Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Concise Asymmetric Total Synthesis of Bruceolline J

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General Information

All the reactions were carried out under nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. Anhydrous THF and diethyl ether were distilled from sodium-benzophenone and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure material, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrin stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography.

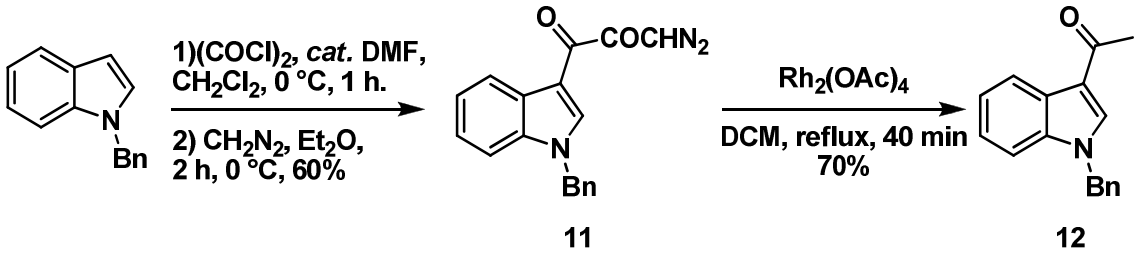
Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Bruker Avance 200 (^{1}H: 200 MHz, ^{13}C: 50MHz), Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100MHz), Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), JEOL ECX 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) Mass spectrometric data were obtained using WATERS-Q-Tof Premier-ESI-MS.

Diastereomeric ratios (dr) were determined by crude ^{1}H NMR.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dm = doublet of a multiplet, m = multiplet, br = broad.

Experimental Procedures and Analytical Data

Synthesis of compound 12

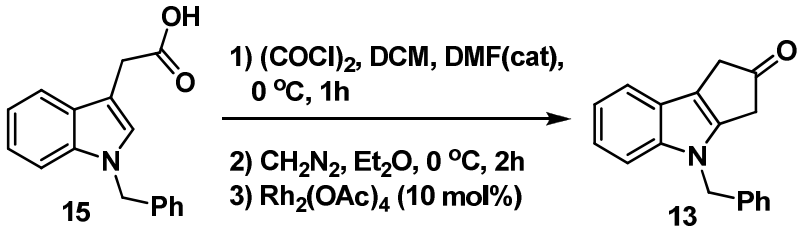


To a cooled solution (0 °C) of 1-benzyl-1*H*-indole (2 g, 7.5 mmol) in dichloromethane (20ml), was added oxalyl chloride (3.2ml, 37.6mmol) slowly, followed by the addition of catalytic amount of DMF. The reaction mixture was stirred at 0 °C for 1 h. Up on the completion of reaction (reaction progress was monitored by TLC by quenching a small portion of the reaction mixture in methanol), solvent was evaporated under reduced pressure at a temperature below 25 °C. The crude product so obtained (**10**) was dissolved in dry diethyl ether (30ml) and cooled to 0 °C. To this, a freshly prepared diazomethane solution in dry diethyl ether (50ml) was added at 0 °C. The reaction mixture was then stirred for 2 h at the same temperature. Upon completion of the reaction, solvent was removed under reduced pressure at a temperature below 25 °C to get a dark green colored crude product which was passed through a column of neutral alumina using DCM (100ml). Solvent was evaporated under reduced pressure at a temperature below 25 °C to get diazoketone (**11**) as a yellow colored oily product (1.3g, 60%).

In a two neck oven dried round bottom flask, $Rh_2(OAc)_4$ (20mg, 10mol%) was dissolved in DCM and heated to reflux. A solution of diazoketone (**11**) (1.3g, 4.4mmol) in DCM was added

very slowly over a period of 45 min. The reaction mixture was stirred at reflux temperature for 1 h and cooled to room temperature. Reaction was quenched by adding ice cold water. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to get a crude product. The residue was purified by flash chromatography (EtOAc-hexane 1:9) to get **12** as a pale yellow oil (0.82 g, 70%); R_f = 0.4 (EtOAc-hexane 1:9); **IR** (thin film): ν_{max}/cm^{-1} 2923, 1726, 1640, 1518, 1465, 1389, 1278, 1169, 1140, 1058, 746, 696; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.46 (s, 1 H), 7.24 - 7.52 (m, 7 H), 7.19 (dd, *J* = 7.6, 1.8 Hz, 2 H), 5.40 (s, 2 H), 3.95 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 177.1, 163.4, 139.9, 137.0, 135.3, 129.6, 129.4, 129.3, 129.3, 129.2, 128.5, 127.4, 127.1, 124.4, 123.8, 123.0, 113.4, 110.6, 52.8, 51.3; **HRMS-ESI**: m/z calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1232; found: 250.1233.

Synthesis of compound 13

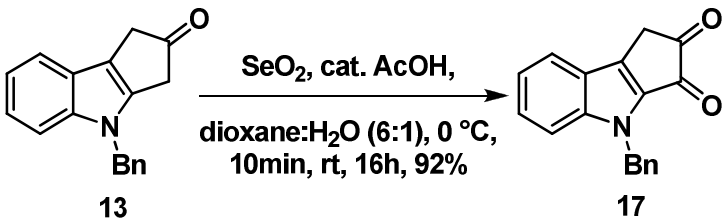


To a cooled solution (0 °C) of **15** (2 g, 7.5 mmol) in dichloromethane (20ml), was added oxalyl chloride (3.2ml, 37.6mmol) slowly, followed by the addition of catalytic amount of DMF. The reaction mixture was stirred at 0 °C for 1 h. Up on completion the of reaction (reaction progress was monitored by TLC), solvent was evaporated under reduced pressure at a temperature below 25 °C. The crude product so obtained was dissolved in dry diethyl ether (30ml) and cooled to 0 °C. To this, a freshly prepared diazomethane solution in dry diethyl ether (50ml) was added at 0 °C. The reaction mixture was then stirred for 2 h at the same temperature. Upon completion of the reaction, solvent was removed under reduced pressure at a temperature below 25 °C to get a

dark green colored crude product which was passed through a column of neutral alumina using DCM (100ml). Solvent was evaporated under reduced pressure at a temperature below 25 °C to get an yellow colored oily product (**14**) (1.3g, 60%).

In a two neck round bottom flask, $Rh_2(OAc)_4$ (20mg, 10mol%) was dissolved in DCM and heated to reflux. A solution of diazoketone (1.3g, 4.4mmol) in DCM was added very slowly over a period of 45 min. The reaction mixture was stirred at reflux temperature for 1 h and was then washed with brine. The organic phase was dried over Na_2SO_4, filtered and concentrated to get a crude product. The residue was purified by flash chromatography (EtOAc-hexane 1:9) to get **13** as a white amorphous powder (0.956g, 78%); R_f = 0.4 (EtOAc-hexane 1:9); **Mp** = 110−115 °C; **IR** (thin film): ν_{max}/cm^{-1} 1743, 1453, 1345, 1107, 733, 697, 673; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.08-7.35 (m, 8H), 5.27 (s, 2H), 3.55 (s, 2H), 3.36 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 213.9, 139.0, 138.8, 137.2, 129.0, 127.9, 126.8, 124.7, 121.8, 120.1, 119.2, 112.5, 110.2, 48.8, 39.9, 38.8; **HRMS-ESI**: m/z calcd for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1232; found: 262.1232.

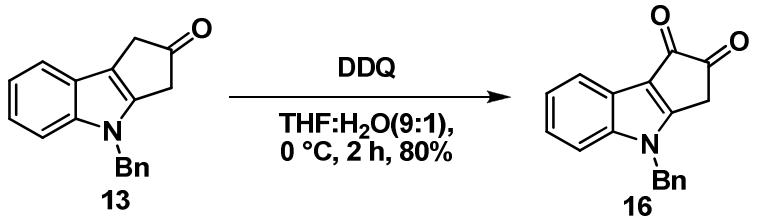
Synthesis of compound 17



Compound **13** was dissolved in dioxane: H_2O (1:6) and cooled to 0 ^oC. After stirring at 0 ^oC for 5 min., solid selenium dioxide was added in one portion followed by the addition of catalytic amount of glacial acetic acid and stirred for 10 min. at 0 ^oC to furnish a dark greenish

suspension. The reaction mixture was then warmed to room temperature and continued stirring for 16 h. Upon the completion of starting material as noticed in TLC, the reaction mixture was passed through celite bed, washed with ethyl acetate. After evaporating the solvent completely, the crude compound was dissolved in ethyl acetate, washed first with water then with brine. The organic portion was dried over Na_2SO_4, filtered and evaporated to get a dark green colored residue which was purified by flash chromatography (EtOAc-hexane 1:4) to get shiny yellow crystals of **17** (115 mg, 92%); R_f = 0.5 (EtOAc : hexane (1:4)); **Mp** = 190 °C ; **IR** (thin film): ν_{max}/cm^{-1} 1760, 1699, 1611, 1512, 1496, 1450, 1433, 1409, 1386, 1269, 1172, 1013, 991, 749, 730, 704, 640, 546, 445, 410; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.73 (d, *J* = 8.0 Hz, 1 H), 7.45 - 7.61 (m, 1 H), 7.42 (d, *J* = 8.6 Hz, 1 H), 7.11 - 7.34 (m, 7 H), 5.59 (s, 2 H), 3.64 (s, 2 H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 200.0, 174.6, 142.9, 141.0, 139.7, 136.5, 130.6, 129.0, 128.1, 127.5, 123.6, 123.3, 122.1, 112.2, 48.4, 32.5; **HRMS-ESI**: m/z calcd for $C_{18}H_{13}NO_2$ $[M]^+$: 276.1025; found: 276.1022.

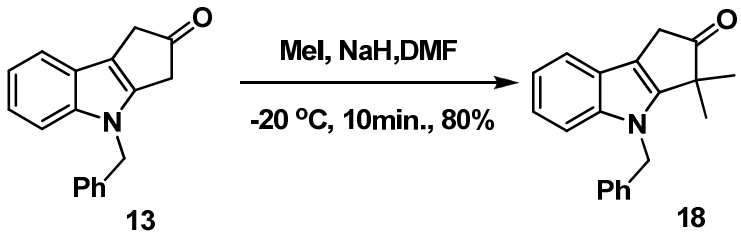
Synthesis of compound 16



Compound **13** (120mg, 0.4mmol) was dissolved in THF: H_2O (9ml:1ml) and cooled to 0 ^oC. DDQ (490 mg, 2.2mmol) was added and stirred at 0 ^oC for 2 h. The reaction mixture was poured into ethyl acetate and washed with excess saturated aq. $NaHCO_3$ (3X20ml). The organic fraction was dried over Na_2SO_4, filtered and evaporated to get a dark red colored residue which was purified by flash chromatography (EtOAc-hexane (1:4)) to get **16** as a brownish red oil (115 mg,

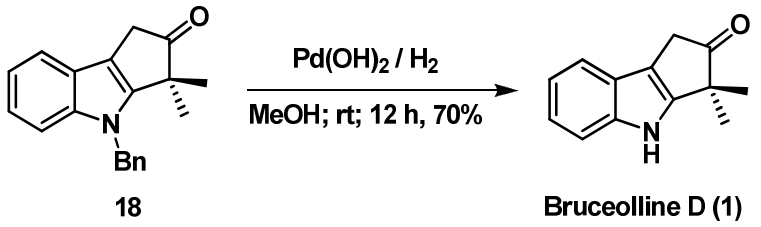
80%); R_f = 0.3 (EtOAc - hexane 1:4); **IR** (thin film): ν_{max}/cm^{-1} 2924, 2854, 1758, 1689, 1609, 1511, 1474, 1450, 1394, 1202, 1130, 1085, 1045, 750, 699, 650, 556, 466, 417; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.09 (d, *J* = 5.2 Hz, 1 H), 7.33 - 7.43 (m, 7 H), 7.18 (d, *J* = 6.7 Hz, 2 H), 5.39 (s, 2 H), 3.44 (s, 2 H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 199.1, 176.7, 162.2, 134.3, 129.5, 128.9, 127.0, 125.9, 124.3, 122.6, 122.3, 111.3, 49.2, 32.7, 32.0, 29.8, 29.5, 22.8, 14.2; **HRMS-ESI**: m/z calcd for $C_{18}H_{13}NO_2$ $[M]^+$: 276.1025; found: 276.1024.

Synthesis of compound 18



To a solution of NaH (153 mg, 3.8mmol) in DMF (5ml), was added **13** (500 mg, 1.9 mmol) in DMF (5ml) at -20 ^{o}C, stirred for 30min. Then MeI (0.3ml, 3.8mmol) was added at the same temperature and stirred for exactly 10 min. keeping the temperature exactly at -20 ^{o}C. Reaction was quenched by adding ice cold water (2ml), then extracted with ethyl acetate and washed with brine. Organic layer was dried over Na_2SO_4, filtered and concentrated to get a crude product. The residue was purified by flash chromatography (EtOAc-hexane (0.2:9.8)) to get **18** as a pale pink semi solid (441 mg, 80%); R_f = 0.6 (EtOAc-hexane (0.5:9.5)); **IR** (thin film): ν_{max}/cm^{-1} 3028, 1745, 1303, 1269, 744, 733, 691; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.60-7.61 (3, 6H), 7.05 (d, *J* = *7*.0 Hz, 2H), 5.46 (s, *2*H), 3.64 (s, 2H), 1.37 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 219.6, 147.1, 139.5, 137.7, 128.9, 127.7, 126.0, 124.5, 122.0, 120.3, 119.5, 110.5, 109.6, 48.0, 37.4, 24.2; **HRMS-ESI**: m/z calcd for $C_{20}H_{19}NO$ $[M]^+$: 289.1500; found: 289.1467.

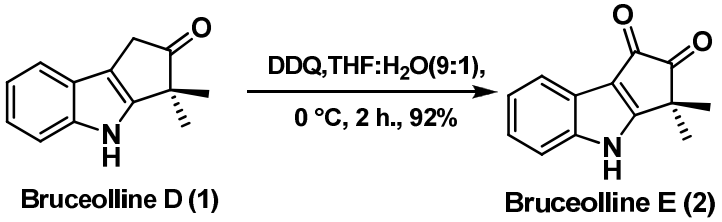
Synthesis of Bruceolline D (1).



18 Bruceolline D (1)

To a solution of **18** (80mg, 0.4mmol) in methanol (3ml), was added catalytic amount of $Pd(OH)_2$ under argon atmosphere at rt. After removing all the argon by using vacuum, the flask was back filled with H_2 by balloon. The reaction was left to stir under H_2 atmosphere at rt for 12 h. Reaction mixture was filtered through celite and washed with ethyl acetate. Solvent was evaporated under reduced pressure to get a white residue which was purified by flash chromatography (EtOAc-hexane (1:9)) to get bruceolline D (**1**) as a pale yellow semi solid (39 mg, 70%); R_f = 0.5 (EtOAc - hexane (1:4)); **IR** (thin film): ν_{max}/cm^{-1} 3392, 2968, 2927, 1747, 1447, 1314, 1051, 767, 755; **^{1}H NMR** (DMSO-D_6, 500 MHz): δ 11.25 (s, 1H), 7.36-7.39 (m, 2H), 6.96-7.06 (m, 2H), 3.45 (s, 2H), 1.26 (s, 6H); **^{13}C NMR** (DMSO-D_6, 125 MHz): δ 220.0, 147.2, 138.7, 124.5, 121.3, 119.6, 119.2, 112.5, 108.2, 47.0, 37.5, 24.3; **HRMS-ESI**: m/z calcd for $C_{13}H_{13}NO$ $[M+Na]^+$: 198.100; found: 198.098.

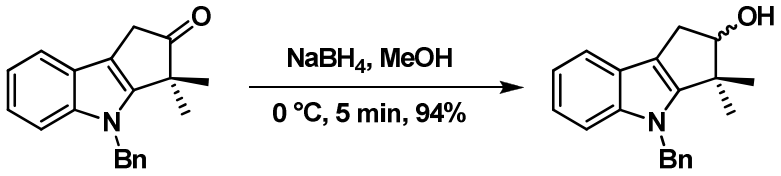
Synthesis of Bruceolline E (2) from Bruceolline D (1):



Bruceolline D (1) Bruceolline E (2)

Bruceolline D (**1**) (120mg, 0.6mmol) was dissolved in THF: H2O (9ml: 1ml) and cooled to 0 ^{o}C. DDQ (490 mg, 1.8mmol) was added in one portion and stirred at 0 ^{o}C for 2 h. The reaction mixture was poured into ethyl acetate and washed with excess saturated aq. $NaHCO_3$ (3X20ml). The organic fraction was dried over Na_2SO_4, filtered and evaporated to get a dark red colored residue which was purified by flash chromatography (EtOAc-hexane (1:4)) to get **bruceolline E** (**2**) as an yellow crystalline compound (115 mg, 92%); R_f = 0.3 (EtOAc-hexane 1:2); **Mp** = 289-291 °C; **IR** (thin film): v_{max}/cm^{-1} 1753, 1676, 1471, 1453, 1215, 753; **^{1}H NMR** (DMSO-D_6, 400 MHz): δ 12.98 (br.s., 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 1.42 (s, 6H); **^{13}C NMR** (DMSO-D_6, 125 MHz): δ 206.6, 175.2,170.9, 139.8, 125.3, 123.4, 121.5, 121.0, 113.5, 41.6, 22.8; **HRMS-ESI**: m/z calcd for $C_{13}H_{11}NO_2$ $[M+H]^+$: 214.0868; found: 214.0865.

Synthesis of compound (±)-18a.

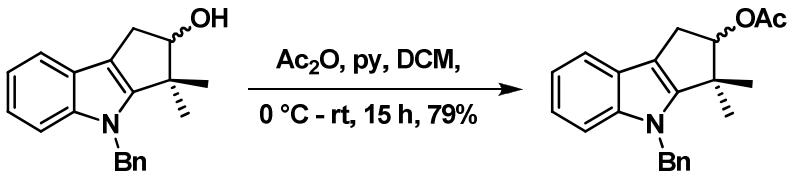


18 **(±)-18a**

Compound **18** (250 mg, 0.9mmol) was dissolved in methanol (5ml) and cooled to 0 ^{o}C. $NaBH_4$ (98mg, 2.6 mmol) was added and the reaction mixture was stirred for 5 min. at 0 ^{o}C. Water was added to the reaction mixture and was extracted by ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered and was evaporated to get a colorless crude substance which was purified by flash chromatography (EtOAc-hexane (1:4)) to get **(±)-18a** as a colorless semi solid (237 mg, 94%). R_f = 0.3 (EtOAc–hexane (1:9)); **IR** (thin film): v_{max}/cm^{-1} 3328, 3050, 2967, 2936, 2845, 1452, 1377, 1347, 1079, 731, 704; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.03-7.55

(m, 9H), 5.40 (s, 2H), 4.44 (t, J = 6.87 Hz, 1H), 3.31 (dd, J = 6.9 Hz, 7.2 Hz, 1H), 2.72 (dd, J = 6.6 Hz, 7.5 Hz, 1H), 2.08 (br s, 1H), 1.34 (s, 3H), 1.17 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 148.6, 140.6, 138.2, 128.8, 127.4, 126.0, 124.6, 120.9, 119.7, 118.9, 111.7, 110.1, 85.3, 47.6, 43.8, 32.6, 25.6, 20.3; **HRMS-ESI**: m/z calcd for $C_{20}H_{21}NO$ $[M+H]^+$: 292.16; found: 292.17.

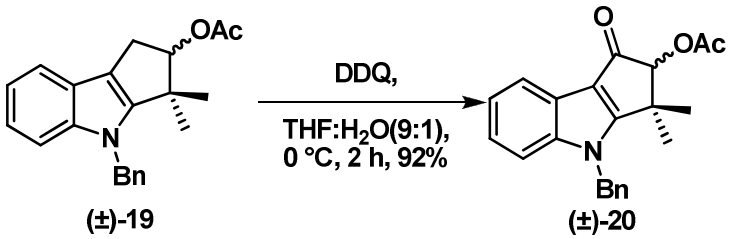
Synthesis of compound (±)-19



(±)-18a (±)-19

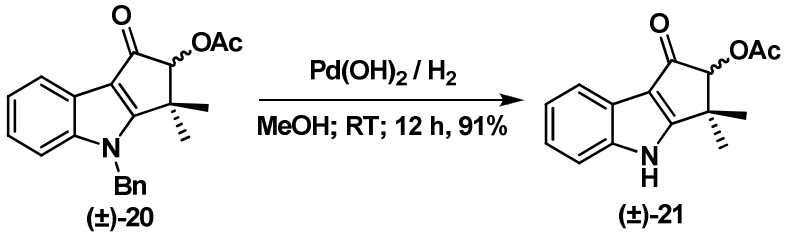
To a solution of **(±)-18a** (180mg, 0.6mmol) in DCM (5ml), was added pyridine (0.3ml, 3.1mmol) at 0 ^oC. After stirring for 2 min., acetic anhydride (0.4ml, 3.3mmol) and catalytic amount of DMAP were added. Then the reaction mixture was slowly allowed to attain room temperature and was stirred for 15 h at rt. Reaction mixture was poured into distilled water and extracted with DCM (2X10ml). The combined organic fractions were washed with saturated $CuSO_4$ solution to remove excess pyridine and were concentrated to get a crude residue which was purified by flash chromatography (EtOAc-hexane (1:9)) to get **(±)-19** as a white semi solid (160 mg, 79%). R_f = 0.5 (EtOAc-hexane (1:4)); **IR** (thin film): ν_{max}/cm^{-1} 2966, 1734, 1456, 1372, 1241, 1105, 740; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.07-7.59 (m, 9H), 5.58-5.61 (m, 1H), 5.44 (s, 2H), 3.48 (dd, J = 7.0 Hz, 14.6 Hz, 1H), 2.87 (dd, J = 5.2 Hz, 14.6 Hz , 1H), 2.20 (s, 3H), 1.42 (s, 3H), 1.30 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 171.1, 148.1, 141.0, 138.2, 128.9, 127.5, 126.0, 124.4, 121.2, 119.9, 119.1, 122.4, 110.3, 85.7, 47.6, 43.7, 30.3, 26.3, 21.5; **HRMS-ESI**: m/z calcd for $C_{22}H_{23}NO_2$ $[M+H]^+$: 334.17; found: 334.18.

Synthesis of compound (±)-20



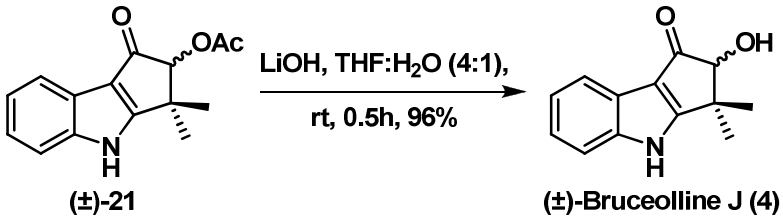
Compound **(±)-19** (120mg, 0.4mmol) was dissolved in THF:H_2O (9ml:1ml) and cooled to 0 ^oC. DDQ (490 mg, 2.2mmol) was added and stirred at 0 ^oC for 2 h. The reaction mixture was poured into ethyl acetate and washed with excess saturated aq. $NaHCO_3$ (3X20ml). The organic fraction was dried over Na_2SO_4, filtered and evaporated to get a dark red colored residue which was purified by flash chromatography (EtOAc-hexane (1:4)) to get **(±)-20** as a white crystalline compound (115 mg, 92%); R_f = 0.3 (EtOAc - hexane (1:4)); **Mp** = 136−139 °C; **IR** (thin film): ν_{max}/cm^{-1} 2926, 1747, 1694, 1522, 1477, 1453, 1371, 1229, 1055, 926, 752; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.00-7.33 (m, 8H), 5.53 (s, 1H), 5.44-5.52 (AB q, *J* = 3.0 Hz, 17.1 Hz, 2H), 2.23 (s, 3H), 1.61 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 188.5, 170.9, 170.0, 142.7, 135.5, 129.2, 128.1, 125.7, 124.4, 123.2, 121.8, 111.2, 85.6, 48.5, 41.1, 29.8, 25.9, 23.0, 20.9; **HRMS-ESI**: m/z calcd for $C_{22}H_{21}NNaO_3$ $[M+Na]^+$: 370.1419; found: 370.1414.

Synthesis of compound (±)-21



To a solution of **(±)-20** (115mg, 0.3mmol) in methanol (3ml), was added catalytic amount of $Pd(OH)_2$ under argon atmosphere at rt. After removing all the argon by using vacuum, the flask was back filled with H_2 by balloon. The reaction was left to stir under H_2 atmosphere at rt for 12 h. Reaction mixture was filtered through celite and washed with ethyl acetate. Solvent was evaporated under reduced pressure to get a white amorphous residue which was purified by flash chromatography (EtOAc-hexane 3:7) to get **(±)-21** as a white amorphous powder (77mg, 91%); R_f = 0.3 (EtOAc-hexane 3:7); **Mp** = 200−205 °C; **IR** (thin film): ν_{max}/cm^{-1} 3187, 2928, 1747, 1671, 1475, 1453, 1371, 1228, 1063, 752; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.91 (brs, 1H), 7.88 (d, J = 7.4 Hz, 1H), 7.23-7.45 (m, 3H), 5.53 (s, 1H), 2.15 (s, 3H), 1.64 (s, 3H), 1.33 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 189.3, 171.7, 170.9, 141.9, 124.6, 123.1, 121.5, 116.0, 112.6, 85.4, 40.4, 26.0, 23.7, 20.8; **HRMS-ESI**: m/z calcd for $C_{15}H_{15}NO_3$ $[M+H]^+$: 258.113; found: 2580.113.

(±) Bruceolline J (4).

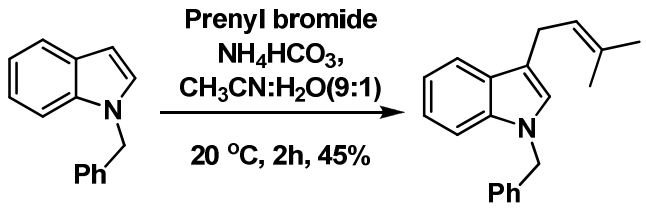


(±)-21 (±)-Bruceolline J (4)

Compound **(±)-21** (60mg, 0.3mmol) was dissolved in THF:H_2O (4ml+1ml) and added with lithium hydroxide (11mg, 0.5mmol). The reaction mixture was stirred for 30min at rt, poured into water and extrated with ethyl acetate (2X5ml). The combined organic fractions were dried over Na_2SO_4, filtered and concentrated to get white colored solid residue which was then purified by flash chromatography (EtOAc-hexane (3:7)) to get **(±)-**bruceolline J (**4)** as a white semi solid (48 mg, 96%); R_f = 0.3 (EtOAc-hexane (3:7)); **IR** (thin film): ν_{max}/cm^{-1} 3193, 2968,

2929, 1667, 1474, 1453, 1082, 1023, 829, 752; **^{1}H NMR** (Acetone-D_6, 500 MHz): δ 11.26 (br.s., 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.16-7.23 (m, 2H), 4.71 (d, *J* = 5.5 Hz, 1H), 4.27 (d, *J* = 5.5 Hz, 1H), 1.55 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (Acetone-D_6, 125 MHz): δ 193.5, 171.1, 142.0, 123.4, 122.0, 120.5, 114.3, 112.7, 86.2, 40.4, 24.5, 23.6; **HRMS-ESI**: m/z calcd. for $C_{13}H_{13}NNaO_2$ $[M+Na]^+$:238.0844; found: 238.0843.

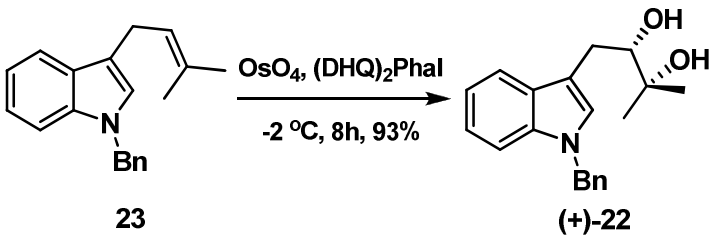
Synthesis of compound 23:



24 **23**

To a solution of 1-benzyl-1*H*-indole **24** (1g, 4.8mmol) in a mixture of acetonitrile and H_2O (18ml+2ml) (9:2), NH_4HCO_3 (1.5g, 19.3mmol) was added at 20 ^{o}C and stirred for 10min. Then prenyl bromide (0.7ml, 6.2mmol) was added and stirred for 2h at the same temperature. The reaction mixture was poured into ethyl acetate (20ml) and washed with brine. Solvent was removed under reduced pressure to get a dark yellowish red colored residue which was purified by flash column chromatography (Hexane) to get **23** as a yellow colored oily liquid (600 mg, 45%); R_f = 0.5 (EtOAc-hexane (0.5:9.5)); **IR** (thin film): ν_{max}/cm^{-1} 2922, 1612, 1495, 1465, 1453, 1356, 1330, 1177, 1013, 737, 698, 425; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.61 - 7.57 (m, 1 H), 7.31 - 7.21 (m, 5 H), 7.18 - 7.07 (m, 5 H), 6.88 (s, 1 H), 5.46 - 5.39 (m, 1 H), 5.26 (s, 2 H), 3.45 (d, *J* = 7.3 Hz, 2 H), 1.79 - 1.72 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 138.1, 137.0, 132.0, 128.9, 128.3, 127.6, 126.9, 125.6, 123.3, 121.9, 121.5, 119.4, 119.0, 115.5, 109.9, 109.8, 50.0, 28.3, 25.9, 24.3; **HRMS-ESI**: m/z calcd for $C_{20}H_{21}N$ $[M+H]^+$: 276.1752; found: 276.1759;

Synthesis of compound (+)-22:

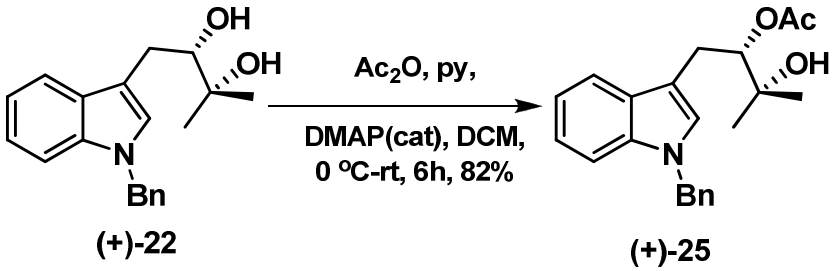


23 (+)-22

$K_3[Fe(CN)_6]$ (2.3g, 7.0mmol) and K_2CO_3 (964mg, 7.0mmol) were dissolved in H_2O (10ml) followed by the addition of *t*-BuOH (10ml) and cooled to -2 °C. OsO_4 (0.1ml, 0.01mmol), methane sulfonamide (221mg, 2.3mmol) and $(DHQ)_2$ Phal (181mg, 0.23mmol) were added consecutively at the same temperature. After stirring the reaction mixture vigorously for 20min, compound **23** (640mg, 2.3mmol) in *t*-BuOH (5ml) was added then the reaction mixture was stirred for 8h at -2 °C. Upon the completion, reaction was quenched by adding solid sodium sulphite, added water and extracted with ethyl acetate (2X20ml). Combined organic fractions were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give an yellow colored residue which was then purified by flash column chromatography (EtOAc-hexane (1:4)) to get **(+)-22** as a yellow colored crystalline compound (671 mg, 93%, 90% *ee*); R_f = 0.2 (EtOAc-hexane (1:4)); $[\alpha]_D^{25}$ = + 124.8 (*c* = 0.2, Chloroform); **Mp** = 66−70 °C; The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralpak IA-3 column, *n*-hexane/2-propanol (9:1) as eluent, flow rate = 1.0 mL/min. t_R (major) = 17.17 min, t_R (minor) = 15.16 min. **IR** (thin film): ν_{max}/cm^{-1} 3422, 3029, 3056, 2973, 2925, 1612, 1495, 1481, 1467, 1357, 1332, 1169, 1104, 1070, 965, 739, 700, 760; **^{1}H NMR** (Acetonitrile-D_3, 400 MHz): δ 7.57 (d, *J* = 7.8 Hz, 1H), 6.99-7.29 (m, 9H), 5.29 (s, 2H), 3.54-3.58 (m, 1H), 3.00-3.04 (m, 1H), 2.80 (d, *J* = 4.6 Hz, 1H), 2.77 (s, 1H), 2.56-2.63 (m, 1H), 1.19 (d, *J* = 5.4 Hz, 6H); **^{13}C NMR** (Acetonitrile-D_3, 100 MHz): δ 138.6, 136.6, 128.7, 127.1, 121.5, 119.2, 118.8, 117.5, 112.9,

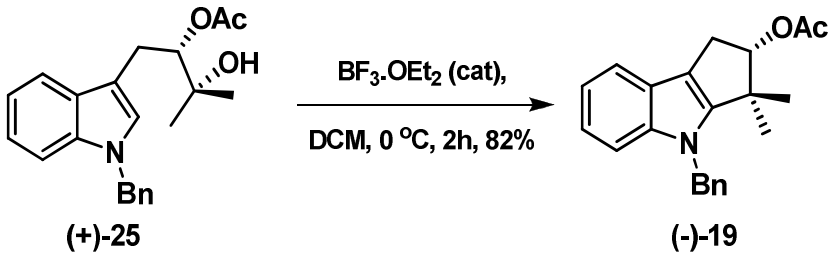
109.9, 78.3, 72.5, 49.5, 27.5, 25.2, 24.3; **HRMS-ESI**: m/z calcd for $C_{20}H_{23}NNaO_2$ $[M+Na]^+$: 332.1626; found: 332.1624.

Synthesis of compound (+)-25:



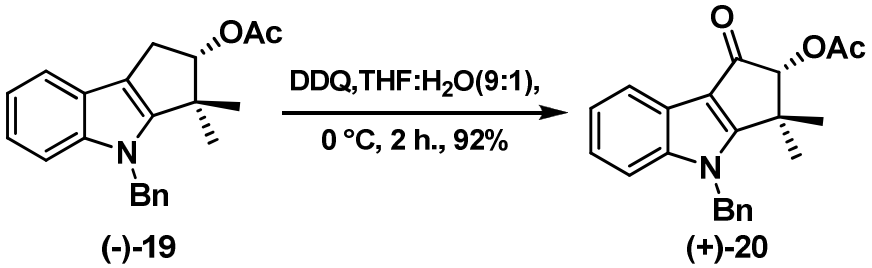
To a stirred solution of **(+)-22** (303mg, 1mmol) in DCM (5ml) was added pyridine (0.4ml, 5mmol) 0 ^oC. After stirring for 10min at the same temperature, Ac_2O (0.5ml, 5mmol) and catalytic amount of DMAP were added. Reaction mixture was stirred for 6h at the same temperature and was added with water, extracted by DCM (2X10ml). Organic phase was washed with saturated $CuSO_4$ solution to remove excess pyridine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to get an yellow colored residue which was then purified by flash column chromatography (EtOAc-hexane (1:4)) to get **(+)-25** as a pale yellow colored amorphous compound (285 mg, 82%); R_f= 0.4 (EtOAc-hexane (1:4)); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = + 11.14 (c = 0.5, Chloroform); **Mp** = 97−100 °C; **IR** (thin film): ν_{max}/cm^{-1} 3400, 2919, 1729, 1466, 1371, 1239, 1028, 739, 700; **^{1}H NMR** (Acetonitrile-D_3, 400 MHz): δ 7.58 (d, J = 7.8 Hz, 1H), 7.01-7.28 (m, 9H), 5.24-5.33 (AB q, J = 5.1 Hz, 16.1 Hz, 2H), 4.96 (dd, J = 2.4 Hz, 8.3 Hz, 1H), 2.80-3.17 (m, 2H), 1.75 (s, 3H), 1.21(s, 3H), 1.20 (s, 3H); **^{13}C NMR** (Acetonitrile-D_3, 100 MHz): δ 170.1, 138.6, 136.4, 128.6, 127.4, 127.1, 126.8, 121.5, 119.0, 118.8, 111.7, 109.8, 79.6, 49.3, 20.3; **HRMS-ESI**: m/z calcd for $C_{22}H_{25}NNaO_3$ $[M+Na]^+$: 374.1732; found: 374.1738.

Synthesis of compound (-)-19:



To a stirred solution of **(+)-25** (75mg, 0.26mmol) in DCM, was added $BF_3.OEt_2$ at 0 ^oC and stirred for 2h at the same temperature. Reaction was quenched by adding water, extracted by DCM (2X10ml). Combined organic fractions were dried over Na_2SO_4, filtered and concentrated under reduced pressure to get a colorless residue which was then purified by flash column chromatography (EtOAc-hexane (1:9)) to get (-)-**19** as a colorless semi solid (50 mg, 82%); R_f = 0.5 (EtOAc-hexane (1:9)); $[\alpha]_D^{25}$ = -43.20 (*c* 0.2, Chloroform); The spectroscopic data was exactly matching with that of **(±)-19.**

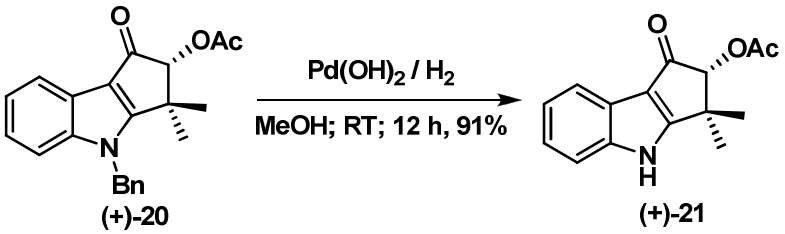
Synthesis of compound (+)-20:



Compound **(-)-19** (120mg, 0.4mmol) was dissolved in THF: H_2O (9ml:1ml) and cooled to 0 ^oC. DDQ (490 mg, 2.2mmol) was added and stirred at 0 ^oC for 2 h. The reaction mixture was poured into ethyl acetate and washed with excess saturated aq. $NaHCO_3$ (3X20ml). The organic fraction was dried over Na_2SO_4, filtered and evaporated to get a dark red colored residue which was purified by flash chromatography (EtOAc-hexane (1:4)) to get **(+)-20** as a white crystalline

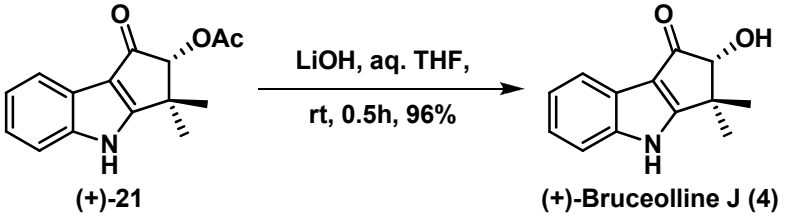
compound (115 mg, 92%); R_f = 0.3 (EtOAc - hexane (1:4)); **Mp** = 136−139 °C. The spectroscopic data was matching exactly with that of **(±)-20.** $[\alpha]_D^{25}$ = +14.40 (*c* 0.1, Chloroform).

Synthesis of compound (+)-21:



To a solution of **(+)-20** (115mg, 0.3mmol) in methanol (3ml), was added catalytic amount of $Pd(OH)_2$ under argon atmosphere at rt. After removing all the argon by using vacuum, the flask was back filled with H_2 by balloon. The reaction was left to stir under H_2 atmosphere at rt for 12 h. Reaction mixture was filtered through celite and washed with ethyl acetate. Solvent was evaporated under reduced pressure to get a white amorphous residue which was purified by flash chromatography (EtOAc-hexane 3:7) to get **(+)-21** as a white amorphous powder (77mg, 91%); R_f = 0.3 (EtOAc-hexane 3:7); **Mp** = 200−205 °C. The spectroscopic data was matching exactly with that of **(±)-21.** $[\alpha]_D^{25}$ = + 11.14 (*c* 0.5, Chloroform).

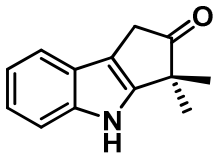
Synthesis of (+)-Bruceolline J (4) :



Compound **(+)-21** (75mg, 0.3mmol) was dissolved in THF:H_2O (3ml+1ml) and added with lithium hydroxide (11mg, 0.5mmol). The reaction mixture was stirred for 30min at rt, poured

into water and extrated with ethyl acetate (2X5ml). The combined organic fractions were dried over Na_2SO_4, filtered and concentrated to get white colored solid residue which was then purified by flash chromatography chromatography (EtOAc-hexane 3:7) to get **(+)-**bruceolline J (**4)** as a white semi solid (60 mg, 96%, 84% ee); R_f = 0.3 (EtOAc-hexane 3:7). The enantiomeric ratio was determined by chiral HPLC using Daicel Chiralcel OD-H column, *n*-hexane/2-propanol (85:15) as eluent, flow rate = 0.8 ml/min. t_R (major) = 5.32 min, t_R (minor) = 7.24 min. $[\alpha]_D^{25}$ = +6 (*c* 0.1, Methanol) {lit. $[\alpha]_D^{20}$: + 8 (*c* 0.1, Methanol)}; R_f = 0.3 (EtOAc-hexane 3:7); **IR** (thin film): v_{max}/cm^{-1} 3193, 2968, 2929, 1667, 1474, 1453, 1082, 1023, 829, 752; **^{1}H NMR** (Acetone-D_6, 500 MHz): δ 11.25 (brs, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.15-7.22 (m, 2H), 4.70 (d, *J* = 5.5 Hz, 1H), 4.27 (d, *J* = 5.5 Hz, 1H), 1.54 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (Acetone-D_6, 125 MHz): δ 194.3, 171.9, 142.9, 124.3, 122.9, 121.4, 115.2, 113.5, 87.1, 41.3, 25.4, 24.5; **HRMS-ESI**: m/z calcd for $C_{13}H_{13}NNaO_2$ $[M+Na]^+$: 238.0844; found: 238.0843.

Bruceolline D (1):



Bruceolline D (1)

^{1}H-NMR Comparision table:

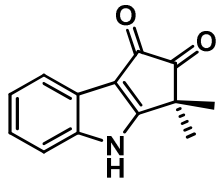
Entry	Bruceolline D (1) (Isolated) Ohmoto et. al. *Phytochemistry* **1994**, *36*, 1543. ^{1}H-NMR	Synthesized Bruceolline D (1) Gribble, et. al. *Org. Lett*., **2013**, *15*, 4485 ^{1}H-NMR	Bruceolline D (1) (present work) ^{1}H-NMR
	δ_H (DMSO-D_6, 500 MHz)	δ_H (DMSO-D_6, 300 MHz)	δ_H (DMSO-D_6, 500 MHz)
1	11.16 (br. S., 1 H)	11.26 (s, 1 H)	11.25 (s., 1 H)
2	7.41 (d, J = 7.6 Hz, 1H)	7.38 (m, 2H)	7.36-7.39 (m, 2H)
3	7.01 (dd, J = 7.6, 7.3 Hz, 1H)		
4	7.08 (dd, J = 8.2, 7.3 Hz, 1H)	7.04 (m, 2H)	6.96-7.06 (m, 2H)
5	7.39 (d, J = 8.2 Hz, 1H)		
6	3.47 (s, 2H)	3.46 (s, 2H)	3.45 (s, 2H)
7	1.38 (s, 3H)	1.28 (s, 6H)	1.26 (s, 6H)
8	1.38 (s, 3H)		

^{13}C-NMR Comparision table:

Entry	Bruceolline D (1) (Isolated) Ohmoto et. al. *Phytochemistry* **1994**, *36*, 1543. ^{13}C-NMR	Synthesized Bruceolline D (1) Gribble, et. al. *Org. Lett*., **2013**, *15*, 4485 ^{13}C-NMR	Bruceolline D (1) (present work) ^{13}C-NMR
	δ_c (DMSO-D_6, 125 MHz)	δ_c (DMSO-D_6, 75 MHz)	δ_c (DMSO-D_6, 125 MHz)
1	219.0	219.5	220.0
2	146.5	146.7	147.2
3	138.2	138.2	138.7
4	123.9	124.0	124.5
5	120.6	120.8	121.3
6	118.9	119.1	119.6
7	118.4	118.7	119.2
8	111.7	112.0	112.5
9	107.5	107.7	108.2
10	46.3	46.5	47.0

11	36.7	37.0	37.5
12	23.5	23.8	24.3
13	23.5		

Bruceolline E (2):



Bruceolline E (2)

^{1}H-NMR Comparision table:

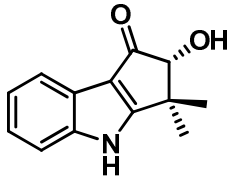
Entry	Bruceolline E (2) (Isolated) Ohmoto et. al. *Phytochemistry* **1994**, *36*, 1543. ^{1}H-NMR	Synthesized Bruceolline E (2) Gribble, et. al. *Org. Lett*., **2013**, *15*, 4485 ^{1}H-NMR	Bruceolline E (2) (present work) ^{1}H-NMR
	δ_H (DMSO-D_6, 500 MHz)	δ_H (DMSO-D_6, 300 MHz)	δ_H (DMSO-D_6, 500 MHz)
1	12.80 (br. S., 1 H)	11.91 (s, 1 H)	11.98 (br. s., 1 H)
2	7.84 (d, J = 7.7 Hz, 1H)	7.83 (d, J = 8.1 Hz, 1H)	7.83 (d, *J* = 7.7 Hz, 1H)
3	7.39 (dd, J = 7.7, 7.3 Hz, 1H)	7.59 (d, J = 7.7 Hz, 1H)	7.60 (d, *J* = 8.1 Hz, 1H)
4	7.31 (dd, J = 8.1, 7.3 Hz, 1H)	7.37 (t, J = 7.3 Hz, 1H)	7.36 (t, J = 7.4 Hz, 1H)
5	7.58 (d, J = 8.1 Hz, 1H)	7.28 (t, J = 7.3 Hz, 1H)	7.28 (t, J = 7.4 Hz, 1H)
6	1.43 (s, 3H)	1.40 (s, 6H)	1.42 (s, 6H)
7	1.43 (s, 3H)		

^{13}C-NMR Comparision table:

Entry	Bruceolline E (2) (Isolated) Ohmoto et. al. *Phytochemistry* **1994**, *36*, 1543. ^{13}C-NMR	Synthesized Bruceolline E (2) Gribble, et. al. *Org. Lett*., **2013**, *15*, 4485 ^{13}C-NMR	Bruceolline E (2) (present work) ^{13}C-NMR
	δ_c (DMSO-D_6, 125 MHz)	δ_c (DMSO-D_6, 75 MHz)	δ_c (DMSO-D_6, 125 MHz)
1	206.4	206.6	206.6
2	175.0	175.2	175.2
3	170.8	170.9	170.9
4	140.0	139.9	139.8
5	125.1	125.3	125.3

6	123.1	123.4	123.4
7	121.4	121.5	121.5
8	121.0	121.1	121.0
9	120.9	121.0	
10	113.4	113.6	113.5
11	41.5	41.6	41.6
12	22.8	22.9	22.8
13	22.8		

(+)-Bruceolline J (4):



(+)-Bruceolline J (4)

^{1}H-NMR Comparision table:

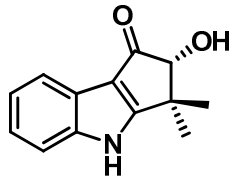
Entry	(+)-Bruceolline J (4) (Isolated) Yu, S. S., et. al. *J. Nat. Prod*. **2011**, *74*, 2438. ^{1}H-NMR	(+)-Bruceolline J (4) (Synthesized) Gribble, et. al. *Org. Lett*., **2013**, *15*, 4485 ^{1}H-NMR	(+)-Bruceolline J (4) (present work) ^{1}H-NMR
	δ_H (Acetone-D_6, 500 MHz)	δ_H (Acetone-D_6, 300 MHz)	δ_H (Acetone-D_6, 500 MHz)
1	11.1 (br. S., 1 H)	11.35 (s, 1 H)	11.26 (brs, 1H)
2	7.74 (d, J = 7.5 Hz, 1H)	7.77 (d, J = 7.0 Hz, 1H)	7.73 (d, *J* = 8.5 Hz, 1H)
3	7.47 (d, J = 8.0 Hz, 1H)	7.52 (d, J = 7.0 Hz, 1H)	7.47 (d, *J* = 7.6 Hz, 1H)
4	7.24 (td, J = 7.5, 1.5 Hz, 1H)	7.27-7.17 (m, 2H)	7.16-7.23 (m, 2H)
5	7.17 (td, J = 8.0, 1.5 Hz, 1H)		
6	4.57 (d, J = 5.5 Hz, 1H)	4.89 (d, J = 5.5 Hz, 1H)	4.71 (d, *J* = 5.5 Hz, 1H)
7	4.26 (d, J = 5.0 Hz, 1H)	4.35 (d, J = 5.1 Hz, 1H)	4.27 (d, *J* = 5.5 Hz, 1H)
8	1.58 (s, 3H)	1.59 (s, 3H)	1.55 (s, 3H)
9	1.32 (s, 3H)	1.36 (s, 3H)	1.31 (s, 3H)

^{13}C-NMR Comparision table:

Entry	(+)-Bruceolline J (4) (Isolated) Yu, S. S., et. al. *J. Nat. Prod*. **2011**, *74*, 2438. ^{13}C-NMR	(+)-Bruceolline J (4) (Synthesized) Gribble, et. al. *Org. Lett*., **2013**, *15*, 4485 ^{13}C-NMR	(+)-Bruceolline J (4) (present work) ^{13}C-NMR
	δ_c (DMSO-D_6, 125 MHz)	δ_c (DMSO-D_6, 75 MHz)	δ_c (DMSO-D_6, 125 MHz)

1	194.3	194.6	194.3
2	171.8	172.1	171.9
3	142.8	142.8	142.9
4	124.1	124.2	124.3
5	122.7	122.8	122.9
6	122.6	122.6	
7	121.2	121.2	121.4
8	115.1	115.0	115.2
9	113.4	113.5	113.5
10	86.9	87.0	87.1
11	41.2	41.2	41.3
12	25.3	25.3	25.4
13	24.4	24.4	24.5

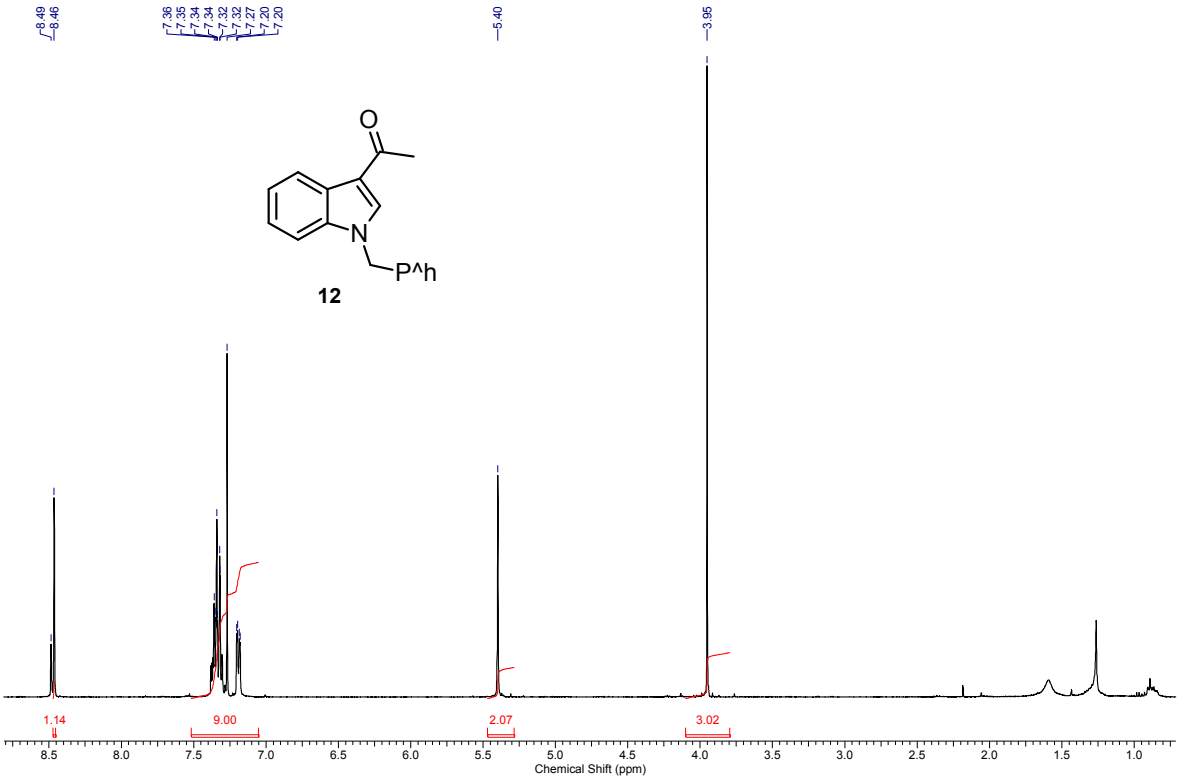
Specific Rotation:

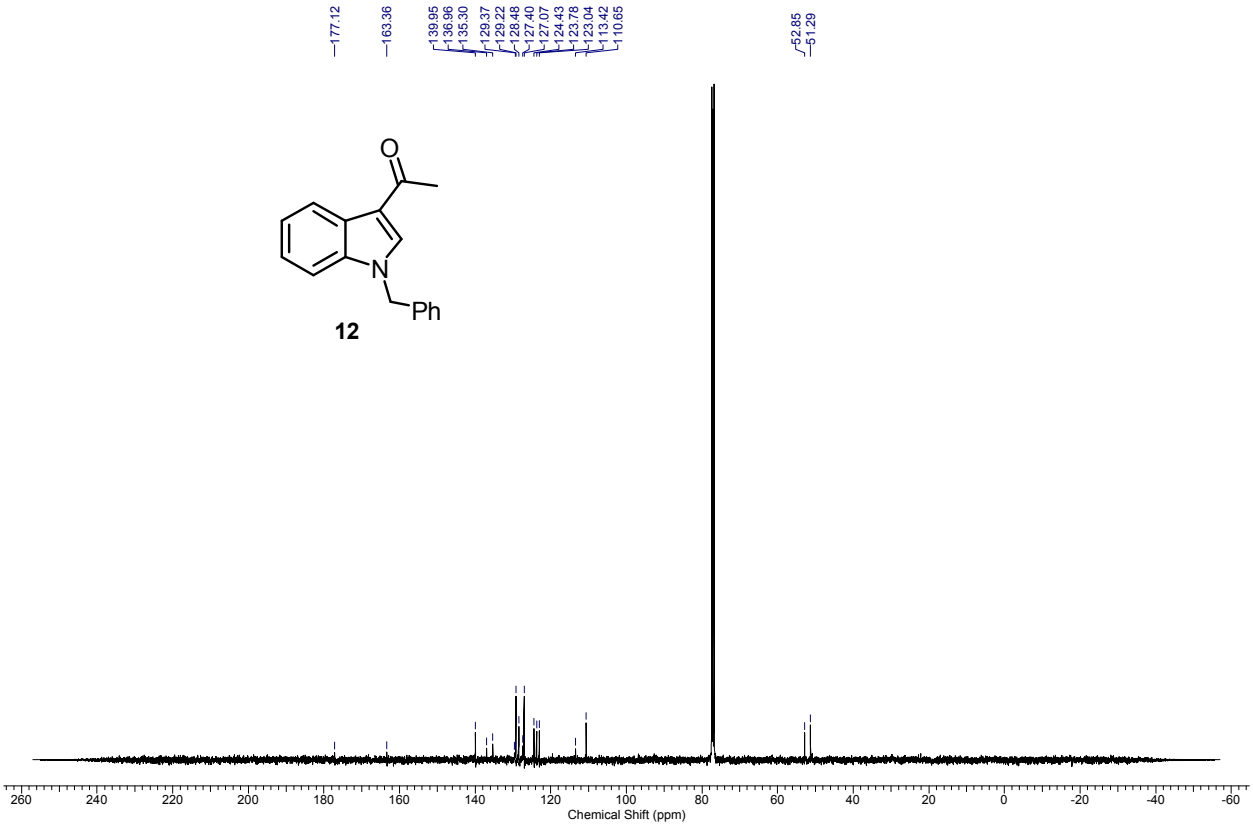


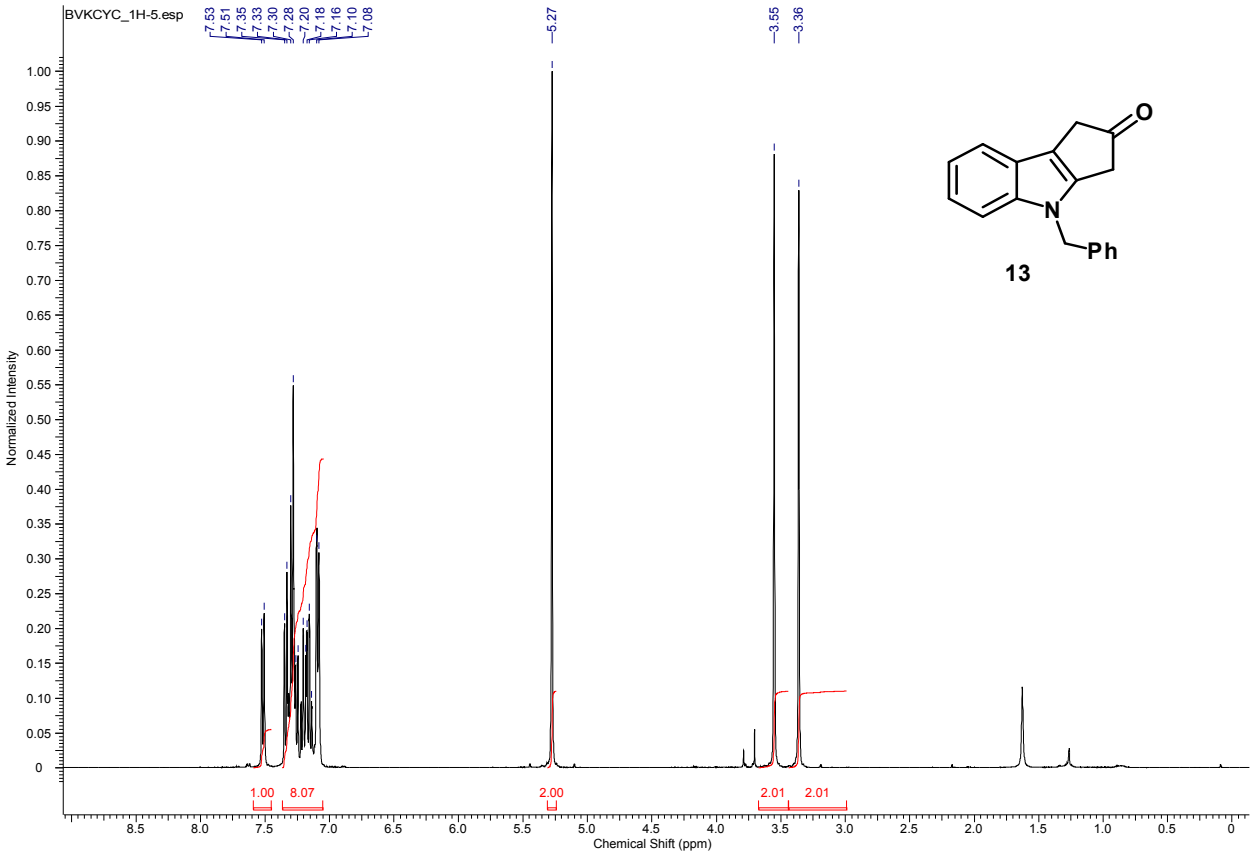
(+)-Bruceolline J (4)

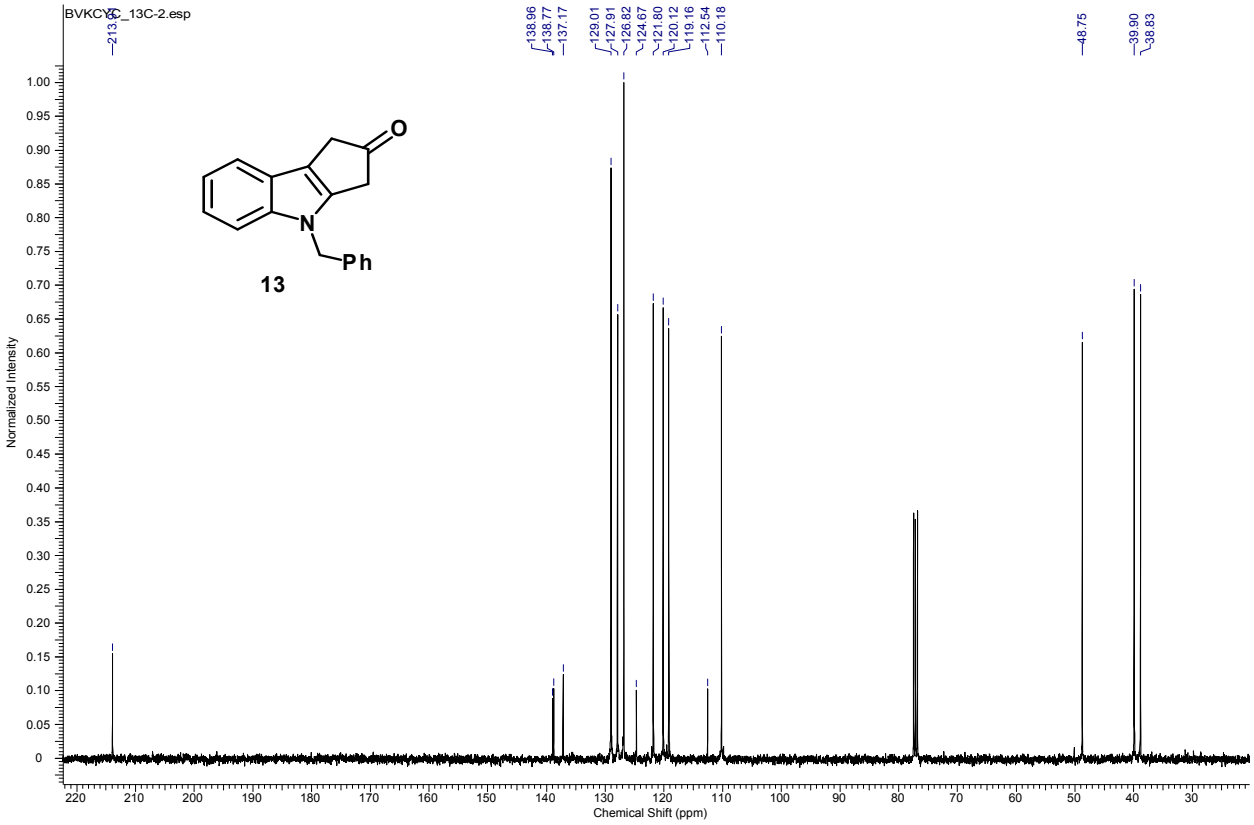
S. No:	(+)-Bruceolline J (4) (Isolated) Yu, S. S., et. al. *J. Nat. Prod*. **2011**, *74*, 2438. Specific Rotation $[\alpha]_D^T$	(+)-Bruceolline E (2) (present work) Specific Rotation $[\alpha]_D^T$
1	+ 8 (*c* 0.1, Methanol) (T=20 ° C)	+ 6 (*c* 0.1, Methanol) (T=25 ° C)

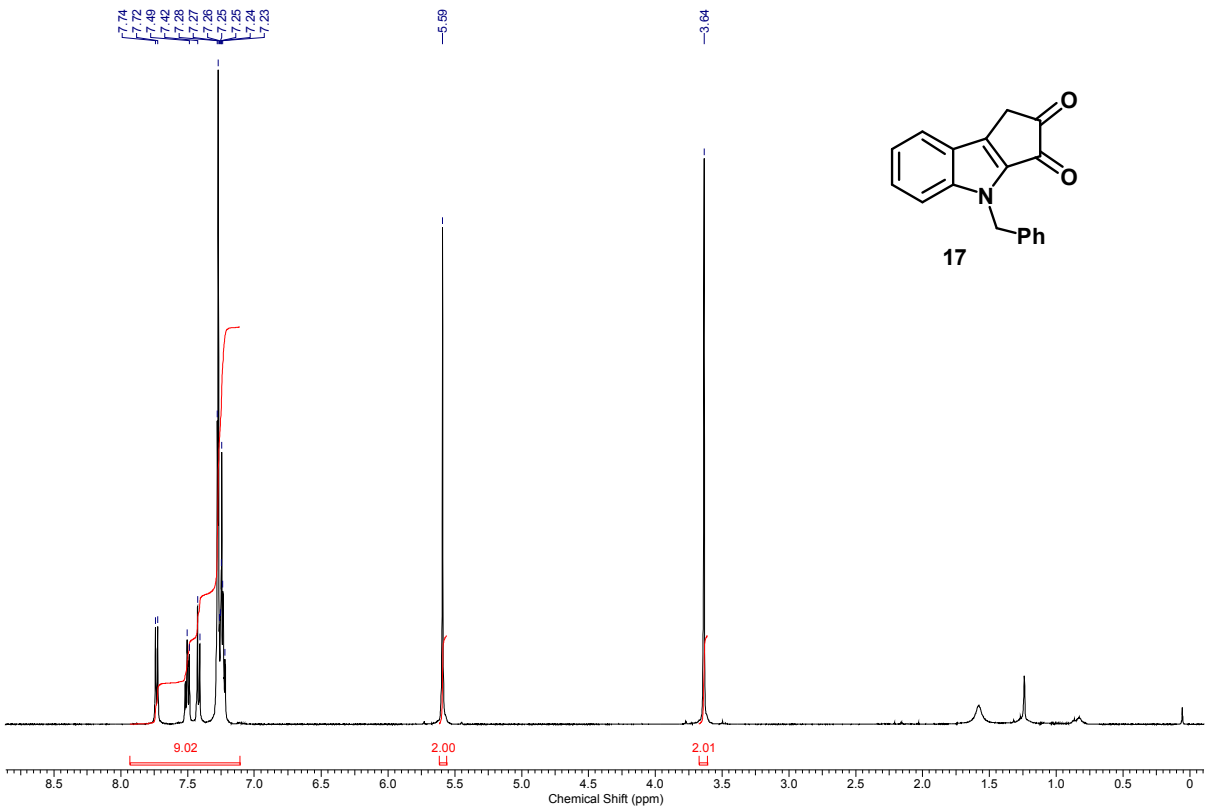
^{1}H and ^{13}C Spectra:

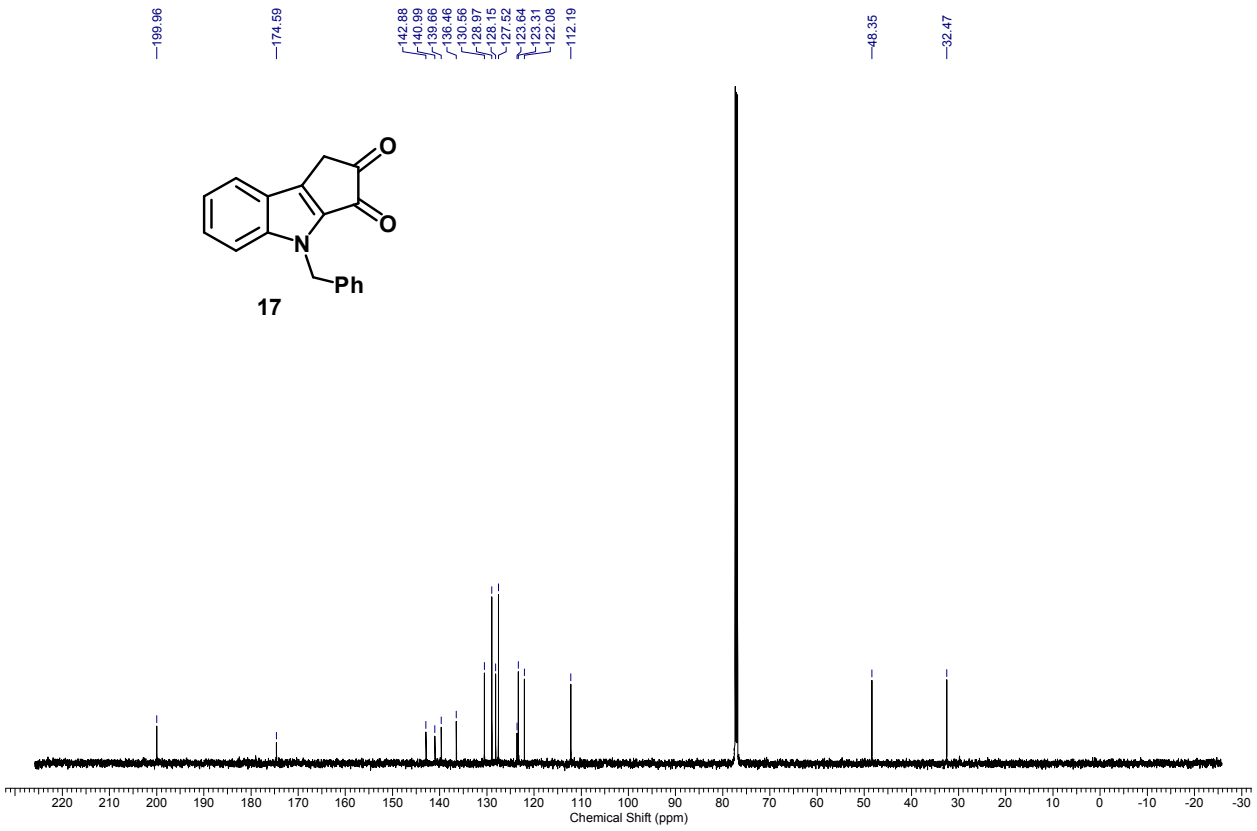


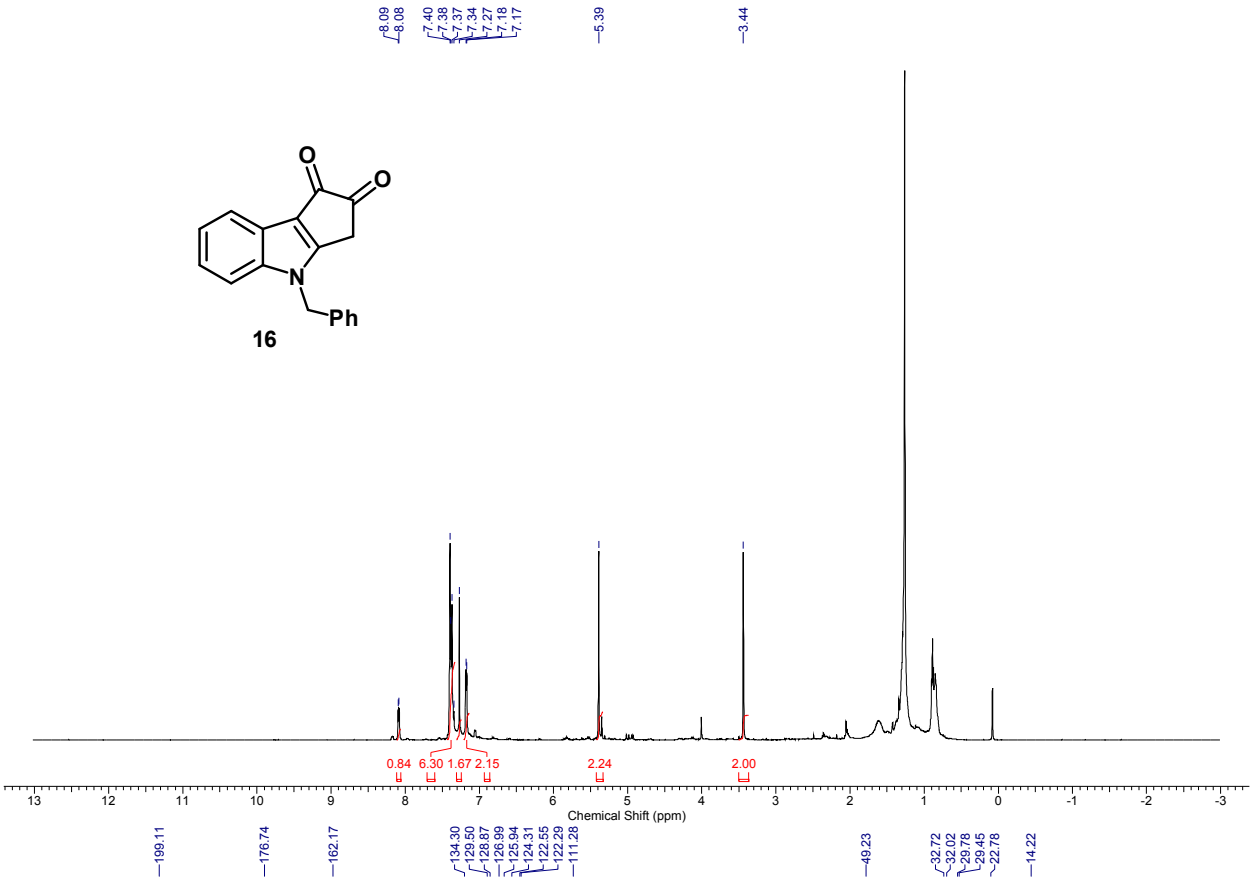


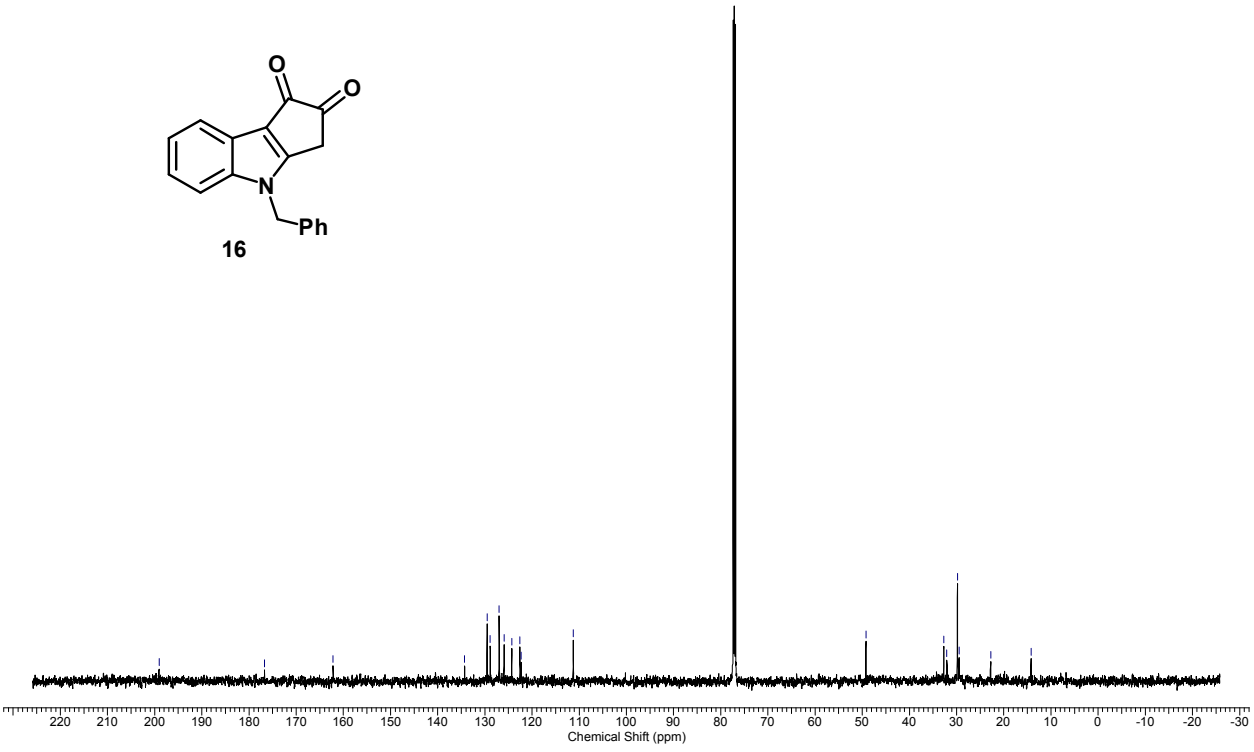

BVKCYC_1H-5.esp
7.53
7.51
7.35
7.33
7.30
7.28
7.20
7.18
7.16
7.10
7.08
5.27
3.55
3.36
1.00
8.07
2.00
2.01
2.01
Normalized Intensity
Chemical Shift (ppm)
O
N
Ph
13

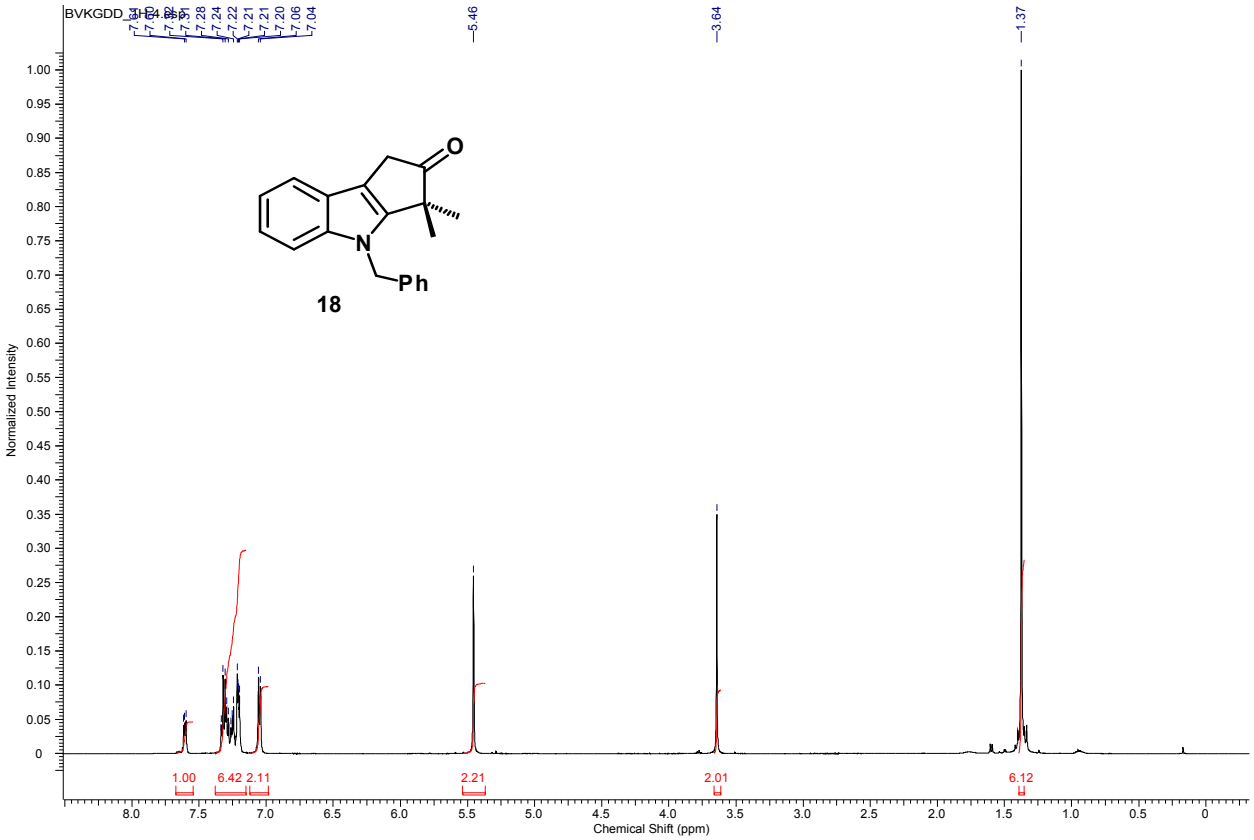

BVKCYC_13C-2.esp
213.60
138.96
138.77
137.17
129.01
127.91
126.82
124.67
121.80
120.12
119.16
112.54
110.18
48.75
39.90
38.83
Normalized Intensity
Chemical Shift (ppm)
O
N
Ph
13

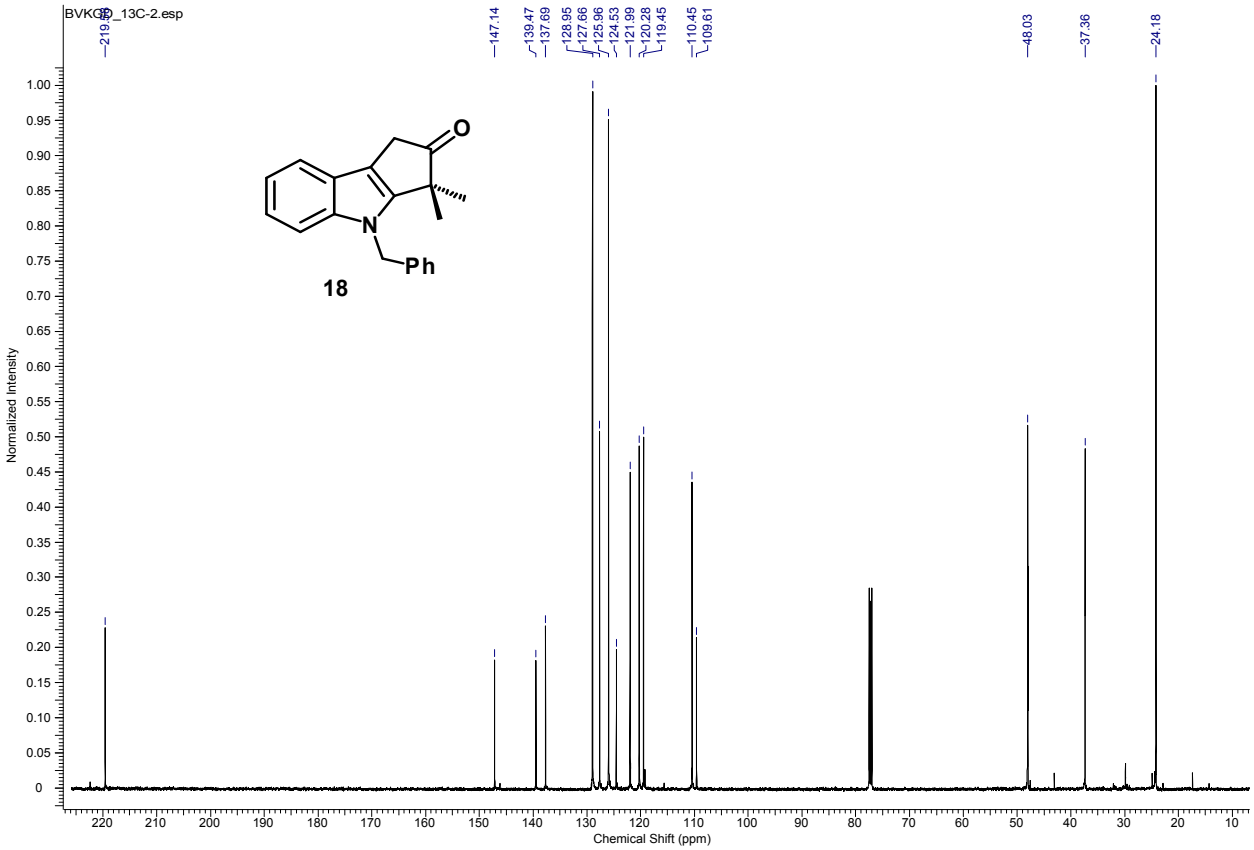

7.74
7.72
7.49
7.42
7.28
7.27
7.26
7.25
7.25
7.24
7.23
5.59
3.64
O
O
N
Ph
17
9.02
2.00
2.01
Chemical Shift (ppm)

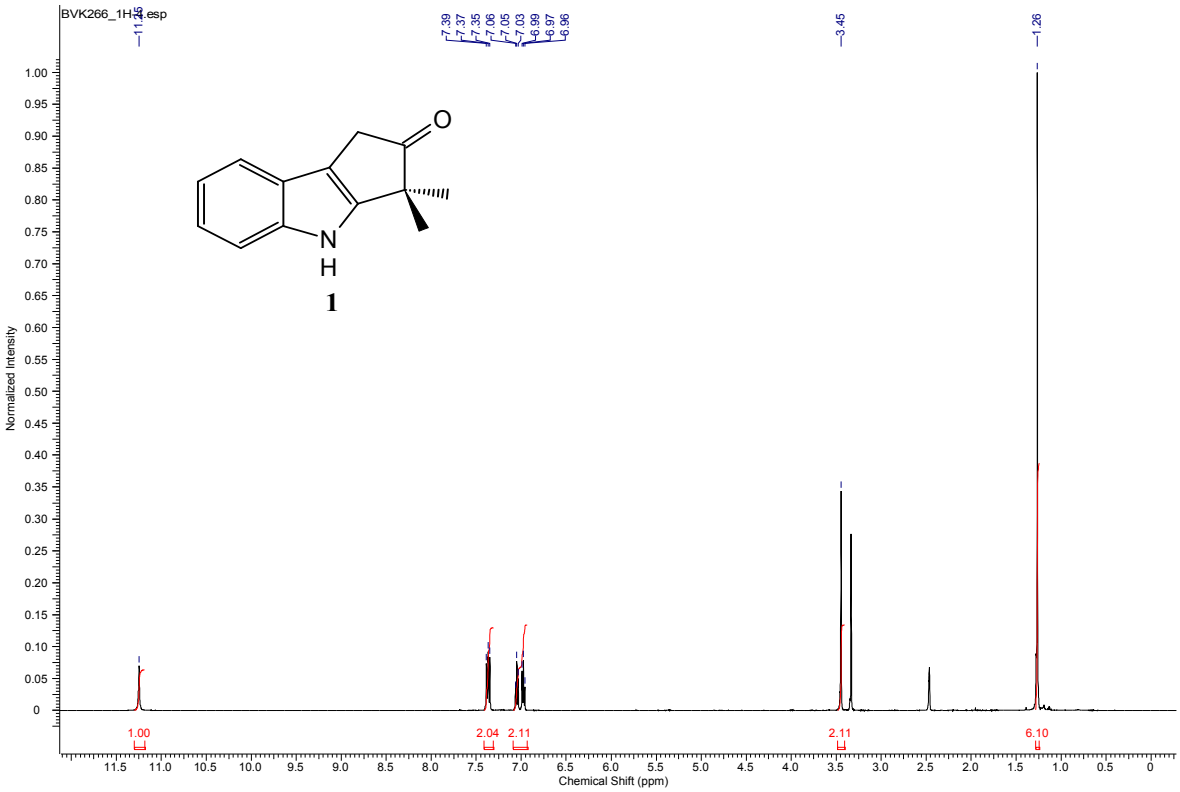

199.96
174.59
142.88
140.99
139.66
136.46
130.56
128.97
128.15
127.52
123.64
123.31
122.08
112.19
48.35
32.47
O
O
N
Ph
17
Chemical Shift (ppm)

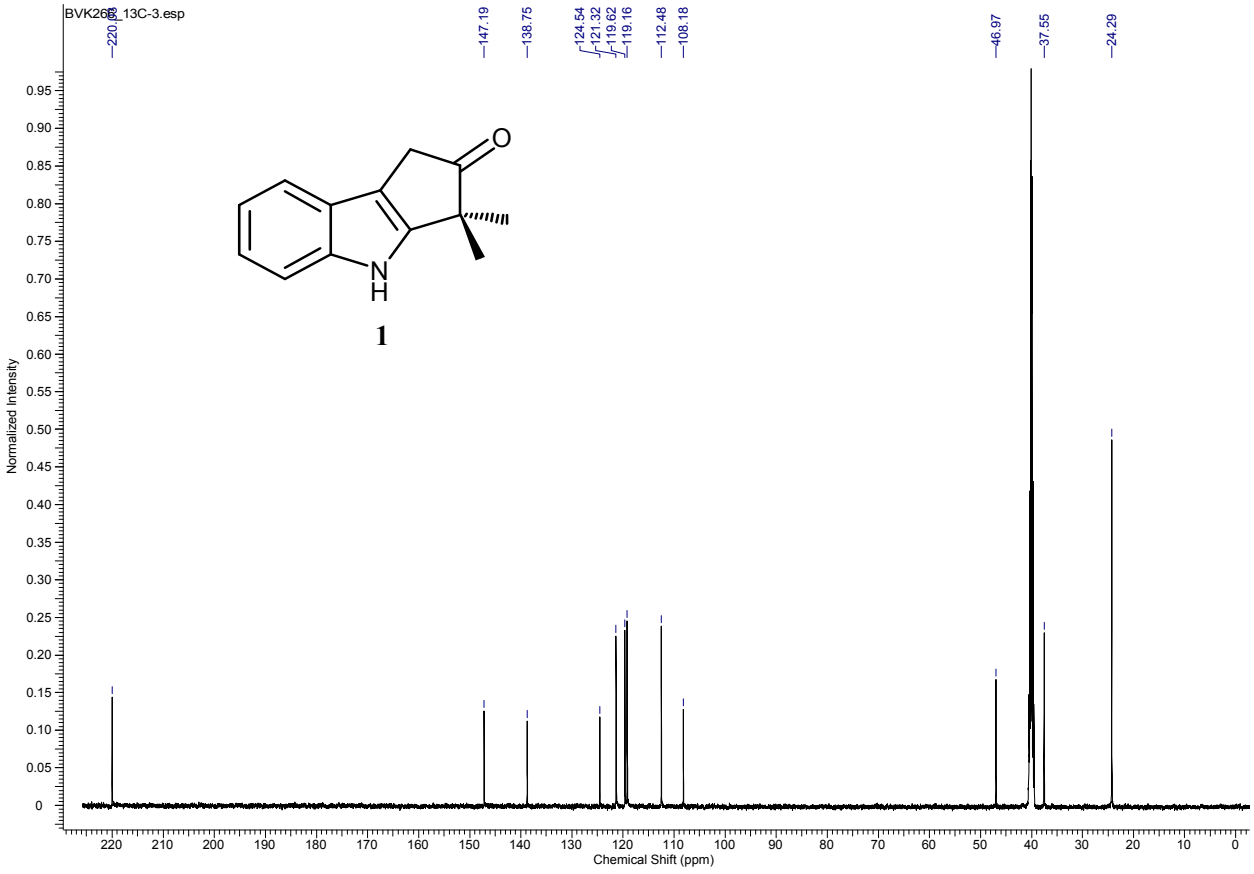

8.09
8.08
7.40
7.38
7.37
7.34
7.27
7.18
7.17
5.39
3.44
O
O
N
Ph
16
0.84
6.30
1.67
2.15
2.24
2.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
Chemical Shift (ppm)

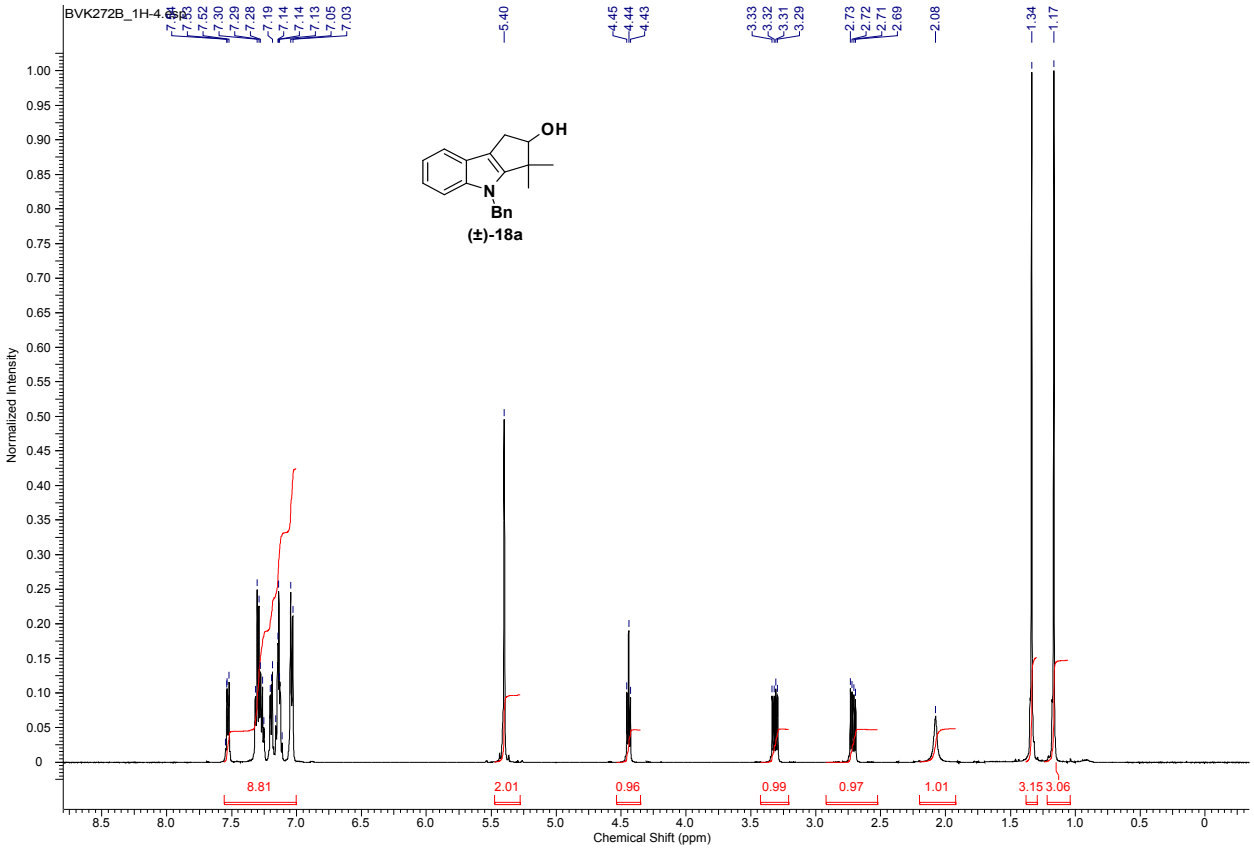

199.11
176.74
162.17
134.30
129.50
128.87
126.99
125.94
124.31
122.55
122.29
111.28
49.23
32.72
32.02
29.78
29.45
22.78
14.22
O
O
N
Ph
16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
Chemical Shift (ppm)

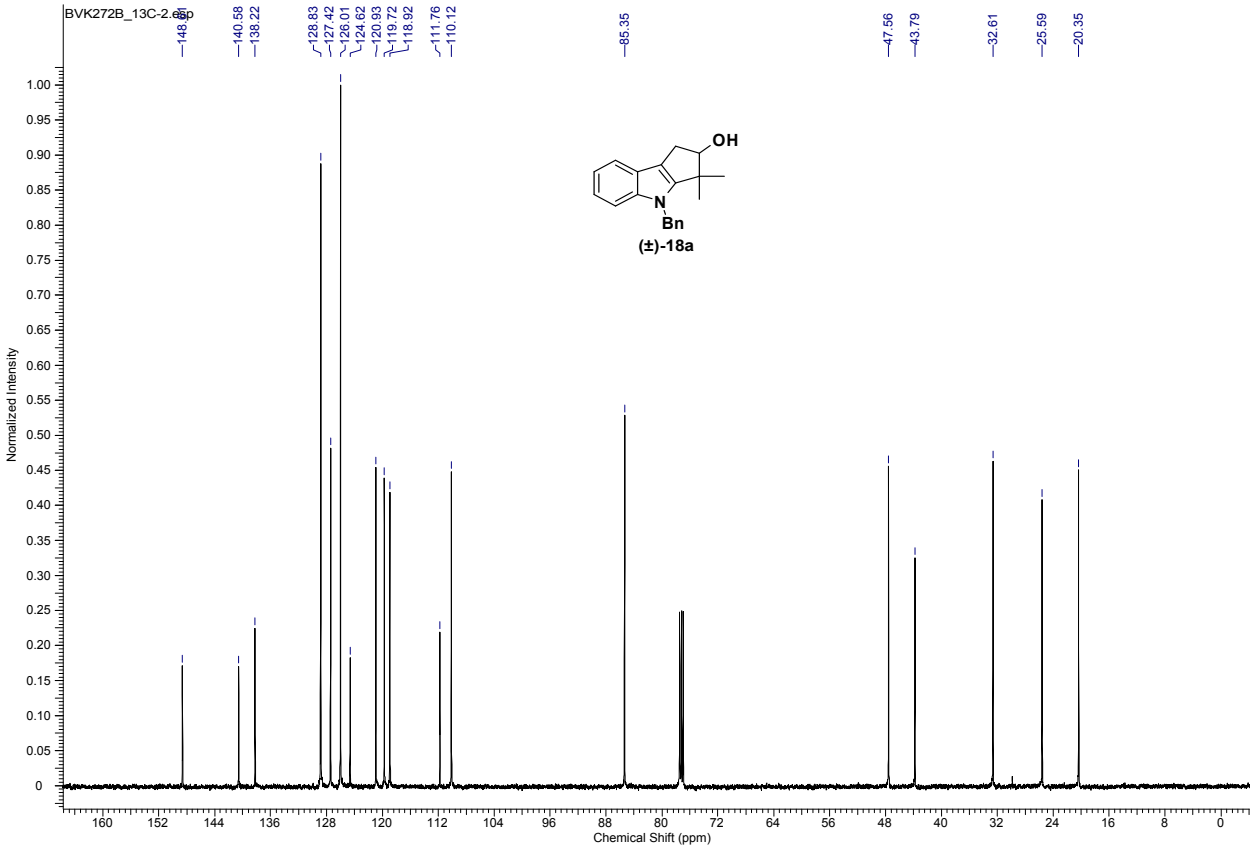

BVKGDD_1H-4.esp
7.40
7.39
7.32
7.31
7.28
7.24
7.22
7.21
7.21
7.20
7.06
7.04
5.46
3.64
1.37
O
N
Ph
18
Normalized Intensity
1.00
6.42
2.11
2.21
2.01
6.12
Chemical Shift (ppm)

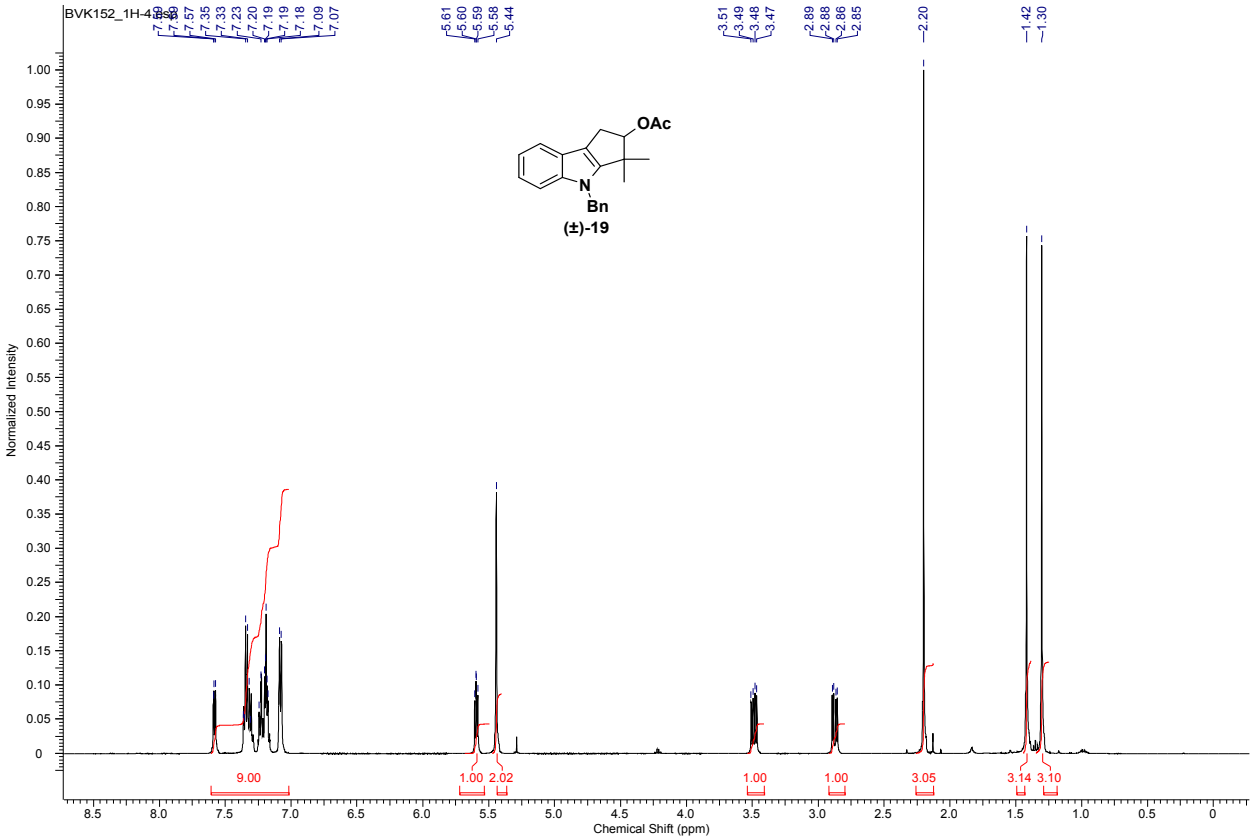

BVKGDD_13C-2.esp
219.41
147.14
139.47
137.69
128.95
127.66
125.96
124.53
121.99
120.28
119.45
110.45
109.61
48.03
37.36
24.18
O
N
Ph
18
Normalized Intensity
Chemical Shift (ppm)

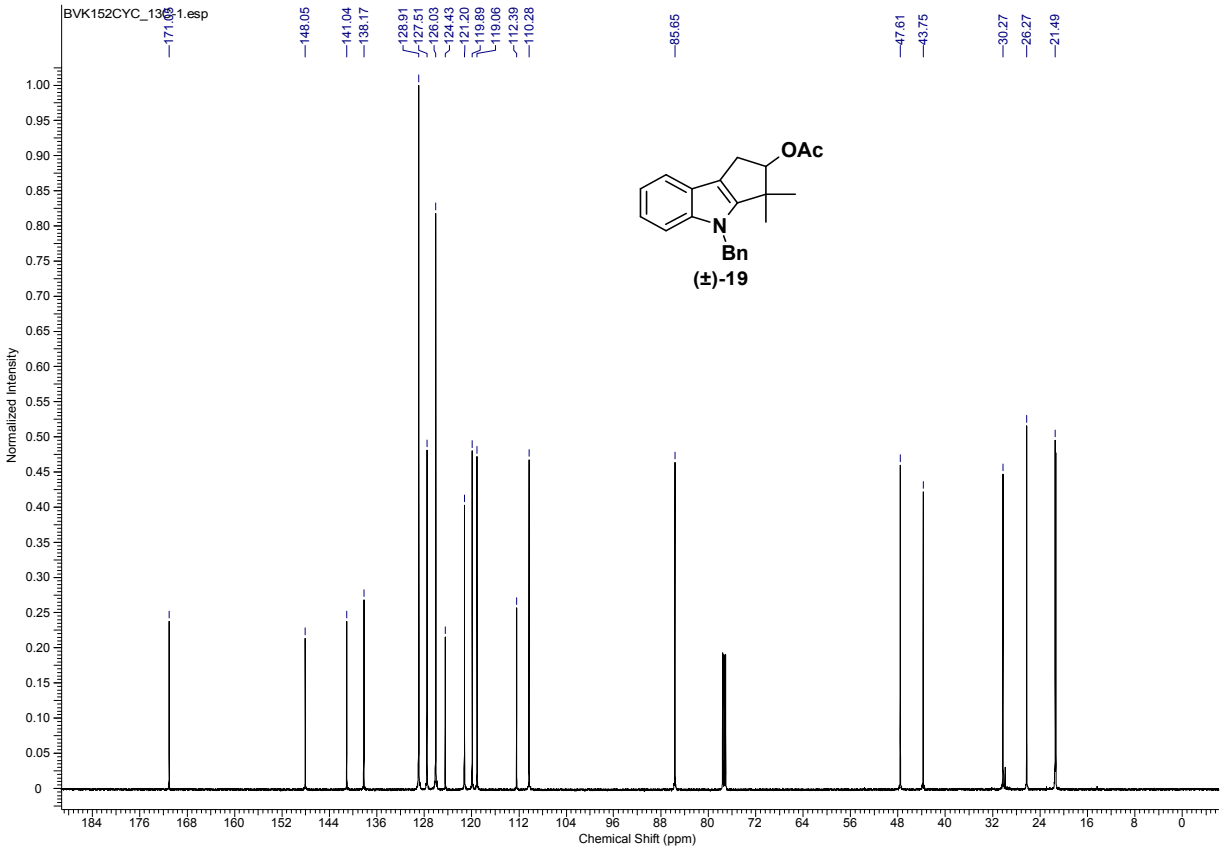

BVK266_1H-4.esp
11.46
7.39
7.37
7.35
7.06
7.05
7.03
6.99
6.97
6.96
3.45
1.26
O
N
H
1
Normalized Intensity
1.00
2.04
2.11
2.11
6.10
Chemical Shift (ppm)

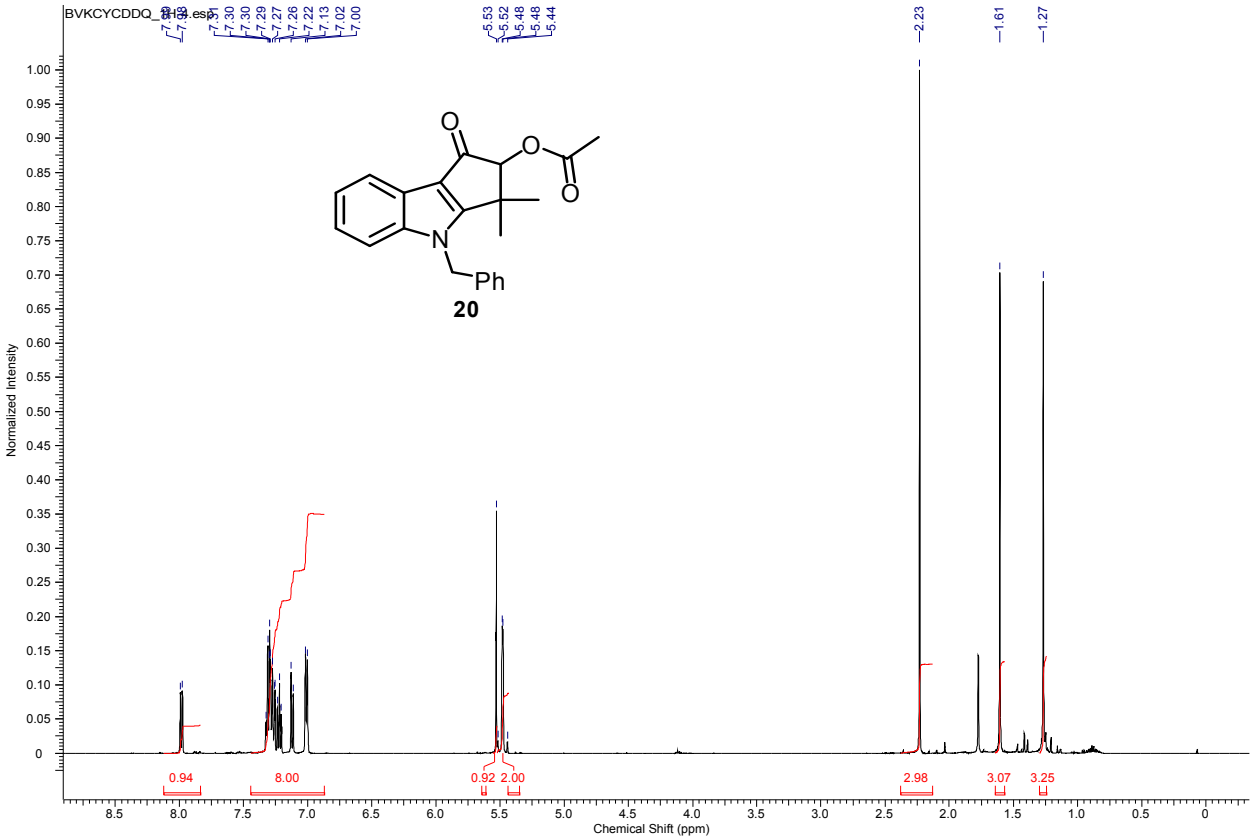

BVK266_13C-3.esp
220.68
147.19
138.75
124.54
121.32
119.62
119.16
112.48
108.18
46.97
37.55
24.29
O
N
H
1
Normalized Intensity
Chemical Shift (ppm)

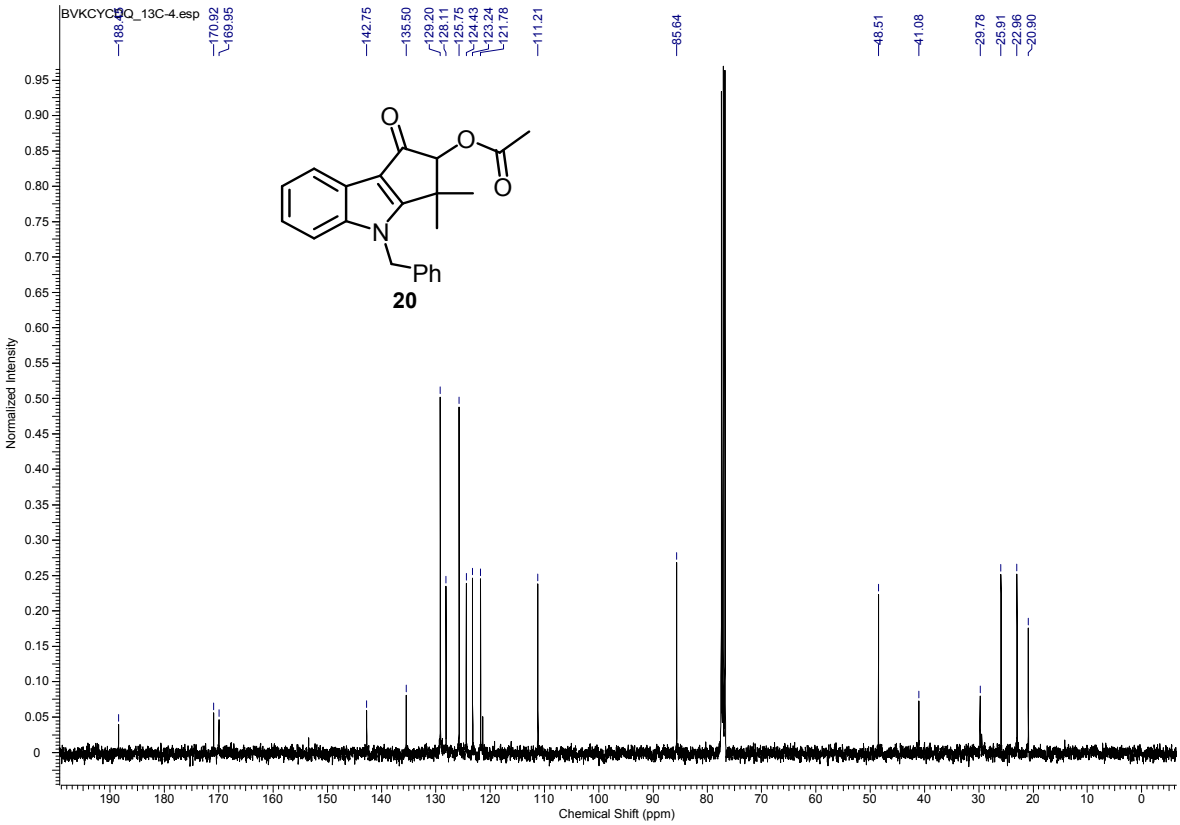

BVK272B_1H-4.esp
7.54
7.53
7.52
7.30
7.29
7.28
7.19
7.14
7.14
7.13
7.05
7.03
5.40
4.45
4.44
4.43
3.33
3.32
3.31
3.29
2.73
2.72
2.71
2.69
2.08
1.34
1.17
OH
N
Bn
(±)-18a
Normalized Intensity
8.81
2.01
0.96
0.99
0.97
1.01
3.15
3.06
Chemical Shift (ppm)

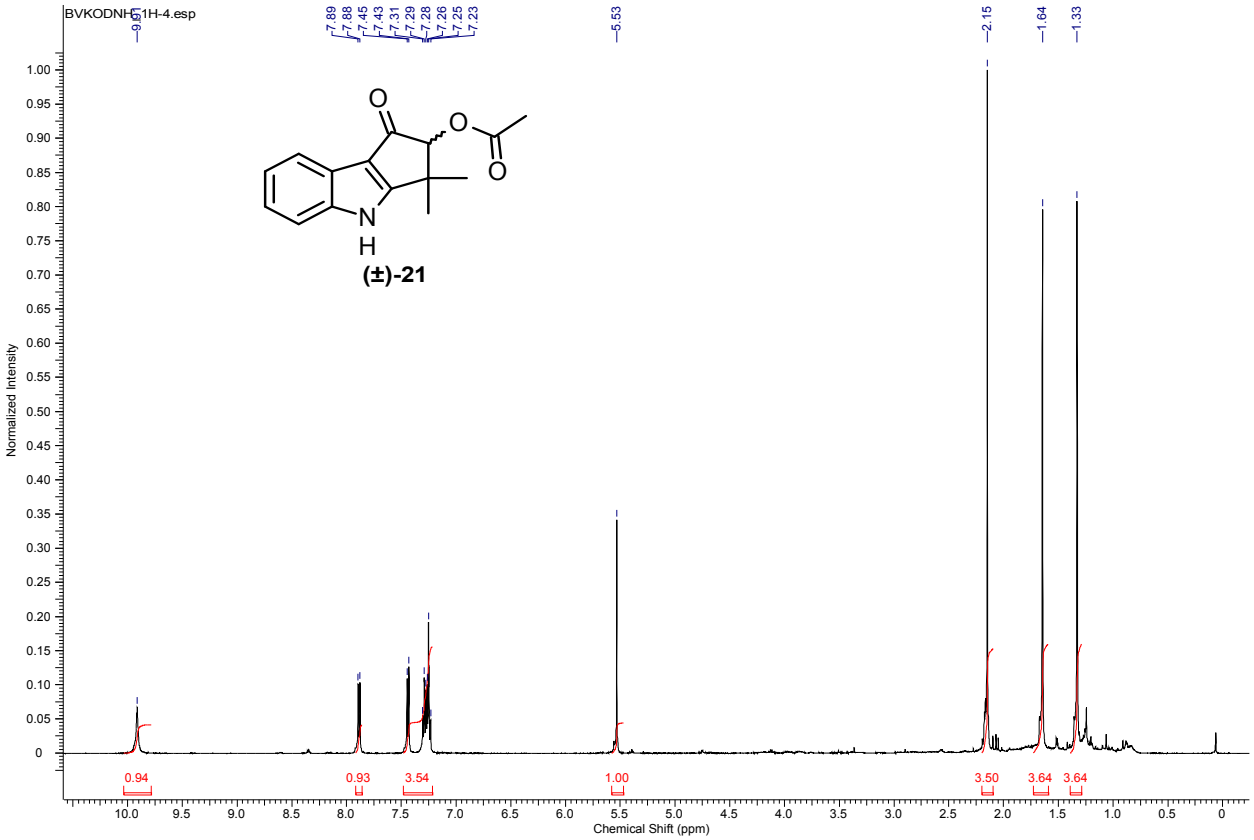

BVK272B_13C-2.esp
148.55
140.58
138.22
128.83
127.42
126.01
124.62
120.93
119.72
118.92
111.76
110.12
85.35
47.56
43.79
32.61
25.59
20.35
OH
N
Bn
(±)-18a
Normalized Intensity
Chemical Shift (ppm)

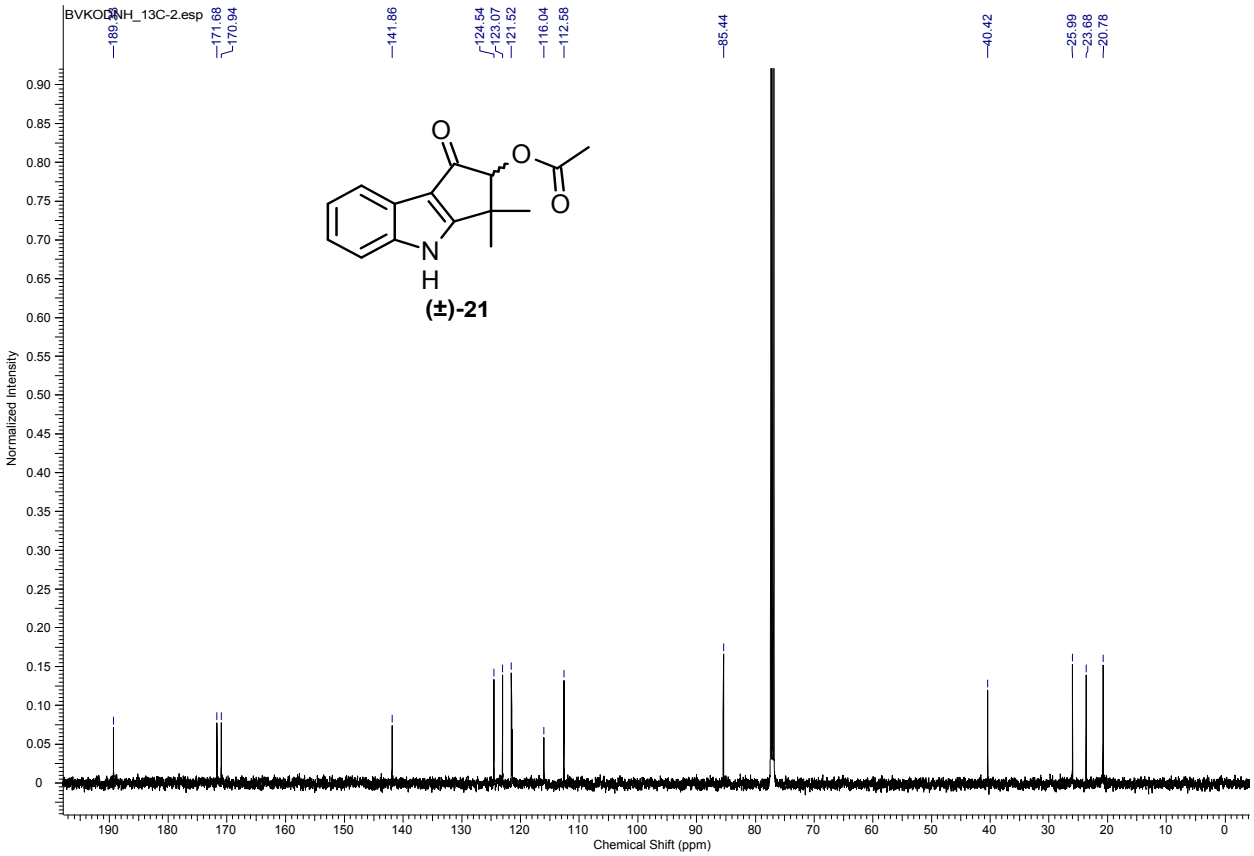

BVK152_1H-4.esp
OAc
N
Bn
(±)-19
Normalized Intensity
Chemical Shift (ppm)
9.00
1.00
2.02
1.00
1.00
3.05
3.14
3.10

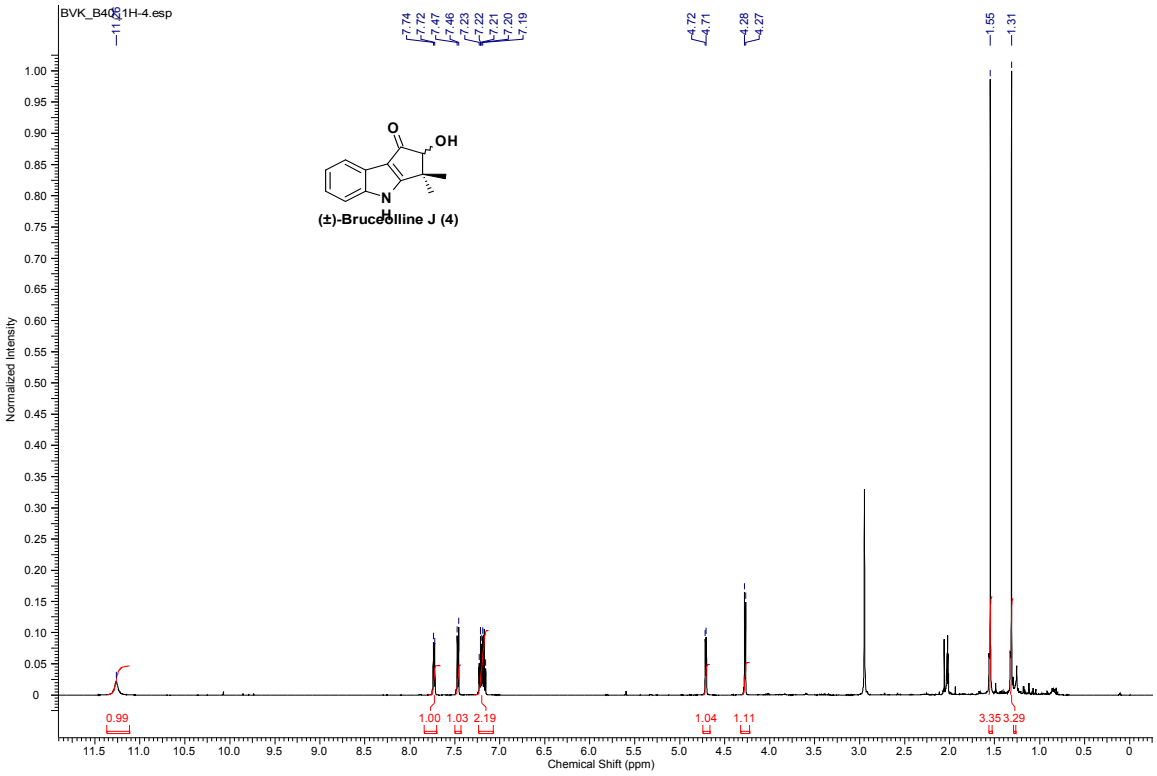

BVK152CYC_13C-1.esp
OAc
N
Bn
(±)-19
Normalized Intensity
Chemical Shift (ppm)

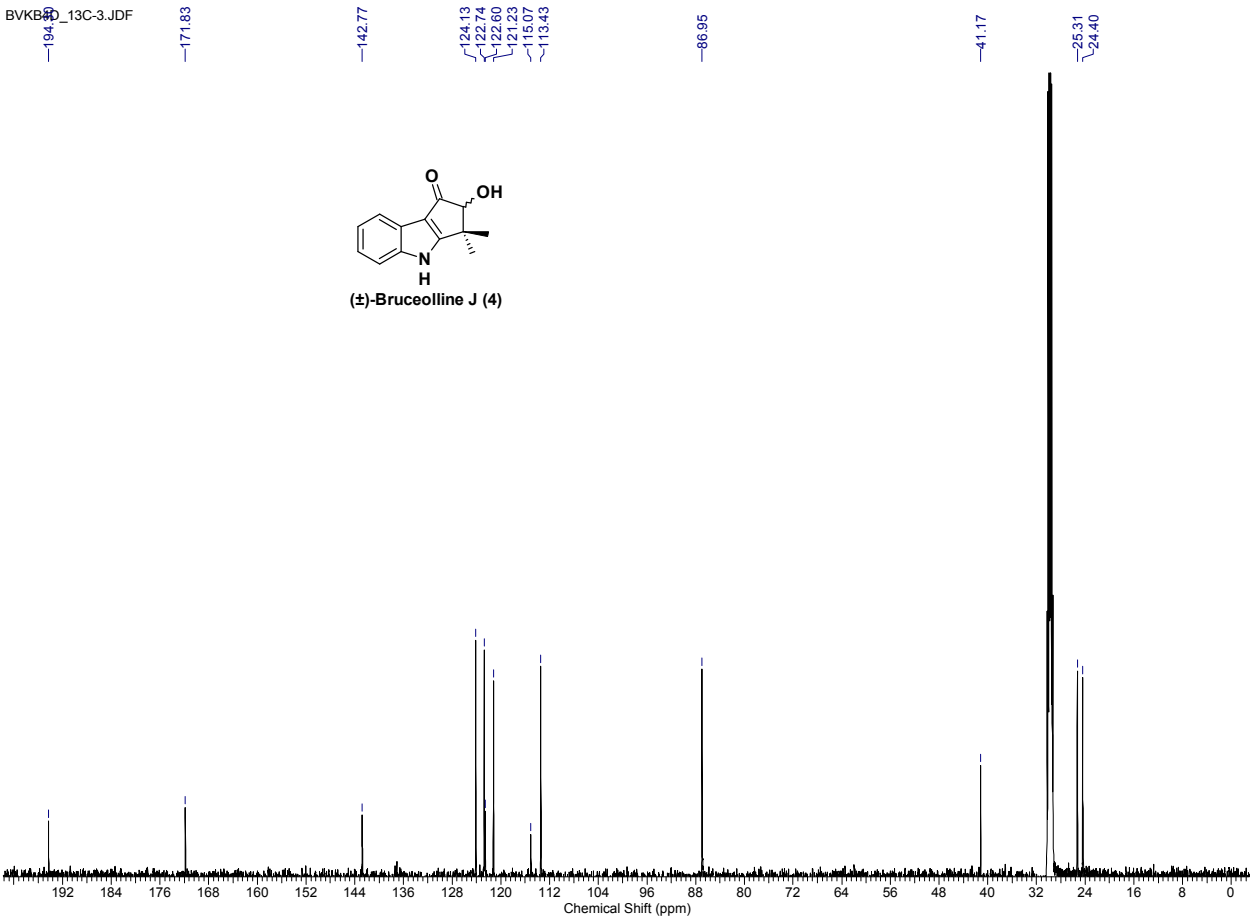

BVKCYCDDQ_1H-3.esp
7.38
7.30
7.30
7.30
7.29
7.27
7.26
7.22
7.13
7.02
7.00
5.53
5.52
5.48
5.48
5.44
2.23
1.61
1.27
O
O
O
N
Ph
20
Normalized Intensity
Chemical Shift (ppm)
0.94
8.00
0.92
2.00
2.98
3.07
3.25

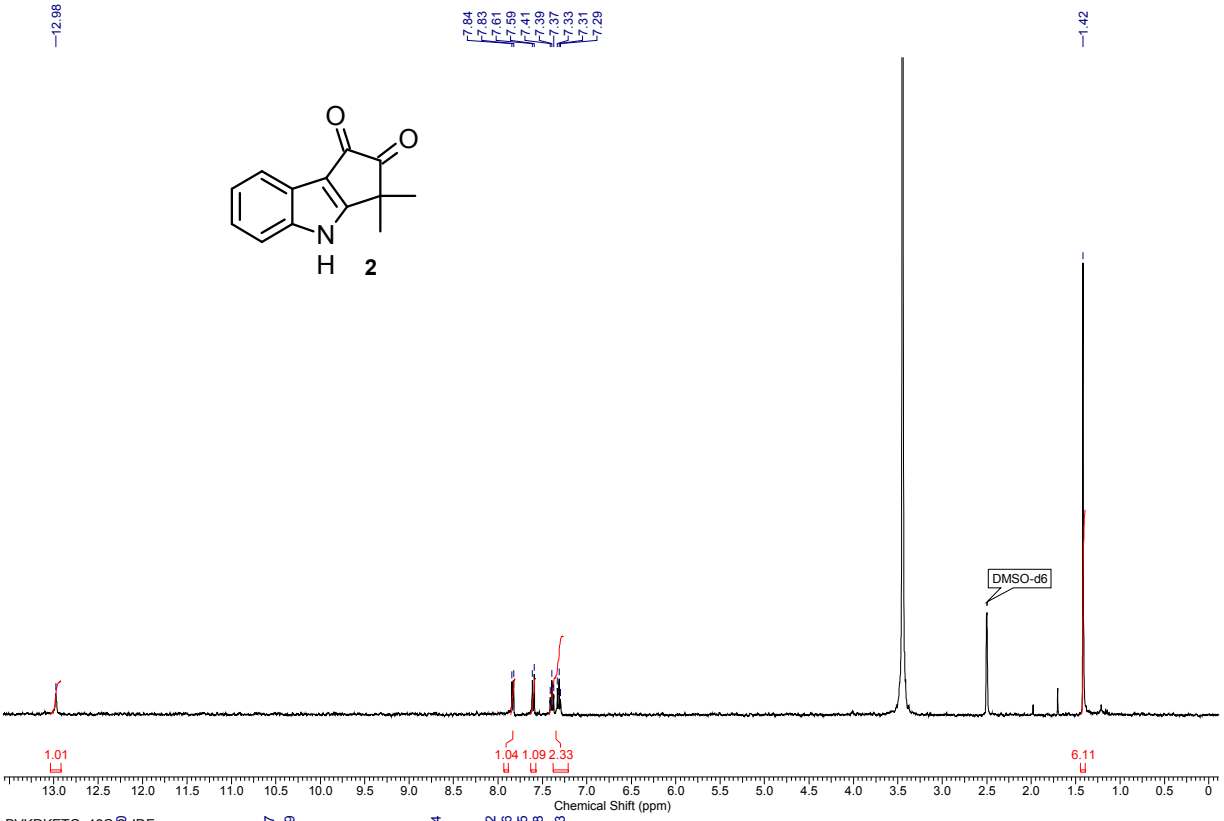

BVKCYCDDQ_13C-4.esp
188.8
170.92
169.95
142.75
135.50
129.20
128.11
125.75
124.43
123.24
121.78
111.21
85.64
48.51
41.08
29.78
25.91
22.96
20.90
O
O
O
N
Ph
20
Normalized Intensity
Chemical Shift (ppm)

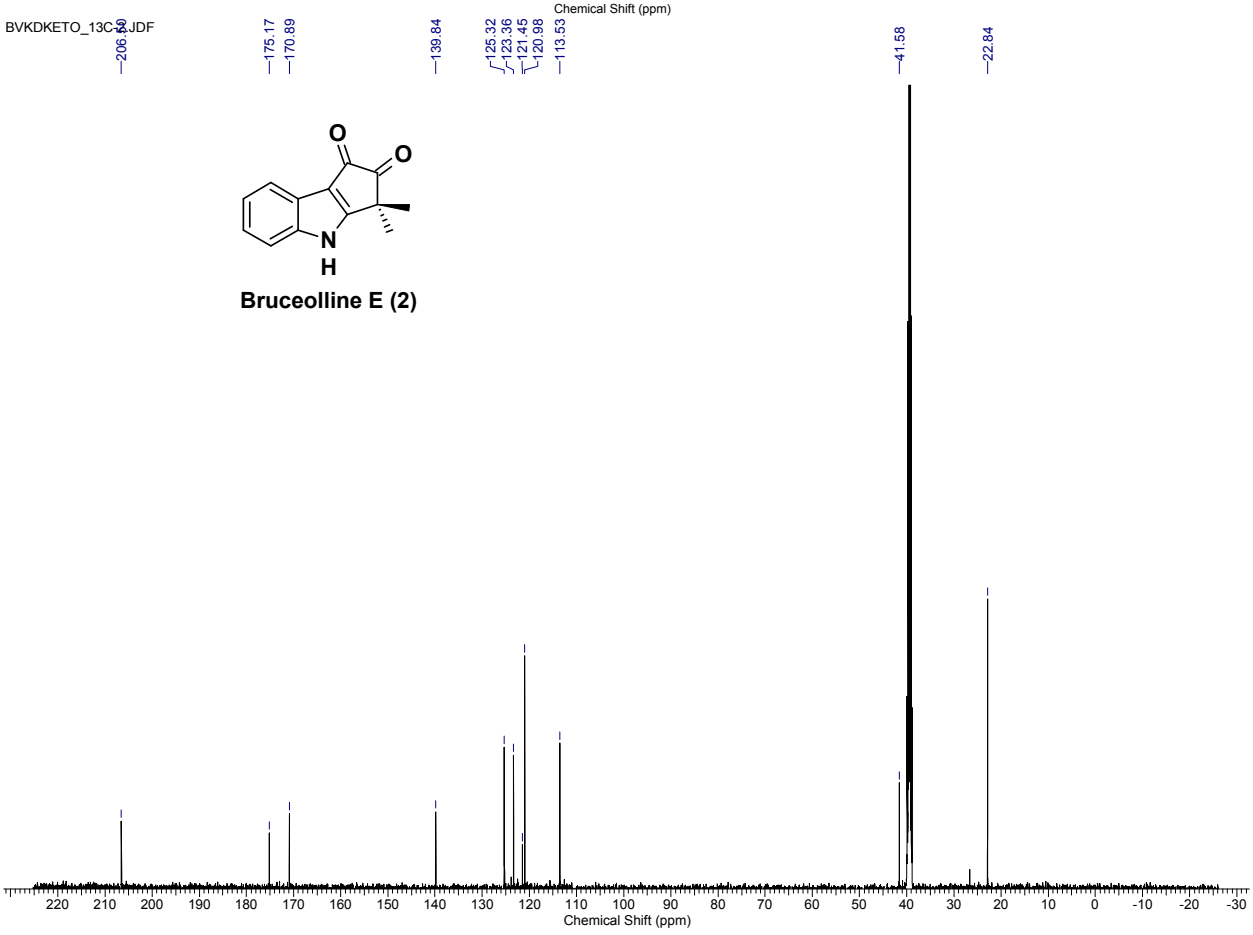

BVKODNH_1H-4.esp
9.67
7.89
7.88
7.45
7.43
7.31
7.29
7.28
7.26
7.25
7.23
5.53
2.15
1.64
1.33
O
O
O
N
H
(±)-21
Normalized Intensity
0.94
0.93
3.54
1.00
3.50
3.64
3.64
Chemical Shift (ppm)

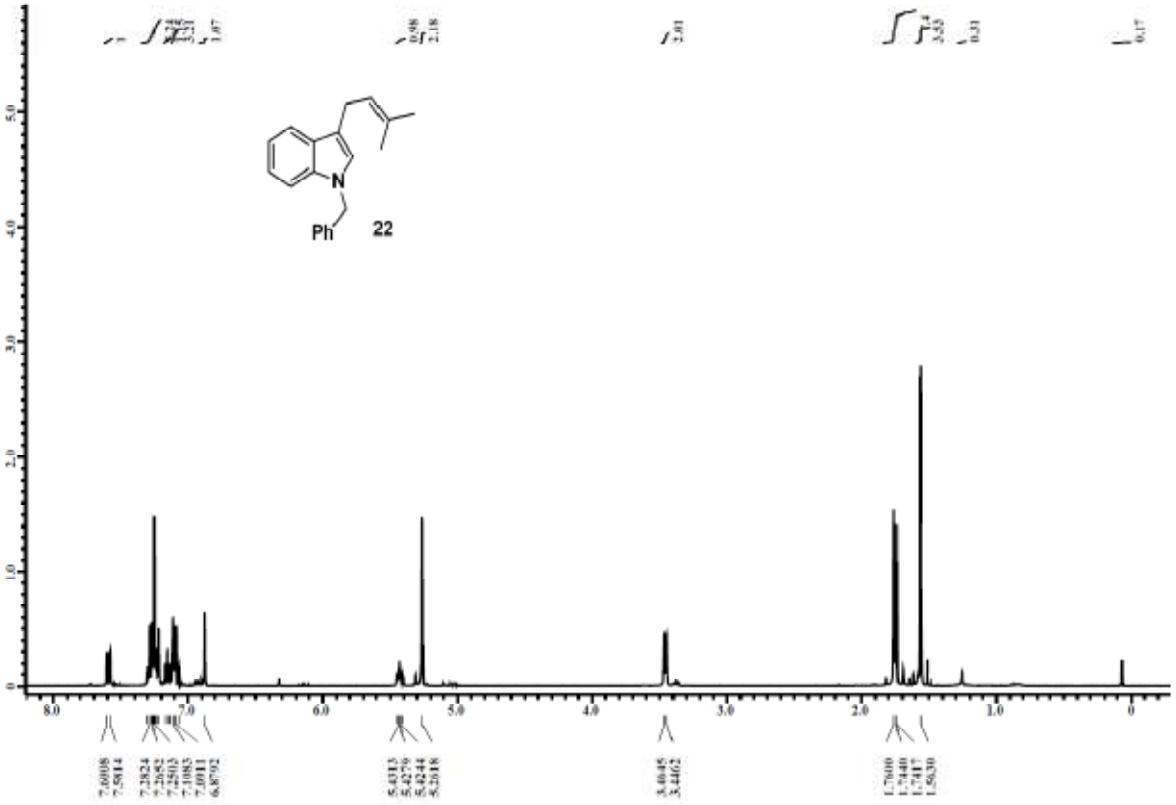

BVKODNH_13C-2.esp
189.38
171.68
170.94
141.86
124.54
123.07
121.52
116.04
112.58
85.44
40.42
25.99
23.68
20.78
O
O
O
N
H
(±)-21
Normalized Intensity
Chemical Shift (ppm)

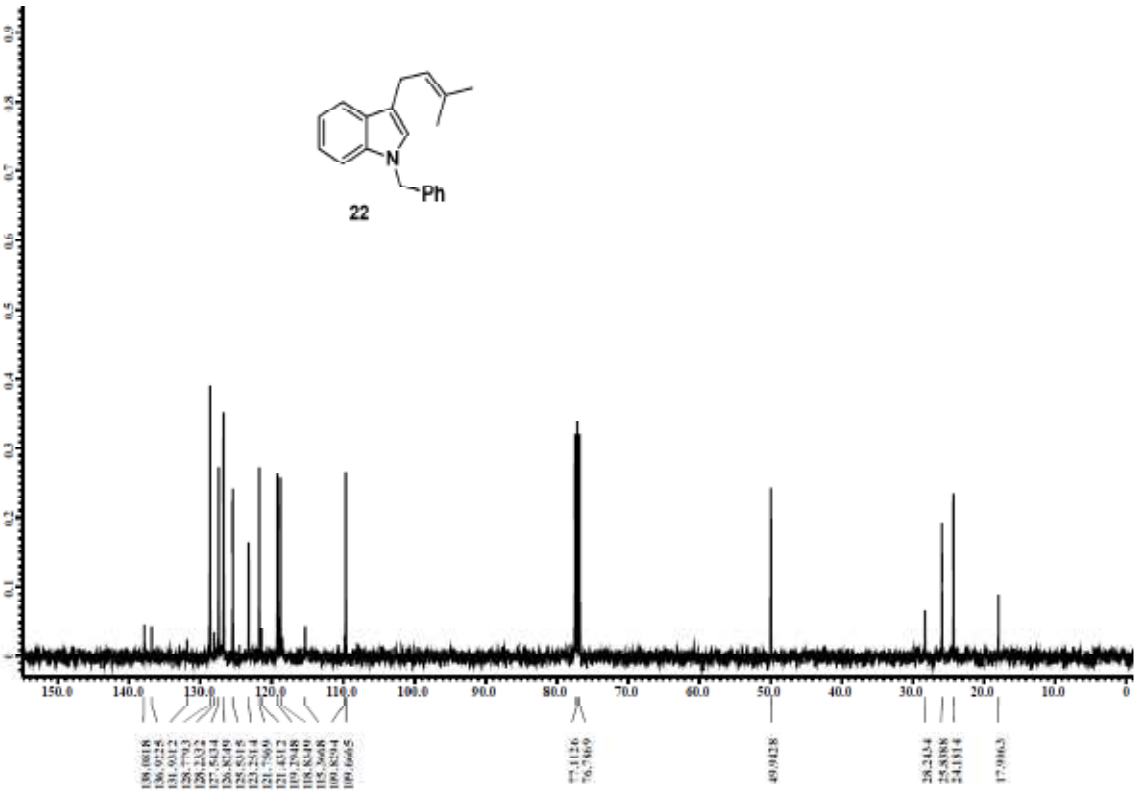

BVK_B40_1H-4.esp
11.68
7.74
7.72
7.47
7.46
7.23
7.22
7.21
7.20
7.19
4.72
4.71
4.28
4.27
1.55
1.31
O
OH
N
H
(±)-Bruceolline J (4)
Normalized Intensity
0.99
1.00
1.03
2.19
1.04
1.11
3.35
3.29
Chemical Shift (ppm)

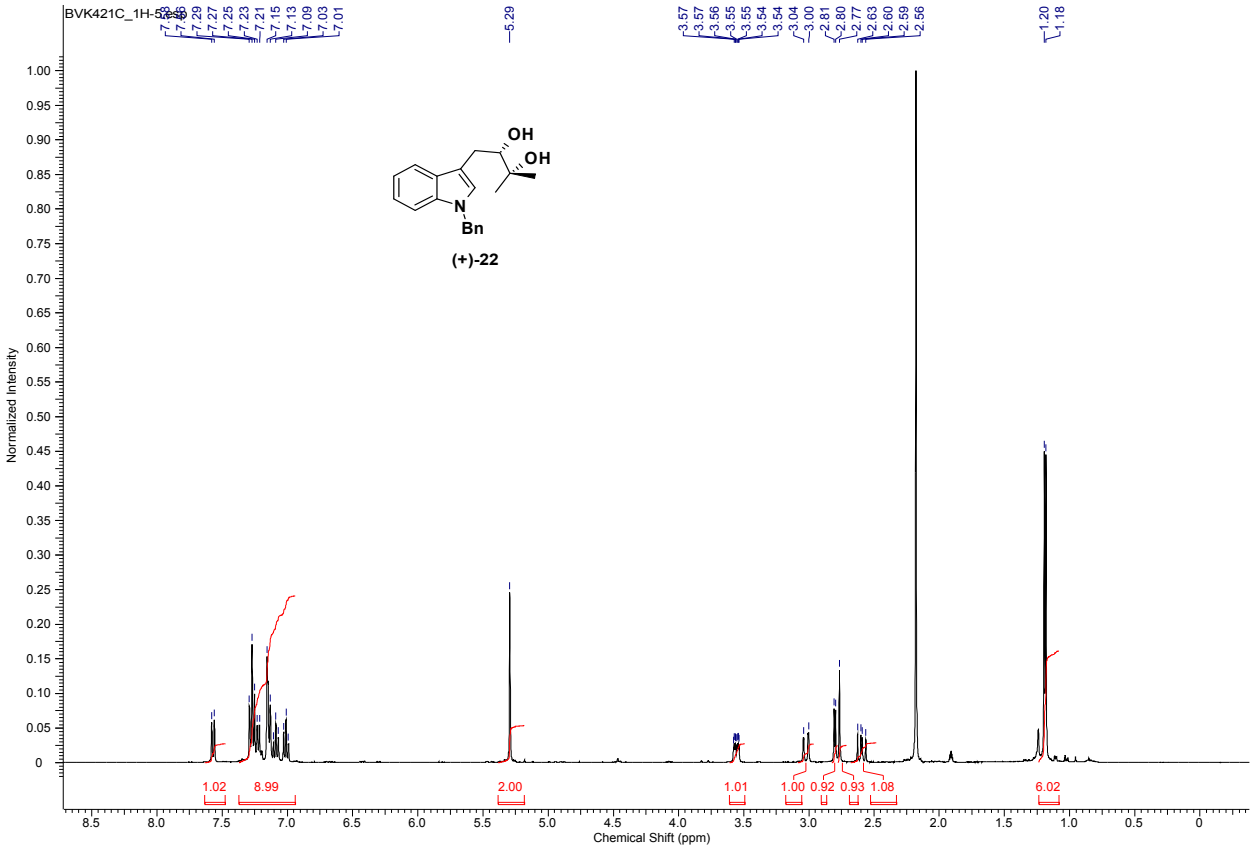

BVKB40_13C-3.JDF
194.10
171.83
142.77
124.13
122.74
122.60
121.23
115.07
113.43
86.95
41.17
25.31
24.40
O
OH
N
H
(±)-Bruceolline J (4)
Chemical Shift (ppm)

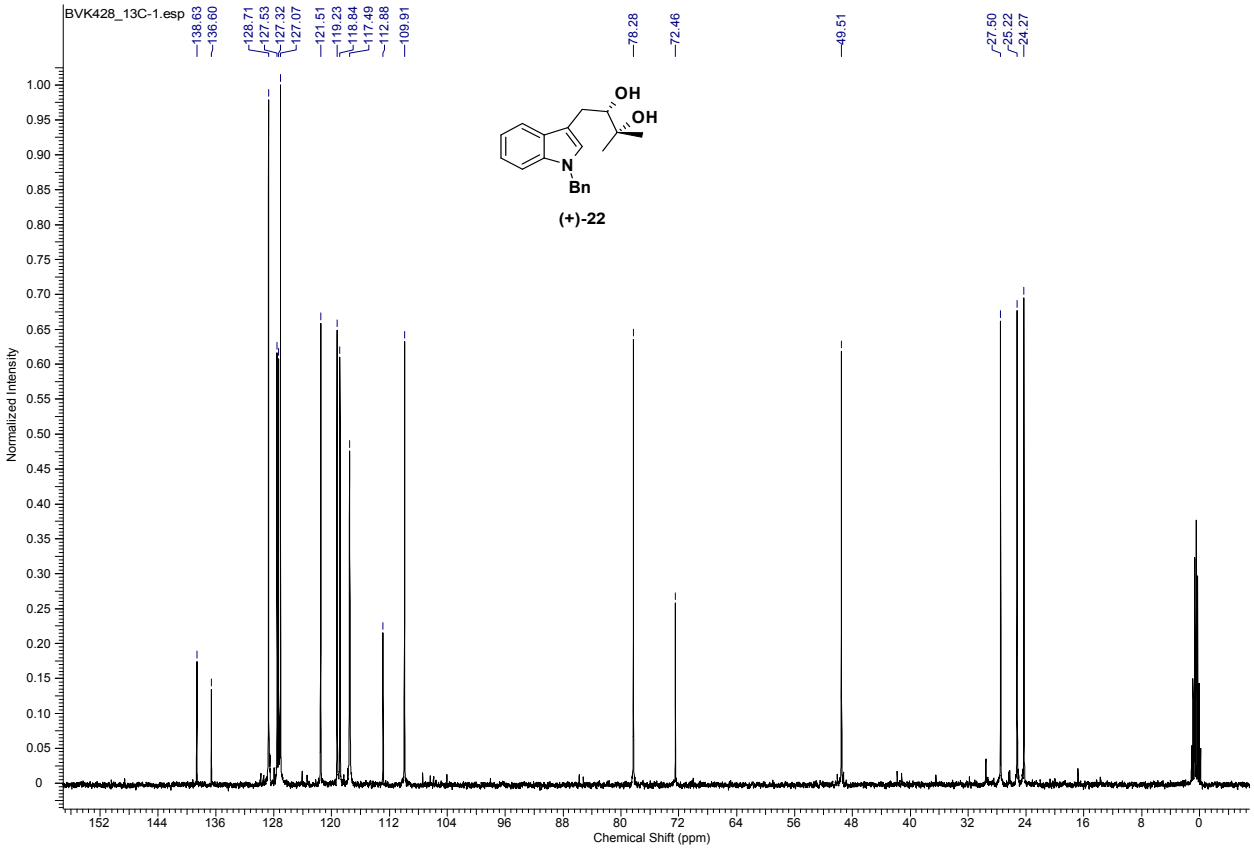

12.98
7.84
7.83
7.61
7.59
7.41
7.39
7.37
7.33
7.31
7.29
1.42
O
O
N
H
2
DMSO-d6
1.01
1.04
1.09
2.33
6.11
Chemical Shift (ppm)

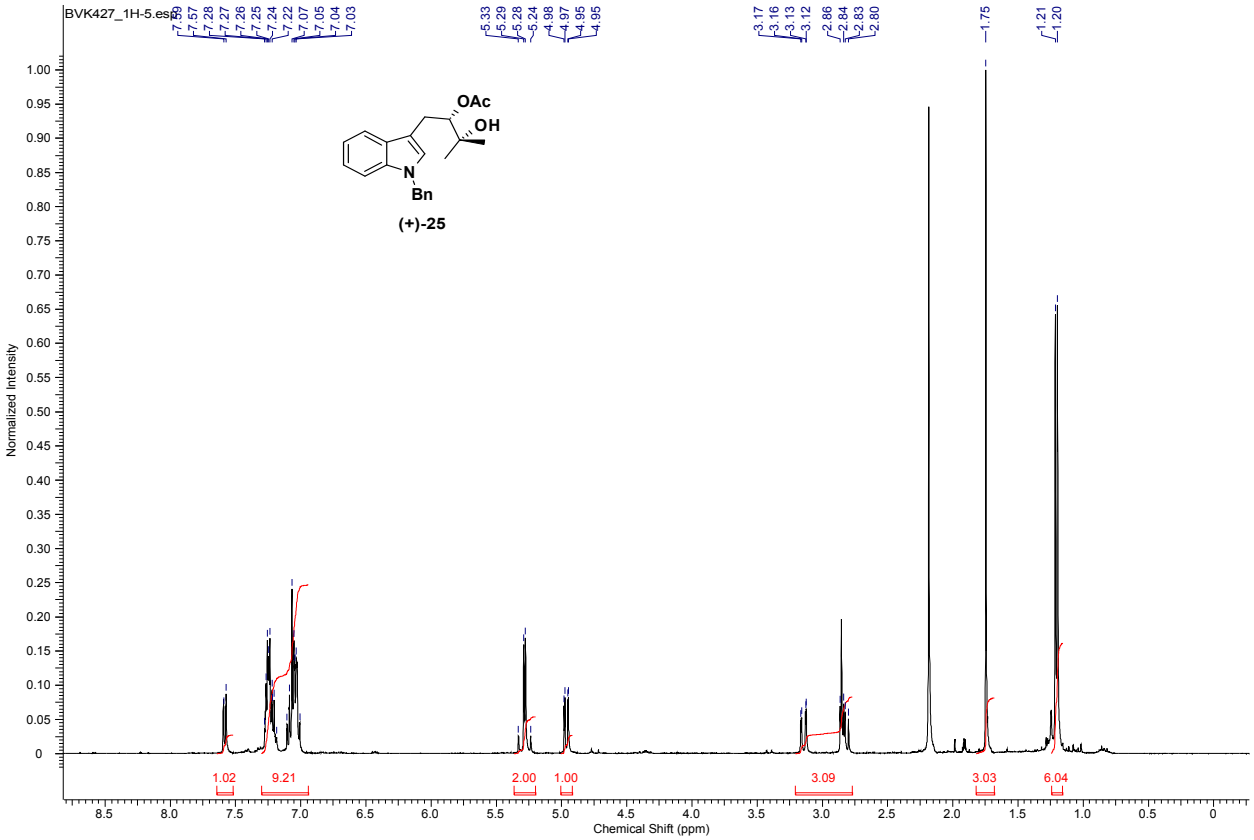

BVKDKETO_13C-1.JDF
206.20
175.17
170.89
139.84
125.32
123.36
121.45
120.98
113.53
41.58
22.84
O
O
N
H
Bruceolline E (2)
Chemical Shift (ppm)

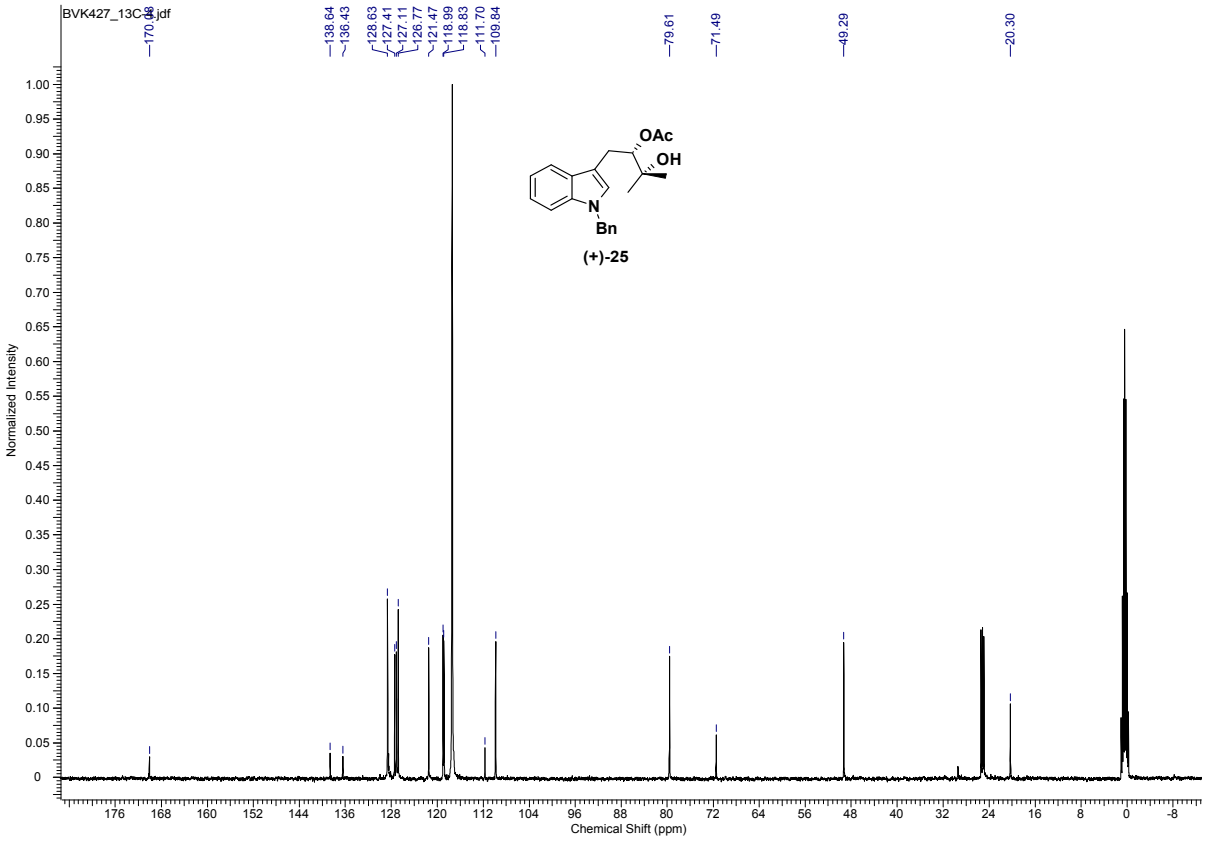

N
Ph
22


N
Ph
22

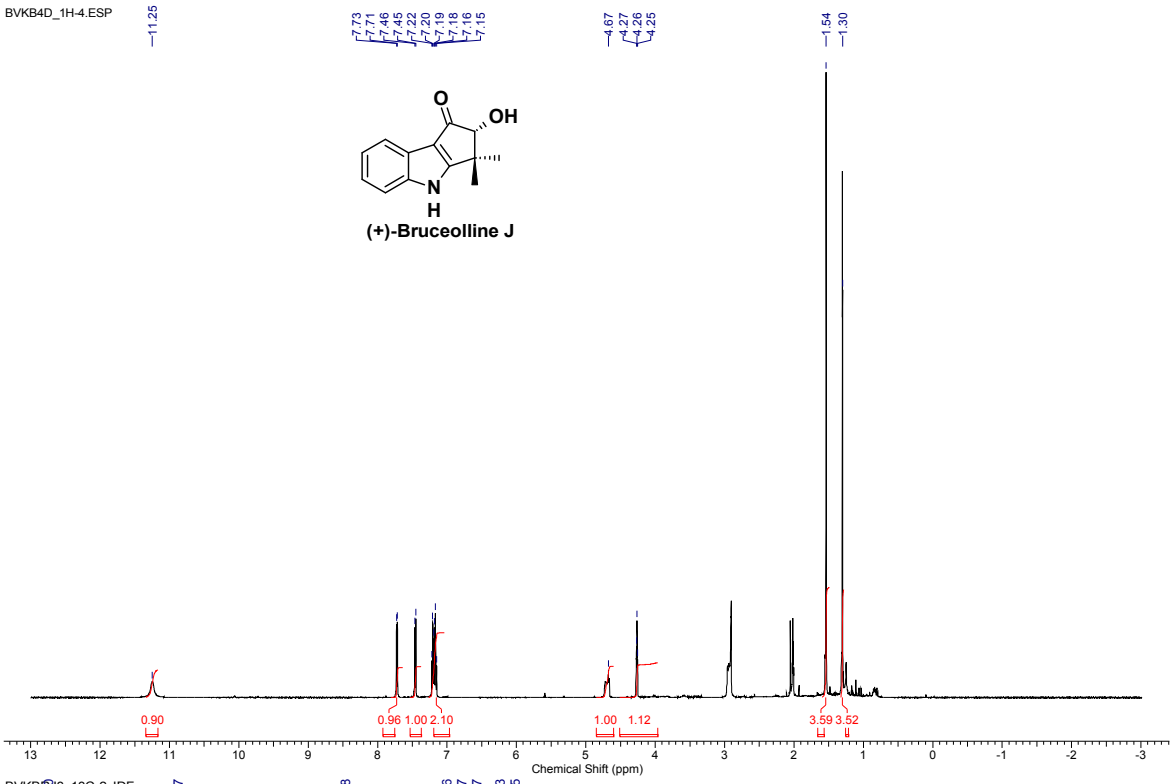

BVK421C_1H-5.esp
OH
OH
N
Bn
(+)-22
Normalized Intensity
Chemical Shift (ppm)
1.02
8.99
2.00
1.01
1.00
0.92
0.93
1.08
6.02

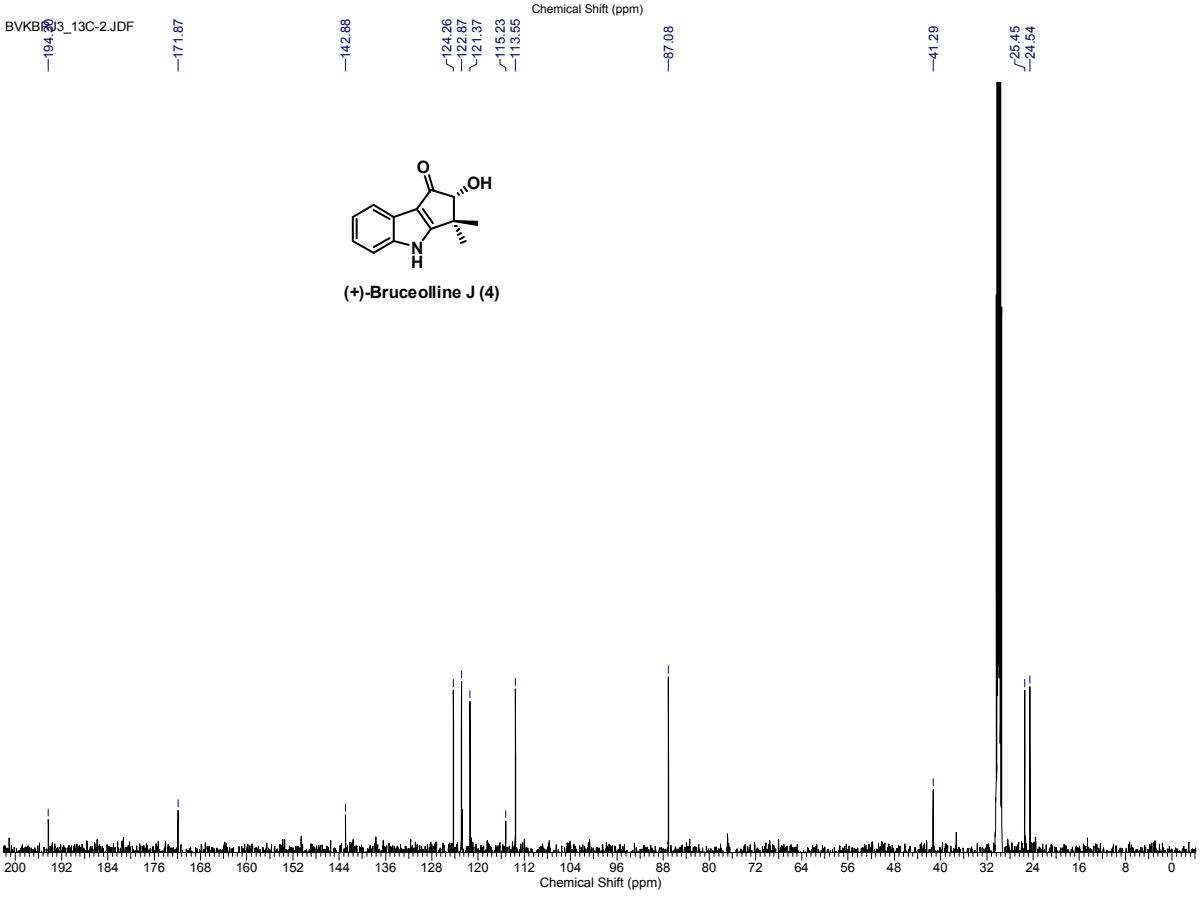

BVK428_13C-1.esp
OH
OH
N
Bn
(+)-22
Normalized Intensity
Chemical Shift (ppm)


BVK427_1H-5.esp
7.59
7.57
7.28
7.27
7.26
7.25
7.24
7.22
7.07
7.05
7.04
7.03
5.33
5.29
5.28
5.24
4.98
4.97
4.95
4.95
3.17
3.16
3.13
3.12
2.86
2.84
2.83
2.80
1.75
1.21
1.20
OAc
OH
N
Bn
(+)-25
Normalized Intensity
1.02
9.21
2.00
1.00
3.09
3.03
6.04
Chemical Shift (ppm)

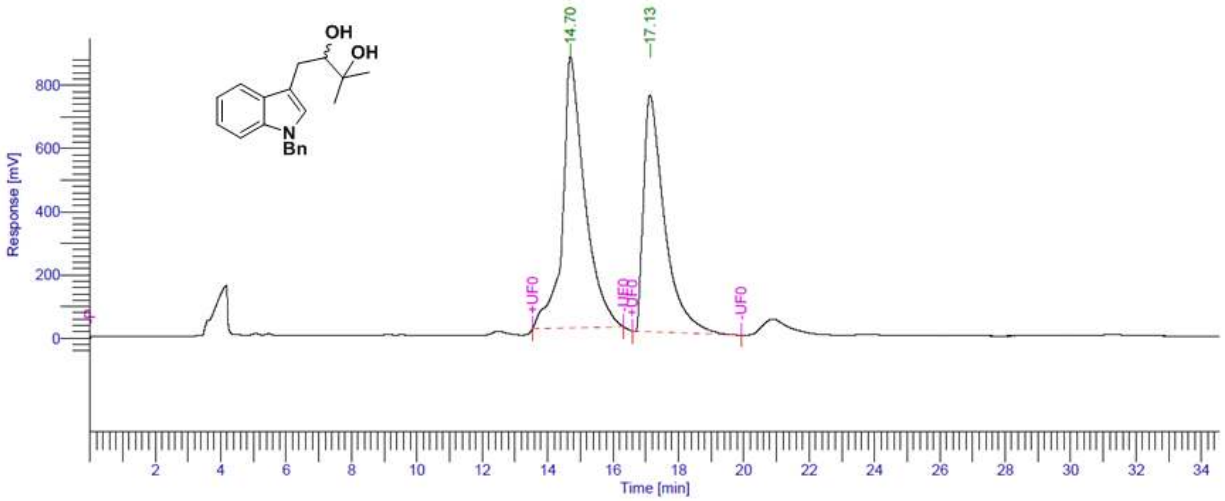

BVK427_13C-3.jdf
170.48
138.64
136.43
128.63
127.41
127.11
126.77
121.47
118.99
118.83
111.70
109.84
79.61
71.49
49.29
20.30
OAc
OH
N
Bn
(+)-25
Normalized Intensity
Chemical Shift (ppm)

^{1}H and ^{13}C NMR spectra of (+)-Bruceolline J:





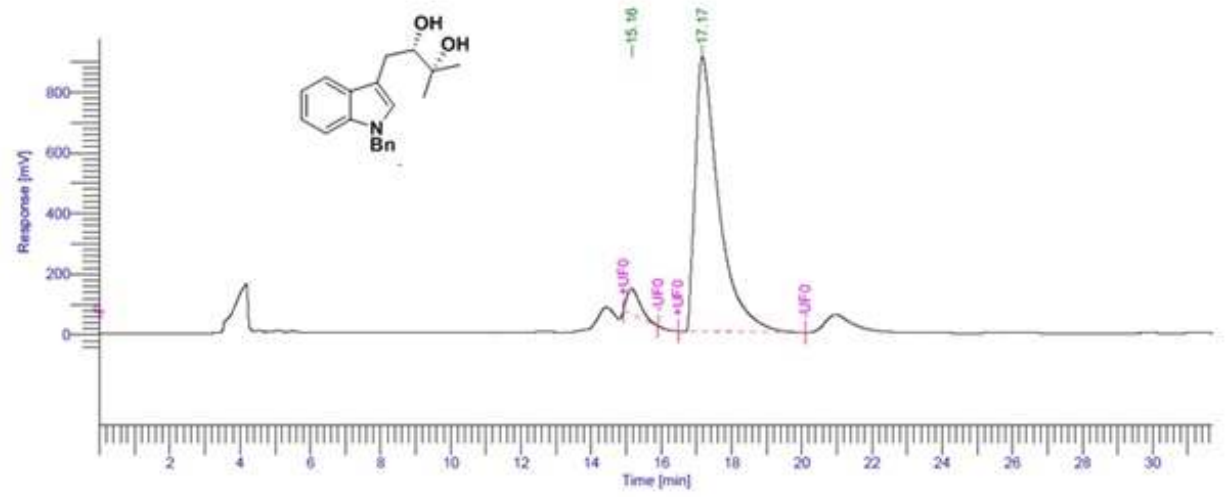
HPLC Chromatogram of racemic (±)-22:



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		14.700	40547577.89	858759.56	54.89	54.89
2		17.133	33321300.34	749935.46	45.11	45.11
			73868878.23	1.61e+06	100.00	100.00

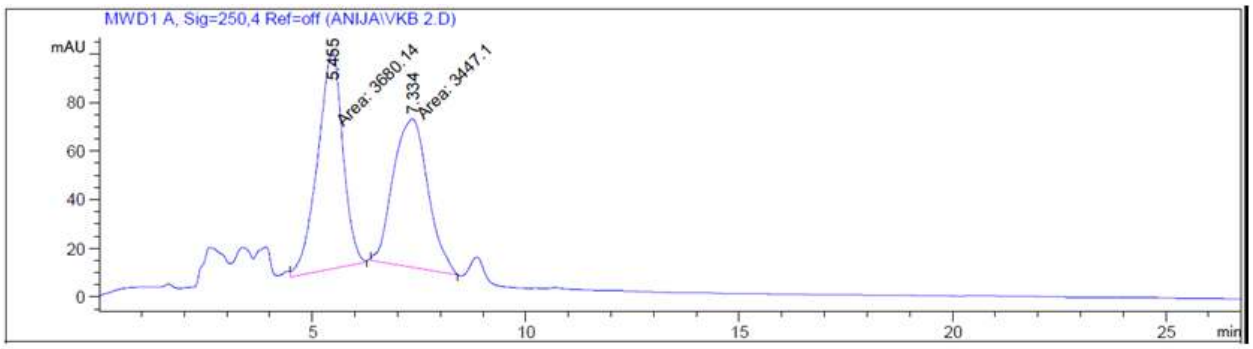
HPLC Chromatogram of Chiral (+)-22:



DEFAULT REPORT

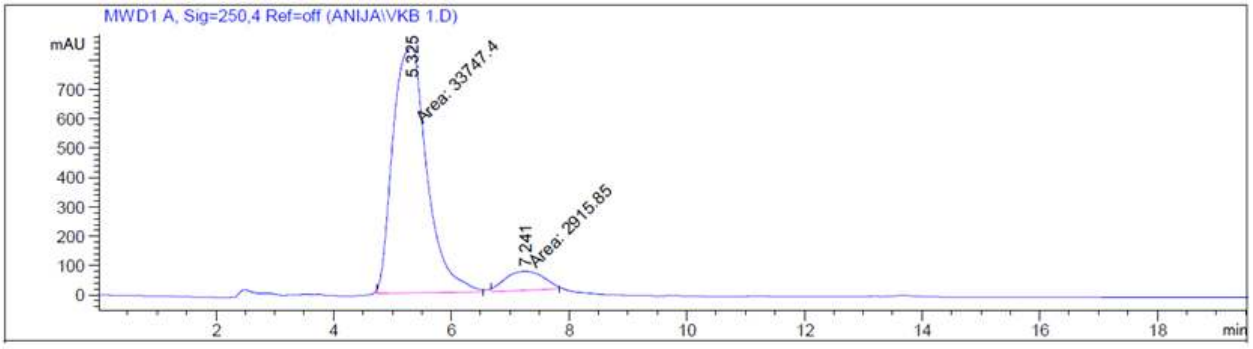
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		15.162	2162564.88	84331.95	4.85	4.85
2		17.168	42426470.76	906332.89	95.15	95.15
			44589035.64	990664.84	100.00	100.00

HPLC Chromatogram of (±)-Bruceolline J (4):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.455	MM	0.6842	3680.14355	89.64825	51.6348
2	7.334	MM	0.9433	3447.10425	60.90742	48.3652

HPLC Chromatogram of (+)-Bruceolline J (4):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.325	MM	0.6726	3.37474e4	836.26556	92.0469
2	7.241	MM	0.7595	2915.85254	63.98799	7.9531

Crystallographic Data of the Compound 17:

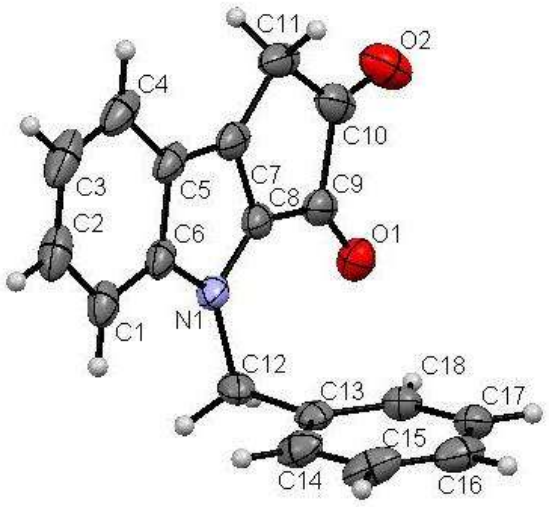


Table 1. Crystal data and structure refinement for compound **17**.

Identification code	22aprbm	
Empirical formula	C18 H13 N O2	
Formula weight	275.29	
Temperature	153(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.159(5) Å	α= 78.846(5)°.
	b = 9.364(5) Å	β= 82.356(5)°.
	c = 10.541(5) Å	γ = 72.557(5)°.
Volume	659.3(7) $Å^3$	
Z	2	
Density (calculated)	1.387 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	288	
Crystal size	0.12 x 0.09 x 0.07 mm^3	
Theta range for data collection	4.09 to 25.03°.	
Index ranges	-8<=h<=7, -11<=k<=11, -12<=l<=11	
Reflections collected	3408	
Independent reflections	2278 [R(int) = 0.0160]	

Completeness to theta = 25.03°	97.5 %
Absorption correction	Empirical
Max. and min. transmission	0.994 and 0.990
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2278 / 0 / 190
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1428
R indices (all data)	R1 = 0.0701, wR2 = 0.1585
Largest diff. peak and hole	0.246 and -0.240 e.$Å^{-3}$