Supplemental material for:

Highly Chemoselective Oxidative Dimerization of Indolosesquiterpene Alkaloids: Biomimetic Approach to Dixiamycin

Mintu Munda,[§a] Ayan Mondal,[§b] Nanda Kishore Roy,[a] Ranjit Murmu,[b] Sovan Niyogi,[b] and Alakesh Bisai*[a,b]

[a]Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhopal, MP - 462 066, India.

[b]Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, Nadia, WB - 741 246, India.

e-Mail: alakesh@iiserkol.ac.in, alakeshb@gmail.com
[§]both authors contributed equally to this work.

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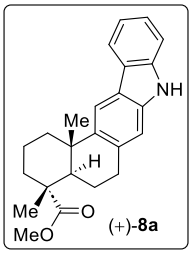
Materials and Methods

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. The Syringe was used to transfer the solvents and liquid reagents. 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 25 °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. Silicagel of particle size 230-400 and 100-200 mesh were used for flash chromatography. Melting points were recorded on a digital melting point apparatus. ^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), $(CD_3)_2SO$ signal (δ = 2.50 for ^1H NMR and δ = 39.5 for ^{13}C NMR) and CD_3OD signal (δ = 3.33 for ^1H NMR and δ = 49.0 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) data was recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. Optical rotations were measured on an automatic polarimeter.

Substrate (Deoxy-xiamycin derivatives) preparation for Oxidative Dimerization:

Compound **8a**[1] was synthesized by the following literature protocol.



(4*R*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8a**]: Following the general procedure (+)-**8a** was obtained as yellow foam (30 mmol scale of reaction; 10% yield over six steps from abietic acid). R_f = 0.35 (20% EtOAc in *n*-hexane).

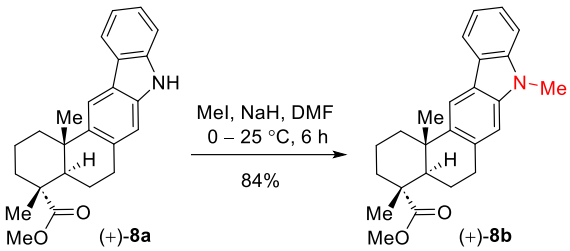
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.85 (s, 1H), 7.37 – 7.32 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.03 (s, 1H), 3.70 (d, *J* = 1.5 Hz, 3H), 3.13 – 3.05 (m, 2H), 2.56 (d, *J* = 12.4 Hz, 1H), 2.39 – 2.33 (m, 1H), 1.95 (ddd, *J* = 22.8, 12.8, 9.2 Hz, 1H), 1.83 (dd, *J* = 21.6, 11.5 Hz, 3H), 1.73 – 1.67 (m, 2H), 1.51 (dt, *J* = 10.6, 3.6 Hz, 1H), 1.35 (d, *J* = 1.5 Hz, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 142.0, 140.2, 138.2, 133.8, 125.4, 123.8, 122.0, 120.0, 119.2, 115.5, 110.6, 110.0, 52.1, 47.9, 45.3, 38.9, 37.6, 36.9, 30.8, 25.9, 22.0, 18.9, 16.7.

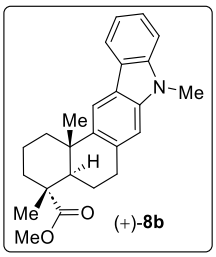
IR (neat) υ_{max} 3402, 2926, 1720, 1465, 1243, 1023, 823, 750, 582 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{24}H_{27}NO_2 + H]^+$ 362.2120, found 362.2113.

$[\alpha]_{589}^{20}$ = +61.3 (c = 0.3, $CHCl_3$).

Methylation of Carbazole derivative (+)**-8a:**



Carbazole (+)-**8a** (250 mg, 0.69 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 4 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (55.2 mg, 1.38 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then iodomethane (65.6 µL, 1.04 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to afford (+)-**8b** as yellow foam (217.6 mg, 84% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,8,13b-trimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8b**]: (+)-**8b** was obtained as yellow foam (0.69 mmol scale of reaction; 84% yield). R_f = 0.7 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.99 (s, 1H), 7.44 – 7.42 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.06 (s, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.19 – 3.15 (m, 2H), 2.60 – 2.56 (m, 1H), 2.37 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.00 – 1.94 (m, 1H), 1.87 – 1.83

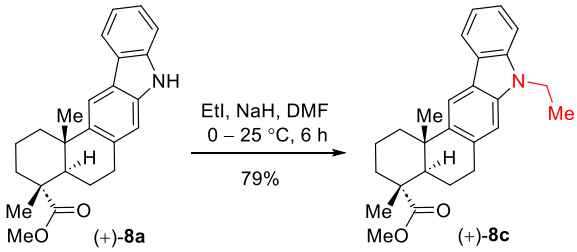
(m, 2H), 1.82 – 1.78 (m, 1H), 1.72 – 1.68 (m, 2H), 1.55 – 1.50 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 141.6, 141.5, 139.8, 133.7, 125.3, 123.2, 121.4, 120.0, 118.6, 115.6, 108.3, 107.9, 52.0, 47.9, 45.4, 39.0, 37.6, 36.9, 31.0, 29.1, 25.9, 22.1, 18.9, 16.8.

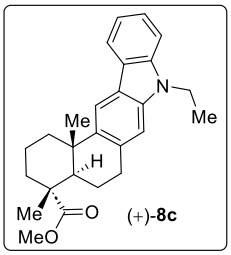
IR (neat) υ_{max} 3320, 2926, 1740, 1465, 1342, 1247, 1023, 853, 750, 682 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{25}H_{29}NO_2 + H]^+$ 376.2277, found 376.2276.

$[\alpha]_{589}^{25}$ = +75.6 (c = 0.6, $CHCl_3$).

Ethylation of Carbazole derivative (+)**-8a:**



Carbazole (+)**-8a** (275 mg, 0.76 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (60.8 mg, 1.52 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then ethyl iodide (92.6 µL, 1.14 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (7 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford (+)**-8c** as white solid (233.9 mg, 79% yield).



(4*R*,4a*R*,13b*S*)-**methyl 8-ethyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8c**]: (+)-**8c** was obtained as white solid (0.76 mmol scale of reaction; 79% yield). R_f = 0.6 (10% EtOAc in *n*-hexane).

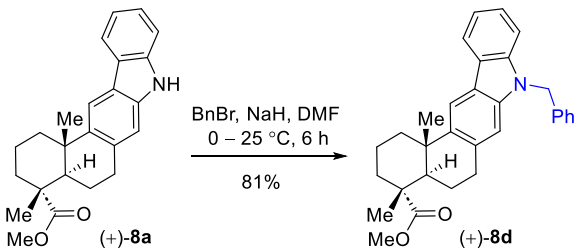
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 8.00 (s, 1H), 7.43 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.20 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.07 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.70 (s, 3H), 3.18 (ddd, *J* = 8.9, 5.4, 3.8 Hz, 2H), 2.61 – 2.56 (m, 1H), 2.37 (dd, *J* = 12.5, 2.4 Hz, 1H), 1.97 (ddd, *J* = 10.6, 8.6, 3.3 Hz, 1H), 1.87 – 1.84 (m, 2H), 1.83 – 1.79 (m, 1H), 1.73 – 1.69 (m, 2H), 1.53 (ddd, *J* = 9.8, 4.8, 2.2 Hz, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.35 (s, 3H), 1.34 – 1.34 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 141.4, 140.5, 138.7, 133.6, 125.2, 123.3, 121.5, 120.1, 118.5, 115.7, 108.3, 107.9, 52.1, 47.9, 45.4, 39.0, 37.6, 37.5, 36.9, 31.0, 25.9, 22.1, 18.9, 16.7, 13.9.

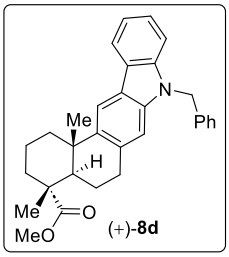
IR (neat) υ_{max} 3320, 2840, 1740, 1650, 1465, 1340, 1247, 1023, 867, 750, 646 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{31}NO_2 + H]^+$ 390.2433, found 390.2426.

$[\alpha]_{589}^{25}$ = +82.1 (c = 0.7, $CHCl_3$).

Benzylation of Carbazole derivative (+)**-8a:**



Carbazole (+)-**8a** (255 mg, 0.71 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (56.4 mg, 1.41 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then benzyl bromide (126.5 µL, 1.07 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford (+)-**8d** as yellow liquid (259.7 mg, 81% yield).



(4*R*,4a*R*,13b*S*)-**methyl 8-benzyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8d**]: (+)-**8d** was obtained as yellow liquid (0.71 mmol scale of reaction; 81% yield). R_f = 0.6 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 8.01 (s, 1H), 7.41 – 7.38 (m, 2H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.29 (s, 1H), 7.27 (d, *J* = 4.4 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.01 (s, 1H), 5.44 (s, 2H), 3.68 (s, 3H), 3.09 (dd, *J* = 10.3, 5.7 Hz, 2H), 2.57 (d, *J* = 12.5 Hz, 1H), 2.34 (dd, *J* = 12.5, 2.5 Hz, 1H), 1.86 – 1.83 (m, 2H), 1.82 – 1.79 (m, 2H), 1.70 (dd, J = 9.2, 3.2 Hz, 2H), 1.51 – 1.47 (m, 1H), 1.33 (s, 3H), 1.33 (s, 3H).

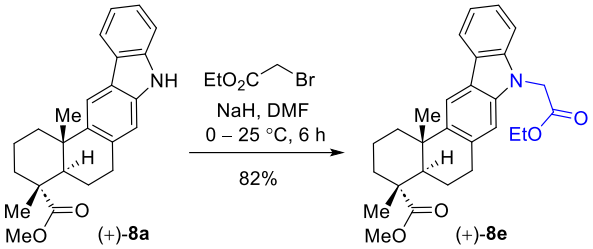
^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 141.8, 141.3, 139.5, 137.6, 133.9, 128.9, 127.5, 126.6, 125.5, 123.5, 121.6, 120.1, 119.0, 115.7, 108.8, 108.3, 52.0, 47.9, 46.7, 45.3, 39.0, 37.6, 36.9, 30.9, 25.8, 22.0, 18.9, 16.8.

IR (neat) υ_{max} 3310, 2840, 1740, 1632, 1465, 1365, 1247, 1015, 900, 867, 750, 610 cm^{-1}.

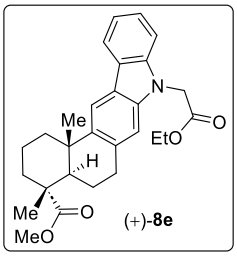
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{31}H_{33}NO_2 + H]^+$ 452.2589, found 452.2614.

$[\alpha]^{25}_{589}$ = +43.0 (c = 0.5, $CHCl_3$).

Synthesis of Carbazole derivative (+)-8e:



Carbazole (+)-**8a** (250 mg, 0.69 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (55.2 mg, 1.38 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then ethyl bromoacetate (119.2 µL, 1.04 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to afford (+)-**8e** as yellow oil (253.3 mg, 82% yield).



(4*R*,4a*R*,13b*S*)-**methyl 8-(2-ethoxy-2-oxoethyl)-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8e**]: (+)-**8e** was obtained as yellow oil (0.69 mmol scale of reaction; 82% yield). R_f = 0.3 (10% EtOAc in *n*-hexane).

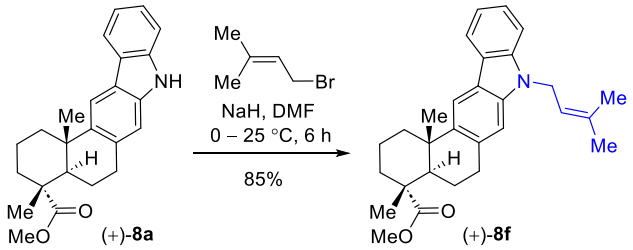
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.96 (s, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 4.90 (s, 2H), 4.20 (d, *J* = 7.0 Hz, 2H), 3.68 (s, 3H), 3.14 – 3.10 (m, 2H), 2.54 (d, *J* = 12.6 Hz, 1H), 2.33 (dd, *J* = 12.5, 2.5 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.83 (d, *J* = 11.8 Hz, 2H), 1.80 – 1.76 (m, 1H), 1.71 – 1.65 (m, 2H), 1.52 – 1.46 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 168.8, 142.2, 141.2, 139.3, 134.0, 125.5, 123.7, 121.8, 120.1, 119.4, 115.8, 108.3, 107.9, 61.7, 61.2, 52.0, 47.9, 45.3, 39.0, 37.6, 36.9, 30.9, 25.8, 22.0, 18.9, 16.7, 14.3.

IR (neat) υ_{max} 3346, 2946, 1735, 1632, 1465, 1163, 1020, 943, 867, 790, 685 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{28}H_{33}NO_4 + H]^+$ 448.2488, found 448.2482.

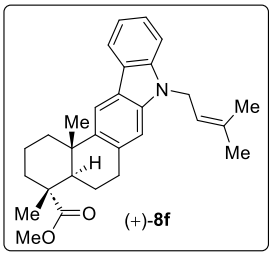
$[\alpha]_{589}^{25}$ = +45.1 (c = 0.4, $CHCl_3$).

Prenylation of Carbazole derivative (+)**-8a:**



Carbazole (+)**-8a** (245 mg, 0.68 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (54.2 mg, 1.36 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then prenyl bromide (152 µL, 1.02 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under

vacuum. The crude product was purified by flash chromatography with 8% EtOAc in *n*-hexane to afford (+)-**8f** as yellow gel (248.3 mg, 85% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-8-(3-methylbut-2-en-1-yl)-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8f**]: (+)-**8f** was obtained as yellow gel (0.68 mmol scale of reaction; 85% yield). R_f = 0.7 (10% EtOAc in *n*-hexane).

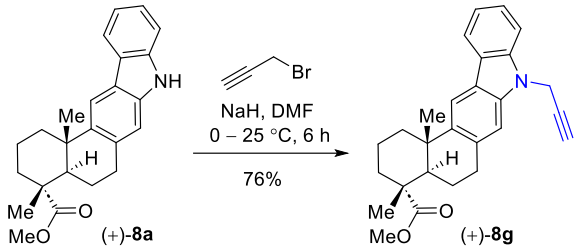
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.98 (s, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.03 (s, 1H), 5.27 (d, *J* = 6.6 Hz, 1H), 4.82 (d, *J* = 6.4 Hz, 2H), 3.69 (s, 3H), 3.18 – 3.14 (m, 2H), 2.57 (d, *J* = 12.6 Hz, 1H), 2.36 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.00 – 1.95 (m, 1H), 1.93 (s, 3H), 1.85 (d, *J* = 11.2 Hz, 2H), 1.80 (d, *J* = 15.7 Hz, 1H), 1.71 (s, 3H), 1.67 (d, *J* = 11.1 Hz, 2H), 1.51 (dd, *J* = 9.0, 4.9 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 141.4, 140.9, 139.1, 135.0, 133.6, 125.2, 123.4, 121.6, 120.4, 120.0, 118.5, 115.6, 108.7, 108.2, 52.0, 47.9, 45.4, 41.1, 39.0, 37.6, 36.9, 31.0, 25.8, 25.7, 22.1, 18.9, 18.3, 16.8.

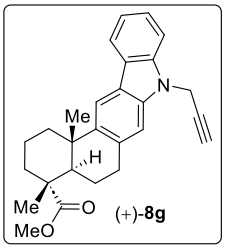
IR (neat) υ_{max} 3310, 2946, 1740, 1632, 1465, 1247, 1064, 900, 867, 790, 665 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{29}H_{35}NO_2 + H]^+$ 430.2746, found 430.2759.

$[\alpha]_{589}^{25}$ = +54.2 (c = 0.5, $CHCl_3$).

Propargylation of Carbazole derivative (+)**-8a:**



Carbazole (+)-**8a** (260 mg, 0.72 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (57.5 mg, 1.44 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then propargyl bromide (81.8 µL, 1.08 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford (+)-**8g** as yellow foam (218.6 g, 76% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-8-(prop-2-yn-1-yl)-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8g**]: (+)-**8g** was obtained as yellow foam (0.72 mmol scale of reaction; 76% yield). R_f = 0.5 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 1H), 7.98 (s, 1H), 7.45 – 7.41 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 4.96 (s, 2H), 3.69 (s, 3H), 3.17 (dd, *J* = 8.3, 3.7 Hz, 2H), 2.56 (d, *J* = 12.7 Hz, 1H), 2.35 (d, *J* = 12.5 Hz, 1H), 2.24 (s, 1H), 1.96 (t, *J* = 11.0 Hz, 1H), 1.84 (d,

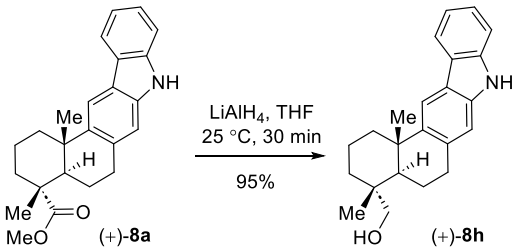
J = 11.4 Hz, 2H), 1.80 (d, *J* = 11.0 Hz, 1H), 1.72 – 1.66 (m, 2H), 1.54 – 1.49 (m, 1H), 1.34 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 142.1, 140.4, 138.6, 134.0, 125.5, 123.7, 121.8, 120.1, 119.4, 115.8, 108.7, 108.2, 78.2, 72.2, 52.1, 47.8, 45.3, 38.9, 37.6, 36.9, 32.4, 31.0, 25.8, 22.0, 18.9, 16.7.

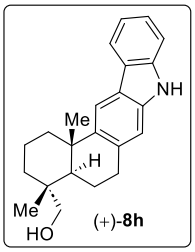
IR (neat) υ_{max} 3466, 2946, 1865, 1632, 1465, 1247, 1064, 943, 867, 790, 643 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{29}NO_2 + H]^+$ 400.2277, found 400.2281.

$[\alpha]_{589}^{25}$ = +25.0 (c = 0.1, $CHCl_3$).

Procedure for the Synthesis of Alcohol (+)**-8h:**



To a stirred solution (+)-**8a** (250 mg, 0.69 mmol, 1 equiv.) in tetrahydrofuran (4 mL), lithium aluminum hydride (26.6 mg, 0.7 mmol, 1.01 equiv.) was added at 0 °C, and the reaction mixture was stirred for 30 min at 25 °C. Distilled water (0.5 ml), 1M aq. NaOH (1 M, 0.5 ml), and distilled water (0.15 ml) was sequentially added at 0 °C and the resulting mixture was warmed to 25 °C. Dried over sodium sulfate and filtered over a pad of celite and washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel with ~40-50% EtOAc in *n*-hexane to provide compound (+)-**8h** as colourless liquid (218.6 mg, 95%).



((4*R*,4a*R*,13b*S*)-**4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazol-4-yl)methanol** [(+)-**8h**]: (+)-**8h** was obtained as colourless liquid (0.69 mmol scale of reaction; 95% yield). R_f = 0.4 (30% EtOAc in *n*-hexane).

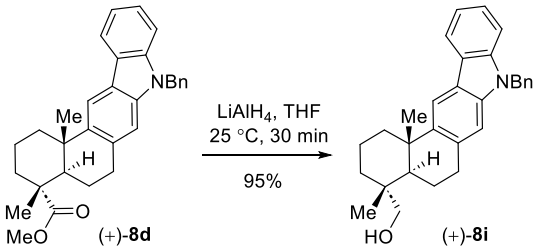
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.97 (s, 1H), 7.79 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.03 (s, 1H), 3.51 (d, *J* = 10.8 Hz, 1H), 3.26 (d, *J* = 10.8 Hz, 1H), 3.14 – 3.04 (m, 2H), 2.54 (d, *J* = 12.6 Hz, 1H), 1.85 (dt, *J* = 11.1, 5.2 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.62 (d, *J* = 13.3 Hz, 1H), 1.56 (dd, *J* = 13.0, 3.9 Hz, 1H), 1.48 (dd, *J* = 12.9, 4.1 Hz, 1H), 1.42 (d, *J* = 4.6 Hz, 1H), 1.32 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 140.1, 138.1, 134.0, 125.4, 123.9, 121.9, 120.0, 119.2, 115.6, 110.5, 109.9, 72.4, 44.3, 39.4, 38.1, 38.0, 35.4, 30.8, 26.0, 19.2, 18.9, 17.6.

IR (neat) υ_{max} 3584, 3300, 1720, 1465, 1243, 1085, 823, 720, 582 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{23}H_{27}NO + H]^+$ 334.2171, found 334.2172.

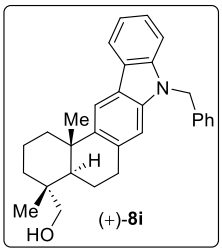
$[\alpha]_{589}^{25}$ = +46.6 (c = 0.5, $CHCl_3$).

Reduction of *N*-Benzyl Carbazole derivative (+)**-8d:**



To a stirred solution (+)**-8d** (265 mg, 0.59 mmol, 1 equiv.) in tetrahydrofuran (6 mL), lithium aluminum hydride (22.5 mg, 0.59 mmol, 1.01 equiv.) was added at 0 °C, and the reaction mixture was stirred for 30 min at 25 °C. Distilled water (0.5 ml), 1M aq. NaOH (1 M, 1.0 ml), and distilled water (0.5 ml) was sequentially added at 0 °C and the resulting mixture was warmed to 25 °C. Dried over sodium sulfate and filtered over a pad of celite and washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure, and the

resulting crude residue was purified by flash column chromatography on silica gel with 20% EtOAc in *n*-Hexane to provide compound (+)-**8i** as white foam (237.4 mg, 95%).



((4*R*,4a*R*,13b*S*)-**8-benzyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazol-4-yl)methanol** [(+)-**8i**]: (+)-**8i** was obtained as white foam (0.59 mmol scale of reaction; 95% yield). R_f = 0.3 (10% EtOAc in *n*-hexane).

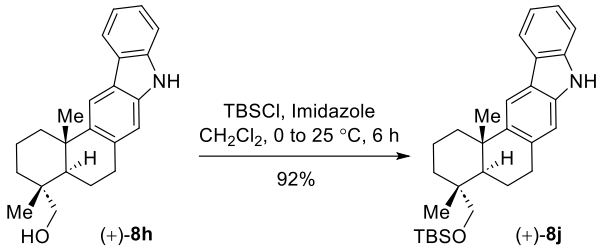
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dt, *J* = 7.8, 0.9 Hz, 1H), 8.06 (s, 1H), 7.40 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.28 – 7.27 (m, 1H), 7.27 – 7.21 (m, 2H), 7.21 – 7.18 (m, 2H), 7.04 (s, 1H), 5.46 (s, 2H), 3.53 (d, *J* = 10.9 Hz, 1H), 3.29 (d, *J* = 11.0 Hz, 1H), 3.16 – 3.07 (m, 2H), 2.59 (dq, *J* = 12.9, 2.8 Hz, 1H), 1.90 – 1.85 (m, 2H), 1.84 – 1.80 (m, 1H), 1.77 (dd, *J* = 10.8, 4.0 Hz, 1H), 1.62 (td, *J* = 13.1, 3.9 Hz, 2H), 1.51 (dd, *J* = 12.9, 4.0 Hz, 1H), 1.49 – 1.44 (m, 1H), 1.37 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 141.2, 139.4, 137.6, 134.1, 128.8, 127.4, 126.6, 125.4, 123.5, 121.5, 120.0, 118.9, 115.8, 108.8, 108.2, 72.4, 46.6, 44.3, 39.4, 38.1, 38.0, 35.3, 31.0, 26.0, 19.2, 18.9, 17.6.

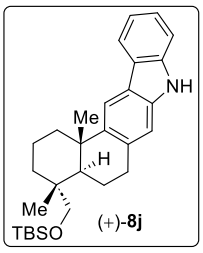
IR (neat) υ_{max} 3630, 3355, 1765, 1420, 1278, 1085, 953, 720, 682 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{30}H_{33}NO + H]^+$ 424.2640, found 424.2643.

$[\alpha]^{25}_{589}$ = +54.9 (c = 0.7, $CHCl_3$).

Procedure for the Synthesis of Silyl ether (+)**-8j:**



To a stirred solution of (+)**-8h** (260 mg, 0.78 mmol, 1 equiv.) in dichloromethane (8 mL), imidazole (79.7 mg, 1.17 mmol, 1.5 eq.), and chlorotrimethylsilane (141.7 mg, 0.94 mmol, 1.2 eq.) was added at 0 °C. The resulting mixture was stirred for 6 h at 25 °C, and then quenched with sat. aq. $NaHCO_3$ at 0 °C. The aqueous layer was extracted twice with dichloromethane. The combined organic layer was dried over Na_2SO_4. After filtration and concentration under reduced pressure, the resulting crude residue was purified by column chromatography on silica gel with ~5-15% EtOAc in *n*-hexane to provide compound (+)**-8j** as white solid (321.3 mg, 92%).



(4*R*,4a*R*,13b*S*)**-4-(((tert-butyldimethylsilyl)oxy)methyl)-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole** [(+)**-8j**]: (+)**-8j** was obtained as white solid (0.78 mmol scale of reaction; 92% yield). R_f = 0.6 (10% EtOAc in *n*-hexane).

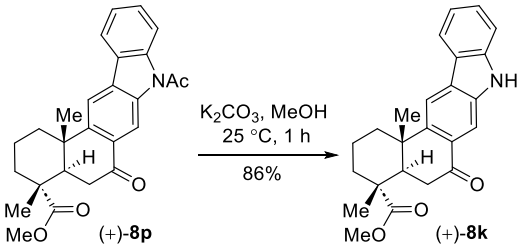
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H), 7.77 (s, 1H), 7.35 (d, *J* = 4.0 Hz, 2H), 7.18 (dt, *J* = 8.3, 4.2 Hz, 1H), 7.07 (s, 1H), 3.47 (d, *J* = 9.6 Hz, 1H), 3.12 (d, *J* = 9.6 Hz, 1H), 3.09 – 3.03 (m, 2H), 2.51 (d, *J* = 12.7 Hz, 1H), 1.86 (t, *J* = 10.4 Hz, 3H), 1.78 – 1.70 (m, 2H), 1.59 – 1.52 (m, 3H), 1.32 (s, 3H), 0.88 (s, 3H), 0.88 – 0.86 (m, 9H), 0.04 (d, *J* = 1.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 140.2, 138.1, 134.4, 125.3, 124.0, 122.0, 120.0, 119.2, 115.8, 110.5, 109.9, 72.0, 44.1, 39.6, 38.3, 38.1, 35.6, 31.4, 26.3, 26.1, 19.2, 19.2, 18.5, 17.8, -5.4, -5.4.

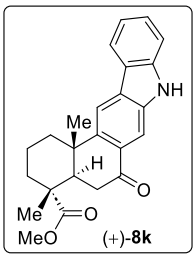
IR (neat) υ_{max} 2950, 1720, 1565, 1300, 1085, 965, 823, 720, 680 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{29}H_{41}NOSi + H]^+$ 448.3036, found 448.3046.

$[\alpha]^{25}_{589}$ = +61.2 (c = 0.3, $CHCl_3$).

Deacetylation of Compound (+)-**8p:**



In an oven-dried round-bottom flask (+)-**8p** (300 mg, 0.72 mmol, 1.0 equiv.) was dissolved in 10 mL of methanol. To the reaction mixture solid K_2CO_3 (198.6 mg, 1.44 mmol, 2.0 equiv.) was added at 25 ºC and stirred for 1 h. After completion of the reaction (monitored by TLC) the reaction mixture was directly evaporated under reduced pressure. The mixture was then extracted with EtOAc (15 mL X 3). The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. Then the crude product was purified by flash chromatography with 50% EtOAc in *n*-hexane to afford (+)-**8k** as yellow foam (232.5 mg, 86% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-6-oxo-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8k**]: (+)-**8k** was obtained as yellow foam (0.72 mmol scale of reaction; 86% yield). R_f = 0.4 (40% EtOAc in *n*-hexane).

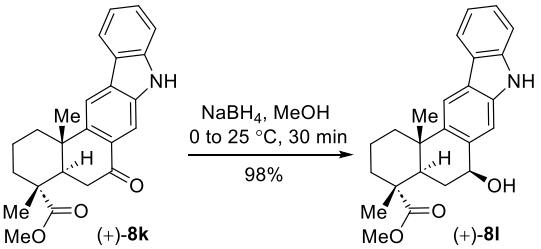
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.20 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.45 (d, *J* = 2.9 Hz, 2H), 7.24 (td, *J* = 5.2, 2.5 Hz, 1H), 3.68 (s, 3H), 2.84 (d, *J* = 2.6 Hz, 2H), 2.58 (d, *J* = 11.5 Hz, 1H), 2.50 – 2.46 (m, 1H), 1.88 (d, *J* = 9.1 Hz, 3H), 1.82 – 1.77 (m, 2H), 1.40 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 178.2, 147.0, 142.0, 137.8, 128.8, 128.4, 127.6, 122.6, 121.2, 119.7, 114.5, 111.3, 110.0, 52.3, 46.9, 44.2, 38.1, 37.9, 37.7, 36.8, 24.6, 18.4, 16.6.

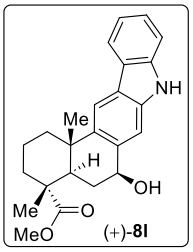
IR (neat) υ_{max} 3525, 2944, 1655, 1460, 1445, 1172, 823, 776, 665 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{24}H_{25}NO_3 + Na]^+$ 398.1732, found 398.1732.

$[\alpha]^{25}_{589}$ = +104.3 (c = 0.2, $CHCl_3$).

Stereoselective reduction of (+)-**8k:**



In an oven-dried round-bottom flask (+)-**8k** (232 mg, 0.62 mmol, 1.0 equiv.) in MeOH (4 mL) was taken at 0 ºC, $NaBH_4$ (28.2 mg, 0.74 mmol, 1.2 equiv.) was added portion wise and the reaction mixture was stirred at 25 ºC temperature for 30 min. After complete consumption of starting material (monitored by TLC analysis), it was quenched with saturated NH_4Cl (2 mL) and extracted with EtOAc (8 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. The crude products were purified by flash chromatography with 60% EtOAc in *n*-hexane to afford (+)-**8l** as colourless liquid (229.4 mg, 98% yield).



(4*R*,4a*R*,6*S*,13b*S*)-**methyl 6-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8l**]: (+)-**8l** was obtained as colourless liquid (0.62 mmol scale of reaction; 98% yield). R_f = 0.3 (40% EtOAc in *n*-hexane).

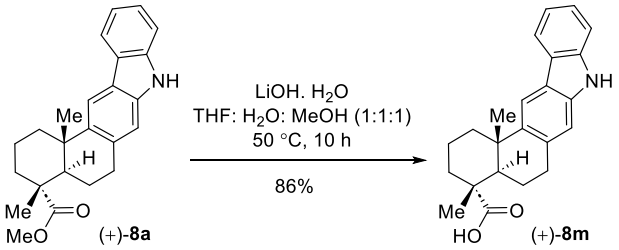
^{1}H NMR (500 MHz, CD_3OD) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.93 (s, 1H), 7.59 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.91 (dt, *J* = 14.2, 7.3 Hz, 1H), 4.09 (p, *J* = 8.7, 8.0 Hz, 1H), 3.69 (s, 3H), 2.58 (d, *J* = 13.0 Hz, 1H), 2.31 (d, *J* = 12.7 Hz, 1H), 2.00 (d, *J* = 6.4 Hz, 1H), 1.93 (d, *J* = 12.2 Hz, 1H), 1.76 (dt, *J* = 13.5, 6.7 Hz, 3H), 1.70 – 1.64 (m, 1H), 1.58 – 1.51 (m, 1H), 1.38 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 180.6, 142.4, 142.0, 140.2, 137.6, 126.4, 124.4, 124.1, 120.8, 119.4, 116.0, 111.6, 110.2, 71.9, 52.6, 45.3, 40.2, 39.2, 37.8, 33.8, 26.7, 19.7, 17.1, 14.4.

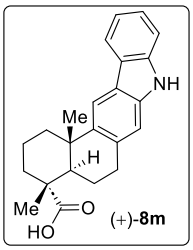
IR (neat) υ_{max} 3610, 3158, 2855, 1764, 1695, 1535, 1430, 1365, 1169, 850 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{24}H_{27}NO_3 + Na]^+$ 400.1889, found 400.1902.

$[\alpha]^{25}_{589}$ = +101.4 (c = 0.4, MeOH).

Procedure for the Synthesis of Acid (+)-**8m:**



In an oven dried round-bottom flask (+)-**8a** (265 mg, 0.73 mmol, 1.0 equiv.) was taken in a mixture of THF, methanol and water [THF: MeOH: H_2O (1:1:1)]. To the solution LiOH. H_2O (1.23 g, 29.3 mmol, 40 equiv.) were added and reaction mixture was refluxed for 10 h at 50 ºC. After completion of the reaction confirmed by TLC, reaction mixture was quenched with 4(N) HCl at 0 ºC and the pH of the reaction mixture was adjusted to ~1-2. Then the reaction mixture was extracted with ethyl acetate (6mL X 3). The organic layer was collected, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography with ~40-60% EtOAc in *n*-Hexane to afford (+)-**8m** as yellow liquid (218.2 mg, 86% yield).



(4*R*,4a*R*,13b*S*)-**4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylic acid** [(+)-**8m**]: (+)-**8m** was obtained as yellow liquid (0.73 mmol scale of reaction; 86% yield). R_f = 0.3 (30% EtOAc in *n*-hexane).

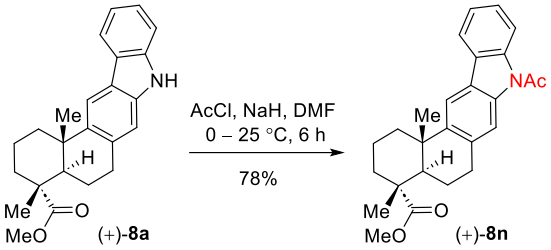
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27 (s, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 3.14 (d, *J* = 7.5 Hz, 2H), 2.60 (d, *J* = 12.6 Hz, 1H), 2.43 (d, *J* = 12.4 Hz, 1H), 2.03 (t, *J* = 10.4 Hz, 1H), 1.95 – 1.88 (m, 2H), 1.85 (s, 1H), 1.81 (d, *J* = 9.9 Hz, 1H), 1.73 – 1.66 (m, 2H), 1.39 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 140.1, 138.2, 133.9, 125.5, 123.6, 121.8, 119.9, 119.2, 115.4, 110.7, 110.2, 47.7, 45.1, 39.0, 37.5, 37.1, 30.8, 25.9, 22.1, 18.9, 16.5.

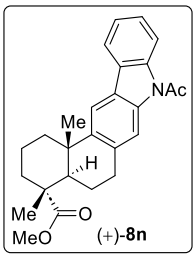
IR (neat) υ_{max} 3000, 2866, 2369, 1760, 1498, 1245, 1123, 915, 768 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{23}H_{25}NO_2 + H]^+$ 348.1964, found 348.1950.

$[\alpha]_{589}^{25}$ = +74.5 (c = 0.5, $CHCl_3$).

Acetylation of Carbazole derivative (+)-**8a:**



Carbazole (+)-**8a** (500 mg, 1.4 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 9 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (112 mg, 2.8 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then acetyl chloride (150 µL, 2.1 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (12 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to afford (+)-**8n** as white foam (440.6 mg, 78% yield).



(4*R*,4a*R*,13b*S*)-**methyl 8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8n**]: Following the general procedure (+)-**8n** was obtained as white foam (1.4 mmol scale of reaction; 78% yield). R_f = 0.3 (10% EtOAc in *n*-hexane).

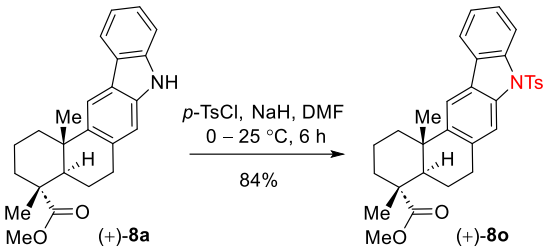
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.86 (s, 1H), 7.85 (s, 1H), 7.43 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.37 – 7.34 (m, 1H), 3.69 (s, 3H), 3.11 (dd, *J* = 9.1, 4.7 Hz, 2H), 2.84 (s, 3H), 2.51 (d, *J* = 12.8 Hz, 1H), 2.31 (dd, *J* = 12.5, 2.4 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.86 – 1.83 (m, 1H), 1.82 – 1.78 (m, 2H), 1.72 – 1.69 (m, 1H), 1.67 – 1.63 (m, 1H), 1.54 – 1.49 (m, 1H), 1.33 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 170.1, 146.0, 139.1, 137.1, 135.3, 127.0, 126.9, 124.8, 123.7, 119.5, 116.5, 116.4, 115.2, 52.1, 47.8, 45.1, 38.6, 37.6, 36.8, 31.1, 27.8, 25.6, 21.9, 18.8, 16.7.

IR (neat) υ_{max} 3402, 2924, 1720, 1660, 1465, 1243, 1032, 823, 705, 528 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{29}NO_3 + H]^+$ 404.2226, found 404.2224.

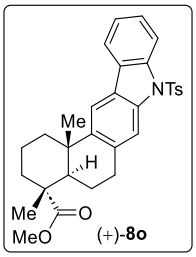
$[\alpha]_{589}^{20}$ = +35.5 (c = 0.2, $CHCl_3$).

Tosylation of Carbazole derivative (+)**-8a:**



Carbazole (+)**-8a** (200 mg, 0.6 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 4 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (48 mg, 1.2 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then solid *p*-toluene sulphonyl chloride (172 mg, 0.9 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary

evaporator under vacuum. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to afford (+)-**8o** as white foam (259.9 mg, 84% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-8-tosyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8o**]: (+)-**8o** was obtained as white foam (0.6 mmol scale of reaction; 84% yield). R_f = 0.35 (20% EtOAc in *n*-hexane).

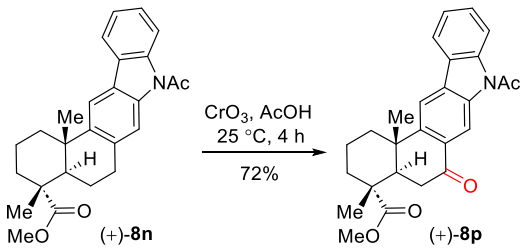
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.70 (s, 3H), 3.13 (dd, *J* = 9.6, 6.7 Hz, 2H), 2.45 (d, *J* = 11.8 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 1H), 1.93 (td, *J* = 12.7, 6.6 Hz, 1H), 1.86 – 1.73 (m, 4H), 1.69 (d, *J* = 9.2 Hz, 1H), 1.51 (dd, *J* = 11.3, 4.7 Hz, 1H), 1.32 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 146.0, 144.6, 138.5, 136.6, 135.4, 135.2, 129.7, 126.8, 126.7, 126.5, 124.4, 123.6, 119.5, 115.2, 115.0, 114.7, 52.0, 47.6, 44.9, 38.4, 37.5, 36.7, 30.8, 25.5, 21.7, 21.5, 18.6, 16.6.

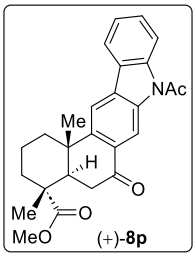
IR (neat) υ_{max} 2921, 1710, 1598, 1368, 1182, 995, 810, 747, 668, 581 cm^{-1}.

$[\alpha]^{25}_{589}$ = +139.2 (c = 0.8, $CHCl_3$).

Benzylic Oxidation of Compound (+)-**8n:**



In an oven-dried round-bottom flask (+)-**8n** (425 mg, 1.05 mmol, 1.0 equiv.) was dissolved in 6 mL of acetic acid. To the reaction mixture solid CrO_3 (210.7 mg, 2.11 mmol, 2.0 equiv.) was added at 25 ºC and stirred for 4 h. After completion of the reaction (monitored by TLC) the reaction mixture was diluted with ethyl acetate and quenched with saturated aqueous sodium bicarbonate solution. The mixture was extracted with EtOAc (12 mL X 3). The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. Then the crude product was purified by flash chromatography with 40% EtOAc in *n*-hexane to afford (+)-**8p** as yellow foam (315.6 mg, 72% yield).



(4*R*,4a*R*,13b*S*)-**methyl 8-acetyl-4,13b-dimethyl-6-oxo-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**8p**]: (+)-**8p** was obtained as yellow foam (1.05 mmol scale of reaction; 72% yield). R_f = 0.2 (20% EtOAc in *n*-hexane).

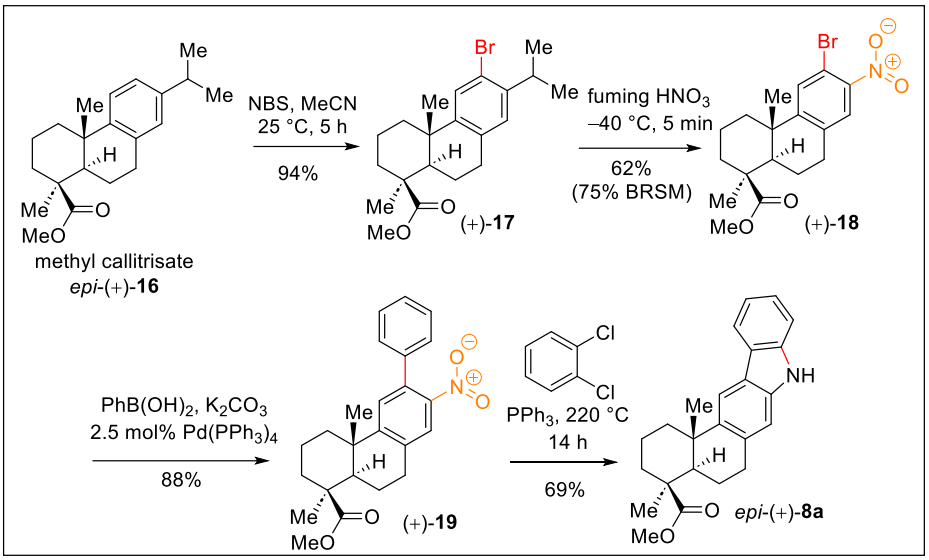
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.97 (s, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 3.68 (s, 3H), 2.92 (s, 3H), 2.80 (s, 1H), 2.57 (d, *J* = 12.0 Hz, 1H), 2.46 (d, *J* = 13.9 Hz, 1H), 1.89 (d, *J* = 7.4 Hz, 3H), 1.85 – 1.75 (m, 3H), 1.39 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 177.9, 170.0, 151.1, 140.9, 136.7, 131.6, 130.0, 129.3, 125.4, 124.2, 120.5, 117.5, 114.7, 114.7, 52.4, 46.9, 44.0, 38.0, 37.9, 37.7, 36.7, 27.8, 24.3, 18.4, 16.6.

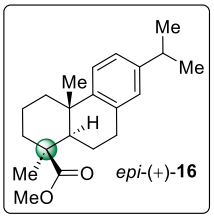
IR (neat) υ_{max} 3500, 2924, 1725, 1660, 1460, 1243, 1132, 823, 767, 528 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{27}NO_4 + H]^+$ 418.2018, found 418.2024.

$[\alpha]_{589}^{25}$ = +49.6 (c = 0.5, $CHCl_3$).

General procedure for the synthesis of compound *epi*-(+)-8a:



Methyl callitrisate *epi*-(+)-16[2] was synthesized by the following literature protocol.



(1*S*,4a*S*,10a*R*)-**methyl 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [*epi*-(+)-**16**]: Following the general procedure *epi*-(+)-**16** was obtained as white solid (130 mmol scale of reaction; 12% overall yield from abietic acid). R_f = 0.6 (5% EtOAc in *n*-hexane).

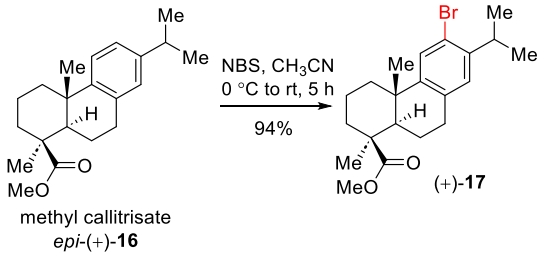
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 3.69 (s, 3H), 2.96 – 2.77 (m, 3H), 2.30 (td, *J* = 8.6, 4.3 Hz, 2H), 2.25 – 2.18 (m, 1H), 2.08 – 1.97 (m, 2H), 1.66 (dq, *J* = 14.4, 3.6 Hz, 1H), 1.58 (dd, *J* = 12.2, 1.8 Hz, 1H), 1.44 (dd, *J* = 13.4, 4.2 Hz, 1H), 1.31 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 1.13 (dd, *J* = 13.7, 4.3 Hz, 1H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 145.7, 145.6, 135.1, 126.9, 125.6, 124.1, 77.5, 53.0, 51.3, 44.1, 39.5, 38.3, 37.8, 33.5, 32.2, 28.7, 24.1, 23.1, 21.2, 20.1.

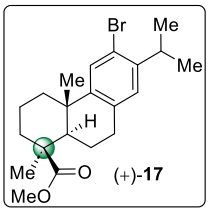
IR (neat) υ_{max} 2958, 2957, 2866, 2369, 1726, 1498, 1243, 1121, 915, 768 cm^{-1}.

$[\alpha]^{25}_{589}$ = +73.9 (c = 2.1, $CHCl_3$); lit.[2] $[\alpha]^{25}_{D}$ = +137 (c = 0.642, EtOH).

Aromatic Electrophilic Bromination of *epi*-(+)-16:



In an oven dried round-bottom flask *epi*-(+)-**16** (8.0 g, 25.5 mmol, 1.0 equiv.) was taken in 108 mL of CH_3CN. To the reaction mixture NBS (5.44 g, 30.6 mmol, 1.2 equiv.) was added at 25 ^{o}C and stirred at the same temperature for 5 h. After completion of the reaction (monitored by TLC), saturated aqueous Na_2S2O_3 solution was added to the reaction mixture. The reaction mixture was then partitioned and extracted with EtOAc (50 mL X 3). The combined organic layers were concentrated in a rotary evaporator under reduced pressure and crude product was purified through column chromatography with 5% EtOAc in *n*-hexane to afford (+)-**17** as yellow gel (9.4 g, 94% yield).



(1*S*,4a*S*,10a*R*)-**methyl 6-bromo-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**17**]: Following the general procedure (+)-**17** was obtained as yellow gel (25.5 mmol scale of reaction; 94% yield). R_f = 0.75 (5% EtOAc in *n*-hexane).

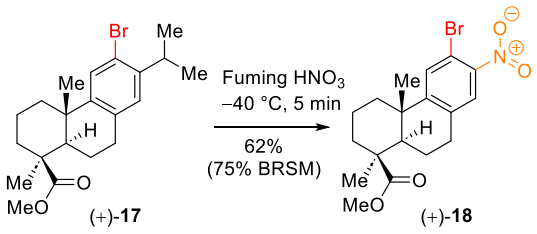
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.93 (s, 1H), 3.66 (s, 4H), 3.26 (p, *J* = 6.9 Hz, 1H), 2.86 (ddd, *J* = 16.9, 5.6, 1.8 Hz, 1H), 2.73 (td, *J* = 11.9, 11.1, 6.3 Hz, 1H), 2.28 (d, *J* = 13.7 Hz, 1H), 2.22 – 2.16 (m, 2H), 1.98 (td, *J* = 8.7, 7.9, 4.5 Hz, 2H), 1.64 – 1.61 (m, 1H), 1.53 – 1.47 (m, 2H), 1.37 (dd, *J* = 13.4, 3.9 Hz, 1H), 1.27 (s, 3H), 1.23 (s, 3H), 1.20 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 147.7, 144.0, 134.9, 129.9, 127.1, 121.7, 52.6, 51.3, 44.0, 39.4, 38.3, 37.7, 32.4, 31.7, 28.6, 23.1, 23.0, 22.9, 21.0, 20.0.

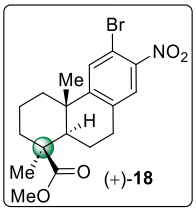
IR (neat) υ_{max} 3015, 1842, 1798, 1641, 1495, 1381, 1332, 1201, 1105, 978, 703 cm^{-1}.

$[\alpha]_{589}^{25}$ = +296.9 (c = 0.8, $CHCl_3$).

***Ipso*-nitration of (+)-17:**



In an oven-dried round-bottom flask 4 mL of fuming nitric acid was taken and set at – 40 °C. Then solid compound (+)-**17** (800 mg, 2.03 mmol, 1.0 equiv.) was directly charged into the previously cooled fuming nitric acid system and the whole solution was scratched well with a spatula maintaining the –40 °C temperature. After scratching the solution for 5 minutes, the reaction was quenched with excess of water. The reaction mixture was then partitioned between water and dichloromethane. The organic layer was then washed with saturated bicarbonate solution. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by column chromatography with 15% EtOAc in *n*-hexane to afford (+)-**18** as yellow foam [602.8 mg, 75% yield (brsm)].



(1*S*,4a*S*,10a*R*)-**methyl 6-bromo-1,4a-dimethyl-7-nitro-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**18**]: (+)-**18** was obtained as yellow foam (2.03 mmol scale of reaction; 75% yield). R_f = 0.4 (10% EtOAc in *n*-hexane).

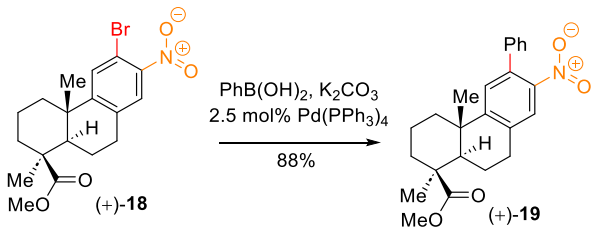
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.58 (s, 1H), 3.68 (s, 3H), 2.96 – 2.91 (m, 1H), 2.81 – 2.73 (m, 1H), 2.30 (dt, *J* = 13.7, 3.6 Hz, 1H), 2.24 (ddd, *J* = 10.7, 8.6, 5.3 Hz, 2H), 2.03 – 1.95 (m, 2H), 1.70 – 1.65 (m, 1H), 1.50 (dd, *J* = 12.4, 1.8 Hz, 1H), 1.38 (dd, *J* = 13.2, 4.2 Hz, 1H), 1.29 (s, 3H), 1.11 (dd, *J* = 13.6, 4.3 Hz, 1H), 1.05 – 1.02 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 154.9, 136.7, 132.8, 126.4, 125.7, 111.4, 52.0, 51.6, 44.1, 39.2, 39.2, 37.4, 31.4, 28.6, 23.0, 20.5, 19.9.

IR (neat) υ_{max} 2932, 1721, 1527, 1450, 1365, 1248, 1112, 981, 883, 734 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{18}H_{22}BrNO_4 + Na]^+$ 418.0630, found 418.0624.

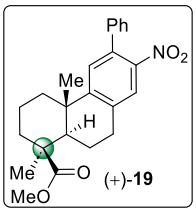
$[\alpha]_{589}^{25}$ = +52.6 (c = 0.1, $CHCl_3$).

Suzuki-Miyaura Coupling of (+)-18 with Phenylboronic acid:



In an oven-dried round-bottom flask, compound (+)-**18** (6.6 g, 16.7 mmol, 1 equiv.) was taken in 55 mL mixed solvent system of benzene: ethanol: water (2:1:1) equipped with a magnetic stir-bar. Then phenylboronic acid (2.44 g, 20.0 mmol, 1.2 equiv.) and potassium carbonate (4.6 g, 33.4 mmol, 2 equiv.) were directly added to the reaction mixture. After the complete

dissolution of the solid materials the reaction mixture was degassed for 10 mins using N_2 gas balloon. Then tetrakis(triphenylphosphine)palladium(0) (386.3 mg, 0.33 mmol, 0.02 equiv.) was rapidly added and the reaction mixture was allowed to reflux at 100 °C on a preheated oil-bath for 8 h maintaining N_2 inertness until the full consumption of starting material (monitored by TLC). The mixture was cooled and was poured into an aqueous ammonium chloride solution. The mixture was extracted with 20% EtOAc in *n*-hexane (25 mL X 3). The combined organic layers were washed with brine (20 mL X 1), dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. Now the crude product was purified by flash chromatography with 25% EtOAc in *n*-hexane to afford (+)-**19** as yellow foam (5.8 g, 88% yield).



(1*S*,4a*S*,10a*R*)-**methyl 1,4a-dimethyl-7-nitro-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**19**]: (+)-**19** was obtained as yellow foam (16.7 mmol scale of reaction; 88% yield). R_f = 0.4 (10% EtOAc in *n*-hexane).

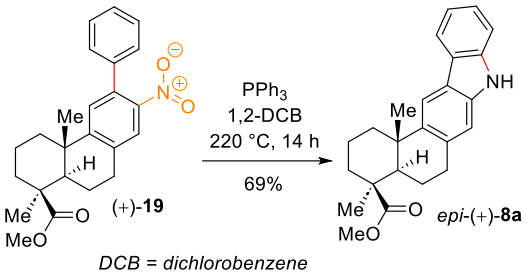
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.42 – 7.36 (m, 3H), 7.30 – 7.25 (m, 3H), 3.68 (s, 3H), 3.05 – 2.98 (m, 1H), 2.91 – 2.83 (m, 1H), 2.34 – 2.21 (m, 4H), 2.07 – 1.97 (m, 2H), 1.47 – 1.39 (m, 1H), 1.30 (s, 3H), 1.27 – 1.24 (m, 1H), 1.15 – 1.09 (m, 1H), 1.07 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 153.3, 146.6, 138.2, 136.4, 134.0, 129.7, 128.7, 128.1, 128.0, 124.8, 124.2, 120.9, 52.4, 51.6, 44.1, 39.3, 39.1, 37.5, 31.6, 28.6, 23.1, 20.7, 19.9.

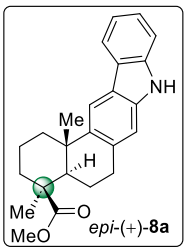
IR (neat) υ_{max} 3015, 1842,1798, 1641, 1495, 1381, 1332, 1201, 1105, 978, 703 cm^{-1}.

$[\alpha]^{25}_{589}$ = +95.0 (c = 0.3, $CHCl_3$).

Cadogan Reaction of (+)**-19:**



In an oven-dried round-bottom flask compound (+)-**19** (5.5 g, 14.0 mmol, 1.0 equiv.) was taken in 30 mL of 1, 2-dichlorobenzene maintaining N_2 inertness. Then to the reaction mixture solid triphenyl phosphine (11.0 g, 41.9 mmol, 3.0 equiv.) was added and refluxed at 220 °C on a preheated oil-bath for 14 h until the full consumption of starting material (monitored by TLC). Now the crude product was purified by flash chromatography with 25% EtOAc in *n*-hexane to afford *epi*-(+)-**8a** as white foam (3.5 g, 69% yield).



(4*S*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [*epi*-(+)-**8a**]: *epi*-(+)-**8a** was obtained as white foam (14.0 mmol scale of reaction; 69% yield). R_f = 0.35 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.80 (s, 1H), 7.38 – 7.35 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.02 (s, 1H), 3.71 (s, 3H), 3.14 – 3.07 (m, 1H), 3.06 – 2.96 (m, 1H), 2.53 (d, *J* = 13.0 Hz, 1H), 2.34 (d, *J* = 13.7 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.10 (ddd, *J* = 17.7, 8.2, 4.8 Hz, 2H), 1.72 (tt, *J* = 7.5, 3.1 Hz, 1H), 1.67 (dd, *J* = 12.2, 1.9 Hz, 1H), 1.58 – 1.51 (m, 1H), 1.34 (s, 3H), 1.30 – 1.27 (m, 1H), 1.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 140.4, 140.2, 138.2, 134.2, 125.5, 123.7, 122.2, 120.0, 119.2, 117.0, 110.5, 109.8, 53.4, 51.4, 44.2, 40.5, 38.8, 37.9, 33.1, 28.8, 24.0, 21.4, 20.3.

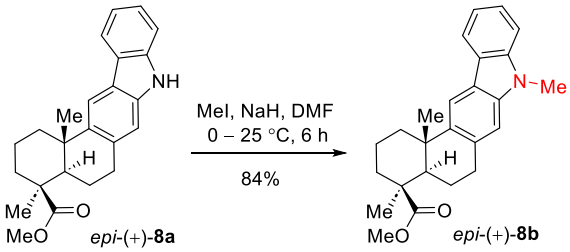
IR (neat) υ_{max} 3402, 2926, 1720, 1465, 1243, 1023, 823, 750, 582 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{24}H_{27}NO_2 + Na]^+$ 362.2120, found 362.2108.

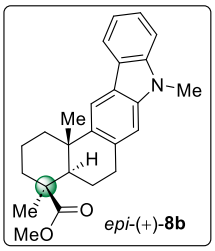
$[\alpha]^{25}_{589}$ = +95.1 (c = 0.8, $CHCl_3$).

Substrate (Deoxy-oridamycin derivatives) preparation for Oxidative Dimerization:

Methylation of Carbazole derivative *epi*-(+)-8a:



Carbazole *epi*-(+)-**8a** (230 mg, 0.64 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 4 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (50.9 mg, 1.27 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then iodomethane (60.6 µL, 0.96 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford *epi*-(+)-**8b** as colourless gel (201.7 mg, 84% yield).



(4*S*,4a*R*,13b*S*)-**methyl 4,8,13b-trimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [*epi*-(+)-**8b**]: *epi*-(+)-**8b** was obtained as colourless gel (0.64 mmol scale of reaction; 84% yield). R_f = 0.6 (10% EtOAc in *n*-hexane).

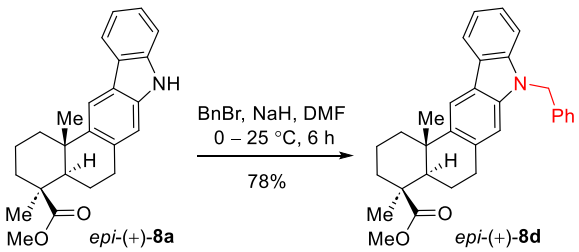
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 7.7, 0.9 Hz, 1H), 8.04 (s, 1H), 7.45 – 7.41 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.06 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.22 – 3.15 (m, 1H), 3.11 – 3.05 (m, 1H), 2.55 (d, *J* = 13.2 Hz, 1H), 2.35 (dd, *J* = 13.6, 3.0 Hz, 1H), 2.32 – 2.26 (m, 1H), 2.19 – 2.07 (m, 3H), 1.75 – 1.71 (m, 1H), 1.69 (dd, *J* = 12.2, 1.9 Hz, 1H), 1.54 (dd, *J* = 13.4, 4.0 Hz, 1H), 1.35 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 141.6, 139.8, 139.7, 134.0, 125.3, 123.1, 121.6, 120.0, 118.6, 117.1, 108.3, 107.7, 53.5, 51.4, 44.2, 40.5, 38.8, 37.9, 33.4, 29.0, 28.8, 24.0, 21.5, 20.3.

IR (neat) υ_{max} 3350, 2974, 1740, 1465, 1310, 1250, 1023, 853, 750, 665 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{25}H_{29}NO_2 + H]^+$ 376.2277, found 376.2278.

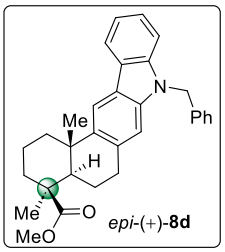
$[\alpha]_{589}^{25}$ = +40.2 (c = 1.0, $CHCl_3$).

Benzylation of Carbazole derivative *epi*-(+)-8a:



Carbazole *epi*-(+)-**8a** (255 mg, 0.71 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 6 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (56.4 mg, 1.41 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then benzyl bromide (126.5 µL, 1.07 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc

and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford *epi*-(+)-**8d** as colourless gel (250.1 mg, 78% yield).



(4*S*,4a*R*,13b*S*)-**methyl 8-benzyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [*epi*-(+)-**8d**]: *epi*-(+)-**8d** was obtained as colourless gel (0.71 mmol scale of reaction; 78% yield). R_f = 0.6 (10% EtOAc in *n*-hexane).

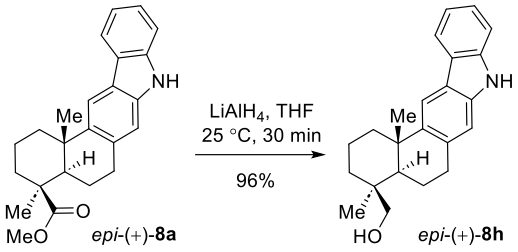
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.09 (m, 1H), 8.08 (s, 1H), 7.44 – 7.41 (m, 1H), 7.40 – 7.37 (m, 1H), 7.30 (d, *J* = 1.0 Hz, 1H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.27 (d, *J* = 0.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 1.9 Hz, 1H), 7.17 (d, *J* = 1.8 Hz, 1H), 7.03 (s, 1H), 5.43 (s, 2H), 3.72 (s, 3H), 3.14 – 3.09 (m, 1H), 3.06 – 2.98 (m, 1H), 2.57 (d, *J* = 13.1 Hz, 1H), 2.38 – 2.34 (m, 1H), 2.29 – 2.24 (m, 1H), 2.15 – 2.08 (m, 2H), 1.77 – 1.73 (m, 1H), 1.69 – 1.66 (m, 1H), 1.62 – 1.56 (m, 1H), 1.34 (s, 3H), 1.32 – 1.30 (m, 1H), 1.20 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 141.2, 140.2, 139.4, 137.6, 134.2, 128.8, 127.4, 126.5, 126.5, 125.5, 123.3, 121.8, 120.1, 119.0, 117.2, 108.8, 108.1, 53.4, 51.3, 46.6, 44.2, 40.4, 38.8, 37.8, 33.3, 28.7, 24.0, 21.4, 20.3.

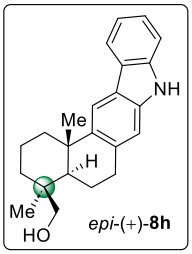
IR (neat) υ_{max} 3450, 2942, 1751, 1624, 1476, 1356, 1258, 1004, 924, 876, 762, 632 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{31}H_{33}NO_2 + H]^+$ 452.2589, found 452.2592.

$[\alpha]_{589}^{25}$ = +28.2 (c = 1.6, $CHCl_3$).

Procedure for the Synthesis of Alcohol *epi*-(+)-8h:



To a stirred solution *epi*-(+)-**8a** (252 mg, 0.7 mmol, 1.0 equiv.) in tetrahydrofuran (4 mL), lithium aluminum hydride (26.8 mg, 0.70 mmol, 1.01 equiv.) was added at 0 °C, and the reaction mixture was stirred for 30 min at 25 °C. Distilled water (0.5 mL), 1M aq. NaOH (1 M, 1.0 mL), and distilled water (0.5 mL) was sequentially added at 0 °C and the resulting mixture was warmed to 25 °C. Dried over sodium sulfate and filtered over a pad of celite and washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel with ~30-40% EtOAc in *n*-hexane to provide compound *epi*-(+)-**8h** as colourless gel (224.1 mg, 96%).



((4*S*,4a*R*,13b*S*)-**4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazol-4-yl)methanol** [*epi*-(+)-**8h**]: *epi*-(+)-**8h** was obtained as colourless gel (0.7 mmol scale of reaction; 96% yield). R_f = 0.3 (20% EtOAc in *n*-hexane).

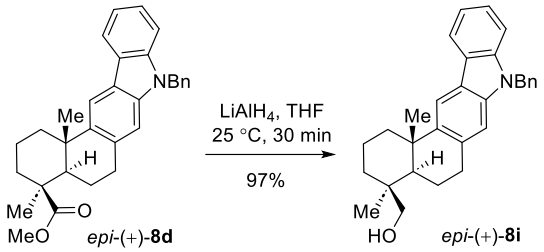
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.97 (s, 1H), 7.81 (s, 1H), 7.37 – 7.32 (m, 2H), 7.19 (ddd, *J* = 8.0, 6.5, 1.6 Hz, 1H), 7.04 (s, 1H), 3.93 (d, *J* = 11.0 Hz, 1H), 3.61 (d, *J* = 11.0 Hz, 1H), 3.16 – 3.10 (m, 1H), 3.05 (ddd, *J* = 17.4, 11.2, 7.3 Hz, 1H), 2.57 (d, *J* = 12.4 Hz, 1H), 2.08 – 2.02 (m, 1H), 1.96 – 1.92 (m, 1H), 1.81 (ddd, *J* = 13.8, 8.0, 4.2 Hz, 2H), 1.72 (tdd, *J* = 14.0, 7.0, 3.5 Hz, 2H), 1.62 (dd, *J* = 13.0, 2.7 Hz, 2H), 1.28 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 140.2, 138.2, 133.7, 125.4, 123.8, 122.0, 120.0, 119.2, 115.9, 110.5, 109.9, 65.5, 51.7, 39.9, 38.9, 38.1, 35.4, 31.8, 27.0, 26.6, 19.5, 19.3.

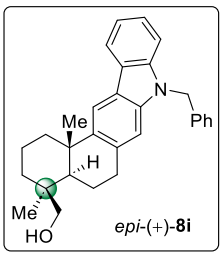
IR (neat) υ_{max} 3610, 3365, 1720, 1465, 1243, 1085, 876, 720, 552 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{23}H_{27}NO + H]^+$ 334.2171, found 334.2172.

$[\alpha]^{25}_{589}$ = +78.4 (c = 0.5, $CHCl_3$).

Reduction of *N*-Benzyl Carbazole derivative *epi*-(+)-8d:



To a stirred solution *epi*-(+)-**8d** (225 mg, 0.5 mmol, 1 equiv.) in tetrahydrofuran (4 mL), lithium aluminum hydride (19.1 mg, 0.5 mmol, 1.01 equiv.) was added at 0 °C, and the reaction mixture was stirred for 30 min at 25 °C. Distilled water (0.5 mL), 1M aq. NaOH (1 M, 1.0 mL), and distilled water (0.5 mL) was sequentially added at 0 °C and the resulting mixture was warmed to 25 °C. Dried over sodium sulfate and filtered over a pad of celite and washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel with ~20-30% EtOAc in *n*-hexane to provide compound *epi*-(+)-**8i** as colourless gel (205.4 mg, 97%).



((4*S*,4a*R*,13b*S*)-**8-benzyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazol-4-yl)methanol** [*epi*-(+)-**8i**]: *epi*-(+)-**8i** was obtained as colourless gel (0.5 mmol scale of reaction; 97% yield). R_f = 0.2 (10% EtOAc in *n*-hexane).

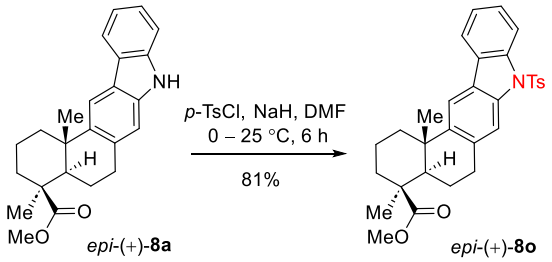
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 3.2 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 6.5 Hz, 3H), 7.01 (s, 1H), 5.43 (s, 2H), 3.96 – 3.91 (m, 1H), 3.62 (dd, *J* = 18.4, 10.1 Hz, 2H), 3.12 (dd, *J* = 17.8, 6.3 Hz, 1H), 3.04 (q, *J* = 8.8 Hz, 1H), 2.59 (d, *J* = 12.8 Hz, 1H), 2.04 (d, *J* = 11.8 Hz, 1H), 1.95 (s, 1H), 1.79 (t, *J* = 13.6 Hz, 2H), 1.69 (s, 1H), 1.62 (d, *J* = 11.9 Hz, 2H), 1.29 (s, 3H), 1.08 (d, *J* = 3.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 141.3, 139.4, 137.6, 133.8, 128.9, 127.5, 126.6, 126.6, 125.5, 121.7, 120.1, 119.0, 116.0, 108.8, 108.2, 65.5, 51.7, 46.6, 39.9, 38.9, 38.1, 35.4, 32.0, 27.0, 26.6, 19.6, 19.3.

IR (neat) υ_{max} 3612, 3346, 1756, 1453, 1248, 1067, 935, 752, 663 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{30}H_{33}NO + H]^+$ 424.2640, found 424.2634.

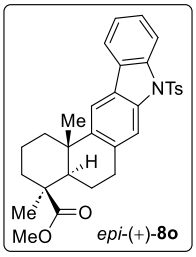
$[\alpha]_{589}^{25}$ = +31.1 (c = 0.3, $CHCl_3$).

Tosylation of Carbazole derivative *epi*-(+)-8a:



Carbazole *epi*-(+)-**8a** (200 mg, 0.6 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 4 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (48 mg, 1.2 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then solid *p*-toluene sulphonyl chloride (172 mg, 0.9 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was

quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to afford *epi*-(+)-**8o** as white foam (250.6 mg, 81% yield).



(4*S*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-8-tosyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [*epi*-(+)-**8o**]: Following the general procedure *epi*-(+)-**8o** was obtained as white foam (0.6 mmol scale of reaction; 81% yield). R_f = 0.5 (20% EtOAc in *n*-hexane).

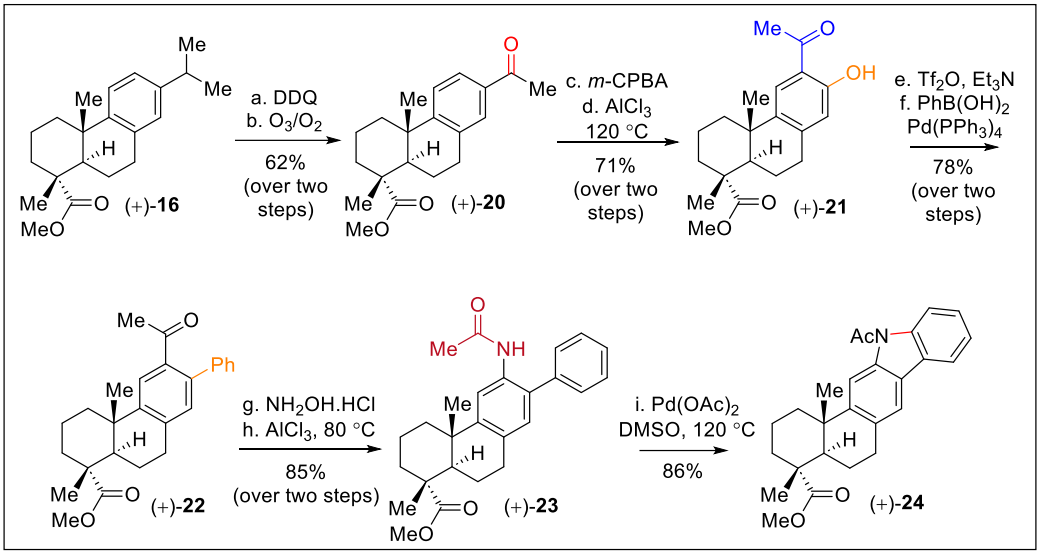
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 1H), 7.97 (s, 1H), 7.85 – 7.81 (m, 1H), 7.79 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.41 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.68 (s, 3H), 3.16 (ddd, *J* = 17.2, 5.3, 1.8 Hz, 1H), 3.07 – 2.98 (m, 1H), 2.44 – 2.38 (m, 1H), 2.31 (dd, *J* = 14.2, 3.7 Hz, 1H), 2.25 (s, 4H), 2.12 – 2.02 (m, 2H), 1.70 – 1.65 (m, 1H), 1.63 (dd, *J* = 12.4, 1.8 Hz, 1H), 1.46 (td, *J* = 12.8, 12.2, 3.5 Hz, 1H), 1.32 (s, 3H), 1.27 (ddd, *J* = 11.3, 5.8, 3.1 Hz, 1H), 1.10 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9, 144.6, 144.5, 138.5, 136.6, 135.8, 135.3, 129.6, 126.8, 126.69, 126.5, 124.6, 123.7, 119.6, 116.8, 115.0, 114.6, 52.8, 51.3, 44.1, 40.0, 38.7, 37.6, 33.2, 28.6, 23.6, 21.5, 21.1, 20.1.

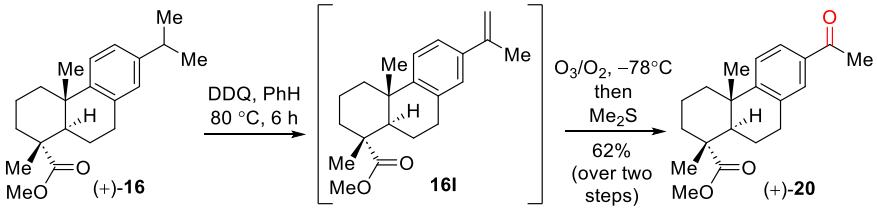
IR (neat) υ_{max} 2921, 1710, 1598, 1368, 1182, 995, 810, 747, 668, 581 cm^{-1}.

$[\alpha]^{25}_{589}$ = +78.8 (c = 0.8, $CHCl_3$).

General procedure for the synthesis of compound (+)-24:

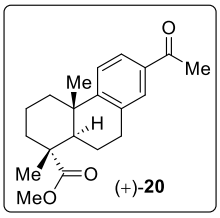


Synthesis of Acetophenone derivative (+)-20:



A solution of Methyl dehydroabietate (+)-**16** (10 g, 31.8 mmol, 1.0 equiv.) and dichloro dicyano quinone (8.7 g, 38.2 mmol, 1.2 equiv.) in benzene was refuxed at 80 ºC for 6 h under N_2 atmosphere. Then, the mixture was cooled and filtered through a short pad of Celite 512 washing with 15 mL of fresh benzene and concentrated to give the crude alkene-ester **16I** (8.6 g) as a brown semisolid which was used in the next step without further purification (same R_f).

The crude alkene-ester **16I** (8.6 g) obtained above was dissolved in a 5:1 mixture of CH_2Cl_2:MeOH (36 mL). An ozone stream was bubbled through this suspension at −78 °C until complete consumption of **16I** was observed by TLC analysis. Then Dimethyl sulfide (DMS) (4 mL) was added, and the reaction mixture was warmed to room temperature over four hours. The solvent was removed in vacuo and after evaporation of the solvent the residue was purified by flash column chromatography with ~15-20% EtOAc in *n*-hexane to afford (+)-**20** as colourless gel (6.2 g, 62%).



(1*R*,4a*S*,10a*R*)-**methyl 7-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**20**]: (+)-**20** was obtained as colorless gel (31.8 mmol scale of reaction; 62% yield). R_f = 0.35 (10% EtOAc in *n*-hexane).

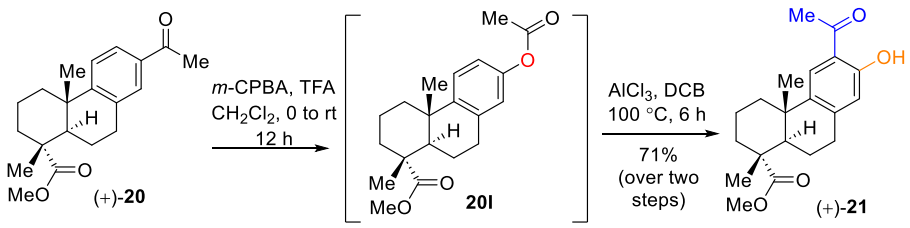
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 1H), 7.63 (dd, *J* = 2.0, 1.1 Hz, 1H), 7.32 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.67 (d, *J* = 1.3 Hz, 3H), 2.97 – 2.91 (m, 2H), 2.55 (s, 3H), 2.36 – 2.29 (m, 1H), 2.21 (dt, *J* = 12.5, 1.8 Hz, 1H), 1.90 – 1.70 (m, 4H), 1.70 – 1.62 (m, 1H), 1.53 – 1.42 (m, 2H), 1.28 (d, *J* = 1.3 Hz, 3H), 1.21 (d, *J* = 1.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 178.9, 155.0, 135.5, 134.6, 129.4, 125.9, 124.7, 52.1, 47.7, 44.6, 37.8, 37.8, 36.7, 30.0, 26.6, 24.9, 21.6, 18.6, 16.7.

IR (neat) υ_{max} 2932, 2872, 1780, 1674, 1602, 1451, 1232, 1206, 1155, 865 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{20}H_{26}O_3 + H]^+$ 315.1955, found 315.1945.

$[\alpha]_{589}^{20}$ = +112.2 (c = 0.1, $CHCl_3$).

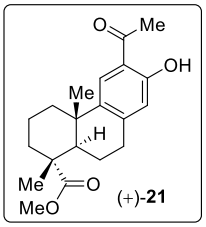
Synthesis of *o*-hydroxy Acetophenone (+)-21:



In an oven-dried round-bottom flask compound (+)-**20** (6.2 g, 19.7 mmol, 1.0 equiv.) was taken in 65 mL of DCM and *m*-CPBA (10.3 g, 59.1 mmol, 3 equiv.) was added at 0 ˚C. Then to the reaction mixture TFA (1.9 mL, 23.64 mmol, 1.2 equiv.) was added in a drop-wise manner at 0

°C. Then reaction mixture was run for 12 h at rt After completion of reaction monitored by TLC it was quenched with saturated aqueous $NaHCO_3$ solution. The reaction mixture was then partitioned between water and DCM. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product **20I** was charged for next step.

In an oven-dried round-bottom flask compound **20I** was taken in 55 mL of 1,2-dichloro benzene and anhydrous $AlCl_3$ (6.6 g, 49.25 mmol, 2.5 equiv.) was added at 25 ºC. Then reaction mixture was run at 100 °C for 4 h. After completion of reaction monitored by TLC, the reaction mixture was then partitioned between water and ethyl acetate. Finally, the crude products were purified by flash chromatography with 10% EtOAc in *n*-hexane to afford product (+)-**21** as yellow liquid (4.62 g, 71%).



(1*R*,4a*S*,10a*R*)-**methyl 6-acetyl-7-hydroxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**21**]: (+)-**21** was obtained as yellow liquid (19.7 mmol scale of reaction; 71% yield). R_f = 0.5 (10% EtOAc in *n*-hexane).

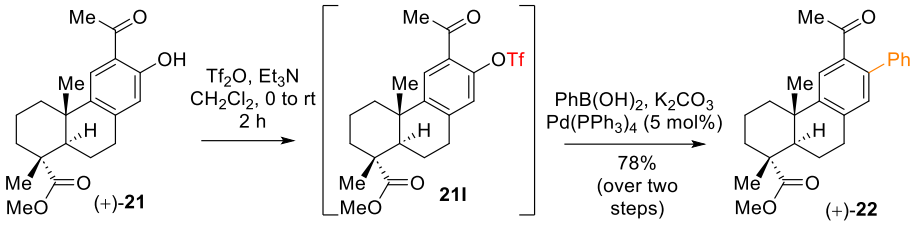
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.94 (s, 1H), 7.57 (s, 1H), 6.64 (s, 1H), 3.68 (s, 3H), 2.89 (dt, *J* = 8.6, 4.6 Hz, 2H), 2.60 (s, 3H), 2.33 – 2.29 (m, 1H), 2.17 (dd, *J* = 12.6, 2.4 Hz, 1H), 1.82 (d, *J* = 8.7 Hz, 1H), 1.79 (s, 1H), 1.75 (d, *J* = 11.3 Hz, 2H), 1.68 (d, *J* = 6.9 Hz, 1H), 1.51 (d, *J* = 12.1 Hz, 1H), 1.46 – 1.42 (m, 1H), 1.28 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 204.1, 179.0, 159.7, 146.0, 141.2, 126.4, 118.3, 117.6, 52.2, 47.6, 44.8, 38.4, 36.8, 36.8, 30.3, 26.6, 25.5, 21.3, 18.60, 16.6.

IR (neat) υ_{max} 3320, 2958, 2848, 2396, 1745, 1489, 1234, 1105, 956, 790, 737 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{20}H_{26}O_4 + H]^+$ 331.1909, found 331.1905.

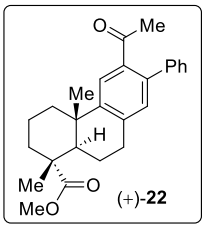
$[\alpha]^{25}_{589}$ = +35.6 (c = 0.2, $CHCl_3$).

Synthesis of Biaryl derivative (+)-22:



To a stirred solution of *ortho*-hydroxy acetophenone (+)-**21** (4.5 g, 13.62 mmol, 1.0 equiv.) in CH_2Cl_2 (36 mL) at 0 °C was added triethyl amine (2.8 mL, 20.43 mmol, 1.5 equiv.) and trifluoromethanesulfonic anhydride (2.8 mL, 15 mmol, 1.1 equiv.) consecutively dropwise over 5 min. Then the reaction was allowed to run at room temperature. After 6 h the reaction was quenched with water, extracted into CH_2Cl_2 (15 mL X 3) and the organic phase washed with 1 M hydrochloric acid (10 mL), water (5 mL) and brine (5 mL). The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent removed *in vacuo*. The crude product **21I** was charged for next step.

A sealed tube or a round-bottom flask equipped with reflux condenser with N_2 atmosphere was charged with K_2CO_3 (3.8 g, 27.24 mmol, 2.0 equiv.), Phenylboronic acid (2 g, 16.34 mmol, 1.2 equiv), compound **21I** and $Pd(PPh_3)_4$ (157 mg, 0.14 mmol, 0.01 equiv.), using a mixture of Benzene (12 mL), EtOH (6 mL) in H_2O (6 mL). The reaction mixture was heated at 100 °C (oil bath) with stirring for 8 h. The resulting mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 × 20 mL). The organic layer was dried (Na_2SO_4) and then filtered. The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography with 20% EtOAc in *n*-hexane to afford the product (+)-**22** as yellow foam (4.15 g, 78%).



(1*R*,4a*S*,10a*R*)-**methyl 6-acetyl-1,4a-dimethyl-7-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**22**]: (+)-**22** was obtained as yellow foam (13.62 mmol scale of reaction; 78% yield). R_f = 0.35 (10% EtOAc in *n*-hexane).

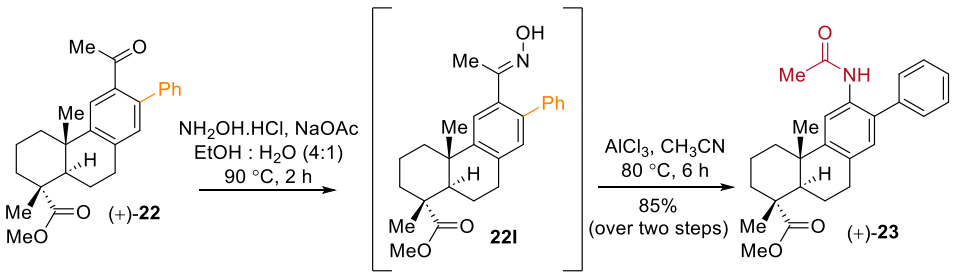
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.69 (s, 1H), 7.60 – 7.57 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 6.97 (s, 1H), 3.68 (s, 3H), 2.95 (dd, *J* = 8.8, 4.7 Hz, 2H), 2.60 (s, 3H), 2.34 (d, *J* = 13.1 Hz, 1H), 2.19 (dd, *J* = 12.5, 2.2 Hz, 1H), 1.86 – 1.82 (m, 1H), 1.79 – 1.74 (m, 3H), 1.70 (d, *J* = 2.9 Hz, 1H), 1.54 – 1.47 (m, 2H), 1.29 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 179.1, 149.1, 138.7, 138.6, 138.1, 131.1, 131.1, 129.0, 128.7, 127.7, 124.6, 52.1, 47.7, 44.8, 38.0, 37.4, 36.8, 30.6, 25.1, 21.5, 18.6, 16.6, 14.2.

IR (neat) υ_{max} 2958, 2848, 2369, 1710, 1489, 1234, 1112, 965, 786, 720 cm^{-1}.

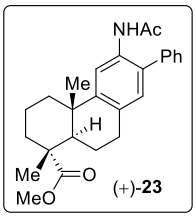
$[\alpha]_{589}^{25}$ = +46.5 (c = 0.5, $CHCl_3$).

Synthesis of Biaryl Acetanilide derivative (+)-**23:**



The ketone (+)-**22** (4.1 g, 10.5 mmol, 1.0 equiv.) was dissolved in EtOH (44 mL) in H_2O (11 mL). Sodium acetate (1.03 g, 12.6 mmol, 1.2 equiv.) and hydroxylamine hydrochloride (1.61 g, 23.1 mmol, 2.2 equiv.) were added before heating the mixture to reflux. After 1 h, the reaction was allowed to cool to ambient temperature and concentrated to dryness *in vacuo*. To the residue was added EtOAc (15 mL X 3) and washed with H_2O (10 mL X 2). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the crude product **22I**, which was used in the next reaction without further purification.

A mixture of oxime **22I** (1.0 equiv.) and anhydrous $AlCl_3$ (1.40 g, 10.5 mmol, 1.0 equiv.) in acetonitrile (40 mL) was stirred for 4 h at 80˚C under N_2. The mixture was evaporated under reduced pressure to dryness. The residue was washed with dichloromethane (25 mL X 2) and the mixture was evaporated under reduced pressure. Finally, the crude products were purified by flash chromatography with 60% EtOAc in *n*-hexane to afford product (+)-**23** as brown foam (3.62 g, 85%).



(1*R*,4a*S*,10a*R*)-**methyl 6-acetamido-1,4a-dimethyl-7-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**23**]: Following the general procedure (+)-**23** was obtained as brown foam (10.5 mmol scale of reaction; 85% yield). R_f = 0.2 (20% EtOAc in *n*-hexane).

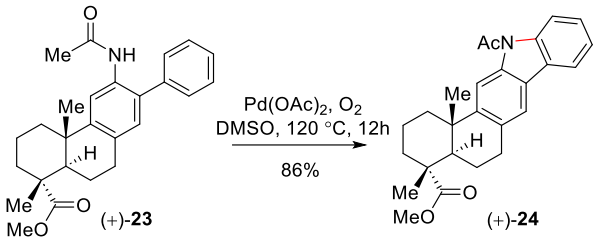
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.36 – 7.34 (m, 2H), 7.07 (s, 1H), 6.92 (s, 1H), 3.67 (s, 3H), 2.91 – 2.84 (m, 2H), 2.41 – 2.36 (m, 1H), 2.26 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.00 (s, 3H), 1.89 – 1.80 (m, 2H), 1.80 – 1.75 (m, 2H), 1.66 (d, *J* = 8.0 Hz, 1H), 1.56 (d, *J* = 4.6 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6, 168.6, 147.9, 138.4, 132.6, 131.5, 130.6, 130.2, 129.4, 129.1, 127.8, 118.2, 52.1, 47.8, 44.9, 38.1, 37.6, 36.8, 29.6, 25.1, 24.7, 21.8, 18.6, 16.7.

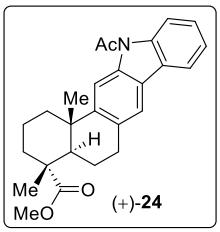
IR (neat) υ_{max} 2968, 1745, 1690, 1564, 1215 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{31}NO_3 + H]^+$ 406.2382, found 406.2387.

$[\alpha]_{589}^{25}$ = +76.2 (c = 0.6, $CHCl_3$).

Synthesis of Carbazole derivative (+)-**24:**



An oven-dried Schlenk tube was cooled under Ar. Biarylamide (+)-**23** (3.5 g, 8.63 mmol, 1.0 equiv.), $Pd(OAc)_2$ (387.5 mg, 1.73 mmol, 0.2 equiv.) were added under air. The tube was evacuated and refilled with Ar. Under a positive Ar pressure, DMSO (25 mL) was added *via* syringe. The reaction mixture was sonicated and degassed under a weak vacuum and refilled with O_2 from the double manifold (this sequence was carried out three times). The sealed Schlenk tube was lowered into an oil bath at 120 °C and stirred for 10 h. After cooling to room temperature, H_2O (15 mL) and EtOAc (45 mL) were added to reaction mixture. The organic phase was separated, and the aqueous phase was further extracted with EtOAc (10 mL X 2). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated. The residue was purified by silica gel chromatography with 15% EtOAc in *n*-hexane to afford the desired carbazole (+)-**24** as white foam (3 g, 86%).



(4*R*,4a*R*,13b*S*)-**methyl 12-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(+)-**24**]: (+)-**24** was obtained as white foam (8.63 mmol scale of reaction; 86% yield). R_f = 0.5 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.63 (s, 1H), 7.43 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.34 (td, *J* = 7.5, 1.0 Hz, 1H), 3.69 (s, 3H), 3.08 (dd, *J* = 8.8, 4.4 Hz, 2H), 2.87 (s, 3H), 2.47 (d, *J* = 12.7 Hz, 1H), 2.36 (d, *J* = 7.5 Hz,

1H), 2.32 (dd, *J* = 12.5, 2.4 Hz, 1H), 1.83 (d, *J* = 2.6 Hz, 1H), 1.81 – 1.80 (m, 1H), 1.69 (d, *J* = 7.4 Hz, 1H), 1.66 – 1.62 (m, 2H), 1.54 – 1.49 (m, 1H), 1.33 (s, 3H), 1.30 (s, 3H).

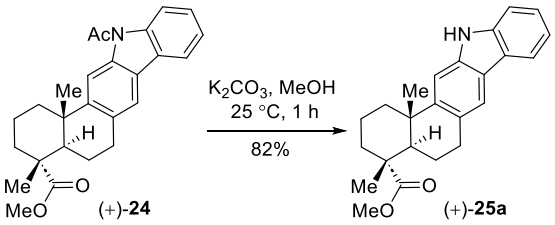
^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2,170.1, 149.8, 139.2, 137.8, 131.2, 127.0, 126.6, 124.4, 123.7, 119.8, 119.8, 116.2, 112.3, 52.2, 47.9, 45.1, 38.7, 38.3, 36.8, 30.0, 27.9, 25.6, 21.9, 18.8, 16.8.

IR (neat) υ_{max} 3437, 2906, 1746, 1651, 1446, 1225, 1023, 834, 714, 546 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{29}NO_3 + H]^+$ 404.2220, found 404.2224.

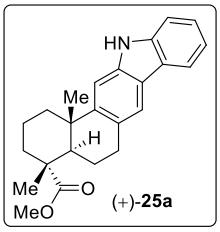
$[\alpha]^{25}_{589}$ = +68.6 (c = 0.3, $CHCl_3$).

Substrate (Regioisomeric deoxy-xiamycin derivatives) preparation for Oxidative Dimerization:

Deacetylation of Compound (+)-**24:**



In an oven-dried round-bottom flask (+)-**24** (2.9 g, 7.2 mmol, 1.0 equiv.) was dissolved in 30 mL of methanol. To the reaction mixture solid K_2CO_3 (2.0 g, 14.4 mmol, 2.0 equiv.) was added at 25 ºC and stirred for 1 h. After completion of the reaction (monitored by TLC) the reaction mixture was directly evaporated under reduced pressure. The mixture was then extracted with EtOAc (15 mL X 3). The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. Then the crude product was purified by flash chromatography with 20% EtOAc in *n*-hexane to afford (+)-**25a** as white foam (2.13 g, 82% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,13b-dimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(+)-**25a**]: (+)-**25a** was obtained as white foam (7.2 mmol scale of reaction; 82% yield). R_f = 0.7 (20% EtOAc in *n*-hexane).

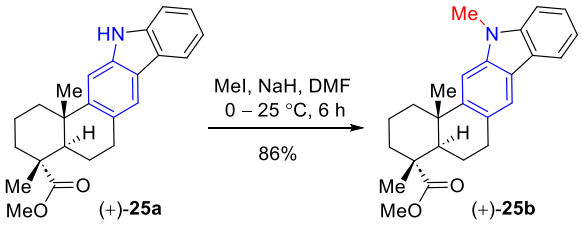
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.73 (s, 1H), 7.37 – 7.34 (m, 2H), 7.29 (s, 1H), 7.19 (td, *J* = 7.0, 6.2, 1.8 Hz, 1H), 3.70 (s, 3H), 3.15 – 3.10 (m, 2H), 2.44 – 2.39 (m, 1H), 2.36 (dd, *J* = 12.5, 2.5 Hz, 1H), 1.95 (ddd, *J* = 14.1, 8.6, 3.3 Hz, 1H), 1.86 – 1.81 (m, 2H), 1.80 – 1.76 (m, 1H), 1.70 (dt, *J* = 10.3, 2.5 Hz, 1H), 1.66 (q, *J* = 6.4, 5.3 Hz, 1H), 1.54 – 1.49 (m, 1H), 1.35 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 148.5, 140.3, 138.7, 126.6, 125.5, 123.3, 120.2, 120.2, 119.2, 110.5, 105.7, 52.1, 47.9, 45.1, 38.7, 38.0, 36.8, 30.1, 25.6, 22.1, 18.9, 16.8.

IR (neat) υ_{max} 3425, 2918, 1742, 1447, 1264, 1045, 814, 705, 593 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{24}H_{27}NO_2 + H]^+$ 362.2120, found 362.2115.

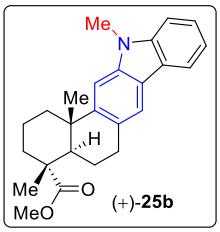
$[\alpha]_{589}^{25}$ = +38.3 (c = 0.7, $CHCl_3$).

Methylation of Carbazole derivative (+)-**25a:**



Carbazole (+)-**25a** (255 mg, 0.71 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium

hydride (56.8 mg, 1.42 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then iodomethane (67.2 µL, 1.07 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford (+)-**25b** as yellow foam (227.8 mg, 86% yield).



(4*R*,4a*R*,13b*S*)-**methyl 4,12,13b-trimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(+)-**25b**]: (+)-**25b** was obtained as yellow foam (0.71 mmol scale of reaction; 86% yield). R_f = 0.7 (10% EtOAc in *n*-hexane).

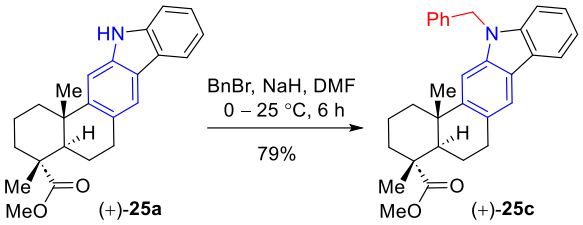
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 1H), 7.79 (s, 1H), 7.49 – 7.44 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.29 (s, 1H), 7.24 – 7.20 (m, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.21 – 3.11 (m, 2H), 2.60 – 2.47 (m, 1H), 2.41 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.24 – 2.04 (m, 1H), 2.04 – 1.94 (m, 1H), 1.89 (dd, *J* = 9.2, 2.4 Hz, 1H), 1.87 – 1.82 (m, 1H), 1.79 – 1.70 (m, 2H), 1.59 – 1.53 (m, 1H), 1.38 (d, *J* = 7.6 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 148.3, 141.7, 140.2, 12.0, 125.3, 122.6, 121.1, 120.2, 120.1, 118.5, 108.2, 103.4, 52.0, 47.9, 45.1, 38.8, 38.1, 36.8, 30.0, 29.1, 25.7, 22.1, 18.8, 16.8.

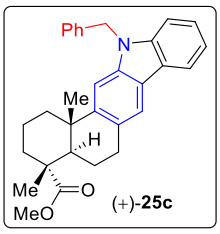
IR (neat) υ_{max} 3355, 2915, 1740, 1465, 1384, 1250, 1005, 853, 760, 647 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{25}H_{29}NO_2 + H]^+$ 376.2277, found 376.2190.

$[\alpha]_{589}^{25}$ = +36.6 (c = 1.5, $CHCl_3$).

Benzylation of Carbazole derivative (+)**-25a:**



Carbazole (+)-**25a** (230 mg, 0.64 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 5 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (51.2 mg, 1.28 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then benzyl bromide (114 µL, 0.96 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 4 h until the full consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (6 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford (+)-**25c** as colourless liquid (228.3 mg, 79% yield).



(4*R*,4a*R*,13b*S*)**-methyl 12-benzyl-4,13b-dimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(+)-**25c**]: (+)-**25c** was obtained as colourless liquid (0.64 mmol scale of reaction; 79% yield). R_f = 0.6 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 10.3 Hz, 2H), 7.31 (d, *J* = 4.6 Hz, 2H), 7.28 (d, *J* = 1.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 5.52 (s, 2H), 3.75 (s, 3H), 3.19 (ddd, *J* = 27.2, 8.3, 4.8 Hz, 2H), 2.52 – 2.38 (m, 2H), 2.05 – 1.96 (m, 1H), 1.92 – 1.83 (m, 2H), 1.80 (dt, *J* =

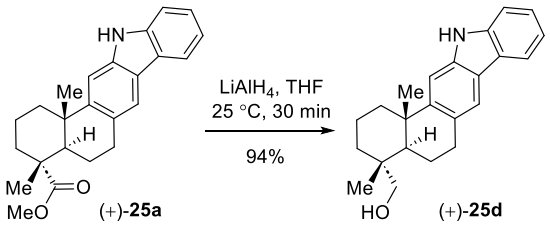
6.2, 3.0 Hz, 1H), 1.76 – 1.72 (m, 1H), 1.67 (dt, *J* = 12.0, 5.8 Hz, 1H), 1.60 – 1.54 (m, 1H), 1.39 (d, *J* = 2.0 Hz, 3H), 1.34 (d, *J* = 1.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 148.5, 141.3, 139.9, 137.5, 128.8, 127.4, 126.6, 126.6, 126.4, 125.5, 122.9, 121.4, 120.3, 118.9, 108.8, 103.9, 52.0, 47.9, 46.6, 45.0, 38.6, 38.1, 36.8, 30.1, 25.6, 22.1, 18.8, 16.8.

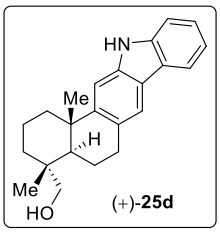
IR (neat) υ_{max} 3529, 2953, 1760, 1615, 1484, 1356, 1249, 1015, 932, 894, 762, 650 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{31}H_{33}NO_2 + H]^+$ 452.2589, found 452.2592.

$[\alpha]_{589}^{25}$ = +35.6 (c = 1.8, $CHCl_3$).

Procedure for the Synthesis of Alcohol (+)-**25d:**



To a stirred solution (+)-**25a** (222 mg, 0.61 mmol, 1 equiv.) in tetrahydrofuran (4 mL), lithium aluminum hydride (23.6 mg, 0.62 mmol, 1.01 equiv.) was added at 0 °C, and the reaction mixture was stirred for 30 min at 25 °C. Water (0.5 mL), 1M aq. NaOH (1 M, 1.0 mL), and distilled water (0.5 mL) was sequentially added at 0 °C and the resulting mixture was warmed to 25 °C. Dried over sodium sulfate and filtered over a pad of celite and washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel with ~20-30% EtOAc in *n*-hexane to provide compound (+)-**25d** as yellow foam (191.2 mg, 94%).



((4*R*,4a*R*,13b*S*)-**4,13b-dimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazol-4-yl)methanol** [(+)-**25d**]: (+)-**25d** was obtained as yellow foam (0.61 mmol scale of reaction; 94% yield). R_f = 0.4 (20% EtOAc in *n*-hexane).

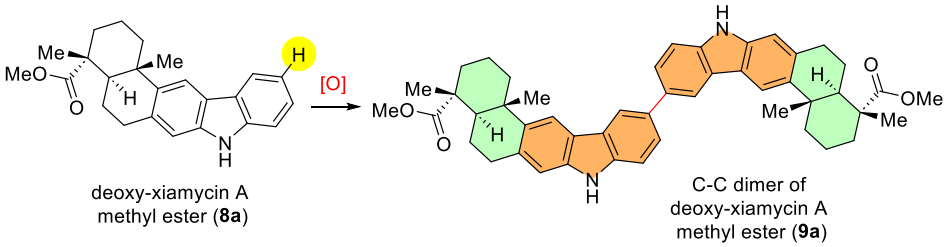
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 6.2 Hz, 1H), 7.73 (d, *J* = 4.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.28 (s, 1H), 7.20 (ddd, *J* = 8.0, 6.7, 1.4 Hz, 1H), 3.53 (dd, *J* = 14.3, 11.0 Hz, 1H), 3.27 (d, *J* = 10.9 Hz, 1H), 3.21 – 3.05 (m, 2H), 2.44 – 2.35 (m, 1H), 1.90 – 1.79 (m, 3H), 1.79 – 1.72 (m, 2H), 1.55 (dd, *J* = 13.1, 3.9 Hz, 1H), 1.50 (dd, *J* = 8.8, 4.0 Hz, 1H), 1.46 – 1.41 (m, 1H), 1.31 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 140.2, 138.7, 126.7, 125.4, 123.3, 121.5, 120.2, 120.0, 119.1, 110.5, 105.8, 72.3, 44.0, 39.2, 38.4, 38.1, 35.2, 30.1, 25.7, 19.3, 18.9, 17.6.

IR (neat) υ_{max} 3662, 3353, 1754, 1456, 1261, 1076, 841, 702, 642 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{23}H_{27}NO + H]^+$ 334.2171, found 334.2172.

$[\alpha]_{589}^{25}$ = +21.9 (c = 0.9, $CHCl_3$).

Dimerizing optimization:



deoxy-xiamycin A methyl ester (**8a**)

C-C dimer of deoxy-xiamycin A methyl ester (**9a**)

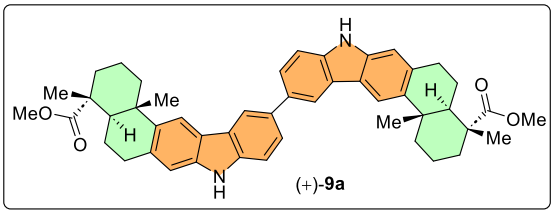
entry	oxidant	additive	solvent	temp	time	yield **9a** (%)
1	$PhI(OCOCF_3)_2$	–	CH_2Cl_2	25 °C	12 h	*NR*
2	$FeCl_3$	–	$CHCl_3$	25 °C	6 h	< 8%
3	DDQ	MsOH	$CHCl_3$	25 °C	6 h	< 15%
4	CAN	–	H_2O	25 °C	12 h	*NR*
5	$AgSbF_6$	TTBP	$(CH_2Cl)_2$	25 °C	2 h	---
6	$PhI(OCOCF_3)_2$	Et_3N	$(CH_2Cl)_2$	0 °C	6 h	*NR*
7	$PhI(OCOCF_3)_2$	$BF_3.OEt_2$	CH_2Cl_2	0 °C	2 h	27
8	$PhI(OCOCF_3)_2$	$BF_3.OEt_2$	CH_2Cl_2	–40 °C	2 h	43
9	**$PhI(OCOCF_3)_2$**	**$BF_3.OEt_2$**	**CH_2Cl_2**	**–78 °C**	**2 h**	**77**
10	$PhI(OCOCF_3)_2$	$BF_3.OEt_2$	HFIP	–78 °C	2 h	64
11	$PhI(OCOCF_3)_2$	BBr_3	CH_2Cl_2	–78 °C	2 h	36
12	$PhI(OCOCF_3)_2$	TMSI	CH_2Cl_2	–78 °C	2 h	55
13	$PhI(OCOCF_3)_2$	$BF_3.OEt_2$	CH_2Cl_2	–78 °C	2 h	31[c]
14	$PhI(OCOCH_3)_2$	$BF_3.OEt_2$	CH_2Cl_2	–78 °C	2 h	62
15	PhIO	$BF_3.OEt_2$	CH_2Cl_2	–78 °C	2 h	< 5%

Table 1. Optimization of reaction conditions for oxidative dimerization of indolosesquiterpenoids. [a] Yield of the isolated product. [b] All reactions were performed on 0.15 mmol scale, oxidant was 1.0 equiv., additive was 1.0 equiv. [c] The catalytic amount of PIFA was 50 mol %. MsOH: methanesulfonic acid; TTBP: 2,4,6-tri-*tert*-butyl-4-methylpyrimidine; CAN: ceric ammonium nitrate; TMSI: iodotrimethylsilane.

General procedure for the Hypervalent Iodine (PIFA)-mediated oxidative dimerization reaction

To a stirred solution of monomeric indolosesquiterpenoids (0.55 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL), PIFA (0.55 mmol, 1.0 equiv.) and $BF_3.OEt_2$ (0.55 mmol, 1.0 equiv.) were quickly added at –78 °C. The reaction mixture was then stirred for 2 hours, while the reaction temperature was maintained at –78 °C. After the reaction completion, saturated aqueous $NaHCO_3$ (ca. 20 mL) was added to the mixture, and then stirred for an additional 10 minutes at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined extract was dried with Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (SiO_2 (neutral)/*n*-hexane-AcOEt) to give C-C dimeric indolosesquiterpenoids.

Substrate Scope of Indolosesquiterpenoids:



(+)-**9a**

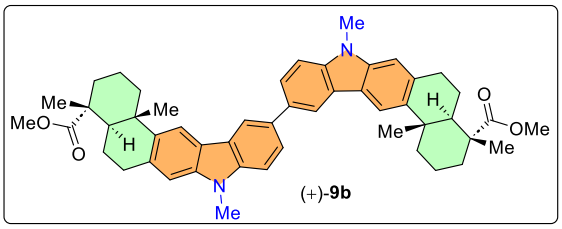
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9a**]: Following the general procedure (+)-**9a** was obtained as yellow amorphous (0.55 mmol scale of reaction; 77% yield). R_f = 0.25 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 10.88 (s, 1H), 8.48 (s, 1H), 8.14 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.46 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.08 (s, 1H), 3.61 (s, 3H), 3.06 (dd, *J* = 17.3, 7.0 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.63 (d, *J* = 12.4 Hz, 1H), 2.15 (d, *J* = 12.3 Hz, 1H), 1.86 (t, *J* = 10.0 Hz, 1H), 1.76 – 1.69 (m, 3H), 1.61 (d, *J* = 11.8 Hz, 1H), 1.51 (t, *J* = 12.7 Hz, 1H), 1.37 (t, *J* = 10.2 Hz, 1H), 1.24 (s, 6H).

^{13}C NMR (125 MHz, DMSO) δ 178.2, 140.8, 139.2, 138.8, 132.7, 131.9, 124.2, 123.6, 121.4, 117.7, 115.6, 110.8, 109.9, 51.8, 47.0, 45.2, 38.6, 37.0, 36.4, 30.1, 25.4, 21.3, 18.2, 16.4.

IR (neat) υ_{max} 3400, 2950, 1720, 1456, 1243, 1010, 823, 750, 582 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{48}H_{52}N_2O_4 + H]^+$ 721.4005, found 721.3997.

$[\alpha]_{589}^{25}$ = +150.8 (c = 1.1, $CHCl_3$).



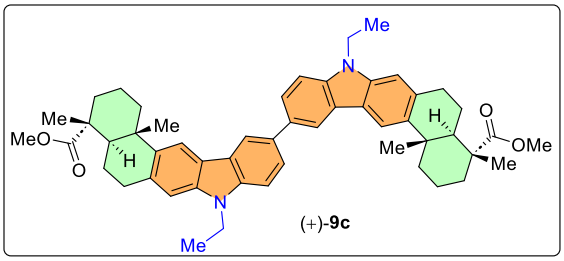
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)**-dimethyl 4,4',8,8',13b,13'b-hexamethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9b**]: Following the general procedure (+)-**9b** was obtained as yellow amorphous (0.55 mmol scale of reaction; 85% yield). R_f = 0.3 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 8.57 (s, 1H), 8.21 (s, 1H), 7.86 – 7.83 (m, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.18 (s, 1H), 3.82 (s, 3H), 3.64 (s, 3H), 3.13 (dd, *J* = 17.2, 6.8 Hz, 1H), 3.05 (q, *J* = 8.6, 8.1 Hz, 1H), 2.66 (d, *J* = 12.8 Hz, 1H), 2.18 (dd, *J* = 12.5, 2.5 Hz, 1H), 1.89 (dd, *J* = 11.8, 7.5 Hz, 1H), 1.83 (d, *J* = 14.6 Hz, 1H), 1.73 (d, *J* = 13.0 Hz, 2H), 1.63 (d, *J* = 10.6 Hz, 1H), 1.52 (t, *J* = 13.4 Hz, 1H), 1.41 (t, *J* = 9.9 Hz, 1H), 1.27 (d, *J* = 4.8 Hz, 6H).

^{13}C NMR (125 MHz, DMSO) δ 178.1, 141.0, 140.1, 139.7, 133.0, 131.8, 124.2, 123.1, 120.9, 117.7, 115.8, 109.0, 108.1, 79.1, 51.8, 47.0, 45.2, 37.0, 36.3, 30.3, 28.9, 25.4, 21.3, 18.2, 16.4.

IR (neat) υ_{max} 3415, 2962, 1752, 1457, 1353, 1258, 1035, 835, 756, 694 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{50}H_{56}N_2O_4]^+$ 748.4240, found 748.4215.

$[\alpha]_{589}^{25}$ = +102.5 (c = 0.6, $CHCl_3$).



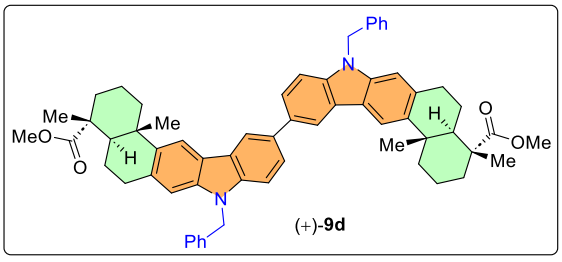
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 8,8'-diethyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9c**]: Following the general procedure (+)-**9c** was obtained as colourless liquid (0.55 mmol scale of reaction; 82% yield). R_f = 0.65 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.29 (m, 1H), 8.09 (d, *J* = 3.7 Hz, 1H), 7.79 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.08 (s, 1H), 4.35 (s, 2H), 3.70 (s, 3H), 3.23 – 3.13 (m, 2H), 2.63 (d, *J* = 11.9 Hz, 1H), 2.47 (dd, *J* = 12.9, 2.3 Hz, 1H), 2.39 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.85 (dd, *J* = 10.8, 7.4 Hz, 2H), 1.71 (d, *J* = 9.2 Hz, 2H), 1.55 – 1.50 (m, 1H), 1.48 – 1.45 (m, 3H), 1.36 (d, *J* = 2.0 Hz, 3H), 1.35 (d, *J* = 2.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 131.3, 125.1, 124.4, 123.9, 122.2, 121.8, 120.9, 119.0, 118.7, 115.9, 115.9, 108.5, 52.1, 47.9, 45.4, 39.1, 37.6, 37.6, 36.9, 31.1, 25.9, 22.1, 18.9, 16.8, 16.6.

IR (neat) υ_{max} 3320, 2840, 1762, 1650, 1465, 1345, 1247, 1032, 867, 750, 669 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{52}H_{60}N_2O_4]^+$ 776.4553, found 776.4553.

$[\alpha]_{589}^{25}$ = +63.9 (c = 0.4, $CHCl_3$).



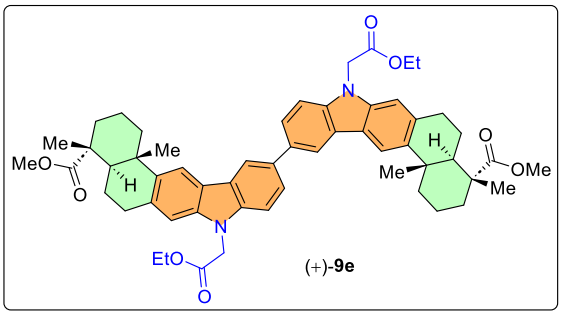
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 8,8'-dibenzyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9d**]: Following the general procedure (+)-**9d** was obtained as yellow foam (0.55 mmol scale of reaction; 76% yield). R_f = 0.25 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.10 (s, 1H), 7.72 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.22 – 7.20 (m, 2H), 7.02 (s, 1H), 5.47 (s, 2H), 3.68 (s, 3H), 3.14 – 3.07 (m, 2H), 2.62 (d, *J* = 12.5 Hz, 1H), 2.36 (dd, *J* = 12.6, 2.4 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.87 – 1.80 (m, 3H), 1.70 (d, *J* = 11.1 Hz, 2H), 1.51 – 1.46 (m, 1H), 1.35 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 141.9, 140.4, 140.0, 137.7, 134.0, 128.9, 128.2, 127.5, 126.7, 125.3, 124.1, 121.9, 118.7, 115.8, 109.0, 108.4, 52.0, 47.9, 46.8, 45.4, 39.1, 37.7, 36.9, 31.0, 25.9, 22.0, 18.9, 16.8.

IR (neat) υ_{max} 3450, 2924, 1751, 1620, 1476, 1359, 1258, 1025, 924, 856, 762, 685 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{62}H_{64}N_2O_4 + H]^+$ 901.4944, found 901.4921.

$[\alpha]_{589}^{25}$ = +98.8 (c = 0.5, $CHCl_3$).



(+)-**9e**

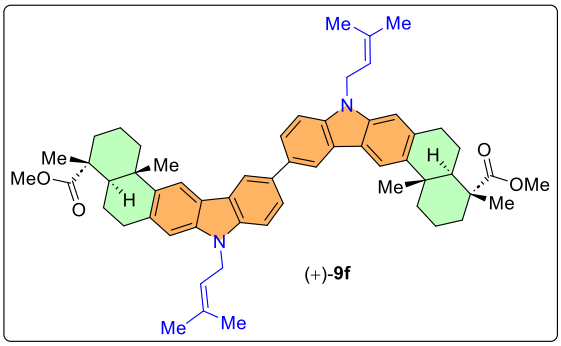
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 8,8'-bis(2-ethoxy-2-oxoethyl)-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9e**]: Following the general procedure (+)-**9e** was obtained as yellow liquid (0.55 mmol scale of reaction; 57% yield). R_f = 0.25 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.8 Hz, 1H), 8.07 (s, 1H), 7.76 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.00 (s, 1H), 4.95 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 3.17 – 3.13 (m, 2H), 2.62 (d, *J* = 12.6 Hz, 1H), 2.36 (dd, *J* = 12.5, 2.3 Hz, 1H), 1.96 (ddd, *J* = 12.2, 9.0, 3.3 Hz, 1H), 1.85 (d, *J* = 12.1 Hz, 2H), 1.81 (s, 1H), 1.73 – 1.69 (m, 2H), 1.54 – 1.49 (m, 1H), 1.34 (d, *J* = 2.2 Hz, 6H), 1.28 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 168.9, 142.2, 140.2, 139.8, 134.1, 134.0, 125.4, 124.3, 122.0, 118.8, 116.0, 108.5, 108.0, 61.8, 52.1, 47.9, 45.3, 45.0, 39.0, 37.6, 36.9, 31.0, 25.9, 22.0, 18.9, 16.8, 14.3.

IR (neat) υ_{max} 3360, 2946, 1768, 1632, 1456, 1163, 1002, 943, 872, 790, 635 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{56}H_{64}N_2O_8 + H]^+$ 893.4741, found 893.4727.

$[\alpha]_{589}^{25}$ = +76.1 (c = 0.2, $CHCl_3$).



(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',13b,13'b-tetramethyl-8,8'-bis(3-methylbut-2-en-1-yl)-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9f**]: Following the general procedure (+)-**9f** was obtained as yellow liquid (0.55 mmol scale of reaction; 48% yield). R_f = 0.5 (5% EtOAc in *n*-hexane).

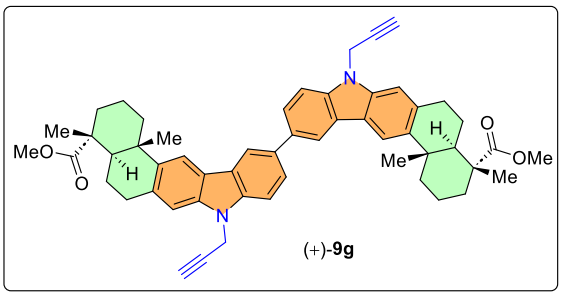
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.08 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 5.31 (d, *J* = 6.7 Hz, 1H), 4.86 (d, *J* = 6.3 Hz, 2H), 3.69 (s, 3H), 3.16 (d, *J* = 7.8 Hz, 2H), 2.62 (d, *J* = 12.6 Hz, 1H), 2.38 (d, *J* = 12.3 Hz, 1H), 1.95 (s, 3H), 1.87 –

1.84 (m, 2H), 1.73 (s, 3H), 1.69 (d, *J* = 5.3 Hz, 2H), 1.57 (d, *J* = 6.7 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 1H), 1.35 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 141.4, 139.9, 139.5, 135.0, 133.6, 133.5, 125.1, 124.0, 121.9, 120.4, 118.6, 115.8, 108.8, 108.3, 52.1, 47.9, 45.4, 41.3, 39.1, 37.6, 36.9, 31.1, 25.9, 25.8, 22.1, 18.9, 18.4, 16.8.

IR (neat) υ_{max} 3325, 2946, 1765, 1632, 1442, 1247, 1046, 900, 852, 790, 656 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{58}H_{68}N_2O_4 + H]^+$ 857.5258, found 857.5268.

$[\alpha]_{589}^{25}$ = +101.7 (c = 0.2, $CHCl_3$).



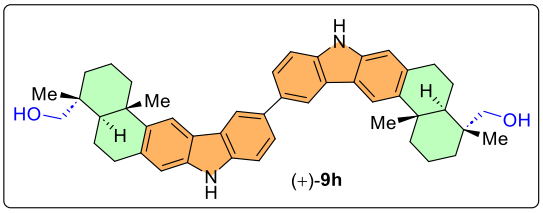
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',13b,13'b-tetramethyl-8,8'-di(prop-2-yn-1-yl)-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9g**]: Following the general procedure (+)-**9g** was obtained as yellow liquid (0.55 mmol scale of reaction; 56% yield). R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.8 Hz, 1H), 8.08 (s, 1H), 7.80 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.15 (s, 1H), 5.00 (d, *J* = 2.5 Hz, 2H), 3.70 (s, 3H), 3.21 – 3.17 (m, 2H), 2.62 (d, *J* = 12.3 Hz, 1H), 2.37 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.28 (t, *J* = 2.4 Hz, 1H), 2.00 – 1.94 (m, 1H), 1.87 – 1.83 (m, 2H), 1.83 – 1.80 (m, 1H), 1.73 – 1.69 (m, 2H), 1.53 (ddd, *J* = 12.8, 5.3, 2.8 Hz, 1H), 1.35 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 142.2, 139.5, 139.1, 134.1, 134.0, 125.4, 124.3, 122.1, 118.8, 116.0, 108.9, 108.3, 78.3, 72.3, 52.1, 47.9, 45.3, 39.0, 37.6, 36.9, 32.5, 31.0, 25.9, 22.0, 18.9, 16.8.

IR (neat) υ_{max} 3466, 2952, 1865, 1665, 1465, 1274, 1064, 965, 867, 778, 643 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{54}H_{56}N_2O_4 + H]^+$ 797.4318, found 797.4338.

$[\alpha]^{25}_{589}$ = +109.7 (c = 0.6, $CHCl_3$).



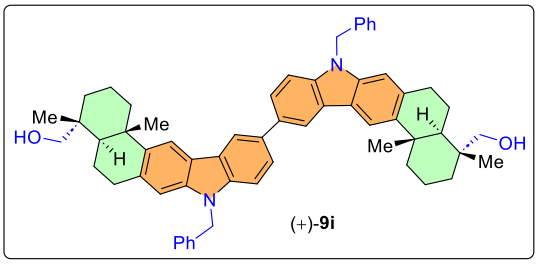
((4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)**-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-diyl)dimethanol** [(+)**-9h**]: Following the general procedure (+)**-9h** was obtained as white amorphous (0.55 mmol scale of reaction; 62% yield). R_f = 0.2 (50% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 10.84 (s, 1H), 8.47 (s, 1H), 8.13 (s, 1H), 7.74 – 7.70 (m, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.07 (s, 1H), 4.50 (t, *J* = 5.6 Hz, 2H), 3.04 – 3.02 (m, 1H), 2.98 – 2.94 (m, 1H), 2.59 (d, *J* = 12.7 Hz, 1H), 1.82 (d, *J* = 8.4 Hz, 2H), 1.71 (s, 1H), 1.68 (s, 2H), 1.54 (t, *J* = 12.6 Hz, 2H), 1.39 (d, *J* = 11.9 Hz, 1H), 1.25 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (125 MHz, DMSO) δ 141.4, 139.1, 138.6, 133.4, 131.8, 124.0, 123.7, 121.2, 117.6, 115.6, 110.8, 109.8, 70.0, 43.3, 39.9, 39.8, 37.6, 37.4, 35.0, 30.3, 25.8, 18.5, 17.6.

IR (neat) υ_{max} 3590, 3317, 1720, 1476, 1243, 1056, 885, 776, 582 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{46}H_{52}N_2O_2 + H]^+$ 665.4107, found 665.4093.

$[\alpha]^{25}_{589}$ = +99.3 (c = 0.3, $CHCl_3$).



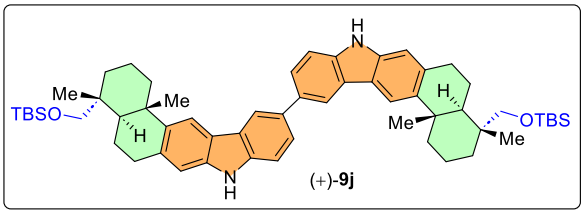
((4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**8,8'-dibenzyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-diyl)dimethanol** [(+)-**9i**]: Following the general procedure (+)-**9i** was obtained as white amorphous (0.55 mmol scale of reaction; 54% yield). R_f = 0.4 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.31 (m, 1H), 8.11 (d, *J* = 3.9 Hz, 1H), 7.72 (dt, *J* = 11.1, 9.1 Hz, 1H), 7.43 (dd, *J* = 8.6, 4.5 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.21 – 7.19 (m, 2H), 7.03 (d, *J* = 4.2 Hz, 1H), 5.47 (s, 2H), 3.51 (d, *J* = 10.9 Hz, 1H), 3.26 (d, *J* = 11.0 Hz, 1H), 3.10 (q, *J* = 8.8, 7.4 Hz, 2H), 2.60 (d, *J* = 11.9 Hz, 1H), 1.88 – 1.84 (m, 2H), 1.79 – 1.74 (m, 2H), 1.62 (h, *J* = 6.3, 4.6 Hz, 2H), 1.52 – 1.47 (m, 2H), 1.35 (d, *J* = 1.6 Hz, 3H), 0.95 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.3, 139.9, 137.7, 134.1, 133.6, 128.9, 127.5, 127.5, 126.7, 126.6, 125.6, 125.2, 125.1, 124.5, 124.1, 122.9, 122.1, 121.8, 121.7, 121.0, 118.7, 115.9, 109.0, 108.7, 108.3, 72.4, 46.8, 44.4, 44.3, 44.1, 39.5, 39.5, 38.1, 38.1, 38.0, 38.0, 37.8, 35.4, 32.1, 31.1, 29.8, 29.8, 26.0, 22.8, 19.3, 19.0, 17.6, 17.6.

IR (neat) υ_{max} 3634, 3337, 1765, 1415, 1220, 1085, 965, 720, 628 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{60}H_{64}N_2O_2]^+$ 844.4968, found 844.4971.

$[\alpha]_{589}^{25}$ = +42.8 (c = 0.2, $CHCl_3$).



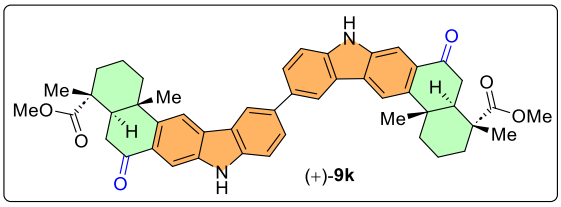
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**4,4'-bis(((tert-butyldimethylsilyl)oxy)methyl)-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-11,11'-binaphtho[2,1-b]carbazole** [(+)-**9j**]: Following the general procedure (+)-**9j** was obtained as yellow amorphous (0.55 mmol scale of reaction; 61% yield). R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.9 Hz, 1H), 8.08 (s, 1H), 7.79 (s, 1H), 7.72 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.09 (s, 1H), 3.47 (d, *J* = 9.6 Hz, 1H), 3.13 (d, *J* = 9.6 Hz, 1H), 3.11 – 3.06 (m, 2H), 2.57 (d, *J* = 12.6 Hz, 1H), 1.89 (dd, *J* = 12.4, 2.3 Hz, 2H), 1.84 (dq, *J* = 9.3, 4.9, 4.2 Hz, 2H), 1.79 – 1.73 (m, 2H), 1.60 (ddd, *J* = 11.6, 7.2, 4.1 Hz, 2H), 1.34 (s, 3H), 0.89 (s, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 139.2, 138.6, 134.4, 133.9, 125.2, 124.6, 122.3, 118.6, 116.0, 110.6, 110.1, 72.0, 44.1, 39.6, 38.3, 38.1, 35.6, 31.4, 26.4, 26.1, 19.2, 19.2, 18.5, 17.8, -5.4, -5.4.

IR (neat) υ_{max} 2945, 1712, 1556, 1354, 1058, 965, 823, 702, 692 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{58}H_{80}N_2O_2Si_2 + H]^+$ 893.5837, found 893.5852.

$[\alpha]_{589}^{25}$ = +125.5 (c = 0.2, $CHCl_3$).



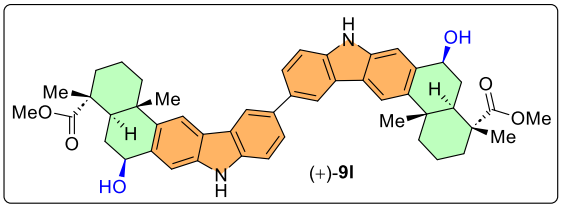
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',13b,13'b-tetramethyl-6,6'-dioxo-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9k**]: Following the general procedure (+)-**9k** was obtained as yellow amorphous (0.55 mmol scale of reaction; 41% yield). R_f = 0.25 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 11.43 (s, 1H), 8.72 (s, 1H), 8.40 (s, 1H), 8.02 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 3.63 (s, 3H), 2.89 (dd, *J* = 17.6, 14.2 Hz, 1H), 2.73 (d, *J* = 12.5 Hz, 1H), 2.64 (dd, *J* = 14.1, 3.2 Hz, 1H), 2.24 – 2.18 (m, 1H), 1.87 (t, *J* = 13.5 Hz, 1H), 1.79 (d, *J* = 14.0 Hz, 2H), 1.70 (d, *J* = 12.8 Hz, 2H), 1.33 (d, *J* = 4.4 Hz, 6H).

^{13}C NMR (125 MHz, DMSO) δ 197.4, 177.4, 146.2, 141.0, 138.2, 132.2, 128.2, 127.7, 126.6, 122.7, 119.2, 115.4, 111.6, 109.1, 52.1, 46.2, 44.2, 37.7, 37.7, 37.4, 36.3, 24.2, 17.8, 16.2.

IR (neat) υ_{max} 3552, 2944, 1640, 1460, 1476, 1172, 832, 776, 675 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{48}H_{48}N_2O_6 + H]^+$ 749.3591, found 749.3583.

$[\alpha]_{589}^{25}$ = +9.7 (c = 0.5, MeOH).



(4*R*,4a*R*,4'*R*,4'a*R*,6*S*,6'*S*,13b*S*,13'b*S*)-**dimethyl 6,6'-dihydroxy-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**9l**]: Following the general procedure (+)-**9l** was obtained as white amorphous (0.55 mmol scale of reaction; 34% yield). R_f = 0.5 (70% EtOAc in *n*-hexane).

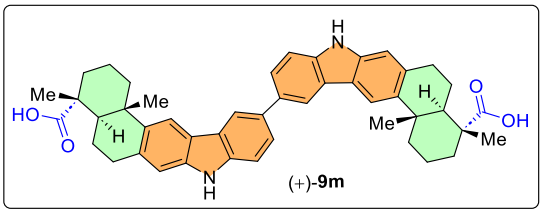
^{1}H NMR (500 MHz, CD_3OD) δ 8.65 (s, 1H), 7.87 – 7.86 (m, 1H), 7.84 (s, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 4.91 (s, 1H), 3.68 (s, 3H), 2.19 (d, *J* = 12.4 Hz, 2H), 1.90 – 1.83 (m, 1H), 1.72 – 1.65 (m, 2H), 1.55 (d, *J* = 14.3 Hz, 1H), 1.51 – 1.46 (m, 2H), 1.41 – 1.35 (m, 1H), 1.24 (s, 3H), 1.15 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 180.6, 142.0, 141.4, 140.7, 137.6, 134.7, 126.3, 125.2, 124.4, 119.3, 116.5, 111.9, 110.2, 72.0, 52.5, 45.2, 39.9, 39.1, 37.7, 33.7, 33.1, 30.7, 26.5, 17.0.

IR (neat) υ_{max} 3614, 3198, 2855, 1743, 1695, 1565, 1430, 1376, 1169, 845 cm^{-1}.

HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{48}H_{52}N_2O_6]^+$ 752.3825, found 752.4019.

$[\alpha]^{25}_{589}$ = +64.5 (c = 0.2, MeOH).



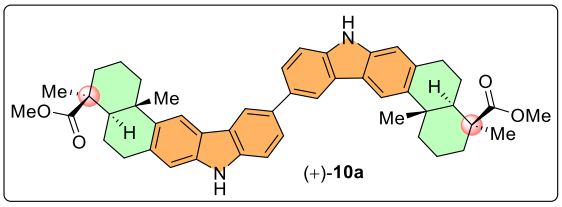
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylic acid** [(+)-**9m**]: Following the general procedure (+)-**9m** was obtained as yellow amorphous (0.55 mmol scale of reaction; 59% yield). R_f = 0.2 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 12.15 (s, 1H), 10.89 (s, 1H), 8.50 (d, *J* = 1.9 Hz, 1H), 8.16 (s, 1H), 7.75 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.11 (s, 1H), 3.10 (dd, *J* = 16.9, 6.8 Hz, 1H), 3.01 (dt, *J* = 17.5, 9.1 Hz, 1H), 2.68 – 2.64 (m, 1H), 2.18 (dd, *J* = 12.4, 2.4 Hz, 1H), 1.88 (dd, *J* = 11.7, 7.3 Hz, 1H), 1.86 – 1.80 (m, 1H), 1.76 (s, 1H), 1.74 (d, *J* = 4.3 Hz, 1H), 1.66 – 1.62 (m, 1H), 1.55 – 1.48 (m, 2H), 1.27 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (125 MHz, DMSO) δ 179.5, 140.9, 139.1, 138.7, 132.8, 131.9, 124.1, 123.6, 121.4, 117.7, 115.6, 110.8, 109.9, 46.4, 45.0, 38.7, 37.0, 36.4, 30.2, 25.5, 21.4, 18.3, 16.5.

IR (neat) υ_{max} 3016, 2857, 2378, 1779, 1487, 1256, 1145, 937, 776 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{46}H_{48}N_2O_4 + H]^+$ 693.3693, found 693.3685.

$[\alpha]^{25}_{589}$ = +77.9 (c = 0.2, MeOH).



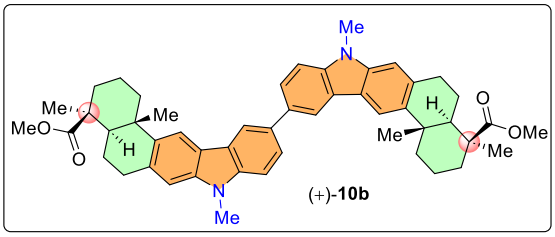
(4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**10a**]: Following the general procedure (+)-**10a** was obtained as brown amorphous (0.55 mmol scale of reaction; 75% yield). R_f = 0.45 (30% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.31 (d, *J* = 17.0 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.84 (s, 1H), 7.78 – 7.70 (m, 2H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.28 (s, 1H), 7.06 (d, *J* = 4.9 Hz, 1H), 3.72 – 3.69 (m, 6H), 3.37 (td, *J* = 13.6, 13.1, 6.9 Hz, 1H), 3.13 – 2.97 (m, 2H), 2.56 (dd, *J* = 10.2, 6.6 Hz, 1H), 2.47 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.41 – 2.38 (m, 1H), 2.33 (dd, *J* = 13.5, 3.5 Hz, 2H), 2.29 – 2.23 (m, 1H), 2.19 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.13 – 2.04 (m, 3H), 1.75 (s, 3H), 1.71 – 1.63 (m, 3H), 1.56 (td, *J* = 13.1, 3.7 Hz, 1H), 1.50 – 1.41 (m, 2H), 1.35 (d, *J* = 4.8 Hz, 3H), 1.33 (s, 3H), 1.18 (s, 3H), 1.18 (d, *J* = 1.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 140.5, 139.7, 139.2, 139.0, 138.7, 137.9, 134.3, 131.5, 131.5, 125.1, 124.9, 124.3, 124.1, 122.5, 122.1, 121.8, 121.3, 121.2, 118.9, 117.2, 110.7, 110.6, 110.0, 108.6, 53.5, 52.8, 51.4, 44.3, 44.2, 40.5, 38.9, 38.6, 37.9, 37.8, 33.2, 31.1, 29.8, 28.8, 28.8, 28.7, 24.1, 23.2, 21.5, 20.9, 20.3.

IR (neat) υ_{max} 3487, 2950, 1776, 1456, 1243, 1068, 823, 735, 579 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{48}H_{52}N_2O_4 + H]^+$ 721.4005, found 721.3986.

$[\alpha]^{25}_{589}$ = +302.3 (c = 0.2, $CHCl_3$).



(4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',8,8',13b,13'b-hexamethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-**

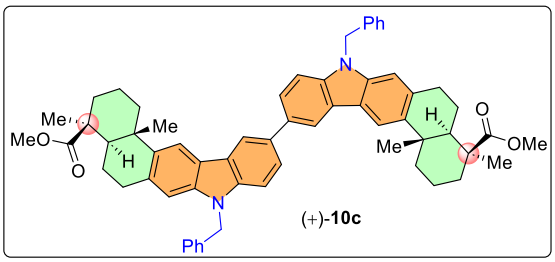
b]carbazole]-4,4'-dicarboxylate [(+)-**10b**]: Following the general procedure (+)-**10b** was obtained as yellow foam (0.55 mmol scale of reaction; 82% yield). R_f = 0.6 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 2H), 7.81 (s, 4H), 7.49 (d, *J* = 1.8 Hz, 2H), 7.47 (d, *J* = 1.9 Hz, 2H), 3.71 (s, 3H), 3.71 (s, 3H), 3.70 (s, 6H), 3.19 (dd, *J* = 16.6, 5.2 Hz, 2H), 3.10 (d, *J* = 13.2 Hz, 2H), 2.59 (d, *J* = 13.2 Hz, 2H), 2.48 (td, *J* = 8.5, 7.6, 4.0 Hz, 2H), 2.41 (d, *J* = 12.8 Hz, 2H), 2.36 – 2.32 (m, 4H), 2.12 – 2.09 (m, 3H), 1.76 – 1.74 (m, 2H), 1.70 (d, *J* = 10.4 Hz, 3H), 1.34 (s, 3H), 1.19 (s, 3H), 1.19 (d, *J* = 1.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 140.7, 140.4, 139.8, 139.1, 131.6, 124.9, 124.3, 124.3, 123.8, 123.6, 122.1, 121.9, 121.8, 120.6, 118.8, 117.3, 117.3, 108.5, 108.3, 107.9, 106.5, 53.5, 52.9, 51.4, 44.3, 44.2, 38.9, 38.6, 37.9, 37.8, 33.4, 32.1, 31.1, 31.1, 29.8, 28.8, 28.8, 28.7, 24.0, 23.2, 22.8, 21.5, 20.9, 20.3.

IR (neat) υ_{max} 3322, 2965, 1749, 1456, 1345, 1285, 1013, 853, 760, 688 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{50}H_{56}N_2O_4]^+$ 748.4240, found 748.4255.

$[\alpha]_{589}^{25}$ = +97.9 (c = 0.5, $CHCl_3$).



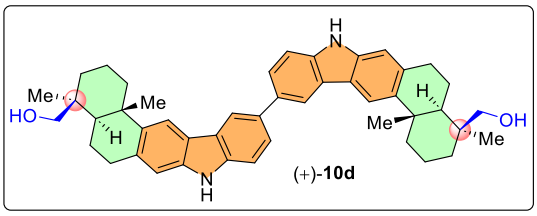
(4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 8,8'-dibenzyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**10c**]: Following the general procedure (+)-**10c** was obtained as yellow gel (0.55 mmol scale of reaction; 69% yield). R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.48 (m, 1H), 8.39 – 8.33 (m, 1H), 8.14 (d, *J* = 1.7 Hz, 1H), 7.76 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.9, 3.1 Hz, 2H), 7.39 – 7.37 (m, 1H), 7.30 (d, *J* = 1.7 Hz, 1H), 7.29 – 7.28 (m, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.23 – 7.22 (m, 1H), 7.21 (d, *J* = 1.9 Hz, 2H), 7.20 – 7.19 (m, 2H), 7.03 (d, *J* = 6.9 Hz, 1H), 5.52 (d, *J* = 3.5 Hz, 2H), 5.46 (d, *J* = 5.8 Hz, 2H), 3.71 (d, *J* = 1.5 Hz, 3H), 3.70 (s, 3H), 3.40 (td, *J* = 11.7, 6.1 Hz, 1H), 3.13 – 3.08 (m, 1H), 3.03 (dq, *J* = 11.3, 6.6, 6.0 Hz, 1H), 2.59 (d, *J* = 12.9 Hz, 1H), 2.49 (dt, *J* = 14.3, 7.6 Hz, 2H), 2.38 – 2.30 (m, 4H), 2.25 – 2.19 (m, 2H), 2.13 – 2.04 (m, 4H), 1.75 (dd, *J* = 12.4, 1.9 Hz, 2H), 1.69 – 1.66 (m, 2H), 1.59 – 1.56 (m, 1H), 1.48 – 1.44 (m, 1H), 1.36 (d, *J* = 5.5 Hz, 3H), 1.32 (s, 3H), 1.19 (d, *J* = 2.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 140.2, 140.0, 139.5, 139.2, 137.6, 134.3, 134.1, 131.6, 128.9, 128.7, 127.5, 127.5, 127.1, 126.7, 126.6, 125.1, 124.6, 124.1, 122.2, 120.8, 118.9, 117.4, 109.0, 108.8, 108.2, 106.9, 53.5, 52.9, 51.4, 51.4, 46.7, 44.3, 44.2, 40.5, 38.9, 38.6, 37.9, 37.8, 33.4, 31.2, 29.8, 28.8, 28.8, 28.7, 24.1, 23.2, 22.8, 21.5, 20.9, 20.3.

IR (neat) υ_{max} 3445, 2920, 1740, 1635, 1476, 1359, 1285, 1025, 942, 856, 726, 680 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{62}H_{64}N_2O_4]^+$ 900.4866, found 900.4888.

$[\alpha]^{25}_{589}$ = +89.3 (c = 0.5, $CHCl_3$).



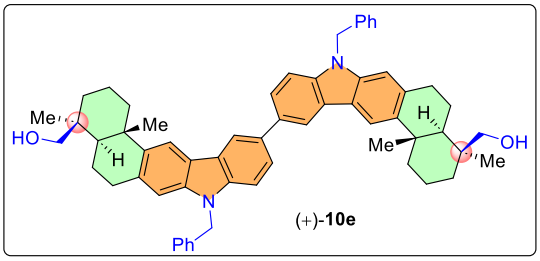
((4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)**-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-diyl)dimethanol** [(+)-**10d**]: Following the general procedure (+)-**10d** was obtained as yellow amorphous (0.55 mmol scale of reaction; 57% yield). R_f = 0.3 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 11.18 – 10.79 (m, 2H), 8.43 (dd, *J* = 40.4, 1.9 Hz, 1H), 8.32 (dd, *J* = 5.1, 1.8 Hz, 1H), 8.12 (d, *J* = 4.5 Hz, 1H), 7.75 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.43 (m, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.06 (s, 1H), 4.32 – 4.24 (m, 2H), 3.71 – 3.66 (m, 2H), 3.56 (dd, *J* = 17.2, 6.5 Hz, 1H), 3.07 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.64 – 2.58 (m, 1H), 2.40 (d, *J* = 12.5 Hz, 1H), 2.21 – 2.15 (m, 1H), 1.98 – 1.85 (m, 4H), 1.82 (dd, *J* = 12.2, 6.4 Hz, 1H), 1.72 (dq, *J* = 12.8, 7.3, 5.4 Hz, 3H), 1.61 – 1.57 (m, 1H), 1.56 – 1.51 (m, 3H), 1.48 – 1.42 (m, 2H), 1.37 – 1.30 (m, 2H), 1.22 (s, 3H), 1.21 – 1.20 (m, 3H), 1.01 (d, *J* = 1.5 Hz, 3H), 0.98 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (125 MHz, DMSO) δ 141.3, 140.2, 140.2, 139.1, 138.9, 138.7, 138.0, 133.0, 132.5, 132.5, 132.3, 130.0, 124.1, 123.9, 123.6, 122.6, 121.3, 120.7, 120.0, 118.0, 110.8, 109.8, 108.7, 62.6, 62.6, 51.4, 51.1, 38.5, 38.4, 37.7, 37.4, 35.1, 35.0, 31.3, 29.9, 29.0, 27.4, 27.3, 27.3, 26.4, 26.1, 26.0, 22.1, 18.9, 18.7.

IR (neat) υ_{max} **IR** (neat) υ_{max} 3534, 3320, 1767, 1439, 1243, 1035, 823, 706, 572 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{46}H_{52}N_2O_2 + H]^+$ 665.4107, found 665.4101.

$[\alpha]_{589}^{25}$ = +32.5 (c = 0.5, MeOH).



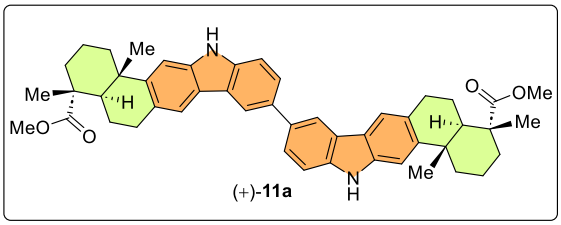
((4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**8,8'-dibenzyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-diyl)dimethanol** [(+)-**10e**]: Following the general procedure (+)-**10e** was obtained as yellow amorphous (0.55 mmol scale of reaction; 61% yield). R_f = 0.3 (30% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 59.7 Hz, 1H), 7.73 (d, *J* = 20.2 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.31 – 7.26 (m, 2H), 7.25 (dd, *J* = 5.7, 1.1 Hz, 1H), 7.20 (td, *J* = 6.0, 5.5, 2.3 Hz, 2H), 5.49 (d, *J* = 27.8 Hz, 2H), 3.94 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.77 – 3.67 (m, 1H), 3.66 – 3.59 (m, 1H), 3.20 – 2.95 (m, 1H), 2.76 – 2.59 (m, 1H), 2.44 (d, *J* = 12.8 Hz, 1H), 2.27 (dd, *J* = 12.9, 7.6 Hz, 1H), 2.03 (d, *J* = 9.1 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.81 – 1.70 (m, 2H), 1.69 – 1.60 (m, 2H), 1.50 (d, *J* = 13.1 Hz, 1H), 1.31 (s, 3H), 1.11 (d, *J* = 14.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 140.1, 139.2, 137.6, 134.1, 133.9, 131.1, 128.9, 127.5, 127.5, 126.7, 126.6, 126.6, 125.6, 125.0, 124.5, 124.0, 123.1, 122.3, 122.1, 120.8, 118.9, 118.7, 116.2, 109.0, 108.8, 108.3, 106.8, 65.5, 65.5, 51.8, 51.5, 51.4, 46.7, 40.0, 38.9, 38.9, 38.2, 38.0, 35.4, 35.4, 32.0, 30.6, 29.8, 27.0, 27.0, 27.0, 26.6, 26.2, 19.6, 19.3, 19.3.

IR (neat) υ_{max} 3600, 3337, 1751, 1415, 1240, 1085, 969, 720, 678 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{60}H_{64}N_2O_2]^+$ 844.4968, found 844.4984.

$[\alpha]^{25}_{589}$ = +11.8 (c = 0.4, $CHCl_3$).



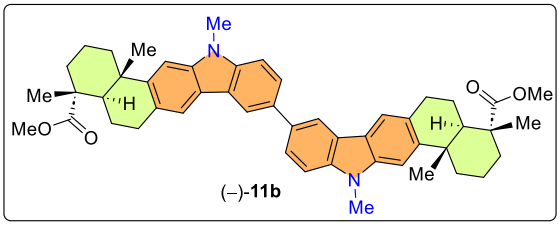
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',12,12',13b,13'b-hexadecahydro-1H,1'H-[9,9'-binaphtho[1,2-b]carbazole]-4,4'-dicarboxylate** [(+)-**11a**]: Following the general procedure (+)-**11a** was obtained as brown amorphous (0.55 mmol scale of reaction; 72% yield). R_f = 0.3 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.90 (s, 1H), 7.77 (s, 1H), 7.72 – 7.70 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.28 (s, 1H), 3.71 (s, 3H), 3.11 (s, 2H), 2.40 (d, *J* = 12.5 Hz, 1H), 2.36 (dd, *J* = 12.5, 2.5 Hz, 1H), 1.98 – 1.92 (m, 1H), 1.86 – 1.82 (m, 2H), 1.77 (q, *J* = 2.8 Hz, 1H), 1.71 – 1.68 (m, 1H), 1.66 – 1.63 (m, 1H), 1.51 (ddd, *J* = 13.0, 5.6, 3.1 Hz, 1H), 1.34 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 148.6, 139.3, 139.2, 133.8, 126.6, 125.4, 124.0, 122.0, 120.3, 118.7, 110.6, 105.8, 52.1, 47.9, 45.1, 38.7, 38.0, 36.9, 30.1, 25.6, 22.1, 18.9, 16.8.

IR (neat) υ_{max} 3443, 2906, 1720, 1456, 1267, 1010, 823, 790, 576 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{48}H_{52}N_2O_4]^+$ 720.3927, found 720.3920.

$[\alpha]^{25}_{589}$ = +12.7 (c = 0.4, $CHCl_3$).



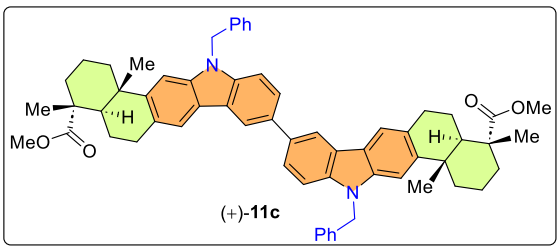
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)**-dimethyl 4,4',12,12',13b,13'b-hexamethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',12,12',13b,13'b-hexadecahydro-1H,1'H-[9,9'-binaphtho[1,2-b]carbazole]-4,4'-dicarboxylate** [(–)-**11b**]: Following the general procedure (–)-**11b** was obtained as colourless amorphous (0.55 mmol scale of reaction; 78% yield). R_f = 0.3 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.84 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 3.86 (d, *J* = 9.7 Hz, 3H), 3.70 (s, 3H), 3.16 (s, 2H), 2.53 (d, *J* = 12.4 Hz, 1H), 2.39 (dd, *J* = 12.5, 2.4 Hz, 1H), 1.97 (ddd, *J* = 12.6, 9.0, 3.6 Hz, 1H), 1.88 – 1.79 (m, 3H), 1.71 (d, *J* = 11.1 Hz, 2H), 1.56 – 1.51 (m, 1H), 1.35 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 148.4, 140.8, 140.7, 133.2, 126.1, 125.2, 123.2, 121.4, 120.4, 118.7, 108.4, 103.5, 52.1, 47.9, 45.2, 38.9, 38.2, 36.8, 30.1, 29.3, 25.7, 22.2, 18.9, 16.8.

IR (neat) υ_{max} 3420, 2926, 1750, 1459, 1345, 1258, 1035, 940, 853, 756, 650 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{50}H_{56}N_2O_4]^+$ 748.4240, found 748.4237.

$[\alpha]^{25}_{589}$ = –3.9 (c = 0.4, $CHCl_3$).



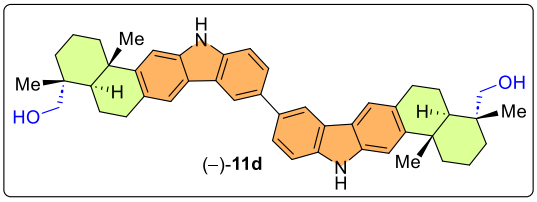
(4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 12,12'-dibenzyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',12,12',13b,13'b-hexadecahydro-1H,1'H-[9,9'-binaphtho[1,2-b]carbazole]-4,4'-dicarboxylate** [(+)-**11c**]: Following the general procedure (+)-**11c** was obtained as colourless gel (0.55 mmol scale of reaction; 68% yield). R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.89 (s, 1H), 7.73 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.27 (s, 2H), 7.24 – 7.21 (m, 2H), 5.53 (s, 2H), 3.71 (s, 3H), 3.23 – 3.13 (m, 2H), 2.39 (dd, *J* = 12.6, 2.5 Hz, 2H), 1.84 (q, *J* = 5.0 Hz, 2H), 1.77 (t, *J* = 3.3 Hz, 1H), 1.70 (d, *J* = 8.0 Hz, 1H), 1.66 – 1.59 (m, 2H), 1.56 – 1.51 (m, 1H), 1.35 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 148.6, 140.4, 140.4, 137.6, 133.5, 128.9, 127.5, 126.7, 126.5, 125.4, 123.5, 121.7, 120.4, 118.8, 109.0, 104.0, 52.1, 47.9, 46.8, 45.1, 38.7, 38.1, 36.8, 30.1, 25.7, 22.1, 18.8, 16.8.

IR (neat) υ_{max} 3405, 2922, 1765, 1690, 1467, 1395, 1285, 1020, 942, 856, 735, 680 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ calcd. for $[C_{62}H_{64}N_2O_4]^+$ 900.4866, found 900.4851.

$[\alpha]_{589}^{25}$ = +1.6 (c = 0.4, $CHCl_3$).



((4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)-**4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',12,12',13b,13'b-hexadecahydro-1H,1'H-[9,9'-binaphtho[1,2-**

b]carbazole]-4,4'-diyl)dimethanol [(–)-**11d**]: Following the general procedure (–)-**11d** was obtained as white amorphous (0.55 mmol scale of reaction; 55% yield). R_f = 0.35 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, DMSO) δ 10.87 (s, 1H), 8.37 (s, 1H), 7.83 (s, 1H), 7.72 – 7.67 (m, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.32 (s, 1H), 4.54 – 4.49 (m, 1H), 3.05 (d, *J* = 8.9 Hz, 2H), 2.96 (dd, *J* = 10.7, 5.5 Hz, 1H), 2.38 (d, *J* = 12.4 Hz, 1H), 1.98 (dd, *J* = 3.1, 1.3 Hz, 1H), 1.88 – 1.81 (m, 1H), 1.80 – 1.74 (m, 1H), 1.72 (s, 1H), 1.65 (d, *J* = 12.1 Hz, 1H), 1.54 (q, *J* = 14.1, 11.6 Hz, 2H), 1.40 (t, *J* = 12.9 Hz, 1H), 1.24 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (125 MHz, DMSO) δ 148.5, 139.3, 139.2, 131.8, 125.6, 124.1, 123.0, 120.8, 119.7, 117.6, 110.8, 105.8, 70.0, 42.9, 37.8, 37.6, 34.9, 29.6, 25.5, 22.1, 18.6, 18.5, 17.7.

IR (neat) υ_{max} 3500, 3320, 1720, 1439, 1243, 1085, 823, 760, 572 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{46}H_{52}N_2O_2 + H]^+$ 665.4107, found 665.4119.

$[\alpha]_{589}^{25}$ = –10.3 (c = 0.2, $CHCl_3$).

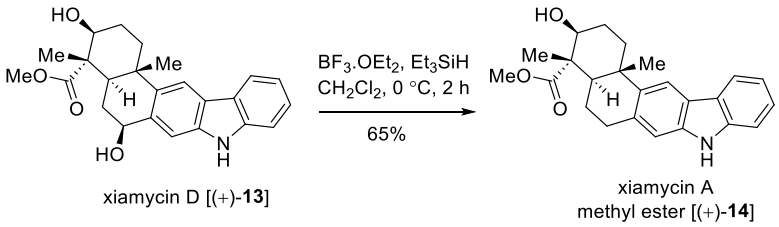
Procedure for the trapping of radical intermediate in hypervalent iodine (PIFA)-mediated oxidative dimerization reaction.

To a stirred solution of monomeric indolosesquiterpenoid **8a** (50 mg, 0.14 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL), $BF_3.OEt_2$ (40 μL, 0.14 mmol, 1.0 equiv.), PIFA (60 mg, 0.14 mmol, 1.0 equiv.) at –78 °C, TEMPO (23 mg, 0.14mmol, 1 equiv.) was quickly added. The reaction mixture was then stirred for 2 hours, while the reaction temperature was maintained at –78 °C. After 2h of the reaction saturated aqueous $NaHCO_3$ (ca. 20 mL) was added to the mixture, and then stirred for an additional 10 minutes at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined extract was dried with Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (SiO_2 (neutral)/*n*-hexane-EtOAc) to give C-C dimeric indolosesquiterpenoid **9a**. The crude reaction mixture before quenching was taken for mass spectrometry. From the mass spectrum

we got the two required mass peaks, one of which is in compliance with TEMPO adduct with one unit of model substrate and another is the C-C dimer product.

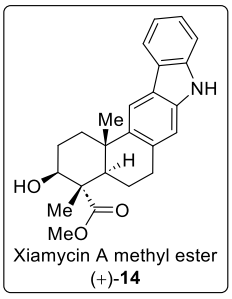
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{33}H_{44}N_2O_3 + H]^+$ 517.3430, found 517.3439.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{48}H_{52}N_2O_4 + H]^+$ 721.4005, found 721.4002.

Dehydroxylation of Xiamycin D (+)**-13:**



xiamycin D [(+)-**13**] → xiamycin A methyl ester [(+)-**14**]

A flame-dried round-bottom flask was charged with Xiamycin D (+)-**13** (172 mg, 0.44 mmol, 1.0 equiv.) in dichloromethane (10 mL) under an inert atmosphere. To this reaction mixture, $BF_3.OEt_2$ (81.4 µL, 0.66 mmol, 1.5 equiv.) was added at 0 °C temperature followed by the addition of triethylsilane (140.2 µL, 0.88 mmol, 2.0 equiv.). Finally, the reaction mixture was allowed to run at 25 °C for 2 h. Upon completion of the reaction, the reaction mixture was diluted with 15 mL of dichloromethane and then it was extracted with 10 mL of saturated sodium bicarbonate. The organic layers were dried over sodium sulphate and the crude materials were purified by flash chromatography using EtOAc in *n*-hexane to afford Xiamycin A methyl ester (+)-**14** as white foam (108 mg, 65%).



Xiamycin A methyl ester (+)-**14**

(3*S*,4*S*,4a*R*,13b*S*)-**methyl 3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate** [(+)-**14**]: Xiamycin A methyl ester (+)-**14** was

obtained as white foam (0.44 mmol scale of reaction; 65% yield). R_f = 0.5 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.94 (s, 1H), 7.85 (s, 1H), 7.37 – 7.36 (m, 2H), 7.21 – 7.18 (m, 1H), 7.07 (s, 1H), 4.10 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.75 (s, 3H), 3.12 – 3.05 (m, 2H), 2.59 (dt, *J* = 12.7, 2.8 Hz, 1H), 2.23 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.90 – 1.80 (m, 2H), 1.50 (ddd, *J* = 13.1, 6.8, 2.8 Hz, 1H), 1.31 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 141.3, 140.2, 138.4, 133.5, 125.6, 123.8, 122.2, 120.1, 119.3, 115.8, 110.6, 110.0, 75.5, 54.0, 52.4, 46.0, 37.6, 37.4, 30.9, 27.6, 26.0, 21.7, 10.9.

IR (neat) υ_{max} 3409, 2926, 2854, 1715, 1612, 1466, 1320, 1244, 1133, 1069, 940, 800, 735, 606, 536 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{24}H_{27}NO_3 + Na]^+$ 400.1889, found 400.1901.

$[\alpha]^{25}_{589}$ = +49.5 (c = 0.2, $CHCl_3$); lit.[4] $[\alpha]^{20}_{D}$ = +75.9 (c = 0.216, $CHCl_3$).

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Xiamycin A methyl ester (+)**-14**

This Report (500 MHz, $CDCl_3$)	**Natural**[3] **(300 MHz, CD_3OD)**	**Dethe**[4] **(500 MHz, $CDCl_3$)**
8.01 (dd, *J* = 7.8, 0.9 Hz, 1H)	7.96 (dd, *J* = 7.7, 1.1 Hz, 1H)	7.99 (d, *J* = 7.8 Hz, 1H)
7.94 (s, 1H)	7.92 (s, 1 H)	7.92 (s, 1H)
7.85 (s, 1H)	-	7.84 (s, 1H)
7.37 – 7.36 (m, 2H)	7.34 (dd, *J* = 8.0, 1.1 Hz, 1H)	7.36 – 7.32 (m, 2H)

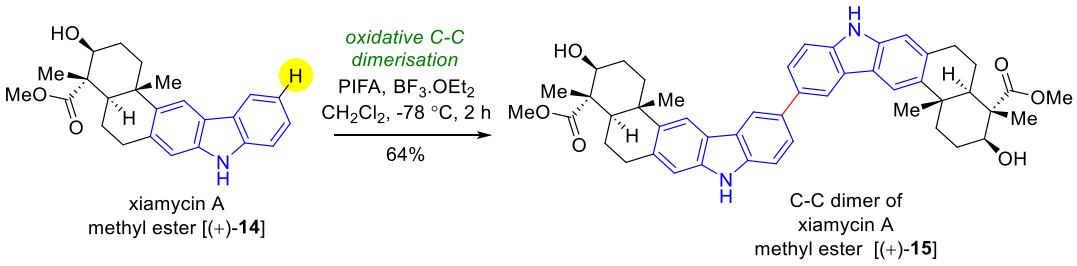
	7.27 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H)	
7.21 – 7.18 (m, 1H)	7.08 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H)	7.18 (dt, *J* = 8.0, 5.5, 2.6 Hz, 1H)
7.07 (s, 1H)	7.05 (s, 1H)	7.04 (s, 1H)
4.10 (dd, *J* = 11.2, 4.4 Hz, 1H)	4.05 (dd, *J* = 9.1, 7.1 Hz, 1H)	4.08 (dd, *J* = 11.2, 4.4 Hz, 1H)
3.75 (s, 3H)	3.71 (s, 3H)	3.73 (s, 3H)
3.12 – 3.05 (m, 2H)	3.09 (dd, *J* = 16.7, 6.1 Hz, 1H) 2.98 (m, 1H)	3.11 – 3.04 (m, 2H)
2.59 (dt, *J* = 12.7, 2.8 Hz, 1H)	2.61 (td, *J* = 13.1, 3.0 Hz, 1H)	2.57 (d, *J* = 12.7 Hz, 1H)
2.23 (dd, *J* = 12.5, 2.4 Hz, 1H)	2.13 (dd, *J* = 12.5, 2.0 Hz, 1H)	2.21 (dd, *J* = 12.5, 2.3 Hz, 1H)
2.03 – 1.94 (m, 2H)	2.00 (ddd, *J* = 13.4, 12.8, 7.0 Hz, 1H) 1.88 (m, 1H)	2.03−1.93 (m, 2H)
1.90 – 1.80 (m, 2H)	1.88 (m, 1H) 1.74 (m, 1H)	1.87 − 1.78 (m, 2H)
1.50 (ddd, *J* = 13.1, 6.8, 2.8 Hz, 1H)	1.38 (m, 1H)	1.48 (dd, *J* = 11.7, 5.2 Hz, 1H)
1.31 (s, 6H)	1.29 (s, 3H) 1.23 (s, 3H)	1.29 (s, 6H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Xiamycin A methyl ester (+)-**14**

This Report **(125 MHz, $CDCl_3$)**	**Natural**[3] **(125.76 MHz, CD_3OD)**	**Dethe**[4] **(125 MHz, $CDCl_3$)**
178.0	179.8	177.8
141.3	142.0	141.0
140.2	141.8	139.9
138.4	140.2	138.1

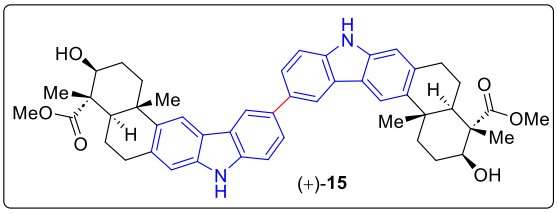
133.5	133.9	133.3
125.6	126.1	125.4
123.8	124.6	123.5
122.2	123.1	121.9
120.1	120.5	119.8
119.3	119.4	119.1
115.8	116.3	115.6
110.6	111.5	110.44
110.0	110.8	109.80
75.5	76.3	75.28
54.0	55.4	53.79
52.4	52.6	52.25
46.0	48.1	45.86
37.6	39.0	37.37
37.4	38.4	37.24
30.9	31.9	30.74
27.6	28.5	27.42
26.0	26.3	25.81
21.7	22.6	21.48
10.9	11.3	10.71

Oxidative Dimerization of Xiamycin A methyl ester (+)**-14:**



To a stirred solution of Xiamycin A methyl ester (+)**-14** (45 mg, 0.12 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL), PIFA (51.6 mg, 0.12 mmol, 1.0 equiv.) and $BF_3.OEt_2$ (17 µL, 0.12 mmol, 1.0

equiv.) were quickly added at –78 °C. The reaction mixture was then stirred for 2 hour, while the reaction temperature was maintained at –78 °C. After the reaction completion, saturated aqueous $NaHCO_3$ (ca. 2 mL) was added to the mixture, and then stirred for an additional 10 minutes at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined extract was dried with Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography using EtOAc in *n*-hexane to afford dimer (+)-**15** as brown amorphous (28.9 mg, 64%).



(3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**dimethyl 3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**15**]: (+)-**15** was obtained as brown amorphous (0.12 mmol scale of reaction; 64% yield). R_f = 0.5 (70% EtOAc in *n*-hexane).

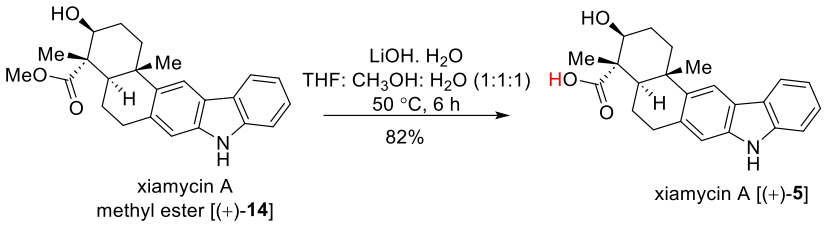
^{1}H NMR (500 MHz, DMSO) δ 10.91 (s, 1H), 8.50 (s, 1H), 8.18 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.11 (s, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 3.93 (t, *J* = 9.8 Hz, 1H), 3.65 (s, 3H), 3.14 – 3.08 (m, 1H), 2.97 (dt, *J* = 17.8, 9.4 Hz, 1H), 2.66 (d, *J* = 11.2 Hz, 1H), 2.06 (d, *J* = 12.7 Hz, 1H), 1.95 (t, *J* = 9.9 Hz, 1H), 1.79 (d, *J* = 16.1 Hz, 3H), 1.69 (d, *J* = 13.5 Hz, 1H), 1.26 (s, 6H).

^{13}C NMR (125 MHz, DMSO) δ 177.3, 140.4, 139.1, 138.8, 132.6, 131.9, 124.2, 123.5, 121.5, 117.7, 115.9, 110.9, 109.8, 74.0, 59.7, 53.6, 51.8, 46.2, 36.8, 31.3, 30.2, 29.0, 27.5, 25.5, 22.1, 14.1, 10.9.

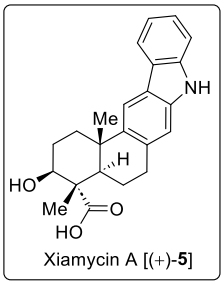
IR (neat) υ_{max} 3430, 2925, 1765, 1653, 1466, 1385, 1290, 1052, 953, 845, 762, 669 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{48}H_{52}N_2O_6 + H]^+$ 753.3904, found 753.3896.

$[\alpha]_{589}^{25}$ = +87.3 (c = 0.5, MeOH).

Hydrolysis of Xiamycin A methyl ester (+)**-14:**



In an oven dried round-bottom flask Xiamycin A methyl ester [(+)-**14**] (63 mg, 0.17 mmol, 1.0 equiv.) was taken in a mixture of THF, methanol and water [THF: MeOH: H_2O (1:1:1)]. To the solution LiOH. H_2O (280.4 mg, 6.68 mmol, 40 equiv.) were added and reaction mixture was refluxed for 10 h at 50 ºC. After completion of the reaction confirmed by TLC, reaction mixture was quenched with 4(N) HCl at 0 ºC and the pH of the reaction mixture was adjusted to ~1-2. Then the reaction mixture was extracted with ethyl acetate (8 mL X 2). The organic layer was collected, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography with ~80-90% EtOAc in *n*-hexane to afford Xiamycin A [(+)-**5**] as white solid (50.7 mg, 82% yield).



(3*S*,4*S*,4a*R*,13b*S*)-**3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylic acid** [(+)-**5**]: Xiamycin A (+)-**5** was obtained as white solid (0.17 mmol scale of reaction; 82% yield). R_f = 0.3 (70% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, CD_3OD) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.96 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 4.14 – 4.10 (m, 1H), 3.13 (dd, *J* = 16.9, 6.6 Hz, 1H), 3.05 (ddd, *J* = 17.3, 11.1, 7.5 Hz, 1H), 2.65 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.17 (d, *J* = 2.1 Hz, 1H), 2.07 – 2.02 (m, 1H), 1.92 (td, *J* = 9.9, 9.4, 3.2 Hz, 2H), 1.77 (dd, *J* = 12.8, 7.5 Hz, 1H), 1.56 (ddd, *J* = 12.7, 6.1, 3.9 Hz, 1H), 1.32 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 181.2, 142.0, 141.8, 140.0, 134.1, 126.0, 124.7, 123.1, 120.5, 119.4, 116.3, 111.5, 110.8, 76.3, 54.9, 47.9, 39.0, 38.3, 32.0, 28.7, 26.3, 22.6, 11.4.

IR (neat) υ_{max} 3340, 2926, 2854, 2454, 1652, 1460, 1320, 1244, 1133, 1069, 940, 735, 606, 563 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{23}H_{25}NO_3 + H]^+$ 364.1913, found 364.1906.

$[\alpha]^{25}_{589}$ = +118.6 (c = 1.0, MeOH); lit.[5] $[\alpha]^{22}_{D}$ = +123.5 (c = 0.4, MeOH).

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Xiamycin A (+)-**5**

Bisai (500 MHz, CD_3OD)	**Natural[3] (500 MHz, CD_3OD)**	**Sarpong[5] (700 MHz, CD_3OD)**
7.99 (d, *J* = 7.7 Hz, 1H)	7.96 (d, *J* = 8.0 Hz, 1H)	7.97 (d, *J* = 8.0 Hz, 1H)
7.96 (s, 1H)	7.91 (s, 1H)	7.94 (s, 1H)
7.37 (d, *J* = 8.1 Hz, 1H)	7.35 (d, *J* = 8.0 Hz, 1H)	7.35 (d, *J* = 8.0 Hz, 1H)
7.33 – 7.28 (m, 1H)	7.28 (dt, *J* = 7.0, 1.0 Hz, 1H)	7.29 (t, *J* = 7.9 Hz, 1H)
7.11 (d, *J* = 7.5 Hz, 1H)	7.08 (dt, *J* = 7.0, 1.0 Hz, 1H)	7.09 (t, *J* = 7.5 Hz, 1H)
7.09 (s, 1H)	7.07 (s, 1H)	7.07 (s, 1H)
4.14 – 4.10 (m, 1H)	4.09 (dd, *J* = 10.5, 7.5 Hz, 1H)	4.10 (dd, *J* = 10.5, 7.5 Hz, 1H)
3.13 (dd, *J* = 16.9, 6.6 Hz, 1H) 3.05 (ddd, *J* = 17.3, 11.1, 7.5 Hz, 1H)	3.09 (m, 2H)	3.15-3.08 (m, 1H) 3.08-2.99 (m, 1H)
2.65 (dt, *J* = 13.2, 3.5 Hz, 1H)	2.58 (dt, *J* = 13.1, 1.5 Hz, 1H)	2.64 (d, *J* = 12.8 Hz, 1H)
2.17 (d, *J* = 2.1 Hz, 1H)	2.18 (dd, *J* = 12.6, 2.3 Hz, 1H)	2.14 (d, *J* = 11.8 Hz, 1H)
2.07 – 2.02 (m, 1H)	2.00 (qd, *J* = 12.6, 7.3 Hz, 1H)	2.08-1.98 (m, 1H)

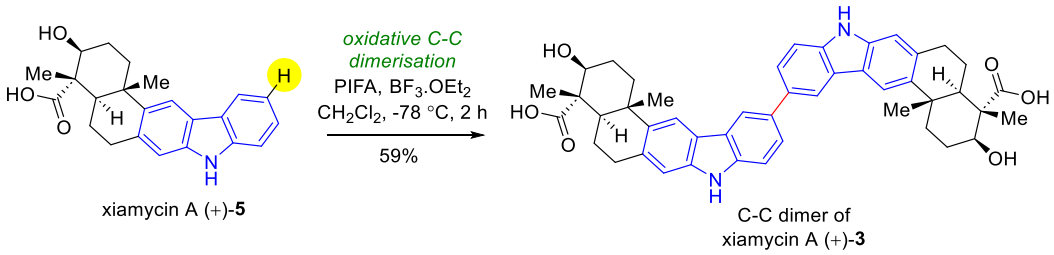
1.92 (td, *J* = 9.9, 9.4, 3.2 Hz, 2H)	1.90 (m, 1H) 1.86 (qd, *J* = 13.1, 2.9 Hz, 1H)	1.93-1.88 (m, 2H)
1.77 (dd, *J* = 12.8, 7.5 Hz, 1H)	1.76 (dt, *J* = 12.3, 6.7 Hz, 1H)	1.78-1.72 (m, 1H)
1.56 (ddd, *J* = 12.7, 6.1, 3.9 Hz, 1H)	1.56 (m, 1H)	1.58-1.53 (m, 1H)
1.32 (s, 3H)	1.28 (s, 3H)	1.30 (s, 3H)
1.27 (s, 3H)	1.23 (s, 3H)	1.25 (s, 3H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Xiamycin A (+)-**5**

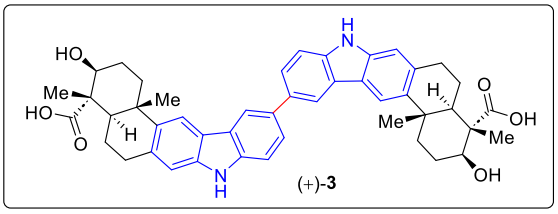
Bisai **(125 MHz, CD_3OD)**	**Natural**[3] **(151 MHz, CD_3OD)**	**Sarpong**[5] **(176 MHz, CD_3OD)**
181.2	181.3	181.3
142.0	142.0	142.0
141.8	141.8	141.8
140.0	140.1	140.1
134.1	134.0	134.0
126.0	126.0	126.0
124.7	124.7	124.6
123.1	123.1	123.1
120.5	120.5	120.6
119.4	119.3	119.3
116.3	116.3	116.4
111.5	111.5	111.4
110.8	110.8	110.8
76.3	76.3	76.3
54.9	54.9	54.9
47.9	47.9	47.9
39.0	39.0	39.0
38.3	38.3	38.3

32.0	32.0	32.1
28.7	28.6	28.7
26.3	26.3	26.3
22.6	22.6	22.6
11.4	11.4	11.4

Oxidative Dimerization of Xiamycin A (+)-5:



To a stirred solution of xiamycin A [(+)-**5**] (50 mg, 0.14 mmol, 1.0 equiv.) in DMF (0.5 mL) and CH_2Cl_2 (3.5 mL), PIFA (60.2 mg, 0.14 mmol, 1.0 equiv.) and $BF_3.OEt_2$ (17.3 µL, 0.14 mmol, 1.0 equiv.) were quickly added at –78 °C. The reaction mixture was then stirred for 2 hour, while the reaction temperature was maintained at –78 °C. After the reaction completion, saturated aqueous $NaHCO_3$ (ca. 2 mL) was added to the mixture, and then stirred for an additional 10 minutes at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined extract was dried with Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography using EtOAc in *n*-hexane to afford dimer (+)-**3** as white amorphous (29.9 mg, 59%).



(3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)**-3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1H,1'H-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylic acid** [(+)-**3**]: Following the general procedure (+)-**3** was

obtained as white amorphous (0.14 mmol scale of reaction; 59% yield). R_f = 0.1 (10% MeOH in CH_2Cl_2).

^{1}H NMR (500 MHz, DMSO) δ 12.11 (s, 1H), 10.91 (s, 1H), 8.49 (s, 1H), 8.17 (s, 1H), 7.74 (d, *J* = 6.7 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.10 (s, 1H), 4.71 (s, 1H), 3.92 (s, 1H), 3.14 – 3.08 (m, 1H), 2.99 – 2.95 (m, 1H), 2.66 – 2.62 (m, 1H), 2.04 – 1.98 (m, 2H), 1.93 (s, 1H), 1.78 (s, 3H), 1.64 (s, 2H), 1.44 (s, 1H), 1.34 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (125 MHz, DMSO) δ 178.8, 140.6, 139.2, 138.8, 132.7, 131.9, 123.6, 121.5, 117.7, 115.9, 114.6, 110.9, 109.9, 74.0, 52.8, 36.8, 31.6, 31.3, 28.7, 25.6, 22.1, 14.0, 11.0.

IR (neat) υ_{max} 3360, 2962, 2834, 2454, 1625, 1400, 1325, 1270, 1135, 1075, 968, 735, 630, 556 cm^{-1}.

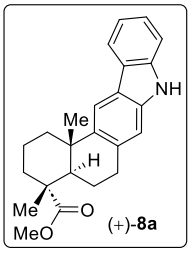
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{46}H_{48}N_2O_6 + Na]^+$ 747.3410, found 747.3448.

$[\alpha]_{589}^{25}$ = +128.3 (c = 0.3, MeOH).

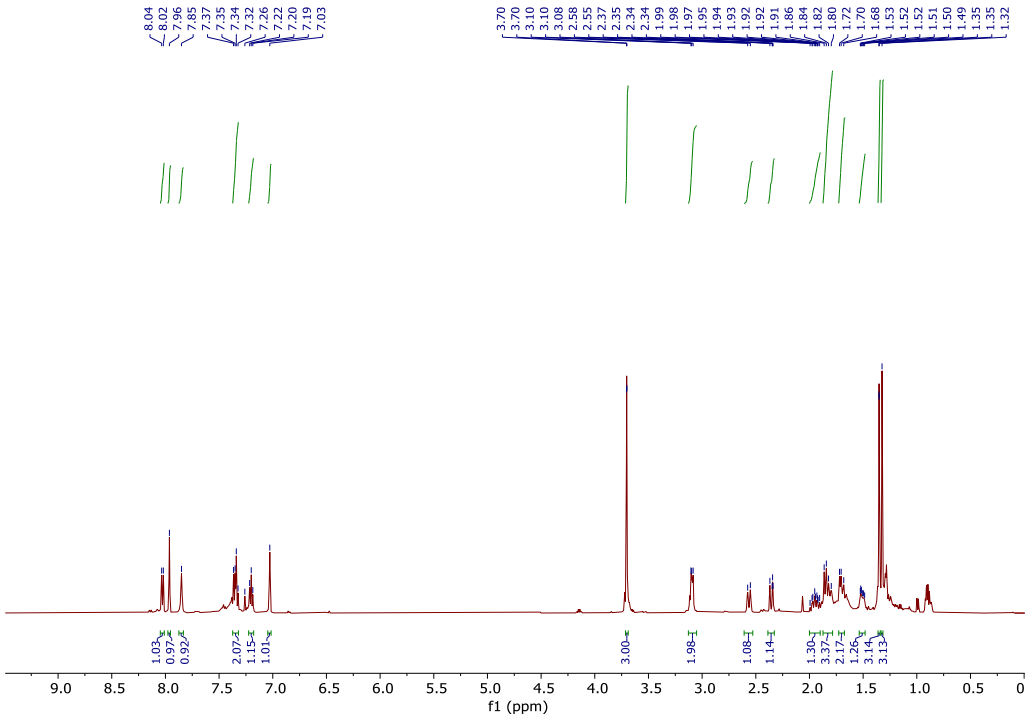
References:

1. M. Munda,[£] R. Nandi,[£] V. R. Gavit, S. Kundu, S. Niyogi and A. Bisai, *Chem. Sci.*, 2022, **13**, 11666–11671. [[£] contributed equally]
2. S. W. Pelletier and D. L. Herald, jun, *J. Chem. Soc. D*, 1971, 10b-11.
3. L. Ding, J. Münch, H. Goerls, A. Maier, H. H. Fiebig, W. H. Lin and C. Hertweck, *Bioorg. Med. Chem. Lett*., 2010, **20**, 6685–6687.
4. D. H. Dethe and M. Shukla, *Chem. Commun*., 2021, **57**, 10644-10646.
5. M. Pfaffenbach, I. Bakanas, N. R. O'Connor, J. L. Herrick and R. Sarpong, *Angew. Chem. Int. Ed.*, 2019, **58**, 15304–15308.

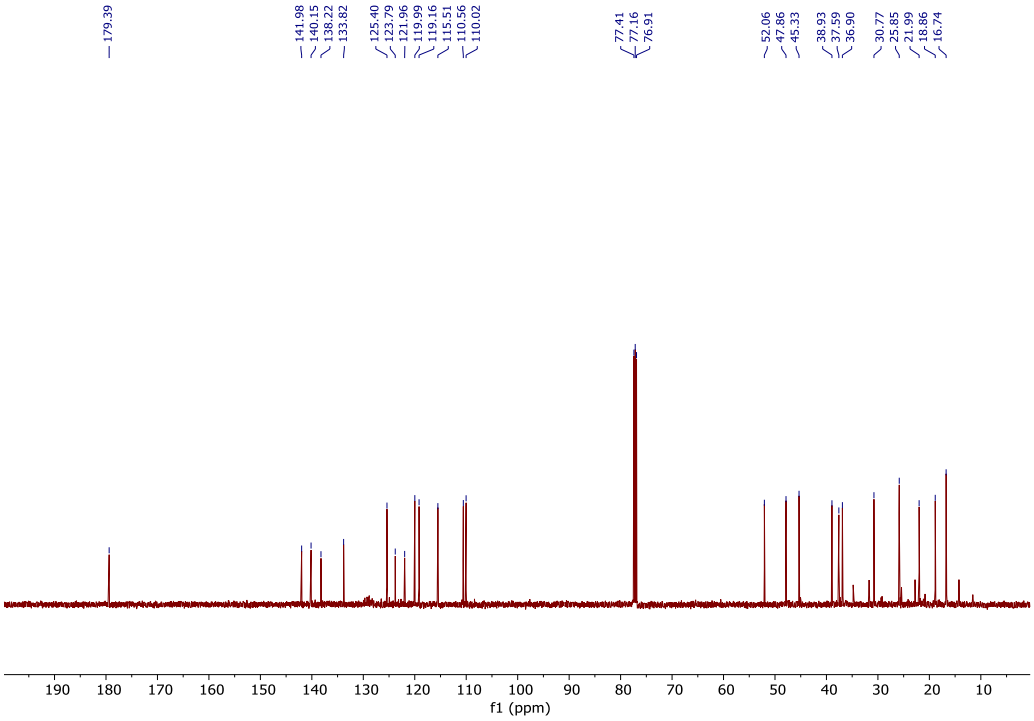
Spectral Data



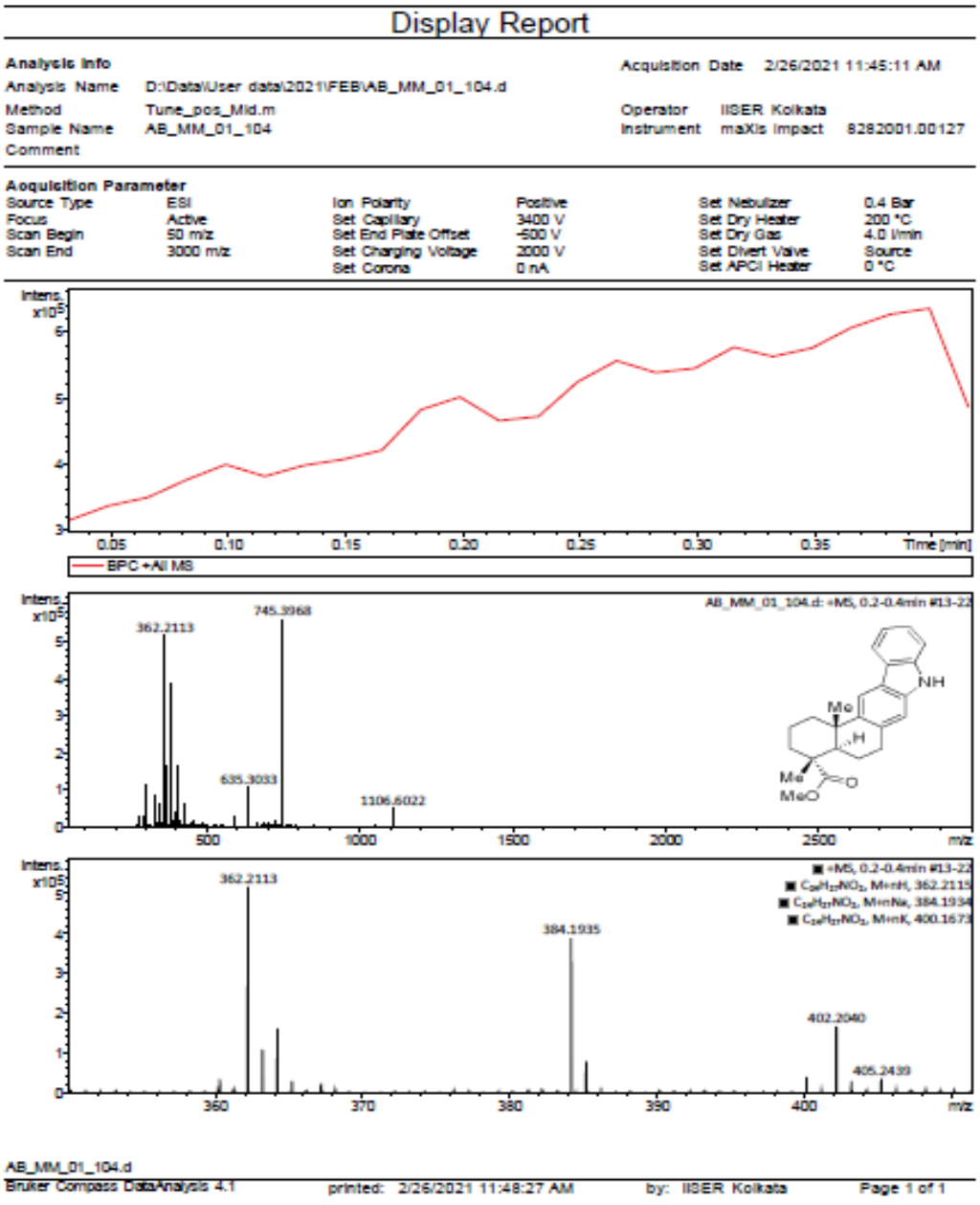
(+)-**8a**



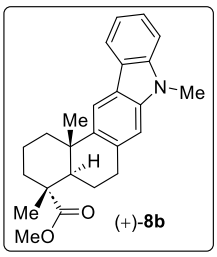
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8a**

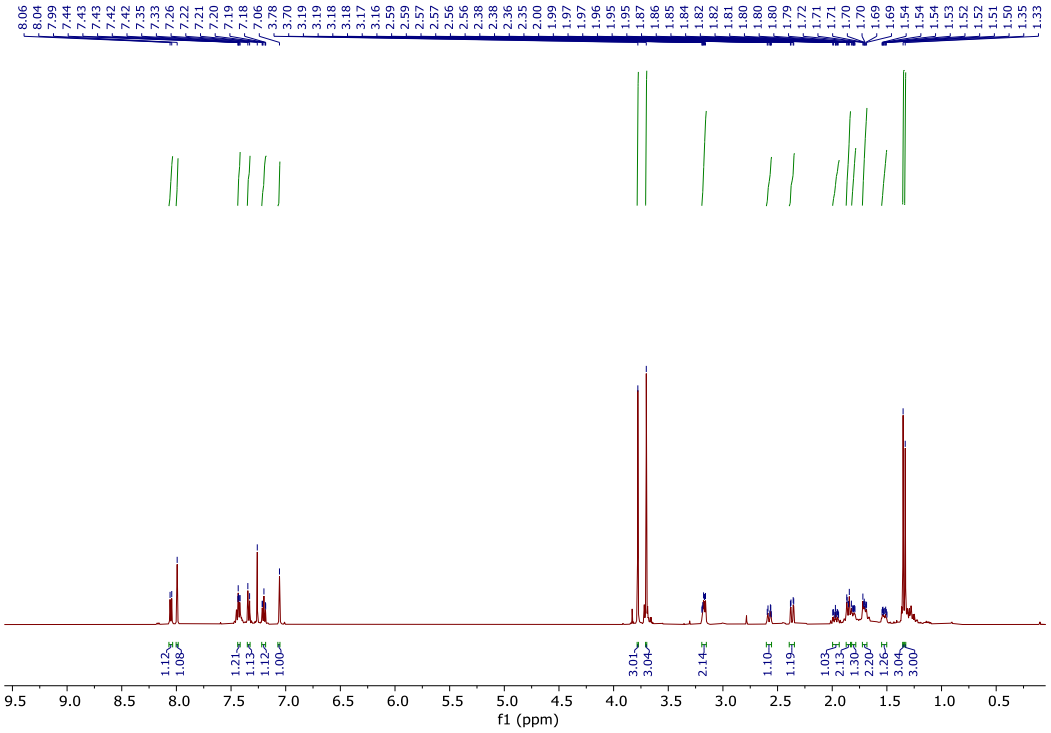


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8a**

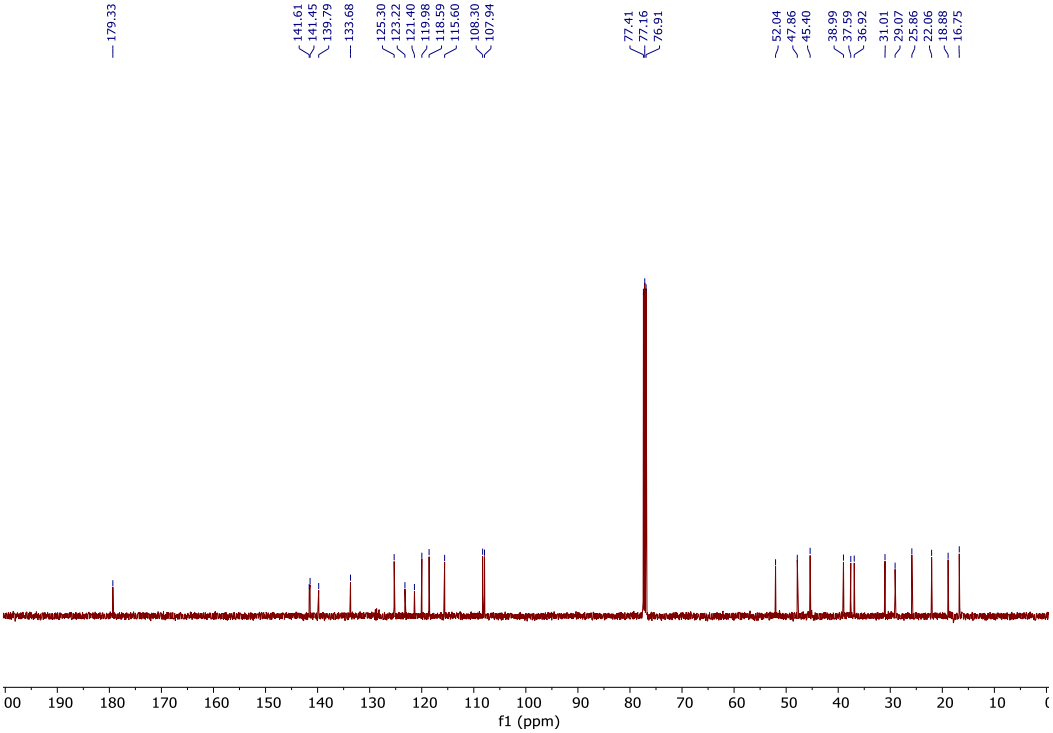


HRMS data of (+)-**8a**

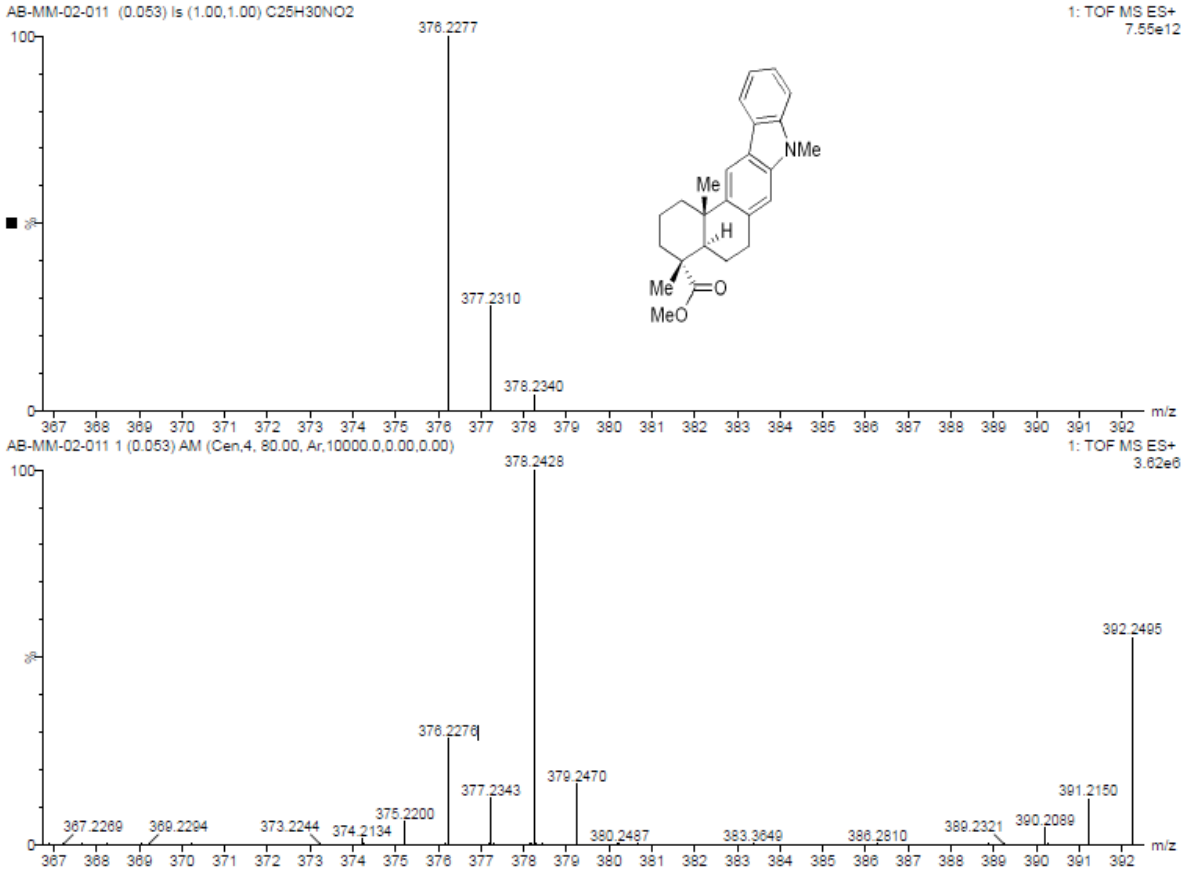




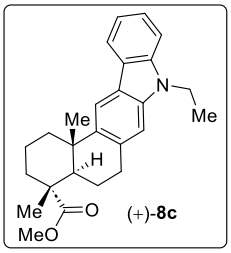
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8b**

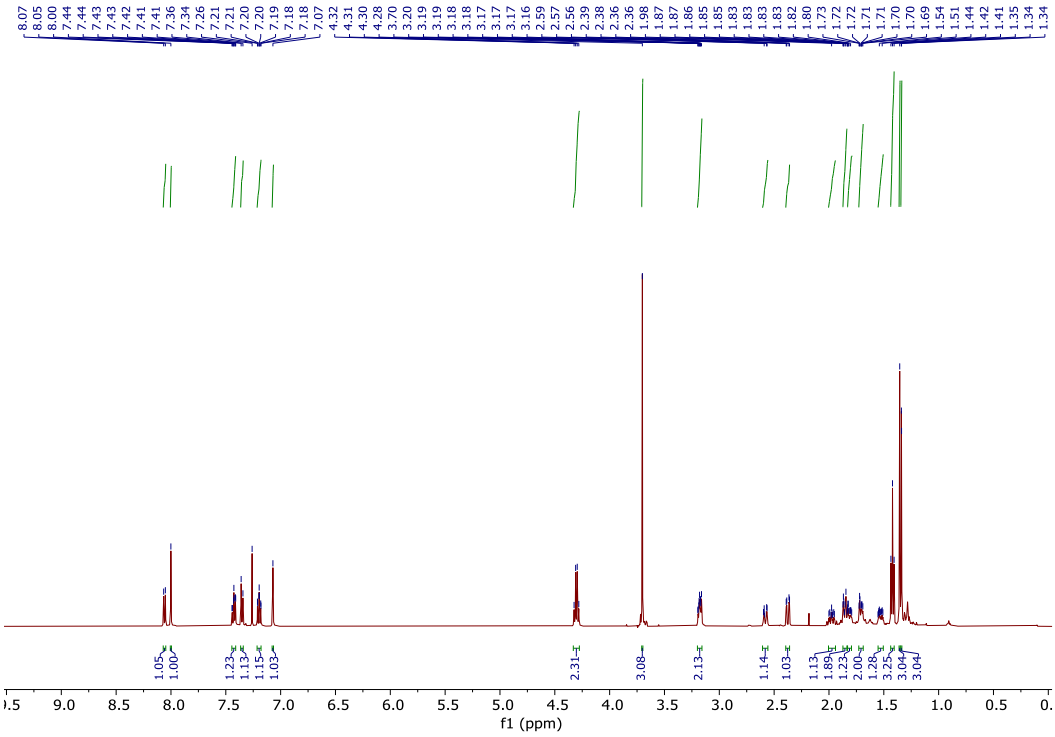


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8b**

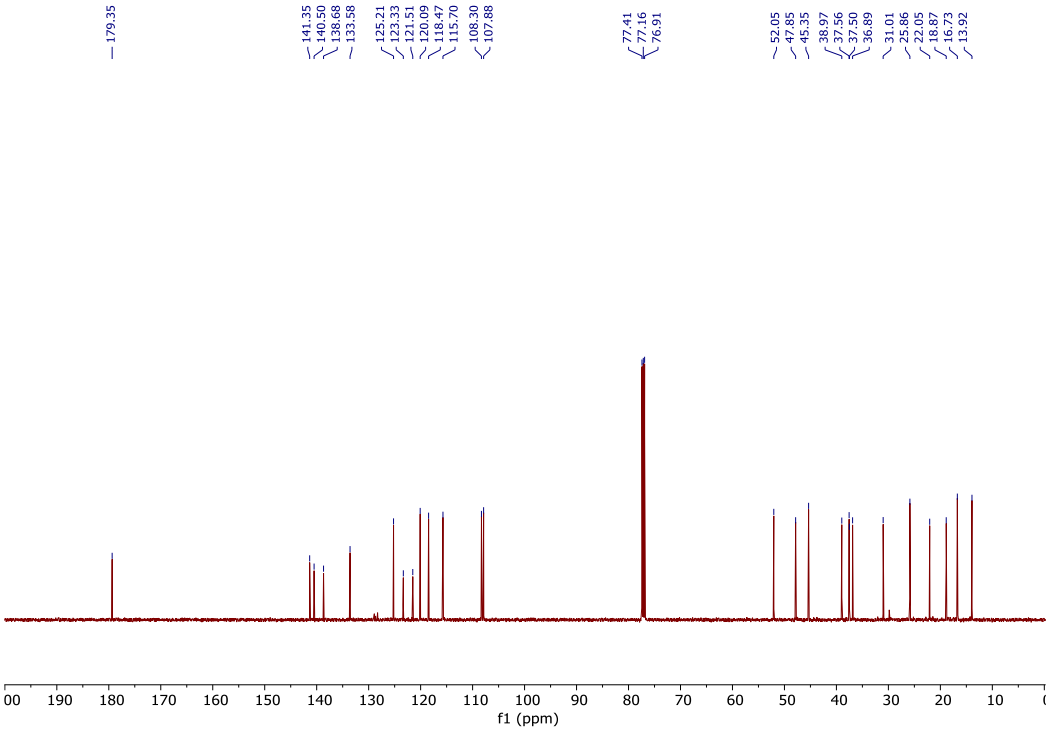


HRMS data of (+)-**8b**

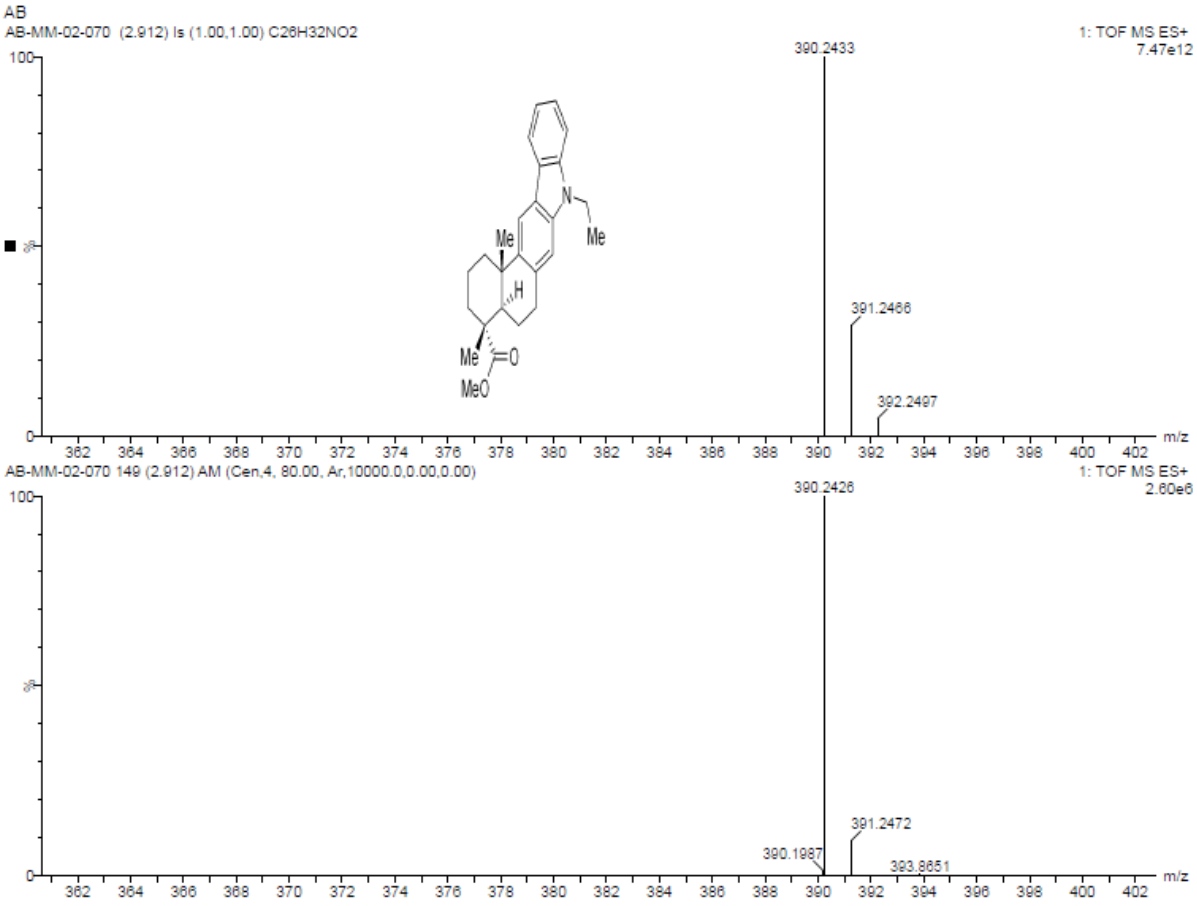




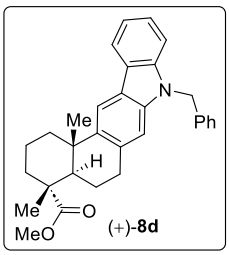
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8c**

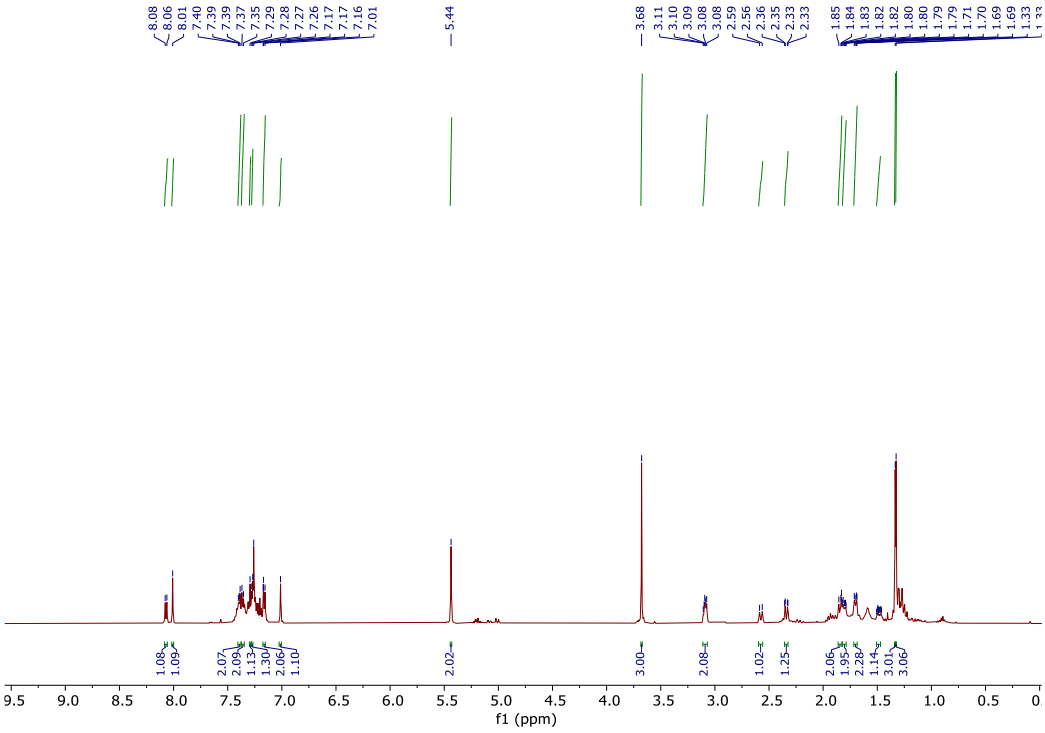


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8c**

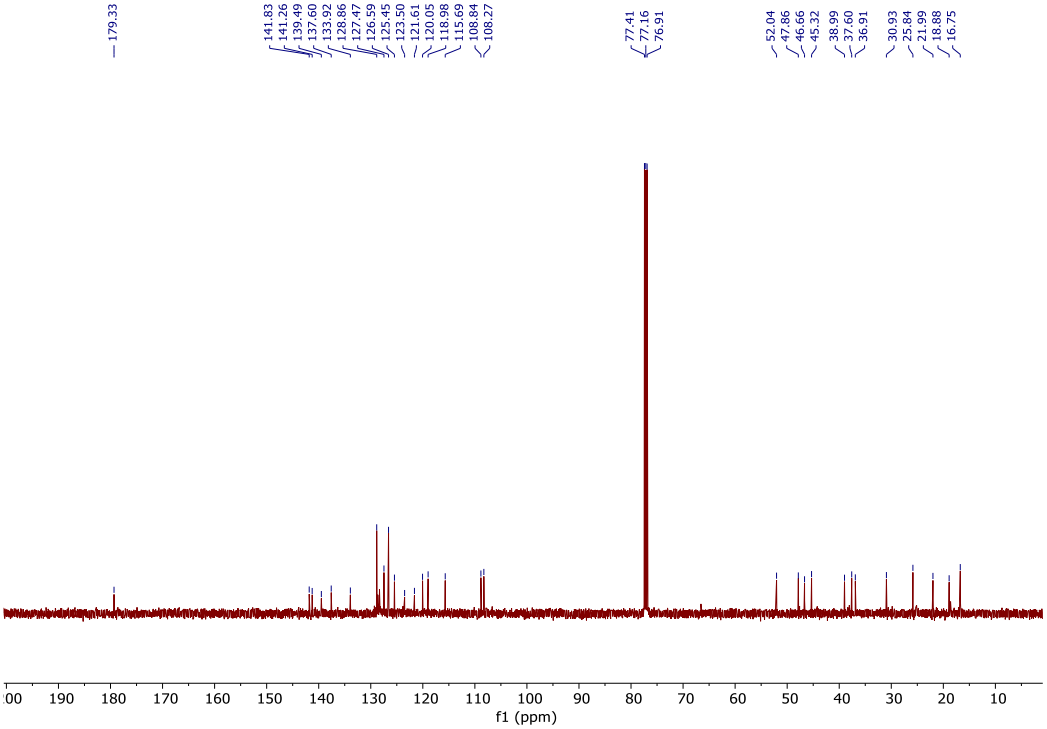


HRMS data of (+)-**8c**

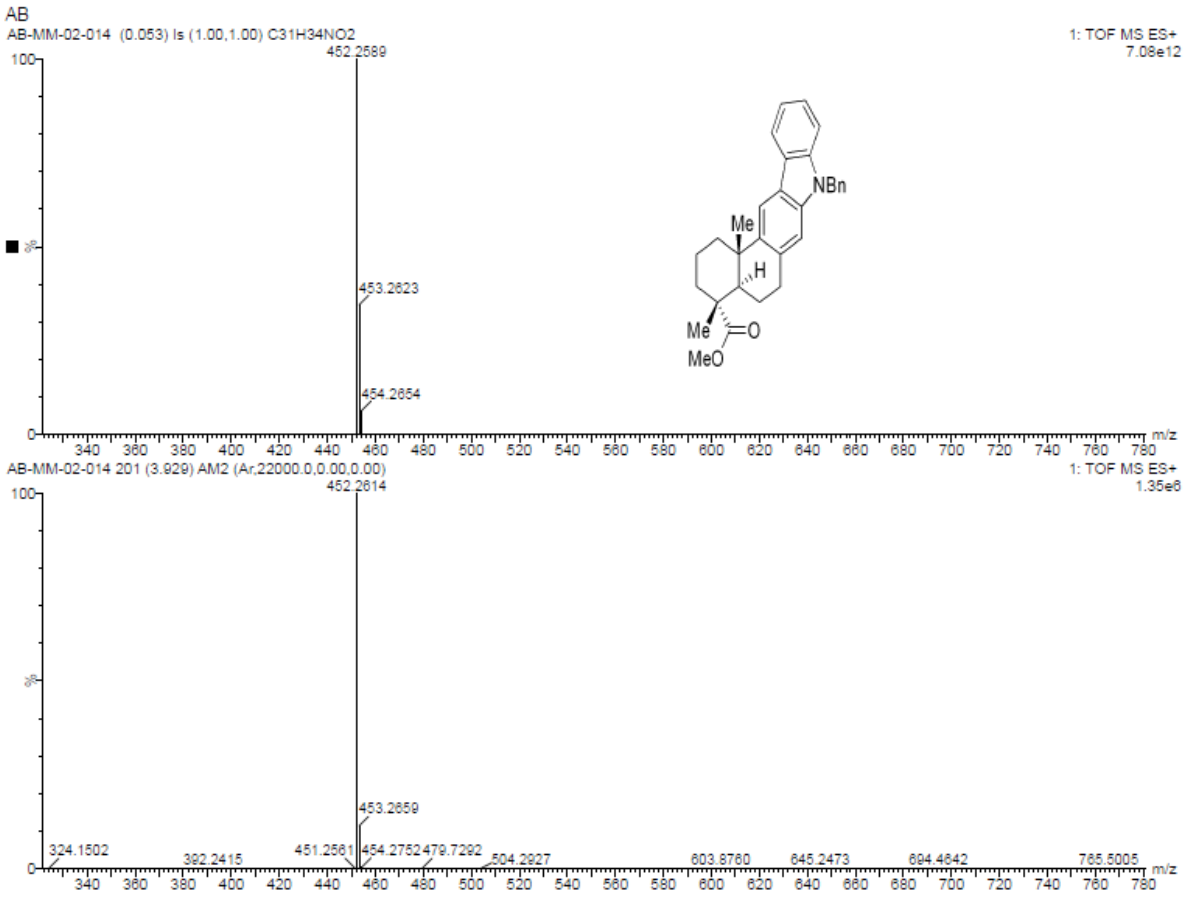




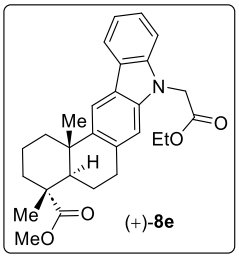
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8d**

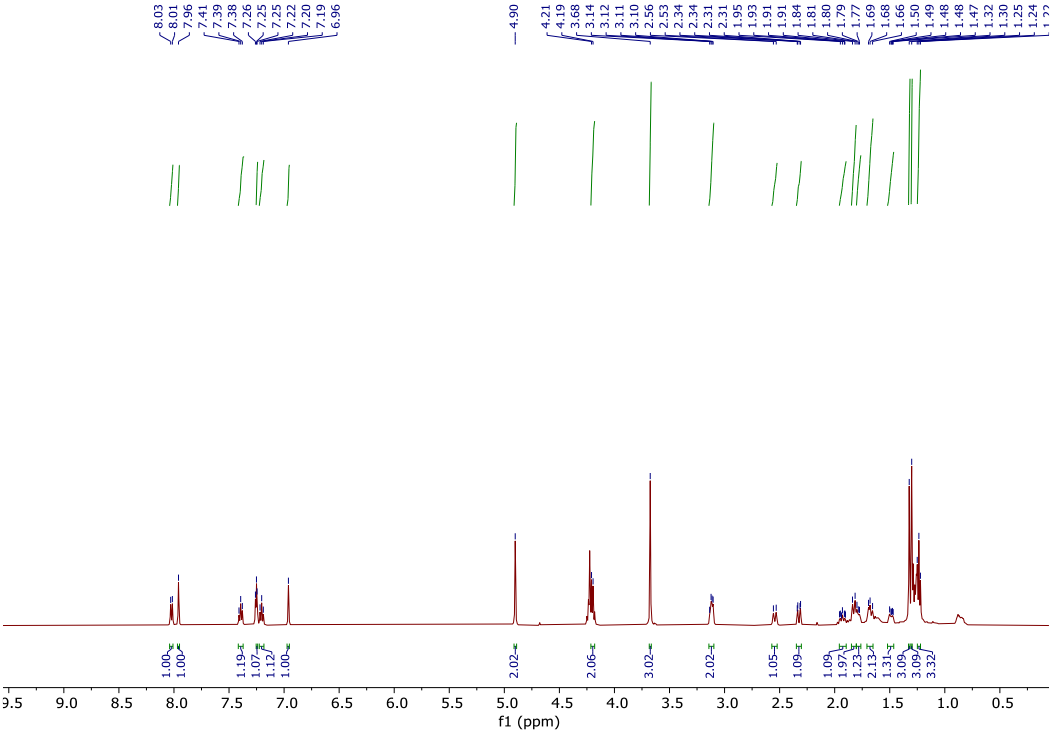


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8d**

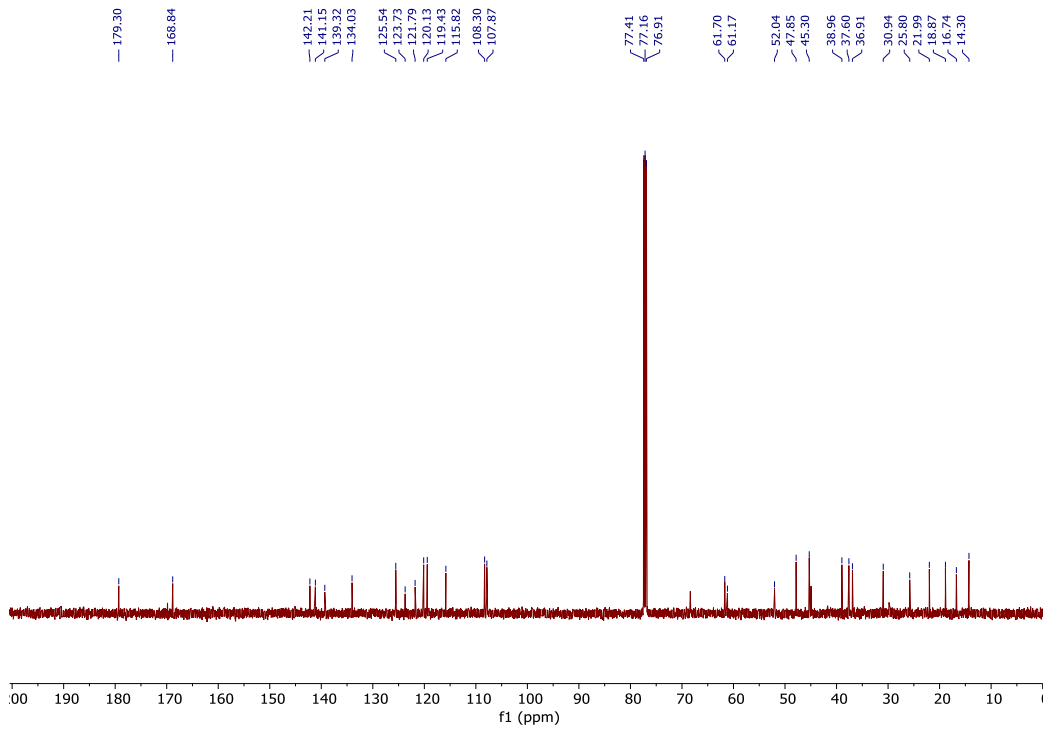


HRMS data of (+)-**8d**

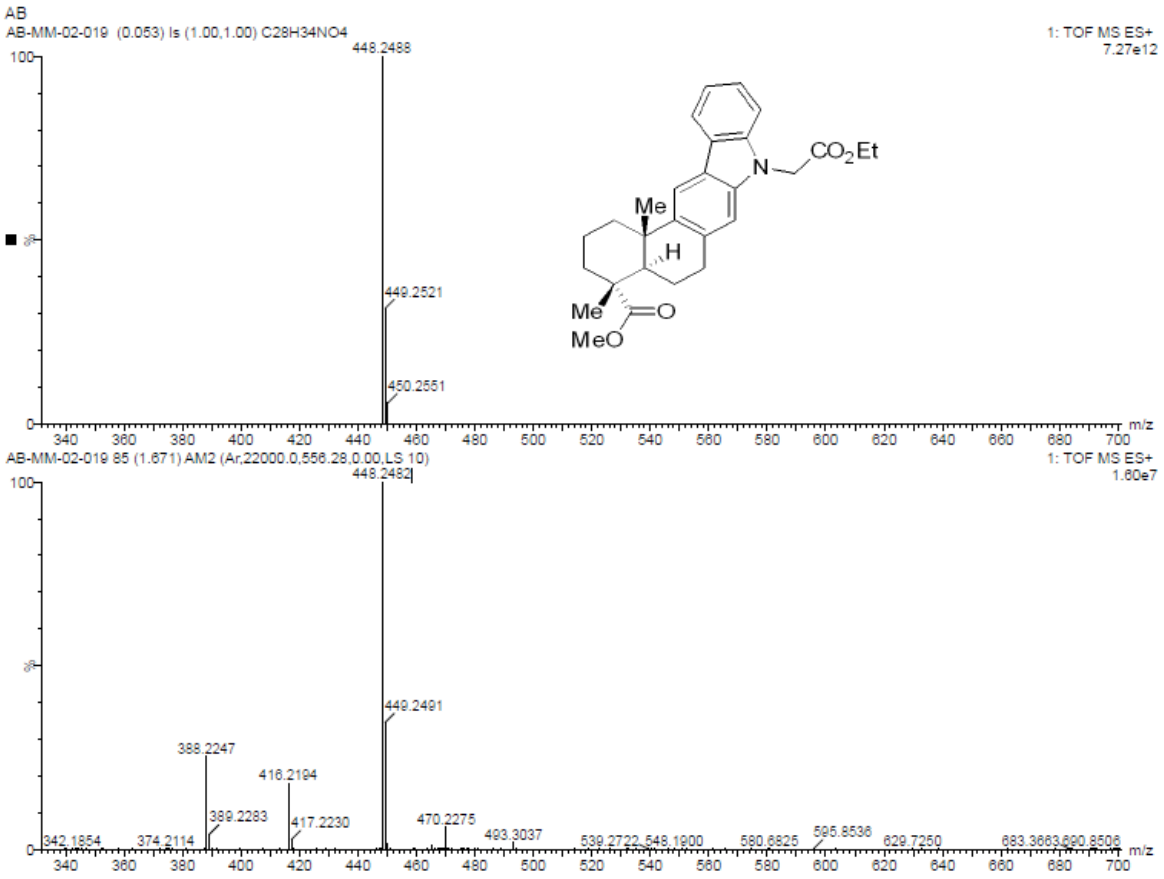




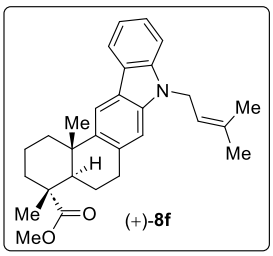
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8e**



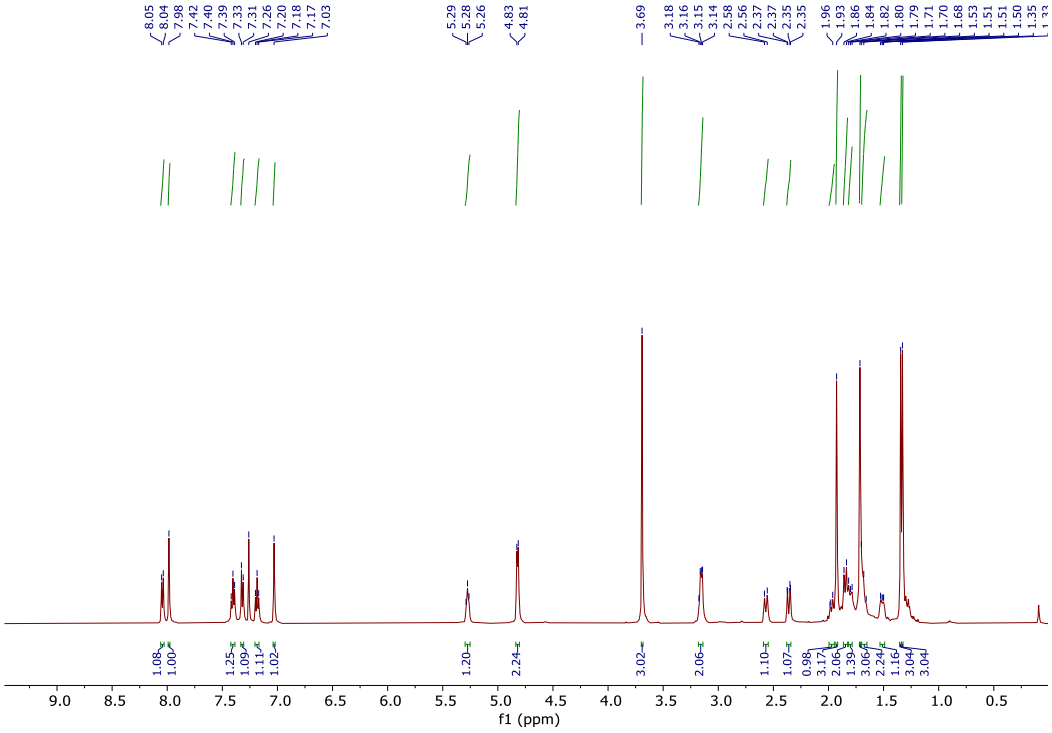
^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8e**



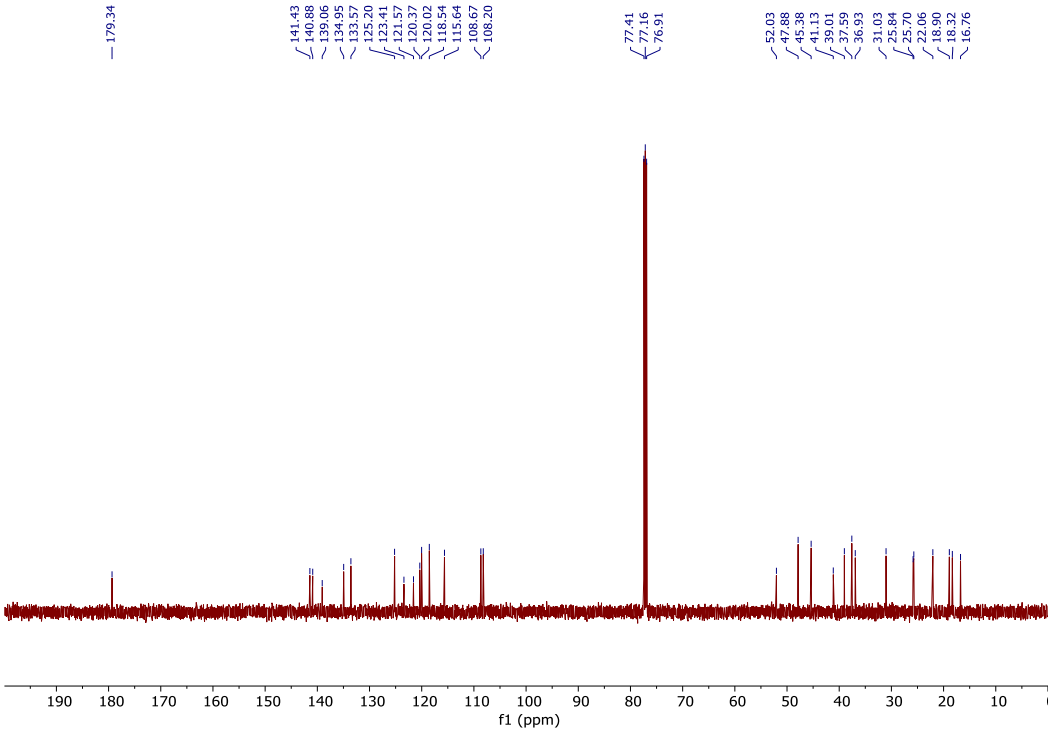
HRMS data of (+)-**8e**



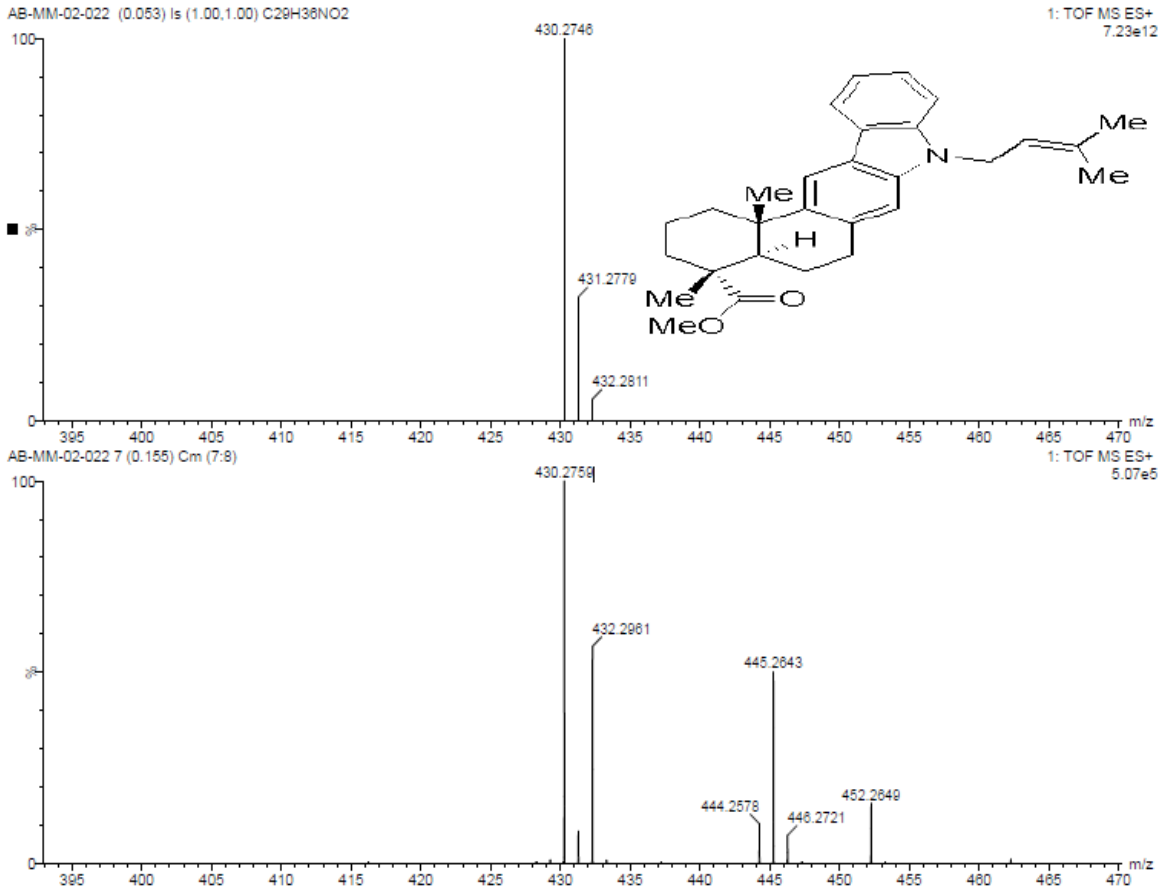
(+)-**8f**



^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8f**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8f**



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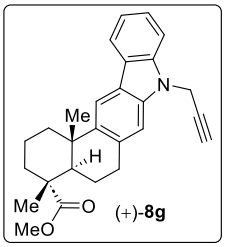
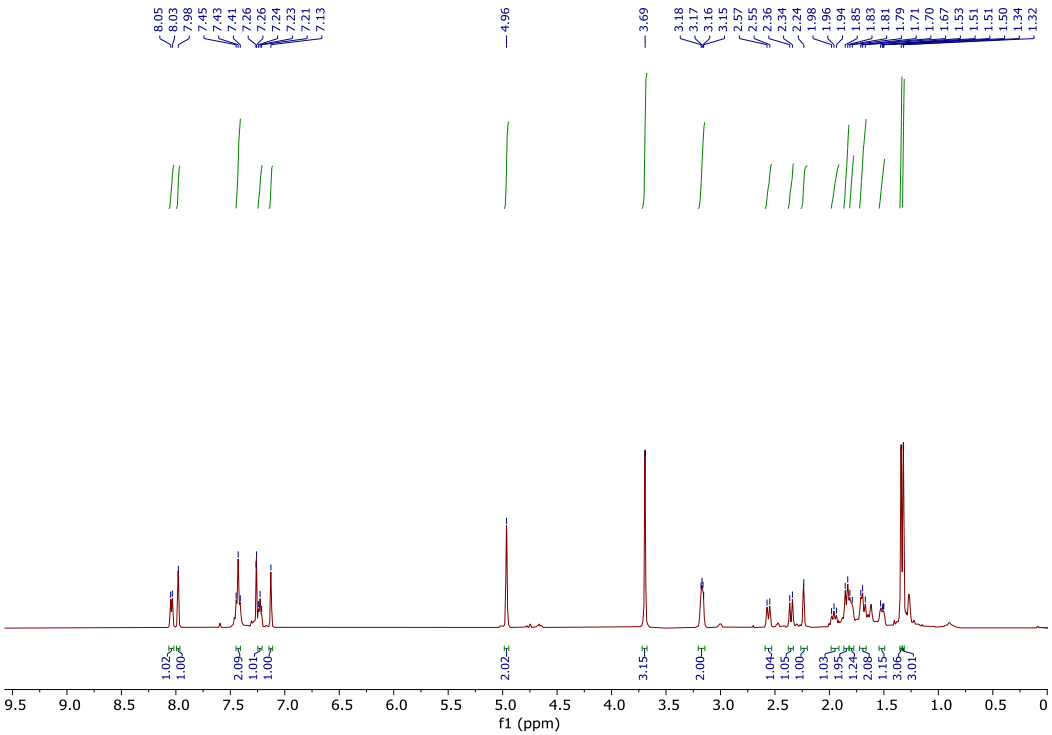
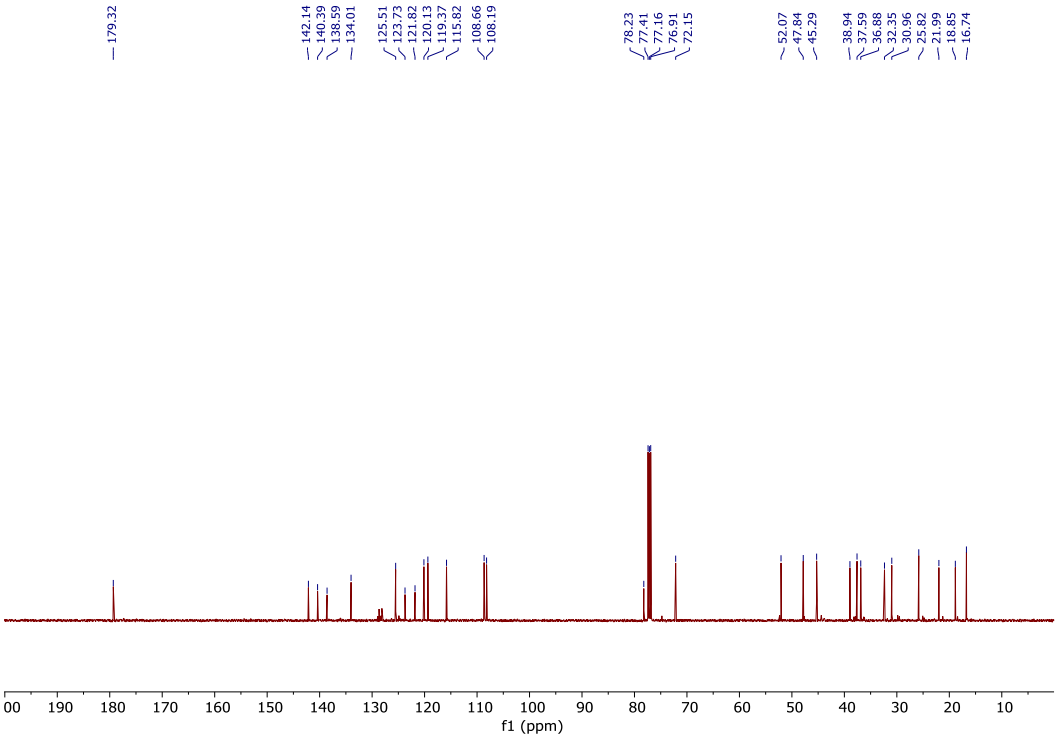
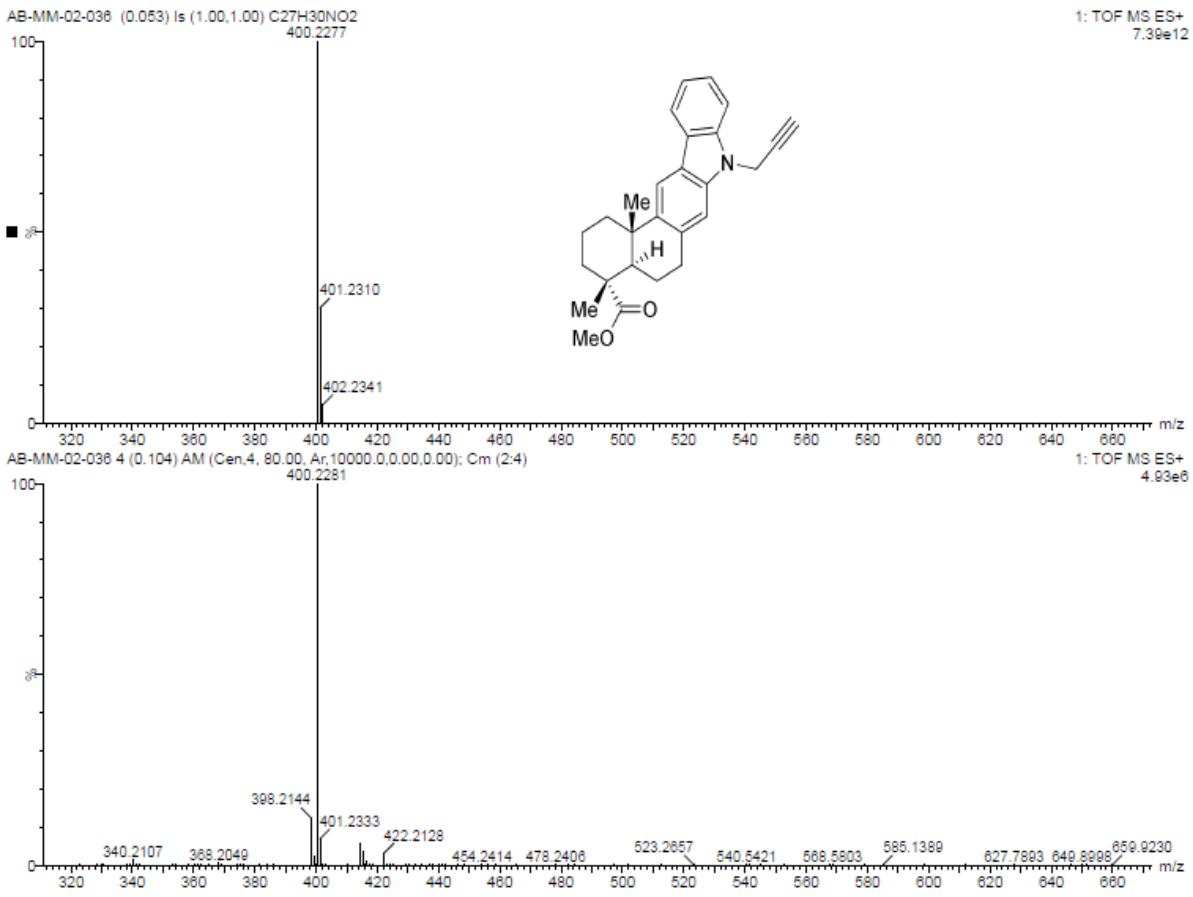




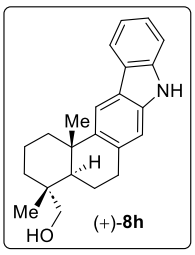
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8g**

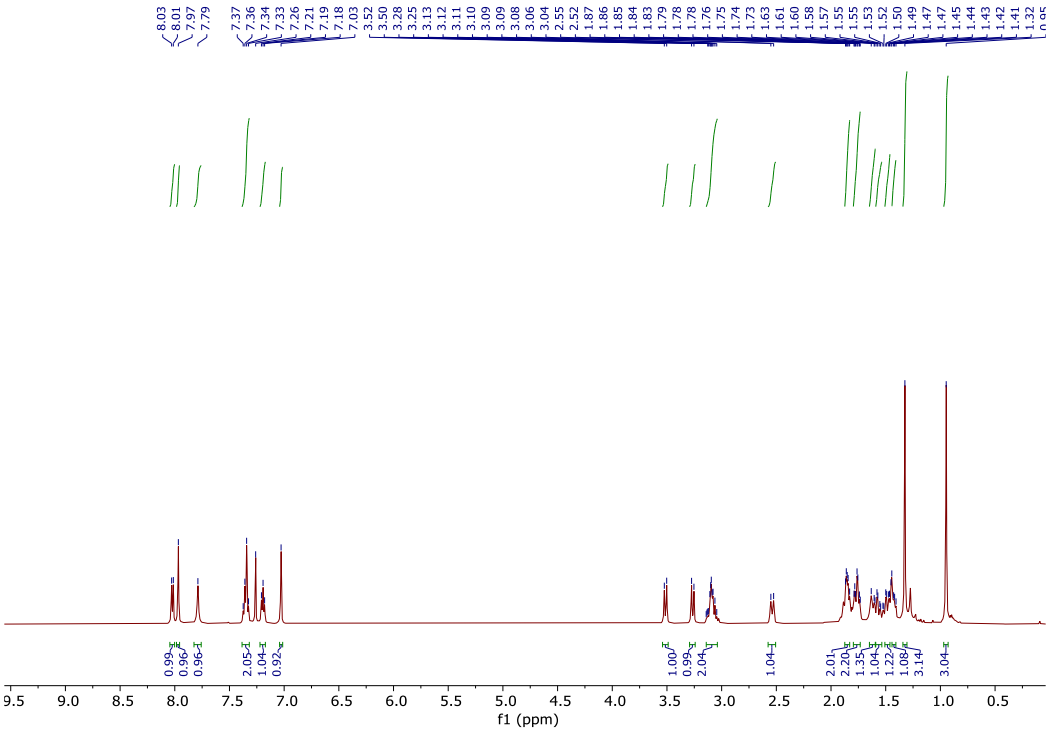


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8g**

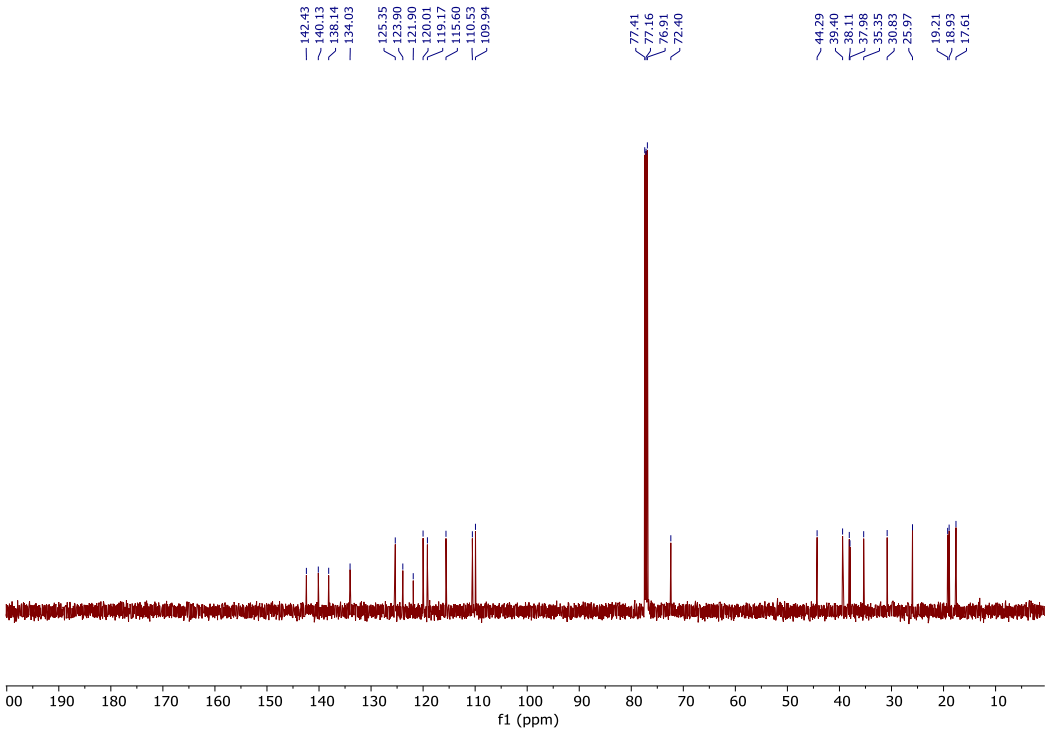


HRMS data of (+)-**8g**

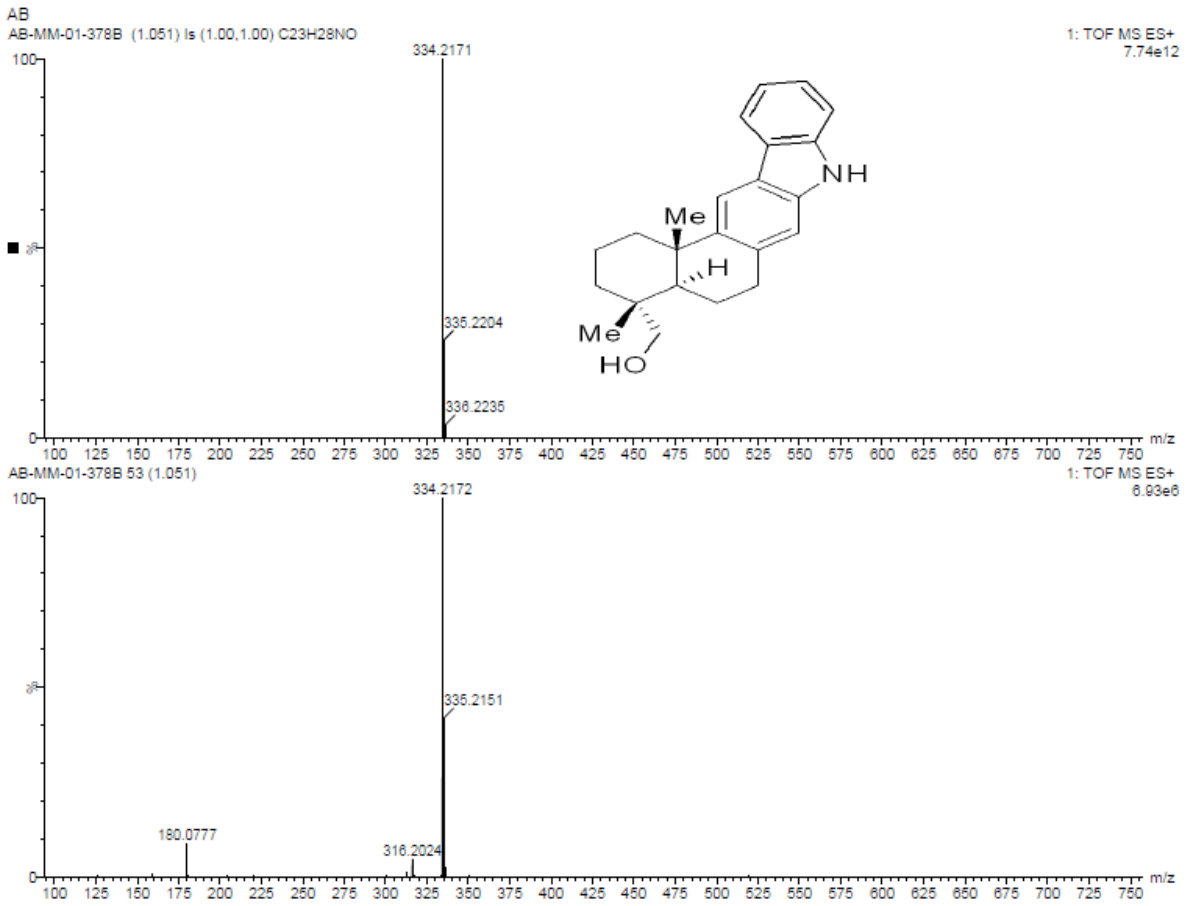




^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8h**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8h**



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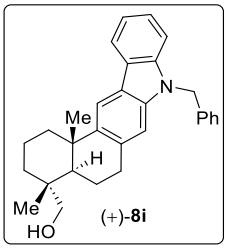
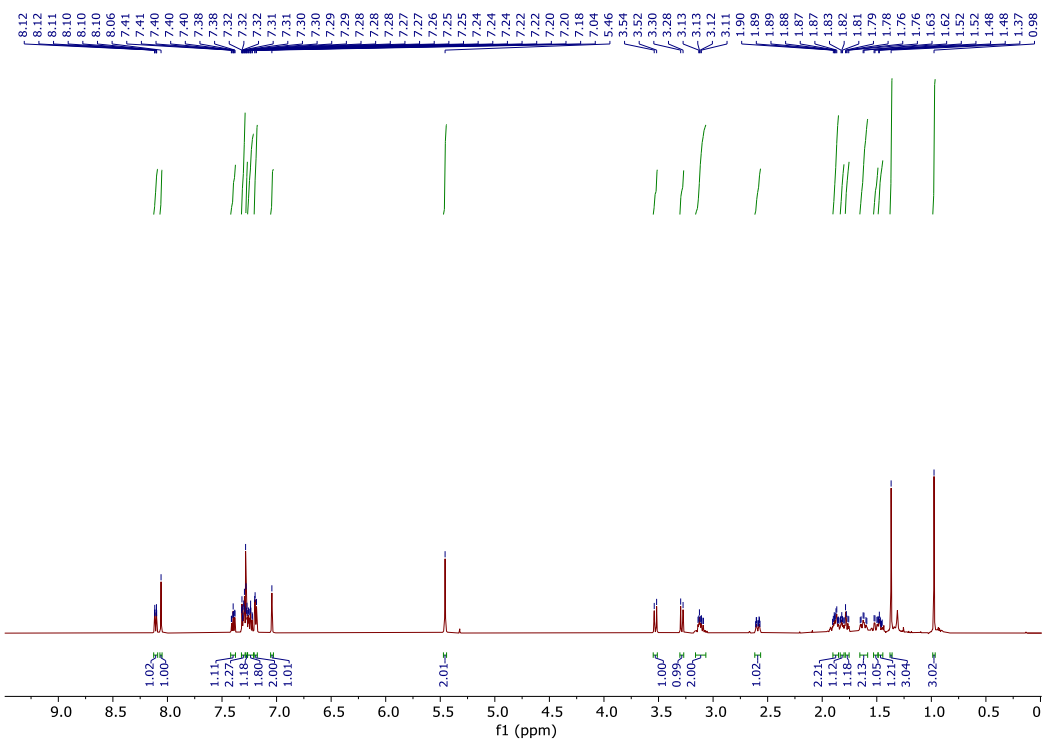
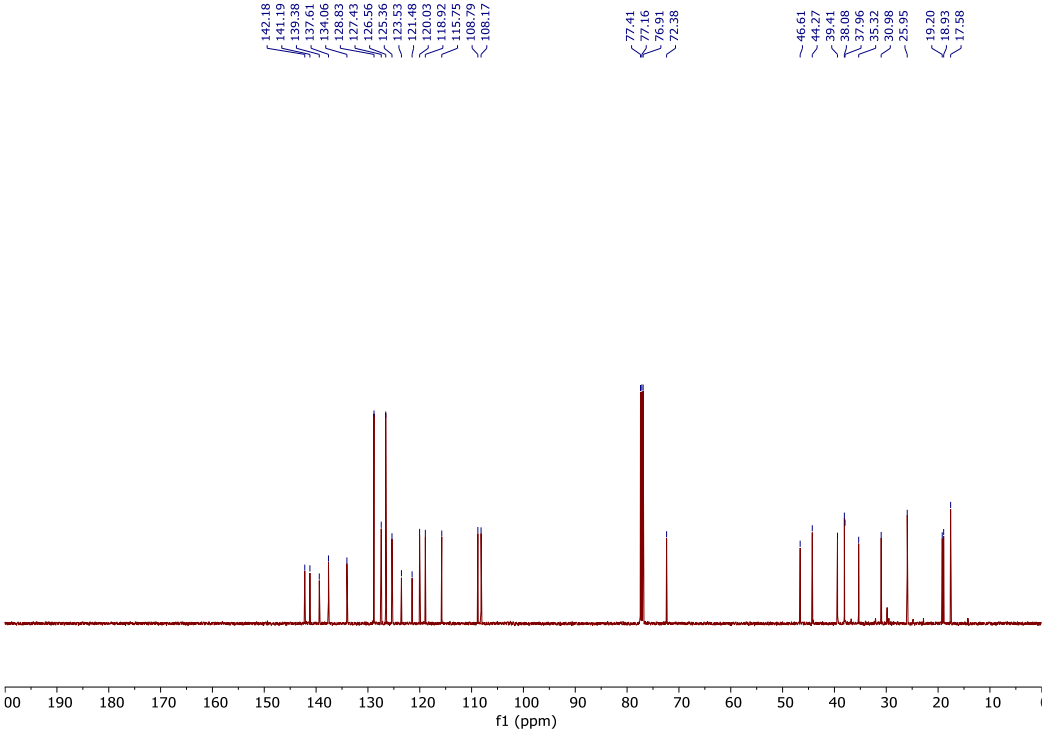


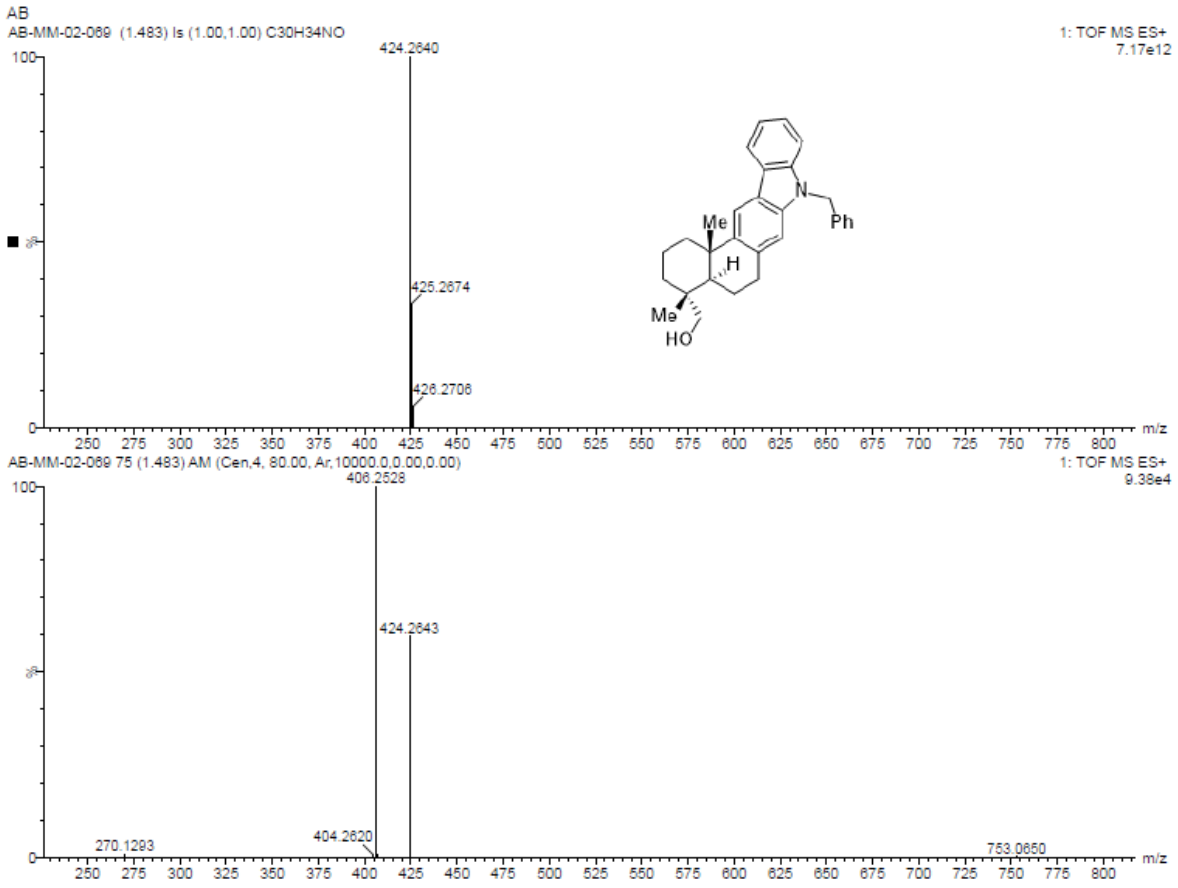
(+)-**8i**



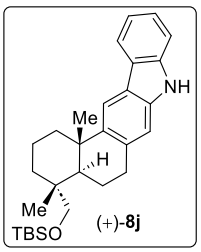
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8i**

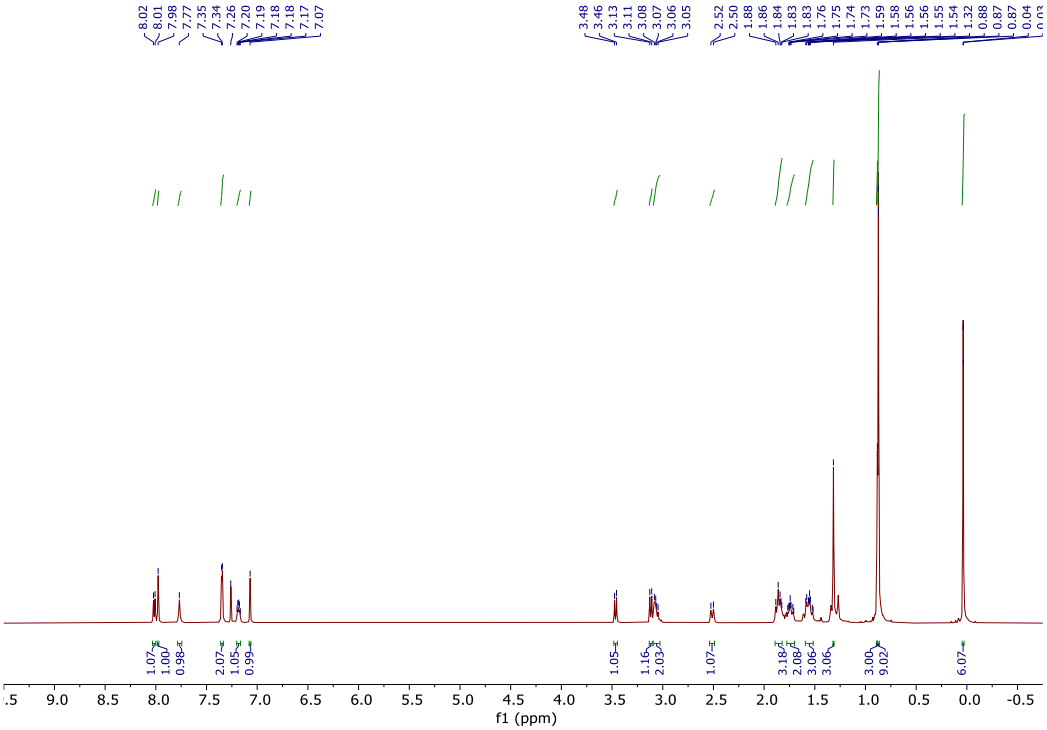


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8i**

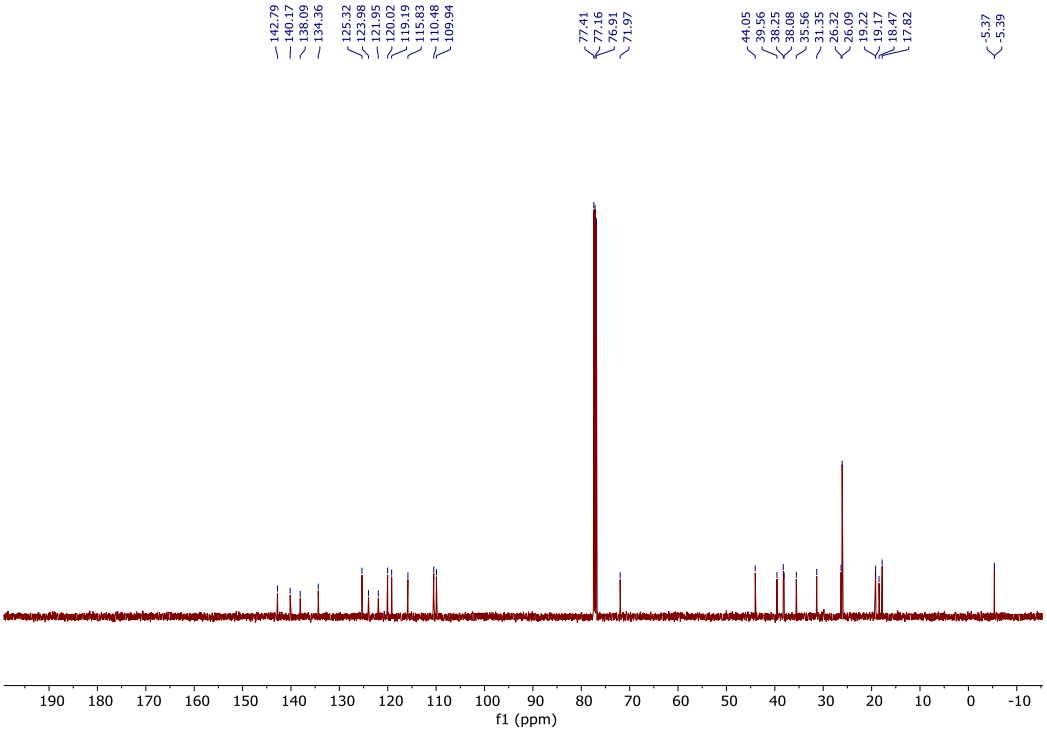


HRMS data of (+)-**8i**

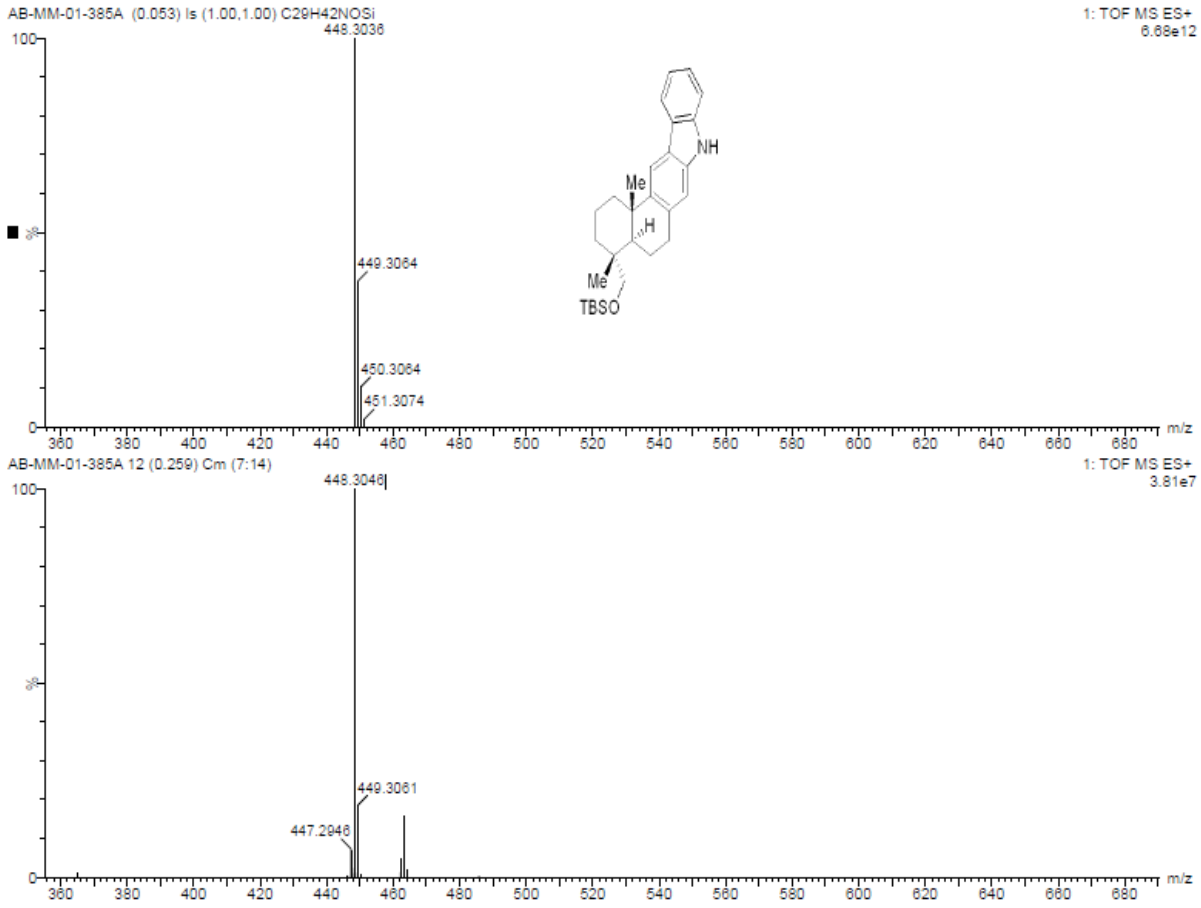




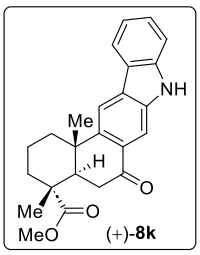
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8j**

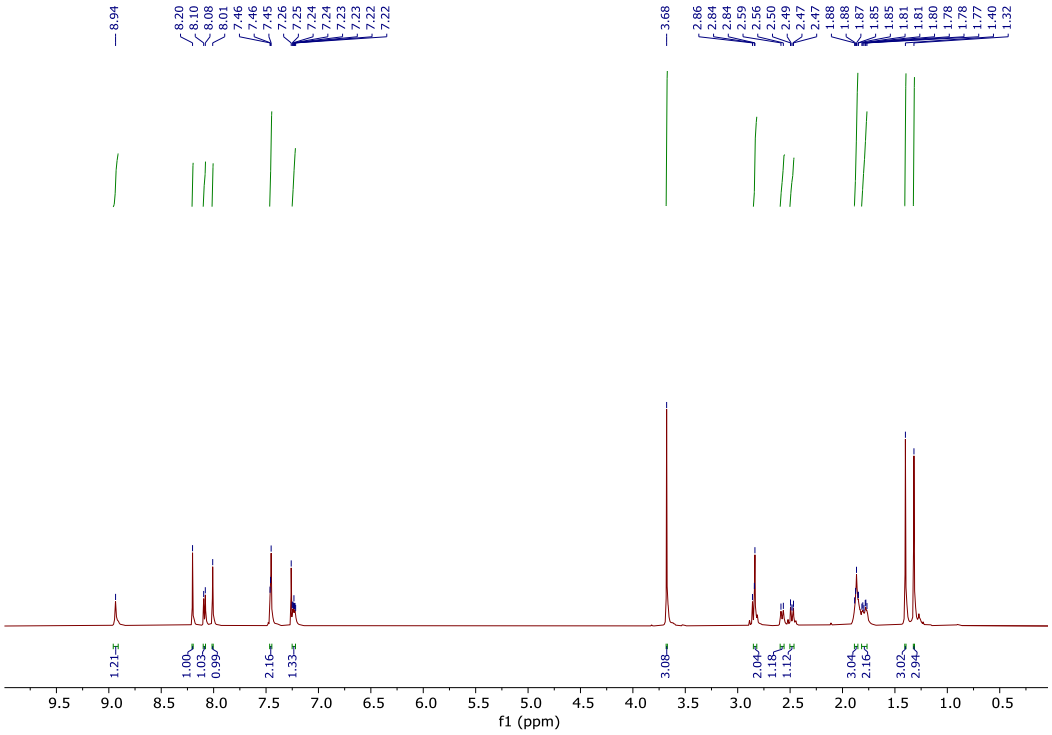


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8j**

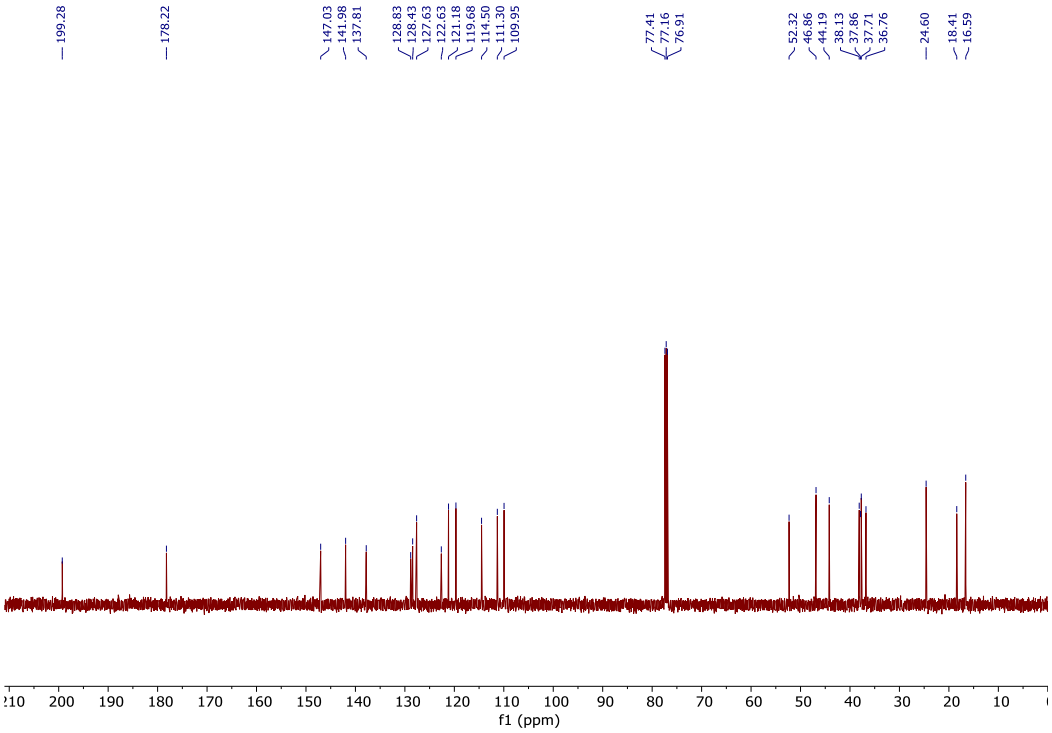


HRMS data of (+)-**8j**

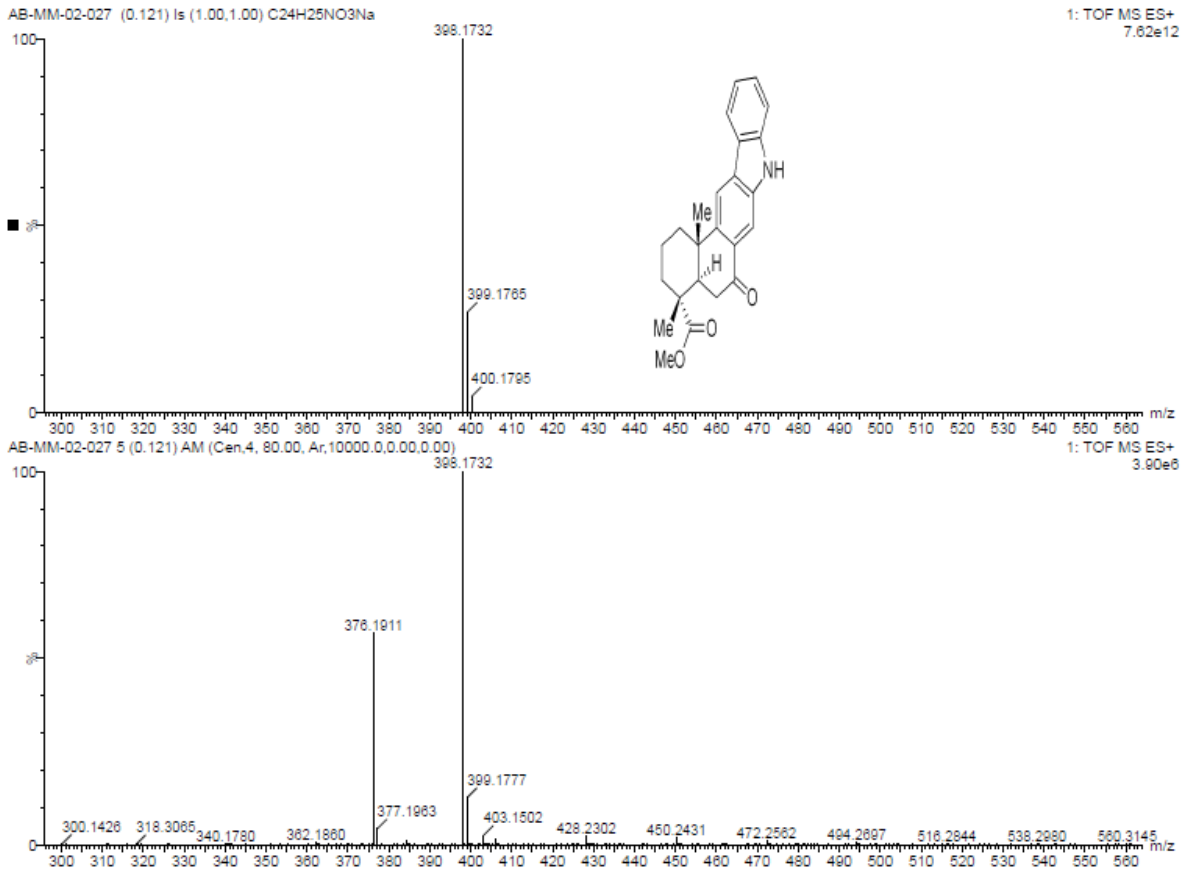




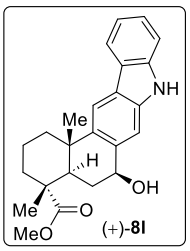
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8k**

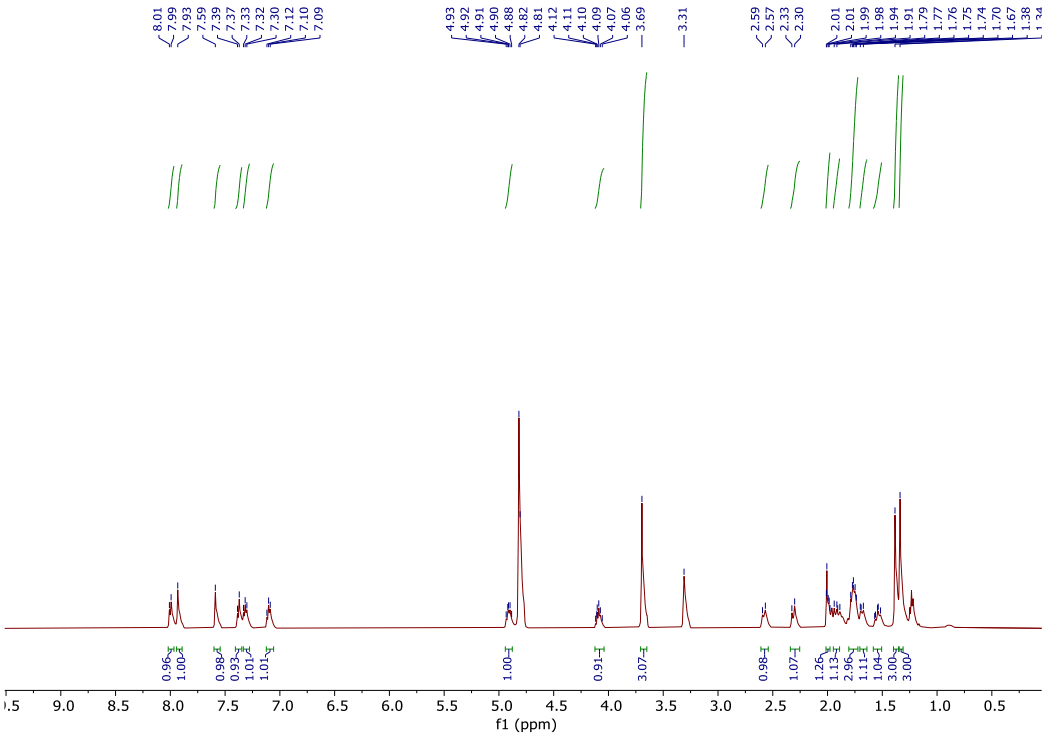


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8k**

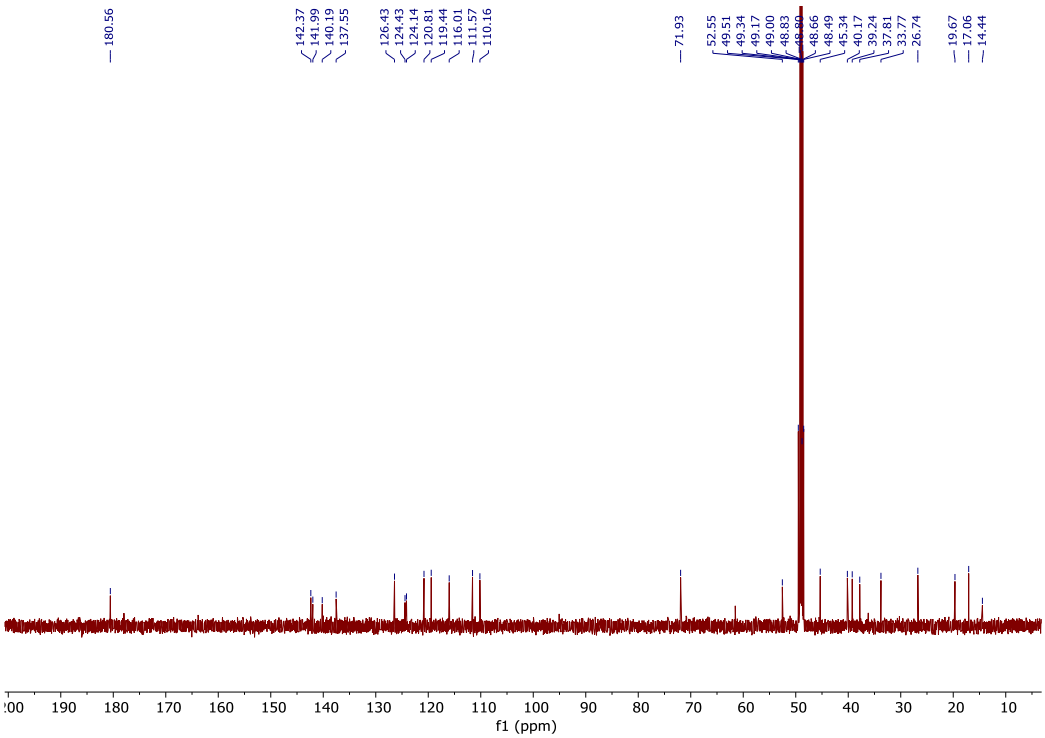


HRMS data of (+)-**8k**

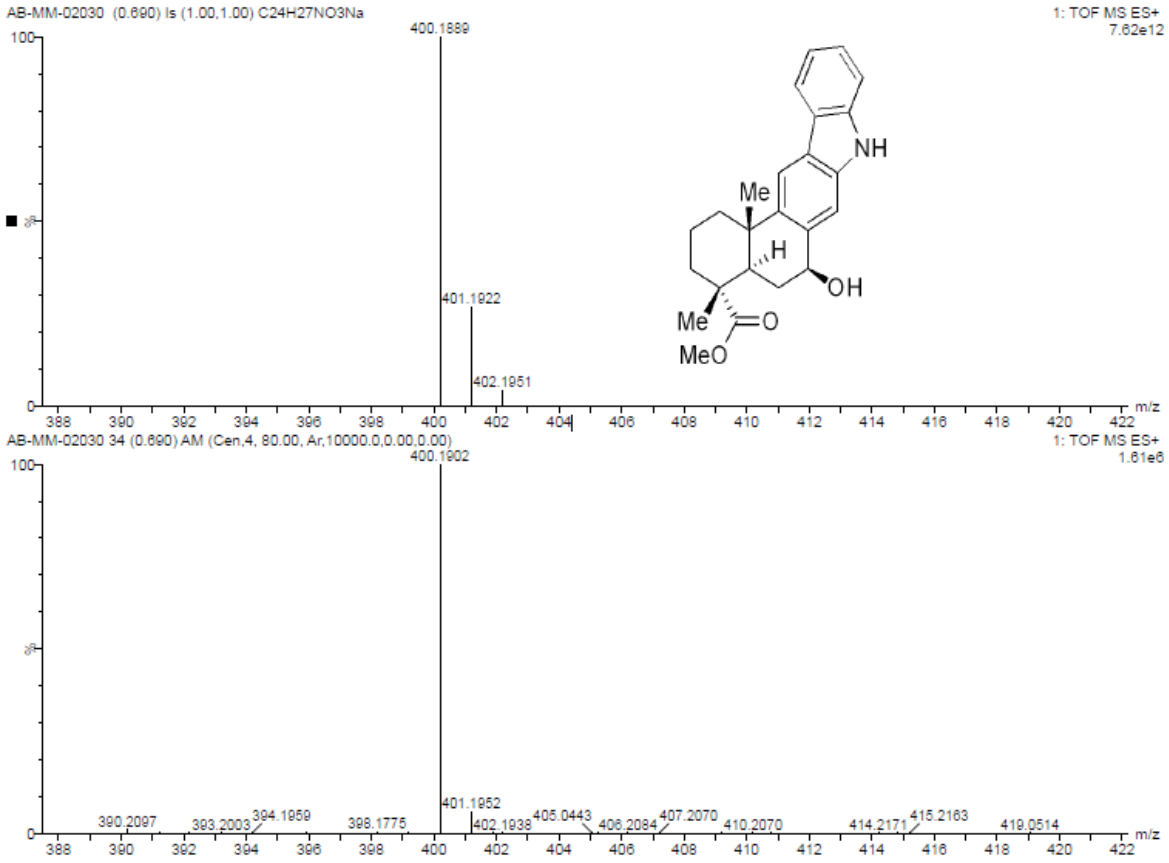




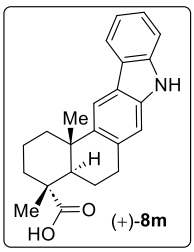
^{1}H NMR (500 MHz, CD_3OD) of (+)-**8l**

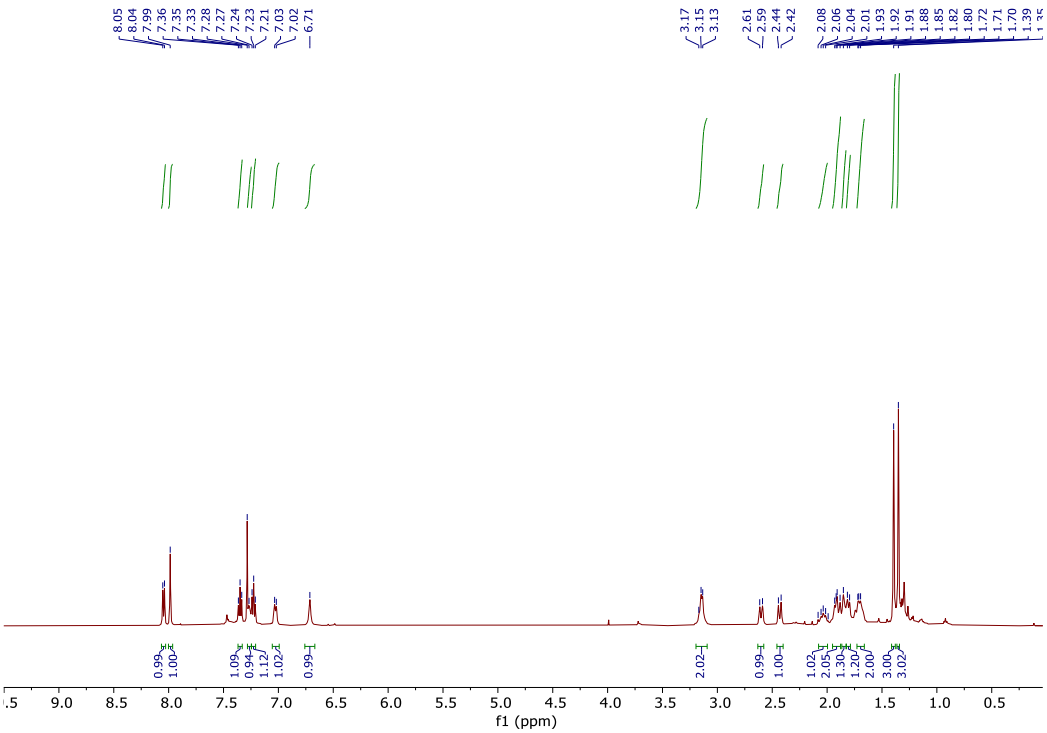


^{13}C NMR (125 MHz, CD_3OD) of (+)-**8l**

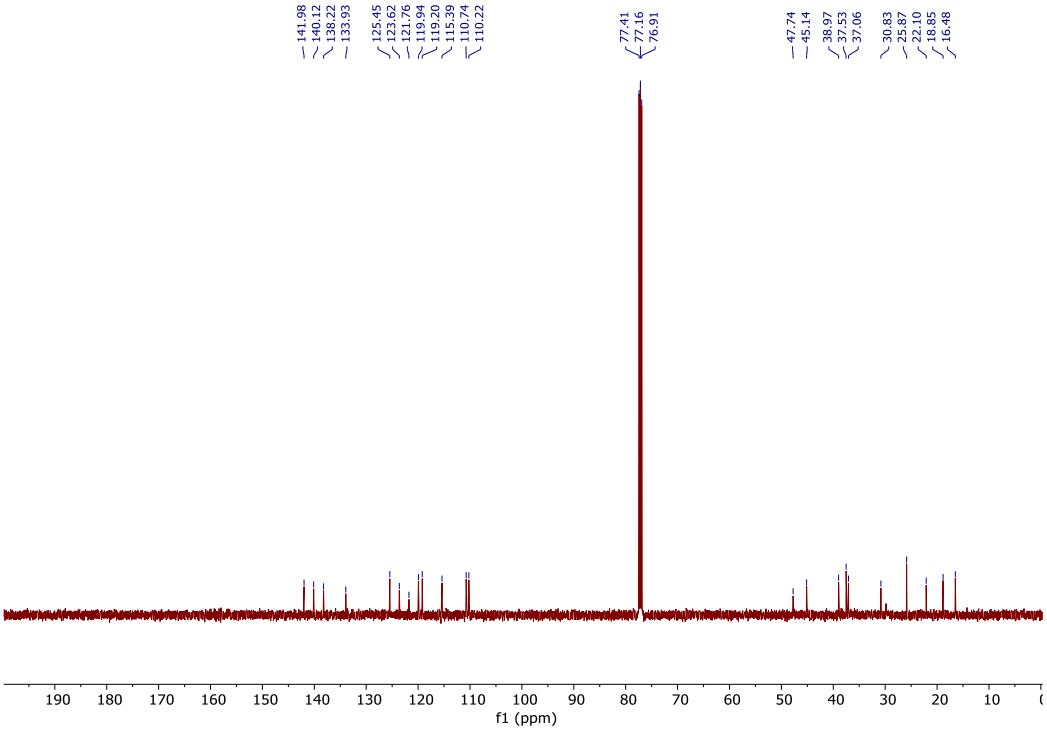


HRMS data of (+)-**8l**

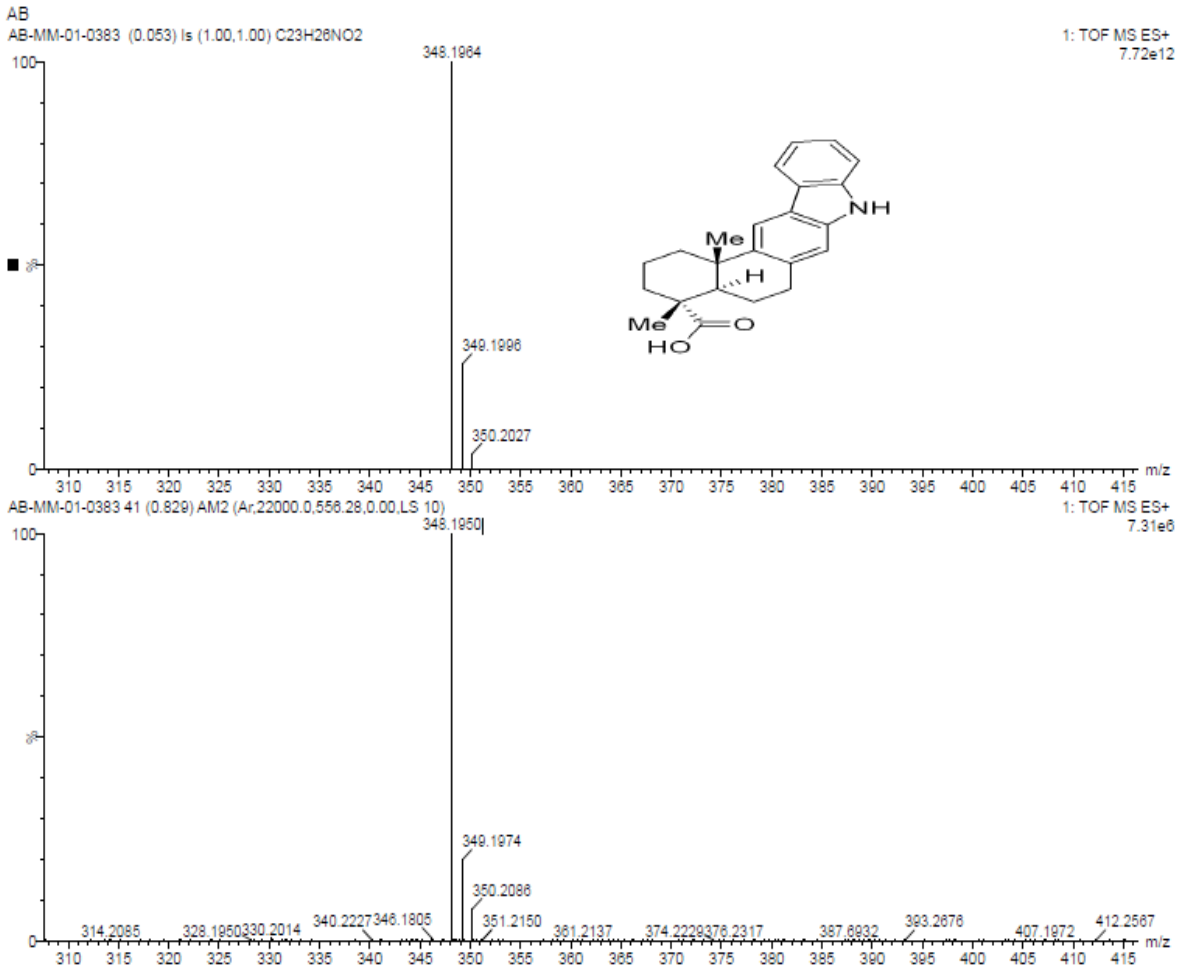




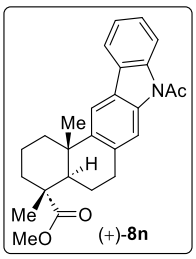
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8m**

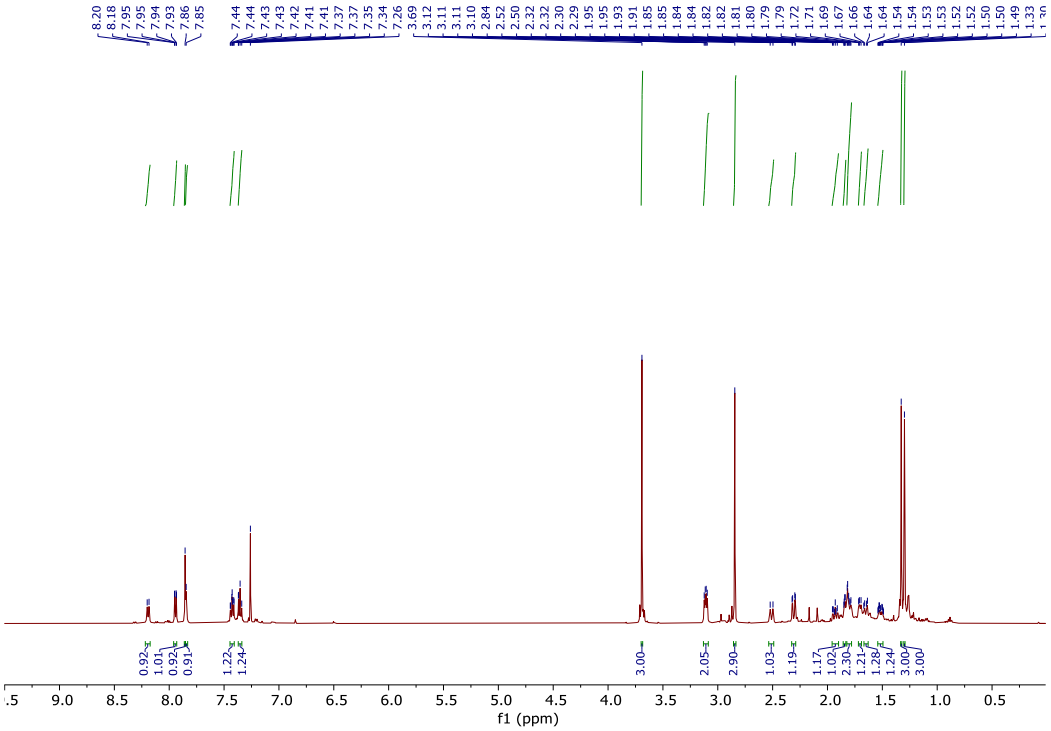


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8m**

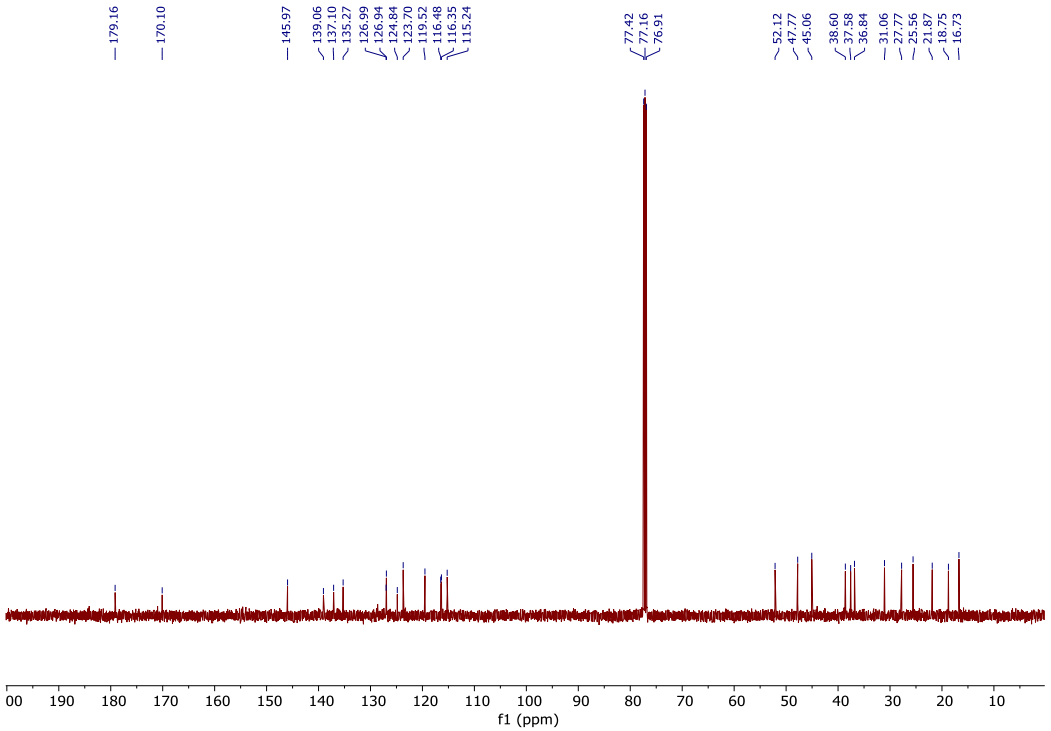


HRMS data of (+)-**8m**





^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8n**



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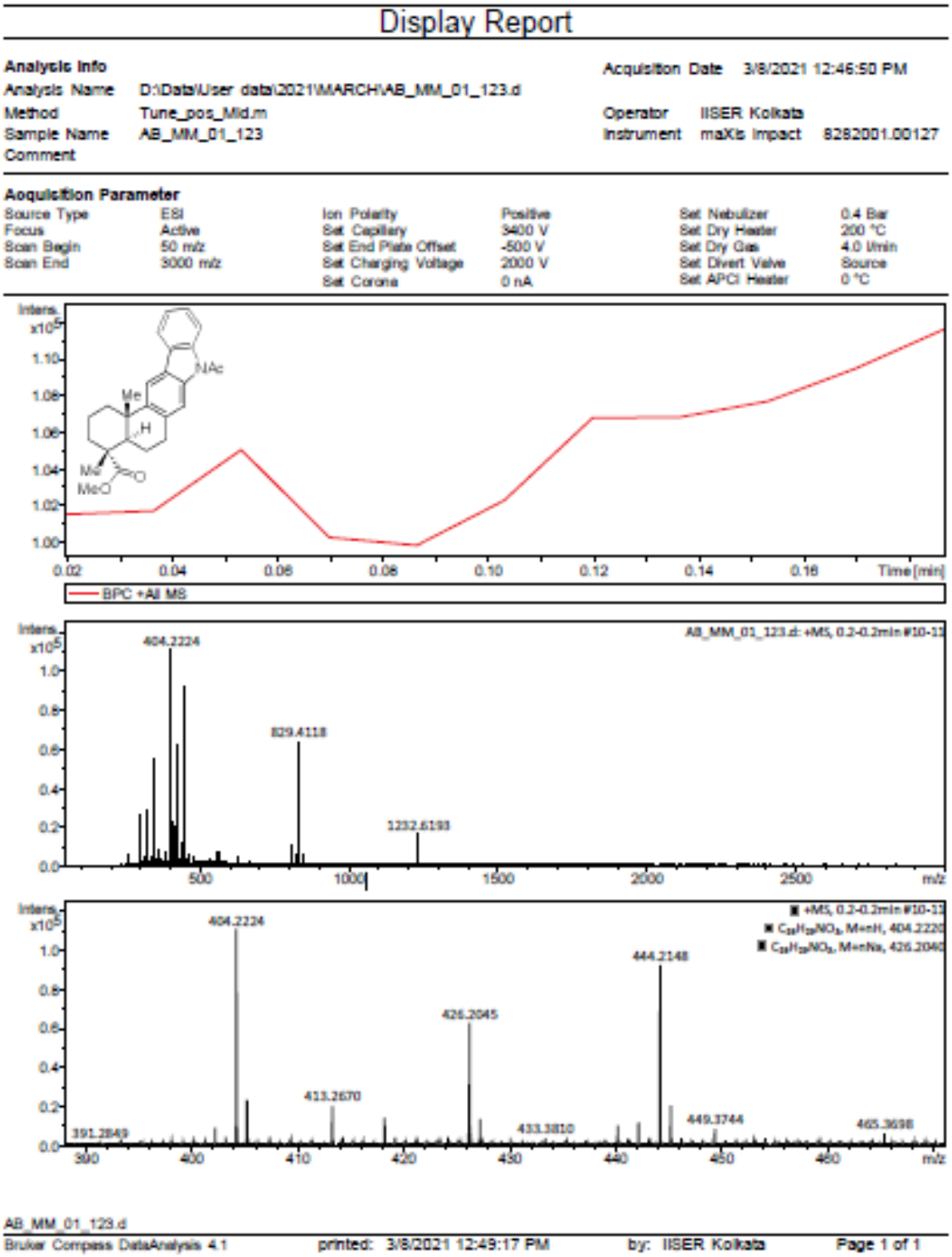
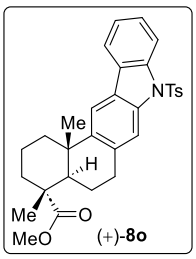
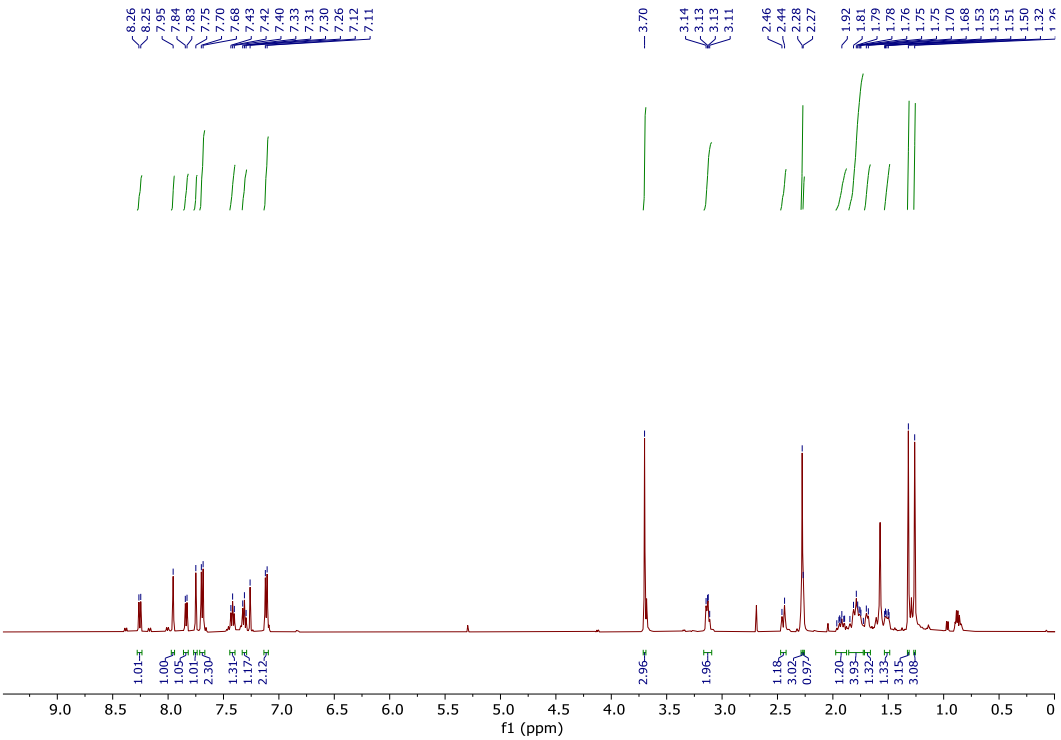
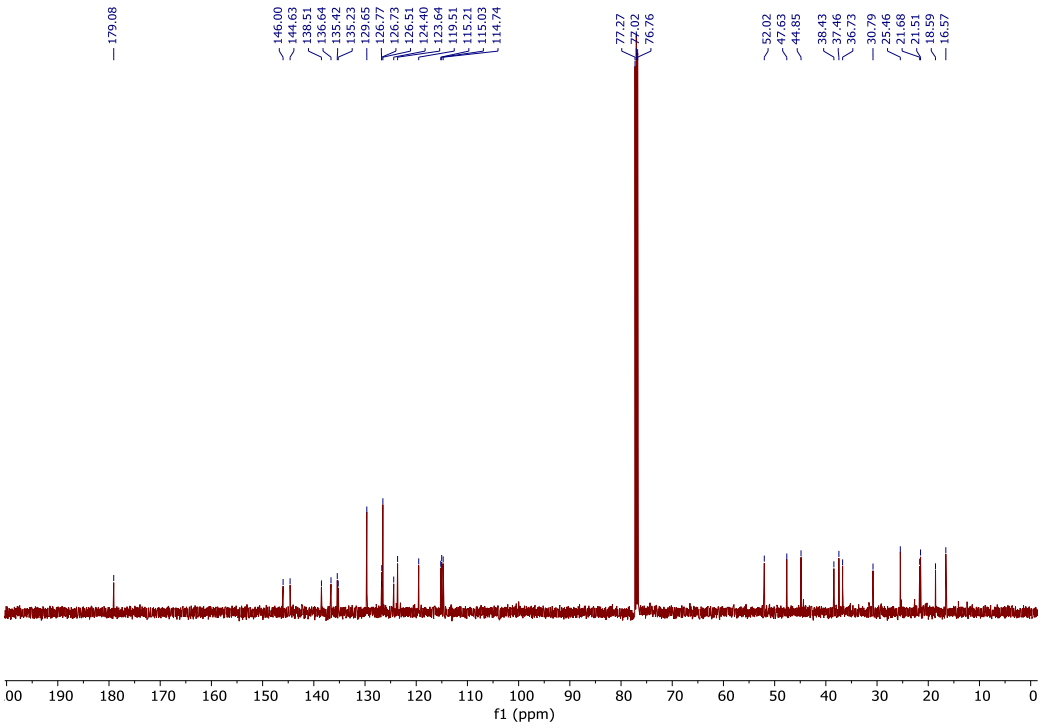


HRMS data of (+)-**8n**

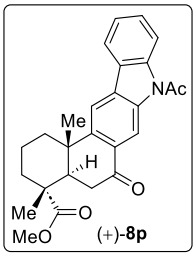


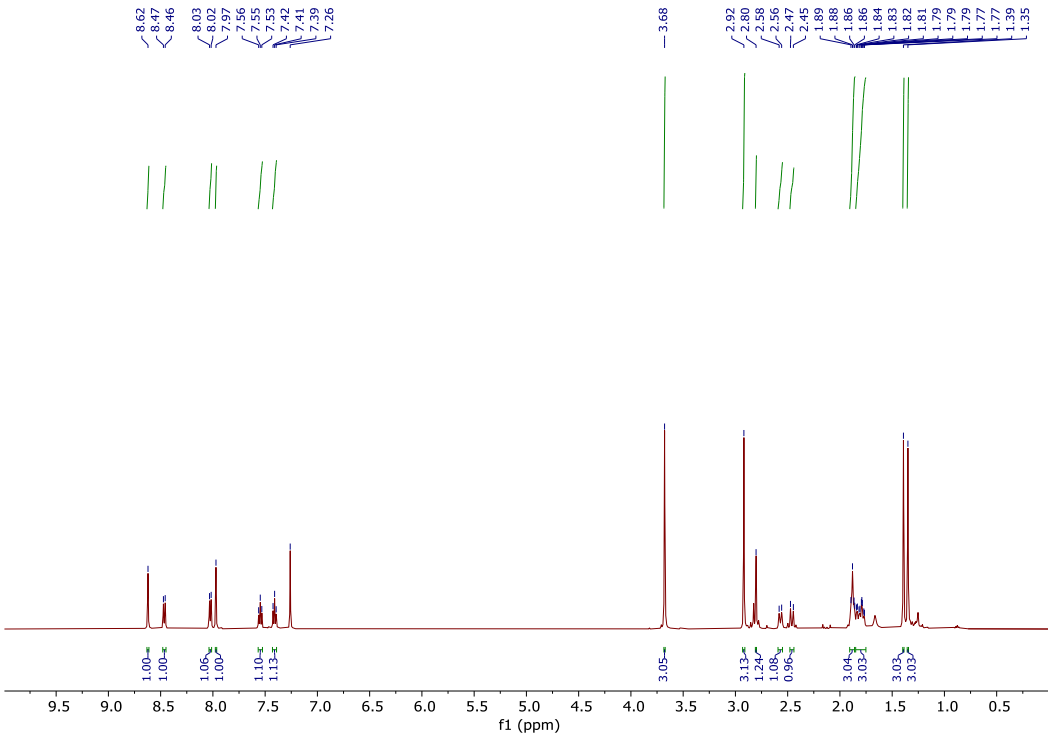


^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8o**

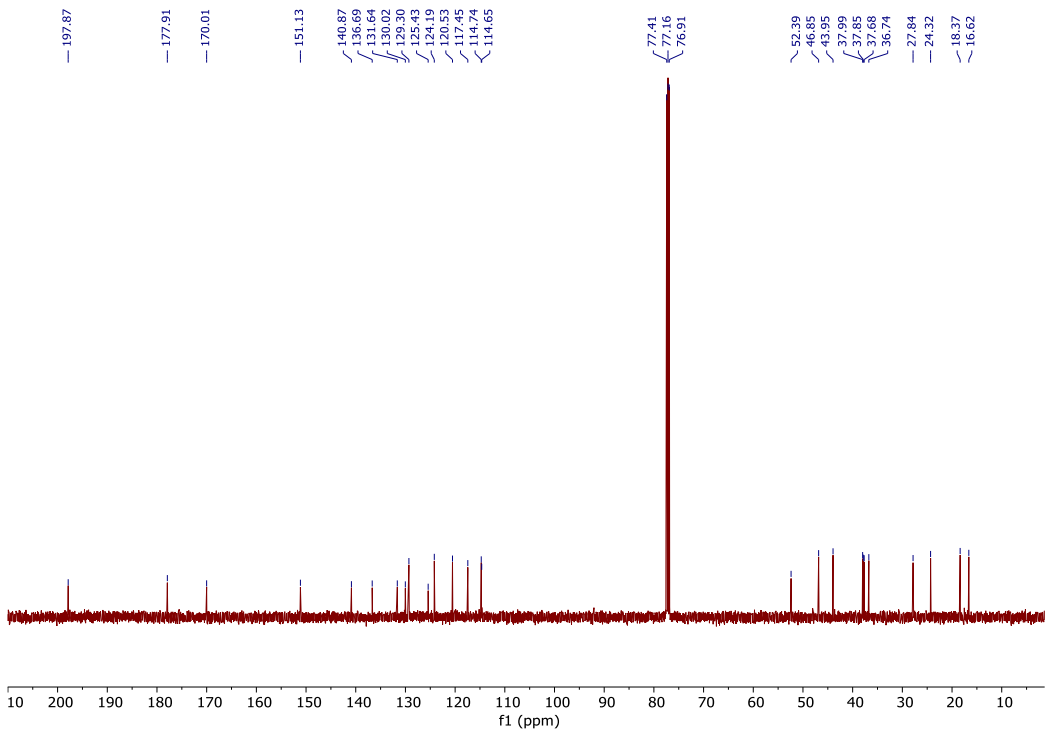


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8o**

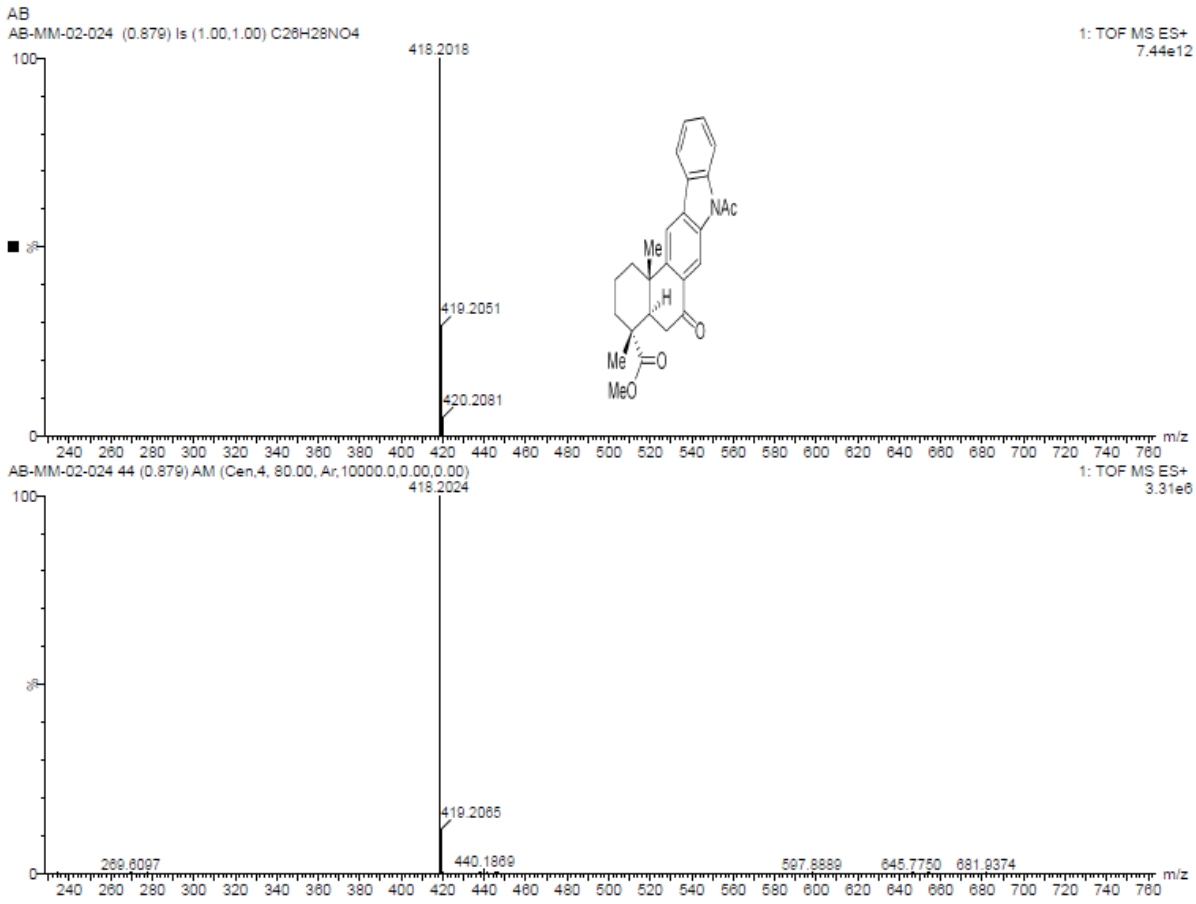




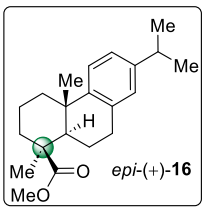
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8p**

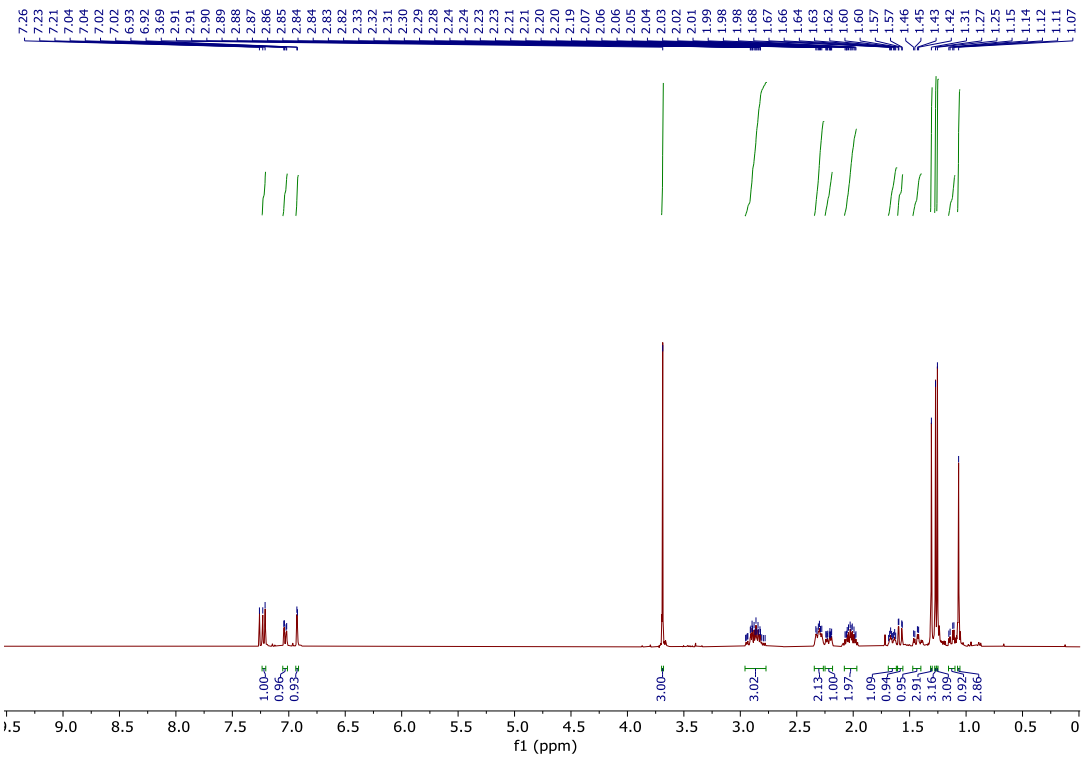


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8p**

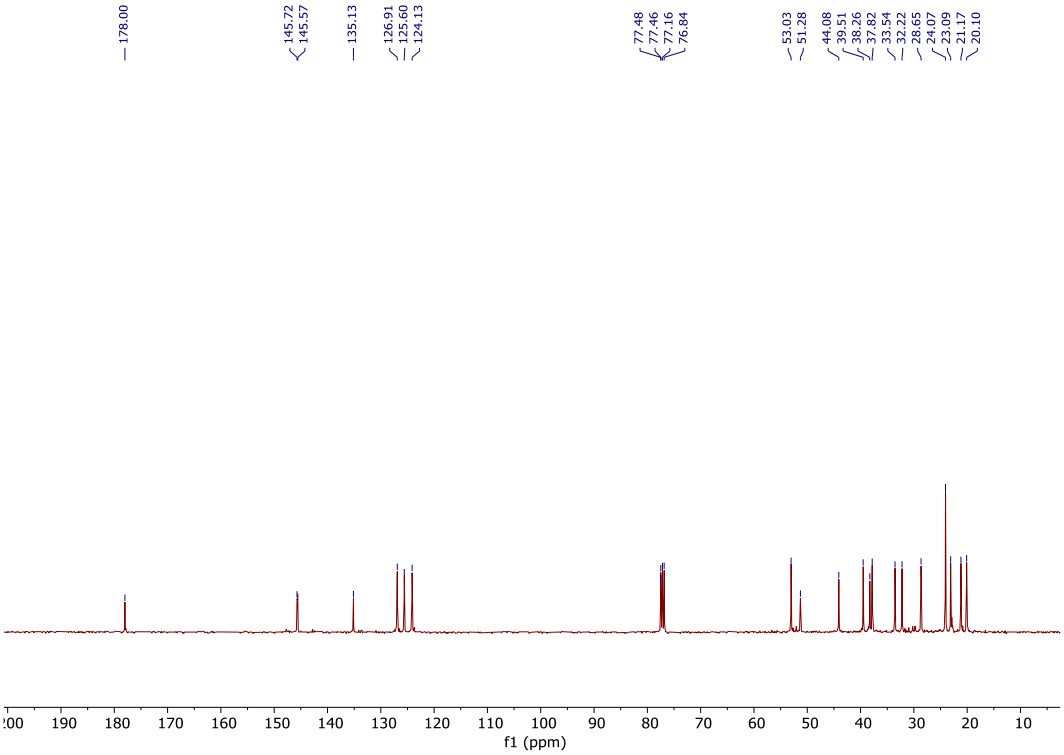


HRMS data of (+)-**8p**

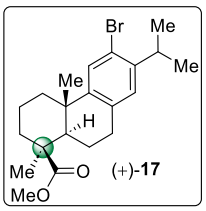


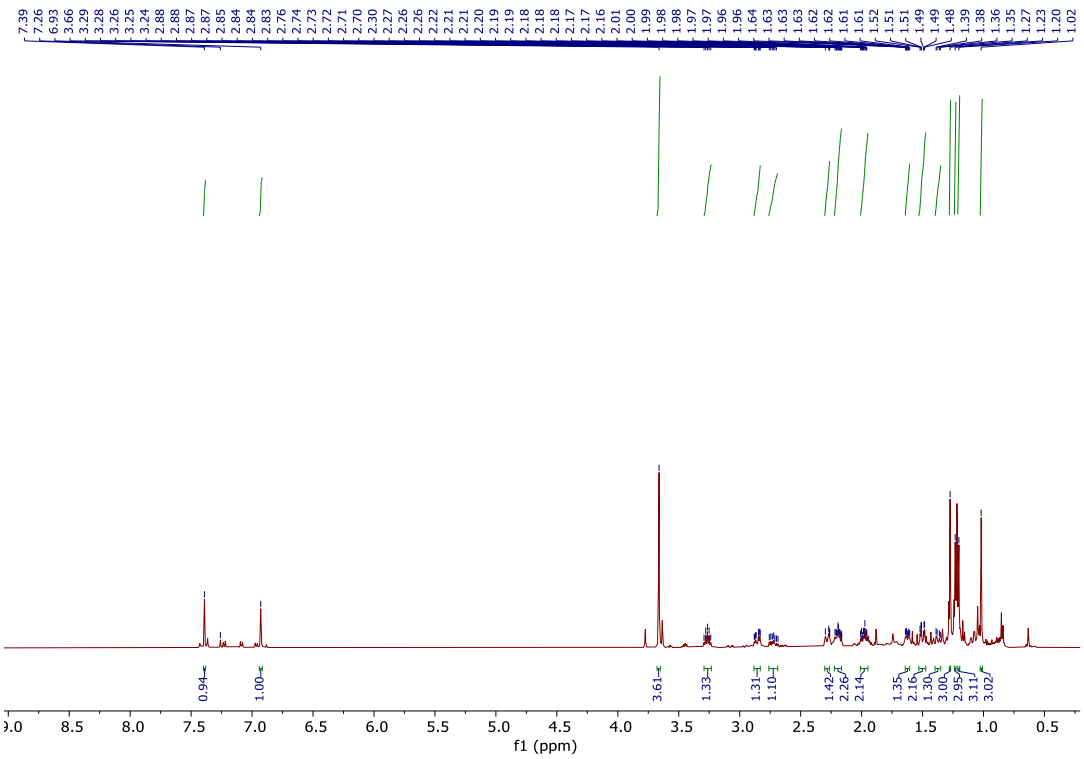


^{1}H NMR (400 MHz, $CDCl_3$) of *epi*-(+)-**16**

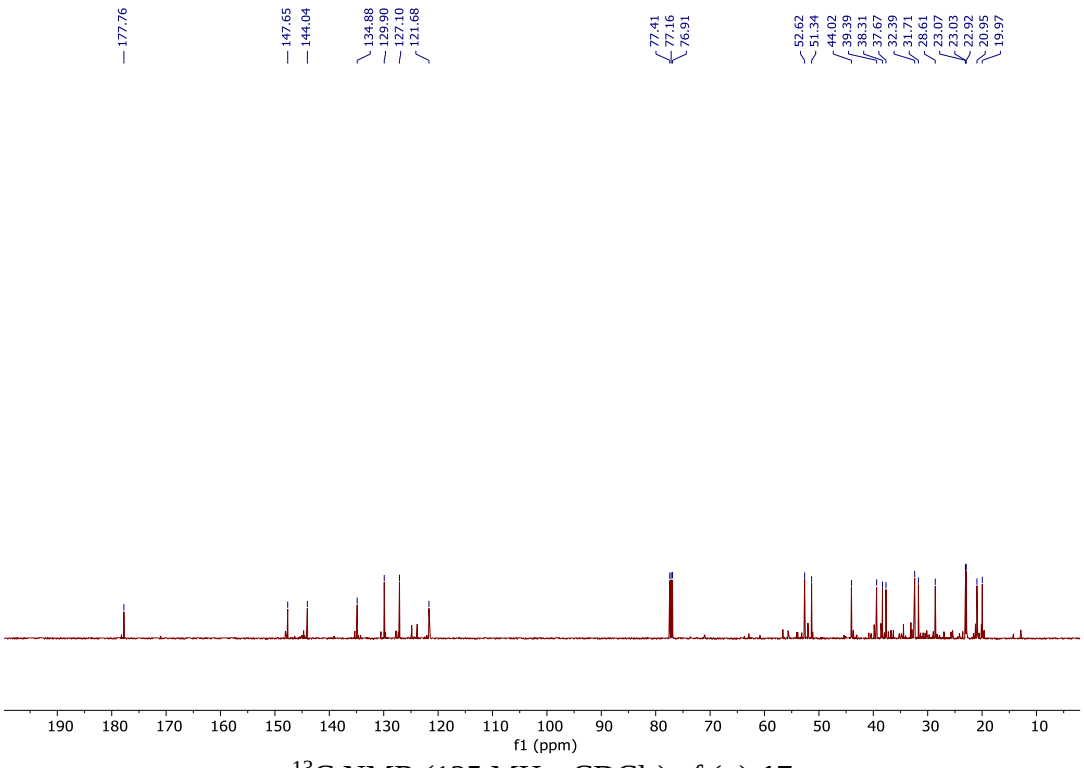


^{13}C NMR (100 MHz, $CDCl_3$) of *epi*-(+)-**16**

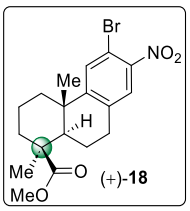


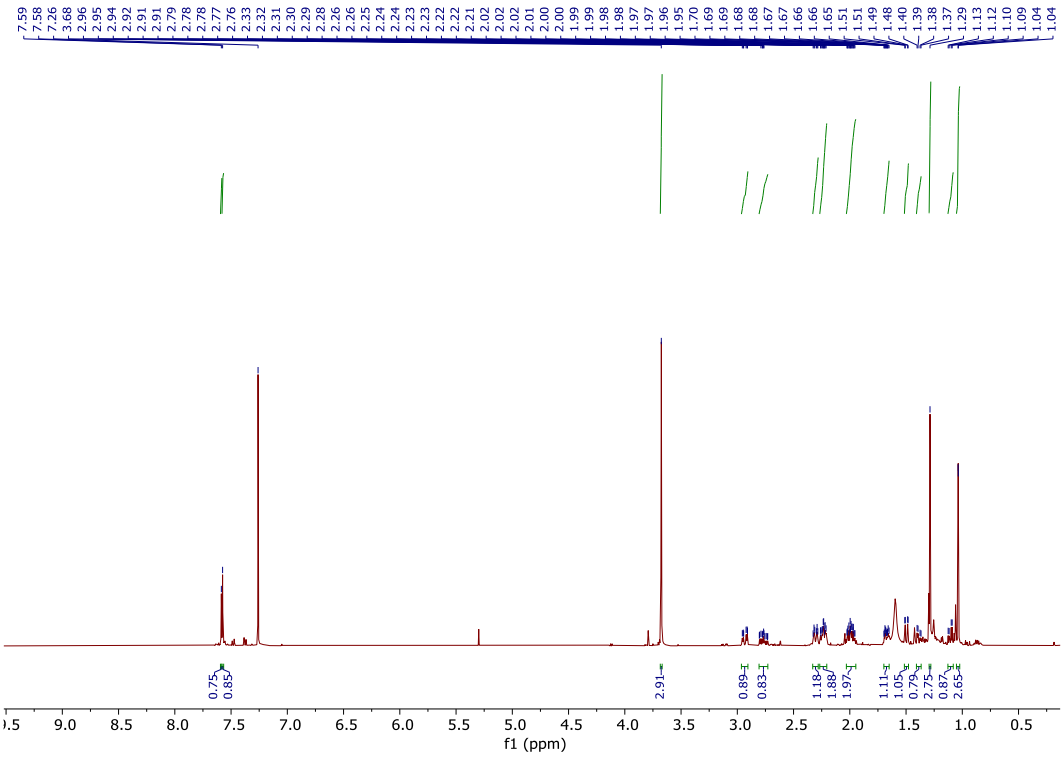


^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**17**

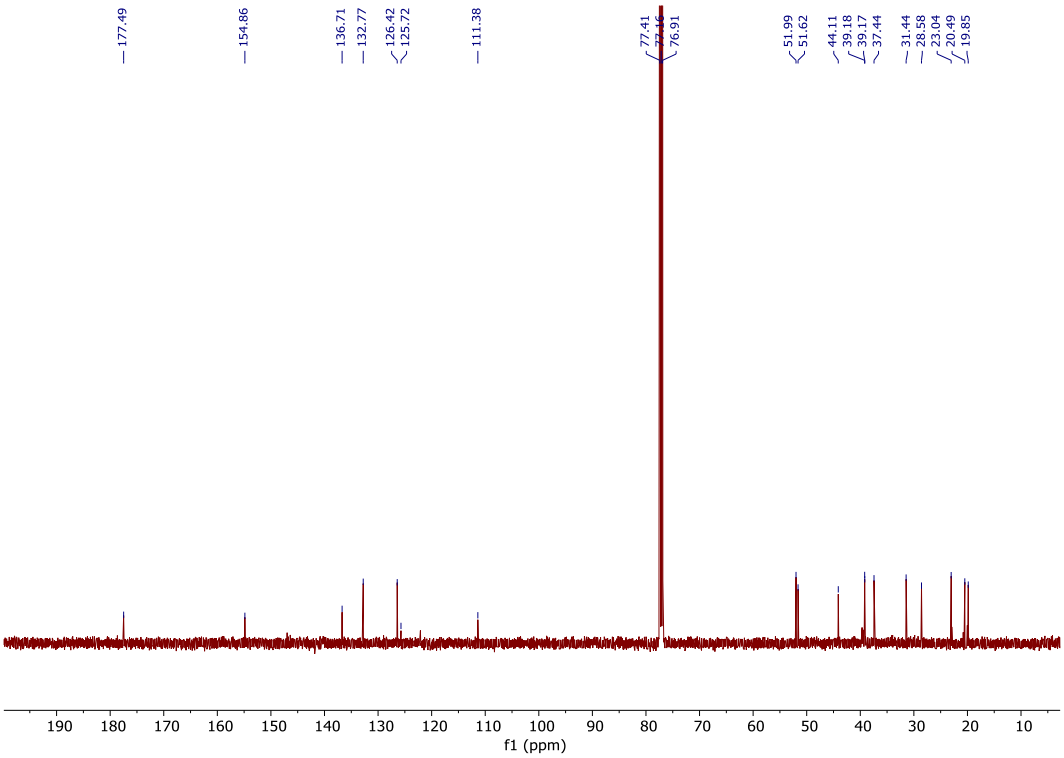


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**17**

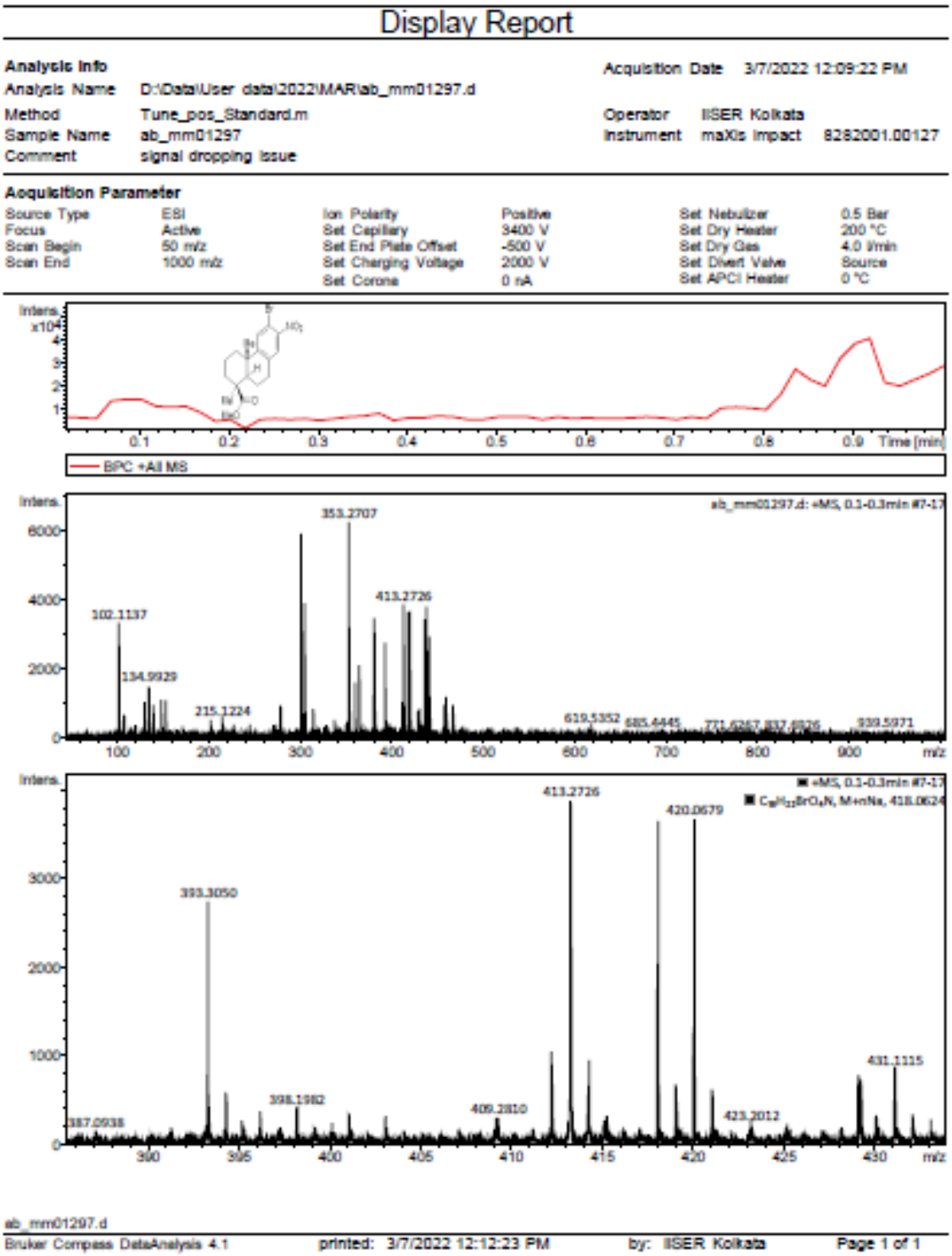




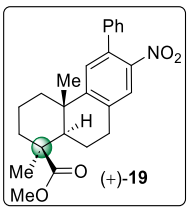
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**18**

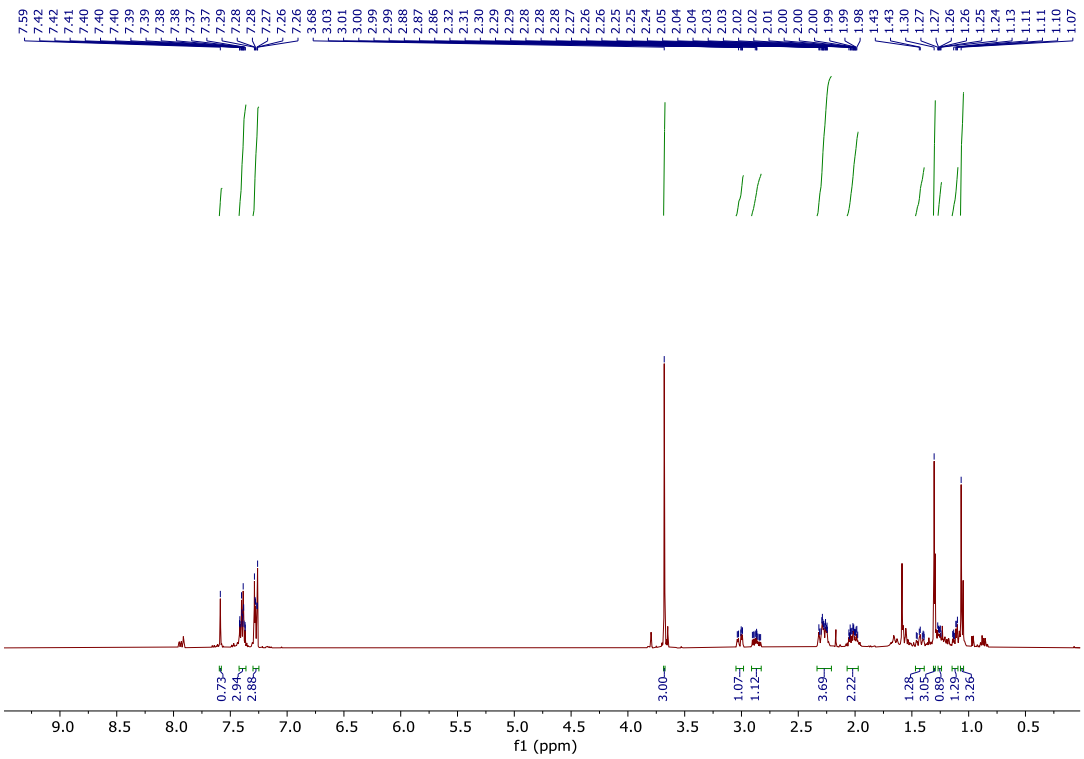


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**18**

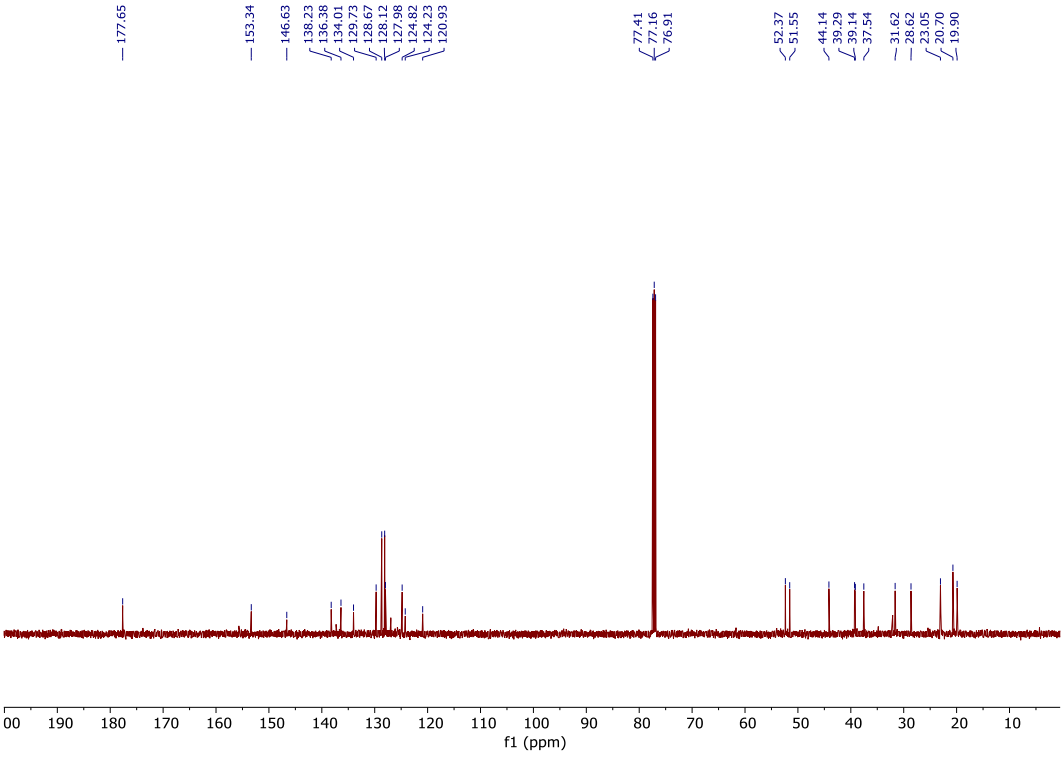


HRMS data of (+)-**18**

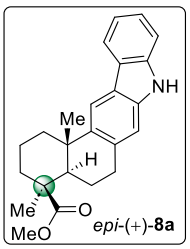


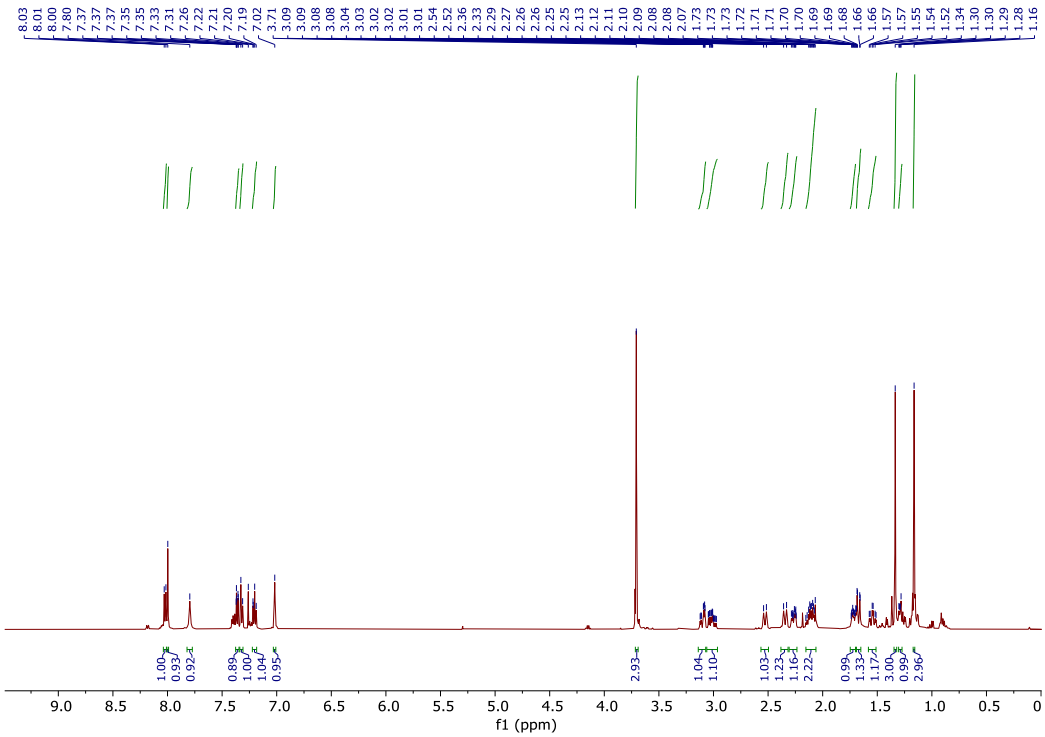


^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**19**

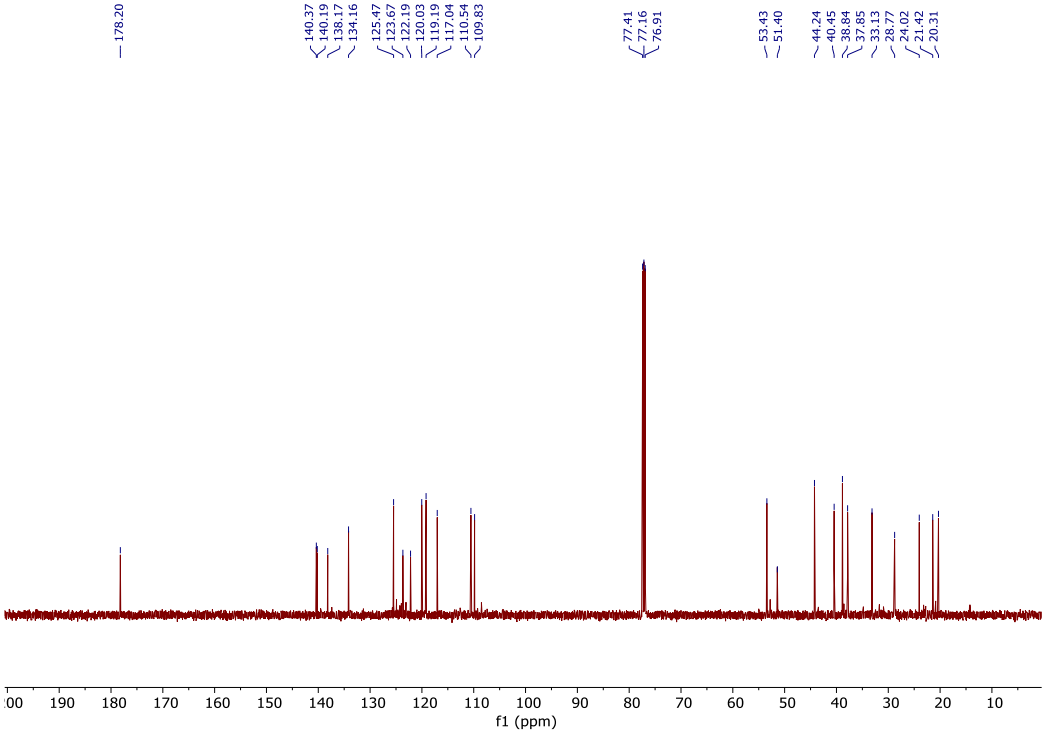


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**19**

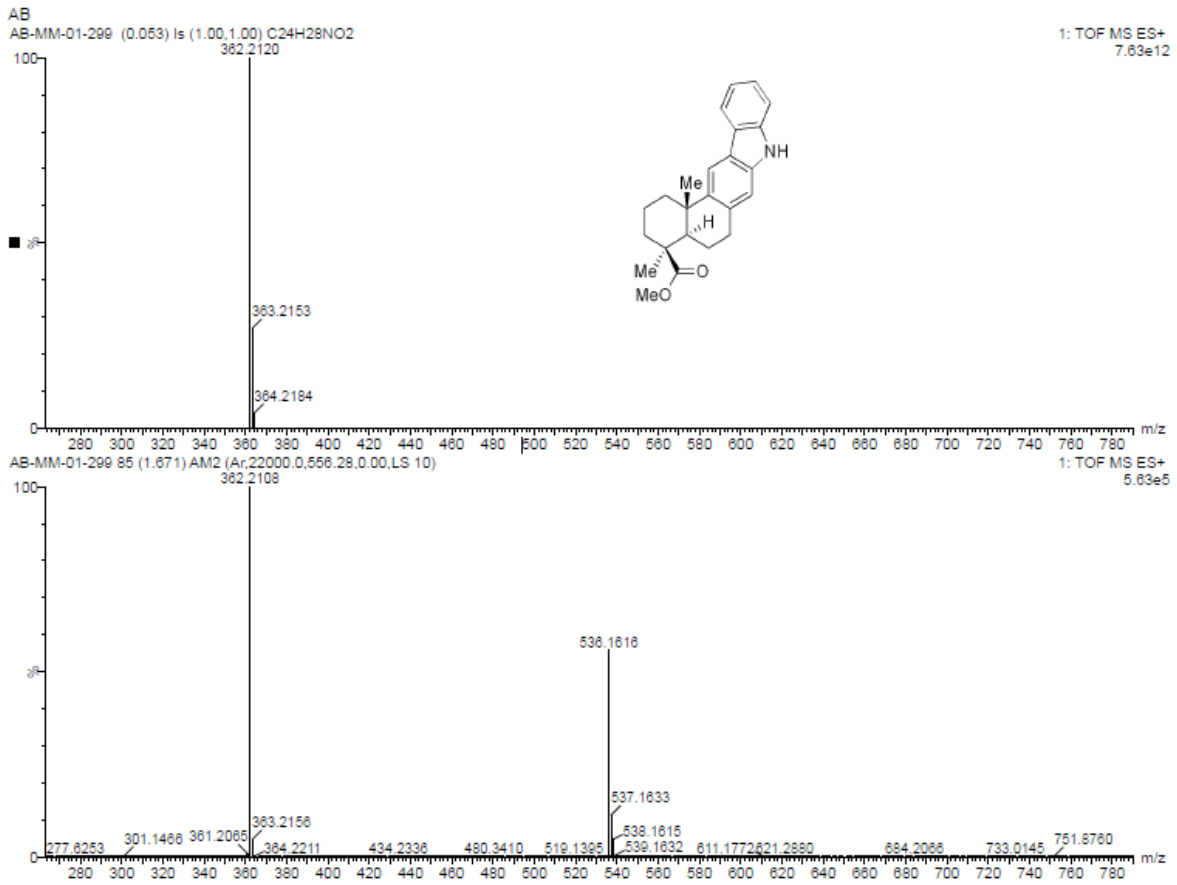




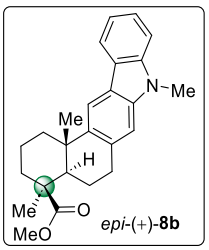
^{1}H NMR (500 MHz, $CDCl_3$) of *epi*-(+)-**8a**

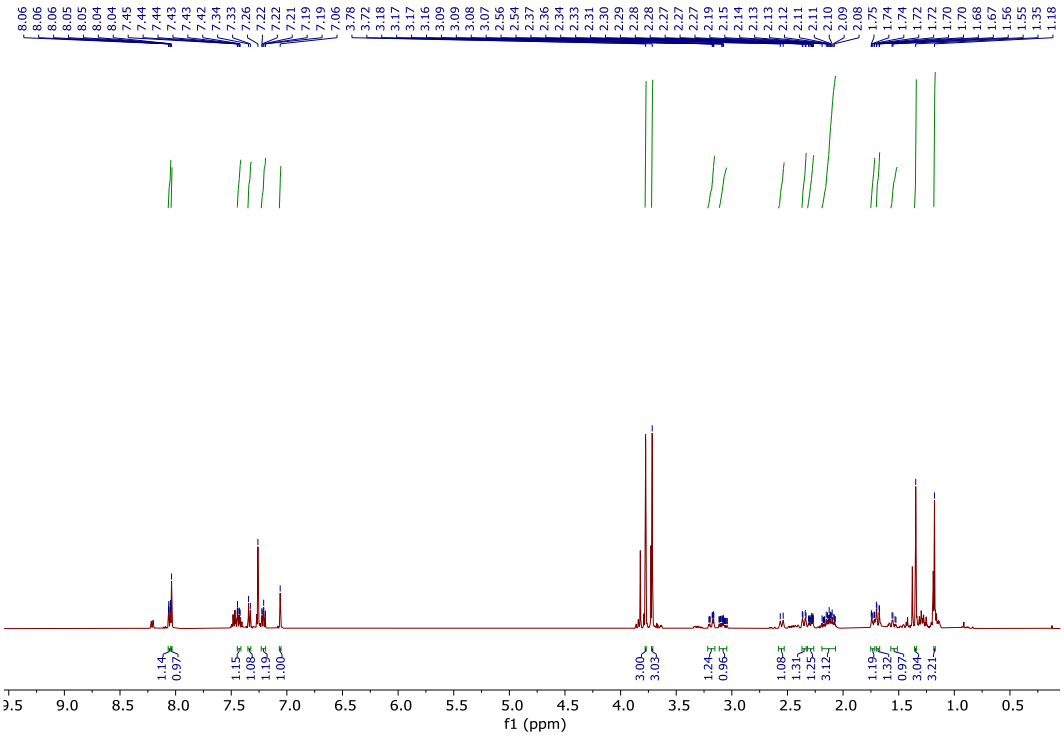


^{13}C NMR (125 MHz, $CDCl_3$) of *epi*-(+)-**8a**

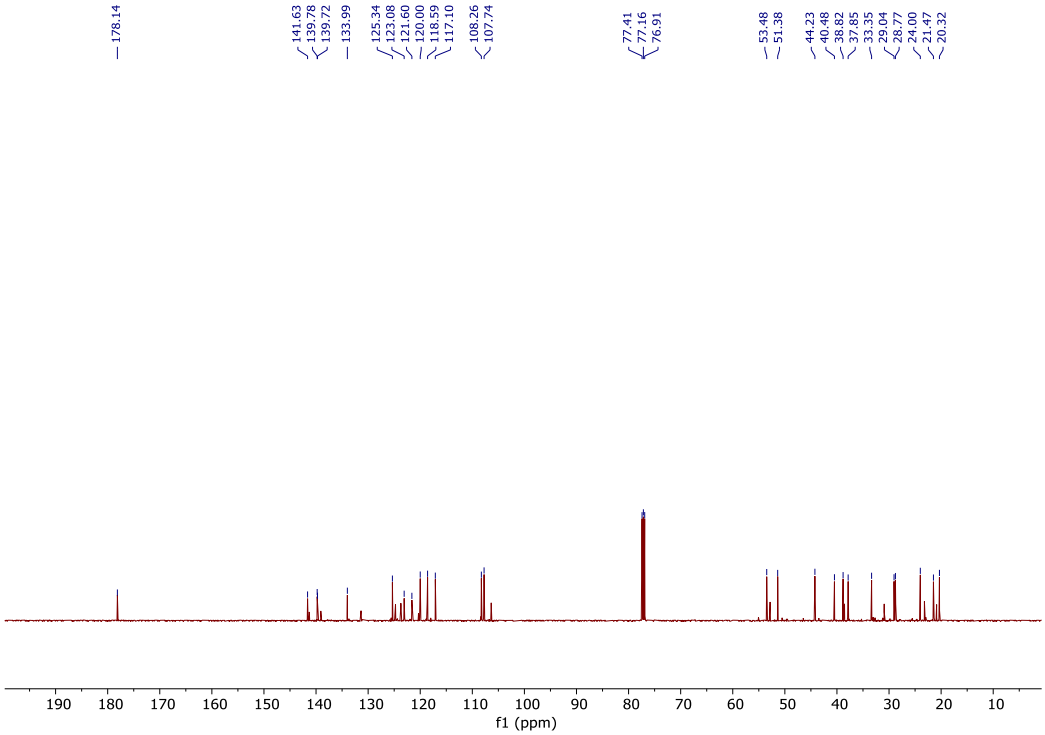


HRMS data of *epi*-(+)-**8a**

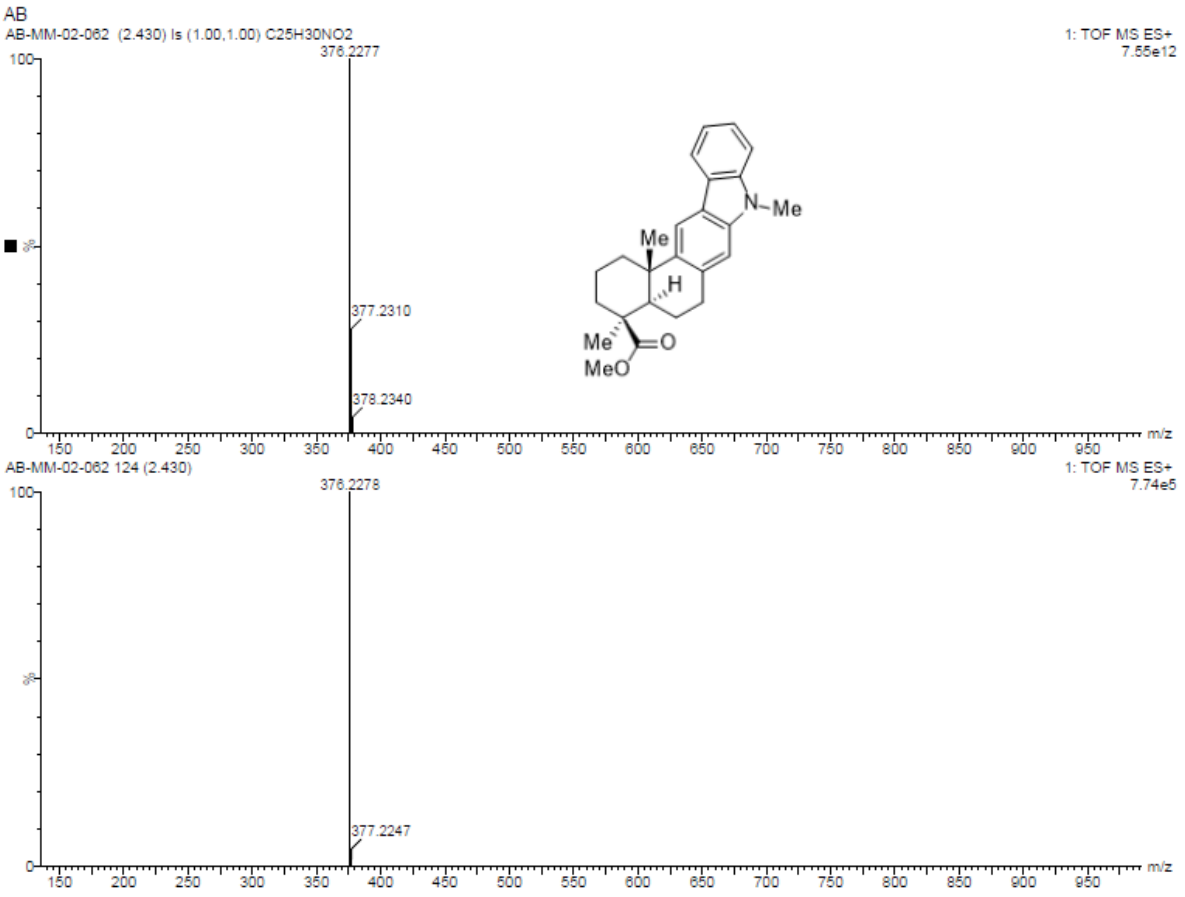




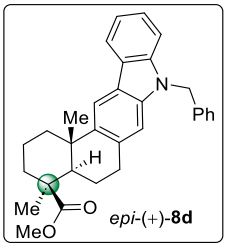
^{1}H NMR (500 MHz, $CDCl_3$) of *epi*-(+)-**8b**



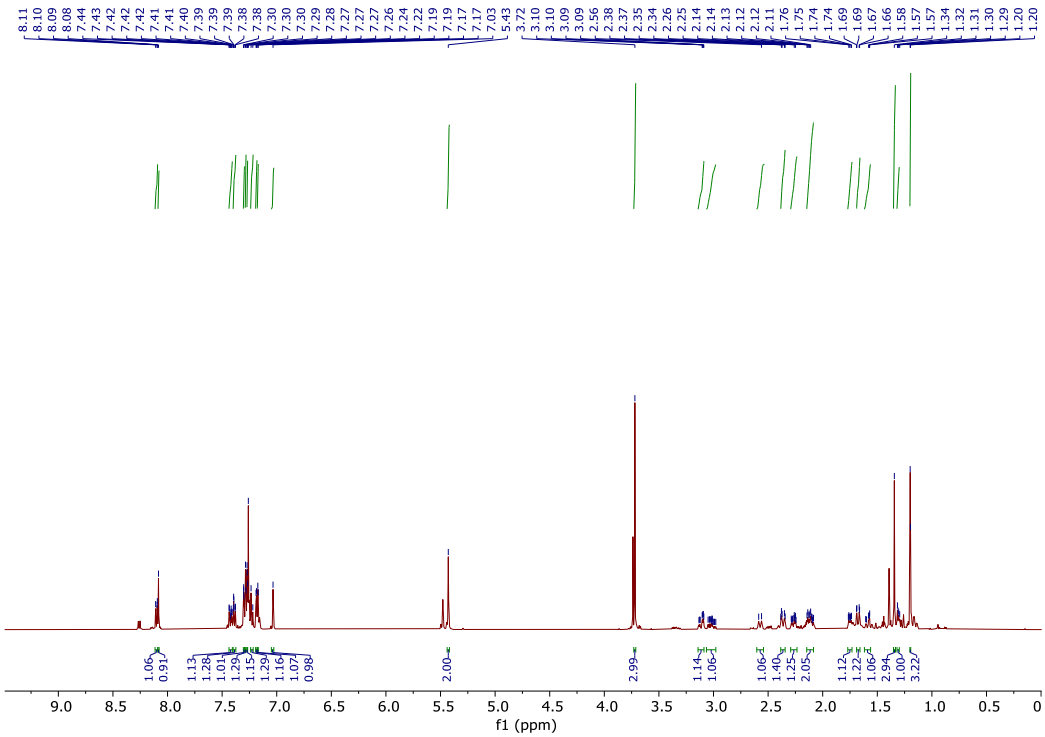
^{13}C NMR (125 MHz, $CDCl_3$) of *epi*-(+)-**8b**



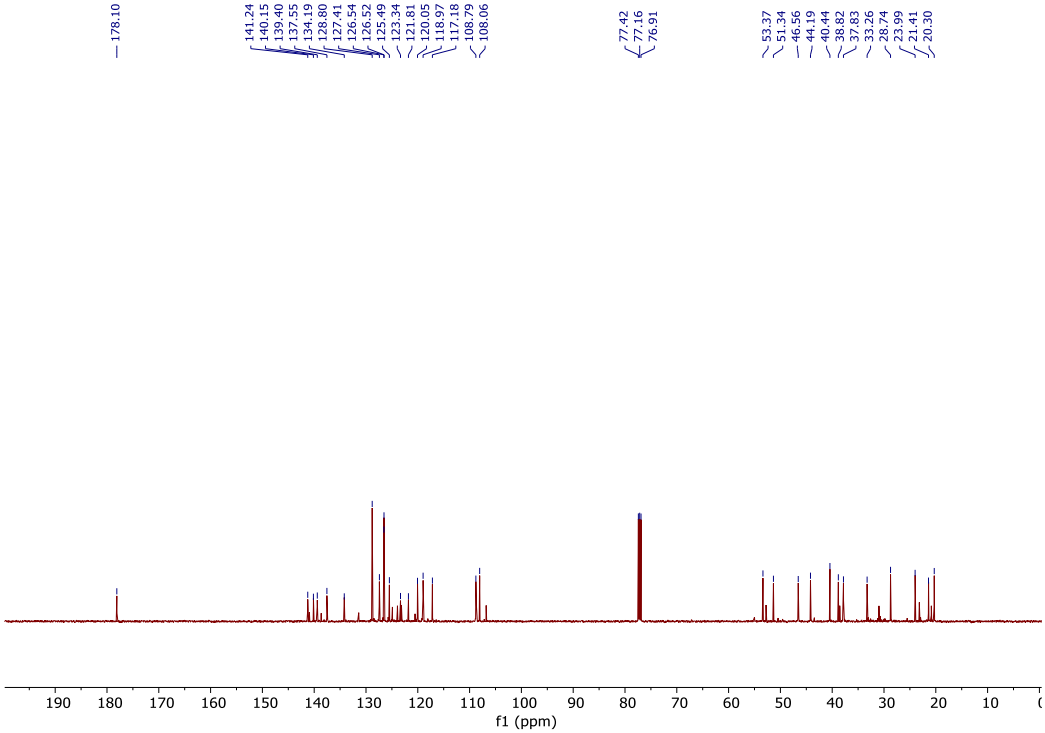
HRMS data of *epi*-(+)-**8b**



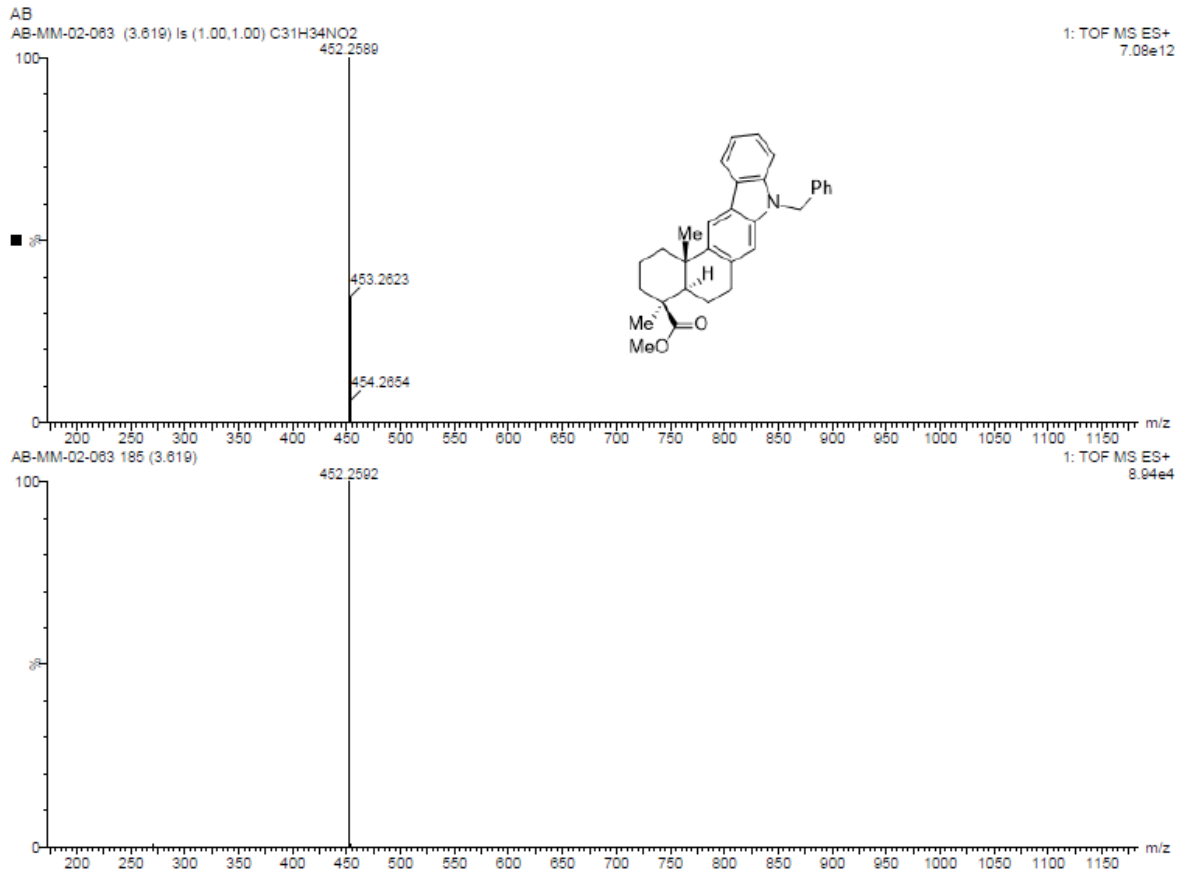
epi-(+)-**8d**



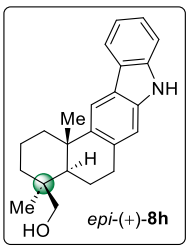
^{1}H NMR (500 MHz, $CDCl_3$) of *epi*-(+)-**8d**

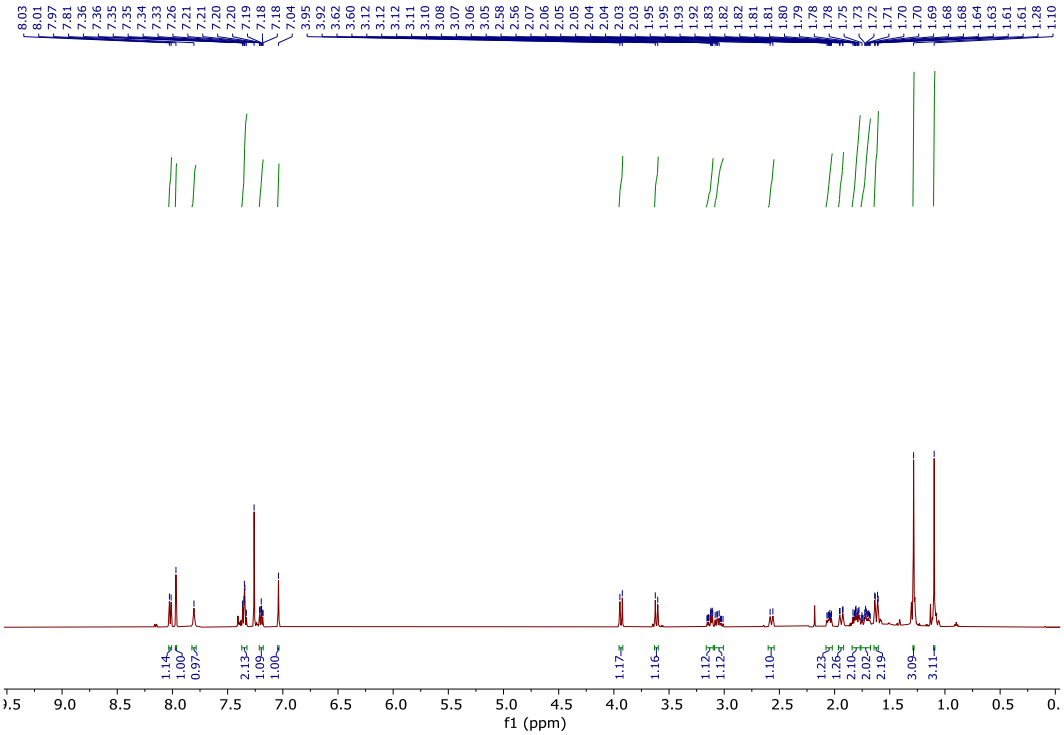


^{13}C NMR (125 MHz, $CDCl_3$) of *epi*-(+)-**8d**

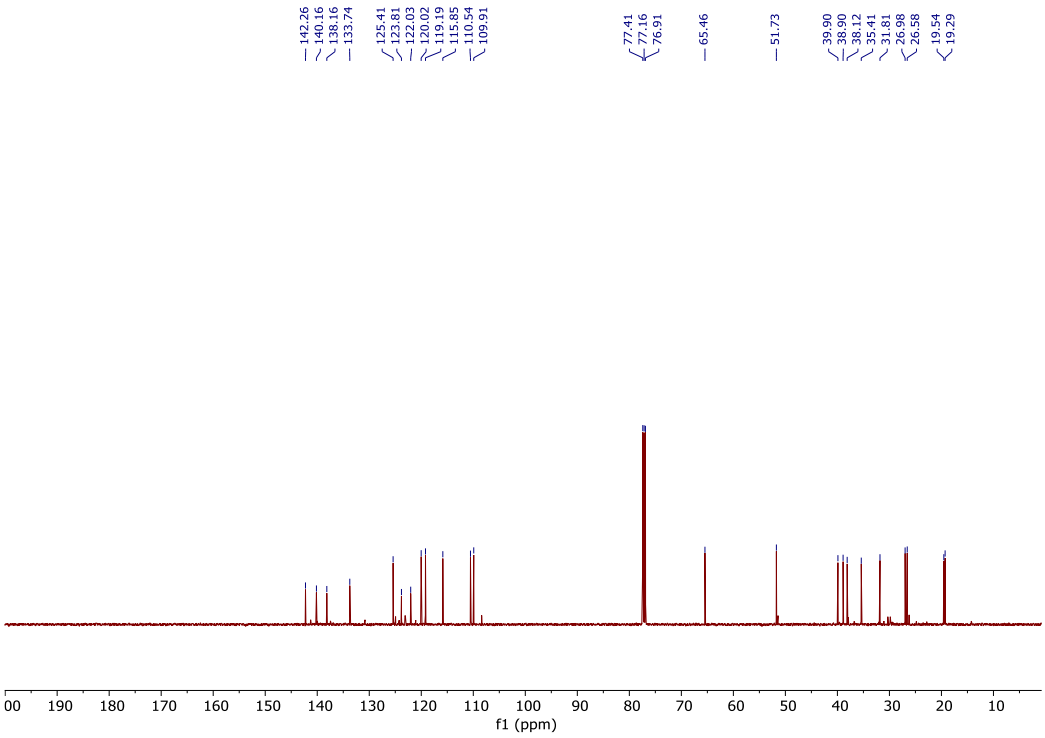


HRMS data of *epi*-(+)-**8d**

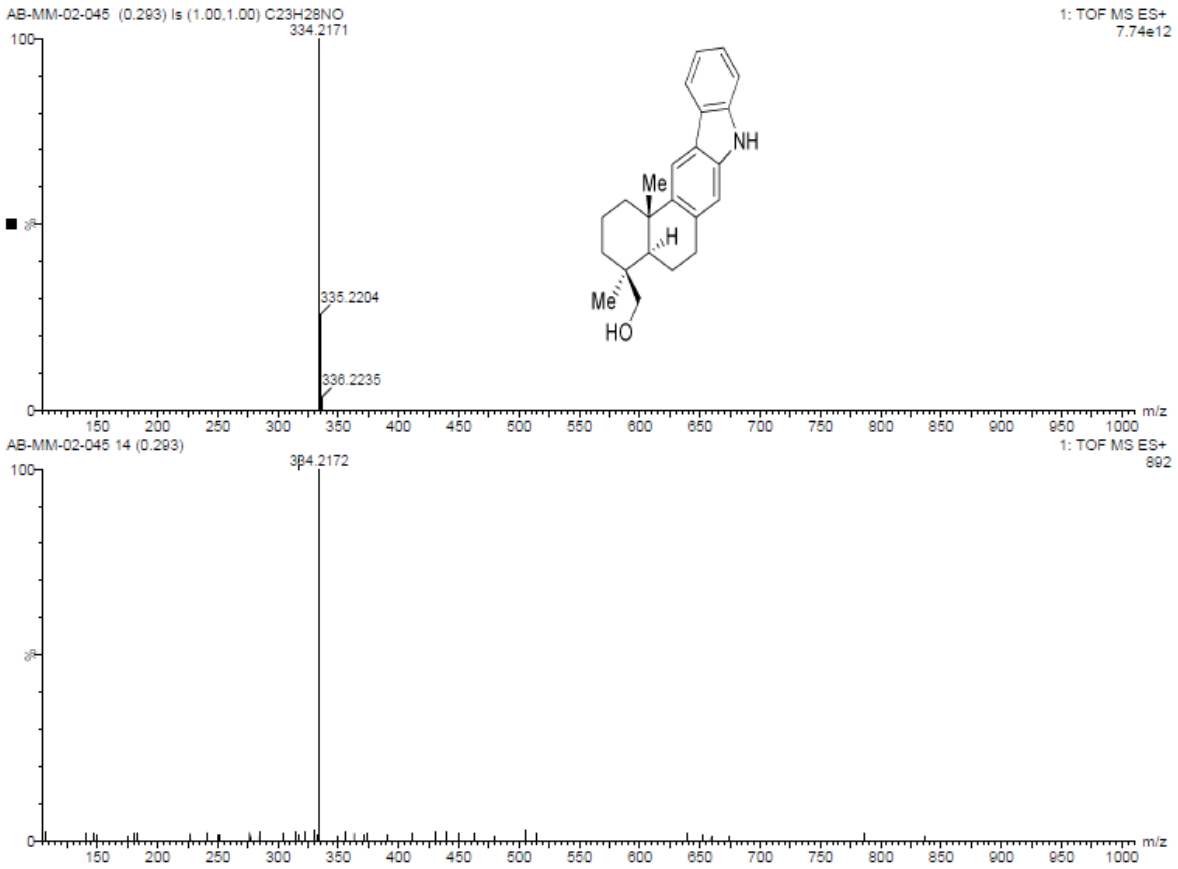




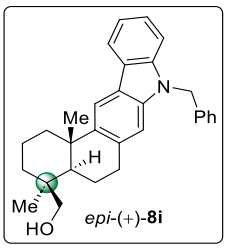
^{1}H NMR (500 MHz, $CDCl_3$) of *epi*-(+)-**8h**



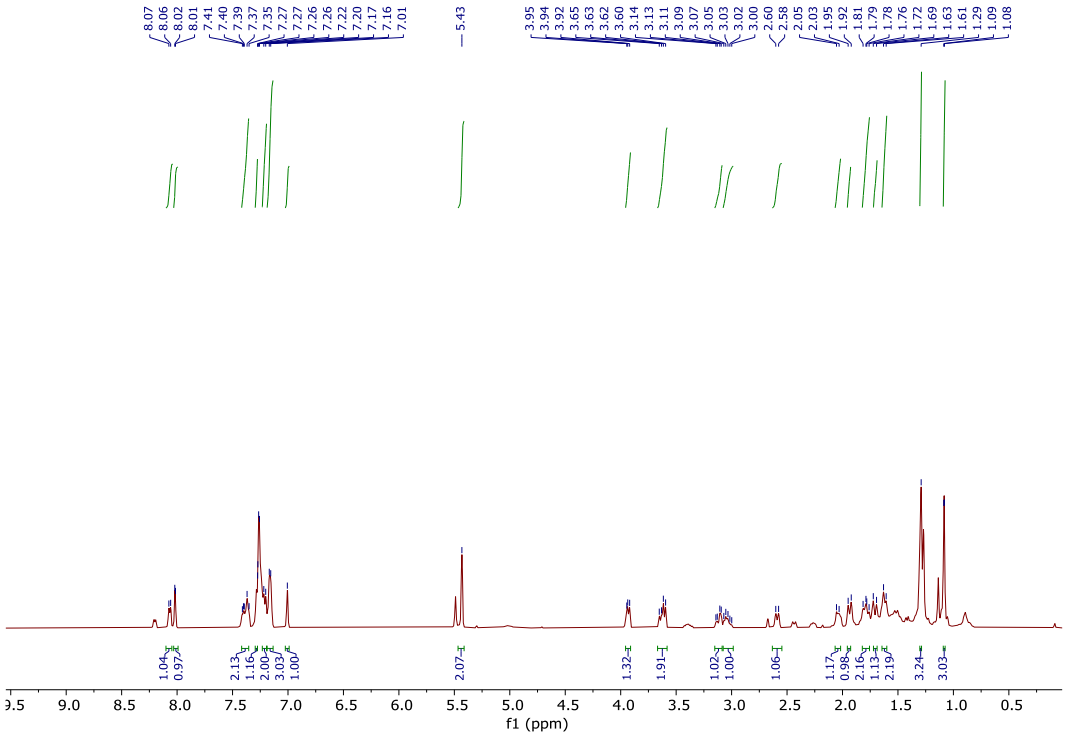
^{13}C NMR (125 MHz, $CDCl_3$) of *epi*-(+)-**8h**



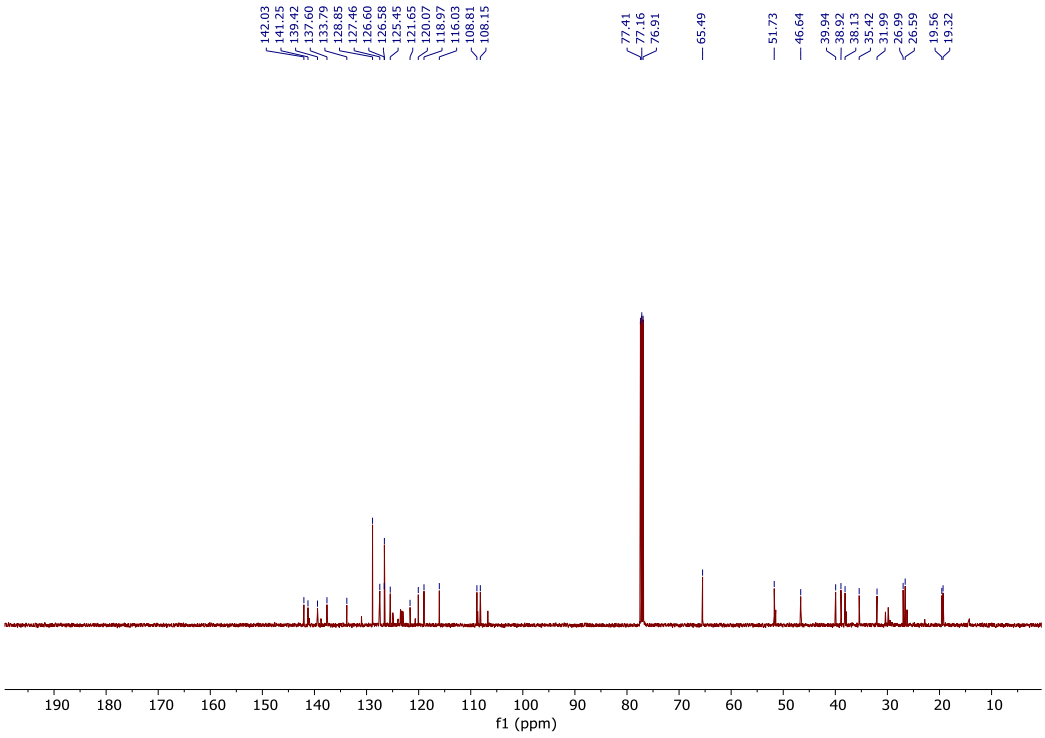
HRMS data of *epi*-(+)-**8h**



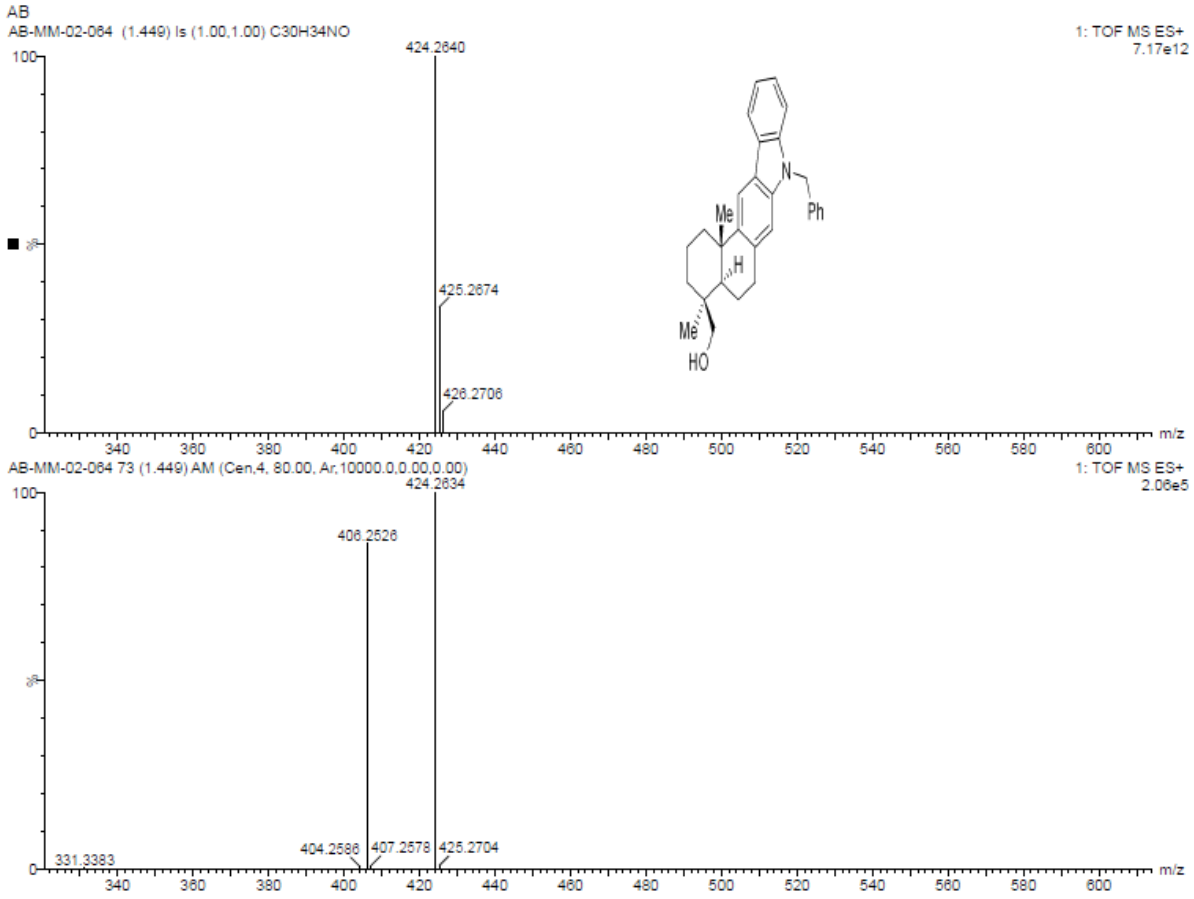
epi-(+)-**8i**



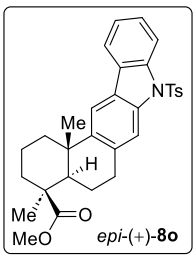
^{1}H NMR (500 MHz, $CDCl_3$) of *epi*-(+)-**8i**

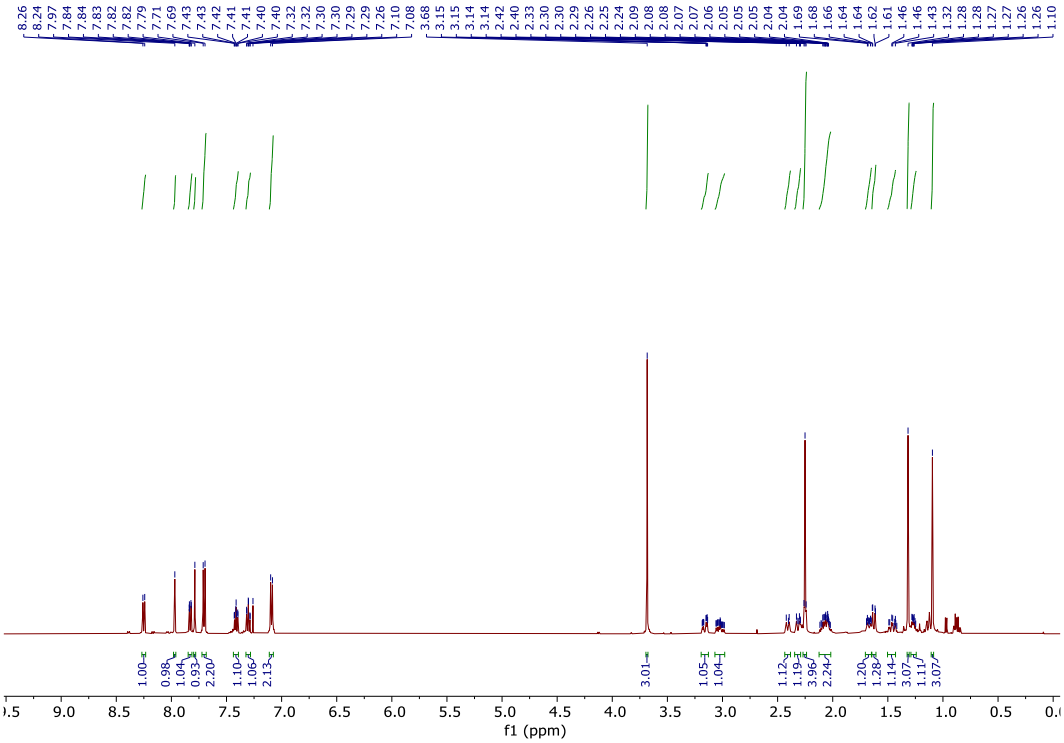


^{13}C NMR (125 MHz, $CDCl_3$) of *epi*-(+)-**8i**

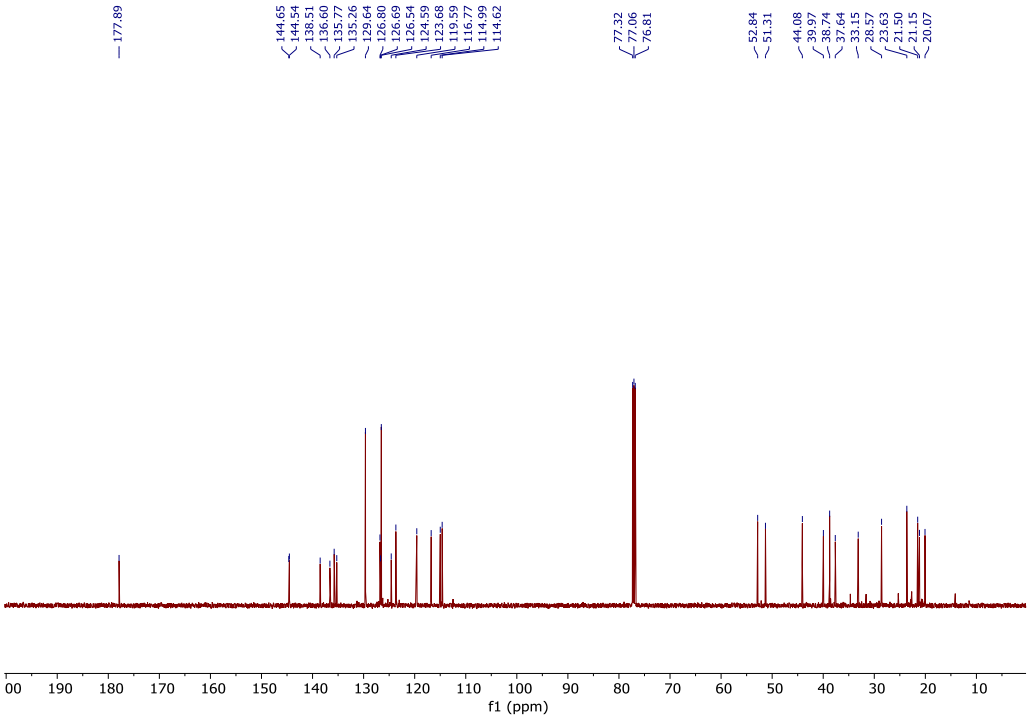


HRMS data of *epi*-(+)-**8i**

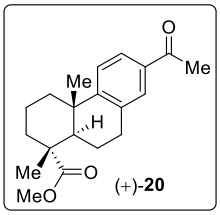


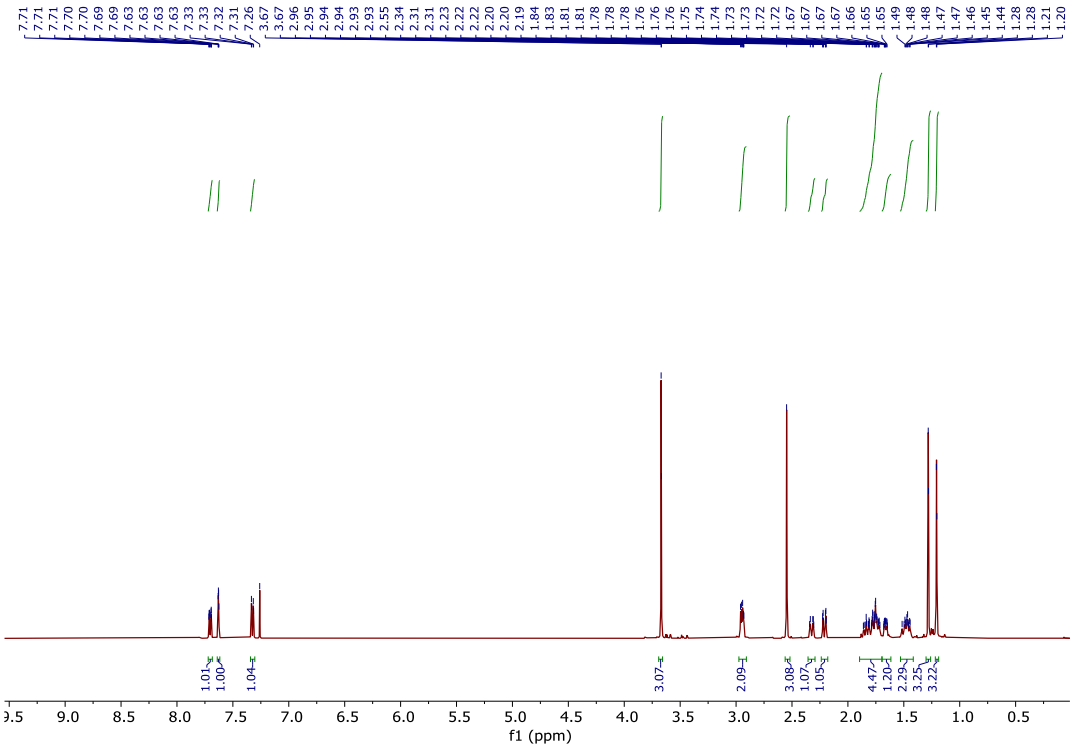


^{1}H NMR (500 MHz, $CDCl_3$) of *epi*-(+)-**8o**

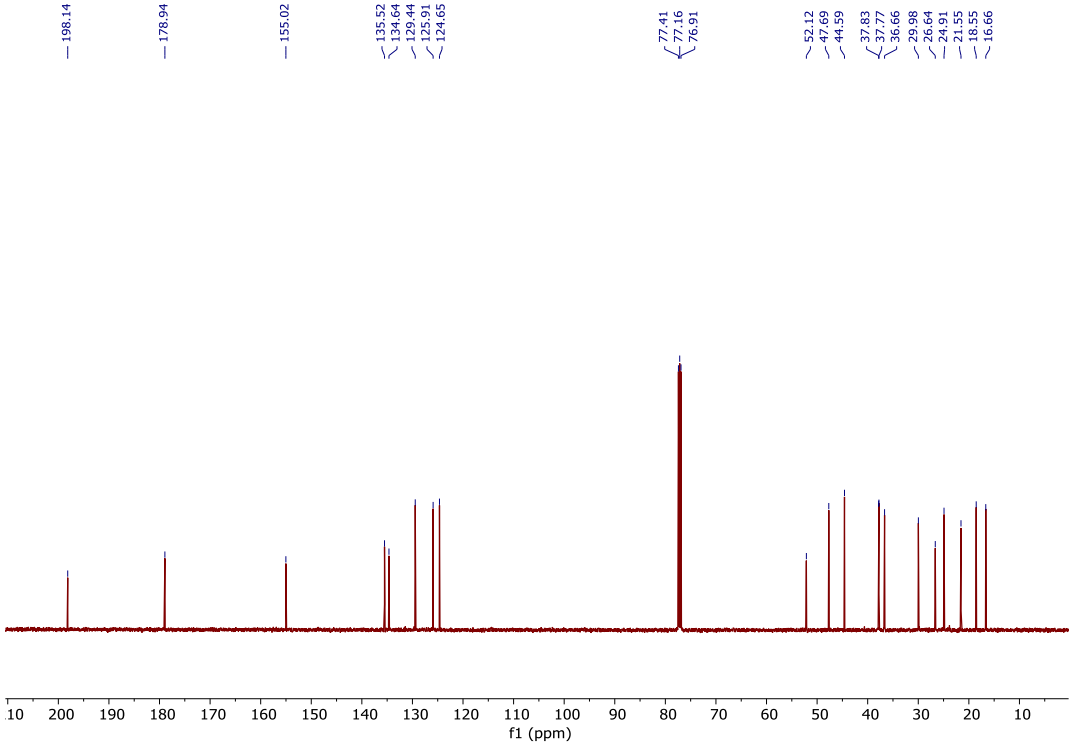


^{13}C NMR (125 MHz, $CDCl_3$) of *epi*-(+)-**8o**

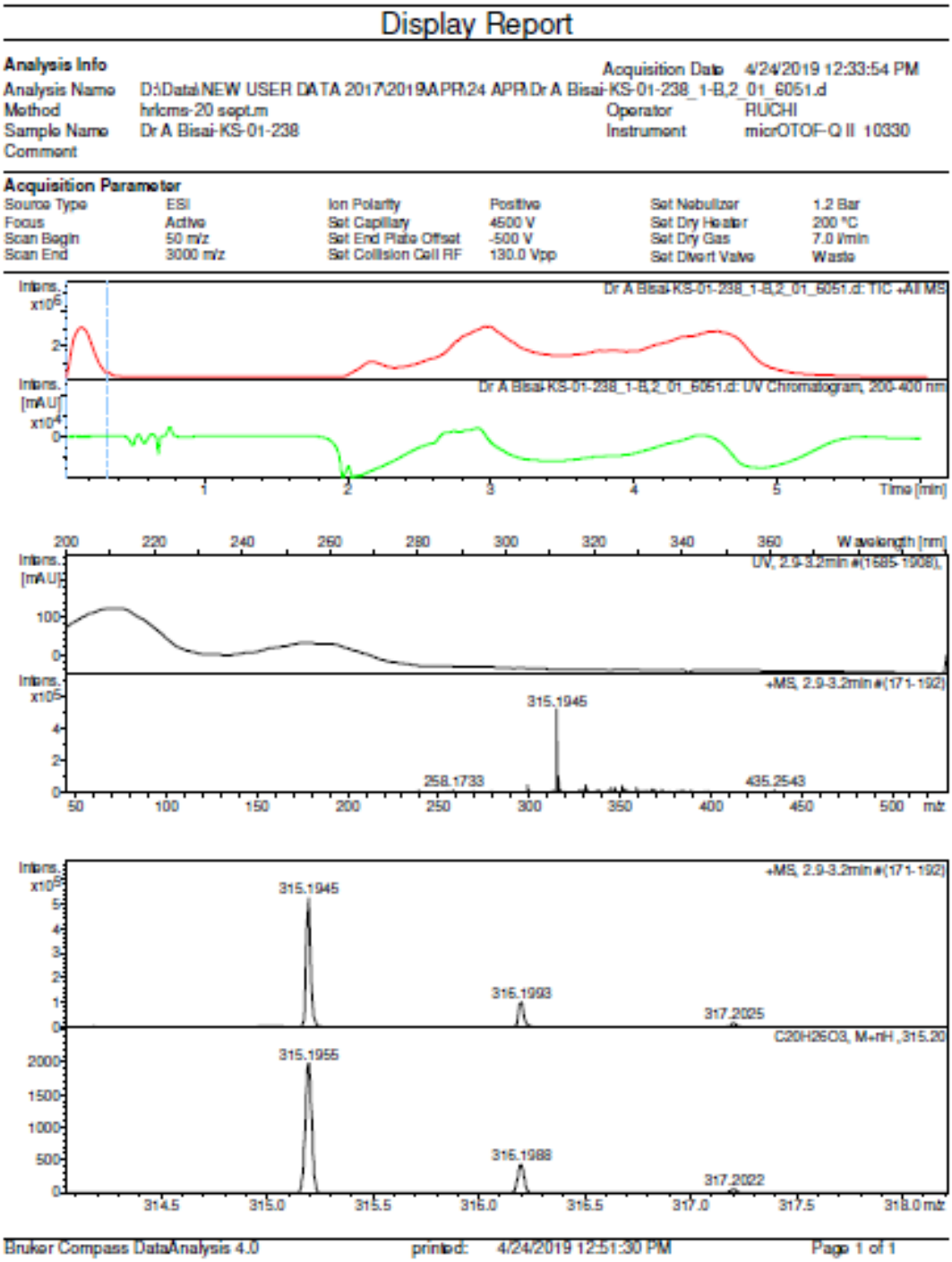




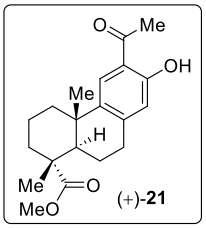
^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**20**



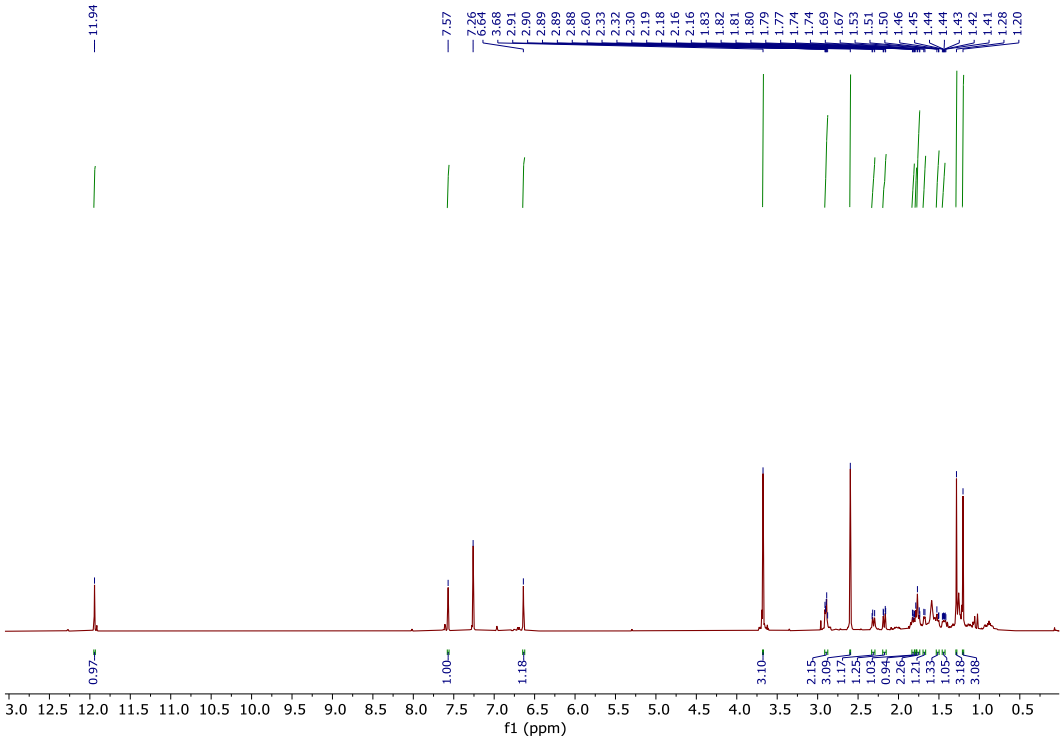
^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**20**



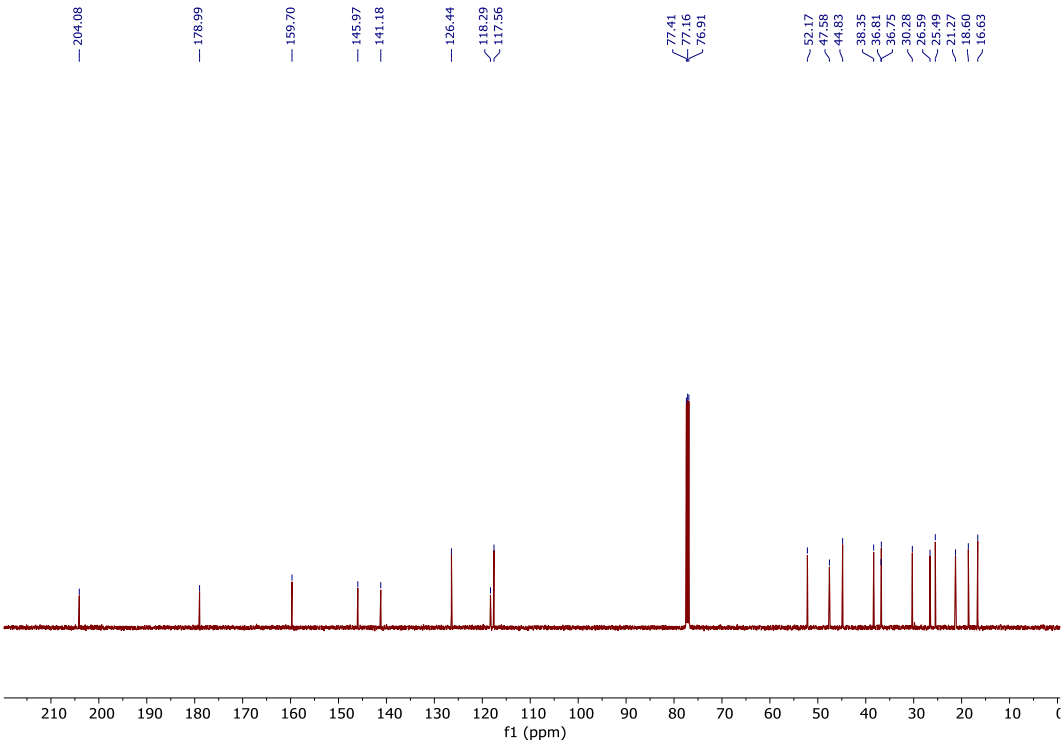
HRMS data of (+)-**20**



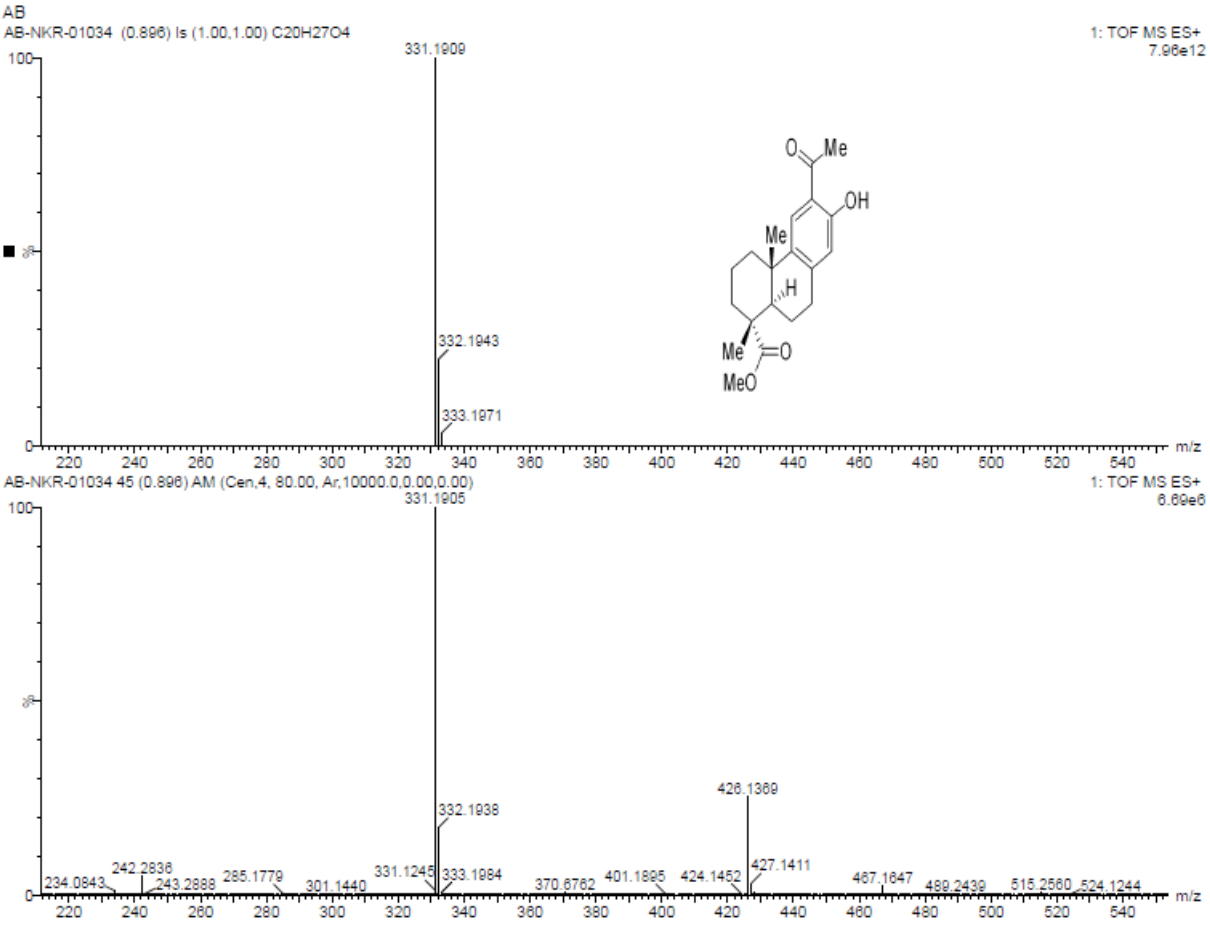
(+)-**21**



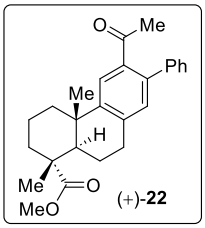
^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**21**

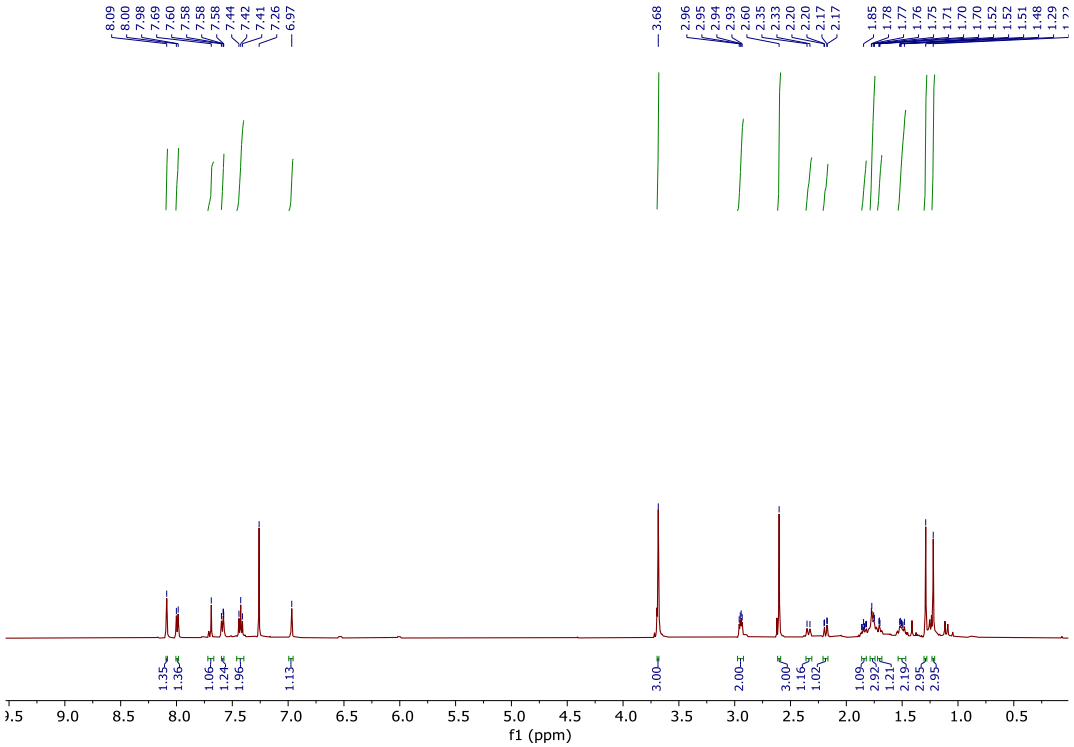


^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**21**

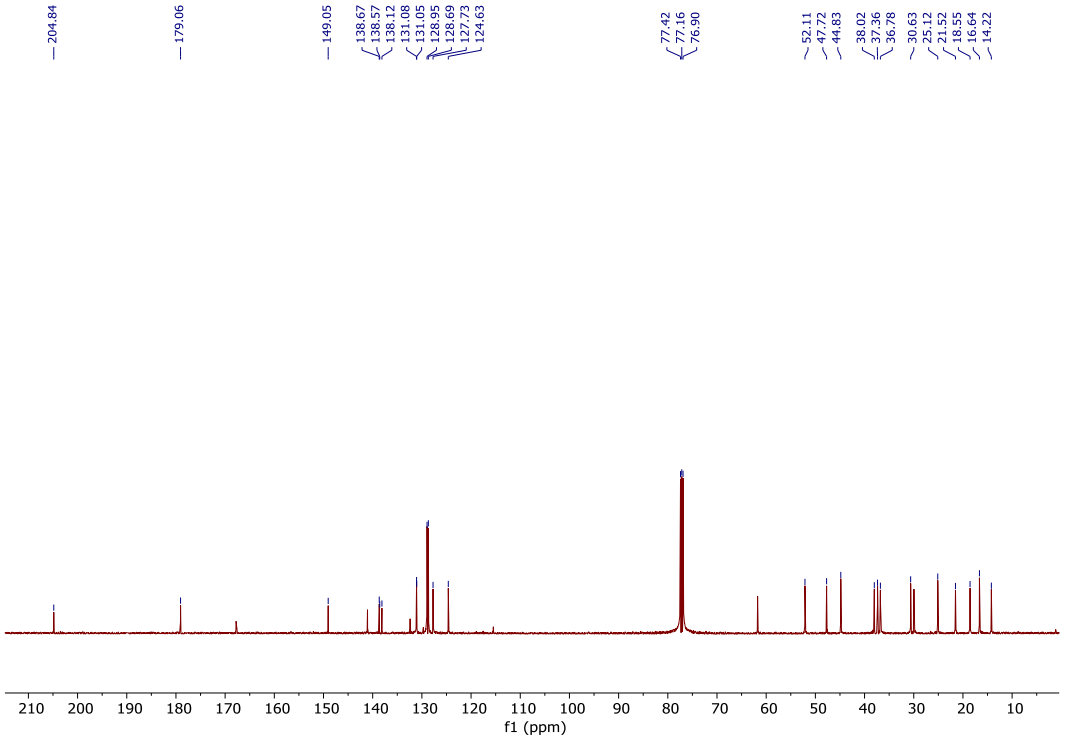


HRMS data of (+)-**21**

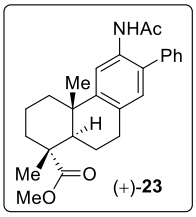


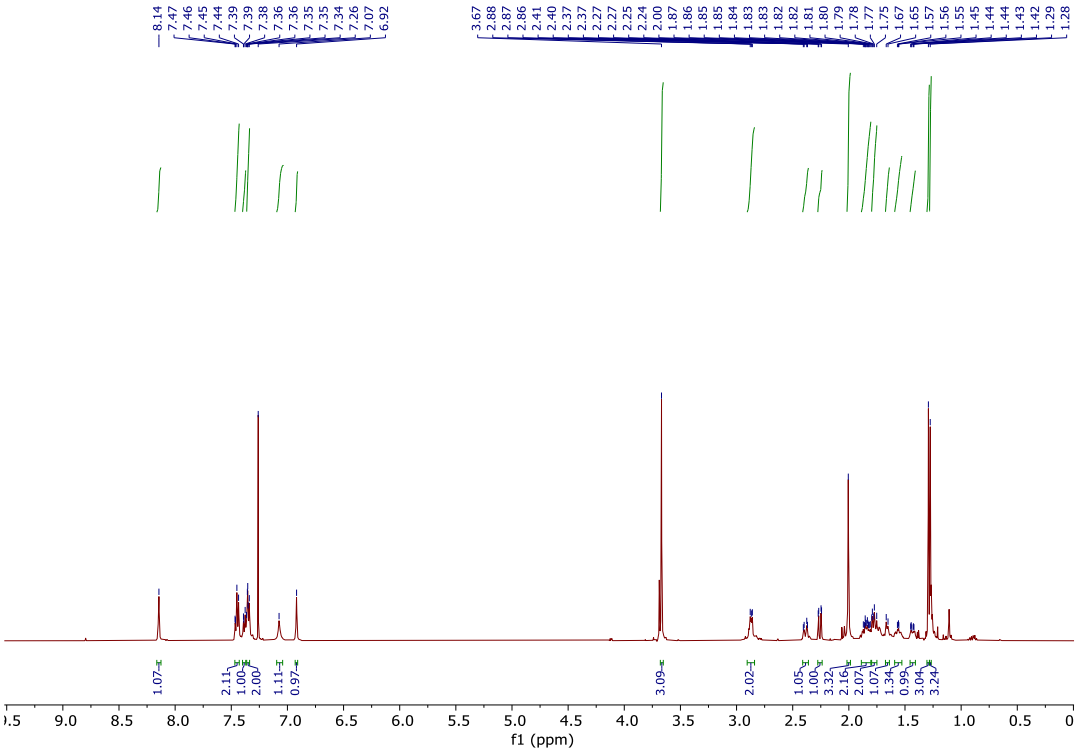


^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**22**

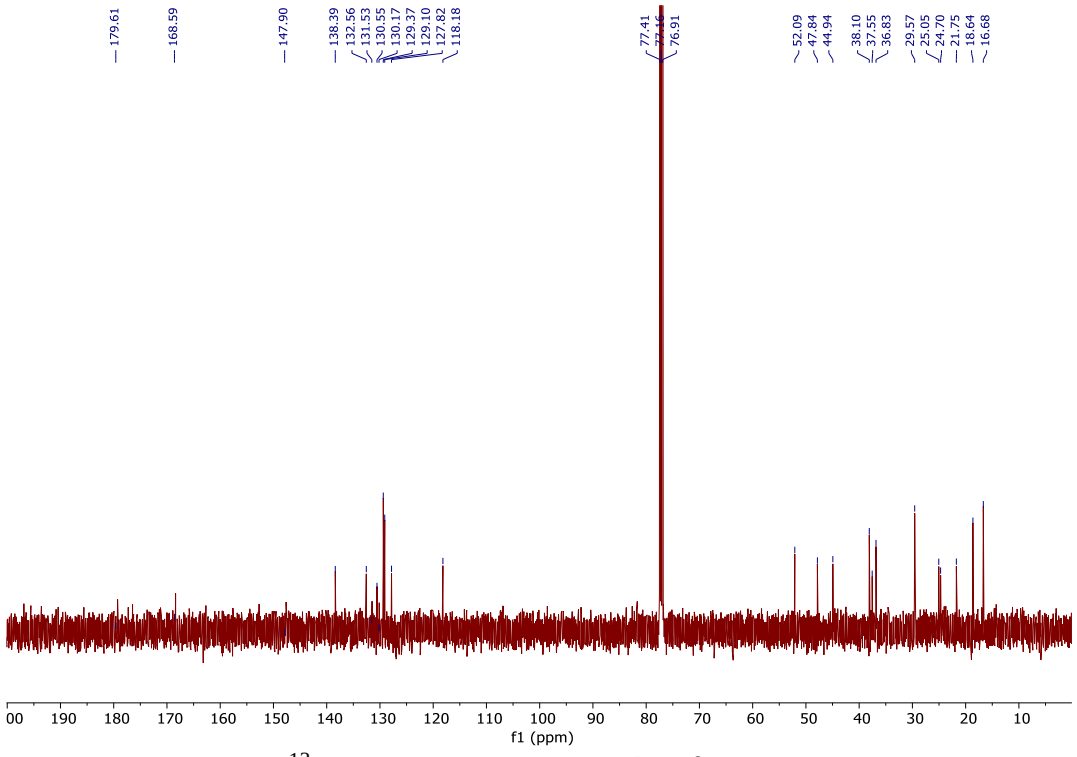


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**22**





^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**23**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**23**

Display Report

Analysis Info

Analysis Name	D:\Data\User data\2022\MAR\ab_mm_01_322.d	Acquisition Date	3/21/2022 1:07:47 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_mm_01_322	Instrument	maXis Impact 8282001.00127
Comment	signal dropping issue		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
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Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
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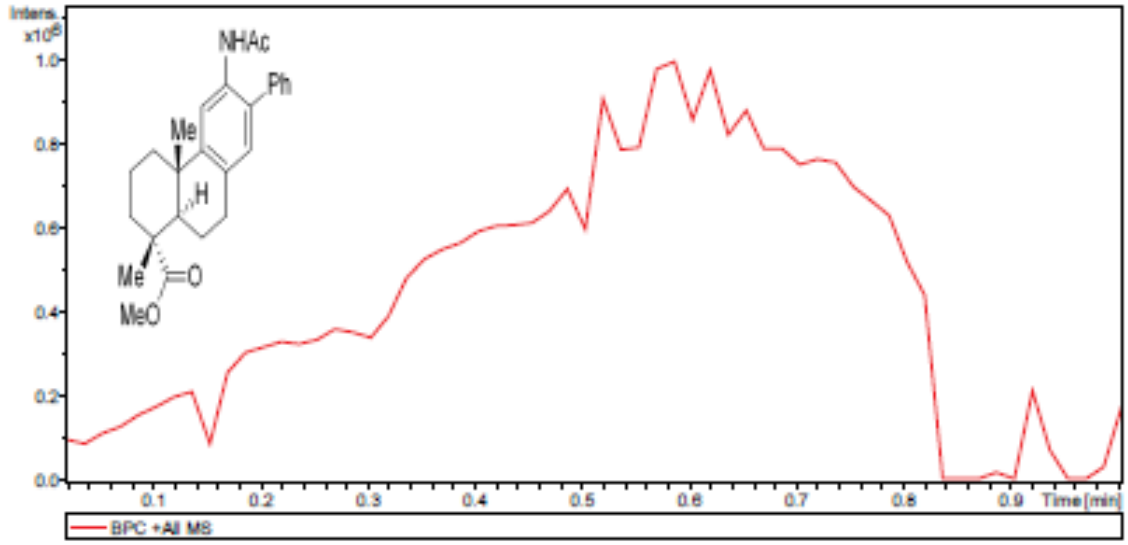

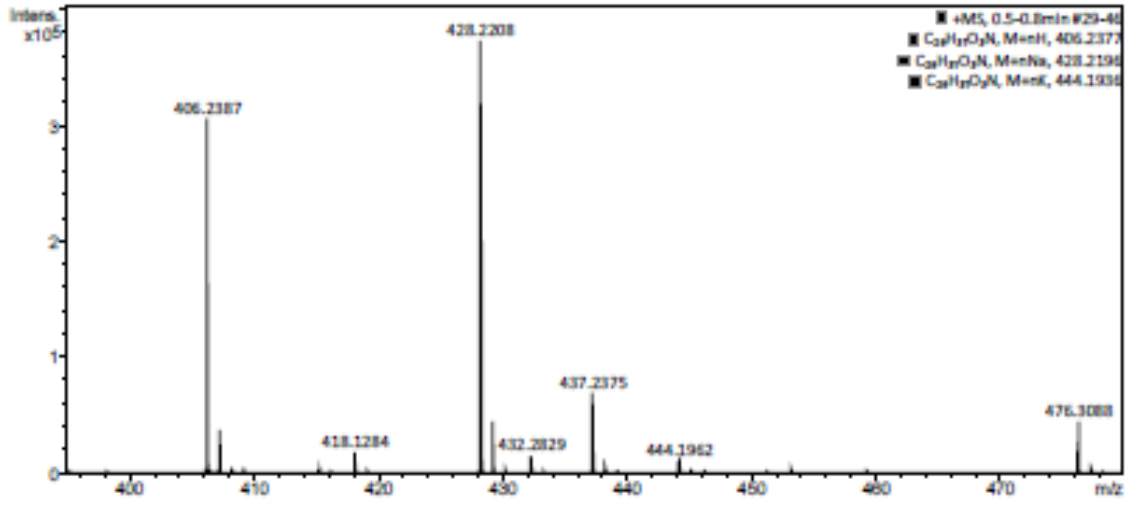

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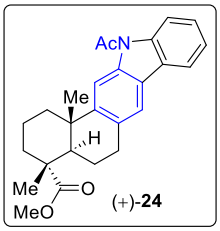
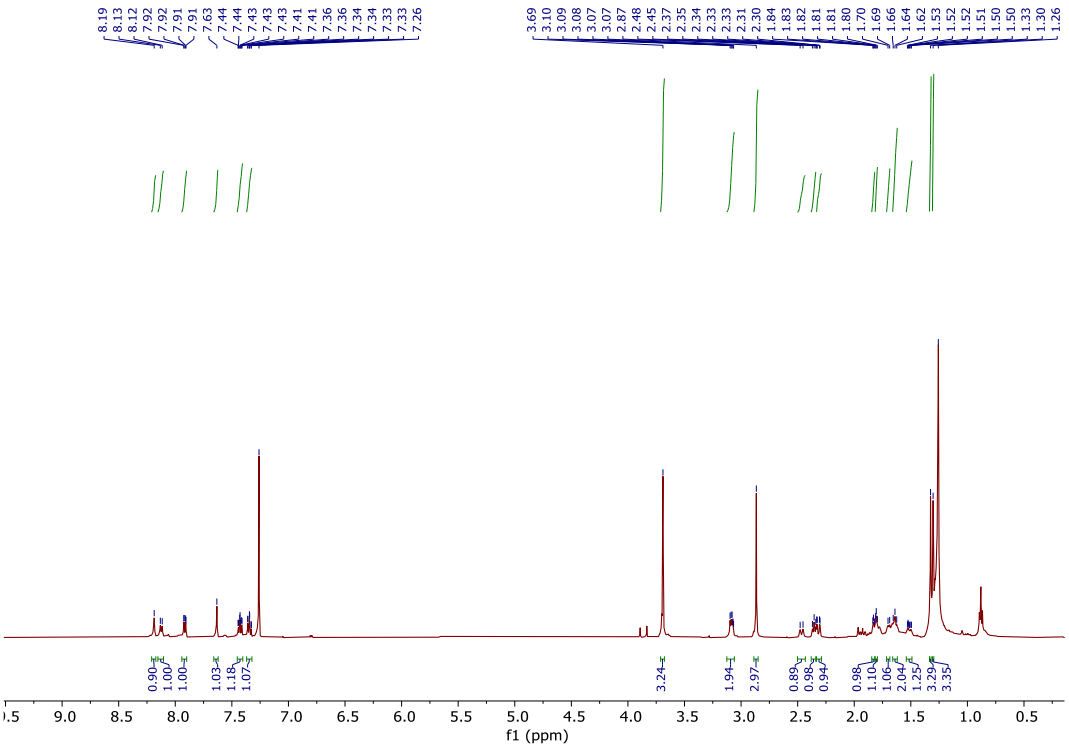
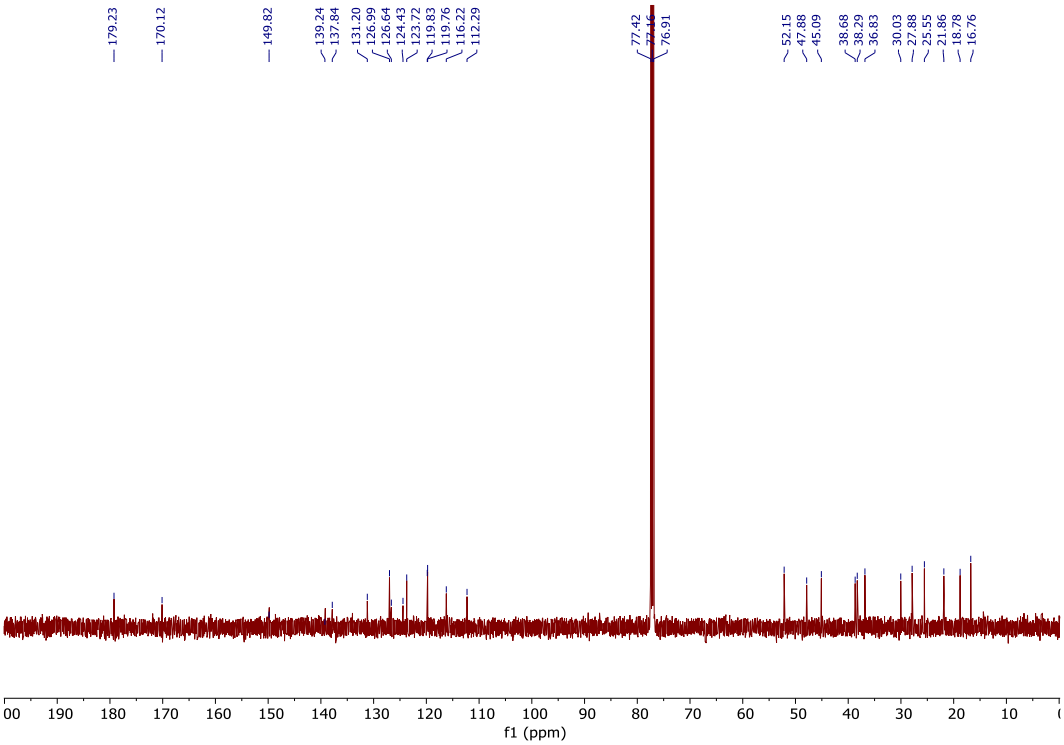
Bruker Compass DataAnalysis 4.1 printed: 3/21/2022 1:10:25 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**23**

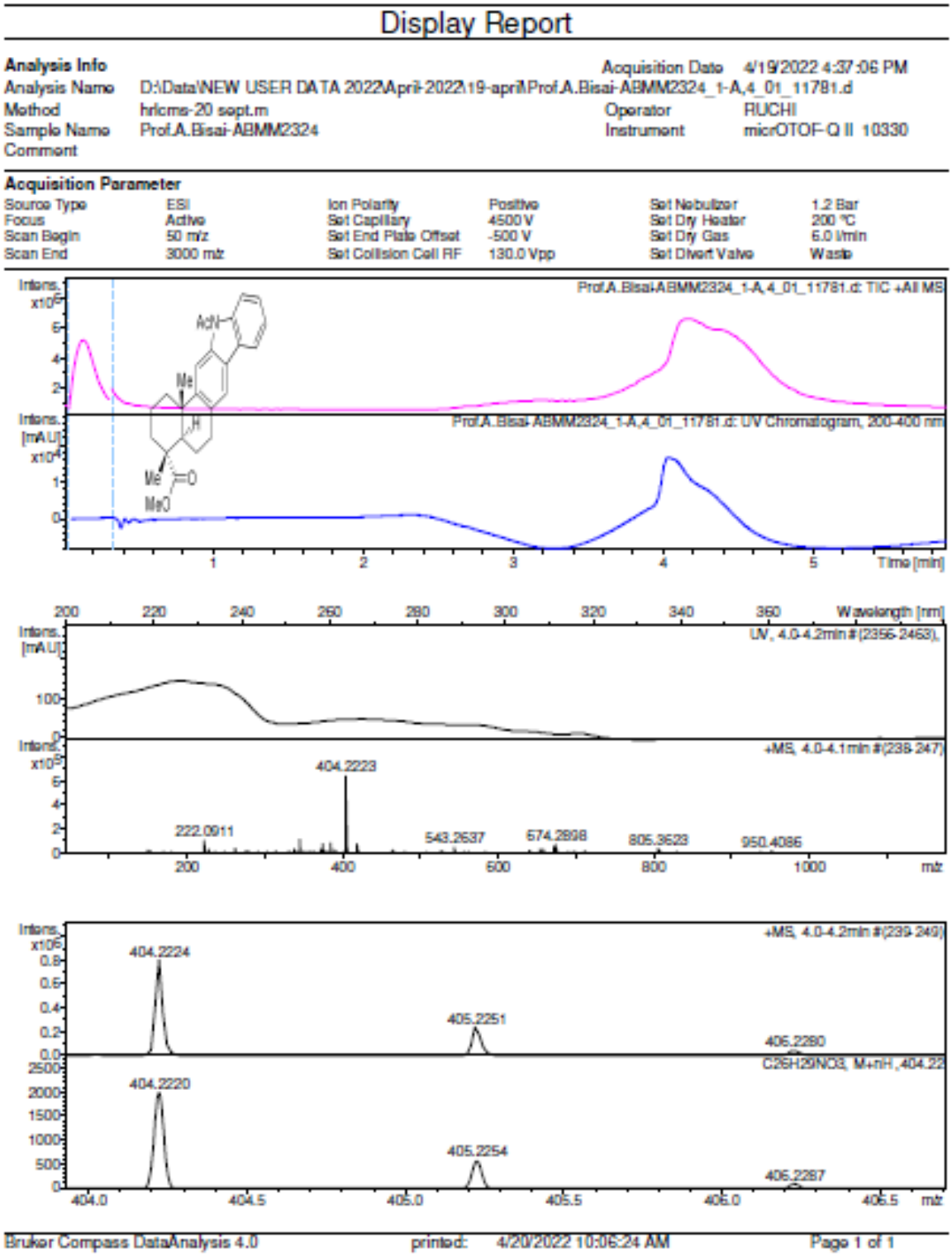




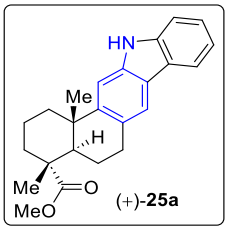
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**24**

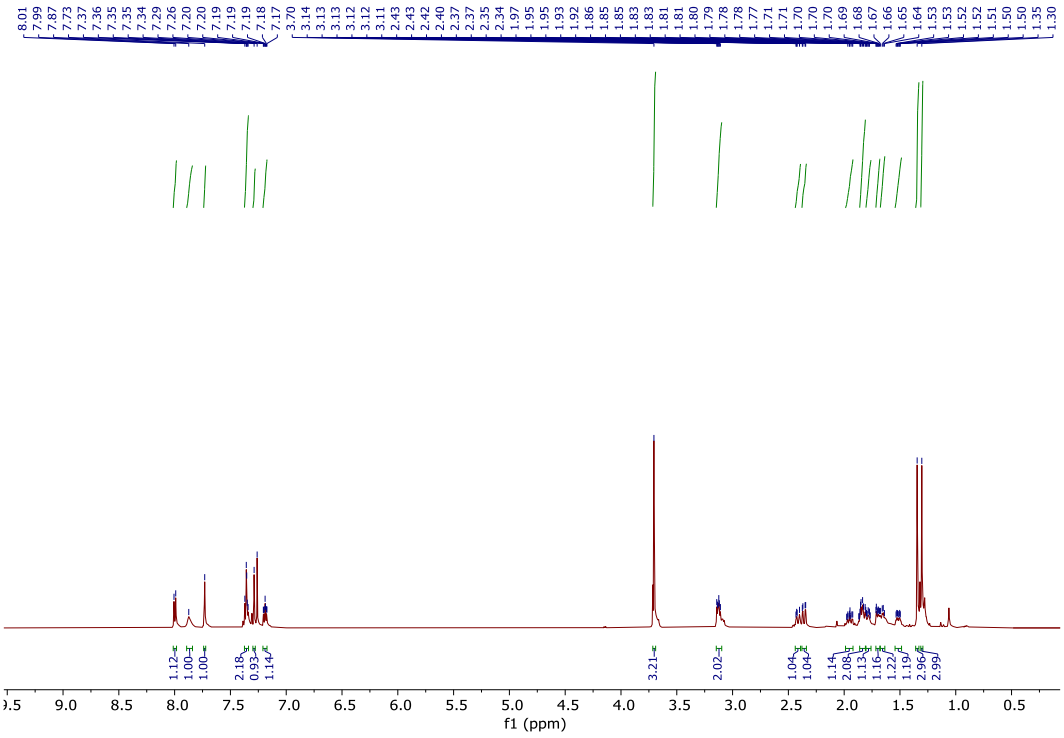


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**24**

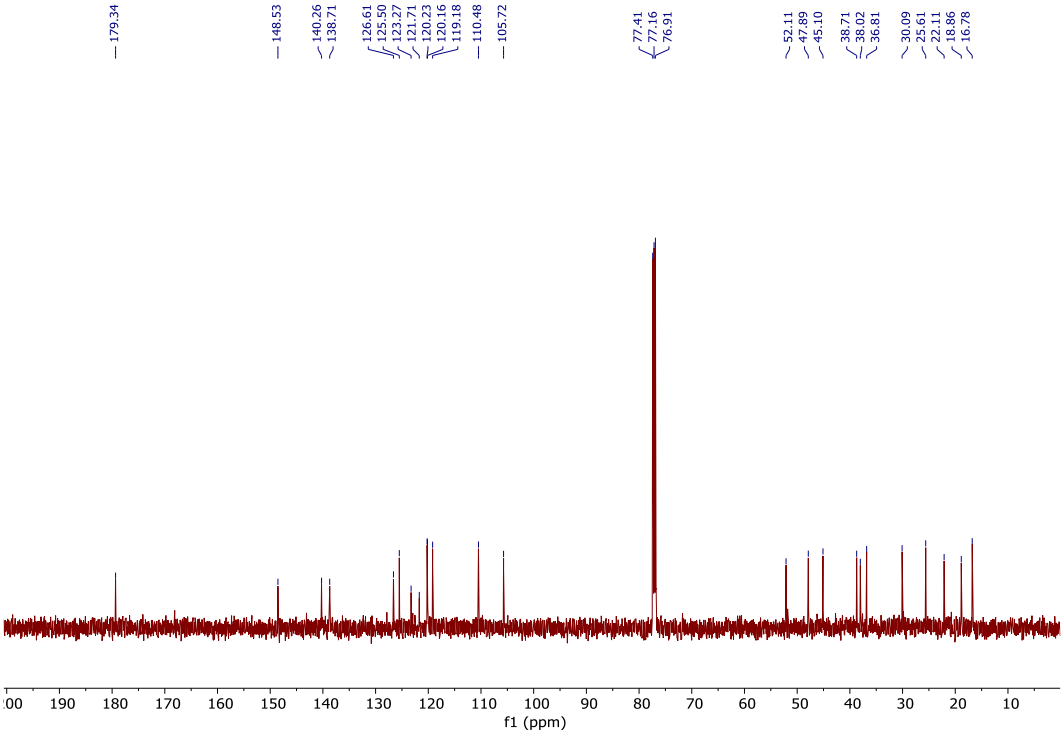


HRMS data of (+)-**24**

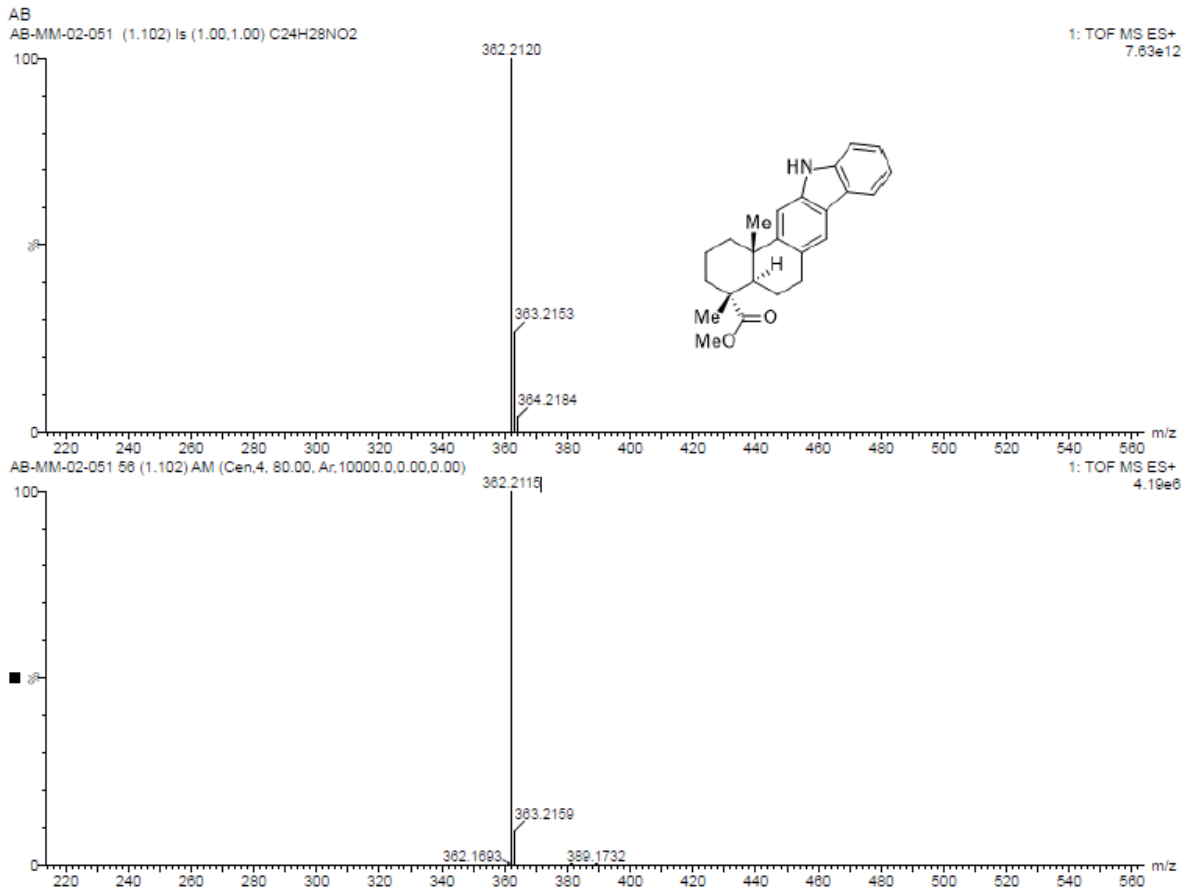




^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**25a**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**25a**



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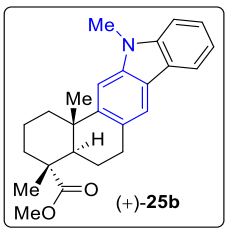
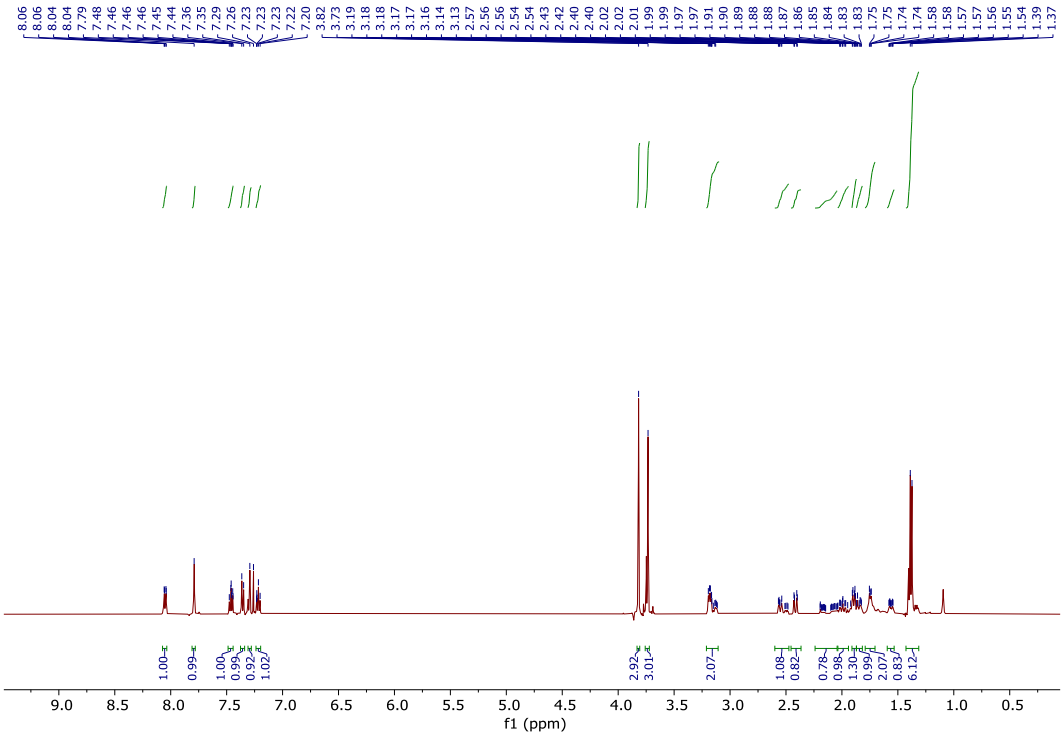
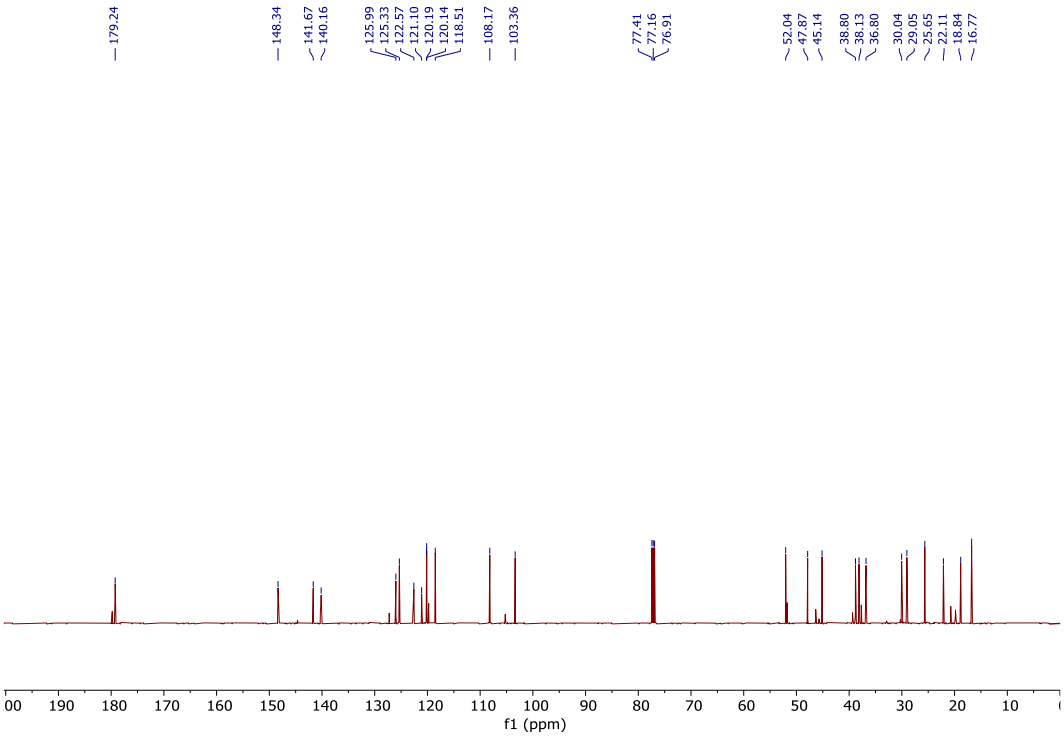


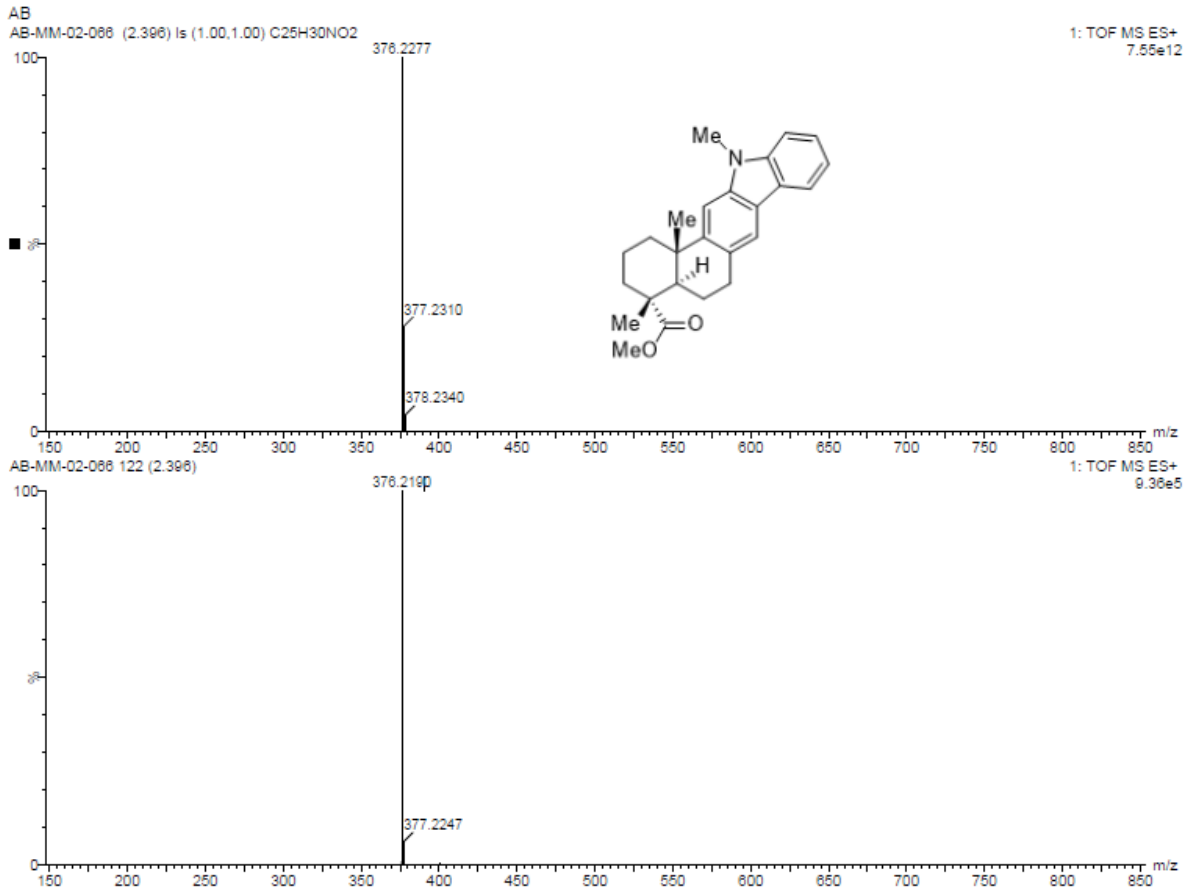
(+)-**25b**



^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**25b**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**25b**



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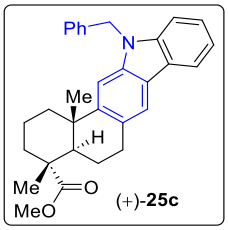
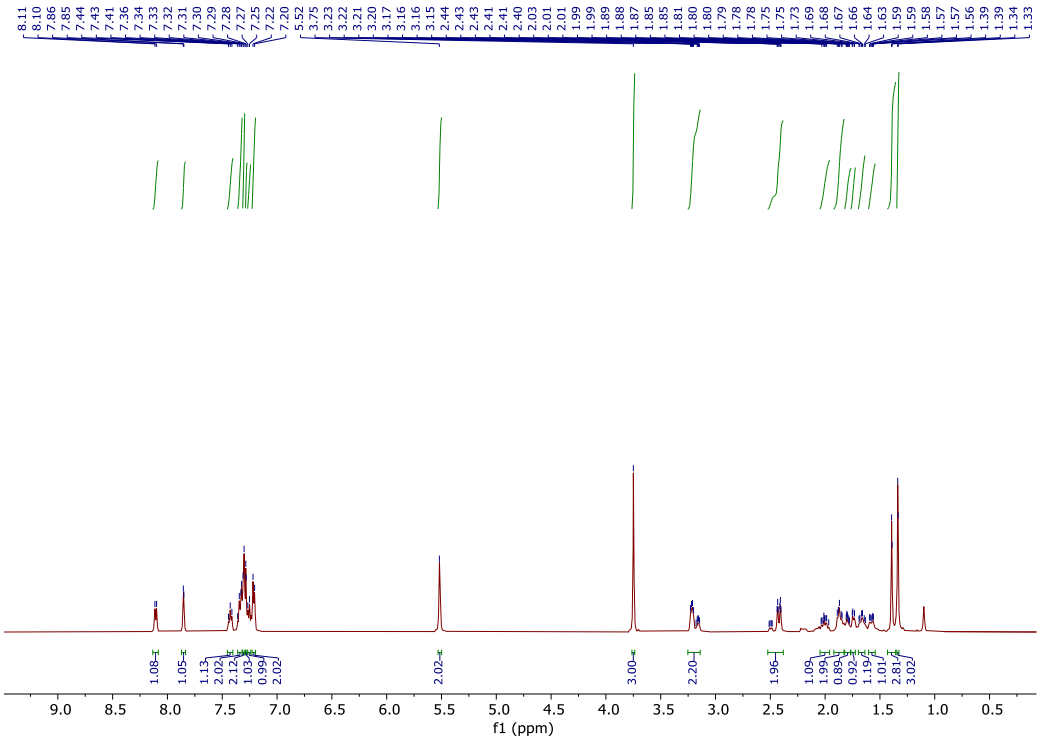
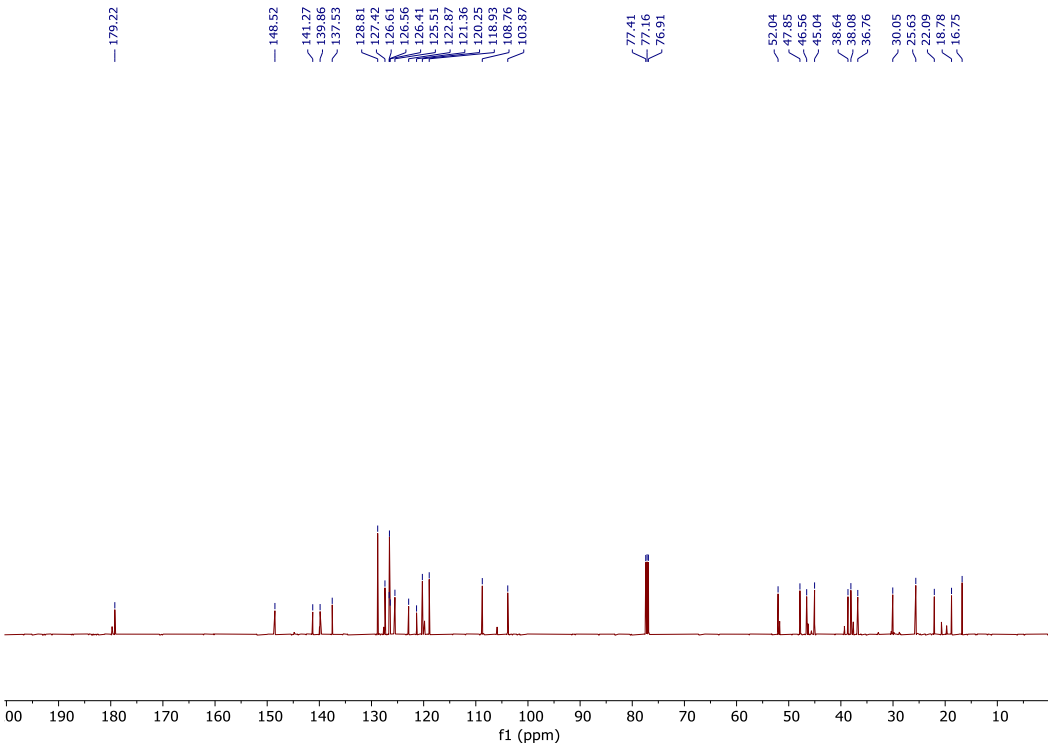
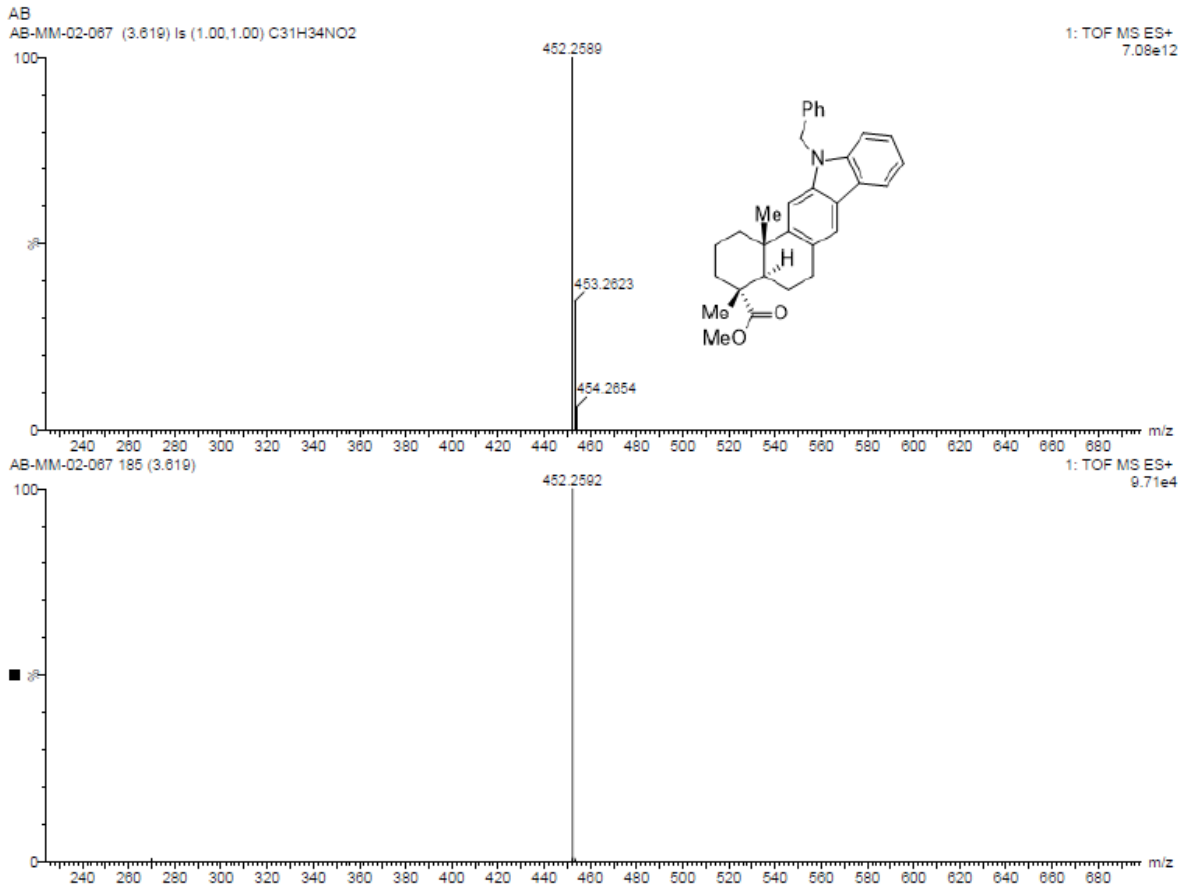




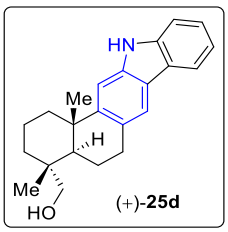
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**25c**



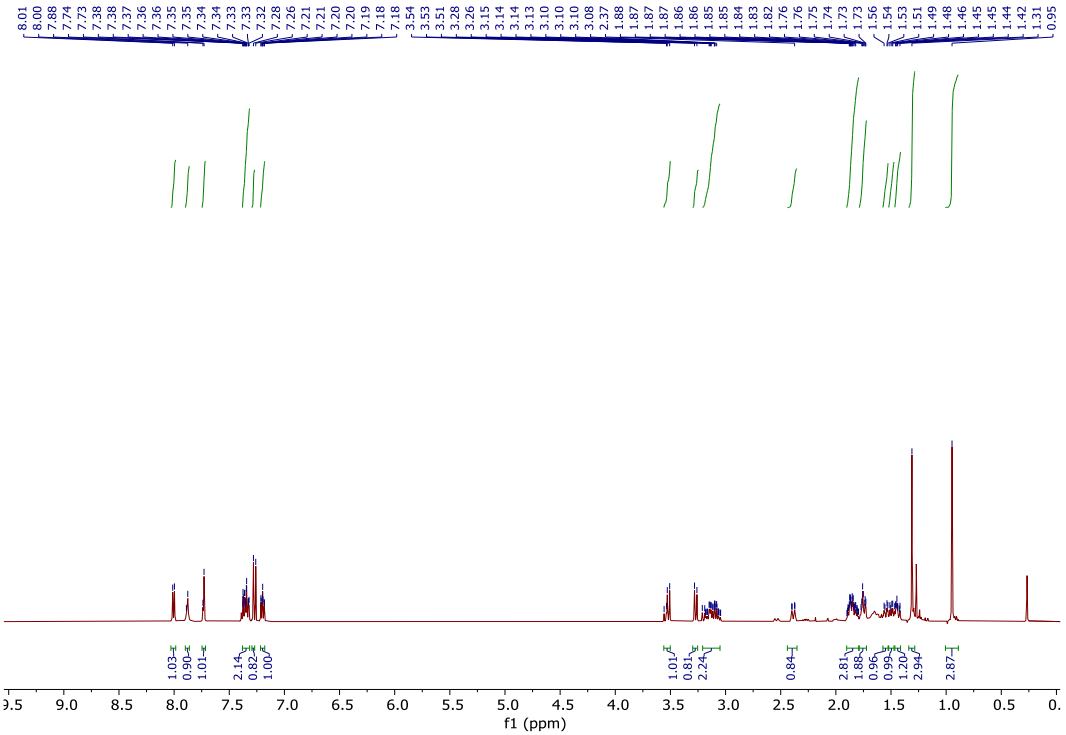
^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**25c**



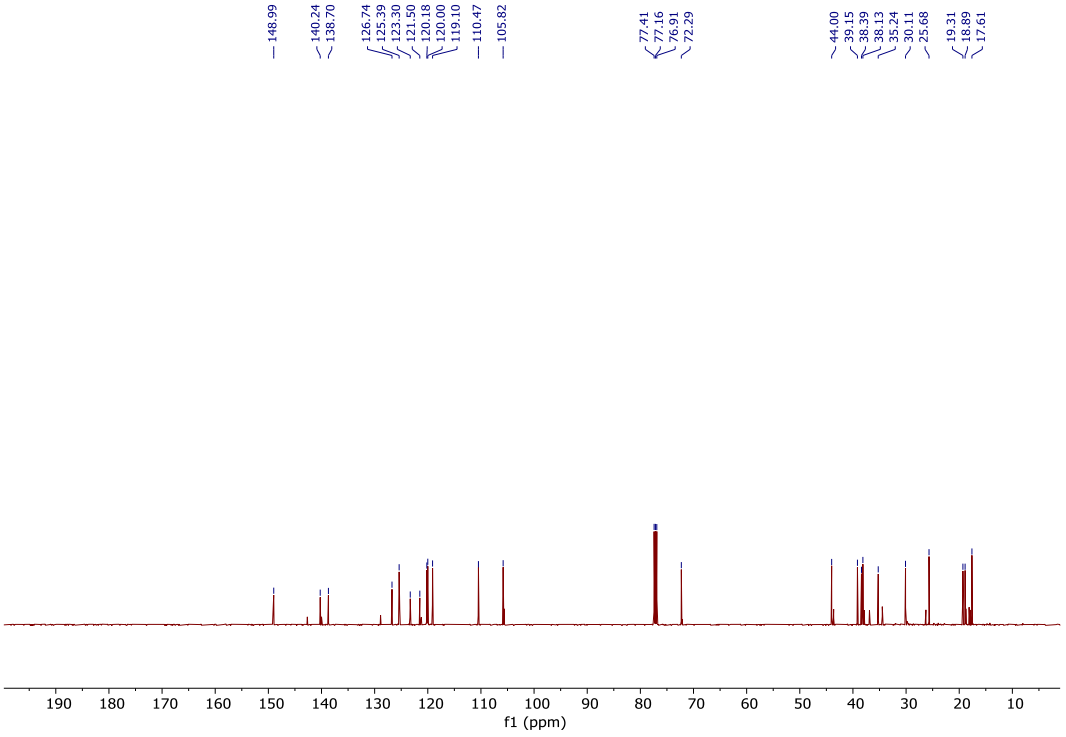
HRMS data of (+)-**25c**



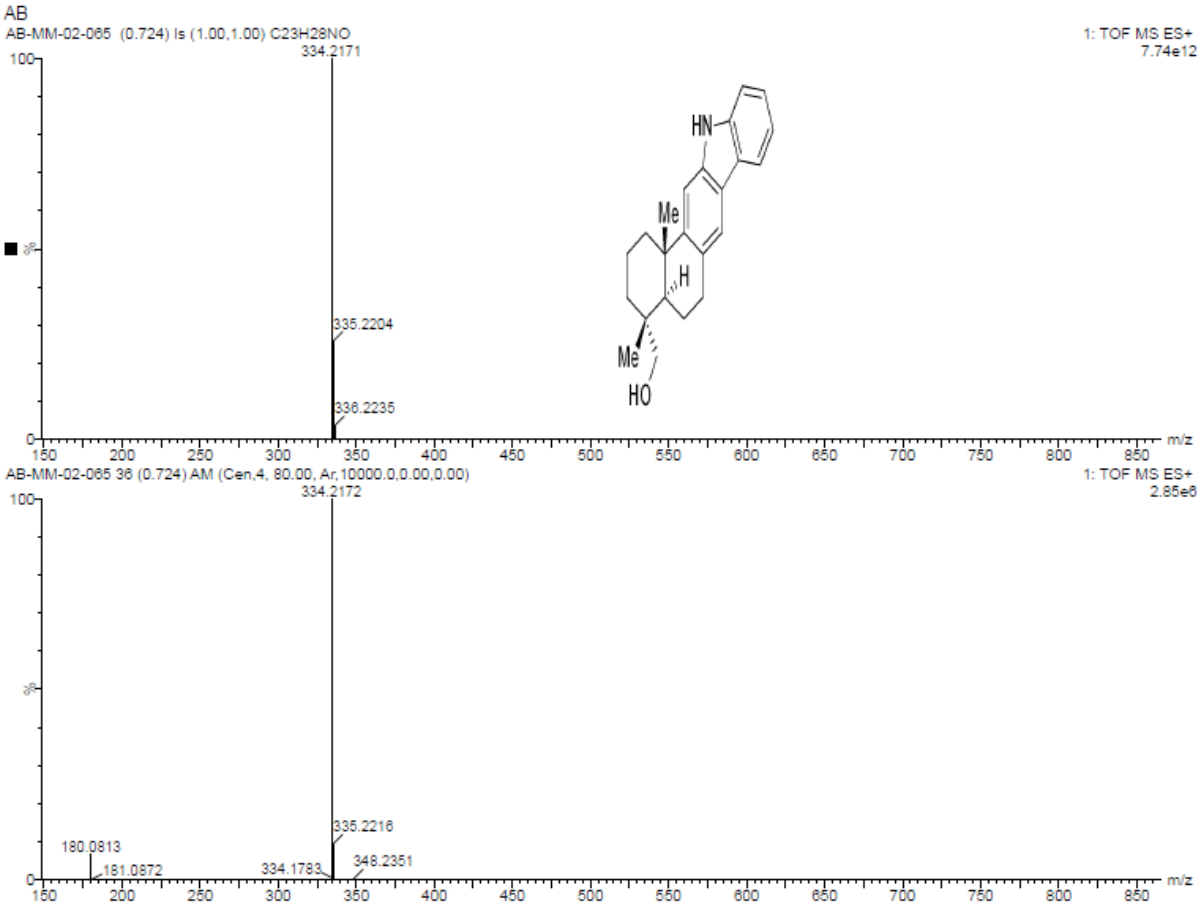
(+)-**25d**



^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**25d**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**25d**



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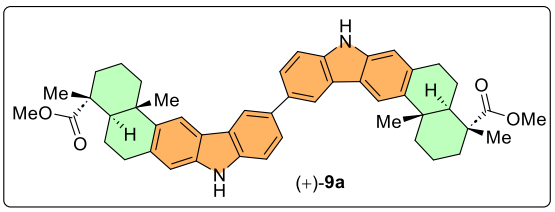
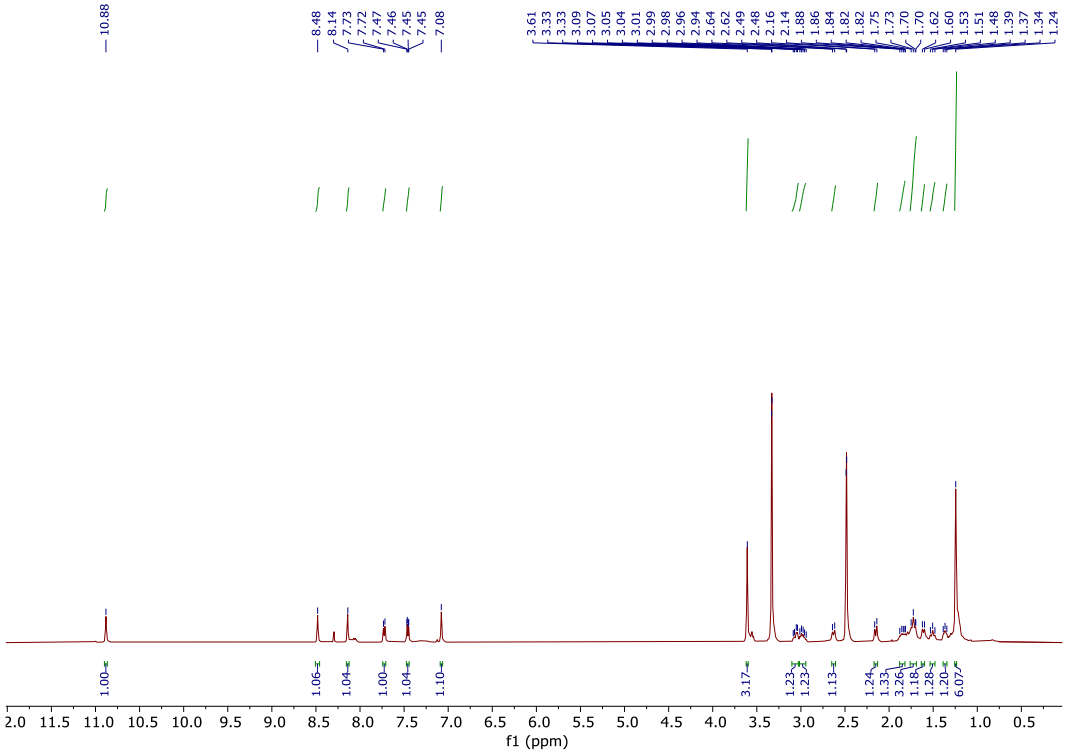
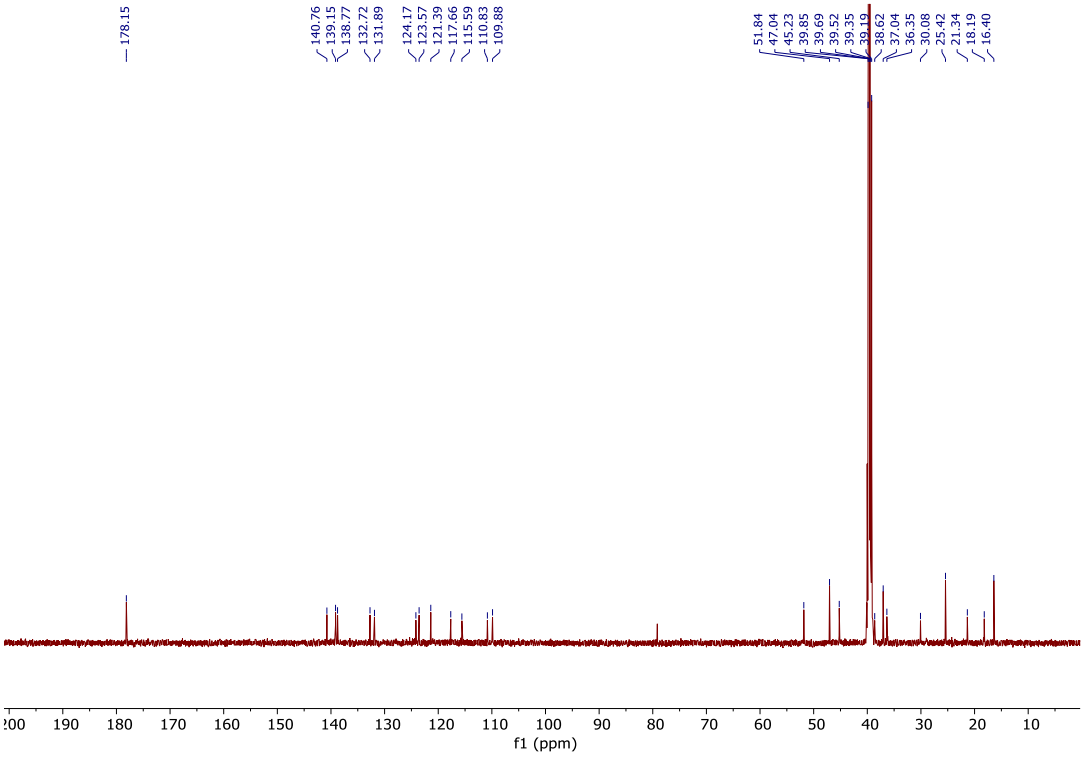
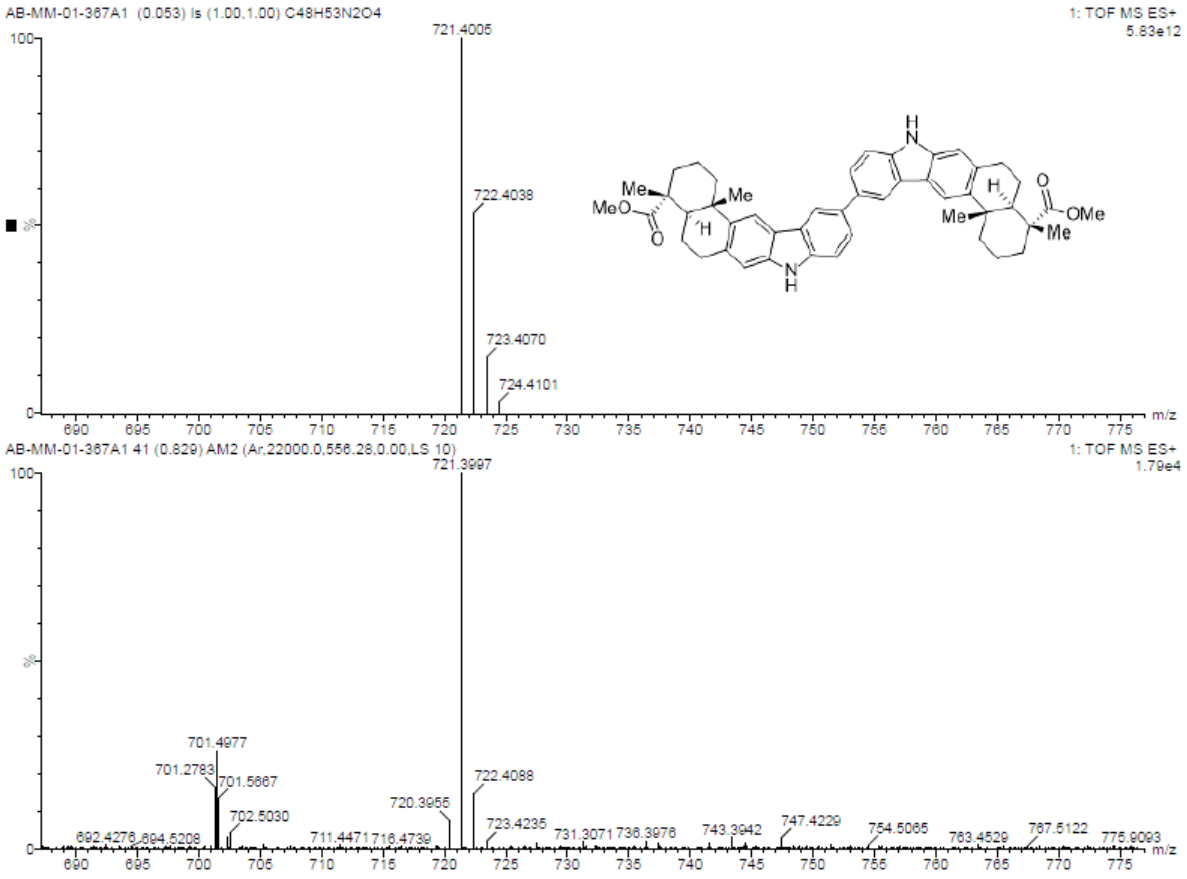




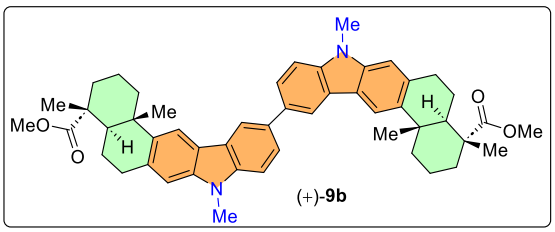
^{1}H NMR (500 MHz, DMSO) of (+)-**9a**

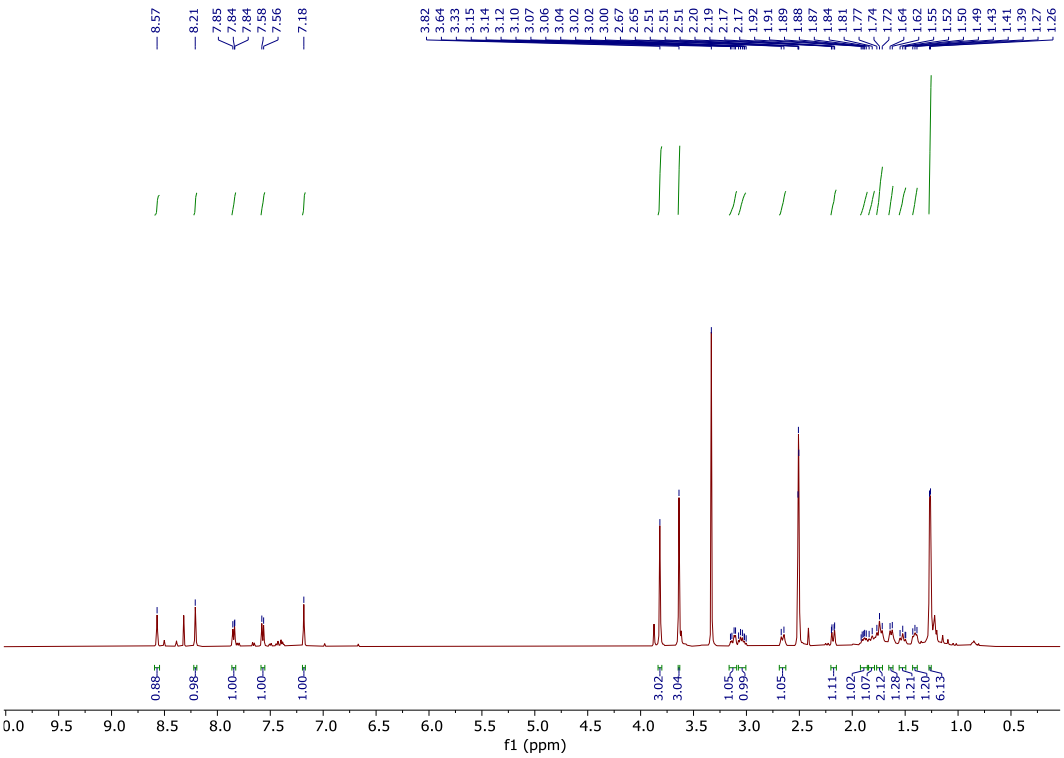


^{13}C NMR (125 MHz, DMSO) of (+)-**9a**

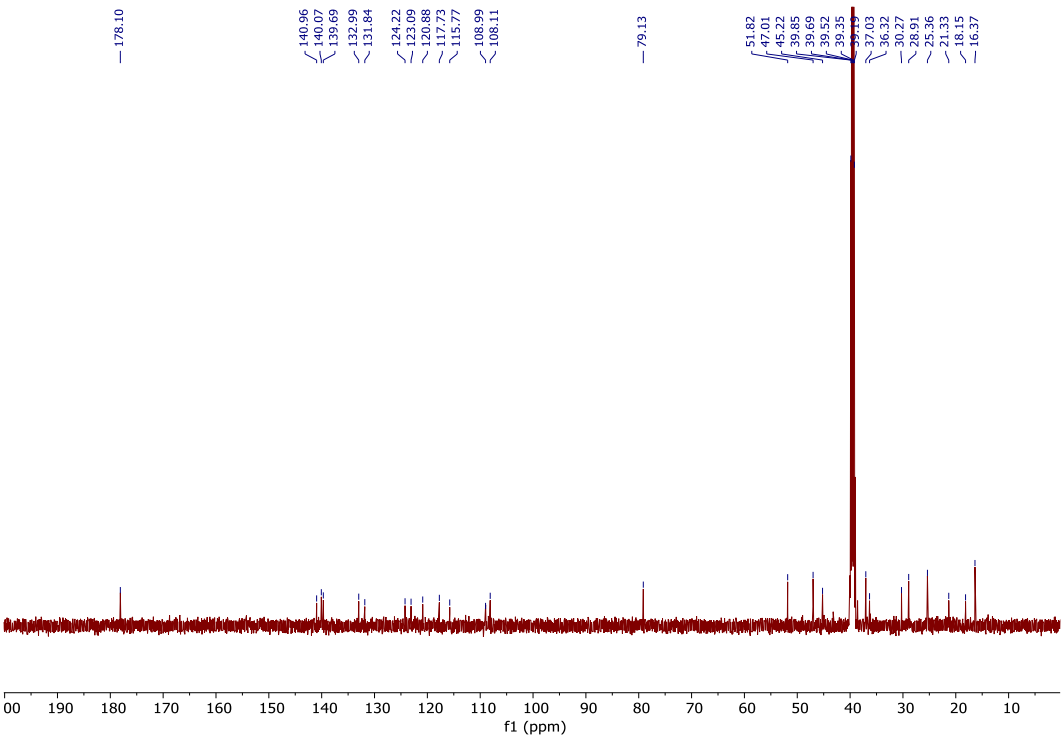


HRMS data of (+)-**9a**

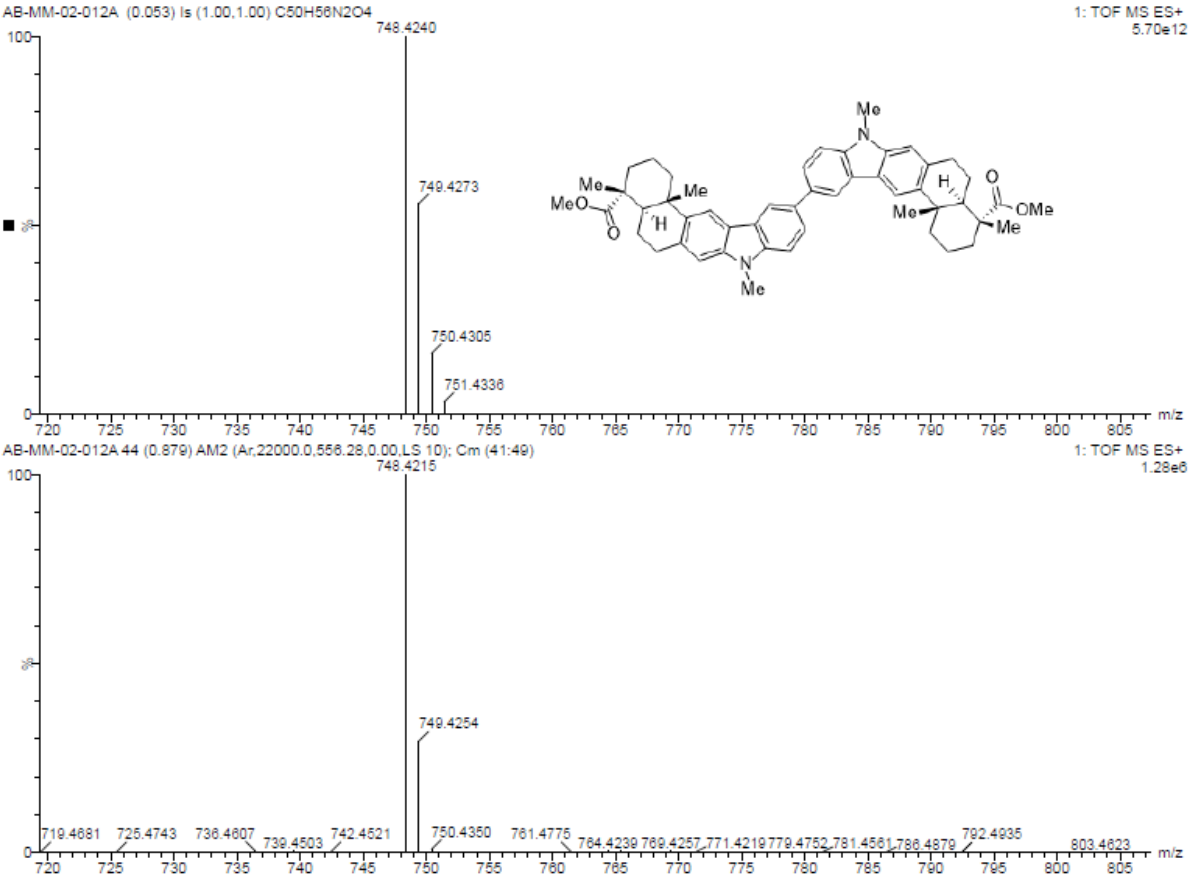




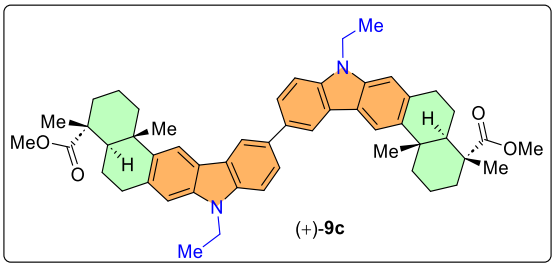
^{1}H NMR (500 MHz, DMSO) of (+)-**9b**

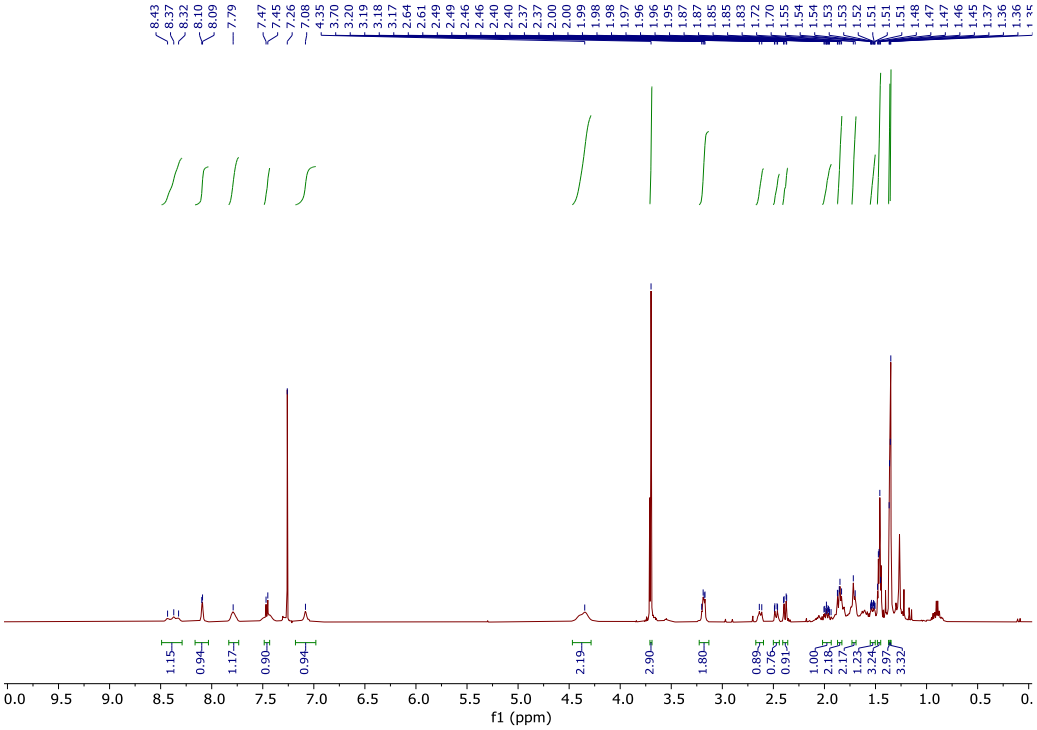


^{13}C NMR (125 MHz, DMSO) of (+)-**9b**

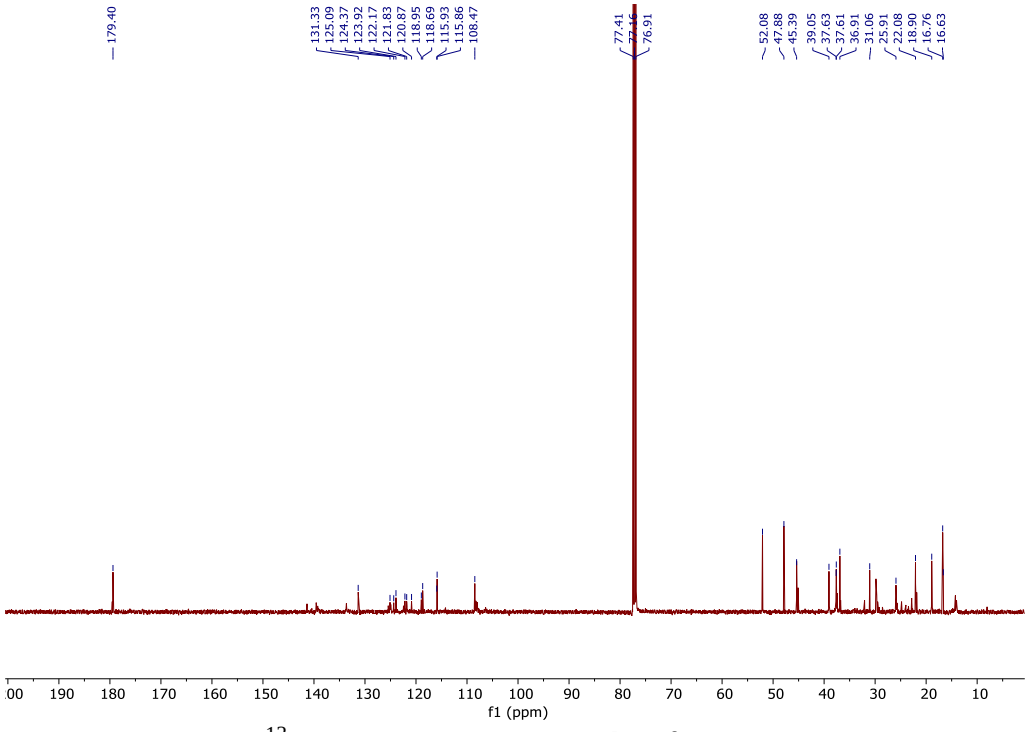


HRMS data of (+)-**9b**





^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**9c**



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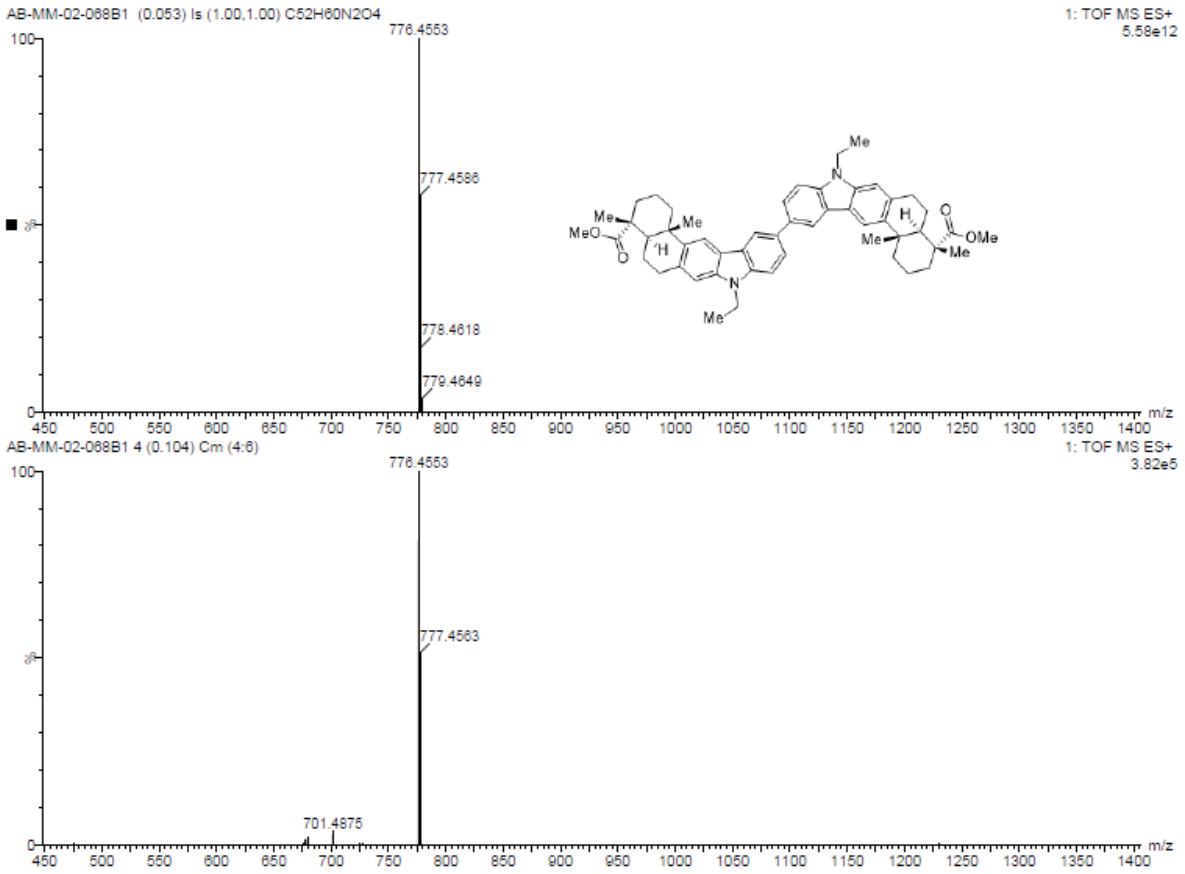

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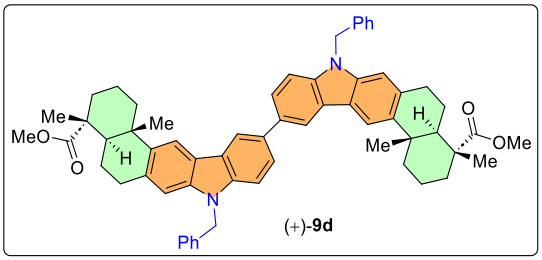

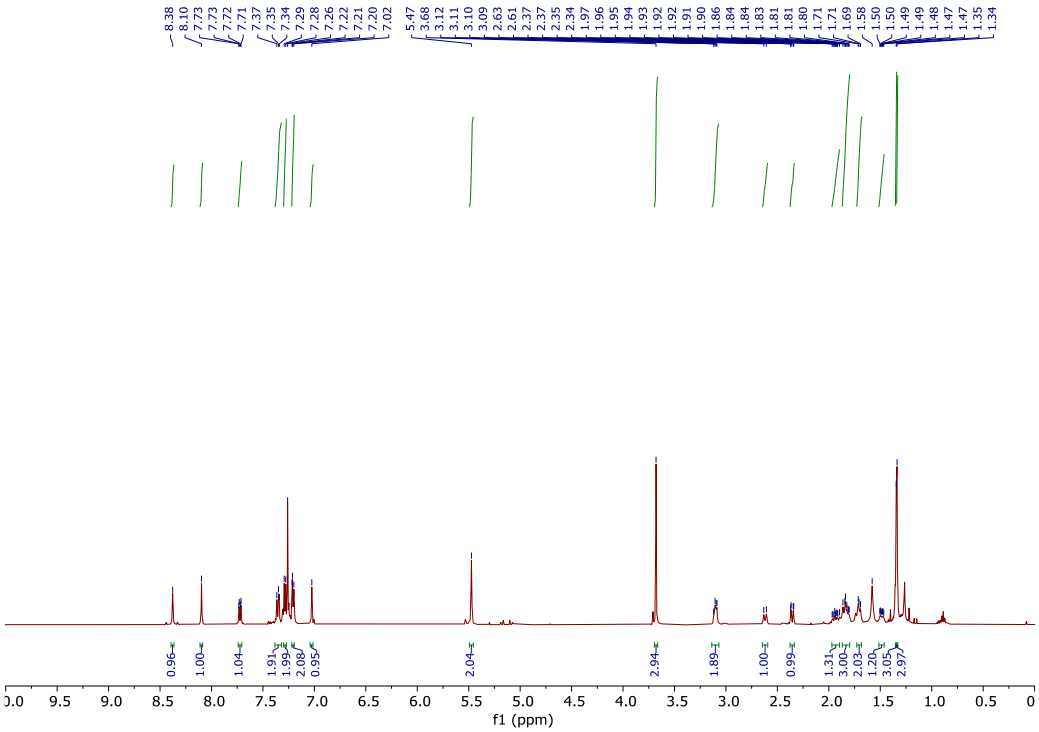

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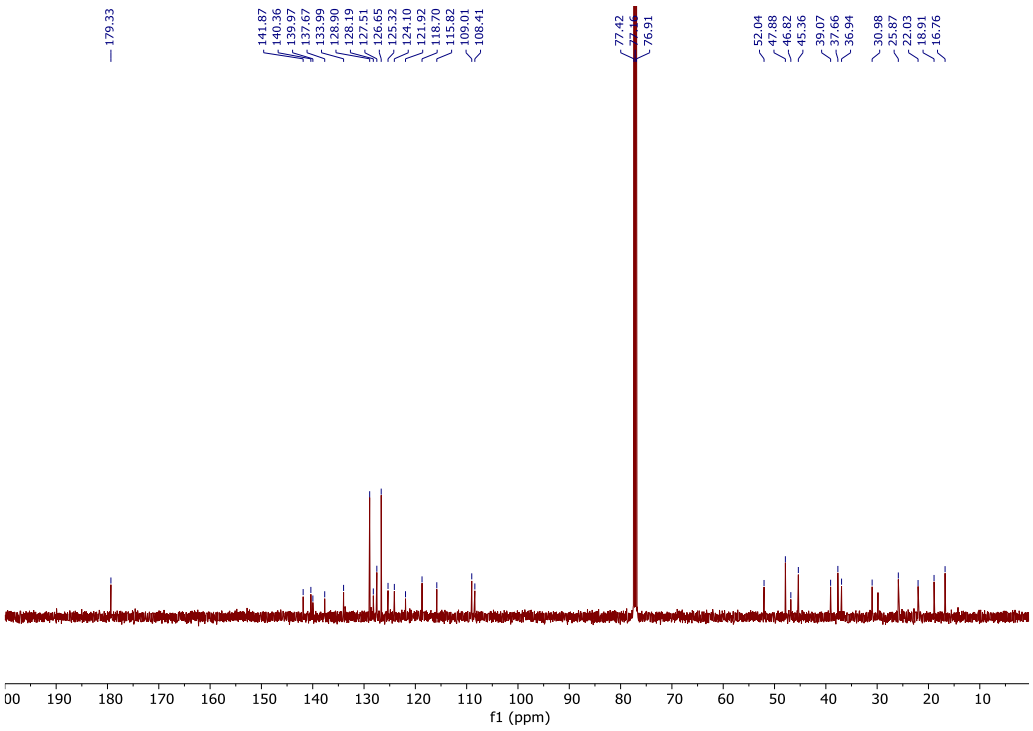

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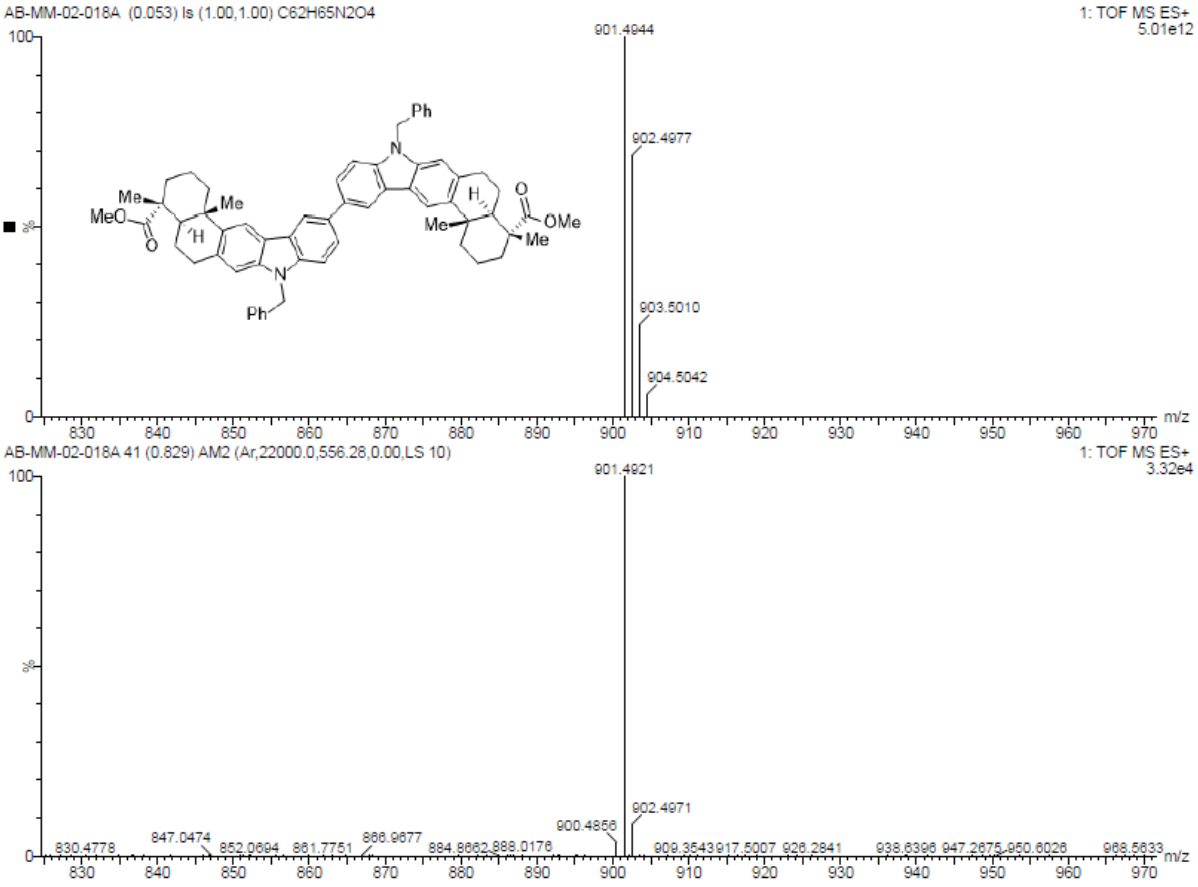

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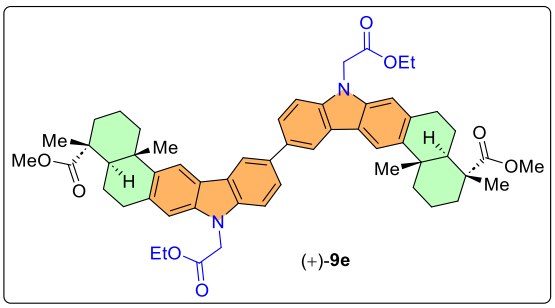
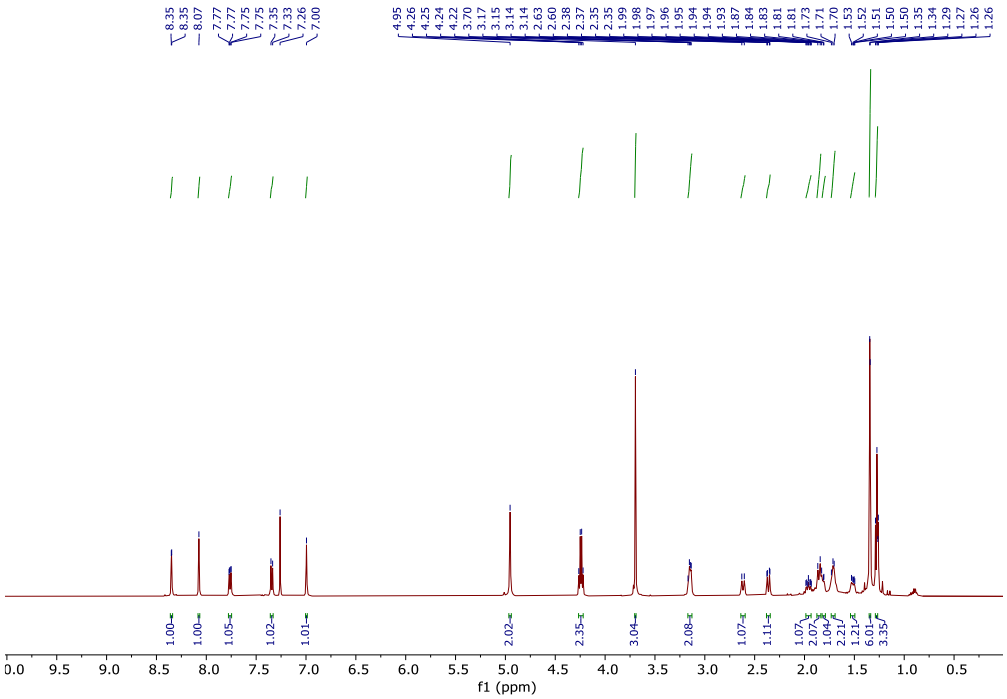
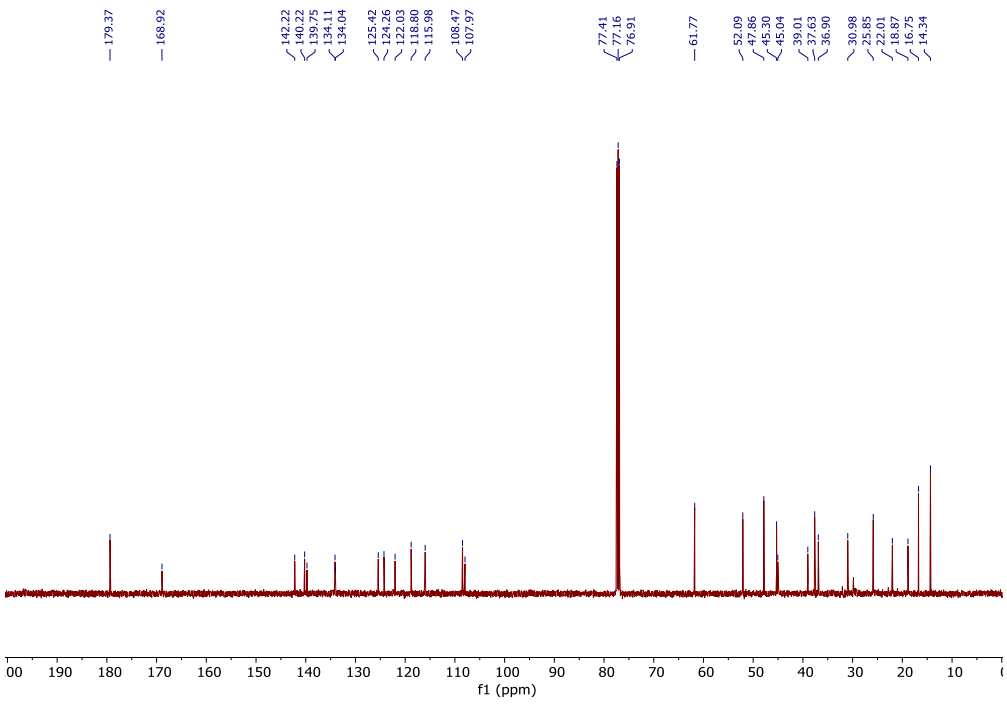


(+)-**9e**



^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**9e**



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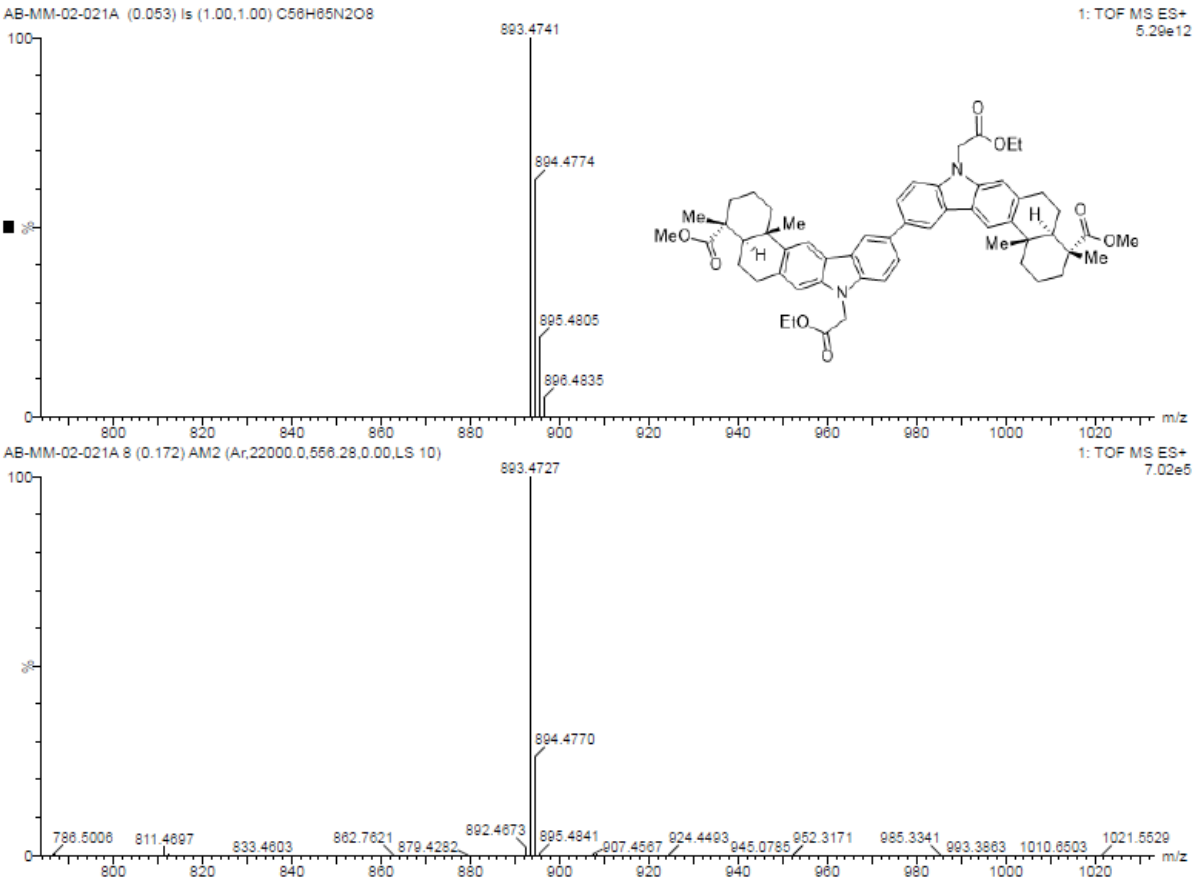
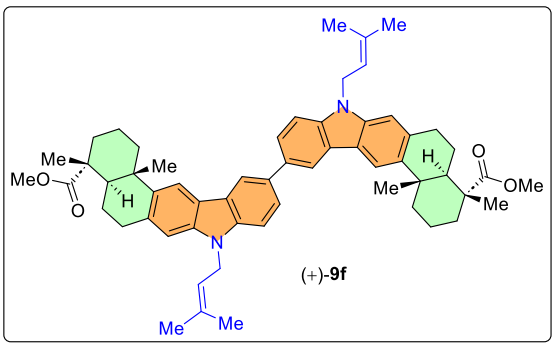
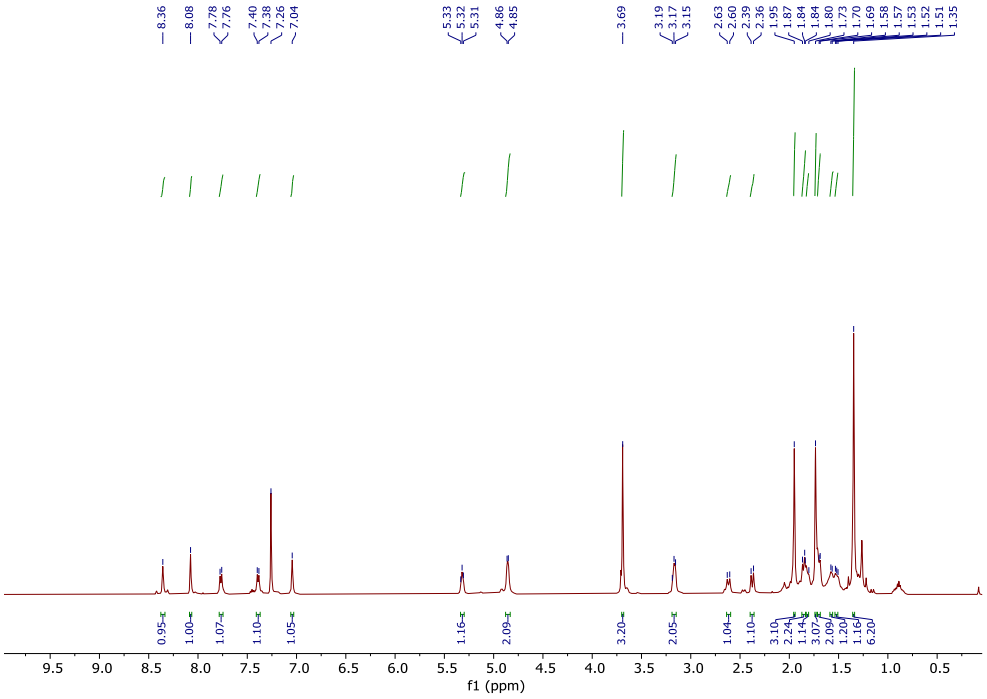


HRMS data of (+)-**9e**



(+)-**9f**



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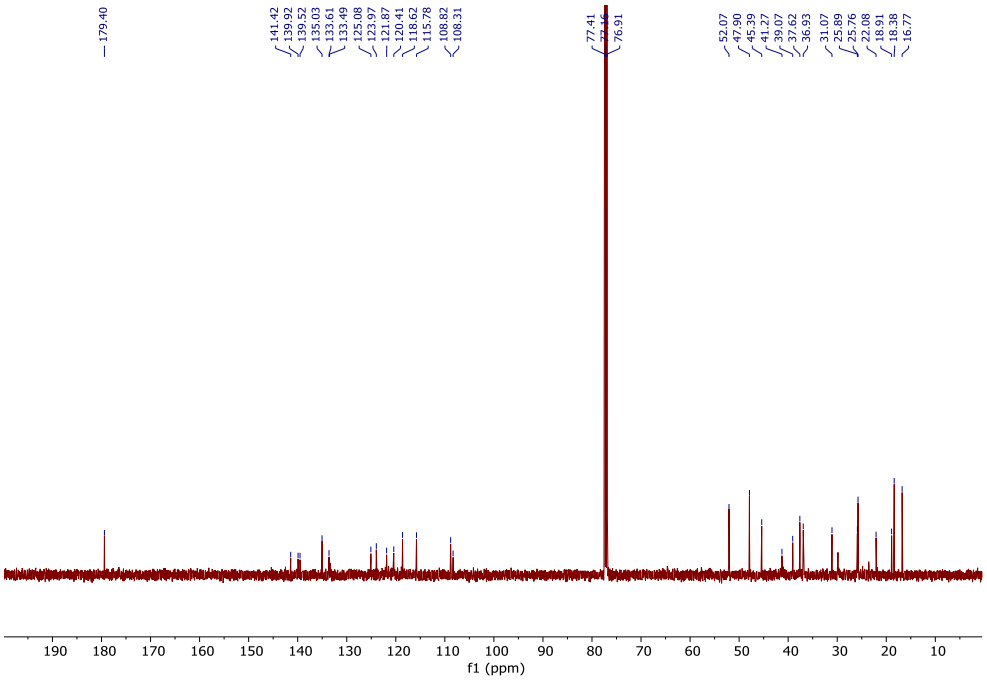

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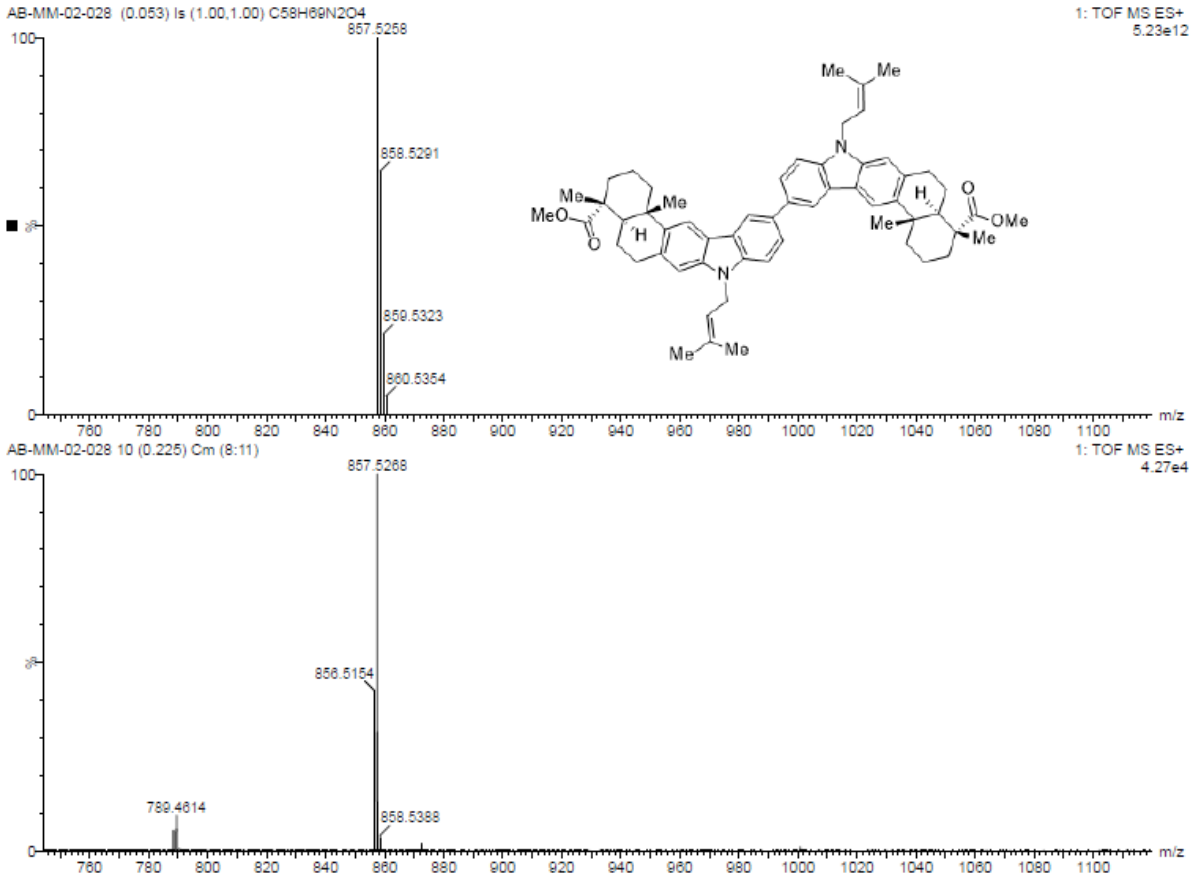

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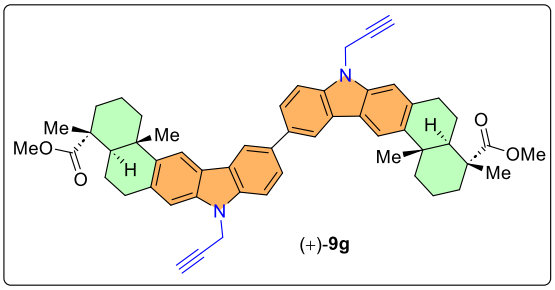
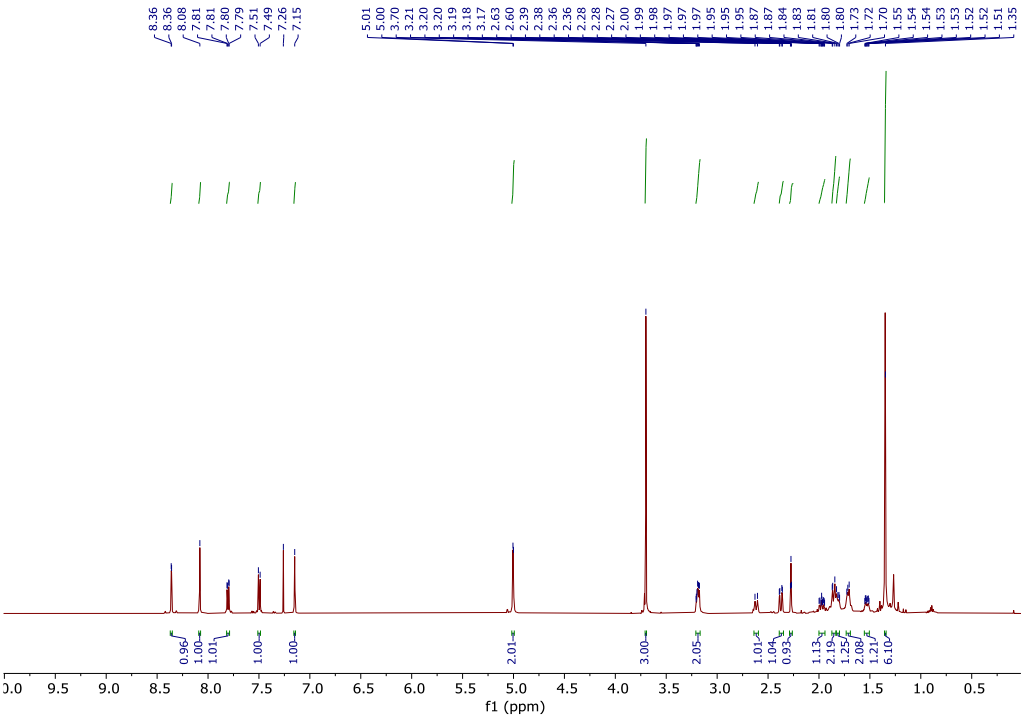
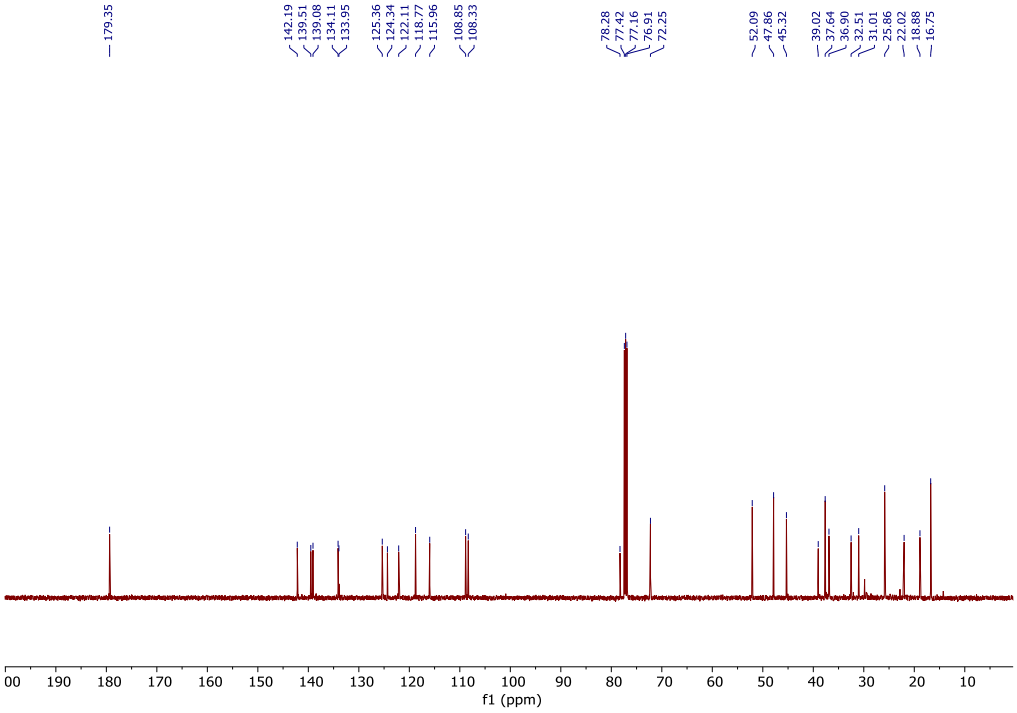




^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**9g**



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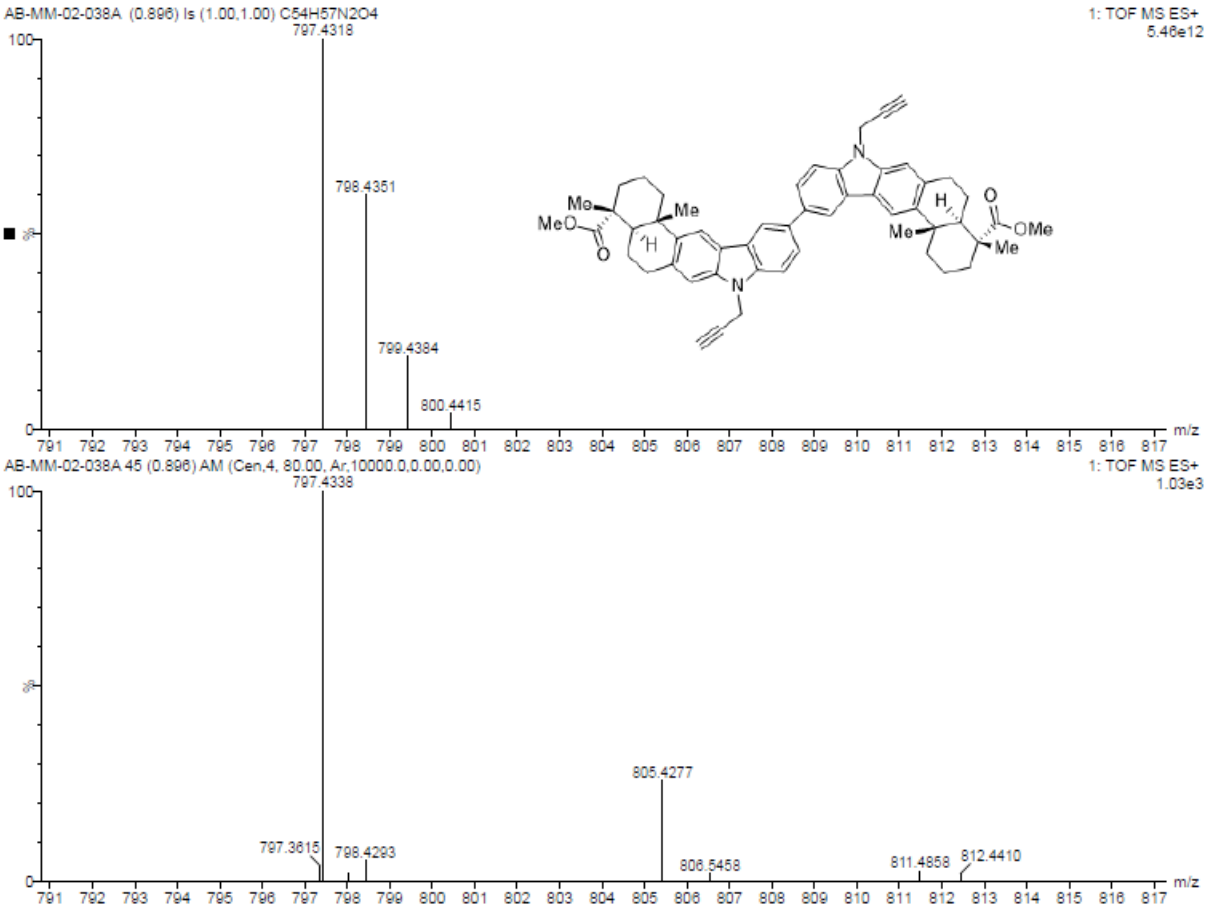
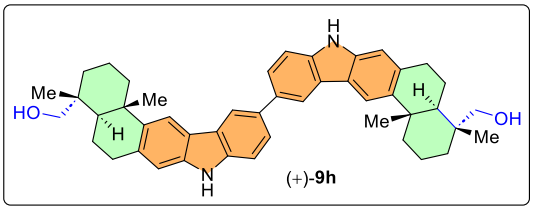
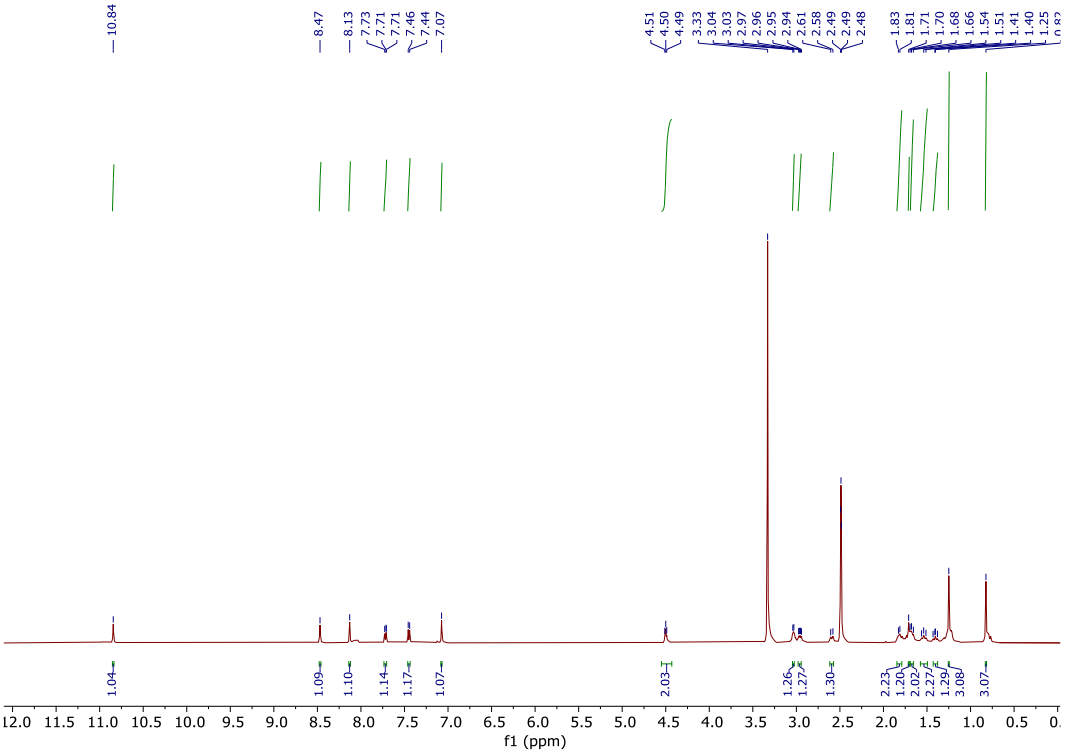
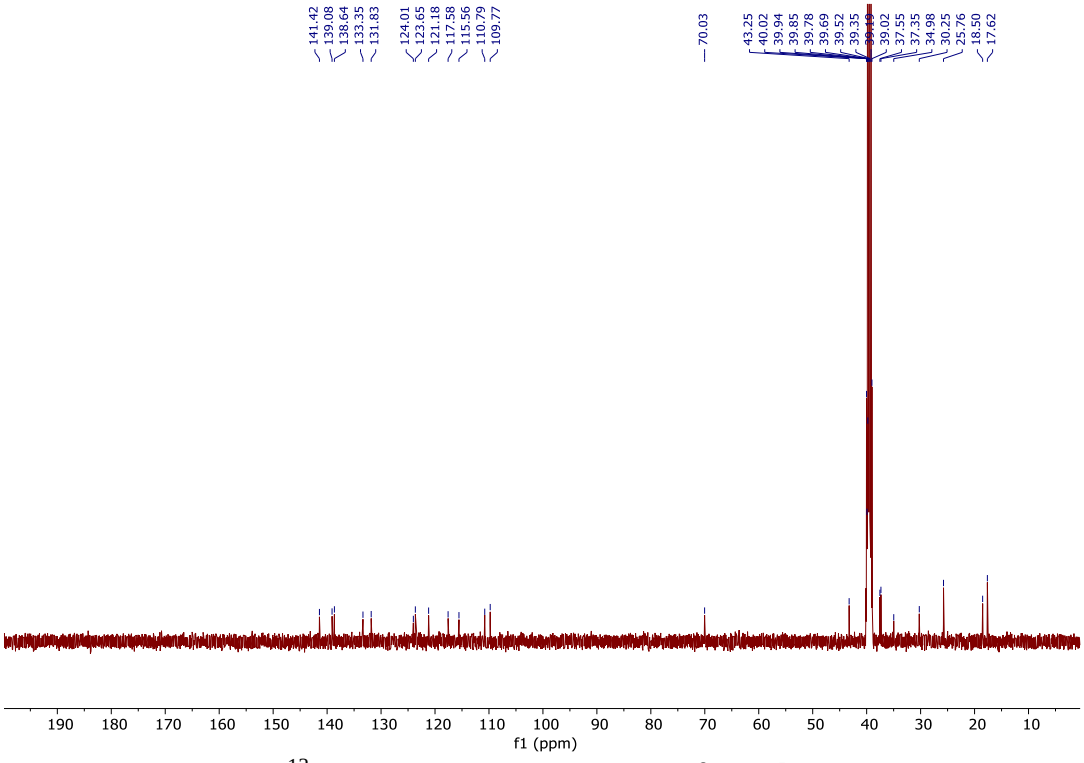


HRMS data of (+)-**9g**

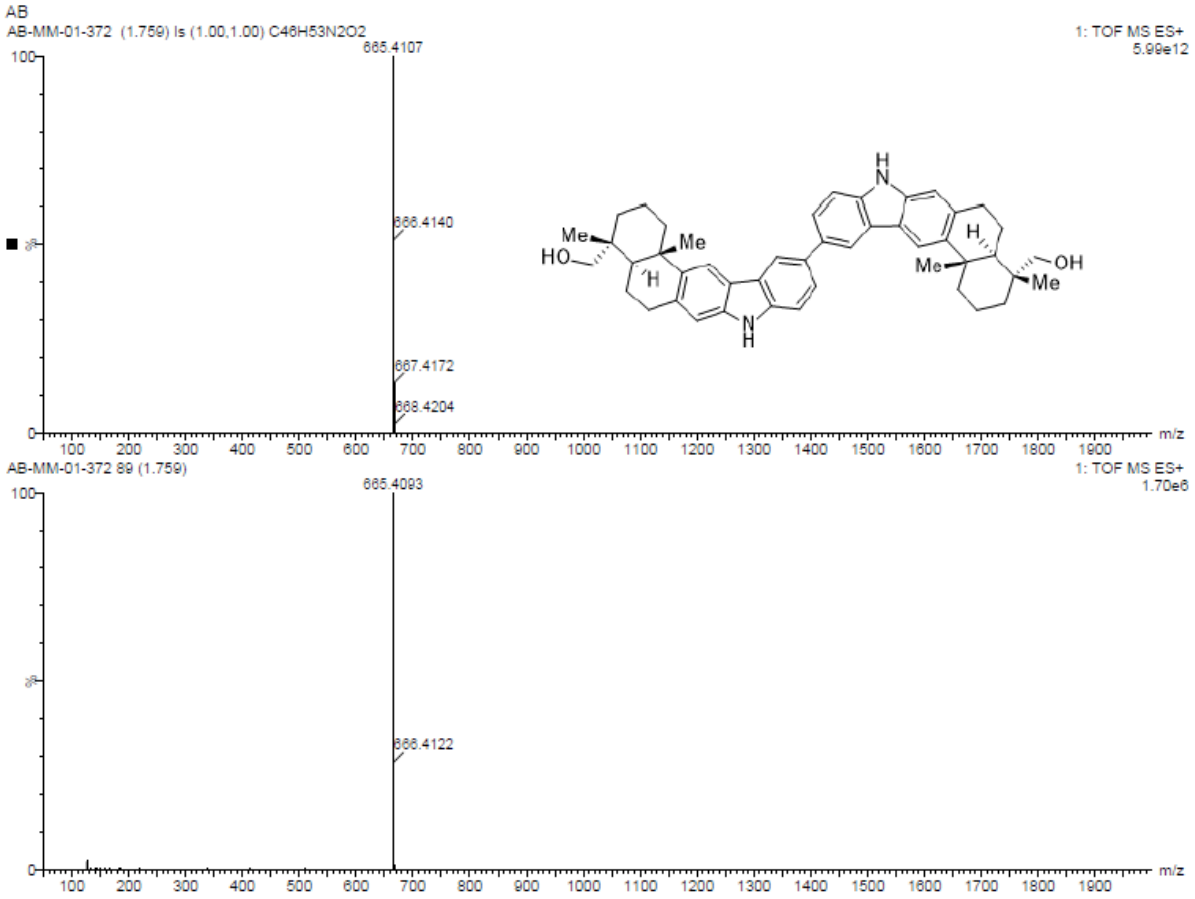




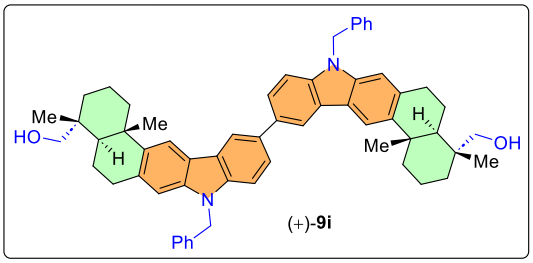
^{1}H NMR (500 MHz, DMSO) of (+)-**9h**

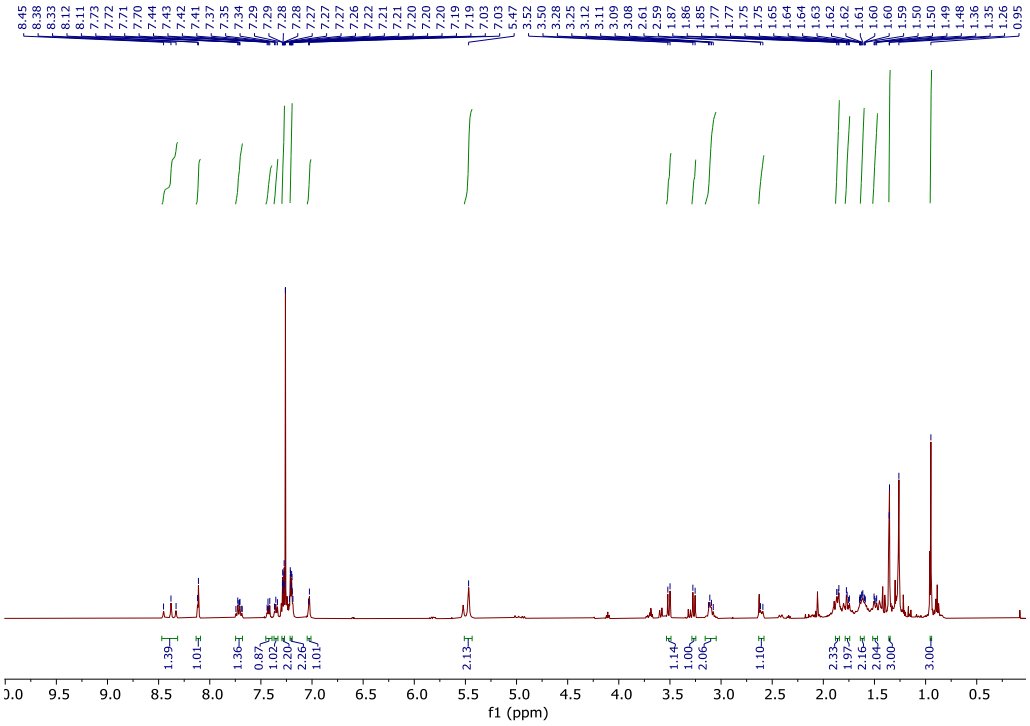


^{13}C NMR (125 MHz, DMSO) of (+)-**9h**

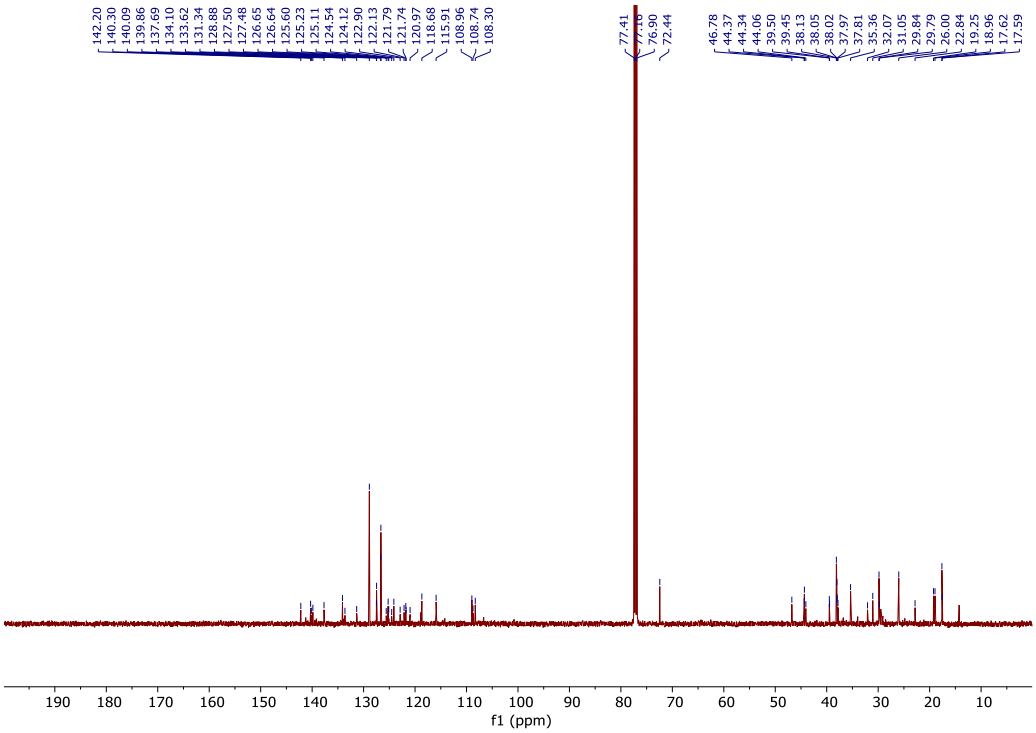


HRMS data of (+)-**9h**

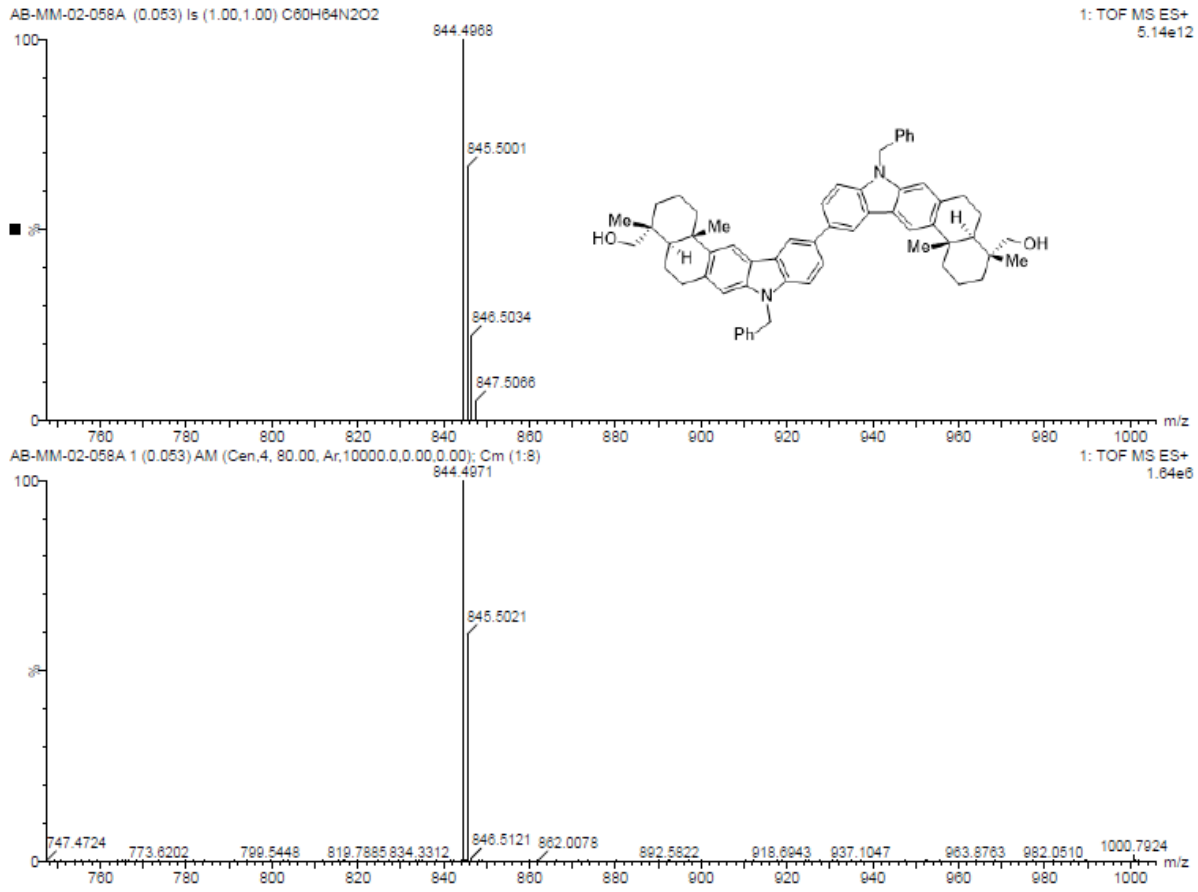




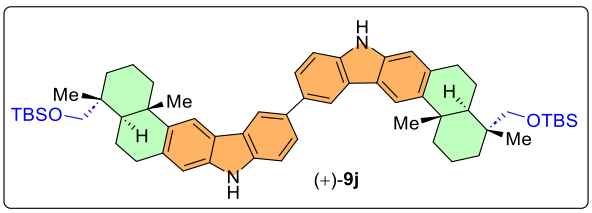
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**9i**



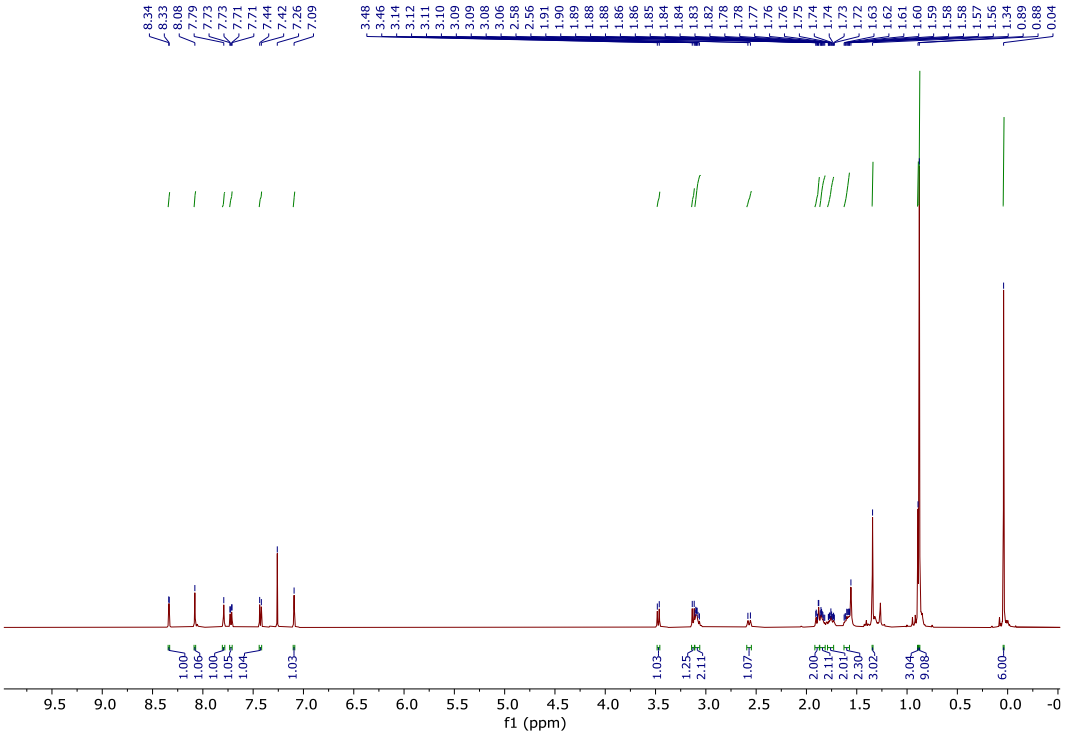
^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**9i**



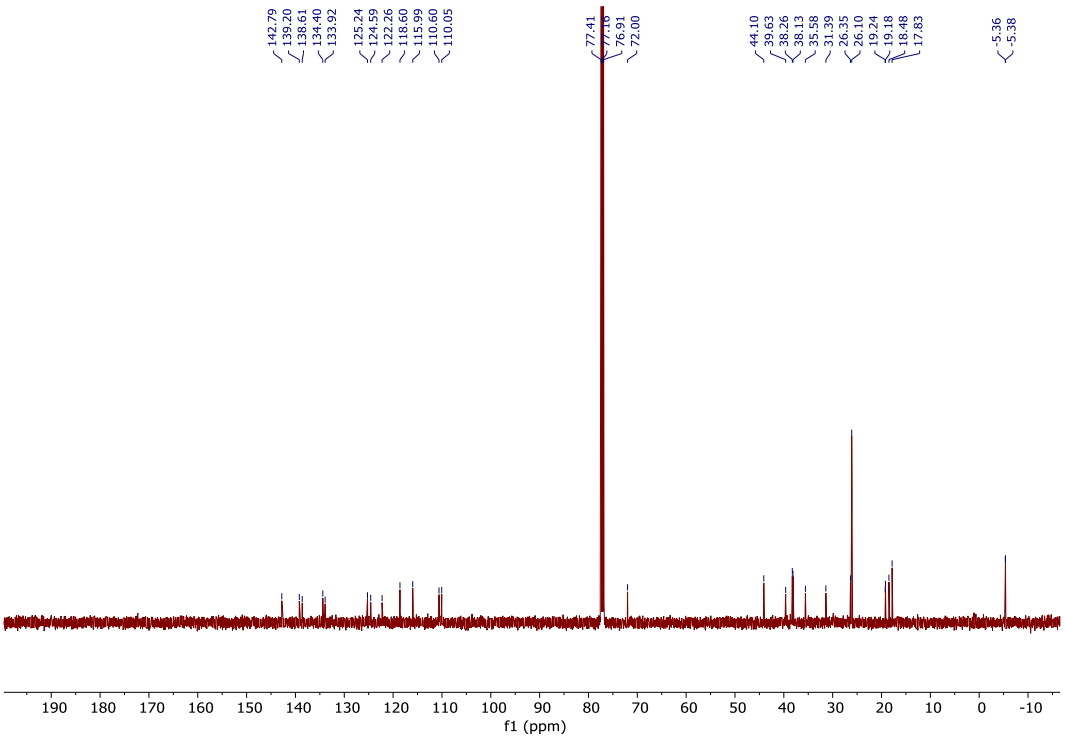
HRMS data of (+)-**9i**



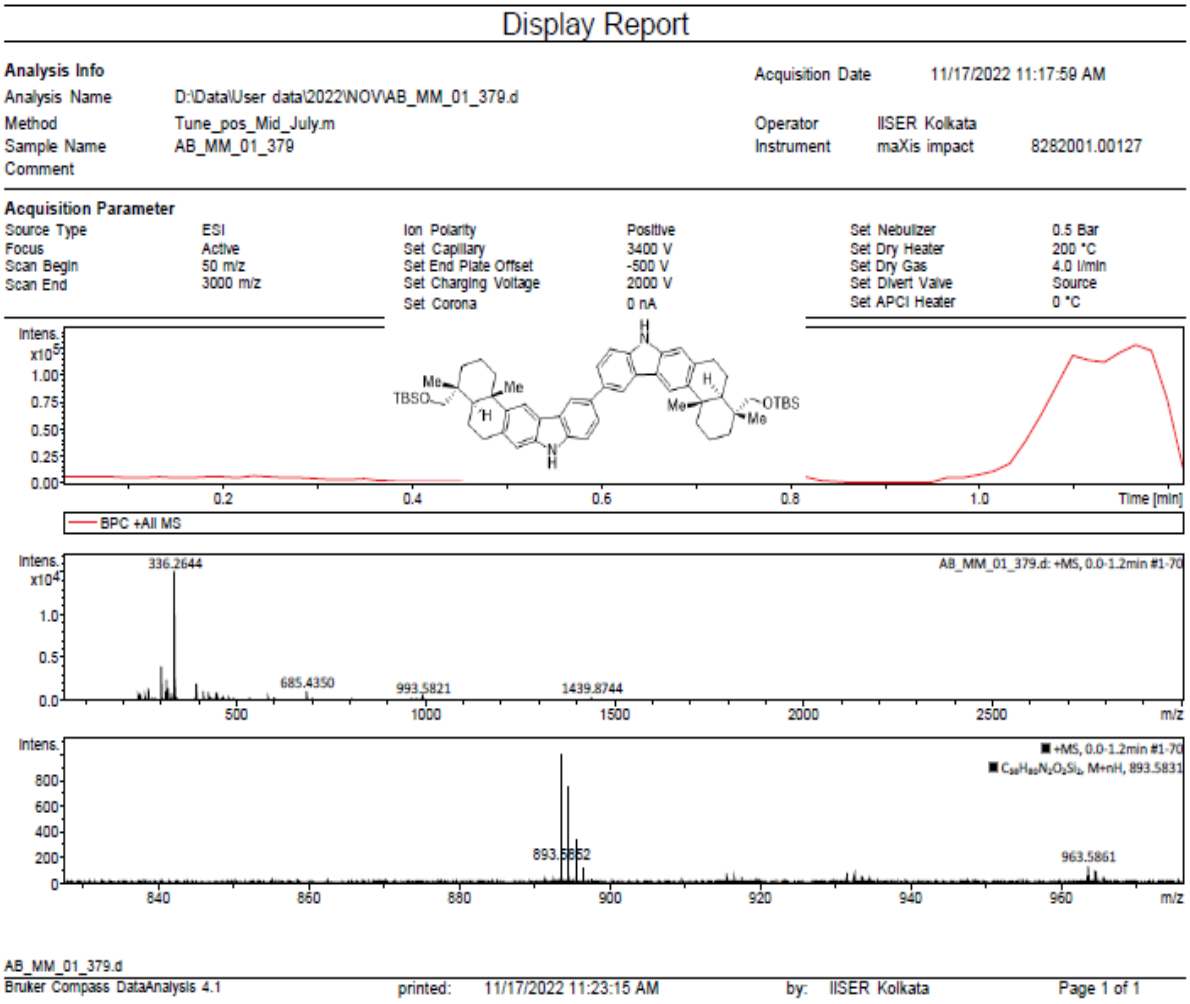
(+)-**9j**



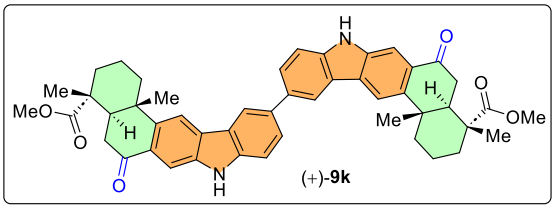
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**9j**

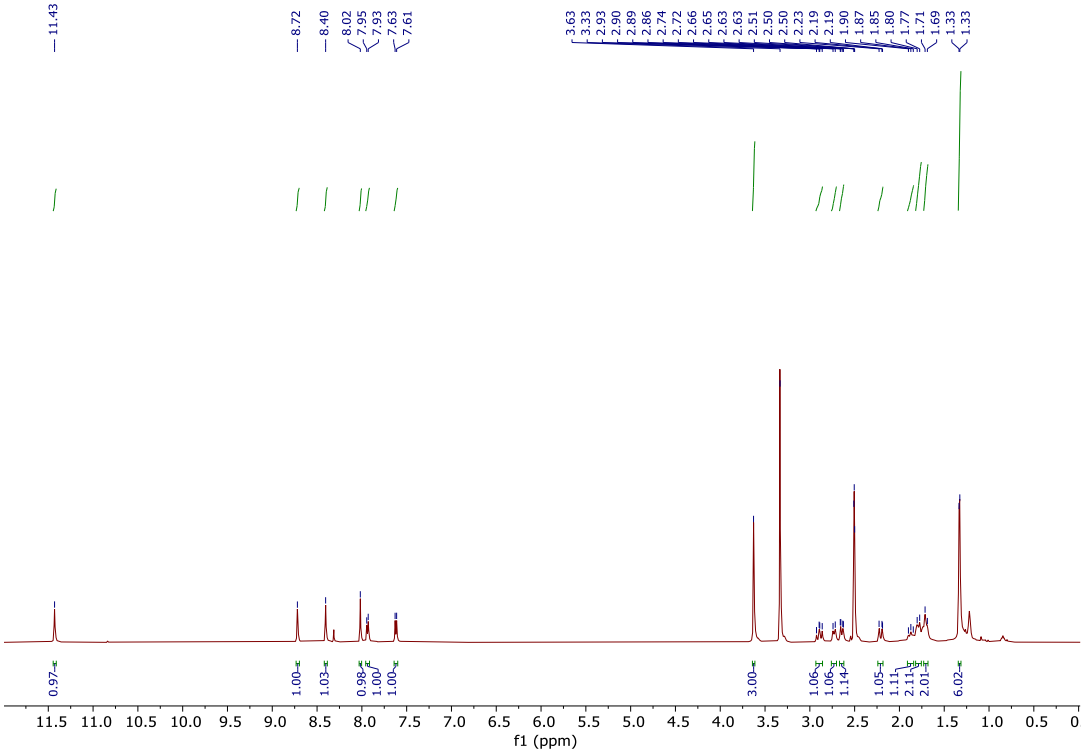


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**9j**

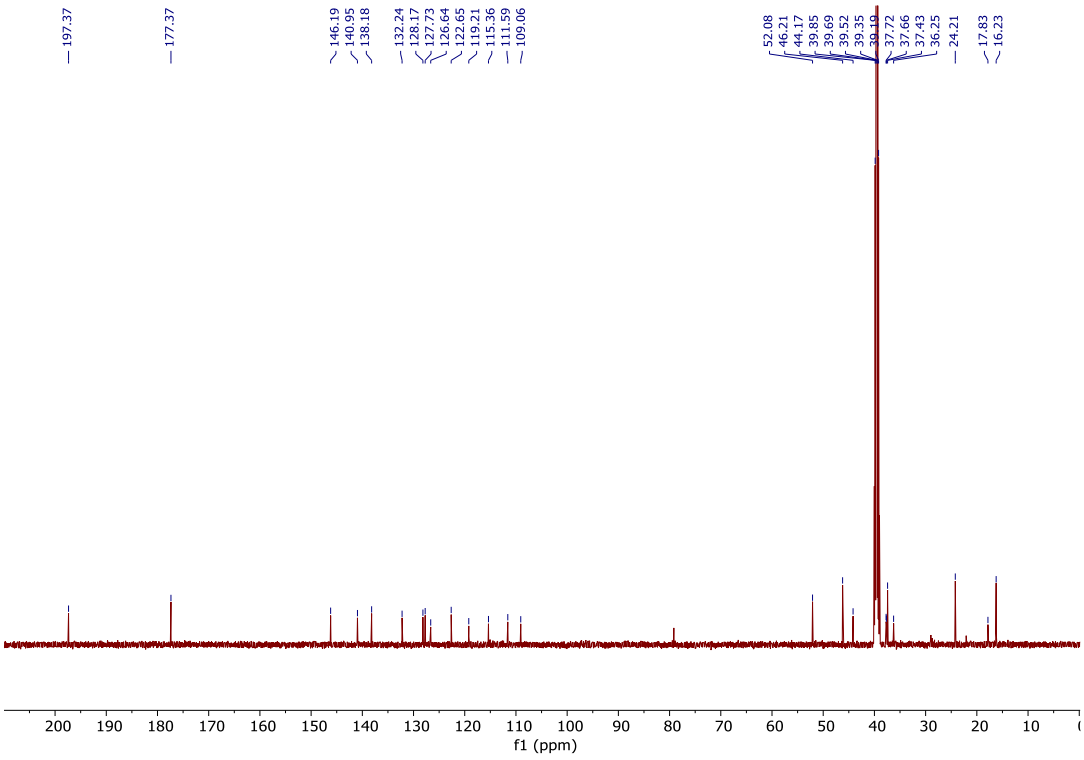


HRMS data of (+)-**9j**

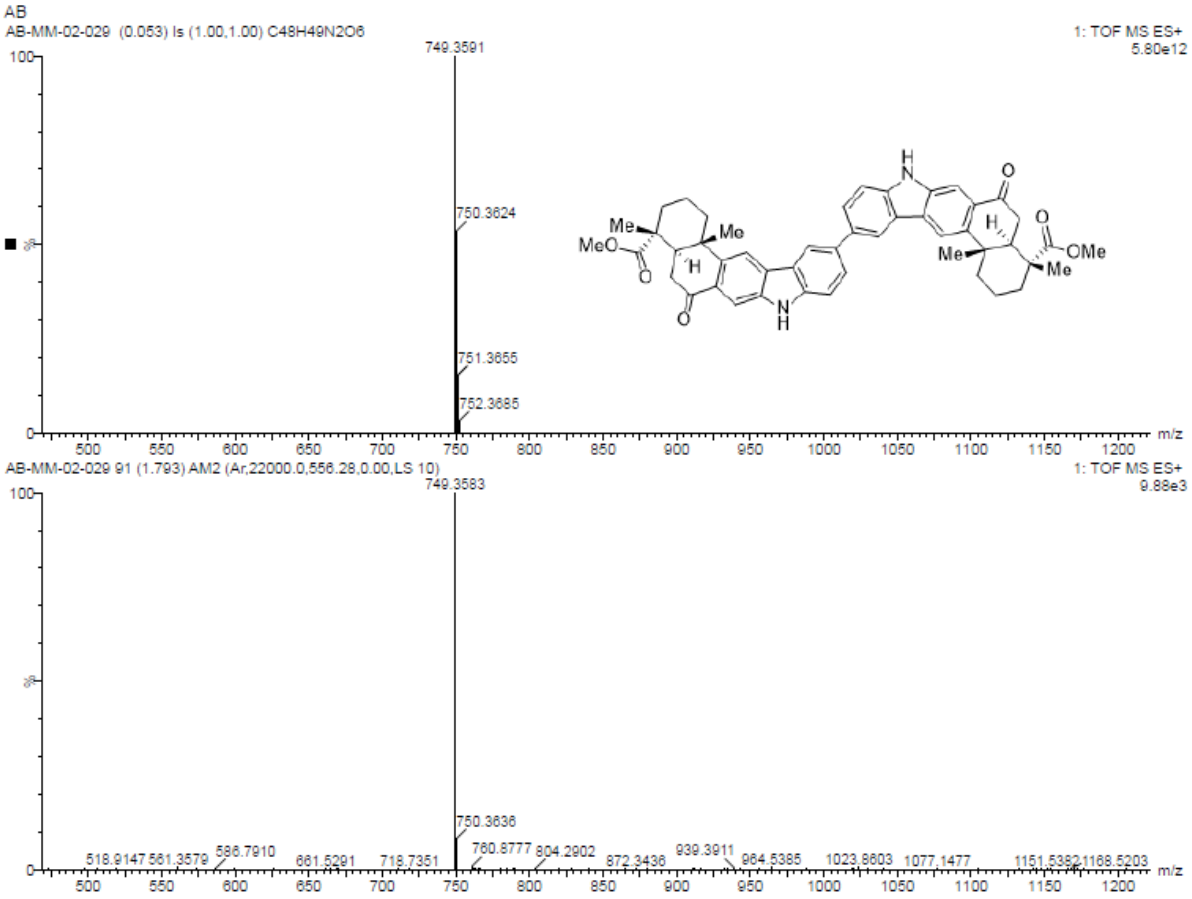




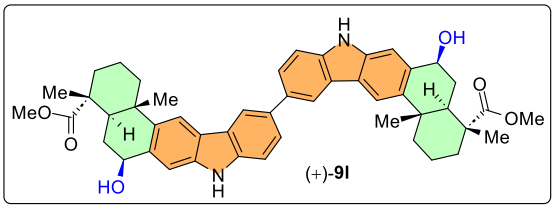
^{1}H NMR (500 MHz, DMSO) of (+)-**9k**

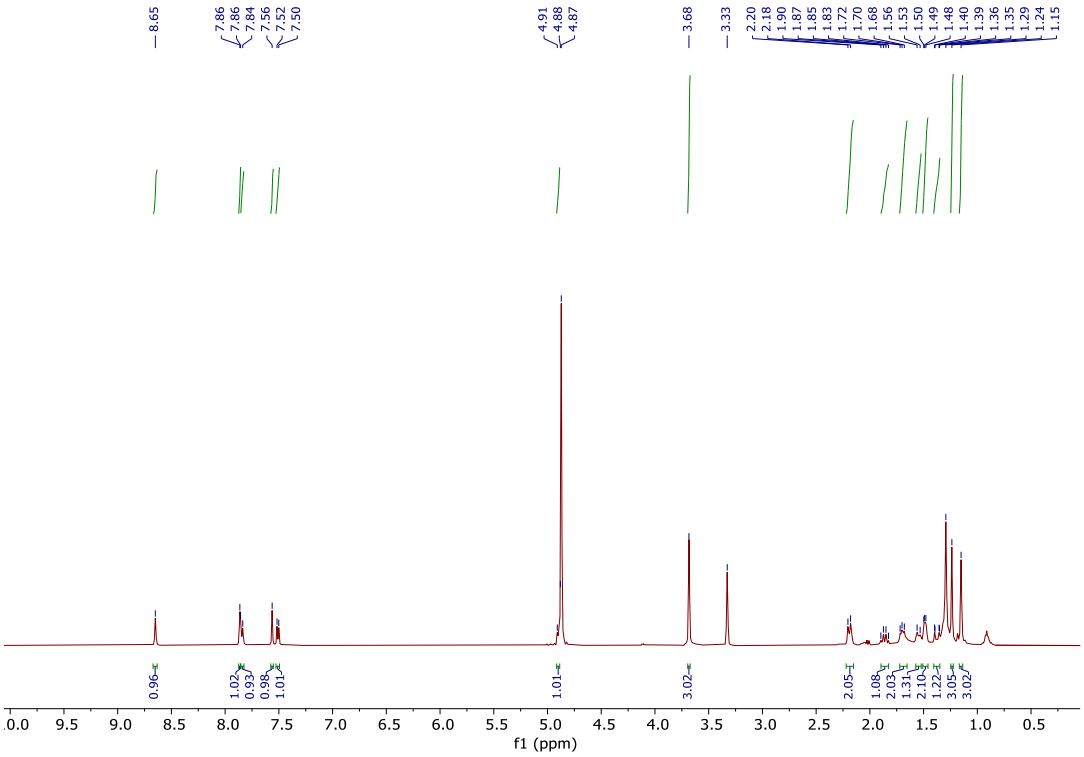


^{13}C NMR (125 MHz, DMSO) of (+)-**9k**

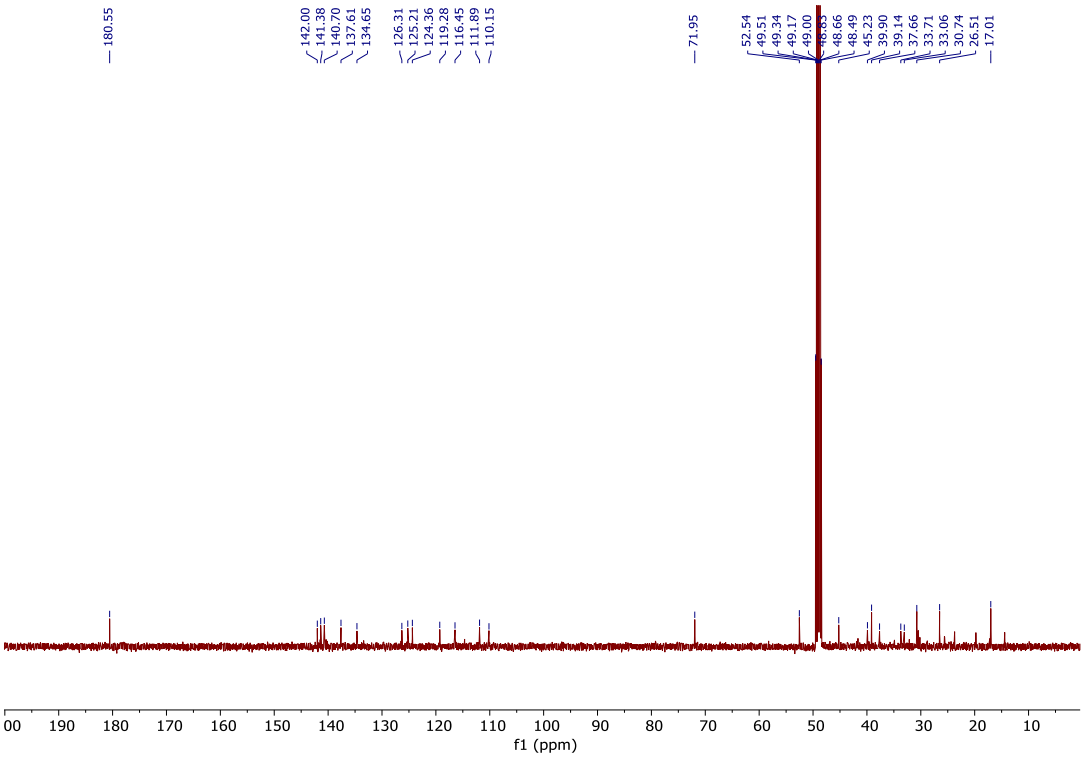


HRMS data of (+)-**9k**

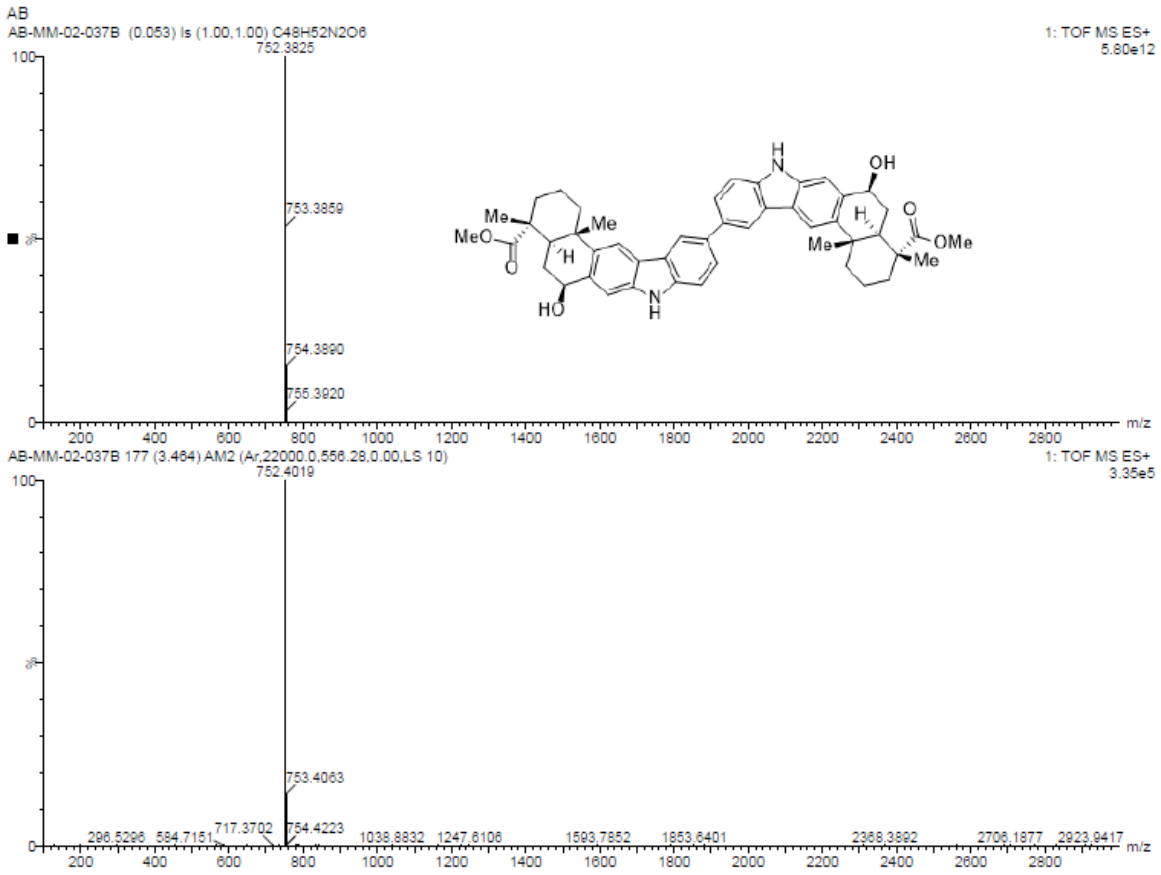




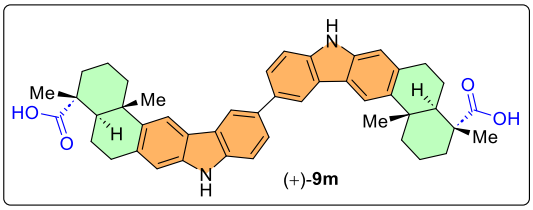
^{1}H NMR (500 MHz, CD_3OD) of (+)-**9l**



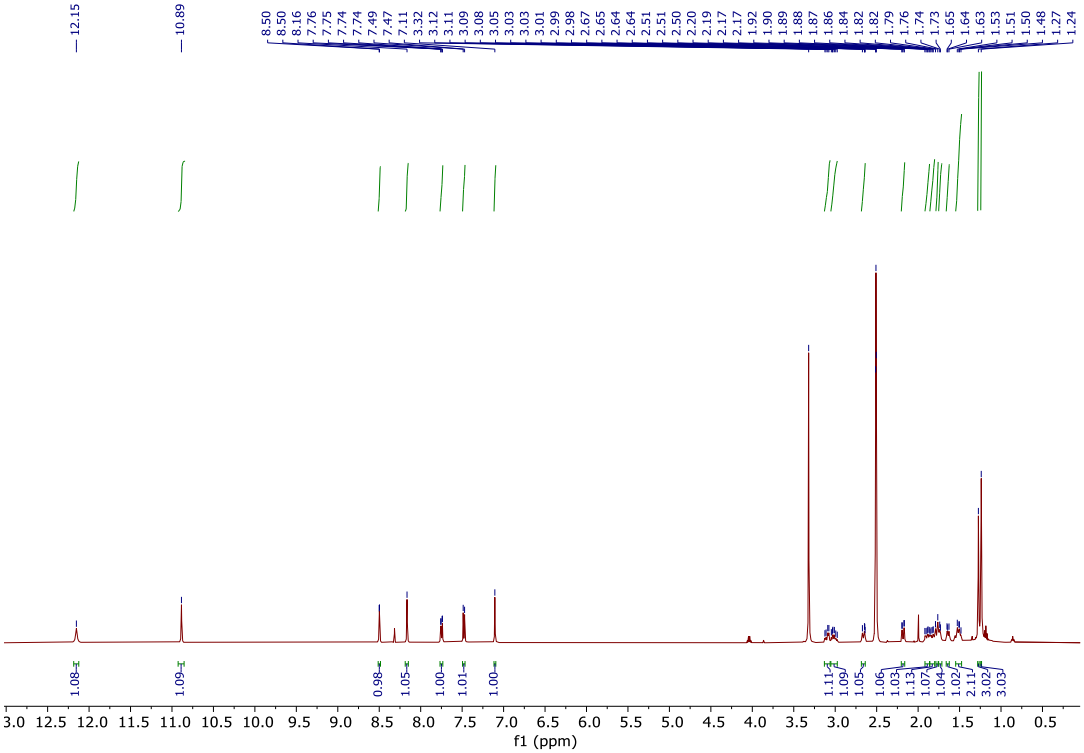
^{13}C NMR (125 MHz, CD_3OD) of (+)-**9l**



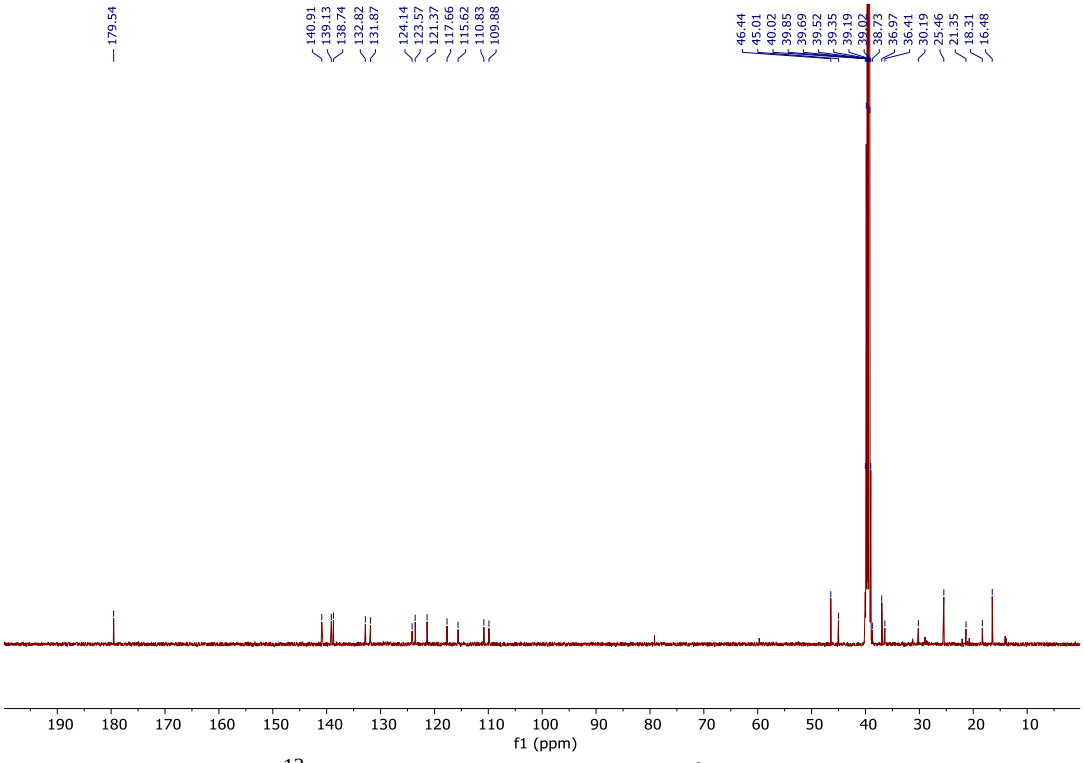
HRMS data of (+)-**9l**



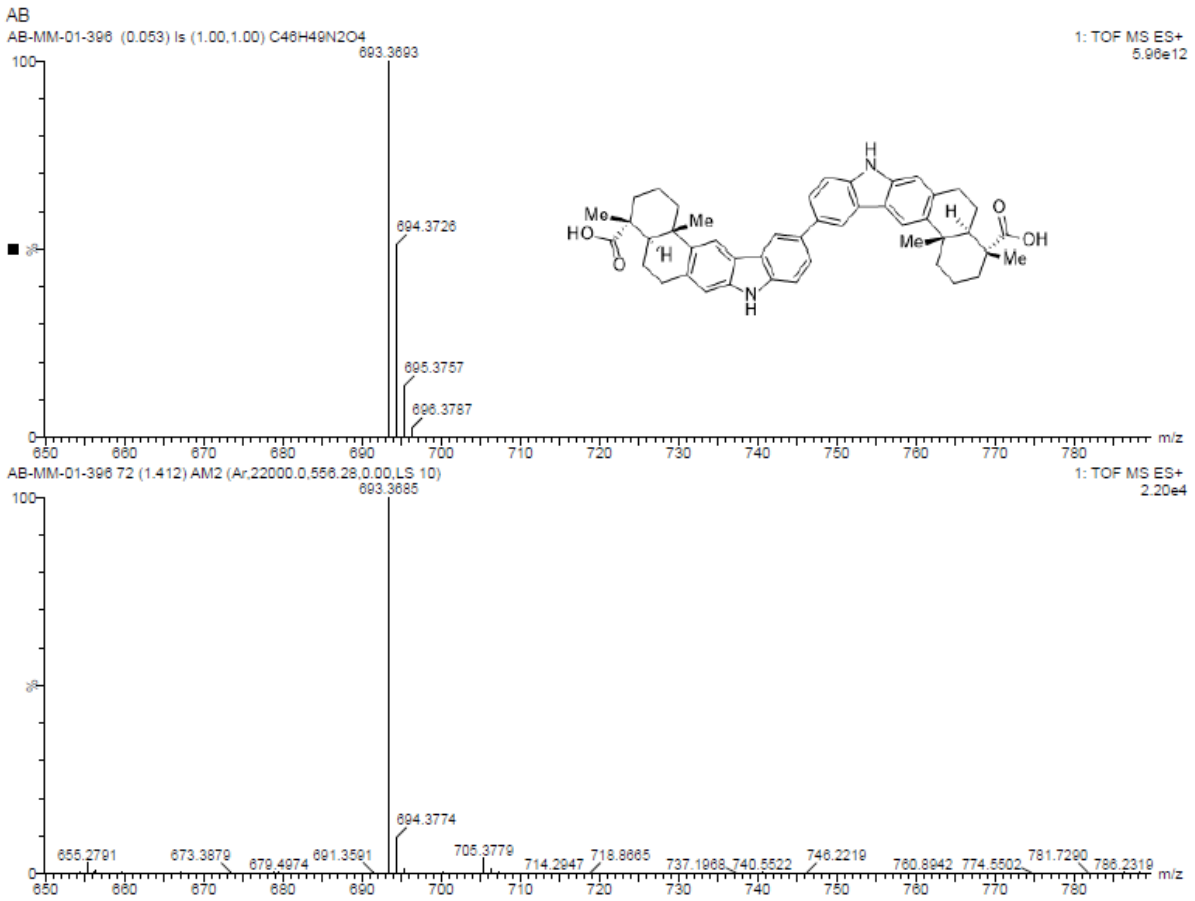
(+)-**9m**



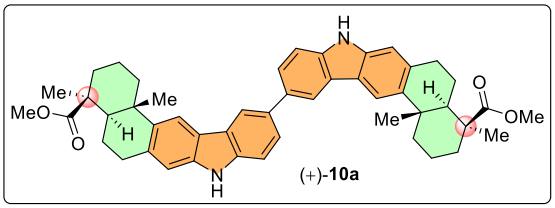
^{1}H NMR (500 MHz, DMSO) of (+)-**9m**

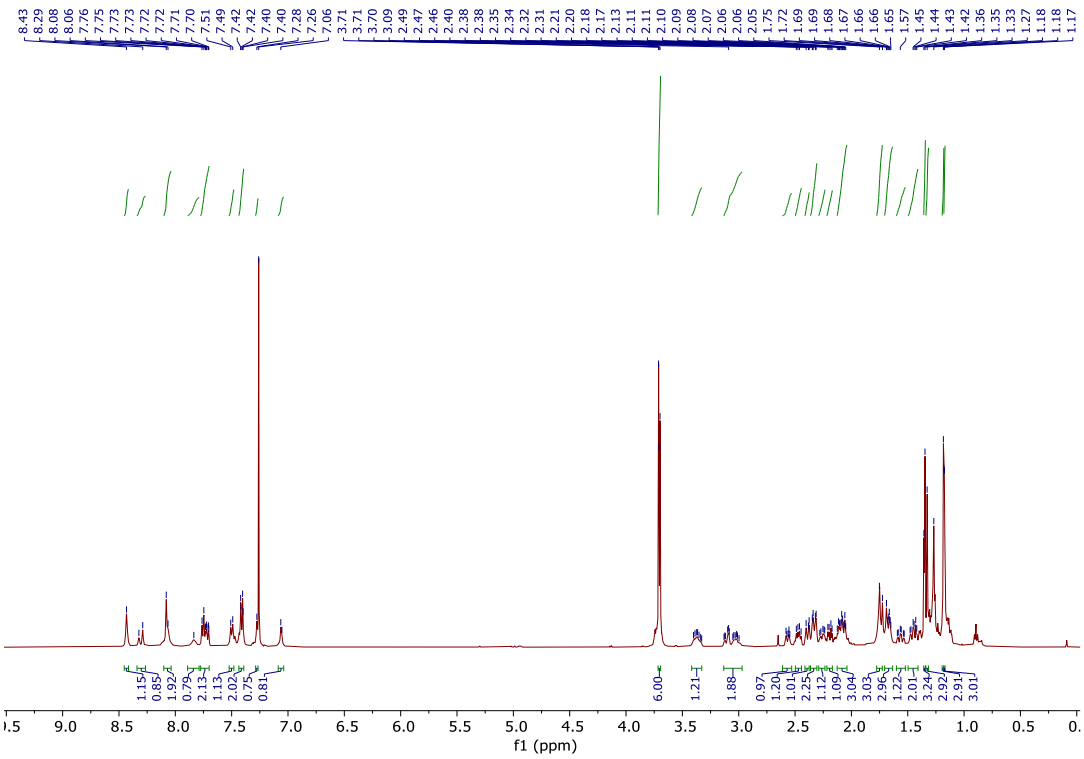


^{13}C NMR (125 MHz, DMSO) of (+)-**9m**

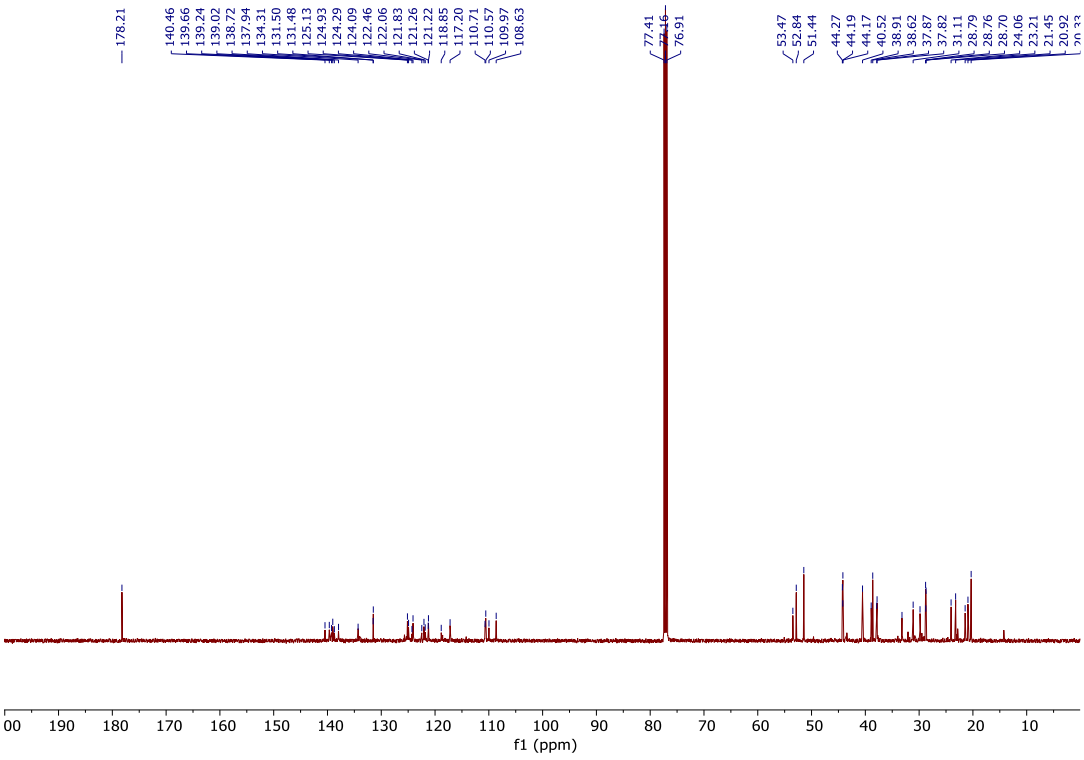


HRMS data of (+)-**9m**

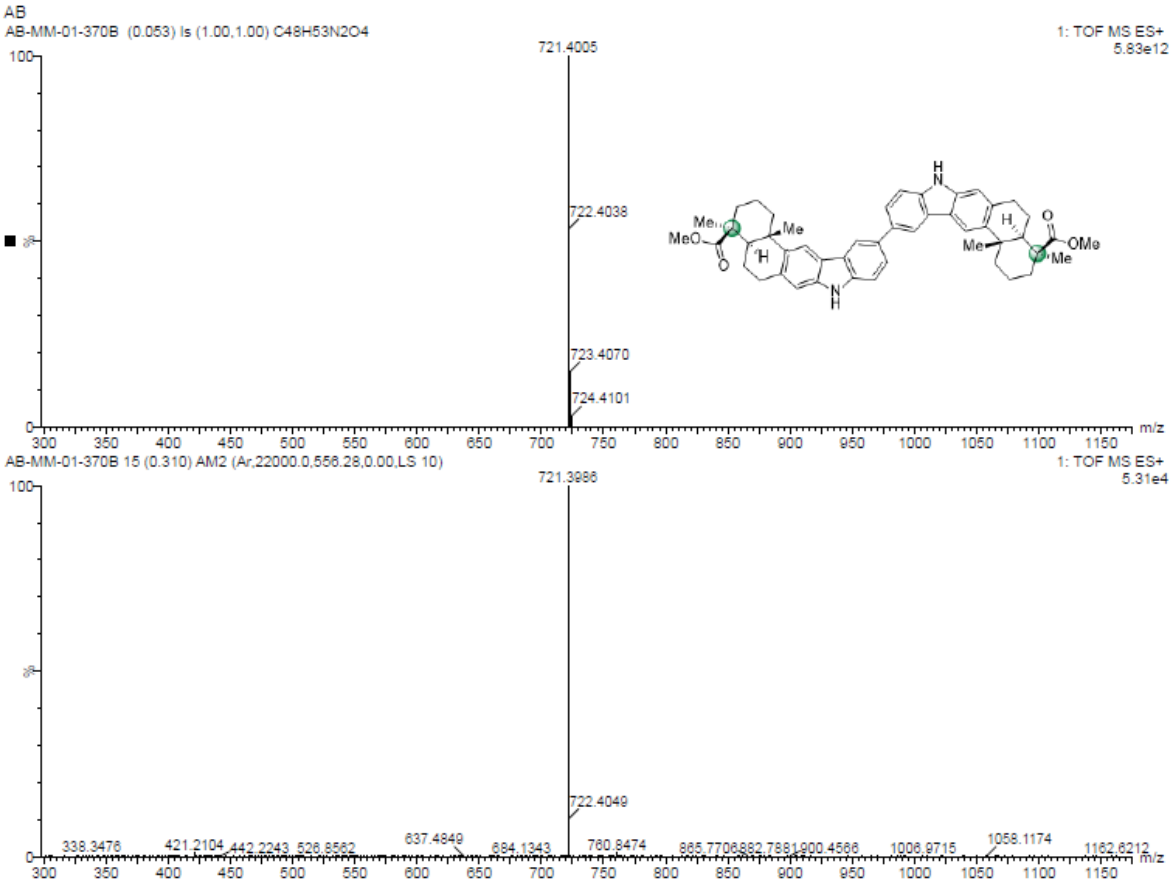




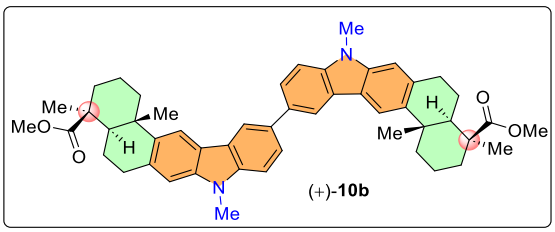
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**10a**

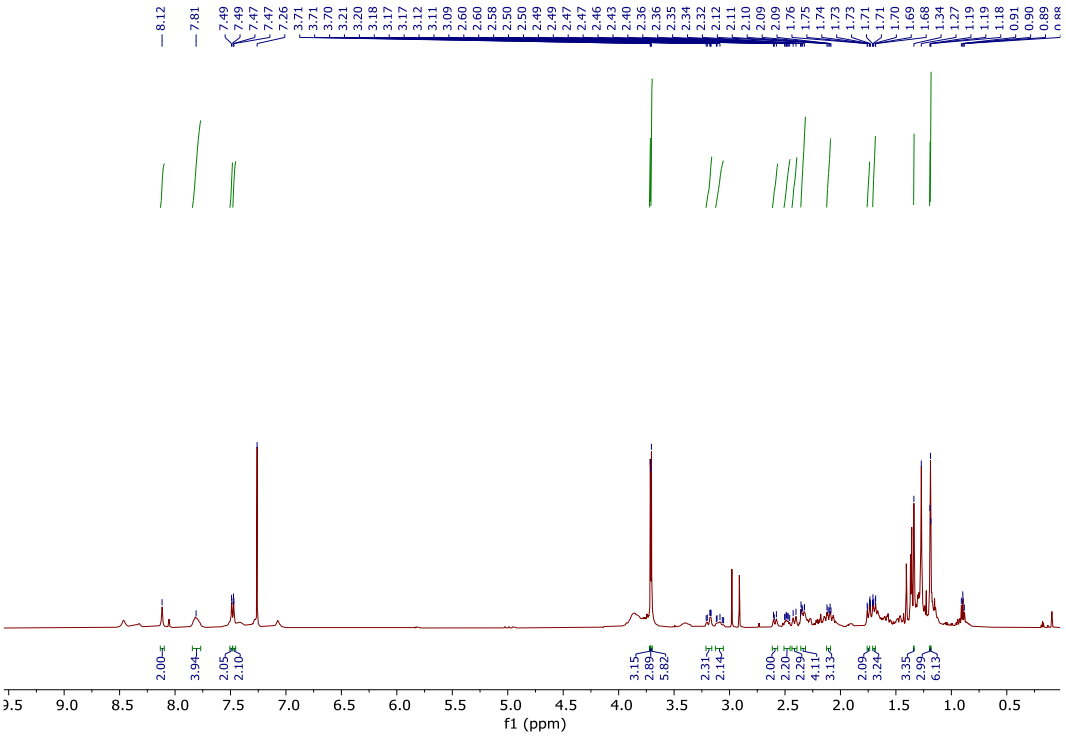


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**10a**

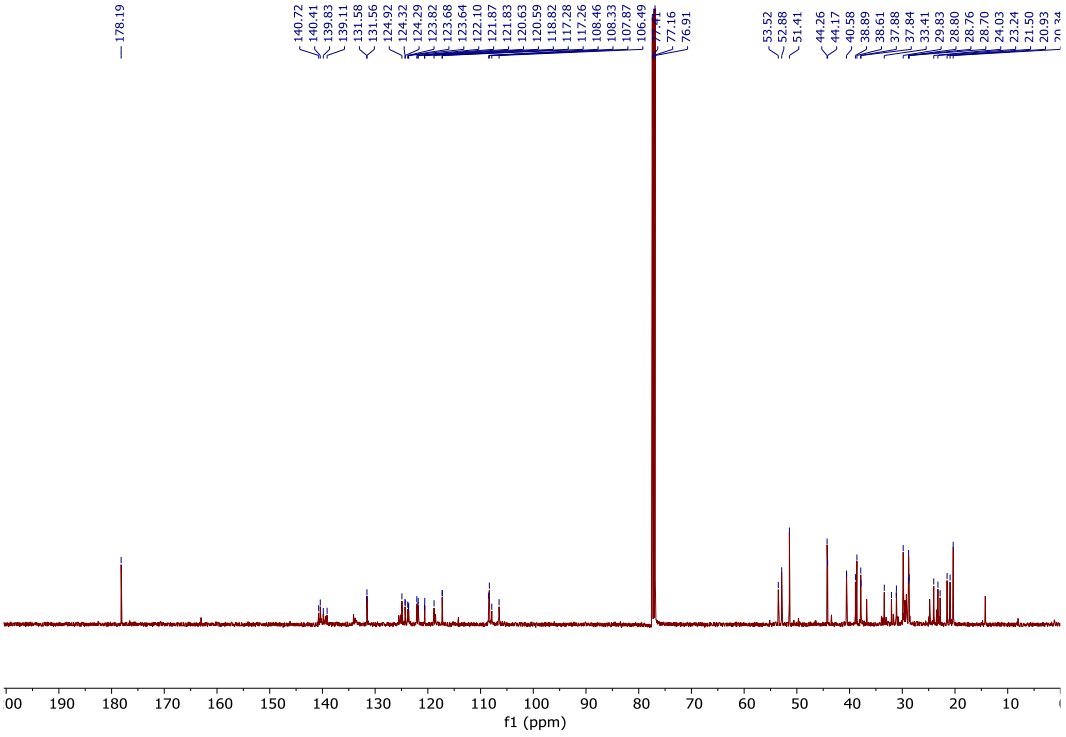


HRMS data of (+)-**10a**

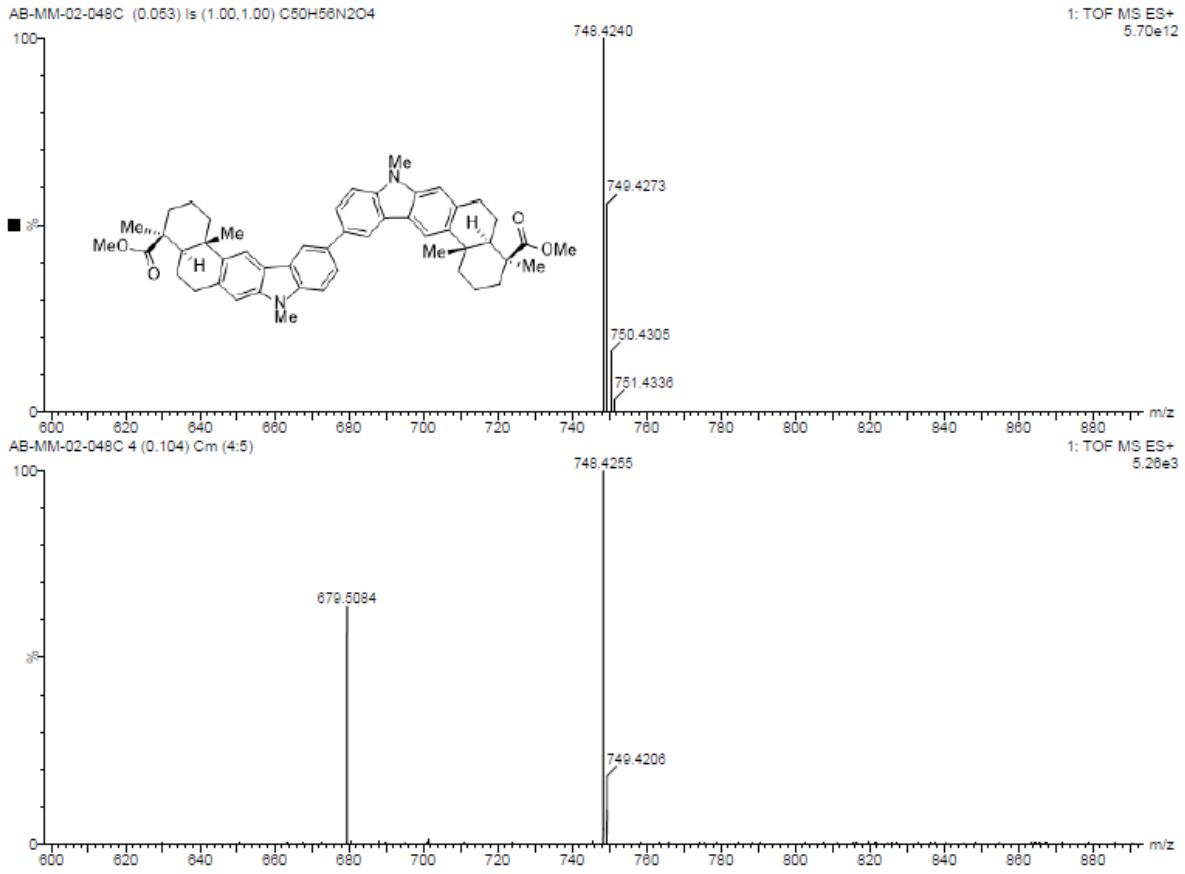




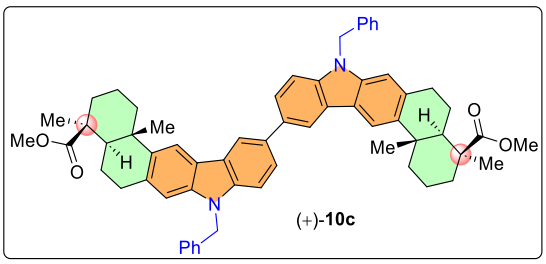
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**10b**

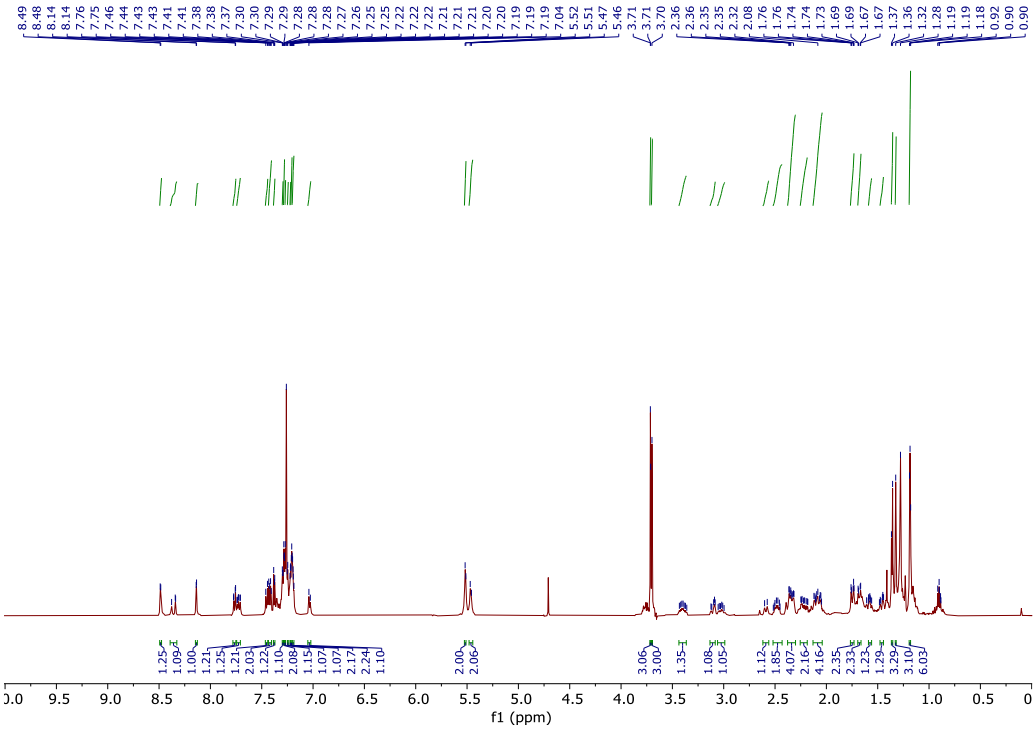


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**10b**

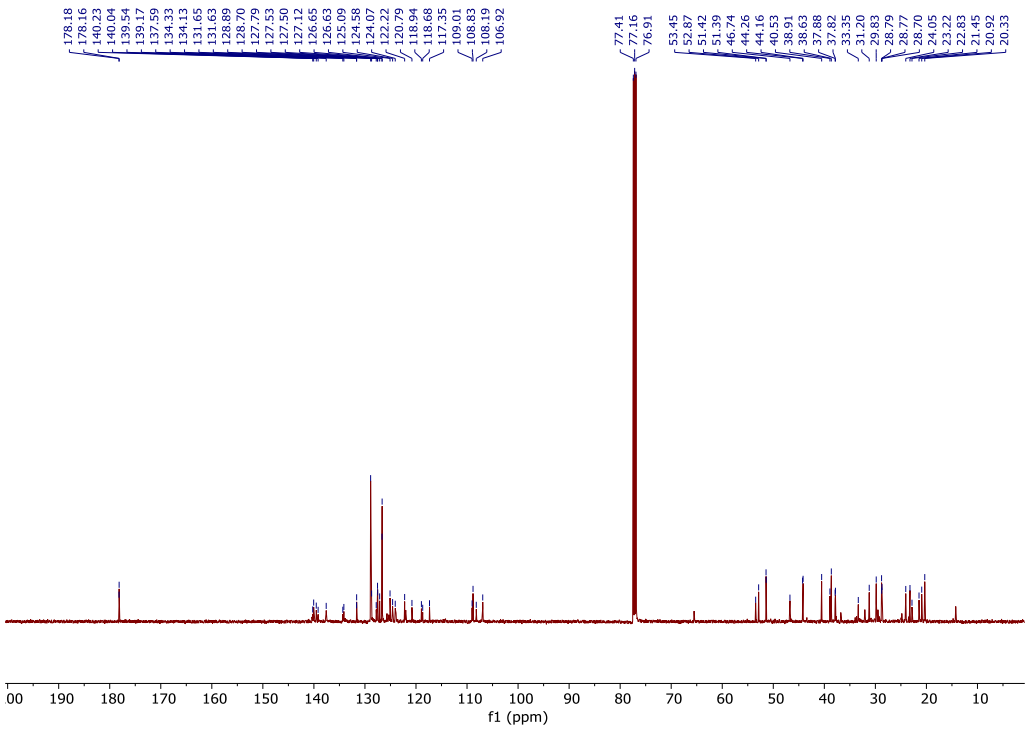


HRMS data of (+)-**10b**

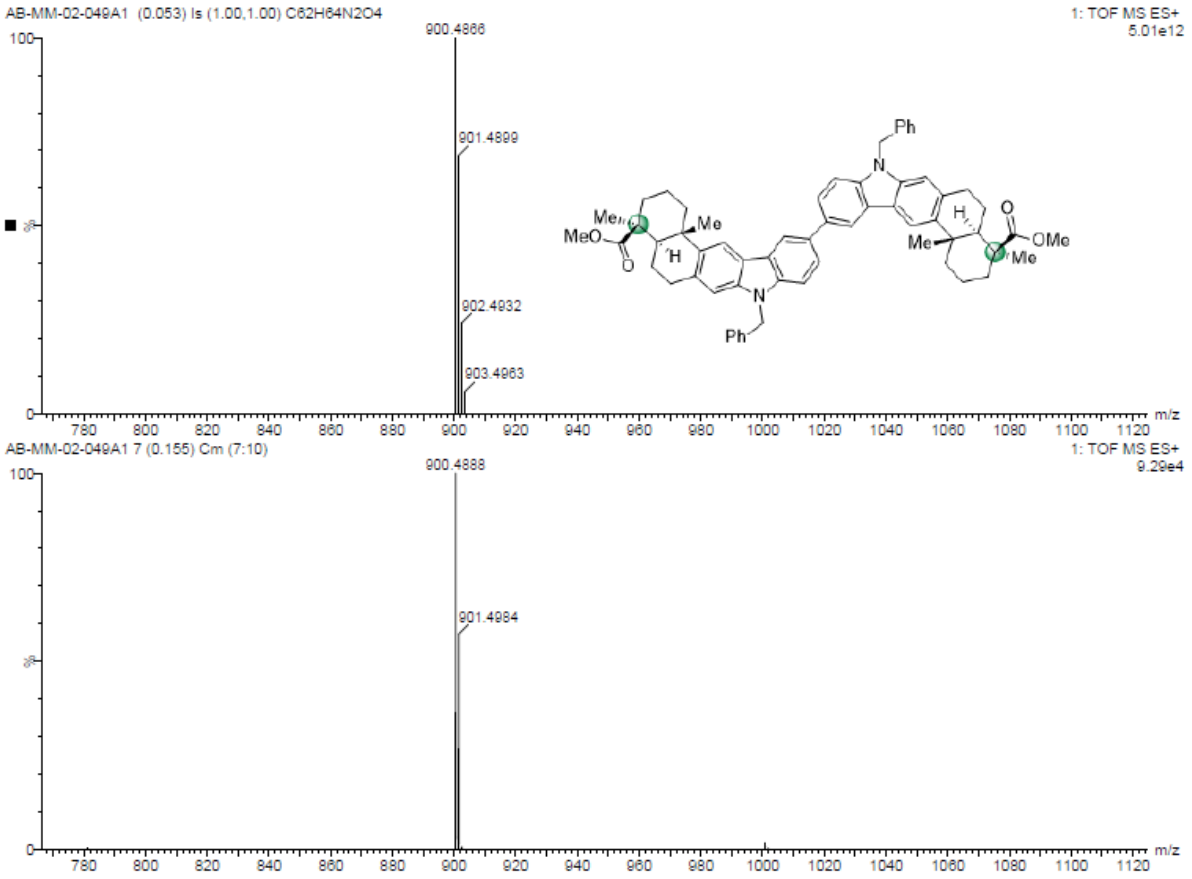




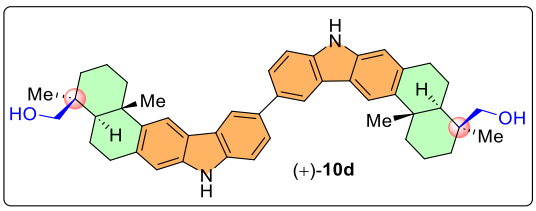
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**10c**

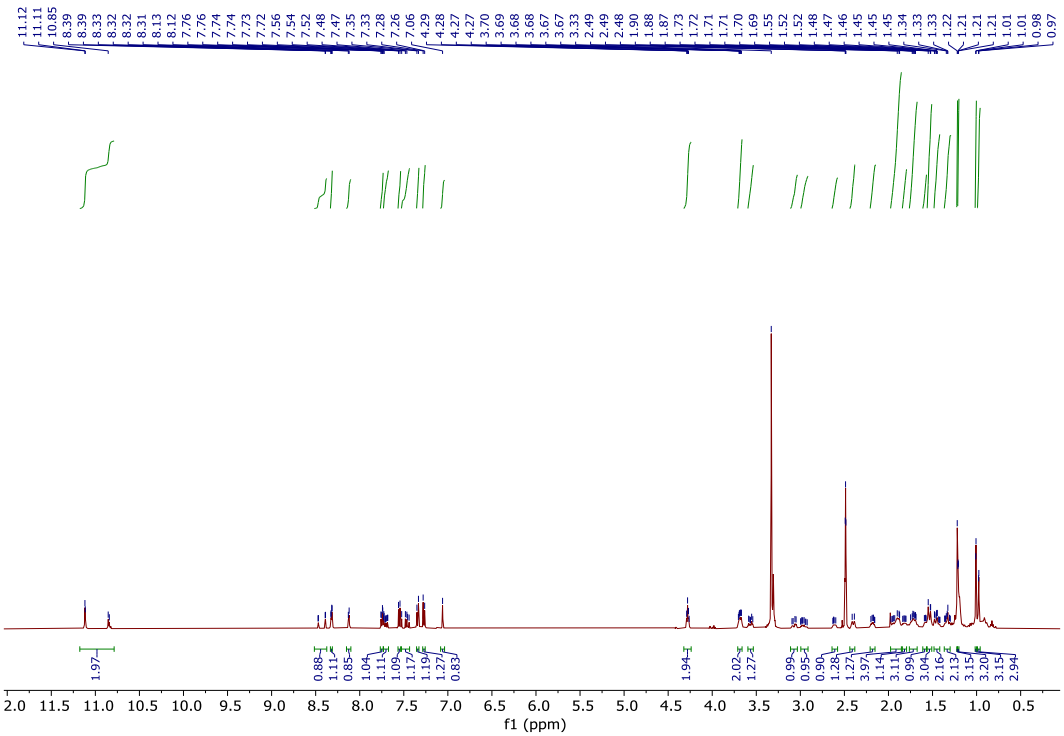


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**10c**

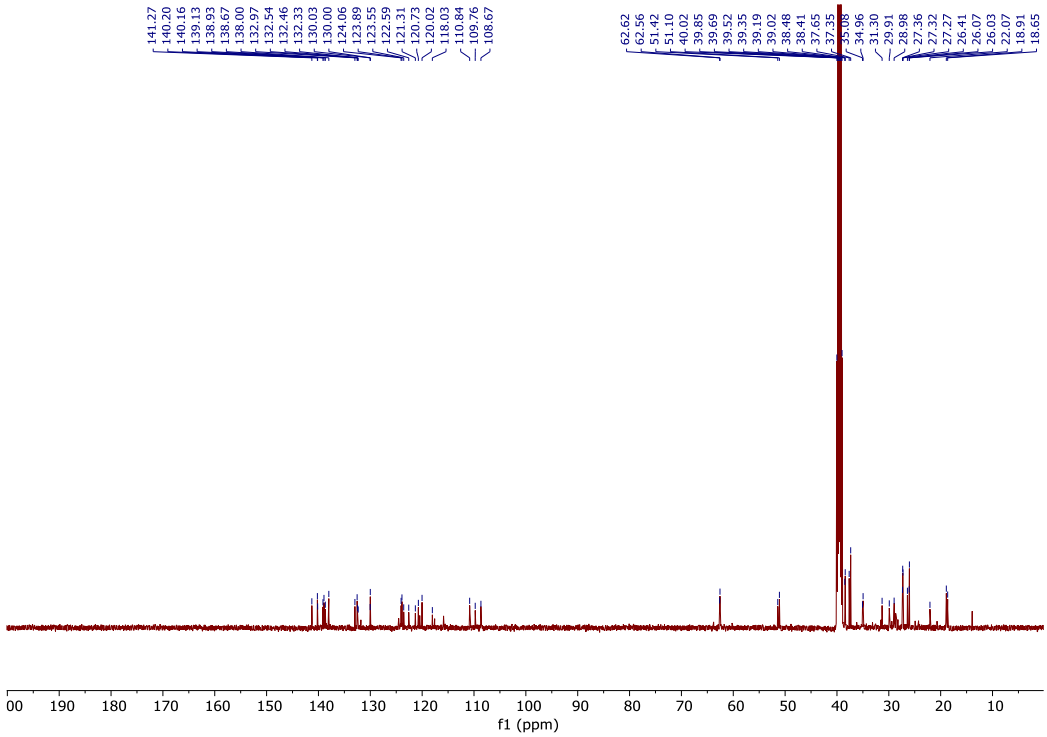


HRMS data of (+)-**10c**

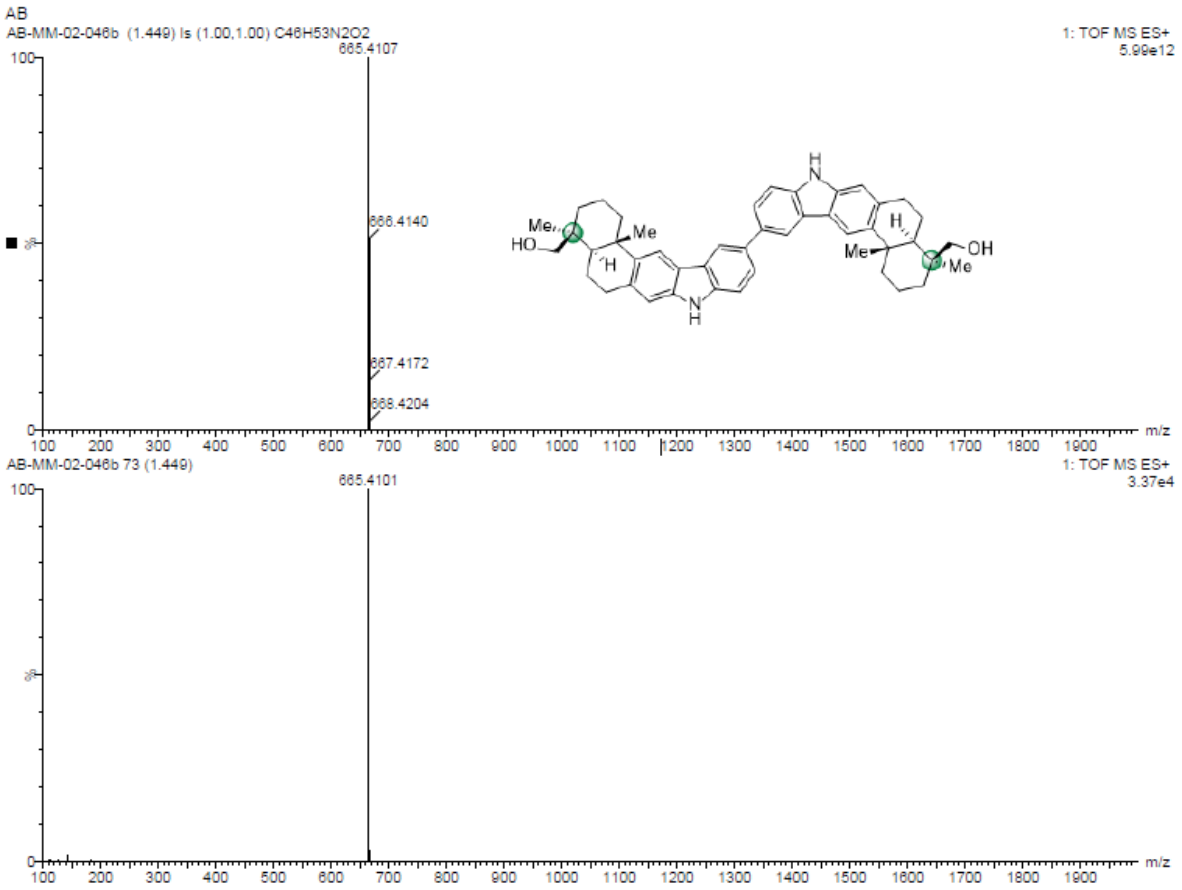




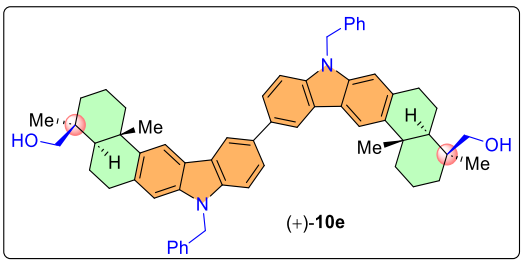
^{1}H NMR (500 MHz, DMSO) of (+)-**10d**

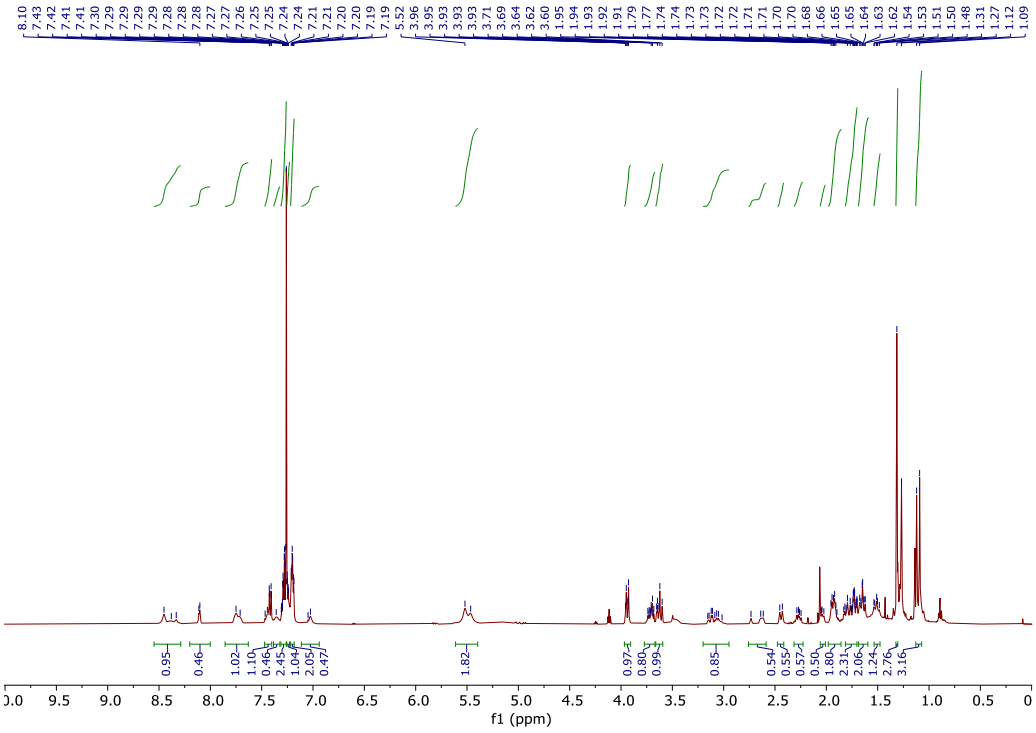


^{13}C NMR (125 MHz, DMSO) of (+)-**10d**

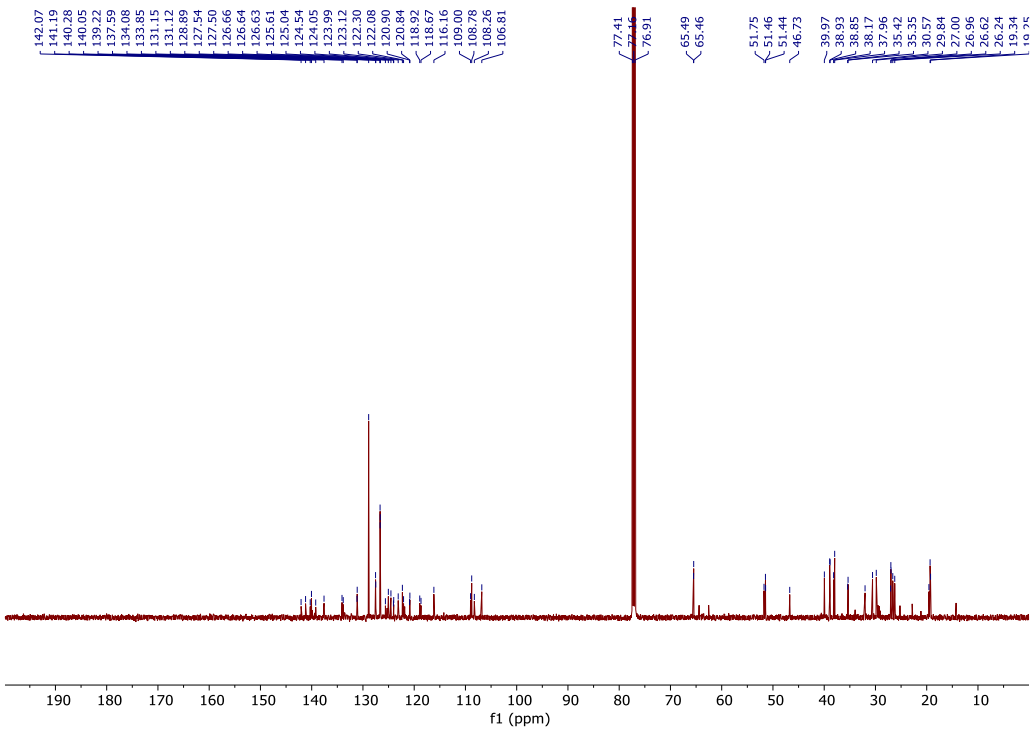


HRMS data of (+)-**10d**

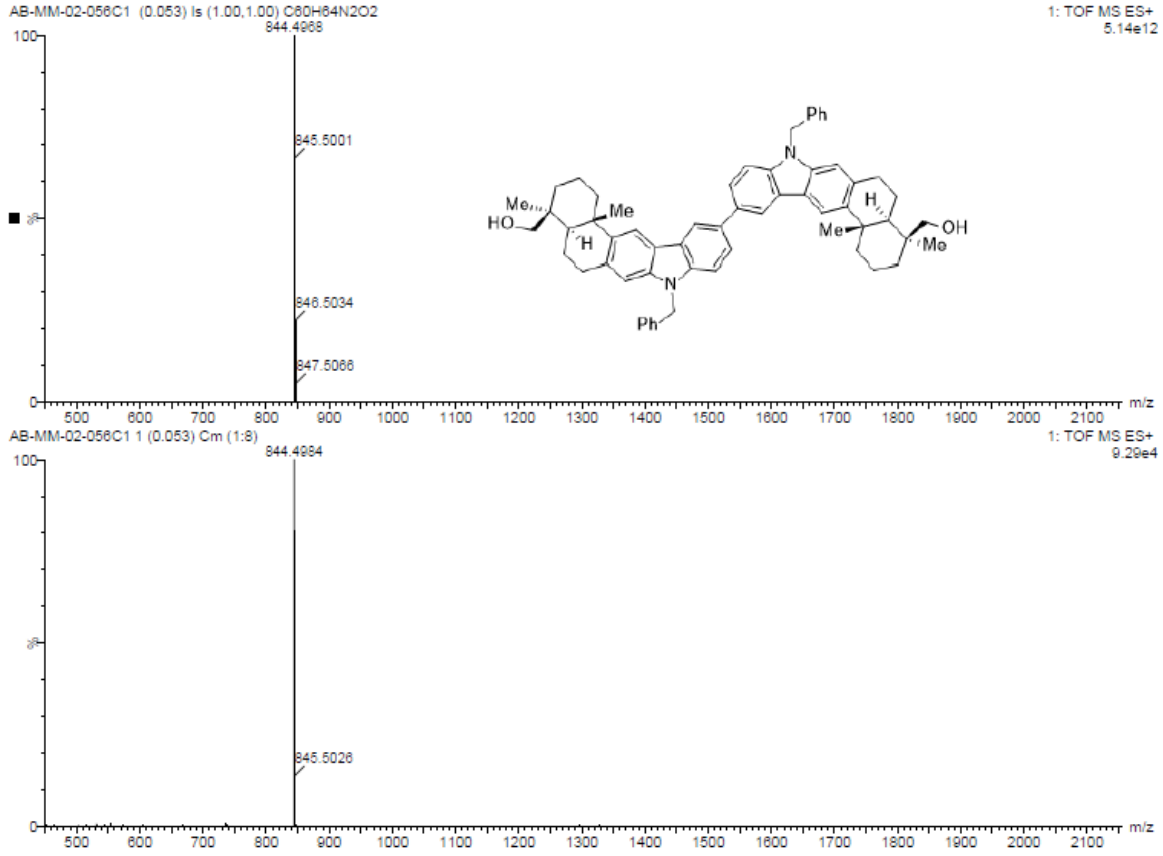




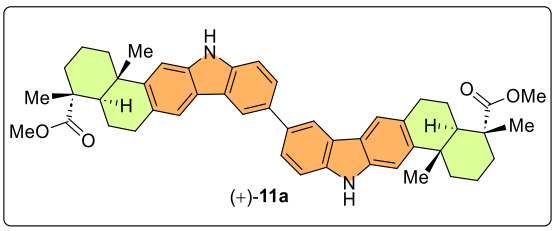
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**10e**

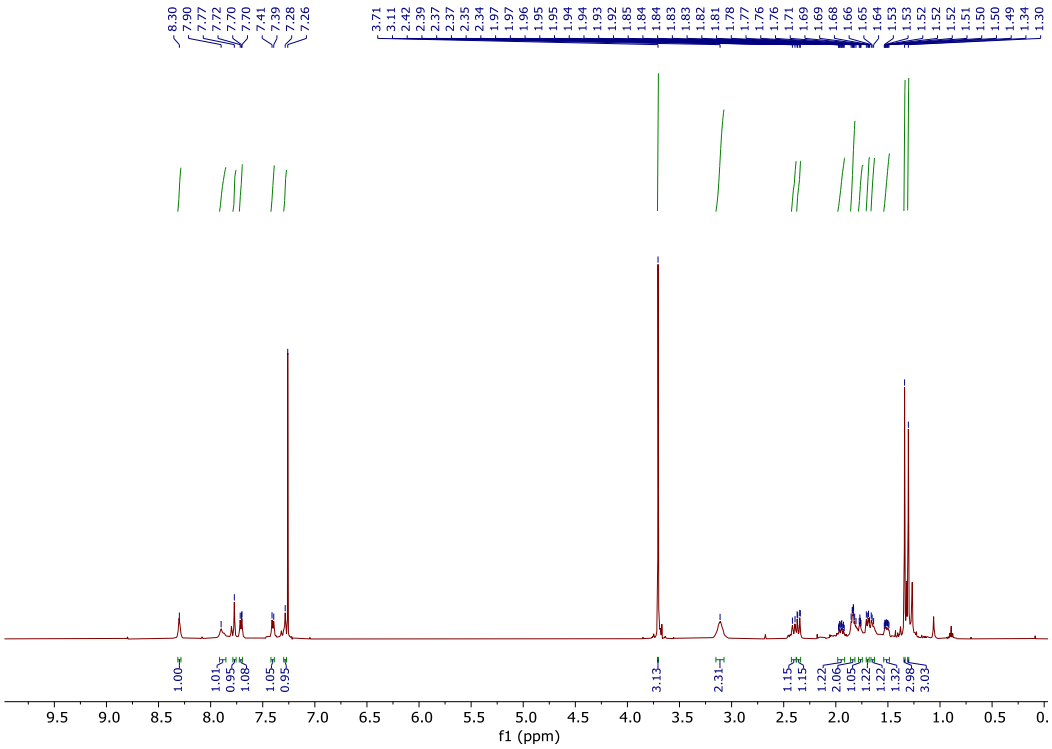


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**10e**

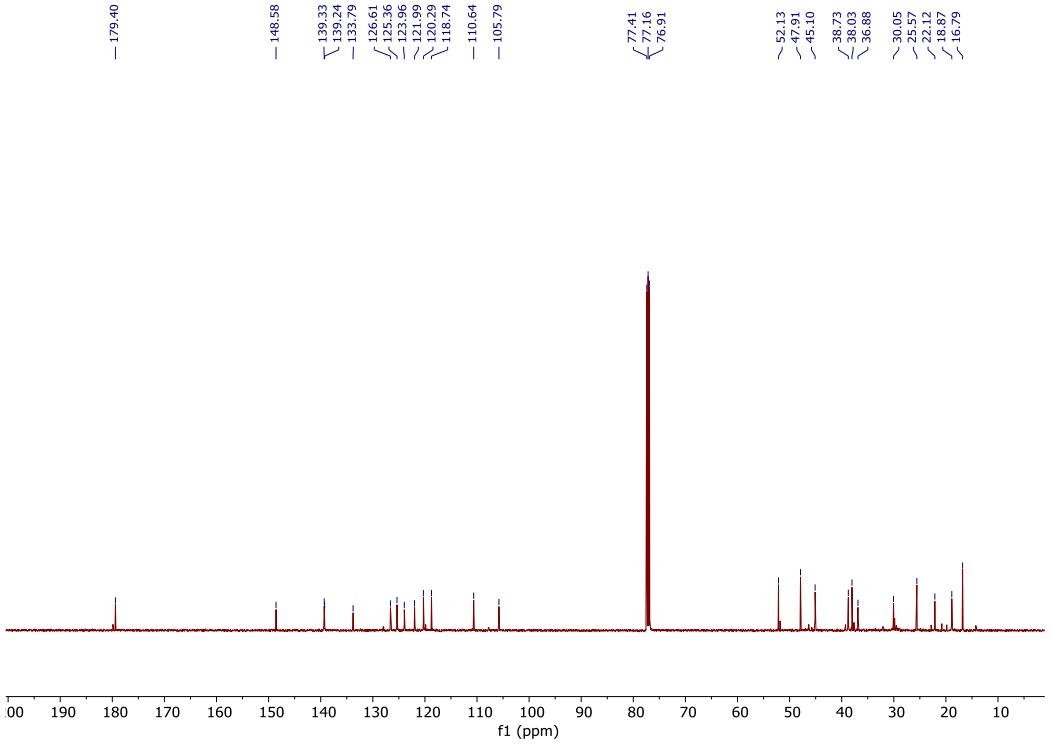


HRMS data of (+)-**10e**

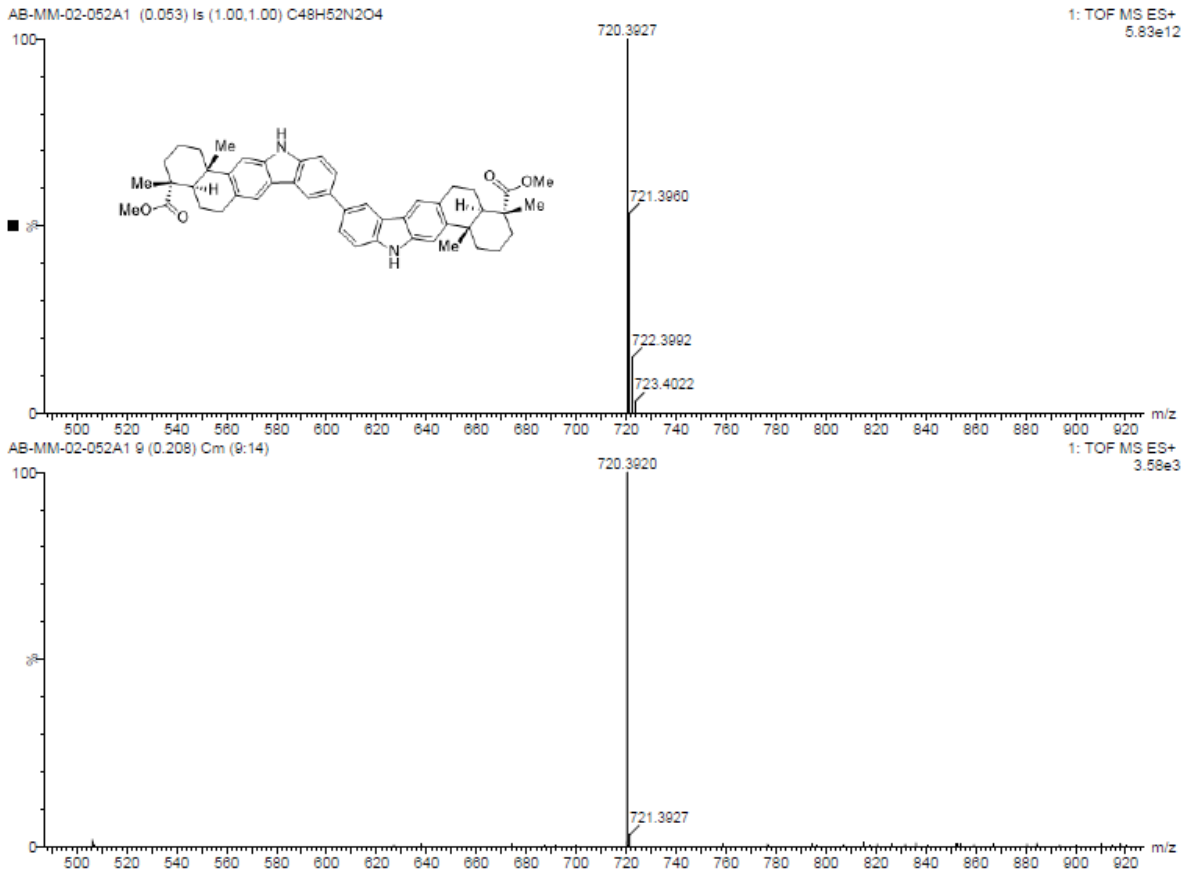




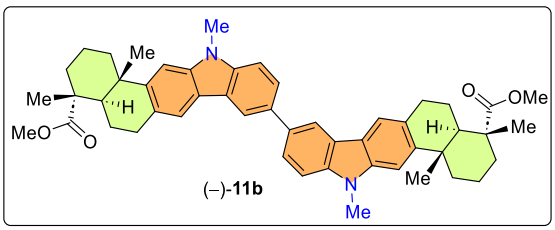
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**11a**

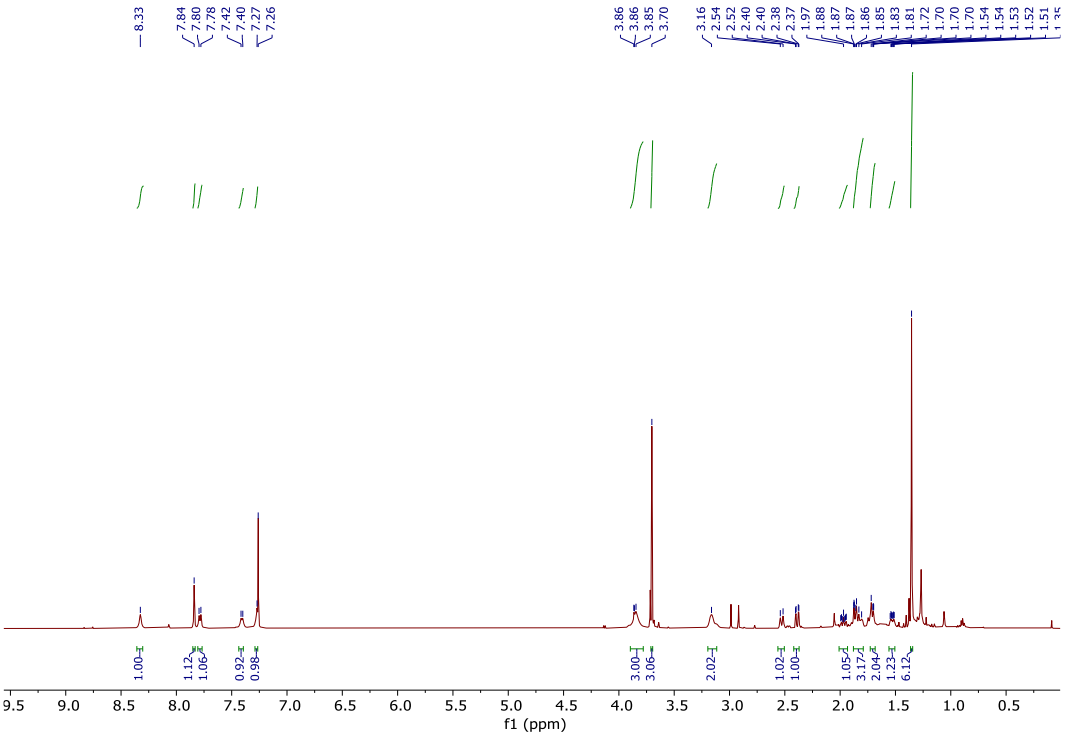


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**11a**

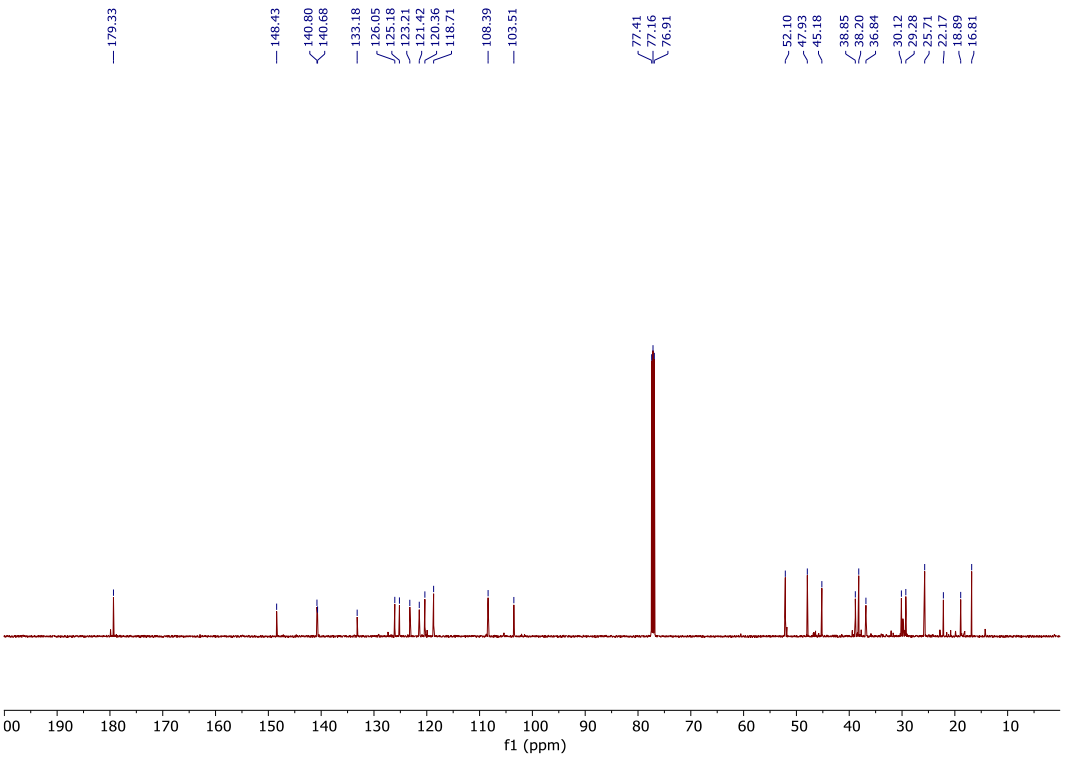


HRMS data of (+)-**11a**

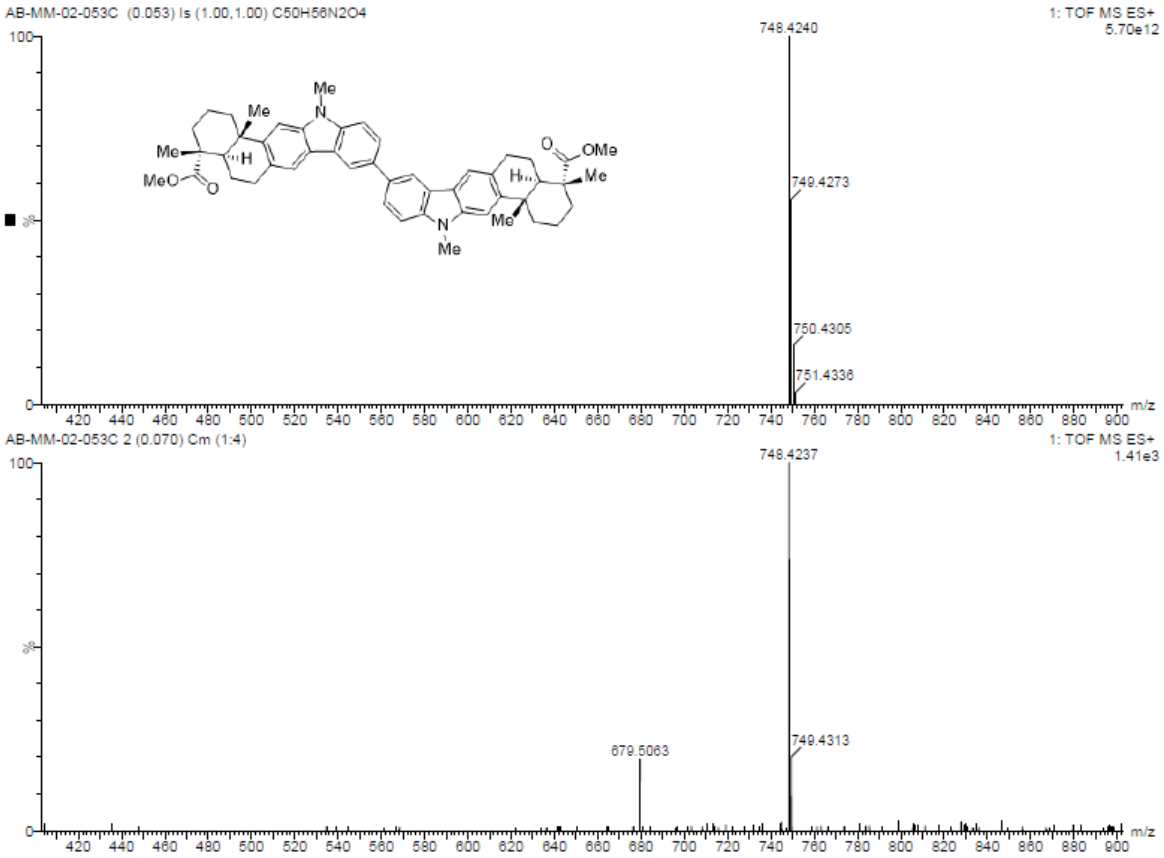




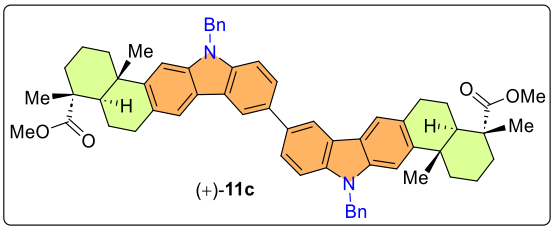
^{1}H NMR (500 MHz, $CDCl_3$) of (–)-**11b**



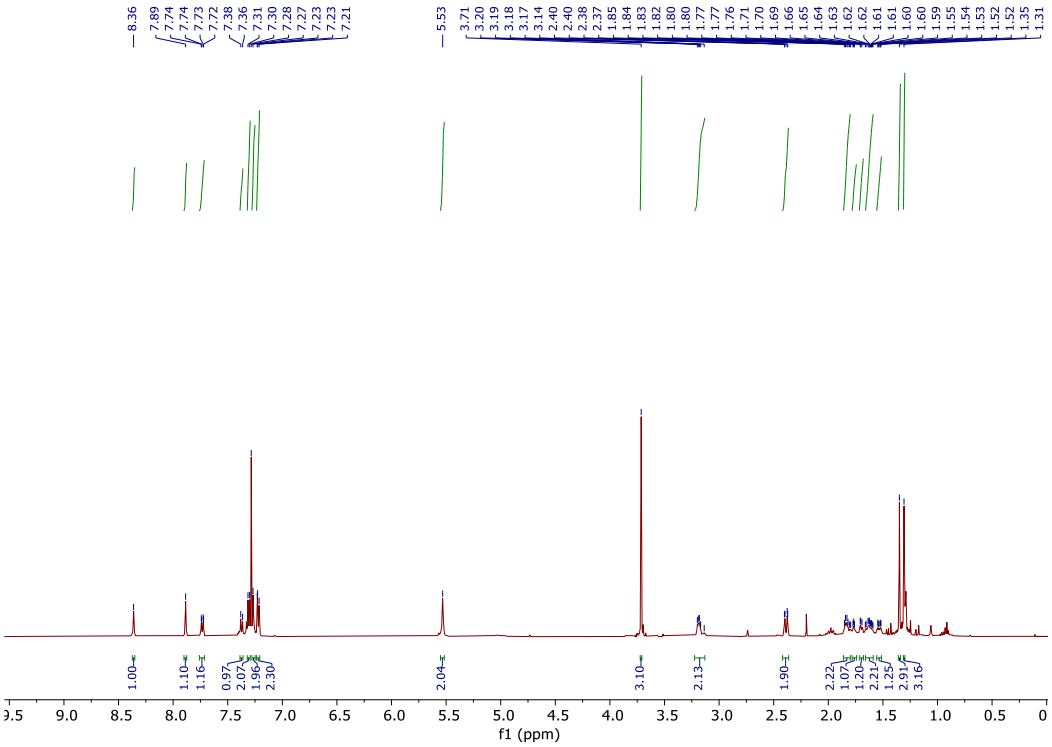
^{13}C NMR (125 MHz, $CDCl_3$) of (–)-**11b**



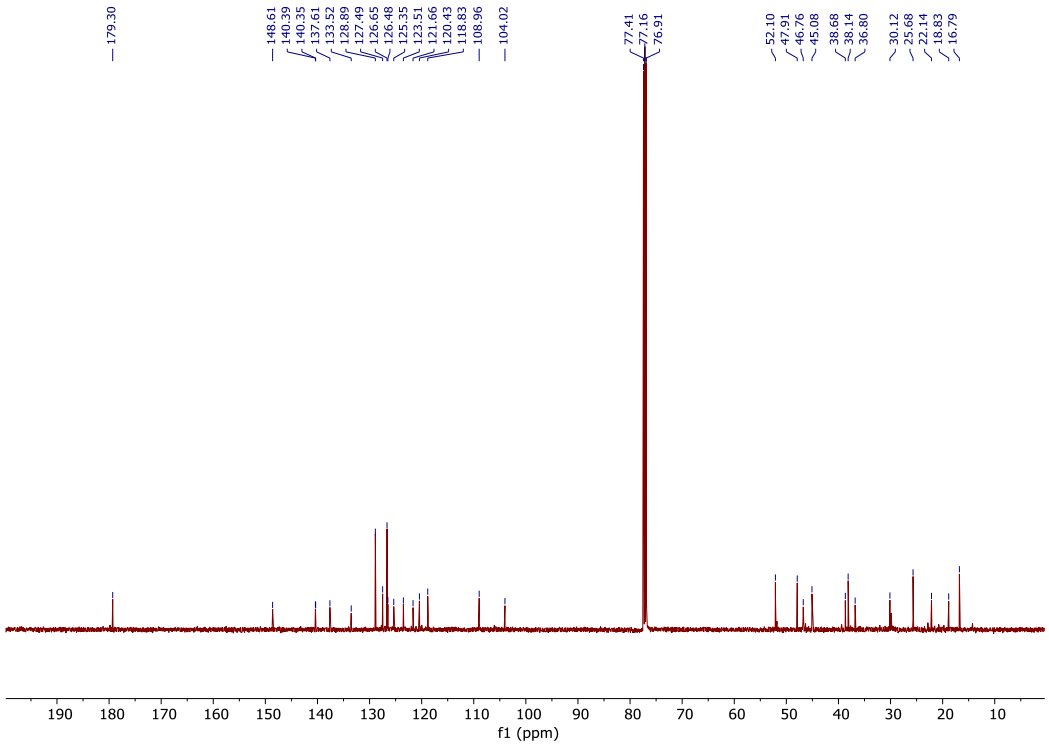
HRMS data of (–)-**11b**



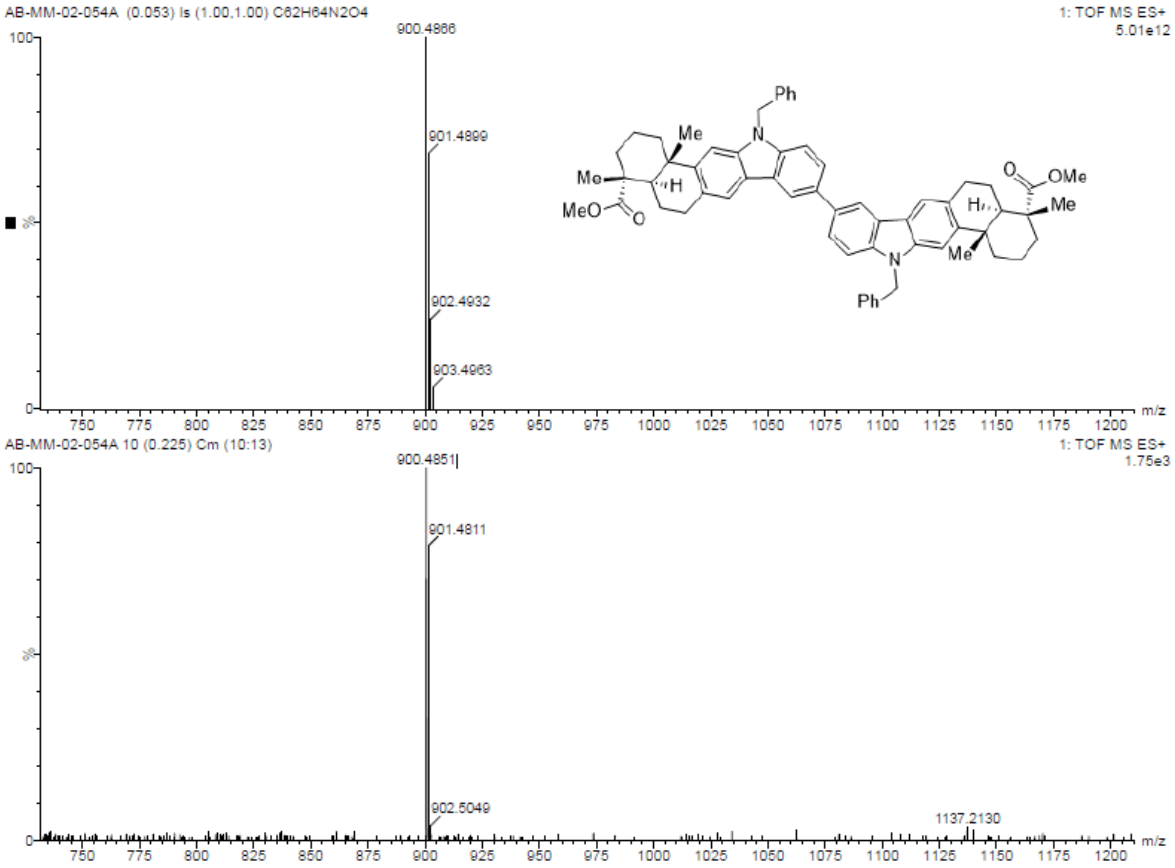
(+)-**11c**



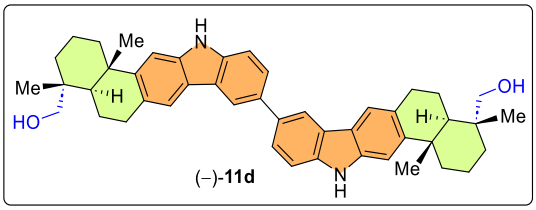
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**11c**



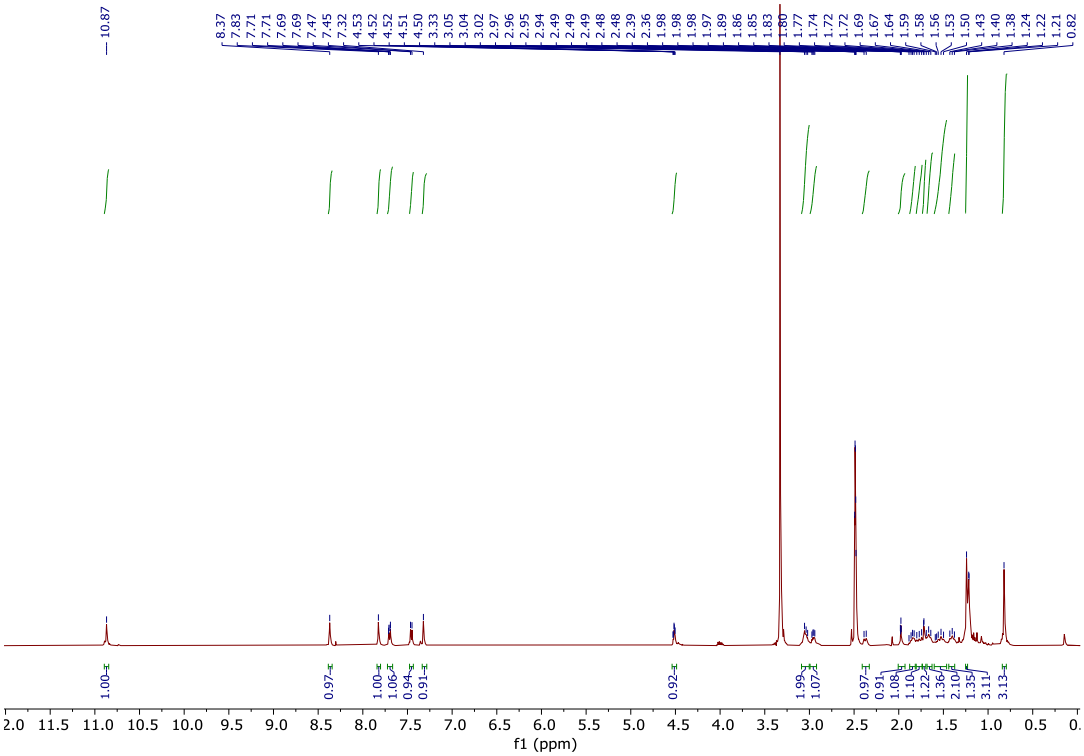
^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**11c**



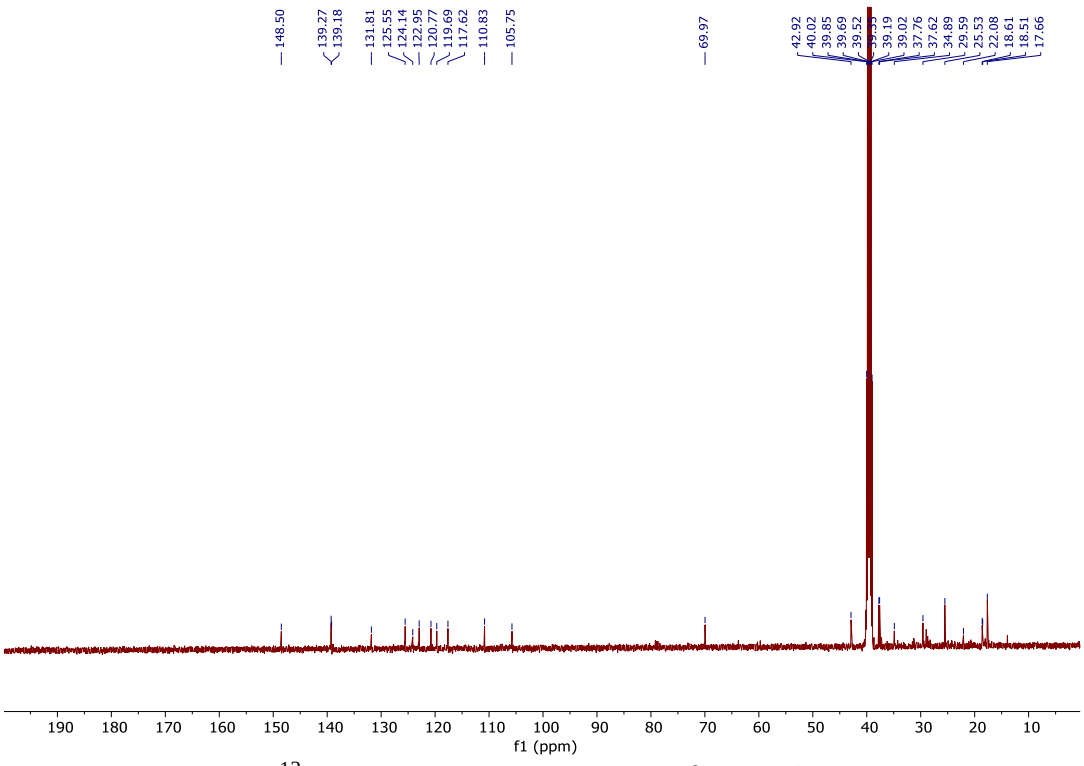
HRMS data of (+)-**11c**



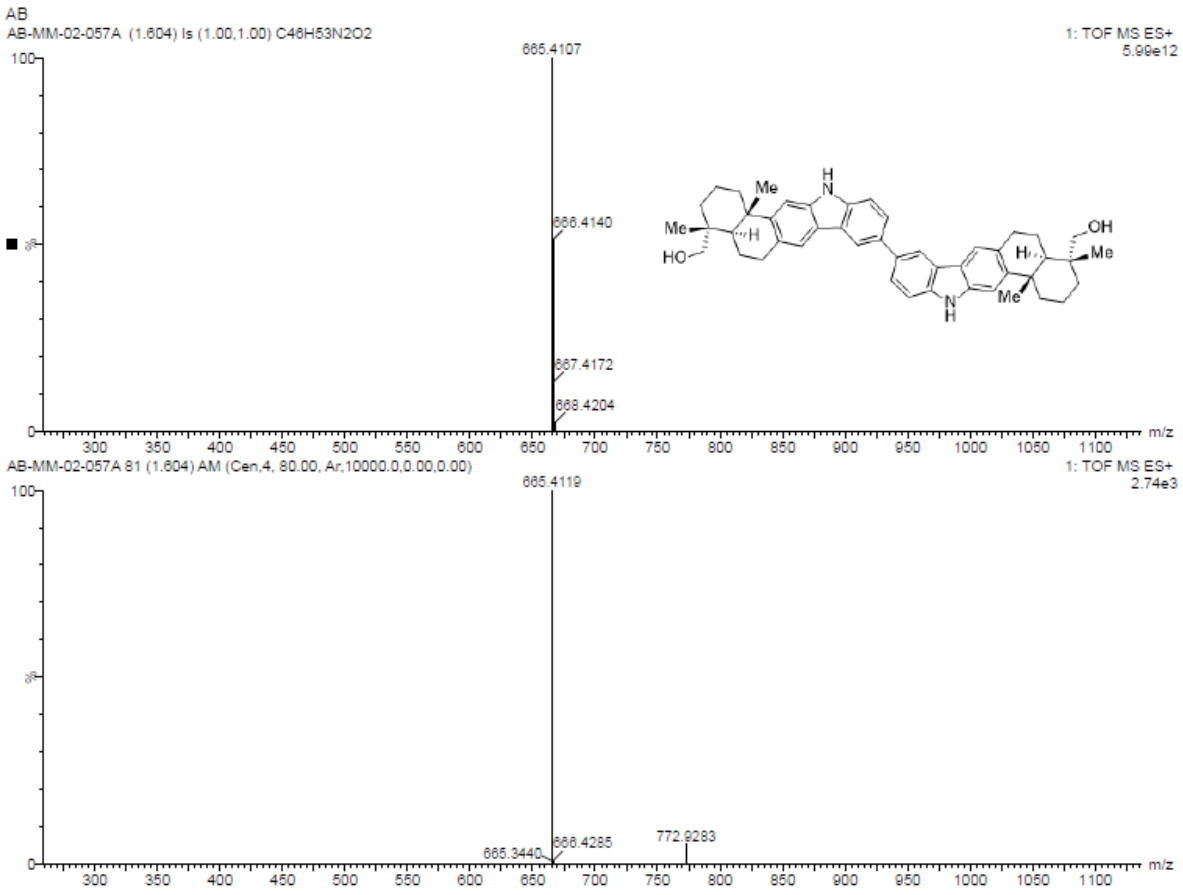
(–)-**11d**



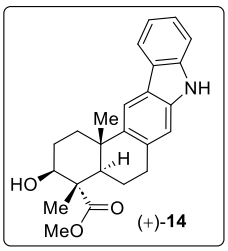
^{1}H NMR (500 MHz, DMSO) of (–)-**11d**

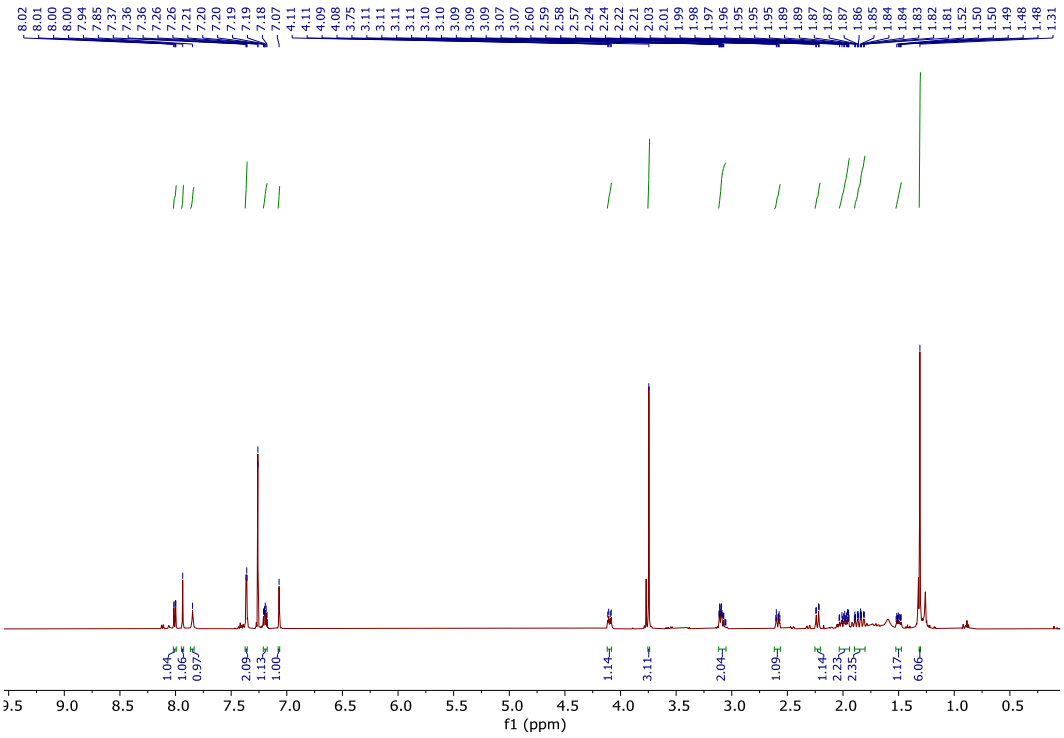


^{13}C NMR (125 MHz, DMSO) of (–)-**11d**

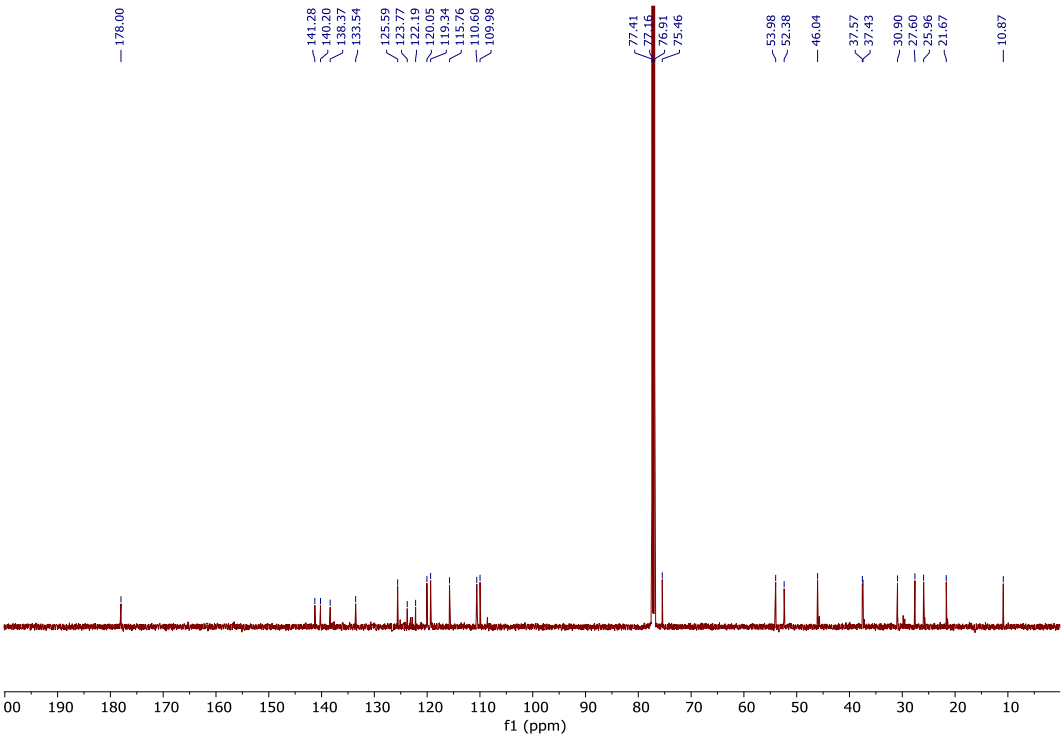


HRMS data of (–)-**11d**

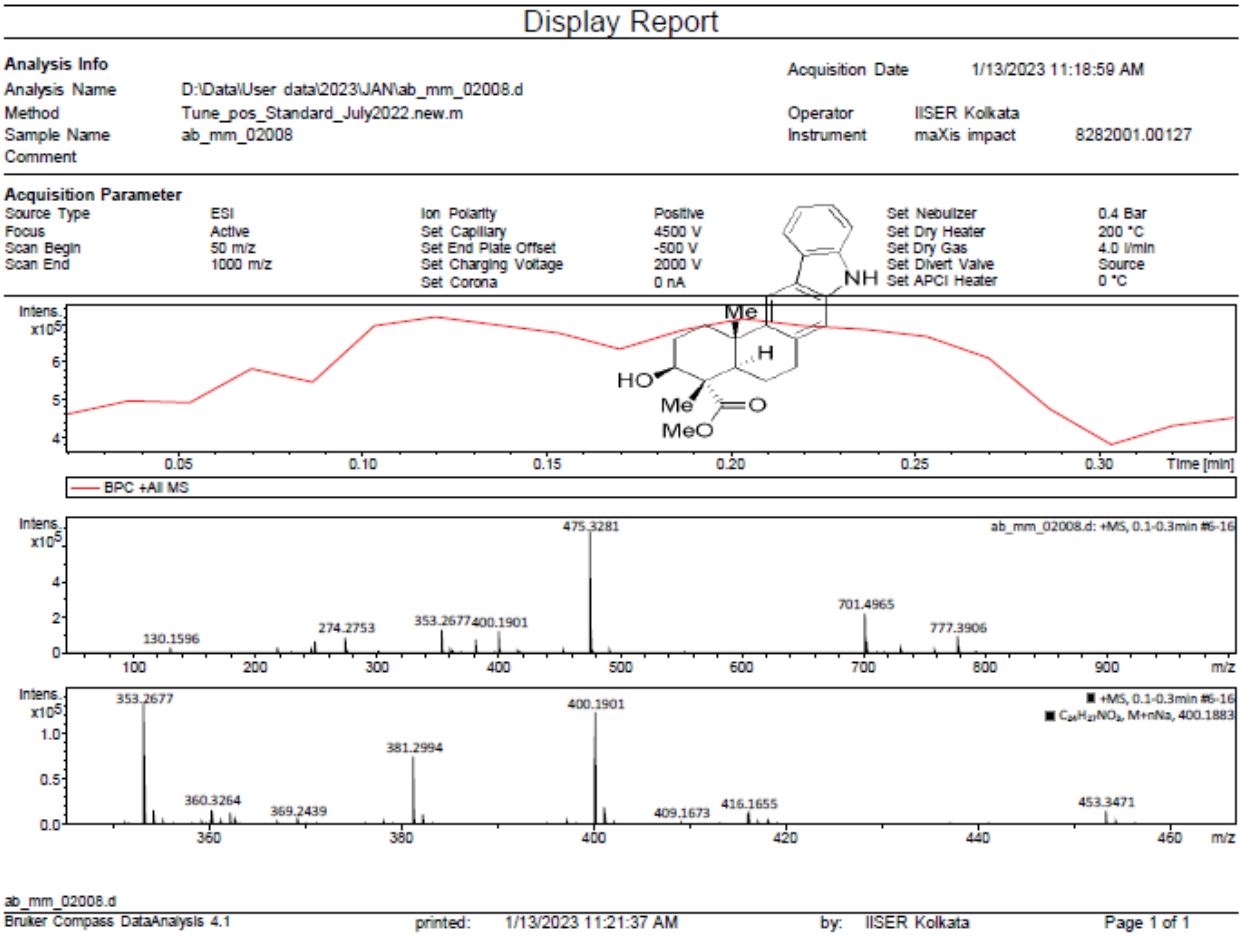




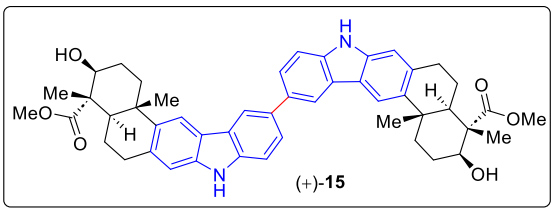
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**14**

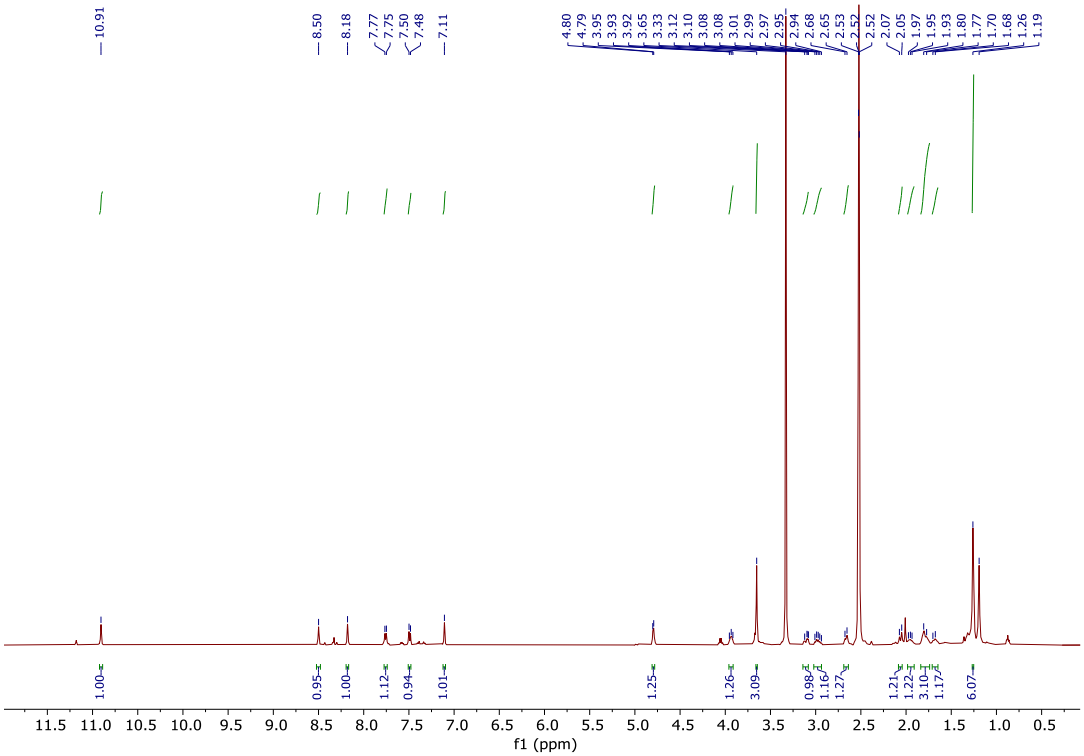


^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**14**

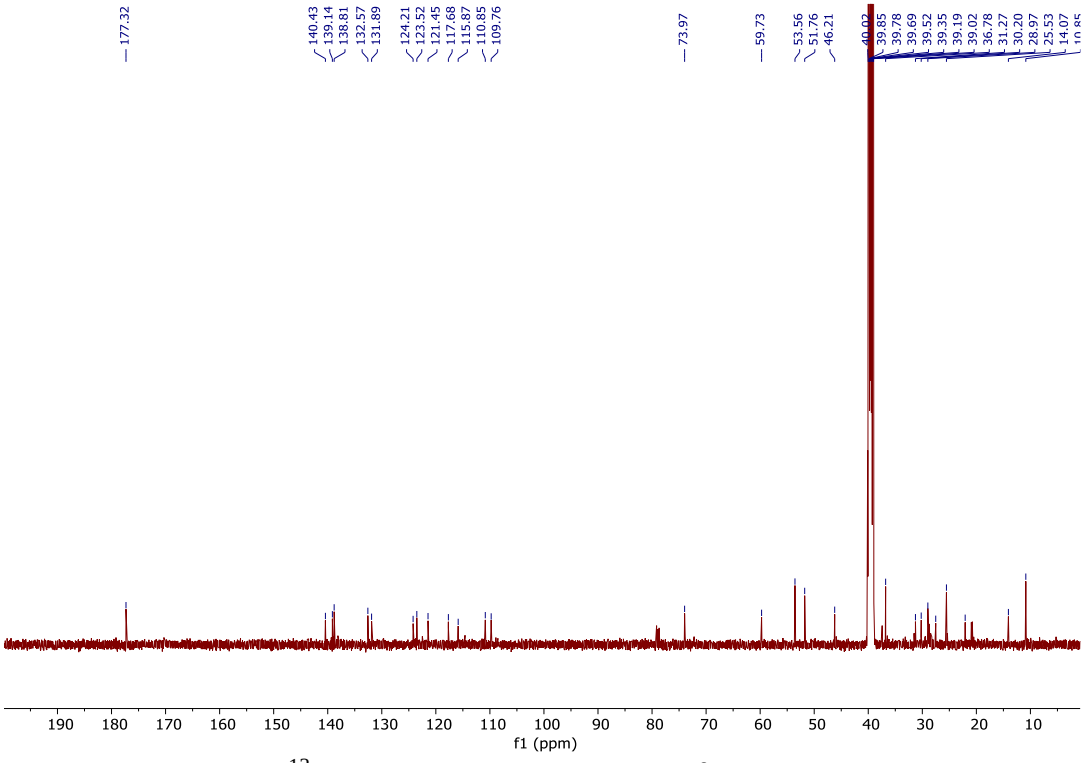


HRMS data of (+)-**14**

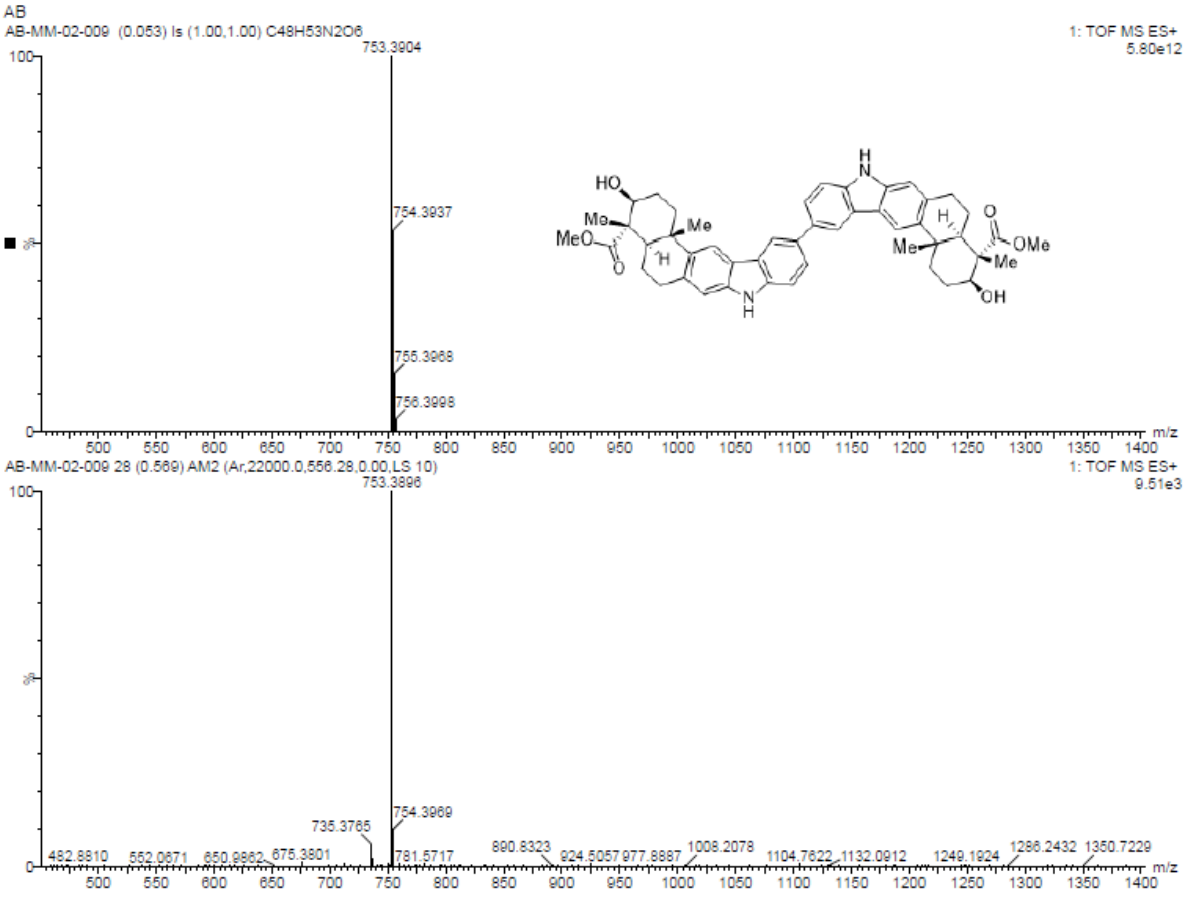




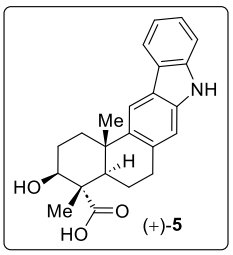
^{1}H NMR (500 MHz, DMSO) of (+)-**15**

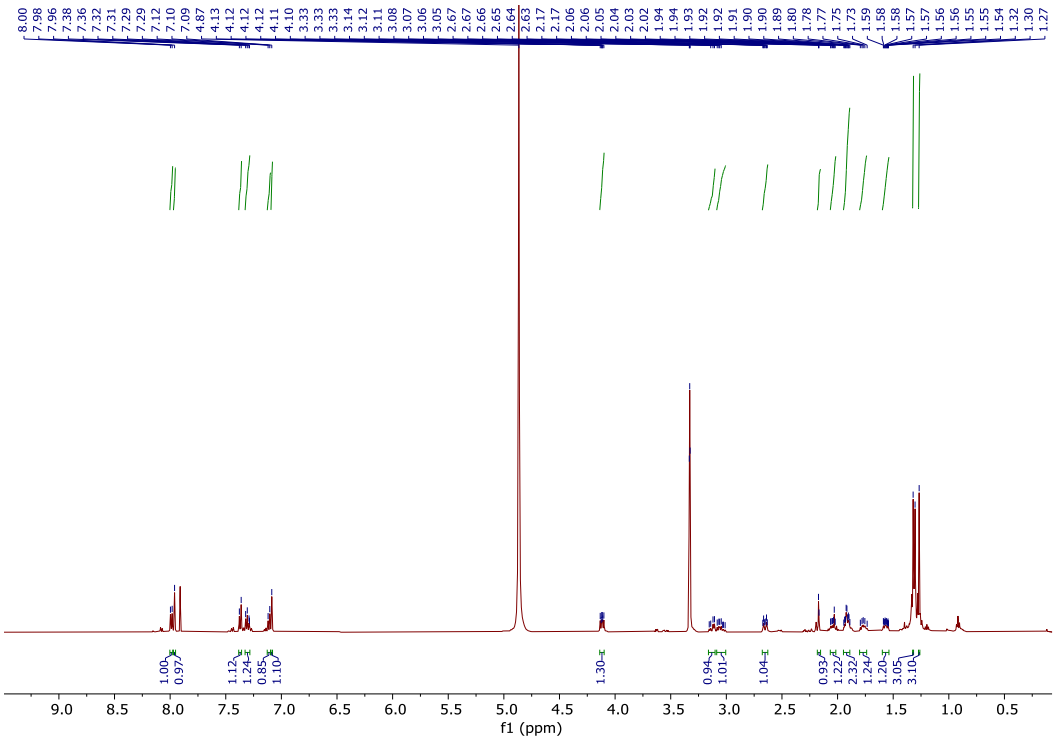


^{13}C NMR (125 MHz, DMSO) of (+)-**15**

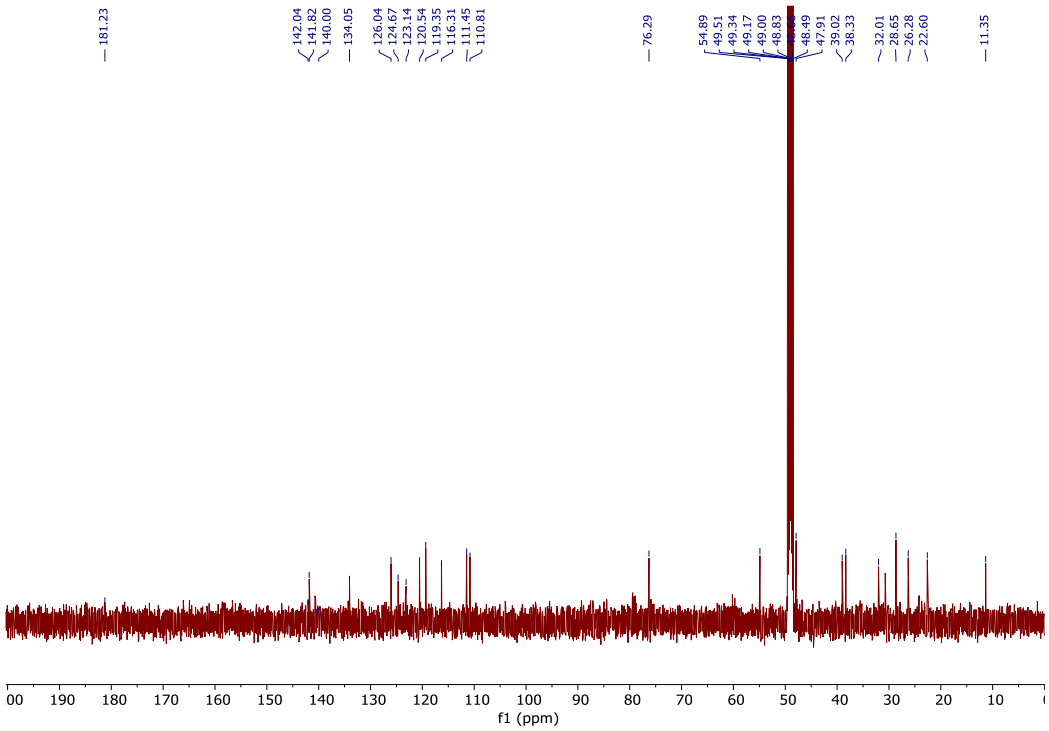


HRMS data of (+)-**15**

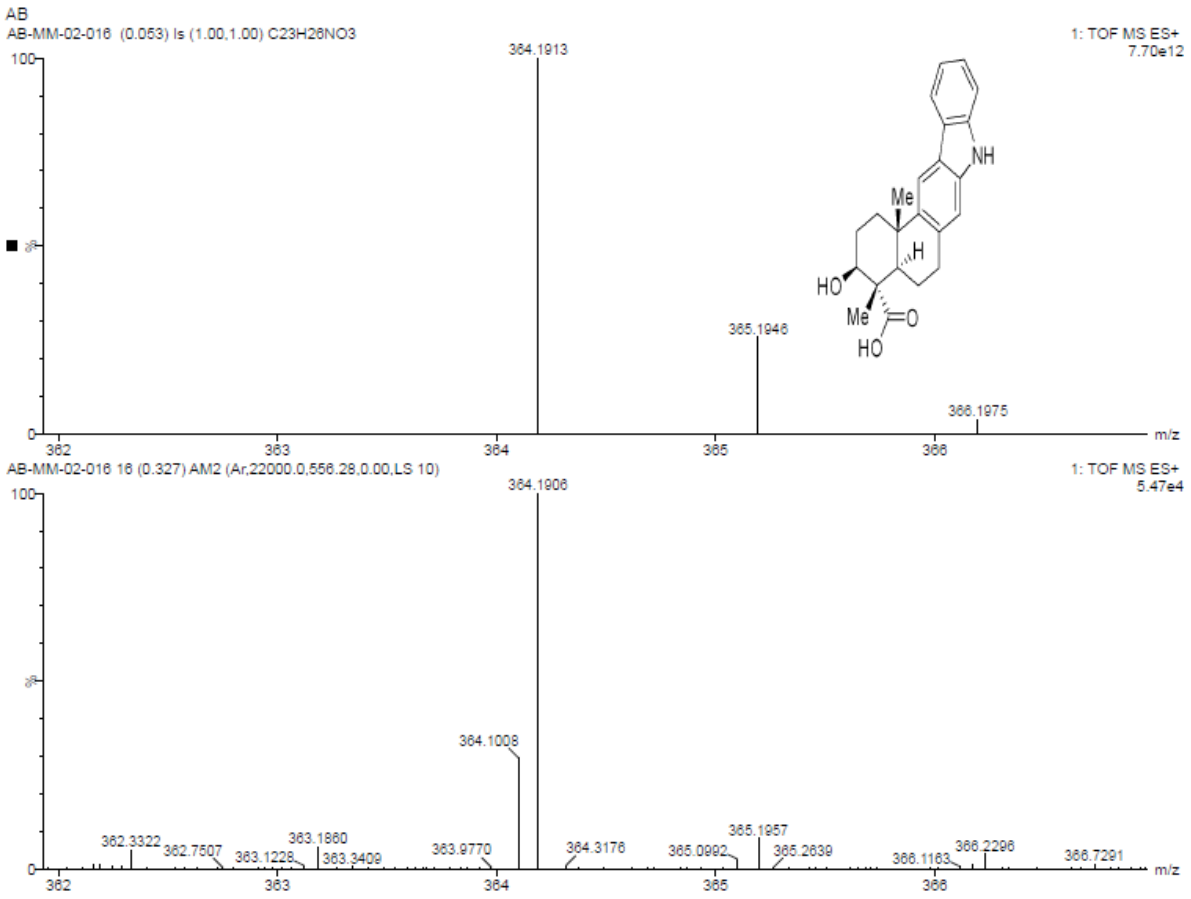




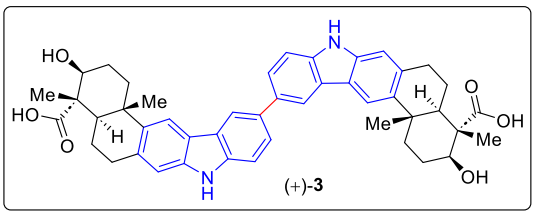
^{1}H NMR (500 MHz, CD_3OD) of (+)-**5**

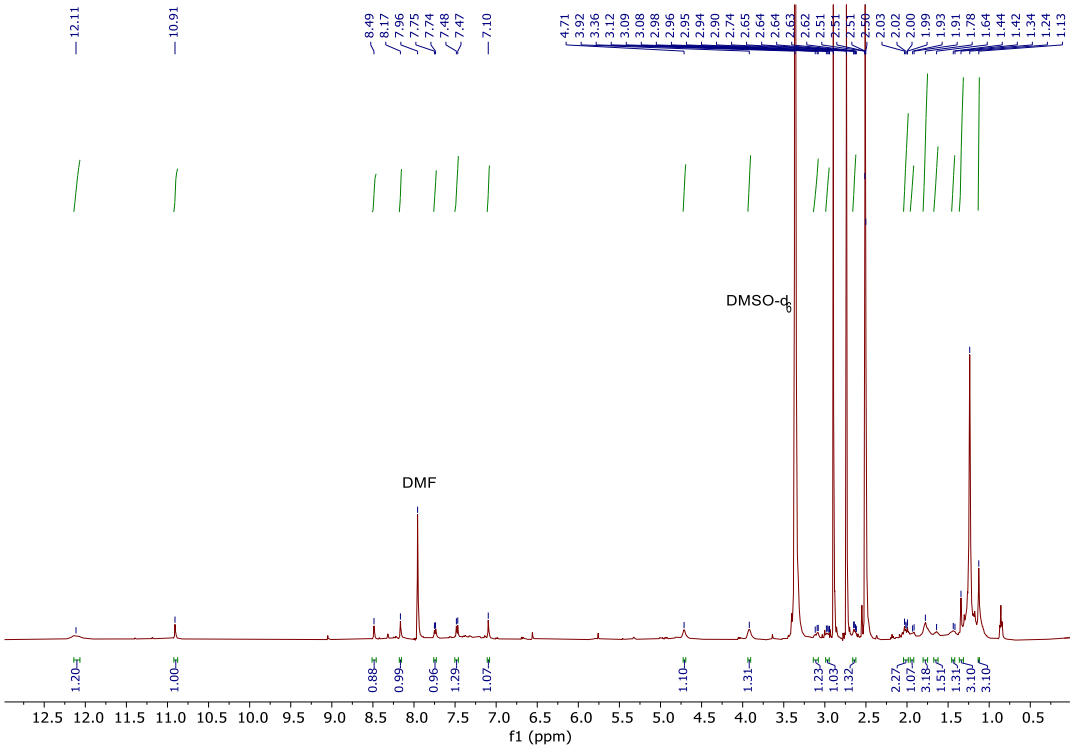


^{13}C NMR (125 MHz, CD_3OD) of (+)-**5**

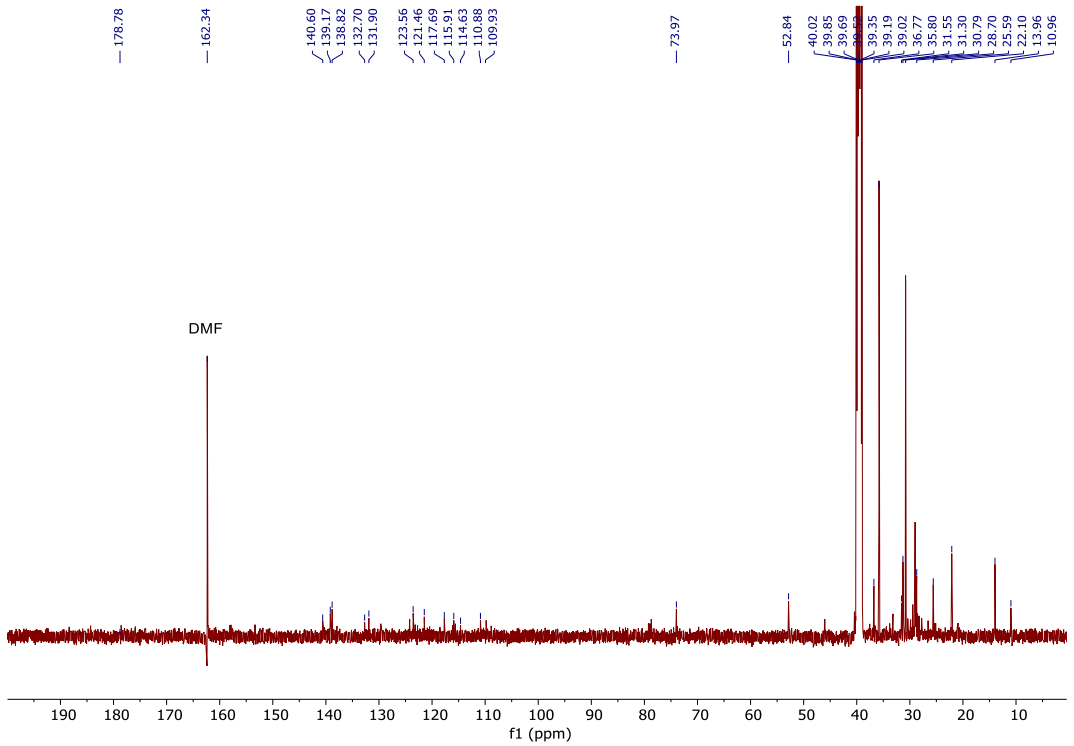


HRMS data of (+)-**5**

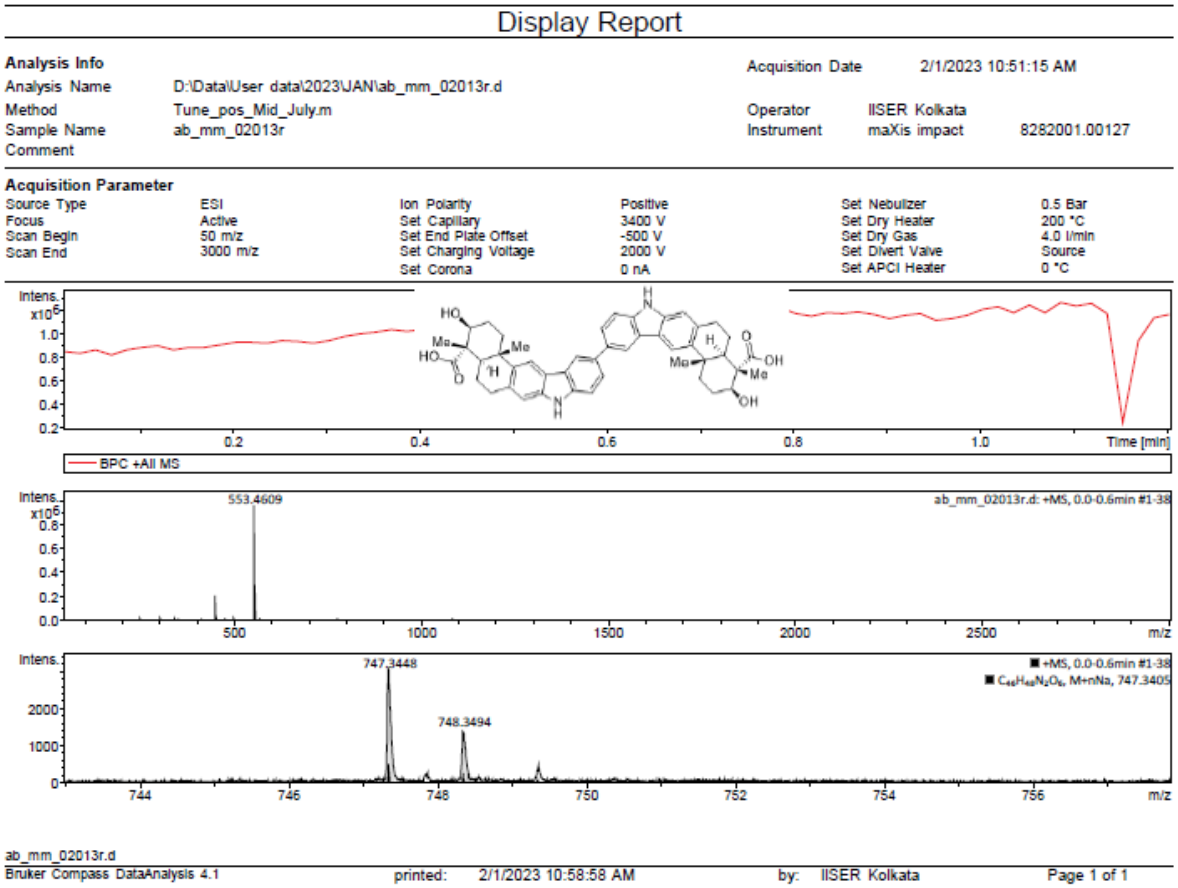




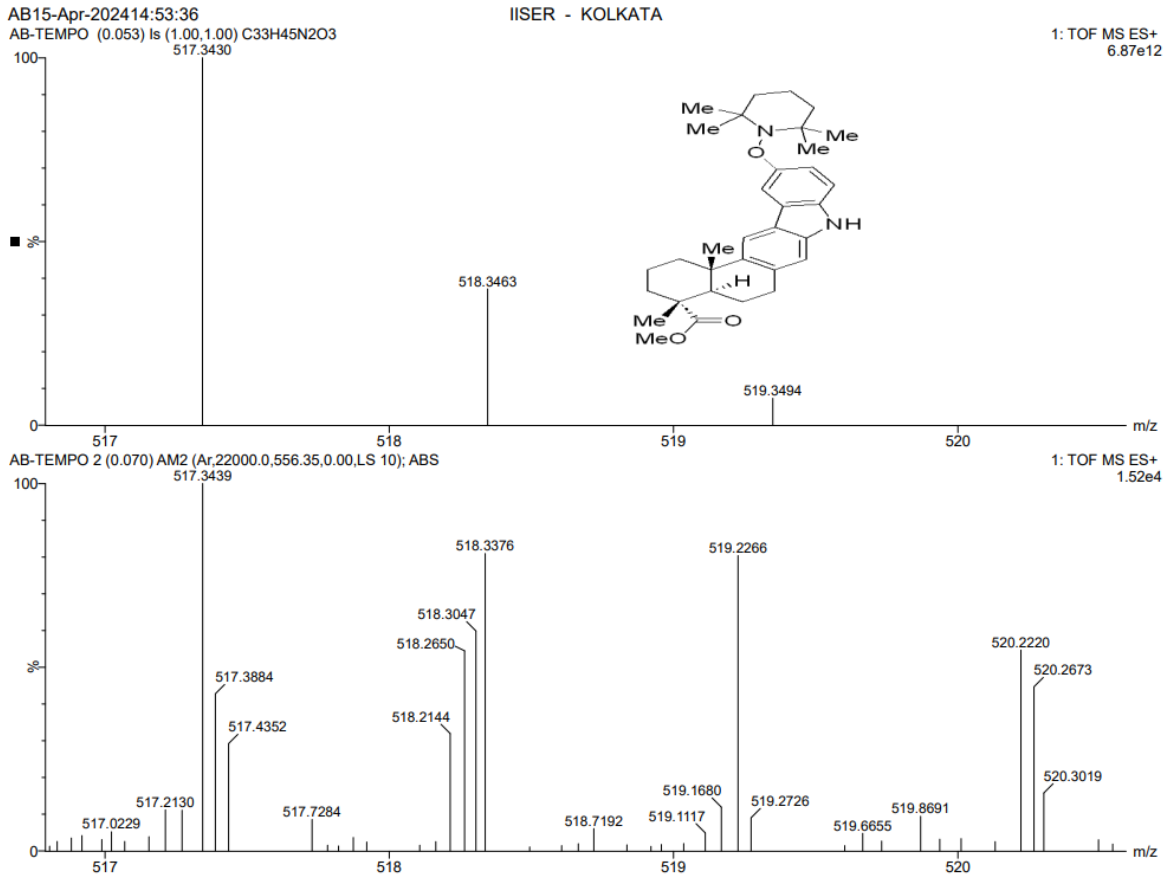
^{1}H NMR (500 MHz, DMSO) of (+)-**3**



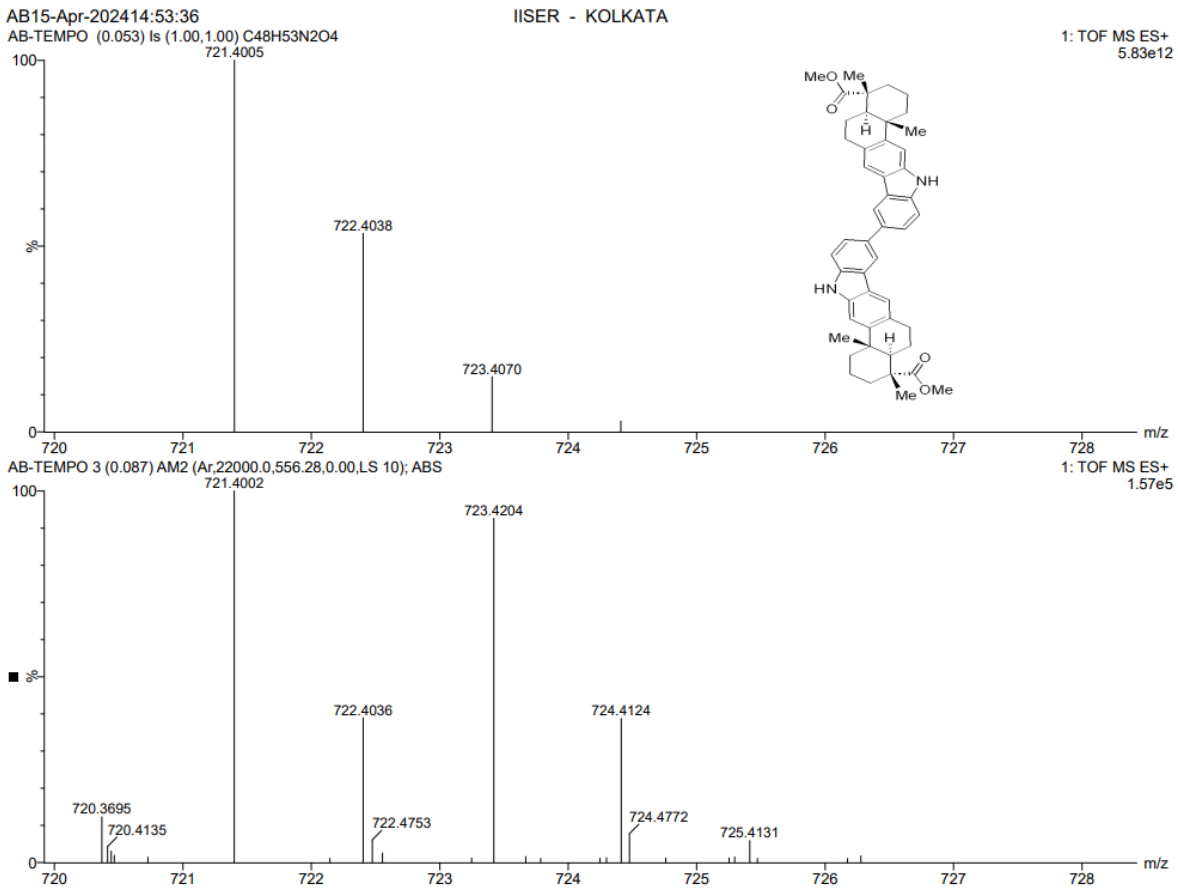
^{13}C NMR (125 MHz, DMSO) of (+)-**3**



HRMS data of (+)-**3**



HRMS data of TEMPO-adduct with deoxy xiamycin A methyl ester



HRMS data of **9a**