Supporting Information

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Total Synthesis of Myristinins A-F and 3'-Hydroxy-5,7-dimethoxy-4-O-2'-cycloflavan by Iterative Generation of *o*-Quinone Methides

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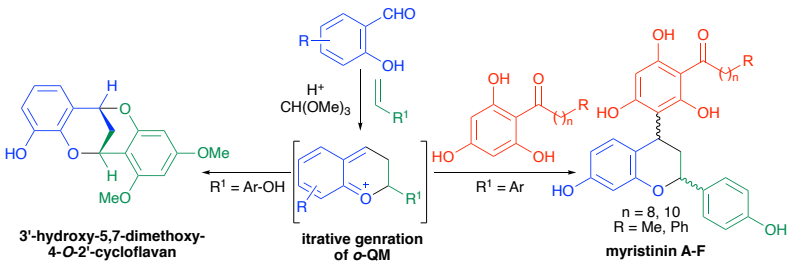


An iterative generation of *o*-quinone methides (*o*-QMs) and [4+2] cycloaddition followed by inter/intra-molecular Michael addition in the cascade sequence.

General experimental

Melting points are recorded using Tempo melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer and JASCO, FT/IR-4100 spectrophotometer. ^{1}H (400 and 500 MHz) and ^{13}C (100 and 125MHz) spectra were recorded on Bruker Avance 400 and 500 spectrophotometers. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to internal chloroform (at 7.26 ppm for ^{1}H and the central line 77.16 ppm for ^{13}C of $CDCl_3$). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment and is given in parentheses. NOE spectrum was recorded in Bruker Avance 400 spectrophotometer. ^{1}H-^{1}H NOESY spectrum was recorded in Bruker Avance 500 spectrometer. High resolution mass measurements were carried out using Micro mass Q-ToF instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with Merck silica gel G containing 13% calcium sulphate as binder or on pr 0.2 mm thick Merck 60 F245 silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by exposure to iodine vapour and $KMnO_4$ stains. All compounds were purified using silica gel [Acme's silica gel (100-200 mesh)] chromatography (approximately 15-20 g per 1 g of the crude product) and gave spectroscopic data consistent with being ≥95% the assigned structure. All small-scale dry reactions were carried out using standard syringe septum technique. Dry THF was obtained by distillation over sodium-benzophenone ketyl. dichloromethane, benzene, acetonitrile and chloroform were distilled from calcium hydride prior to use.

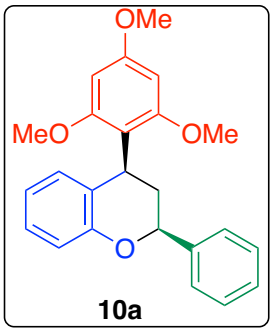
EXPERIMENTAL PROCEDURES AND SPECTRAL DATA

Note: *In the cases wherein diastereomeric mixtures of products were obtained, the data for the major isomer have been mentioned and the diastereomeric ratio measured on the crude reaction mixture by ^1H NMR.*

Experimental Procedure for the synthesis of cassiaflavans

***(2S*,4S*)-2-phenyl-4-(2,4,6-trimethoxyphenyl)chroman* (10a):**

To a cold (0 °C) magnetically stirred solution of salicylaldehyde (**7a**) (87 μL, 0.82 mmol), (±)-camphor sulphonic acid (CSA) (9.5 mg, 0.04 mmol), in dry CH_3CN (8 mL), was added trimethyl orthoformate (136 μL, 1.23 mmol) and stirred for 10 min. Then the styrene (**8a**) (141 μL, 1.23 mmol) was added slowly at 0 °C the resulting mixture was stirred at room temperature, and then the trimethoxy benzene (**9a**) (207 mg, 1.23 mmol,) in dry CH_3CN (2 mL), was slowly added at 0 °C the resulting mixture was stirred for 1h at 0 °C then slowly warmed to room temperature. After completion of the reaction (TLC control), the reaction mixture was carefully quenched with saturated sodium hydrogen carbonate solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL), the combined organic layer was washed with brine and dried over anhydrous sodium sulphate. Evaporation of the solvent and purification of the residue on silica gel column, using EtOAc:petroleum ether (from 1% to 15% ethyl acetate) as an eluent afforded the required bicyclic product **10a** (205 mg, 66%).



10a

Physical appearance: white foamy solid.

R_f: 0.6 (1: 3, EtOAc:petroleum ether).

IR (neat): 2925, 2854, 1626, 1599, 1427, 1221, 1135, 1107, 1121, 902, 753cm^{-1}.

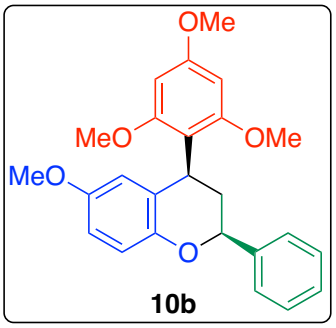
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.62-7.56 (m, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.38 (d, J = 7.3 Hz, 1H), 7.12 (ddd, J = 8.5, 6.0, 2.7 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.82 (q, J = 4.6, 3.9 Hz, 2H), 6.29 (d, J = 2.4 Hz, 1H), 6.18 (d, J = 2.4 Hz, 1H), 5.26 (dd, J = 11.6, 1.9 Hz, 1H), 5.05 (dd, J = 12.0, 5.9 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 3.50 (s, 3H), 2.77 (q, J = 12.3 Hz, 1H), 2.19 (ddd, J = 13.3, 5.9, 1.9 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*, DEPT): δ 160.0 (C), 159.8 (C), 159.3 (C), 155.3 (C), 142.0 (C), 128.5 (2 x CH), 127.8 (CH), 127.5 (CH), 127.4 (C), 126.3 (CH), 126.3 (2 x CH), 120.2 (CH), 116.5 (CH), 112.7 (C), 92.3 (CH), 90.7 (CH), 78.8 (CH), 56.1 (OCH_3), 55.6 (OCH_3), 55.3 (OCH_3), 35.1 (CH_2), 32.1 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{24}H_{24}NaO_4$ 433.1985, found 433.1987.

***(2S*,4S*)-6-methoxy-2-phenyl-4-(2,4,6-trimethoxyphenyl)chroman* (10b):**

The reaction of salicylaldehyde **7b** (82 μL, 0.66 mmol), styrene (**8a**) (115 μL, 0.99 mmol) and trimethoxy benzene (**9a**) (166 mg, 0.99 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (7.6 mg, 0.03 mmol) and trimethyl orthoformate (110 μL, 0.9858 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10b** (191 mg, 71%).



10b

Physical appearance: White solid.

R_f: 0.6 (1:3, EtOAc:petroleum ether).

IR (neat): 2815, 2794, 1624, 1600, 1428, 1231, 1138, 1109, 1100, 901, 752 cm^{-1}.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 8.7 Hz, 1H), 6.66 (ddd, J = 14.8, 8.9, 3.1 Hz, 2H), 6.34 (dd, J = 10.9, 3.1 Hz, 2H), 6.28-6.19 (m, 1H), 6.17 (s, 2H), 4.94 (dd, J = 12.0, 6.1 Hz, 1H), 4.53 (t, J = 6.6 Hz, 1H), 3.65 (s, 6H), 3.60 (s, 3H), 3.49 (s, 3H), 2.67 (q, J = 12.2 Hz, 1H), 2.31 (dt, J = 13.9, 7.0 Hz, 1H).

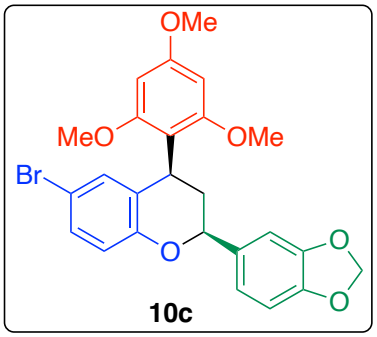
^{13}C NMR (100 MHz, Chloroform-*d*, DEPT): δ 161.6 (C), 159.8 (C), 159.4 (C), 153.7 (C), 149.8 (C), 142.5 (C), 128.5 (2 x CH), 127.9 (CH), 126.3 (2 x CH), 116.8 (CH), 114.9 (CH), 113.3 (CH), 112.3 (C),111.6 (C), 92.3 (CH), 90.7 (CH), 78.9 (CH), 56.2 (CH_3), 55.9 (CH_3), 55.4 (CH_3), 55.2 (CH_3), 35.1 (CH_2), 32.4 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{25}H_{26}NaO_5$ 429.1672, found 429.1675.

***(2S*,4S*)-2-(benzo[d][1,3]dioxol-5-yl)-6-bromo-4-(2,4,6-trimethoxyphenyl)chroman* (10c):**

The reaction of salicylaldehyde **7c** (100 mg, 0.4974 mmol), styrene **8b** (111 mg, 0.75 mmol) and trimethoxy benzene (**9a**) (126 mg, 0.75 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (5.7 mg, 0.03 mmol) and trimethyl orthoformate (83 μL, 0.75 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10c** (194 mg, 78%).

Physical appearance: White Solid.



R_f: 0.4 (1: 3, EtOAc:petroleum ether).

IR (neat): 2925, 2854, 1626, 1609, 1437, 1221, 1146, 1131, 1101, 904, 756cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.12 (d, J = 8.8 Hz, 1H), 7.00 (s, 1H), 6.91 (dd, J = 19.4, 10.4 Hz, 1H), 6.85-6.79 (m, 2H), 6.76 (d, J = 8.5 Hz, 1H), 6.21 (s, 1H), 6.11 (s, 1H), 5.96 (s, 2H), 5.05 (d, J = 11.5 Hz, 1H), 4.87 (dd, J = 12.1, 5.9 Hz, 1H), 3.84 (d, J = 12.6 Hz, 6H), 3.48 (s, 3H), 2.58 (q, J = 12.3 Hz, 1H), 2.04 (dd, J = 13.6, 5.7 Hz, 1H).

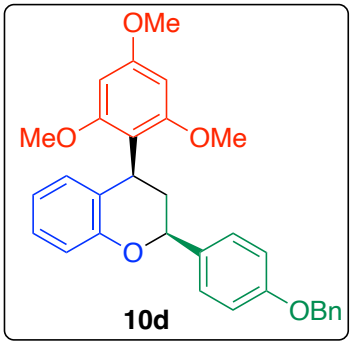
^{13}C NMR (125 MHz, Chloroform-*d*, DEPT): δ 160.3 (C), 159.6 (C), 159.2 (C), 154.5 (C), 147.9 (C), 147.4 (C), 135.5 (C), 130.7 (C), 130.0 (C), 129.9 (CH), 120.0 (CH), 112.5 (C), 111.7 (CH), 108.3 (CH), 107.0 (C), 106.8 (CH), 101.1 (CH_2), 92.3 (CH), 90.8 (CH), 78.9 (CH), 56.1 (CH_3), 55.6 (CH_3), 55.4 (CH_3), 34.7 (CH_2), 32.1 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{25}H_{23}BrNaO_6$ 521.0570, found 521.0572.

***(2S*,4S*)-2-(4-(benzyloxy)phenyl)-4-(2,4,6-trimethoxyphenyl)chroman* (10d):**

The reaction of salicylaldehyde (**7a**) (87 μL, 0.82 mmol), styrene **8c** (258 mg, 1.23 mmol,) and trimethoxy benzene (**9a**) (207 mg, 1.23 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (0.0497 mmol, 9.5 mg) and trimethyl orthoformate (136 μL, 1.23 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10d** (312 mg, 78%).

Physical appearance: white solid.



R_f: 0.6 (1: 3, EtOAc:petroleum ether).

IR (neat): 2945, 2866, 1637, 1587, 1436, 1231, 1144, 1102, 1131, 908, 753cm^{-1}.

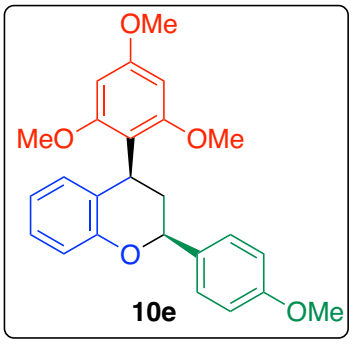
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50-7.34 (m, 4H), 7.34 (td, J = 4.4, 2.1 Hz, 2H), 7.13-6.94 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.85-6.70 (m, 2H), 6.24 (d, J = 2.3 Hz, 2H), 6.19-6.10 (m, 2H), 5.15 (dd, J = 11.6, 1.8 Hz, 1H), 5.10 (s, 2H), 4.96 (dd, J = 11.9, 5.9 Hz, 1H), 3.86 (d, J = 15.1 Hz, 6H), 3.46 (s, 3H), 2.71 (dt, J = 13.3, 11.8 Hz, 1H), 2.10 (ddd, J = 13.7, 6.2, 2.1 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*, DEPT): δ 160.0 (C), 159.8 (C), 159.3 (C), 158.5 (C), 155.4 (C), 137.2 (C), 134.5 (C), 128.7 (2 x CH), 128.0 (CH), 127.7 (CH), 127.6 (C), 127.5 (2 x CH), 127.3 (2 x CH), 126.3 (CH), 120.2 (CH), 116.5 (CH), 114.8 (2 x CH), 112.8 (CH), 92.4 (CH), 90.7 (CH), 78.6 (CH), 70.1 (CH_2), 56.2 (OCH_3), 55.7 (CH_3), 55.4 (CH_3), 34.9 (CH_2), 32.2 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{31}H_{30}NaO_5$ 505.1985, found 505.1987.

***(2S*,4S*)-2-(4-methoxyphenyl)-4-(2,4,6-trimethoxyphenyl)chroman* (10e):**

The reaction of salicylaldehyde (**7a**) (87 μL, 0.82 mmol), styrene **8d** (165 mg, 1.23 mmol) and trimethoxy benzene (**9a**) (207 mg, 1.23 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (9.5 mg, 0.05 mmol) and trimethyl orthoformate (136 μL, 1.23 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10e** (251 mg, 75%).



10e

Physical appearance: Pale red foamy solid.

R_f: 0.6 (1: 3, EtOAc:petroleum ether).

IR (neat): 2926, 2864, 1625, 1596, 1422, 1228, 1132, 1105, 1129, 904, 751cm^{-1}.

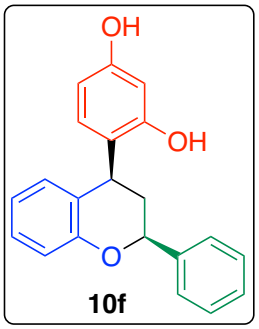
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.45 (d, J = 8.2 Hz, 2H), 7.08 (dd, J = 11.9, 5.9 Hz, 1H), 7.07-7.01 (m, 1H), 6.93 (dt, J = 15.5, 9.1 Hz, 4H), 6.79 (s, 1H), 6.23 (s, 1H), 5.15 (d, J = 11.5 Hz, 1H), 4.96 (dd, J = 12.0, 5.9 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H), 3.45 (s, 3H), 2.71 (q, J = 12.2 Hz, 1H), 2.09 (dd, J = 13.4, 6.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*, DEPT): δ 160.0 (C), 159.8 (C), 159.6 (C), 159.3 (C), 155.4 (C), 134.2 (C), 127.7 (2 x CH), 127.5 (CH), 127.3 (C), 126.3 (2 x CH), 120.2 (CH), 116.5 (CH), 113.9 (CH), 112.8 (C), 92.4 (CH), 90.7 (CH), 78.6 (CH), 56.3 (CH_3), 55.9 (CH_3), 55.7 (CH_3), 55.4 (CH_3), 34.9 (CH_2), 32.2 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{25}H_{26}NaO_5$ 429.1672, found 429.1675.

***4-((2S*,4R*)-2-phenylchroman-4-yl)benzene-1,3-diol* (10f):**

The reaction of salicylaldehyde (**7a**) (87 μL, 0.82 mmol,), styrene **8a** (145 μL, 1.23 mmol) and resorcinol (**9b**) (135 mg, 1.23 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (9.5 mg, 0.05 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using ethyl acetate:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10f** (179 mg, 69%).



Physical appearance: Pale brown foamy solid.

R_f: 0.4 (1:3, EtOAc:petroleum ether).

IR (neat): 3341, 2925, 2854, 1626, 1599, 1427, 1221, 1135, 1107, 1121, 902, 753cm^{-1}.

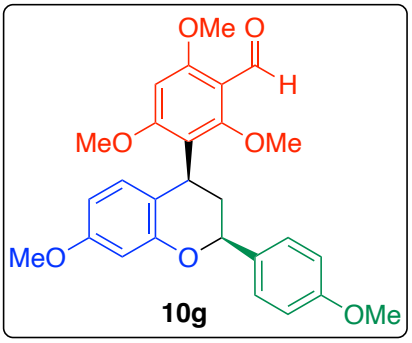
^{1}H NMR (400 MHz, CD_3CN): δ 7.52-7.21 (m, 2H), 7.16 (dd, J = 16.2, 8.5 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 7.01-6.82 (m, 2H), 6.75 (h, J = 7.5 Hz, 1H), 6.48 (d, J = 8.2 Hz, 1H), 6.40-6.21 (m, 4H), 5.01 (dd, J = 10.0, 2.9 Hz, 1H), 4.44-4.28 (m, 1H), 2.41 (s, 2H), 2.35-2.17 (m, 2H).

^{13}C NMR (100 MHz, CD_3CN, DEPT): δ 157.4 (C), 156.7 (C), 155.8 (C), 142.8 (C), 132.0 (CH), 131.6 (CH), 131.2 (CH), 129.5 (2 x CH), 128.7 (CH), 127.2 (2 x CH), 127.1 (C), 125.1 (CH), 121.5 (CH), 117.6 (CH), 107.9 (CH), 103.4 (CH), 74.7 (CH), 36.8 (CH_2), 34.5 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{21}H_{18}NaO_3$ 341.1149, found 341.1149.

***2,4,6-trimethoxy-3-((2S*,4S*)-7-methoxy-2-(4-methoxyphenyl)chroman-4-yl)benzaldehyde* (10g):**

The reaction of salicylaldehyde **7d** (125 mg, 0.8215 mmol), styrene **8c** (166 mg, 1.23 mmol) and trimethoxy benzene **9c** (242 mg, 1.23 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (9.5 mg, 0.04 mmol,) and trimethyl orthoformate (136 μL, 1.23 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10g** (272 mg, 71%).



Physical Appearance: Pale red foamy solid.

R_f: 0.4 (1:4, EtOAc:petroleum ether).

IR (neat): 2932, 2835, 1614, 1728, 1620, 1455, 1432, 1386, 1327, 1248, 1159, 1104, 1016, 831, 807, 739 cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 10.31 (d, J = 2.1 Hz, 1H), 7.34 (dd, J = 8.6, 2.3 Hz, 2H), 6.42 (dt, J = 6.7,

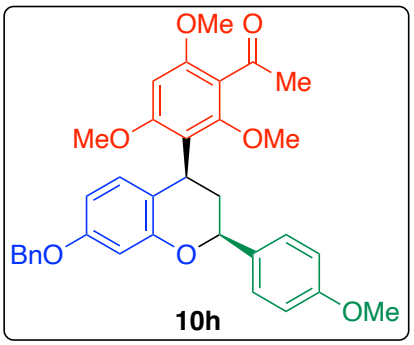
2.4 Hz, 2H), 6.28 (s, 1H), 6.28-6.18 (m, 2H), 6.17 (d, J = 2.1 Hz, 1H), 4.96 (d, J = 11.3 Hz, 1H), 4.79 (ddd, J = 25.2, 11.9, 6.2 Hz, 1H), 3.93 (s, 3H), 3.78 – 3.67 (m, 6H), 3.65 (dd, J = 8.5, 2.1 Hz, 3H), 3.52 (d, J = 2.2 Hz, 3H), 2.63-2.51 (m, 1H), 2.07-1.93 (m, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*, DEPT): δ 187.7 (CH), 164.6 (C), 163.1 (C), 162.1 (C), 159.3 (C), 158.5 (C), 155.9 (C), 133.9 (C), 128.8 (CH), 128.2 (2 x CH), 126.8 (2 x CH), 119.6 (CH), 118.3 (C), 113.8 (CH), 107.3 (CH), 101.4 (CH), 92.4 (CH), 78.4 (CH), 55.9 (2 x CH_3), 55.7 (CH_3), 55.2 (2 x CH_3), 35.3 (CH_2), 31.8 (CH).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{27}H_{28}NaO_7$ 487.1727, found 487.1722.

***1-(3-((2S*,4S*)-7-(benzyloxy)-2-(4-(benzyloxy)phenyl)chroman-4-yl)-2,4,6-trimethoxyphenyl)ethanone* (10h):**

The reaction of salicylaldehyde **7e** (100 mg, 0.44 mmol,), styrene **8d** (89 mg, 0.67 mmol) and trimethoxy benzene **9c** (139 mg, 0.6572 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (0.0219 mmol, 5 mg) and trimethyl orthoformate (73 μL, 0.66 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10h** (192 mg, 79%).



10h

Physical Appearance: white foamy solid.

m.p.: 80-82 °C.

R_f: 0.3 (1:4, EtOAc:petroleum ether).

IR (neat): 2924, 2852, 1698, 1595, 1502, 1456, 1402, 1247, 1153, 1108, 1018, 831, 738 cm^{-1}.

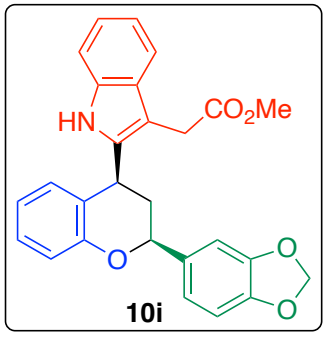
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.48-7.25 (m, 7H), 6.98-6.84 (m, 2H), 6.67-6.55 (m, 2H), 6.43 (dd, J = 8.5, 2.6 Hz, 1H), 6.28 (d, J = 23.7 Hz, 1H), 5.15 (dd, J = 11.7, 1.8 Hz, 1H), 5.11-4.98 (m, 2H), 4.71 (dd, J = 11.9, 5.8 Hz, 1H), 3.91 (s, 3H), 3.52 (s, 6H), 2.95 (s, 3H), 2.69 (q, J = 12.2 Hz, 1H), 2.54 (d, J = 16.7 Hz, 3H), 2.09 (ddd, J = 13.3, 6.0, 1.9 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*, DEPT): δ 202.5 (C), 160.7 (C), 159.5 (C), 158.3 (C), 157.8 (C), 157.2 (C), 156.7 (C), 137.3 (C), 128.6 (2 x CH), 127.9 (CH), 127.8 (C), 127.8 (2 x CH), 127.7 (2 x CH), 127.6 (2 x CH), 127.5 (C), 118.1 (C), 114.0 (CH), 113.9 (CH), 108.1 (CH), 102.5 (CH), 93.3 (CH), 78.6 (CH), 70.1 (CH_2), 56.2 (CH_3), 55.9 (CH_3), 55.9 (CH_3), 55.4 (CH_3), 35.2 (CH_2), 32.8 (CH), 31.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{34}H_{34}NaO_7$ 577.2195, found 577.2195.

***methyl 2-(2-((2S*,4S*)-2-(benzo[d][1,3]dioxol-5-yl)chroman-4-yl)-1H-indol-3-yl)acetate* (10i):**

The reaction of salicylaldehyde (**7a**) (87 μL, 0.82 mmol), styrene **8b** (183 mg, 1.23 mmol) and indole **9d** (233 mg, 1.23 mmol) in the presence of (±)-camphor sulphonic acid (CSA) (9.5 mg, 0.05 mmol) and trimethyl orthoformate (136 μL, 1.23 mmol) in dry CH_3CN (8 mL) at 0 °C to room temperature as described for the bicyclic product **10a** followed by purification on a silica gel column using EtOAc:petroleum ether (from 1% to 25% ethyl acetate) as eluent furnished the bicyclic product **10i** (290 mg, 80%).



10i

Physical appearance: Off-white foamy solid.

R_f: 0.4 (1: 3, EtOAc:petroleum ether).

IR (neat): 3491, 2937, 2873, 1745, 1647, 1597, 1438, 1215, 1137, 1107, 1126, 904, 759cm^{-1}.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.68-7.60 (m, 1H), 7.19-7.14 (m, 1H), 7.16-6.96 (m, 3H), 6.98-6.85 (m, 2H), 6.88 – 6.72 (m, 3H), 5.99-5.88 (m, 1H), 5.95 (s, 2H), 5.10 (dd, J = 9.6, 3.0 Hz, 1H), 4.56 (t, J = 4.6 Hz, 1H), 3.88-3.74 (m, 2H), 3.74-3.66 (s, 3H), 2.46 (qdt, J = 13.9, 7.1, 3.3 Hz, 2H).

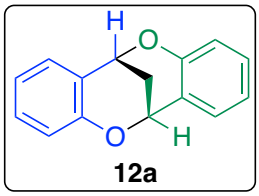
^{13}C NMR (125 MHz, Chloroform-*d*, DEPT): δ 172.3 (C), 155.4 (C), 148.0 (C), 139.2 (C), 136.0 (C), 134.8 (C), 130.7 (CH), 130.3 (CH), 129.1 (CH), 128.7 (CH), 122.0 (C), 120.8 (C), 120.1 (CH), 119.6 (CH), 118.6 (C), 117.7 (CH), 111.0 (C), 109.6 (CH), 108.3 (CH), 106.7 (CH), 104.9 (CH), 101.2 (CH_2), 74.5 (CH), 52.1 (CH_3),36.4 (CH_2), 32.4 (CH), 30.4 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{27}H_{23}NNaO_5$ 464.1468, found 464.1466.

Experimental Procedure for the synthesis of cycloflavans

***6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine* (12a):**

To a magnetically stirred solution of salicylaldehyde **7a** (51 µL, 0.48 mmol) and styrene **11a** (85 mg, 0.7 mmol) in dry CH_2Cl_2 (3 ml) was added TMOF (80 µL, 0.7 mmol) followed by (±) CSA (11 mg, 0.048 mmol) at 0 °C. Reaction mixture slowly brought to room temperature and monitored by TLC. After disappearance of intermediate spot on TLC reaction was quenched with 5% aqueous NaOH solution (4 ml). After stirring for 5 minute extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished methanodibenzo[b,f][1,5]dioxocine derivative **12a** (77 mg, 82 %).



12a

Physical appearance: white solid.

M.P.: 155-157 ^{0}C

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 3026, 1606, 1585, 1483, 1218, 1115, 990, 756, cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 1.2, 7.6 Hz, 2H), 7.20 (td, *J* = 1.2, 8.4 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.35 (t, *J* = 2.8 Hz, 2H), 2.33 (t, *J* = 2.8 Hz, 2H).

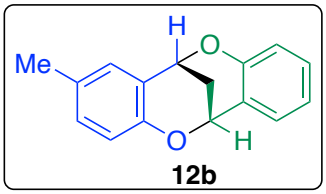
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.2 (2 × C), 130.9 (2 × CH), 130.7 (2 × CH), 121.4 (2 × C), 120.7 (2 × CH), 117.2 (2 × CH), 67.6 (2 × CH), 26.6 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{15}H_{12}NaO_2$ 247.0730, found 247.0737.

***2-methyl-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine* (12b):**

Salicylaldehyde derivative **7e** (66 mg, 0.48 mmol) was reacted with styrene **11a** (87 mg, 0.7 mmol) in presence of TMOF (80 µL, 0.7 mmol) and (±) CSA (11 mg, 0.048 mmol) in dry CH_2Cl_2 (3 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12b** (97.8 mg, 85%).

Physical appearance: sticky white solid.



12b

M.P.: 128-130 ^{0}C

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 2960, 1612, 1586, 1497, 1461, 1219, 1050, 1029, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 0.8, 7.2 Hz, 1H), 7.22-7.16 (m, 2H), 7.00 (dd, *J* = 1.6, 8.4 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H) 5.32 (t, *J* = 2.8 Hz, 2H), 2.31 (d, *J* = 2.8 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.2 (C), 150.9 (C), 131.5 (CH), 131.1 (CH), 131.0 (CH), 130.6 (CH), 129.9 (C), 121.6 (C), 121.0 (C), 120.6 (CH), 117.1 (CH), 116.9 (CH), 67.8 (CH), 67.5 (CH), 26.7 (CH_2), 20.5 (CH_3).

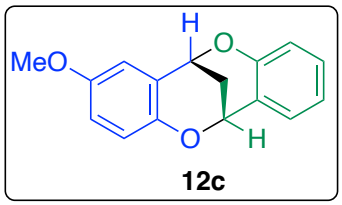
HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{16}H_{14}NaO_2$ 261.0886, found 261.0888.

***2-methoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine* (12c):**

Salicylaldehyde derivative **7b** (60 µL, 0.48 mmol) was reacted with styrene **11a** (87 mg, 0.7 mmol) in presence of TMOF (80 µL, 0.7 mmol) and (±) CSA (11 mg, 0.048 mmol) in dry CH_2Cl_2 (3 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel

column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12c** (87.2 mg, 87%).

Physical appearance: Stick white solid.



12c

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 2959, 1610, 1583, 1495, 1461, 1217, 1220, 1052 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.20 (td, *J* = 1.2, 8.4 Hz, 1H), 6.93-6.88 (m, 2H), 6.84-6.74 (m, 3H), 5.30 (s, 2H), 3.75 (s, 3H), 2.31 (d, *J* = 2.4 Hz, 2H).

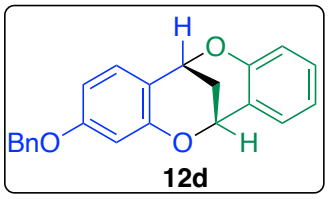
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.5 (C), 153.2 (C), 147.0 (C), 130.9 (CH), 130.6 (CH), 121.5 (C), 120.7 (CH), 117.9 (CH), 117.6 (CH), 117.0 (CH), 114.4 (CH), 67.9 (CH), 67.4 (CH), 55.8 (CH_3), 26.7 (CH_2).

HRMS (ESI, M+H^+): m/z calcd. for $C_{16}H_{15}O_3$ 255.1016, found 255.1017.

3-(benzyloxy)-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine **(12d):**

Salicylaldehyde derivative **7e** (68 mg, 0.3 mmol) was reacted with styrene **11a** (55 mg, 0.45 mmol) in presence of TMOF (50 µL, 0.45 mmol) and (±) CSA (7 mg, 0.03 mmol) in dry CH_2Cl_2 (2.5 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12d** (91.9 mg, 91%).

Physical appearance: Pale yellow liquid.



12d

M.P.: 115-117 °C

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 3028, 2960, 1618, 1585. 1501, 1484, 1436, 1214, 1160, 1125, 1050, 756 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.21 (td, *J* = 1.2, 8.4 Hz, 1H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 5.32 (d, *J* = 2.8 Hz, 2H), 4.97 (s, 2H), 2.31 (t, *J* = 2.8 Hz, 2H).

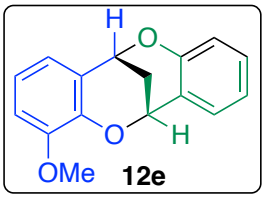
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 160.8 (C), 154.3 (C), 153.3 (C), 136.9 (C), 131.7 (CH), 130.9 (CH), 130.7 (CH), 128.7 (2 × CH), 128.1 (CH), 127.6 (2 ×CH), 126.5 (C), 120.6 (CH), 117.3 (CH), 114.3 (C), 108.7 (CH), 102.3 (CH), 70.1 (CH_2), 67.8 (CH), 67.4 (CH), 26.8 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{22}H_{18}NaO_3$ 353.1148, found 353.1159.

***4-methoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine* (12e):**

Salicylaldehyde derivative **7f** (45.6 mg, 0.3 mmol) was reacted with styrene **11a** (55 mg, 0.45 mmol) in presence of TMOF (50 µL, 0.45 mmol) and (±) CSA (7 mg, 0.03 mmol) in dry CH_2Cl_2 (2.5 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12e** (74.4 mg, 91%).

Physical appearance: Pale yellow solid.



12e

M.P.: 125-127 °C

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 2959, 1610, 1586, 1487, 1463, 1288, 1264, 1219, 1048, 1030, 991, 894, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.19 (td, *J* = 1.6, 8.8 Hz, 1H), 6.98 (dd, *J* = 1.2, 7.6 Hz, 1H), 6.91-6.75 (m, 4H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.35-5.34 (m, 1H), 3.81 (s, 3H), 2.32 (d, *J* = 2.8 Hz, 2H).

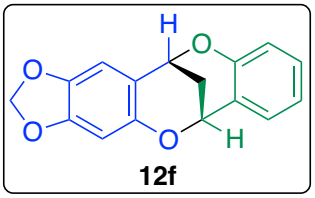
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.2 (C), 148.6 (C), 142.7 (C), 131.2 (CH), 130.7 (CH), 122.5 (CH), 122.0 (C), 121.3 (C), 120.7 (CH), 120.4 (CH), 117.1 (CH), 112.1 (CH), 67.9 (CH), 67.4 (CH), 56.0 (CH_3), 26.4 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{16}H_{14}NaO_3$ 277.0835, found 277.0833.

***6H,12H-6,12-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f][1,5]dioxocine* (12f):**

Salicylaldehyde derivative **7f** (50 mg, 0.3 mmol) was reacted with styrene **11a** (55 mg, 0.45 mmol) in presence of TMOF (50 µL, 0.45 mmol) and (±) CSA (7 mg, 0.03 mmol) in dry CH_2Cl_2 (2.5 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12f** (65 mg, 81%).

Physical appearance: White solid.



12f

M.P.: 154-156 °C

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 2914, 1628, 1607, 1480, 1447, 1253, 1213, 1086, 1045, 763 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.20 (td, *J* = 1.6, 8.4 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.77 (s, 1H), 6.32 (s, 1H), 5.87 (s, 1H), 5.80 (s, 1H), 5.27 (s, 1H), 5.22 (s, 1H), 2.27 (t, *J* = 2.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.2 (C), 149.3 (C), 148.6 (C), 141.8 (C), 130.9 (CH), 130.7 (CH), 121.5 (C), 120.7 (CH), 117.1 (CH), 112.9 (C), 109.0 (CH), 101.2 (CH_2), 98.6 (CH), 67.9 (CH), 67.6 (CH), 26.7 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{16}H_{12}NaO_4$ 291.0628, found 291.0620.

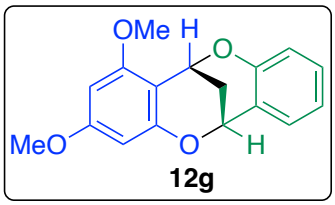
***1,3-dimethoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine* (12g):**

Salicylaldehyde derivative **7g** (71.4 mg, 0.3 mmol) was reacted with styrene **11a** (67 mg, 0.45 mmol) in presence of TMOF (50 µL, 0.45 mmol) and (±) CSA (7 mg, 0.03 mmol) in dry CH_2Cl_2 (2.5 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12g** (25.8 mg, 31%).

Physical appearance: Sticky solid.

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 3004, 2960, 2853, 1614, 1593, 1484, 1335, 1304, 1217, 1175, 1145, 1108, 1055, 998, 878, 756 cm^{-1}.



12g

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.92-6.88 (m, 2H), 6.04 (s, 1H), 5.99 (s, 1H), 5.70 (s, 1H), 5.32 (s, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 2.28 (d, *J* = 13.5 Hz, 1H), 2.19 (d, *J* = 13.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 161.9 (C), 159.2 (C), 154.9 (C), 153.8 (C), 130.9 (CH), 130.6 (CH), 121.3 (C), 120.4 (CH), 117.4 (CH), 103.5 (C), 93.0 (CH), 91.8 (CH), 67.8 (CH), 62.0 (CH), 56.0 (CH_3), 55.3 (CH_3), 26.6 (CH_2).

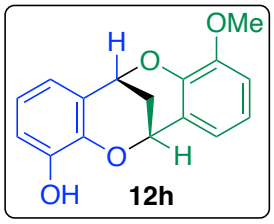
HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{17}H_{16}NaO_4$ 307.0941, found 307.0946.

***10-methoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocin-4-ol* (12h)**:

To a magnetically stirred solution of salicylaldehyde **7h** (70 mg, 0.50 mmol) and hydroxy-styrene **11b** (114 mg, 0.76 mmol) in dry CH_2Cl_2 (5 ml) was added $CH(OMe)_3$ (84 µL, 0.76 mmol) followed by (±) CSA (11.7 mg, 0.050 mmol) at 0 °C. Reaction mixture slowly brought to room temperature and monitored by TLC. After disappearances of intermediate spots on TLC reaction was quenched with saturated aqueous $NaHCO_3$ solution (4 mL). After stirring for 5 minute extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether (8:92) as eluent furnished cycloflavan derivative **12h** (105 mg, 76 %).

Physical appearance: white solid.

M.P.: 165-167 ^{0}C



12h

R_f: 0.3 (8:2 EtOAc:petroleum ether).

IR (neat): 3427, 2960, 1588, 1486, 1336, 1264, 1214, 1078, 1038, 1012, 890, 737 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.85-6.76 (m, 4H), 5.64 (s, 1H), 5.49 (s, 1H), 5.43 (s, 1H), 3.79 (s, 3H), 2.33 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 148.6 (C), 144.8 (C), 142.8 (C), 140.4 (C), 122.4 (CH), 121.9 (CH), 121.5 (C), 121.4 (C), 121.0 (CH), 120.4 (CH), 115.6 (CH), 112.2 (CH), 68.0 (CH), 67.4 (CH), 55.0 (CH_3), 26.5 (CH_2).

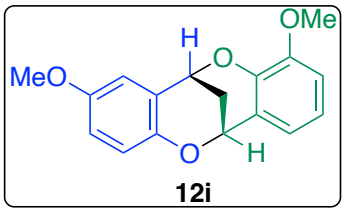
HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{15}O_4$ 271.0970, found 271.0969.

***2,10-dimethoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine* (12i):**

Salicylaldehyde derivative **7b** (60.8 mg, 0.4 mmol) was reacted with styrene **11b** (90 mg, 0.6 mmol) in presence of TMOF (65 µL, 0.6 mmol) and (±) CSA (9.3 mg, 0.04 mmol) in dry CH_2Cl_2 (3 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12i** (79 mg, 70%).

Physical appearance: White solid.

M.P.: 130-132 °C



12i

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 2959, 2833, 1587, 1494, 1469, 1283, 1265, 1214, 1081, 1049, 1028, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.95 (m, 2H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.80-6.72 (m, 3H), 5.44 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.30 (t, *J* = 2.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.5 (C), 148.5 (C), 147.0 (C), 142.7 (C), 122.5 (CH), 122.1 (C), 121.3 (C), 120.4 (CH), 117.9 (CH), 117.8 (CH), 114.5 (CH), 111.9 (CH), 68.2 (CH), 67.2 (CH), 55.9 (CH_3), 55.8 (CH_3), 26.8 (CH_2).

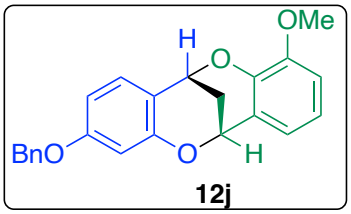
HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{17}H_{16}NaO_4$ 307.0941, found 307.0934.

***(6R*,12R*)-3-(benzyloxy)-10-methoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine*(12j)**:

To a magnetically stirred solution of salicylaldehyde **7e** (114 mg, 0.49 mmol) and hydroxy-styrene derivative **11b** (112.5 mg, 0.74 mmol) in dry CH_2Cl_2 (5 ml) was added $CH(OMe)_3$ (82

µL, 0.74 mmol) followed by (±) CSA (11.6 mg, 0.049 mmol) at 0 °C. Reaction mixture slowly brought to room temperature and monitored by TLC. After disappearances of intermediate spots on TLC reaction was quenched with saturated aqueous $NaHCO_3$ solution (4 mL). After stirring for 5 minute extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether (8:92) as eluent furnished cycloflavan derivative **12j** (147 mg, 84 %).

Physical appearance: white solid.



12j

M.P.: 124-126 °C

R_f: 0.3 (8:2: EtOAc:petroleum ether).

IR (neat): 2940, 1616, 1591, 1486, 1466, 1265, 1210, 1146, 1108, 1082, 1002, 755, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 5H), 6.98 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 5.47 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 1.6 Hz, 1H), 4.96 (s, 2H), 3.82 (s, 3H), 2.30 (t, *J* = 2.4 Hz, 2H).

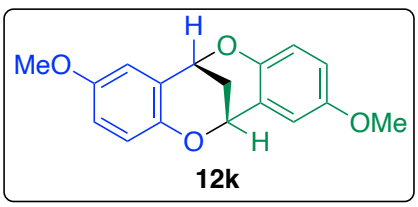
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 160.8 (C), 154.3 (C), 148.6 (C), 142.7 (C), 136.8 (C), 131.9 (CH), 128.7 (CH), 128.1 (CH), 127.6 (CH), 122.5(C), 122.0(CH), 120.3(CH), 114.1 (C), 112.0 (CH), 108.6 (CH), 102.2 (CH), 70.0 (OCH_2), 67.6 (CH), 67.5 (CH), 55.9 (OCH_3), 26.6 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{23}H_{20}NaO_4$ 383.1254, found 383.1254.

2,8-dimethoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocine **(12k):**

Salicylaldehyde derivative **7b** (46 mg, 0.30 mmol) was reacted with styrene **11c** (55 mg, 0.45 mmol) in presence of TMOF (50 µL, 0.45 mmol) and (±) CSA (7 mg, 0.03 mmol) in dry CH_2Cl_2 (2.5 ml) at 0 °C to room temperature as described for the methanodibenzo[b,f][1,5]dioxocine derivative **12a** followed by purification on a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished the methanodibenzo[b,f][1,5]dioxocine derivative **12k** (79.6 mg, 90%).

Physical appearance: White solid.



12k

M.P.: 107-109 °C

R_f: 0.5 (2:8 EtOAc:petroleum ether).

IR (neat): 2959, 2833, 16118, 1494, 1466, 1429, 1284, 1207, 1153, 993, 880, 817, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 2.8 Hz, 2H), 6.80-6.72 (m, 4H), 5.24 (t, *J* = 2.8 Hz, 2H), 3.75 (s, 6H), 2.29 (d, *J* = 2.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.6 (2 × C), 147.0 (2 × C), 121.7 (2 × C), 117.8 (2 × CH), 117.6 (2 × CH), 114.5 (2 × CH), 67.7 (2 × CH), 55.8 (2 × CH_3), 26.8 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{16}NaO_4$ 307.0941, found 307.0939.

Gram Scale Total Synthesis of Myristinin A-F

***1-(2,4,6-trihydroxy-3-((2R*,4S*)-7-hydroxy-2-(4-hydroxyphenyl)chroman-4-yl)phenyl)dodecan-1-one* (1/2):**[2]

To a cold (0 ºC) magnetically stirred solution of salicylaldehyde **7e** (1.0 g, 4.3813 mmol), (±)-camphor sulphonic acid (CSA) (50.8 mg, 0.2190 mmol), in dry CH_3CN (8 mL), was added trimethyl orthoformate (727 μL, 6.5720 mmol) and stirred for 10 min. Then the styrene **8b** (1.38 g, 6.5720 mmol) was added slowly at 0 ºC the resulting mixture was stirred at room temperature, and then the phenol **9e** (2.026 g, 6.5720 mmol) in dry CH_3CN (2 mL), was slowly added at 0 ºC the resulting mixture was stirred for 1h at 0 ºC then slowly warmed to room temperature. After completion of the reaction (TLC control), the reaction mixture was carefully quenched with saturated sodium hydrogen carbonate solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL), the combined organic layer was washed with brine and dried over anhydrous sodium sulphate. Evaporation of the solvent followed by the addition of dry THF and dry MeOH in 1:1 ratio and 10% $Pd(OH)_2/C$ (420 mg) was added to the crude reaction mixture. Then the reaction mixture was stirred at room temperature in an atmosphere of hydrogen created by evacuative displacement of air by H_2 (balloon, 1 atm). After completion of the reaction the catalyst filtered off through a celite pad. Evaporation and purification of the residue on silica gel column, using Pet. Ether: CH_2Cl_2: MeOH: AcOH (70:25:3:1) as an eluent afforded the required bicyclic product **1** in (337 mg, 14%) and mixture of phenol **9e** and **2a/b.** and further purification of the mixture on silica gel column, using Pet. Ether: $CHCl_3$: MeOH: AcOH (70:25:3:1) as an eluent afforded the required bicyclic product **2a/b** in (1.037 g, 43%).

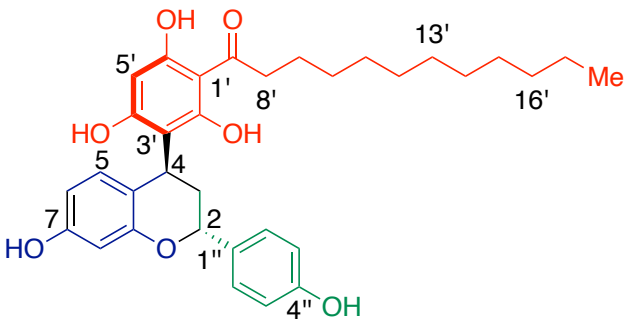
***1-(2,4,6-trihydroxy-3-((2R*,4S*)-7-hydroxy-2-(4-hydroxyphenyl)chroman-4-yl)phenyl)dodecan-1-one* (1):**

Physical Appearance: Pale Brown colour foamy solid

R_f: 0.4 (1:4, Petroleum Ether: CH_2Cl_2: MeOH (AcOH))

R_t: 10.4 min (CH_3CN: H_2O) [C18 column, 4ml/min]

IR (neat): 3459, 2952, 2845, 1728, 1620, 1614,1465, 1452, 1386, 1337, 1236, 1160, 1144, 1066, 841, 802, 735 cm^{-1}.

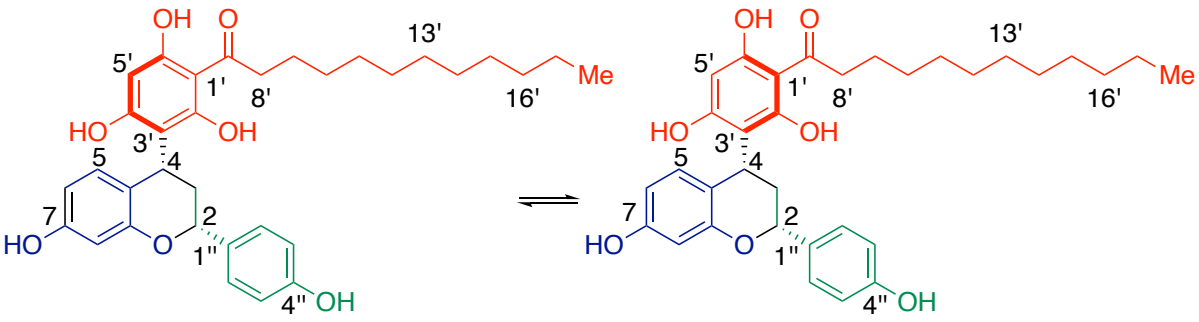


myristinin A (**1**)

^{1}H NMR (500 MHz, DMSO-d6): δ 14.30 (br s, 1H), 10.57 (br s, 1H), 10.18 (br s, 1H), 9.32 (s, 1H), 8.99 (s, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 6.35 (d, *J* = 8.4Hz, 1H), 6.22 (d, *J* = 2.1 Hz, 1H), 6.11 (dd, *J* = 8.1, 2.4 Hz, 1H), 5.94 (s, 1H), 5.36 (d, *J* = 4.2 Hz, 1H), 4.15 (dd, *J* = 8.4, 6.3 Hz, 1H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.57 (m, 1H), 2.08 (m, 1H), 1.55 (t, *J* = 6.6 Hz, 2H), 1.23 (bs, 16H), 0.84 (t, *J* = 6.3 Hz, 3H,).

^{13}C NMR (125 MHz, DMSO-d6, DEPT): δ205.5 (C), 164.3 (C), 163.0 (C), 160.4 (C), 156.3 (C), 155.9 (C), 154.5 (C), 132.3 (C), 128.0 (C), 126.7 (CH), 116.9 (CH), 115.0 (C), 108.1 (C), 107.5 (CH), 103.5 (C), 102.5 (C), 102.2 (CH), 94.3 (CH), 74.58 (CH), 43.2 (CH_2), 32.1 (CH_2), 31.4 (CH_2), 31.25 (CH), 29.0 (CH_2), 28.8 (CH_2), 25.5 (CH_2), 24.6 (CH_2), 22.2 (CH_2), 14.0 (CH_3).

HRMS (ESI, M+Na^{+}): m/z calcd. for $C_{33}H_{40}NaO_7$ 571.2666, found 571.2663.



myristinin B (**2a**) myristinin C (**2b**)

1-(2,4,6-trihydroxy-3-((2R*,4R*)-7-hydroxy-2-(4-hydroxyphenyl)chroman-4-yl)phenyl)dodecan-1-one **(2a/b):**

Physical Appearance: Pale Brown colour foamy solid

R_f: 0.4 (1:4, Petroleum Ether: $CHCl_3$: MeOH (AcOH))

R_t: 15.6 min (CH_3CN: H_2O) [C18 column, 4ml/min]

IR (neat): 3445, 2832, 2815, 1714, 1632, 1620, 1455, 1432, 1386, 1327, 1248, 1169, 1104, 1055, 835, 807, 739 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d6): δ14.52 (s, 1H), 14.10 (s, 1H), 10.55 (bs, 1H), 10.07 (bs, 1H), 9.39 (s, 1H), 8.97 (s, 1H), 7.24 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.75 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.42 (d, *J* = *9.0 Hz*, 1H), 6.08 (s, 1H), 6.15 (m, 2H), 5.91 (s, 1H), 5.00 (dd, *J* = 11.0, 10.0 Hz,

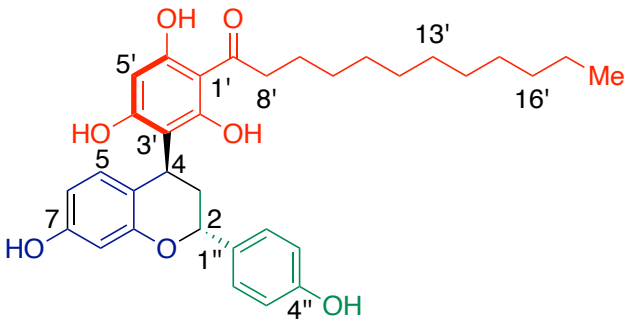
1H), 4.69 (dd, J = 11.5, 5.5 Hz, 1H), 4.60 (dd, J = 12.0, 5.5 Hz, 1H), 3.01 (t, J = 8.0 Hz, 1H), 2.96 (m, 1H), 2.81 (q, J = 12.5 Hz, 1H), 2.58 (q, J = 12.5 Hz, 1H, 1H), 1.67 (m, 2H), 1.89 (m, 1H), 1.33 (m, 16H), 0.82 (t, J = 5.8 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d6, DEPT): δ205.7 (C), 163.8 (C), 162.0 (C), 160.2 (C), 158.0 (C), 155.4 (C), 155.3 (C), 135.3 (C), 128.5 (C), 127.8 (CH), 117.2 (CH), 114.9 (C), 114.9 (C), 106.4 (CH), 104.1 (C), 102.4 (C), 102.2 (CH), 94.3 (CH), 67.9 (CH), 43.1 (CH_2), 35.8 (CH_2), 33.64 (CH_2), 31.25 (CH), 28.97 (CH_2), 28.97 (CH_2), 28.95 (CH_2), 28.9 (CH_2), 28.87 (CH_2), 28.65 (CH_2), 24.45 (CH_2), 22.04 (CH_2), 13.89 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{33}H_{40}NaO_7$ 571.2666, found 571.2665.

Comparison of ^{1}H NMR spectral data of myristinin-A (1) in DMSO-d$_6$

Reported [a]	Synthesized	Reported [a]	Synthesized
14.23 (br s, 1H)	14.30 (br s, 1H)	6.12 (dd, J = 8.3, 2.1 Hz, 1H)	6.11 (dd, J = 8.1, 2.4 Hz, 1H)
10.57 (br s, 1H)	-	5.97 (s, 1H)	5.94 (s, 1H)
10.18 (br s, 1H)	-	5.38 (dd, J = 4.3, 3.9 Hz, 1H)	5.36 (d, J = 4.2Hz, 1H)
9.32 (br s, 1H)	9.32 (s, 3H)	4.17 (dd, J = 8.0, 7.0 Hz, 1H)	4.15 (dd, J = 8.4, 6.3 Hz, 1H)
9.00 (br s, 1H)	8.99 (s, 1H)	2.97 (t, J = 7.3Hz, 2H)	2.96 (t, J = 7.5 Hz, 2H)
7.10 (br d, J = 8.4 Hz, 2H)	7.08 (d, J = 8.7 Hz, 2H)	2.07, (m, 1H) 2.59, (m, 1H)	2.57 (m, 1H), 2.08 (m, 1H)
6.71 (br d, J = 8.4 Hz, 2H)	6.69 (d, J = 8.4 Hz, 2H)	1.56 (m, 2H)	1.55 (t, J = 6.6 Hz, 2H)
6.38 (d, J = 8.4 Hz, 1H)	6.35 (d, J = 8.4Hz, 1H)	1.25 (m, 18H)	1.23 (br s, 16H)
6.24 (d, J = 2.2Hz, 1H)	6.22 (d, J = 2.1 Hz, 1H)	0.84 (t, J = 6.5 Hz, 3H)	0.84 (t, J = 6.3 Hz, 3H)

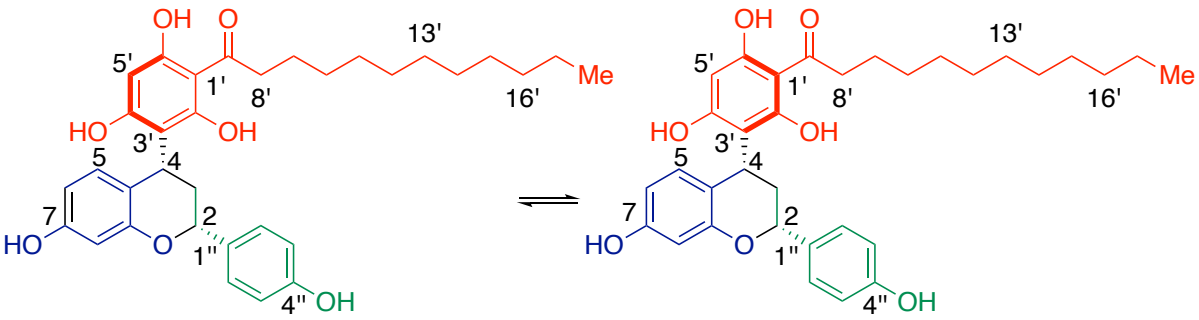


myristinin A (**1**)

Comparison of ^{13}C NMR spectral data of myristinin-A (1) in DMSO-d_6

Position #	Reported [a]	Synthesized	Position #	Reported [a]	Synthesized
2	74.6	74.63	8'	43.2	43.24
3	32.1	32.18	9'	24.6	24.62
4	25.2	25.57	10'	28.7	28.78
4a	116.8	116.91	11'	28.7	28.03
5	127.9	127.98	12'	29	29.08
6	107.5	107.59	13'	29	29.1
7	155.9	155.99	14'	29	29.1
8	102.5	102.58	15'	29	29.02
8a	154.6	154.61	16'	31.3	31.37
1'	103.5	103.58	17'	22.1	22.17
2'	164.3	164.41	18'	13.9	14.02
3'	108.1	108.2	1"	132.3	132.35
4'	163	163.01	2", 6"	126.7	126.71
5'	94.5	95.03	3", 5"	115	115.1
6'	160.4	160.43	4"	156.3	156.35
7'	205.5	205.56			

[a]isolated values *J. Org. Chem*, **2002**, *67*, 5470.



myristinin B (**2a**) myristinin C (**2b**)

Comparison of ^{1}H NMR spectral data of myristinin-B/C (2a/b) in DMSO-d$_6$

Reported [a]	**Synthesized**
14.52 (br s, 1H)	14.52 (s, 1H)
14.10 (br s, 1H)	14.10 (s, 1H
10.57 (br s, 1H)	10.55 (br s, 1H)
10.07 (br s, 1H)	10.07 (br s, 1H)
9.42 (br s, 1H)	9.39 (s, 1H)
9.00 (br s, 1H)	8.97 (s, 1H)
7.24 (br d, *J* = 7.8 Hz, 2H)	7.24 (dd, *J* = 9.0 and 2.0 Hz, 2H)
6.76 (br d, *J* = 8.4, 2H)	6.75 (dd, *J* = 9.0 and 2.0 Hz, 2H)
6.42 (d, *J* = 8.7Hz, 1H)	6.42 (d, *J* = 9.0 Hz, 1H)
6.15 (m, 1H)	6.08 (s, 1H)
6.09 (s, 1H)	6.15 (m, 2H)
5.92 (s, 1H)	5.91 (s, 1H)
5.00 (dd, *J* = 11.4, 7.0 Hz, 1H)	5.00 (dd, *J* = 11.0 and 10.0 Hz, 1H)
4.69 (dd, *J* = 11.9, 5.8 Hz, 1H)	4.69 (dd, *J* = 11.5 and 5.5 Hz, 1H)
4.62 (dd, *J* = 11.9 5.8 Hz, 1H)	4.60 (dd, *J* = 12.0 and 5.5 Hz, 1H)
3.05 (t, *J* = 8.3 Hz, 2H)	3.01 (t, *J* = 8.0 Hz, 2H)
2.97 (m, 2H)	2.96 (m, 2H)
2.61 (ddd, *J* = 12.4, 11.9, 11.4Hz, 1H)	2.81 (q, *J* = 12.5 Hz, 1H)
2.71 (ddd. *J* = 12.4, 11.9, 11.4 Hz, 1H)	2.58 (q, *J* = 12.5 Hz, 1H)
1.79 (m, 2H),	1.81 (m, 2H)
1.60 (m, 1H)	1.67 (m, 2H)
1.54 (m, 1H)	1.89 (m, 1H)
1.23 (m, 16H)	1.33 (m, 16H)
0.84 (t, 5.8Hz, 3H)	0.82 (t, *J* = *5.8 Hz*, 3H)

Comparison of ^{13}C NMR spectral data of myristinin-B/C (2a/b) in DMSO-d_6

Position #	Reported [a]	Synthesized	Position #	Reported [a]	Synthesized
2	78	73.95	8'	43.2	43.18
3	34	34.5	9'	24.5	24.47
4	30.4	30.3	10'	28.7	28.61
4a	117	117	11'	28.9	28.74
5	127.6	127.66	12'	28.9	28.93
6	107.8	105.38	13'	29	28.99
7	155.7	155.06	14'	29	29.04
8	102.7	102.68	15'	29	29.04
8a	155.6	156.48	16'	31.3	31.33
1'	103.2	104.34	17'	22.1	22.13
2'	164.1	161.86	18'	13.9	13.98
3'	107.6	107.7	1"	132.1	130.65
4'	163.1	163.72	2", 6"	127.4	127.55
5'	95.1	94.24	3", 5"	115	115.16
6'	160.6	160.24	4"	156.9	157.35
7'	205.5	205.78			

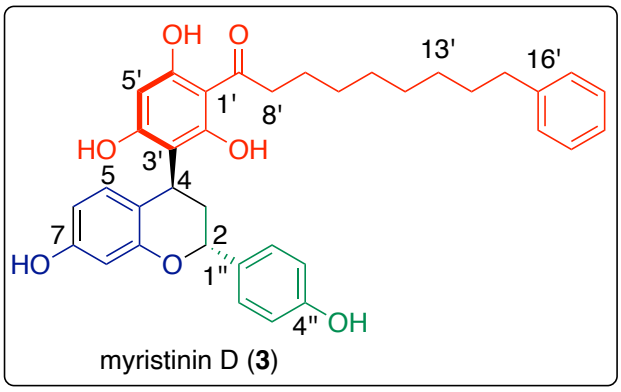
[a]isolated values *J. Org. Chem*, **2002**, *67*, 5470.

***9-phenyl-1-(2,4,6-trihydroxy-3-((2R*,4S*)-7-hydroxy-2-(4-hydroxyphenyl)chroman-4-yl)phenyl)nonan-1-one*(3/4):**

To a cold (0 °C) magnetically stirred solution of salicylaldehyde **7e** (1.0 g, 4.3813 mmol), (±)-camphor sulphonic acid (CSA) (50.8 mg, 0.2190 mmol), in dry CH_3CN (8 mL), was added trimethyl orthoformate (727 μL, 6.5720 mmol) and stirred for 10 min. Then the styrene **8b** (1.38 g, 6.5720 mmol) was added slowly at 0 °C the resulting mixture was stirred at room temperature, and then the phenol **9f** (2.25 g, 6.5720 mmol) in dry CH_3CN (2 mL), was slowly added at 0 °C the resulting mixture was stirred for 1h at 0 °C then slowly warmed to room temperature. After completion of the reaction (TLC control), the reaction mixture was carefully quenched with saturated sodium hydrogen carbonate solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL), the combined organic layer was washed with brine and dried over anhydrous sodium sulphate. Evaporation of the solvent followed by the addition of dry THF and dry MeOH in 1:1 ratio and 10% $Pd(OH)_2/C$ (420 mg) was added to the crude reaction mixture. Then the reaction mixture was stirred at room temperature in an atmosphere of hydrogen created by evacuative displacement of air by H_2 (balloon, 1 atm). After completion of the reaction the catalyst filtered off through a celite pad. Evaporation and purification of the residue on silica gel column, using Pet. Ether: CH_2Cl_2: MeOH: AcOH (70:25:3:1) as an eluent

afforded the required bicyclic product **3** in (230 mg, 9%) and mixture of phenol **9f** and **4a/b.** and further purification of the mixture on silica gel column, using Pet. Ether: $CHCl_3$: MeOH: AcOH (70:25:3:1) as an eluent afforded the required bicyclic product **4a/b** in (897 mg, 35%).

1-(2,4,6-trihydroxy-3-((2R*,4S*)-7-hydroxy-2-(4-hydroxyphenyl)chroman-4-yl)phenyl)dodecan-1-one **(3):**



myristinin D (**3**)

Physical Appearance: Pale Brown colour foamy solid

R_f: 0.3 (Petroleum Ether: CH_2Cl_2: MeOH: AcOH [70:25:3:1])

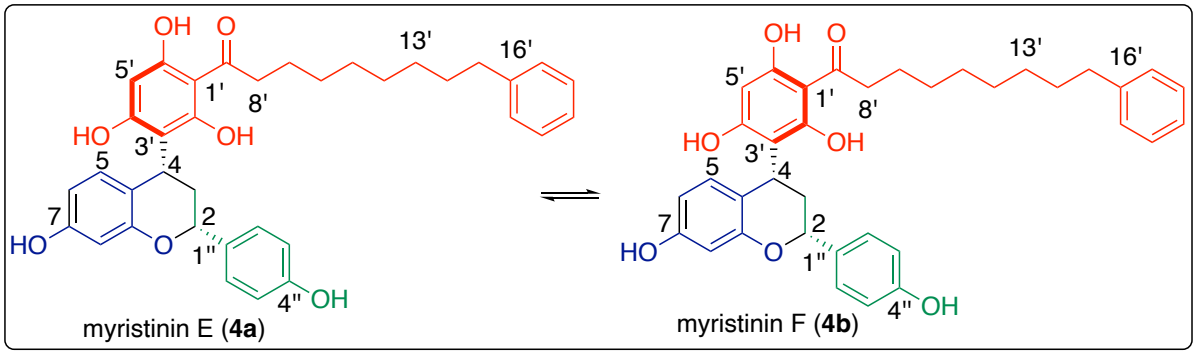
R_t: 48.4 min (MeOH: H_2O) [C18 column, 4ml/min]

IR (neat): 3409, 2931, 2835, 1708, 1639, 1454, 1439, 1375, 1335, 1258, 1169, 1104, 1055, 817, 719 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d6): δ 14.30 (bs, 1H) , 10.57 (bs, 1H) , 10.18 (bs, 1H) , 9.32 (s, 1H) , 8.99 (s, 1H) , 7.08 (d, J = 8.7 Hz, 2H) , 6.69 (d, J = 8.4 Hz, 2H) , 6.35 (d, J = 8.4 Hz, 1H), 6.22 (d, J = 2.1 Hz, 1H) , 6.11 (dd, J = 8.1, 2.4 Hz, 1H) , 5.94 (s, 1H) , 5.36 (t, J = 4.2 Hz, 1H), 4.15 (dd, J = 8.4, 6.3 Hz, 1H) , 2.96 (t, J = 7.5 Hz, 2H) , 2.57 (m, 1H) , 2.08 (m, 2H), 1.55 (bs, J = 6.6 Hz, 4H) and 1.23 (s, 8H).

^{13}C NMR (125 MHz, DMSO-d6, DEPT): δ205.5 (C), 164.3 (C), 162.9 (C), 160.3 (C), 155.9 (C), 156.3 (C), 154.5 (C), 142.3 (C), 132.3 (C), 128.2 (4 x CH), 128.1 (CH), 126.6 (2 x CH), 125.5 (CH), 116.8 (C), 115.0 (2 x CH), 108.2 (C), 107.5 (CH), 103.5 (C), 102.5 (CH), 94.6 (CH), 74.5 (CH), 43.1 (CH_2), 35.1 (CH_2), 32.2 (CH_2), 30.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 25.5 (CH), 24.5 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{36}H_{38}NaO_7$ 605.2510, found 605.2514.



1-(2,4,6-trihydroxy-3-((2R*,4R*)-7-hydroxy-2-(4-hydroxyphenyl)chroman-4-yl)phenyl)dodecan-1-one (**4a/b**):

Physical Appearance: Pale Brown colour foamy solid

R_f: 0.5 (Petroleum Ether: $CHCl_3$: MeOH: AcOH [70:25:3:1])

R_t: 53.3 min (MeOH: H_2O) [C18 column, 4ml/min]

IR (neat): 3429, 2931, 2845, 1704, 1629, 1465, 1442, 1386, 1337, 1249, 1159, 1124, 1061, 807, 729 cm^{-1}.

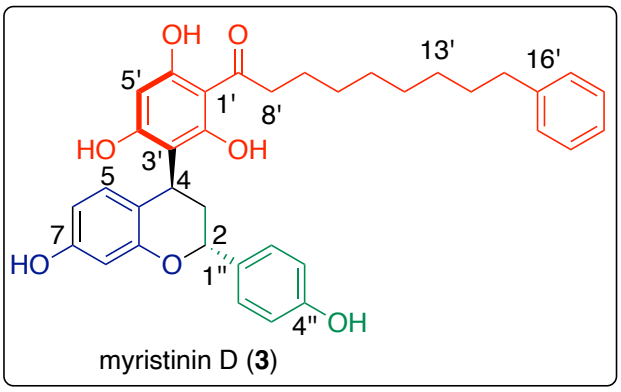
^{1}H NMR (500 MHz, DMSO-d6): δ 14.52 (s, 1H), 14.10 (s, 1H) , 10.55 (br s, 1H), 10.07 (br s, 1H), 9.39 (s, 1H), 8.97 (s, 1H), 7.24 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.75 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.42 (d, *J* = 9.0 Hz, 1H), 6.08 (s, 1H), 6.15 (s, 1H), 5.91 (s, 1H), 5.00 (dd, *J* = 11.0, 10.0 Hz, 1H), 4.69 (dd, *J* = 11.5, 5.5 Hz, 1H,), 4.60 (dd, *J* = 12.0, 5.5 Hz, 1H), 3.01 (t, *J* = 8.0 Hz, , 1H), 2.96 (m, 1H), 2.81 (q, *J* = 12.5 Hz, 1H), 2.58 (q, *J* = 12.3 Hz, 1H), 1.89 (m, 2H), 1.67 (bs, 4H), 1.33 (bs, 8H).

^{13}C NMR (125 MHz, DMSO-d6, DEPT): δ 205.6 (C), 164.6 (C), 163.02 (C), 160.6 (C), 156.9 (C), 155.8 (C), 155.7 (C), 142.3 (C), 132.1 (C), 128.3 (CH), 128.2 (CH), 127.6 (CH), 127.4 (CH), 125.6 (CH), 117.1 (C), 115.1 (CH), 107.8 (CH), 107.6 (C), 104.1 (C), 102.7 (CH), 95.1 (CH), 78.1 (CH), 43.2 (CH_2), 35.1 (CH_2), 34.0 (CH_2), 31.0 (CH_2), 30.9 (CH), 28.9 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 24.6 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{36}H_{38}NaO_7$ 605.2510, found 605.2512.

Comparison of ^{1}H NMR spectral data of myristinin-D (3)in DMSO-d_6

Reported [a]	Synthesized
14.33 (br s, 1H)	14.30 (br s, 1H)
10.61 (br s, 1H)	10.57 (br s, 1H)
10.23 (br s, 1H)	10.18 (br s, 1H)
9.36 (br s, 1H)	9.32 (s, 1H)
9.04 (br s, 1H)	8.99 (s, 1H)
7.25-7.18 (m, 5H)	7.25-7.15 (m, 5H)
7.09 (br d, J = 8.4 Hz, 2H)	7.08 (d, J = 8.7 Hz, 2H)
6.71 (br d, 8.4, 2H)	6.69 (d, J = 8.4 Hz, 2H)
6.38 (d, J = 8.4 Hz, 1H)	6.35 (d, J = 8.4Hz, 1H)
6.25 (d, J = 2.3Hz, 1H)	6.22 (d, J = 2.1 Hz, 1H)
6.12 (dd, J = 8.4, 2.2Hz, 1H)	6.11 (dd, J = 8.1 and 2.4 Hz, 1H)
5.97 (s, 1H)	5.94 (s, 1H)
5.38 (dd, J = 4.3, 4.1 Hz, 1H)	5.36 (t, J = 4.2Hz, 1H)
4.17 (dd, J = 8.0, 7.0 Hz, 1H)	4.15 (dd, J = 8.4, 6.3 Hz, 1H)
2.97 (t, J = 7.3 Hz, 2H)	2.96 (t, J = 7.5 Hz, 2H)
2.04 (m, 1H)	2.05 (m, 1H)
2.59 (m, 1H)	2.57 (m, 1H)
1.54 (m, 2H)	1.54 (m, 2H)
1.26 (m, 9H)	1.23 (s, 8H).

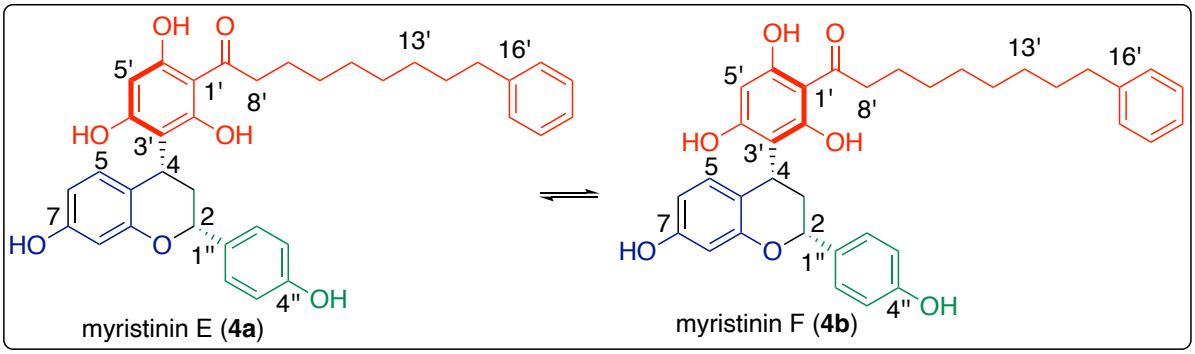


myristinin D (**3**)

Comparison of ^{13}C NMR spectral data of myristinin-D (3) in DMSO-d_6

Reported [a]	Synthesized	Reported [a]	Synthesized
205.5	205.47	115.1	115.01
164.4	164.29	115.1	115.01
163	162.92	108.2	108.16
160.4	160.32	107.6	107.5
156.3	155.9	103.6	103.5
156	156.27	102.6	102.49
154.6	154.54	94.6	94.57
142.4	142.3	74.6	74.54
132.3	132.27	43.2	43.11
128.3	128.22	35.2	35.12
128.3	128.22	32.2	32.16
128.3	128.22	31	30.93
128.3	128.22	28.9	28.85
128	128.17	28.9	28.85
126.7	126.62	28.8	28.74
126.7	126.62	28.7	28.58
125.6	125.53	25.6	25.52
116.9	116.82	24.6	24.52

[a]isolated values *J. Org. Chem*, **2002**, *67*, 5470.



Comparison of ^{1}H NMR spectral data of myristinin-E/F (4a/b) in DMSO-d_6

Reported [a]	Synthesized	Reported [a]	Synthesized
14.58 (br s, 1H)	14.52 (s, 1H)	6.16-6.19 (br d, J = 8.1 Hz, 1H)	6.16-6.19 (br s, 1H)
14.17 (br s, 1H)	14.10 (s, 1H)	6.13 (s, 1H)	6.15 (s, 1H)
10.65 (br s, 1H)	-	5.96 (s, 1H)	5.91 (s, 1H)
10.63 (br s, 1H)	-	5.02 (dd, J = 11.3, 7.0 Hz, 1H)	5.00 (dd, J = 11.0 and 10.0 Hz, 1H)
10.56 (br s, 1H)	10.55 (br s, 3H)	4.74 (dd, J = 11.7, 5.8 Hz, 1H)	4.69 (dd J = 11.5 and 5.5 Hz, 1H,)
10.11 (br s, 1H)	10.07 (br s, 1H)	4.67 (dd, J = 11.7, 5.8 Hz, 1H)	4.60 (dd, J = 12.0 and 5.5 Hz, 1H)
9.46 (br s, 1H)	9.39 (s, 1H)	3.03 (t, J = 7.2 Hz, 2H)	3.01 (t, J = 8.0 Hz, 2H)
9.06 (br s, 1H)	8.97 (s, 1H)	2.76 (ddd, J = 12.2, 11.7, 11.3 Hz, 1H)	2.82 (ddd, J = 12.3, 11.5, 11.7 Hz, 1H)
7.24 (m, 2H)	7.27 (m, 2H)	2.65 (ddd, J = 12.2, 11.7, 11.3 Hz, 1H)	2.81 (q, J = 12.5 Hz, 1H)
7.24 (br d, J = 8.4 Hz, 2H)	7.24 (dd, J = 9.0 and 2.0 Hz, 2H)	2.50 (t, J = 7.7 Hz, 1H)	2.58 (q, J = 12.3 Hz, 1H)
7.12 (m, 3H)		1.82 (m, 2H)	1.89 (m, 2H)
6.79 (br d, J = 8.4 Hz, 2H)	6.75 (dd, J = 9.0 and 2.0 Hz, 2H)	1.60 (m, 1H)	1.63 (m, 1H)
6.47 (d, J = 8.1 Hz, 1H)	6.42 (d, J = 9.0 Hz, 1H)	1.52 (m, 1H)	1.67 (bs, 4H)
6.19 (br s, 1H)	6.08 (s, 1H)	1.25 (m, 4H)	1.33 (bs, 8H).

Comparison of ^{13}C NMR spectral data of myristinin-E/F (4a/b) in DMSO-d_6

Reported [a]	Synthesized	Reported [a]	Synthesized
205.691	205.61	107.737	107.58
205.605	205.53	107.429	107.31
164.803	164.61	104.173	104.06
164.34	164.14	103.374	103.25
163.226	163.17	102.828	102.7
162.901	162.81	102.785	102.67
160.716	160.6	95.177	95.13
160.518	160.32	93.98	93.93
157.049	156.94	78.294	78.14
155.877	155.79	78.18	78.05
155.702	155.75	43.335	43.16
155.652	155.57	35.292	35.15
142.423	142.34	34.17	34.03
132.26	132.15	33.718	33.59
128.319	128.26	31.115	30.96
128.268	128.21	30.997	30.86
127.794	127.62	30.558	30.44
127.651	127.53	29.064	28.9
127.565	127.44	29.029	28.76
125.628	125.57	28.926	28.72
117.215	117.06	28.881	28.61
117.144	117.01	24.7	24.56
115.16	115.06	24.6	24.52
107.937	107.82		

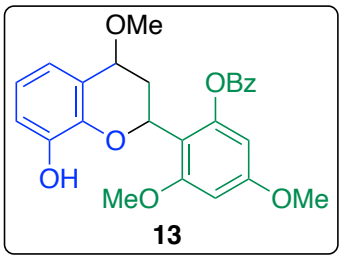
[a]isolated values *J. Org. Chem*, **2002**, *67*, 5470.

Total Synthesis of (±)-3'-hydroxy-5,7-dimethoxy-4-O-2'-cycloflavan (5)

***2-((2S*,4S*)-8-hydroxy-4-methoxychroman-2-yl)-3,5-dimethoxyphenyl benzoate* (13)**:

To a magnetically stirred solution of salicylaldehyde **7i** (70 mg, 0.50 mmol) and styrene derivative **11d** (216 mg, 0.76 mmol) in dry CH_2Cl_2 (7 ml) was added trimethyl orthoformate (84 µL, 0.76 mmol) followed by (±) CSA (11.7 mg, 0.050 mmol) at 0 ºC. Reaction mixture slowly brought to room temperature and monitored by TLC. After disappearances of intermediate spots on TLC reaction was quenched with saturated aqueous $NaHCO_3$ solution (4 ml). After stirring for 5 minute extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc:petroleum ether (8:92) as eluent furnished flavan derivative **13** (141 mg, 64 %).

Physical appearance: sticky solid.



13

R_f: 0.5 (1:9 EtOAc:petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07-8.02 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.35-7.32 (m, 2H), 6.65-6.63 (m, 3H), 6.47 (s, 1H), 6.39 (s, 1H), 5.84 (d, *J* = 12.5 Hz, 1H), 5.57 (s, 1H), 4.24 (s, 1H), 3.84 (s, 6H), 3.36 (s, 3H), 2.54 (t, *J* = 14.5 Hz, 1H), 2.26 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 166.0 (C), 160.9 (C), 159.3 (C), 151.5 (C), 144.9 (C), 142.3 (C), 133.6 (CH), 130.1 (2 x CH), 128.9 (C), 128.5 (2 x CH), 121.4 (CH), 120.7 (C), 119.6 (CH), 114.4 (CH), 100.7 (CH), 97.3 (CH), 72.5 (CH), 66.8 (CH), 56.1 (CH_3), 55.8 (CH_3), 55.6 (CH_3), 31.3 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{25}H_{24}NaO_7$ 459.1414, found 459.1410

***(6R*,12R*)-7,9-dimethoxy-6H,12H-6,12-methanodibenzo[b,f][1,5]dioxocin-4-ol* (5)**:

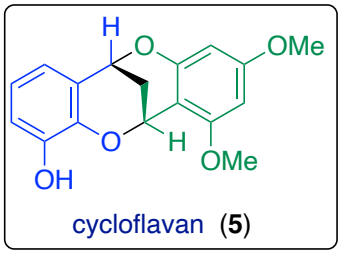
The compound **13** (140 mg, 0.32 mmol) was subjected to de-benzoylation under 3N NaOH (6 ml) under room temperature in MeOH solvent (3 mL) and monitored by TLC. After completion of the starting material the reaction mixture was cooled to 0 ºC the pH was adjusted to 3 by adding HCl. After stirring for 5 minute extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and the crude mixture was treated with (±) CSA (5.2 mg, 0.022 mmol) at 0 ºC. Reaction mixture slowly brought to room temperature and monitored by TLC. After disappearances of starting material on TLC reaction was quenched with saturated aqueous $NaHCO_3$ solution (4 ml). After stirring for 5 minute extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc:petroleum ether (25:75) as eluent furnished cycloflavan derivative (**5**) (54 mg, 56 % over 2 steps).

Physical appearance: brown solid.

M.P.: 147-149 °C

R_f: 0.3 (2:8 EtOAc:petroleum ether).

IR (neat): 3466, 2929, 2846, 1617, 1592, 1477, 1273, 1220, 1145, 1108, 1040, 986, 944, 911, 817, 795, 760, 740 cm^{-1}.



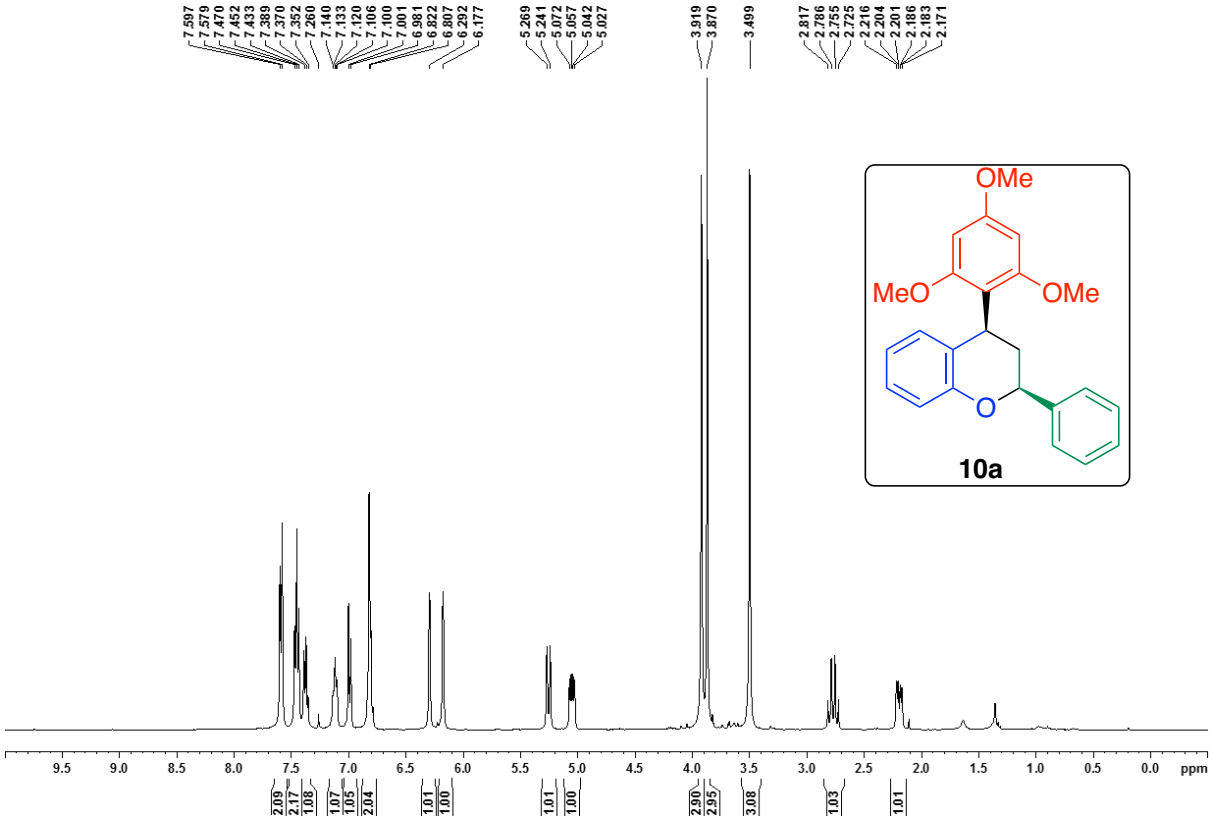
cycloflavan (**5**)

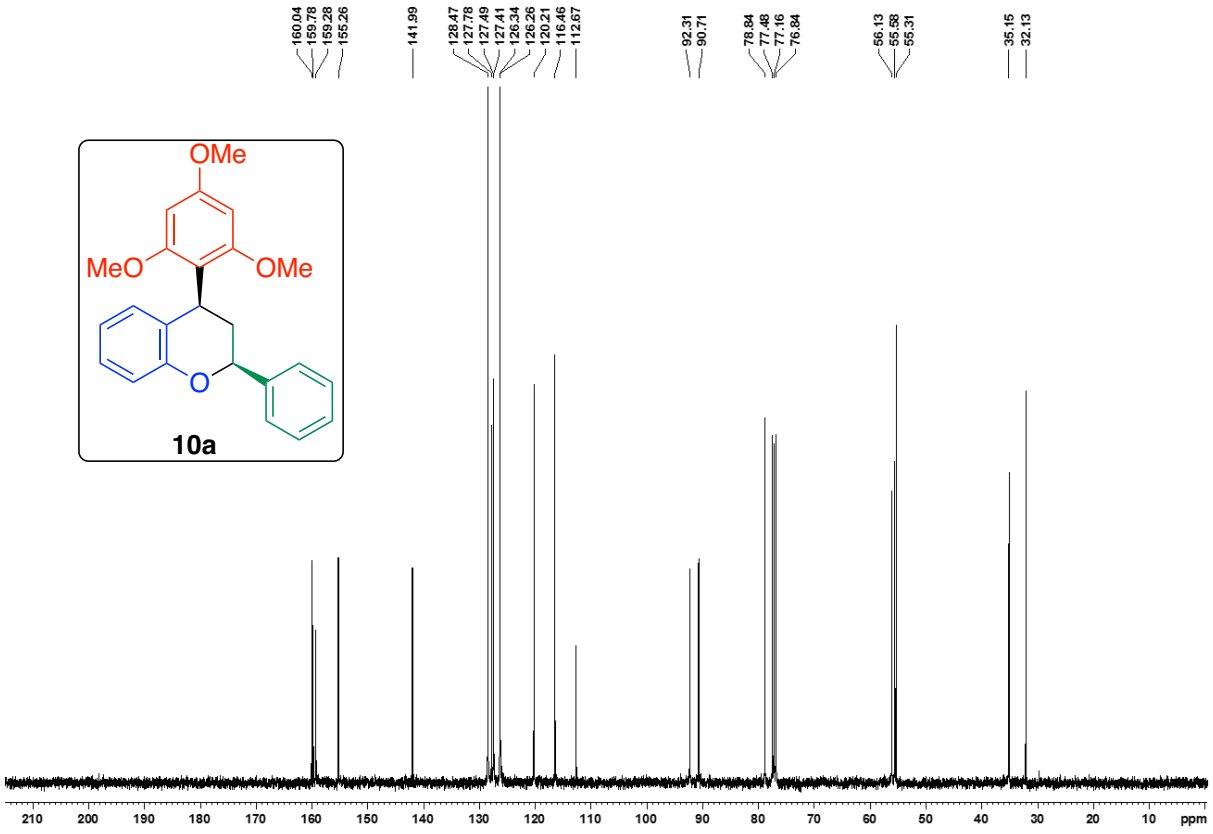
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.80 (dd, *J* = 1.5, 7.2 Hz, 1H), 6.70 (d, *J* = 1.6 Hz, 1H), 6.68 (d, *J* = 7.4, 1H), 6.11 (d, *J* = 2.3 Hz, 1H), 5.97 (d, *J* = 2.3 Hz, 1H), 5.62 (br s, 1H), 5.34 (br s, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 2.16 (dt, *J* = 2.5, 14.0 Hz, 1H), 2.08 (dt, *J* = 2.5, 14.0 Hz, 1H).

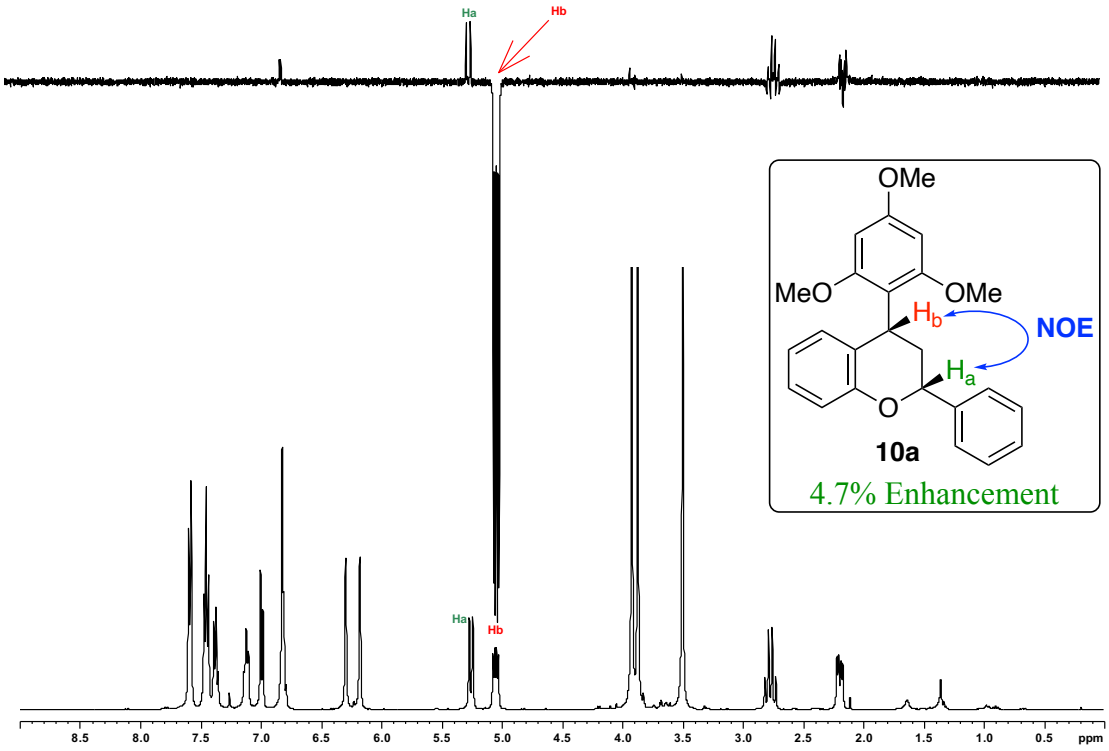
^{13}C NMR (100 MHz, DMSO-d_6, DEPT): δ 161.9 (C), 159.3 (C), 155.0 (C), 146.1 (C), 142.2 (C), 122.5 (C), 121.4 (CH), 120.1 (CH), 116.5 (CH), 103.5 (C), 93.4 (CH), 91.8 (CH)67.2 (CH), 61.5 (CH), 56.1 (OCH_3), 55.6 (OCH_3), 26.5 (CH_2).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{16}NaO_5$ 323.0895, found 323.089

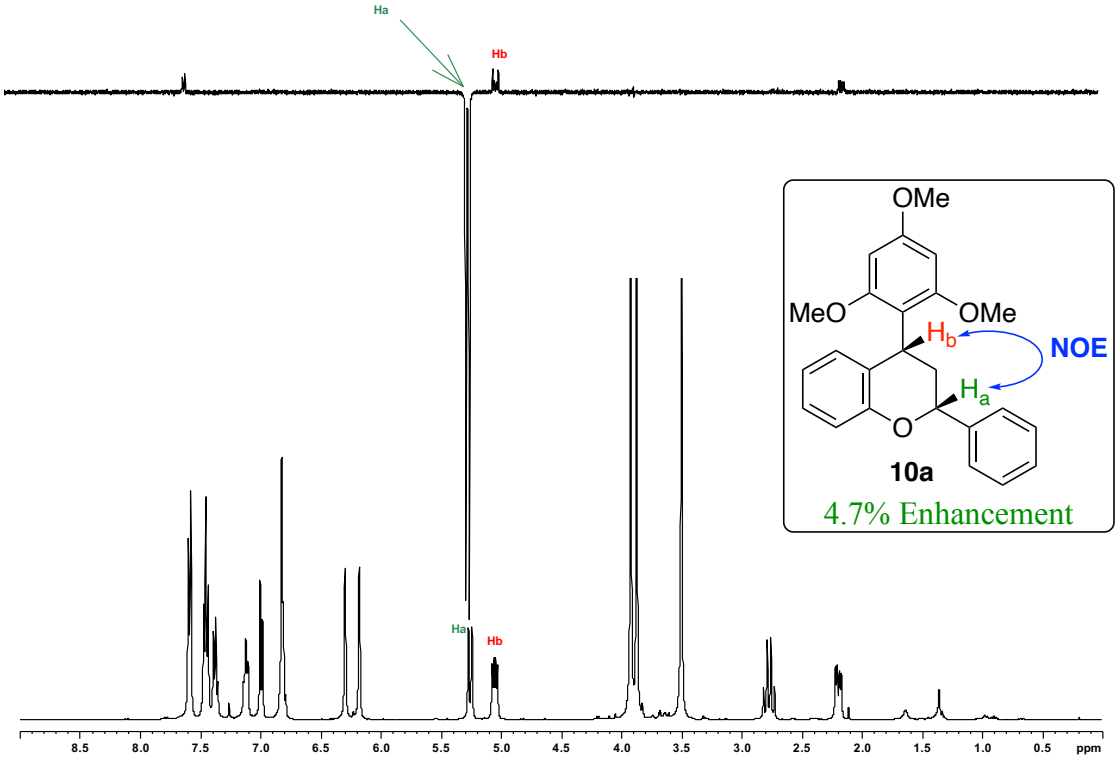
^{1}H and ^{13}C NMR spectra of cassiaflavans



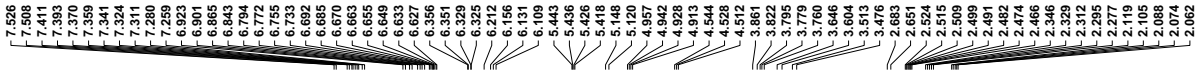




NOE spectrum of cassiaflavan **10a**



NOE spectrum of cassiaflavan **10a**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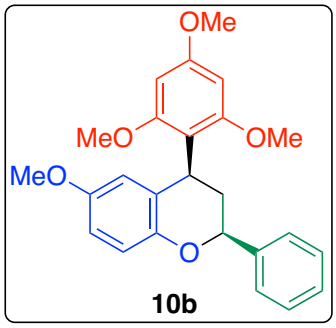
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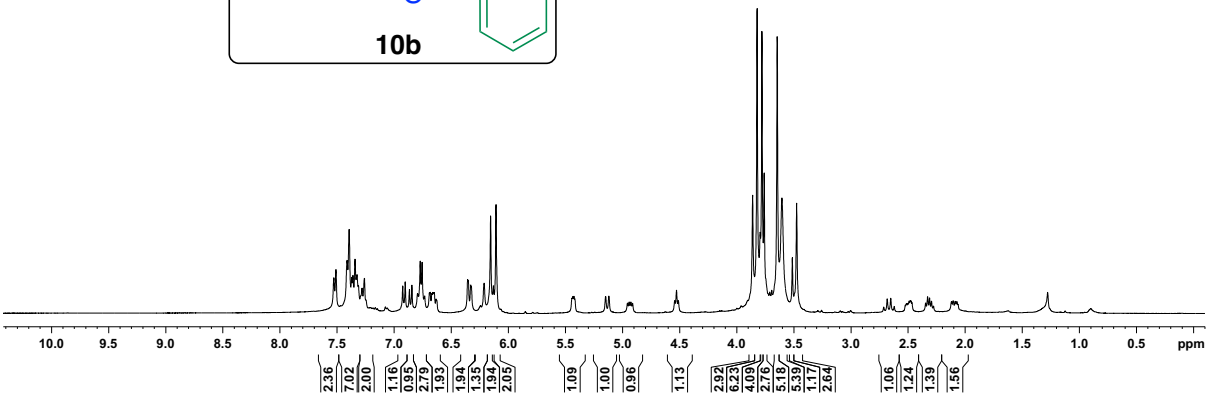
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1.94
1.35
1.94
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1.09
1.00
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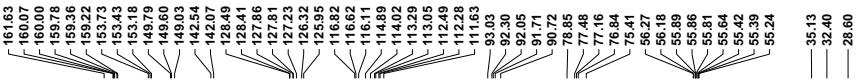
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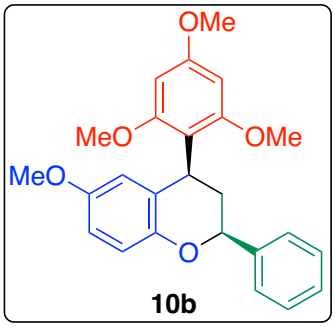
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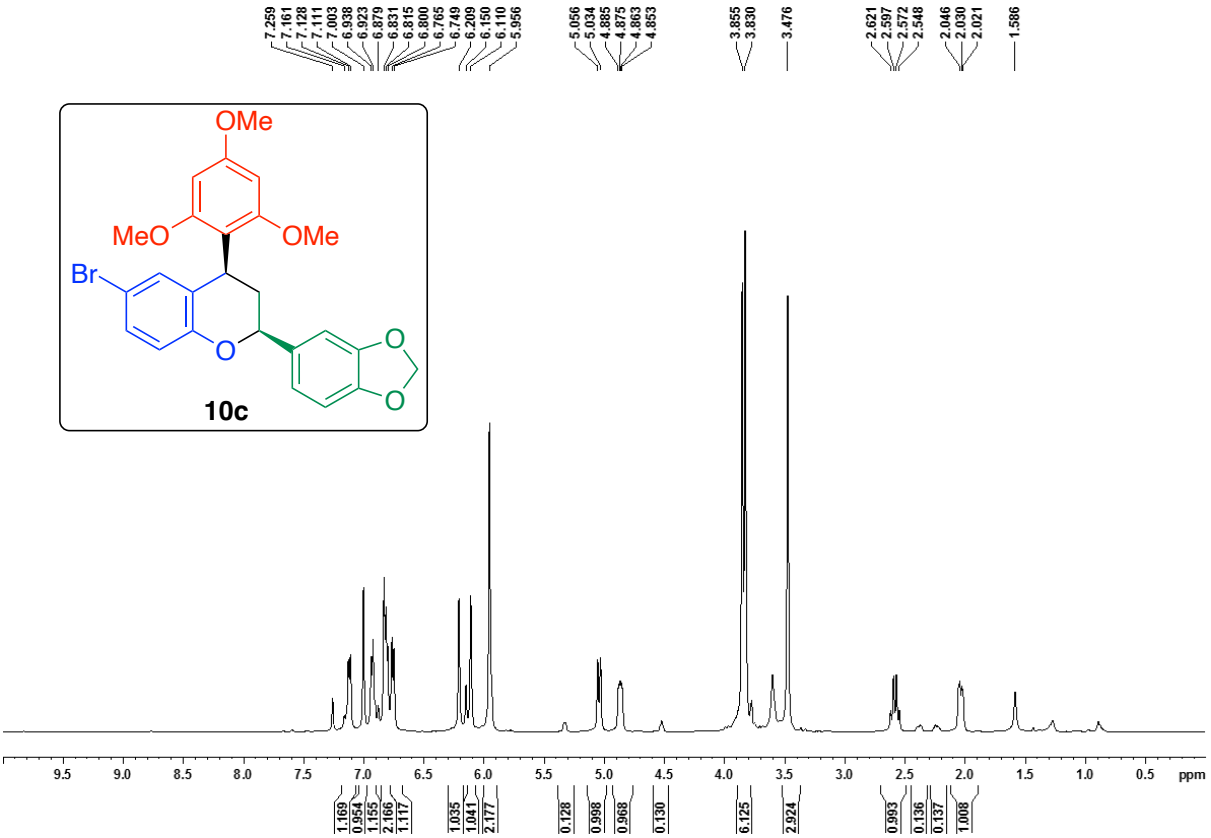
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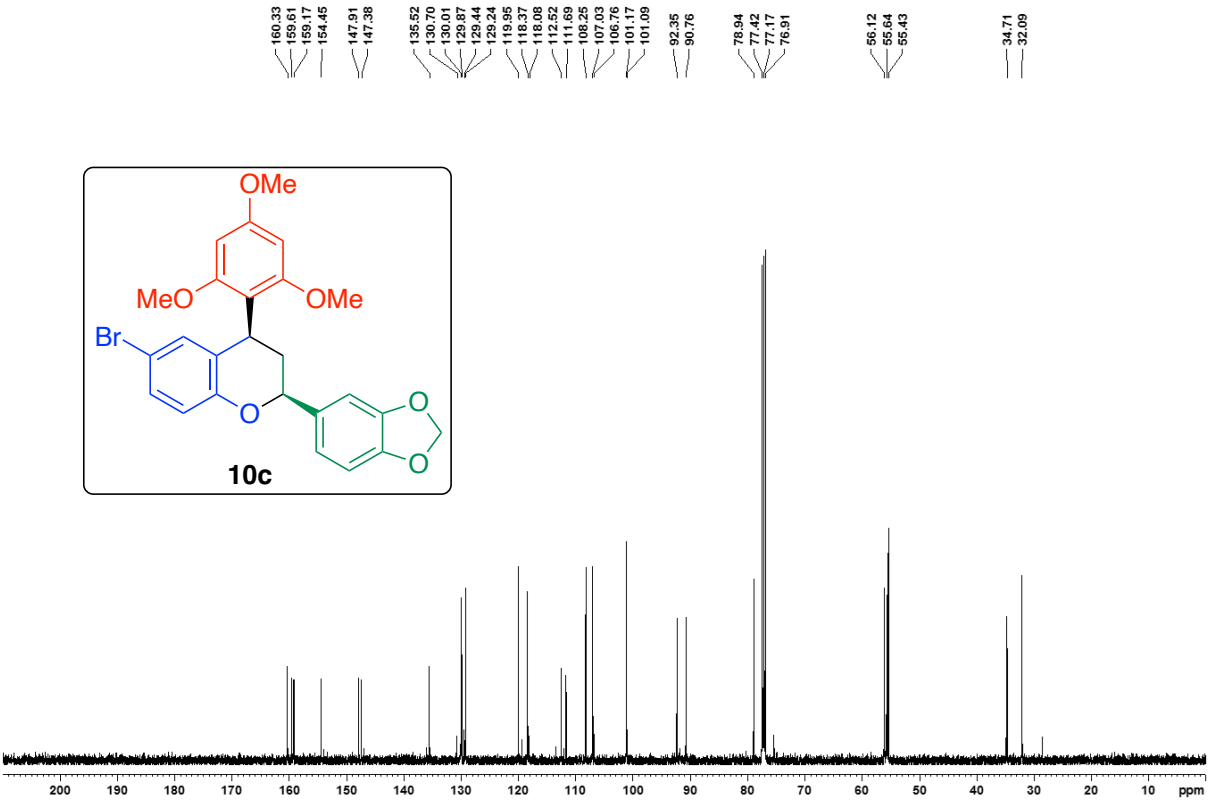
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34.71
32.09
OMe
MeO
OMe
Br
O
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10c
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170
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150
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120
110
100
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60
50
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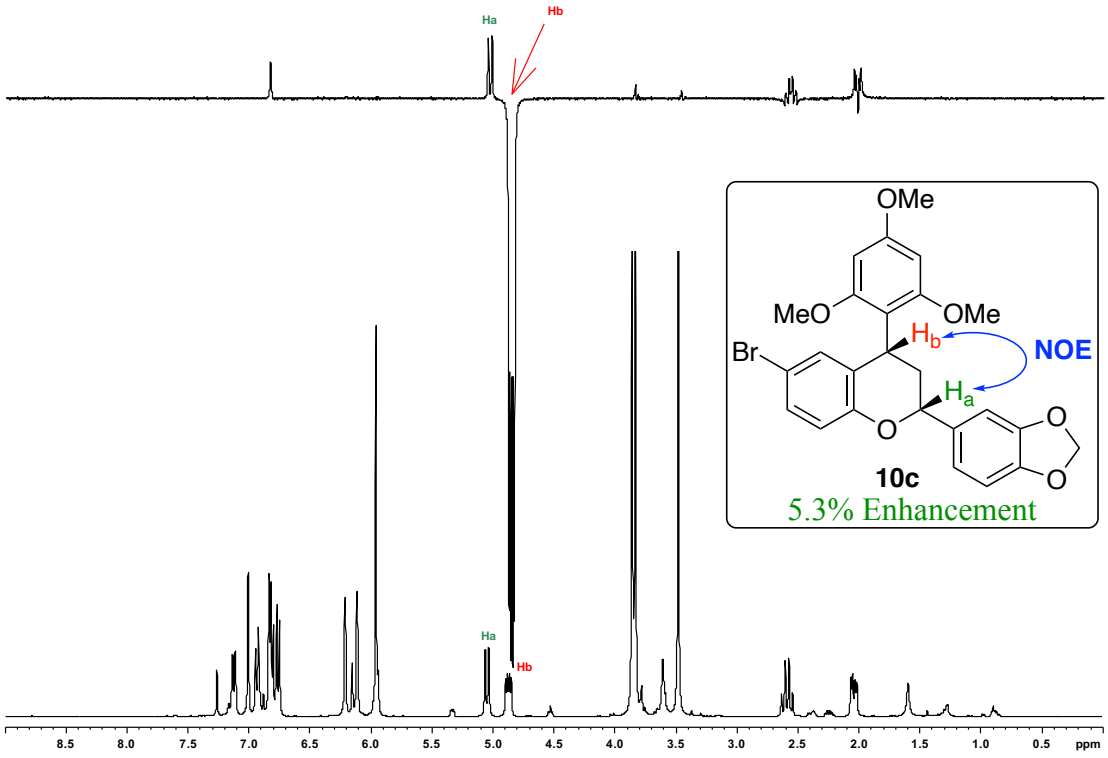
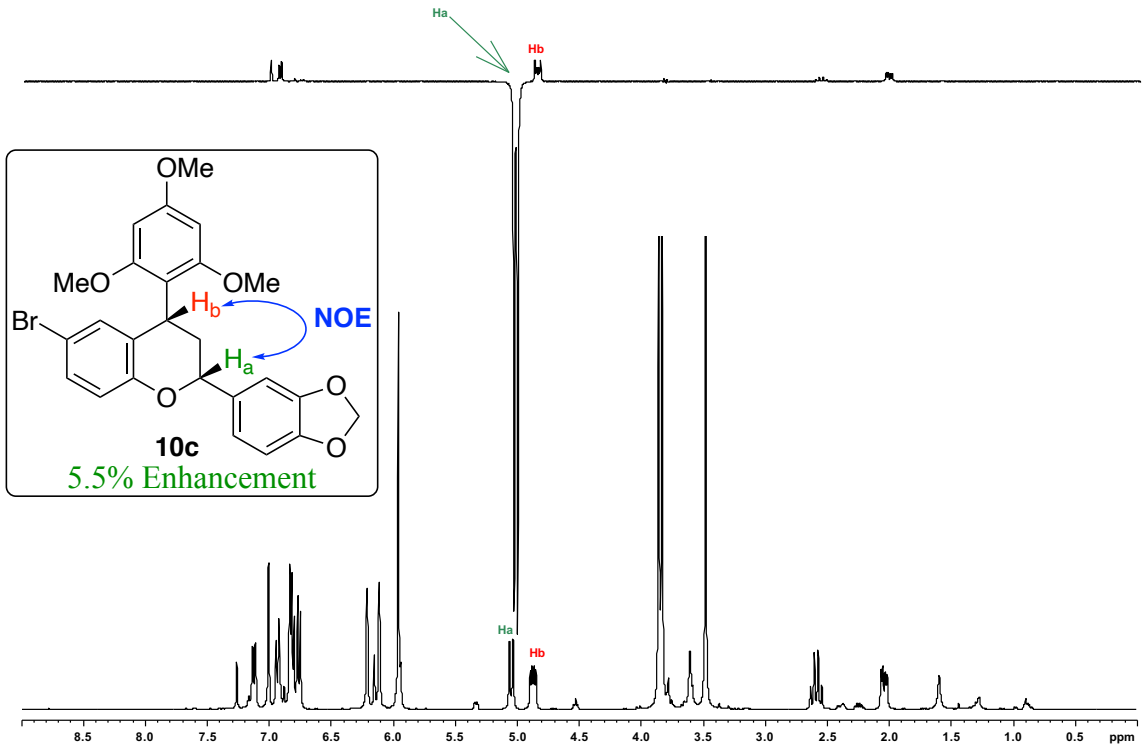
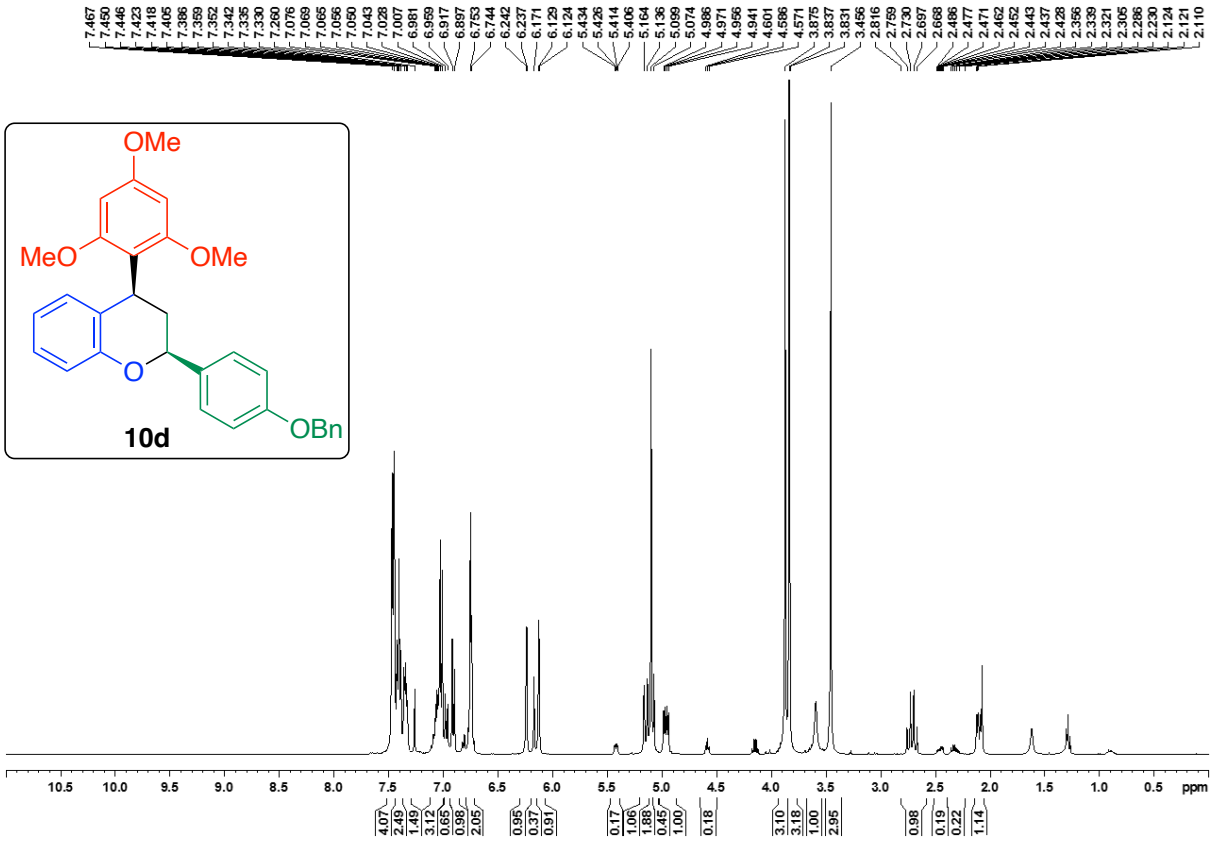
30
20
10
ppm

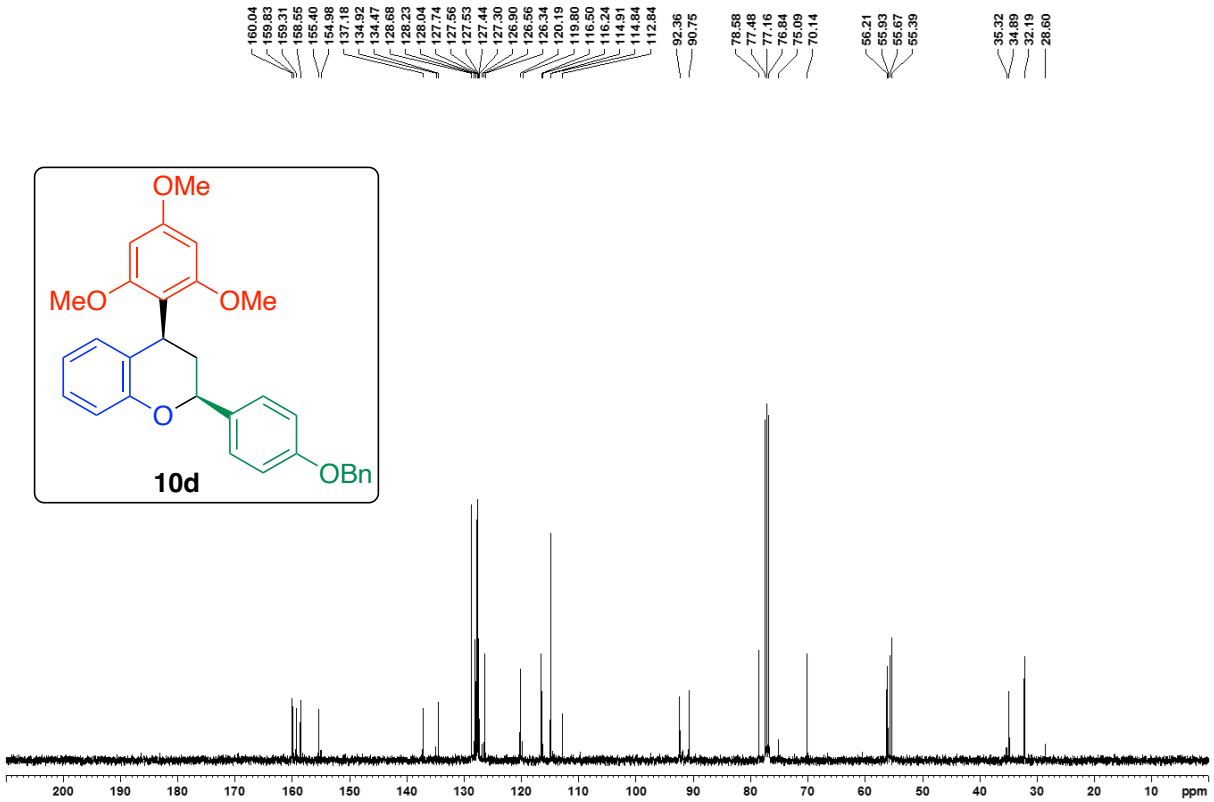


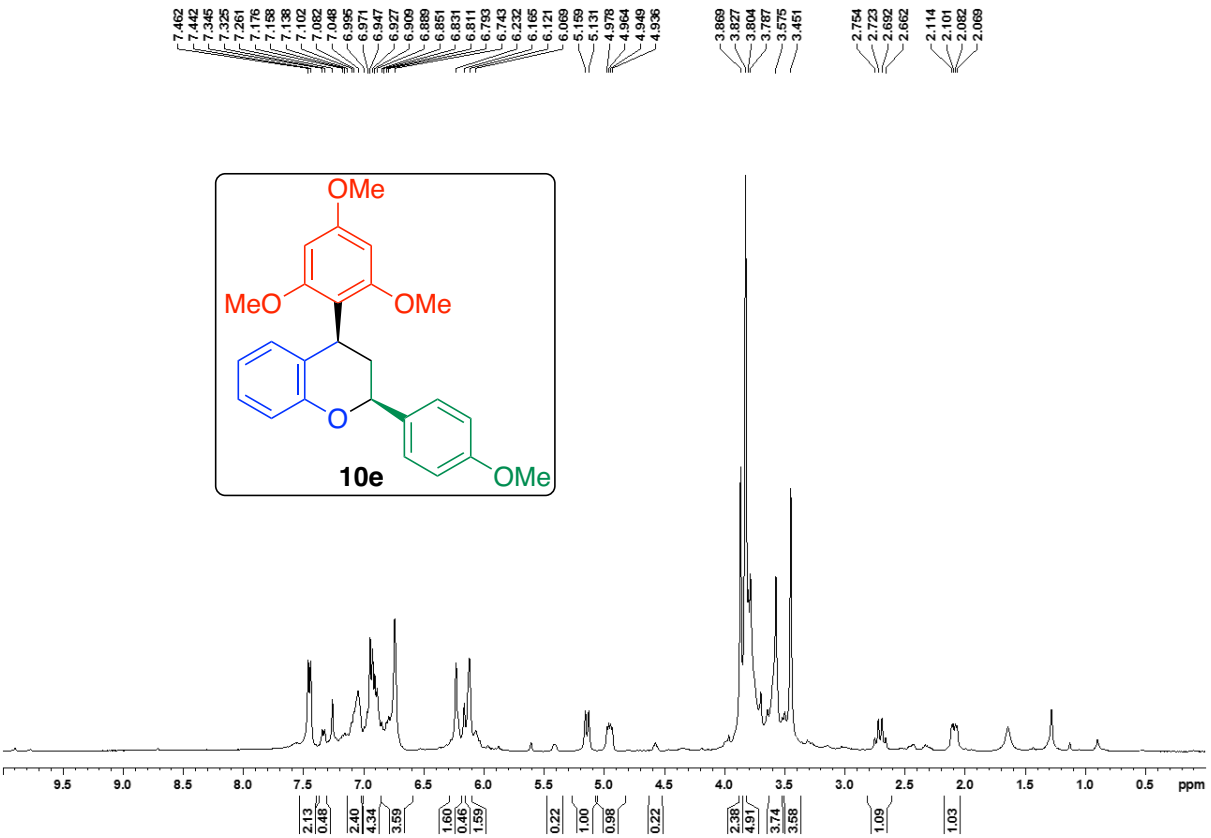
NOE spectrum of cassiaflavan **10c**



NOE spectrum of cassiaflavan **10c**


OMe
MeO
OMe
OBn
10d
ppm


OMe
MeO
OMe
OBn
10d
ppm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7.345
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7.261
7.176
7.158
7.138
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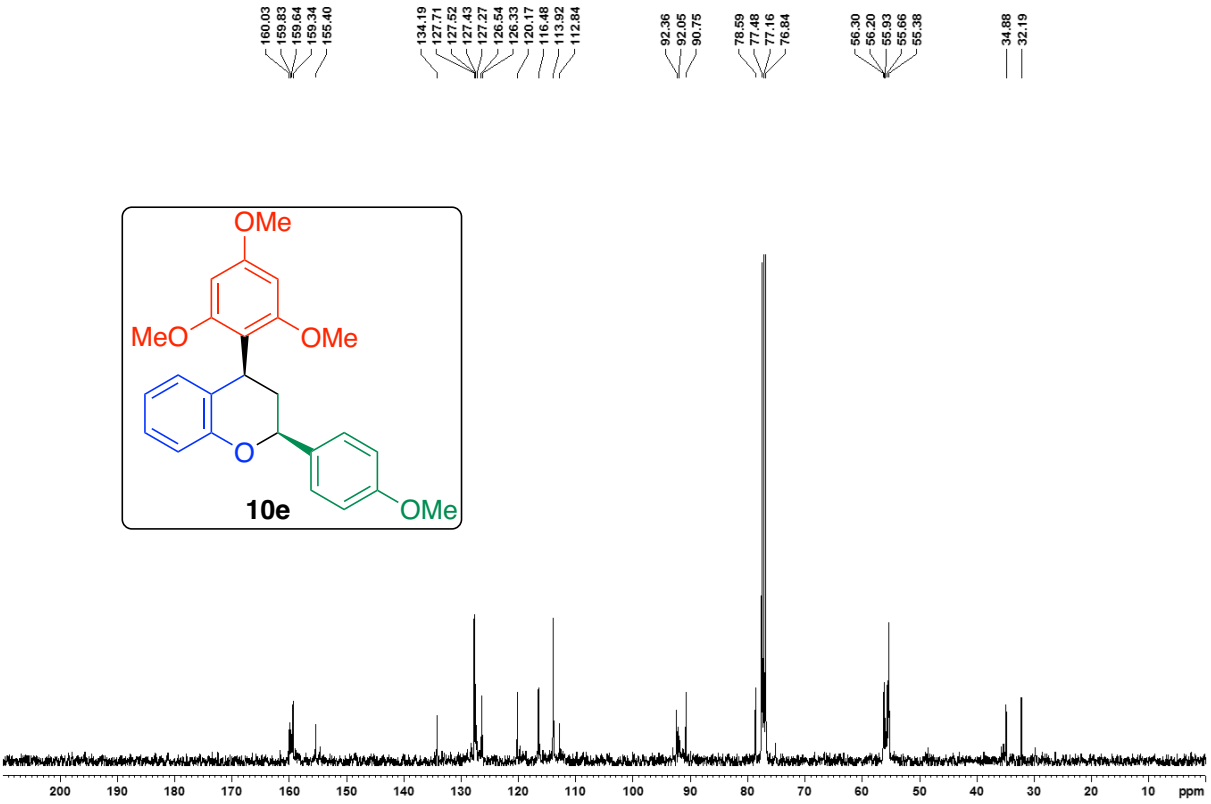
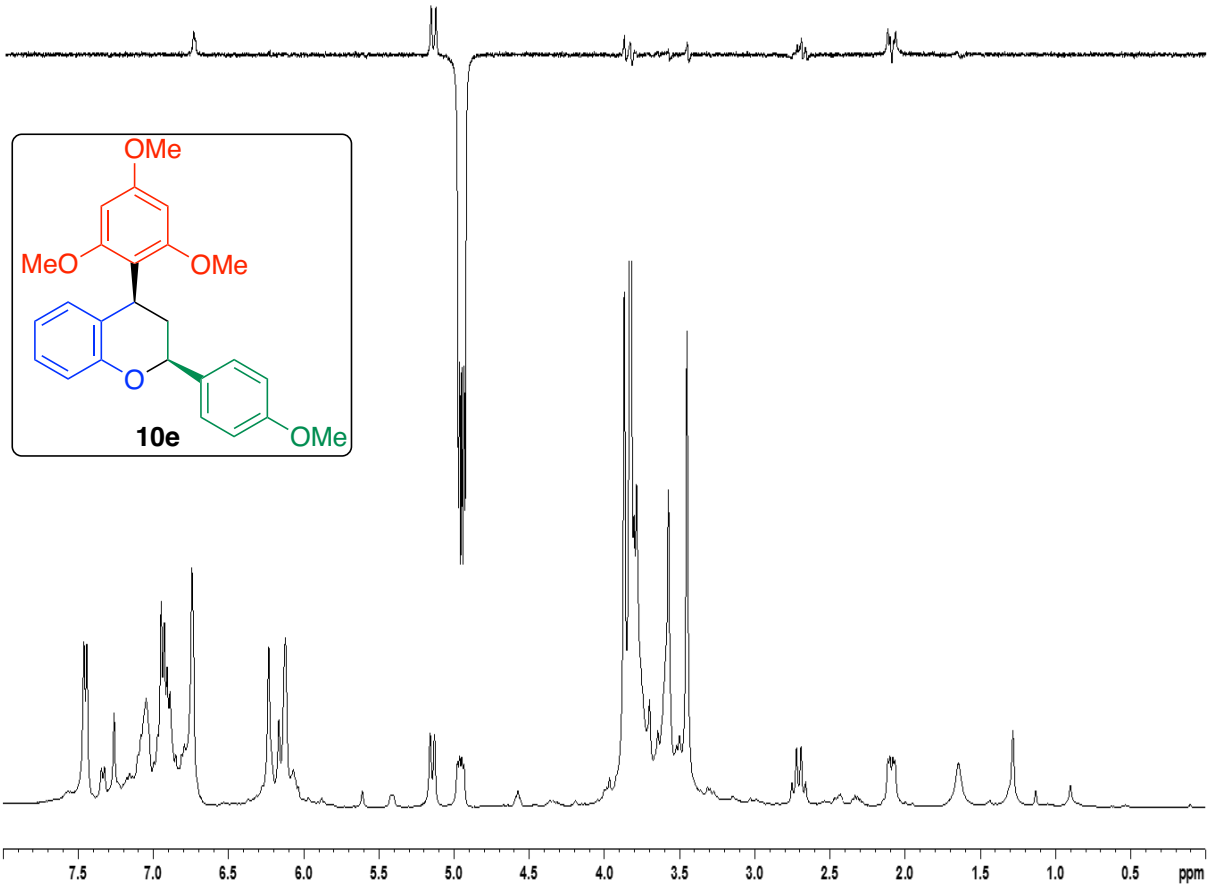
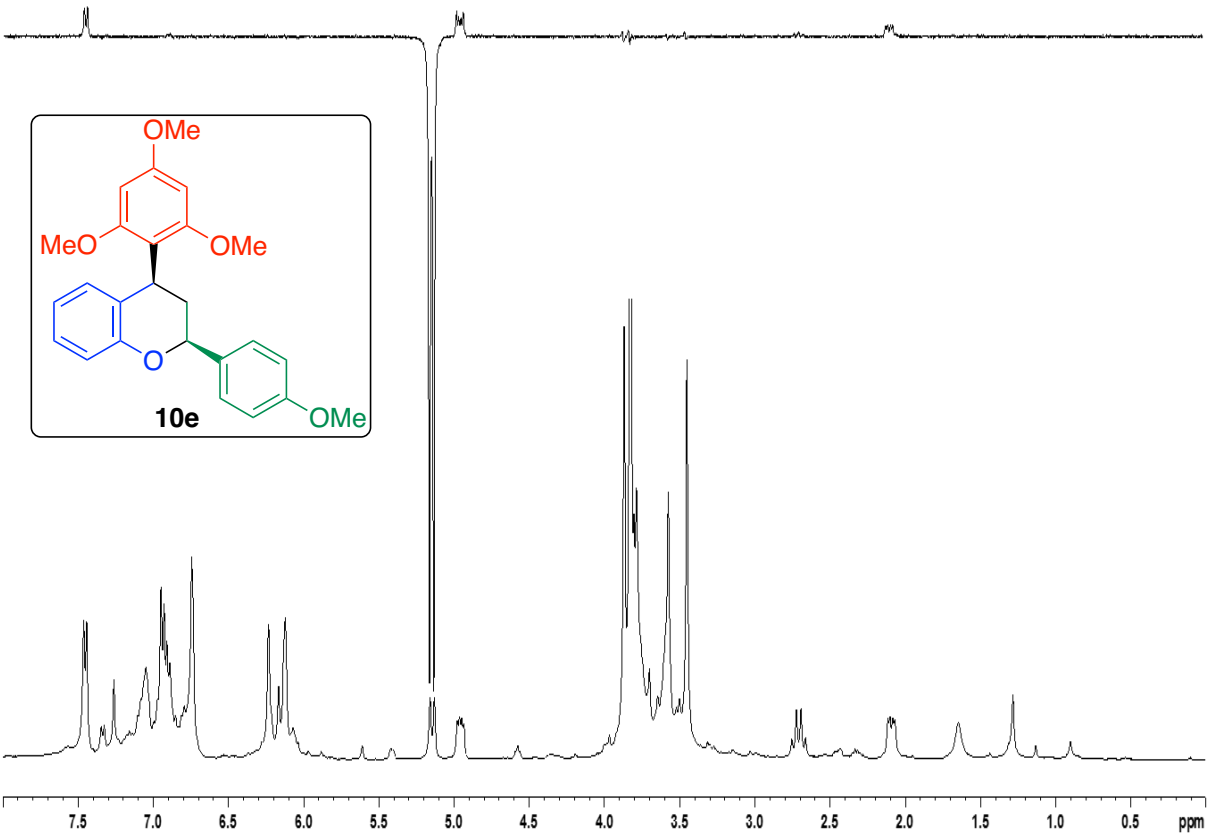
7.082
7.048
6.995
6.971
6.947
6.927
6.909
6.889
6.851
6.831
6.811
6.793
6.743
6.232
6.165
6.121
6.069
5.159
5.131
4.978
4.964
4.949
4.936
3.869
3.827
3.804
3.787
3.575
3.451
2.754
2.723
2.692
2.662
2.114
2.101
2.082
2.069
OMe
MeO
OMe
O
OMe
10e
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.13
0.48
2.40
4.34
3.59
1.60
0.46
1.59
0.22
1.00
0.98
0.22
2.38
4.91
3.74
3.58
1.09
1.03

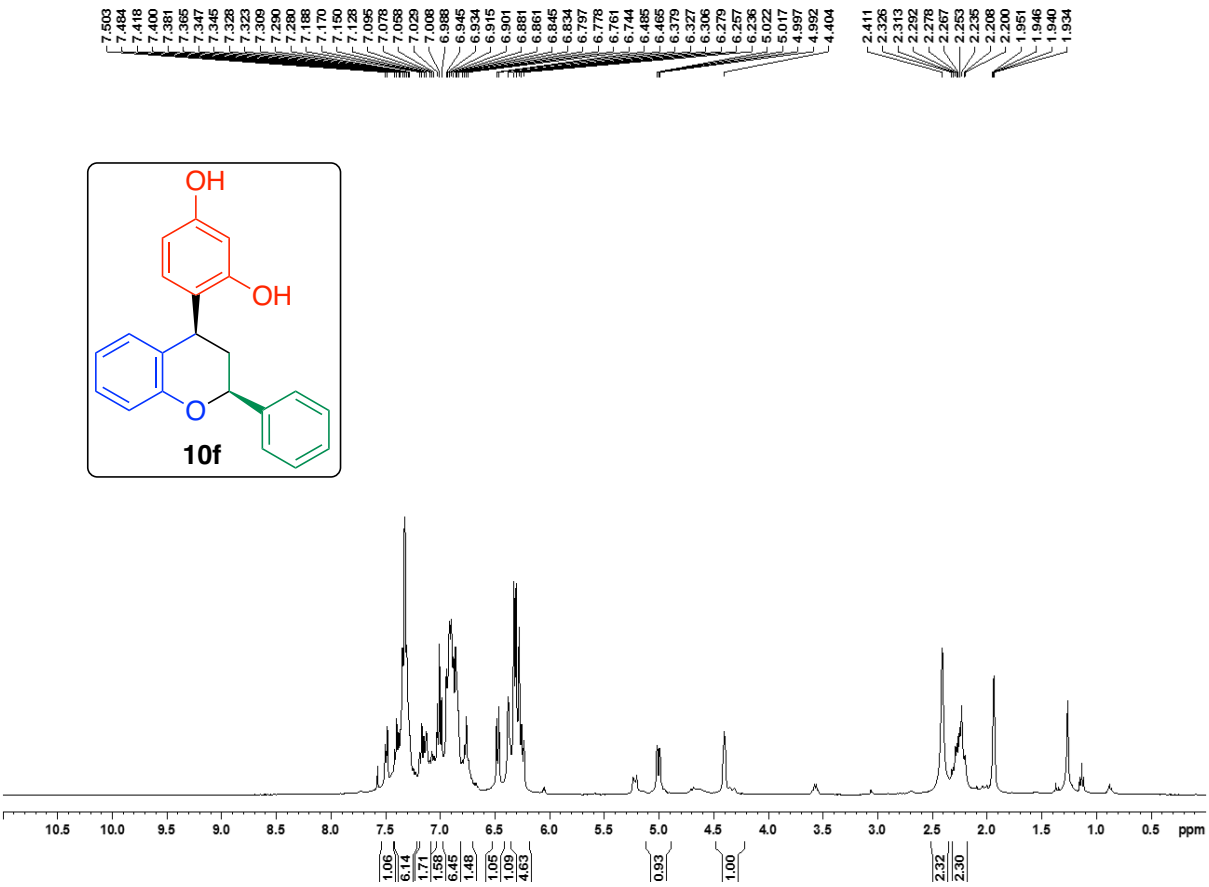

160.03
159.83
159.64
159.34
155.40
134.19
127.71
127.52
127.43
127.27
126.54
126.33
120.17
116.48
113.92
112.84
92.36
92.05
90.75
78.59
77.48
77.16
76.84
56.30
56.20
55.93
55.66
55.38
34.88
32.19
OMe
MeO
OMe
O
OMe
10e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



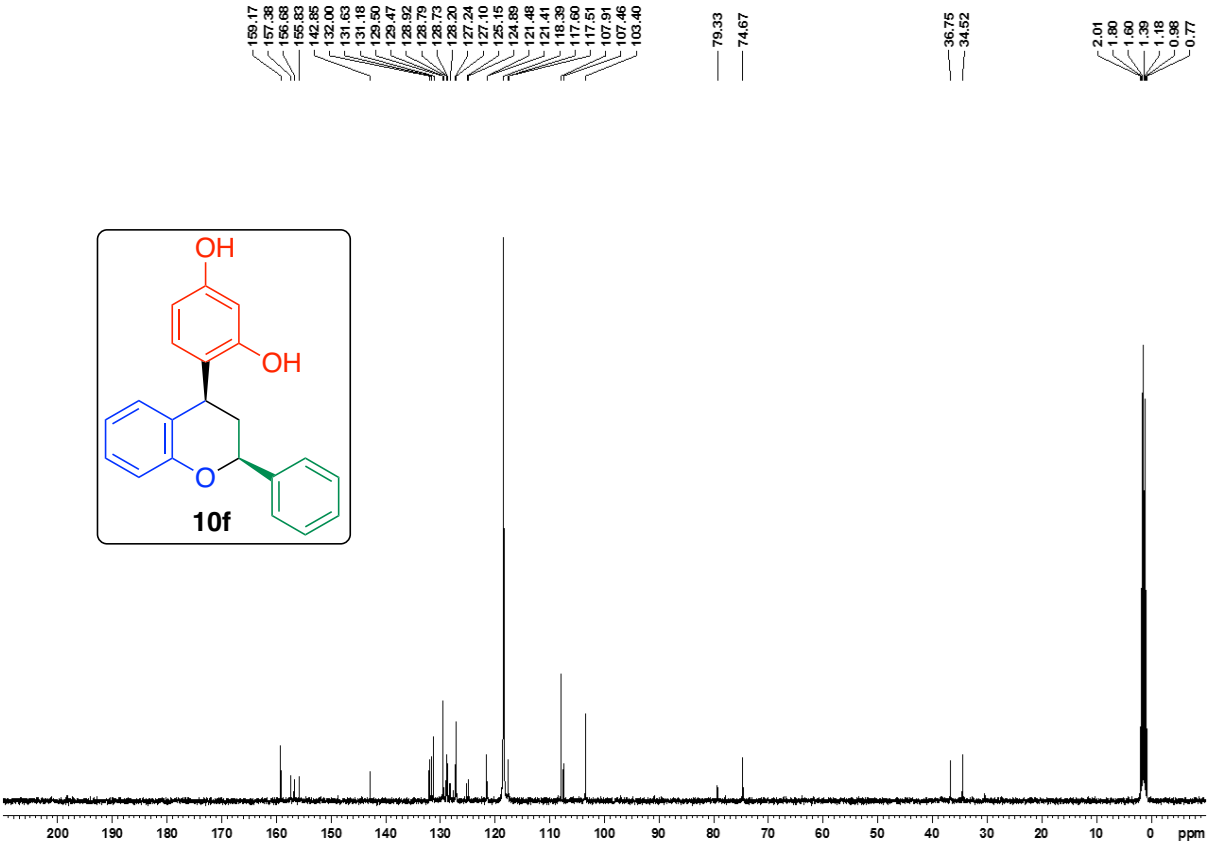
NOE spectrum of cassiaflavan **10e**



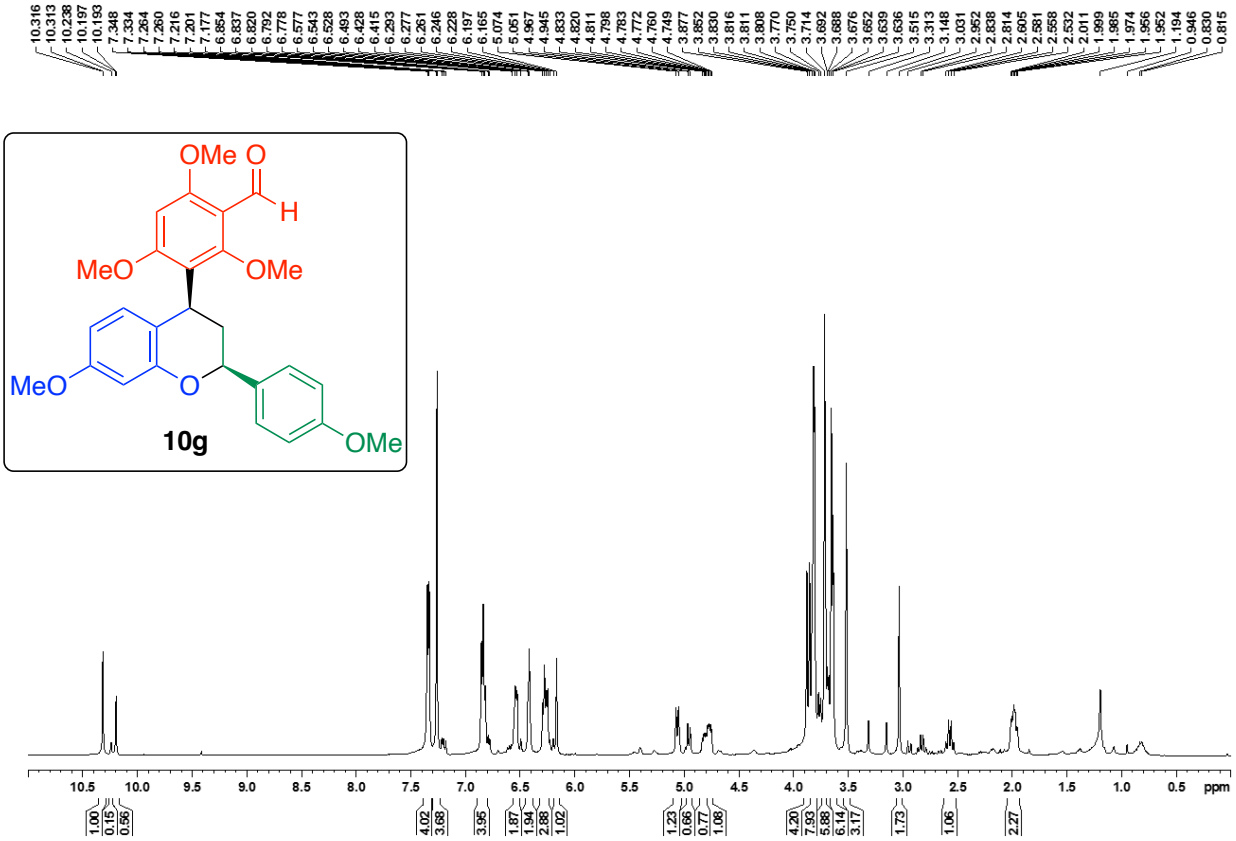
NOE spectrum of cassiaflavan **10e**

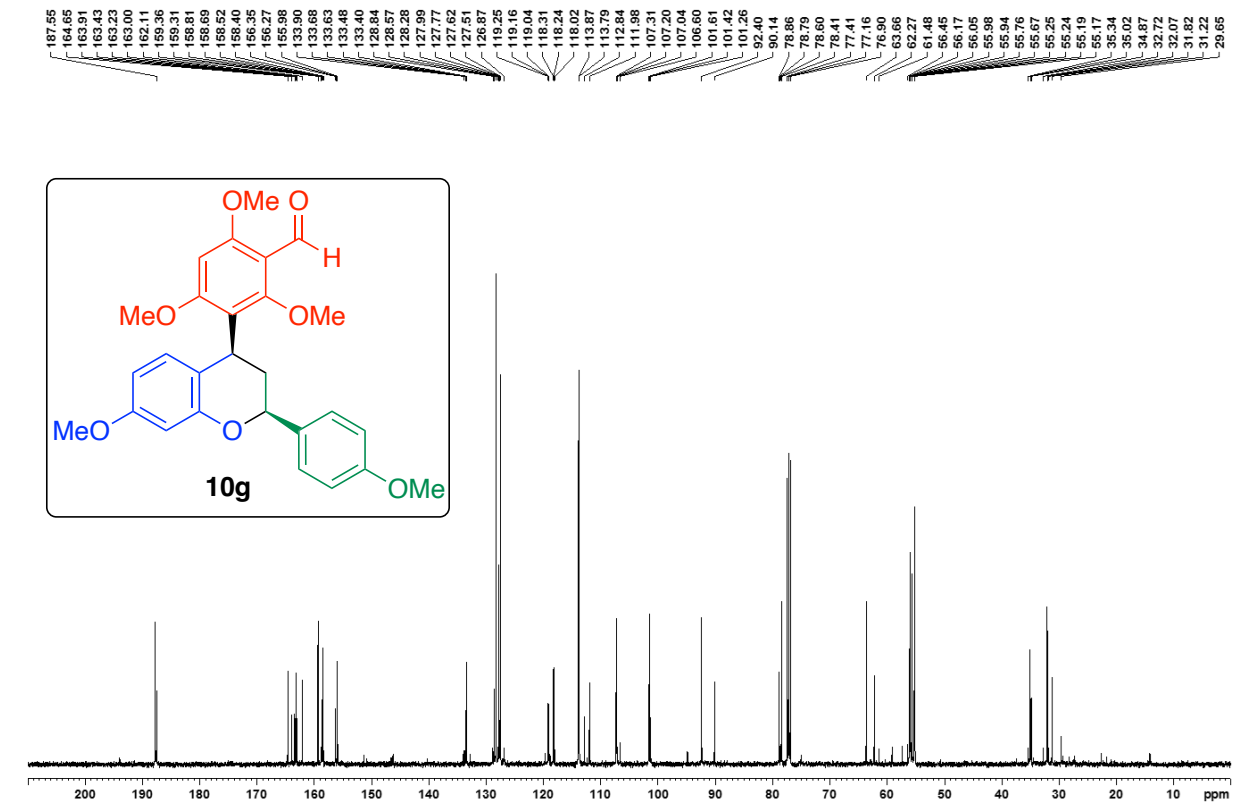


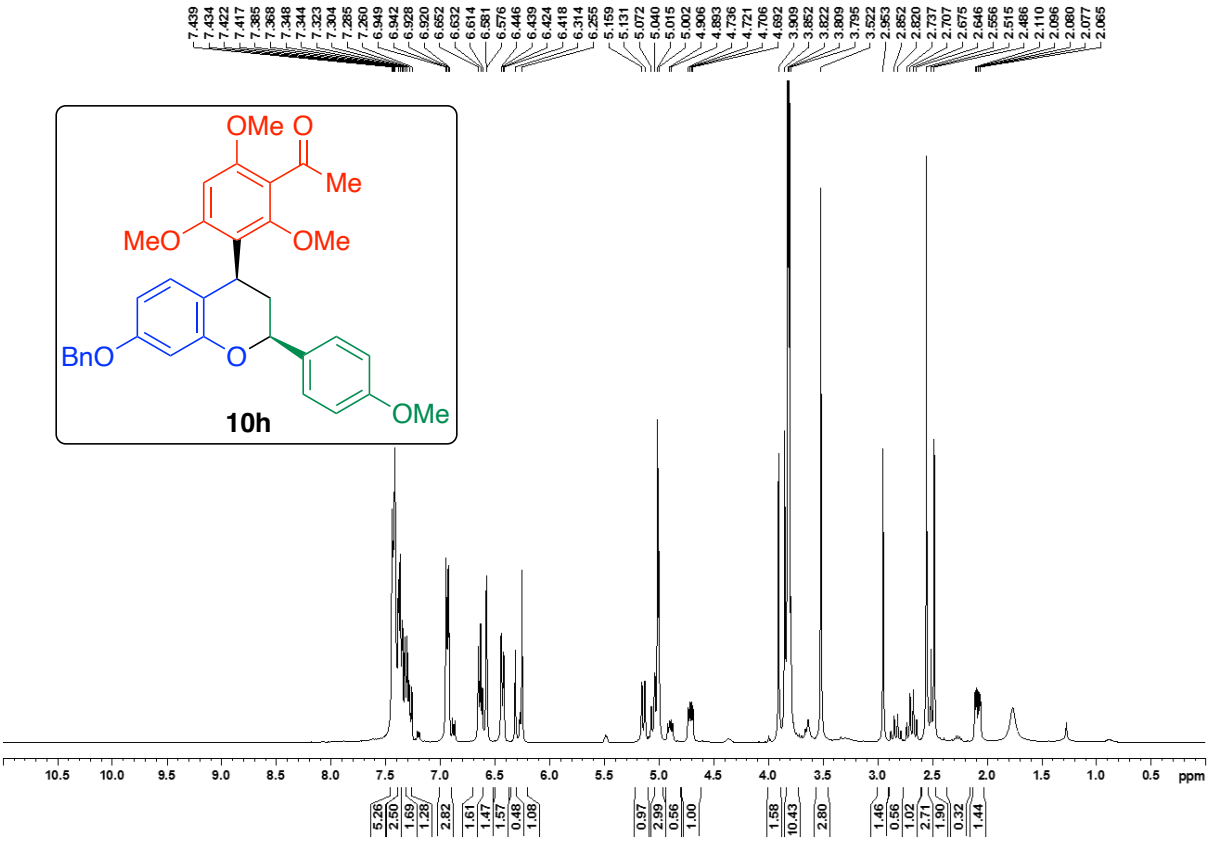
^{1}H NMR spectrum of cassiaflavan **10f** (400MHz, CD_3CN)

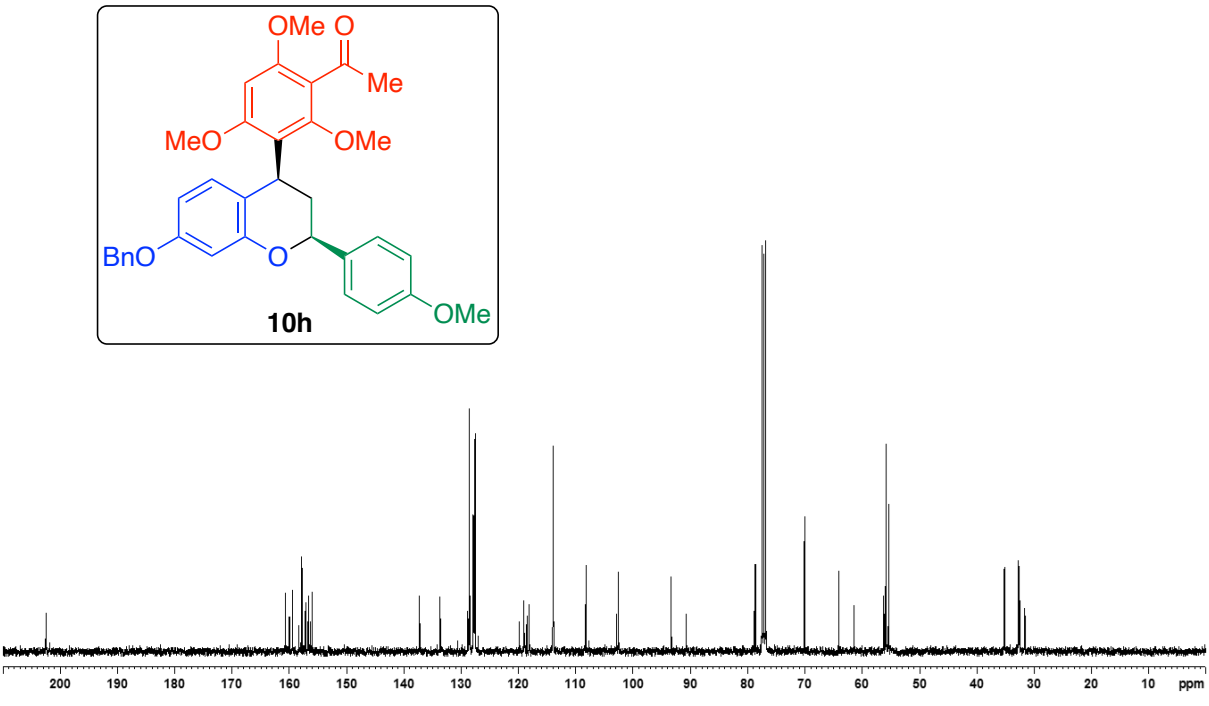


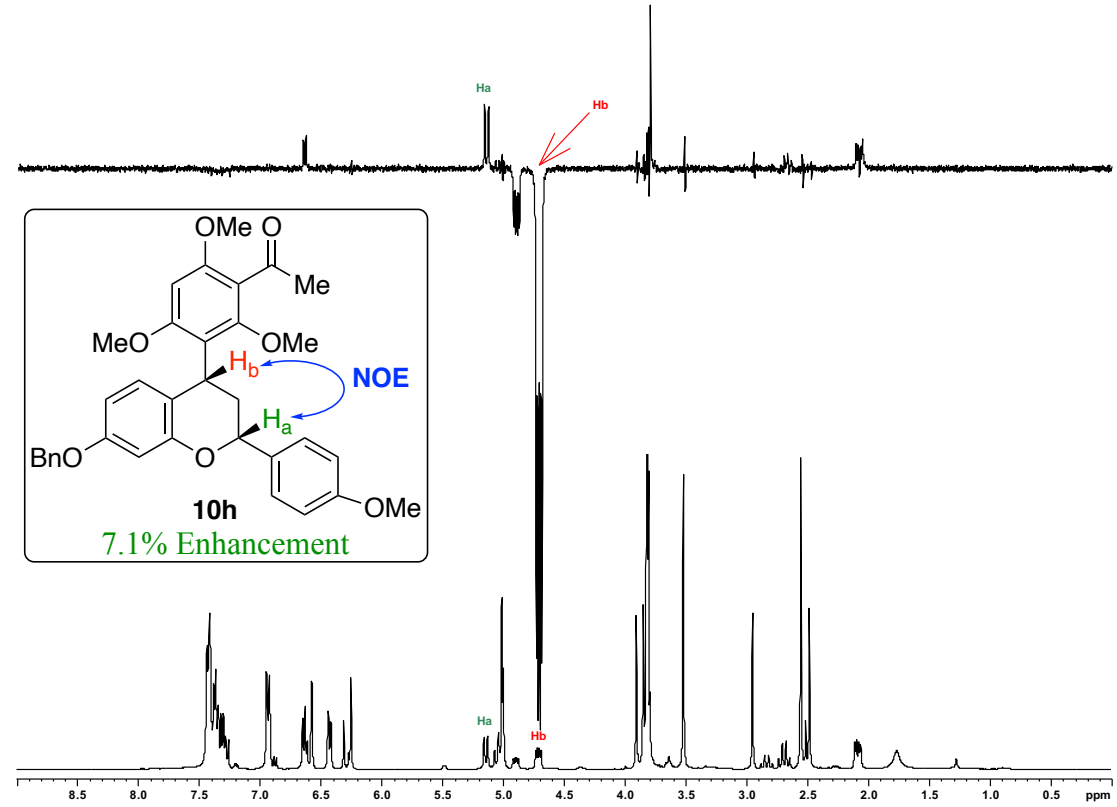
^{13}C NMR spectrum of cassiaflavan **10f** (100MHz, CD_3CN)


OMe O
H
MeO
OMe
MeO
O
OMe
10g

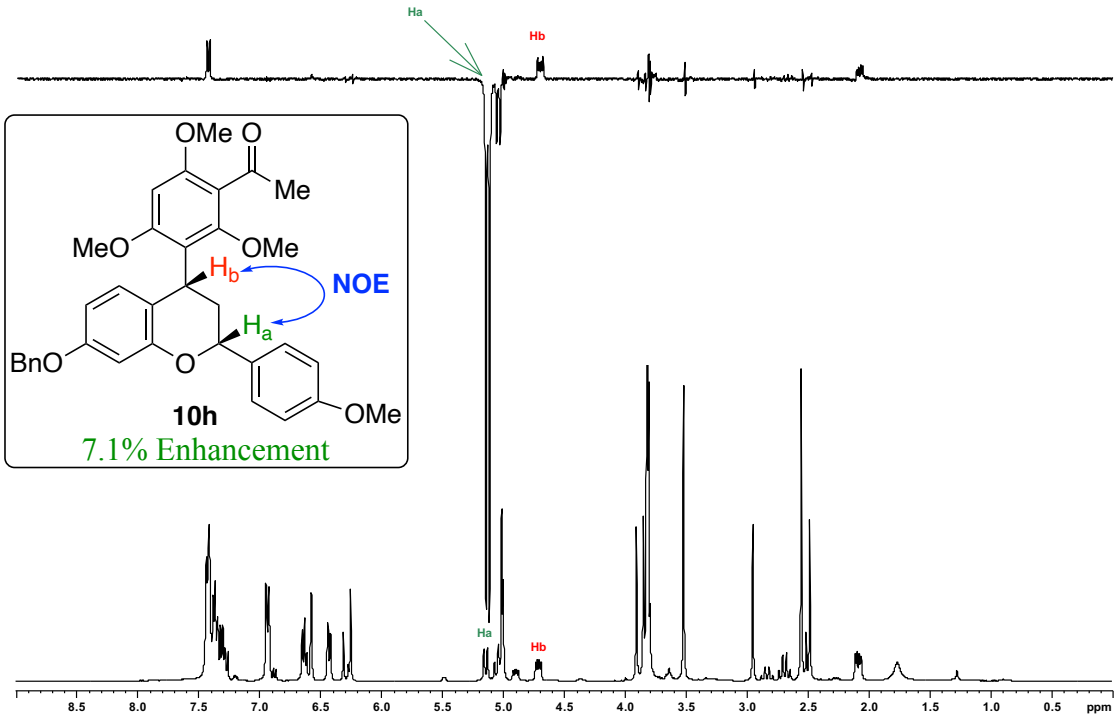

OMe O
H
MeO
OMe
MeO
O
OMe
10g


OMe O
Me
MeO
OMe
BnO
O
OMe
10h

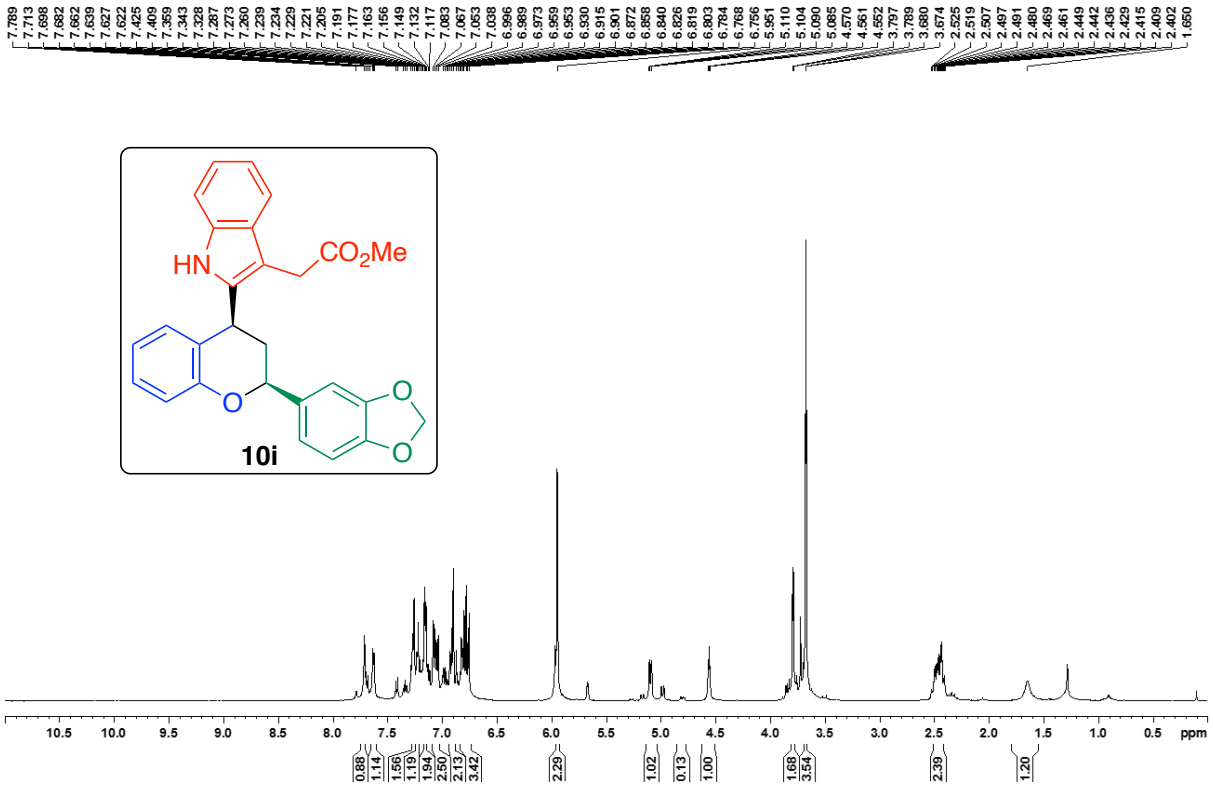

OMe O
Me
MeO
OMe
BnO
O
OMe
10h

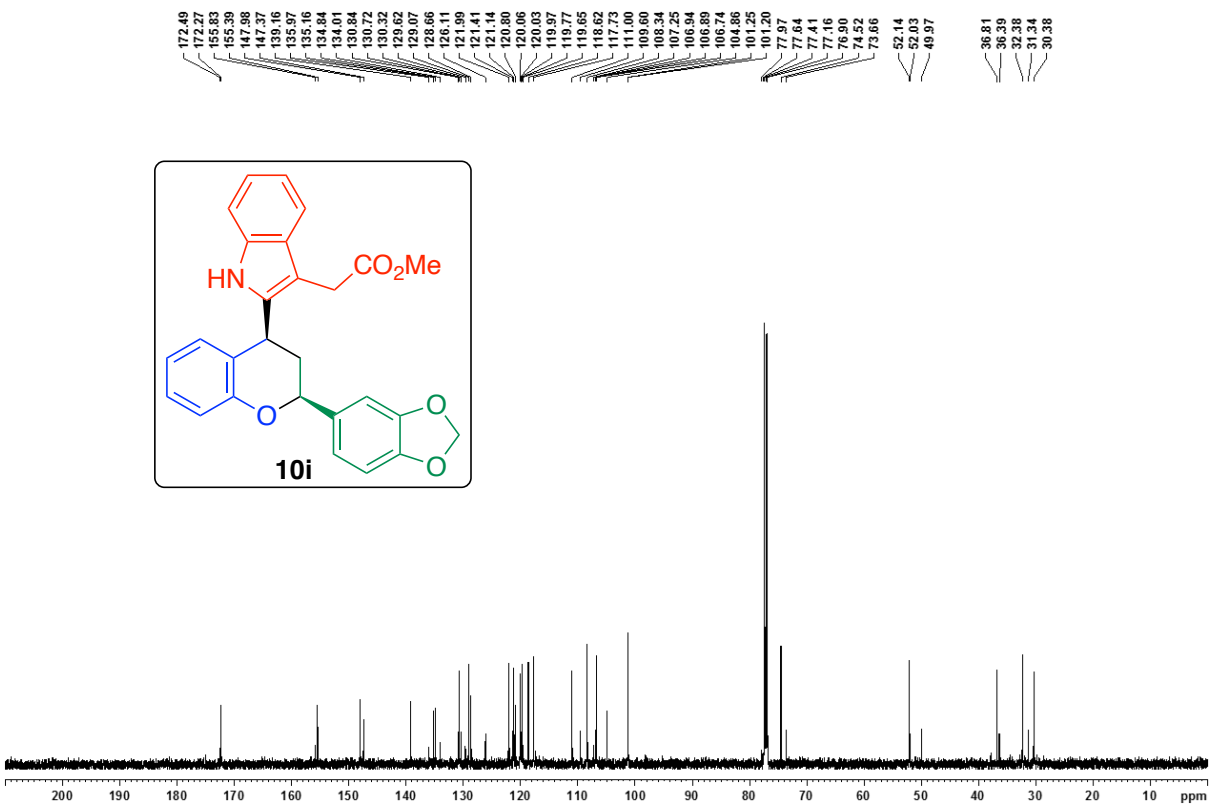


NOE spectrum of cassiaflavan **10g**

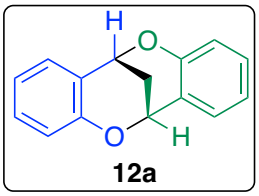


NOE spectrum of cassiaflavan **10h**

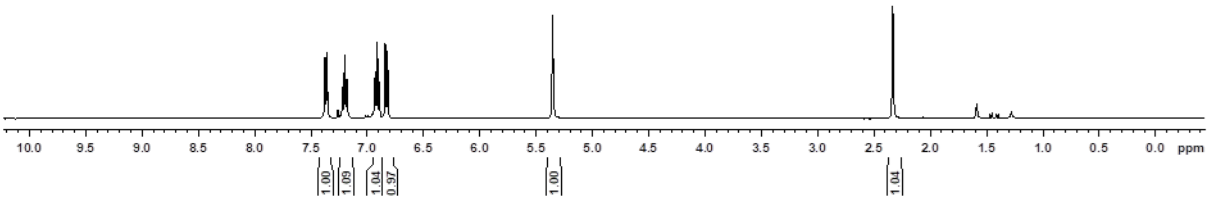

HN
CO2Me
O
O
O
10i

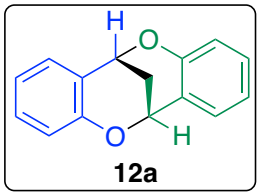

HN
CO2Me
O
O
O
10i

^{1}H and ^{13}C NMR spectra of cycloflavans

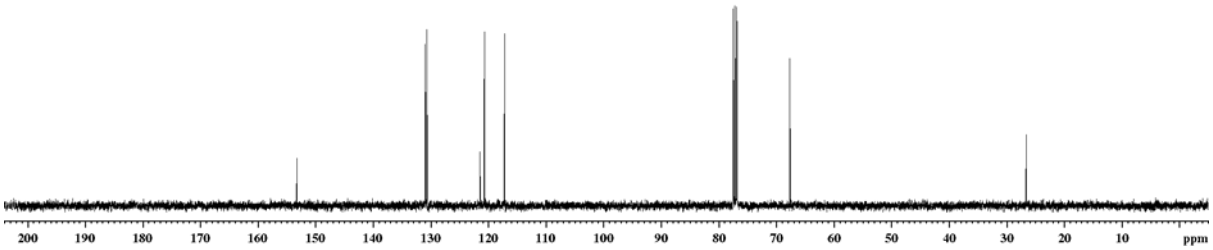


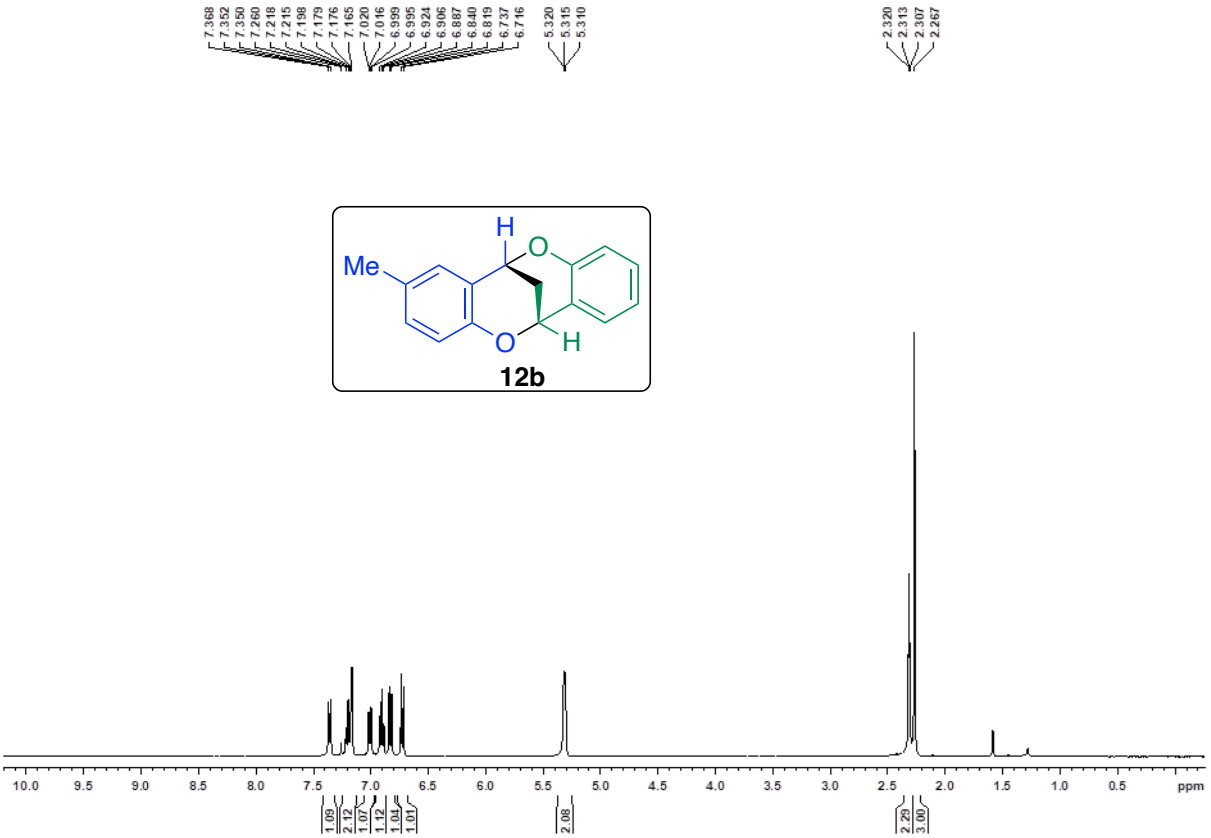
12a





12a




7.368
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7.350
7.260
7.218
7.215
7.198
7.179
7.176
7.165
7.020
7.016
6.999
6.995
6.924
6.906
6.887
6.840
6.819
6.737
6.716
5.320
5.315
5.310
2.320
2.313
2.307
2.267
H
O
Me
O
H
12b
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.09
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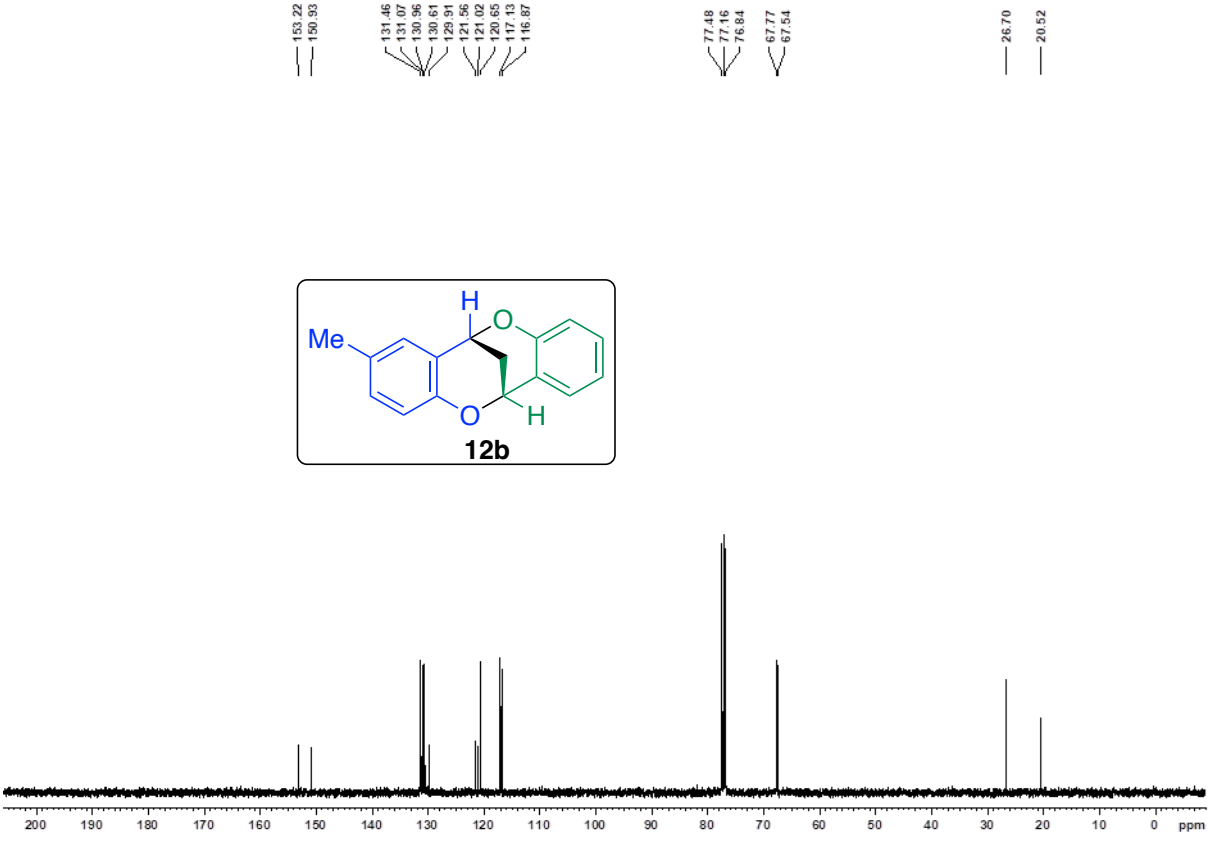
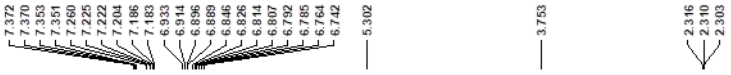
1.07
1.12
1.04
1.01
2.08
2.29
3.00


153.22
150.93
131.46
131.07
130.96
130.61
129.91
121.56
121.02
120.65
117.13
116.87
77.48
77.16
76.84
67.77
67.54
26.70
20.52
H
O
Me
O
H
12b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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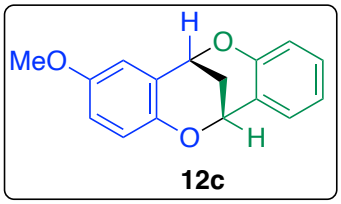
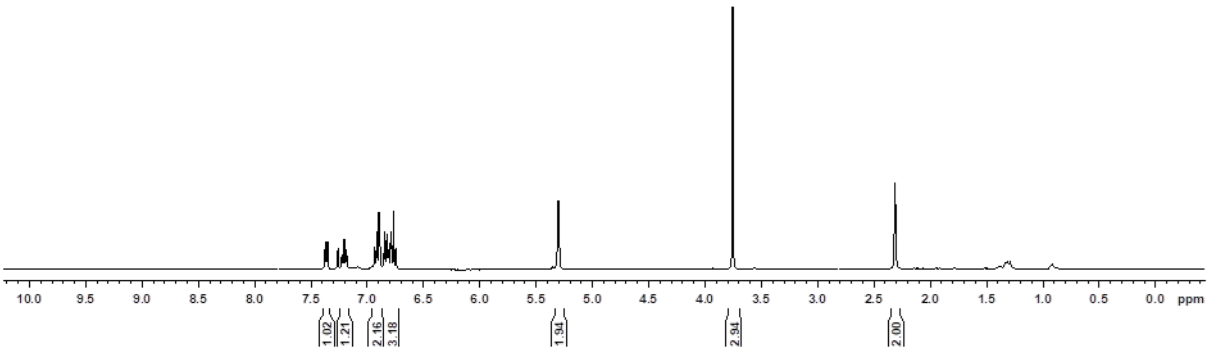
7.222
7.204
7.186
7.183
6.933
6.914
6.896
6.889
6.846
6.826
6.814
6.807
6.792
6.785
6.764
6.742
5.302
3.753
2.316
2.310
2.303


H
O
MeO
O
H

12c


10.0
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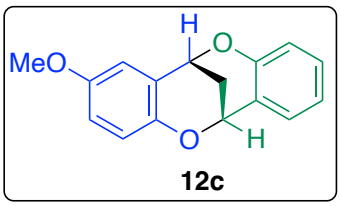
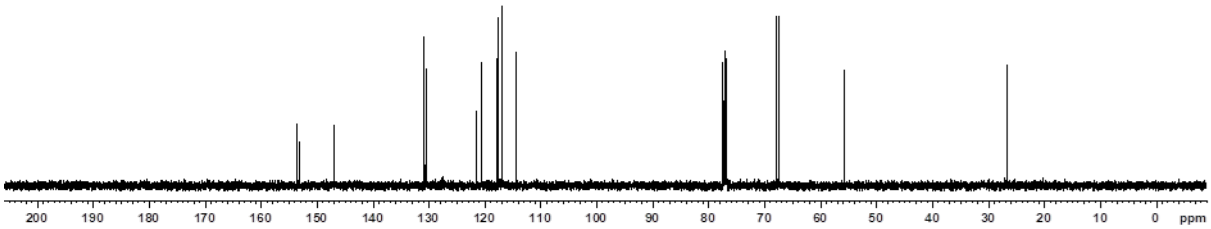
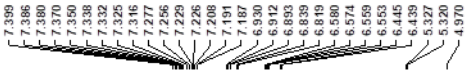
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.02
1.21
2.16
3.18
1.94
2.94
2.00


153.55
153.17
147.03
130.92
130.59
121.53
121.51
120.70
117.86
117.59
117.05
114.45
77.47
77.16
76.84
67.89
67.43
55.81
26.66


H
O
MeO
O
H

12c


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.350
7.338
7.332
7.325
7.316
7.277
7.256
7.229
7.226
7.208
7.191
7.187
6.930
6.912
6.893
6.839
6.819
6.580
6.574
6.559
6.553
6.445
6.439
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5.320
4.970
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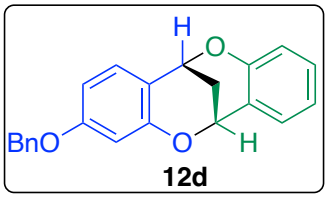
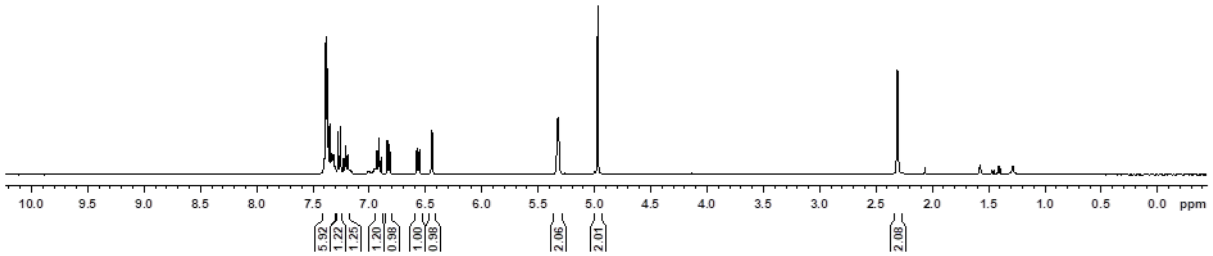
2.308
2.301


H
O
BnO
O
H

12d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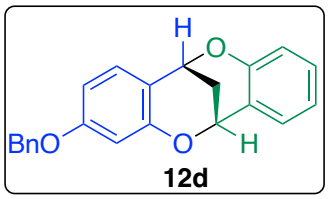
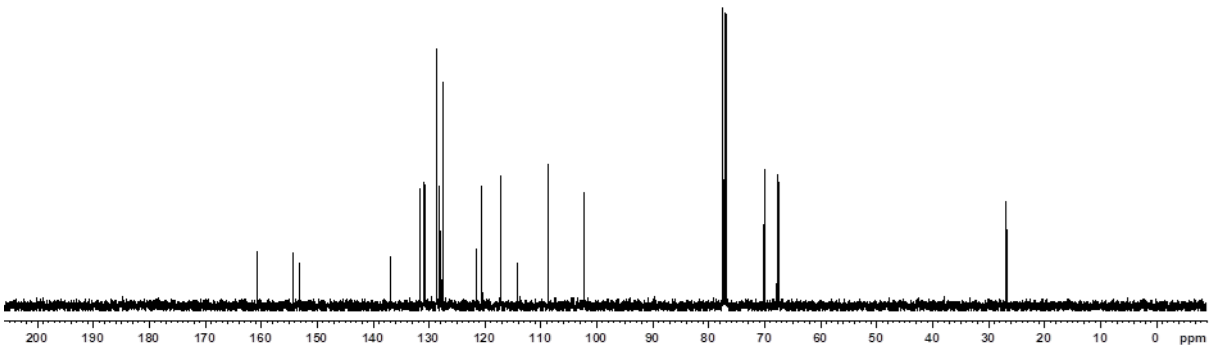
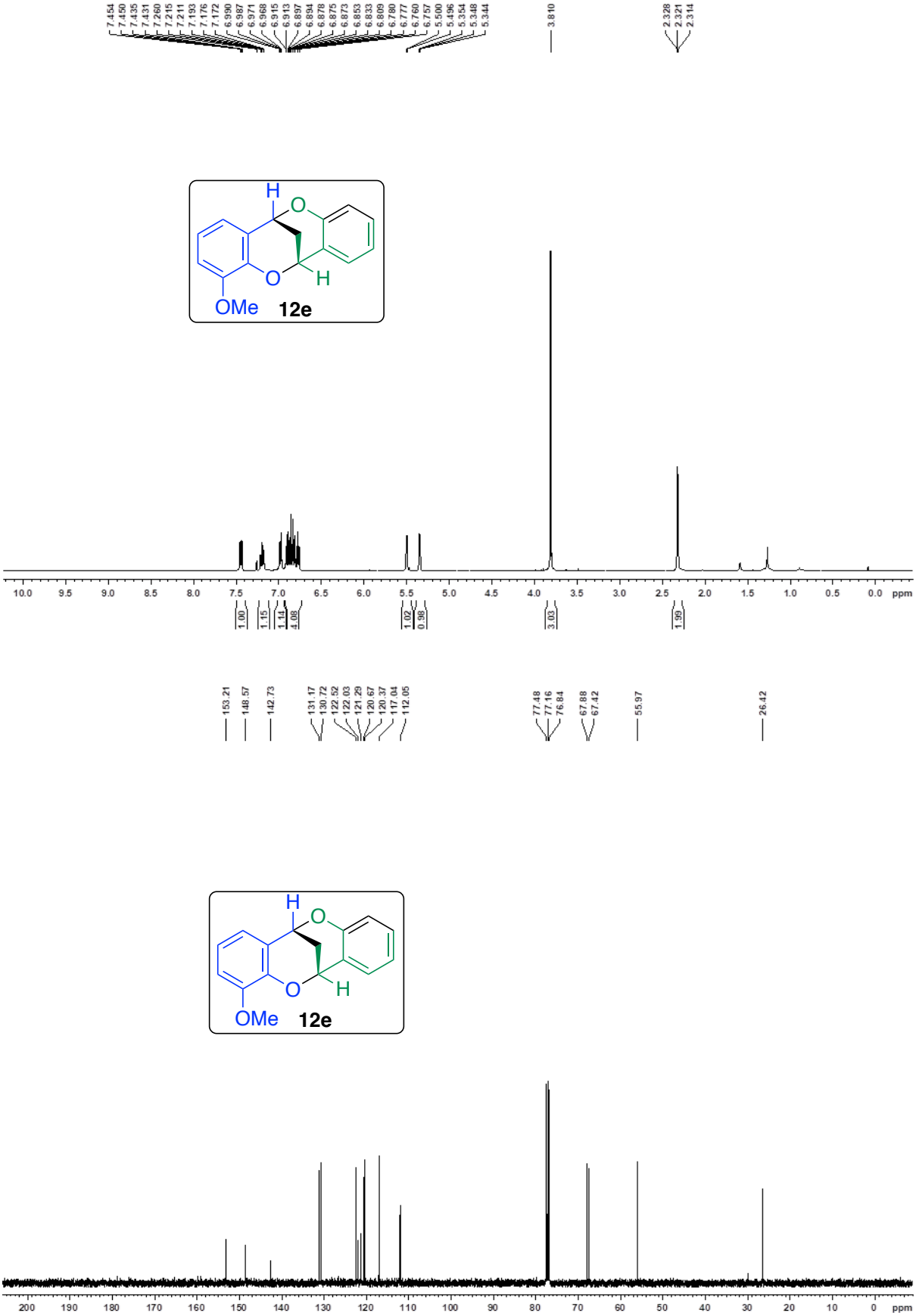
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.92
1.22
1.25
1.20
0.98
1.00
0.98
2.06
2.01
2.08


160.78
154.35
153.26
136.86
131.66
130.92
130.69
128.70
128.11
127.63
121.46
120.60
117.27
114.30
108.70
102.35
77.48
77.16
76.84
70.11
67.79
67.42
26.81


H
O
BnO
O
H

12d


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.435
7.431
7.260
7.215
7.211
7.193
7.176
7.172
6.990
6.987
6.971
6.968
6.915
6.913
6.897
6.894
6.878
6.875
6.873
6.853
6.833
6.809
6.780
6.777
6.760
6.757
5.500
5.496
5.354
5.348
5.344
3.810
2.328
2.321
2.314
H
O
O
H
OMe
12e
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.15
1.14
4.08
1.02
0.98
3.03
1.99
153.21
148.57
142.73
131.17
130.72
122.52
122.03
121.29
120.67
120.37
117.04
112.05
77.48
77.16
76.84
67.88
67.42
55.97
26.42
H
O
O
H
OMe
12e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.346
7.343
7.327
7.324
7.225
7.221
7.204
7.186
7.183
6.924
6.905
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6.767
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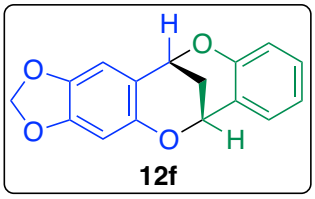
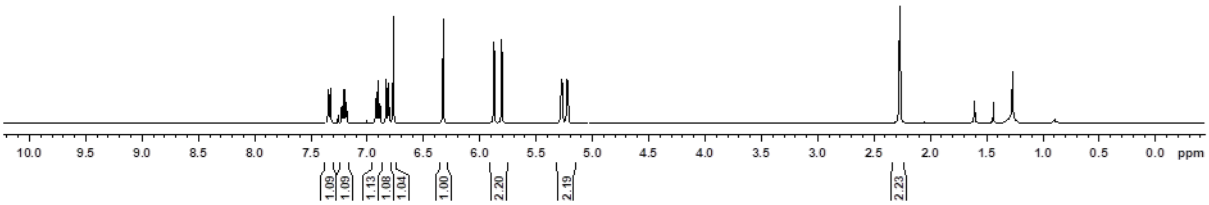
2.272
2.266


H
O
O
O
O
H

12f


10.0
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7.5
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6.5
6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
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ppm
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1.13
1.08
1.04
1.00
2.20
2.19
2.23


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149.29
148.56
141.84
130.91
130.69
121.45
120.67
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112.93
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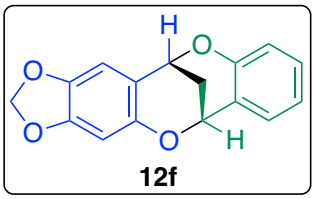
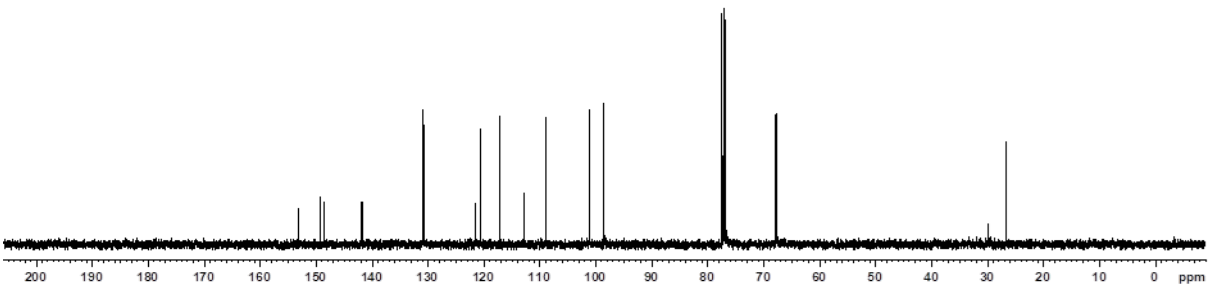
101.24
98.56
77.48
77.16
76.84
67.88
67.65
26.73


H
O
O
O
O
H

12f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100
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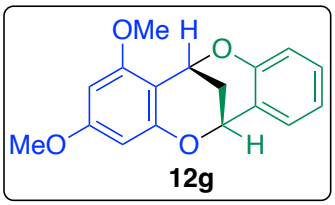
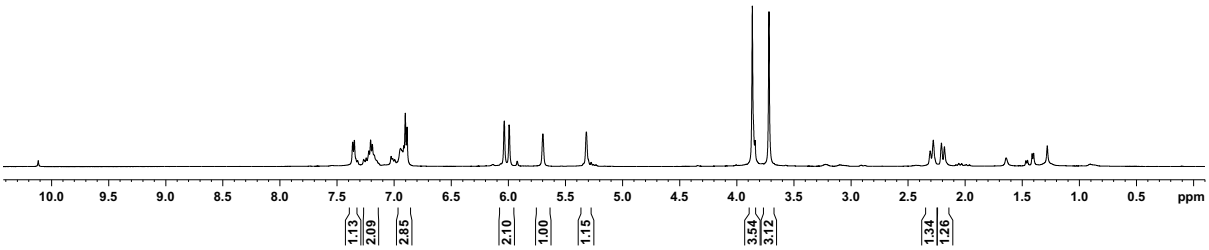
80
70
60
50
40
30
20
10
0
ppm


7.363
7.349
7.245
7.222
7.206
7.191
7.027
7.013
6.944
6.916
6.902
6.887
6.036
5.994
5.698
5.317
3.864
3.718
2.307
2.279
2.208
2.182


OMe
H
O
MeO
O
H

12g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7.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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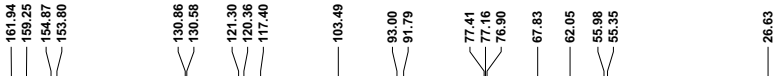
2.10
1.00
1.15
3.54
3.12
1.34
1.26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159.25
154.87
153.80
130.86
130.58
121.30
120.36
117.40
103.49
93.00
91.79
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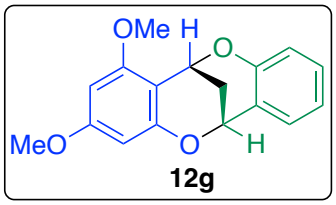
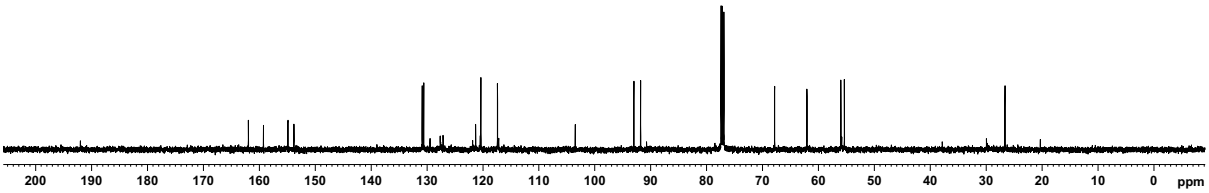
76.90
67.83
62.05
55.98
55.35
26.63


OMe
H
O
MeO
O
H

12g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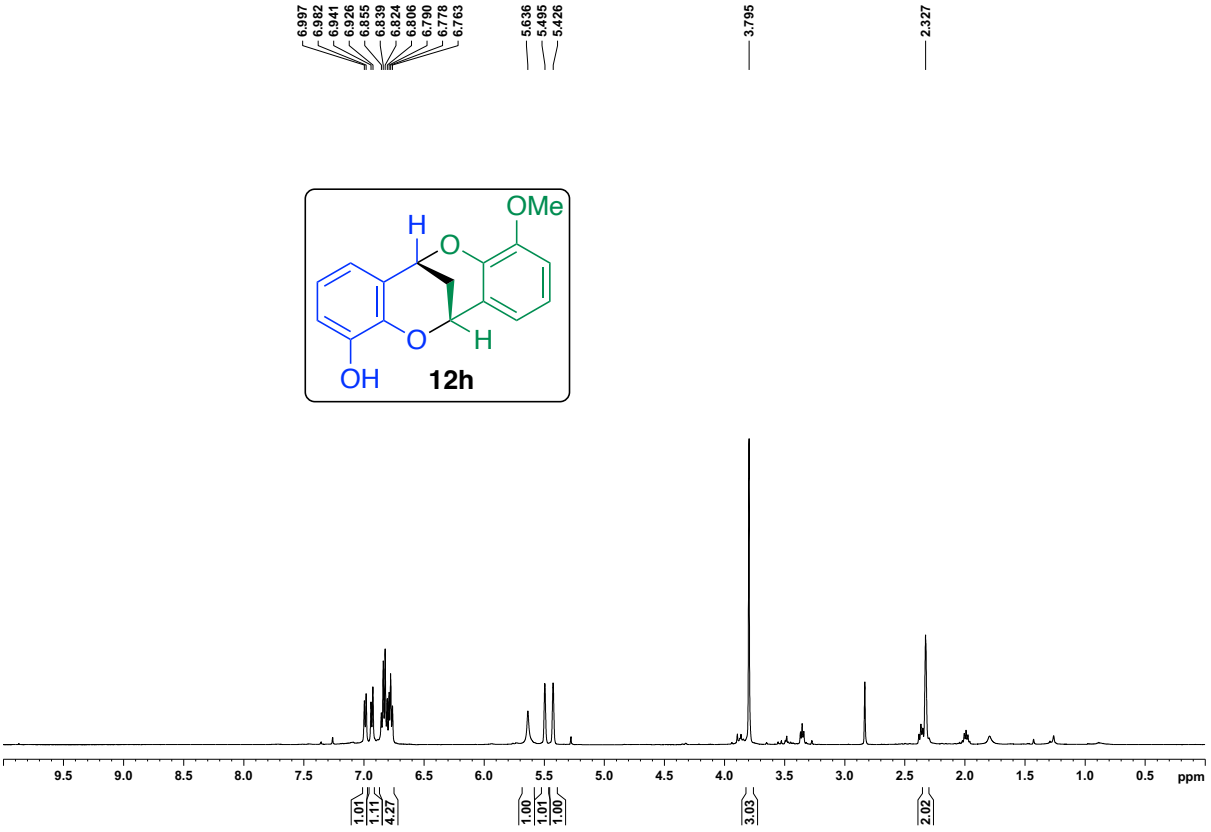
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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6.982
6.941
6.926
6.855
6.839
6.824
6.806
6.790
6.778
6.763
5.636
5.495
5.426
3.795
2.327
OMe
H
O
O
H
OH
12h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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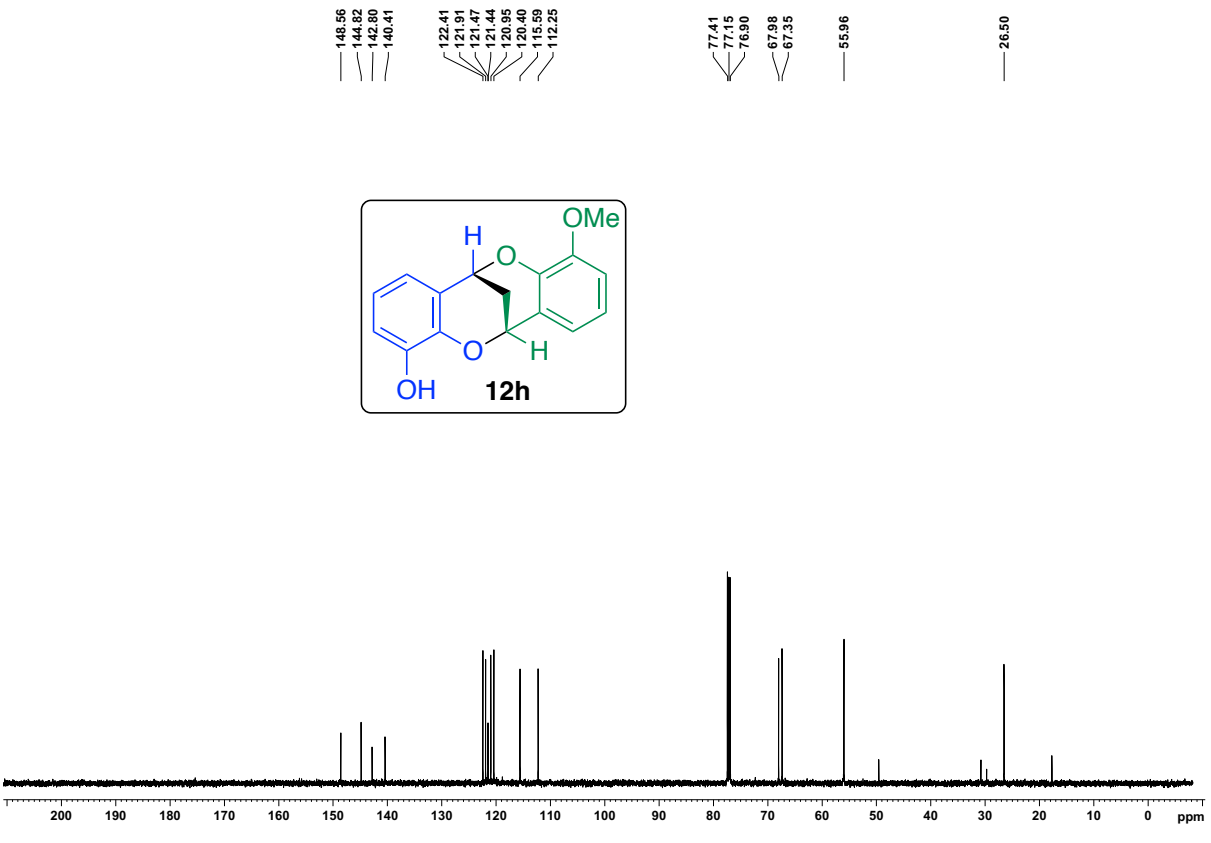
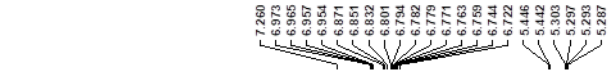
1.11
4.27
1.00
1.01
1.00
3.03
2.02


148.56
144.82
142.80
140.41
122.41
121.91
121.47
121.44
120.95
120.40
115.59
112.25
77.41
77.15
76.90
67.98
67.35
55.96
26.50
OMe
H
O
O
H
OH
12h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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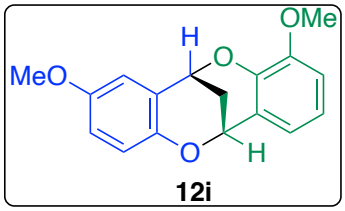
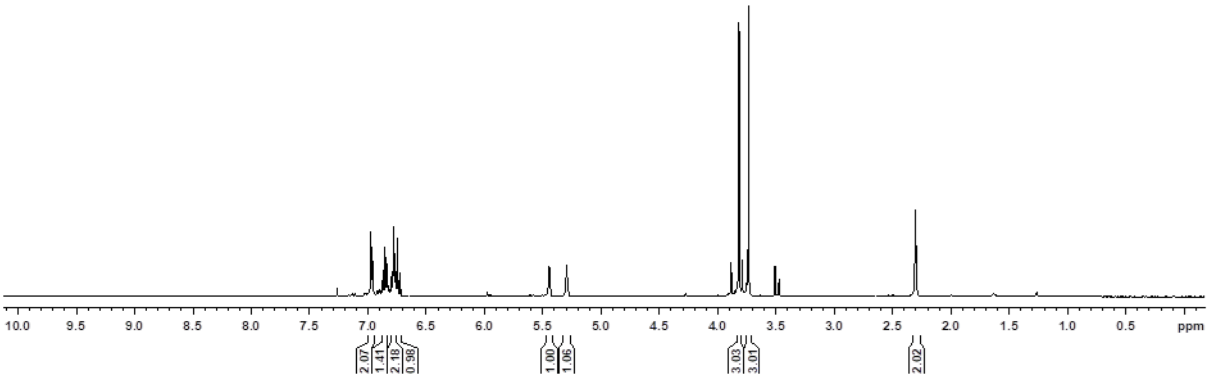
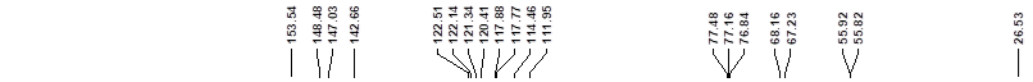
6.973
6.965
6.957
6.954
6.871
6.851
6.832
6.801
6.794
6.782
6.779
6.771
6.763
6.759
6.744
6.722
5.446
5.442
5.303
5.297
5.293
5.287
3.817
3.736
2.308
2.301
2.295


OMe
H
O
MeO
O
H

12i


10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.07
1.41
2.18
0.98
1.00
1.06
3.03
3.01
2.02


153.54
148.48
147.03
142.66
122.51
122.14
121.34
120.41
117.88
117.77
114.46
111.95
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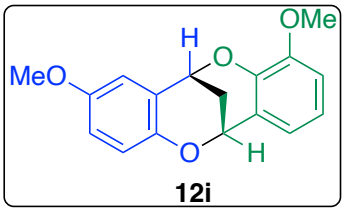
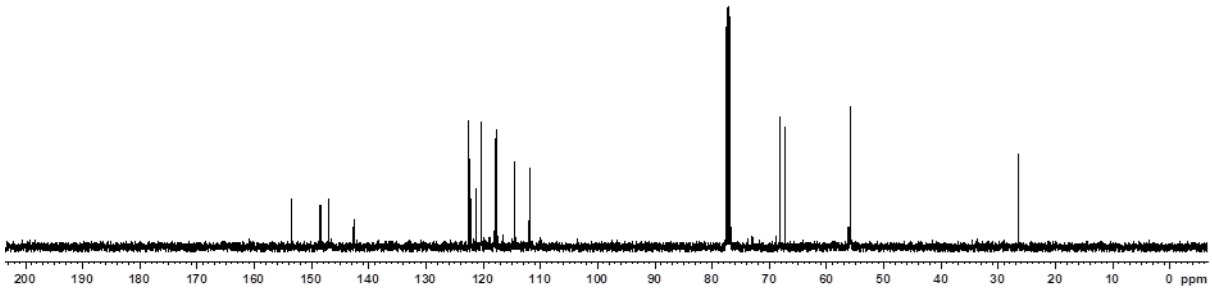
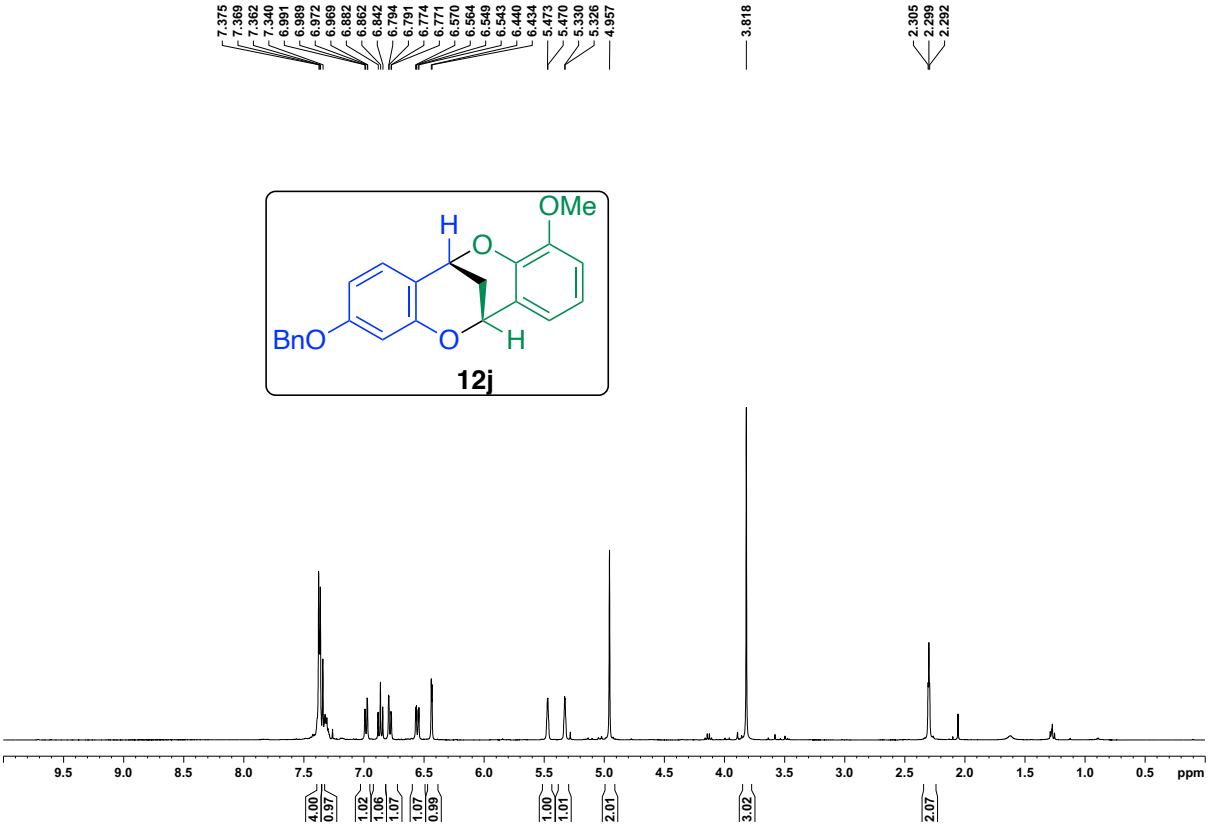
76.84
68.16
67.23
55.92
55.82
26.53


OMe
H
O
MeO
O
H

12i


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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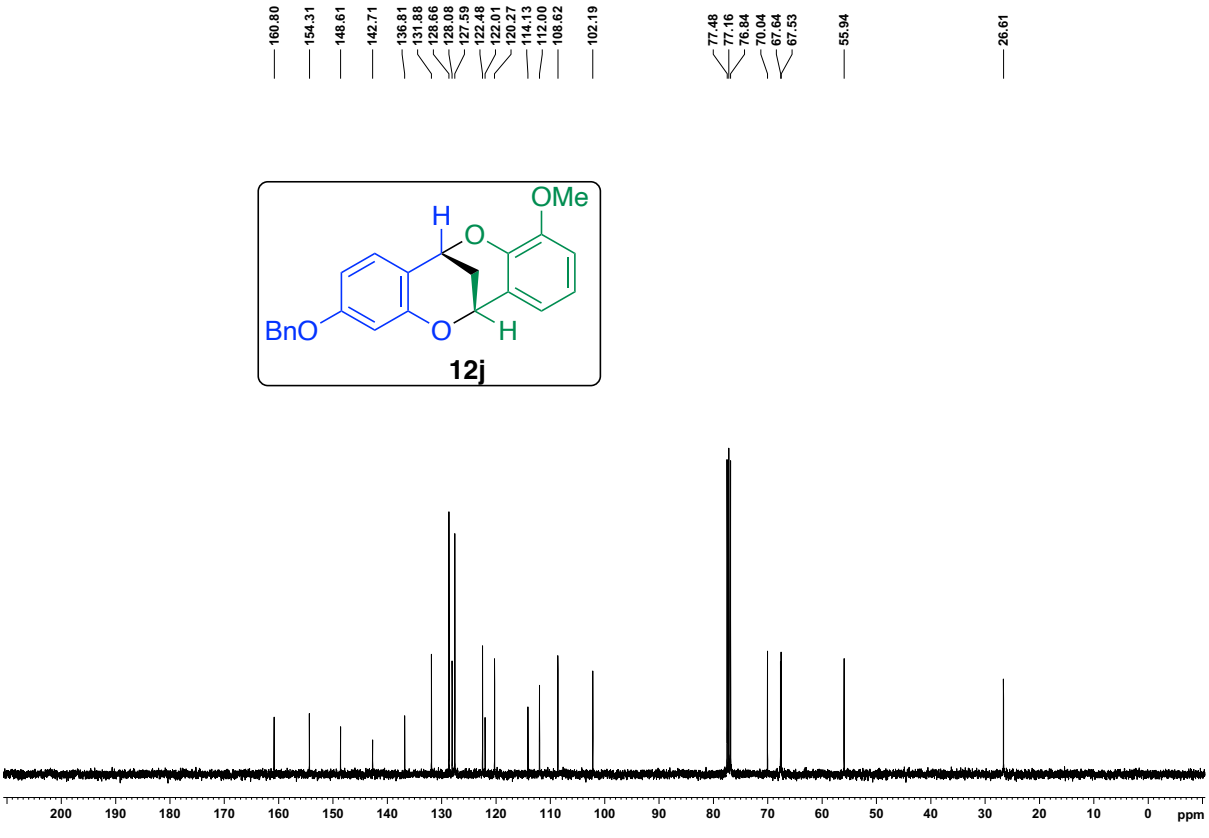
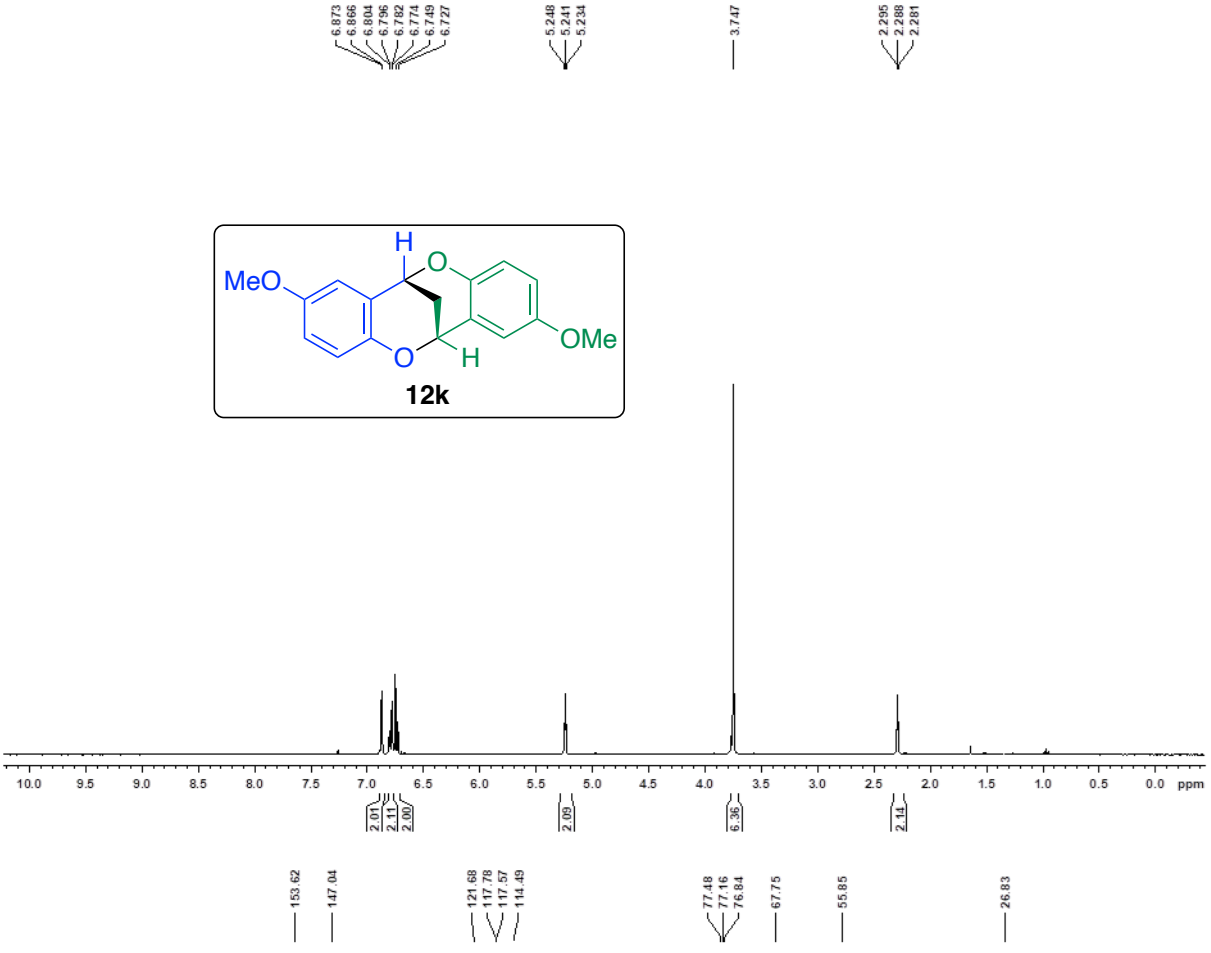
7.369
7.362
7.340
6.991
6.989
6.972
6.969
6.882
6.862
6.842
6.794
6.791
6.774
6.771
6.570
6.564
6.549
6.543
6.440
6.434
5.473
5.470
5.330
5.326
4.957
3.818
2.305
2.299
2.292
OMe
H
O
BnO
O
H
12j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
0.97
1.02
1.06
1.07
1.07
0.99
1.00
1.01
2.01
3.02
2.07


160.80
154.31
148.61
142.71
136.81
131.88
128.66
128.08
127.59
122.48
122.01
120.27
114.13
112.00
108.62
102.19
77.48
77.16
76.84
70.04
67.64
67.53
55.94
26.61
OMe
H
O
BnO
O
H
12j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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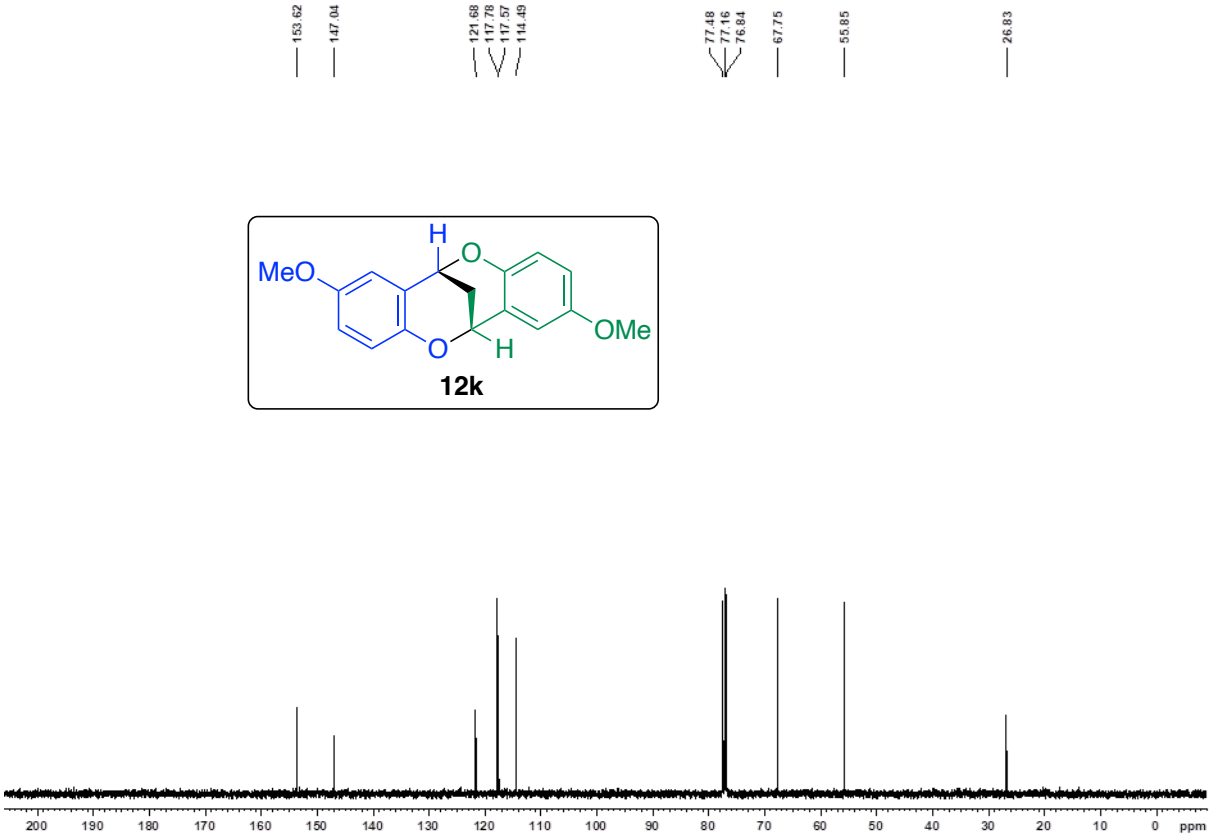
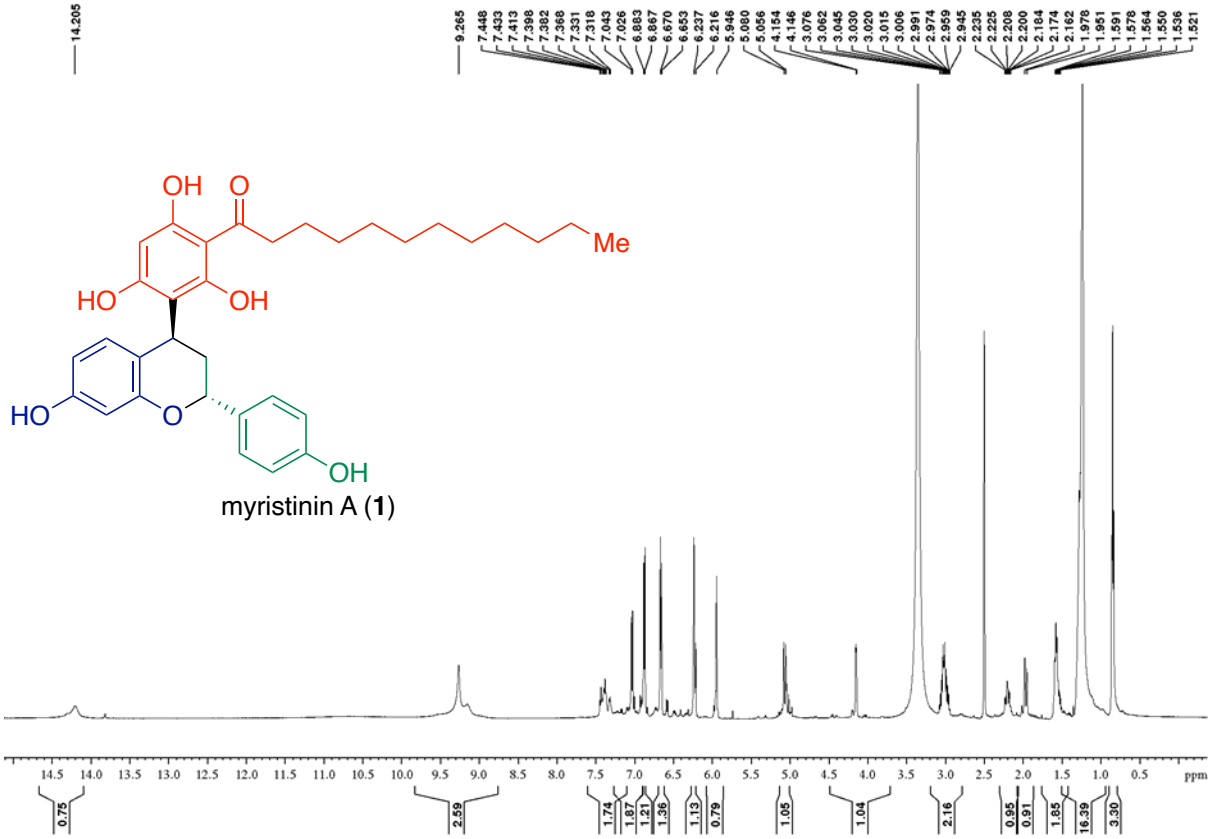
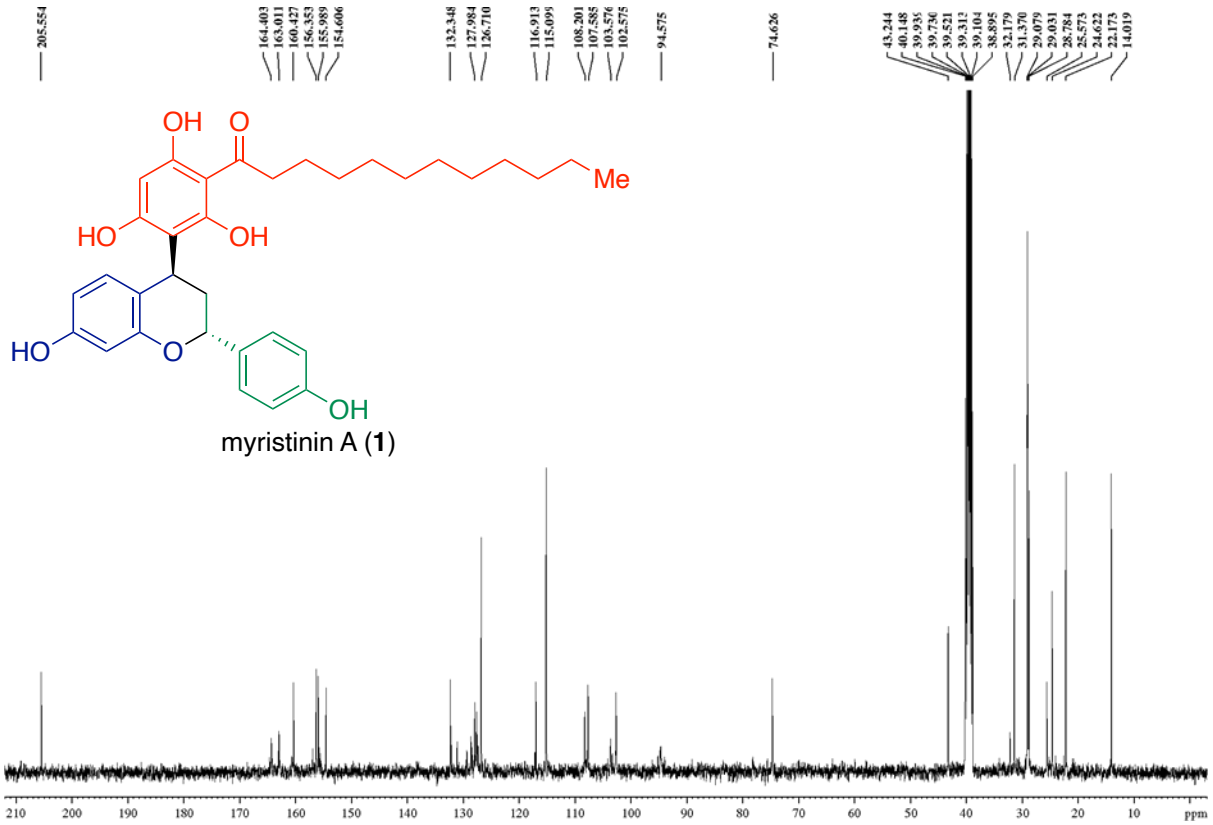
6.804
6.796
6.782
6.774
6.749
6.727
5.248
5.241
5.234
3.747
2.295
2.288
2.281
MeO
H
O
OMe
O
H
12k
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
2.11
2.00
2.09
6.36
2.14


153.62
147.04
121.68
117.78
117.57
114.49
77.48
77.16
76.84
67.75
55.85
26.83
MeO
H
O
OMe
O
H
12k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

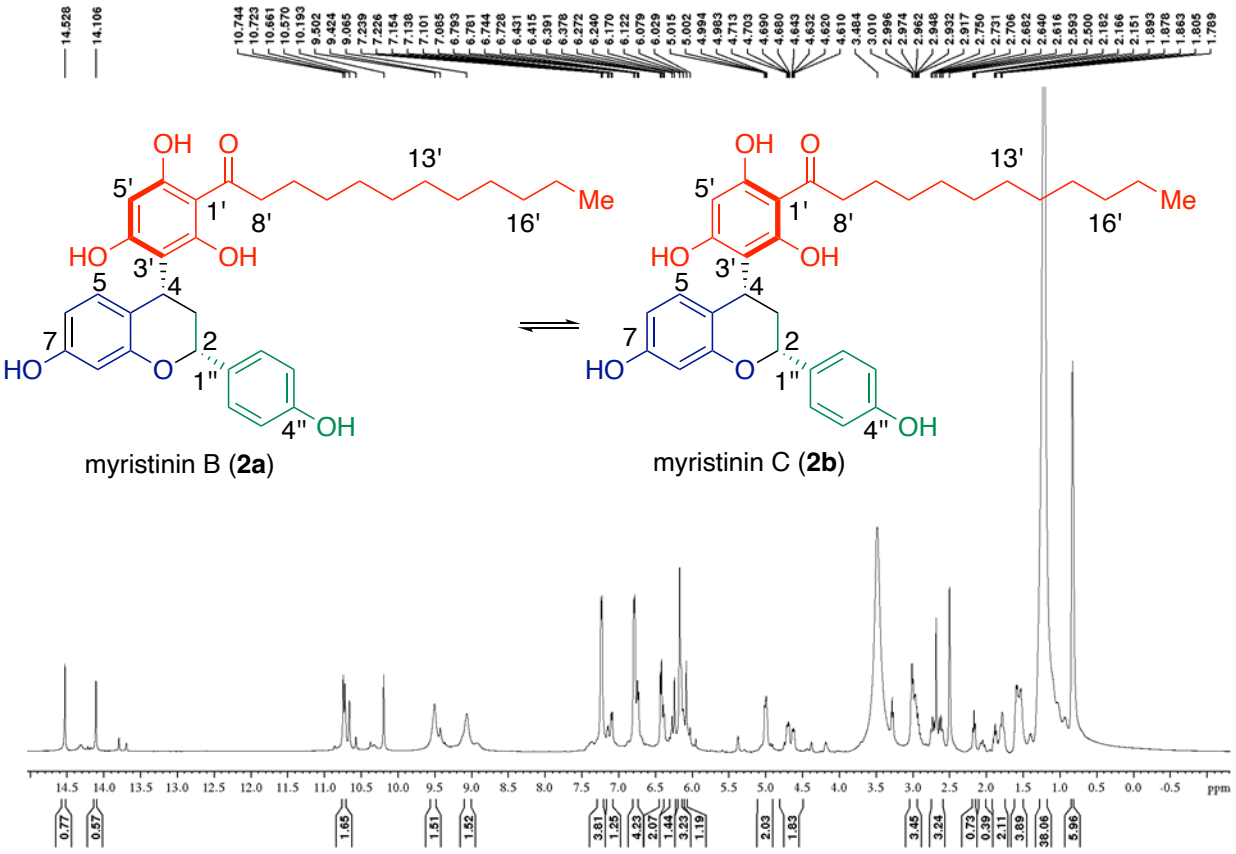
^{1}H and ^{13}C NMR spectra of total synthesis of myristinin A-F



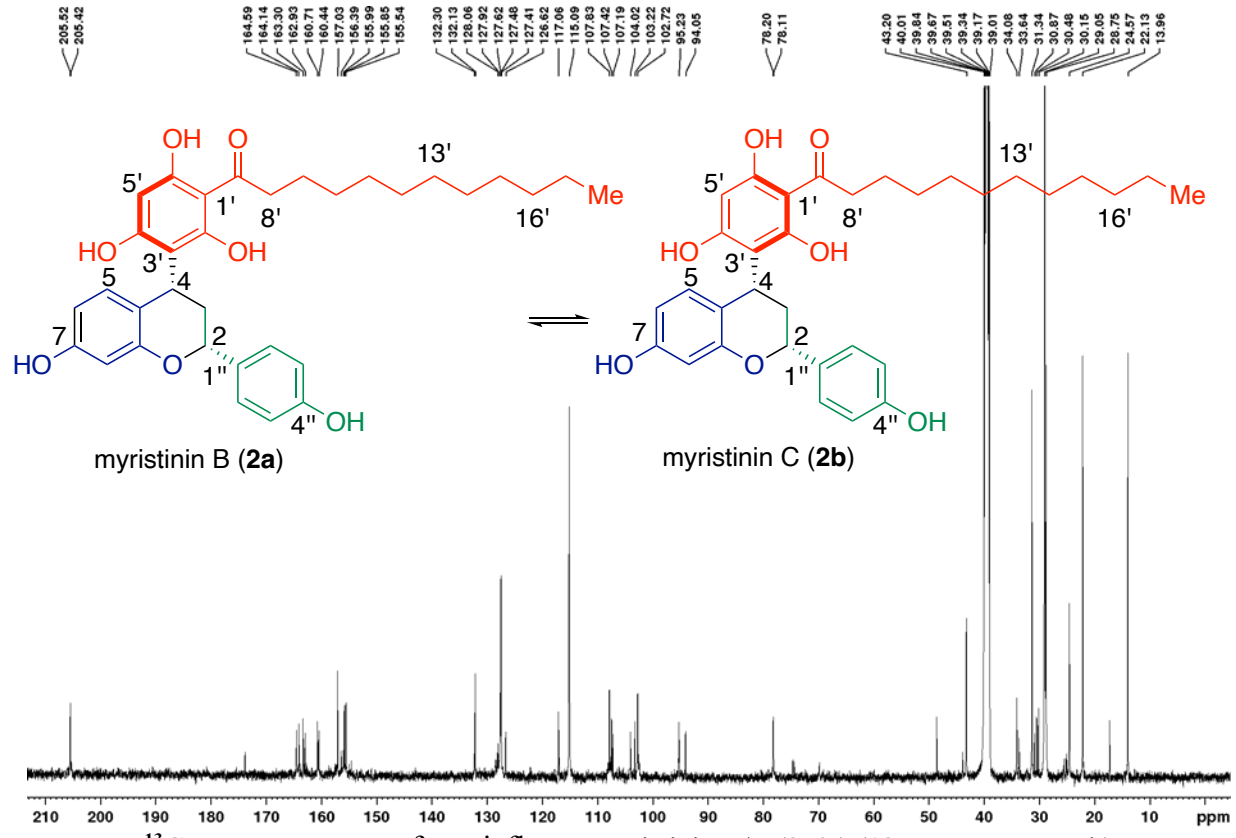
NMR spectrum of myristinin A (**1**) (500MHz, DMSO-D6)



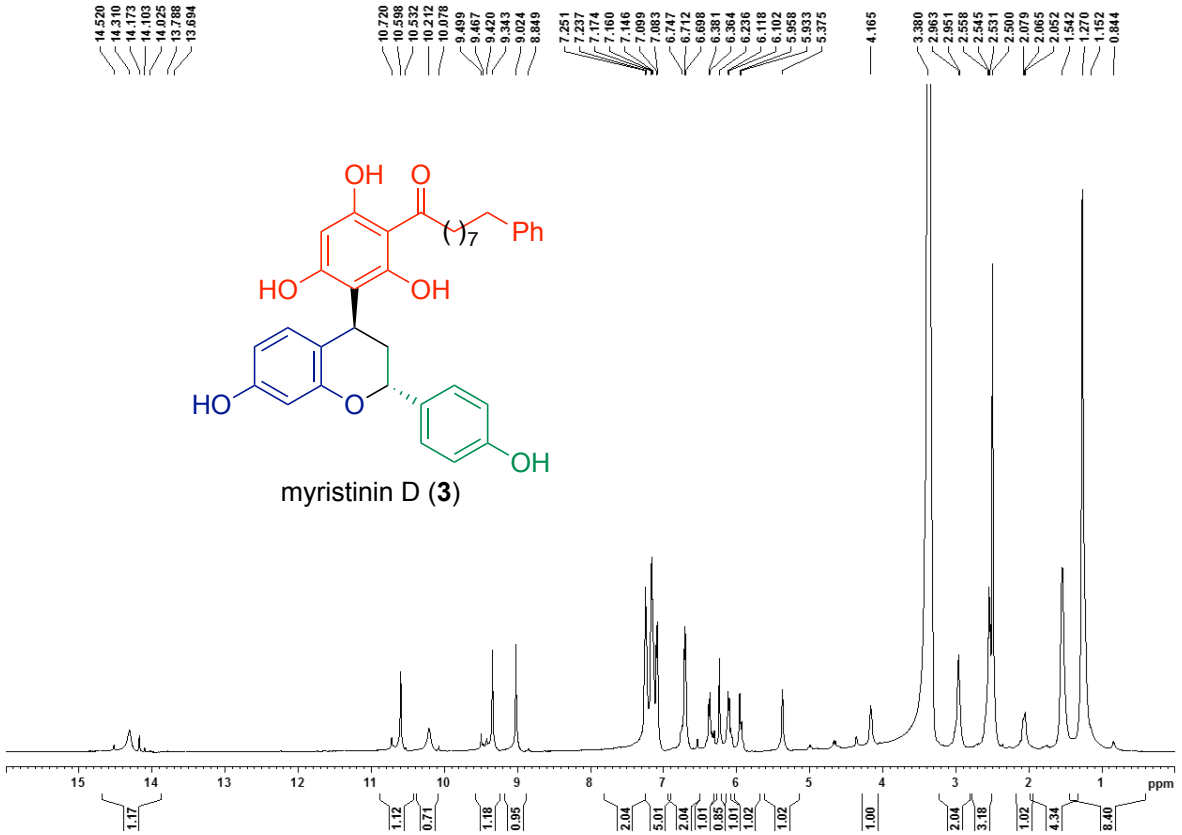
^{13}C NMR spectrum of myristinin A (**1**) (125MHz, DMSO-D6)



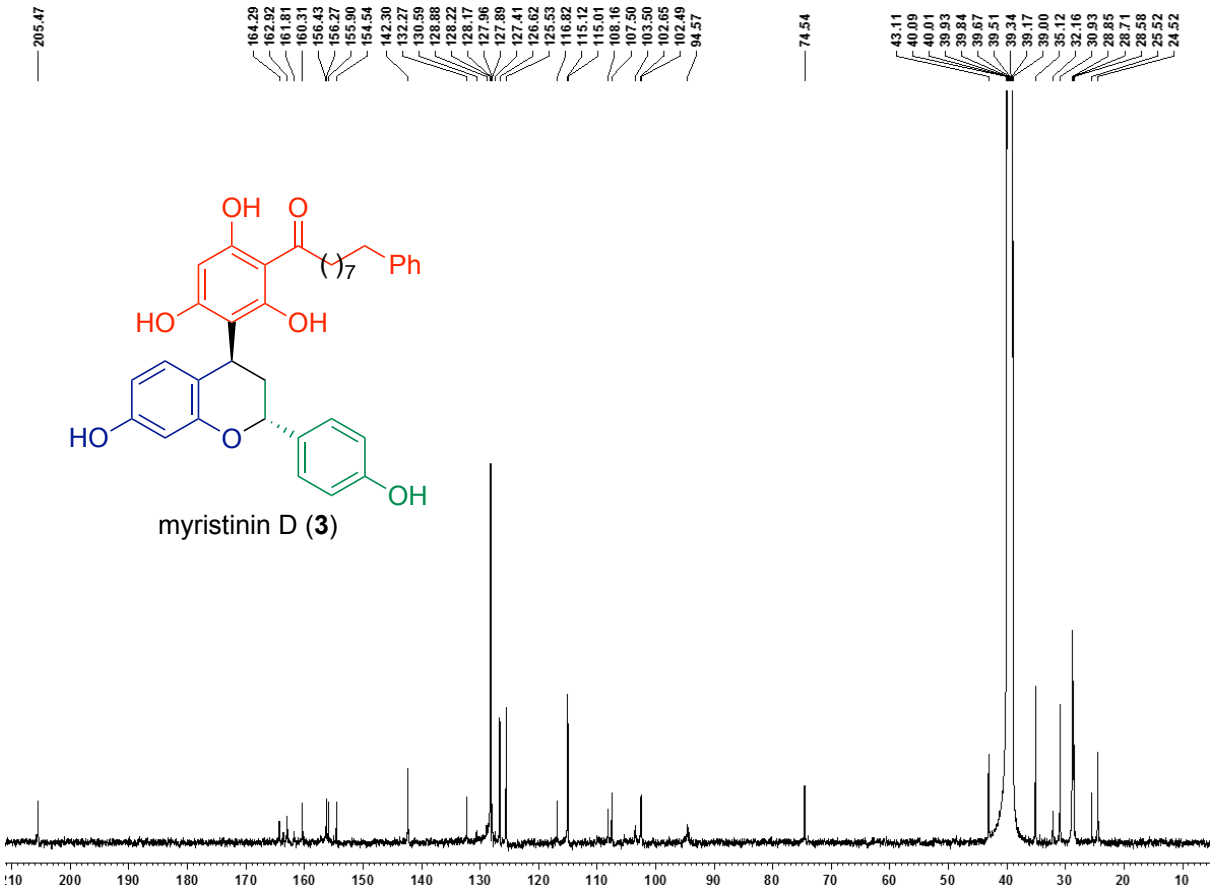
^{1}H NMR spectrum of cassiaflavan myristinin B/C (**2a/b**) (125MHz, DMSO-d_6)



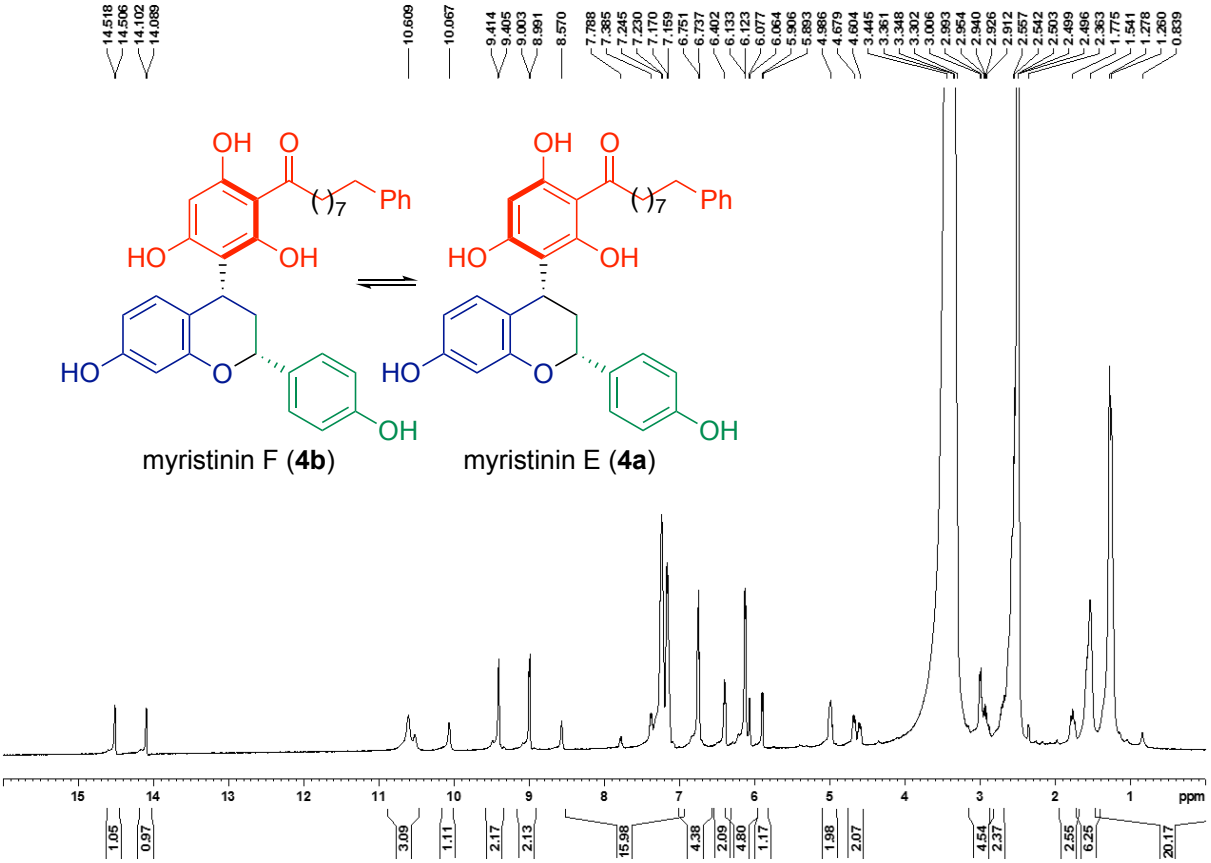
^{13}C NMR spectrum of cassiaflavan myristinin B/C (**2a/b**) (125MHz, DMSO-d_6)



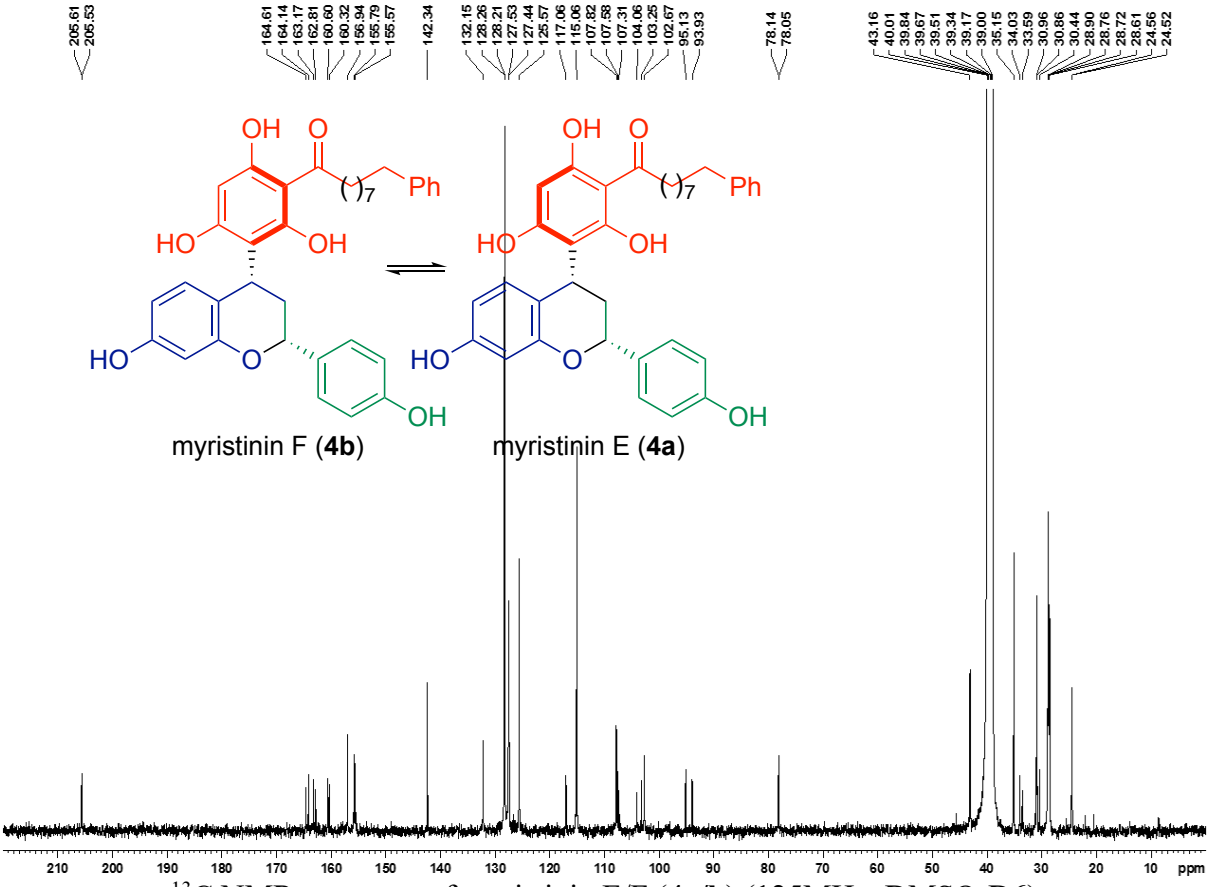
^{1}H NMR spectrum of myristinin D (**3**) (500MHz, DMSO-D6)



^{13}C NMR spectrum of myristinin D (**3**) (125MHz, DMSO-D6)

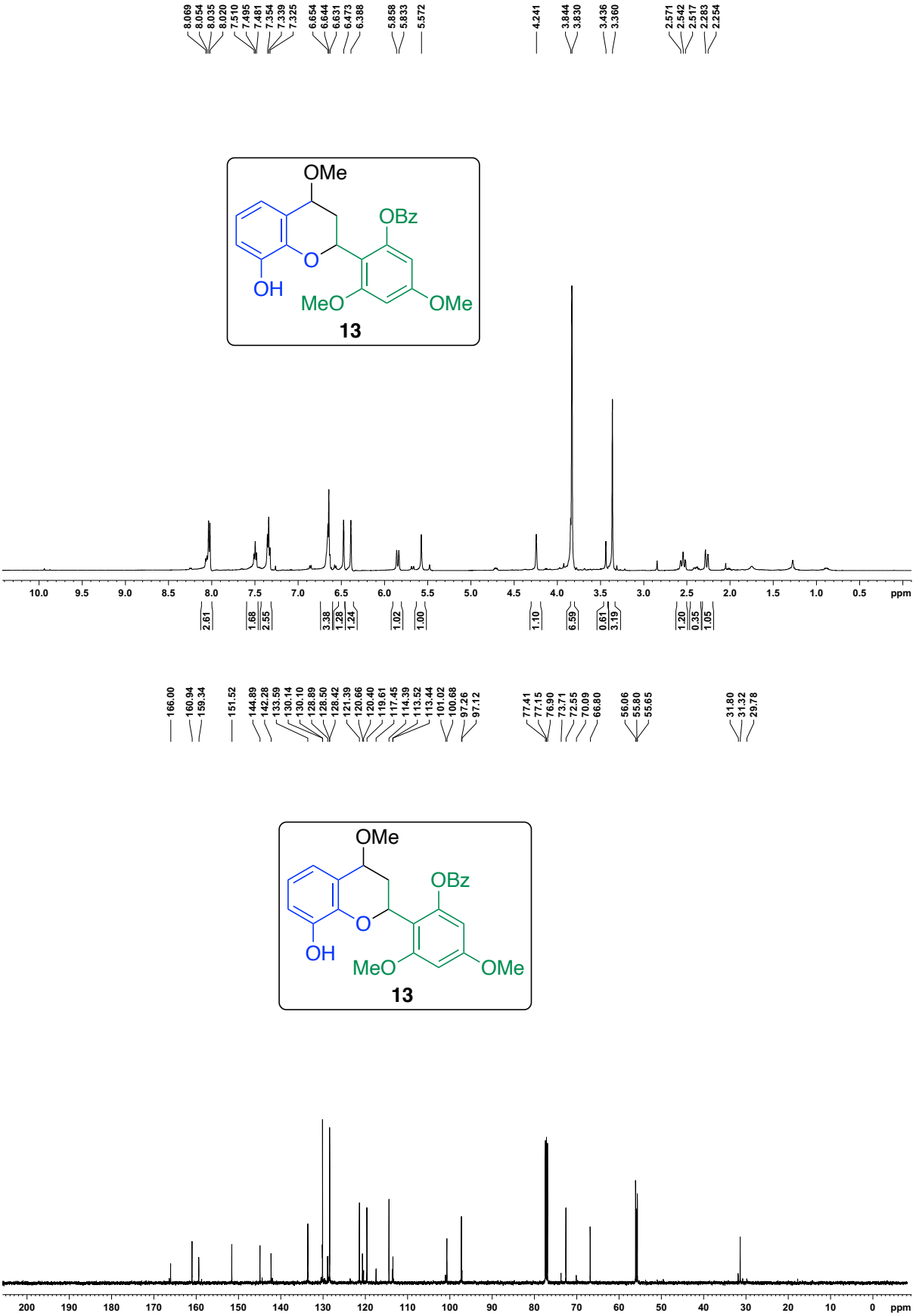


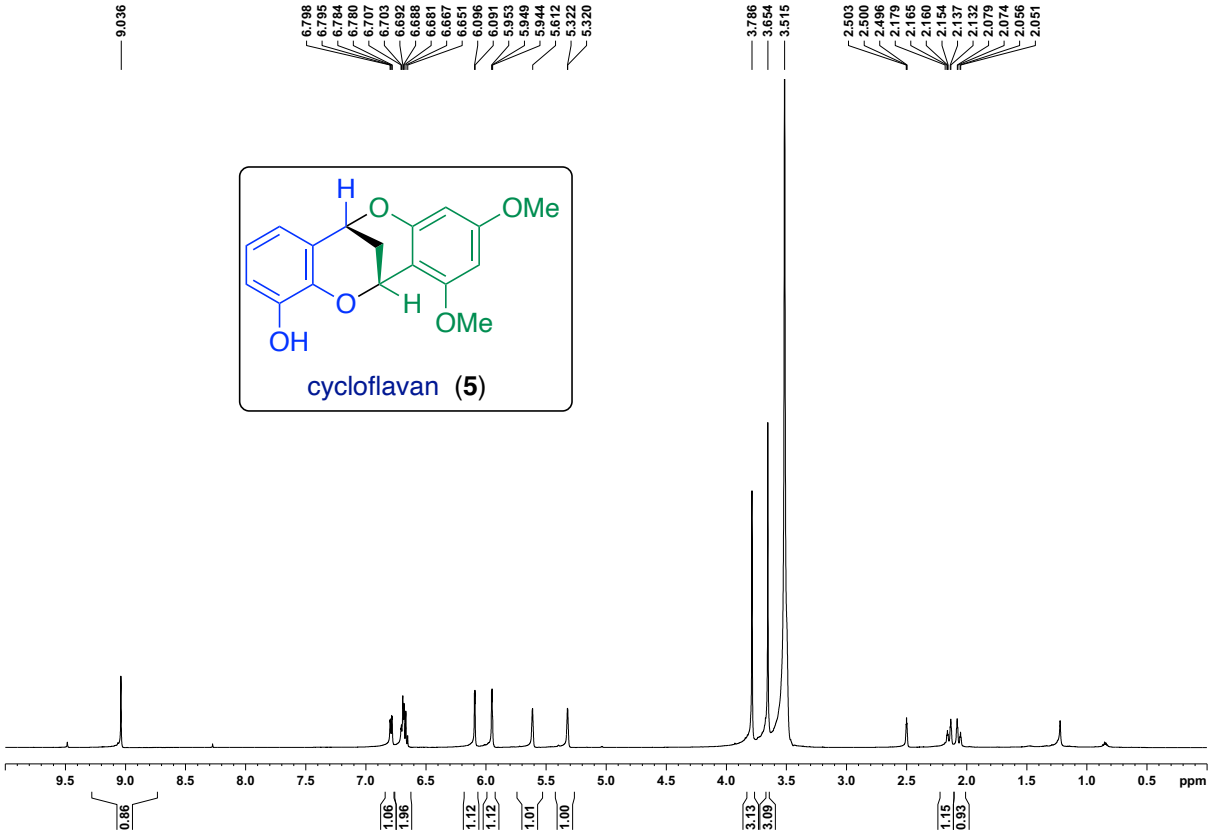
^{1}H NMR spectrum of myristinin E/F (**4a**/**b**) (500MHz, DMSO-D6)



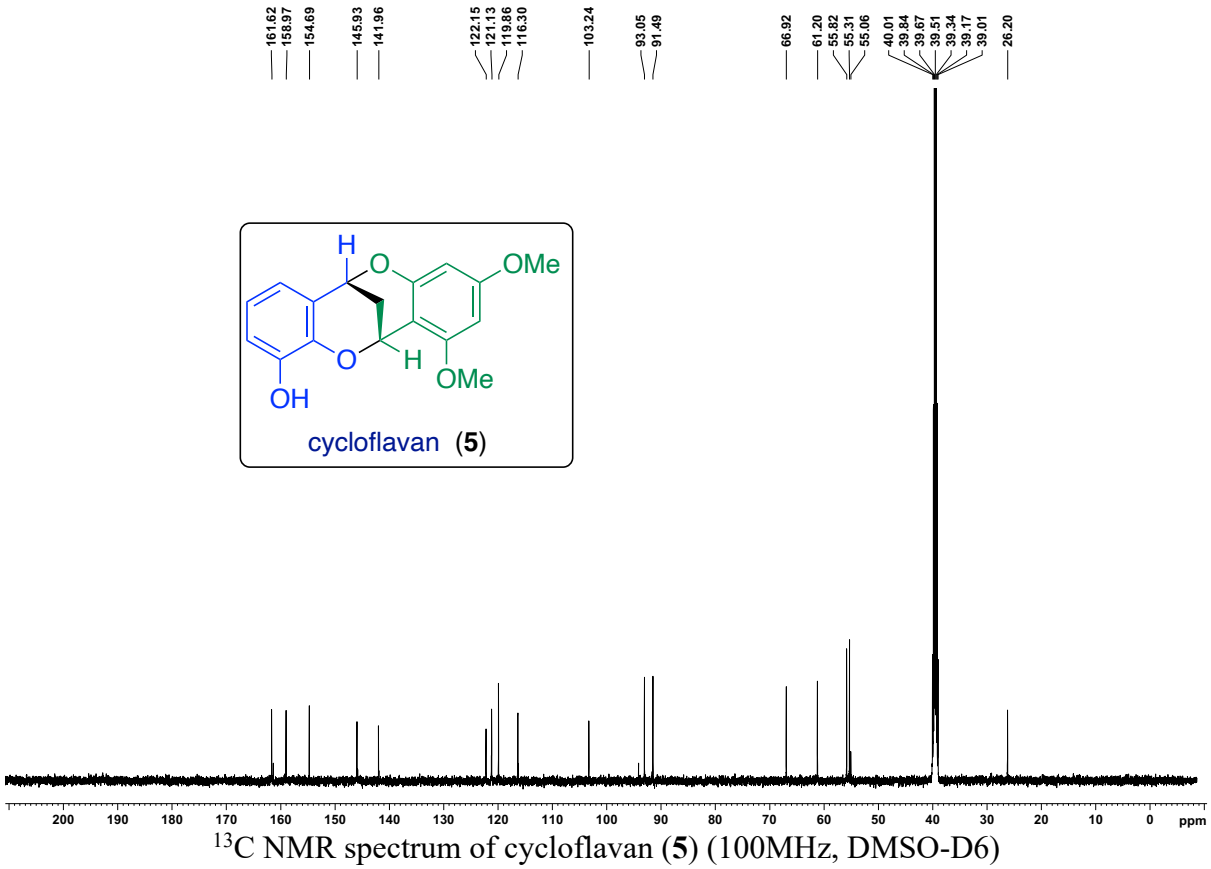
^{13}C NMR spectrum of myristinin E/F (**4a**/**b**) (125MHz, DMSO-D6)

^{1}H and ^{13}C NMR spectra of total synthesis of cycloflavan (5)





^{1}H NMR spectrum of cycloflavan (**5**) (400MHz, DMSO-D6)



^{13}C NMR spectrum of cycloflavan (**5**) (100MHz, DMSO-D6)

X-Ray crystallographic analysis and data

Crystal data and structure refinement for cassiaflavan 10a

Identification code		**10a**	
Solvent		Pet. Ether:Ethylacetate	
CCDC		2097416	
Bond precision:	C-C = 0.0019 A	Wavelength= 0.71073	
Cell:	a= 14.3203(6) alpha= 90	b= 11.9892(12) beta= 97.938(6)	c= 11.4344(17) gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	1944.4(4)	1944.3(4)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C24 H24 O4	0.5(C24 H24 O4)	
Sum formula	C24 H24 O4	C12 H12 O2	
Mr	376.43	188.22	
Dx, g cm-3	1.286	1.286	
Z	4	8	
Mu (mm-1)	0.087	0.087	
F000	800.0	800.0	
F000’	800.40		
h,k,l max	17,14,13	17,13,13	
Nref	3426	3342	
Tmin,Tmax	0.983,0.994	0.826,1.000	
Tmin’	0.981		
Correction method=	NUMERICAL		
Data completeness =	0.975	Theta(max)= 24.993	
R(reflections) =	0.0382(2973)	wR2(reflections)= 0.0993(3342)	
S = 1.040	Npar = 256		

Crystal data and structure refinement for doubly linked flavan 10b

Identification code		**10b**	
Solvent		Pet. Ether:Benzene	
CCDC		2097417	
Bond precision:	C-C = 0.0053 A	Wavelength= 0.71073	
Cell:	a= 9.1365(7) alpha= 101.064(6)	b= 10.0584(7) beta= 106.529(6)	c= 13.1688(9) gamma=104.988(6)
Temperature:	150 K		
	Calculated	Reported	
Volume	1073.68(15)	1073.67(14)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C25 H26 O5	0.4(C25 H26 O5)	
Sum formula	C25 H26 O5	C10 H10.40 O2	
Mr	406.46	162.58	
Dx, g cm-3	1.257	1.257	
Z	2	5	
Mu (mm-1)	0.087	0.087	
F000	432.0	432.0	
F000’	432.22		
h,k,l max	10,11,15	10,11,15	
Nref	3780	3720	
Tmin,Tmax	0.986,0.995	0.778,1.000	
Tmin’	0.982		
Correction method=	NUMERICAL		
Data completeness =	0.984	Theta(max)= 24.996	
R(reflections) =	0.0743(2308)	wR2(reflections)= 0.2269(3720)	
S = 1.053	Npar = 275		

Crystal data and structure refinement for cassiaflavan 10c

Identification code		**10c**	
Solvent		Pet. Ether:Ethylacetate	
CCDC		2097419	
Bond precision:	C-C = 0.0038 A	Wavelength= 0.71073	
Cell:	a=9.1036 (4) alpha= 101.354(3)	b=9.9813 (4) beta= 107.907 (4)	c= 14.0392 (6) gamma=101.361(3)
Temperature:	150 K		
	Calculated	Reported	
Volume	1143.89 (9)	1143.89 (8)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C25 H23 Br O6	C25 H23 Br O6	
Sum formula	C25 H23 Br O6	C25 H23 Br O6	
Mr	499.33	500.35	
Dx, g cm-3	1.450	1.453	
Z	2	2	
Mu (mm-1)	1.835	1.835	
F000	512.0	514.0	
F000’	511.67		
h,k,l max	10,11,16	10,11,16	
Nref	4026	3932	
Tmin,Tmax	0.785, 0.863	0.445, 1.000	
Tmin’	0.719		
Correction method=	NUMERICAL		
Data completeness =	0.977	Theta(max)= 24.996	
R(reflections) =	0.0344 (3430)	wR2(reflections)= 0.0817 (3932)	
S = 1.002	Npar = 292		

Crystal data and structure refinement for cassiaflavan 10d

Identification code		**10d**	
Solvent		Pet. Ether:Diethyl Ether	
CCDC		2097418	
Bond precision:	C-C = 0.0030 A	Wavelength= 0.71073	
Cell:	a= 8.0204(4) alpha= 83.198(4)	b= 9.7166(5) beta= 89.949(4)	c= 16.0604(8) gamma=82.176(4)
Temperature:	150 K		
	Calculated	Reported	
Volume	1231.08(11)	1231.08(11)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C31 H30 O5	C31 H30 O5	
Sum formula	C31 H30 O5	C31 H30 O5	
Mr	482.55	482.55	
Dx, g cm-3	1.302	1.302	
Z	2	2	
Mu (mm-1)	0.087	0.087	
F000	512.0	512.0	
F000’	512.25		
h,k,l max	9,11,18	9,11,18	
Nref	4099	3939	
Tmin,Tmax	0.988,0.993	0.855, 1.000	
Tmin’	0.986		
Correction method=	NUMERICAL		
Data completeness =	0.961	Theta(max)= 24.500	
R(reflections) =	0.0485(3309)	wR2(reflections)= 0.1277(3939)	
S = 1.034	Npar = 328		

Crystal data and structure refinement for cassiaflavan 12b

Identification code		**12b**	
Solvent		CH_2Cl_2	
CCDC		2097420	
Bond precision:	C-C = 0.0028 A	Wavelength= 1.54184	
Cell:	a= 7.7629(2) alpha= 90	b= 17.0020(5) beta= 90	c= 17.7065(6) gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2336.99(12)	2336.99(12)	
Space group	P b c a	P b c a	
Hall group	-P 2ac 2ab	-P 2ac 2ab	
Moiety formula	C16 H14 O2	C16 H14 O2	
Sum formula	C16 H14 O2	C16 H14 O2	
Mr	238.27	238.27	
Dx, g cm-3	1.354	1.354	
Z	8	8	
Mu (mm-1)	0.704	0.704	
F000	1008.0	1008.0	
F000’	1010.99		
h,k,l max	9,21,21	9,20,21	
Nref	2332	2277	
Tmin,Tmax	0.915,0.945	0.308,1.000	
Tmin’	0.869		
Correction method=	NUMERICAL		
Data completeness =	0.976	Theta(max)= 72.985	
R(reflections) =	0.0520(1834)	wR2(reflections)= 0.1493(2277)	
S = 1.066	Npar = 164		

Crystal data and structure refinement for cassiaflavan 12f

Identification code		**12f**	
Solvent		CH_2Cl_2	
CCDC		2097421	
Bond precision:	C-C = 0.0047 A	Wavelength= 1.54184	
Cell:	a=20.0353(7) alpha= 90	b=7.8785(2) beta= 97.267(4)	c=31.1858(12) gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	4883.1(3)	4883.1(3)	
Space group	C 2/c	C 1 2/c 1	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C16 H12 O4	2(C16 H12 O4)	
Sum formula	C16 H12 O4	C32 H24 O8	
Mr	268.26	536.51	
Dx, g cm-3	1.460	1.460	
Z	16	8	
Mu (mm-1)	0.872	0.872	
F000	2240.0	2240.0	
F000’	2247.53		
h,k,l max	24,9,38	24,9,38	
Nref	4908	4792	
Tmin,Tmax	0.893,0.957	0.617,1.000	
Tmin’	0.877		
Correction method=	NUMERICAL		
Data completeness =	0.976	Theta(max)= 73.139	
R(reflections) =	0.0399(2560)	wR2(reflections)= 0.1049(3315)	
S = 1.014	Npar = 361		

Crystal data and structure refinement for cassiaflavan 12i

Identification code		**12i**	
Solvent		CH_2Cl_2	
CCDC		2097422	
Bond precision:	C-C = 0.0019 A	Wavelength= 0.71073	
Cell:	a=17.3610(14) alpha= 90	b= 10.1907(8) beta= 100.301(3)	c= 15.3314(10) gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2668.7(3)	2668.7(3)	
Space group	C 2/c	C 1 2/c 1	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C17 H16 O4	C17 H16 O4	
Sum formula	C17 H16 O4	C17 H16 O4	
Mr	284.30	284.30	
Dx, g cm-3	1.415	1.415	
Z	8	8	
Mu (mm-1)	0.101	0.101	
F000	1200.0	1200.0	
F000’	1200.65		
h,k,l max	23,13,20	23,13,20	
Nref	3336	3315	
Tmin,Tmax	0.982,0.998	0.702,0.746	
Tmin’	0.980		
Correction method=	NUMERICAL		
Data completeness =	0.994	Theta(max)= 28.329	
R(reflections) =	0.0399(2560)	wR2(reflections)= 0.1049(3315)	
S = 1.071	Npar = 192		