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Supporting Information

Brønsted acid-catalysed intramolecular ring opening of 2-(aryloxymethyl)-3-aryloxiranes leading to *trans*-4-arylchroman-3-ols: scope and limitations

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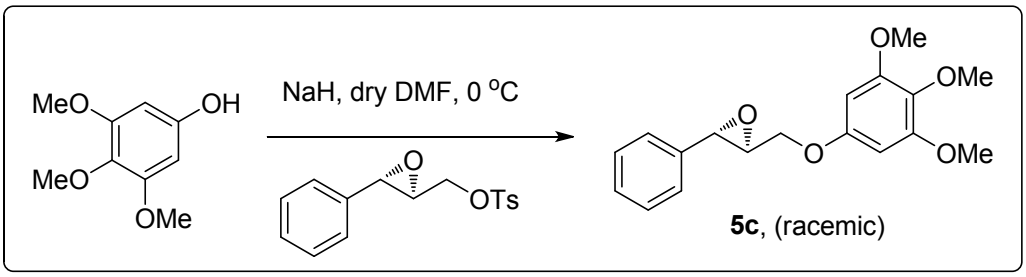
1 General information

All dry reactions were carried out under nitrogen in oven-dried glassware using standard gas-light syringes, cannulas, and septa. Commercial reagents were used without further purification unless otherwise stated. Progress of reactions was monitored by TLC on precoated Merck silica gel plates (60F-254). Visualization of reactants and products was accomplished with UV light. Column chromatography was performed over silica gel (60–120 mesh) procured from Merck using freshly distilled solvents. Melting points were determined with a Buchi-545 apparatus. Perkin Elmer 20 analyzer was utilized for elemental analysis of all compounds. ^{1}H NMR and ^{13}C NMR spectra were run on a JEOL 400 MHz spectrometer in $CDCl_3$ as solvent. Tetramethylsilane (0.00 ppm) served as an internal standard in ^{1}H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR. All spectra were recorded at 25 °C. Coupling constants (*J* values) are given in hertz (Hz). Chemical shifts are expressed in parts per million (ppm).

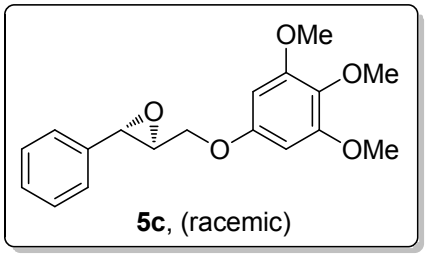
2 Preparation of starting materials:

Starting materials **5a**, **5b**, **5e**, **5g**, **5h**, **5j**, **5k, 5l**, and **5m** were prepared according to literature procedures[1-3] whereas the syntheses of **5c**, **5d**, **5f**, **5i**, **5n, 5o**, and **5p** are described below. Enantiomerically pure [(2*S*,3*S*)-2-((3,5- dimethoxyphenoxy)methyl)-3-phenyloxirane] **5b** and (3*S*,4*R*)-4-(4-bromophenyl)-5,7-dimethoxychroman-3-ol **5m** were also prepared according to the literature prodedures.[2]

Preparation of racemic 2-((3,4,5-trimethoxyphenoxy)methyl)-3-phenyloxirane 5c:



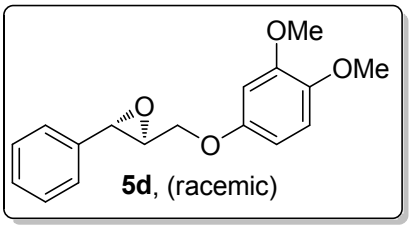
To a stirred suspension of sodium hydride (25 mg, 1.07 mmol,) in DMF (3 mL), a solution of 3,4,5-trimethoxyphenol (130 mg, 0.70 mmol) in dry DMF (5 mL) was added at 0 °C under N_2 atmosphere. The resulting mixture was stirred for 5 min, and a solution of racemic (3-phenyloxiran-2-yl)methyl 4-methylbenzenesulfonate[2] (0.23 g, 0.76 mmol) in DMF (5 mL) was added dropwise. The solution was stirred for an additional 10 h at 0 ºC. The reaction was terminated by the addition of 10% aqueous ammonium chloride (10 mL) and diethyl



ether (50 mL) was added. The organic layer was separated, washed by brine (50 mL), dried over anhyd. Na_2SO_4, and filtered. Evaporation of the solvent under reduced pressure gave the crude product which was subjected to silica gel column chromatography using hexane:EtOAc (90:10/80:20) as eluent to get the title compound **5c** (170 mg, 74%) as a colourless gum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.29 (m, 5H), 6.22 (s, 2H), 4.29 (dd, *J* = 3.1 and 11.1 Hz, 1H), 4.11 (dd, *J* = 5.2 and 11.2 Hz, 1H), 3.91 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 6H), 3.79 (s, 3H), 3.40-3.38 (m, 1H). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: 68.22; H, 6.44.

2-((3,4-Dimethoxyphenoxy)methyl)-3-phenyloxirane 5d:

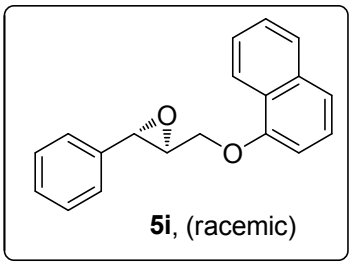
Starting from 3,4-dimethoxyphenol (150 mg, 0.97 mmol), the title compound was prepared in the same manner as that described for **5c**. After the usual work-up, the title compound was **5d** (225 mg, 81%) was obtained as a colourless semi-solid in the pure form which was used for the next step without further purification and characterisation.



5d, (racemic)

2-((Naphthalen-1-yloxy)methyl)-3-phenyloxirane 5i:

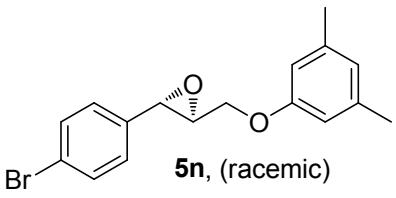
Starting from 1-naphthol (0.15 g, 1.04 mmol), the title compound was prepared in the same manner as that described for **5c**. Silica gel column chromatography of the crude product using hexane:EtOAc (98:2/90:10) as eluent furnished the title compound **5i** (0.23 g, 80%) as a colourless semi-solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 6.5 Hz, 1H), 7.44-7.38 (m, 3H), 7.31-7.17 (m, 6H), 6.77 (d, *J* = 7.5 Hz, 1H), 4.42 (dd, *J* = 2.0 and 11.0 Hz, 1H), 4.25 (dd, *J* = 5.0 and 11.0 Hz, 1H), 3.94 (d, *J* = 2.0 Hz, 1H), 3.48-3.37 (m, 1H). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.66; H, 5.76.



5i, (racemic)

2-(4-Bromophenyl)-3-((3,5-dimethylphenoxy)methyl)oxirane 5n:

Starting from 3,5-dimethylphenol (0.11 g, 0.90 mmol), the title compound was prepared in the same manner as that described for **5c**. After the usual work-up, the title compound was **5n** (0.25 g, 83%) was obtained as a as a light

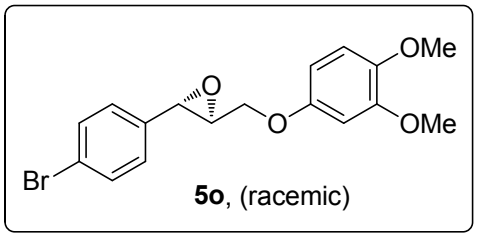


5n, (racemic)

yellow liquid in the pure form which was used for the next step without further purification and characterisation.

2-(4-Bromophenyl)-3-((3,4-dimethoxyphenoxy)methyl)oxirane 5o:

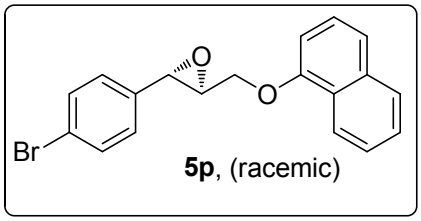
Starting from 3,4-dimethoxyphenol (0.11 g, 0.71 mmol), the title compound was prepared in the same manner as that described for **5c**. Silica gel column chromatography of the crude product using hexane:EtOAc (98:2/80:20) as eluent furnished the title compound **5o** (0.19 g, 73%) as a white solid. M.P.: 122-123˚C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.34 (dd, *J* = 3.0 and 9.0 Hz, 1H), 4.18 (dd, *J* = 3.0 and 11.0 Hz, 1H), 4.01 (dd, *J* = 4.5 and 11.0 Hz, 1H), 3.79-3.75 (m, 7H), 3.24 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 149.9, 144.0, 135.6, 131.7, 127.3, 122.3, 111.6, 104.0, 101.2, 68.2, 60.4, 56.4, 55.8, 55.7. Anal. Calcd for $C_{17}H_{17}BrO_4$: C, 55.91; H, 4.69. Found: C, 55.88; H, 4.62.



5o, (racemic)

2-(4-Bromophenyl)-3-((naphthalen-1-yloxy)methyl)oxirane 5p:

Starting from 1-naphthol (0.15 g, 1.04 mmol), the title compound was prepared in the same manner as that described for **5c**. Silica gel column chromatography of the crude product using hexane:EtOAc (98:2/90:10) as eluent furnished the title compound **5p** (0.28 g, 76%) as a white solid. M.P.: 144-145˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.27 (m, 1H), 7.80 (d, *J* = 2.3 Hz, 1H), 7.51-7.45 (m, 5H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.48 (dd, *J* = 3.2 and 11.0 Hz, 1H), 4.31 (dd, *J* = 5.0 and 11.0 Hz, 1H), 3.97 (d, *J* = 1.8 Hz, 1H), 3.48-3.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 135.7, 134.6, 131.7, 127.5, 127.4, 126.6, 125.7, 125.6, 125.4, 122.3, 121.9, 121.0, 105.1, 67.9, 60.3, 55.8. Anal. Calcd for $C_{19}H_{15}BrO_2$: C, 64.24; H, 4.26. Found: C, 64.29; H, 4.34.

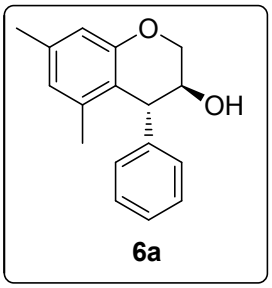


5p, (racemic)

3 Synthesis of racemic *trans*-4-arylchroman-3-ols:

***trans*-5,7-Dimethyl-4-phenylchroman-3-ol 6a:**[3]

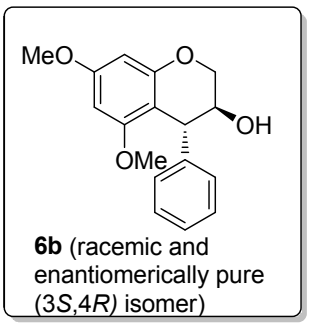
TsOH.H_2O (0.0074 g, 0.039 mmol) was added to a solution of compound **5a** (50 mg, 0.196 mmol) in toluene (5 mL) and the resulting solution was heated at 70˚C for 30 min. After cooling, EtOAc (50 mL) was added to the reaction mixture, and then the whole mixture was poured in a beaker containing saturated aq. $NaHCO_3$ solution (25 mL) with vigorous stirring. The combined organic layers were washed with brine (50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (5-12% ethyl acetate in hexane) afforded compound **7a** (45 mg, 90%) as a white solid. M.P.: 125-126 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, J = 7.2 Hz, 2H), 7.21 (t, J =7.3 Hz, 1H), 7.07 (d, J = 7.2 Hz, 2H), 6.66 (s, 1H), 6.64 (s, 1H), 4.13 (m, 1H), 4.05-4.04 (m, 1H), 4.01-3.96 (m, 2H), 2.28 (s, 4H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 142.6, 139.2, 138.0, 128.7, 128.5, 126.7, 124.5, 116.0, 114.9, 69.9, 64.4, 46.5, 21.1, 18.9. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.36; H, 7.19.



6a

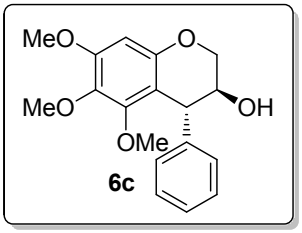
***trans*-5,7-Dimethoxy-4-phenylchroman-3-ol 6b and its (3*S*, 4*R*) isomer:**[2,3]

Starting from **5b** (50 mg, 0.17 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6b** (44 mg, 88%) as a white solid. M.P.: 101-112 ^oC. Compound **6b** in the enantiomerically pure form [(3*S*,4*R*)-5,7-Dimethoxy-4-phenylchroman-3-ol] was also similarly synthesised from [(2*S*,3*S*)-2-((3,5- dimethoxyphenoxy)methyl)-3-phenyloxirane]. $[\alpha]_D^{27}$ = +51.5 (c = 1.0 in $CHCl_3$). Literature: $[\alpha]_D^{20}$ = +53.0 (c = 1.0 in $CHCl_3$)[2] and $[\alpha]_D^{27}$ = +52.3 (c = 1.1 in $CHCl_3$)[3]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.24 (m, 2H), 7.19-7.16 (m, 1H), 7.08 (d, J = 7.3 Hz), 6.15 (d, J = 2.3 Hz, 1H), 6.08 (d, J = 2.3 Hz, 1H), 4.22 (m, 1H), 4.02-3.92 (m, 3H), 3.78 (s, 3H), 3.55 (s, 3H), 2.1 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.2, 159.6, 154.9, 143.3, 128.3, 128.0, 126.3, 101.6, 92.8, 92.3, 69.2, 64.9, 55.4, 55.2, 43.2. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.40; H, 6.36.



6b (racemic and enantiomerically pure (3*S*,4*R*) isomer)

***trans*-5,6,7-Trimethoxy-4-phenylchroman-3-ol 6c:**

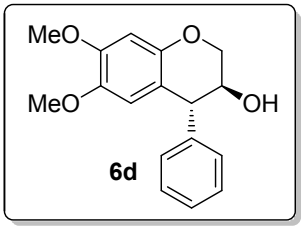


6c

Starting from **5c** (50 mg, 0.158 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6c** (38.5 mg, 77%) as a white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 3H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.31 (s, 1H), 4.23 (m, 1H), 3.99 (m, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 149.8, 143.8, 136.6, 128.3, 128.1, 126.5, 106.9, 95.5, 69.1, 64.9, 60.6, 60.1, 55.7, 44.1. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.41; H, 6.39.

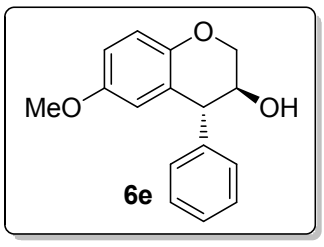
***trans*-6,7-Dimethoxy-4-phenylchroman-3-ol 6d:**

Starting from **5d** (50 mg, 0.17 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6d** (0.0375 g, 75%) as a white solid. M.P.: 118-119 ℃. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.19 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.49 (s, 1H), 6.33 (s, 1H), 4.09-4.06 (m, 1H), 4.03 (d, *J* = 2.0 Hz, 2H), 3.98-3.93 (m, 1H), 3.88 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.9, 147.9, 143.8, 142.8, 128.9, 128.5, 126.8, 113.1, 111.9, 100.2, 69.9, 66.2, 56.2, 55.7, 49.3. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.25; H, 6.42.

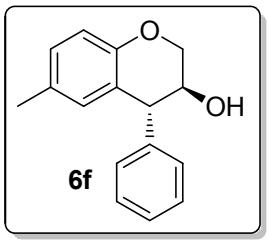


***trans*-6-Methoxy-4-phenylchroman-3-ol 6e:**[3]

Starting from **5e** (50 mg, 0.195 mmol), the title compound was prepared in the same manner as that described for **6e**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **7e** (40 mg, 80%) as a white solid. M.P.: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 2H), 7.30-7.25 (m, 1H), 7.18-7.16 (m, 2H), 6.89 (d, *J* = 9.1 Hz, 1H), 6.79 (dd, *J* = 3.0, 9.1 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 4.15 (d, *J* = 10.5 Hz, 1H), 4.09-4.12 (m, 2H), 3.99-3.97 (m, 1H), 3.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 148.0, 142.5, 129.0, 128.6, 126.9, 122.5, 117.2, 115.2, 114.6, 69.7, 66.5, 55.5, 50.2. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.91; H, 6.22.



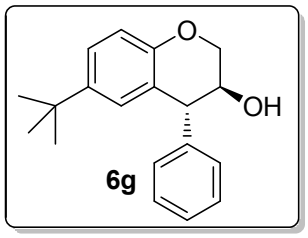
***trans*-6-Methyl-4-phenylchroman-3-ol 6f:**



Starting from **5f** (50 mg, 0.208 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6f** (36 mg, 72%) as a white solid. M.P.: 102-103 ^{o}C. ^{1}H NMR (400 MHz, CDCl3): δ 7.35-7.11 (m, 5H), 6.98-6.95 (m, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.67 (br. s, 1H), 4.15-4.04 (m, 3H), 3.998-3.95 (m, 1H), 2.17 (s, 3H), 2.01 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 142.7, 131.4, 130.2, 129.1, 128.9, 128.6, 126.9, 121.5, 116.3, 69.8, 66.5, 50.1, 20.4. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.78.

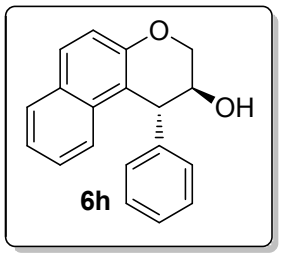
***trans*-6-(tert-Butyl)-4-phenylchroman-3-ol 6g:**[3]

Starting from **5g** (50 mg, 0.208 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15% ethyl acetate in hexane) furnished compound **6g** (0.035 g, 70%) as a white solid. M.P.: 108-109 oC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 4H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.15-4.08 (m, 3H), 4.08-3.99 (m, 1H), 1.98 (bs, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 144.1, 142.9, 129.1, 128.7, 128.1, 127.9, 125.3, 120.8, 116.0, 70.1, 66.5, 50.2, 34.1, 31.1. Anal.Calcd for $C_{19}H_{22}O_2$: C, 80.52; H, 7.59. Found: C, 80.57; H, 7.53.

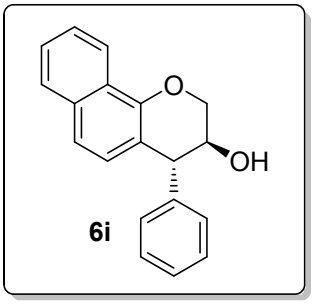


***trans*-1-Phenyl-2,3-dihydro-1H-benzo[f]chromen-2-ol 6h:**[3]

Starting from compound **5h** (50 mg, 0.18 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15% ethyl acetate in hexane) furnished compound **6a** (35 mg, 70%) as a white solid. M.P.: 119-120 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.73 (m, 2H), 7.48–7.45 (m, 1H), 7.30-7.15 (m, 8H), 4.68 (br s, 1H), 4.22–4.14 (m, 3H), 2.30 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 143.0, 133.4, 129.8, 129.3, 128.5, 126.8, 126.7, 123.5, 122.9, 118.5, 111.7, 69.7, 64.8, 45.9. Anal.Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.66; H, 5.89.



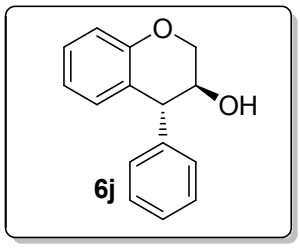
***trans*-4-Phenyl-3,4-dihydro-2H-benzo[h]chromen-3-ol 6i:**



Starting from compound **5i** (50 mg, 0.18 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15% ethyl acetate in hexane) furnished compound **6i** (37.5 mg, 75%) as a white solid. M.P.: 130-131˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.23 (m, 1H), 7.72-7.70 (m, 1H), 7.48-7.42 (m, 2H), 7.31-7.08 (m, 6H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.24-4.21 (m, 1H), 4.14-4.05 (m, 3H), 2.38 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 142.8, 133.6, 129.2, 128.7, 128.5, 127.4, 127.0, 126.3, 125.6, 124.8, 121.8, 120.8, 115.2, 69.9, 66.7, 50.1. Anal.Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.52; H, 5.89.

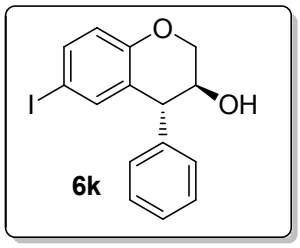
***trans*-4-Phenylchroman-3-ol 6j:**[3]

Starting from compound **5j** (50 mg, 0.22 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound **6j** (27 mg, 54%) as a white solid. M.P.: 122-123˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.13 (m, 6H), 6.92-6.84 (m, 3H), 4.18 (dd, *J* = 2.1, 11.0 Hz, 1H), 4.09 (m, 2H), 4.02-3.98 (m, 1H), 2.08 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 142.6, 131.3, 129.1, 128.5, 128.2, 127.1, 122.1, 121.2, 116.6, 69.7, 66.7, 50.1. Anal.Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.68; H, 6.19.

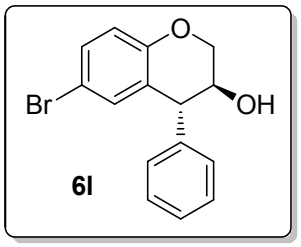


***trans*-6-Iodo-4-phenylchroman-3-ol 6k:**[3]

Starting from compound **5j** (50 mg, 0.14 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound **6j** (25 mg, 50%) as a white solid. M.P.: 108-109˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.12 (m, 7H), 6.72 (d, *J* = 8.5 Hz, 1H), 4.18 (d, *J* = 2.1, 11.0 Hz, 1H), 4.12-3.98 (m, 3H), 2.10 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 141.9, 139.8, 137.1, 129.0, 129.0, 127.5, 124.8, 119.0, 83.5, 69.4, 66.5, 49.9. Anal.Calcd for $C_{15}H_{13}IO_2$: C, 51.16; H, 3.72. Found: C, 51.26; H, 3.76.



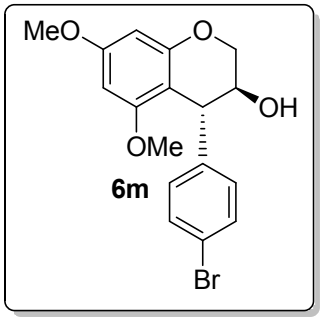
***trans*-6-Bromo-4-phenylchroman-3-ol 6l:**[3]



Starting from compound **5j** (50 mg, 0.16 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound **6j** (22.5 mg, 45%) as a white solid. M.P.: 118-119˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.19 (m, 4H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 1H), 4.18 (d, *J* = 2.1, 10.9 Hz, 1H), 4.11-3.97 (m, 3H), 1.58 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 141.9, 139.8, 137.1, 129.0, 129.0, 127.5, 124.8, 119.0, 83.5, 69.4, 66.5, 49.9. Anal.Calcd for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 59.10; H, 4.21.

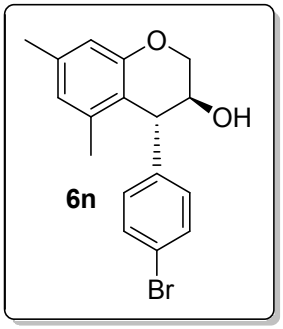
***trans*-4-(4-bromophenyl)-5,7-dimethoxychroman-3-ol 6m and its (3*S*, 4*R*) isomer:**[3]

Starting from compound **5m** (50 mg, 0.136 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound **6m** (42 mg, 84%) as a white solid. M.P.: 76-77˚C. Compound **6m** in the enantiomerically pure form (3*S*,4*R*)-4-(4-bromophenyl)-5,7-dimethoxychroman-3-ol was also similarly synthesised from [(2*S*,3*S*)-2-(4-bromophenyl)-3-((3,5-dimethoxyphenoxy)methyl)oxirane]. $[\alpha]_D^{27}$ = +33.8 (c = 0.5 in $CHCl_3$). Literature: $[\alpha]_D^{27}$ = +35.2 (c = 0.5 in $CHCl_3$)[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.14 (d, *J* = 2.3 Hz, 1H), 6.08 (d, *J* = 2.3 Hz, 1H), 4.16 (m, 1H), 4.02-3.95 (m, 2H), 3.89 (d, *J* = 11.1 Hz, 1H), 3.78 (s, 3H), 3.56 (s, 3H), 2.30 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 159.5, 155.0, 142.5, 131.4, 129.7, 120.2, 101.3, 92.9, 92.4, 69.0, 64.9, 55.4, 55.3, 42.8. Anal.Calcd for $C_{17}H_{17}BrO_4$: C, 55.91; H, 4.69. Found: C, 55.99; H, 4.61.



***trans*-(3S,4R)-4-(4-bromophenyl)-5,7-dimethylchroman-3-ol 6n:**

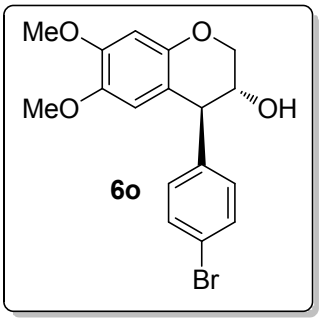
Starting from compound **5m** (50 mg, 0.15 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound **6n** (43 mg, 86 %) as a white solid.



M.P.: 86-87˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 6.8 Hz, 1H), 4.07 (m, 1H), 4.03-3.99 (m, 2H), 3.92-88 (m, 1H), 2.28 (s, 3H), 1.97 (bs, 1H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 141.7, 139.1, 138.4, 131.9, 130.3, 124.7, 115.5, 115.08, 69.7, 64.3, 46.0, 21.2, 18.9. Anal.Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.37; H, 5.31.

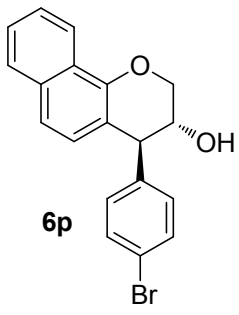
***trans*-4-(4-bromophenyl)-6,7-dimethoxychroman-3-ol 6o:**

Starting from compound **5o** (50 mg, 0.136 mmol), the title compound was prepared in the same manner as that described for **6a**. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound **6o** (35 mg, 69%) as a white solid. M.P.: 89-90˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.49 (s, 1H), 6.29 (s, 1H), 4.06 (d, *J* = 10.1 Hz, 1H), 4.01-3.99 (m, 3H), 3.86 (s, 3H), 3.68 (s, 3H), 1.83 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 144.1, 141.9, 131.7, 130.6, 120.9, 112.8, 111.3, 100.3, 69.8, 66.2, 56.2, 55.8, 48.9. Anal.Calcd for $C_{17}H_{17}BrO_4$: C, 55.91; H, 4.69. Found: C, 55.97; H, 4.78.



***trans*-4-(4-Bromophenyl)-3,4-dihydro-2H-benzo[h]chromen-3-ol 6p:**

Starting from **5p** (50 mg, 0.14 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-12% ethyl acetate in hexane) furnished the title compound **6p** (33 mg, 66%) as a white solid. M.P.: 128-129℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.23 (m, 1H), 7.77-7.75 (m, 1H), 7.51-7.47 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 4.28-4.21 (m, 1H), 4.23-4.11 (m, 3H), 2.43 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 141.9, 133.6, 131.8, 130.8, 128.2, 127.4, 126.5, 125.7, 124.8, 121.8, 121.1, 114.7, 69.8, 66.7, 49.5. Anal. Calcd for $C_{19}H_{15}BrO_2$: C, 64.24; H, 4.26. Found: C, 64.29; H, 4.38.



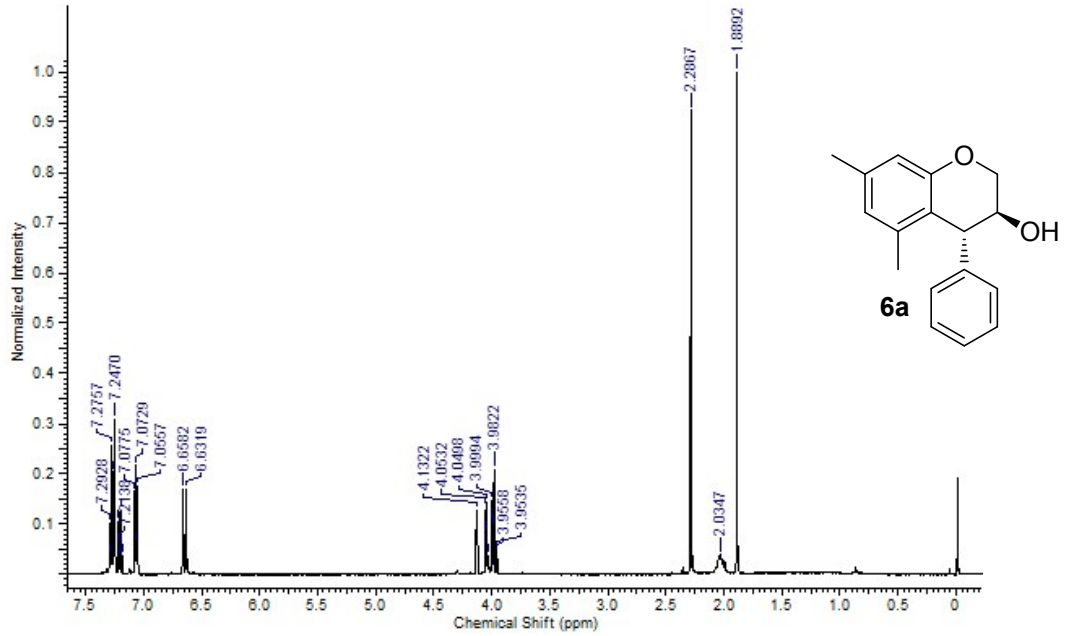
4 References

1. Z.-J. Shi and C. He, *J. Am. Chem. Soc.*, 2004, **126**, 5964.

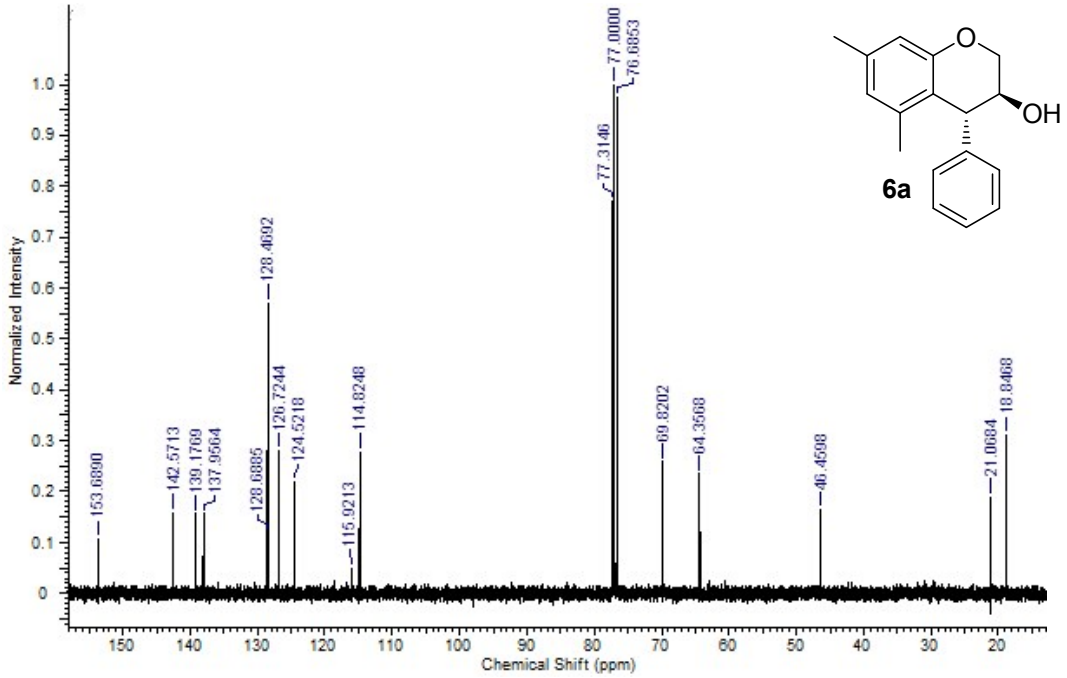
2. R. Marcos, C. Rodrıguez-Escrich, C. Herrerıas and M. A. Pericas, *J. Am. Chem. Soc*., 2008, **130**, 16838.

3. G.-X. Li and J. Qu, *Chem. Commun*., 2010, **46**, 2653

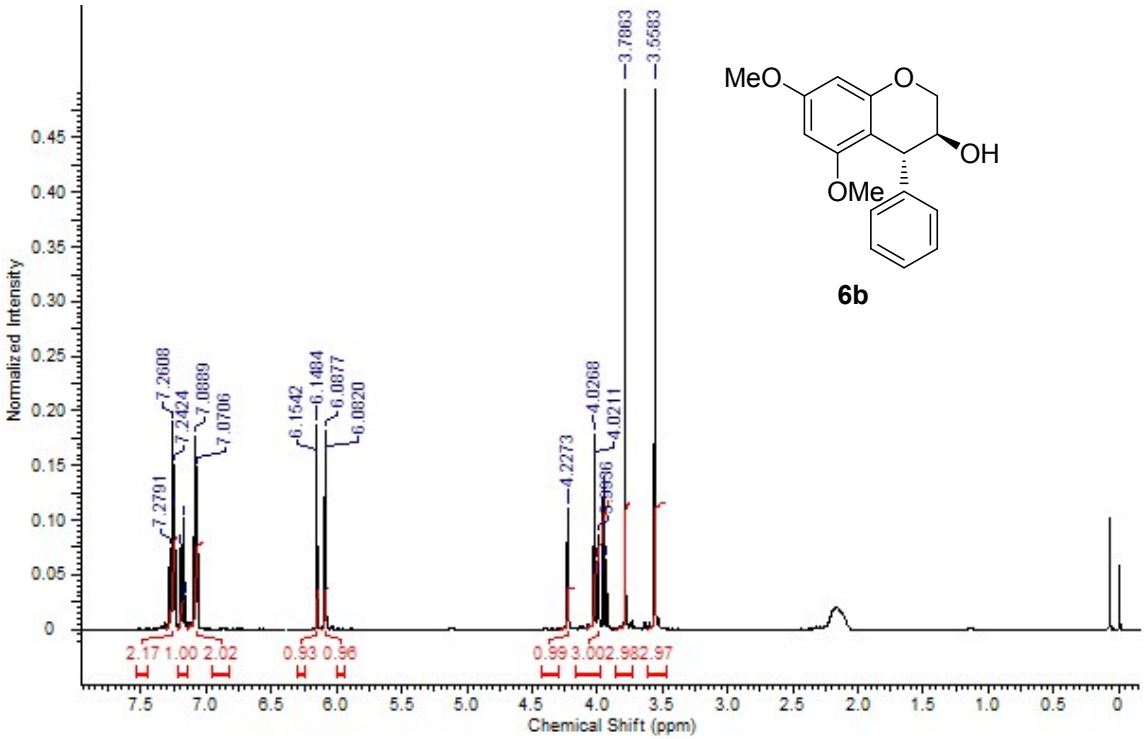
4 Copies of ^{1}H and ^{13}C NMR spectra for *trans*-4-aryl-chroman-3-ols



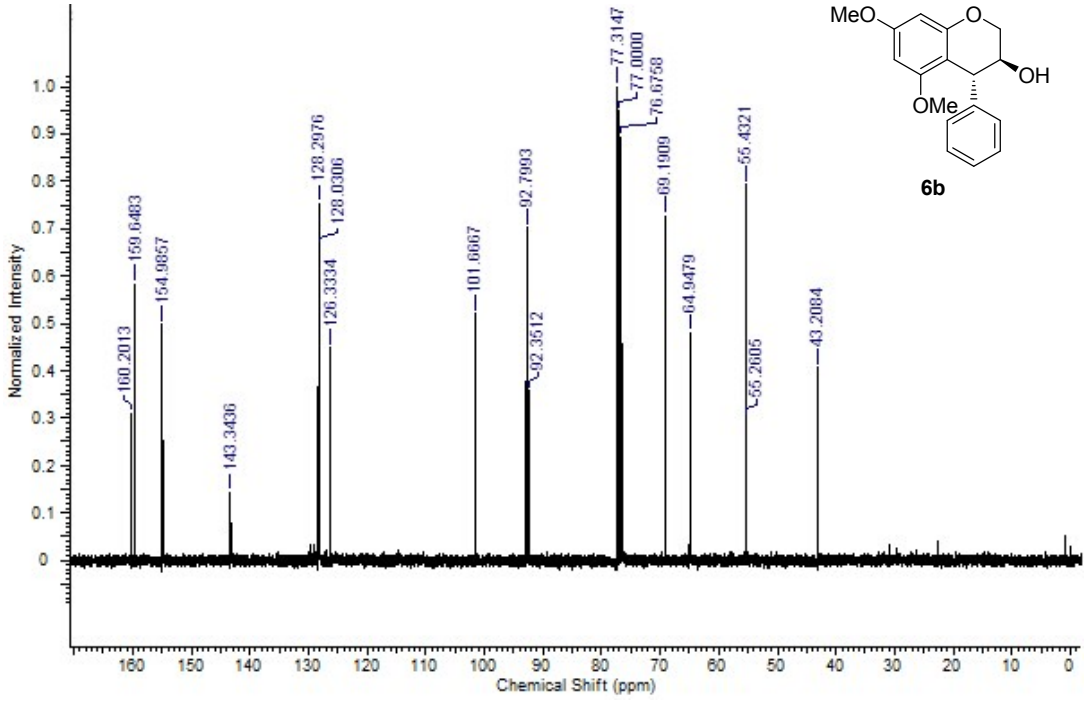
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6a**.



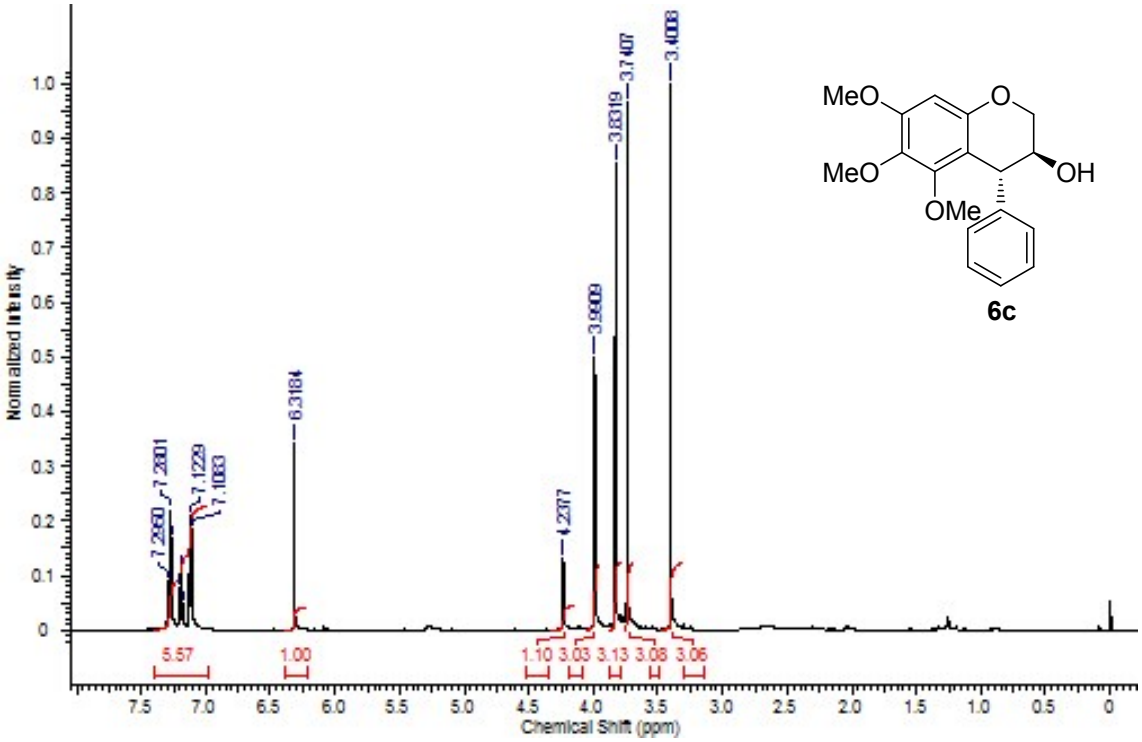
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6a**.



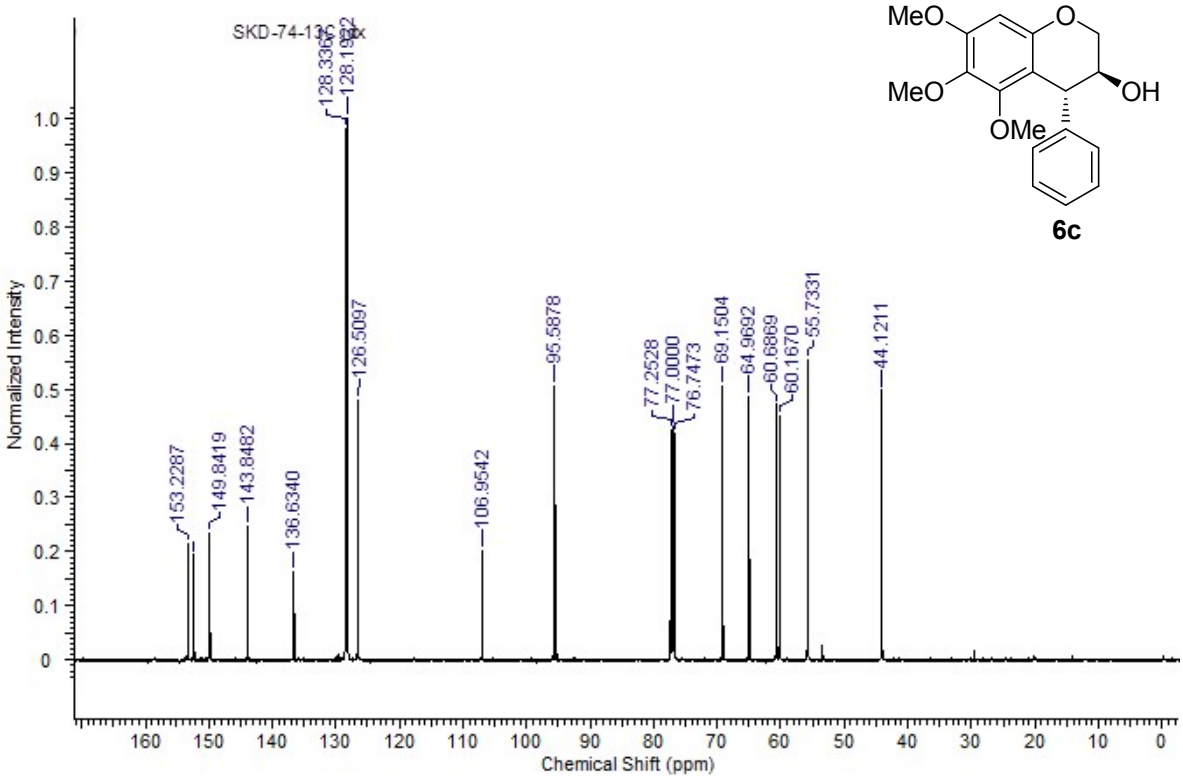
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6b**.



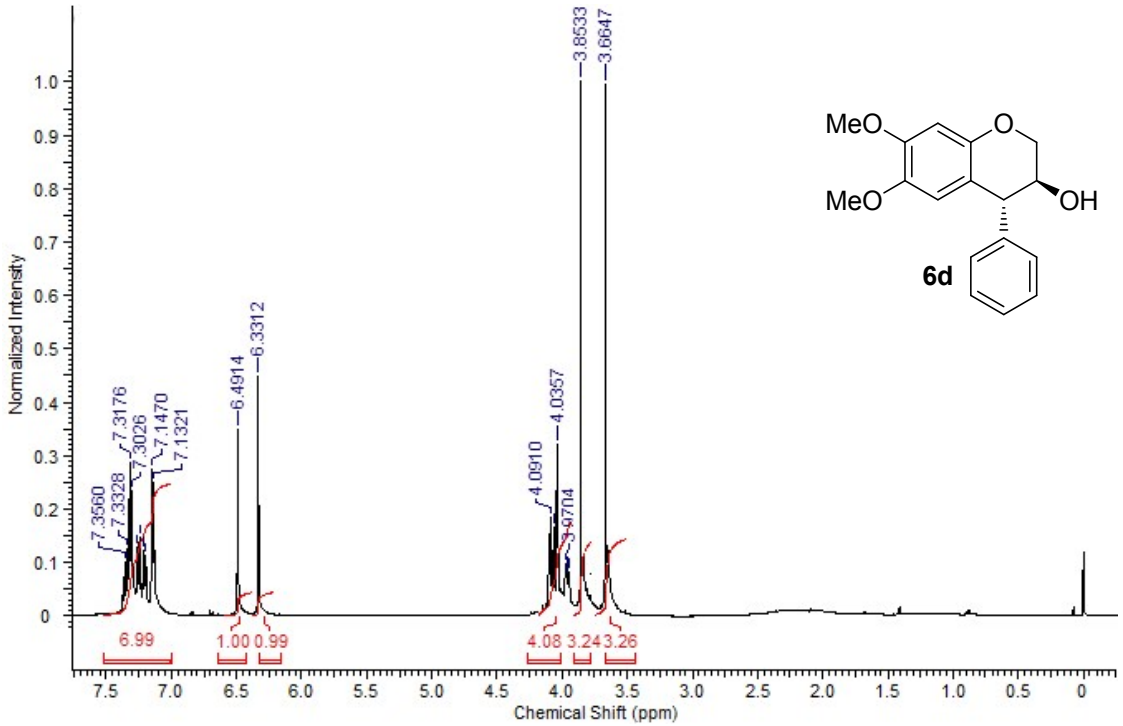
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6b**.



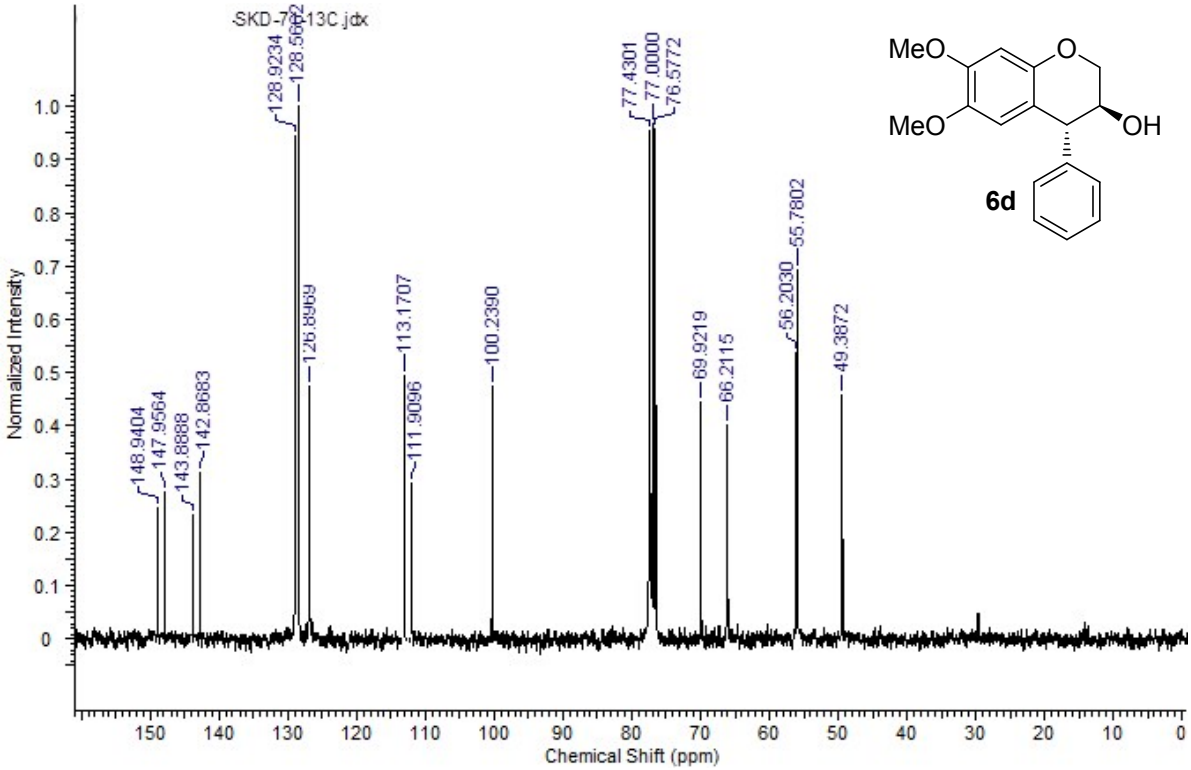
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6c**.



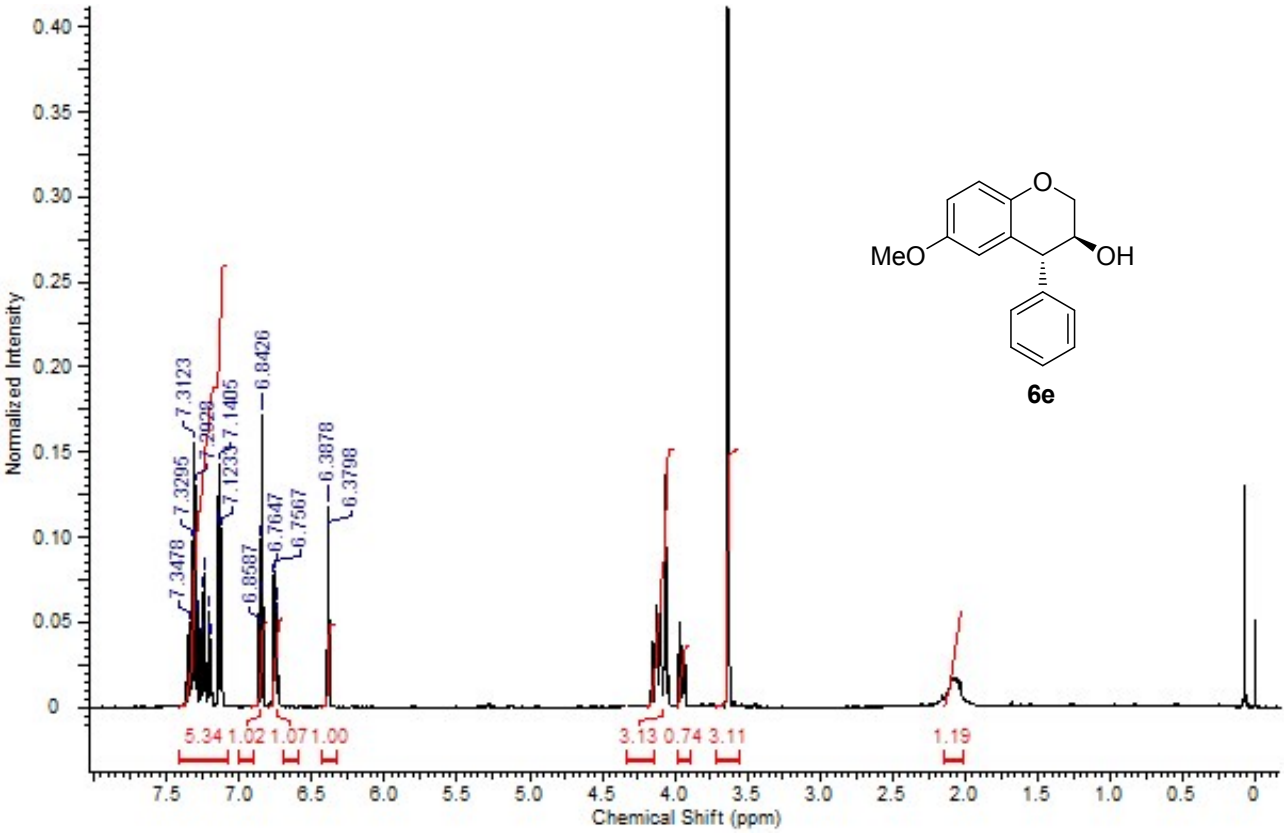
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6c**.



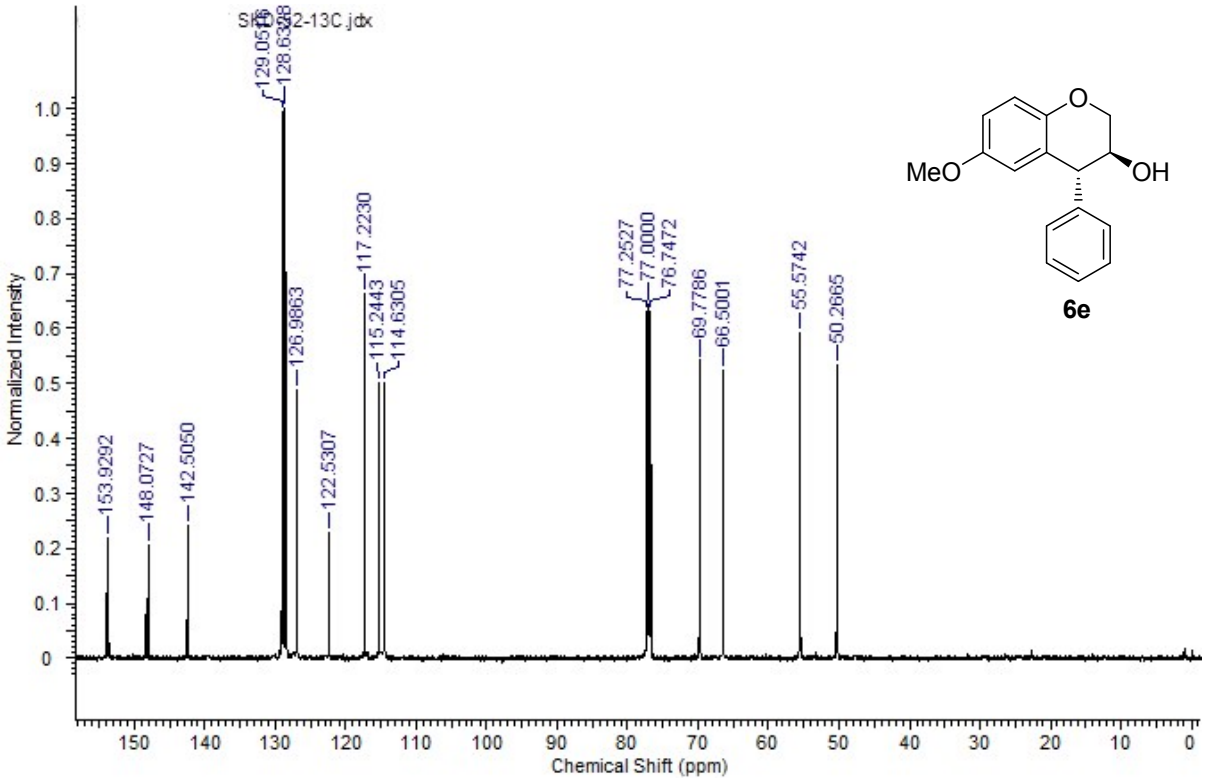
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6d**.



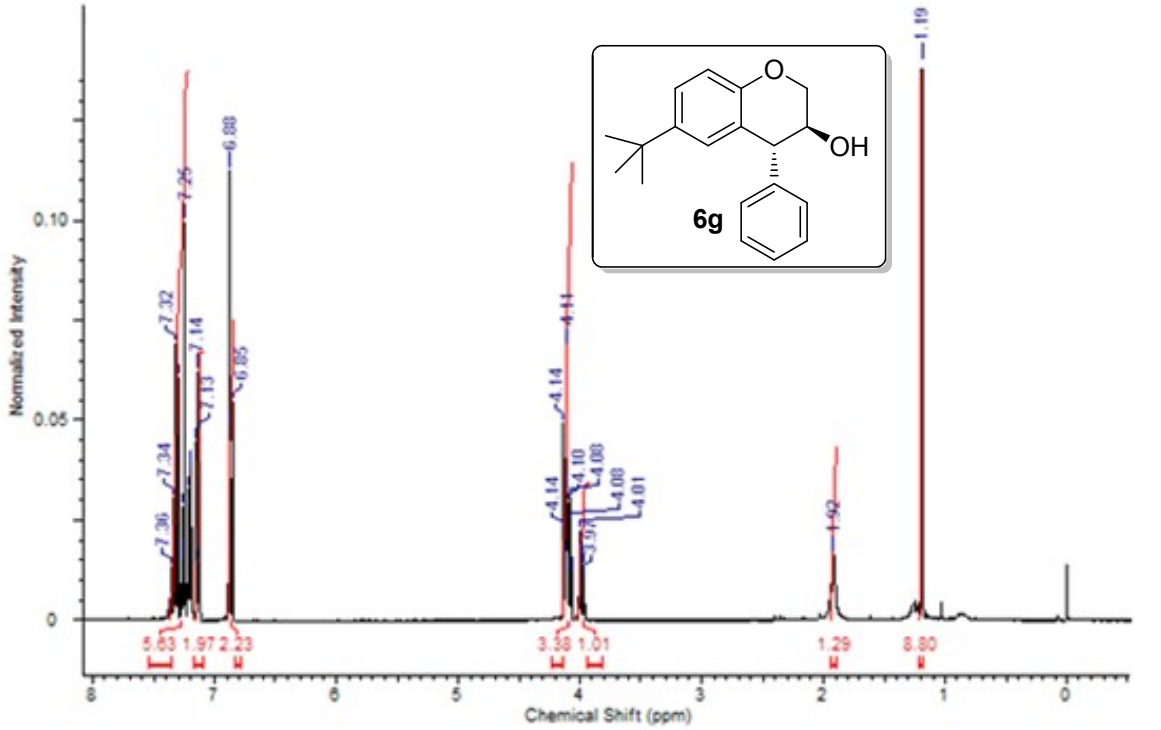
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6d**.



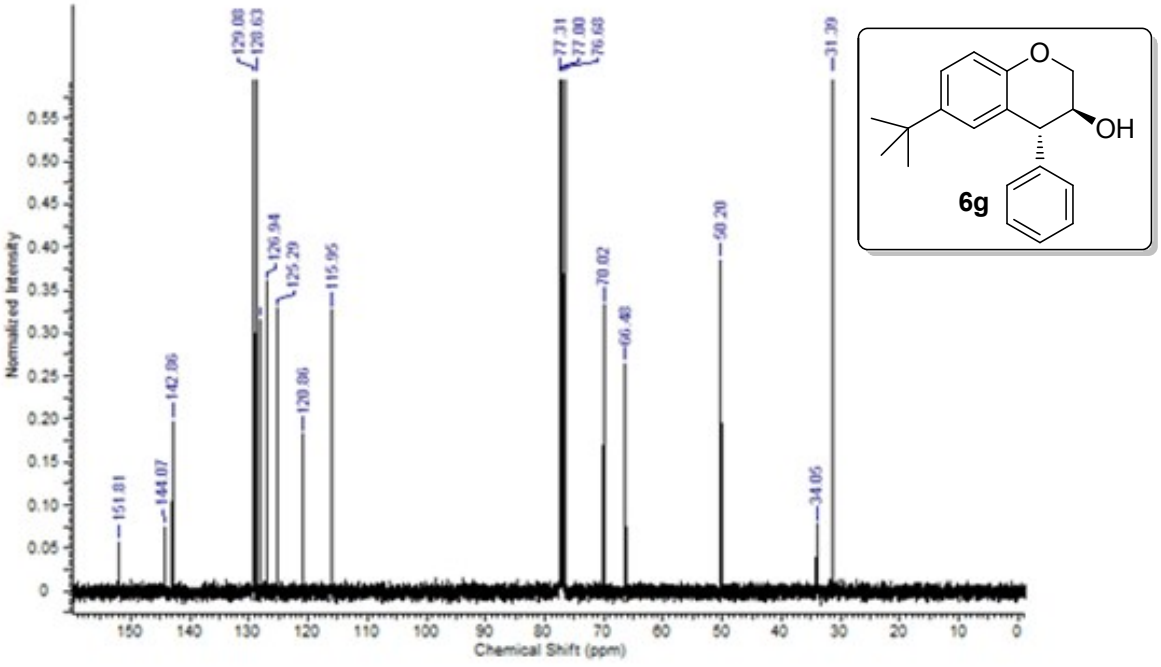
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6e**.



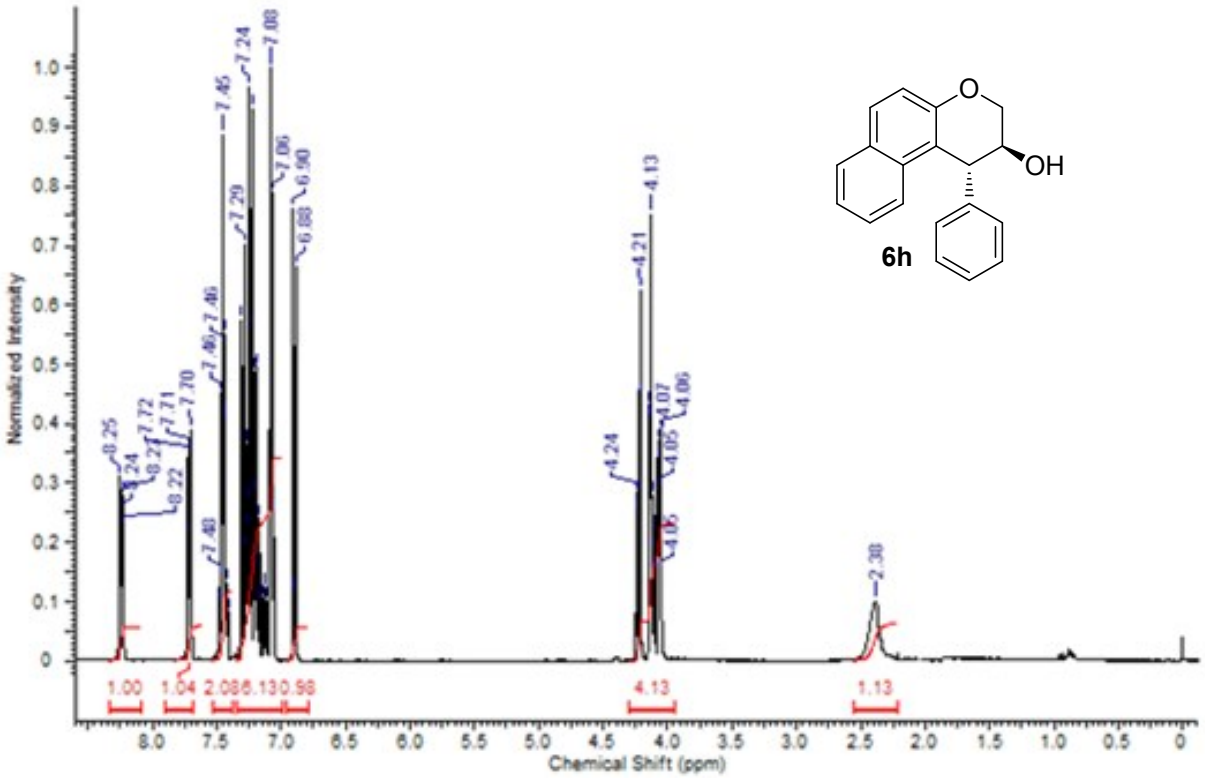
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6e**.



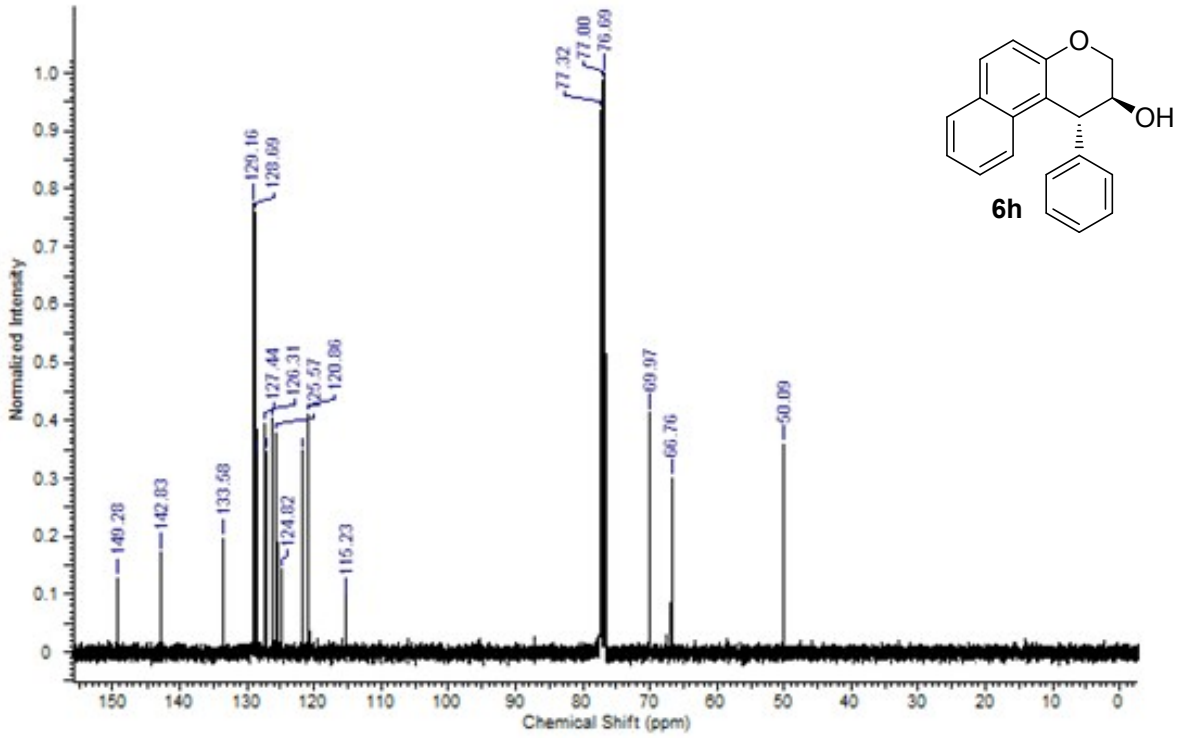
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6g**.



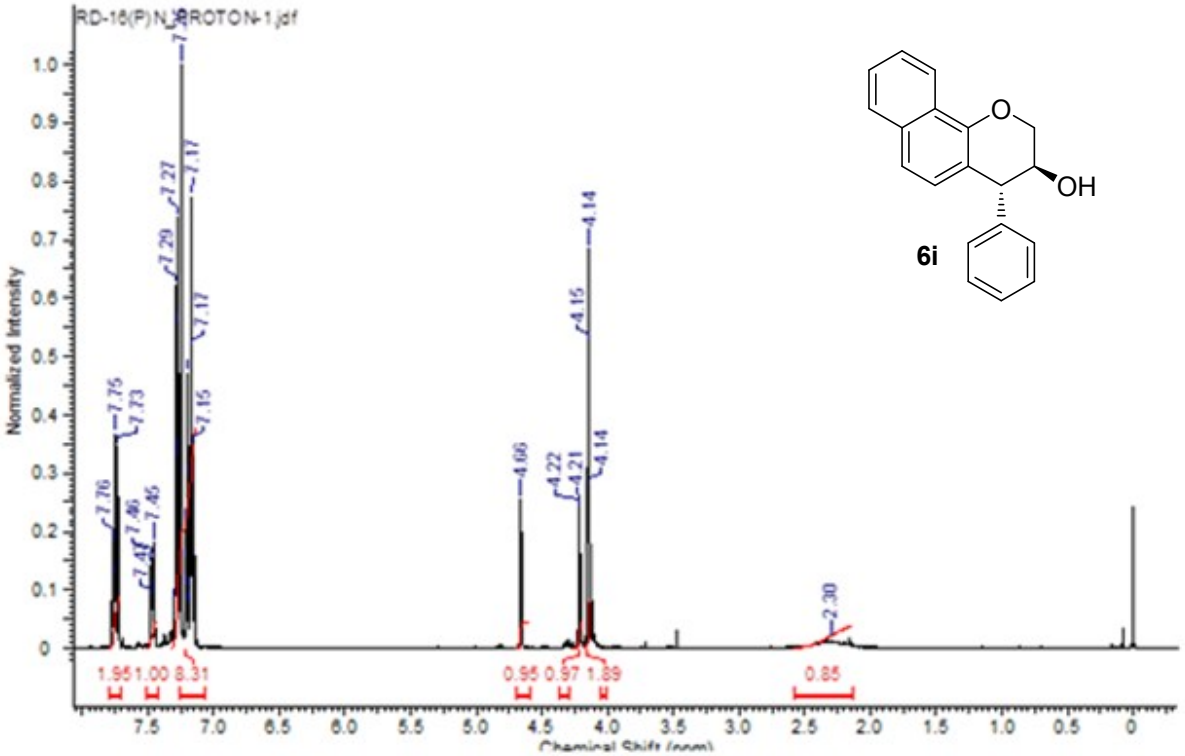
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6g**.



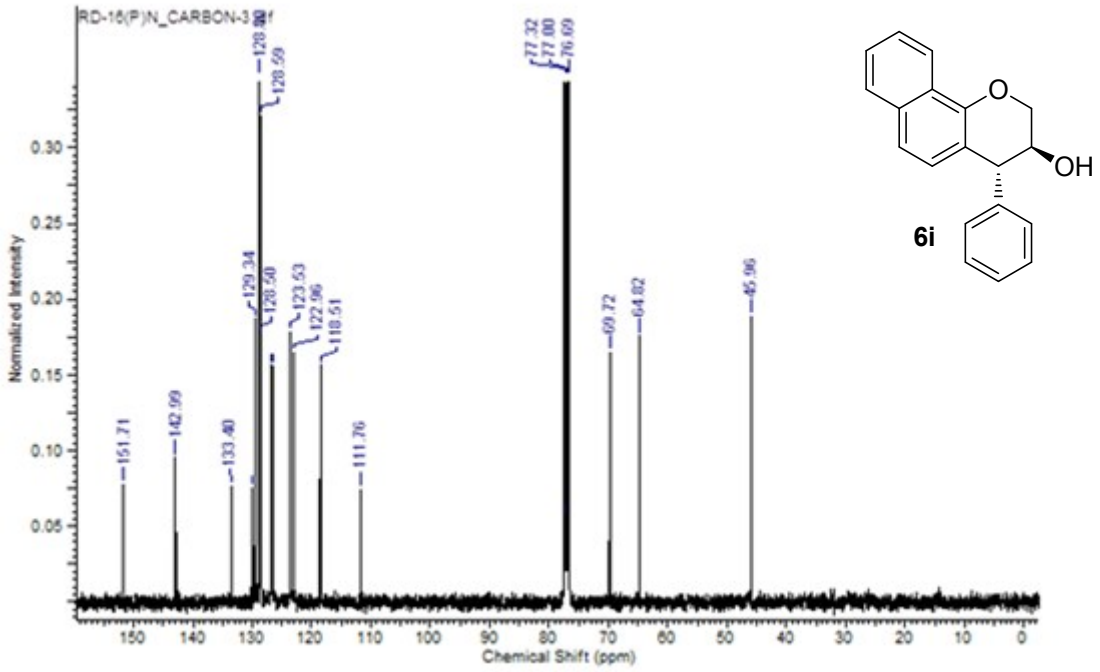
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6h**.



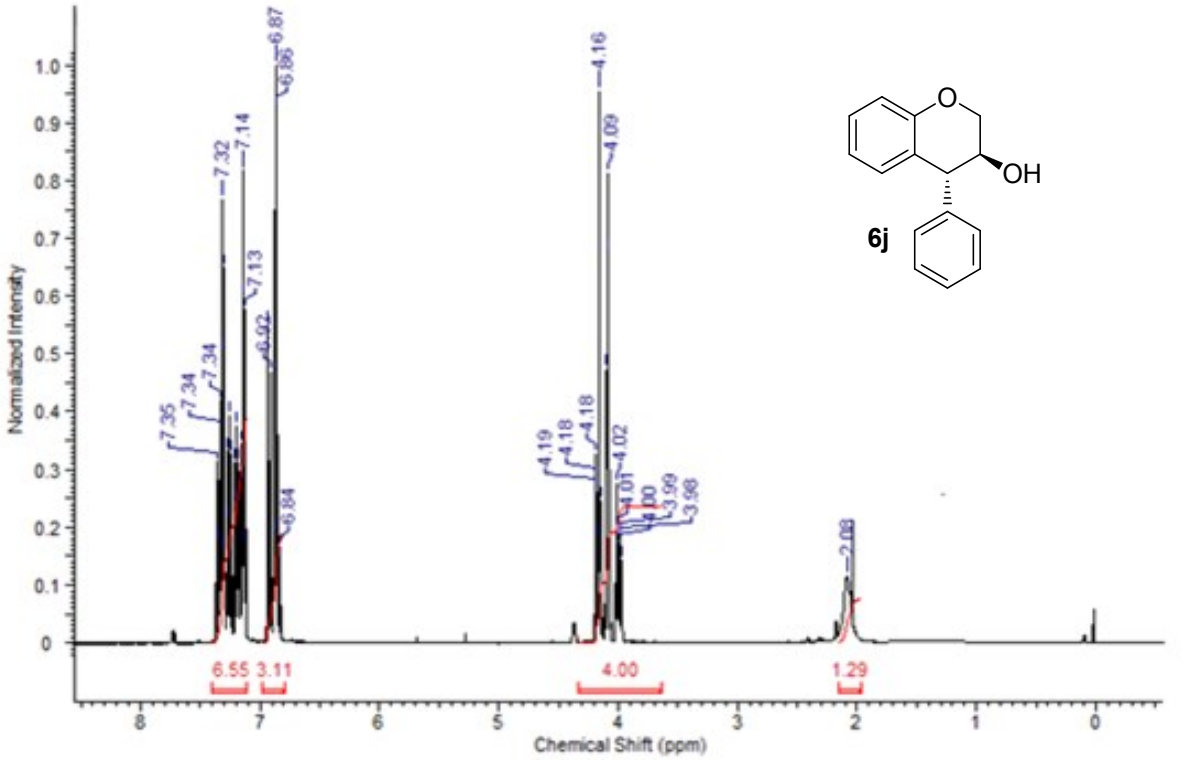
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6h**.



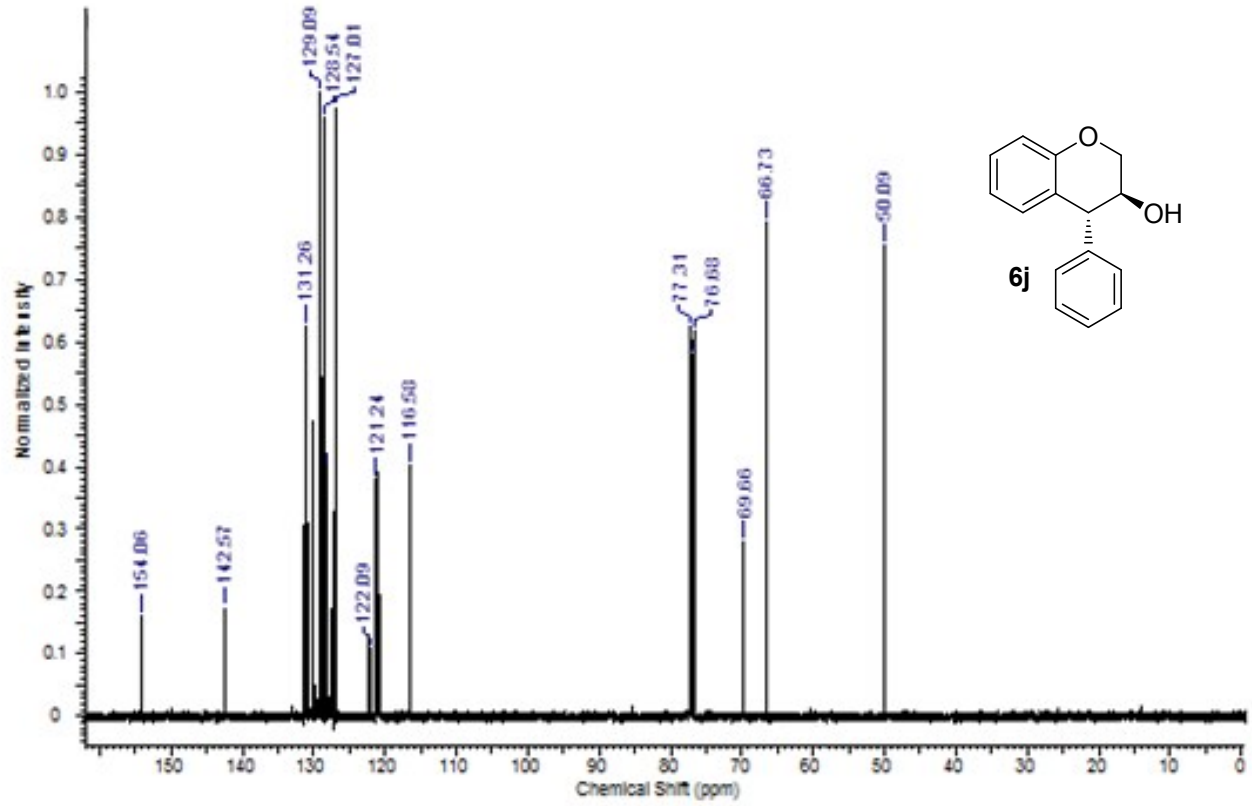
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6i**.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6i**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6j**



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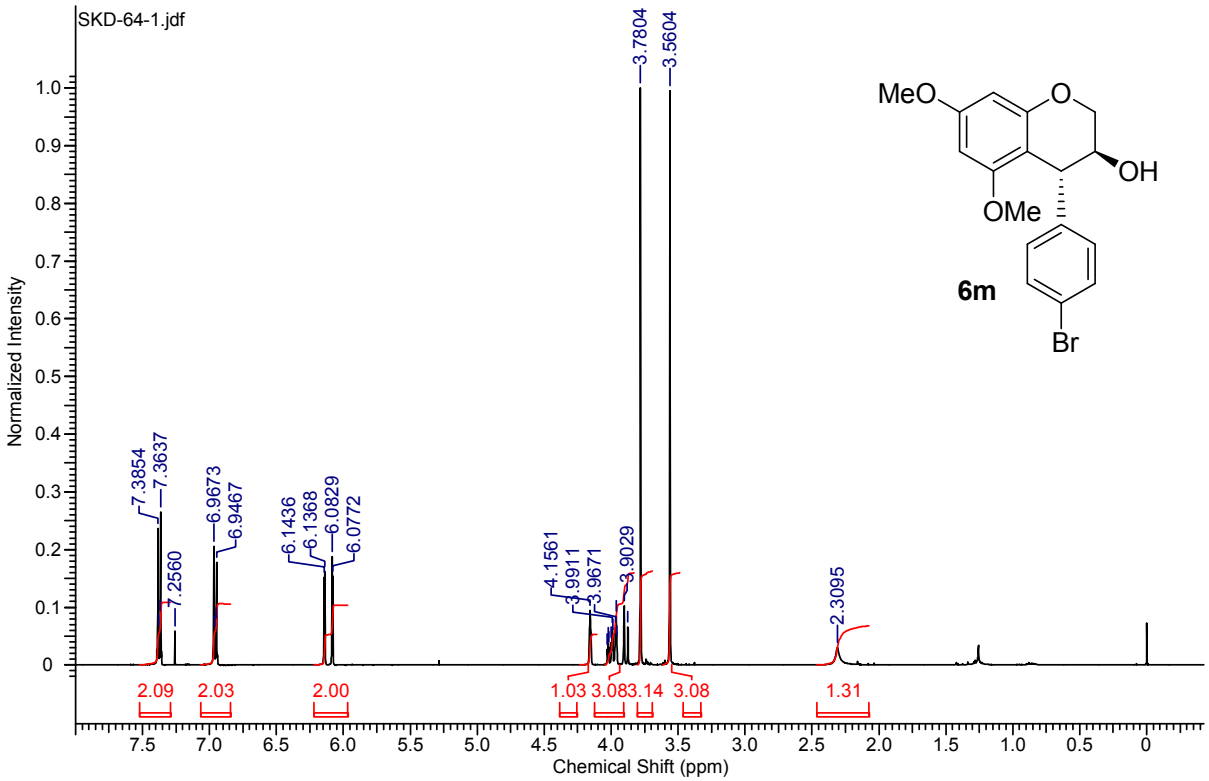
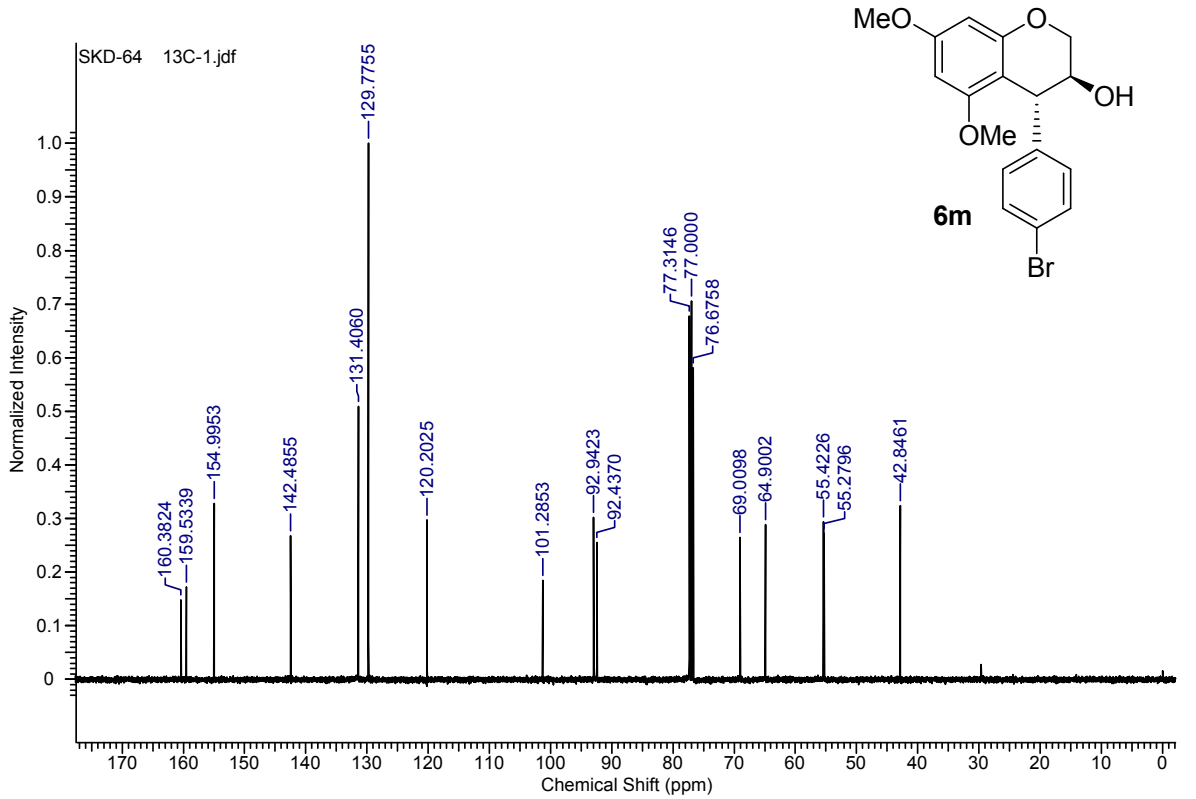
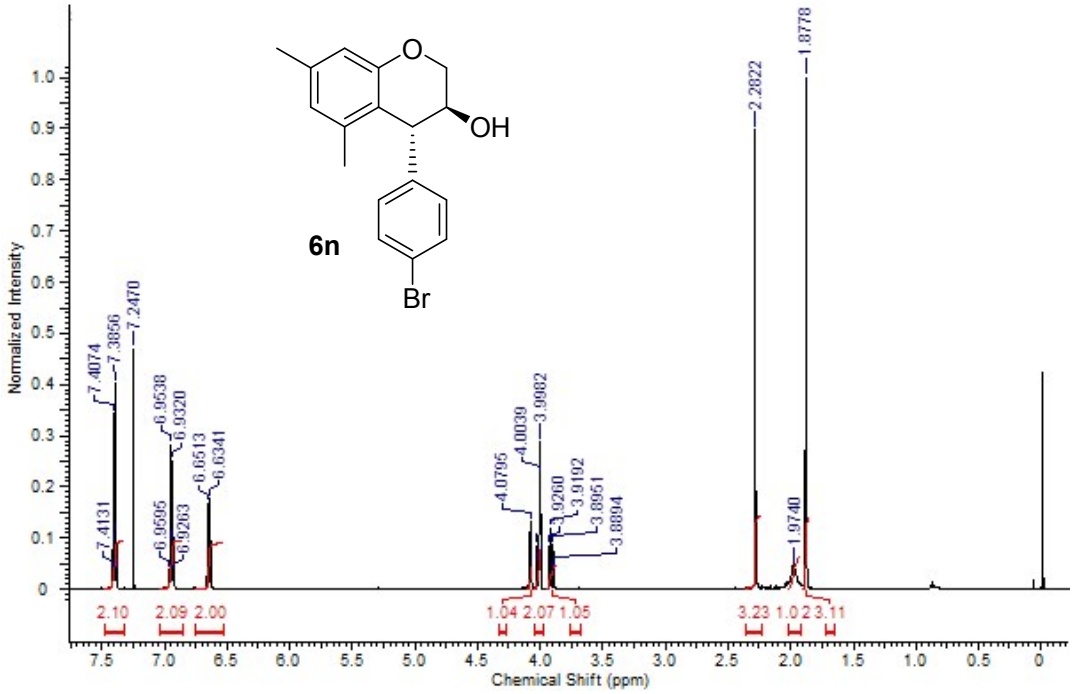


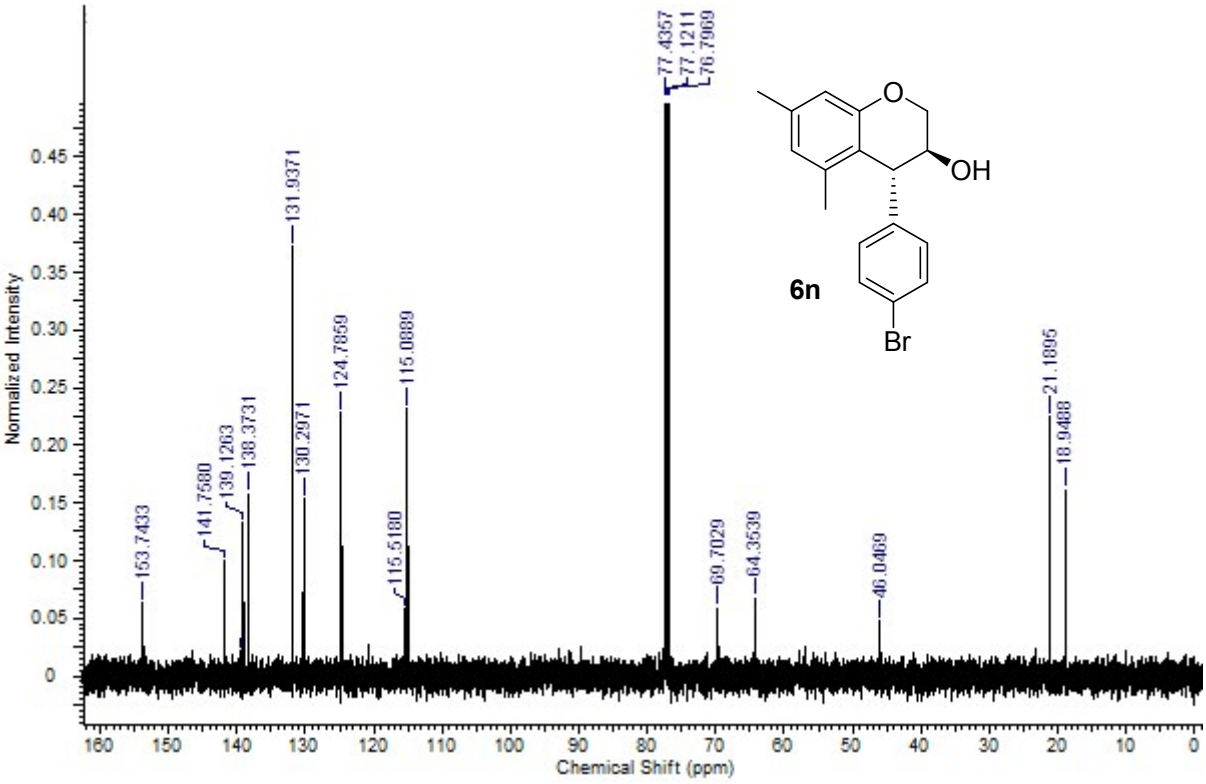
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6m**.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6m.**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6n**.



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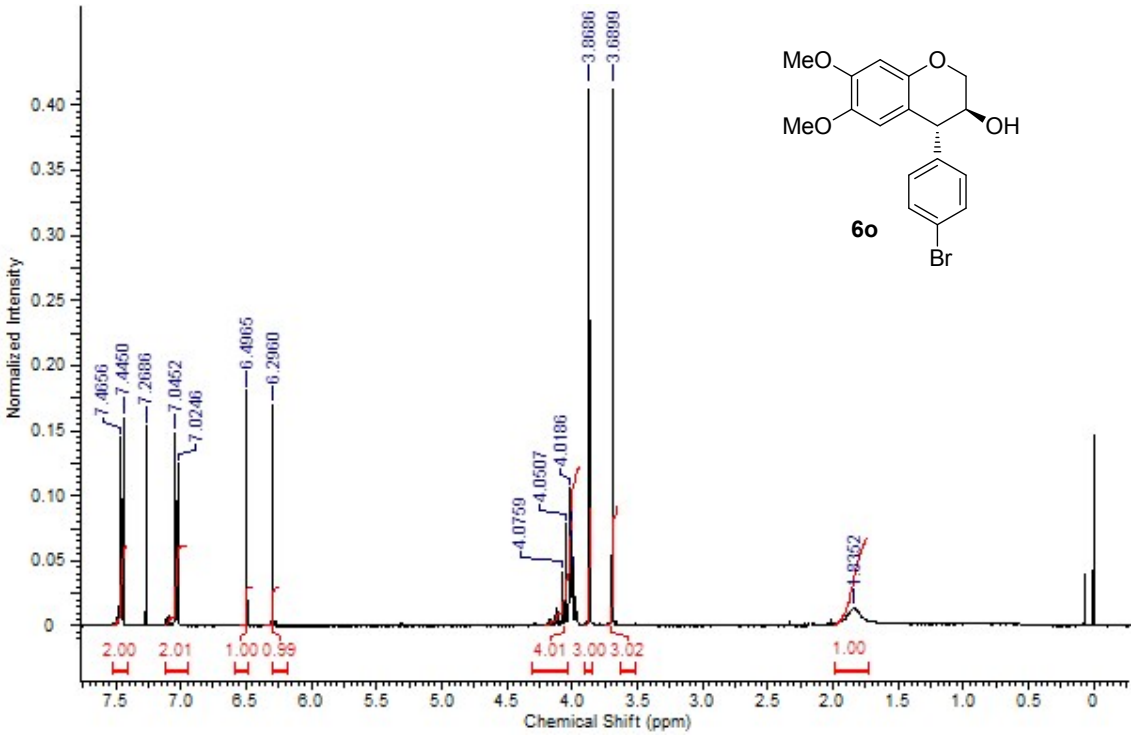
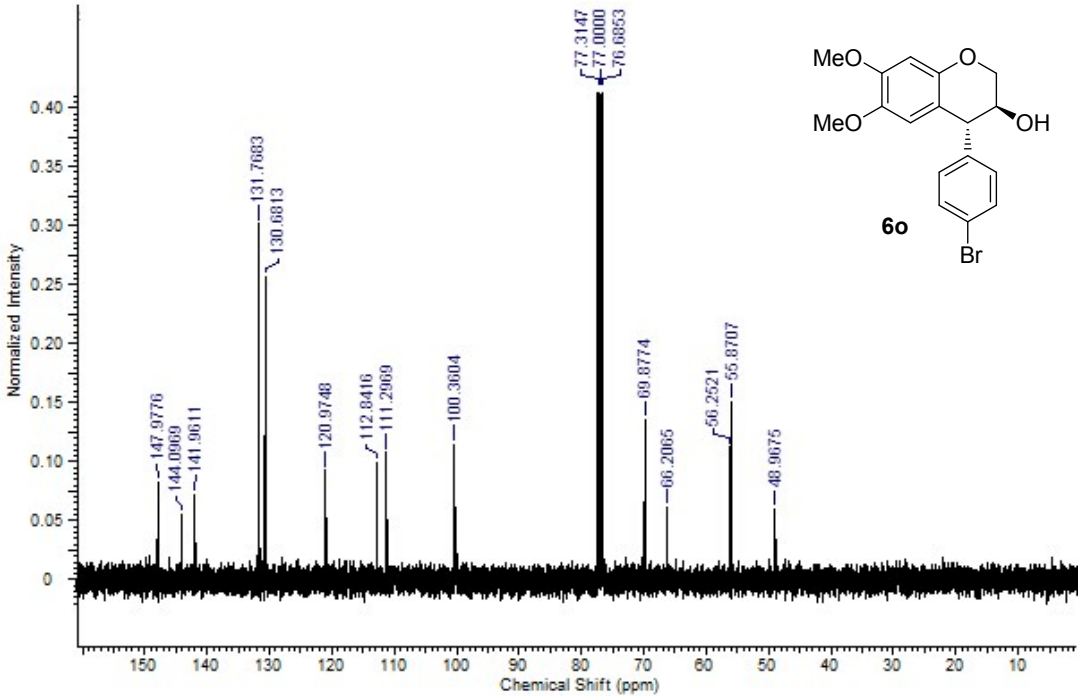
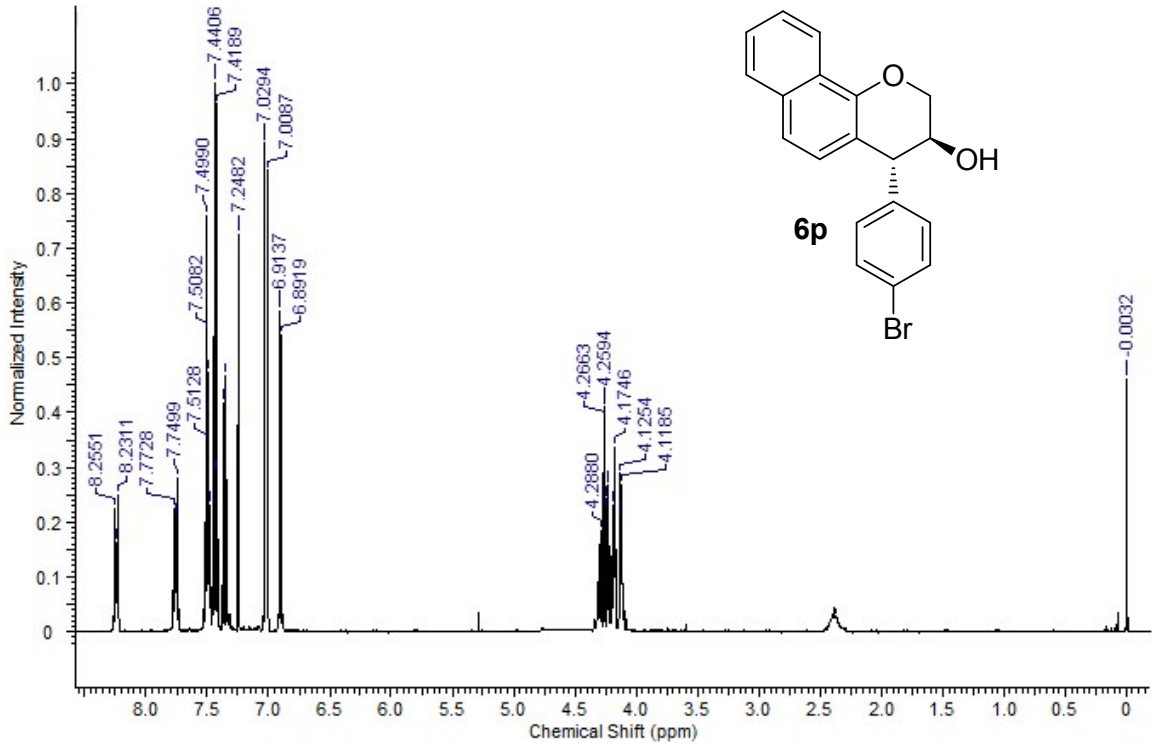


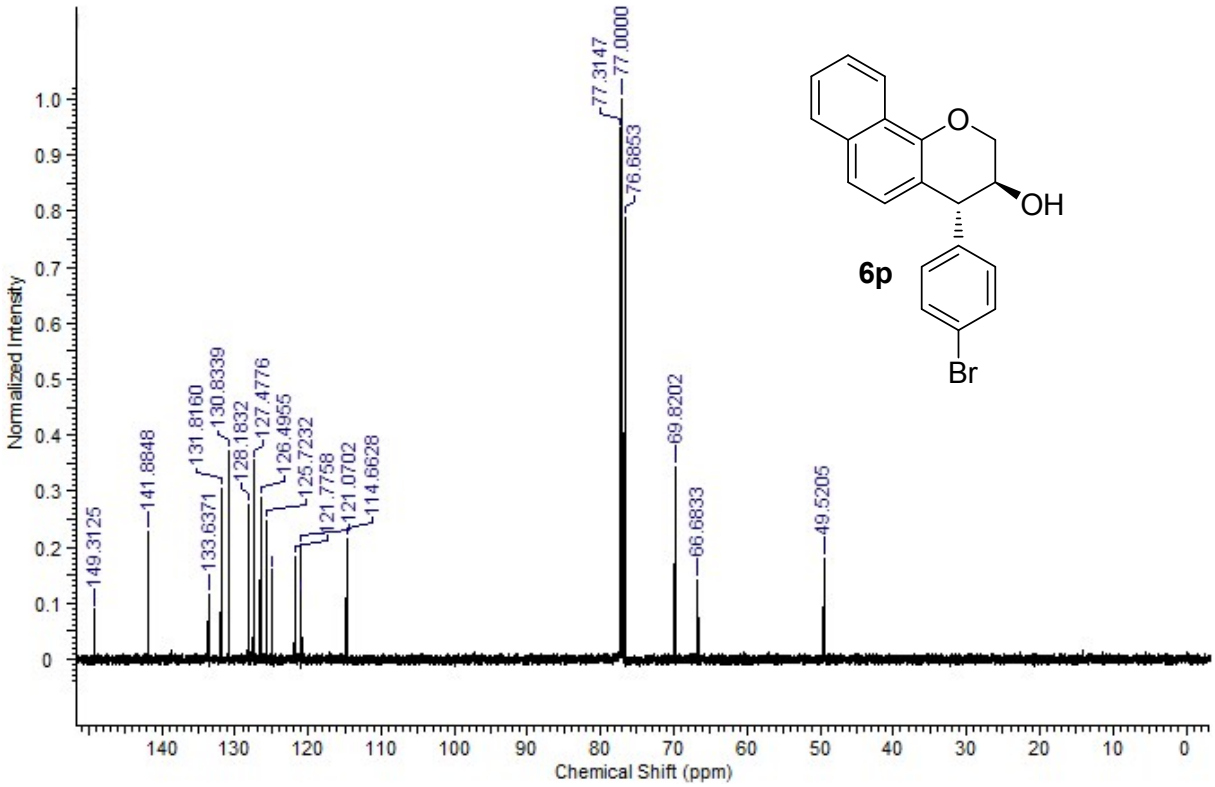
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6o**.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6o.**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6p**.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6p**.