Electronic Supplementary Material (ESI) for Chemical Communications.

Dynamic resolution of 2-cyclohexylidene acetaldehydes through organocatalytic dienamine [4+2] cycloaddition

Jakob Blom, Tore Kiilerich Johansen, Frank Jensen and Karl Anker Jørgensen*

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

E-mail: kaj@chem.au.dk

Contents

1. General methods.

All solvents used were of high-performance liquid chromatography grade and were used as received, with the exception of solvents specified as dry, which were dried over activated alumina in a M-Braun MB-SPS 800.

All chemicals were brought at commercial suppliers and used as received without any further purification.

Moisture sensitive reactions were performed in flame-dried glassware, under argon atmosphere.

TLC analysis was performed using pre-coated aluminium-backed plates (Merck® Silica gel 60 F_{254}) and visualized by exposure to ultraviolet radiation, or by staining with a basic aqueous solution of $KMnO_4$ or an acidic ethanolic solution of *p*-anisaldehyde.

Flash column chromatography (FC) was performed using Fluka® Silica gel 60 (230-400 mesh).

Mass spectra were recorded on a Bruker MicroTOF-Q High-performance LC-MS system.

^{1}H NMR and ^{13}C NMR spectra were acquired on a Bruker NanoBay III spectrometer, running at 400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported relative to the residual solvent peak of chloroform δ(C<u>H</u>Cl_3): 7.26 ppm and δ(<u>C</u>HCl_3): 77.16 ± 0.06 ppm. The following abbreviations are used for NMR data: s, singlet; bs, broad singlet; d, doublet; dd, double doublet; t, triplet; tt, triple triplet; q, quartet; p, pentet; m, multiplet. Coupling constants are reported as the mean value between electronically coupled hydrogen atoms. For characterization of diastereomeric mixtures, * denotes minor diastereomer, + denotes overlap of signals from both diastereoisomers, while no signs denotes signals of major diastereomer. The number of protons given in the parenthesis is the sum over both diastereomers. ^{13}C NMR spectra were acquired on a broad band decoupled mode.

Single-crystal X-ray analysis was performed on a SuperNova Single Source At Offset Atlas (Mo X-ray source).

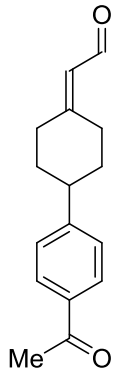
Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

The enantiomeric excess of the products was determined by Ultraperformance Convergence Chromatography (UPC^2) using Daicel Chrialpak IA, IB, IC or ID, or Trefoil^{TM} CEL2 columns as chiral stationary phases.

2. Synthesis of α,β-unsaturated aldehydes 1a-i

General procedure: The 2-step transformation of cyclohexanone derivatives into their corresponding α,β-unsaturated aldehydes was followed and afforded **1a-g** in accordance to literature.[1]

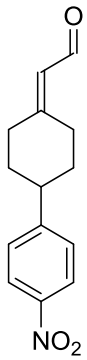
2-(4-(4-Acetylphenyl)cyclohexylidene)acetaldehyde 1h



Acylation of 2-(4-phenylcyclohexylidene)acetonitrile was achieved by following the general procedure.[2] FC (CH_2Cl_2) afforded the acylated nitrile in 84% yield as a white solid. The acylated nitrile (1.7 mmol, 1 eq) was dissolved in dry CH_2Cl_2 (13 mL, 0.13 M) and the mixture was cooled to -78 ^oC. A 1 M solution of diisobutylaluminum hydride in CH_2Cl_2 (3.7 mmol, 2.2 eq) was added drop wise to the cooled mixture. The mixture was allowed to react for 4 h, gradually warming to -40 ^oC, after which a sat. aq. solution of Rochelle salt (20 mL) was added. The biphasic mixture was stirred vigorously at rt overnight. Extracted with CH_2Cl_2 (3 x 20 mL), washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Without further purifications the crude was dissolved in dry CH_2Cl_2 (10 mL, 1.7 M) and added Dess-Martin periodinane (2.5 mmol, 1.5 eq). The mixture was allowed to react for 3 h at rt, after which it was concentrated *in vacuo* and subject to FC (40% Et_2O in pentane) affording the α,β-unsaturated aldehyde in 29% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (d, *J*=8.0 Hz, 1H), 7.91 (d, *J*=8.0 Hz, 2H), 7.31 (d, *J*=8.0 Hz, 2H), 5.91 (d, *J*=8.4 Hz, 1H), 3.53 (d, *J*=12.4 Hz, 1H), 2.91 (tt, *J*=12.0, 3.6 Hz, 1H), 2.50-2.62 (m, 4H), 2.40-2.50 (m, 1H), 2.23-2.34 (m, 1H), 2.10-2.21 (m, 2H), 1.65-1.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.9, 190.6, 165.5, 150.9, 135.8, 128.9 (2C), 127.1 (2C), 126.1, 44.1, 37.6, 35.0, 34.8, 29.2, 26.7. **HRMS** (ESI+) *m/z* calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380; found: 243.1377.

2-(4-(4-Nitrophenyl)cyclohexylidene)acetaldehyde 1i



In a flame dried flask, under Ar, was added 4-phenylcyclohexanone (10 mmol, 1.0 eq) to dry MeCN (80 ml, 0.12 M). The mixture was cooled to -78 ^oC and NO_2BF_4 (13 mmol, 1.3 eq) was added in one portion. After 10 min the mixture was warmed to 0 ^oC and then allowed to react at 0 ^oC for 2 h. The mixture was then warmed to rt and allowed to react for 1 h after which full consumption of 4-phenylcyclohexanone was observed. To the mixture was added 100 mL crushed ice and the organic phase was reduced *in vacuo*. The remaining was extracted with Et_2O (3 x 25 mL). The combined organic phases was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude was subject to FC (20% EtOAc in pentane) affording the *para*-nitrated ketone in 57% yield as a yellow solid.

The ketone was then subjected to the general two-step procedure.[1] FC (Iatrobeads, 20-0 % pentane in CH_2Cl_2) afforded the desired α,β-unsaturated aldehyde in 17% (over two steps) yield as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (d, *J*=8.0 Hz, 1H), 8.18 (d, *J*=8.8 Hz, 2H), 7.38 (d, *J*=8.8 Hz, 2H), 5.92 (d, *J*=8.0 Hz, 1H), 3.50-3.59 (m, 1H), 2.97 (tt, *J*=12.0, 3.6 Hz, 1H), 2.52-2.59 (m, 1H), 2.42-2.51 (m, 1H), 2.24-2.35 (m, 1H), 2.11-2.23 (m, 2H), 1.65-1.81 (m, 2H). **^{13}C NMR (100 MHz,**

[1] H. Jiang, K. S. Halskov, T. K. Johansen, and K. A Jørgensen, *Chem. Eur. J.* **2011**, *17*, 3842

[2] **Beecham Group Limited Patent:** US4309443 A1, **1982**

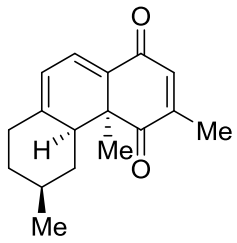
$CDCl_3$): δ 190.4, 164.7, 152.9, 146.8, 127.8 (2C), 126.2, 124.1 (2C), 44.0, 37.4, 34.9, 34.7, 29.0. **HRMS** (ESI+) *m/z* calcd. for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1125; found: 246.1123.

3. DTR-controlled cycloaddition

General procedure: α,β-Unsaturated aldehyde (100 μmol, 1.0 eq), 2,6-dimethylbenzoquinone (120 μmol, 1.2 eq) and benzoic acid (20 μmol, 0.2 eq) were added to a flask. $CHCl_3$ (0.50 mL, 0.2 M), water (18 μL, 10 eq) and finally catalyst **III** (5.0 μmol, 0.05 eq)* were added and the stirred mixture was allowed to react for 1-6 h at rt, after which full conversion of aldehyde was determined by crude ^{1}H NMR. The crude mixture was subject to FC on silica gel affording the cycloaddition adducts **3a-i**.

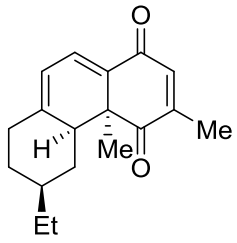
* For the synthesis of racemates, a 1:1 mixture of the *R*- and *S*-catalyst **III** was used.

(4a*S*,4b*S*,6*S*)-3,4a,6-Trimethyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3a



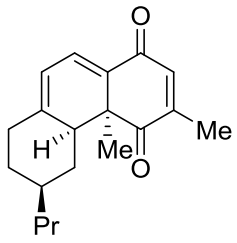
Following the general procedure compound **3a** was obtained after 1.5 h. FC (CH_2Cl_2/pentane 75-100%) affords the compound in 66% yield (combined yield of diastereomers, d.r. 4.3:1) and 99% ee as a yellow sticky oil. $[\alpha]_D^{28}$ = +880.0 (*c* = 0.8, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06+ (d, *J*=5.6 Hz, 2H), 6.80+ (s, 2H), 5.93+ (d, *J*=5.6 Hz, 2H), 2.93* (d, *J*=12.4 Hz, 1H), 2.68 (d, *J*=12.0 Hz, 1H), 2.51-2.35+ (m, 2H), 2.32-2.15+ (m, 2H), 2.03+ (s, 6H), 1.84-1.68+ (m, 4H), 1.34+ (s, 6H), 1.29-1.20+ (m, 2H), 1.18* (d, *J*=7.2 Hz, 3H), 1.11-0.97+ (m, 2H), 0.83 (d, *J*=6.4 Hz, 3H), 0.80-0.69+ (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.2, 201.1*, 185.1*, 185.0, 159.0*, 158.2, 147.0, 147.0*, 140.4, 140.4*, 131.9*, 131.9, 131.5, 131.2*, 115.2, 115.0*, 49.7, 48.5, 48.3*, 44.7*, 40.5, 37.9, 37.3*, 36.9, 35.3*, 33.2, 33.1*, 28.1*, 27.9, 27.8*, 21.7, 18.5*, 16.7, 16.7*. **HRMS** (ESI+) *m/z* calcd. for $C_{17}H_{21}O_2$ $[M+H]^+$: 257.1536; found: 257.1538. **UPC^2:** IA, CO_2/iPrOH gradient 99:1 to 90:10, 3 mL·min^{-1}; t_{major} = 3.62 min, t_{minor} = 3.47 min.

(4a*S*,4b*S*,6*S*)-6-Ethyl-3,4a-dimethyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3b



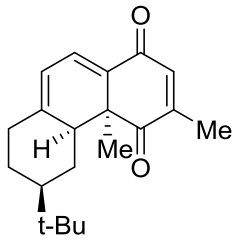
Following the general procedure compound **3b** was obtained after 1.5 h. FC (CH_2Cl_2/pentane 75-100%) affords the compound in 59% yield (combined yield of diastereomers, d.r. 1:5.4) and 99% ee as a yellow sticky oil. $[\alpha]_D^{27}$ = +860.9 (*c* = 0.8, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06+ (d, *J*=5.6 Hz, 2H), 6.80+ (s, 2H), 5.92+ (d, *J*=5.6 Hz, 2H), 2.85* (d, *J*=12.4 Hz, 1H), 2.67 (d, *J*=12.0 Hz, 1H), 2.46-2.38+ (m, 2H), 2.32-2.21+ (m, 2H), 2.13-2.05+ (m, 2H), 2.03+ (s, 6H), 1.91* (d, *J*=12.4 Hz, 1H), 1.78 (d, *J*=11.6 Hz, 1H), 1.69-1.50+ (m, 4H), 1.34+ (s, 6H), 1.23-1.07+ (m, 2H), 1.06-0.92+ (m, 2H), 0.82+ (t, *J*=7.6 Hz, 6H), 0.79-0.68+ (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.1, 201.1*, 185.0+, 159.0*, 158.5, 147.0, 147.0*, 140.4, 140.3*, 131.9*, 131.9, 131.5, 131.1*, 115.0, 115.0*, 49.8, 48.6, 48.3*, 44.9*, 39.7, 37.9, 36.8, 35.7, 35.5*, 35.3*, 33.5*, 32.8*, 29.8*, 29.2, 28.0, 27.8*, 24.9*, 16.7, 12.6*, 11.7. **HRMS** (ESI+) *m/z* calcd. for $C_{18}H_{23}O_2$ $[M+H]^+$: 271.1693; found: 271.1698. **UPC^2:** IA, CO_2/iPrOH gradient 99:1 to 90:10, 3 mL·min^{-1}; t_{major} = 3.90 min, t_{minor} = 3.73 min.

(4a*S*,4b*S*,6*S*)-3,4a-Dimethyl-6-propyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3c



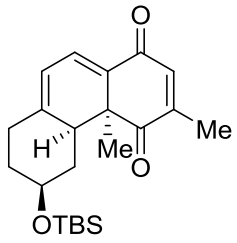
Following the general procedure compound **3c** was obtained after 1.5 h. FC (CH_2Cl_2/pentane 75-100%) affords the compound in 64% yield (combined yield of both diastereomers, d.r. 1:5.5) and 99% ee as a yellow sticky oil. $[\alpha]_D^{29}$ = +916.0 (*c* = 0.9, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06+ (d, *J*=5.6 Hz, 2H), 6.80+ (s, 2H), 5.92+ (d, *J*=5.6 Hz, 2H), 2.87* (d, *J*=12.0 Hz, 1H), 2.67 (d, *J*=11.6 Hz, 1H), 2.48-2.37+ (m, 2H), 2.32-2.21+ (m, 2H), 2.11-2.07+ (m, 2H), 2.03+ (s, 6H), 1.90* (d, *J*=12.0 Hz, 1H), 1.77 (d, *J*=11.2, 1H), 1.71-1.59+ (m, 2H), 1.34+ (s, 6H), 1.30-1.19+ (m, 4H), 1.16-1.04+ (m, 4H), 1.03-0.92+ (m, 2H), 0.89-0.80+ (t, *J*=7.2 Hz, 6H), 0.79-0.69+ (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.1, 201.1*, 185.1*, 185.0, 159.1*, 158.5, 147.0, 147.0*, 140.4, 140.3*, 132.0*, 131.9, 131.5, 131.1*, 115.0, 115.0*, 49.8, 48.6, 48.3*, 44.9*, 38.8, 38.4, 37.8, 36.9, 36.1, 35.6*, 34.4*, 33.5*, 33.4*, 33.3*, 27.9, 27.8*, 21.2*, 20.3, 16.7+, 14.4*, 14.4. **HRMS** (ESI+) *m/z* calcd. for $C_{19}H_{25}O_2$ $[M+H]^+$: 285.1849; found: 285.1854. **UPC^2:** IA, CO_2/iPrOH gradient 99:1 to 95:5, 3 mL·min^{-1}; t_{major} = 4.99 min, t_{minor} = 4.81 min.

(4a*S*,4b*S*,6*S*)-6-(*tert*-Butyl)-3,4a-dimethyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3d



Following the general procedure compound **3d** was obtained after 1.5 h. FC (CH_2Cl_2/pentane 75-100%) affords the compound in 49% yield (combined yield of diastereomers, d.r. >20:1) and 99% ee as a yellow sticky oil. $[\alpha]_D^{27}$ = +815.7 (*c* = 0.7, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.08 (d, *J*=5.2 Hz, 1H), 6.81 (s, 1H), 5.91 (d, *J*=5.6 Hz, 1H), 2.64 (d, *J*=11.6 Hz, 1H), 2.48-2.41 (m, 1H), 2.30-2.19 (m, 1H), 2.14-2.06 (m, 1H), 2.04 (s, 3H), 1.85 (d, *J*=11.6 Hz, 1H), 1.50-1.41 (m, 1H), 1.34 (s, 3H), 1.19-1.07 (m, 1H), 0.97-0.82 (m, 1H), 0.80 (s, 9H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.1, 185.0, 158.8, 147.1, 140.4, 132.0, 131.5, 114.7, 50.0, 48.7, 48.4, 37.0, 33.2, 32.7, 30.7, 28.1, 27.8 (3C), 16.8. **HRMS** (ESI+) *m/z* calcd. for $C_{20}H_{27}O_2$ $[M+H]^+$: 299.2006; found: 299.2008. **UPC^2:** IA, CO_2/iPrOH 95:5, 3 mL·min^{-1}; t_{major} = 2.49 min, t_{minor} = 2.12 min.

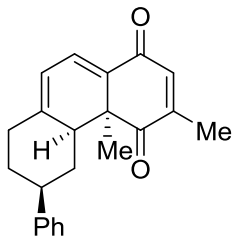
(4a*S*,4b*S*,6*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-3,4a-dimethyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3e



Following the general procedure compound **3e** was obtained after 1.5 h. FC (Et_2O/pentane 10%) affords compound as separate diastereoisomers in 75% yield (combined yield of diastereomers, d.r. 1.6:1) and 98/99% ee as a yellow sticky oil. Major; $[\alpha]_D^{28}$ = +226.4 (*c* = 0.7, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.06 (d, *J*=5.7 Hz, 1H), 6.91-6.71 (m, 1H), 5.93 (d, *J*=5.8 Hz, 1H), 4.07 (s, 1H), 3.41-3.19 (m, 1H), 2.70 (td, *J*=11.9, 4.4 Hz, 1H), 2.39-2.18 (m, 1H), 2.02 (s, 3H), 1.97 (s, 1H), 1.80 (dd, *J*=12.3, 3.3 Hz, 1H), 1.60-1.42 (m, 1H), 1.35 (s, 3H), 1.18 (td, *J*=12.3, 2.2 Hz, 1H), 0.98 (d, *J*=1.9 Hz, 9H), 0.14 (s, 3H), 0.06 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.3, 185.2, 158.9, 147.3, 140.0, 133.0, 131.3, 115.0, 67.1, 48.0, 43.6, 39.9, 37.1, 32.5, 27.9, 26.0 (3C), 18.3, 16.9, -4.8, -4.9. **HRMS** (ESI+) *m/z* calcd. for $C_{22}H_{33}O_3Si$ $[M+H]^+$: 373.2193; found: 373.2198. **UPC^2:** IA, CO_2/iPrOH 95:5, 3 mL·min^{-1}; t_{major} = 2.64 min t_{minor} = 2.57 min.

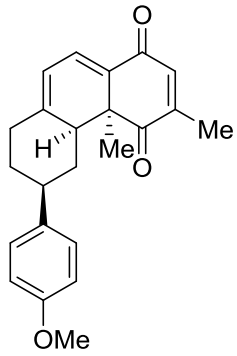
Minor; $[\alpha]_D^{28}$ = +403.2 (*c* = 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.03 (d, *J*=5.8 Hz, 1H), 6.77 (s, 1H), 5.92 (d, *J*=5.8 Hz, 1H), 3.86 (dt, *J*=10.8, 6.0 Hz, 1H), 2.54 (d, *J*=12.8 Hz, 1H), 2.38-2.32 (m, 1H), 2.24-2.18 (m, 1H), 2.18-2.08 (m, 1H), 2.00 (s, 3H), 1.94-1.83 (m, 1H), 1.39-1.27 (m, 1H), 1.29 (s, 3H), 1.00 (q, *J*=11.4 Hz, 1H), 0.81 (s, 9H), 0.01 (s, 3H), -0.00 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.7, 184.8, 155.6, 147.2, 140.4, 131.6, 131.5, 116.1, 70.8, 48.5, 46.1, 40.3, 38.0, 34.0, 28.0, 26.0 (3C), 18.2, 16.8, -4.5, -4.6.
HRMS (ESI+) *m/z* calcd. for $C_{22}H_{33}O_3Si$ $[M+H-SiC_3H_8]^+$: 259.1329; found: 259.1308. **UPC^2:** IA, CO_2/iPrOH 95:5, 3 mL·min^{-1}; t_{major} = 2.38 min, t_{minor} = 2.20 min.

(4a*S*,4b*S*,6*S*)-3,4a-Dimethyl-6-phenyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3f



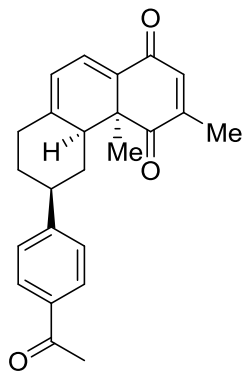
Following the general procedure compound **3f** was obtained after 5 h. FC (CH_2Cl_2/pentane 75-100%) affords the compound in 70% yield (combined yield of diastereomers, d.r. 15:1) and 99% ee as a yellow solid. $[\alpha]_D^{26}$ = +903.9 (*c* = 1.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46-7.52* (m, 2H), 7.36-7.42* (m, 3H), 7.20-7.29 (m, 2H), 7.08-7.15 (m, 3H), 7.15-7.19+ (m, 2H), 6.82* (d, *J*=1.4 Hz, 1H), 6.80 (d, *J*=1.5 Hz, 1H), 6.03+ (d, *J*=5.9 Hz, 2H), 2.95+ (tt, *J*=12.4, 3.9 Hz, 2H), 2.84+ (dd, *J*=12.2, 3.3 Hz, 2H), 2.50-2.59+ (m, 2H), 2.45+ (td, *J*=12.0, 4.4 Hz, 2H), 2.16-2.25+ (m, 2H), 2.04* (d, *J*=1.2 Hz, 3H), 1.98 (d, *J*=1.2 Hz, 3H), 1.89-1.96+ (m, 2H), 1.52-1.65+ (m, 2H), 1.39+ (s, 6H), 1.30+ (q, *J*=12.1 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.9+, 184.9+, 157.0+, 147.1+, 145.2+, 140.4+, 131.7+, 131.7+, 128.6+ (2C), 127.0+ (2C), 126.5+, 115.7+, 49.8+, 48.5+, 44.8+, 39.5+, 37.0+, 36.9+, 28,0+, 16.7+.
HRMS (ESI+) *m/z* calcd. for $C_{22}H_{23}O_2$ $[M+H]^+$: 319.1693; found: 319.1693. **UPC^2:** IB, CO_2/iPrOH gradient 99:1 to 40:60, 3 mL·min^{-1}; t_{major} = 3.18 min, t_{minor} = 3.13 min.

(4a*S*,4b*S*,6*S*)-6-(4-Methoxyphenyl)-3,4a-dimethyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3g



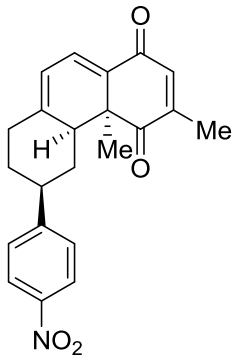
Following the general procedure compound **3g** was obtained after 3 h. FC (Et_2O/pentane 16%) affords the compound in 69% yield (combined yield of diastereomers, d.r. >20:1) and 98% ee as a yellow sticky oil. $[\alpha]_D^{28}$ = +882.0 (*c* = 1.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.11 (d, *J*=5.9 Hz, 1H), 7.04 (d, *J*=8.5 Hz, 2H), 6.83-6.74 (m, 3H), 6.02 (d, *J*=5.8 Hz, 1H), 3.75 (s, 3H), 3.03-2.86 (m, 1H), 2.84-2.77 (m, 1H), 2.64-2.48 (m, 1H), 2.50-2.35 (m, 1H), 2.28-2.12 (m, 1H), 1.98 (d, *J*=1.8 Hz, 3H), 1.89 (d, *J*=12.2 Hz, 1H), 1.38 (s, 3H), 1.33-1.25 (m, 1H), 1.25-1.18 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.9, 184.9, 158.2, 157.1, 147.1, 140.4, 137.5, 131.7, 131.7, 127.9 (2C), 115.6 (2C), 113.9, 55.4, 49.8, 48.5, 44.0, 39.7, 37.2, 37.0, 28.9, 16.7.
HRMS (ESI+) *m/z* calcd. for $C_{23}H_{25}O_3$ $[M+H]^+$: 349.1798; found: 349.1801. **UPC^2:** IA, CO_2/iPrOH 95:5, 3 mL·min^{-1}; t_{major} = 4.25 min, t_{minor} = 3.08 min.

(4a*S*,4b*S*,6*S*)-6-(4-Acetylphenyl)-3,4a-dimethyl-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3h



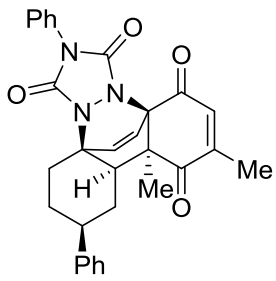
Following the general procedure compound **3h** was obtained after 6 h. FC (Et_2O/CH_2Cl_2 4%) affords the compound in 76% yield (combined yield of diastereomers, d.r. 19:1) and 90% ee as a yellow oil. $[\alpha]_D^{26}$ = +898.0 (*c* = 1.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.08* (d, *J*=8.4 Hz, 2H), 7.85 (d, *J*=8.4 Hz, 2H), 7.61* (d, J=8.4 Hz, 2H), 7.22 (d, *J*=8.4 Hz, 2H), 7.12+ (d, *J*=5.6 Hz, 2H), 6.78-6.83+ (m, 2H), 6.04+ (d, *J*=5.6 Hz, 2H), 2.97-3.11+ (m, 2H), 2.89* (dd, *J*=12.4, 4.4 Hz, 1H), 2.83 (dd, *J*=12.0, 3.2 Hz, 1H), 2.52-2.62+ (m, 8H), 2.37-2.50+ (m, 2H), 2.14-2.16+ (m, 2H), 2.03-2.06* (m, 3H), 1.96-2.01 (m, 3H), 1.89-1.96+ (m, 2H), 1.51-1.64+ (m, 2H), 1.34-1.43+ (m, 6H), 1.22-1.33+ (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.8+, 197.8+, 184.8+, 156.3+, 150.7+, 147.1+, 140.4+, 135.6+, 131.7+, 131.6+, 128.8+ (2C), 127.3+ (2C), 115.9+, 49.5+, 48.5+, 44.8+, 39.1+, 36.8+, 36.3+, 28.0+, 26.7+, 16.7+. **HRMS** (ESI+) *m/z* calcd. for $C_{24}H_{25}O_3$ $[M+H]^+$: 361.1798; found: 361.1804. **UPC^2:** ID, CO_2/iPrOH gradient 99:1 to 40:60, 3 mL·min^{-1}; t_{major} = 5.19 min, t_{minor} = 5.03 min.

(4a*S*,4b*S*,6*S*)-3,4a-Dimethyl-6-(4-nitrophenyl)-4a,4b,5,6,7,8-hexahydrophenanthrene-1,4-dione 3i



Following the general procedure compound **3i** was obtained after 6 h. FC (CH_2Cl_2/pentane 75-100 %) affords the compound in 64% yield (combined yield of diastereomers, d.r. 19:1) and 99% ee as a yellow solid. $[\alpha]_D^{26}$ = +741.6 (*c* = 1.2, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.27* (d, *J*=9,2 Hz, 2H), 8.12 (d, *J*=8.8 Hz, 2H), 7.69* (d, J=8.8 Hz, 2H), 7.30 (d, *J*=8.8 Hz, 2H), 7.08-7.14+ (m, 2H), 6.78-6.85+ (m, 2H), 6.03-6.08+ (m, 2H), 3.03-3.15+ (m, 2H), 2.84+ (dd, *J*=12.0, 3.2 Hz, 2H), 2.55-2.63+ (m, 2H), 2.39-2.51+ (m, 2H), 2.15-2.28+ (m, 2H), 2.05* (d, *J*=1.6 Hz, 3H), 2.00 (d, *J*=1.6 Hz, 3H), 1.92-1.98+ (m, 2H), 1.52-1.65+ (m, 2H), 1.40+ (bs, 6H), 1.24-1.36+ (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.8+, 184.7+, 155.6+, 152.7+, 147.2+, 146.7+, 140.5+, 131.7+, 131.5+, 127.9+ (2C), 123.9+ (2C), 116.1+, 49.3+, 48.5+, 44.7+, 39.0+, 36.7+, 36.1+, 28.0+, 16.8+. **HRMS** (ESI+) *m/z* calcd. for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1543; found: 364.1545. **UPC^2:** IC, CO_2/iPrOH gradient 99:1 to 60:40, 3 mL·min^{-1}; t_{major} = 4.72 min, t_{minor} = 4.86 min.

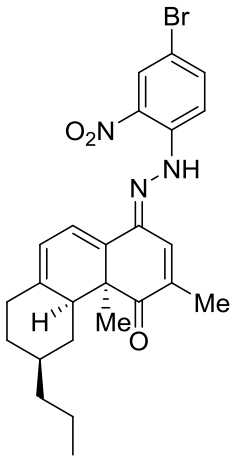
(4a*R*,8a*S*,8b*R*,10*S*,12a*S*)-7,8a-Dimethyl-2,10-diphenyl-8a,8b,9,10,11,12-hexahydro-1*H*-4a,12a-ethenobenzo[*c*][1,2,4]triazolo[1,2-*a*]cinnoline-1,3,5,8(2*H*)-tetraone 5



The cycloaddition adduct **3f** (0.5 mmol, 1 eq) was dissolved in $CHCl_3$ (1.0 ml, 0.5 M). To the stirred solution at rt was added 4-phenyl-1,2,4-triazoline-3,5-dione (0.6 mmol, 1.2 eq) as two equal size portions with a 20 min interval. The mixture was allowed to react for 40 min at rt, after which it was concentrated *in vacuo*. FC (EtOAc/pentane 10-20%) afforded the compound in 88% (0.44 mmol) yield as a clear solid. Crystals suitable for single crystal X-ray were obtained by dissolving the compound in a heptane/Et_2O mixture, which was allowed to slowly concentrate at rt. $[\alpha]_D^{27}$ = -28.2 (*c* = 0.7, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39-7.46 (m, 4H), 7.19-7.37 (m, 6H), 7.05 (d, *J*=8.0 Hz, 1H), 6.91 (d, *J*=1.6 Hz, 1H), 6.43 (d, *J*=8.0 Hz, 1H), 3.31-3.39 (m, 1H), 2.99 (d,

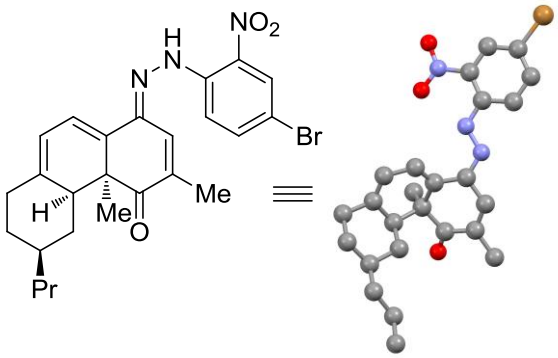
J=13.6 Hz, 1H), 2.63-2.73 (m, 1H), 2.12-2.26 (m, 1H), 1.90-2.03 (m, 5H), 1.76 (dd, *J*=12.4, 3.6 Hz, 1H), 1.58 (q, *J*=12.4 Hz, 1H), 1.14 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.4, 189.4, 155.4, 154.3, 147.2, 146.0, 135.4, 135.0, 131.0, 129.2 (2C), 128.6 (2C), 128.6, 127.1 (2C), 126.5, 125.6 (2C), 124.8, 69.7, 63.1, 54.0, 50.5, 44.8, 34.2, 32.4, 28.4, 27.0, 16.9. **HRMS** (ESI+) *m/z* calcd. for $C_{30}H_{28}N_3O_4$ $[M+H]^+$: 494.2074; found: 494.2076.

(4a*S*,4b*S*,6*S*,*E*)-1-(2-(4-Bromo-2-nitrophenyl)hydrazono)-3,4a-dimethyl-6-propyl-4a,4b,5,6,7,8-hexahydrophenanthren-4(1*H*)-one 6



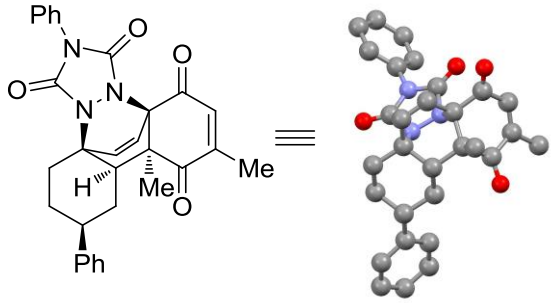
The cycloaddition adduct **3c** (0.1 mmol, 1 eq) was dissolved in $CHCl_3$ (0.5 mL, 0.2 M). To the stirred solution at rt was added 4-bromo-2-nitrophenylhydrazine hydrochloride (0.105 mmol, 1.05 eq). The mixture was allowed to react for 16 h at 60 °C after which it was concentrated *in vacuo*. FC (EtOAc/pentane 5%) afforded the compound in 62% yield (combined yield of *E*:*Z*, 1.2:1) as a red solid. Crystals suitable for single crystal X-ray were obtained by dissolving the compound in Et_2O, which was allowed to slowly concentrate at rt. $[\alpha]_D^{28}$ = +882.0 (*c* = 1.1, CH_2Cl_2) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.54 (s, 1H), 11.47* (s, 1H), 8.27+ (d, *J*=2.3 Hz, 2H), 7.87* (d, *J*=4.7 Hz, 1H), 7.85 (d, *J*=4.7 Hz, 1H), 7.56+ (td, *J*=9.5, 2.4 Hz, 2H), 7.24* (d, *J*=1.6 Hz, 1H), 7.04 (d, *J*=1.4 Hz, 1H), 6.82+ (dd, *J*=13.2, 6.0 Hz, 2H), 5.84 (d, *J*=6.0 Hz, 1H), 5.74* (d, *J*=6.0 Hz, 1H), 2.64-2.47+ (m, 2H), 2.40-2.25+ (m, 2H), 2.23-2.09+ (m, 2H), 2.01+ (d, J = 1.4 Hz, 3H), 2.01-1.94+ (m, 2H), 1.89+ (d, *J*=1.3 Hz, 3H), 1.63-1.50+ (m, 4H), 1.48+ (s, 6H), 1.26+ (s, 6H), 1.22-0.80+ (m, 6H), 0.77+ (t, *J*=7.3 Hz, 6H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.4, 201.1, 152.7, 150.4, 143.0, 142.8, 140.9, 140.6, 140.5, 139.8, 139.2, 139.1, 135.8, 132.3, 131.8, 130.4, 128.3, 127.3, 125.6, 125.6, 121.4, 118.2, 118.1, 114.6, 113.5, 111.2, 110.6, 100.1, 50.0, 49.1, 48.9, 48.8, 39.1, 39.0, 38.4, 38.3, 38.0, 37.9, 37.3, 36.4, 36.4, 36.1, 27.4, 26.3, 20.3 (2C), 17.4, 15.9, 14.5 (2C). **HRMS** (ESI+) *m/z* calcd. for $C_{25}H_{29}BrN_3O_3$ $[M+H]^+$: 498.1387; found: 498.1314.

4. X-Ray structures



Item	Value
Molecular formula	$C_{25}H_{28}BrN_3O_3$
Formula weight	498.42
Crystal system	monoclinic
Space Group	P 1 2 1
a (Å)	10.064
b (Å)	8.502
c (Å)	13.718
α (°)	90
β (°)	100.284
γ (°)	90
Volume ($Å^3$)	1154.9
Z	2
T (K)	100
ρ (g cm^{-1})	1.4331
λ (Å)	0.56086
μ (mm^{-1})	0.977
# measured refl	29092
# unique refl	5929
R_{int}	0.0602
# parameters	291
$R(F^2)$, all refl	0.0463
$R_w(F^2)$, all refl	0.1016
Goodness of fit	1.003

Crystal data for **6**: $C_{25}H_{28}BrN_3O_3$, M = 498.42, monoclinic, space group P 1 2 1 (no. 3), a = 10.064(3) Å, b = 8.502(2) Å, c = 13.718(4) Å, β = 100.284(7)°, Flack parameter = 0.029, V = 1154.9(5) $Å^3$, T = 100 K, Z = 2, d_c = 1.4331 g cm^{-3}, μ(Mo Kα, λ = 0.56086 Å) = 0.977 mm^{-1}, 29092 reflections collected, 5929 unique [R_{int} = 0.0602], which were used in all calculations. Refinement on F^2, final R(F) = 0.0463, R_w(F2) = 0.1016. CCDC number 1457544.



Item	Value
Molecular formula	$C_{30}H_{27}N_3O_4$
Formula weight	493.57
Crystal system	monoclinic
Space Group	P 1 2 1
a (Å)	12.983
b (Å)	10.976
c (Å)	16.961
α (°)	90
β (°)	99.955
γ (°)	90
Volume (Å^3)	2380.6
Z	4
T (K)	100
ρ (g cm^{-1})	1.377
λ (Å)	0.56086
μ (mm^{-1})	0.058
# measured refl	34349
# unique refl	11189
R_{int}	0.0841
# parameters	670
R(F^2), all refl	0.0545
R_w(F^2), all refl	0.1
Goodness of fit	1.0081

Crystal data for **5** $C_{30}H_{27}N_3O_4$, M = 493.57, monoclinic, space group P 1 2 1 (no. 3), a = 12.983(3) Å, b = 10.976(3) Å, c = 16.961(4) Å, β = 99.955(8)°, V = 2380.6(9) Å^3, T = 100 K, Z = 4, d_c = 1.377 g cm^{-3}, μ(Mo Kα, λ = 0.56086 Å) = 0.058 mm^{-1}, 34349 reflections collected, 11189 unique [R_{int} = 0.0841], which were used in all calculations. Refinement on F^2, final R(F) = 0.0545, R_w(F2) = 0.1. CCDC number 1457564.

5. Computational data

Coordinates for the optimized structures:

S-*trans-syn* dienamine
Energy = -1666.1431136000

C	-3.041299	0.203848	-0.801454
C	-4.486573	0.690031	-0.813743
C	-5.322031	-0.003805	0.265123
C	-5.354366	-1.503023	-0.053948
C	-4.000633	-2.047516	-0.418344
C	-2.926462	-1.302239	-0.733231
C	-1.619727	-1.918489	-0.966001
C	-0.503555	-1.203591	-1.233312
N	0.762534	-1.686486	-1.381712
C	1.052401	-3.108619	-1.405027
C	2.575383	-3.186329	-1.503825
C	2.988345	-1.827201	-2.077984
C	1.920484	-0.838377	-1.592380
H	-2.495576	0.645887	0.047172
H	-2.534560	0.574464	-1.702804
H	-4.925907	0.478736	-1.799748
H	-4.498010	1.779667	-0.692156
H	-4.777186	0.104398	1.219030
H	-6.069069	-1.703488	-0.869774
H	-5.731163	-2.066904	0.809400
H	-3.890215	-3.134129	-0.389693
H	-1.561704	-3.002665	-0.861775
H	-0.568825	-0.122638	-1.322221
H	0.549913	-3.577170	-2.267433
H	0.671750	-3.600232	-0.497756
H	2.900454	-4.018998	-2.136139
H	3.013408	-3.335872	-0.510845
H	2.962845	-1.855078	-3.174155
H	3.994241	-1.517126	-1.781872
H	1.714142	-0.100228	-2.376846
C	2.359315	-0.007057	-0.323900
C	3.333683	-2.971382	2.687049
C	4.337552	-2.232133	2.072935
C	4.014887	-1.251929	1.138414
C	2.688298	-0.986998	0.801896
C	1.684454	-1.737603	1.427792
C	2.004376	-2.717106	2.359944
H	3.583633	-3.740812	3.415025
H	5.382421	-2.421986	2.311711
H	4.810686	-0.706283	0.641031
H	0.639133	-1.572848	1.177043
H	1.205861	-3.288337	2.829884

C	-0.659033	3.002791	0.563496
C	-0.092243	2.896103	-0.703717
C	0.869413	1.927692	-0.956432
C	1.282667	1.032322	0.038284
C	0.728895	1.172708	1.309948
C	-0.235211	2.144446	1.569471
H	-1.418851	3.755328	0.765226
H	-0.397984	3.572663	-1.499435
H	1.311834	1.874013	-1.948662
H	1.053792	0.529869	2.122412
H	-0.654363	2.227576	2.570369
O	3.519682	0.674624	-0.757660
Si	4.314812	2.045746	-0.159931
C	3.832377	3.555275	-1.150697
H	4.502486	4.389892	-0.901495
H	3.921257	3.365029	-2.228193
H	2.804257	3.871983	-0.940030
C	6.123969	1.680795	-0.452274
H	6.737049	2.554133	-0.192018
H	6.477165	0.833476	0.148821
H	6.306289	1.445502	-1.508883
C	3.974492	2.332799	1.656193
H	4.067473	1.409752	2.241939
H	4.701387	3.058209	2.047876
H	2.969358	2.740508	1.816901
C	-6.723018	0.635056	0.493493
C	-7.499563	0.791393	-0.820403
H	-8.509814	1.173709	-0.621601
H	-7.010600	1.498037	-1.502148
H	-7.608214	-0.165608	-1.346968
C	-6.547471	2.017768	1.138370
H	-5.965184	2.698478	0.505793
H	-7.523932	2.488554	1.314427
H	-6.035129	1.936067	2.106495
C	-7.546063	-0.232482	1.456402
H	-8.476182	0.281704	1.733101
H	-7.823980	-1.193606	1.007326
H	-6.989415	-0.438552	2.381159

S-*trans*-*anti* dienamine

Energy = -1666.1433431700

C	-3.054987	0.227062	-0.378668
C	-4.338431	0.715233	0.284242
C	-5.564051	-0.014879	-0.271320
C	-5.426433	-1.502899	0.070800
C	-4.043234	-2.035560	-0.183697
C	-2.955022	-1.281876	-0.419391
C	-1.657693	-1.893536	-0.711062

C	-0.562851	-1.172425	-1.041272
N	0.687428	-1.649274	-1.300350
C	0.970797	-3.069778	-1.398055
C	2.479874	-3.142437	-1.626747
C	2.844200	-1.766307	-2.192252
C	1.823166	-0.793521	-1.587179
H	-2.192568	0.640800	0.161492
H	-2.984565	0.624951	-1.403583
H	-4.421144	1.800201	0.149863
H	-4.268193	0.535795	1.367341
H	-5.513195	0.062402	-1.371352
H	-6.137186	-2.096715	-0.518837
H	-5.699791	-1.678129	1.124637
H	-3.936430	-3.122894	-0.193498
H	-1.601071	-2.981402	-0.655211
H	-0.637101	-0.090245	-1.105875
H	0.396287	-3.507848	-2.231074
H	0.667346	-3.593552	-0.479753
H	2.750621	-3.955216	-2.308446
H	2.997442	-3.320612	-0.678155
H	2.724421	-1.760624	-3.282503
H	3.872290	-1.464710	-1.974078
H	1.549687	-0.033656	-2.329166
C	2.374036	0.000696	-0.339371
C	3.623031	-3.035574	2.493356
C	2.269029	-2.787252	2.283987
C	1.864938	-1.787239	1.408448
C	2.807370	-1.010123	0.721931
C	4.159191	-1.271318	0.937998
C	4.566389	-2.271561	1.816872
H	3.938594	-3.819507	3.179213
H	1.517596	-3.379149	2.803389
H	0.801481	-1.625947	1.247561
H	4.905796	-0.705566	0.389457
H	5.628723	-2.456351	1.965270
C	-0.542598	2.973497	0.930504
C	-0.097361	2.912210	-0.387399
C	0.833246	1.953581	-0.764005
C	1.335380	1.023836	0.155660
C	0.902545	1.117936	1.477573
C	-0.030411	2.078868	1.861059
H	-1.277611	3.718243	1.229196
H	-0.473700	3.616638	-1.126730
H	1.180195	1.935683	-1.794916
H	1.299275	0.446232	2.232781
H	-0.352921	2.125637	2.899410
O	3.488599	0.698735	-0.857926
Si	4.331617	2.062443	-0.312902

C	3.739572	3.591396	-1.211811
H	3.643780	3.404585	-2.289311
H	2.769457	3.936967	-0.835595
H	4.466069	4.404712	-1.076090
C	6.102778	1.717251	-0.796976
H	6.738586	2.581962	-0.564172
H	6.513560	0.848179	-0.267809
H	6.180694	1.523628	-1.874657
C	4.177505	2.302693	1.534780
H	4.362431	1.371910	2.085378
H	4.917065	3.045319	1.865376
H	3.181986	2.670715	1.809816
C	-6.926620	0.613499	0.141489
C	-7.075102	1.987760	-0.527973
H	-8.050944	2.430508	-0.288020
H	-6.306206	2.696352	-0.197750
H	-7.006027	1.900564	-1.620765
C	-7.039569	0.784943	1.661817
H	-8.032165	1.172996	1.927446
H	-6.905443	-0.167022	2.191402
H	-6.295881	1.493552	2.047071
C	-8.079913	-0.273899	-0.348786
H	-9.043780	0.227568	-0.189218
H	-7.985835	-0.485381	-1.422998
H	-8.117701	-1.232395	0.182628

Cycloaddition intermediate **4a**
Energy = -2126.3050867300

C	-3.361034	0.479406	-3.114033
C	-4.040640	1.528758	-2.213339
C	-3.201655	1.775343	-0.951389
C	-3.218656	0.494140	-0.095465
C	-3.216787	-0.798227	-0.951707
C	-2.565941	-0.487313	-2.275996
C	-1.357548	-0.932388	-2.613280
C	-0.472779	-1.786323	-1.738948
C	-1.032698	-1.900357	-0.326295
C	-2.574295	-2.028395	-0.275620
C	-0.384902	-2.995235	0.486429
C	-0.925363	-3.155569	1.854301
C	-2.150887	-2.736353	2.202147
C	-3.061208	-2.150358	1.170300
O	0.515895	-3.709863	0.091048
O	-4.200124	-1.852121	1.475139
H	-2.695385	0.966467	-3.837424
H	-4.122288	-0.063031	-3.693001
H	-5.038555	1.177583	-1.916613
H	-4.199175	2.451005	-2.782871

H	-2.160808	1.931296	-1.283705
H	-4.102372	0.480338	0.552364
H	-2.348067	0.487665	0.570227
H	-4.265545	-1.056536	-1.155799
H	-0.931478	-0.628597	-3.571723
H	-0.281133	-3.670306	2.566222
C	-3.042570	-3.316382	-0.986242
H	-4.125104	-3.438517	-0.868649
H	-2.820407	-3.261144	-2.057330
H	-2.551719	-4.208963	-0.578458
C	-2.705340	-2.871298	3.582270
H	-3.603045	-3.500342	3.581147
H	-1.965272	-3.301644	4.263232
H	-3.009774	-1.888621	3.961674
C	-3.592521	3.058123	-0.164826
C	-2.833626	3.109174	1.168132
H	-2.997083	4.074208	1.665759
H	-3.165427	2.324687	1.858871
H	-1.752135	2.999191	1.013212
C	-5.099253	3.112243	0.117088
H	-5.337951	3.980353	0.745804
H	-5.681665	3.206366	-0.807679
H	-5.448590	2.216165	0.645939
C	-3.186951	4.293320	-0.981801
H	-3.448343	5.214468	-0.444214
H	-2.103136	4.306419	-1.160387
H	-3.689405	4.329578	-1.955782
H	-0.415670	-2.802000	-2.154359
H	-0.787595	-0.978578	0.211712
C	1.157913	0.102728	-1.433986
N	0.911360	-1.306067	-1.732159
C	1.650885	-1.711038	-2.936684
C	2.524153	-0.521651	-3.332224
C	1.803356	0.672580	-2.707648
H	0.210458	0.621537	-1.234157
H	0.950418	-1.953768	-3.751972
H	2.240485	-2.616994	-2.739427
H	2.620829	-0.431973	-4.420116
H	3.533446	-0.626067	-2.921853
H	1.003183	1.022218	-3.373432
H	2.457941	1.523338	-2.500929
C	2.064134	0.354209	-0.161852
C	0.022291	-0.317978	3.622161
C	1.173392	-1.037540	3.333720
C	1.824348	-0.874236	2.112327
C	1.339151	0.012675	1.152339
C	0.176970	0.729695	1.459654
C	-0.476764	0.570207	2.673960

H	-0.483597	-0.445316	4.577143
H	1.581131	-1.732415	4.065600
H	2.741077	-1.426718	1.934292
H	-0.212221	1.444974	0.737337
H	-1.376450	1.146296	2.882056
C	5.811505	-1.753335	-0.751615
C	4.629124	-2.462086	-0.551507
C	3.431766	-1.791691	-0.335628
C	3.391084	-0.390547	-0.316060
C	4.579471	0.307395	-0.519085
C	5.780659	-0.364290	-0.733506
H	6.748354	-2.280583	-0.922816
H	4.634889	-3.550623	-0.570001
H	2.509863	-2.356911	-0.221752
H	4.564827	1.391513	-0.545390
H	6.694217	0.205104	-0.895866
O	2.273681	1.756738	-0.180381
Si	2.679790	2.914936	0.977675
C	3.438691	2.164876	2.512133
H	3.898264	2.959392	3.116595
H	2.688941	1.656252	3.130110
H	4.220510	1.437721	2.257739
C	1.166555	3.928102	1.413564
H	0.591001	4.176968	0.511779
H	0.501853	3.407532	2.112506
H	1.473643	4.872667	1.883547
C	3.900153	4.042079	0.117391
H	3.491682	4.398020	-0.837555
H	4.106631	4.922256	0.741336
H	4.858457	3.548649	-0.086837

Cycloaddition intermediate **4b**
Energy = -2126.2934301200

C	-3.574278	-2.426828	0.116516
C	-4.986588	-2.131876	0.616343
C	-5.648187	-1.001388	-0.197965
C	-4.585087	0.024577	-0.668316
C	-3.377317	0.097084	0.280949
C	-2.664641	-1.235128	0.290904
C	-1.349761	-1.353159	0.452456
C	-0.411727	-0.183212	0.505288
C	-1.180981	1.088829	0.990910
C	-2.452743	1.329917	0.146695
C	-0.287477	2.308842	1.003853
C	-0.181964	3.063851	-0.259191
C	-0.916388	2.751479	-1.340251
C	-1.971883	1.677945	-1.261624
O	0.338195	2.645534	1.997174

O	-2.450576	1.232516	-2.286446
H	-3.621668	-2.676226	-0.955573
H	-3.150797	-3.303767	0.620024
H	-4.934875	-1.869158	1.682815
H	-5.594333	-3.041646	0.557138
H	-6.047117	-1.471579	-1.109735
H	-5.034546	1.015209	-0.785721
H	-4.224454	-0.245223	-1.664318
H	-3.789825	0.198842	1.297975
H	-0.890550	-2.342609	0.460452
H	0.546586	3.874550	-0.280963
C	-3.224964	2.555393	0.694026
H	-4.156159	2.713469	0.139250
H	-3.481258	2.379351	1.745355
H	-2.648147	3.483548	0.640341
C	-0.778934	3.441799	-2.656891
H	-1.718039	3.941798	-2.925461
H	0.025705	4.182358	-2.635581
H	-0.578603	2.710023	-3.447139
C	-6.883374	-0.369079	0.509020
C	-7.660028	0.492434	-0.497404
H	-8.554406	0.922762	-0.027668
H	-7.060402	1.326677	-0.881400
H	-7.987976	-0.107420	-1.357114
C	-6.484331	0.503628	1.705929
H	-7.381142	0.895196	2.204522
H	-5.914312	-0.060589	2.455334
H	-5.880894	1.366423	1.398380
C	-7.823193	-1.481402	0.997335
H	-8.758752	-1.050831	1.378464
H	-8.080092	-2.170841	0.181211
H	-7.379226	-2.069100	1.809685
H	0.355119	-0.371657	1.261252
H	-1.470767	0.902128	2.033486
C	1.575402	0.533820	-0.905724
N	0.231688	-0.002752	-0.794712
C	-0.082194	-0.838303	-1.948686
C	0.675431	-0.159680	-3.090885
C	1.745990	0.721113	-2.421938
H	1.601089	1.500904	-0.390247
H	-1.161029	-0.846009	-2.129046
H	0.241759	-1.882935	-1.819255
H	-0.013349	0.453212	-3.682492
H	1.116219	-0.899268	-3.768030
H	1.592286	1.777871	-2.666784
H	2.759278	0.478480	-2.754511
C	2.721693	-0.283196	-0.202106
C	2.184908	-4.404525	-1.421639

C	1.751449	-3.974074	-0.172455
C	1.970865	-2.660518	0.230534
C	2.620250	-1.753731	-0.605043
C	3.071222	-2.202092	-1.850302
C	2.853758	-3.513302	-2.256379
H	2.011465	-5.430518	-1.740595
H	1.233627	-4.662058	0.493464
H	1.617113	-2.323749	1.200592
H	3.603307	-1.524139	-2.514179
H	3.210941	-3.840605	-3.231102
C	6.668703	1.447958	-0.738841
C	5.535280	2.251216	-0.819403
C	4.269040	1.693249	-0.688834
C	4.104608	0.319416	-0.486687
C	5.251216	-0.475330	-0.414606
C	6.520974	0.080638	-0.534174
H	7.659964	1.886552	-0.835737
H	5.636584	3.323438	-0.974917
H	3.406641	2.353186	-0.731962
H	5.153049	-1.546925	-0.257081
H	7.397266	-0.561542	-0.468130
O	2.450419	-0.146896	1.178315
Si	3.335799	-0.084383	2.607647
C	4.382720	-1.618536	2.843730
H	3.790861	-2.534403	2.721748
H	5.219184	-1.656838	2.136211
H	4.805754	-1.622638	3.858136
C	1.971677	-0.012176	3.877105
H	2.372862	0.121717	4.890609
H	1.302712	0.828874	3.651010
H	1.376850	-0.935141	3.866425
C	4.410009	1.440941	2.697093
H	4.817107	1.548196	3.712355
H	5.252286	1.392994	1.995794
H	3.824856	2.341485	2.470252

Cycloaddition intermediate **4c**

Energy = -2126.3100840000

C	-3.073611	0.651216	-3.013347
C	-2.989050	1.907627	-2.135464
C	-3.497539	1.669344	-0.704391
C	-2.782191	0.461814	-0.068935
C	-2.945959	-0.784753	-0.960206
C	-2.345235	-0.449550	-2.302916
C	-1.165796	-0.926581	-2.698027
C	-0.270376	-1.815443	-1.868662
C	-0.844091	-2.090695	-0.476569
C	-2.385967	-2.114542	-0.418096

C	-0.275074	-3.349079	0.133539
C	-0.849036	-3.735222	1.443506
C	-2.037077	-3.286834	1.876584
C	-2.865811	-2.392307	1.003355
O	0.597709	-4.026848	-0.374524
O	-3.934395	-1.980733	1.412308
H	-2.630747	0.846016	-3.997498
H	-4.127458	0.377654	-3.170319
H	-3.540713	2.726973	-2.612044
H	-1.933619	2.214047	-2.100265
H	-4.560840	1.383548	-0.781916
H	-3.216198	0.256358	0.912267
H	-1.711837	0.676321	0.076086
H	-4.027629	-0.930877	-1.097956
H	-0.756241	-0.604107	-3.657609
H	-0.263431	-4.439350	2.035157
C	-2.953949	-3.282623	-1.260886
H	-4.044698	-3.325158	-1.160537
H	-2.714989	-3.138610	-2.319247
H	-2.545540	-4.250571	-0.945688
C	-2.620866	-3.640185	3.204405
H	-3.594888	-4.127439	3.082400
H	-1.954470	-4.300362	3.766689
H	-2.794755	-2.727066	3.786234
C	-3.469733	2.959999	0.171110
C	-2.100563	3.647356	0.116147
H	-2.044516	4.454515	0.858877
H	-1.290256	2.943372	0.336019
H	-1.902381	4.093147	-0.866727
C	-3.792171	2.622792	1.634414
H	-3.943047	3.546584	2.208322
H	-4.710069	2.024513	1.714780
H	-2.980810	2.066374	2.119093
C	-4.542983	3.936493	-0.331922
H	-4.530587	4.860385	0.261585
H	-4.387294	4.219295	-1.379715
H	-5.545353	3.495858	-0.245689
H	-0.148631	-2.778513	-2.379398
H	-0.495309	-1.278991	0.181419
C	1.217434	0.160478	-1.508110
N	1.087476	-1.279452	-1.716068
C	2.062781	-1.677079	-2.725587
C	2.187752	-0.482727	-3.674630
C	1.950551	0.722069	-2.756138
H	0.214030	0.590406	-1.422740
H	1.748402	-2.601832	-3.219382
H	3.027609	-1.880947	-2.240317
H	1.417214	-0.535470	-4.454145

H	3.160016	-0.440195	-4.179272
H	1.349621	1.498968	-3.241746
H	2.897446	1.196936	-2.479769
C	1.915918	0.507401	-0.145538
C	5.252517	-2.246463	0.054306
C	5.422321	-1.003231	-0.544948
C	4.371784	-0.090461	-0.573009
C	3.136780	-0.398015	0.004843
C	2.981363	-1.648705	0.602534
C	4.025219	-2.564604	0.628907
H	6.069575	-2.965414	0.070700
H	6.374828	-0.740154	-1.001197
H	4.527433	0.870379	-1.058254
H	2.018346	-1.912182	1.026323
H	3.872678	-3.539072	1.088920
C	2.591448	4.766403	0.378802
C	1.512480	4.304866	-0.369143
C	1.335213	2.942437	-0.573049
C	2.225126	2.006629	-0.037274
C	3.302056	2.485229	0.712471
C	3.486576	3.849488	0.917717
H	2.731641	5.833043	0.542441
H	0.796013	5.008542	-0.788791
H	0.472999	2.612244	-1.145805
H	4.007288	1.786996	1.155680
H	4.332748	4.193103	1.509718
O	0.943773	0.199868	0.850093
Si	0.843826	0.619294	2.485582
C	2.412418	0.210059	3.420128
H	3.267004	0.816194	3.097857
H	2.249564	0.407575	4.489085
H	2.685997	-0.845667	3.306948
C	-0.555108	-0.449862	3.103916
H	-0.797478	-0.191160	4.143685
H	-1.463423	-0.307191	2.503828
H	-0.287548	-1.512162	3.074895
C	0.398479	2.412283	2.767609
H	0.286271	2.573945	3.849342
H	1.156963	3.111783	2.398122
H	-0.557670	2.665031	2.296185

Cycloaddition intermediate **4d**

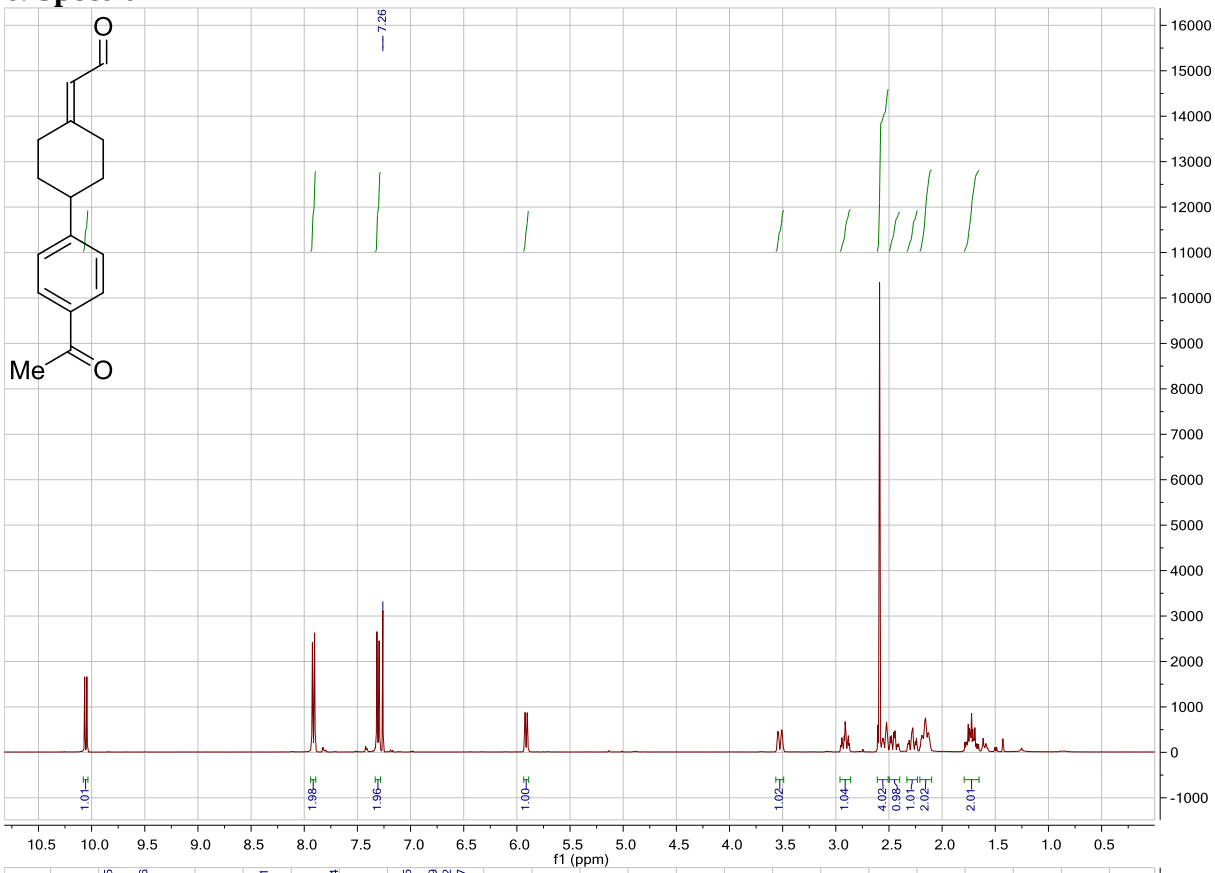
Energy = -2126.2977258900

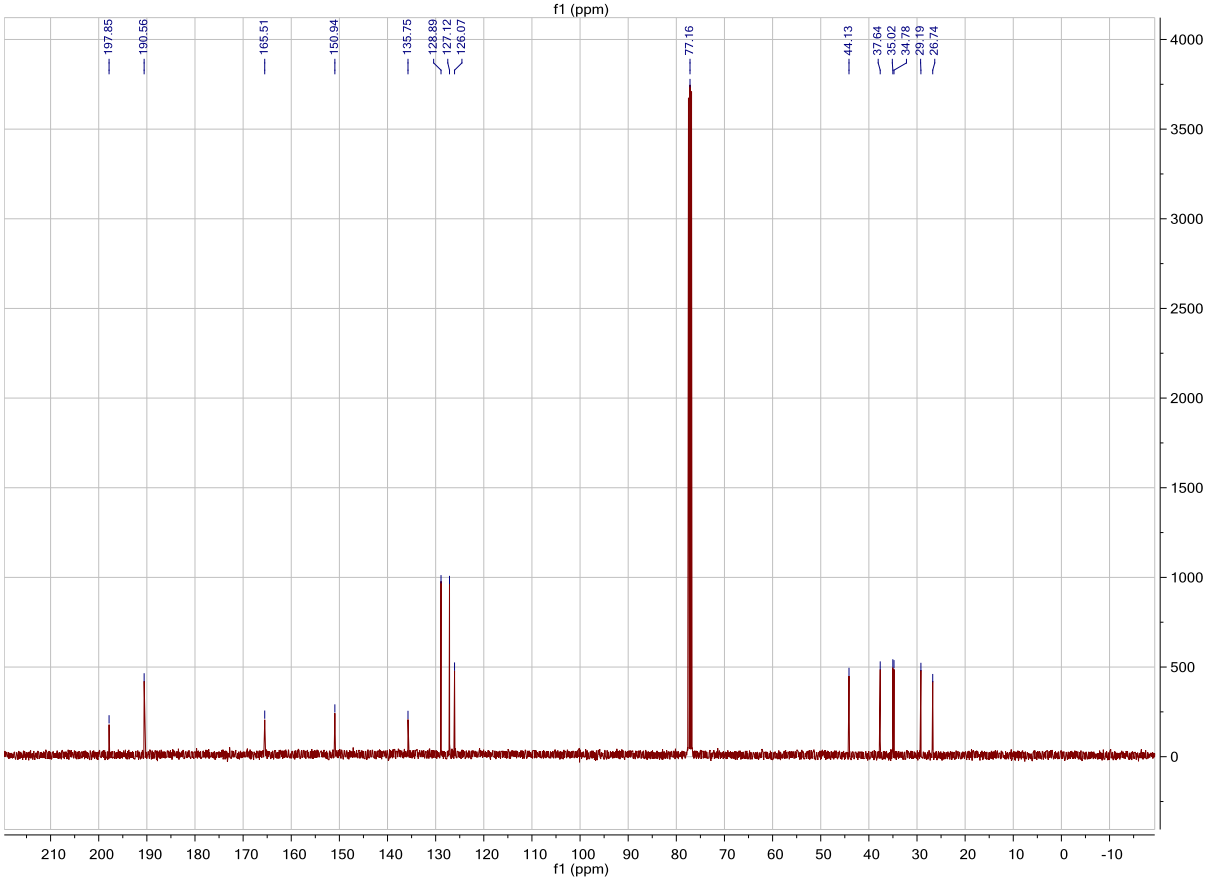
C	3.564628	1.826495	1.731821
C	4.781838	1.973689	0.818098
C	5.480746	0.626618	0.607490
C	4.459058	-0.353014	0.020325
C	3.259163	-0.570859	0.959641

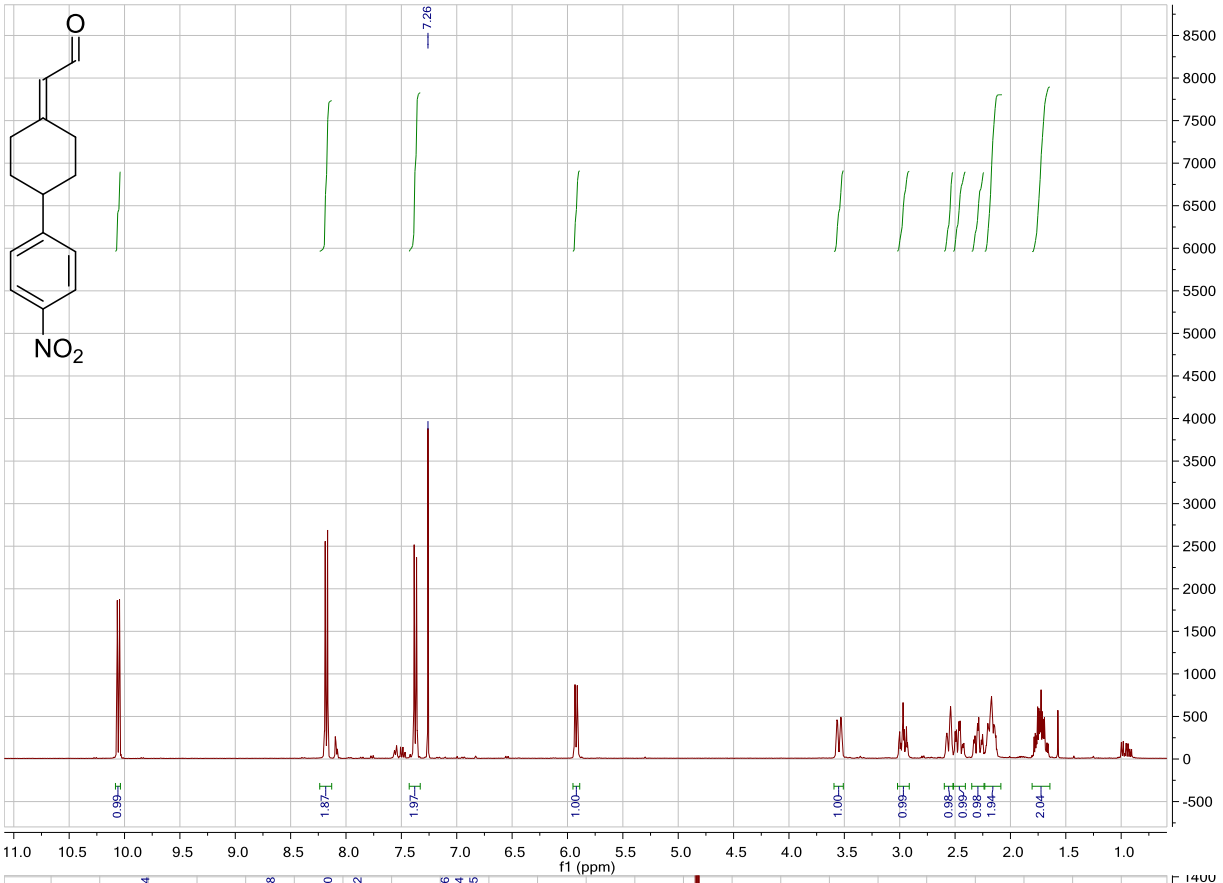
C	2.608330	0.754675	1.281483
C	1.293365	0.950421	1.237274
C	0.316256	-0.133776	0.892054
C	0.942434	-1.511146	1.284762
C	2.284347	-1.717607	0.554912
C	-0.033212	-2.638680	1.044759
C	-0.041520	-3.232406	-0.301906
C	0.838169	-2.859090	-1.245572
C	1.949780	-1.887821	-0.932536
O	-0.806000	-3.019283	1.911165
O	2.589979	-1.418370	-1.853191
H	3.036175	2.782624	1.828315
H	3.919802	1.560255	2.740781
H	5.461981	2.709542	1.260946
H	4.459661	2.379642	-0.152153
H	5.773354	0.256028	1.606292
H	4.924086	-1.320718	-0.195105
H	4.095530	0.032480	-0.935701
H	3.689014	-0.909022	1.919113
H	0.881741	1.937030	1.451510
H	-0.813738	-3.974726	-0.504967
C	2.944896	-3.044875	1.004974
H	3.938945	-3.152352	0.555905
H	3.062790	-3.040247	2.094841
H	2.360210	-3.929349	0.733414
C	0.815774	-3.391114	-2.640635
H	1.738324	-3.947344	-2.849969
H	-0.042296	-4.050420	-2.800223
H	0.781457	-2.567241	-3.361568
C	6.800564	0.705426	-0.217123
C	7.528615	-0.645520	-0.144967
H	8.494952	-0.587569	-0.663348
H	7.725231	-0.930402	0.897762
H	6.957057	-1.454333	-0.614776
C	7.732972	1.766807	0.386058
H	8.721718	1.717333	-0.088705
H	7.351642	2.784133	0.239046
H	7.871248	1.607793	1.464559
C	6.536769	1.054056	-1.687659
H	7.487699	1.160881	-2.226771
H	5.955839	0.274307	-2.194951
H	5.993389	2.002113	-1.790172
H	-0.570871	-0.015887	1.519294
H	1.117834	-1.476916	2.367760
C	-1.427011	-0.421388	-0.930530
N	-0.080881	-0.068480	-0.511423
C	0.509466	0.889965	-1.439518
C	-0.087117	0.486241	-2.788950

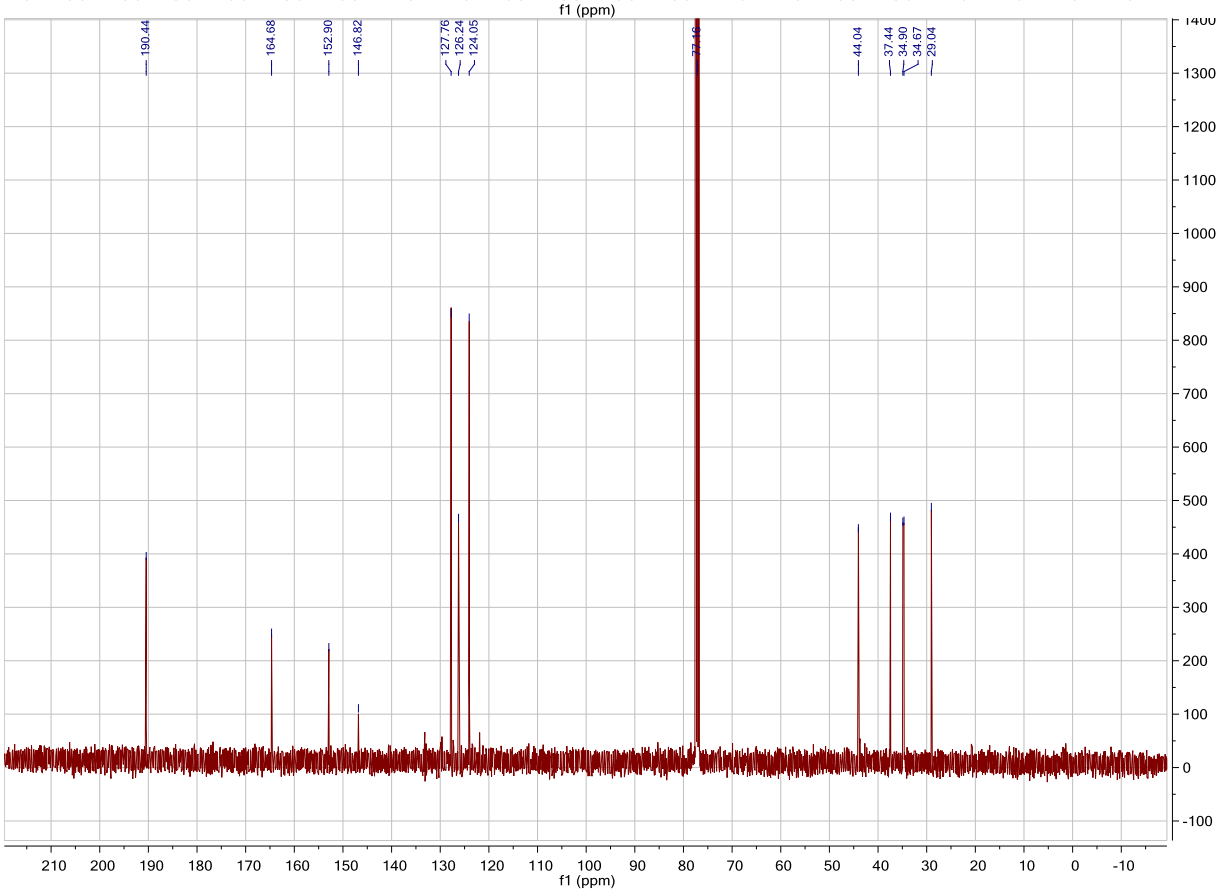
C	-1.332498	-0.358980	-2.463694
H	-1.630338	-1.444347	-0.591654
H	1.599743	0.795934	-1.437763
H	0.265237	1.933751	-1.186413
H	0.640628	-0.103388	-3.356834
H	-0.335769	1.367657	-3.389873
H	-1.226694	-1.376607	-2.854816
H	-2.243090	0.044599	-2.915133
C	-2.605532	0.412904	-0.303521
C	-1.503352	4.581868	-0.711231
C	-2.064322	3.900334	-1.788101
C	-2.463514	2.576896	-1.648113
C	-2.303415	1.905253	-0.432321
C	-1.763365	2.604487	0.644842
C	-1.363228	3.930566	0.509016
H	-1.187584	5.617445	-0.822465
H	-2.193424	4.401936	-2.745320
H	-2.908431	2.066704	-2.499537
H	-1.642091	2.095392	1.596527
H	-0.935631	4.453337	1.362703
C	-6.530178	-0.717718	-1.777940
C	-5.479988	-1.629421	-1.819268
C	-4.211825	-1.259340	-1.386276
C	-3.961593	0.032612	-0.914360
C	-5.024029	0.938930	-0.883906
C	-6.297177	0.569364	-1.305809
H	-7.524230	-1.009163	-2.111771
H	-5.648626	-2.640963	-2.183379
H	-3.419581	-2.002642	-1.409859
H	-4.857077	1.950017	-0.519002
H	-7.107770	1.294487	-1.266293
O	-2.611469	0.042599	1.059960
Si	-3.749668	-0.147971	2.285732
C	-4.678360	1.442929	2.621394
H	-5.396051	1.681128	1.827586
H	-5.240405	1.346404	3.560993
H	-3.991260	2.291956	2.727421
C	-2.658251	-0.592095	3.730309
H	-1.988001	0.238340	3.989142
H	-3.252469	-0.837283	4.620956
H	-2.038717	-1.461640	3.472157
C	-4.953748	-1.528400	1.918405
H	-4.421645	-2.437832	1.611246
H	-5.526180	-1.763758	2.826838
H	-5.665489	-1.261451	1.127550

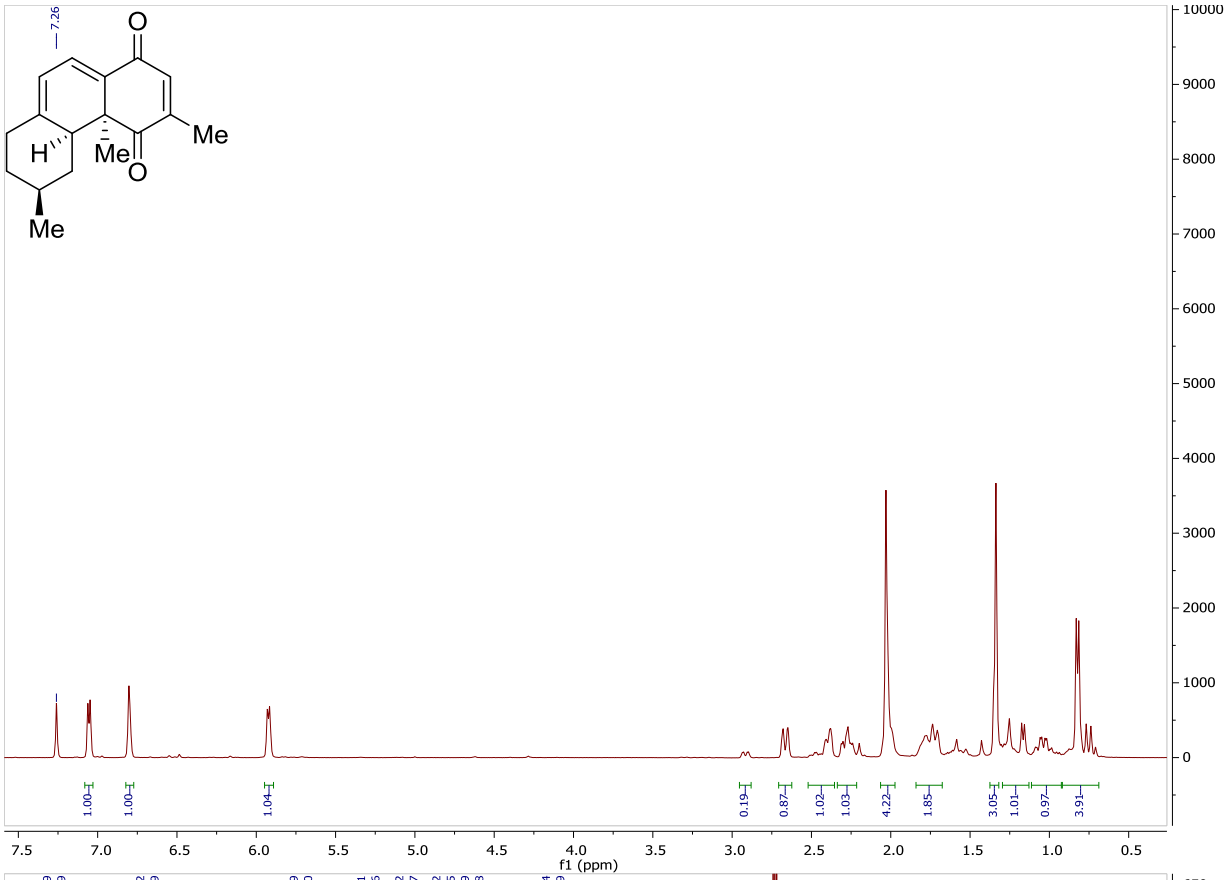
6. **Spectra**

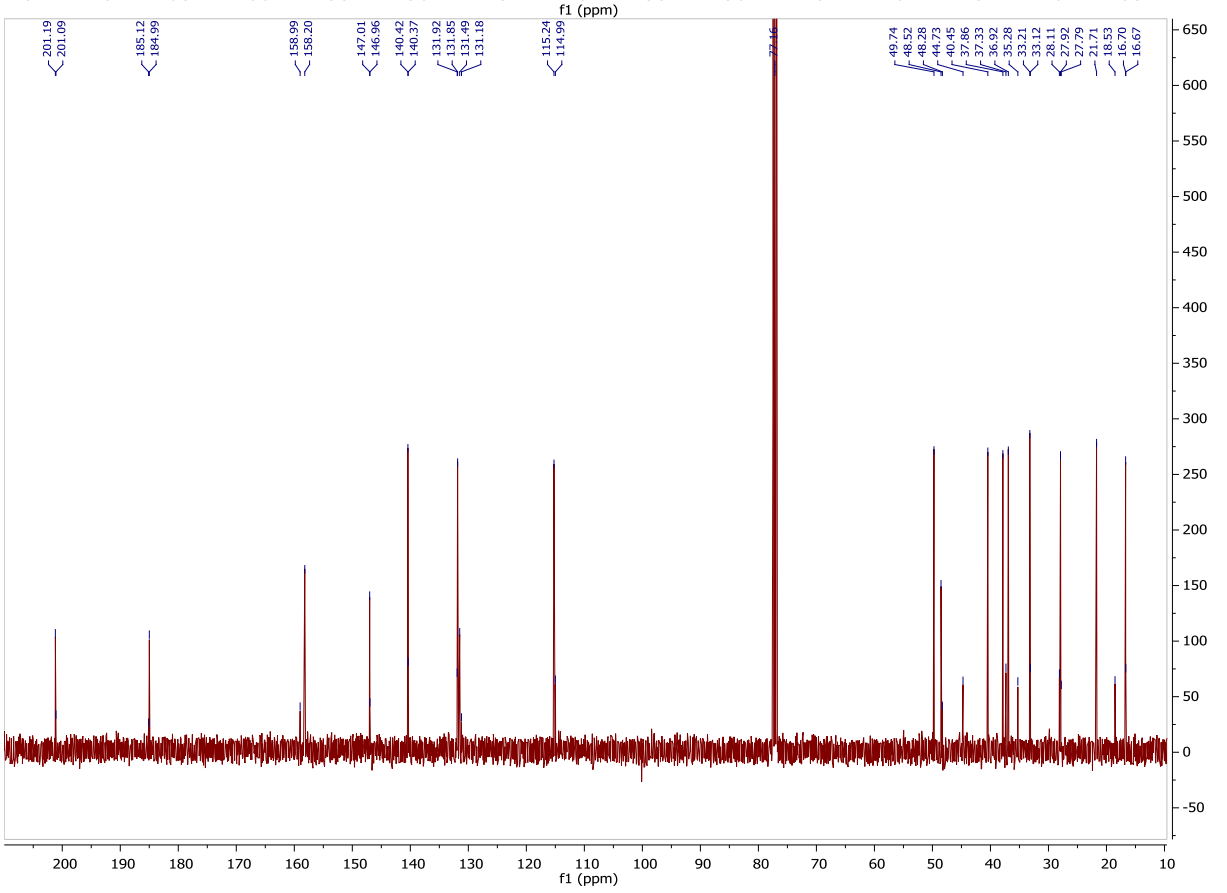

O
Me
O
7.26
1.01
1.98
1.96
1.00
1.02
1.04
4.02
0.98
1.01
2.02
2.01
f1 (ppm)

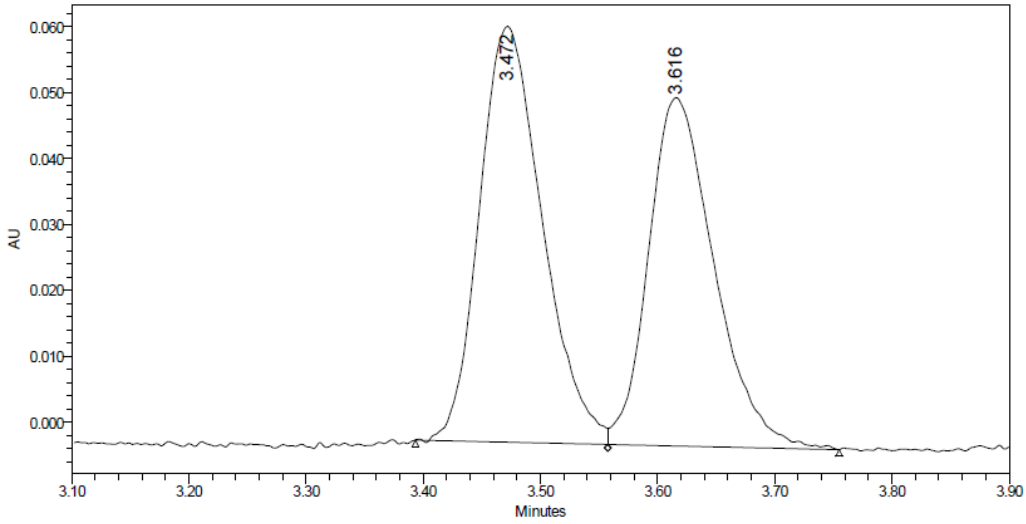

197.85
190.56
165.51
150.94
135.75
128.89
127.12
126.07
77.16
44.13
37.64
35.02
34.78
29.19
26.74
f1 (ppm)


O
NO2
7.26
0.99
1.87
1.97
1.00
1.00
0.99
0.98
0.99
0.98
1.94
2.04
f1 (ppm)

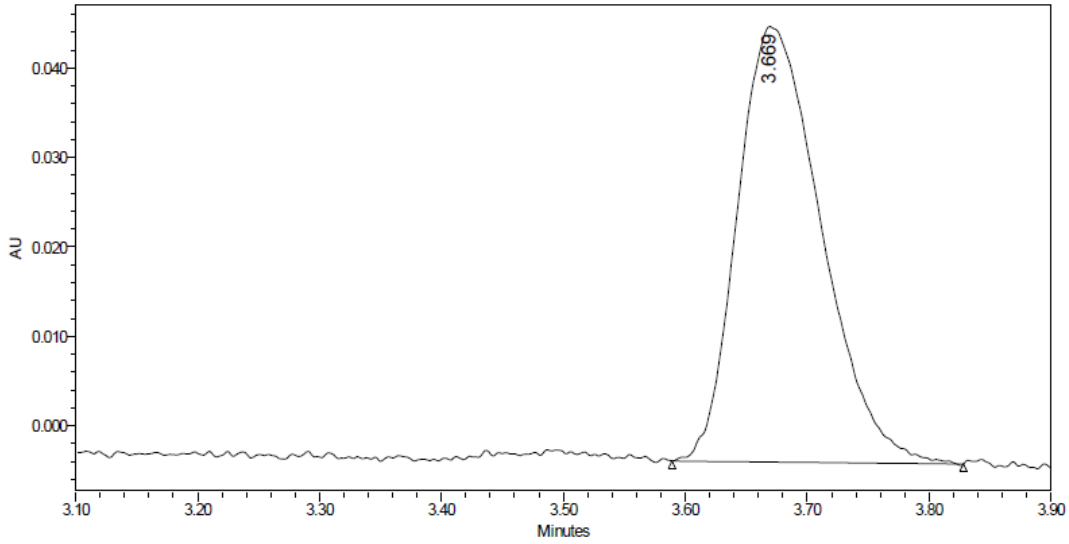

190.44
164.68
152.90
146.82
127.76
126.24
124.05
77.46
44.04
37.44
34.90
34.67
29.04
f1 (ppm)


7.26
O
Me
H
Me
O
Me
1.00
1.00
1.04
0.19
0.87
1.02
1.03
4.22
1.85
3.05
1.01
0.97
3.91
f1 (ppm)

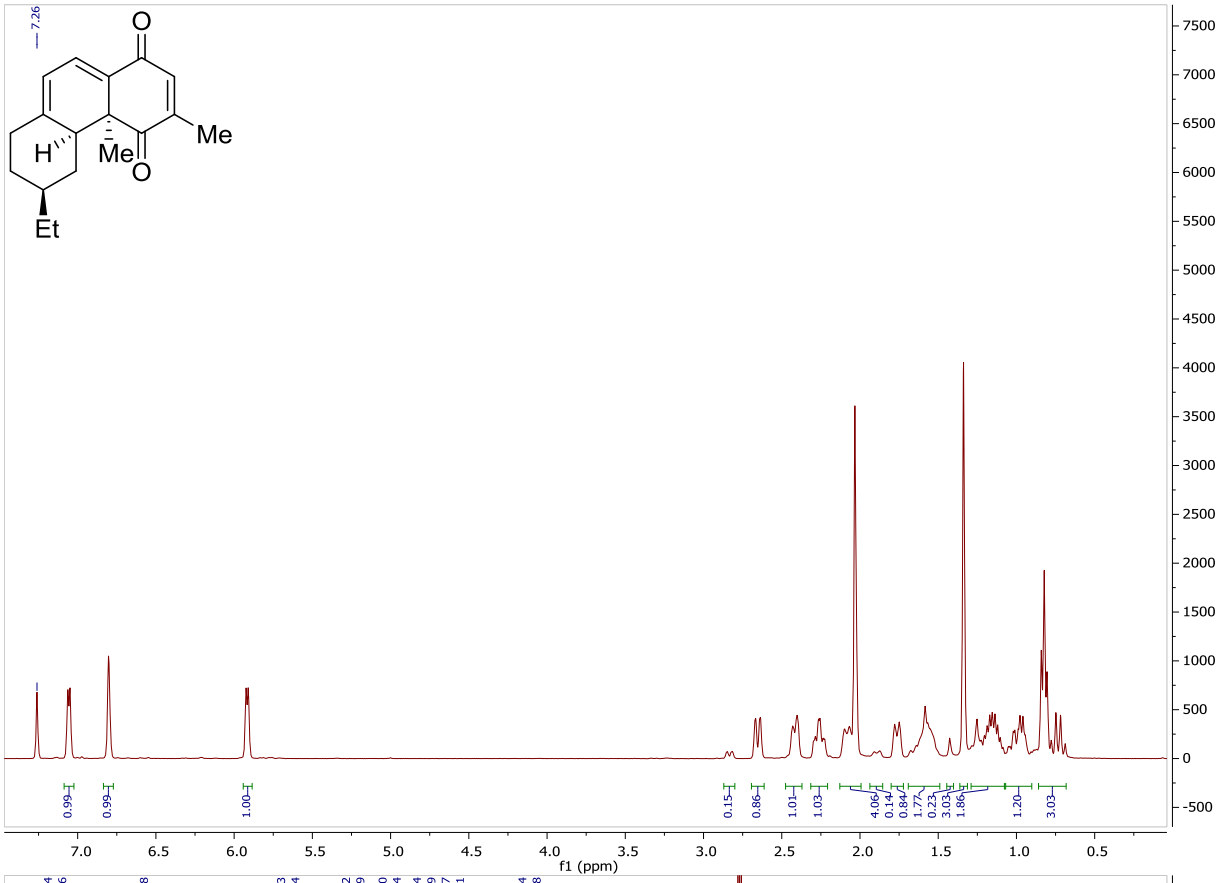

201.19
201.09
185.12
184.99
158.99
158.20
147.01
146.96
140.42
140.37
131.92
131.85
131.49
131.18
115.24
114.99
77.16
49.74
48.52
48.28
44.73
40.45
37.86
37.33
36.92
35.28
33.21
33.12
28.11
27.92
27.79
21.71
18.53
16.70
16.67
f1 (ppm)

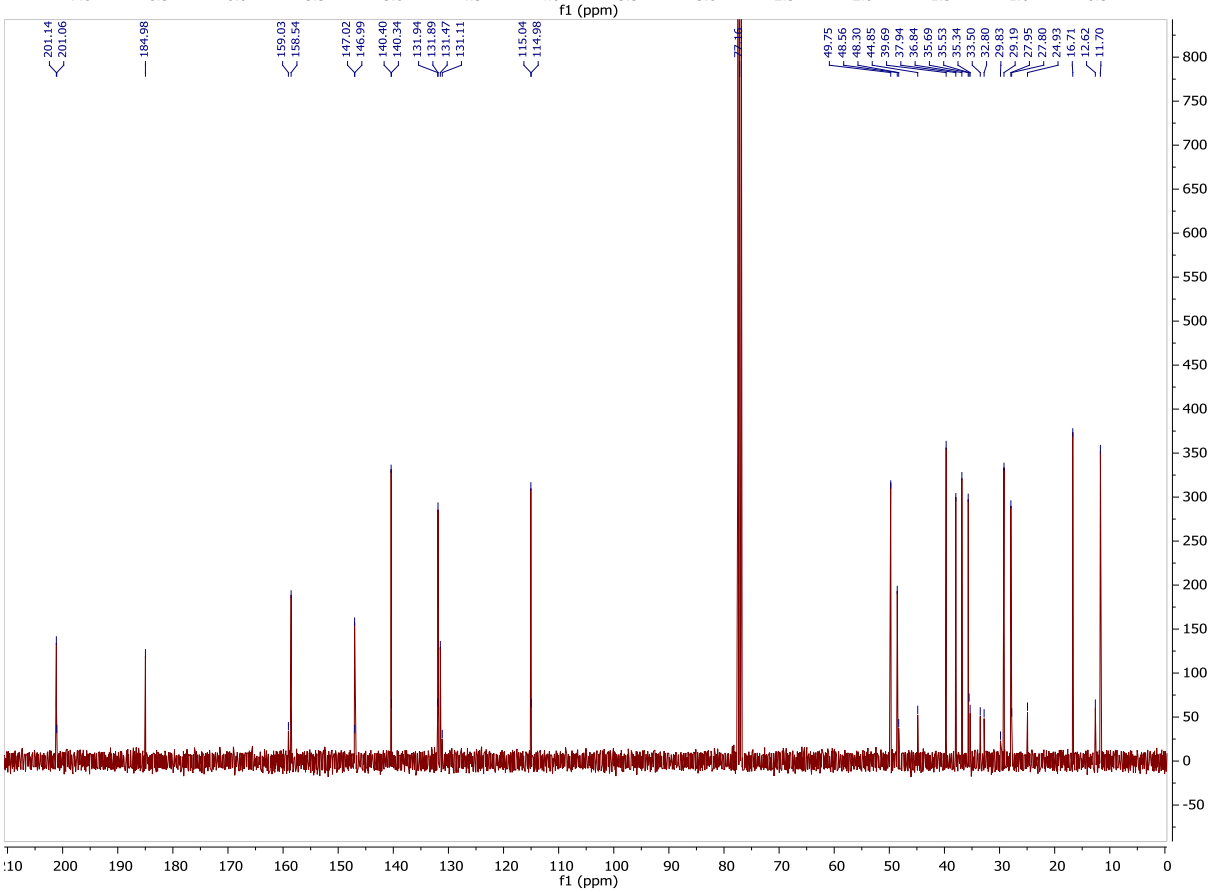


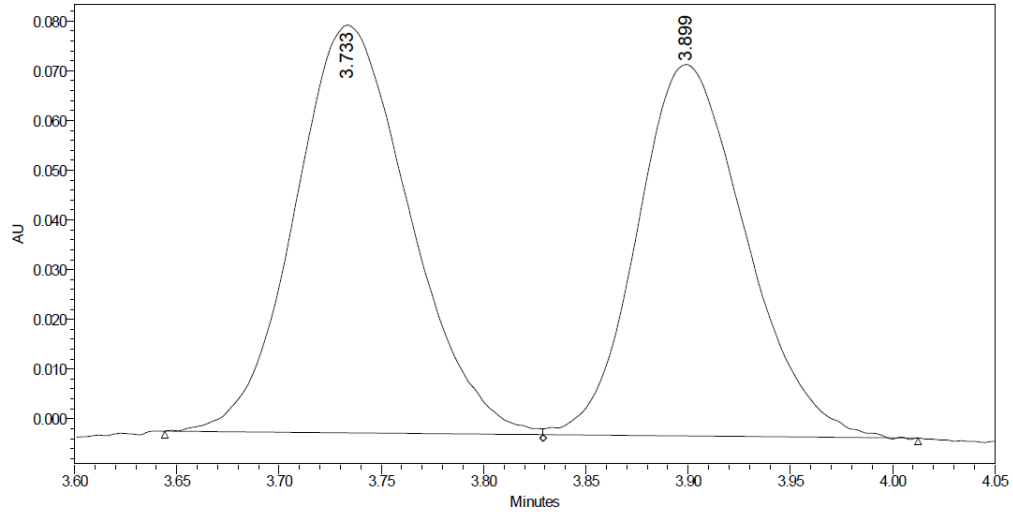
	Retention Time (min)	% Area
1	3.472	53.31
2	3.616	46.69



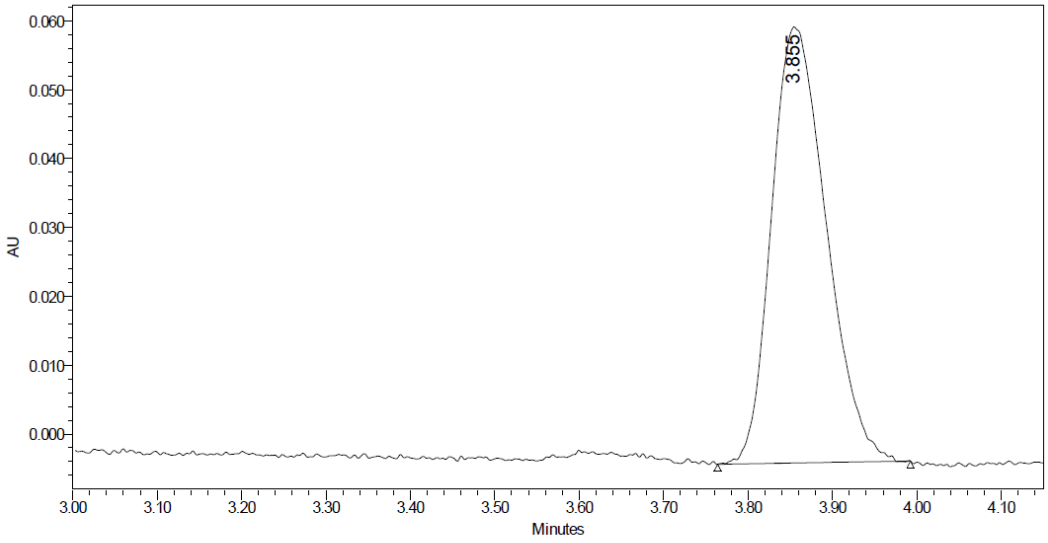
	Retention Time (min)	% Area
1	3.669	100.00


7.26
O
Me
H
Me
O
Et
0.99
0.99
1.00
0.15
0.86
1.01
1.03
4.06
0.14
0.84
1.77
0.23
3.03
1.86
1.20
3.03
f1 (ppm)

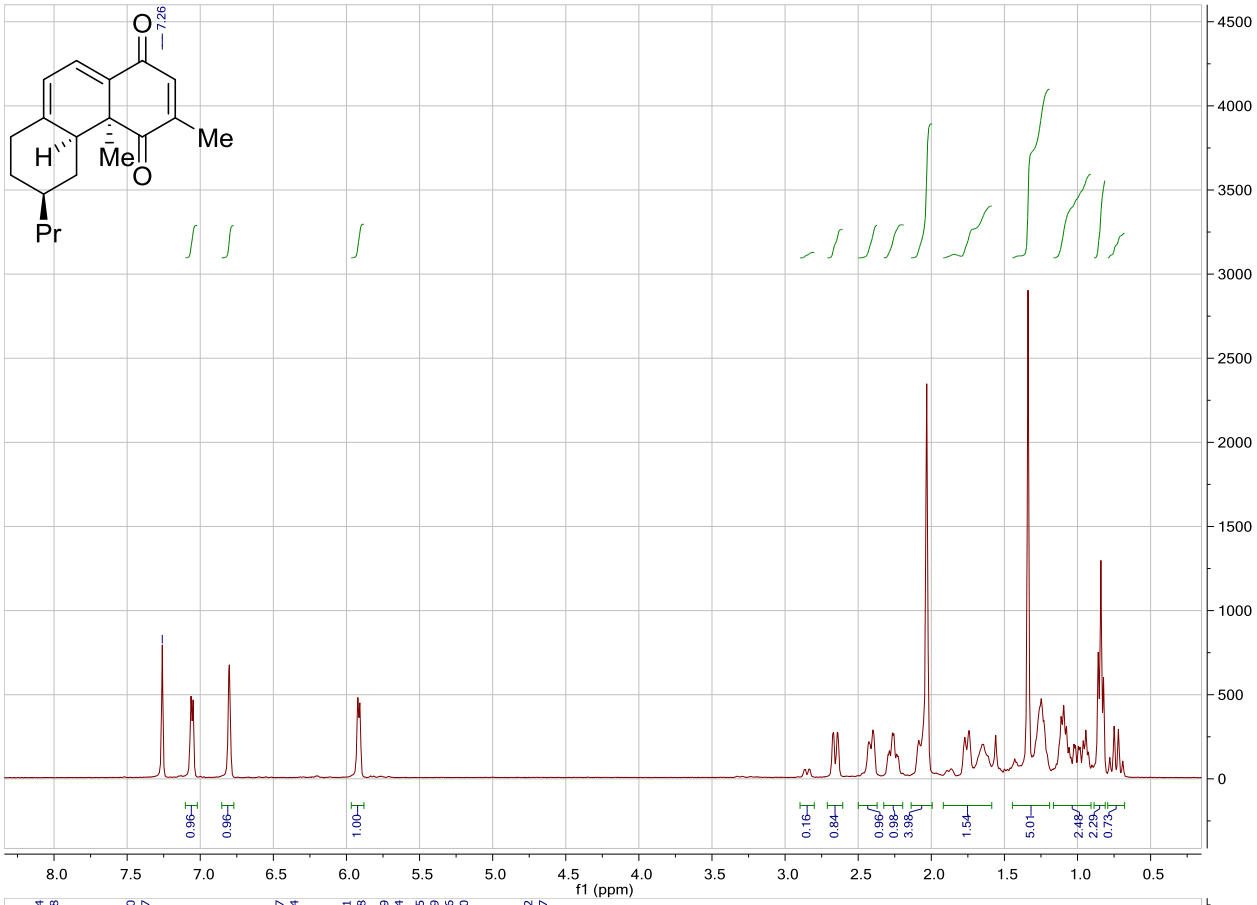

201.14
201.06
184.98
159.03
158.54
147.02
146.99
140.40
140.34
131.94
131.89
131.47
131.11
115.04
114.98
77.16
49.75
48.56
48.30
44.85
39.69
37.94
36.84
35.69
35.53
35.34
33.50
32.80
29.83
29.19
27.95
27.80
24.93
16.71
12.62
11.70
f1 (ppm)

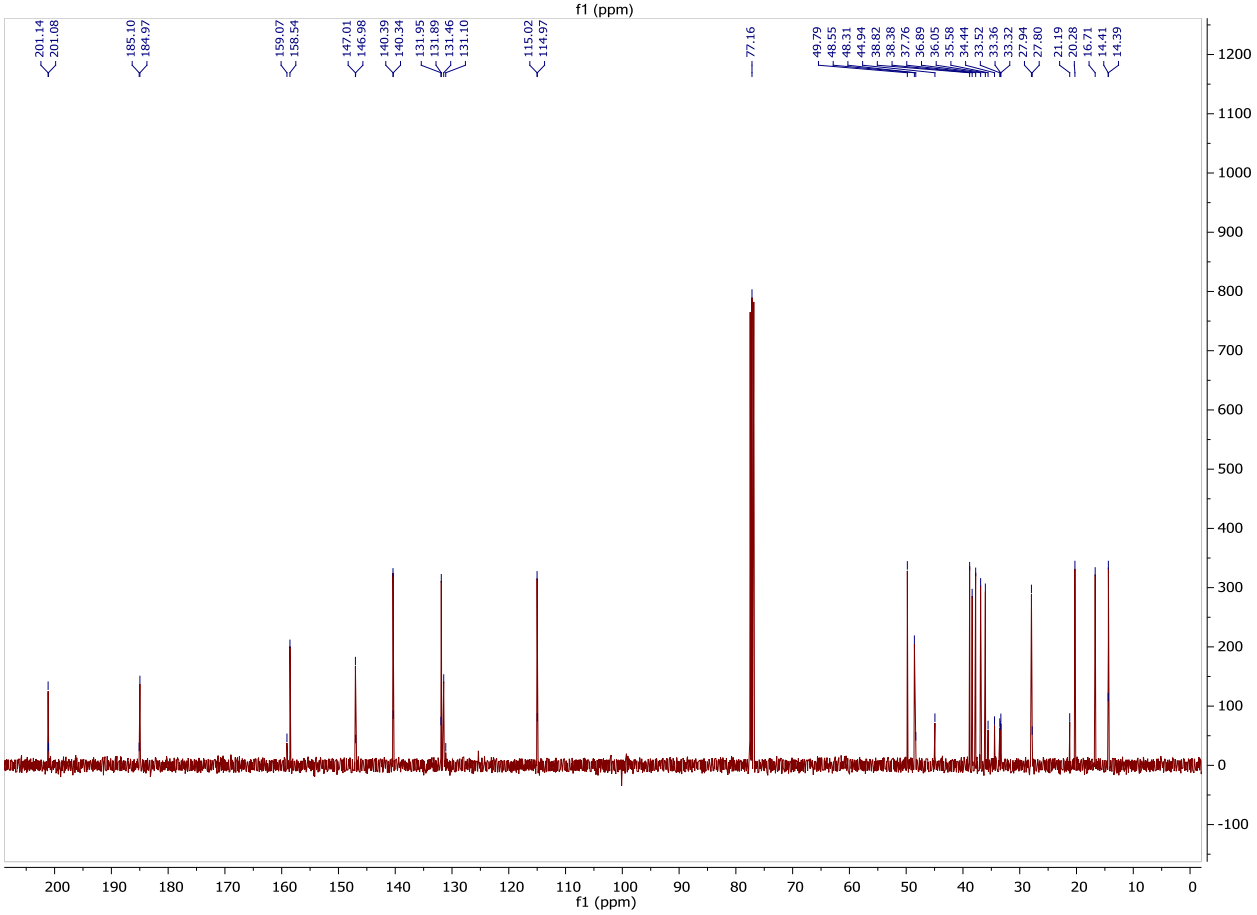


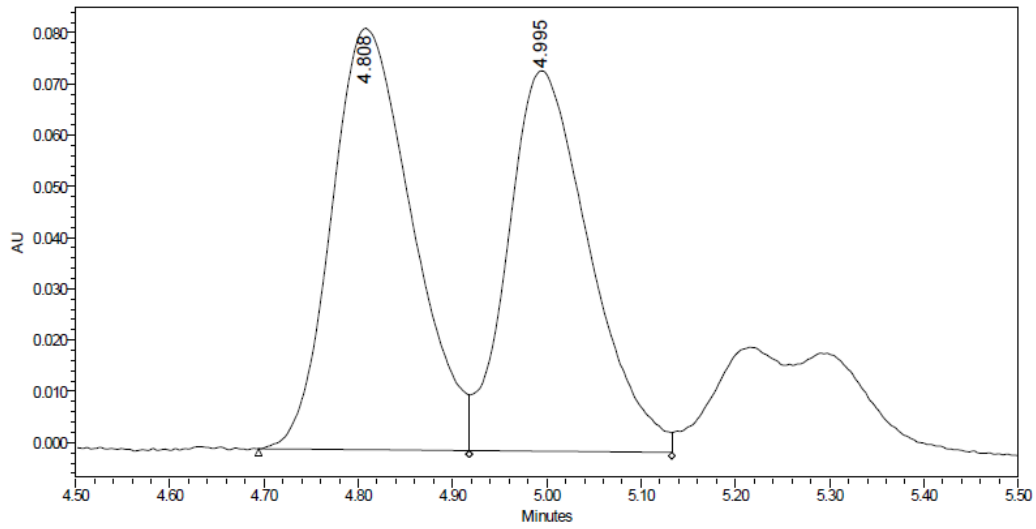
	Retention Time (min)	% Area
1	3.733	53.68
2	3.899	46.32



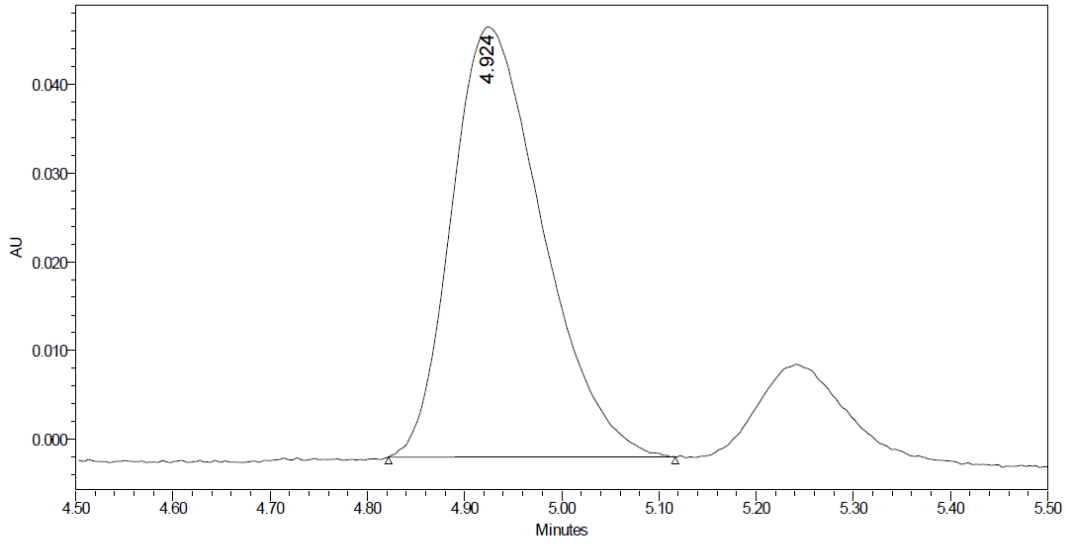
	Retention Time (min)	% Area
1	3.855	100.00


O
7.26
Me
H
Me
O
Pr
0.96
0.96
1.00
0.16
0.84
0.96
0.98
3.98
1.54
5.01
2.48
2.29
0.73
f1 (ppm)

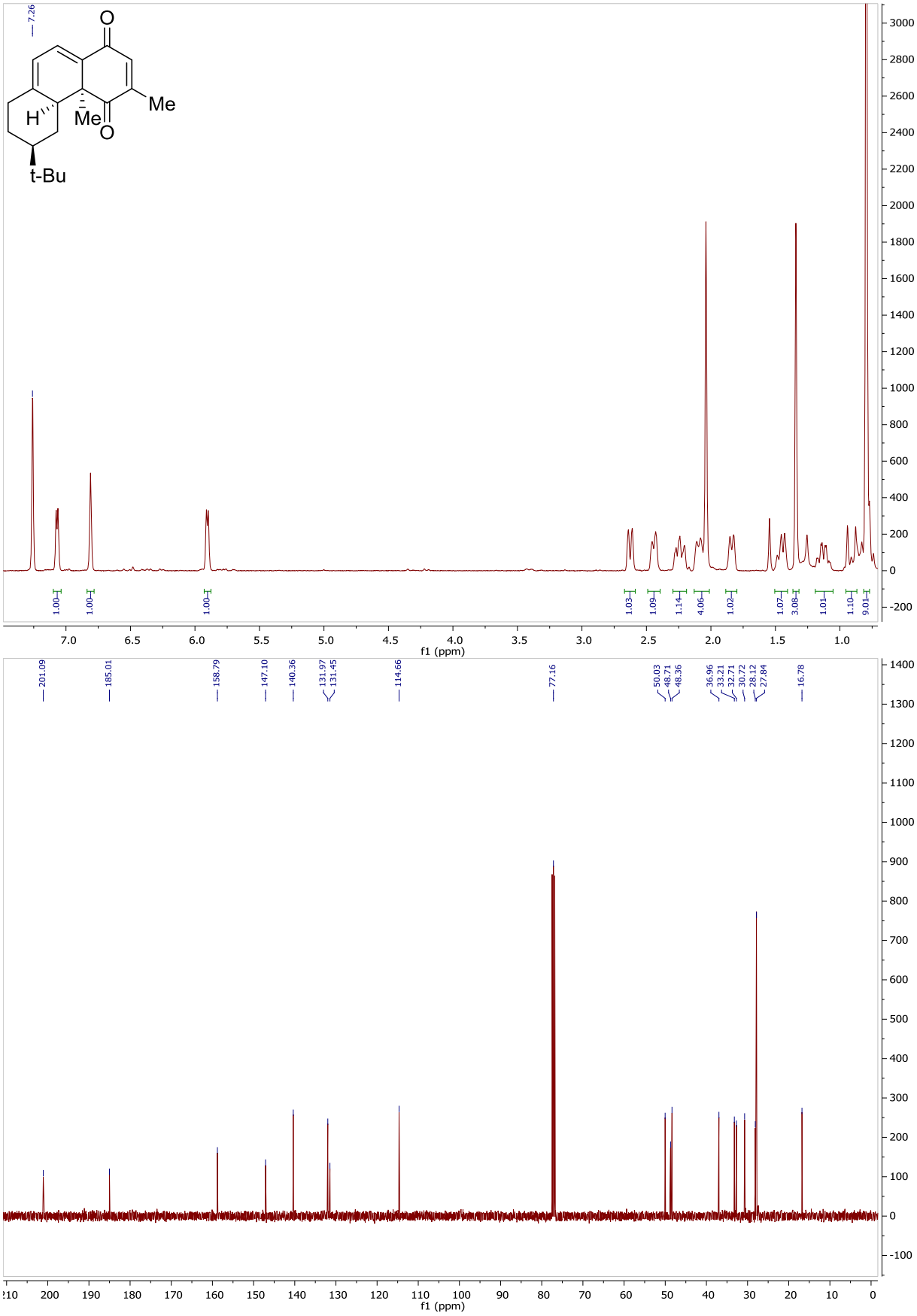

201.14
201.08
185.10
184.97
159.07
158.54
147.01
146.98
140.39
140.34
131.95
131.89
131.46
131.10
115.02
114.97
77.16
49.79
48.55
48.31
44.94
38.82
38.38
37.76
36.89
36.05
35.58
34.44
33.52
33.36
33.32
27.94
27.80
21.19
20.28
16.71
14.41
14.39
f1 (ppm)

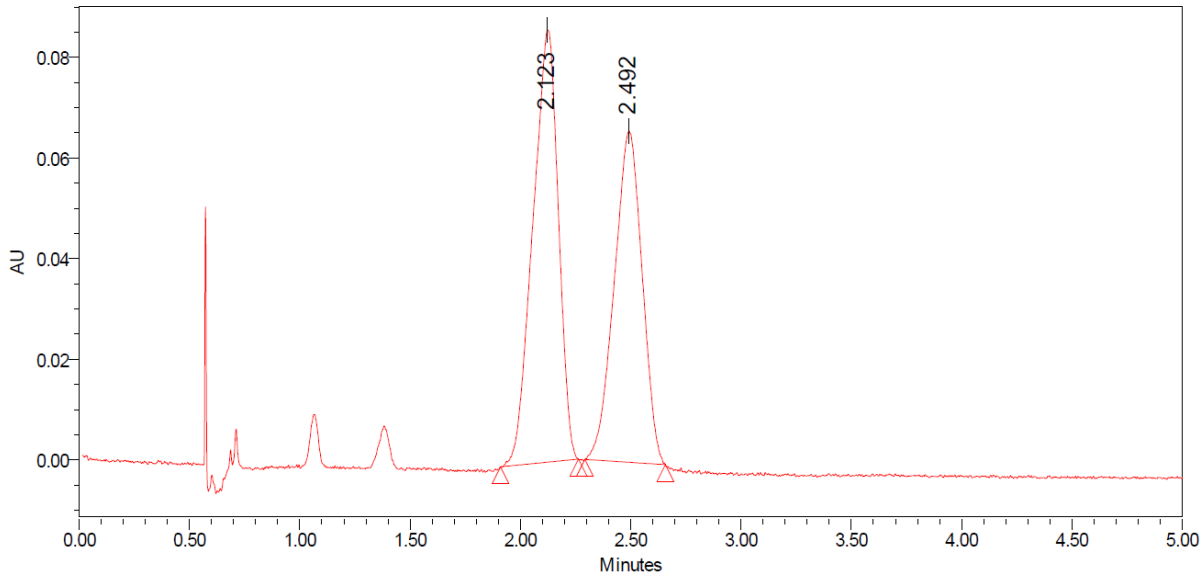


	Retention Time (min)	% Area
1	4.808	52.18
2	4.995	47.82



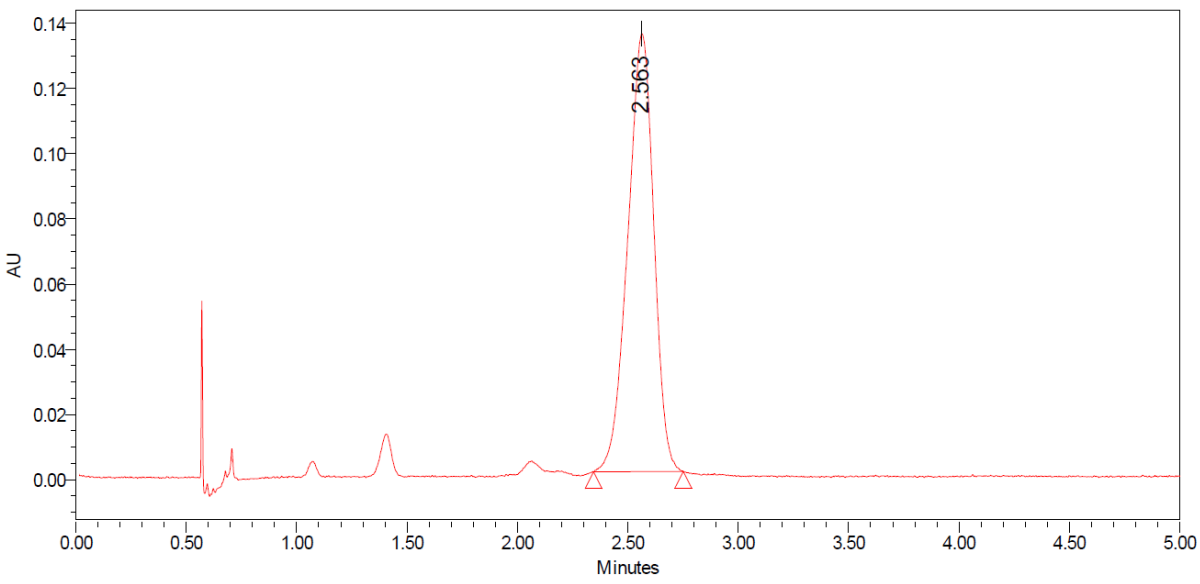
	Retention Time (min)	% Area
1	4.924	100.00


7.26
O
Me
H
Me
O
t-Bu
1.00
1.00
1.00
1.03
1.09
1.14
4.06
1.02
1.07
3.08
1.01
1.10
9.01
f1 (ppm)
201.09
185.01
158.79
147.10
140.36
131.97
131.45
114.66
77.16
50.03
48.71
48.36
36.96
33.21
32.71
30.72
28.12
27.84
16.78
f1 (ppm)



Peak Results

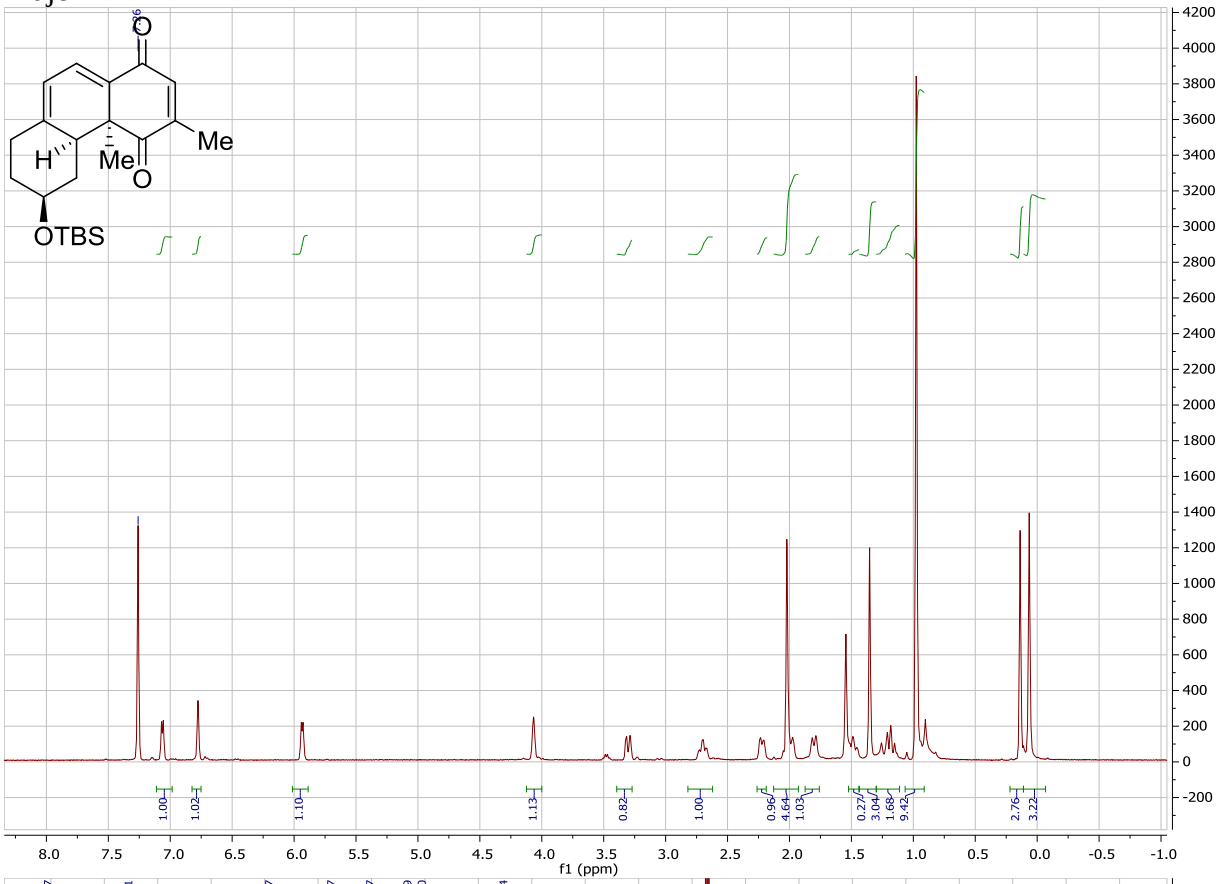
	RT	% Area
1	2.123	54.36
2	2.492	45.64

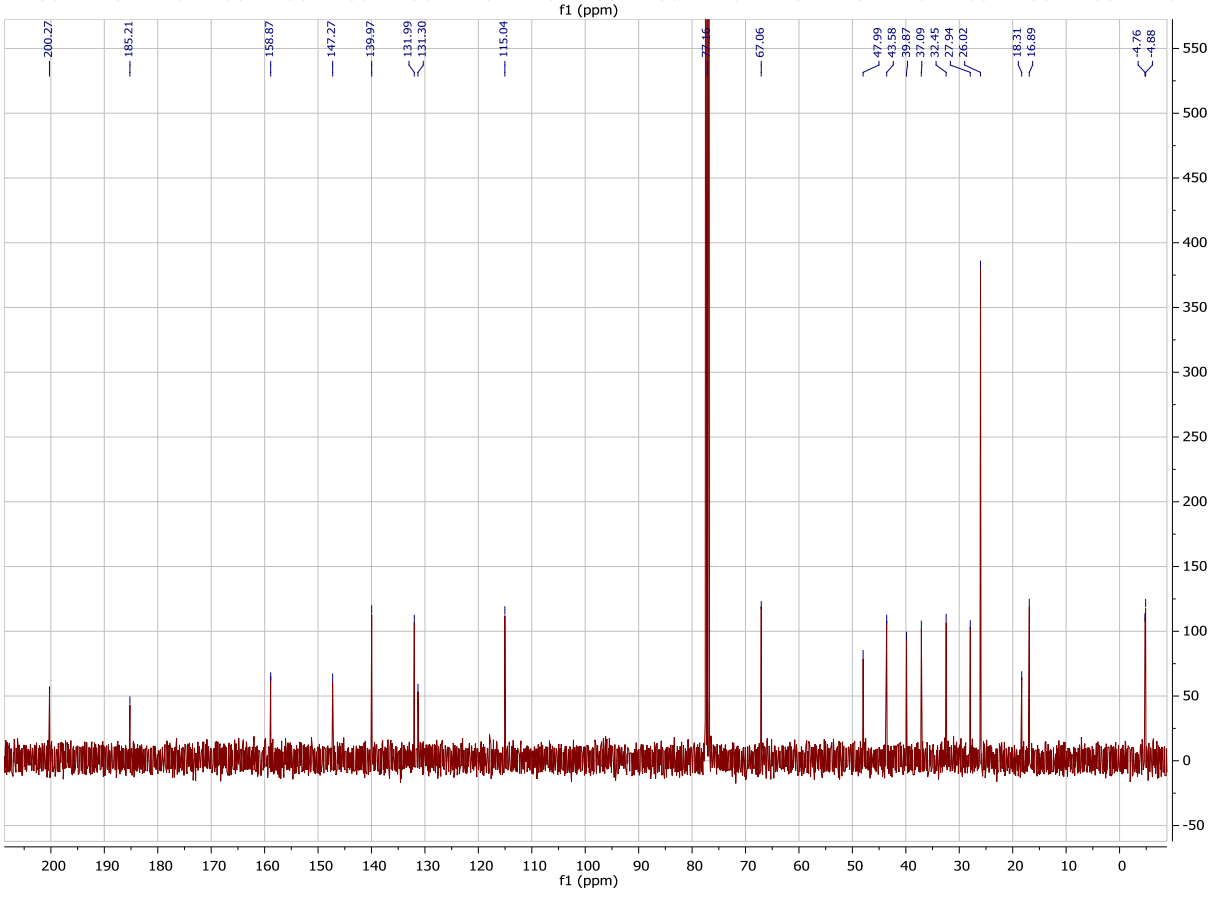


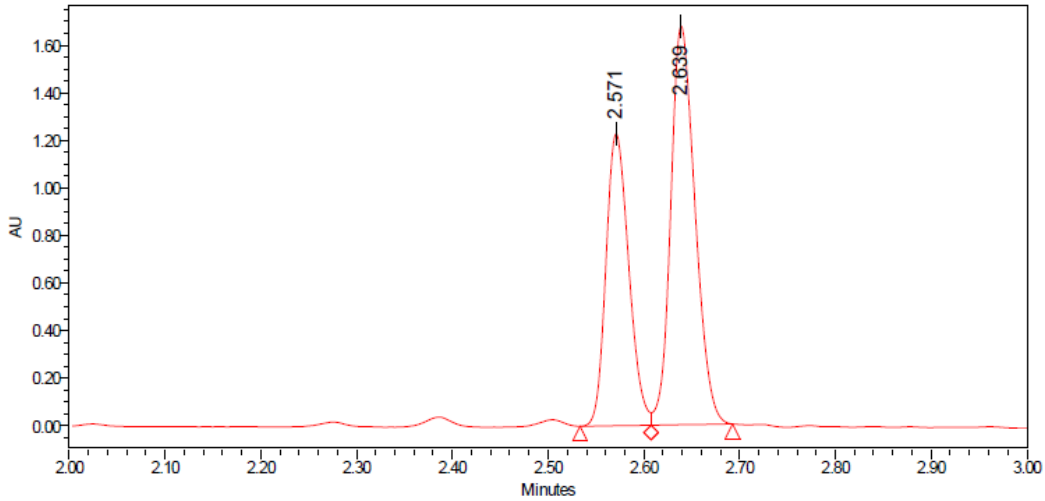
Peak Results

	RT	% Area
1	2.563	100.00

Major

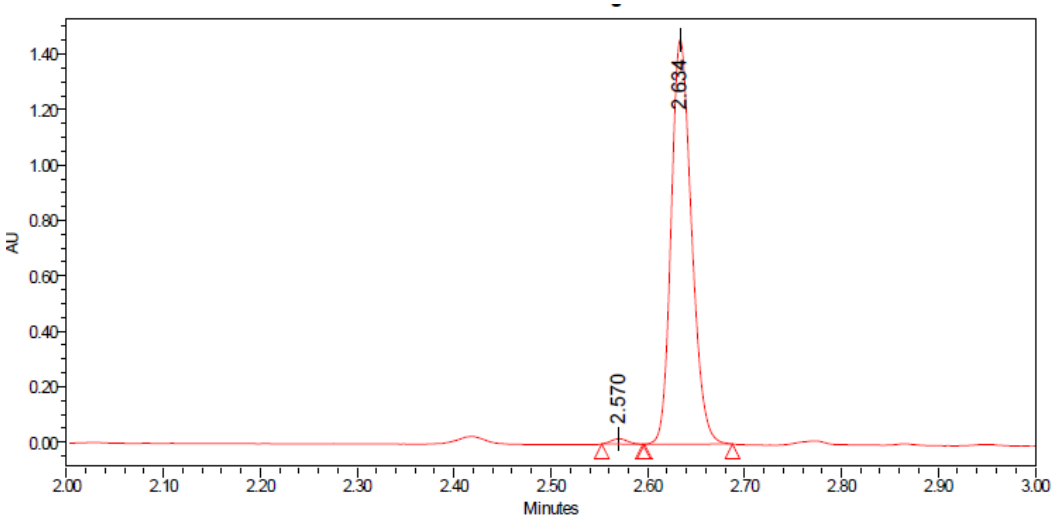

O
Me
H
Me
O
OTBS
f1 (ppm)


200.27
185.21
158.87
147.27
139.97
131.99
131.30
115.04
77.16
67.06
47.99
43.58
39.87
37.09
32.45
27.94
26.02
18.31
16.89
-4.76
-4.88
f1 (ppm)



Peak Results

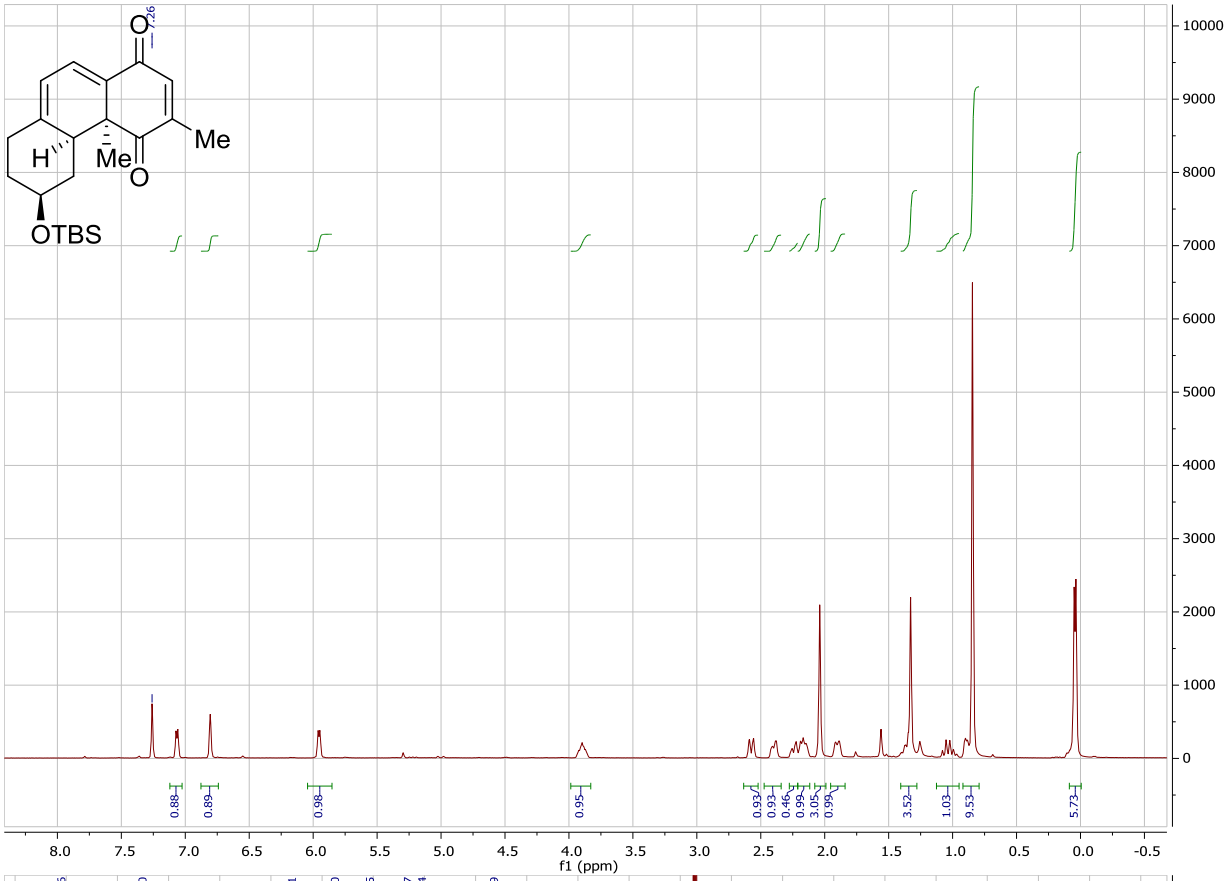
	RT	% Area
1	2.571	40.68
2	2.639	59.32

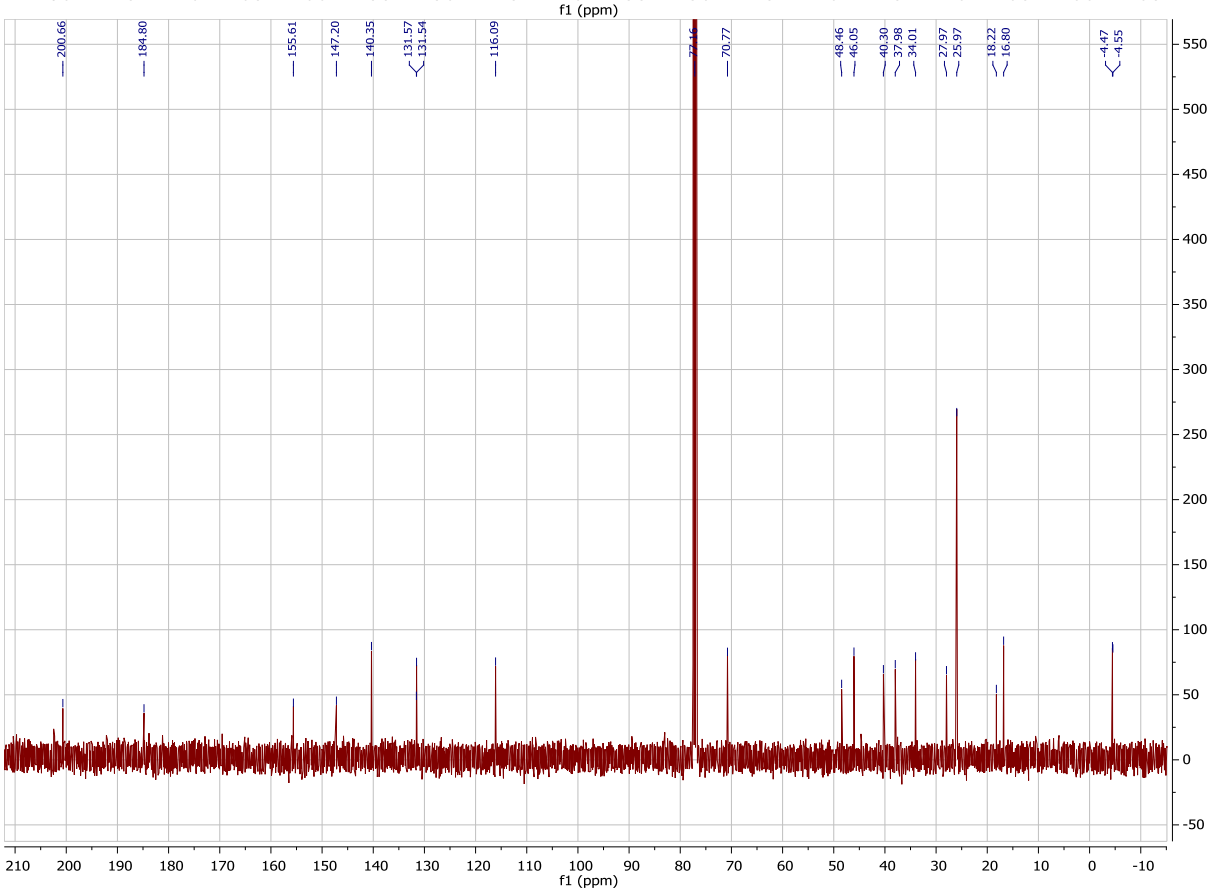


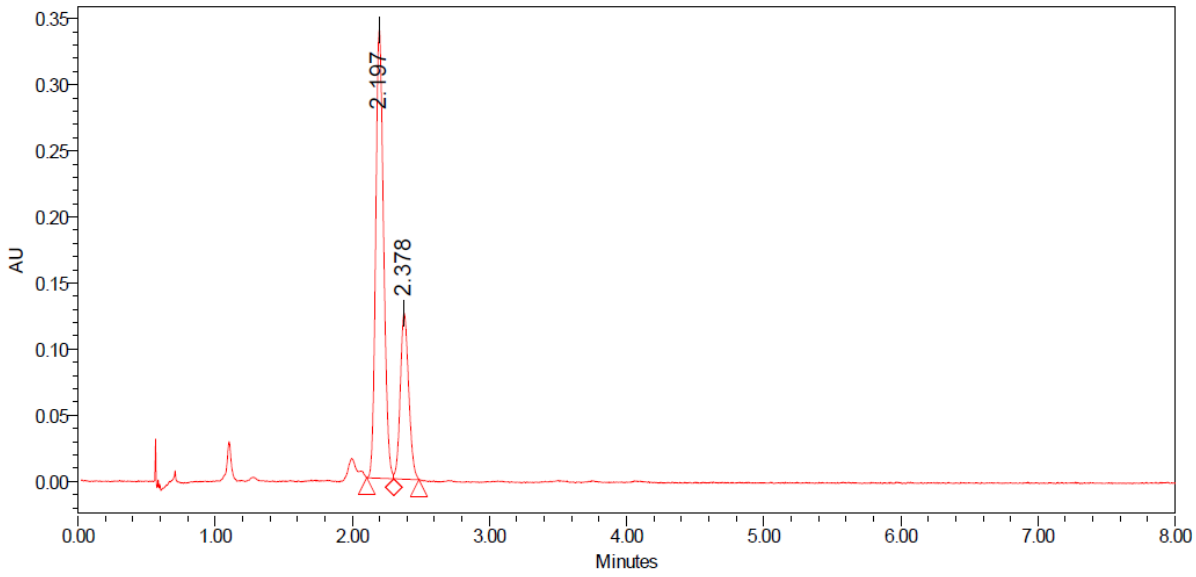
Peak Results

	RT	% Area
1	2.570	1.04
2	2.634	98.96

Minor

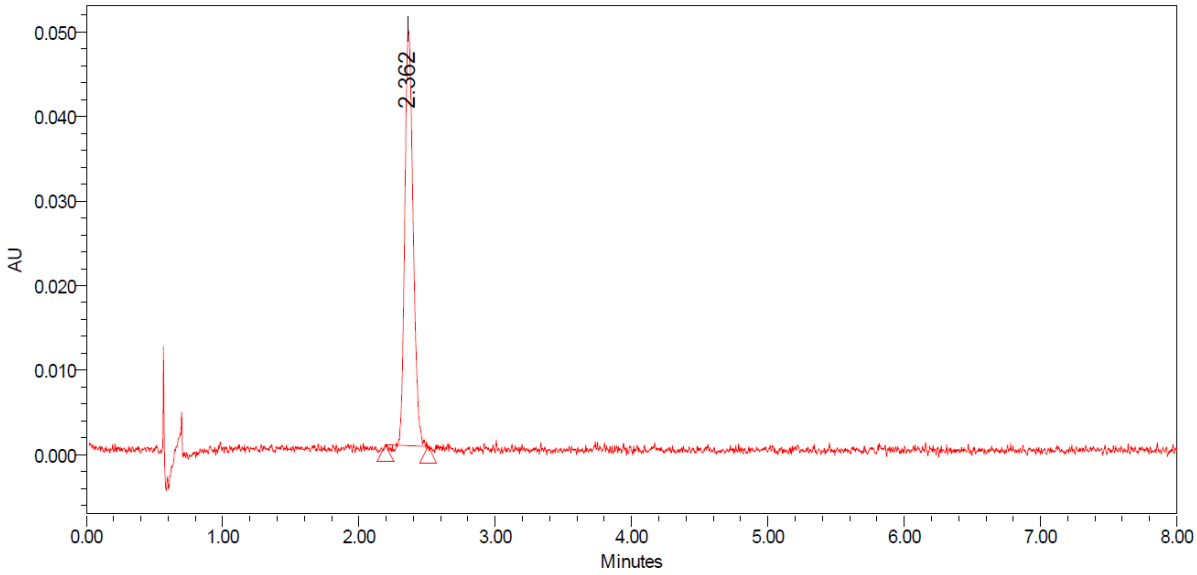

O
Me
H
Me
O
OTBS
7.26
0.88
0.89
0.98
0.95
0.93
0.93
0.46
0.99
3.05
0.99
3.52
1.03
9.53
5.73
f1 (ppm)


200.66
184.80
155.61
147.20
140.35
131.57
131.54
116.09
73.46
70.77
48.46
46.05
40.30
37.98
34.01
27.97
25.97
18.22
16.80
-4.47
-4.55
f1 (ppm)



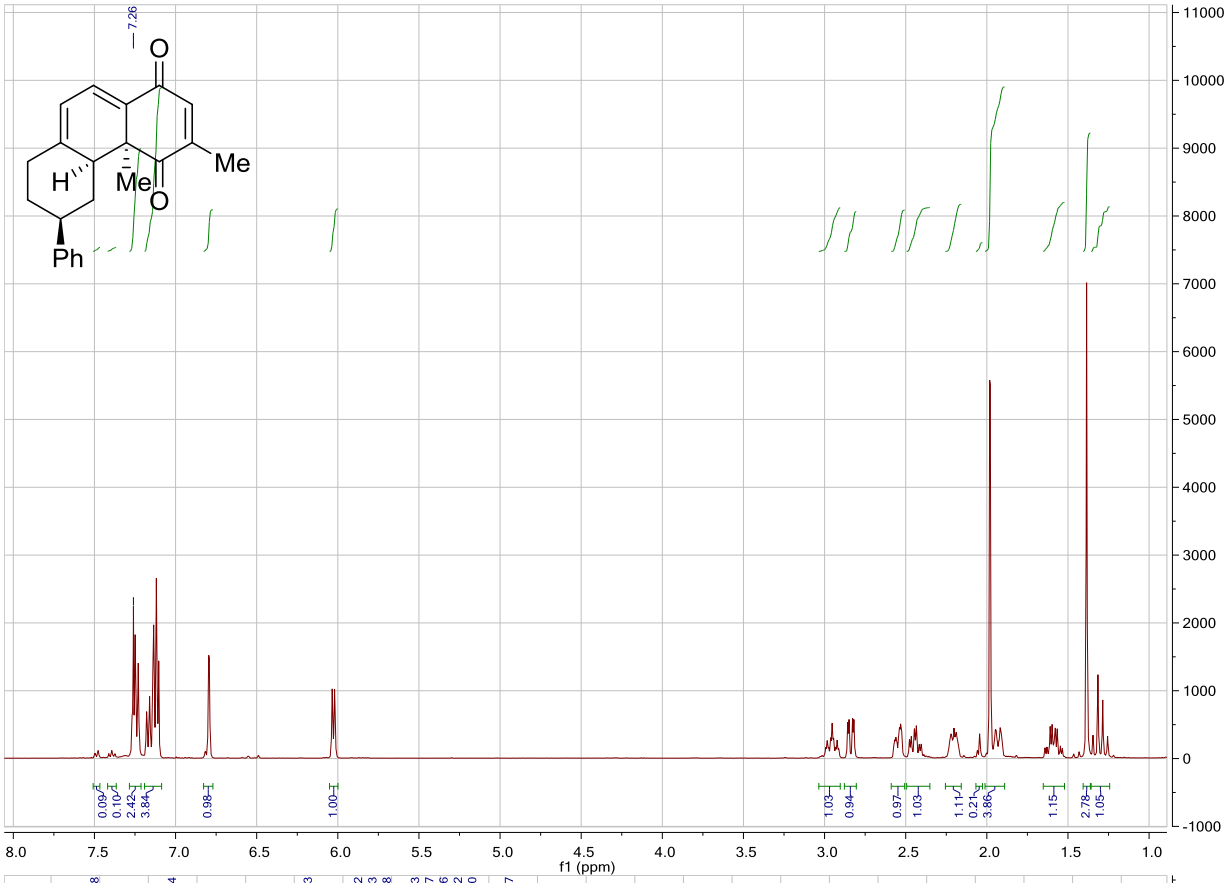
Peak Results

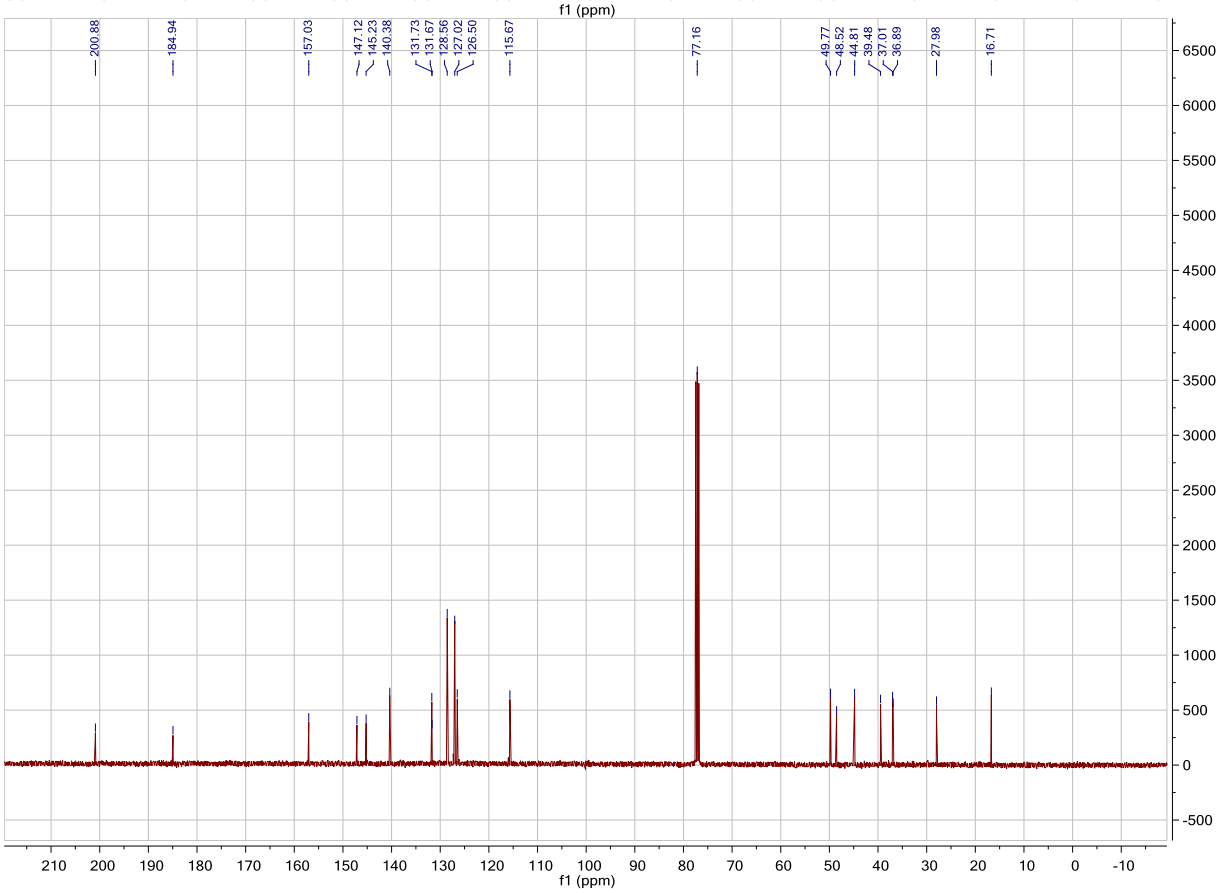
	RT	% Area
1	2.197	71.77
2	2.378	28.23

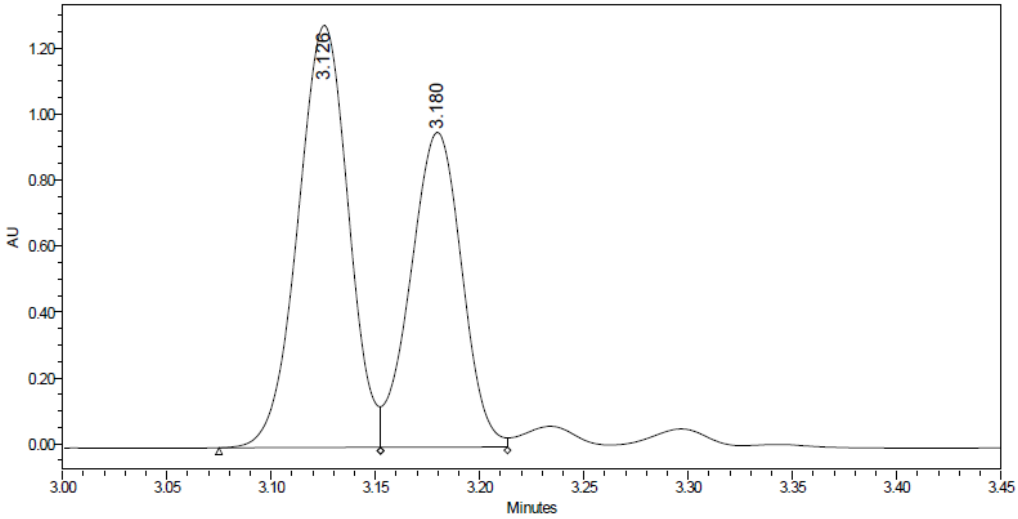


Peak Results

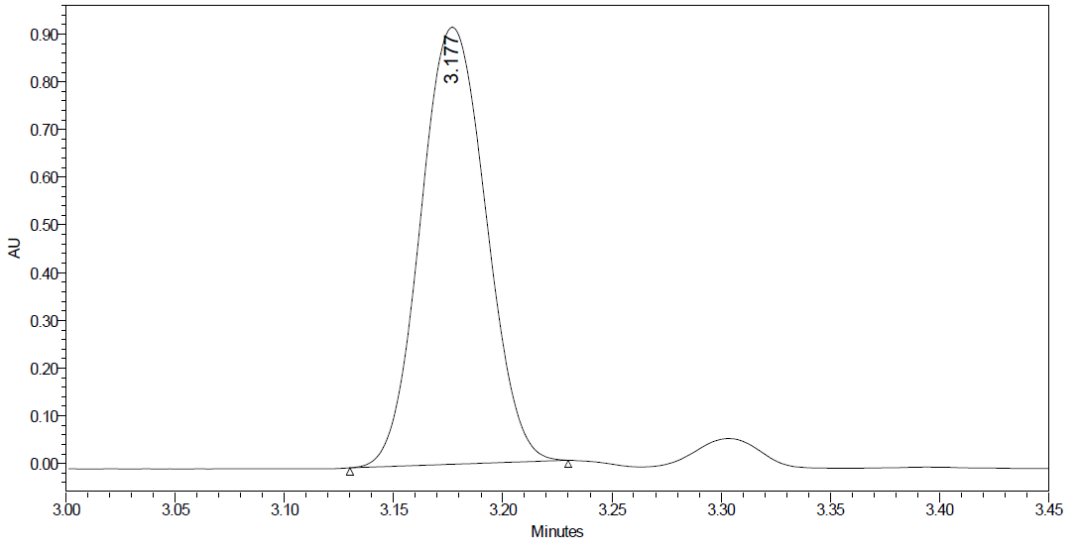
	RT	% Area
1	2.362	100.00


7.26
O
Me
H
Me
O
Ph
0.09
0.10
2.42
3.84
0.98
1.00
1.03
0.94
0.97
1.03
1.11
0.21
3.86
1.15
2.78
1.05
f1 (ppm)

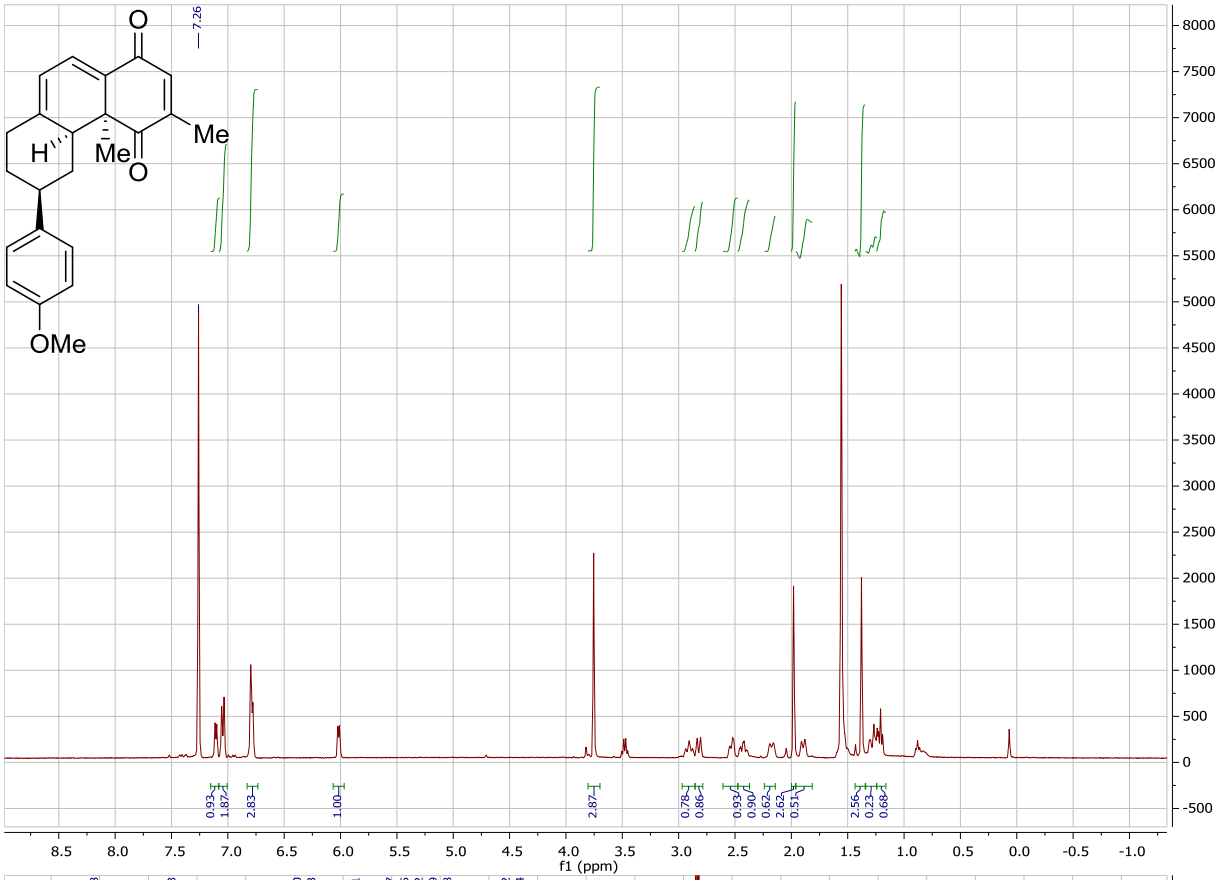

200.88
184.94
157.03
147.12
145.23
140.38
131.73
131.67
128.56
127.02
126.50
115.67
77.16
49.77
48.52
44.81
39.48
37.01
36.89
27.98
16.71
f1 (ppm)

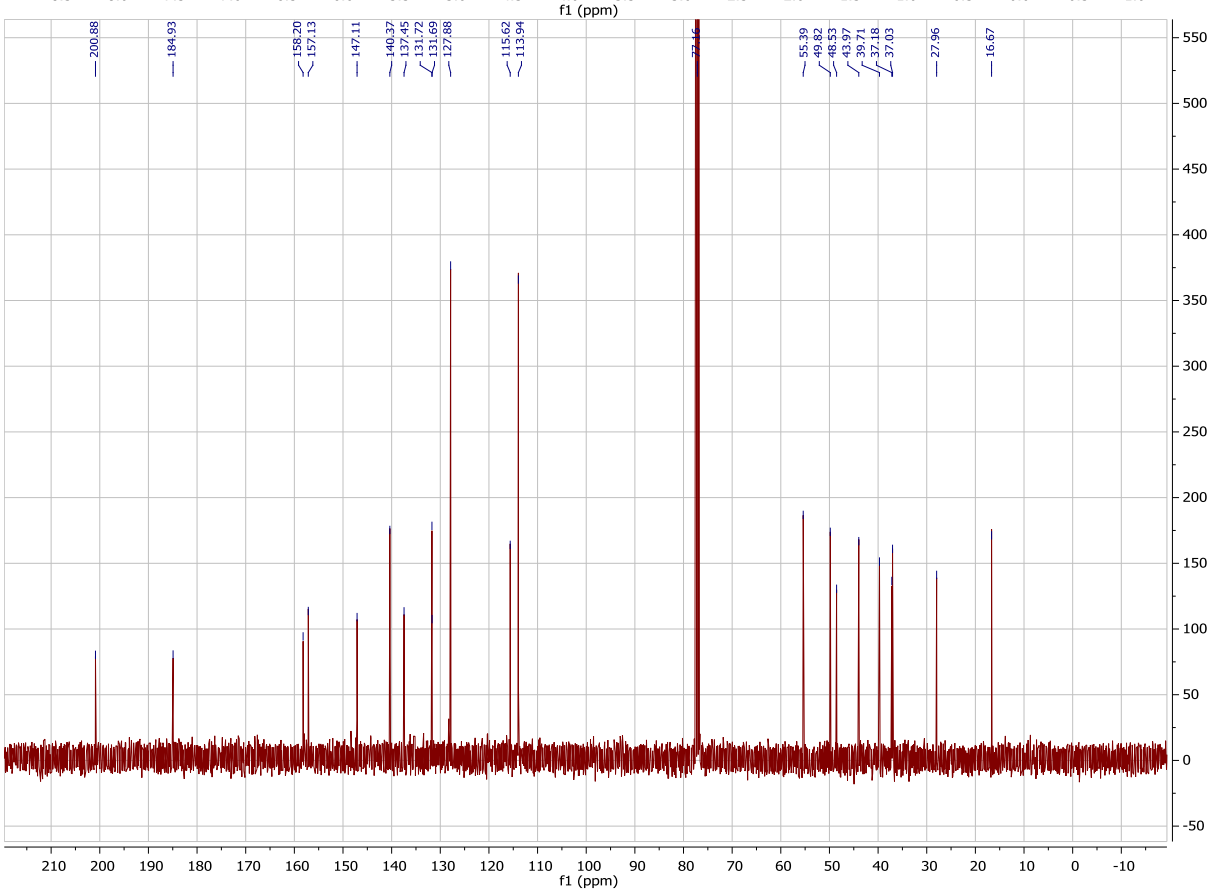


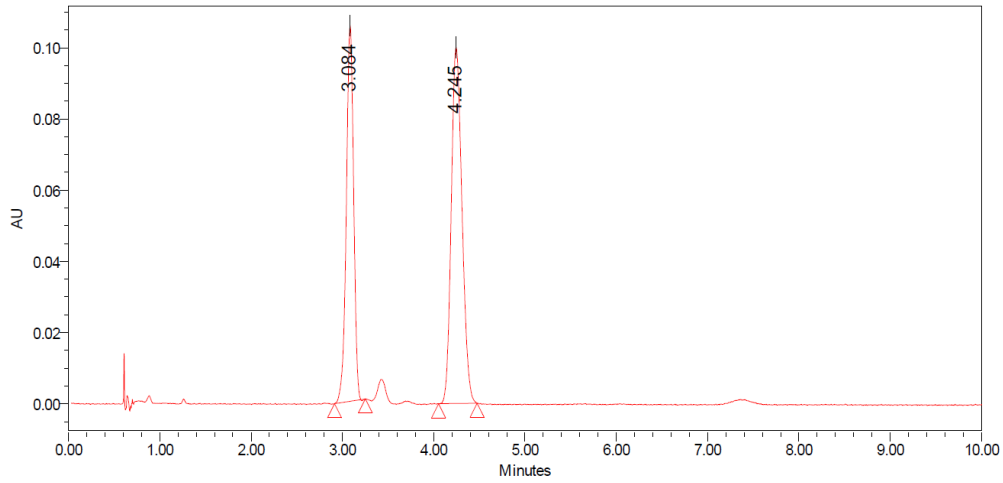
	Retention Time (min)	% Area
1	3.126	56.90
2	3.180	43.10



	Retention Time (min)	% Area
1	3.177	100.00

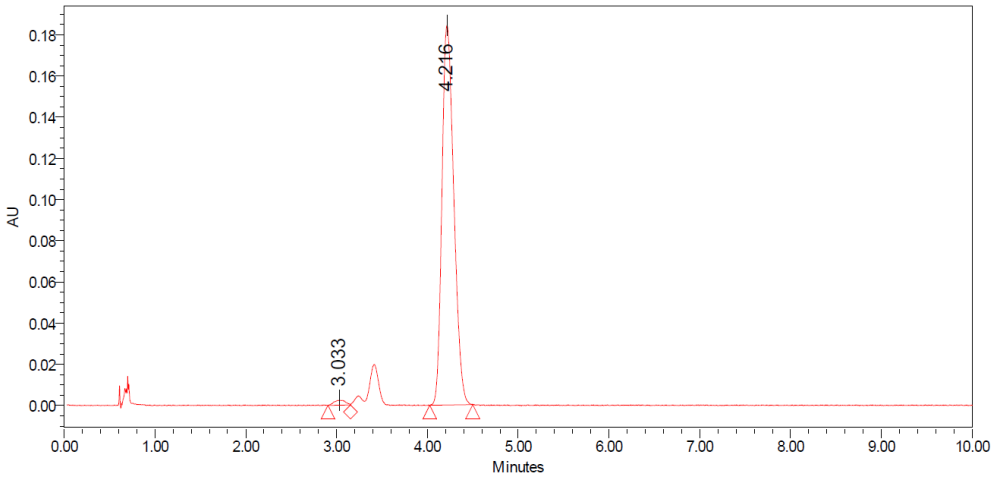

O
Me
H
Me
O
OMe
7.26
0.93
1.87
2.83
1.00
2.87
0.78
0.86
0.93
0.90
0.62
2.62
0.51
2.56
0.23
0.68
f1 (ppm)


200.88
184.93
158.20
157.13
147.11
140.37
137.45
131.72
131.69
127.88
115.62
113.94
77.16
55.39
49.82
48.53
43.97
39.71
37.18
37.03
27.96
16.67
f1 (ppm)



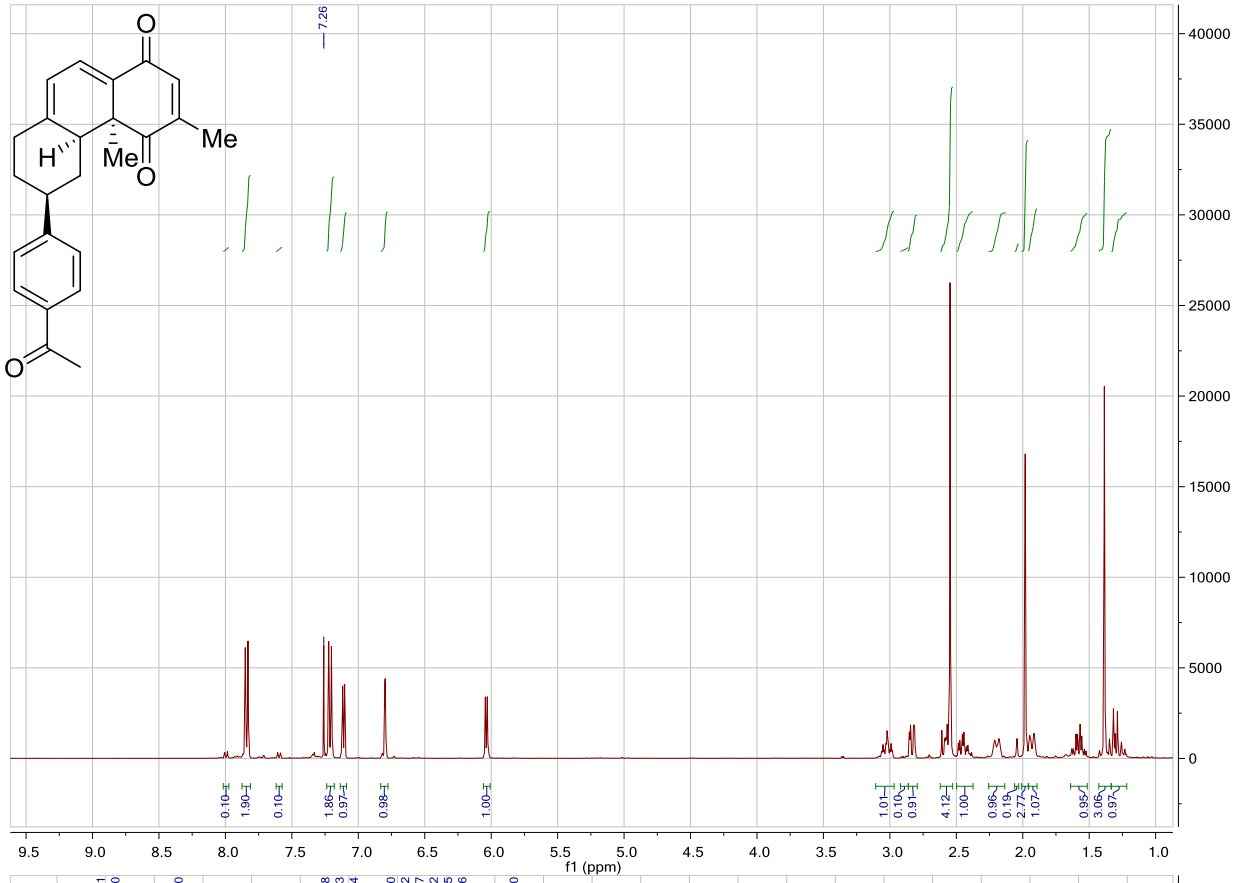
Peak Results

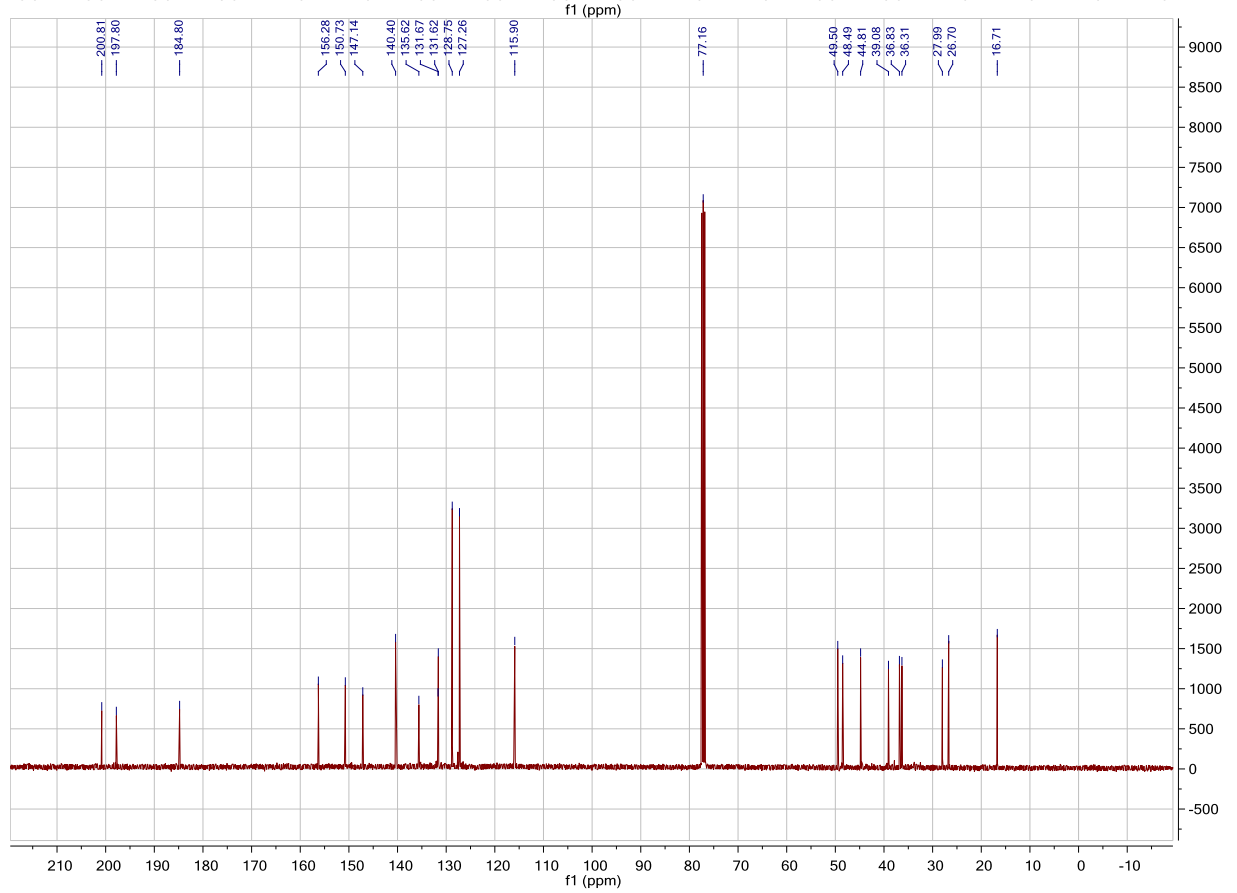
	RT	% Area
1	3.084	41.82
2	4.245	58.18

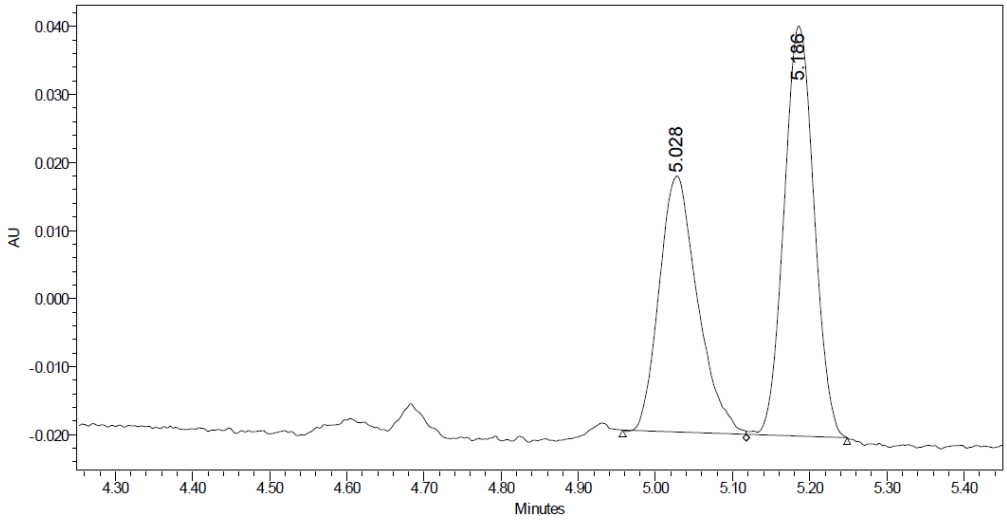


Peak Results

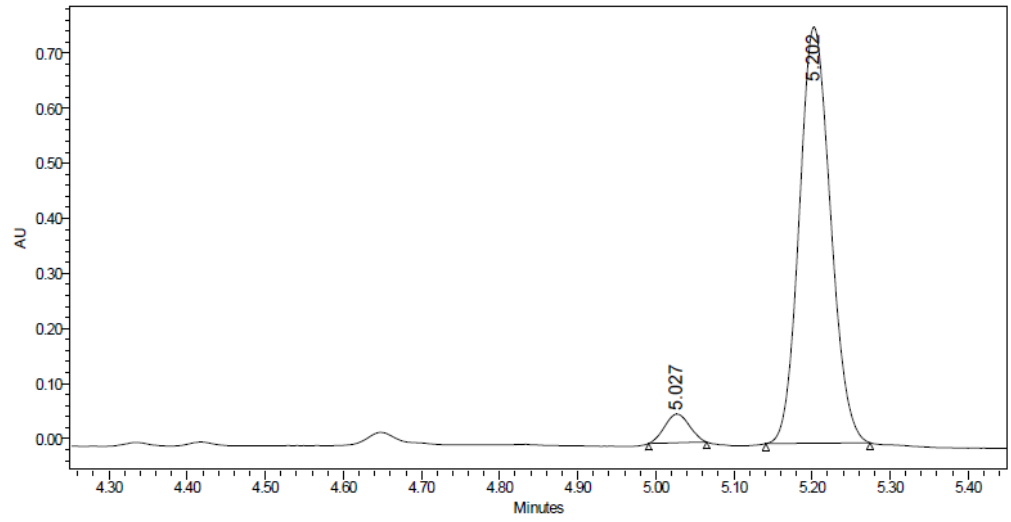
	RT	% Area
1	3.033	1.23
2	4.216	98.77


O
H
Me
Me
O
O
7.26
0.10
1.90
0.10
1.86
0.97
0.98
1.00
1.01
0.10
0.91
4.12
1.00
0.96
0.19
2.77
1.07
0.95
3.06
0.97
f1 (ppm)

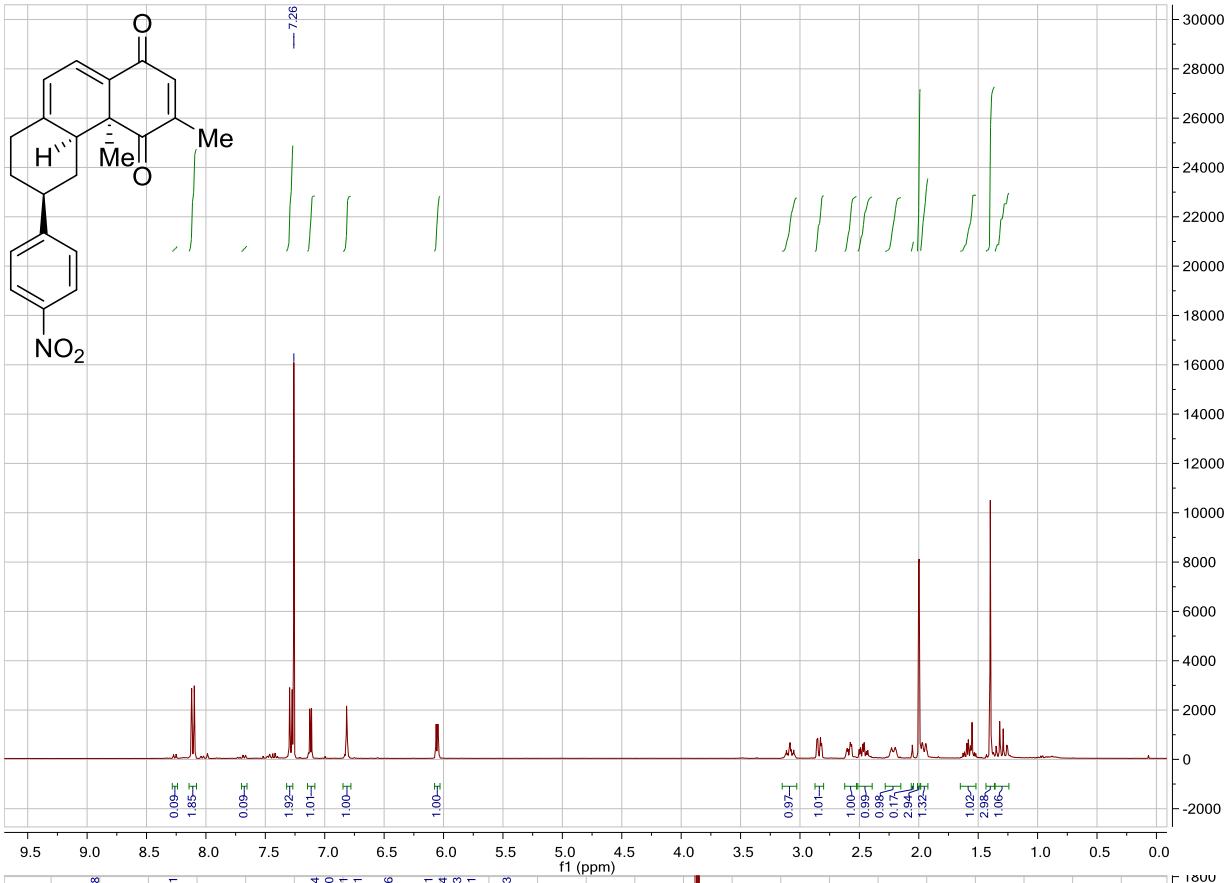

200.81
197.80
184.80
156.28
150.73
147.14
140.40
135.62
131.67
131.62
128.75
127.26
115.90
77.16
49.50
48.49
44.81
39.08
36.83
36.31
27.99
26.70
16.71
f1 (ppm)

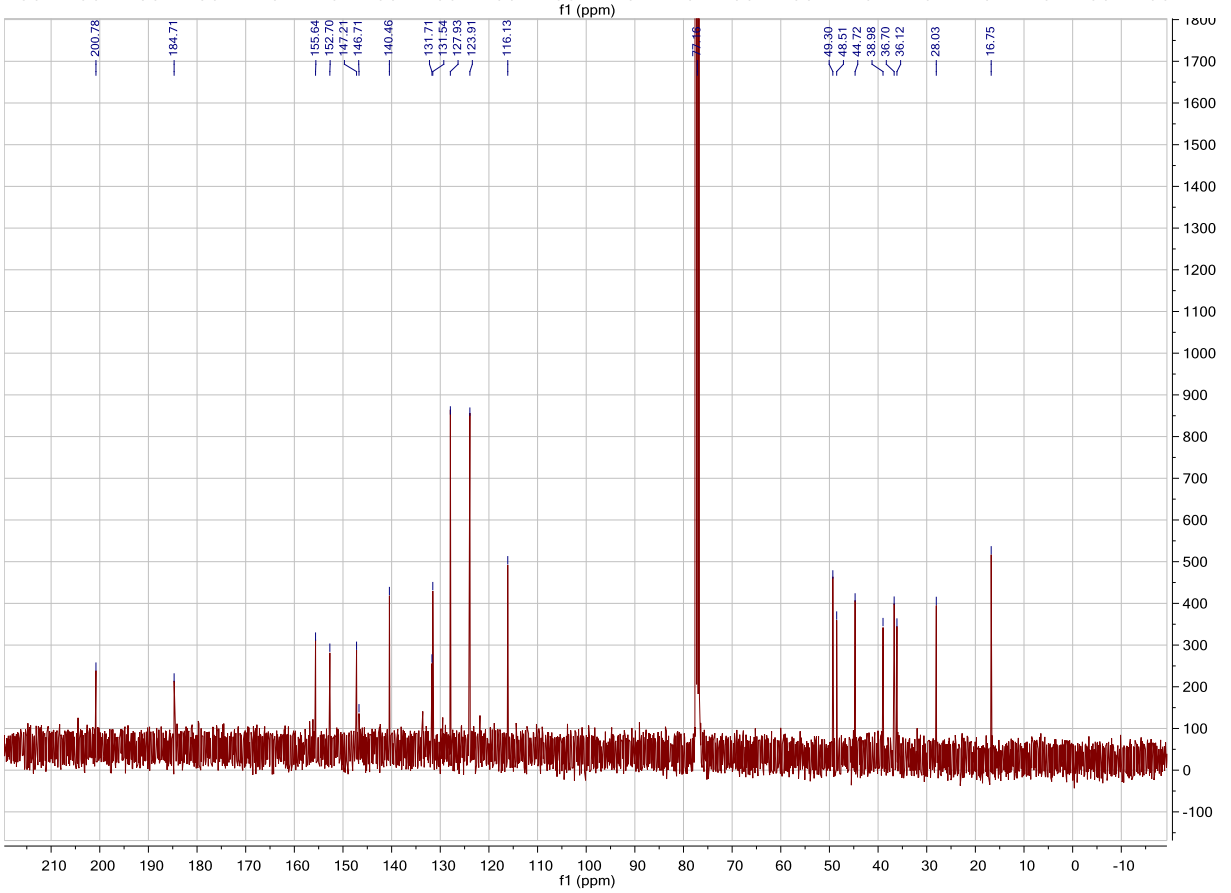


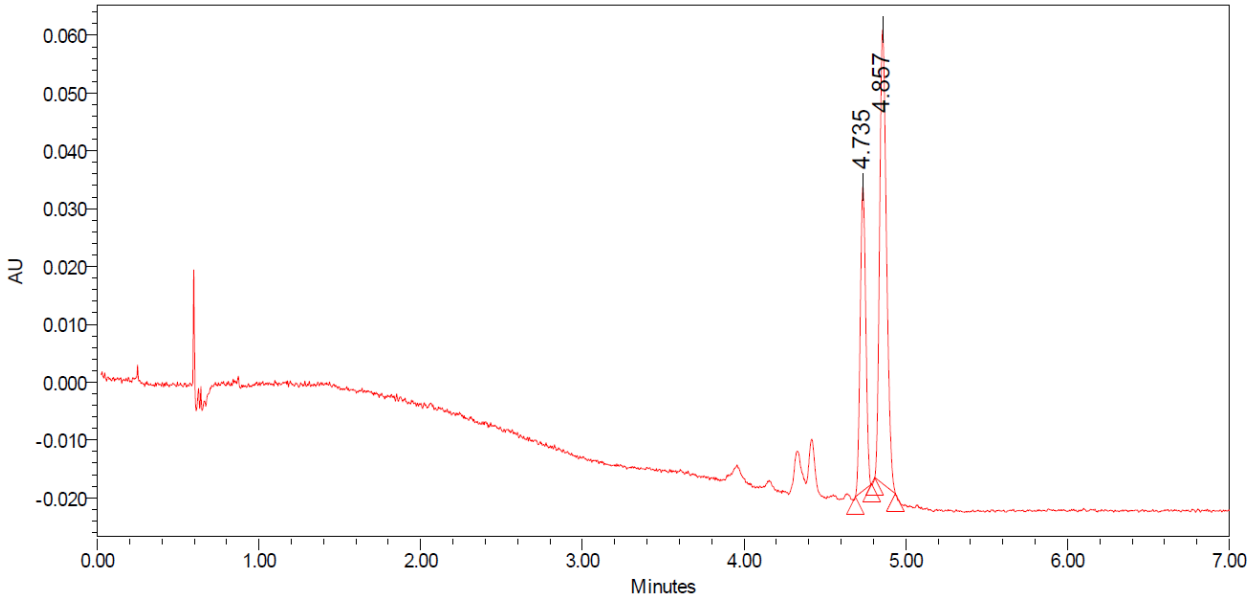
	Retention Time (min)	% Area
1	5.028	44.25
2	5.186	55.75



	Retention Time (min)	% Area
1	5.027	5.19
2	5.202	94.81

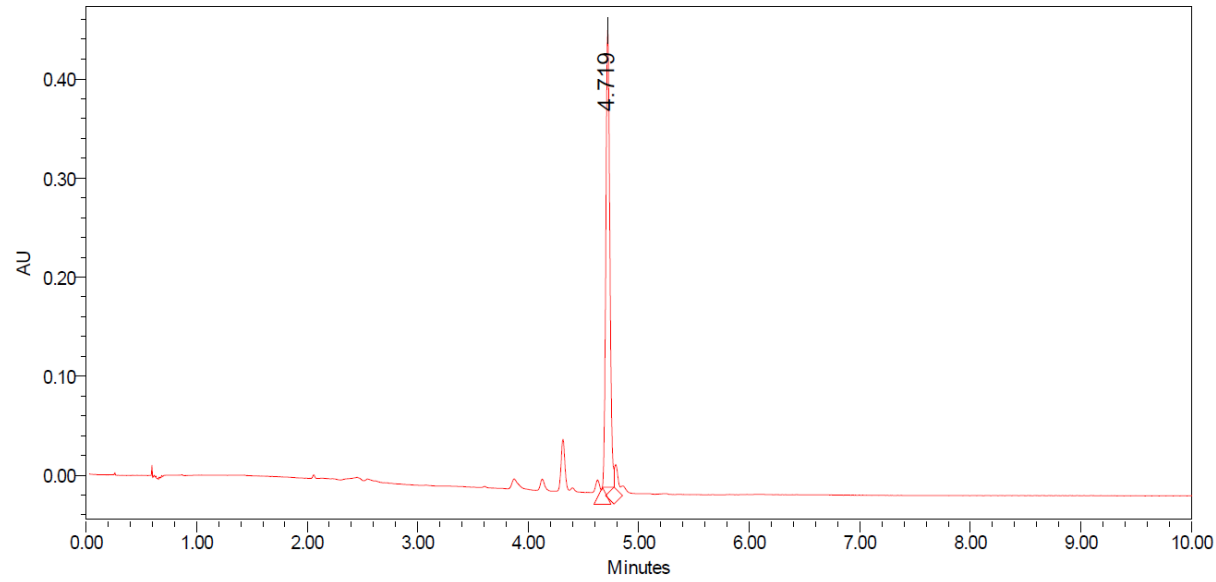

O
H
Me
Me
O
NO2
7.26
0.09
1.85
0.09
1.92
1.01
1.00
1.00
0.97
1.01
1.00
0.99
0.98
0.17
2.94
1.32
1.02
2.98
1.06
f1 (ppm)


200.78
184.71
155.64
152.70
147.21
146.71
140.46
131.71
131.54
127.93
123.91
116.13
77.48
49.30
48.51
44.72
38.98
36.70
36.12
28.03
16.75
f1 (ppm)



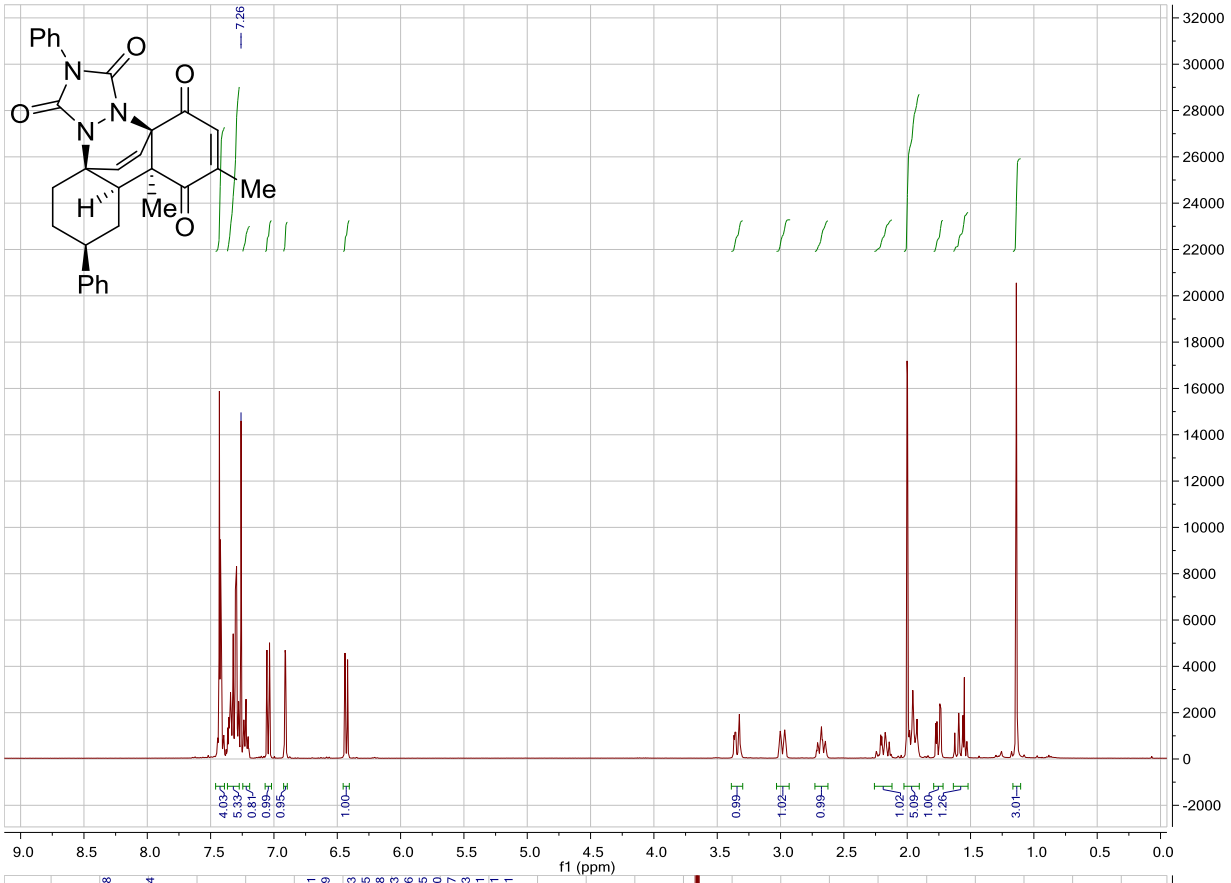
Peak Results

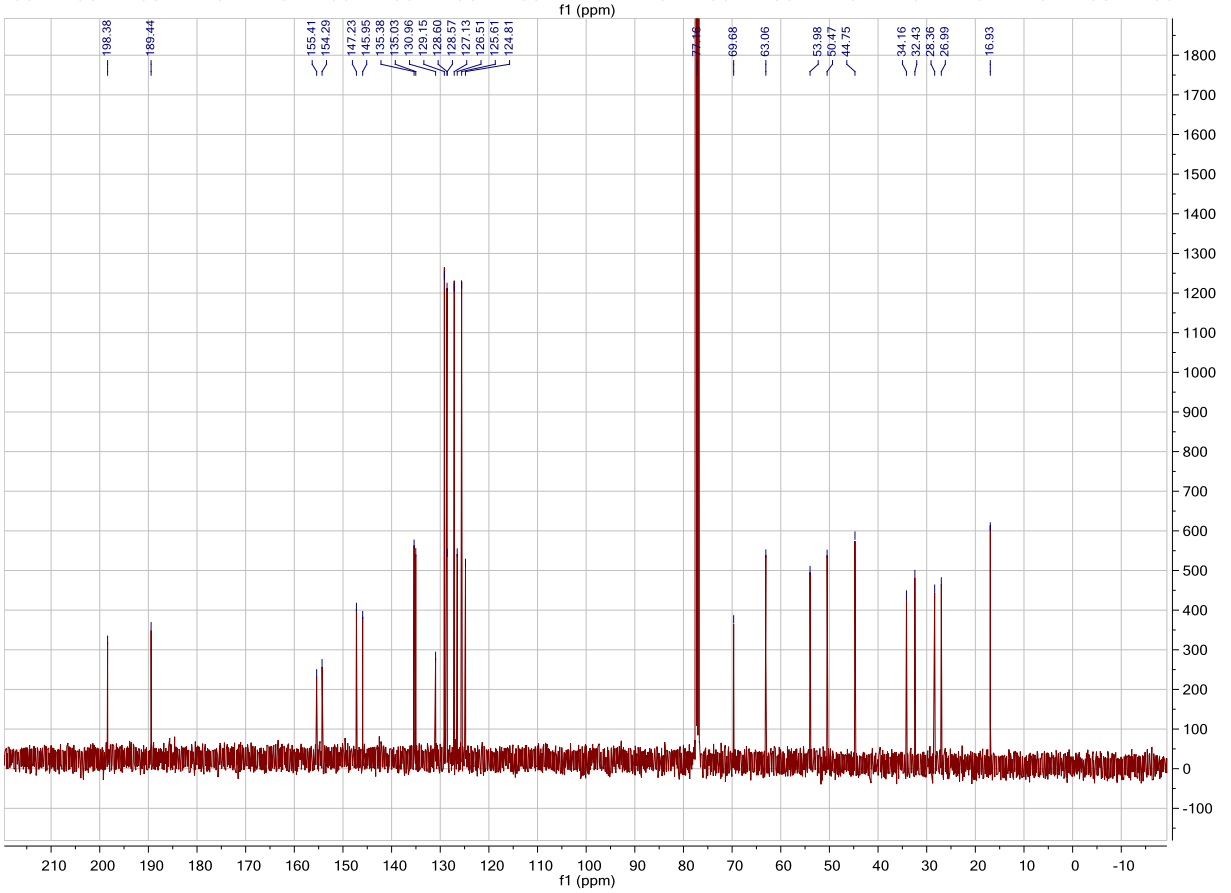
	RT	% Area
1	4.735	35.11
2	4.857	64.89

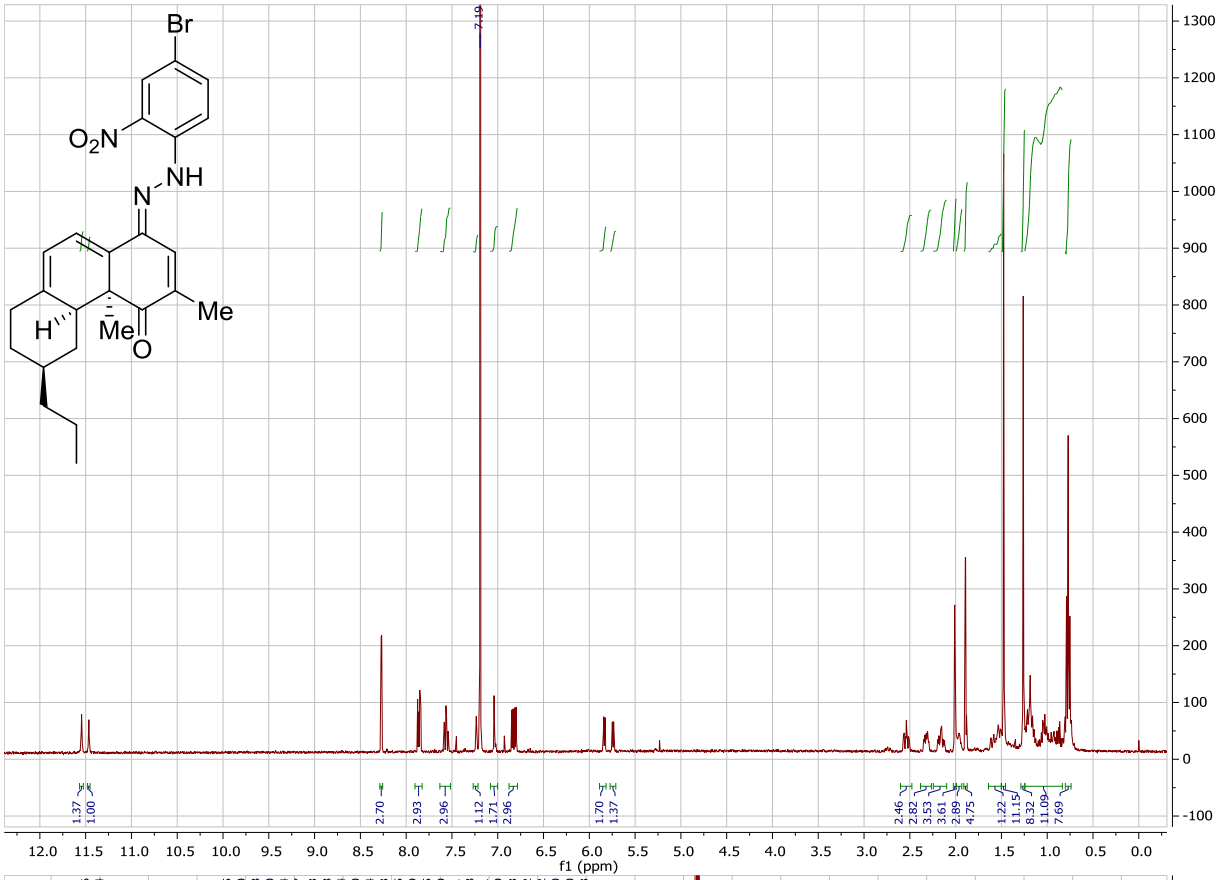


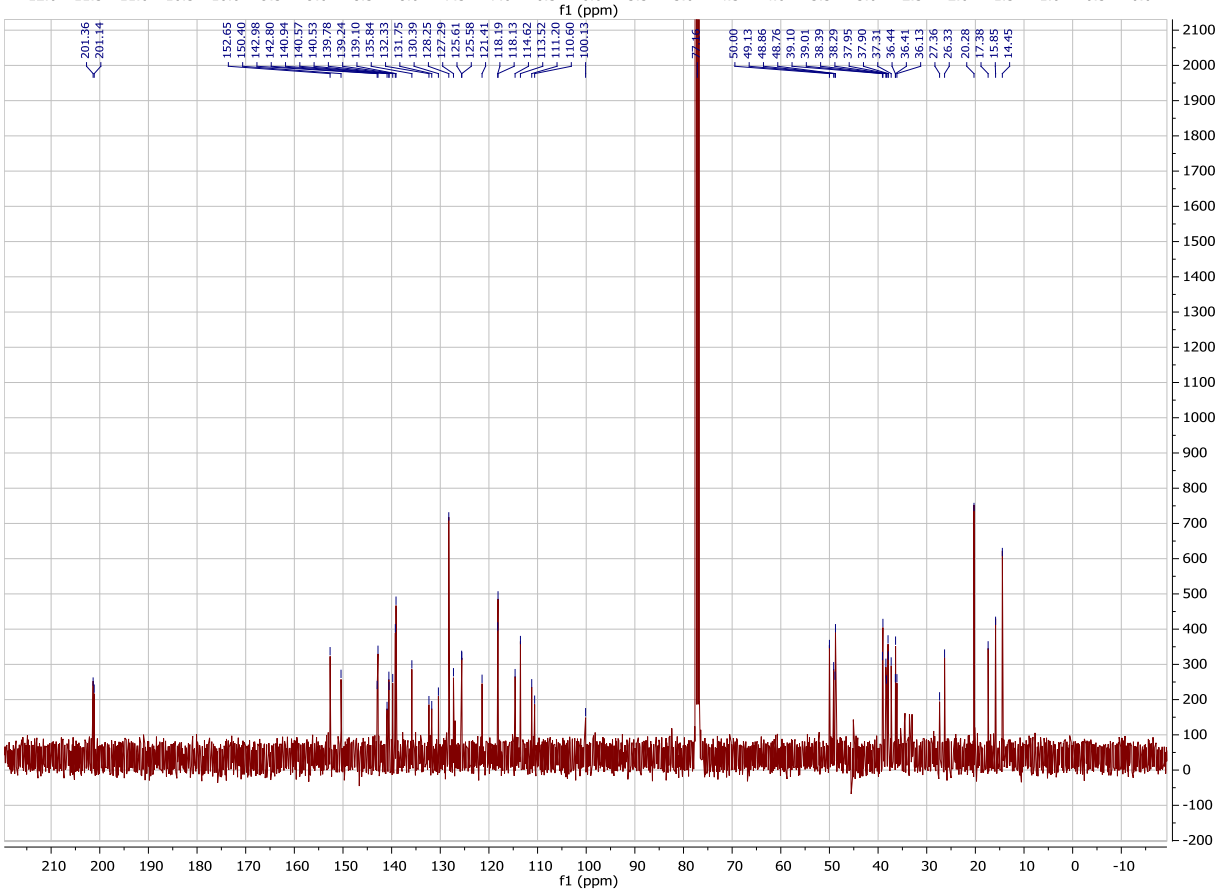
Peak Results

	RT	% Area
1	4.719	100.00


Ph
N
O
O
N
N
O
H
Me
Me
O
Ph
7.26
4.03
5.33
0.81
0.99
0.95
1.00
0.99
1.02
0.99
1.02
5.09
1.00
1.26
3.01
f1 (ppm)


198.38
189.44
155.41
154.29
147.23
145.95
135.38
135.03
130.96
129.15
128.60
128.57
127.13
126.51
125.61
124.81
77.46
69.68
63.06
53.98
50.47
44.75
34.16
32.43
28.36
26.99
16.93
f1 (ppm)


Br
O2N
NH
N
Me
H
Me
O
7.19
1.37
1.00
2.70
2.93
2.96
1.12
1.71
2.96
1.70
1.37
2.46
2.82
3.53
3.61
2.89
4.75
1.22
11.15
8.32
11.09
7.69
f1 (ppm)


201.36
201.14
152.65
150.40
142.98
142.80
140.94
140.57
140.53
139.78
139.24
139.10
135.84
132.33
131.75
130.39
128.25
127.29
125.61
125.58
121.41
118.19
118.13
114.62
113.52
111.20
110.60
100.13
77.46
50.00
49.13
48.86
48.76
39.10
39.01
38.39
38.29
37.95
37.90
37.31
36.44
36.41
36.13
27.36
26.33
20.28
17.38
15.85
14.45
f1 (ppm)