Supplimentary Material for:

Total Synthesis of (+)-*ar*-Macrocarpene†

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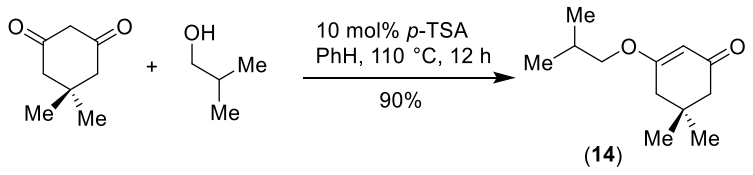
Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2), toluene, and benzene were distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silica gel of particle size 100-200 mesh was used for flash chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$) signal (δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) and Low-Resolution Mass Spectrometry (LRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

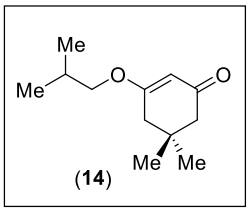
Procedure for the synthesis of vinylogous ester (**14**):



(**14**)

A round bottomed flask was charged with 1,3-cyclohexadione (5.0 g, 35.6 mmol, 1.0 eq) in benzene (60 mL). *p*-TsOH·H_2O (1.0g, 5.34 mmol, 0.15 eq) was added, followed by isobutanol (16.5 mL, 178 mmol, 5.0 eq). The reaction was tapped with a Dean-Stark apparatus and a condenser, and heated to 110 ^oC overnight, then concentrated to produce brown oil. The crude

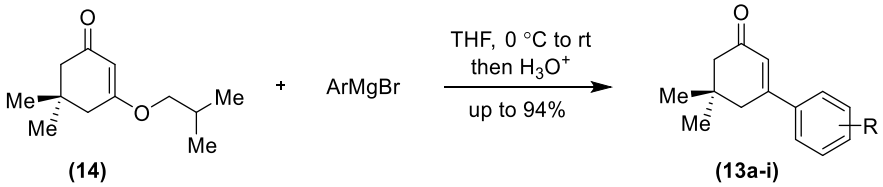
product was purified by silica gel chromatography (10% ethylacetate in petroleum ether) to afford **14** as a yellow oil (6.28 g, 90% yield).



(**14**)

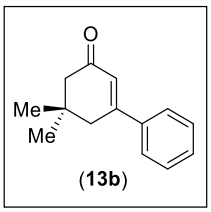
3-Isobutoxy-5,5-dimethylcyclohex-2-en-1-one (**14**): R_f = 0.45 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.33 (s, 1H), 3.60 (d, *J* = 6.5 Hz, 2H), 2.28 (s, 2H), 2.21 (s, 2H), 2.03 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.07 (s, 6H), 0.98 (s, 3H), 0.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 199.5, 176.4, 101.5, 74.7, 50.7, 42.9, 32.4, 28.3, 27.7, 19.0; **IR** (film) υ_{max}: 2755, 2173, 1676, 1166, 1051, 835, 774 cm^{-1}.

General procedure for the synthesis of compound (**13a-i**):



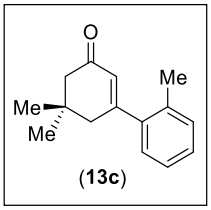
(**14**) (**13a-i**)

A solution of vinylogous ester (49 mg, 0.25 mmol, 1.0 eq.) in THF was added dropwise to a solution of aryl Grignard reagent in THF (0.3 mmol, 1.2 eq.) at 0 ºC. After that the reaction mixture temperature was slowly increased to room temperature, and stirred for 5 h. After that, 1(*N*) aqueous HCl solution was added to the reaction mixture dropwise and stirred for another 1h. The mixture was then poured on brine, dichloromethane was added, the layers were separated, and the aqueous layer was extracted 2 times with the same amount of dichloromethane. The combined organic layers were dried over Na_2SO_4, concentrated. Finally, the crude products were purified by flash chromatography (hexanes: EtOAc = 92:8) to afford product (**13a-i**).



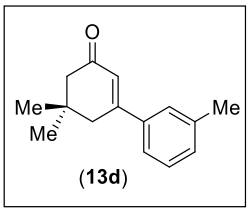
(**13b**)

5,5-Dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13b**): According to the general procedure, compound **13b** was obtained as colourless oil (0.25 mmol scale, 45.0 mg, 90% yield); R_f = 0.55 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.30 (m, 5H), 6.73 (s, 1H), 2.65 (dd, *J* = 7.4, 6.2 Hz, 2H), 2.01 – 1.96 (m, 2H), 1.28 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 197.8, 157.3, 137.3, 136.4, 128.7, 128.0, 127.6, 36.0, 35.3, 33.5, 28.0; **IR** (film) υ_{max}: 2943, 2873, 2735, 2143, 2028, 1673, 1176, 1031, 865, 754 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}O$: 201.1274, found: 201.1259.



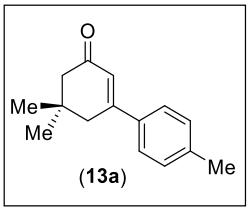
(**13c**)

2',5,5-Trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13c**): According to the general procedure, compound **13c** was obtained as yellow oil (0.25 mmol scale of reaction, 49.3 mg of product, 92% yield); R_f = 0.6 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.28 – 7.21 (m, 2H), 7.10 (dd, *J* = 6.8, 1.5 Hz, 2H), 6.03 (t, *J* = 1.7 Hz, 1H), 2.51 (d, *J* = 1.7 Hz, 2H), 2.38 (s, 2H), 2.34 (s, 3H), 1.18 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 199.9, 161.3, 140.6, 134.0, 130.7, 128.3, 127.6, 126.8, 125.9, 51.0, 45.4, 34.1, 28.3, 20.0; **IR** (film) υ_{max}: 3013, 2853, 2775, 2167, 1678, 1461, 1061, 1018, 938, 756 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{18}ONa$: 237.1250, found: 237.1250.



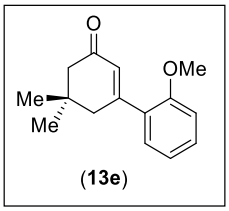
(**13d**)

3',5,5-Trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13d**): According to the general procedure, compound **13d** was obtained as yellow oil (0.25 mmol scale of reaction, 47.7 mg of product, 89% yield); R_f = 0.62 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.33 (m, 1H), 7.33 – 7.30 (m, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.41 (t, *J* = 1.5 Hz, 1H), 2.63 (d, *J* = 1.7 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 2H), 1.12 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 200.1, 158.0, 139.0, 138.4, 130.7, 128.7, 126.8, 124.2, 123.3, 50.9, 42.3, 33.7, 28.4, 21.5; **IR** (film) υ_{max}: 3023, 2853, 2735, 2067, 1684, 1338, 1054, 987, 827 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}O$: 215.1430, found: 215.1424.



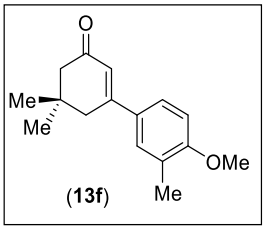
(**13a**)

4',5,5-Trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13a**): According to the general procedure, compound **13a** was obtained as colourless gel (0.76 mmol scale of reaction, 151.5 mg of product, 93% yield); R_f = 0.64 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.48 – 7.44 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 1.5 Hz, 1H), 2.65 (d, *J* = 1.6 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 2H), 1.14 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:200.3, 157.7, 140.9, 136.0, 129.5, 126.1, 123.5, 50.9, 42.2, 33.7, 28.4, 21.3; **IR** (film) υ_{max}: 3021, 2953, 2825, 2038, 1693, 1221, 1158, 984, 865 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}O$: 215.1430, found: 215.1415.



(**13e**)

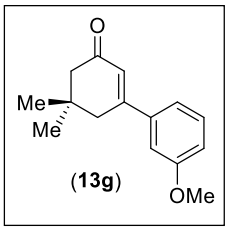
2'-Methoxy-5,5,5'-trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13e**): According to the general procedure, compound **13e** was obtained as orange gel (0.25 mmol scale of reaction, 50.1 mg of product, 87% yield); R_f = 0.50 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 – 7.27 (m, 1H), 7.16 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.98 – 6.88 (m, 2H), 6.16 (t, *J* = 1.6 Hz, 1H), 3.80 (s, 3H), 2.61 (d, *J* = 1.8 Hz, 2H), 2.31 (s, 2H), 1.10 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 200.1, 159.7, 156.6, 130.3, 129.9, 128.6, 127.1, 120.72, 111.2, 55.4, 51.2, 44.0, 34.2, 28.2; **IR**(film) υ_{max}: 2933, 2863, 2735, 1674, 1587, 1164, 948, 836, 757 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}O_2$: 231.1380, found: 231.1362.



(**13f**)

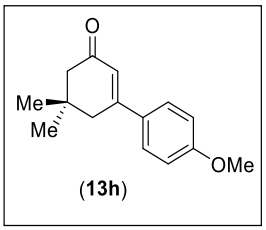
4'-Methoxy-3',5,5-trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13f**): According to the general procedure, compound **13f** was obtained as orange gel (0.25 mmol scale of reaction,

52.5 mg of product, 86% yield); R_f = 0.52 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38 (dd, *J* = 2.4, 0.9 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.71 – 6.68 (m, 1H), 6.45 – 6.42 (m, 1H), 3.88 (s, 3H), 2.35 (s, 2H), 2.26 (s, 3H), 2.19 (d, *J* = 0.7 Hz, 2H), 1.14 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 197.7, 159.2, 157.4, 137.8, 137.2, 129.0, 121.2, 114.5, 113.2, 55.2, 36.0, 35.3, 33.5, 28.0; **IR** (film) υ_{max}: 2969, 2823, 2741, 2138, 1678, 1321, 1086, 976, 813 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{21}O_2$: 245.1536, found: 245.1518.



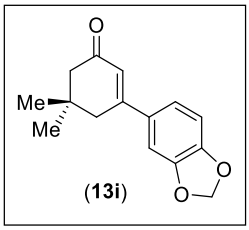
(**13g**)

3'-Methoxy-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13g**): According to the general procedure, compound **13g** was obtained as colorless gel (0.25 mmol scale of reaction, 52.4 mg of product, 91% yield); R_f = 0.48 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 (t, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* = 7.7, 1.7, 0.9 Hz, 1H), 7.07 (dd, *J* = 2.5, 1.7 Hz, 1H), 6.98 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.43 (t, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 2.66 (d, *J* = 1.6 Hz, 2H), 2.37 (s, 2H), 1.15 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 200.2, 159.8, 157.6, 140.6, 129.7, 124.6, 118.6, 115.4, 111.8, 55.4, 51.0, 42.4, 33.8, 28.4; **IR** (film) υ_{max}: 3043, 2963, 2825, 2162, 2038, 1686, 1485, 1161, 1045, 956, 767 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}O_2$: 231.1380, found: 231.1365.



(**13h**)

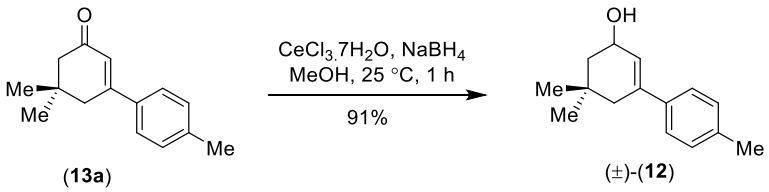
4'-Methoxy-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**13h**): According to the general procedure, compound **13h** was obtained as colourless gel (0.25 mmol scale of reaction, 51.2 mg of product, 89% yield); R_f = 0.45 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.61 – 7.48 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.41 (t, *J* = 1.4 Hz, 1H), 3.86 (s, 3H), 2.35 (s, 2H), 2.30 (s, 1H), 2.24 (s, 1H), 1.14 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:-198.1, 156.5, 148.3, 136.8, 129.2, 121.0, 110.8, 55.9, 36.0, 35.4, 33.5, 28.1; **IR** (film) υ_{max} 3153, 2886, 2723, 1694, 1251, 1042, 1026, 936, 854, 786 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}O_2$: 231.1380, found: 231.1375.



(**13i**)

3-(Benzo[d][1,3]dioxol-5-yl)-5,5-dimethylcyclohex-2-en-1-one (**13i**): According to the general procedure, compound **13i** was obtained as colourless oil (0.19 mmol scale, 56.2 mg of product, 92% yield); R_f = 0.45 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.84 – 6.82 (m, 1H), 6.80 – 6.76 (m, 2H), 6.66 (d, *J* = 1.0 Hz, 1H), 5.97 (s, 2H), 2.63 (dd, *J* = 7.4, 6.2 Hz, 2H), 1.96 (ddd, *J* = 7.8, 6.3, 0.9 Hz, 2H), 1.26 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 197.9, 156.7, 147.2, 147.1, 136.8, 130.3, 122.2, 109.5, 108.0, 101.0, 36.0, 35.3, 33.5, 28.0; **IR** (film) υ_{max}: 3053, 2954, 2763, 1718, 1321, 1031, 1012, 936, 864, 722 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{16}O_3Na$: 267.0992, found: 267.1014.

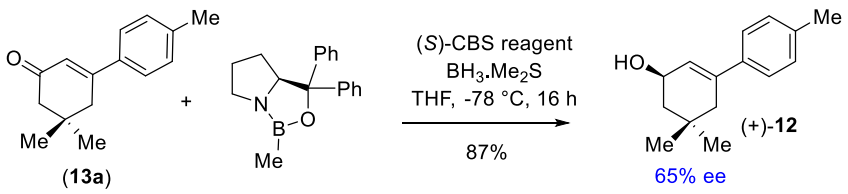
Synthesis of allylalcohol (±)**-12**:



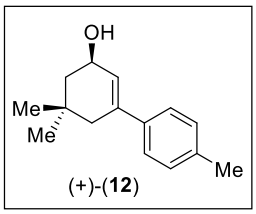
(**13a**) (±)-(**12**)

To a solution of **13a** (39.0 mg, 0.18 mmol, 1.0 equiv.) in methanol was added $CeCl_3.7H_2O$ (67.0 mg, 0.18 mmol, 1.0 equiv.). Under ice bath cooling condition, $NaBH_4$ (7.0 mg, 0.18 mmol, 1.0 equiv.) was added slowly. Then the reaction mixture was allowed to stir at same temperature for 1h. Then, the mixture was quenched with water and extracted with EtOAc (2 x 3mL). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Finally, the crude product was purified by column chromatography (hexanes: EtOAc = 90:10) to afford the product (±)-**12** (35.4 mg, 91 % yield) as a colorless oil.

Procedure A for the synthesis of enantioenriched allylalcohol (+)**-12 via CBS reduction of enone 13a**:

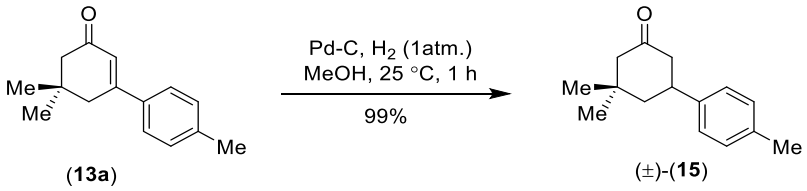


Compound **13a** (39.0 mg, 0.18 mmol, 1.0 eq.) was taken in dry THF (2 mL) and the reaction vessel was cooled to -78 ºC. After 15 min of stirring, (*S*)-(−)-2-Methyl-CBS-oxazaborolidine (18µL, 0.018 mmol, 0.1 eq.) was added to the reaction mixture and stirred it for another 30 min. Later, $BH_3.Me_2S$ (11µL, 0.108 mmol, 0.6 eq.) was added dropwise at -78 ºC and the reaction temperature was allowed to warm to rt. After completion of the reaction (as judged by running TLC, 16 h), 1 mL water was added followed by ethyl acetate (3 mL) and the organic filtrate was extracted. The crude product was purified by flash chromatography using 8-10% EtOAc/hexane as eluent to afford product (+)- **12** (33.9 mg, 87% yield) as a colorless oil.

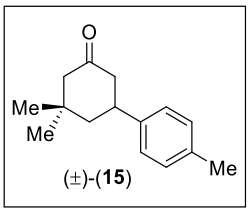


(*S*)-4',5,5-Trimethyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol [(+)-12]: R_f = 0.42 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.09 (s, 1H), 4.47 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 2H), 2.16 (d, *J* = 17.1 Hz, 1H), 1.91 (dd, *J* = 12.7, 6.2 Hz, 1H), 1.40 (t, *J* = 10.9 Hz, 1H), 1.13 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.5, 137.8, 137.1, 129.0, 125.4, 125.1, 67.3, 45.1, 41.5, 31.3, 26.1, 21.1; **IR** (film) υ_{max} 3443, 2965, 2821, 2735, 2138, 1181, 1061, 1022, 936, 821, 768 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+ Na]^+$ calcd for $C_{15}H_{20}ONa$; calc.: 239.1406, found: 239.1422; Enantiomeric excess was determined to be 65 % ee via HPLC analysis using Chiralpak AD-H column: solvent: 2-propanol/ hexane = 5/95: 1.0 mL/ min: detection at 273 nm): ^tR major = 13.36 min, ^tR minor = 15.36 min; $[\alpha]^{28.6}_{589}$ = +122.0 (c = 0.1, $CHCl_3$ for 65 % ee).

Hydrogenation of enone (±)**-13a**:

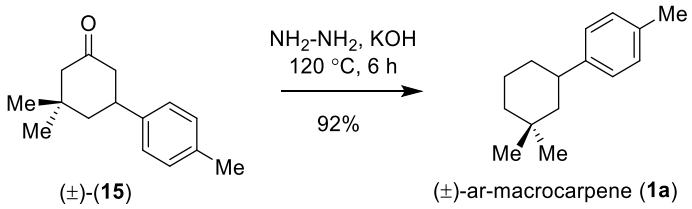


In an oven-dried round-bottom flask, compound **13a** (60.0 mg, 0.28 mmol, 1.0 equiv.) was taken in MeOH (4 mL) under argon atmosphere. To this reaction mixture Pd-C (0.028 mmol; 0.1 equiv.) was added and it was stirred for another 5 min at room temperature under argon atmosphere. Then the reaction mixture was stirred for 1 h under H_2 (g) balloon (1 atm.). Upon completion of the reaction, (TLC showed complete consumption of **13a**) the reaction mixture was filtered through celite and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash column chromatography using 8-10% EtOAc/hexane as eluent to afford (±)-**15** (60.0 mg, 99% yield) as colorless gel.



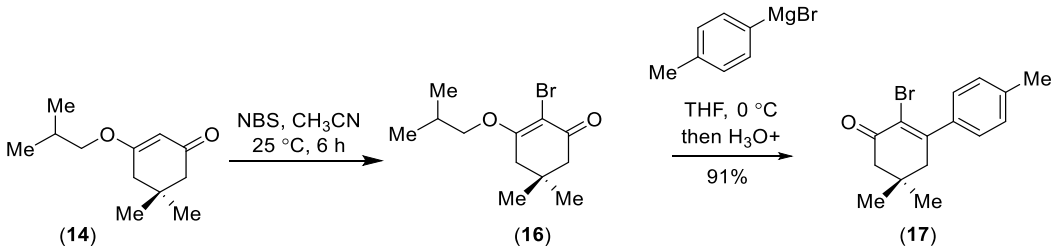
3,3-Dimethyl-5-(*p*-tolyl)cyclohexan-1-one [(±)-**15**]: R_f = 0.6 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.19 – 7.13 (m, 4H), 2.59 – 2.52 (m, 1H), 2.50 – 2.40 (m, 1H), 2.36 (s, 3H), 2.31 (d, *J* = 8.7 Hz, 1H), 2.20 (dt, *J* = 13.4, 2.2 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.15 (s, 3H), 1.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 211.2, 141.3, 136.3, 129.4, 126.5, 54.3, 48.3, 46.5, 40.0, 35.4, 32.2, 25.7, 21.0; **IR** (film) υ_{max}: 3062, 2947, 2360, 2333, 1720, 1354, 1217, 1139,772 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}ONa$: 239.1406, found: 239.1401.

Wolf-Kishner reduction of ketone (±)-**15**:



In an oven-dried round-bottom flask, the compound (±)**-15** (30.0 mg, 0.14 mmol, 1.0 equiv.) was taken in hydrazine hydrate (4 mL) under argon atmosphere. To this reaction mixture potassium hydroxide (23.5 mg, 0.42 mmol; 3.0 equiv.) was added and the reaction mixture was refluxed for 4 h. Upon completion of the reactions, (TLC showed complete consumption of **15** after 6 h) the reaction mixture was concentrated in a rotary evaporator under vacuum. Then the mixture was quenched with water and extracted in ethyl acetate. Then the product was purified by flash column chromatography using (01-02)% EtOAc/hexane as eluent to afford (±)**-1a** (26.0 mg, 92% yield) as colorless oil.

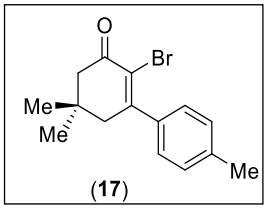
Synthesis of 2-bromo cyclohex-2-enone (**17**) **from vinylogoues ester** (**14**):



In a solution of the vinylogous ester **14** (100 mg, 0.51 mmol, 1.0 eq) in CH_3CN solvent, *N*-Bromo Succinamide (99.84 mg, 0.56 mmol, 1.1 eq) portion wise added to the solution at 25 ºC. After that the reaction mixture was stirred for 6 h at this temperature. Then saturated $Na_2S_2O_3$ solution was added.After that ethyl acetate(5 mL x 2) was used to extract the compound.The combined organic layers were dried over Na_2SO_4, concentrated, and dried and directly used for next step without any purification.

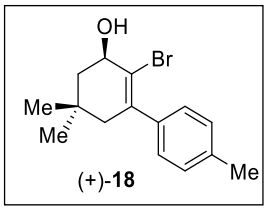
A solution of the crude bromo vinylogous ester **16** (1.0 eq) in THF was added dropwise to a solution of *p*-Tolyl Magnesium Bromide in THF (1.2 eq) at 0 ºC. After that the reaction mixture temperature was slowly increased to room temperature, and stirred for 6 h at this temperature. Then 1(*N*) aqueous HCl solution was added. The mixture was slowly warmed to room temperature and stirred overnight. The mixture was then poured on brine, dichloromethane was added, the layers were separated, and the aqueous layer was extracted 2 times with the same amount of dichloromethane. The combined organic layers were dried over Na_2SO_4,

concentrated, and purified by flash column chromatography using 10-12% EtOAc/hexane as eluent to afford **17**.



(**17**)

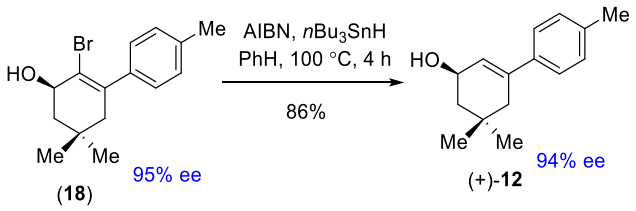
2-Bromo-4',5,5-trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**17)**: According to the experimental procedure The compound **17** was obtained as yellow gel (0.51 mmol scale of reaction, 136.0 mg of product, 91% yield)(after two step); R_f = 0.6 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.25 – 7.20 (m, 2H), 7.09 (dd, *J* = 6.8, 1.5 Hz, 2H), 2.50 (d, *J* = 1.7 Hz, 2H), 2.36 (s, 2H), 2.35 (s, 3H), 1.17 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 200.1, 163.3, 136.0, 130.7, 127.3, 127.6, 126.8, 51.0, 45.4, 34.1, 28.3, 20.0; **IR** (film) υ_{max}: 2957, 2942, 2835, 1724, 1540, 1492, 1201, 1048, 936, 857, 727 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{17}BrONa$: 315.0365, found: 315.0343.



(+)-**18**

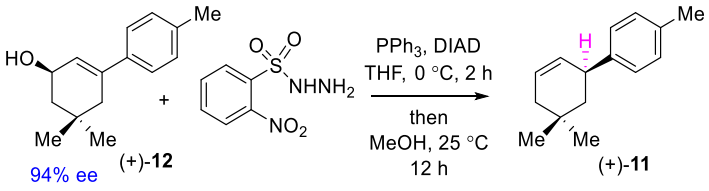
(*S*)-2-Bromo-4',5,5-trimethyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol [(+)-18]: According to the experimental procedure **A** the compound (+)-**18** was obtained as yellow gel (0.44 mmol scale of reaction, 121.7 mg of product, 93% yield); R_f = 0.5 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.18 (d, *J* = 3.9 Hz, 1H), 3.98 (d, *J* = 2.8 Hz, 1H), 2.36 (s, 2H), 2.00 (t, *J* = 13.2 Hz, 1H), 1.86 (dt, *J* = 10.8, 3.4 Hz, 1H), 1.69 – 1.63 (m, 1H), 1.06 (s, 2H), 1.03 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 137.1, 129.0, 125.4, 125.1, 115.2, 67.4, 45.1, 41.5, 31.3, 26.1, 21.1; **IR** (film) υ_{max}: 3343, 2924, 2720, 2643, 2572, 1201, 1051, 908, 892, 756 cm^{-1}. Enantiomericexcess of pure compound was determined via HPLC analysis using a Chiralpak IE-3 column; solvent: hexane/2-propanol = 95/5; flow rate: 1.00 mL/min; detection: at 254 nm): ^{t}Rminor = 9.84 min, ^{t}Rmajor = 13.08 min, $[\alpha]_{589}^{28.6}$ = +131.0 (c = 0.12, $CHCl_3$ for 95% ee).

Synthesis of allylalcohol (+)-12 (94% ee):

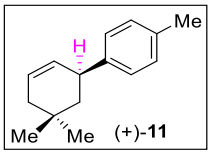


In an oven-dried round-bottm flask, the bromo compound **12** (100.0 mg, 0.34 mmol, 1.0 equiv.) was taken in dry benzene and was purged for 15 mins with Argon. The mixture was immerged in a preheated oil bath. When the solvent started to reflux, a mixture of *n*-Bu_3SnH (98.6 µL, 0.61 mmol, 1.8 equiv.) and AIBN (14.0 mg, 0.085 mmol, 0.25 equiv.) in benzene was added slowly over 1.5 h and then the reaction mixture was cooled after 2 h and evaporated. Then the residue was purified by flash column chromatography using (08-10)% EtOAc/hexane as eluent to afford **12** (63.2 mg, 86%). Enantiomeric excess was determined to be 94 % ~~ee~~ via HPLC analysis using Chiralpak IE-3 column: solvent: 2-propanol/ hexane = 5/95: 1.0 mL/ min: detection at 273 nm): ^{t}R major = 12.48 min, ^{t}R minor = 9.128. $[\alpha]^{28.6}_{589}$ = +154.0 (c = 0.18, $CHCl_3$ for 94 % ee).

Procedure for the synthesis of compound (+)-11:

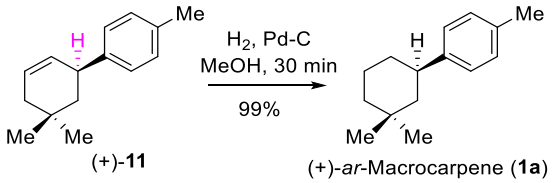


To a solution of the enol (35 mg, 0.16 mmol, 1.0 eq), *o*-nitrophenylsulfonylhydrazine (86.8 mg, 0.4 mmol, 2.5 eq) and triphenylphosphine (146.9 mg, 0.56 mmol, 3.5 eq) in benzene was added dropwise diisopropylazadicaboxylate (110.2 µL, 0.56 mmol, 3.5 eq). The reaction mixture was stirred for 2 h at 25 °C, concentrated, and diluted with methanol (0.5 mL). The resulting solution was stirred for 18 h at 20 °C and purified directly by flash chromatography on silica gel (elution with 5% EtOAc in hexane) to afford **11** (20.8 mg, 65%) as colorless gel.

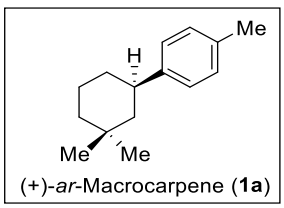


(*S*)-3,3,4'-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (+)-11: R_f = 0.5(5% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 2.5, 1.3 Hz, 2H), 7.23 (d, *J* = 1.2 Hz, 2H), 6.16 – 6.11 (m, 1H), 6.09 – 5.72 (m, 1H), 4.04 (tt, *J* = 6.3, 3.0 Hz, 1H), 2.38 (s, 3H), 2.24 – 2.09 (m, 2H), 2.03 – 1.81 (m, 2H), 1.12 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.78, 138.56, 137.75, 128.13, 126.36, 122.67, 55.75, 41.77, 40.76, 31.06, 26.30, 21.49; **IR** (film) υ_{max}: 2963, 2835, 2267, 1724, 1201, 1048, 956, 847, 757 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{21}$: 201.1635, found: 201.1645. $[\alpha]^{28.6}_{589}$ = +171.0 (c = 0.12, $CHCl_3$).

Synthesis of naturally occurring (+)-*ar*-Macrocarpene [(+)-**1a**]:



In an oven-dried round-bottom flask, the compound **11** (20.8 mg, 0.10 mmol, 1.0 equiv) was taken in MeOH (2 mL) under argon atmosphere. To this reaction mixture Pd on Carbon (0.010 mmol; 0.1 equiv) was added portion wise and it was stirred for another 10 min at room temperature under argon atmosphere. Then the reaction mixture was stirred for 30 min under H_2 (g) balloon. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was filtered through Celite and concentrated in a rotary evaporator under vacuum. Then the product was purified by flash column chromatography using (01-02)% EtOAc/hexane as eluent to afford (+)-**1a** (20.0 mg, 99% yield) as colorless oil.



1-(3,3-Dimethylcyclohexyl)-4-methylbenzene [(+)-**1a**]: R_f = 0.80 (5% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.03 (s, 4H), 2.59 (tt, *J* = 12.5, 3.5 Hz, 1H), 2.24 (s, 3H), 1.81 – 1.69 (m, 4H), 1.61 – 1.54 (m, 2H), 1.50 – 1.44 (m, 2H), 0.92 (s, 3H), 0.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.9, 135.2, 129.0, 126.7, 47.7, 39.5, 38.9, 34.2, 33.5, 31.2, 24.6, 22.8, 21.0; **IR** (film) υ_{max}: 2963, 2835, 1481, 1261, 1048, 936, 727 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M]^+$ calcd for $C_{15}H_{22}$: 202.1716, found: 202.1692; $[\alpha]_{589}^{28.6}$ = +7.9 (c = 1.2, *n*-hexane) [Literature report: $[\alpha]_{589}^{22}$ = +7.2 (c = 5.1, *n*-hexane)][2]

Comparison of NMR Data of (+)-*ar*-Macrocarpene (**1a**) of this report with literature of (±)-(**1a)** by A. Srikrishna.[1]

Comparison of **^{1}H-NMR** Data:

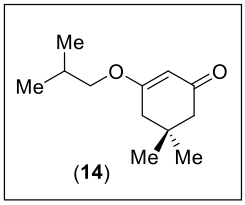
A. Srikrishna's report (±)-*ar*-Macrocarpene (**1a**) (^{1}H-NMR, 300 MHz, $CDCl_3$+CCl_4)			
δ (ppm)	Int.	mult.	*J* (Hz)
7.04	4H	s	-
2.63	1H	tt	12.3, 6.6
2.30	3H	s	-
1.90-1.79	1H	m	-
1.70-1.10	7H	m	-
0.99	3H	s	-
0.94	3H	s	-
This report (+)-*ar*-Macrocarpene (**1a**) (^{1}H-NMR, 400 MHz, $CDCl_3$)			
δ (ppm)	Int.	mult.	*J* (Hz)
7.03	4H	s	-
2.59	1H	tt	12.5, 3.5
2.24	3H	s	-
1.81-1.69	4H	m	-
1.61-1.54	2H	m	-
1.50-1.44	2H	m	-
0.92	3H	s	-
0.87	3H	s	-

Comparison of **^{13}C-NMR** Data:

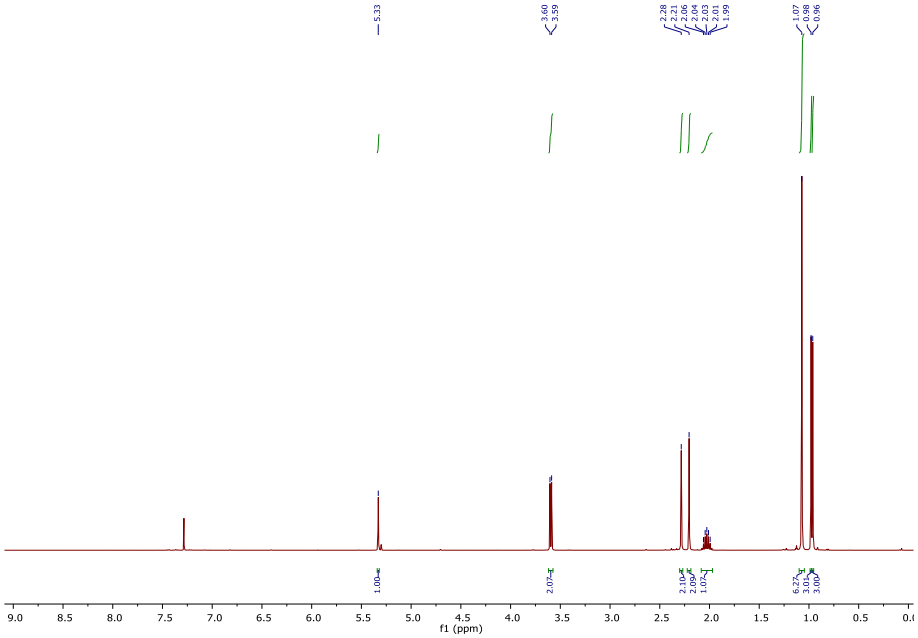
A. Srikrishna's report (±)-*ar*-Macrocarpene (**1a**) (^{13}C-NMR, 75 MHz, $CDCl_3$+CCl_4)	This report (+)-*ar*-Macrocarpene (**1a**) (^{13}C-NMR, 100 MHz, $CDCl_3$)
144.7	144.9
135.0	135.2
129.0	129.0
126.8	126.7
47.8	47.7
39.7	39.5
39.1	38.9
34.3	34.2
33.7	33.5
31.4	31.2
24.8	24.6
22.9	22.8
21.1	21.0

1. A. Srikrishna and B. Beeraiah. *Synth. Commun.* 2007, 37(**17**), 2855–2860.
2. L. G. Cool, *Phytochemistry* **2005**, *66*, 249–260.

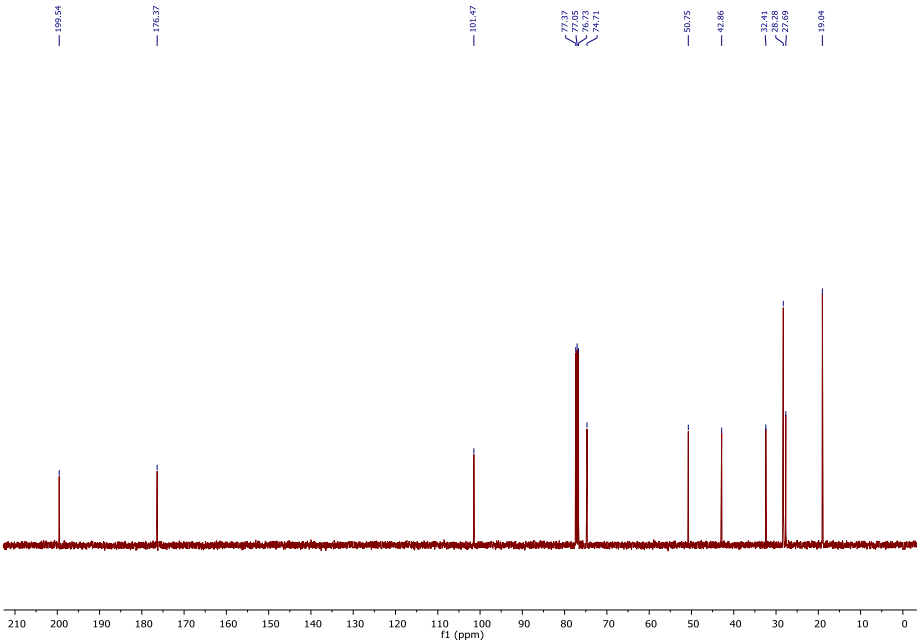
Spectral Data



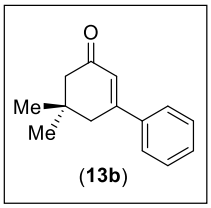
(**14**)



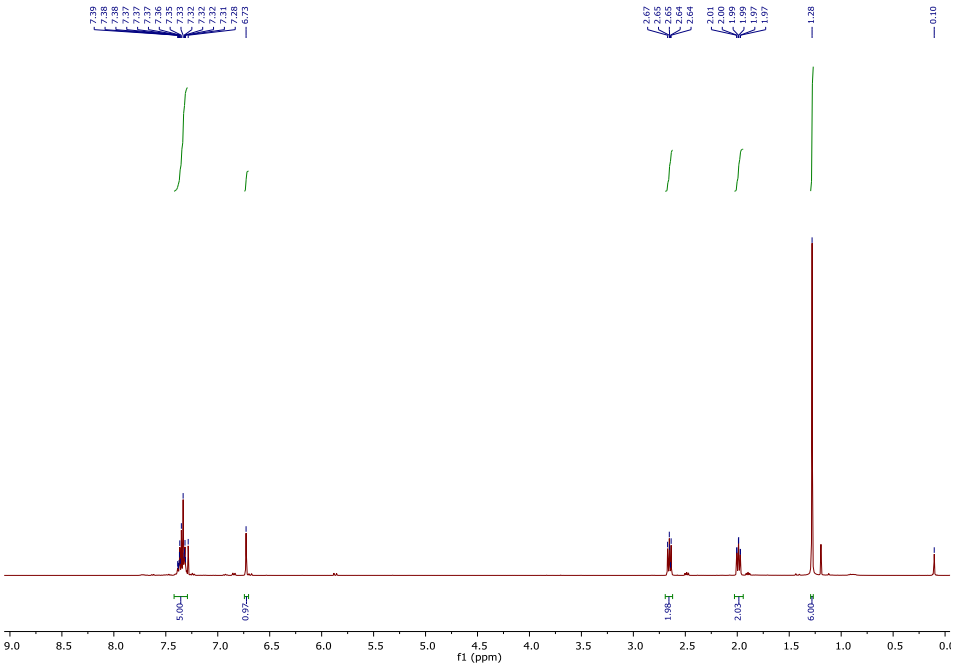
^{1}H NMR (400 MHz, $CDCl_3$) of compound **14**



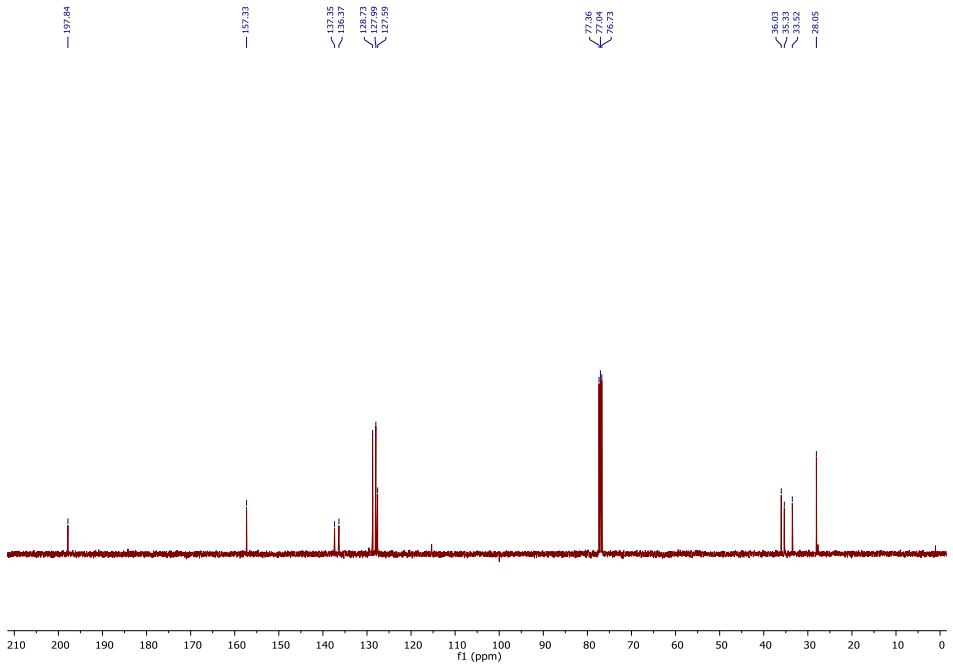
^{13}C NMR (100 MHz, $CDCl_3$) of compound **14**



(**13b**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound **13b**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13b**

Display Report

Analysis Info

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Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\30 APR\Dr A Bisai-AK-01-174_1-A,6_01_6104.d		
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Sample Name	Dr A Bisai-AK-01-174	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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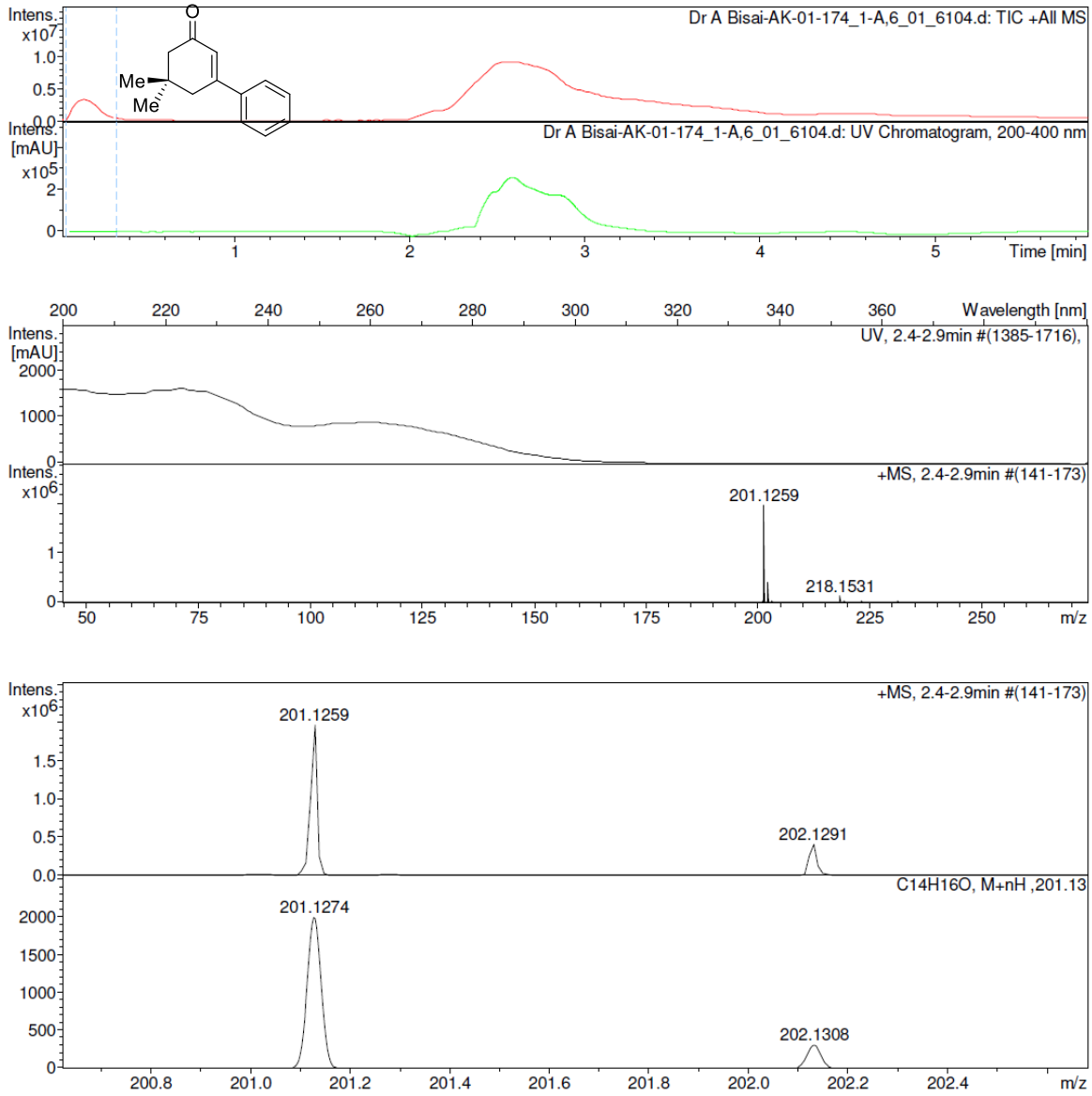
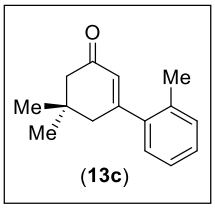
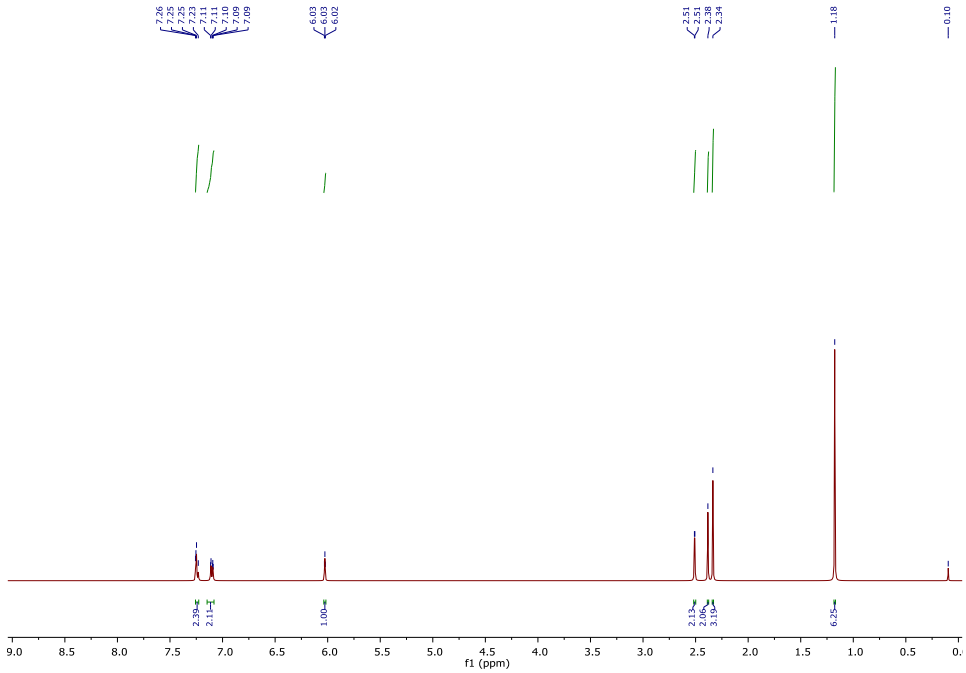


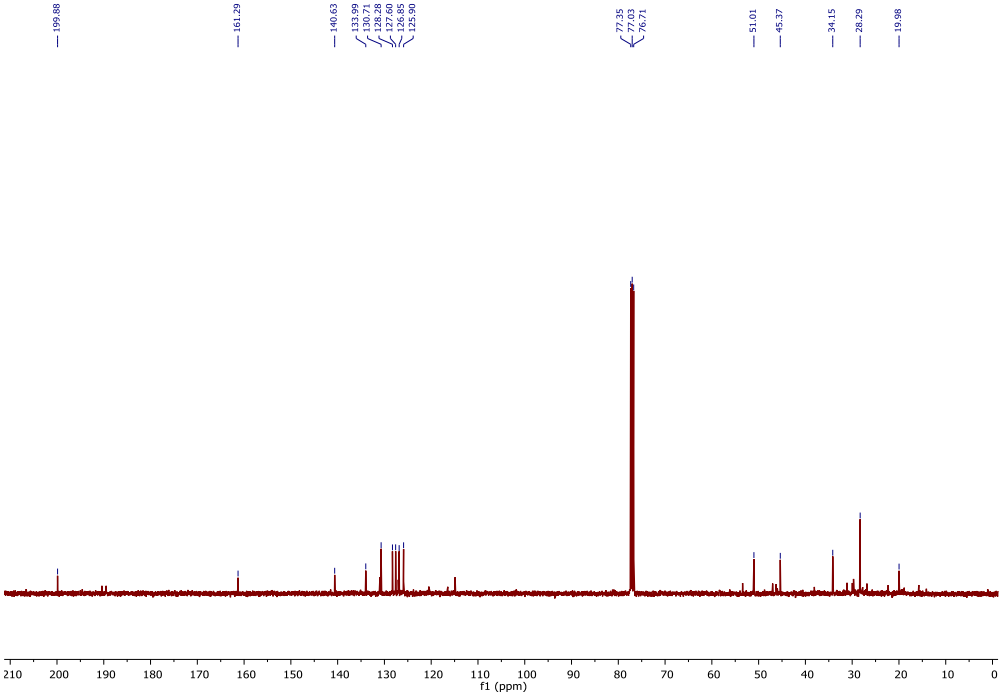
Bruker Compass DataAnalysis 4.0 printed: 4/30/2019 11:45:52 AM Page 1 of 1

Scanned copy of mass spectrum of **13b**





^{1}H NMR (400 MHz, $CDCl_3$) of compound **13c**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13c**

Display Report

Analysis Info

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Sample Name	-AB-AR-01-570	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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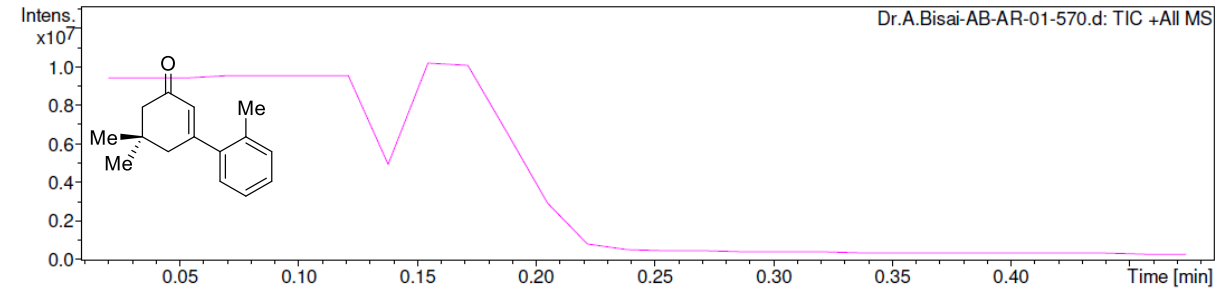
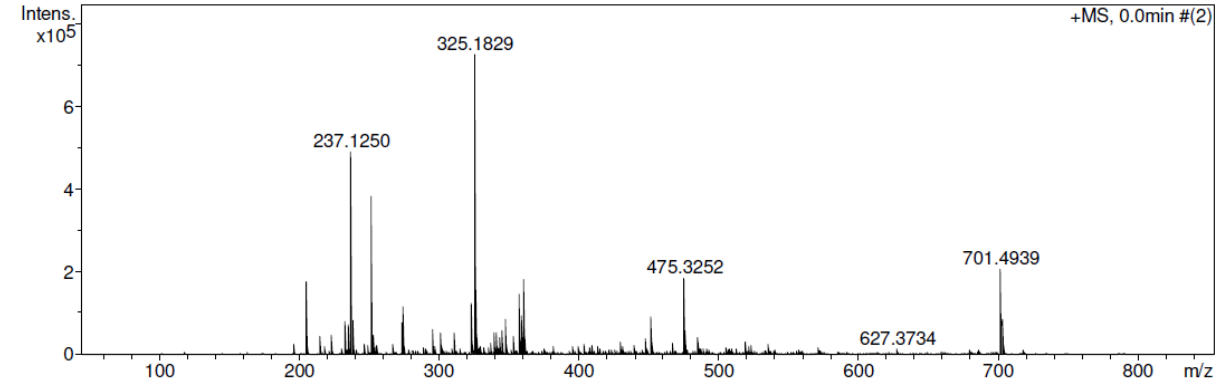
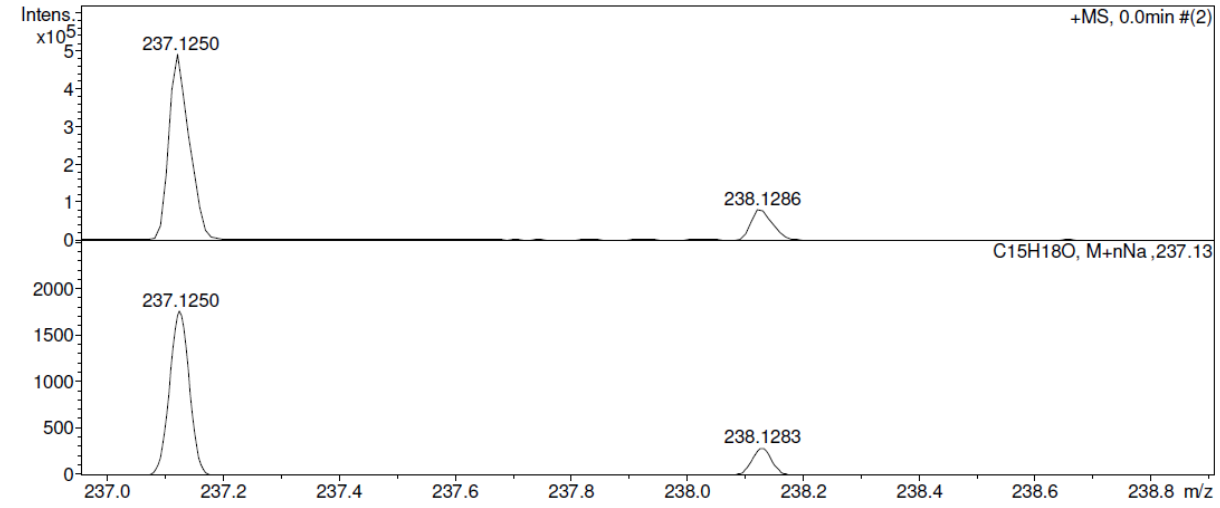
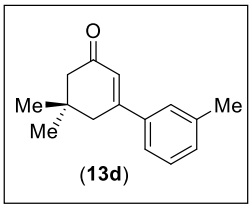


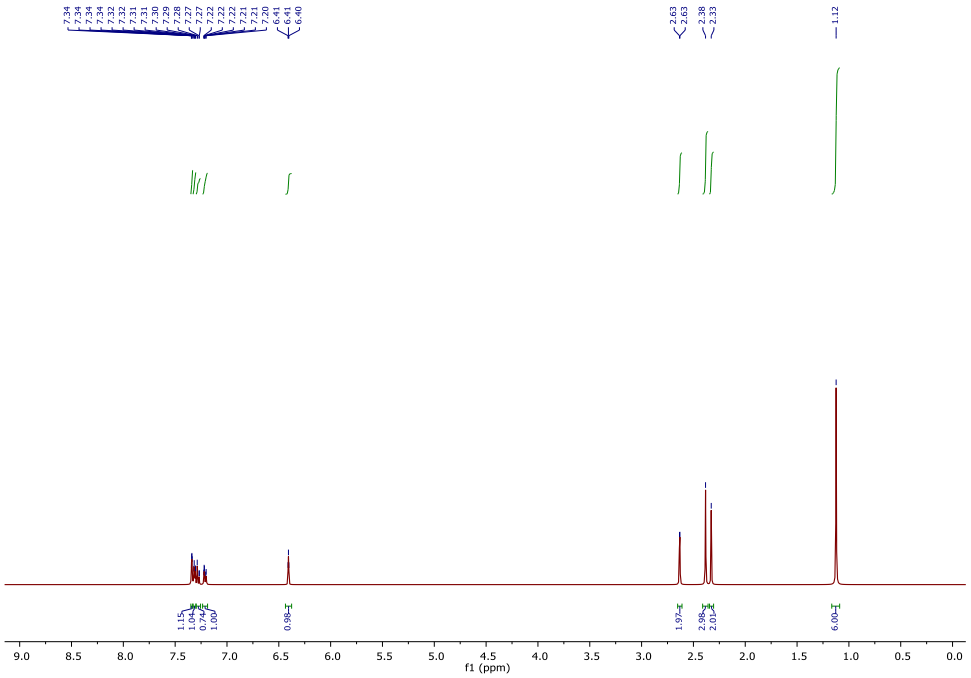




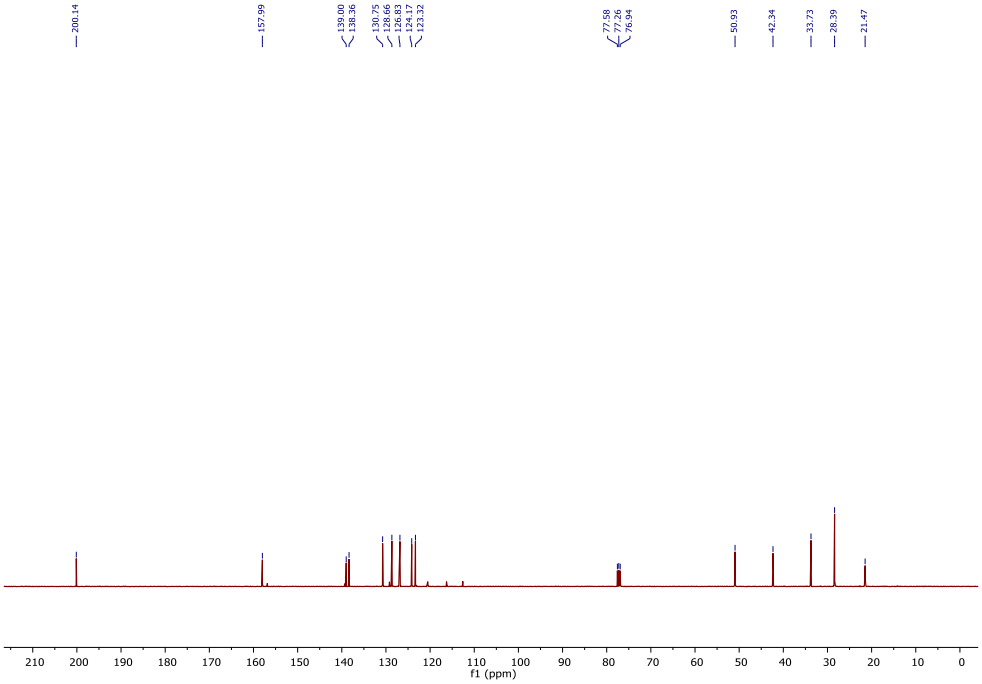
Bruker Compass DataAnalysis 4.0 printed: 4/26/2019 4:56:36 PM Page 1 of 1

Scanned copy of mass spectrum of **13c**





^{1}H NMR (400 MHz, $CDCl_3$) of compound **13d**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13d**

Display Report

Analysis Info

Acquisition Date	4/26/2019 10:30:56 AM		
Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\26 APR\Dr A Bisai-AK-01-169_1-A,4_01_6059.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-169	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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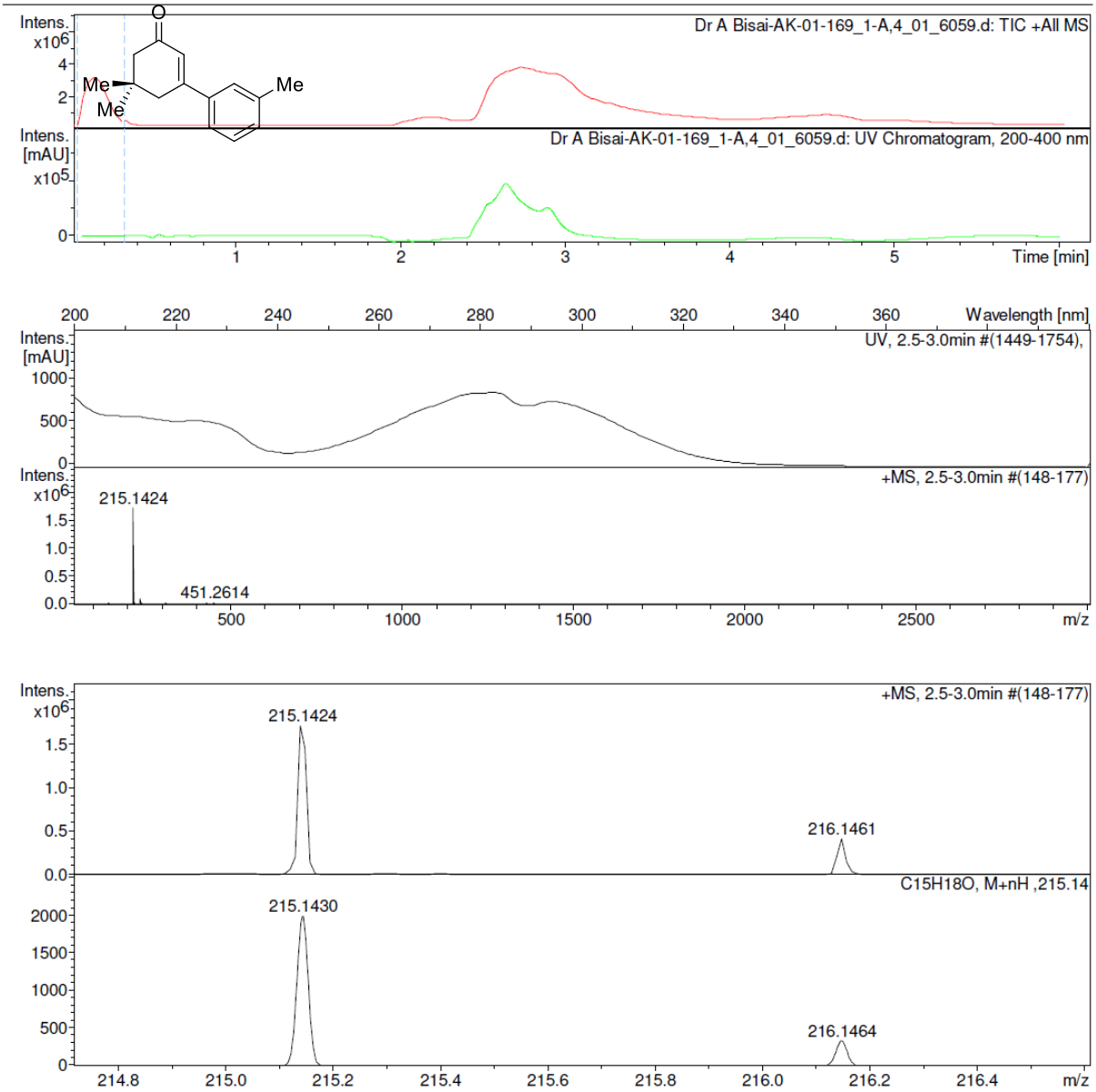
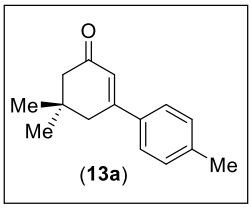
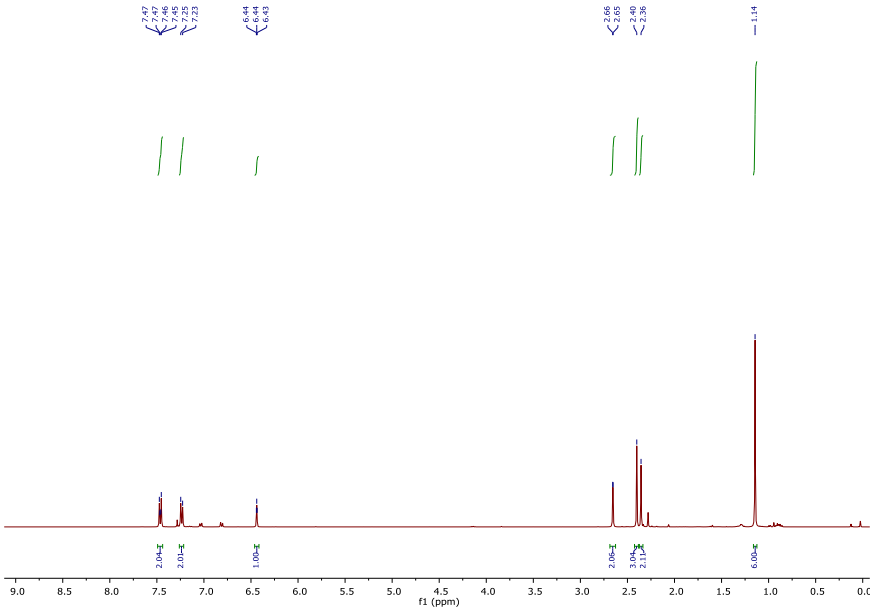
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

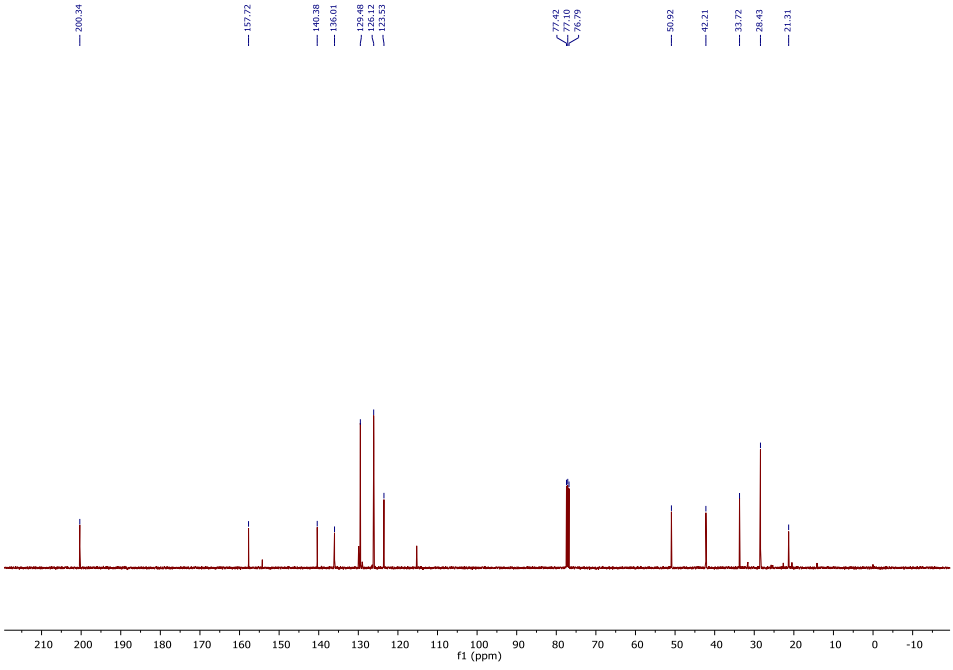


Scanned copy of mass spectrum of **13d**





^{1}H NMR (400 MHz, $CDCl_3$) of compound **13a**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13a**

Display Report

Analysis Info

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Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-168	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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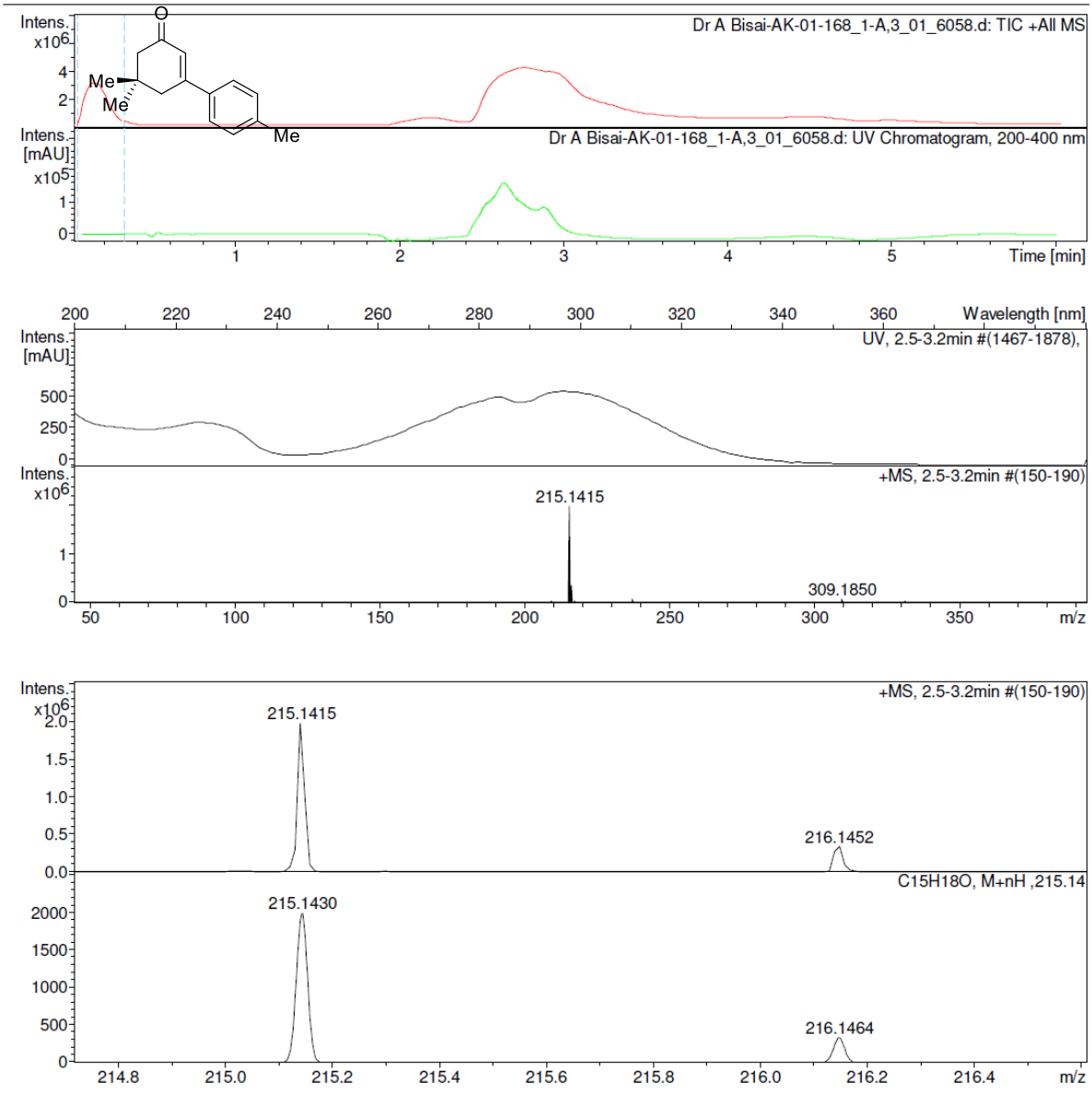
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



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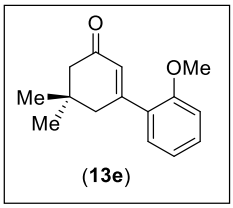
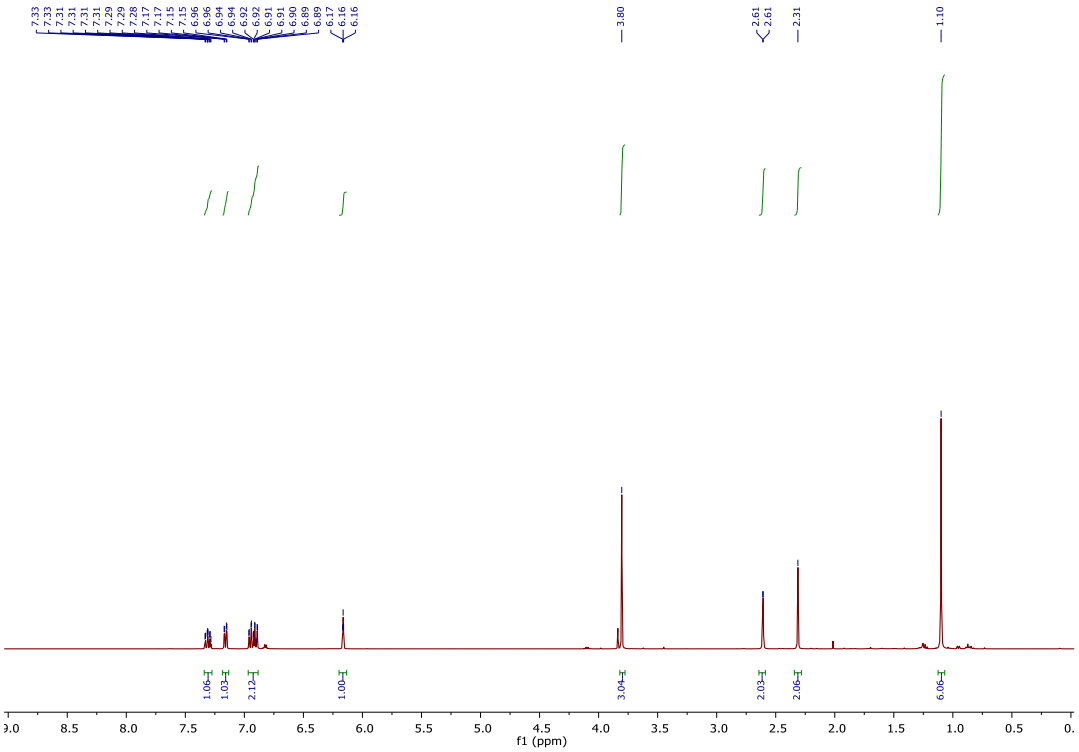
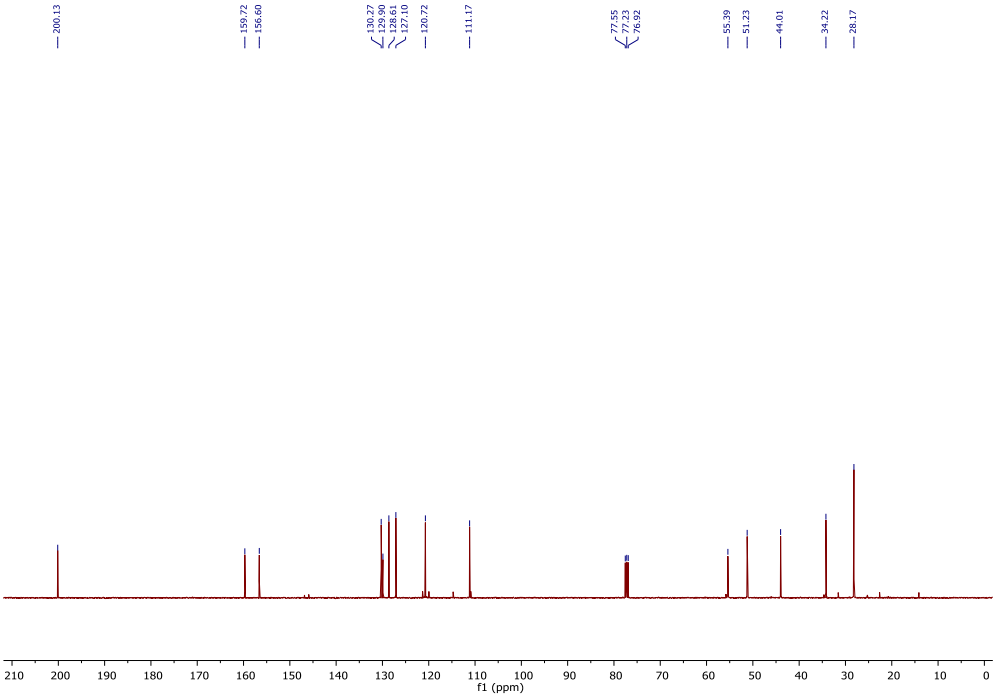
Scanned copy of mass spectrum of **13a**





^{1}H NMR (400 MHz, $CDCl_3$) of compound **13e**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13e**

Display Report

Analysis Info

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Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\30 APR\Dr A Bisai-AK-01-179_1-A,7_01_6105.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-179	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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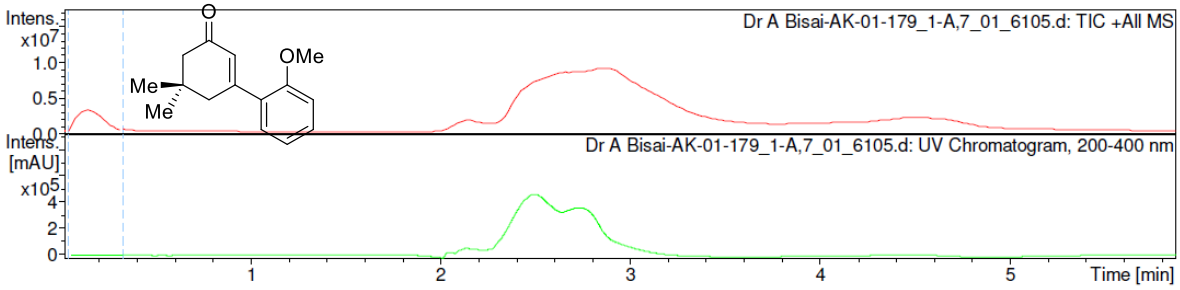
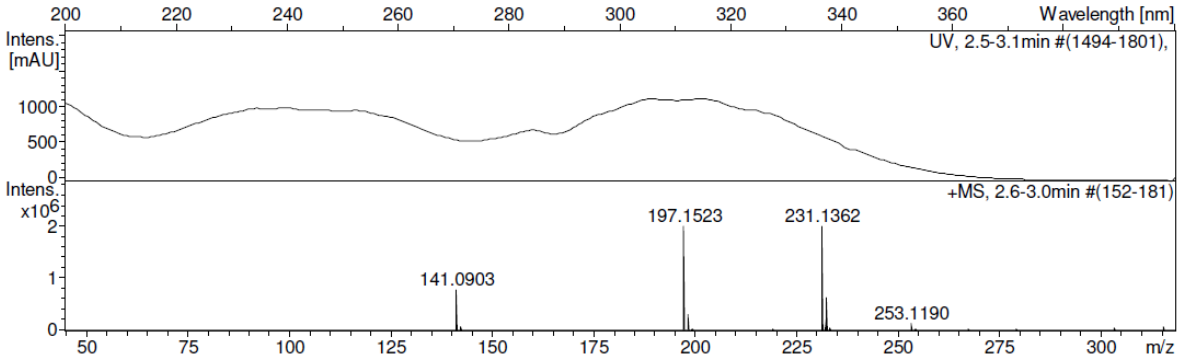
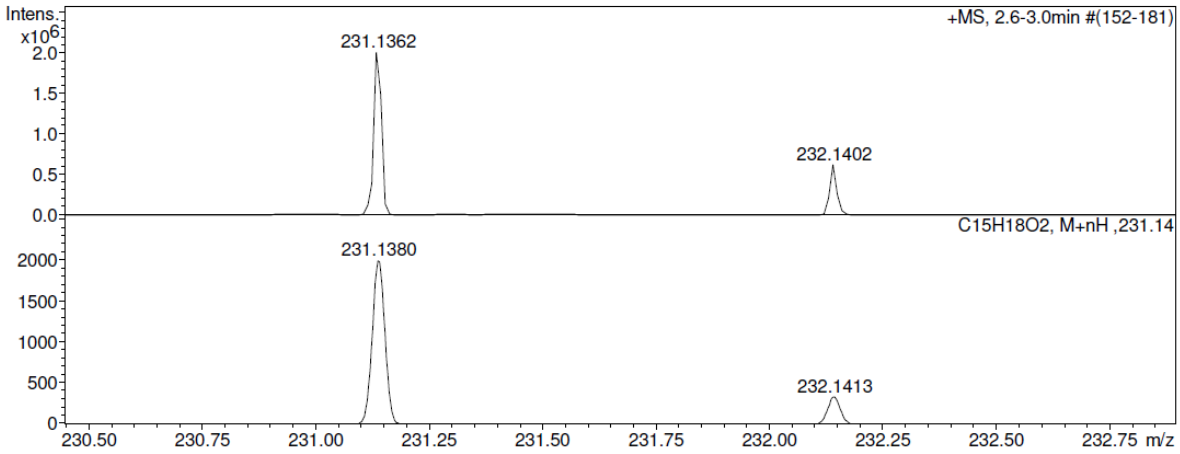
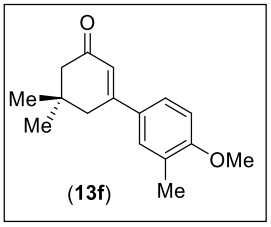
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



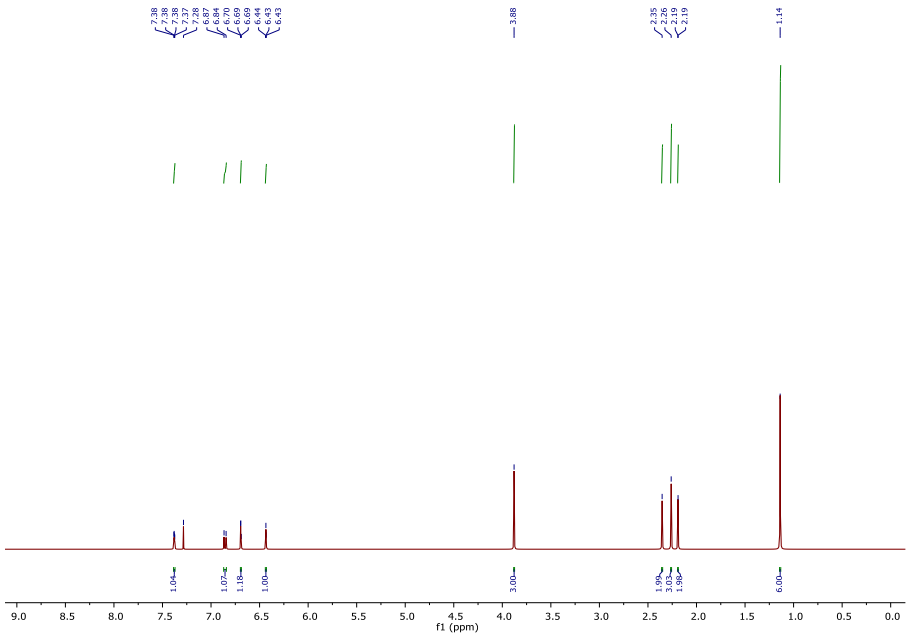




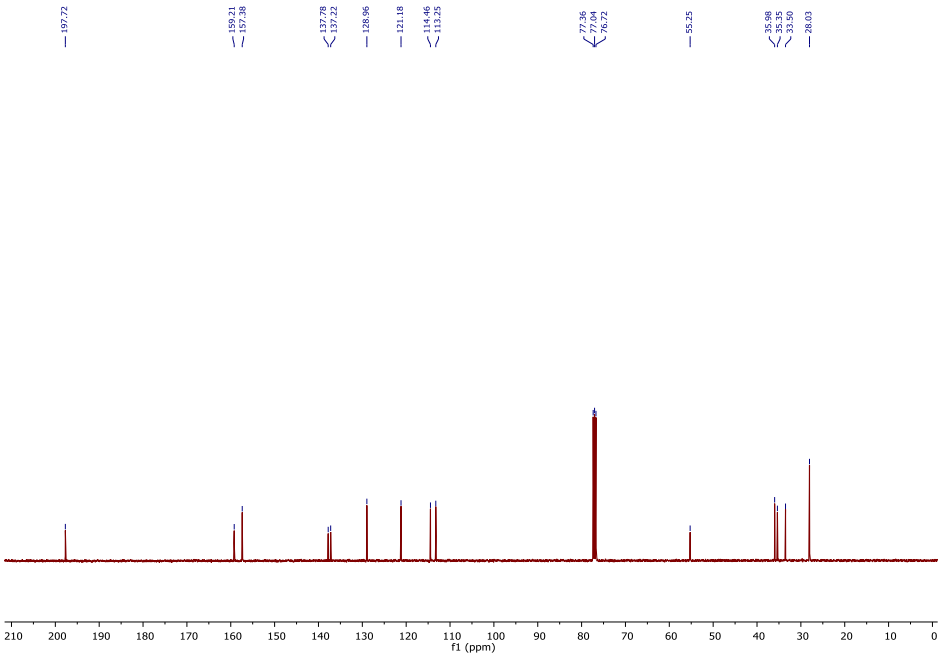
Scanned copy of mass spectrum of (±)-**13e**



(**13f**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**13f**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**13f**

Display Report

Analysis Info

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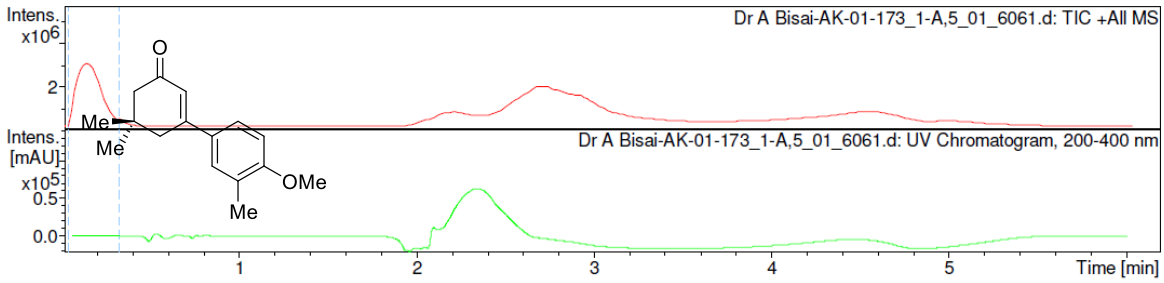
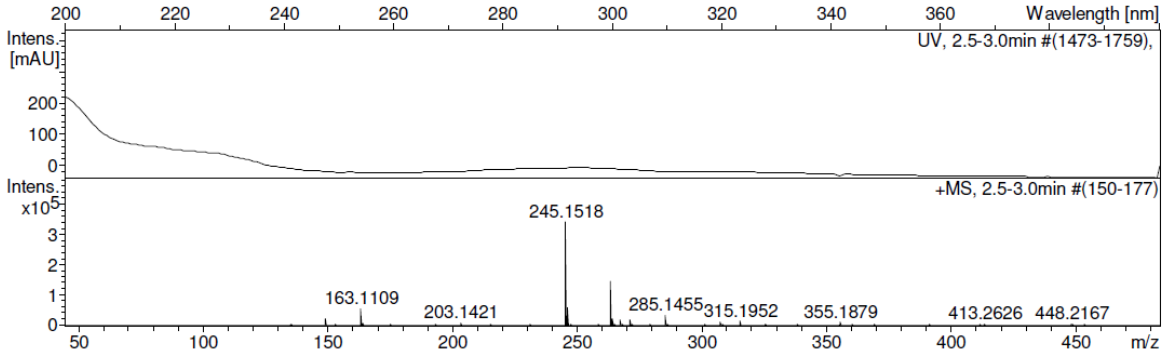
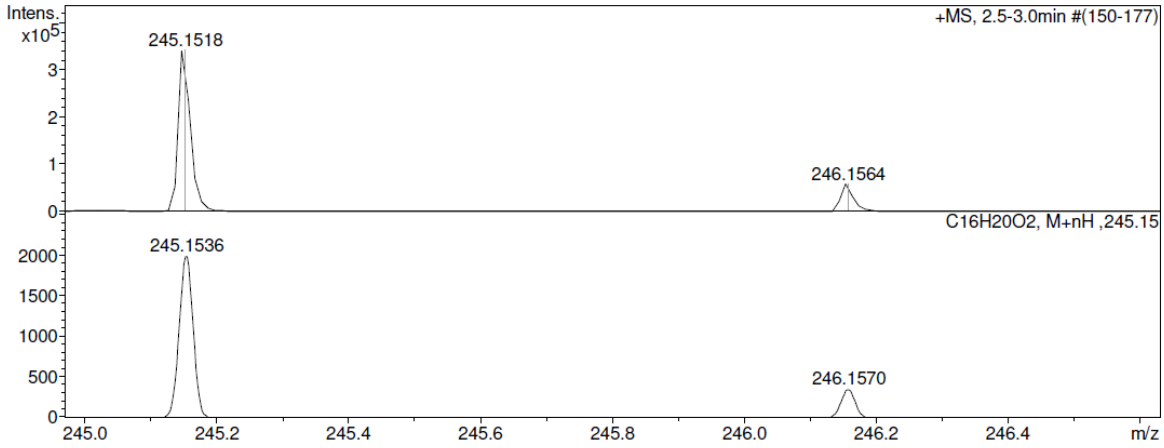
Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\26 APR\Dr A Bisai-AK-01-173_1-A,5_01_6061.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-173	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

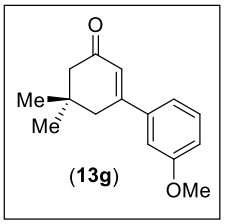
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

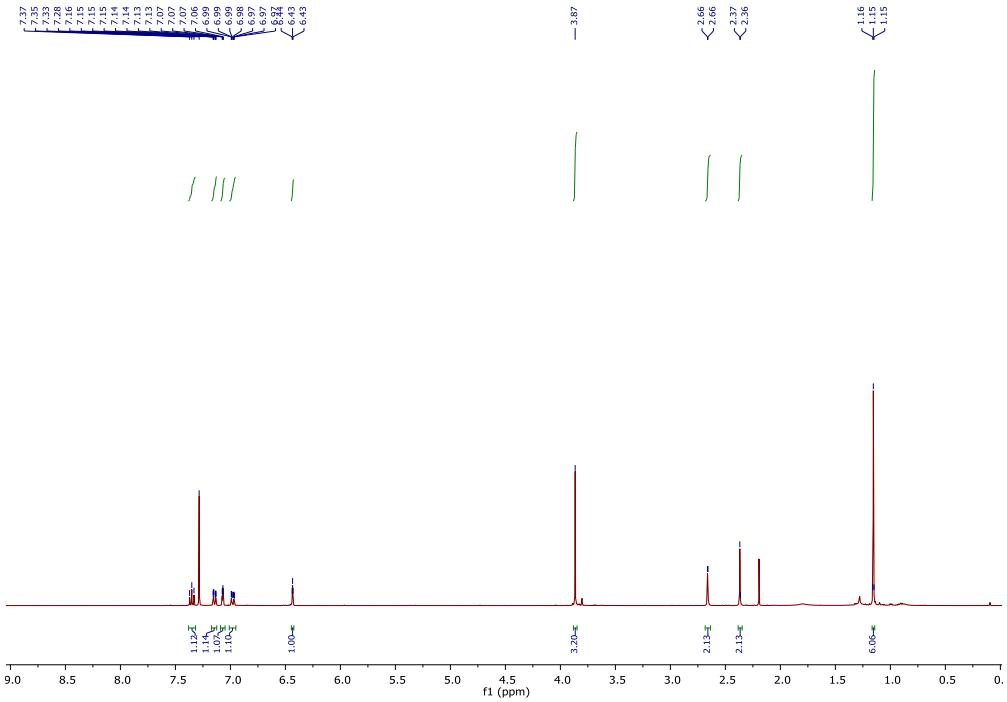




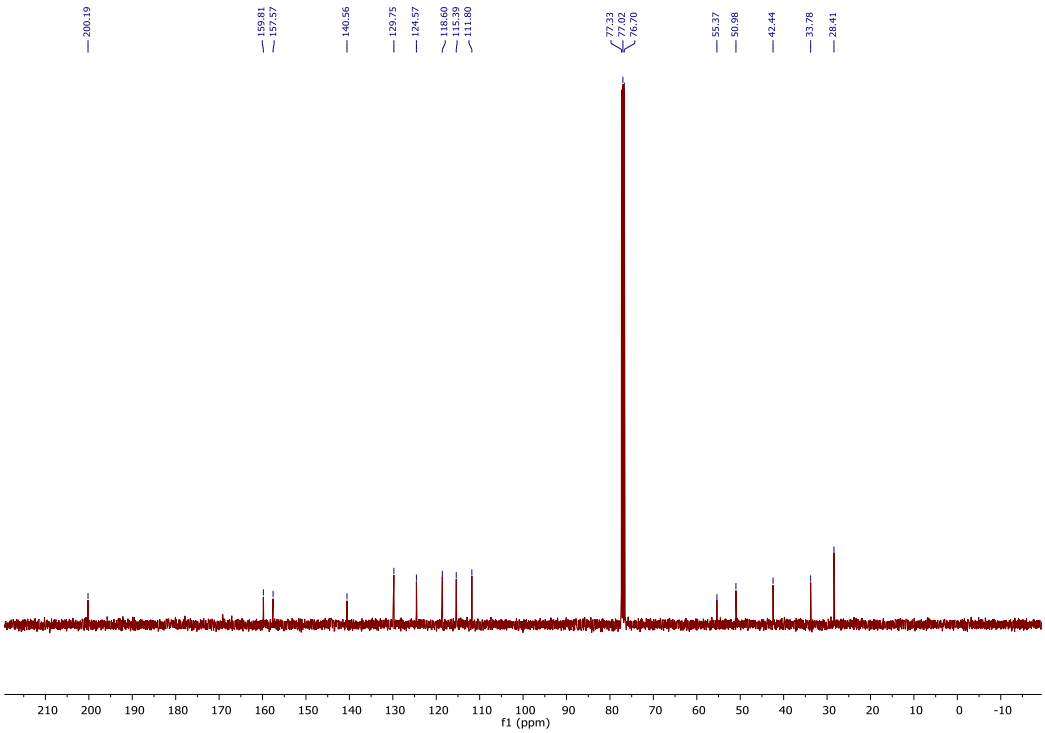


Scanned copy of mass spectrum of (±)-**13f**





^{1}H NMR (400 MHz, $CDCl_3$) of compound **13g**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13g**

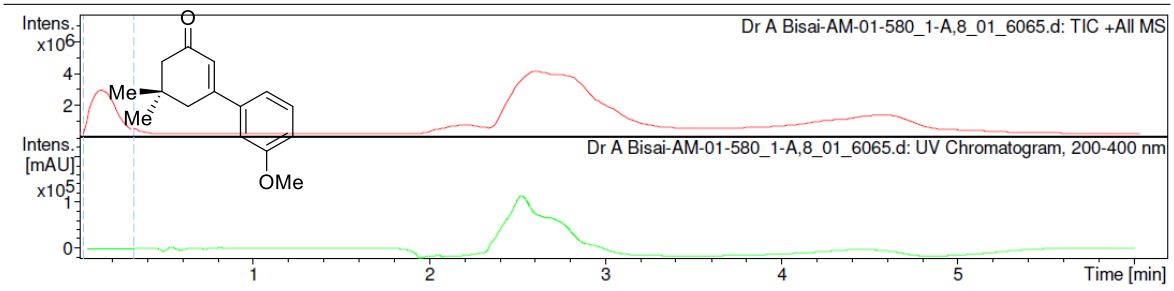
Display Report

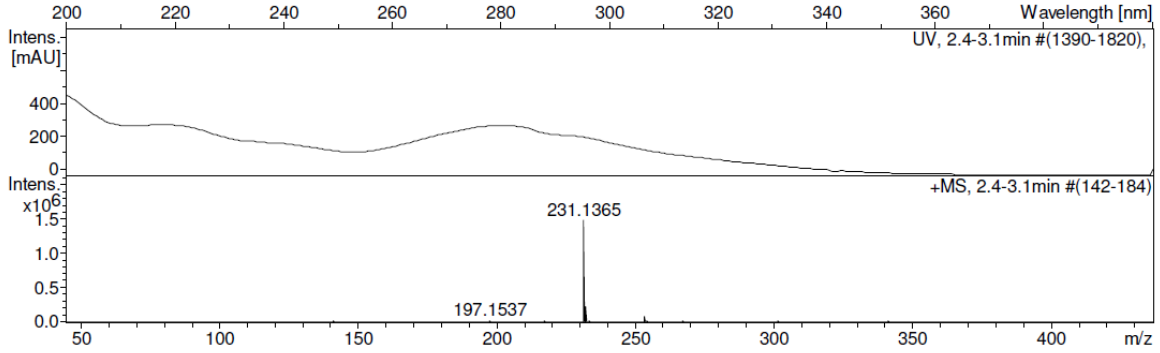
Analysis Info

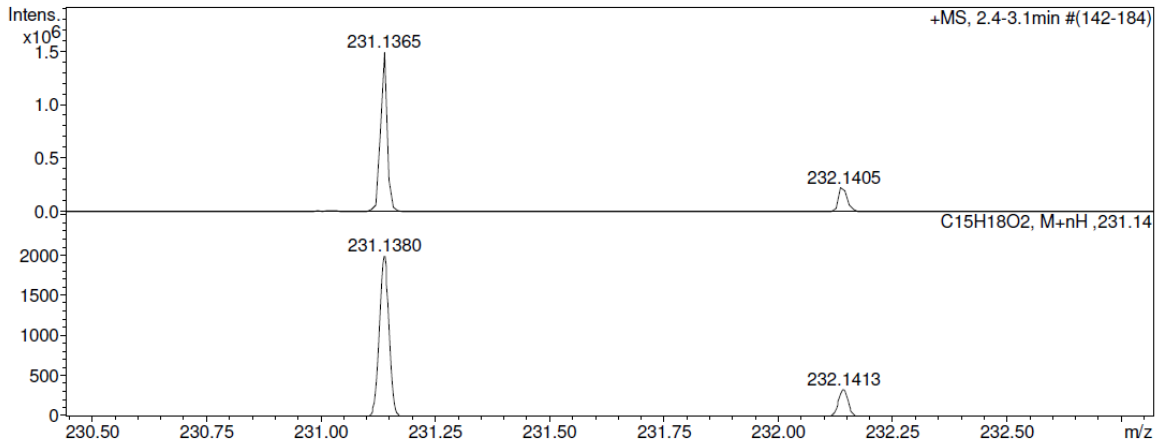
Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\26 APR\Dr A Bisai-AM-01-580_1-A,8_01_6065.d	Acquisition Date	4/26/2019 11:14:11 AM
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AM-01-580	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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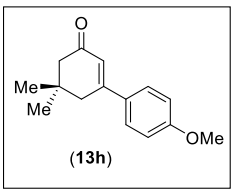
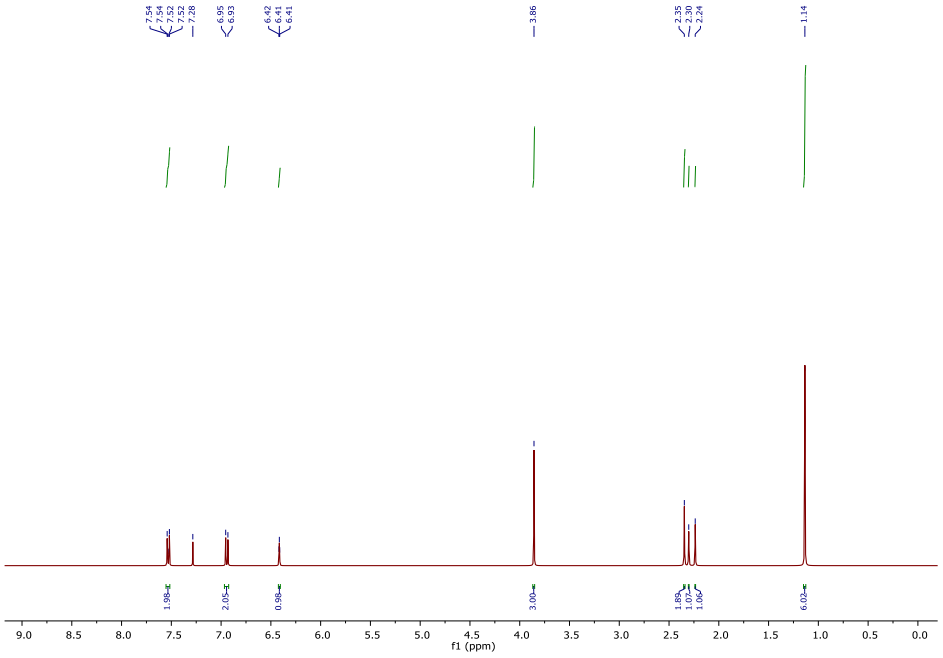
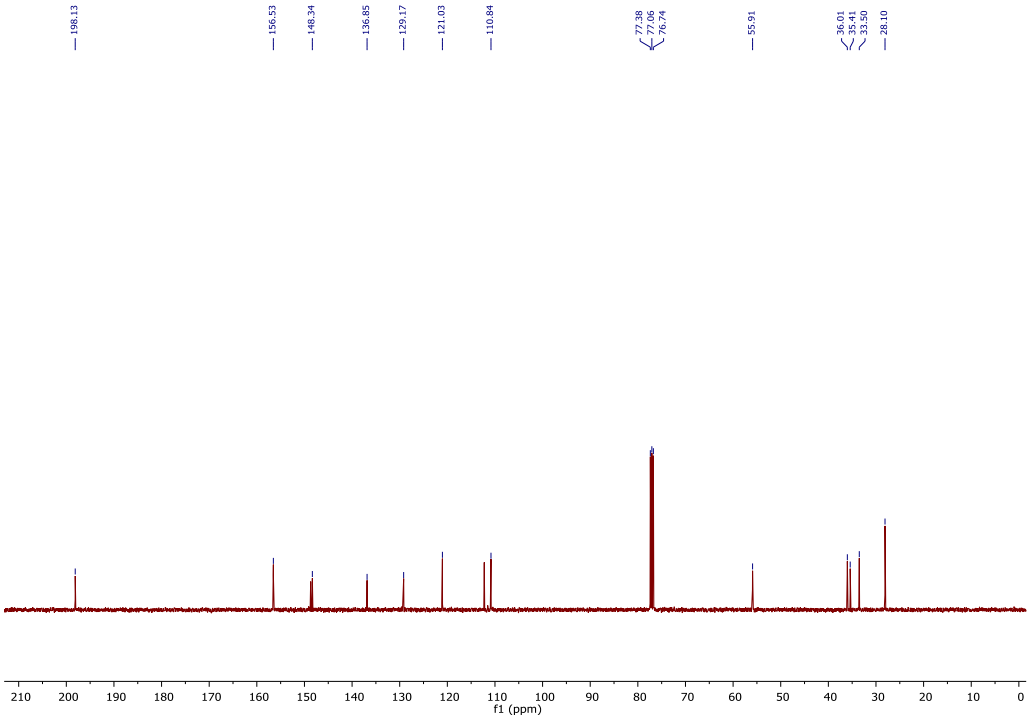
Scanned copy of mass spectrum of **13g**



(**13h**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound **13h**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13h**

Display Report

Analysis Info

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Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AM-01-578	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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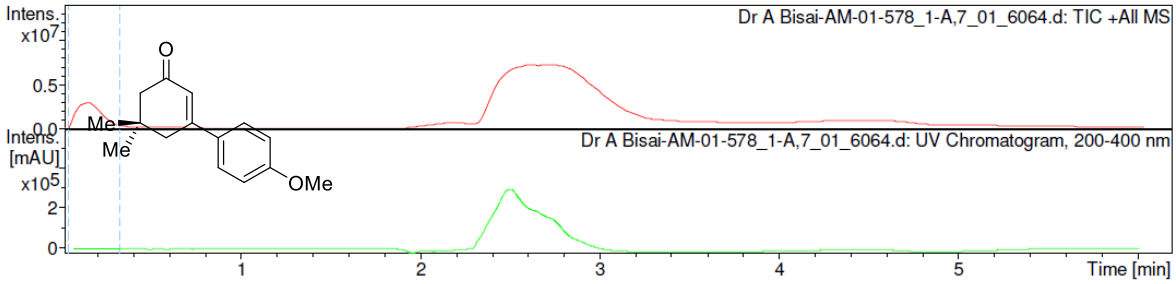
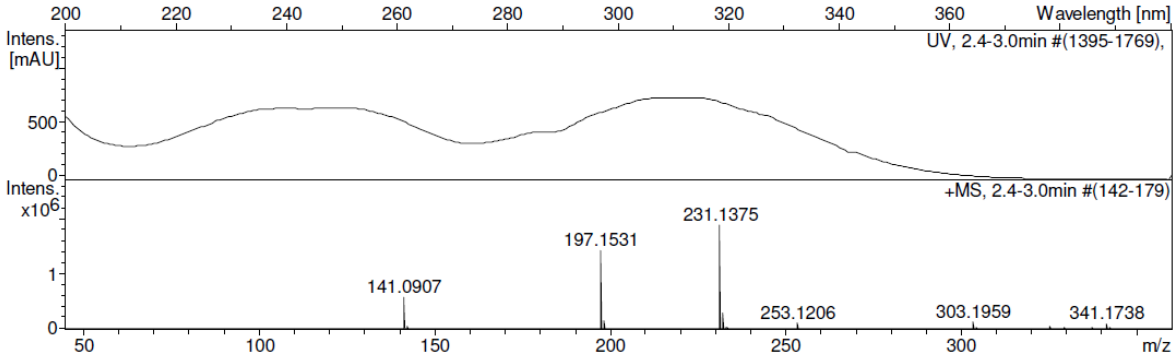
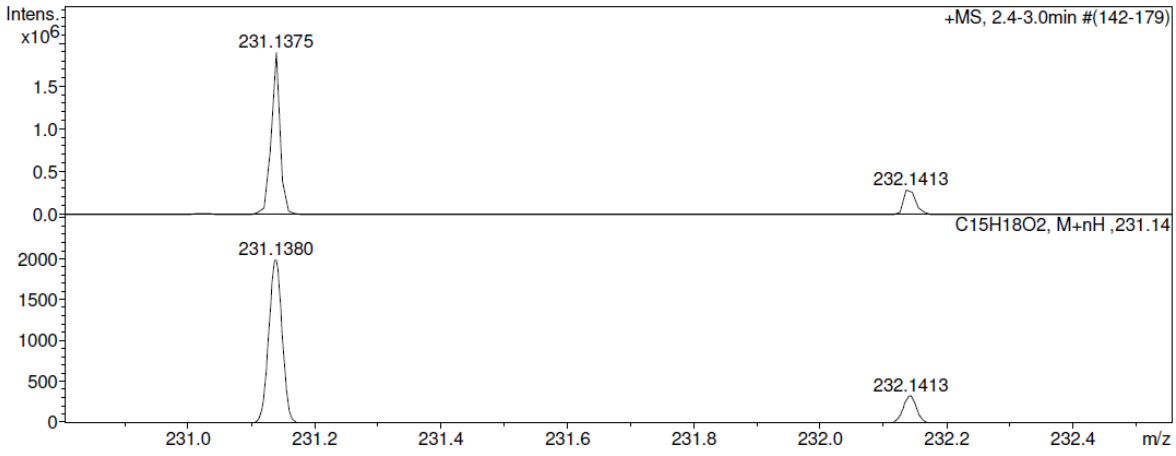
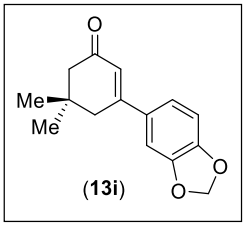
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



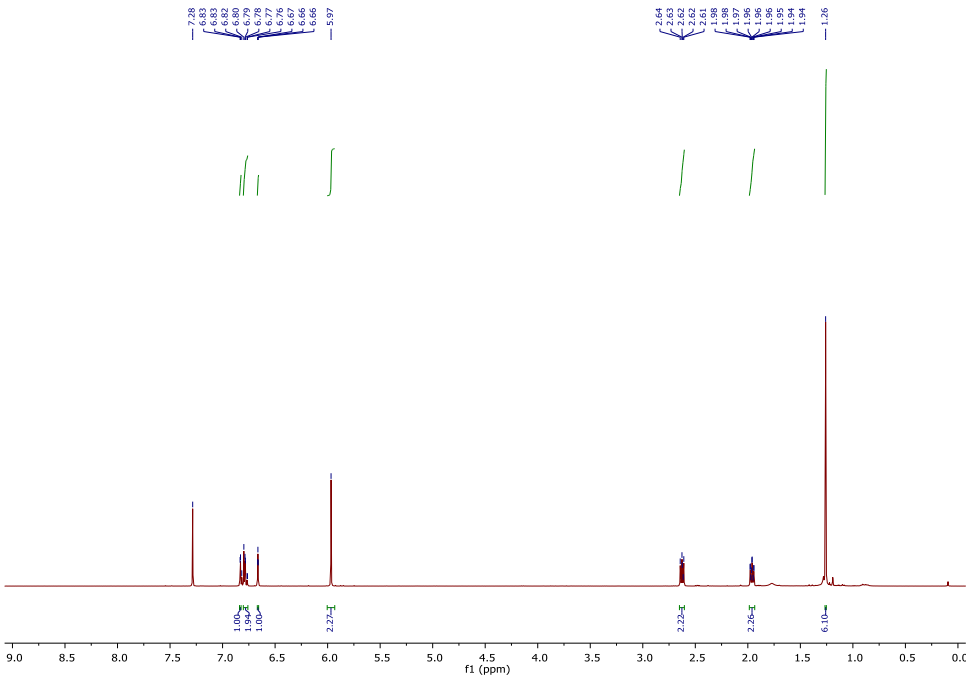




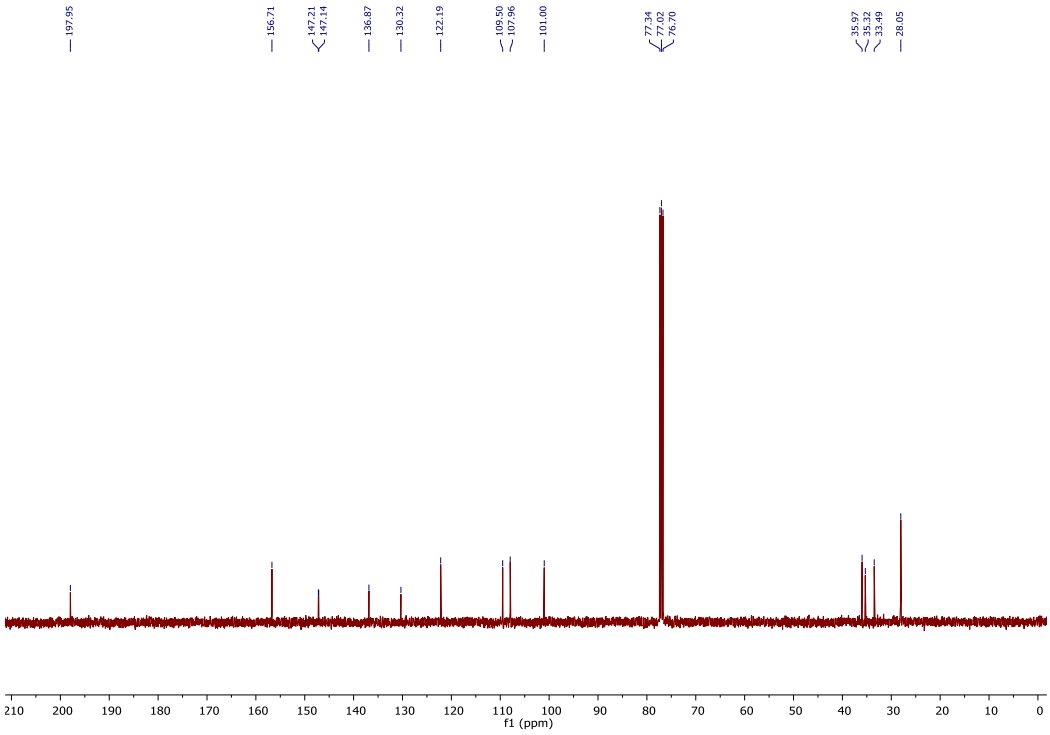
Scanned copy of mass spectrum of **13h**



(**13i**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound **13i**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **13i**

Display Report

Analysis Info

Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\26 APR\Dr.A.Bisai-AB-AR-01-586.d	Acquisition Date	4/26/2019 4:59:00 PM
Method	tune_low.m	Operator	RUCHI
Sample Name	-AB-AR-01-586	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
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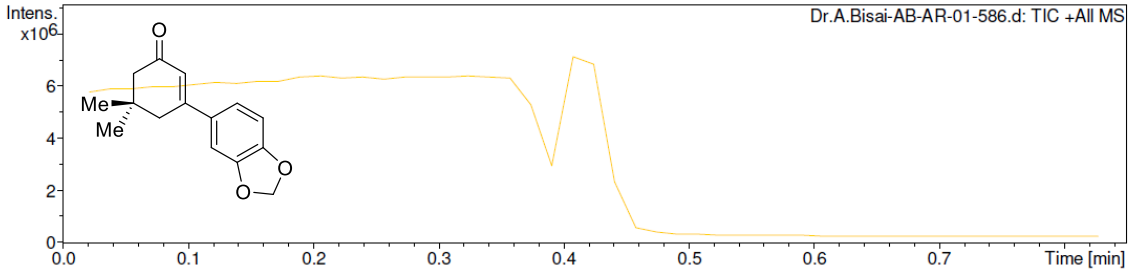
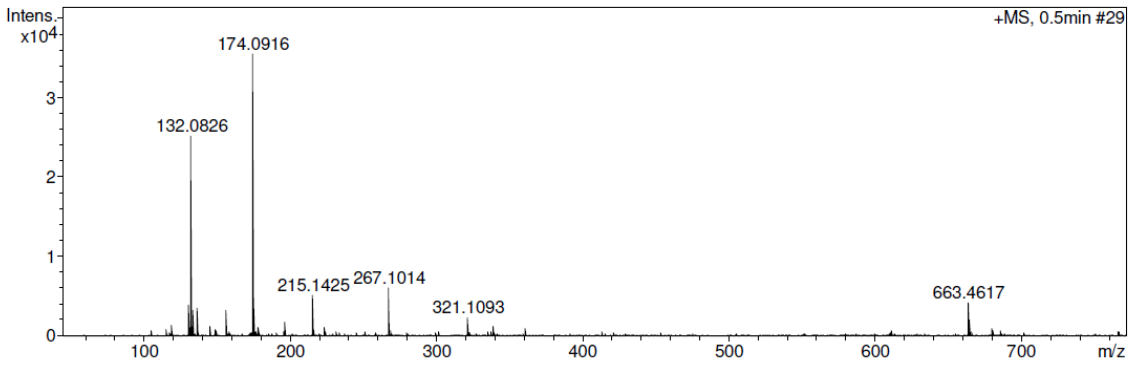
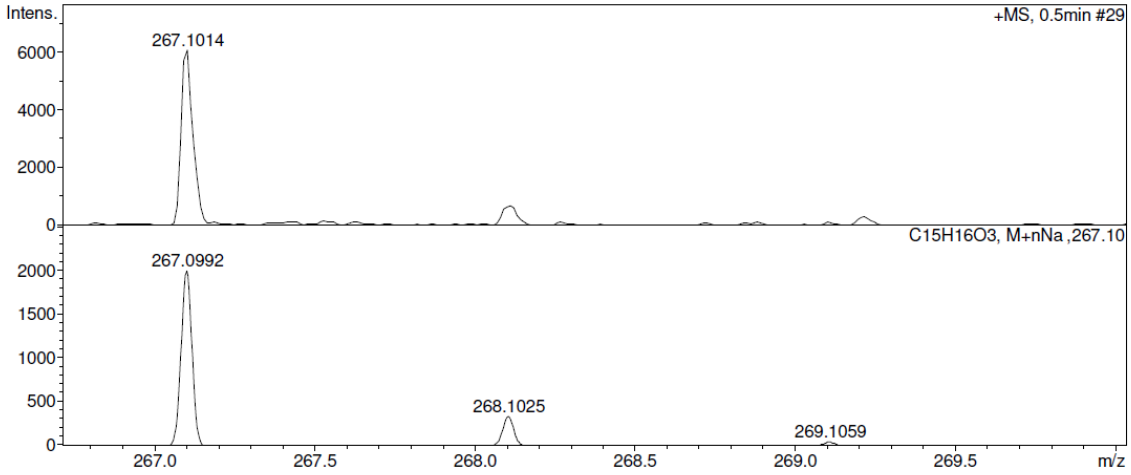
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste







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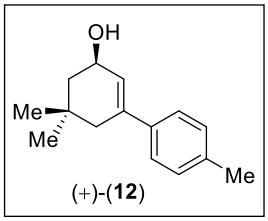
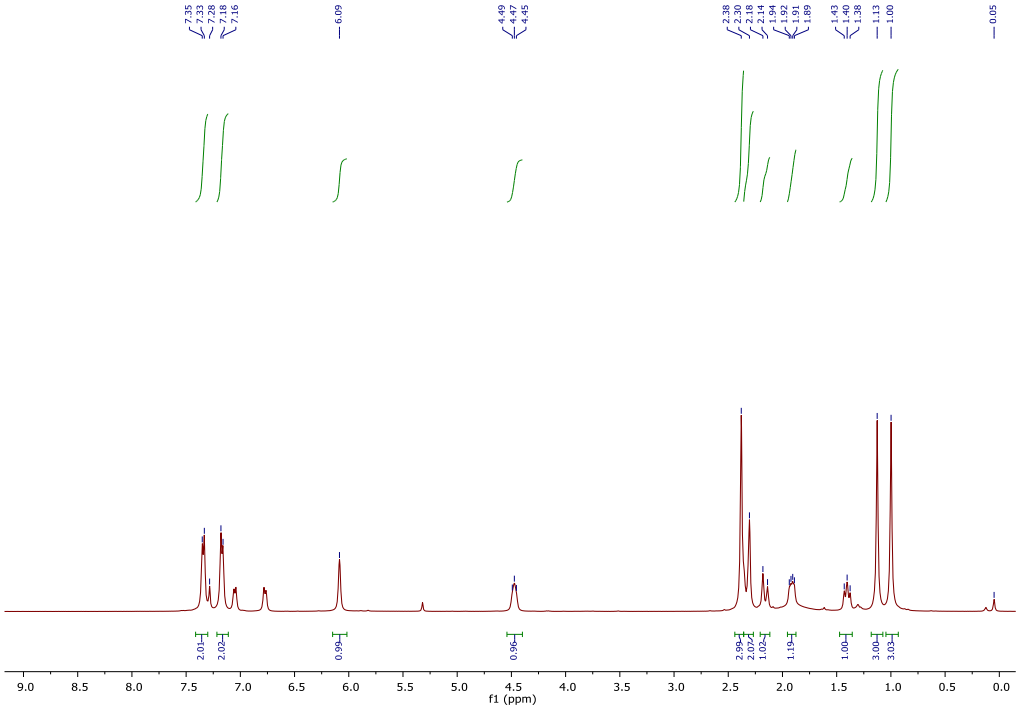
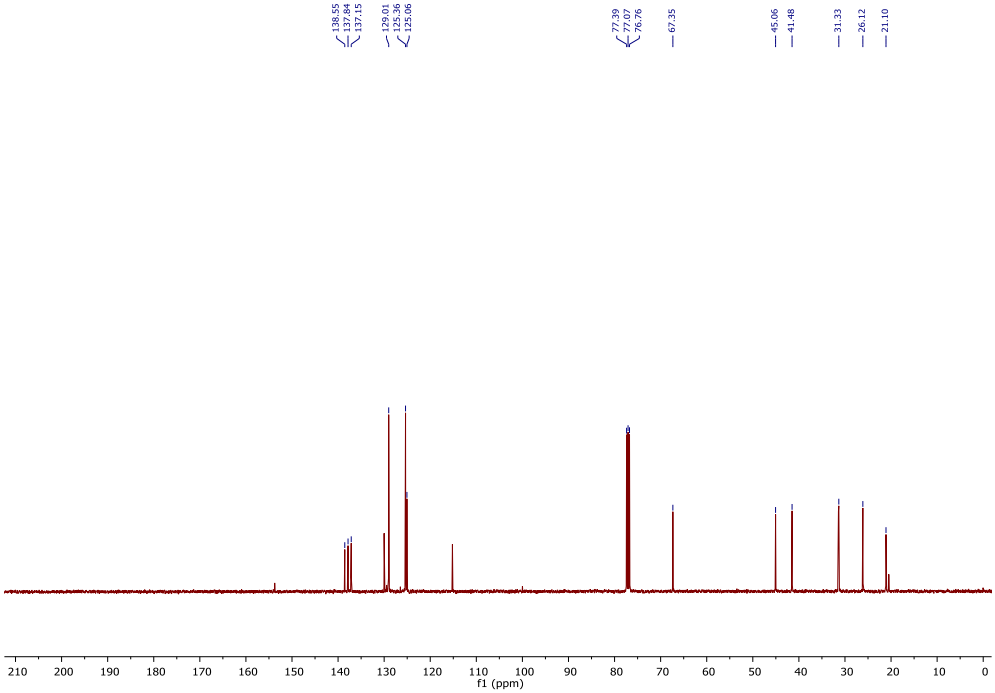
Scanned copy of mass spectrum of **13i**



(+)-(**12**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**12**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (+)-**12**

Display Report

Analysis Info

Analysis Name	D:\Data\NEW USER DATA 2017\2019\MAY\10 may\Dr A Bisai-AK-01-244_1-A,7_01_6230.d	Acquisition Date	5/10/2019 10:25:23 AM
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-244	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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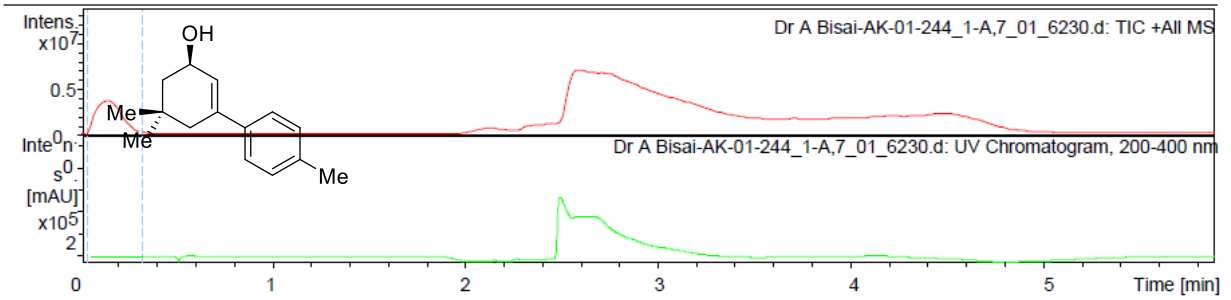
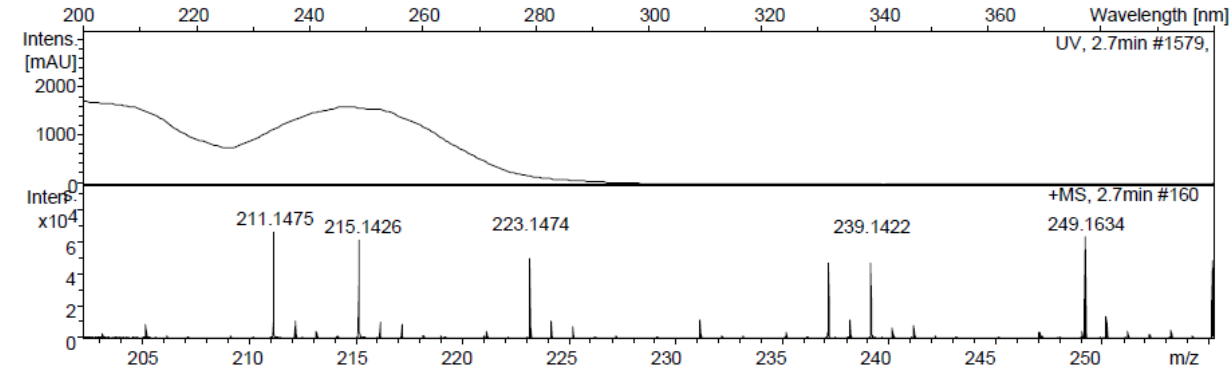
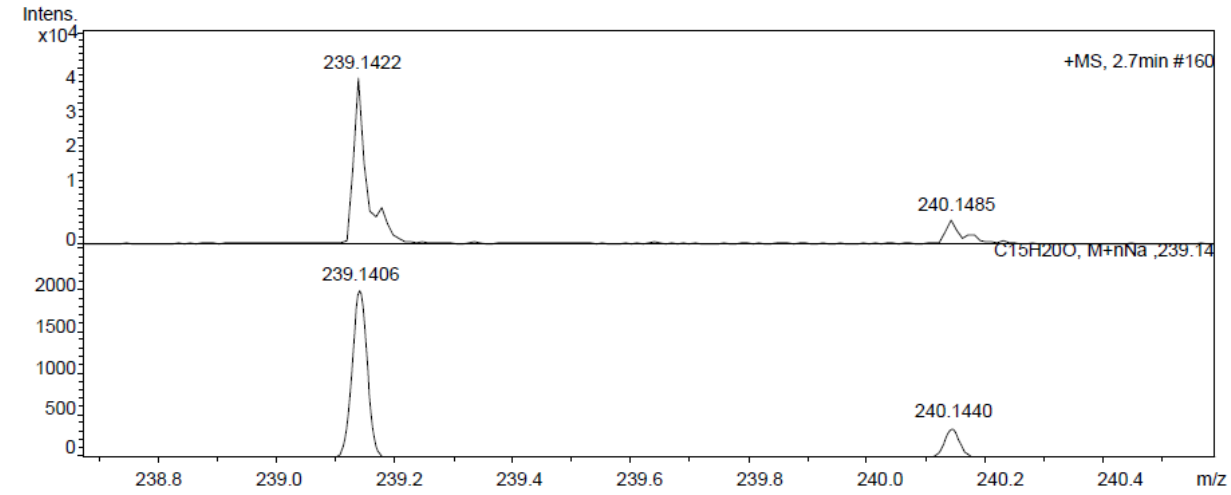
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

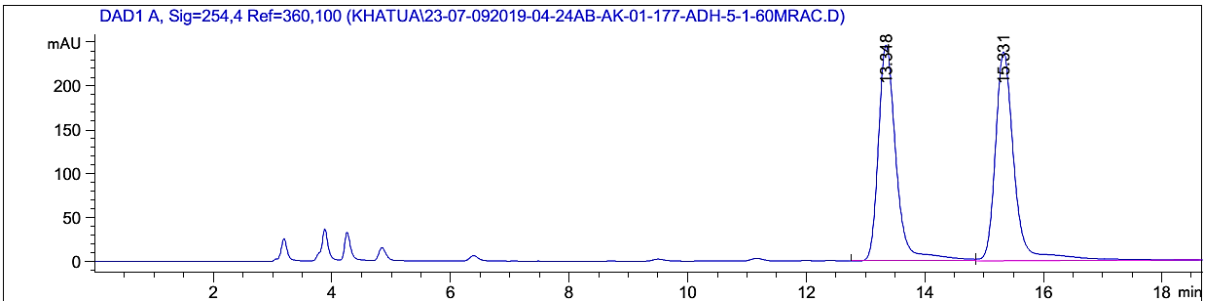






Scanned copy of mass spectrum of (+)-**12**

Data File C:\CHEM32\1\DATA\KHATUA\23-07-092019-04-24AB-AK-01-177-ADH-5-1-60MRAC.D
Sample Name: AB-AK-01-177-ADH-5-1-60MRAC



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.348	BV	0.3169	5126.65918	246.19289	49.1960
2	15.331	VBA	0.3355	5294.22656	238.05228	50.8040
Totals :				1.04209e4	484.24516	

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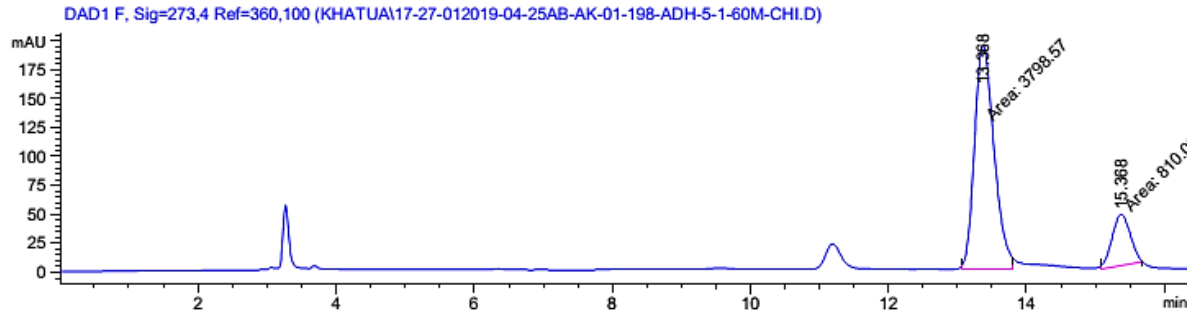
*** End of Report ***

HPLC Data for (±)-12

Data File C:\CHEM32\1\DATA\KHATUA\17-27-012019-04-25AB-AK-01-198-ADH-5-1-60M-CHI.D
Sample Name: AB-AK-01-198-ADH-5-1-60M-CHI



Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.368	MM	0.3269	3798.56763	193.66483	82.4235
2	15.368	MM	0.3047	810.03217	44.31486	17.5765
Totals :				4608.59979	237.97968	

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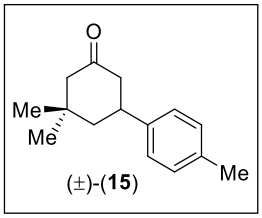
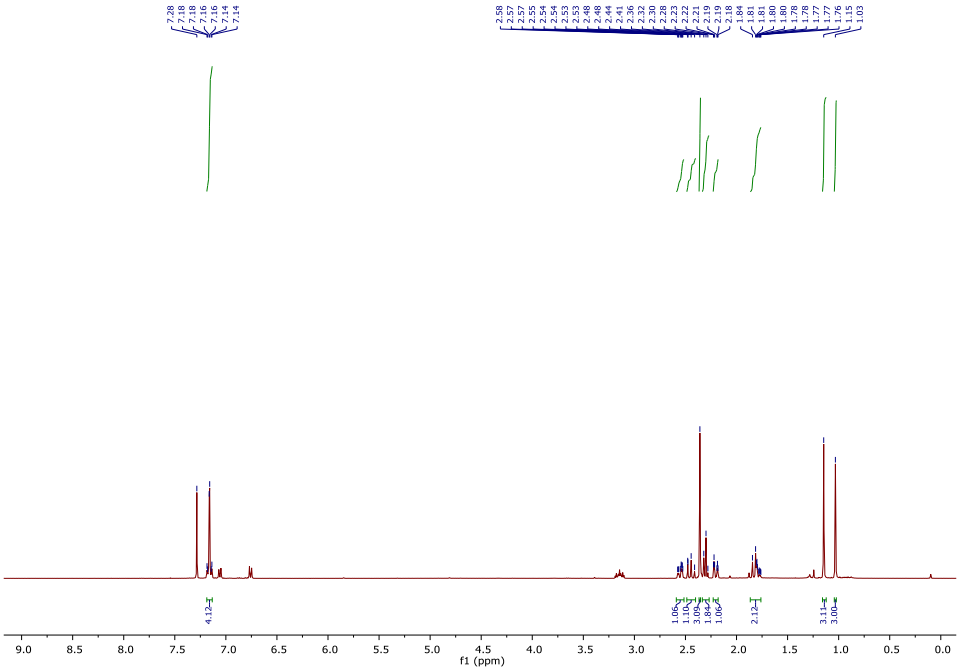
*** End of Report ***

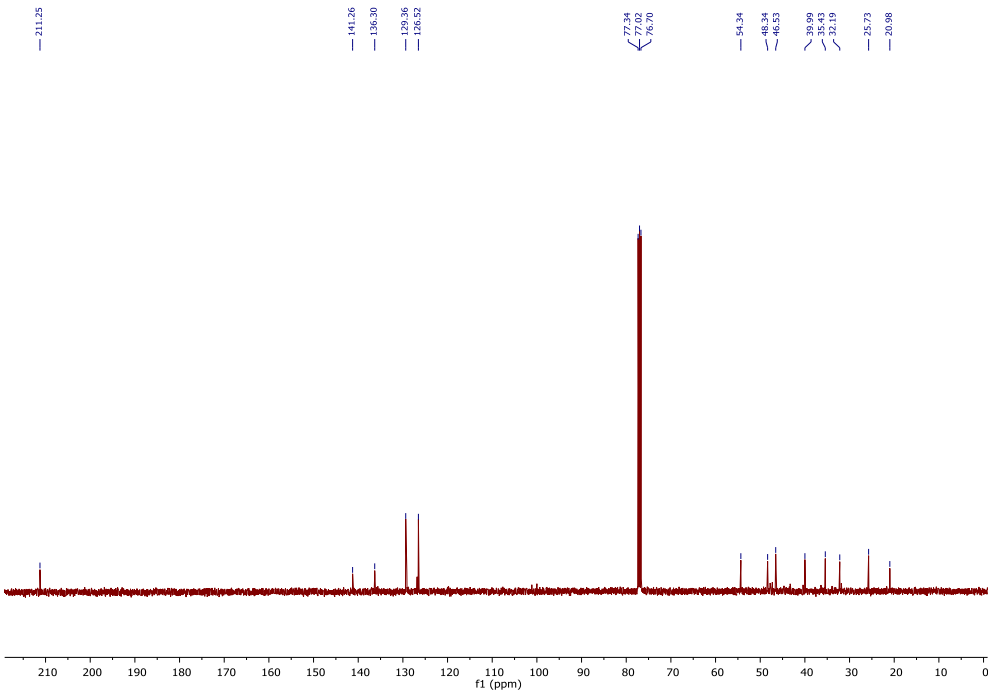
HPLC Data for (+)-12



(±)-(**15**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**15**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**15**

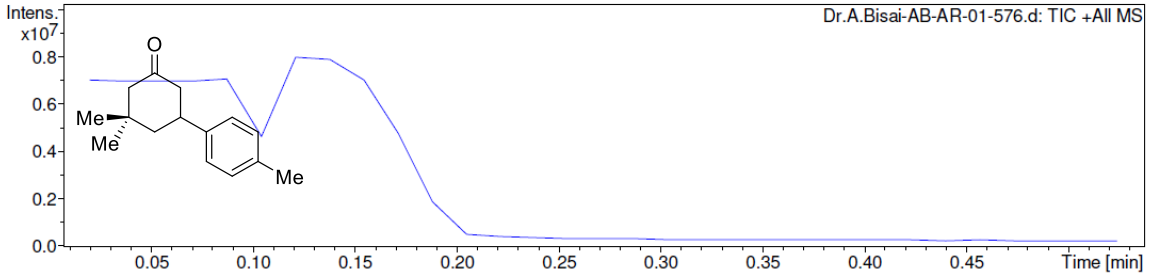
Display Report

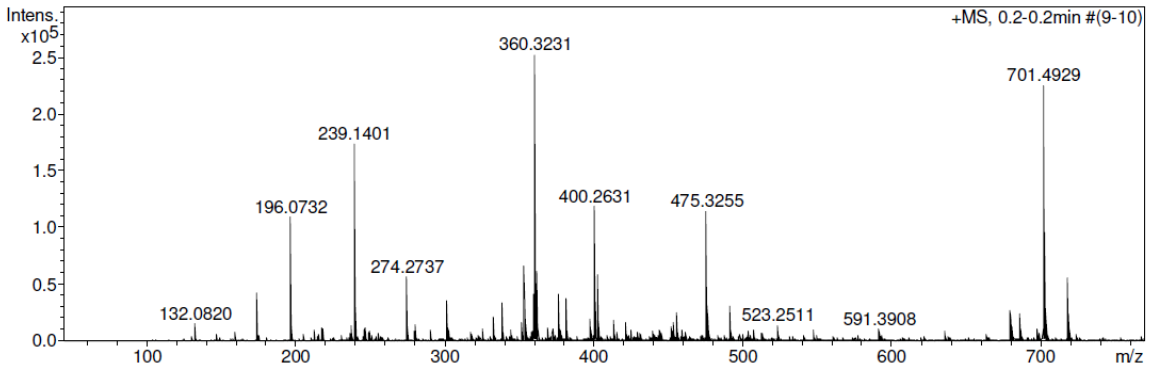
Analysis Info

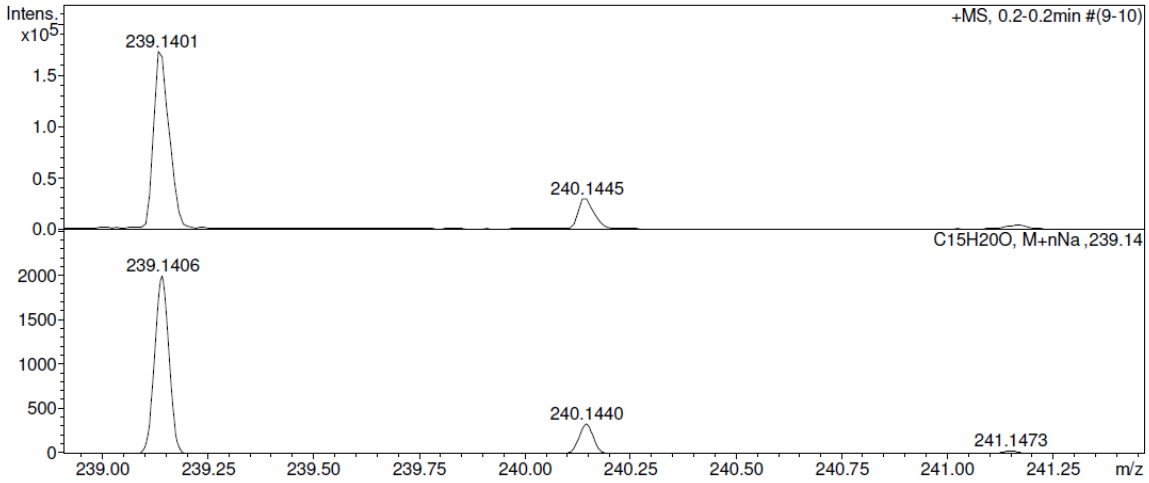
Acquisition Date	4/26/2019 4:57:26 PM		
Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\26 APR\Dr.A.Bisai-AB-AR-01-576.d		
Method	tune_low.m	Operator	RUCHI
Sample Name	-AB-AR-01-576	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

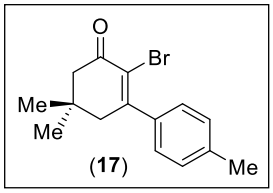
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

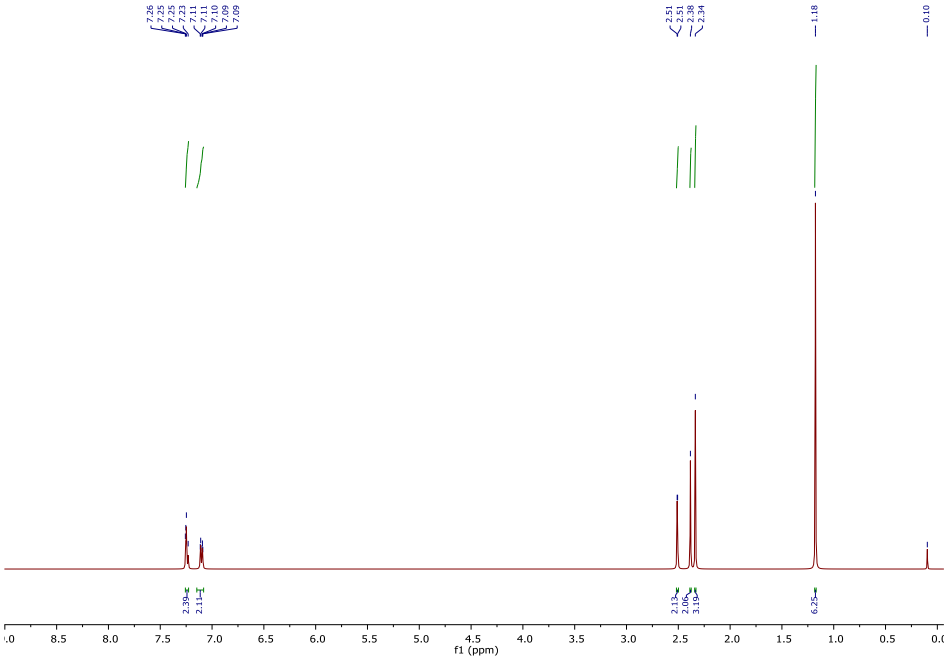




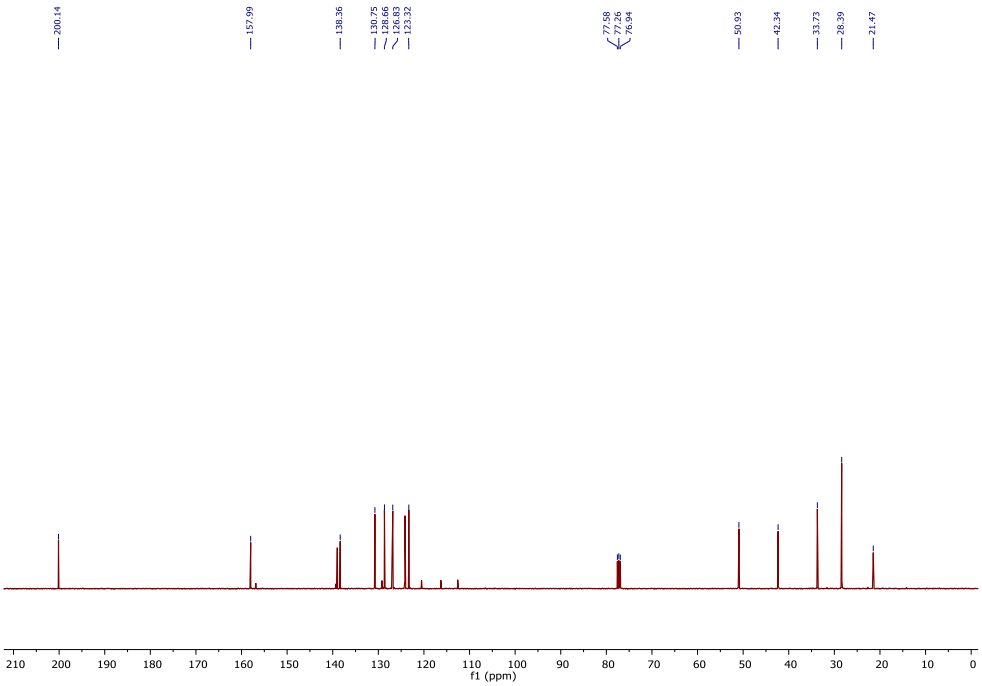


Scanned copy of mass spectrum of (±)-**15**





^{1}H NMR (400 MHz, $CDCl_3$) of compound **17**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **17**

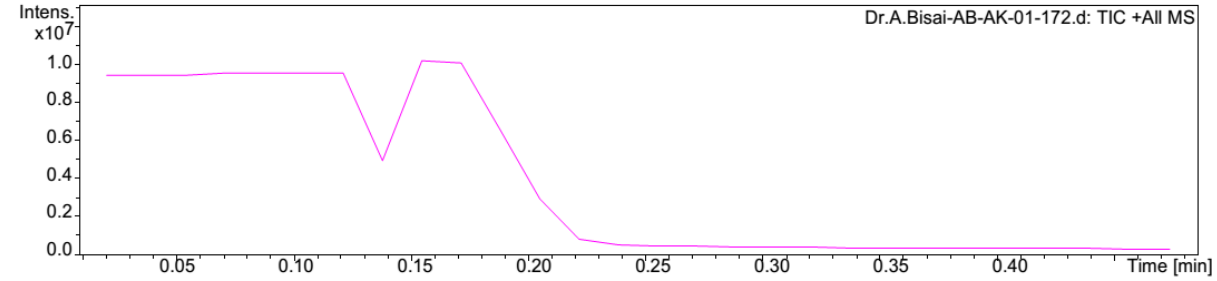
Display Report

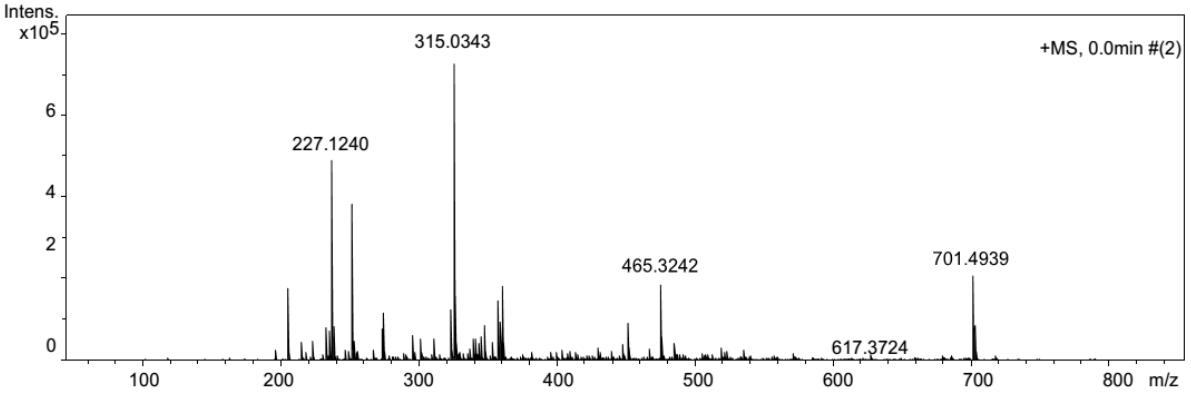
Analysis Info

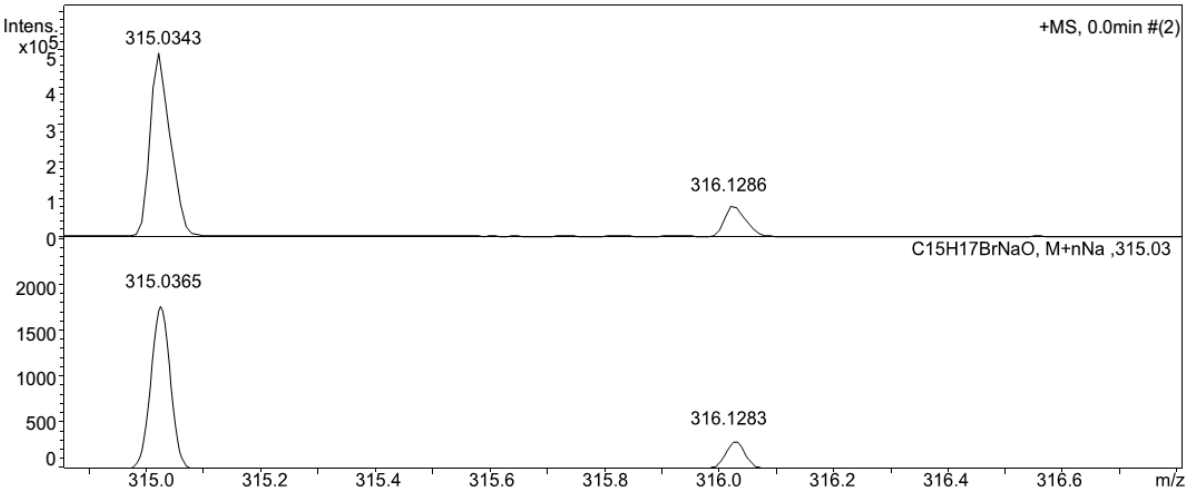
Acquisition Date	4/20/2019 3:15:28 PM		
Analysis Name	D:\Data\NEW USER DATA 2017\2019\APR\20 APR\Dr.A.Bisai-AB-AK-01-172.d		
Method	tune_low.m	Operator	RUCHI
Sample Name	-AB-AK-01-172	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

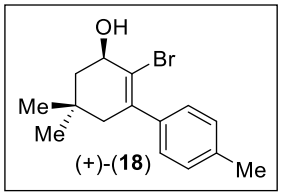
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

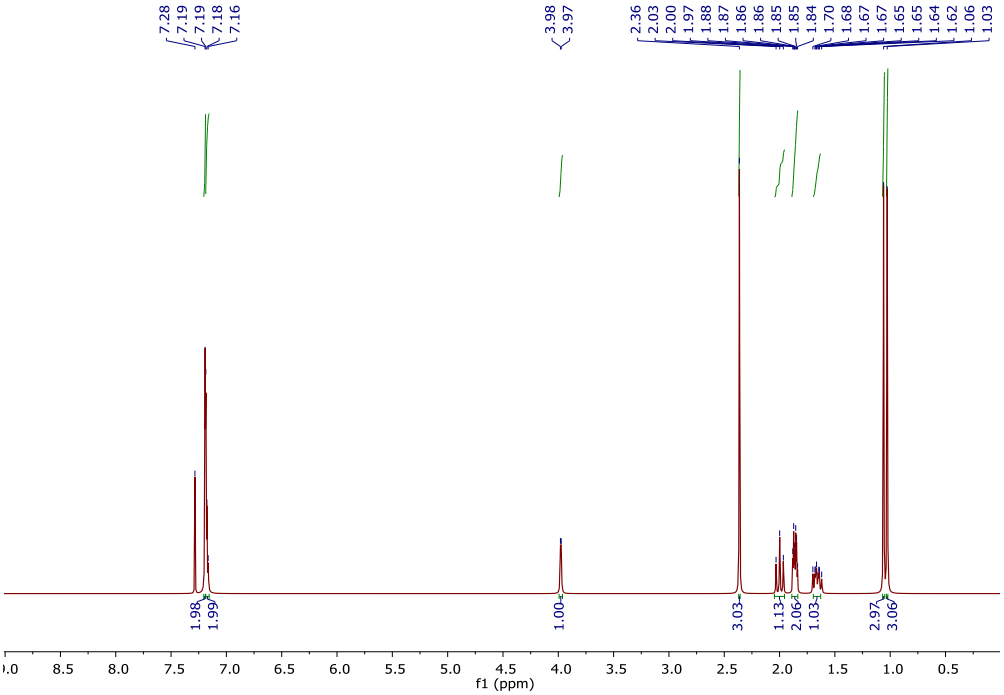




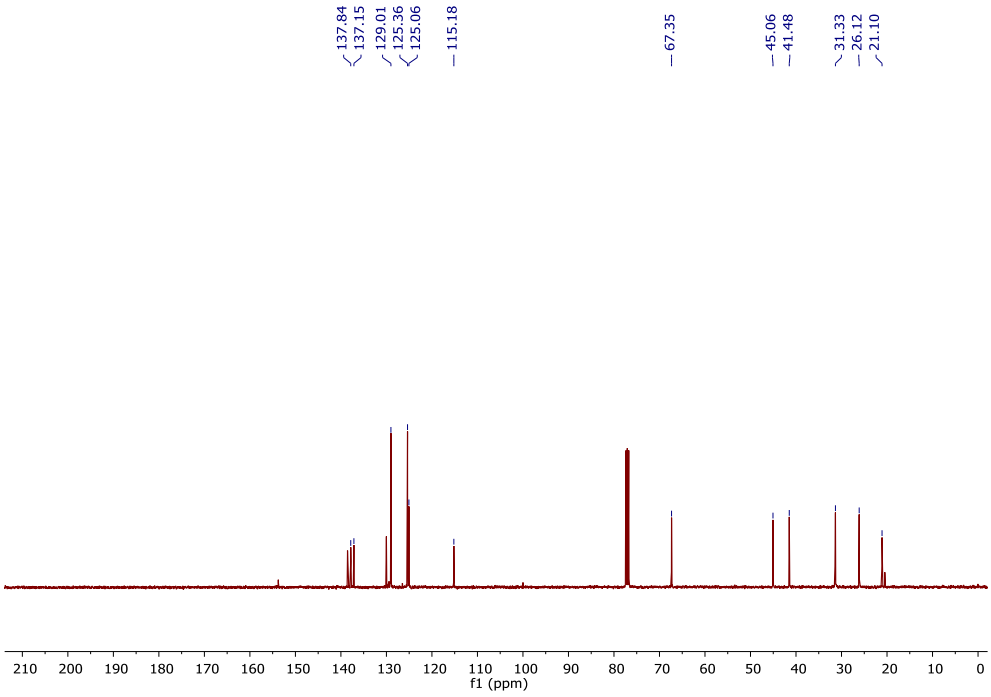


Scanned copy of mass spectrum of **17**



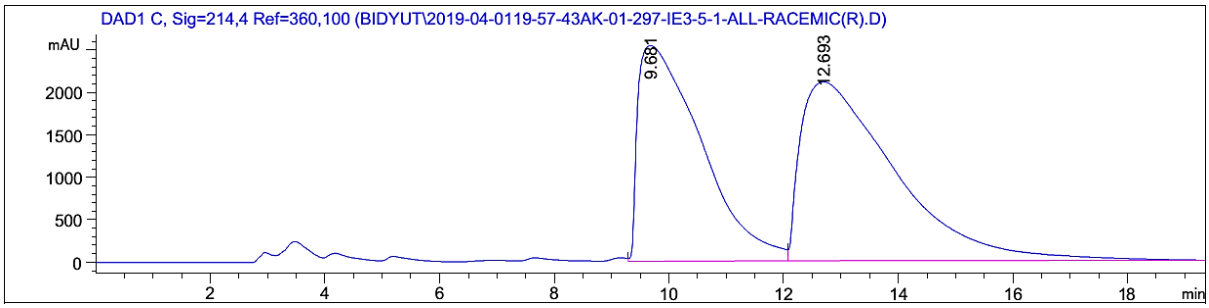


^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**18**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (+)-**18**

Data File C:\CHEM32\1\DATA\BIDYUT\2019-04-0119-57-43AK-01-297-IE3-5-1-ALL-RACEMIC(R).D
Sample Name: AK-01-297-IE3-5-1-all-racemic(R)

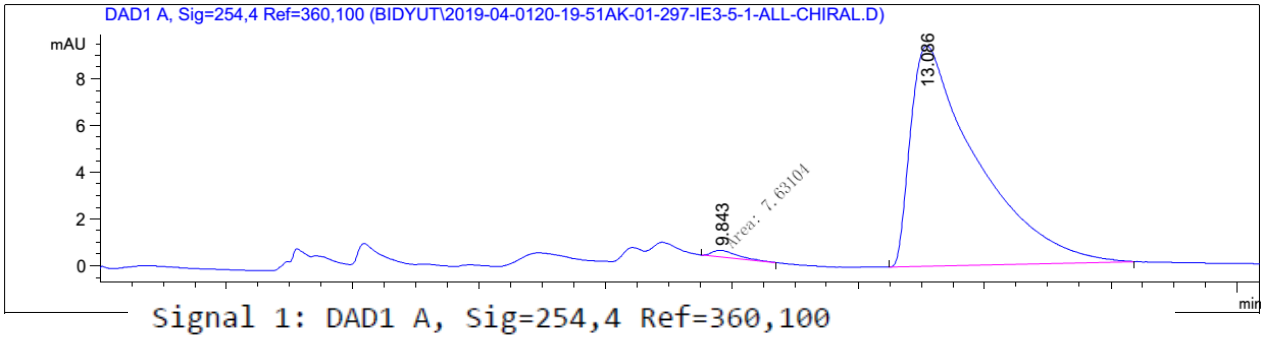


Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.681	VV	1.0718	1.94820e5	2537.29590	44.6674
2	12.693	VBA	1.6225	2.41337e5	2106.67236	55.3326
Totals :				4.36157e5	4643.96826	

HPLC Data for (±)-18

Data File C:\CHEM32\1\DATA\BIDYUT\AB-AK-01-297-20-1-ALL-IE3(C).D Sample Name: AB-AK-01-297-CHI-10-1-all-IE3(C)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.843	MM	0.2406	541.86804	37.54002	2.1152
2	13.086	BB	0.4617	2.50761e4	905.19739	97.8848
Totals :				2.56179e4	942.73740	

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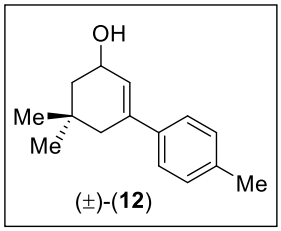
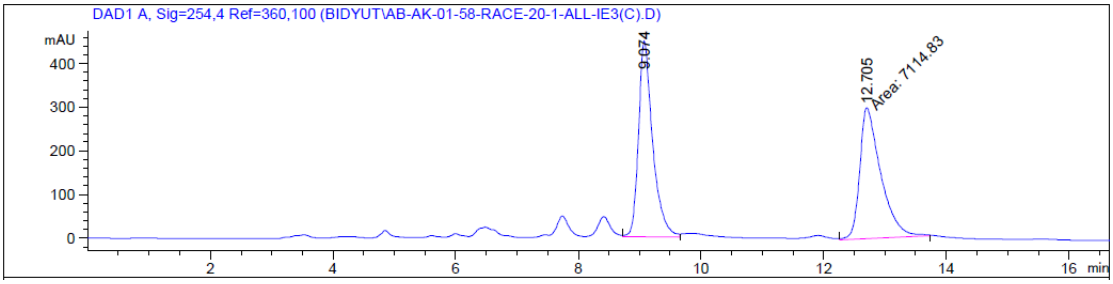
*** End of Report ***

HPLC Data for (+)-18



(±)-(**12**)

Data File C:\CHEM32\1\DATA\BIDYUT\AB-AK-01-58-RACE-20-1-ALL-IE3(C).D
Sample Name: AB-AK-01-58-race-10-1-all-IE3(C)

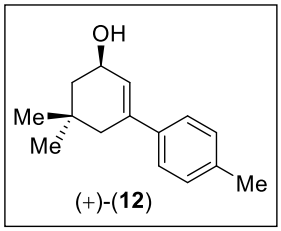


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.074	VV	0.2331	7197.45313	448.69098	50.2886
2	12.705	MM	0.3960	7114.82910	299.44119	49.7114
Totals :				1.43123e4	748.13217	

*** End of Report ***

HPLC Data for (±)-12



(+)-(**12**)

```
Data File C:\CHEM32\1\DATA\BIDYUT\AB-AK-01-59-CHIRAL-20-1-ALL-IE3(C).D
Sample Name: AB-AK-01-59-chiral-20-1-all-IE3(C)
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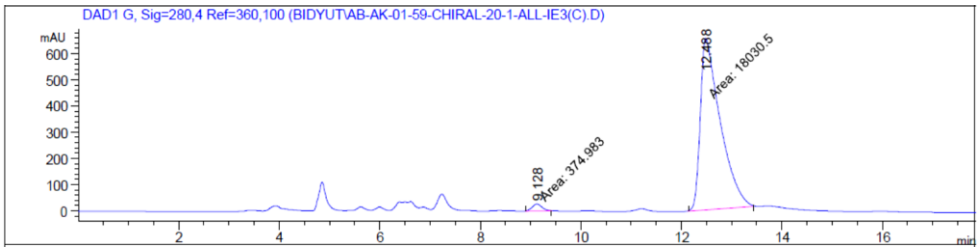


```
Signal 7: DAD1 G, Sig=280,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.128 MM    0.2322  374.98264   26.91870   3.0373
   2  12.488 MM    0.4582 1.80305e4   655.89880  96.9627

Totals :                  1.84055e4   682.81750

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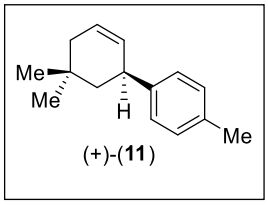
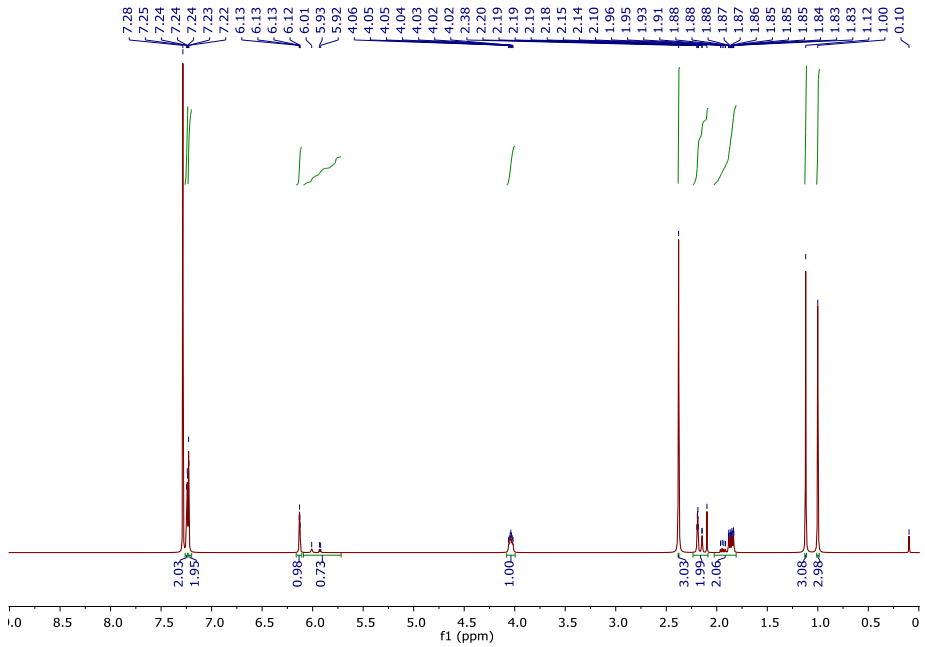
                      *** End of Report ***
```

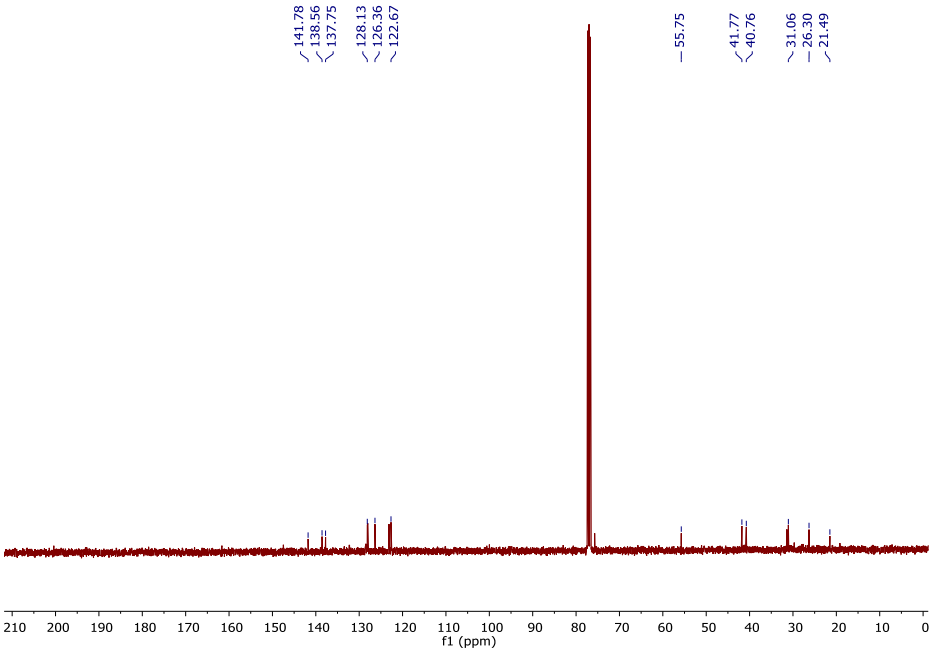
HPLC Data for (+)-12



(+)-(**11**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**11**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (+)-**11**

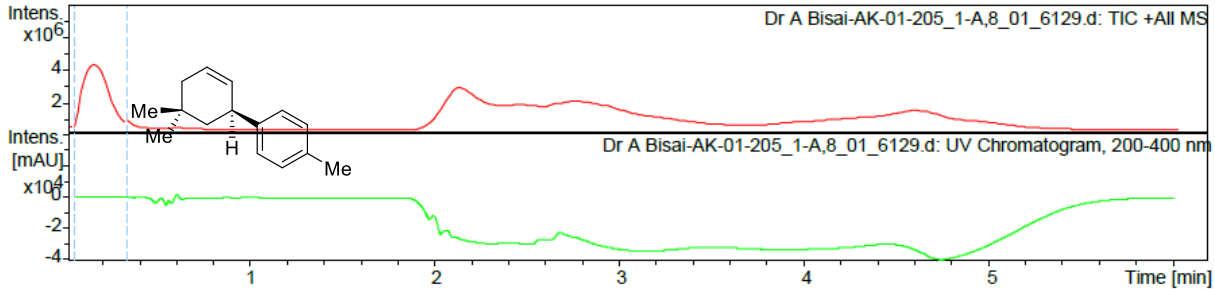
Display Report

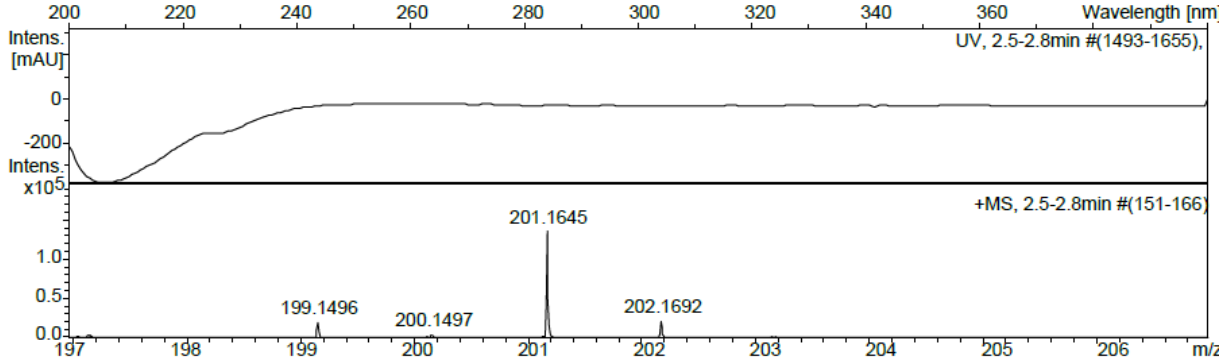
Analysis Info

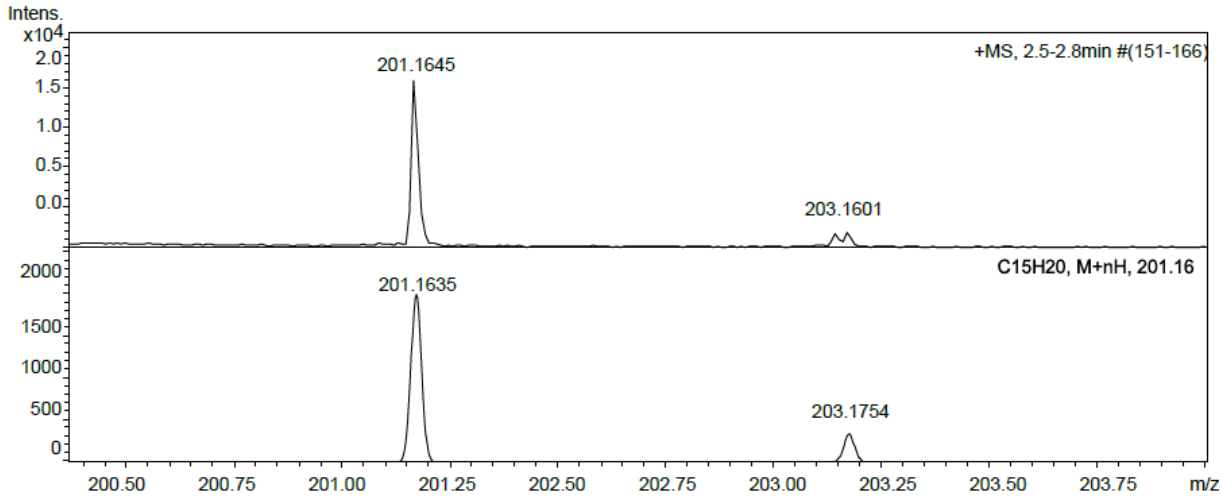
Analysis Name	D:\Data\NEW USER DATA 2017\2019\MAY\15 MAY\Dr A Bisai-AK-01-205_1-A,8_01_6129.d	Acquisition Date	5/15/2019 3:12:35 PM
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-205	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

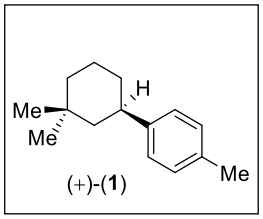
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

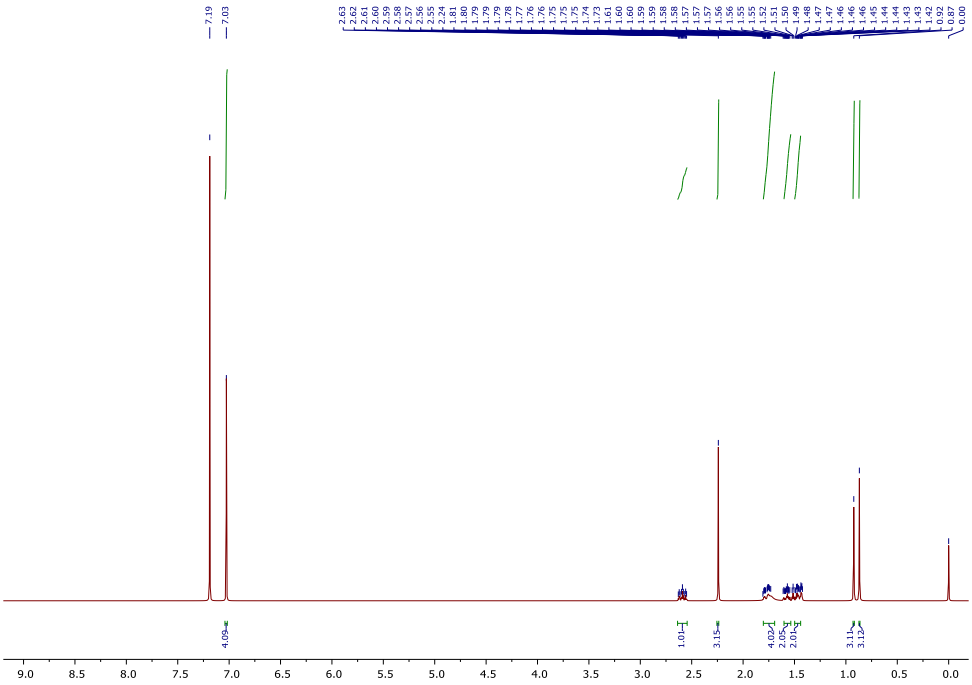




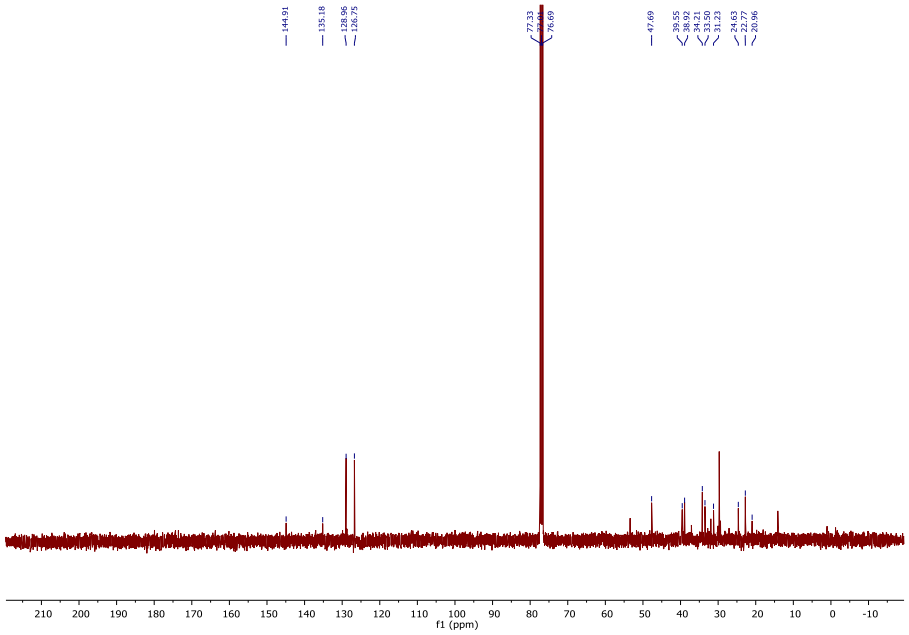


Scanned copy of mass spectrum of (+)-**11**





^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**1**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (+)-**1**

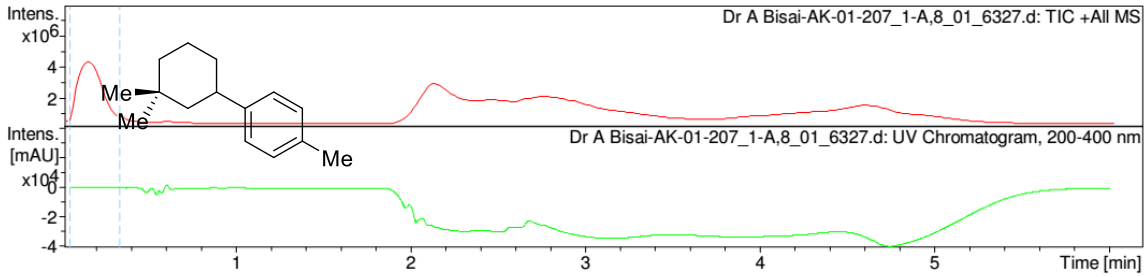
Display Report

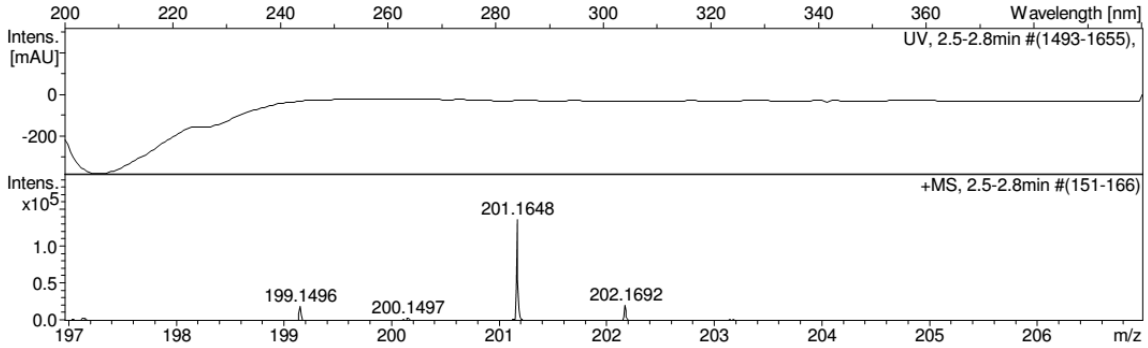
Analysis Info

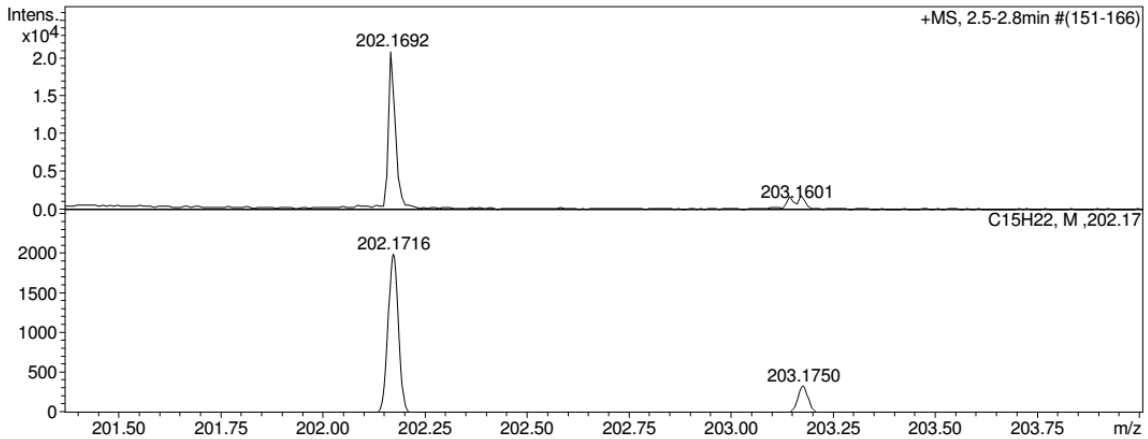
Acquisition Date	5/10/2019 11:16:18 AM		
Analysis Name	D:\Data\NEW USER DATA 2017\2019\MAY\10 MAY\Dr A Bisai-AK-01-207_1-A,8_01_6327.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr A Bisai-AK-01-207	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







Scanned copy of mass spectrum of (+)-**1**