

Multicomponent Condensation Reactions via ortho- Quinone Methides

Emily E. Allen, Calvin Zhu, James S. Panek, and Scott E. Schaus*

*Department of Chemistry and Center for Molecular Discovery (BU-CMD),
Life Sciences and Engineering Building, Boston University,
24 Cummington Mall, Boston, Massachusetts 02215, United States*

Supporting Information

Table of Contents

I. General Information	S3
Instrumentation and Methods	S3
Solvents and Reagents	S3
II. Experimental procedures and characterization	S4
General Experimental Procedures for Starting Materials	S4
General Experimental Procedure for the reaction of Hydroxybenzyl Alcohols and Olefins. S6	
General Experimental Procedure for MCR of phenols, aldehydes and dienophiles	S6
General Experimental Procedure for MCR of phenols, acetals and dienophiles	S7
Additional Experiments	S8
Compound synthesis and characterization	S10
Selected Spectra	S35

I. General Information

A. Instrumentation and Methods

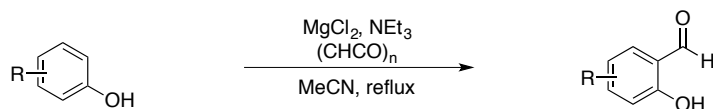
All ^1H NMR and ^{13}C NMR spectra were recorded using a Agilent 500 MHz VNMR spectrometer featuring a Varian ultra shielded magnet at ambient temperature in CDCl_3 unless otherwise noted. Select ^1H NMR and ^{13}C NMR spectra were recorded on a Agilent 400 MHz VNMR unity plus spectrometer with an Oxford Instruments superconducting magnet. Chemical shifts were reported in parts per million relative to the CDCl_3 as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constants and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm at 25°C, and were reported as $[\alpha]_D^{25}$ (concentration). Optical rotations for benzopyran substrates were reported as diastereomeric mixtures. High-resolution mass spectra were obtained using a Waters Q-TOF API US by electrospray (ESI) at the Boston University Chemical Instrumentation Center. Mass correction was done by an external reference using a Waters Lockspray accessory. This mass spectrometer was purchased with funding from the National Science Foundation (CHE 0443618). Analytical thin layer chromatography (TLC) was performed using SORBTECH 0.25 mm Silica Gel HL TLC Plates w/UV 254. Flash chromatography was performed using ZEOprep 60 ECO 40-63 μm ZEOCHEM silica gel or Sigma Aldrich Alumina Oxide. All reactions were run in oven-dried glassware with magnetic stirring.

B. Chemical reagents and Solvents

HPLC grade toluene, methylene chloride, diethyl ether and tetrahydrofuran were purchased from Fischer and Sigma Aldrich and were dried by passing through a Solvent Purification System. Chloroform purchased from Pharmco-AAPER was used for the multicomponent reactions. Anhydrous chloroform stabilized with amylenes purchased from Sigma Aldrich was used for the two component diol reactions. Reagents were purchased from Sigma Aldrich, Strem, Alfa Aesar and TCI America and were used without further purification unless otherwise noted.

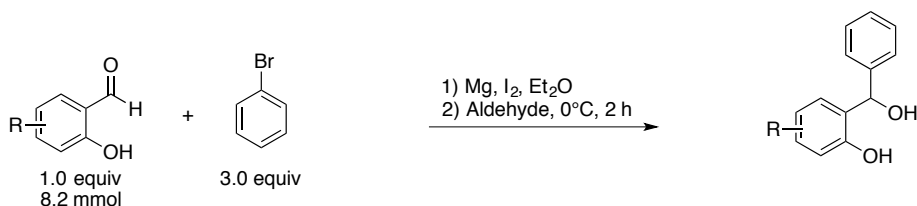
II. Experimental procedures and characterization

Representative procedure for the preparation of salicylaldehyde derivatives:



An oven dried round bottom flask equipped with a magnetic stir bar was charged with phenol (5 mmol) sealed with a rubber septa and flushed with N_2 . The material was dissolved in 25 mL of dry MeCN. After dissolution, MgCl_2 (7.5 mmol, 1.5 eq.), and NEt_3 (18.75 mmol, 3.75 eq.) were added sequentially, at which time, paraformaldehyde (33.75 mmol, 6.75 eq.) was added. The solution was heated to reflux and monitored by TLC. After completion the reaction flask was cooled to room temperature and quenched with a 10% HCl (aq) solution. The biphasic reaction was extracted with 3 x 15 mL diethyl ether. The combined extracts were washed with saturated sodium chloride. The organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated by rotary evaporation. The crude product was purified by column chromatography over SiO_2 with 99:1 to 97:3 hexanes:EtOAc.¹

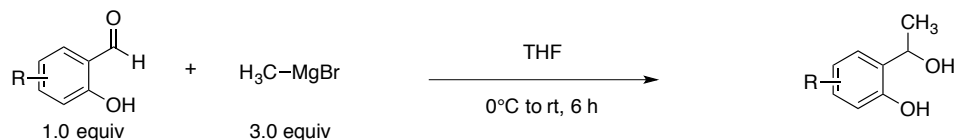
General procedure for the diol preparation from salicylaldehyde derivatives with bromobenzene:



An oven dried flask equipped with a magnetic stir bar was charged with Mg turnings (0.717 g, 29.9 mmol), and an iodine crystal. The round bottom was fitted with an oven dried reflux condenser and anhydrous diethyl ether (8.2 mL) was added. The mixture stirred for 5 minutes, and was treated dropwise with bromobenzene (2.45 mL, 24.6 mmol, 3 equiv). The Grignard mixture was allowed to stir at room temperature for 30-45 minutes. A solution of salicylaldehyde (8.2 mmol, 1 equiv) in 41 mL of diethyl ether was added to the Grignard mixture slowly at 0°C . The reaction was monitored by TLC until completion and was quenched with NH_4Cl (aq) (30 mL). The reaction mixture was extracted with 2 x 30 mL Ether. The combined organic extracts were washed with brine, and dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography over SiO_2 with 85:15 hexanes:EtOAc. The product was a white powder-like solid. Diols were stored under argon in an -80°C freezer.

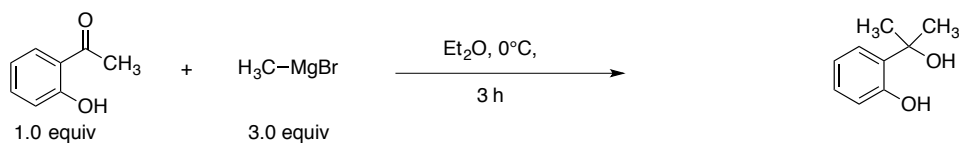
¹ Moon, N.G.; Harend, A.M.; *Org. Lett.*, **2015**, *17*, 2218–2221.

General procedure for the diol preparation from salicaldehyde derivatives with methylmagnesium bromide:



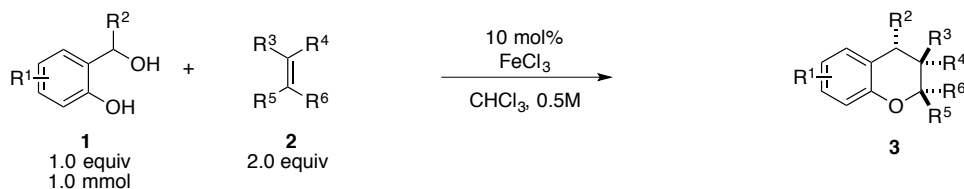
An oven dried round bottom flask equipped with a magnetic stir bar was charged with methyl magnesium bromide (3.0 equiv., 3.0 M in THF) and cooled to 0 °C in an ice bath. A solution of aldehyde (1.0 g) in 36 mL dry THF was added slowly over 15 min. After 6 hours, the reaction was quenched with saturated NH₄Cl. The biphasic solution was extracted twice with ether. The combined organic extracts were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated. The crude product was purified by flash chromatography with SiO₂ and eluted with 100 to 80:20 hexanes:EtOAc.

General procedure for the geminal diol preparation:



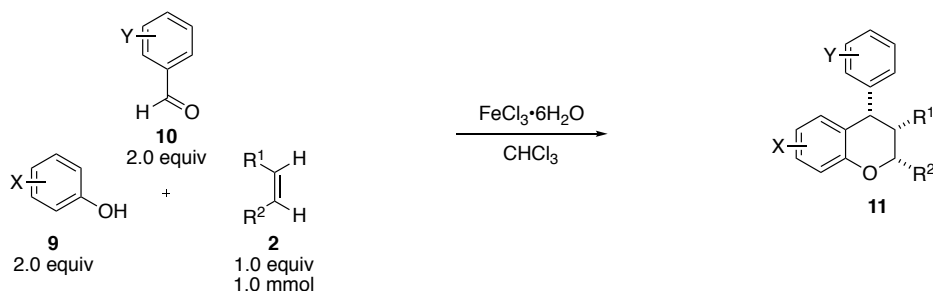
An oven dried flask equipped with a stir bar was charged with methyl-magnesium bromide (7.34 mL, 29.4 mmol, 3.0 M in diethyl ether). A solution of 2-hydroxy acetophenone (884 μL, 7.34 mmol, 1 equiv), dissolved in 36.7 mL of diethyl ether, was added to the Grignard at 0 °C. Upon reaction completion, the reaction was quenched with NH₄Cl (35 mL) at 0 °C. The biphasic solution was extracted with 2 x 20 mL ether. Combined organic extracts were washed with brine and dried over anhydrous Na₂SO₄. The product was filtered, concentrated under reduced pressure and was used without further purification. The product is an off-white to yellow solid. The diols were stored under argon in a -80 °C freezer.

General procedure for the two-component reaction of diols and dienophiles to afford benzopyrans:



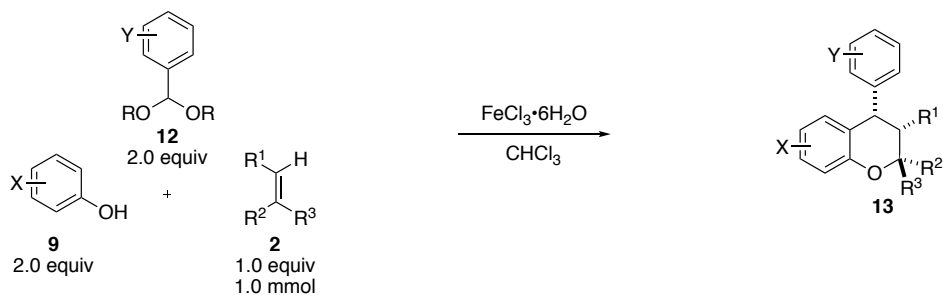
To an oven dried flask equipped with a magnetic stir bar was added diol (1.0 mmol, 1 equiv), dienophile (2.0 mmol, 2 equiv), anhydrous chloroform stabilized with amylene 2.0 mL, and lastly anhydrous FeCl₃ (16 mg, 10 mol% with respect to diol). The reaction vessel was capped with a septa and parafilm. The reactions were monitored by TLC. TLC conditions: silica plate, eluted with 85:15 hexanes:EtOAc and stained with cerium ammonium nitrate stain. Upon consumption of the limiting reagent, the reactions were quenched with a basic aqueous workup with saturated sodium bicarbonate. Extracted with 3 x 30mL EtOAc, combined organic layers were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purified by flash chromatography with SiO₂ and ethyl acetate in hexanes.

General procedure for the multicomponent reaction of phenols, aldehydes and dienophiles to afford benzopyrans:



To an oven dried flask equipped with a magnetic stir bar was added phenol (2.0 mmol, 2 equiv), aldehyde (2.0 mmol, 2 equiv), dienophile (1.0 mmol, 1 equiv), chloroform 2.0 mL, and lastly FeCl₃•6H₂O (54 mg, 10 mol% with respect to phenol). The reaction vessel was capped with a septa, parafilm and monitored by TLC. Generally monitored with 90:10 or 85:15 hexanes:EtOAc. Upon consumption of the limiting reagent, the reactions were quenched with a basic aqueous workup with saturated sodium bicarbonate. Extracted with 3 x 30 mL chloroform, combined organic layers were rinsed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. Purified by flash chromatography with SiO₂ and ethyl acetate in hexanes.

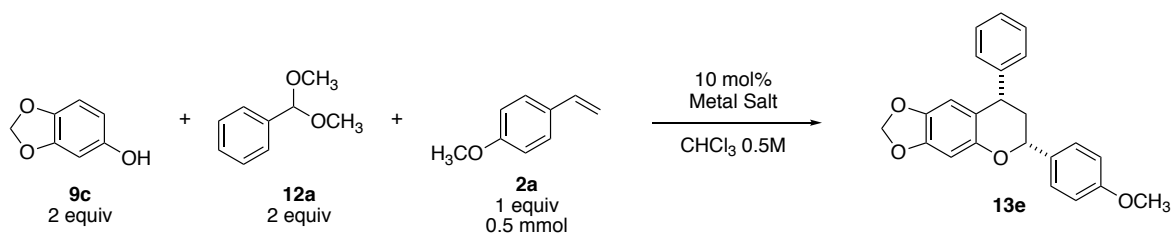
General procedure for the multicomponent reaction of phenols, acetals and dienophiles to afford benzopyrans:



To an oven dried flask equipped with a magnetic stir bar was added phenol (2.0 mmol, 2 equiv), aldehyde (2.0 mmol, 2 equiv), dienophile (1.0 mmol, 1 equiv), chloroform 2.0 mL, and lastly FeCl₃•6H₂O (54 mg, 10 mol% with respect to phenol). The reaction vessel was capped with a septa, parafilm and monitored by TLC. Generally monitored with 90:10 or 85:15 hexanes:EtOAc. Upon consumption of the limiting reagent, the reactions were quenched with a basic workup with saturated sodium bicarbonate. Extracted with 3 x 30 mL chloroform, combined organic layers were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purified by flash chromatography over SiO₂ and ethyl acetate in hexanes.

Additional Experiments

Multicomponent Reaction: Catalyst Optimization^a



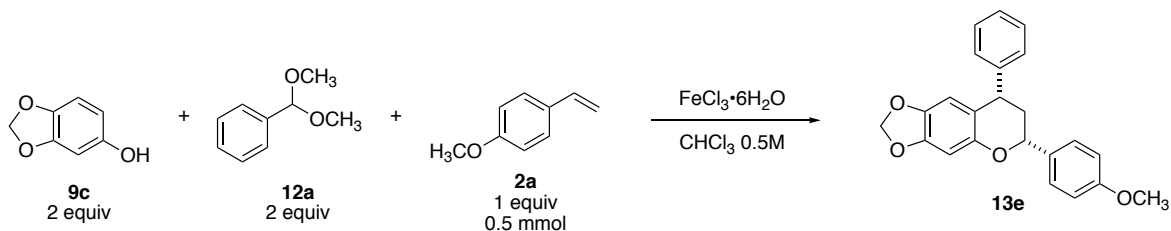
entry	metal salt	time (h)	temp	yield ^b	dr ^c
1	FeCl ₃	2	rt	53%	3:1
2	FeCl ₃ •6H ₂ O	1	rt	50%	3:1
3	FeCl ₃ •6H ₂ O	2	rt	56%	5:1
4	FeCl ₃ •6H ₂ O	5	rt	54%	5:1
5	FeCl ₃ •6H ₂ O	5	4°C	53%	3:1
6	FeCl ₃ •6H ₂ O	10	rt	56%	4:1
7	Sc(OTf) ₃	2	rt	58%	5:1
8	Cu(OTf) ₂	2	rt	49%	3:1
10	RuCl ₃ •H ₂ O	2	rt	46%	4:1
11	ZrCl ₄	2	rt	25%	3:1
12	IrCl ₃	2	rt	<4%	--

^aReactions conditions: 1.0 mmol sesamol, 1.0 mmol acetal and 0.5 mmol styrene, 0.5M with respect to styrene and 10 mol% with respect to sesamol, ^bisolated yields, ^cdiastereomeric ratio determined by ¹H NMR.

Note: Additional reaction pathways from this substrate combination were identified. *p*-Methoxy styrene is very electron-rich and it is able to nucleophilically attack the benzaldehyde oxonium ion directly. An equivalent of methanol can trap the carbocation leading to a diastereomeric mixture of undesired side products. A gold mediated reaction of styrenes and aryl acetals has been reported in the literature.² Additionally, *p*-methoxy styrene can polymerize. Although this reaction can be heated, a greater product yield was isolated at room temperature. These side products were only observed when *p*-methoxy styrene was used as the dienophile likely due to its electron-rich nature and ability to stabilize a secondary carbocation through resonance.

² Dong, W.; Zhang, M.; Xiao, F.; Wang, Y.; Liu, W.; Hu, X.;* Yuan, Q.; Zhanga, S. *Synlett*, **2012**, 23, 2799–2802.

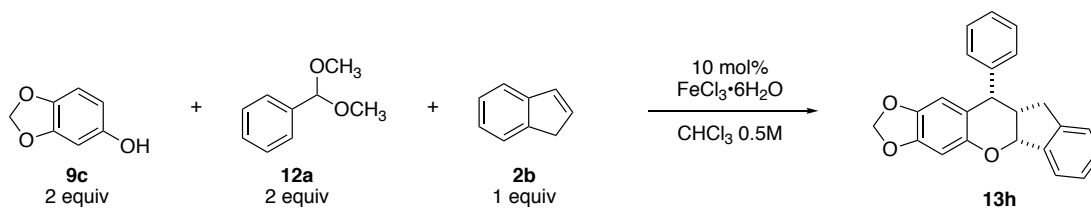
Multicomponent Reaction: Catalyst Loading



Entry	Catalyst Loading	Time	Yield	dr
1	20 mol%	2 h	60%	4:1
2	10 mol%	2 h	56%	5:1
3	5 mol%	4 h	51%	5:1
4	2.5 mol%	6 h	53%	5:1

The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reactions were run at 0.5 mmol scale and 0.5M concentration with respect to dienophile. The catalyst loading is respect to phenol. Reported yields are isolated yields after flash chromatography over SiO_2 and dr is the diastereomeric ratio determined by ^1H NMR.

Multicomponent Reaction: Scale Up

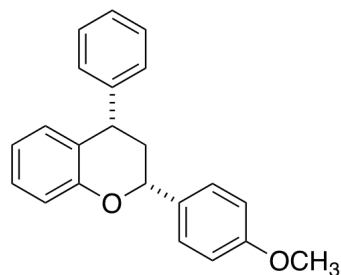


Entry	Scale	Time	Yield	dr	Yield (trituated)	dr (trituated)
1	1.0 mmol	6 h	86%	6:1		
2	3.0 mmol	6 h	79%	4:1	60%	single
3	3.0 mmol	24 h			73%	9:1
4	9.0 mmol	24 h	71%	3:1	64%	5:1

The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reactions were run at 60 °C, 0.5M concentration with respect to dienophile. The catalyst loading is 10 mol% with respect to phenol. The reactions were purified by flash chromatography and afforded a white solid. The solid could be further purified by trituration in hot hexanes.

Compound synthesis and characterization

2-(4-methoxyphenyl)-4-phenylchromane (3a):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction was run at 0 °C in an ice bath for two hours and allowed to stir at room temperature for an additional two hours. The reaction was monitored by TLC with conditions: 15% Ethyl Acetate in Hexanes, stained with CAM, silica plate. The reaction was quenched with a basic workup with saturated sodium bicarbonate and extracted with 3x30mL CHCl₃. The combined organic layers were rinsed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude reaction was purified by flash chromatography, packed with silica and eluted with 98:2 Hexanes:EtOAc. **(3a)** was isolated as a white solid, in 81% yield, 0.2562 g, 0.810mmol, 3:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.41 (d, J = 9.0 Hz, 2H), 7.32 (dd, J = 7.5, 7.5 Hz, 2H) 7.27-7.22 (m, 3H), 7.12 (dd, J = 1.5, 8.5 Hz, 1H), 6.93 (dd, J = 8.5, 3 Hz, 2H), 6.81-6.75 (overlap, 2H), 5.17 (dd, J = 1.7, 11.3 Hz, 1H), 4.35 (dd, J = 5.8, 12.1, 1H), 3.82 (s, 3H), 2.38 (ddd, J = 1.7, 5.8, 13.6 Hz, 1H), 2.29 (ddd, J = 11.3, 12.1, 13.6)

¹³C NMR (125 MHz, CDCl₃): δ 159.4, 155.6, 144.6, 133.3, 129.8, 128.6, 128.6, 127.7, 127.5, 126.7, 125.7, 120.5, 117.0, 114.0, 77.8, 55.3, 43.6, 40.4.

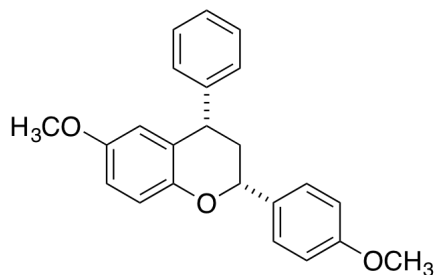
IR (thin film, cm⁻¹): 2918.28, 1513.57, 1483.80, 1452.01, 1244.09, 1227.23, 1177.95, 1111.85, 1061.05, 1031.07, 1016.56, 758.74, 699.74.

HRMS (m/z): [M+Na]⁺ calculated for C₂₂H₂₀O₂ 339.1361; found 339.1355.

SMILES: COC(C=C1)=CC=C1[C@@H]2OC3=CC=CC=C3[C@H](C4=CC=CC=C4)C2

InChI=1S/C22H20O2/c1-23-18-13-11-17(12-14-18)22-15-20(16-7-3-2-4-8-16)19-9-5-6-10-21(19)24-22/h2-14,20,22H,15H2,1H3/t20-,22+/m0/s1

6-methoxy-2-(4-methoxyphenyl)-4-phenylchromane (3b):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction was run at 0 °C in an ice bath for two hours and allowed to stir at room temperature for an additional two hours. The reaction was quenched with a basic aqueous workup with sat. sodium bicarbonate and the crude reaction was purified by flash chromatography over SiO₂ and eluted with 95:5 hexanes:EtOAc to afford **(3b)** in 70% yield, 0.2410g, 69.6 mmol, 3:1 dr, as a white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.39 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2 H), 7.23 (overlap, 3H), 6.91 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 9.0 Hz, 1H), 6.71 (dd, J = 9.0, 3.0 Hz, 1H), 6.31 (d, J = 3.0 Hz, 1H), 5.09 (dd, J = 11.0, 1.5 Hz, 1H), 4.32 (dd, J = 12.0, 6.0 Hz, 1H), 3.81 (s, 3H), 3.61 (s, 3H), 2.36 (ddd, J = 13.5, 6.0, 1.5 Hz, 1H), 2.25 (ddd, J = 13.5, 12.0, 11.0 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 159.4, 153.4, 149.8, 144.5, 133.4, 128.7, 128.5, 127.5, 126.8, 126.2, 117.5, 114.6, 113.9, 113.6, 77.7, 55.6, 55.3, 43.8, 40.5.

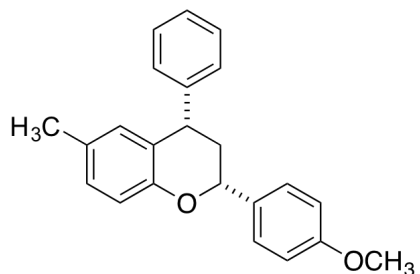
IR (thin film, cm⁻¹): 2952.85, 2932.00, 2917.99, 1514.01, 1489.53, 1244.21, 1207.81, 1178.03, 1152.32, 1061.59, 1052.11, 1027.59, 832.17, 826.57, 737.23, 700.23.

HRMS (*m/z*): [M+Na]⁺ calculated for C₂₃H₂₂O₃ 369.1467; found 369.1459.

SMILES: COC1=CC=C(O[C@@H](C2=CC=C(OC)C=C2)C[C@H]3C4=CC=CC=C4)C3=C1

InChI=1S/C23H22O3/c1-24-18-10-8-17(9-11-18)23-15-20(16-6-4-3-5-7-16)21-14-19(25-2)12-13-22(21)26-23/h3-14,20,23H,15H2,1-2H3/t20-,23+/m0/s1

2-(4-methoxyphenyl)-6-methyl-4-phenylchromane (3c):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C and was quenched with a basic workup after 1 hour with saturated sodium bicarbonate. The crude organic reaction was purified by flash chromatography with an elution of 98.5:1.5 to 95:5 hexanes:EtOAc. Upon concentrating under reduced pressure (**3c**) was afforded as white solid, 84% yield, 0.277

g, 0.838 mmol, 2:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.41 (d, J = 8.5 Hz, 2H), 7.33 (dd, J = 8.0, 7.5 Hz, 2H), 7.27 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 6.93 (overlap, 3H), 6.84 (d, J = 8.0 Hz, 1H), 6.58 (s, 1H), 5.12 (d, J = 11.5 Hz, 1H), 4.32 (dd, J = 12.0, 6.0 Hz, 1H), 3.82 (s, 3H), 2.36 (ddd, J = 14.0, 6.0, 1.0 Hz), 2.28 (m, 1H), 2.15 (s, 3H)

¹³C NMR (125 MHz, CDCl₃): δ 159.4, 153.5, 144.8, 133.4, 129.9, 129.7, 128.61, 128.57, 128.4, 127.5, 126.7, 125.2, 116.7, 113.9, 77.7, 55.3, 43.6, 40.7, 20.6.

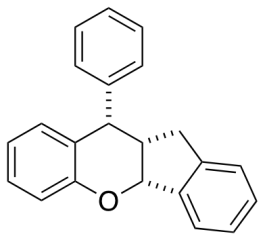
IR (thin film, cm⁻¹): 3024.11, 2945.41, 2903.80, 1493.00, 1452.79, 1244.15, 1216.10, 945.27, 815.64, 750.12, 701.70.

HRMS (*m/z*): [M+H]⁺ calculated for C₂₃H₂₂O₂ 331.1698; found 331.1708.

SMILES: CC1=CC=C(O[C@@H](C2=CC=C(OC)C=C2)C[C@H]3C4=CC=CC=C4)C3=C1

InChI=1S/C23H22O2/c1-16-8-13-22-21(14-16)20(17-6-4-3-5-7-17)15-23(25-22)18-9-11-19(24-2)12-10-18/h3-14,20,23H,15H2,1-2H3/t20-,23+/m0/s1

10-phenyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (3d):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C for 2 hours and stirred at room temp for a total reaction time of 24 hours. The reaction was quenched with a basic workup and purified by flash chromatography with silica and eluted with 100 to 95:5 hexanes:EtOAc to afford (**3d**) as a clear oil in 77% yield, 0.2307g, 0.773 mmol, 4:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.60-7.73 (overlap, 13H), 5.51 (d, *J* = 5.0 Hz, 1H), 4.68 (d, *J* = 6.0 Hz, 1H), 3.06 (m, 1H), 2.97 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.49 (dd, *J* = 15.2, 7.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 156.10, 155.15*, 144.34, 143.12*, 142.53*, 142.36, 142.02, 141.95*, 129.45, 129.26, 129.20*, 129.17, 129.02*, 128.79*, 128.73*, 128.50, 127.69*, 127.49, 126.97*, 126.85, 126.81*, 126.78, 125.22, 125.06, 123.60, 120.78*, 120.49, 116.92, 116.85*, 81.12, 80.47*, 45.74, 45.63*, 43.12*, 43.11, 36.22*, 33.48. (* indicates peaks arising from the minor diastereomer.)

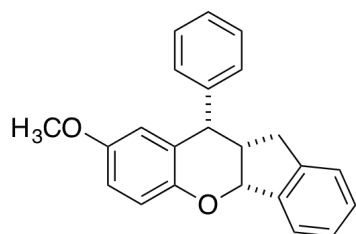
IR (thin film, cm⁻¹): 3061.36, 3026.25, 2913.91, 2850.00, 1602.10, 1580.04, 1483.12, 1453.19, 1303.61, 1239.76, 1221.64, 1202.55, 1111.02, 1075.69, 1051.07, 1030.28, 1003.85, 942.49, 909.81, 749.43, 735.87, 699.08.

MS (*m/z*): [M+Na]⁺ calculated for C₂₂H₁₈O 321.1; found 321.1.

SMILES: C12=CC=CC=C1[C@H](C3=CC=CC=C3)[C@H]4[C@H](C5=CC=CC=C5C4)O2

InChI=1S/C22H18O/c1-2-8-15(9-3-1)21-18-12-6-7-13-20(18)23-22-17-11-5-4-10-16(17)14-19(21)22/h1-13,19,21-22H,14H2/t19-,21-,22-/m0/s1

8-methoxy-10-phenyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (**3e**):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C for 2 hours and was then allowed to warm to room temperature. The reaction ran for a total time of 24 hours. The reaction was then quenched with a basic workup with saturated sodium bicarbonate. Upon concentration of the organic layer, the crude reaction was purified by flash

chromatography over SiO₂ and an elution of 98:2 to 95:5 hexanes:EtOAc (**3e**) was afforded as a clear oil, 85%, 0.2782 g, 0.847 mmol, 4:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.54 (dd, *J* = 5.0, 4.0 Hz, 1H), 7.39-7.35 (overlap, 2H), 7.32-7.29 (overlap 3H), 7.26-7.23 (overlap 2H), 7.13 (dd, *J* = 4.5, 3.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.65 (dd, *J* = 3.0, 0.5 Hz, 1H), 6.50 (dd, *J* = 3.0, 1.0 Hz, 1H), 5.47 (d, *J* = 5.0 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 3.63 (s, 3H), 3.07 (dddd, *J* = 10.0, 7.5, 6.0, 5.0 Hz, 1H), 2.92 (dd, *J* = 15.5, 10.0 Hz, 1H), 2.50 (dd, *J* = 15.5, 7.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 153.5, 150.0, 144.2, 142.3, 141.7, 129.4, 129.1, 128.5, 126.8, 126.7, 125.2, 125.2, 124.9, 117.6, 114.3, 112.9, 81.4, 55.6, 45.5, 43.5, 33.6.

IR (thin film, cm⁻¹): 2955.10, 2919.32, 2897.53, 1489.03, 1464.79, 1450.51, 1423.38, 1273.26, 1244.83, 1202.71, 1157.12, 1048.59, 947.46, 887.26, 820.05, 811.80, 756.90, 739.38, 710.74, 703.36

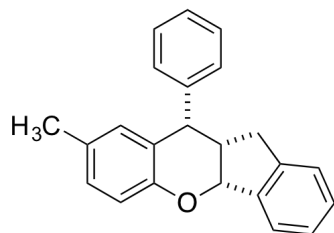
HRMS (*m/z*): [M+Na]⁺ calculated for C₂₃H₂₀O₂ 351.1361; found 351.1353.

SMILES:

COC1=CC=C(O[C@@H](C(C=CC=C2)=C2C3)[C@@H]3[C@H]4C5=CC=CC=C5)C4=C1

InChI=1S/C23H20O2/c1-24-17-11-12-21-19(14-17)22(15-7-3-2-4-8-15)20-13-16-9-5-6-10-18(16)23(20)25-21/h2-12,14,20,22-23H,13H2,1H3/t20-,22-,23-/m0/s1

8-methyl-10-phenyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (3f):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0°C for 2 hours, and then stirred at rt for a total stir time of 24 h. The reaction was quenched with a basic workup after 24 hours. The crude reaction was purified by flash column chromatography over SiO₂ with an elution of 98.5:1.5 to 98:2 hexanes:EtOAc. (**3f**) was isolated as a white solid in 81% yield,

0.2530g, 0.810 mmol, 3:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.55 (m, 1H), 7.40-7.35 (overlap, 2H), 7.33-7.21 (overlap, 6H), 7.14 (dd, *J* = 4.8, 3.5 Hz, 1H), 6.89 (ddd, *J* = 8.0, 1.5, 0.8 Hz, 1H), 6.75 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.46 (d, *J* = 4.5 Hz, 1H), 4.64 (d, *J* = 6.5 Hz, 1H), 3.04 (dddd, *J* = 10.0, 7.5, 6.5, 4.5 Hz, 1H), 2.94 (dd, *J* = 15.5, 10.0 Hz, 1H), 2.46 (dd, *J* = 15.5, 7.5 Hz, 1H), 2.17 (s, 3H)

¹³C NMR (125 MHz, CDCl₃): δ 153.94, 144.38, 142.51, 142.23, 129.74, 129.51, 129.48, 129.13, 128.51, 128.14, 126.78, 125.24, 125.05, 123.51, 116.78, 81.09, 45.79, 43.20, 33.60, 20.70.

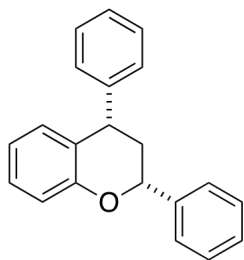
IR (thin film, cm⁻¹): 2917.47, 2903.54, 1515.40, 1492.32, 1485.17, 1453.18, 1244.61, 1215.53, 815.15, 757.87, 749.47, 736.29, 701.27.

HRMS (*m/z*): [M+Na]⁺ calculated for C₂₃H₂₀O 335.1412; found 335.1401.

SMILES: CC1=CC=C(O[C@@H](C(C=CC=C2)=C2C3)[C@@H]3[C@H]4C5=CC=CC=C5)C4=C1

InChI=1S/C23H20O/c1-15-11-12-21-19(13-15)22(16-7-3-2-4-8-16)20-14-17-9-5-6-10-18(17)23(20)24-21/h2-13,20,22-23H,14H2,1H3/t20-,22-,23-/m0/s1

2,4-diphenylchromane (3g):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C for 6 hours and stirred at room temp for a total reaction time of 48 hours. The reaction was quenched with a basic workup, saturated sodium bicarbonate, extracted with 3x30 mL Ethyl Acetate, combined organic layers were rinsed with Brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude reaction

was purified by flash chromatography with silica and eluted with 100 to 95:5 hexanes:EtOAc to afford (**3g**) as a white solid, 0.2296, 0.802 mmol, 80% yield, 2:1 dr. The NMR spectra are in agreement with literature values.³

¹H NMR (500 MHz, CDCl₃): δ 7.51-6.75 (overlap, 14H), 5.22 (dd, *J* = 11.5, 1.8 Hz, 1H), 4.37 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.42 (ddd, *J* = 13.7, 6.0, 1.8Hz, 1H), 2.29 (ddd, *J* = 13.7, 12.0, 11.5Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 155.63, 155.53*, 146.19*, 144.63, 141.52*, 141.32, 130.92*, 129.93, 128.81*, 128.79, 128.71, 128.69*, 128.59*, 128.27*, 128.17, 127.91, 127.90*, 126.91, 126.56*, 126.21, 126.16*, 125.82, 123.20*, 120.72, 120.66*, 117.21*, 117.14,

³ (a) Inoue, T.; Inoue, S.; Sato, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 6, 1647–1652. (b) Pagar, V. V.; Tseng, C-C.; Liu, R-S. *Chem. Eur. J.* **2014**, *20*, 10519–10526.

78.17, 73.32*, 43.60, 40.75, 40.31*, 38.44*. (*indicates peaks arising from the minor diastereomer).

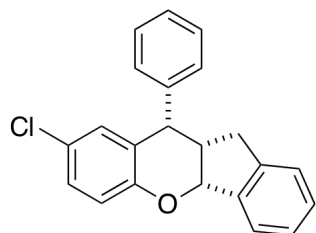
IR (thin film, cm⁻¹): 3023.93, 2918.66, 1579.39, 1484.54, 1451.34, 1271.83, 1233.96, 1110.60, 1061.05, 1024.83, 1011.54, 913.09, 899.86, 756.56, 746.03, 697.36, 525.52.

MS (m/z): [M+H⁺] calculated for C₂₁H₁₈O 287.1 m/z; found 287.2 m/z.

SMILES: C1(O2)=CC=CC=C1[C@H](C3=CC=CC=C3)C[C@@H]2C4=CC=CC=C4

InChI= 1S/C21H18O/c1-3-9-16(10-4-1)19-15-21(17-11-5-2-6-12-17)22-20-14-8-7-13-18(19)20/h1-14,19,21H,15H2/t19-,21+/m0/s1

8-chloro-10-phenyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (3h):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C for 2 hours and stirred at room temp for a total reaction time of 24 hours. The reaction was quenched with a basic workup and purified by flash chromatography with silica and eluted with 100 to 95:5 hexanes:EtOAc to afford **(3h)**, 0.2650g, 0.796 mmol, 80% yield, 3:1 dr, white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.53 (m, 1H), 7.42-7.21 (overlap, 7H), 7.16 (m, 1H), 7.03 (ddd, *J* = 9.0, 2.7, 1.0 Hz, 1H), 6.92 (dd, *J* = 2.7, 1.5 Hz, 1H), 6.75 (d, *J* = 9.0 Hz, 1H), 5.51 (d, *J* = 5.0 Hz, 1H), 4.62 (d, *J* = 6.0 Hz, 1H), 3.07 (dddd, *J* = 10.0, 7.0, 6.0, 5.0 Hz, 1H), 2.92 (dd, *J* = 15.5, 10.0 Hz, 1H), 2.51 (dd, *J* = 15.5, 7.0 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 154.64, 153.71, 144.07, 142.21, 141.88, 141.74, 141.00, 129.32, 129.28, 128.93, 128.88, 128.84, 128.78, 128.69, 128.67, 128.06, 127.63, 127.45, 127.13, 127.08, 127.03, 126.85, 125.52, 125.48, 125.23, 125.20, 125.08, 125.05, 125.04, 125.03, 118.26, 118.17, 81.50, 80.70, 45.32, 45.30, 44.14, 43.15, 36.13, 33.43.

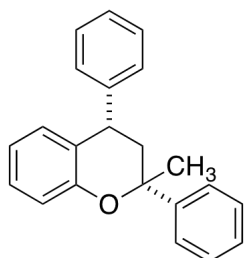
IR (thin film, cm⁻¹): 2937.29, 2931.29, 2910.17, 1474.18, 1460.81, 1452.13, 1407.68, 1249.54, 1223.92, 1198.69, 1175.00, 1121.11, 1077.07, 1047.01, 939.08, 887.17, 878.74, 872.61, 821.71, 768.28, 750.83, 731.68, 711.67, 701.34, 656.89, 626.63, 617.42, 610.52, 607.00, 588.20, 578.29, 569.19, 559.10, 543.60, 538.70, 530.30,

HRMS (m/z): [M-H]⁺ calculated for C₂₂H₁₇ClO 331.0890; found 331.0901.

SMILES: ClC1=CC=C(O[C@@H]2[C@H]3CC4=C2C=CC=C4)C([C@H]3C5=CC=CC=C5)=C1

InChI= 1S/C22H17ClO/c23-16-10-11-20-18(13-16)21(14-6-2-1-3-7-14)19-12-15-8-4-5-9-17(15)22(19)24-20/h1-11,13,19,21-22H,12H2/t19-,21-,22-/m0/s1

2-methyl-2,4-diphenylchromane (3i):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C for 2 hours and then room temperature for an additional 2 hours. The reaction was monitored by TLC, 15% EtOAc/HEX, stained with cam, silica plate. The reaction was quenched after 4 hours with sat. sodium bicarbonate, extracted with 3x30mL CHCl₃, combined organic layers were rinsed with brine, dried over anhydrous sodium sulfate and

concentrated under reduced pressure. The reaction was purified by column chromatography with silica and an elution of 100 to 98:2 hexanes:EtOAc to afford **(3i)** 0.2909g, 0.968 mmol, 97%, white solid, 1:1 dr. The spectral assignments are in agreement with literature values.⁴

¹H NMR (500 MHz, CDCl₃): δ 7.59-6.84 (overlap, 13H), 6.73 (m, 1H), 4.28 (dd, *J* = 12.1, 6.0 Hz, 1H), 2.43 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.25 (m, 1H), 1.75 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 154.33, 153.94, 146.93, 145.29, 144.55, 144.51, 129.84, 129.67, 128.83, 128.64, 128.60, 128.32, 127.97, 127.87, 127.03, 126.84, 126.74, 126.68, 125.51, 124.98, 124.66, 124.45, 120.25, 120.18, 117.68, 116.78, 79.04, 77.71, 44.49, 42.76, 40.15, 39.85, 32.28, 24.90.

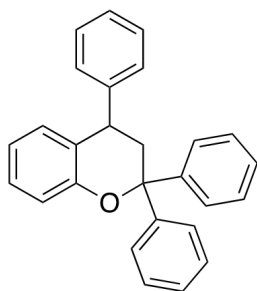
IR (thin film, cm⁻¹): 2942.87, 1482.80, 1442.84, 1300.85, 1239.07, 1178.23, 1117.59, 1068.47, 759.39, 697.95, 578.42, 575.55, 558.52, 551.17.

MS (*m/z*): [M+H]⁺ calculated for C₂₂H₂₀O 301.1; found 301.1.

SMILES: C[C@@](C1)(C2=CC=CC=C2)OC3=CC=CC=C3[C@@H]1C4=CC=CC=C4

InChI=1S/C22H20O/c1-22(18-12-6-3-7-13-18)16-20(17-10-4-2-5-11-17)19-14-8-9-15-21(19)23-22/h2-15,20H,16H2,1H3/t20-,22+/m0/s1

2,2,4-triphenylchromane (**3j**):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0 °C for 2 hours and then room temperature for an additional 2 hours. The reaction was quenched after 4 hours with sat. sodium bicarbonate, extracted with 3x30mL CHCl₃, combined organic layers were rinsed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The reaction was purified by column chromatography with silica and an elution of 100 to 98:2 hexanes:EtOAc to afford **(3j)** as a pale yellow solid, 0.3356g, 0.926

mmol, 93% yield. The spectral assignments are in agreement with literature values.⁵

¹H NMR (500 MHz, CDCl₃): δ 7.53 (overlap, 4H), 7.37-7.00 (overlap, 13H), 6.75 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.91 (dd, *J* = 12.7, 5.5 Hz, 1H), 3.12 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.64 (dd, *J* = 13.9, 12.7 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 154.15, 145.75, 144.34, 143.48, 129.58, 128.83, 128.63, 128.26, 127.82, 127.33, 127.11, 126.78, 126.31, 125.67, 125.35, 120.43, 117.22, 81.85, 42.03, 40.10.

IR (thin film, cm⁻¹): 3061.93, 3034.28, 2930.00, 1601.29, 1577.32, 1483.83, 1446.98, 1318.26, 1298.16, 1275.76, 1246.74, 1229.08, 1205.17, 1104.25, 1065.39, 1029.41, 1014.04, 916.33, 784.76, 762.62, 747.44, 727.71, 697.16.

MS (*m/z*): [M+H]⁺ calculated for C₂₇H₂₂O 363.1; found 363.1.

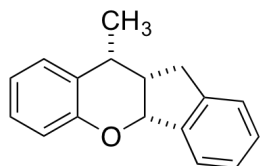
SMILES: C1(OC(C2=CC=CC=C2)(C3=CC=CC=C3)C4)=CC=CC=C1C4C5=CC=CC=C5

⁴ Aoyama, * T.; Furukawa, T.; Hayakawa, M.; Takido, T.; Kodomari, M. *Synlett*. **2015**, 26, 1875–1879.

⁵ Aoyama, * T.; Furukawa, T.; Hayakawa, M.; Takido, T.; Kodomari, M. *Synlett*. **2015**, 26, 1875–1879.

InChI=1S/C27H22O/c1-4-12-21(13-5-1)25-20-27(22-14-6-2-7-15-22,23-16-8-3-9-17-23)28-26-19-11-10-18-24(25)26/h1-19,25H,20H2

(4bR,10R,10aS)-10-methyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (3k):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at 0°C and was allowed to warm to rt after 2 hours and went for total time of 24 hours. The reaction was quenched with a basic workup and the crude reaction was purified by flash chromatography with an elution 100 to 95:5 hexanes:EtOAc. Upon concentrating under reduced

pressure, **(3k)** was afforded as a clear oil in 76% yield, 0.1796 g, 0.760 mmol, 5:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.54 (dd, *J* = 5.3, 3.5 Hz, 1H), 7.25-7.22 (overlap 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.12 (dd, *J* = 4.5, 3.5 Hz, 1H), 7.02 (m, 1H), 6.89 (m, 1H), 6.70 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.64 (d, *J* = 7.1 Hz, 1H), 3.33 (m, 1H), 3.11 (m, 1H), 2.84 (dd, *J* = 16.0, 8.3 Hz, 1H), 2.57 (dd, *J* = 16.0, 8.6 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 155.59, 154.96*, 143.95, 143.25*, 142.56*, 142.50, 129.11, 128.98*, 128.44, 128.29*, 128.01*, 127.29*, 127.08, 126.93*, 126.88, 126.08, 125.78, 125.78, 125.49*, 125.06*, 124.90, 121.01, 120.93*, 117.22, 117.22*, 83.01, 80.19*, 77.45, 77.20, 76.95, 45.72*, 44.83, 36.69*, 32.58, 32.54*, 30.04, 21.24*, 16.01. (* indicates minor diastereomer).

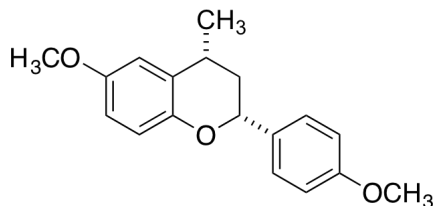
IR (thin film, cm⁻¹): 3068.37, 3029.43, 2965.65, 2929.84, 2848.42, 1604.21, 1581.27, 1480.71, 1450.01, 1431.20, 1375.03, 1345.99, 1223.19, 1202.97, 1186.91, 1122.66, 1037.89, 1018.76, 943.61, 933.42, 748.75.

MS (*m/z*): [M+H]⁺ calculated for C₁₇H₁₆O 237.1; found 237.1.

SMILES: C[C@@H]1[C@H]2[C@H](C(C=CC=C3)=C3C2)OC4=CC=CC=C41

InChI=1S/C17H16O/c1-11-13-7-4-5-9-16(13)18-17-14-8-3-2-6-12(14)10-15(11)17/h2-9,11,15,17H,10H2,1H3/t11-,15-,17-/m0/s1

6-methoxy-2-(4-methoxyphenyl)-4-methylchromane (3l):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction stirred at to stir at 0°C for 1 hour. The reaction was quenched with a basic workup and after concentrating under reduced pressure, the crude reaction was purified by flash chromatography with an elution of

95:5 to 93:7 hexanes:EtOAc. **(3l)** was isolated in 54 % yield, 0.1538 g, 0.541 mmol, 3:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.37 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.82-6.76(overlap, 2H), 6.70 (m, 1H), 4.96 (dd, *J* = 11.5, 1.5 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.17 (m, 1H), 2.16 (ddd, *J* = 1.5, 6.0, 13.5 Hz, 1H), 1.82 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 159.33, 159.22*, 153.52, 153.36*, 149.06, 148.63*, 133.95, 127.87, 127.78*, 127.46, 127.45*, 117.53*, 117.36, 113.91, 113.90*, 113.34*, 112.80, 112.47,

77.58, 73.10*, 55.77, 55.32, 39.82, 36.92*, 30.43, 29.01*, 23.99*, 20.34. (* indicates peaks arising from the minor diastereomer).

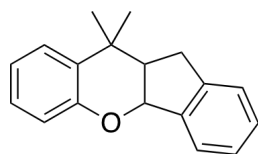
IR (thin film, cm⁻¹): 2956.35, 2933.90, 2917.66, 1514.86, 1490.82, 1459.28, 1273.64, 1239.16, 1207.80, 1177.71, 1157.64, 1049.71, 1033.88.

HRMS (m/z): [M+H]⁺ calculated for C₁₈H₂₀O₃ 285.1491; found 285.1478.

SMILES: C[C@@H]1C[C@H](C2=CC=C(OC)C=C2)OC3=CC=C(OC)C=C31

InChI=1S/C18H20O3/c1-12-10-18(13-4-6-14(19-2)7-5-13)21-17-9-8-15(20-3)11-16(12)17/h4-9,11-12,18H,10H2,1-3H3/t12-,18-/m1/s1

10,10-dimethyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (3m):



The general procedure for the two-component reaction of diols and dienophiles to afford benzopyrans was followed. The reaction was clear prior to the addition of the iron and brown after it was added. The reaction stirred at 0°C and was allowed to warm to room temperature after 2 hours and went for total time of 24 hours. After basic workup,

the crude reaction was purified by flash chromatography, with SiO₂ and 100 to 95:5 hexanes:EtOAc to afford **(3m)** as a clear oil, 72% yield, 0.1812 g, 0.724 mmol.

¹H NMR (500 MHz, CDCl₃): δ 7.55 (m, 1H), 7.31-7.23 (overlap, 3H), 7.17 (dd, *J* = 4.5, 3.5 Hz, 1H), 7.03 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 6.87 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 6.71 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.61 (d, *J* = 6.5 Hz, 1H), 2.89 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.73-2.61 (overlap, 3H), 1.48 (s, 3H), 1.45 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 154.6, 144.1, 142.6, 130.3, 129.0, 127.0, 126.8, 125.6, 125.5, 124.8, 120.5, 116.9, 79.9, 51.0, 34.3, 33.5, 31.3, 25.7.

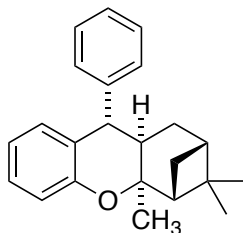
IR (thin film, cm⁻¹): 2957.19, 1483.29, 1449.27, 1439.48, 1221.00, 1196.37, 1004.83, 948.58, 938.52, 747.54.

HRMS (m/z): [M+H-CH₃]⁺ calculated for C₁₈H₁₈O 236.1201; found 236.1210.

SMILES: CC1(C)C2C(C(C=CC=C3)=C3C2)OC4=CC=CC=C41

InChI=1S/C18H18O/c1-18(2)14-9-5-6-10-16(14)19-17-13-8-4-3-7-12(13)11-15(17)18/h3-10,15,17H,11H2,1-2H3

3,3,4a-trimethyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-2,4-methanoxanthene (3n):



To an oven dried test tube equipped with a magnetic stir bar was added diol (0.100 g, 0.5 mmol, 1 equiv), (-)-α-Pinene ⁶ (0.159 mL, 1.0 mmol, 2 equiv), CHCl₃ 1 mL, anhydrous FeCl₃ (16 mg, 20 mol% with respect to diol). The reaction stirred at room temperature for 24 hours, was monitored by TLC. The TLC conditions were 15% Ethyl Acetate in Hexanes, silica plate stained with CAM. After 24 hours, the reaction was quenched with saturated sodium bicarbonate, extracted with 3x30 mL DCM. Combined organic layers were rinsed with brine, dried over anhydrous

⁶ (-)-α-Pinene from Sigma Aldrich, catalog no. 274399. Used without further purification, 99%, optical purity ee: ≥86% (GLC).

Na₂SO₄ and concentrated under reduced pressure. The crude reaction was purified by flash chromatography with silica and 98:2 hexanes:EtOAc. After concentrating the fractions under reduced pressure, **(3n)** was afforded as a clear oil, 0.0942 g, 0.296 mmol, 59% yield, 3:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.38 (dd, *J* = 7.5 Hz, 2H), 1.30-7.24 (overlap, 3H), 7.15 (m, 1H), 6.90 (d, *J* = 8.0, 1.0 Hz, 1H), 6.84 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.60 (m, 1H), 3.65 (d, *J* = 9.5 Hz, 1H), 2.45 (ddd, *J* = 9.5, 9.5, 4.5 Hz, 1H), 2.27 (ddd, *J* = 10.0, 6.0, 2.0 Hz, 1H), 2.22 (ddd, *J* = 5.5, 5.5, 5.5 Hz, 1H), 2.00 (m, 1H), 1.93 (m, 1H), 1.69-1.61 (overlap 2H), 1.30 (s, 3H), 1.15 (s, 3H), 0.96 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 13C NMR (126 MHz, cdcl3) δ 155.46, 141.34, 131.31, 129.60, 128.59, 127.39, 127.16, 126.74, 121.40, 118.23, 84.61, 53.90, 52.30, 43.67, 40.19, 39.09, 34.50, 29.31, 27.40, 26.51, 23.64.

IR (thin film, cm⁻¹): 3061.84, 3027.43, 2988.51, 2923.65, 2869.47, 1586.10, 1493.33, 1481.24, 1453.89, 1257.86, 1245.23, 1234.79, 700.84.

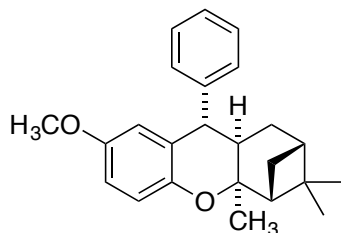
MS (*m/z*): [M+H]⁺ calculated for C₂₃H₂₆O 319.2; found 319.2.

[α]_D²⁰ = -3.1 ° (*c* = 5.1 mg/mL, CHCl₃)

SMILES:CC1(C)[C@H]2C[C@@H]1CC3[C@]2(C)OC4=CC=CC=C4[C@@H]3C5=CC=CC=C5

InChI=1S/C23H26O/c1-22(2)16-13-18-21(15-9-5-4-6-10-15)17-11-7-8-12-19(17)24-23(18,3)20(22)14-16/h4-12,16,18,20-21H,13-14H2,1-3H3/t16-,18?,20+,21?,23-/m0/s1

7-methoxy-3,3,4a-trimethyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-2,4-methanoxanthene (**3o**):



To a flame dried round bottom flask equipped with a magnetic stir bar was added diol (0.115 g, 0.5 mmol, 1 equiv), (-)-α-Pinene⁷ (0.159 mL, 1.0 mmol, 2 equiv), CHCl₃ 1 mL, FeCl₃ (16 mg, 20 mol% with respect to diol). The reaction turned black upon addition of the iron and was allowed to stir at room temperature. The reaction was monitored by TLC, with TLC conditions: 85:15 hexanes:EtOAc, silica plate, stained with CAM. The reaction ran

for 24 hours and was subsequently quenched with a basic workup, saturated sodium bicarbonate, extracted with 3x30 mL DCM, rinsed with brine, and dried over anhydrous Na₂SO₄. Purified by flash chromatography with silica and 100 to 98:2 hexanes:EtOAc. **(3o)** was isolated as a white solid, 0.0833 g, 0.239 mmol, 48% 2:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.39 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.33-7.26 (overlap 3H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.18 (d, *J* = 2.5 Hz, 1H), 3.67-3.61 (overlap 4H), 2.39 (ddd, *J* = 9.5, 9.5, 4.5 Hz, 1H), 2.30 (m, 1H), 2.23 (dd, *J* = 5.5, 5.5 Hz, 1H), 2.02-1.92 (overlap 2H), 1.71-1.64 (overlap 2H), 1.32 (s, 3H), 1.17 (s, 3H), 0.97 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 154.3, 149.0, 140.8, 132.9, 129.6, 128.6, 126.8, 118.6, 113.5, 111.5, 84.3, 55.5, 53.8, 52.9, 43.5, 40.2, 39.0, 34.4, 29.1, 27.4, 26.4, 23.7.

IR (thin film, cm⁻¹): 2924.94, 2869.10, 1489.85, 1452.80, 1428.36, 1373.11, 1245.40, 1212.96, 1134.75, 1073.57, 1040.72, 700.47, 513.46, 508.15, 501.41.

⁷ (-)-α-Pinene from Sigma Aldrich, catalog no. 274399. Used without further purification, 99%, optical purity ee: ≥86% (GLC).

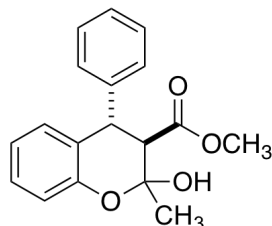
MS (*m/z*): [M+H]⁺ calculated for C₂₄H₂₈O₂ 349.2; found 349.2.

[α]_D²⁰ = -16.1 ° (c = 10.1 mg/mL, CHCl₃)

SMILES: COC1=CC=C(OC(C(C2)C(C)(C)C2C3)(C)C3C4C5=CC=CC=C5)C4=C1

InChI=1S/C24H28O2/c1-23(2)16-12-19-22(15-8-6-5-7-9-15)18-14-17(25-4)10-11-20(18)26-24(19,3)21(23)13-16/h5-11,14,16,19,21-22H,12-13H2,1-4H3

methyl 2-hydroxy-2-methyl-4-phenylchromane-3-carboxylate (**5**):



To an oven dried round bottom flask equipped with a magnetic stir bar was added diol (200 mg, 1.0 mmol, 1 equiv) Methyl Acetoacetate (.216mL, 2.0mmol, 2 equiv), 2 mL Chloroform (From Sigma Aldrich, stabilized with amylenes, not ethanol). This stirred at rt to allow for dissolution of the diol. Next FeCl₃ (16 mg, 10 mol % with respect to diol was added). The reaction stirred for 1 h at 0 °C. After 1 hour the reaction was quenched with a basic workup with sat. sodium

bicarbonate, extracted with 3x30mL EtOAc, combined organic layers were rinsed with brine, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude reaction was purified by flash chromatography on silica and an elution of 95:5 to 85:15 hexanes:EtOAc. (**5**) was afforded as a white solid, 76% yield, 0.2256 g, 0.756 mmol.

¹H NMR (500 MHz, CDCl₃): δ 7.32-7.28 (m, 3H), 7.13-7.19 (m, 3H), 7.90 (dd, *J* = 8.5, 1.0, Hz, 1H), 6.82 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 12.5 Hz, 1H), 3.51 (s, 3H), 3.10 (d, *J* = 12.5 Hz, 1H), 1.68 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 173.2, 151.3, 141.4, 129.3, 129.2, 128.0, 127.3, 124.3, 121.4, 117.0, 95.1, 55.4, 52.1, 42.6, 27.8.

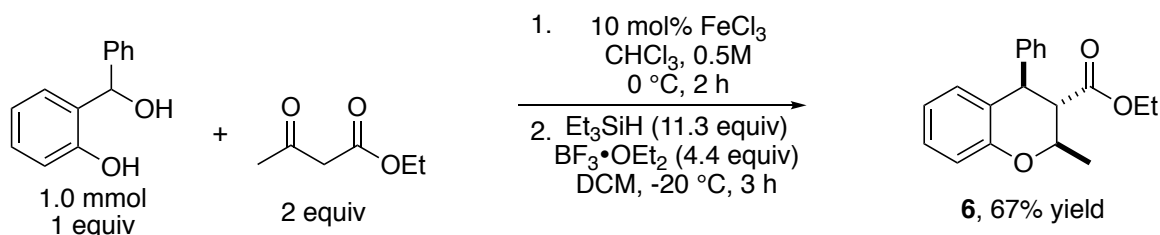
IR (thin film, cm⁻¹): 2921.84, 1739.17, 1487.12, 1452.62, 1247.41, 1165.37, 1087.31, 760.01, 701.00, 582.55, 553.30.

HRMS (*m/z*): [M + Na]⁺ calculated for C₁₈H₁₈O₄: 321.1103 *m/z*; found 321.1100.

SMILES: CC1(O)OC2=CC=CC=C2C(C3=CC=CC=C3)C1C(OC)=O

InChI=InChI=1S/C18H18O4/c1-18(20)16(17(19)21-2)15(12-8-4-3-5-9-12)13-10-6-7-11-14(13)22-18/h3-11,15-16,20H,1-2H3

ethyl -2-methyl-4-phenylchromane-3-carboxylate (**6**):



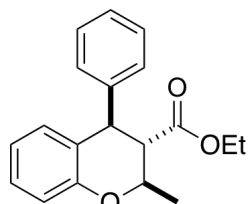
Step1:

To an oven dried test tube equipped with a magnetic stir bar was added diol (0.200mg, 1.0 mmol, 1.0 equiv) Ethyl acetoacetate (0.253mL, 2.0 mmol, 2.0 equiv) followed by CHCl₃ 2mL,

the reaction stirred at 0 °C in an ice bath for 2 hours. The reaction was quenched with a basic workup with saturated sodium bicarbonate, extracted with 3x30mL EtOAc, combined extracts were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated. The reaction was purified by column chromatography with silica and eluted with 95:5 to 85:15 hexanes:EtOAc. After concentrating, the chroman was afforded, 0.2451 g, 0.785 mmol, 78% yield 18:3:2:1 dr, off-white solid.

Step 2:

To a flame dried flask equipped with a magnetic stir bar was added chroman (0.2451 g, 0.785 mmol, 1 equiv) 50 mL DCM, followed by Triethylsilane dropwise (1.425 ml, 8.9 mmol, 11.3 equiv). This stirred at -20 °C and BF₃-OEt₂ (0.440 mL, 3.47 mmol, 4.4 equiv) was added slowly at -20 °C. The reaction stirred at -20 °C for 3 hours and was monitored by TLC (TLC conditions: silica plate, 85:15 hexanes:EtOAc, stained with CAM). The TLC showed consumption of starting material and the reaction was quenched with saturated sodium bicarbonate. The crude reaction was concentrated under reduced pressure and purified by column chromatography with silica and an elution of 100 to 98:2 hexanes:EtOAc. Two aliquots were collected. **(6)** was isolated 0.1988g, 0.674 mmol, 86% yield, clear oil. This procedure was adapted from a literature precedent.⁸



ethyl-2-methyl-4-phenylchromane-3-carboxylate (6):

¹H NMR (500 MHz, CDCl₃): δ 4.41 (d, *J* = 11.5 Hz, 1H), 4.32 (dt, *J* = 9.7, 6.0 Hz, 1H), 2.81 (dd, *J* = 11.5, 9.7 Hz, 1H), 1.43 (d, *J* = 6.0 Hz, 3H)

¹³C NMR (125 MHz, CDCl₃): δ 172.4, 154.4, 141.9, 129.7, 128.9, 128.6, 127.8, 127.2, 124.7, 120.7, 116.4, 73.1, 60.6, 54.6, 46.6, 19.6, 14.0.

IR (thin film, cm⁻¹): 3061.00, 3028.87, 2974.21, 2932.81, 2895.95, 2875.74, 1724.70, 1585.40, 1485.92, 1450.81, 1375.59, 1344.34, 1323.92, 1298.14, 1233.88, 1210.89, 1176.82, 1155.08, 1106.52, 1089.09, 1030.46, 945.36, 753.02, 700.86.

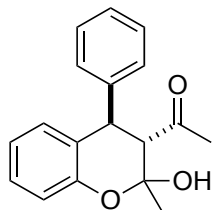
MS (*m/z*): [M+H]⁺ calculated for C₁₉H₂₀O₃ 297.1; found 297.1.

SMILES: C[C@H]1OC2=CC=CC=C2[C@@H](C3=CC=CC=C3)[C@@H]1C(OCC)=O

InChI=1S/C19H20O3/c1-3-21-19(20)17-13(2)22-16-12-8-7-11-15(16)18(17)14-9-5-4-6-10-14/h4-13,17-18H,3H2,1-2H3/t13-,17-,18-/m1/s1

1-(2-hydroxy-2-methyl-4-phenylchroman-3-yl)ethan-1-one (7):

⁸ Zhu, Y-H.; Zhang, M.; Li, Q-Y.; Liu, Q.; Zhang, J.; Yuan, Y-Y.; Nan, F-J.; Wang, M-W. *Chin. Chem. Lett.* **2014**, *25*, 693–698.



To an oven dried test tube with a magnetic stir bar was added 2-(hydroxy(phenyl)methyl)phenol (0.200 g, 1.0 mmol, 1 equiv), pentane-2,4-dione (0.205 mL, 2.0 mmol, 2 equiv), CHCl₃ 2mL, FeCl₃ (16 mg, 10 mol% with respect to the diol). The reaction stirred at 0 °C for 2 hours and was monitored by TLC, TLC conditions: silica plate, 85:15 hexanes:EtOAc, stained with CAM. The diol was consumed after 2 hours,

Saturated sodium bicarbonate (aq) was added and the biphasic mixture was extracted with 3x20 mL CHCl₃. The combined organic layers were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude reaction was purified by flash chromatography with silica and an elution of 95:5 to 85:15 hexanes:EtOAc. **(7)** was afforded as a white solid, 92%, 0.261, 0.924 mmol, 5:1 dr

¹H NMR (500 MHz, CDCl₃): δ 7.35-7.27 (overlap 3H), 7.19-7.11 (overlap 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 8.81 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.39 (d, *J* = 12.2 Hz, 1H), 4.03 (s, 1H), 3.32 (d, *J* = 12.2 Hz, 1H), 1.83 (s, 3H), 1.61 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 212.71, 151.42, 141.19, 129.83*, 129.14, 129.07*, 129.00, 128.70, 128.06, 127.95*, 127.53, 127.11*, 124.40, 124.32*, 121.32, 121.24*, 117.06, 116.96*, 98.72*, 95.18, 61.40*, 60.64, 44.58*, 43.72, 34.16*, 32.85, 27.69, 21.73*. (* indicates prominent peaks corresponding to the minor diastereomer.)

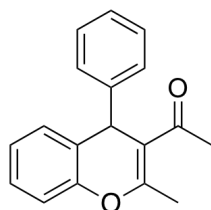
IR (thin film, cm⁻¹): 3459.59, 1694.44, 1486.93, 1452.10, 1357.83, 1241.65, 1120.98, 1096.14, 952.25, 757.95, 747.15, 701.62, 604.67, 582.41, 579.30.

HRMS (*m/z*): [M+H]⁺ calculated for C₁₈H₁₈O₃ 305.1154; found 305.1187.

SMILES: CC1(O)OC2=CC=CC=C2[C@H](C3=CC=CC=C3)[C@H]1C(C)=O

InChI= 1S/C18H18O3/c1-12(19)17-16(13-8-4-3-5-9-13)14-10-6-7-11-15(14)21-18(17,2)20/h3-11,16-17,20H,1-2H3/t16-,17+,18?/m0/s1

1-(2-methyl-4-phenyl-4H-chromen-3-yl)ethan-1-one (**8**):



To a round bottom flask equipped with a magnetic stir bar was added chroman **3v** (0.267 mg, 0.947 mmol) PTSA-mono-hydrate (17 mg, 0.09 mmol), Toluene 10 mL. This stirred at 100 °C for 4h and was monitored by TLC. TLC conditions 85:15 hexanes:EtOAc, stained with CAM, silica plate. The crude mixture was purified directly by column chromatography with SiO₂ and an elution of 95:5 to 85:15 hexanes:EtOAc. **(8)** was afforded as a clear oil, 96% yield, 0.240g, 0.908 mmol. The overall yield from the diol

was 91%, in two steps. The spectral assignments are in agreement with literature values.⁹

¹H NMR (500 MHz, CDCl₃): δ 7.29-7.26 (m, 1H), 7.26-7.23 (overlap, 3H), 7.19-7.11 (overlap, 3H), 7.01-6.97 (overlap, 2H), 5.02 (s, 1H), 2.46 (s, 3H), 2.17 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 198.8, 159.1, 149.0, 145.8, 128.91, 128.87, 127.6, 127.5, 126.9, 124.9, 124.5, 116.3, 114.2, 42.3, 30.1, 20.1

IR (thin film, cm⁻¹): 3061.70, 3024.82, 1681.27, 1616.85, 1600.95, 1575.29, 1487.41, 1457.44, 1425.25, 1378.56, 1356.27, 1332.66, 1217.72, 1194.08, 1132.26, 1103.85, 1075.14, 029.84, 937.76, 748.90, 720.81, 698.44, 616.61.

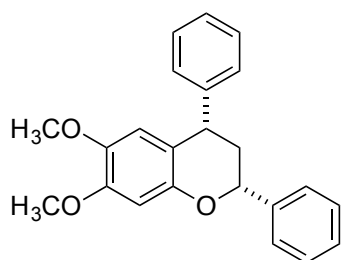
⁹ Aoyama, T.; Yamamoto, T.; Miyota, S.; Hayakawa, M.; Takido, T.; Kodomaro, M. *Synlett*. **2014**, 25, 11, 1571–1576.

HRMS (*m/z*): [M+H]⁺ calculated for C₁₈H₁₆O₂ 265.1150; found 265.1142.

SMILES: CC1=C(C(C)=O)C(C2=CC=CC=C2)C3=CC=CC=C3O1

InChI=1S/C18H16O2/c1-12(19)17-13(2)20-16-11-7-6-10-15(16)18(17)14-8-4-3-5-9-14/h3-11,18H,1-2H3

6,7-dimethoxy-2,4-diphenylchromane (**11a**):



The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles to afford benzopyrans was followed. The reaction was run at 60 °C for 8 hours. The crude reaction was purified by flash chromatography with SiO₂ and an elution of 95:5 to 90:10 hexanes:EtOAc. (**11a**) was isolated in 90% yield, 0.3105g, 3:1 dr, pale yellow solid.

¹H NMR (500 MHz, CDCl₃): δ 7.49 (d, *J* = 7.5 Hz, 2 H), 7.41-7.37 (overlap, 2H), 7.32 (m, 3H), 7.27-7.21 (overlap 3H), 6.55 (s, 1H), 6.27 (s, 1H), 5.15 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.32 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.85 (s, 3H), 3.62 (s, 3H), 2.40 (ddd, *J* = 13.7, 6.0, 1.5 Hz, 1H), 2.23 (*J* = 13.7, 12.0, 11.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 149.82, 149.58*, 149.14*, 148.84, 146.46*, 144.87, 143.55*, 143.34, 141.46*, 141.27, 128.73, 128.71*, 128.62, 128.54*, 128.51, 128.10, 127.86*, 126.83, 126.49*, 126.20, 126.17*, 116.13, 113.29*, 112.99*, 112.61, 101.00, 100.87*, 78.18, 73.14*, 56.43, 56.35*, 56.34*, 55.88, 43.18, 41.28, 40.15*, 38.81* (*Indicates prominent peaks arising from the minor diastereomer).

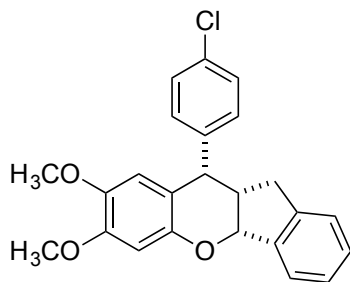
IR (thin film, cm⁻¹): 2951.52, 1618.14, 1504.98, 1464.00, 1451.98, 1406.15, 1259.94, 1217.03, 1194.51, 1169.74, 1126.35, 1062.44, 1050.01, 1021.73, 828.40, 744.56, 728.47, 698.27.

HRMS (*m/z*): [M+H]⁺ calculated for C₂₃H₂₂O₃ 347.1647; found 347.1638.

SMILES: COC1=C(OC)C=C(O[C@@H](C2=CC=CC=C2)C[C@H]3C4=CC=CC=C4)C3=C1

InChI=1S/C23H22O3/c1-24-22-14-19-18(16-9-5-3-6-10-16)13-20(17-11-7-4-8-12-17)26-21(19)15-23(22)25-2/h3-12,14-15,18,20H,13H2,1-2H3/t18-,20+/m0/s1

10-(4-chlorophenyl)-7,8-dimethoxy-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (**11b**):



The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles to afford benzopyrans was followed. The reaction was run at 60°C for 3 hours. The crude reaction was purified by flash chromatography with an elution of 95:5 to 90:10 hexanes:EtOAc to afford (**11b**) in 86% yield, 0.3398 g, 4:1 dr, off-white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.52 (m, 1H), 7.33 (dd, *J* = 6.7, 2.0 Hz, 2H), 7.27-7.24 (overlap, 2H), 7.21 (dd, *J* = 6.7, 2.0 Hz, 2H), 7.16 (m, 1H), 6.45 (s, 1H), 6.38 (m, 1H), 5.37 (d, *J* = 4.5 Hz, 1H), 4.63 (d, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.96 (dddd, *J* = 10.5, 6.5, 6.5, 4.5 Hz, 1H), 2.87 (dd, 15.3, 10.5 Hz, 1H), 2.35 (dd, *J* = 15.3, 6.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 150.2, 148.5, 144.1, 143.2, 142.3, 141.1, 132.5, 130.5, 129.2, 128.6, 126.8, 125.1, 125.0, 112.8, 111.9, 101.0, 80.5, 56.4, 55.8, 45.7, 42.0, 33.3.

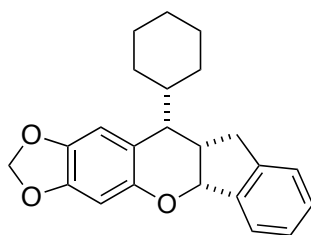
IR (thin film, cm⁻¹): 2946.47, 2903.10, 1510.87, 1487.05, 1463.37, 1446.90, 1216.12, 1195.05, 1169.15, 1139.64, 1132.60, 1099.12, 1011.02, 826.35, 766.42.

MS (m/z): [M+H]⁺ calculated for C₂₄H₂₁ClO₃ 393.1; found 393.1.

SMILES: COC1=C(OC)C=C(O[C@@H](C2=C3C=CC=C2)[C@@H](C3)[C@H]4C5=CC=C(Cl)C=C5)C4=C1

InChI=1S/C24H21ClO3/c1-26-21-12-18-20(13-22(21)27-2)28-24-17-6-4-3-5-15(17)11-19(24)23(18)14-7-9-16(25)10-8-14/h3-10,12-13,19,23-24H,11H2,1-2H3/t19-,23-,24-/m0/s1

11-cyclohexyl-5a,10,10a,11-tetrahydro-[1,3]dioxolo[4,5-g]indeno[1,2-b]chromene (11c):



The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles was followed. The reaction stirred at 60°C and was monitored by TLC. The reaction was quenched after 9 hours with a basic workup. The crude reaction was purified by column chromatography with 98:2 to 90:10 hexanes:EtOAc to afford (**11c**) as a white solid, 80% yield, 0.2802g, 2:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.48 (m, 1H), 7.21-7.16 (overlap, 2H), 7.01 (m, 1H), 6.68 (s, 1H), 6.25 (s, 1H), 5.80 (dd, *J* = 9.0, 0.5 Hz, 2H), 5.67 (d, *J* = 8.5 Hz, 1H), 3.36 (ddt, *J* = 12.5, 8.5, 4.0 Hz, 1H), 2.81-2.73 (overlap, 2H), 2.45 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.12 (d, *J* = 14.5 Hz, 1H), 1.96 (d, *J* = 12.0 Hz, 1H), 1.88 (m, 1H), 1.81-1.73 (overlap, 3H), 1.44-1.35 (overlap, 2H), 1.30-1.23 (overlap, 2H), 1.12 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 150.30, 145.28, 144.28, 142.12, 141.58, 128.90, 126.67, 125.91, 124.45, 122.67, 106.17, 101.18, 100.63, 85.82, 41.64, 40.50, 36.54, 33.47, 33.14, 30.41, 26.81, 26.66, 26.35.

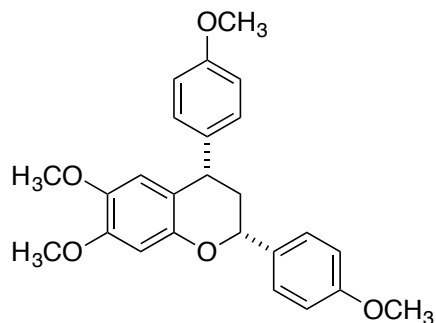
IR (thin film, cm⁻¹): 2919.96, 2903.71, 1480.96, 1146.31, 1042.13, 755.16.

HRMS (m/z): [M+H]⁺ calculated for C₂₃H₂₄O₃ 349.1804.1753; found 349.1809.

SMILES: C1(OCO2)=C2C=C(O[C@@H](C(C=CC=C3)=C3C4)[C@@H]4[C@H]5C6CCCCC6)C5=C1

InChI=1S/C23H24O3/c1-2-6-14(7-3-1)22-17-11-20-21(25-13-24-20)12-19(17)26-23-16-9-5-4-8-15(16)10-18(22)23/h4-5,8-9,11-12,14,18,22-23H,1-3,6-7,10,13H2/t18-,22-,23-/m0/s1

6,7-dimethoxy-2,4-bis(4-methoxyphenyl)chromane (11d):



The general procedure for the multicomponent reaction of phenols, aldehydes, and dienophiles to afford benzopyrans was followed. The reaction stirred at room temperature. After 3 hours, the styrene was consumed and the reaction was quenched with a basic workup. The reaction was quenched with saturated sodium bicarbonate and extracted with 3 x 30mL CHCl₃. The combined organic layers were rinsed with brine, dried over anhydrous sodium sulfate, filtered and concentrated

under reduced pressure. The crude reaction was purified by column chromatography with SiO₂ and an elution of 93:7 to 90:10 hexanes:EtOAc. **(11d)** was isolated as a white solid in 65% yield, 0.2646 g, 3:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.39 (m, 2H), 7.13 (m, 2H), 6.92 (m, 2H), 6.85 (m, 2H), 6.51 (s, 1H), 6.27 (s, 1H), 5.08 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.24 (dd, *J* = 12.7, 6.0 Hz, 1H), 3.83 (3s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.62 (s, 3H), 2.33 (ddd, *J* = 12.7, 6.0, 1.5 Hz, 1H), 2.19 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 159.43, 158.31, 149.71, 148.61, 143.11, 136.79, 133.32, 129.35, 127.54, 116.35, 113.98, 113.94, 112.45, 100.79, 77.97, 56.43, 55.83, 55.31, 55.25, 42.38, 40.98.

IR (thin film, cm⁻¹): 2956.67, 2945.74, 2935.82, 2918.73, 1610.53, 1507.35, 1465.32, 1454.86, 1441.53, 1247.64, 1215.90, 1195.76, 1174.11, 1124.93, 1103.63, 1044.99, 1029.57, 1020.13, 922.71, 859.94, 812.49, 583.26.

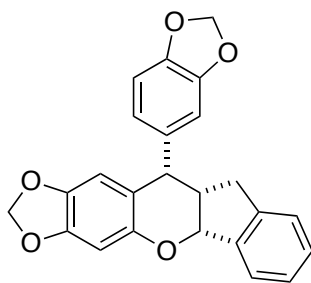
HRMS (*m/z*): [M+H]⁺ calculated for C₂₅H₂₆O₅ 407.1858; found 407.1859.

SMILES:

COC1=C(OC)C=C(O[C@@H](C2=CC=C(OC)C=C2)C[C@H]3C4=CC=C(OC)C=C4)C3=C1

InChI=1S/C25H26O5/c1-26-18-9-5-16(6-10-18)20-13-22(17-7-11-19(27-2)12-8-17)30-23-15-25(29-4)24(28-3)14-21(20)23/h5-12,14-15,20,22H,13H2,1-4H3/t20-,22+/m0/s1

11-(benzo[d][1,3]dioxol-5-yl)-5a,10,10a,11-tetrahydro-[1,3]dioxolo[4,5-g]indeno[1,2-b]chromene (11e):



The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles was followed. The reaction ran at 60 °C for 6 hours and was quenched with a basic workup. The crude reaction was subjected to reducing conditions to remove excess aldehyde. The reaction mixture was diluted with 2 mL DCM, 18 mL MeOH and 76 mg of NaBH₄ was added. This stirred at room temperature overnight. The reaction was quenched with saturated NH₄Cl, extracted with EtOAc, combined organic layers

were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude reaction was purified by column chromatography with SiO₂ and an elution of 95:5 hexanes:EtOAc. **(11e)**: was afforded as a white solid in 58% yield, 0.2245g, 4:1 dr. Recrystallization in Hexanes afforded 11:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.52 (dd, *J* = 6.5, 3.0 Hz, 1H), 7.28 (overlap, 2H), 7.16 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.72 (d, *J* = 1.5 Hz, 1H), 6.41

(s, 1H), 6.37 (s, 1H), 5.98 (s, 2H), 5.84 (dd, $J = 4.0, 1.2$ Hz, 2H), 5.40 (d, $J = 5.0$ Hz, 1H), 4.48 (d, $J = 6.0$ Hz, 1H), 3.00 (dddd, $J = 10.5, 7.5, 6.0, 5.0$ Hz, 1H), 2.91 (dd, $J = 15.2, 10.5$ Hz, 1H), 2.52 (dd, $J = 15.1, 7.5$ Hz, 1H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 150.7, 147.7, 146.4, 146.3, 144.3, 142.2, 141.5, 135.9, 129.2, 126.7, 125.2, 125.0, 122.5, 116.0, 109.4, 108.2, 108.0, 101.0, 100.8, 99.0, 81.4, 45.7, 42.9, 33.6.

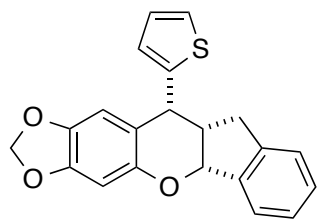
IR (thin film, cm^{-1}): 2895.75, 1503.43, 1487.98, 1474.89, 1442.28, 1431.14, 1337.32, 1236.60, 1202.21, 1187.62, 1177.50, 1149.80, 1131.91, 1117.14, 1030.39, 938.71, 930.99, 923.40, 914.57, 888.09, 866.82, 837.33, 821.61, 773.25, 750.28, 742.47.

HRMS (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{18}\text{O}_5$ 387.1232; found 387.1219.

SMILES: C1(OCO2)=C2C=C(O[C@@H](C3=C4C=CC=C3)[C@@H](C4)[C@H]5C6=CC(OCO7)=C7C=C6)C5=C1

InChI=1S/C24H18O5/c1-2-4-15-13(3-1)7-17-23(14-5-6-18-20(8-14)26-11-25-18)16-9-21-22(28-12-27-21)10-19(16)29-24(15)17/h1-6,8-10,17,23-24H,7,11-12H2/t17-,23-,24-/m0/s1

11-(thiophen-2-yl)-5a,10,10a,11-tetrahydro-[1,3]dioxolo[4,5-g]indeno[1,2-b]chromene (**11f**):



The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles was followed. The aldehyde was black and once added the flask, the solution was black in color. Upon addition of the iron, the solution had a dark purple appearance. The reaction flask was capped with a septa, parafilm and set to stir at 60 °C. The reaction was monitored by

TLC and was quenched after 24 hours with a basic workup with saturated sodium bicarbonate, extracted with 3x30 mL EtOAc, combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . The resulting solution was concentrated under reduced pressure. The crude residue was subjected to reducing conditions to remove excess aldehyde. The crude brown oil was dissolved in 2 mL DCM, and 18 mL MeOH and NaBH_4 (75.3 mg, 2 mmol) was added. This stirred at room temperature for 3 hours and was quenched with saturated ammonium chloride, extracted 3x30 mL EtOAc, combined organic layers were pooled, rinsed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography with SiO_2 and an elution of 98:2 to 93:7 hexanes:EtOAc. (**11f**) was afforded in 55% yield, 0.1929g, 9:1 dr. The product was recrystallized with boiling hexanes to afford 46% yield, 11:1 dr.

$^1\text{H NMR}$ (500MHz, CDCl_3): δ 7.53 (m, 1H), 7.28-7.24 (overlap, 3H), 7.15 (m, 1H), 7.04 (dd, $J = 5.0, 3.5$ Hz, 1H), 7.01 (d, $J = 3.5$ Hz, 1H), 6.47 (s, 1H), 6.33 (s, 1H), 5.58 (d, $J = 6.5$ Hz, 1H), 4.82 (d, $J = 5.5$ Hz, 1H), 3.28 (dddd, $J = 8.5, 8.0, 6.5, 5.5$ Hz, 1H), 2.96 (dd, $J = 8.5$ Hz, 1H) 2.86 (dd, $J = 8.0$ Hz, 1 H).

$^{13}\text{C NMR}$ (126MHz, CDCl_3): δ 149.9, 146.5, 143.9, 143.8, 141.78, 141.75, 129.2, 126.9, 126.7, 126.5, 125.5, 124.9, 124.3, 118.4, 107.5, 100.8, 99.6, 82.8, 45.4, 38.9, 34.2.

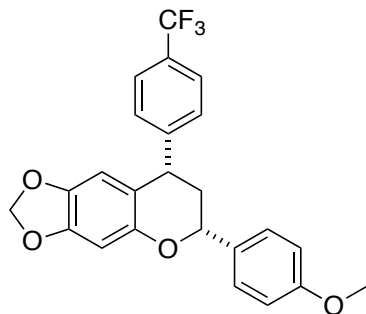
IR (thin film, cm^{-1}): 2922.25, 1497.10, 1473.77, 1434.28, 1134.85, 1031.94, 1018.82, 764.49.

HRMS (m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{16}\text{O}_3\text{S}$ 349.0898; found 349.0911.

SMILES: C1(OCO2)=C2C=C(O[C@@H](C(C=CC=C3)=C3C4)[C@@H]4[C@H]5C6=CC=CS6)C5=C1

InChI=1S/C21H16O3S/c1-2-5-13-12(4-1)8-15-20(19-6-3-7-25-19)14-9-17-18(23-11-22-17)10-16(14)24-21(13)15/h1-7,9-10,15,20-21H,8,11H2/t15-,20-,21-/m0/s1

6-(4-methoxyphenyl)-8-(4-(trifluoromethyl)phenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (11g):



The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles was followed. The reaction stirred at room temperature for 3 hours. The reaction was quenched with a basic workup. The crude reaction was purified by column chromatography over SiO₂ with an elution of 95:5 to 93:7 hexanes:EtOAc to afford **(11g)** in 43% yield, 0.1835 g, 5:1 dr. The spectral assignments correlate to those previously reported in the literature.¹⁰ The NMR spectra are provided to confirm compound purity.

¹H NMR (500 MHz, CDCl₃): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.93 (m, 2H), 6.51 (s, 1H), 6.15 (s, 1H), 5.85 (dd, *J* = 7.5, 1.0 Hz, 2H), 5.07 (dd, *J* = 11.5, 1.2 Hz, 1H), 4.34 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.81 (s, 3H), 2.36 (ddd, *J* = 13.5, 6.0, 1.2 Hz, 1H), 2.20 (ddd, *J* = 13.5, 12.0, 11.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 159.56, 159.37*, 150.66, 150.38*, 149.19, 147.52*, 147.04, 141.89*, 141.78, 132.95*, 132.88, 128.99, 128.79, 127.49, 127.39, 125.69, 116.12, 114.00, 113.92*, 108.13, 101.05*, 101.00, 98.85, 77.69, 72.71*, 55.39*, 55.30, 43.44, 40.49, 40.39*, 37.88* (*indicates prominent peaks corresponding to the minor diastereomer).

IR (thin film, cm⁻¹): 2918.80, 1616.49, 1514.68, 1501.83, 1479.40, 1435.57, 1419.40, 1322.81, 1245.53, 1146.96, 1120.49, 1088.91, 1066.51, 1035.61, 1017.24, 939.31, 917.95, 864.02, 829.87, 761.51.

MS (*m/z*): [M+H]⁺ calculated for C₂₄H₁₉F₃O₄ 429.1; found 429.1.

SMILES:

FC(C(C=C1)=CC=C1[C@@H]2C[C@H](C3=CC=C(OC)C=C3)OC4=CC5=C(OCO5)C=C42)(F)F

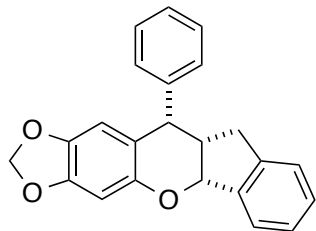
InChI=1S/C24H19F3O4/c1-28-17-8-4-15(5-9-17)20-10-18(14-2-6-16(7-3-14)24(25,26)27)19-11-22-23(30-13-29-22)12-21(19)31-20/h2-9,11-12,18,20H,10,13H2,1H3/t18-,20+/m0/s1

11-phenyl-5a,10,10a,11-tetrahydro-[1,3]dioxolo[4,5-g]indeno[1,2-b]chromene (11h):

The general procedure for the multicomponent reaction of phenols, aldehydes and dienophiles was followed. This was allowed to stir at 60 °C for 6 hours. The crude reaction was quenched with a basic workup with saturated sodium bicarbonate. The crude residue was subjected to reducing conditions to remove excess aldehyde. The crude reaction was dissolved in 2 mL dry DCM, 18 mL MeOH and NaBH₄ (80 mg, 2.0 mmol). This stirred for 2

¹⁰ Barbato, K. S.; Luan, Y.; Ramella, D.; Panek, J. S.; Schaus, S. E. *Org. Lett.* **2015**, *17*, 23, 5812–5815.

hours at room temp and was quenched with aqueous NH₄Cl extracted with 3 x 30mL EtOAc, combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography with silica and an elution of 95:5 to 90:10 hexanes:EtOAc to afford (**11h**) in 48% yield, 3:1 dr, white solid.



¹H NMR (500MHz, CDCl₃): δ 7.50 (m, 1H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.26-7.32 (overlap 3H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.14 (m, 1H), 6.39 (s, 1H), 6.38 (s, 1H), 5.83 (dd, *J* = 6.0, 1.5, Hz, 2H), 5.43 (d, *J* = 5.0 Hz, 1H), 4.56 (d, *J* = 6.3 Hz, 1H) 3.05 (dddd, *J* = 10.0, 7.3, 6.3, 5.0 Hz, 1H), 2.92 (dd, *J* = 15.5, 10.0 Hz, 1 H), 2.46 (dd, *J* = 15.5, 7.3 Hz, 1H).

¹³C NMR (126MHz, CDCl₃): δ 150.8, 146.4, 144.3, 142.2, 142.1, 141.5, 129.3, 129.1, 128.5, 126.8, 126.7, 125.2, 125.0, 116.0, 108.1, 100.8, 99.0, 81.5, 45.5, 43.2, 33.6.

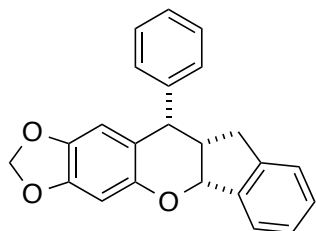
IR (thin film, cm⁻¹): 2912.19, 1504.71, 1486.89, 1477.53, 1451.37, 1426.24, 1333.84, 1235.28, 1194.96, 1176.59, 1147.90, 1117.35, 1051.45, 1030.37, 933.94, 926.77, 887.00, 866.05, 826.37, 759.52, 745.59721.31, 704.23.

HRMS (*m/z*): [M+H]⁺ calculated for C₂₃H₁₈O₃ 343.1334; found 343.1339.

SMILES: C1(OCO2)=C2C=C(O[C@@H](C(C=CC=C3)=C3C4)[C@@H]4[C@H]5C6=CC=CC=C6)C5=C1

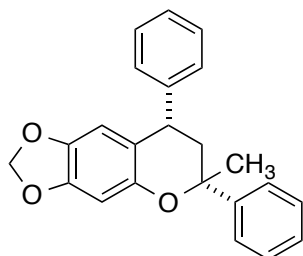
InChI=1S/C23H18O3/c1-2-6-14(7-3-1)22-17-11-20-21(25-13-24-20)12-19(17)26-23-16-9-5-4-8-15(16)10-18(22)23/h1-9,11-12,18,22-23H,10,13H2/t18-,22-,23-/m0/s1

11-phenyl-5a,10,10a,11-tetrahydro-[1,3]dioxolo[4,5-g]indeno[1,2-b]chromene (**13a**):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The solution turned red upon addition of iron and was allowed to stir at 60 °C for 6 hours. The crude mixture was purified by column chromatography with silica and an elution of 95:5 to 90:10 hexanes:EtOAc. (**13a**) was isolated as a white solid in 86% yield, 0.2929 g, 6:1 dr. A trituration in hexanes afforded 0.2474g, 0.724 mmol, 72% yield, 11:1 dr. The spectra data is in agreement with compound (**11h**).

6-methyl-6,8-diphenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (**13b**):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles to afford benzopyrans was followed. Upon addition of the iron, the reaction turned green and then red after a couple minutes of stirring. The reaction was allowed to stir at 60 °C and was quenched after 6 hours with a basic workup up. The crude reaction was purified by column chromatography with neutral

alumina and an elution 98:2 to 95:5 hexanes:EtOAc. **(13b)** was afforded in 93% yield, 0.3203 g, dr 1.0: 1.55 as a white solid.

¹H NMR (500MHz, CDCl₃): δ 7.51 (m, 2H), 7.38-7.09 (overlap, 8H), 6.55 (s, 1H), 6.23 (s, 1H), 5.80 dd, *J* = 9.0, 1.5 Hz, 2H), 4.11 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.33 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.13 (dd, *J* = 13.6, 12.0 Hz, 1H), 1.65 (s, 3H).

¹³C NMR (126MHz, CDCl₃): δ 149.03, 148.61, 147.08, 146.92, 146.83, 145.19, 144.75, 144.72, 141.48, 141.32, 128.71, 128.68, 128.64, 128.61, 128.30, 127.03, 126.84, 126.77, 126.70, 125.03, 124.44, 117.11, 116.17, 108.42, 108.38, 100.88, 100.84, 99.18, 98.41, 79.01, 77.68, 44.50, 42.76, 40.32, 40.00, 32.22, 24.59.

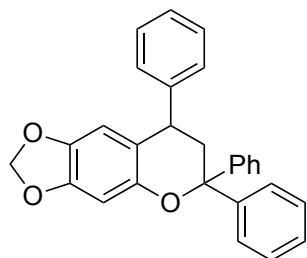
IR (thin film, cm⁻¹): 2977.98, 2879.49, 1499.65, 1477.47, 1452.68, 1427.40, 1373.53, 1271.70, 1244.45, 1213.54, 1149.45, 1094.99, 1065.02, 1037.53, 939.11, 909.11, 856.37, 759.23, 736.14, 726.36, 697.45.

HRMS (*m/z*): [M+H]⁺ calculated for C₂₃H₂₀O₃ 345.1491; found 345.1478.

SMILES: C[C@@]1(C2=CC=CC=C2)OC3=CC4=C(OCO4)C=C3[C@H](C5=CC=CC=C5)C1.

InChI=1S/C23H20O3/c1-23(17-10-6-3-7-11-17)14-19(16-8-4-2-5-9-16)18-12-21-22(25-15-24-21)13-20(18)26-23/h2-13,19H,14-15H2,1H3/t19-,23+/m0/s1

6,6,8-triphenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (**13c**):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles to afford benzopyrans was followed. The reaction was run at 60 °C for 24 hours and quenched with a basic work up. The crude reaction was subjected to reducing conditions, dissolved in 2 mL dry DCM, 18 mL MeOH, and NaBH₄ (80 mg, 2.0 mmol) to reduce the excess aldehyde. This ran at room temperature for 3 hours and was quenched with saturated NH₄Cl, extracted 3 x

30mL EtOAc, combined organic extracts were rinsed with saturated sodium chloride, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purified by column chromatography with silica and an elution of 100 to 95:5 hexanes:EtOAc. The spectra assignments are in agreement with literature values.¹¹ The NMR spectras have been provided for evidence of compound purity. **(13c)** was afforded in 95% yield, 0.3874 g, as a white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.53-7.46 (overlap 4H), 7.18-7.36 (overlap 11 H), 6.67 (s, 1H), 6.06 (s, 1H), 5.82 (dd, *J* = 14.5, 1.5 Hz, 2 H), 3.78 (dd, *J* = 12.5, 5.5 Hz, 1H), 3.08 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.55(dd, *J* = 13.7, 12.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 148.83, 146.87, 145.65, 144.55, 143.34, 141.50, 128.68, 128.65, 128.57, 128.22, 127.31, 127.11, 126.78, 126.30, 125.61, 108.27, 100.83, 98.80, 81.87, 42.10, 40.26.

IR (thin film, cm⁻¹): 2955.26, 2874.27, 1498.37, 1480.38, 1455.10, 1448.25, 1427.41, 1241.21, 1184.76, 1151.84, 1099.56, 1077.06, 1063.18, 1045.50, 1034.50, 936.05, 923.30, 910.15, 872.42, 833.02, 781.54, 759.28, 744.86, 727.01, 701.85, 696.33, 590.23.

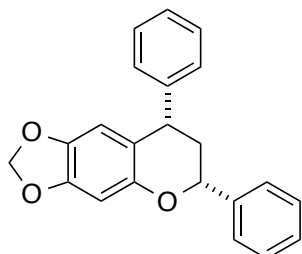
MS (*m/z*): [M+H]⁺ calculated for C₂₈H₂₂O₃ 407.1; found 407.1.

SMILES: C1(OCO2)=C2C=C(OC(C3=CC=CC=C3))(C4=CC=CC=C4)CC5C6=CC=CC=C6)C5=C1.

¹¹ Taheri, A.; Lai, B.; Yang, J.; Zhang, J.; Gu, Y. *Tetrahedron*. **2016**, *72*, 479–488.

InChI=1S/C28H22O3/c1-4-10-20(11-5-1)24-18-28(21-12-6-2-7-13-21,22-14-8-3-9-15-22)31-25-17-27-26(16-23(24)25)29-19-30-27/h1-17,24H,18-19H2

6,8-diphenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (13d):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reaction stirred at 60 °C and was monitored by TLC. After 6 hours the TLC showed consumption of the dienophile, the reaction was subsequently quenched with a basic workup. The crude reaction was purified by flash chromatography on alumina with an elution of 98:2 to 95:5 hexanes:EtOAc. **(13d)** was afforded in 70%, 0.2296g, 3:1 dr as a white solid. A recrystallization with hexanes afforded 40% yield, 0.1926g, 4:1 dr. The spectra assignments are in agreement with the literature values.¹² The NMR data is provided to support the compound purity.

¹H NMR (500 MHz, CDCl₃): δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.37 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.31-7.28 (overlap 3H), 7.23-7.14 (overlap 3H), 6.50 (s, 1H), 6.22 (s, 1H), 5.80 (d, *J* = 7.0 Hz, 2H), 5.10 (d, *J* = 11.0 Hz, 1H), 4.24 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.36 (ddd, *J* = 14.0, 6.0, 1.5 Hz, 1H), 2.21 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 150.39, 150.20*, 147.23*, 146.77, 146.24*, 144.79, 141.74*, 141.66, 141.33*, 141.14, 128.73, 128.66*, 128.58, 128.49*, 128.48, 128.08, 127.81*, 126.83, 126.50*, 126.11, 126.06*, 117.34, 114.49*, 109.06*, 108.46, 100.96*, 100.91, 98.67, 98.58*, 78.20, 73.21*, 43.55, 40.81, 40.37*, 38.36* (* corresponds to peaks arising from the minor diastereomer).

IR (thin film, cm⁻¹): 3028.26, 2881.13, 1498.57, 1477.29, 1452.88, 1431.52, 1232.59, 1180.55, 1145.53, 1092.34, 1036.65, 938.82, 920.87, 862.69, 834.14, 748.85, 696.76.

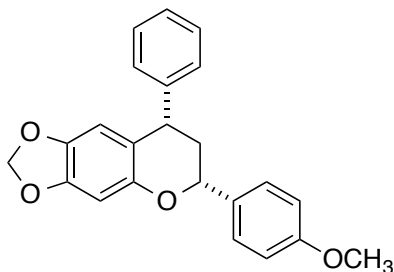
MS (*m/z*): [M+H]⁺ calculated for C₂₂H₁₈O₃ 331.1; found 331.3.

SMILES:C1(OCO2)=C2C=C(O[C@@H])(C3=CC=CC=C3)C[C@H]4C5=CC=CC=C5)C4=C1

InChI= 1S/C22H18O3/c1-3-7-15(8-4-1)17-11-19(16-9-5-2-6-10-16)25-20-13-22-21(12-18(17)20)23-14-24-22/h1-10,12-13,17,19H,11,14H2/t17-,19+/m0/s1

6-(4-methoxyphenyl)-8-phenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (13e):

¹² Barbato, K. S.; Luan, Y.; Ramella, D.; Panek, J. S.; Schaus, S. E. *Org. Lett.* **2015**, *17*, 23, 5812–5815.



The general procedure for the multicomponent reaction with phenols, acetals, and dienophiles as followed. The reaction was clear prior to the addition of the metal. After the iron was added the reaction turned brown. The reaction stirred at room temperature beginning for 2 hours and was then quenched with a basic workup. Purified by column chromatography with silica and an elution of 100 to 90:10 hexanes:EtOAc. After concentration, **(13e)** was isolated as a

white solid, 56% yield, 0.1006 g, 5:1 dr. The spectra assignments are consistent with literature values.¹³ The NMR spectra are provided to confirm purity.

¹H NMR (500 MHz, CDCl₃): δ 7.39 (m, 2H), 7.32 (m, 2H), 7.27-7.19 (overlap, 3H), 6.92 (m, 2H), 6.48 (s, 1H), 6.21 (s, 1H), 5.84 (dd, *J* = 8.5, 1.5 Hz, 2H), 5.07 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.25 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.82 (s, 3H), 2.25 (ddd, *J* = 13.5, 6.0, 1.5 Hz, 1H), 2.20 (ddd, *J* = 13.5, 12.0, 11.5).

¹³C NMR (125 MHz, CDCl₃): δ 159.43, 150.48, 146.67, 144.84, 141.53, 133.19, 128.67, 128.42, 127.50, 126.75, 117.27, 113.93, 108.41, 100.85, 98.60, 77.87, 55.32, 43.58, 40.51.

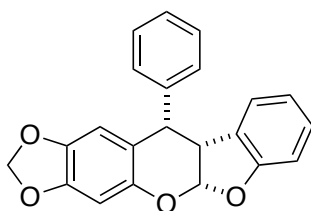
IR (thin film, cm⁻¹): 2916.05, 2901.18, 2883.12, 1611.43, 1513.80, 1497.77, 1475.95, 1452.31, 1430.68, 1243.71, 1174.79, 1141.76, 1085.96, 1028.05, 943.66, 918.98, 869.30, 834.26, 774.41, 752.99, 703.14, 568.51, 553.55.

MS (*m/z*): [M+H]⁺ calculated for C₂₃H₂₀O₄ 361.1; found 361.1.

SMILES: COC(C=C1)=CC=C1[C@@H]2OC3=CC4=C(OCO4)C=C3[C@H](C5=CC=CC=C5)C2

InChI= 1S/C23H20O4/c1-24-17-9-7-16(8-10-17)20-11-18(15-5-3-2-4-6-15)19-12-22-23(26-14-25-22)13-21(19)27-20/h2-10,12-13,18,20H,11,14H2,1H3/t18-,20+/m0/s1

11-phenyl-5a,10b-dihydro-11H-benzofuro[2,3-b][1,3]dioxolo[4,5-g]chromene (**13f**):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed with the exception that 5 mol% Iron Trichloride hexahydrate was added: To an oven dried test tube equipped with a magnetic stir bar was added sesamol (0.276 g, 2.0 mmol, 2 equiv), benzaldehyde dimethyl acetal (0.300 mL, 2.0 mmol, 2.0 equiv), 2,3-benzofuran (0.110 mL, 1.0 mmol, 1 equiv) CHCl₃ 2mL, and lastly FeCl₃·6H₂O (27 mg, 5 mol% with respect to phenol). The reaction vessel was capped with a septa, parafilm and set to stir at 60 °C for 24 hours. The crude reaction was purified by column chromatography, with SiO₂ and an elution of 98:2 to 95:5 hexanes:EtOAc to afford **(13f)** in 38% yield, 0.132g, white solid.

¹H NMR (500MHz, CDCl₃): δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 7.3, 7.5 Hz, 1H), 7.19 (m, 1 H), 6.91 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H), 6.26 (s, 1H), 5.92 (d, *J* = 7.5 Hz, 1H), 5.77 (dd, *J* = 11.5, 1.5 Hz, 2H), 5.37 (dd, *J* = 7.5, 2.5 Hz, 1H), 4.27 (d, *J* = 2.5 Hz, 1H).

¹³C NMR (126MHz, CDCl₃): δ 160.7, 148.3, 146.3, 142.6, 137.3, 131.0, 130.5, 128.6, 127.6, 126.2, 125.5, 120.9, 120.6, 110.1, 107.5, 100.8, 100.7, 85.7, 80.2, 44.5.

¹³ Barbato, K. S.; Luan, Y.; Ramella, D.; Panek, J. S.; Schaus, S. E. *Org. Lett.*, **2015**, *17*, 23, 5812–5815.

IR (thin film, cm⁻¹): 2927.43, 1474.38, 1467.67, 1439.40, 1235.62, 1186.47, 1139.53, 1040.36, 1032.08, 934.20, 872.68, 760.45, 700.85.

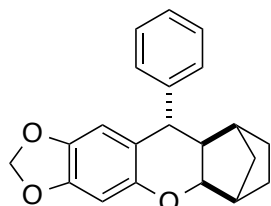
HRMS (*m/z*): [M+H]⁺ calculated for C₂₂H₁₆O₄ 345.1127; found 345.1114.

SMILES: C1(OCO2)=C2C=C(O[C@@H]

(OC3=C4C=CC=C3)[C@@H]4[C@H]5C6=CC=CC=C5=C1

InChI=1S/C22H16O4/c1-2-6-13(7-3-1)20-15-10-18-19(24-12-23-18)11-17(15)26-22-21(20)14-8-4-5-9-16(14)25-22/h1-11,20-22H,12H2/t20-,21-,22+/m0/s1

10-phenyl-5a,6,8,9,9a,10-hexahydro-7H-6,9-methano[1,3]dioxolo[4,5-b]xanthene (13g):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles to afford benzopyrans was followed. The reaction was run at 60 °C for 6 hours and was subsequently quenched with a basic workup. The crude reaction mixture was purified by column chromatography with an elution of 97.5:1.5 to 98:2 Hexanes:EtOAc to afford (**13g**) as a white solid in 29% yield, 0.0934g,

14:1dr.

¹H NMR (500MHz, CDCl₃): δ 7.41-7.26 (overlap 5H), 6.54 (s, 1H), 6.05 (s, 1H), 5.82 (dd, *J* = 4.5, 1.5, Hz, 2H), 3.88 (d, *J* = 6.5 Hz, 1H), 3.40 (d, *J* = 11.0 Hz, 1H), 2.56 (d, *J* = 5.0 Hz, 1H), 2.15-2.09 (overlap, 2H), 2.03 (d, *J* = 3.0 Hz, 1H), 1.61 (m, 1H), 1.44 (m, 1H), 1.23 (m, 1H), 1.16 (m, 1H), 1.06 (m, 1H).

¹³C NMR (126MHz, CDCl₃): δ 150.3, 145.9, 142.0, 141.3, 129.6, 128.7, 126.9, 125.6, 106.9, 100.7, 99.7, 85.2, 55.1, 44.8, 43.2, 40.2, 33.4, 28.9, 24.7.

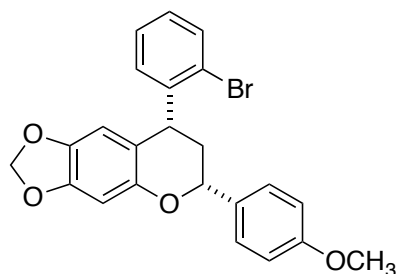
IR (thin film, cm⁻¹): 2957.32, 2924.44, 2873.25, 2853.87, 1474.03, 1440.50, 1141.45, 1032.86.

HRMS (*m/z*): [M+H]⁺ calculated for C₂₁H₂₀O₃ 321.1491; found 321.1482.

SMILES: C1(OCO2)=C2C=C(O[C@H]([C@@H]3CC[C@H]4C3)[C@H]4[C@H]5C6=CC=CC=C6)C5=C1

InChI=1S/C21H20O3/c1-2-4-12(5-3-1)19-15-9-17-18(23-11-22-17)10-16(15)24-21-14-7-6-13(8-14)20(19)21/h1-5,9-10,13-14,19-21H,6-8,11H2/t13-,14+,19-,20+,21+/m0/s1

8-(2-bromophenyl)-6-(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (13h):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reaction stirred at room temperature for 4 hours. The reaction was quenched with a basic workup and the crude reaction was purified by column chromatography with silica and an elution of 95:5 to 93:7 hexanes:EtOAc. (**13h**) was isolated in

44% yield, 0.1935 g, 4:1 dr, as a white solid. The spectra data is in agreement with literature values.¹⁴ The spectra have been provided to confirm purity.

¹H NMR (500MHz, CDCl₃): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.5Hz, 2H), 7.25 (m, 1H), 7.10 (m, 2H), 6.93 (d, *J* = 8.5Hz, 2H), 6.51 (s, 1H), 6.22 (s, 1H), 5.86(d, *J* = 12.5Hz, 1H), 5.08 (d, *J* = 11.5 Hz, 1H), 4.88 (m, 1H), 3.82 (s, 3H), 2.48 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.05 (m, 1H).

¹³C NMR (126MHz, CDCl₃): δ 159.51, 159.38, 151.00, 150.77, 147.42, 146.86, 144.86, 144.27, 141.93, 141.79, 133.09, 133.04, 132.72, 131.51, 129.55, 128.25, 128.16, 128.07, 127.64, 127.60, 127.28, 125.01, 124.17, 116.28, 113.98, 113.90, 113.68, 108.92, 108.20, 101.03, 100.97, 98.92, 98.63, 77.80, 72.76, 55.35, 55.26, 41.98, 40.39, 38.85, 35.66.

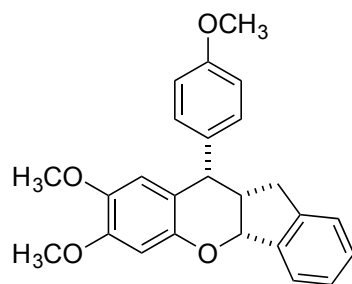
IR (thin film, cm⁻¹): 2889.19, 1514.86, 1497.77, 1478.30, 1243.48, 1179.96, 1147.90, 1119.99, 1082.81, 1028.65, 933.83, 913.23, 871.47, 833.90, 753.24.

MS (*m/z*): [M+H]⁺ calculated for C₂₃H₁₉BrO₄ 439.1, 441.1; found 439.2, 441.3.

SMILES: BrC(C=CC=C1)=C1[C@@H]2C[C@H](C3=CC=C(OC)C=C3)OC4=CC5=C(OCOC5)C=C4

InChI=1S/C23H19BrO4/c1-25-15-8-6-14(7-9-15)20-10-17(16-4-2-3-5-19(16)24)18-11-22-23(27-13-26-22)12-21(18)28-20/h2-9,11-12,17,20H,10,13H2,1H3/t17-,20+/m0/s1

7,8-dimethoxy-10-(4-methoxyphenyl)-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (**13i**):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reaction stirred at 60 °C and was monitored by TLC and quenched after 24 h with a basic work up. The crude reaction mixture was purified by column chromatography, with SiO₂ and an elution of 90:10 hexanes:EtOAc. (**13i**) was isolated as a white solid upon concentrating under reduced pressure, 77% yield, 0.299 g, 6:1 dr, white solid; recrystallized with hexanes to give 68%,

0.2632g, 12:1 dr.

¹H NMR (500 MHz, CDCl₃): δ 7.52 (dd, *J* = 6.3, 3.2 Hz, 1H), 7.27-7.21 (overlap, 2H), 9.19 (d, *J* = 9.0 Hz, 2H), 7.16 (dd, *J* = 6.3, 3.2 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.44 (s, 1H), 6.43 (s, 1H), 5.39 (d, *J* = 4.5 Hz, 1H), 4.89 (d, *J* = 6.5 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.65 (s, 3H), 2.79 (dddd, *J* = 10.5, 6.5, 6.5, 4.5 Hz, 1H), 2.90 (dd, *J* = 15.0, 10.5 Hz, 1H), 2.38 (dd, *J* = 15.0, 6.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 158.4, 150.2, 148.3, 144.4, 143.0, 142.5, 134.4, 130.2, 129.1, 126.7, 125.1, 125.0, 113.83, 113.77, 112.2, 100.9, 80.7, 56.5, 55.8, 55.3, 46.2, 41.7, 33.3.

IR (thin film, cm⁻¹): 2925.69, 1507.87, 1244.57, 1192.02, 1009.09, 760.19.

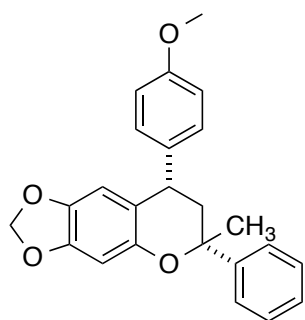
HRMS (*m/z*): [M+H]⁺ calculated for C₂₅H₂₄O₄ 389.1753; found 389.1764.

SMILES: COC1=C(OC)C=C(O[C@@H](C(C=CC=C2)=C2C3)[C@@H]3[C@H]4C5=CC=C(OC)C=C5)C4=C1

¹⁴ Barbato, K. S.; Luan, Y.; Ramella, D.; Panek, J. S.; Schaus, S. E. *Org. Lett.* **2015**, *17*, 23, 5812–5815.

InChI=1S/C25H24O4/c1-26-17-10-8-15(9-11-17)24-19-13-22(27-2)23(28-3)14-21(19)29-25-18-7-5-4-6-16(18)12-20(24)25/h4-11,13-14,20,24-25H,12H2,1-3H3/t20-,24-,25-/m0/s1

8-(4-methoxyphenyl)-6-methyl-6-phenyl-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (13j):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reaction was stirred at 60 °C for 6 hours. The crude reaction mixture was quenched with a basic workup. The crude reaction mixture was purified by column chromatography with silica and an elution of 98:2 to 93:7 hexanes:EtOAc to afford **(13j)** 89% yield, 0.334 g, 1:1 dr, white solid. The spectra are in agreement with literature values.¹⁵

¹H NMR (500MHz, CDCl₃): δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.43-7.33 (overlap 2H), 7.29 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.87 (dd, *J* = 8.5, 8.5 Hz, 2H), 6.61 (s, 1H), 6.31 (s, 1H), 5.87 (dd, *J* = 9.0, 1.0 Hz, 1H), 4.13 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.82 (s, 3H), 2.37 (m, 1H), 2.16 (t, *J* = 12.5 Hz, 1H), 1.71 (s, 3H).

¹³C NMR (126MHz, CDCl₃): δ 158.34, 158.29, 148.87, 148.45, 146.92, 146.84, 146.77, 145.16, 141.35, 141.21, 136.64, 136.61, 129.56, 128.52, 128.24, 126.95, 126.75, 124.96, 124.37, 117.45, 116.52, 113.98, 113.96, 108.34, 108.28, 100.82, 100.78, 99.06, 98.30, 79.00, 77.67, 55.29, 44.48, 42.75, 39.37, 39.03, 32.17, 24.51.

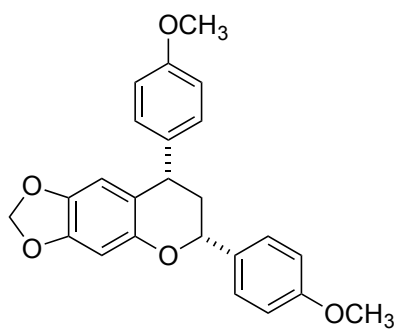
IR (thin film, cm⁻¹): 2973.40, 2927.19, 1610.26, 1511.16, 1476.44, 1445.53, 1428.44, 1373.43, 1272.87, 1243.96, 1163.70, 1149.01, 1107.80, 1095.62, 1072.79, 1035.40, 938.83, 911.00, 895.01, 858.75, 829.18, 758.98, 731.59, 699.19.

HRMS (*m/z*): [M+Na]⁺ calculated for C₂₄H₂₂O₄ 397.1416 *m/z*; found 397.1413.

SMILES:C[C@@]1(C2=CC=CC=C2)OC3=CC4=C(OCO4)C=C3[C@H](C5=CC=C(OC)C=C5)C1

InChI=1S/C24H22O4/c1-24(17-6-4-3-5-7-17)14-20(16-8-10-18(25-2)11-9-16)19-12-22-23(27-15-26-22)13-21(19)28-24/h3-13,20H,14-15H2,1-2H3/t20-,24+/m0/s1

6,8-bis(4-methoxyphenyl)-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]chromene (13k):



The general procedure for the multicomponent reaction of phenols, acetals and dienophiles was followed. The reaction stirred at room temperature 3 hours. The reaction was quenched with a basic workup with saturated sodium bicarbonate, extracted with 3 x 30 mL EtOAc, combined organic layers were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude reaction was subjected to reducing conditions because the excess aldehyde and the product had the same rf. The crude reaction was dissolved in 2 mL dry DCM, 18 mL MeOH, NaBH₄ (80 mg) was

¹⁵ Wonga, Y. F.; Wanga, Z.; Hongb, W-X.; Suna, J. *Tetrahedron*. **2016**, *82*, 22, 2748–2751.

added and stirred at room temperature for 2 hours. The reaction was quenched with saturated NH₄Cl, extracted with 3 x 30 mL EtOAc, combined organic layers were rinsed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude reaction was purified by flash chromatography with silica and an elution of 95:5 to 90:10 hexanes:EtOAc. **(13k)** was isolated in 63% yield, 0.2472 g, 4:1 dr. The spectra assignments are in agreement with literature values.¹⁶ The NMR spectra are provided to support the spectral values.

¹H NMR (500 MHz, CDCl₃): δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.94-6.82 (overlap 4H), 5.06 (dd, *J* = 8.0, 1.0 Hz, 2H), 5.06 (dd, *J* = 11.5, 2.0 Hz, 1H), 4.20 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.36 (ddd, *J* = 13.5, 6.0, 2.0 Hz, 1H), 2.18 (ddd, *J* = 13.5, 12.0, 11.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 159.41, 158.37, 150.38, 146.60, 141.49, 136.80, 133.26, 129.34, 127.48, 117.64, 114.04, 113.92, 108.36, 100.82, 98.54, 77.94, 55.31, 55.28, 42.73, 40.55.

IR (thin film, cm⁻¹): 2953.56, 2937.18, 1613.81, 1511.13, 1476.64, 1434.97, 1305.73, 1255.02, 1239.89, 1173.92, 1144.73, 1085.03, 1050.54, 1031.00, 935.26, 911.97, 874.04, 831.63, 761.32, 564.20, 558.97, 545.00, 530.88, 526.97.

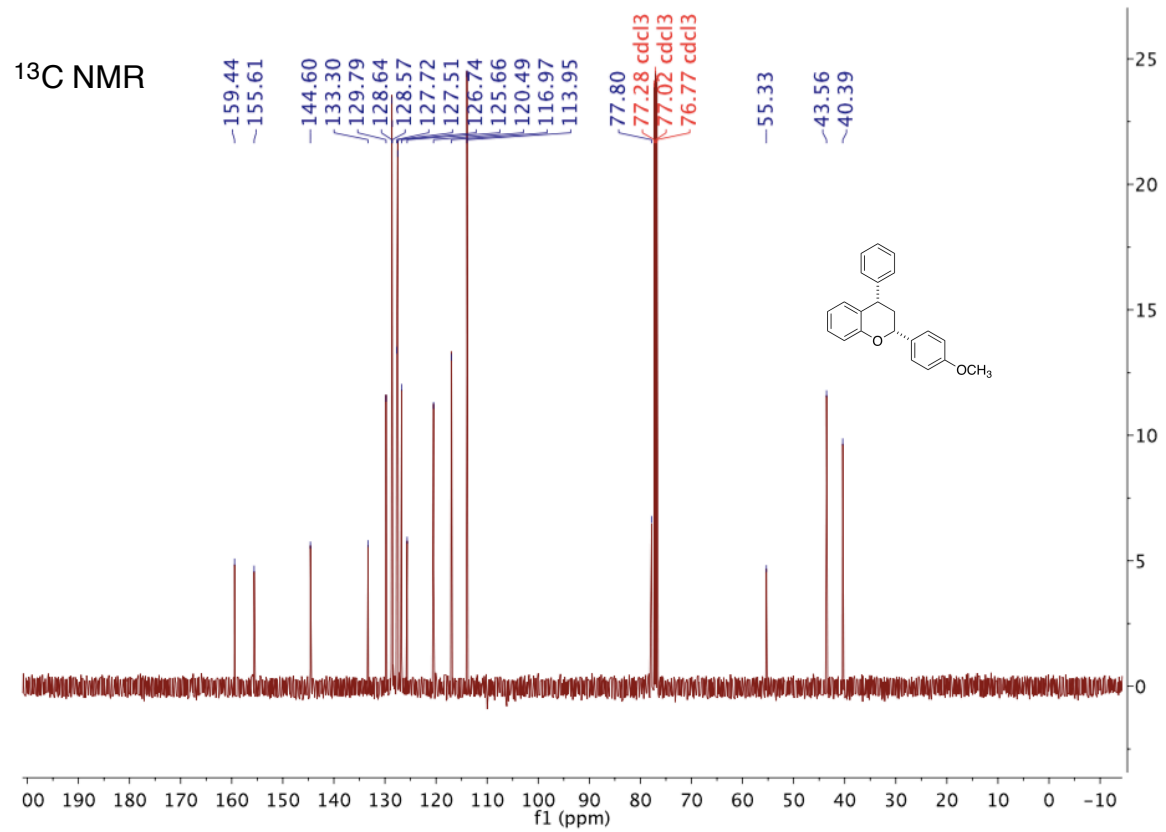
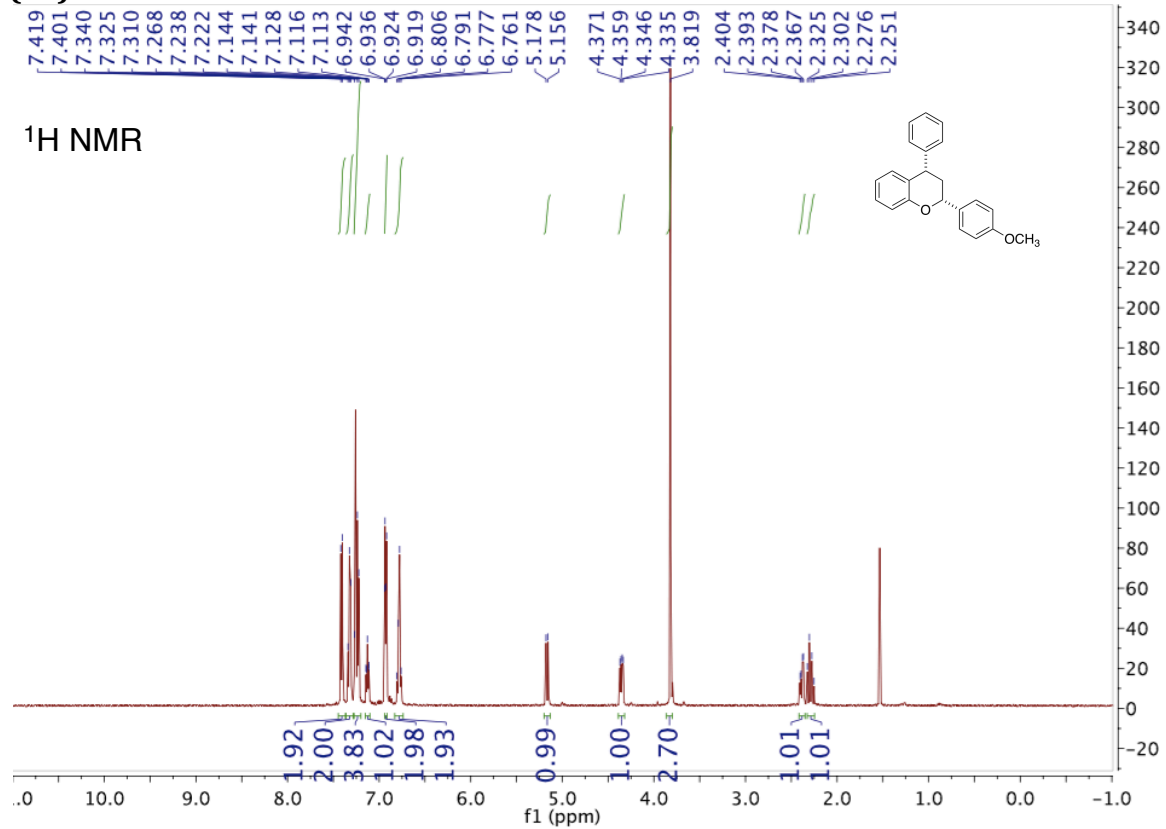
MS (*m/z*): [M+H]⁺ calculated for C₂₄H₂₂O₅ 391.1; found 391.3.

SMILES: COC(C=C1)=CC=C1[C@@H]2OC3=CC4=C(OCO4)C=C3[C@H](C5=CC=C(OC)C=C5)C2

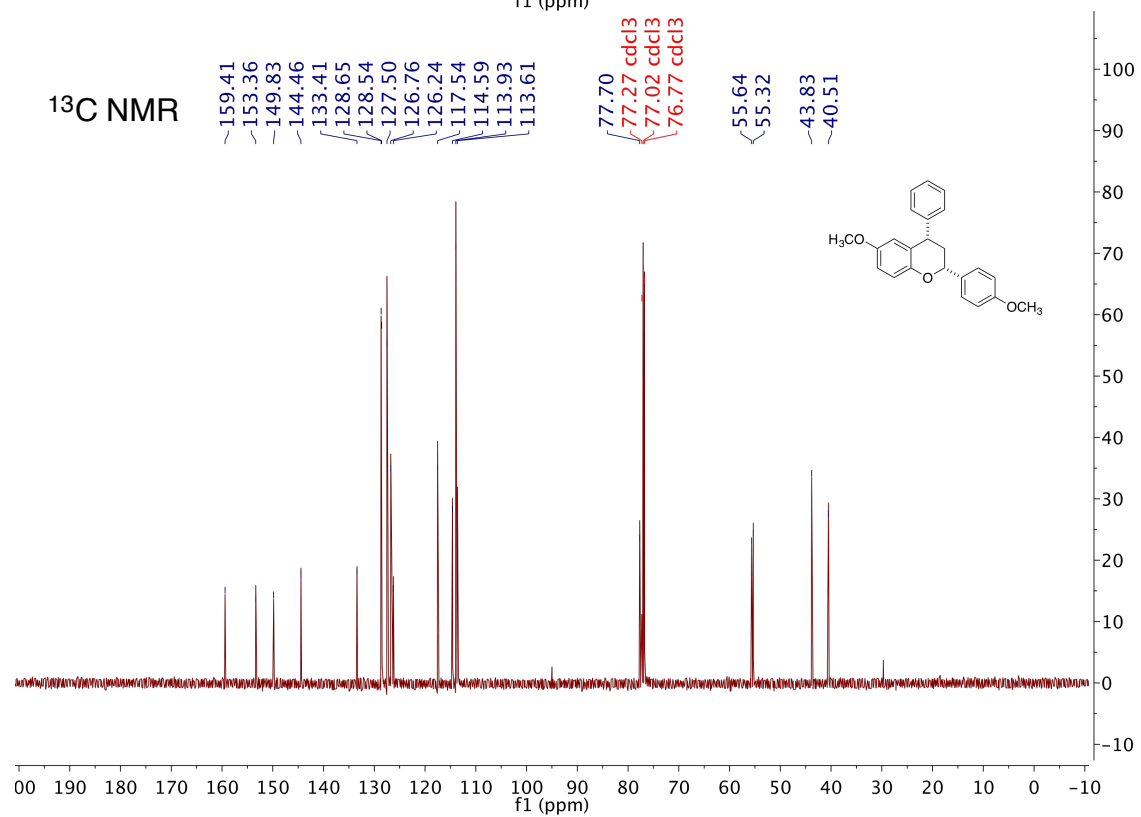
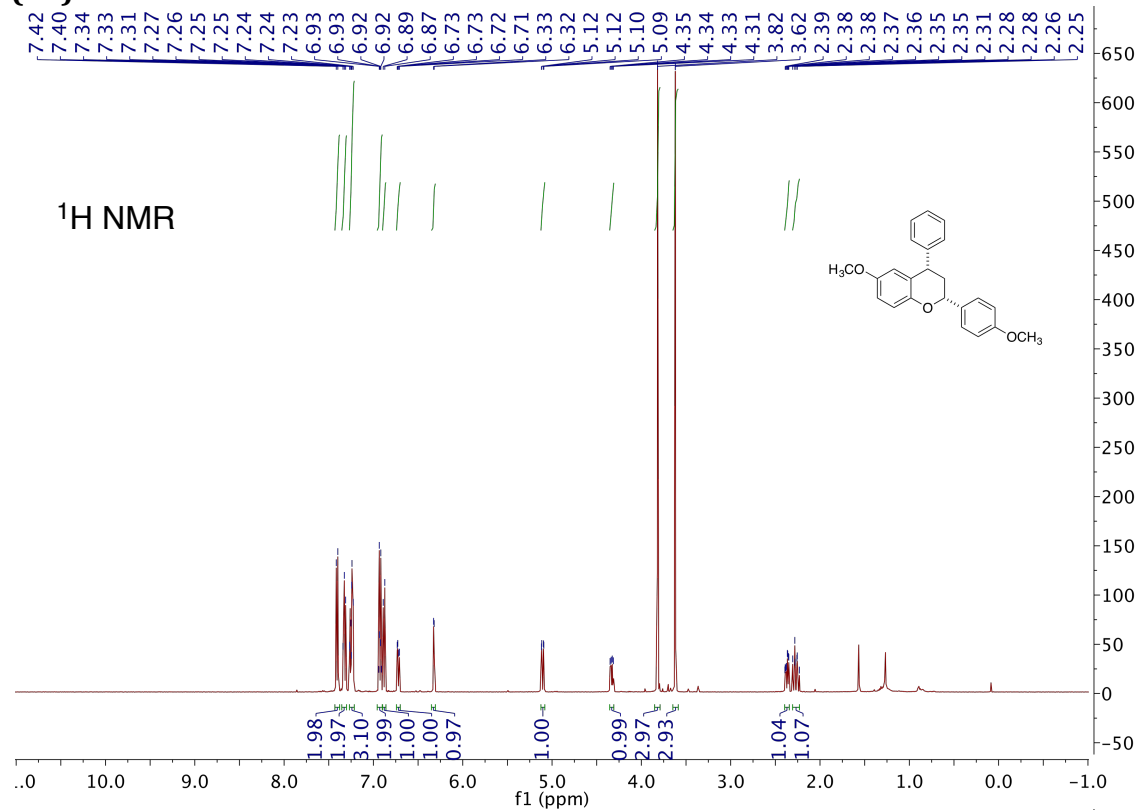
InChI=1S/C24H22O5/c1-25-17-7-3-15(4-8-17)19-11-21(16-5-9-18(26-2)10-6-16)29-22-13-24-23(12-20(19)22)27-14-28-24/h3-10,12-13,19,21H,11,14H2,1-2H3/t19-,21+/m0/s1

¹⁶ Barbato, K. S.; Luan, Y.; Ramella, D.; Panek, J. S.; Schaus, S. E. *Org. Lett.*, **2015**, *17*, 23, 5812–5815.

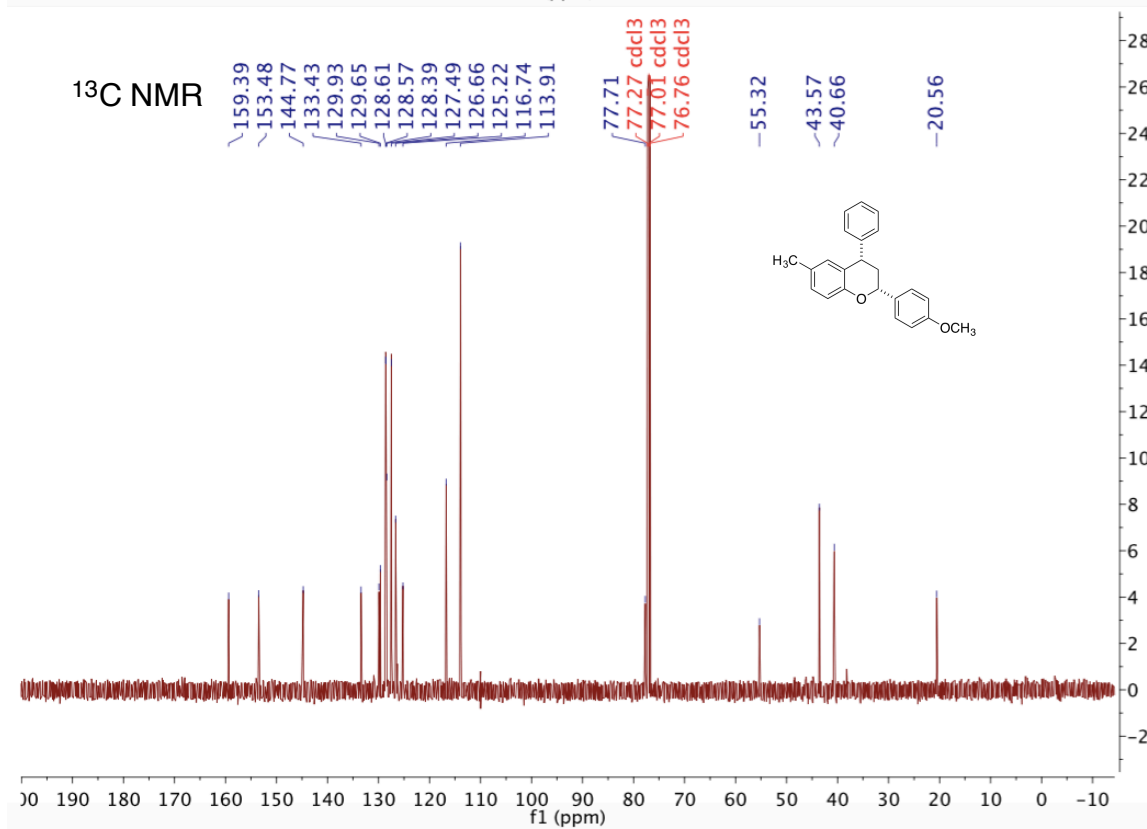
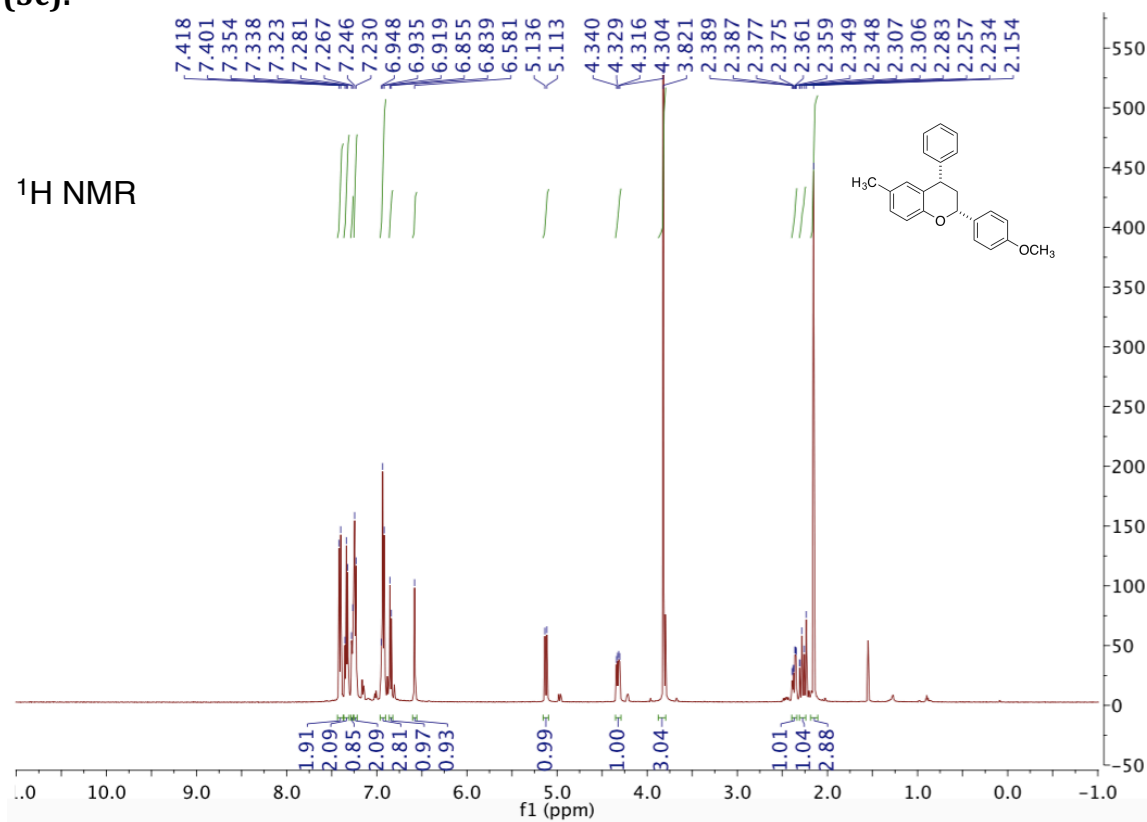
(3a):



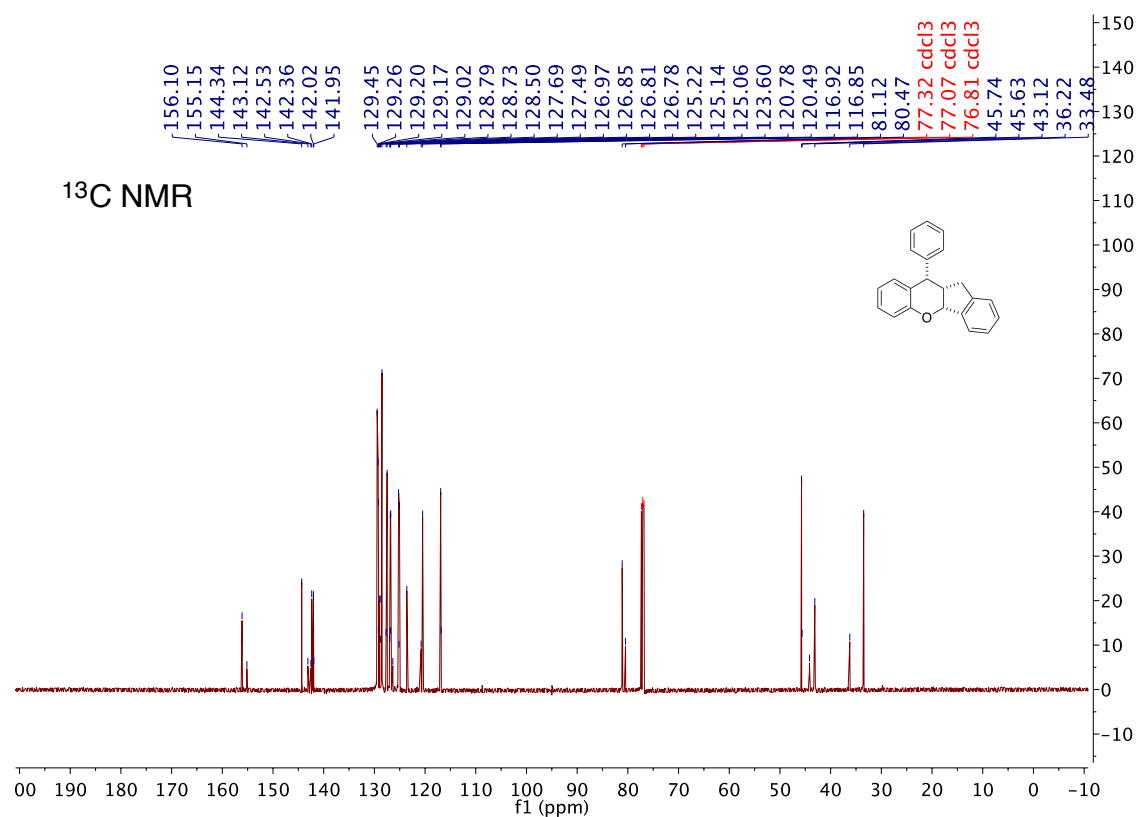
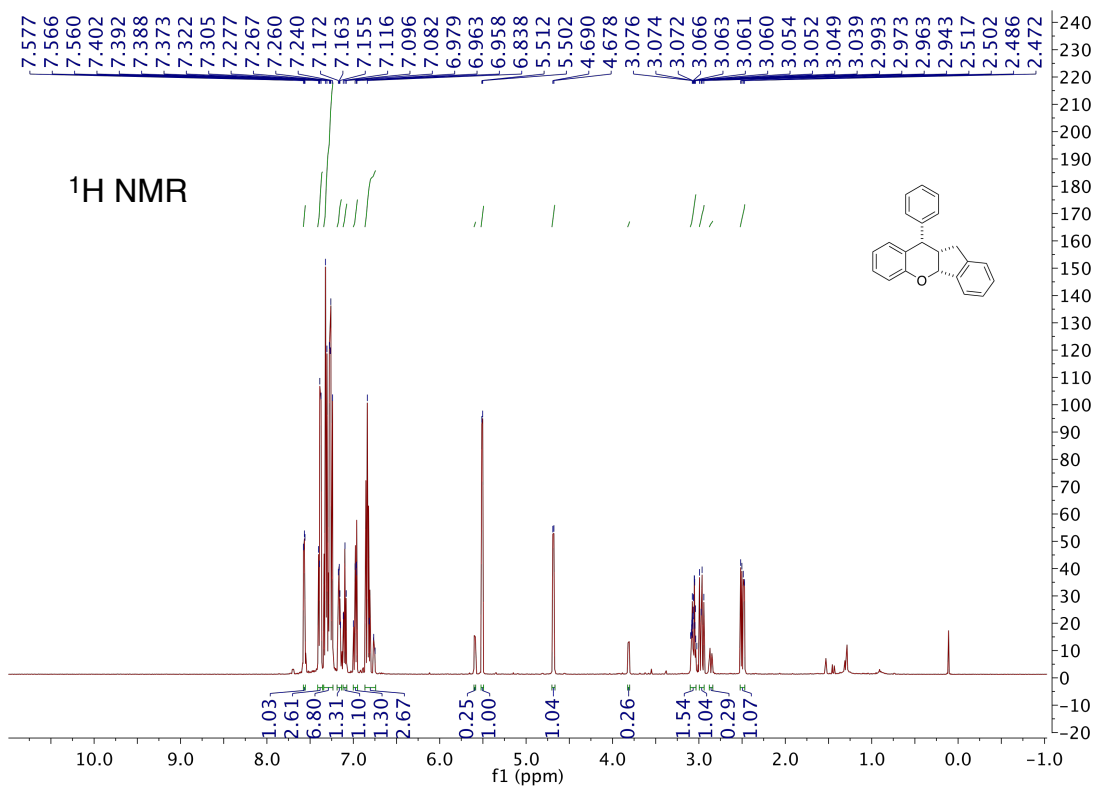
(3b):



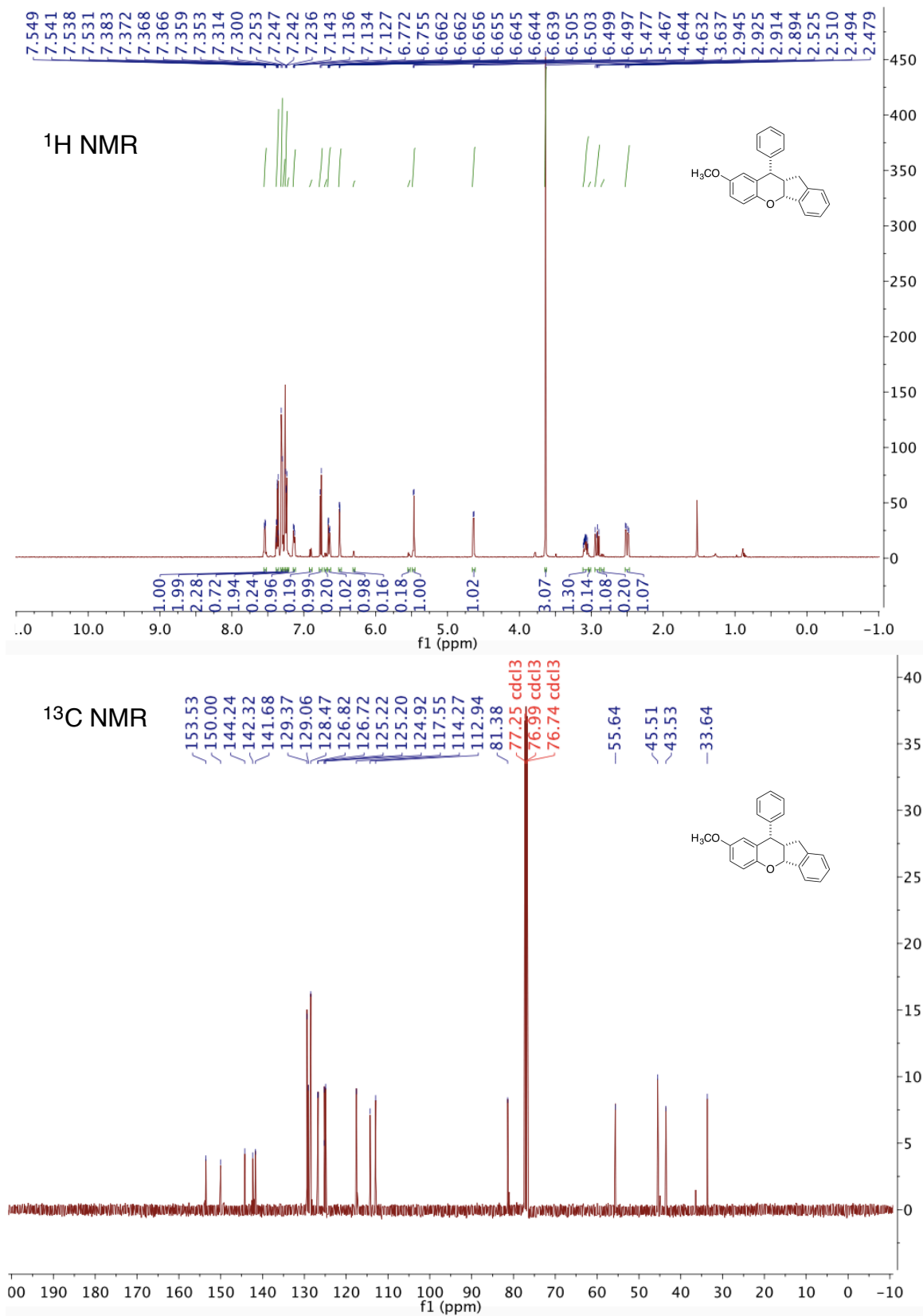
(3c):



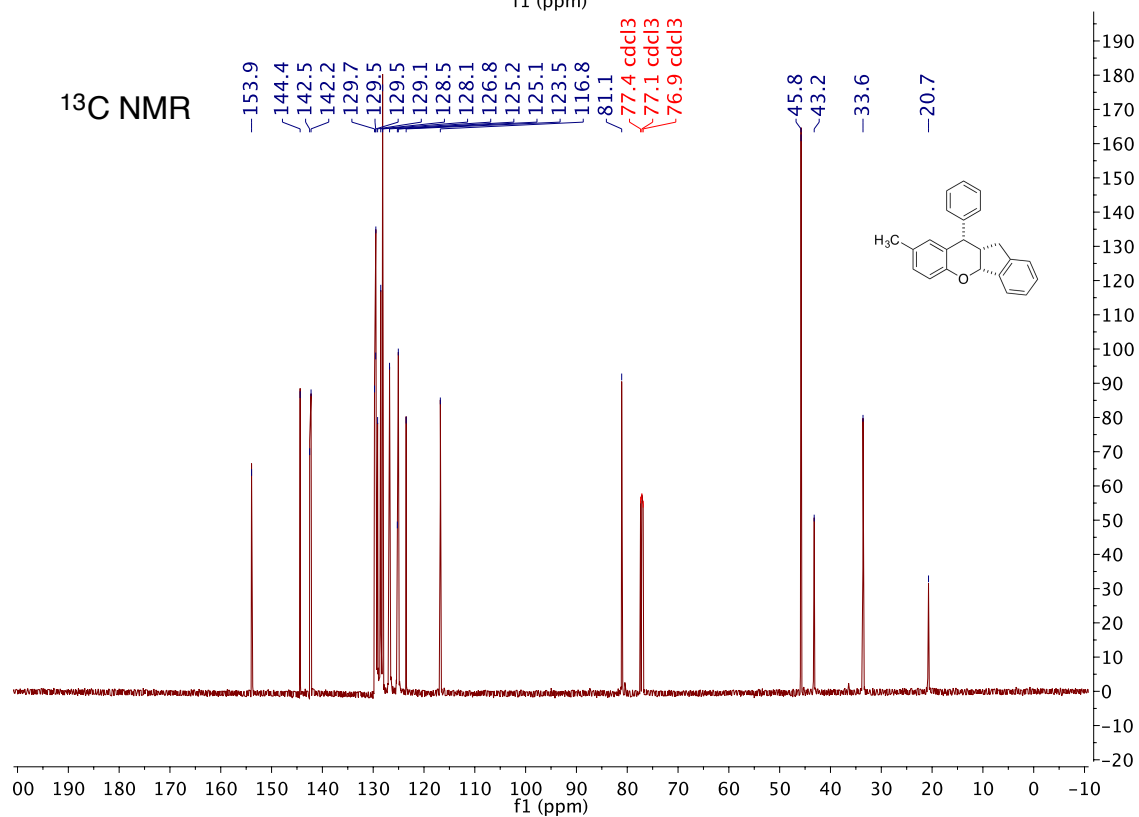
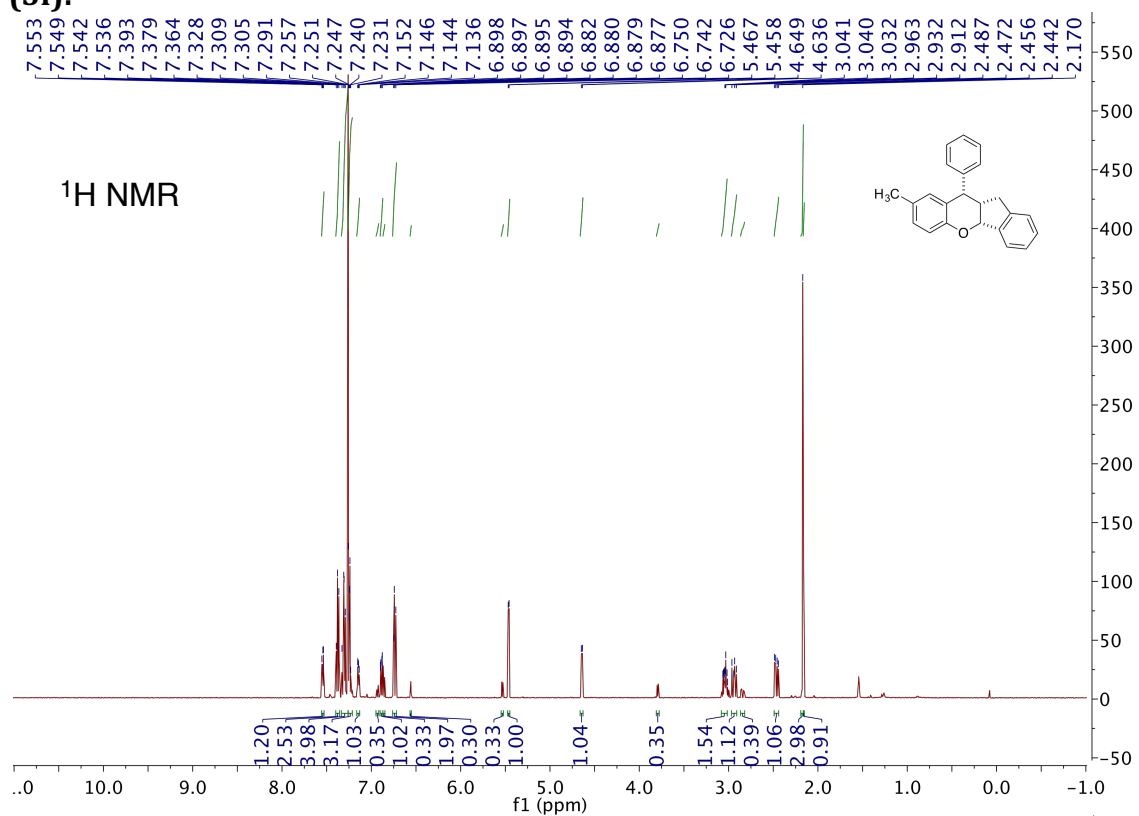
(3d):



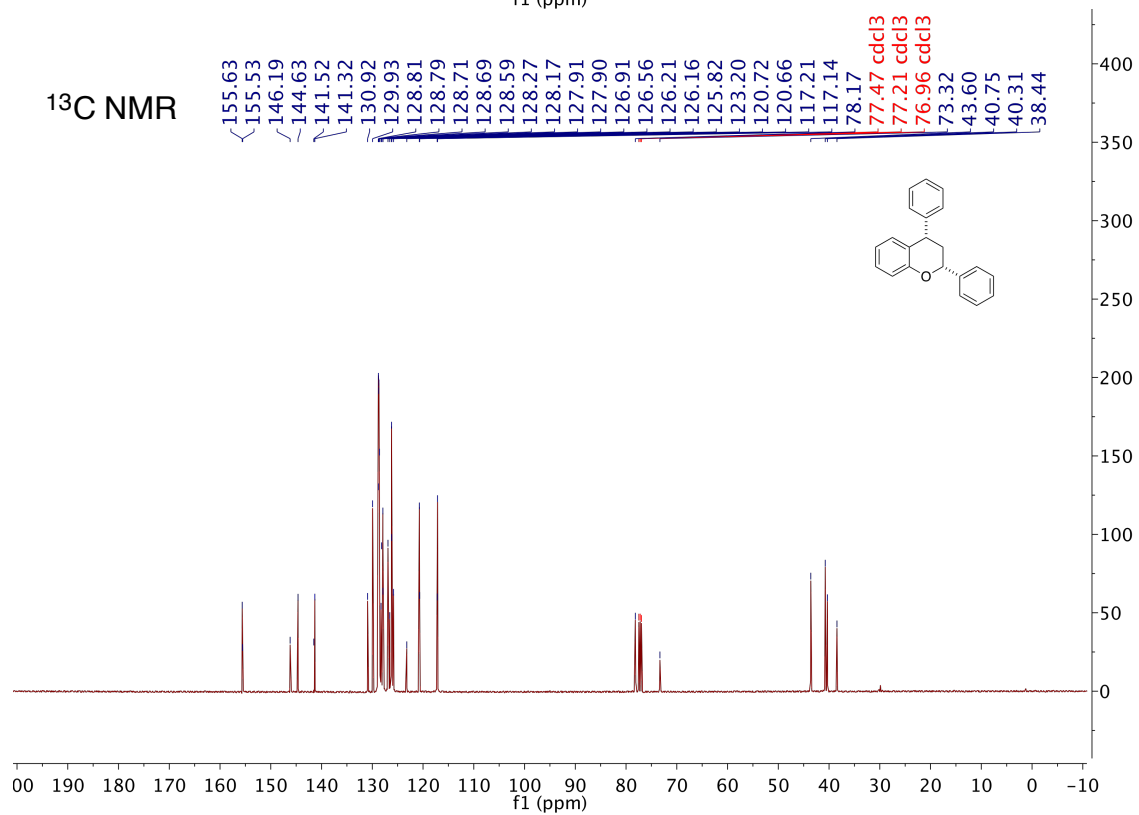
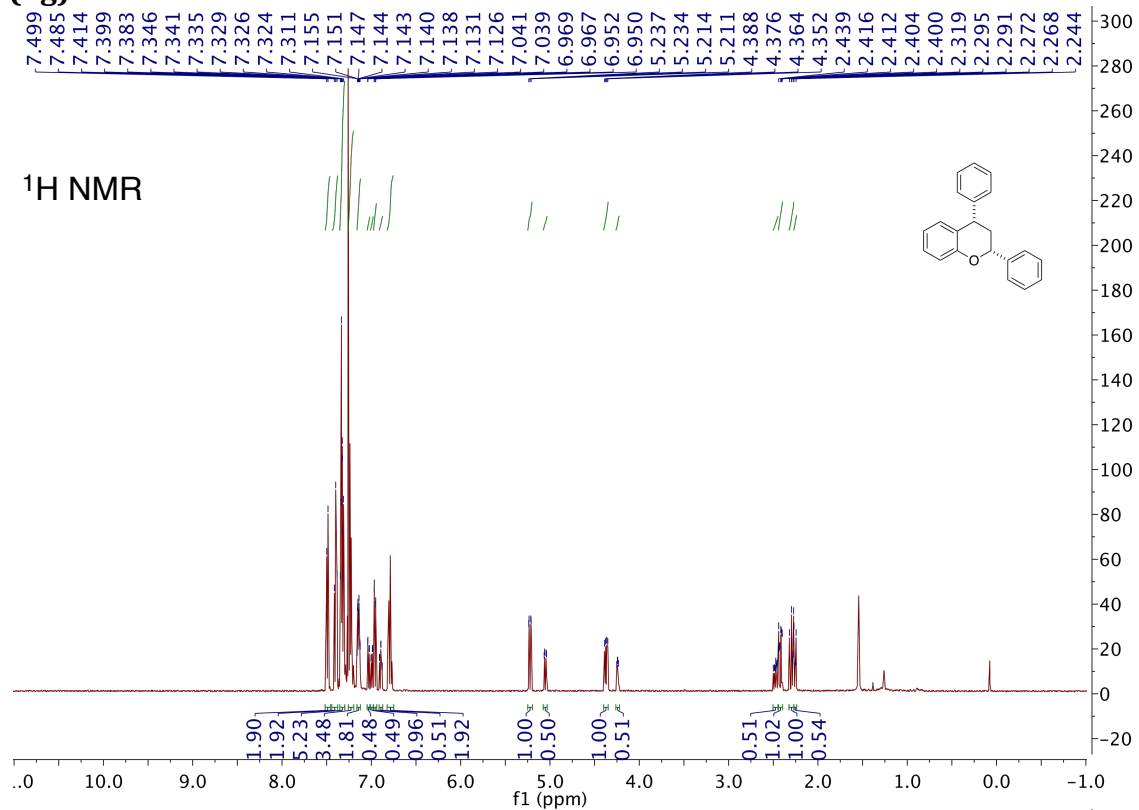
(3e):



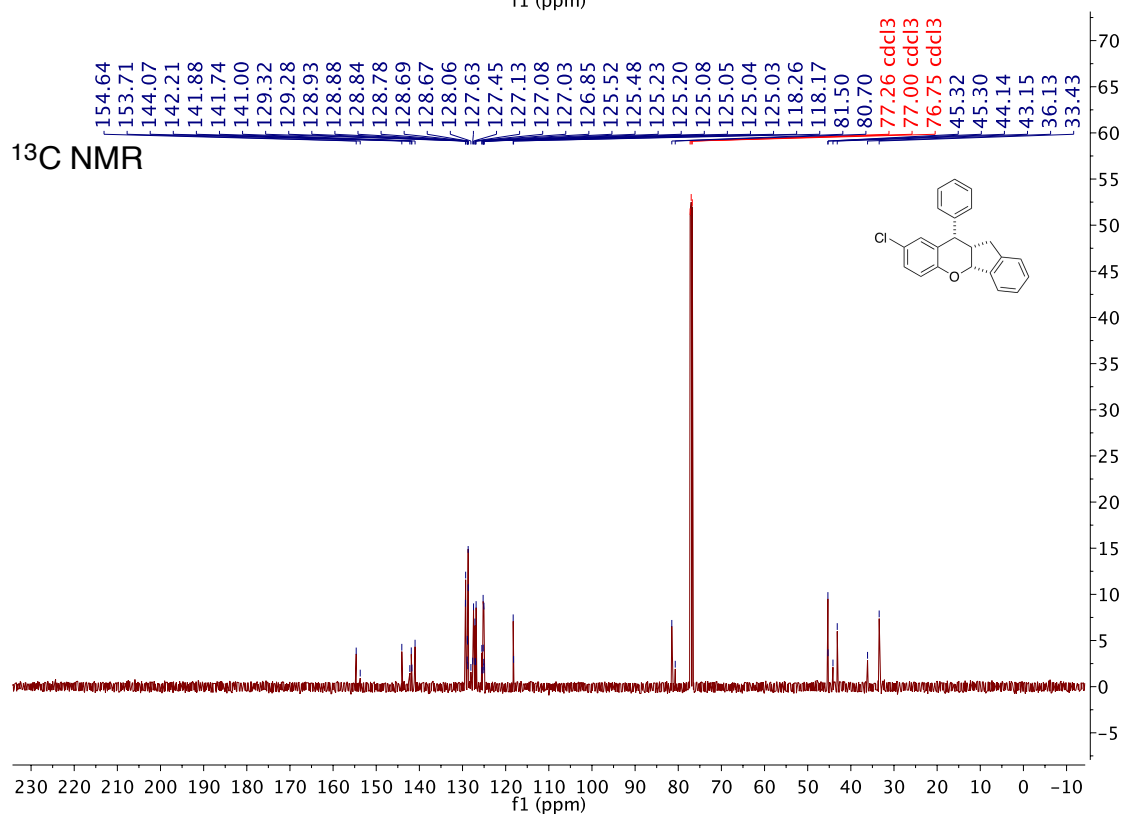
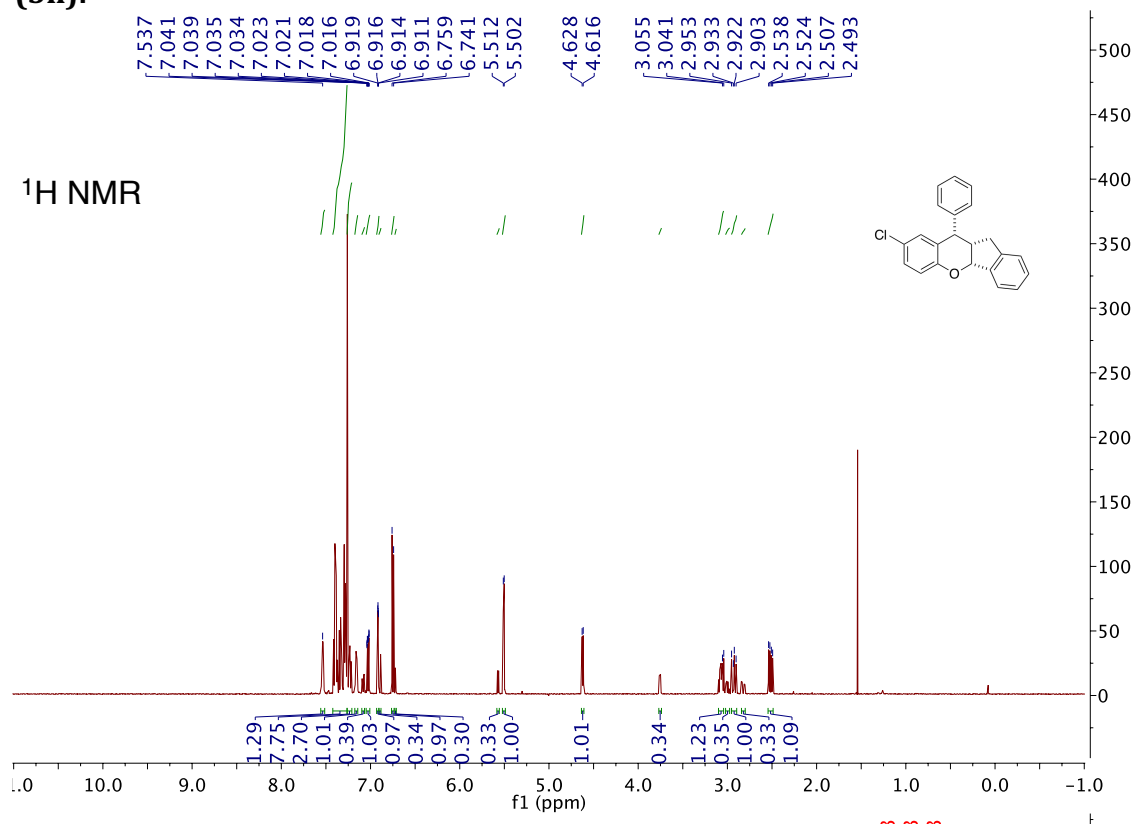
(3f):



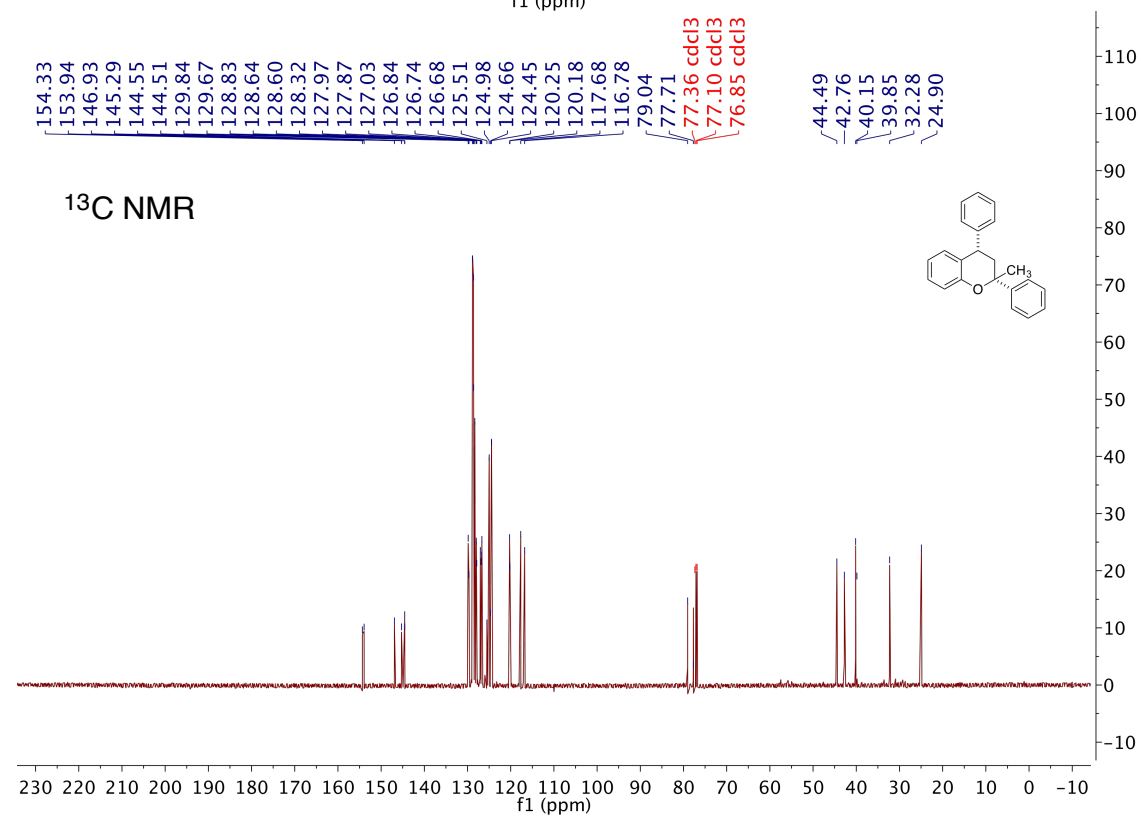
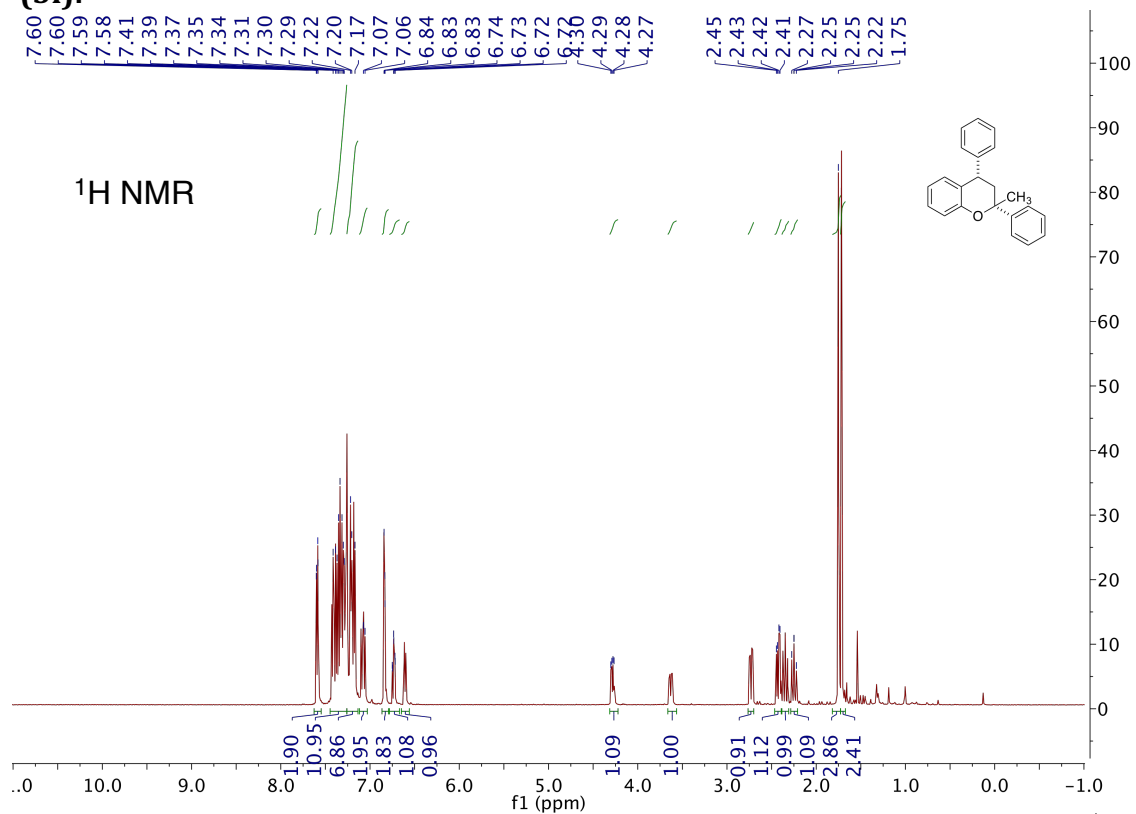
(3g):



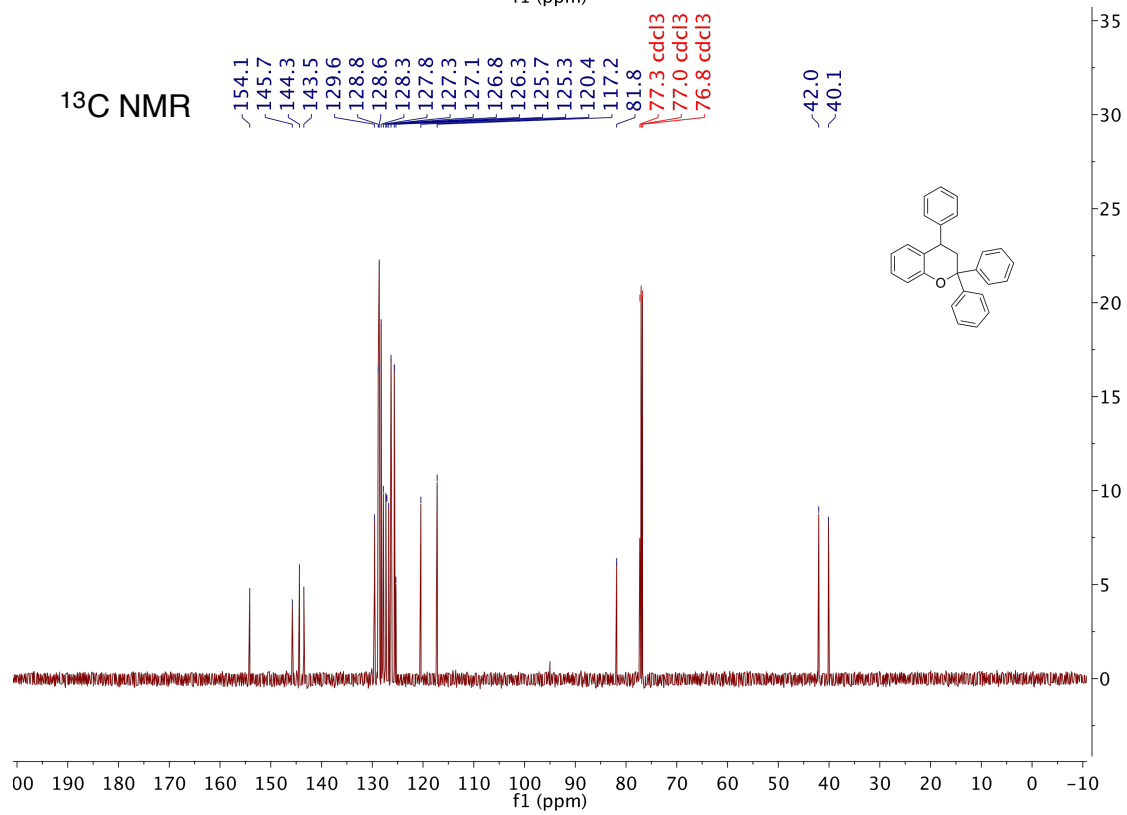
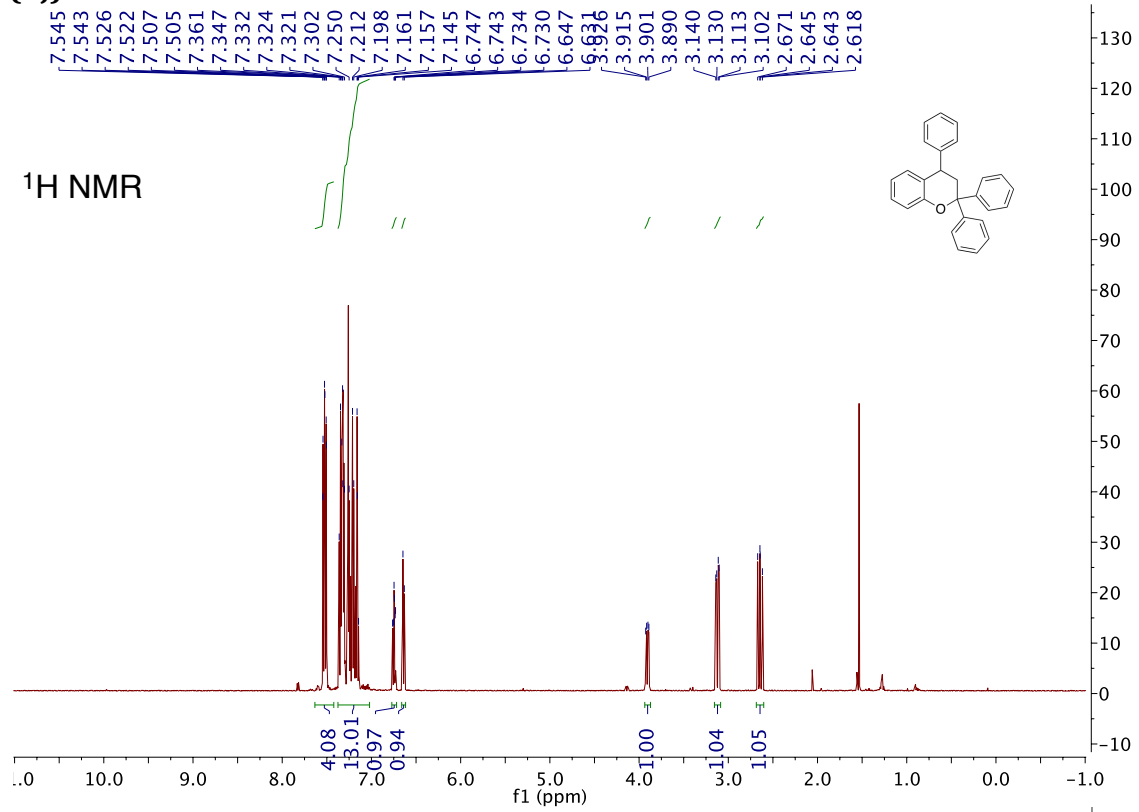
(3h):



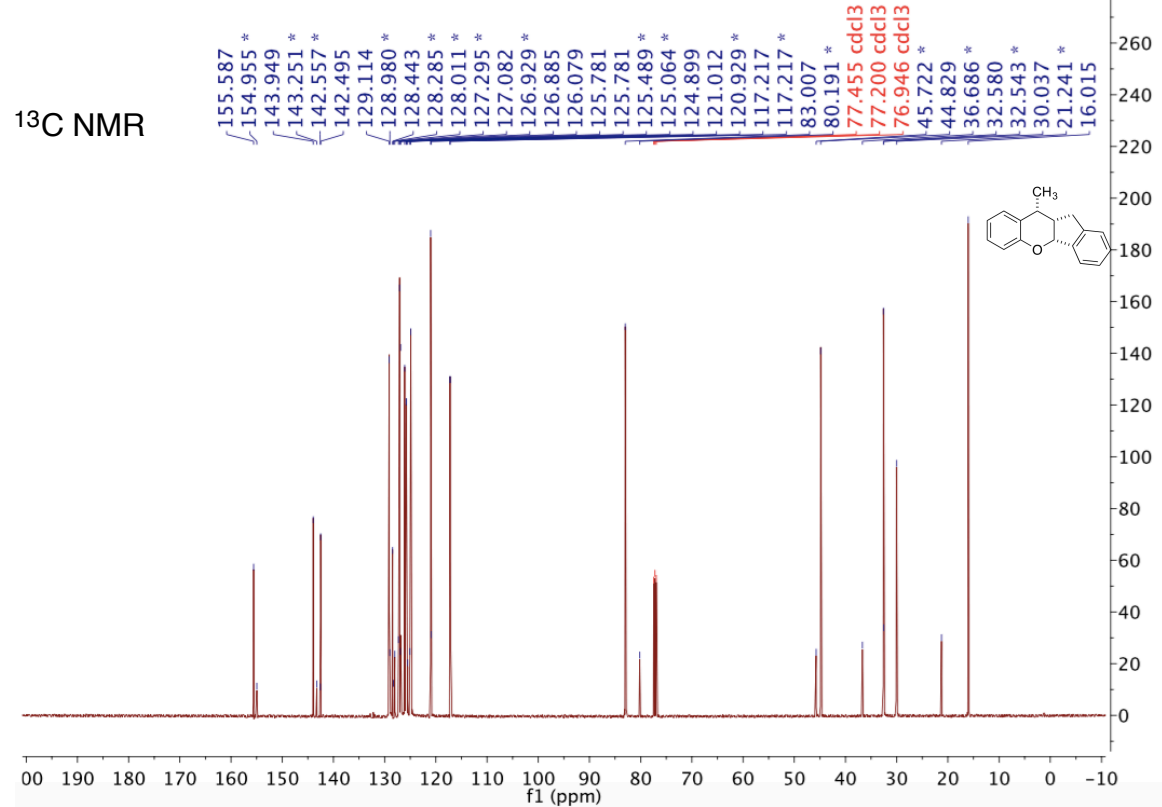
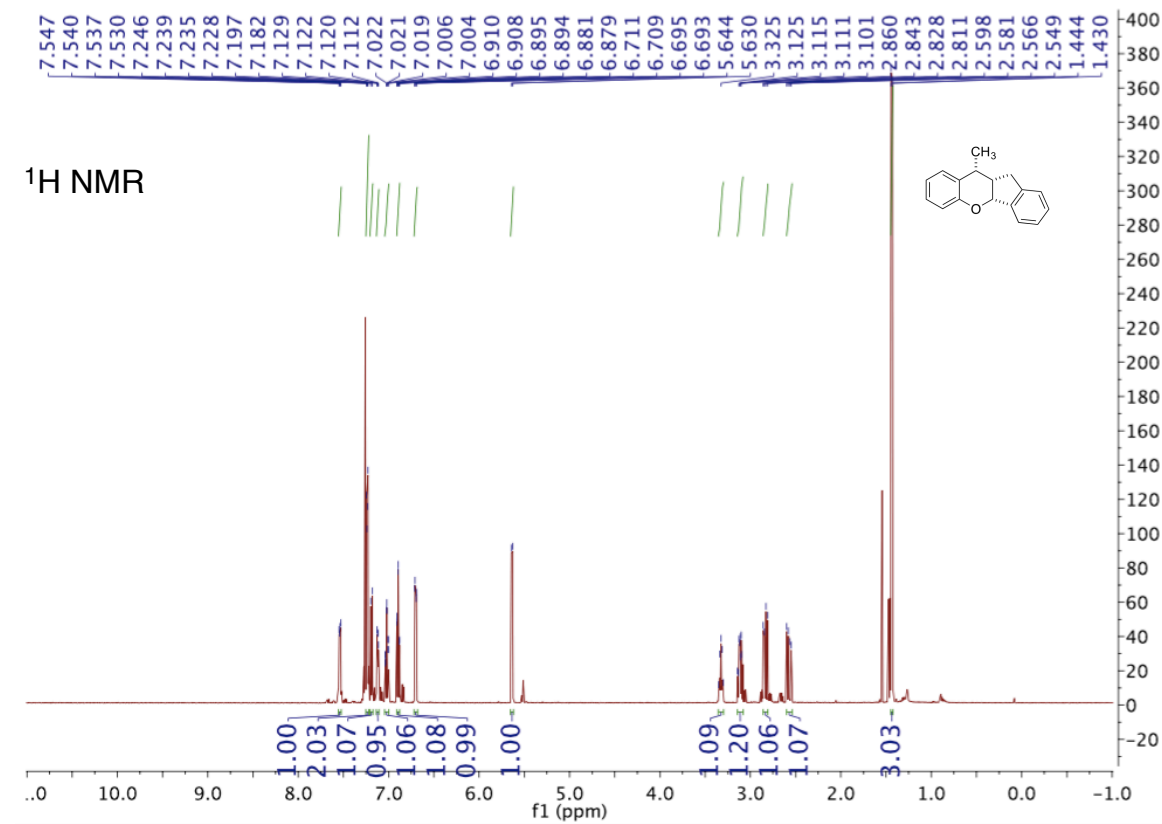
(3i):



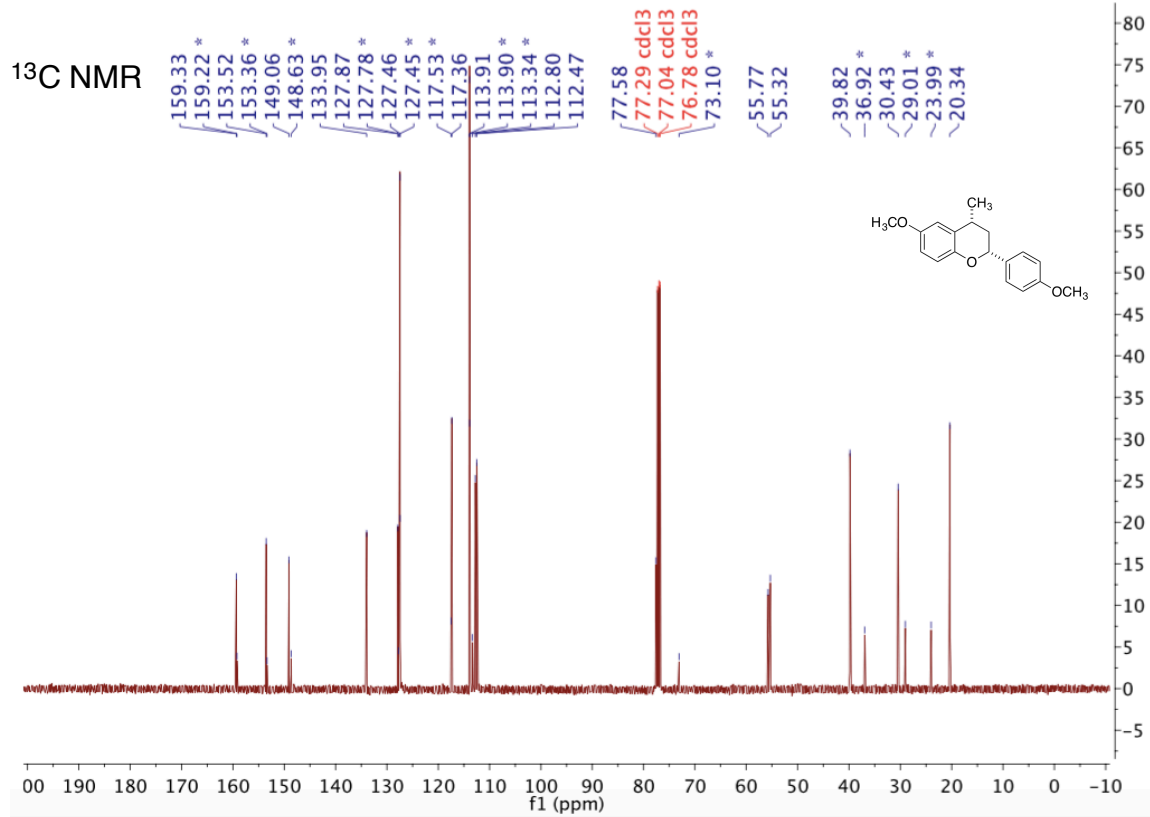
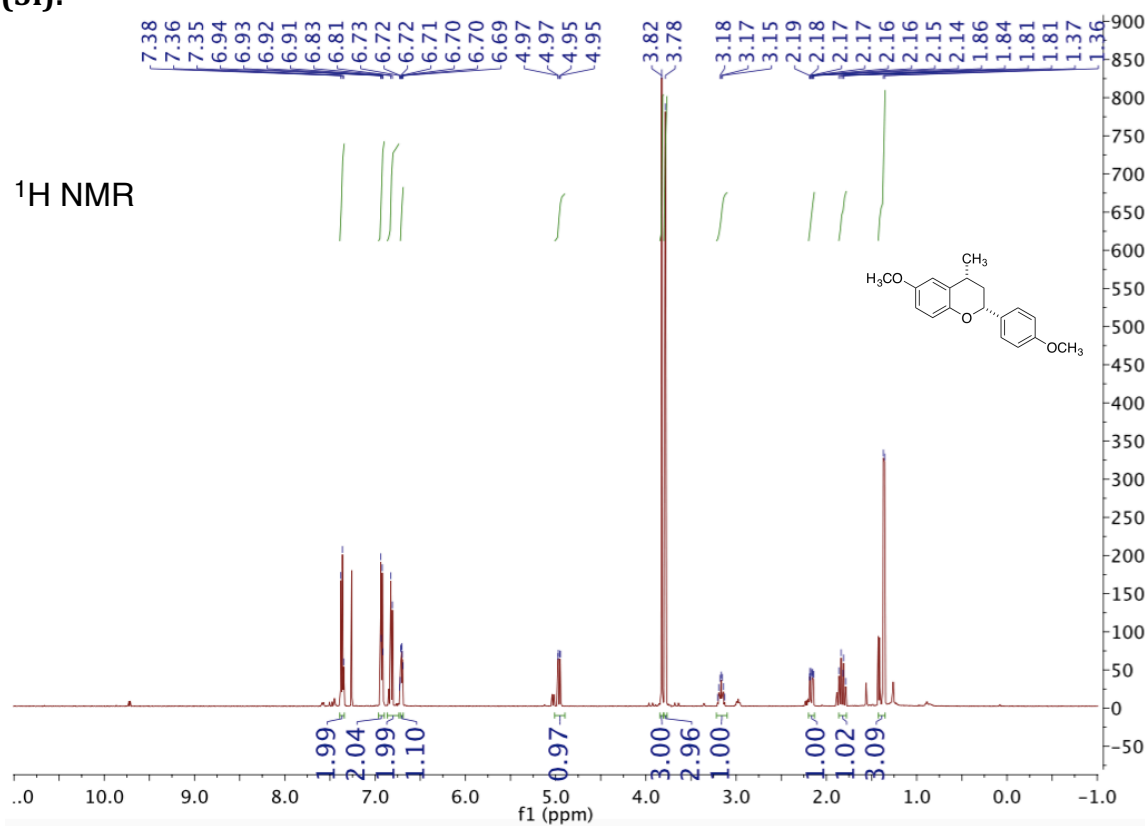
(3j):



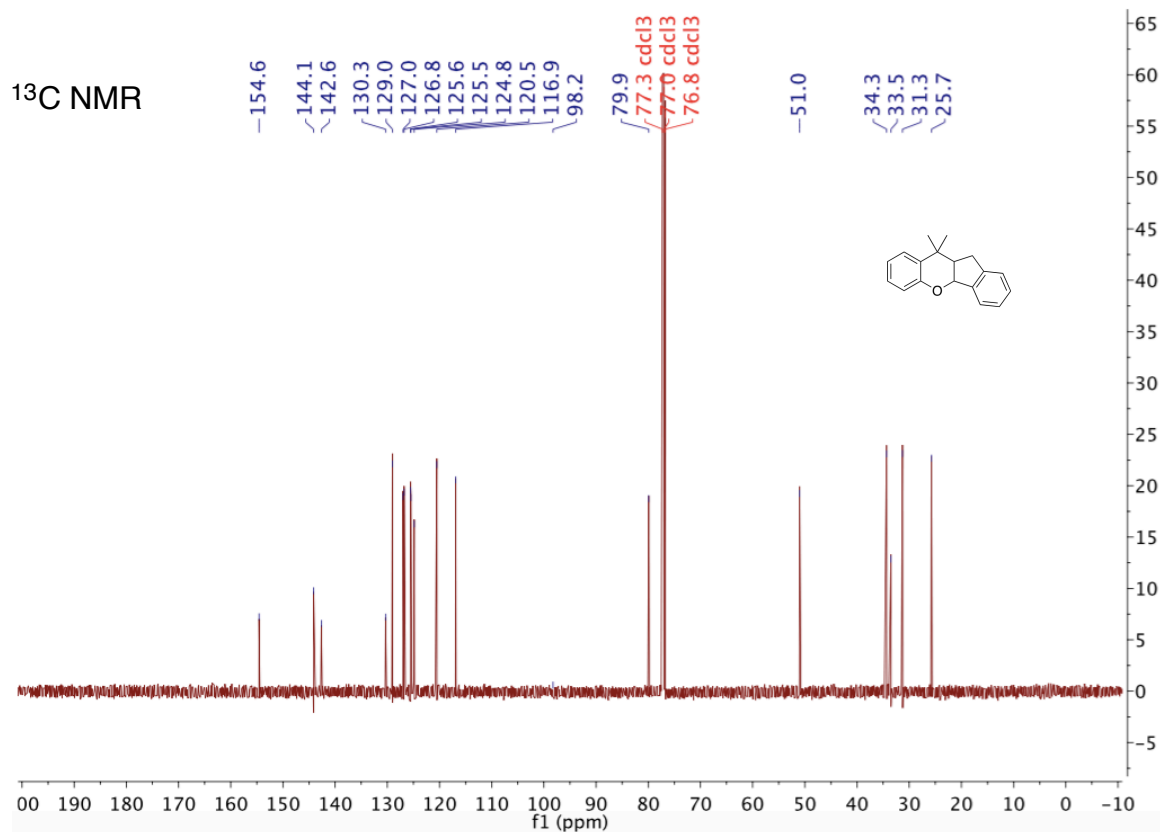
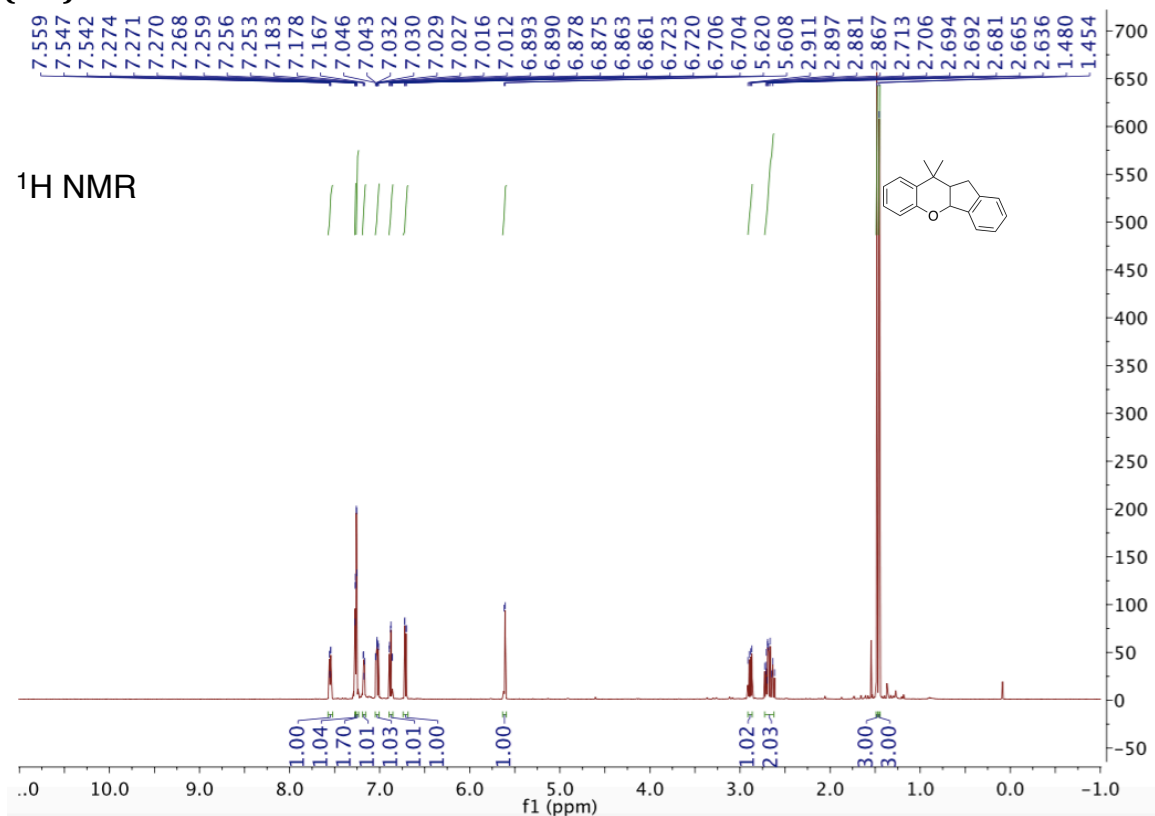
(3k):



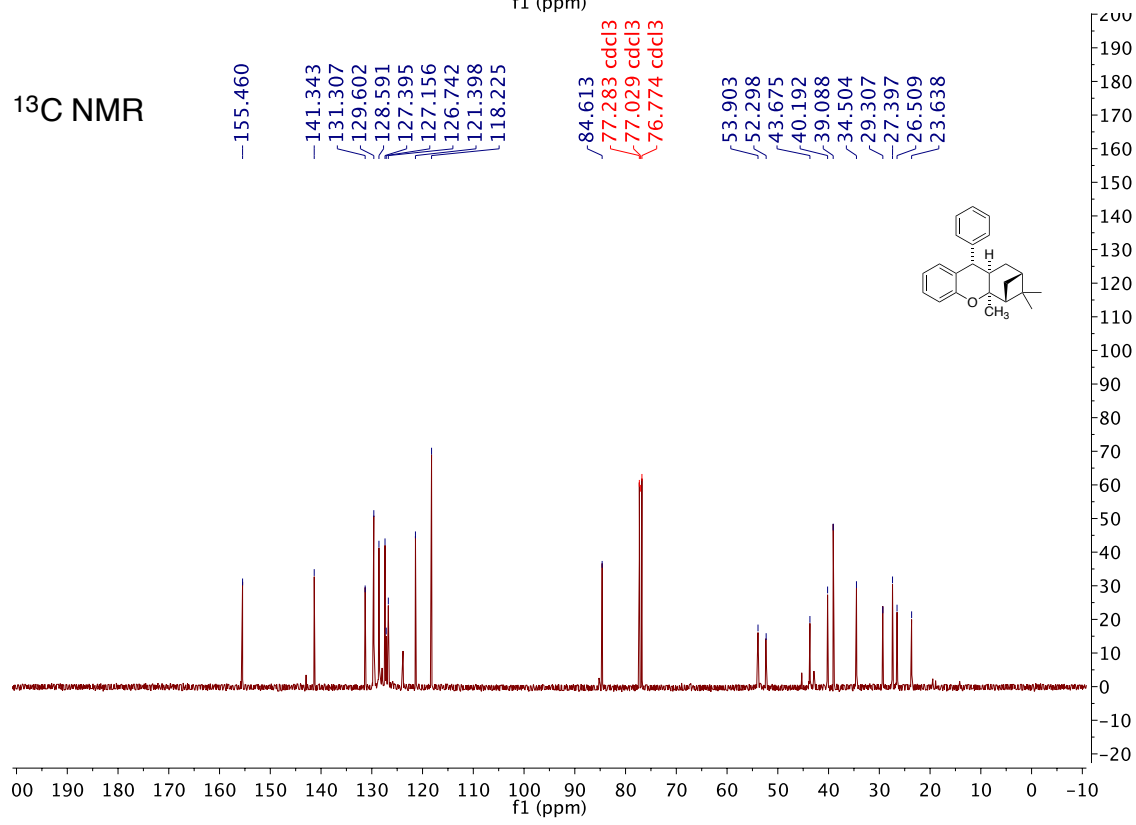
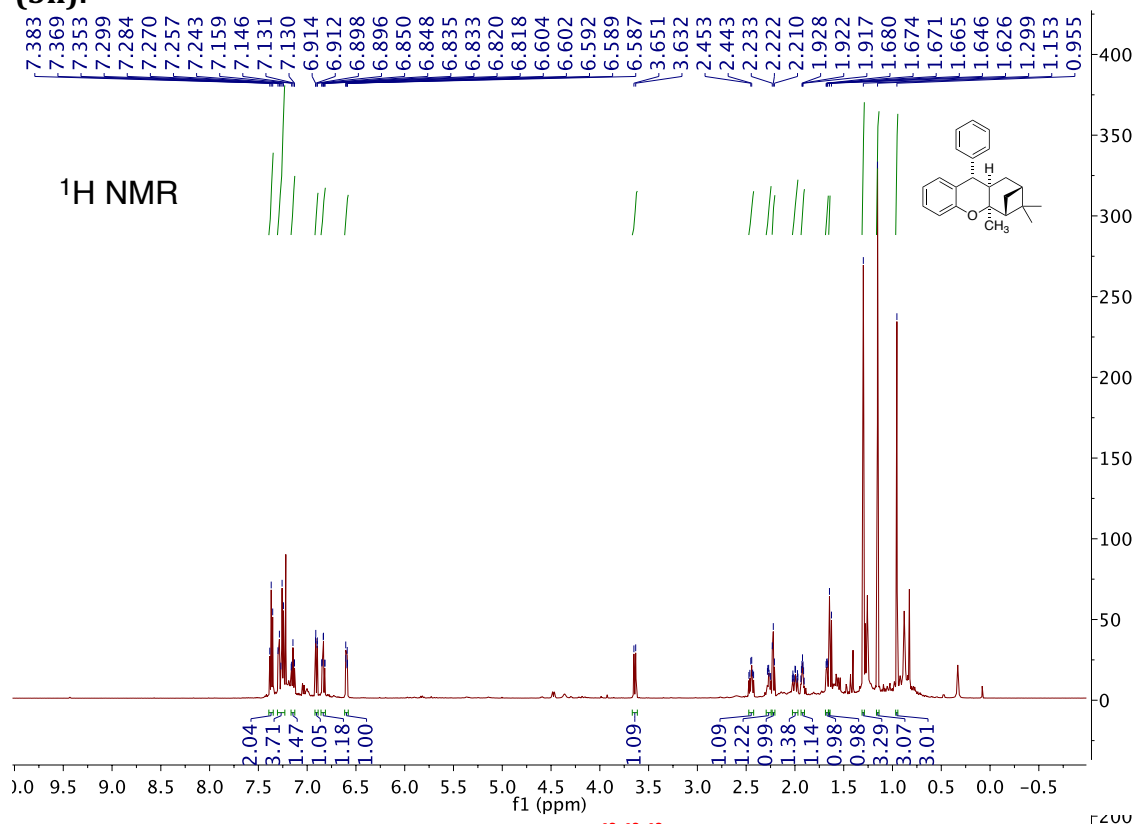
(31):



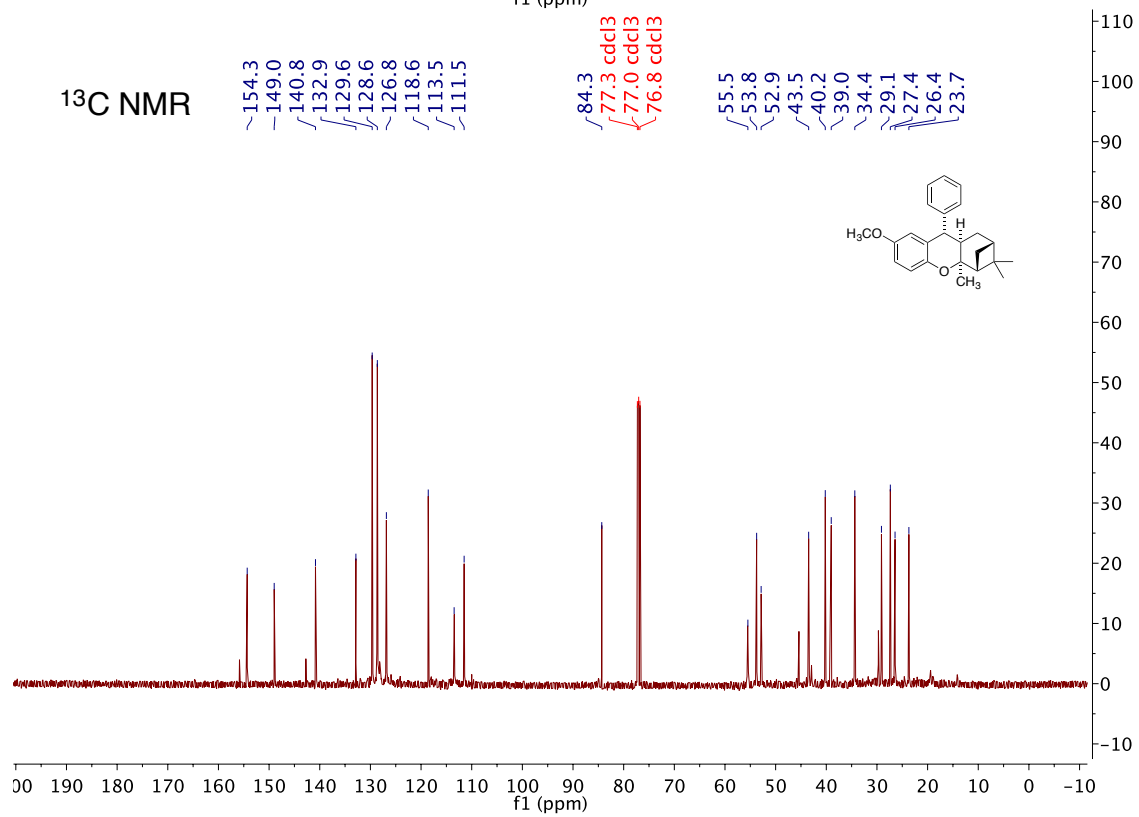
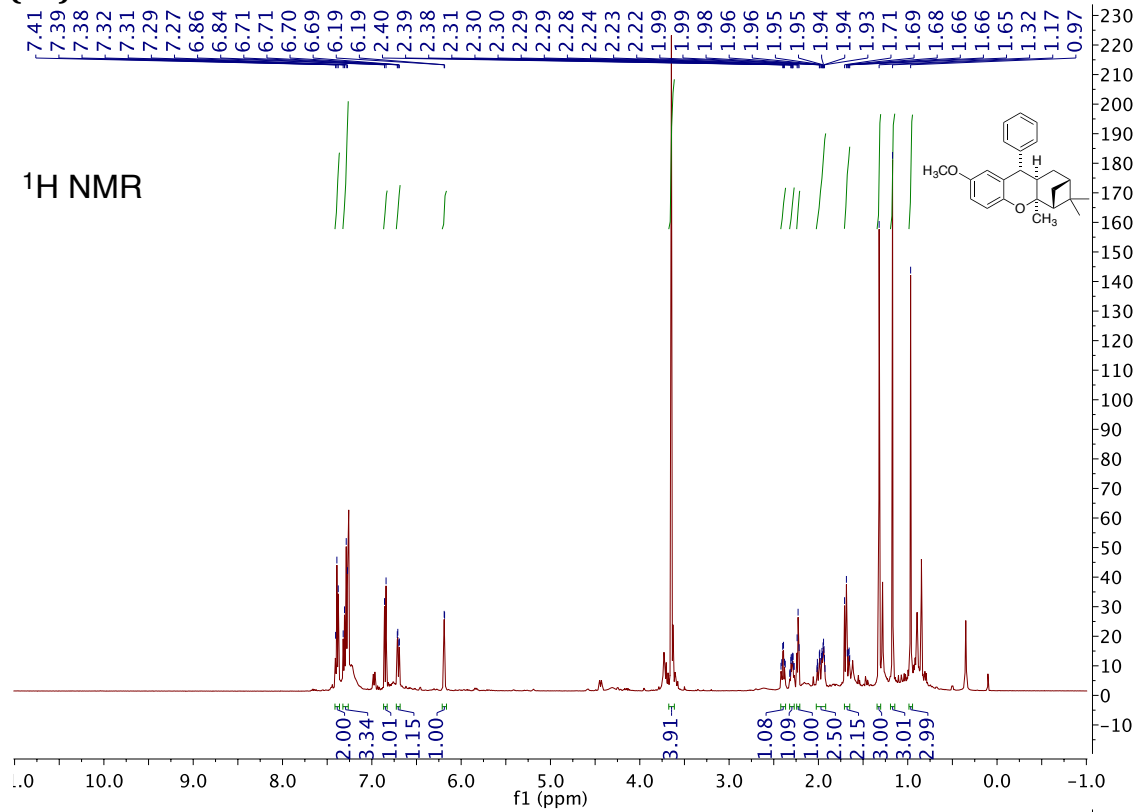
(3m):



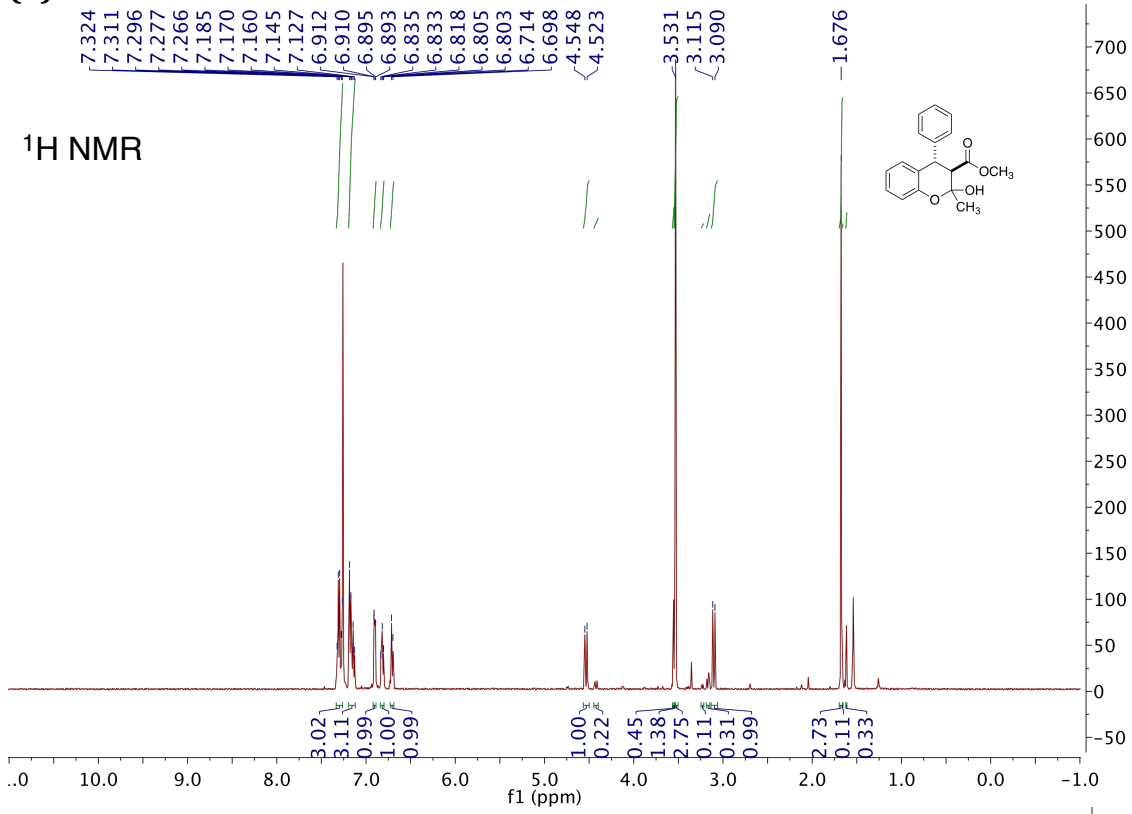
(3n):



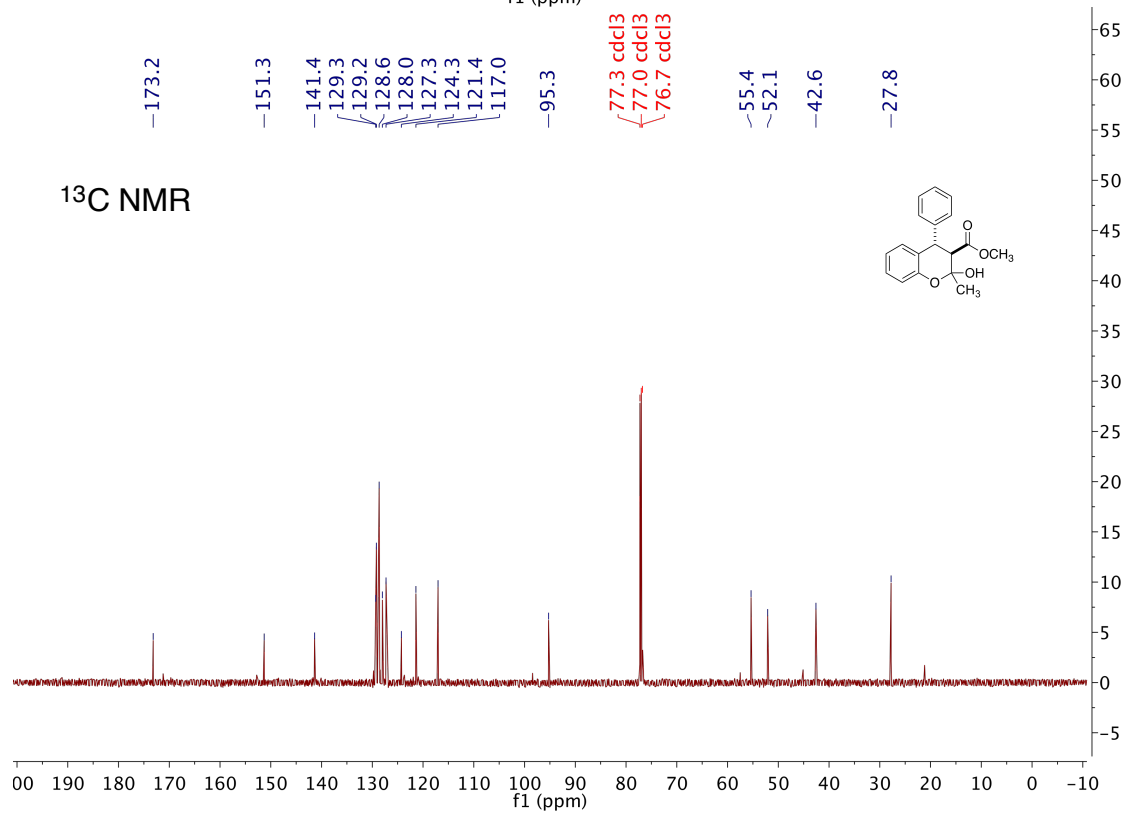
(3o):



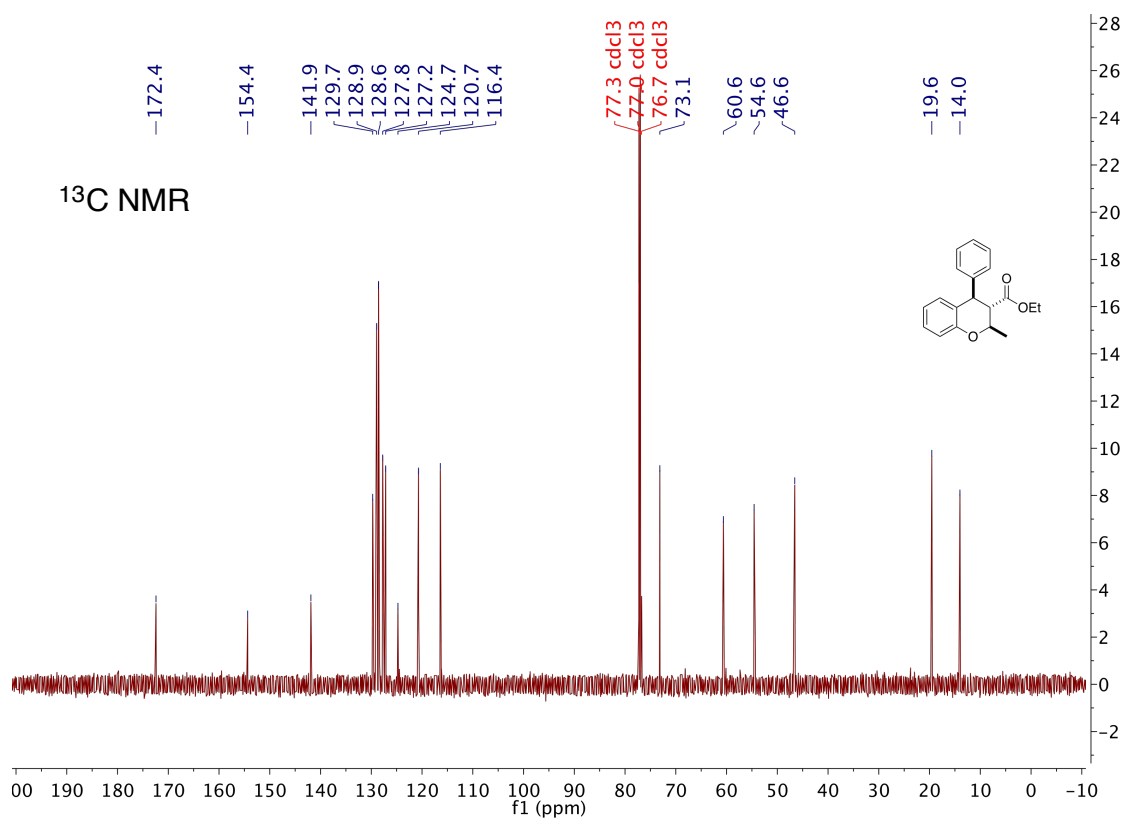
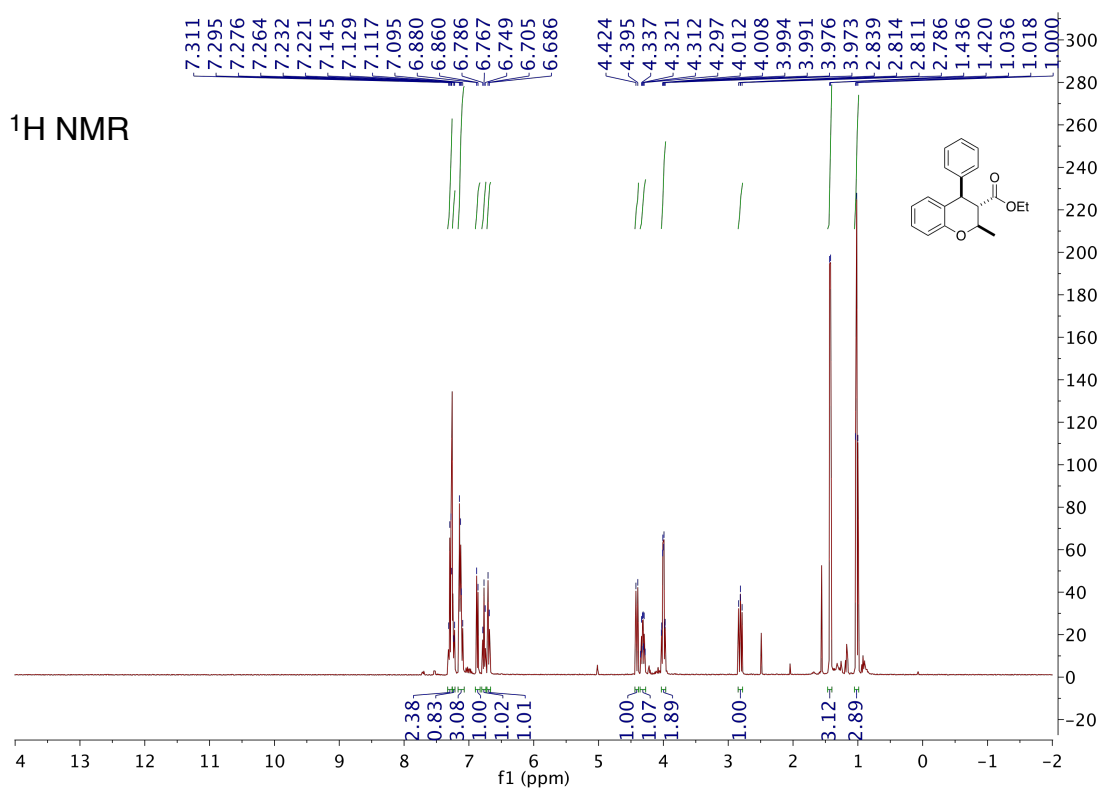
(5):



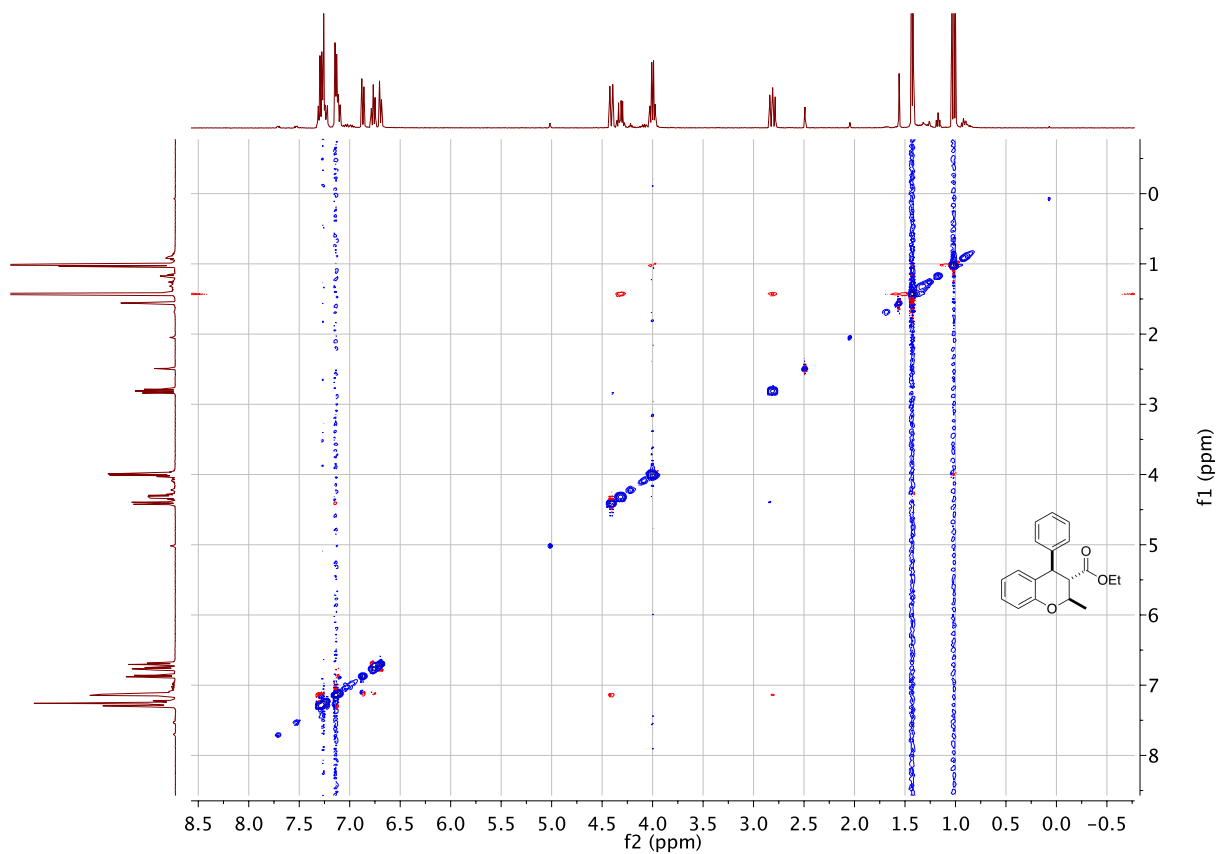
¹³C NMR



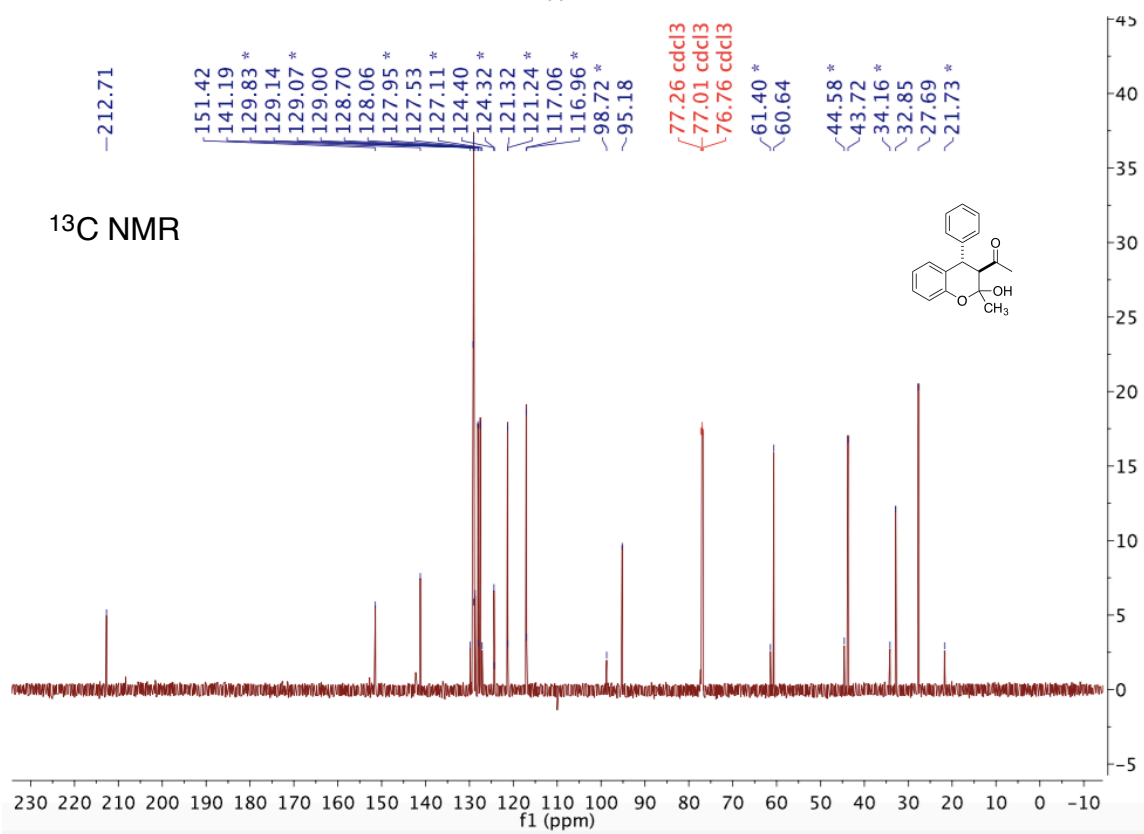
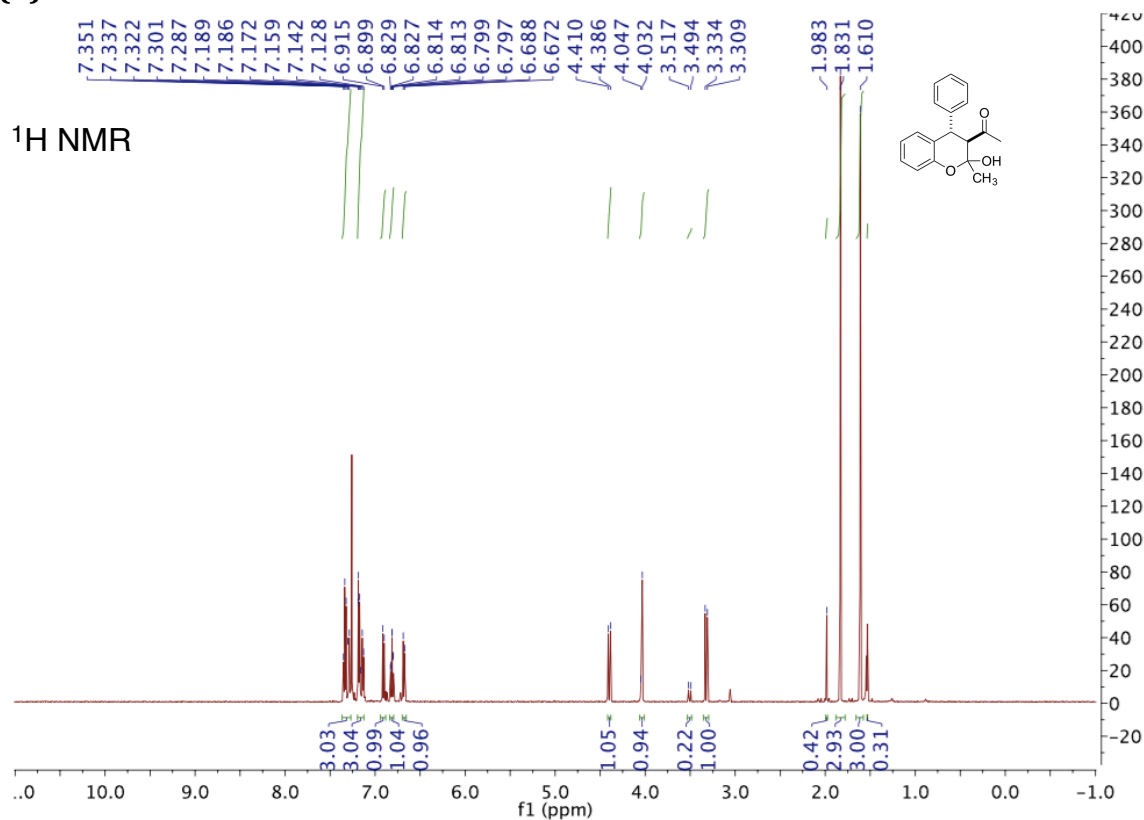
(6):



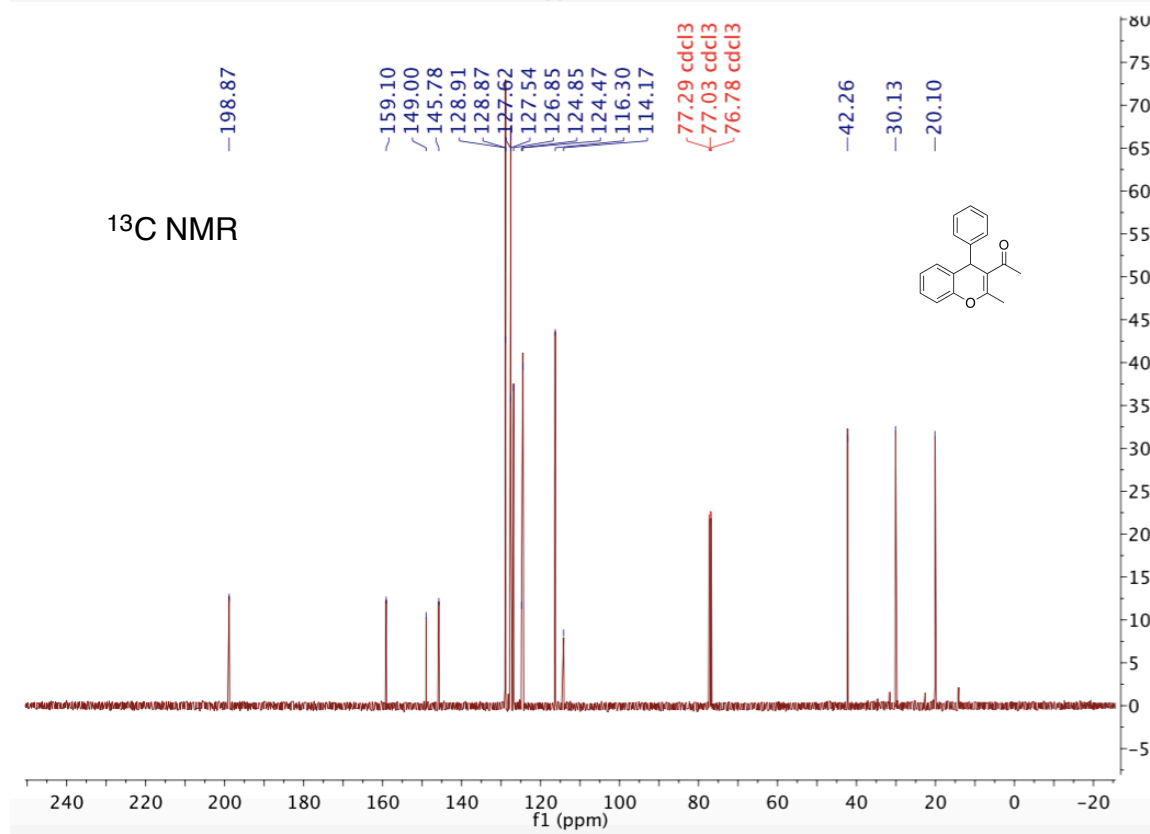
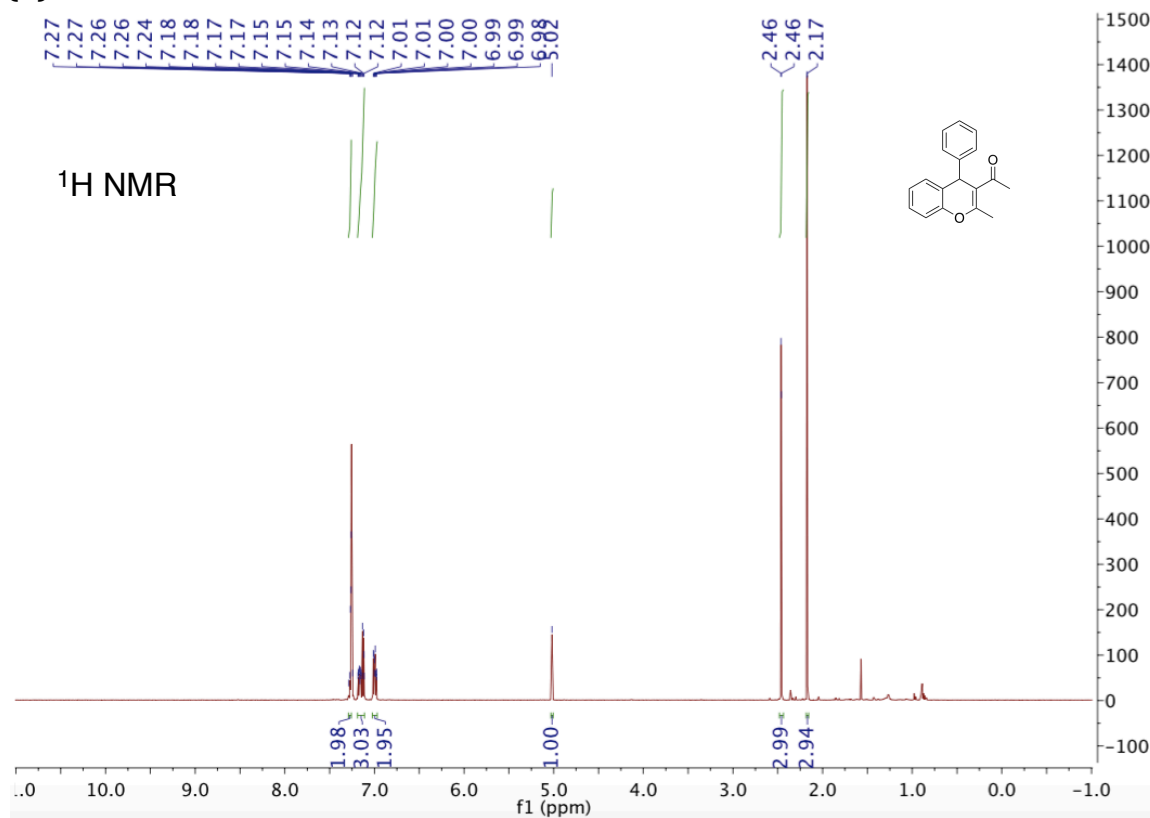
NOESY NMR (400 MHz, CDCl₃):



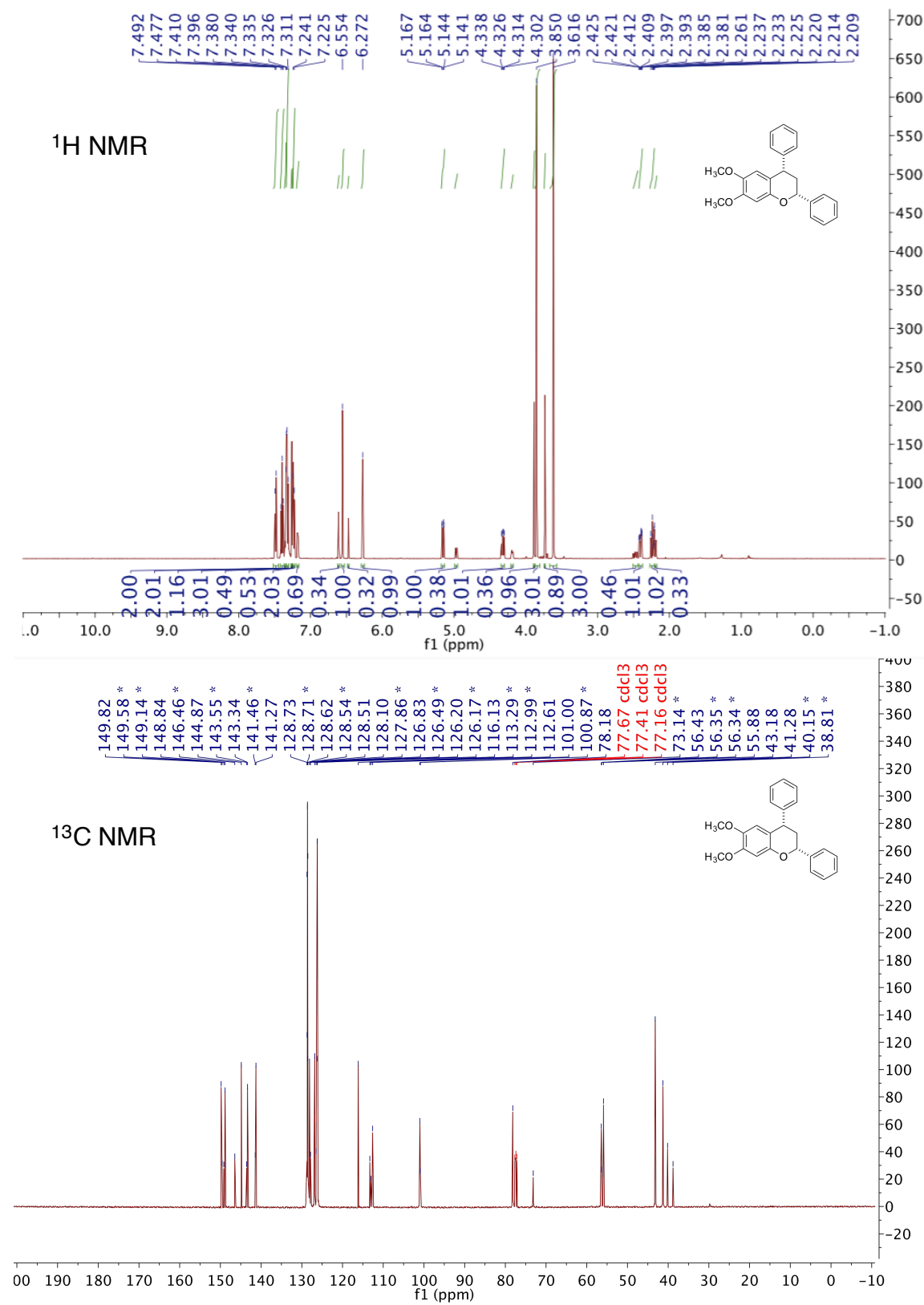
(7):



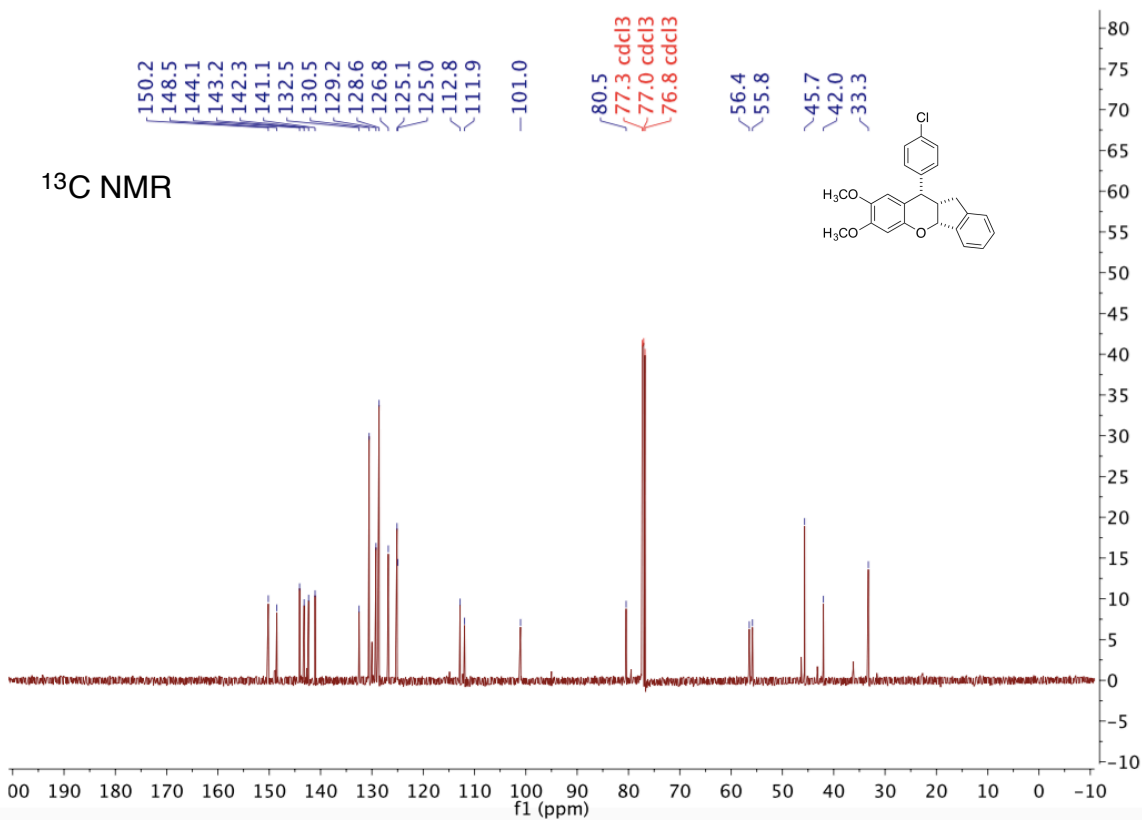
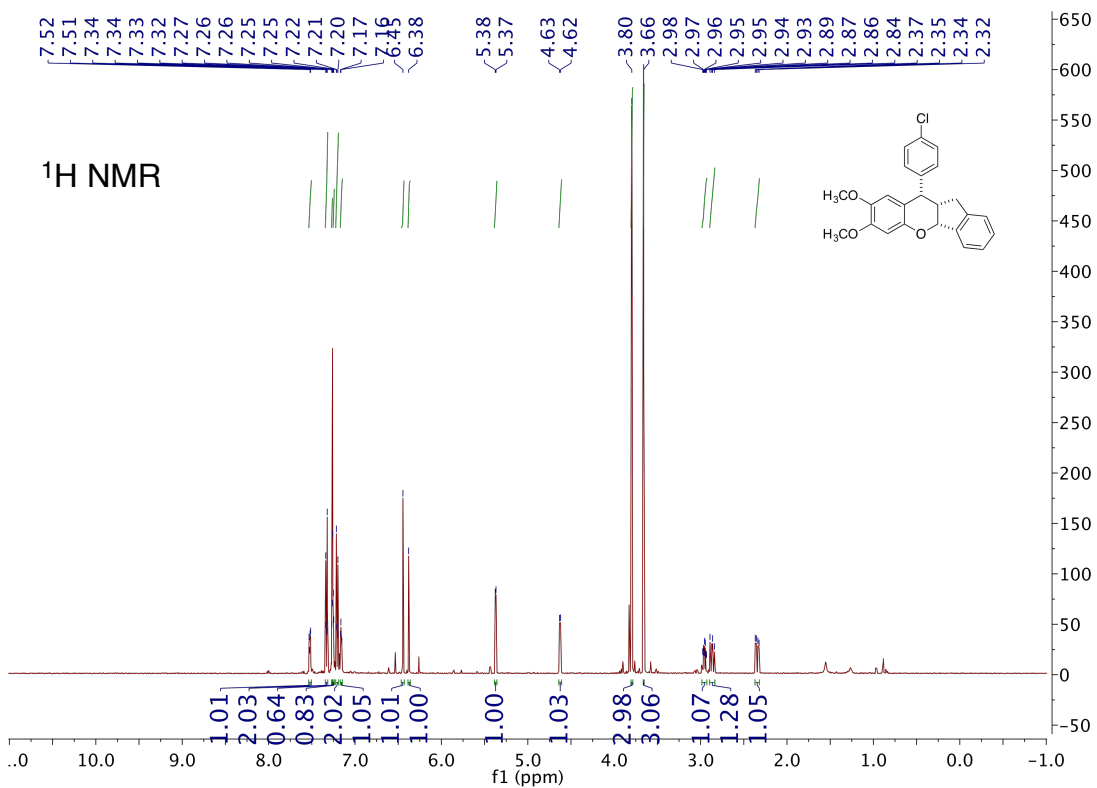
(8):



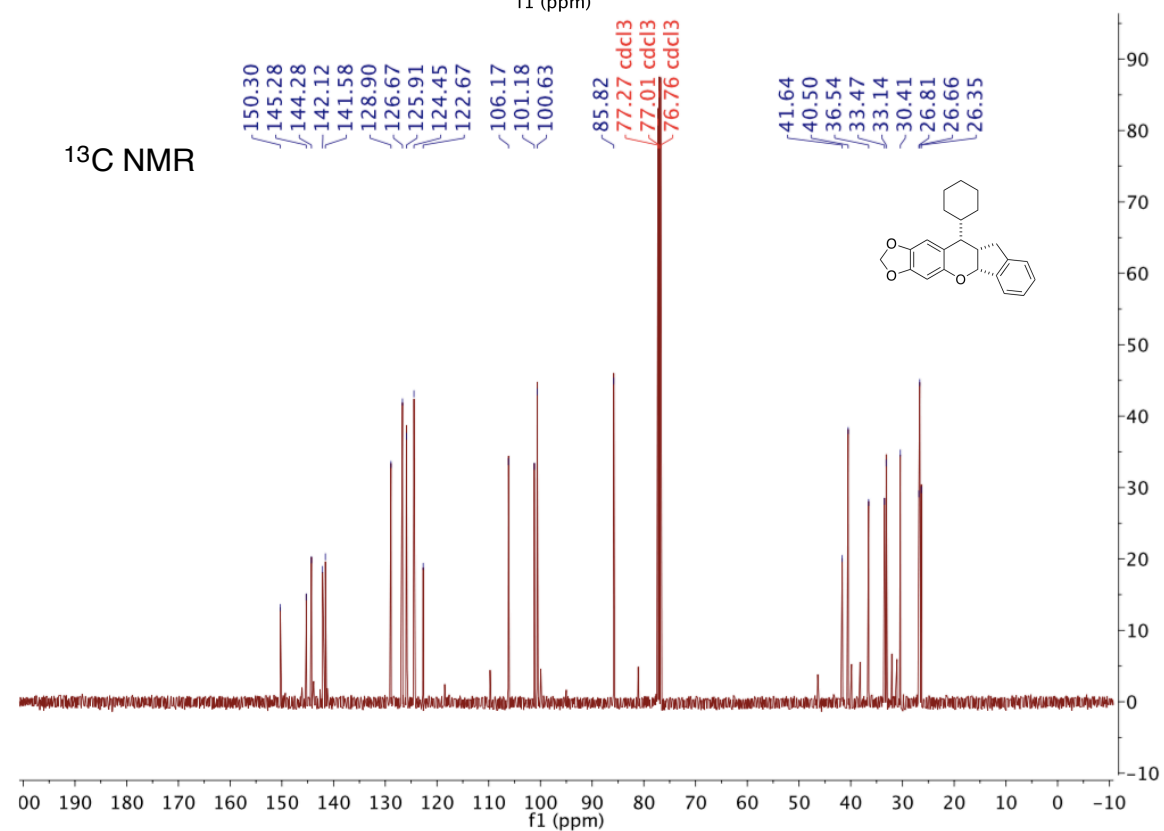
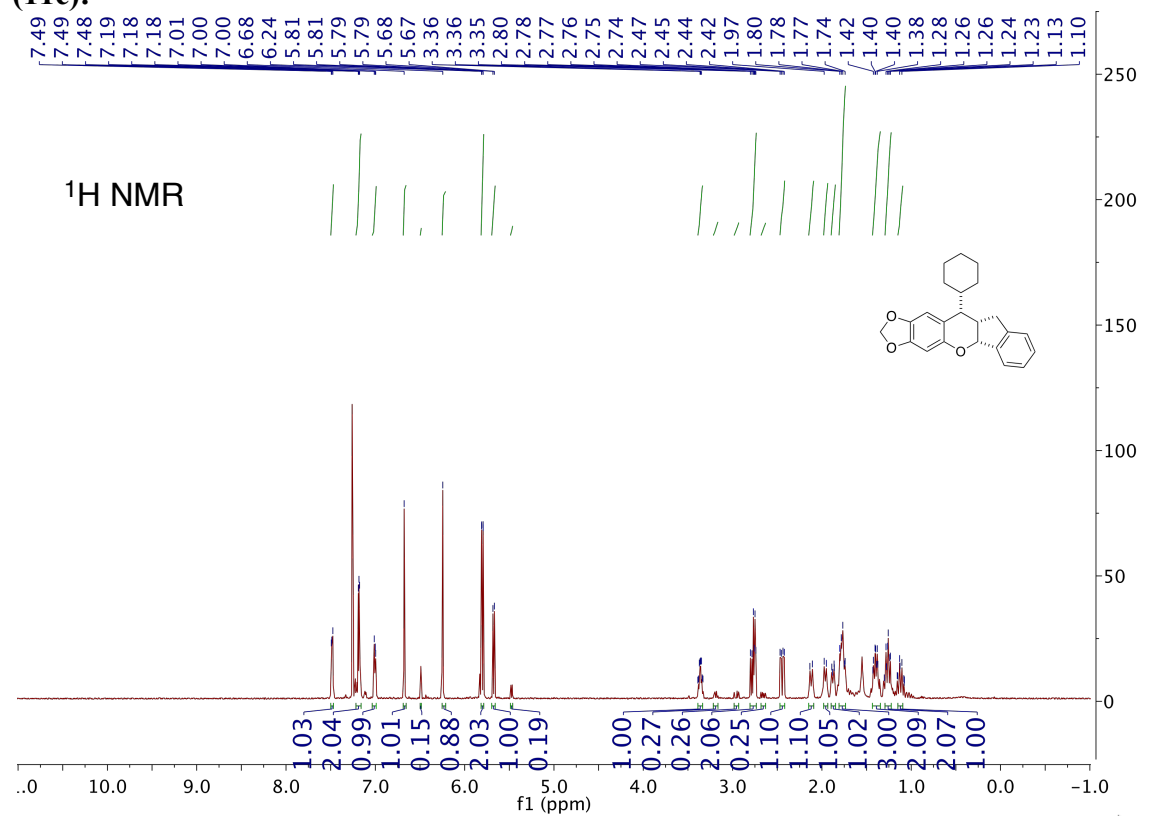
(11a):



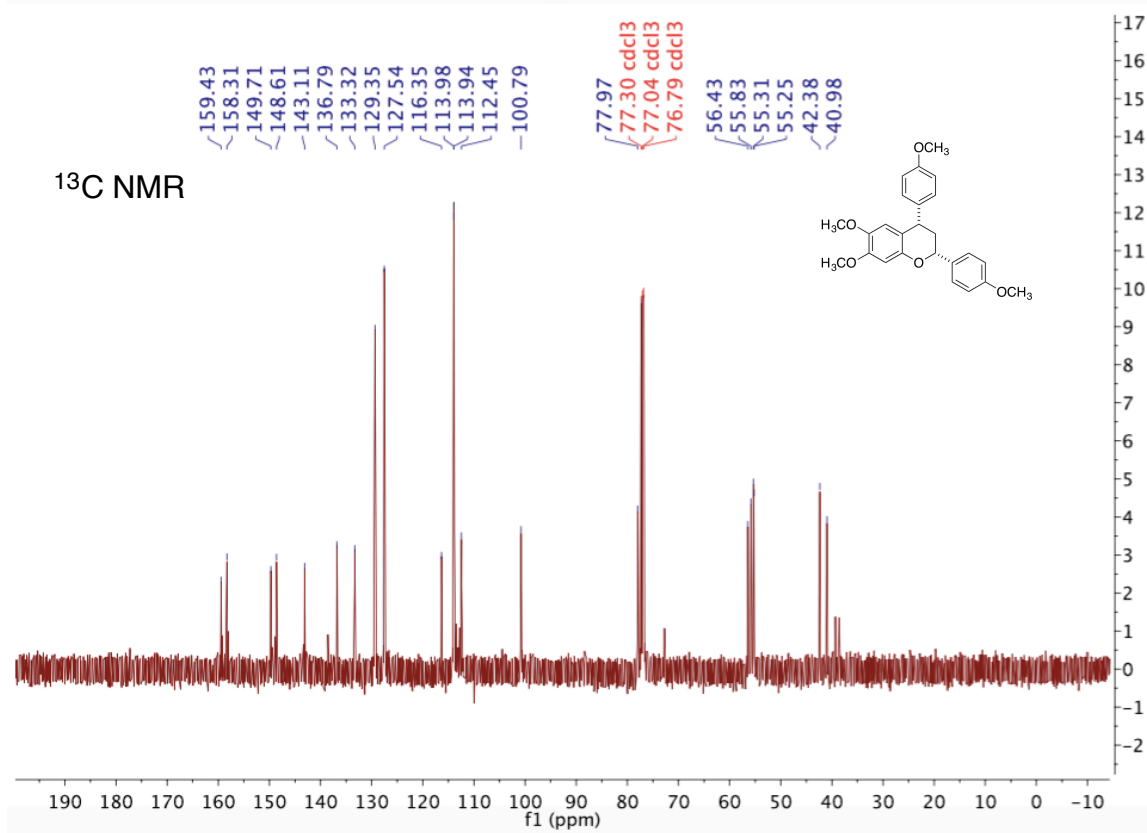
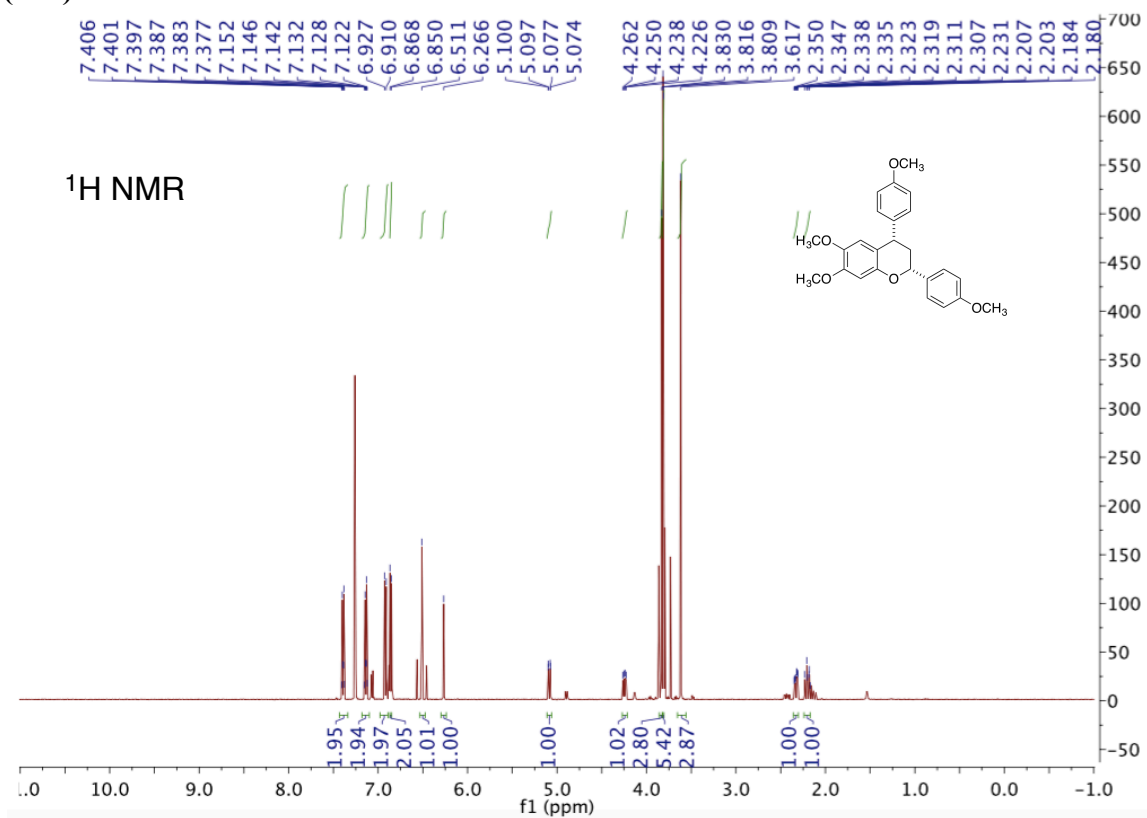
(11b):



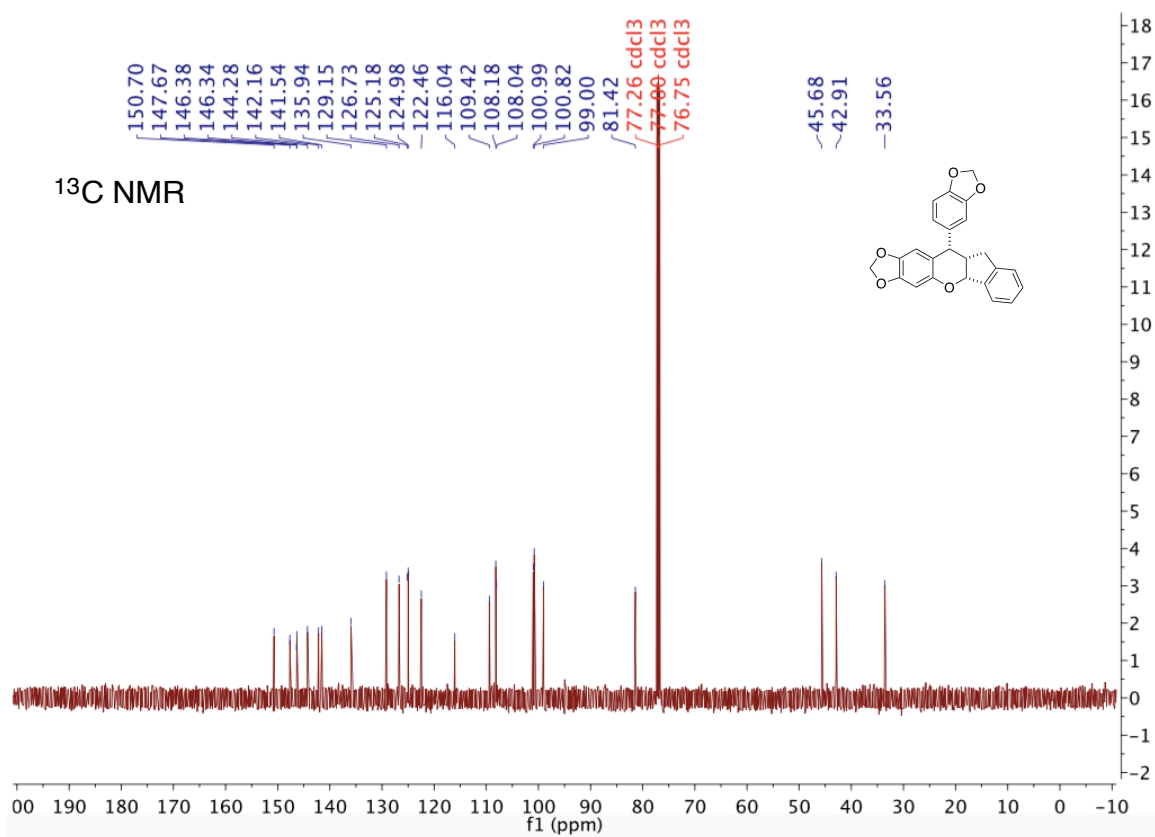
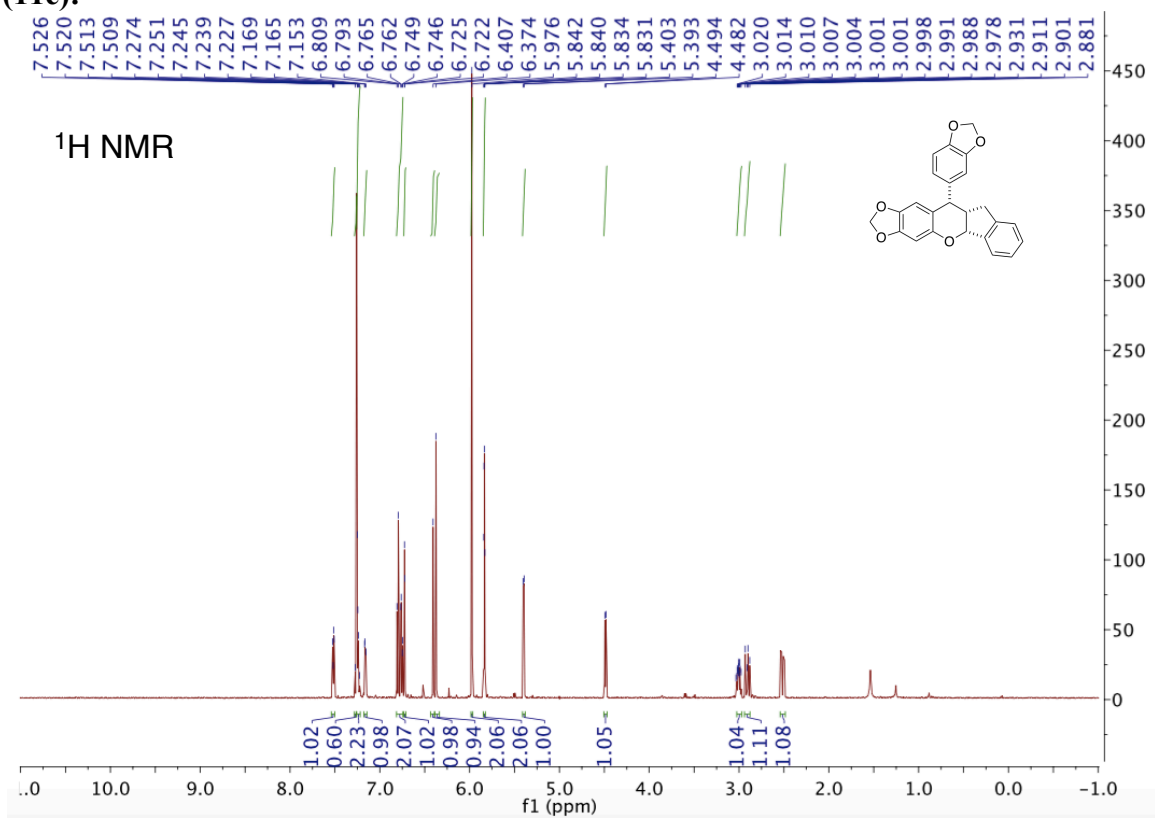
(11c):



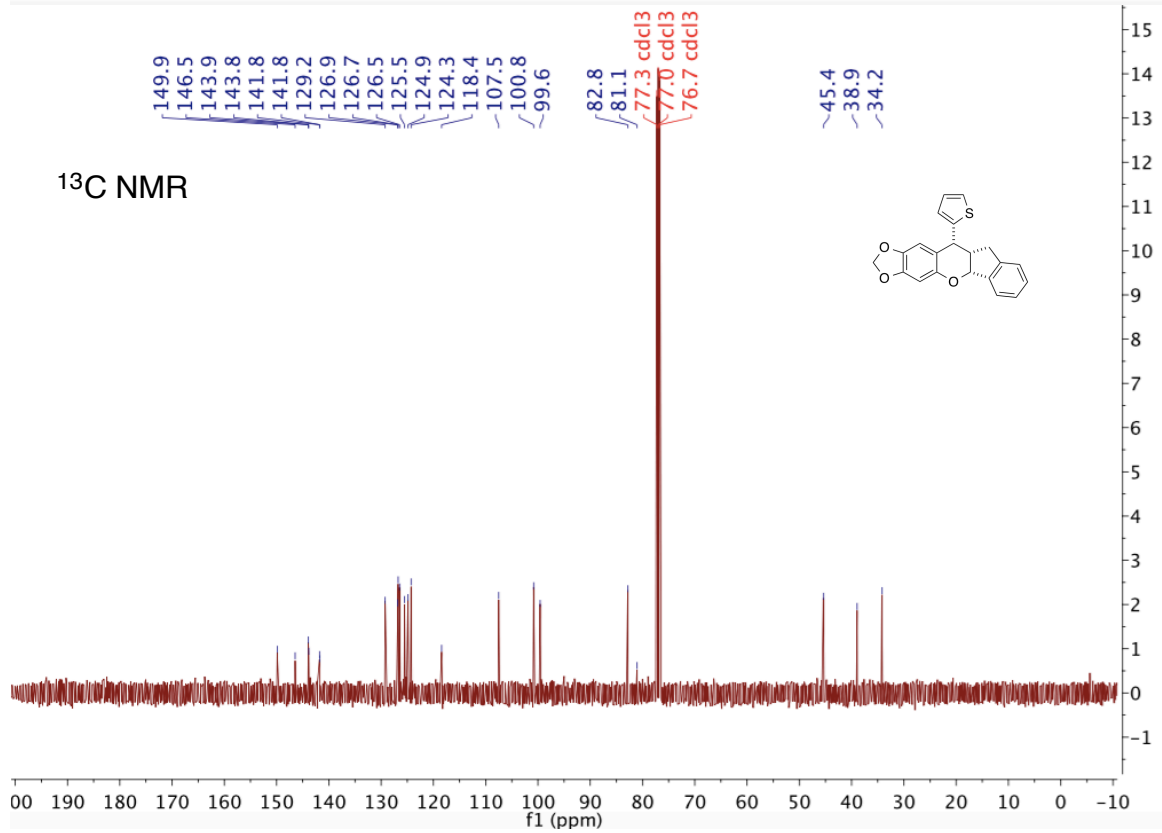
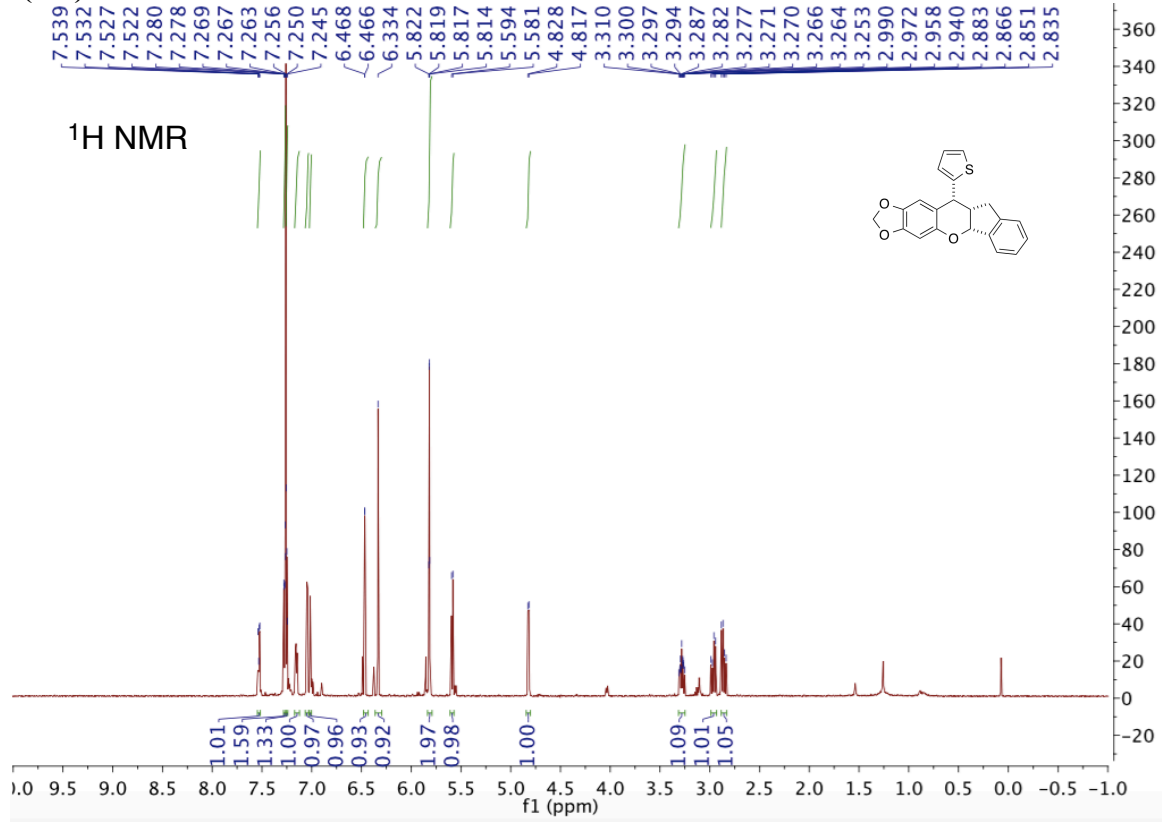
(11d):



(11e):

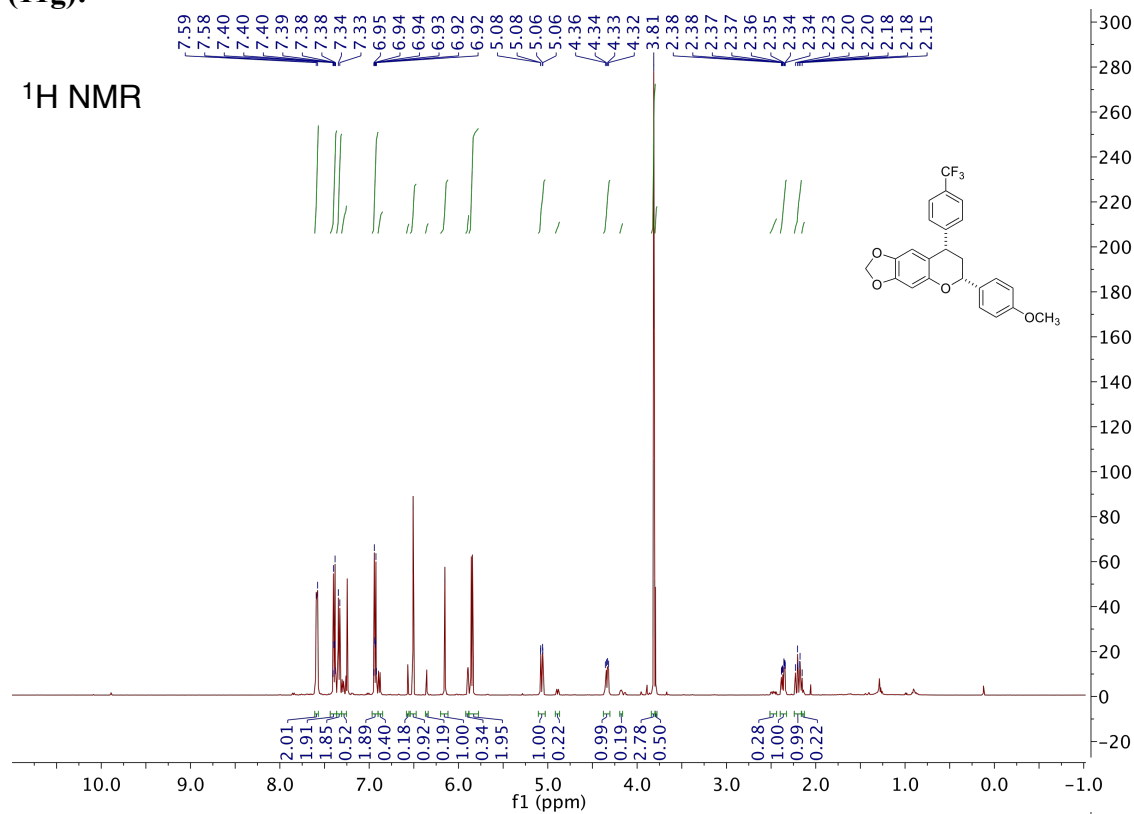


(11f):

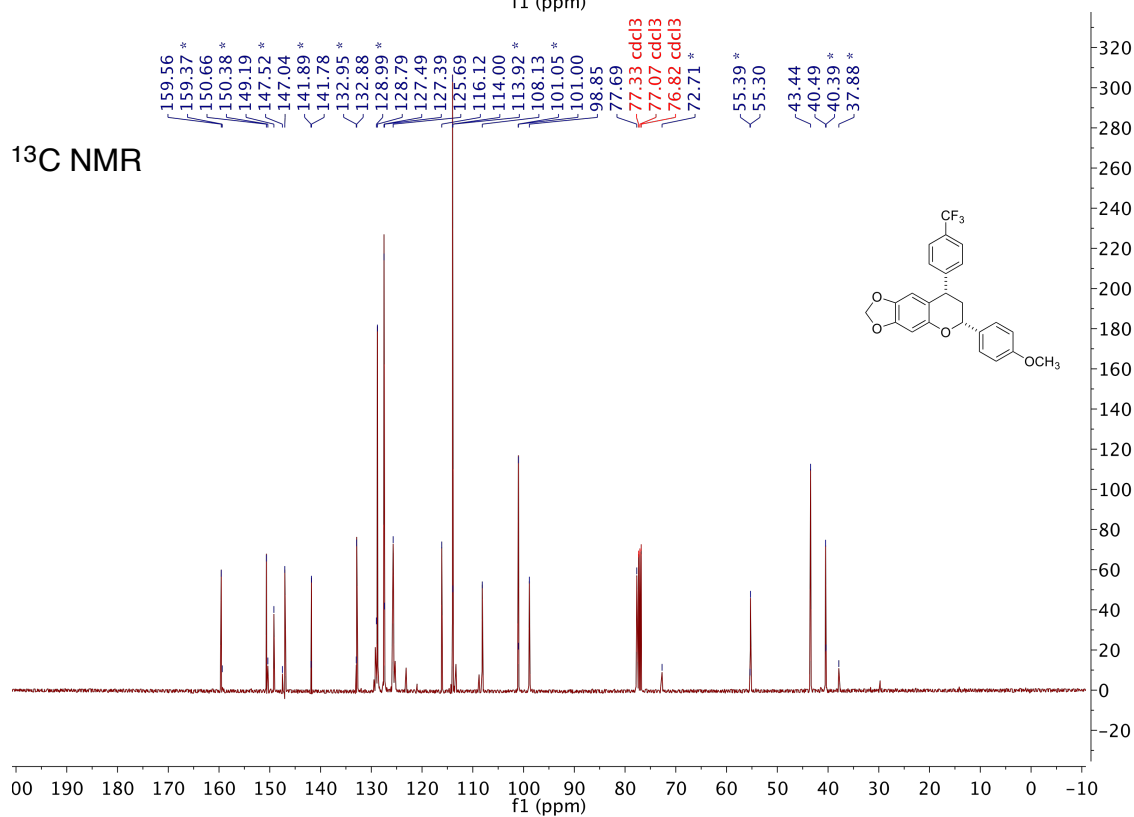


(11g):

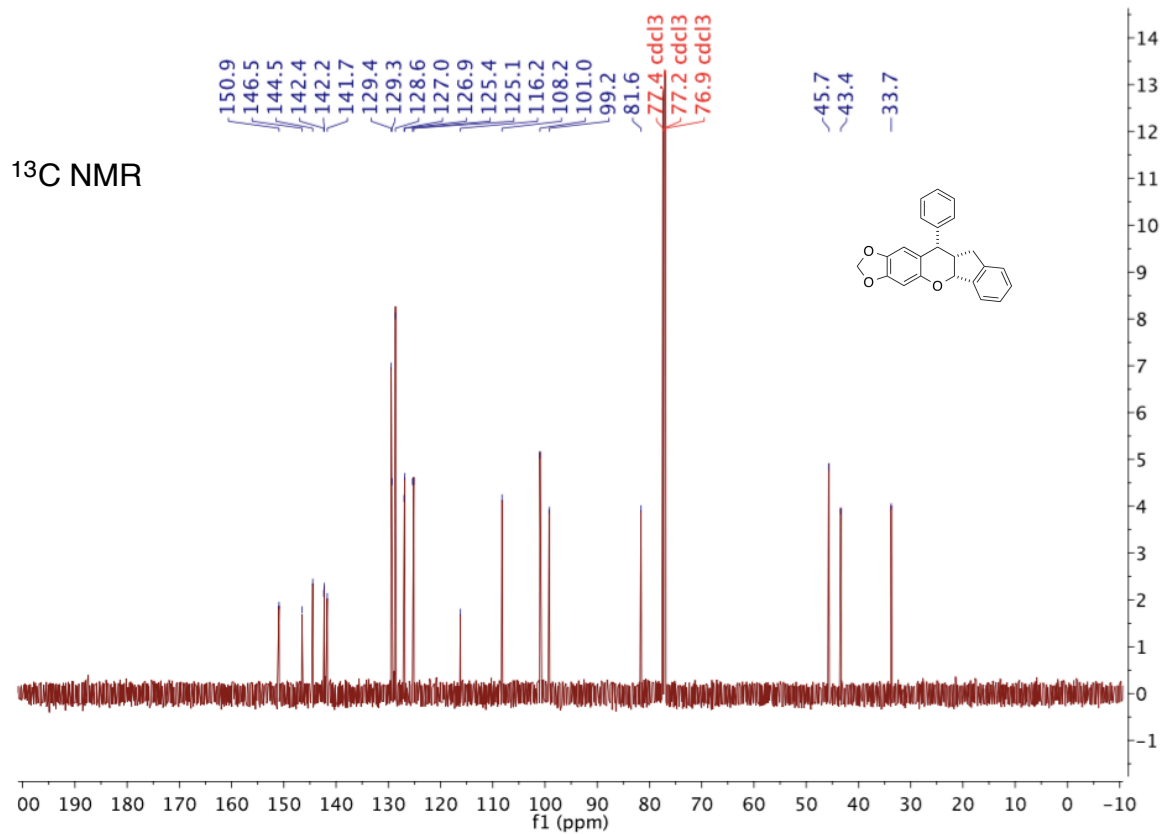
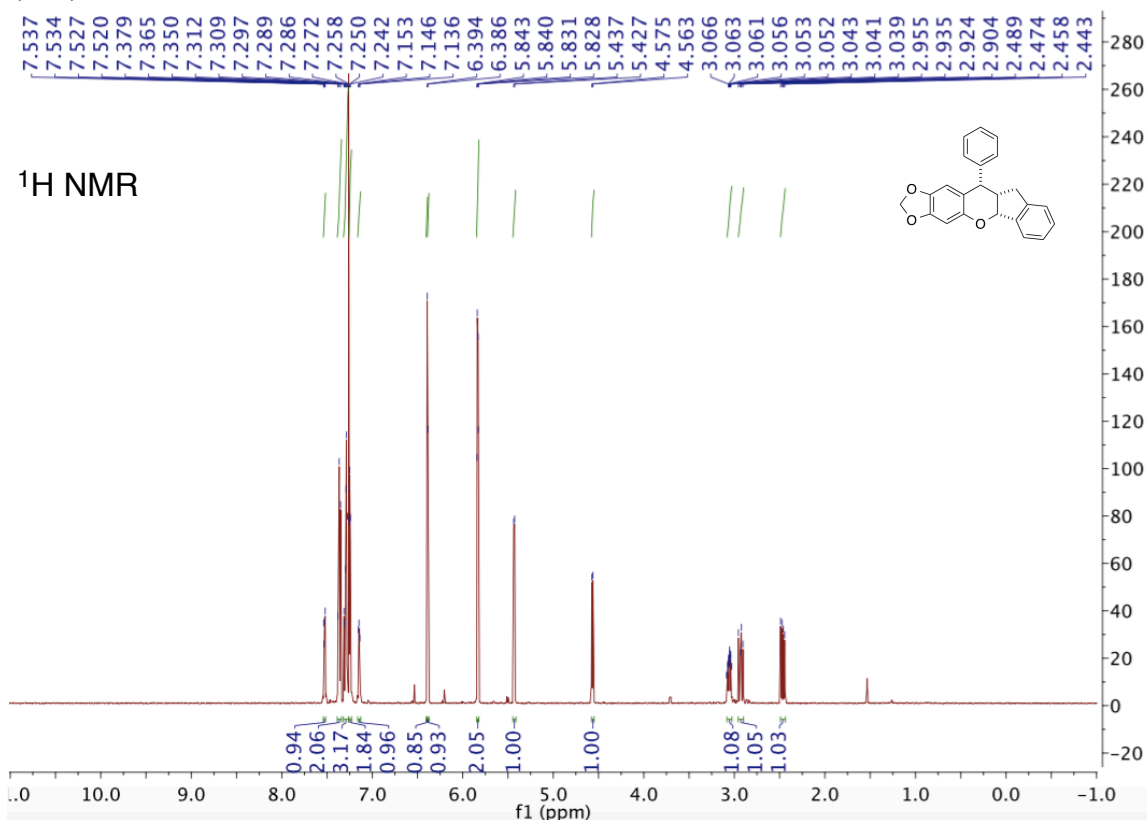
¹H NMR



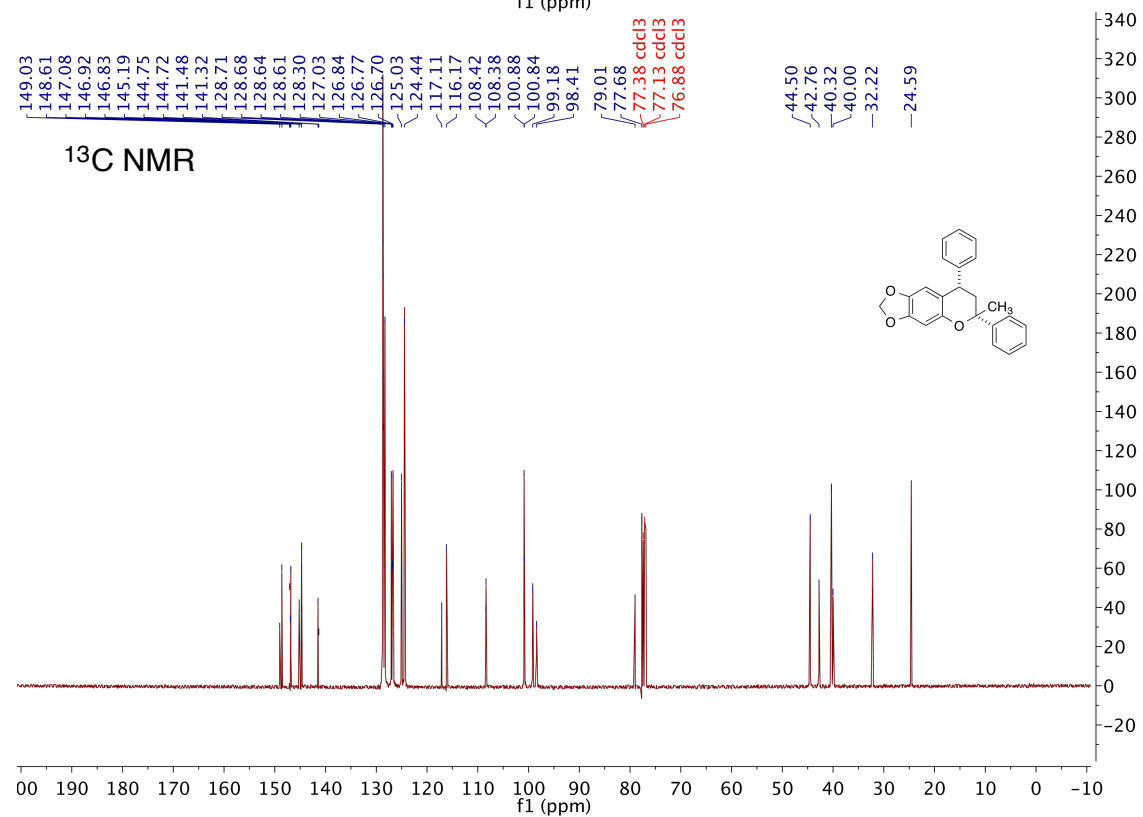
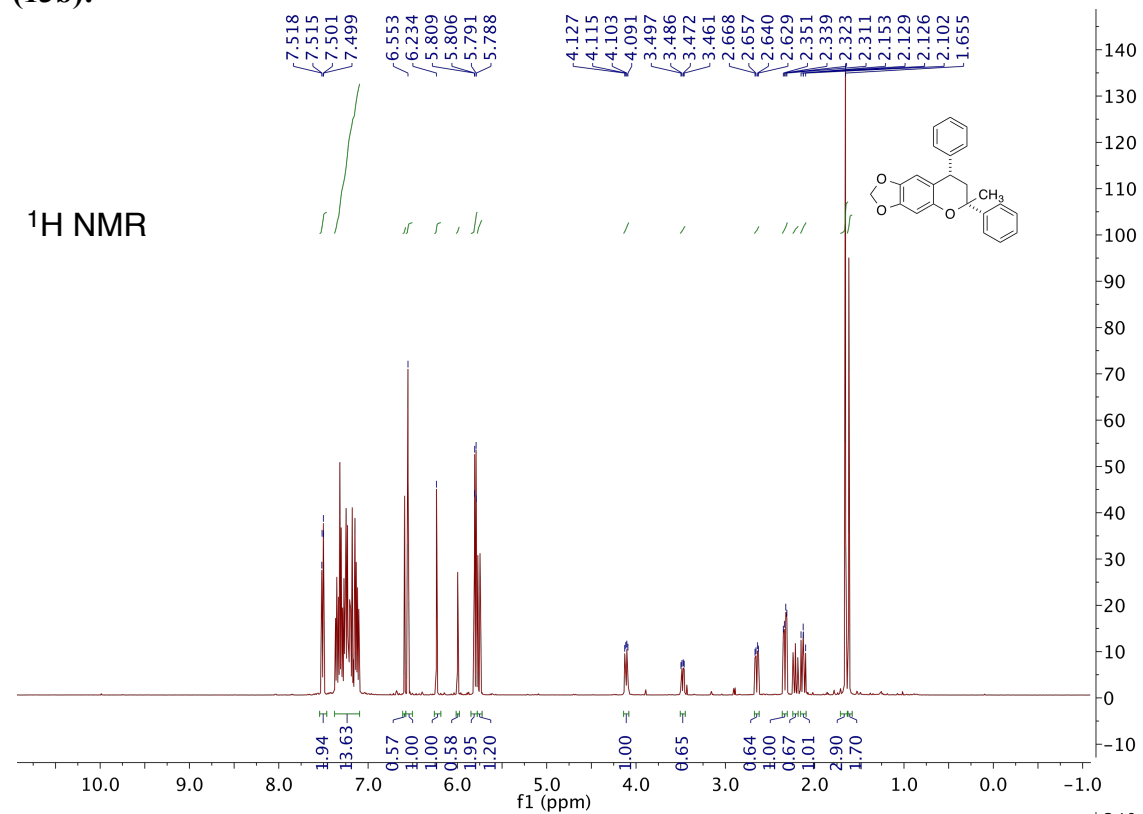
¹³C NMR



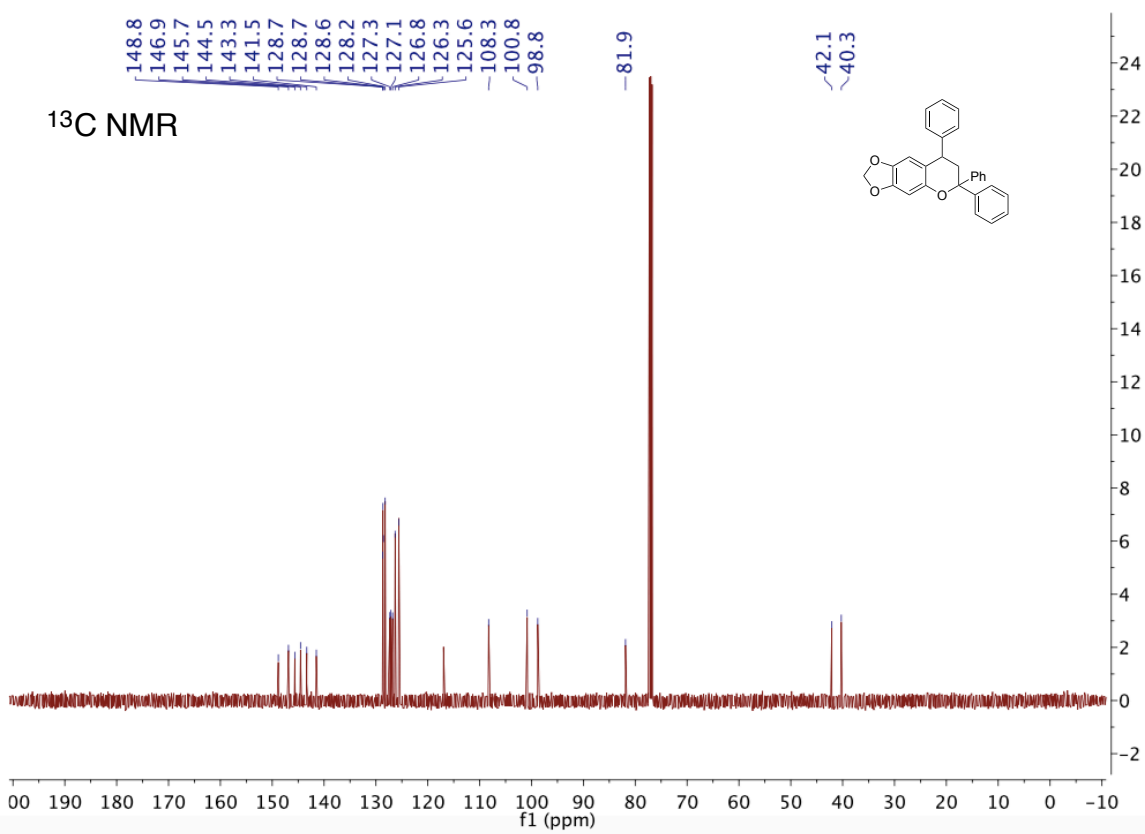
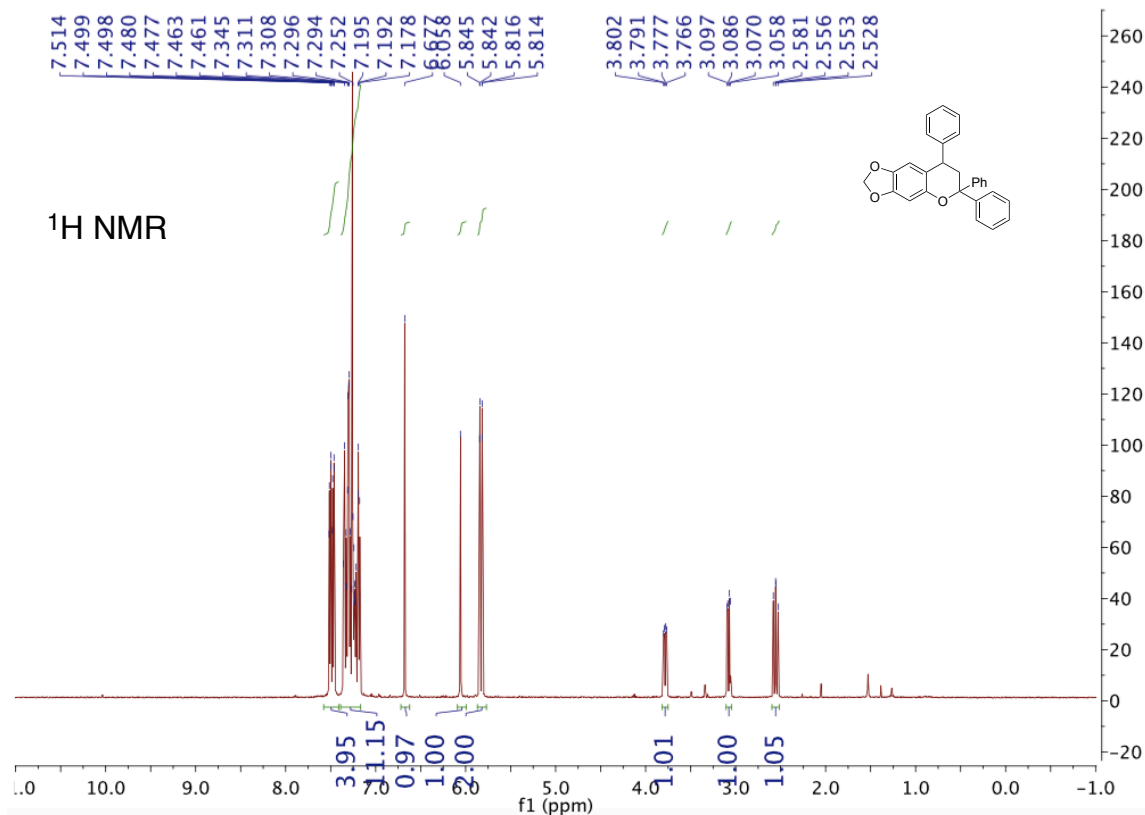
(11h):



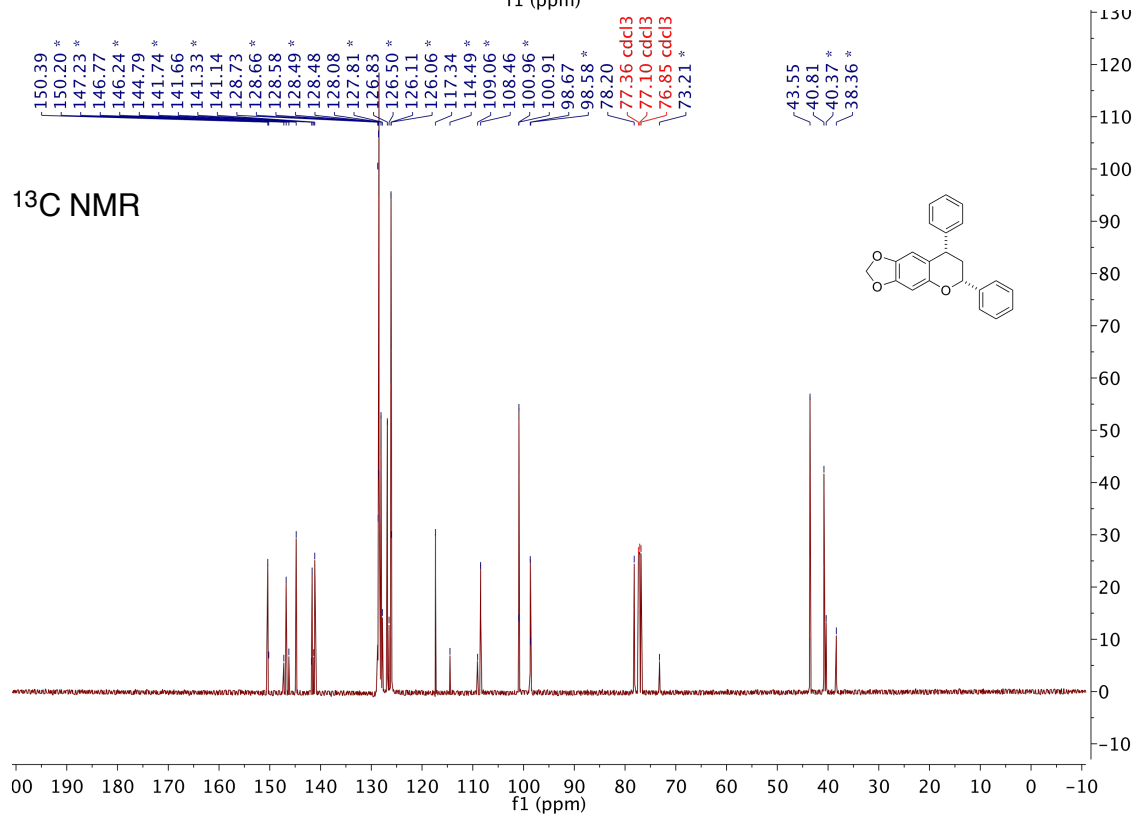
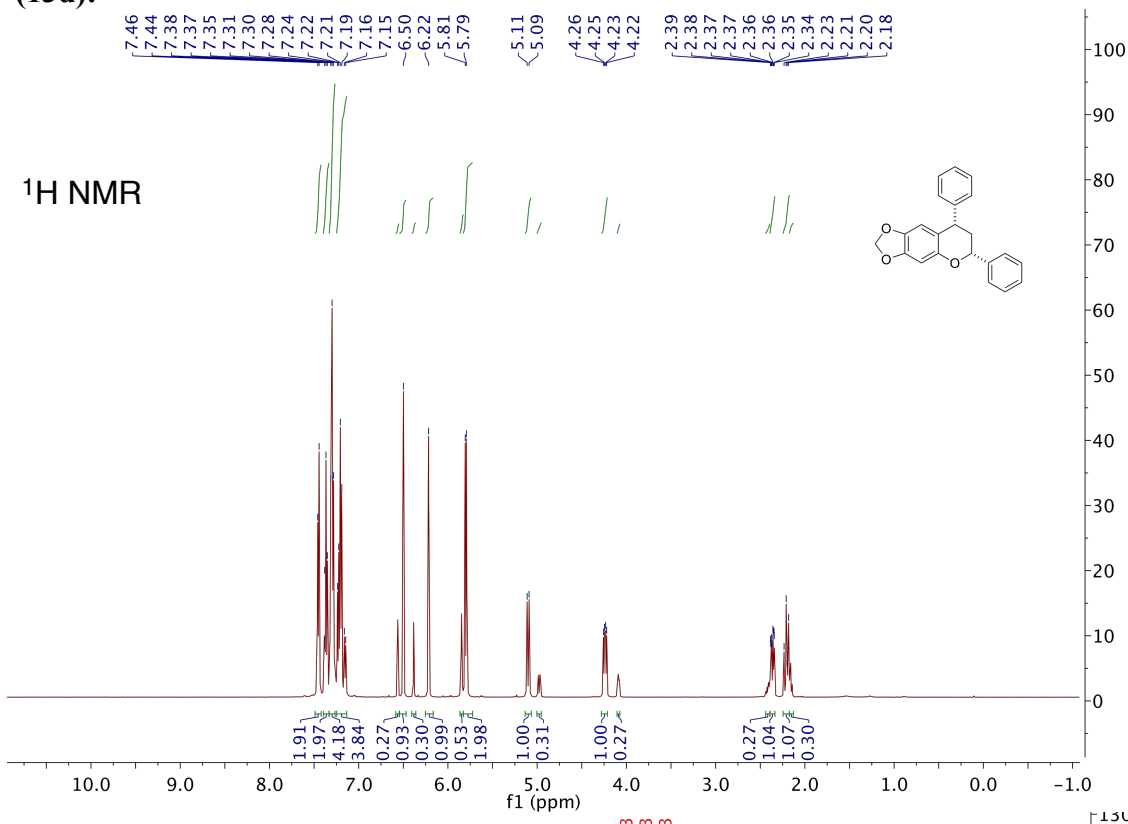
(13b):



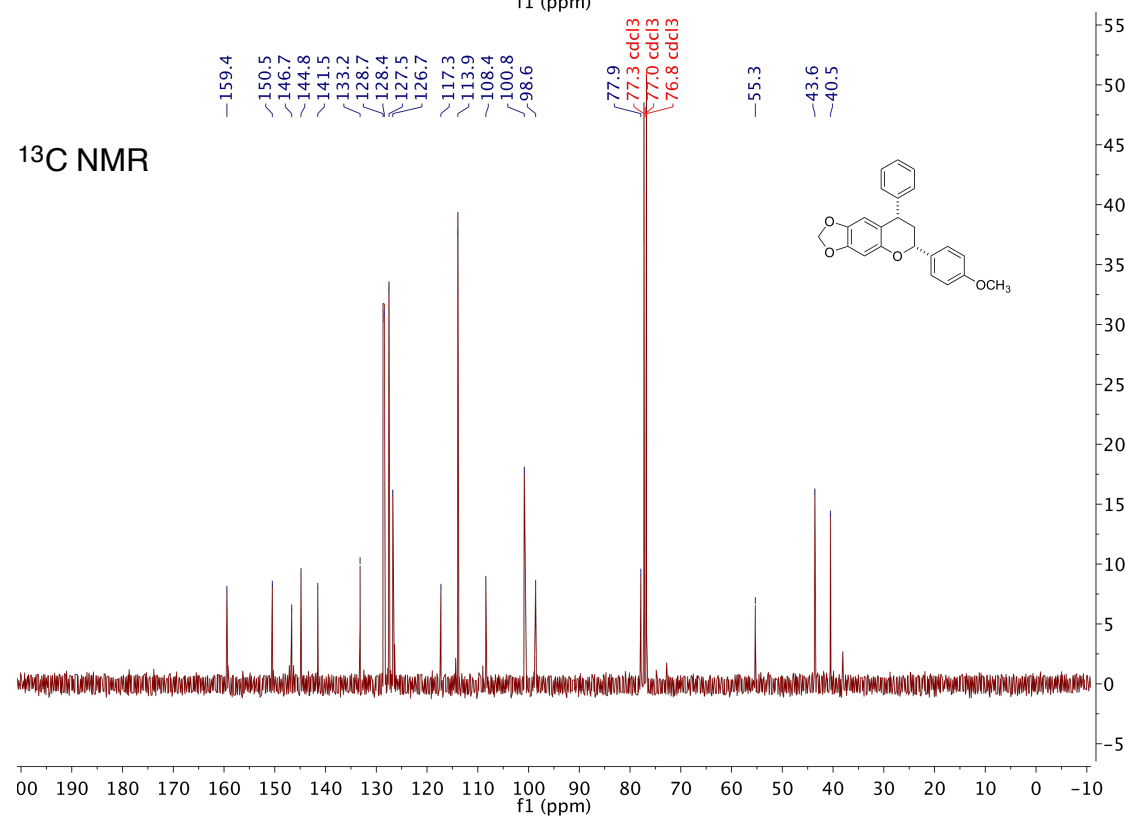
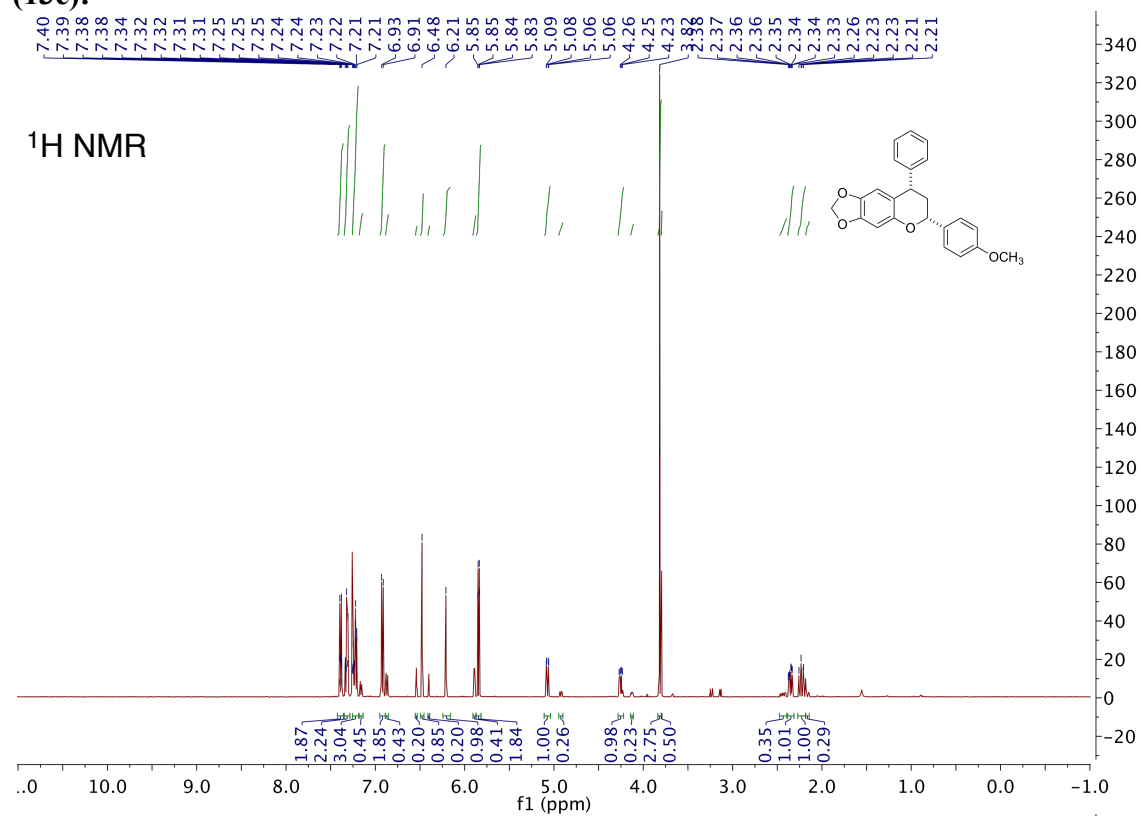
(13c):



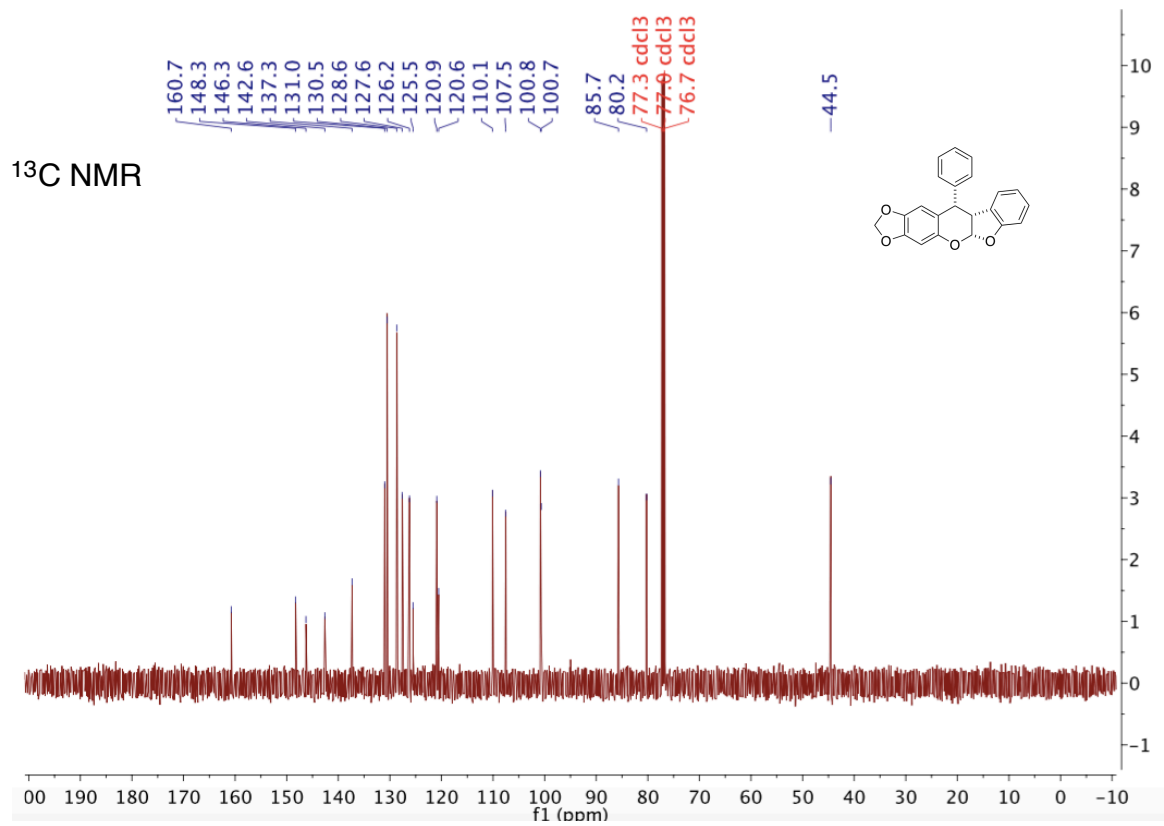
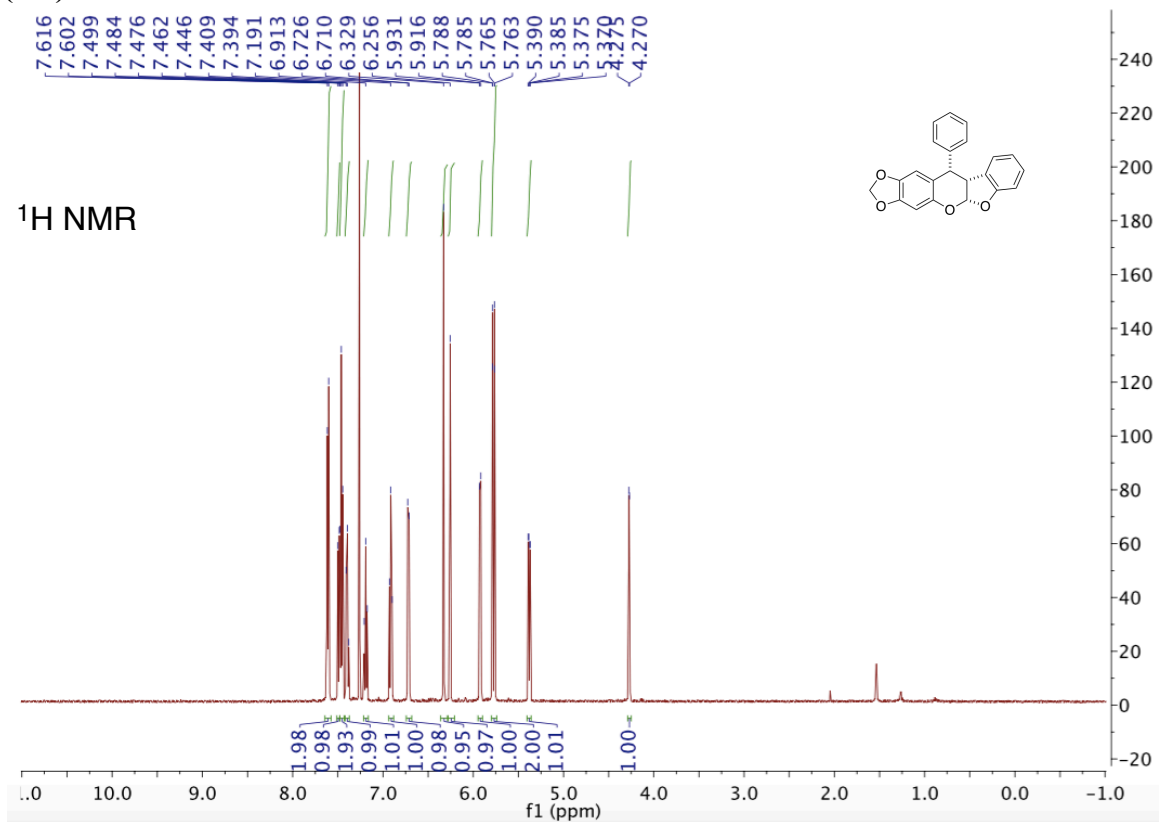
(13d):



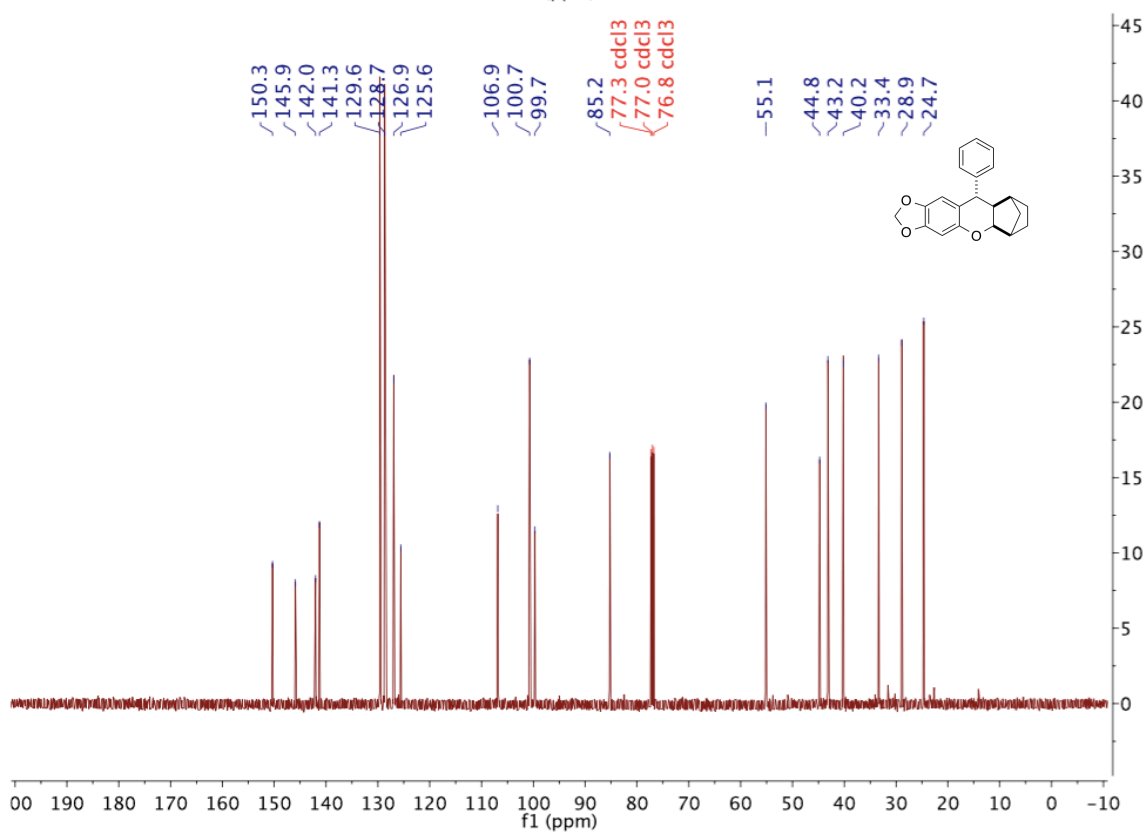
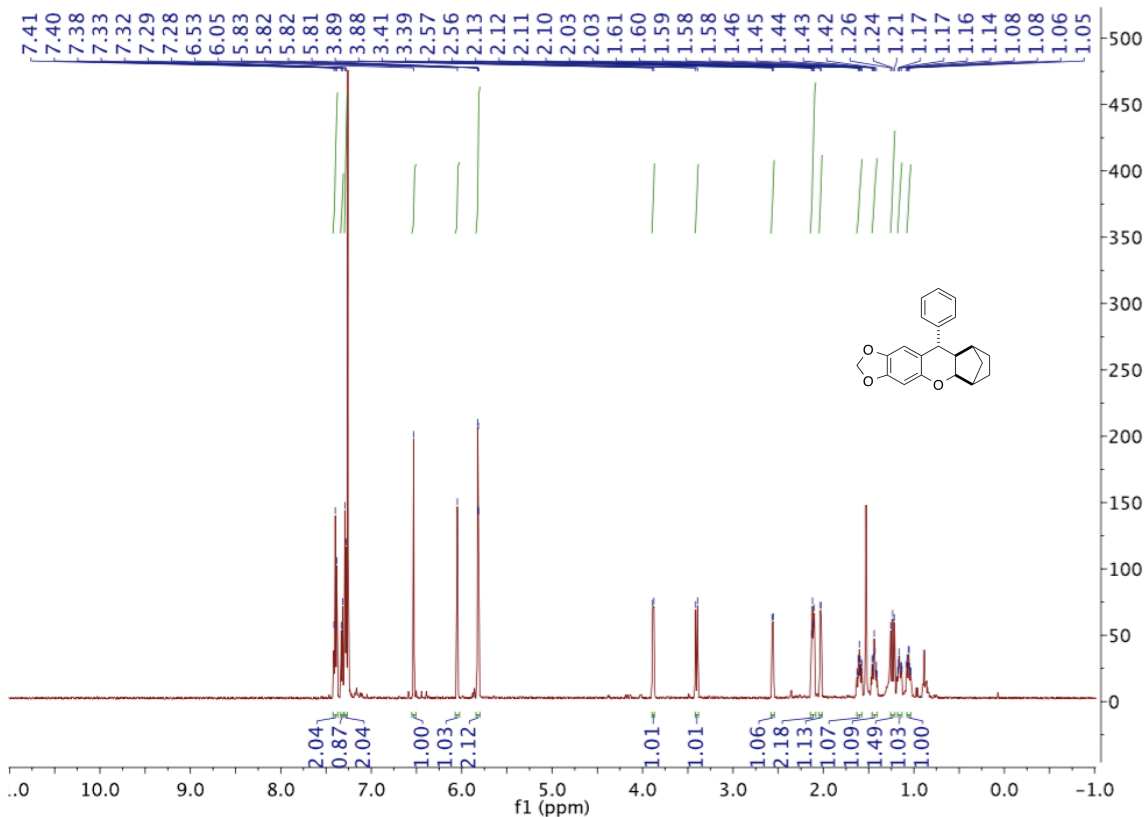
(13e):

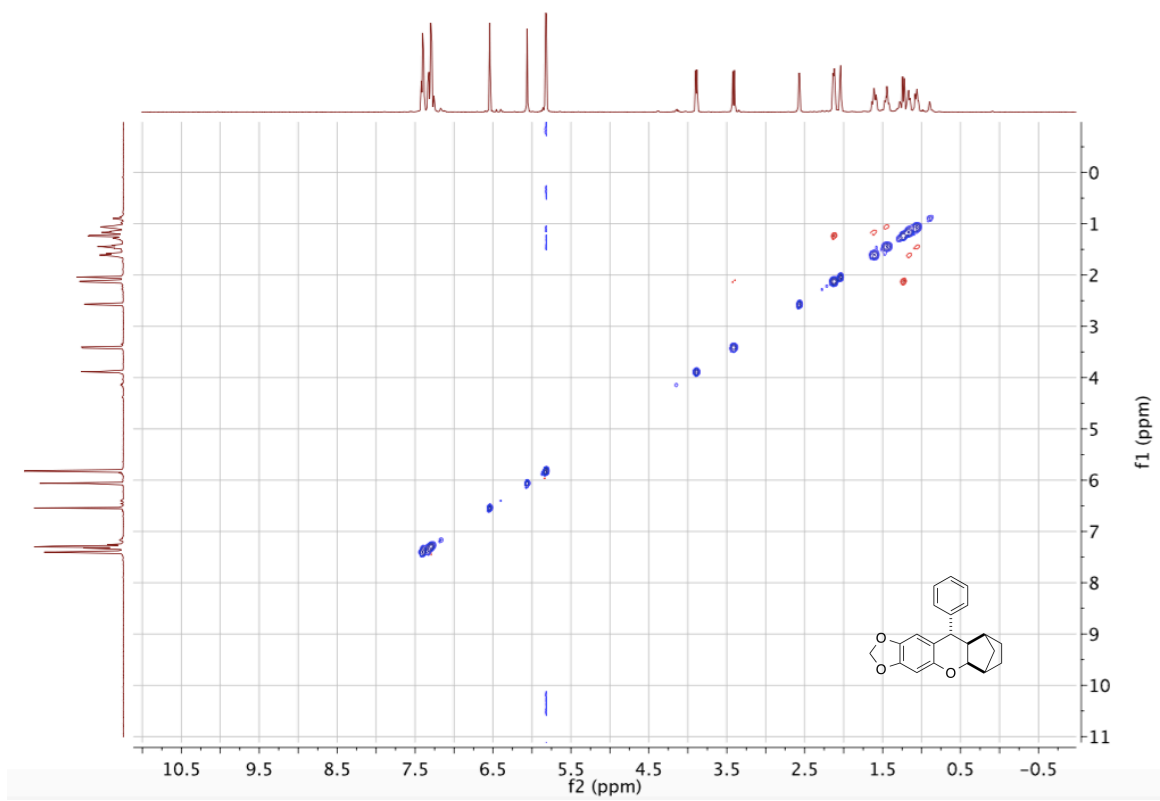


(13f):



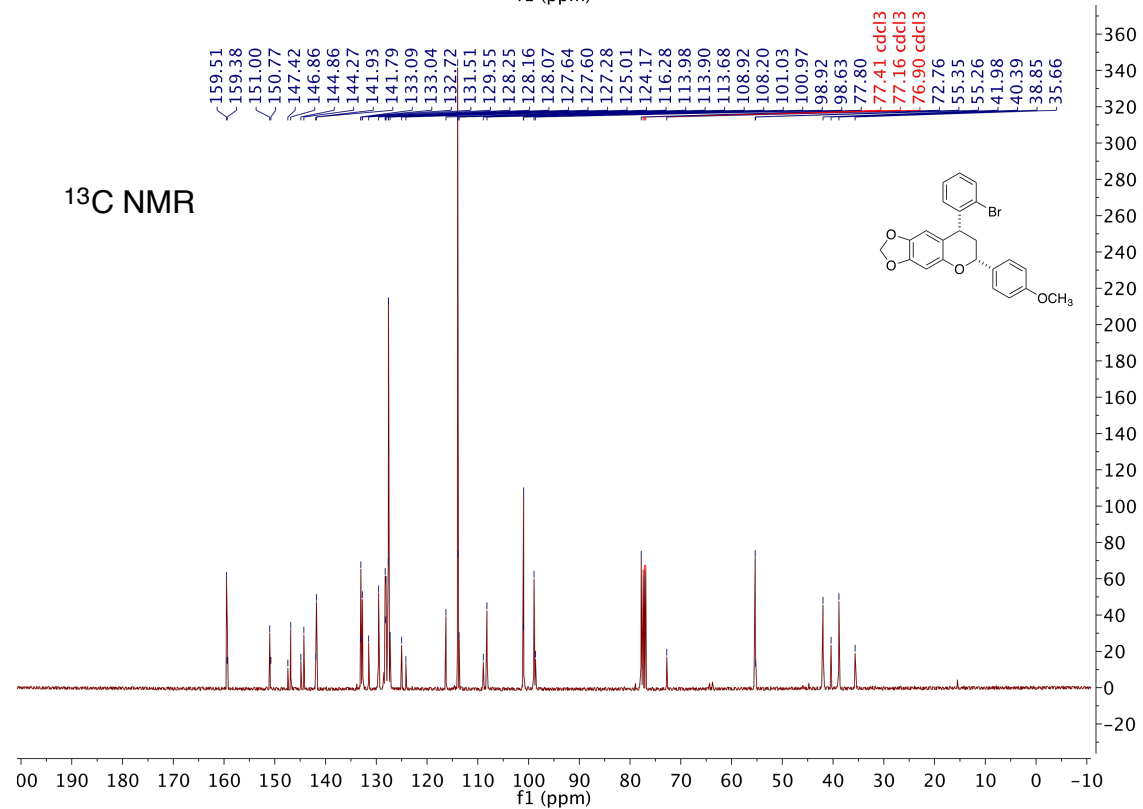
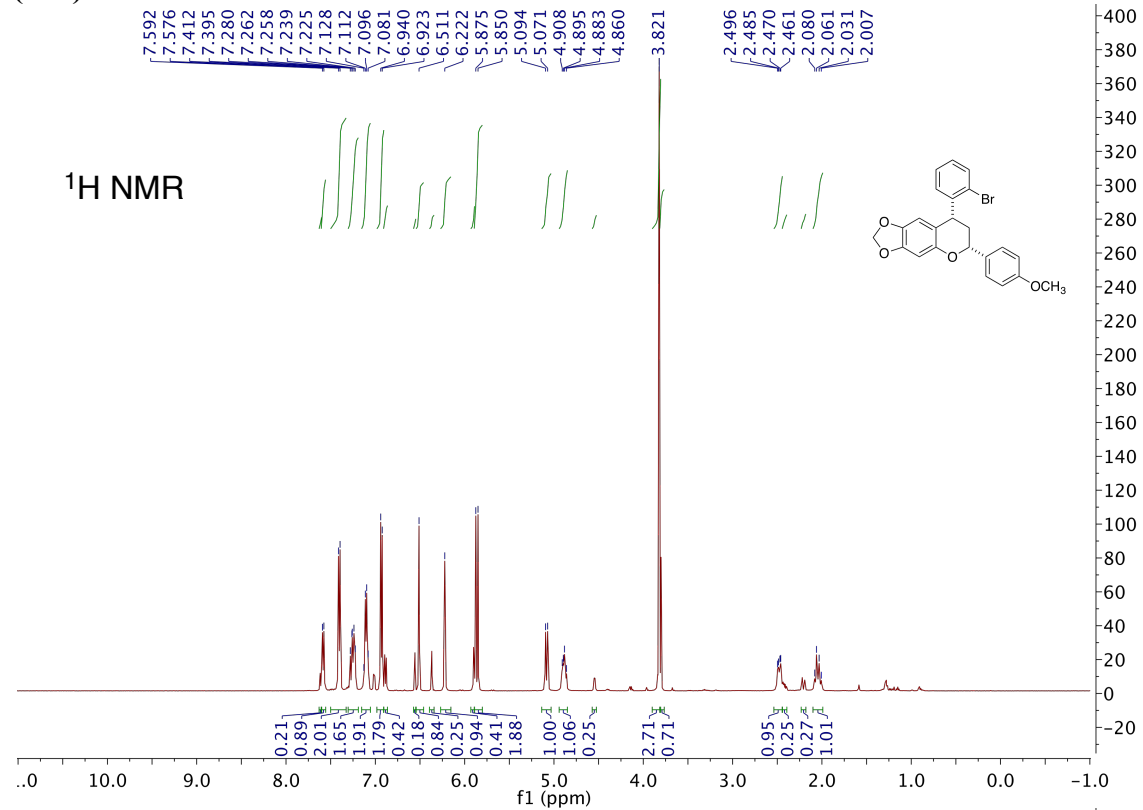
(13g):



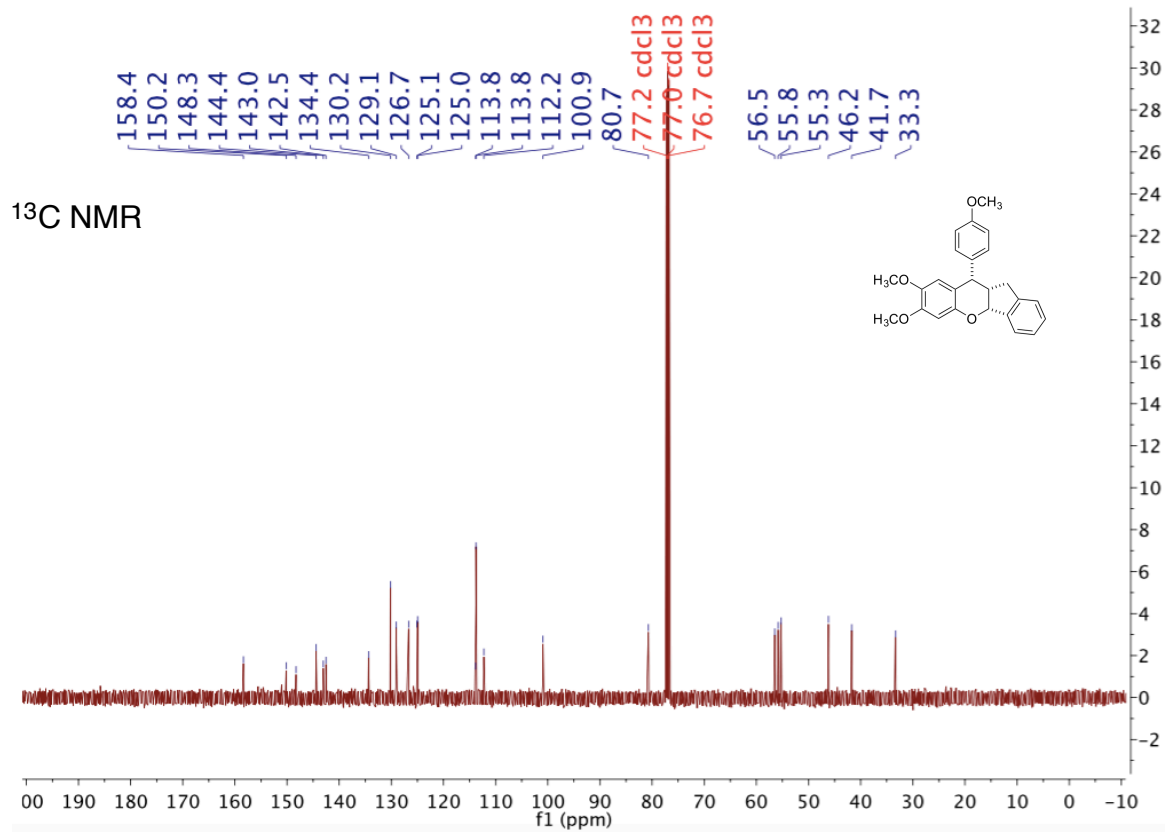
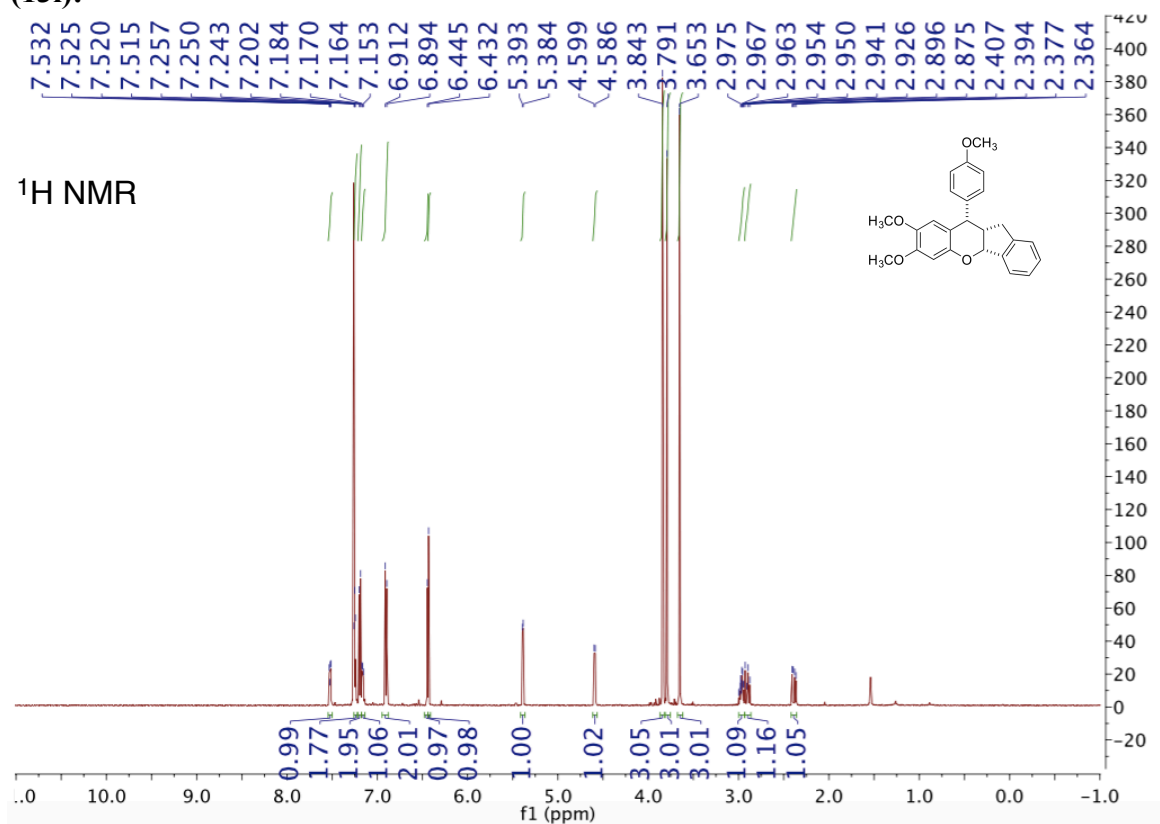


NOESY on the 400??? Double check

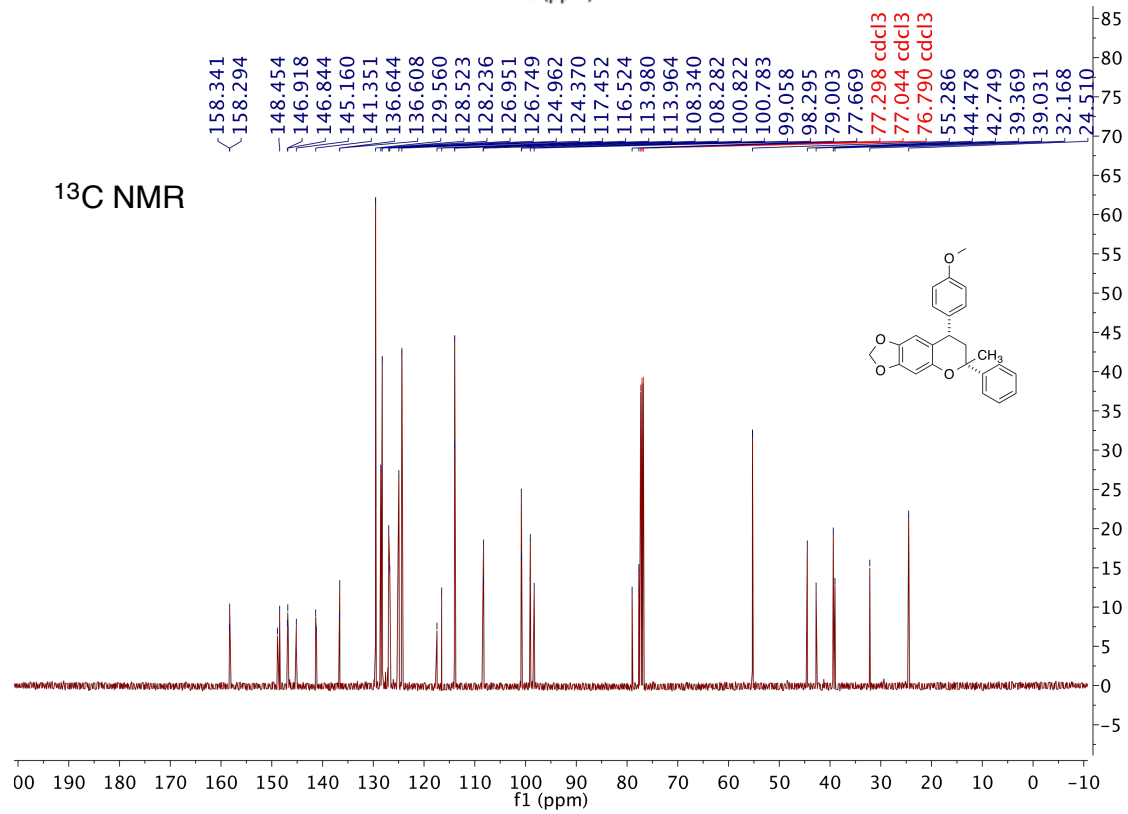
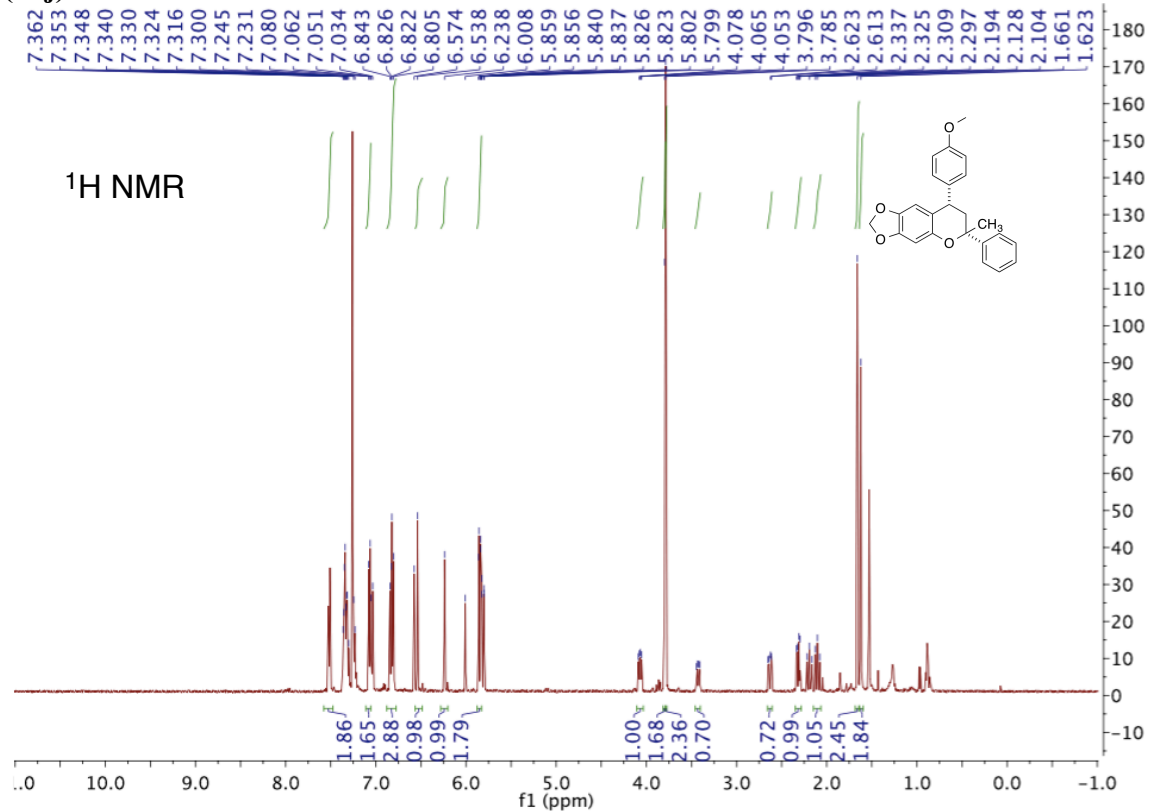
(13h):



(13i):



(13j):



(13k):

