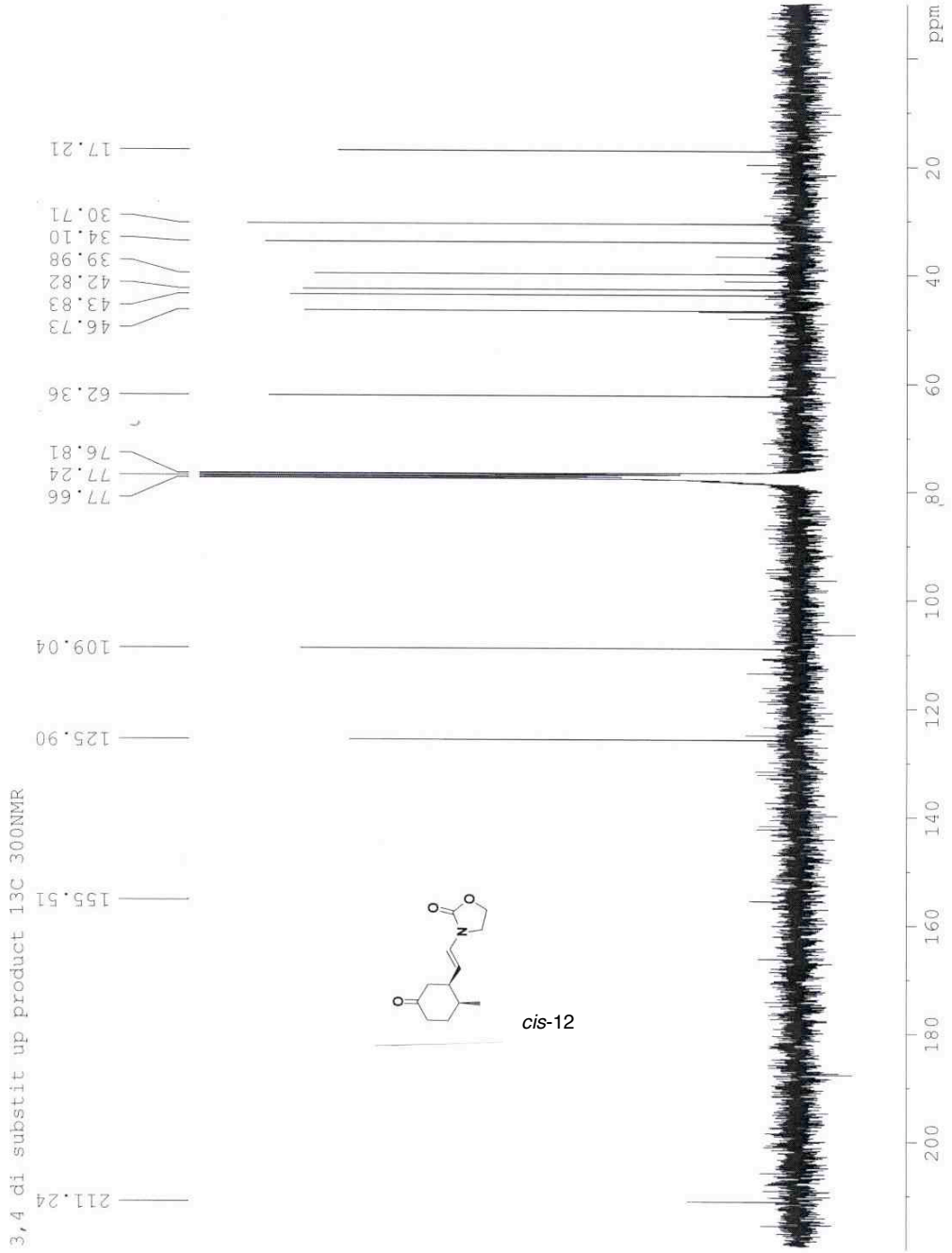

3,4 disubstituted substrate 13C 301a
169.40
156.73
155.59
125.13
109.28
101.35
77.64
77.22
76.80
62.29
42.83
37.27
33.20
33.10
31.19
21.30
19.37
ppm
20
40
60
80
100
120
140
160
180
200
AcO
11


3,4-disubstitued, lower spot
7.2705
6.6671
6.6386
4.6529
4.6349
4.6244
4.6064
4.4553
4.4394
4.4365
4.4229
3.7069
3.6905
3.6746
2.3762
2.3693
2.3601
2.3488
2.3408
2.3377
2.2572
2.2322
2.2046
2.0862
2.0793
2.0708
2.0635
2.0595
2.0529
2.0438
2.0349
2.0264
1.6267
1.6174
1.6115
1.6042
1.5973
1.5910
1.4386
1.4262
1.4128
1.3985
0.9633
0.9502
12
9
8
7
6
5
4
3
2
1
ppm
0.84
0.95
1.98
2.00
2.85
0.99
1.95
1.00
1.01
3.01
BRUKER
Current Data Parameters
NAME Lei07100802
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080710
Time 11.17
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 16
DW 48.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

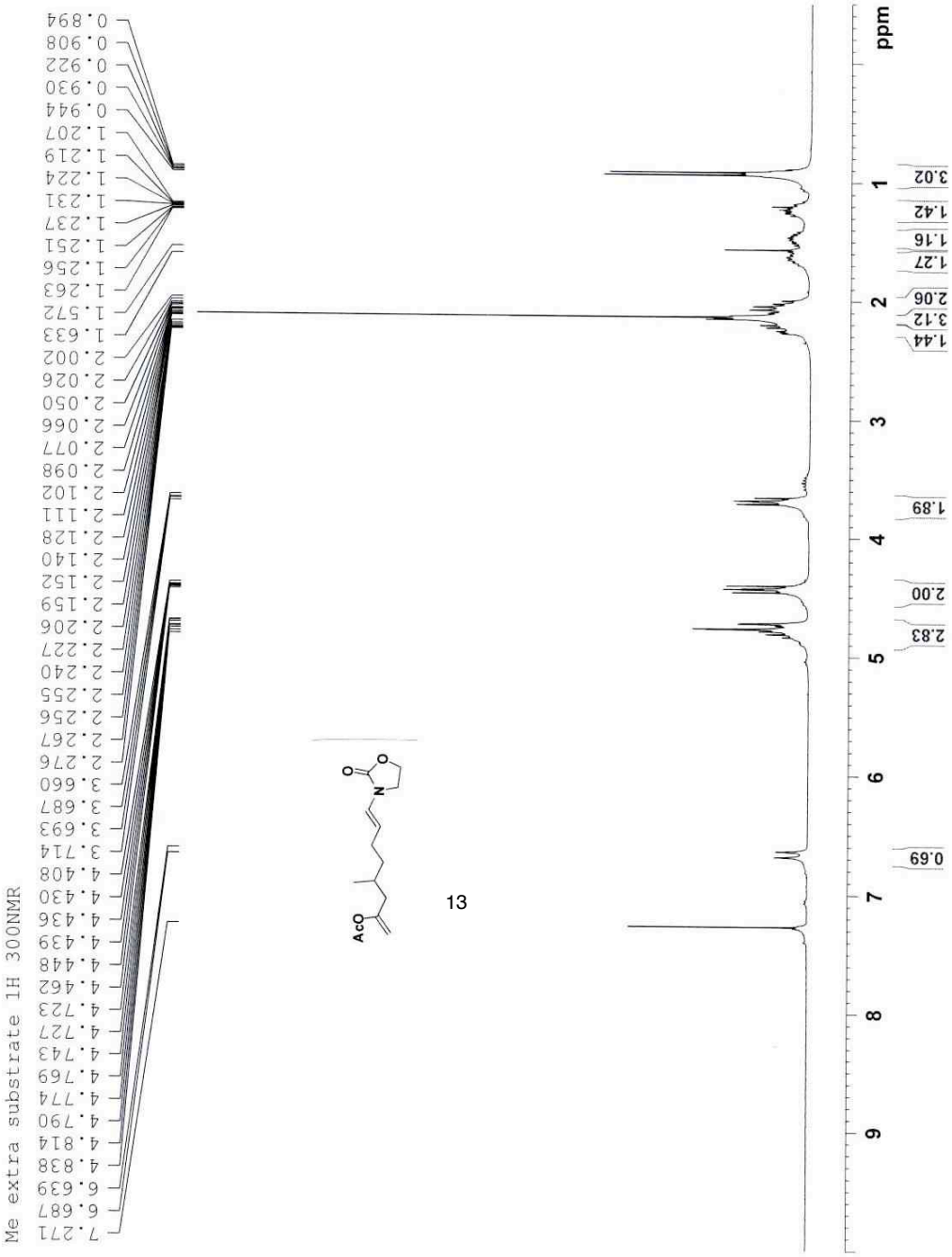

3,4 disubsti product 13C 300NMR
210.47
155.53
124.85
113.54
77.66
77.23
76.81
62.32
48.10
46.90
42.71
41.22
36.62
34.09
19.64
ppm
20
40
60
80
100
120
140
160
180
200

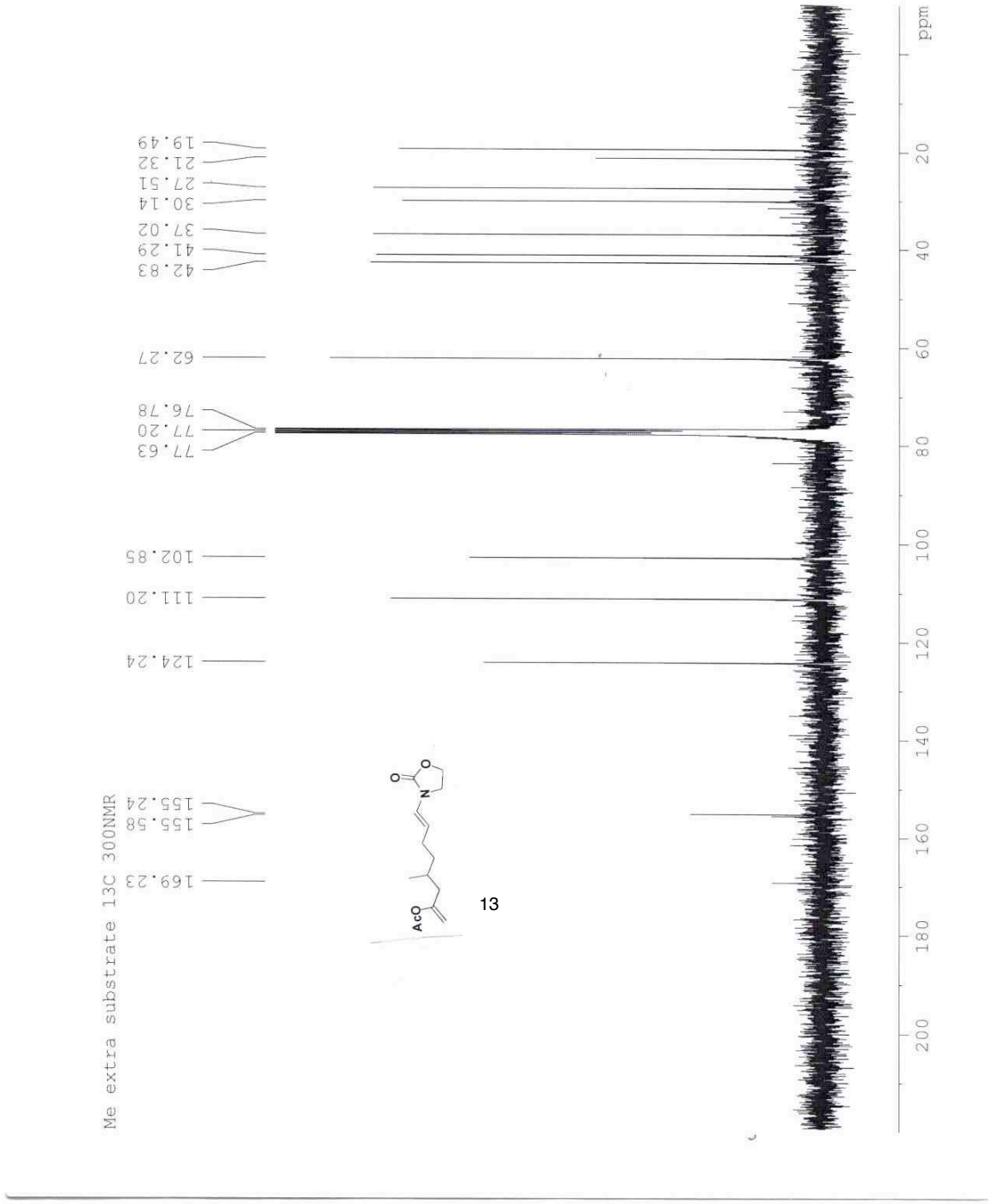
12


3,4-disubstitued, upper spot
7.2703
6.7051
6.6767
4.6454
4.6267
4.6170
4.5983
4.4663
4.4502
4.4341
3.7095
3.6929
3.6749
3.6580
2.7577
2.7475
2.6040
2.5936
2.5765
2.5659
2.3985
2.3845
2.3706
2.3518
2.3404
2.3240
2.3126
2.1574
2.1529
2.1507
2.1446
2.1373
1.8698
1.8675
1.8607
1.6847
1.6653
1.6574
1.6379
1.5924
1.2599
0.9904
0.9805
0.9667
BRUKER
Current Data Parameters
NAME Lei07100801
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080710
Time 11.11
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 143.7
DW 48.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300085 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
cis-12
9
8
7
6
5
4
3
2
1
ppm
0.97
1.05
2.27
2.51
1.00
1.05
2.36
1.21
1.41
1.27
1.35
3.24

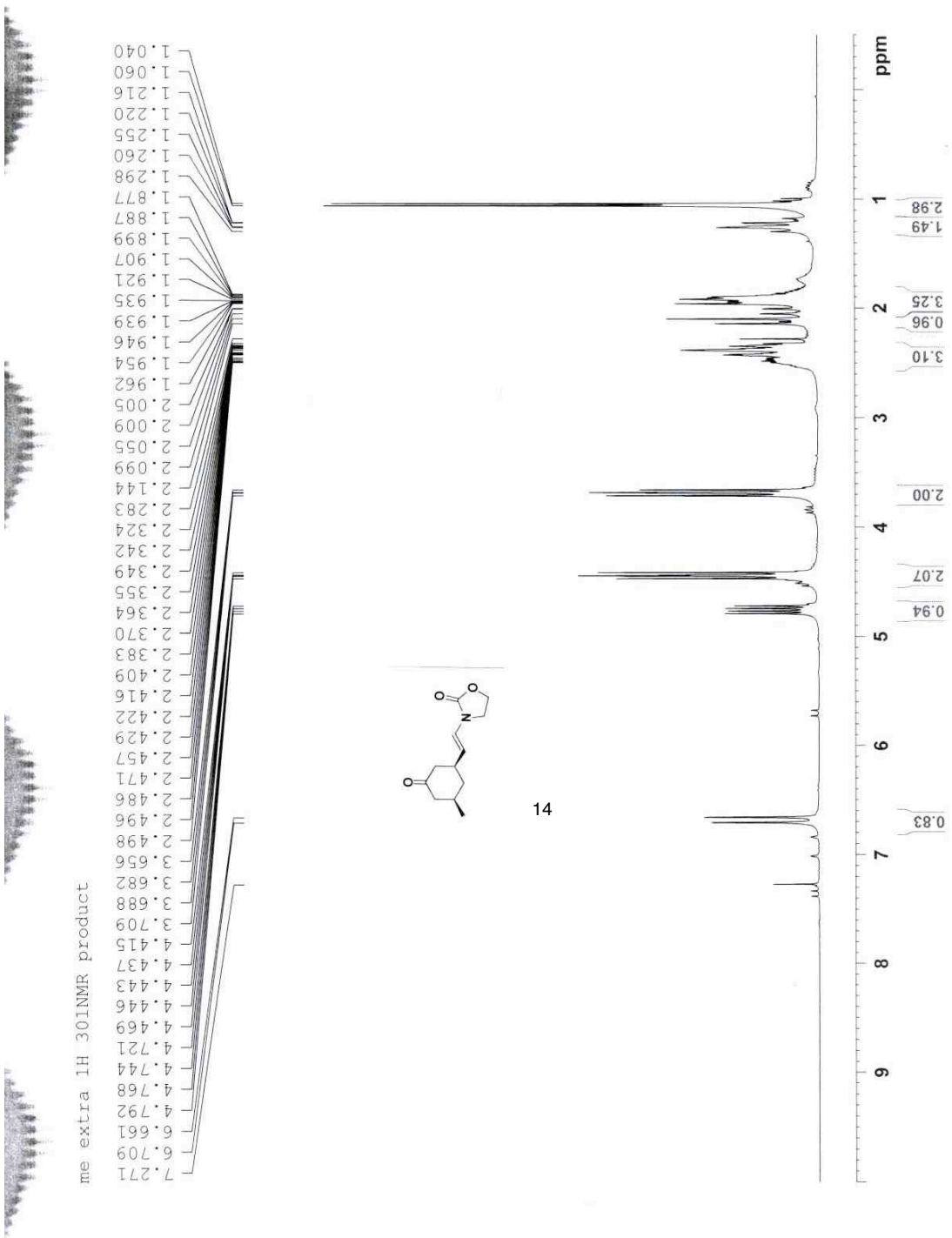

3,4 di substit up product 13C 300NMR
211.24
155.51
125.90
109.04
77.66
77.24
76.81
62.36
46.73
43.83
42.82
39.98
34.10
30.71
17.21
ppm
20
40
60
80
100
120
140
160
180
200

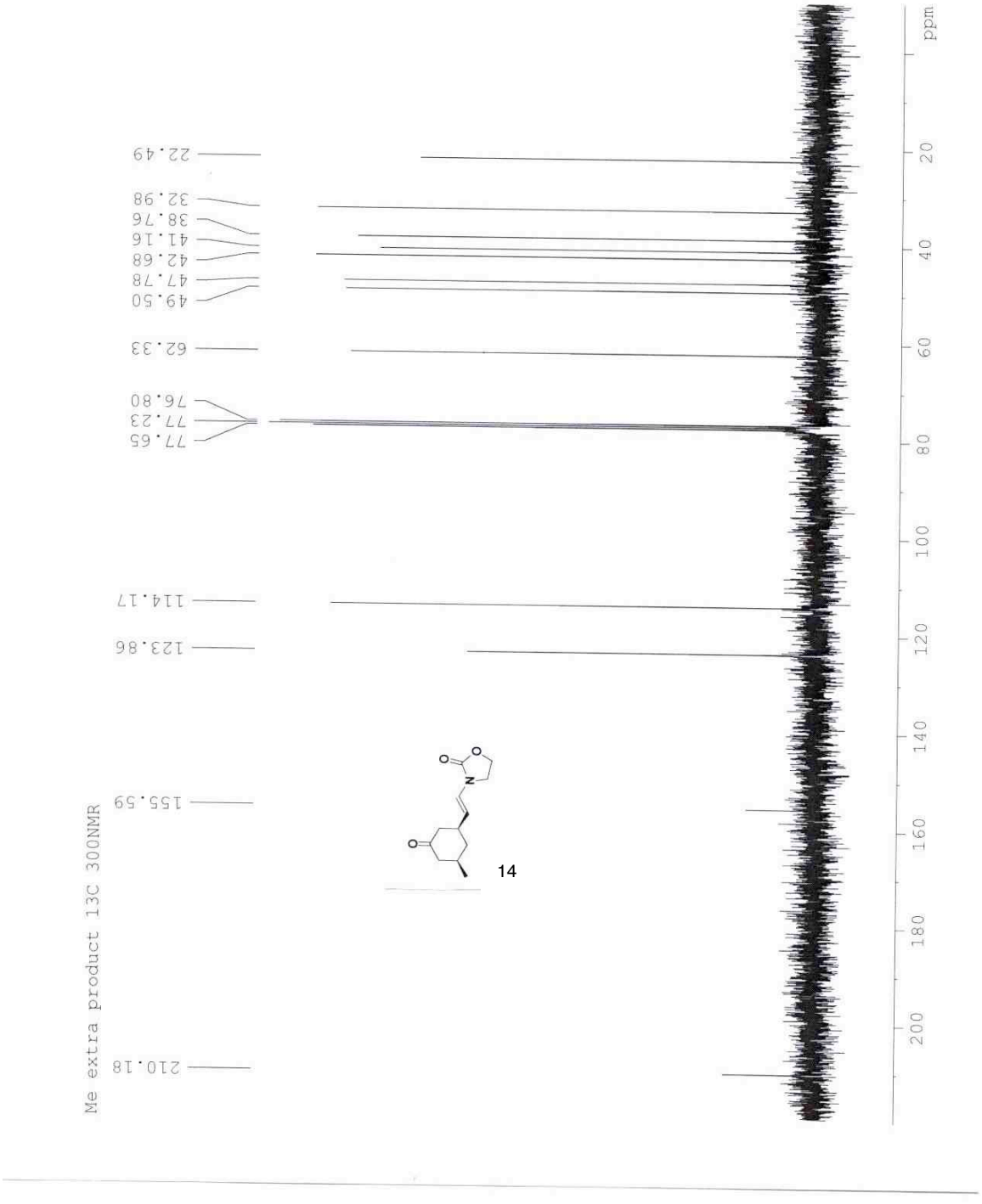
cis-12

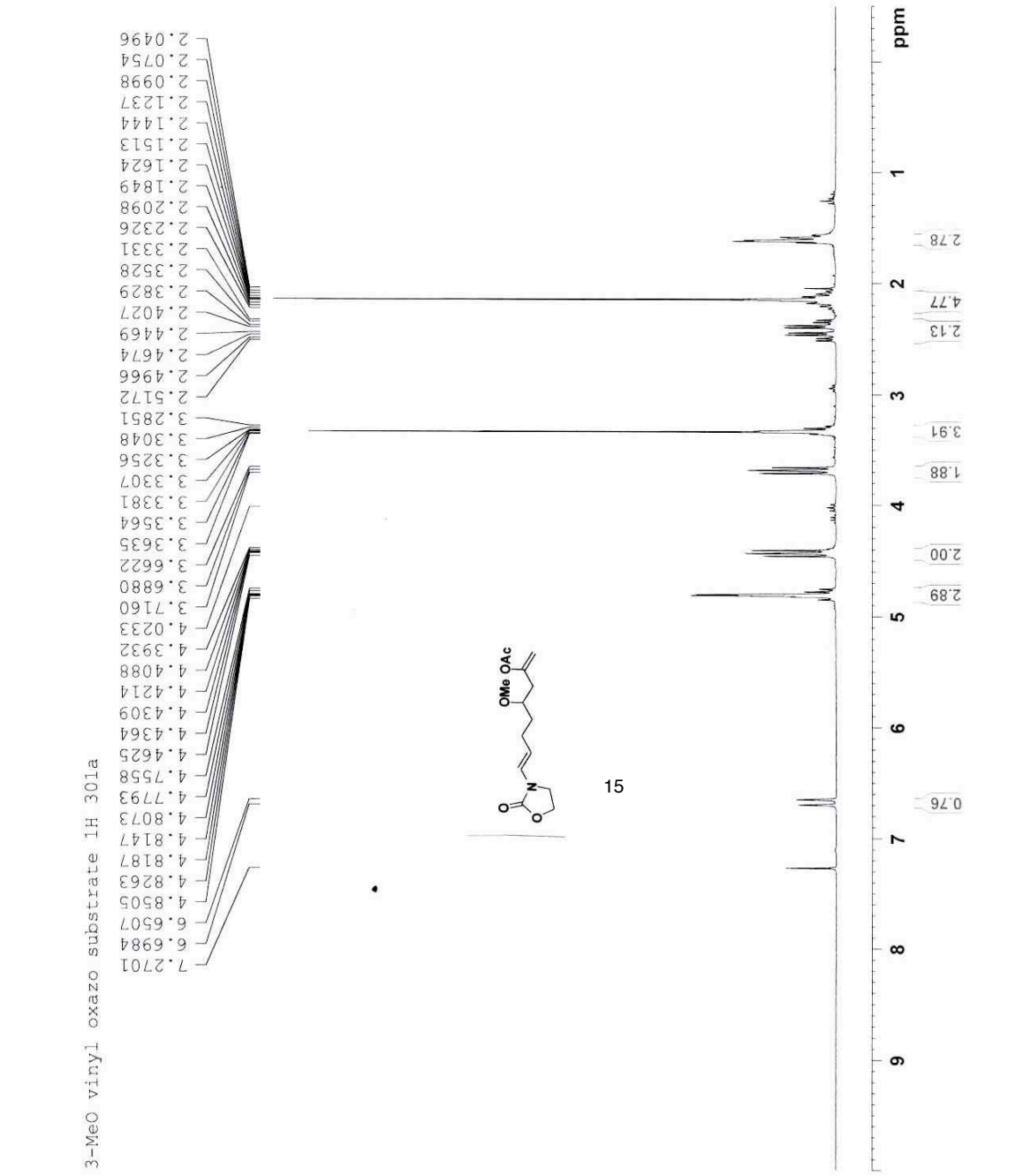

Me extra substrate 1H 300NMR
7.271
6.687
6.639
4.838
4.814
4.790
4.774
4.769
4.743
4.727
4.723
4.462
4.448
4.439
4.436
4.430
4.408
3.714
3.693
3.687
3.660
2.276
2.267
2.256
2.255
2.240
2.227
2.206
2.159
2.152
2.140
2.128
2.111
2.102
2.098
2.077
2.066
2.050
2.026
2.002
1.633
1.572
1.263
1.256
1.251
1.237
1.231
1.224
1.219
1.207
0.944
0.930
0.922
0.908
0.894
AcO
13
ppm
9
8
7
6
5
4
3
2
1
0.69
2.83
2.00
1.89
1.44
3.12
2.06
1.27
1.16
1.42
3.02

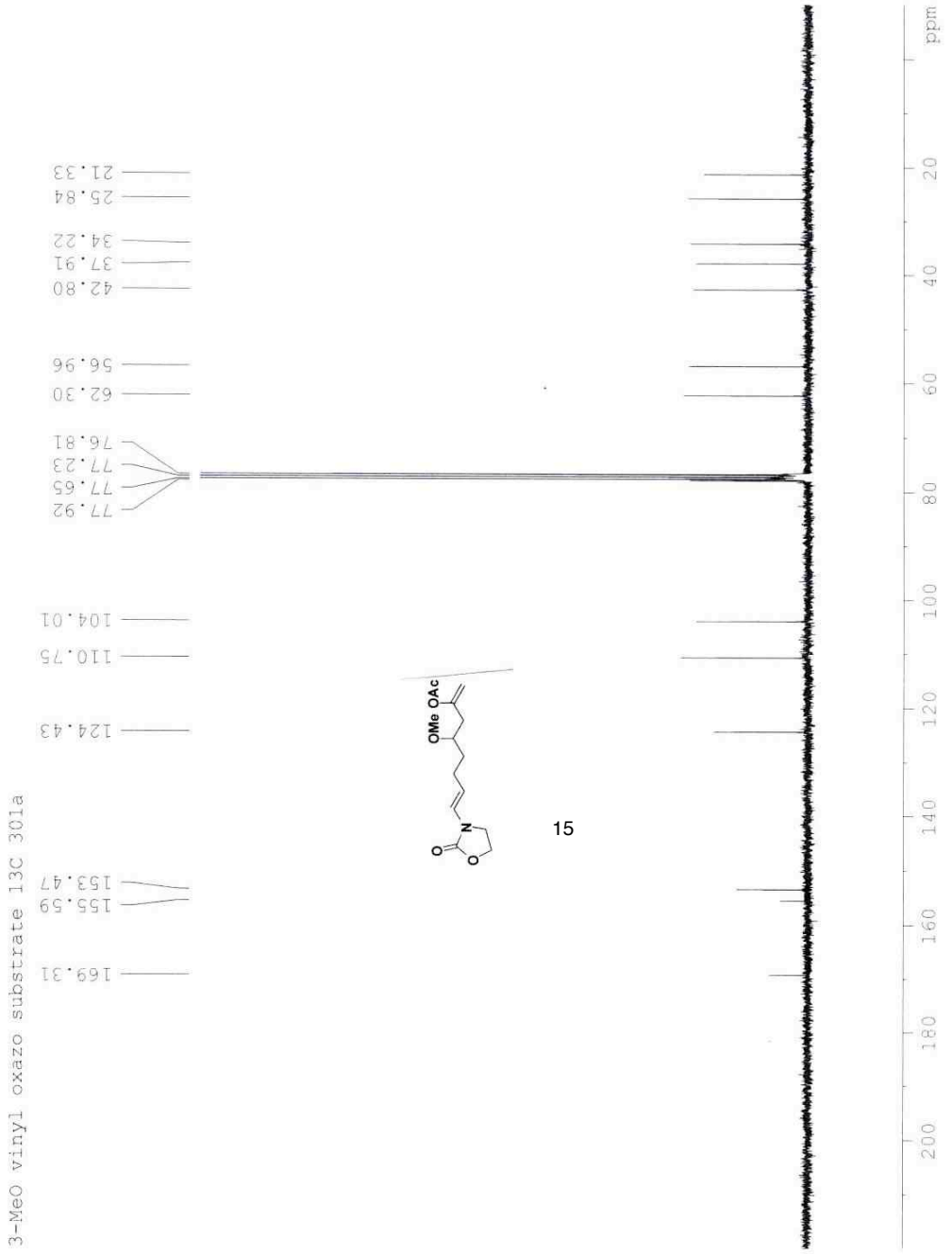

Me extra substrate 13C 300NMR
169.23
155.58
155.24
124.24
111.20
102.85
77.63
77.20
76.78
62.27
42.83
41.29
37.02
30.14
27.51
21.32
19.49
ppm
20
40
60
80
100
120
140
160
180
200
AcO
O
N
O
O

13

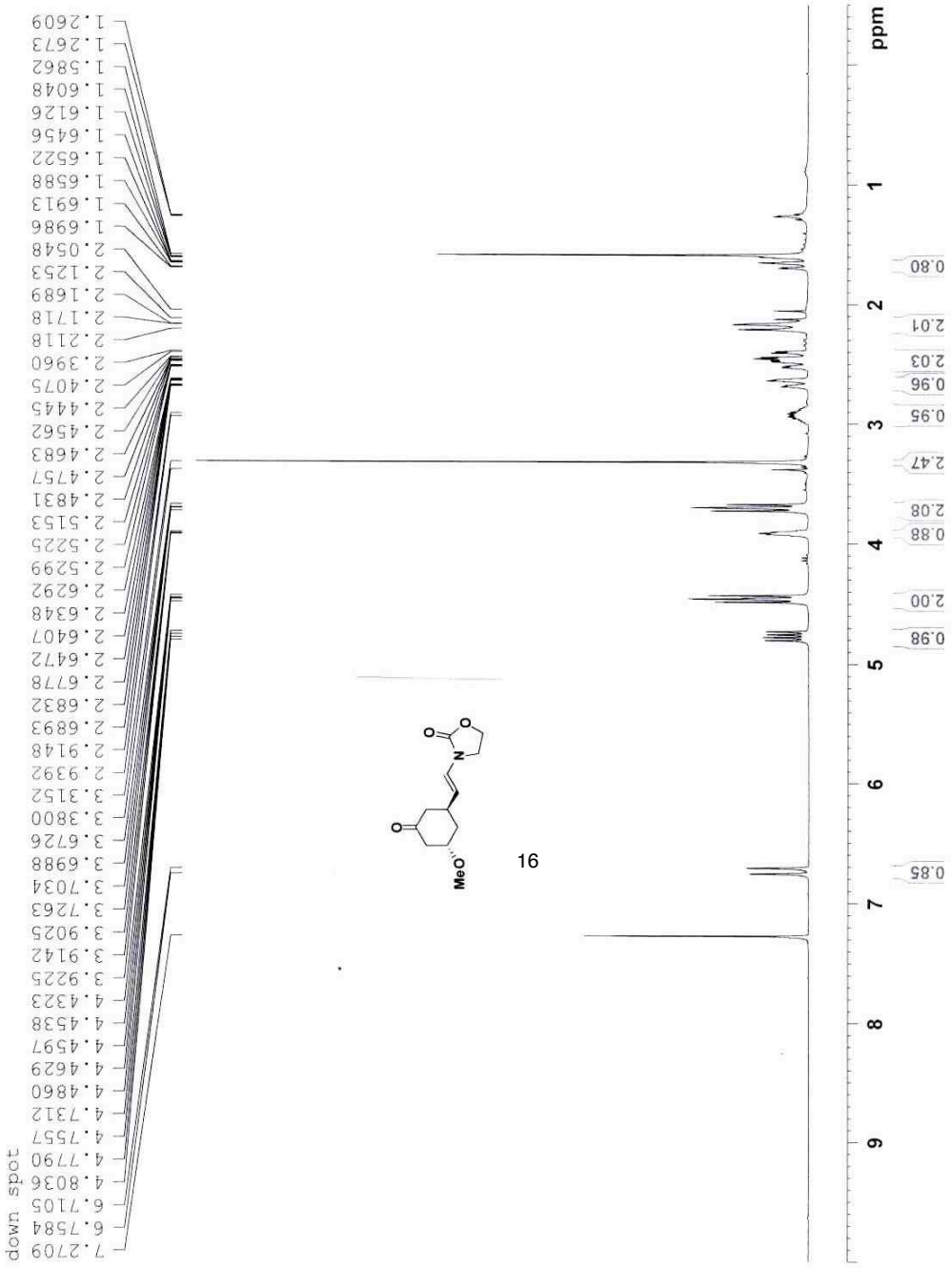

me extra 1H 301NMR product
7.271
6.709
6.661
4.792
4.768
4.744
4.721
4.469
4.446
4.443
4.437
4.415
3.709
3.688
3.682
3.656
2.498
2.496
2.486
2.471
2.457
2.429
2.422
2.416
2.409
2.383
2.370
2.364
2.355
2.349
2.342
2.324
2.283
2.144
2.099
2.055
2.009
2.005
1.962
1.954
1.946
1.939
1.935
1.921
1.907
1.899
1.887
1.877
1.298
1.260
1.255
1.220
1.216
1.060
1.040
ppm
1
2
3
4
5
6
7
8
9
2.98
1.49
3.25
0.96
3.10
2.00
2.07
0.94
0.83
O
O
N
O
14

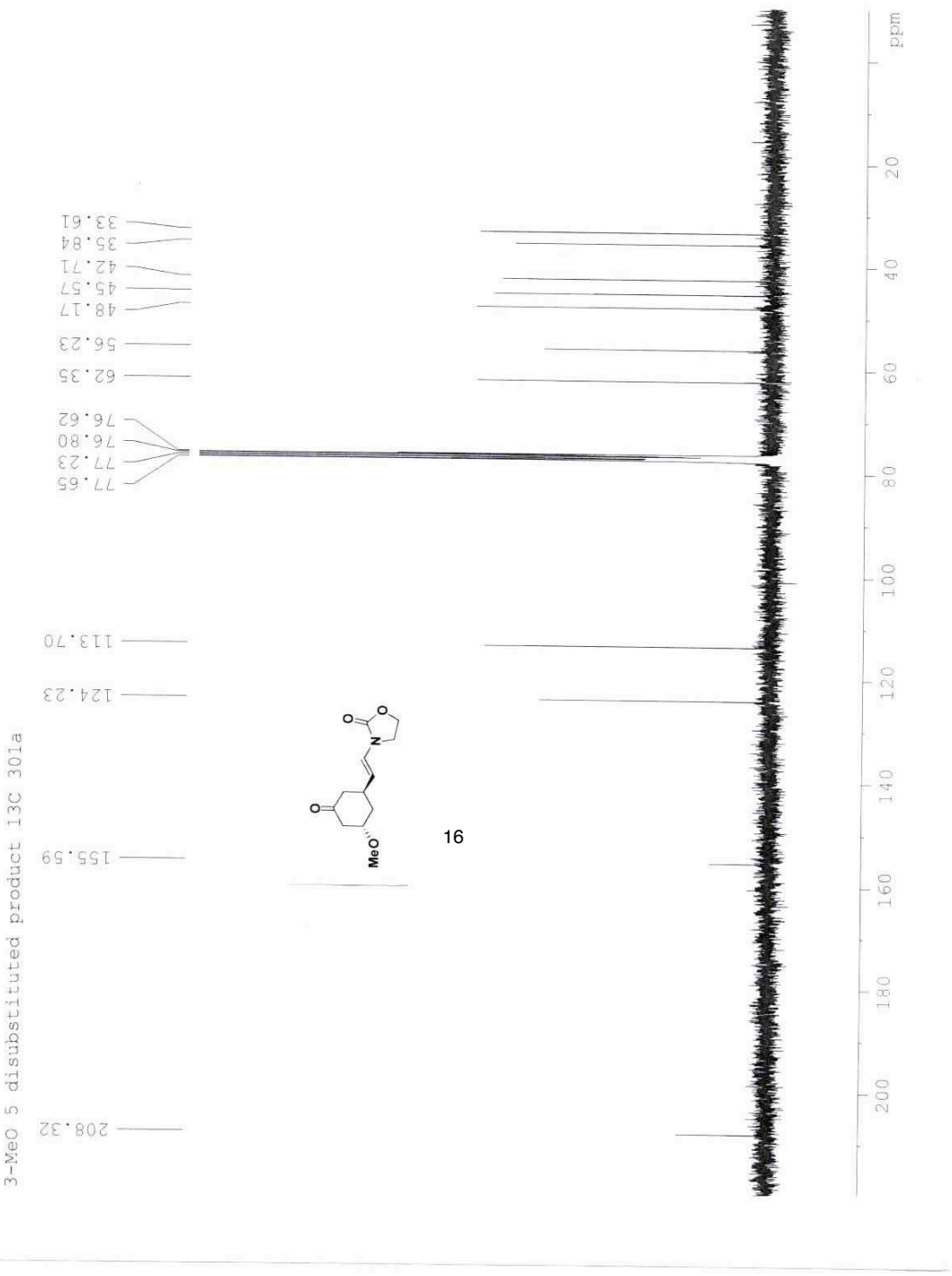

Me extra product 13C 300NMR
210.18
155.59
123.86
114.17
77.65
77.23
76.80
62.33
49.50
47.78
42.68
41.16
38.76
32.98
22.49
ppm
20
40
60
80
100
120
140
160
180
200
14

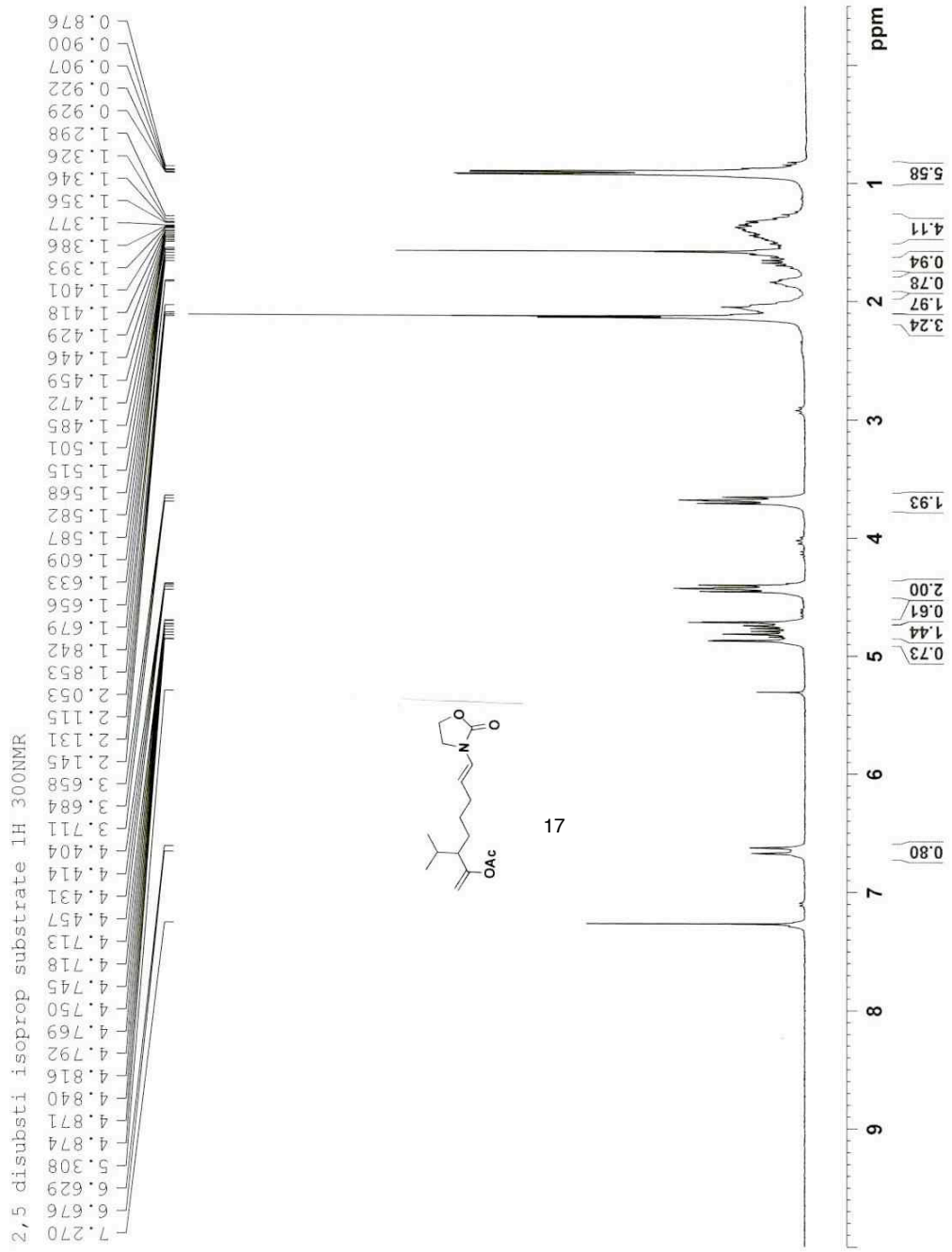

3-MeO vinyl oxazo substrate 1H 301a
7.2701
6.6984
6.6507
4.8505
4.8263
4.8187
4.8147
4.8073
4.7793
4.7558
4.4625
4.4364
4.4309
4.4214
4.4088
4.3932
4.0233
3.7160
3.6880
3.6622
3.6635
3.5564
3.3381
3.3307
3.3256
3.3048
3.2851
2.5172
2.4966
2.4674
2.4469
2.4027
2.3829
2.3528
2.3331
2.2326
2.2098
2.1849
2.1624
2.1513
2.1444
2.1237
2.0998
2.0754
2.0496
OMe OAc
15
ppm
9
8
7
6
5
4
3
2
1
0.76
2.89
2.00
1.88
3.91
2.13
4.77
2.78


3-MeO vinyl oxazo substrate 13C 301a
169.31
155.59
153.47
124.43
110.75
104.01
77.92
77.65
77.23
76.81
62.30
56.96
42.80
37.91
34.22
25.84
21.33
OMe OAc
N
O
O
ppm
200
180
160
140
120
100
80
60
40
20

15


down spot
7.2709
6.7584
6.7105
4.8036
4.7790
4.7557
4.7312
4.4860
4.4629
4.4597
4.4538
4.4323
3.9225
3.9142
3.9025
3.7263
3.7034
3.6988
3.6726
3.3800
3.3152
2.9392
2.9148
2.6893
2.6832
2.6778
2.6472
2.6407
2.6348
2.6292
2.5299
2.5225
2.5153
2.4831
2.4757
2.4683
2.4562
2.4445
2.4075
2.3960
2.2118
2.1718
2.1689
2.1253
2.0548
1.6986
1.6913
1.6588
1.6522
1.6456
1.6126
1.6048
1.5862
1.2673
1.2609
MeO
16
ppm
0.80
2.01
2.03
0.96
0.95
2.47
2.08
0.88
2.00
0.98
0.85

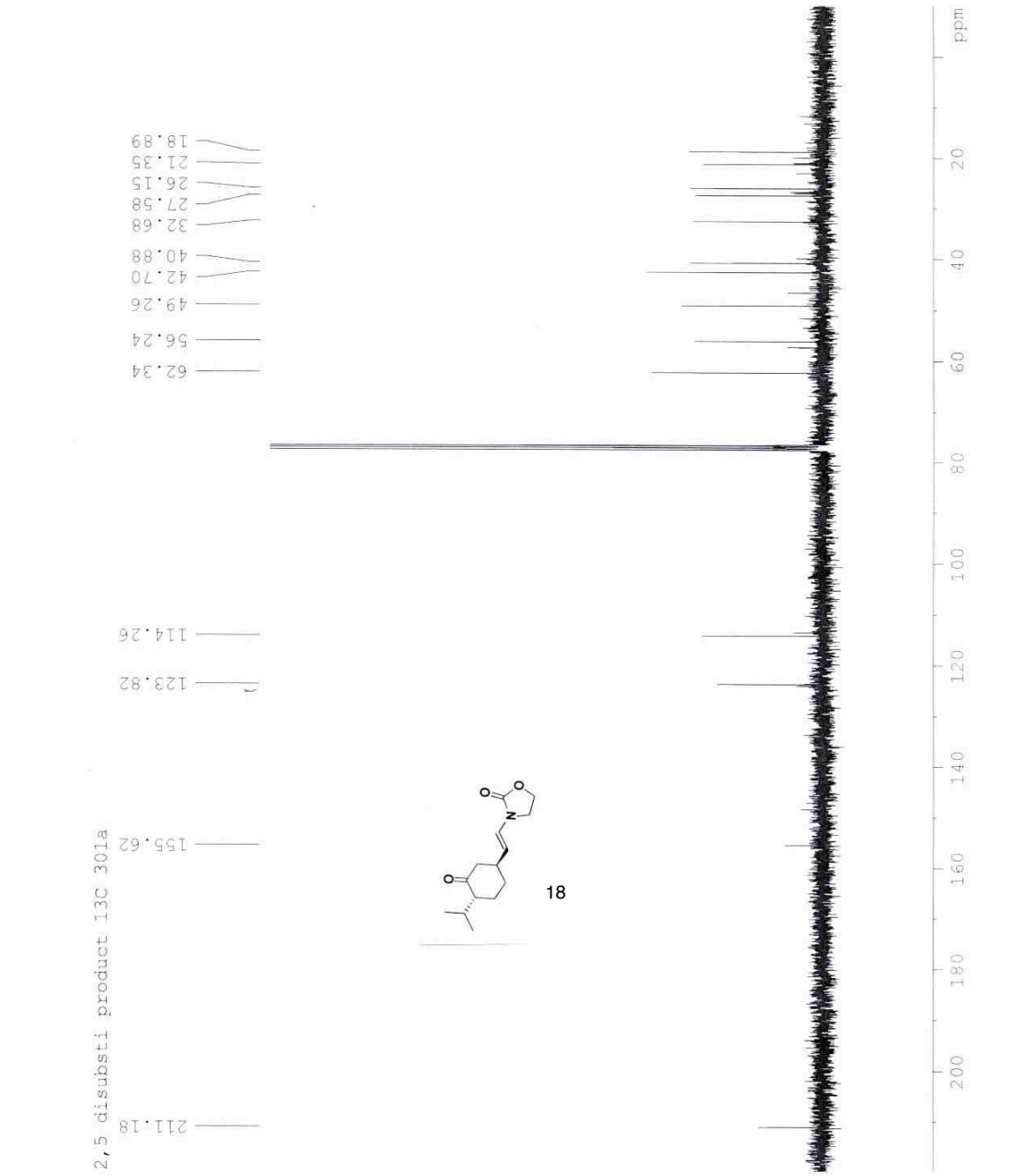

3-MeO 5 disubstituted product 13C 301a
208.32
155.59
124.23
113.70
77.65
77.23
76.80
76.62
62.35
56.23
48.17
45.57
42.71
35.84
33.61
MeO
16
ppm
20
40
60
80
100
120
140
160
180
200

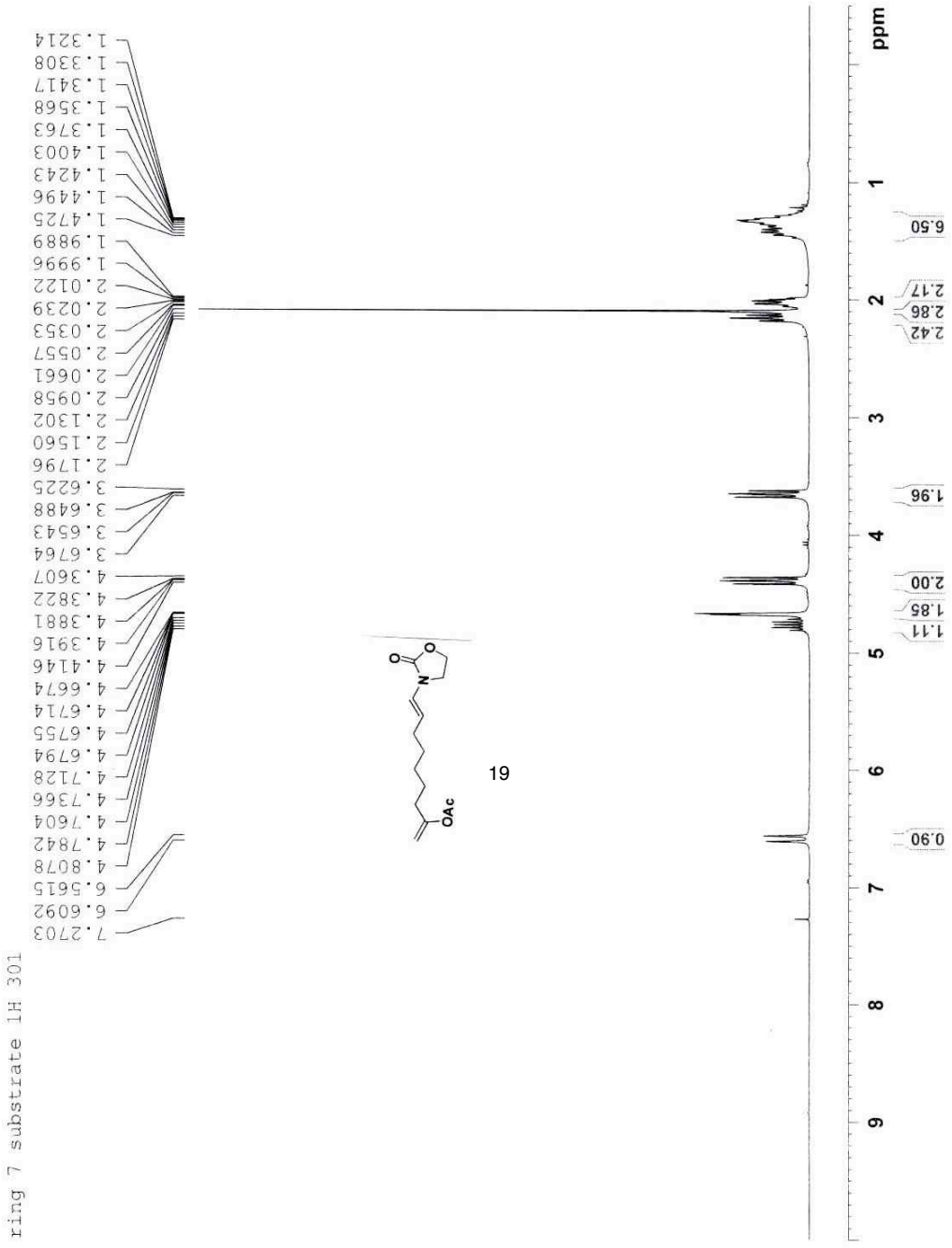

2,5 disubsti isoprop substrate 1H 300NMR
7.270
6.676
6.629
5.308
4.874
4.871
4.840
4.816
4.792
4.769
4.750
4.745
4.718
4.713
4.457
4.431
4.414
4.404
3.711
3.684
3.658
2.145
2.131
2.115
2.053
1.853
1.842
1.679
1.656
1.633
1.609
1.587
1.582
1.568
1.515
1.501
1.485
1.472
1.459
1.446
1.429
1.418
1.401
1.393
1.386
1.377
1.356
1.346
1.326
1.298
0.929
0.922
0.907
0.900
0.876
ppm
1
2
3
4
5
6
7
8
9
5.58
4.11
0.94
0.78
1.97
3.24
1.93
2.00
0.61
1.44
0.73
0.80
O
O
N
O
OAc

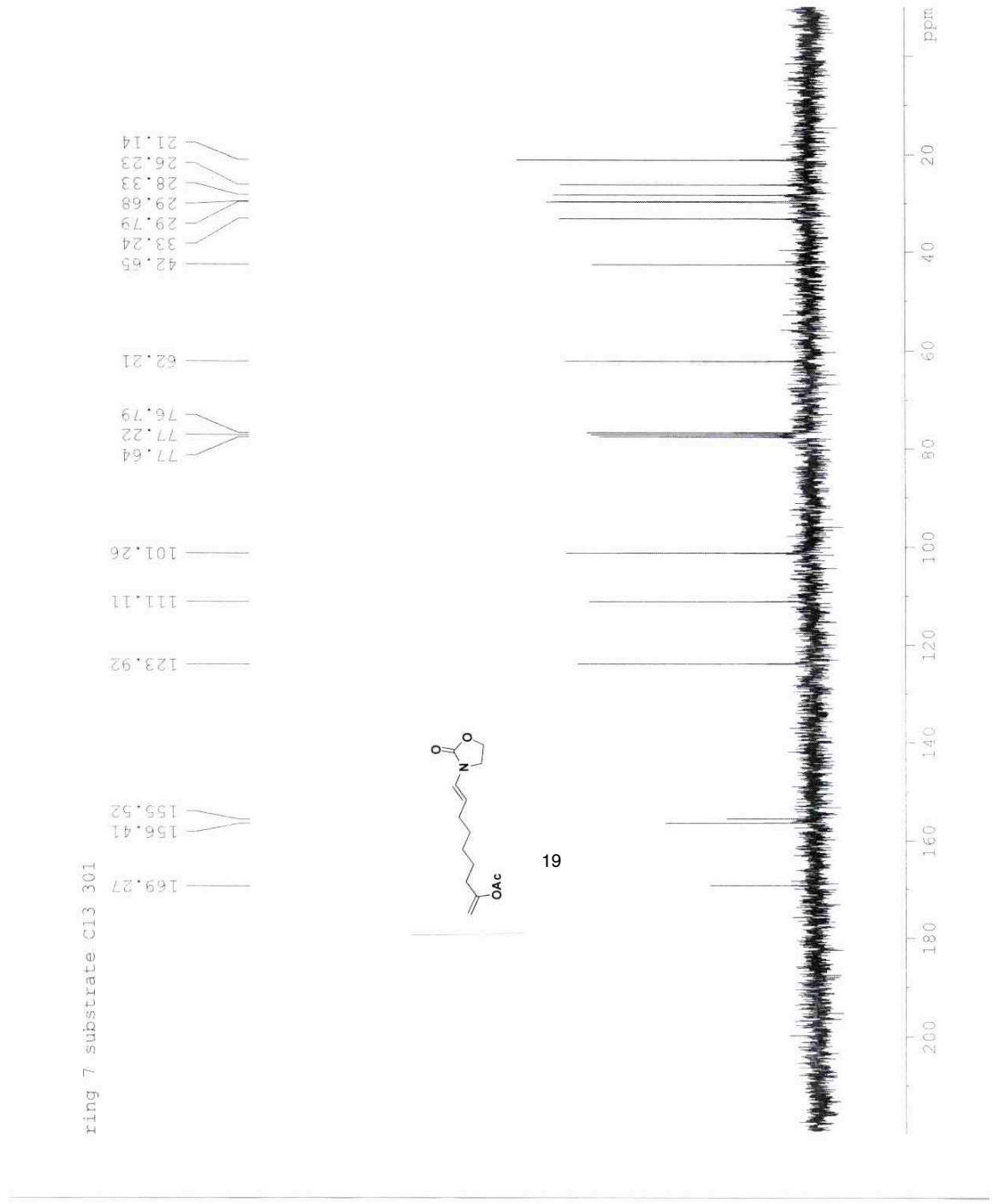
17

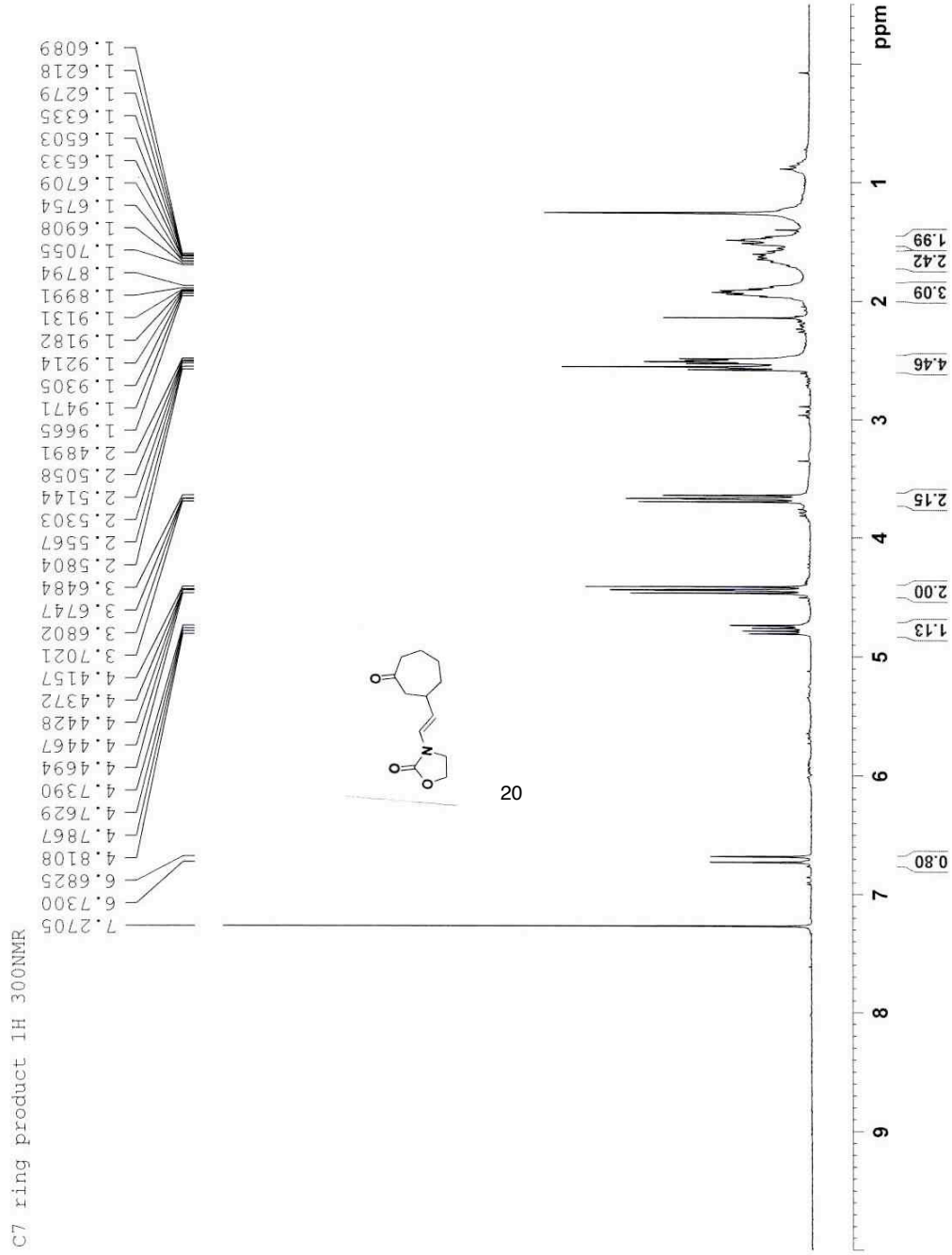
C13 isopropyl substrate 301a
168.87
156.12
155.43
123.89
111.16
102.47
77.47
77.05
76.63
62.10
51.15
42.60
29.88
29.85
28.40
27.96
21.42
20.42
20.20
OAc
17
ppm
200
180
160
140
120
100
80
60
40
20

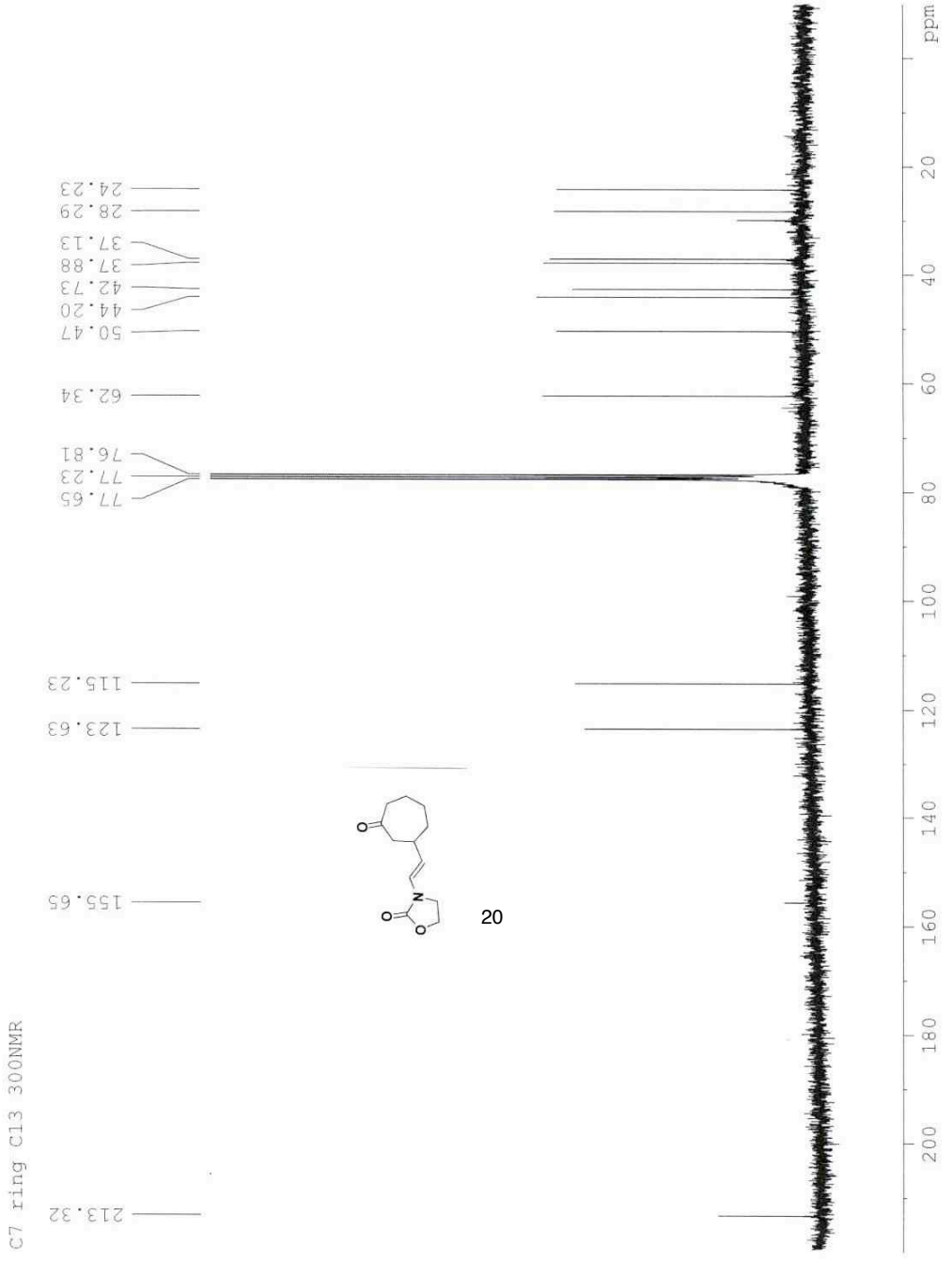
2,5 disubsti product 1H 301a
7.2702
6.7126
6.6647
4.7981
4.7746
4.7503
4.7268
4.4736
4.4474
4.4421
4.4199
3.7159
3.7041
3.6937
3.6883
3.6622
2.4742
2.4661
2.4313
2.4243
2.4177
2.3361
2.3311
2.2089
2.2070
2.1655
2.1549
2.1319
2.1204
2.0996
2.0880
2.0780
2.0596
2.0491
2.0199
2.0115
1.9866
1.9782
1.4929
1.4562
0.9368
0.9147
0.8798
0.8574
BRUKER
Current Data Parameters
NAME 1e1071920801
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080719
Time 22.10
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 181
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 16384
SF 300.3799991 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
18
ppm
9
8
7
6
5
4
3
2
1
6.06
1.69
0.67
4.78
1.82
2.10
0.21
2.27
1.00
0.10
0.88


2,5 disubsti product 13C 301a
211.18
155.62
123.82
114.26
62.34
56.24
49.26
42.70
40.88
32.68
27.58
26.15
21.35
18.89
ppm
20
40
60
80
100
120
140
160
180
200
18

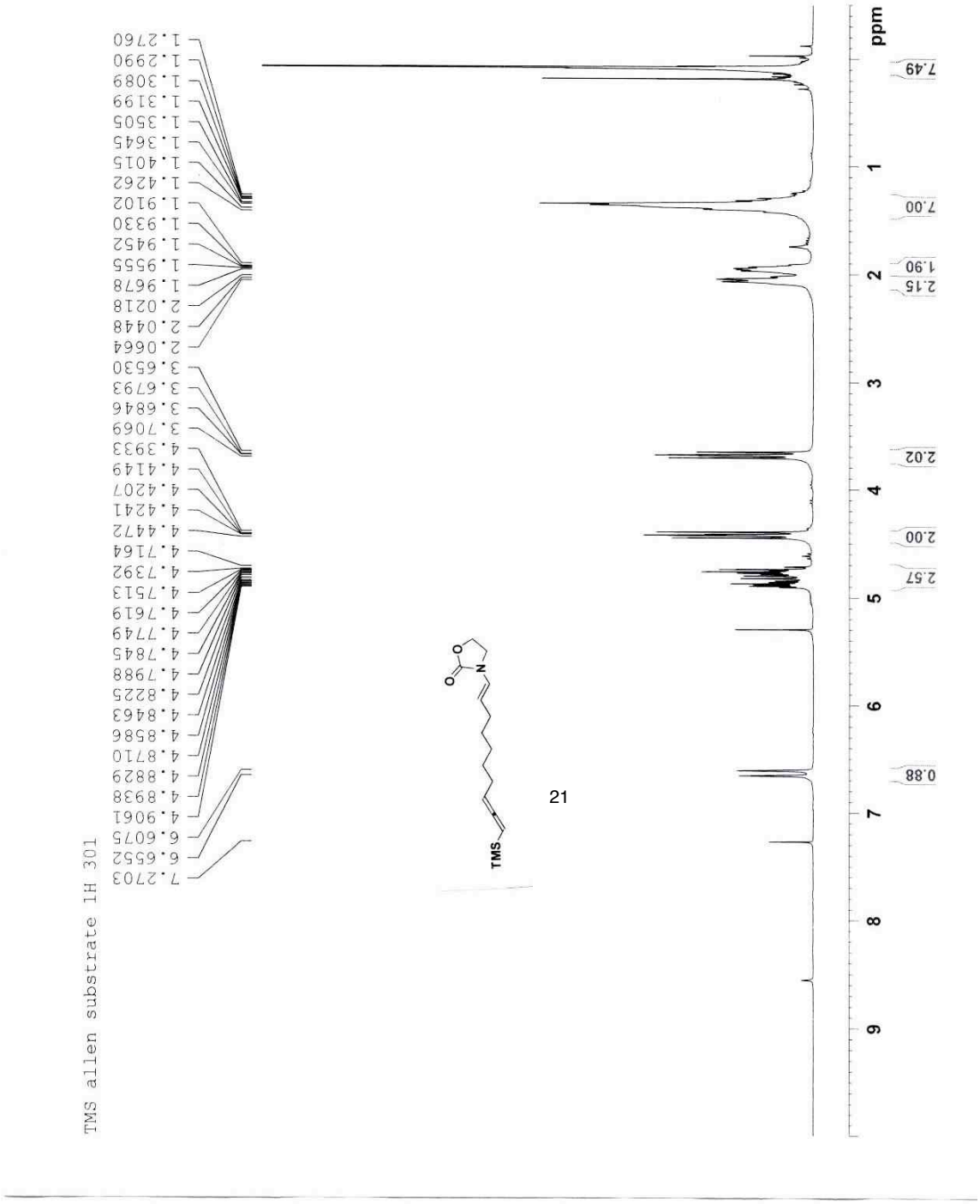

ring 7 substrate 1H 301
7.2703
6.6092
6.5615
4.8078
4.7842
4.7604
4.7366
4.7128
4.6794
4.6755
4.6714
4.6674
4.4146
4.3916
4.3881
4.3822
4.3607
3.6764
3.6543
3.6488
3.6225
2.1796
2.1560
2.1302
2.0958
2.0661
2.0557
2.0353
2.0239
2.0122
1.9996
1.9889
1.4725
1.4496
1.4243
1.4003
1.3763
1.3568
1.3417
1.3308
1.3214
ppm
0.90
1.11
1.85
2.00
1.96
2.42
2.86
2.17
6.50
19
OAc

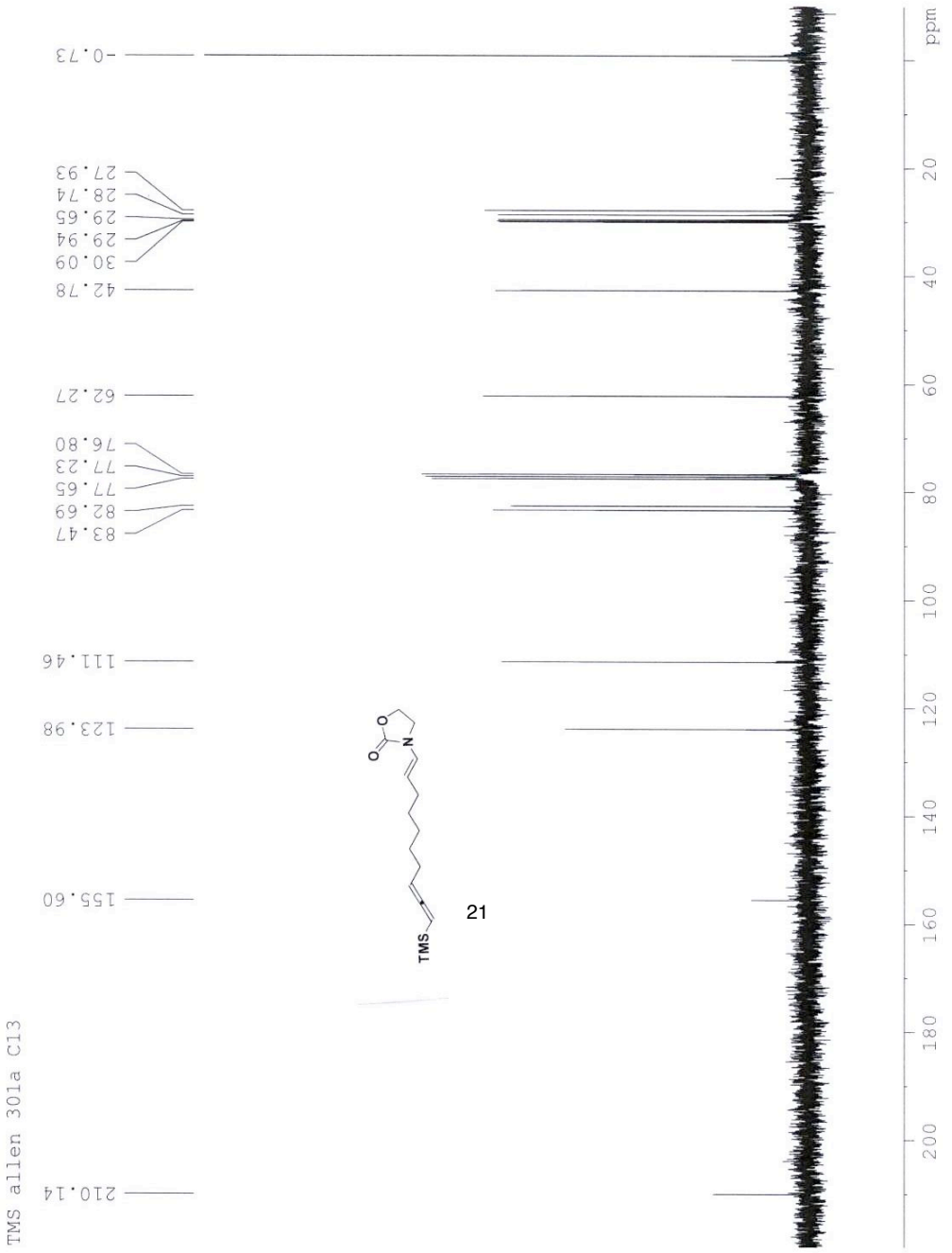

ring 7 substrate C13 301
169.27
156.41
155.52
123.92
111.11
101.26
77.64
77.22
76.79
62.21
42.65
33.24
29.79
29.68
28.33
26.23
21.14
OAc
19
ppm


C7 ring product 1H 300NMR
7.2705
6.7300
6.6825
4.8108
4.7867
4.7629
4.7390
4.4694
4.4467
4.4428
4.4372
4.4157
3.7021
3.6802
3.6747
3.6484
2.5804
2.5567
2.5303
2.5144
2.5058
2.4891
1.9665
1.9471
1.9305
1.9214
1.9182
1.9131
1.8991
1.8794
1.7055
1.6908
1.6754
1.6709
1.6533
1.6503
1.6335
1.6279
1.6218
1.6089
ppm
0.80
1.13
2.00
2.15
4.46
3.09
2.42
1.99
20

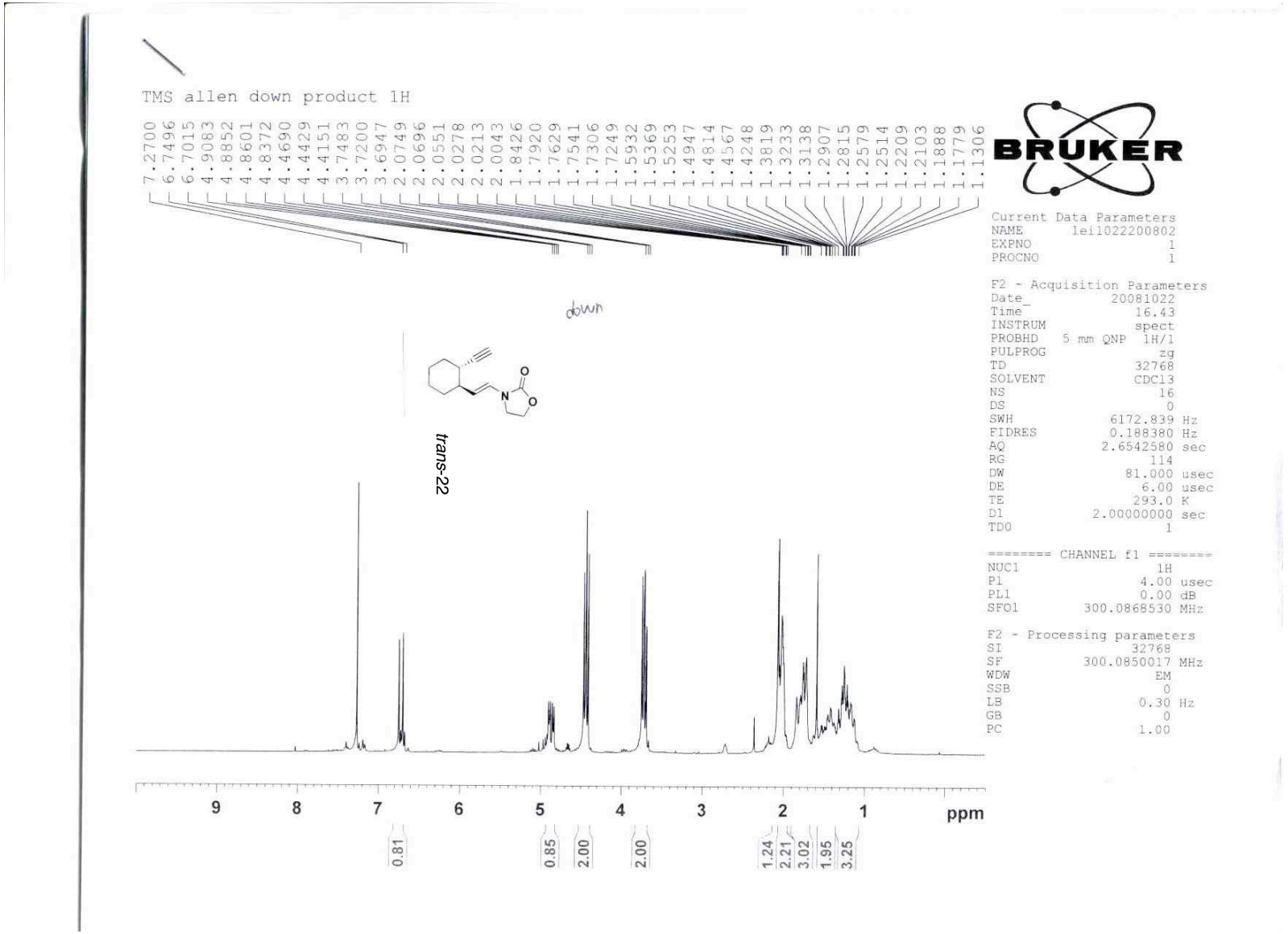

C7 ring C13 300NMR
213.32
155.65
123.63
115.23
77.65
77.23
76.81
62.34
50.47
44.20
42.73
37.88
37.13
28.29
24.23
ppm
20
40
60
80
100
120
140
160
180
200

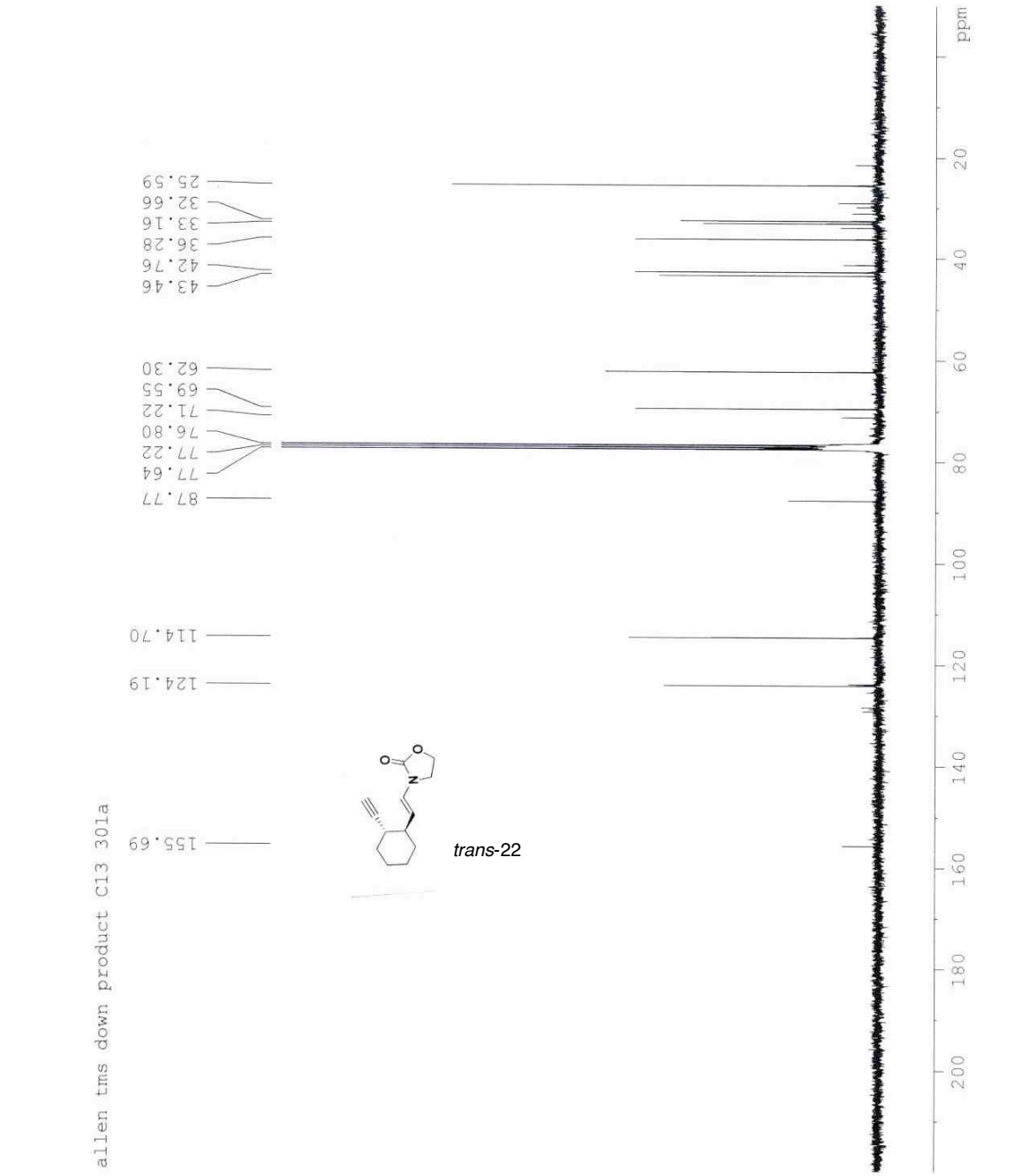
20


TMS allen substrate 1H 301
1.2760
1.2990
1.3089
1.3199
1.3505
1.3645
1.4015
1.4262
1.9102
1.9330
1.9452
1.9555
1.9678
2.0218
2.0448
2.0664
3.6530
3.6793
3.6846
3.7069
4.3933
4.4149
4.4207
4.4241
4.4472
4.7164
4.7392
4.7513
4.7619
4.7749
4.7845
4.7988
4.8225
4.8463
4.8586
4.8710
4.8829
4.8938
4.9061
6.6075
6.6552
7.2703
TMS
O
O
N
21
ppm
0
1
2
3
4
5
6
7
8
9
7.49
7.00
1.90
2.15
2.02
2.00
2.57
0.88


TMS allen 301a C13
210.14
155.60
123.98
111.46
83.47
82.69
77.65
77.23
76.80
62.27
42.78
30.09
29.94
29.65
28.74
27.93
-0.73
ppm
20
40
60
80
100
120
140
160
180
200
O
O
N
TMS

21

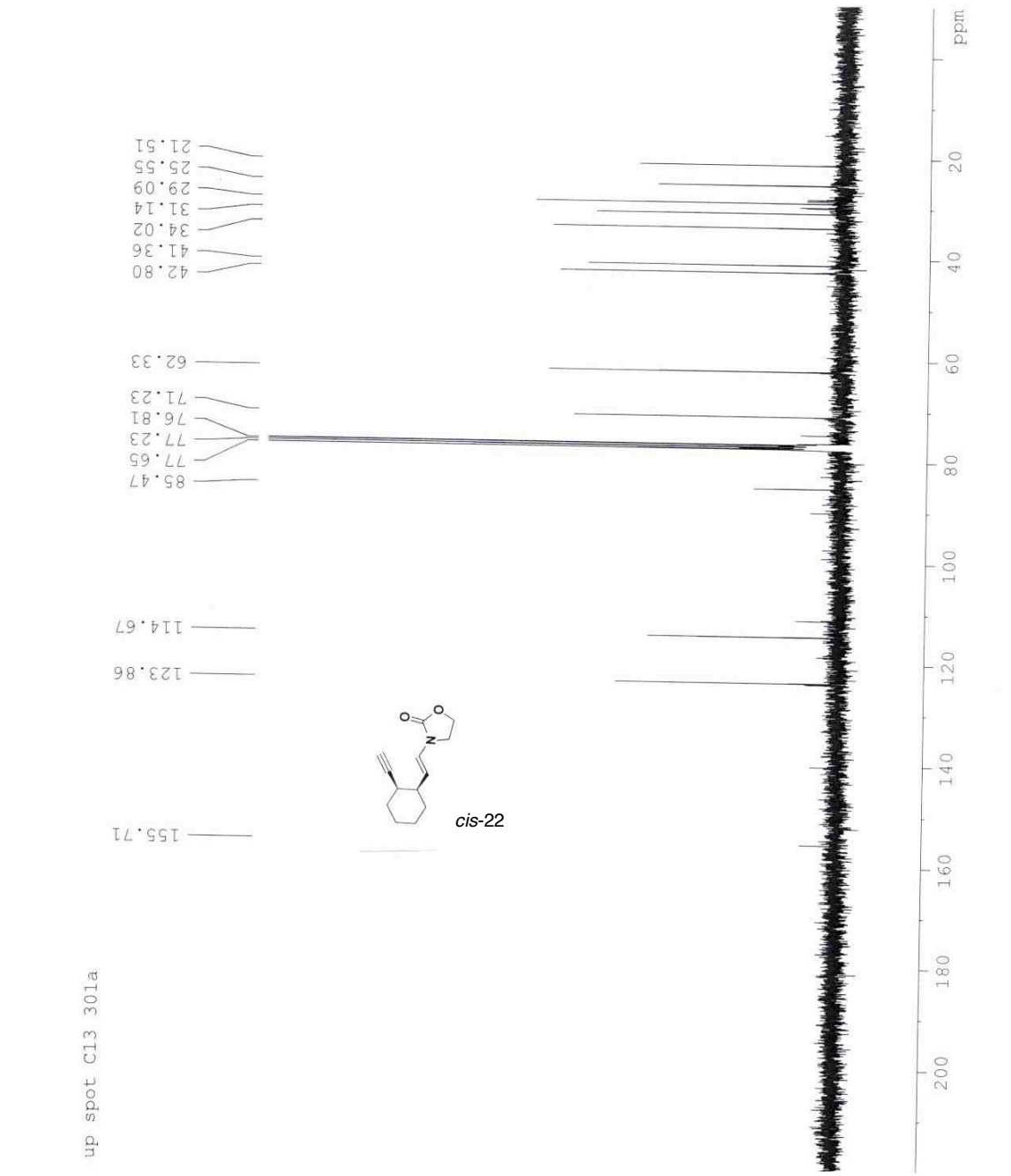

TMS allen down product 1H
7.2700
6.7496
6.7015
4.9083
4.8852
4.8601
4.8372
4.4690
4.4429
4.4151
3.7483
3.7200
3.6947
2.0749
2.0696
2.0551
2.0278
2.0213
2.0043
1.8426
1.7920
1.7629
1.7541
1.7306
1.7249
1.5932
1.5369
1.5253
1.4947
1.4814
1.4567
1.4248
1.3819
1.3233
1.3138
1.2907
1.2815
1.2579
1.2514
1.2209
1.2103
1.1888
1.1779
1.1306
BRUKER
down
trans-22
Current Data Parameters
NAME lei1022200802
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081022
Time 16.43
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 114
DW 81.000 usec
DE 6.00 usec
TE 293.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 4.00 usec
PL1 0.00 dB
SFO1 300.0868530 MHz
F2 - Processing parameters
SI 32768
SF 300.0850017 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
0.81
0.85
2.00
2.00
1.24
2.21
3.02
1.95
3.25


allen tms down product C13 301a
155.69
124.19
114.70
87.77
77.64
77.22
76.80
71.22
69.55
62.30
43.46
42.76
36.28
33.16
32.66
25.59
ppm
20
40
60
80
100
120
140
160
180
200

trans-22

TMS Allen up product
7.270
6.724
6.676
4.970
4.942
4.922
4.894
4.669
4.464
4.438
4.433
4.410
3.751
3.728
3.721
3.696
2.726
2.715
2.705
2.195
2.184
2.079
2.071
1.837
1.832
1.755
1.742
1.718
1.713
1.709
1.701
1.697
1.684
1.676
1.638
1.633
1.626
1.606
1.594
1.587
1.582
1.577
1.573
1.566
1.561
1.557
1.553
1.545
1.535
1.524
1.511
1.494
1.481
1.291
1.252
ppm
0.78
1.95
2.00
0.26
0.82
0.78
0.89
0.80
0.42
0.92
1.39
1.52
2.88
2.06

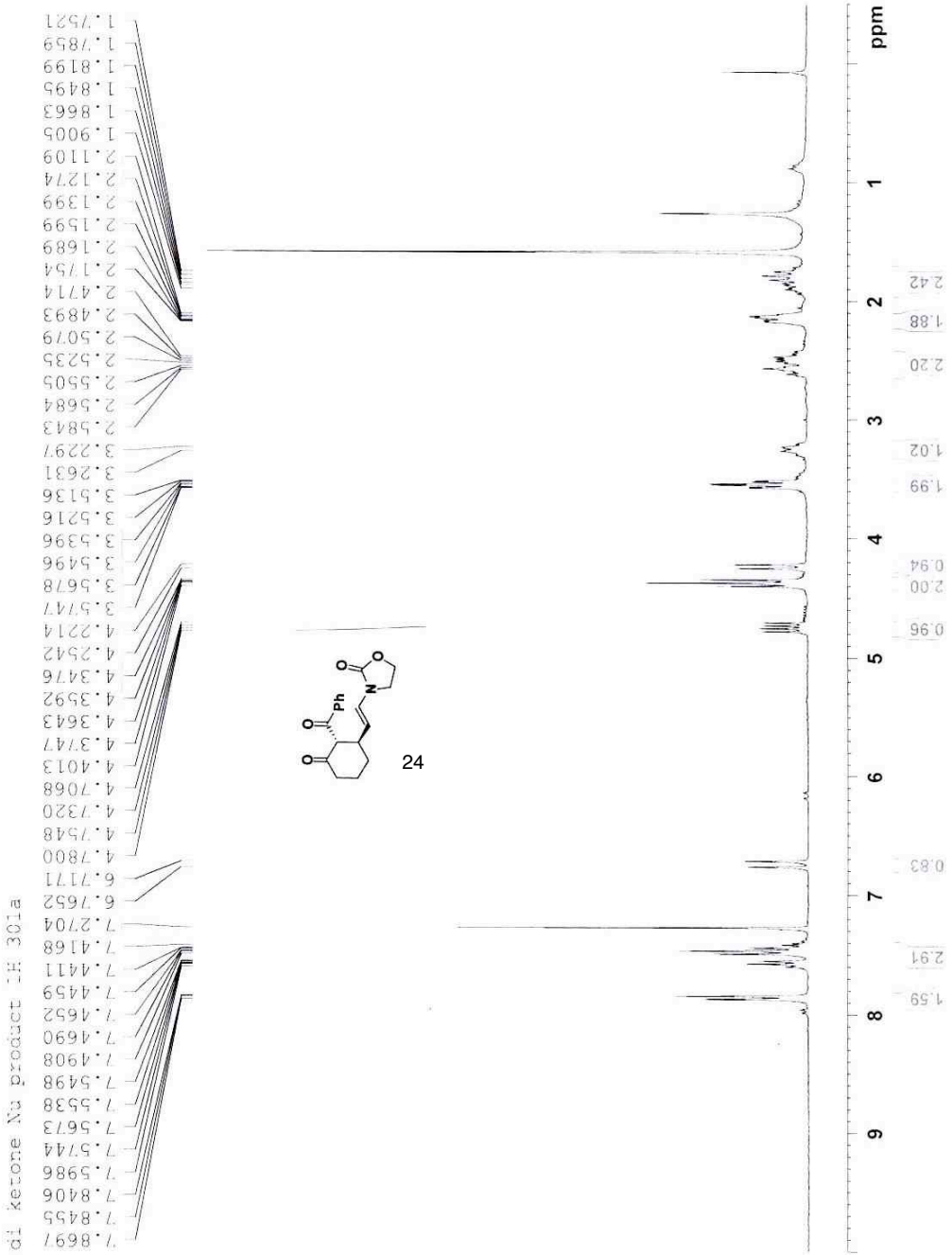
cis-22

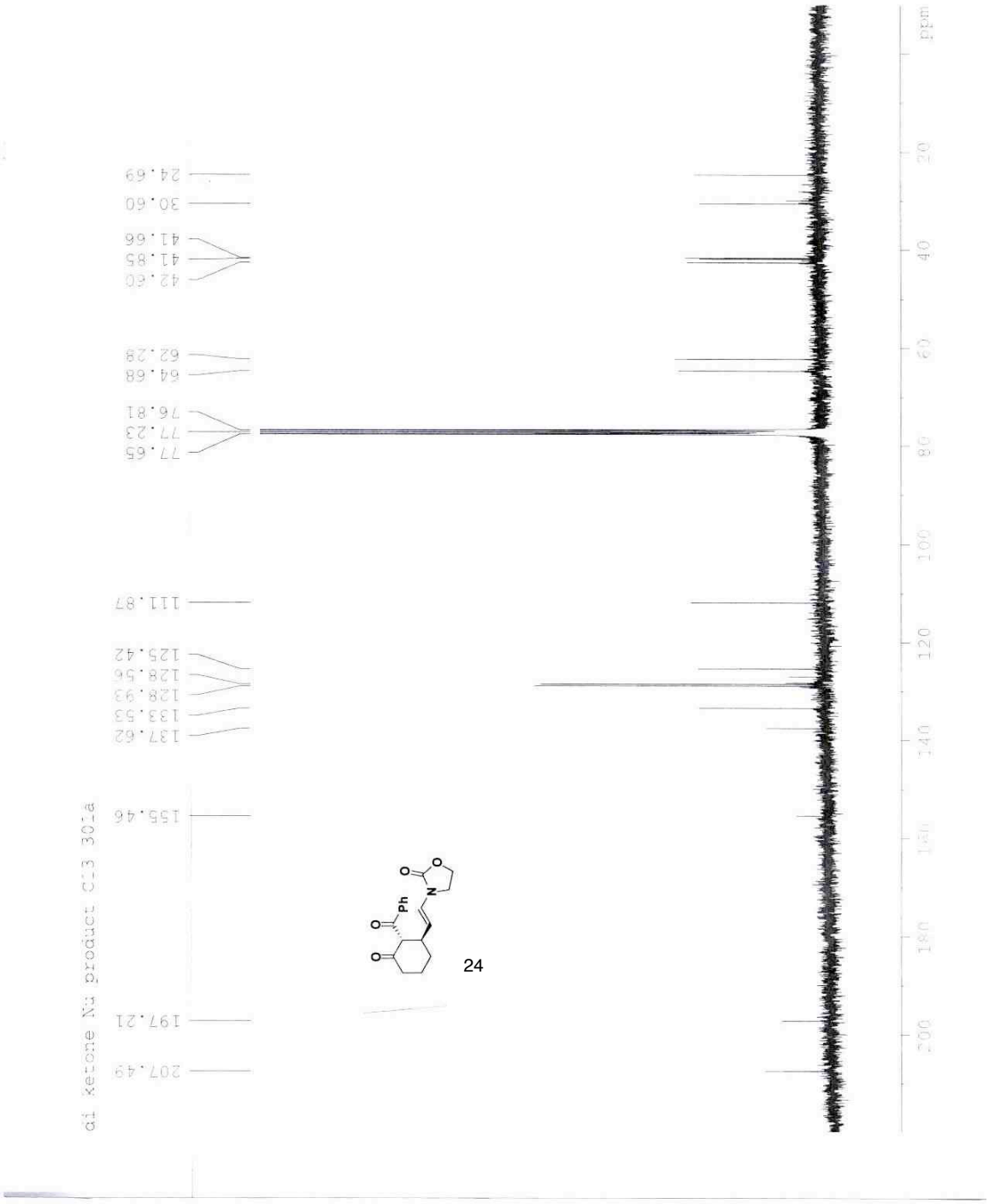

up spot C13 301a
155.71
123.86
114.67
85.47
77.65
77.23
76.81
71.23
62.33
42.80
41.36
34.02
31.14
29.09
25.55
21.51
ppm
20
40
60
80
100
120
140
160
180
200

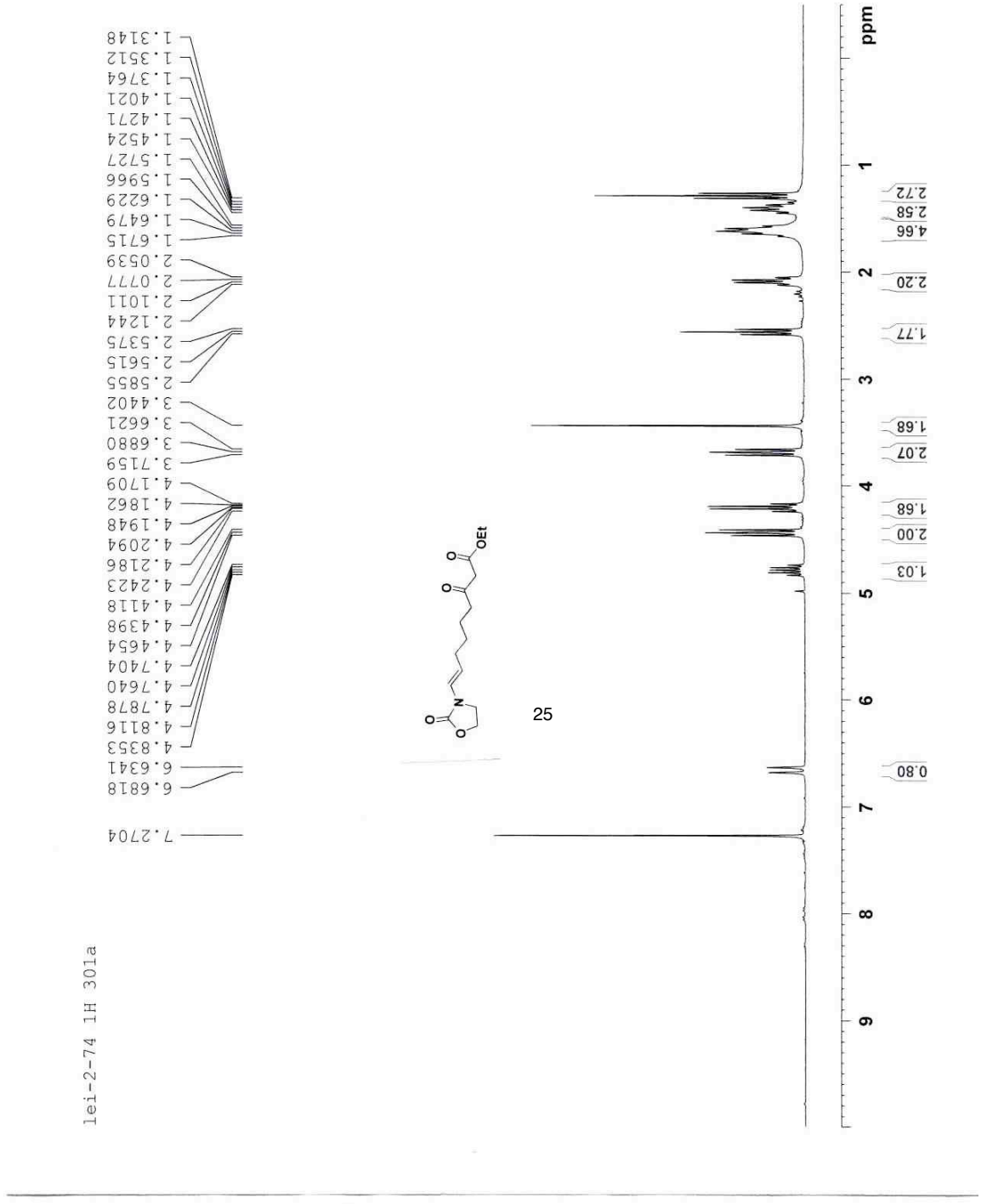
cis-22

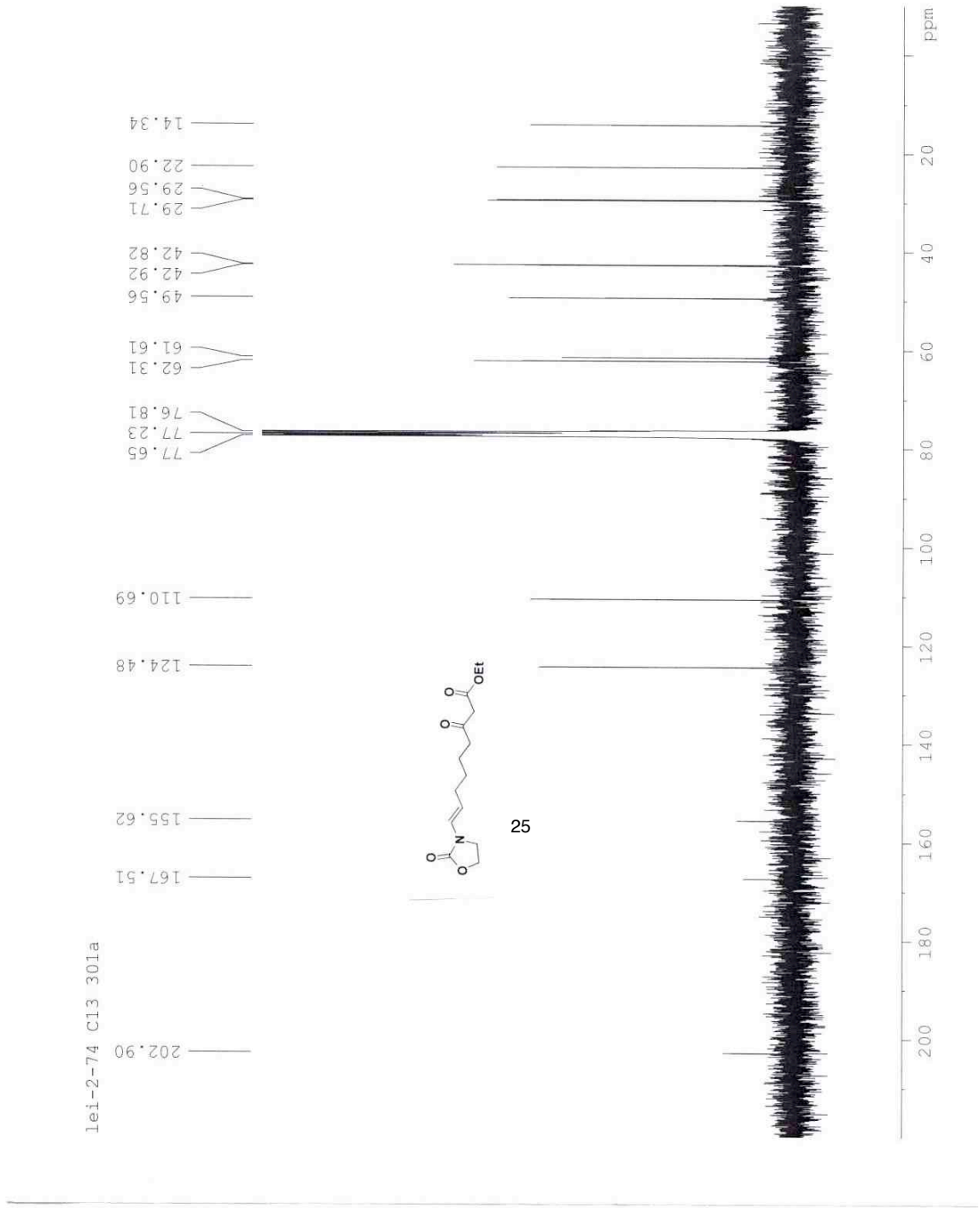
BRUKER
Current Data Parameters
NAME 1e10812200802
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080812
Time 21.54
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 161.3
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 16384
SF 300.3799993 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
16.1873
7.9023
7.8788
7.5343
7.5107
7.4833
7.4584
7.4352
7.2705
6.9969
6.6492
6.1788
4.8480
4.8243
4.8004
4.7766
4.7529
4.4504
4.4242
4.3968
3.7094
3.6816
3.6555
2.4696
2.4450
2.4197
2.1591
2.1355
2.1116
2.0863
2.09
1.81
2.01
1.69
2.02
2.00
0.95
0.80
0.77
2.55
1.76
0.51
Ph
O
N
O
O
O
O
23
di ketone substrate 1H 301a

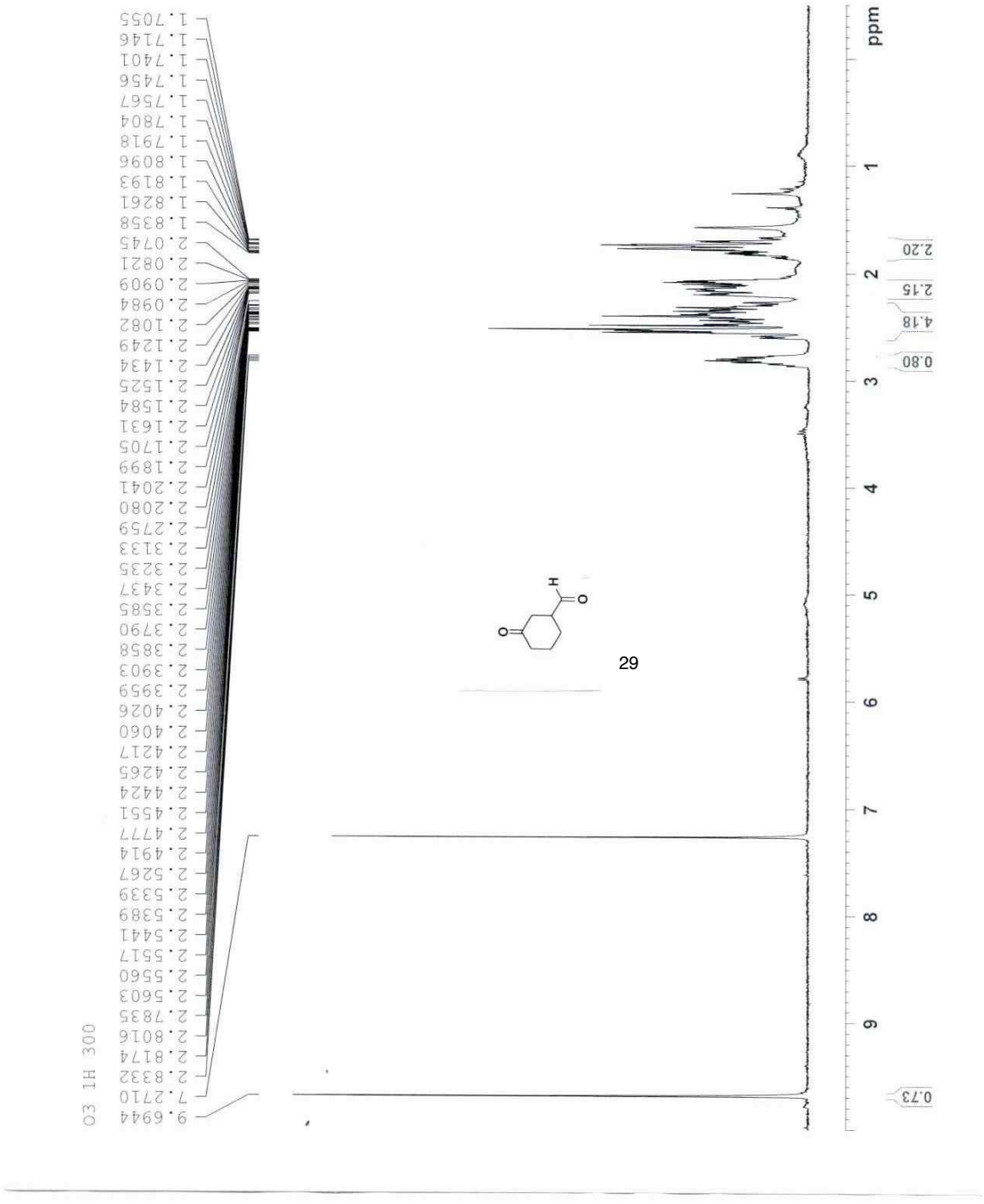
di ketone substrate CD3 301a
196.93
183.61
155.62
135.17
132.50
128.83
127.21
124.45
110.76
96.37
77.66
77.24
76.82
62.31
42.80
39.22
29.82
29.74
25.31
ppm
20
40
60
80
100
120
140
160
180
200
Ph
O
O
N
O
O
23


dl ketone Nu product 1H 301a
7.8697
7.8455
7.8406
7.5986
7.5744
7.5673
7.5538
7.5498
7.4908
7.4690
7.4652
7.4459
7.4411
7.4168
7.2704
6.7652
6.7171
4.7800
4.7548
4.7320
4.7068
4.4013
4.3747
4.3643
4.3592
4.3476
4.2542
4.2214
3.5747
3.5678
3.5496
3.5396
3.5216
3.5136
3.2631
3.2297
2.5843
2.5684
2.5505
2.5235
2.5079
2.4893
2.4714
2.1754
2.1689
2.1599
2.1399
2.1274
2.1109
2.0005
1.8663
1.8495
1.8199
1.7859
1.7521
ppm
1
2
3
4
5
6
7
8
9
2.42
1.88
2.20
1.02
1.99
0.94
2.00
0.96
0.83
2.91
1.59
Ph
O
O
O
O
N
24

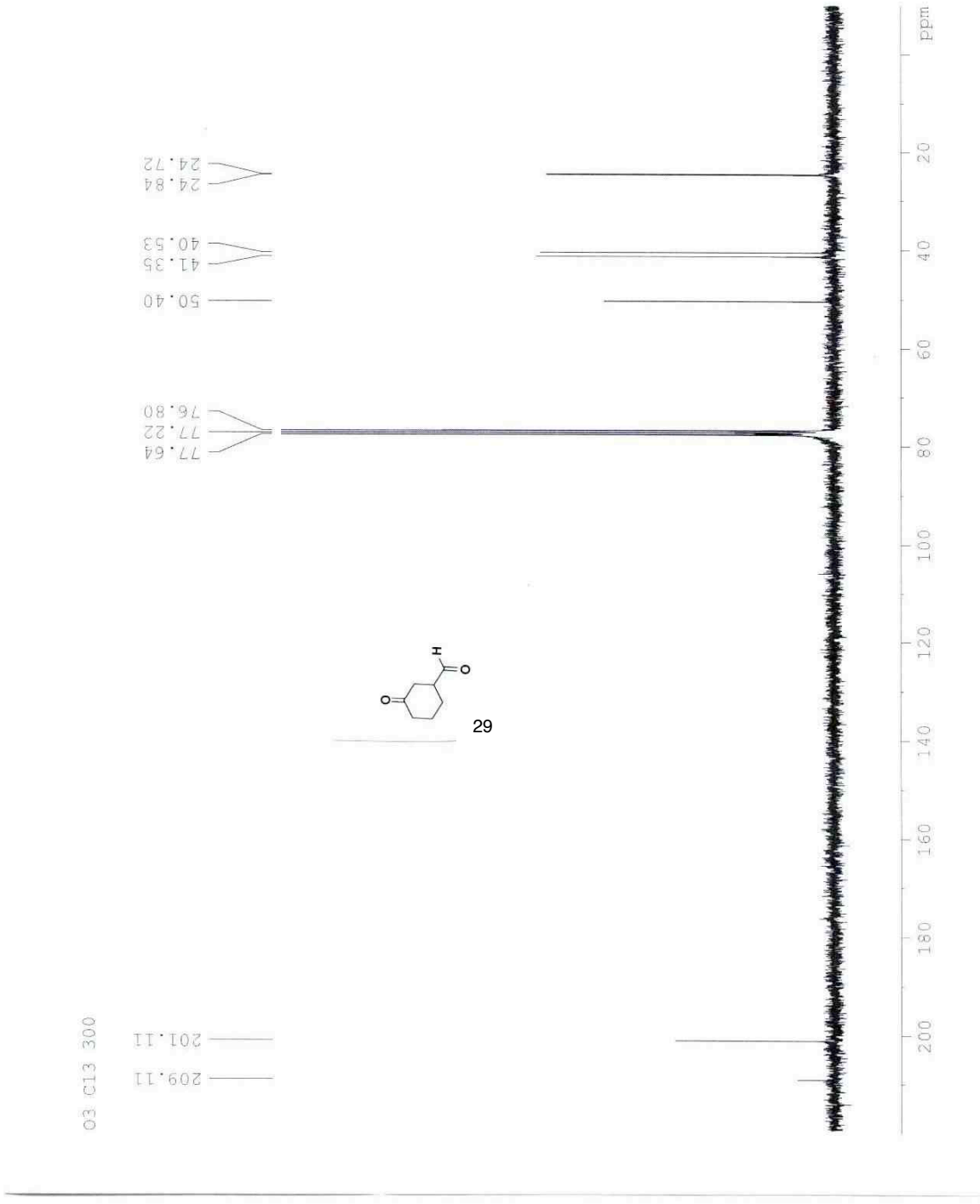

24.69
30.60
41.66
41.85
42.60
62.28
64.68
76.81
77.23
77.65
111.87
125.42
128.56
128.93
133.53
137.62
155.46
197.21
207.49
ppm
20
40
60
80
100
120
140
160
180
200
Ph
N
O
O
O
O
24

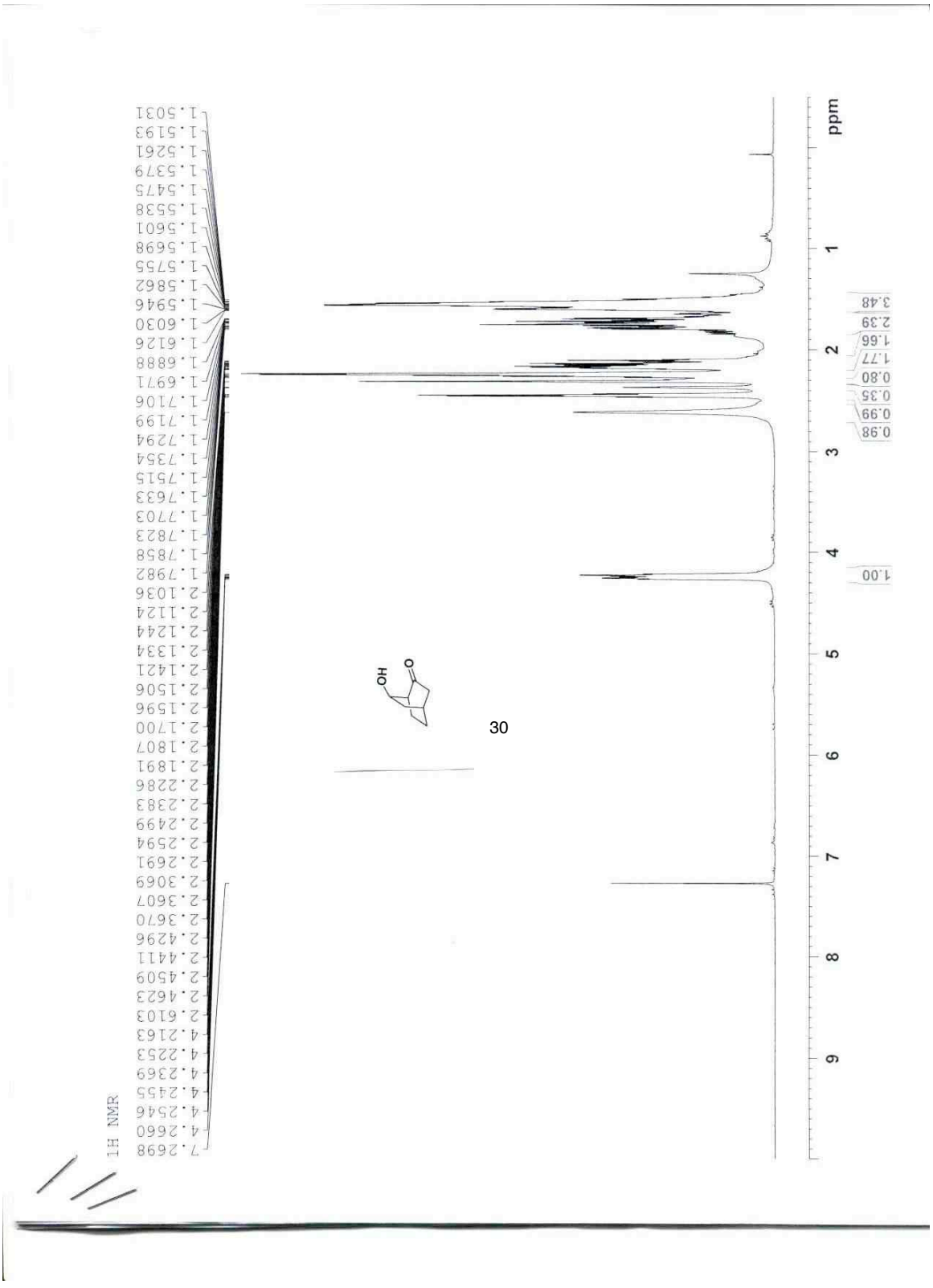

lei-2-74 1H 301a
7.2704
6.6818
6.6341
4.8353
4.8116
4.7878
4.7640
4.7404
4.4654
4.4398
4.4118
4.2423
4.2186
4.2094
4.1948
4.1862
4.1709
3.7159
3.6880
3.6621
3.4402
2.5855
2.5615
2.5375
2.1244
2.1011
2.0777
2.0539
1.6715
1.6479
1.6229
1.5966
1.5727
1.5524
1.4271
1.4021
1.3764
1.3512
1.3148
25
ppm
0.80
1.03
2.00
1.68
2.07
1.68
2.20
1.77
4.66
2.58
2.72

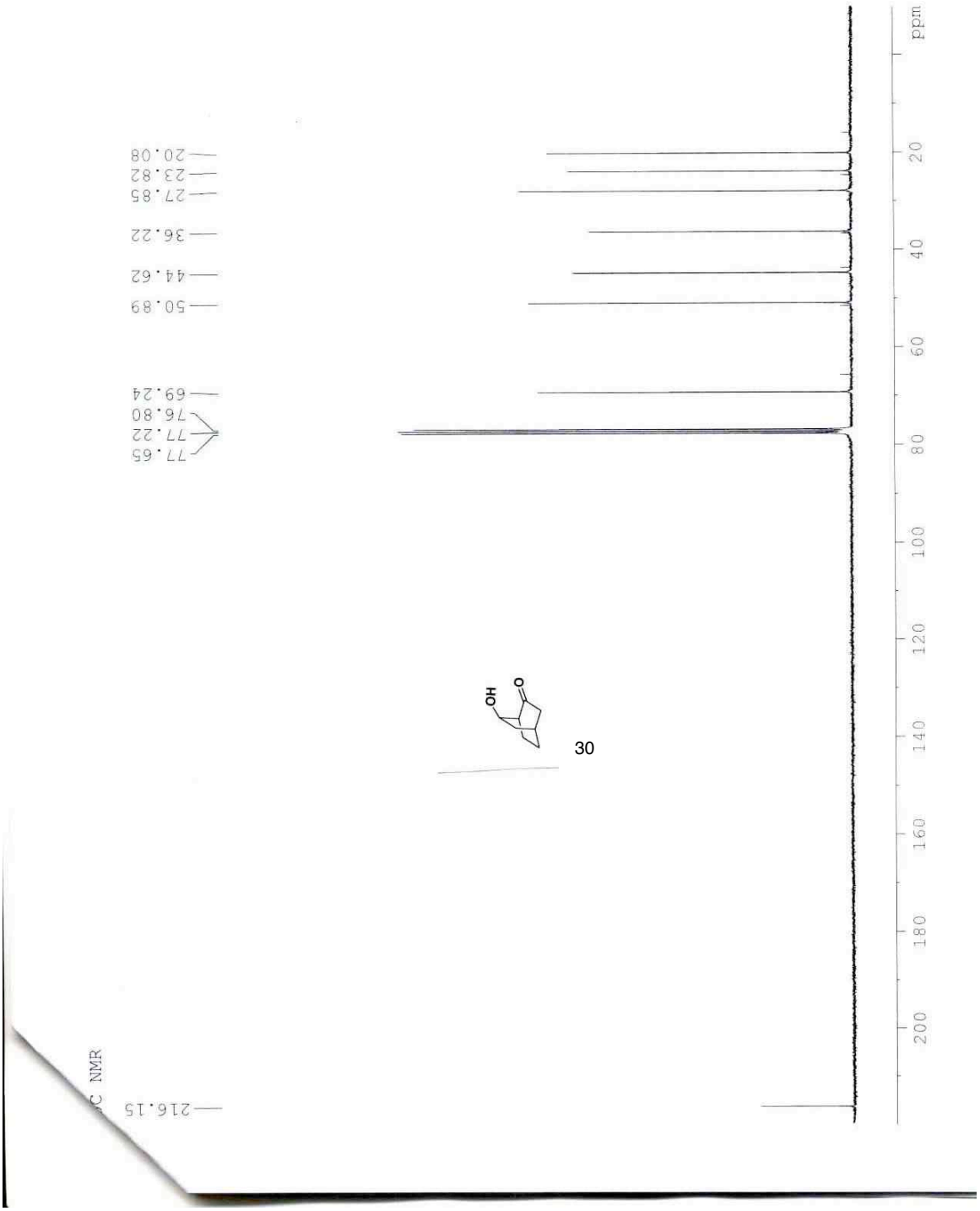

lei-2-74 C13 301a
202.90
167.51
155.62
124.48
110.69
77.65
77.23
76.81
62.31
61.61
49.56
42.92
42.82
29.71
29.56
22.90
14.34
ppm
20
40
60
80
100
120
140
160
180
200
OEt
25

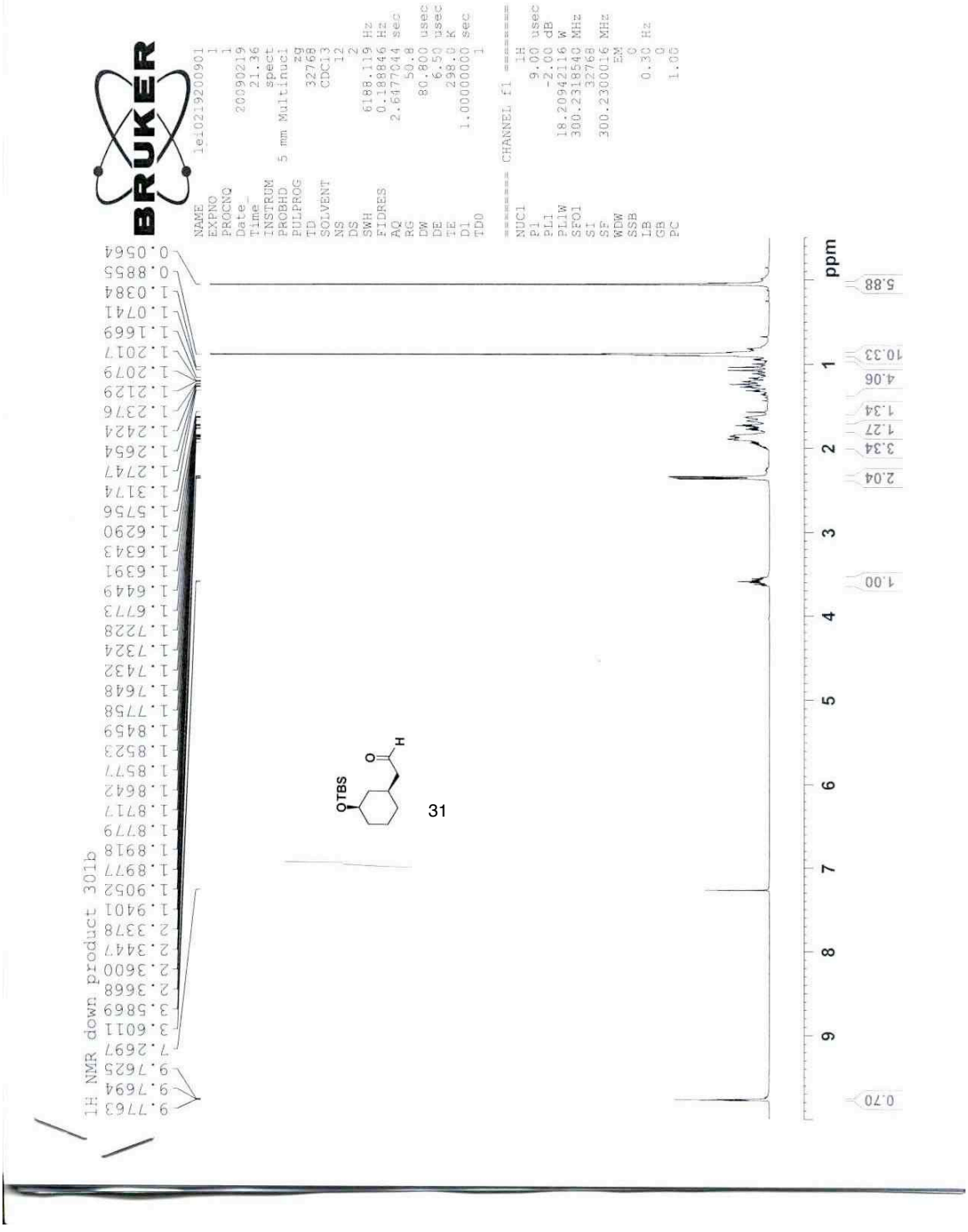

O3 1H 300
9.6944
7.2710
2.8332
2.8174
2.8016
2.7835
2.5603
2.5560
2.5517
2.5441
2.5389
2.5339
2.5267
2.4914
2.4777
2.4551
2.4424
2.4265
2.4217
2.4060
2.4026
2.3959
2.3903
2.3858
2.3790
2.3585
2.3437
2.3235
2.3133
2.2759
2.2080
2.2041
2.1899
2.1705
2.1631
2.1584
2.1525
2.1434
2.1249
2.1082
2.0984
2.0909
2.0821
2.0745
1.8358
1.8261
1.8193
1.8096
1.7918
1.7804
1.7567
1.7456
1.7401
1.7146
1.7055
ppm
0.73
2.20
2.15
4.18
0.80
O
O
H

29


O3 C13 300
201.11
209.11
24.72
24.84
40.53
41.35
50.40
76.80
77.22
77.64
ppm
20
40
60
80
100
120
140
160
180
200
O
O
H
29


1H NMR
ppm
30


C NMR
216.15
77.65
77.22
76.80
69.24
50.89
44.62
36.22
27.85
23.82
20.08
ppm
20
40
60
80
100
120
140
160
180
200
OH
O
30


1H NMR down product 301b
BRUKER
NAME 1e1021920090l
EXPNO 1
PROCNO 1
Date_ 20090219
Time 21.36
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 50.8
DW 80.800 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
PL1W 18.20942116 W
SFO1 300.2318540 MHz
SI 32768
SF 300.2300016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
O
H
31
ppm

NMR down product 301b
202.47
77.66
77.23
76.81
71.13
51.12
42.90
35.90
32.21
31.52
26.11
24.06
18.39
-4.35
-4.39
OTBS
O
H
31
ppm
200
180
160
140
120
100
80
60
40
20