SUPPORTING INFORMATION

Hetero Diels-Alder Reaction of Olefin with *o*-Quinone Methides Generated Using (±)-Binolphosphoric Acid for the Stereoselective Synthesis of 2,4 Diarylbenzopyrans: Application to the Formal Synthesis of Myristinin B/C

General experimental:

Melting points are recorded using Sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on JASCO FT-IR 4100 and Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). 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. ^{1}H-^{1}H NOESY spectrum was recorded in Bruker Avance 500 spectrometer. High resolution mass measurements were carried out using Micromass Q-ToF instrument using direct inlet mode. CHN analysis was carried out using Elemental analyzer VSM-VT. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain. Acme's silica gel (100-200 mesh) was used for column chromatography (approximately 15-20 g per 1 g of the crude product).

All small-scale dry reactions were carried out using standard syringe septum technique. Low temperature reactions were conducted in a bath made of acetone and liquid nitrogen. Dry THF and dry ether were obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane and dry DMF were prepared by distilling over calcium hydride. Dry pyridine and triethylamine were obtained by distillation over KOH and stored over KOH. NaH dispersion in oil was obtained from Aldrich. $BF_3{\cdot}OEt_2$ was obtained from E. Merck. Requisite styrene derivatives were either obtained commercially or were readily

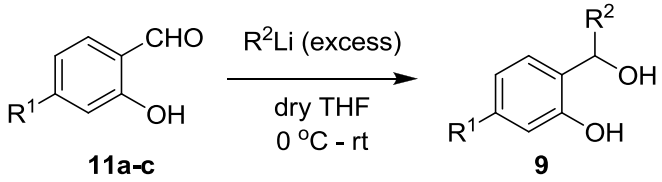
prepared from their respective aldehydes by Wittig olefination reaction. All the commercial reagents were used as such without further purification.

Note: *In the cases wherein diastereomeric mixtures of products were obtained, the data for the major isomer have been mentioned.*

General Procedure for the synthesis of alcohol 9:

To a cold (-78 ^{o}C), magnetically stirred solution of respective organic halides (2.2 equiv.) in dry THF was added *n*-BuLi (2.1 equiv.) and stirred for 20 min. The aldehyde **11** (1 equiv.) was added slowly; the resulting mixture was slowly warmed to rt and stirred for 2h. Upon completion (TLC control), the reaction was carefully quenched with saturated aq. NH_4Cl (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL); combined organic layer was washed with brine and dried (*anhyd*. Na_2SO_4). Evaporation of the solvent followed by purification of the residue on a silica gel column, doped with Et_3N, using ethyl acetate-hexanes as the eluent afforded their respective alcohols **9**.

Table 1 Synthesis of *o*-hydroxy benzylic alcohols 9



11a-c **9**

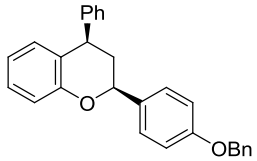
Entry	Aldehyde		Organolithium	Alcohol	Yield (%)
	Aldehyde	R^1	R^2		
1	**11a**	H	PhMgBr	**9a**	83
2	**11a**	H	4-(MeO)-C_6H_4-Li	**9b**	34
3	**11a**	H	2,4,6-$(MeO)_3$-C_6H_2-Li	**9c**	69
4	**11b**	-OMe	2,4,6-$(MeO)_3$-C_6H_2-Li	**9d**	75
5	**11b**	-OMe	3-I-2,4,6-$(MeO)_3$-C_6H-Li	**9e**	82
6	**11a**	H	*n*-BuLi	**9f**	82

Procedure for the synthesis of 2,4-diarylbenzopyran 8:

(±)-(2*S,4*R**)-2-(4-(benzyloxy)phenyl)-4-phenylchroman (8a):**

Using (±)-binolphosphoric acid:

To a magnetically stirred solution of the alcohol **9a** (30 mg, 0.15 mmol) and olefin **10a** (35 mg, 0.16 mmol) in CH_2Cl_2 (4 mL) was added (±)-binolphosphoric acid [(±)-BPA] (16 mg, 0.05 mmol). The reaction mixture was stirred at rt for 20h (TLC control) and quenched by adding saturated $NaHCO_3$. The reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL), washed with brine and dried (*anhyd*. Na_2SO_4). Evaporation of the solvent followed by purification of the residue on a silica gel column using ethyl acetate-hexanes (1:19) as eluent furnished the chroman **8a** (53 mg, 90%) as a white solid.



Physical Appearance: white solid

m.p.:124-126 ^oC

R_f: 0.5 (1:9, EtOAc:Hexanes)

IR (neat): 3027, 2919, 1611, 1580, 1515, 1485, 1467, 1454, 1384, 1346, 1300, 1272, 1218, 1177, 1115, 1078, 1042, 1012, 939, 916, 897, 862, 845, 834 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.20 (m, 9H), 7.20-7.10 (m, 4H), 7.10-7.00 (m, 1H), 6.95-6.90 (m, 2H), 6.90-6.85 (m, 1H), 6.75-6.65 (m, 2H), 5.09 (dd, *J* = 11.3, 1.8 Hz, 1H), 5.01 (s, 2H), 4.27 (dd, *J* = 12.0, 6.0, Hz, 1H), 2.31 (ddd, *J* = 13.6, 6.0, 2.0 Hz, 1H), 2.21 (ddd, *J* = 13.6, 12.0, 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 158.83 (C), 155.76 (C), 144.75 (C), 137.12 (C), 133.75 (C), 129.94 (CH), 128.80 (CH x 2), 128.73 (CH x 4), 128.11 (CH), 127.87 (CH), 127.67 (CH x 2), 127.59 (CH x 2), 126.90 (CH), 125.81 (C), 120.66 (CH), 117.13 (CH), 115.09 (CH x 2), 77.94 (CH), 70.21 (CH_2), 43.70 (CH), 40.56 (CH_2).

HRMS (ESI, M+Na): m/z calcd. for $C_{28}H_{24}O_2Na$ 415.1674, found 415.1650.

Elemental analysis: Calcd. for $C_{28}H_{24}O_2$ C 85.68%, H 6.16%, O 8.15%, found C 85.30%, H 6.59%, O 7.95%.

By Thermolysis:

Reaction of the alcohol **9a** (168 mg, 0.84 mmol) and olefin **10a** (952 mg, 4.52 mmol) in toluene (1 mL) at 110 ^oC in a sealed tube for 24h (TLC control) followed by purification of the residue on a silica gel column using ethyl acetate-hexanes (1:49 to 1:19) as the eluent furnished the requisite chroman **8a** (32 mg, 53%) as a white solid.

Using $BF_3{\cdot}OEt_2$:

Reaction of alcohol **9a** (30 mg, 0.15 mmol), olefin **10a** (35 mg, 0.16 mmol) and $BF_3{\cdot}OEt_2$ (5 μL, 0.04 mmol) in CH_2Cl_2 (2 mL) at rt for 1h (TLC control), as described for the chroman **8a** using (±)-BPA, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8a** (35 mg, 59%) as a white solid.

Using $Bi(OTf)_3$:

Reaction of alcohol **9a** (30 mg, 0.15 mmol), olefin **10a** (35 mg, 0.16 mmol) and $Bi(OTf)_3$ (30 mg, 0.04 mmol) in CH_2Cl_2 (2 mL) at rt for 4h (TLC control), as described for the chroman **8a** using (±)-BPA, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8a** (51 mg, 86%) as a white solid.

Using *p*-TSA:

Reaction of alcohol **9a** (30.0 mg, 0.15 mmol), olefin **10a** (35.0 mg, 0.16 mmol) and *p*-TSA (9.0 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) at rt for 2.5 h (TLC control), as described for the chroman **8a** using (±)-BPA, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8a** (35.5 mg, 60%) as a white solid.

Using $HClO_4$:

Reaction of alcohol **9a** (30 mg, 0.15 mmol), olefin **10a** (36 mg, 0.16 mmol) and $HClO_4$ (10 μL, 0.05 mmol) in CH_2Cl_2 (2 mL) at rt for 3h (TLC control), as described for the chroman **8a** using (±)-BPA, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent did not furnish the requisite chroman **8a**.

Using TFA:

Reaction of alcohol **9a** (30 mg, 0.15 mmol), olefin **10a** (35 mg, 0.16 mmol) and TFA (5 μL, 0.05 mmol) in CH_2Cl_2 (2 mL) at rt for 4h (TLC control), as described for the chroman **8a** using (±)-BPA, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8a** (36 mg, 60%) as a white solid.

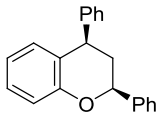
Using H_3PO_4:

Reaction of alcohol **9a** (30 mg, 0.15 mmol), olefin **10a** (36 mg, 0.16 mmol) and H_3PO_4 (10 μL, 0.05 mmol) in CH_2Cl_2 (2 mL) at rt for 3h (TLC control), as described for the chroman **8a** using (±)-BPA, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent did not furnish the requisite chroman **8a**.

(±)-(2*S,4*R**)-2,4-diphenylchroman (8b):**

Reaction of alcohol **9a** (100 mg, 0.50 mmol), styrene (**10b**) (1 mL, 8.73 mmol) and (±)-BPA (52 mg, 0.15 mmol) in CH_2Cl_2 (4 mL) at rt for 24h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:49) as the eluent furnished the requisite chroman **8b** (86 mg, 60%) as a white solid.

Physical Appearance: white solid



m.p.:116-118 ^oC

R_f: 0.6 (1:9, EtOAc:Hexanes)

IR (neat): 3061, 3030, 2952, 2923, 2853, 1605, 1582, 1487, 1453, 1309, 1272, 1235, 1113, 1066, 1025, 918, 902, 754, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.40 (m, 2H), 7.35-7.20 (m, 5H), 7.20-7.10 (m, 3H), 71.0-7.00 (m, 1H), 6.90-6.85 (m, 1H), 6.75-6.65 (m, 2H), 5.14 (dd, *J* = 11.6, 2.0 Hz, 1H), 4.29 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.34 (ddd, *J* = 13.6, 7.6, 2.0 Hz, 1H), 2.25-2.10 (m, 1H).

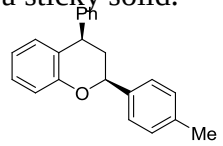
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 155.65 (C), 144.65 (C), 141.35 (C), 129.93 (CH), 128.80 (CH x 2), 128.71 (CH x 3), 128.60 (CH), 128.91 (CH), 127.91 (CH), 126.92 (CH), 126.22 (CH x 2), 125.84 (C), 120.72 (CH), 117.14 (CH), 78.24 (CH), 43.65 (CH), 40.78 (CH_2).

HRMS (ESI, M+Na): m/z calcd. for $C_{21}H_{18}ONa$ 309.1255, found 309.1251.

(±)-(2*S,4*R**)-4-phenyl-2-p-tolylchroman (8c):**

Reaction of alcohol **9a** (50 mg, 0.25 mmol), olefin **10c** (32 mg, 0.27 mmol) and (±)-BPA (26 mg, 0.08 mmol) in CH_2Cl_2 (2 mL) at rt for 22h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8c** (46 mg, 61%) as a sticky solid.

Physical Appearance: sticky solid



R_f: 0.4 (1:49, EtOAc:Hexanes)

IR (neat): 3057, 3032, 2924, 2867, 1581, 1487, 1452, 1266, 1232, 1111, 1071, 1017, 909, 810, 749 cm^{-1}.

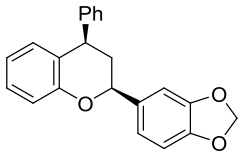
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.00 (m, 9H), 6.95-6.75 (m, 2H), 6.75-6.65 (m, 2H), 5.10 (d, *J* = 11.2 Hz, 1H), 4.27 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.45-2.10 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 155.73 (C), 144.72 (C), 138.33 (C), 137.93 (C), 130.90 (C), 129.91 (CH), 129.36 (CH x 2), 128.78 (CH x 2), 128.72 (CH x 2), 127.85 (CH), 126.88 (CH), 126.24 (CH x 2), 120.62 (CH), 117.13 (CH), 78.14 (CH), 43.67 (CH), 40.58 (CH_2), 21.37 (CH_3).

HRMS (ESI, M+H): m/z calcd. for $C_{22}H_{21}O$ 301.1592, found 301.1594.

(±)-(2*S,4*R**)-2-(benzo[*d*][1,3]dioxol-5-yl)-4-phenylchroman (8d):**

Reaction of alcohol **9a** (100 mg, 0.50 mmol), olefin **10d** (81 mg, 0.55 mmol) and (±)-BPA (52 mg, 0.15 mmol) in CH_2Cl_2 (4 mL) at rt for 22h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8d** (134 mg, 79%) as a white solid.



Physical Appearance: white solid

m.p.:138-140 °C

R_f: 0.5 (1:9, EtOAc:Hexanes)

IR (neat): 3061, 3027, 2953, 2922, 2887, 2876, 2777, 1606, 1580, 1504, 1487, 1444, 1391, 1331, 1314, 1294, 1273, 1246, 1234, 1201, 1112, 1100, 1067, 1038, 1014, 934, 916, 883, 862, 822, 808, 795, 758, 751, 742, 717, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.20 (m, 4H), 7.14 (td, *J* = 8.4, 2.0 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.85-6.70 (m, 3H), 5.97 (s, 2H), 5.13 (dd, *J* = 11.2, 2.0 Hz, 1H), 4.34 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.37 (ddd, *J* = 13.6, 6.0, 2.0 Hz, 1H), 2.35-2.20 (m, 1H).

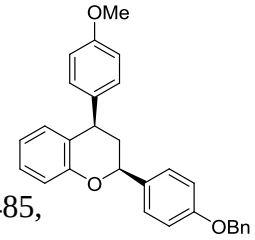
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 155.58 (C), 148.00 (C), 147.51 (C), 144.61 (C), 135.24 (C), 129.92 (CH), 128.80 (CH x 2), 128.71 (CH x 2), 127.90 (CH), 126.92 (CH), 125.74 (C), 120.73 (CH), 119.91 (CH), 117.09 (CH), 108.37 (CH), 106.94 (CH), 101.24 (CH_2), 78.11 (CH), 43.60 (CH), 40.66 (CH_2).

HRMS (ESI, M+Na): m/z calcd. for $C_{22}H_{18}O_3Na$ 353.1154, found 353.1148.

Elemental analysis: Calcd. for $C_{22}H_{18}O_3$ C 79.98%, H 5.49%, O 14.53%, found C 80.25%, H 5.35%, O 14.28%.

(±)-(2*S,4*R**)-2-(4-(benzyloxy)phenyl)-4-(4-methoxyphenyl)chroman (8e):**

Reaction of alcohol **9b** (26 mg, 0.11 mmol), olefin **10a** (26 mg, 0.12 mmol) and (±)-BPA (12 mg, 0.03 mmol) in CH_2Cl_2 (4 mL) at rt for 23h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8e** (45 mg, 94%) as a white solid.



Physical Appearance: white solid

m.p.:126-128 ^oC

R_f: 0.3 (1:9, EtOAc:Hexanes)

IR (neat): 3062, 3033, 2951, 2922, 2867, 2838, 1610, 1582, 1512, 1485, 1455, 1379, 1338, 1303, 1249, 1175, 1112, 1070, 1034, 1013, 937, 907, 830, 757, 738 cm^{-1}.

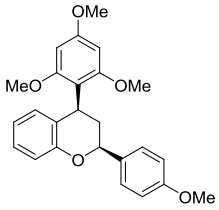
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.35 (m, 6H), 7.35-7.30 (m, 1H), 7.16 (d, *J* = 6.8 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 2H), 7.00-6.90 (m, 2H), 6.88 (d, *J* = 6.4 Hz, 2H), 6.85-6.75 (m, 2H), 5.20-5.15 (m, 1H), 5.10 (s, 2H), 4.31 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.82 (s, 3H), 2.37 (ddd, *J* = 10.8, 4.8, 1.6 Hz, 1H), 2.35-2.20 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 158.76 (C), 158.52 (C), 155.68 (C), 137.09 (C), 136.70 (C), 133.79 (C), 129.86 (CH), 129.62 (CH x 2), 128.72 (CH x 2), 128.09 (CH), 127.64 (CH x 2), 127.57 (CH x 3), 126.16 (C), 120.59 (CH), 117.05 (CH), 115.05 (CH x 2), 114.16 (CH x 2), 77.99 (CH), 70.18 (CH_2), 55.39 (CH_3), 42.83 (CH), 40.58 (CH_2).

HRMS (ESI, M+Na): m/z calcd. for $C_{29}H_{26}O_3Na$ 445.1780, found 445.1780.

(±)-(2*S,4*S**)-2-(4-methoxyphenyl)-4-(2,4,6-trimethoxyphenyl)chroman (8f):**

Reaction of alcohol **9c** (44 mg, 0.15 mmol), olefin **10e** (40 mg, 0.30 mmol) and (±)-BPA (18 mg, 0.05 mmol) in CH_2Cl_2 (4 mL) at rt for 24h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8f** (55 mg, 90%) as a white solid.



Physical Appearance: white solid

m.p.: 140-142 ^oC

R_f: 0.3 (1:9, EtOAc:Hexanes)

IR (neat): 2924, 2848, 1597, 1501, 1455, 1233, 1116, 1036, 819, 756 cm^{-1}.

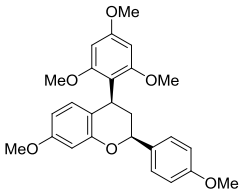
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.6, 2H), 7.05-7.00 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 4.2 Hz, 1H), 6.71 (d, *J* = 4.2 Hz, 2H), 6.21 (d, *J* = 2.2 Hz, 1H), 6.10 (d, *J* = 2.2 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.93 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 6H), 3.44 (s, 3H), 2.68 (q, *J* = 12.0 Hz, 1H), 2.06 (ddd, *J* = 12.0, 6.0, 1.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 160.08 (C), 159.89 (C), 159.40 (C x 2), 155.46 (C), 134.25 (C), 127.75 (CH x 2), 127.56 (CH), 127.48 (C), 126.36 (CH), 120.20 (CH), 116.53 (CH), 113.97 (CH x 2), 112.96 (C), 92.46 (CH), 90.34 (CH), 78.63 (CH), 56.27 (CH_3), 55.98 (CH_3), 55.71 (CH_3), 55.43 (CH_3), 34.94 (CH_2), 32.25 (CH).

HRMS (ESI, M+Na): m/z calcd. for $C_{25}H_{26}O_5Na$ 429.1678, found 429.1670.

(±)-(2*S,4*S**)-7-methoxy-2-(4-methoxyphenyl)-4-(2,4,6-trimethoxyphenyl)chroman (8g):**

Reaction of alcohol **9d** (430 mg, 1.34 mmol), olefin **10e** (200 mg, 1.49 mmol) and (±)-BPA (140 mg, 0.40 mmol) in CH_2Cl_2 (4 mL) at rt for 22h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8g** (486 mg, 83%) as a white solid.



Physical Appearance: white solid

m.p.: 72-74 °C

R_f: 0.3 (1:9, EtOAc:Hexanes)

IR (neat): 2942, 1597, 1504, 1456, 1314, 1250, 1207, 1155, 1115, 1037, 953, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 2.6 Hz, 1H), 6.35 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.23, (d, *J* = 2.1 Hz, 1H), 6.13 (d, *J* = 2.1 Hz, 1H), 5.14 (d, *J* = Hz, 1H), 4.90 (dd, *J* = 11.8, 5.8 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 6H), 3.76 (s, 3H), 3.49 (s, 2H), 2.71 (q, *J* = 11.9 Hz, 1H), 2.07 (ddd, *J* = 13.4, 5.8, 1.6 Hz, 1H).

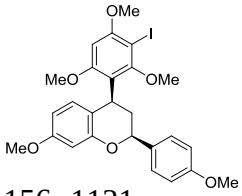
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 159.94 (C), 159.90 (C), 159.36 (C), 159.29 (C), 158.32 (C), 156.02 (C), 134.06 (C), 128.06 (CH), 127.77 (CH x 2), 119.58 (C), 113.93 (CH x 2), 112.79 (C), 107.16 (CH), 101.20 (CH), 92.30 (CH), 90.69 (CH), 78.95 (CH),

56.21 (CH_3), 55.78 (CH_3), 55.43 (CH_3), 55.39 (CH_3), 55.35 (CH_3), 34.81 (CH_2), 31.60 (CH).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{26}H_{29}O_6$ 437.1964, found 437.1957.

(±)-(2*S,4*S**)-4-(3-iodo-2,4,6-trimethoxyphenyl)-7-methoxy-2-(4-methoxyphenyl)chroman (8h):**

Reaction of alcohol **9e** (966 mg, 2.16 mmol), olefin **10e** (580 mg, 4.32 mmol) and (±)-BPA (376 mg, 1.08 mmol) in CH_2Cl_2 (15 mL) at rt for 2 h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:49 to 1:19) as the eluent furnished the requisite chroman **8h** (810 mg, 67%) as a sticky solid.



Physical Appearance: sticky solid

R_f: 0.3 (1:9, EtOAc:Hexanes)

IR (neat): 2933, 2845, 1614, 1584, 1504, 1458, 1388, 1249, 1201, 1156, 1121, 1105, 1036, 956, 917, 833, 813, 739 cm^{-1}.

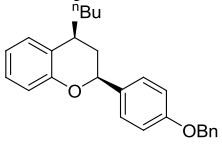
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.62 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.34 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.27 (s, 1H), 5.14 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.78 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 3.75 (s, 3H), 3.51 (s, 3H), 2.69 (q, *J* = 12.0 Hz, 1H), 2.08 (ddd, *J* = 13.2, 6.0, 2.0 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 160.58 (C), 159.81 (C), 159.52 (C), 158.68 (C), 156.05 (C), 133.74 (C), 129.30 (C), 127.83 (CH), 127.70 (CH x 2), 119.46 (C), 118.84 (C), 114.04 (CH x 2), 107.33 (CH), 101.48 (CH), 94.20 (CH), 78.67 (CH), 73.40 (C), 62.16 (CH_3), 56.63 (CH_3), 56.05 (CH_3), 55.46 (CH_3), 55.37 (CH_3), 35.33 (CH_2), 34.35 (CH).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{26}H_{28}O_6I$ 563.0931, found 563.0938.

(±)-(2*S,4*S**)-2-(4-(benzyloxy)phenyl)-4-butylchroman (8i):**

Reaction of alcohol **9f** (50 mg, 0.28 mmol), olefin **10a** (58 mg, 0.28 mmol) and (±)-BPA (29 mg, 0.08 mmol) in CH_2Cl_2 (4 mL) at rt for 22h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **8i** (76 mg, 74%) as a sticky solid.



Physical Appearance: sticky solid

R_f: 0.5 (1:9, EtOAc:Hexanes)

IR (neat): 3034, 2927, 2863, 1610, 1515, 1458, 1377, 1301, 1232, 1172, 1116, 1017, 902, 826, 748 cm^{-1}.

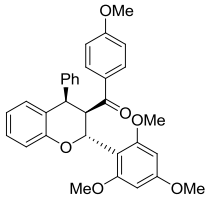
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.25 (m, 8H), 7.20-7.10 (m, 1H), 7.10-7.00 (m, 2H), 7.00-6.85 (m, 2H), 5.10 (s, 2H), 4.98 (dd, *J* = 11.6, 1.6 Hz, 1H), 3.15-3.05 (m, 1H), 2.26 (ddd, *J* = 13.6, 6.0, 2.0 Hz, 1H), 2.15-2.00 (m, 2H), 1.81 (q, *J* = 11.6 Hz, 1H), 1.55-1.25 (m, 4H), 1.00-0.90 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 158.68 (C), 155.51 (C), 137.11 (C), 134.43 (C), 128.73 (CH x 2), 128.10 (CH), 127.65 (CH x 2), 127.61 (CH x 2), 127.32 (CH), 127.26 (CH), 126.38 (C), 120.64 (CH), 117.23 (CH), 115.02 (CH x 2), 77.83 (CH), 70.17 (CH_2), 36.89 (CH_2), 34.87 (CH), 34.49 (CH_2), 28.64 (CH_2), 23.09 (CH_2), 14.23 (CH_3).

HRMS (ESI, M+Na): m/z calcd. for $C_{26}H_{28}O_2Na$ 395.1987, found 395.1985.

(±)-(4-methoxyphenyl)((2*R,3*R**,4*R**)-4-phenyl-2-(2,4,6-trimethoxyphenyl)chroman-3-yl)methanone (8j):**

Reaction of alcohol **9a** (150 mg, 0.75 mmol), enone **10f** (250 mg, 0.75 mmol) and (±)-BPA (79 mg, 0.22 mmol) in CH_2Cl_2 (4 mL) at rt for 10h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:4) as the eluent furnished the requisite chroman **8j** (345 mg, 90%) as a yellow solid.



Physical Appearance: yellow solid

m.p.:198-200 ^oC

R_f: 0.3 (1:4, EtOAc:Hexanes)

IR (neat): 3060, 3008, 2964, 2939, 2840, 1674, 1600, 1484, 1456, 1421, 1366, 1313, 1262, 1231, 1207, 1169, 1155, 1124, 1034, 842, 815, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.20-7.05 (m, 5H), 7.00-6.95 (m, 3H), 6.85-6.80 (m, 3H), 6.13 (d, *J* = 10.8 Hz, 1H), 6.04 (s, 2H), 5.40 (dd, *J* = 10.8, 5.2 Hz, 1H), 4.60 (d, *J* = 5.2 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 6H), 3.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 197.14 (C), 163.37 (C), 161.30 (C), 160.35 (C x 2), 155.95 (C), 141.77 (C), 130.80 (C), 130.50 (CH x 2), 129.89 (CH x 2), 129.19 (CH), 128.58 (CH), 127.86 (CH x 2), 126.84 (CH), 124.26 (C), 120.18 (CH), 117.35 (CH),

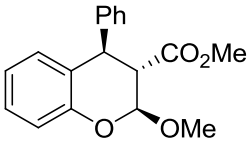
114.03 (CH), 108.02 (C), 91.62 (CH x 2), 67.51 (CH), 56.21 (CH_3), 55.60 (CH_3), 55.29 (CH_3 x 2), 47.81 (CH), 46.32 (CH).

HRMS (ESI, M+Na): m/z calcd. for $C_{32}H_{30}O_6Na$ 533.1940, found 533.1942.

Elemental analysis: Calcd. for $C_{32}H_{30}O_6$ C 75.28%, H 5.92%, O 18.80%, found C 75.08%, H 5.84%, O 18.7%.

(±)-(2*S,3*S**,4*R**)-methyl 2-methoxy-4-phenylchroman-3-carboxylate (8k):**

Reaction of alcohol **9a** (40 mg, 0.20 mmol), acrylate **10g** (25 μL, 0.23 mmol) and (±)-BPA (21 mg, 0.06 mmol) in CH_2Cl_2 (2 mL) at rt for 12h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite acetal **8k** (43 mg, 74%) as a viscous liquid.



Physical Appearance: viscous liquid

R_f: 0.5 (1:9, EtOAc:Hexanes)

IR (neat): 3023, 2949, 2846, 1736, 1590, 1488, 1447, 1365, 1216, 1003, 930, 761, cm^{-1}.

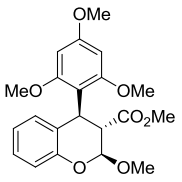
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.25 (m, 4H), 7.25-7.15 (m, 2H), 7.05-6.95 (m, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 5.24 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 3.66 (s, 3H), 3.57 (s, 3H), 3.11 (dd, *J* = 10.8, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.09 (C), 152.71 (C), 141.26 (C), 129.44 (CH), 129.00 (CH x 2), 128.82 (CH x 2), 128.26 (CH), 127.50 (CH), 124.66 (C), 121.51 (CH), 117.09 (CH), 101.25 (CH), 56.94 (CH_3), 53.13 (CH_3), 52.12 (CH), 45.81 (CH).

HRMS (ESI, M+Na): m/z calcd. for $C_{18}H_{18}O_4Na$ 321.1103, found 321.1097.

(±)-(2*S,3*S**,4*S**)-methyl 2-methoxy-4-(2,4,6-trimethoxyphenyl)chroman-3-carboxylate (8l)**

Reaction of alcohol **9c** (250 mg, 0.86 mmol), acrylate **10g** (100 μL, 0.95 mmol) and (±)-BPA (91 mg, 0.26 mmol) in CH_2Cl_2 (5 mL) at rt for 3.5h (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite acetal **8l** (241 mg, 73%) as a sticky solid.



Physical Appearance: sticky solid

R_f: 0.6 (1:4, EtOAc:Hexanes)

IR (neat): 3004, 2947, 2844, 1735, 1602, 1461, 1365, 1329, 1212, 1153, 1119, 1038, 1004, 909, 817, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.16 (d, *J* = 2.0 Hz, 1H), 6.08 (d, *J* = 2.0 Hz, 1H), 5.17 (d, *J* = 8.8 Hz, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 3.60-3.50 (m ,4H), 3.45 (s, 3H).

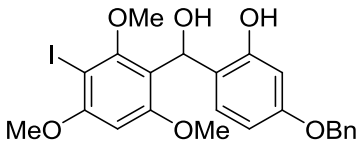
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.75 (C), 160.60 (C), 159.77 (C), 159.88 (C), 152.53 (C), 127.00 (CH), 126.92 (CH), 126.07 (C), 121.04 (CH), 116.33 (CH), 109.13 (C), 102.32 (CH), 92.08 (CH), 90.70 (CH), 57.16 (CH_3), 56.34 (CH_3), 55.62 (CH_3), 55.32 (CH3), 51.81 (CH3), 48.44 (CH), 35.05 (CH).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{21}H_{25}O_7$ 389.1600, found 389.1591.

Formal Synthesis of Myristinin B/C

(±)-5-(benzyloxy)-2-(hydroxy(3-iodo-2,4,6-trimethoxyphenyl)methyl)phenol (9h):

To a cold (-78 ^oC), magnetically stirred solution of diiodide **12a** (8.3 g, 19.73 mmol) in dry THF (75 mL) was added *n*-BuLi (11 mL, 17.54 mmol, 1.6M in hexane) and stirred for 20 min. The aldehyde **11c** (1 g, 4.38 mmol) in dry THF (15 mL) was added slowly; the resulting mixture was slowly warmed to rt and stirred for 2h. Upon completion (TLC control), the reaction was carefully quenched with saturated aq. NH_4Cl (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL) combined organic layer was washed with brine and dried (*anhyd*. Na_2SO_4). Evaporation of the solvent followed by purification of the residue by repeated washing with ethyl acetate-hexanes (1:9) furnished the iodoalcohol **9h** (1.43 g, 62%) as a white solid.



Physical Appearance: white solid

m.p.: 78-79 ^oC

R_f: 0.4 (1:3, EtOAc:Hexanes)

IR (neat): 3415, 1579, 1449, 1390, 1314, 1260, 1150, 1097, 1017, 967, 834, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.45-7.30 (m, 5H), 6.60 (d, *J* = 2.3 Hz, 1H), 6.40-6.25 (m, 4H), 5.00 (s, 2H), 4.63 (d, *J* = 11.3 Hz, 1H), 3.94 (s, 3H), 3.82 (s, 3H), 3.64 (s, 3H).

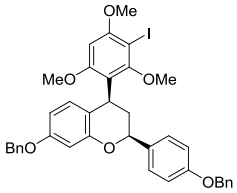
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 159.93 (C x 2), 159.10 (C), 157.80 (C), 137.01 (C), 128.65 (CH x 2), 128.04 (CH), 127.62 (CH x 2), 127.44 (CH), 119.92 (C), 115.82

(C), 106.27 (CH), 103.16 (CH), 92.63 (CH), 74.06 (C), 70.04 (CH_2), 69.40 (CH), 62.19 (CH_3), 56.75 (CH_3), 56.22 (CH_3).

HRMS (ESI, M+Na): m/z calcd. for $C_{23}H_{23}O_6NaI$ 545.0437, found 545.0417.

(±)-(2*S,4*S**)-7-(benzyloxy)-2-(4-(benzyloxy)phenyl)-4-(3-iodo-2,4,6-trimethoxyphenyl)chroman (13):**

Reaction of alcohol **9h** (130 mg, 0.25 mmol), olefin **10a** (255 mg, 1.21 mmol) and (±)-BPA (50 mg, 0.14 mmol) in CH_2Cl_2 (4 mL) at rt for 20 min (TLC control), as described for the chroman **8a**, followed by purification on a silica gel column using ethyl acetate-hexanes (1:19) as the eluent furnished the requisite chroman **13** (162 mg, 91%) as a white solid.



Physical Appearance: white solid

m.p.: 68-70 ^oC

R_f: 0.2 (1:9, EtOAc:Hexanes)

IR (neat): 2932, 2856, 1615, 1583, 1500, 1456, 1433, 1387, 1328, 1245, 1160, 1104, 1015, 831, 809, 801, 738 cm^{-1}.

^{1}H NMR (400 MHz, CD_3CN): δ 7.40-7.10 (m, 12H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.45 (t, *J* = 8.5 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 6.33 (s, 1H), 6.29 (dd, *J* = 8.5, 2.4, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 4.99 (s, H) 4.90 (s, 2H), 4.68 (dd, *J* = 12.0, 5.8 Hz, 1H) 3.75 (s, 3H), 3.69 (s, 3H), 3.41 (s, 3H), 2.57 (q, *J* = 12.0 Hz, 1H), 1.93 (dd, *J* = 12.0, 5.8 Hz, 1H).

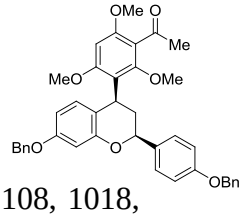
^{13}C NMR (100 MHz, CD_3CN, DEPT): δ 161.45 (C), 160.59 (C), 159.58 (C), 159.34 (C), 158.56 (C), 156.84 (C), 138.45 (C), 138.26 (C), 134.93 (C), 129.44 (CH x 2), 129.39 (CH x 2), 128.81 (CH), 128.71 (CH), 128.64 (CH x 2), 128.57 (CH x 2), 128.52 (CH x 2), 120.14 (C), 119.68 (C), 115.63 (CH x 3), 108.51 (CH), 103.28 (CH), 95.29 (CH), 79.19 (CH), 73.50 (C), 70.52 (CH_2), 70.45 (CH_2), 62.66 (CH_3), 57.27 (CH_3), 57.20 (CH_3), 35.56 (CH_2), 34.86 (CH),

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{38}H_{36}O_6I$ 715.1557, found 715.1548.

(±)-1-(3-((2*S,4*S**)-7-(benzyloxy)-2-(4-(benzyloxy)phenyl)chroman-4-yl)-2,4,6-trimethoxyphenyl)ethanone (14):**

To a magnetically stirred suspension of iodoflavan **13** (715 mg, 1.01 mmol), PPh_3 (55 mg, 0.21 mmol) and $Pd(OAc)_2$ (28 mg, 0.12 mmol) in degassed dry DMF (5 mL) in a sealed tube, was added ethyl vinyl ether (**10h**) (1 mL, 10.44 mmol) and dry Et_3N (2.2

mL, 15.03 mmol) and heated at 110 ^{o}C for 22h (TLC control). The reaction mixture was quenched with 2N HCl (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 20 mL), combined organic layer was washed with brine and dried (*anhyd*. Na_2SO_4). Evaporation of the solvent and purification of residue on a silica gel column using ethyl acetate-hexanes (1:4) afforded the ketone **14** (565 mg, 90%) as a white solid.



Physical Appearance: white solid

m.p.: 80-82 ^{o}C

R_f: 0.3 (1:4, EtOAc:Hexanes)

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

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.25 (m, 12H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.61 (m, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.41 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.24 (s, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 5.09 (s, 2H), 5.00 (s, 2H), 4.69 (dd, *J* = 12.0, 5.7 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.51 (s, 3H), 2.67 (q, *J* = 12.0, 1H), 2.54 (s, 3H), 2.07 (ddd, *J* = 12.0, 5.8, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 202.33 (C), 160.72 (C), 158.66 (C), 157.84 (C), 157.19 (C), 156.67 (C), 156.04 (C), 137.32 (C), 137.10 (C), 133.98 (C),128.67 (CH x 2), 128.58 (CH x 2), 128.04 (CH), 127.90 (CH), 127.84 (CH), 127.80 (CH), 127.70 (CH x 2), 127.53 (CH x 2), 119.04 (C), 118.56 (C), 118.13 (C), 114.98 (CH x 3), 108.18 (CH), 102.54 (CH), 93.34 (CH), 78.64 (CH), 70.14 (CH_2), 70.08 (CH_2), 64.07 (CH_3), 56.24 (CH_3), 55.88 (CH_3), 35.19 (CH_2), 32.77 (CH), 32.68 (CH_3).

HRMS (ESI, M+H^{+}): m/z calcd. for $C_{40}H_{39}O_7$ 631.2696, found 631.2696.

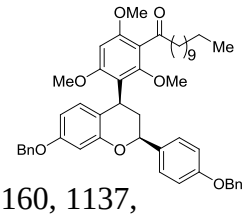
(±)-1-(3-((2*S,4*S**)-7-(benzyloxy)-2-(4-(benzyloxy)phenyl)chroman-4-yl)-2,4,6-trimethoxyphenyl)dodecan-1-one (15):**

To a cold (0 °C), magnetically stirred solution of ketone **14** (900 mg, 1.43 mmol) in dry THF (12 mL), was added *t*-BuOK (200 mg, 1.78 mmol) and the resulting mixture was stirred for 1h at rt. The iodide **16** (370 μL, 1.72 mmol) was added slowly, the resulting mixture was stirred for 24h at rt and then reaction was carefully quenched with saturated aq. NH_4Cl (10 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL), combined organic layer was washed with brine and dried (*anhyd*. Na_2SO_4). Evaporation of the solvent and purification of residue on a silica gel column using ethyl acetate-

hexanes (1:19) afforded the flavan **15** (228 mg, 21%) as a sticky solid and the unreacted ketone **14** (610 mg, 68%) as a sticky solid.

Second iteration:

Reaction of ketone **14** (610 mg, 0.97 mmol), *t*-BuOK (130 mg, 1.16 mmol) and iodide **16** (250 μL, 1.16 mmol) in dry THF (10 mL) as described above, furnished the unreacted ketone **14** (416 mg, 68%) and the flavan **15** (162 mg, 22%) [Overall yield (390 mg, 36%, 66% brsm) after two iterations].



Physical Appearance: Sticky solid

R_f: 0.3 (1:9, EtOAc:Hexanes)

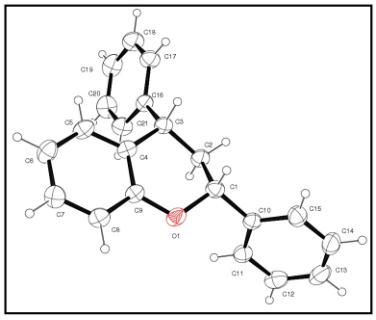
IR (neat): 2925, 2853, 1699, 1596, 1501, 1456, 1403, 1323, 1246, 1160, 1137, 1107, 830, 810, 738 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.10 (m, 12H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.53 (dd, *J* = 8.4, 6.6 Hz, 1H), 6.48 (d, *J* = 2.0 , 1H), 6.33 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.15 (s, 1H), 5.04 (d, *J* = 11.3 Hz, 1H), 4.99 (s, 2H), 4.91 (s, 2H), 4.59 (dd, *J* = 11.7, 5.7 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.41 (s, 3H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.65-2.55 (m, 1H), 1.99 (dd, *J* = 13.0, 5.7 Hz, 1H), 1.65-1.55 (m, 2H), 1.20-1.10 (m, 16H), 0.85-0.75 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 205.48 (C), 160.44 (C), 158.65 (C), 157.82 (C), 156.93 (C), 156.33 (C), 156.02 (C), 137.31 (C), 137.09 (C), 133.97 (C), 128.68 (CH x 2), 128.59 (CH x 2), 128.05 (CH), 127.91 (CH), 127.81 (CH), 127.71 (CH), 127.58 (CH x 2), 127.53 (CH x 2), 119.06 (C), 118.75 (C), 118.00 (C), 114.96 (CH x 3), 108.16 (CH), 102.51 (CH), 93.40 (CH), 78.67 (CH), 70.12 (CH_2), 70.06 (CH_2), 64.19 (CH_3), 55.90 (CH_3), 55.84 (CH_3), 45.22 (CH_2), 35.18 (CH_2), 32.78 (CH), 32.02 (CH_2), 29.74 (CH_2 x 2), 29.66 (CH_2), 29.59 (CH_2), 29.46 (CH_2), 29.30 (CH_2), 23.97 (CH_2), 22.80 (CH_2), 14.24 (CH_3).

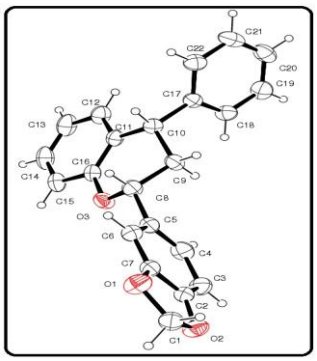
HRMS (ESI, M+Na): m/z calcd. for $C_{50}H_{58}O_7Na$ 793.4080, found 793.4086.

Crystal data and structure refinement for 8b



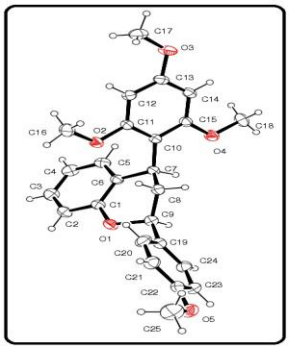
Identification code	**8b**	
CCDC No.	**932658**	
Empirical formula	$C_{21}H_{18}O$	
Formula weight	330.36	
Temperature	298(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P2(1)/c	
Unit cell dimensions	a = 13.2722(19) A	alpha = 90 deg.
	b = 5.7365(6) A	beta = 103.844(4) deg.
	c = 21.383(3) A	gamma = 90 deg.
Volume	1580.7(4) A^3	
Z, Calculated density	4, 1.203 Mg/m^3	
Absorption coefficient	0.072 mm^-1	
F(000)	608	
Crystal size	0.25 x 0.20 x 0.18 mm	
Theta range for data collection	1.96 to 24.85 deg.	
Limiting indices	-14<=h<=15, -6<=k<=6, -21<=l<=25	
Reflections collected / unique	8164 / 2662 [R (int) = 0.0379]	
Completeness to theta = 24.85	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9871 and 0.9822	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2662 / 0 / 199	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1178	
R indices (all data)	R1 = 0.0910, wR2 = 0.1388	
Largest diff. peak and hole	0.181 and -0.214 e.A^-3	

Crystal data and structure refinement for 8d



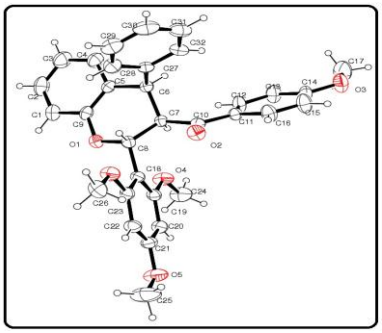
Identification code	**8d**	
CCDC No.	**932655**	
Empirical formula	$C_{22}H_{18}O_3$	
Formula weight	330.36	
Temperature	298(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P2(1)/c	
Unit cell dimensions	a = 10.1432(3) A	alpha = 90 deg.
	b = 8.1265(2) A	beta = 97.036(2) deg.
	c = 20.3620(6) A	gamma = 90 deg.
Volume	1665.77(8) A^3	
Z, Calculated density	4, 1.317 Mg/m^3	
Absorption coefficient	0.087 mm^-1	
F(000)	696	
Crystal size	0.25 x 0.20 x 0.18 mm	
Theta range for data collection	2.02 to 28.45 deg.	
Limiting indices	-13<=h<=13, -9<=k<=10, -27<=l<=24	
Reflections collected / unique	12682 / 4171 [R(int) = 0.0217]	
Completeness to theta = 25.00	100%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9845 and 0.9786	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4171 / 0 / 226	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1319	
R indices (all data)	R1 = 0.0959, wR2 = 0.1551	
Largest diff. peak and hole	0.332 and -0.209 e.A^-3	

Crystal data and structure refinement for 8f



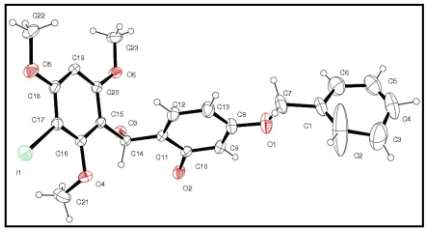
Identification code	**8f**	
CCDC No.	**932656**	
Empirical formula	$C_{25}H_{26}O_5$	
Formula weight	406.46	
Temperature	298(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P2(1)/c	
Unit cell dimensions	a = 8.2985(3) A	alpha = 90 deg.
	b = 28.7950(11) A	beta = 111.617(2) deg.
	c = 9.4916(3) A	gamma = 90 deg.
Volume	2108.55(13) A^3	
Z, Calculated density	4, 1.280 Mg/m^3	
Absorption coefficient	0.088 mm^-1	
F(000)	864	
Crystal size	0.45 x 0.25 x 0.15 mm	
Theta range for data collection	2.41 to 30.04 deg.	
Limiting indices	-11<=h<=11, -36<=k<=39, -9<=l<=13	
Reflections collected / unique	17954 / 6038 [R(int) = 0.0296]	
Completeness to theta = 25.00	99.9%	
Absorption correction	None	
Max. and min. transmission	0.9869 and 0.9613	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6038 / 0 / 275	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1175	
R indices (all data)	R1 = 0.1012, wR2 = 0.1384	
Largest diff. peak and hole	0.338 and -0.205 e.A^-3	

Crystal data and structure refinement for 8j



Identification code	**8j**	
CCDC No.	**932657**	
Empirical formula	$C_{32}H_{30}O_6$	
Formula weight	510.56	
Temperature	298(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P2(1)/n	
Unit cell dimensions	a = 8.2911(6) A	alpha = 90 deg.
	b = 19.7700(18) A	beta = 96.314(3)deg.
	c = 17.1314(14) A	gamma = 90 deg.
Volume	2791.1(4) A^3	
Z, Calculated density	4, 1.215 Mg/m^3	
Absorption coefficient	0.083 mm^-1	
F(000)	1080	
Crystal size	0.25 x 0.22 x 0.15 mm	
Theta range for data collection	1.58 to 18.86 deg.	
Limiting indices	-7<=h<=6, -17<=k<=17, -15<=l<=15	
Reflections collected / unique	9049 / 2192 [R(int) = 0.0475]	
Completeness to theta = 18.86	99.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9876 and 0.9795	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2192 / 0 / 347	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0951	
R indices (all data)	R1 = 0.0555, wR2 = 0.1083	
Largest diff. peak and hole	0.190 and -0.150 e.A^-3	

Crystal data and structure refinement for 9h



Identification code	**9h**	
CCDC No.	**932659**	
Empirical formula	C23H20IO6	
Formula weight	519.29	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Triclinic, P1	
Unit cell dimensions	a = 9.3330(4) A	alpha = 107.576(2) deg.
	b = 9.5986(4) A	beta = 92.267(2) deg.
	c = 14.6529(7) A	gamma = 90.024(2) deg.
Volume	1250.30(10) A^3	
Z, Calculated density	2, 1.379 Mg/m^3	
Absorption coefficient	1.312 mm^-1	
F(000)	518	
Crystal size	0.38 x 0.31 x 0.25 mm	
Theta range for data collection	1.46 to 28.58 deg.	
Limiting indices	-12<=h<=11, -12<=k<=12, -19<=l<=19	
Reflections collected / unique	15676 / 5737 [R(int) = 0.0179]	
Completeness to theta = 25.00	95.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9845 and 0.9786	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5737 / 1 / 313	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0600, wR2 = 0.1982	
R indices (all data)	R1 = 0.0691, wR2 = 0.2301	
Largest diff. peak and hole	2.812 and -0.675 e.A^-3	

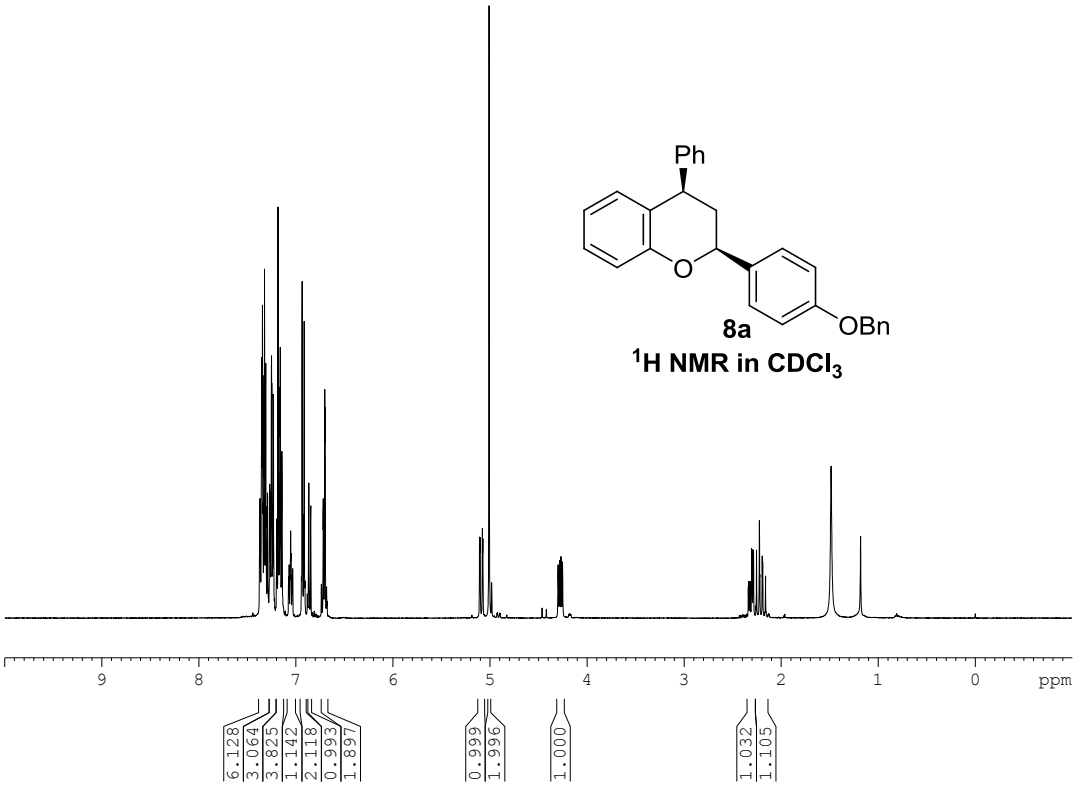


Fig. 1 ^{1}H NMR Spectrum of chroman 8a

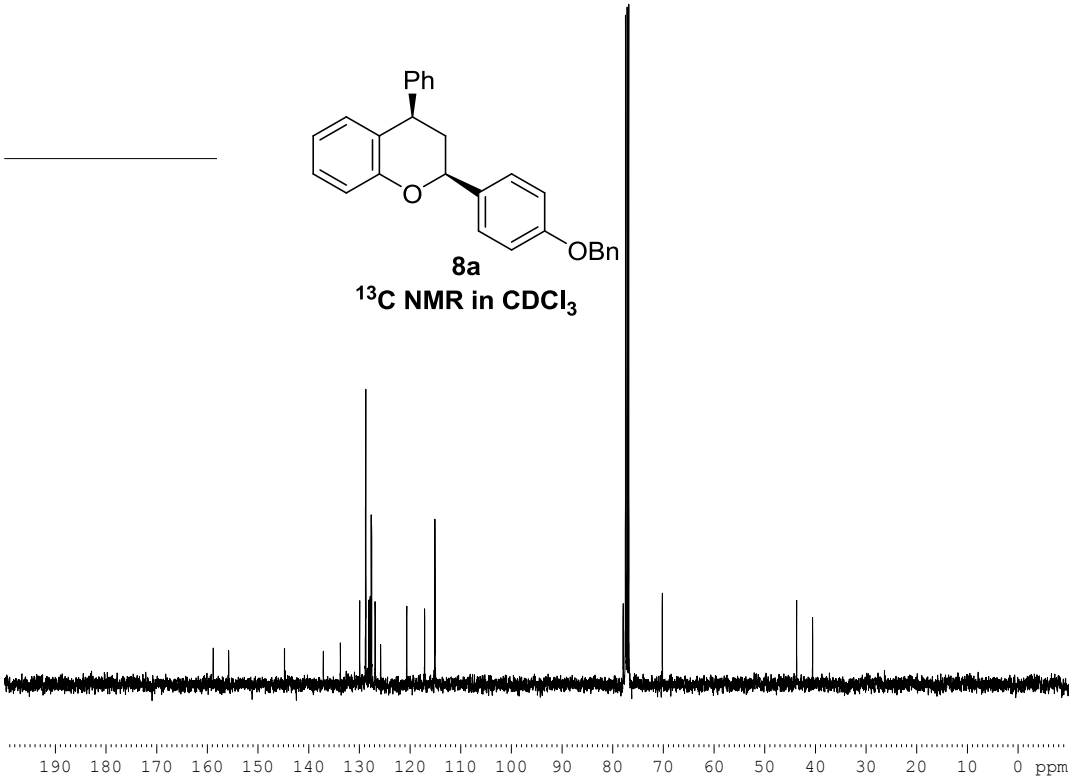


Fig. 2 ^{13}C NMR Spectrum of chroman 8a

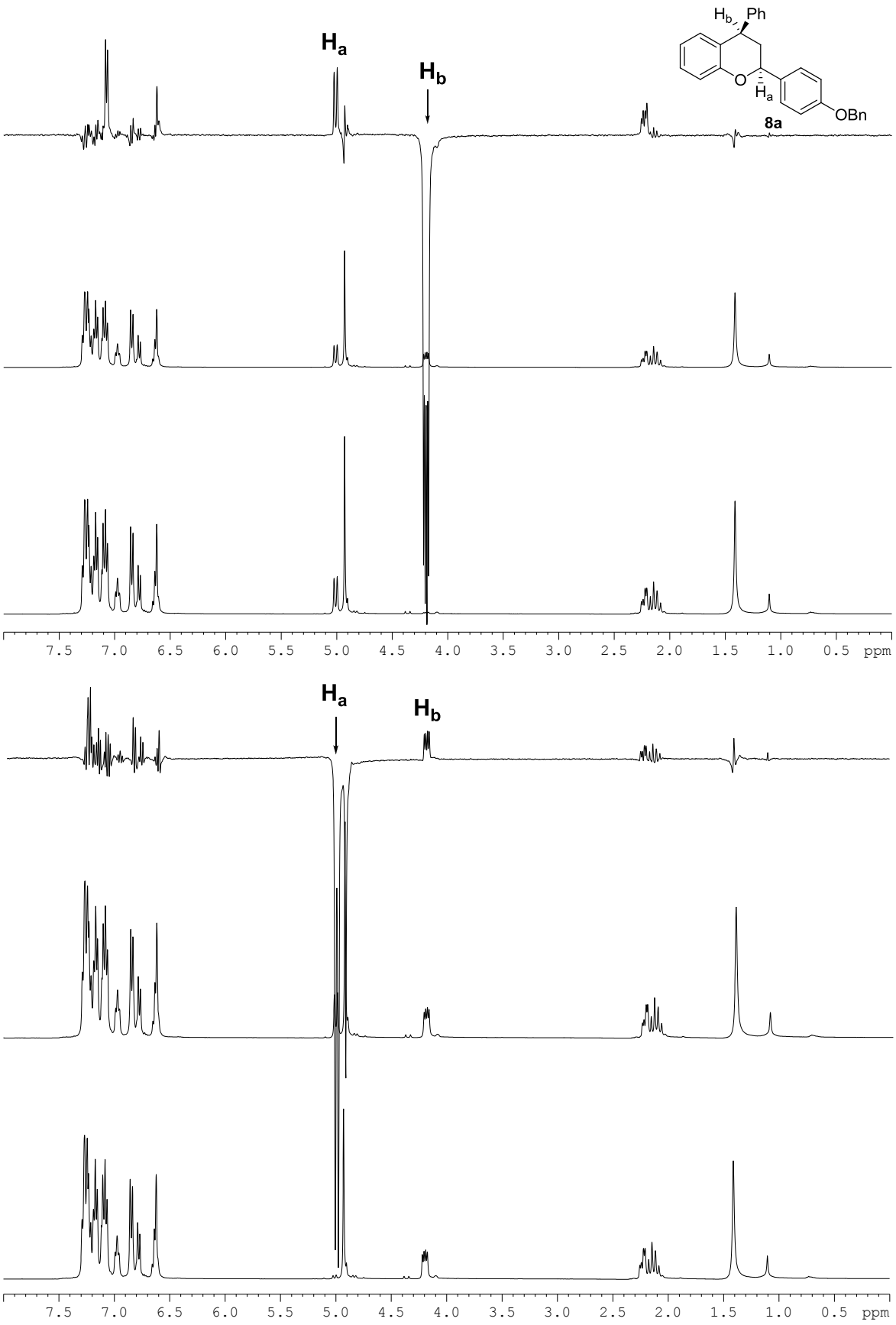


Fig. 3 NOE Spectra of chroman 8a

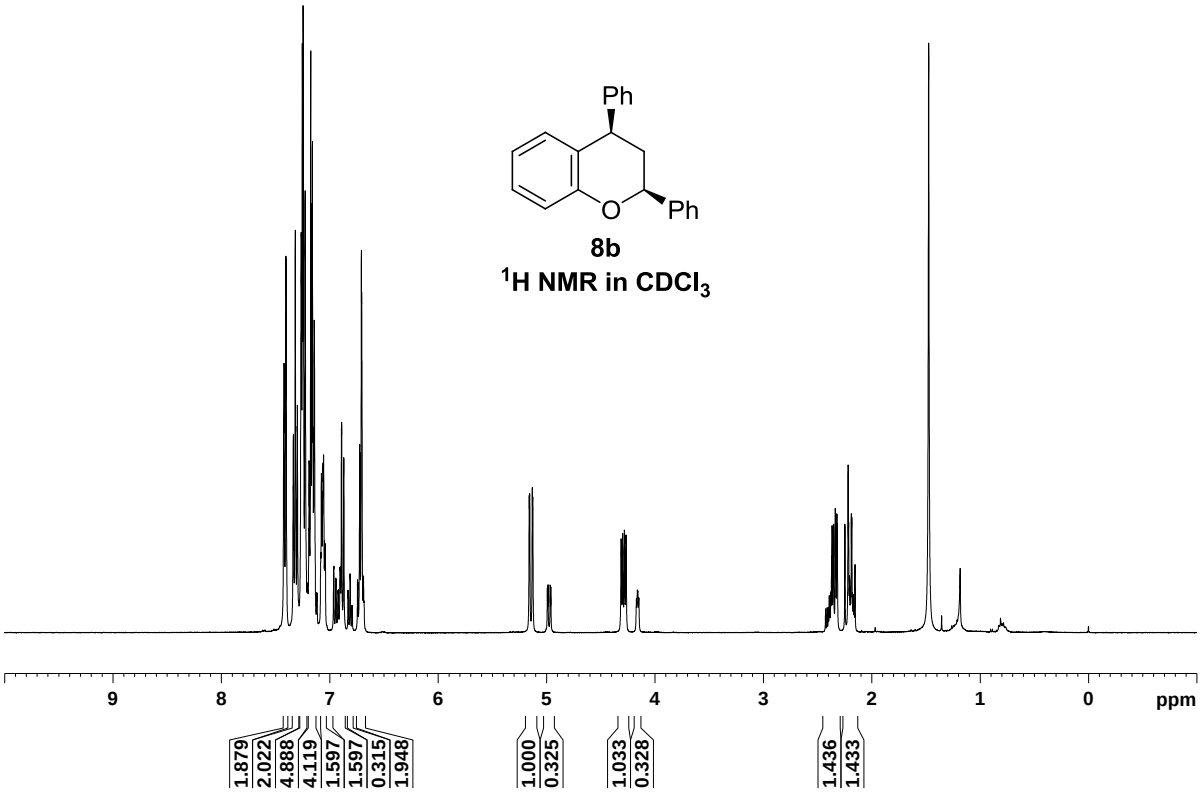


Fig. 4 ^{1}H NMR Spectrum of chroman 8b

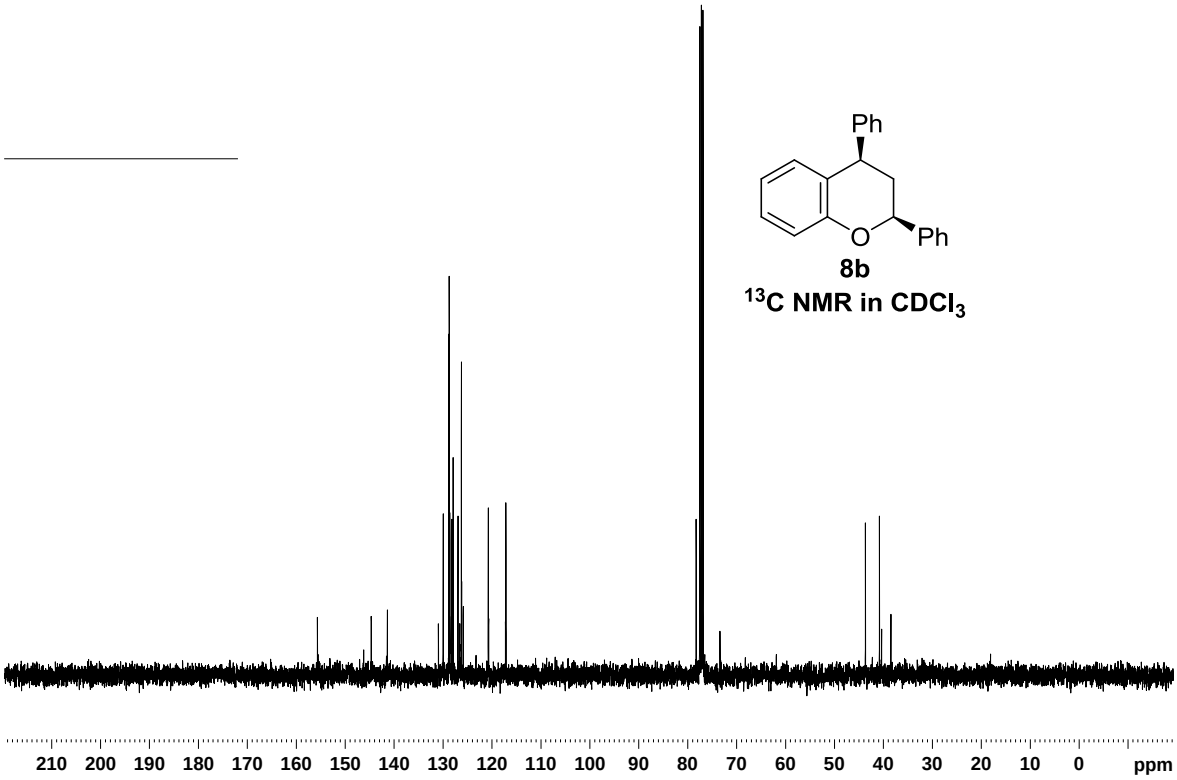


Fig. 5 ^{13}C NMR Spectrum of chroman 8b

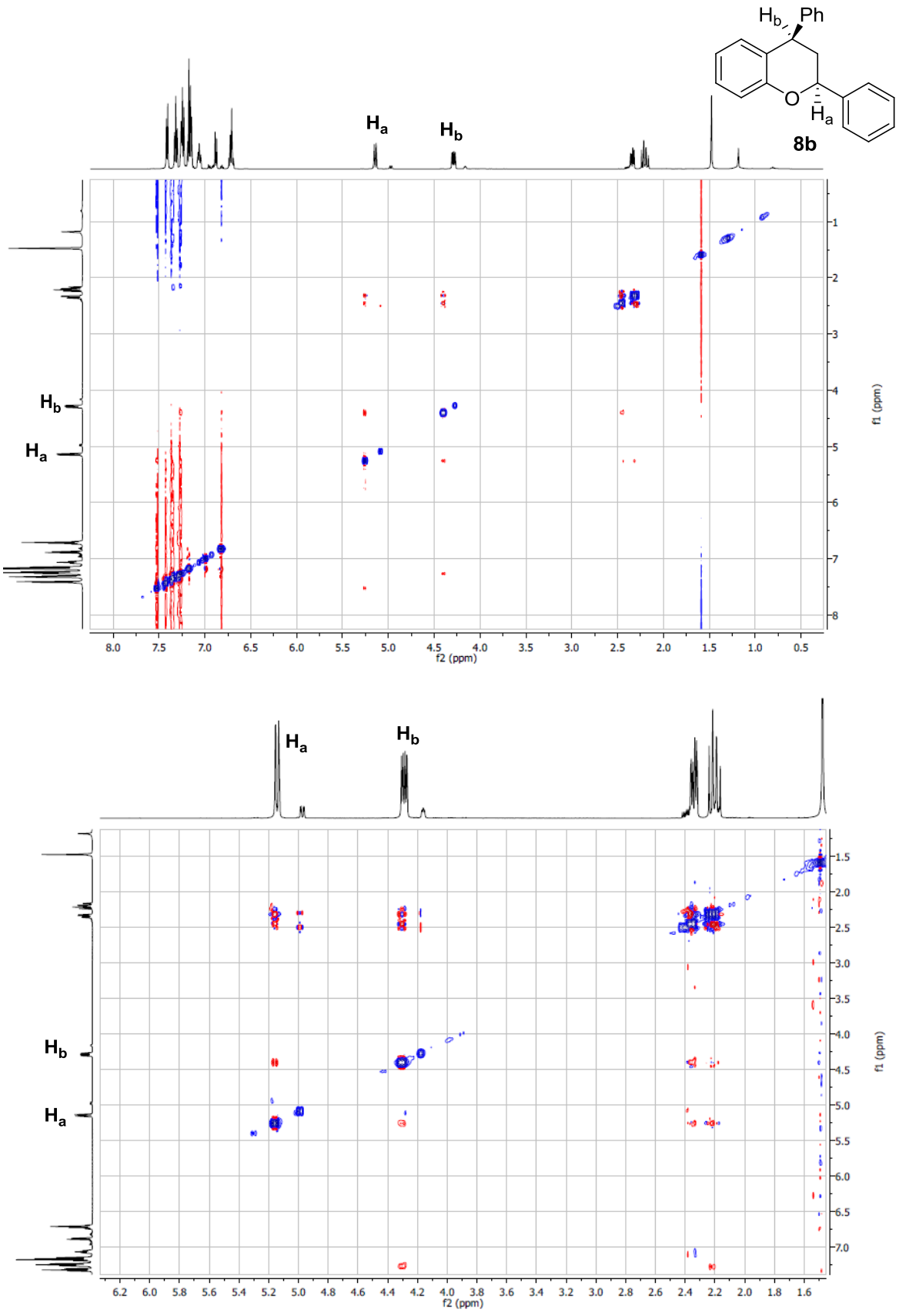


Fig. 6 NOESY Spectrum of chroman 8b

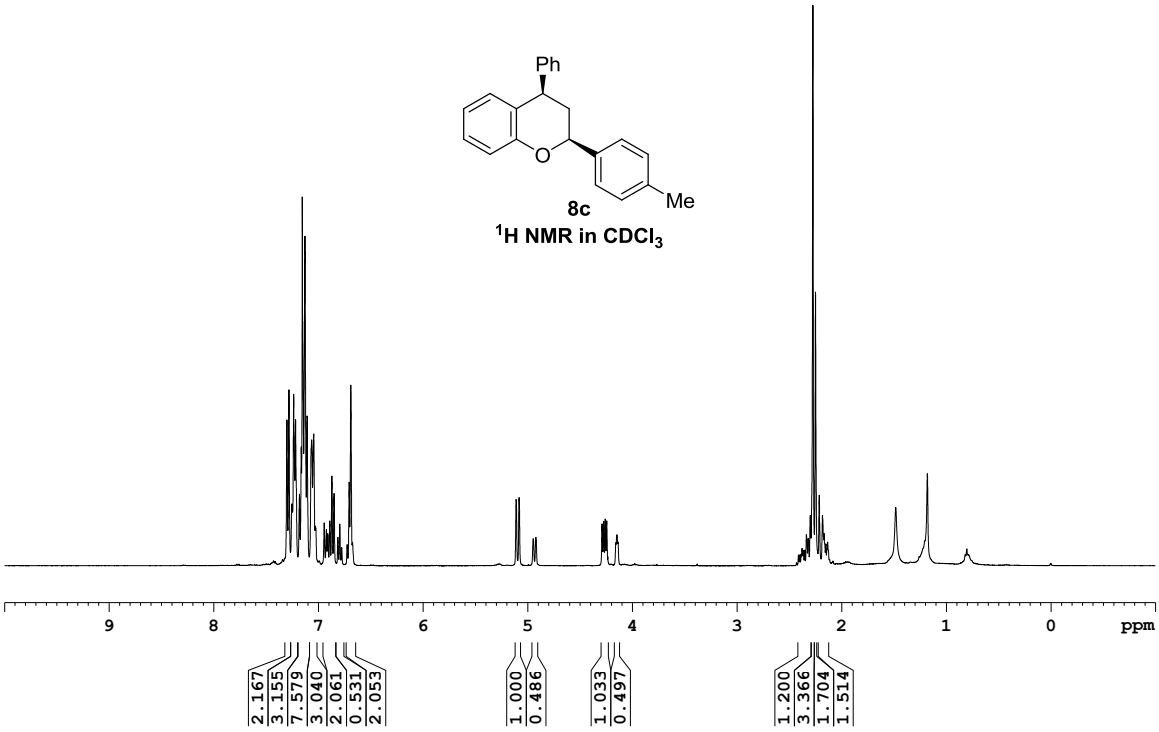


Fig. 7 ^{1}H NMR Spectrum of chroman 8c

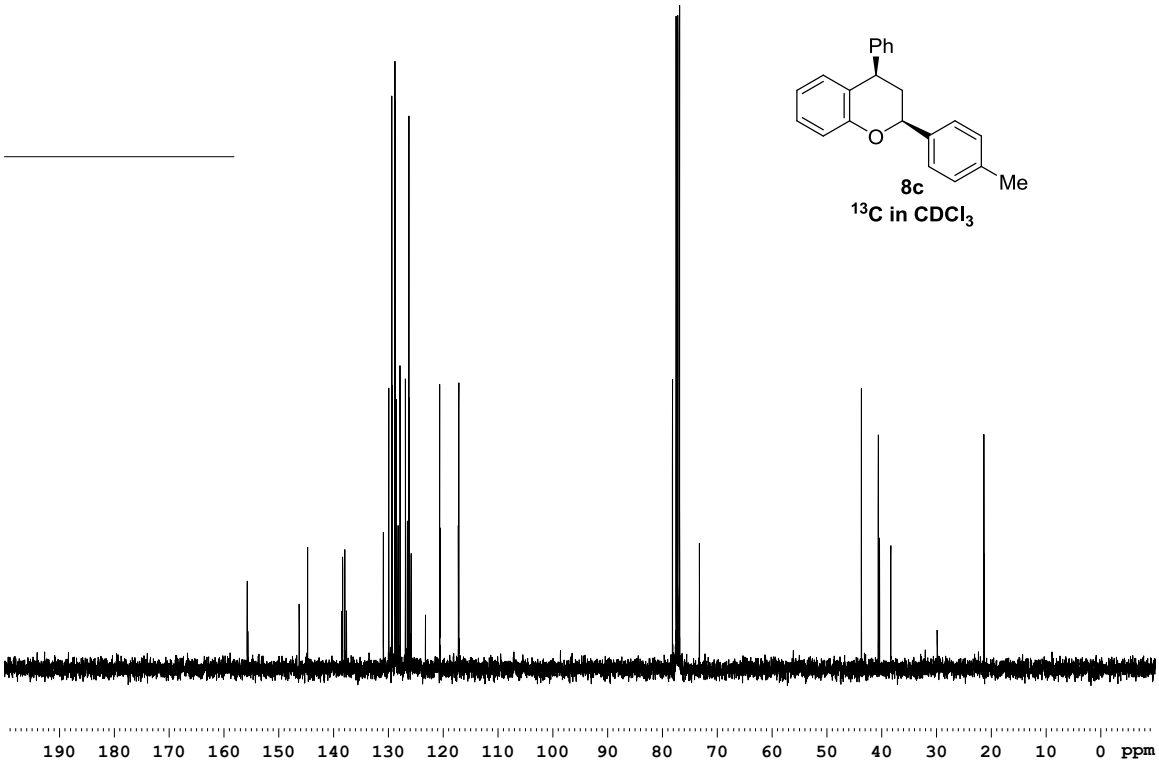


Fig. 8 ^{13}C NMR Spectrum of chroman 8c

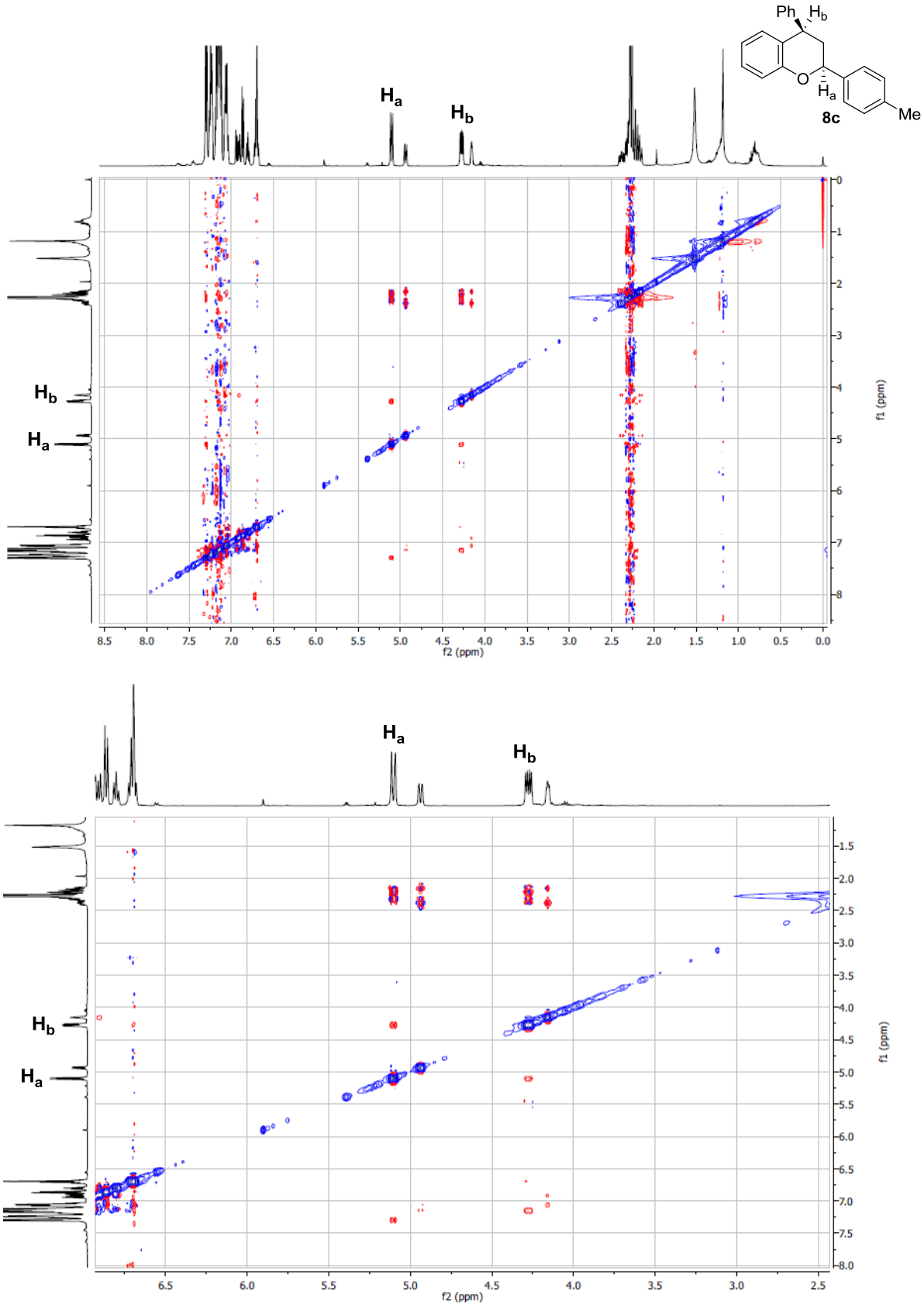


Fig. 9 NOESY Spectrum of chroman 8c

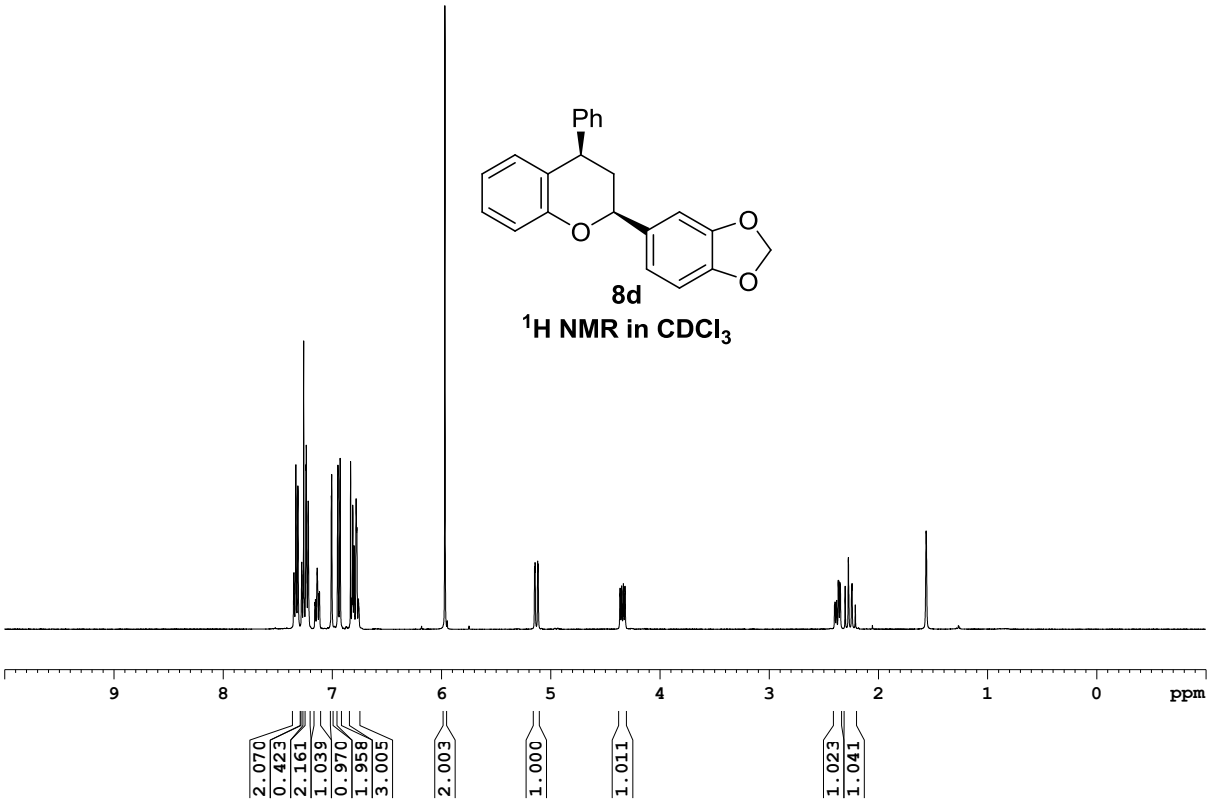


Fig. 10 ^{1}H NMR Spectrum of chroman 8d

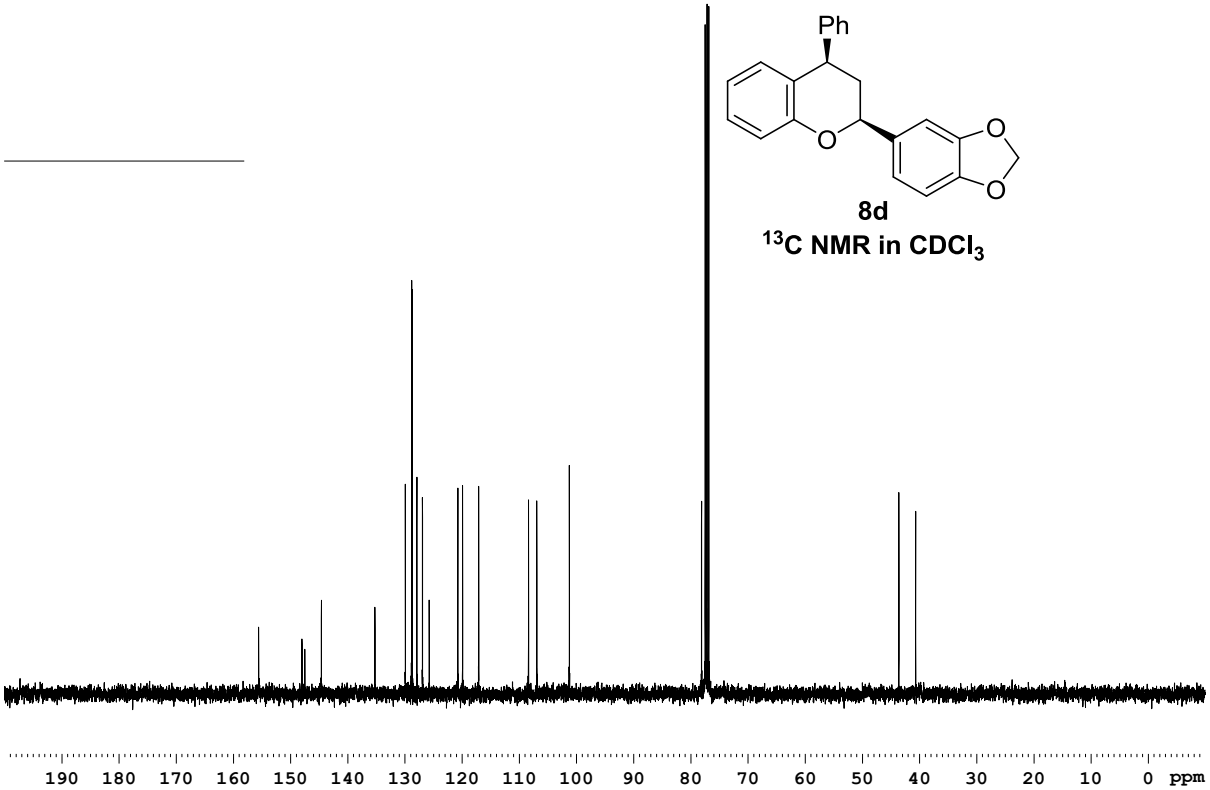


Fig. 11 ^{13}C NMR Spectrum of chroman 8d

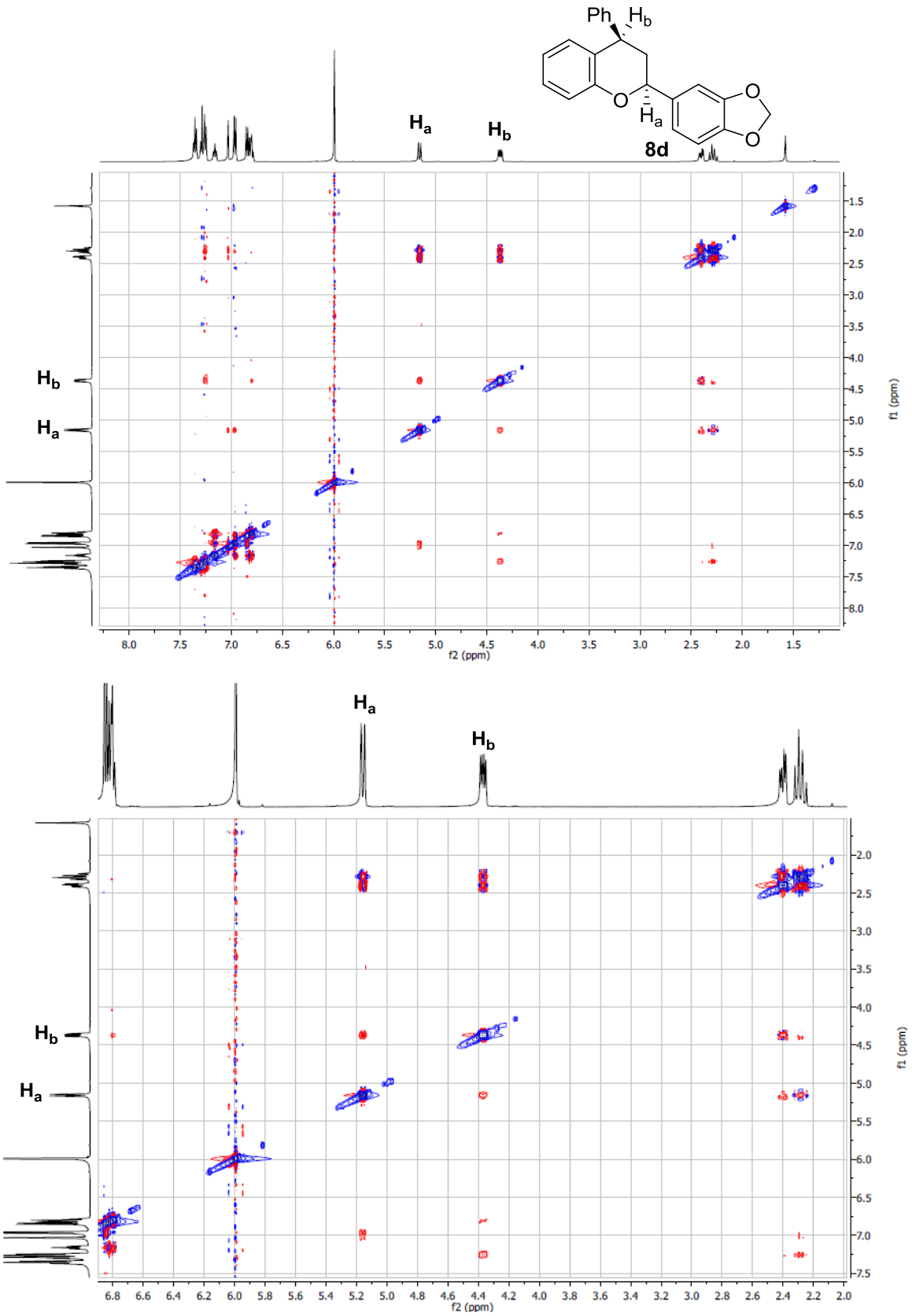


Fig. 12 NOESY Spectrum of chroman 8d

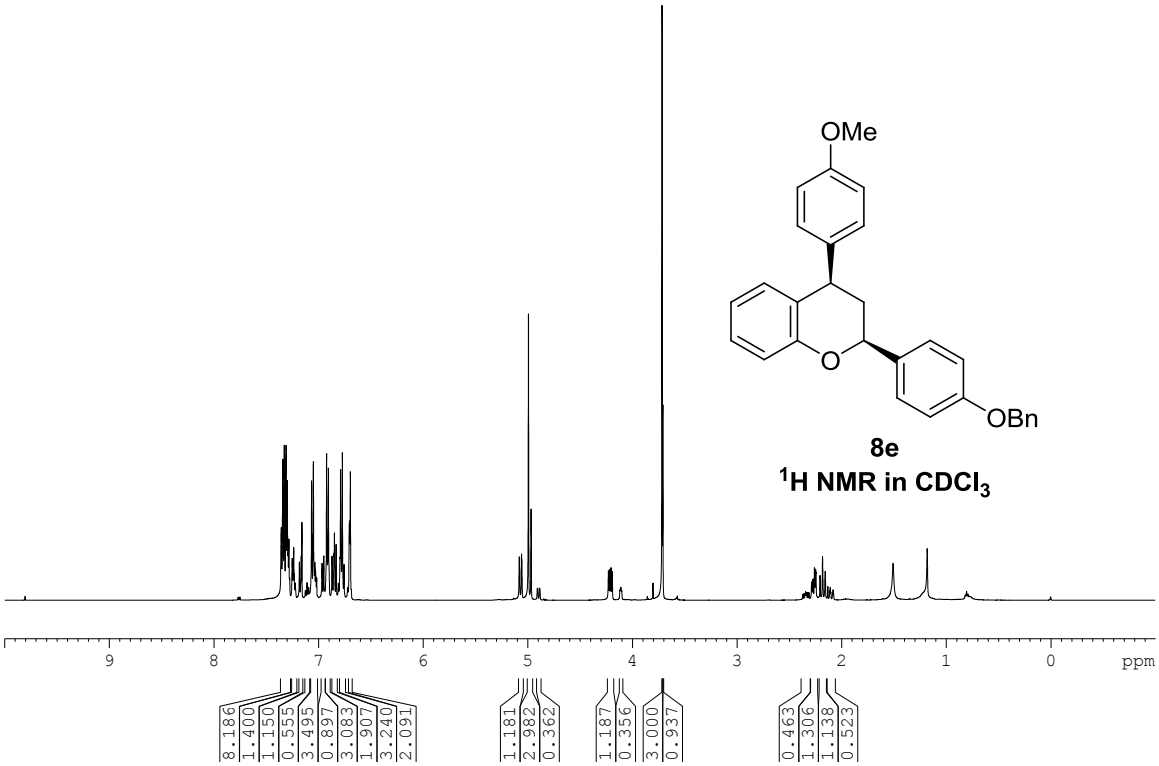


Fig. 13 ^{1}H NMR Spectrum of chroman 8e

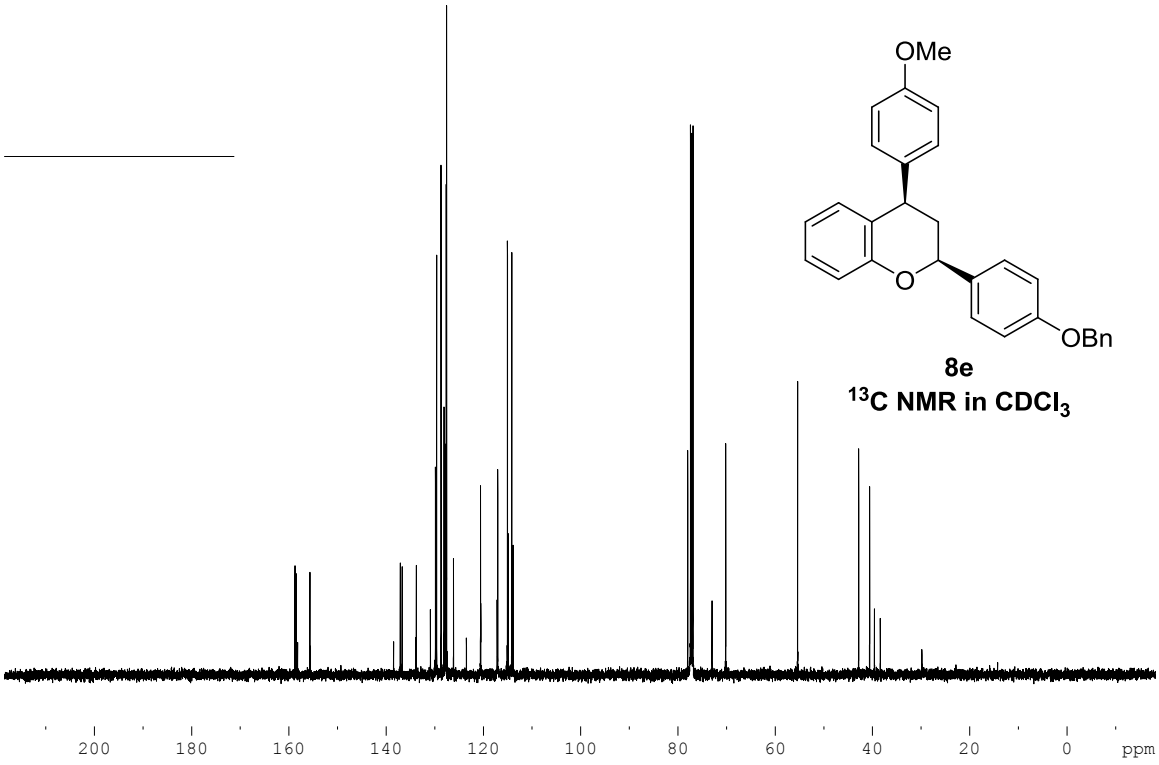


Fig. 14 ^{13}C NMR Spectrum of chroman 8e

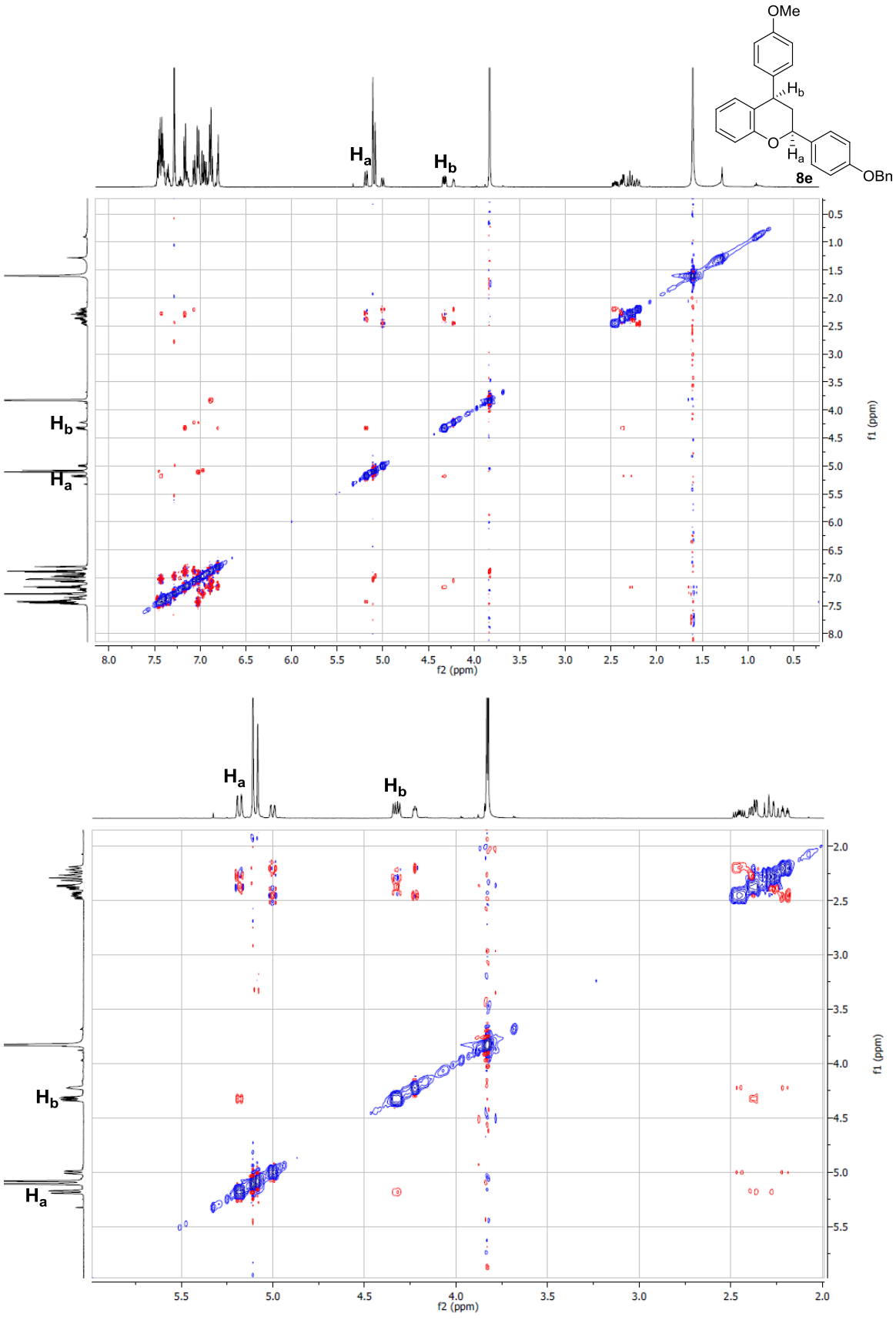


Fig. 15 NOESY Spectrum of chroman 8e

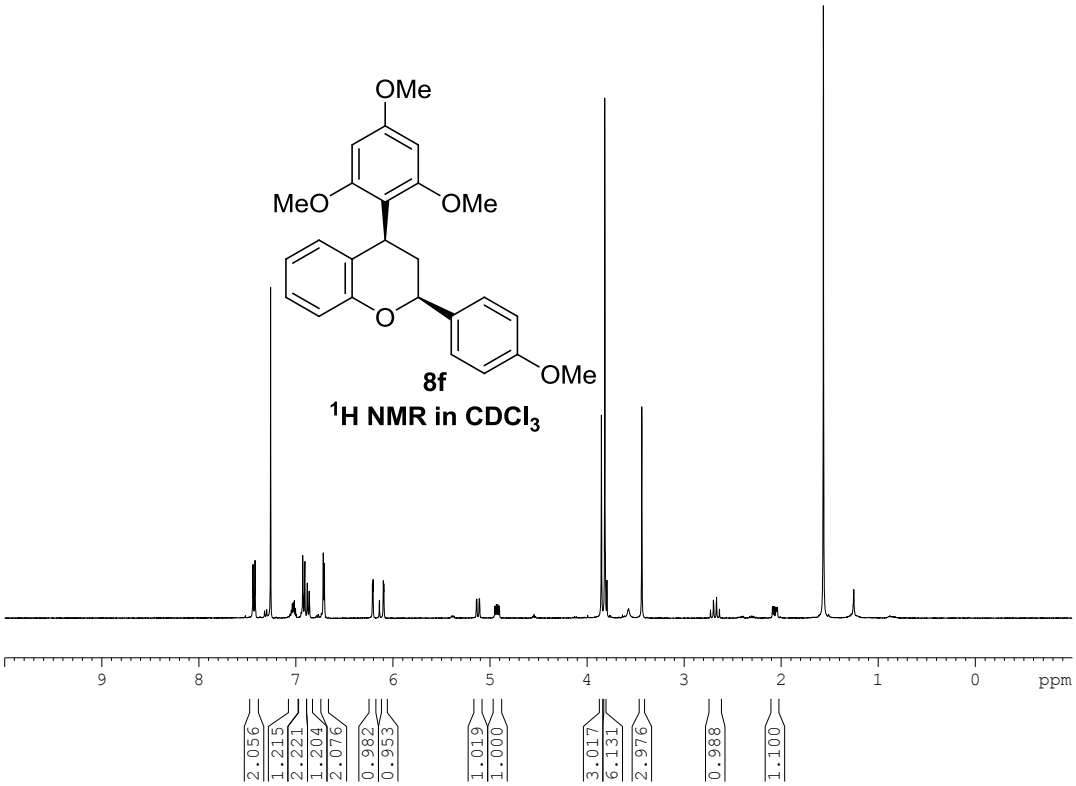


Fig. 16 ^{1}H NMR Spectrum of chroman 8f

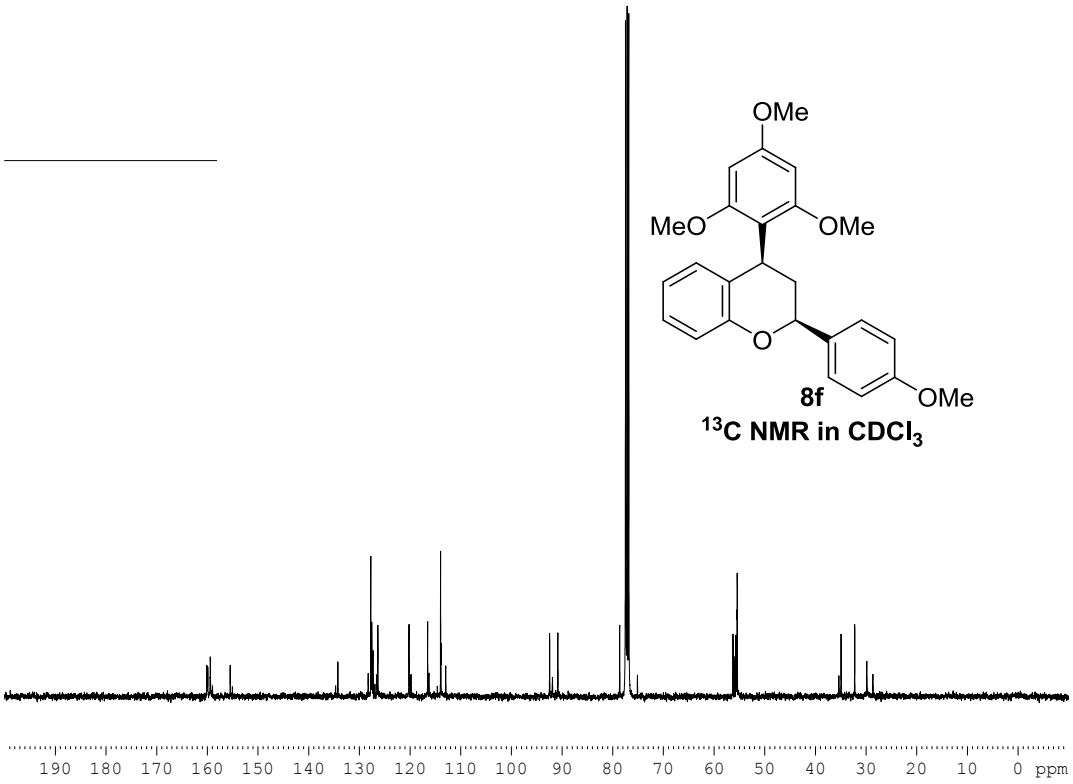


Fig. 17 ^{13}C NMR Spectrum of chroman 8f

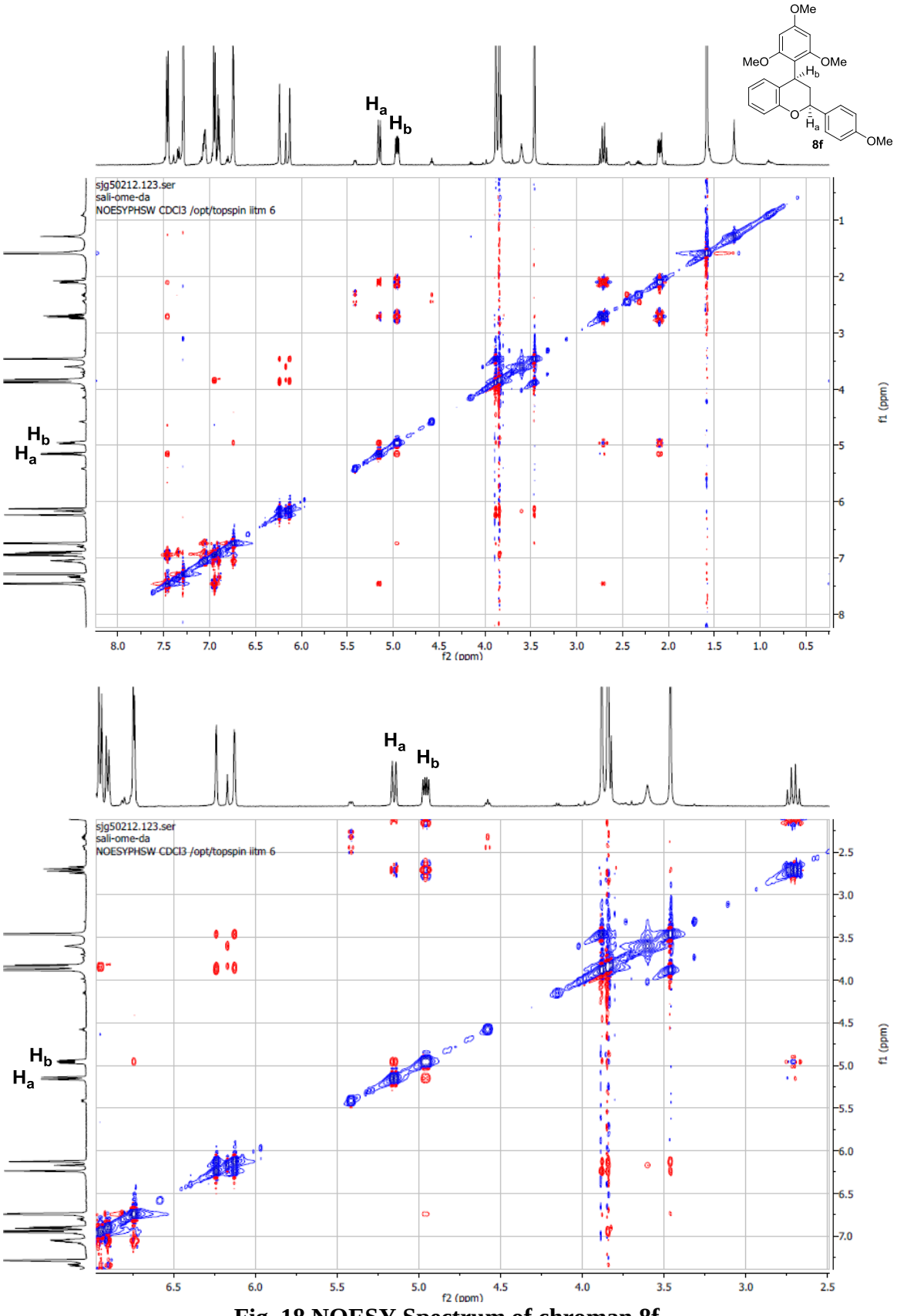


Fig. 18 NOESY Spectrum of chroman 8f

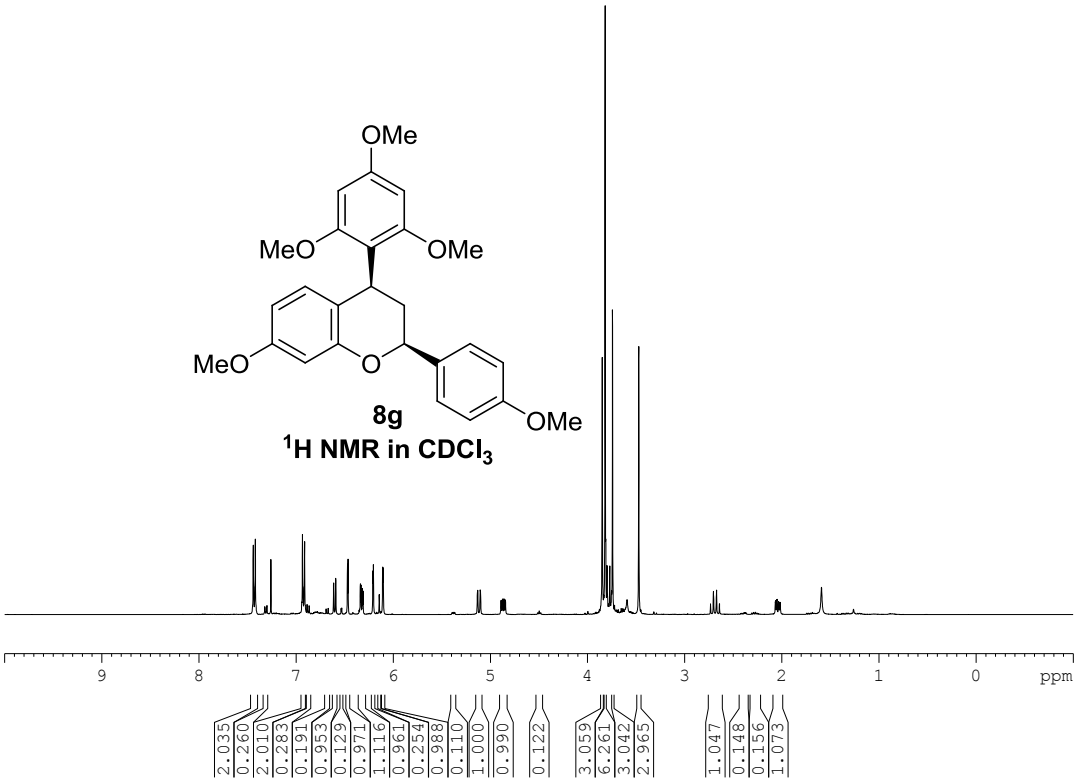


Fig. 19 ^{1}H NMR Spectrum of chroman 8g

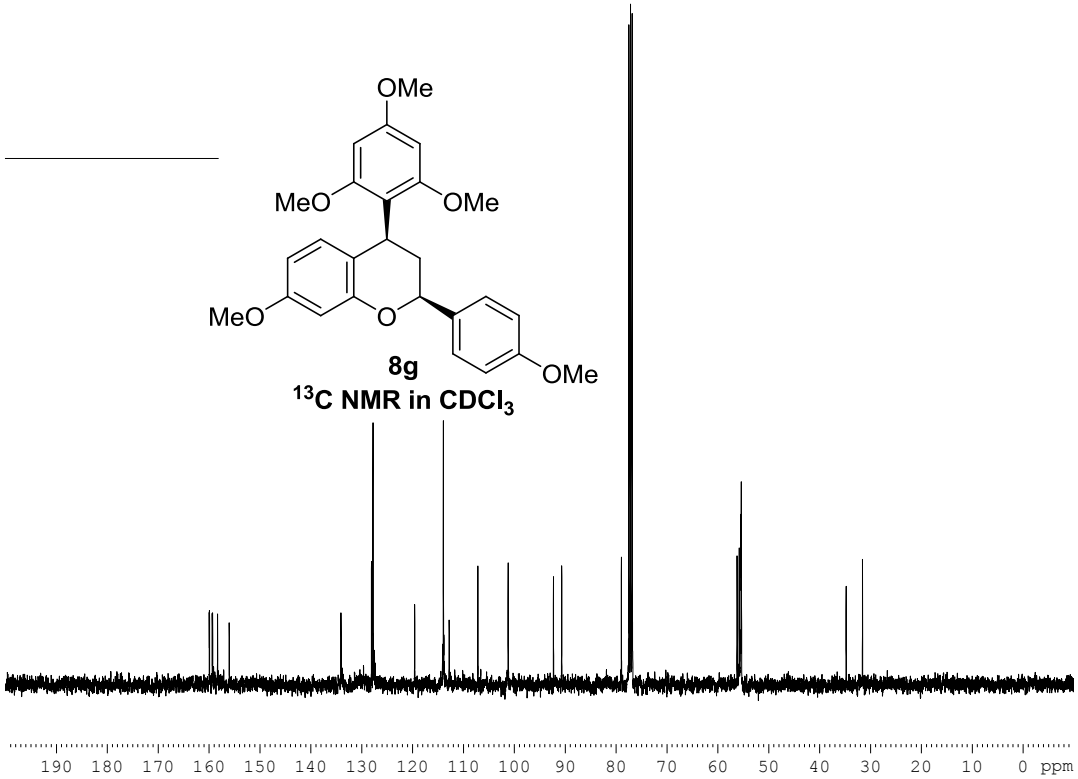


Fig. 20 ^{13}C NMR Spectrum of chroman 8g

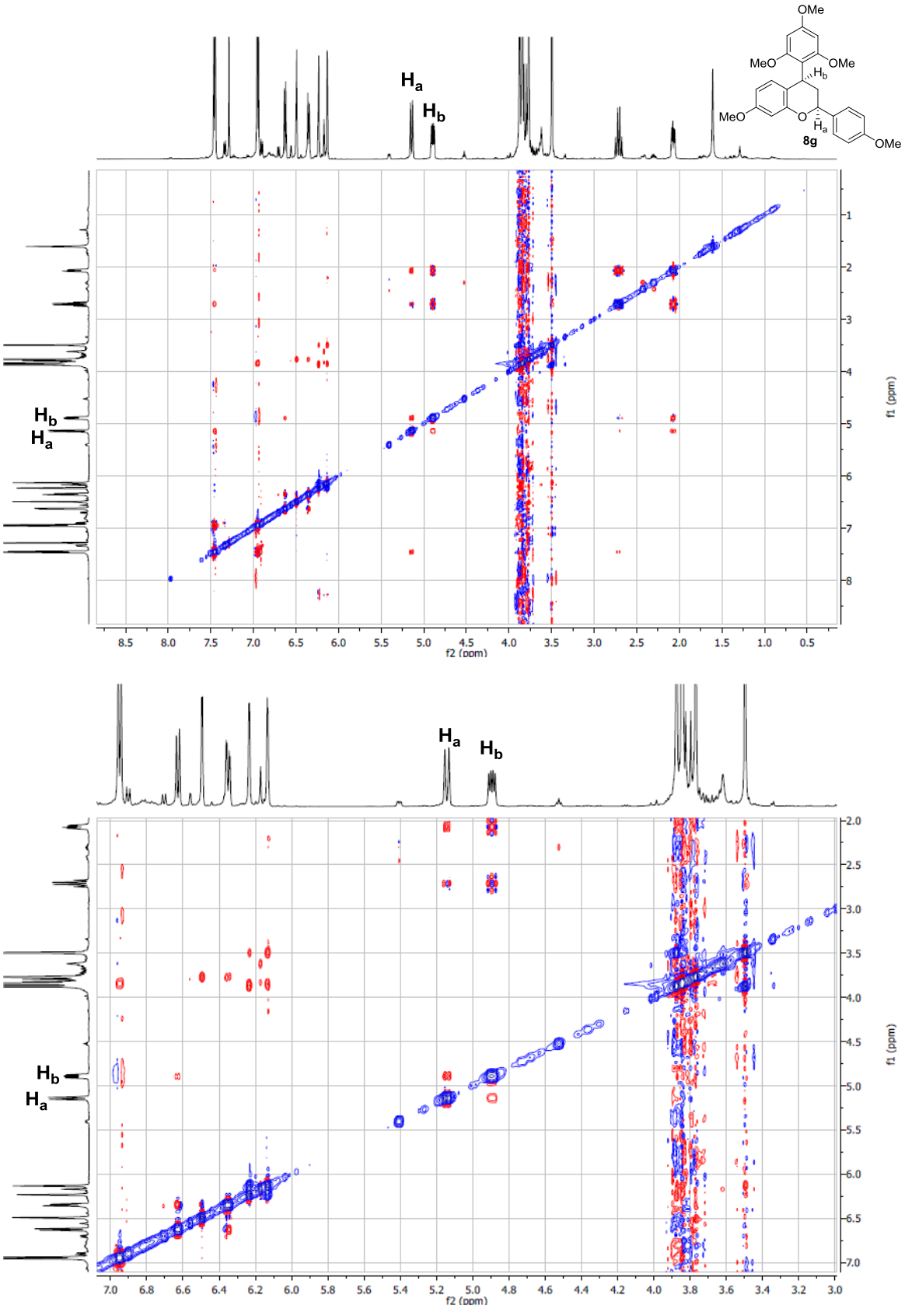


Fig. 21 NOESY Spectrum of chroman 8g

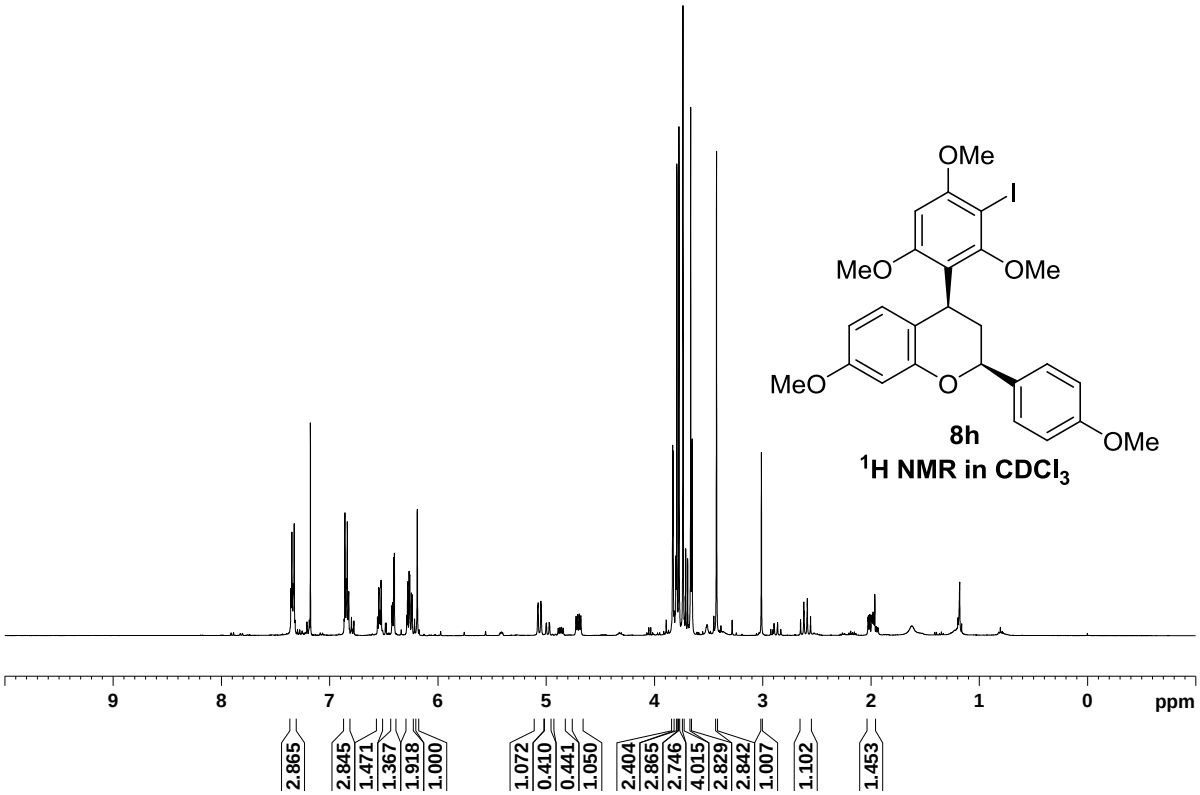


Fig. 22 ^{1}H NMR Spectrum of chroman 8h

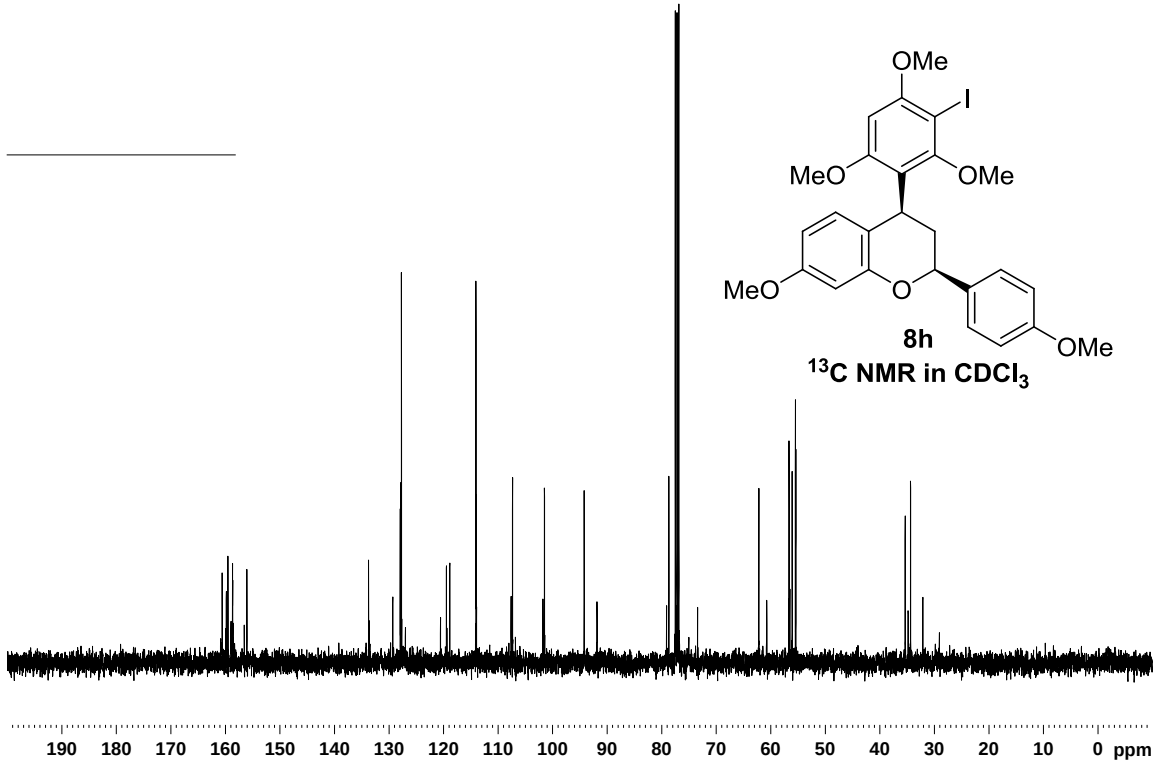


Fig. 23 ^{13}C NMR Spectrum of chroman 8h

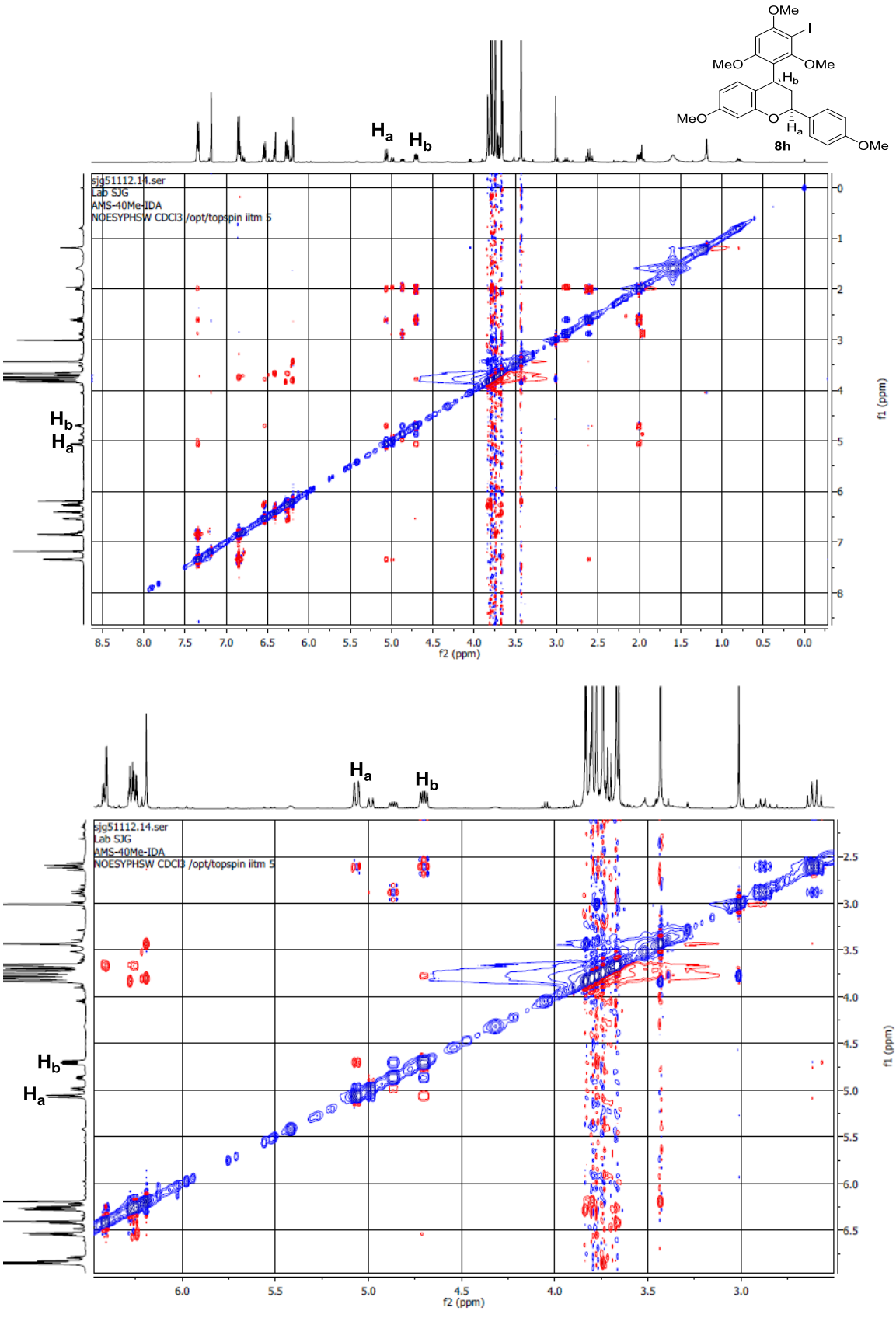


Fig. 24 NOESY Spectrum of chroman 8h

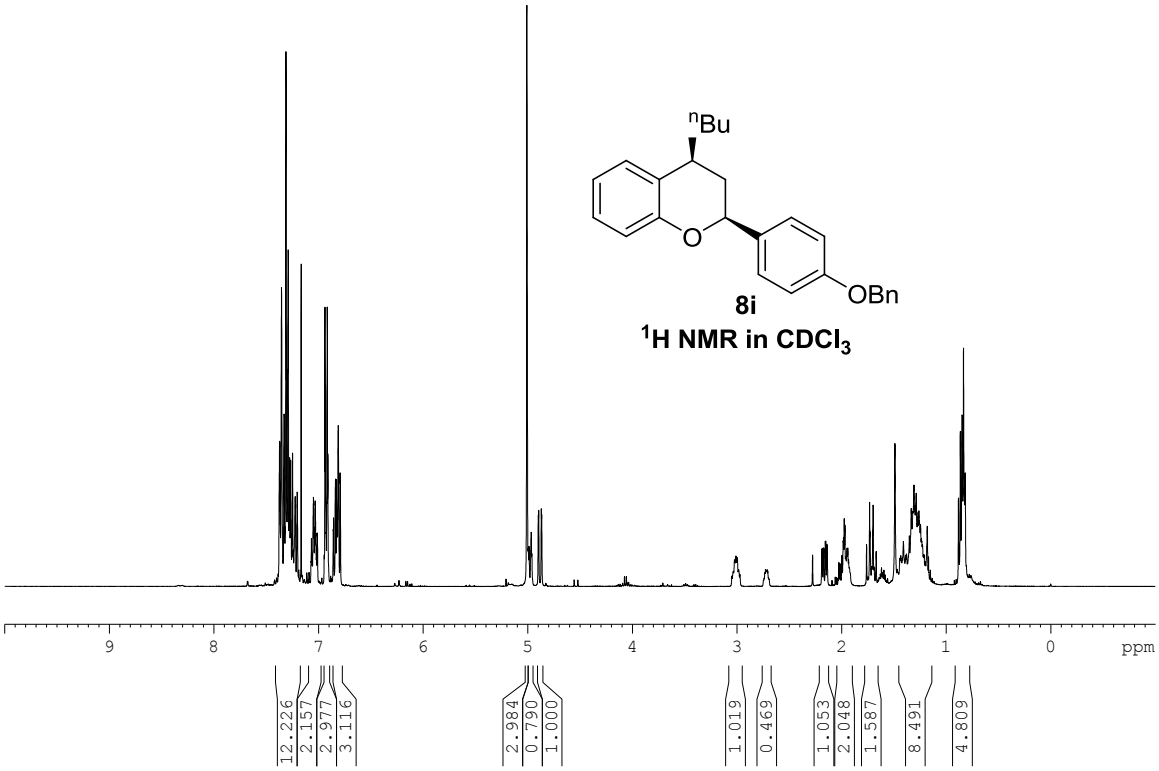


Fig. 25 ^{1}H NMR Spectrum of chroman 8i

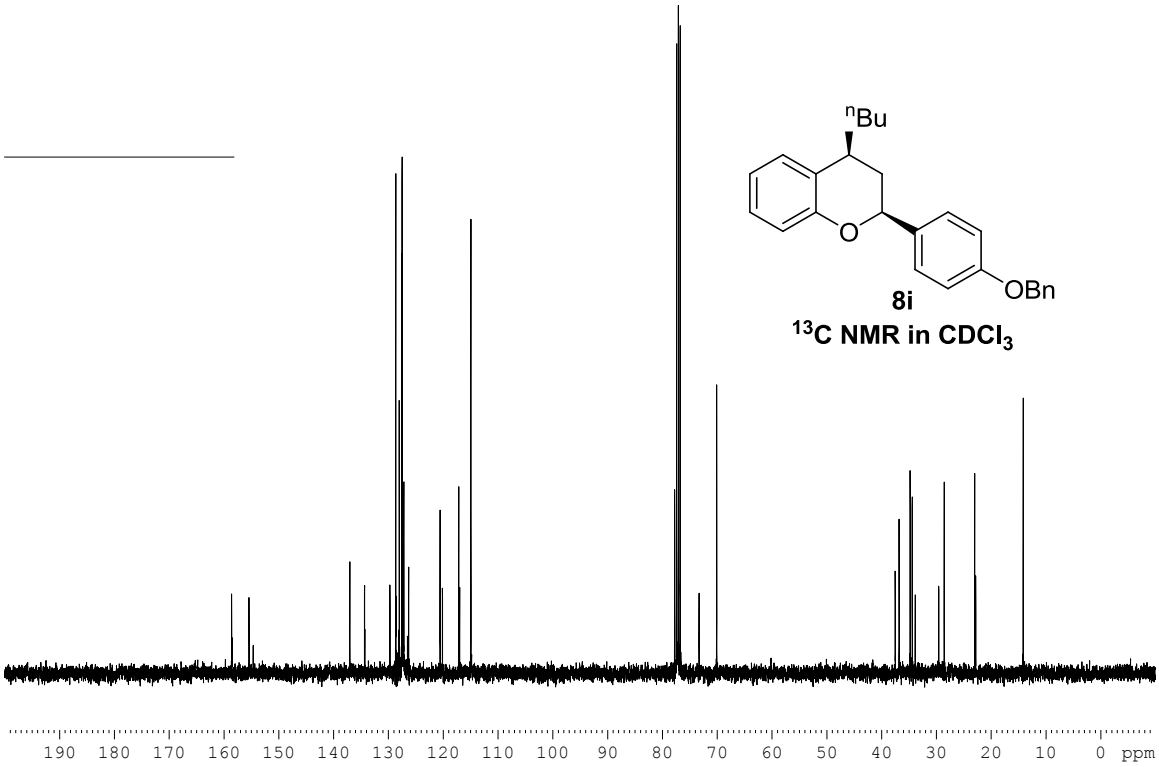


Fig. 26 ^{13}C NMR Spectrum of chroman 8i

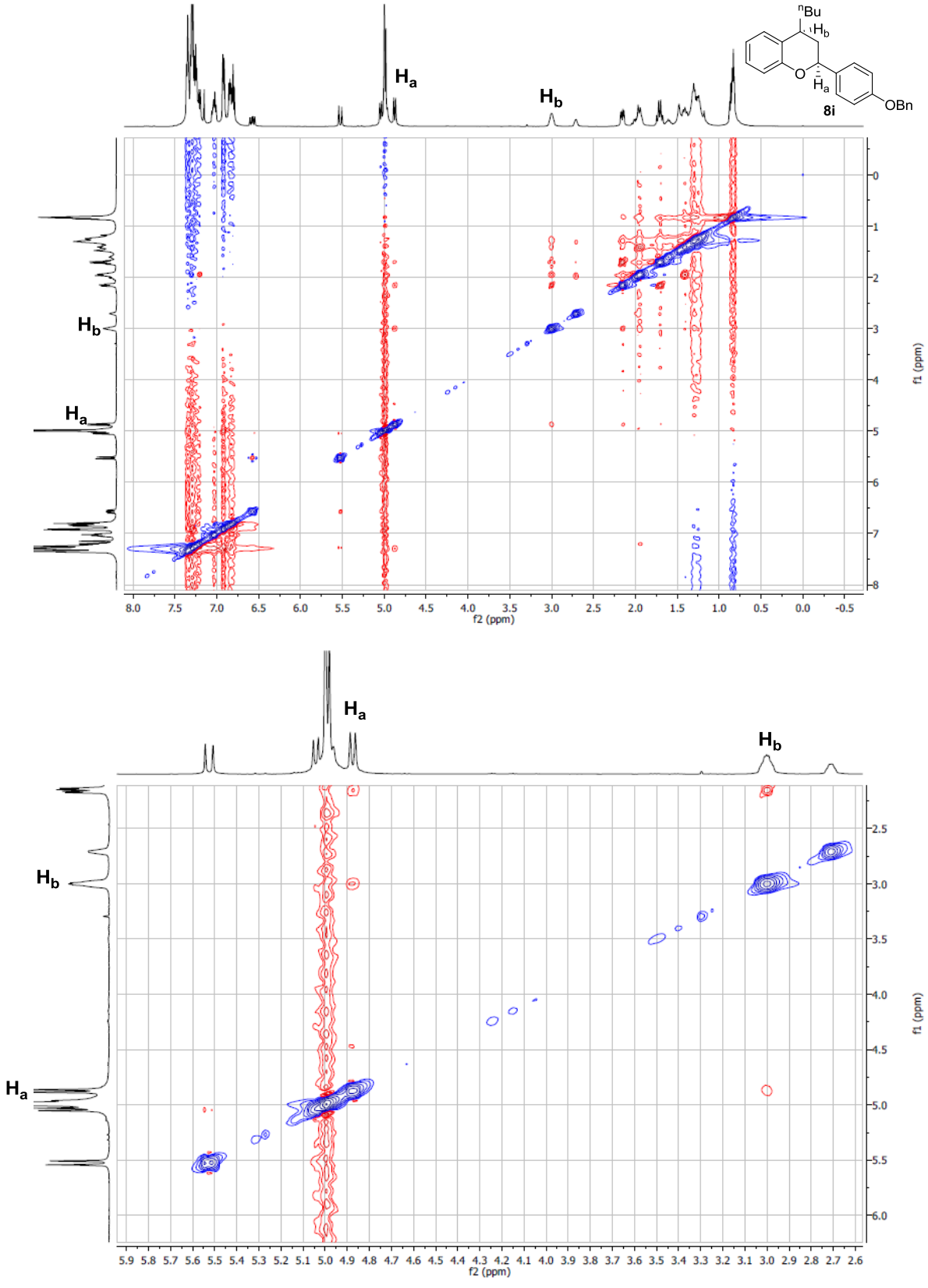


Fig. 27 NOESY Spectrum of chroman 8i

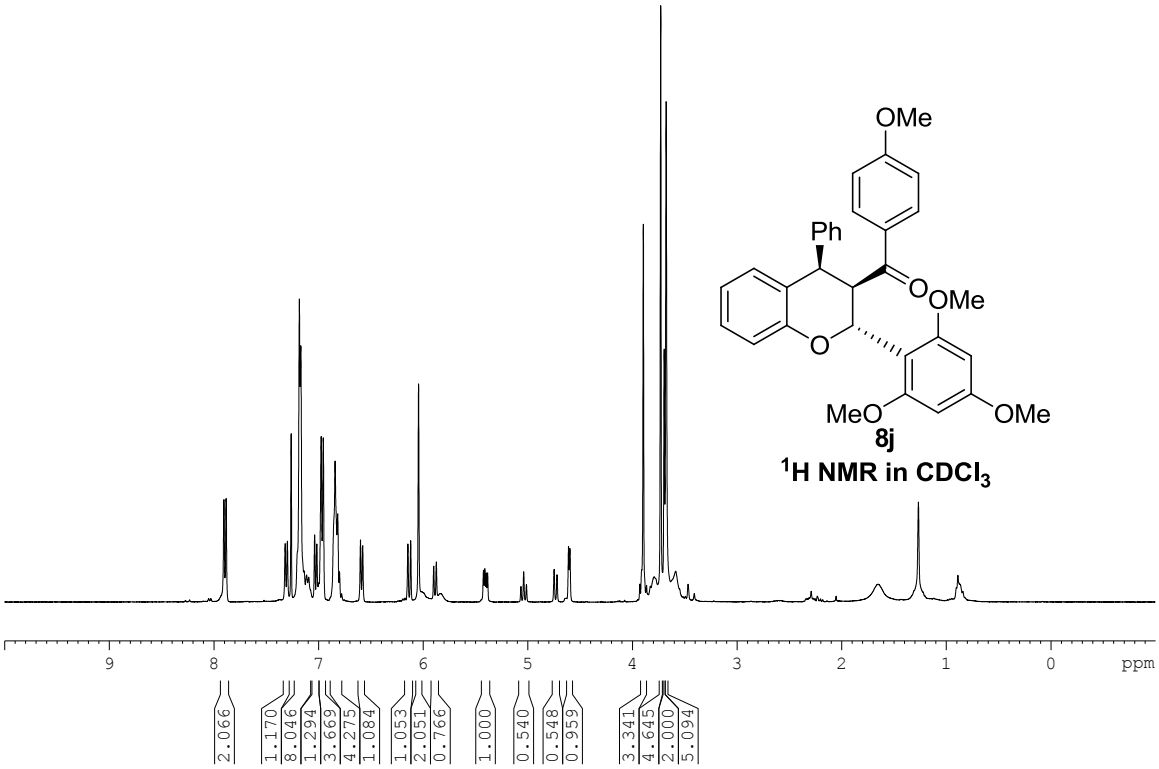


Fig. 28 ^{1}H NMR Spectrum of chroman 8j

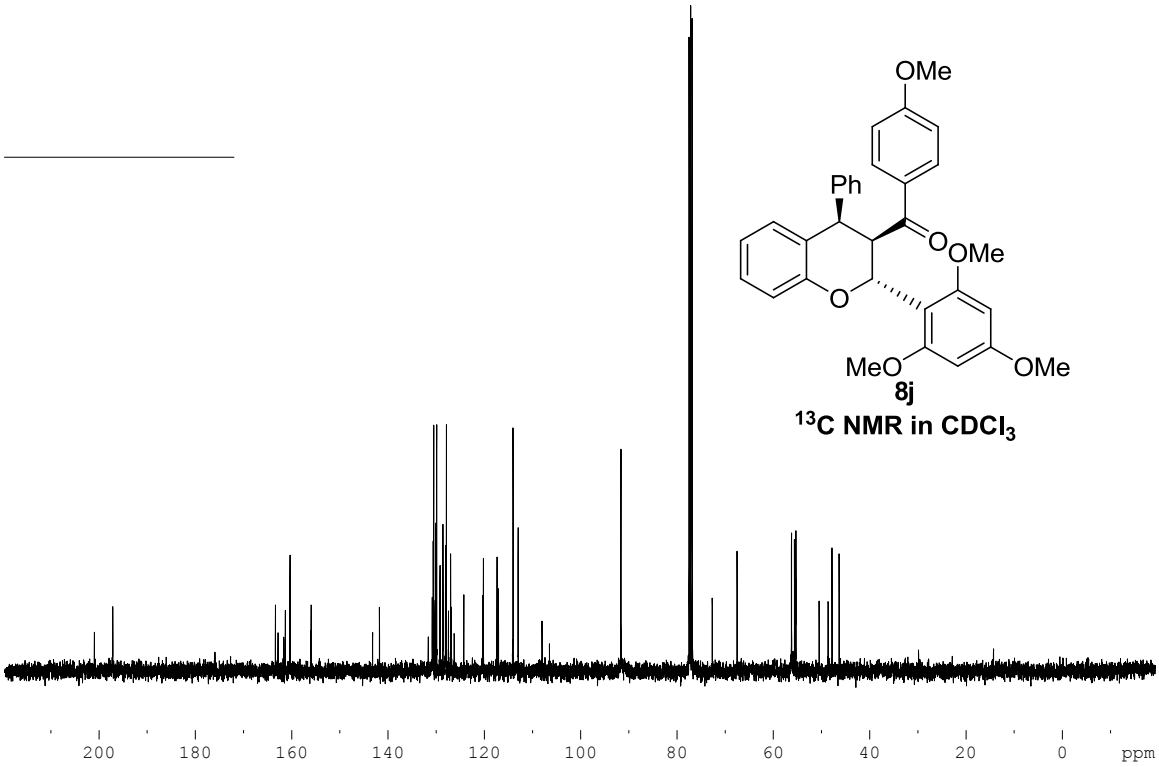


Fig. 29 ^{13}C NMR Spectrum of chroman 8j

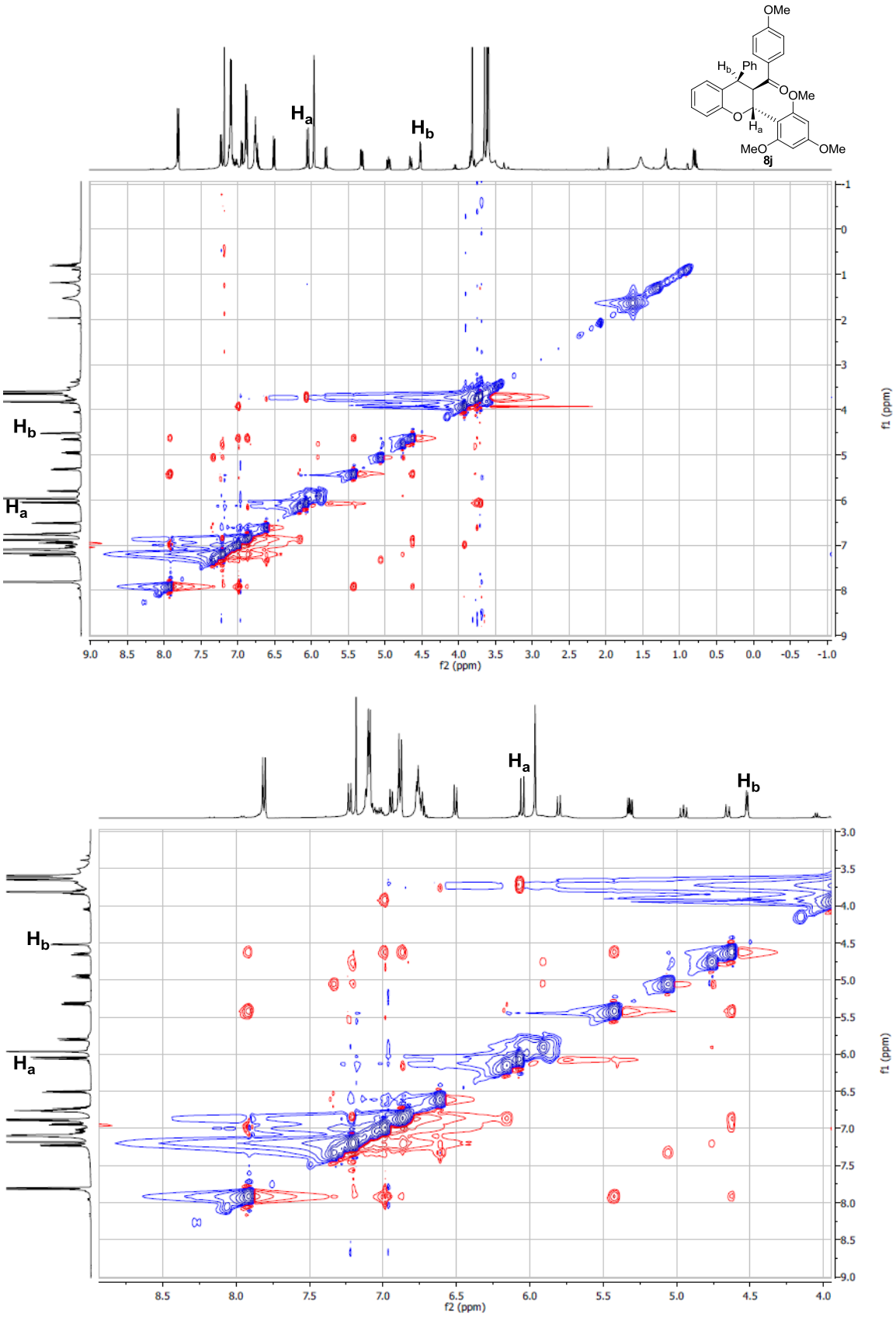


Fig. 30 NOESY Spectrum of chroman 8j

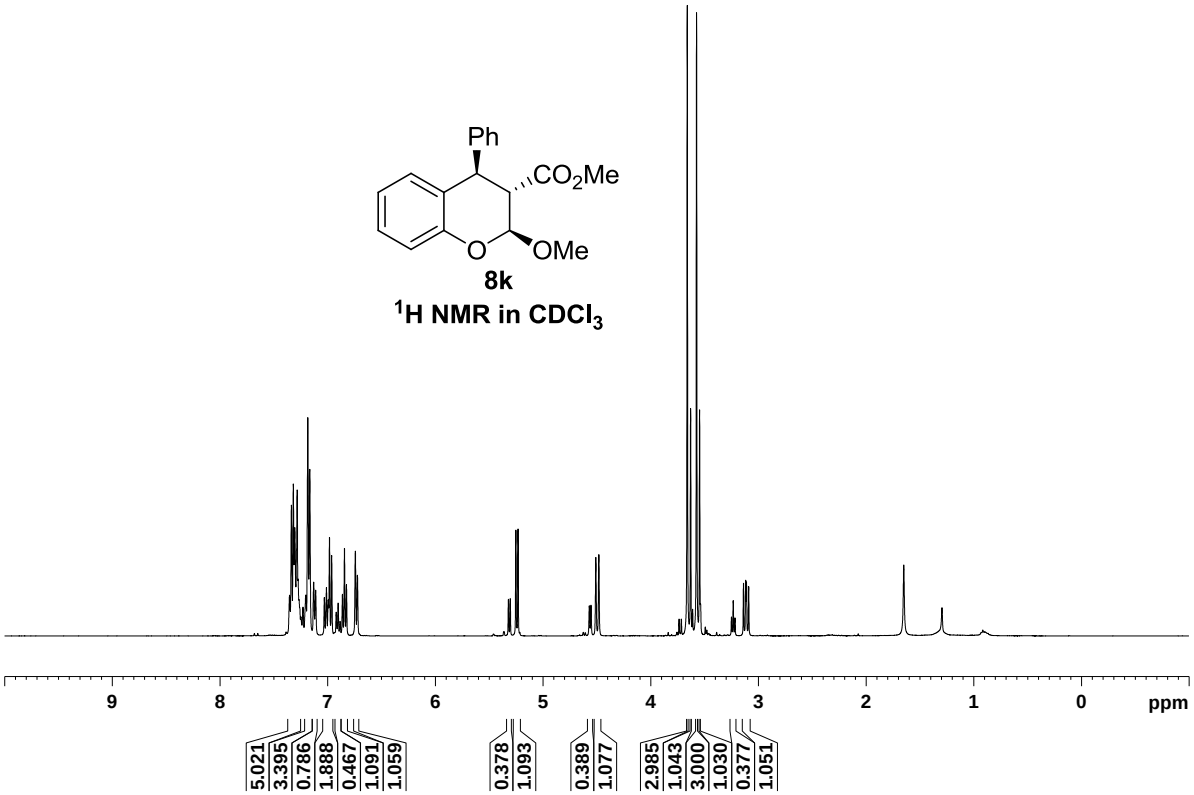


Fig 31 ^{1}H NMR spectrum of acetal 8k

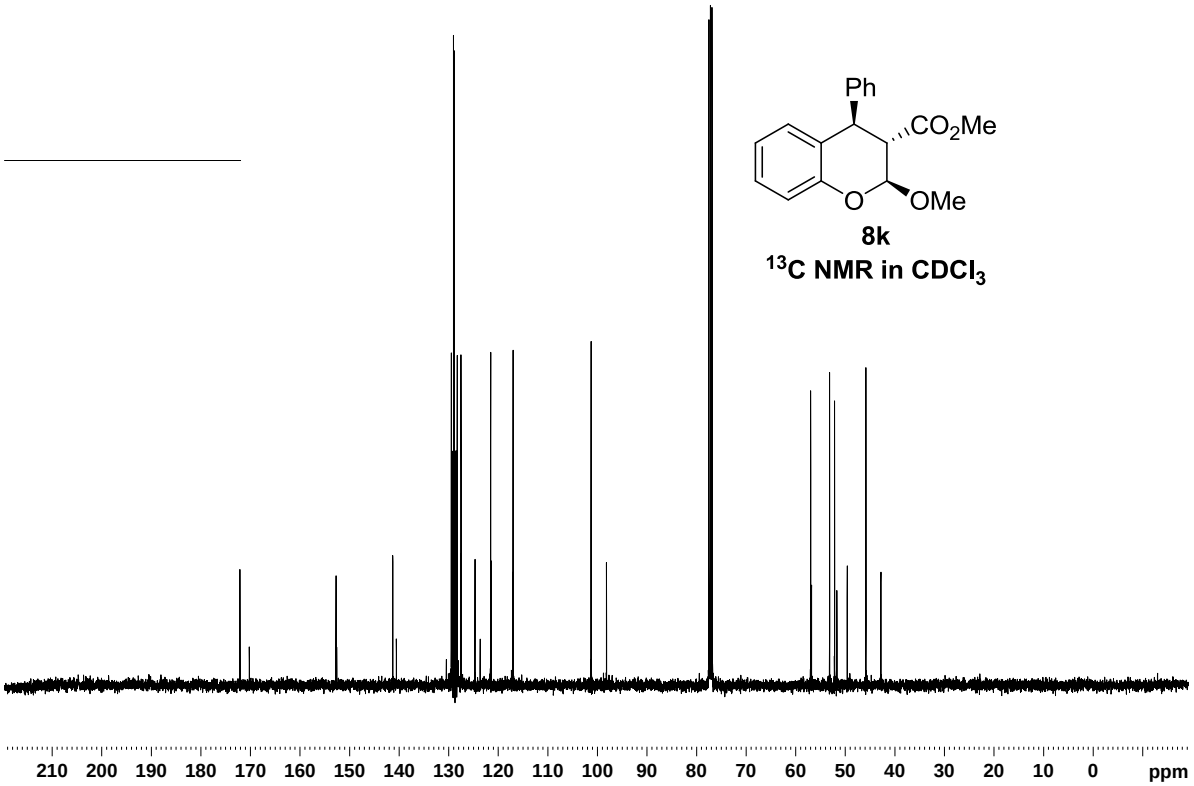


Fig 32 ^{13}C NMR spectrum of acetal 8k

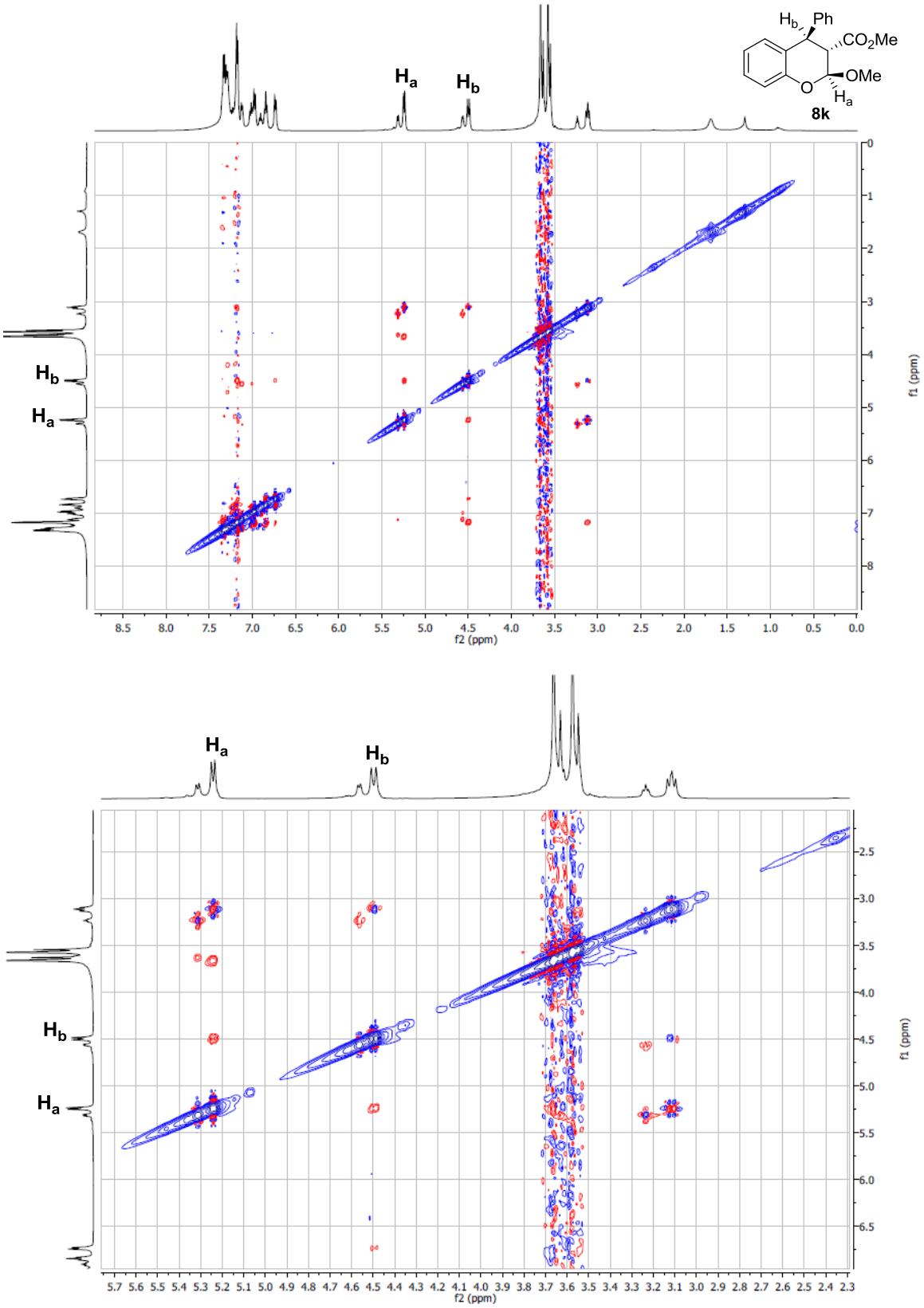


Fig. 33 NOESY Spectrum of acetal 8k

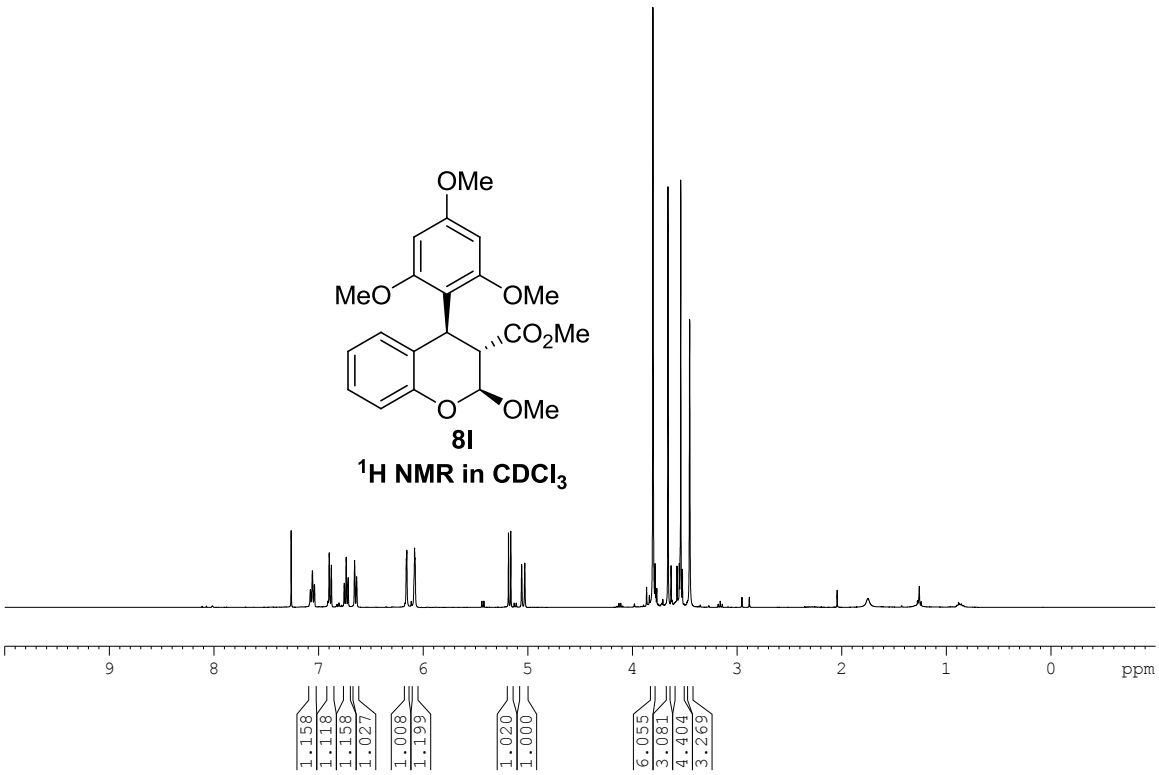


Fig. 34 ^{1}H NMR Spectrum of acetal 8l

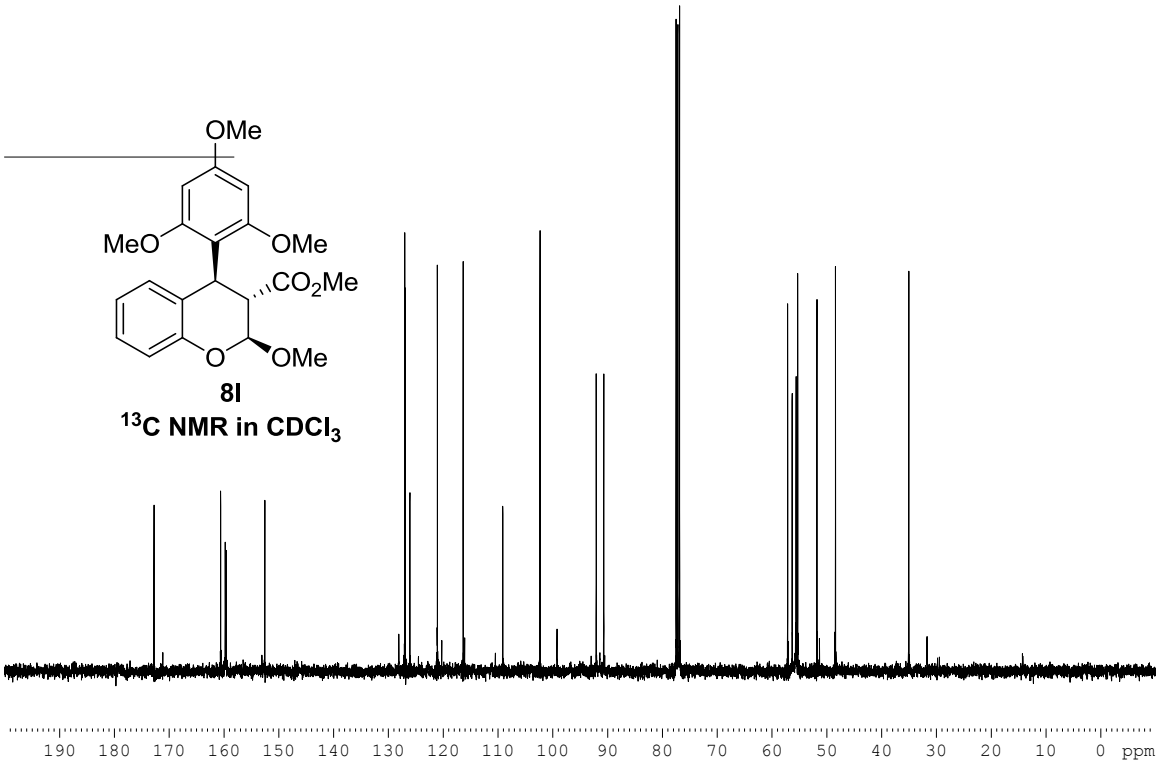


Fig. 35 ^{13}C NMR Spectrum of acetal 8l

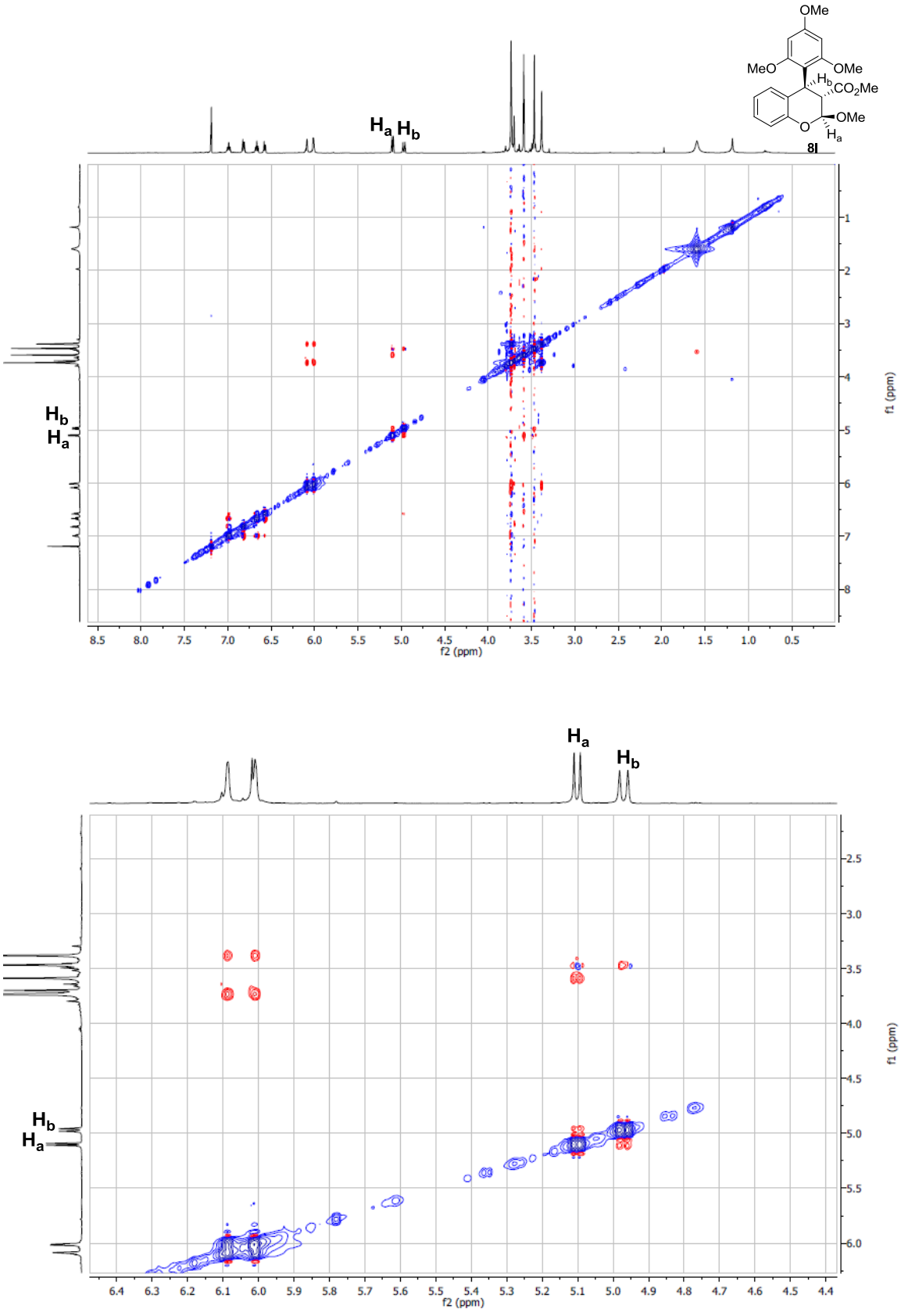


Fig. 36 NOESY Spectrum of acetal 8l

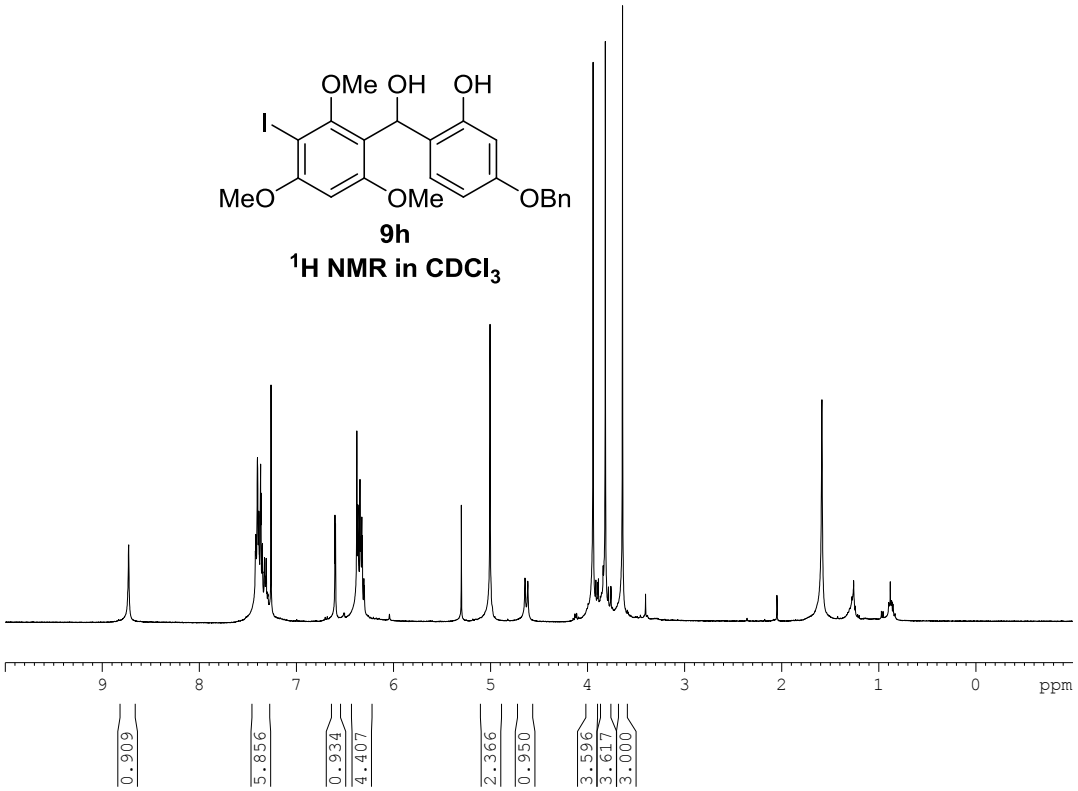


Fig. 37 ^{1}H NMR Spectrum of alcohol 9h

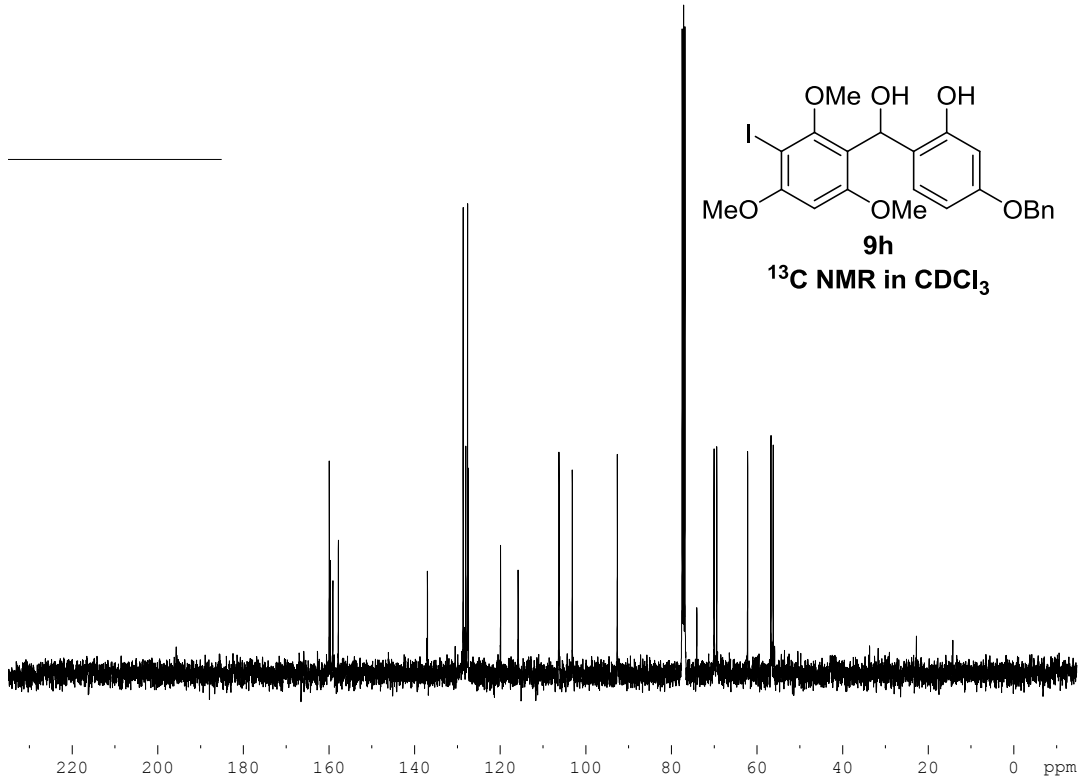


Fig. 38 ^{13}C NMR Spectrum of alcohol 9h

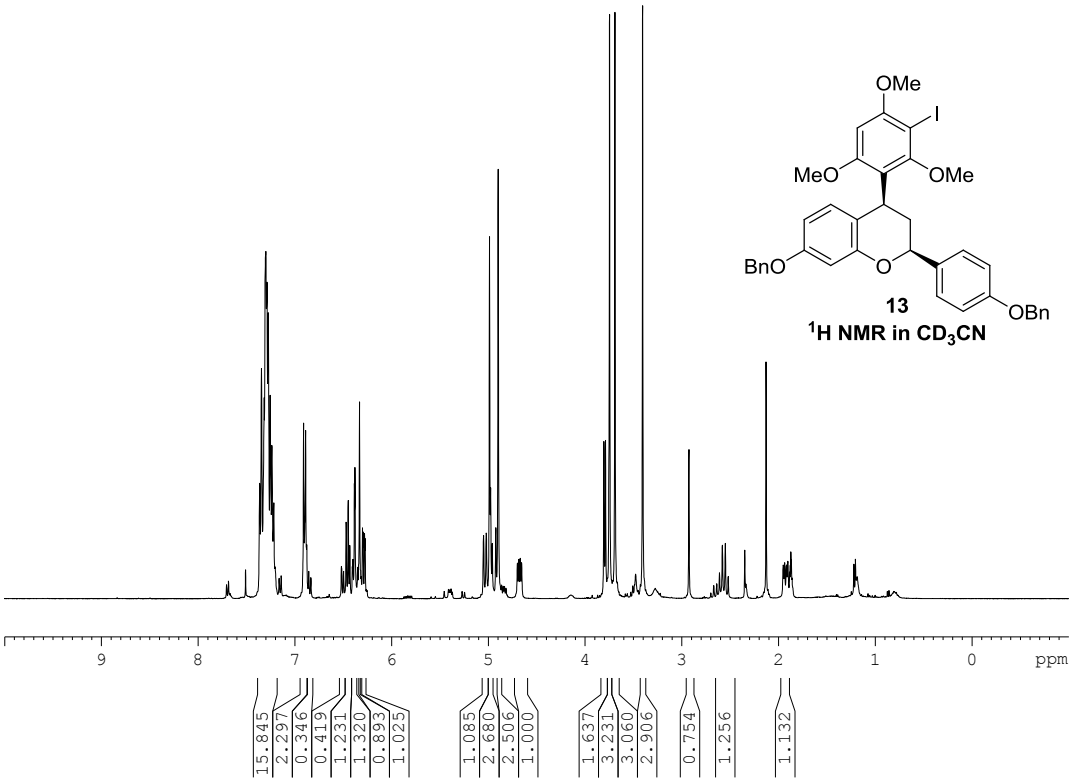


Fig. 39 ^{1}H NMR Spectrum of chroman 13

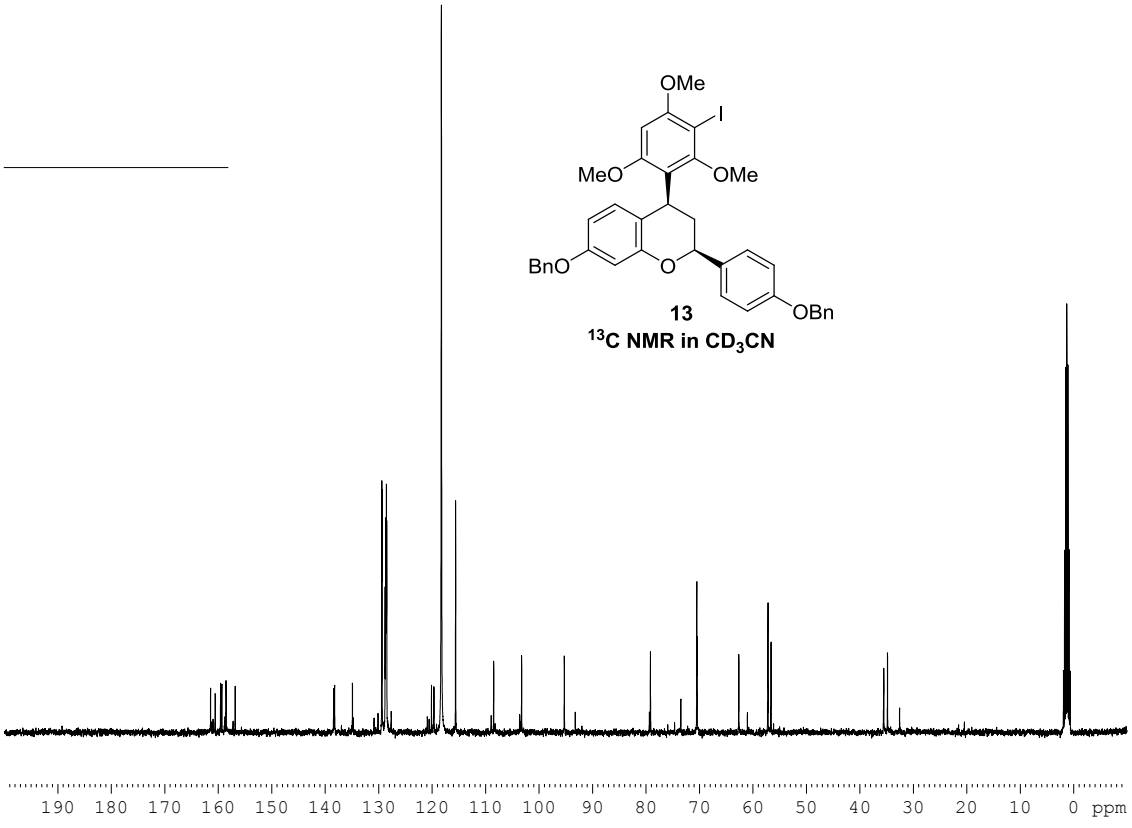


Fig. 40 ^{13}C NMR Spectrum of chroman 13

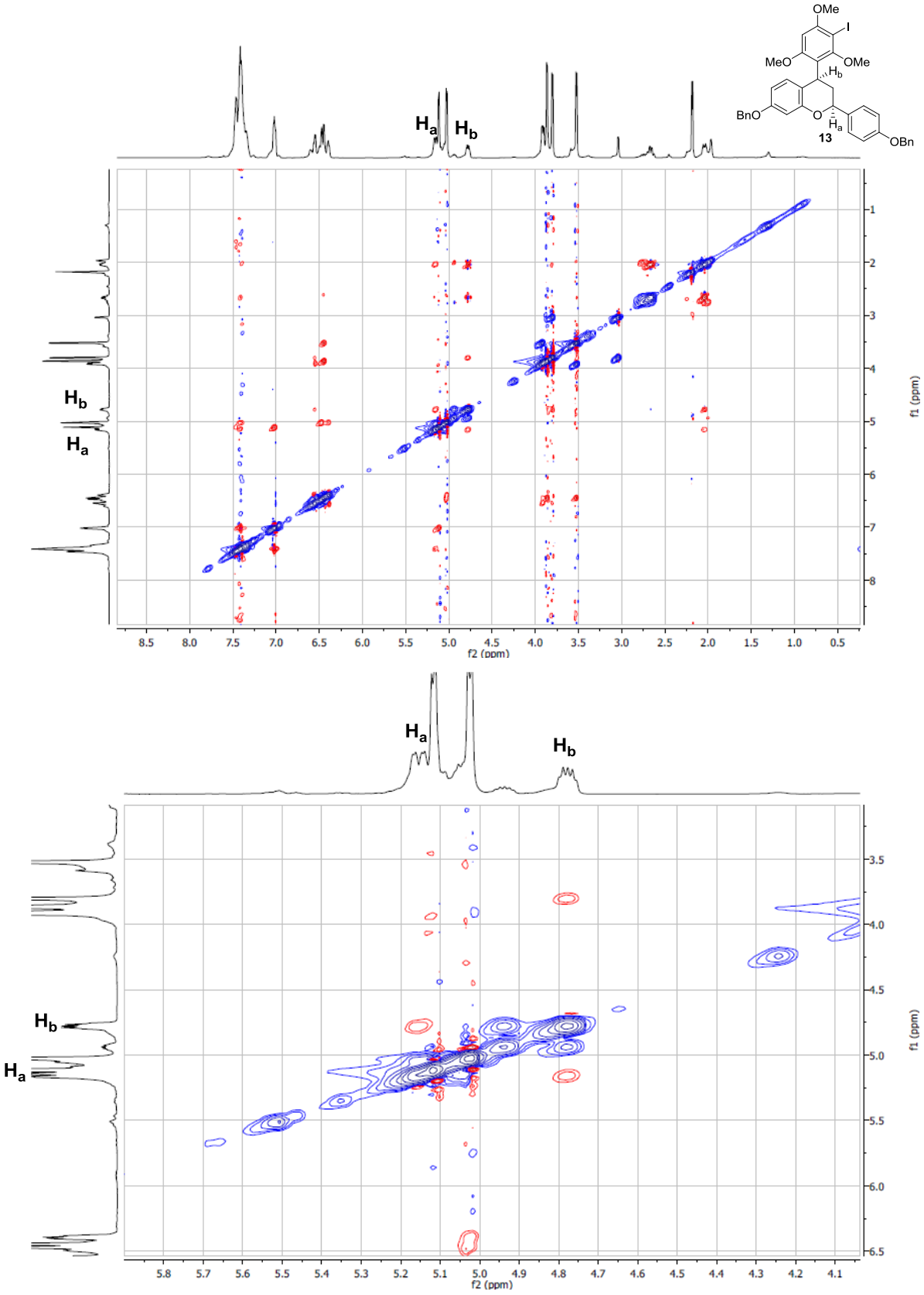


Fig. 41 NOESY Spectrum of chroman 13

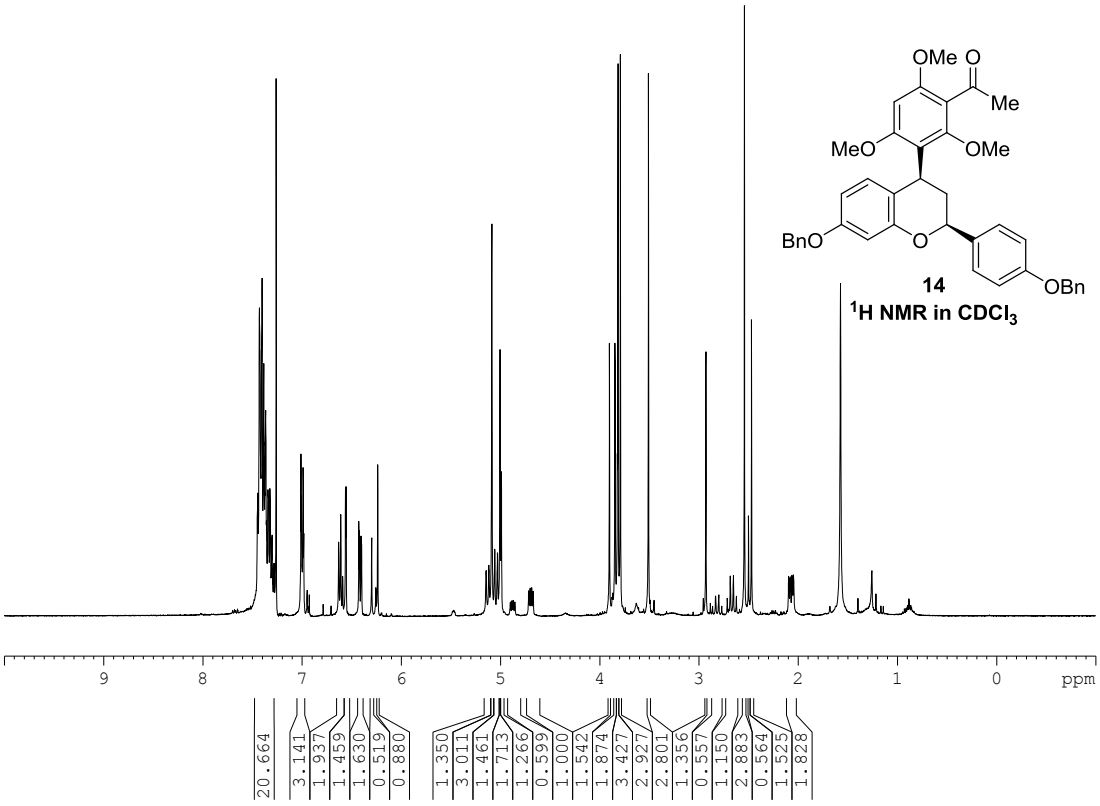


Fig. 42 ^{1}H NMR Spectrum of ketone 14

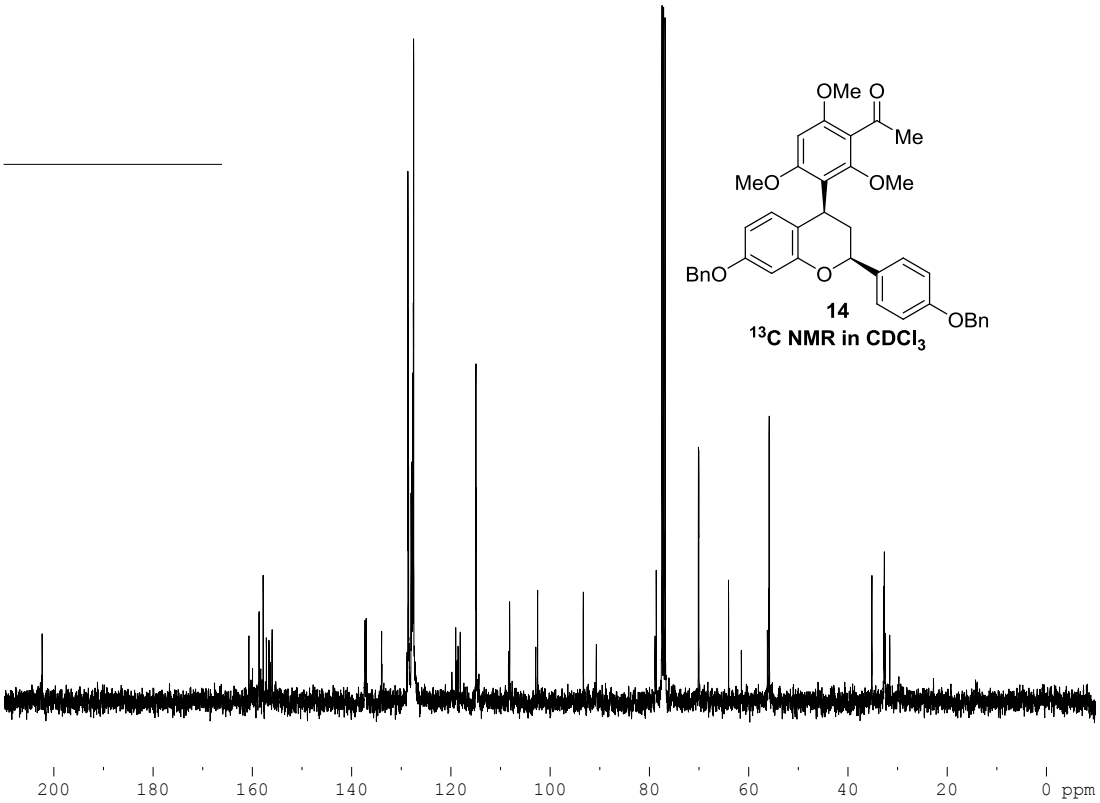


Fig. 43 ^{13}C NMR Spectrum of ketone 14

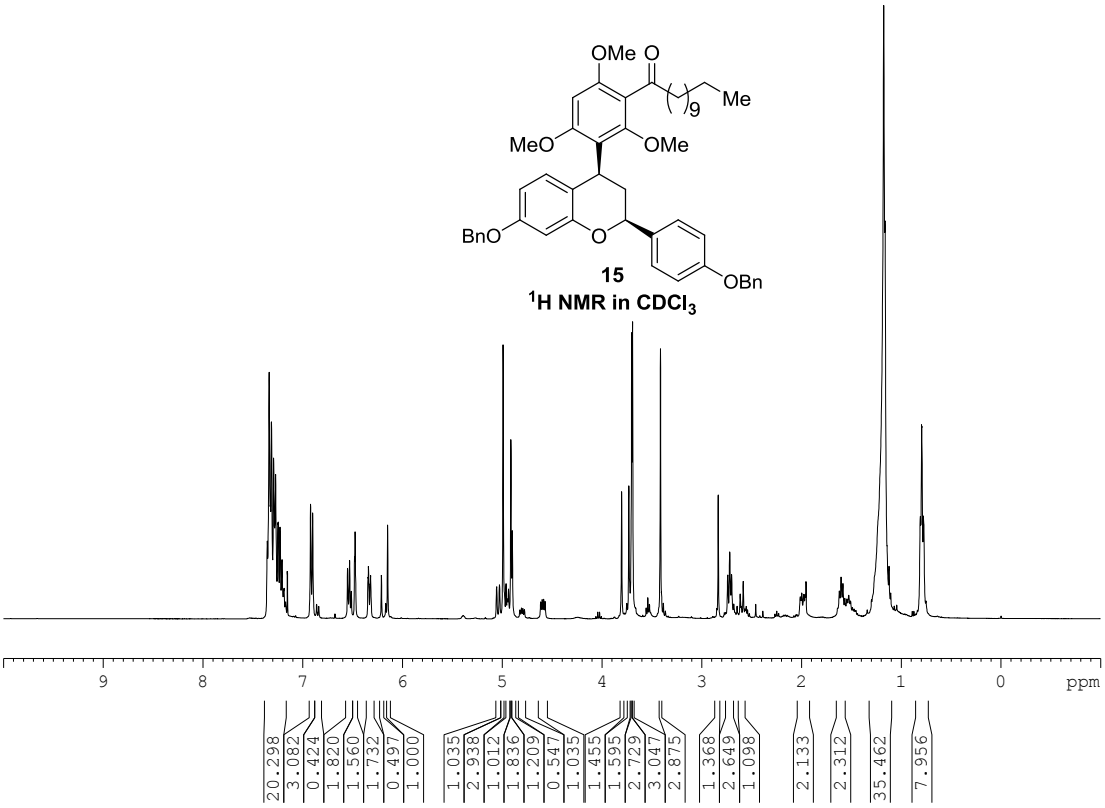


Fig. 44 ^{1}H NMR Spectrum of ketone 15

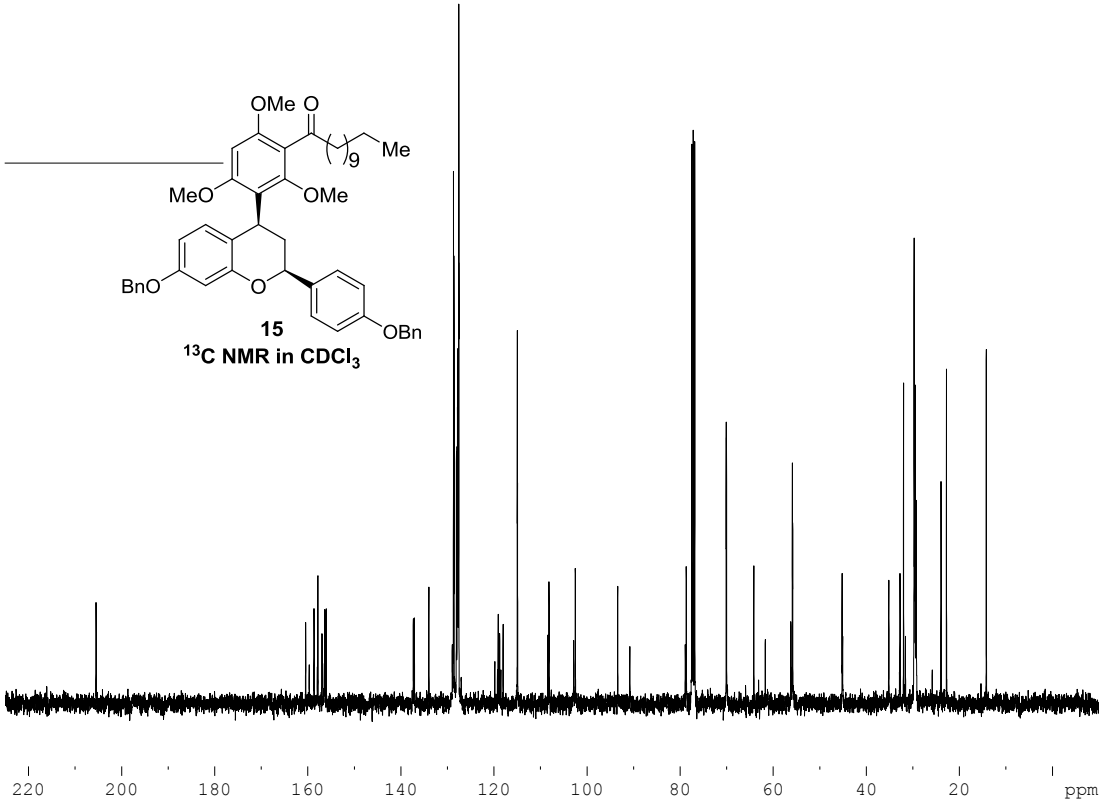


Fig. 45 ^{13}C NMR Spectrum of ketone 15