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Electronic Supplementary Information

for

Iridium-catalyzed highly stereoselective deoxygenation of tertiary cycloalkanols: stereoelectronic insights and synthetic applications

Tingting Wang [a], Yang Chen [a], Ning Chen [a], Jiaxi Xu [a] and Zhanhui Yang *[a]

Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

Corresponding author: zhyang@mail.buct.edu.cn

Contents

1. General Information

Unless otherwise noted, all starting materials were purchased from commercial suppliers. Tetrahydrofuran was refluxed over sodium with benzophenone as indicator under nitrogen atmosphere prior to distillation. Column chromatography was performed using silica gel (normal phase, 200-300 mesh) from branch of Anhui Liangchen Silicon Material Co. Ltd, with petroleum ether (60-90 $^{\circ}$C fraction), dichloromethane, and ethyl acetate as eluents. Reactions were monitored by thin-layer chromatography (TLC) on GF_{254} silica gel plates (0.2 mm) from Anhui Liangchen Silicon Material Co. Ltd. The plates were visualized under UV light, as well as other TLC stains (1.5 g of $KMnO_4$, 10 g of K_2CO_3, and 1.25 mL of 10 % NaOH in 200 mL water; 12 g of 2,4-dinitrophenylhydra zine dissolved in 60 mL of conc. H_2SO_4 and 80 mL of H_2O in 200 mL of 95% EtOH.). ^{1}H, ^{13}C , and NOE NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$, acetone-d_6, or dimethyl sulfoxide-d_6, with tetramethylsilane (TMS) as an internal standard. The chemical shifts (δ) are reported in parts per million (ppm), and multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), tt (triple triplet), dq (double quartet), m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer or a Thermo scientific Q Exactive spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. PE, EA, DCM, THF, DMSO and HFIP are abbreviations for petroleum ether, ethyl acetate, dichloromethane, tetrahydrofuran, dimethyl sulfoxide and hexafluoroisopropanol respectively.

Catalysts (***C1*** *and* ***C2***) were prepared according to our previous publications.[1] Compounds **1h**, ***e*-4h**, ***a*-5h**, **4k**, **4l** and **4n** were reported in our previous work.[2] For their analytical data and spectra, please see the supporting information of our previous publications.[2]

2. DFT Calculations

A density functional theory (DFT) study was performed using Gaussian 09 B01 program.[3,4] Structural optimizations and Frequency calculations were obtained at the M06-2X-D3[2]/6-311G(d,p)[5] level. Topology analysis of Electron Localization Function (ELF)[6] for 3a was performed to simulate Bürgi-Dunitz angle with Multifwn program[7], which was also utilized to get Lowest Unoccupied Molecular Orbital (LUMO) of **3a** with an isovalue of 0.080 a.u. Unless otherwise specified, molecular structures were showed by the Cylview visualization package. [8]

Topology analysis of Electron Localization Function (ELF) for **3a**.

Topology analysis Electron Localization Function (ELF) was performed to calculate the angle of nucleophilic attack from nucleophile to carbanyl group. In both pictures, these small yellow balls represent critical points, eg: critical point 35 (c35) and critical point58 (c58). Two pictures are derived from the same calculation, but all labels are removed in order to observe the angle expediently in the right one. The simulated angle were consistent with the Bürgi-Dunitz angle (100-110°).

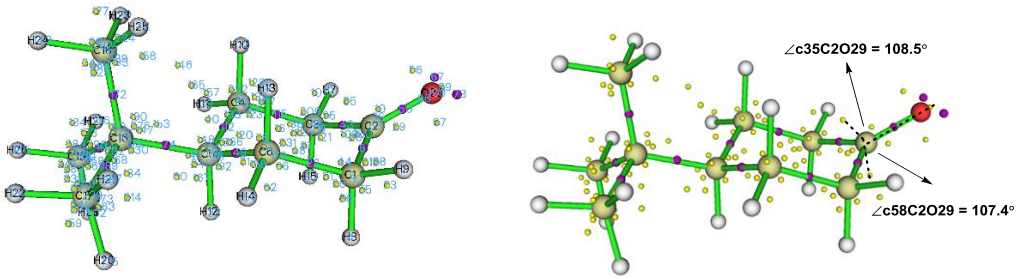
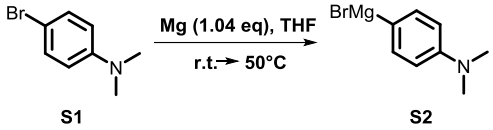


Figure S1. The profile of Topology analysis of Electron Localization Function (ELF) for 3a.

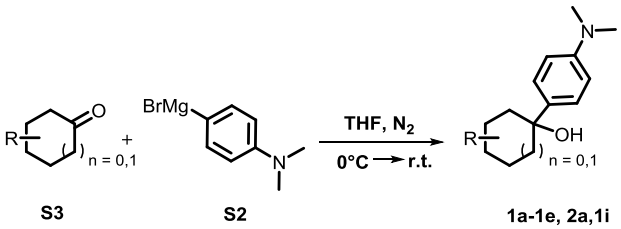
3. Synthesis of starting materials

3.1 *Procedure A:*



Scheme S1. Preparation of Grinard reagent.

(1) To an oven-dried 25-mL three-necked round bottom flask equipped with a magnetic stirring bar, and a constant-pressure dropping funnel was added magnesium powder (12.5 mmol, 0.30 g). The equipment was sealed with a rubber septum, then evacuated and back filled with nitrogen for three times using a nitrogen balloon. To the funnel was added 1M solution of 4-bromo-*N,N*-dimethylaniline **S1** (12 mmol) in THF (12 mL) by syringe. The above solution was added dropwise at r.t. within 30 min. When 1 mL of the solution was added, 1 drop of 1,2-dibromoethane was added via syringe to initiate the reaction. Upon addition, the flask was immersed in a preheated 50 °C oil-bath for 2 h. The prepared (4-(dimethylamino)phenyl)magnesium bromide (**S2**) (ca. 1.0 M in THF) was stored under nitrogen atmosphere and used in the next step.

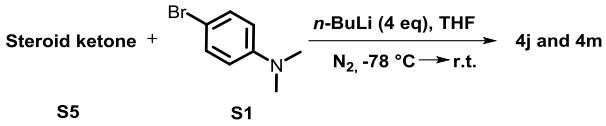


Scheme S2. Preparation of tertiary cyclohexanols and cyclopentanols

(2) To a 50-mL oven-dried round-bottom flask equipped with a magnetic stirring bar were sequentially added ketones (**S3**) (5 mmol) under nitrogen atmosphere and 10 mL of dry THF via syringe. The resultant mixture was stirred for 5 minutes at 0 °C. Then (4-(dimethylamino)phenyl)magnesium bromide **S2** (1.0 M solution in THF, 6 mL) was added dropwise. The solution was kept at 0 °C for another 30 min and further stirred at r.t. overnight. The reaction mixture was quenched by adding saturated NH_4Cl solution and extracted with ethyl acetate. The organic extracts were dried over Na_2SO_4. After concentration in vacuo, the resulting residue was purified by flash chromatography on silica gel with PE and EA as eluent to give **1a-1e**, **2a**, and **1i**.

3.2 Procedure B:

For ketones containing active OH group:

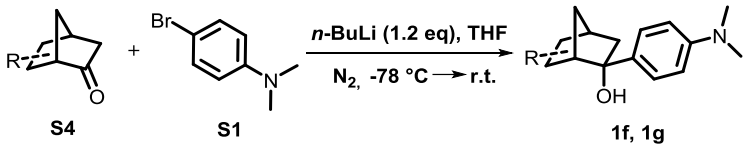


Scheme S3. Preparation of tertiary alkanols from steroidal ketones

To a solution of 4-bromo-*N,N*-dimethylaniline **S1** (800 mg, 4 mmol) in dry THF (20 mL) was added dropwise a solution of *n*-butyllithium (5 mL, 1.6 M in hexanes) at -78 °C. The mixture was stirred at -78°C for 30 minutes, and then, 2 mmol of ketones (**S5**) in dry THF (5 mL) was added dropwise. The resulting mixture was stirred for a further 30 minutes at -78°C, followed by removal of the cooling bath. The mixture was warmed to room temperature and stirred overnight. Then water (5 mL) and saturated aqueous NH_4Cl solution (20 mL) was sequentially added and the mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4, After concentrating in vacuo, the resulting residue was purified by flash chromatography on silica gel with a mixture of PE (or DCM) and EA as eluent to give **4j** and **4m**.

3.3 Procedure C:

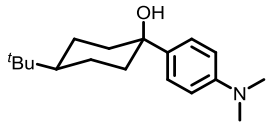
For bulky ketones:



Scheme S4. Preparation of tertiary alkanols bridged bicyclic ketones

To a solution of 4-bromo-*N,N*-dimethylaniline **S1** (0.72 g, 3.6 mmol) in THF (50 mL) at -78°C was added dropwise a solution of n-butyllithium (2.25 mL, 1.6 M in hexanes). The mixture was stirred at -78°C for 30 minutes, and then, 3.0 mmol of ketones (**S4**) in THF (6 mL) was added dropwise. Similar workup as in *Procedure B* afforded desired products **1f** and **1g**.

4. Data of cycloalkanol starting materials



***cis*-4-(*tert*-butyl)-1-(4-(dimethylamino)phenyl)cyclohexan-1-ol (1a)**

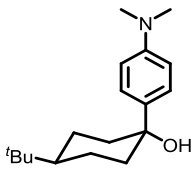
Prepared according to *procedure A*.

The configurations were assigned based on published synthesis of similar compounds: According to Garner and coworkers' report,[9] the *cis*-4-(*tert*-butyl)-1-phenylcyclohexan-1-ol and its *trans*-isomers exhibited significant differences in polarity on silica gel TLC, with the *trans*-isomer being more polar (R_f = 0.14 for *trans*-isomer; R_f = 0.28 for the *cis*-isomer, using 10% ethyl acetate in hexane). Moreover, *cis*-4-(*tert*-butyl)-1-phenylcyclohexan-1-ol has the following ^{1}H NMR characteristic peak: (500 MHz, Acetone-d_6) δ (ppm): 0.92 (^{t}Bu, s, 9H). In contrast, the *trans*-isomer has a different characteristic peak: 500 MHz, Acetone-d_6) δ (ppm): 0.78 (^{t}Bu, s, 9H).[9] The two isomers obtained in our experiment possessed similar polar difference and *tert*-butyl ^{1}H NMR signals as compared to those reported in the literature.

White solid, m.p. 125-127 °C, 5 mmol scale, yield: 280 mg, 20%, **R_f = 0.25** (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 7.35 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 3.32 (s, 1H), 2.89 (s, 6H), 1.83-1.69 (m, 4H),

1.66-1.60 (m, 4H), 1.16-1.05 (m, 1H), **0.91 (s, 9H)**. ^{13}C NMR {^{1}H} (101 MHz, DMSO-d_6) δ (ppm): 154.1, 144.3, 130.4, 117.2, 75.6, 53.8, 52.2, 45.6, 37.4, 32.8, 27.8.

HRMS (positive ESI): m/z calculated for $C_{18}H_{29}NO$ $[M+H]^+$: 276.2322; found: 276.2318.

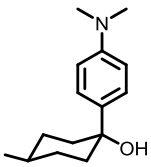


***trans*-4-(*tert*-butyl)-1-(4-(dimethylamino)phenyl)cyclohexan-1-ol (2a)**

Prepared according to *procedure A* from Grignard reagent.

White solid, m.p. 158-161 °C, 5 mmol scale, yield: 596 mg, 44%, **R_f = 0.15** (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 7.37 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 3.35 (s, 1H), 2.91 (s, 6H), 2.51-2.45 (m, 2H), 1.79-1.49 (m, 4H), 1.19-1.12 (m, 1H), 1.10-0.98 (m, 2H), **0.77 (s, 9H)**. ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 149.5, 137.7, 125.3, 112.4, 72.2, 47.6, 40.7, 39.4, 32.5, 27.6, 23.0.

HRMS (positive ESI): m/z calculated for $C_{18}H_{29}NO$ $[M+H]^+$: 276.2322; found: 276.2294.



***trans*-1-(4-(dimethylamino)phenyl)-4-methylcyclohexan-1-ol (1b)** [CAS No. 30689- 84-0]

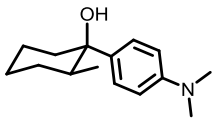
Prepared according to *procedure A*.

The configurations were assigned based on published work. According to Woodal and coworkers' report,[10] the *cis*-1-phenyl-4-methylcyclohexan-1-ol has the following ^{1}H NMR characteristic peak: ($CDCl_3$) δ (ppm): 0.99 (CH_3, m, 3H). In contrast, the *trans*-isomer has a different characteristic peak: ($CDCl_3$) δ (ppm): 0.92 (CH_3, d, *J* = 7 Hz, 3H).

In our prepration, two isomers were obtained using *procedure A*, but the polarity difference between the two isomers (R_f = 0.3 for *trans*, R_f = 0.25 for *cis*, PE/EA = 5:1, *v/v*) is too small and both products were prone to easy elimination in the separation process on silica gel. So only the major stereomer was obtained and characterized.

White solid, m.p. 68-70 °C (Lit.[10] 66-67 °C); 5 mmol scale, yield: 483 mg, 41%, ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 7.35 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 3.34 (s, 1H), 2.89 (s, 6H), 1.82-1.67 (m, 4H), 1.61-1.48 (m, 4H), 1.48-1.35 (m, 1H), **0.94 (d, *J* = 6.2 Hz, 3H)**. ^{13}C NMR{^{1}H} (101 MHz, Acetone-d_6) δ (ppm): 149.4, 139.0, 125.2, 112.2, 71.1, 40.0, 39.0, 32.0, 30.7, 22.1.

HRMS (positive ESI): m/z calculated for $C_{15}H_{23}NO$ $[M+H]^+$: 234.1852; found: 234.1863.



***cis*-1-(4-(dimethylamino)phenyl)-2-methylcyclohexan-1-ol (1c)**

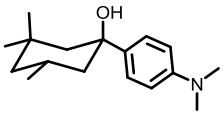
Prepared according to *procedure A*.

The configurations were assigned based on published work on similar compounds: According to Canonne and Bernatchez's report,[11] *trans*-1-phenyl-2-methylcyclohexan-1-ol has the following ^{1}H NMR characteristic peak: ($CDCl_3$) δ (ppm): 0.81 (CH_3, d, 3H, *J* = 7.0 Hz). In contrast, the *cis*-isomer has a different characteristic peak: ($CDCl_3$) δ (ppm): 0.60 (CH_3, d, 3H, *J* = 7.0 Hz). In other words, the *cis*-Me has smaller 1H NMR chemical shift than the *trans*-Me.

In our synthesis, two isomers were generated by using *procedure A*, but the yield of the *trans*-isomer is too low and the polarity difference between the two isomers is too small (R_f = 0.2 for *cis*-isomer, R_f = 0.15 for *trans*-isomer, PE/EA = 5:1, *v/v*). So only the major stereomer was obtained and characterized.

White solid, m.p. 68-70 °C, 5 mmol scale, yield: 420 mg, 48%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.23 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 4.22 (s, 1H), 2.84 (s, 6H), 1.87-1.27 (m, 9H), **0.50 (d, *J* = 6.7 Hz, 3H)**. ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6) δ (ppm): 149.0, 138.1, 125.9, 112.4, 74.2, 41.2, 40.8, 40.5, 30.6, 26.5, 22.2, 16.3.

HRMS (positive ESI): m/z calculated for $C_{15}H_{23}NO$ $[M+H]^+$: 234.1852; found: 234.1848.



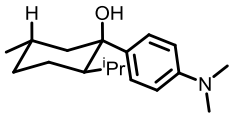
1,5-*trans*-1-(4-(dimethylamino)phenyl)-3,3,5-trimethylcyclohexan-1-ol (1d)

Prepared according to *procedure A*.

The configurations were assigned based on published synthesis of similar compounds using similar method. According to Manoharan and Eliel's report,[12] *1,5-trans*-1-Phenyl-3,3,5-trimethylcyclohexan-1-ol has the following ^{1}H NMR characteristic peak: (360 MHz, CDCl3) δ (ppm): 0.91-0.93 (d, *J* = 6.5 Hz, 3H, 5-CH_3); 2.0-2.2 (symmetrical, 15 lines, 1H, H-5). The chemical shifts in our work is consistent with those reported.[12]

White solid, m.p. 73-75 °C, 5 mmol scale, yield: 643 mg, 50 %, R_f = 0.25 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 7.34 (d, *J* = 8.90 Hz, 2H), 6.69 (d, *J* = 8.87 Hz, 2H), 3.23 (s, 1H), 2.89 (s, 6H), **2.23–2.11 (m, 1H)**, 1.87-1.67 (m, 1H), 1.58 (dt, *J* = 14.0, 2.3 Hz, 1H), 1.54–1.43 (m, 2H), 1.33 (dd, *J* = 13.3, 11.9 Hz, 1H), 1.23 (s, 3H), 0.95–0.89 (m, 1H), **0.92 (d, *J* = 6.3 Hz, 3H)**, 0.91 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6) δ (ppm): 149.3, 140.0, 125.7, 112.4, 73.5, 50.7, 48.7, 48.0, 40.9, 35.0, 32.0, 28.1, 24.6, 23.0.

HRMS (positive ESI): m/z calculated for $C_{17}H_{27}NO$ $[M+H]^+$: 262.2165; found: 262.2162.



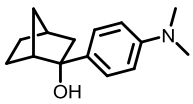
(1*R*,2*R*,5*S*)-1-(4-(dimethylamino)phenyl)-2-isopropyl-5-methylcyclohexan-1-ol (1e)

Prepared according to *procedure A*.

The configurations were assigned based on published synthesis of similar compounds using similar method. In Panev and Dimitrov's report, the aryl magnesium reagent all attacked menthone from equatorial directions. [13]

White solid, m.p. 53-54 °C, 5 mmol scale, yield: 404 mg, 30 %, R_f = 0.15 (PE/EA = 10:1, *v/v*). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.23 (d, *J* = 8.25 Hz, 2H), 6.66 (d, *J* = 9.12 Hz, 2H), 4.22 (s, 1H), 2.85 (s, 6H), 1.92–1.81 (m, 1H), 1.78–1.73 (m, 1H), 1.60 (qd, *J* = 12.8, 3.4 Hz, 1H), 1.50–1.31 (m, 5H), 0.98 (qd, *J* = 12.8, 3.4 Hz, 1H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H), 0.63 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, DMSO-d_6) δ 148.9, 138.2, 125.9, 112.4, 76.7, 51.6, 50.5, 40.8, 35.5, 28.1, 26.7, 22.8, 21.3, 18.8.

HRMS (positive ESI): m/z calculated for $C_{18}H_{29}NO$ $[M+H]^+$: 276.2322; found: 276.2319.



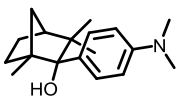
(1*R*,2*S*,4*S*)-2-(4-(dimethylamino)phenyl)bicyclo[2.2.1]heptan-2-ol (1f) [CAS No. 64618-89-9]

Prepared according to *procedure C.*

The configurations were assigned based on published synthesis of the same compounds using the same method.[14]

White solid, m.p. 90-92 °C (Lit.[14] 102-103 °C), 3 mmol scale, yield: 407 mg, 60 %, R_f = 0.15 (PE/EA = 10:1, *v/v*). ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 7.57-7.21 (m, 2H), 7.00–6.59 (m, 2H), 3.51 (s, 1H), 2.90 (s, 6H), 2.44 (d, *J* = 3.7 Hz, 1H), 2.32–2.20 (m, 3H), 1.63–1.53 (m, 1H), 1.53–1.47 (m, 1H), 1.45–1.35 (m, 3H), 1.23 (ddt, *J* = 9.7, 3.3, 1.6 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, Acetone-d_6) δ (ppm): 149.3, 138.0, 126.6, 112.1, 79.2, 47.8, 46.0, 39.9, 38.1, 37.5, 29.1, 22.1.

HRMS (positive ESI): m/z calculated for $C_{15}H_{21}NO$ $[M+H]^+$: 232.1696; found: 232.1694.



(1*S*,2*R*,4*S*)-2-(4-(dimethylamino)phenyl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol (1g)

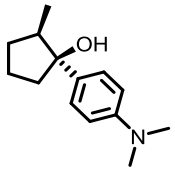
Prepared according to *procedure C.*

The configurations were assigned based on published synthesis of similar compounds using the

same method.[15]

White solid, m.p. 45-47 °C, 3 mmol scale, yield: 544 mg, 66 %, R_f = 0.1 (PE/EA = 20:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (d, *J* = 8.90 Hz, 2H), 6.68 (d, *J* = 8.86 Hz, 2H), 2.94 (s, 6H), 2.30 (dq, *J* = 10.4, 2.3 Hz, 1H), 2.26–2.15 (m, 1H), 1.82–1.75 (m, 2H), 1.49 (s, 1H), 1.48–1.42 (m, 1H), 1.35 (dd, *J* = 10.4, 1.6 Hz, 1H), 1.16 (td, *J* = 12.6, 4.6 Hz, 1H), 1.11 (s, 3H), 1.02 (s, 3H), 0.46 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 148.6, 133.5, 128.3, 111.3, 83.9, 52.8, 49.0, 45.8, 41.7, 40.5, 33.4, 30.2, 24.3, 21.5, 17.5.

HRMS (positive ESI): m/z calculated for $C_{18}H_{27}NO$ $[M+H]^+$: 274.2165; found: 274.2159.



cis-1-(4-(dimethylamino)phenyl)-2-methylcyclopentan-1-ol (1i)

Prepared according to *procedure A* .

Its phenyl analogues *cis*- and *trans*-1-phenyl-2-methylcyclopentan-1-ols were prepared by Chodklewlcz and coworkers from PhMgBr in THF.[16] In their work, a 99:1 *cis/trans* ratio was obtained. *Trans*-1-phenyl-4-methylcyclopentan-1-ol has the following ^{1}H NMR characteristic peak:($CDCl_3$) δ (ppm): 0.51 (d, 3 H, *J* = 6.98 Hz). In contrast, the *cis*-isomer has a different characteristic peak: ($CDCl_3$) δ (ppm): 0.82 (d, 3 H, *J* = 6.67 Hz).

In our preparation following procedure *A*, two isomers were obtained, the yield of the *trans*-isomer is too low and the polarity difference between the two isomers is too small, and they were prone to easy elimination in the separation process on silica gel. A mixture *cis*-stereoisomers and one elimination product were collected together and subjected to the deoxygenation.

Colorless oil, 4 mmol scale, yield: 370 mg, 36%, R_f = 0.75 (alkene, PE/EA = 10:1, *v/v*), R_f = 0.2 for *cis*-isomer. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.25 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 1H), 2.84 (s, 6H), 2.03–1.42 (m, 7H), 0.70 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 149.3, 133.7, 125.8, 112.4, 83.6, 44.5, 43.0, 40.7, 31.7, 21.5, 12.2.

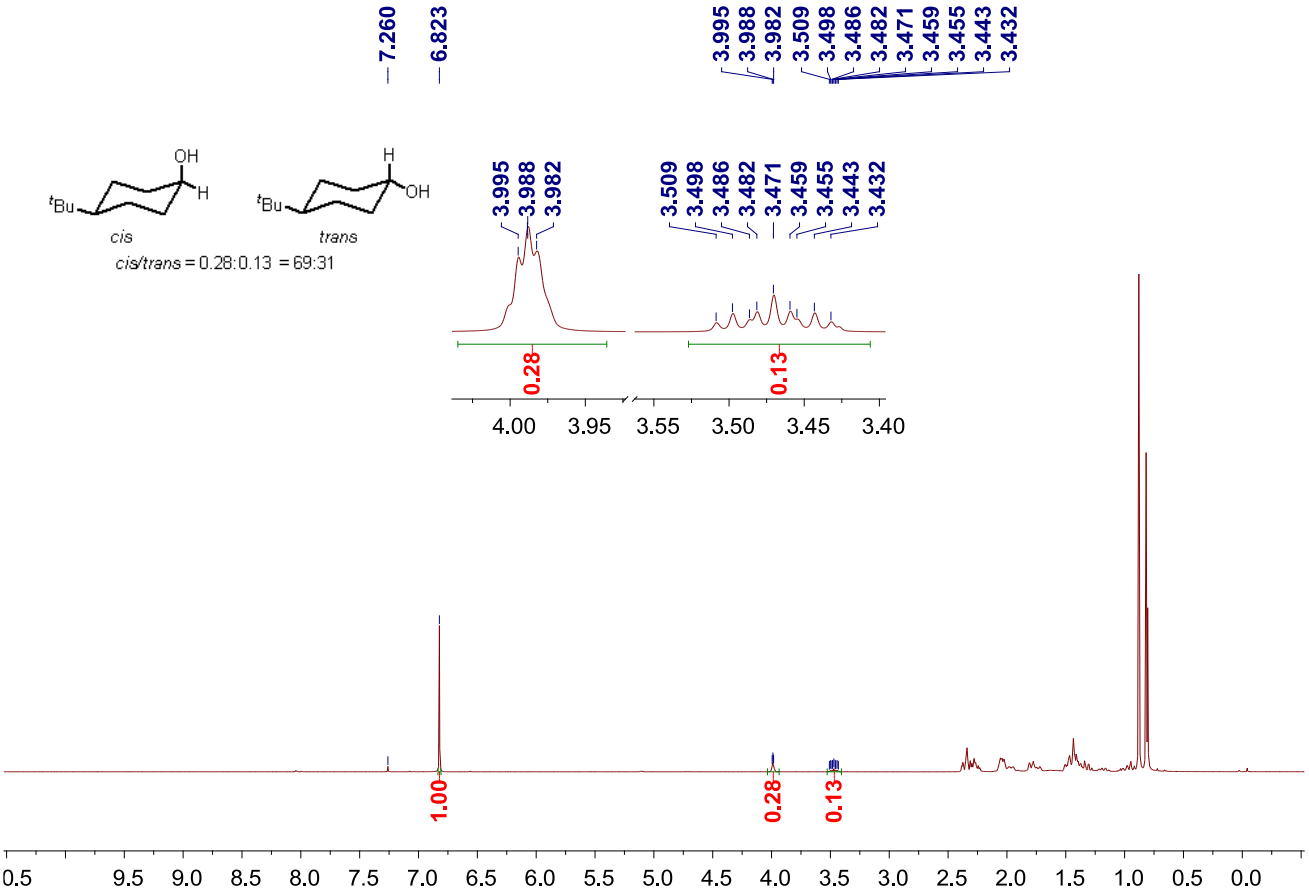
HRMS (positive ESI): m/z calculated for $C_{14}H_{21}NO$ $[M+H]^+$: 220.1696; found: 220.1694.

5. General procedure for iridium-catalyzed reduction of 4-tert-butylcyclohexanone

To a 10-mL tube was sequentially added 4-(tert-butyl)cyclohexan-1-one (0.5 mmol), 1 mL of the ***C2*** catalyst solution in deionized water (0.0005 mol/L for *S/C* = 1000). The tube was immersed in a preheated 80°C oil-bath for 5 min, followed by slow addition of formic acid (300 μL, 8 mmol) in 1 min. The reaction process was monitored by TLC (1h). After cooling to room temperature, diluting with saturated sodium bicarbonate solution (5 mL), extracting with ethyl acetate (5 mL x 3), and drying over Na_2SO_4, concentration of the organic phase under reduced pressure followed by ^{1}H NMR determination of the crude reaction mixture with $CHBr_3$ as an internal standard (126.4 mg, 0.5 mmol) gave the yield and diastereoselectivity.

4-(*tert*-butyl)cyclohexan-1-ol(*e*-6a and *a*-7a): 41% yield, cis/trans = 69:31

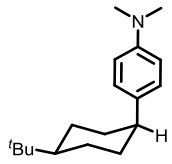
The configurations were determined based on published work. According to Glorius and coworkers' report, *trans*-4-*tert*-butylcyclohexan-1-ol has the following ^{1}H NMR characteristic peak: (600 MHz, $CDCl_3$) δ (ppm): δ 3.51 (tt, $^3J_{ax,ax}$ = 11.0 Hz, $^3J_{ax,\,eq}$ = 4.4 Hz, 1H, H_{ax} C1). In contrast, the *cis*-isomer has a different characteristic peak: (400 MHz, $CDCl_3$) δ (ppm): 4.03 (m, 1H, H_{eq}-C1). [17]



6. General procedure for deoxygenation of cycloalkanols

To a 10-mL tube was sequentially added alcohol (**1a-1i, 2a**) (0.25 mmol), 0.5 mL of HFIP and 0.5 mL of the **C1** catalyst solution in deionized water (0.0001 mol/L for *S/C* = 5000; 0.00025 mol/L for *S/C* = 2000; 0.0005 mol/L for *S/C* = 1000; 0.001 mol/L for *S/C* = 500; 0.0025 mol/L for *S/C* = 200; 0.005 mol/L for *S/C* = 100; and 0.01 mol/L for *S/C* = 50) . The tube was immersed in a preheated 80 °C oil-bath for 5 min, followed by slow addition of formic acid (38 µL, 1 mmol; 57 µL, 1.5 mmol; 228 µL, 6 mmol) with in 1 min. The resultant reaction mixture was stirred for indicated time (see the tables in main text). After cooling to room temperature, diluting with saturated sodium bicarbonate solution (5 mL), extracting with ethyl acetate (5 mL x 3), and drying over Na_2SO_4, concentration of the organic phase under reduced pressure followed by purification by column chromatography on silica gel with afforded desired products. The two diastereomeric deoxygenation products had the same polarity, and isolation of them on silica gel was unreliable. Our experiments also revealed that the ^{1}H NMR spectra of the crude reaction mixture and the isolated products showed the same diastereomeric ratio.

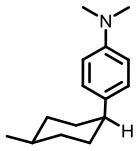
7. Data of deoxygenation products



***cis*-(4-(tert-butyl)cyclohexyl)-*N,N*-dimethylaniline (*e*-4a) *S/C* = 1000, HCOOH = 4 eq.**

The configurations were assigned based on published synthesis of similar compounds. For example, trans-1-tert-butyl-4-phenylcyclohexane has the following ^{1}H NMR characteristic peak: (300 MHz, $CDCl_3$) δ (ppm) 2.45 (benzylic H, tt, *J* = 12.2, 3.5, 1H). The coupling constant *J* = 12.2 indicates the presence of an axial hydrogen. [18]

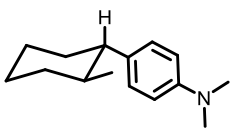
White solid, m.p. 75-78 °C, 0.25 mmol scale, yield: 64 mg, 99%, R_f = 0.15 (PE/EA = 40:1, *v/v*), *d.r.* = 98 : 2, characterization of the major stereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), **2.98–2.95 (H-benzyl, m, 1H)**, 2.93 (s, 6H), 2.23–2.18 (m, 2H), 1.73 (tt, *J* = 13.2, 4.4 Hz, 2H), 1.56 (dd, *J* = 13.1, 3.6 Hz, 2H), 1.21 (qd, *J* = 12.6, 3.4 Hz, 2H), 1.14–1.04 (m, 1H), 0.81 (s, 9H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.4, 133.5, 128.3, 112.8, 48.4, 40.9, 35.5, 32.7, 31.0, 27.6, 22.8.
HRMS (positive ESI): m/z calculated for $C_{18}H_{29}N$ $[M+H]^+$: 260.2373; found: 260.2367.



***cis*-*N,N*-dimethyl-4-(4-methylcyclohexyl)aniline (*e*-4b) S/C = 1000, HCOOH = 4eq.**

The configurations were assigned based on published synthesis of similar compounds. For example, *trans*-1-methyl-4-phenylcyclohexane has the following ^{1}H NMR characteristic peak: (300 MHz, $CDCl_3$) δ (ppm): 2.45 (benzyl-H, tt, *J* = 12.2, 3.3, 1H), 0.94 (CH_3, d, *J* = 6.5 Hz, 3H). The coupling constant *J* = 12.2 indicates the presence of an axial hydrogen. [19] In contrast, the *cis*-isomer has a different characteristic peak: (300 MHz, $CDCl_3$) δ (ppm): 2.60-2.51 (benzyl-H, m, 1H); δ (ppm) 1.03 (CH_3, d, *J* = 7.1 Hz, 3H).[19]

Colorless oil, 0.25 mmol scale, yield: 40 mg, 74%, R_f = 0.8 (PE/EA = 10:1, *v/v*), mixture of 2 stereomers, *d.r.* = 85 : 15. Characterization of the *cis*-stereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.17 (d, *J* = 10.4 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 2.95 (s, 6H), **2.56-2.46 (H-benzyl, m, 1H)**, 2.02–1.88 (m, 1H), 1.83–1.62 (m, 6H), 1.62–1.51 (m, 2H), **1.06 (CH_3, dd, *J* = 7.2, 1.6 Hz, 3H)**. ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 149.0, 136.1, 127.5, 113.0, 42.6, 41.0, 32.1, 28.9, 27.7, 18.4. Characterization of the *trans*-stereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): **2.40 (H-benzyl, t, *J* = 12.0 Hz, 1H)**, **0.97 (CH_3, d, *J* = 6.4 Hz, 3H)**.
HRMS (positive ESI): m/z calculated for $C_{15}H_{23}N$ $[M+H]^+$: 218.1903; found: 218.1925.



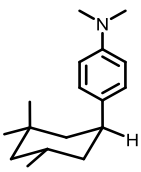
***trans*-*N,N*-dimethyl-4-(2-methylcyclohexyl)aniline (*a*-5c) *S/C* = 1000, HCOOH = 4 eq.**

The configurations were assigned based on published synthesis of similar compounds. For example, *trans*-1-methyl-2-phenylcyclohexane has the following ^{1}H NMR characteristic peak: δ (ppm): (300 MHz, $CDCl_3$) 2.14 (benzyl-H, td, *J* = 11.1, 3.1, 1H), δ (ppm) 0.73 (CH_3, d, *J* = 6.5 Hz, 3H). The coupling constant *J* = 11.1 indicates the presence of an axial hydrogen. [20]

Colorless oil, 0.25 mmol scale, yield: 52 mg, 96%, R_f = 0.15 (PE/EA = 40:1, *v/v*), mixture of 2 stereomers, *d.r.* = 65 : 35 characterization of the major stereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): for *trans*-isomer δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 2.94 (s, 6H), **2.00 (H-benzyl, td, *J* = 11.2, 3.1 Hz, 1H)**, 1.93–1.74 (m, 3H), 1.76–1.60 (m, 1H), 1.62–1.27 (m, 4H), 1.10 (qd, *J* = 12.9, 3.4 Hz, 1H), 0.71 (d, *J* = 6.5 Hz, 3H); for *cis*-isomer δ 2.13-2.06 (m, 1H), 0.73 (d, *J* = 7.2 Hz, 3H). ^{13}C

NMR (two isomers): 148.8, 135.6, 135.0, 128.1, 128.1, 113.0, 112.8, 51.4, 45.5, 41.0, 37.9, 35.9, 35.9, 34.7, 33.5, 27.1, 27.0, 26.8, 24.9, 20.9, 20.3, 12.4.

HRMS (positive ESI): m/z calculated for $C_{15}H_{23}N$ $[M+H]^+$: 218.1903; found: 218.1900.

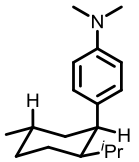


***1,5-trans-N,N*-dimethyl-4-(3,3,5-trimethylcyclohexyl)aniline (*e*-4d) S/C = 1000, HCOOH = 4eq.**

The configurations were assigned based on published synthesis of similar compounds.[12] For example, 1,5-*trans*-1-phenyl-3,3,5-trimethylcyclohexane has the following ^{1}H NMR characteristic peak: (360 MHz, CD_2Cl_2) δ (ppm) 2.98-3.02 (benzylic H, m, 7 lines, 1H). In contrast, the *cis*-isomer has a different characteristic peak: (250 MHz, $CDCl_3$) δ (ppm) 2.98-3.02 (benzylic H, tt, *J* = 12, 4.6 Hz, 1H).[12]

White solid, m.p. 50-51 °C, 0.25 mmol scale; yield: 61 mg, 99%, R_f = 0.5 (PE/EA = 5:1, *v/v*), *d.r.* = 95 : 5 characterization of the major stereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 2.92 (s, 6H), **2.89–2.86 (benzylic H, m, 1H)**, 2.11–2.00 (m, 1H), 1.76 (ddd, *J* = 14.1, 9.7, 5.1 Hz, 1H), 1.63–1.46 (m, 3H), 1.40 (dd, *J* = 13.5, 5.2 Hz, 1H), 1.20 (dd, *J* = 13.5, 5.8 Hz, 1H), 1.09 (d, *J* = 7.2 Hz, 3H), 1.02 (s, 3H), 0.80 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.9, 135.9, 127.5, 113.0, 46.5, 45.6, 41.0, 39.1, 34.3, 32.6, 31.4, 30.1, 27.2, 21.9.

HRMS (positive ESI): m/z calculated for $C_{17}H_{27}N$ $[M+H]^+$: 246.2216; found: 246.2212.

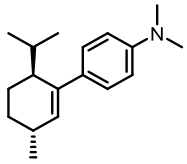


1,2-*cis*-1,5-*trans*-2-isopropyl-5-methylcyclohexyl)-*N,N*-dimethylaniline (*e*-4e) S/C = 50, HCOOH = 6 eq.

The configurations were assigned based on published synthesis of similar compounds.[21] For example, 1,2-*trans*-1,3-*cis*-1-phenyl-2-isopropyl-5-methylcyclohexane (with equatorial phenyl group) has the following ^{1}H NMR characteristic peak: (400 MHz, $CDCl_3$) δ (ppm) 2.42 (benzylic H, dt, *J* = 11.6, 3.2 Hz, 1H).[21] The coupling constant *J* = 11.6 indicates the presence of an axial hydrogen. However, in our experimental results, the coupling constants of benzyl hydrogen are 5.3 and 2.7 Hz, indicating the existence of an equatorial benzylic hydrogen.

Colorless oil, 0.25 mmol scale, yield: 48 mg, 74%, R_f = 0.8 (PE/EA = 10:1, *v/v*), *d.r.* = 94 : 6. Characterization of the major stereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), **3.07 (benzylic H, dt, *J* = 5.3, 2.7 Hz, 1H)**, 2.91 (s, 6H), 1.89–1.80 (m, 2H), 1.77–1.52 (m, 3H), 1.39–1.28 (m, 2H), 1.26–1.16 (m, 1H), 0.98 (qd, *J* = 13.4, 4.8 Hz, 1H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.78 (t, *J* = 6.2 Hz, 6H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.5, 134.8, 130.8, 115.1, 47.5, 43.5, 42.1, 40.7, 35.6, 30.2, 26.6, 26.0, 22.9, 21.4, 21.2.

HRMS (positive ESI): m/z calculated for $C_{18}H_{29}N$ $[M+H]^+$: 260.2373; found: 260.2407.

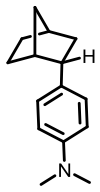


(2'*S*,5'*R*)-2'-isopropyl-*N,N*,5'-trimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-amine (S6) *S/C* = 1000, HCOOH = 4eq.

White solid, 0.25 mmol scale, yield: 57 mg, 88%, R_f = 0.2 (PE/EA = 20:1, *v/v*). Characterization of the major stereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.17 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 1H), 2.95 (s, 6H), 2.72 – 2.65 (m, 1H), 2.25 – 2.18 (m, 1H), 1.97 – 1.89 (m, 1H),

1.87 – 1.80 (m, 2H), 1.53 – 1.43 (m, 1H), 1.24 – 1.10 (m, 1H), 1.02 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 149.2, 141.1, 132.9, 132.0, 127.2, 112.4, 41.4, 40.8, 31.3, 31.1, 28.5, 22.3, 21.7, 20.8, 15.7.

HRMS (positive ESI): m/z calculated for $C_{18}H_{27}N$ [M+H]$^+$: 258.2216; found: 258.2211.

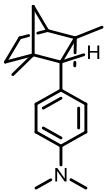


***endo*-4-bicyclo[2.2.1]heptan-2-yl)-*N,N*-dimethylaniline (*e*-4f) S/C = 1000, HCOOH = 4eq.**

The configuration was assigned by comparing our NMR data with those reported for *exo*-(4-*N,N*-dimethylaminophenyl) norbornane.[22] According to Li and coworker's work, the *exo* isomer of *e*-**4f** has the following ^{1}H NMR characteristic peak: (500 MHz, $CDCl_3$) δ (ppm) 2.68 (exo-benzylic H, dd, *J* = 6.0, 8.5 Hz, 1H). According to Uemura and coworkers' work, *endo*-1-phenylnorbornane has the following ^{1}H NMR characteristic peak: (270 MHz, $CDCl_3$) δ (ppm) 3.17-3.26 (endo-benzyl-H, m, 1H).

Colorless oil, 0.125 mmol scale, yield: 18 mg, 67%, R_f = 0.2 (PE/EA = 20:1, *v/v*), *d.r.* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.12 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), **3.19–3.13 (H-benzyl, m, 1H)**, 2.94 (s, 6H), 2.35 (dt, *J* = 19.4, 4.5 Hz, 2H), 1.97 (tt, *J* = 12.1, 3.9 Hz, 1H), 1.62–1.49 (m, 2H), 1.48–1.32 (m, 3H), 1.31–1.22 (m, 2H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.8, 131.9, 128.8, 112.7, 45.1, 42.7, 41.0, 40.6, 37.6, 34.5, 30.3, 22.9.

HRMS (positive ESI): m/z calculated for $C_{15}H_{21}N$ [M+H]$^+$: 216.1747; found: 216.1743.

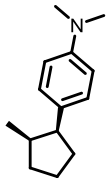


***endo*-2-isopropyl-5-methylcyclohexyl)-*N,N*-dimethylaniline (*e*-5g) S/C = 100, HCOOH = 24 eq.**

The configurations were determined based on NOE spectra (vide post)

Colorless oil; 0.125 mmol scale; yield: 23 mg, 72%, R_f = 0.2 (PE/EA = 30:1, *v/v*), *d.r.* = 94 : 6: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.15 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 2.93 (s, 6H), 2.43 (d, *J* = 2.0 Hz, 1H), 2.08–1.96 (m, 1H), 1.89–1.76 (m, 2H), 1.70 (dq, *J* = 9.5, 2.3 Hz, 1H), 1.51 (tt, *J* = 12.5, 4.7 Hz, 1H), 1.27 (dd, *J* = 9.5, 1.4 Hz, 1H), 1.21–1.13 (m, 1H), 1.12 (s, 3H), 1.04 (s, 3H), 0.77 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.7, 131.0, 128.7, 112.0, 62.6, 49.7, 49.0, 46.2, 40.7, 40.2, 33.3, 28.3, 26.2, 24.0, 21.3.

HRMS (positive ESI): m/z calculated for $C_{18}H_{27}N$ [M+H]$^+$: 258.2216; found: 258.2234.



***cis*-*N,N*-dimethyl-4-(2-methylcyclopentyl)aniline (*pe*-4i) S/C = 100, HCOOH = 4eq.**

The configurations were assigned based on published synthesis of similar compounds.[23] For example, 1,2-*trans*-1-phenyl-2-methylcyclopentane has the following ^{1}H NMR characteristic peak: (300 MHz, $CDCl_3$) δ (ppm) 2.42((benzylic H, m, 1H), 0.92 (CH_3, d, *J* = 6.22 Hz, 3H).[23] In contrast, the *cis*-isomer has a different characteristic peak: (300 MHz, $CDCl_3$) δ (ppm) 3.14 (benzylic H, m, 1H), 0.58 (CH_3, d, *J* = 7 Hz, 3H). The methyl of the *trans*-isomer displayed larger chemical shift than the methyl of cis-isomer.

Colorless oil, 0.125 mmol scale, yield: 20 mg, 80%, R_f = 0.65 (PE/EA = 10:1, *v/v*), *d.r.* = 95 : 5. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.06 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), **3.11–3.01 (H-benzyl, m, 1H)**, 2.92 (s, 6H), 2.24 (qd, *J* = 7.0, 5.5 Hz, 1H), 2.02–1.77 (m, 4H), 1.77–1.59 (m, 1H); 1.47–1.33 (m, 1H); **0.60 (CH_3, d, *J* = 7.1 Hz, 3H)**. ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.9, 131.8, 129.0, 112.6, 48.3, 40.9, 38.3, 33.4, 29.2, 23.2, 17.0.

HRMS (positive ESI): m/z calculated for $C_{14}H_{21}N$ [M+H]$^+$: 204.1747; found: 204.1757.

8. Other procedures for deoxygenation of *cis*-4-(tertbutyl)-1-(4-(dimethylamino)phenyl)cyclohexan-1-ol (1a)

Procedure A (with $LiAlH_4$):

To a 10-mL dry tube were sequentially added *cis*-4-(tertbutyl)-1-(4-(dimethylamino)phenyl)cyclohexan-1-ol (**1a**) (0.125 mmol), 1 mL of dry THF, and $LiAlH_4$ (11.9 mg, 0.313 mmol). Anhydrous $AlCl_3$ (41.7 mg, 0.3125 mmol) was slowly added at 0 °C (ice water bath), the mixture was warmed to room temperature and stirred at for 30 min. then 1 mL of H_2O, 0.5 mL of NaOH (10%) and 0.5 mL of H_2O were added successively, followed by extraction with diethyl ether (3 mL x 3), washing with 5 mL saturated sodium chloride solution, and drying over Na_2SO_4. After concentration of the organic phase under reduced pressure, the crude reaction mixture was analyzed by ^{1}H NMR.

Procedure B (with $NaBH_3CN$):

To a 10-mL dry tube were sequentially added **1a** (0.125 mmol), 1 mL of HFIP, and $NaBH_3CN$ (23.6 mg, 0.75 mmol). Then HCl (0.25 mL 1M, 0.25 mmol) was added dropwise, and the reaction process was monitored by TCL. Upon complete consumption of **1a**, diluting with H_2O (1 mL), extracting with ethyl acetate (3 mL x 3), and drying over Na_2SO_4, concentration of the organic phase under reduced pressure afforded the crude reaction mixture, which was analyzed by ^{1}H NMR.

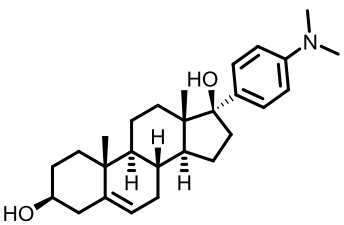
Procedure C (with BH_3·THF):

BH_3·THF (1 mol/L, 0.275 mL, 0.275 mmol) was diluted in 1.5 mL of dry THF. The solution was added to a 10-mL dry tube charged with **1a** (0.125 mmol) and 1 mL of dry THF via a syringe, and was stirred at 65 °C. The reaction process was monitored by TCL. Upon complete consumption of **1a**, diluting with saturated sodium chloride solution (3 mL), extracting with ethyl acetate (3 mL x 3), and drying over Na_2SO_4, concentration of the organic phase under reduced pressure afforded the crude reaction mixture, which was analyzed by ^{1}H NMR.

9. General procedure for structure modification of Prasterone and Stanolone

To a solution of 4-bromo-*N,N*-dimethylaniline (800 mg, 4 mmol) in THF (20 mL) at -78°C was added dropwise a solution of *n*-butyllithium (3.75 mL, 1.6 M in hexanes, 3 equiv.). The mixture was stirred at -78°C for 30 minutes, and then 2 mmol of Prasterone or Stanolone dissolved in THF (5 mL) was added dropwise via a syringe. The resulting mixture was stirred for a further 30 minutes at -78 °C, followed by removal of the cooling bath and stirring at room temperature overnight. Then water (5 mL) and saturated aqueous NH_4Cl solution (10 mL) were added, and the mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the crude tertiary alcohols, which were directly submitted to the above deoxygenation procedure with water-HFIP (1:1, v/v) as solvent.

10. Data of Prasterone and Stanolone derivatives.



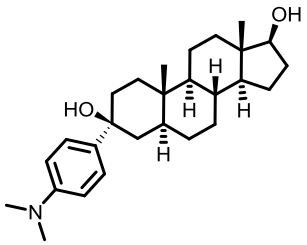
(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-17-(4-(dimethylamino)phenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-3,17-diol

Prepared according to *procedure B*. The stereochemistry is assigned according to published stereochemical results.[24]

White solid, m.p. 169-170 °C, 2 mmol scale, yield: 123 mg, 15 %, R_f = 0.3 (DCM/EA = 10:1, *v/v*). ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 7.21 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.29 (dt, *J* =

5.1, 1.8 Hz, 1H), 3.65 (s, 1H), 3.61 (d, *J* = 4.6 Hz, 1H), 3.37–3.28 (m, 1H), 2.90 (s, 6H), 2.81–2.80 (m, 1H), 2.30–2.09 (m, 4H), 1.86–1.66 (m, 3H), 1.59–1.36 (m, 7H), 1.23–1.12 (m, 1H), 1.04 (s, 3H), 1.00 (s, 3H), 0.98–0.88 (m, 1H), 0.67–0.55 (m, 1H), 0.53–0.41 (m, 1H). ^{13}C NMR{1H} (101 MHz, Acetone-d_6) δ (ppm): 149.3, 141.6, 135.2, 128.0, 118.8, 111.1, 84.6, 70.8, 50.2, 49.5, 46.4, 42.4, 39.8, 38.0, 37.3, 36.4, 33.5, 32.7, 31.6, 24.3, 20.6, 18.9, 14.0.

HRMS (positive ESI): m/z calculated for $C_{27}H_{39}NO_2$ $[M+H]^+$: 410.3054; found: 410.3059.

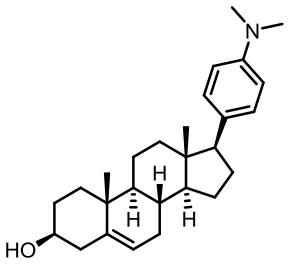


(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-3-(4-(dimethylamino)phenyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,17-diol

Prepared according to *procedure B*. The stereochemistry is assigned according to published stereochemical results.[25]

White solid, m.p. 193-195 °C, 2 mmol scale, yield: 332 mg, 40 %, R_f = 0.2 (DCM/EA = 10:1, *v/v*). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.25 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.41 (d, *J* = 4.6 Hz, 1H), 4.37 (s, 1H), 3.48–3.41 (m, 1H), 2.86 (s, 2H), 2.83 (s, 4H), 1.85–1.09 (m, 20H), 1.01–0.90 (m, 2H), 0.82 (s, 3H), 0.64 (s, 3H). ^{13}C NMR{1H} (101 MHz, DMSO-d_6) δ (ppm): 149.3, 139.6, 125.6, 112.5, 80.6, 71.8, 54.6, 54.0, 51.2, 51.0, 42.3, 40.9, 37.2, 35.8, 35.7, 35.3, 34.5, 32.0, 31.5, 30.3, 28.8, 28.6, 23.6, 20.7, 12.2, 11.8, 11.7.

HRMS (positive ESI): m/z calculated for $C_{27}H_{41}NO_2$ $[M+H]^+$: 412.3210; found: 412.3213.

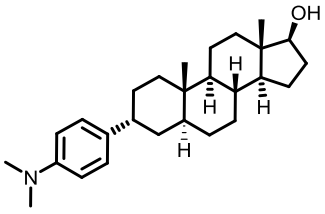


(*3S*,8*S*,9*S*,10*R*,13*S*,14*S*)-17-(4-(dimethylamino)phenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (4j) S/C = 1000, HCOOH = 4eq.

The configurations were determined based on NOE spectra (*vide post*).

White solid, m.p. 213-215 °C , 0.05 mmol scale, yield: 14 mg, 71%, R_f = 0.4 (PE/EA = 3:1, *v/v*), *d.r.* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.39–5.37 (m, 1H), 3.57–3.49 (m, 1H), 2.92 (s, 6H), 2.58 (t, *J* = 9.9 Hz, 1H), 2.43–2.15 (m, 2H), 2.12–1.99 (m, 2H), 1.98–1.89 (m, 1H), 1.88–1.72 (m, 3H), 1.65–1.59 (m, 3H), 1.55–1.47 (m, 3H), 1.43–1.28 (m, 2H), 1.28–1.16 (m, 2H), 1.10 (td, *J* = 13.8, 4.0 Hz, 1H), 1.00 (s, 3H), 0.997 (td, *J* = 11.2, 4.8 Hz, 1H), 0.49 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 149.1, 140.9, 129.2, 121.7, 112.4, 71.8, 56.4, 56.1, 50.5, 43.9, 42.3, 40.9, 37.6, 37.3, 36.7, 32.4, 32.0, 31.7, 26.4, 24.5, 20.8, 19.5, 12.5.

HRMS (positive ESI): m/z calculated for $C_{27}H_{39}NO$ $[M+H]^+$: 394.3104; found: 394.3115.



(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-3-(4-(dimethylamino)phenyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol (4m) S/C = 100, HCOOH = 4eq.

The configurations were assigned based on published synthesis of similar compounds.[26] which displayed the following ^{1}H NMR characteristic peak: for 3α-arylated compounds, (400 MHz, $CDCl_3$) δ (ppm) 2.61-2.51 (m, 1H, H_{ax}-benzyl); for 3β-arylated compounds, (300 MHz, $CDCl_3$) δ (ppm) 3.09 (t, *J* = 6.0Hz, 1H, H_{eq}-benzyl). [26]

White solid, m.p. 150-151 °C; 0.3 mmol scale, yield: 55 mg, 46%, R_f = 0.8 (PE/EA = 10:1, *v/v*), *d.r.* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 3.58 (td, *J* = 8.6, 3.9 Hz, 1H), **2.99 (t, *J* = 5.7 Hz, 1H)**, 2.92 (s, 6H), 2.09–1.97 (m, 2H), 1.98–1.86 (m, 1H), 1.84–1.71 (m, 2H), 1.69 (d, *J* = 2.3 Hz, 1H), 1.67–1.58 (m, 3H), 1.56–1.49 (m, 3H), 1.47–1.31 (m, 3H), 1.24–1.15 (m, 6H), 0.97 (td, *J* = 12.8, 4.2 Hz, 1H),

0.88 (s, 3H), 0.72 (s, 3H), 0.61 (ddd, *J* = 12.4, 10.5, 4.1 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ (ppm): 148.9, 134.6, 128.5, 112.7, 82.0, 54.7, 51.1, 43.0, 40.9, 36.8, 36.4, 35.5, 34.4, 33.4, 31.5, 30.5, 28.8, 25.2, 23.4, 20.3, 12.1, 11.1. HRMS (positive ESI): m/z calculated for $C_{27}H_{41}NO$ $[M+H]^+$: 396.3261; found: 396.3269.

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12. Copies of Spectra

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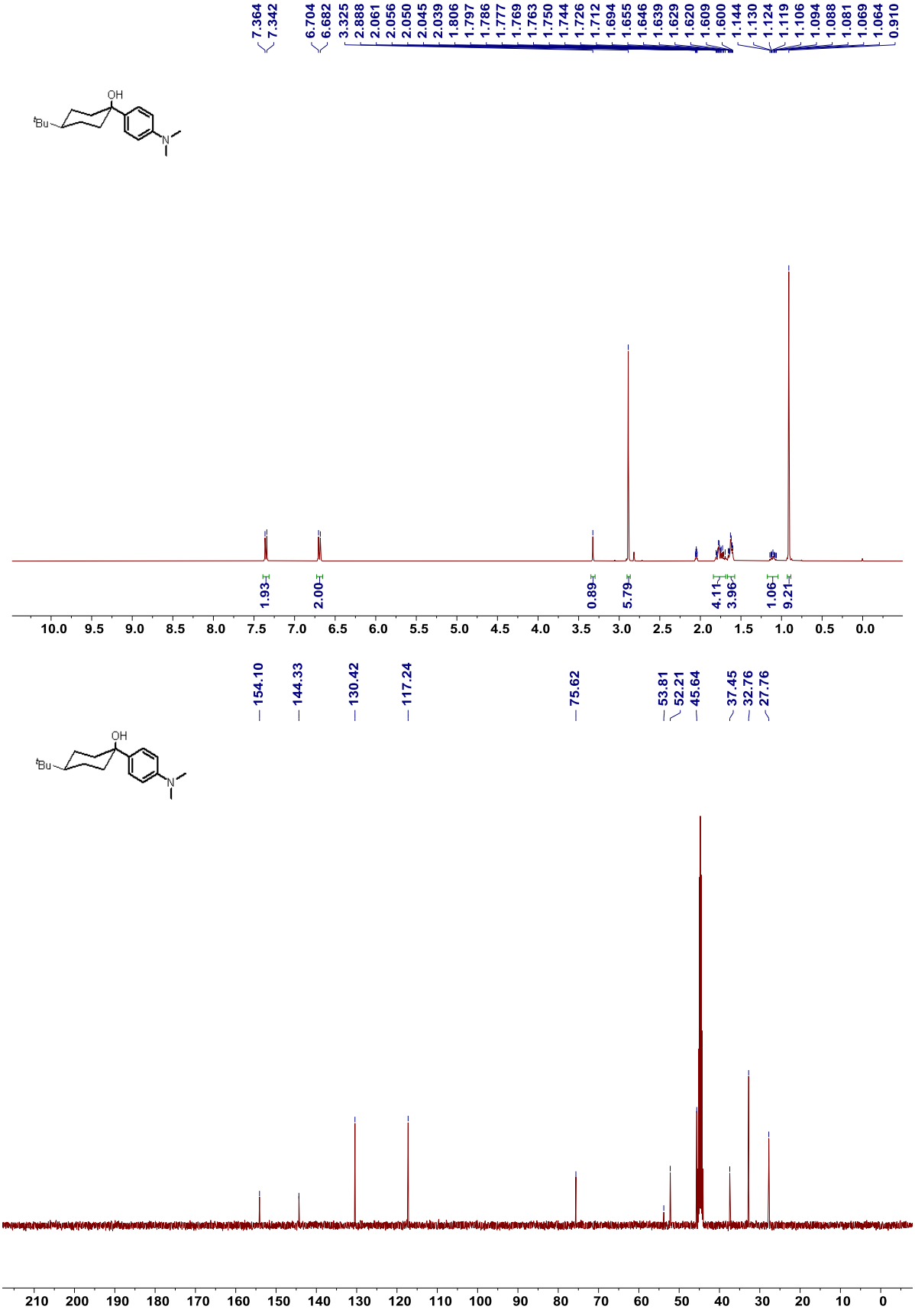

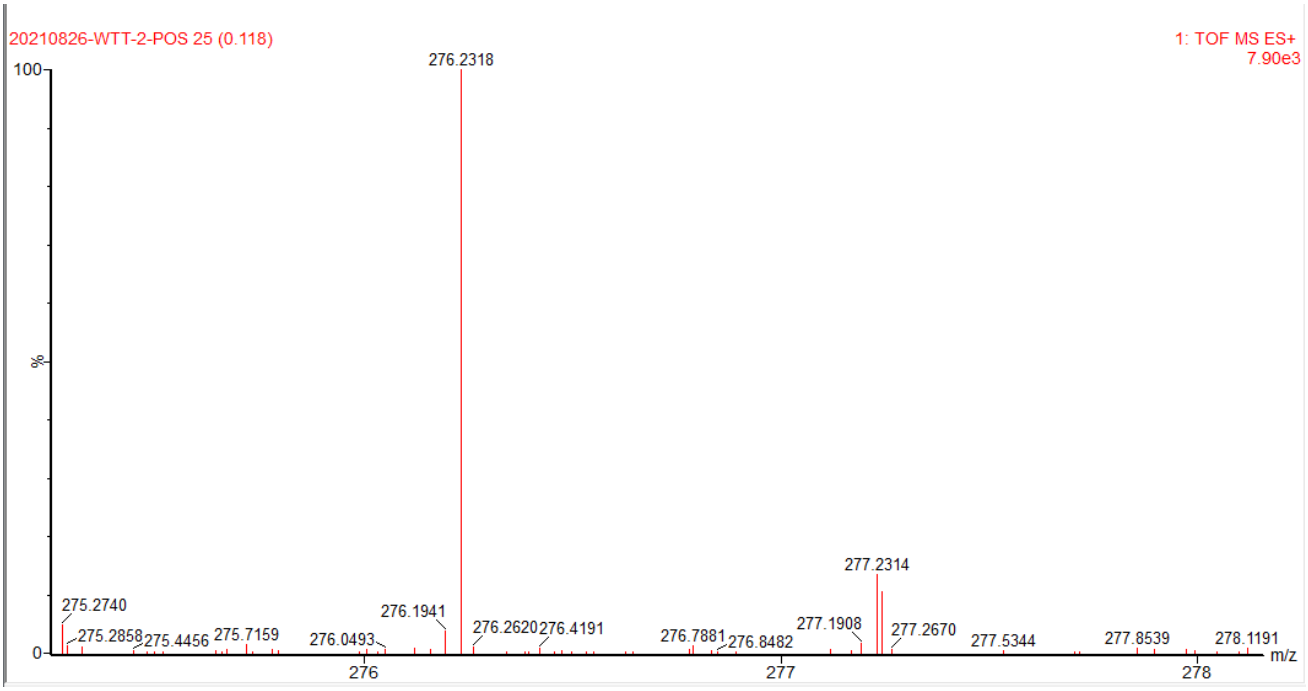
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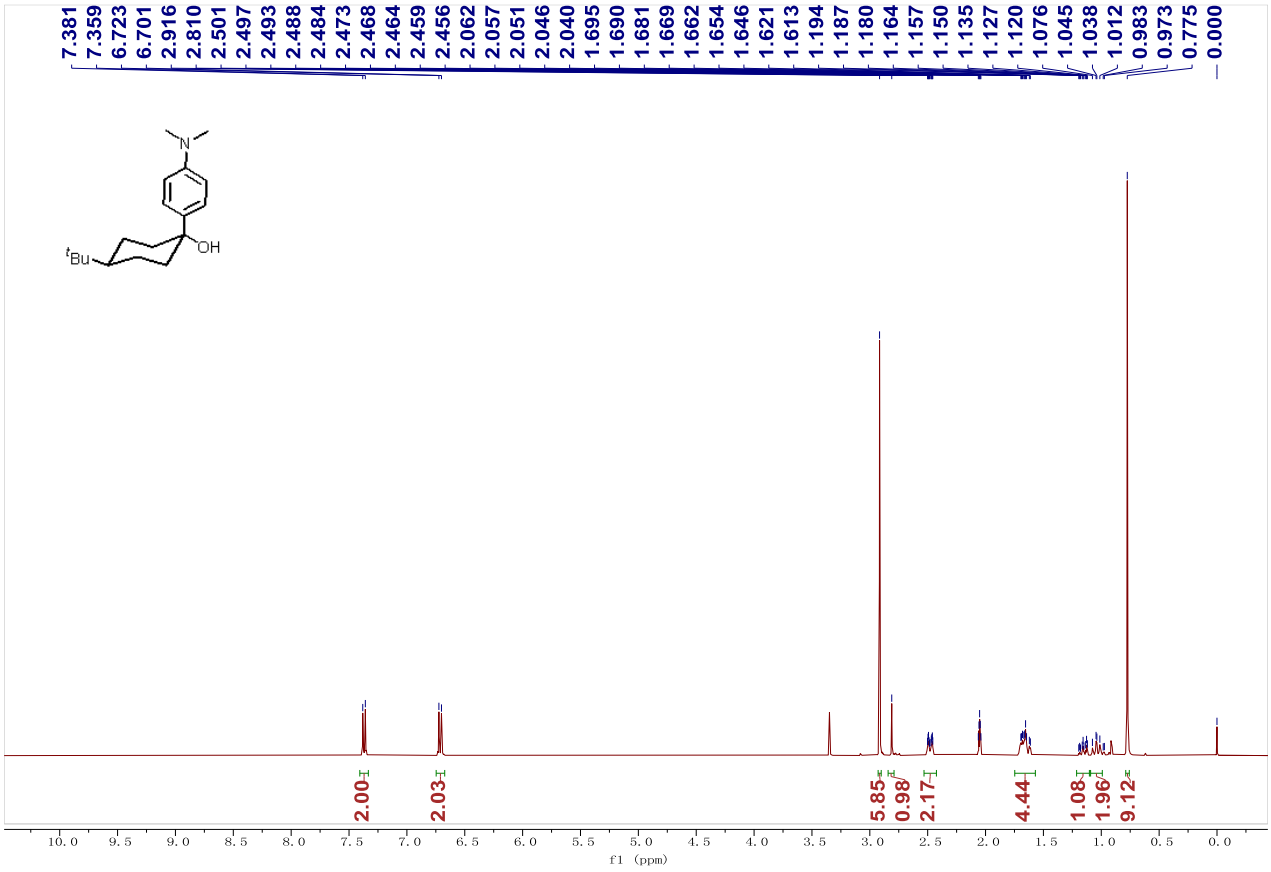

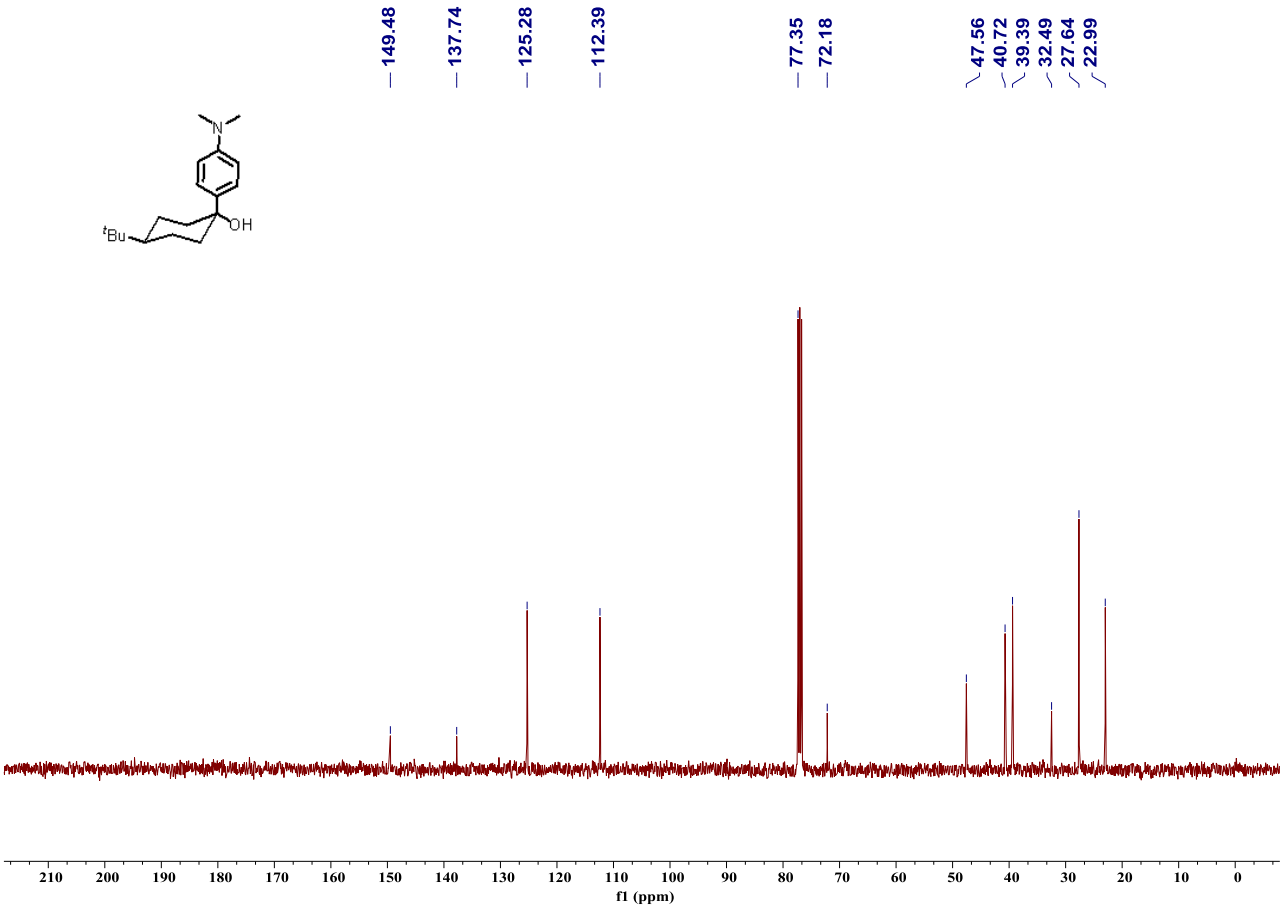

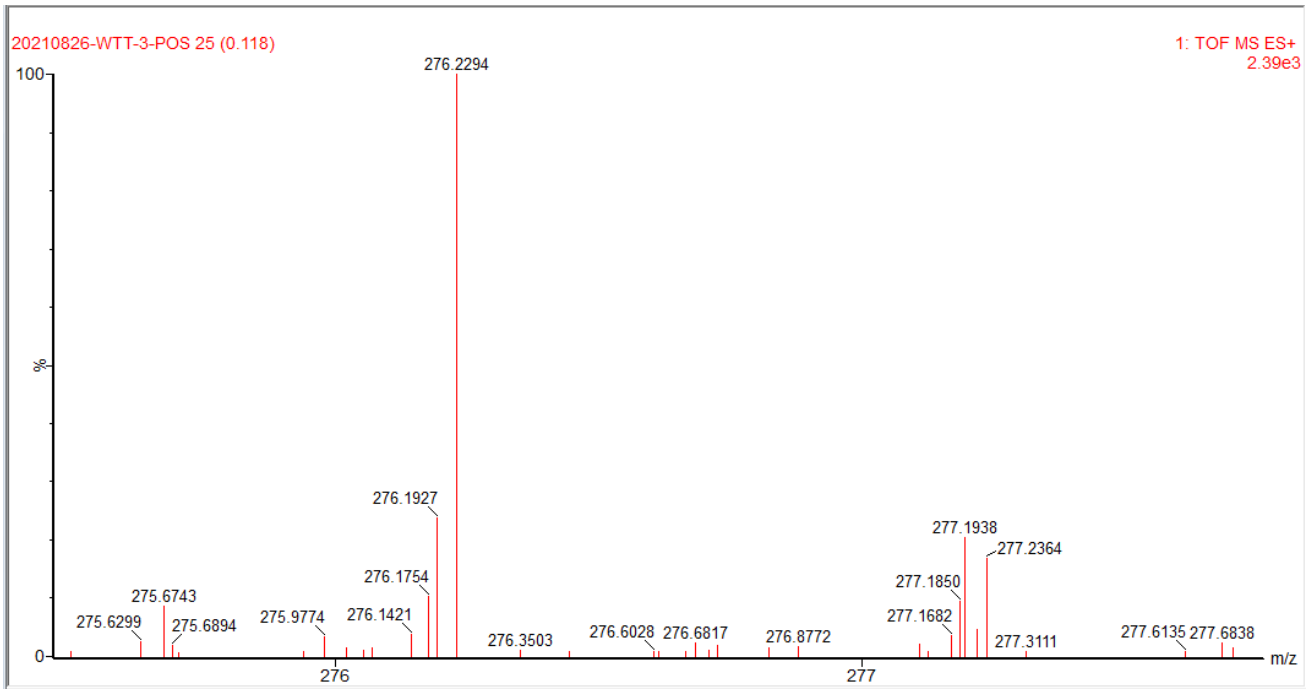
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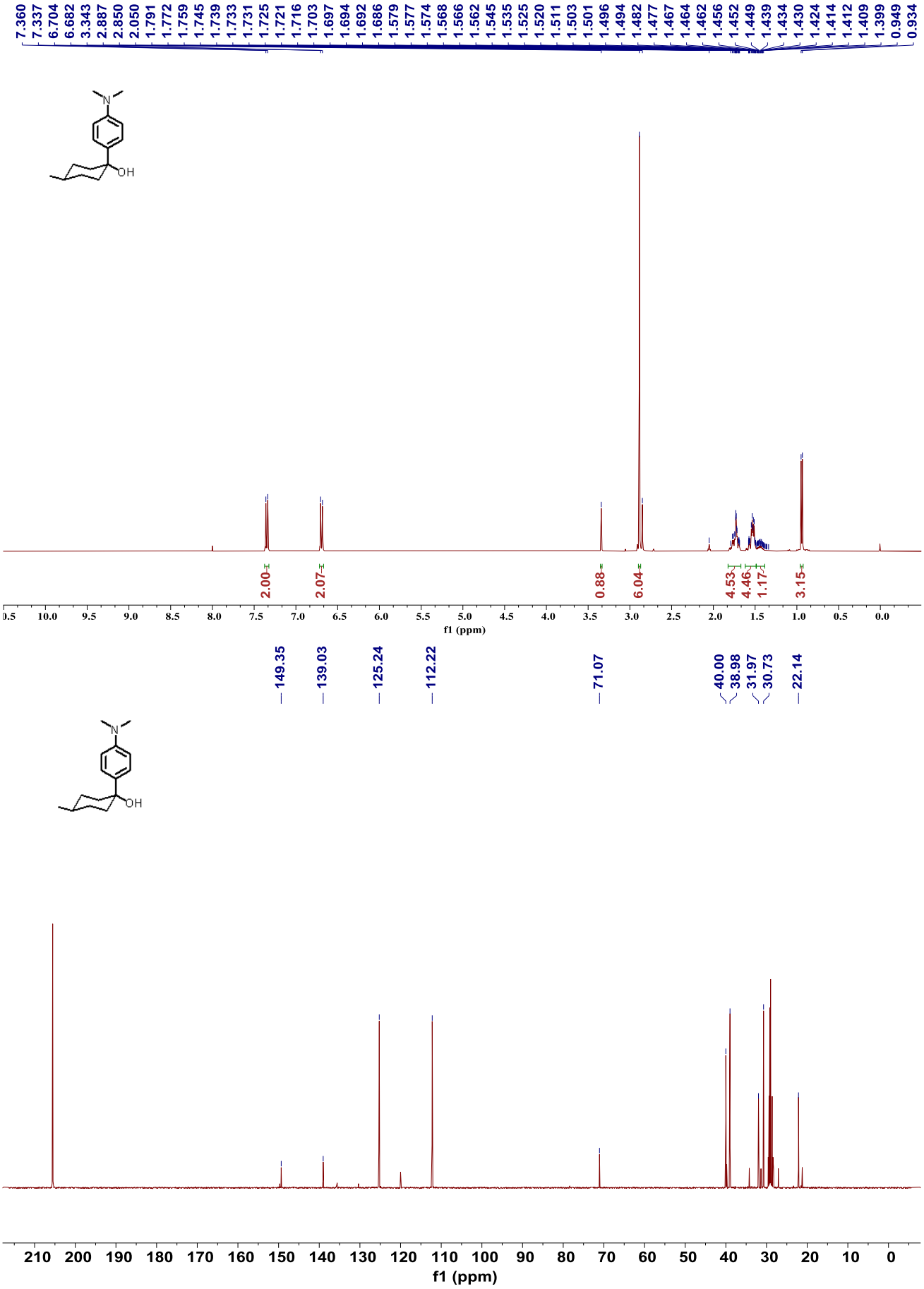

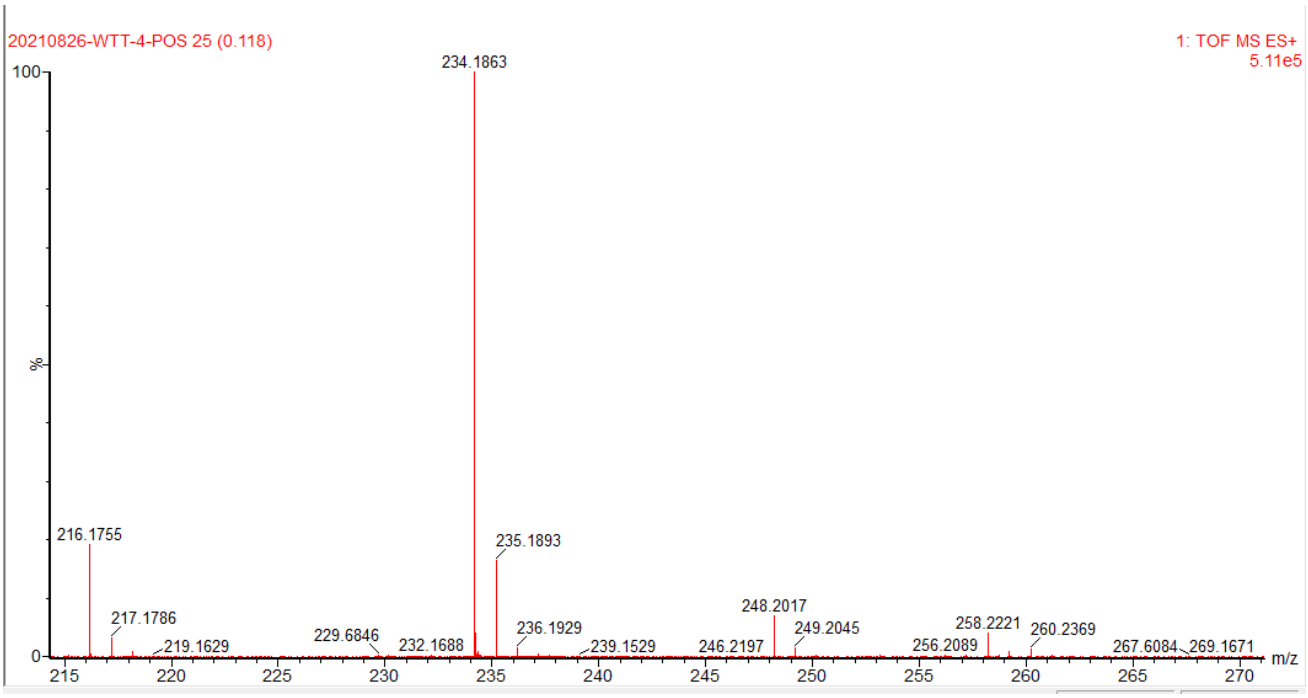
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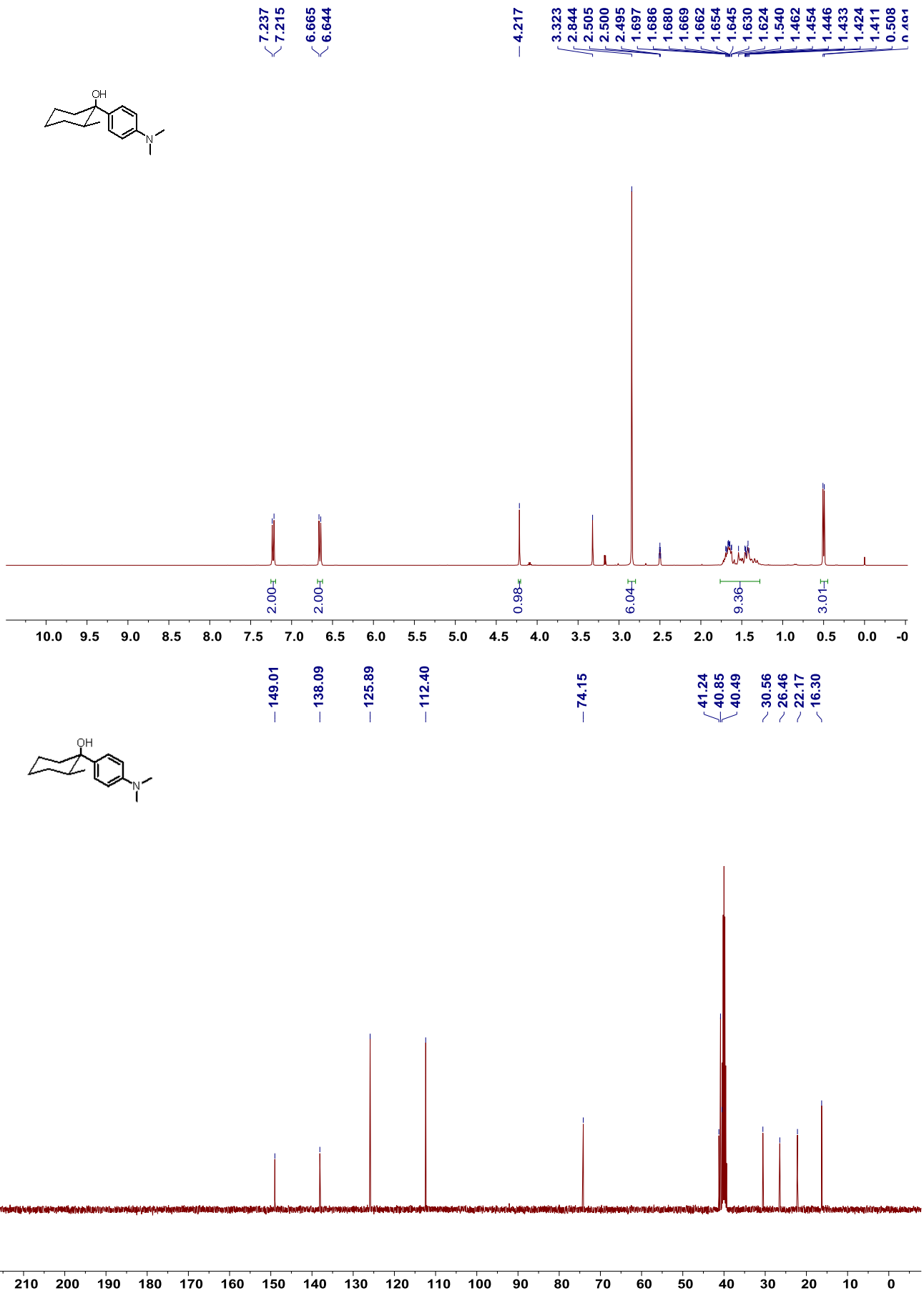

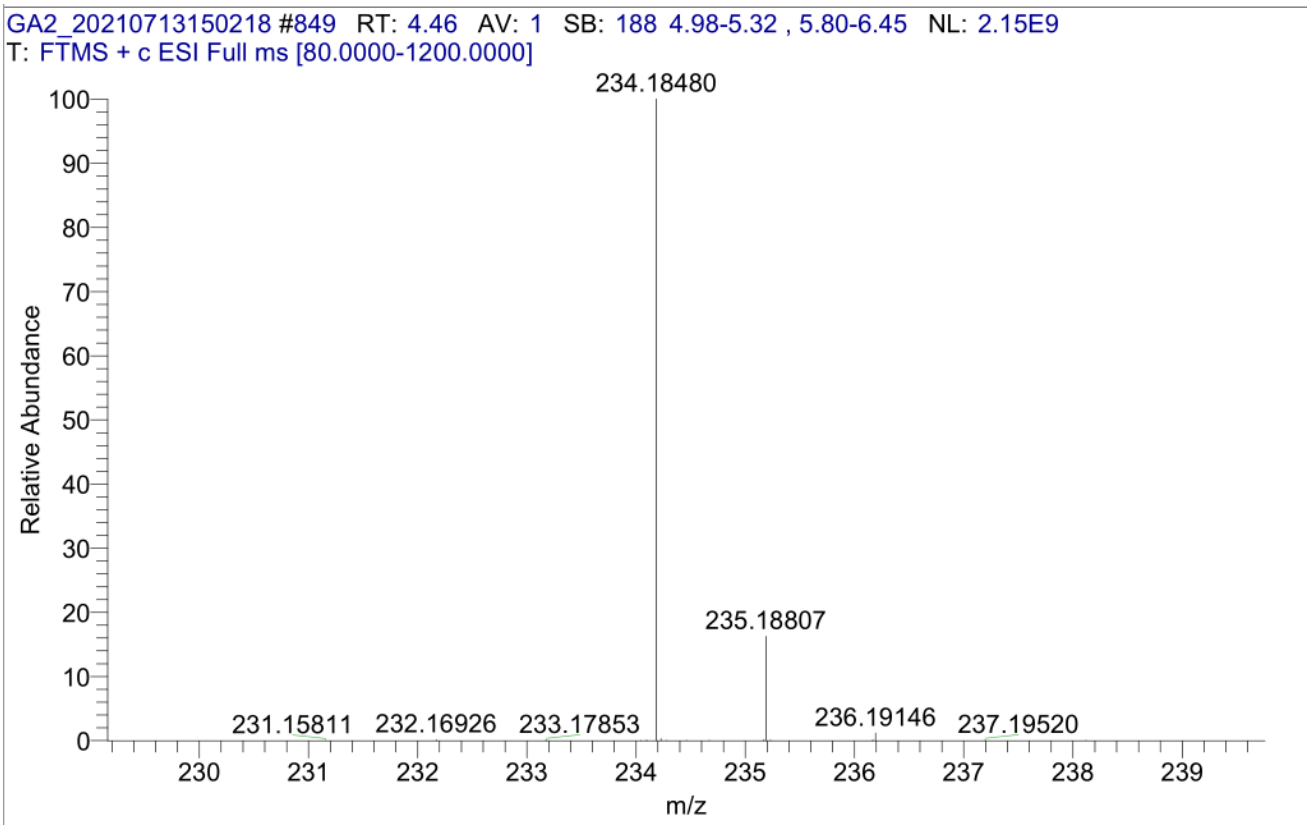
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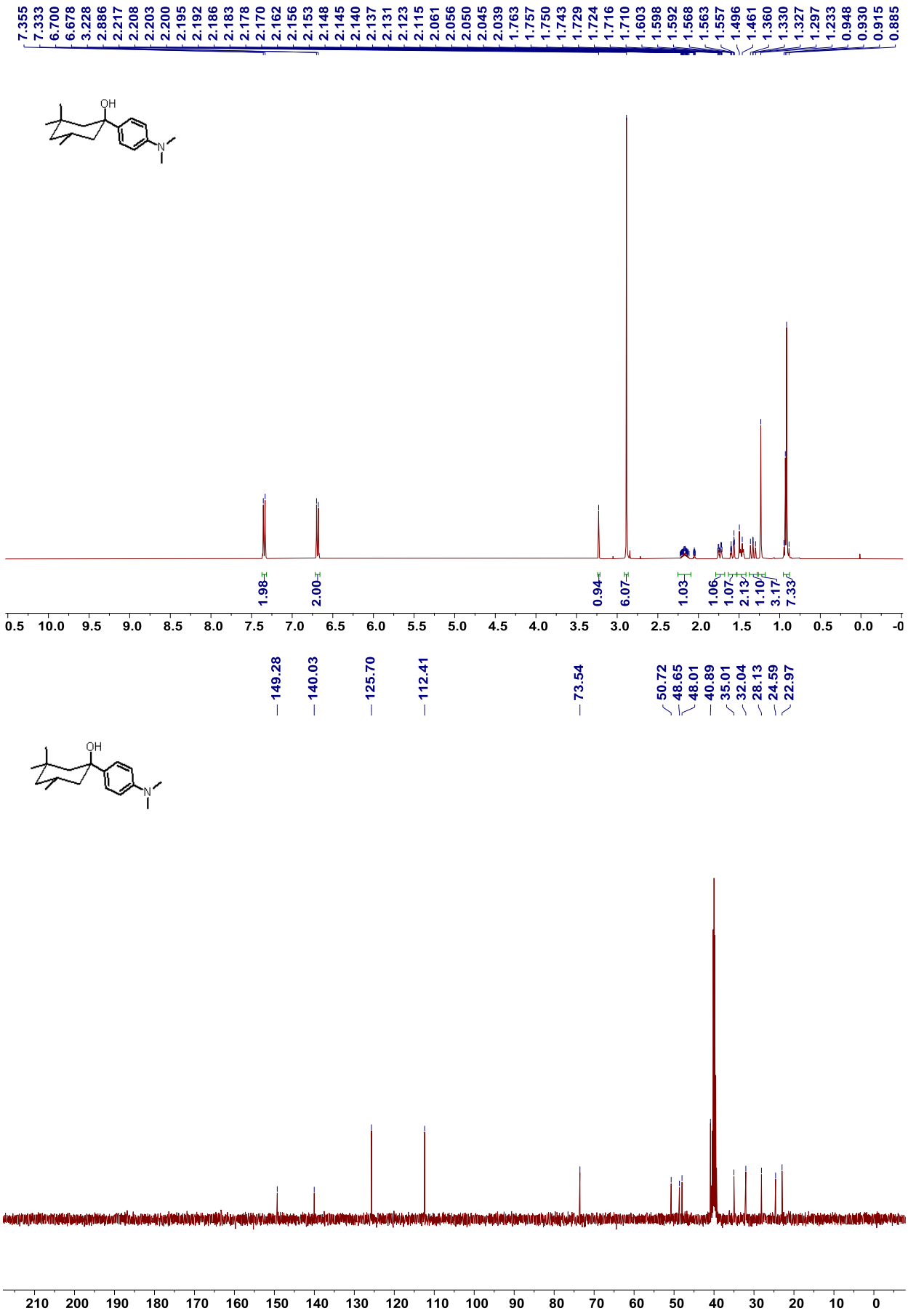

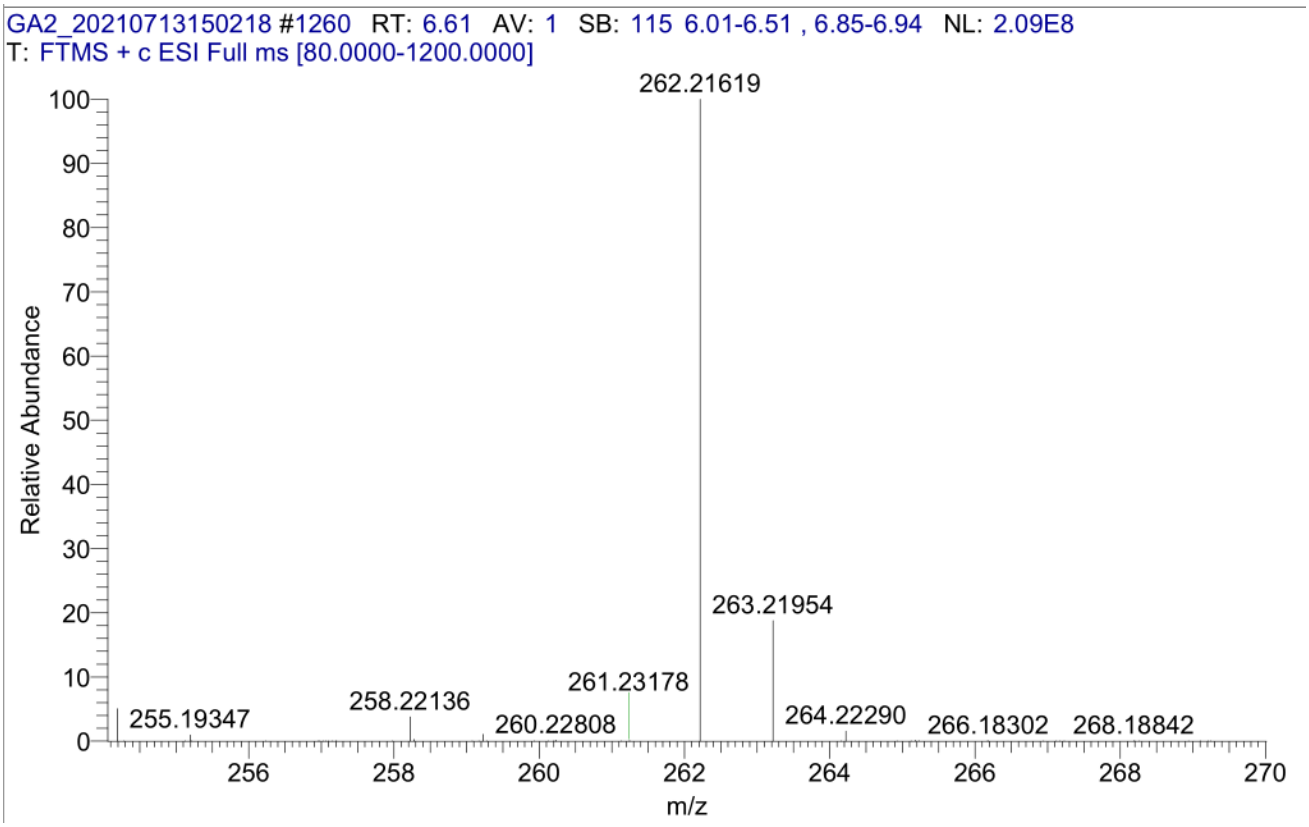
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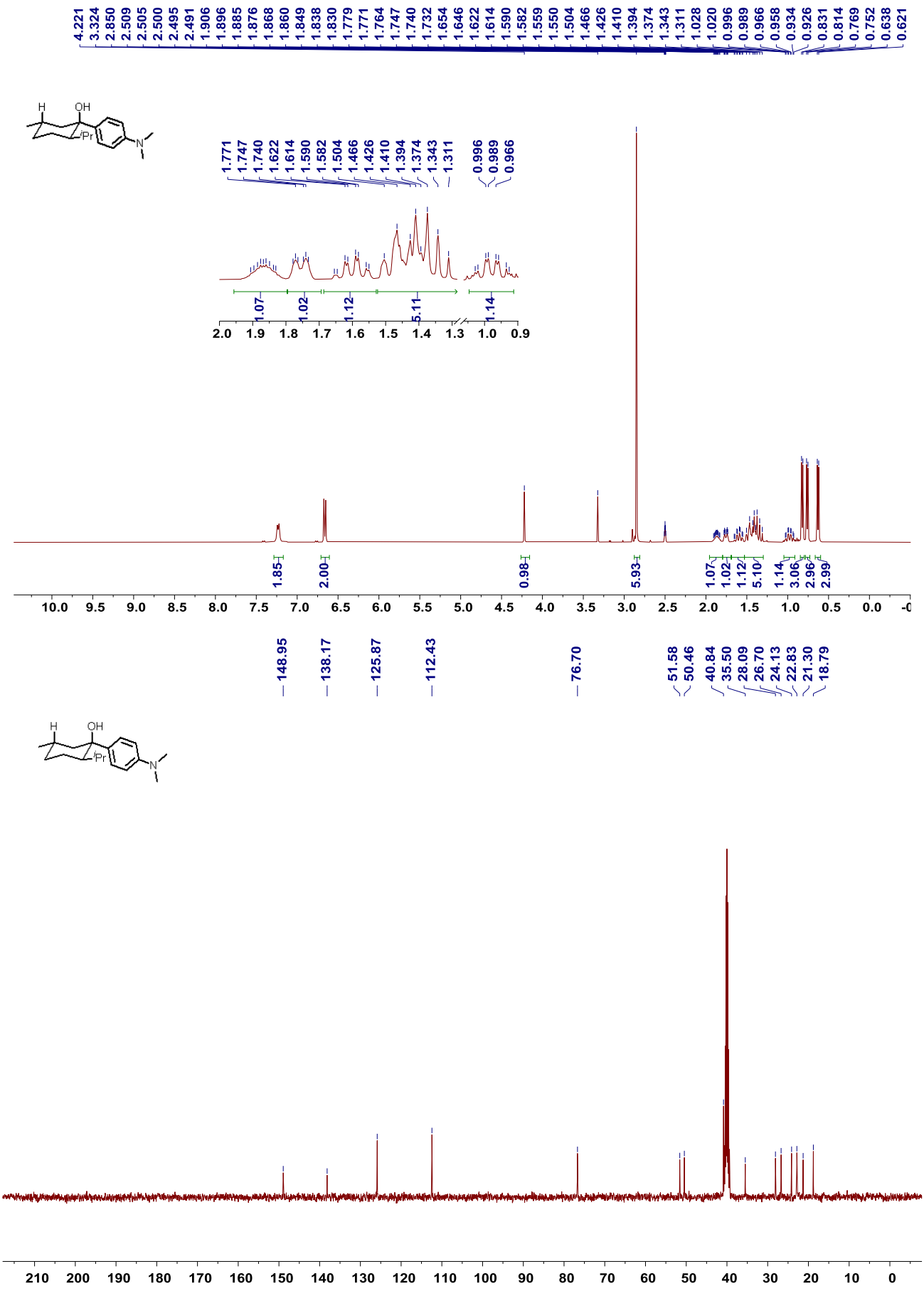
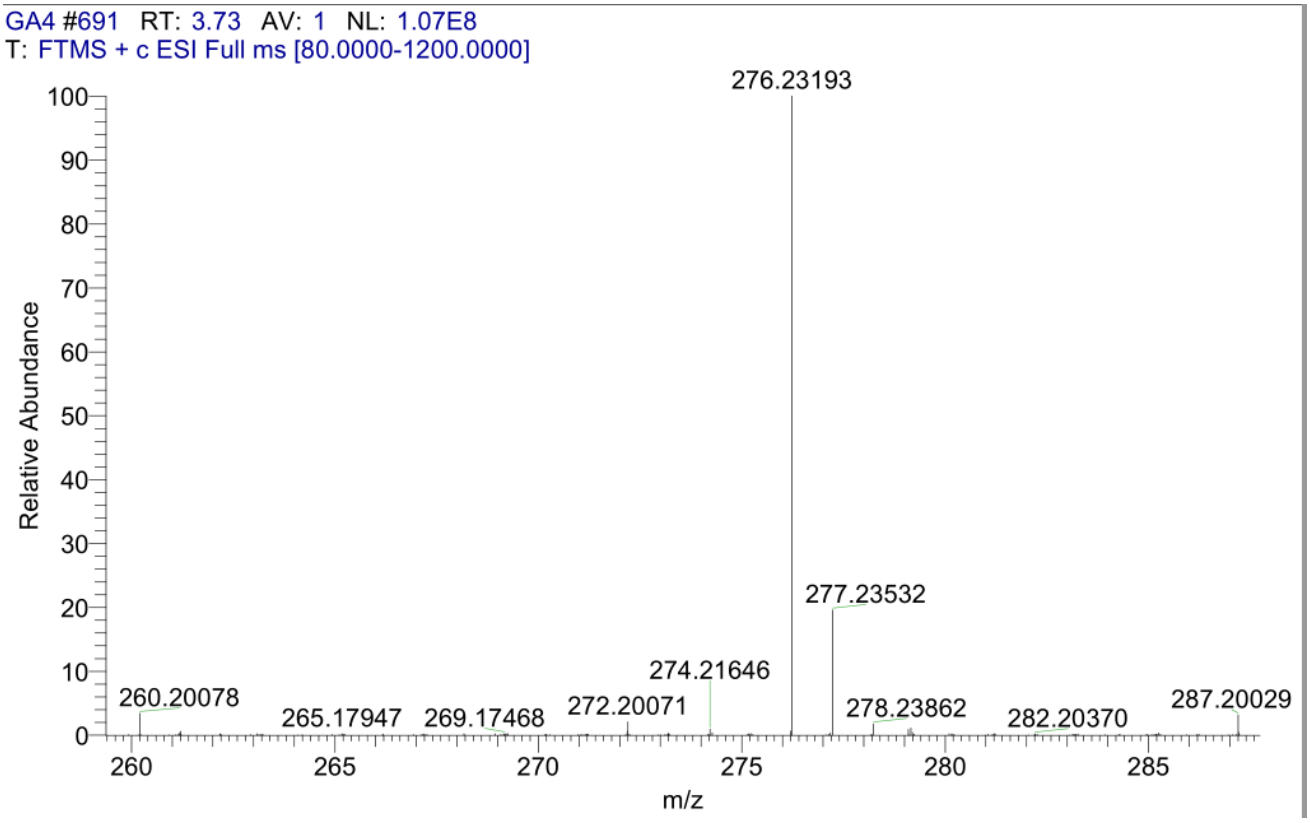
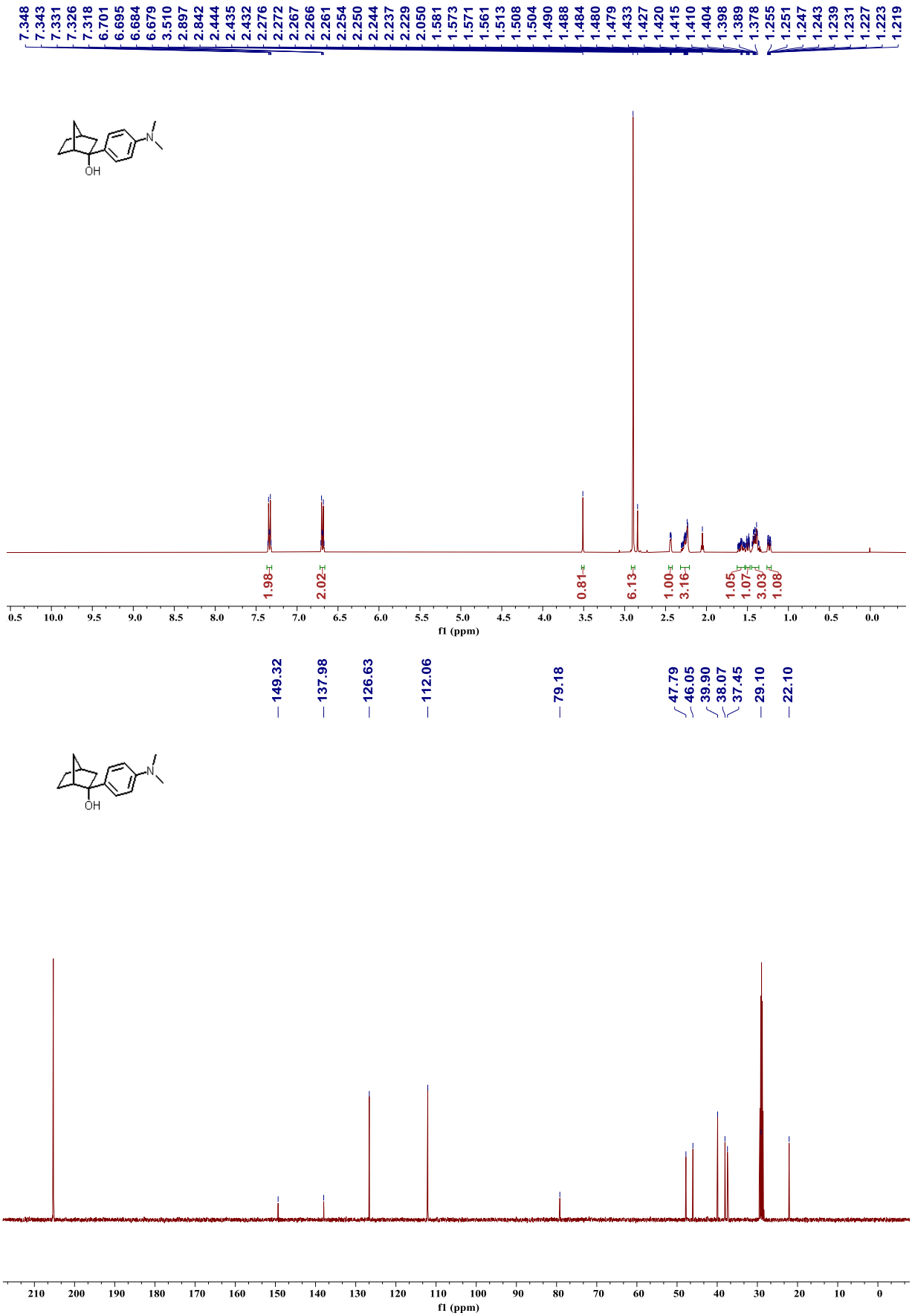
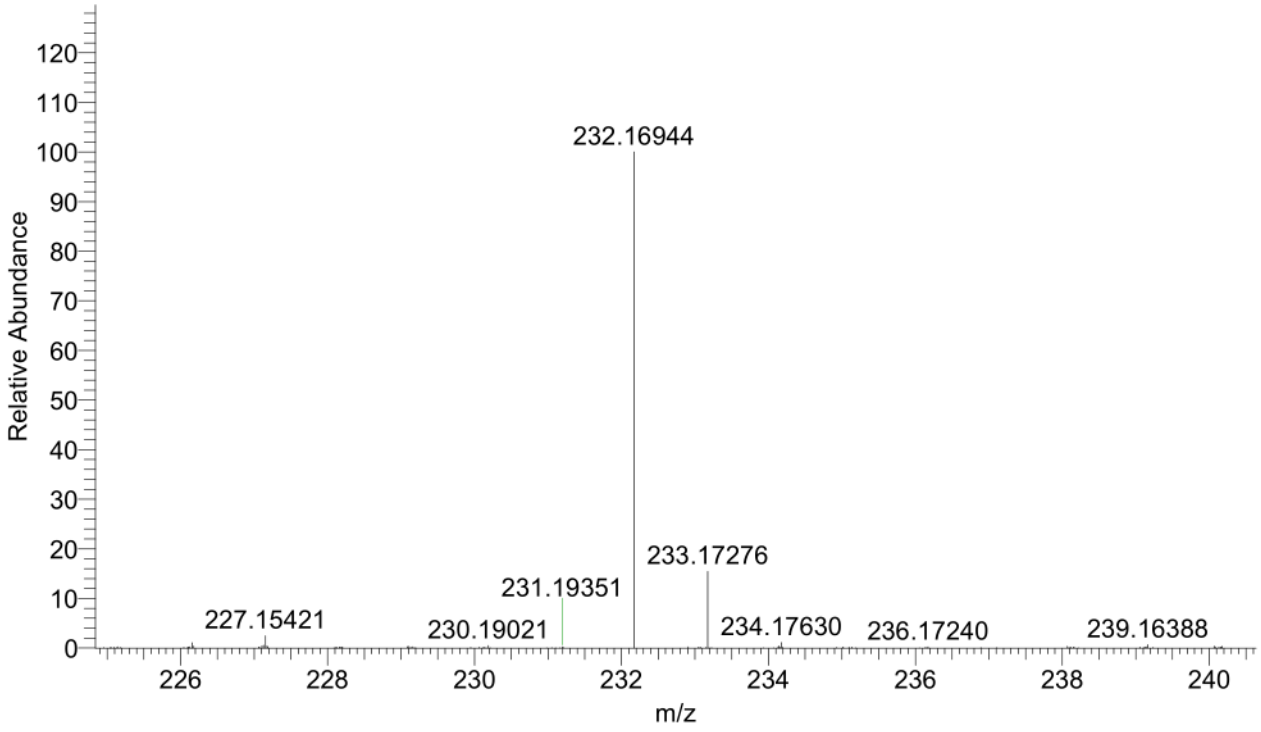



GA4 #691 RT: 3.73 AV: 1 NL: 1.07E8
T: FTMS + c ESI Full ms [80.0000-1200.0000]
276.23193
277.23532
274.21646
260.20078
265.17947
269.17468
272.20071
278.23862
282.20370
287.20029
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
260
265
270
275
280
285

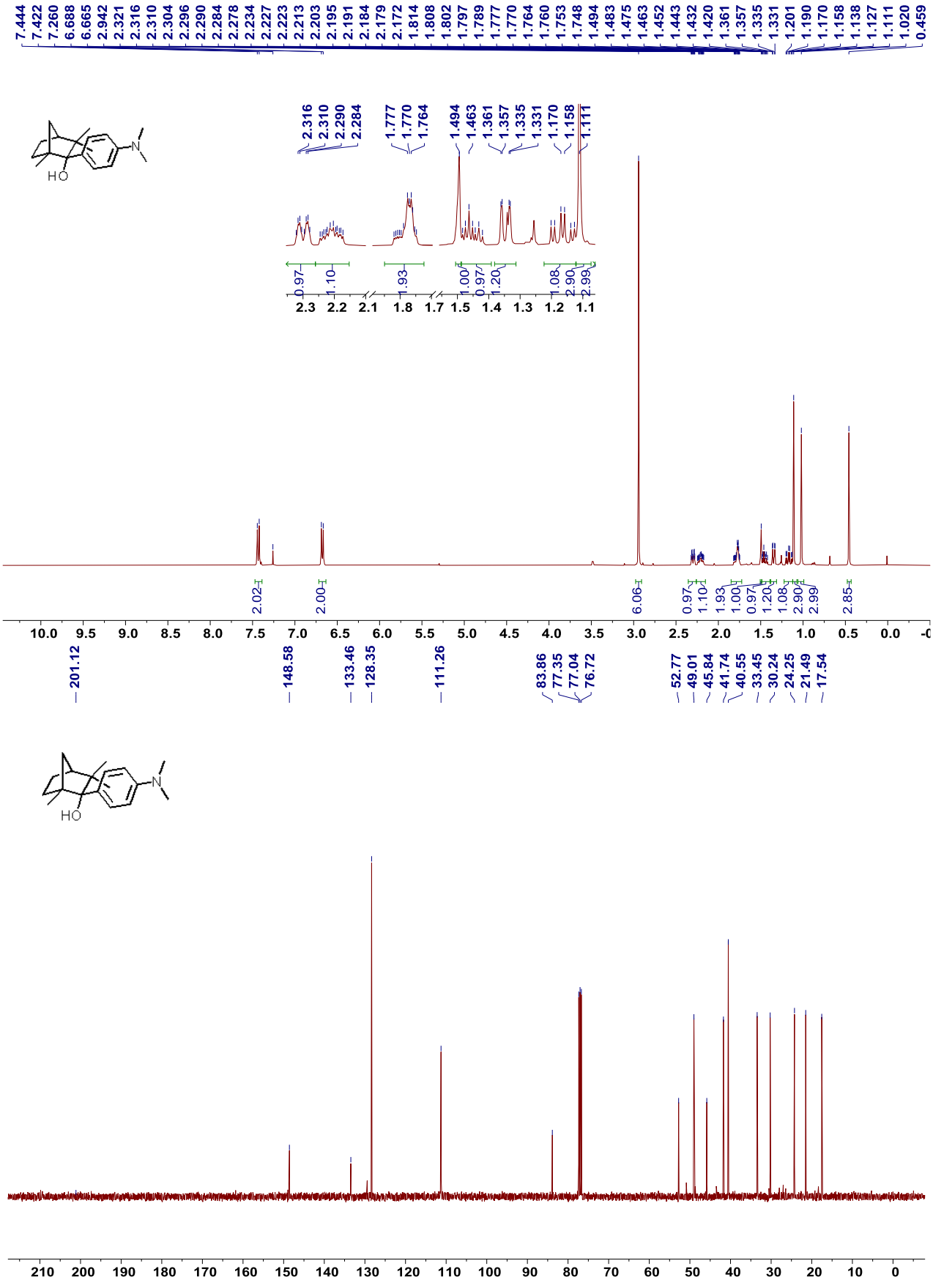
***rel*-(1*R*,2*S*,4*S*)-2-(4-(dimethylamino)phenyl)bicyclo[2.2.1]heptan-2-ol (1f)**

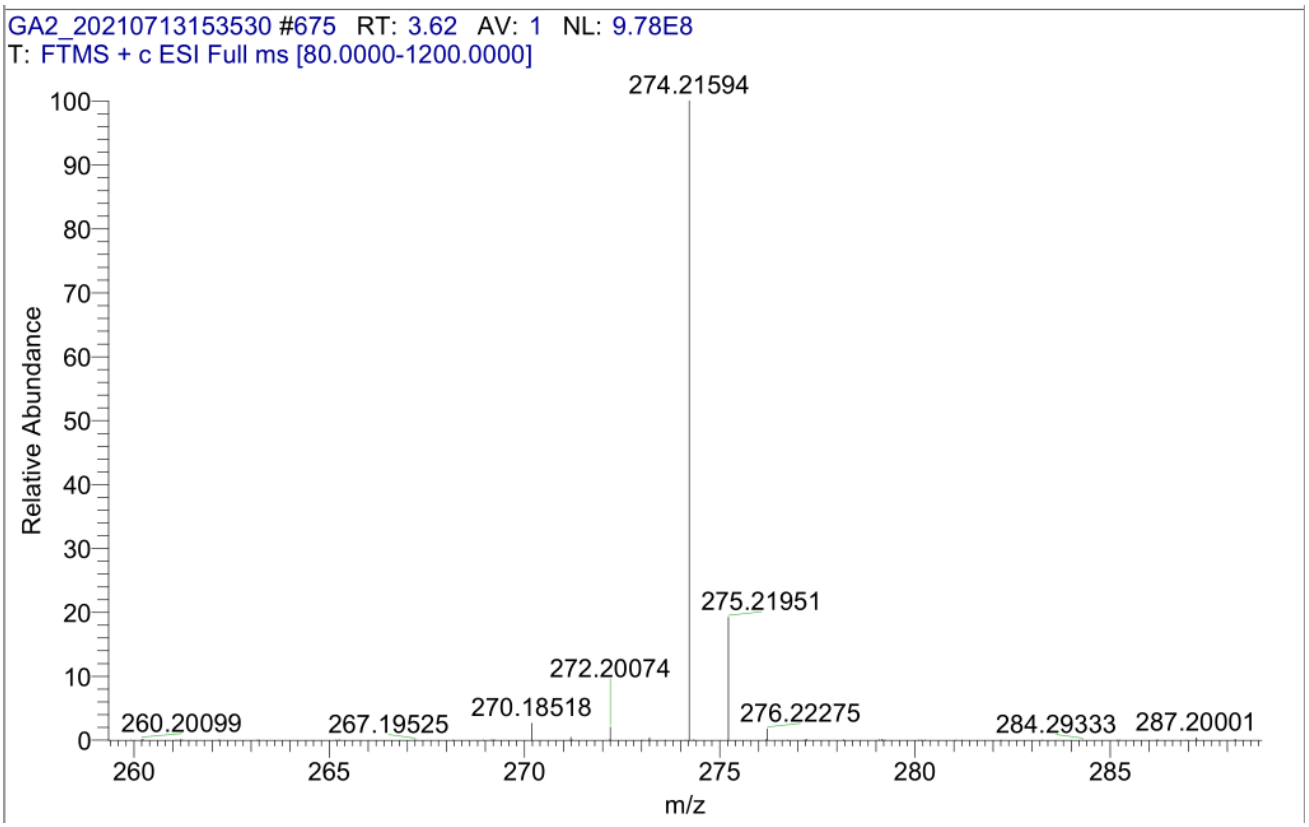


GA4 #426 RT: 2.30 AV: 1 SB: 697 1.02-2.05 , 2.53-5.25 NL: 1.46E7
T: FTMS + c ESI Full ms [80.0000-1200.0000]

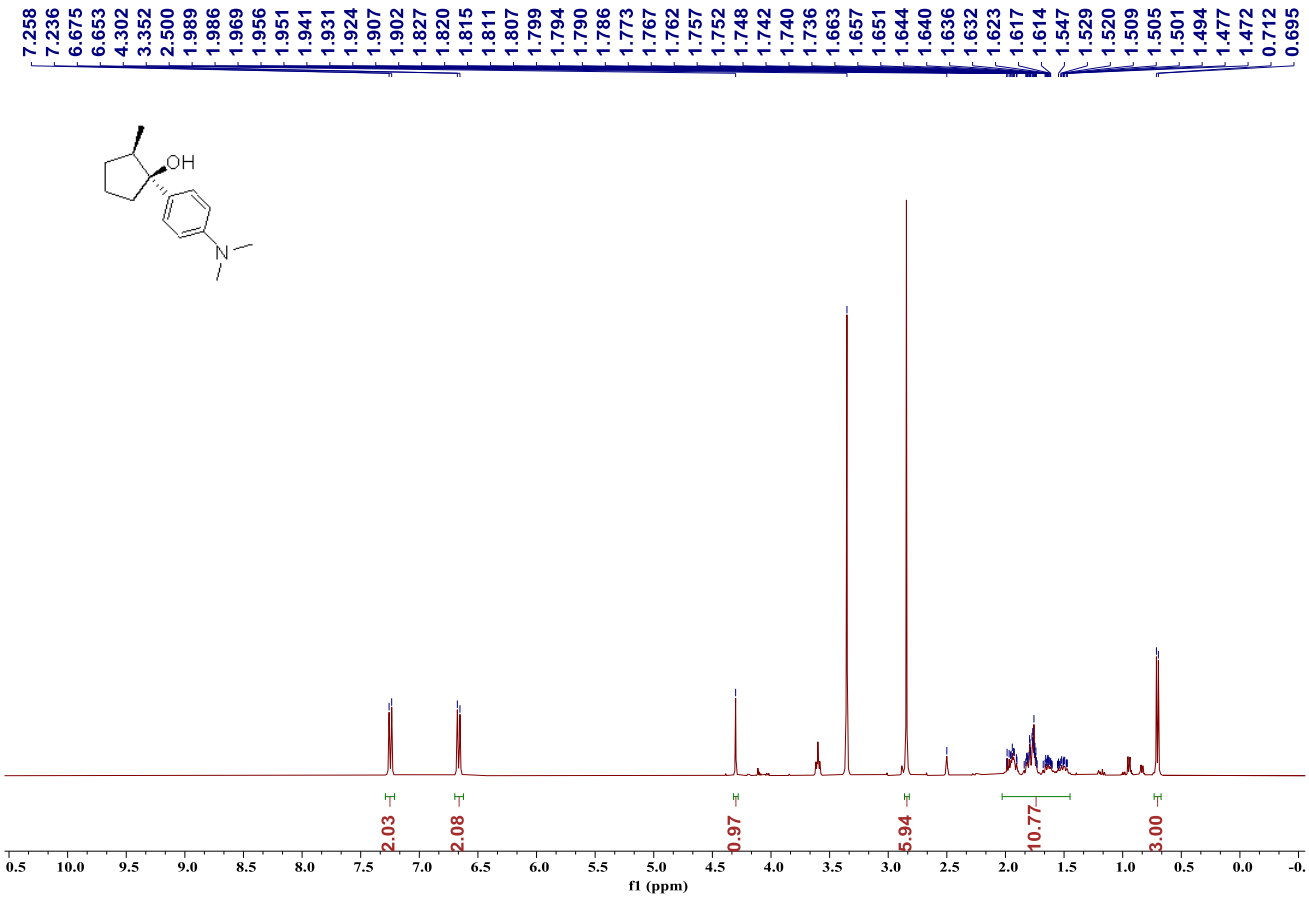


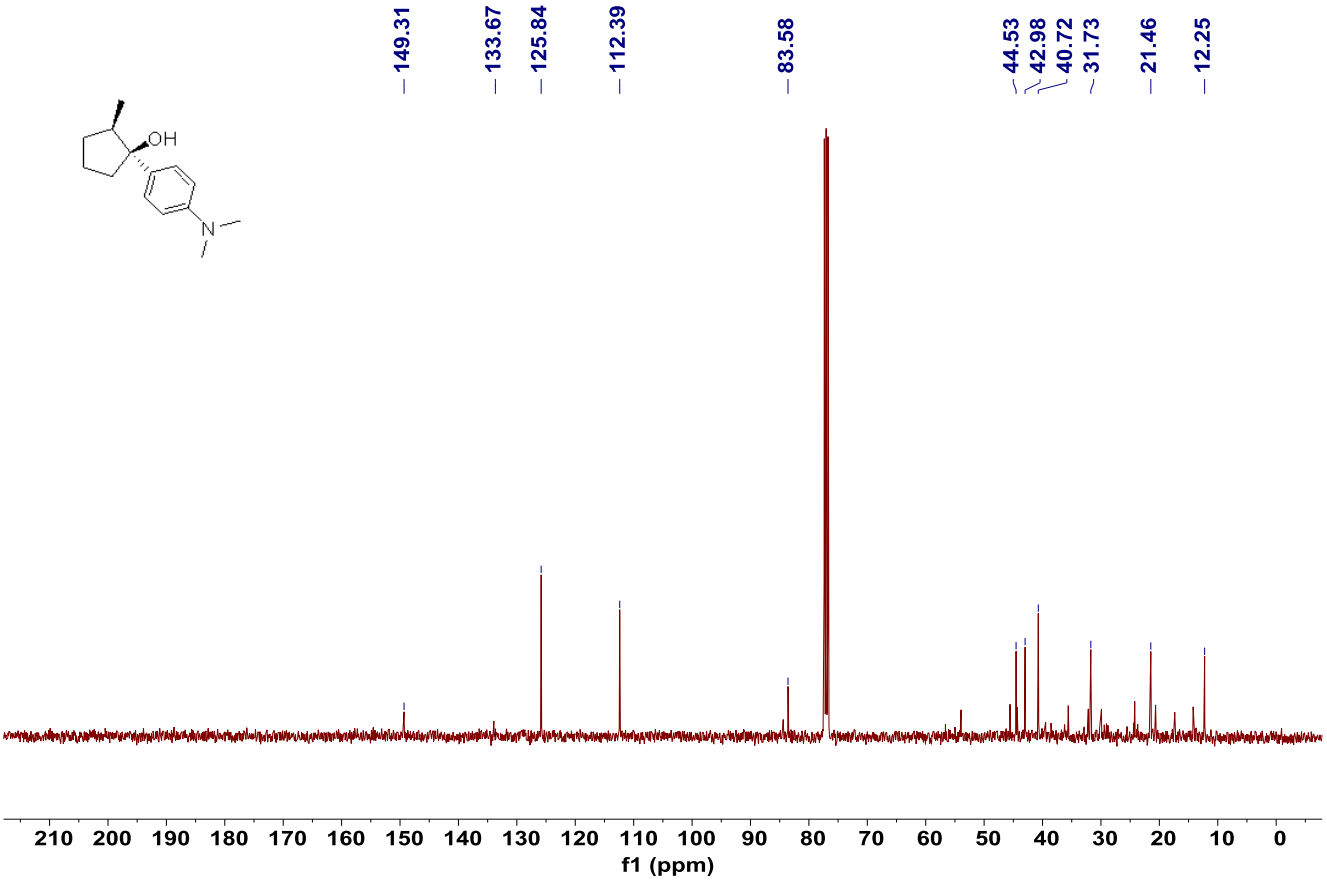
***Rel*-(*1S,2R,4S*)-2-(4-(dimethylamino)phenyl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol (1g)**

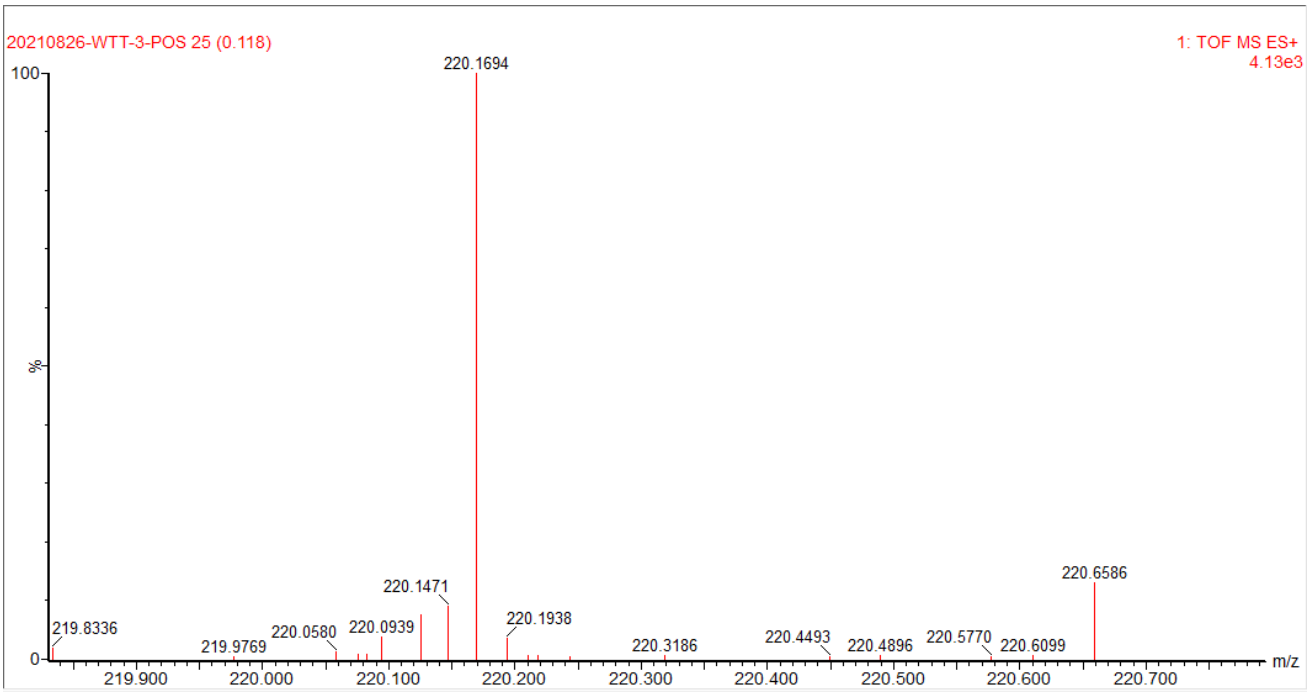



GA2_20210713153530 #675 RT: 3.62 AV: 1 NL: 9.78E8
T: FTMS + c ESI Full ms [80.0000-1200.0000]
274.21594
275.21951
272.20074
270.18518
260.20099
267.19525
276.22275
284.29333
287.20001
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
260
265
270
275
280
285

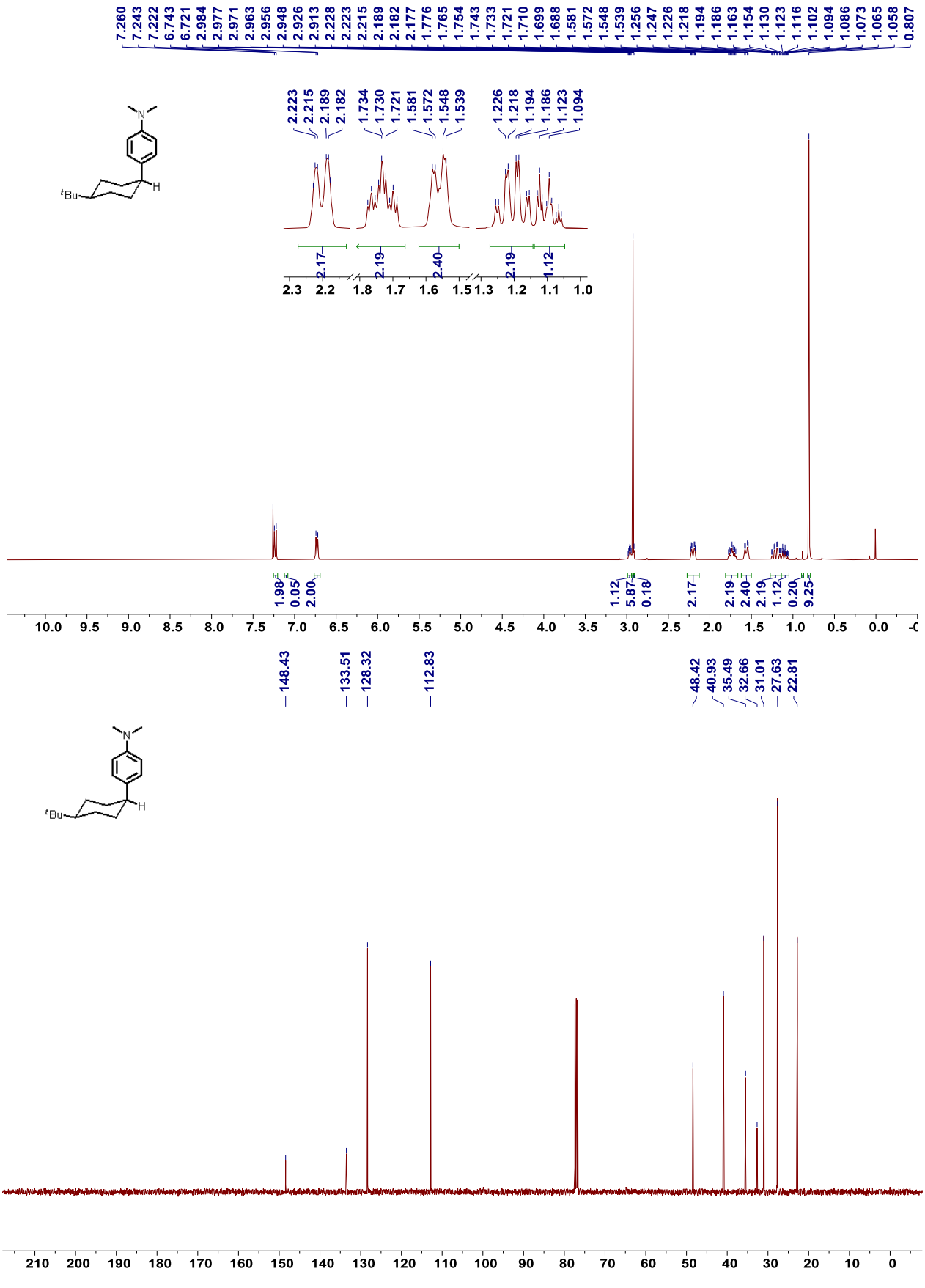
***cis*-1-(4-(dimethylamino)phenyl)-2-methylcyclopentan-1-ol (1i)**

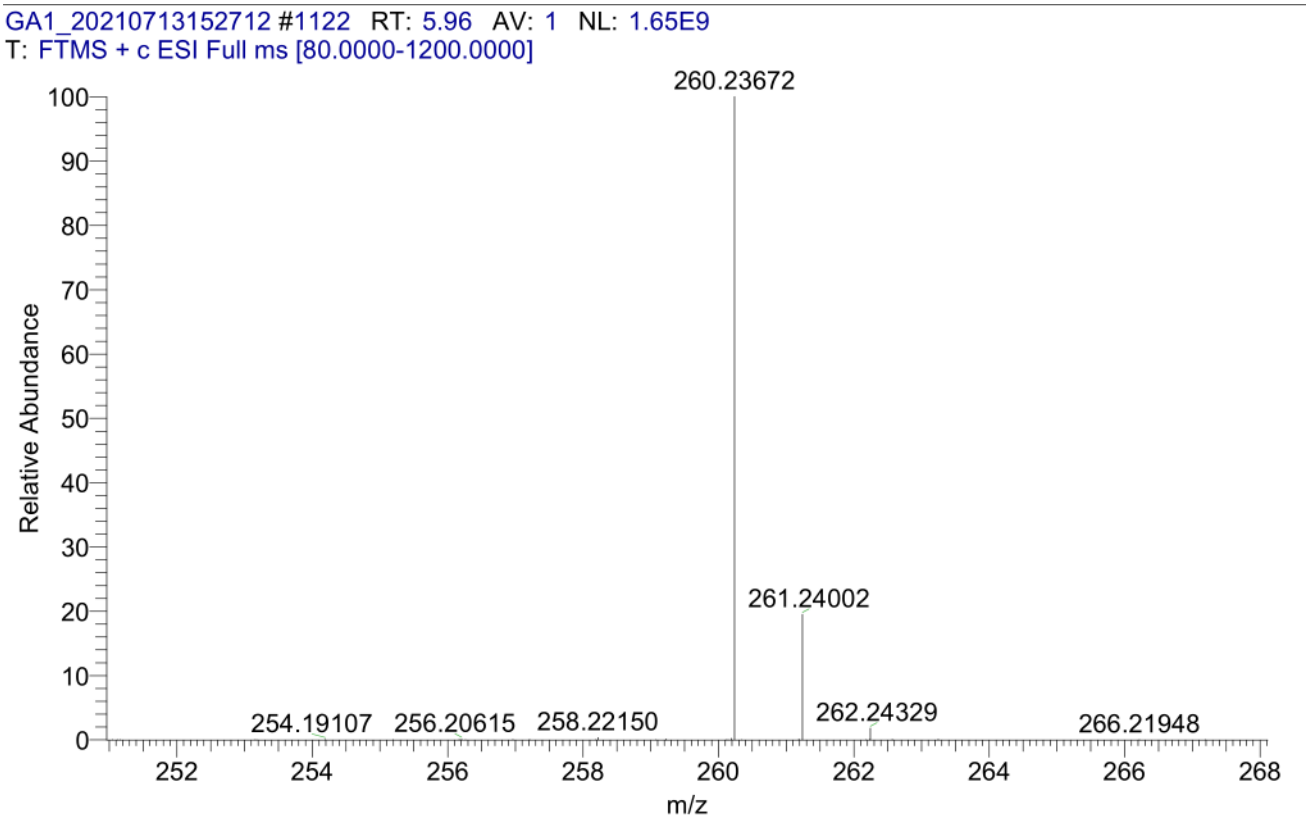




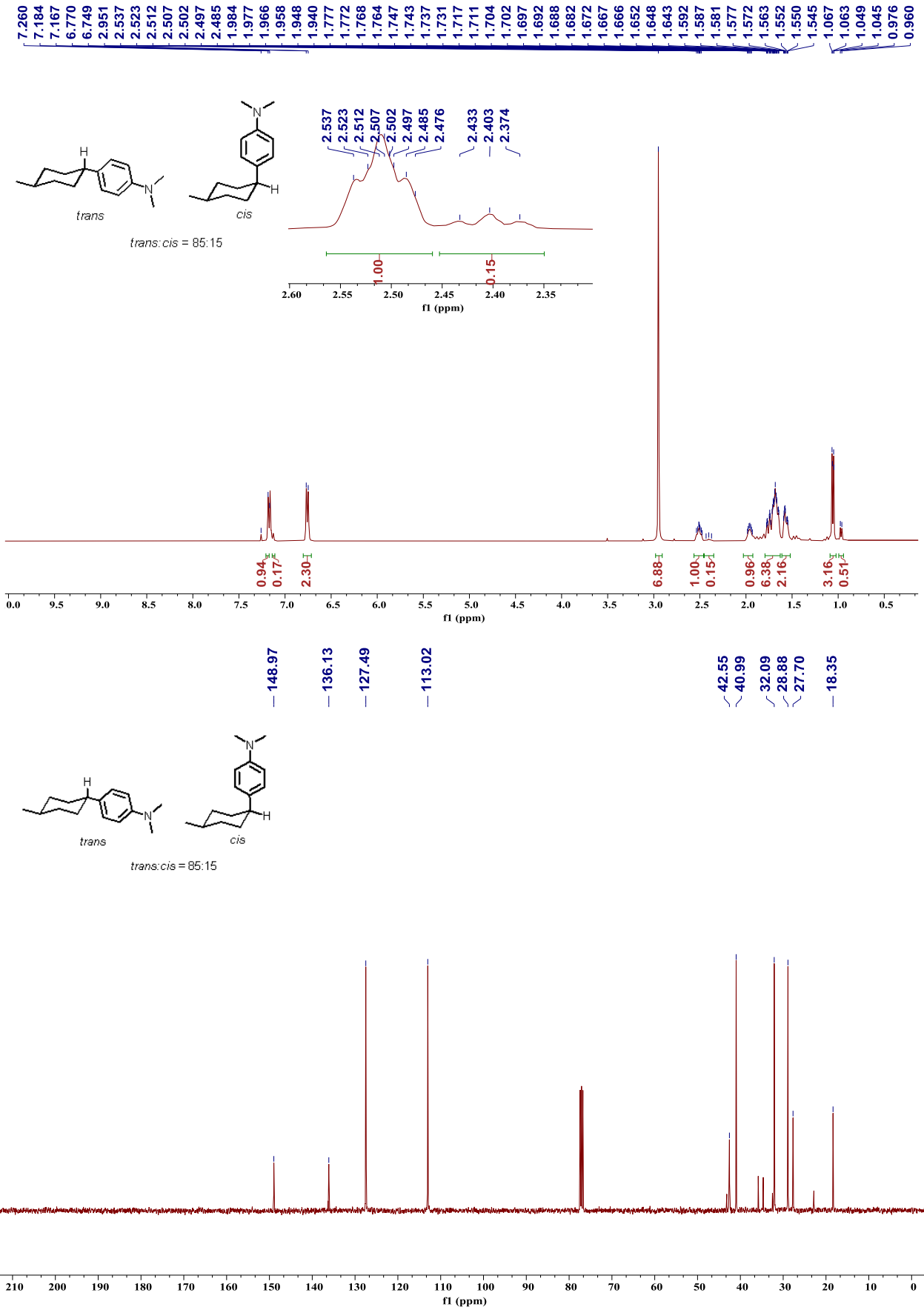

20210826-WTT-3-POS 25 (0.118)
1: TOF MS ES+
4.13e3
100
%
0
220.1694
220.6586
220.1471
220.1938
219.8336
219.9769
220.0580
220.0939
220.3186
220.4493
220.4896
220.5770
220.6099
219.900
220.000
220.100
220.200
220.300
220.400
220.500
220.600
220.700
m/z

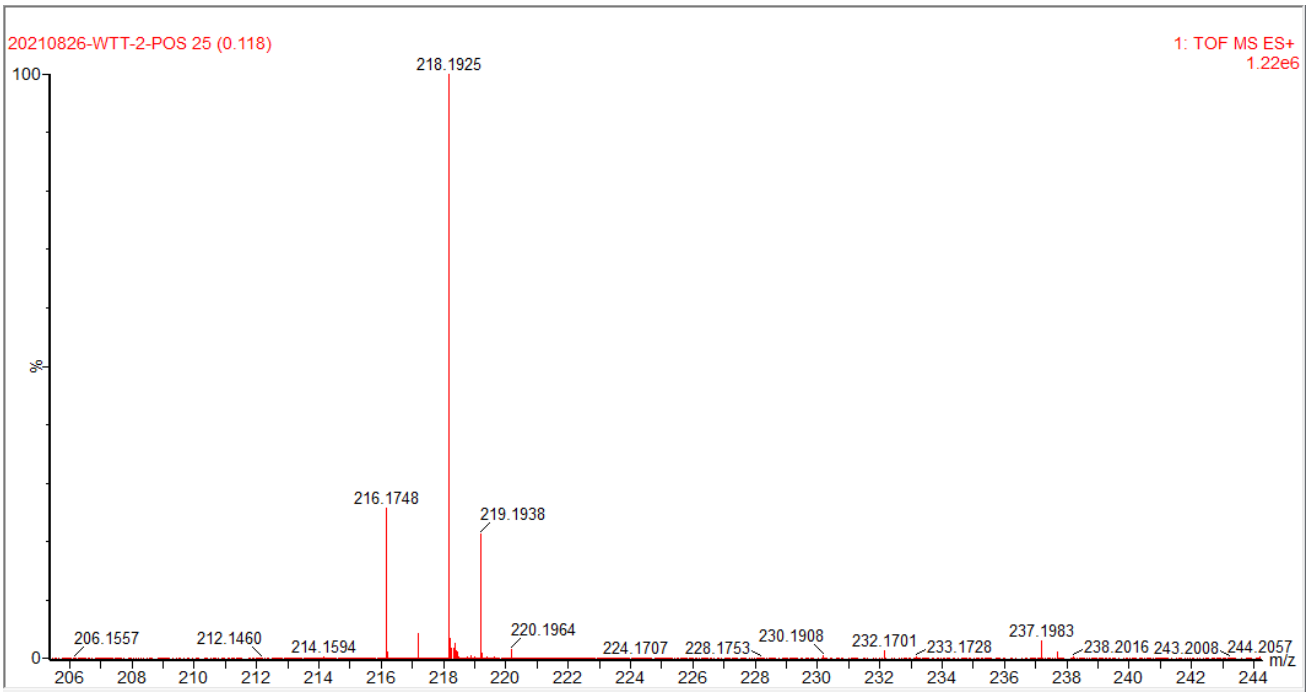
***cis*-(4-(tert-butyl)cyclohexyl)-*N,N*-dimethylaniline (*e*-4a) (mixture of 2 stereomers, *d.r.* = 98 : 2)**



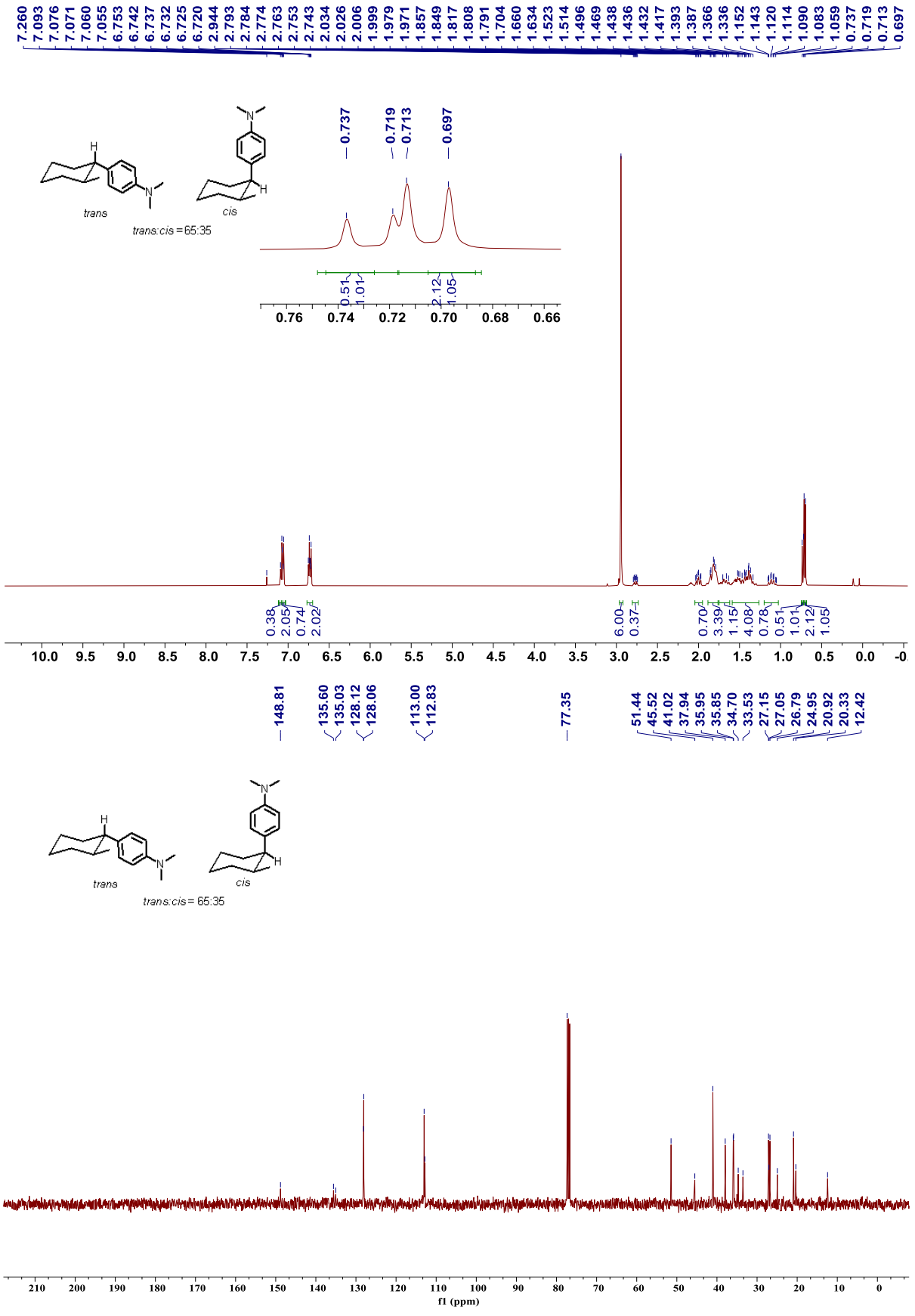

GA1_20210713152712 #1122 RT: 5.96 AV: 1 NL: 1.65E9
T: FTMS + c ESI Full ms [80.0000-1200.0000]
260.23672
261.24002
254.19107
256.20615
258.22150
262.24329
266.21948
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
252
254
256
258
260
262
264
266
268

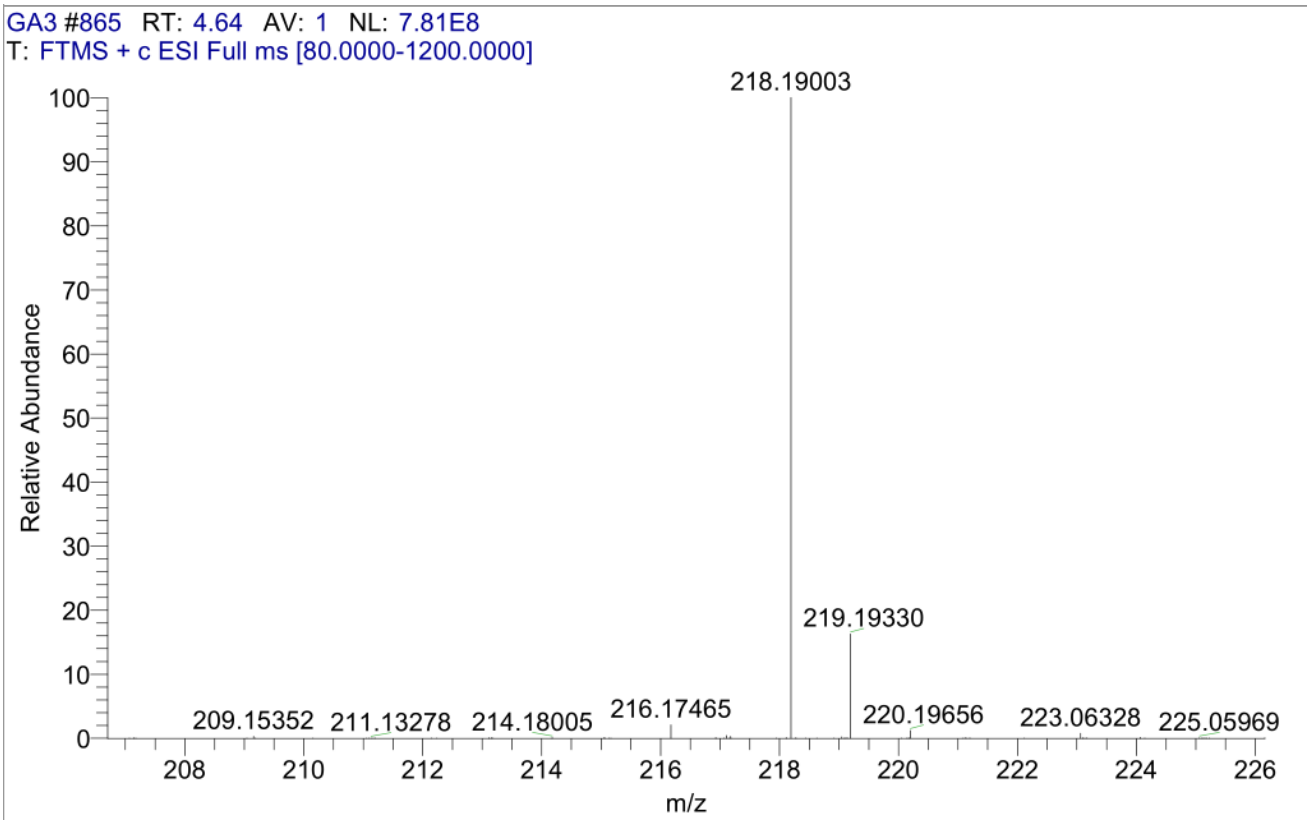
***cis*-*N*,*N*-dimethyl-4-(4-methylcyclohexyl)aniline (*e*-4b) (mixture of 2 stereomers, *d.r.* = 85 : 15)**



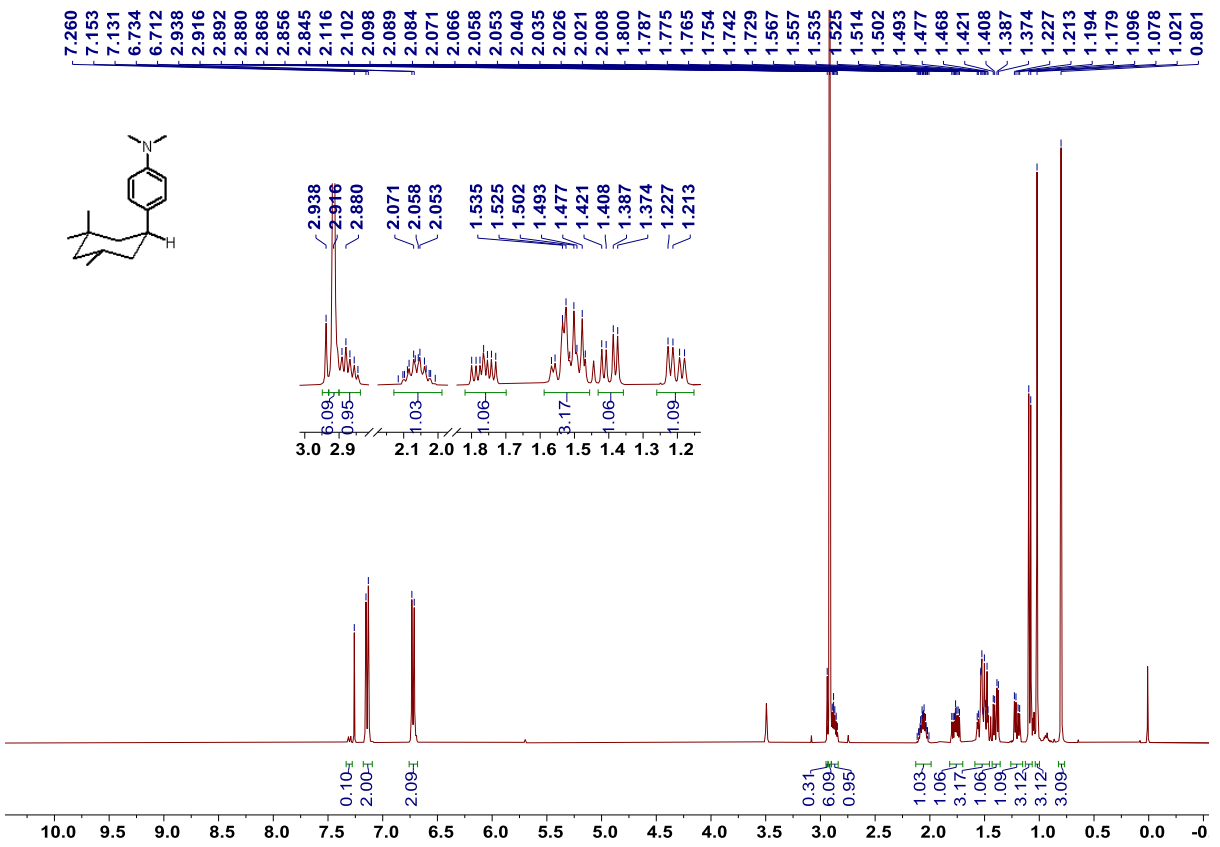

20210826-WTT-2-POS 25 (0.118)
1: TOF MS ES+
1.22e6
100
%
0
218.1925
216.1748
219.1938
206.1557
212.1460
214.1594
220.1964
224.1707
228.1753
230.1908
232.1701
233.1728
237.1983
238.2016
243.2008
244.2057
m/z
206
208
210
212
214
216
218
220
222
224
226
228
230
232
234
236
238
240
242
244

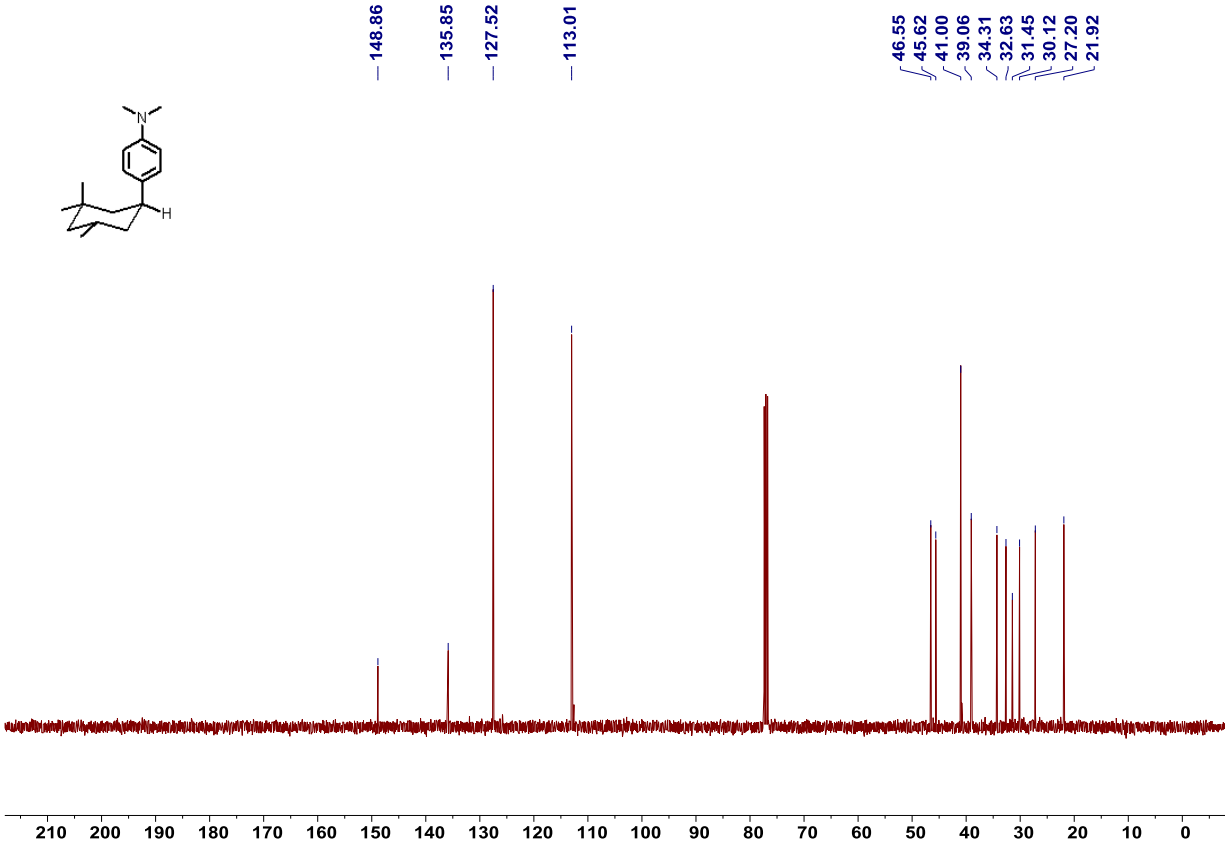
***trans*-*N*,*N*-dimethyl-4-(2-methylcyclohexyl)aniline (*a*-5c) (mixture of 2 stereomers, *d.r.* = 65 : 35)**

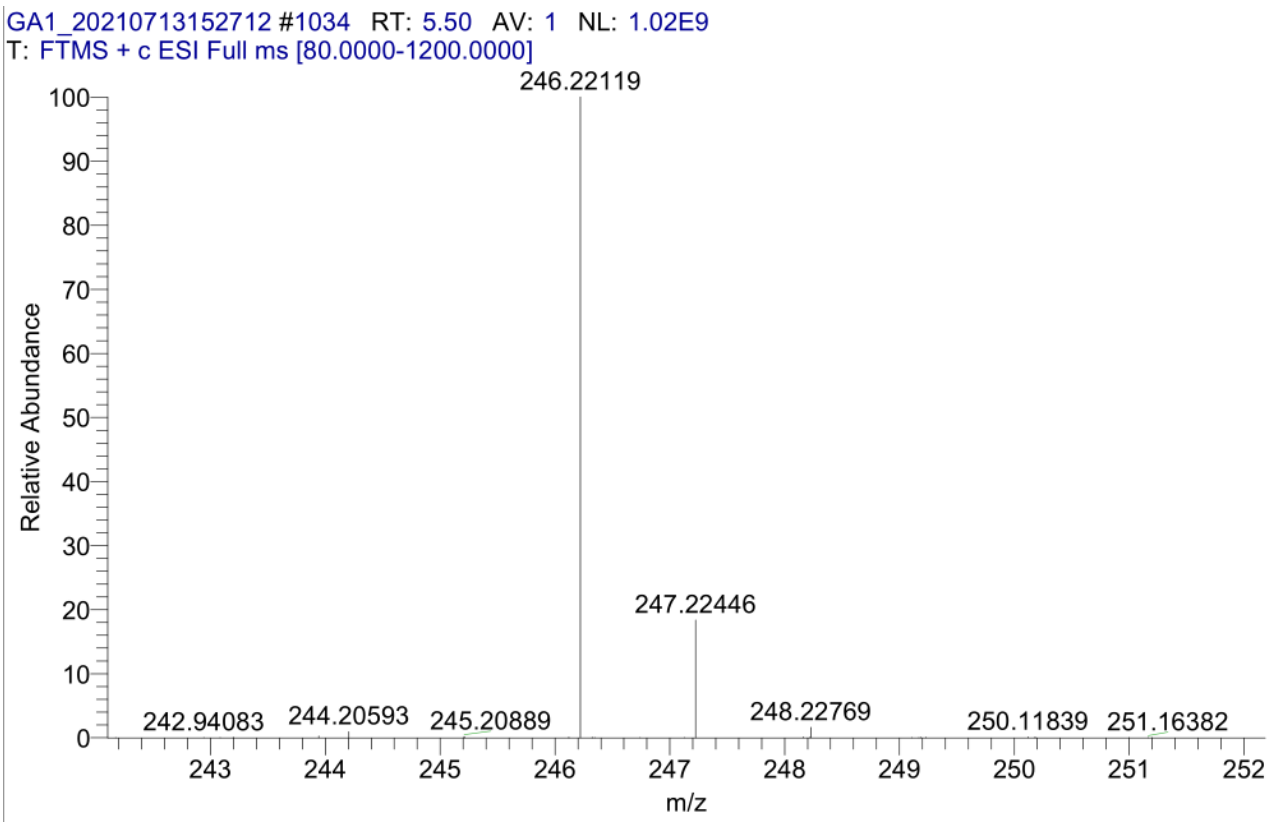



GA3 #865 RT: 4.64 AV: 1 NL: 7.81E8
T: FTMS + c ESI Full ms [80.0000-1200.0000]
218.19003
219.19330
209.15352
211.13278
214.18005
216.17465
220.19656
223.06328
225.05969
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
208
210
212
214
216
218
220
222
224
226

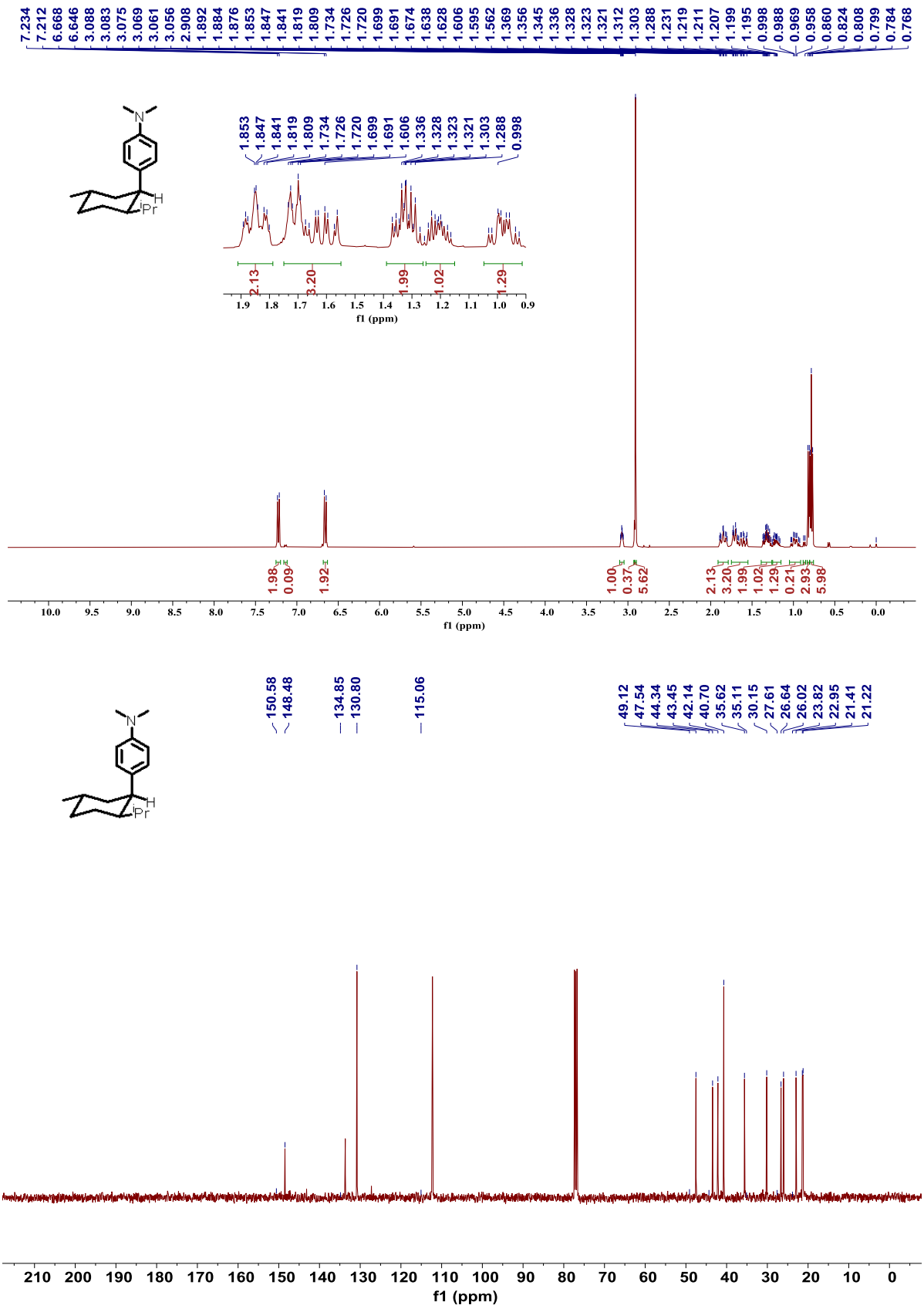
***1,5-trans-N,N*-dimethyl-4-(3,3,5-trimethylcyclohexyl)aniline (*e*-4d) (mixture of 2 stereomers, *d.r.* = 95 : 5)**

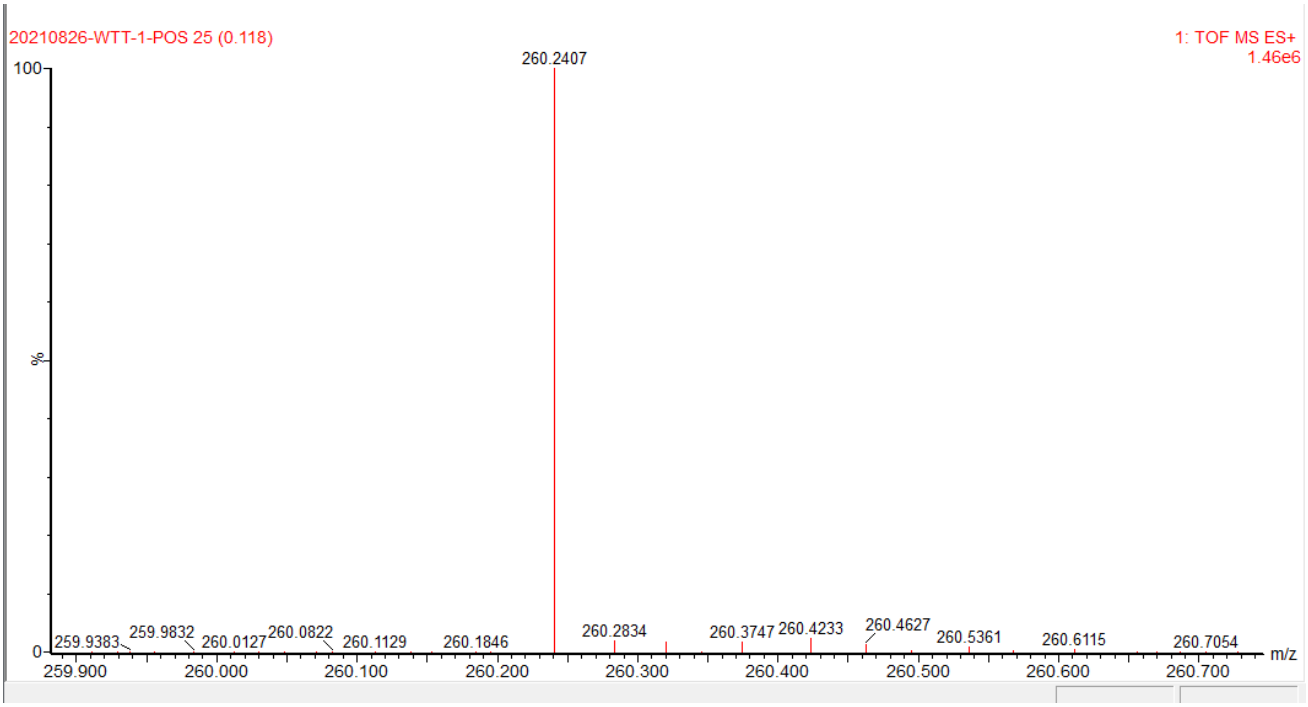




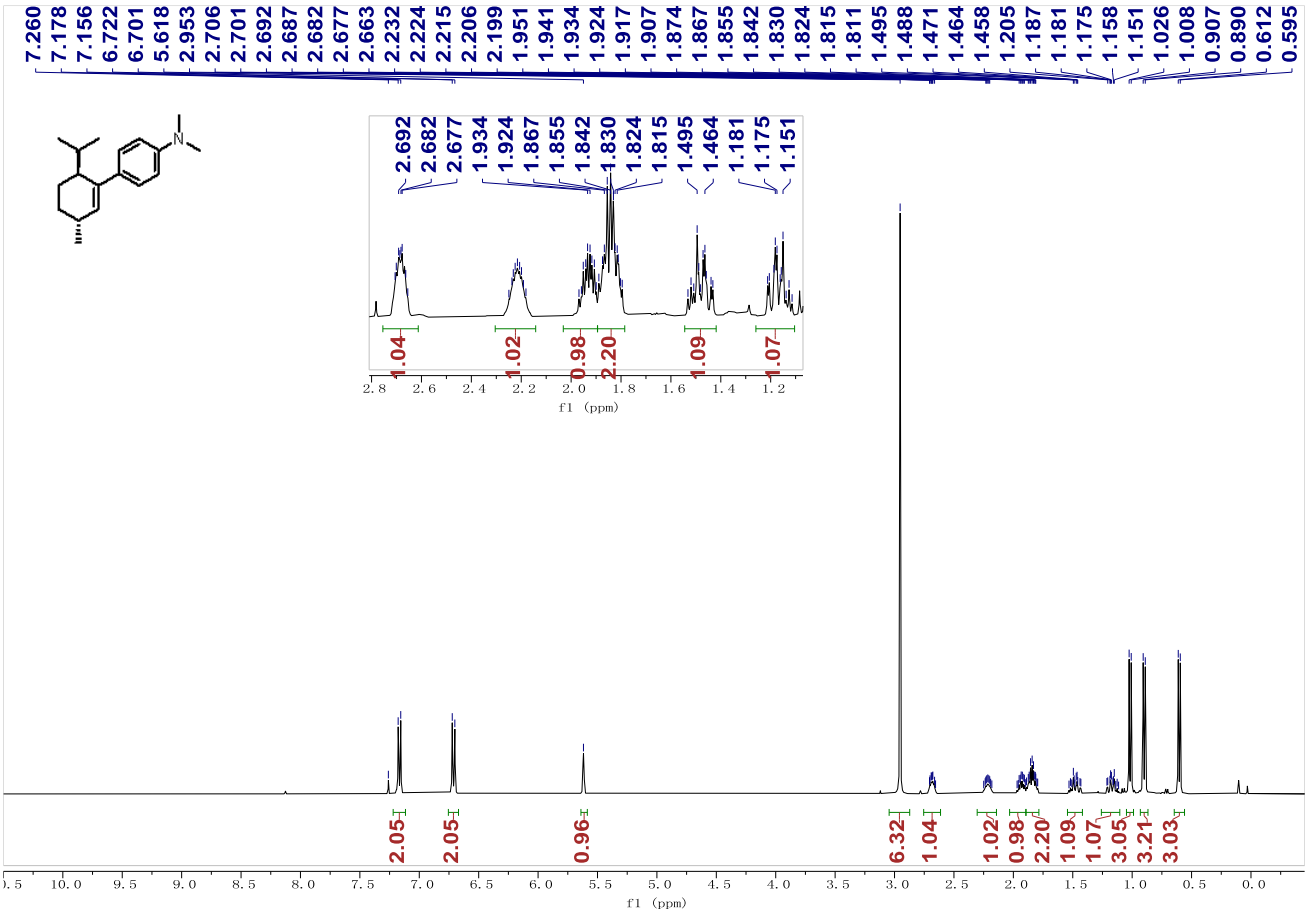

GA1_20210713152712 #1034 RT: 5.50 AV: 1 NL: 1.02E9
T: FTMS + c ESI Full ms [80.0000-1200.0000]
246.22119
247.22446
242.94083
244.20593
245.20889
248.22769
250.11839
251.16382
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
243
244
245
246
247
248
249
250
251
252

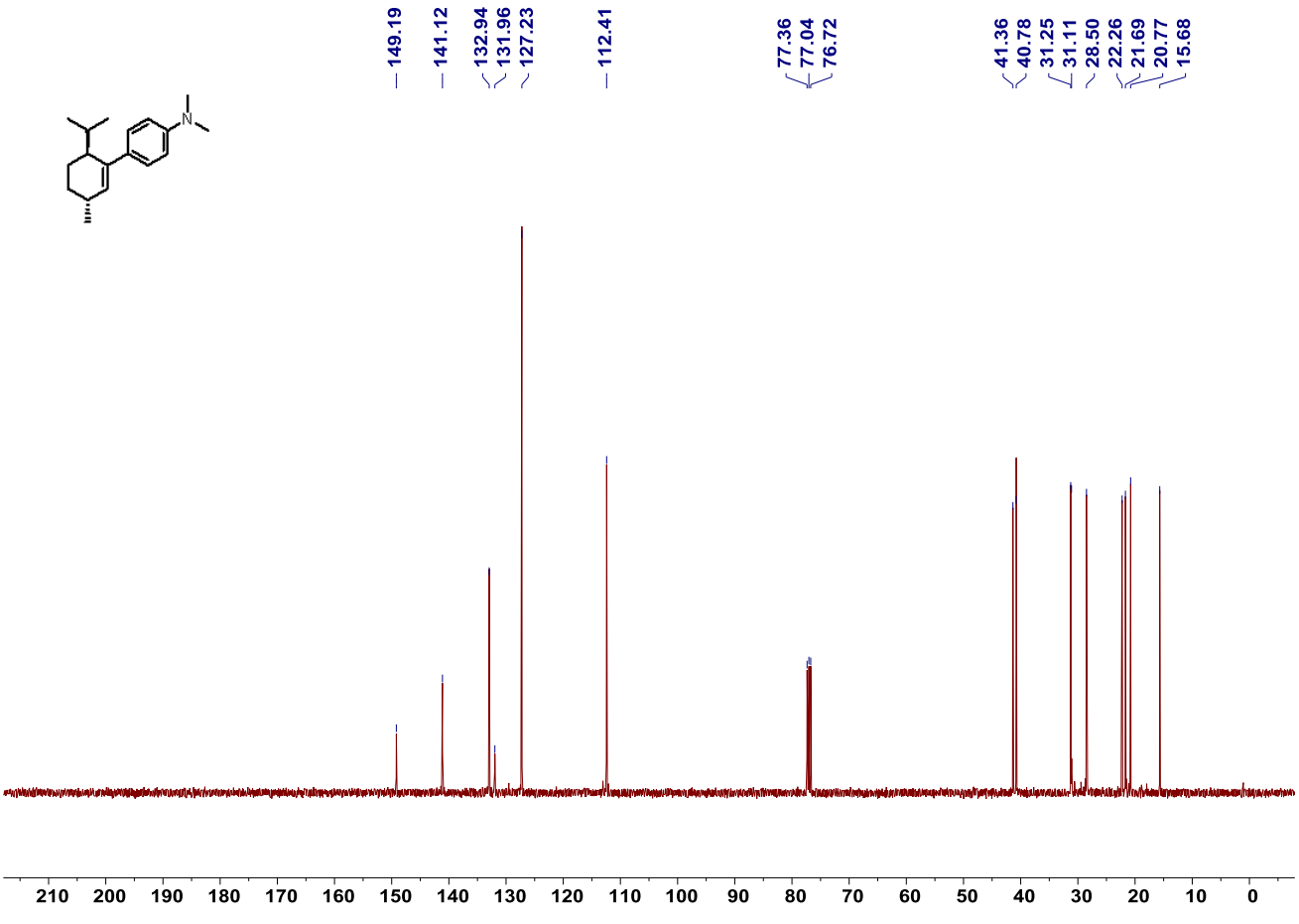
1,2-*cis*-1,5-*trans*-2-isopropyl-5-methylcyclohexyl)-*N, N*-dimethylaniline (*e*-4e) (mixture of 2 stereomers, *d.r.* = 94 : 6)

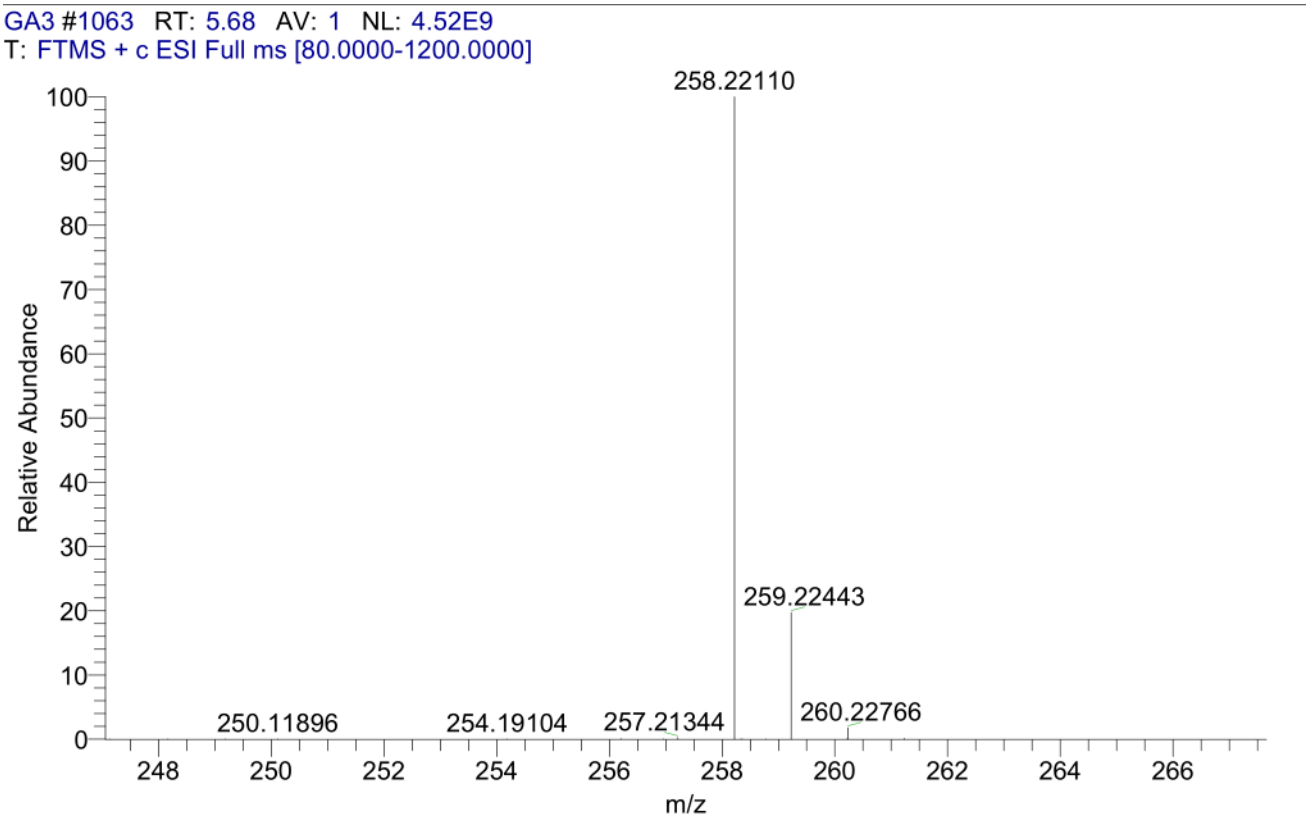



20210826-WTT-1-POS 25 (0.118)
1: TOF MS ES+
1.46e6
100
%
0
260.2407
259.9383
259.9832
260.0127
260.0822
260.1129
260.1846
260.2834
260.3747
260.4233
260.4627
260.5361
260.6115
260.7054
m/z
259.900
260.000
260.100
260.200
260.300
260.400
260.500
260.600
260.700

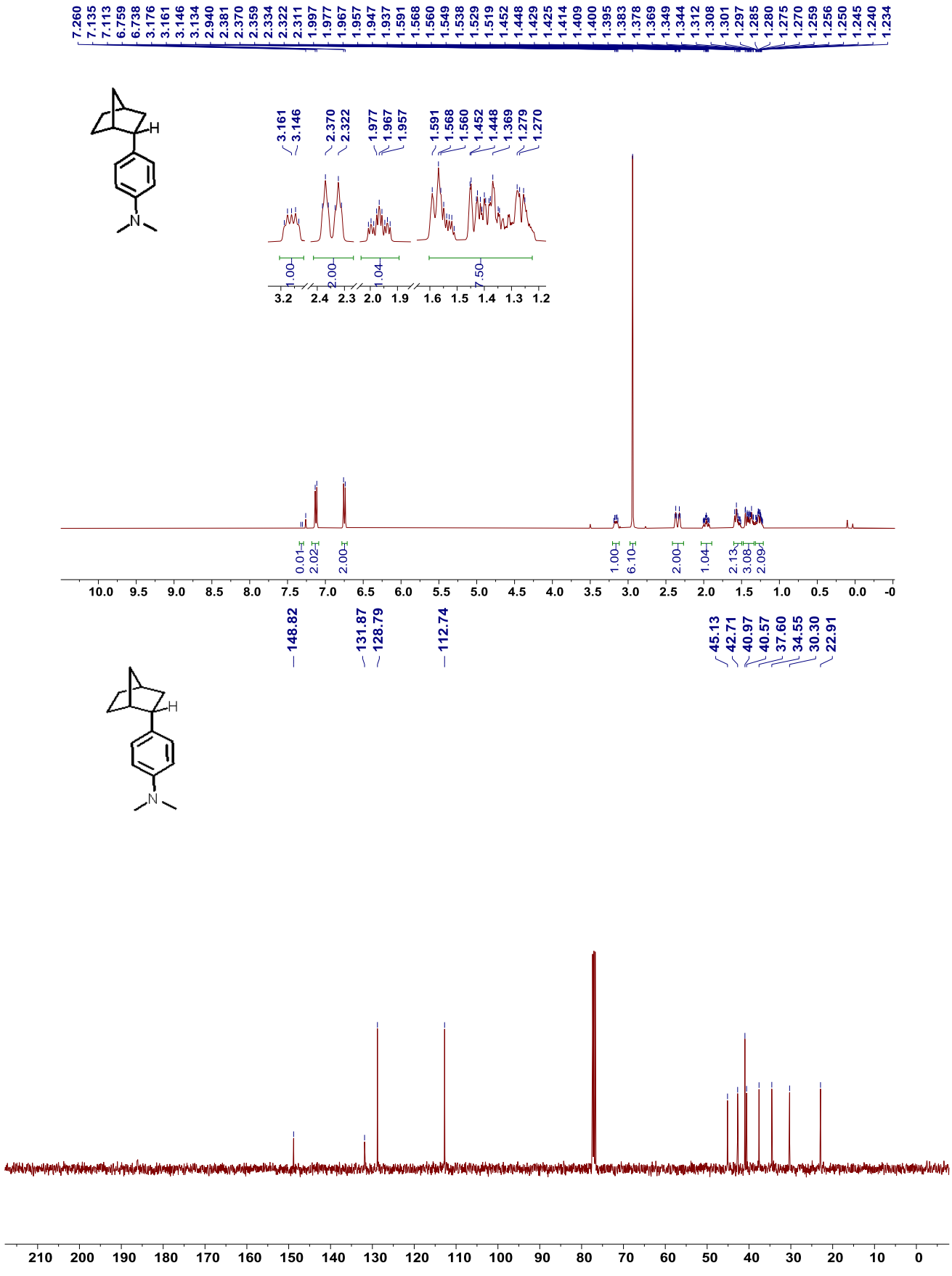
(2'*S*,5'*R*)-2'-isopropyl-*N*,*N*,5'-trimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-amine (S6)

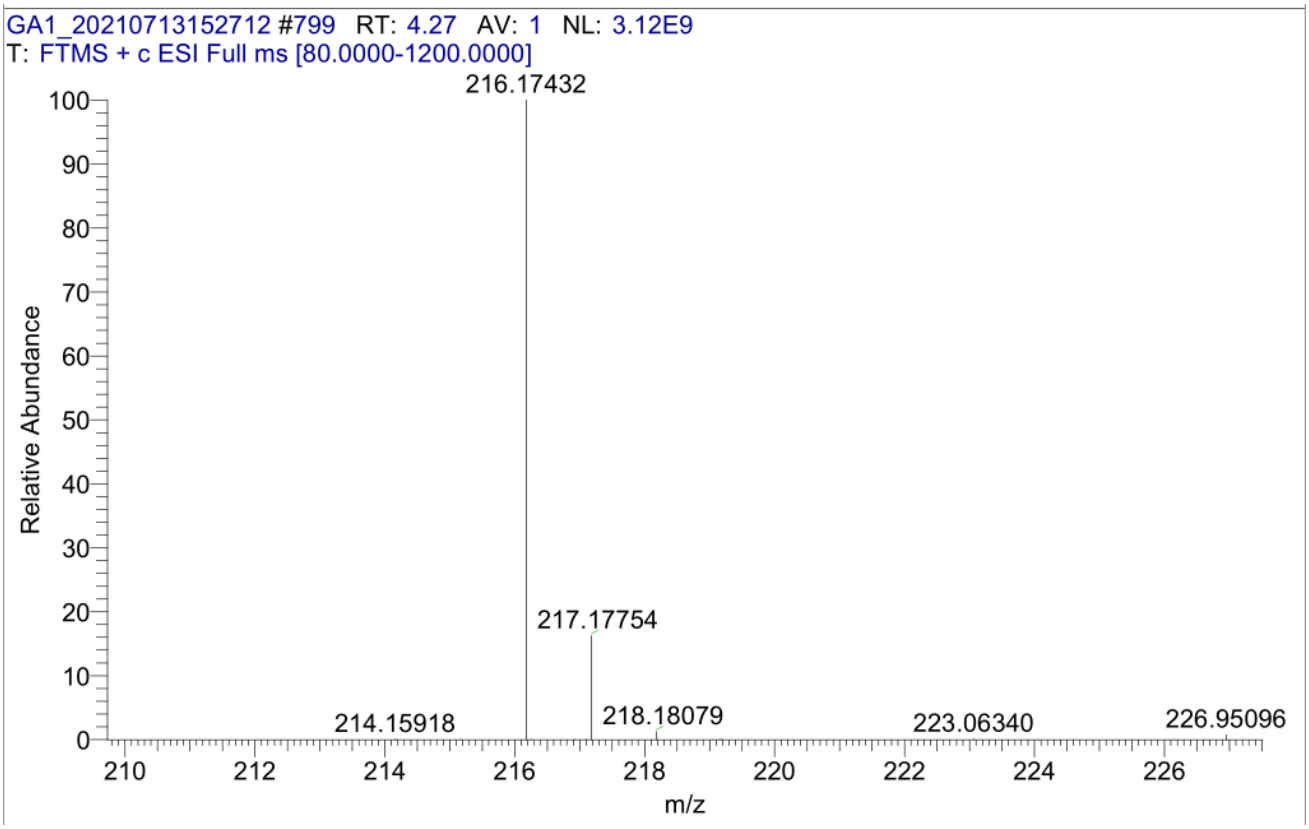




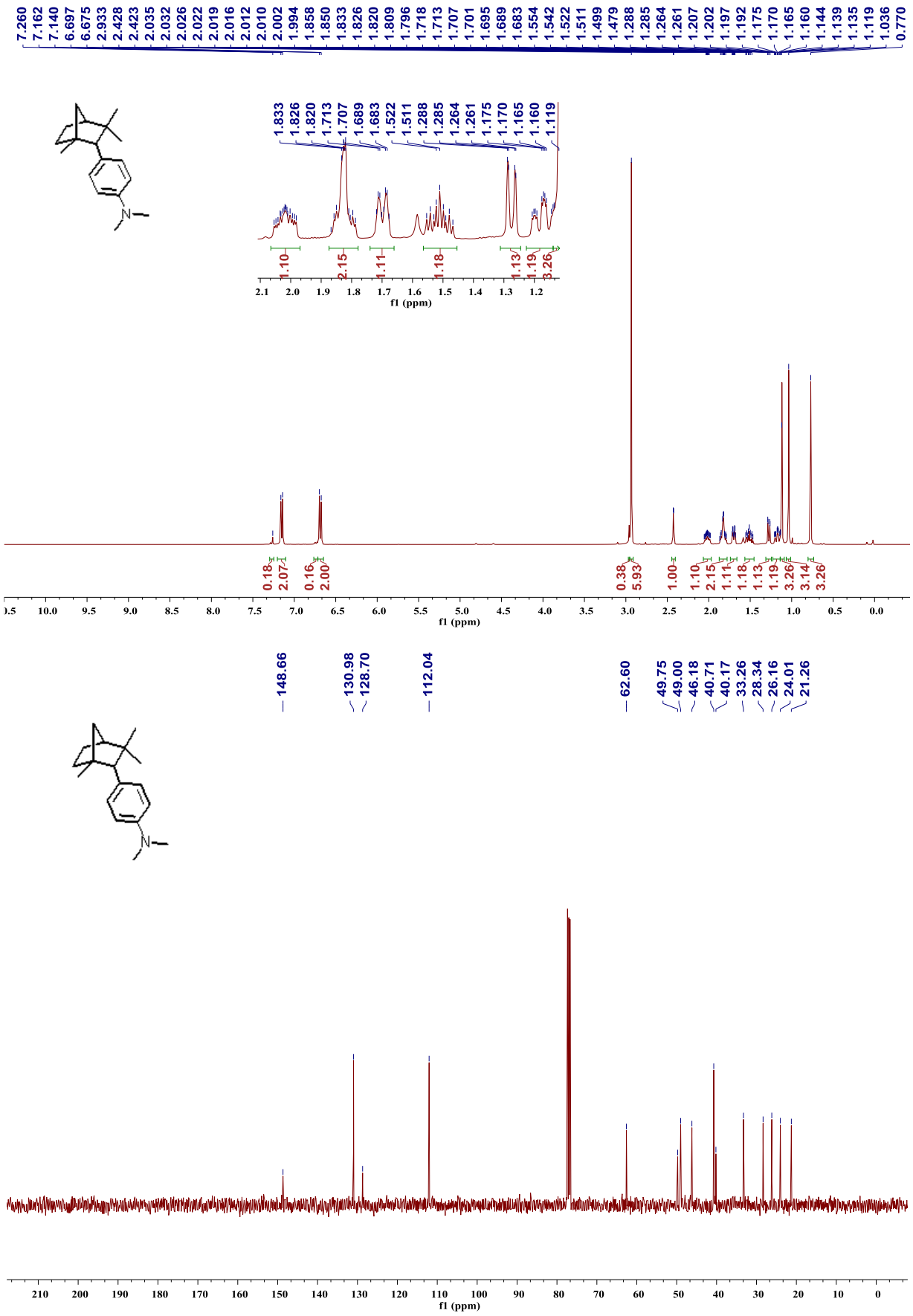

GA3 #1063 RT: 5.68 AV: 1 NL: 4.52E9
T: FTMS + c ESI Full ms [80.0000-1200.0000]
258.22110
259.22443
260.22766
250.11896
254.19104
257.21344
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
248
250
252
254
256
258
260
262
264
266

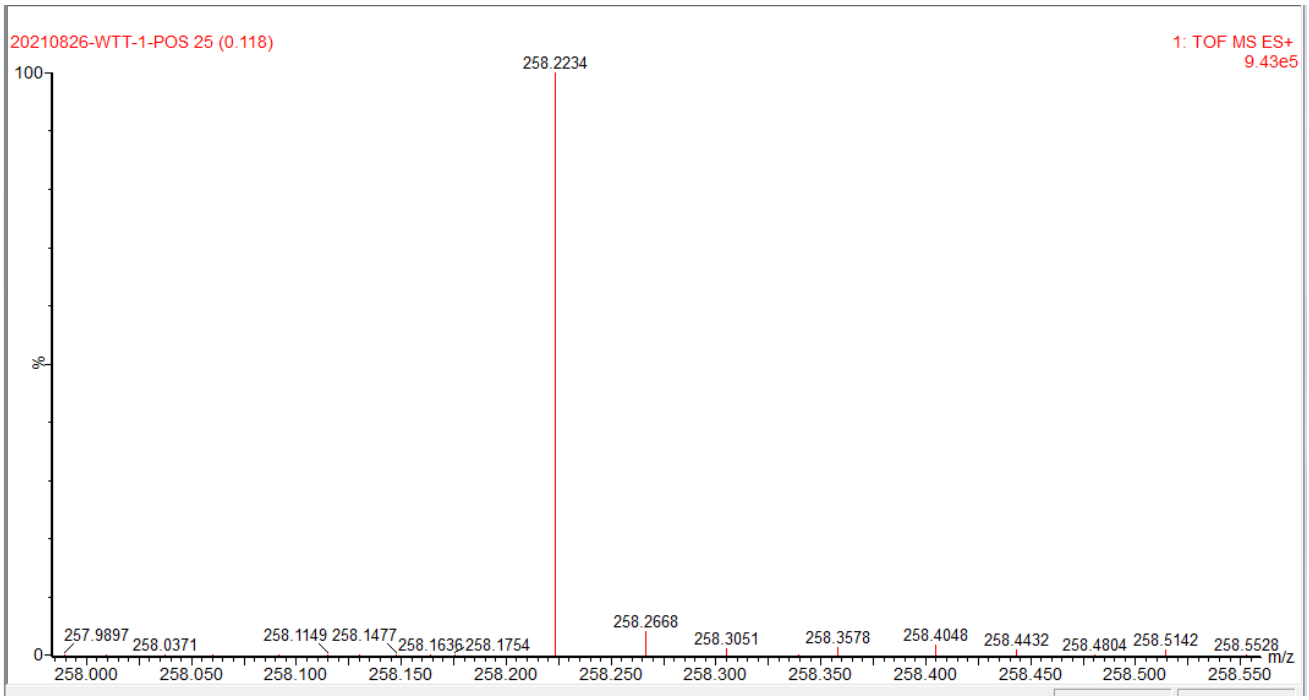
***endo*-4-bicyclo[2.2.1]heptan-2-yl)-*N,N*-dimethylaniline (*e*-4f) (*d.r.* > 99%)**



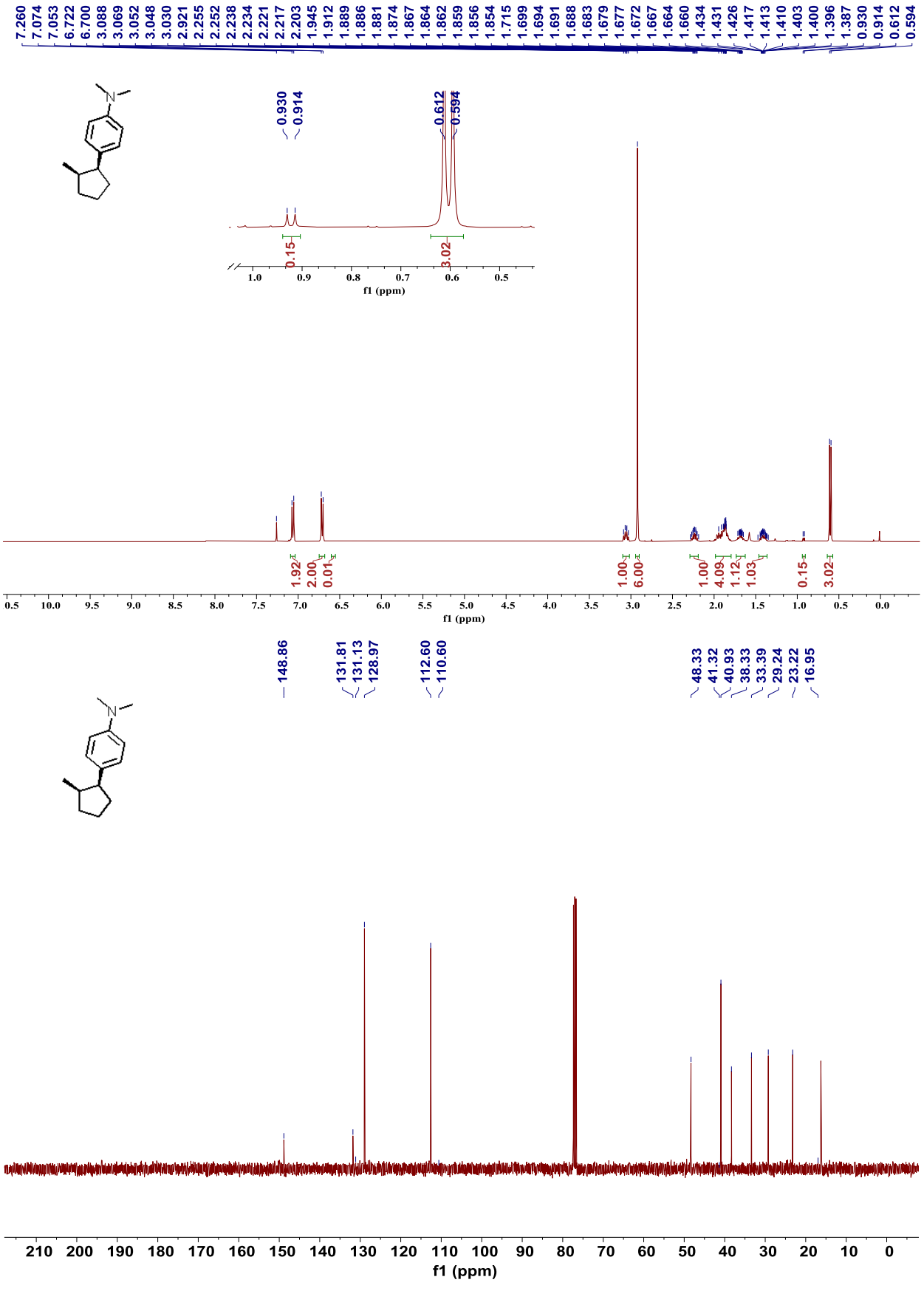

GA1_20210713152712 #799 RT: 4.27 AV: 1 NL: 3.12E9
T: FTMS + c ESI Full ms [80.0000-1200.0000]
216.17432
217.17754
214.15918
218.18079
223.06340
226.95096
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
210
212
214
216
218
220
222
224
226

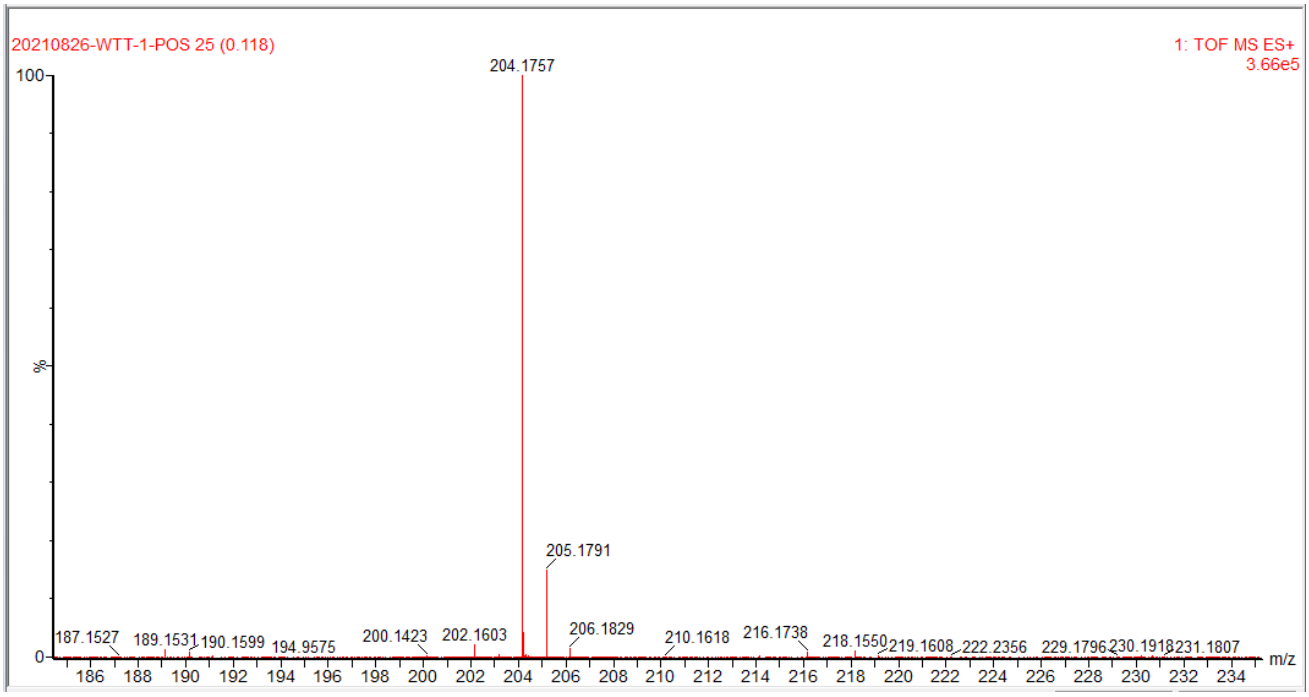
***endo*-2-isopropyl-5-methylcyclohexyl)-*N,N*-dimethylaniline (*e*-5g) (mixture of 2 stereomers, *d.r.* = 94 : 6)**



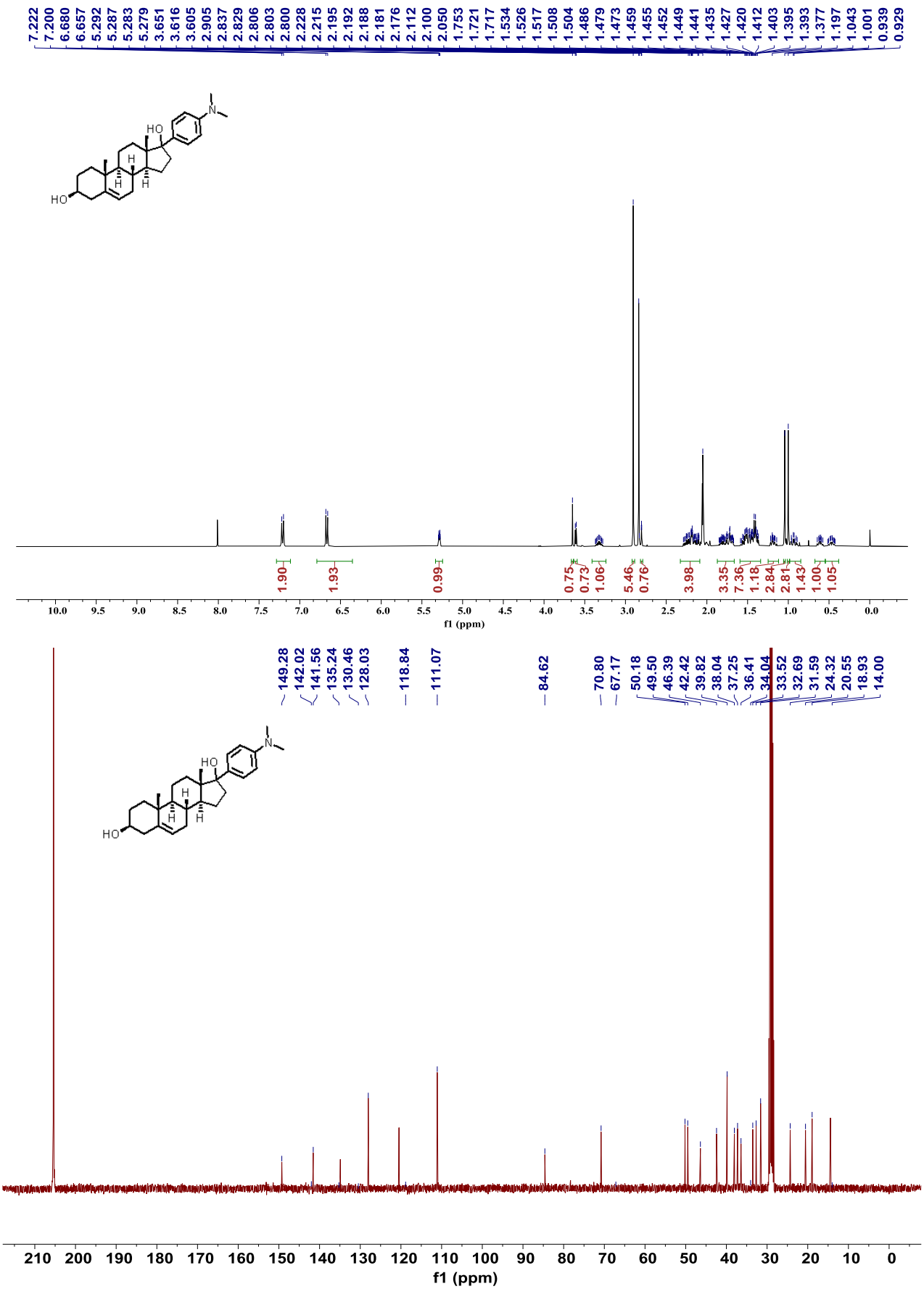

20210826-WTT-1-POS 25 (0.118)
1: TOF MS ES+
9.43e5
100
%
0
258.2234
257.9897
258.0371
258.1149
258.1477
258.1636
258.1754
258.2668
258.3051
258.3578
258.4048
258.4432
258.4804
258.5142
258.5528
m/z
258.000
258.050
258.100
258.150
258.200
258.250
258.300
258.350
258.400
258.450
258.500
258.550

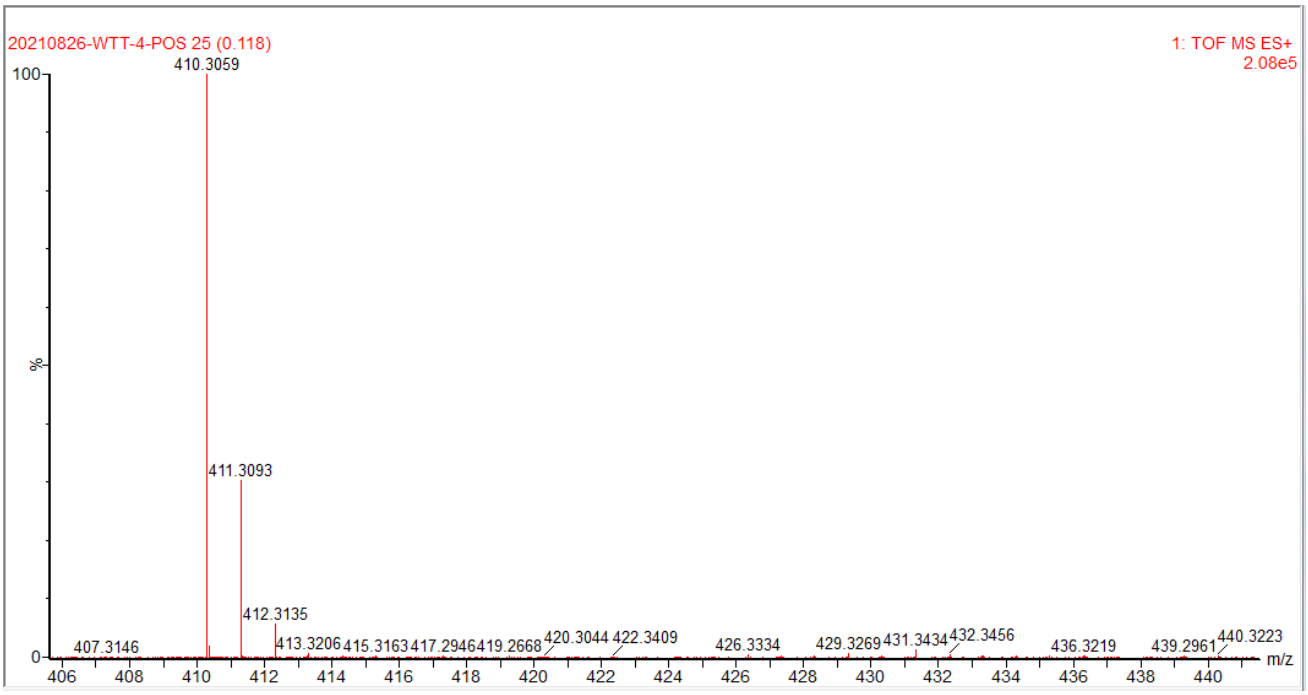
***cis*-*N*,*N*-dimethyl-4-(2-methylcyclopentyl)aniline (*pe*-4i) (d.r. = 95 : 5)**



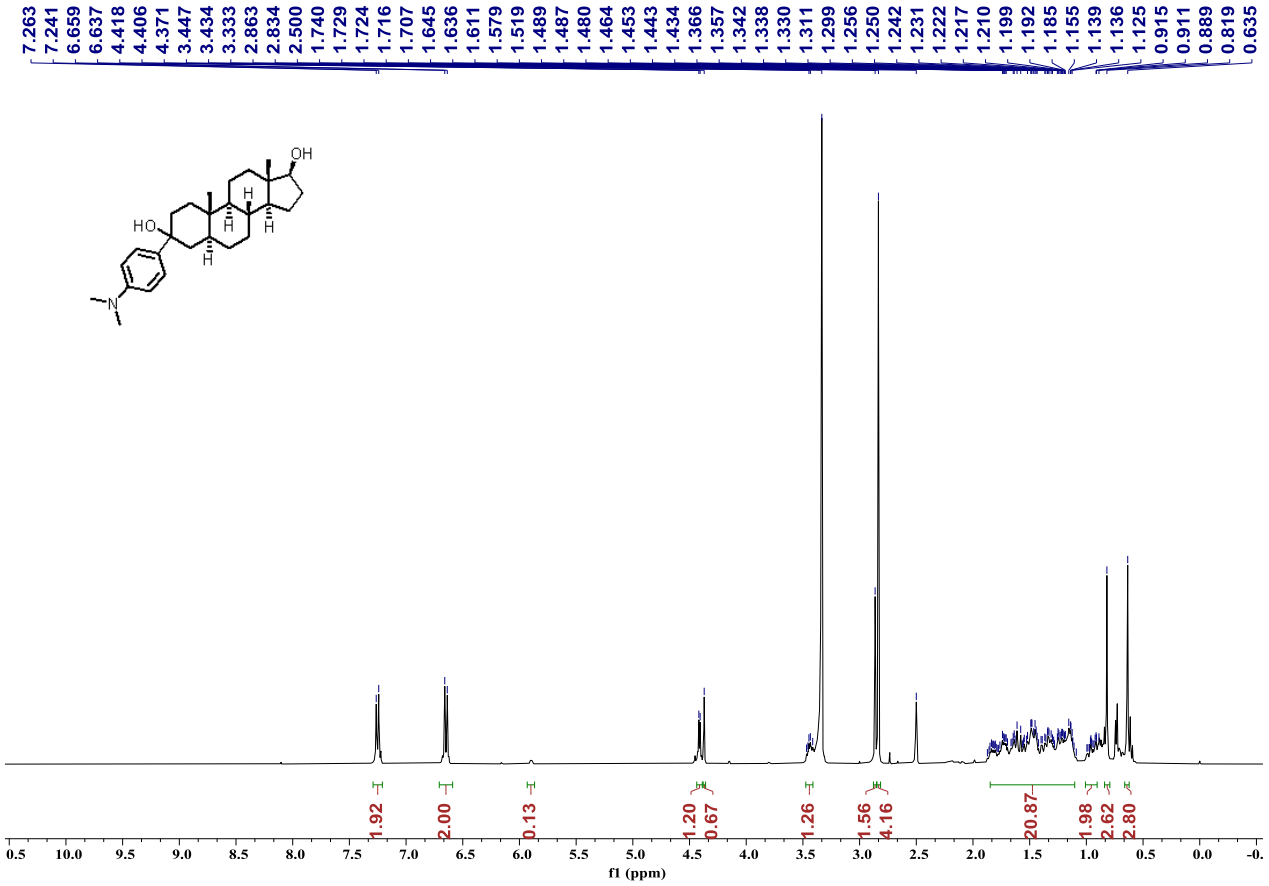

20210826-WTT-1-POS 25 (0.118)
1: TOF MS ES+
3.66e5
100
%
0
204.1757
205.1791
206.1829
187.1527
189.1531
190.1599
194.9575
200.1423
202.1603
210.1618
216.1738
218.1550
219.1608
222.2356
229.1796
230.1918
231.1807
m/z
186 188 190 192 194 196 198 200 202 204 206 208 210 212 214 216 218 220 222 224 226 228 230 232 234

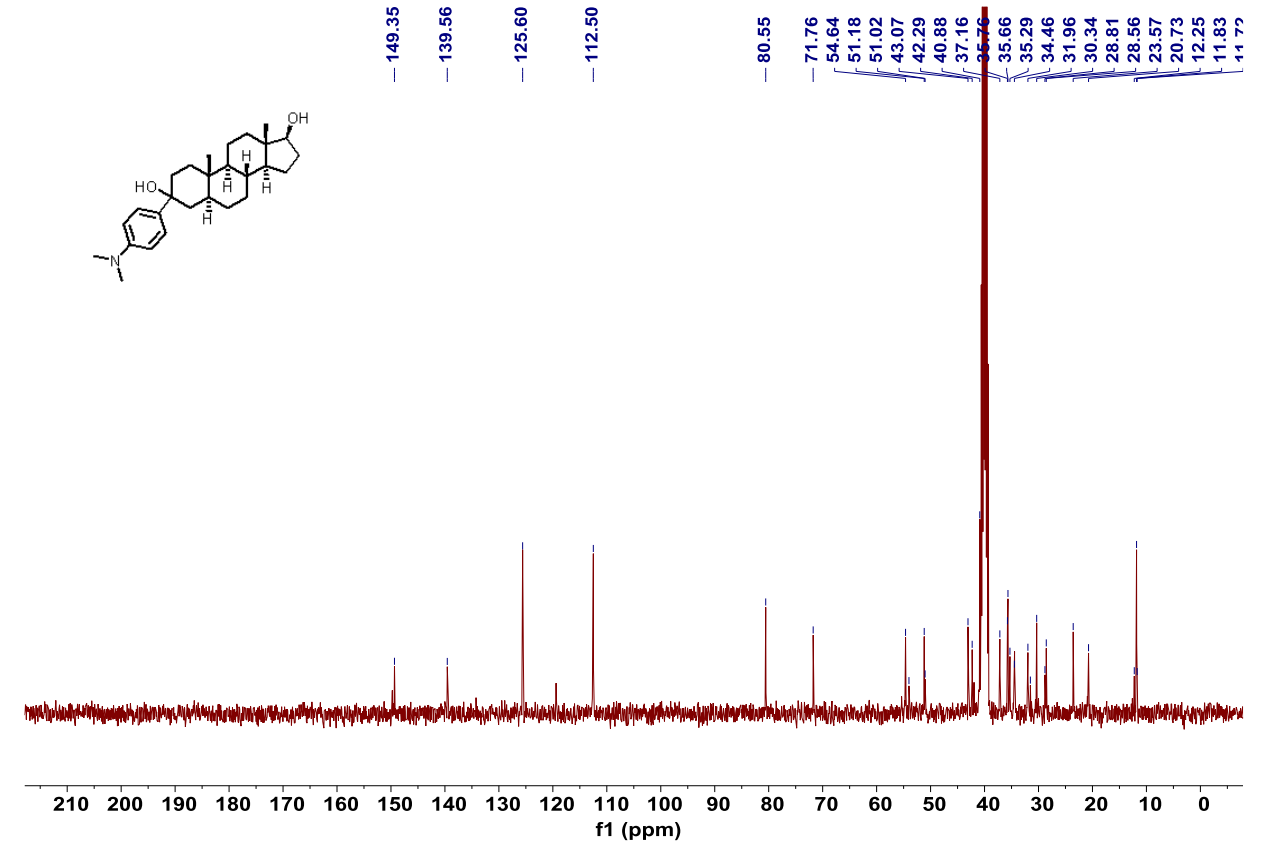
(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-17-(4-(dimethylamino)phenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-3,17-diol

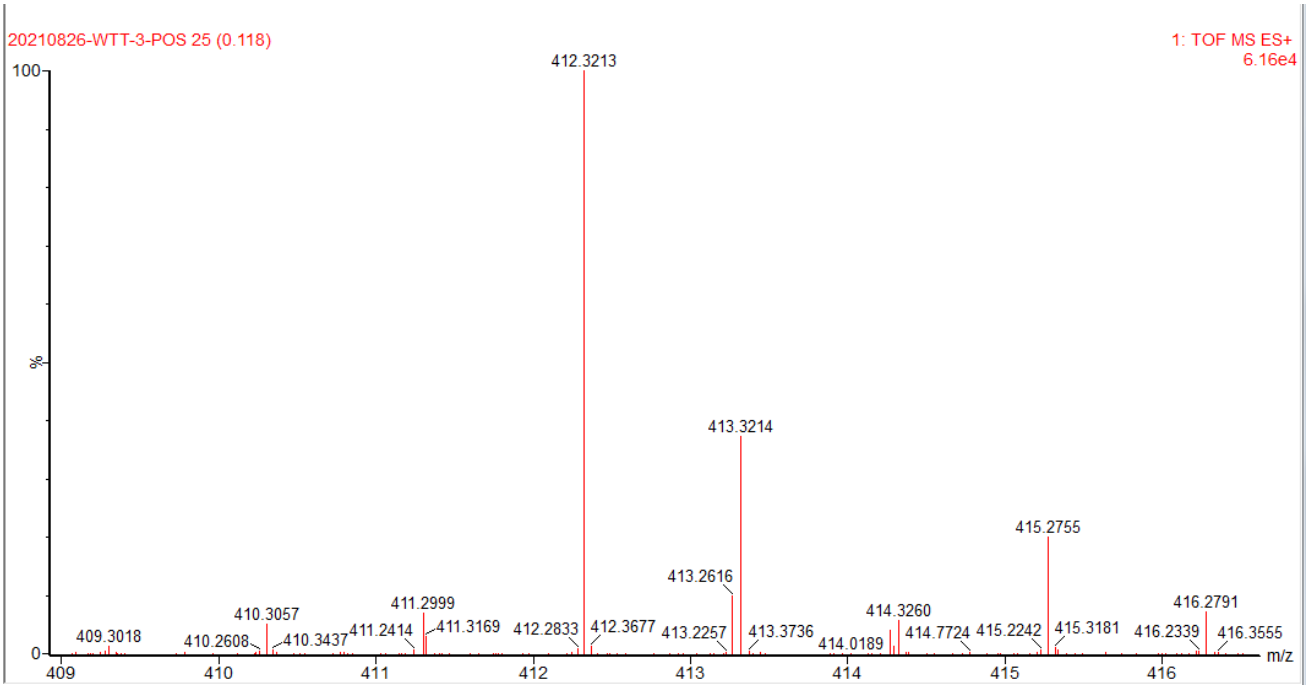



20210826-WTT-4-POS 25 (0.118)
1: TOF MS ES+
2.08e5
100
%
0
410.3059
411.3093
412.3135
407.3146
413.3206
415.3163
417.2946
419.2668
420.3044
422.3409
426.3334
429.3269
431.3434
432.3456
436.3219
439.2961
440.3223
406
408
410
412
414
416
418
420
422
424
426
428
430
432
434
436
438
440
m/z

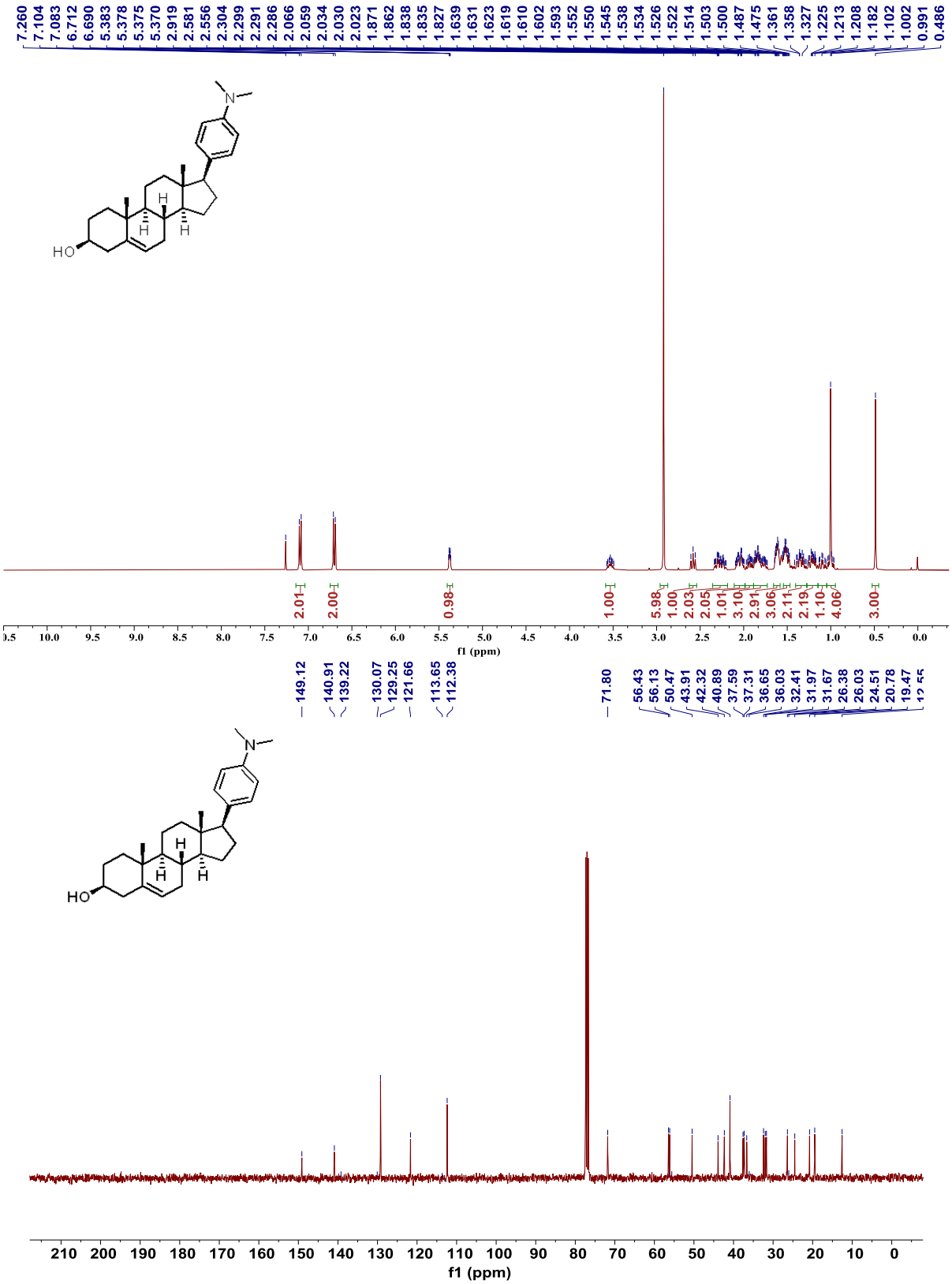
(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-3-(4-(dimethylamino)phenyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,17-diol

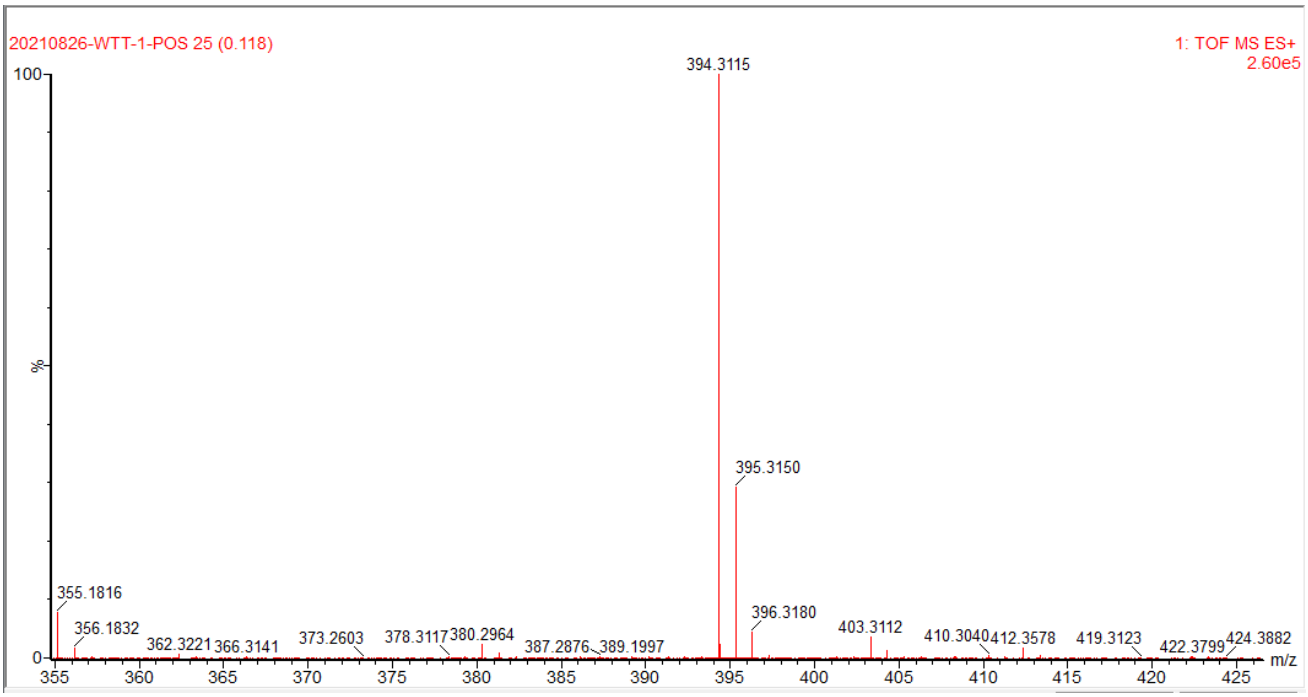




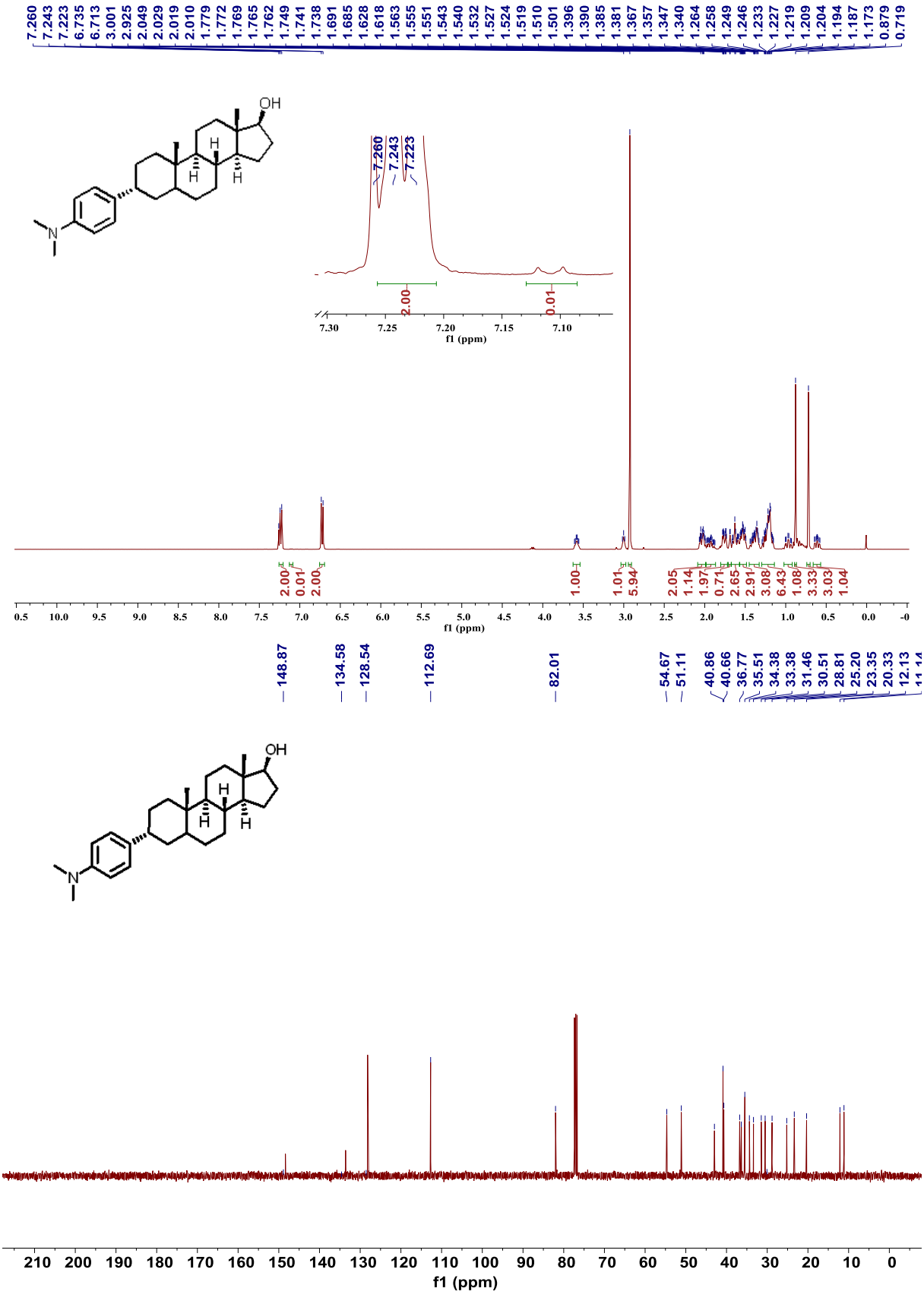

20210826-WTT-3-POS 25 (0.118)
1: TOF MS ES+
6.16e4
100
%
0
412.3213
413.3214
415.2755
413.2616
411.2999
410.3057
414.3260
416.2791
409.3018
410.2608
410.3437
411.2414
411.3169
412.2833
412.3677
413.2257
413.3736
414.0189
414.7724
415.2242
415.3181
416.2339
416.3555
409
410
411
412
413
414
415
416
m/z

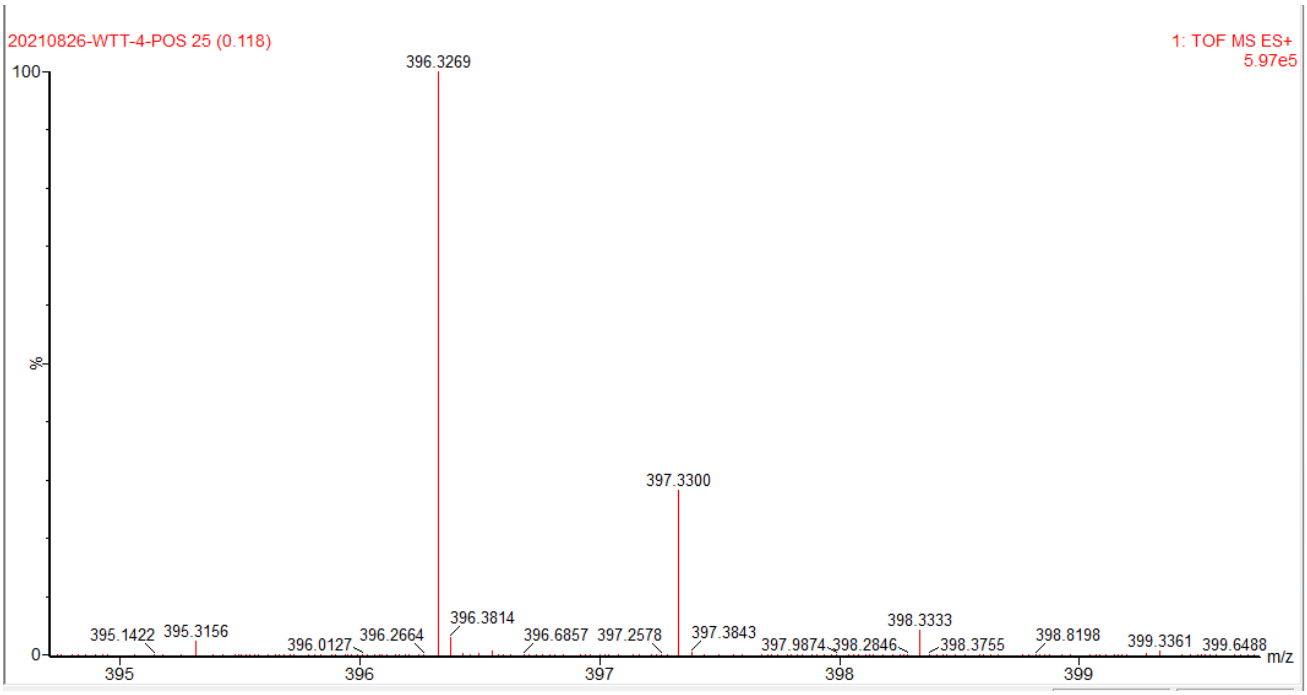
(*3S,8S,9S,10R,13S,14S*)-17-(4-(dimethylamino)phenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (4j) (*d.r.* > 99%)




20210826-WTT-1-POS 25 (0.118)
1: TOF MS ES+
2.60e5
100
%
0
394.3115
395.3150
355.1816
356.1832
362.3221
366.3141
373.2603
378.3117
380.2964
387.2876
389.1997
396.3180
403.3112
410.3040
412.3578
419.3123
422.3799
424.3882
355
360
365
370
375
380
385
390
395
400
405
410
415
420
425
m/z

(*8R,9S,10S,13S,14S,17S*)-3-(4-(dimethylamino)phenyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol (4m) (*d.r.* > 99%)

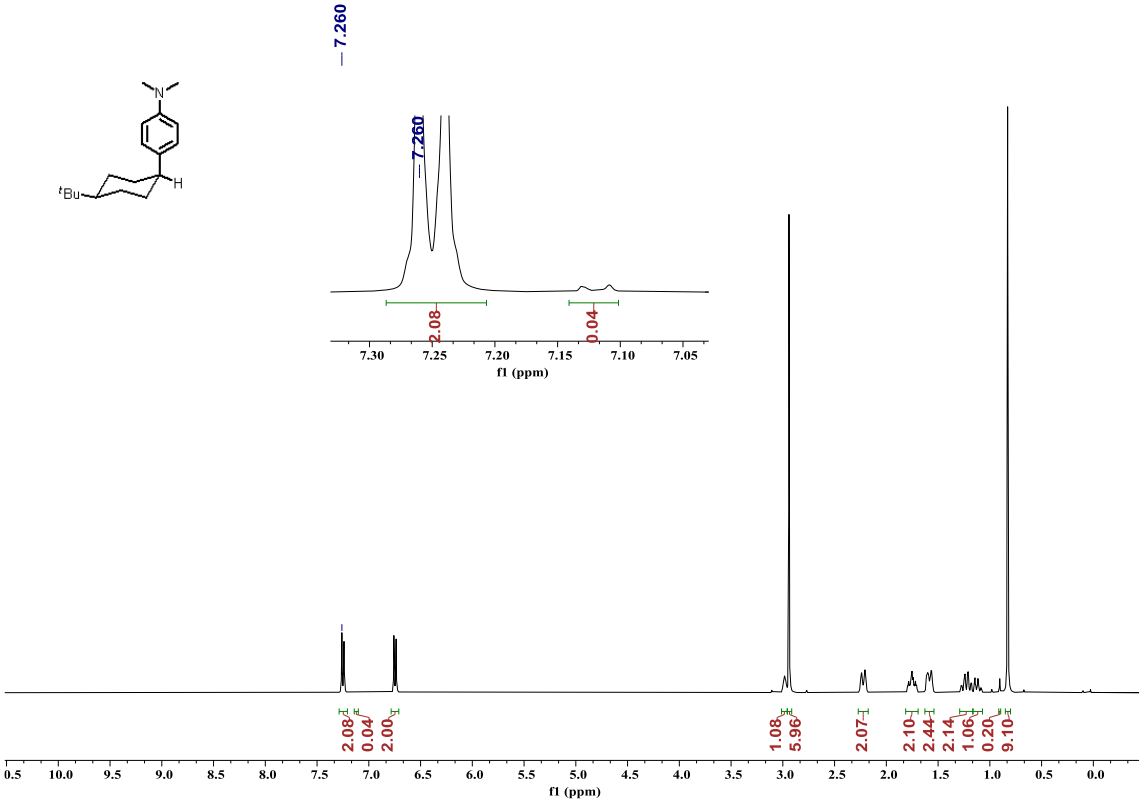



20210826-WTT-4-POS 25 (0.118)
1: TOF MS ES+
5.97e5
100
%
0
396.3269
397.3300
395.1422
395.3156
396.0127
396.2664
396.3814
396.6857
397.2578
397.3843
397.9874
398.2846
398.3333
398.3755
398.8198
399.3361
399.6488
395
396
397
398
399
m/z

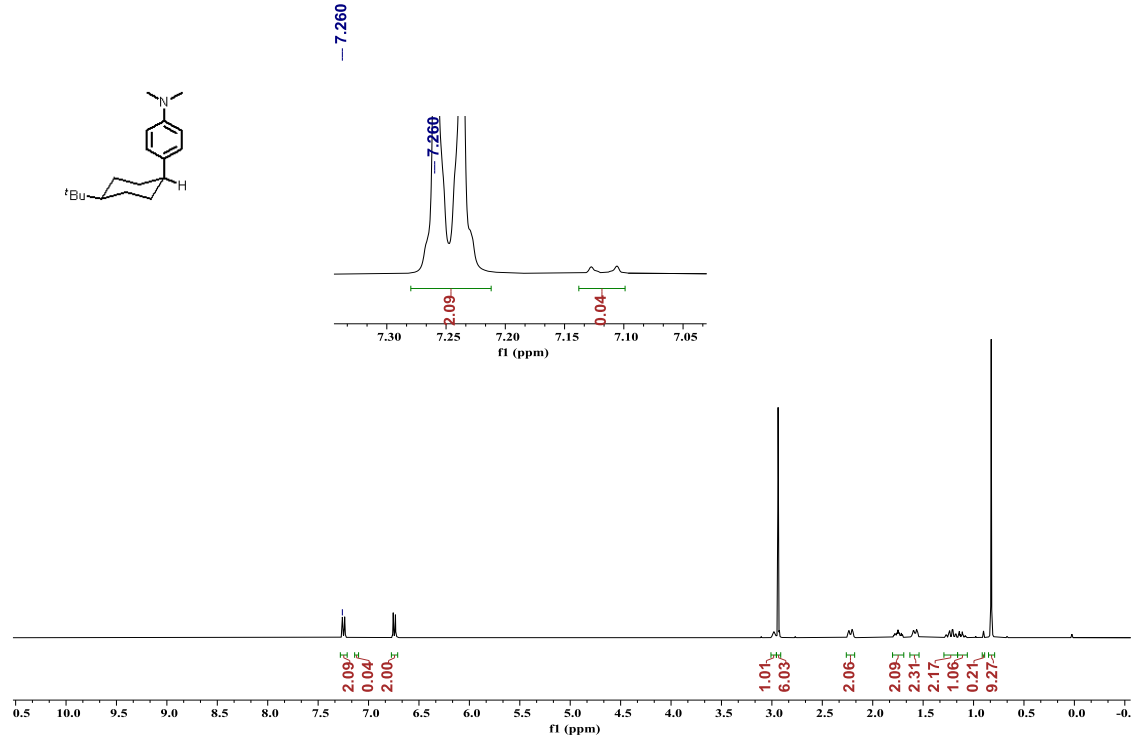
13. Influence of catalyst dosage on stereochemistry of deoxygenation reactions

4-((*1s,4s*)-4-(tert-butyl)cyclohexyl)-*N,N*-dimethylaniline (*e*-4a and *a*-5a) (from (*1s,4s*)-4-(tert-butyl)-1-(4-(dimethyl amino)phenyl)cyclohexan-1-ol (1a))

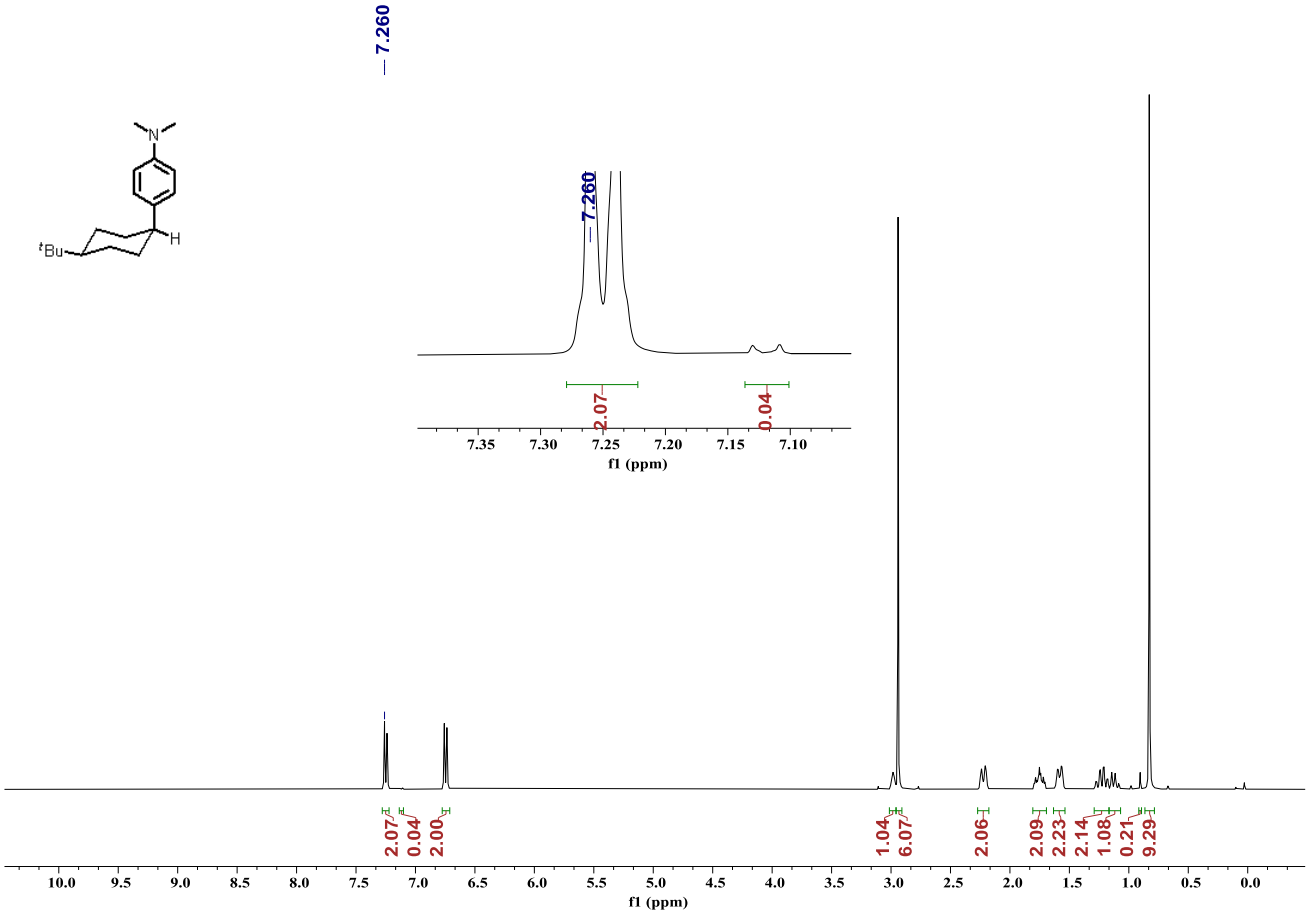
1. S/C = 5000; *d.r.* = 98 : 2



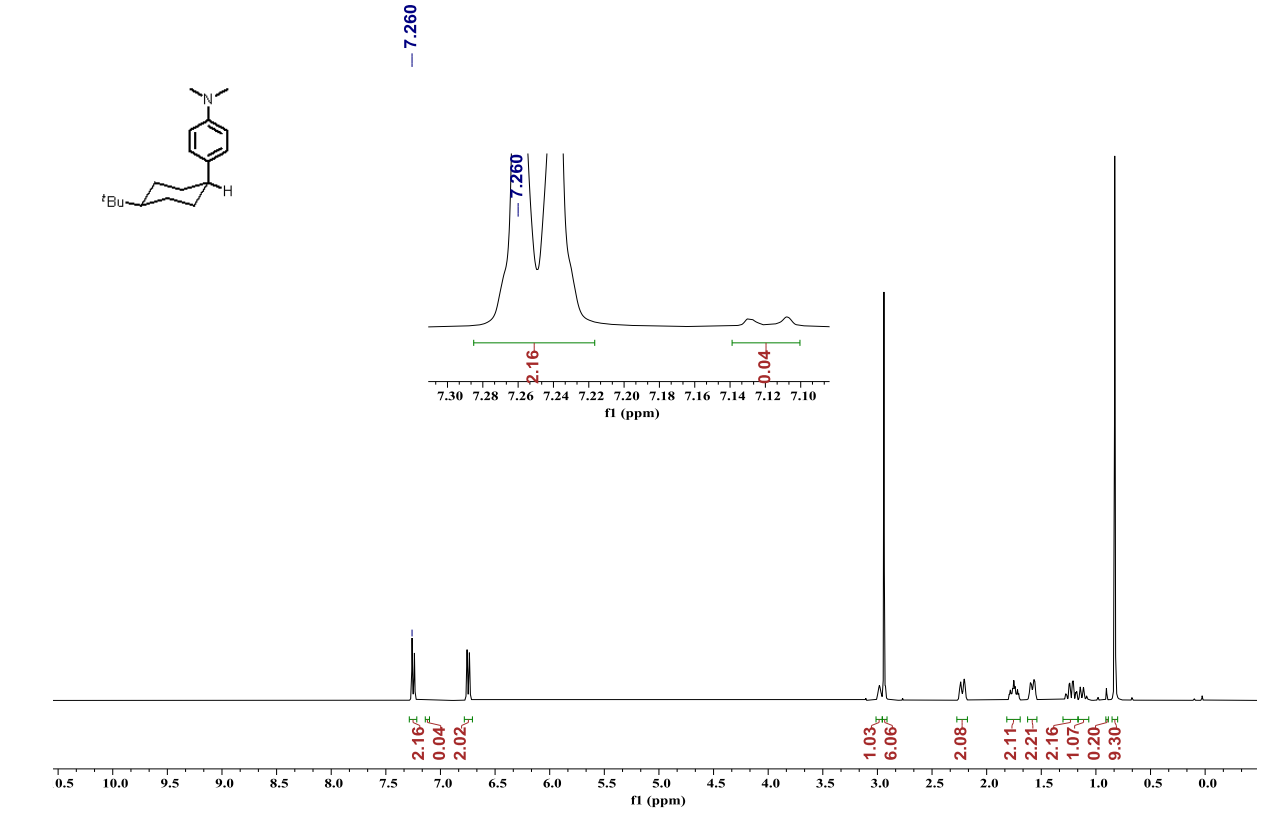
2. S/C = 2000; *d.r.* = 98 : 2



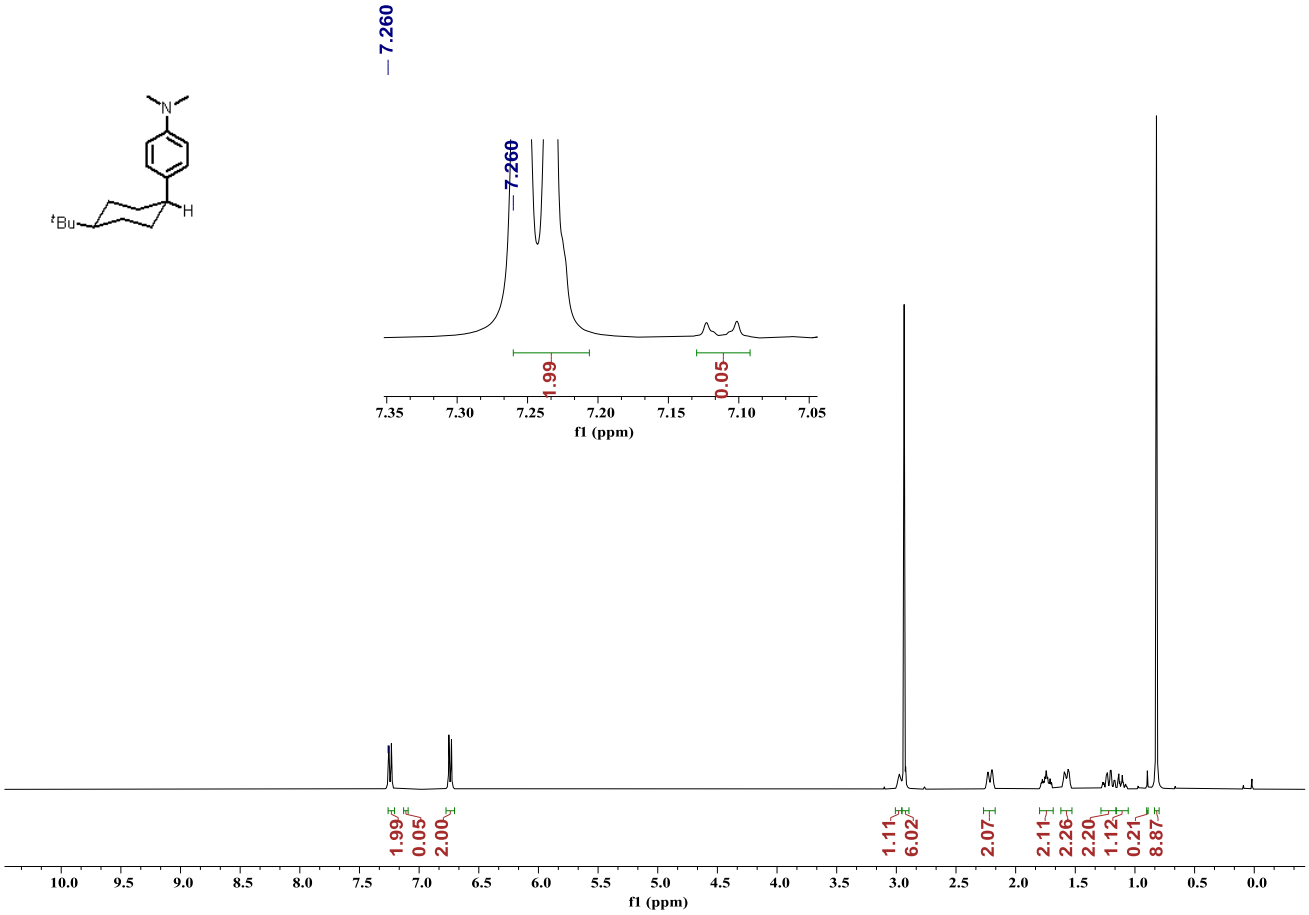
3. S/C = 500; *d.r.* = 98 : 2



4. S/C = 200; *d.r.* = 98 : 2

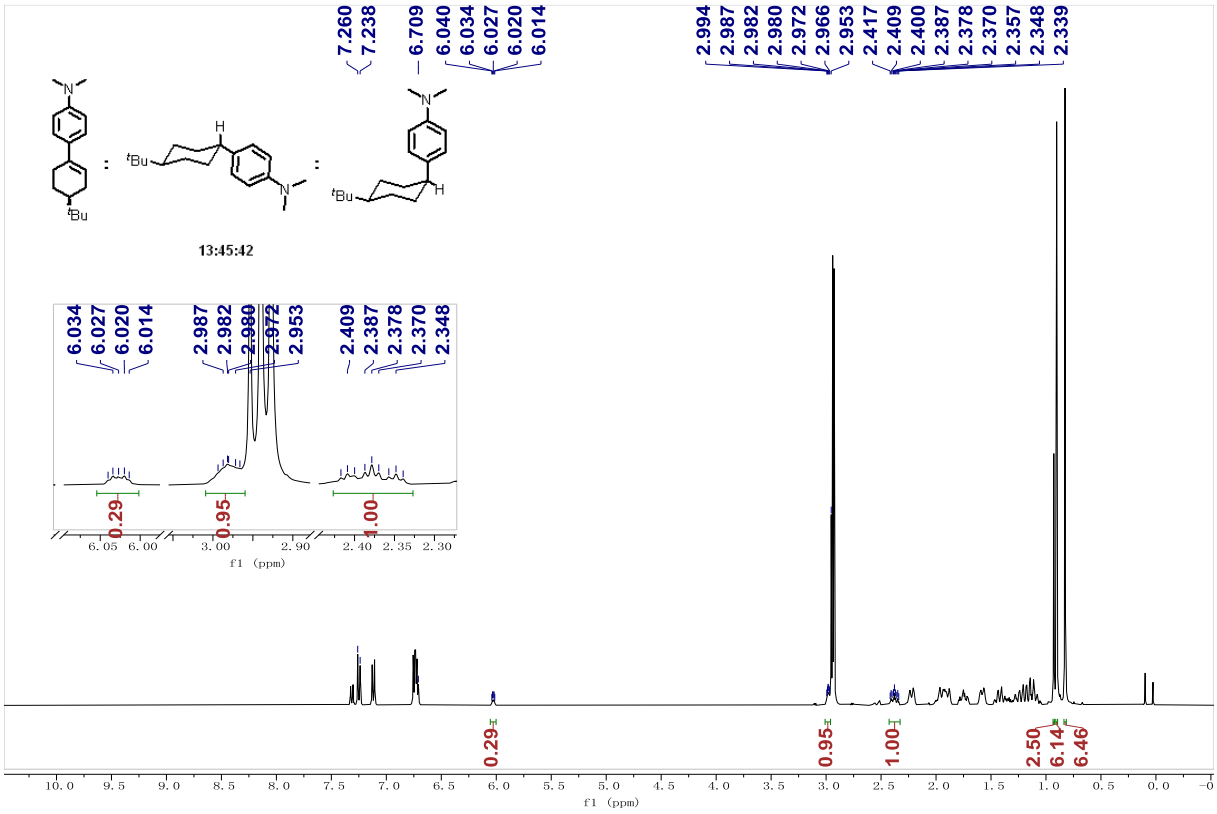


5. S/C = 100; *d.r.* = 98 : 2

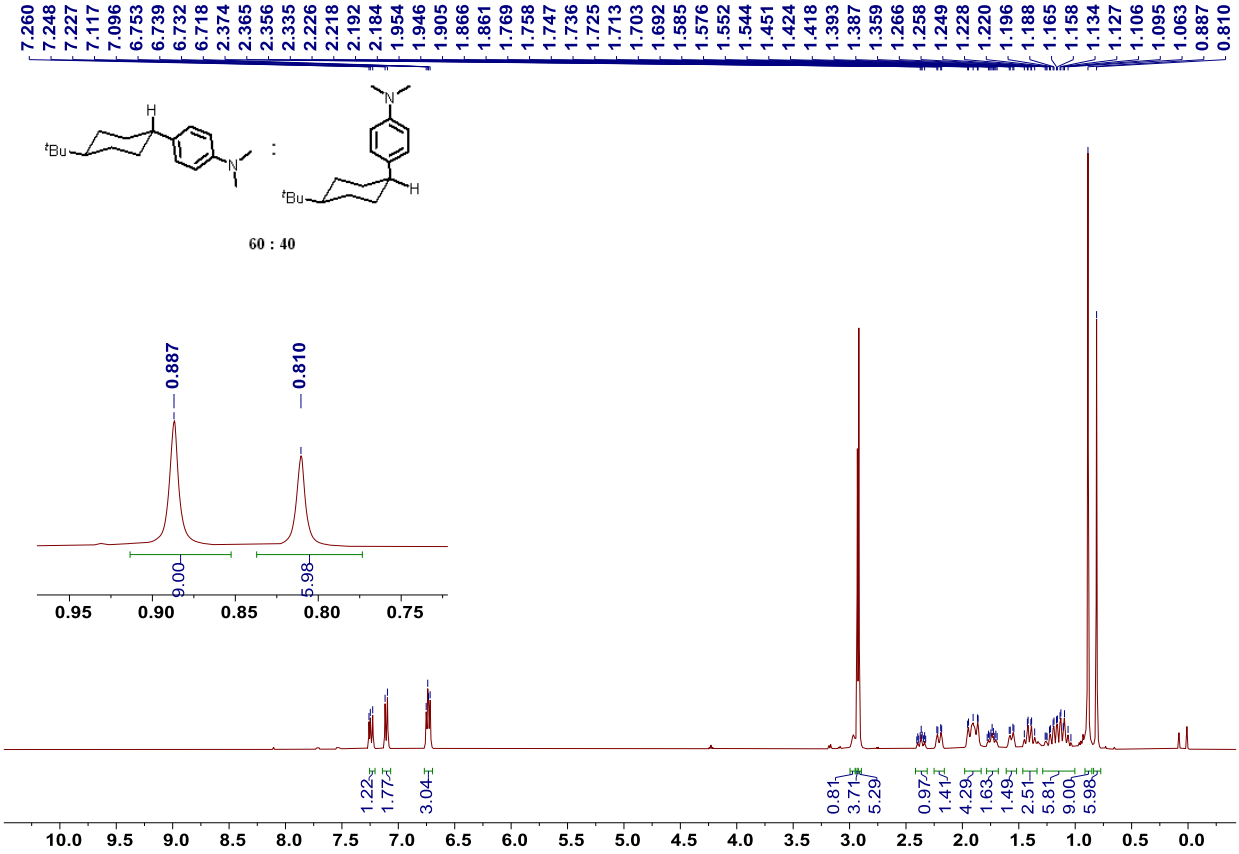


14. Spectra of other procedures for deoxygenation of (*1S,4S*)-4-(tert-butyl)-1-(4-(dimethylamino)phenyl)cyclohexan-1-ol

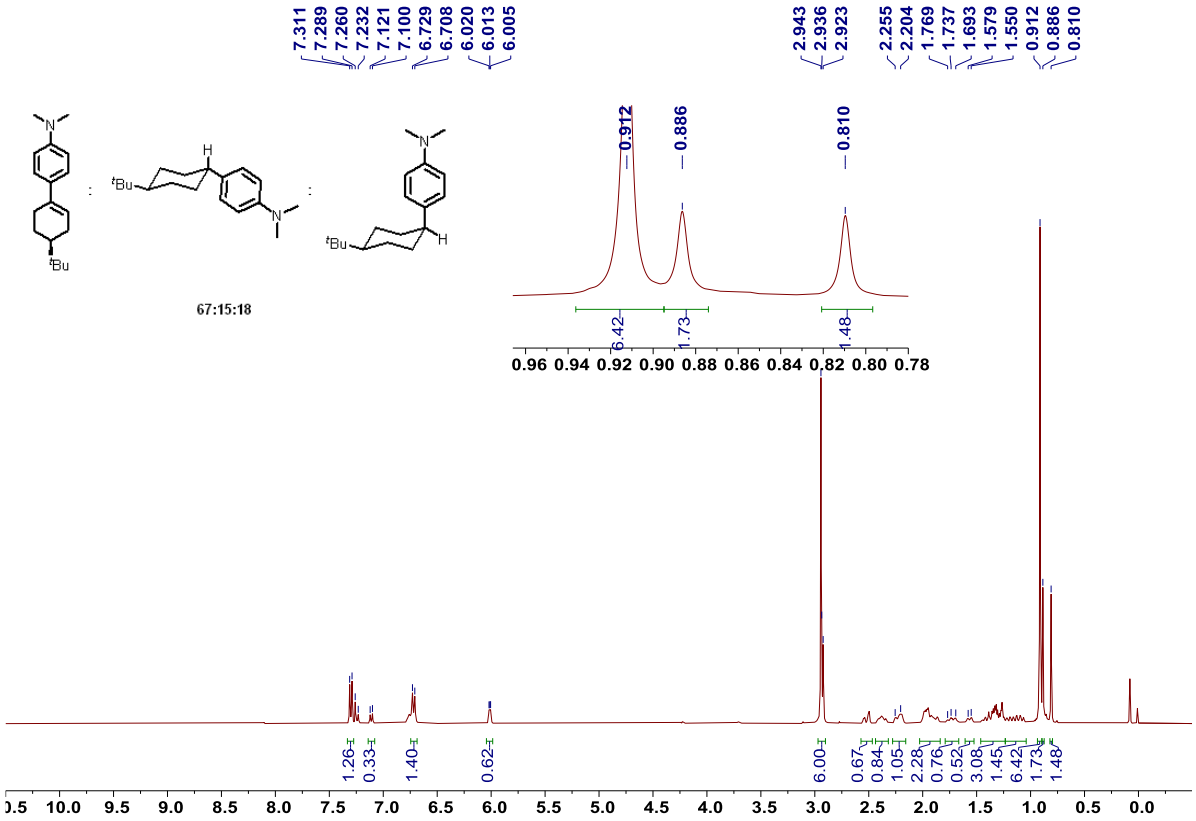
1. with $LiAlH_4$:



2. with $NaBH_3CN$:

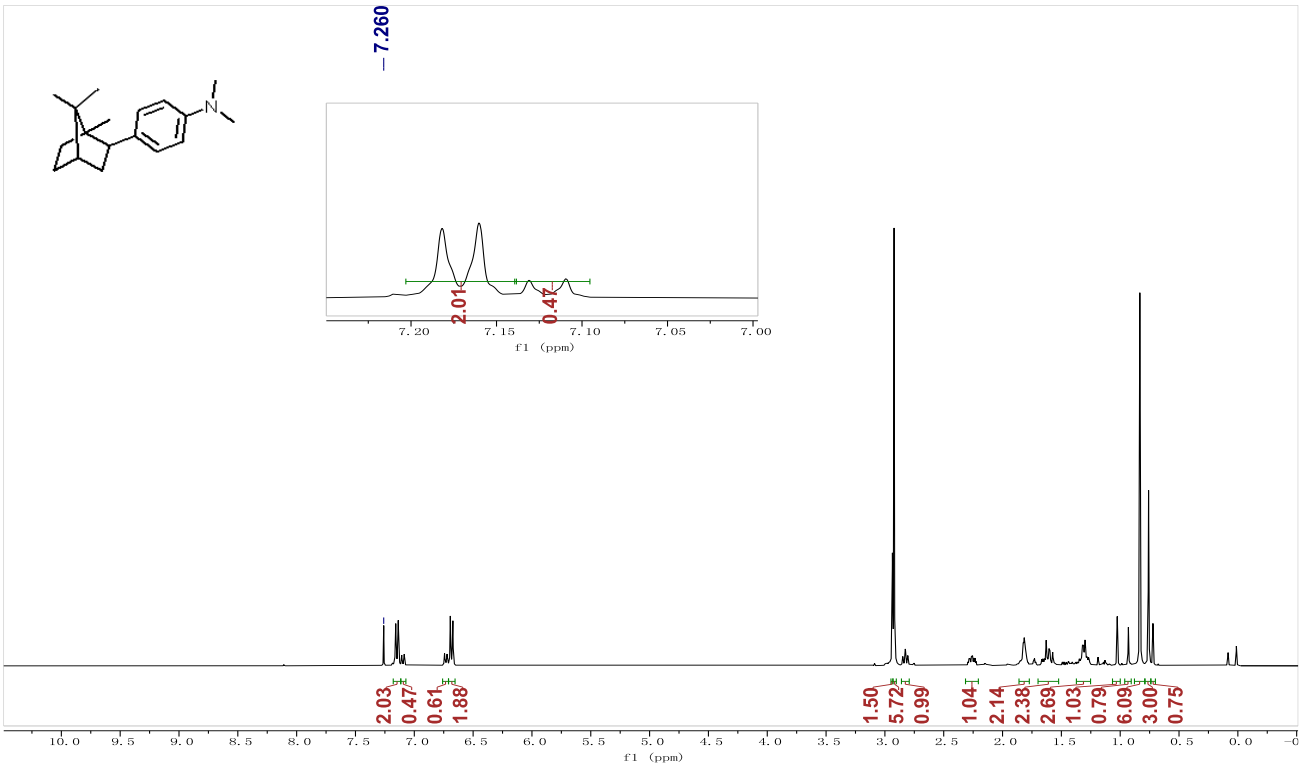


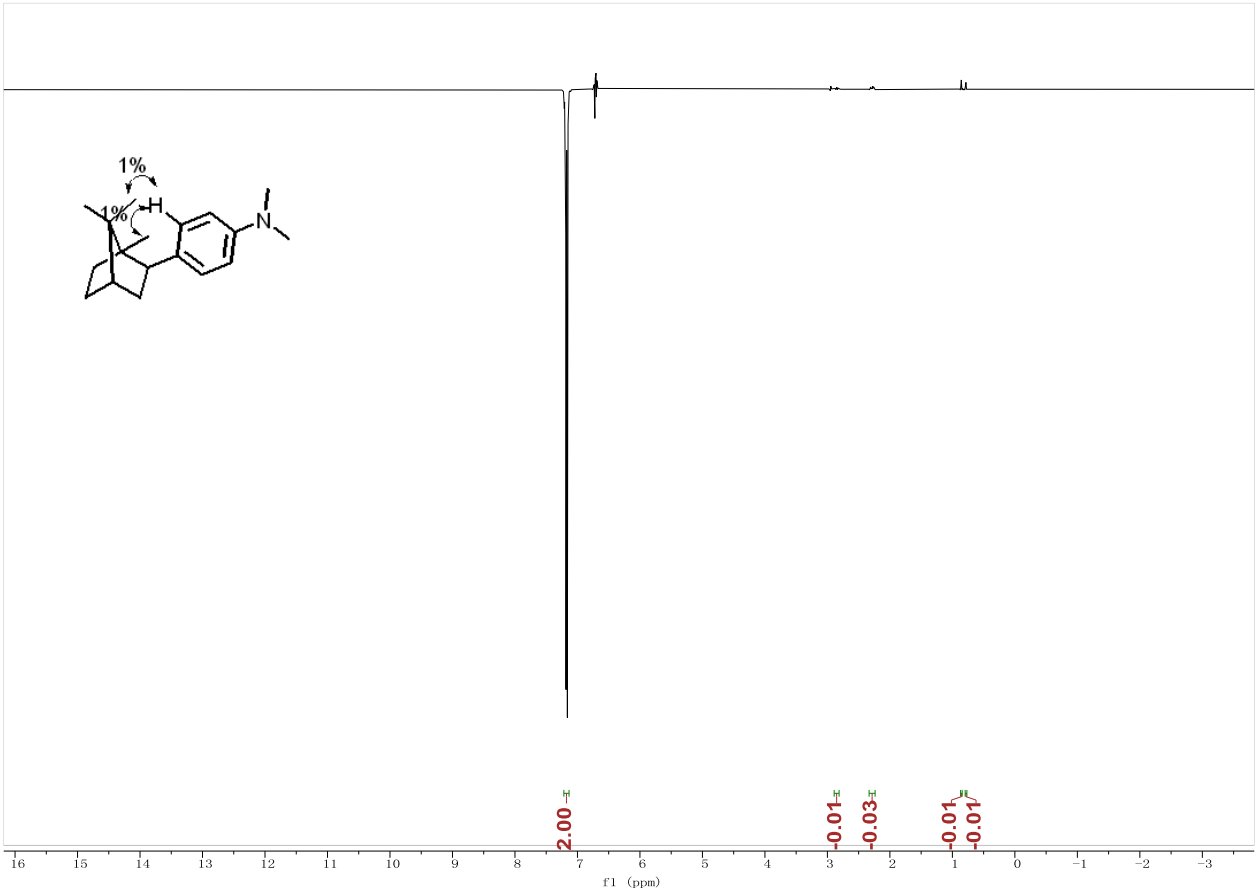
3. with BH_3·THF:



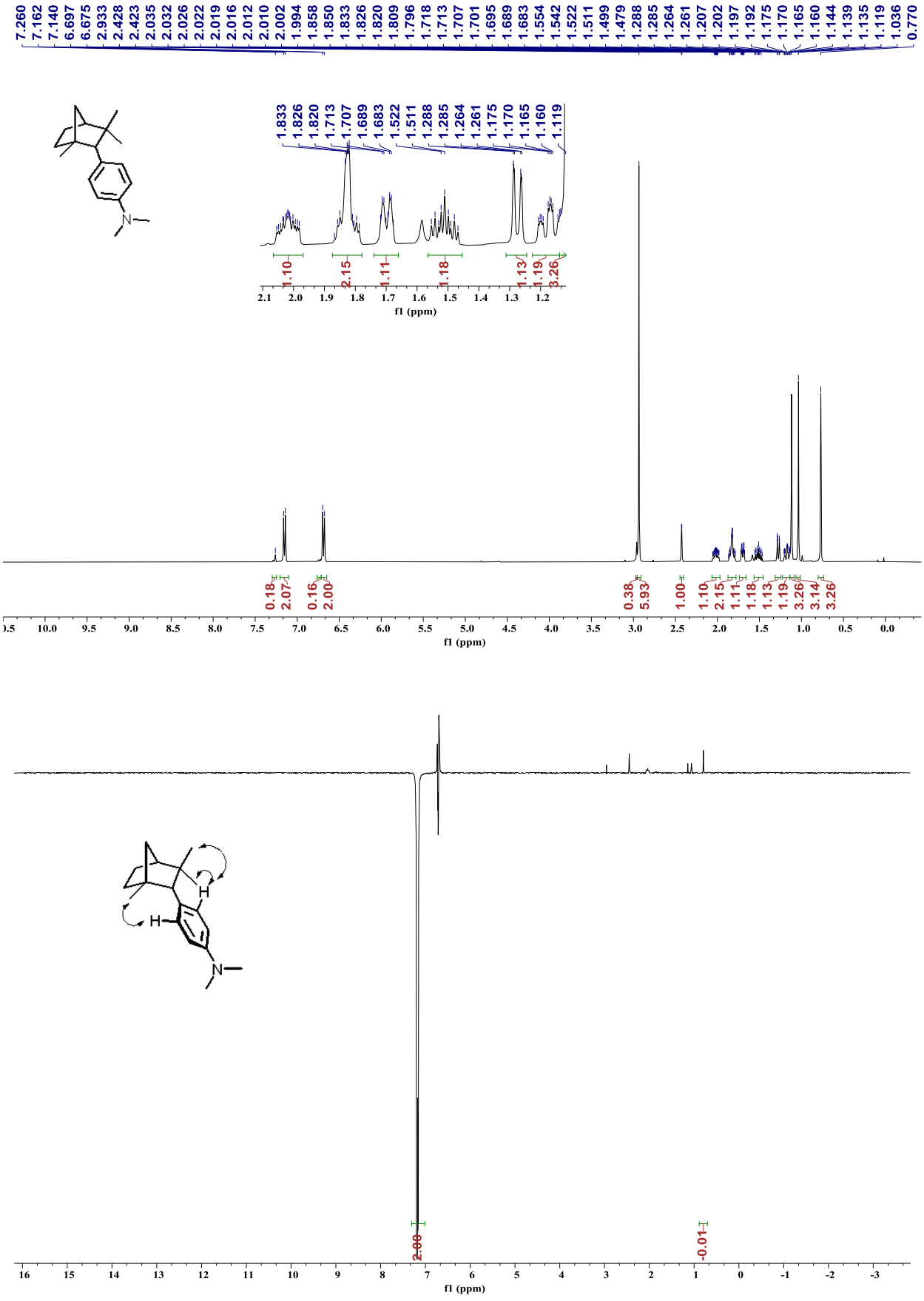
15. NOE spectra

***N,N*-dimethyl-4-((*1R,4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)aniline (*e*-4h and *a*-5h):**

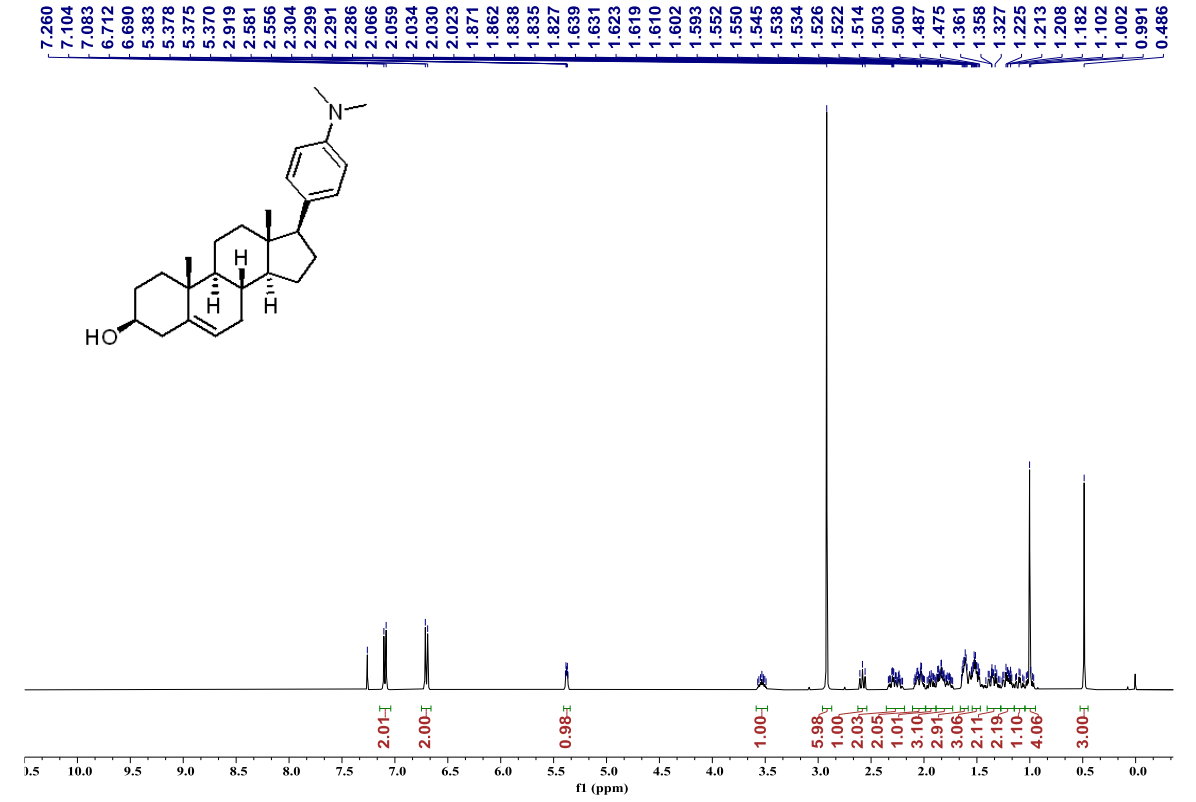


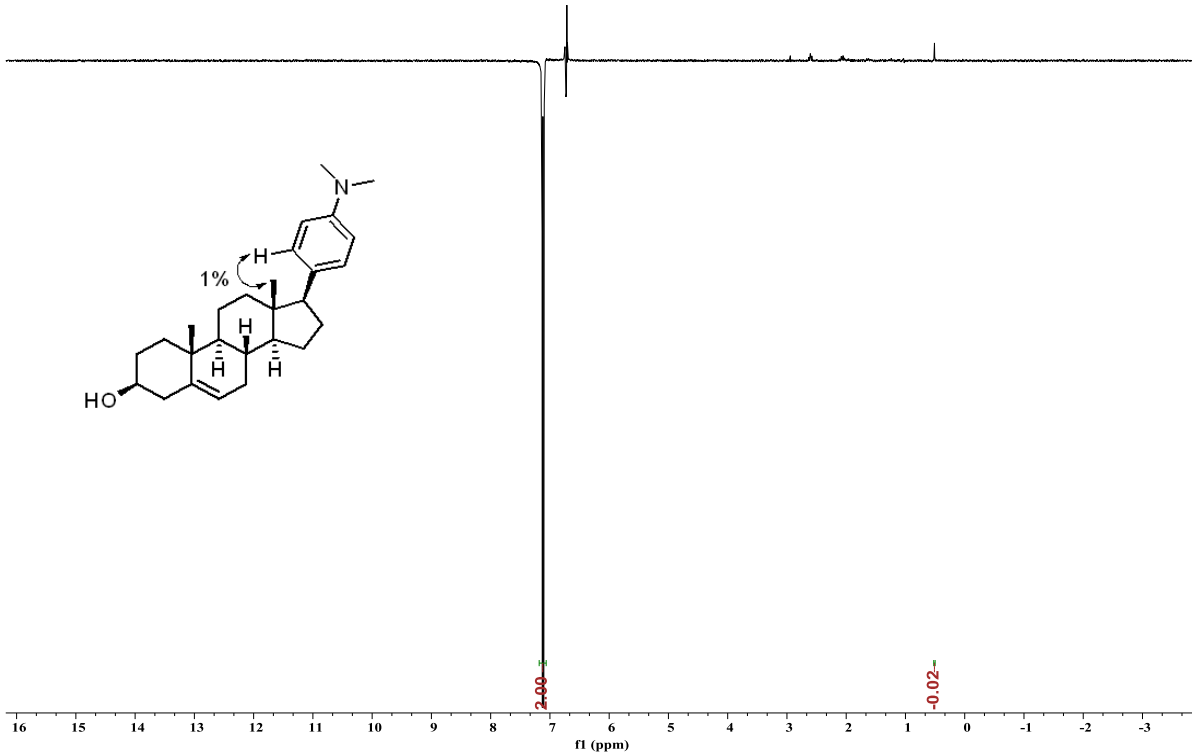


***N,N*-dimethyl-4-((*1S,4S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)aniline (*e*-4g and *a*-5g)**

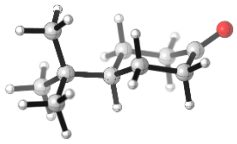


(*3S,8S,9S,10R,13S,14S*)-17-(4-(dimethylamino)phenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta*[a]*phenanthren-3-ol



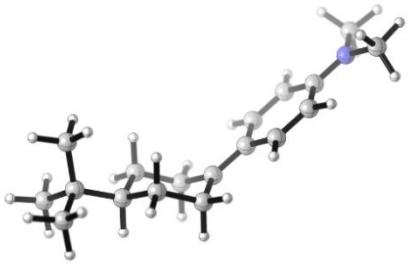


16. Cartesian Coordinates



3a

C	-1.83736400	1.27585400	-0.39097900
C	-2.56619000	-0.00367200	-0.03492800
C	-1.82827000	-1.27181400	-0.41202900
C	-0.38752500	-1.23744300	0.12057200
C	0.37168200	0.00773300	-0.36113800
C	-0.38385000	1.25910500	0.11112900
H	-2.38769800	-2.12474600	-0.02712300
H	-1.83317200	1.36051800	-1.48481400
H	-2.39931500	2.11765500	0.01432000
H	-0.41979600	-1.23785900	1.21570600
H	0.12369600	-2.15270400	-0.18295400
H	0.34127700	0.00921800	-1.46201800
H	-0.38531000	1.29505200	1.20645500
H	0.11012100	2.16699000	-0.23776900
H	-1.80544800	-1.33804100	-1.50660100
C	1.87927600	-0.00234100	0.02486700
C	2.54178100	1.31169300	-0.41327500
C	2.08562900	-0.18031700	1.53470700
C	2.58922700	-1.14941500	-0.70938900
H	2.31215300	1.53921100	-1.45929400
H	2.22043300	2.15618100	0.19955800
H	3.62790600	1.23314400	-0.31795800
H	1.73823200	-1.15725700	1.87841500
H	3.15001100	-0.10682400	1.77452800
H	1.56539300	0.59040700	2.10926800
H	3.66164600	-1.12276200	-0.49896600
H	2.22187000	-2.12893300	-0.39792400
H	2.45723300	-1.06163400	-1.79200900
O	-3.63570000	-0.01173800	0.51899500



INTa

C	1.14142600	1.23312900	-1.36927700

C	1.14143500	-1.23318000	-1.36927200
C	2.25713100	-1.25035700	-0.29176400
C	3.13984500	-0.00001100	-0.36733700
C	2.25723700	1.25042000	-0.29188800
H	0.56939300	-2.15581700	-1.33120900
H	1.61756300	1.18007200	-2.35423300
H	0.56937600	2.15576200	-1.33121800
H	1.78836100	-1.32832000	0.69463000
H	2.84418000	-2.15600100	-0.44705400
H	3.61500300	-0.00002000	-1.35961900
H	1.78864100	1.32871600	0.69456400
H	2.84436500	2.15595300	-0.44752700
H	1.61763000	-1.18014100	-2.35419800
C	4.30562000	-0.00003400	0.66455400
C	5.17896700	1.24367700	0.44470000
C	3.80328500	-0.00225500	2.11396700
C	5.18152800	-1.24142800	0.44177600
H	5.49582400	1.32565600	-0.59949500
H	4.66247000	2.16490000	0.72238900
H	6.07877700	1.18178200	1.06066700
H	3.21051200	-0.89090500	2.34390000
H	4.65777500	-0.00112400	2.79506100
H	3.20693200	0.88361400	2.34541800
H	6.08079000	-1.17955100	1.05854800
H	4.66668300	-2.16446200	0.71646000
H	5.49926600	-1.31978100	-0.60242800
C	-0.99821600	-0.00002300	-0.76395200
C	-1.72552500	-1.21878900	-0.52463300
C	-1.72546900	1.21875500	-0.52453200
C	-3.01251000	-1.22904700	-0.09828600
H	-1.24197900	-2.17218500	-0.68363000
C	-3.01245500	1.22903800	-0.09818900
H	-1.24187100	2.17214300	-0.68342700
C	-3.71982400	0.00000200	0.13214900
H	-3.50569200	-2.17573300	0.06546200
H	-3.50558600	2.17573200	0.06566100
N	-4.98283800	0.00001400	0.54161900
C	-5.69461200	1.26024900	0.77691400
H	-5.73551400	1.85510800	-0.13738200
H	-6.70980500	1.03637200	1.08881700
H	-5.20641900	1.83573900	1.56585600
C	-5.69462500	-1.26020800	0.77694300
H	-5.73576000	-1.85497900	-0.13740300
H	-5.20628800	-1.83579800	1.56572100
H	-6.70973200	-1.03631100	1.08910600
C	0.32092200	-0.00002700	-1.18433400