SUPPORTING INFORMATION

for the article entitled

Bio-inspired Polyene Cyclization: Aziridinyl Polyene Cyclization Catalyzed by $InBr_3$

Authored by

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1.General

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification with the following exceptions: THF, CH_2Cl_2 and dried Et_2O was taken from solvent purification system (PS-400-5, innovative technology Inc.). HPLC grade *iso*-propanol was used without further purification.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating on a hot plate.

Flash chromatography was performed using Merck silica gel 60 with distilled solvents. Columns were typically packed as slurry and equilibrated with hexane prior to use.

Infrared spectra were recorded on a Shimadzu IR Prestige-21 FT-IR Spectrometer. Liquid samples were examined as film between NaCl or KBr salt plates.

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Advance 300, 400 and 500 NMR spectrometers. Chemical shifts ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); ddd (doublet of doublets of doublets); dddd (doublet of doublets of doublets of doublets); dt (doublet of triplets); m (multiplets) and etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as d in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet). Enantiomeric excess (*ee*) was determined by chiral HPLC analysis.

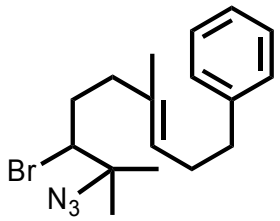
Low resolution mass spectrum analysis was performed on Finnigan polaris Q, GCMS XP mass spectrometer (Thermo Electron Corporation). High-resolution mass spectral analysis (HRMS) was performed on Q-Tof Premier mass spectrometer (Waters Corporation).

X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter.

2.Synthesis of Aziridinyl Olefin Cyclization Substrates

To a 50 mL round-bottom flask quipped with a magnetic stirring bar was added 1,5 diene substrate (448 mg, 2.0 mmol, 1.0 equiv), NaN_3 (780 mg, 12.0 mmol, 6.0 equiv.), $(MeOCH_2)_2$ (14 mL) and water (3.0 mL). The reaction mixture was cooled to -10 ^{o}C with ice-ethanol bath. Solid NBS (500 mg, 2.8 mmol, 1.4 equiv.) was added in small portion.[1] The reaction was warmed up to room temperature and stirred for 1 hour. The reaction mixture was poured into water (10 mL) and the aqueous layer was extracted with ethyl acetate (40 mL × 2). The combined organic extracts were washed with brine (30 mL) and dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was used directly for the next step without further purification. (The azidobromide product is isolable using silica gel column chromatography).

[1] (a) Van Ende, D.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 279–280. (b) Riddiford, L. M.; Ajami, A. M.; Corey, E. J.; Yamamoto, H.; Anderson, J. E. *J. Am. Chem. Soc.* **1971**, *93, 1815*–1816.



(*E*)-(8-Azido-7-bromo-4,8-dimethylnon-3-enyl)benzene

R_f: 0.90 (Hexane : Ethyl Acetate = 4:1)

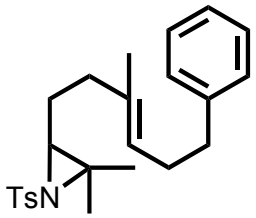
^{1}H NMR (500 MHz, $CDCl_3$): 7.34–7.14 (m, 5H), 5.26 (t, *J* = 6.96 Hz, 1H), 3.91 (dd, *J* = 11.44, 1.77 Hz, 1H), 2.65 (dt, *J* = 7.23, 4.27 Hz, 2H), 2.32 (dd, *J* = 14.55, 6.94 Hz, 2H), 2.15–2.07 (m, 1H), 1.98–1.86 (m, 1H), 1.81–1.71 (m, 1H), 1.65 (dd, *J* = 14.20, 0.97 Hz, 1H), 1.53 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): 142.1, 133.7, 128.4, 128.2, 125.7, 125.5, 64.1, 63.8, 37.7, 36.0, 31.6, 30.0, 25.1, 23.0, 15.7.

HRMS (ESI): *m*/*z* calculated for $C_{17}H_{25}{}^{79}BrN_1$ $[M+H-N_2]^+$: 322.1170, Found: 322.1167, $C_{17}H_{25}{}^{81}BrN_1$ $[M+H-N_2]^+$: 324.1151, Found: 324.1151.

$LiAlH_4$ (>20.0 equiv, 1.6 g) was placed in a 25 mL round-bottom flask quipped with a magnetic stirring bar and cooled to 0 ^oC. Dry Et_2O (25 mL) was added via syringe. An Et_2O solution (4 mL) of previous crude azidobromide substrate was added slowly via syringe. The reaction mixture was warmed up to room temperature and stirred for 12 hours. The reaction was quenched by added H_2O (3 mL) and KOH solution (4 *N,* 10 mL). The white oily mixture was extracted with ethyl acetate (50 mL × 4). The combined organic extracts were washed with brine (30 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired amine product as colorless oil.

The amine product (24.3 mg, 0.1 mmol, 1.0 equiv.) was placed in a 25 mL round-bottom flask quipped with a magnetic stirring bar. THF (10 mL), pyridine (0.1 mL, 0.4 mmol, 4.0 equiv.) and DMAP (20 mg, cat.) were added accordingly. TsCl (40 mg, 0.2 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 12 hours. The organic solvent was removed *in vacuo*. The residual crude product was purified by column chromatography to afford the desired product as colorless oil.



1

(*E*)-2,2-Dimethyl-3-(3-methyl-6-phenylhex-3-enyl)-1-tosylaziridine, a colorless oil, 44% yield over 3 steps.

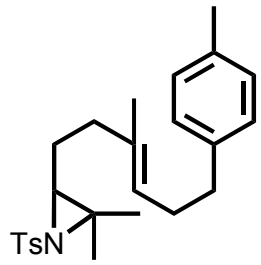
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7. 89–7.78 (m, 2H), 7.34–7.22 (m, 5H), 7.20–7.12 (m. 2H), 5.08 (t, *J* = 7.03 Hz, 1H), 2.81 (t, *J* = 7.2, 6.1 Hz, 1H), 2.62 (t, *J* = 7.60 Hz, 2H), 2.41 (s, 3H), 2.27 (dd, *J* = 15.1, 7.4 Hz, 2H), 1.91–1.82 (m, 1H), 1.82–1.73 (m, 1H), 1.70 (s, 3H), 1.56–1.48 (m, 1H), 1.47 (s, 3H), 1.44–1.30 (m, 1H), 1.26 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 142.1, 138.4, 134.3, 129.3, 128.4, 128.2, 127.3, 125.7, 124.3, 52.4, 51.8, 37.0, 35.9, 29.8, 26.4, 21.5, 21.3, 21.1, 15.8

HRMS (ESI): *m*/*z* calculated for $C_{24}H_{31}NO_2SNa$ $[M+Na]^+$: 420.1970, Found: 420.1973.

FTIR (NaCl): ν 2992, 2926, 1598, 1494, 1454, 1379, 1319, 1157, 1089, 931 cm^{-1}



1a

(*E*)-2,2-Dimethyl-3-(3-methyl-6-*p*-tolylhex-3-enyl)-1-tosylaziridine, a colorless oil, 35% yield over 3 steps.

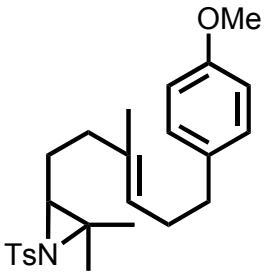
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.84–7.80 (m, 2H), 7.31–7.26 (m, 2H), 7.10–7.03 (m, 4H), 5.08 (t, *J* = 7.03 Hz, 1H), 2.81 (dd, *J* = 7.07, 6.27 Hz, 1H), 2.57 (t, *J* = 7.87 Hz, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 2.24 (dd, *J* = 15.24, 7.45 Hz, 2H), 1.91–1.82 (m 1H), 1.81–1.72 (m, 1H), 1.69 (s, 3H), 1.58–1.48 (m, 1H), 1.45 (s, 3H), 1.45–1.36 (m, 1H), 1.27 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 139.0, 138.4, 135.1, 134.2, 129.3, 128.9, 128.2, 127.3, 124.5, 52.4, 51.8, 37.0, 35.5, 30.0, 26.4, 21.5, 21.3, 21.1, 20.9, 15.9

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{33}NO_2SNa$ $[M+Na]^+$: 434.2126, Found: 434.2130.

FTIR (NaCl): ν 2961, 2922, 1599, 1514, 1454, 1379, 1319, 1157, 1090, 931 cm^{-1}



1b

(*E*)-3-(6-(4-Methoxyphenyl)-3-methylhex-3-enyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 40% yield over 3 steps.

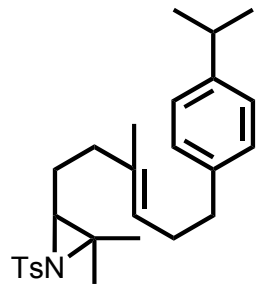
R_f: 0.50 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.84–7.78 (m, 2H), 7.30–7.21 (m, 2H), 7.10–7.04 (m, 2H), 6.84–6.74 (m, 2H), 5.06 (t, *J* = 6.83 Hz, 1H), 3.55 (s, 3H), 2.81 (t, *J* = 6.63 Hz, 1H), 2.55 (t, *J* = 7.69 Hz, 2H), 2.38 (s, 3H), 2.23 (dd, *J* = 14.7, 7.36 Hz, 2H), 1.91–1.81 (m, 1H), 1.80–1.72 (m, 1H), 1.69 (s, 3H), 1.58–1.48 (m, 1H), 1.43 (s, 3H), 1.46–1.34 (m, 1H), 1.26 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 157.7, 143.5, 138.5, 134.3, 134.2, 129.4, 129.3, 127.3, 124.4, 113.6, 55.2, 52.4, 51.8, 37.0, 35.0, 30.1, 26.4, 21.5, 21.3, 21.2, 15.9

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{33}NO_3SNa$ $[M+Na]^+$: 450.2061, Found: 450.2079.

FTIR (NaCl): ν 2957, 2928, 1611, 1599, 1512, 1458, 1319, 1246, 1155, 1090, 1038, 931 cm^{-1}



1c

(*E*)-3-(6-(4-Isopropylphenyl)-3-methylhex-3-enyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 22% yield over 3 steps.

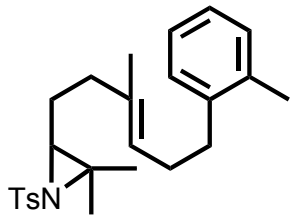
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.84–7.78 (m, 2H), 7.30–7.25 (m, 2H), 7.15–7.05 (m, 4H), 508 (t, *J* = 6.83 Hz, 1H), 2.86 (septet, *J* = 6.90 Hz, 1H), 2.82 (t, *J* = 6.66 Hz, 1H), 2.58 (t, *J* = 2.58 Hz, 2H), 2.40 (s, 3H), 2.25 (dd, *J* = 15.3, 7.45 Hz, 2H), 1.91–1.81 (m, 1H), 1.81–1.71 (m, 1H), 1.69 (s, 3H), 1.59–1.48 (m, 1H), 1.46 (s, 3H), 1.46–1.36 (m, 1H), 1.28 (s, 3H), 1.22 (d, *J* = 6.90 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): 146.1, 143.4, 139.3, 138.4, 134.1, 129.2, 128.2, 127.2, 126.1, 124.4, 52.3, 51.7, 36.9, 35.4, 33.6, 29.8, 26.4, 24.0, 21.4, 21.2, 21.1, 15.8

HRMS (ESI): *m*/*z* calculated for $C_{27}H_{37}NO_2SNa$ $[M+Na]^+$: 462.2443, Found: 462.2443.

FTIR (NaCl): ν 2959, 2926, 1599, 1512, 1458, 1379, 1321, 1157, 1090, 931 cm^{-1}



1d

(E)-2,2-Dimethyl-3-(3-methyl-6-o-tolylhex-3-enyl)-1-tosylaziridine, a colorless oil, 20% yield over 3 steps.

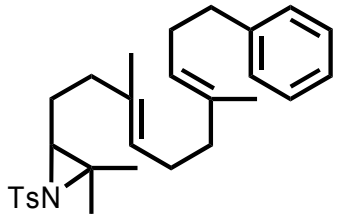
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.85–7.80 (m, 2H), 7.34–7.26 (m, 2H), 7.15–7.06 (m, 4H), 5.11 (t, *J* = 7.05 Hz, 1H), 2.82 (t, *J* = 6.53 Hz, 1H), 2.59 (t, *J* = 7.41 Hz, 2H), 2.42 (s, 3H), 2.30 (s, 3H), 2.21 (dd, *J* = 15.3, 7.29 Hz, 2H), 1.94–1.84 (m, 1H), 1.84–1.72 (m, 1H), 1.70 (s, 3H), 1.60–1.48 (m, 1H), 1.45 (s, 3H), 1.45–1.36 (m, 1H), 1.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 140.2, 138.4, 135.8, 134.3, 130.0, 129.3, 128.7, 127.3, 125.9, 125.8, 124.4, 52.4, 51.8, 37.0, 33.2, 28.5, 26.4, 21.5, 21.3, 21.1, 19.2, 15.8

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{33}NO_2SNa$ $[M+Na]^+$: 434.2130, Found: 434.2130.

FTIR (NaCl): ν 2965, 2928, 1599, 1493, 1458, 1379, 1319, 1155, 1090, 931 cm^{-1}



3

3-((3*E*,7*E*)-3,7-Dimethyl-10-phenyldeca-3,7-dienyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 11% yield over 3 steps.

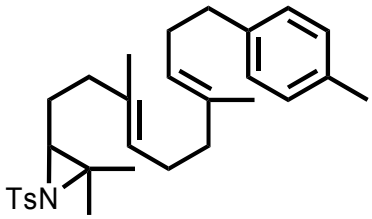
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.84–7.80 (m, 2H), 7.30–7.23 (m, 4H), 7.20–7.15 (m, 3H), 5.16 (t, *J* = 7.04 Hz, 1H), 5.01 (t, *J* = 6.72 Hz, 1H), 2.82 (t, *J* = 6.66 Hz, 1H), 2.62 (t, *J* = 7.49 Hz, 2H), 2.42 (s, 3H), 2.29 (dd, *J* = 15.22, 7.42 Hz, 2H), 2.03 (dd, *J* = 14.78, 6.98 Hz, 2H), 1.96 (dd, *J* = 12.4, 6.12 Hz, 2H), 1.92–1.82 (m, 1H), 1.82–1.74 (m, 1H), 1.70 (s, 3H), 1.56–1.48 (m, 1H), 1.54 (s, 3H), 1.48 (s, 3H), 1.48–1.36 (m, 1H), 1.28 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 143.4, 142.3, 138.4, 135.5, 133.5, 129.3, 128.4, 128.1, 127.3, 125.6, 124.9, 123.6, 52.4, 51.8, 39.5, 37.0, 36.0, 29.9, 26.6, 26.5, 21.5, 21.3, 21.1, 15.9, 15.9

HRMS (ESI): *m*/*z* calculated for $C_{29}H_{39}NO_2SNa$ $[M+Na]^+$: 488.2593, Found: 488.2599.

FTIR (NaCl): ν 2924, 2855, 1601, 1495, 1454, 1379, 1321, 1157, 1090, 931 cm^{-1}



3b

3-((3*E*,7*E*)-3,7-Dimethyl-10-p-tolyldeca-3,7-dienyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 14% yield over 3 steps.

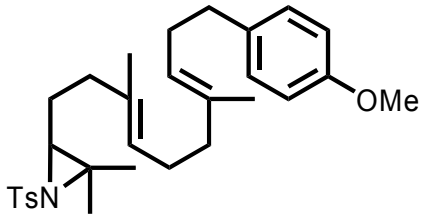
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (300 MHz, $CDCl_3$): 7.85–7.79 (m, 2H), 7.30–7.24 (m, 2H), 7.10–7.04 (m, 4H), 5.17 (t, J = 7.13 Hz, 1H), 5.01 (t, *J* = 6.61 Hz, 1H), 2.82 (t, *J* = 6.63 Hz, 1H), 2.58 (dd, *J* = 8.95, 6.76 Hz, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 2.27 (dd, *J* = 15.41, 7.18 Hz, 2H), 2.10–1.90 (m, 4H), 1,90–1.70 (m, 2H), 1.70 (s, 3H), 1.60–1.36 (m, 2H), 1.56 (s, 3H), 1.48 (s, 3H), 1.28 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 143.4, 139.2, 138.4, 135.3, 135.0, 133.5, 129.3, 128.8, 128.2, 127.3, 124.9, 123.8, 52.4, 51.7, 39.5, 37.0, 35.6, 30.0, 26.5, 26.4, 21.5, 21.3, 21.1, 20.9, 16.0, 15.9

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_2SNa$ $[M+Na]^+$: 502.2755, Found: 502.2756.

FTIR (NaCl): ν 2922, 2855, 1599, 1514, 1454, 1379, 1321, 1157, 1090, 931 cm^{-1}



3b

3-((3*E*,7*E*)-10-(4-Methoxyphenyl)-3,7-dimethyldeca-3,7-dienyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 21% yield over 3 steps.

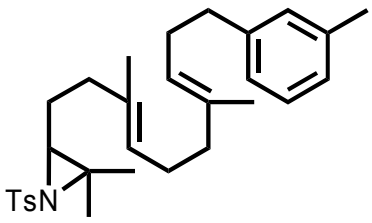
R_f: 0.65 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.84–7.78 (m, 2H), 7.32–7.24 (m, 2H), 7.12–7.06 (m, 2H), 6.84–6.76 (m, 2H), 5.16 (t, *J* = 6.95 Hz, 1H), 5.01 (t, *J* = 6.61 Hz, 1H), 3.76 (s, 3H), 2.82 (t, *J* = 6.64 Hz, 1H), 2.56 (t, *J* = 7.77 Hz, 2H), 2.40 (s, 3H), 2.26 (dd, *J* = 15.00, 7.37 Hz, 2H), 2.03 (dd, *J* = 14.54, 7.06 Hz, 2H), 1.96 (dd, *J* = 13.6, 6.80 Hz, 2H), 1.93–1.83 (m, 1H), 1.82–1.74 (m, 1H), 1.70 (s, 3H), 1.57–1.48 (m, 1H), 1.54 (s, 3H), 1.49 (s, 3H), 1.45–1.38 (m, 1H), 1.27 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 143.4, 138.3, 135.3, 134.3, 133.4, 129.3, 129.2, 127.2, 124.9, 123.7, 113.5, 55.1, 52.4, 51.7, 39.4, 36.9, 35.1, 30.1, 26.5, 26.4, 21.4, 21.2, 21.1, 15.9, 15.8.

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_3SNa$ $[M+Na]^+$: 518.2709, Found: 518.2705.

FTIR (NaCl): ν 2957, 2926, 1611, 1512, 1454, 1379, 1319, 1246, 1157, 1090, 1038, 931 cm^{-1}



3c

3-((3*E*,7*E*)-3,7-Dimethyl-10-m-tolyldeca-3,7-dienyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 19% yield over 3 steps.

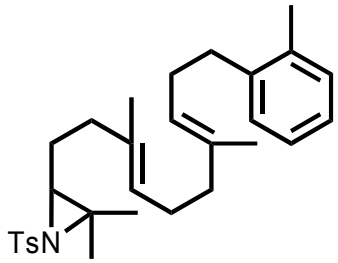
R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.84–7.78 (m, 2H), 7.30–7.24 (m, 2H), 7.18–7.12 (m, 1H), 7.02–6.96 (m, 3H), 5.17 (t, *J* = 7.02 Hz, 1H), 5.01 (t, *J* = 6.74 Hz, 1H), 2.82 (t, *J* = 6.66 Hz, 1H), 2.58 (dd, *J* = 8.91, 6.97 Hz, 2H), 2.40 (s, 3H), 2.32 (s, 3H), 2.27 (dd, *J* = 15.57, 7.30 Hz, 2H), 2.03 (dd, *J* = 14.66, 7.16 Hz, 2H), 1.97 (dd, *J* = 15.00, 7.48 Hz, 2H), 1.92–1.82 (m, 1H), 1.82–1.73 (m, 1H), 1.69 (s, 3H), 1.56 (s, 3H), 1.56–1.48 (m, 1H), 1.50 (s, 3H), 1.48–1.38 (m, 1H), 1.27 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 143.4, 142.2, 138.4, 137.6, 135.3, 133.4, 129.2, 129.1, 128.0, 127.2, 126.3, 125.3, 124.9, 123.7, 52.4, 51.7, 39.5, 37.0, 36.0, 29.9, 26.5, 26.4, 21.4, 21.3, 21.2, 21.1, 15.9, 15.8

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_2SNa$ $[M+Na]^+$: 502.2759, Found: 502.2756.

FTIR (NaCl): ν 2961, 2922, 2855, 1599, 1487, 1452, 1379, 1321, 1157, 1090, 931 cm^{-1}



3d

3-((3*E*,7*E*)-3,7-Dimethyl-10-o-tolyldeca-3,7-dienyl)-2,2-dimethyl-1-tosylaziridine, a colorless oil, 16% yield over 3 steps.

R_f: 0.70 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.84–7.78 (m, 2H), 7.28–7.25 (m, 2H), 7.14–7.05 (m, 4H), 5.21 (t, *J* = 6.77 Hz, 1H), 5.02 (t, *J* = 6.43 Hz, 1H), 2.82 (t, *J* = 6.67 Hz, 1H), 2.60 (dd, *J* = 9.00, 6.92 Hz, 2H), 2.40 (s, 3H), 2.30 (s, 3H), 2.25 (dd, J = 15.58, 7.39 Hz, 2H), 2.05 (dd, *J* = 15.55, 7.79 Hz, 2H), 1.98 (dd, *J* = 12.5, 6.23 Hz, 2H), 1.92–1.84 (m, 1H), 1.82–1/74 (m, 1H), 1.70 (s, 3H), 1.56–1.46 (m, 1H), 1.55 (s, 3H), 1.50 (s, 3H), 1.46–1.40 (m, 1H), 1.27 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 143.4, 140.3, 138.4, 135.7, 135.4, 133.5, 129.9, 129.2, 128.7, 127.2, 125.7, 125.7, 124.9, 123.7, 52.4, 51.7, 39.5, 36.9, 33.3, 28.6, 26.5, 26.4, 21.4, 21.2, 21.1, 19.2, 15.9, 15.8

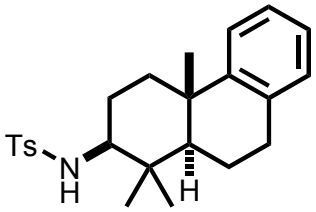
HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_2SNa$ $[M+Na]^+$: 502.2757, Found: 502.2756.

FTIR (NaCl): ν 2959, 2926, 2862, 1599, 1493, 1456, 1379. 1321, 1157, 1090, 931 cm^{-1}

3.Genaral Procedure for Polyene Cyclization Reaction Catalyzed by $InBr_3$

To a 10 mL round-bottom flask quipped with a magnetic stirring bar was added $InBr_3$ (7 mg, 0.02 mmol, 0.20 equiv.). CH_2Cl_2 (1.5 mL) was added via syringe. Aziridinyl olefin substrate **1** (40 mg, 0.1 mmol, 1.0 equiv) was added as CH_2Cl_2 solution via syringe.

The reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was quenched by 5 mL aqueous $NaHCO_3$ saturated solution. The mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired amine product as colorless solid.



2

4-Methyl-*N*-((2*S*,4a*S*,10a*R*)-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl)benzenesulfonamide, a colorless solid, 69% yield. Mp: 223.5-225 ºC

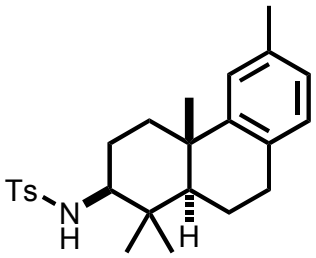
R_f: 0.50 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.78–7.72 (m, 2H), 7.31–7.26 (m, 2H), 7.16–6.98 (m, 4H), 4.27 (d, *J* = 9.33 Hz, 1H), 2.97–2.89 (m, 2H), 2.89–2.78 (m, 1H), 2.43 (s, 3H), 2.19 (dt, *J* = 13.10, 3.10 Hz, 1H), 1.86 (dd, *J* = 13.27, 7.39 Hz, 1H), 1.75–1.65 (m, 1H), 1.60–1.53 (m, 1H), 1.51–1.45 (m, 1H), 1.44–1.36 (m, 1H), 1.35–1.28 (m, 1H), 1.11 (s, 3H), 0.90 (s, 3H), 0.82 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 148.7, 143.2, 138.1, 134.8, 129.6, 128.9, 127.1, 125.7, 125.5, 124.3, 62.0, 50.8, 38.2, 37.6, 37.2, 30.5, 28.1, 26.7, 24.7, 21.5, 19.2, 16.2

HRMS (ESI): *m*/*z* calculated for $C_{24}H_{32}NO_2S$ $[M+H]^+$: 398.2159, Found: 398.2154.

FTIR (NaCl): ν 3462 (br), 2957, 2928, 1700 (br), 1645 (br), 1450, 1159 cm^{-1}



2a

4-Methyl-*N*-((2*S*,4a*S*,10a*R*)-1,1,4a,6-tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl)benzenesulfonamide, a colorless solid, 70% yield. Mp: 221-222 ºC

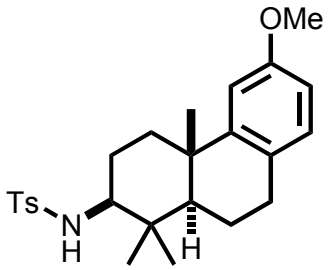
R_f: 0.60 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.78–7.73 (m, 2H), 7.31–7.26 (m, 2H), 6.97–6.84 (m, 3H), 4.40–4.36 (b, 1H), 2,94–2.84 (m, 2H), 2.82–2.72 (m, 1H), 2.42 (s, 3H), 2.26 (s, 3H), 2.18 (dt, *J* = 13.04, 3.13 Hz, 1H), 1.85 (dd, *J* = 13.15, 7.30 Hz, 1H), 1.73–1.63 (m, 1H), 1.63–1.52 (m, 1H), 1.500–1.43 (m, 1H), 1.42–1.34 (m, 1H), 1.33–1.26 (m, 1H), 1.11 (s, 3H), 0.92 (s, 3H), 0.83 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 148.6, 143.2, 138.1, 135.0, 131.6, 129.6, 128.9, 127.1, 126.4, 124.8, 62.0, 50.9, 38.2, 37.6, 37.2, 30.1, 28.1, 26.7, 24.6, 21.5, 21.2, 19.3, 16.2

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{34}NO_2S$ $[M+H]^+$: 412.2302, Found: 412.2310.

FTIR (NaCl): ν 2968, 2932, 1500, 1435 (br), 1319, 1157, 1090, 1047 cm^{-1}



2b

***N*-((2*S*,4a*S*,10a*R*)-6-Methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl)-4-methylbenzenesulfonamide,** a colorless solid, 75% yield. Mp: 221-222 ºC.

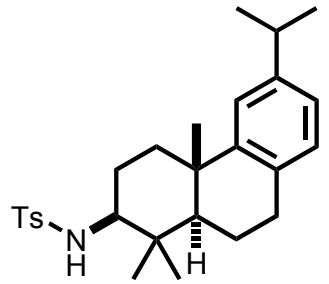
R_f: 0.25 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.80–7.74 (m, 2H), 7.31–7.26 (m, 2H), 6.96–6.91 (m, 1H), 6.71–6.61 (m, 2H), 4.61 (d, *J* = 9.54 Hz, 1H), 3.55 (s, 3H), 2.95–2.81 (m, 2H), 2.80–2.69 (m, 1H), 2.42 (s, 3H), 2.12 (dt, *J* = 12.96, 3.20 Hz, 1H), 1.84 (dd, *J* = 13.15, 6.96 Hz, 1H), 1.74–1.50 (m, 2H), 1.50–1.46 (m, 1H), 1.39 (td, J = 13.47, 3.20 Hz, 1H), 1.30 (dd, *J* = 12.16, 1,51 Hz, 1H), 1.12 (s, 3H), 0.92 (s, 3H), 0.82 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 150.0, 143.2, 138.1, 129.7, 129.6, 127.1, 127.0, 110.9, 110.1, 62.0, 55.2, 50.8, 38.2, 37.6, 37.4, 29.7, 28.1, 26.6, 24.6, 21.5, 19.3, 16.2

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{33}NO_3SNa$ $[M+Na]^+$: 450.2072, Found: 450.2079.

FTIR (NaCl): ν 3443 (br), 3260, 2968, 2943, 1650 (br), 1609, 1495, 1427, 1317, 1157, 1090, 1041 cm^{-1}



2c

***N*-((2*S*,4a*S*,10a*R*)-6-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl)-4-methylbenzenesulfonamid e,** a colorless solid, 74% yield. Mp: 201-201.5 ºC.

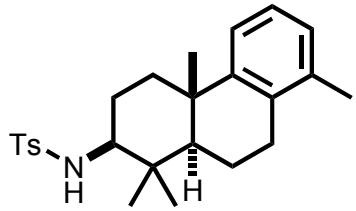
R_f: 0.60 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (500 MHz, $CDCl_3$): 7.80–7.75 (m, 2H), 7.31–7.26 (m, 2H), 7.01–6.92 (m, 3H), 4.54–4.50 (m, 1H), 2.94–2.84 (m, 2H), 2.84–2.73 (m, 2H), 2.42 (s, 3H), 2.20 (dt, *J* = 13.09, 3.13 Hz, 1H), 1.84 (dd, *J* = 13.14, 7.25 Hz, 1H), 1.72–1.54 (m, 2H), 1.52–1.45 (m, 1H), 1.40 (td, *J* = 13.43, 3.30 Hz, 1H), 1.32 (dd, *J* = 12.10, 1.74 Hz, 1H), 1.20 (d, *J* = 6.90 Hz, 6H), 1.13 (s, 3H), 0.92 (s, 3H), 0.84 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 148.6, 146.2, 143.1, 138.2, 132.2, 129.6, 128.8, 127.1, 123.4, 122.4, 62.1, 50.9, 38.2, 37.6, 37.3, 34.0, 30.2, 28.2, 26.6, 24.7, 24.2, 24.1, 21.5, 19.3, 16.2

HRMS (ESI): *m*/*z* calculated for $C_{27}H_{37}NO_2SNa$ $[M+Na]^+$: 462.2453, Found: 462.2443.

FTIR (NaCl): ν 3441 (br), 3265, 2963, 2870, 1645 (br), 1599, 1497, 1435, 1323, 1159, 1092, 1047 cm^{-1}



2d

4-Methyl-*N*-((2*S*,4a*S*,10a*R*)-1,1,4a,8-tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl)benzenesulfonamide, a colorless solid, 70% yield. Mp: 241.5-243 ºC.

R_f: 0.63 (Hexane : Ethyl Acetate = 4:1)

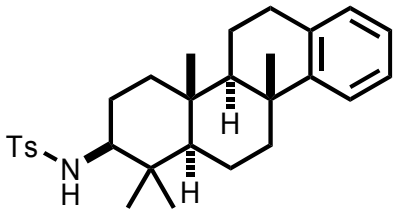
^{1}H NMR (500 MHz, $CDCl_3$): 7.79–7.73 (m, 2H), 7.31–7.26 (m, 2H), 7.07–7.00 (m, 2H), 6.97–6.92 (m, 1H), 5.52 (d, *J* = 9.65 Hz, 1H), 2.88 (ddd, *J* = 12.71, 9.89, 4.04 Hz, 1H), 2.79 (dd, *J* = 17.44, 6.27 Hz, 1H), 2.59 (ddd, *J* = 18.10, 11.49, 7.88 Hz, 1H), 2.42 (s, 3H), 2,20–2.12 (m, 1H), 2.18 (s, 3H), 1.93 (dd, *J* = 13.10, 7.67 Hz, 1H), 1.69 (qd, *J* = 12.51, 6.80 Hz, 1H), 1.58 (ddd, *J* = 15.56, 13.48, 2.91 Hz, 1H), 1.440 (ddd, *J* = 11.02, 6.93, 3.25 Hz, 1H), 1.36 (td, *J* = 13.71, 3.00 Hz, 1H), 1.31 (dd, *J* = 12.50, 1.63 Hz, 1H), 1.10 (s, 3H), 0.93 (s, 3H), 0.83 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 148.8, 143.2, 138.1, 136.3, 133.4, 129.6, 127.1, 127.0, 125.5, 122.1, 62.0, 50.2, 38.1, 38.0, 37.3, 28.4, 28.1, 26.7, 24.7, 21.5, 19.8, 19.1, 16.1

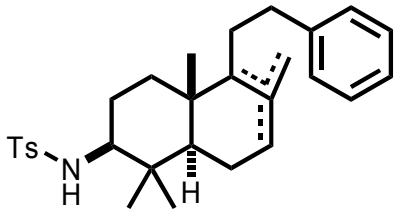
HRMS (ESI): *m*/*z* calculated for $C_{25}H_{33}NO_2SNa$ $[M+Na]^+$: 434.2132, Found: 434.2130.

FTIR (NaCl): ν 1450, 1421, 1331, 1157, 1303, 1157, 1088, 1045 cm^{-1}

*For tetracyclic products formation, bicyclized isomers **4'** were always obtained which were inseparable from desired products **4** by column chromatography.*



4 Tetracyclic Product



4' Bicyclized Isomers

4-Methyl-*N*-((2*S*,4a*R*,4b*R*,10b*R*,12a*R*)-1,1,4a,10b-tetramethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysen-2-yl)benzenesulfonamide, a colorless solid, 63% yield. Tetracyclic product : Bicyclized isomer = 82:18, Mp: 217-219 ^{o}C.

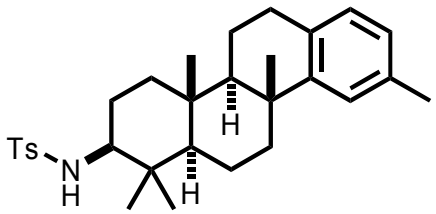
R_f: 0.50 (Hexane : Ethyl Acetate = 4:1) ,

^{1}H NMR (400 MHz, $CDCl_3$): 7.82–7.74 (m, 2H), 7.35–7.24 (m, 2H), 7.24–6.95 (m, 4H), 4.50–4.30 (m, 1H), 2.94–2.70 (m, 2H), 2.68–2.50 (m, 1H), 2.41 (s, 3H). 2.37 (dt, *J* = 12.62, 2.77 Hz, 1H), 1.80–1.00 (m, 11H), 1.16 (s, 3H), 0.85 (s, 3H), 0.84 (s, 3H), 0.76 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 149.8, 143.1, 138.4, 134.8, 129.6, 128.3, 127.0, 125.7, 125.2, 124.5, 62.2, 56.1, 54.9, 40.3, 38.8, 38.0, 37.8, 37.0, 30.7, 28.0, 26.1, 26.0, 21.5, 19.2, 18.0, 16.1, 16.1

HRMS (ESI): *m*/*z* calculated for $C_{29}H_{39}NO_2SNa$ $[M+Na]^+$: 488.2596, Found: 488.2599.

FTIR (NaCl): ν 3447 (br), 3252, 2965, 2932, 1650 (br), 1599, 1447, 1321, 1159, 1094 cm^{-1}



4a

4-Methyl-*N*-((2*S*,4a*R*,4b*R*,10b*R*,12a*R*)-1,1,4a,9,10b-pentamethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysen-2-yl)benzenesulfonamide, a colorless solid, 51% yield. Tetracyclic product : Bicyclized isomer = 84:16. Mp: 244-247 °C.

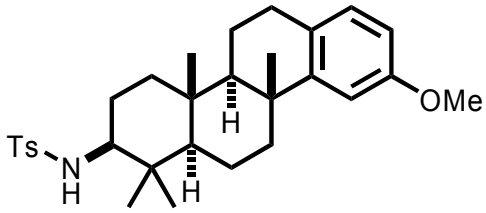
R_f: 0.50 (Hexane : Ethyl Acetate = 4:1),

^{1}H NMR (400 MHz, $CDCl_3$): 7.82–7.76 (m, 2H), 7.34–7.22 (m, 2H), 7.14–7.00 (m, 1H), 6.94–6.84 (m, 2H), 4.41 (d, *J* = 9.71, 1H), 2.90–2.78 (m, 2H), 2.78–2.64 (m, 1H), 2.41 (s, 3H), 2.40–2.30 (m, 1H), 2.27 (s, 3H), 1.58–1.00 (m, 11H), 1.15 (s, 3H), 0.84 (s, 6H), 0.75 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 149.7, 143.1, 138.4, 135.0, 131.7, 129.6, 128.7, 127.0, 126.1, 125.1, 62.2, 56.2, 55.0, 40.4, 38.9, 38.1, 37.8, 37.1, 30.3, 28.0, 26.1, 26.0, 21.5, 21.2, 19.3, 18.1, 16.2, 16.1

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_2SNa$ $[M+Na]^+$: 502.2751, Found: 502.2756.

FTIR (NaCl): ν 3250, 2934, 1445, 1319, 1157, 1093, 914 cm^{-1}



4b

***N*-((2*S*,4a*R*,4b*R*,10b*R*,12a*R*)-9-Methoxy-1,1,4a,10b-tetramethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysen-2-yl)-4-methylbenzenesulfonamide,** a colorless solid, 55% yield. Tetracyclic product : Bicyclized isomer = 87:13. Mp: 233-236 °C.

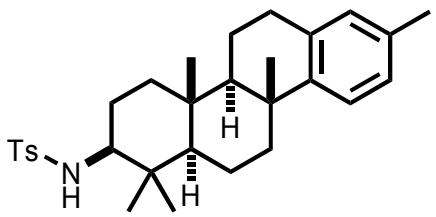
R_f: 0.49 (Hexane : Ethyl Acetate = 4:1),

^{1}H NMR (400 MHz, $CDCl_3$): 7.80–7.72 (m, 2H), 7.34–7.24 (m, 2H), 7.00–6.60 (m, 3H), 4.32 (d, *J* = 9.59 Hz, 1H), 3.76 (s, 3H), 2.90–2.80 (m, 2H), 2.76–2.64 (m, 1H), 2.42 (s, 3H), 2.33 (dt, *J* = 11.56, 2.72 Hz, 1H), 1.80–1.10 (m, 11H), 1.16 (s, 3H), 0.84 (s, 3H), 0.83 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 157.8, 151.2, 144.5, 138.4, 137.1, 129.6, 129.4, 127.2, 127.1, 110.9, 110.3, 62.3, 56.2, 55.3, 55.0, 40.4, 38.9, 38.1, 37.1, 29.8, 28.0, 26.2, 26.0, 21.6, 19.3, 18.2, 16.2, 16.2

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_3SNa$ $[M+Na]^+$: 518.2701, Found: 518.2705.

FTIR (NaCl): ν 3250, 2934, 1610, 1510, 1443, 1321, 1250, 1159, 1094, 1045, 910 cm^{-1}



4c

4-Methyl-*N*-((2*S*,4a*R*,4b*R*,10b*R*,12a*R*)-1,1,4a,8,10b-pentamethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysen-2-yl)benzenesulfonamide, a colorless solid, 52% yield. Tetracyclic product : Bicyclized isomer = 87:13. Mp: 190-193 °C.

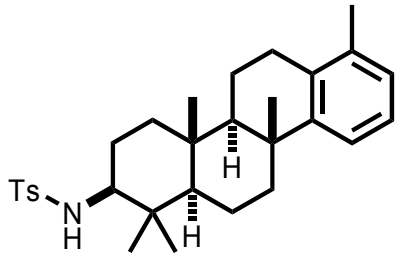
R_f: 0.50 (Hexane : Ethyl Acetate = 4:1),

^{1}H NMR (400 MHz, $CDCl_3$): 7.82–7.71 (m, 2H), 7.32–7.24 (m, 2H), 7.14–6.78 (m, 3H), 4.33 (d, *J* = 9.87 Hz, 1H), 2.90–2.80 (m, 2H), 2.78–2.68 (m 1H), 2.41 (s, 3H), 2.35 (dt, *J* = 11.26, 2.81 Hz, 1H), 2.25 (s, 3H), 1.78–1.04 (m, 11H), 1.14 (s, 3H), 0.84 (s, 3H), 0.83 (s, 3h), 0.75 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 147.0, 143.1, 138.4, 134.7, 134.6, 129.6, 129.3, 127.0, 126.6, 124.5, 62.2, 56.2, 55.1, 40.4, 38.8, 38.1, 37.5, 37.0, 30.6, 28.0, 26.1, 26.0, 21.5, 20.7, 19.2, 18.0, 16.0, 16.1

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_2SNa$ $[M+Na]^+$: 502.2758, Found: 502.2756.

FTIR (NaCl): ν 3420 (br), 3281 (br), 2965, 2940, 1636 (br), 1599, 1497, 1450 (br), 1323, 1159, 1094, 1047 cm^{-1}



4d

4-Methyl-*N*-((2*S*,4a*R*,4b*R*,10b*R*,12a*R*)-1,1,4a,7,10b-pentamethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysen-2-yl)benzenesulfonamide, a colorless solid, 65% yield. Tetracyclic product : Bicyclized isomer = 86:14. Mp: 183-184 ^oC.

R_f: 0.50 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.81–7.70 (m, 2H), 7.32–7.20 (m, 2H), 7.18–6.90 (m, 3H), 4.33 (d, *J* = 9.73 Hz, 1H), 2.90–2.70 (m, 2H), 2.60–2.45 (m, 1H), 2.42 (s, 3H), 2.40–2.28 (m, 1H), 2.16 (s, 3H), 2.00–1.00 (m, 11H), 1.16 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H), 0.74 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 149.9, 143.1, 138.4, 136.1, 133.4, 129.6, 127.0, 126.8, 125.5, 122.4, 62.2, 56.1, 54.4, 40.8, 38.8, 38.0, 37.9, 36.9, 28.5, 28.0, 26.2, 26.0, 21.5, 19.8, 19.3, 17.9, 16.2, 16.1

HRMS (ESI): *m*/*z* calculated for $C_{30}H_{41}NO_2SNa$ $[M+Na]^+$: 502.2756, Found: 502.2756.

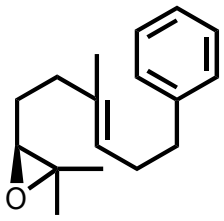
FTIR (NaCl): ν 3443 (br), 3285 (br), 2966, 2941, 1651 (br), 1599, 1454, 1321, 1159, 1094 cm^{-1}

4.Functionalization of Cyclization Products

The chiral epoxide was synthesized according to Sharpless and Corey's procedures.[2] Diene substrate (674 mg, 3.0 mmol, 1.0 equiv.) was mixture with $MeSO_2NH_2$ (300 mg, 3.0 mmol, 1.0 equiv), *t*-BuOH (10 mL) and H_2O (10 mL) at room temperature. Sharpless dihydroxylation reagent AD-mix-β (3.36 g, 0.8 equiv.) was added in small portions. The reaction was stirred at room temperature for 12 hours. The aqueous layer was extracted with ethyl acetate (40 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired diol product in 67% yield as colorless oil.

To a 50 mL round-bottom flask quipped with a magnetic stirring bar was added diol (0.2884 g, 1.1 mmol, 1.0 equiv.), Et_3N (1.0 mL), pyridine (1.0 mL), DMAP (20 mg, cat) and THF (20 mL). MsCl (126 mg, 1.2 mmol, 1.1 equiv.) was added via syringe at room temperature. The reaction mixture was refluxed for 12 hours. The reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (40 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired chiral epoxide product in 75% yield as colorless oil.

[2] (a) Crispino, G. A.; Sharpless, K. B. *Tetrahedron Lett*. **1992**, *33*, 4273. (b) Corey, E. J.; Noe, M. C.; Lin, S. Z.; *Tetrahedron Lett*. **1995**, *36*, 8741-8744.



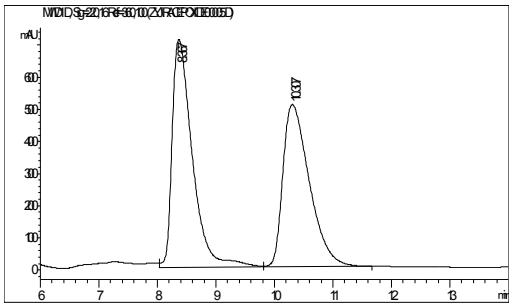
5

(*S*,*E*)-2,2-dimethyl-3-(3-methyl-6-phenylhex-3-enyl)oxirane

50% yield (2 steps), 97% ee, $[\alpha]^{D}_{20}$ = **–**43.6° (*c* = 4.0). (Hexane : Ethyl Acetate = 4:1)

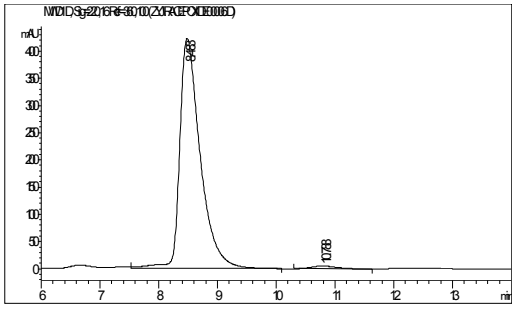
The other spectrum data were the same as reference.[3]

The enantiomeric excess was determined by HPLC analysis employing Daicel Chiral OB-H column (Hexane : *i*-propanol = 99.7, 0.3 mL/min): t_1 = 8.48 min (major) , t_2 = 10.79 min (minor)



Signal 4: MWD1 D, Sig=220,16 Ref=360,100

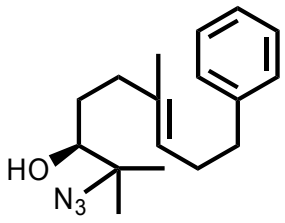
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.367	VV	0.3616	1.71572e4	710.88226	51.8586
2	10.307	VB	0.4857	1.59274e4	505.41504	48.1414
Totals :				3.30846e4	1216.29730	



Signal 4: MWD1 D, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.483	VB	0.3640	1.03100e4	423.47754	98.4492
2	10.788	BB	0.4504	162.40680	5.37646	1.5508
Totals :				1.04724e4	428.85400	

The procedure for selective opening of epoxide was following Fringuelli's.[4] To a 50 mL round-bottom flask quipped with a magnetic stirring bar was added epoxide (0.13 g, 0.53 mmol, 1.0 equiv.), NaN_3 (480 mg, 6.0 mmol, 10.0 equiv.), AcOH (2.0 mL), H_2O (1.5 mL) and $(MeOCH_2)_2$ (4.5 mL). The reaction mixture was stirred at 35 °C for 48 hours. The pH value was adjusted to be 8 by NaOH (1 *N*) and extracted with ethyl acetate (30 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired amine product in 50% yield as colorless oil.



6

(*S*,*E*)-2-Azido-2,6-dimethyl-9-phenylnon-6-en-3-ol

$[\alpha]^{D}_{20}$ = -11.6° (*c* = 1.5), R_f: 0.63 (Hexane : Ethyl Acetate = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.30–2.23 (m, 2H), 7.20–7.15 (m, 3H), 5.23 (td, *J* = 7.04, 1.14 Hz, 1H), 3.27 (ddd, *J* = 10.50,

[3] Zhao, J. F.; Zhao, Y. J.; Loh, T. P. *Chem. Commun.* **2008**, 1353–1355.

[4] Fringuelli, F.; Poermatti, O.; Pizzo, F.; Vaccaro, L. *J. Org. Chem*. **1999**, *64*, 6094–6096.

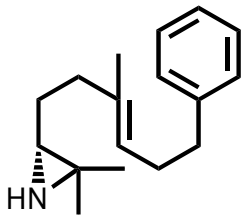
4.79, 1.86 Hz, 1H), 2.65 (t, *J* = 7.69 Hz, 2H), 2.32 (q, *J* = 7.51 Hz, 2H), 2.22 (ddd, *J* = 13.97, 8.67, 5.49 Hz, 1H), 2.04 (dt, *J* = 14.08, 7.87 Hz, 1H), 1.86 (t, *J* = 5.23 Hz, 1H), 1.60–1.55 (m, 1H), 1.55 (s, 3H), 1.39 (dddd, *J* = 12.33, 8.99, 7.83, 4.59 Hz, 1H), 1.26 (s, 3H), 1.25 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.3, 135.3, 128.5, 128.3, 125.8, 124.6, 77.13, 68.0, 36.5, 36.0, 29.9, 29.2, 22.7, 21.1, 15.9

HRMS (ESI): *m*/*z* calculated for $C_{17}H_{25}N_3ONa$ $[M+Na]^+$: 310.1906, Found: 310.1895.

FTIR (NaCl): ν 3437 (br), 2990, 2102, 1643 (br), 1568, 1495, 1454, 1259 (br), 1138, 1076 cm^{-1}

To a 50 mL round-bottom flask quipped with a magnetic stirring bar was added azidohydrin (72 mg, 0.25 mmol, 1.0 equiv.), Ph_3P (excess, 1.0 g) and 1,4-dioxane (15 mL).[5] The reaction mixture was reflux for 48 hours. The reaction mixture was concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired amine product as colorless oil.



7

(*R*,*E*)-2,2-Dimethyl-3-(3-methyl-6-phenylhex-3-enyl)aziridine

$[\alpha]^D_{20}$ = 4.8° (c = 3.6), R_f: 0.05 (Ethyl Acetate)

^{1}H NMR (400 MHz, $CDCl_3$): 7.30–7.15 (m, 5H), 5.23 (t, *J* = 6.78 Hz, 1H), 2.69 (t, *J* = 6.27 Hz, 1H), 2.64 (t, *J* = 7.85 Hz, 2H), 2.31 (dd, *J* = 15.05, 7.44 Hz, 2H), 2.22–2.00 (m, 2H), 1.72–1.54 (m, 2H), 1.54 (s, 3H), 1.30 (s, 3H), 1.24 (s, 3H)

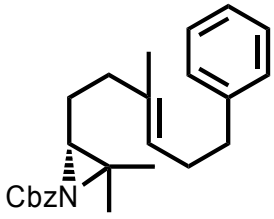
H (N-H) was not observed.

^{13}C NMR (100 MHz, $CDCl_3$): 142.2, 134.8, 128.4, 128.2, 125.7, 124.2, 64.1, 58.3, 36.2, 36.0, 30.0, 27.4, 24.9, 18.7, 15.9

HRMS (ESI): *m*/*z* calculated for $C_{17}H_{26}N$ $[M+H]^+$: 244.2062, Found: 244.2065.

FTIR (NaCl): ν 3026, 2953, 2924, 1603, 1495, 1454, 1381, 1265 cm^{-1}

To a 25 mL round-bottom flask quipped with a magnetic stirring bar was added aziridine (74 mg, 0.29 mmol, 1.0 equiv.), Et_3N (0.5 mL, 0.5 mL, 5.0 equiv.), DMAP (20 mg, cat.) and THF (5 mL). The mixture was cooled to –40 °C. CbzCl (0.2 mL, 1.2 mmol, 4.0 equiv.) was added as a THF solution via syringe. The reaction mixture was stirred for 5 hours. The reaction was poured into ice water. The aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography (neutral Al_2O_3) to afford the desired amine product in 50% yield (over two steps from azidohydrin) as colorless oil.



8

(*R*,*E*)-Benzyl 2,2-dimethyl-3-(3-methyl-6-phenylhex-3-enyl)aziridine-1-carboxylate

50% yield, 96.8% ee, $[\alpha]^D_{20}$ = –48.8° (*c* = 0.75), R_f: 0.6 (Hexane : Ethyl acetate = 4:1)

[5] Voronkov, M. V.; Gontcharov, A. V.; Kanamarlapudi, R. C.; Richardson, P. F.; Wang, Z. M. *Org. Process Res. Dev*. **2005**, *9*, 221–224

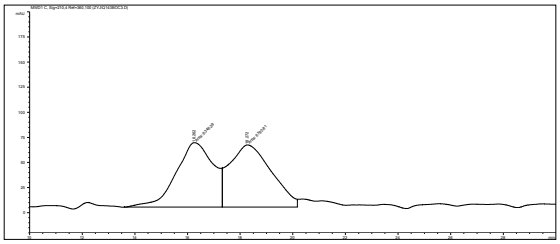
^{1}H NMR (400 MHz, $CDCl_3$): 7.40–7.10 (m, 10H), 5.21 (t, *J* = 6.41 Hz, 1H), 5.15 (d, *J* = 12.35 Hz, 1H), 5.10 (d, *J* = 12.35 Hz, 1H), 2.62 (t, *J* = 12.35 Hz, 2H), 2.29 (q, *J* = 12.35 Hz, 2H), 2.23 (t, *J* = 6.58 Hz, 1H), 2.18–2.06 (m, 2H), 1.65–1.50 (m, 2H), 1.56 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H)

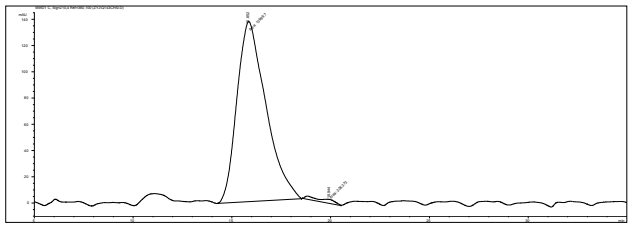
^{13}C NMR (100 MHz, $CDCl_3$): 162.2, 142.3, 136.3, 135.0, 128.5, 128.5, 128.4, 128.3, 128.2, 125.7, 124.2, 67.7, 48.3, 44.6, 37.2, 36.1, 30.1, 27.1, 23.3, 19.5, 16.1

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{32}NO_2$ $[M+H]^+$: 378.2426, Found: 378.2433.

FTIR (NaCl): ν 3028, 2961, 2928, 1715, 1497, 1454, 1379, 1321, 1261, 1246, 1136, 1078 cm^{-1}

The enantiomeric excess was determined by HPLC analysis employing Daicel Chiral OB-H column (Hexane : *i*-propanol = 99.5, 0.5 mL/min): t_1 = 15.82 min (major) , t_2 = 19.94 min (minor)





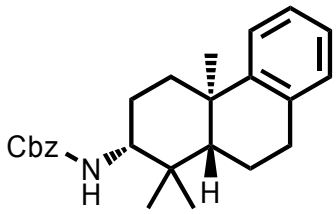
Signal 4: MWD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.262	MM	1.6511	6346.28271	64.06287	48.3449
2	18.272	MM	1.8281	6780.80762	61.81863	51.6551
Totals :				1.31271e4	125.88149	

Signal 4: MWD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.852	MM	1.7002	1.39997e4	137.23798	98.3949
2	19.944	MM	1.2338	228.37294	3.08491	1.6051
Totals :				1.42280e4	140.32289	

Reaction was performed in 0.1 mmol (38 mg) scale using previous standard procedure for polyene cyclization catalyzed by $InBr_3$, 67% isolated yield (25 mg), a colorless oil.



9

Benzyl (2*R*,4a*R*,10a*S*)-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-ylcarbamate

67% yield, 97% ee. $[\alpha]^D_{20}$ = -327.3° (*c* = 2.5), R_f: 0.5 (Hexane : Ethyl acetate = 4:1)

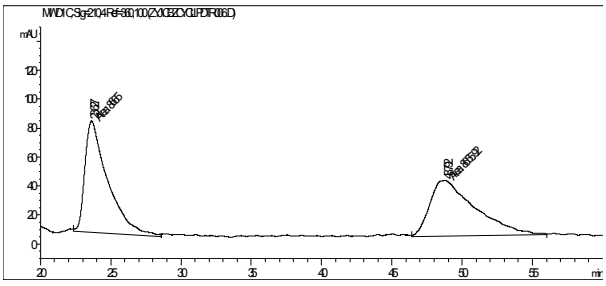
^{1}H NMR (400 MHz, $CDCl_3$): 7.40–7.28 (m, 5H), 7.24–7.18 (m, 1H), 7.16–7.00 (m, 3H), 5.13 (d, *J* = 12.17 Hz, 1H), 5.07 (d, *J* = 12.17 Hz, 1H), 4.69 (d, *J* = 12.19 Hz, 1H), 2.45 (td, *J* = 11.53, 3.89 Hz, 1H), 2.95 (dd, *J* = 16.52, 6.14 Hz, 1H), 2.91–2.80 (m, 1H), 2.35 (dt, *J* = 12.88, 3.26 Hz, 1H), 1.95–1.80 (m, 2H), 1.80–1.54 (m, 3H), 1.44 (dd, *J* = 12.01, 1.38 Hz, 1H), 1.17 (s, 3H), 1.02 (s, 3H), 0.85 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 156.3, 149.0, 136.7, 135.0, 129.0, 128.6, 128.2, 128.2, 125.9, 125.5, 124.6, 66.8, 58.8, 50.7, 38.1, 37.6, 37.6, 30.8, 28.6, 26.7, 25.0, 19.2, 16.4

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{32}NO_2$ $[M+H]^+$: 378.2427, Found: 378.2433.

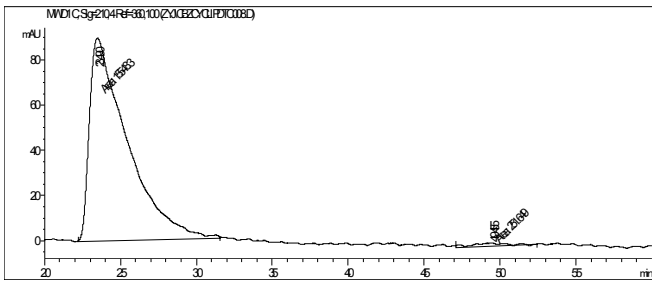
FTIR (NaCl): ν 3441 (br), 2965, 2943, 1701, 1508, 1489, 1454, 1338, 1315, 1234 (br), 1068, 1022 cm^{-1}

The enantiomeric excess was determined by HPLC analysis employing Daicel Chiral OD-H column (Hexane : *i*-propanol = 98 :2, 1 mL/min): t_1 = 23.49 min (major) , t_2 = 49.46 min (minor)



Signal 3: MWD1 C, Sig=210,4 Ref=360,100

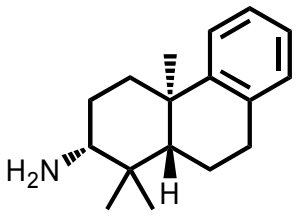
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.627	MM	1.8863	8665.00293	76.56206	50.0262
2	48.792	MM	3.7576	8655.91895	38.39245	49.9738



Signal 3: MWD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.490	MM	2.8831	1.55483e4	89.88303	98.4073
2	49.455	MM	2.7890	251.64857	1.50384	1.5927

To a 25 mL round-bottom flask quipped with a magnetic stirring bar was added Cbz group protected amine *i.e.* cyclization product (38 mg, 0.1 mmol), 10% Pd/C (0.1 g) and ethanol (15 mL). Hydrogen gas was bubbled for 3 hours at room temperature. The reaction mixture was filtered to remove catalyst. The solvent was removed *in vacuo* and the crude product was purified by passing through a pad of silica gel affording desired amine product in 95% yield as colorless oil.



10

(2*R*,4a*R*,10a*S*)-1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-amine

$[\alpha]^{D}_{20}$ = -51.5° (*c* = 1.2), R_f: 0.25 (MeOH)

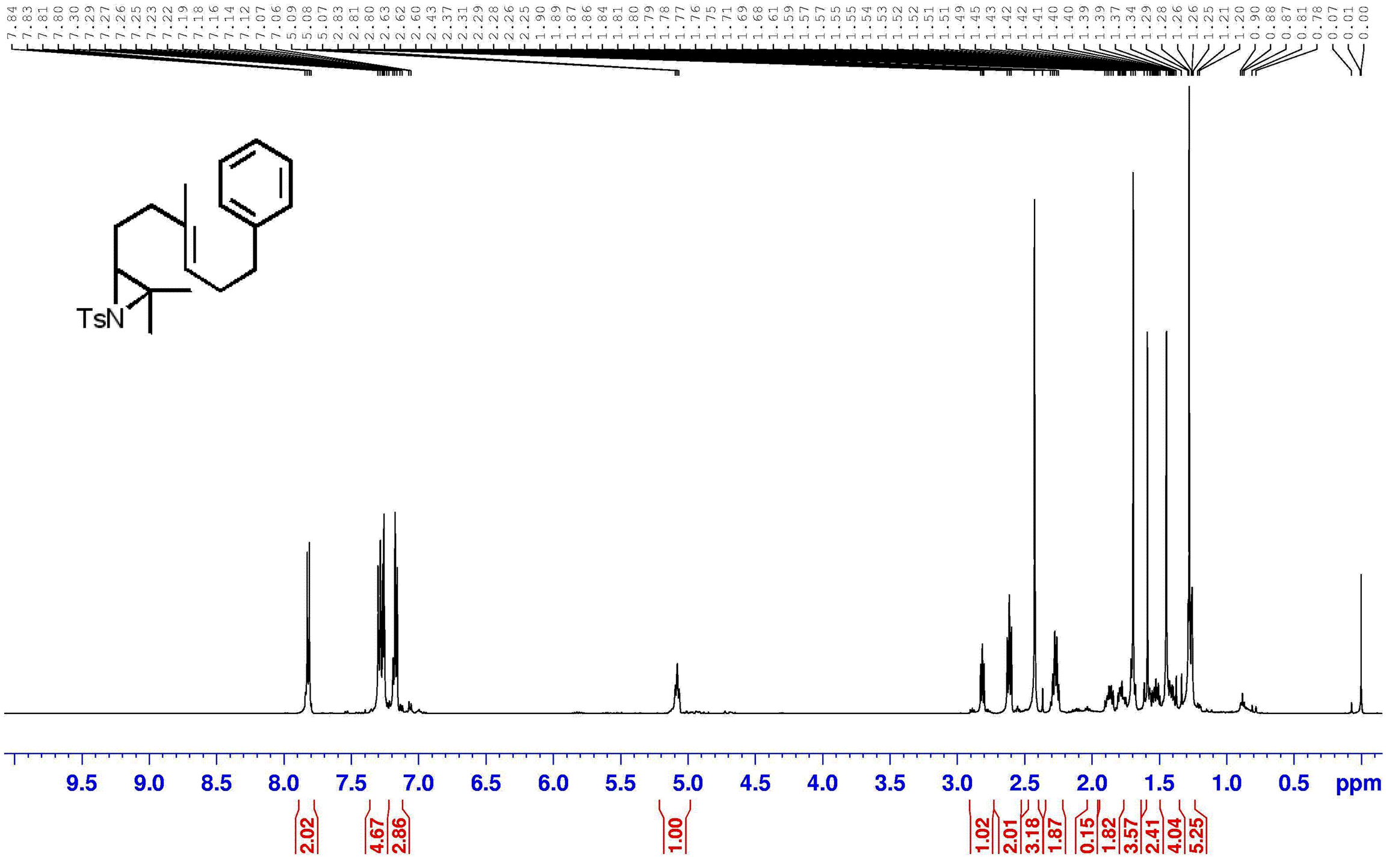
^{1}H NMR (400 MHz, $CDCl_3$): 7.30–7.00 (m, 4H), 5.00–4.00 (m, 2H), 2.90 (dd, *J* = 17.33, 6.02 Hz, 1H), 2.80 (ddd, *J* = 17.95, 11.97, 7.41 Hz, 1H), 2.65 (dd, *J* = 11.41, 4.18 Hz, 1H), 2.28 (dt, *J* = 13.37, 3.04 Hz, 1H), 1.92–1.80 (m, 2H), 1.76–1.60 (m, 2H), 1.47 (td, *J* = 13.0, 4.21 Hz, 1H), 1.29 (dd, *J* = 12.07, 1.65 Hz, 1H),. 1.19 (s, 3H), 1.14 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 149.0, 134.9, 129.0, 125.9, 125.6, 124.5, 60.1, 50.4, 37.8, 37.7, 37.3, 30.8, 28.6, 26.5, 24.9, 19.1, 16.0

HRMS (ESI): *m*/*z* calculated for $C_{17}H_{26}N$ $[M+H]^+$: 244.2065, Found: 244.2060.

FTIR (NaCl): ν 3439 (br), 2854, 1643 (br), 1454, 1371, 1260, 1259, 1026 cm^{-1}

500 MHz H
Q095 Ts_081028.1.1



300 NMR
Q048 Ts Fraction 2_081024.4.1 13C

143.52
142.13
138.46
134.38
129.35
128.43
128.23
127.35
125.72
124.34

77.46
77.03
76.61

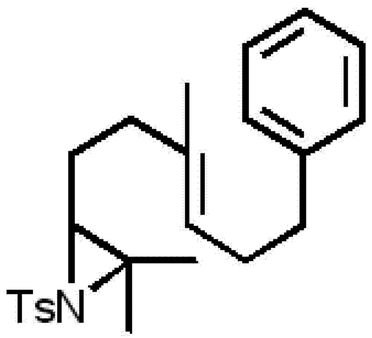
52.43
51.83

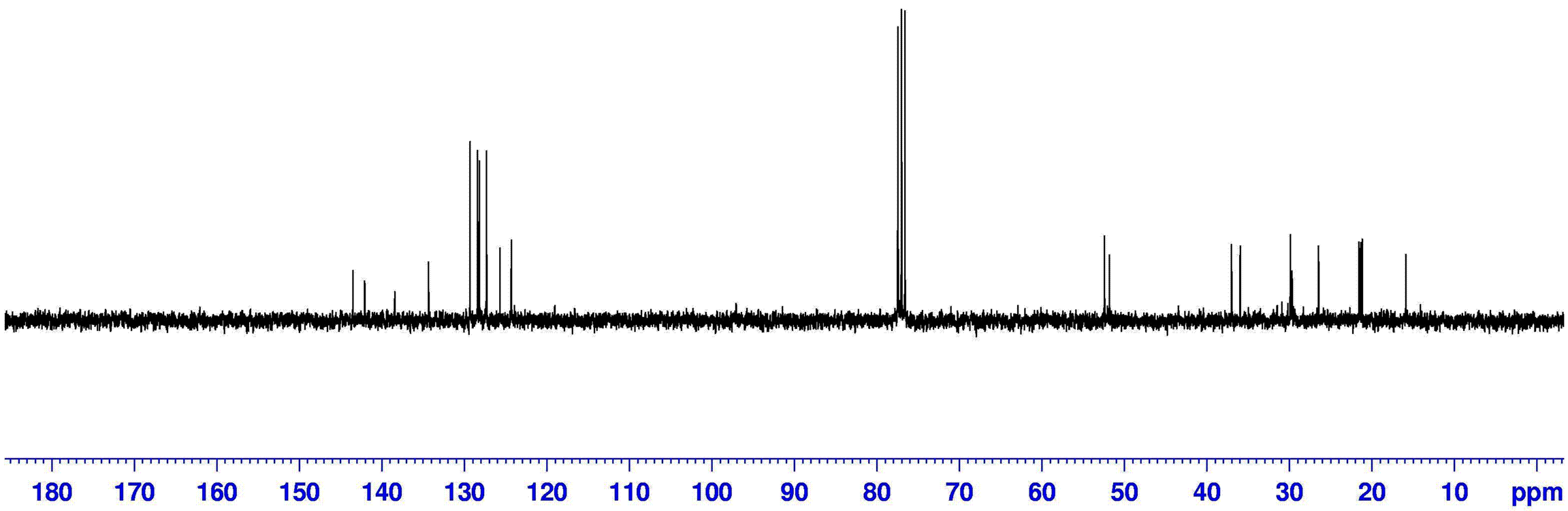
37.01
35.95

29.87
29.69
26.46

21.56
21.34
21.18

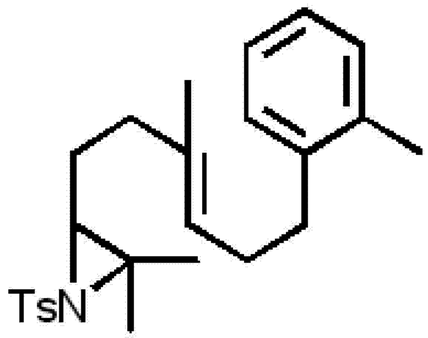
15.88

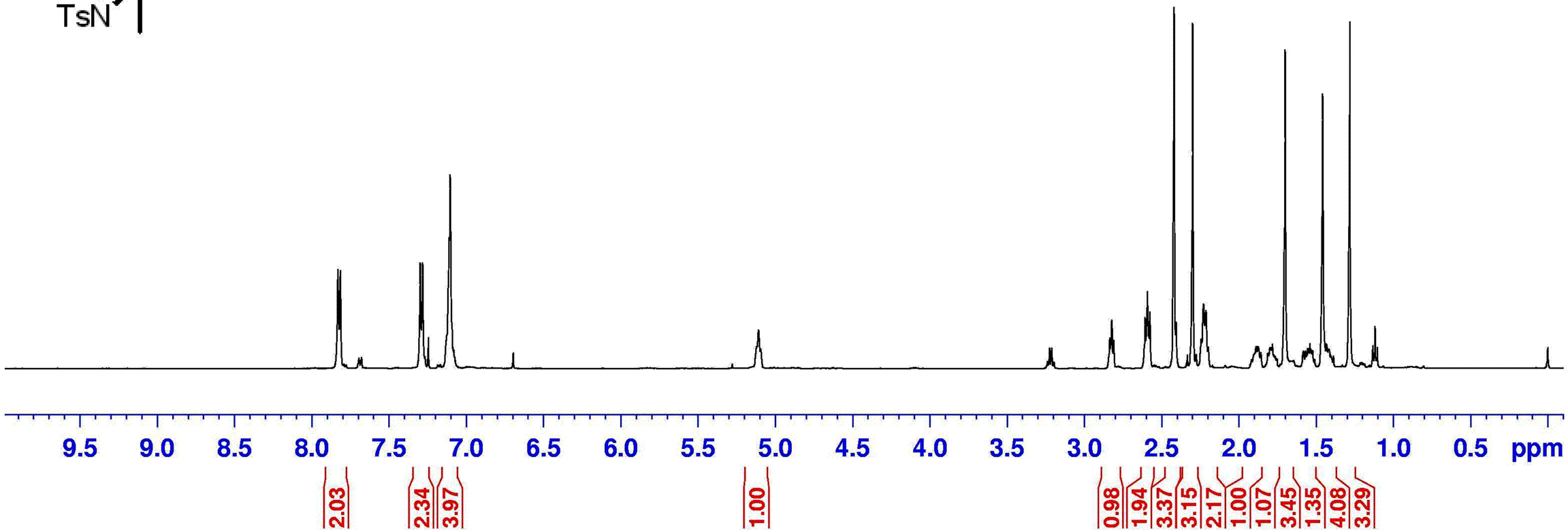




500 MHz H
Q111 Tri, 2 Me_081103.1.1

7.83
7.82
7.30
7.28
7.11
7.11
5.11
2.84
2.82
2.81
2.61
2.59
2.58
2.42
2.41
2.30
2.24
2.23
2.21
2.20
1.89
1.88
1.80
1.79
1.78
1.70
1.58
1.57
1.55
1.54
1.53
1.52
1.46
1.44
1.43
1.42
1.42
1.28





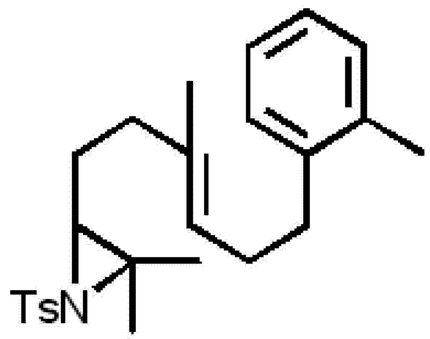
500 MHz H
Q111 Tri, 2 Me_081103.4.1 13C

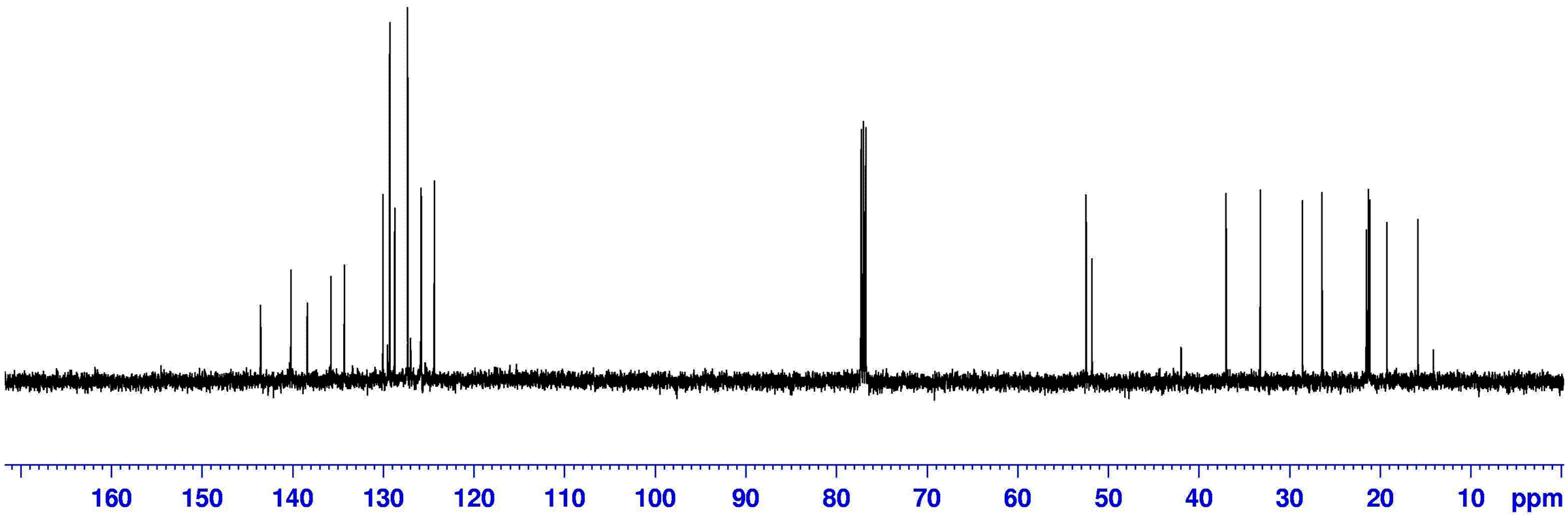
143.52
140.23
138.43
135.80
134.34
130.05
129.34
128.78
127.34
125.87
125.83
124.41

77.29
77.03
76.78

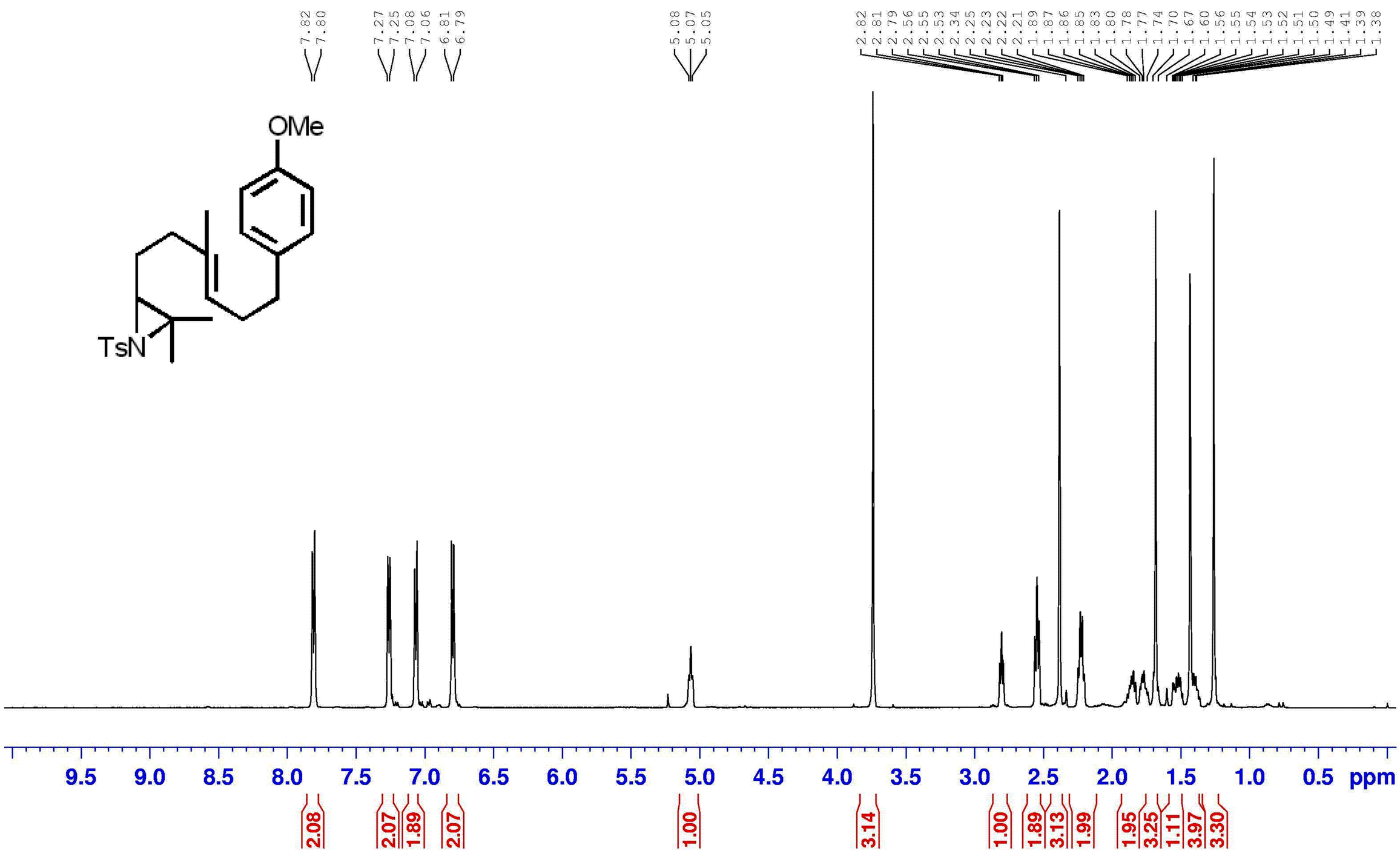
52.46
51.83

37.01
33.23
28.58
26.44
21.54
21.32
21.17
19.28
15.84



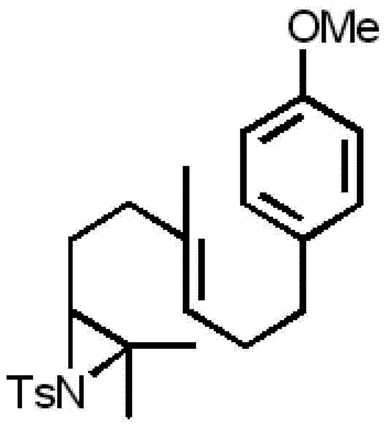


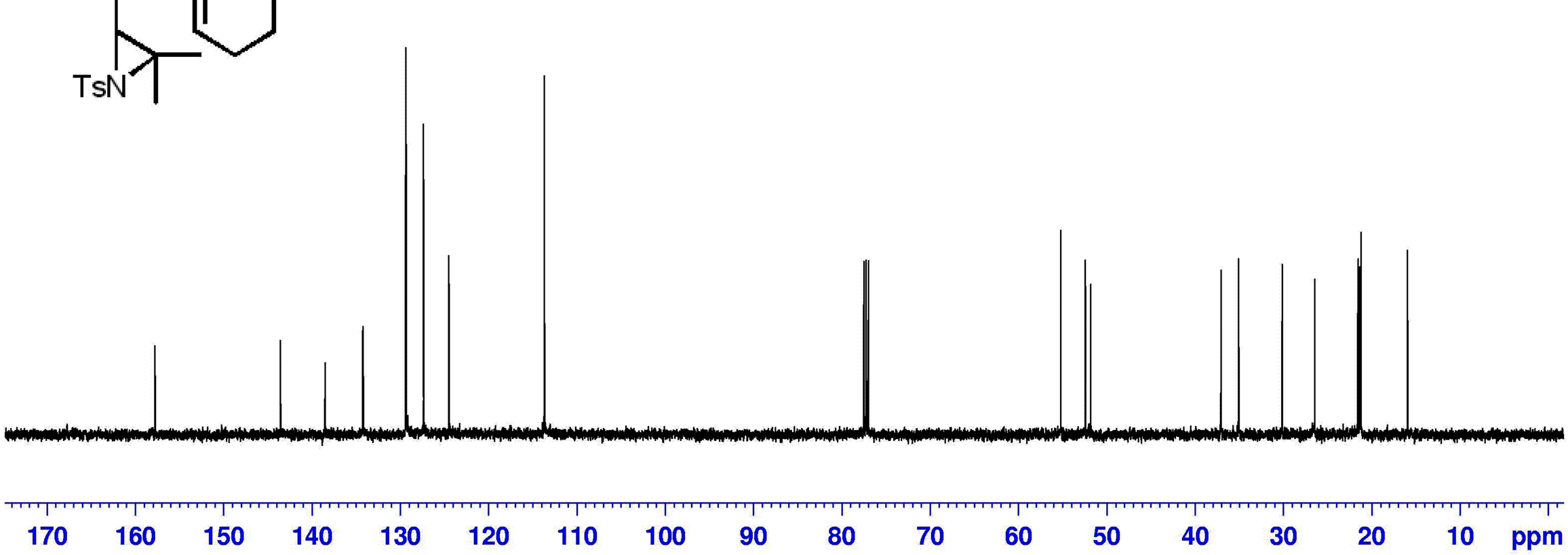
500 MHz H
Q122 Tri, N-Ts OMe_081107.1.1



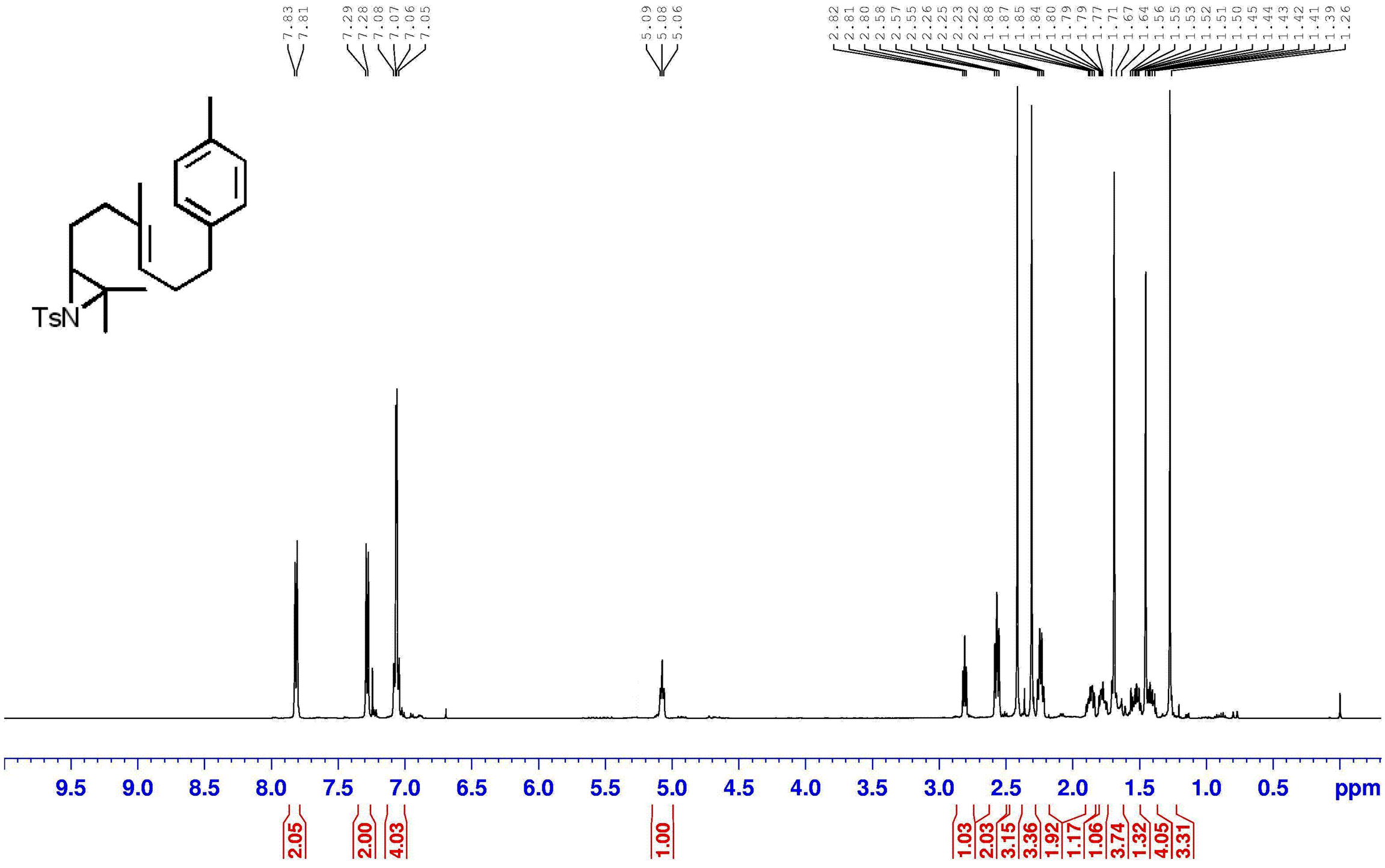
500 MHz H
Q122 Tetra, N-Ts OMe_081107.4.1 13 C

157.78
143.57
138.52
134.28
134.21
129.41
129.34
127.37
124.48
113.69
77.52
77.26
77.01
55.22
52.44
51.82
37.06
35.07
30.15
26.46
21.56
21.36
21.22
15.94





500 MHz H
Q105 Tri p_Me_081030.1.1



500 MHz H
Q105 Tri p_Me_081030.4.1

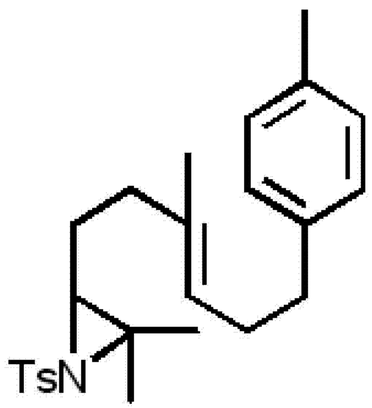
143.51
139.05
138.45
135.12
134.23
129.34
128.91
128.27
127.34
124.47

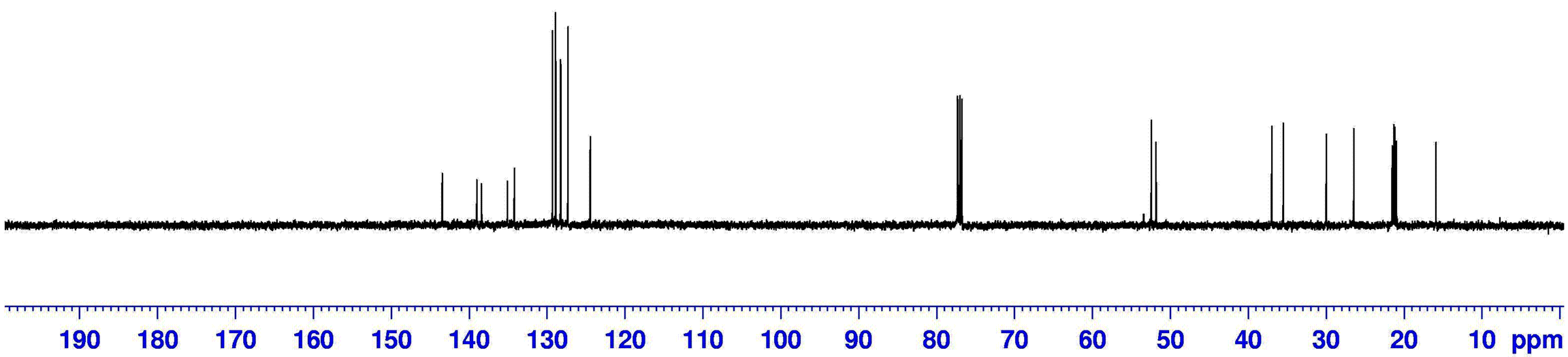
77.29
77.04
76.78

52.45
51.84

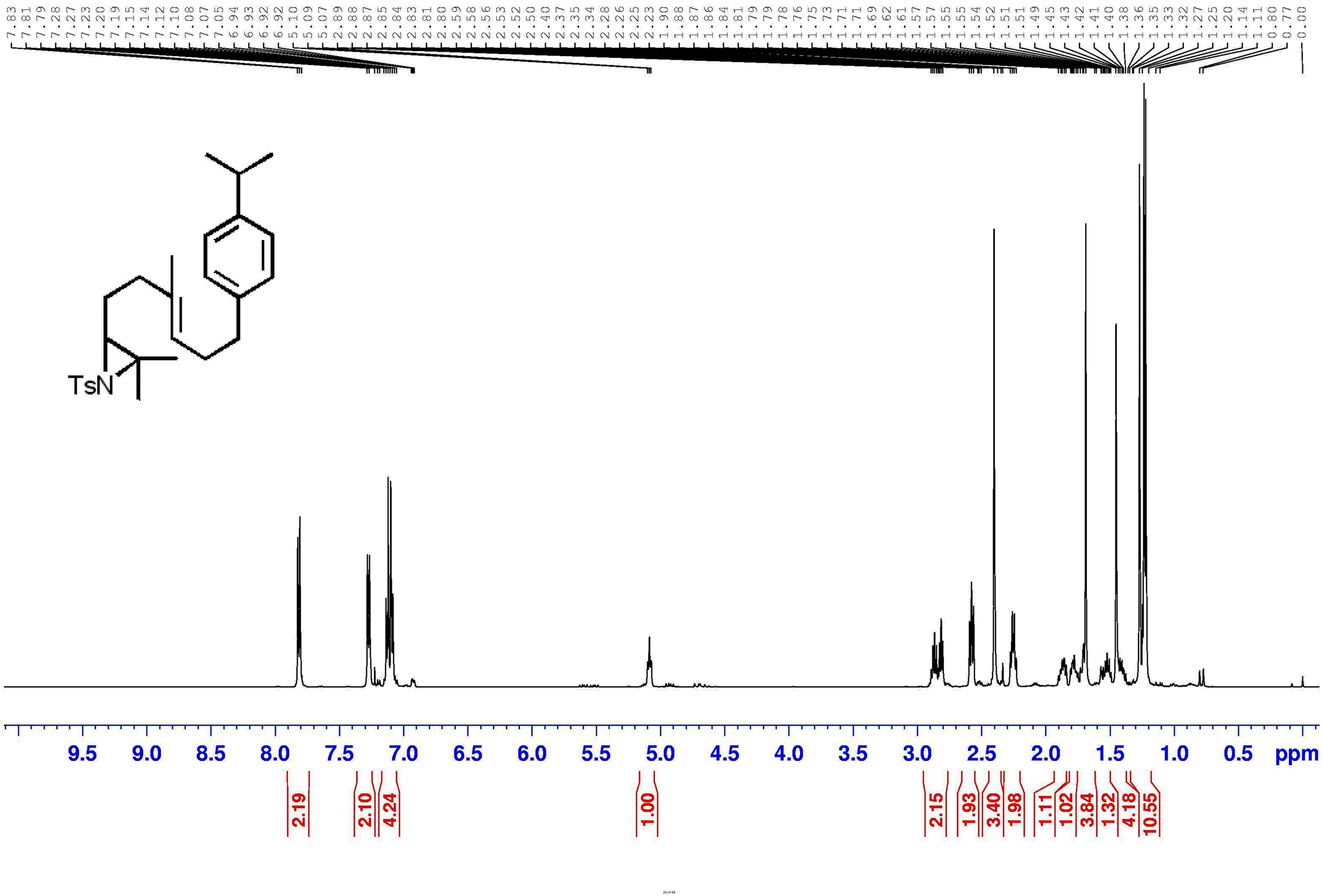
37.00
35.50

29.99
26.44
21.54
21.32
21.17
20.98
15.90

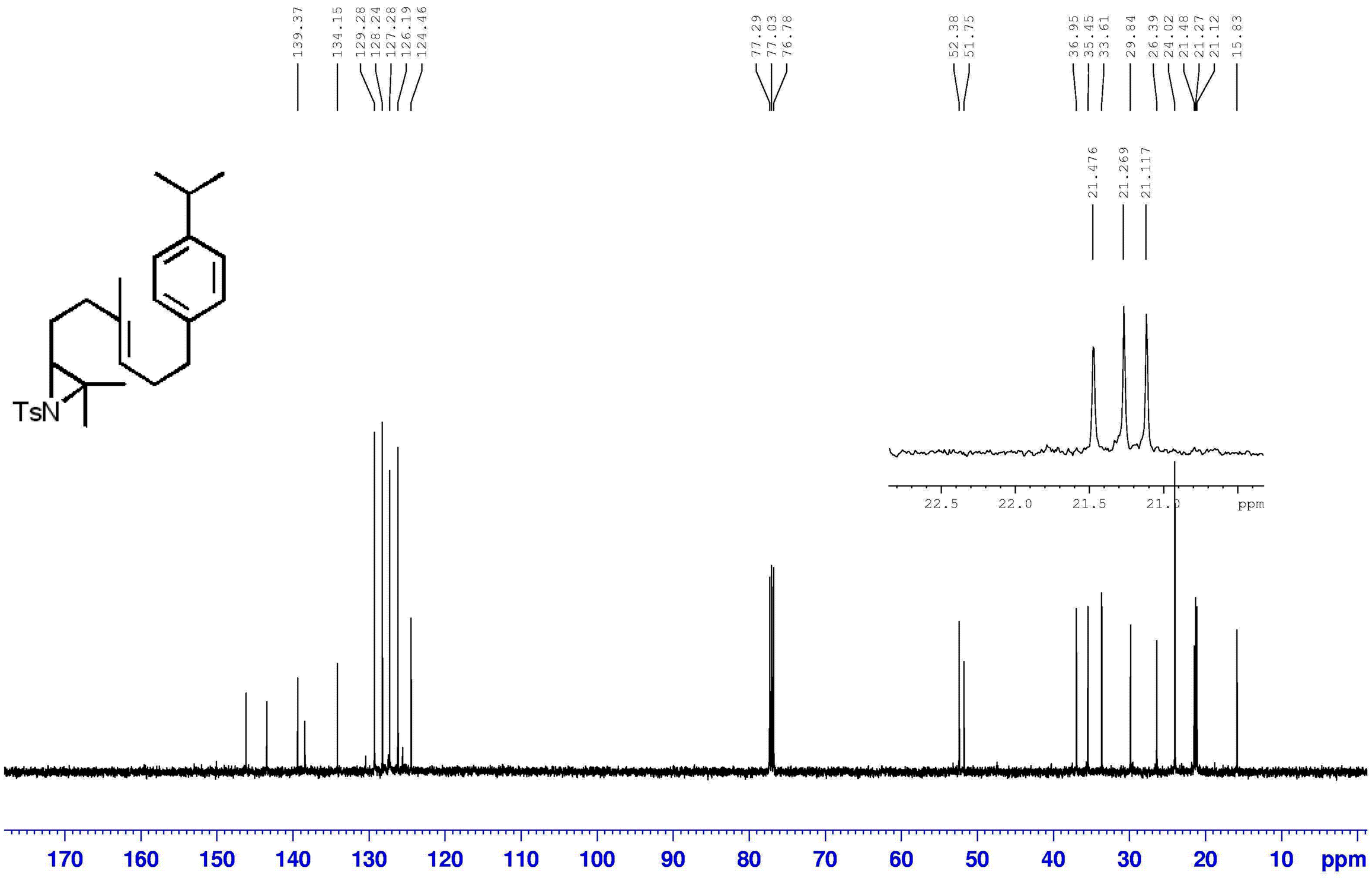




500 MHz H
Q121 Tri, N-Ts i Pr_081107.1.1

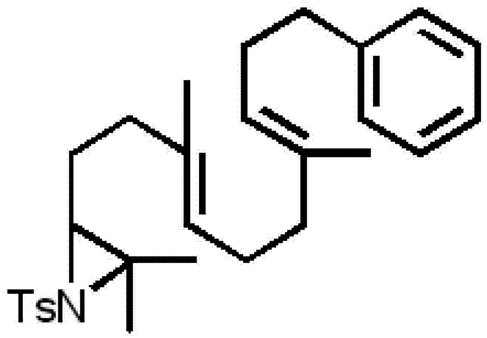


500 MHz H
Q121 Tri, N-Ts i Pr_081107.4.1



500 MHz H
Q103 Tetra No_081030.1.1

7.83 7.81 7.29 7.27 7.26 7.25 7.25 7.18 7.17 7.16 6.69 5.22 5.18 5.17 5.15 5.02 5.01 4.99 3.74 3.54 3.39 2.83 2.82 2.81 2.64 2.62 2.61 2.41 2.32 2.30 2.28 2.27 2.05 2.04 2.02 2.01 1.98 1.97 1.96 1.94 1.91 1.89 1.88 1.86 1.85 1.83 1.82 1.81 1.80 1.79 1.78 1.77 1.77 1.75 1.72 1.71 1.70 1.67 1.67 1.62 1.60 1.57 1.57 1.55 1.54 1.53 1.52 1.51 1.51 1.50 1.47 1.46 1.45 1.44 1.43 1.42 1.41 1.40 1.39 1.29 1.28 1.26 1.25 1.24 1.21 0.95 0.88 0.08 0.00



500 MHz H
Q103 Tetra No_081030.4.1

143.49
142.30
138.44
135.54
133.55
129.33
128.42
128.18
127.32
125.65
124.97
123.67

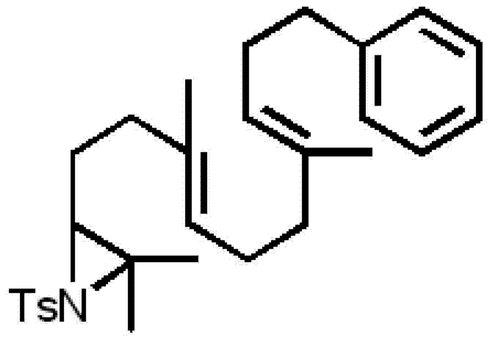
77.29
77.03
76.78

52.49
51.82

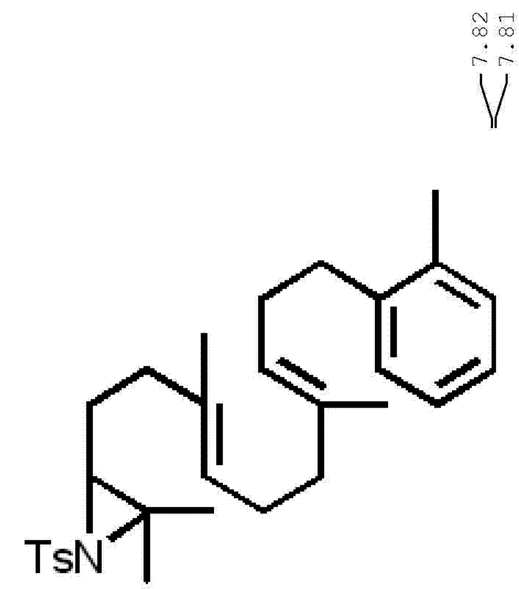
39.54
37.00
36.09

29.91
26.55
26.48
21.53
21.33
21.17

15.94



500 MHz H
Q123 Tetra, N-Ts 2-Me_081107.1.1



500 MHz H
Q123 Tetra, N-Ts 2-Me_081107.4.1

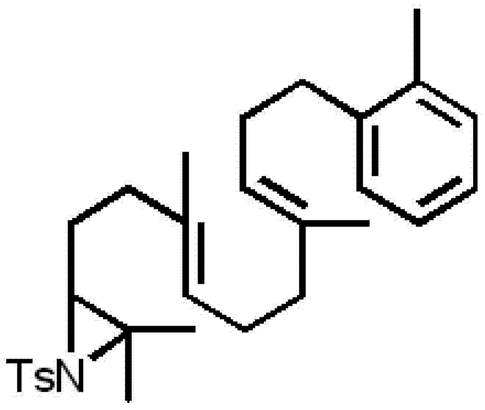
143.42
140.36
138.42
135.74
135.43
133.51
129.98
129.27
128.76
127.26
125.77
124.93
123.75

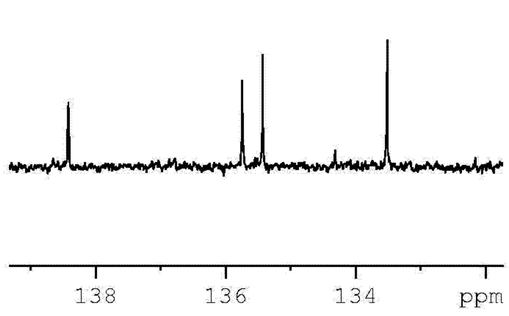
77.29
77.03
76.78

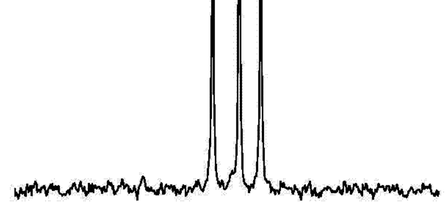
52.41
51.73

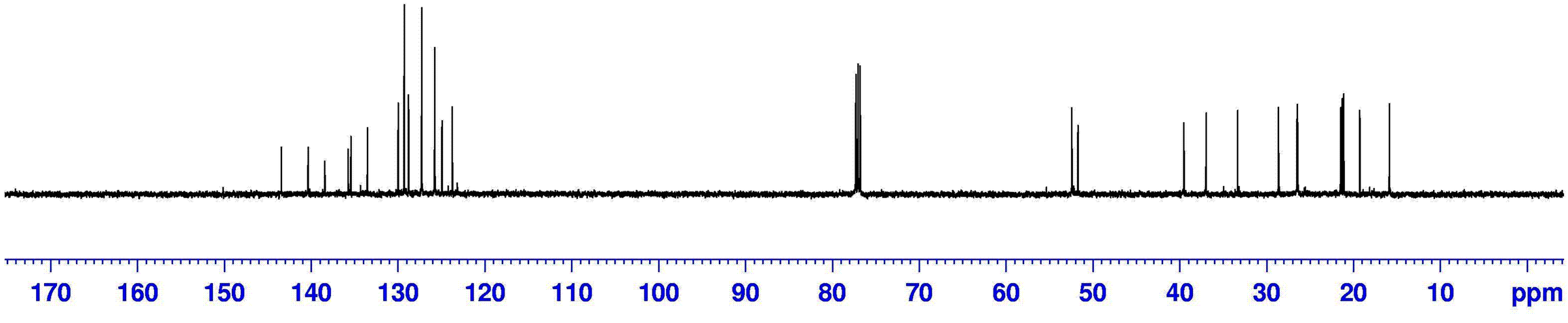
39.51
36.96
33.33
28.62
26.50
26.42
21.47
21.28
21.12
19.25
15.88
15.86

138.417
135.738
135.426
133.512
21.466
21.276
21.119

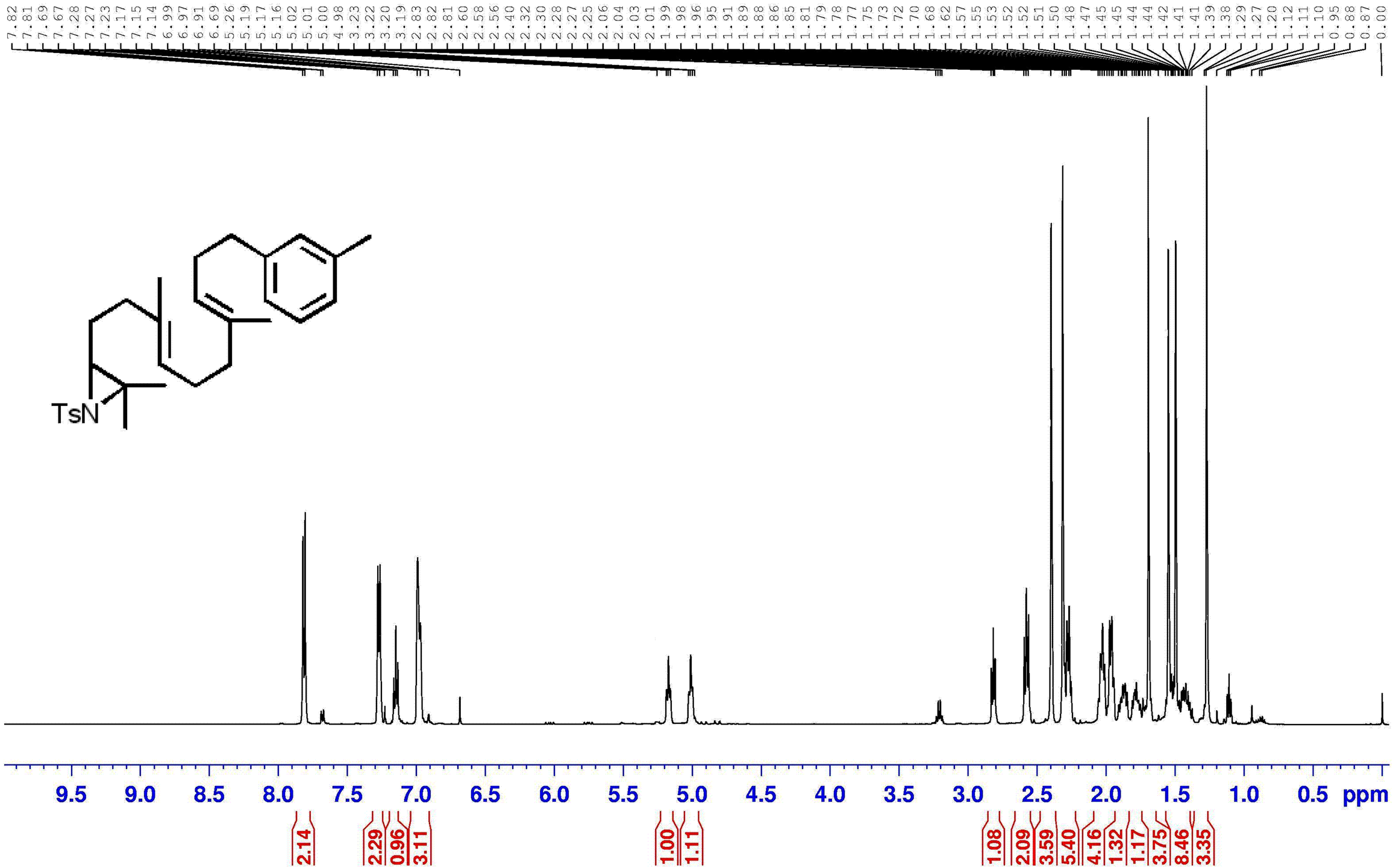








500 MHz H
Q113 Tetra, 3 Me_081103.1.1



500 MHz H
Q113 Tetra, 3 Me_081103.4.1 13C

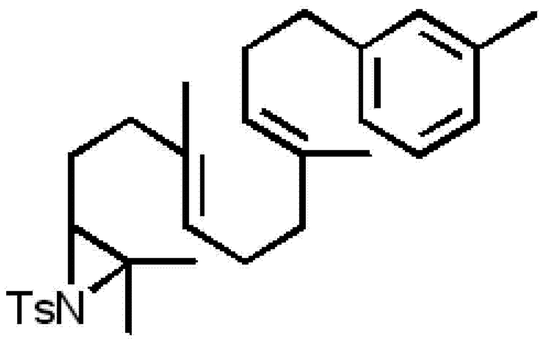
143.44
142.20
138.40
137.60
135.38
133.49
129.28
129.18
128.06
127.27
126.34
125.36
124.94
123.76

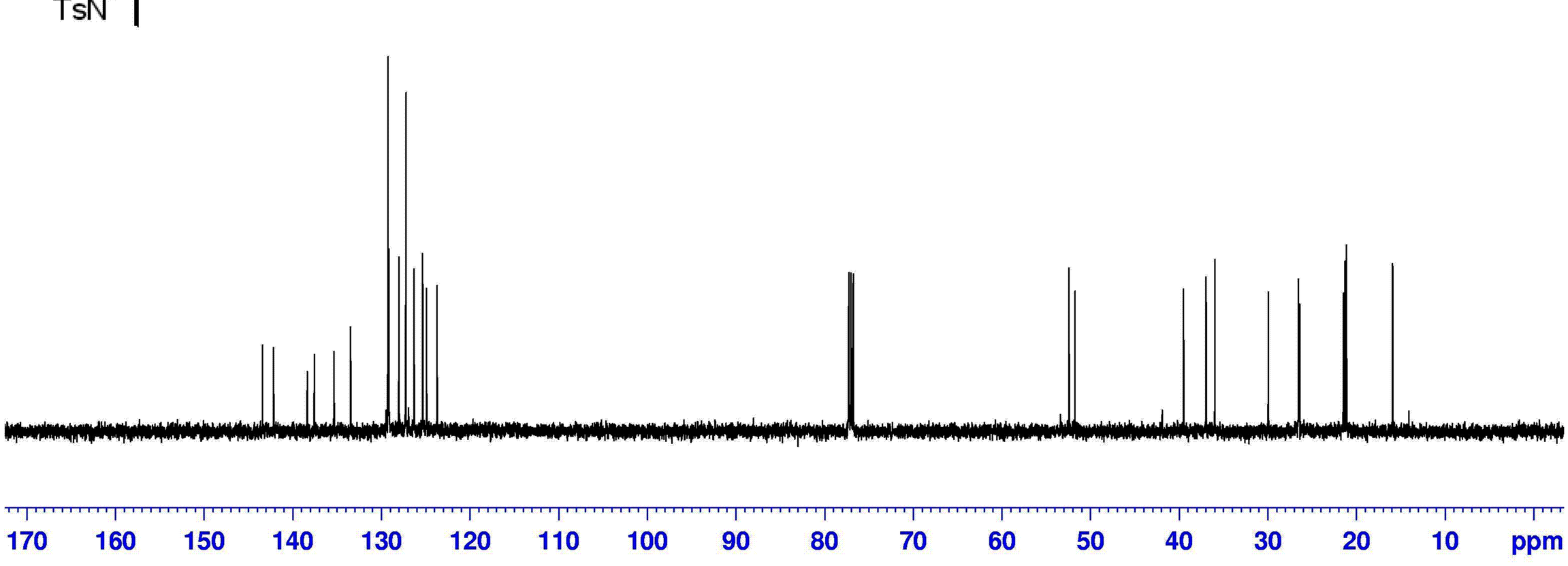
77.29
77.03
76.78

52.44
51.76

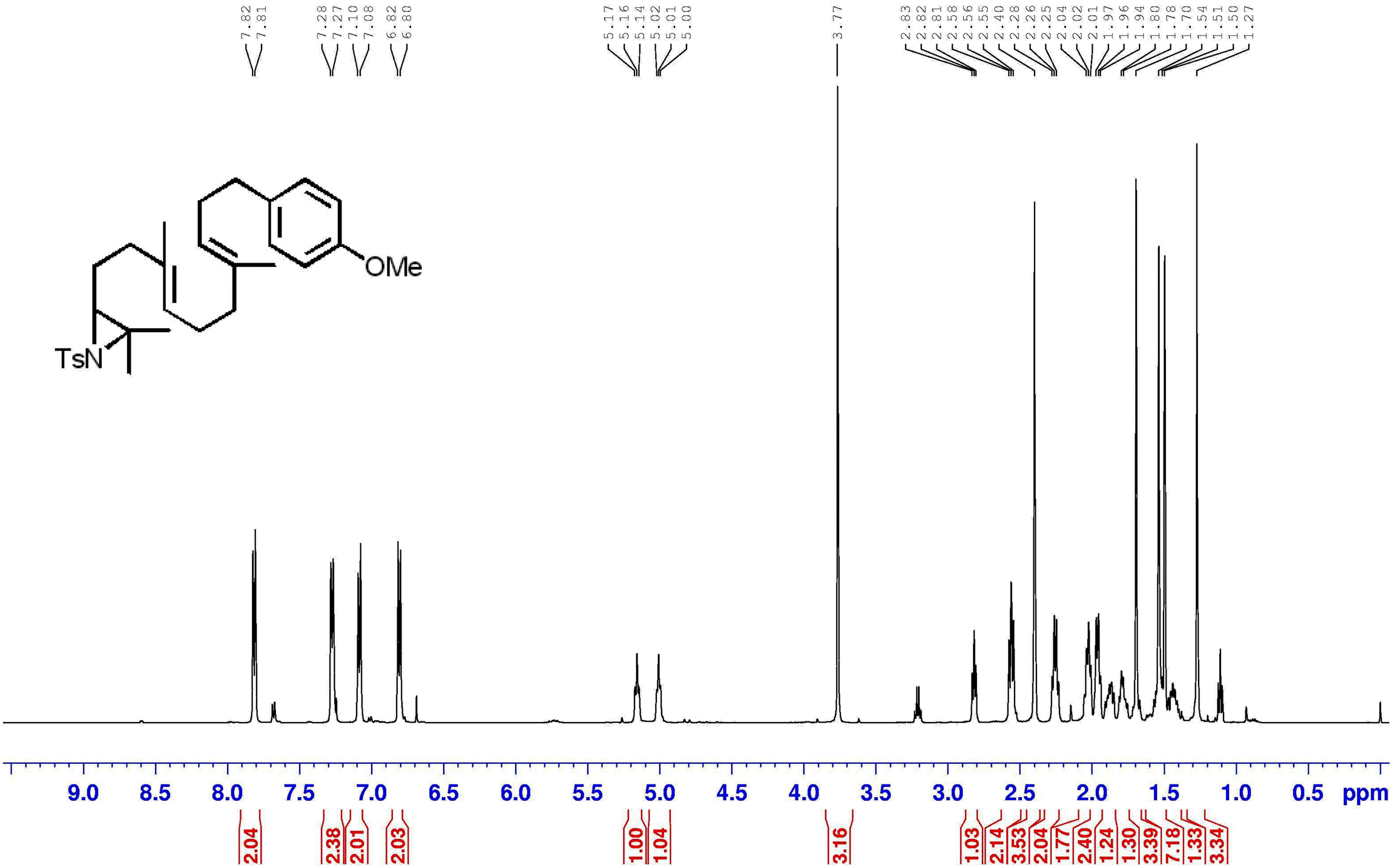
39.51
36.96
35.99

29.94
26.54
26.43
21.47
21.34
21.28
21.12
15.92
15.88



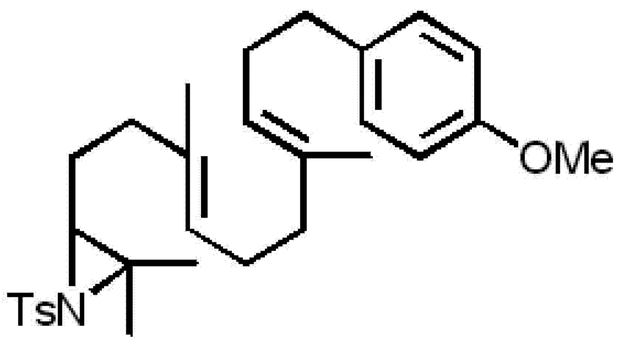


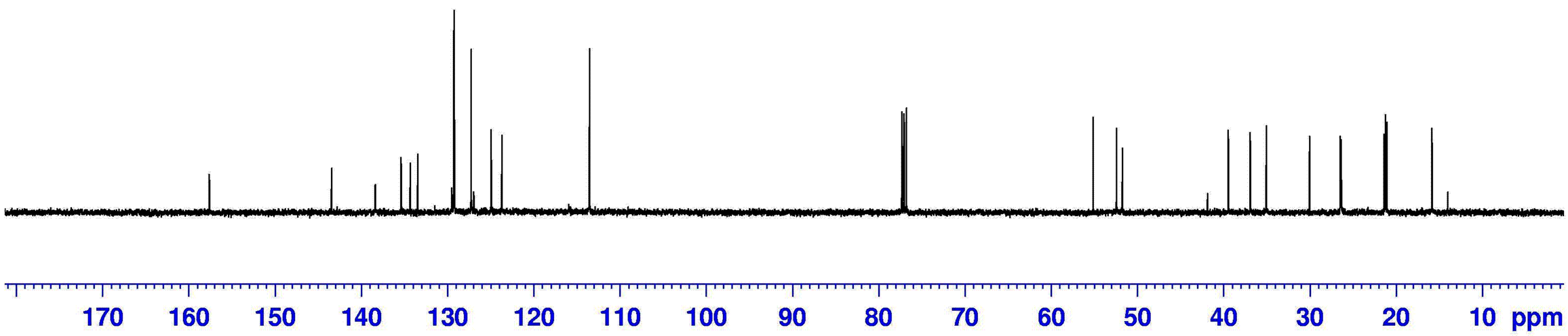
500 MHz H
Q112 Tetra, O Me_081103.1.1



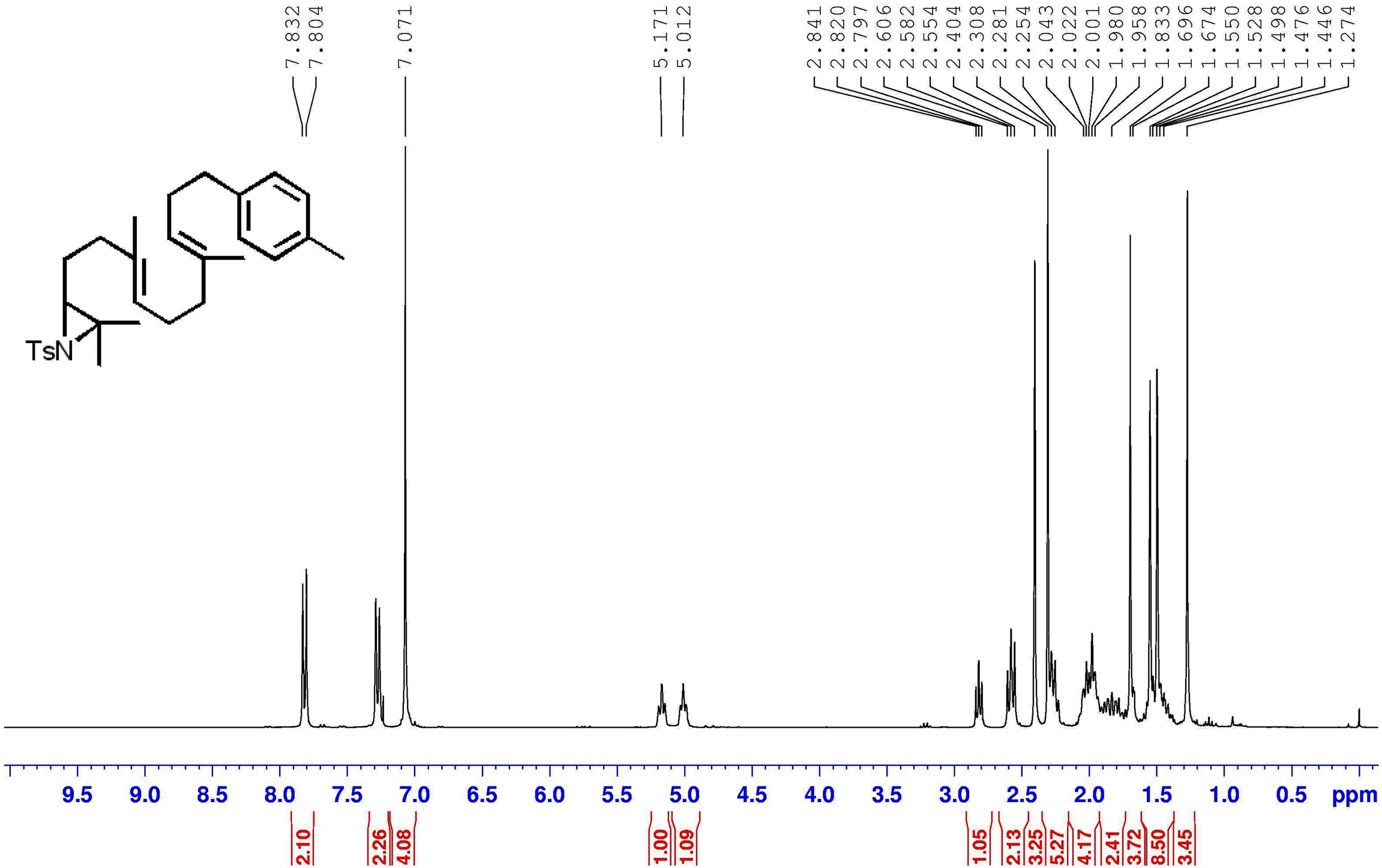
500 MHz H
Q112 Tetra, O Me_081103.4.1 13C

157.60
143.44
138.39
135.36
134.34
133.47
129.28
129.22
127.25
124.94
123.71
113.55
77.29
77.03
76.78
55.13
52.42
51.75
39.49
36.94
35.10
30.10
26.50
26.41
21.46
21.26
21.10
15.90
15.87



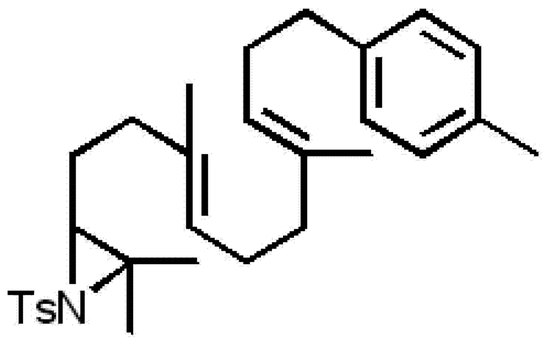


300 NMR
Q107 NTs_081101.2.1



300 NMR
Q107 NTs_081101.14.1 13C

143.46
139.22
138.45
135.37
135.00
133.52
129.31
128.86
128.26
127.30
124.98
123.80

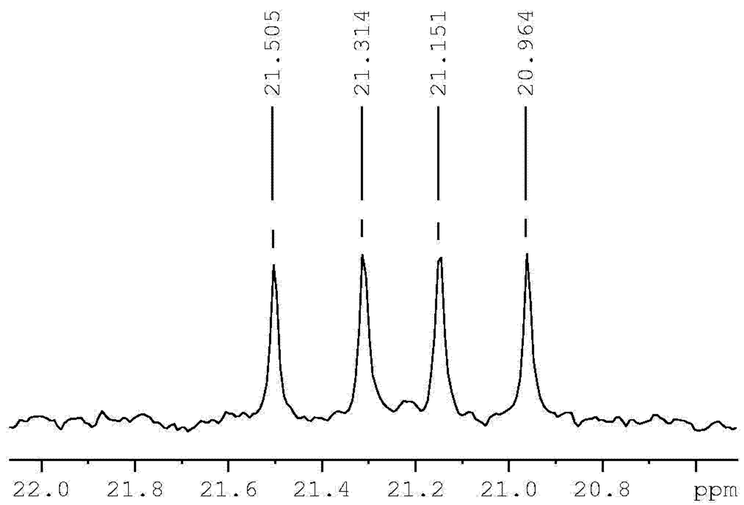


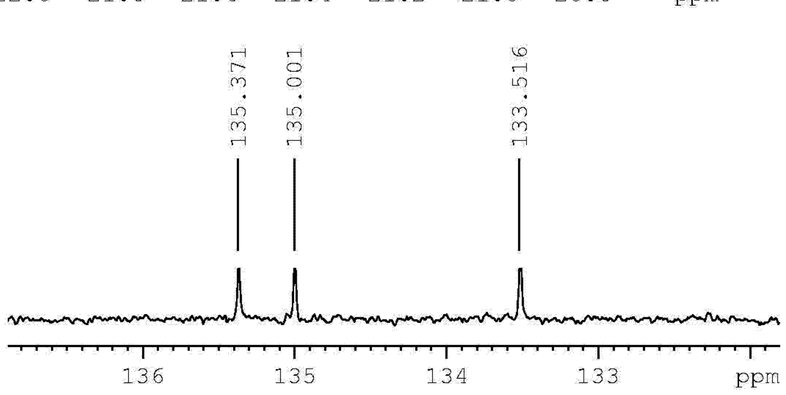
77.46
77.03
76.61

52.46
51.78

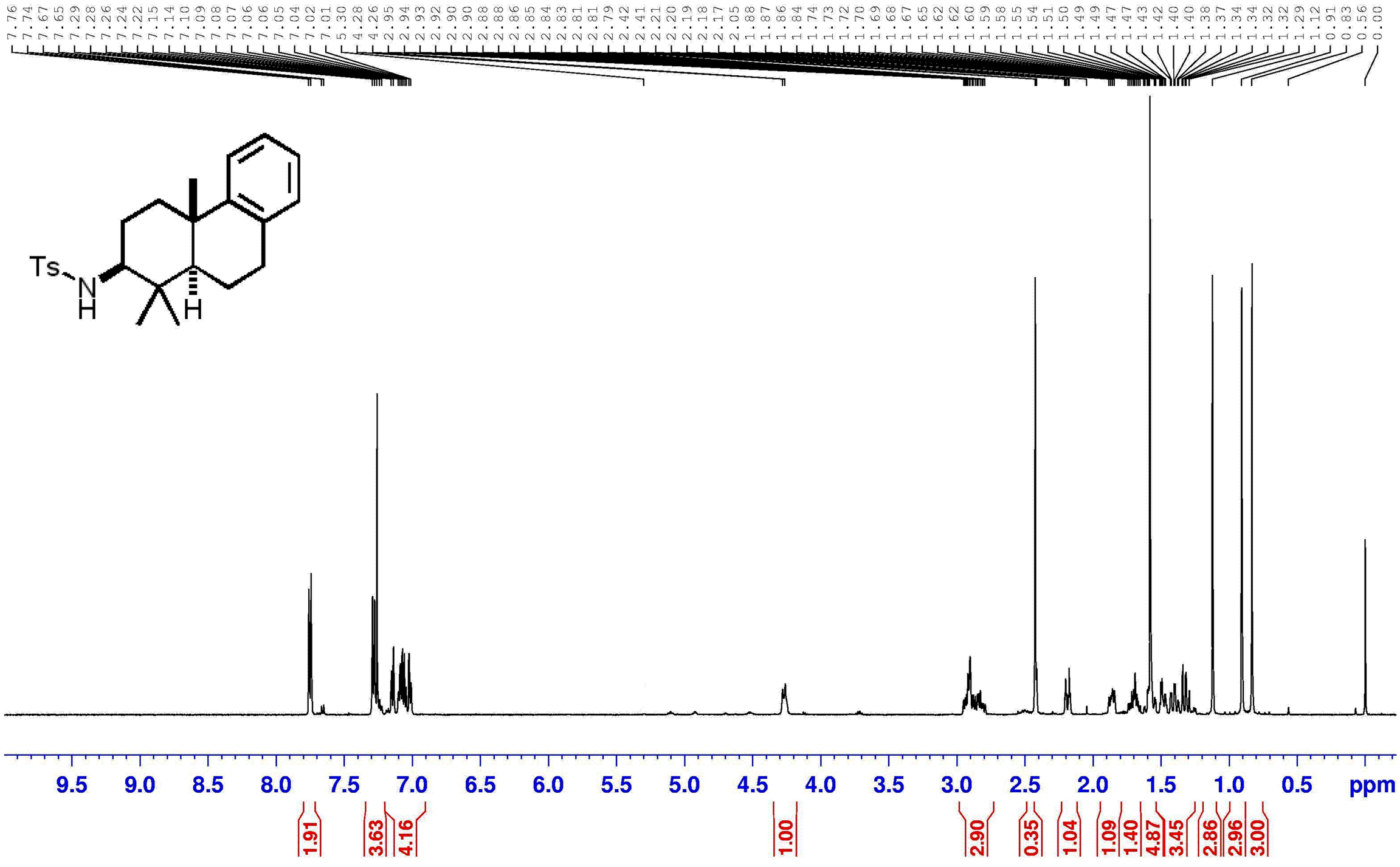
39.52
36.99
35.64

30.05
26.54
26.47
21.51
21.31
21.15
20.96
15.95
15.91



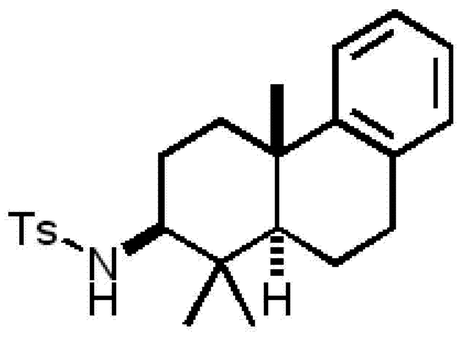


500 MHz H
Q110 TfOH_081031.2.1



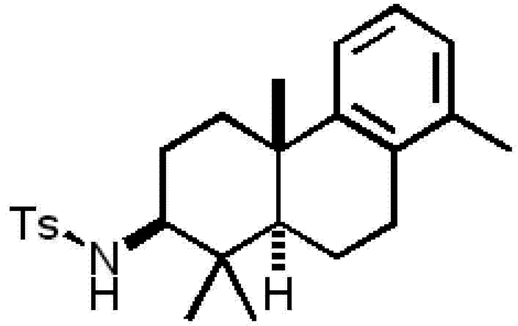
500 MHz H
Q090 InBr3_081025.34.1 13C

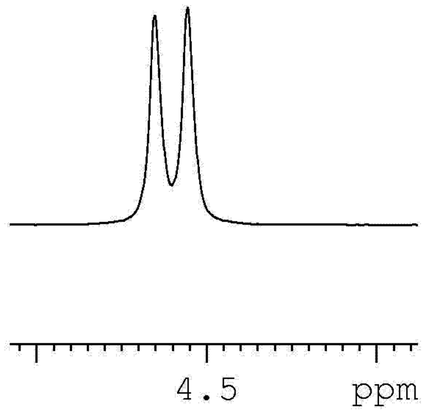
148.76
143.24
138.15
134.83
129.64
128.98
127.10
125.76
125.50
124.36
77.28
77.02
76.77
62.02
50.82
38.26
37.65
37.29
30.56
28.16
26.76
24.72
21.55
19.28
16.22



500 MHz H
Q129 Tri, 2 Me pdt_081108.2.1

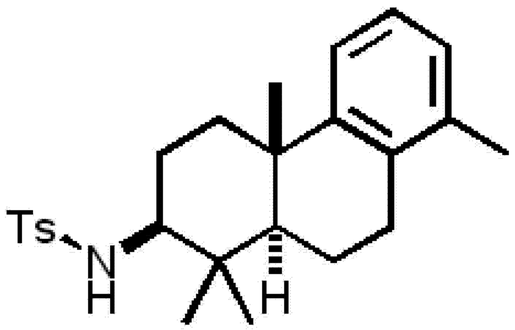
7.77 7.75 7.29 7.27 7.25 7.04 7.03 7.03 7.02 7.01 6.96 6.95 6.94 5.47 5.30 5.29 5.27 5.11 4.53 4.51 2.91 2.90 2.88 2.88 2.86 2.81 2.80 2.77 2.76 2.63 2.61 2.60 2.59 2.58 2.57 2.55 2.42 2.35 2.29 2.25 2.19 2.18 2.17 2.04 1.95 1.93 1.92 1.91 1.73 1.72 1.71 1.70 1.68 1.67 1.66 1.64 1.62 1.60 1.59 1.57 1.57 1.55 1.54 1.46 1.45 1.43 1.42 1.39 1.38 1.36 1.36 1.34 1.33 1.32 1.29 1.25 1.13 1.10 1.05 1.00 0.96 0.93 0.87 0.84 0.80 0.71 0.00



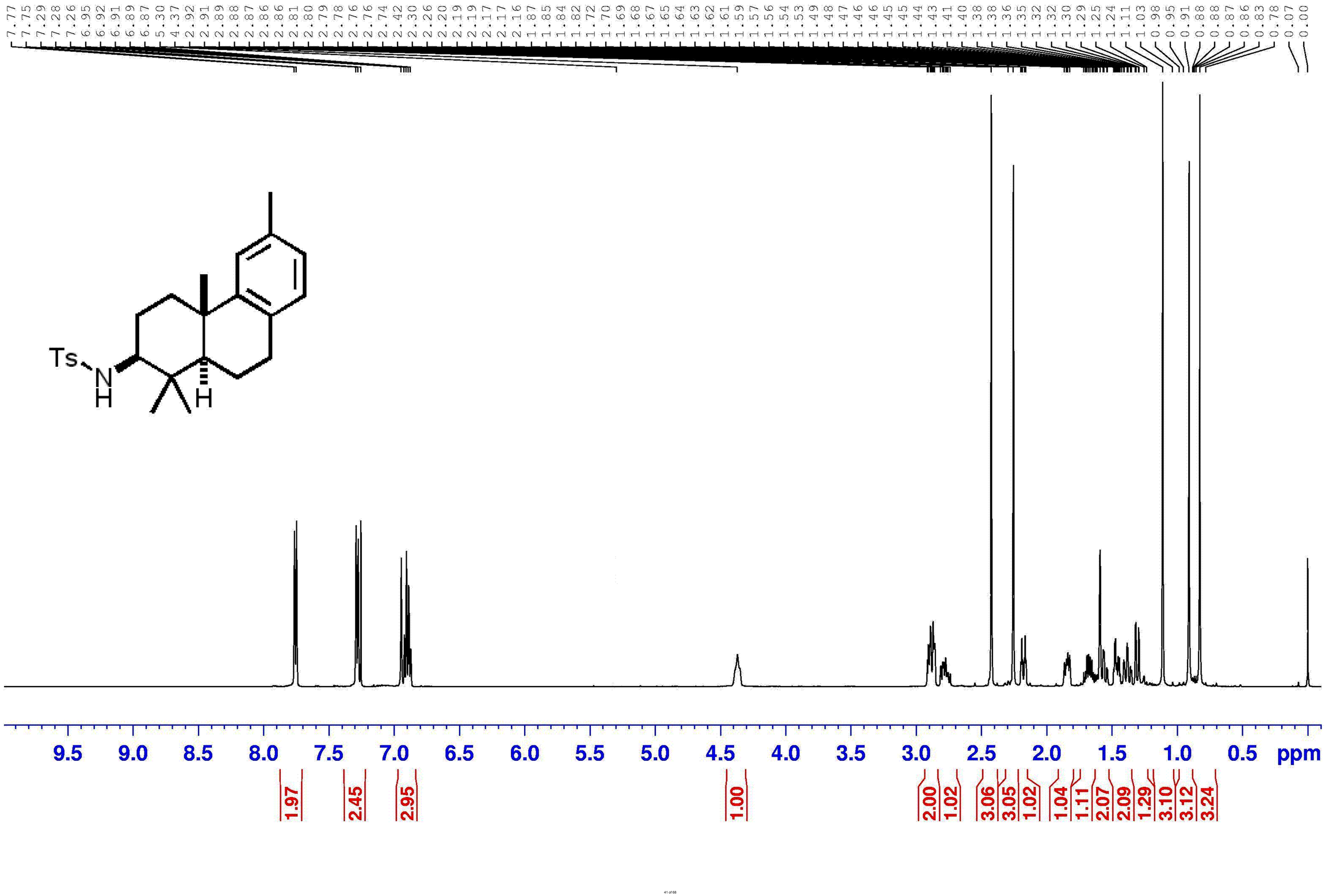


500 MHz H
Q129 Tri, 2 Me pdt_081108.24.1 13C

148.87
143.20
138.16
136.30
133.42
129.61
127.08
127.06
125.53
122.16
77.28
77.03
76.77
62.02
50.29
38.18
38.06
37.35
28.40
28.14
26.74
24.78
21.52
19.85
19.19
16.18



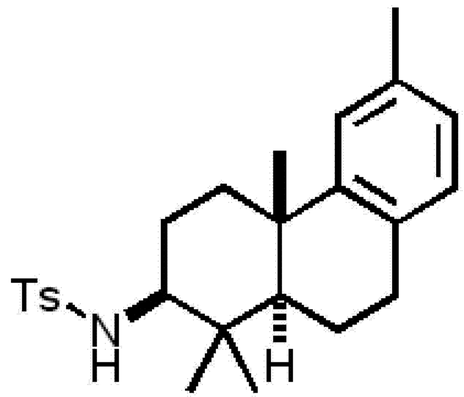
500 MHz H
Q117 No MS 4A_081103.2.1



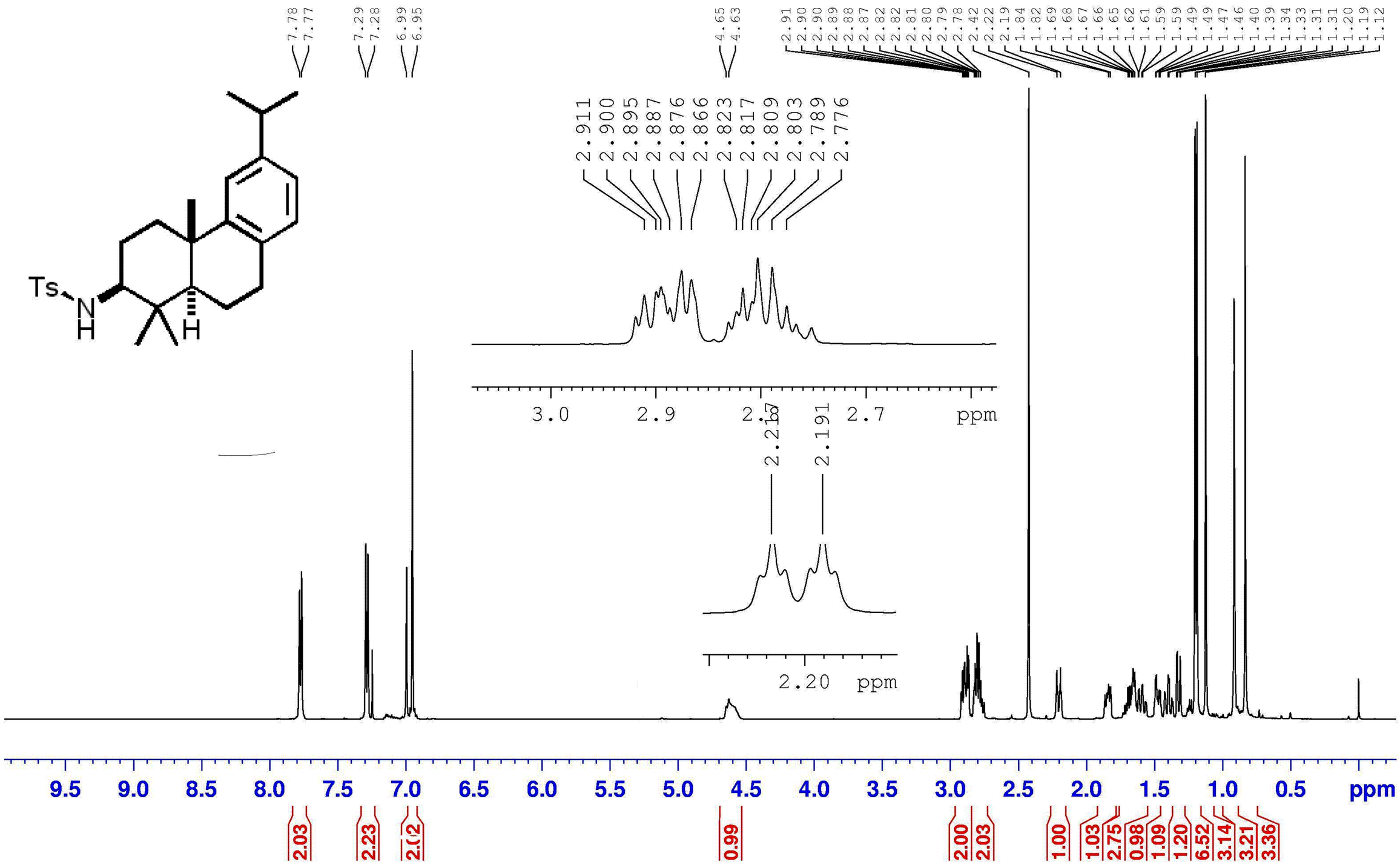
500 MHz H
Q117 No MS 4A_081103.24.1 13C

148.61
143.22
138.17
135.00
131.69
129.63
128.89
127.10
126.40
124.89

77.28
77.02
76.77
62.05
50.94
38.27
37.68
37.22
30.18
28.19
26.75
24.69
21.54
21.24
19.35
16.22



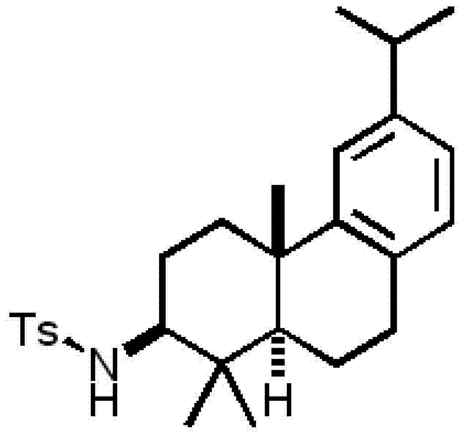
500 MHz H
Q128 Tri, i Pr pdt_081108.2.1



500 MHz H
Q128 Tri, i Pr pdt_081108.24.1

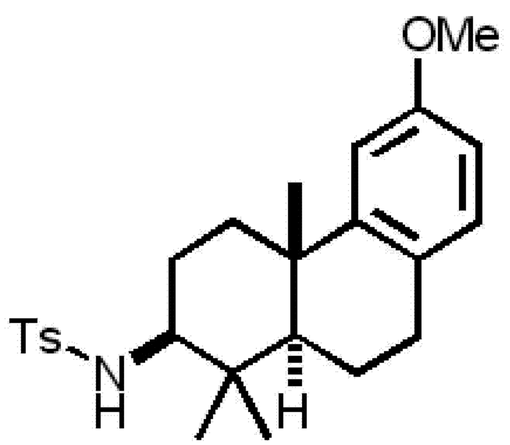
148.61
146.22
143.18
138.22
132.20
129.61
128.87
127.10
123.49
122.44

77.29
77.03
76.78
62.06
50.95
38.28
37.66
37.37
34.01
30.25
28.20
26.69
24.75
24.16
24.14
21.54
19.34
16.22



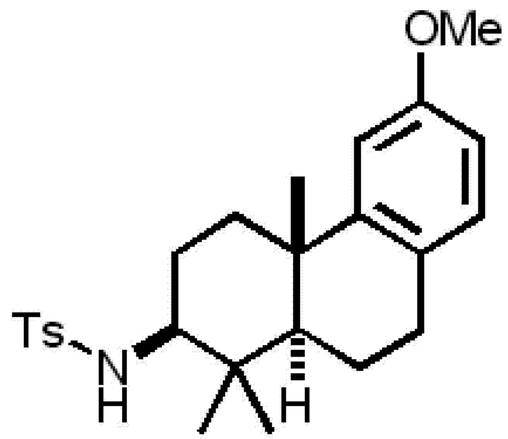
1H 400 NMR
Q127 Tri, OMe, pdt_081108.2.1

7.780 7.759 7.295 7.275 7.255 6.948 6.927 6.700 6.688 6.683 6.660 6.655 6.640 6.634 5.290 4.621 4.597 3.741 2.922 2.912 2.891 2.881 2.868 2.850 2.834 2.791 2.773 2.763 2.745 2.423 2.138 2.105 1.869 1.850 1.836 1.818 1.692 1.675 1.659 1.642 1.603 1.569 1.538 1.462 1.453 1.444 1.421 1.392 1.359 1.320 1.290 1.111 0.921 0.828 0.000

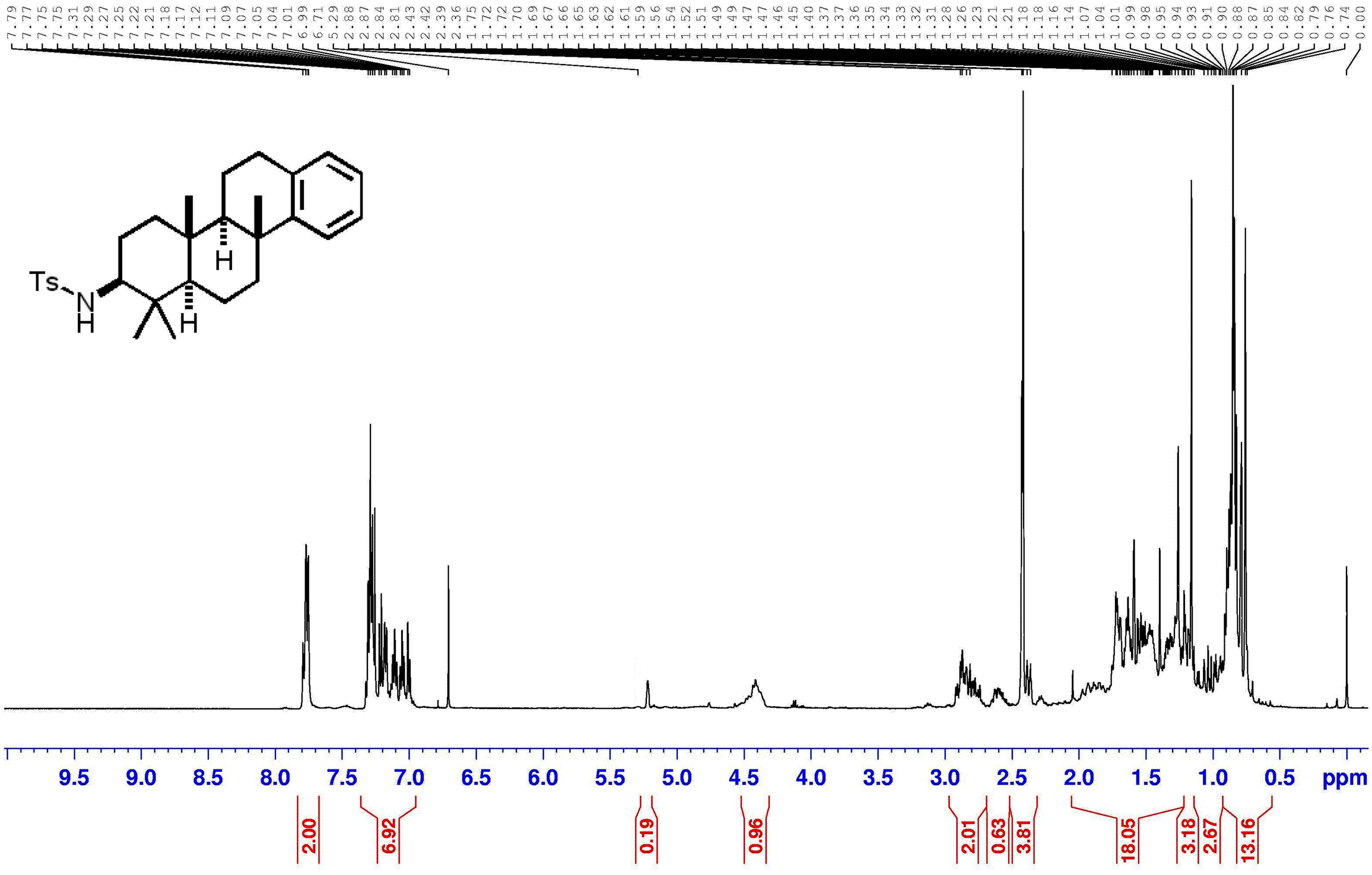


1H 400 NMR
Q127 Tri, OMe, pdt_081108.24.1 13C

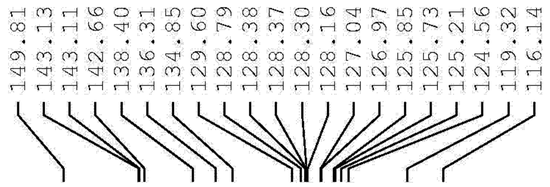
157.67
150.05
143.21
138.17
129.74
129.61
127.07
127.05
110.95
110.18
77.35
77.03
76.71
62.01
55.23
50.81
38.26
37.67
37.45
29.71
28.17
26.62
24.58
21.52
19.38
16.23

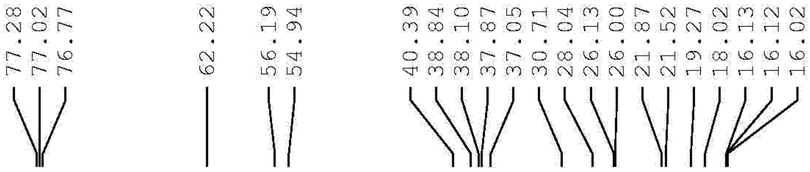


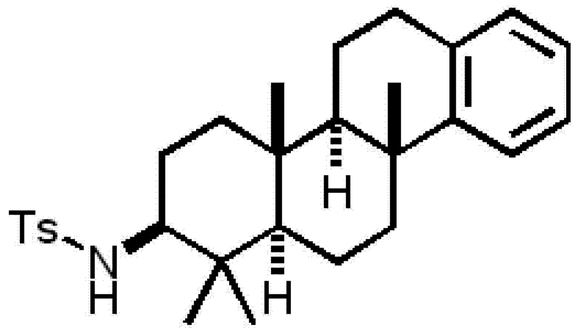
500 MHz H
Q131 Tetra, No, pdt_081111.2.1



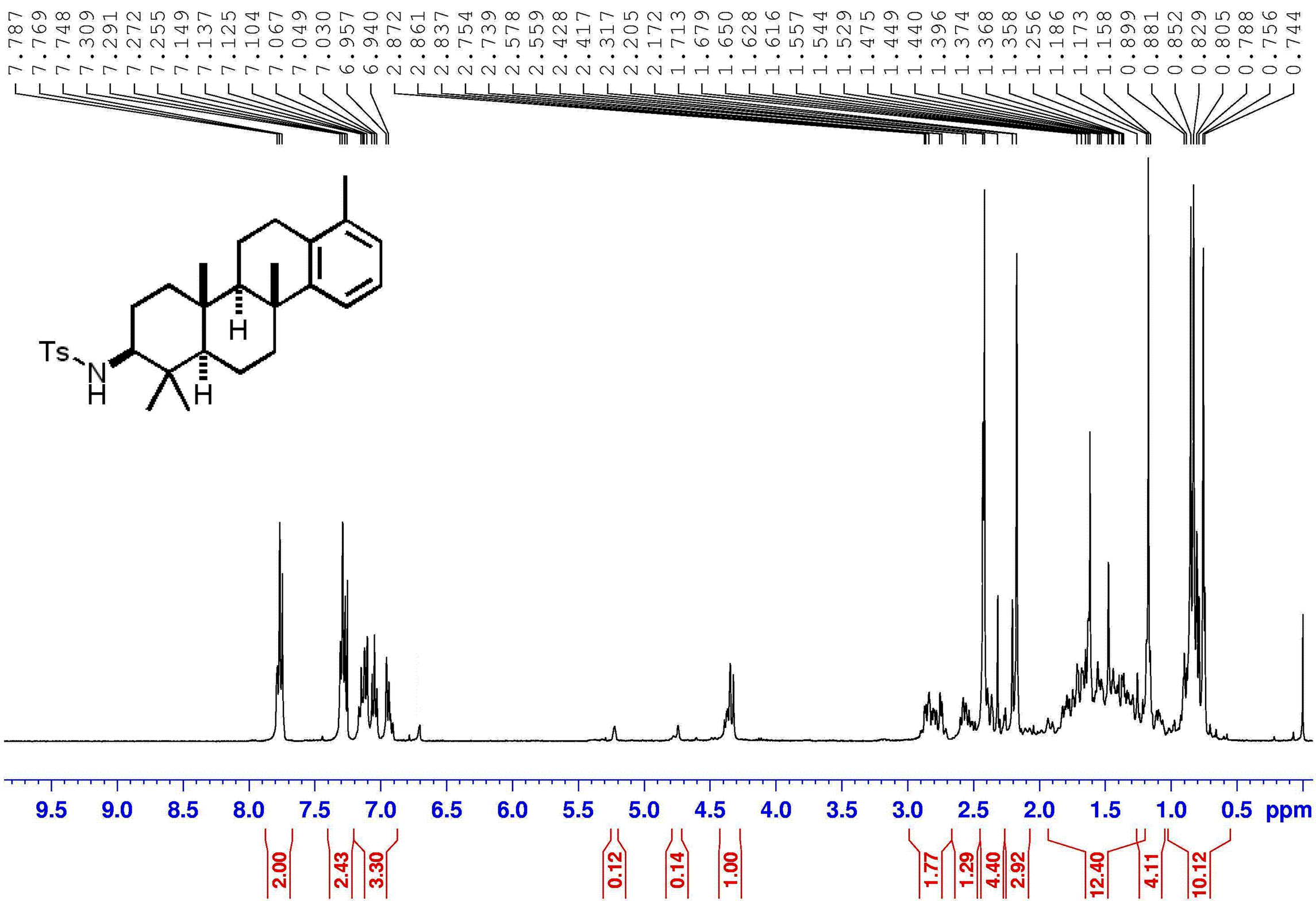
500 MHz H
Q131 Tetra, No, pdt_081111.24.1 13C



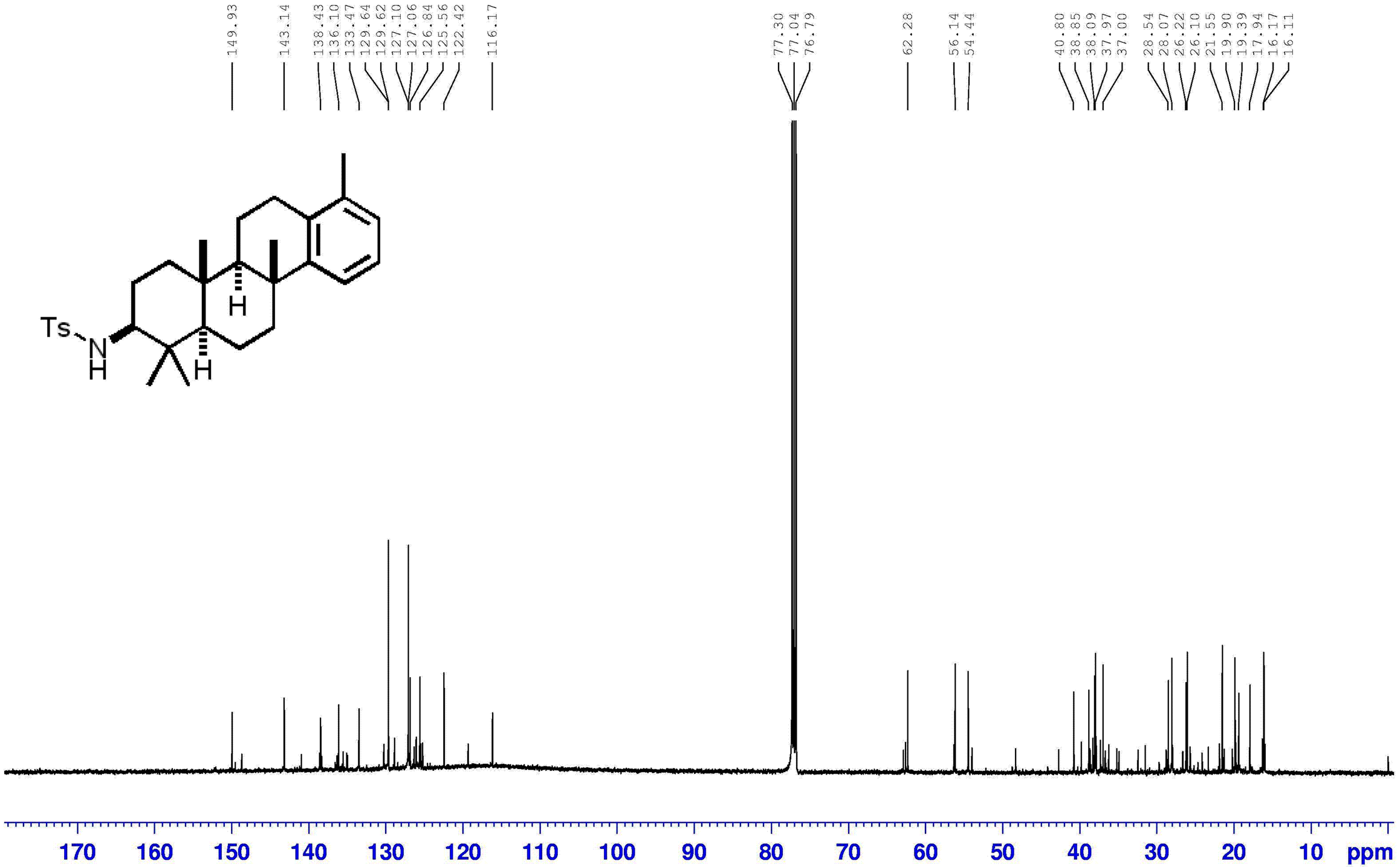




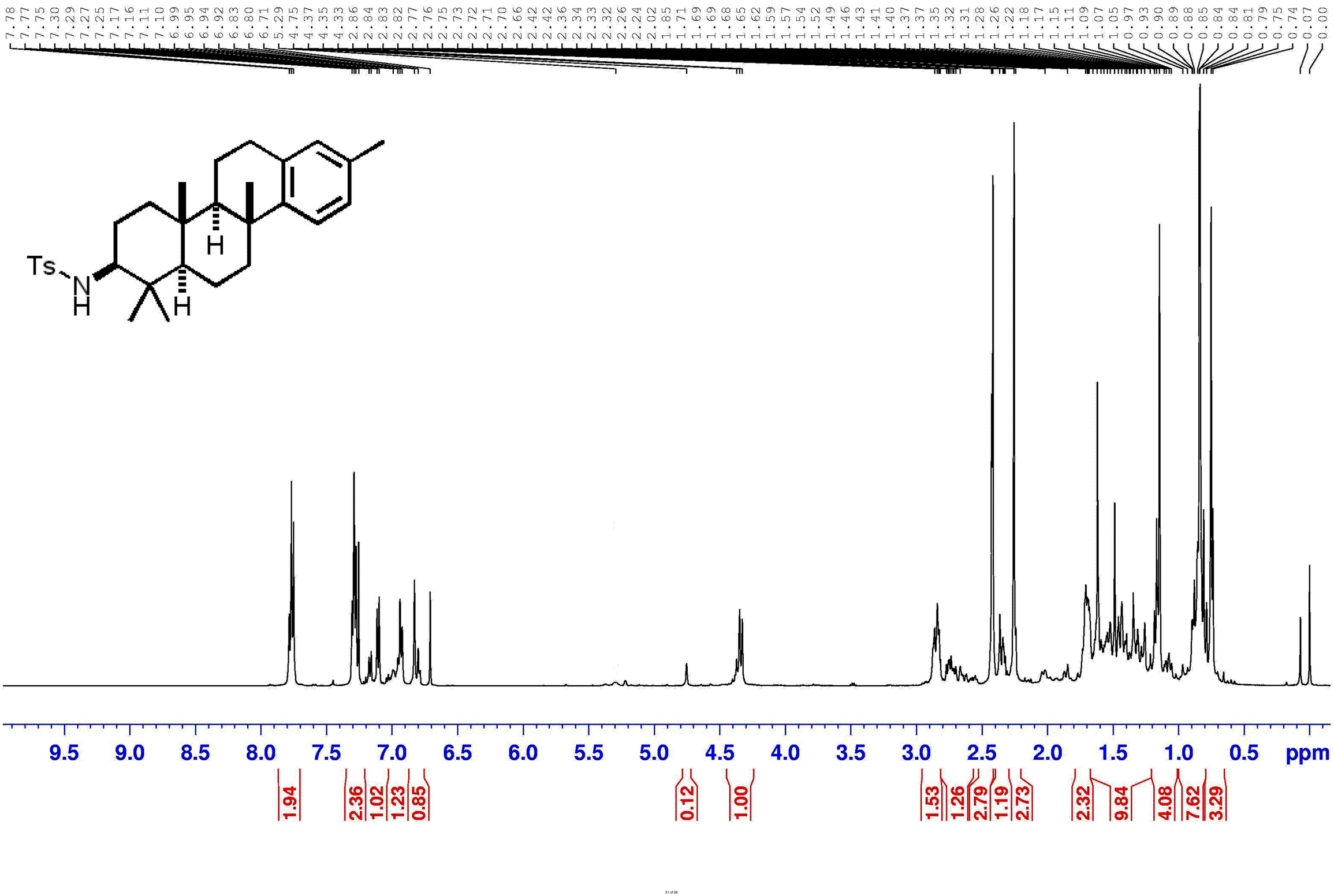
1H 400 NMR
Q130 Tetra, 2 Me, 0.2 pdt_081107.1.1



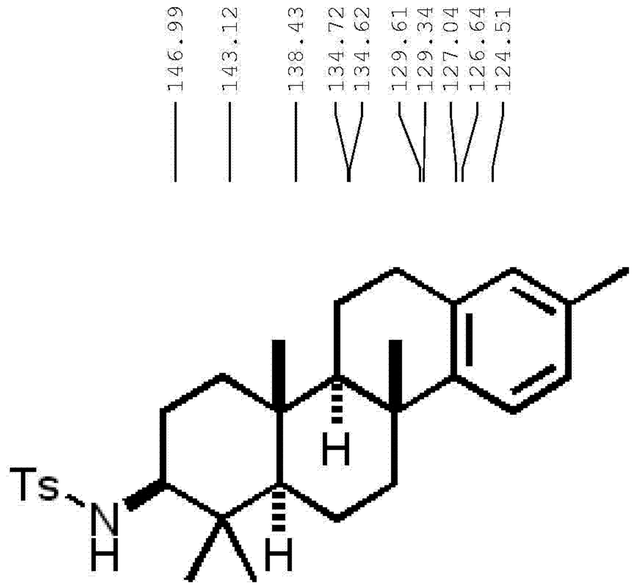
500 MHz H
Q130 Tetra, 2 Me, 0.2 eq_081108.4.1



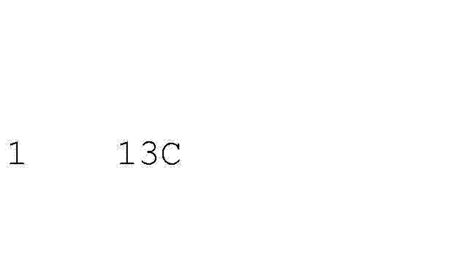
500 MHz H
Q123_3 pdt tetra, 3 Me_081105.1.1

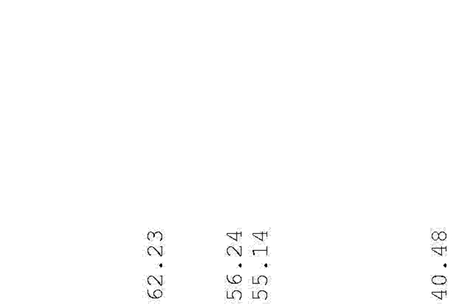


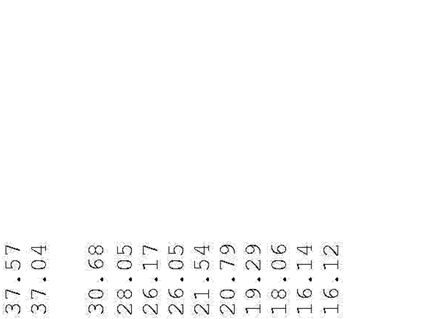
500 MHz H
Q123_3 pdt tetra, 3 Me_081105.4.1 13C



146.99
143.12
138.43
134.72
134.62
129.61
129.34
127.04
126.64
124.51
129.614
129.338
127.035
126.641
62.23
56.24
55.14
40.48
38.85
38.10
37.57
37.04
30.68
28.05
26.17
26.05
21.54
20.79
19.29
18.06
16.14
16.12
26.174
26.049
16.144
16.116

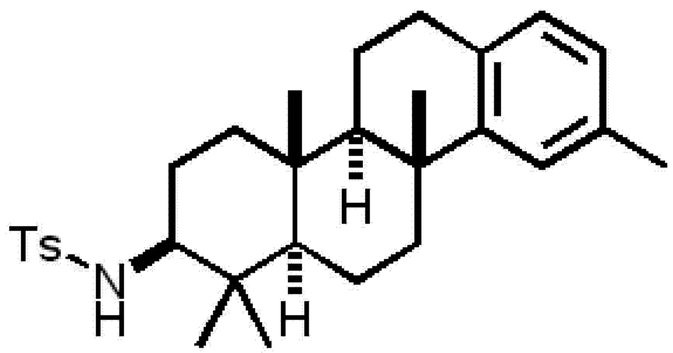






1H 400 NMR
Q132 Tetra, 4Me_081110.1.1

7.792
7.772
7.752
7.305
7.289
7.270
7.251
7.109
7.073
7.054
7.018
6.892
6.884
6.865
5.291
4.417
4.393
2.861
2.837
2.824
2.426
2.416
2.386
2.336
2.277
1.717
1.709
1.685
1.628
1.615
1.600
1.557
1.528
1.496
1.474
1.442
1.395
1.351
1.340
1.329
1.305
1.259
1.214
1.188
1.170
1.152
0.895
0.883
0.859
0.844
0.818
0.784
0.756
0.743
0.000

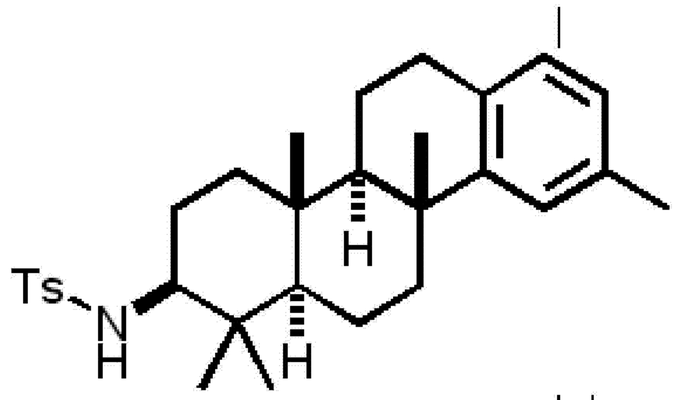


1H 400 NMR
Q132 Tetra, 4Me_081110.4.1 13C

149.69
143.12
138.47
134.98
131.73
129.63
129.07
128.72
128.25
127.09
127.05
126.16
125.11

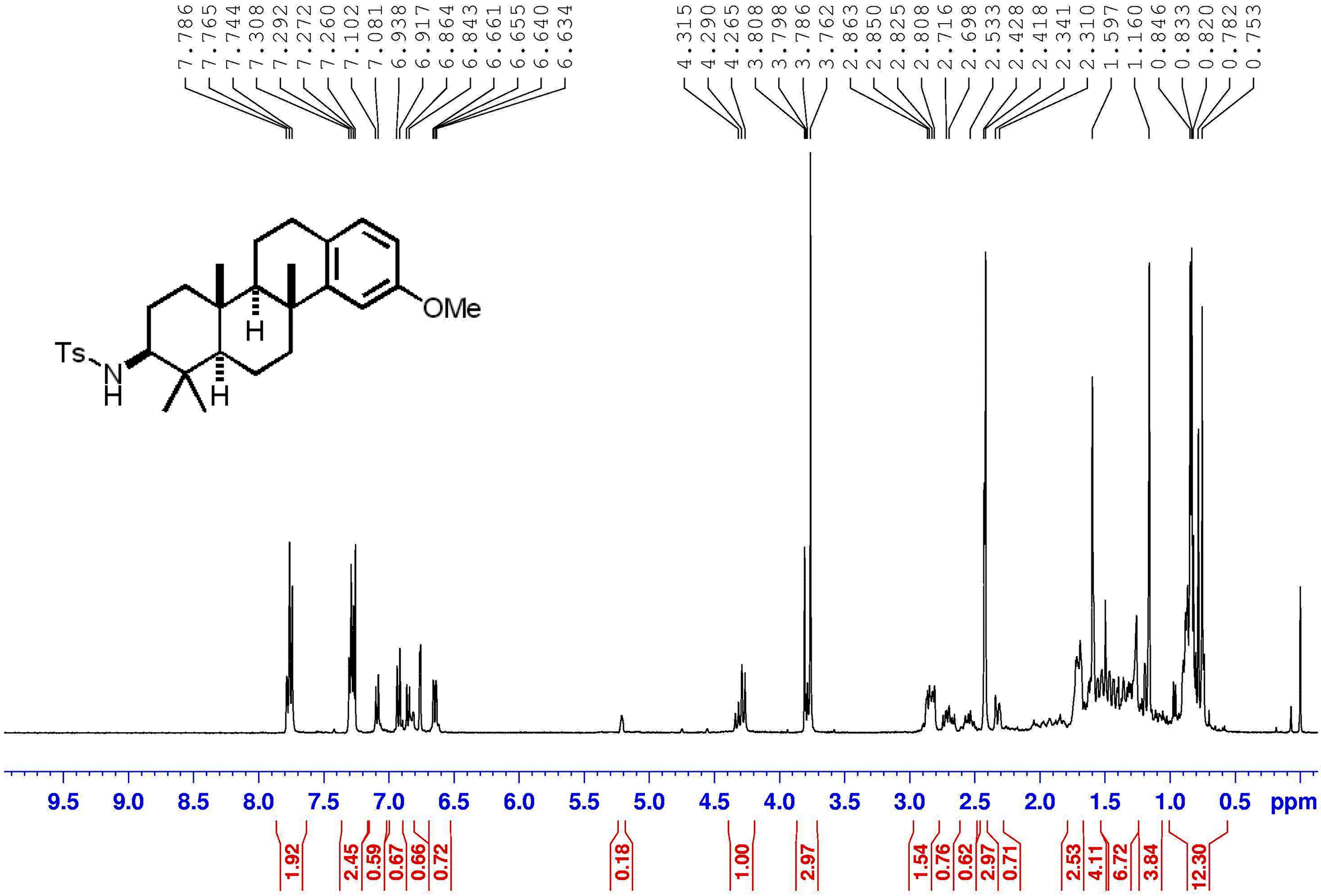
62.25
56.24
55.09

40.45
38.89
38.12
37.83
37.09
30.36
28.07
26.15
26.00
23.36
21.55
21.29
19.30
18.12
16.16
16.15

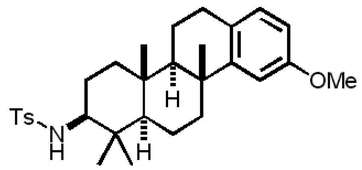


160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1H 400 NMR
Q126 Tetra, OMe DCM_081107.1.1



Q126, tetra, OMe, DCM 13C_081106–3.jdf
Q126, tetra, OMe, DCM 13C_081106



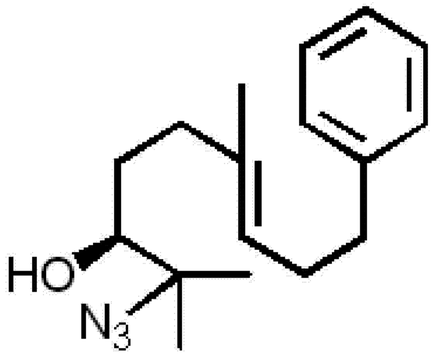
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

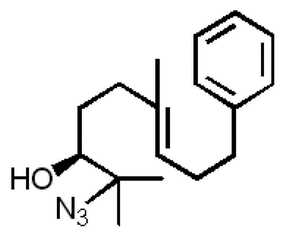
157.7885
151.1781
138.4458
129.6511
127.1219
113.8531
110.9024
110.3372
62.2823
56.2371
55.3366
55.0396
40.4775
38.9255
38.1686
37.1435
29.9870
28.0518
26.2699
25.9921
21.6330
19.3625
18.2320
16.2393
16.2201

X : 13C

500 MHz H
Q139 N3_081117.1.1



Q139 pdt_N3 OH 13C_081118-3.jdf
Q139 pdt_N3 OH 13C_081118



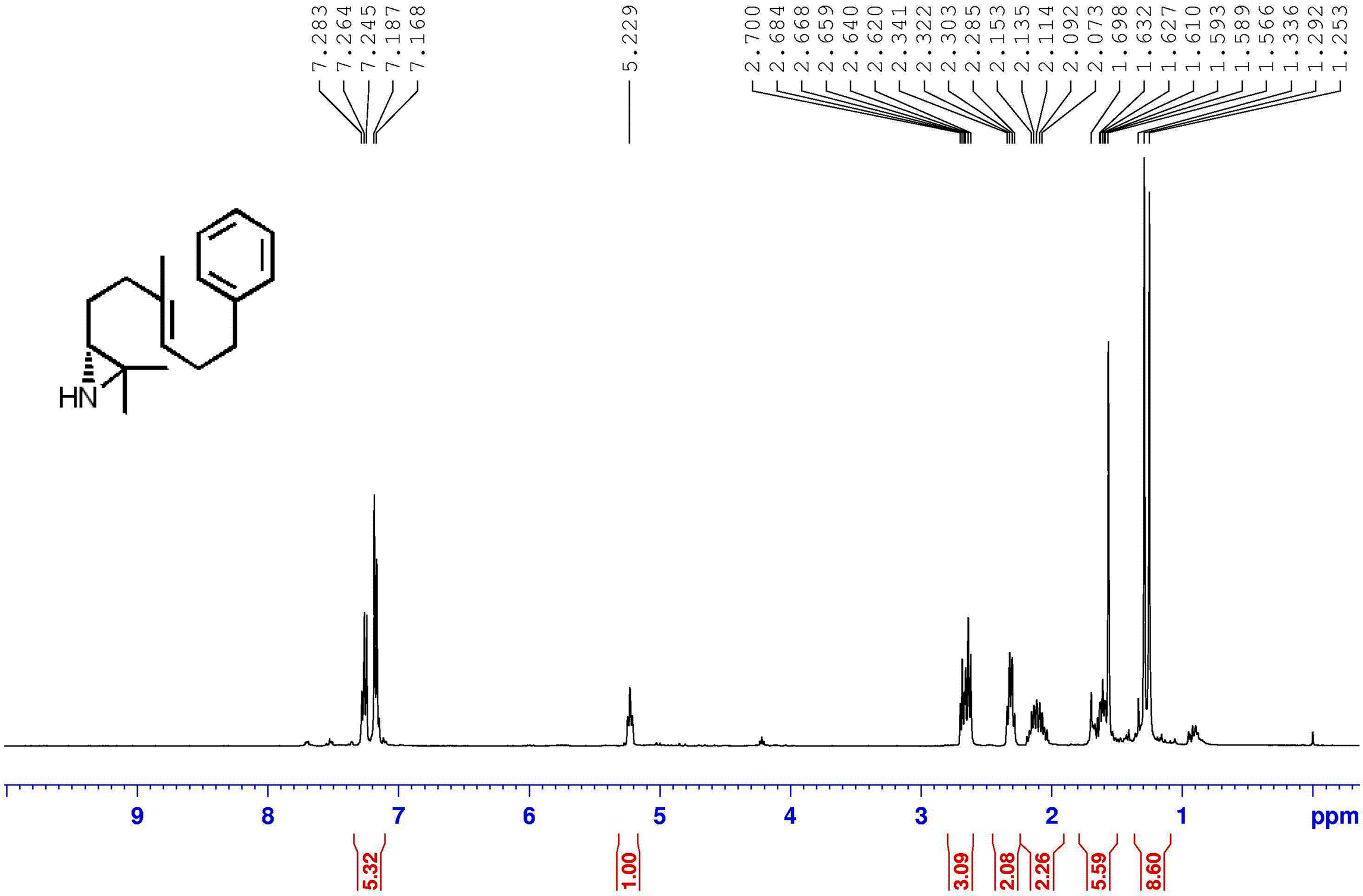
0.3
0.2
0.1
0

180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

142.2971
135.3801
128.5493
128.3290
125.8190
124.6118
68.0688
65.3863
36.5112
36.0705
29.9296
29.2877
25.7046
22.7539
21.1444
15.9423

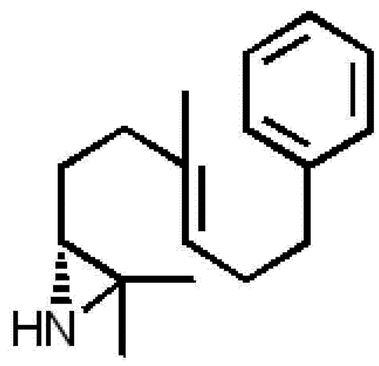
X : 13C

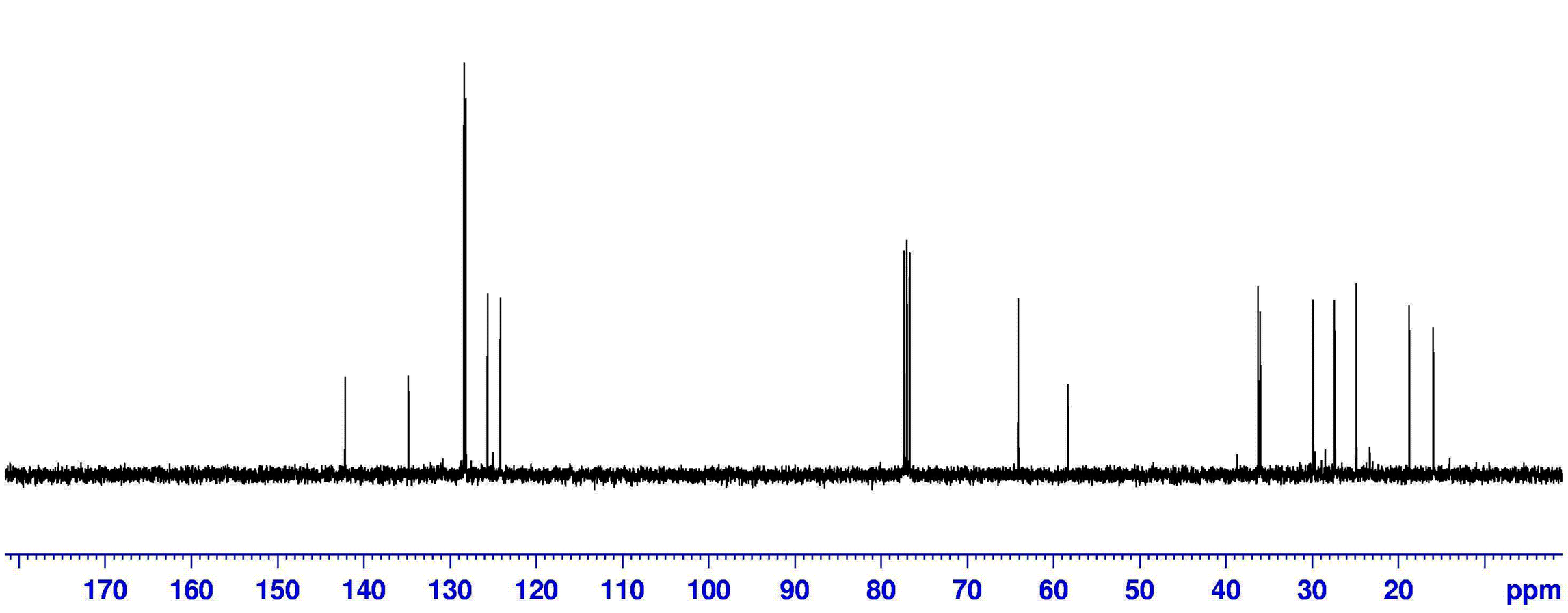
1H 400 NMR
Q078 amine pdt_081107.1.1



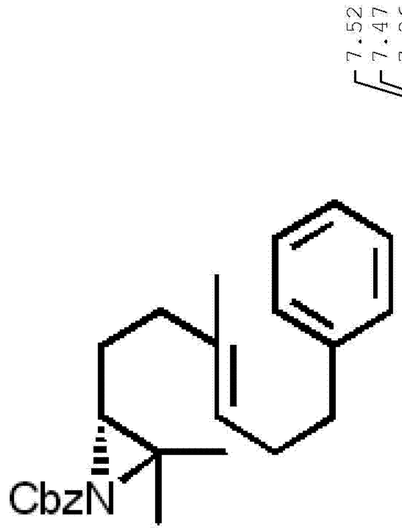
1H 400 NMR
Q078 amine pdt_081107.4.1 13C

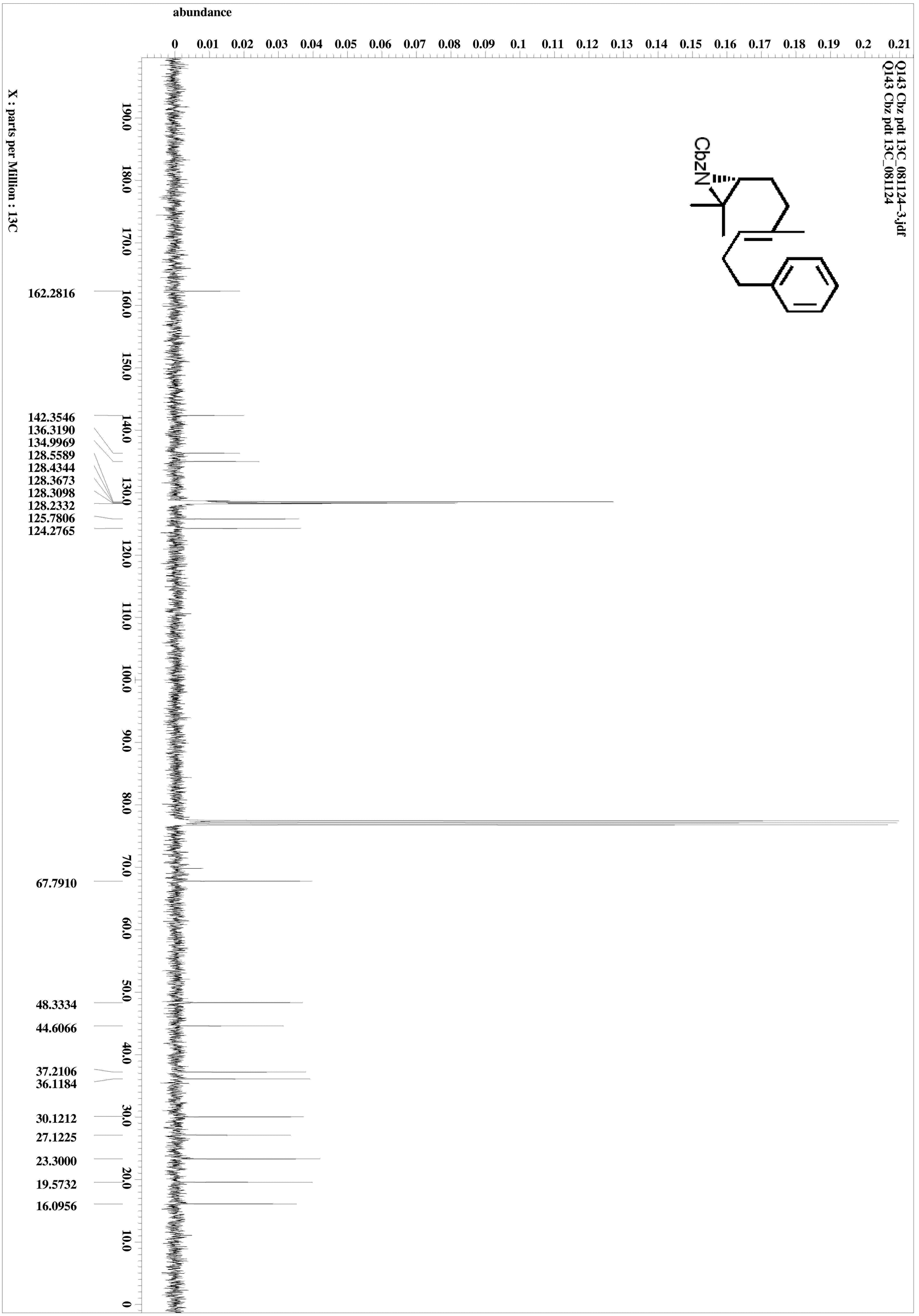
142.20
134.84
128.43
128.20
125.69
124.20
77.35
77.03
76.71
64.11
58.30
36.28
36.01
29.90
27.41
24.88
18.72
15.94





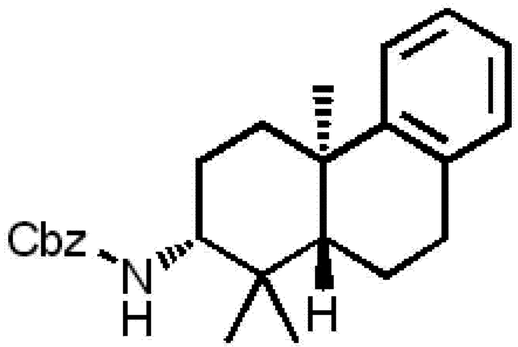
500 MHz H
Q143 chiral Cbz_081127.1.1



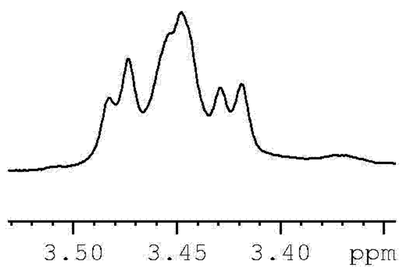

abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.2 0.21
Q143 Cbz pdt 13C_081124-3.jdf
Q143 Cbz pdt 13C_081124
CbzN
X : parts per Million : 13C
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
162.2816
142.3546
136.3190
134.9969
128.5589
128.4344
128.3673
128.3098
128.2332
125.7806
124.2765
67.7910
48.3334
44.6066
37.2106
36.1184
30.1212
27.1225
23.3000
19.5732
16.0956

1H 400MHz
Q146 Chiral Cbz pdt_081127.1.1

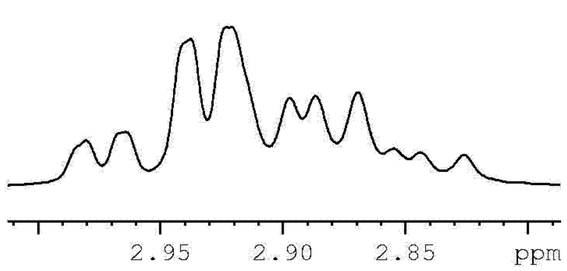
7.374 7.364 7.338 7.328 7.318 7.240 7.234 7.214 7.137 7.120 7.097 7.075 7.057 7.047 7.029 5.279 5.146 5.115 5.092 5.061 4.702 4.678 4.474 4.448 2.938 2.921 2.897 2.887 2.870 2.331 2.307 2.299 1.926 1.908 1.893 1.875 1.863 1.841 1.831 1.823 1.750 1.734 1.720 1.703 1.672 1.637 1.614 1.586 1.460 1.429 1.388 1.170 1.025 0.850 0.000



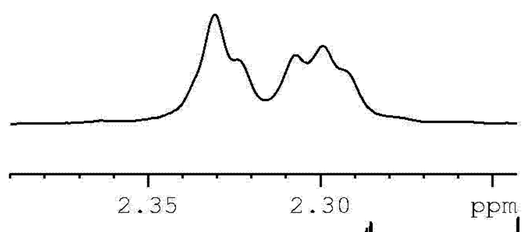
3.483 3.474 3.448 3.429 3.419 3.373



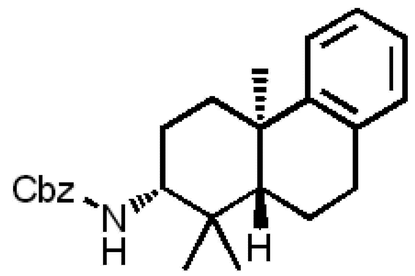
2.981 2.965 2.938 2.921 2.897 2.887 2.870 2.855 2.844 2.826



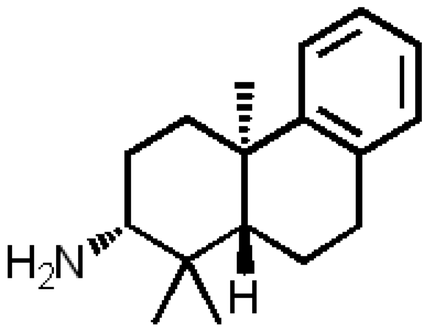
2.331 2.307 2.299



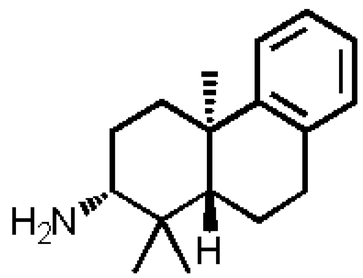
Q146 Cbz cyclization pdt 13_081125–3.jdf
Q146 Cbz cyclization pdt 13_081125



1H 400 NMR
H2, NH2_081209.1.1



H2, NH2 chiral pdt 13C Second_081209−3.jdf
13C



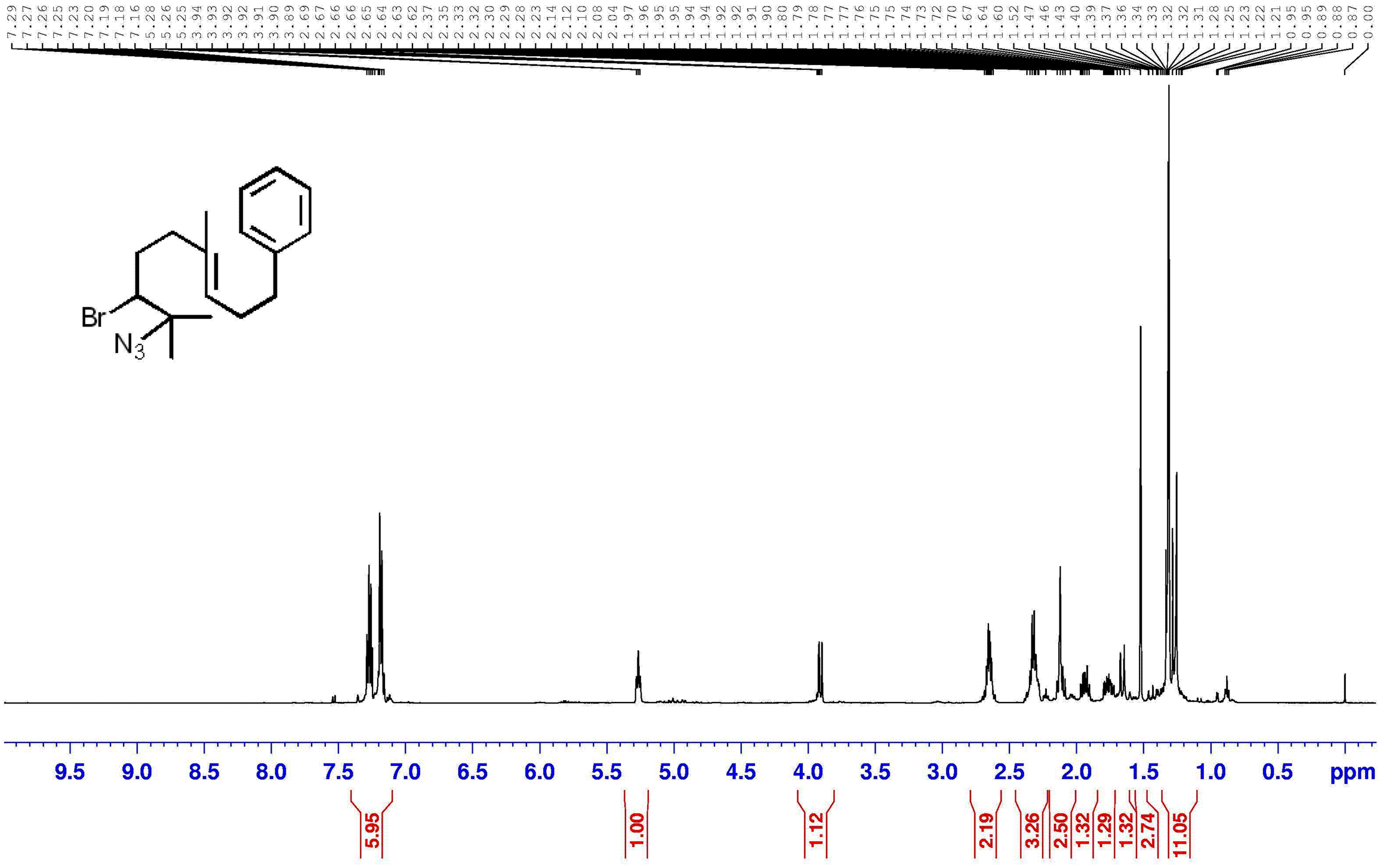
0.24 0.22 0.2 0.18 0.16 0.14 0.12 0.1 0.08 0.06 0.04 0.02 0

170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

149.0033
134.9682
129.0858
125.9339
125.5890
124.5927
60.0884
50.4410
37.8046
37.7567
37.3160
30.8014
28.6458
26.5477
24.9191
19.1517
16.0860

X : 13C

500 MHz H
Q076_081013.2.1



500 MHz H
Q088 pdt BrN3_081024.4.1

142.16
133.69
128.46
128.24
125.71
125.51
77.27
77.01
76.76
64.16
63.78
37.70
35.96
31.56
29.89
25.15
23.01
15.70