Supporting Information

Asymmetric Transfer Hydrogenation of Polyoxygenated 3-Arylidenechroman-4-ones: A Powerful Tool for the Total Synthesis of Natural Homoisoflavonoids

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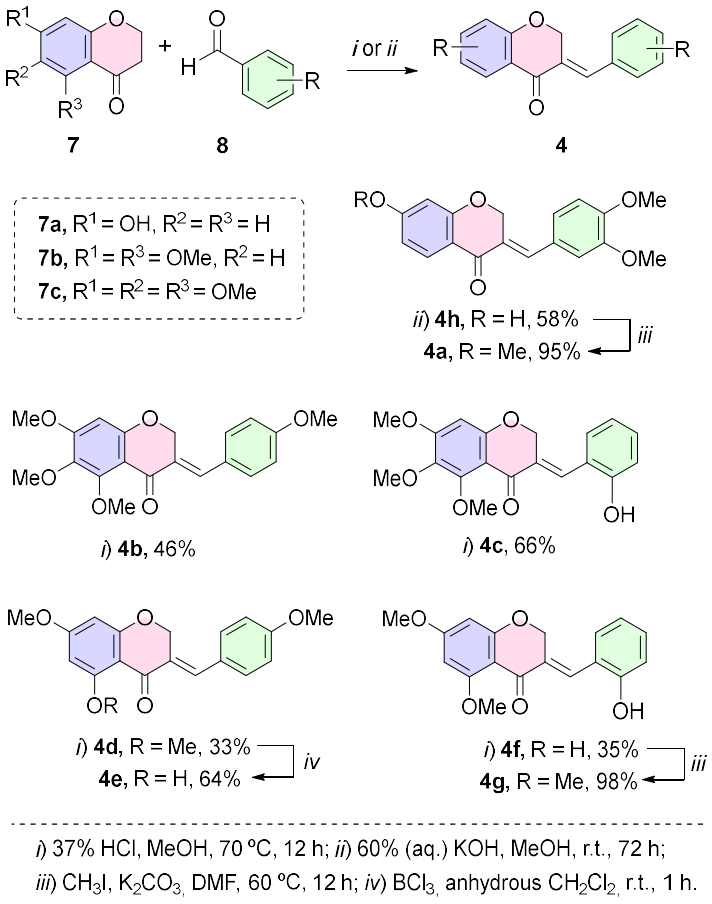


Scheme S1. Aldol condensation reaction of polyoxygenated arylidene chromanones

Computational Study

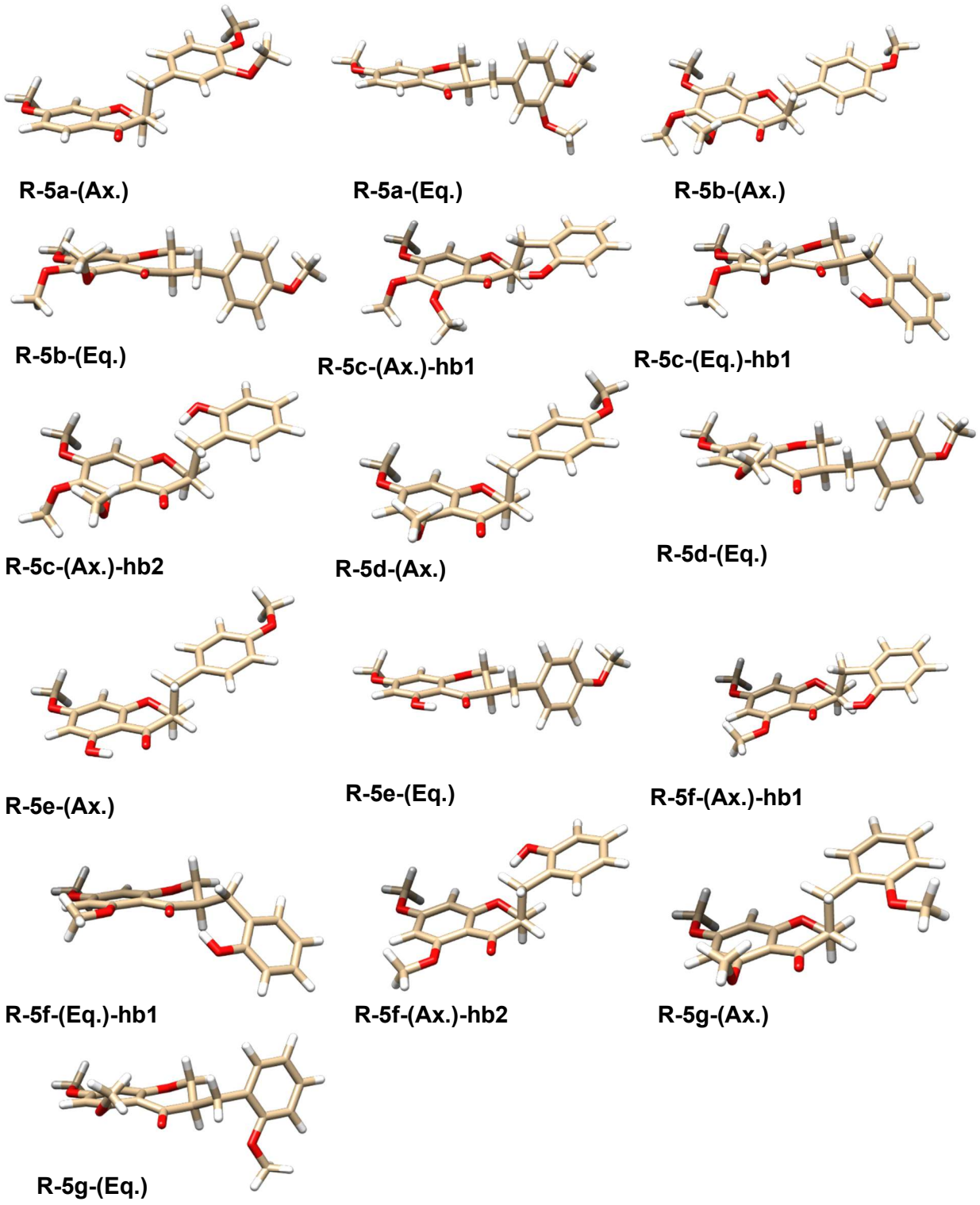


Figure S1. Substrates optimized structures in gas phase at the M062X/ZORA-def2-TZVP/D3zero level. All structures are of **R** configuration. **Ax.** and **Eq.** refers to the spatial orientation of the substituent at the saturated β-carbon of C-ring; and **Hb1** and **Hb2** refers to the type of intramolecular hydrogen bond.

Table S1. Table of descriptors of reactivity and relative energy between different conformations of the substrate including solvent effects (ε=24.70). E, ρN(r), E, ρN+1(r), and E, ρN-1(r) are the energies in Hartree units of the optimized structures at conditions charge/multiplicity: 0/1, -1/2, and +1/2, respectively; ΔE given in kcal/mol is the energy difference of the conformation's relatives to axial conformations; HOMO/LUMO stands for highest occupied molecular orbitals and lowest unoccupied molecular orbital, respectively; IP, EA, μ, η, and ω given in electron volts (eV) are the descriptors of reactivity: ionization potential, electron affinity, chemical potential, hardness, and electrophilic index, respectively

Reactivity Descriptors	Methoxilated A ring							
	5a		5b		5d		5g	
	R/Ax.	R/Eq.	R/Ax.	R/Eq.	R/Ax.	R/Eq.	R/Ax.	R/Eq.
E, ρN(r)	*-1113.09*	*-1113.09*	*-1227.72*	*-1227.72*	*-1113.09*	*-1113.09*	*-1113.09*	*-1113.09*
E, ρN+1(r)	*-1113.16*	*-1113.16*	*-1227.79*	*-1227.78*	*-1113.15*	*-1113.15*	*-1113.15*	*-1113.15*
E, ρN-1(r)	*-1112.85*	*-1112.85*	*-1227.48*	*-1227.48*	*-1112.85*	*-1112.84*	*-1112.85*	*-1112.85*
ΔE	0.00	-3.22	0.00	0.06	0.00	0.48	0.00	0.59
HOMO	-7.36	-7.44	-7.48	-7.48	-7.49	-7.48	-7.60	-7.59
LUMO	-0.96	-0.67	-0.71	-0.62	-0.66	-0.64	-0.67	-0.62
LUMO - HOMO	6.39	6.77	6.77	6.85	6.83	6.85	6.93	6.97
IP	6.53	6.67	6.53	6.48	6.36	6.61	6.44	6.61
EA	1.91	1.76	1.78	1.70	1.73	1.71	1.73	1.70
μ	-4.22	-4.22	-4.16	-4.09	-4.04	-4.16	-4.09	-4.15
η	4.62	4.92	4.75	4.78	4.63	4.90	4.71	4.91
ω	1.93	1.81	1.82	1.75	1.77	1.76	1.77	1.75

Reactivity Descriptors	Phenolic B ring							
	5c			5e		5f		
	R/Ax./Hb1	R/Ax./Hb2	R/Eq./Hb1	R/Ax.	R/Eq.	R/Ax./Hb1	R/Ax./Hb2	R/Eq./Hb1
E, ρN(r)	*-1188.40*	*-1188.41*	*-1188.41*	*-1073.79*	*-1073.79*	*-1073.78*	*-1073.78*	*-1073.78*
E, ρN+1(r)	*-1188.48*	*-1188.47*	*-1188.48*	*-1073.86*	*-1073.86*	*-1073.85*	*-1073.84*	*-1073.85*
E, ρN-1(r)	*-1188.17*	*-1188.16*	*-1188.17*	*-1073.55*	*-1073.55*	*-1073.54*	*-1073.54*	*-1073.55*
ΔE	0.00	-1.35	-1.77	0.00	0.37	0.00	-0.92	-1.26
HOMO	-7.54	-7.71	-7.54	-7.51	-7.50	-7.57	-7.70	-7.51
LUMO	-0.89	-0.79	-0.89	-0.77	-0.76	-0.78	-0.62	-0.73
LUMO - HOMO	6.65	6.92	6.66	6.74	6.74	6.80	7.08	6.78
IP	6.41	6.66	6.37	6.61	6.59	6.41	6.54	6.34
EA	1.96	1.85	1.96	1.85	1.85	1.86	1.69	1.81
μ	-4.18	-4.25	-4.16	-4.23	-4.22	-4.13	-4.12	-4.07
η	4.45	4.81	4.40	4.75	4.74	4.56	4.85	4.53
ω	1.97	1.88	1.97	1.88	1.88	1.87	1.75	1.83

Table S2. Table of descriptors of reactivity and relative energy between different conformations of the substrate computed at gas phase. E, ρN(r), E, ρN+1(r), and E, ρN-1(r) are the energies in Hartree units of the optimized structures at conditions charge/multiplicity: 0/1, -1/2, and +1/2, respectively; ΔE given in kcal/mol is the energy difference of the conformation's relatives to axial conformations; HOMO/LUMO stands for highest occupied molecular orbitals and lowest unoccupied molecular orbital, respectively; IP, EA, μ, η, and ω given in electron volts (eV) are the descriptors of reactivity: ionization potential, electron affinity, chemical potential, hardness, and electrophilic index, respectively.

Reactivity Descriptors	Phenolic B ring							
	5c			5e		5f		
	R/Ax./Hb1	R/Ax./Hb2	R/Eq./Hb1	R/Ax.	R/Eq.	R/Ax./Hb1	R/Ax./Hb2	R/Eq./Hb1
E, ρN(r)	-1188.38	-1188.38	-1188.38	-1073.77	*-1073.76*	-1073.75	-1073.75	-1073.75
E, ρN+1(r)	-1188.39	-1188.39	-1188.40	-1073.77	*-1073.77*	-1073.76	-1073.75	-1073.76
E, ρN-1(r)	-1188.08	-1188.08	-1188.09	-1073.47	*-1073.47*	-1073.46	-1073.45	-1073.47
ΔE	0.00	-1.72	-2.25	0.00	0.50	0.00	-0.35	-1.19
HOMO	-7.33	-7.57	-7.20	-7.56	-7.56	-7.26	-7.52	-7.14
LUMO	-0.91	-0.72	-0.99	-0.66	-0.65	-0.71	-0.51	-0.69
LUMO - HOMO	6.42	6.85	6.21	6.91	6.91	6.54	7.00	6.45
IP	7.92	8.20	7.84	8.09	8.09	7.88	8.14	7.77
EA	0.47	0.26	0.46	0.14	0.13	0.23	0.01	0.21
μ	-4.19	-4.23	-4.15	-4.12	-4.11	-4.06	-4.08	-3.99
η	7.44	7.94	7.38	7.95	7.96	7.65	8.13	7.56
ω	1.18	1.13	1.17	1.07	1.06	1.07	1.02	1.05

Reactivity Descriptors	Methoxilated A ring							
	5a		5b		5d		5g	
	R/Ax.	R/Eq.	R/Ax.	R/Eq.	R/Ax.	R/Eq.	R/Ax.	R/Eq.
E, ρN(r)	*-1113.07*	*-1113.07*	*-1227.69*	*-1227.69*	*-1113.06*	-1113.06	-1113.07	-1113.06
E, ρN+1(r)	*-1113.06*	*-1113.06*	*-1227.70*	*-1227.69*	-1113.06	-1113.06	-1113.06	-1113.06
E, ρN-1(r)	*-1112.77*	*-1112.77*	*-1227.40*	*-1227.40*	-1112.77	-1112.77	-1112.77	-1112.77
ΔE	0.00	-0.16	0.00	0.09	0.00	-0.01	0.00	0.08
HOMO	-7.42	-7.41	-7.42	-7.45	-7.49	-7.50	-7.59	-7.53
LUMO	-0.47	-0.48	-0.50	-0.43	-0.48	-0.46	-0.40	-0.38
LUMO - HOMO	6.94	6.93	6.92	7.02	7.01	7.04	7.18	7.14
IP	7.94	7.92	7.88	7.85	8.03	8.04	8.11	8.04
EA	-0.06	-0.05	0.05	-0.04	-0.02	-0.03	-0.09	-0.11
μ	-3.94	-3.93	-3.96	-3.91	-4.01	-4.01	-4.01	-3.96
η	8.01	7.97	7.83	7.89	8.05	8.07	8.20	8.15
ω	0.97	0.97	1.00	0.97	1.00	0.99	0.98	0.96

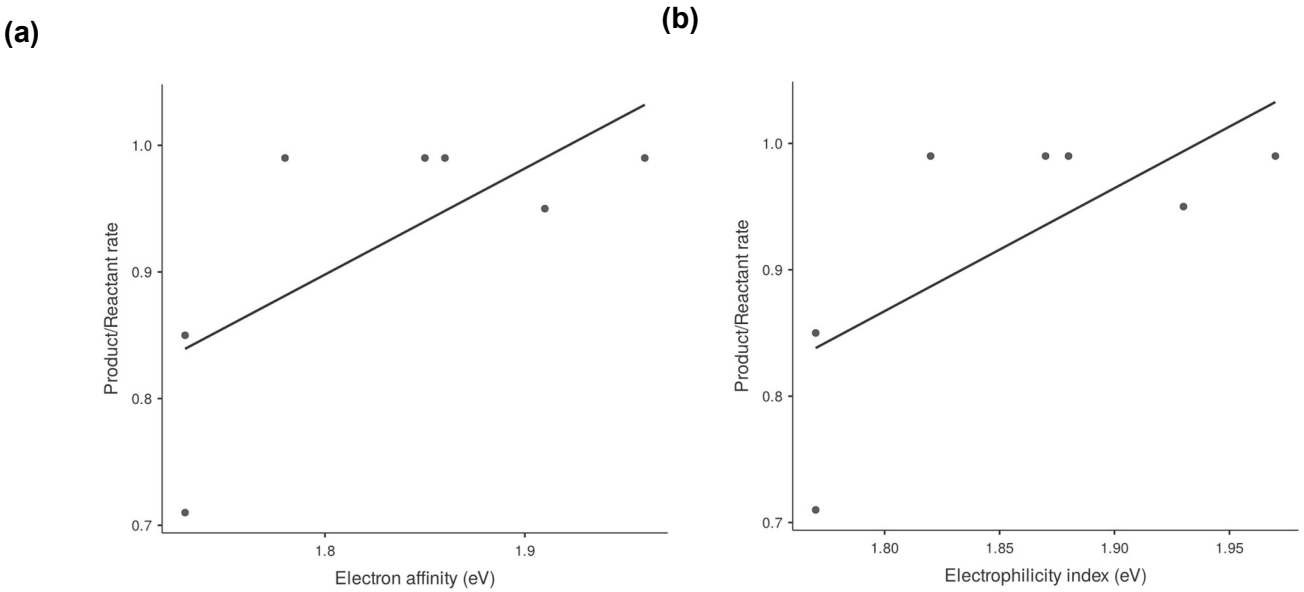


Figure S2. Linear correlation between the experimental Product/Reactant ratios under reactions condition A and computed reactive index with solvent effects included: **(a)** electron affinity (R=0.690, and R^2 = 0.477) and **(b)** electrophilic index (R=0.694, and R^2 = 0.482).

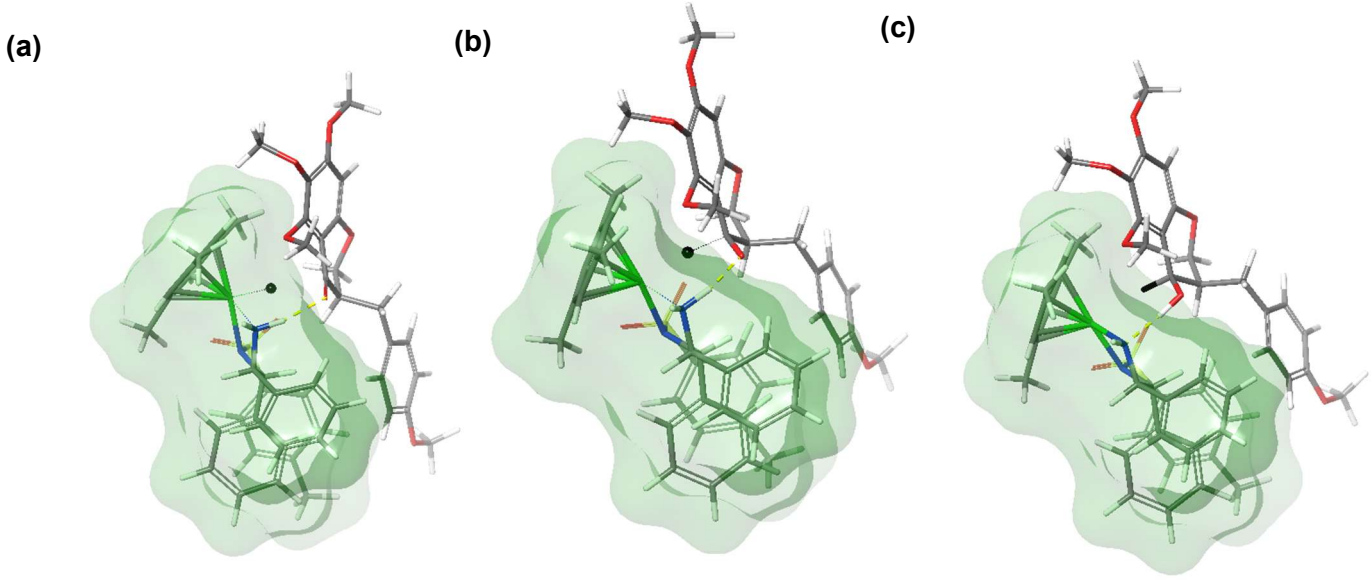


Figure S3. Si-face attack on R-5b-(Ax.). **(a)** Reactant complex; **(b)** Transition State (TS); and **(c)** Intermediate 1 or final adduct (catalyst-(R,R)-6b complex).

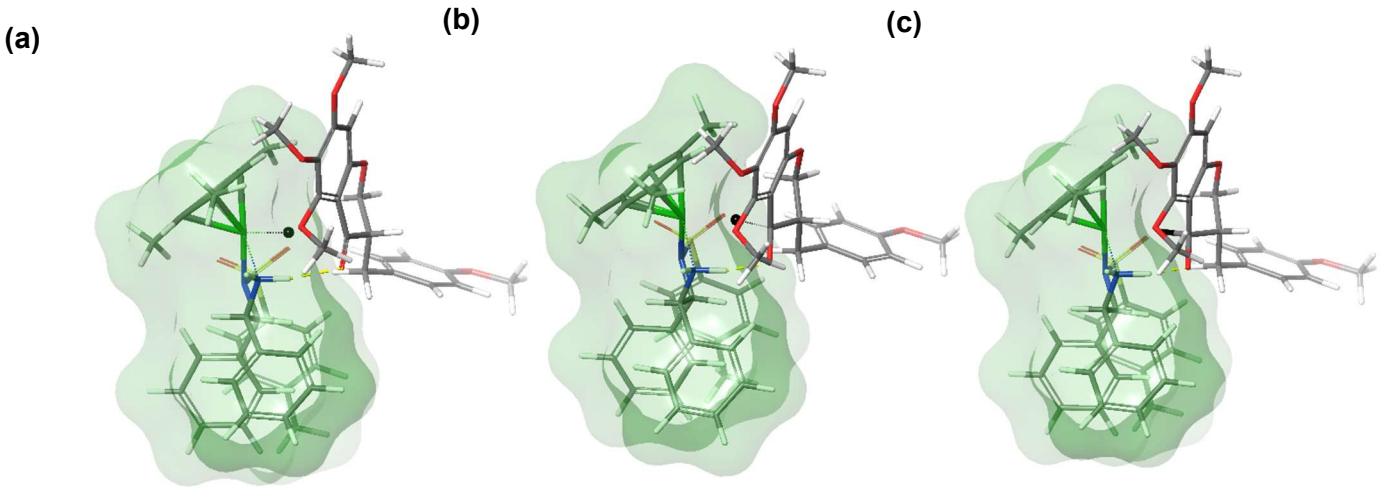


Figure S4. Si-face attack on S-5b-(Eq.). **(a)** Reactant complex; **(b)** Transition State (TS); and **(c)** Intermediate 1 or final adduct (catalyst-(R,S)-6b complex).

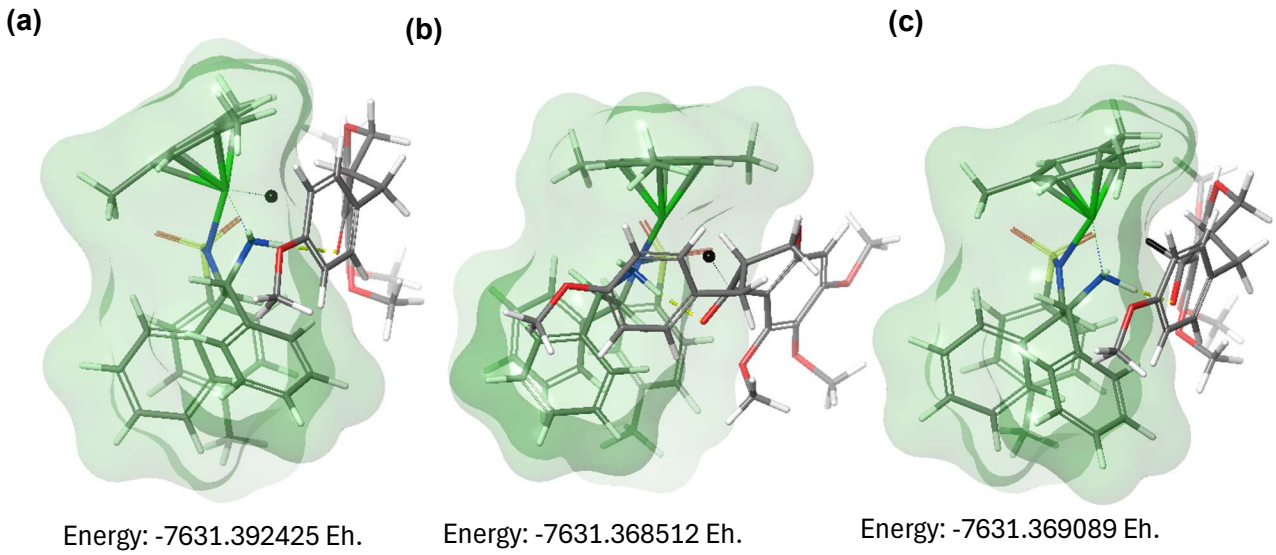


Figure S5. Re-face attack on S-5b-(Eq.). **(a)** Reactant complex; **(b)** Transition State (TS); and **(c)** Intermediate 1 or final adduct (catalyst-(S,S)-6b complex).

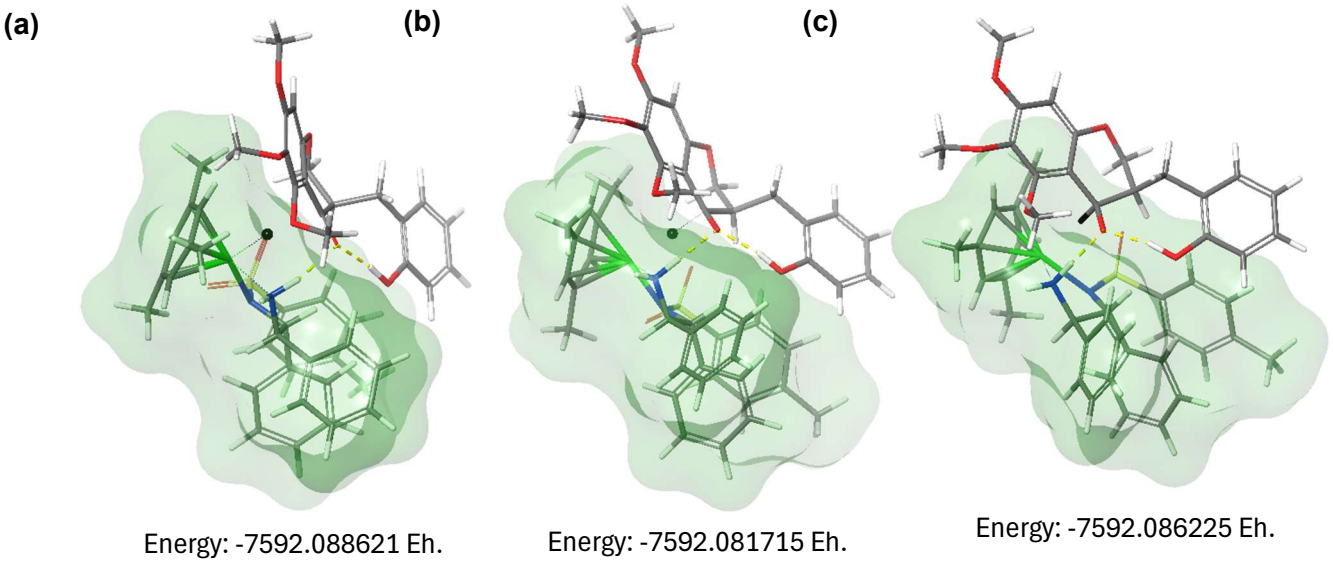


Figure S6. Si-face attack on R-5c-(Ax.). **(a)** Reactant complex; **(b)** Transition State (TS); and **(c)** Intermediate 1 or final adduct (catalyst-(R,R)-6c complex).

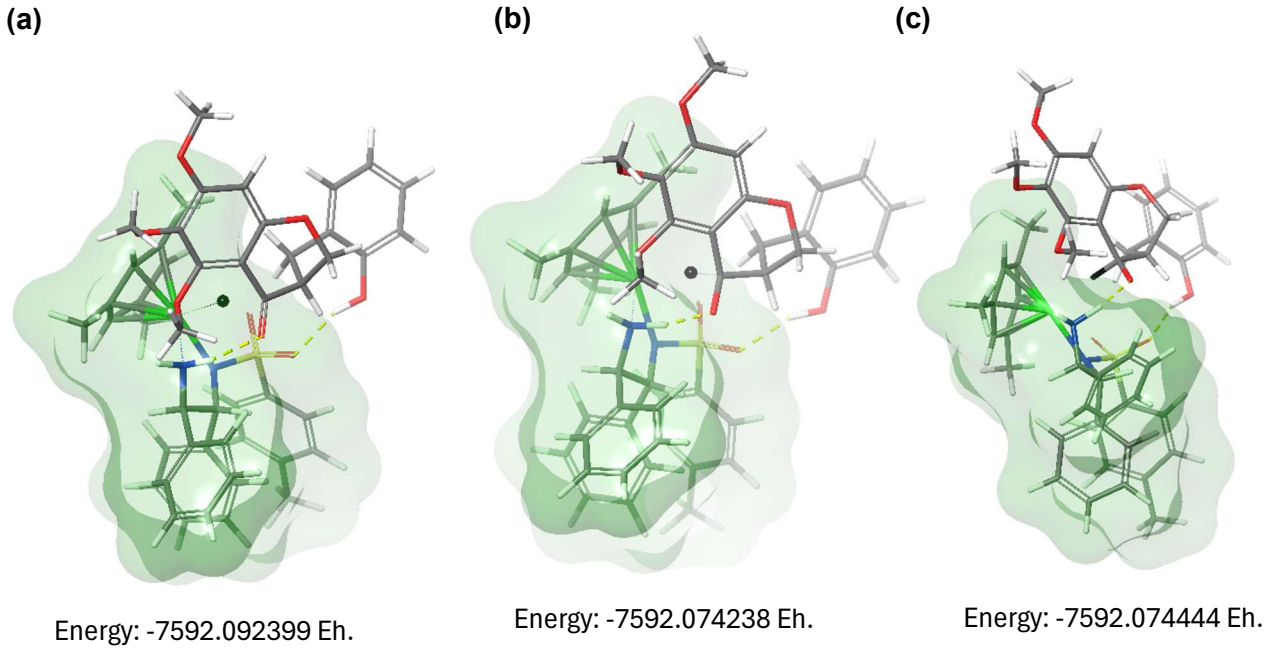


Figure S7. Si-face attack on S-5c-(Ax.). **(a)** Reactant complex; **(b)** Transition State (TS); and **(c)** Intermediate 1 or final adduct (catalyst-(R,S)-6c complex).

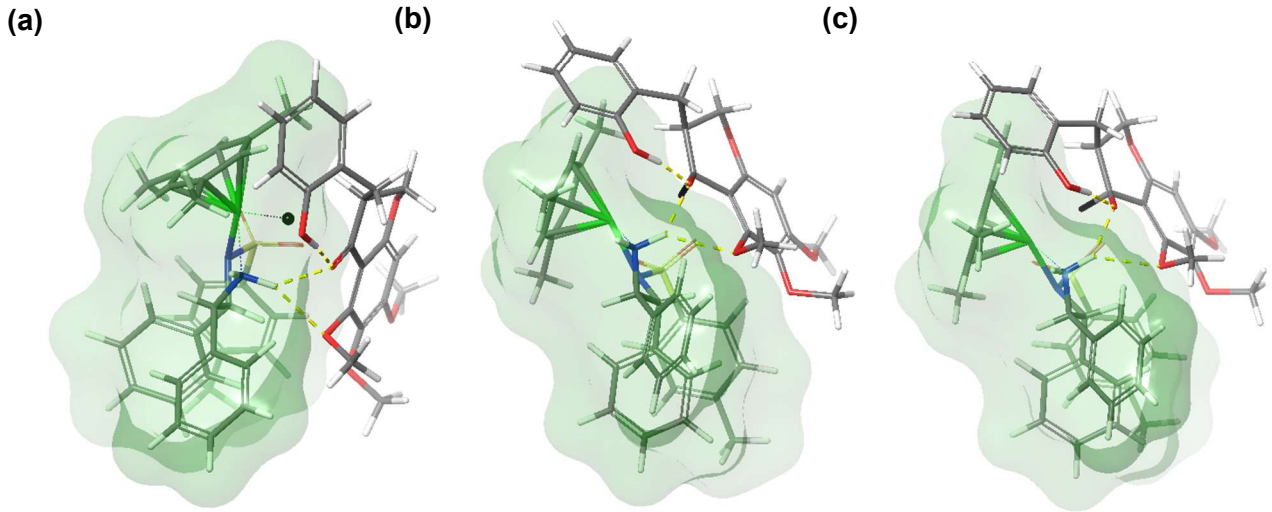


Figure S8. Si-face attack on S-5c-(Eq.). **(a)** Reactant complex; **(b)** Transition State (TS); and **(c)** Intermediate 1 or final adduct (catalyst-(S,S)-6c complex).

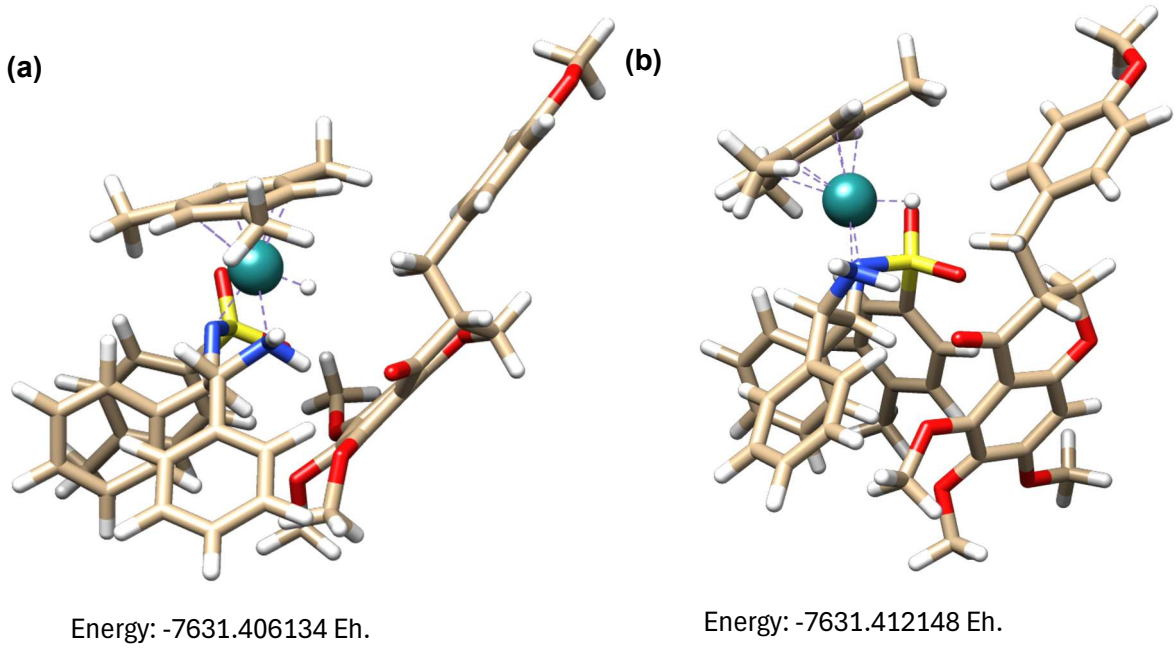
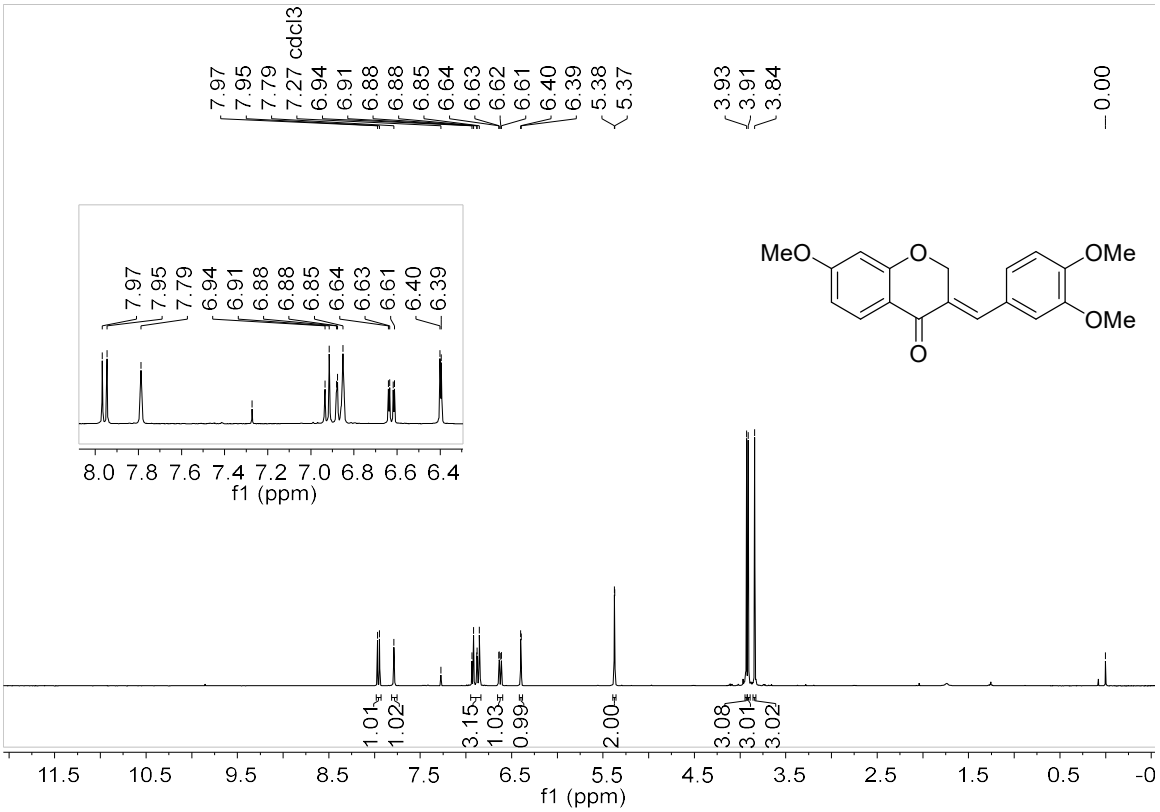


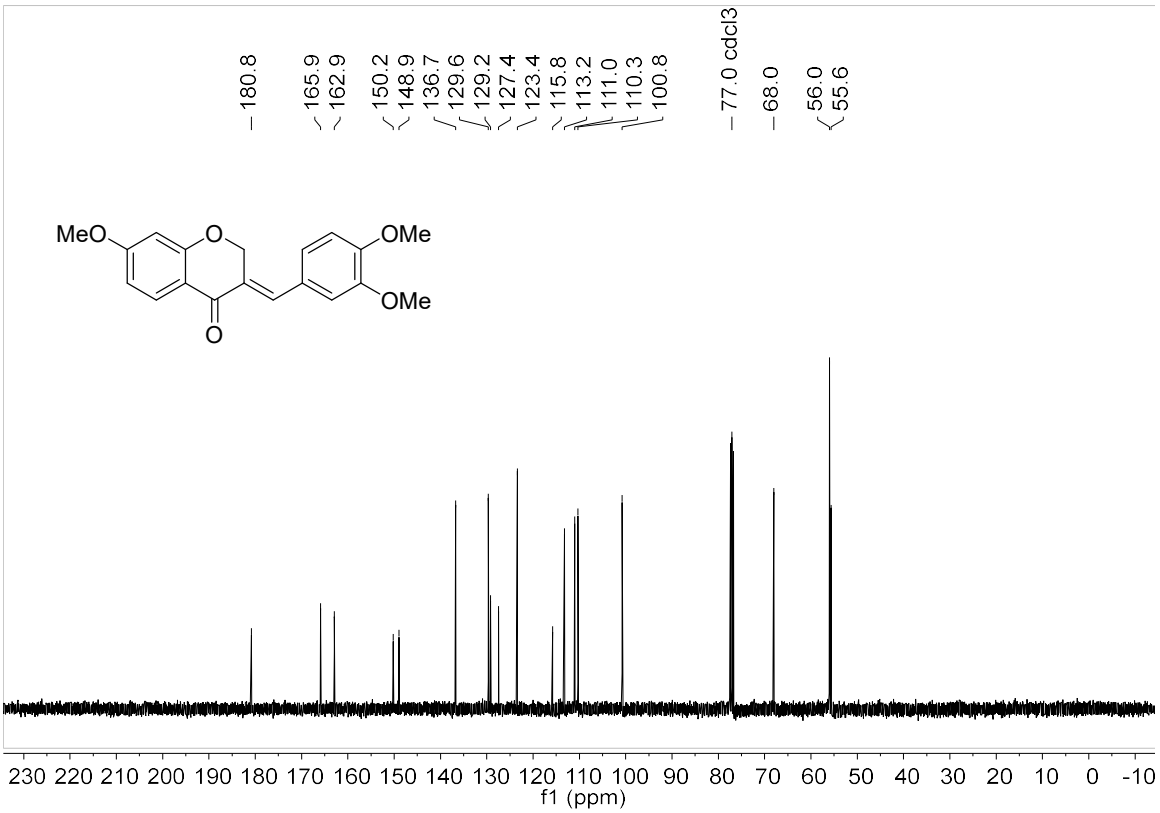
Figure S9. Si-face attack on R-5b. **(a)** Axial conformation; and **(b)** Equatorial conformation.

NMR Spectra of the (*E*)-3-benzylidenechroman-4-ones (4a-h)

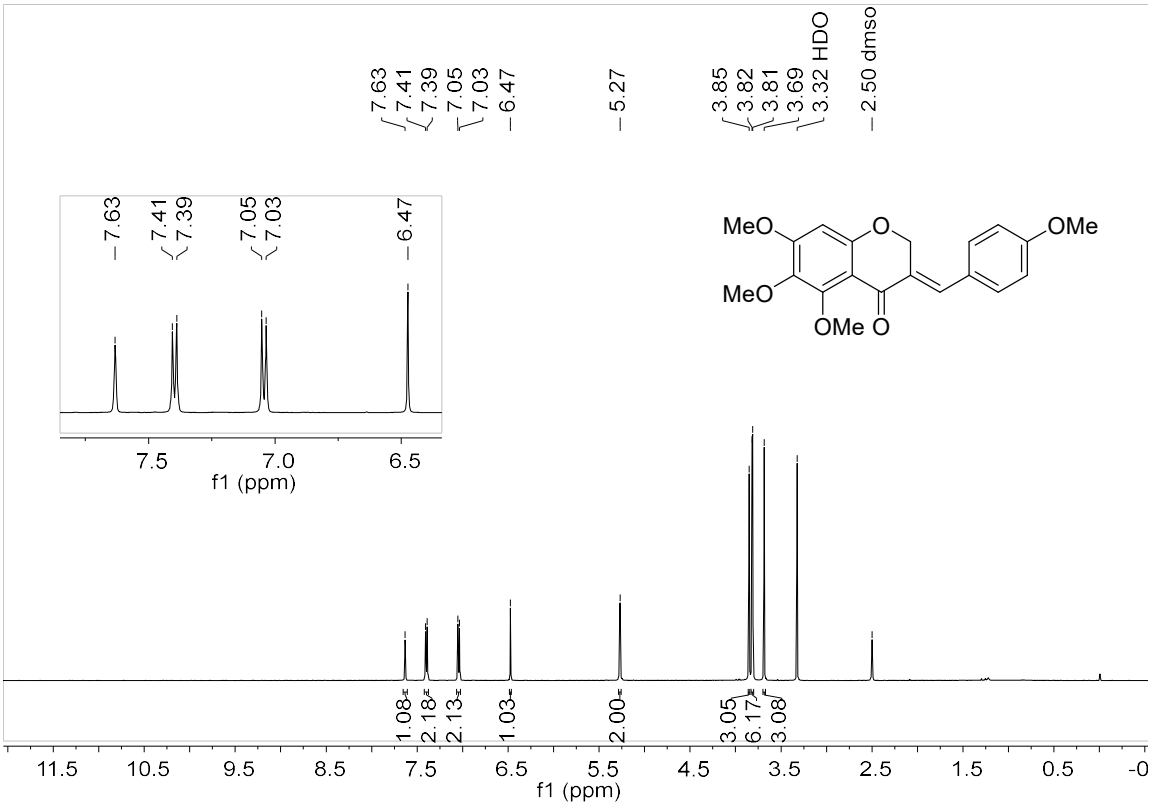
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a



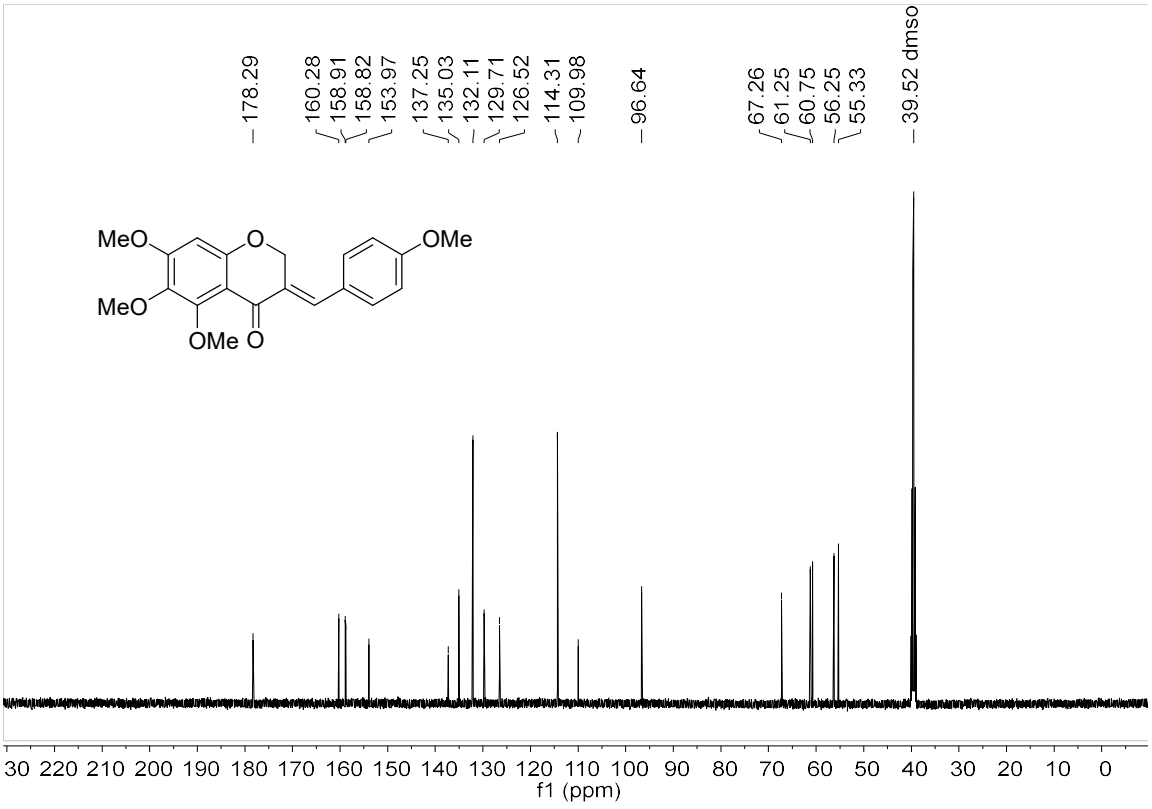
^{13}C NMR (101 MHz, $CDCl_3$) of 4a



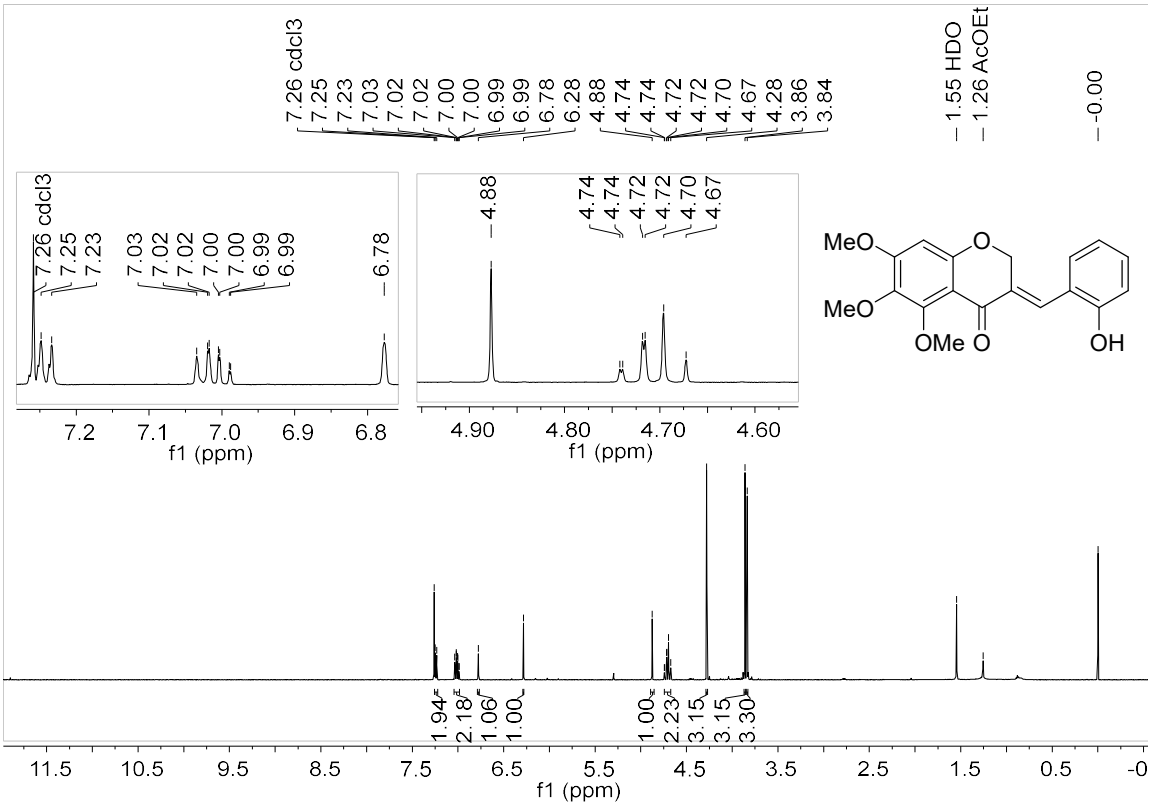
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of 4b



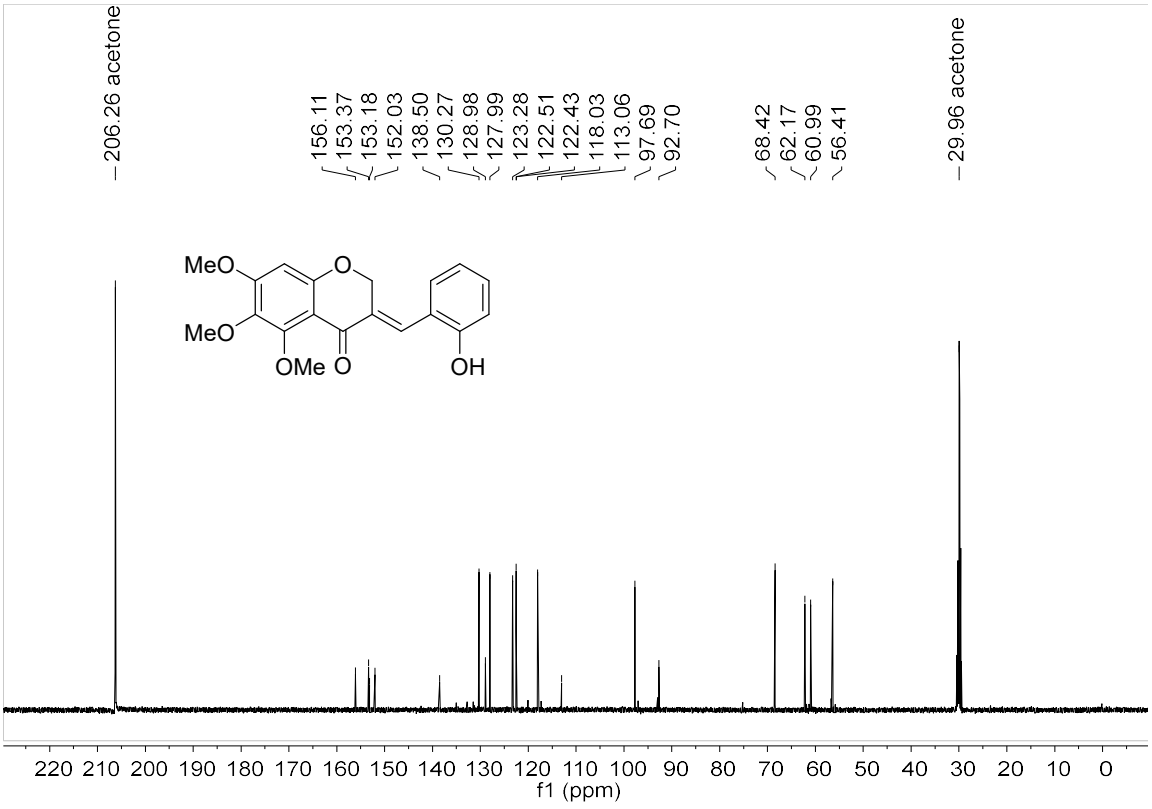
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of 4b



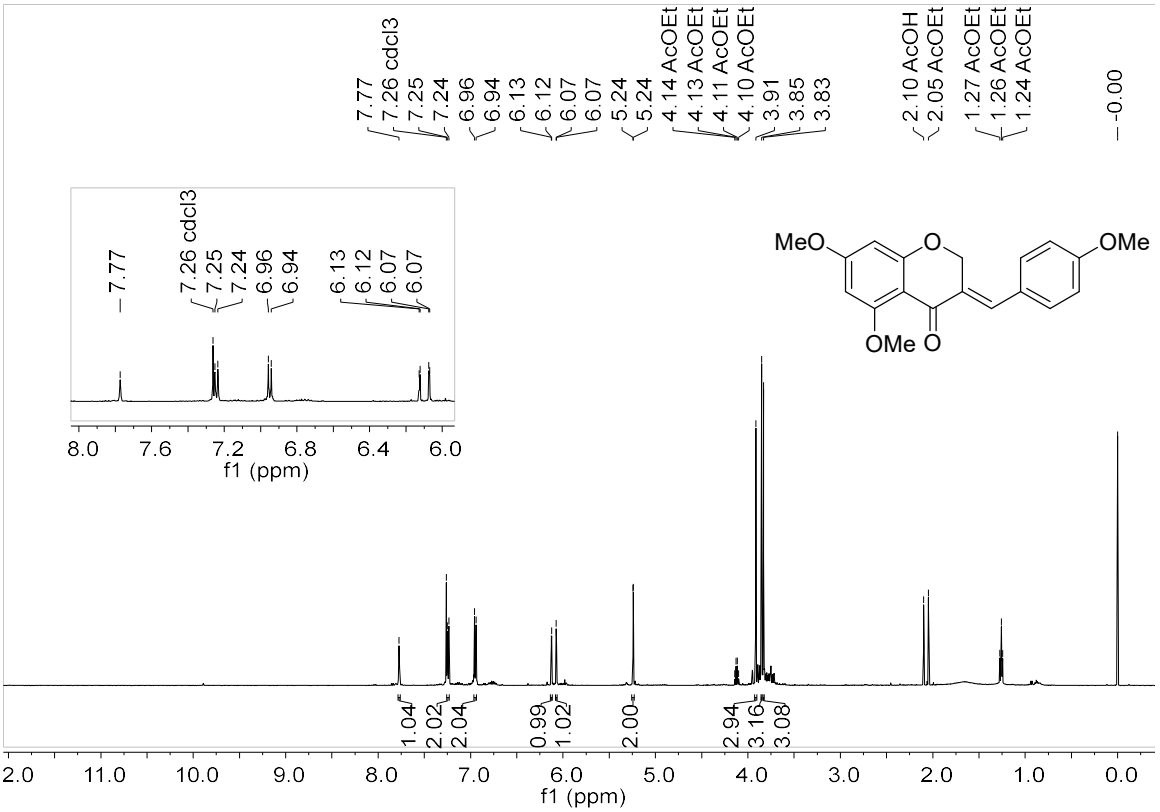
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4c



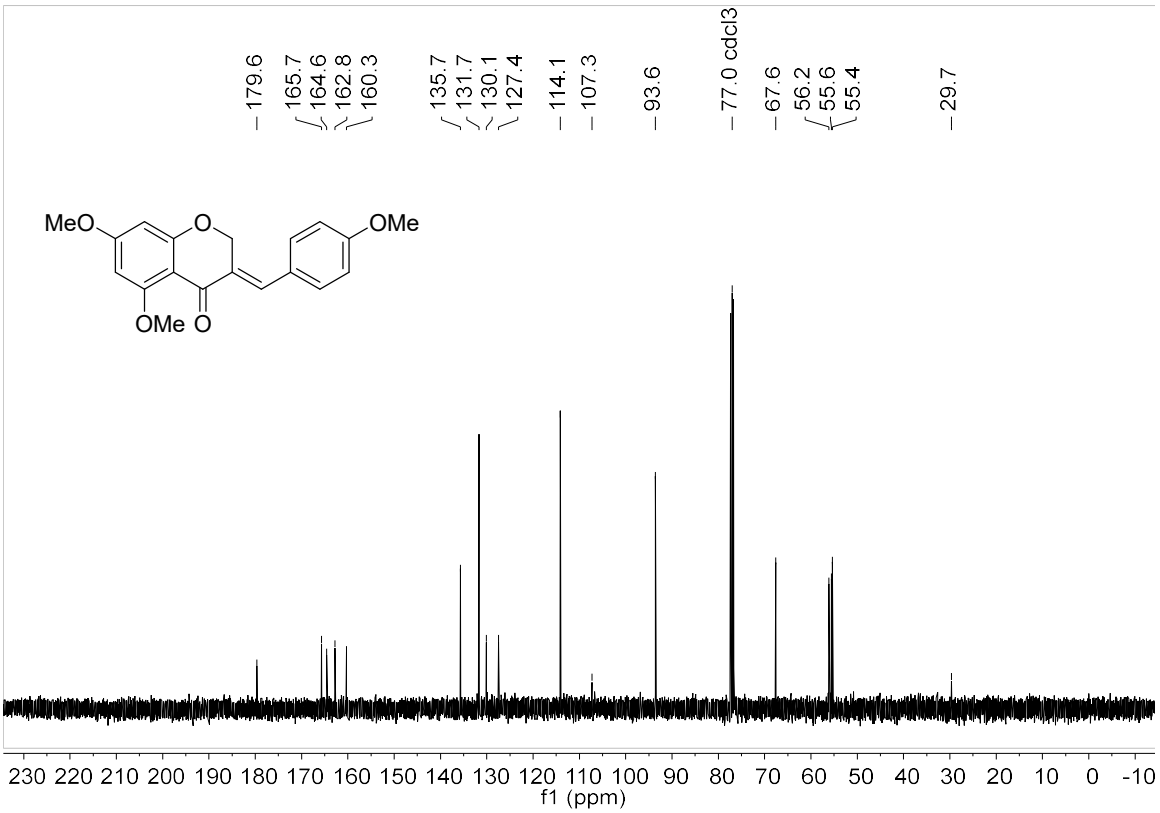
^{13}C NMR (126 MHz, Acetone-d_6) spectrum of 4c



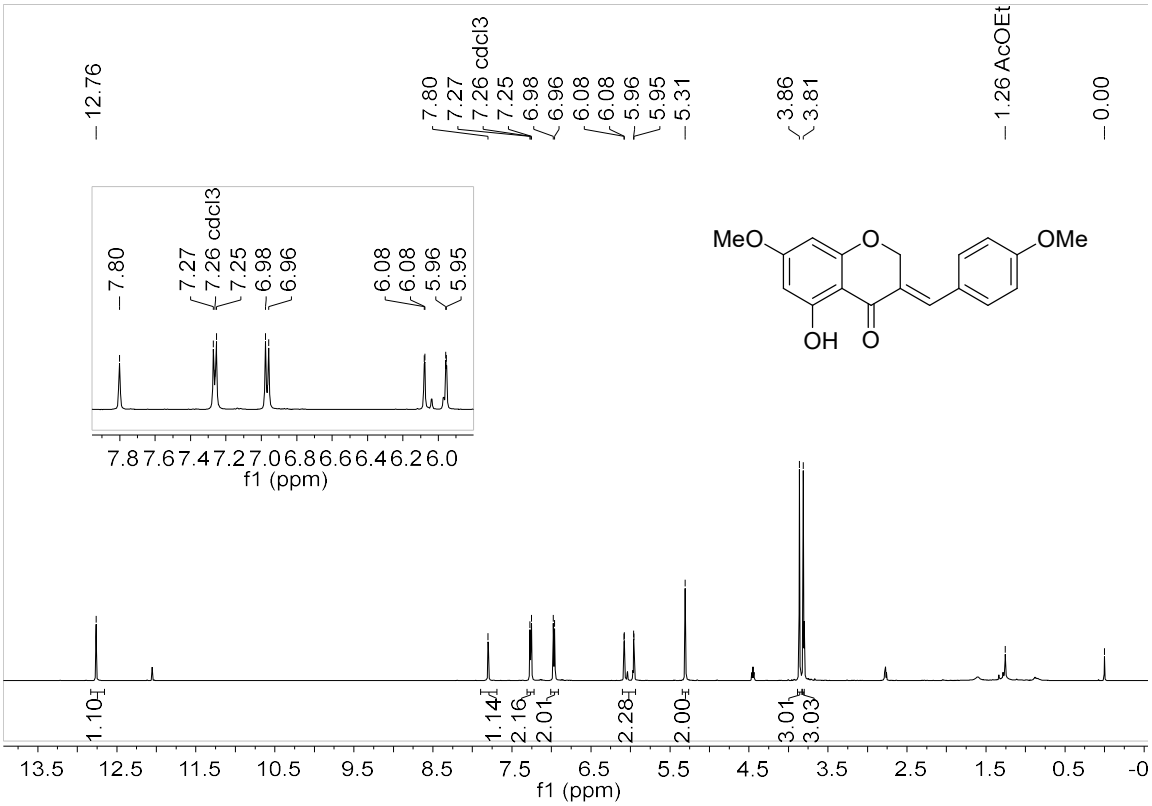
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4d



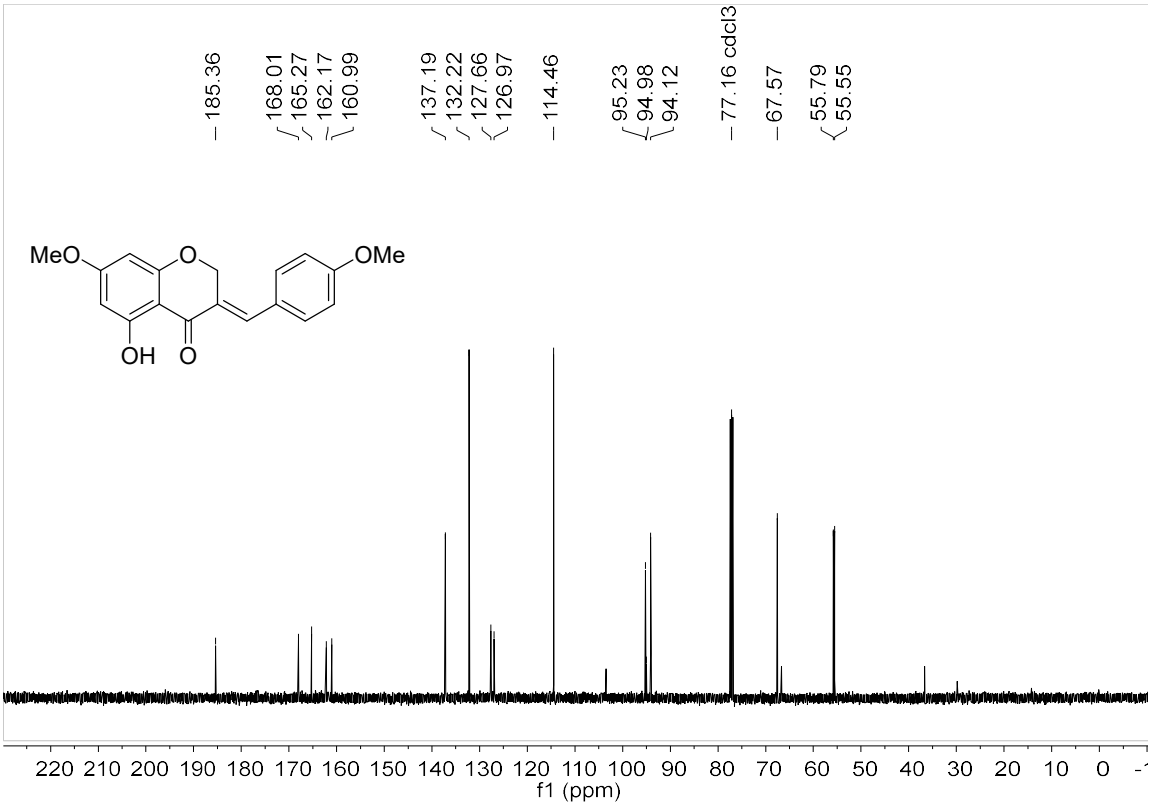
^{13}C NMR (101 MHz, $CDCl_3$) of 4d



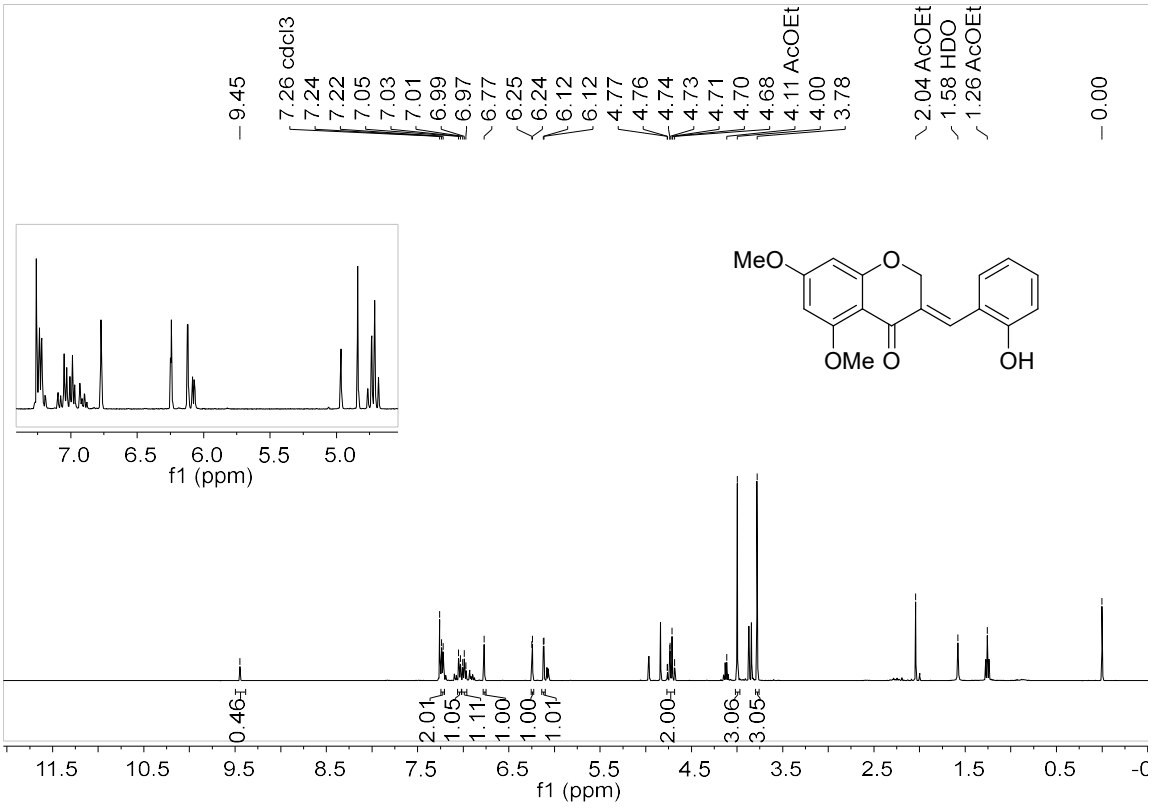
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4e



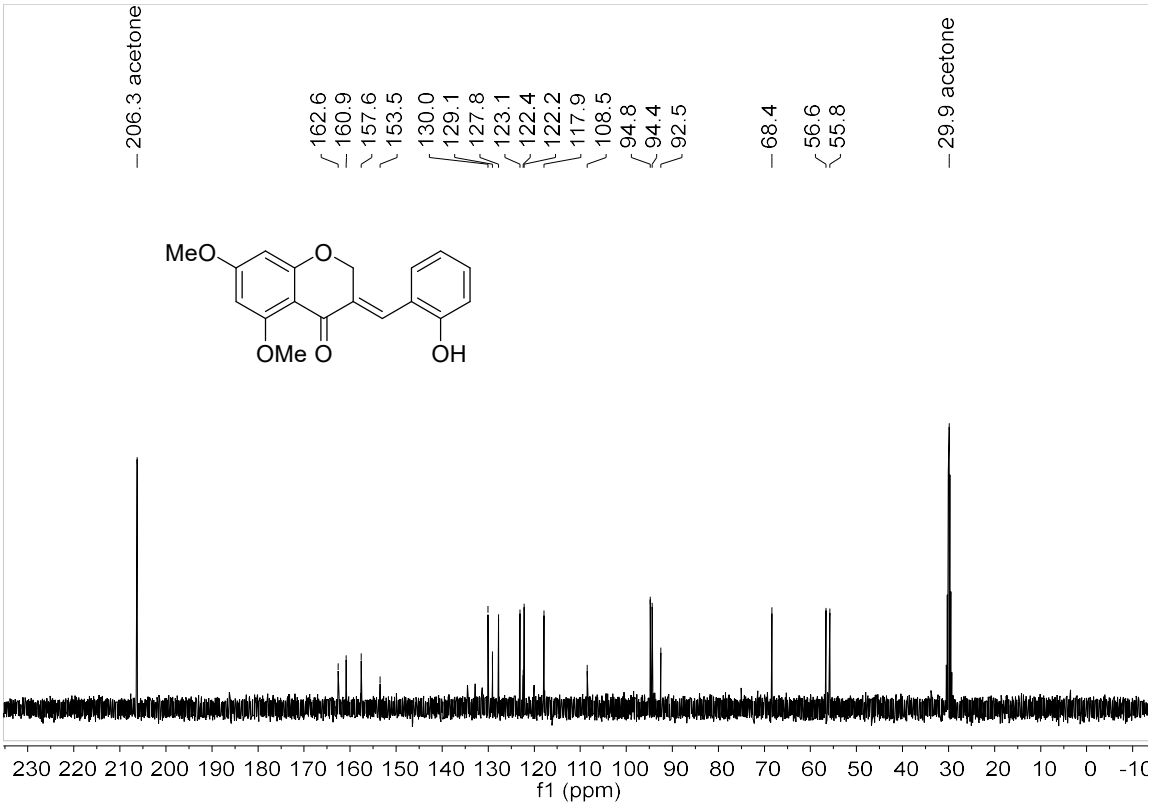
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4e



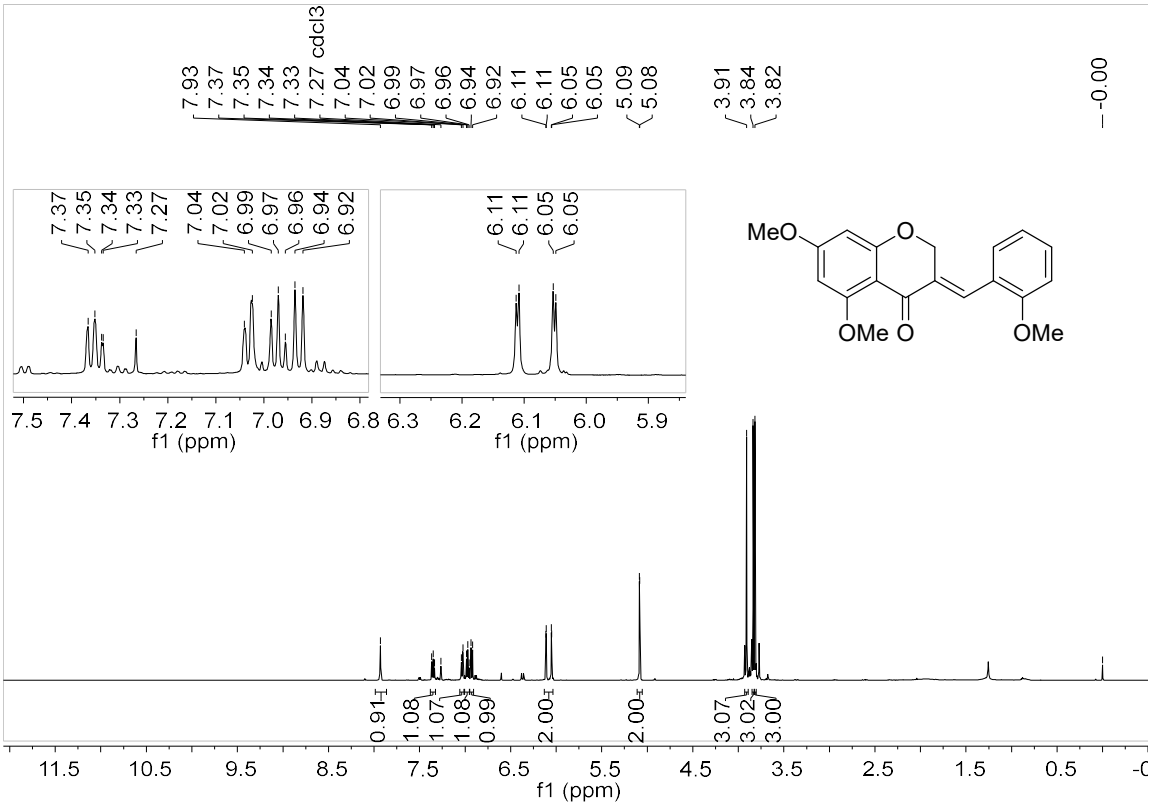
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4f



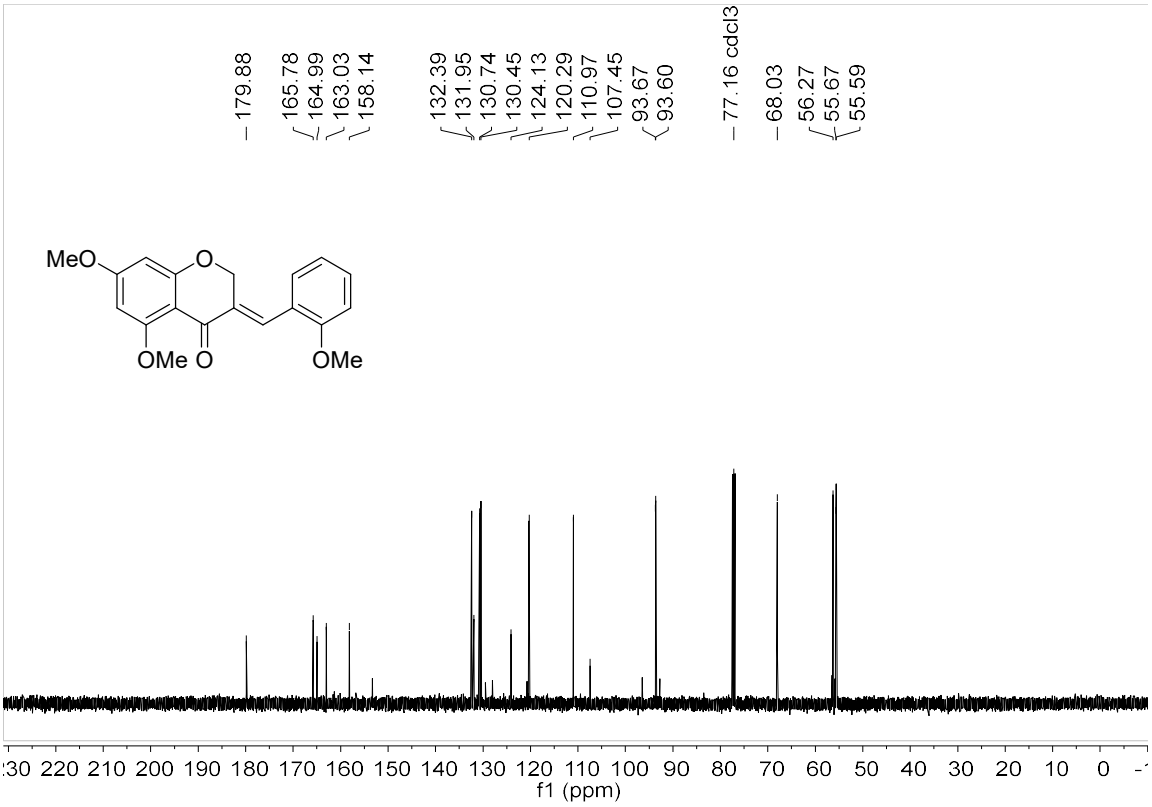
^{13}C NMR (101 MHz, Acetone-d_6) spectrum of 4f



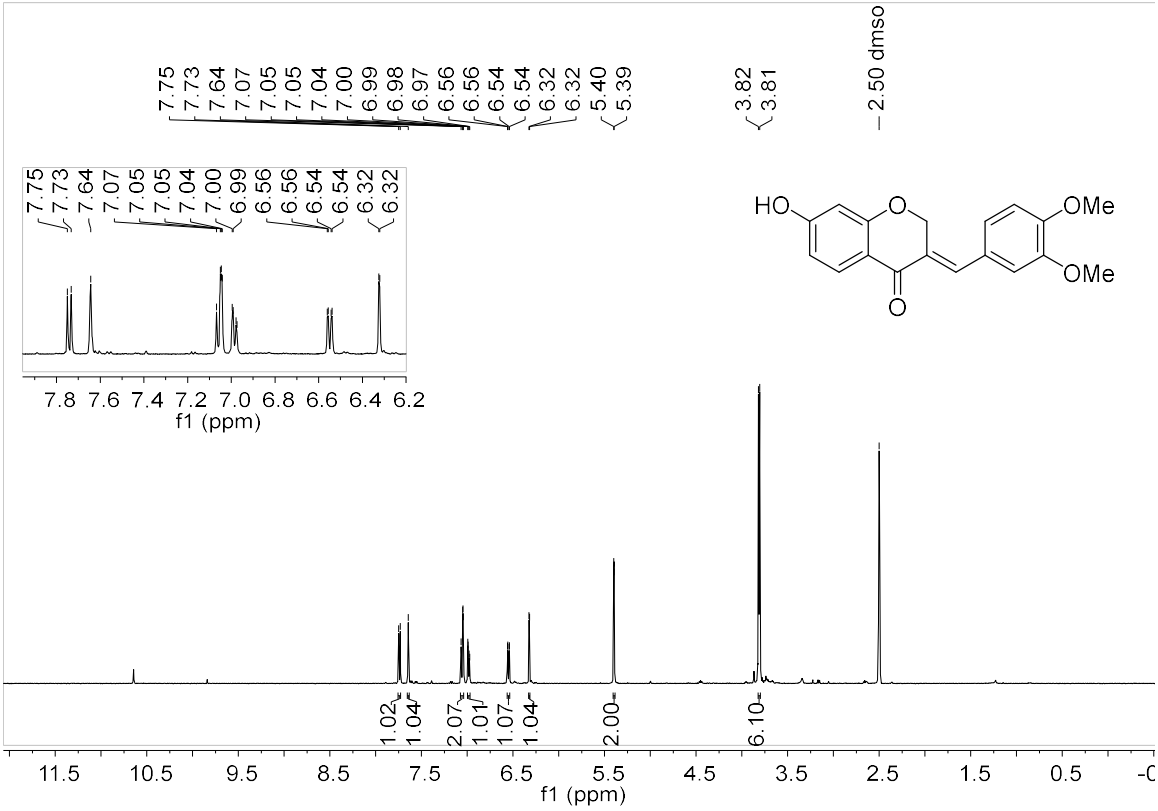
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4g



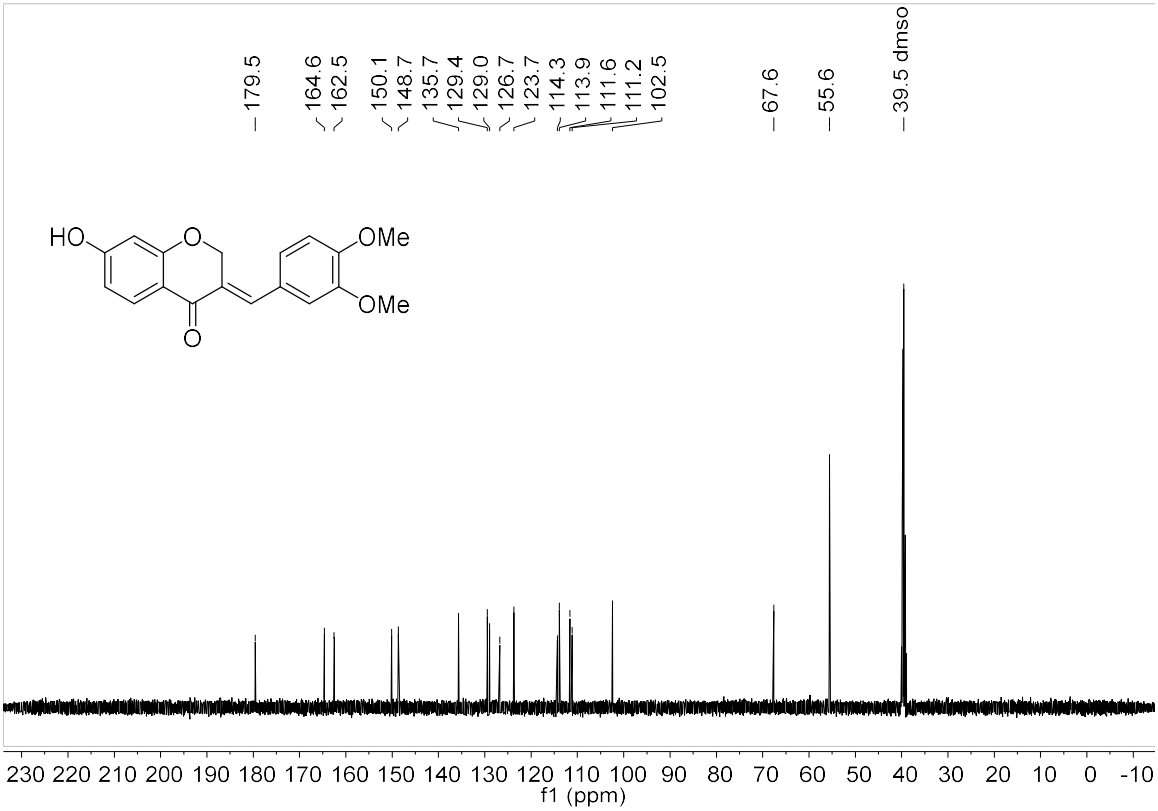
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4g



^{1}H NMR (500 MHz, DMSO-d_6) spectrum of 4h

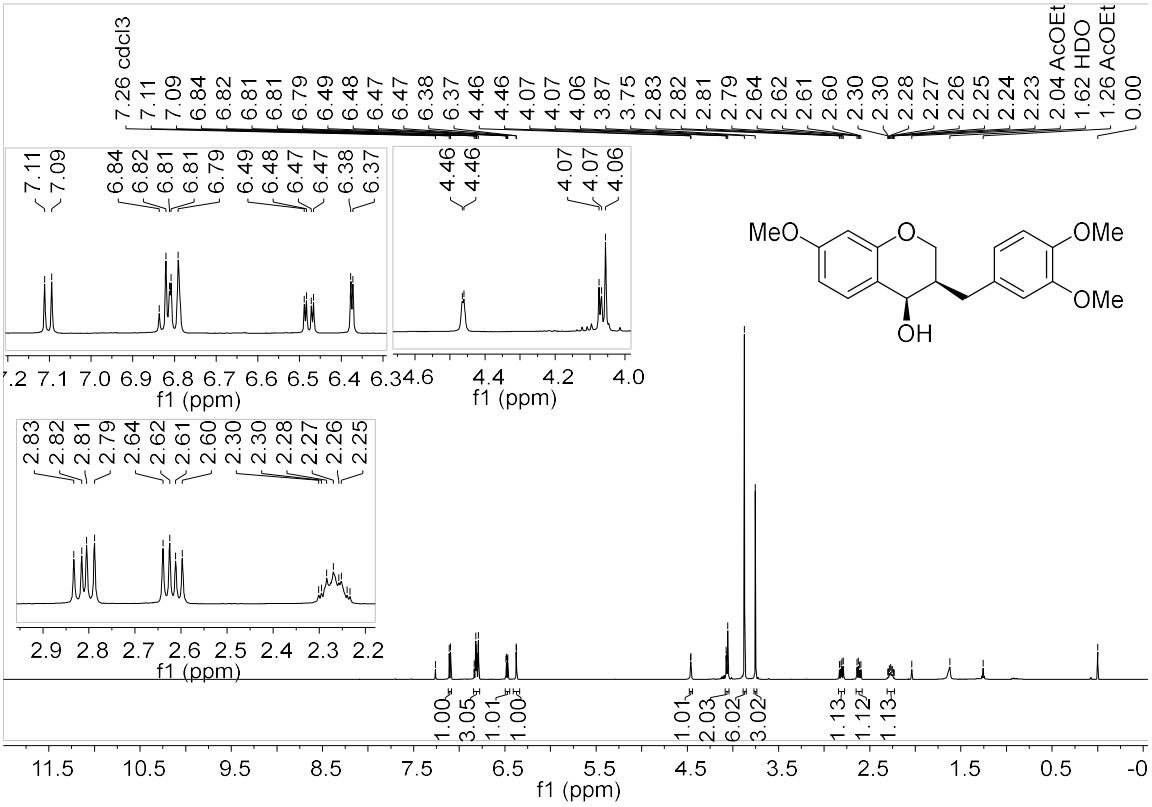


^{13}C NMR (101 MHz, DMSO-d_6) of 4h

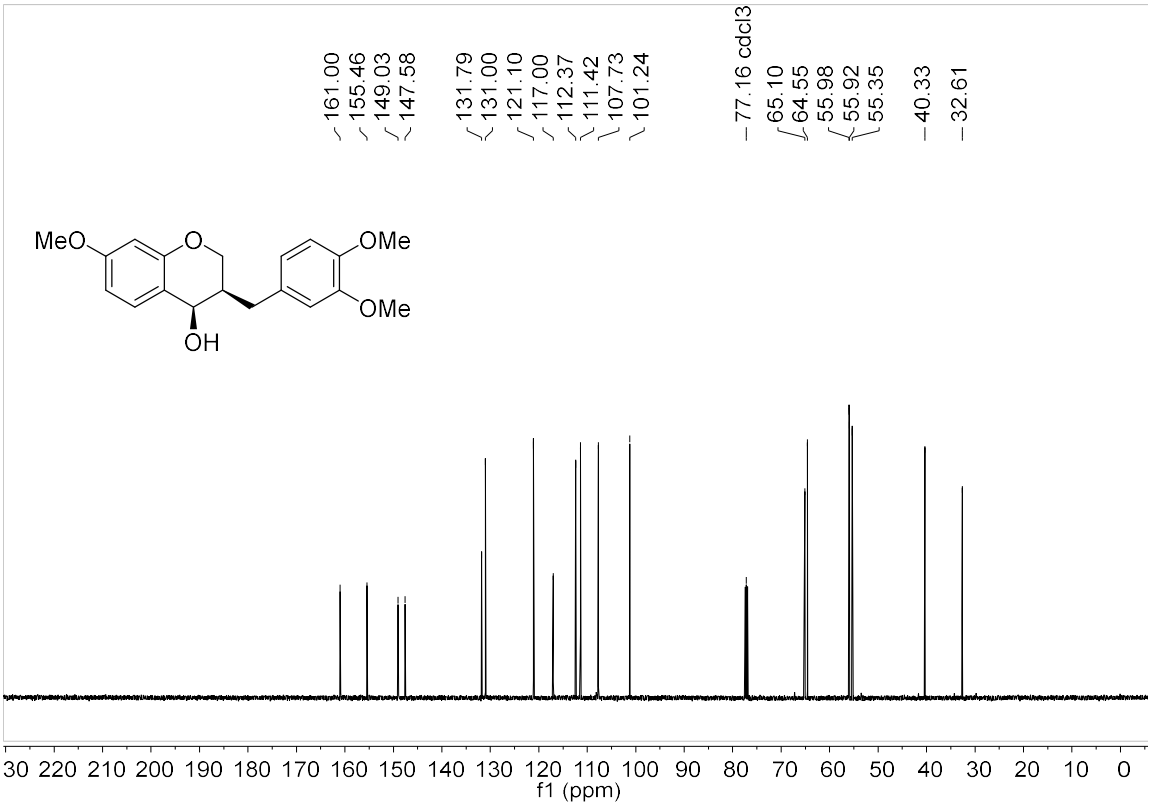


NMR Spectra of the (3*R*,4*R*)-3-benzylchroman-4-ol (6a-g, 7c,f)

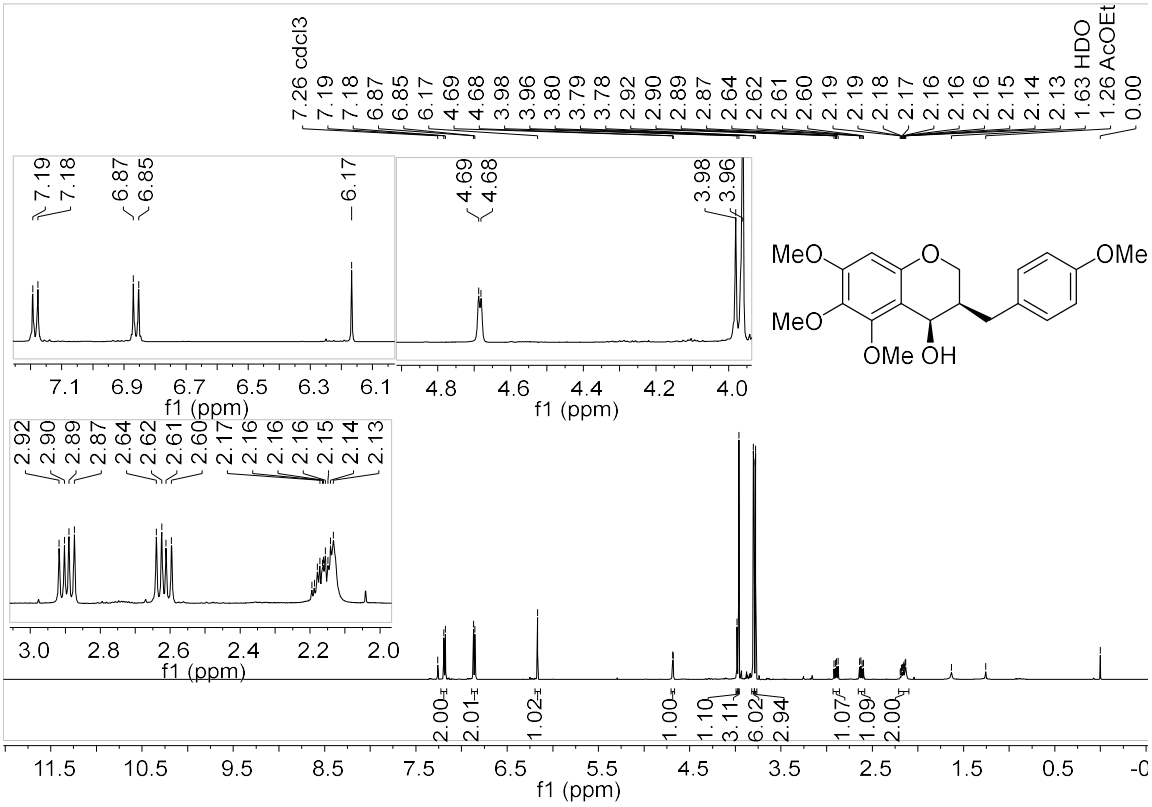
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6a



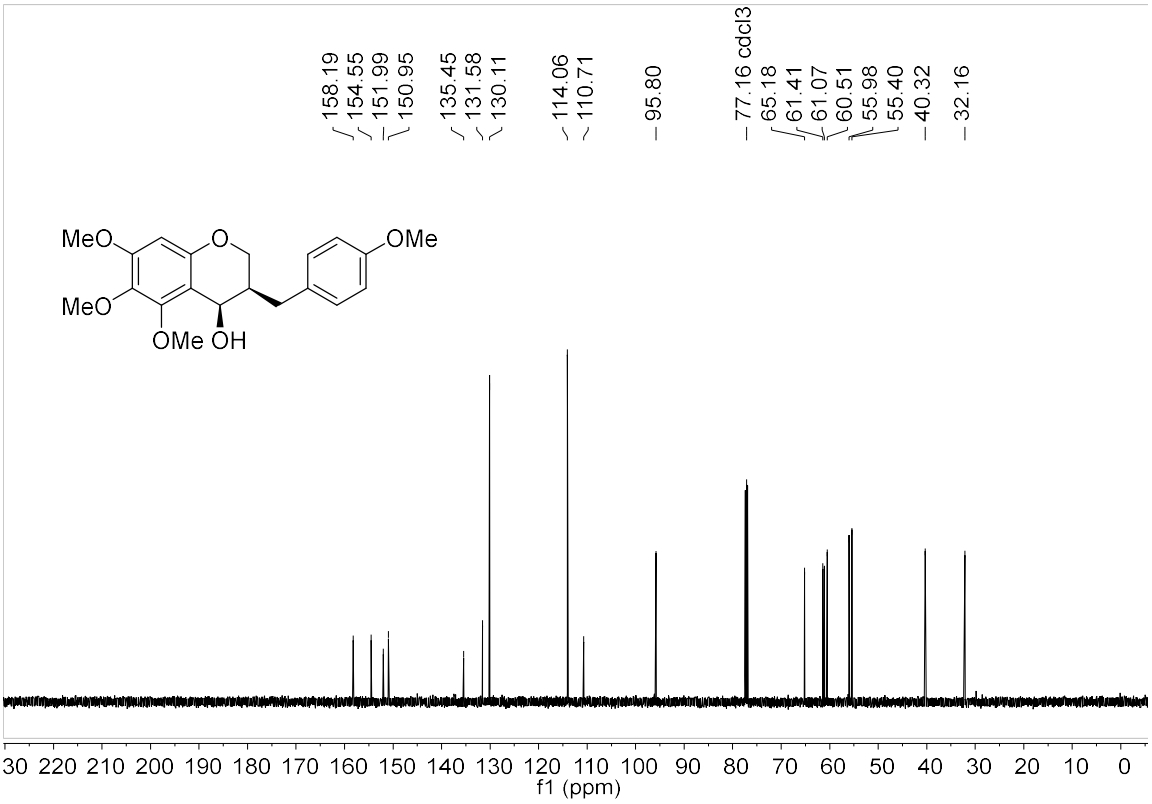
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6a



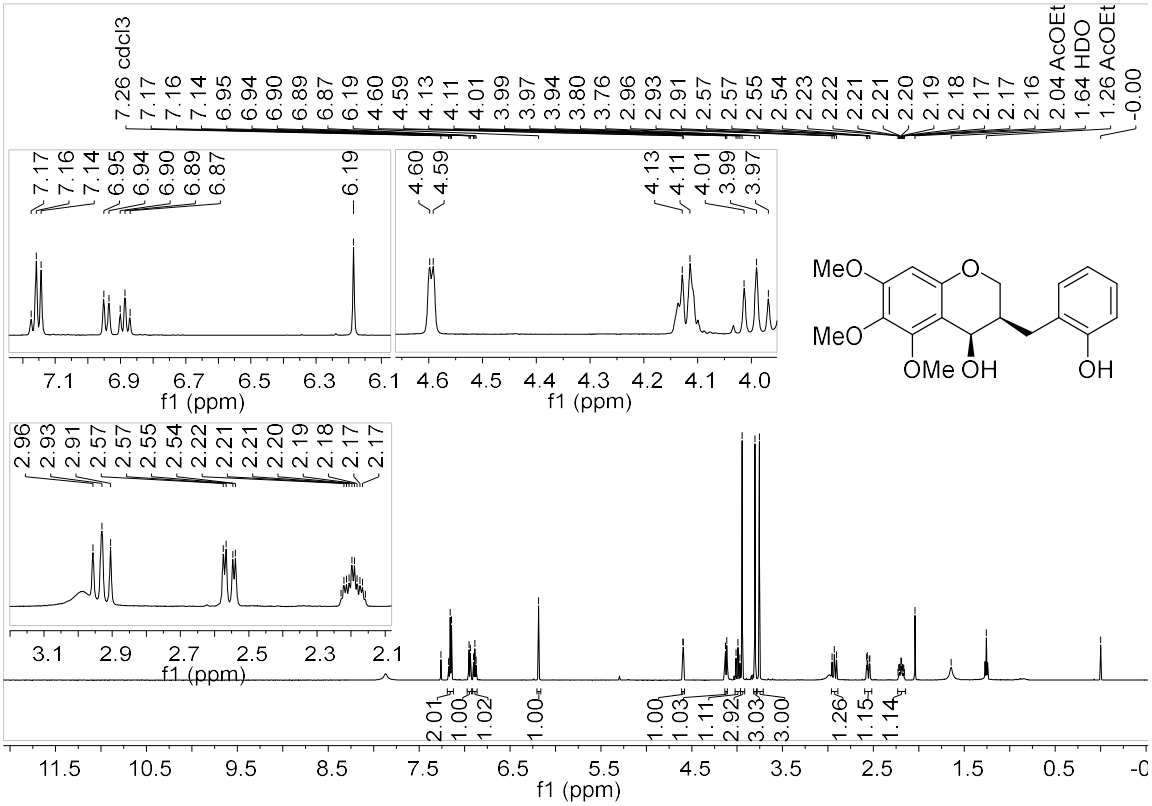
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6b



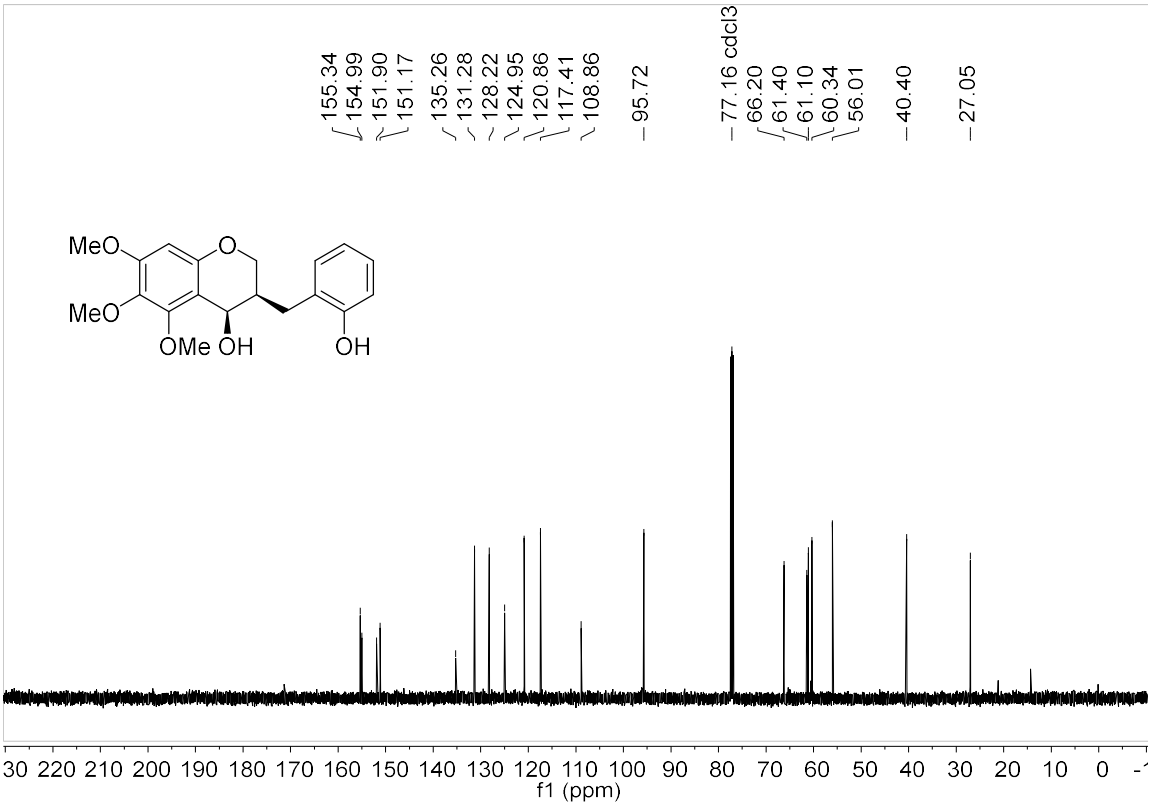
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6b



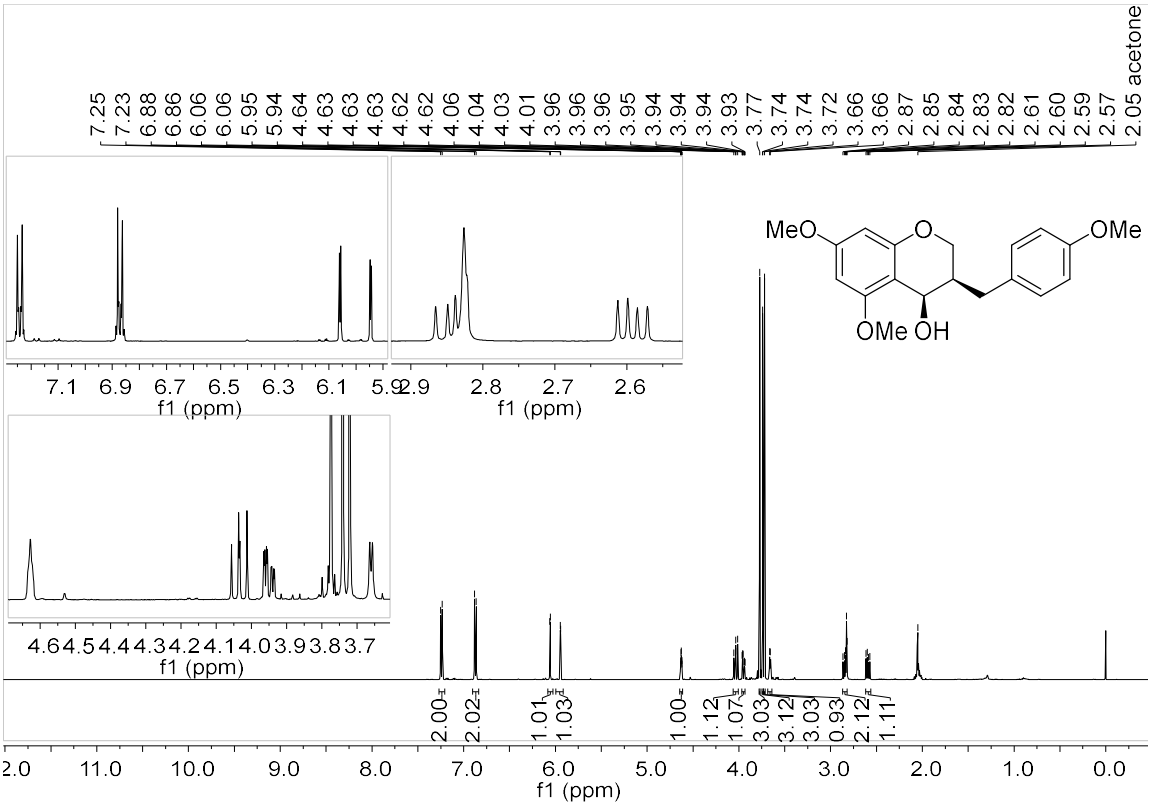
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6c



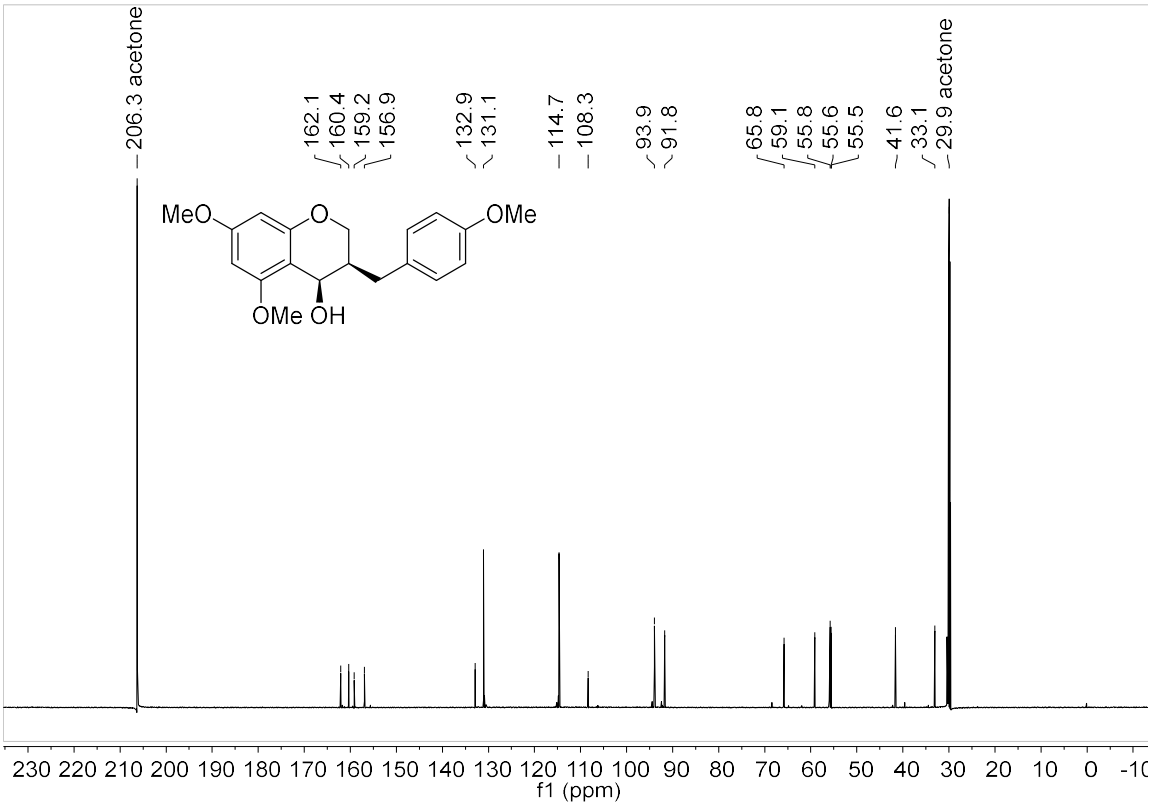
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6c



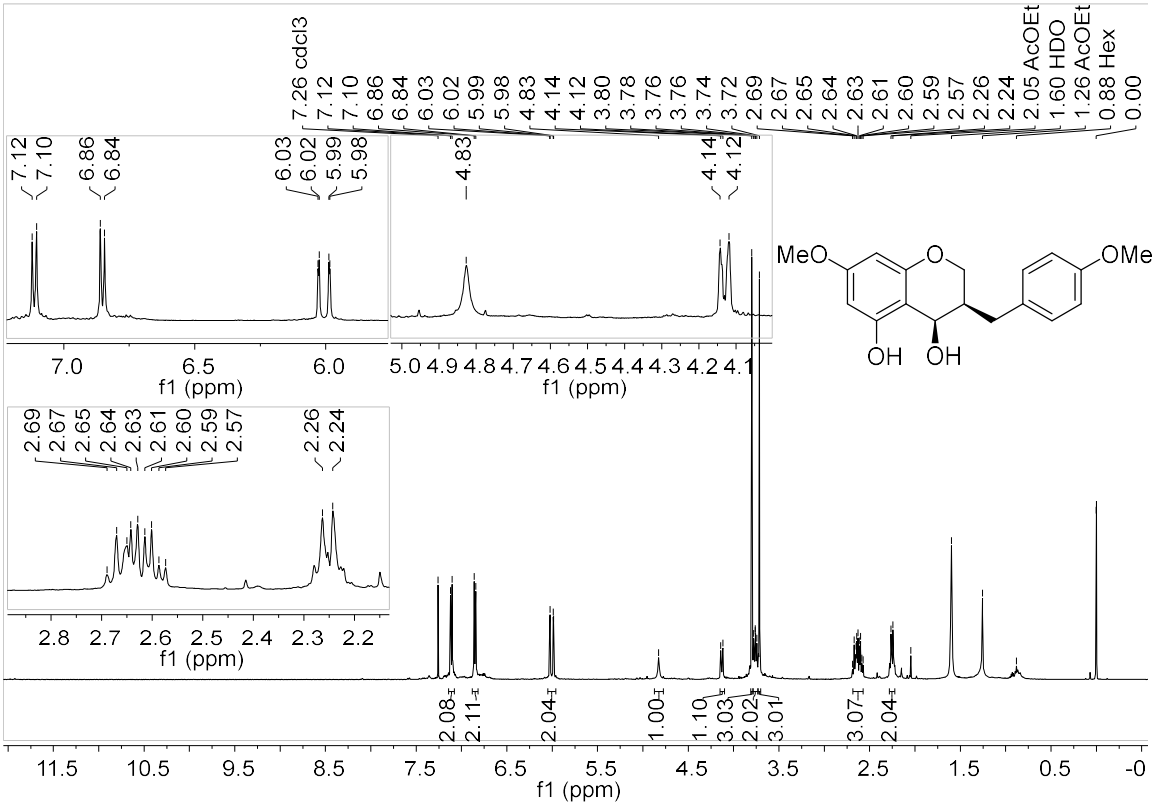
^{1}H NMR (500 MHz, Acetone-d_6) spectrum of 6d



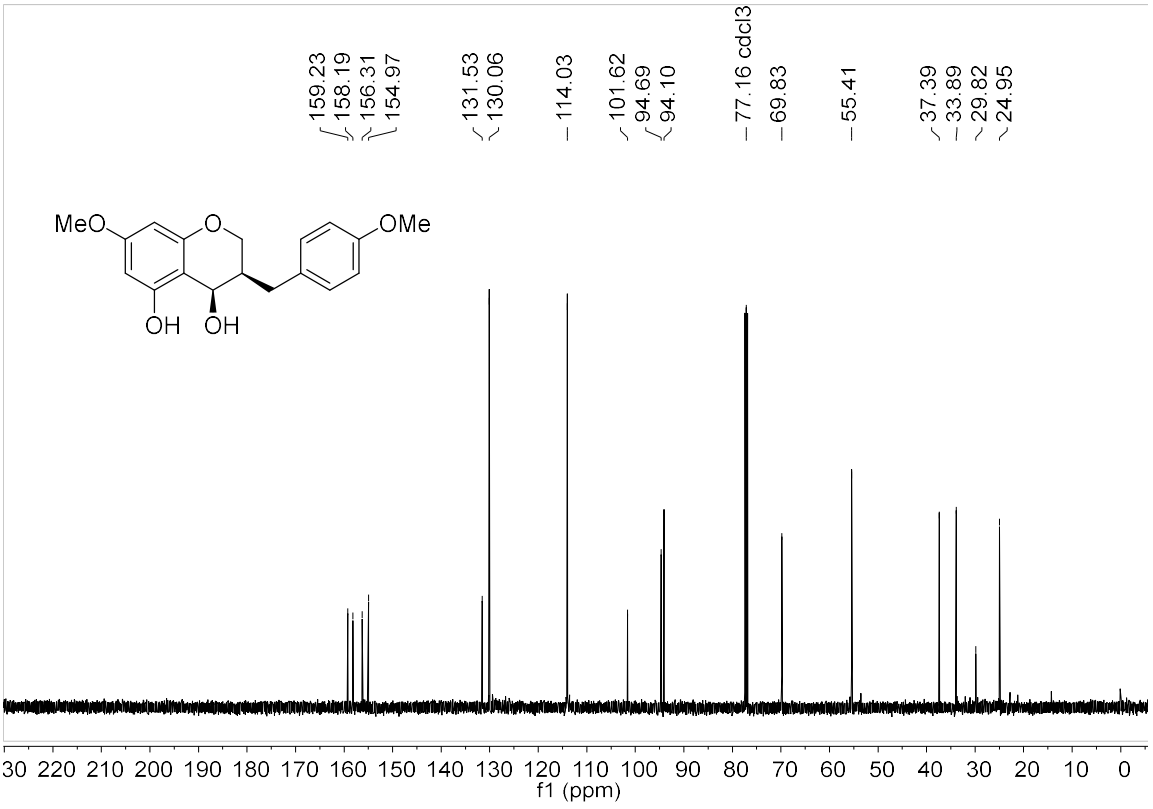
^{13}C NMR (101 MHz, Acetone-d_6) spectrum of 6d



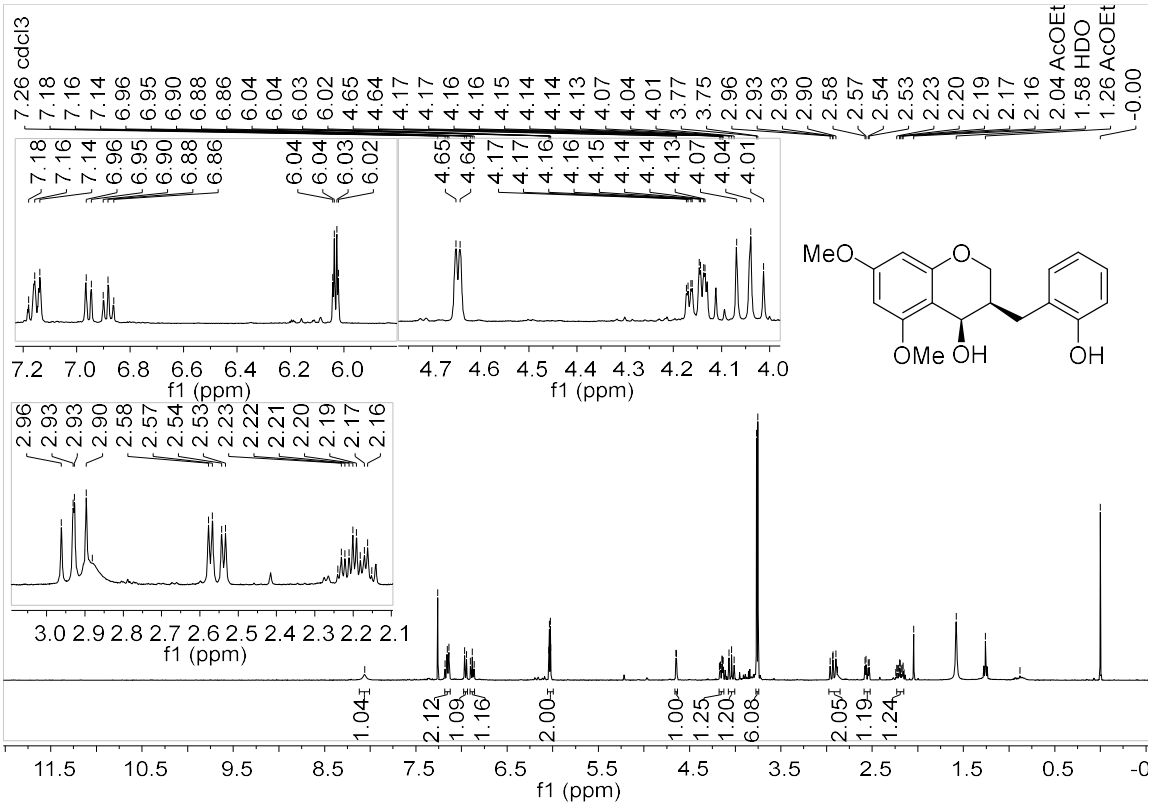
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6e



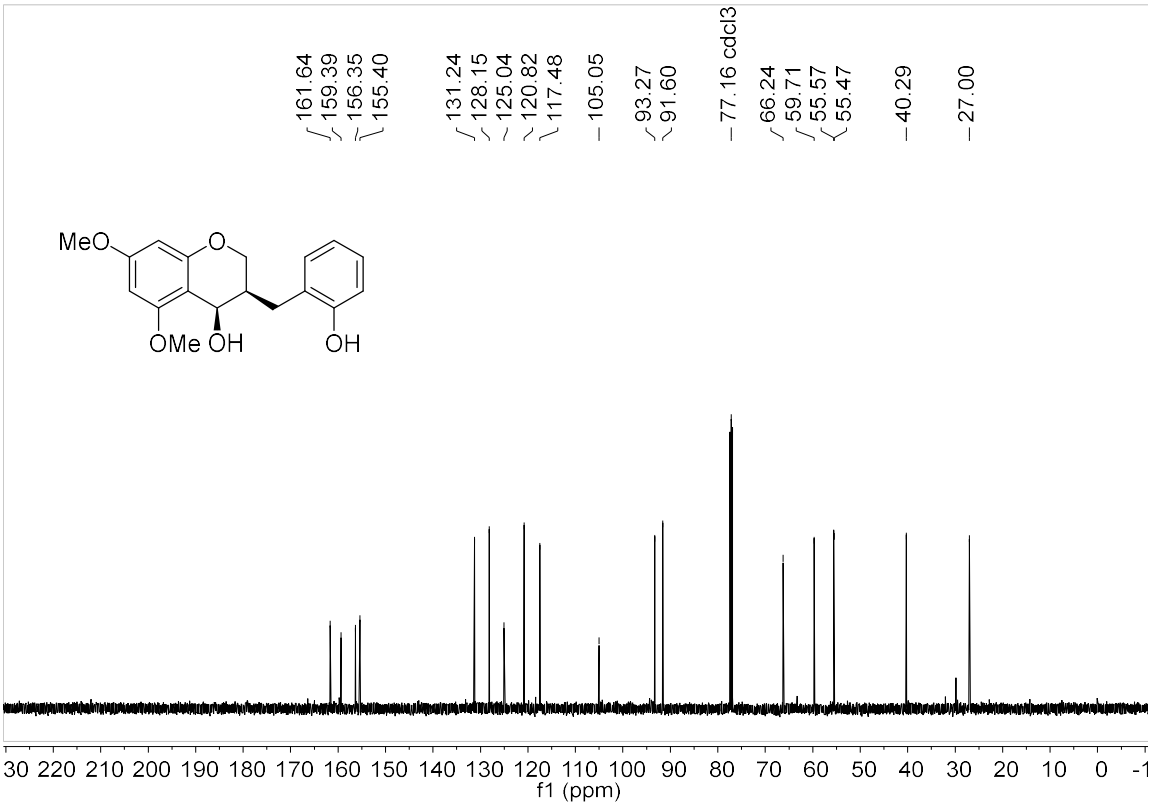
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6e



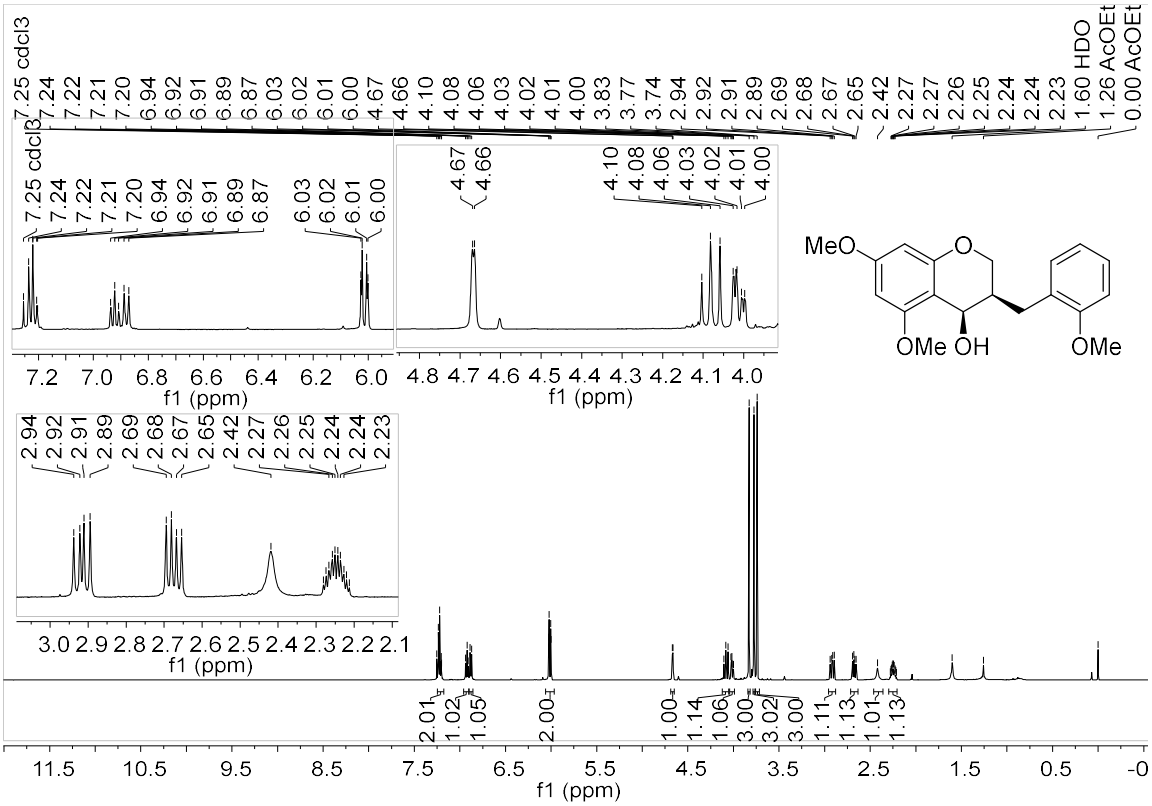
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6f



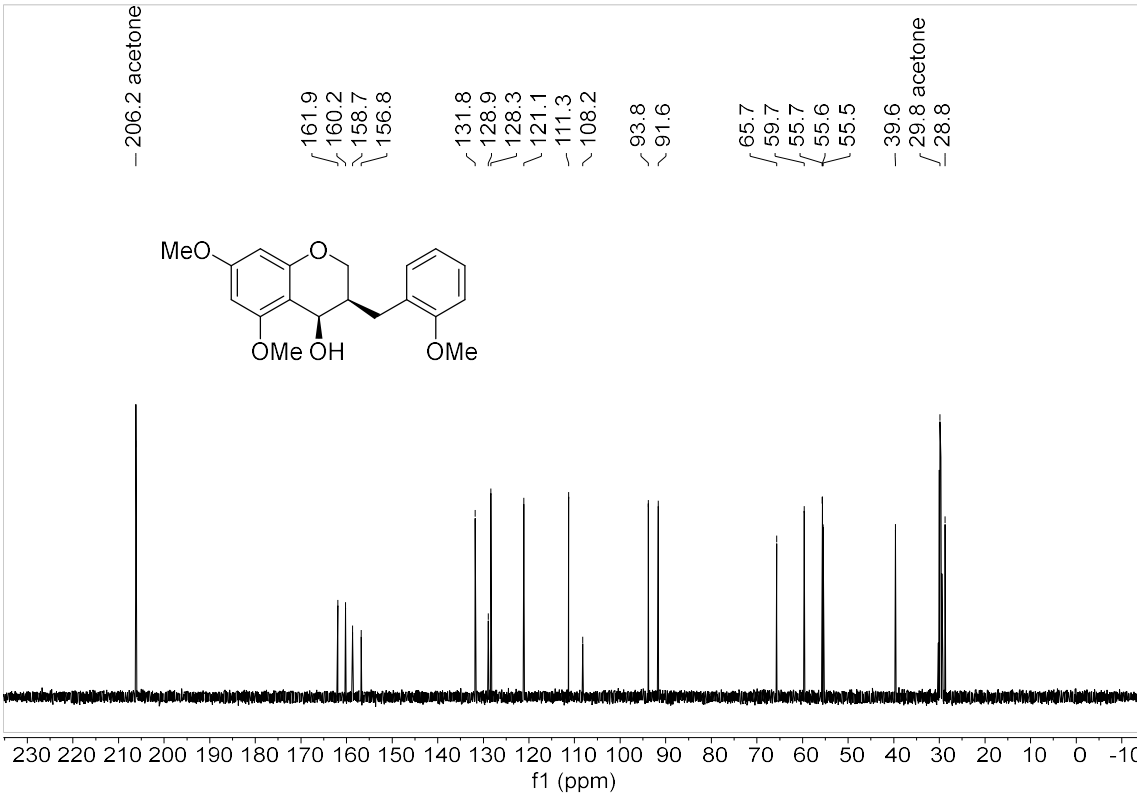
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6f



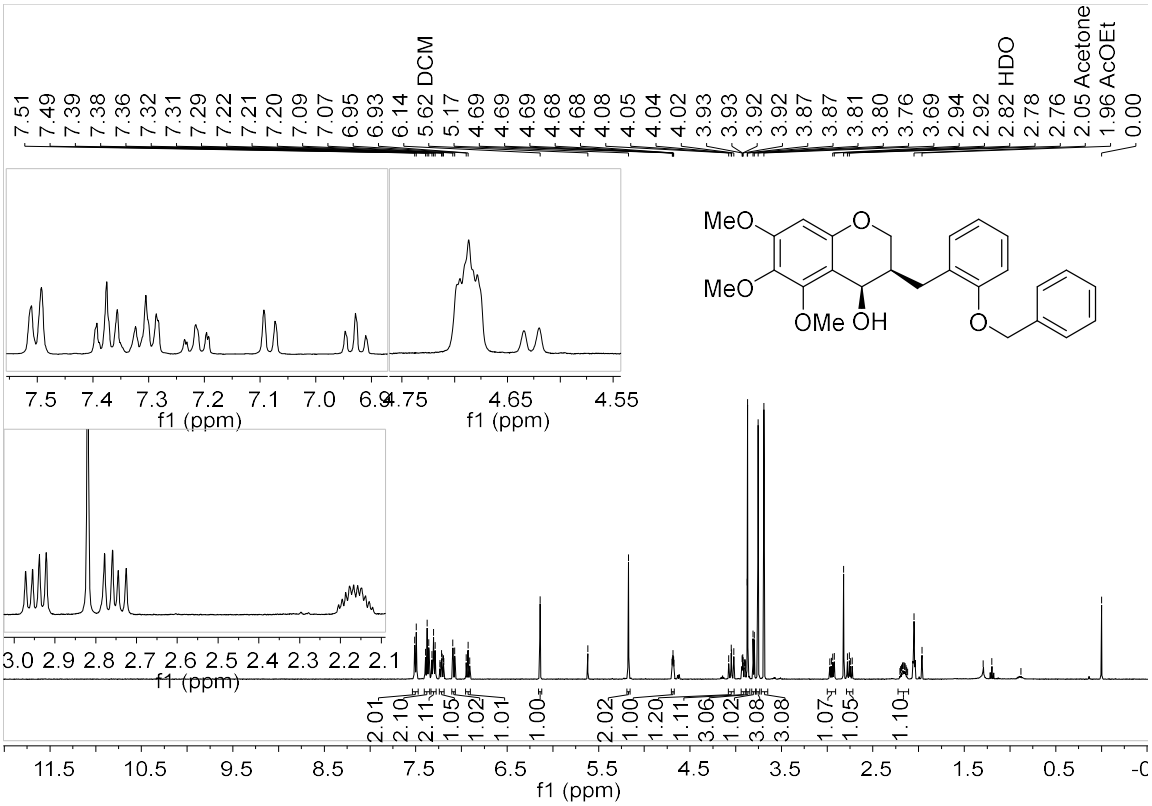
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6g



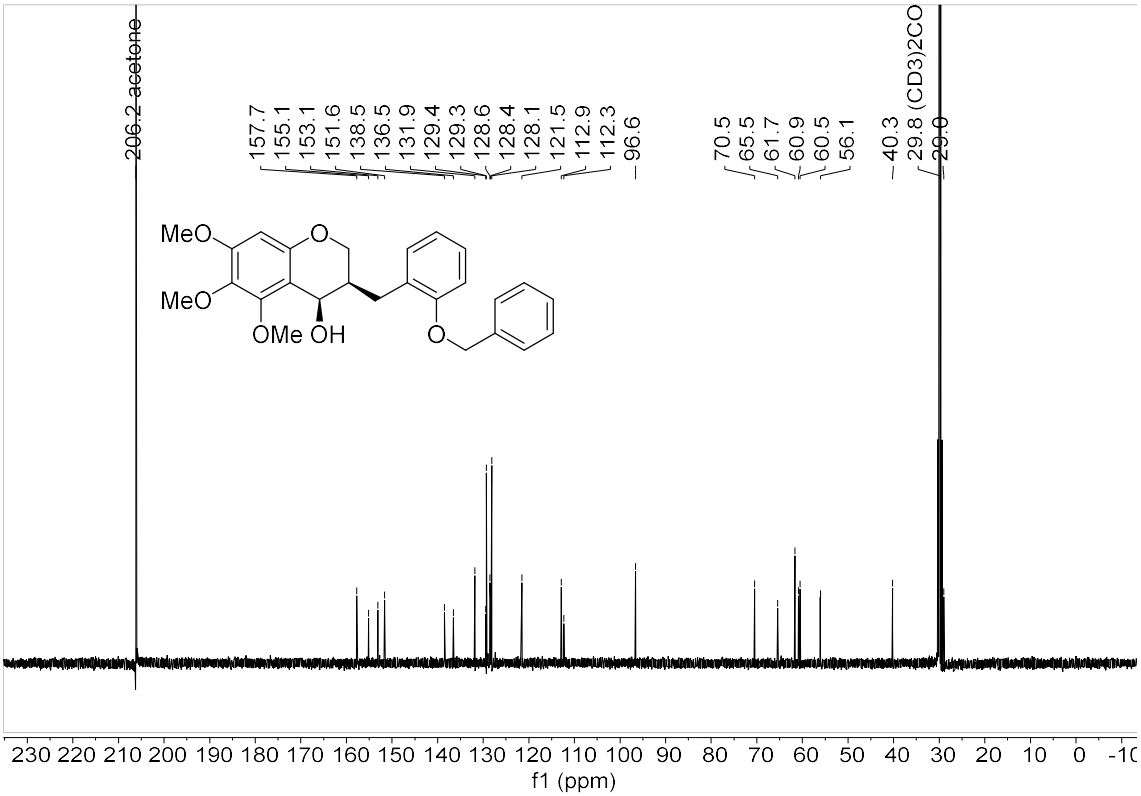
^{13}C NMR (101 MHz, Acetone-d_6) spectrum of 6g



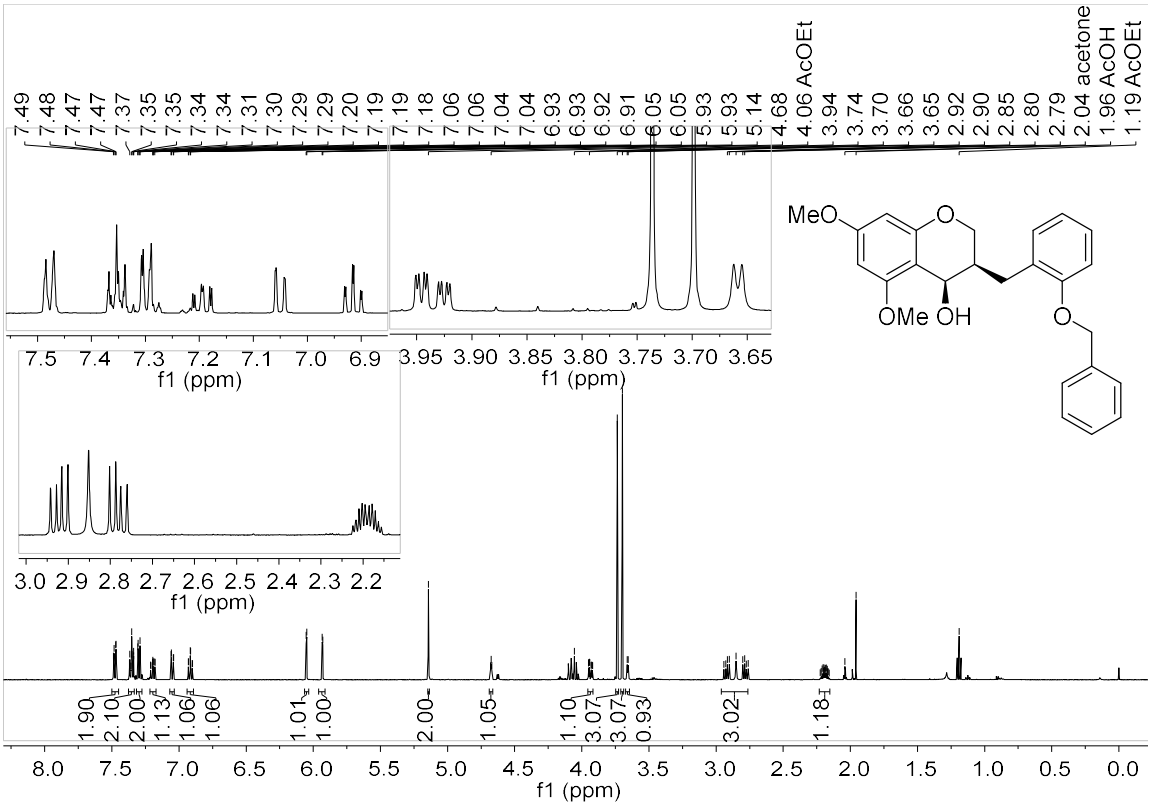
^{1}H NMR (400 MHz, Acetone-d_6) spectrum of 7c



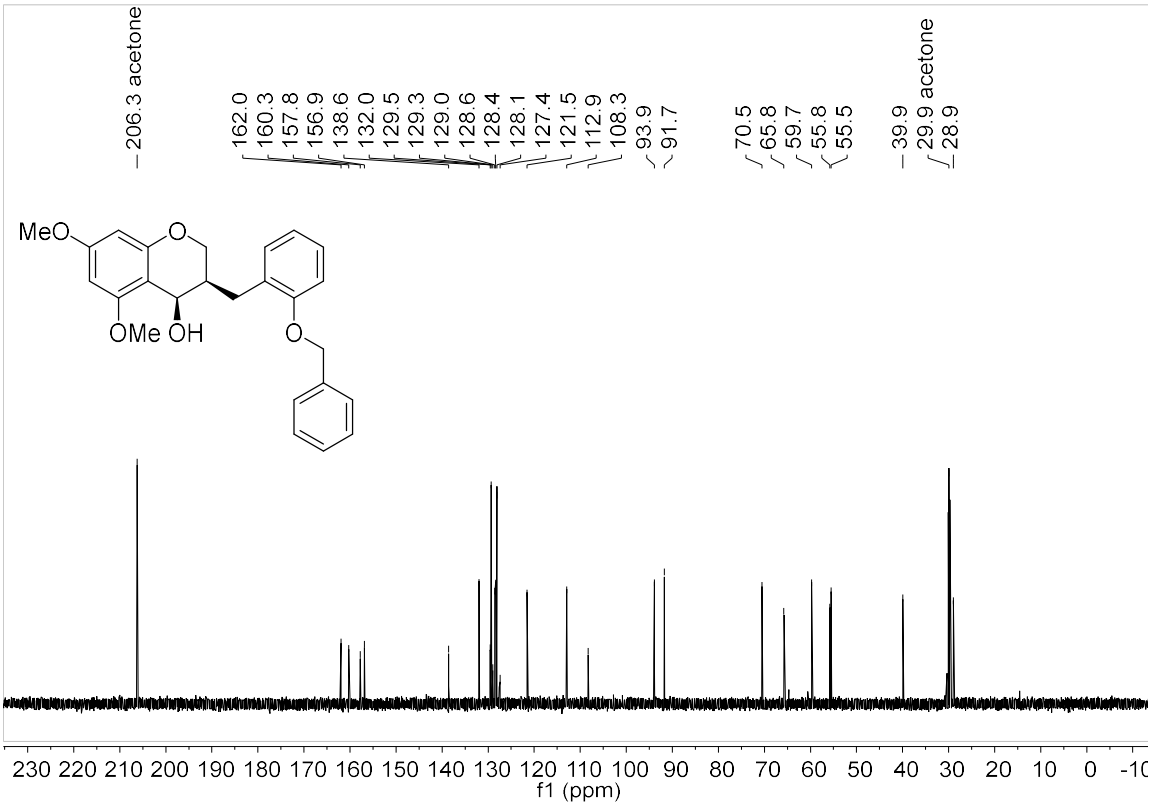
^{13}C NMR (126 MHz, Acetone-d_6) spectrum of 7c



^{1}H NMR (500 MHz, Acetone-*d*) spectrum of 7f

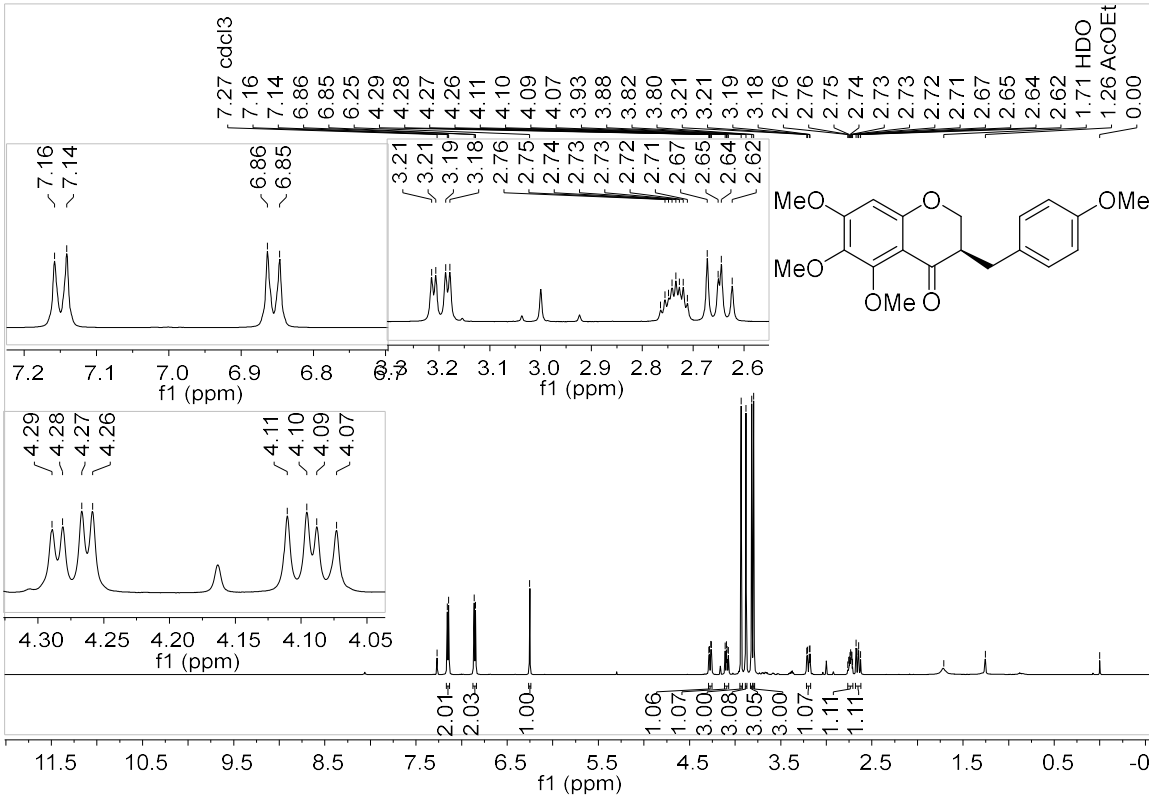


^{13}C NMR (126 MHz, Acetone-*d*) spectrum of 7f

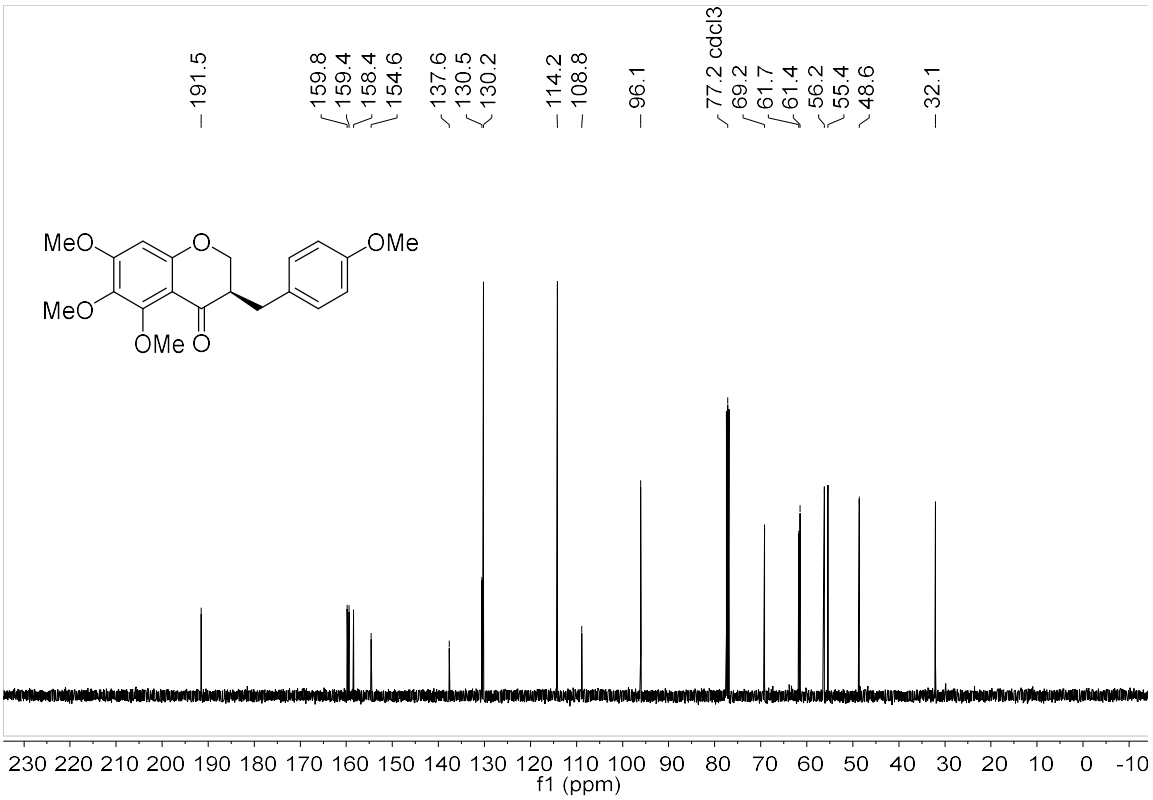


NMR Spectra of the (R)-3-benzylchroman-4-one (1a-d, 8c,f)

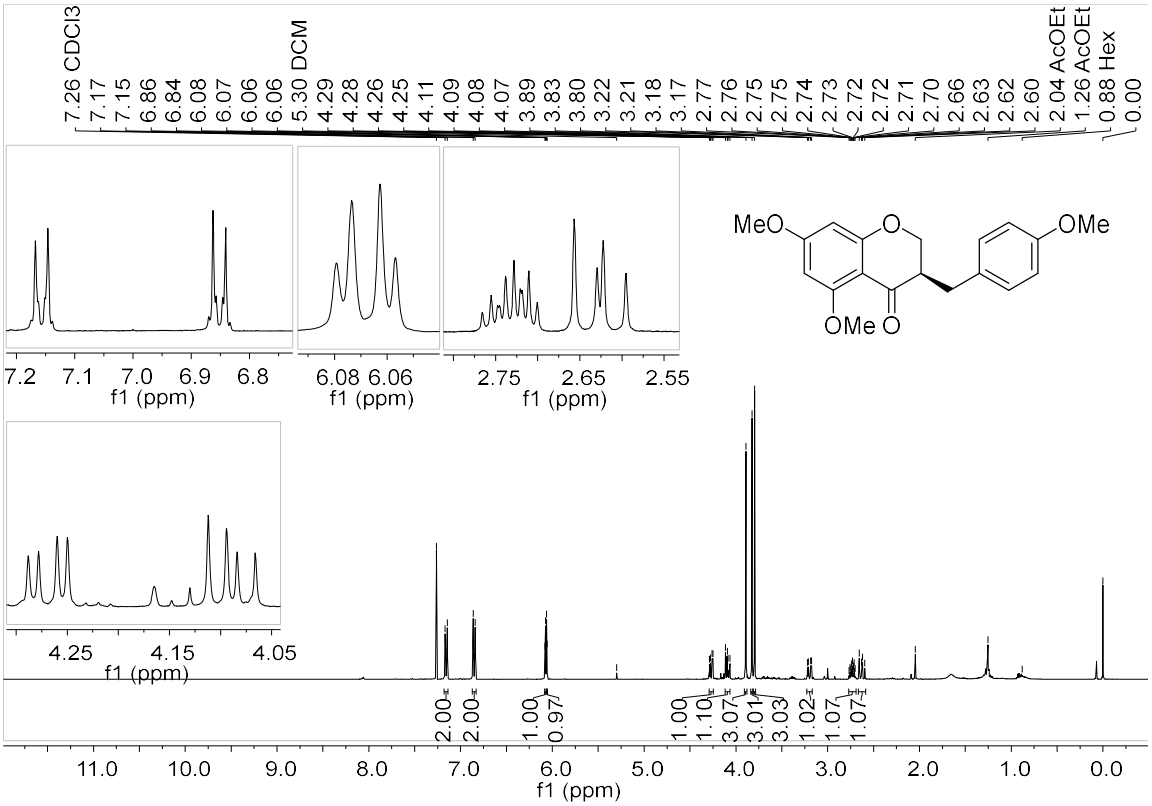
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1a



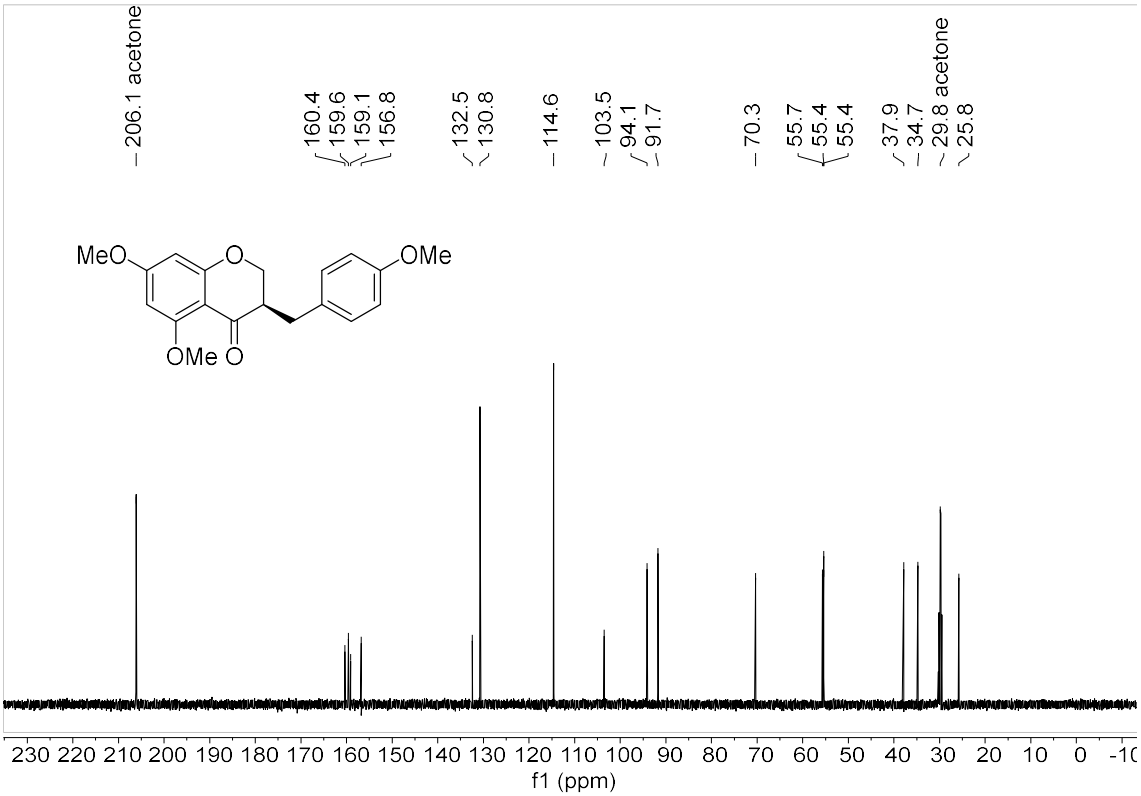
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1a



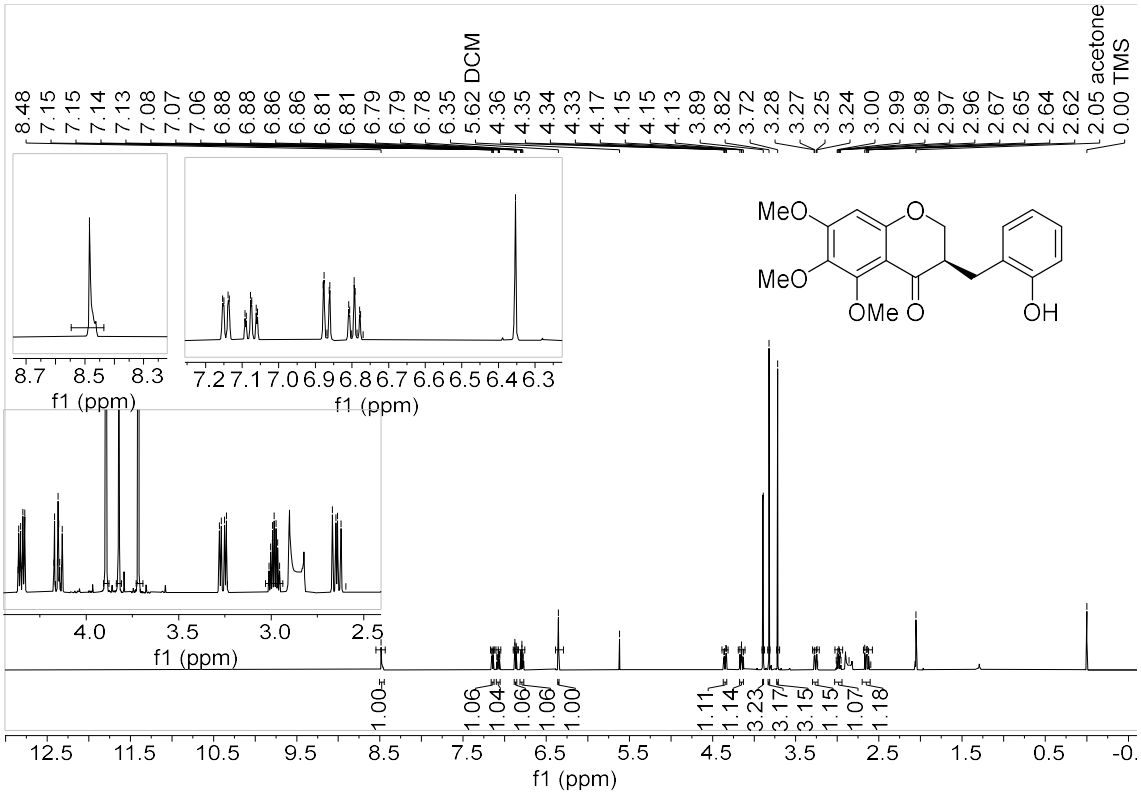
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1b



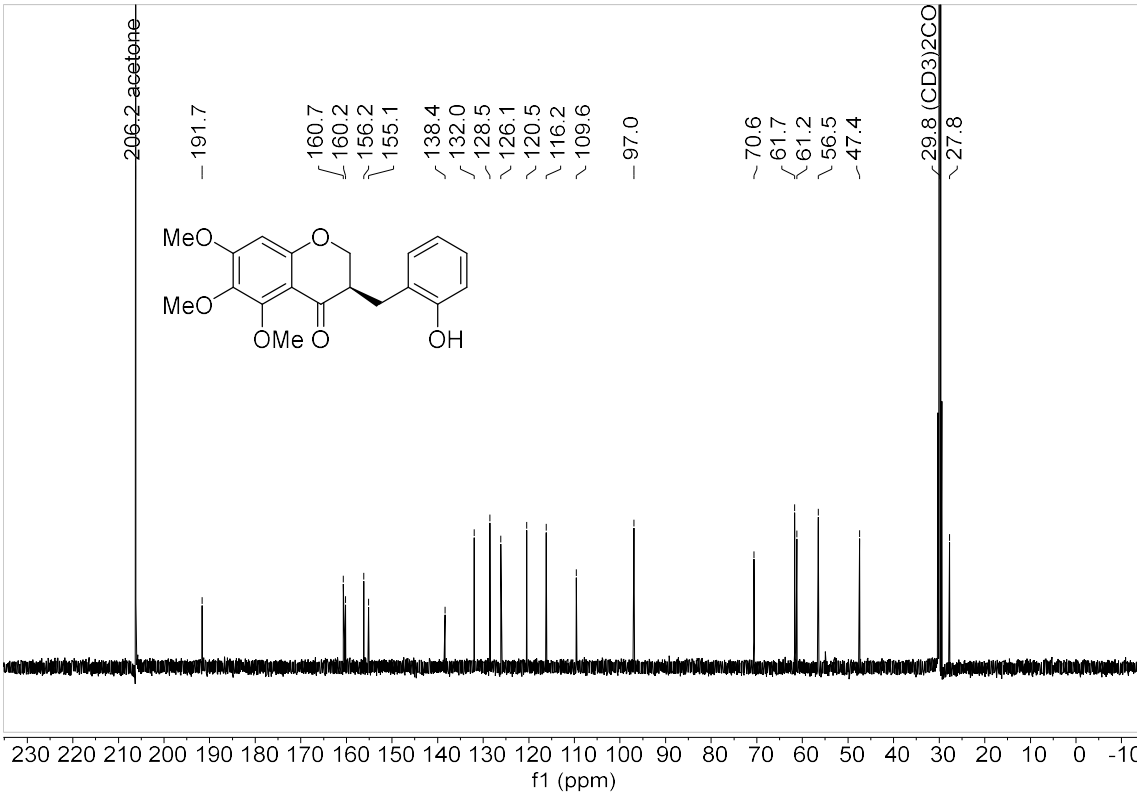
^{13}C NMR (126 MHz, acetone-d_6) spectrum of 1b



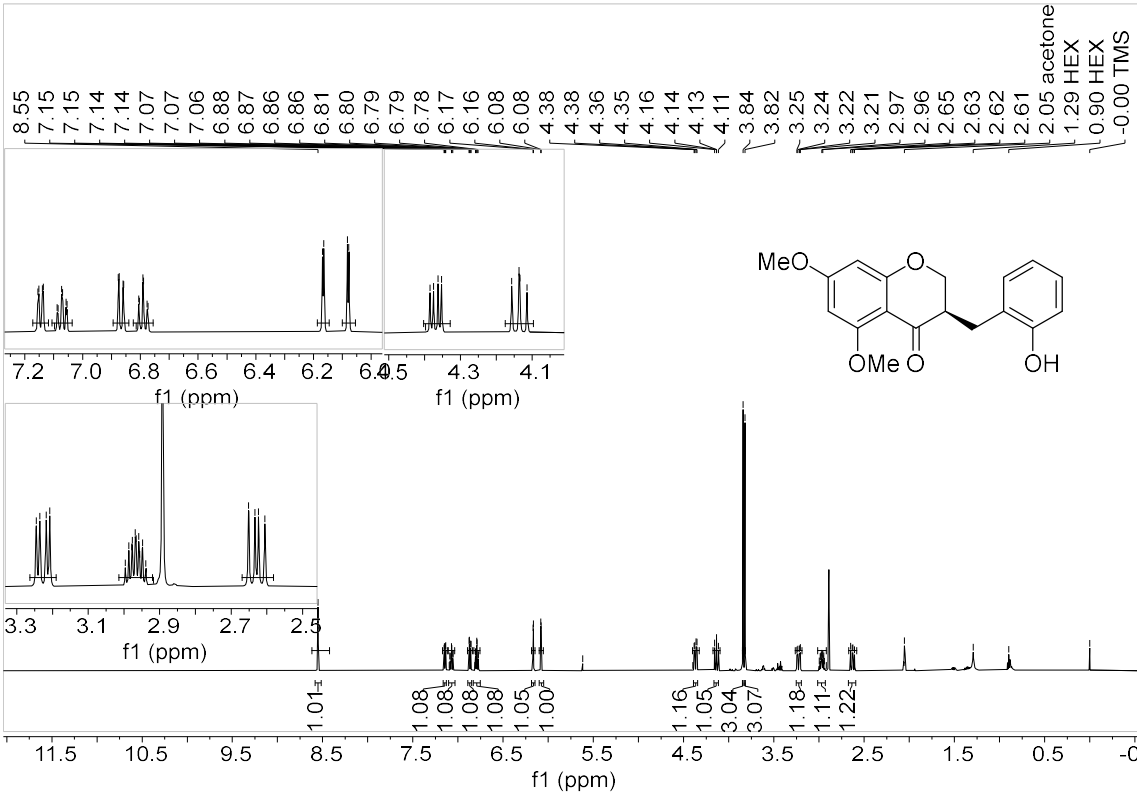
^{1}H NMR (500 MHz, Acetone-d_6) spectrum of 1c



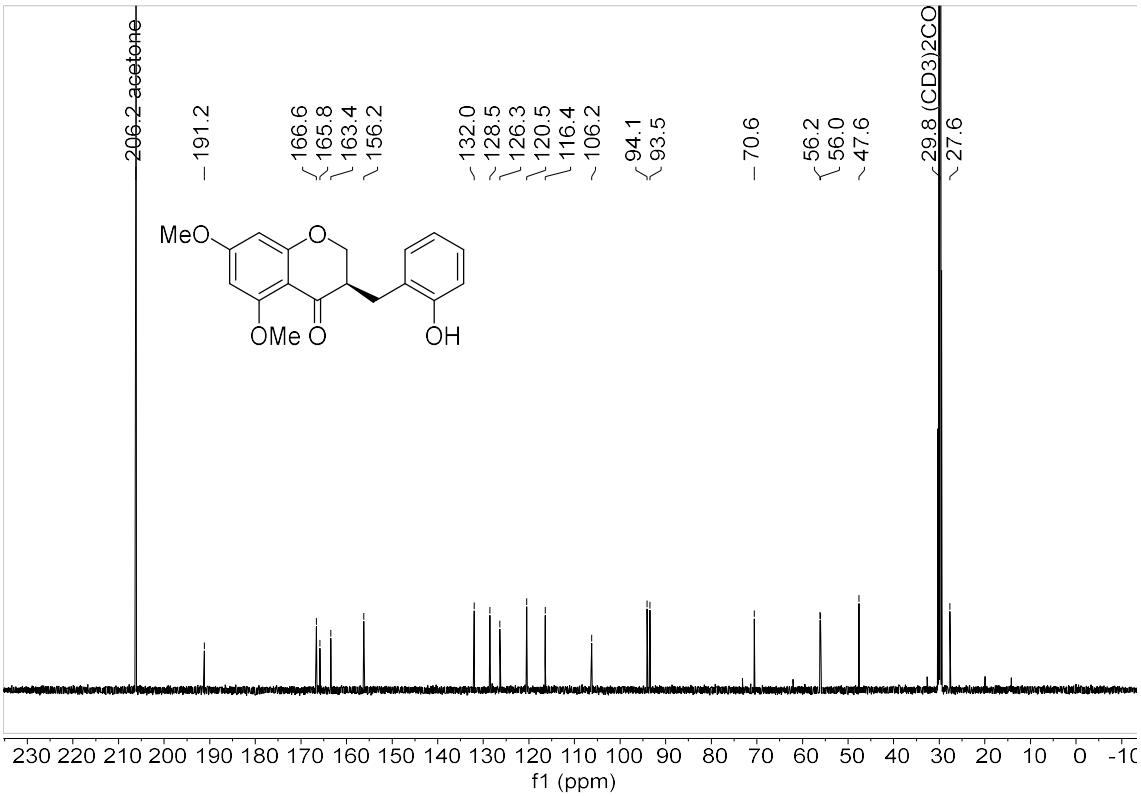
^{13}C NMR (126 MHz, Acetone-d_6) spectrum of 1c



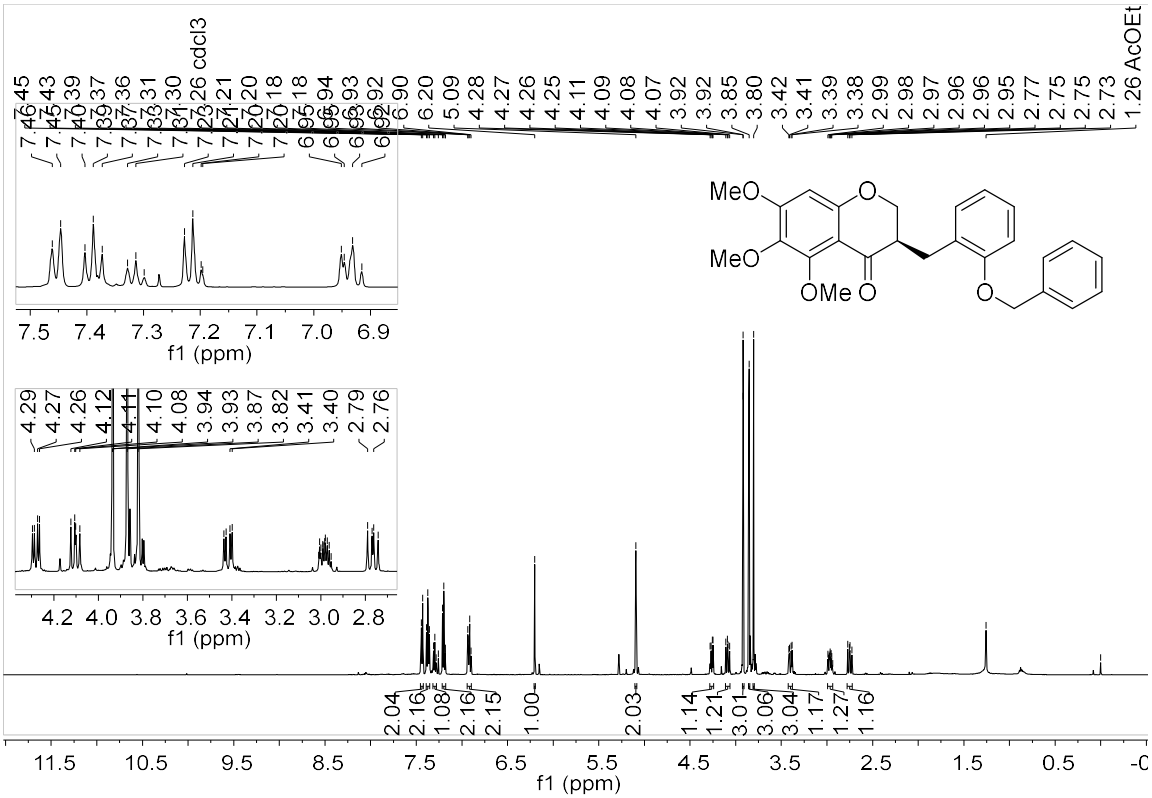
^{1}H NMR (500 MHz, Acetone-d_6) spectrum of 1d



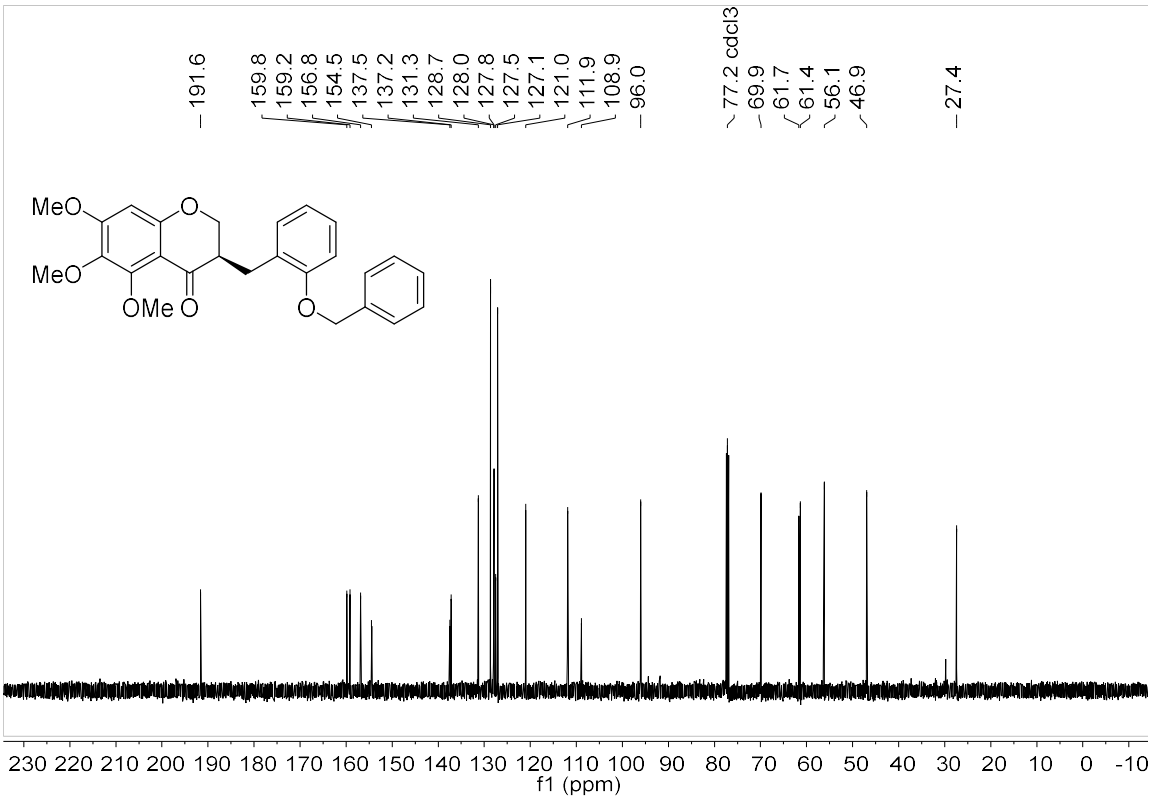
^{13}C NMR (126 MHz, Acetone-d_6) spectrum of 1d



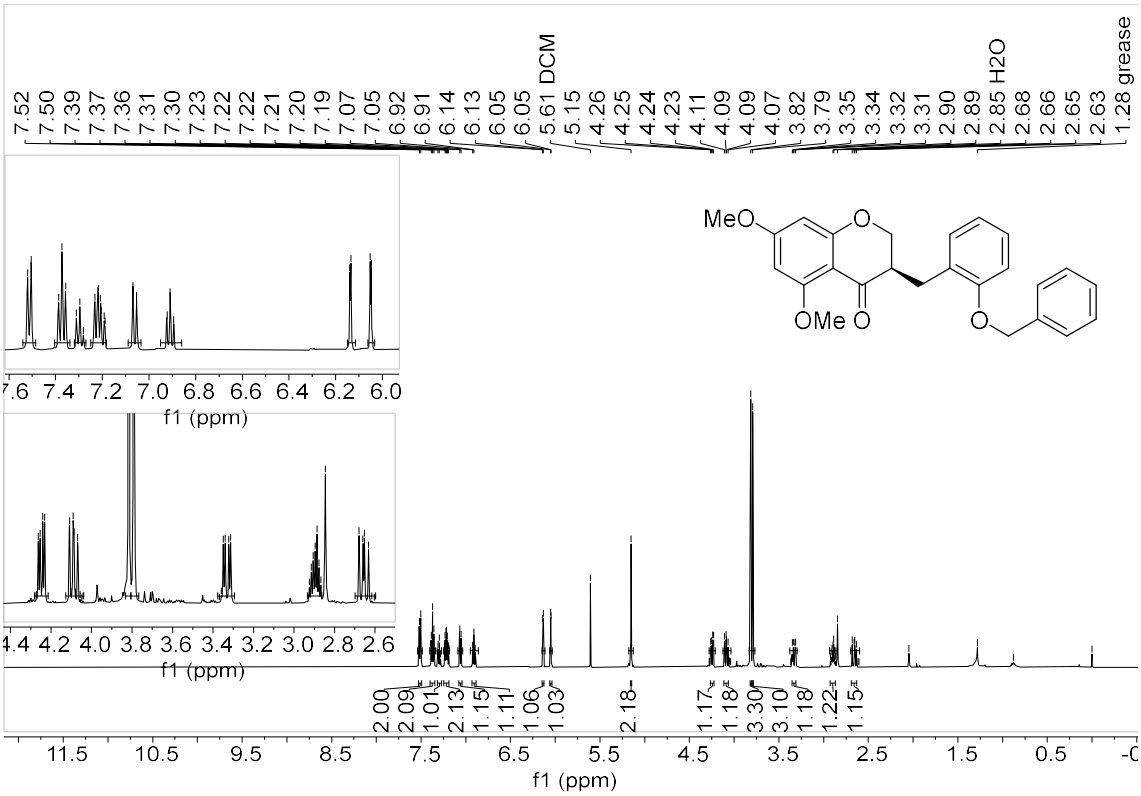
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 8c



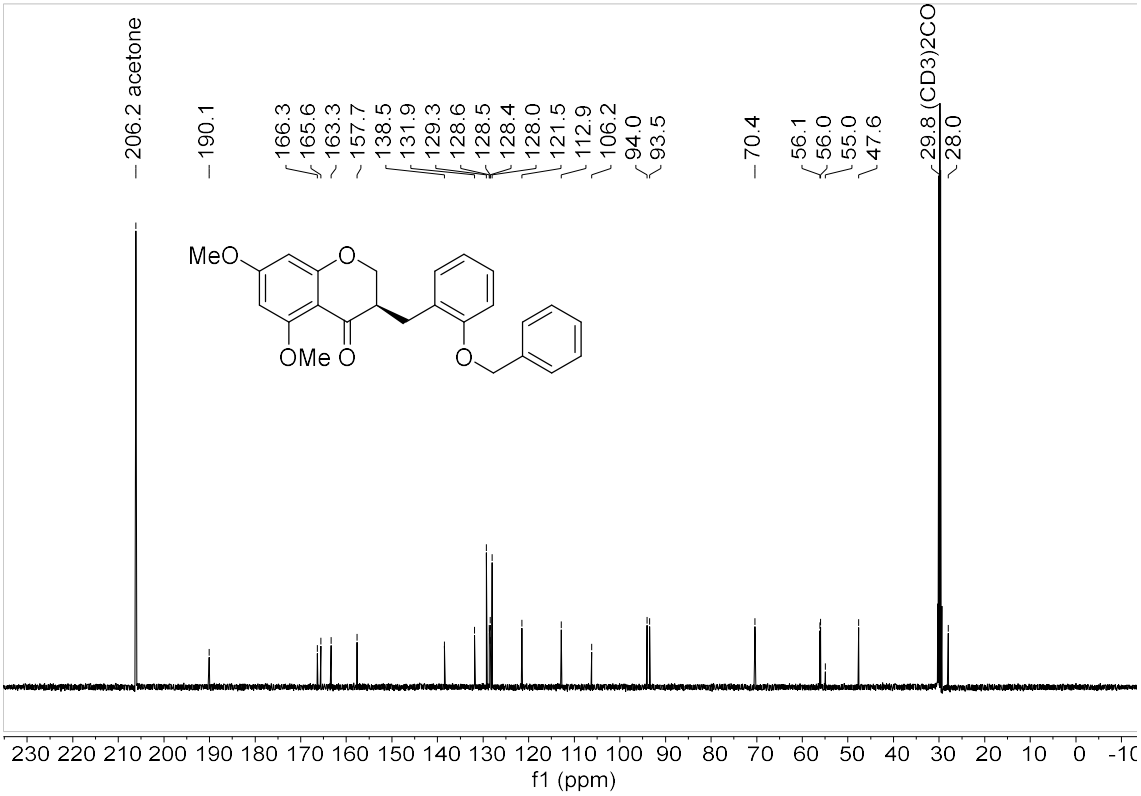
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 8c



^{1}H NMR (500 MHz, Acetone-d_6) spectrum of 8f

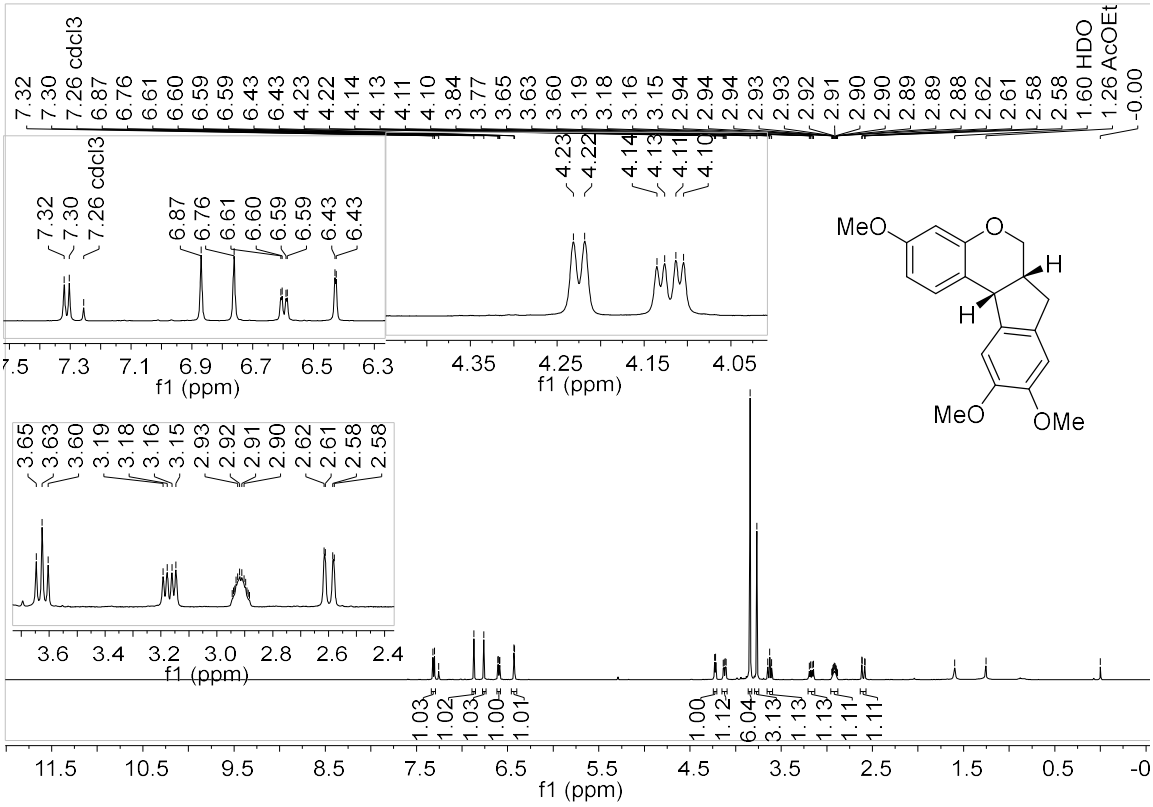


^{13}C NMR (126 MHz, Acetone-d_6) spectrum of 8f

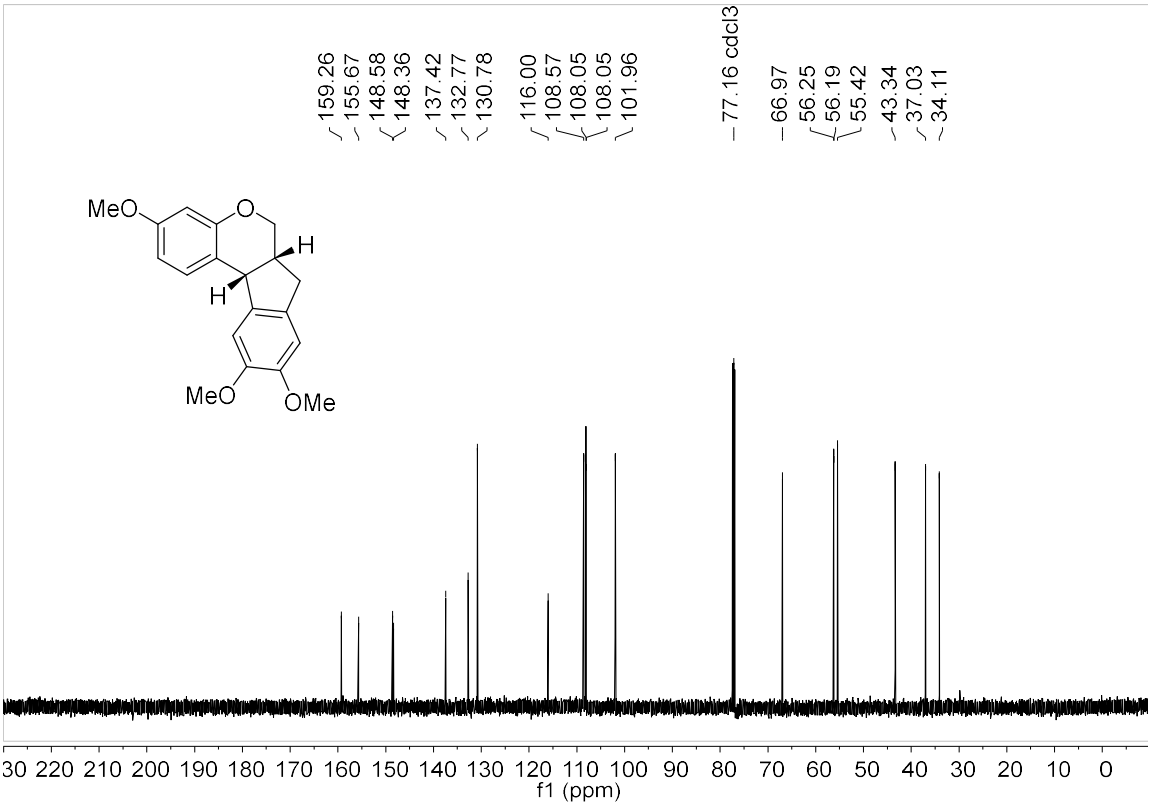


NMR Spectra of the (6aR,11bR)-3,9,10-trimethoxy-brazilane (9a)

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 9a

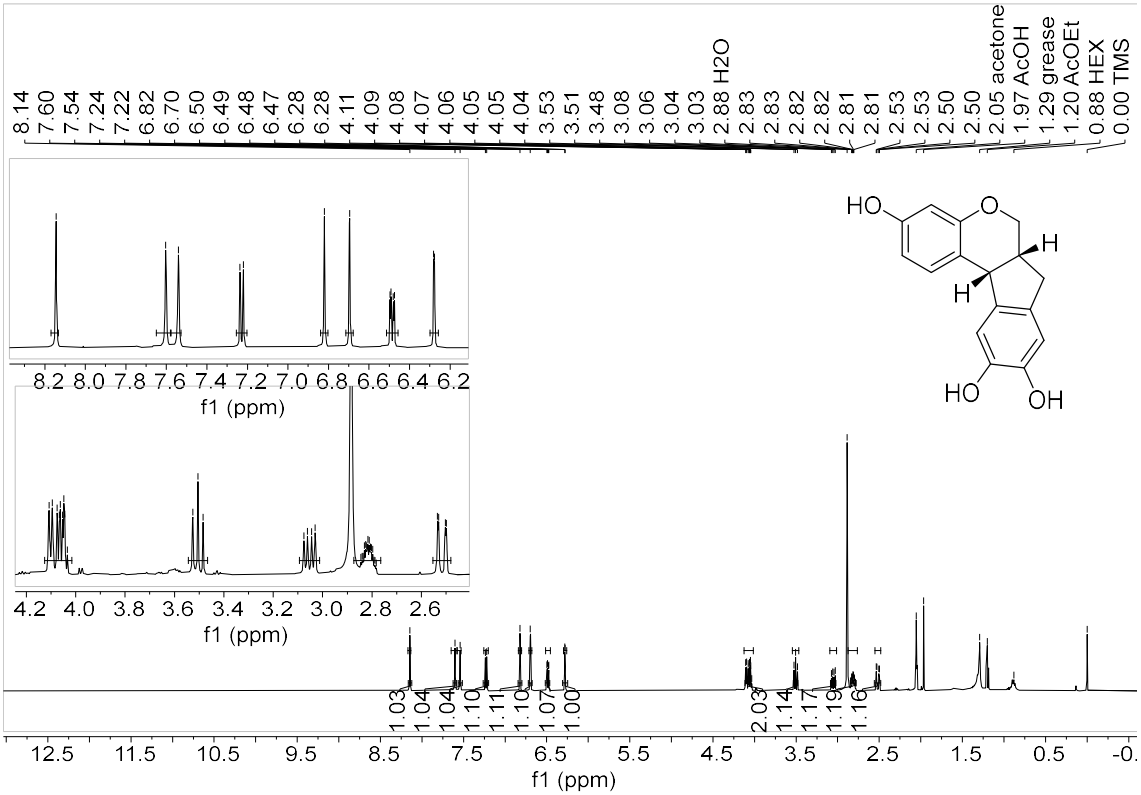


^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 9a

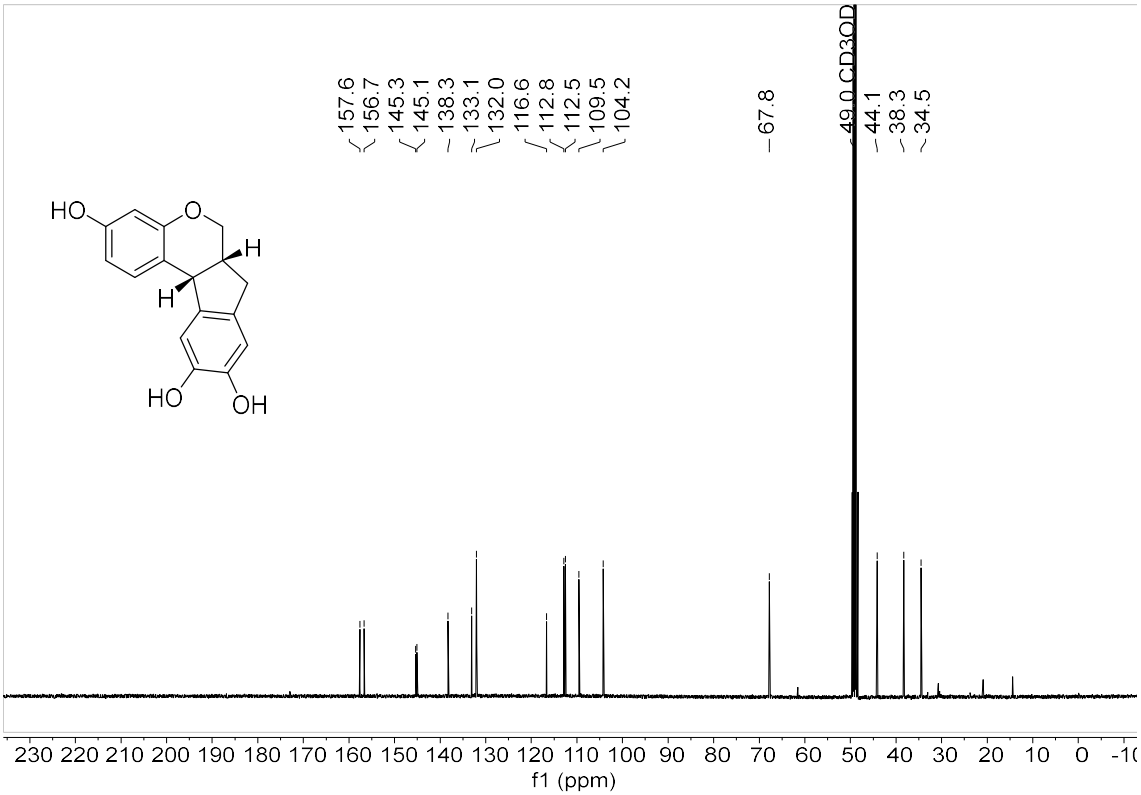


NMR Spectra of the (6aR,11bR)- brazilane (2)

^{1}H NMR (500 MHz, Acetone-d_6) spectrum of 2

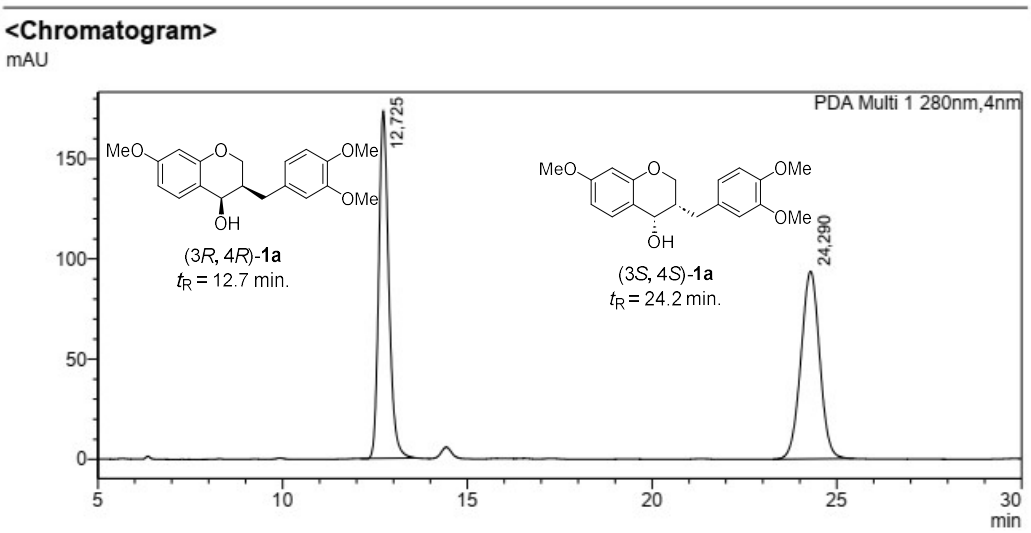


^{13}C NMR (126 MHz, Methanol-d_4) spectrum of 2



HPLC Chromatograms of the 3-benzylchroman-4-ol (6a-g, 7c,f)

HPLC Chromatogram of (rac)-6a

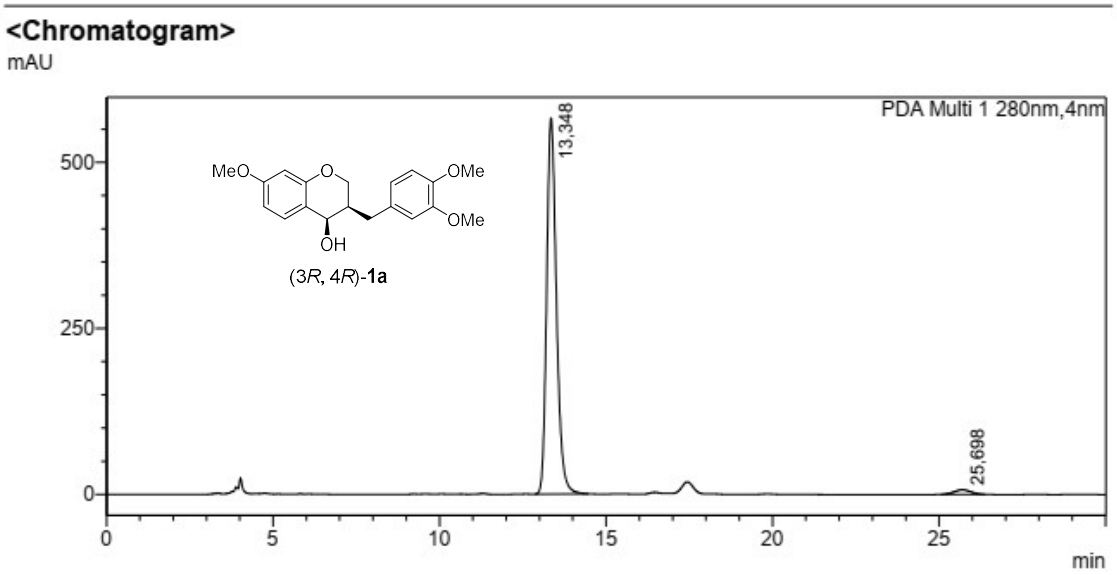


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Area%
1	12,725	3258062	173098	49,680
2	24,290	3300084	93646	50,320
Total		6558146	266744	100,000

HPLC Chromatogram of (3*R*,4*R*)-6a



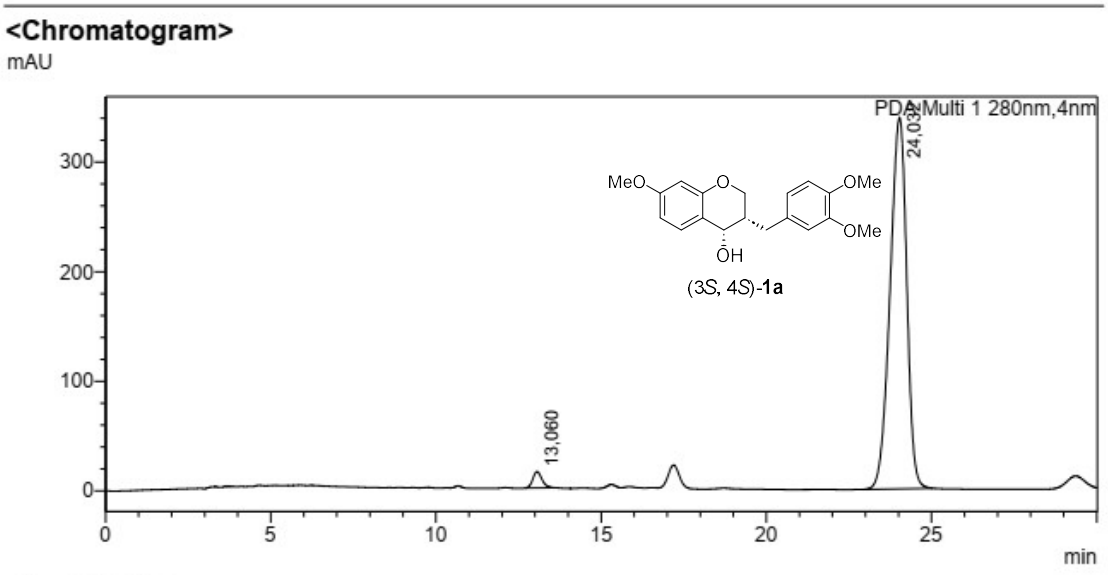
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13,348	11520469	565590	98,801	97,927
2	25,698	243862	6866	1,199	2,073
Total		11764331	572455	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 80:20, 1 mL/min, 28 ºC, t_{Rmaj}: 13.3 min, t_{Rmin}: 25.6 min, 280 nm.

HPLC Chromatogram of (3*S*,4*S*)-6a



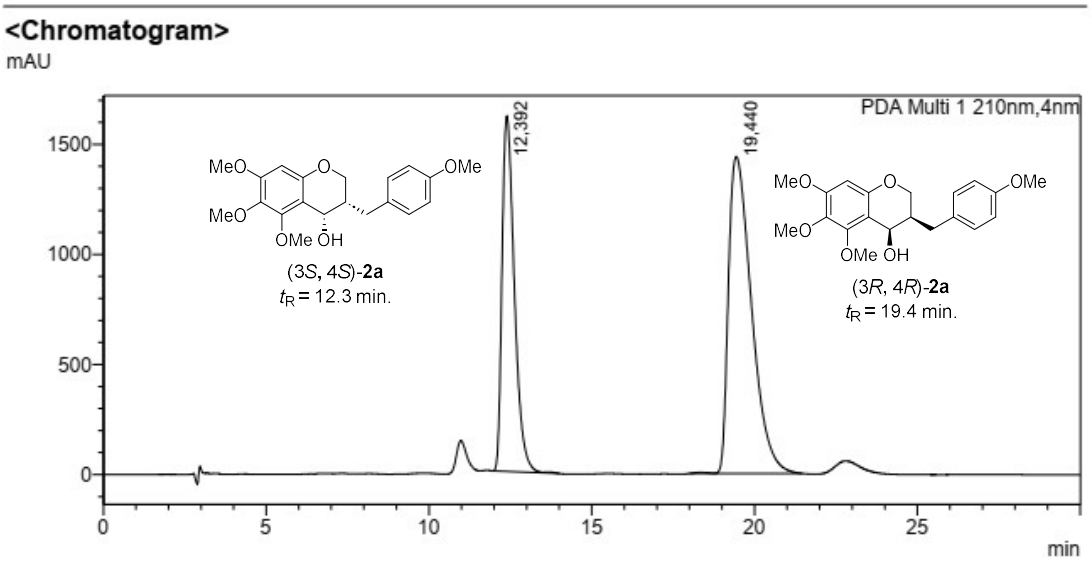
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13,060	287910	14971	4,232	2,367
2	24,032	11873874	338753	95,768	97,633
Total		12161784	353723	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 80:20, 1 mL/min, 28 ºC, t_{Rmaj}: 24.0 min, t_{Rmin}: 13.0 min, 280 nm.

HPLC Chromatogram of (rac)-6b

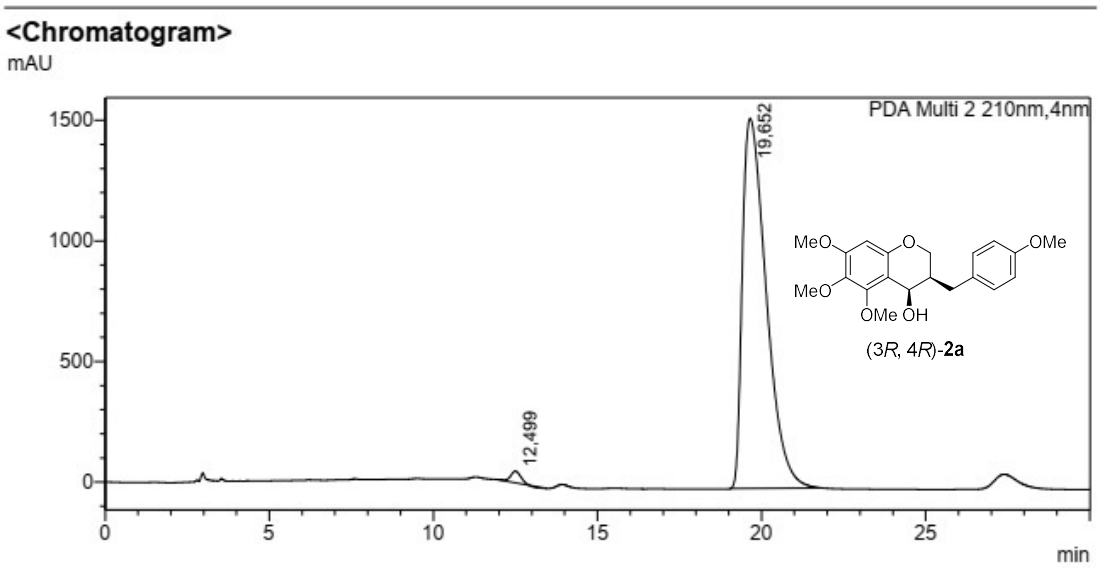


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12,392	42516216	1613424	52,845	37,514
2	19,440	70816876	1439678	47,155	62,486
Total		113333092	3053103	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-6b



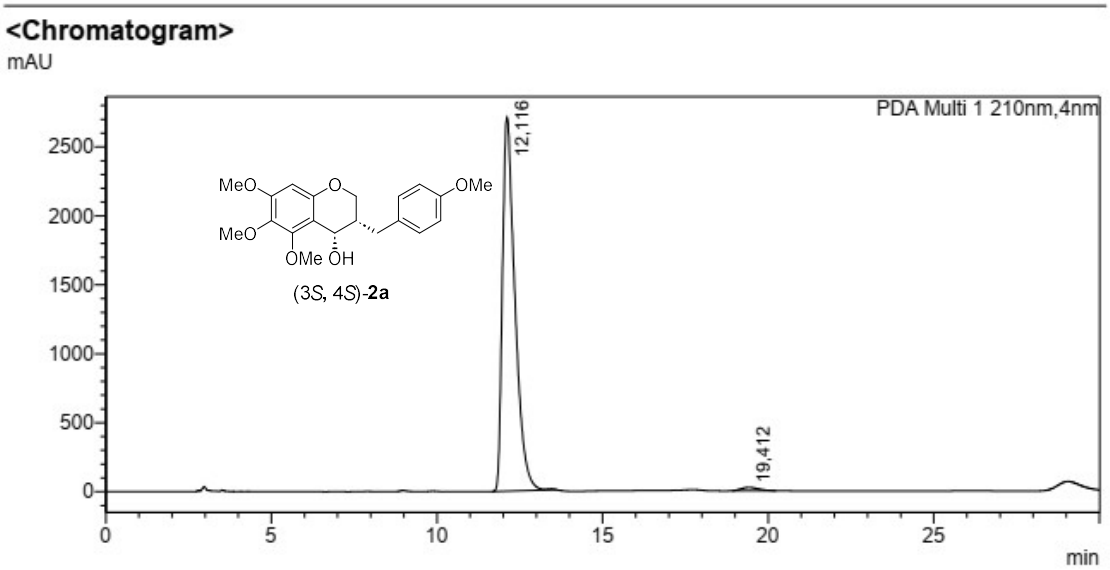
<Peak Table>

PDA Ch2 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12,499	951514	48268	3,049	1,214
2	19,652	77458338	1534888	96,951	98,786
Total		78409852	1583157	100,000	100,000

HPLC method: Chiralpack Celulose column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 19.6 min, t_{Rmin}: 12.4 min, 210 nm.

HPLC Chromatogram of (3*S*,4*S*)-6b



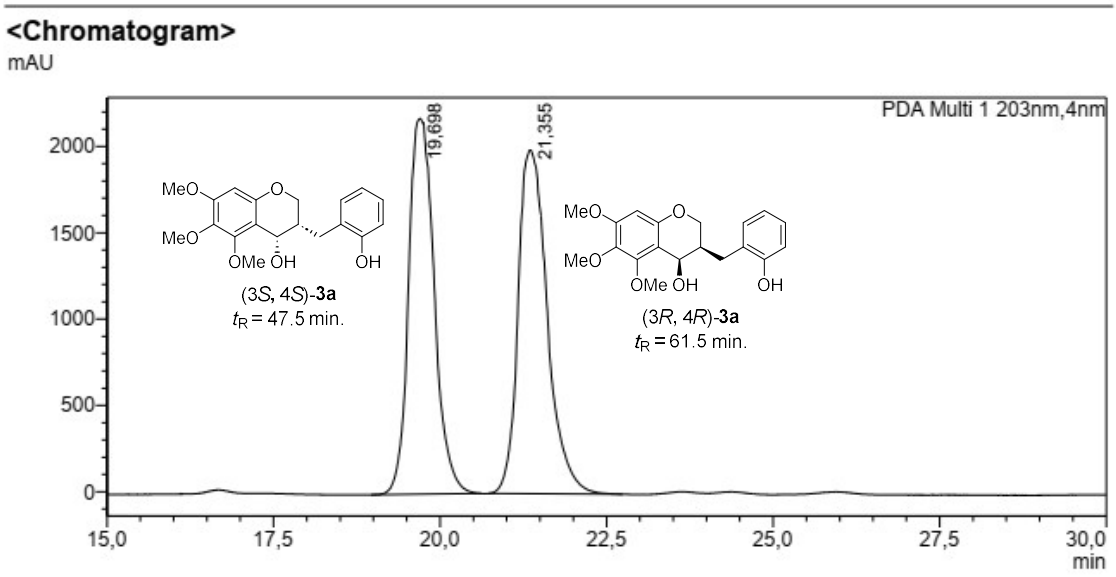
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12,116	71055162	2708758	99,123	98,803
2	19,412	860533	23953	0,877	1,197
Total		71915695	2732711	100,000	100,000

HPLC method: Chiralpack Celulose column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 12.1 min, t_{Rmin}: 19.4 min, 210 nm.

HPLC Chromatogram of (rac)-6c

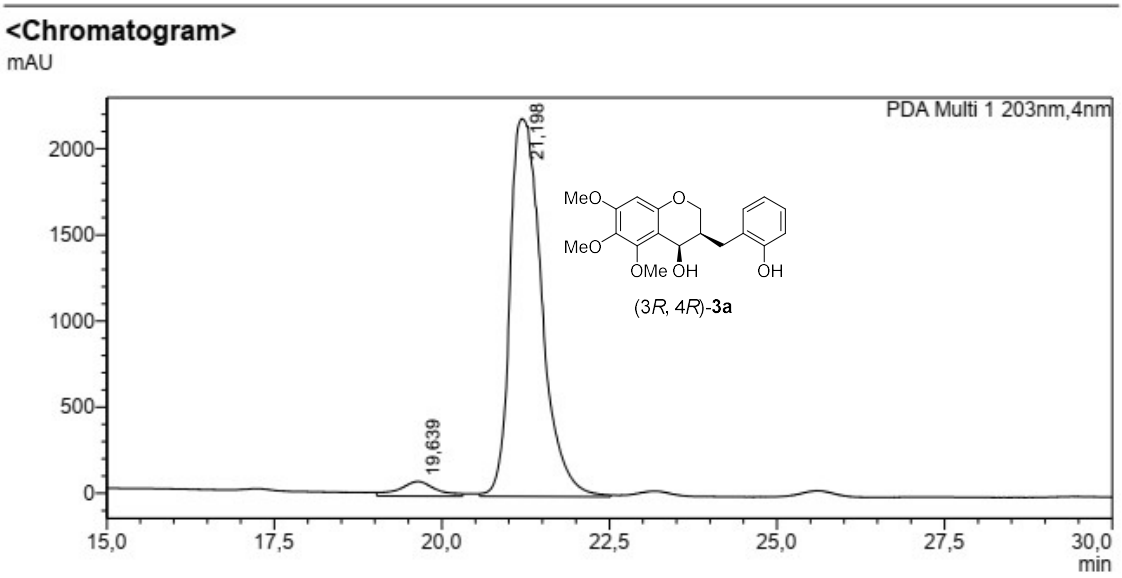


<Peak Table>

PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	19,698	58404618	2174805	52,211	49,027
2	21,355	60722517	1990599	47,789	50,973
Total		119127134	4165404	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-6c



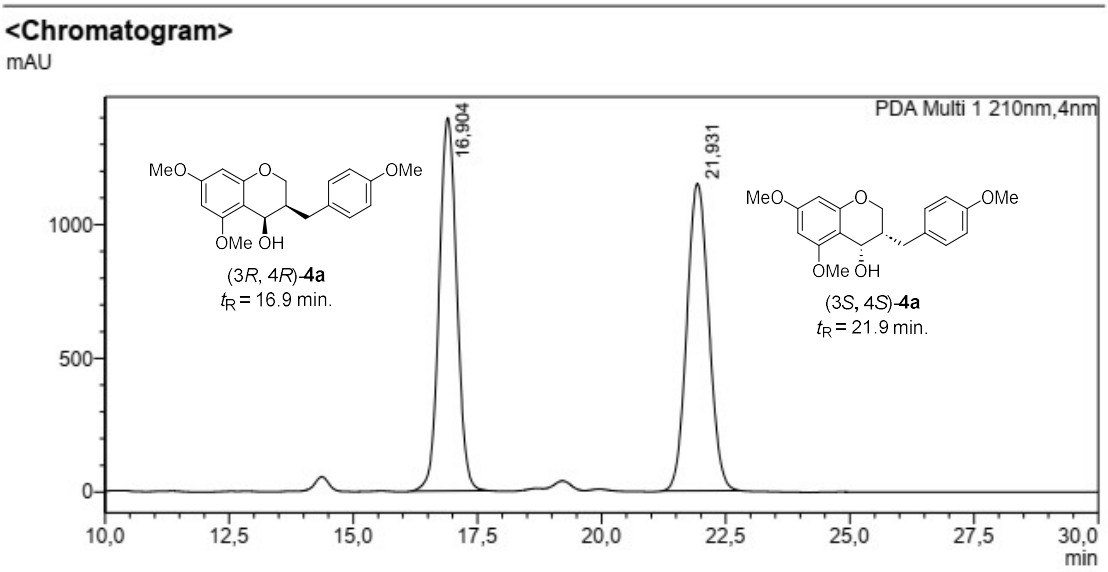
<Peak Table>

PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	19,639	3198346	84633	4,220	3,718
2	21,198	72584852	2191508	95,780	96,282
Total		75783198	2276141	100,000	100,000

HPLC method: Chiralpack IA column, 0.1% DEA, *n*-hexane/EtOH 90:10, 1 mL/min, 28 °C, t_{Rmaj} = 21.1 min, t_{Rmin} = 19.6 min, 203 nm

HPLC Chromatogram of (rac)-6d

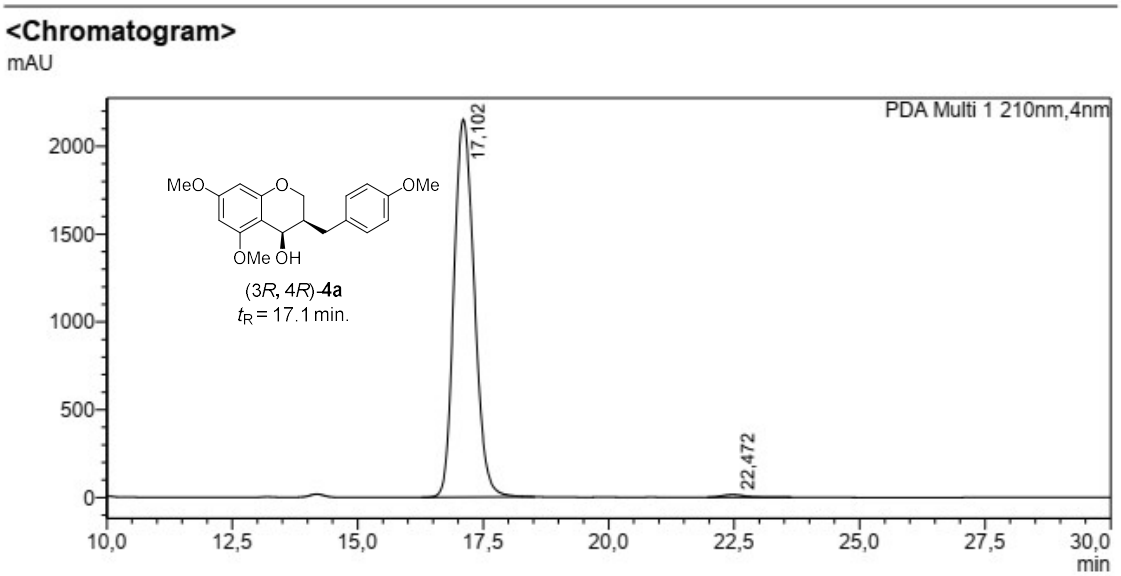


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	16,904	34472857	1395142	54,844	49,391
2	21,931	35323175	1148690	45,156	50,609
Total		69796032	2543832	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-6d



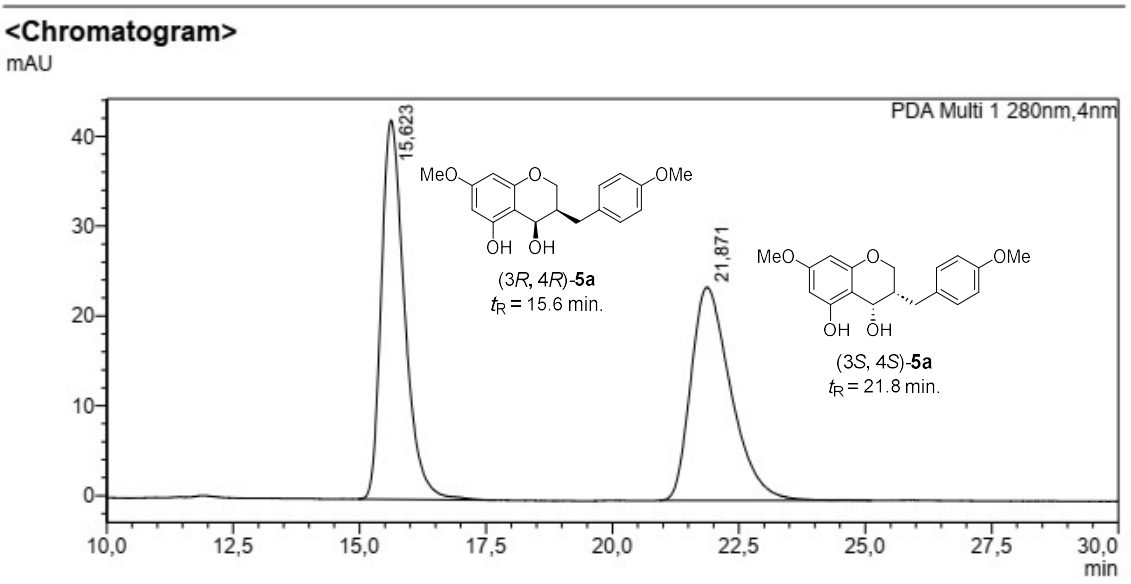
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	17,102	60522297	2151524	99,307	99,170
2	22,472	506449	15020	0,693	0,830
Total		61028746	2166544	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 17.1 min, t_{Rmin}: 22.4 min, 210 nm.

HPLC Chromatogram of (rac)-6e

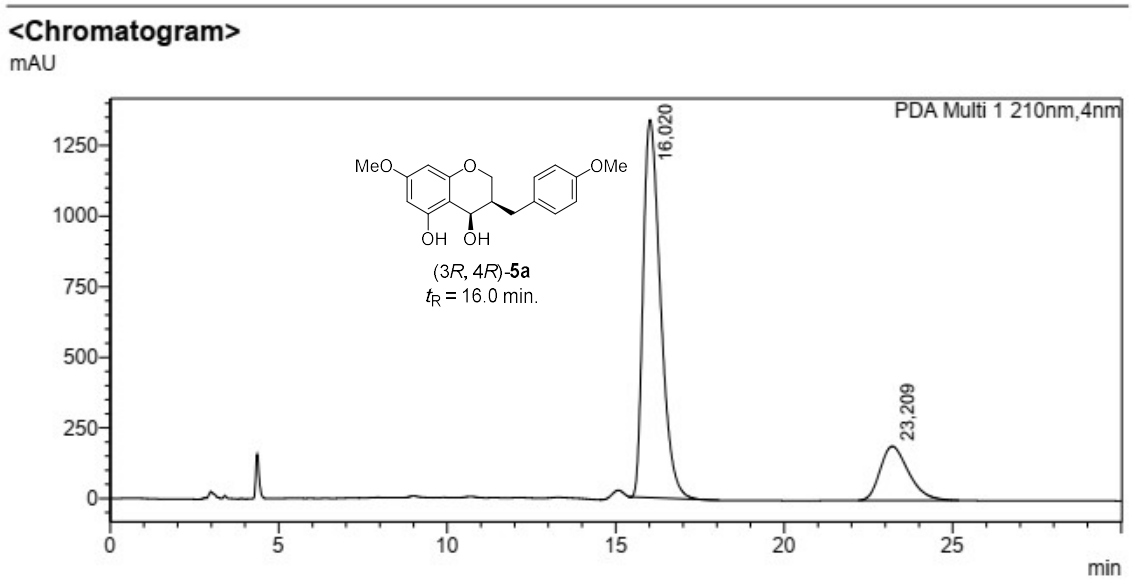


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15,623	1346450	42195	63,991	50,761
2	21,871	1306076	23744	36,009	49,239
Total		2652526	65939	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-6e



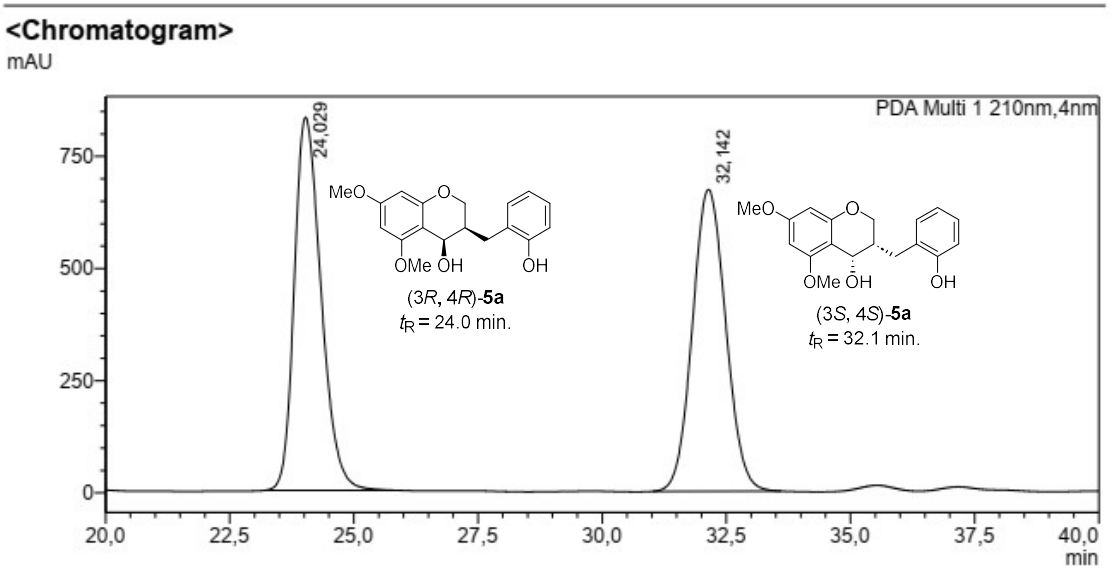
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	16,020	47977255	1338171	87,492	81,070
2	23,209	11202484	191312	12,508	18,930
Total		59179740	1529483	100,000	100,000

HPLC method: Chiralpack Celulose column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 16.0 min, t_{Rmin}: 23.2 min, 210 nm.

HPLC Chromatogram of (rac)-6f

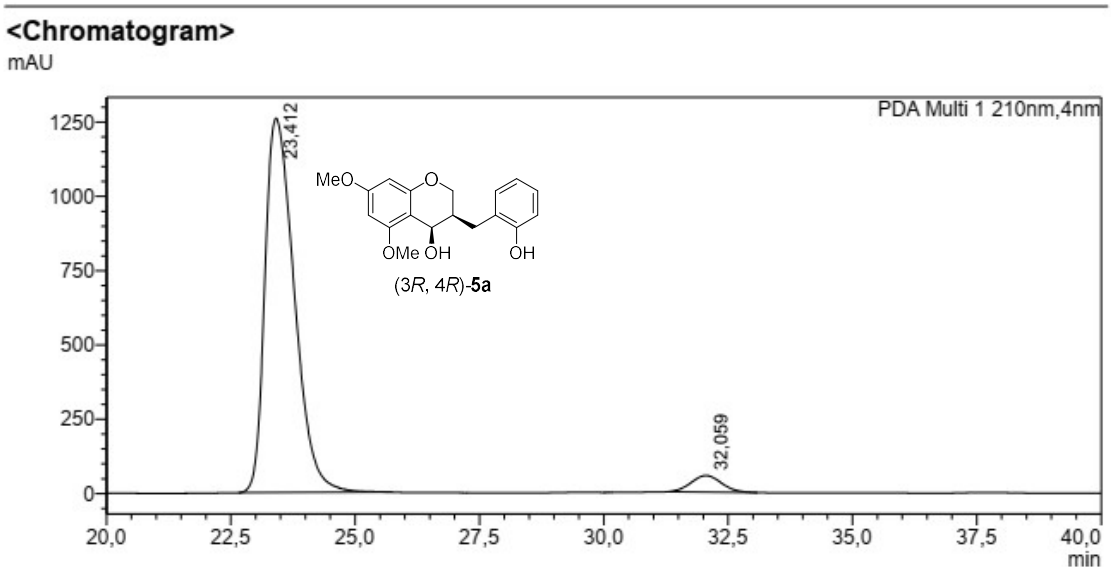


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	24,029	31186555	831277	55,287	49,781
2	32,142	31460616	672301	44,713	50,219
Total		62647171	1503578	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-6f



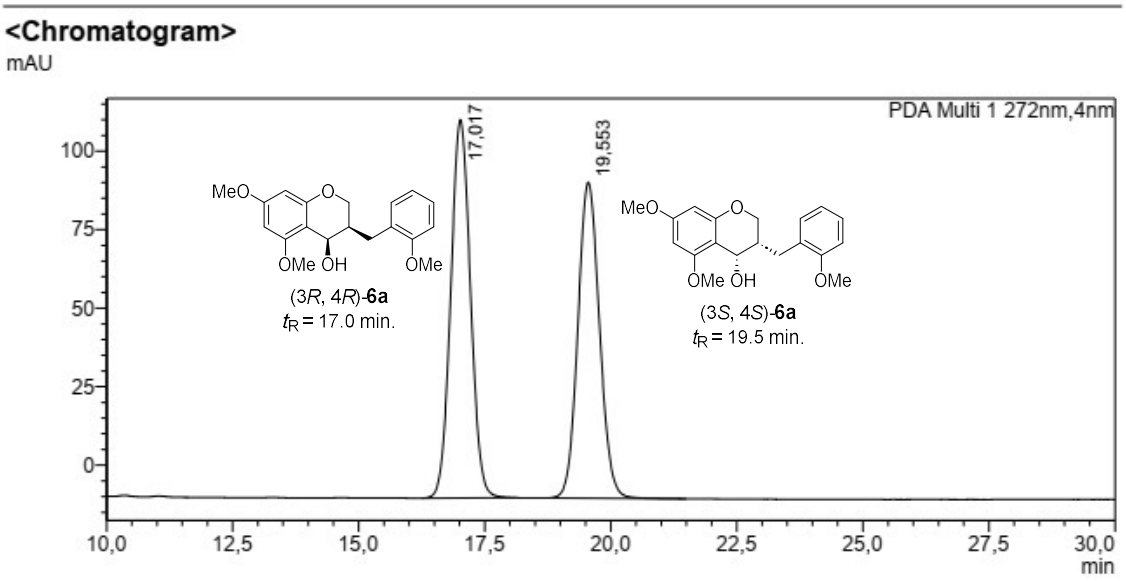
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	23,412	51678781	1259455	95,743	95,567
2	32,059	2397468	56004	4,257	4,433
Total		54076249	1315459	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 90:10, 1 mL/min, 28 ºC, t_{Rmaj}: 24.0 min, t_{Rmin}: 32.1 min, 210 nm.

HPLC Chromatogram of (rac)-6g

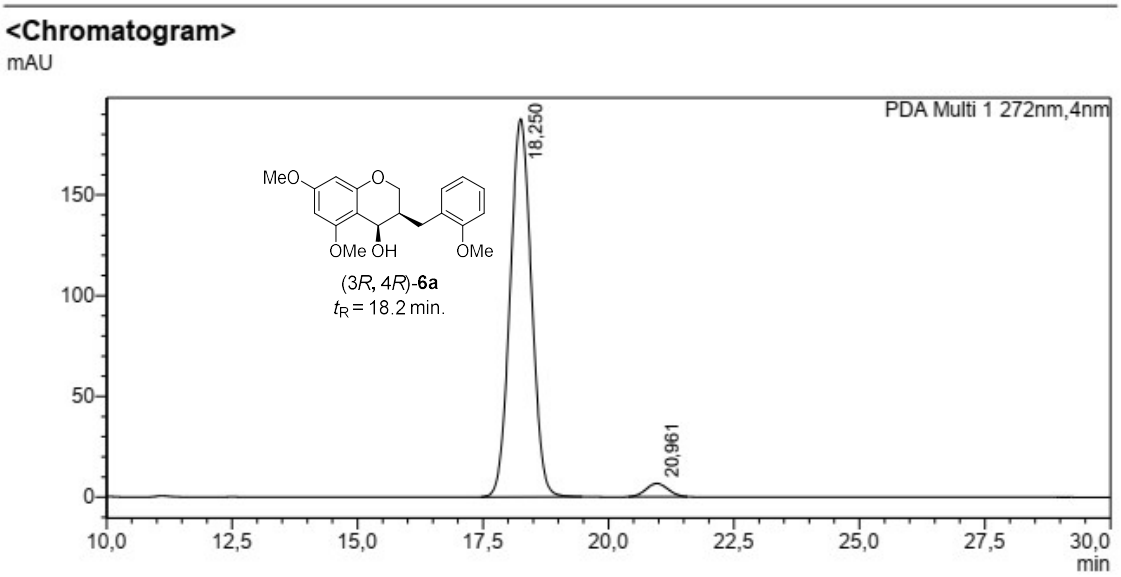


<Peak Table>

PDA Ch1 272nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	17,017	3274026	120449	54,493	52,218
2	19,553	2995846	100588	45,507	47,782
Total		6269871	221037	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-6g



<Peak Table>

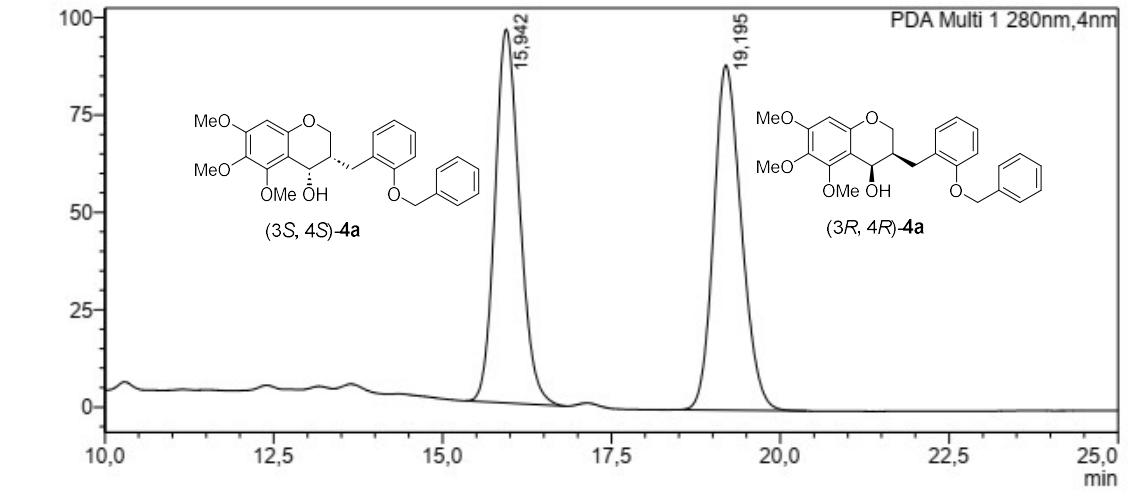
PDA Ch1 272nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	18,250	5544806	187533	96,624	96,530
2	20,961	199346	6553	3,376	3,470
Total		5744152	194086	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 18.2 min, t_{Rmin}: 20.6 min, 272 nm.

HPLC Chromatogram of (rac)-7c

<Chromatogram>



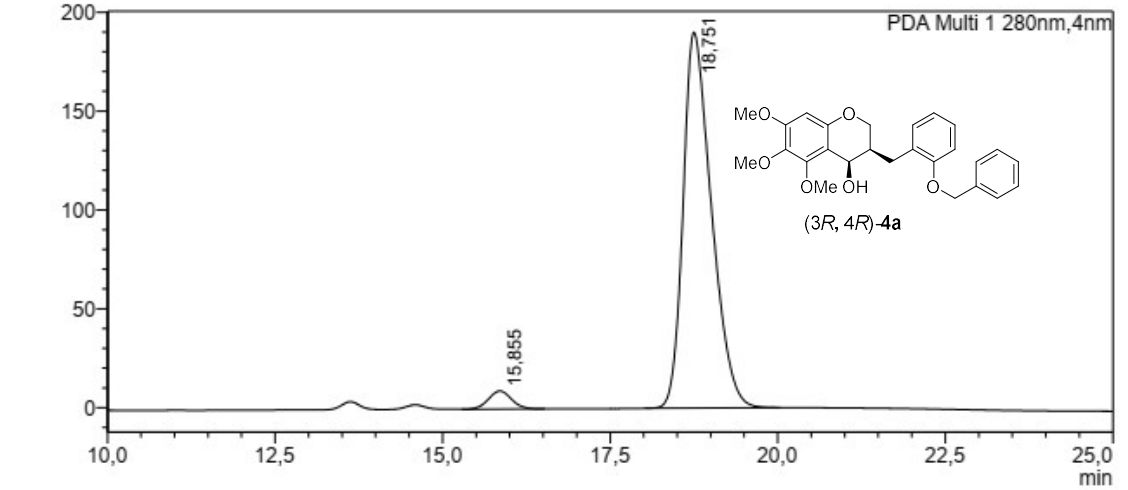
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15,942	2428326	95914	51,988	48,931
2	19,195	2534421	88578	48,012	51,069
Total		4962747	184491	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-7c

<Chromatogram>



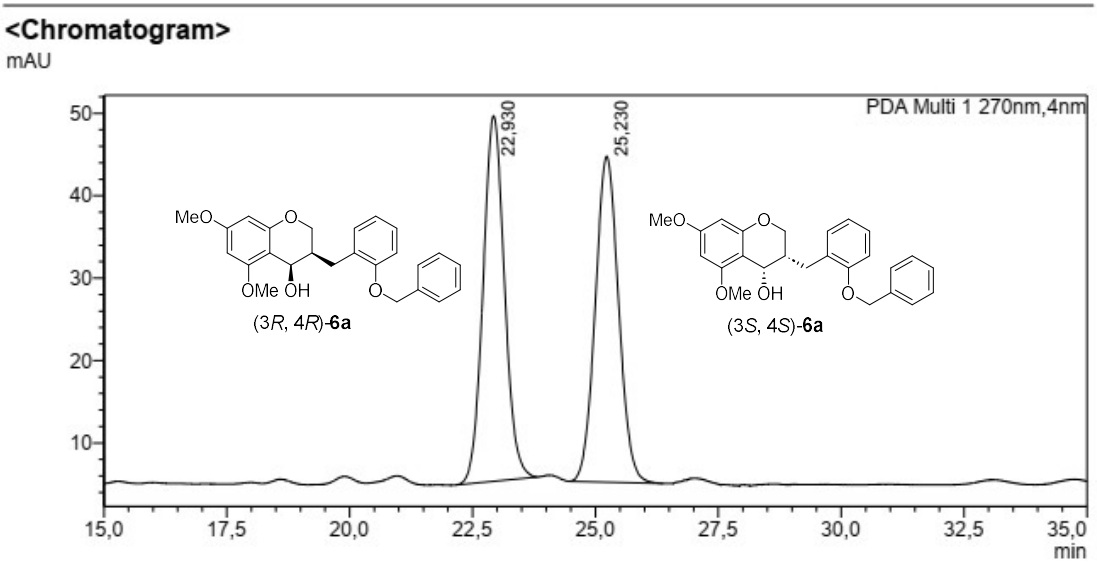
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15,855	220202	9157	4,597	3,790
2	18,751	5589144	190009	95,403	96,210
Total		5809346	199166	100,000	100,000

HPLC method: Chiralpack Celulose column, 0.1% DEA in n-hexane/ethanol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 18.7 min, t_{Rmin}: 15.8 min, 280 nm.

HPLC Chromatogram of (rac)-7f

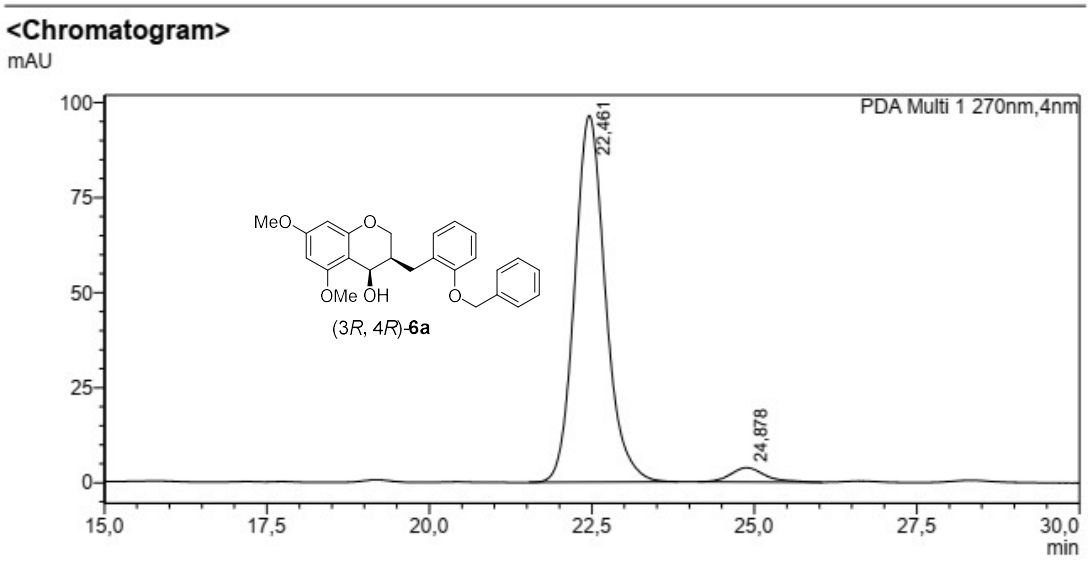


<Peak Table>

PDA Ch1 270nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	22,930	1342818	44333	52,865	50,702
2	25,230	1305609	39528	47,135	49,298
Total		2648427	83860	100,000	100,000

HPLC Chromatogram of (3*R*,4*R*)-7f



<Peak Table>

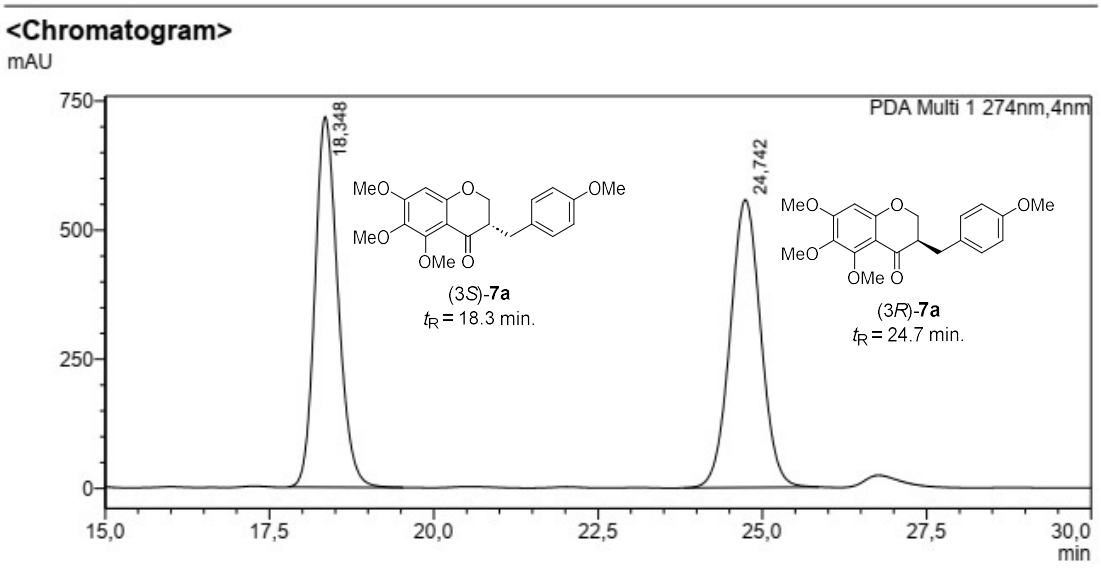
PDA Ch1 270nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	22,461	3176793	96396	96,250	95,827
2	24,878	138337	3756	3,750	4,173
Total		3315131	100152	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 22.4 min, t_{Rmin}: 24.8 min, 270 nm.

HPLC Chromatograms of the 3-benzylchroman-4-one (1a-d, 8c,f)

HPLC Chromatogram of (rac)-1a

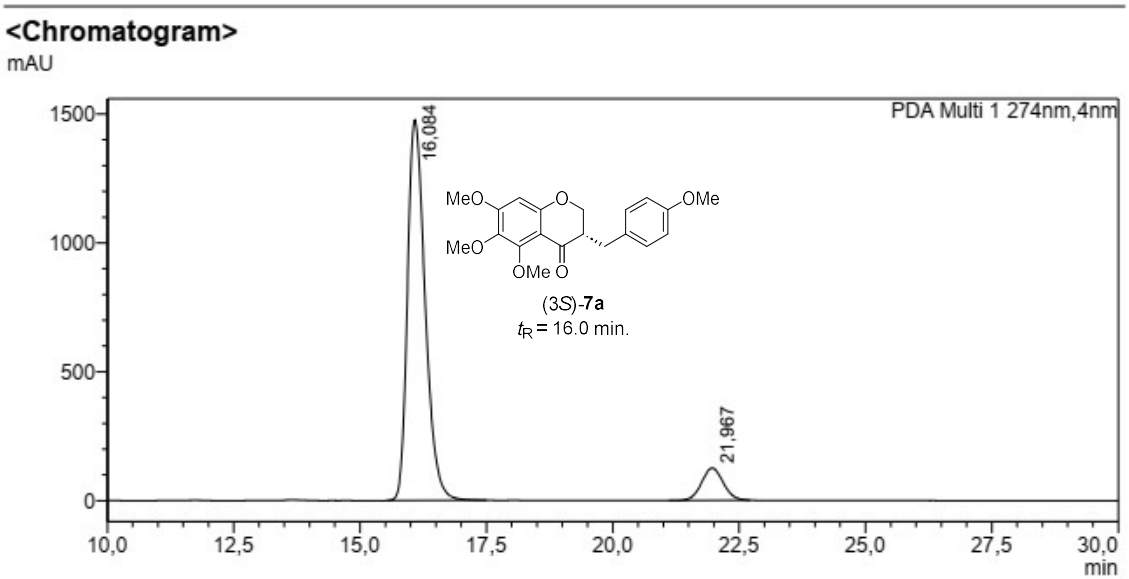


<Peak Table>

PDA Ch1 274nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	18,348	17403516	717014	56,273	49,128
2	24,742	18021245	557151	43,727	50,872
Total		35424761	1274165	100,000	100,000

HPLC Chromatogram of (3*S*)-1a



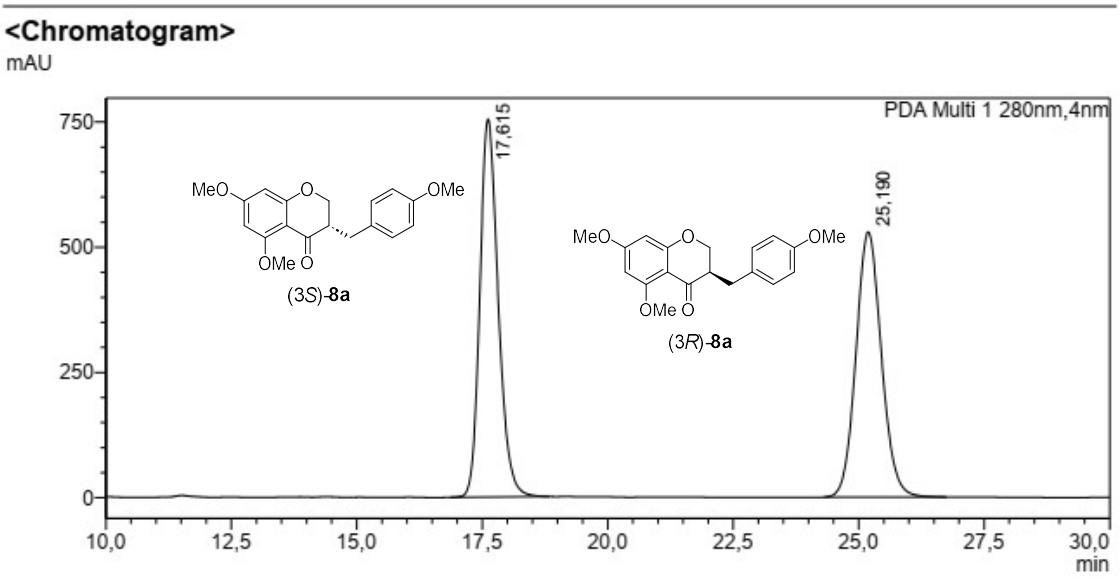
<Peak Table>

PDA Ch1 274nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	16,084	35854640	1476205	92,181	90,560
2	21,967	3737533	125208	7,819	9,440
Total		39592173	1601413	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 24.7 min, t_{Rmin}: 18.4 min, 274 nm.

HPLC Chromatogram of (rac)-1b

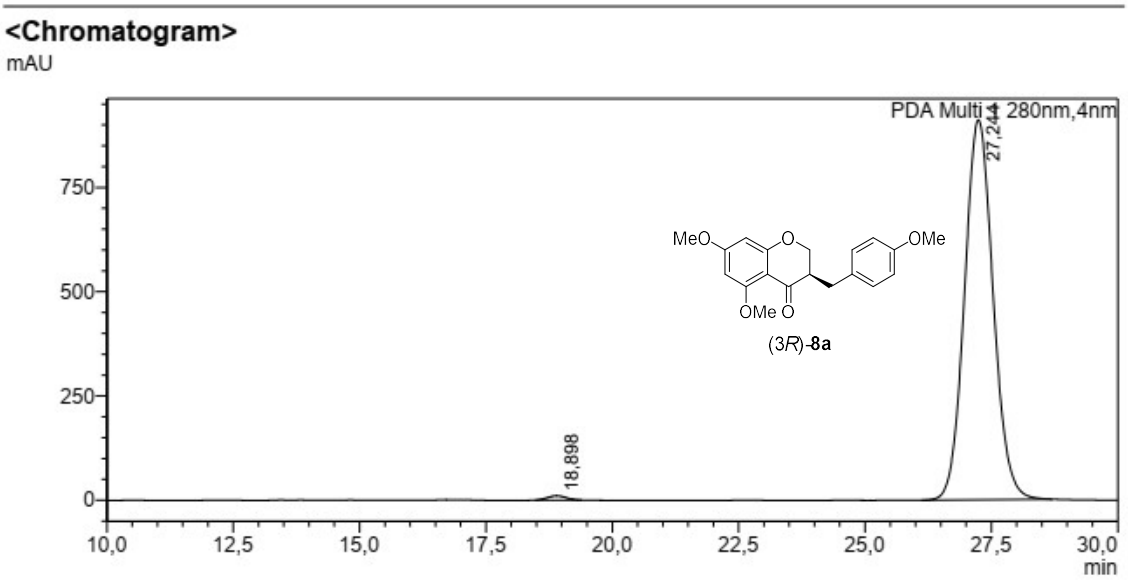


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	17,615	19202206	754155	58,768	50,670
2	25,190	18694154	529114	41,232	49,330
Total		37896360	1283269	100,000	100,000

HPLC Chromatogram of (3*R*)-1b



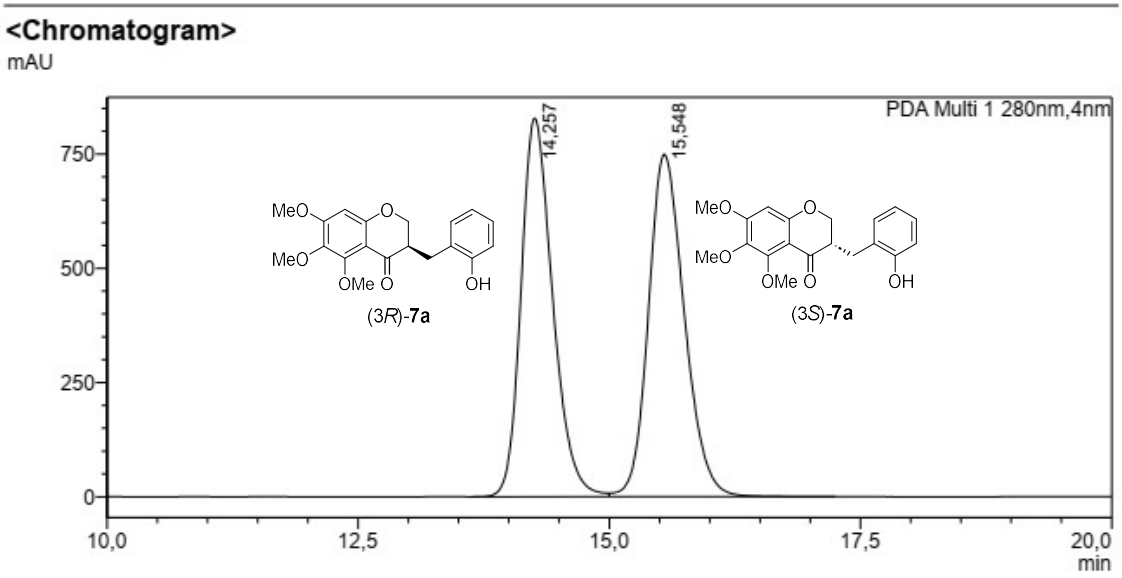
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	18,898	253183	10083	1,094	0,701
2	27,244	35884004	911237	98,906	99,299
Total		36137186	921320	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 80:20, 1 mL/min, 28 ºC, t_{Rmaj}: 27.2 min, t_{Rmin}: 18.8 min, 280 nm.

HPLC Chromatogram of (rac)-1c

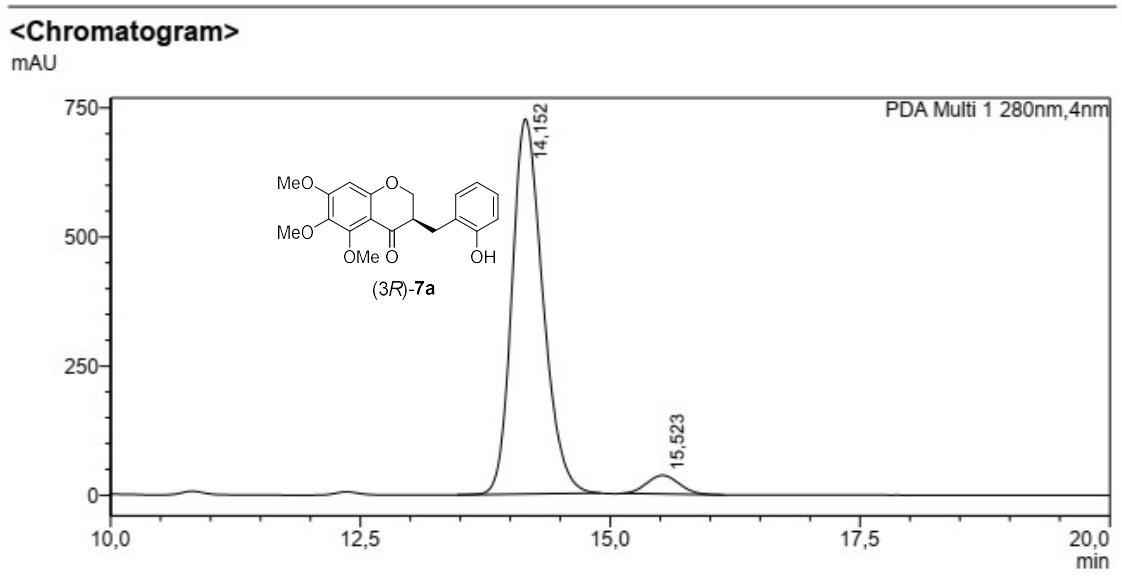


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	14,257	18165743	827968	52,495	49,345
2	15,548	18647995	749264	47,505	50,655
Total		36813738	1577232	100,000	100,000

HPLC Chromatogram of (3*R*)-1c



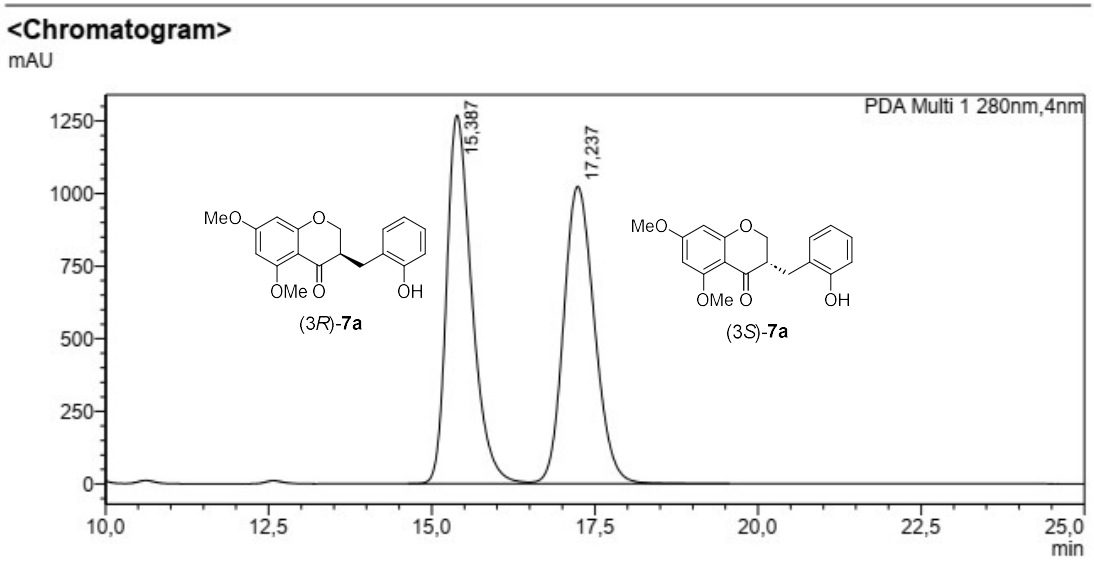
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	14,152	15630687	726562	95,265	95,023
2	15,523	818651	36110	4,735	4,977
Total		16449337	762672	100,000	100,000

HPLC method: Chiralpack IA column 0.1% DEA in n-hexane/ethanol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 14.1 min, t_{Rmin}: 15.5 min, 280 nm.

HPLC Chromatogram of (rac)-1d

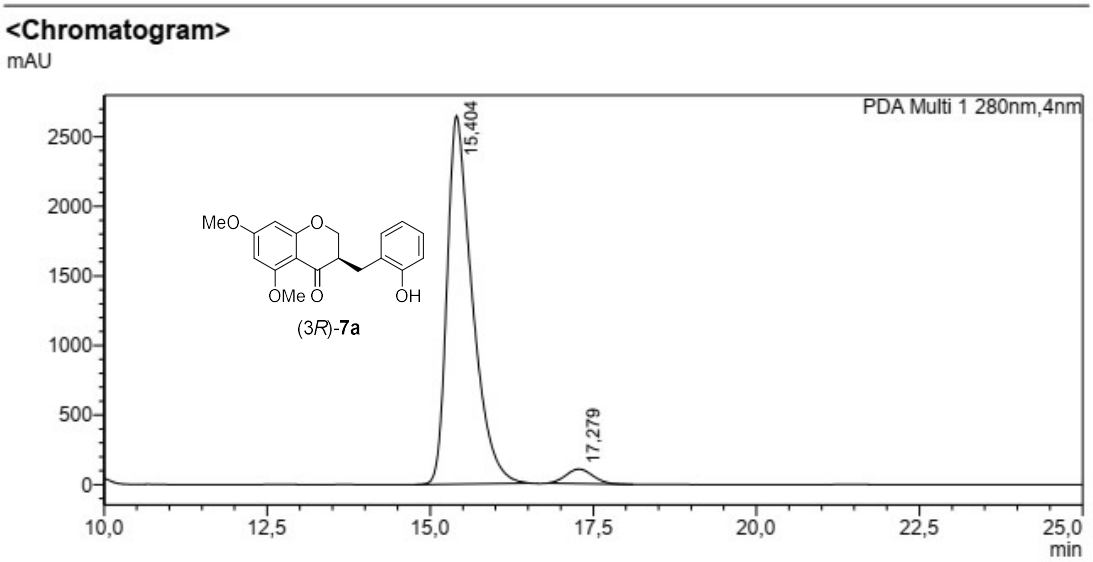


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15,387	34017945	1268367	55,339	50,275
2	17,237	33646271	1023626	44,661	49,725
Total		67664216	2291993	100,000	100,000

HPLC Chromatogram of (3*R*)-1d



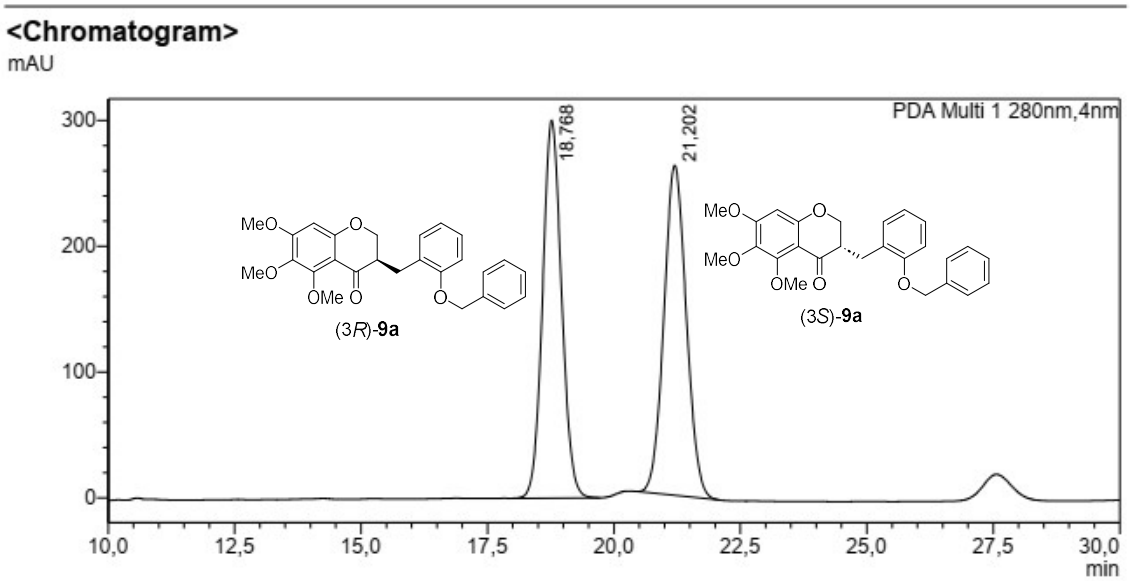
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15,404	71109272	2646812	96,225	95,979
2	17,279	2978876	103829	3,775	4,021
Total		74088148	2750641	100,000	100,000

HPLC method: Chiralpack IA column 0.1% DEA in n-hexane/ethanol 80:20, 1 mL/min, 28 ºC, t_{Rmaj}: 15.4 min, t_{Rmin}: 17.2 min, 280 nm

HPLC Chromatogram of (rac)-8c

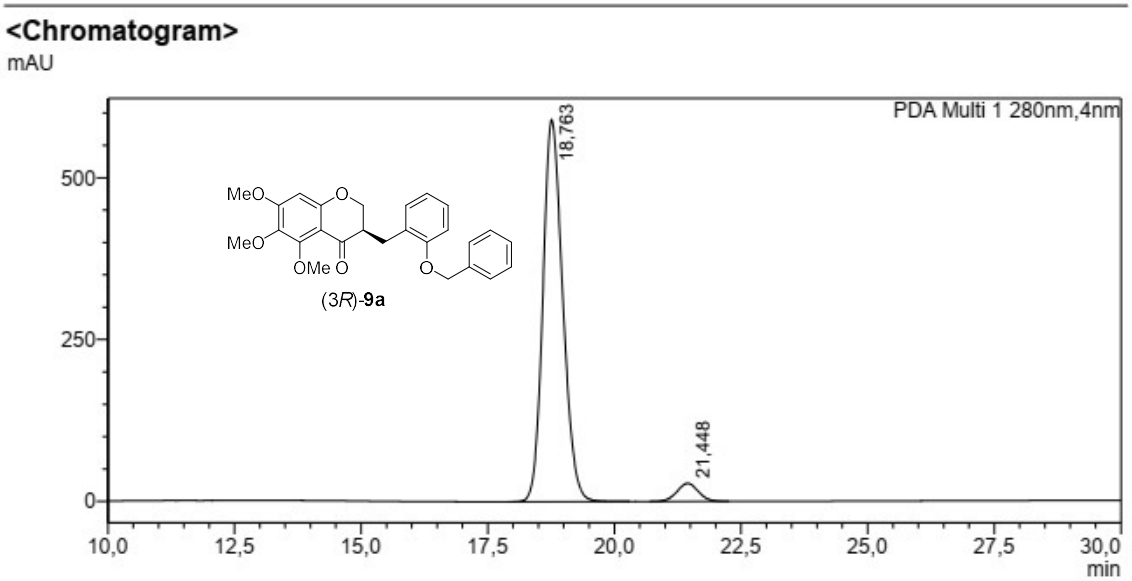


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	18,768	7843678	300267	53,381	49,299
2	21,202	8066742	262232	46,619	50,701
Total		15910420	562499	100,000	100,000

HPLC Chromatogram of (3*R*)-8c



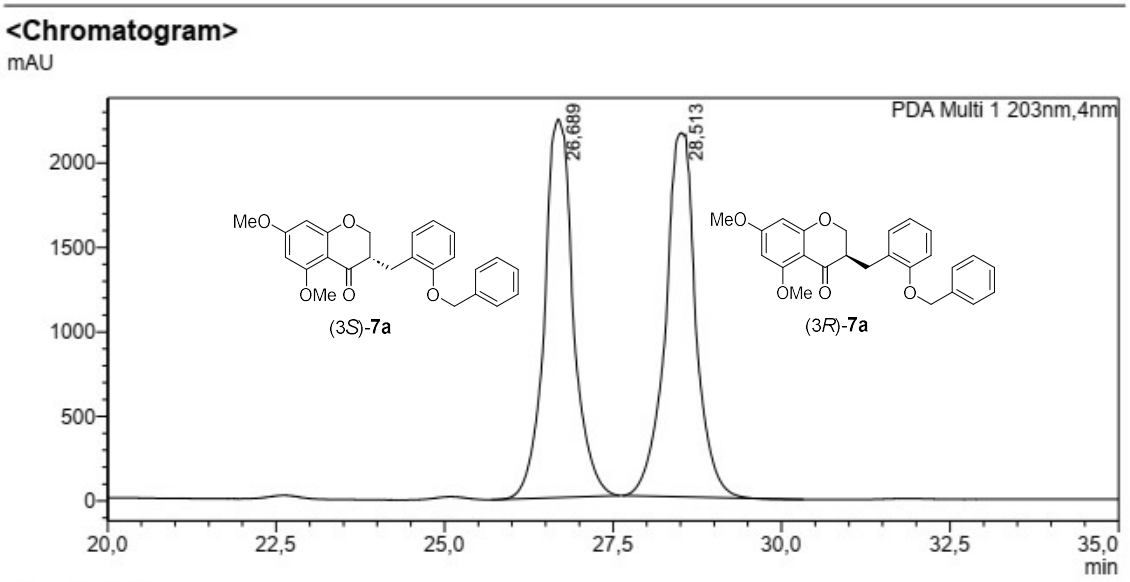
<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	18,763	16074786	590013	95,509	95,179
2	21,448	814163	27742	4,491	4,821
Total		16888950	617755	100,000	100,000

HPLC method: Chiralpack IA column 0.1% DEA in n-hexane/ethanol 90:10, 1 mL/min, 28 ºC, t_{Rmaj}: 18.7 min, t_{Rmin}: 21.4 min, 280 nm.

HPLC Chromatogram of (rac)-8f

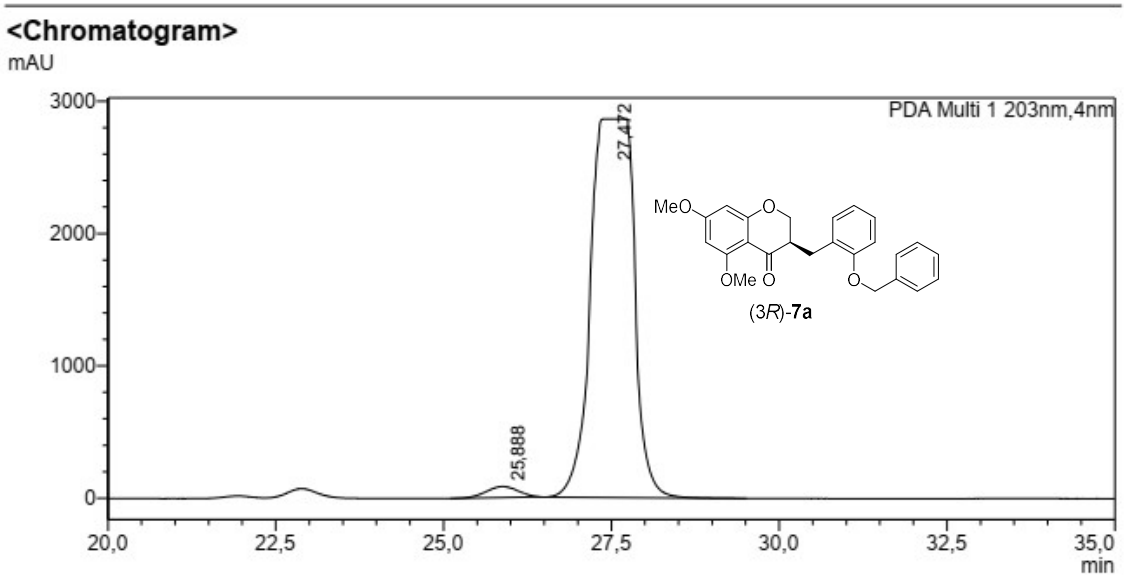


<Peak Table>

PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	26,689	66874506	2239125	50,971	49,727
2	28,513	67607471	2153823	49,029	50,273
Total		134481978	4392948	100,000	100,000

HPLC Chromatogram of (3*R*)-8f



<Peak Table>

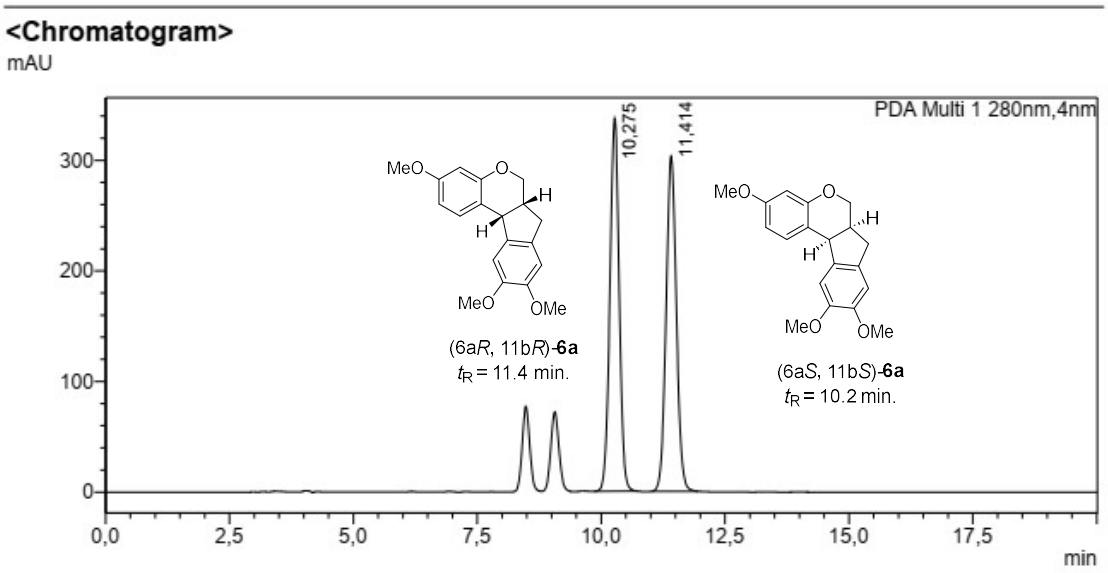
PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	25,888	2764640	83151	2,825	2,111
2	27,472	128168908	2859903	97,175	97,889
Total		130933548	2943055	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 27.4 min, t_{Rmin}: 25.8 min, 203 nm.

HPLC Chromatograms of (*6aR,11bR*)-3,9,10-trimethoxy-brazilane (9a)

HPLC Chromatogram of (rac)-9a

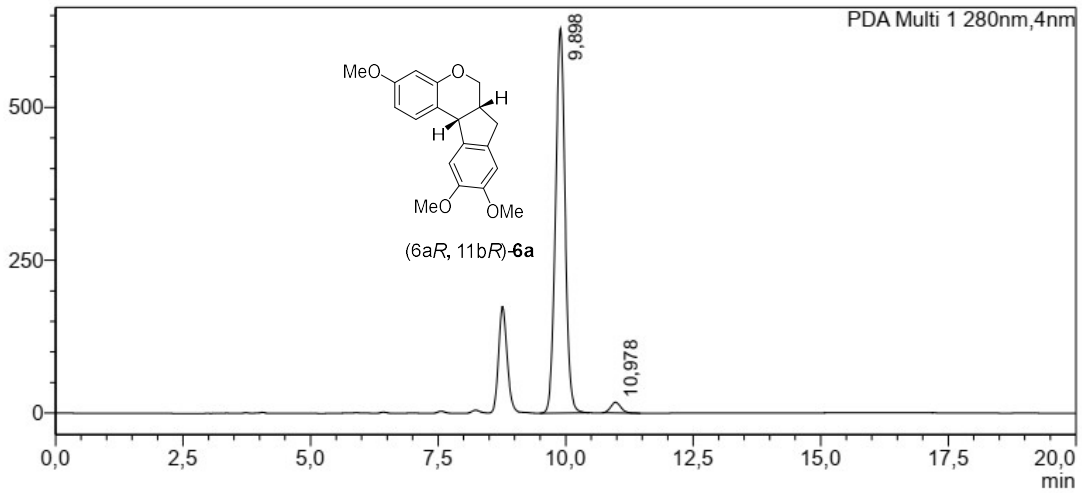


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	10,275	4402256	337024	52,676	50,173
2	11,414	4371861	302777	47,324	49,827
Total		8774117	639801	100,000	100,000

HPLC Chromatogram of (6a*R*,11b*R*)-9a



<Peak Table>

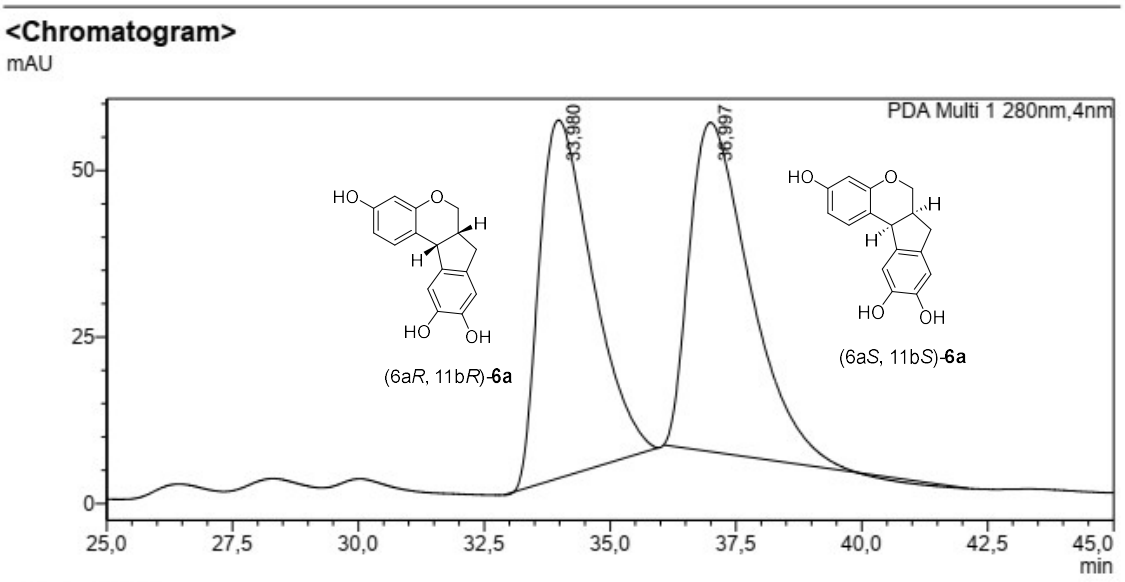
PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	9,898	8224568	628249	97,315	97,138
2	10,978	242298	17335	2,685	2,862
Total		8466867	645584	100,000	100,000

HPLC method: Chiralpack IA column, n-hexane/isopropyl alcohol 85:15, 1 mL/min, 28 ºC, t_{Rmaj}: 9.9 min, t_{Rmin}: 10.9 min, 280 nm.

HPLC Chromatograms of (*6aR,11bR*)-brazilane (2)

HPLC Chromatogram of (rac)-2

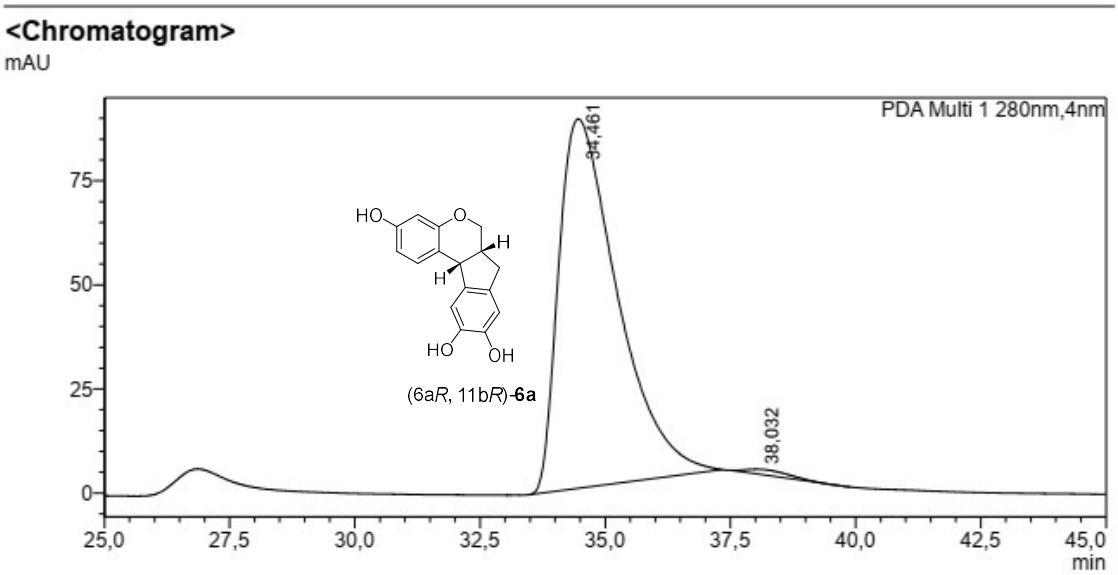


<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	33,980	3968072	53775	52,107	48,926
2	36,997	4142251	49426	47,893	51,074
Total		8110322	103201	100,000	100,000

HPLC Chromatogram of (6a*R*,11b*R*)-2



<Peak Table>

PDA Ch1 280nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	34,461	7244520	88720	98,718	98,989
2	38,032	74016	1152	1,282	1,011
Total		7318536	89872	100,000	100,000

HPLC method: Chiralpack Celulose column, 0.1% DEA in n-hexane/ethanol 90:10, 1 mL/min, 28 °C, t_{Rmaj} = 34.4 min, t_{Rmin} = 38.0 min, 280 nm.