Electronic Supplementary Information

Isoquinoline-Based Chiral Monodentate *N*-Heterocyclic Carbenes

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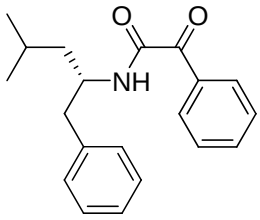
Contents

1. General remarks

All reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon. THF, CH_2Cl_2, Et_2O and toluene were purified under positive pressure of dry nitrogen by Meyer Solvent Dispensing System prior to use. All the chemicals used were purchased from Sigma-Aldrich Co., Acros Organics and Strem Chemicals Inc. and were used as received without further purification. NMR spectra were recorded using a Mercury-300 FT-NMR, operating at 300 MHz for ^{1}H NMR and at 75.4 MHz for ^{13}C NMR. All chemical shifts for ^{1}H and ^{13}C NMR spectroscopy were referenced to residual signals from $CDCl_3$ (^{1}H) 7.27 ppm and (^{13}C) 77.23 ppm. High resolution mass spectra were recorded on a GC/MS spectrometer or a TOF-LC/MS spectrometer. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. Enantiomer ratios were determined by chiral HPLC analysis (Shimadzu) using Chiral Technologies Chiralcel OJ-H, Chiralpak IA and IB columns and Regis Technologies Whelk-01 column. (*Z*)-cinnamic acid,[1] (S)-4-methyl-1-phenylpentan-2-amine (**4**)[2], [6(R),8(R)-Diisobutyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluorenium] chloride (**18**)[2] and [6(S),8(S)-Dicyclohexyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluorenium] chloride (**19**)[2] were prepared according to literature procedure.

2. Ligands synthesis

(S)-N-(4-methyl-1-phenylpentan-2-yl)-2-oxo-2-phenylacetamide (5)



To a flame-dried Schlenk flask was added 2.21 g (12.5 mmol) of (S)-4-methyl-1-phenylpentan-2-amine, 2.18 g (16.1 mmol) of HOBt, 3.09 g (16.2 mmol) of EDCI, 2.05 g (13.7 mmol) of 2-oxo-2-phenylacetic acid and 33 mL (0.377 M) of DMF. The reaction mixture was stirred at room temperature for 12 h. It was quenched by 40 mL of water. The reaction mixture was extracted with ethyl acetate (2 x 40 mL), washed with water (2 x 40 mL) and dried over anhydrous $MgSO_4$. All volatiles were removed in vacuo. Silicagel column chromatography with a 95:5

mixture of hexane and ethyl acetate as the eluent gave 2.91 g (9.41 mmol, 75.3%) of (S)-N-(4-methyl-1-phenylpentan-2-yl)-2-oxo-2-phenylacetamide.

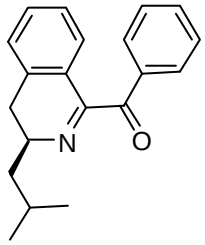
^{1}H NMR (299 MHz, CHLOROFORM-d) δ = 8.18 - 8.29 (m, 2 H), 7.56 - 7.67 (m, 1 H), 7.41 - 7.51 (m, 2 H), 7.16 - 7.36 (m, 5 H), 6.79 (d, *J*=9.3 Hz, 1 H), 4.30 - 4.46 (m, *J*=9.1, 6.0, 6.0, 3.0 Hz, 1 H), 2.75 - 2.97 (m, *J*=13.9, 6.2 Hz, 2 H), 1.67 (td, *J*=13.7, 6.7 Hz, 1 H), 1.43 (ddd, *J*=8.9, 5.4, 3.5 Hz, 2 H), 0.93 (dd, *J*=6.5, 1.4 Hz, 6 H)

^{13}C NMR (75 MHz, CHLOROFORM-d) δ = 161.2, 137.5, 134.3, 131.1, 129.5, 128.4, 126.5, 48.6, 43.3, 41.6, 25.0, 23.2, 21.9

HRMS Calcd. for $C_{20}H_{23}NO_2$ $[M+H]^+$: 310.1802, Found: 310.1826

$[\alpha]^{20}_D$ - 22.2° (*c* 1.33, $CHCl_3$)

(S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone (6)



To a flame-dried Schlenk flask was added 400 mg (1.29 mmol) of (S)-N-(4-methyl-1-phenylpentan-2-yl)-2-oxo-2-phenylacetamide, 472 mg (3.87 mmol) of DMAP and 50 mL (0.025 M) of toluene. The reaction mixture was cooled to 0 °C, and 1.09 mL (6.45 mmol) of Tf_2O was slowly added. After 10 min stirring at 0 °C, the reaction mixture was stirred at 90 °C for 8 h. It was quenched by 10 mL of a saturated Na_2CO_3 aqueous solution. The reaction mixture was extracted with DCM (3 x 40 mL) and dried over anhydrous $MgSO_4$. All volatiles were removed in vacuo. Silicagel column chromatography with a 95:5 mixture of hexane and ethyl acetate as the eluent gave 370 mg (1.27 mmol, 98.4%) of (S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone.

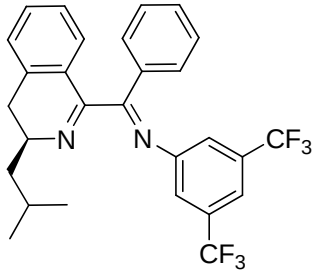
^{1}H NMR (300 MHz, CHLOROFORM-d) δ = 8.01 - 8.14 (m, 2 H), 7.54 - 7.69 (m, 1 H), 7.20 - 7.53 (m, 6 H), 3.84 - 3.98 (m, 1 H), 2.94 (dd, *J*=16.1, 5.6 Hz, 1 H), 2.68 (dd, *J*=16.0, 11.0 Hz, 1 H), 1.88 - 2.04 (m, *J*=13.5, 6.7, 6.7, 6.7, 6.7 Hz, 1 H), 1.70 - 1.84 (m, 1 H), 1.50 (ddd, *J*=13.6, 7.0, 6.9 Hz, 1 H), 0.98 (dd, *J*=6.6, 2.2 Hz, 6 H)

^{13}C NMR (75 MHz, CHLOROFORM-d) δ =194.08, 164.15, 137.16, 135.74, 134.05, 131.72, 130.69, 128.71, 128.33, 127.33, 126.95, 126.62, 55.34, 44.50, 31.43, 25.03, 23.08, 22.80

HRMS Calcd. for $C_{20}H_{21}NO$ $[M+H]^+$: 291.1696, Found: 291.1700

$[\alpha]^{20}_D$ - 13.9° (*c* 1.21, $CHCl_3$)

(S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-3,5-bis(trifluoromethyl)aniline (7a)



37.0 mg (0.0736 mmol, 79.5%) of (S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-3,5-bis(trifluoromethyl)aniline was obtained from 27.0 mg (0.0926 mmol) of (S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone, 25.6 µL (1.85 mmol) of Et_3N, 71.3 µL (0.460 mmol) of 3,5-bis(trifluoromethyl)aniline and 110 µL of $TiCl_4$ (1 M in toluene).

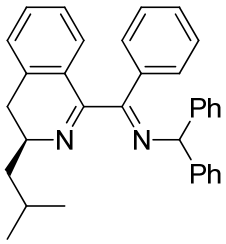
^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.95 (d, *J* = 7.4 Hz, 2 H), 7.55 - 7.34 (m, 4 H), 7.34 - 7.20 (m, 3 H), 7.20 - 7.01 (m, 3 H), 3.78 - 3.55 (m, 1 H), 2.63 (dd, *J* = 5.5, 16.0 Hz, 1 H), 1.88 - 1.65 (m, 1 H), 1.57 (dt, *J* = 6.7, 13.3 Hz, 1 H), 1.40 - 1.15 (m, 1 H), 0.85 (d, *J* = 6.5 Hz, 3 H), 0.88 (d, *J* = 6.8 Hz, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 163.0, 151.9, 136.3, 136.1, 132.0, 131.7, 131.1, 128.7, 128.0, 127.1, 125.7, 124.9, 121.3, 120.7, 116.9, 54.9, 44.2, 30.7, 24.5, 22.6, 22.4

HRMS Calcd. for $C_{28}H_{24}F_6N_2$ $[M+H]^+$: 503.1916, Found: 503.1919

$[\alpha]^{32}_D$ - 43.4° (*c* 0.78, $CHCl_3$)

(S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-1,1-diphenylmethanamine (7b)



46.0 mg (0.100 mmol, 72.9%) of (S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-1,1-diphenylmethanamine was obtained from 40.0 mg (0.137 mmol) of (S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone, 37.9 µL (0.274 mmol) of Et_3N, 118 µL (0.685 mmol) of diphenylmethanamine and 165 µL of $TiCl_4$ (1 M in toluene).

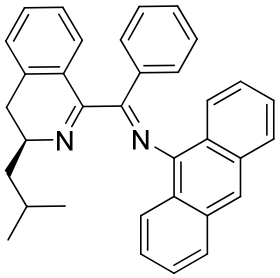
^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.96 (d, *J* = 10.0 Hz, 2 H), 7.52 - 7.12 (m, 15 H), 6.94 (br. s., 1 H), 6.89 - 6.55 (m, 1 H), 5.91 - 5.73 (m, 1 H), 4.09 - 3.85 (m, 1 H), 3.13 - 2.89 (m, 1 H), 2.83 - 2.65 (m, 1 H), 2.12 - 1.66 (m, 2 H), 1.58 - 1.41 (m, 1 H), 0.97 (d, *J* = 6.4 Hz, 6 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 164.5, 144.2, 137.9, 137.7, 136.6, 136.0, 131.6, 130.6, 128.4, 128.3, 127.5, 127.4, 126.9, 70.0, 54.9, 44.8, 31.9, 31.6, 24.8, 23.0

HRMS Calcd. for $C_{33}H_{32}N_2$ $[M+H]^+$: 457.2638, Found: 457.2638

$[\alpha]^{32}_D$ - 88.8° (*c* 1.08, $CHCl_3$)

(S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)anthracen-9-amine (7c)



36.0 mg (0.0773 mmol, 75.0%) of (S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)anthracen-9-amine was obtained from 30.0 mg (0.103 mmol) of (S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone, 100 µL (0.723 mmol) of Et_3N, 100 mg (0.435 mmol) of anthracen-9-aminium chloride and 125 µL of $TiCl_4$ (1 M in toluene).

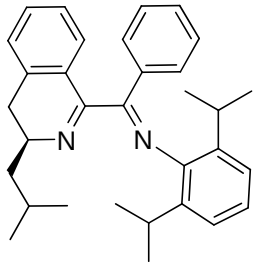
^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 8.27 (d, *J* = 6.7 Hz, 2 H), 8.14 - 7.86 (m, 3 H), 7.86 - 7.65 (m, 2 H), 7.65 - 7.45 (m, 3 H), 7.45 - 7.12 (m, 4 H), 7.03 (d, *J* = 7.6 Hz, 1 H), 6.95 - 6.76 (m, 1 H), 6.76 - 6.52 (m, 2 H), 3.29 (s, 1 H), 1.94 - 1.72 (m, *J* = 7.3 Hz, 1 H), 1.67 - 1.47 (m, 1 H), 1.19 (dt, *J* = 7.1, 13.7 Hz, 1 H), 0.99 - 0.82 (m, 2 H), 0.76 (t, *J* = 7.0 Hz, 6 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 168.0, 163.7, 143.7, 137.2, 131.8, 131.6, 131.4, 130.2, 129.2, 128.9, 127.8, 127.3, 126.9, 126.1, 125.4, 125.3, 125.2, 123.9, 121.7, 54.7, 30.8, 29.9, 24.5, 22.8, 22.7

HRMS Calcd. for $C_{34}H_{30}N_2$ $[M+H]^+$: 467.2482, Found: 467.2487

$[\alpha]^{28}_D$ – 252.9° (*c* 0.5, $CHCl_3$)

(S)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-2,6-diisopropylaniline (7d)



217 mg (0.482 mmol, 70.6%) of (S)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-2,6-diisopropylaniline was obtained from 200 mg (0.686 mmol) of (S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone, 190 µL (1.37 mmol) of Et_3N, 647 µL (3.43 mmol) of 2,6-diisopropylaniline and 820 µL of $TiCl_4$ (1 M in toluene).

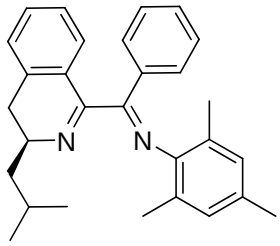
^{1}H NMR (300 MHz, CHLOROFORM-d) δ = 8.07 (d, *J*=6.5 Hz, 2 H), 7.42 - 7.58 (m, 3 H), 7.19 - 7.26 (m, 1 H), 6.80 - 7.15 (m, 6 H), 3.54 (br. s., 1 H), 3.00 - 3.15 (m, 1 H), 2.78 (br. s., 1 H), 2.38 (dd, *J*=15.5, 4.7 Hz, 1 H), 1.84 (dt, *J*=13.1, 6.8 Hz, 2 H), 1.55 (dt, *J*=13.7, 7.1 Hz, 1 H), 0.80 - 1.30 (m, 19 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 163.5, 163.2, 146.2, 137.4, 137.1, 136.7, 135.6, 131.0, 130.4, 128.6, 128.3, 127.5, 126.6, 125.7, 123.1, 121.7, 54.7, 44.2, 31.2, 28.5, 28.4, 24.5, 24.0, 23.0, 22.6, 20.9, 20.8

HRMS Calcd. for $C_{32}H_{38}N_2$ $[M+H]^+$: 451.3108, Found: 451.3106

$[\alpha]^{20}_D$ - 8.7° (*c* 0.96, $CHCl_3$)

(S)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-2,4,6-trimethylaniline (7e)



To a flame-dried Schlenk flask was added 204 mg (0.700 mmol) of (S)-(3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methanone, 194 µL (1.40 mmol) of Et_3N, 492 µL (3.50 mmol) of mesitylamine and 8 mL (0.1 M) of toluene. The reaction mixture was cooled to 0 °C, and 840 µL of $TiCl_4$ solution (1 M in toluene) was slowly added. After 10 min stirring at 0 °C, the reaction mixture was stirred at room temperature for 12 h. It was quenched by 4 mL of a saturated NH_4Cl aqueous solution. The reaction mixture was extracted with DCM (3 x 20 mL) and dried over anhydrous $MgSO_4$. All volatiles were removed in vacuo. Silicagel column chromatography with a 99:1 mixture of hexane and ethyl acetate as the eluent gave 280 mg (0.685 mmol, 97.8%) of (S)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-2,4,6-trimethylaniline.

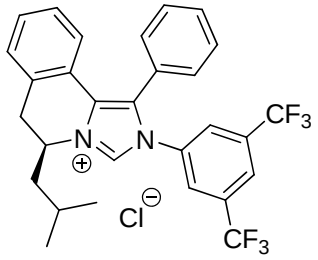
^{1}H NMR (300 MHz, CHLOROFORM-d) δ = 7.95 - 8.14 (m, 2 H), 7.40 - 7.58 (m, 3 H), 7.19 - 7.27 (m, 1 H), 7.01 - 7.14 (m, 3 H), 6.67 (br. s., 1 H), 6.55 (br. s., 1 H), 3.56 (dd, *J*=11.9, 5.4 Hz, 1 H), 2.46 (dd, *J*=15.5, 5.0 Hz, 1 H), 2.17 (s, 3 H), 2.10 (br. s., 3 H), 1.75 - 2.00 (m, 4 H), 1.52 - 1.63 (m, 1 H), 1.23 - 1.34 (m, 2 H), 0.91 (dd, *J*=10.7, 6.6 Hz, 6 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 165.6, 163.2, 145.7, 137.3, 136.9, 131.8, 131.0, 130.6, 128.6, 128.3, 127.9, 127.6, 127.4, 126.2, 126.0, 54.7, 44.4, 31.3, 30.3, 29.7, 24.5, 22.8, 22.6, 20.6

HRMS Calcd. for $C_{29}H_{32}N_2$ $[M+H]^+$: 409.2638, Found: 409.2640

$[\alpha]^{20}_D$ - 28.2° (*c* 0.97, $CHCl_3$)

(S)-2-(3,5-bis(trifluoromethyl)phenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride (8a)



21.0 mg (0.0381 mmol, 70.9%) of (S)-2-(3,5-bis(trifluoromethyl)phenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride was obtained from 27.0 mg (0.0537 mmol) of (S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-3,5-bis(trifluoromethyl)aniline and 29.8 µL (0.322 mmol) of chloromethyl ethyl ether .

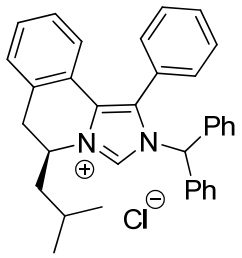
^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 10.88 (br. s., 1 H), 8.32 - 6.48 (m, 12 H), 5.33 (br. s., 1 H), 3.56 (d, *J* = 16.7 Hz, 1 H), 3.06 (d, *J* = 15.6 Hz, 1 H), 2.03 - 1.61 (m, 3 H), 1.20 - 0.76 (m, 6 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 136.7, 134.7, 133.5, 133.1, 131.8, 131.8, 131.3, 131.0, 130.6, 129.9, 129.7, 127.8, 126.9, 124.7, 124.5, 124.0, 123.9, 114.3, 54.4, 41.6, 32.5, 24.9, 22.9, 21.7

HRMS Calcd. for $C_{29}H_{25}F_6N_2$ $[M]^+$: 515.1916, Found: 515.1932

$[\alpha]^{32}_D$ -11.8° (*c* 0.65, $CHCl_3$)

(S)-2-benzhydryl-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride (8b)



30.0 mg (0.0594 mmol, 90.3%) of (S)-2-benzhydryl-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride was obtained from 30.0 mg (0.0658 mmol) of (S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-1,1-diphenylmethanamine and 36.5 µL (0.394 mmol) of chloromethyl ethyl ether .

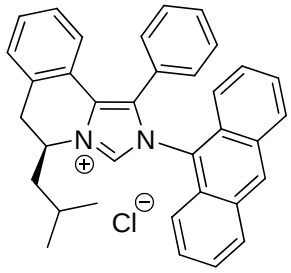
^{1}H NMR (500MHz ,DICHLOROMETHANE-d_2) δ = 10.09 (s, 1 H), 7.64 (d, *J* = 7.0 Hz, 1 H), 7.57 - 7.39 (m, 9 H), 7.39 - 7.19 (m, 7 H), 7.19 - 6.99 (m, 1 H), 6.91 (d, *J* = 7.8 Hz, 1 H), 6.44 (s, 1 H), 5.61 (br. s., 1 H), 3.65 - 3.56 (m, 1 H), 3.08 (d, *J* = 15.9 Hz, 1 H), 1.70 - 1.46 (m, 3 H), 0.98 (t, *J* = 6.2 Hz, 6 H)

^{13}C NMR (126MHz ,DICHLOROMETHANE-d_2) δ = 136.4, 136.2, 135.5, 132.0, 131.3, 131.3, 130.2, 129.9, 129.6, 129.6, 129.5, 129.5, 129.3, 128.8, 128.7, 127.6, 126.7, 125.8, 124.5, 123.1, 66.0, 53.9, 41.9, 32.6, 25.2, 22.9, 21.9

HRMS Calcd. for $C_{34}H_{33}N_2$ $[M]^+$: 469.2638, Found: 469.2641

$[\alpha]^{29}_D$ + 36.6° (*c* 0.73, $CHCl_3$)

(S)-2-(anthracen-9-yl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride (8c)



20.0 mg (0.0388 mmol, 90.4%) of (S)-2-(anthracen-9-yl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride was obtained from 20.0 mg (0.0429 mmol) of (S,E)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)anthracen-9-amine and 24.5 µL (0.264 mmol) of chloromethyl ethyl ether .

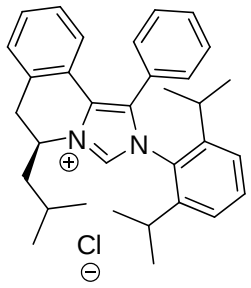
^{1}H NMR (500MHz ,DMSO-d_6) δ = 10.10 (s, 1 H), 8.97 (s, 1 H), 8.31 - 8.23 (m, 2 H), 8.03 - 7.89 (m, 2 H), 7.81 - 7.58 (m, 5 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.36 - 7.22 (m, 4 H), 7.22 - 7.14 (m, 2 H), 7.04 (d, *J* = 7.7 Hz, 1 H), 5.03 - 4.94 (m, *J* = 6.0, 6.0 Hz, 1 H), 3.73 (dd, *J* = 4.9, 16.0 Hz, 1 H), 3.33 - 3.27 (m, 1 H), 2.03 - 1.95 (m, *J* = 6.5, 13.7 Hz, 1 H), 1.95 - 1.85 (m, 1 H), 1.85 - 1.74 (m, 1 H), 1.05 (t, *J* = 6.4 Hz, 6 H)

^{13}C NMR (126MHz ,DMSO-d_6) δ = 137.3, 135.3, 133.8, 133.4, 131.9, 131.6, 131.4, 131.1, 130.9, 130.7, 130.6, 130.3, 129.8, 129.6, 129.4, 129.4, 129.1, 129.1, 129.0, 128.8, 128.1, 127.6, 127.5, 127.1, 126.1, 124.5, 123.8, 122.7, 122.5, 54.7, 41.6, 33.0, 24.9, 23.6, 22.7

HRMS Calcd. for $C_{35}H_{31}N_2$ $[M]^+$: 479.2482, Found: 479.2488

$[\alpha]^{28}_{D}$ +19.2° (*c* 0.7, $CHCl_3$)

(S)-2-(2,6-diisopropylphenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride (8d)



60.0 mg (0.120 mmol, 75.5%) of (S)-2-(2,6-diisopropylphenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride was obtained from 72.0 mg (0.159 mmol) of ((S)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-2,6-diisopropylaniline and 83.5 µL (0.954 mmol) of chloromethyl ethyl ether .

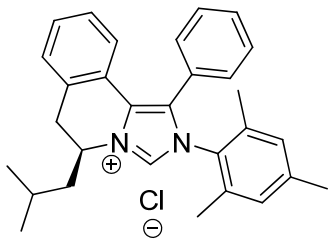
^{1}H NMR (500MHz ,DICHLOROMETHANE-d_2) δ = 11.08 (s, 1 H), 7.54 - 7.33 (m, 7 H), 7.24 (d, *J* = 7.3 Hz, 2 H), 7.21 - 7.07 (m, 3 H), 5.81 (q, *J* = 6.5 Hz, 1 H), 3.76 (dd, *J* = 5.2, 16.1 Hz, 1 H), 3.14 (d, *J* = 16.1 Hz, 1 H), 2.55 (spt, *J* = 6.7 Hz, 1 H), 2.48 - 2.26 (m, *J* = 6.7, 6.7, 13.6 Hz, 1 H), 1.74 - 1.51 (m, 3 H), 1.41 (d, *J* = 6.9 Hz, 3 H), 1.38 - 1.27 (m, 4 H), 1.22 (d, *J* = 6.7 Hz, 3 H), 1.14 (d, *J* = 6.5 Hz, 3 H), 1.00 (d, *J* = 6.5 Hz, 3 H), 0.79 (d, *J* = 6.7 Hz, 3 H)

^{13}C NMR (126MHz ,DICHLOROMETHANE-d_2) δ = 146.3, 146.0, 138.0, 132.3, 131.9, 130.9, 130.5, 130.5, 130.2, 130.1, 129.5, 128.7, 127.6, 126.1, 125.6, 124.9, 124.8, 124.5, 123.0, 53.6, 42.2, 33.4, 29.5, 29.2, 26.1, 25.6, 25.1, 22.6, 22.5, 22.5, 22.2

HRMS Calcd. for $C_{33}H_{39}ClN_2$ $[M]^+$: 463.3108, Found: 463.3108

$[\alpha]^{29}_{D}$ – 38.1° (*c* 0.90, $CHCl_3$)

(S)-5-isobutyl-2-mesityl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride (8e)



To a flame-dried Schlenk flask was added 225 mg (0.551 mmol) of (S)-N-((3-isobutyl-3,4-dihydroisoquinolin-1-yl)(phenyl)methylene)-2,4,6-trimethylaniline, 256 µL (2.75 mmol) of chloromethyl ethyl ether and 28 mL (0.02M) of THF. After 48 h, all volatiles were removed in vacuo. Silicagel column chromatography with a 95:5 mixture of DCM and methanol as the eluent gave 220 mg (0.481 mmol, 87.3%) of (S)-5-isobutyl-2-mesityl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride.

^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 10.34 (s, 1 H), 7.55 - 7.23 (m, 5 H), 7.18 (d, *J* = 7.4 Hz, 2 H), 7.13 - 7.00 (m, 2 H), 6.92 (s, 1 H), 6.76 (s, 1 H), 5.74 - 5.47 (m, 1 H), 3.64 (dd, *J* = 4.4, 16.3 Hz, 1 H), 3.06 (d, *J* = 15.9 Hz, 1 H), 2.18 (s, 3 H), 2.23 (s, 3 H), 1.89 (s, 3 H), 1.78 - 1.43 (m, 3 H), 0.99 (dd, *J* = 6.2, 9.1 Hz, 6 H)

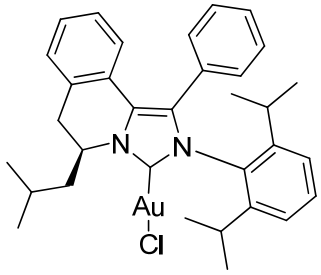
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 141.2, 137.2, 135.5, 134.7, 132.0, 130.9, 130.5, 130.1, 130.1, 130.0, 129.7, 129.6, 129.5, 129.3, 127.7, 126.1, 125.6, 124.7, 122.9, 53.8, 42.1, 33.0, 25.3, 23.1, 22.3, 21.3, 18.2, 18.2

HRMS Calcd. for $C_{30}H_{33}N_2$ $[M]^+$: 421.2638, Found: 421.2646

$[\alpha]^{29}_D$ - 23° (*c* 1.06, $CHCl_3$)

3. Gold complexes synthesis

(S)-chloro(2-(2,6-diisopropylphenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium-3-yl)aurate(I) (9)



To a flame-dried Schlenk flask was added 33.0 mg (0.0661 mmol) of (S)-2-(2,6-diisopropylphenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium chloride, 9.20 mg (0.0396 mmol) of Ag_2O and 1.3 mL (0.05M) of DCM. After stirring for 12 h, the reaction mixture was filtered through a pad of celite. The solvent of the filtrate was removed

under reduced pressure. To another flame-dried Schlenk flask was added the filtered silver complex, 22.0 mg (0.0747 mmol) of AuCl•Me_2S and 1.3 mL (0.05M) of DCM. The reaction mixture was stirred for 12 h at room temperature. The reaction solution was filtered through a pad of celite and evaporated to dryness. The residue was dissolved in ether and the solid was discarded. Then the ethereal solution was concentrated and additional impurities were washed away with hexane. Additionally the residue was purified by silicagel column chromatography with a 80:20 mixture of hexane and ethyl acetate as the eluent to yield 40.0 mg (0.0574 mmol, 86.8 %) of (S)-chloro(2-(2,6-diisopropylphenyl)-5-isobutyl-1-phenyl-5,6-dihydro-2H-imidazo[5,1-a]isoquinolin-4-ium-3-yl)aurate(I).

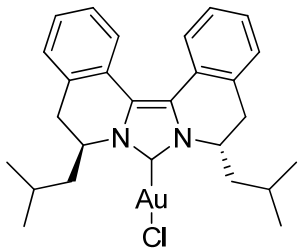
^{1}H NMR (500MHz ,DICHLOROMETHANE-d_2) δ = 7.51 - 7.44 (m, 1 H), 7.43 - 7.28 (m, 6 H), 7.23 (d, *J* = 7.1 Hz, 2 H), 7.16 - 7.01 (m, 3 H), 5.21 (tdd, *J* = 1.5, 5.7, 7.4 Hz, 1 H), 3.60 (dd, *J* = 5.6, 15.7 Hz, 1 H), 3.12 (dd, *J* = 1.5, 15.8 Hz, 1 H), 2.72 (spt, *J* = 6.8 Hz, 1 H), 2.50 - 2.32 (m, *J* = 6.8, 6.8, 6.8, 6.8 Hz, 1 H), 1.89 (dquin, *J* = 6.7, 13.4 Hz, 1 H), 1.66 - 1.59 (m, 1 H), 1.58 - 1.55 (m, 1 H), 1.53 (d, *J* = 6.9 Hz, 3 H), 1.42 - 1.36 (m, 3 H), 1.33 - 1.28 (m, 3 H), 1.10 (d, *J* = 6.6 Hz, 3 H), 1.04 (d, *J* = 6.6 Hz, 3 H), 0.79 (d, *J* = 6.9 Hz, 3 H)

^{13}C NMR (126MHz ,DICHLOROMETHANE-d_2) δ = 170.3, 146.7, 146.3, 133.0, 132.2, 130.7, 130.6, 130.4, 129.9, 129.8, 129.0, 129.0, 128.1, 127.2, 125.3, 125.0, 124.4, 124.3, 124.3, 54.8, 43.1, 33.8, 29.0, 28.7, 26.2, 25.7, 24.9, 23.3, 23.2, 22.5, 22.3

HRMS Calcd. for $C_{33}H_{39}ClN_2Au$ $[M+NH_4]^+$: 712.2727, Found: 712.2739

$[\alpha]^{29}_D$ - 12.8° (*c* 0.84, $CHCl_3$)

[6(*S*),8(*S*)-Diisobutyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluoren-5-ylidene]-chloroaurate(I) (10)



To a flame-dried Schlenk flask was added 15.0 mg (0.0356 mmol) of [6(S),8(S)-Diisobutyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluorenium] chloride, 4.80 mg (0.0207 mmol) of Ag_2O and 700 μL (0.05M) of DCM. After stirring for 12 h, the reaction mixture was filtered through a pad of celite. The solvent of the filtrate was removed under reduced pressure. To another flame-dried Schlenk flask was added the filtered silver complex, 12.0 mg (0.0407 mmol)

of AuCl•Me_2S and 1.3 mL (0.05M) of DCM. The reaction mixture was stirred for 12 h at room temperature. The reaction solution was filtered through a pad of celite and evaporated to dryness. The residue was purified by silicagel column chromatography with a 70:30 mixture of hexane and ethyl acetate as the eluent to give 17.0 mg (0.0275 mmol, 77.2%) of [6(S),8(S)-Diisobutyl-5,6,8,9-tetrahydro-6a,7a-diazadibenzo[c,g]fluoren-5-ylidene]- chloroaurate(I).

^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.94 (d, *J* = 7.5 Hz, 2 H), 7.42 - 7.30 (m, 6 H), 4.96 (dtd, *J* = 1.6, 5.6, 9.1 Hz, 2 H), 3.36 (dd, *J* = 5.2, 15.4 Hz, 2 H), 3.00 (dd, *J* = 1.5, 15.4 Hz, 2 H), 1.86 - 1.69 (m, 2 H), 1.49 (ddd, *J* = 5.8, 8.4, 13.8 Hz, 2 H), 1.35 - 1.29 (m, 2 H), 1.01 (d, *J* = 6.6 Hz, 6 H), 0.96 (d, *J* = 6.6 Hz, 6 H)

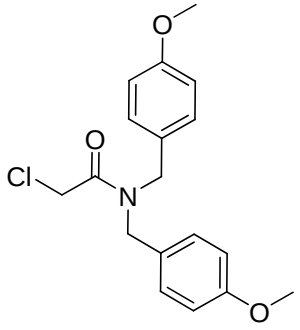
^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 166.6, 132.6, 129.9, 129.4, 127.5, 125.8, 124.2, 124.0, 54.8, 42.1, 33.6, 25.2, 23.7, 22.1

HRMS Calcd. for $C_{27}H_{33}ClN_2Au$ $[M]^+$: 616.1920, Found: 616.1959

$[\alpha]^{29}_D$ - 266.5° (*c* 0.32, $CHCl_3$)

4. Substrates synthesis

2-chloro-N,N-bis(4-methoxybenzyl)acetamide



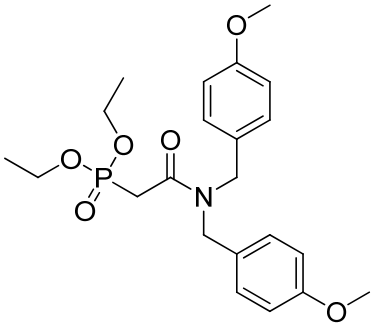
To a flame-dried Schlenk flask was added 618 µL (7.77 mmol) of 2-chloroacetyl chloride and 16 mL (0.5 M) of THF. The reaction mixture was cooled to 0 ºC and 2.00 g (7.77 mmol) of bis(4-methoxybenzyl)amine was added dropwise followed by 1.08 mL (7.77 mmol) of Et_3N. The reaction mixture was stirred at room temperature for 12 h. It was diluted with 20 mL of Et_2O and washed with 1N HCl (2 x 15 mL) followed by a saturated $NaHCO_3$ aqueous solution (2 x 15 mL). It was dried over anhydrous $MgSO_4$. All volatiles were removed in vacuo to yield 2.55 g (7.62 mmol, 98.1%) of 2-chloro-N,N-bis(4-methoxybenzyl)acetamide.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.22 - 6.97 (m, 4 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 4.50 (s, 2 H), 4.40 (s, 2 H), 4.12 (s, 2 H), 3.78 (s, 3 H), 3.80 (s, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.2, 159.6, 129.9, 128.8, 128.1, 127.8, 114.7, 114.3, 55.6, 55.5, 49.8, 48.0, 41.7

HRMS Calcd. for $C_{18}H_{20}ClNO_3$ $[M+H]^+$: 334.1204, Found: 334.1208

Diethyl 2-(bis(4-methoxybenzyl)amino)-2-oxoethylphosphonate



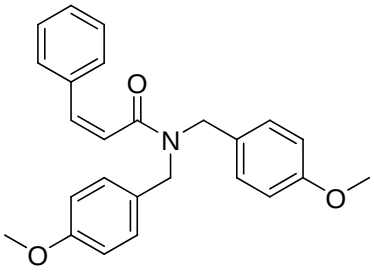
To a flame-dried Schlenk flask was added 970 mg (2.90 mmol) of 2-chloro-N,N-bis(4-methoxybenzyl)acetamide and 1.26 mL (7.25 mmol) of triethyl phosphite. The reaction mixture was stirred at 100 ºC for 60 h. After cooling at room temperature, it was washed with hexane (3 x 5 mL) and concentrated in vacuo to yield 1.13 g (2.59 mmol, 89.3%) of diethyl 2-(bis(4-methoxybenzyl)amino)-2-oxoethylphosphonate.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.19 - 7.11 (m, 2 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 6.93 - 6.73 (m, 4 H), 4.52 (d, *J* = 5.6 Hz, 4 H), 4.24 - 4.06 (m, 4 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 3.13 (s, 1 H), 3.06 (s, 1 H), 1.39 - 1.22 (m, 6 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 165.7, 159.4, 159.2, 129.6, 129.2, 128.4, 128.3, 127.9, 114.6, 114.2, 62.9, 62.8, 55.6, 50.4, 48.0, 34.8, 33.1, 16.6, 16.5

HRMS Calcd. for $C_{22}H_{30}NO_6P$ $[2M+H]^+$: 871.3616, Found: 871.3720

(Z)-N,N-bis(4-methoxybenzyl)-3-phenylacrylamide (Z-17a)



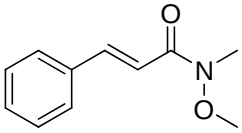
To a flame-dried Schlenk flask was added 150 mg (1.012 mmol) of (*Z*)-cinnamic acid, 137 mg (1.012 mmol) of HOBt and 7 mL (0.14 M) of DCM. The reaction mixture was stirred 30 minutes at room temperature. 12.0 mg (0.100 mmol) of DMAP and 260 mg (1.012 mmol) of bis(4-methoxybenzyl)amine were then added. The reaction mixture was cooled to 0 ºC and a solution of 209 mg (1.012 mmol) of DCC in 5 mL (0.2 M) of DCM was added dropwise. The reaction was stirred 1 h at 0 ºC and 12 h at room temperature. The reaction mixture was concentrated and 15 mL of ethyl acetate was added and the white solid was filtered off. The ethyl acetate solution was concentrated. Silicagel column chromatography with a 75:25 mixture of hexane and ethyl acetate as the eluent gave 245 mg (0.633 mmol, 62.5%) of (Z)-N,N-bis(4-methoxybenzyl)-3-phenylacrylamide.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.42 (d, *J* = 7.3 Hz, 2 H), 7.35 - 7.13 (m, 5 H), 7.01 (d, *J* = 8.2 Hz, 2 H), 6.96 - 6.80 (m, 4 H), 6.70 (d, *J* = 12.6 Hz, 1 H), 6.23 (d, *J* = 12.6 Hz, 1 H), 4.55 (s, 2 H), 4.35 (s, 2 H), 3.83 (s, 3 H), 3.86 (s, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 169.2, 159.4, 159.3, 135.6, 133.9, 130.6, 128.9, 128.8, 128.8, 128.7, 128.7, 128.4, 123.6, 114.4, 114.1, 55.5, 50.0, 45.9

HRMS Calcd. for $C_{25}H_{25}NO_3$ $[M+H]^+$: 388.1907, Found: 388.1905

N-methoxy-N-methylcinnamamide (14a)



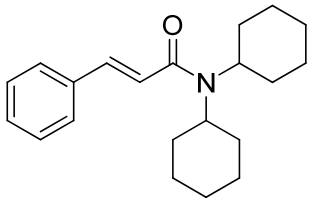
940 mg (4.92 mmol, 95.9%) of N-methoxy-N-methylcinnamamide was obtained from 1.25 g (10.3 mmol) of DMAP, 1.37 g (6.66 mmol) of DCC, 500 mg (5.13 mmol) of N,O-dimethylhydroxylammonium chloride and 986 mg (6.66 mmol) of *trans*-cinnamic acid.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.74 (d, *J* = 15.8 Hz, 1 H), 7.62 - 7.52 (m, 2 H), 7.45 - 7.29 (m, 3 H), 7.04 (d, *J* = 15.8 Hz, 1 H), 3.76 (s, 3 H), 3.30 (s, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.2, 143.6, 135.4, 130.0, 129.0, 128.2, 116.0, 62.1, 32.7

HRMS Calcd. for $C_{11}H_{13}NO_2$ $[M+H]^+$: 192.1019, Found: 192.1024

N,N-dicyclohexylcinnamamide (15a)



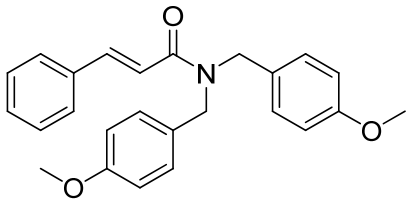
400 mg (1.28 mmol, 37.9%) of N,N-dicyclohexylcinnamamide was obtained from 42 mg (0.344 mmol) of DMAP, 765 mg (3.71 mmol) of DCC, 455 mg (3.37 mmol) of HOBt, 670 µL (3.37 mmol) of dicyclohexylamine and 500 mg (3.37 mmol) of *trans*-cinnamic acid.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.80 - 7.43 (m, 3 H), 7.43 - 7.15 (m, 3 H), 6.84 (d, *J* = 15.2 Hz, 1 H), 3.56 (br. s., 2 H), 2.26 (br. s., 2 H), 1.80 (br. s., 6 H), 1.64 (br. s., 6 H), 1.48 - 1.21 (m, 4 H), 1.18 (br. s., 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 166.5, 140.9, 136.0, 129.4, 128.9, 127.8, 121.3, 57.6, 56.1, 32.3, 30.6, 26.6, 25.7

HRMS Calcd. for $C_{21}H_{29}NO$ $[M+H]^+$: 312.2322, Found: 312.2320

N,N-bis(4-methoxybenzyl)cinnamamide (E-17a)



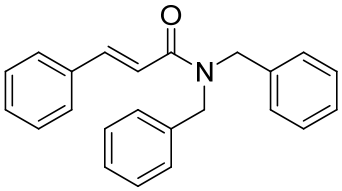
To a flame-dried Schlenk flask was added 60.2 mg (2.51 mmol) of sodium hydride and 2 mL (1.3 M) of DMF. A solution of 100 mg (0.679 mmol) of *trans*-cinnamide in 2 mL (0.33 M) of DMF was then added dropwise at room temperature. The reaction mixture was heated to 70 ºC for 1 h. Then 276 µL (2.04 mmol) of 1-(chloromethyl)-4-methoxybenzene was added dropwise to the reaction mixture. It was stirred at 70 ºC for 2 h. It was cooled to room temperature and quenched by 10 mL of water. The reaction mixture was extracted with Et_2O (2 x 15 mL), washed with water (2 x 15 mL) and dried over anhydrous $MgSO_4$ All volatiles were removed in vacuo. Silicagel column chromatography with a 80:20 mixture of hexane and ethyl acetate as the eluent gave 260 mg (0.671 mmol, 98.8%) of N,N-bis(4-methoxybenzyl)cinnamamide.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.84 (d, *J* = 15.2 Hz, 1 H), 7.55 - 7.40 (m, 2 H), 7.40 - 7.07 (m, 7 H), 7.02 - 6.76 (m, 5 H), 4.62 (s, 2 H), 4.52 (s, 2 H), 3.80 (s, 6 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.2, 159.4, 159.2, 143.8, 135.5, 130.0, 129.9, 129.8, 129.0, 128.9, 128.1, 117.7, 114.6, 114.2, 55.5, 49.5, 48.2

HRMS Calcd. for $C_{25}H_{25}NO_3$ $[M+H]^+$: 388.1907, Found: 388.1926

N,N-dibenzylcinnamamide (16a)



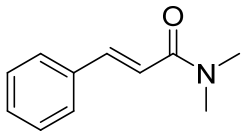
197 mg (0.602 mmol, 88.7%) of N,N-dibenzylcinnamamide was obtained from 60.2 mg (2.51 mmol) of sodium hydride, 100 mg (0.679 mmol) of *trans*-cinnamide and 242 µL (2.04 mmol) of benzyl bromide.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.87 (d, *J* = 15.2 Hz, 1 H), 7.56 - 7.17 (m, 15 H), 6.92 (d, *J* = 15.2 Hz, 1 H), 4.73 (s, 2 H), 4.62 (s, 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.4, 144.1, 137.6, 137.0, 135.4, 129.9, 129.2, 129.0, 128.9, 128.6, 128.1, 128.0, 127.7, 126.8, 117.5, 50.3, 49.1

HRMS Calcd. for $C_{23}H_{21}NO$ $[M+H]^+$: 328.1696, Found: 328.1704

N,N-dimethylcinnamamide (13a)



90.0 mg (0.514 mmol, 75.7%) of N,N-dimethylcinnamamide was obtained from 60.2 mg (2.51 mmol) of sodium hydride, 100 mg (0.679 mmol) of *trans*-cinnamide and 127 µL (2.04 mmol) of methyl iodide.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.67 (d, *J* = 15.2 Hz, 1 H), 7.59 - 7.46 (m, 2 H), 7.46 - 7.22 (m, 3 H), 6.89 (d, *J* = 15.5 Hz, 1 H), 3.17 (s, 3 H), 3.06 (s, 3 H)

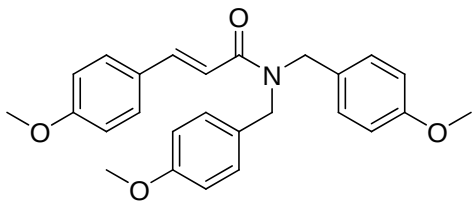
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 166.9, 142.5, 135.6, 129.7, 129.0, 128.0, 117.7, 37.6, 36.1

HRMS Calcd. for $C_{11}H_{13}NO$ $[M+H]^+$: 176.1070, Found: 176.1068

General procedure for the Horner-Wadsworth-Emmons olefination for aryl substrates **20a-23a**:

To a flame-dried Schlenk flask was added 1.10 mmol of sodium hydride and 1.6 mL (0.7 M) of THF. The reaction was cooled to 0 ºC and a solution of 0.919 mmol of diethyl 2-(bis(4-methoxybenzyl)amino)-2-oxoethylphosphonate in 1.6 mL (0.7 M) of THF was added dropwise. The reaction mixture was stirred at room temperature for 1 h. 1.10 mmol of aryl aldehyde was then added and the mixture was stirred for 12 h at room temperature. It was quenched by 4 mL of water. The reaction mixture was extracted with Et_2O (2 x 10 mL), washed several times with water (2 x 5 mL) and dried over anhydrous $MgSO_4$. All volatiles were removed in vacuo. Silicagel column chromatography with a mixture of hexane and ethyl acetate as the eluent gave the desired (*E*)-α,β-unsaturated amide.

(E)-N,N-bis(4-methoxybenzyl)-3-(4-methoxyphenyl)acrylamide (20a)

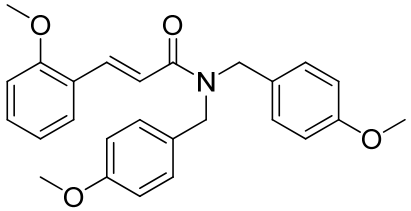


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.79 (d, *J* = 15.2 Hz, 1 H), 7.40 (d, *J* = 7.9 Hz, 2 H), 7.30 - 7.00 (m, 4 H), 7.00 - 6.70 (m, 7 H), 4.60 (s, 2 H), 4.50 (s, 2 H), 3.92 - 3.64 (m, 9 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.5, 161.1, 159.3, 159.2, 143.5, 130.0, 129.6, 129.0, 128.1, 115.2, 114.5, 114.4, 114.2, 55.5, 49.4, 48.1

HRMS Calcd. for $C_{26}H_{27}NO_4$ $[M+H]^+$: 418.2013, Found: 418.2009

(E)-N,N-bis(4-methoxybenzyl)-3-(2-methoxyphenyl)acrylamide (21a)

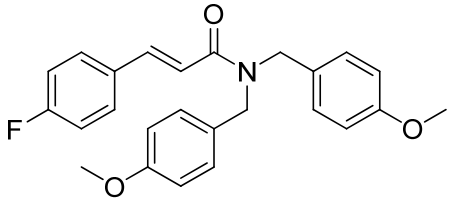


^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 8.08 (d, *J* = 15.3 Hz, 1 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.30 - 7.01 (m, 6 H), 6.95 - 6.80 (m, 6 H), 4.61 (s, 2 H), 4.50 (s, 2 H), 3.85 - 3.74 (m, 9 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.6, 159.0, 158.9, 158.2, 139.1, 130.7, 129.8, 129.2, 128.9, 127.9, 124.3, 120.6, 118.5, 114.2, 113.9, 111.1, 55.4, 55.3, 49.2, 47.9

HRMS Calcd. for $C_{26}H_{27}NO_4$ $[M+H]^+$: 418.2013, Found: 418.2008

(E)-3-(4-fluorophenyl)-N,N-bis(4-methoxybenzyl)acrylamide (22a)

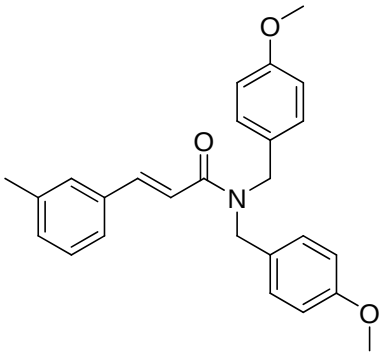


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.78 (d, *J* = 15.5 Hz, 1 H), 7.43 (dd, *J* = 5.6, 8.5 Hz, 2 H), 7.31 - 7.06 (m, 4 H), 7.00 (t, *J* = 8.5 Hz, 2 H), 6.93 - 6.68 (m, 5 H), 4.60 (s, 2 H), 4.50 (s, 2 H), 3.78 (s, 3 H), 3.78 - 3.75 (m, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.0, 165.4, 162.0, 159.4, 159.2, 142.5, 131.7, 130.0, 129.9, 129.8, 129.7, 128.8, 128.0, 117.5, 116.2, 115.9, 114.6, 114.2, 55.5, 49.5, 48.2

HRMS Calcd. for $C_{25}H_{24}FNO_3$ $[M+H]^+$: 406.1813, Found: 406.1818

(E)-N,N-bis(4-methoxybenzyl)-3-m-tolylacrylamide (23a)

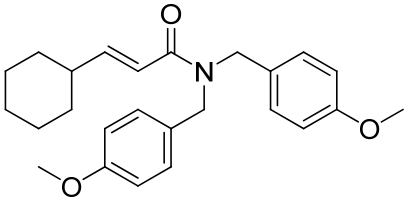


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.85 (d, *J* = 15.2 Hz, 1 H), 7.40 - 7.05 (m, 8 H), 7.05 - 6.77 (m, 5 H), 4.64 (s, 2 H), 4.55 (s, 2 H), 3.79 (s, 6 H), 2.34 (s, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.3, 159.4, 159.3, 144.0, 138.6, 135.5, 130.8, 130.1, 129.8, 128.9, 128.8, 128.2, 125.3, 117.5, 114.6, 114.2, 55.5, 49.5, 48.1, 21.6

HRMS Calcd. for $C_{26}H_{27}NO_3$ $[M+H]^+$: 402.2064, Found: 402.2045

(E)-3-cyclohexyl-N,N-bis(4-methoxybenzyl)acrylamide (24a)



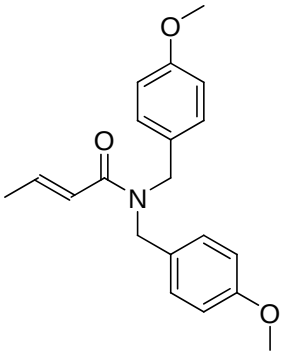
To a flame-dried Schlenk flask was added 200 mg (0.459 mmol) of diethyl 2-(bis(4-methoxybenzyl)amino)-2-oxoethylphosphonate, 146 µL (0.834 mmol) of Hunig's base, 36.0 mg (0.834 mmol), 51.0 µL (0.417 mmol) of cyclohexanecarbaldehyde and 3 mL (0.15 M) of acetonitrile. It was stirred at room temperature for 12 h. The reaction mixture was extracted with ethyl acetate (2 x 10 mL), washed with water (2 x 10 mL) and dried over anhydrous $MgSO_4$. All volatiles were removed in vacuo. Silicagel column chromatography with a 70:30 mixture of hexane and ethyl acetate as the eluent gave 140 mg (0.356 mmol, 85.4%) of (E)-3-cyclohexyl-N,N-bis(4-methoxybenzyl)acrylamide.

^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.12 (t, *J* = 7.6 Hz, 4 H), 6.97 (dd, *J* = 7.0, 15.0 Hz, 1 H), 6.84 (dd, *J* = 8.4, 12.2 Hz, 4 H), 6.22 (d, *J* = 15.0 Hz, 1 H), 4.52 (s, 2 H), 4.40 (br. s., 2 H), 3.77 (s, 3 H), 3.76 (s, 3 H), 2.18 - 2.03 (m, 1 H), 1.81 - 1.58 (m, 5 H), 1.30 - 1.05 (m, 5 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.7, 159.3, 159.1, 152.9, 130.0, 128.9, 128.1, 118.0, 114.4, 114.1, 55.4, 49.3, 47.8, 41.0, 32.2, 26.1, 25.9

HRMS Calcd. for $C_{25}H_{31}NO_3$ $[M+H]^+$:394.2377, Found: 394.2393

(E)-N,N-bis(4-methoxybenzyl)but-2-enamide (25a)



^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.16 (d, *J* = 7.6 Hz, 2 H), 7.12 - 6.93 (m, 3 H), 6.82 (d, *J* = 8.2 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 6.30 (d, *J* = 15.0 Hz, 1 H), 4.53 (br. s., 2 H), 4.40 (br. s., 2 H), 3.77 (s, 3 H), 3.78 (s, 3 H), 1.85 (d, *J* = 6.7 Hz, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 167.3, 159.3, 159.2, 142.9, 129.9, 128.9, 128.0, 122.0, 114.5, 114.1, 55.5, 49.2, 47.7, 18.5

HRMS Calcd. for $C_{20}H_{23}NO_3$ $[M+H]^+$: 326.1751, Found: 326.1735

5. Products from the copper catalyzed borylation

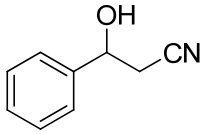
General procedure for copper catalyzed borylation of α,β-unsaturated substrates:

To a flame-dried Schlenk flask was added copper (I) bromide-dimethylsulfide complex (3 mol%), NHC ligand (3.5 mol%), potassium tert-butoxide (9 mol%) and THF (0.16 M). The reaction mixture was stirred for 30 minutes at room temperature. Then bis(pinacolato)diboron (0.178 mmol) was added followed by substrate (0.162 mmol) and methanol (0.324 mmol) when used. Then the reaction mixture was stirred at room temperature for 12 h or at 40 ºC for 6 h.

$NaBO_3•(H_2O)_4$ (0.810 mmol) and water (0.16 M) were added and the reaction mixture was stirred an additional 3 h at room temperature. The suspension was then extracted with Et_2O (3 x 10 mL), dried with $MgSO_4$ and concentrated in vacuo. Silicagel column chromatography with a mixture of hexane and ethyl acetate as the eluent gave the chiral β alcohol.

The racemic compound was obtained by using IMes as racemic NHC ligand.

3-hydroxy-3-phenylpropanenitrile (11b)

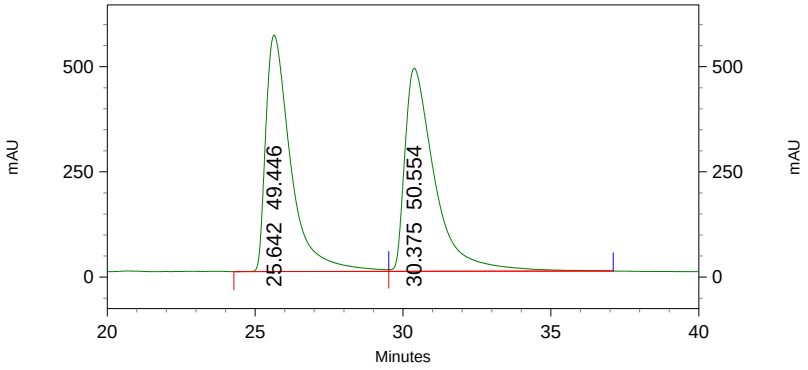


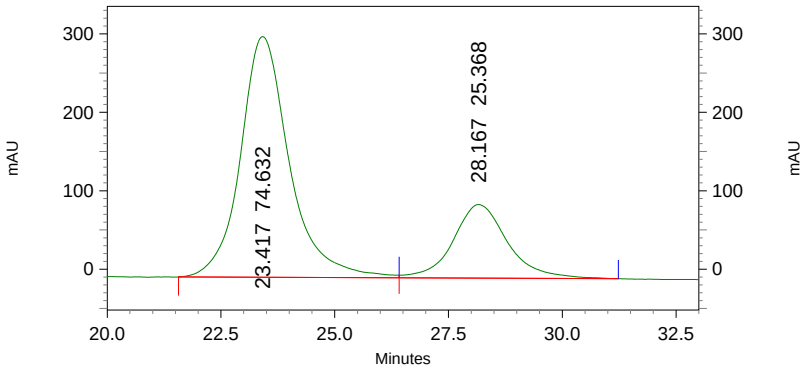
^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.53 - 7.24 (m, 5 H), 4.98 (t, *J* = 6.3 Hz, 1 H), 3.10 (br. s., 1 H), 2.71 (d, *J* = 6.2 Hz, 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 141.3, 129.1, 129.0, 125.8, 117.7, 70.1, 28.1

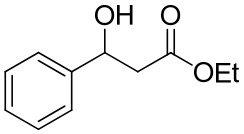
HRMS Calcd. for C_9H_9NO $[M+H]^+$: 148.0757, Found: 148.0753

Ee was measured by chiral HPLC with a OJ-H column (UV 215 nm, 10% isopropanol/hexane, 1.0 ml/min).





Ethyl 3-hydroxy-3-phenylpropanoate (12b)

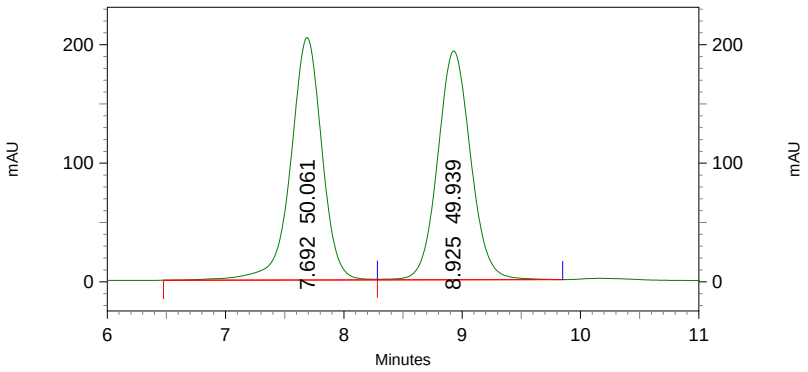


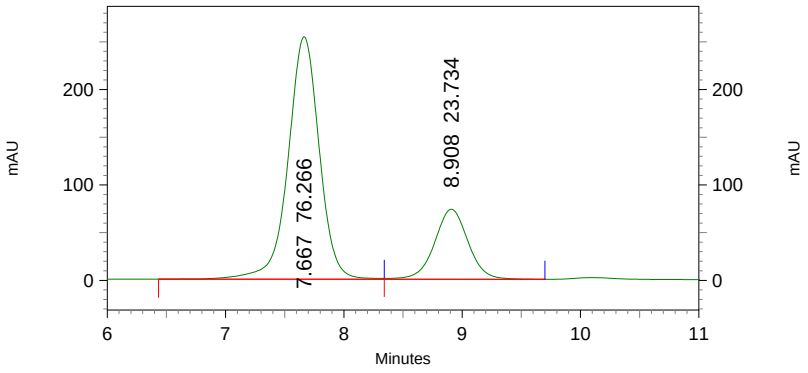
^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 7.49 - 7.17 (m, 5 H), 5.13 (dd, *J* = 4.2, 8.2 Hz, 1 H), 4.18 (q, *J* = 7.1 Hz, 2 H), 3.34 (br. s., 1 H), 2.83 - 2.62 (m, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 172.6, 142.7, 128.7, 128.0, 125.9, 70.5, 61.1, 43.6, 14.4

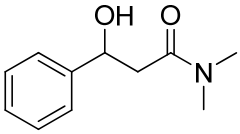
HRMS Calcd. for $C_{11}H_{14}O_3$ $[M+Na]^+$: 217.0835, Found: 217.0830

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 10% isopropanol/hexane, 1.0 ml/min).





3-hydroxy-N,N-dimethyl-3-phenylpropanamide (13b)

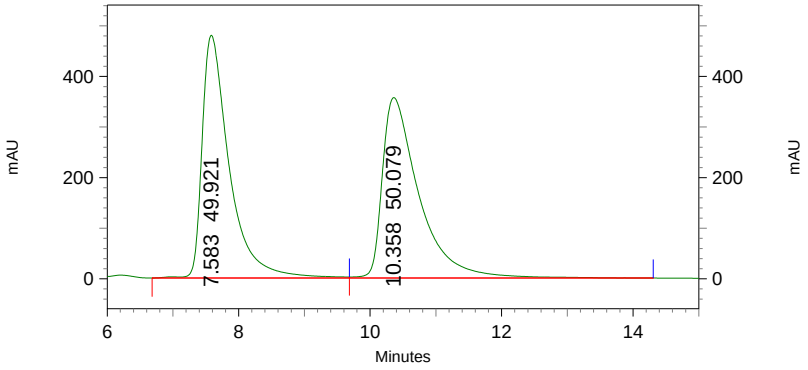


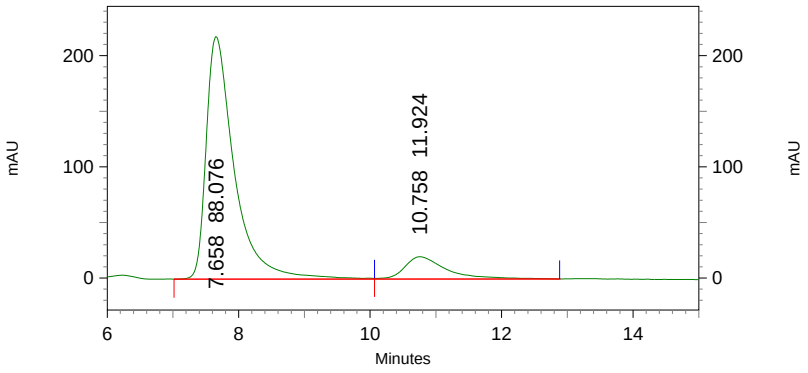
^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 7.47 - 7.17 (m, 5 H), 5.13 (dd, *J* = 3.1, 9.1 Hz, 1 H), 4.79 (br. s., 1 H), 2.93 (s, 3 H), 2.97 (s, 3 H), 2.73 - 2.58 (m, 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 172.5, 143.2, 128.7, 127.7, 125.9, 70.6, 42.1, 37.3, 35.4

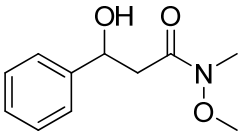
HRMS Calcd. for $C_{11}H_{15}NO_2$ $[M+H]^+$: 194.1176, Found: 194.1172

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 30% isopropanol/hexane, 1.5 ml/min).





3-hydroxy-N-methoxy-N-methyl-3-phenylpropanamide (14b)

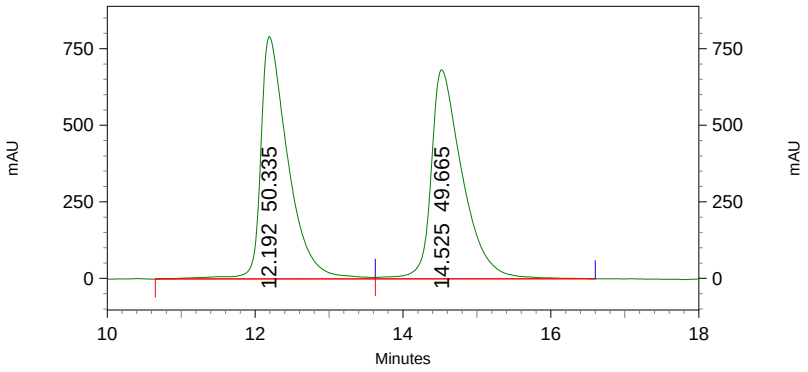


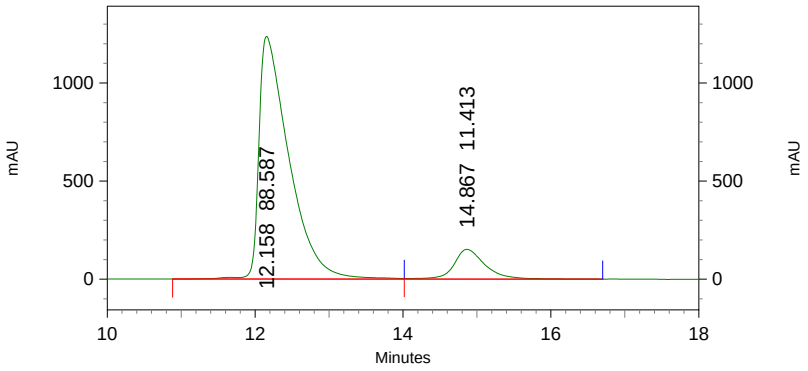
^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.55 - 7.18 (m, 5 H), 5.15 (d, *J* = 9.1 Hz, 1 H), 4.29 - 4.22 (m, 1 H), 3.62 (s, 3 H), 3.20 (s, 3 H), 2.92 - 2.75 (m, 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.5, 143.3, 128.7, 127.8, 126.0, 70.4, 61.5, 40.7, 32.1

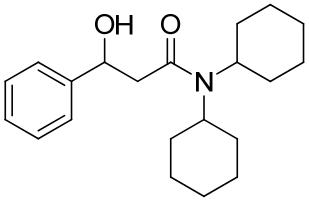
HRMS Calcd. for $C_{11}H_{15}NO_3$ $[M+Na]^+$: 232.0944, Found: 232.0948

Ee was measured by chiral HPLC with a IB column (UV 215 nm, 5% isopropanol/hexane, 1.4 ml/min).





N,N-dicyclohexyl-3-hydroxy-3-phenylpropanamide (15b)

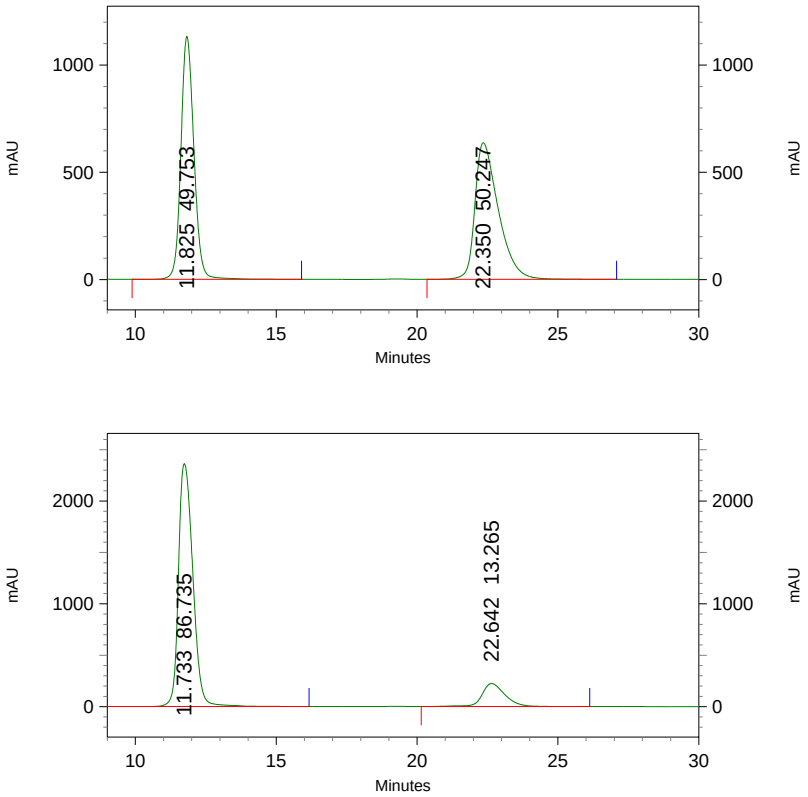


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.54 - 7.23 (m, 5 H), 5.12 (d, *J* = 9.1 Hz, 1 H), 4.99 (br. s., 1 H), 3.34 (t, *J* = 11.6 Hz, 1 H), 3.13 - 2.81 (m, 1 H), 2.78 - 2.49 (m, 2 H), 2.45 (br. s., 2 H), 1.92 - 1.69 (m, 4 H), 1.61 (br. s., 4 H), 1.49 (t, *J* = 12.5 Hz, 4 H), 1.33 - 0.98 (m, 6 H)

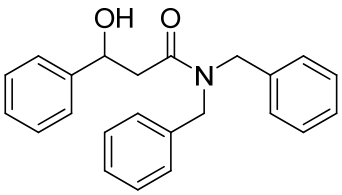
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 171.6, 143.5, 128.6, 127.6, 126.1, 70.8, 57.8, 56.4, 43.7, 31.2, 30.5, 30.1, 26.8, 26.0, 25.6, 25.4

HRMS Calcd. for $C_{21}H_{31}NO_2$ $[M+H]^+$: 330.2428, Found: 330.2423

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 10% isopropanol/hexane, 1.0 ml/min).



N,N-dibenzyl-3-hydroxy-3-phenylpropanamide (16b)

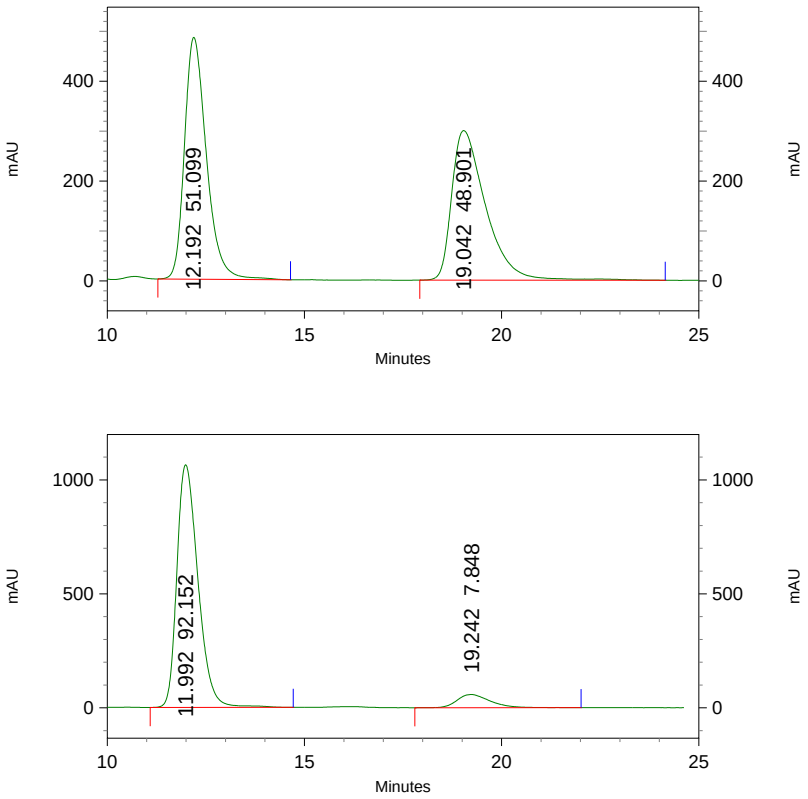


^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 7.49 - 7.17 (m, 13 H), 7.17 - 7.05 (m, 2 H), 5.29 - 5.20 (m, 1 H), 4.84 (d, *J* = 2.8 Hz, 1 H), 4.75 (d, *J* = 14.7 Hz, 1 H), 4.54 (d, *J* = 15.0 Hz, 1 H), 4.48 - 4.33 (m, 2 H), 2.88 - 2.77 (m, 2 H)

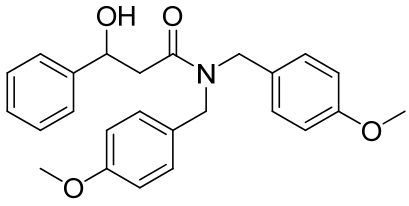
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.2, 143.1, 137.0, 136.0, 129.3, 129.0, 128.7, 128.5, 128.1, 127.8, 127.8, 126.6, 126.0, 70.9, 50.1, 48.4, 41.9

HRMS Calcd. for $C_{23}H_{23}NO_2$ $[M+H]^+$: 346.1802, Found: 346.1802

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 30% isopropanol/hexane, 1.5 ml/min).



3-hydroxy-N,N-bis(4-methoxybenzyl)-3-phenylpropanamide (17b)



^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.45 - 7.23 (m, 5 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.95 - 6.79 (m, 4 H), 5.22 (br. s., 1 H), 4.87 (d, *J* = 2.9 Hz, 1 H), 4.61 (d, *J* = 14.7 Hz, 1 H), 4.45 (d, *J* = 14.4 Hz, 1 H), 4.30 (d, *J* = 4.1 Hz, 2 H), 3.81 (s, 3 H), 3.81 - 3.79 (m, 3 H), 2.87 - 2.75 (m, 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 172.6, 159.1, 159.0, 142.9, 129.6, 128.8, 128.4, 127.6, 127.4, 125.7, 114.3, 114.0, 70.6, 55.3, 49.0, 47.2, 41.6

HRMS Calcd. for $C_{25}H_{27}NO_4$ $[M+H]^+$: 406.2013, Found: 406.2011

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 30% isopropanol/hexane, 1.5 ml/min).

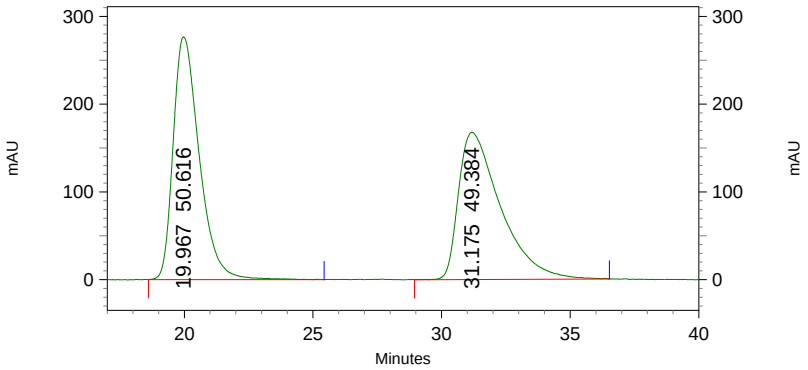
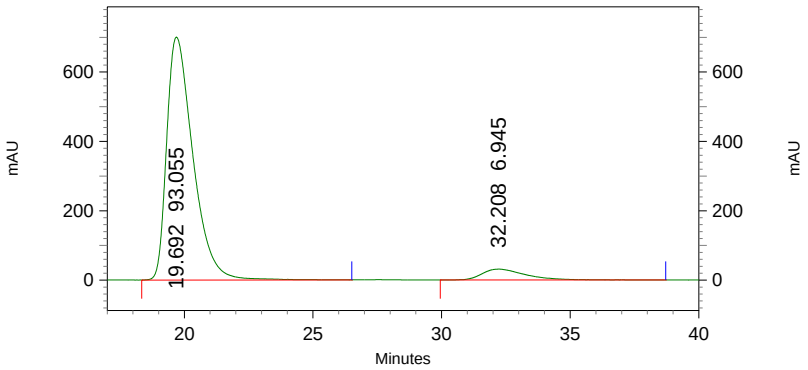
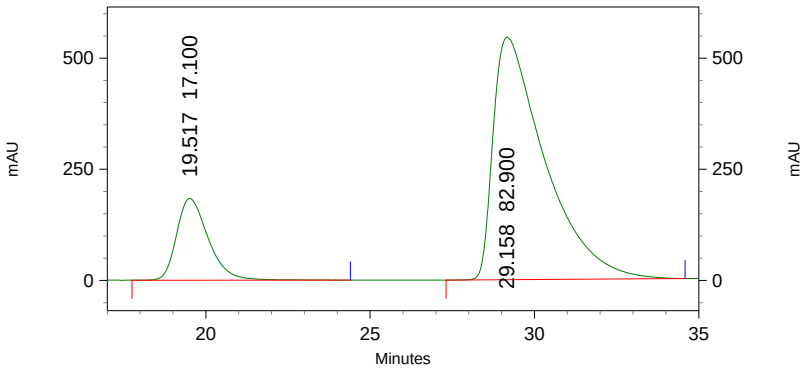


Table 1 entry 7:



Scheme 2 line 2:



Scheme 2 line 3:

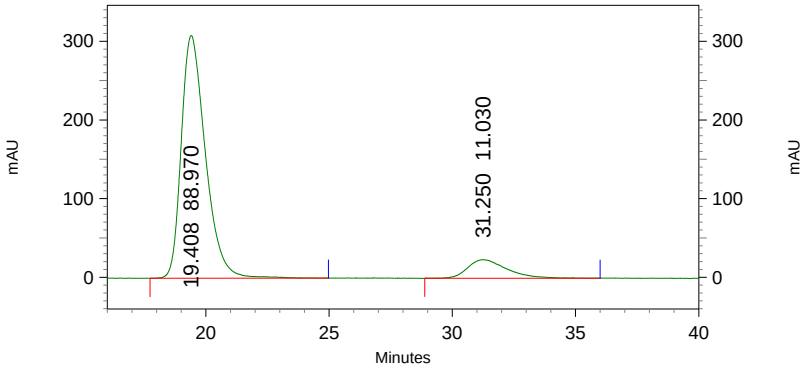


Figure 3 ligand **8a**:

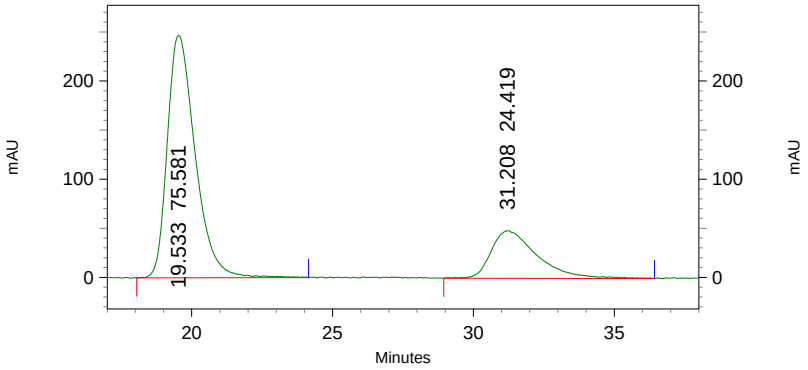


Figure 3 ligand **8b**:

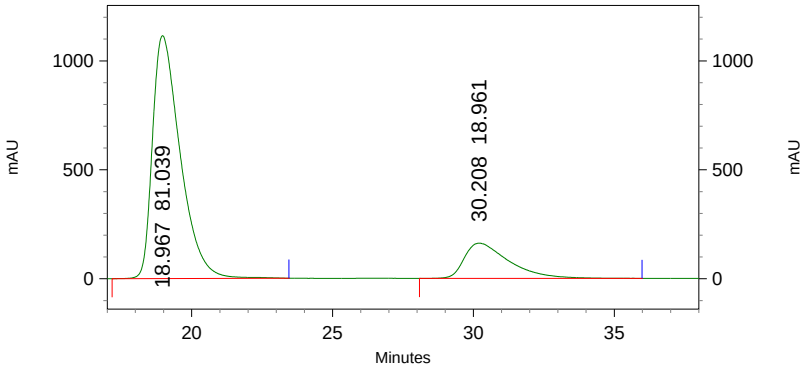


Figure 3 ligand **8c**:

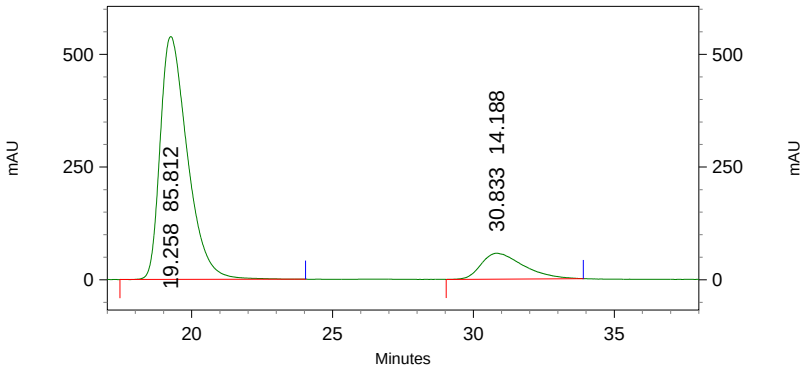


Figure 3 ligand **8d**:

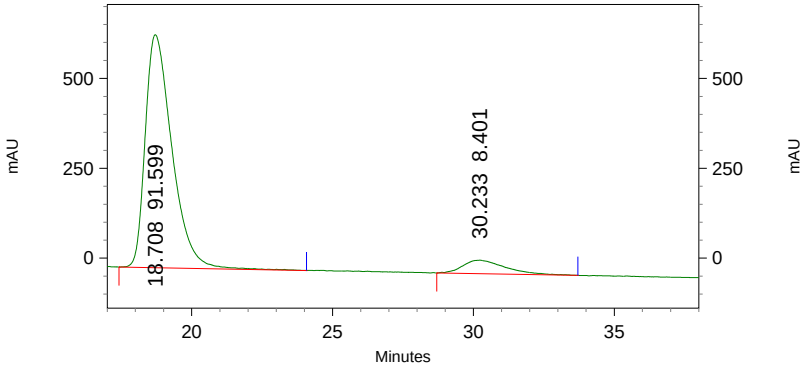


Figure 3 ligand **8e**:

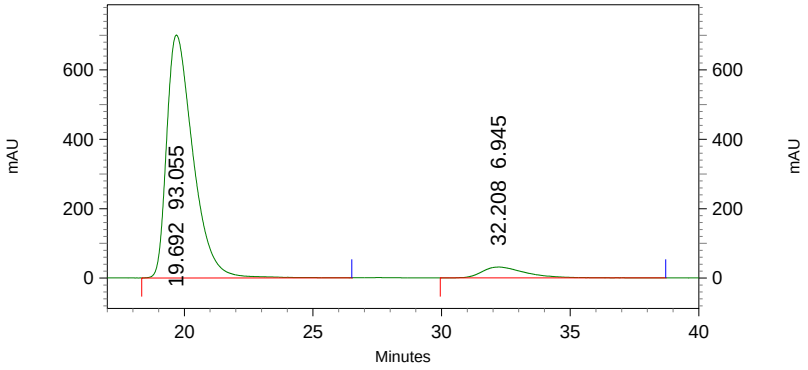


Figure 3 ligand **18**:

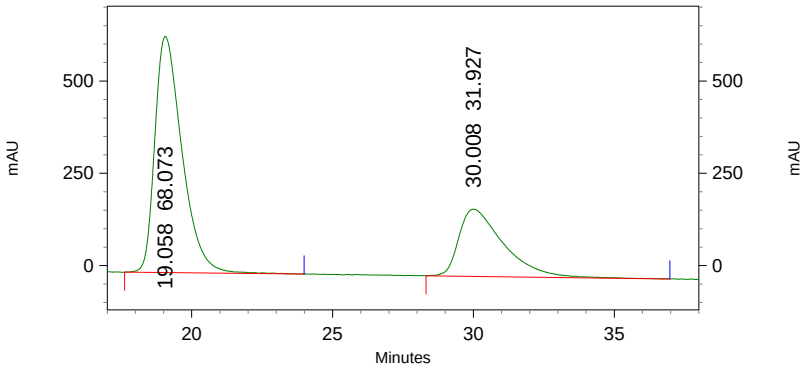


Figure 3 ligand **19**:

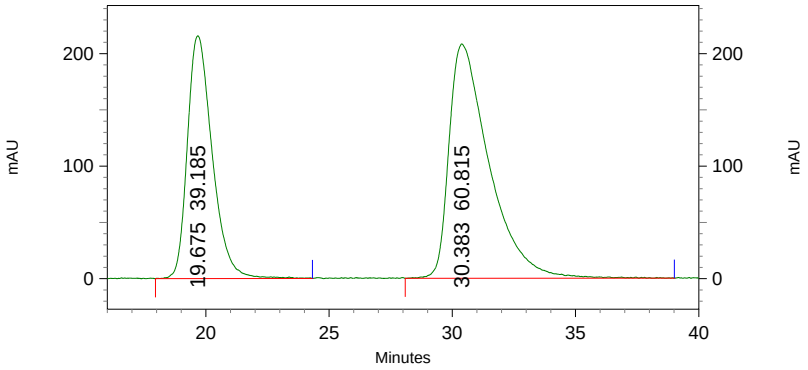
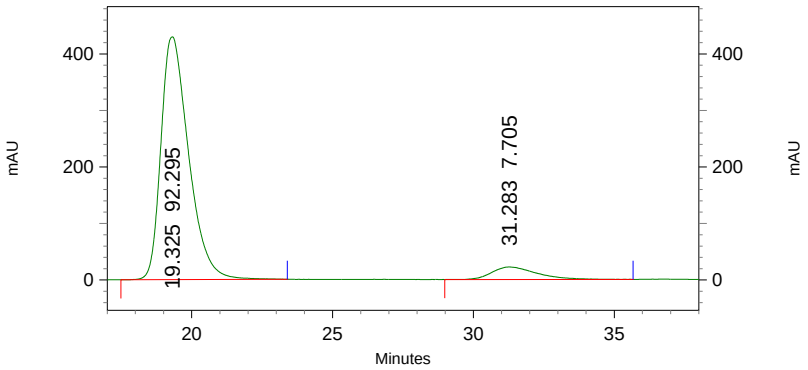
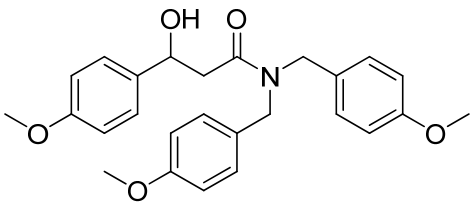


Table 2 entry 1:



3-hydroxy-N,N-bis(4-methoxybenzyl)-3-(4-methoxyphenyl)propanamide (20b)

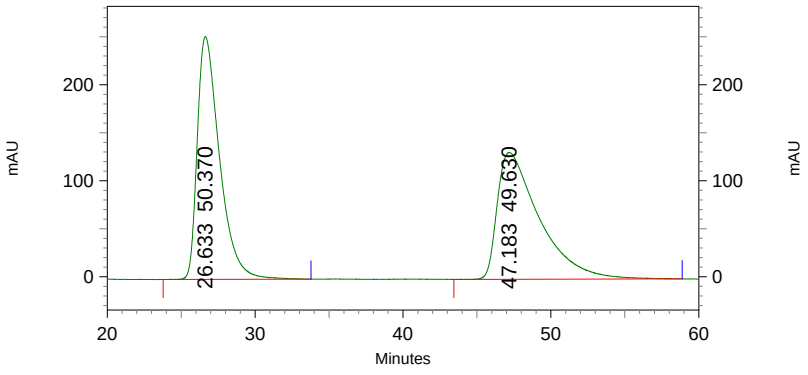


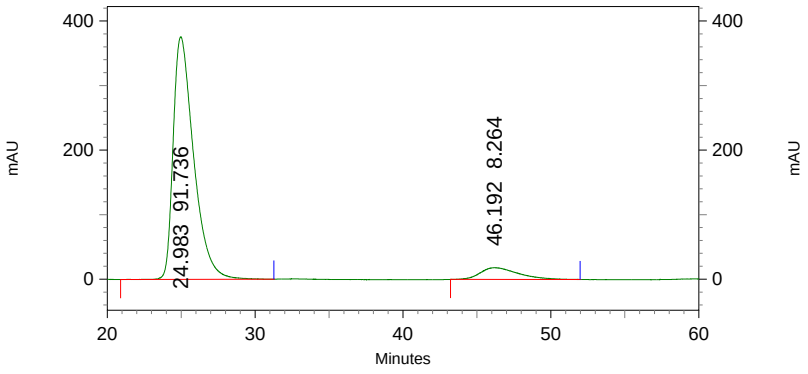
^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 7.36 - 7.29 (m, 2 H), 7.17 (d, *J* = 8.5 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 6.99 - 6.83 (m, 6 H), 5.20 (t, *J* = 5.5 Hz, 1 H), 4.84 (br. s., 1 H), 4.65 (d, *J* = 14.4 Hz, 1 H), 4.48 (d, *J* = 14.7 Hz, 1 H), 4.34 (d, *J* = 4.2 Hz, 2 H), 3.97 - 3.76 (m, 9 H), 2.81 (d, *J* = 6.2 Hz, 2 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.5, 159.3, 159.2, 155.7, 131.3, 129.8, 129.2, 128.3, 128.1, 127.9, 126.7, 121.0, 114.5, 114.2, 110.2, 66.1, 55.5, 55.5, 55.3, 49.1, 47.2, 39.6

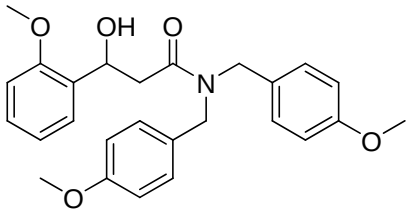
HRMS Calcd. for $C_{26}H_{29}NO_5$ $[M+H]^+$: 436.2118, Found: 436.2105

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 40% isopropanol/hexane, 1.5 ml/min).





3-hydroxy-N,N-bis(4-methoxybenzyl)-3-(2-methoxyphenyl)propanamide (21b)

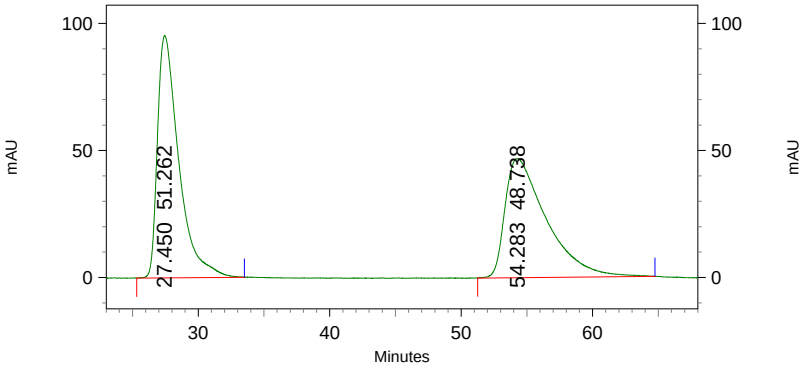


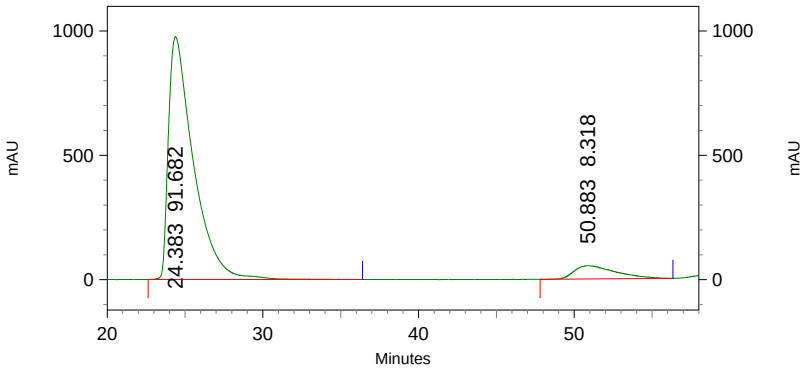
^{1}H NMR (299MHz ,CHLOROFORM-d) δ = 7.59 (d, *J* = 7.6 Hz, 1 H), 7.36 - 6.68 (m, 11 H), 5.47 (d, *J* = 8.5 Hz, 1 H), 5.03 (d, *J* = 3.4 Hz, 1 H), 4.66 (d, *J* = 14.4 Hz, 1 H), 4.47 - 4.15 (m, 3 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.71 (s, 3 H), 2.99 (dd, *J* = 2.4, 16.0 Hz, 1 H), 2.69 (dd, *J* = 8.8, 15.9 Hz, 1 H)

^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.5, 159.3, 159.2, 155.7, 131.3, 129.8, 129.2, 128.3, 128.0, 127.9, 126.7, 121.0, 114.5, 114.2, 110.2, 66.1, 55.5, 55.5, 55.3, 49.1, 47.2, 39.6

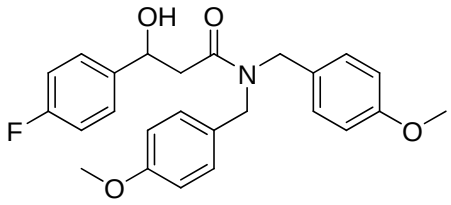
HRMS Calcd. for $C_{26}H_{29}NO_5$ $[M+H]^+$: 436.2118, Found: 436.2108

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 40% isopropanol/hexane, 1.5 ml/min).





3-(4-fluorophenyl)-3-hydroxy-N,N-bis(4-methoxybenzyl)propanamide (22b)

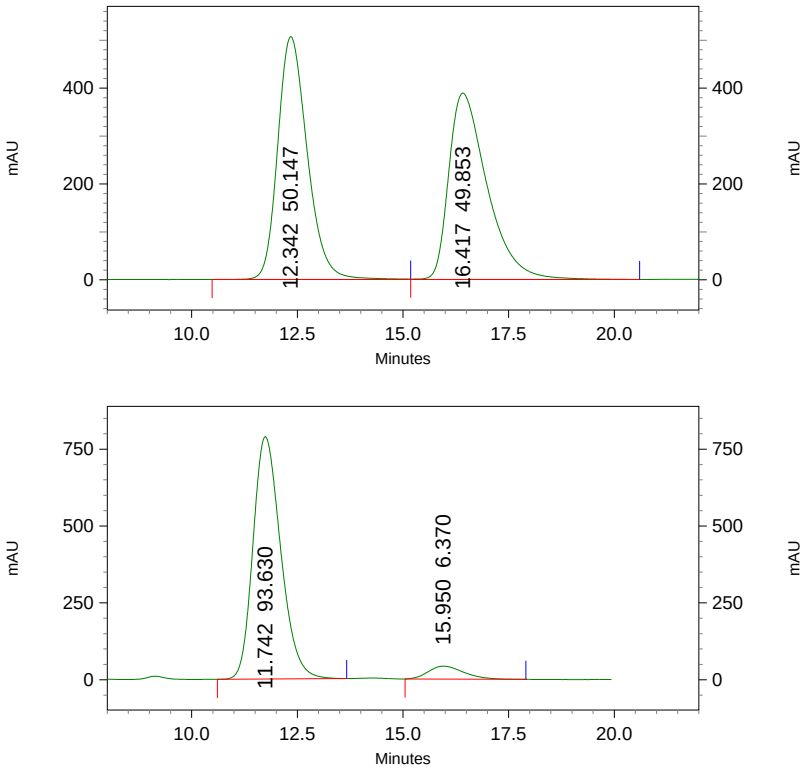


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.38 - 7.20 (m, 2 H), 7.19 - 6.80 (m, 10 H), 5.15 (dd, *J* = 4.3, 7.8 Hz, 1 H), 4.90 (br. s., 1 H), 4.58 (d, *J* = 14.4 Hz, 1 H), 4.43 (d, *J* = 14.7 Hz, 1 H), 4.28 (d, *J* = 2.3 Hz, 2 H), 3.79 (d, *J* = 2.1 Hz, 6 H), 2.77 - 2.69 (m, 2 H)

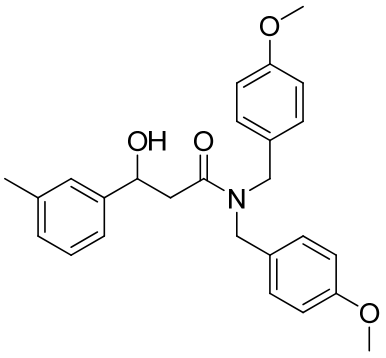
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 172.7, 159.4, 159.3, 138.9, 129.9, 129.0, 127.8, 127.7, 127.6, 115.6, 115.3, 114.6, 114.3, 70.3, 55.5, 55.5, 49.3, 47.5, 41.8

HRMS Calcd. for $C_{25}H_{26}FNO_4$ $[M+H]^+$: 424.1919, Found: 424.1916

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 40% isopropanol/hexane, 1.5 ml/min).



3-hydroxy-N,N-bis(4-methoxybenzyl)-3-m-tolylpropanamide (23b)

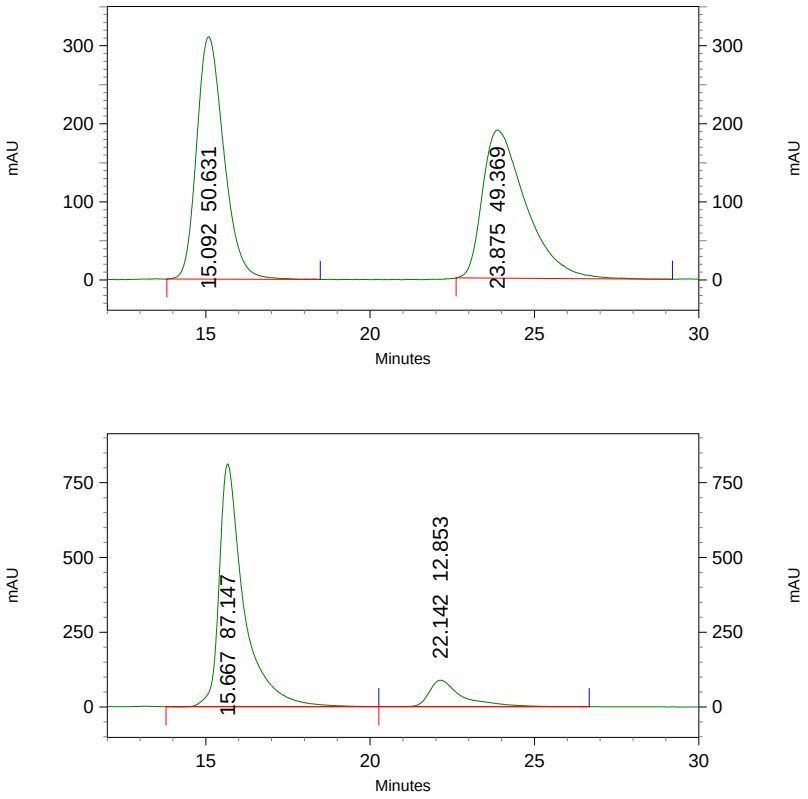


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.34 - 6.95 (m, 8 H), 6.95 - 6.72 (m, 4 H), 5.18 (br. s., 1 H), 4.83 (d, *J* = 2.9 Hz, 1 H), 4.61 (d, *J* = 14.7 Hz, 1 H), 4.45 (d, *J* = 14.4 Hz, 1 H), 4.30 (d, *J* = 3.8 Hz, 2 H), 3.81 (d, *J* = 2.1 Hz, 6 H), 2.85 - 2.73 (m, 2 H), 2.34 (s, 3 H)

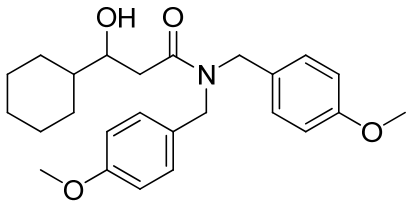
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.0, 159.4, 159.3, 143.1, 138.3, 129.9, 129.1, 128.6, 128.5, 127.9, 126.6, 123.0, 114.6, 114.3, 70.9, 55.6, 55.5, 49.3, 47.4, 42.0, 21.7

HRMS Calcd. for $C_{26}H_{29}NO_4$ $[M+H]^+$: 344.1856, Found: 344.1859

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 40% isopropanol/hexane, 1.5 ml/min).



3-cyclohexyl-3-hydroxy-N,N-bis(4-methoxybenzyl)propanamide (24b)

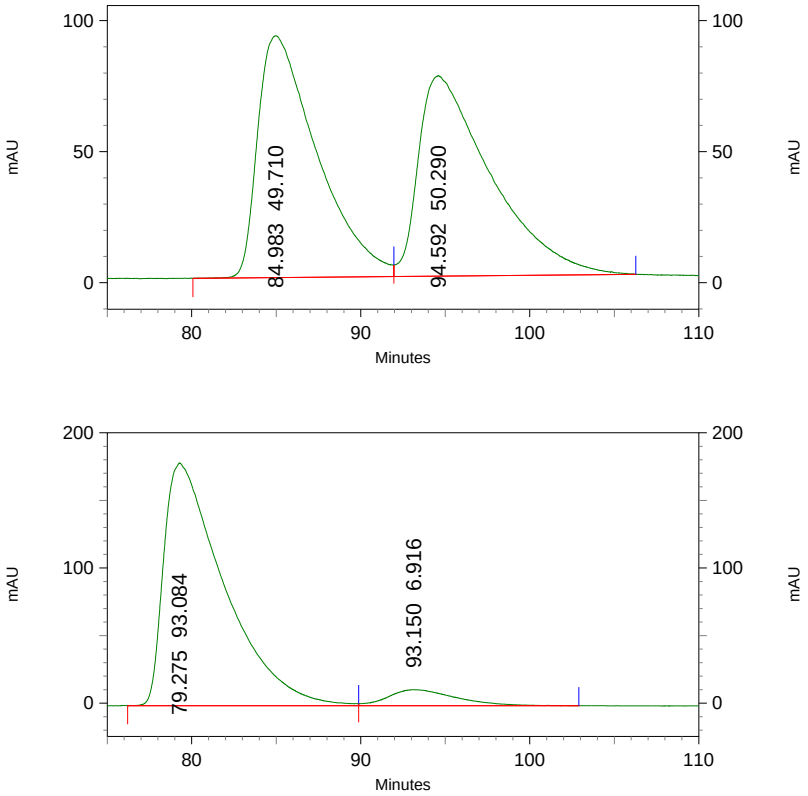


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.22 - 6.98 (m, 4 H), 6.98 - 6.69 (m, 4 H), 4.66 - 4.41 (m, 2 H), 4.36 (d, *J* = 4.4 Hz, 2 H), 4.25 (d, *J* = 2.6 Hz, 1 H), 3.82 (s, 3 H), 3.80 (s, 3 H), 2.58 (d, *J* = 2.1 Hz, 1 H), 2.48 (d, *J* = 9.7 Hz, 1 H), 1.87 (br. s., 1 H), 1.81 - 1.58 (m, 4 H), 1.43 - 1.10 (m, 4 H), 1.10 - 0.98 (m, 2 H)

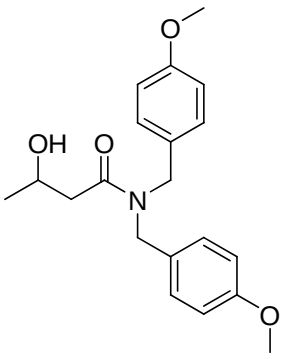
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.8, 159.4, 159.3, 129.9, 129.3, 128.1, 127.9, 114.6, 114.2, 72.6, 55.6, 55.5, 49.3, 47.4, 43.2, 36.8, 29.2, 28.6, 26.7, 26.4, 26.3

HRMS Calcd. for $C_{25}H_{33}NO_4$ $[M+H]^+$:412.2482, Found: 412.2482

Ee was measured by chiral HPLC with a Whelk-01 column (UV 215 nm, 5% isopropanol/hexane, 1.5 ml/min).



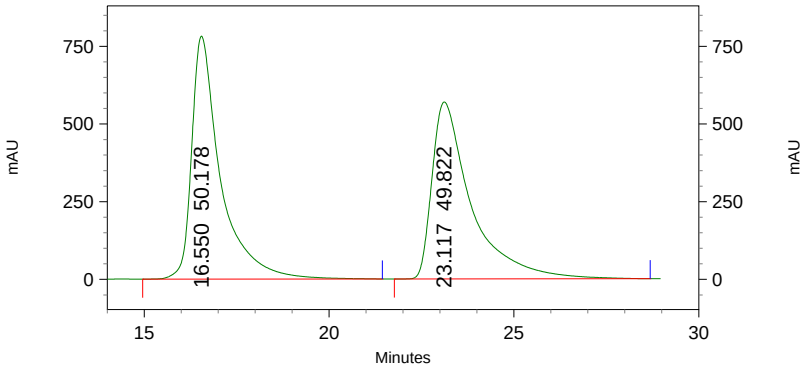
3-hydroxy-N,N-bis(4-methoxybenzyl)butanamide (25b)

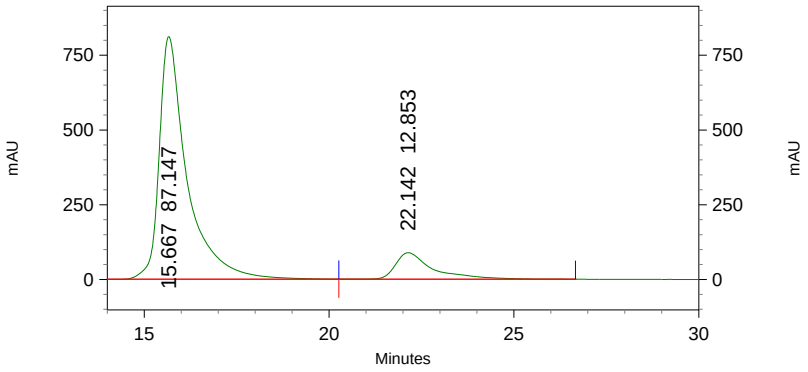


^{1}H NMR (300MHz ,CHLOROFORM-d) δ = 7.20 - 6.98 (m, 4 H), 6.96 - 6.78 (m, 4 H), 4.58 (d, *J* = 14.7 Hz, 1 H), 4.43 (d, *J* = 14.4 Hz, 2 H), 4.38 - 4.22 (m, 3 H), 3.80 (s, 6 H), 2.57 (dd, *J* = 2.6, 16.4 Hz, 1 H), 2.42 (dd, *J* = 9.4, 16.7 Hz, 1 H), 1.23 - 1.18 (m, 3 H)

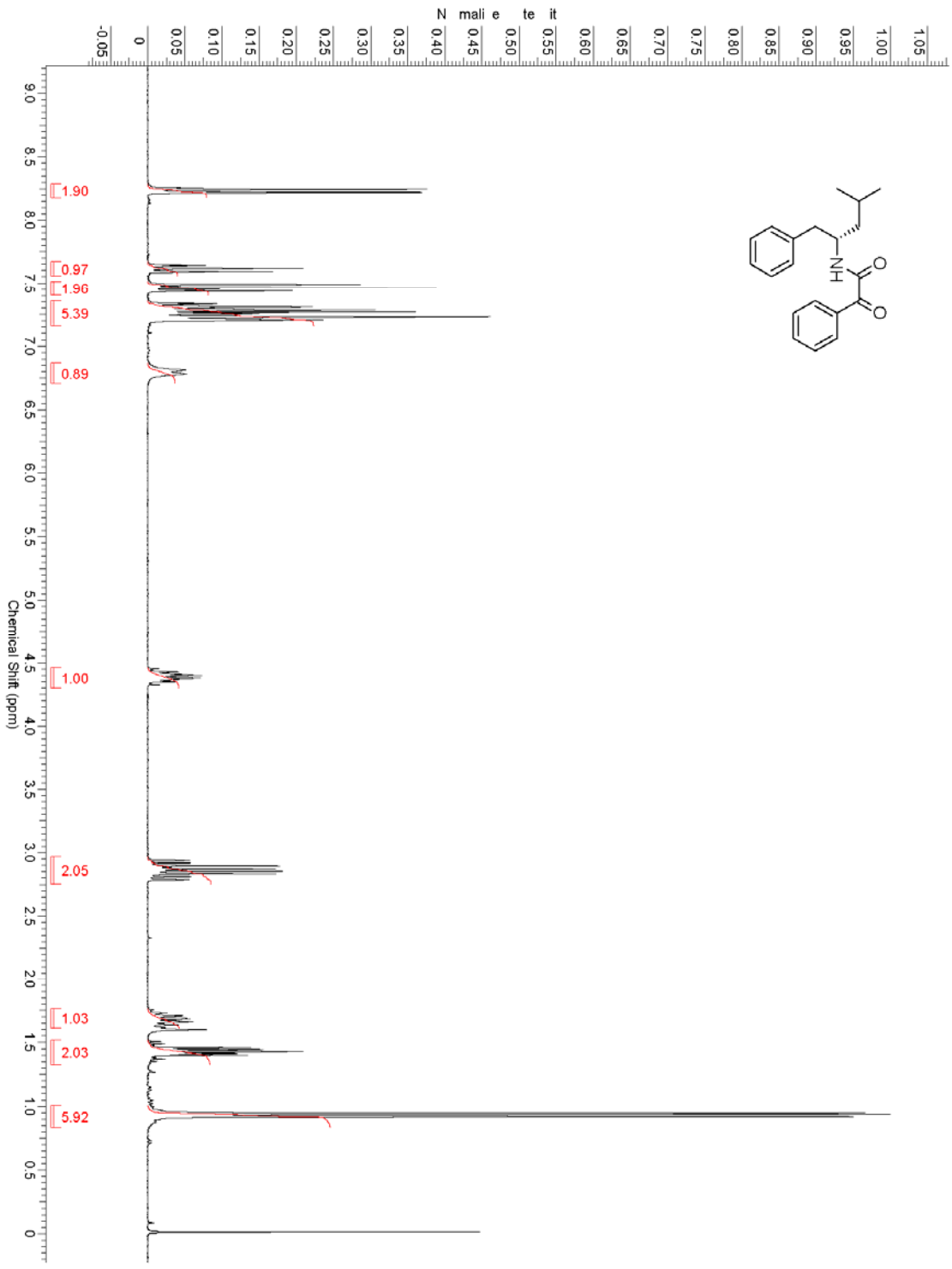
^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 173.4, 159.4, 159.3, 129.9, 129.2, 128.0, 127.9, 114.7, 114.3, 64.7, 55.6, 55.5, 49.2, 47.3, 41.2, 22.5

Ee was measured by chiral HPLC with a IA column (UV 215 nm, 10% isopropanol/hexane, 1.2 ml/min).





6. NMR spectra for ligands


N mali e te it
Chemical Shift (ppm)
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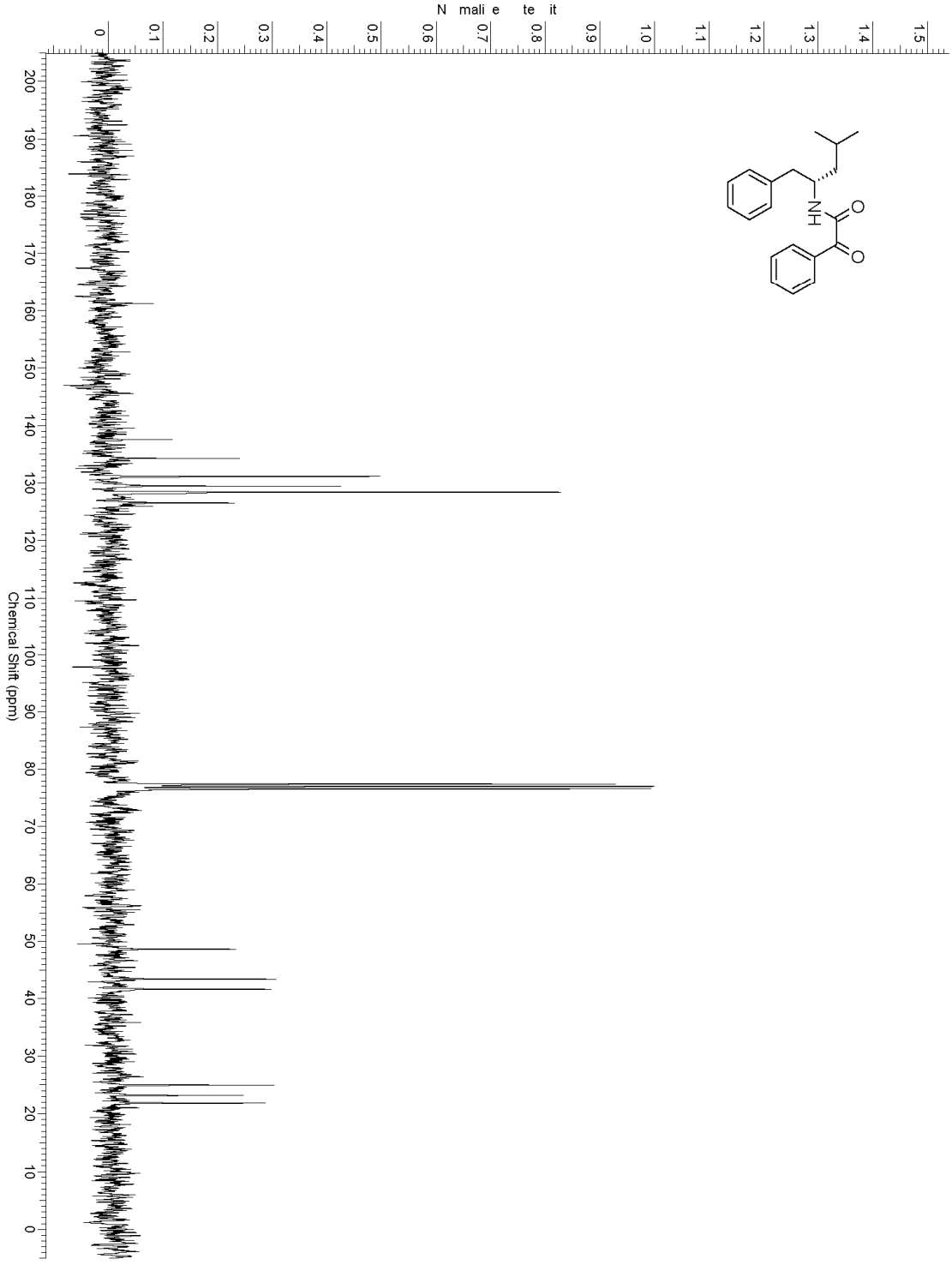
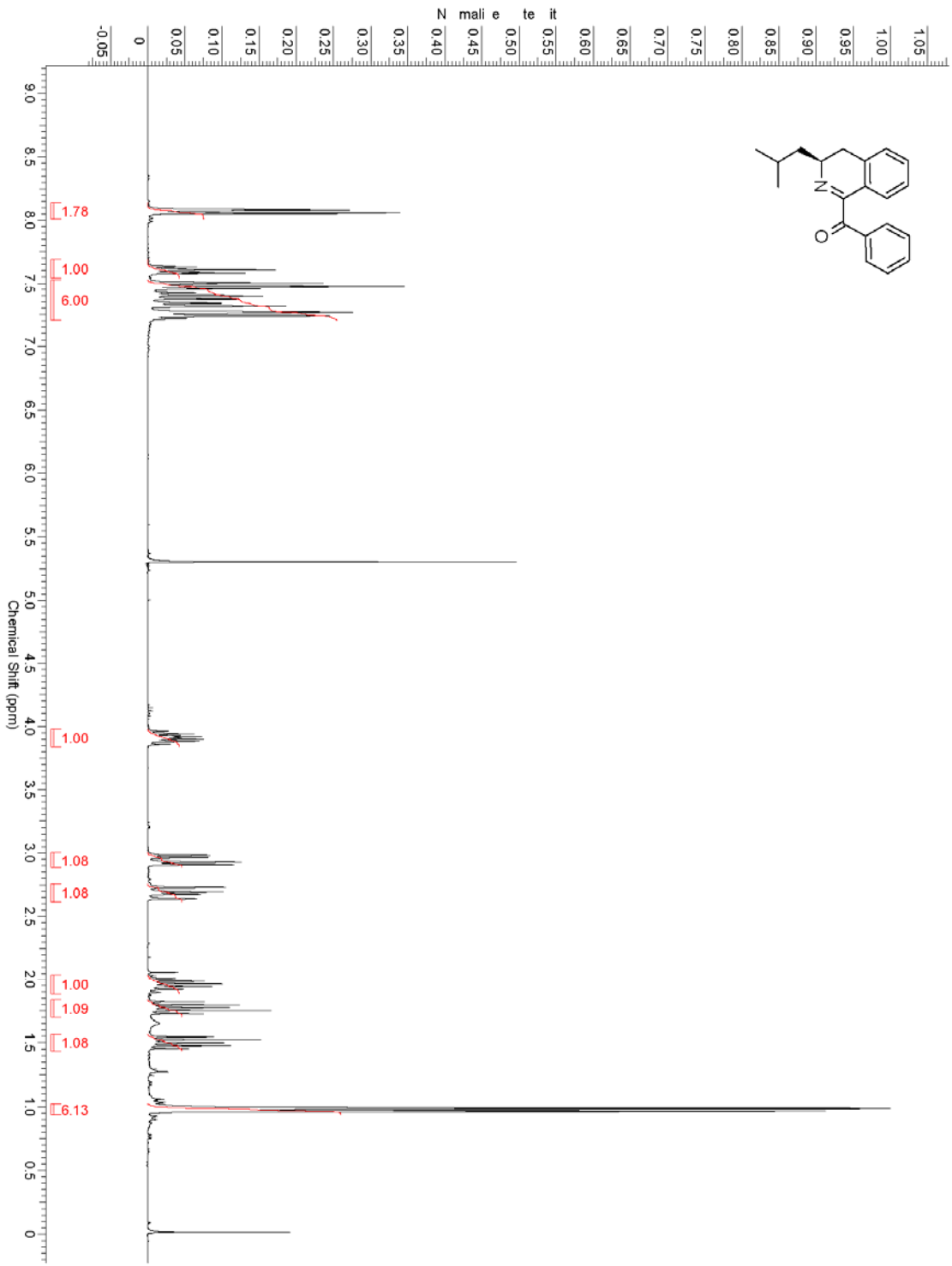
1.96
5.39
0.89
1.00
2.05
1.03
2.03
5.92
NH
O
O


N mali e te it
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NH
O
O


N mali e te it
Chemical Shift (ppm)
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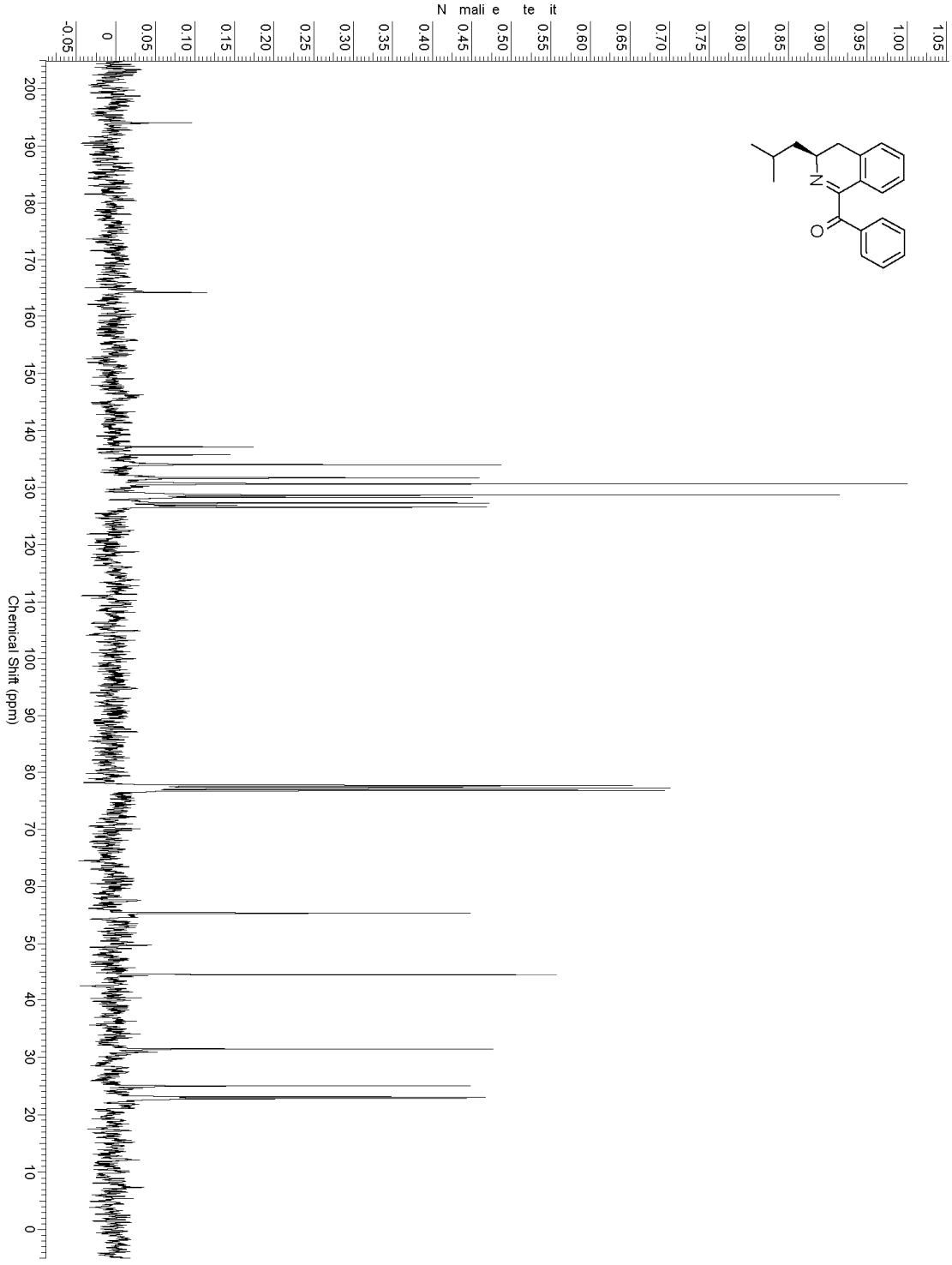
1.00
1.08
1.08
1.00
1.09
1.08
6.13
N
O


N mali e te it
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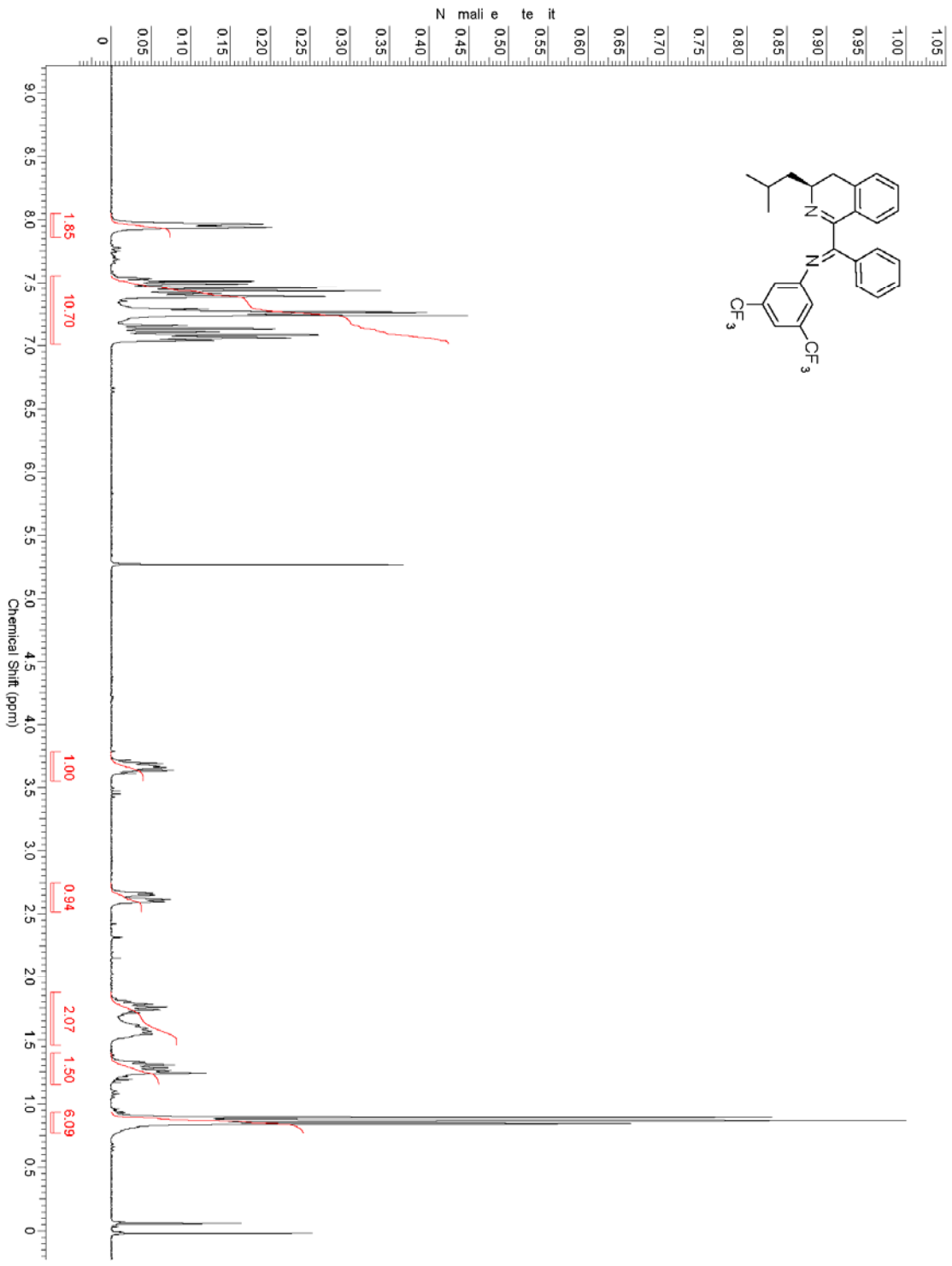
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
O


N mali e te it
Chemical Shift (ppm)
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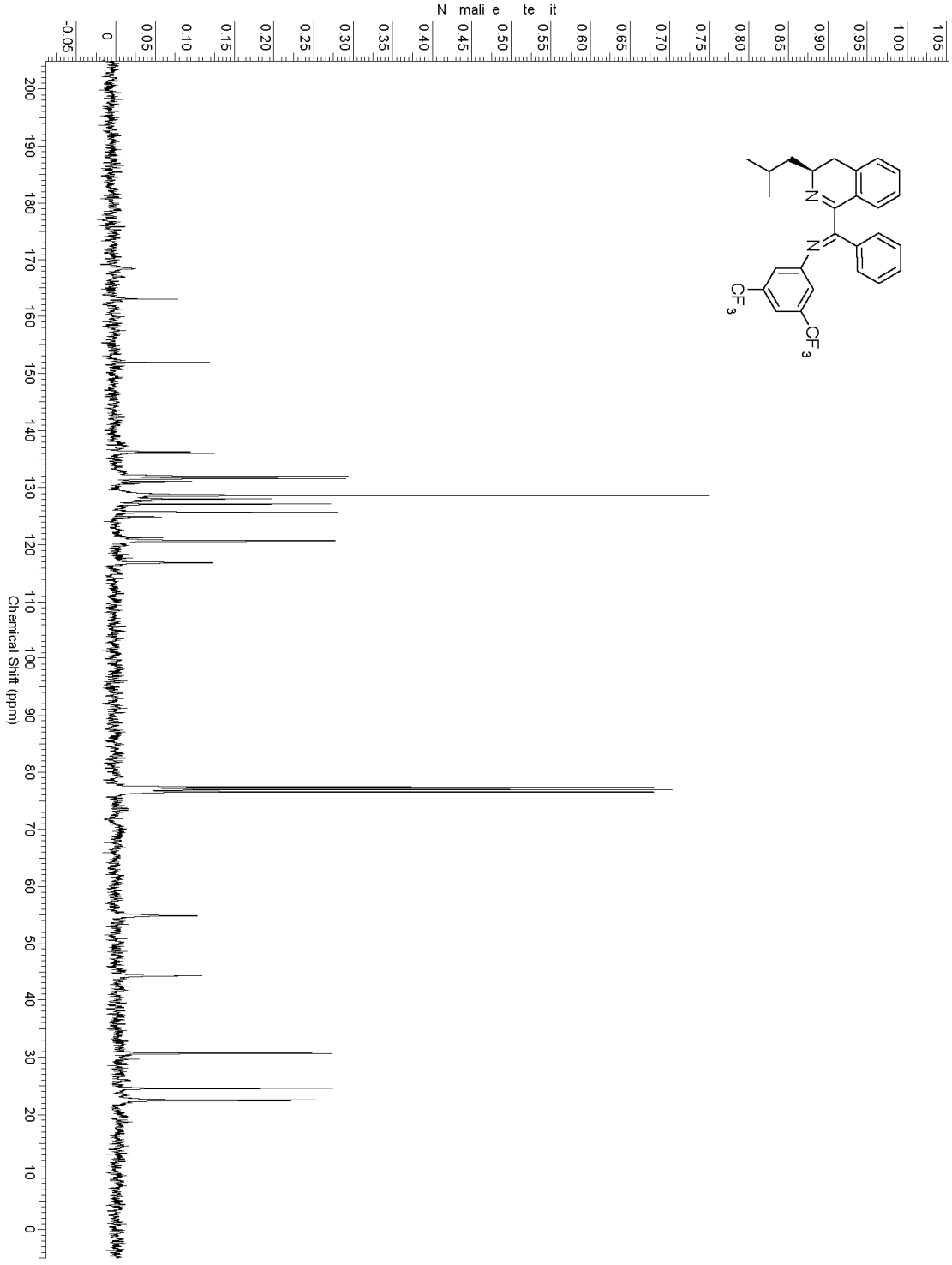
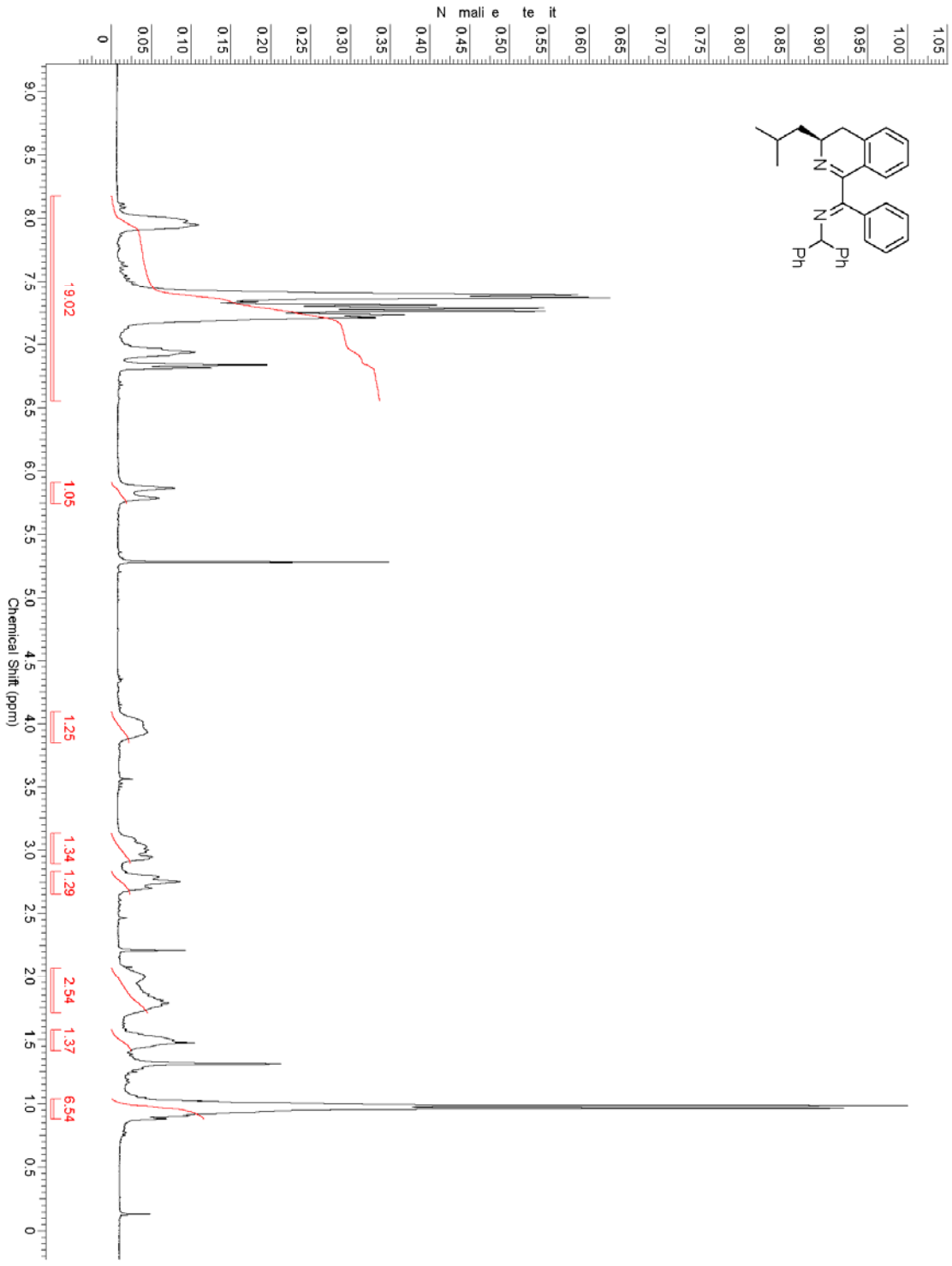
6.09
N
N
CF3
CF3


N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
N
N
CF3
CF3


N mali e te it
Chemical Shift (ppm)
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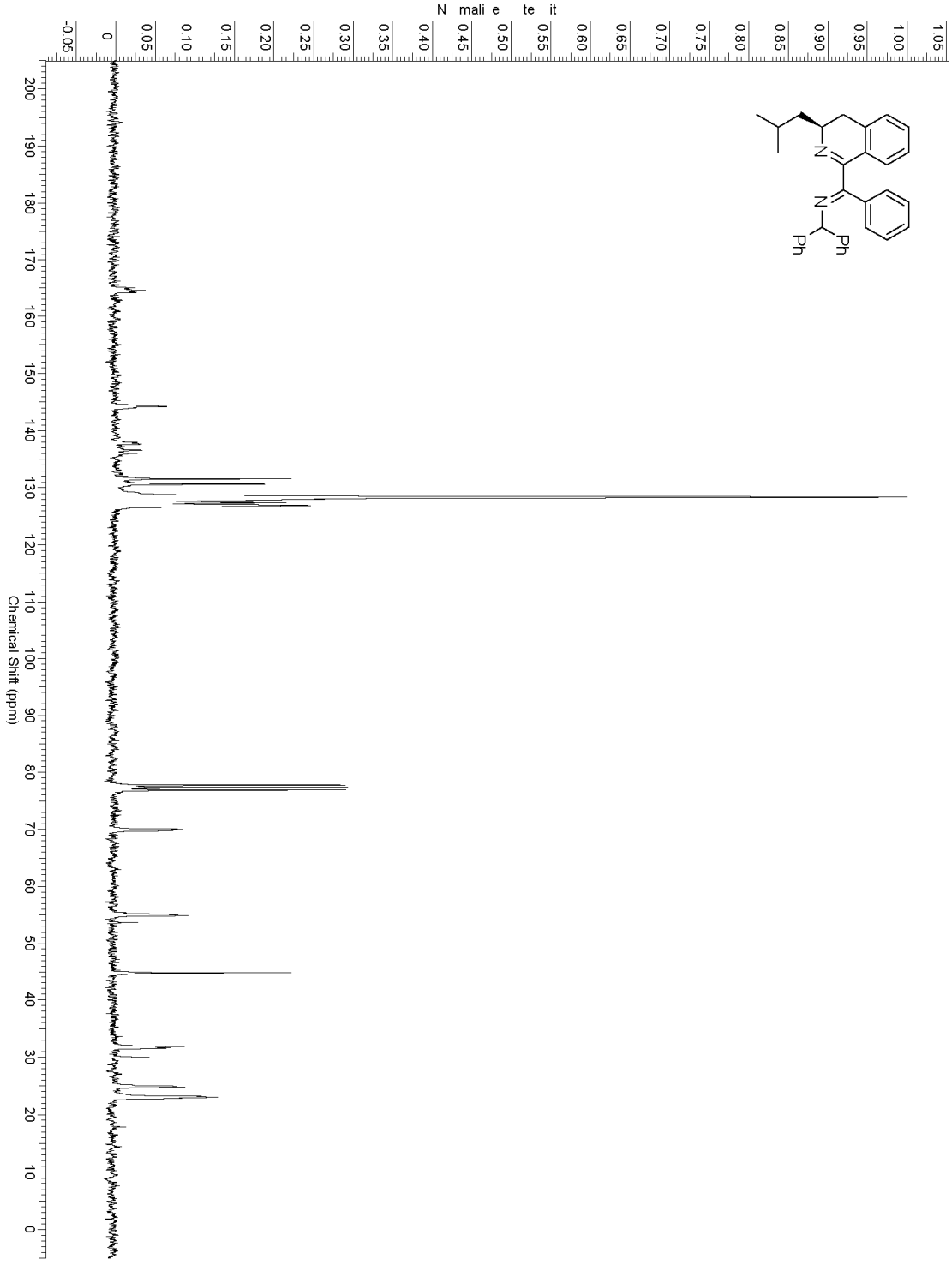
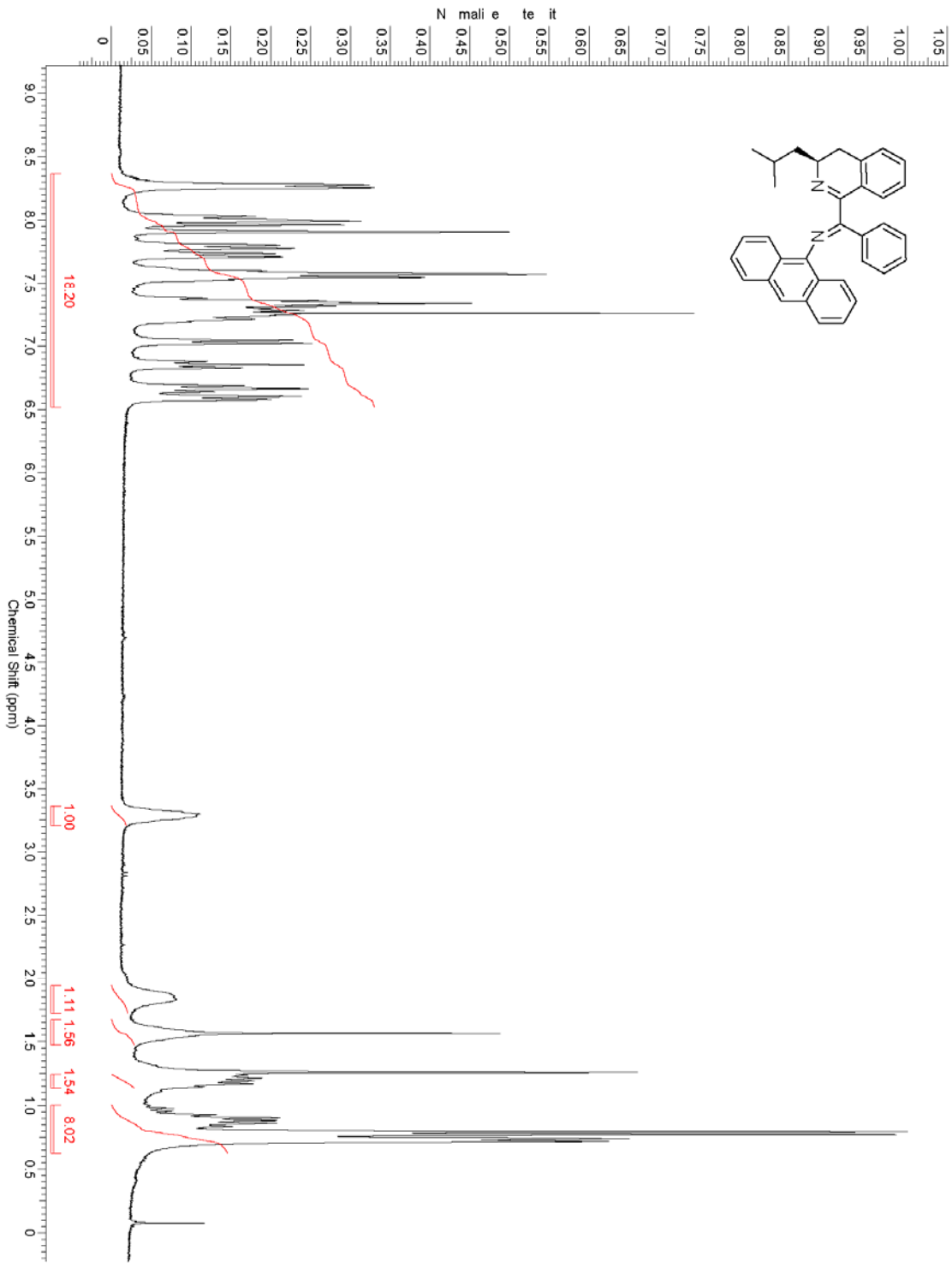
1.34
1.29
2.54
1.37
6.54
N
N
Ph
Ph


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N
Ph
Ph


N mali e te it
Chemical Shift (ppm)
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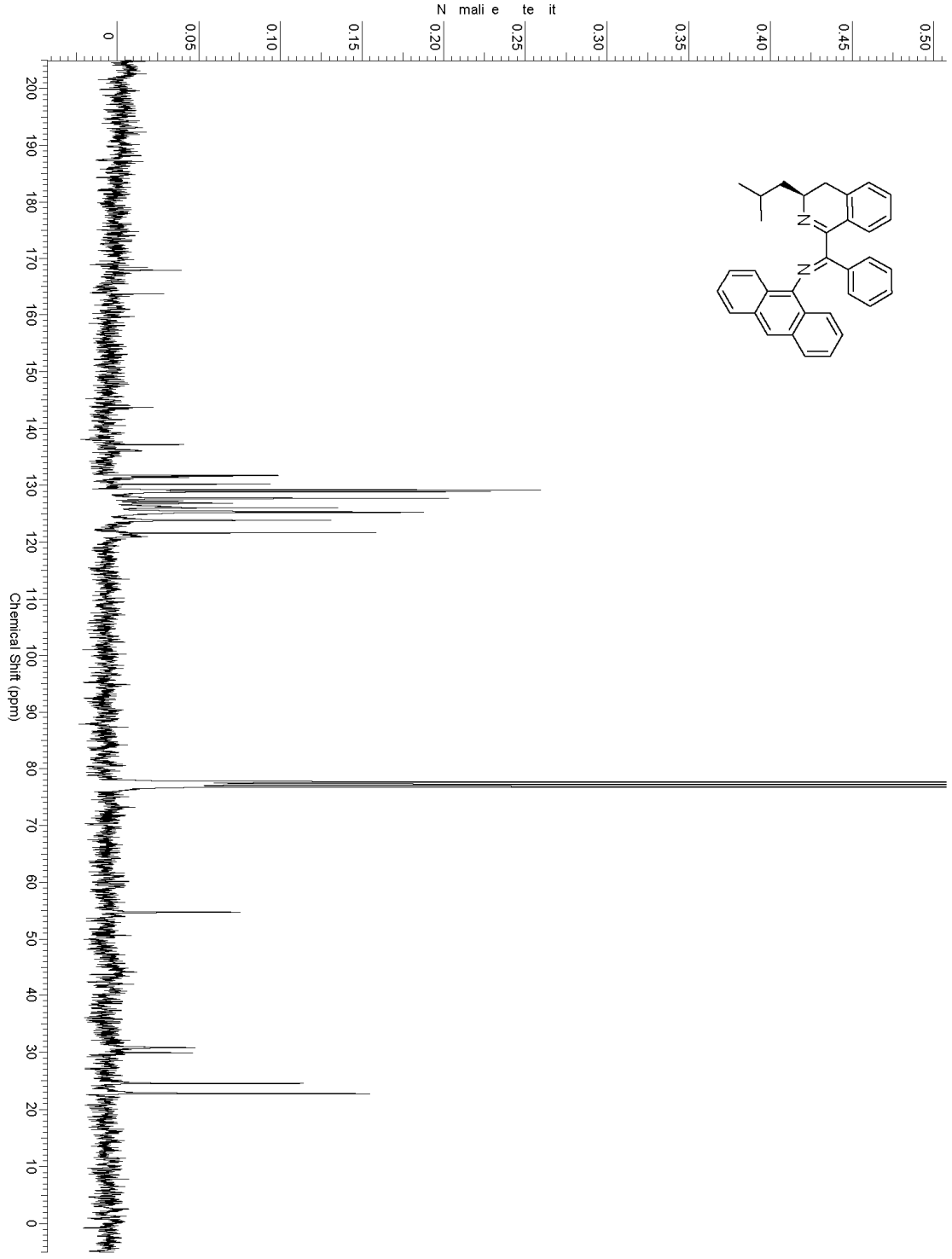
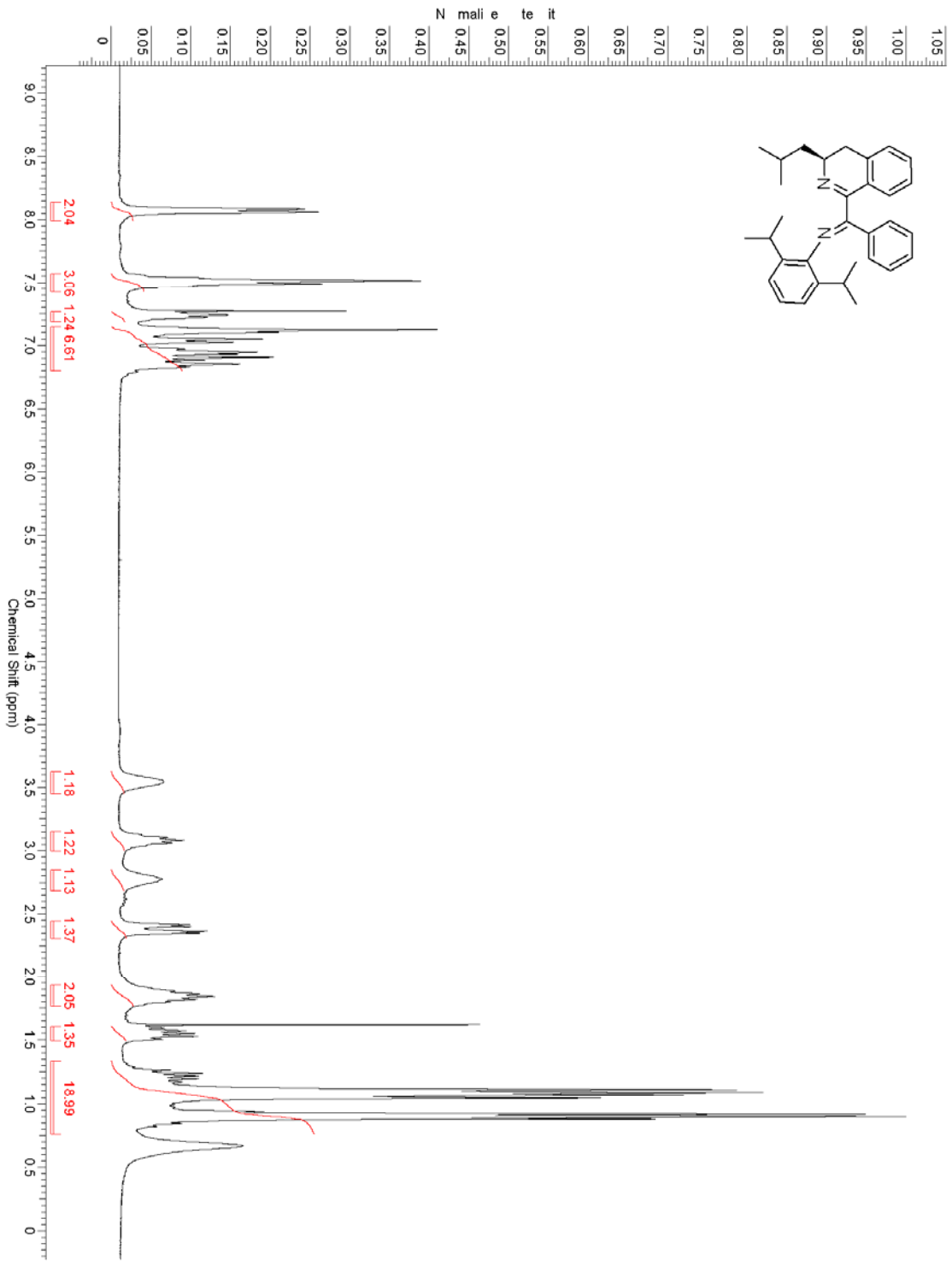
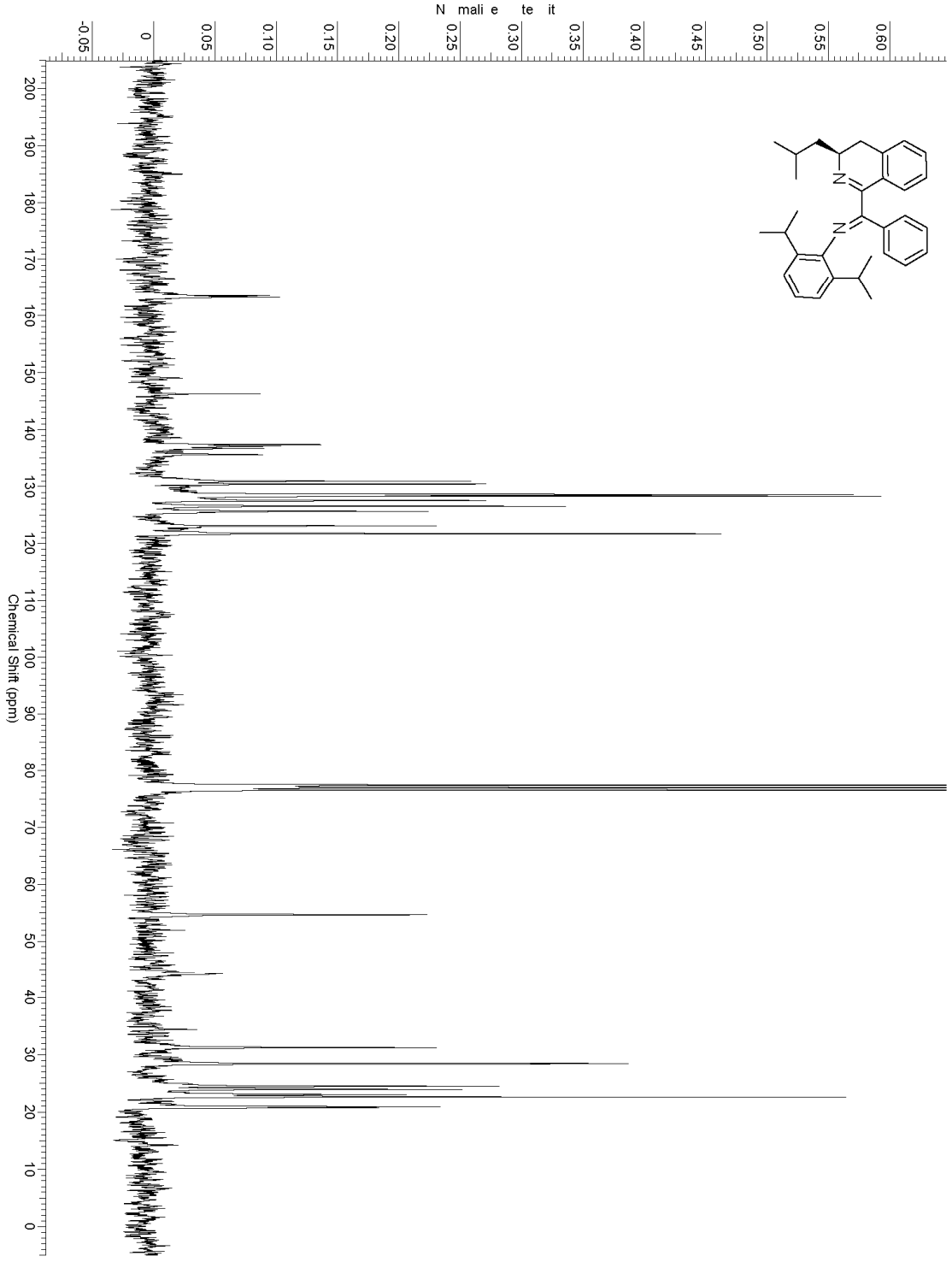
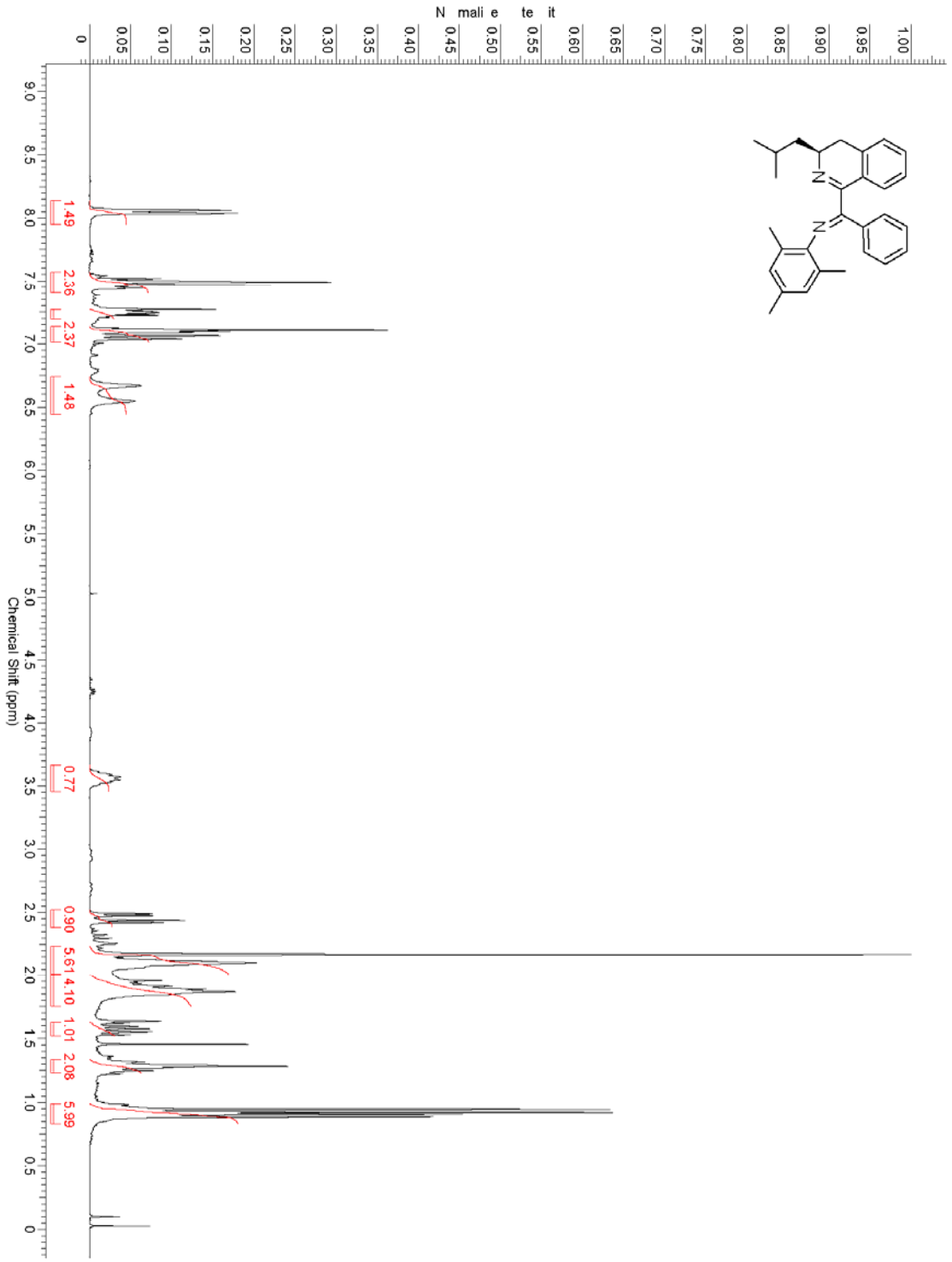
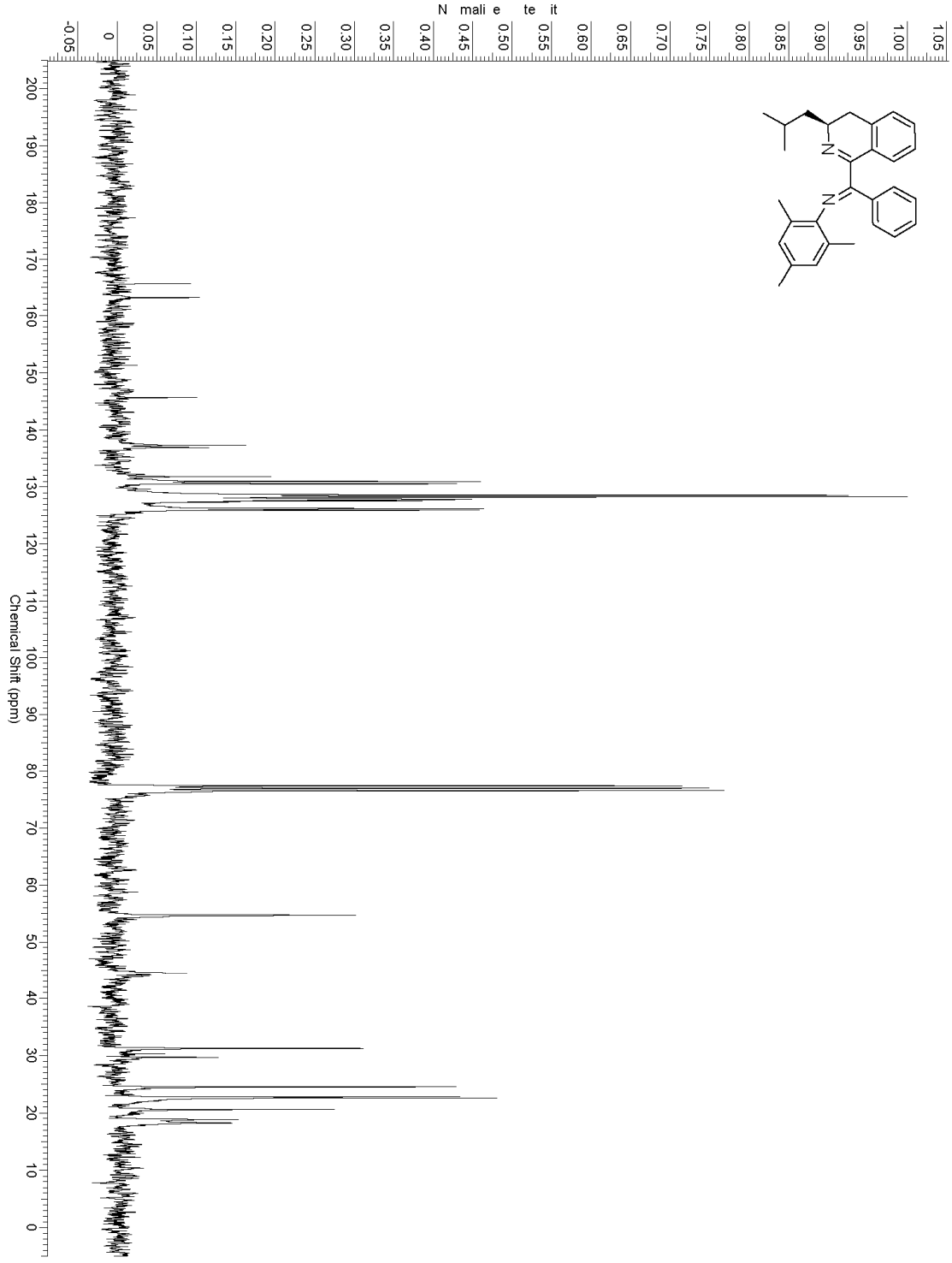
1.00
1.11
1.56
1.54
8.02
N
N

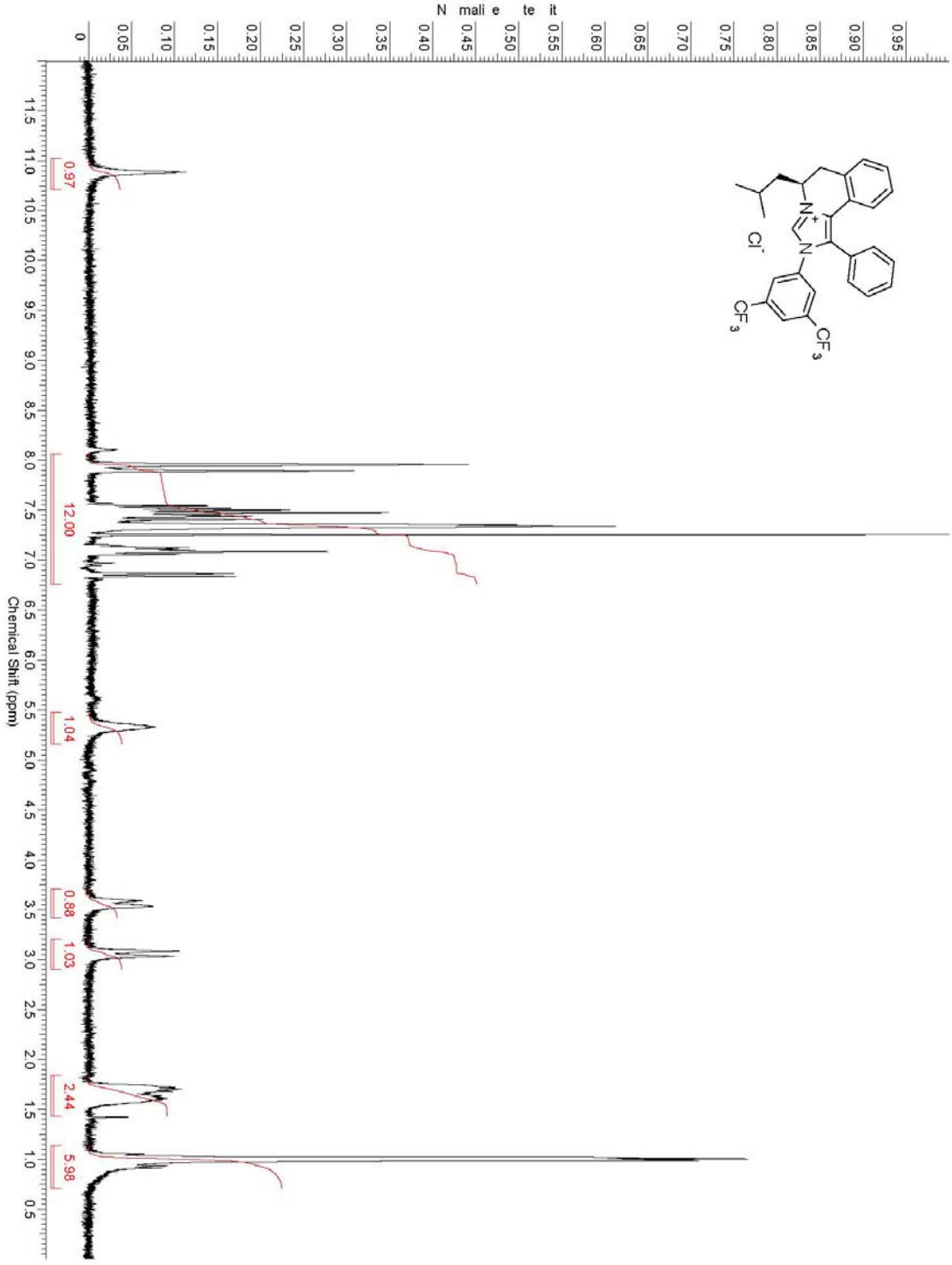

N mali e te it
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N

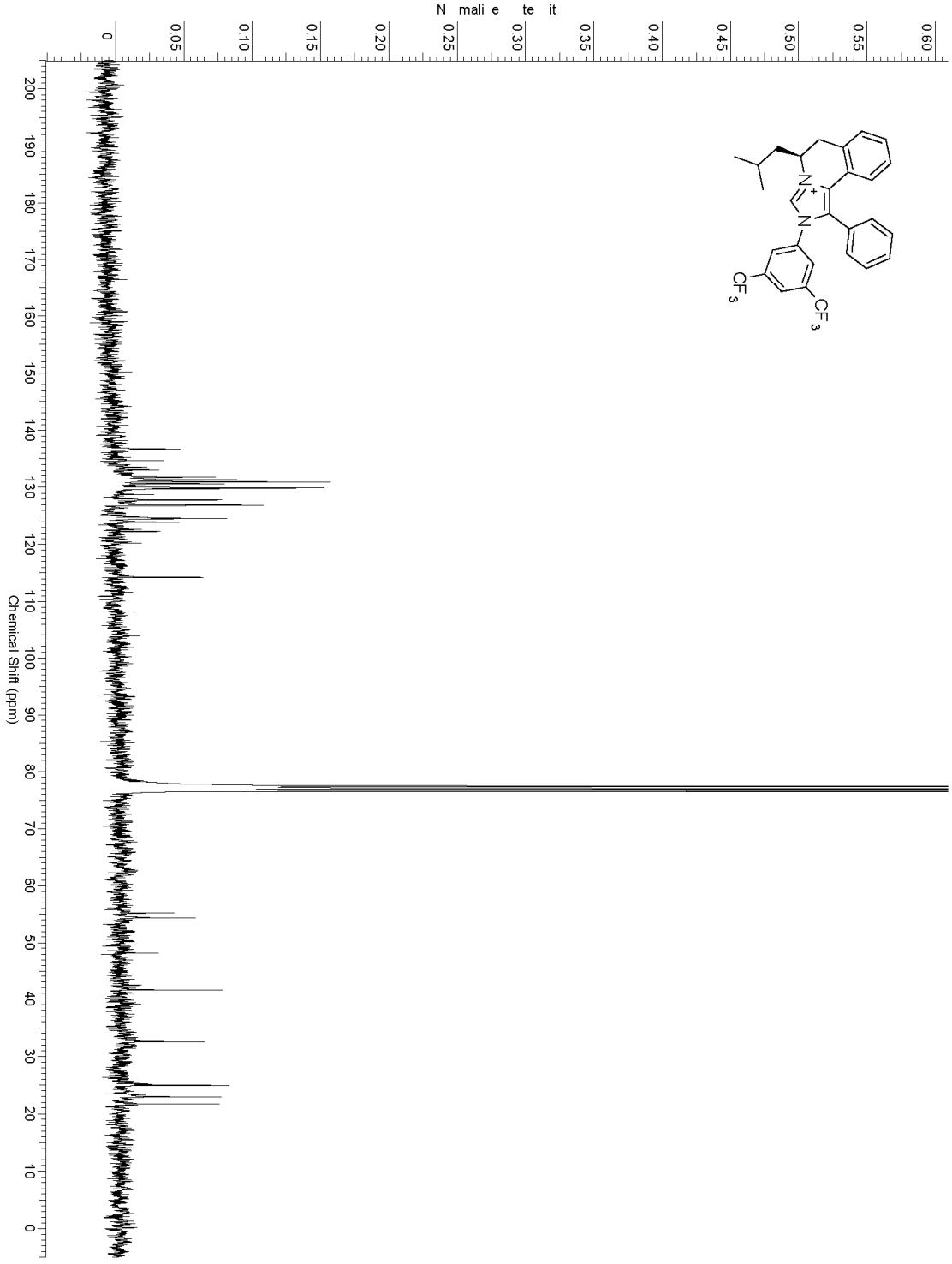

N mali e te it
Chemical Shift (ppm)
2.04
3.06
1.24
6.61
1.18
1.22
1.13
1.37
2.05
1.35
18.99

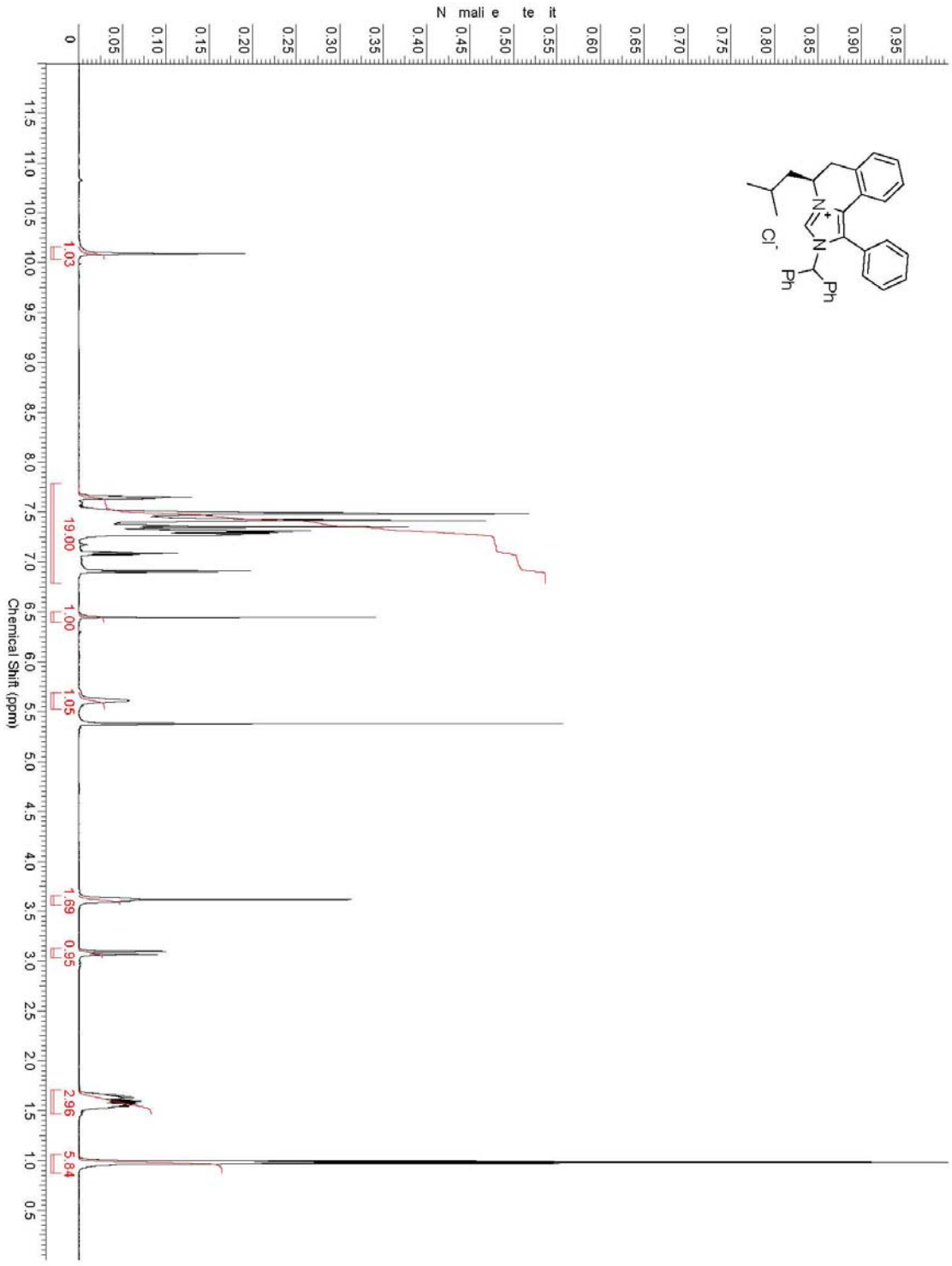

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N

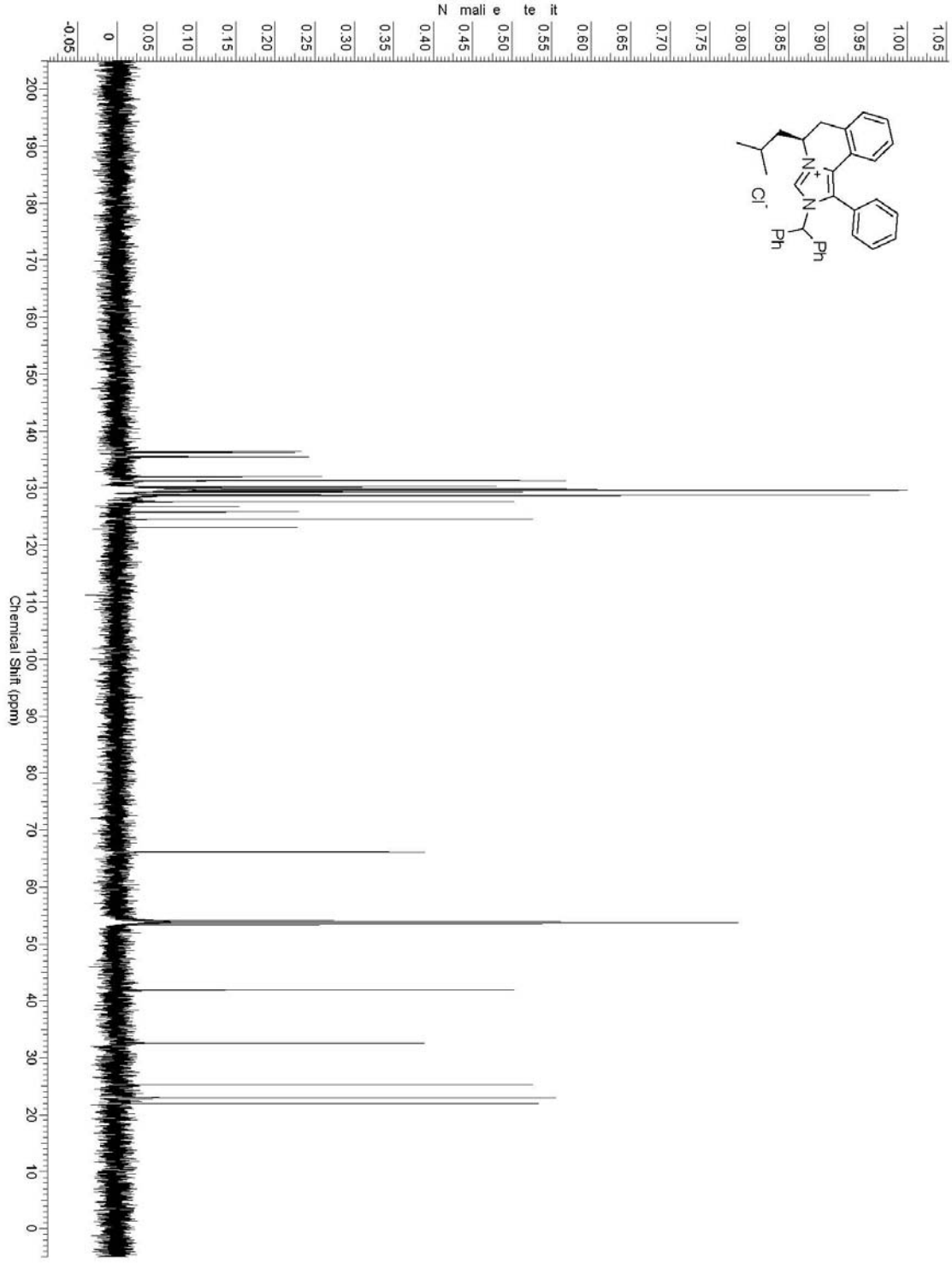

N mali e te it
0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00
Chemical Shift (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
1.49 2.36 2.37 1.48 0.77 0.90 5.61 4.10 1.01 2.08 5.99
N
N

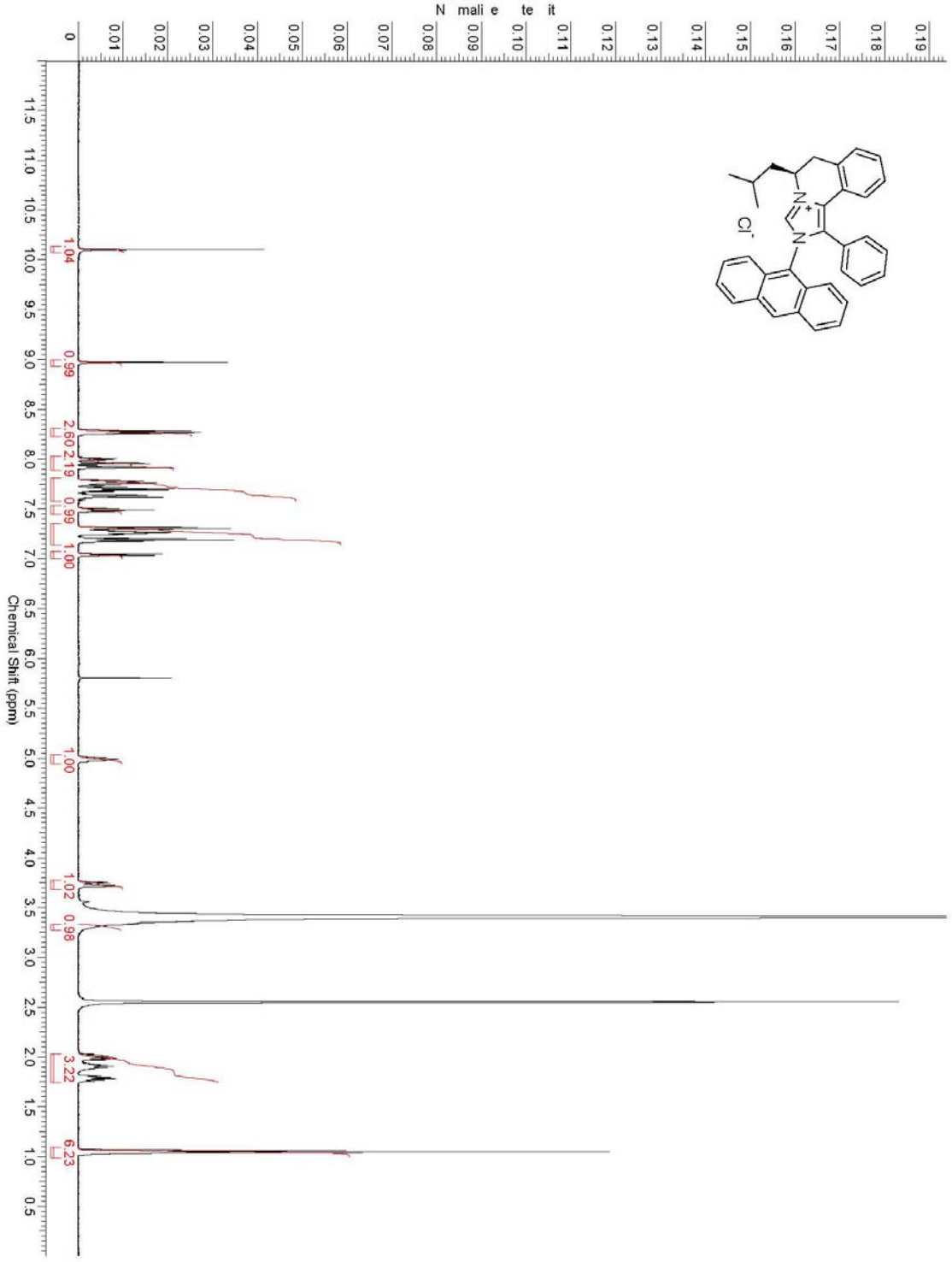

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
N
N

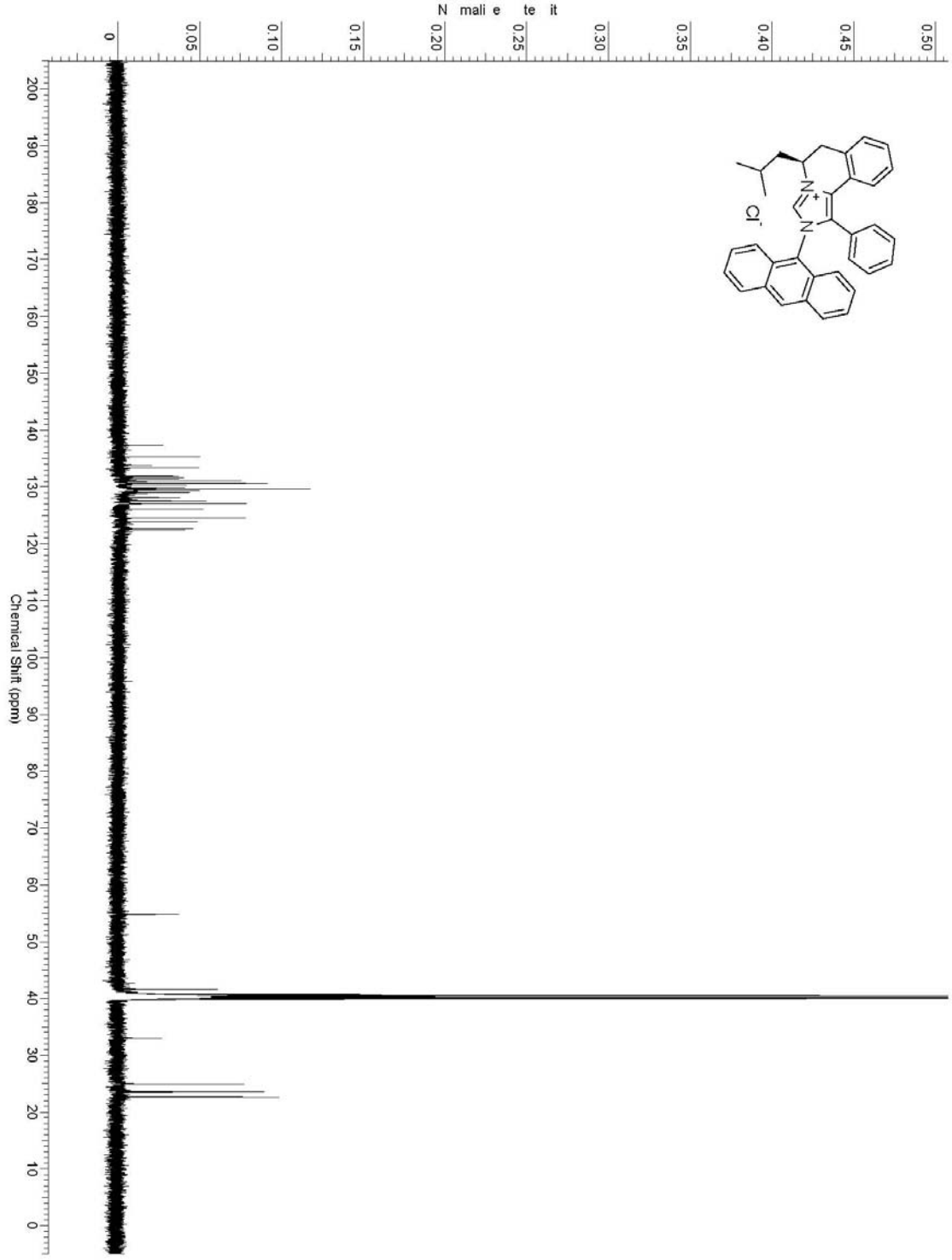

Normalized Intensity
Chemical Shift (ppm)
0.97
12.00
1.04
0.88
1.03
2.44
5.98
Cl⁻
CF3
CF3

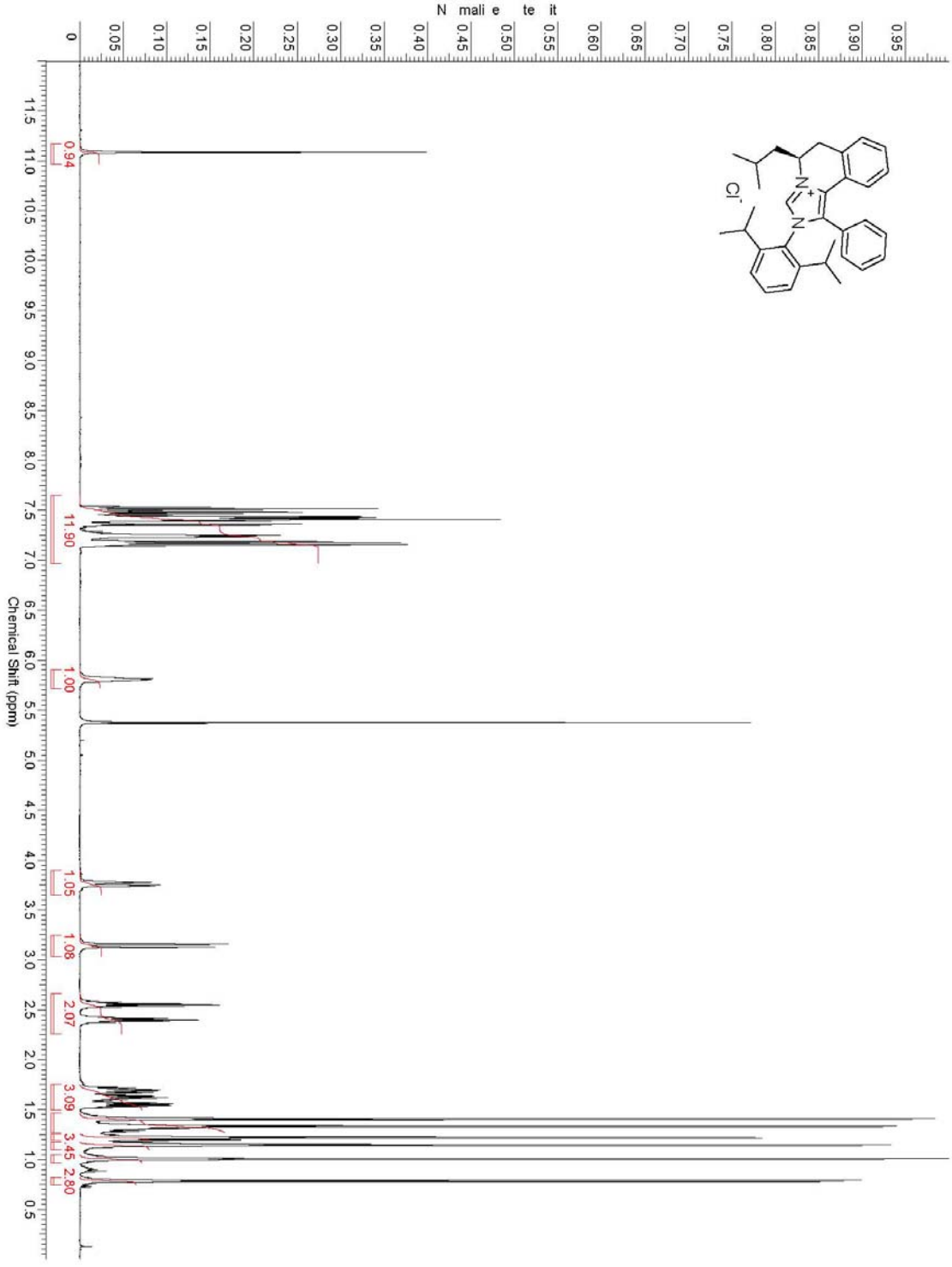

N mali e te it
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N+
N
CF3
CF3

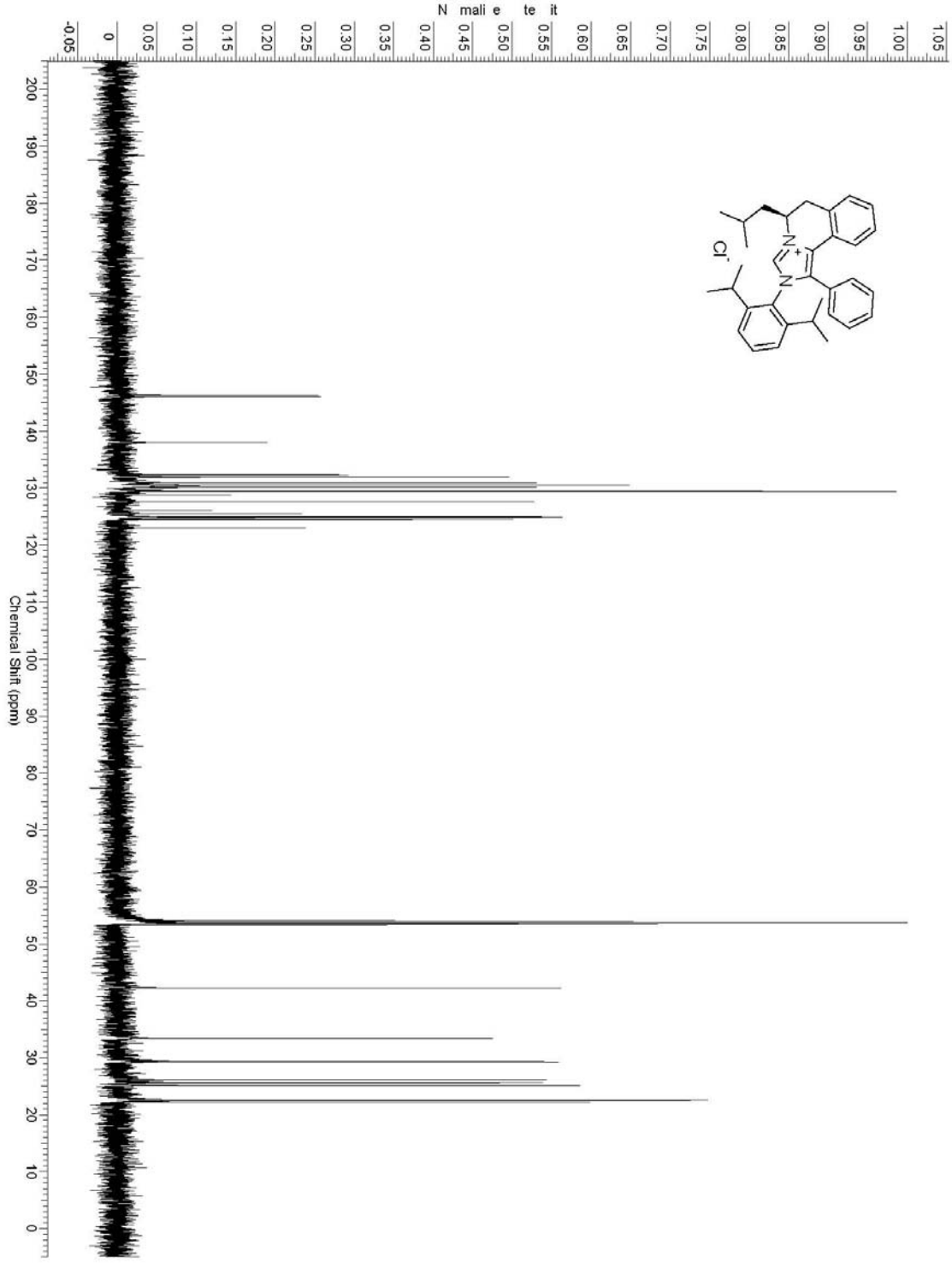

N mali e te it
Chemical Shift (ppm)
1.03
19.00
1.00
1.05
1.69
0.95
2.96
5.84
Cl
N
N
Ph
Ph

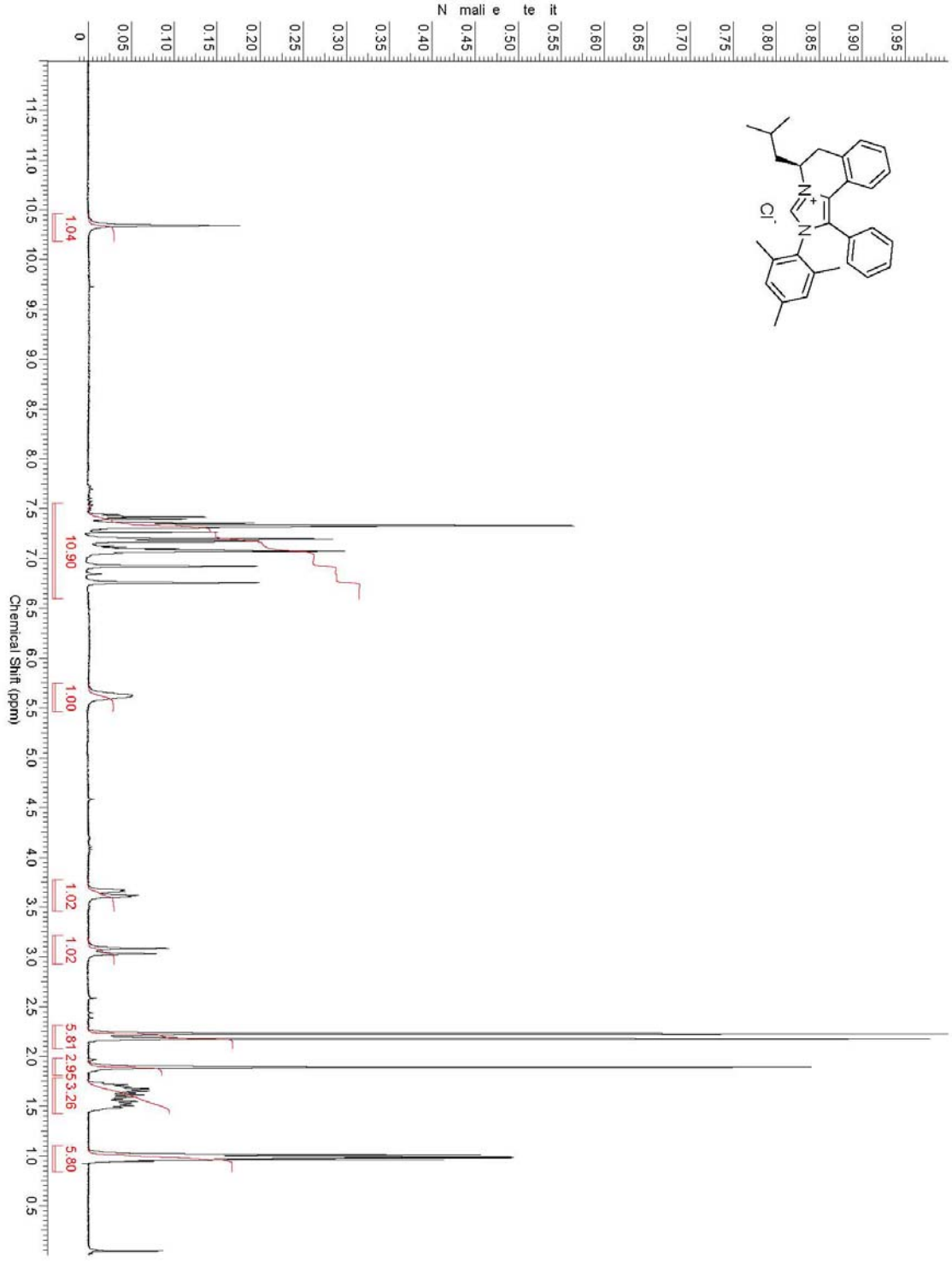

Normalized Intensity
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N+
N
Cl-
Ph
Ph

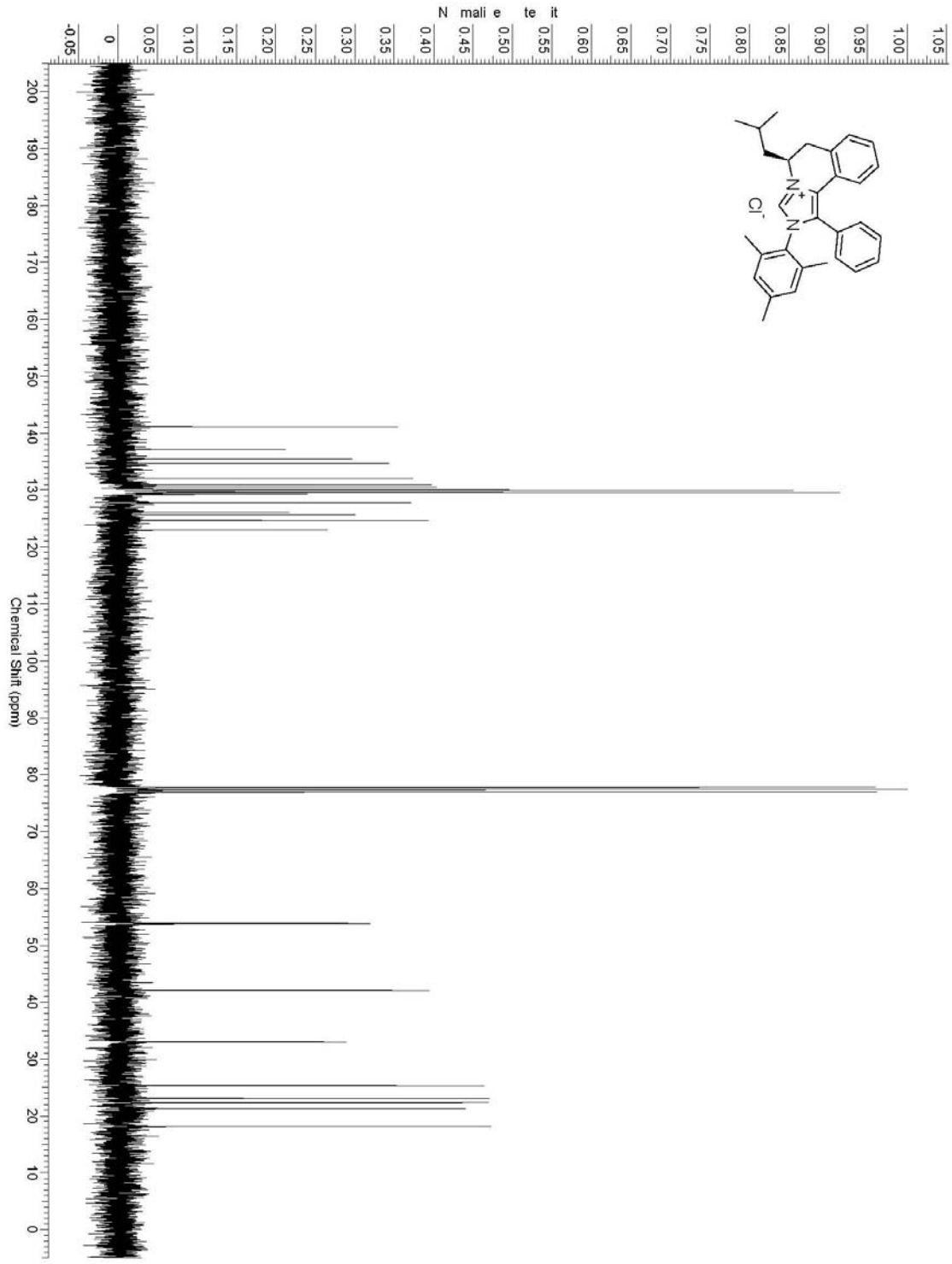

N mali e te it
Chemical Shift (ppm)
1.04
0.99
2.60
2.19
0.99
1.00
1.00
1.02
0.98
3.22
6.23
Cl⁻

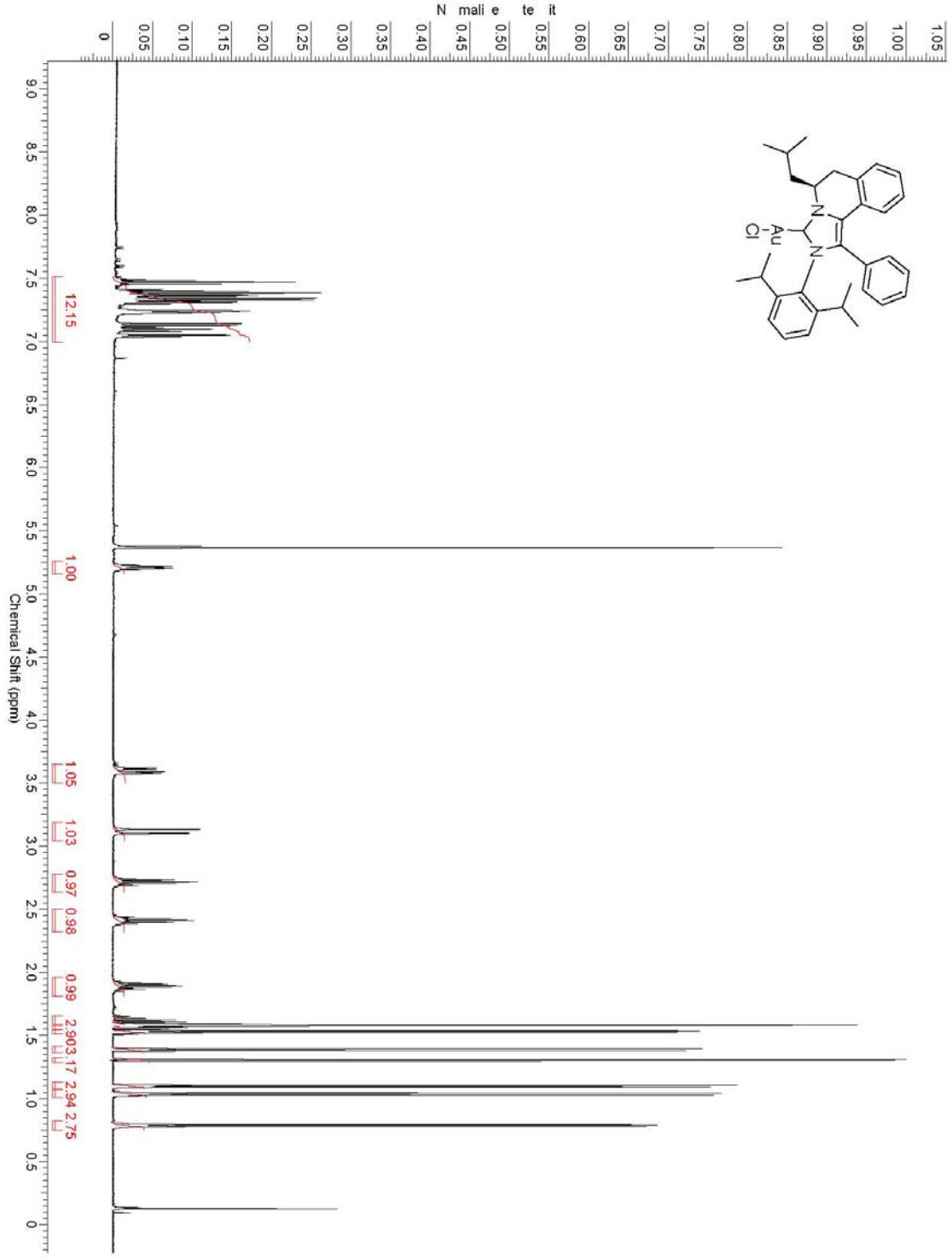

N mali e te it
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl-

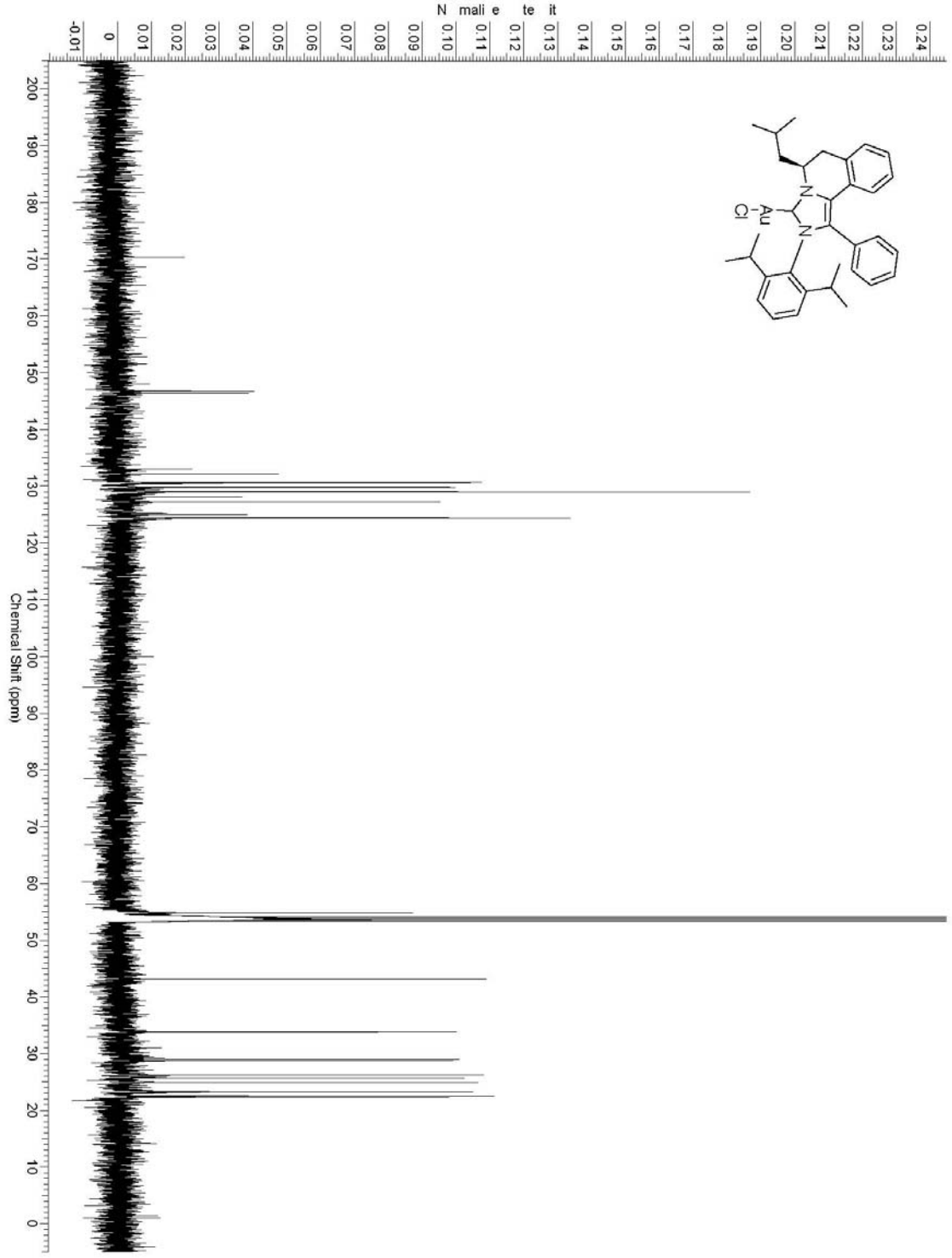

Normalized to
Chemical Shift (ppm)
0.94
11.90
1.00
1.05
1.08
2.07
3.09
3.45
2.80
Cl⁻

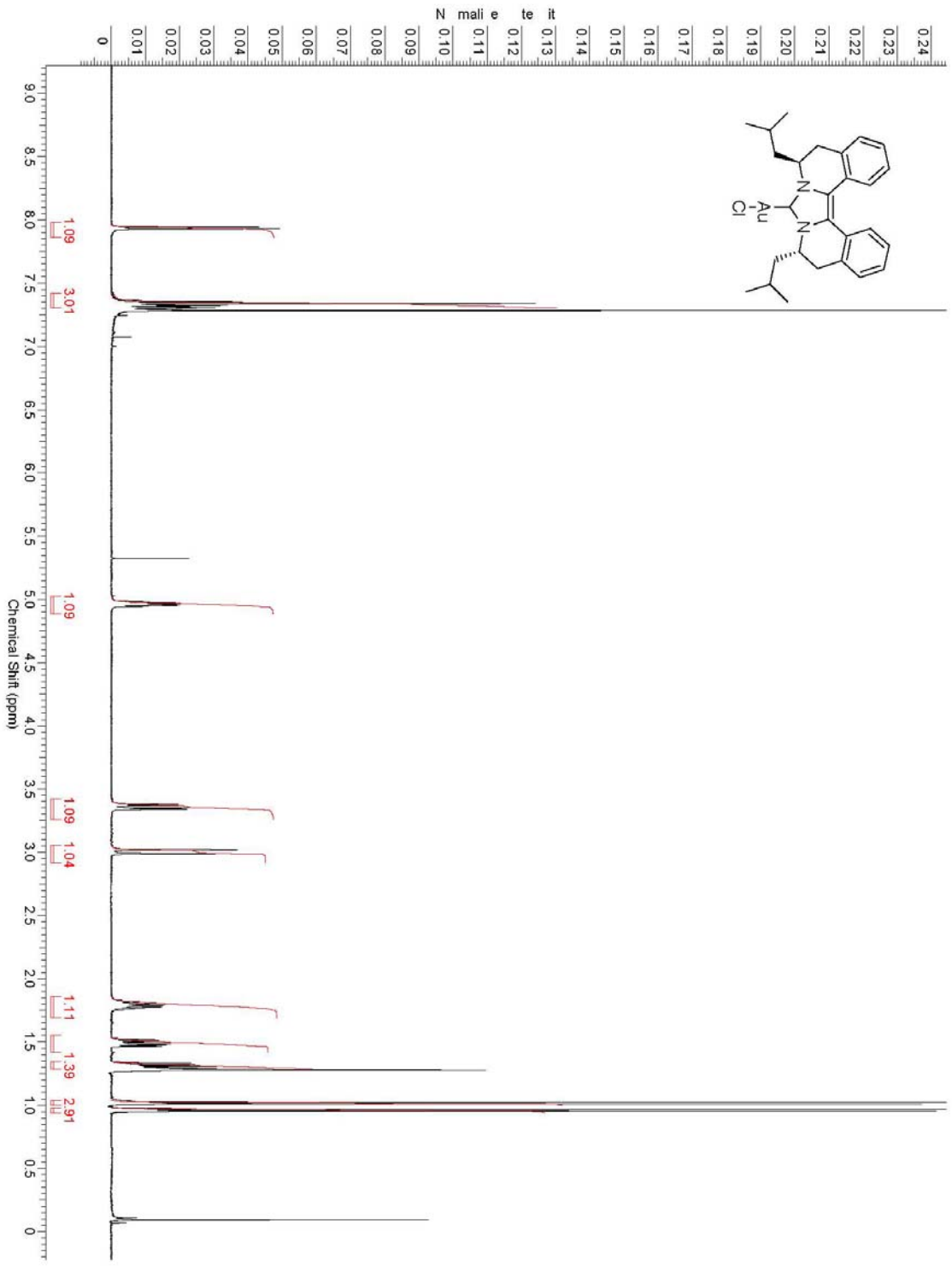

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl-
N+
N

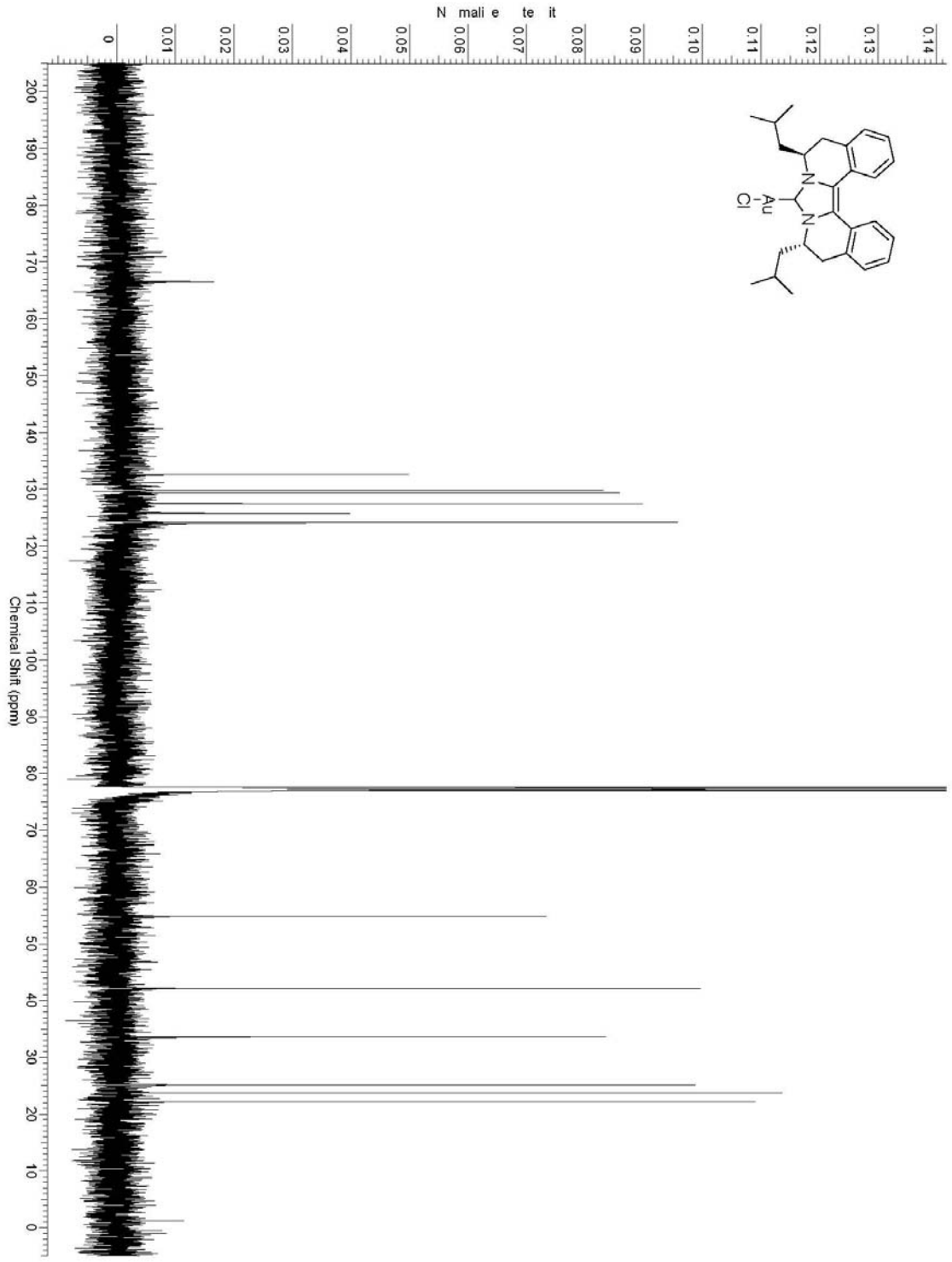

N mali e te it
Chemical Shift (ppm)
1.04
10.90
1.00
1.02
1.02
5.81
2.95
3.26
5.80
Cl-


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N+
N
Cl-

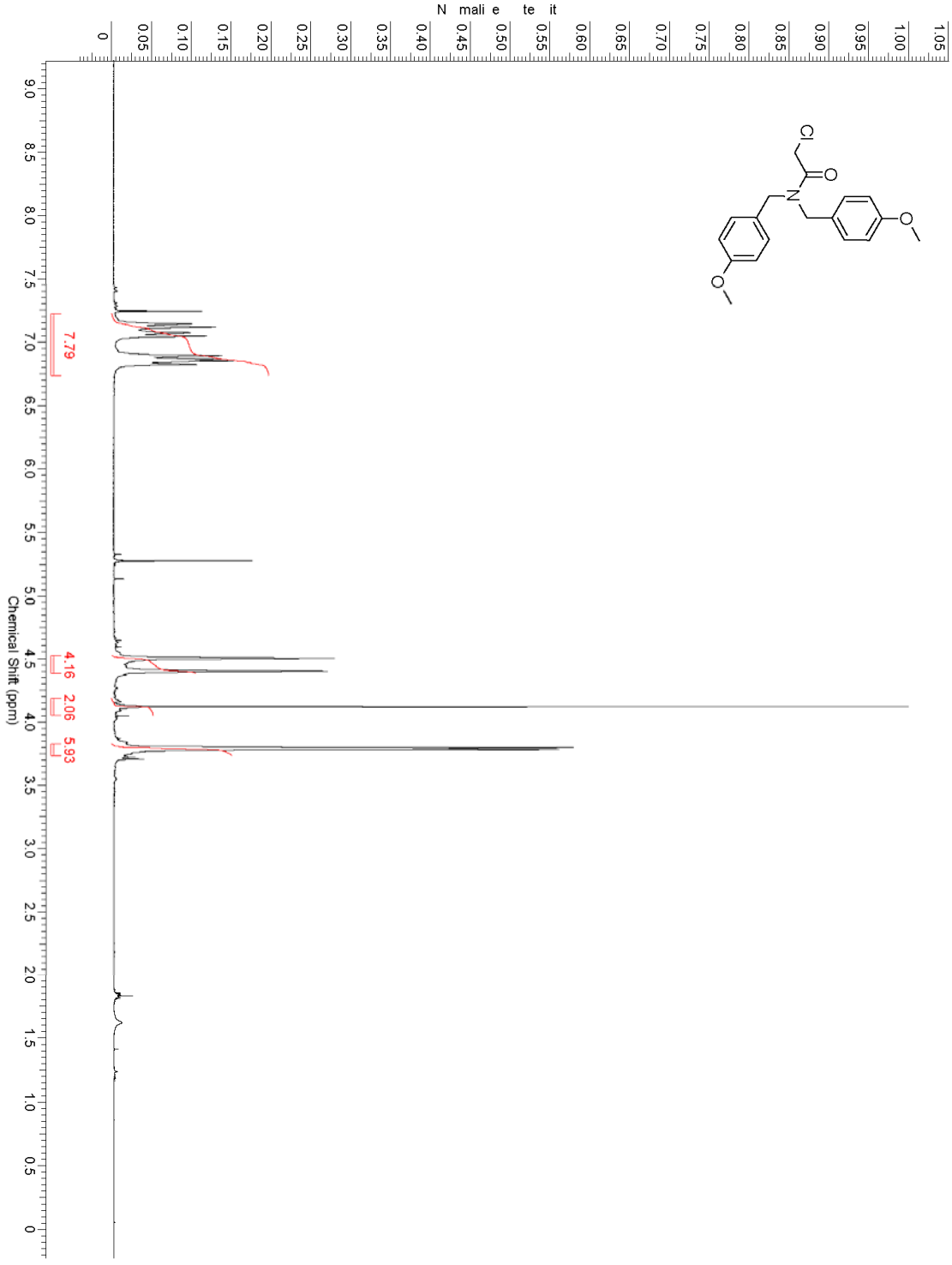

N mali e te it
Chemical Shift (ppm)
12.15
1.00
1.05
1.03
0.97
0.98
0.99
2.90
3.17
2.94
2.75
N
Au
Cl

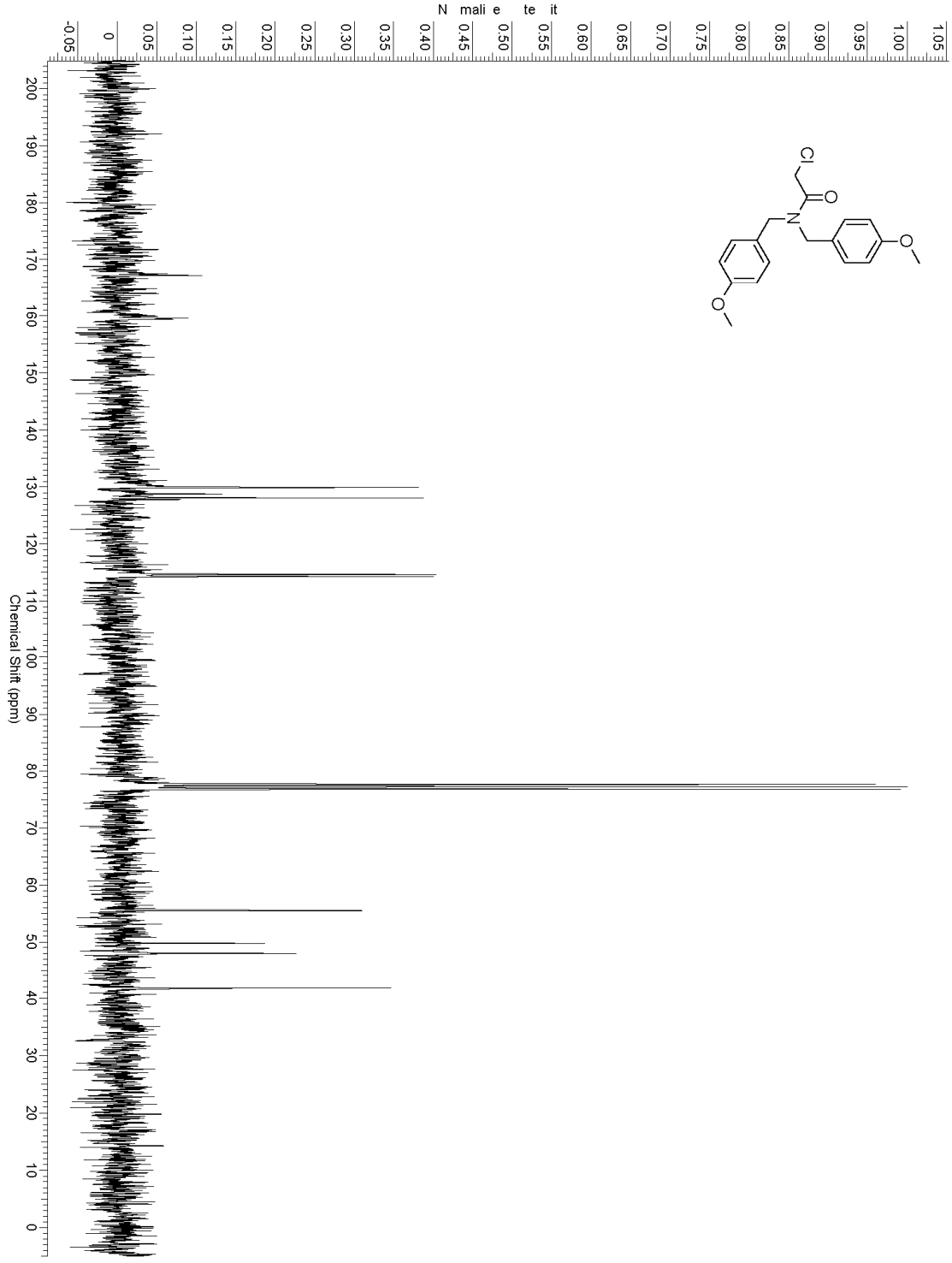

N mali e te it
-0.01
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.20
0.21
0.22
0.23
0.24
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
Au
Cl
N

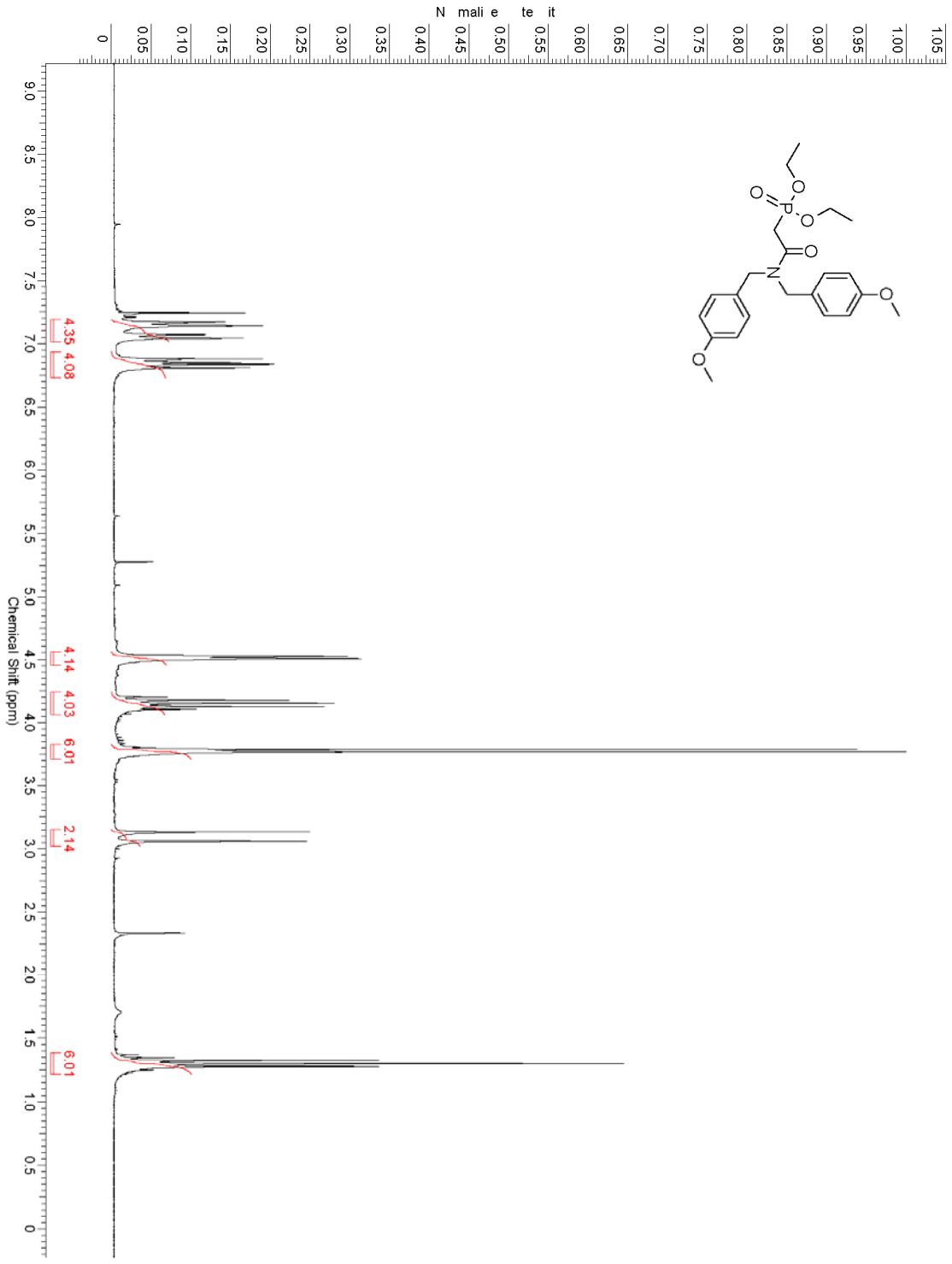

N mali e te it
Chemical Shift (ppm)
1.09
3.01
1.09
1.09
1.04
1.11
1.39
2.91
Cl
Au
N
N

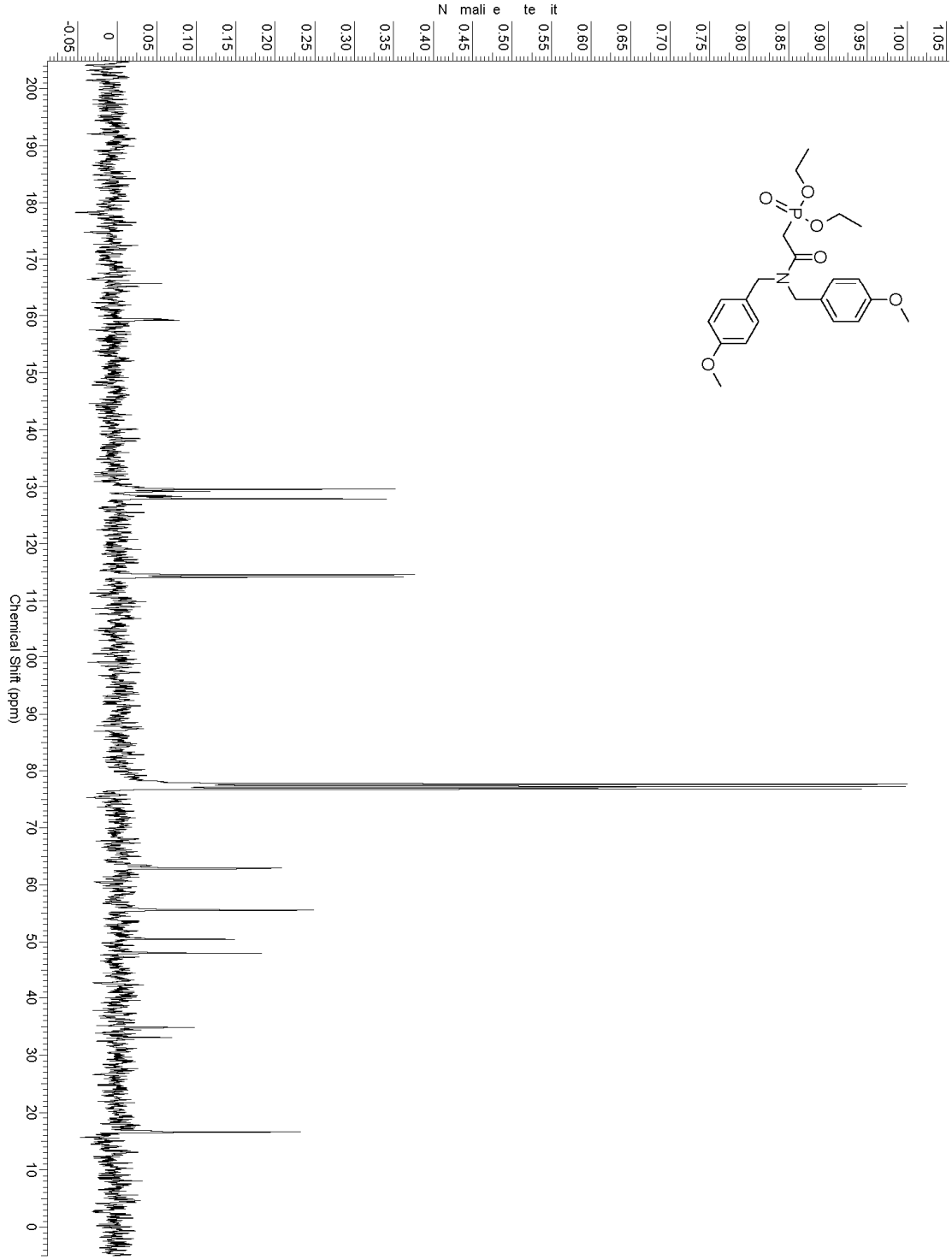

N mali e te it
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
0.13
0.14
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N
Au
Cl

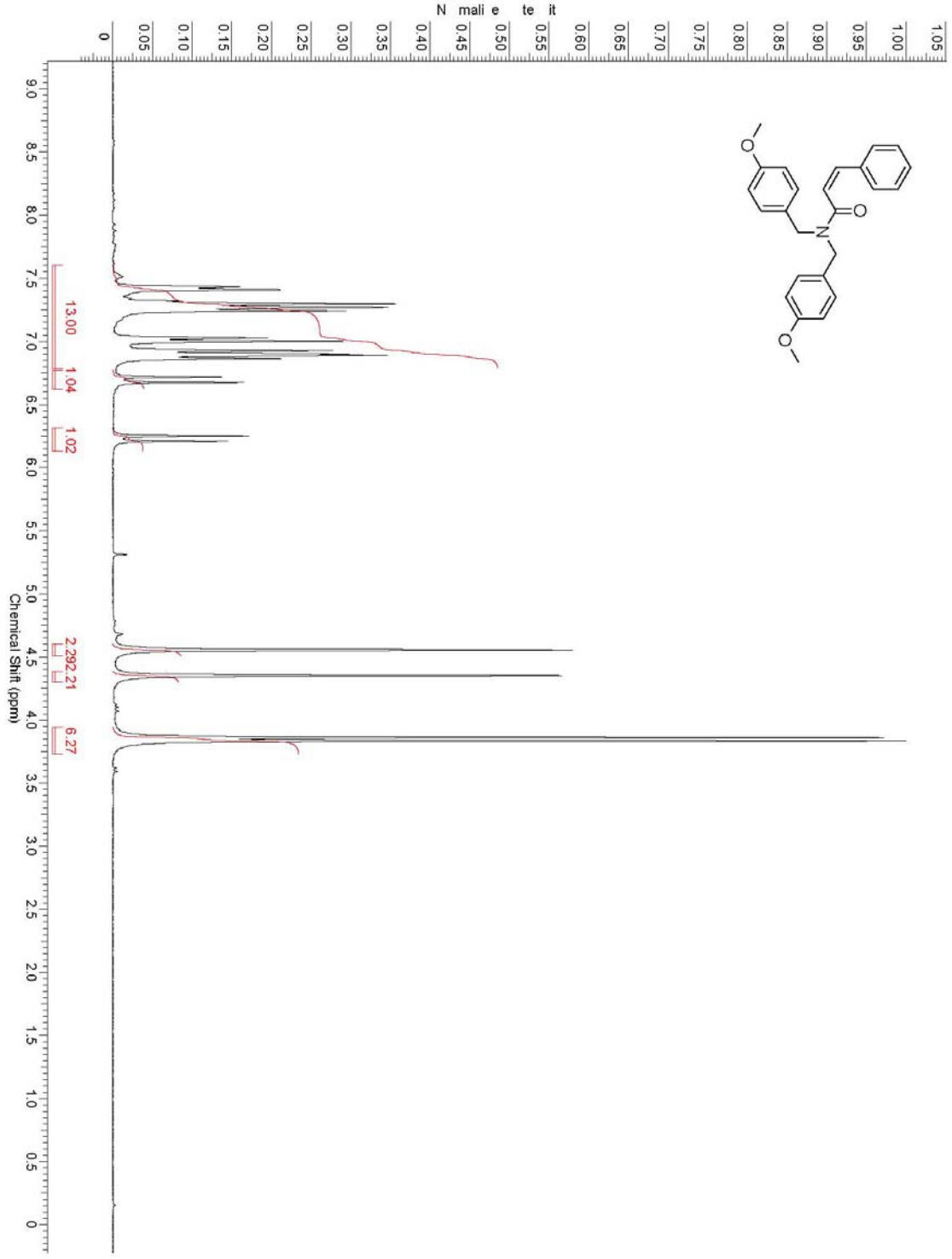
7. NMR spectra for substrates

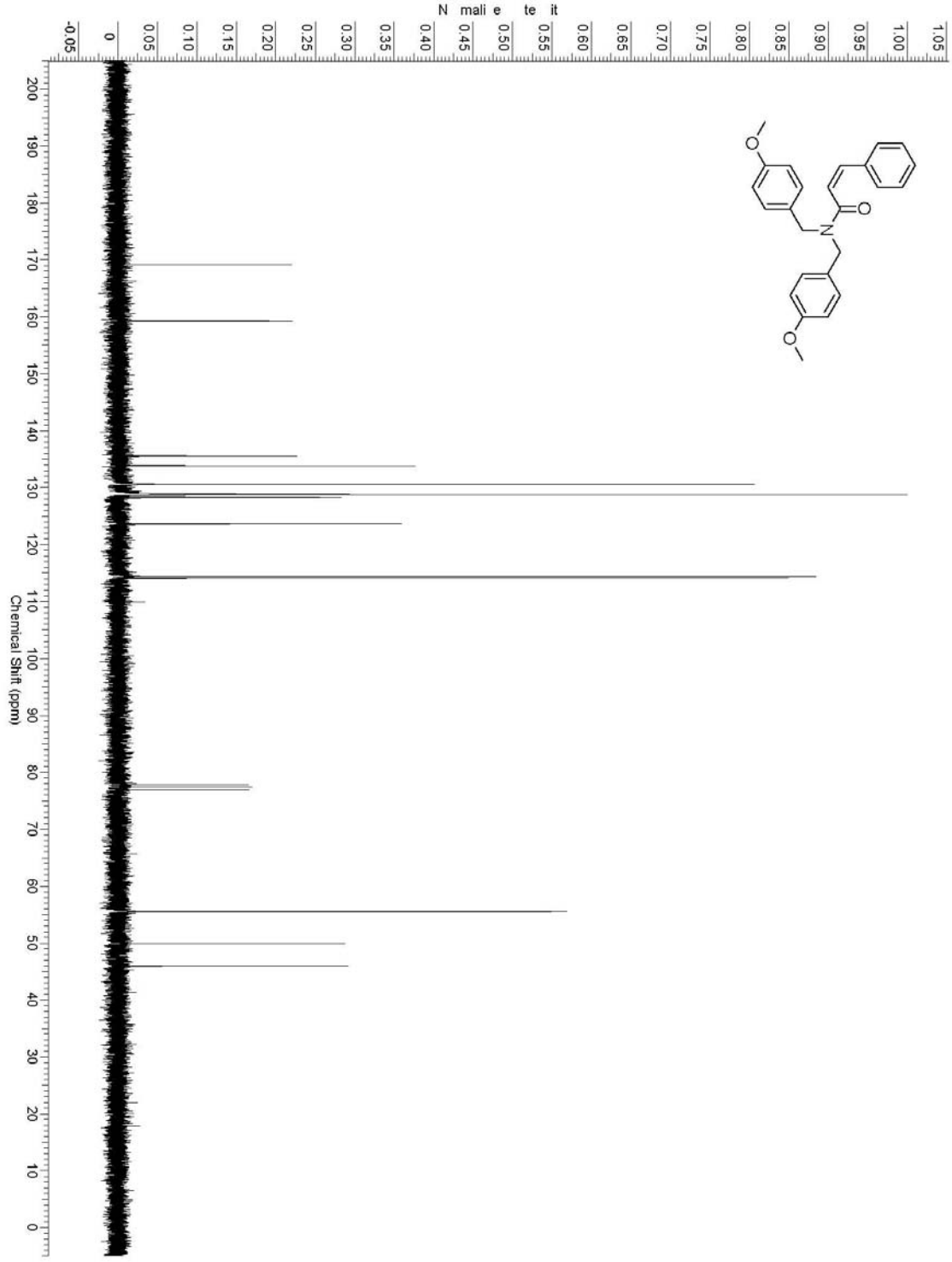

N mali e te it
Chemical Shift (ppm)
7.79
4.16
2.06
5.93
Cl
O
N
O
O

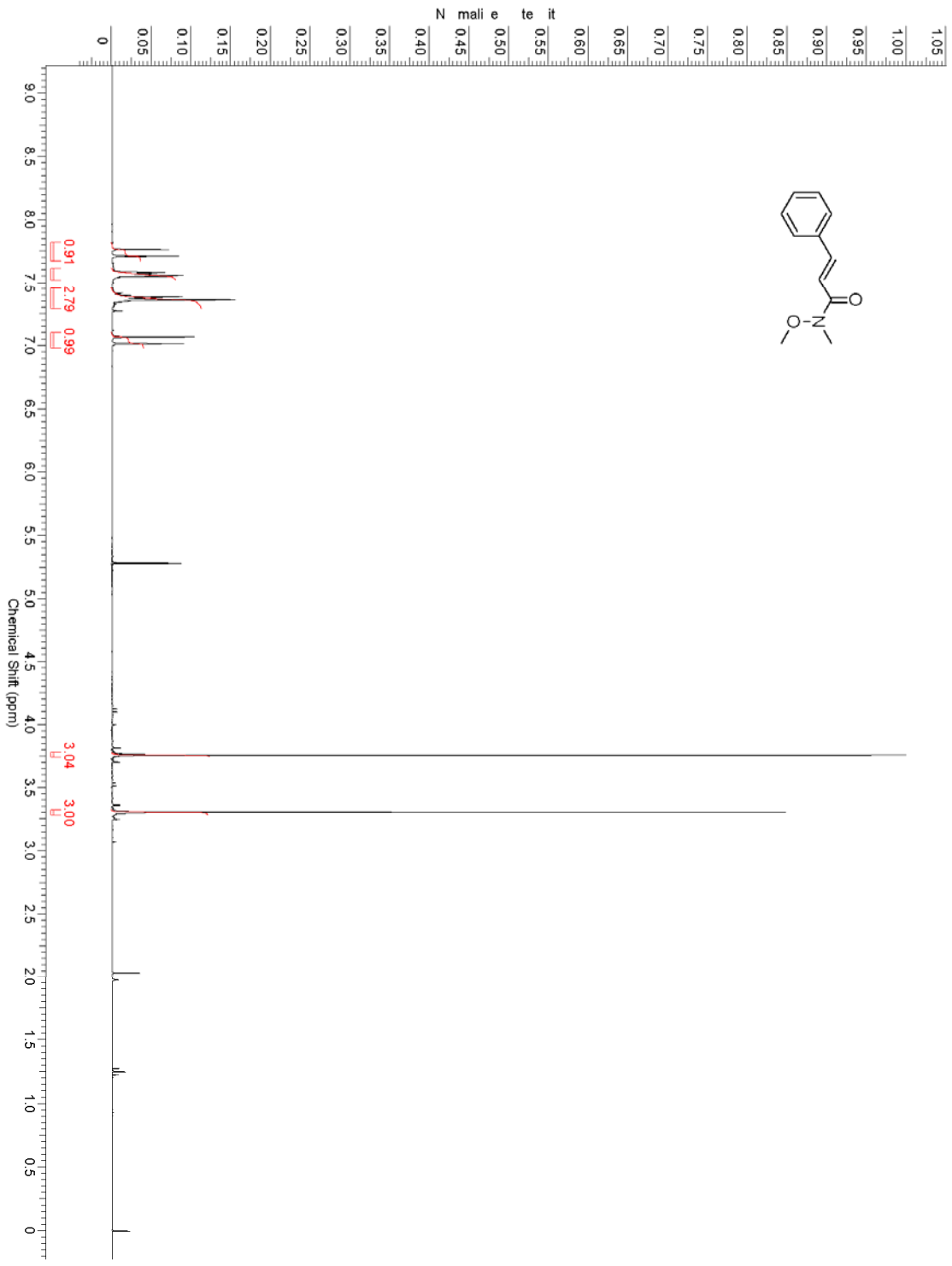

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl
O
N
O
O

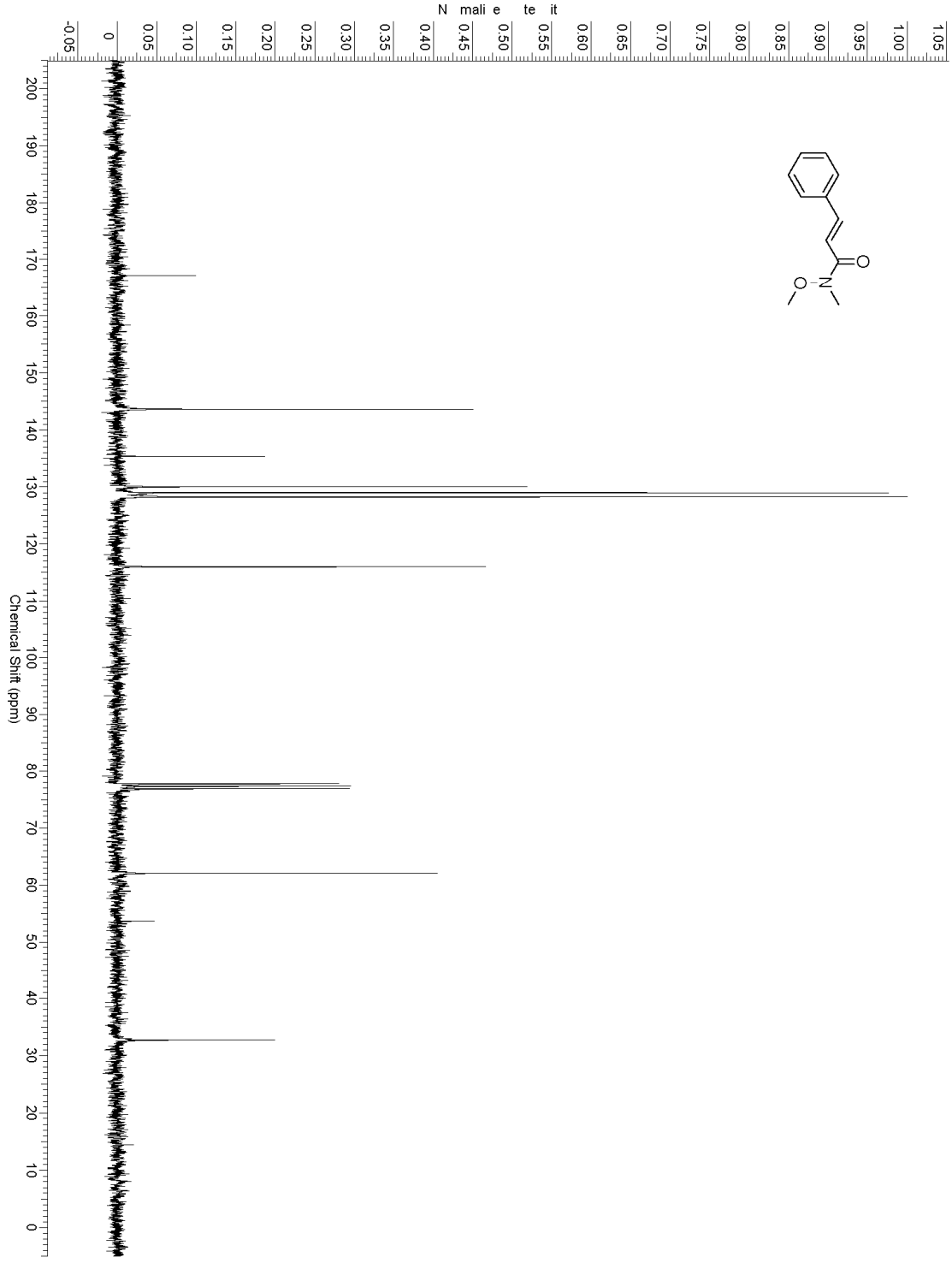

N mali e te it
Chemical Shift (ppm)
4.35
4.08
4.14
4.03
6.01
2.14
6.01

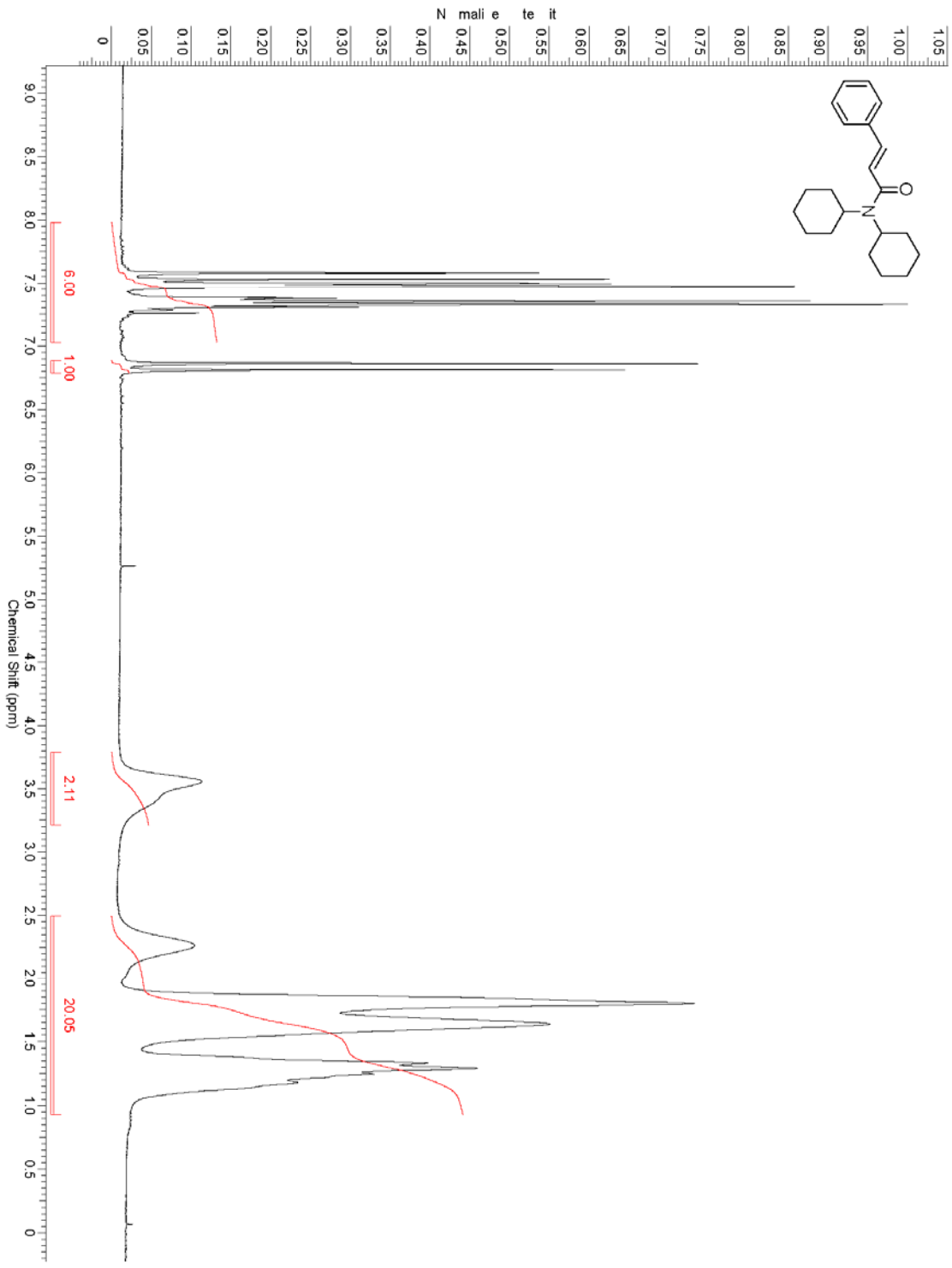

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
O
P
O
O
O
N
O
O

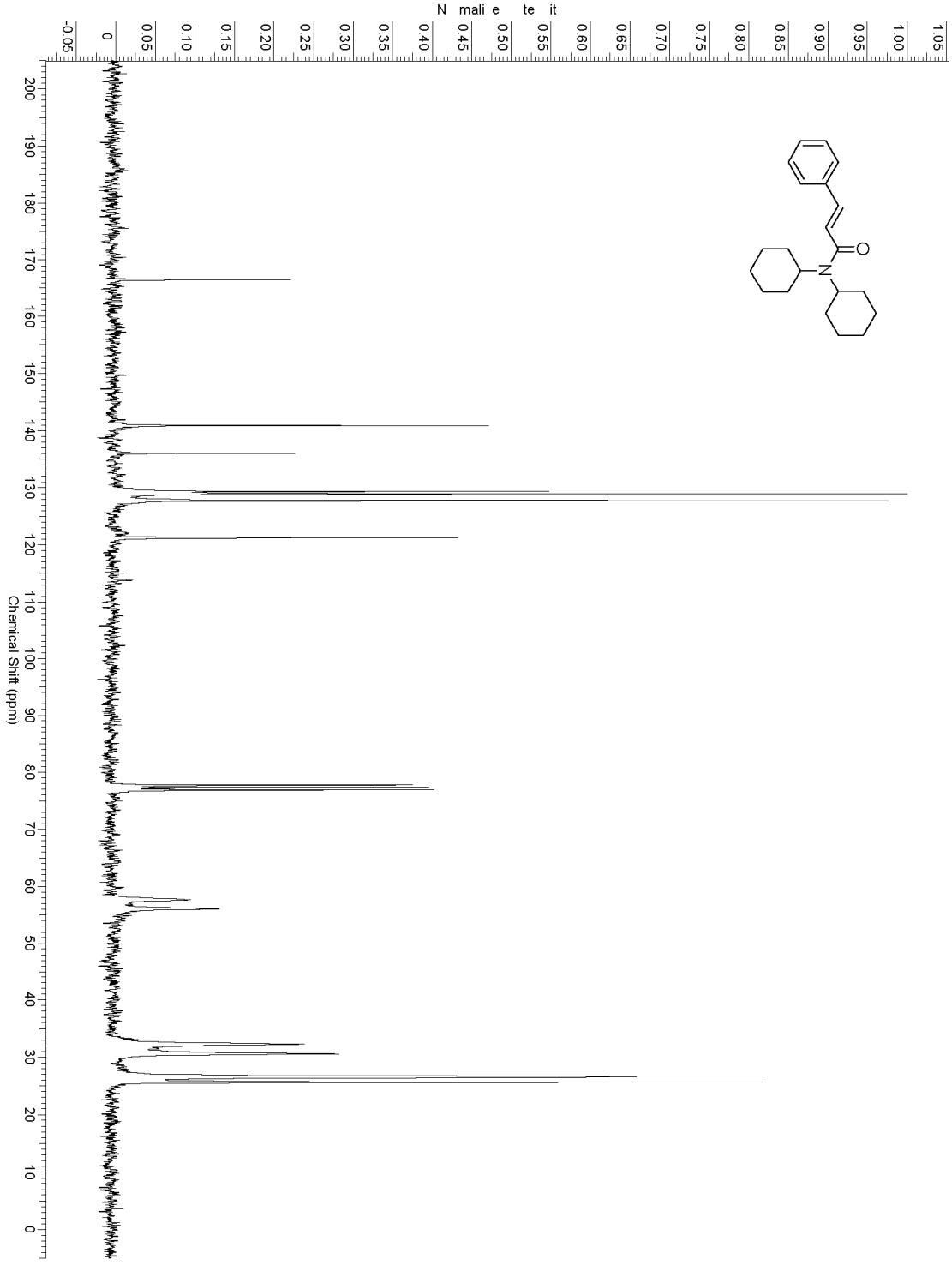

N mali e te it
Chemical Shift (ppm)
13.00
1.04
1.02
2.29
2.21
6.27
O
O
N
O

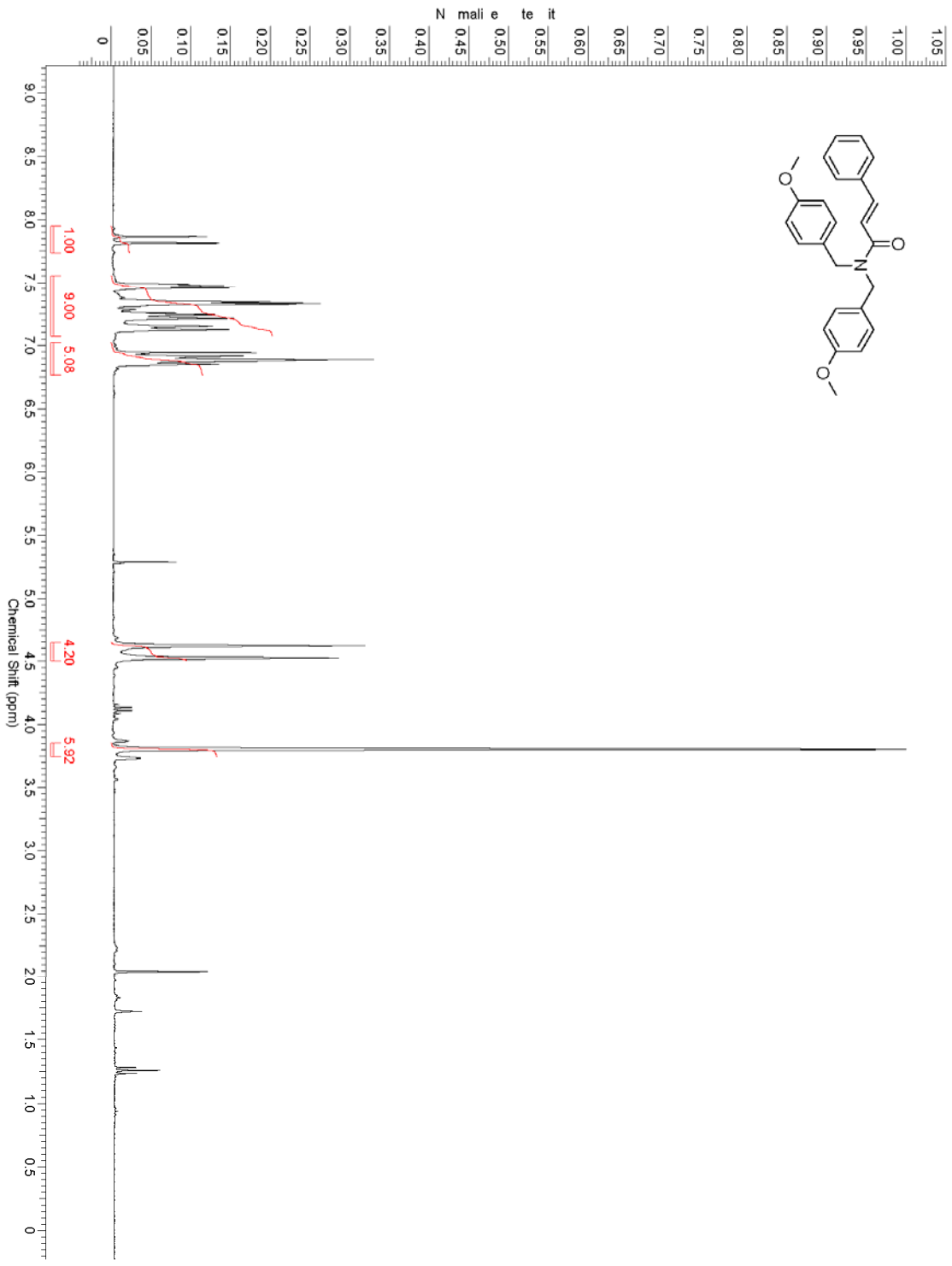

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
N
O
O

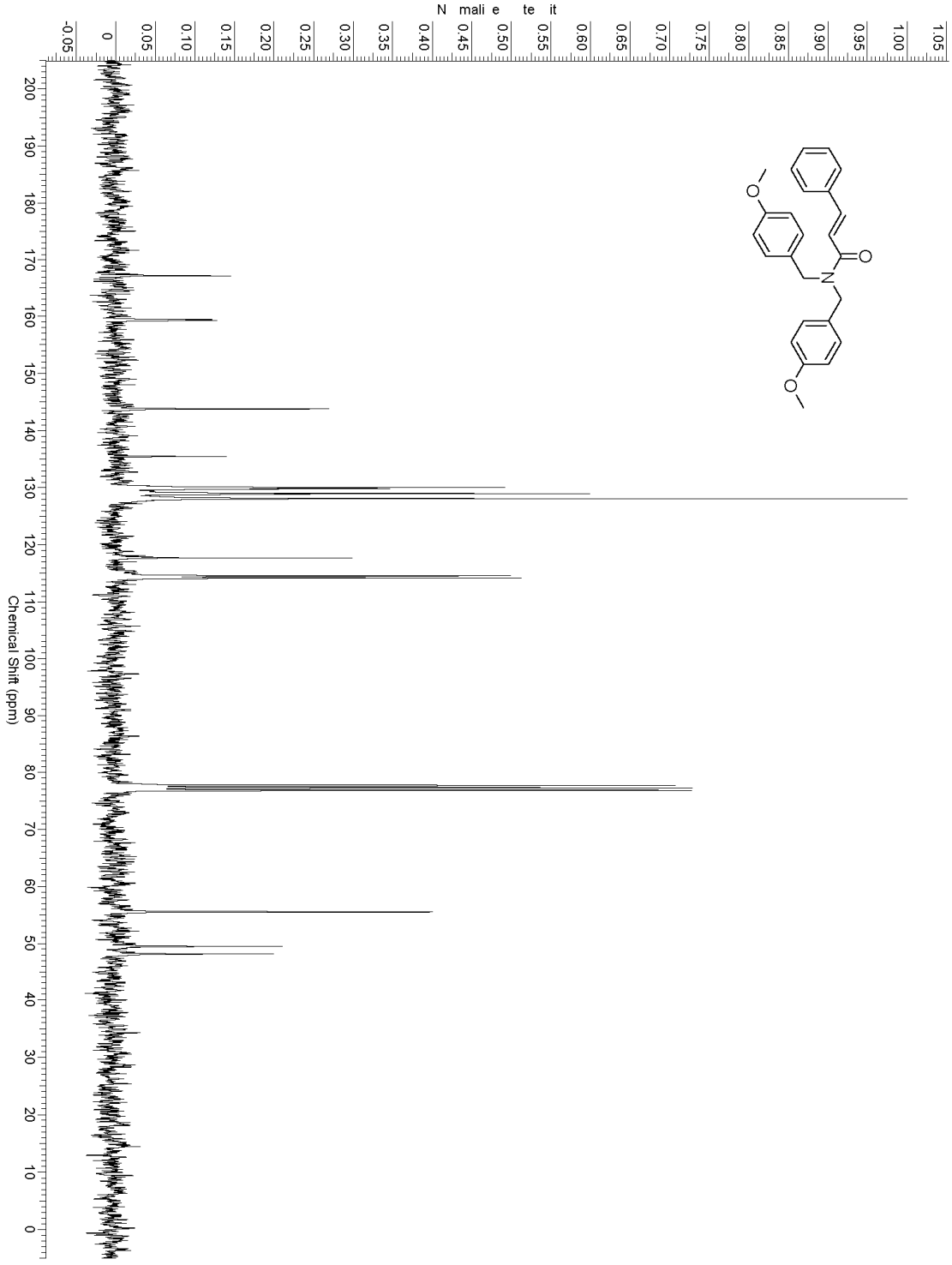

N mali e te it
Chemical Shift (ppm)
0.91
2.79
0.99
3.04
3.00
O
O
N

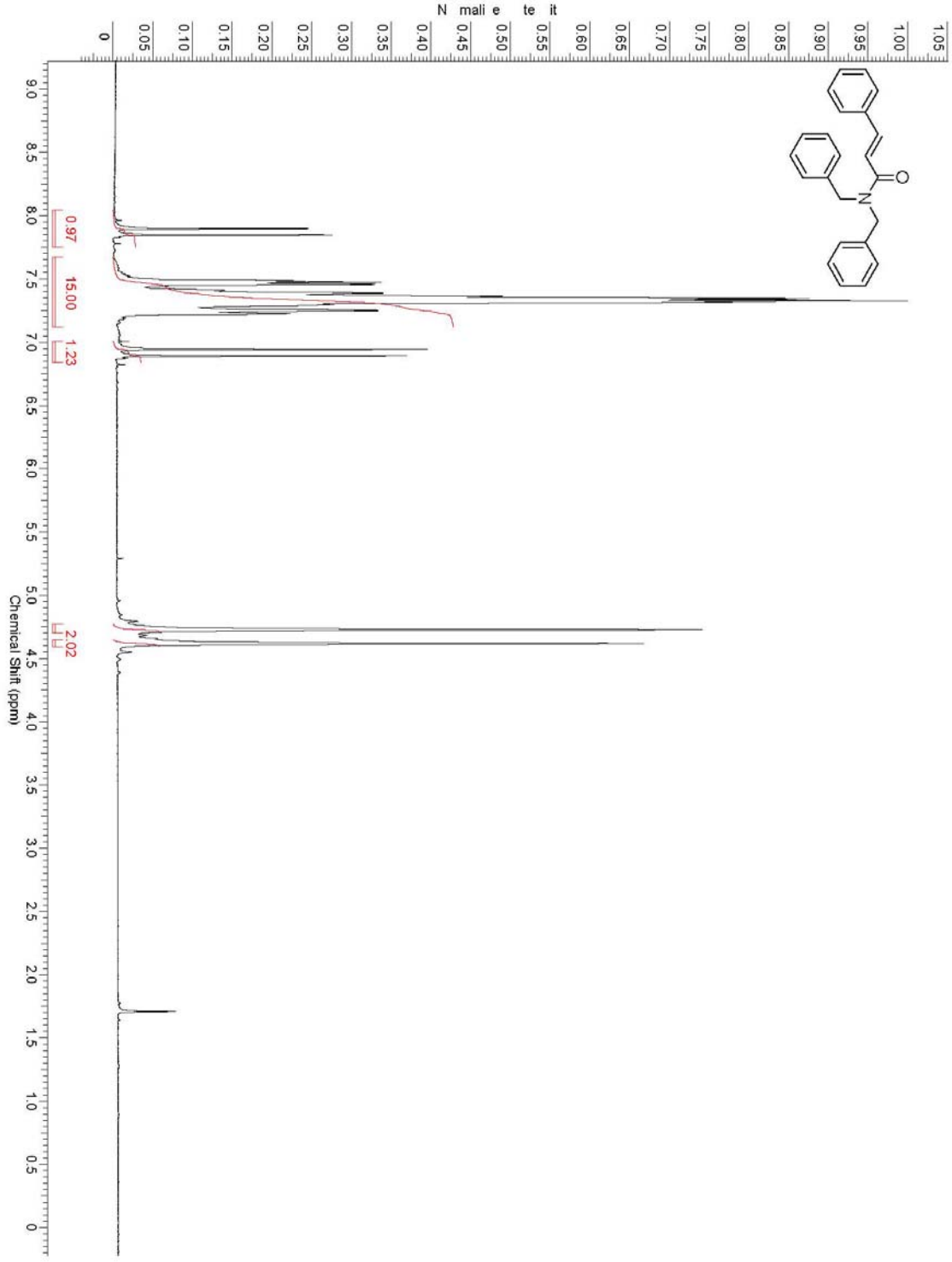

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
N
O

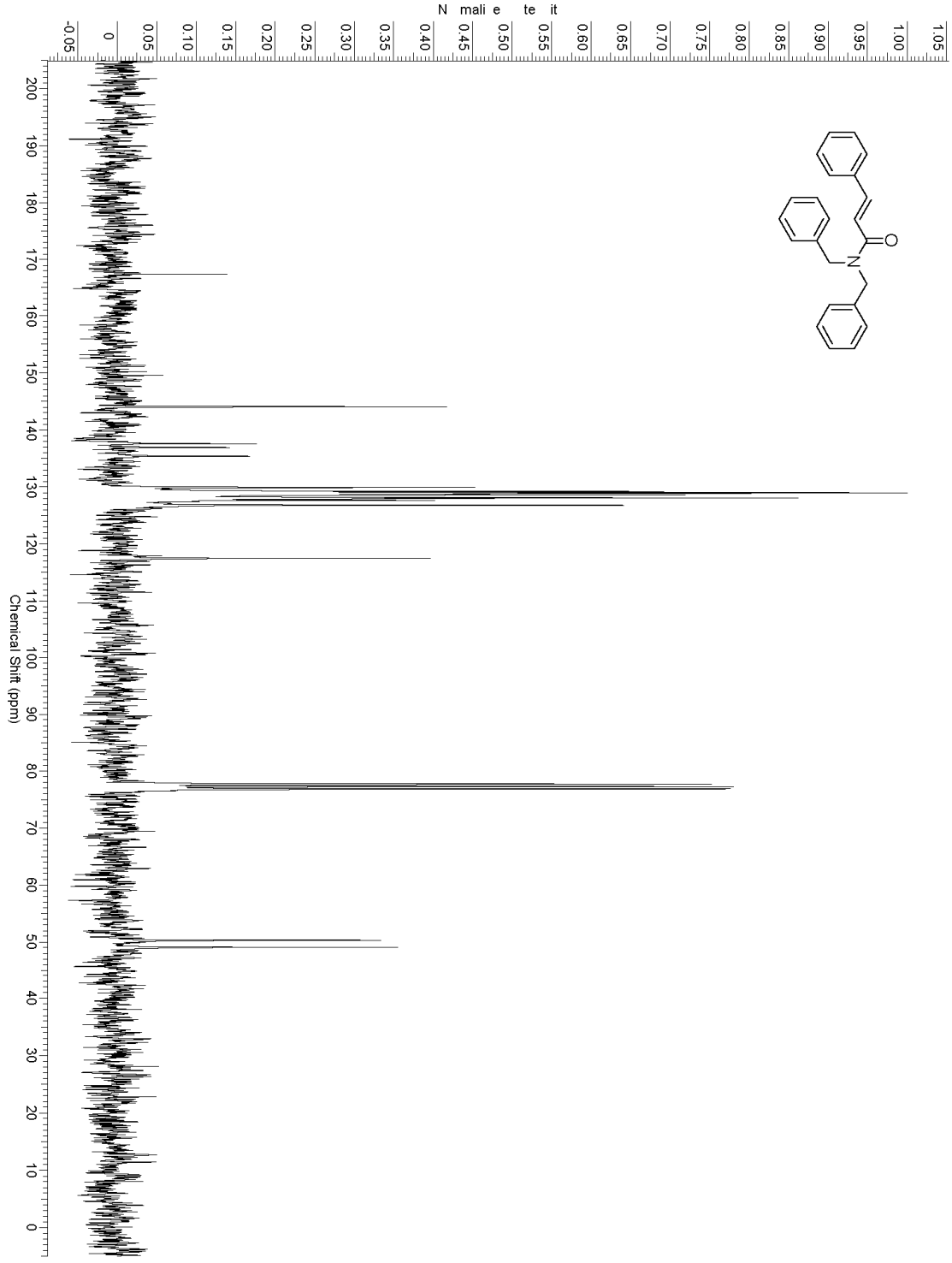

N mali e te it
Chemical Shift (ppm)
6.00
1.00
2.11
20.05
O
N

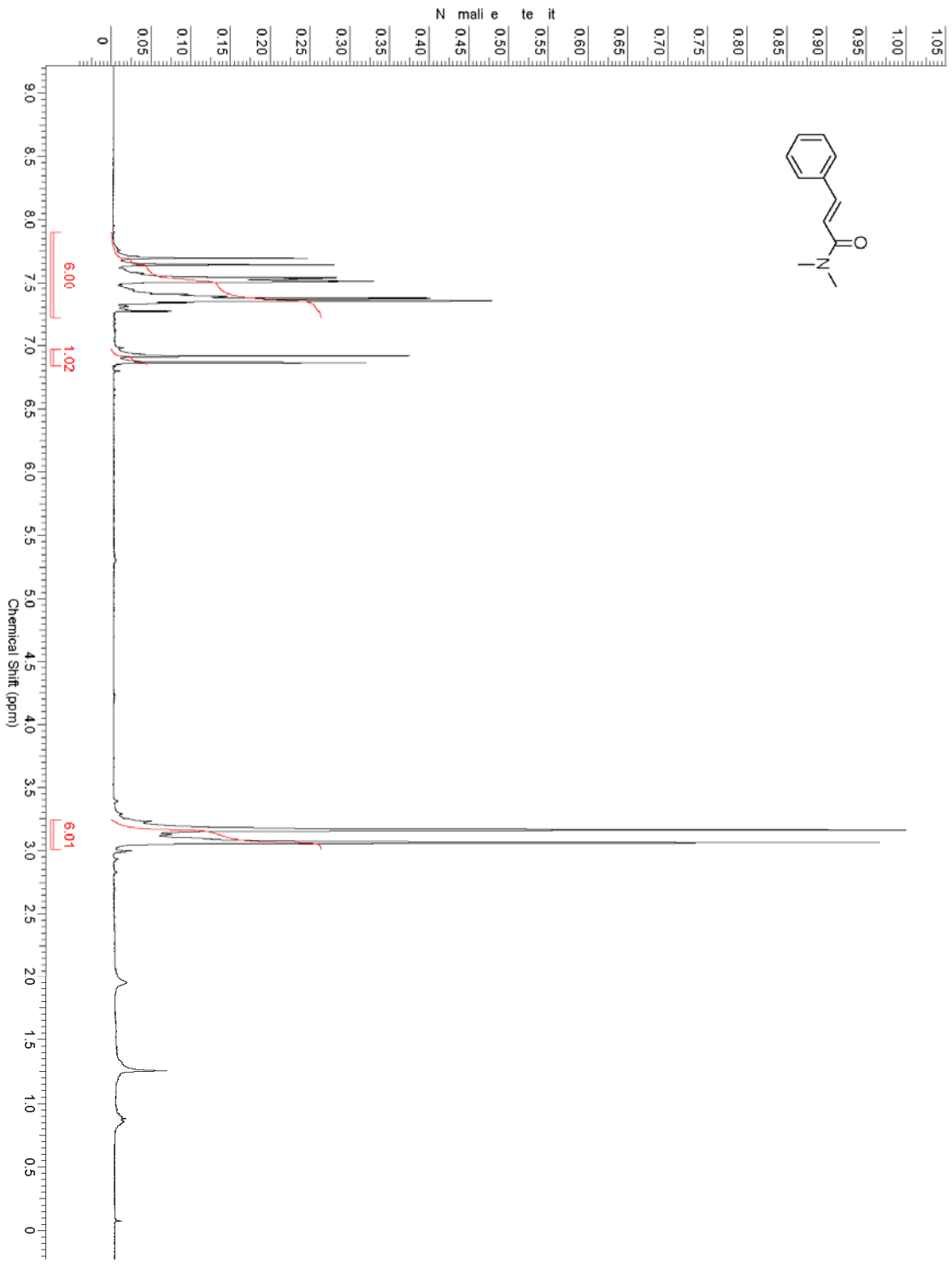

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O
N

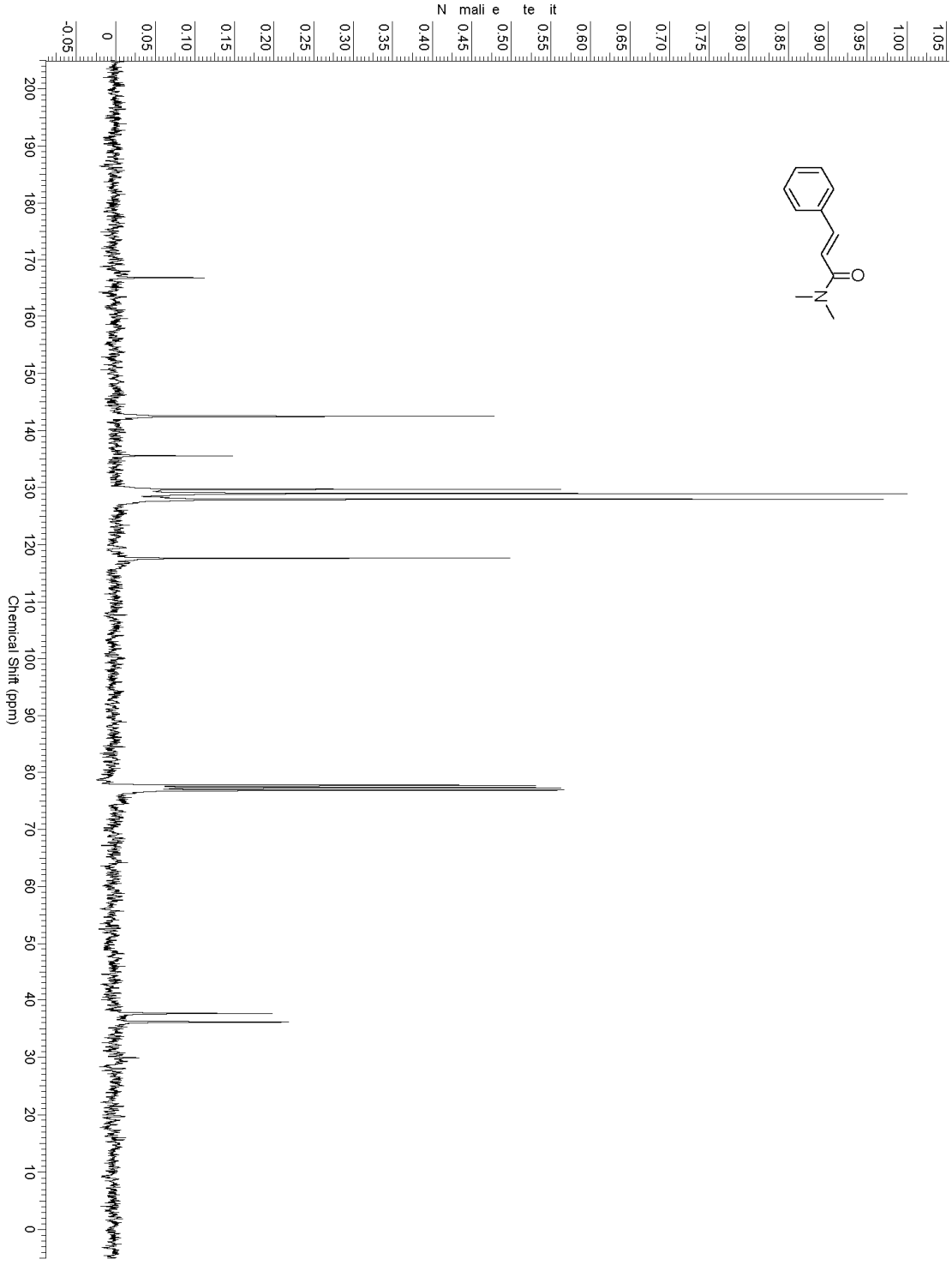

N mali e te it
Chemical Shift (ppm)
1.00
9.00
5.08
4.20
5.92
O
N
O
O

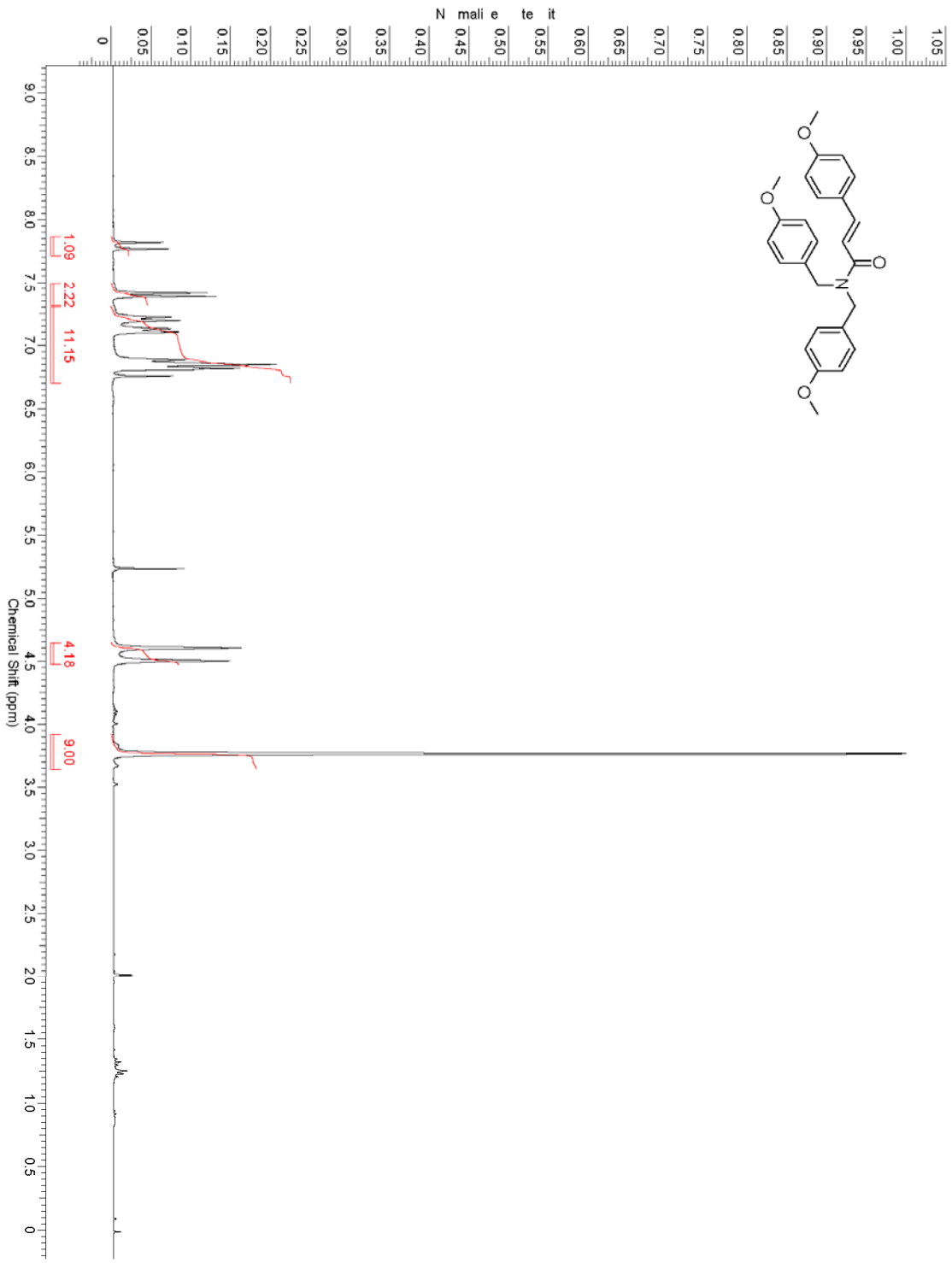

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O
O
N
O

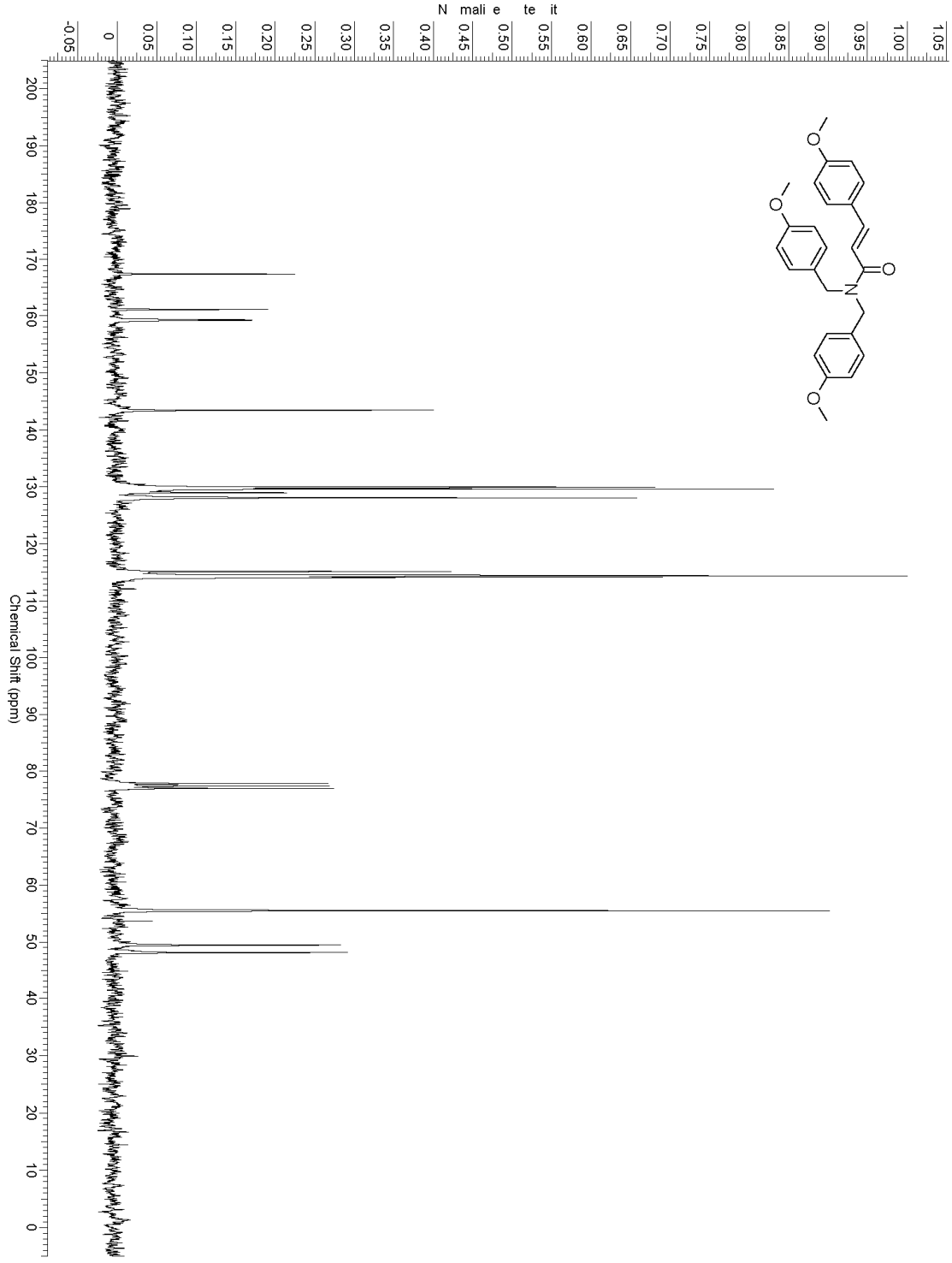

N mali e te it
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
O
N
0.97
15.00
1.23
2.02
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

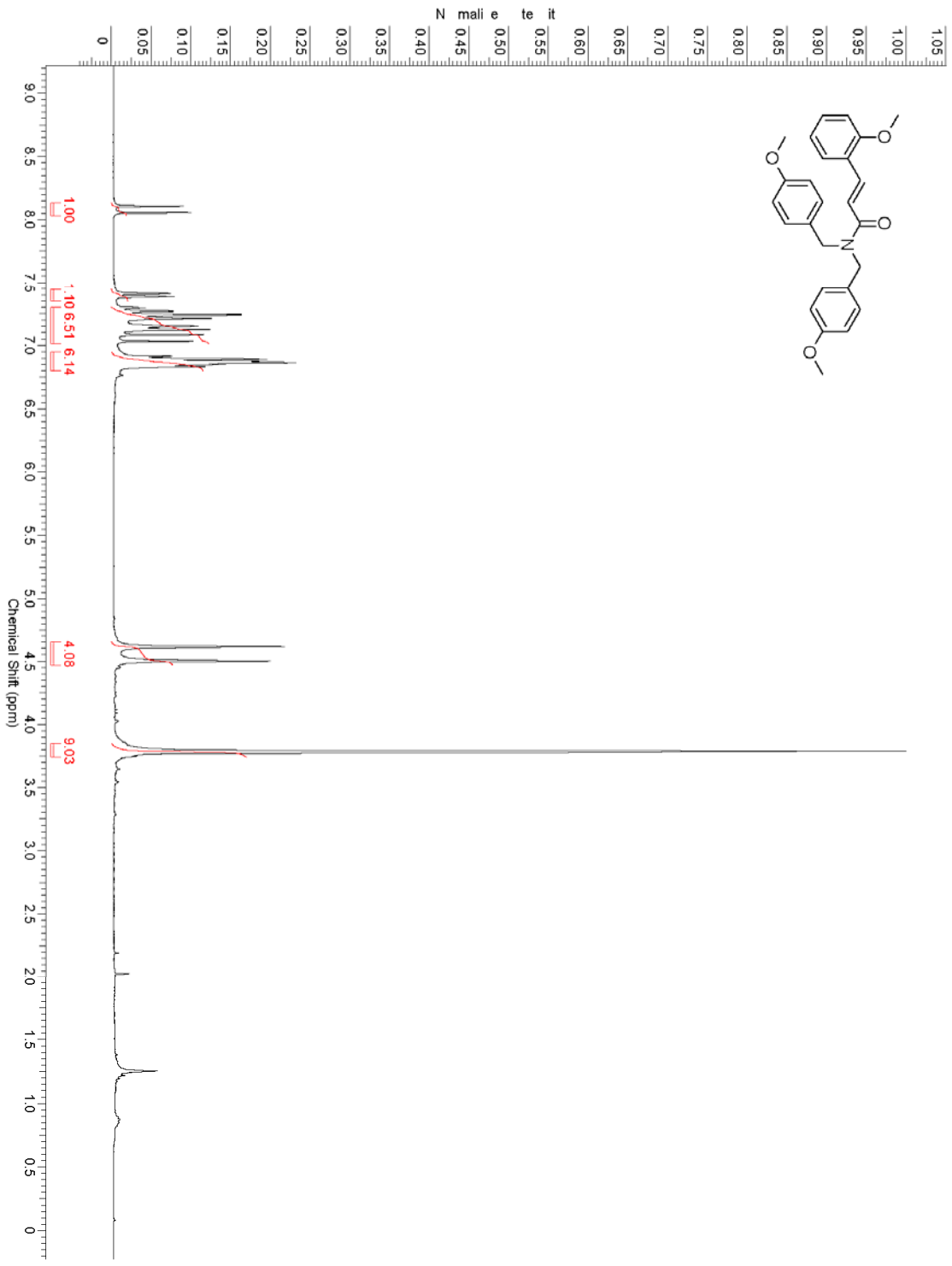

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O
N

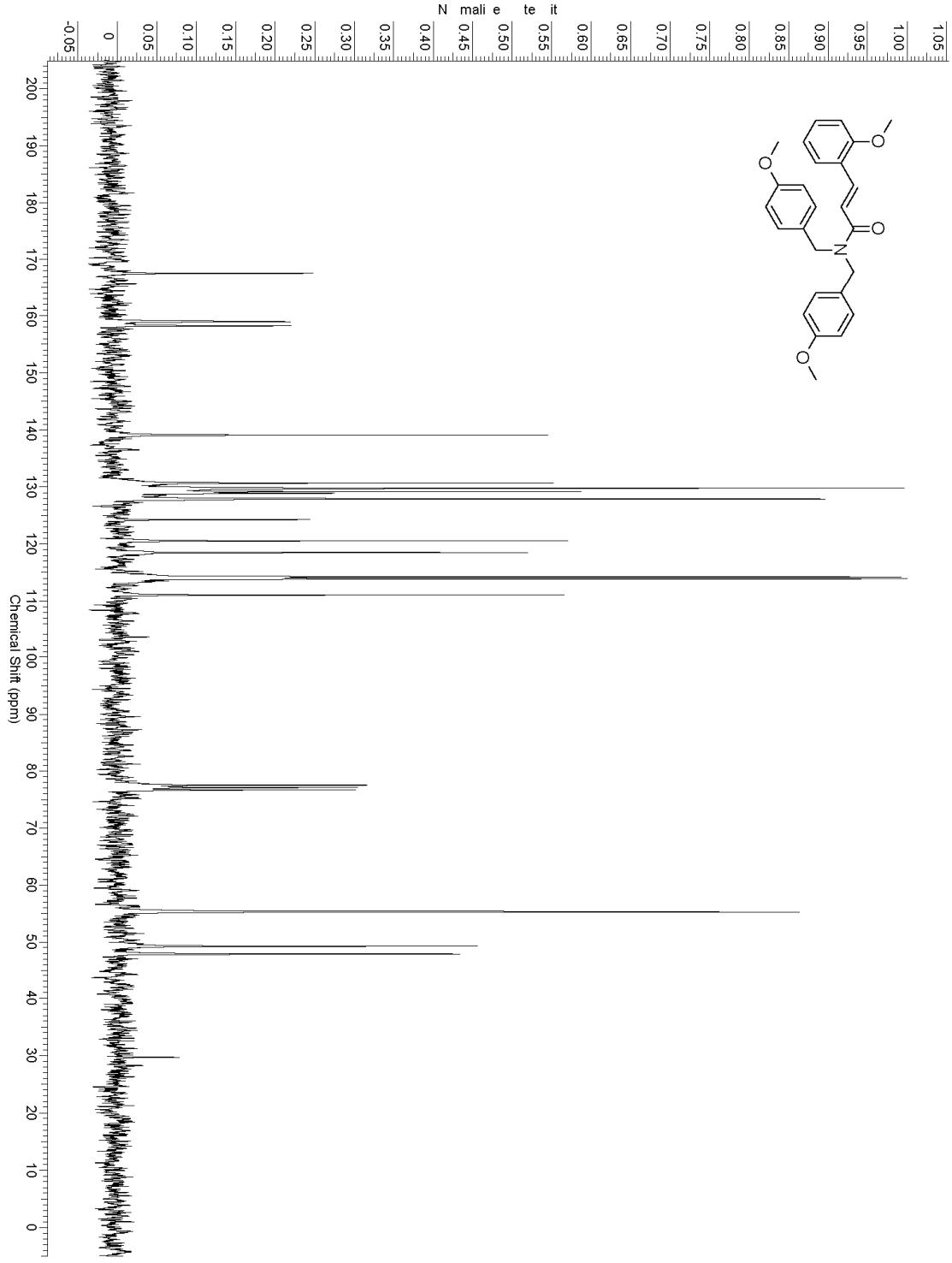

N mali e te it
Chemical Shift (ppm)
6.00
1.02
6.01
O
N

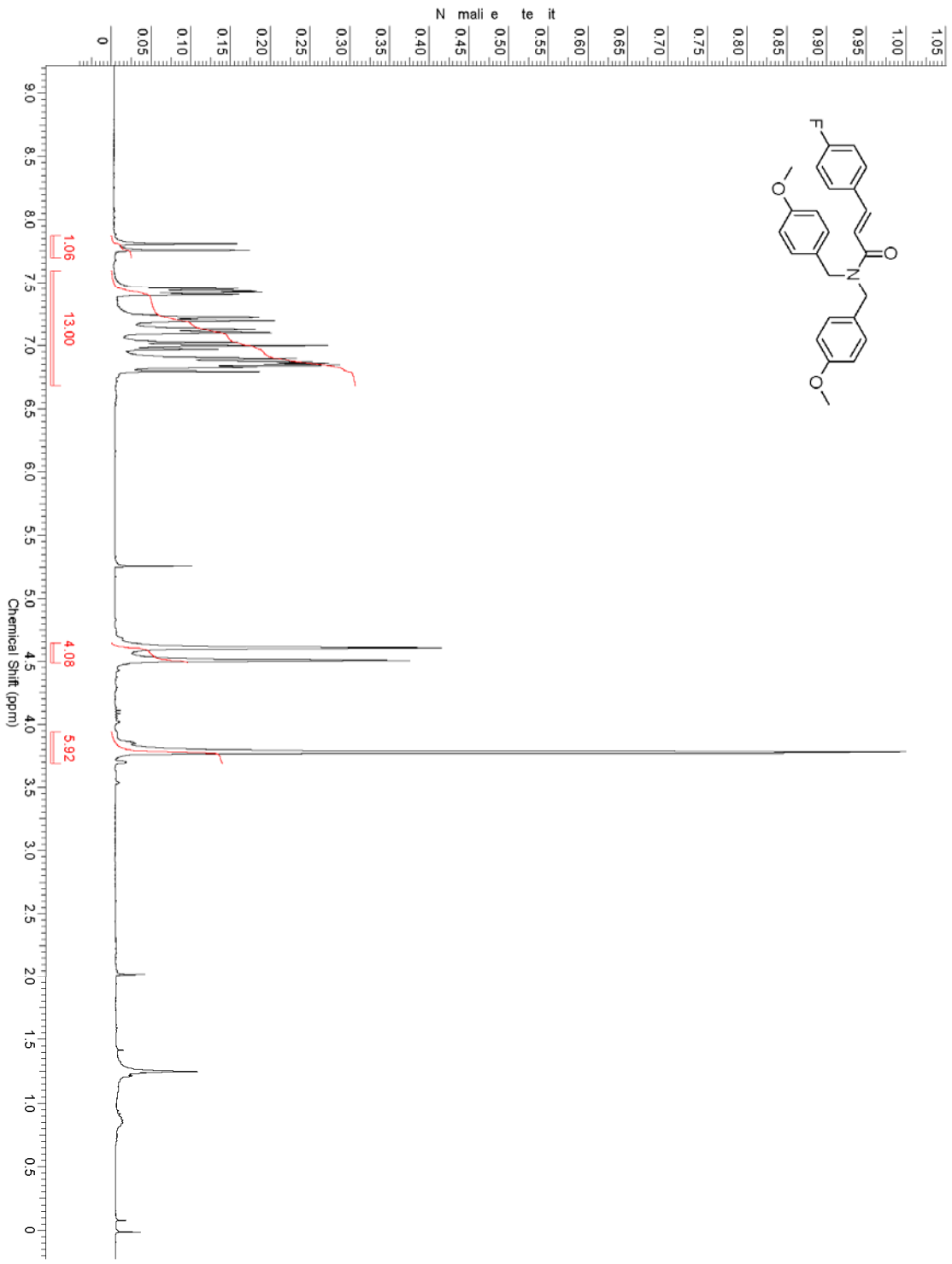

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O
N

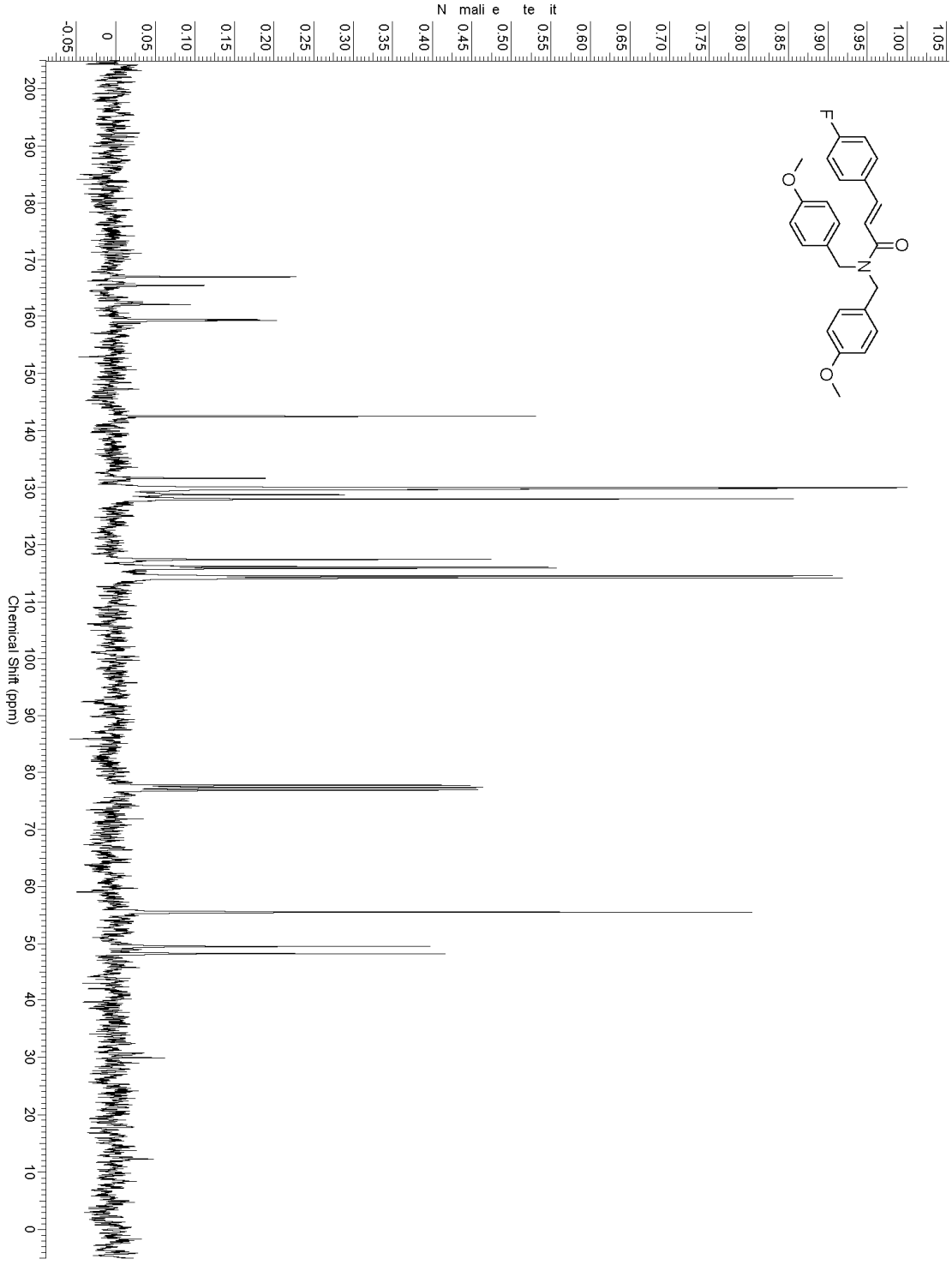

N mali e te it
Chemical Shift (ppm)
1.09
2.22
11.15
4.18
9.00

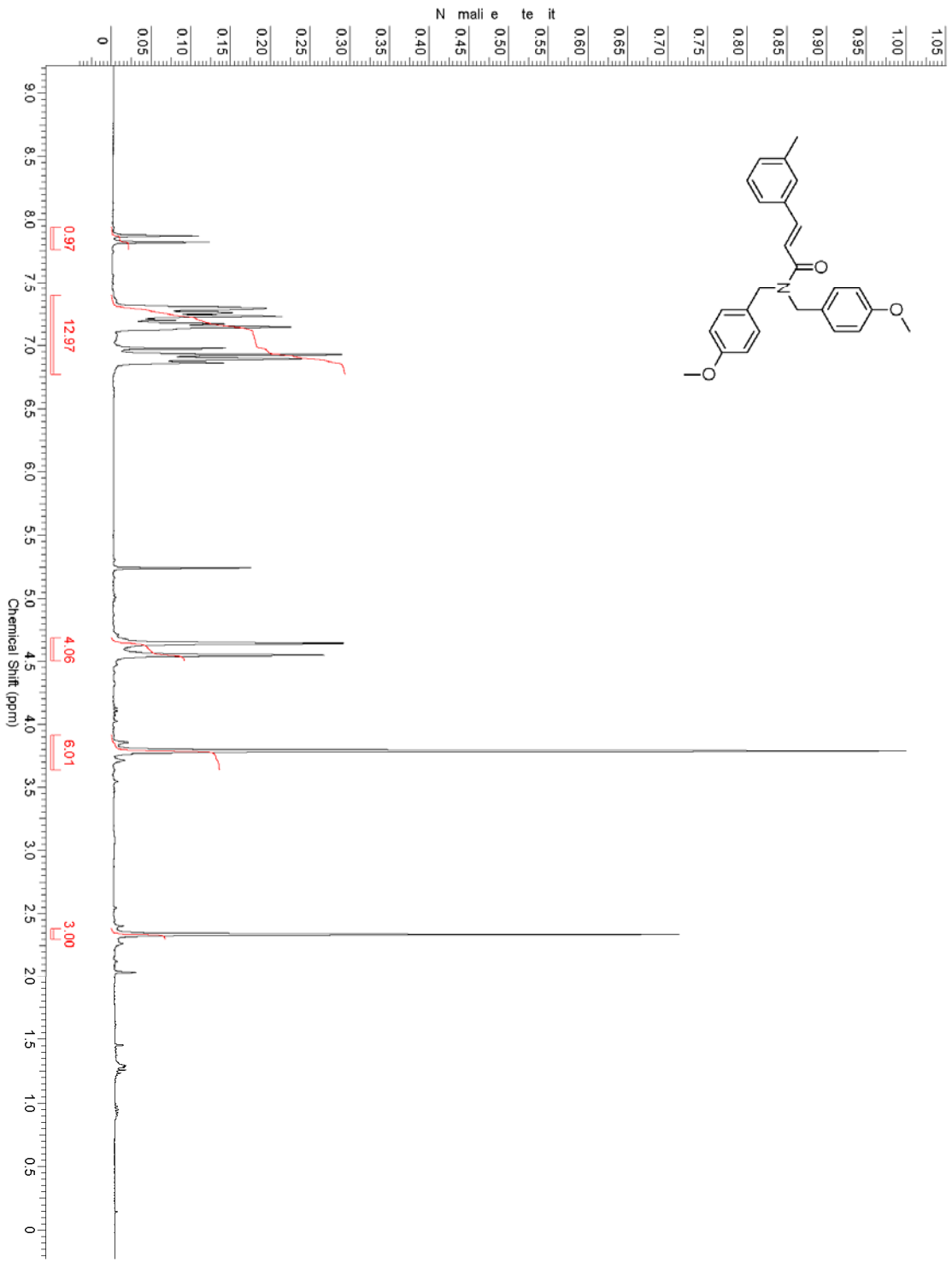

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
N
O
O

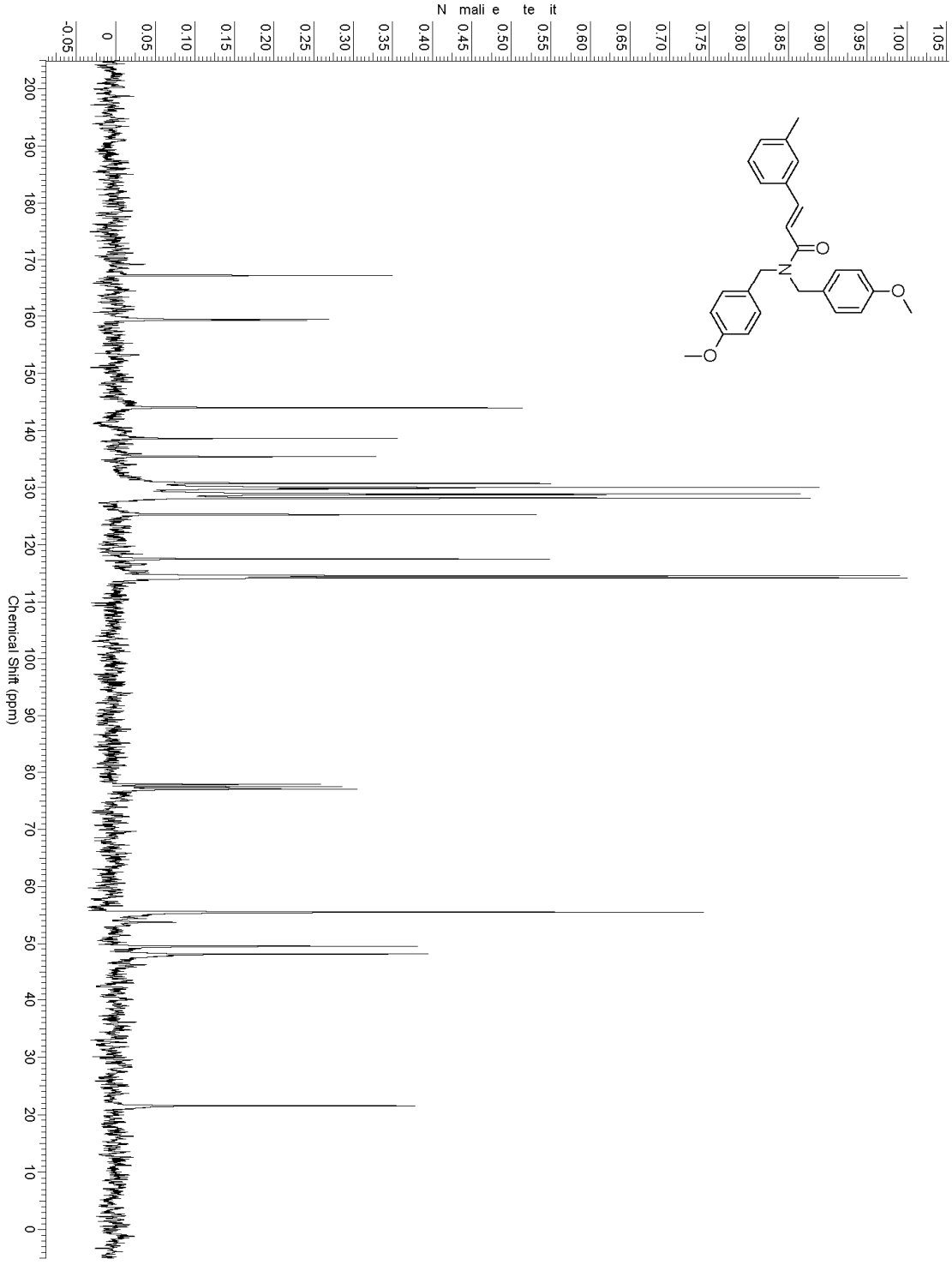

N mali e te it
Chemical Shift (ppm)
1.00
1.10
6.51
6.14
4.08
9.03
O
O
O
O
N

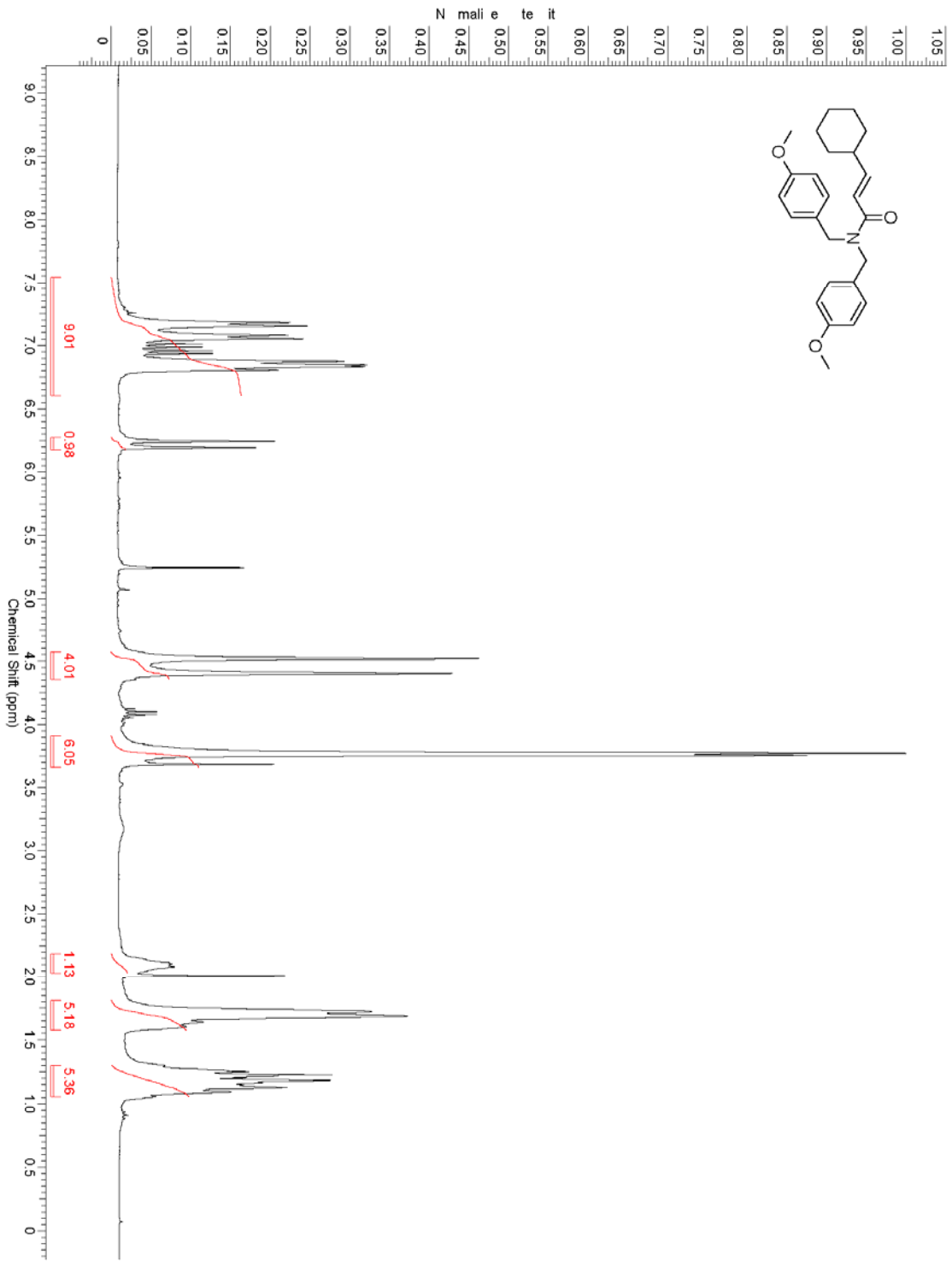

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
N
O
O

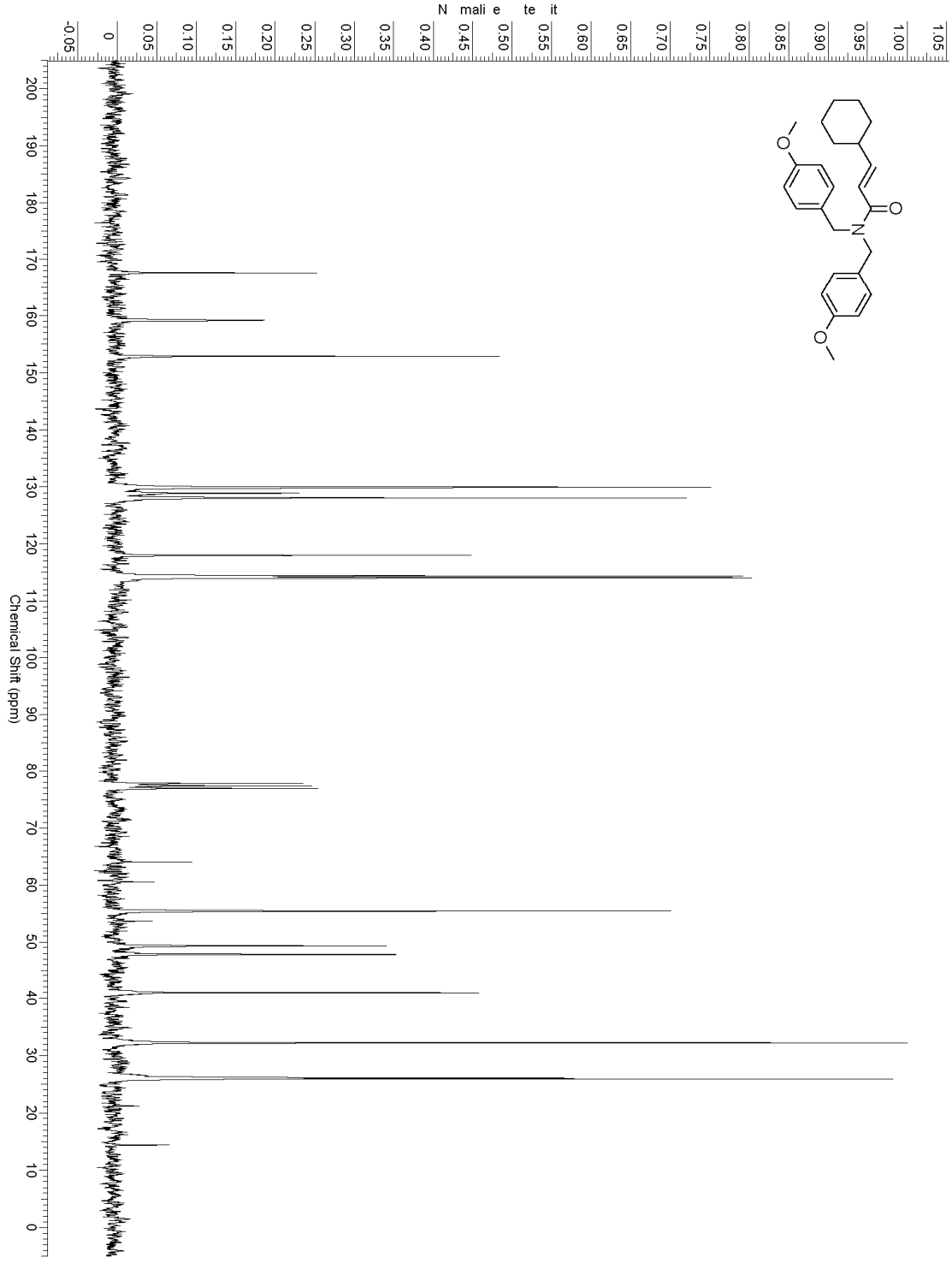

N mali e te it
Chemical Shift (ppm)
1.06
13.00
4.08
5.92
F
O
N
O
O

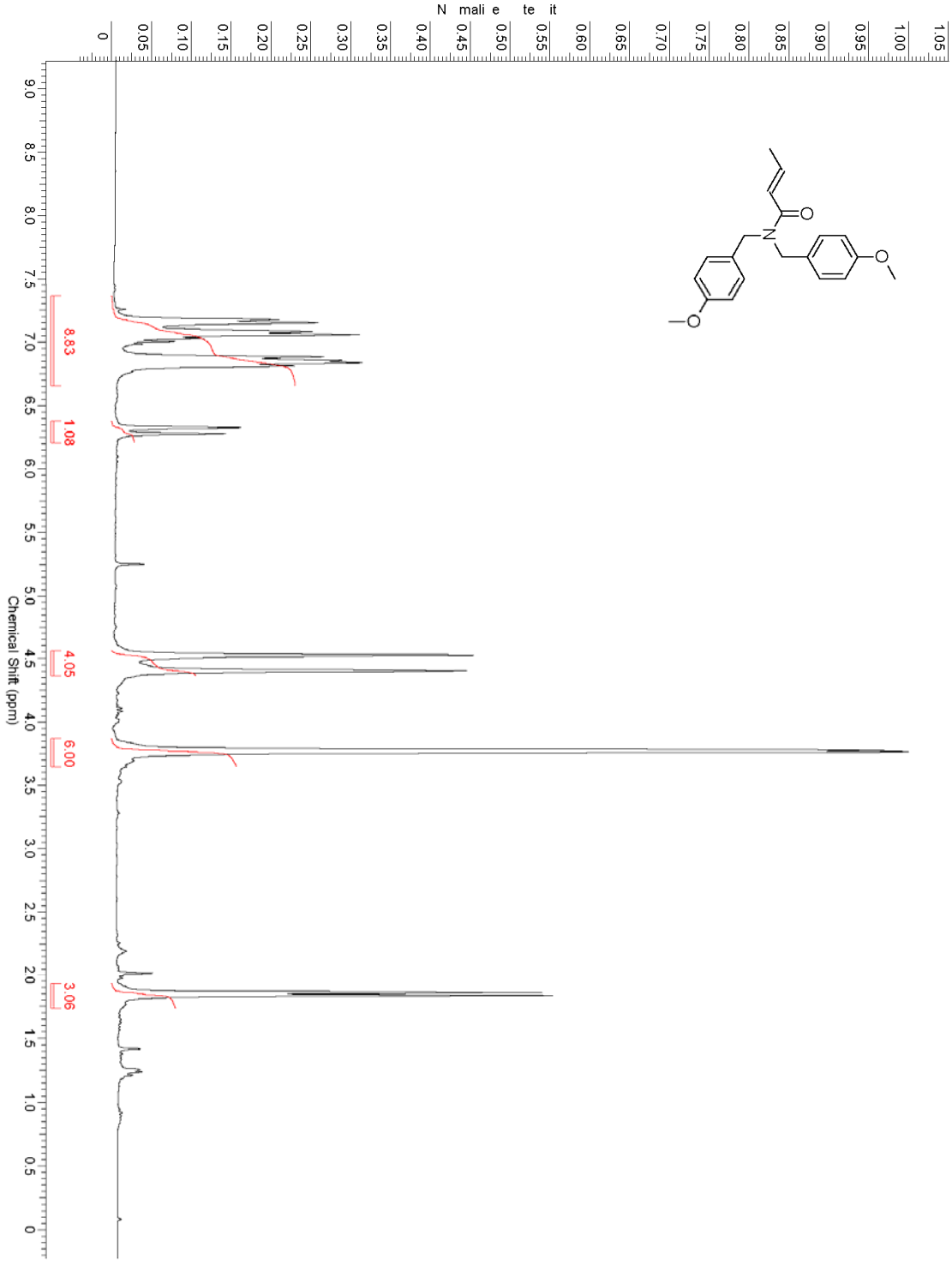

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
F
O
O
N
O

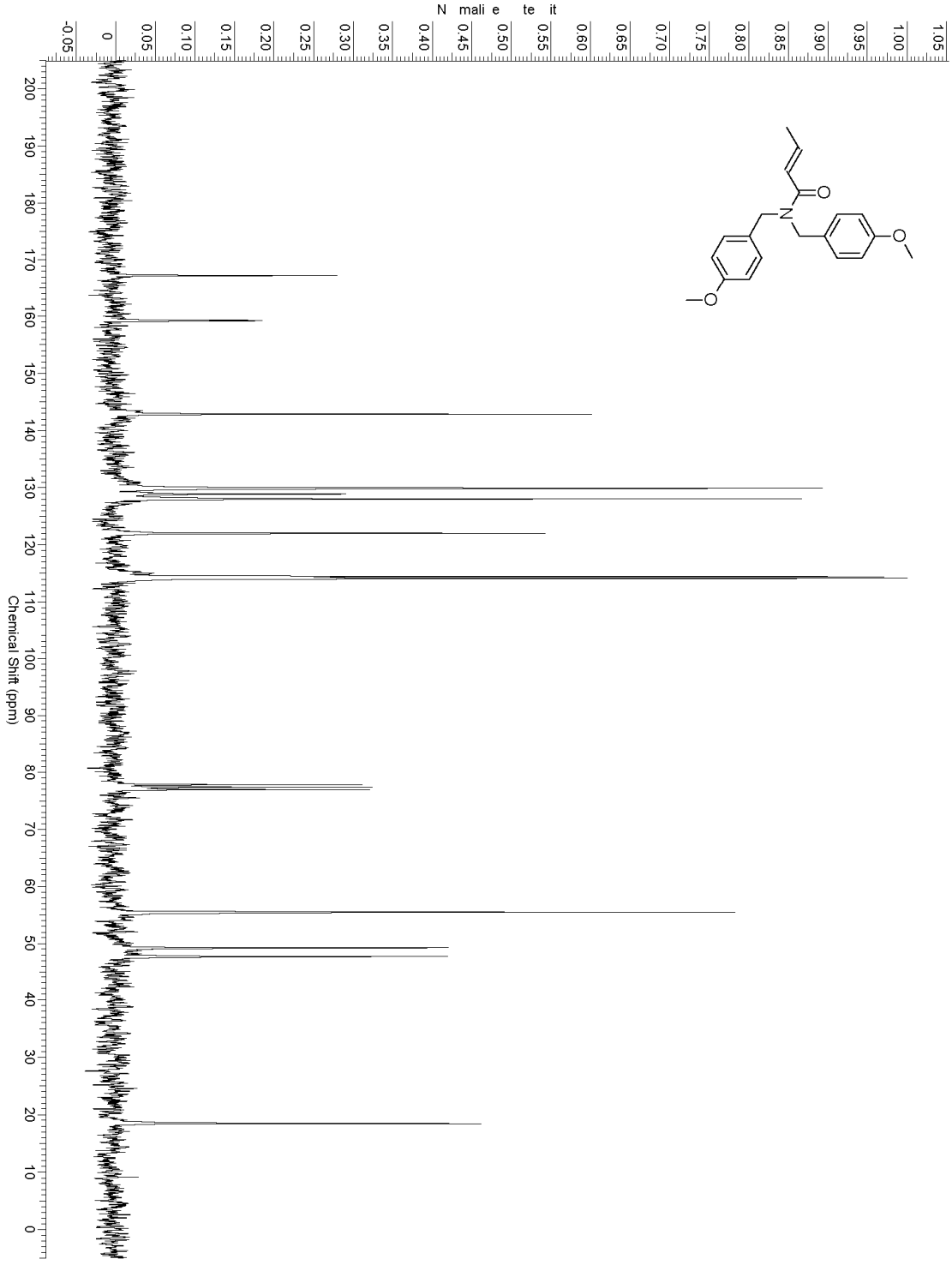

N mali e te it
Chemical Shift (ppm)
0.97
12.97
4.06
6.01
3.00
O
N
O
O


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
N
O
O

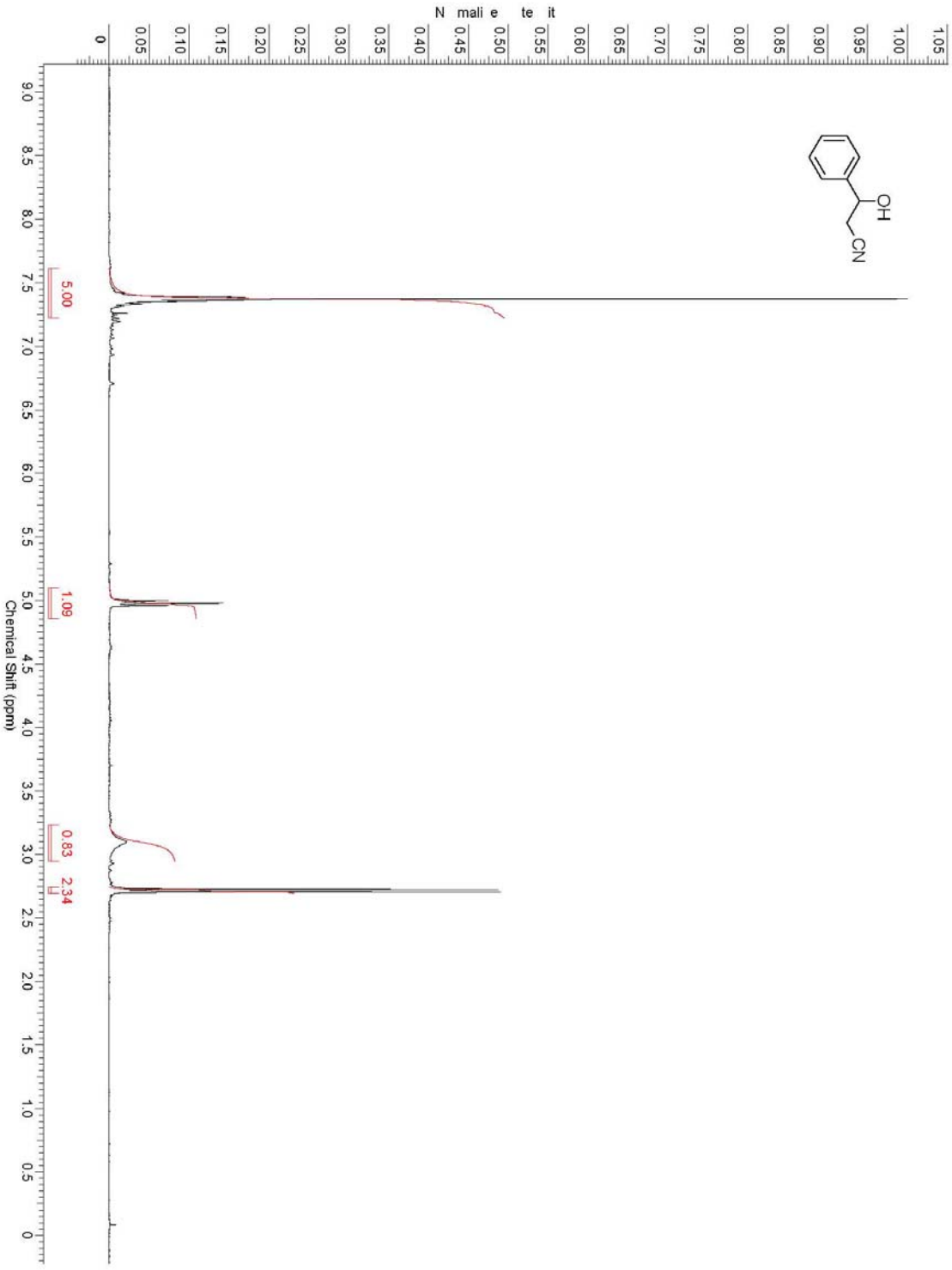

N mali e te it
Chemical Shift (ppm)
9.01
0.98
4.01
6.05
1.13
5.18
5.36
O
N
O
O

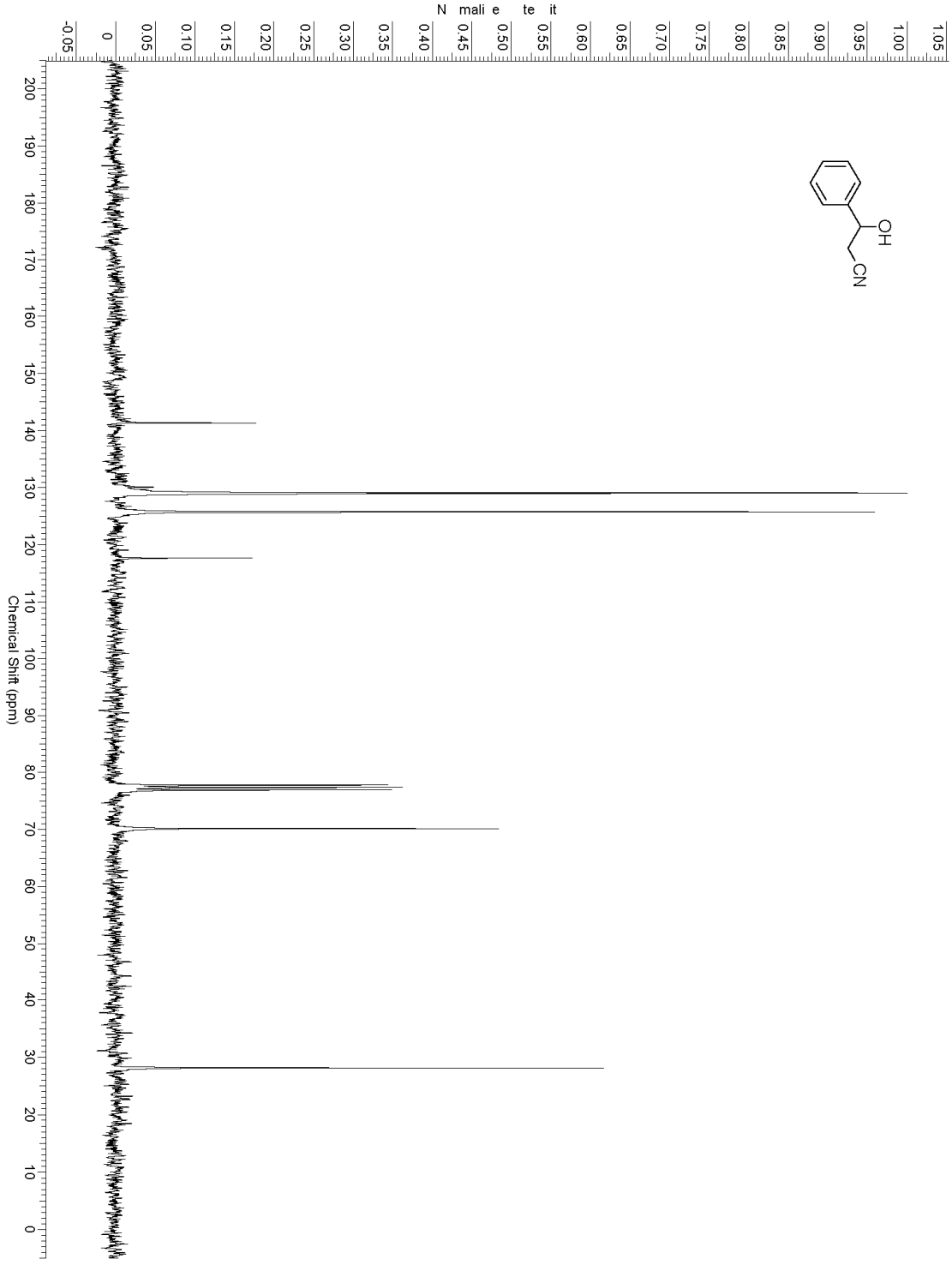

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
N
O

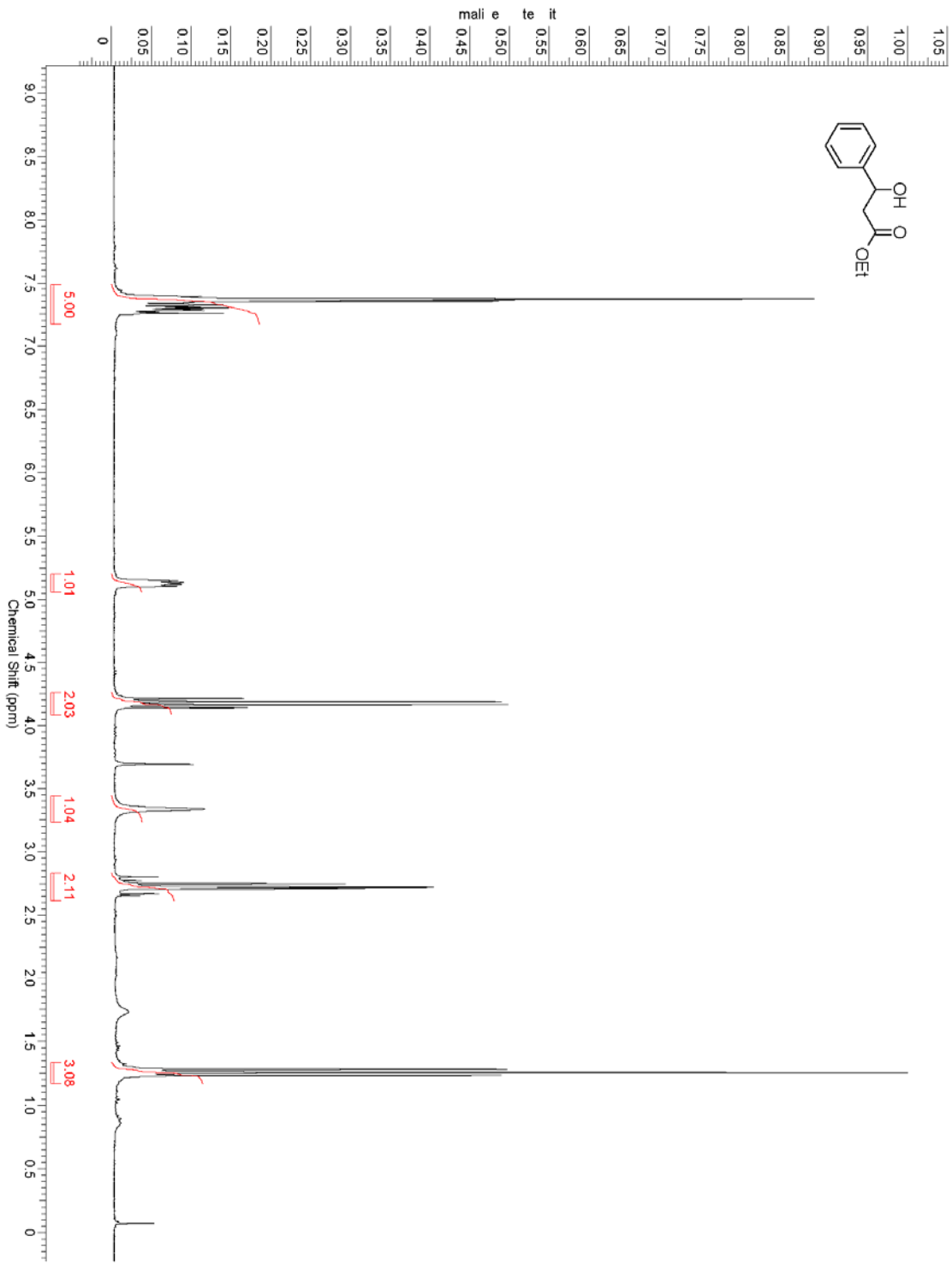

N mali e te it
Chemical Shift (ppm)
8.83
1.08
4.05
6.00
3.06

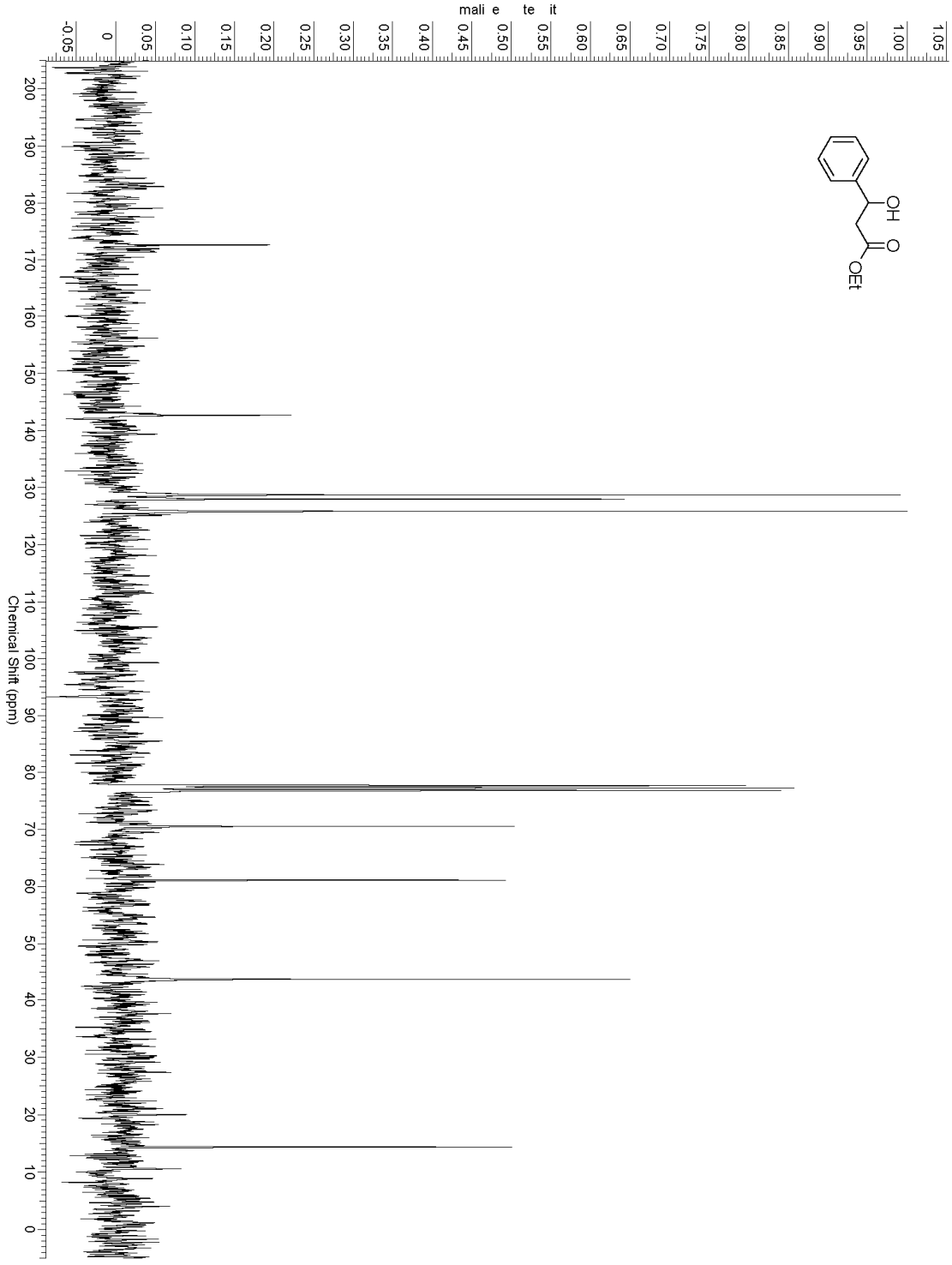

N mali e te it
-0.05 0 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O
N
O
O

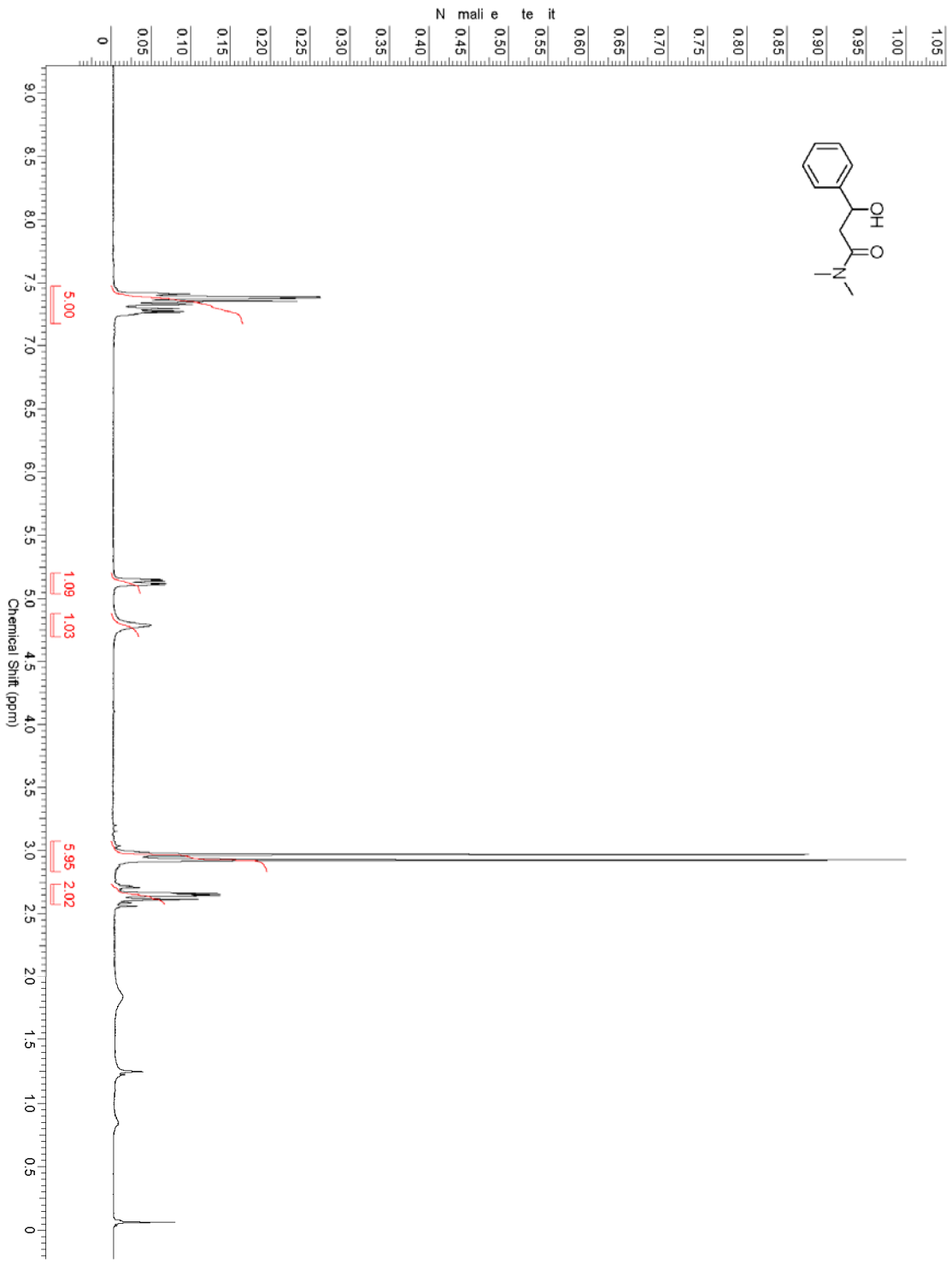
8. NMR spectra for products from copper catalyzed borylation

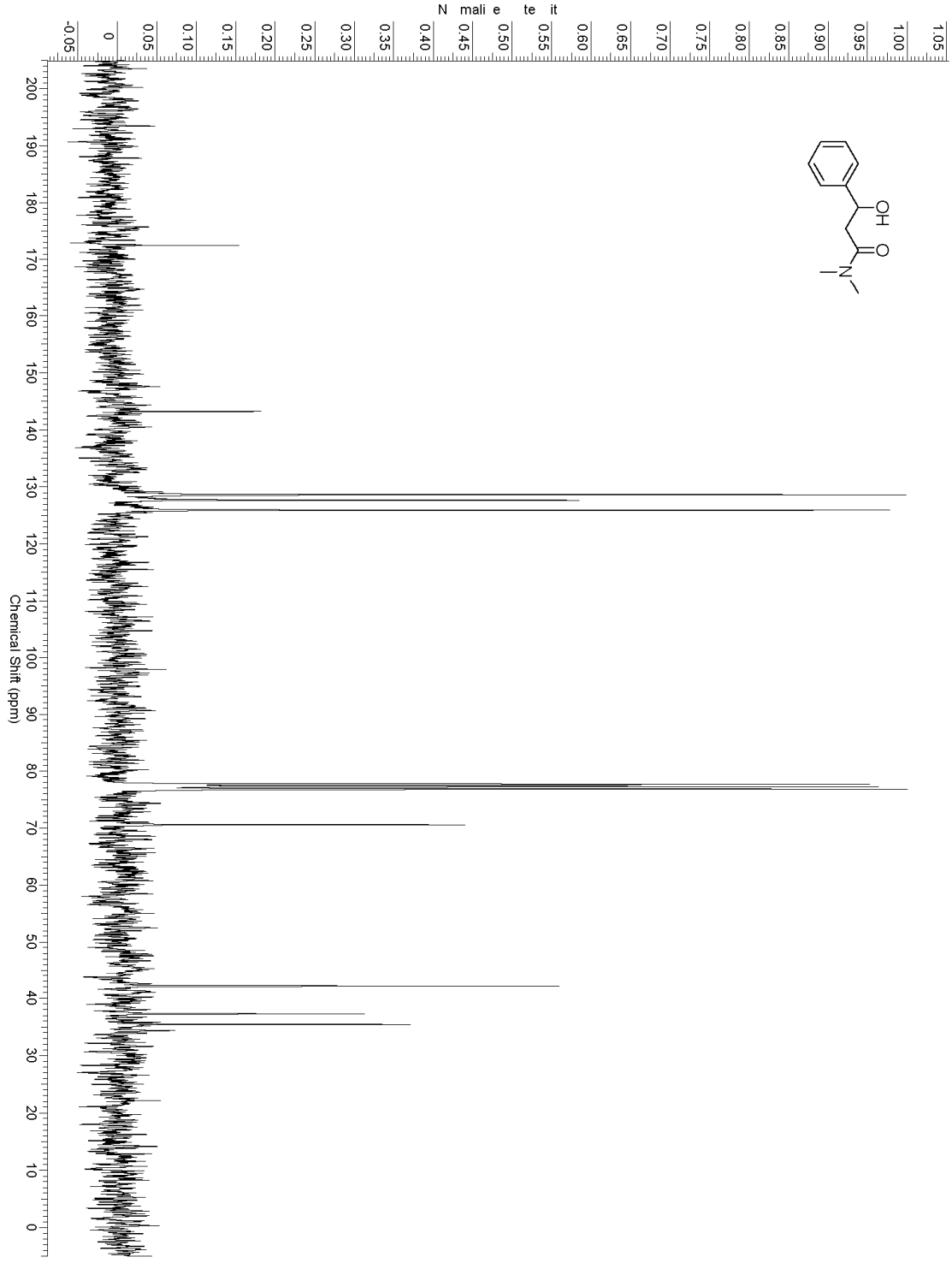

N mali e te it
OH
CN
5.00
1.09
0.83
2.34
Chemical Shift (ppm)

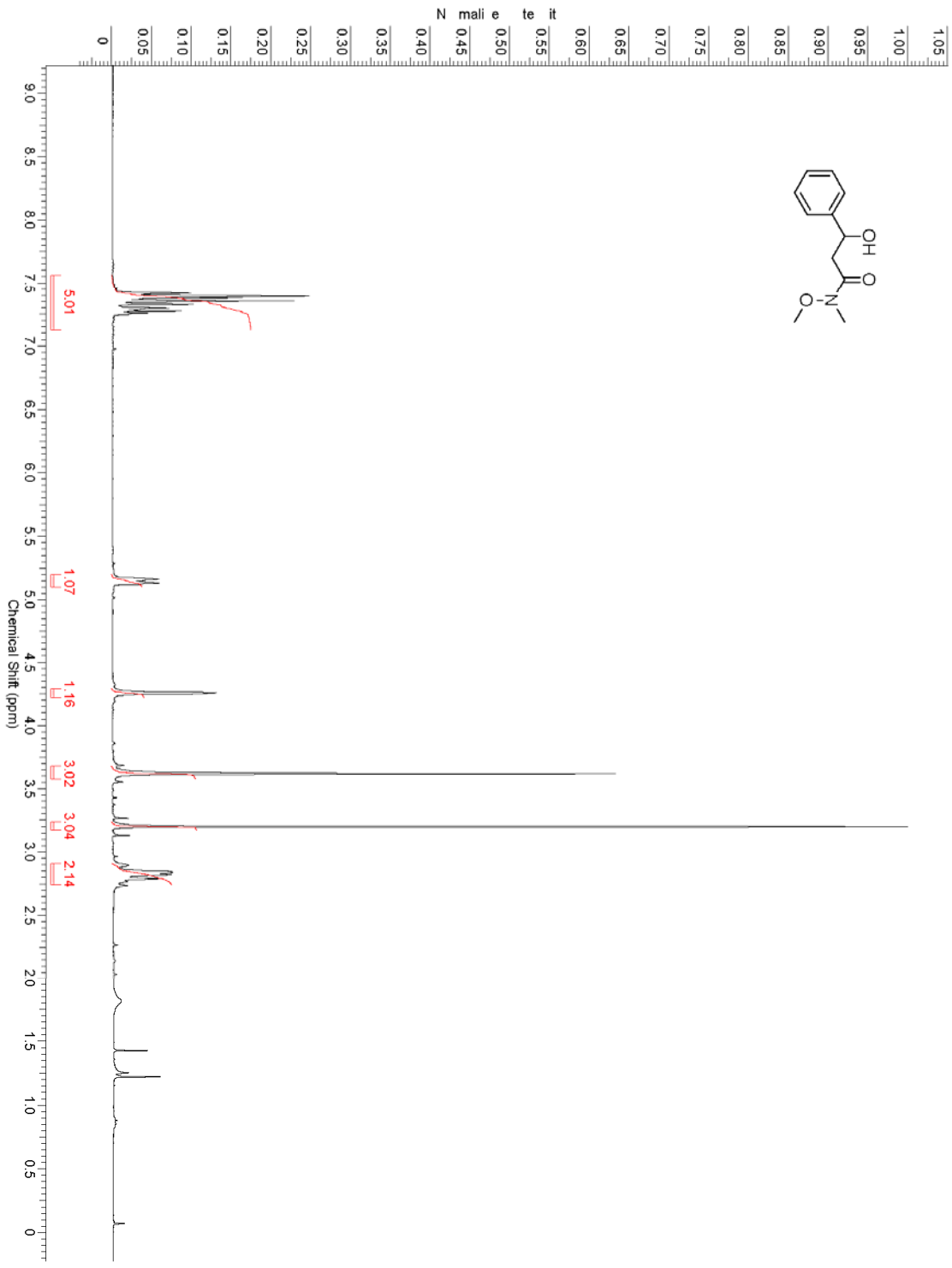

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
CN

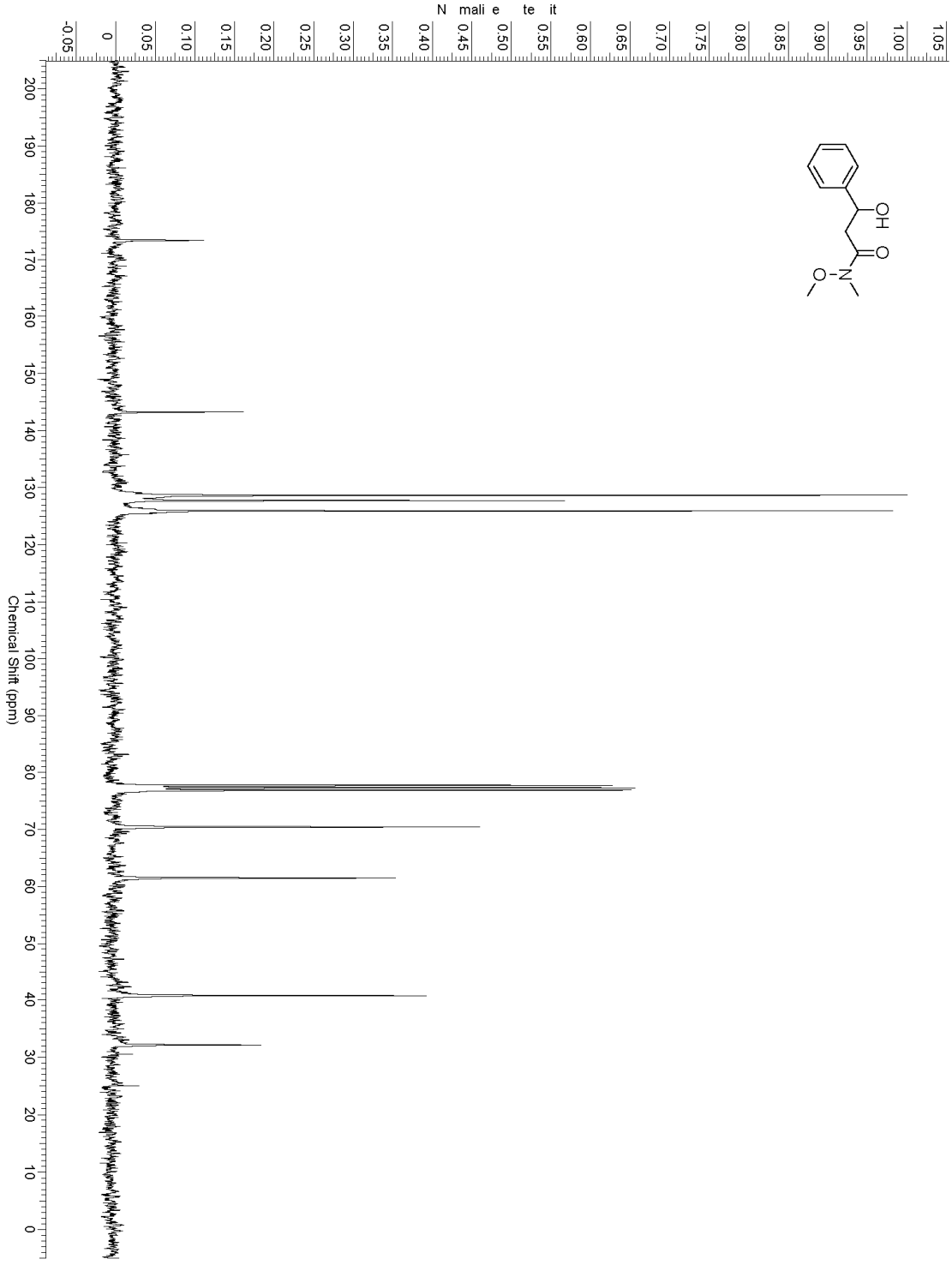

mali e te it
OH O
OEt
5.00
1.01
2.03
1.04
2.11
3.08
Chemical Shift (ppm)

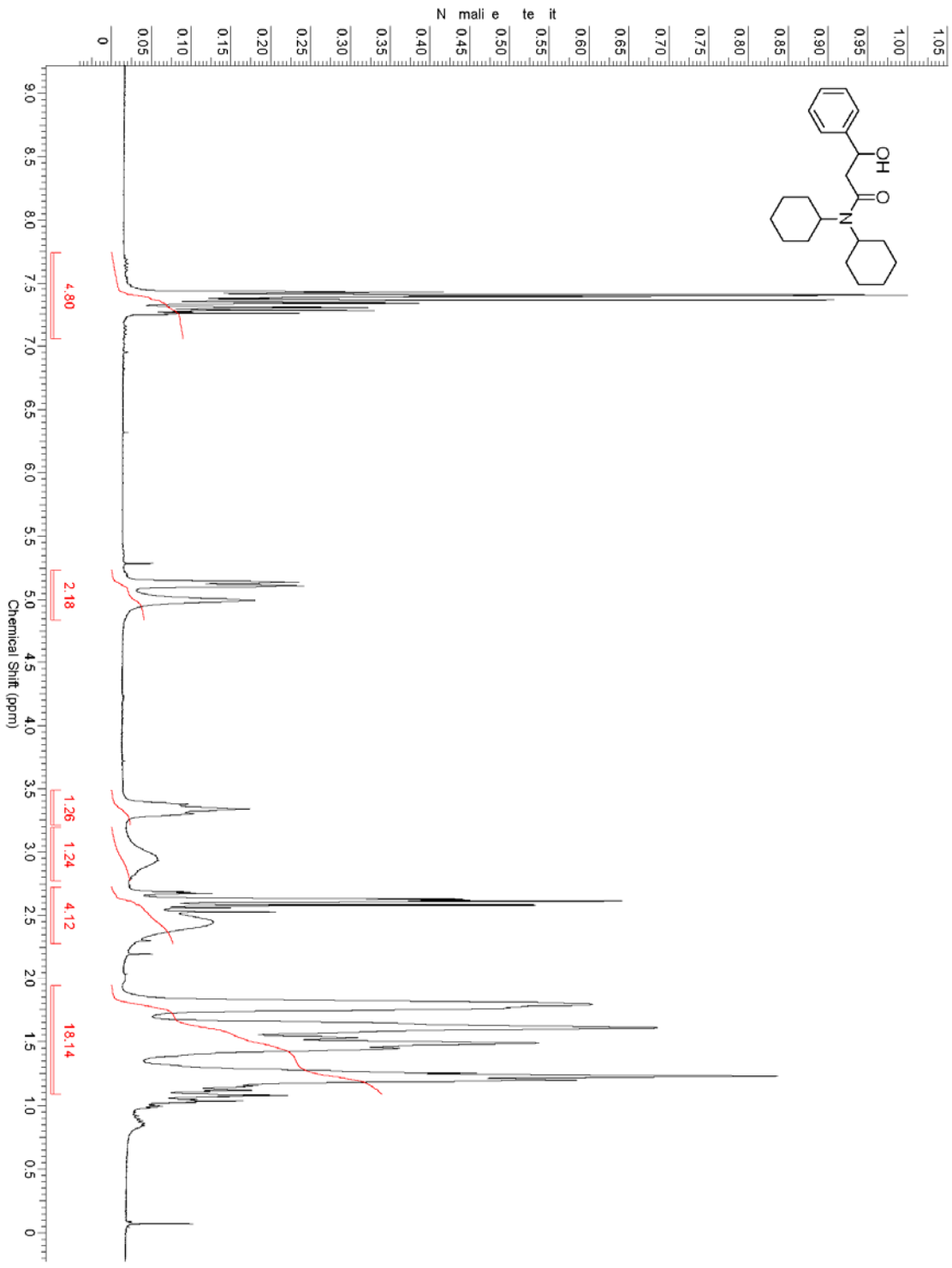

mali e te it
Chemical Shift (ppm)
OH
O
OEt

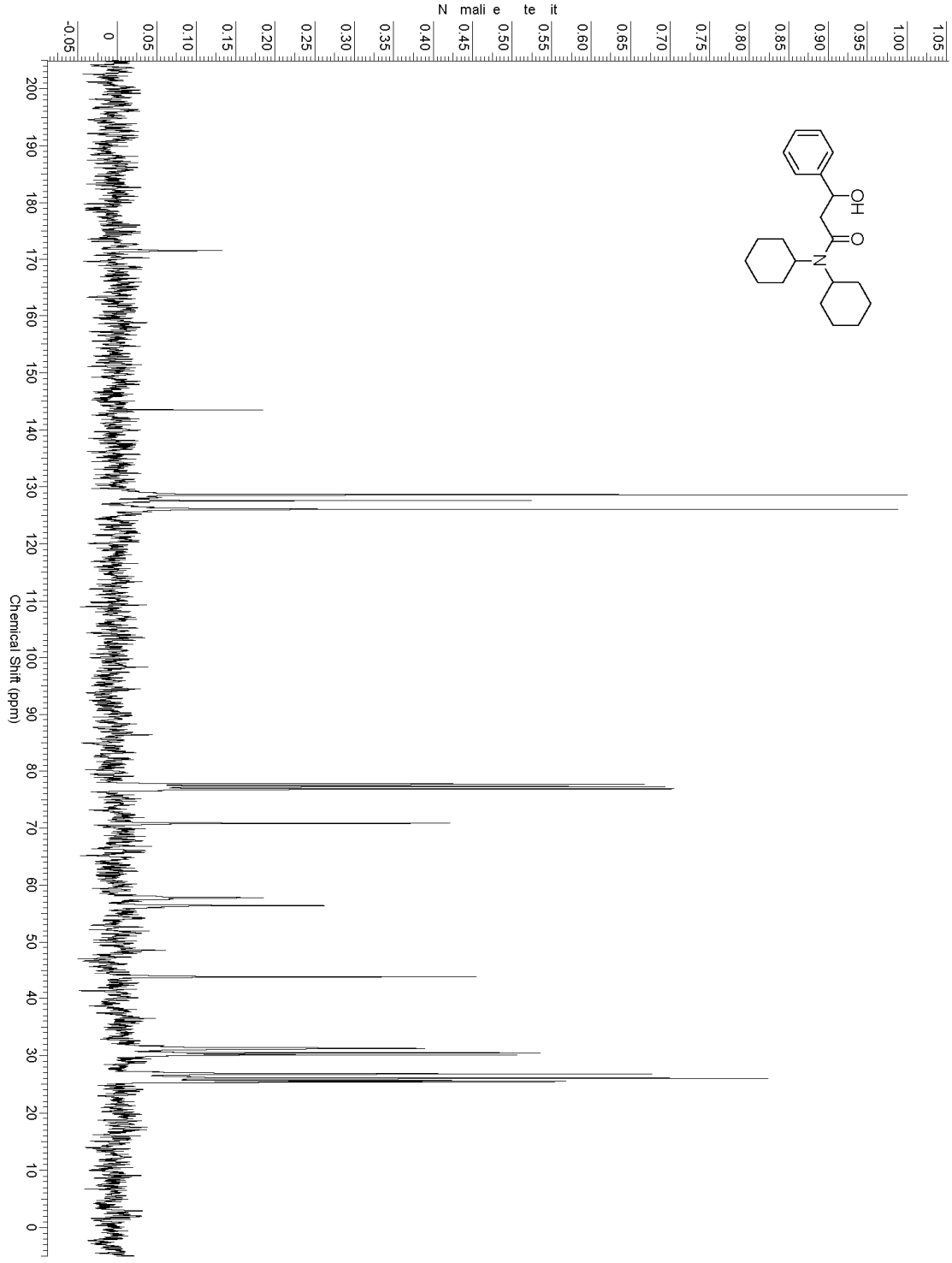

N mali e te it
Chemical Shift (ppm)
5.00
1.09
1.03
5.95
2.02
OH
O
N

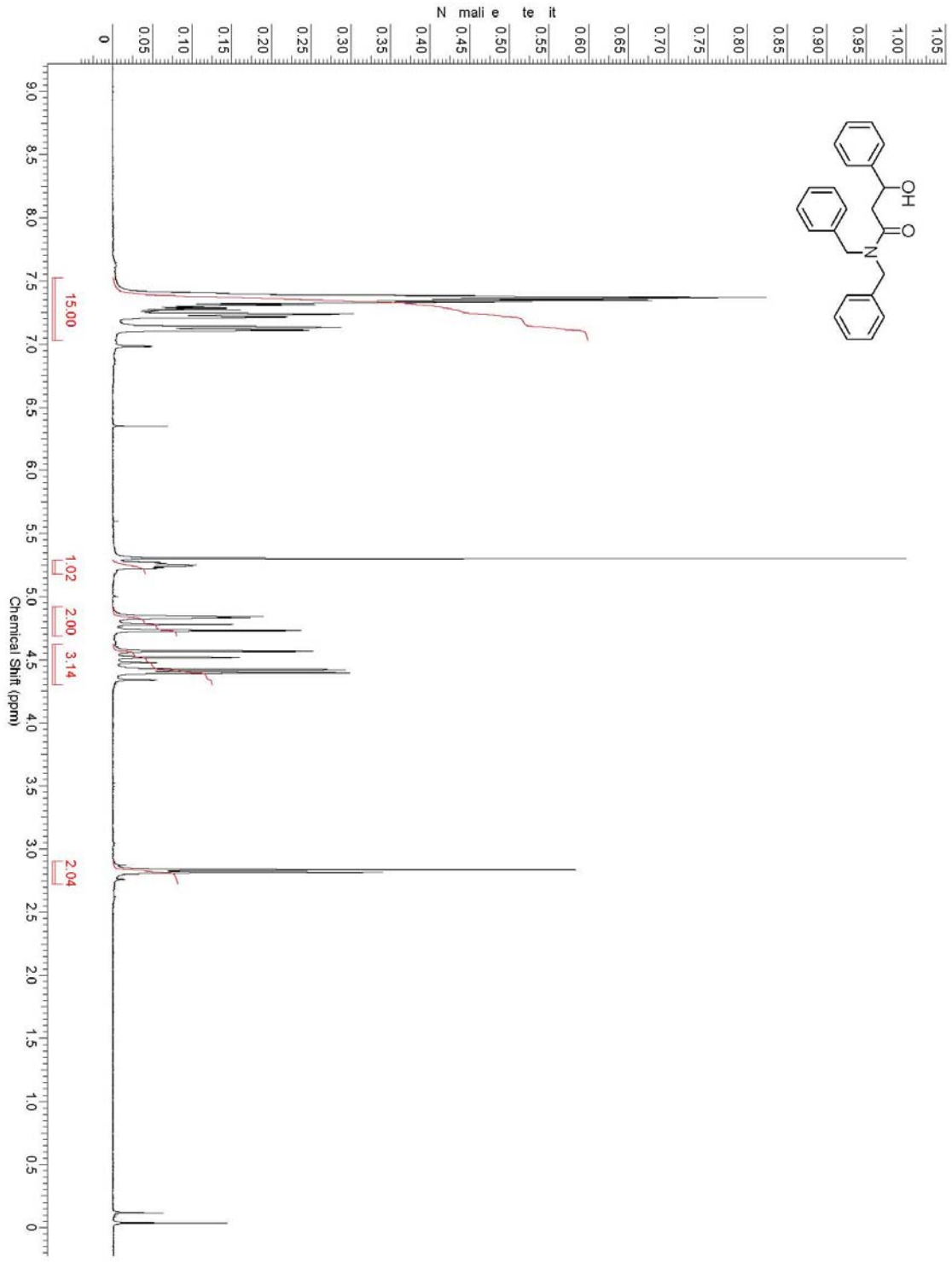

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
O
N

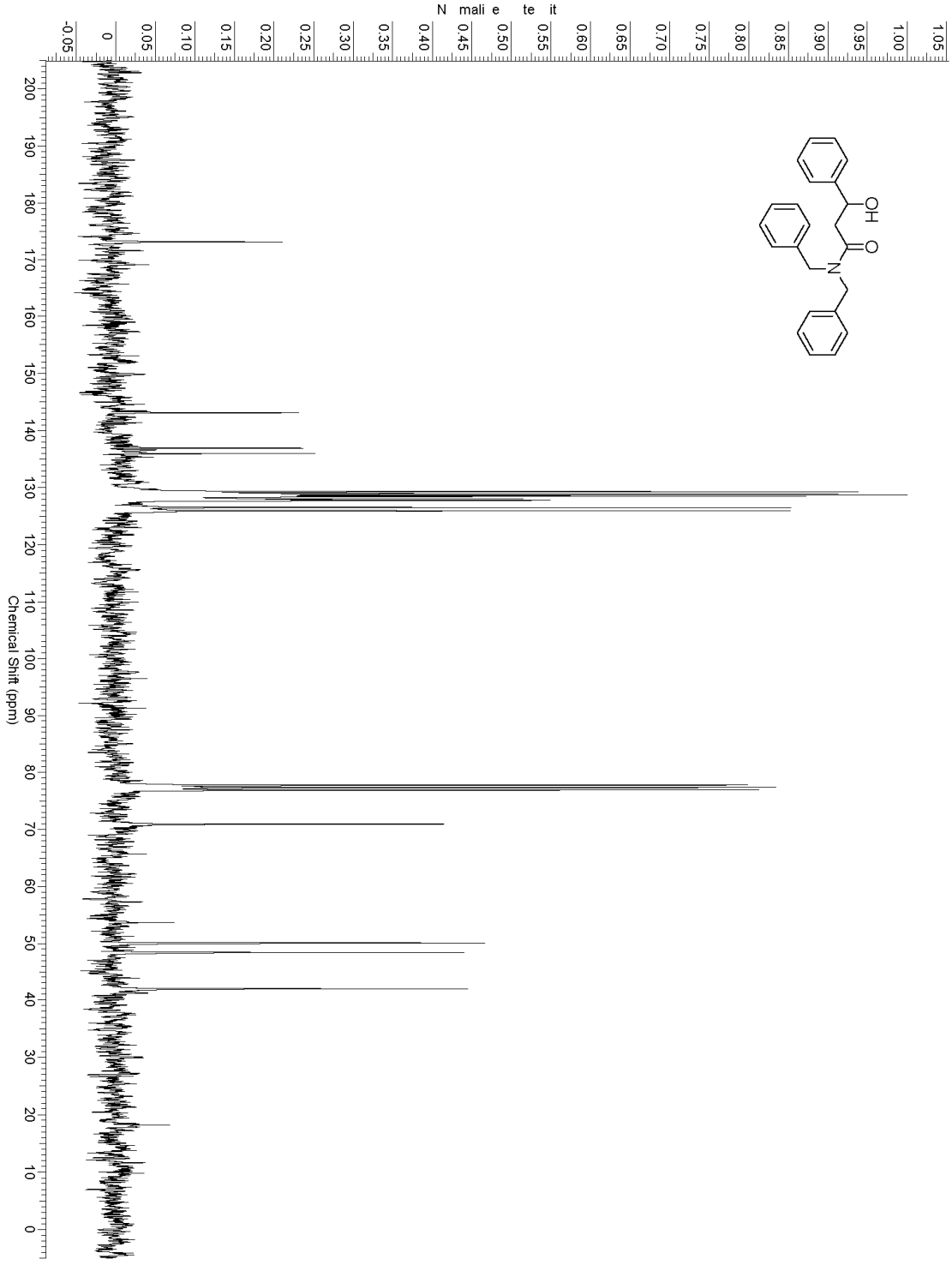

N mali e te it
Chemical Shift (ppm)
5.01
1.07
1.16
3.02
3.04
2.14
OH
O
O
N

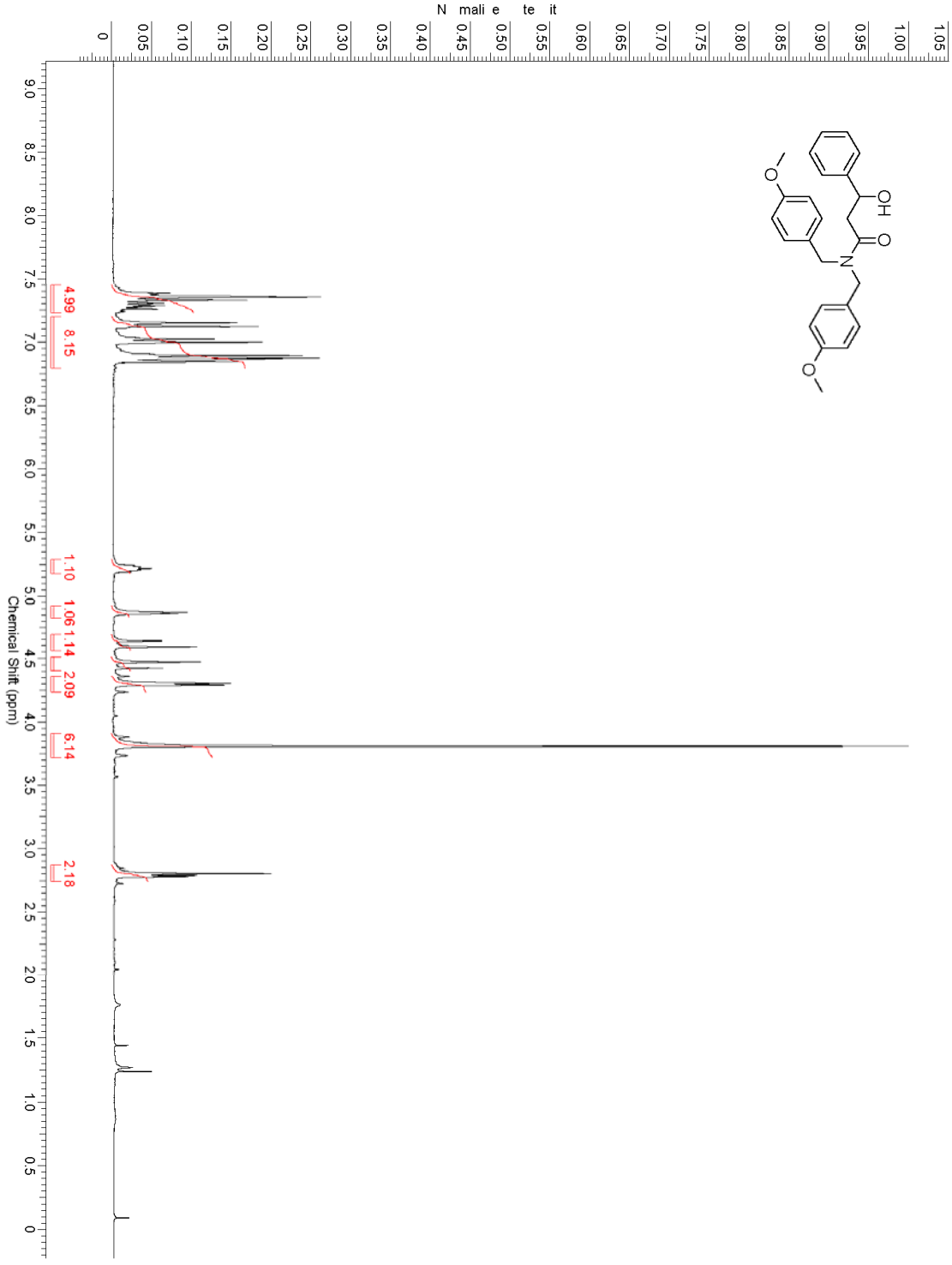

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
O
O
N

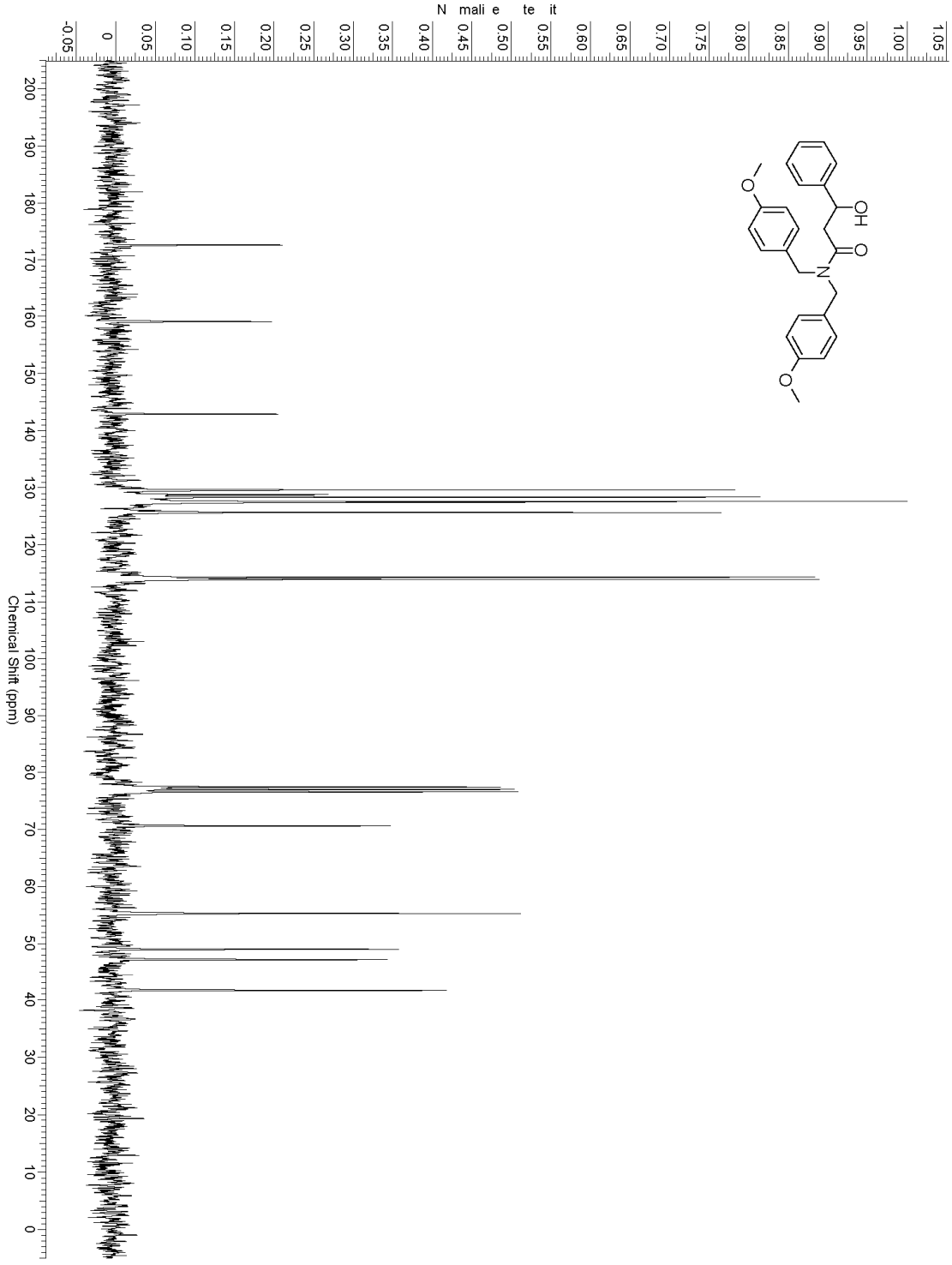

N mali e te it
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
OH
O
N
4.80
2.18
1.26
1.24
4.12
18.14
Chemical Shift (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

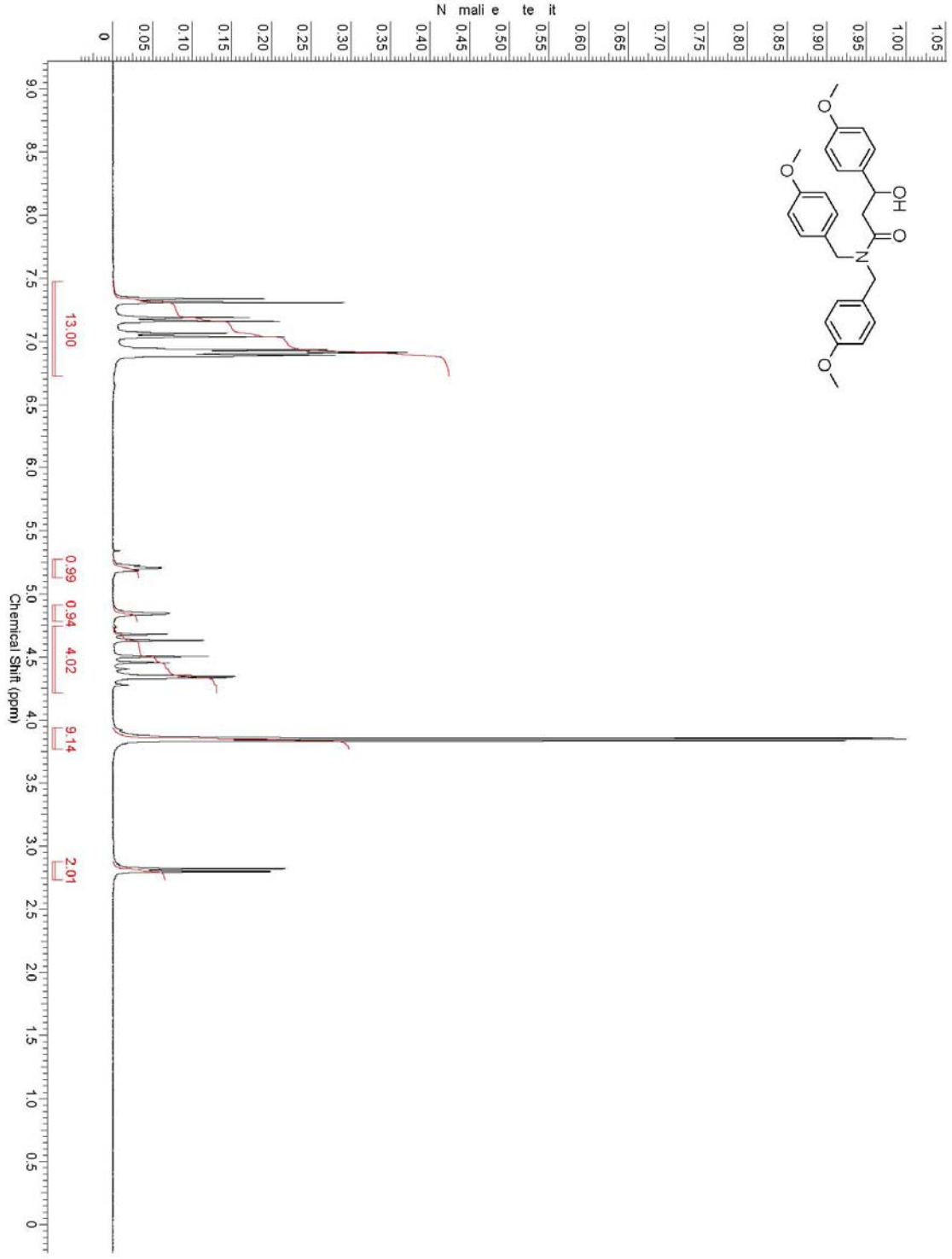

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
O
N

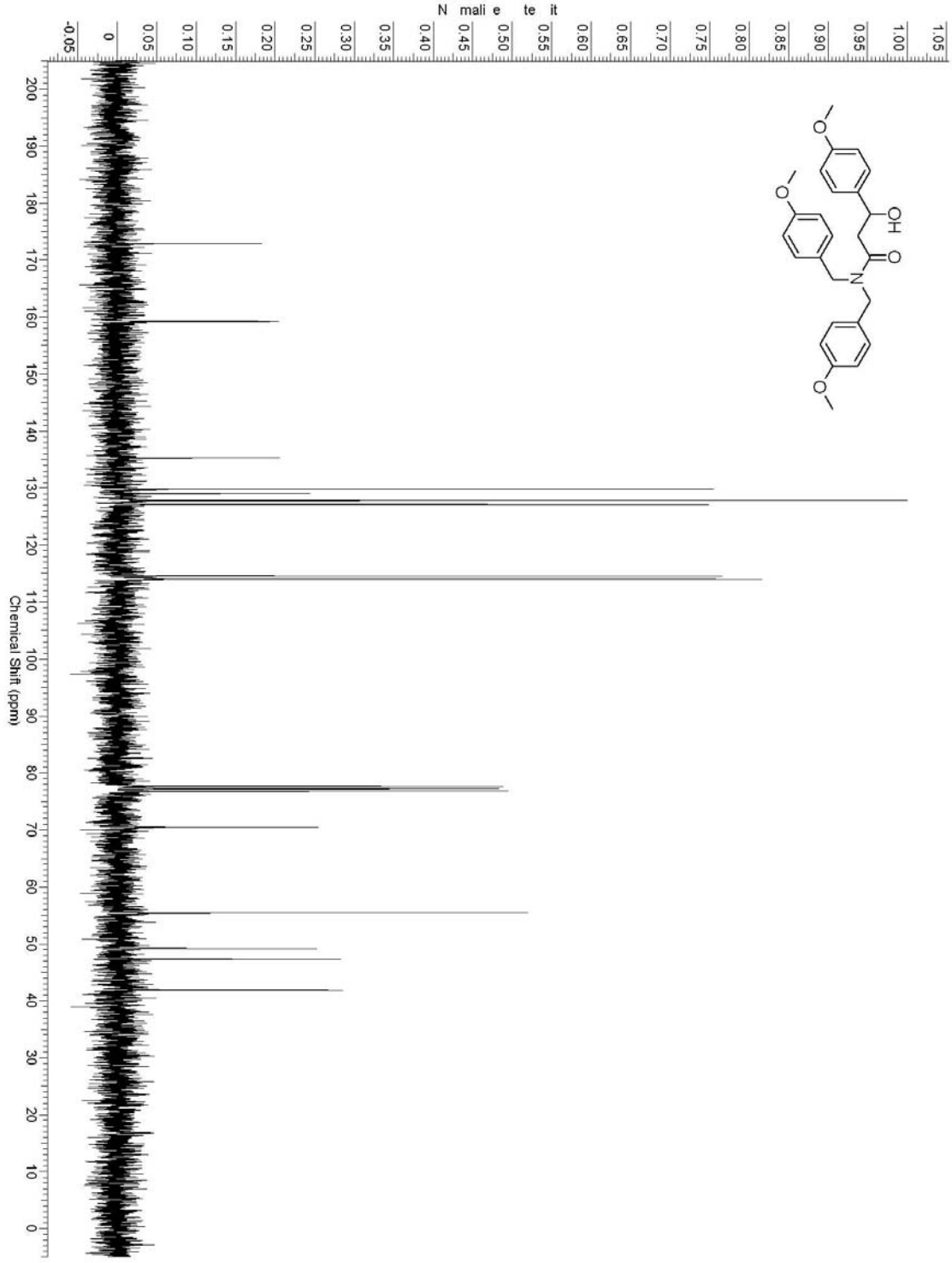

N mali e te it
Chemical Shift (ppm)
15.00
1.02
2.00
3.14
2.04
OH
O
N

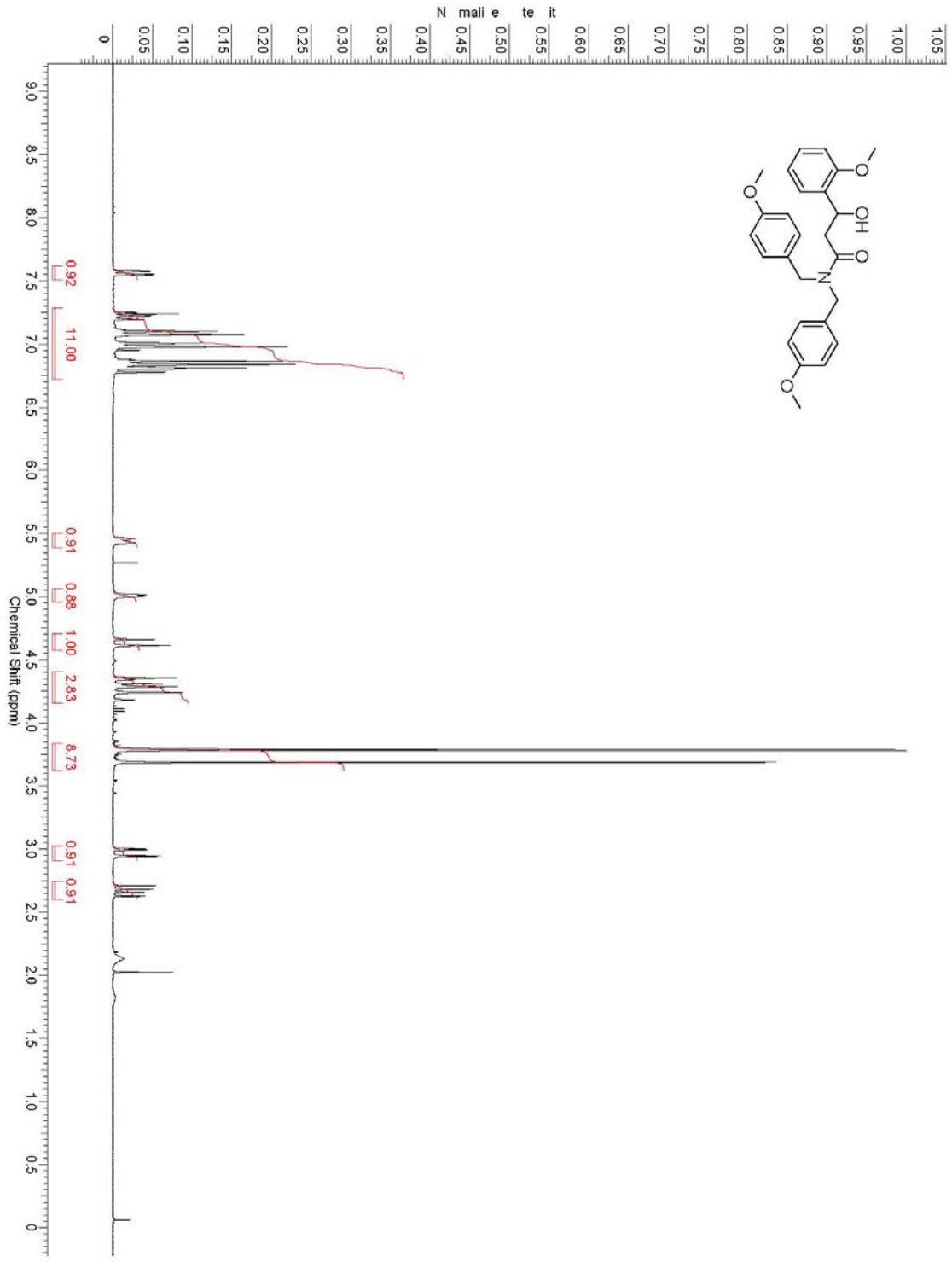

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
O
N

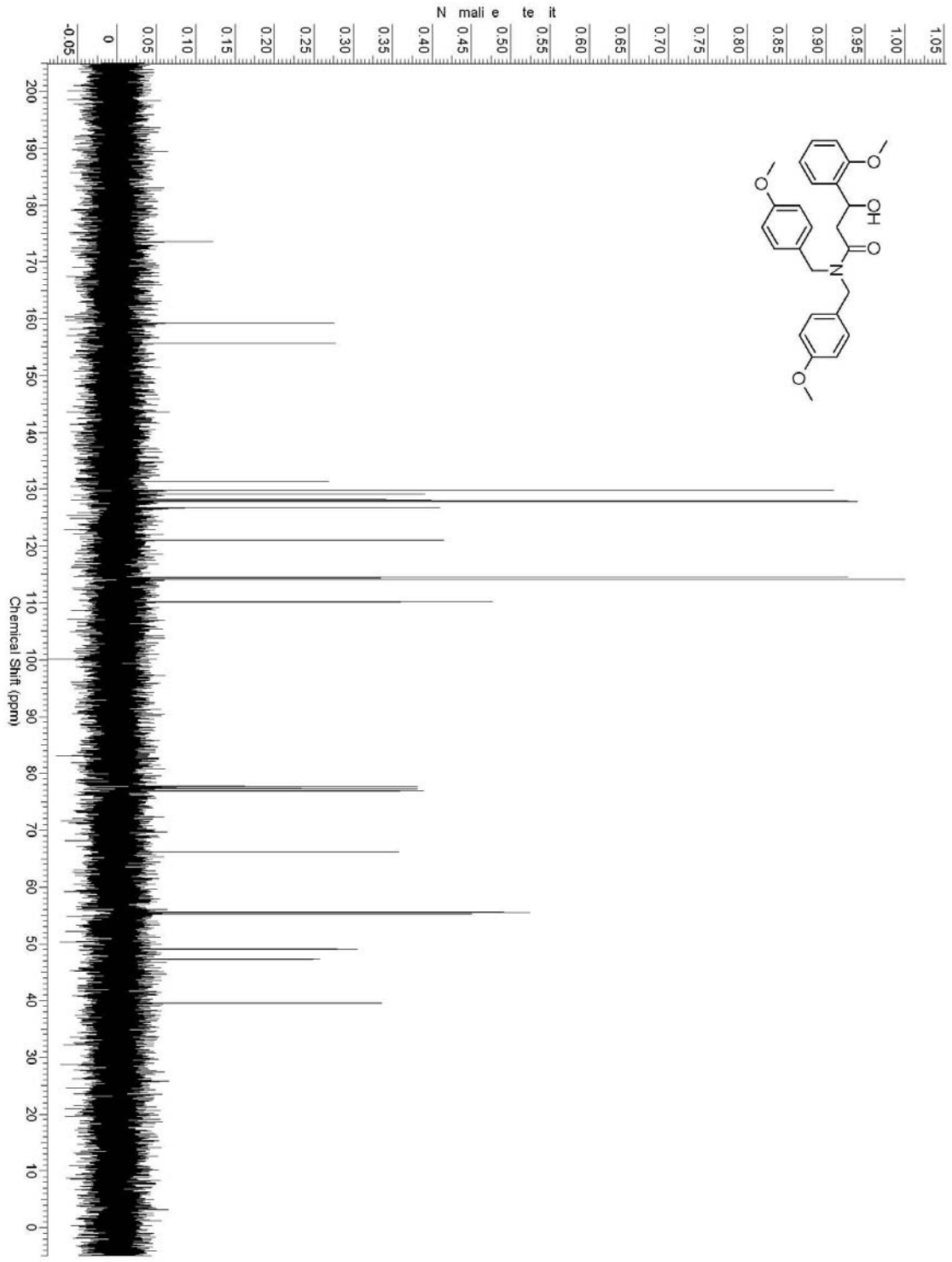

N mali e te it
Chemical Shift (ppm)
4.99
8.15
1.10
1.06
1.14
2.09
6.14
2.18
OH
O
N
O
O

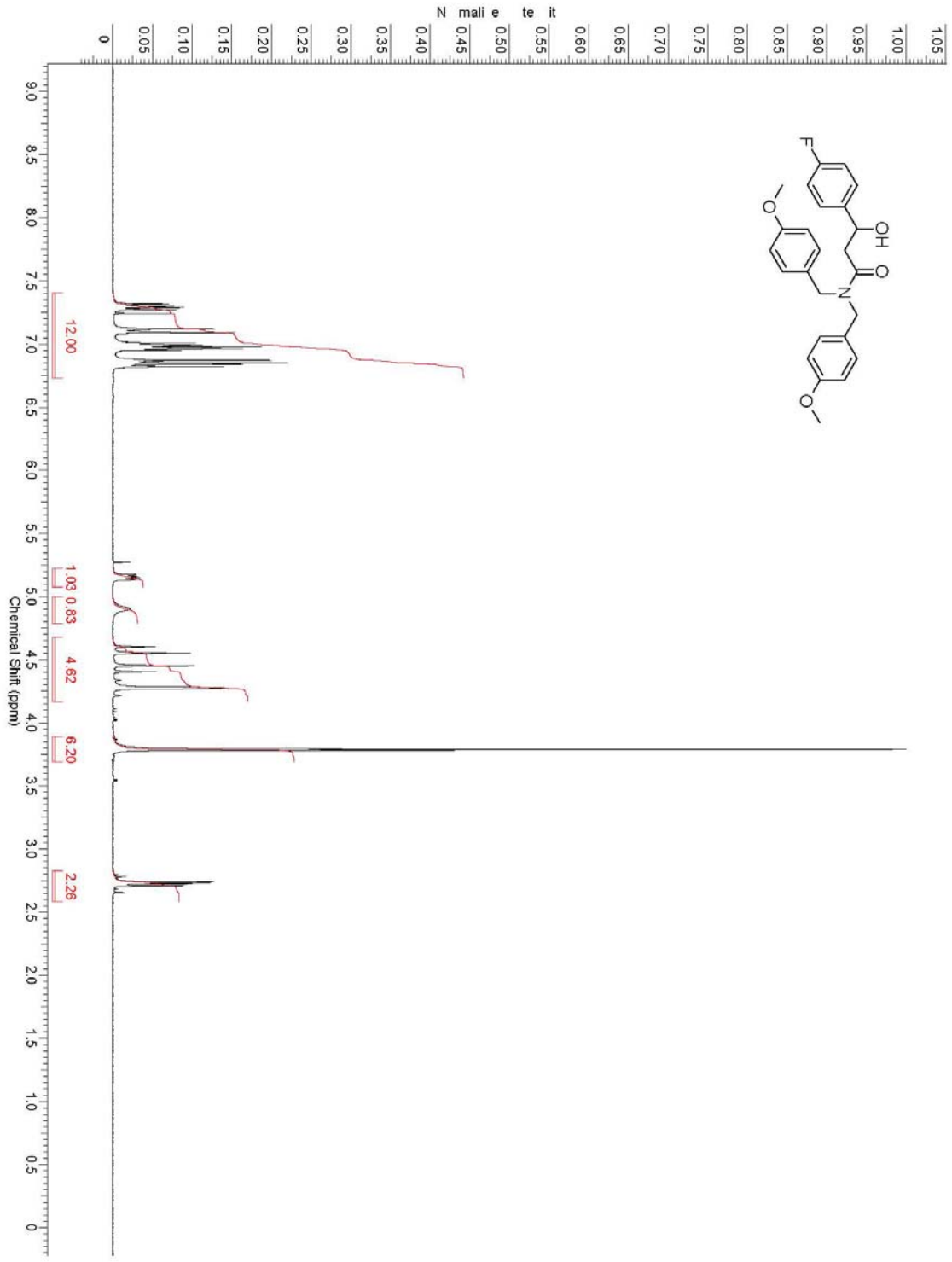

N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
OH
O
N
O


N mali e te it
Chemical Shift (ppm)
13.00
0.99
0.94
4.02
9.14
2.01
OH
O
N
O
O
O


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
OH
O
N
O


N mali e te it
Chemical Shift (ppm)
0.92
11.00
0.91
0.88
1.00
2.83
8.73
0.91
0.91
OH
O
N


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
OH
O
N
O
O


N mali e te it
Chemical Shift (ppm)
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0.83
4.62
6.20
2.26
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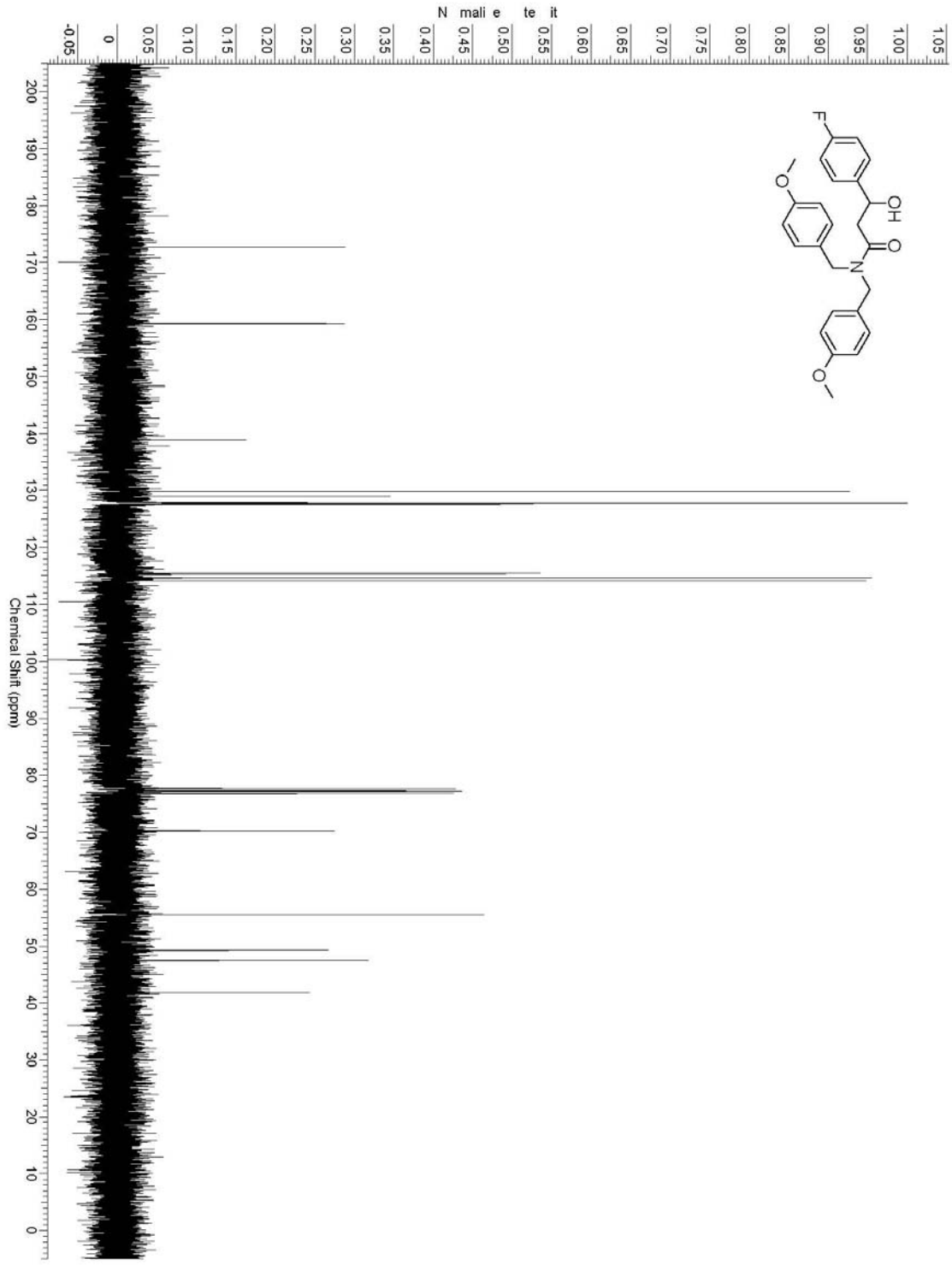
OH
O
N
O


N mali e te it
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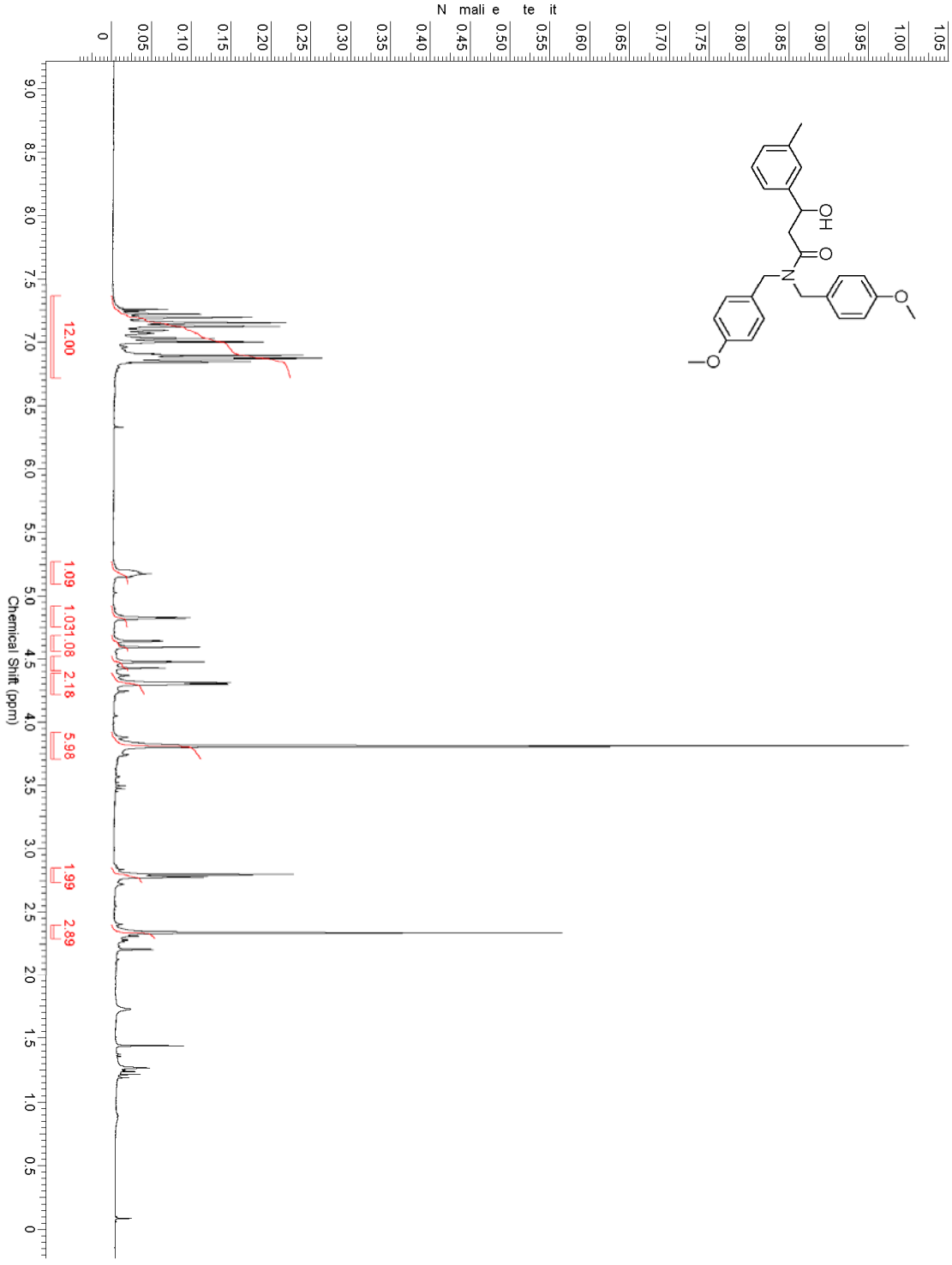
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
F
O
OH
O
N
O


N mali e te it
Chemical Shift (ppm)
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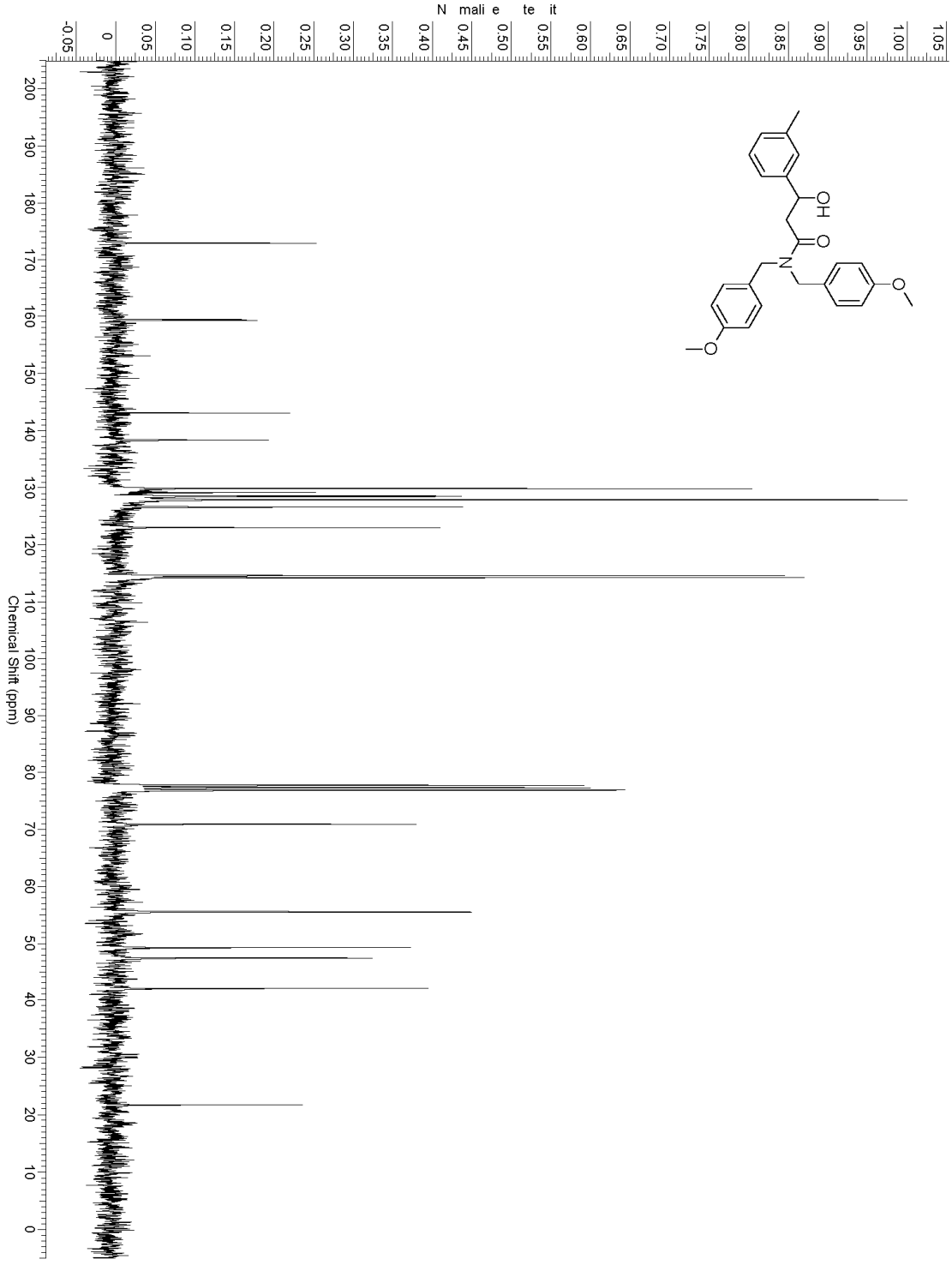
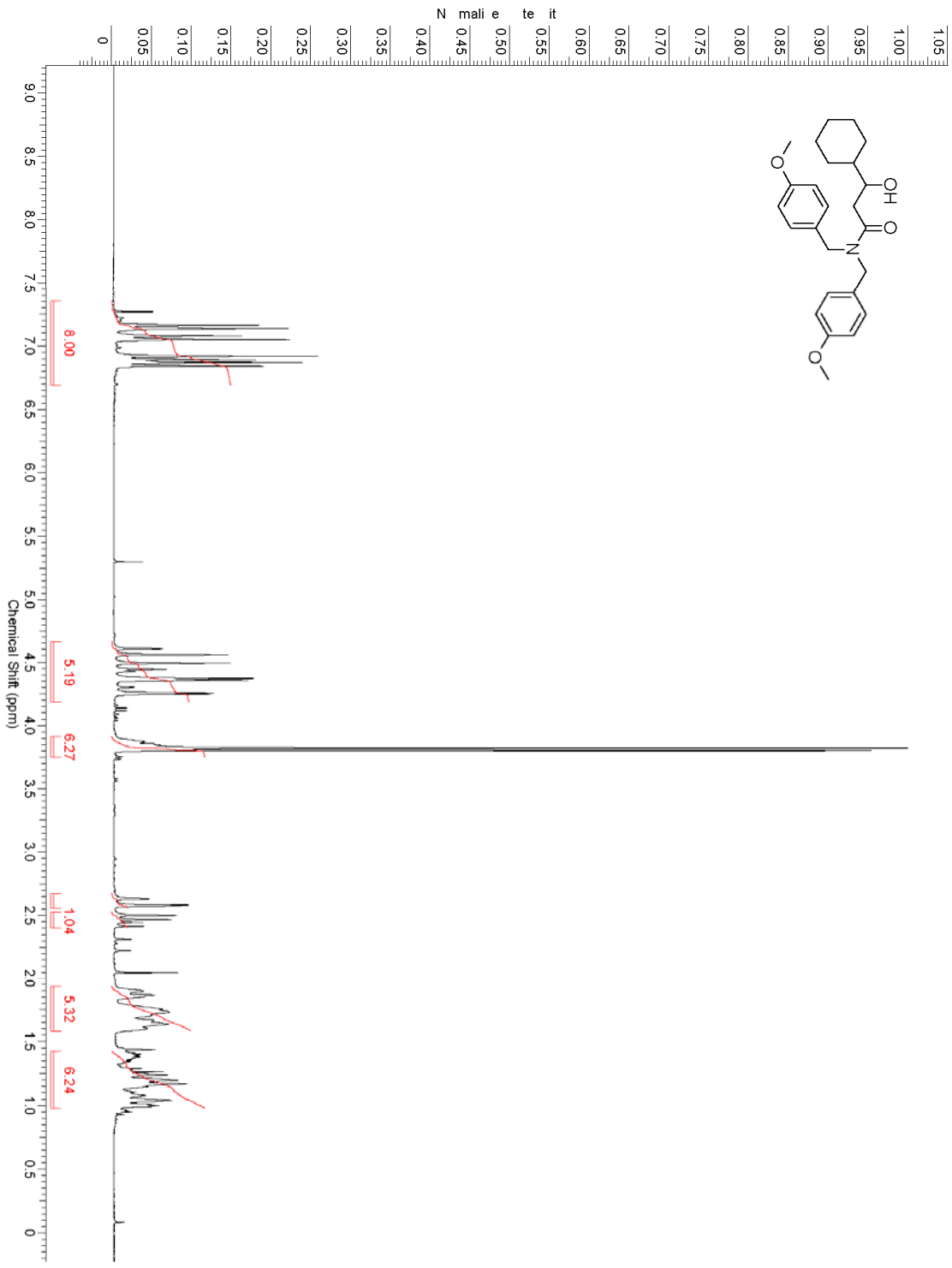
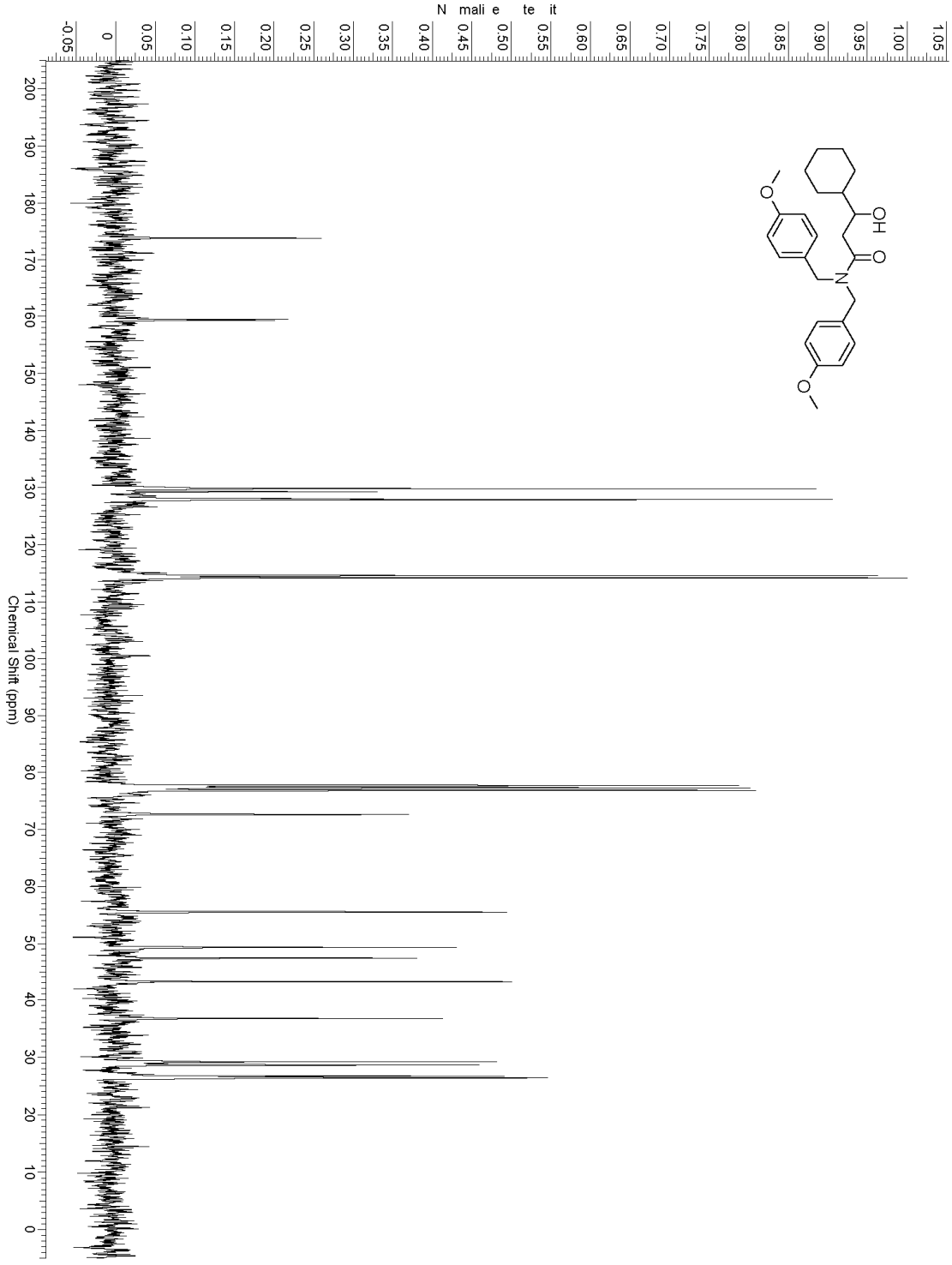
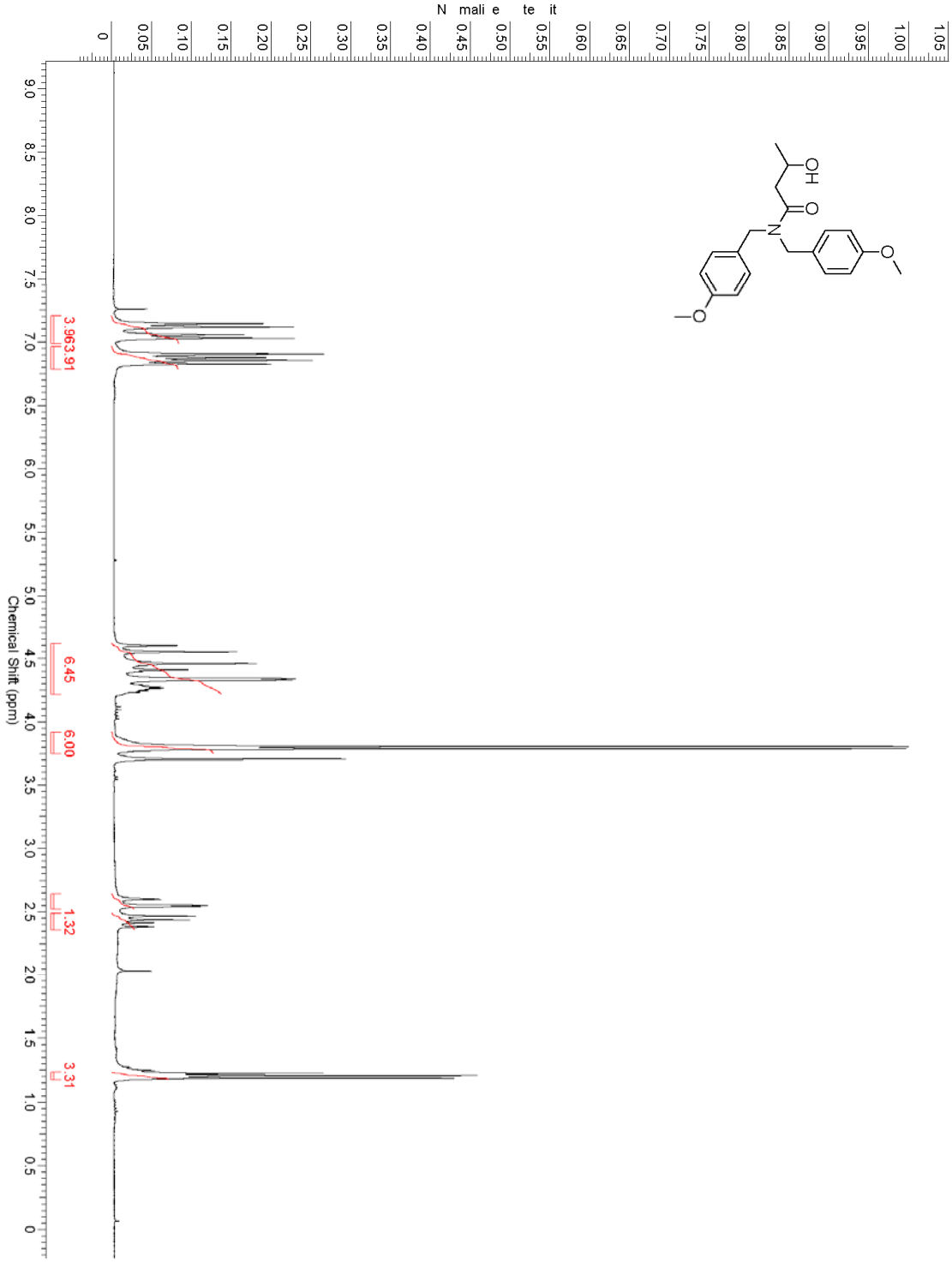
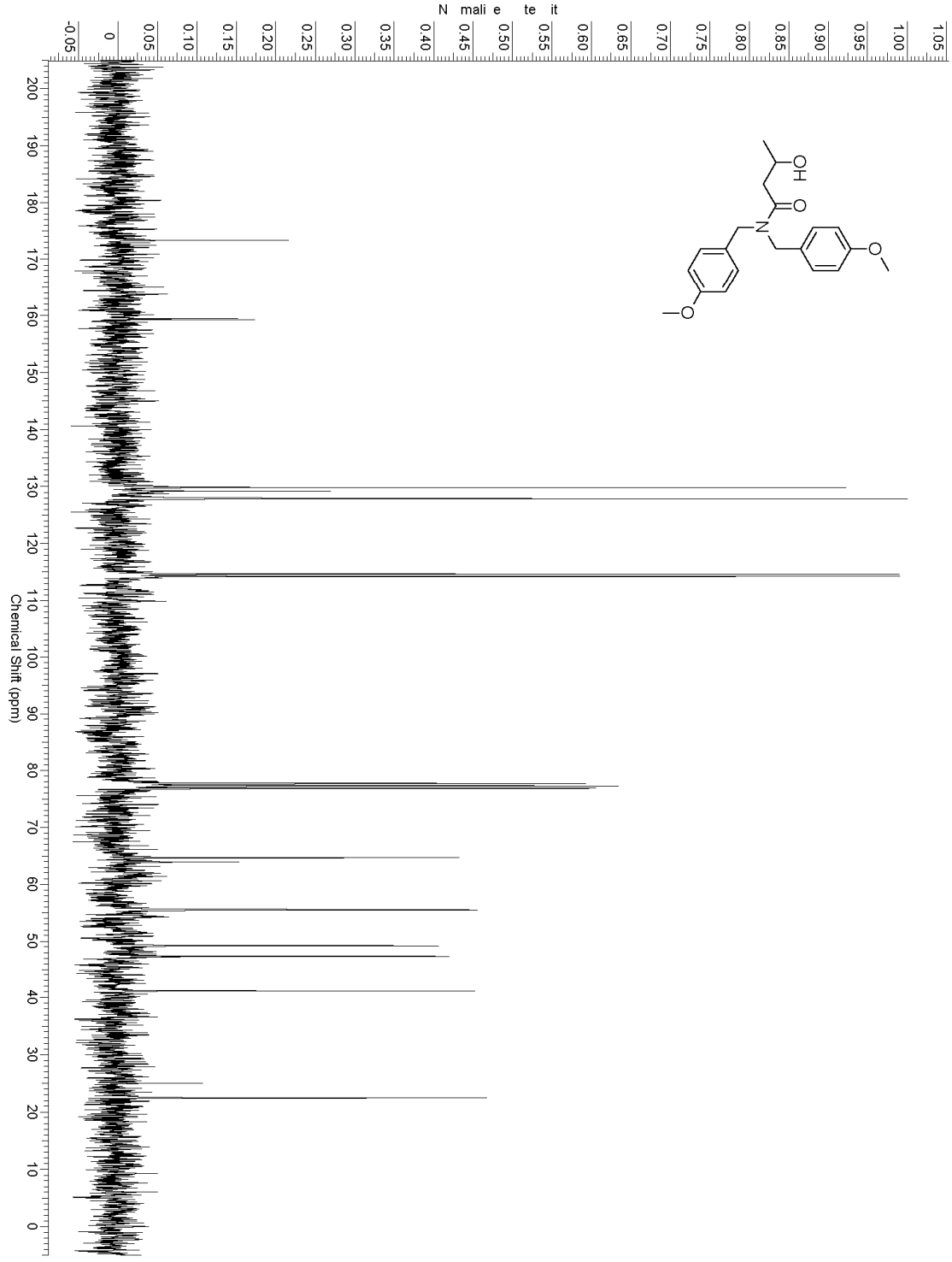
1.09
1.03
1.08
2.18
5.98
1.99
2.89
OH
O
N
O
O


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
O
N
O
O


N mali e te it
Chemical Shift (ppm)
8.00
5.19
6.27
1.04
5.32
6.24
OH
O
N
O
O


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
OH
O
N
O


N mali e te it
Chemical Shift (ppm)
3.96
3.91
6.45
6.00
1.32
3.31
OH
O
N
O
O


N mali e te it
-0.05
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
Chemical Shift (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OH
O
N
O
O

9. X-ray analysis for gold complexes

X-ray experimental for MIQ-AuCl (9): Data were collected at 100 K on a Bruker DUO system equipped with an APEX II area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 9999 reflections. A hemisphere of data was collected using the ω-scan method (0.5° frame width). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of two chemically equivalent but crystallographically independent. The data was checked for higher symmetry, in specific checked for the possibility of the space group being $P2_1/m$. No possible solution was found. Additionally, the two molecules in the asymmetric unit do not have neither a mirror symmetry nor an inversion symmetry. A total of 679 parameters were refined in the final cycle of refinement using 11154 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.32% and 4.24%, respectively. Refinement was done using F^2.

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement:

Identification code	dhw6	
Empirical formula	C33 H38 Au Cl N2	
Formula weight	695.07	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.074(12) Å	α= 90°.
	b = 11.168(12) Å	β= 93.82(2)°.
	c = 22.31(2) Å	γ = 90°.
Volume	3002(5) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	5.013 mm^{-1}	
F(000)	1384	
Crystal size	0.15 x 0.13 x 0.03 mm^3	
Theta range for data collection	1.69 to 27.50°.	
Index ranges	-15≤h≤15, -14≤k≤13, -28≤l≤28	
Reflections collected	31564	
Independent reflections	12574 [R(int) = 0.0246]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Nnumerical	

Max. and min. transmission	0.8642 and 0.5221
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12574 / 1 / 679
Goodness-of-fit on F^2	0.919
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0424 [11154]
R indices (all data)	R1 = 0.0300, wR2 = 0.0442
Absolute structure parameter	0.006(4)
Largest diff. peak and hole	1.341 and -0.688 e.Å^{-3}

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for dhw6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au1	9423(1)	7488(1)	10139(1)	17(1)
Au2	5631(1)	2554(1)	5028(1)	18(1)
Cl1	9807(1)	8323(1)	11066(1)	24(1)
Cl2	6385(1)	3340(1)	4203(1)	25(1)
N1	9468(2)	6994(3)	8816(1)	16(1)
N2	8287(2)	5883(3)	9215(1)	17(1)
N3	4151(2)	2106(2)	6045(1)	16(1)
N4	5589(2)	969(3)	6102(1)	17(1)
C1	9037(3)	6734(3)	9345(2)	16(1)
C2	7551(3)	5321(3)	9640(2)	21(1)
C3	7474(3)	3999(4)	9482(2)	24(1)
C4	7101(3)	3816(3)	8826(2)	23(1)
C5	6397(3)	2909(3)	8628(2)	29(1)
C6	6092(3)	2737(4)	8025(2)	31(1)
C7	6496(3)	3506(4)	7604(2)	28(1)
C8	7199(3)	4436(3)	7791(2)	21(1)
C9	7510(3)	4600(3)	8393(2)	17(1)
C10	8249(3)	5561(4)	8605(2)	16(1)

C11	9011(3)	6265(3)	8358(2)	15(1)
C12	9439(3)	6293(3)	7751(2)	17(1)
C13	9961(3)	5283(3)	7528(2)	21(1)
C14	10427(3)	5332(4)	6975(2)	27(1)
C15	10376(3)	6369(4)	6643(2)	28(1)
C16	9847(3)	7367(5)	6852(2)	29(1)
C17	9380(3)	7326(4)	7405(1)	22(1)
C18	10285(3)	7922(3)	8754(2)	17(1)
C19	11401(3)	7600(5)	8758(1)	20(1)
C20	12180(3)	8520(4)	8728(2)	23(1)
C21	11846(3)	9687(4)	8703(2)	28(1)
C22	10730(3)	9992(4)	8696(2)	25(1)
C23	9920(3)	9109(3)	8703(2)	19(1)
C24	11789(3)	6299(4)	8811(2)	22(1)
C25	12265(4)	6034(4)	9434(2)	39(1)
C26	12608(4)	5983(4)	8342(2)	37(1)
C27	8702(3)	9445(4)	8638(2)	22(1)
C28	8432(4)	10298(4)	8096(2)	33(1)
C29	8328(4)	10018(4)	9203(2)	34(1)
C30	6421(3)	5928(4)	9611(2)	24(1)
C31	6379(3)	7228(4)	9843(2)	28(1)
C32	6609(3)	7302(4)	10520(2)	34(1)
C33	5255(3)	7770(5)	9672(2)	48(1)

C34	5076(3)	1832(3)	5763(2)	18(1)
C35	6659(3)	384(4)	6000(2)	21(1)
C36	6536(3)	-932(3)	6162(2)	26(1)
C37	6146(3)	-1109(3)	6786(2)	22(1)
C38	6495(3)	-2051(3)	7152(2)	33(1)
C39	6103(3)	-2211(4)	7709(2)	41(1)
C40	5341(3)	-1404(4)	7915(2)	36(1)
C41	4959(3)	-464(4)	7558(2)	30(1)
C42	5363(3)	-296(3)	6991(2)	21(1)
C43	4980(3)	676(3)	6591(2)	16(1)
C44	4081(3)	1394(3)	6562(2)	18(1)
C45	3094(3)	1464(3)	6924(2)	18(1)
C46	2301(3)	577(4)	6879(2)	31(1)
C47	1339(4)	688(5)	7183(2)	42(1)
C48	1183(3)	1680(4)	7537(2)	32(1)
C49	1991(3)	2544(6)	7606(1)	29(1)
C50	2950(3)	2433(5)	7299(1)	26(1)
C51	3308(3)	2948(3)	5820(2)	18(1)
C52	2444(2)	2537(5)	5436(1)	18(1)
C53	1654(3)	3378(4)	5218(2)	25(1)
C54	1751(3)	4554(4)	5374(2)	23(1)
C55	2608(3)	4940(3)	5770(2)	22(1)
C56	3406(3)	4146(3)	6006(2)	18(1)

C57	4323(3)	4556(4)	6455(2)	22(1)
C58	3916(3)	5452(4)	6918(2)	29(1)
C59	5280(3)	5111(4)	6134(2)	25(1)
C60	2337(3)	1229(3)	5232(2)	23(1)
C61	2533(3)	1107(4)	4570(2)	33(1)
C62	1202(3)	693(4)	5361(2)	31(1)
C63	7614(3)	988(4)	6369(2)	23(1)
C64	7899(3)	2277(4)	6194(2)	25(1)
C65	8718(3)	2818(4)	6667(2)	40(1)
C66	8395(3)	2334(5)	5584(2)	31(1)

Table 3. Bond lengths [Å] and angles [°] for dhw6.

Au1-C1	1.988(4)
Au1-Cl1	2.289(2)
Au2-C34	1.984(4)
Au2-Cl2	2.2824(19)
N1-C1	1.353(4)
N1-C11	1.391(4)
N1-C18	1.444(4)
N2-C1	1.331(5)
N2-C10	1.407(5)
N2-C2	1.481(4)
N3-C34	1.353(4)
N3-C44	1.409(4)
N3-C51	1.451(4)
N4-C34	1.349(5)
N4-C43	1.396(5)
N4-C35	1.478(5)
C2-C3	1.519(5)
C2-C30	1.521(5)
C2-H2A	1.0000
C3-C4	1.515(5)
C3-H3A	0.9900

C3-H3B	0.9900
C4-C5	1.376(5)
C4-C9	1.417(5)
C5-C6	1.386(5)
C5-H5A	0.9500
C6-C7	1.385(6)
C6-H6A	0.9500
C7-C8	1.389(5)
C7-H7A	0.9500
C8-C9	1.382(5)
C8-H8A	0.9500
C9-C10	1.454(5)
C10-C11	1.354(5)
C11-C12	1.483(5)
C12-C17	1.387(6)
C12-C13	1.400(5)
C13-C14	1.391(5)
C13-H13A	0.9500
C14-C15	1.374(6)
C14-H14A	0.9500
C15-C16	1.381(6)
C15-H15A	0.9500
C16-C17	1.391(5)

C16-H16A	0.9500
C17-H17A	0.9500
C18-C19	1.393(5)
C18-C23	1.400(5)
C19-C20	1.398(6)
C19-C24	1.529(7)
C20-C21	1.364(6)
C20-H20A	0.9500
C21-C22	1.389(5)
C21-H21A	0.9500
C22-C23	1.390(5)
C22-H22A	0.9500
C23-C27	1.515(5)
C24-C25	1.499(6)
C24-C26	1.527(5)
C24-H24A	1.0000
C25-H25A	0.9800
C25-H25B	0.9800
C25-H25C	0.9800
C26-H26A	0.9800
C26-H26B	0.9800
C26-H26C	0.9800
C27-C29	1.508(6)

C27-C28	1.557(6)
C27-H27A	1.0000
C28-H28A	0.9800
C28-H28B	0.9800
C28-H28C	0.9800
C29-H29A	0.9800
C29-H29B	0.9800
C29-H29C	0.9800
C30-C31	1.544(6)
C30-H30A	0.9900
C30-H30B	0.9900
C31-C33	1.512(5)
C31-C32	1.520(5)
C31-H31A	1.0000
C32-H32A	0.9800
C32-H32B	0.9800
C32-H32C	0.9800
C33-H33A	0.9800
C33-H33B	0.9800
C33-H33C	0.9800
C35-C36	1.523(6)
C35-C63	1.529(5)
C35-H35A	1.0000

C36-C37	1.511(5)
C36-H36A	0.9900
C36-H36B	0.9900
C37-C38	1.381(5)
C37-C42	1.409(5)
C38-C39	1.371(6)
C38-H38A	0.9500
C39-C40	1.389(6)
C39-H39A	0.9500
C40-C41	1.379(6)
C40-H40A	0.9500
C41-C42	1.397(5)
C41-H41A	0.9500
C42-C43	1.462(5)
C43-C44	1.347(5)
C44-C45	1.486(5)
C45-C46	1.376(5)
C45-C50	1.385(6)
C46-C47	1.389(6)
C46-H46A	0.9500
C47-C48	1.382(6)
C47-H47A	0.9500
C48-C49	1.373(7)

C48-H48A	0.9500
C49-C50	1.390(4)
C49-H49A	0.9500
C50-H50A	0.9500
C51-C52	1.384(5)
C51-C56	1.404(5)
C52-C53	1.401(6)
C52-C60	1.533(6)
C53-C54	1.361(6)
C53-H53A	0.9500
C54-C55	1.384(5)
C54-H54A	0.9500
C55-C56	1.388(5)
C55-H55A	0.9500
C56-C57	1.513(5)
C57-C59	1.531(5)
C57-C58	1.542(5)
C57-H57A	1.0000
C58-H58A	0.9800
C58-H58B	0.9800
C58-H58C	0.9800
C59-H59A	0.9800
C59-H59B	0.9800

C59-H59C	0.9800
C60-C61	1.517(5)
C60-C62	1.540(5)
C60-H60A	1.0000
C61-H61A	0.9800
C61-H61B	0.9800
C61-H61C	0.9800
C62-H62A	0.9800
C62-H62B	0.9800
C62-H62C	0.9800
C63-C64	1.537(6)
C63-H63A	0.9900
C63-H63B	0.9900
C64-C65	1.524(5)
C64-C66	1.525(5)
C64-H64A	1.0000
C65-H65A	0.9800
C65-H65B	0.9800
C65-H65C	0.9800
C66-H66A	0.9800
C66-H66B	0.9800
C66-H66C	0.9800

C1-Au1-Cl1	177.79(10)
C34-Au2-Cl2	176.17(10)
C1-N1-C11	111.0(3)
C1-N1-C18	122.9(3)
C11-N1-C18	126.1(3)
C1-N2-C10	111.8(3)
C1-N2-C2	126.3(3)
C10-N2-C2	121.9(3)
C34-N3-C44	110.4(3)
C34-N3-C51	124.6(3)
C44-N3-C51	124.8(3)
C34-N4-C43	111.0(3)
C34-N4-C35	127.1(3)
C43-N4-C35	121.9(3)
N2-C1-N1	105.0(3)
N2-C1-Au1	127.7(3)
N1-C1-Au1	127.3(3)
N2-C2-C3	107.1(3)
N2-C2-C30	111.0(3)
C3-C2-C30	112.5(3)
N2-C2-H2A	108.7
C3-C2-H2A	108.7
C30-C2-H2A	108.7

C4-C3-C2	111.4(3)
C4-C3-H3A	109.4
C2-C3-H3A	109.4
C4-C3-H3B	109.4
C2-C3-H3B	109.4
H3A-C3-H3B	108.0
C5-C4-C9	118.1(4)
C5-C4-C3	123.1(3)
C9-C4-C3	118.7(3)
C4-C5-C6	122.2(4)
C4-C5-H5A	118.9
C6-C5-H5A	118.9
C7-C6-C5	119.3(4)
C7-C6-H6A	120.3
C5-C6-H6A	120.3
C6-C7-C8	119.7(4)
C6-C7-H7A	120.2
C8-C7-H7A	120.2
C9-C8-C7	120.9(4)
C9-C8-H8A	119.5
C7-C8-H8A	119.5
C8-C9-C4	119.7(3)
C8-C9-C10	122.3(3)

C4-C9-C10	117.9(3)
C11-C10-N2	105.3(3)
C11-C10-C9	135.7(4)
N2-C10-C9	118.9(3)
C10-C11-N1	106.8(3)
C10-C11-C12	132.1(3)
N1-C11-C12	120.9(3)
C17-C12-C13	118.7(3)
C17-C12-C11	121.2(3)
C13-C12-C11	120.0(3)
C14-C13-C12	120.1(4)
C14-C13-H13A	119.9
C12-C13-H13A	119.9
C15-C14-C13	120.3(4)
C15-C14-H14A	119.9
C13-C14-H14A	119.9
C14-C15-C16	120.2(4)
C14-C15-H15A	119.9
C16-C15-H15A	119.9
C15-C16-C17	119.8(4)
C15-C16-H16A	120.1
C17-C16-H16A	120.1
C12-C17-C16	120.8(4)

C12-C17-H17A	119.6
C16-C17-H17A	119.6
C19-C18-C23	123.0(4)
C19-C18-N1	118.8(3)
C23-C18-N1	118.3(3)
C18-C19-C20	117.6(4)
C18-C19-C24	122.5(4)
C20-C19-C24	119.9(3)
C21-C20-C19	120.4(4)
C21-C20-H20A	119.8
C19-C20-H20A	119.8
C20-C21-C22	121.2(4)
C20-C21-H21A	119.4
C22-C21-H21A	119.4
C21-C22-C23	120.6(4)
C21-C22-H22A	119.7
C23-C22-H22A	119.7
C22-C23-C18	117.0(4)
C22-C23-C27	120.1(4)
C18-C23-C27	122.8(3)
C25-C24-C26	111.4(4)
C25-C24-C19	110.8(3)
C26-C24-C19	112.1(3)

C25-C24-H24A	107.4
C26-C24-H24A	107.4
C19-C24-H24A	107.4
C24-C25-H25A	109.5
C24-C25-H25B	109.5
H25A-C25-H25B	109.5
C24-C25-H25C	109.5
H25A-C25-H25C	109.5
H25B-C25-H25C	109.5
C24-C26-H26A	109.5
C24-C26-H26B	109.5
H26A-C26-H26B	109.5
C24-C26-H26C	109.5
H26A-C26-H26C	109.5
H26B-C26-H26C	109.5
C29-C27-C23	111.6(4)
C29-C27-C28	109.3(4)
C23-C27-C28	112.2(3)
C29-C27-H27A	107.9
C23-C27-H27A	107.9
C28-C27-H27A	107.9
C27-C28-H28A	109.5
C27-C28-H28B	109.5

H28A-C28-H28B	109.5
C27-C28-H28C	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5
C27-C29-H29A	109.5
C27-C29-H29B	109.5
H29A-C29-H29B	109.5
C27-C29-H29C	109.5
H29A-C29-H29C	109.5
H29B-C29-H29C	109.5
C2-C30-C31	117.0(3)
C2-C30-H30A	108.1
C31-C30-H30A	108.1
C2-C30-H30B	108.1
C31-C30-H30B	108.1
H30A-C30-H30B	107.3
C33-C31-C32	109.3(3)
C33-C31-C30	109.9(3)
C32-C31-C30	112.1(3)
C33-C31-H31A	108.5
C32-C31-H31A	108.5
C30-C31-H31A	108.5
C31-C32-H32A	109.5

C31-C32-H32B	109.5
H32A-C32-H32B	109.5
C31-C32-H32C	109.5
H32A-C32-H32C	109.5
H32B-C32-H32C	109.5
C31-C33-H33A	109.5
C31-C33-H33B	109.5
H33A-C33-H33B	109.5
C31-C33-H33C	109.5
H33A-C33-H33C	109.5
H33B-C33-H33C	109.5
N4-C34-N3	105.4(3)
N4-C34-Au2	125.8(3)
N3-C34-Au2	128.8(3)
N4-C35-C36	106.9(3)
N4-C35-C63	110.9(3)
C36-C35-C63	112.4(3)
N4-C35-H35A	108.9
C36-C35-H35A	108.9
C63-C35-H35A	108.9
C37-C36-C35	112.7(3)
C37-C36-H36A	109.1
C35-C36-H36A	109.1

C37-C36-H36B	109.1
C35-C36-H36B	109.1
H36A-C36-H36B	107.8
C38-C37-C42	118.9(4)
C38-C37-C36	122.9(4)
C42-C37-C36	118.2(3)
C39-C38-C37	121.7(4)
C39-C38-H38A	119.1
C37-C38-H38A	119.1
C38-C39-C40	119.4(4)
C38-C39-H39A	120.3
C40-C39-H39A	120.3
C41-C40-C39	120.5(4)
C41-C40-H40A	119.8
C39-C40-H40A	119.8
C40-C41-C42	120.1(4)
C40-C41-H41A	120.0
C42-C41-H41A	120.0
C41-C42-C37	119.4(4)
C41-C42-C43	122.4(4)
C37-C42-C43	118.2(3)
C44-C43-N4	106.8(3)
C44-C43-C42	133.8(3)

N4-C43-C42	119.3(3)
C43-C44-N3	106.4(3)
C43-C44-C45	132.7(3)
N3-C44-C45	120.7(3)
C46-C45-C50	119.5(3)
C46-C45-C44	120.1(3)
C50-C45-C44	120.4(3)
C45-C46-C47	120.0(4)
C45-C46-H46A	120.0
C47-C46-H46A	120.0
C48-C47-C46	120.0(4)
C48-C47-H47A	120.0
C46-C47-H47A	120.0
C49-C48-C47	120.3(4)
C49-C48-H48A	119.9
C47-C48-H48A	119.9
C48-C49-C50	119.5(5)
C48-C49-H49A	120.2
C50-C49-H49A	120.2
C45-C50-C49	120.5(4)
C45-C50-H50A	119.7
C49-C50-H50A	119.7
C52-C51-C56	123.0(4)

C52-C51-N3	118.8(4)
C56-C51-N3	118.1(3)
C51-C52-C53	117.3(5)
C51-C52-C60	123.0(4)
C53-C52-C60	119.6(3)
C54-C53-C52	120.9(4)
C54-C53-H53A	119.5
C52-C53-H53A	119.5
C53-C54-C55	120.7(4)
C53-C54-H54A	119.6
C55-C54-H54A	119.6
C54-C55-C56	121.0(4)
C54-C55-H55A	119.5
C56-C55-H55A	119.5
C55-C56-C51	116.9(3)
C55-C56-C57	121.2(4)
C51-C56-C57	121.9(3)
C56-C57-C59	110.8(3)
C56-C57-C58	112.8(3)
C59-C57-C58	109.5(3)
C56-C57-H57A	107.9
C59-C57-H57A	107.9
C58-C57-H57A	107.9

C57-C58-H58A	109.5
C57-C58-H58B	109.5
H58A-C58-H58B	109.5
C57-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5
C57-C59-H59A	109.5
C57-C59-H59B	109.5
H59A-C59-H59B	109.5
C57-C59-H59C	109.5
H59A-C59-H59C	109.5
H59B-C59-H59C	109.5
C61-C60-C52	111.0(3)
C61-C60-C62	110.2(3)
C52-C60-C62	111.9(3)
C61-C60-H60A	107.8
C52-C60-H60A	107.8
C62-C60-H60A	107.8
C60-C61-H61A	109.5
C60-C61-H61B	109.5
H61A-C61-H61B	109.5
C60-C61-H61C	109.5
H61A-C61-H61C	109.5

H61B-C61-H61C	109.5
C60-C62-H62A	109.5
C60-C62-H62B	109.5
H62A-C62-H62B	109.5
C60-C62-H62C	109.5
H62A-C62-H62C	109.5
H62B-C62-H62C	109.5
C35-C63-C64	116.8(3)
C35-C63-H63A	108.1
C64-C63-H63A	108.1
C35-C63-H63B	108.1
C64-C63-H63B	108.1
H63A-C63-H63B	107.3
C65-C64-C66	109.1(3)
C65-C64-C63	109.9(3)
C66-C64-C63	112.0(3)
C65-C64-H64A	108.6
C66-C64-H64A	108.6
C63-C64-H64A	108.6
C64-C65-H65A	109.5
C64-C65-H65B	109.5
H65A-C65-H65B	109.5
C64-C65-H65C	109.5

H65A-C65-H65C	109.5
H65B-C65-H65C	109.5
C64-C66-H66A	109.5
C64-C66-H66B	109.5
H66A-C66-H66B	109.5
C64-C66-H66C	109.5
H66A-C66-H66C	109.5
H66B-C66-H66C	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for dhw6. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au1	17(1)	18(1)	17(1)	-2(1)	4(1)	-2(1)
Au2	15(1)	21(1)	19(1)	1(1)	2(1)	1(1)
Cl1	27(1)	24(1)	20(1)	-4(1)	3(1)	-4(1)
Cl2	26(1)	26(1)	24(1)	4(1)	6(1)	-2(1)
N1	14(2)	18(2)	17(2)	-4(1)	6(1)	1(1)
N2	12(2)	15(2)	24(2)	0(1)	5(1)	0(1)
N3	9(1)	18(2)	21(2)	0(1)	4(1)	1(1)
N4	13(2)	17(2)	21(2)	0(1)	1(1)	2(1)
C1	17(2)	12(2)	20(2)	3(2)	5(2)	4(2)
C2	15(2)	25(2)	24(2)	4(2)	9(2)	-4(2)
C3	21(2)	21(2)	31(2)	3(2)	9(2)	-5(2)
C4	18(2)	17(2)	33(2)	0(2)	6(2)	2(2)
C5	21(2)	23(2)	44(3)	0(2)	5(2)	-6(2)
C6	20(2)	22(3)	51(2)	-6(2)	0(2)	-7(2)
C7	21(2)	29(2)	32(2)	-8(2)	-4(2)	1(2)
C8	14(2)	24(2)	26(2)	-2(2)	1(2)	2(2)
C9	10(2)	15(2)	27(2)	-3(2)	3(2)	2(2)
C10	13(2)	19(2)	16(2)	-1(2)	-2(2)	0(2)

C11	15(2)	14(2)	16(2)	-3(2)	1(1)	2(2)
C12	13(2)	21(2)	17(2)	0(2)	1(1)	-6(2)
C13	23(2)	19(2)	22(2)	-1(2)	2(2)	-2(2)
C14	25(2)	33(3)	23(2)	-10(2)	6(2)	1(2)
C15	27(2)	39(3)	17(2)	-5(2)	9(2)	-6(2)
C16	38(2)	29(3)	22(2)	9(2)	7(1)	-4(3)
C17	25(2)	22(3)	20(2)	-2(2)	3(1)	1(2)
C18	21(2)	17(2)	12(2)	-1(1)	6(2)	-5(2)
C19	17(2)	27(2)	15(2)	-2(2)	3(1)	-6(2)
C20	12(2)	34(3)	23(2)	-3(2)	2(2)	-5(2)
C21	27(2)	30(3)	28(2)	2(2)	1(2)	-16(2)
C22	34(2)	20(2)	20(2)	1(2)	2(2)	-5(2)
C23	22(2)	22(2)	15(2)	-1(2)	4(2)	-4(2)
C24	9(2)	28(3)	30(2)	-2(2)	7(2)	-2(2)
C25	49(3)	36(3)	34(3)	5(2)	4(2)	11(2)
C26	32(3)	38(3)	43(3)	-12(2)	11(2)	4(2)
C27	21(2)	17(2)	29(2)	3(2)	2(2)	1(2)
C28	39(3)	30(3)	30(2)	2(2)	1(2)	8(2)
C29	33(3)	36(3)	33(3)	3(2)	13(2)	9(2)
C30	14(2)	29(2)	30(2)	-1(2)	9(2)	-2(2)
C31	22(2)	28(3)	34(2)	6(2)	13(2)	5(2)
C32	26(2)	29(3)	47(2)	-7(2)	10(2)	6(2)
C33	44(3)	54(4)	45(2)	10(2)	15(2)	25(2)

C34	11(2)	23(2)	19(2)	-2(2)	0(1)	1(2)
C35	11(2)	27(2)	24(2)	0(2)	-1(2)	4(2)
C36	17(2)	19(2)	40(2)	-5(2)	-4(2)	7(2)
C37	12(2)	20(2)	33(2)	3(2)	-3(2)	-2(2)
C38	21(2)	19(2)	59(3)	9(2)	-7(2)	4(2)
C39	33(2)	35(3)	53(3)	23(2)	-8(2)	6(2)
C40	30(2)	38(3)	38(3)	20(2)	-2(2)	-3(2)
C41	28(2)	28(2)	32(2)	8(2)	1(2)	-2(2)
C42	13(2)	20(2)	28(2)	4(2)	-4(2)	-3(2)
C43	15(2)	20(2)	15(2)	3(2)	1(2)	2(2)
C44	18(2)	14(2)	21(2)	2(2)	1(2)	0(2)
C45	17(2)	22(2)	16(2)	5(2)	3(2)	5(2)
C46	34(2)	36(3)	25(2)	-6(2)	10(2)	-11(2)
C47	30(3)	61(4)	36(3)	-3(2)	11(2)	-26(2)
C48	22(2)	50(3)	25(2)	10(2)	10(2)	7(2)
C49	30(2)	27(2)	31(2)	2(3)	14(1)	4(3)
C50	22(2)	23(2)	33(2)	3(3)	9(1)	-3(3)
C51	14(2)	23(2)	19(2)	4(1)	10(2)	9(2)
C52	16(2)	21(2)	18(2)	3(3)	6(1)	-4(2)
C53	12(2)	35(3)	27(2)	1(2)	-1(2)	7(2)
C54	18(2)	28(2)	25(2)	10(2)	6(2)	9(2)
C55	21(2)	19(2)	28(2)	2(2)	6(2)	4(2)
C56	13(2)	20(2)	20(2)	1(2)	6(2)	3(2)

C57	19(2)	23(2)	23(2)	2(2)	2(2)	2(2)
C58	27(2)	32(3)	27(2)	-6(2)	5(2)	-2(2)
C59	18(2)	23(2)	32(2)	2(2)	-1(2)	-3(2)
C60	13(2)	22(2)	34(2)	1(2)	-2(2)	0(2)
C61	32(3)	27(3)	42(3)	-13(2)	12(2)	-4(2)
C62	22(2)	29(3)	44(3)	-4(2)	12(2)	-5(2)
C63	14(2)	28(2)	28(2)	-2(2)	-2(2)	4(2)
C64	16(2)	26(3)	32(2)	-8(2)	2(1)	1(2)
C65	28(2)	48(4)	45(3)	-14(2)	0(2)	-2(2)
C66	21(2)	29(3)	43(2)	-2(2)	4(2)	-3(2)

X-ray experimental for BIQ-AuCl (10): Data were collected at 100 K on a Bruker DUO system equipped with an APEX II area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 9999 reflections. A hemisphere of data was collected using the ω-scan method (0.5° frame width). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of the complex and a disordered dichloromethane solvent molecule. The latter molecules was disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Judging by the total count of electrons calculated by program SQUEEZE, it looks like the solvent exists in about 80% occupancy and disordered by the 2_1 screw axis of symmetry along the a-axis. A total of 281 parameters were refined in the final cycle of refinement using 6106 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.01% and 5.62%, respectively. Refinement was done using F^2.

P. van der Sluis & A.L. Spek (1990). SQUEEZE, Acta Cryst. A46, 194-201

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.

Spek, A.L. (1990). PLATON, Acta Cryst. A46, C-34

Table 1. Crystal data and structure refinement for BIQ-AuCl.

Identification code	dhw10	
Empirical formula	C27 H32 Au Cl N2	
Formula weight	616.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.4129(6) Å	α= 90°.
	b = 16.7290(11) Å	β= 90°.
	c = 17.6201(12) Å	γ = 90°.
Volume	2774.6(3) $Å^3$	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	5.413 mm^{-1}	
F(000)	1216	
Crystal size	0.28 x 0.17 x 0.13 mm^3	
Theta range for data collection	1.68 to 27.50°.	
Index ranges	-12≤h≤12, -21≤k≤21, -20≤l≤22	
Reflections collected	43949	
Independent reflections	6356 [R(int) = 0.0281]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Nnumerical	

Max. and min. transmission	0.5441 and 0.3165
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6356 / 0 / 281
Goodness-of-fit on F^2	0.849
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0562 [6106]
R indices (all data)	R1 = 0.0216, wR2 = 0.0569
Absolute structure parameter	0.009(6)
Largest diff. peak and hole	1.156 and -1.026 e.Å^{-3}

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for dhw10. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au1	5489(1)	5405(1)	3821(1)	21(1)
Cl1	7049(1)	6134(1)	3111(1)	32(1)
N1	2738(3)	4622(2)	4250(2)	22(1)
N2	4276(3)	4469(2)	5130(2)	20(1)
C1	4101(4)	4787(2)	4433(2)	20(1)
C2	2042(4)	4812(2)	3527(2)	24(1)
C3	487(4)	5018(2)	3727(3)	30(1)
C4	-198(4)	4339(2)	4122(2)	20(1)
C5	-1556(4)	4069(2)	3950(2)	24(1)
C6	-2138(4)	3399(3)	4323(2)	25(1)
C7	-1363(4)	3008(2)	4872(2)	23(1)
C8	0(4)	3260(2)	5051(2)	20(1)
C9	592(4)	3926(2)	4688(2)	19(1)
C10	2051(4)	4203(2)	4828(2)	20(1)
C11	3022(4)	4132(2)	5406(2)	20(1)
C12	2999(4)	3831(2)	6188(2)	21(1)
C13	1744(4)	3759(2)	6611(2)	22(1)
C14	1787(5)	3461(3)	7338(2)	27(1)

C15	3085(5)	3237(2)	7664(2)	29(1)
C16	4334(5)	3333(2)	7256(2)	25(1)
C17	4309(4)	3623(2)	6522(2)	21(1)
C18	5639(4)	3718(2)	6057(2)	25(1)
C19	5598(4)	4492(2)	5574(2)	22(1)
C20	2108(5)	4141(3)	2938(3)	31(1)
C21	3576(5)	3822(3)	2715(2)	32(1)
C22	4081(5)	3155(3)	3263(3)	38(1)
C23	3541(7)	3481(4)	1895(3)	47(1)
C24	5689(4)	5264(2)	6039(2)	21(1)
C25	7033(5)	5347(3)	6522(2)	30(1)
C26	7084(6)	6178(3)	6878(3)	39(1)
C27	8384(5)	5204(3)	6049(3)	43(1)

Table 3. Bond lengths [Å] and angles [°] for dhw10.

Au1-C1	1.985(4)
Au1-Cl1	2.2829(10)
N1-C1	1.352(5)
N1-C10	1.395(5)
N1-C2	1.467(5)
N2-C1	1.348(5)
N2-C11	1.396(5)
N2-C19	1.470(5)
C2-C20	1.531(7)
C2-C3	1.544(6)
C2-H2A	1.0000
C3-C4	1.479(5)
C3-H3A	0.9900
C3-H3B	0.9900
C4-C5	1.390(5)
C4-C9	1.423(5)
C5-C6	1.411(6)
C5-H5A	0.9500
C6-C7	1.377(6)
C6-H6A	0.9500
C7-C8	1.387(6)

C7-H7A	0.9500
C8-C9	1.400(5)
C8-H8A	0.9500
C9-C10	1.470(6)
C10-C11	1.373(6)
C11-C12	1.468(6)
C12-C13	1.402(5)
C12-C17	1.410(5)
C13-C14	1.375(6)
C13-H13A	0.9500
C14-C15	1.402(6)
C14-H14A	0.9500
C15-C16	1.388(6)
C15-H15A	0.9500
C16-C17	1.382(5)
C16-H16A	0.9500
C17-C18	1.505(6)
C18-C19	1.550(5)
C18-H18A	0.9900
C18-H18B	0.9900
C19-C24	1.531(5)
C19-H19A	1.0000
C20-C21	1.533(7)

C20-H20A	0.9900
C20-H20B	0.9900
C21-C22	1.551(7)
C21-C23	1.553(7)
C21-H21A	1.0000
C22-H22A	0.9800
C22-H22B	0.9800
C22-H22C	0.9800
C23-H23A	0.9800
C23-H23B	0.9800
C23-H23C	0.9800
C24-C25	1.531(5)
C24-H24A	0.9900
C24-H24B	0.9900
C25-C26	1.526(7)
C25-C27	1.540(7)
C25-H25A	1.0000
C26-H26A	0.9800
C26-H26B	0.9800
C26-H26C	0.9800
C27-H27A	0.9800
C27-H27B	0.9800
C27-H27C	0.9800

C1-Au1-Cl1	178.86(11)
C1-N1-C10	111.6(3)
C1-N1-C2	125.9(3)
C10-N1-C2	122.4(3)
C1-N2-C11	111.9(3)
C1-N2-C19	125.3(3)
C11-N2-C19	122.7(3)
N2-C1-N1	104.6(3)
N2-C1-Au1	128.4(3)
N1-C1-Au1	126.9(3)
N1-C2-C20	114.3(3)
N1-C2-C3	105.9(3)
C20-C2-C3	110.9(3)
N1-C2-H2A	108.5
C20-C2-H2A	108.5
C3-C2-H2A	108.5
C4-C3-C2	110.4(3)
C4-C3-H3A	109.6
C2-C3-H3A	109.6
C4-C3-H3B	109.6
C2-C3-H3B	109.6
H3A-C3-H3B	108.1

C5-C4-C9	118.4(3)
C5-C4-C3	123.2(4)
C9-C4-C3	118.4(3)
C4-C5-C6	120.9(4)
C4-C5-H5A	119.5
C6-C5-H5A	119.5
C7-C6-C5	119.9(4)
C7-C6-H6A	120.0
C5-C6-H6A	120.0
C6-C7-C8	120.4(4)
C6-C7-H7A	119.8
C8-C7-H7A	119.8
C7-C8-C9	120.4(4)
C7-C8-H8A	119.8
C9-C8-H8A	119.8
C8-C9-C4	119.9(4)
C8-C9-C10	123.1(3)
C4-C9-C10	116.9(3)
C11-C10-N1	106.0(3)
C11-C10-C9	136.0(4)
N1-C10-C9	117.9(3)
C10-C11-N2	105.6(3)
C10-C11-C12	135.7(4)

N2-C11-C12	118.6(3)
C13-C12-C17	119.7(4)
C13-C12-C11	122.7(3)
C17-C12-C11	117.6(3)
C14-C13-C12	120.1(4)
C14-C13-H13A	120.0
C12-C13-H13A	120.0
C13-C14-C15	120.3(4)
C13-C14-H14A	119.8
C15-C14-H14A	119.8
C16-C15-C14	119.7(4)
C16-C15-H15A	120.1
C14-C15-H15A	120.1
C15-C16-C17	120.7(4)
C15-C16-H16A	119.6
C17-C16-H16A	119.6
C16-C17-C12	119.5(4)
C16-C17-C18	122.2(4)
C12-C17-C18	118.3(3)
C17-C18-C19	111.4(3)
C17-C18-H18A	109.3
C19-C18-H18A	109.3
C17-C18-H18B	109.3

C19-C18-H18B	109.3
H18A-C18-H18B	108.0
N2-C19-C24	110.7(3)
N2-C19-C18	106.9(3)
C24-C19-C18	114.2(3)
N2-C19-H19A	108.3
C24-C19-H19A	108.3
C18-C19-H19A	108.3
C2-C20-C21	117.7(4)
C2-C20-H20A	107.9
C21-C20-H20A	107.9
C2-C20-H20B	107.9
C21-C20-H20B	107.9
H20A-C20-H20B	107.2
C22-C21-C20	111.5(4)
C22-C21-C23	108.8(4)
C20-C21-C23	110.3(4)
C22-C21-H21A	108.7
C20-C21-H21A	108.7
C23-C21-H21A	108.7
C21-C22-H22A	109.5
C21-C22-H22B	109.5
H22A-C22-H22B	109.5

C21-C22-H22C	109.5
H22A-C22-H22C	109.5
H22B-C22-H22C	109.5
C21-C23-H23A	109.5
C21-C23-H23B	109.5
H23A-C23-H23B	109.5
C21-C23-H23C	109.5
H23A-C23-H23C	109.5
H23B-C23-H23C	109.5
C19-C24-C25	114.9(3)
C19-C24-H24A	108.6
C25-C24-H24A	108.6
C19-C24-H24B	108.6
C25-C24-H24B	108.6
H24A-C24-H24B	107.5
C26-C25-C24	109.7(4)
C26-C25-C27	109.8(4)
C24-C25-C27	111.5(4)
C26-C25-H25A	108.6
C24-C25-H25A	108.6
C27-C25-H25A	108.6
C25-C26-H26A	109.5
C25-C26-H26B	109.5

H26A-C26-H26B	109.5
C25-C26-H26C	109.5
H26A-C26-H26C	109.5
H26B-C26-H26C	109.5
C25-C27-H27A	109.5
C25-C27-H27B	109.5
H27A-C27-H27B	109.5
C25-C27-H27C	109.5
H27A-C27-H27C	109.5
H27B-C27-H27C	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for dhw10. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au1	18(1)	21(1)	25(1)	1(1)	3(1)	-2(1)
Cl1	26(1)	32(1)	38(1)	6(1)	10(1)	-5(1)
N1	18(2)	18(1)	30(2)	7(2)	1(1)	4(1)
N2	16(2)	20(2)	25(2)	-1(1)	2(1)	-1(1)
C1	19(2)	15(2)	27(2)	-2(1)	0(1)	1(1)
C2	18(2)	23(2)	30(2)	11(2)	-2(2)	3(1)
C3	20(2)	27(2)	45(2)	13(2)	-2(2)	6(2)
C4	15(2)	26(2)	20(2)	1(1)	2(1)	-2(1)
C5	17(2)	29(2)	27(2)	5(2)	0(2)	2(2)
C6	18(2)	28(2)	30(2)	-2(2)	0(2)	0(2)
C7	21(2)	22(2)	27(2)	-3(2)	5(2)	-1(2)
C8	19(2)	19(2)	23(2)	1(1)	3(1)	1(1)
C9	17(2)	18(2)	23(2)	1(1)	0(2)	1(2)
C10	19(2)	17(2)	23(2)	4(1)	4(1)	-2(2)
C11	17(2)	16(2)	28(2)	-1(1)	3(1)	-1(1)
C12	22(2)	18(2)	24(2)	-3(2)	-1(2)	-2(1)
C13	25(2)	20(2)	20(2)	-4(1)	3(1)	0(2)
C14	33(2)	26(2)	24(2)	-6(2)	7(2)	-9(2)

C15	41(3)	23(2)	21(2)	-1(2)	-3(2)	-8(2)
C16	33(2)	20(2)	23(2)	1(1)	-4(2)	-5(2)
C17	26(2)	14(2)	22(2)	-4(1)	-2(2)	-3(1)
C18	21(2)	20(2)	33(2)	-2(2)	0(2)	-2(2)
C19	18(2)	22(2)	26(2)	-1(1)	1(2)	-1(2)
C20	25(2)	43(3)	26(2)	10(2)	-3(2)	-5(2)
C21	27(2)	37(2)	32(2)	4(2)	2(2)	-8(2)
C22	37(3)	37(3)	42(3)	-1(2)	-2(2)	2(2)
C23	52(3)	57(3)	33(3)	-4(2)	9(2)	-16(3)
C24	25(2)	18(2)	21(2)	-1(1)	1(1)	-2(1)
C25	36(2)	27(2)	29(2)	0(2)	-7(2)	-4(2)
C26	47(3)	40(3)	29(2)	-7(2)	-3(2)	-10(2)
C27	27(2)	41(3)	62(3)	-19(2)	-4(2)	-6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for dhw10.

	x	y	z	U(eq)
H2A	2503	5299	3308	29
H3A	464	5497	4057	37
H3B	-44	5142	3257	37
H5A	-2100	4339	3575	29
H6A	-3065	3217	4196	30
H7A	-1764	2563	5130	28
H8A	535	2980	5423	24
H13A	862	3916	6395	26
H14A	932	3408	7621	33
H15A	3109	3020	8162	34
H16A	5217	3198	7484	30
H18A	5746	3250	5717	30
H18B	6473	3733	6398	30
H19A	6417	4480	5213	27
H20A	1634	4334	2471	37
H20B	1541	3686	3132	37
H21A	4274	4272	2734	38

H22A	4113	3364	3782	58
H22B	5031	2974	3114	58
H22C	3418	2704	3241	58
H23A	4486	3281	1759	71
H23B	3263	3905	1541	71
H23C	2852	3043	1869	71
H24A	4852	5293	6377	26
H24B	5639	5724	5686	26
H25A	6998	4941	6938	37
H26A	6226	6265	7182	59
H26B	7137	6582	6477	59
H26C	7923	6221	7205	59
H27A	9222	5259	6374	65
H27B	8431	5598	5638	65
H27C	8358	4664	5833	65

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