A facile 2*H*-chromene dimerization through an *ortho*-quinone methide intermediate catalyzed by a sulfonyl derived MIL-101 MOF

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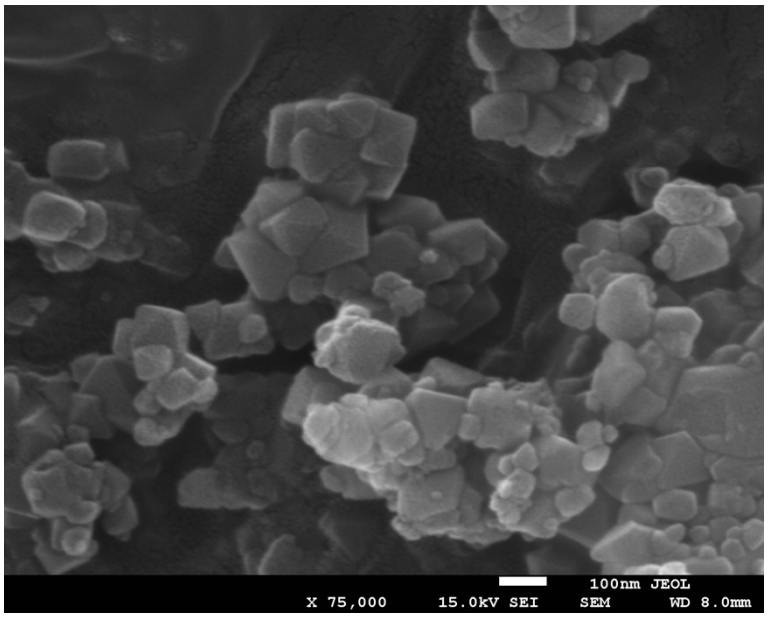


Fig. S1 SEM image of recycled MIL-101-SO_3H.

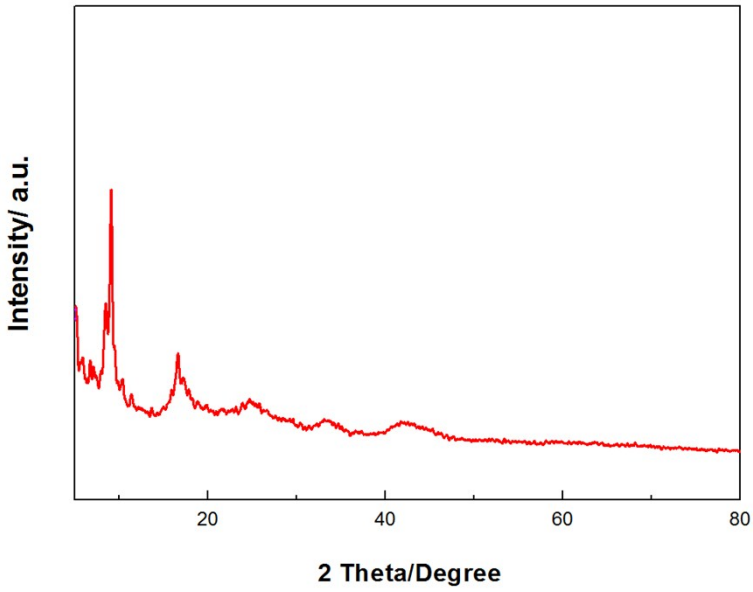
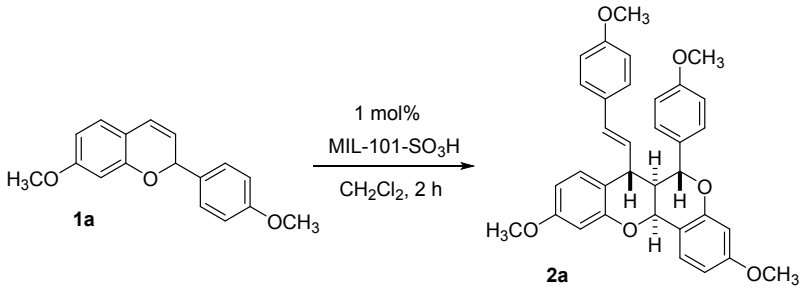


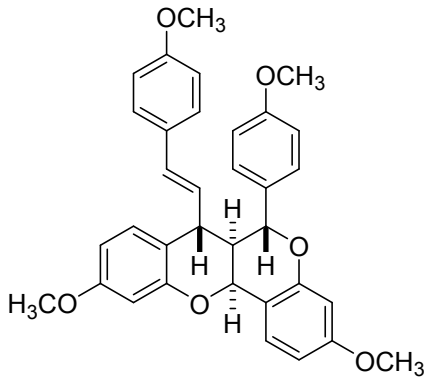
Fig. S2 XRD pattern of recycled MIL-101-SO_3H.

General procedure used for the preparation of homodimers 2 by MIL-101-SO_3H catalyst (Table 2).

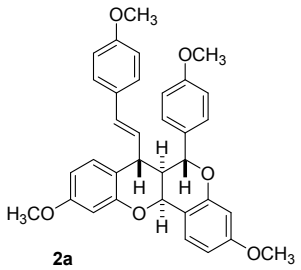


To a reaction vessel equipped with stir bar in air was added 2*H*-chromene **1a** (134 mg, 0.5 mmol) and MIL-101-SO_3H catalyst (1 mol%) in 10 mL dichloromethane. The mixture was stirred at room temperature for 2 hours. Then the crude product was subjected to ^{1}H-NMR analysis for the determination of diastereoselectivity. The reaction was purified without work-up by flash chromatography over silica gel column (elution with 98:2 – 95:5, hexanes:EtOAc) to afford the product **2a** as a single diastereomer (white solid, 263 mg, 98% yield).

(*E*)-3,10-dimethoxy-6-(4-methoxyphenyl)-7-(4-methoxystyryl)-6,6a,7,12a-tetrahydrochromeno[4,3-b]chromene (2a)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 263 mg, 98%. **Single diastereomer**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.11 (m, 9H), 7.12 (d, J = 1.5 Hz, 1H), 6.91 – 6.83 (m, 2H), 6.80 – 6.68 (m, 3H), 6.51 (ddd, J = 8.4, 2.5, 1.3 Hz, 1H), 6.43 (dd, J = 8.3, 2.0 Hz, 3H), 6.03 (ddd, J = 15.7, 6.3, 1.3 Hz, 1H), 5.91 (d, J = 15.7 Hz, 1H), 5.01 (t, J = 1.8 Hz, 1H), 4.93 (d, J = 10.7 Hz, 1H), 3.78 (d, J = 1.4 Hz, 3H), 3.77 – 3.60 (m, 9H), 3.07 (d, J = 6.3 Hz, 1H), 2.40 (dq, J = 10.8, 2.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.59 , 159.89 , 159.81 , 159.07 , 155.91 , 153.53 , 131.30 , 131.20 , 131.09 , 131.07 , 130.69 , 129.61 , 128.68 , 127.37 , 114.14 , 113.92 , 113.67 , 112.39 , 108.32 , 108.04 , 101.30 , 101.24 , 76.56 , 67.27 , 55.37 , 55.34 , 55.28 , 41.59 , 38.02 . **IR** (thin film, cm^{-1}): 3006, 2956, 2909, 2836, 1618, 1587, 1511, 1464, 1443, 1303, 1251, 1160, 1112, 1034, 833, 755. **HRMS** *m/z* 537.2277 [(M + H^+) calc'd for $C_{34}H_{32}O_6H^+$: 537.2278].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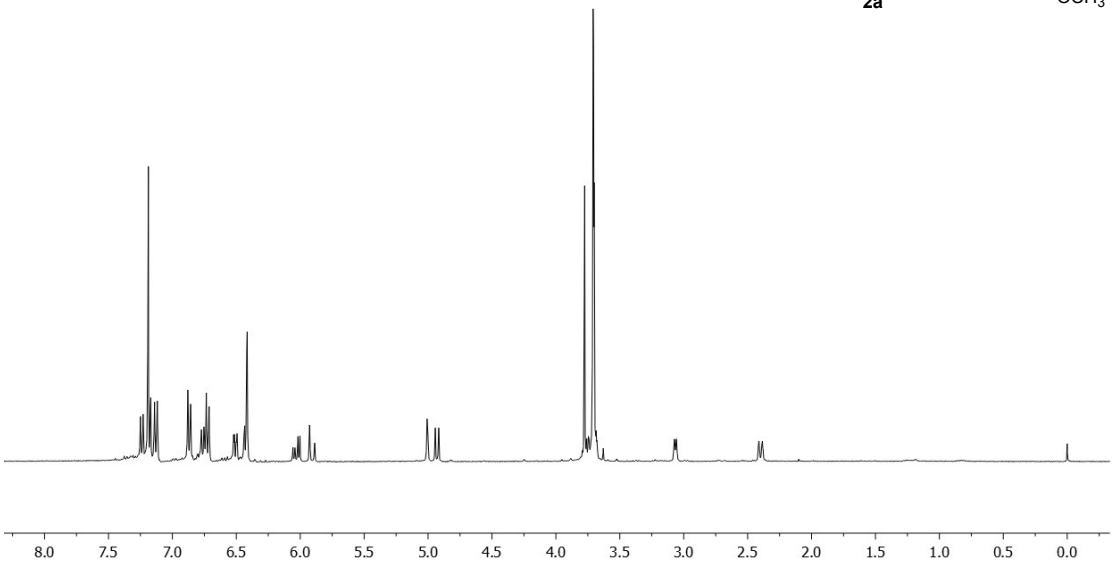
OCH3
H
H
H
O
H3CO
O
H
OCH3

2a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7.0
6.5
6.0
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2.0
1.5
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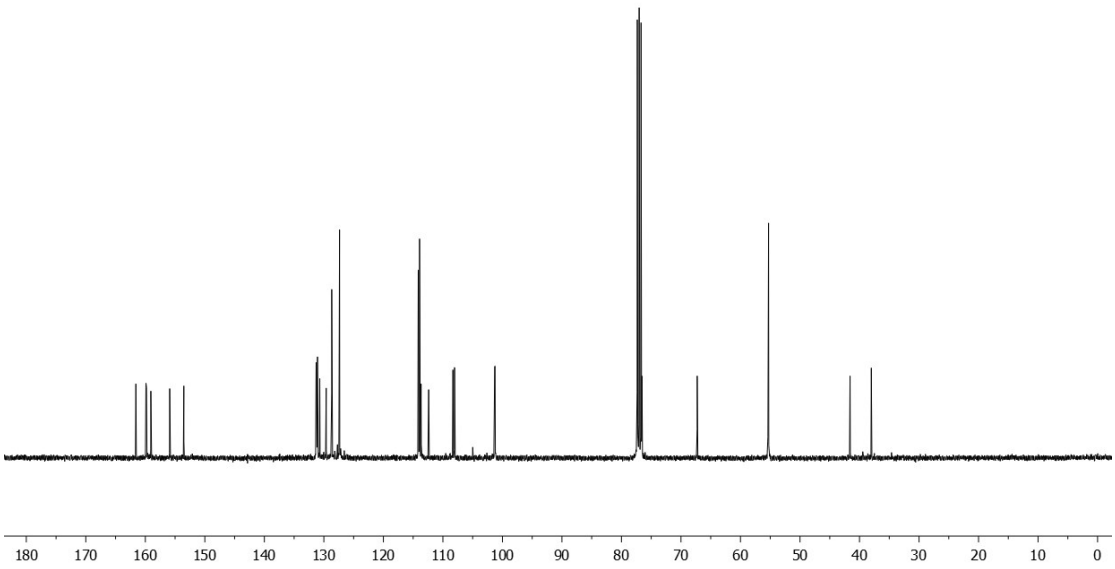
0.0


180
170
160
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130
120
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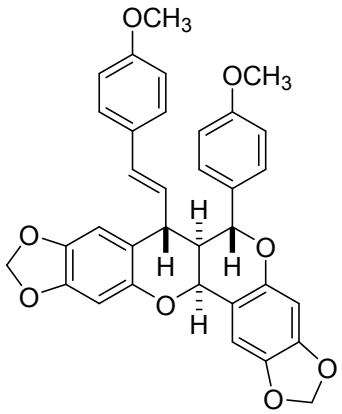
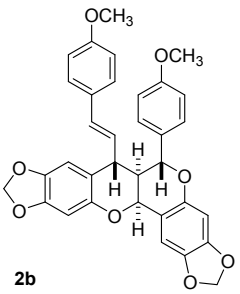
100
90
80
70
60
50
40
30
20
10
0

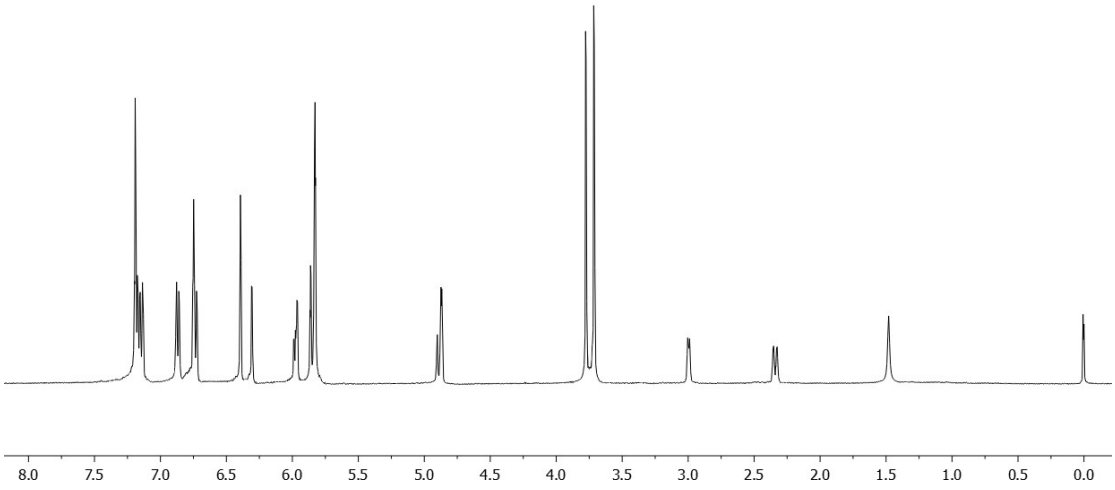
(*E*)-6-(4-methoxyphenyl)-7-(4-methoxystyryl)-6,6a,7,13a-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3-b][1,3]dioxolo[4,5-g]chromene (2b)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 90:10, hexanes:EtOAc. **Yield:** 259 mg, 92%. **Single diastereomer**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 6H), 6.91 – 6.83 (m, 2H), 6.75 (s, 2H), 6.81 – 6.69 (m, 2H), 6.39 (q, J = 1.4 Hz, 2H), 6.37 – 6.28 (m, 1H), 6.06 – 5.93 (m, 2H), 5.95 – 5.76 (m, 5H), 4.93 – 4.84 (m, 2H), 3.80 – 3.67 (m, 6H), 3.03 – 2.96 (m, 1H), 2.39 – 2.26 (m, 1H), 1.17 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.85 , 150.14 , 147.38 , 147.20 , 141.80 , 131.10 , 131.01 , 130.65 , 129.47 , 128.60 , 127.37 , 114.12 , 113.93 , 112.69 , 111.98 , 108.69 , 108.64 , 101.17 , 100.95 , 98.60 , 98.57 , 67.64 , 55.33 , 55.28 , 41.37 , 38.60 . **IR** (thin film, cm^{-1}): 3010, 2903, 1610, 1511, 1480, 1456, 1439, 1248, 1152, 1076, 1037, 755. **HRMS** *m/z* 565.1862 [(M + H^+) calc'd for $C_{34}H_{28}O_8H^+$: 565.1860].


OCH3
OCH3
H
H
H
H
O
O
O
O
O
O

2b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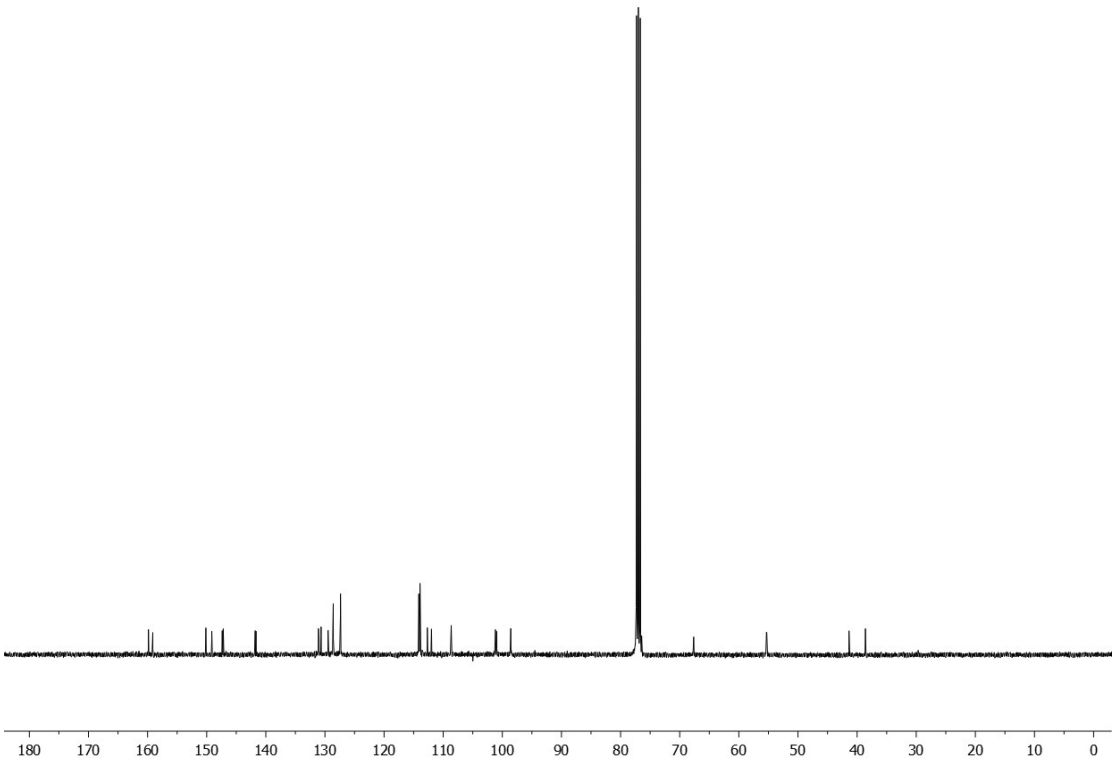
180
170
160
150
140
130
120
110
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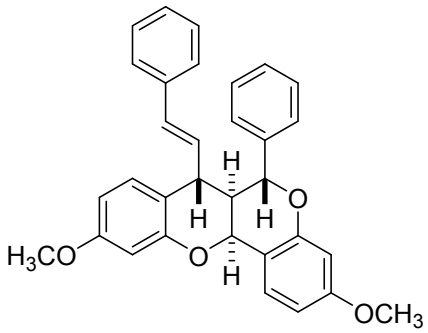
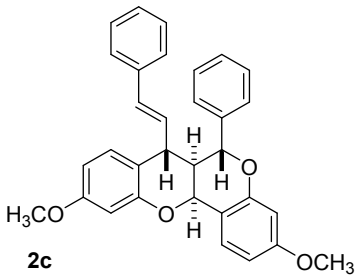
90
80
70
60
50
40
30
20
10
0

(6R,6aS,7R,12aS)-3,10-dimethoxy-6-phenyl-7-((E)-styryl)-6a,12a-dihydro-6H,7H-chromeno[4,3-b]chromene (2c)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 193 mg, 81%. **Single diastereomer**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.08 (m, 5H), 6.90 – 6.82 (m, 2H), 6.84 – 6.68 (m, 3H), 6.65 – 6.38 (m, 2H), 6.41 (s, 2H), 6.02 (ddd, *J* = 15.7, 6.3, 1.5 Hz, 1H), 5.90 (d, *J* = 15.7 Hz, 1H), 5.00 (t, *J* = 1.9 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 3.06 (d, *J* = 6.2 Hz, 1H), 2.39 (dq, *J* = 10.9, 2.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.59 , 155.91 , 153.53 , 131.30 , 131.20 , 131.09 , 131.07 , 130.69 , 129.61 , 128.68 , 127.37 , 114.14 , 113.92 , 113.67 , 112.39 , 108.32 , 108.04 , 101.30 , 101.24 , 67.27 , 55.37 , 55.28 , 41.59 , 38.02 . **IR** (thin film, cm^{-1}): 3004, 2951, 2901, 1611, 1582, 1465, 1442, 1301, 1254, 1108, 1031, 829, 748. **HRMS** *m/z* 477.2066 [(M + Na^+) calc'd for $C_{32}H_{28}O_4H^+$: 477.2068].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H
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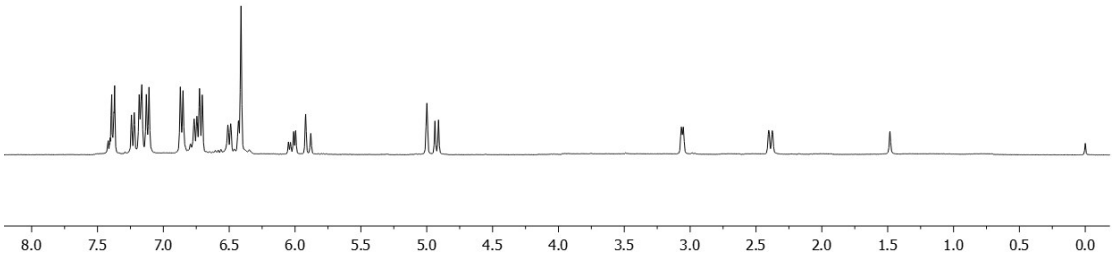
O
H
H3CO
OCH3

2c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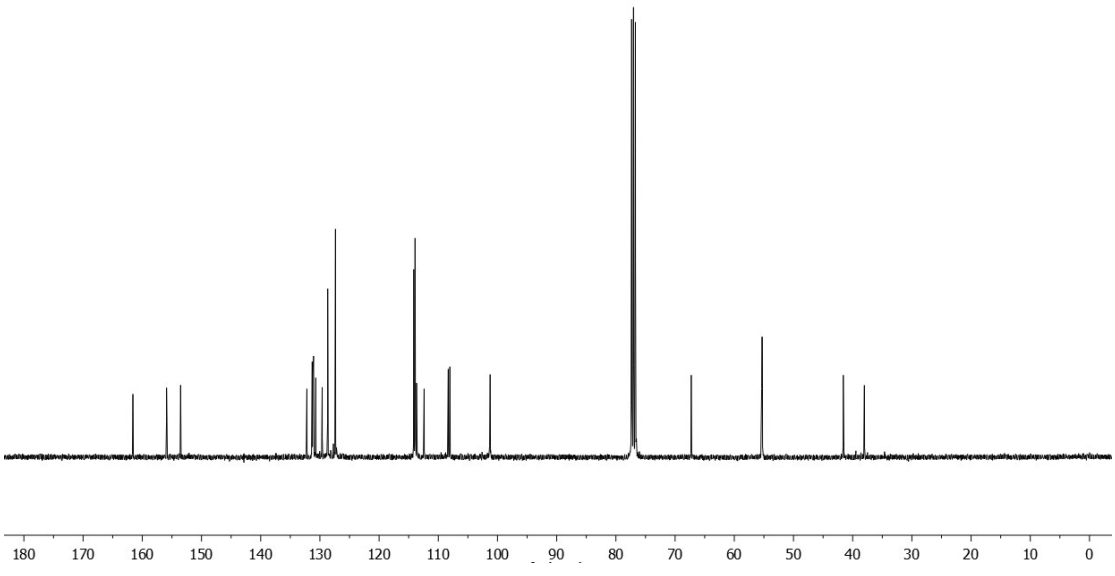
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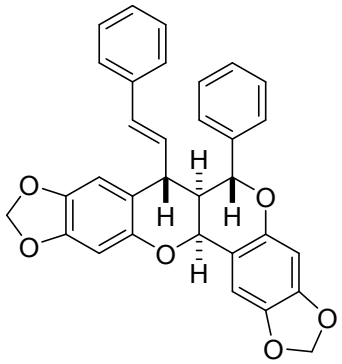
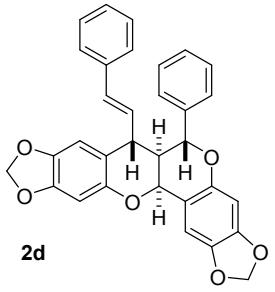
(6R,6aS,7R,13aS)-6-phenyl-7-((E)-styryl)-6a,13a-dihydro-6H,7H-[1,3]dioxolo[4',5':6,7]chromeno[4,3-b][1,3]dioxolo[4,5-g]chromene (2d)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 90:10, hexanes:EtOAc. **Yield:** 259 mg, 86%. **Single diastereomer**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (s, 1H), 7.51 – 7.48 (d, 1H), δ 7.32 – 7.12 (m, 7H), 6.91 – 6.83 (m, 2H), 6.75 – 6.62 (m, 2H), 6.43 – 6.28 (s, 2H), 6.05 – 5.91 (m, 1H), 5.90 – 5.84 (m, 3H), 5.01 (t, J = 1.8 Hz, 1H), 4.93 (s, 1H), 3.01 (d, J = 6.3 Hz, 1H), 2.38 (dq, J = 10.8, 2.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.15 , 147.22 , 141.81 , 131.11 , 131.02 , 130.66 , 129.48 , 128.60 , 127.45 , 127.38 , 114.13 , 113.93 , 112.70 , 111.99 , 108.70 , 108.65 , 101.17 , 100.96 , 98.61 , 98.57 , 76.45 , 67.64 , 41.38 , 38.61 . **IR** (thin film, cm^{-1}): 3010, 2903, 1610, 1511, 1480, 1456, 1439, 1248, 1152, 1076, 1037, 755. **HRMS** *m/z* 505.1651 [(M + H^+) calc'd for $C_{32}H_{24}O_6H^+$: 505.1652].


O
O
O
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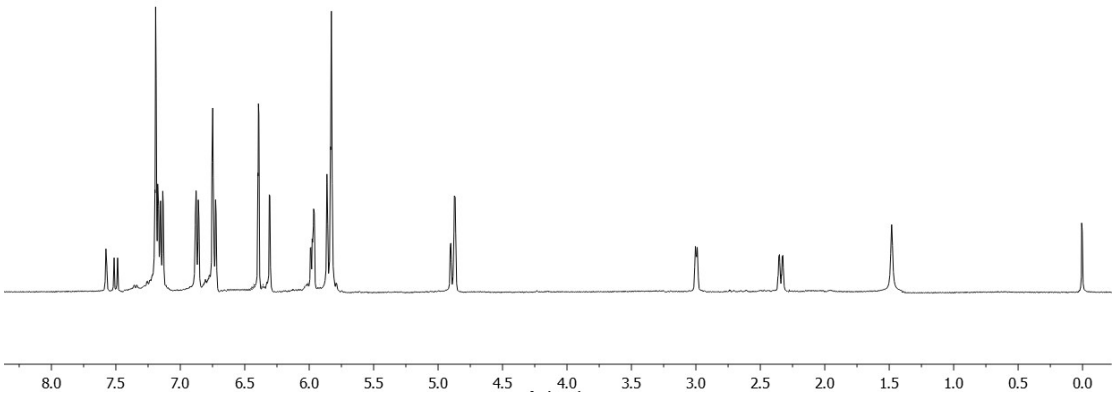
O
H
H
H
H

2d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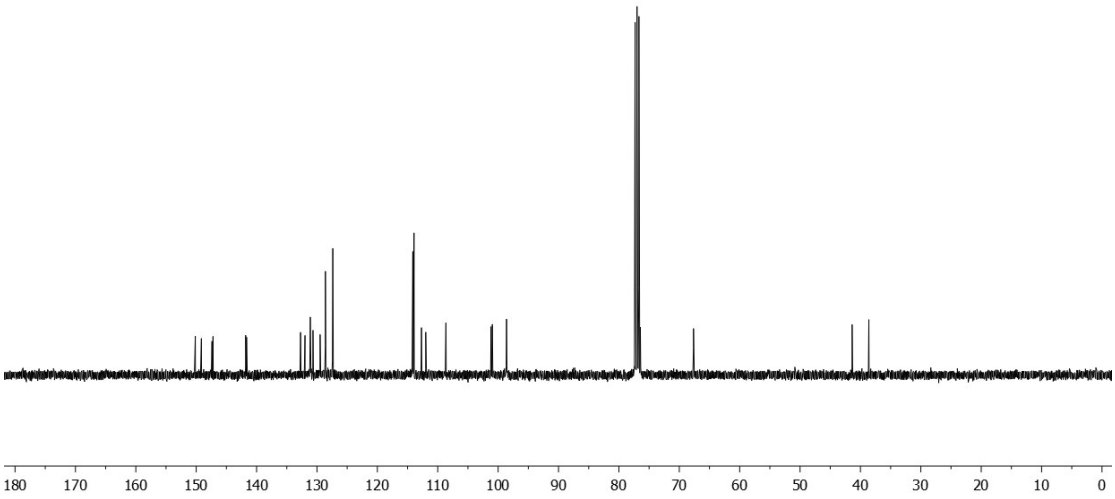
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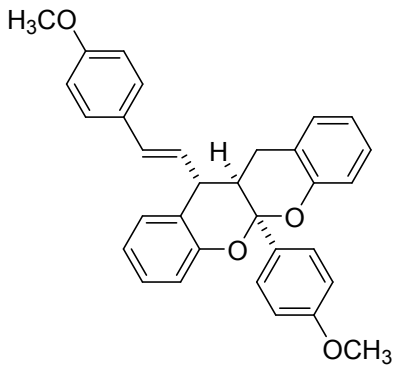
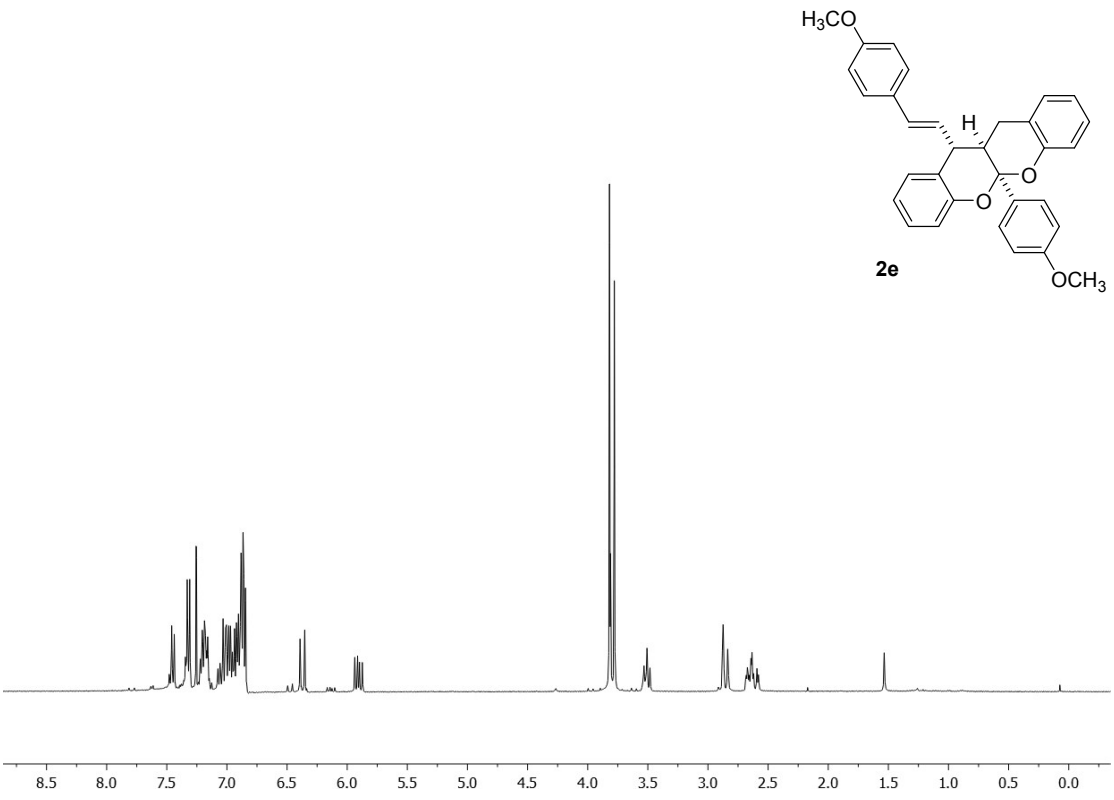
(*E*)-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2e)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 214 mg, 90%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.53 –6.77 (m, 16H), 6.37 (d, *J* = 15.7 Hz, 1H), 5.91 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.51 (dd, *J* = 9.9 Hz, 9.9 Hz, 1H), 2.91 – 2.56 (m, 3H). Minor: δ 7.53 – 6.77 (m, 16H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.15 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.51 (m, 1H), 2.91 – 2.56 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 159.91, 159.85, 159.33, 159.28, 152.97, 152.35, 151.81, 151.46, 133.74, 133.52, 132.76, 132.52, 129.62, 129.57, 129.36, 129.10, 128.71, 128.07, 128.03, 127.82, 127.53, 127.50, 127.46, 127.28, 127.22, 125.85, 123.67, 122.24, 121.68, 121.57, 121.37, 121.12, 119.36, 117.13, 116.98, 116.55, 116.48, 114.09, 114.07, 113.99, 113.86, 101.09, 100.83, 55.36, 55.26, 42.24, 40.08, 38.11, 37.19, 27.43, 23.19. **IR** (thin film, cm^{-1}): 3008, 2933, 2836, 1609, 1584, 1512, 1486, 1455, 1249, 1177, 1054, 754. **HRMS** *m/z* 477.2066 [(M + H^+) calc'd for $C_{32}H_{28}O_4H^+$: 477.2069].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O
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OCH3
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7.5
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6.0
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2.0
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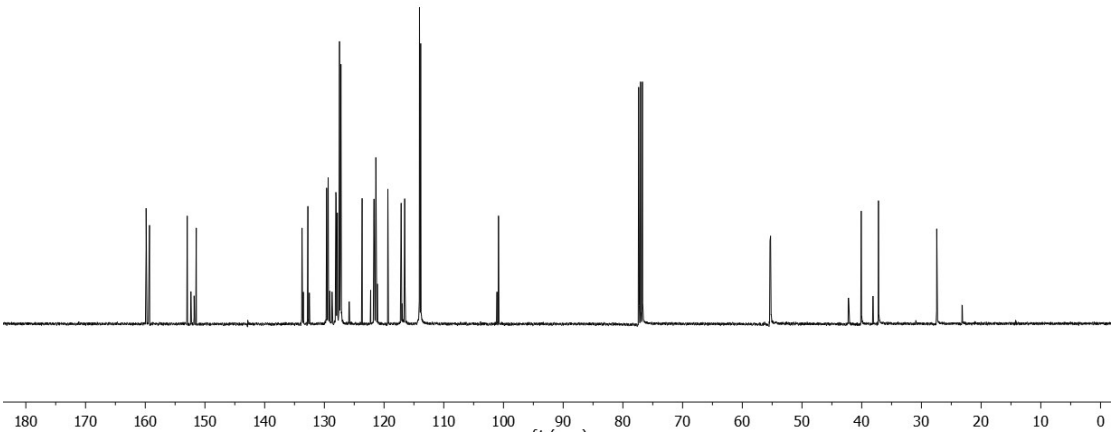
180
170
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120
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80
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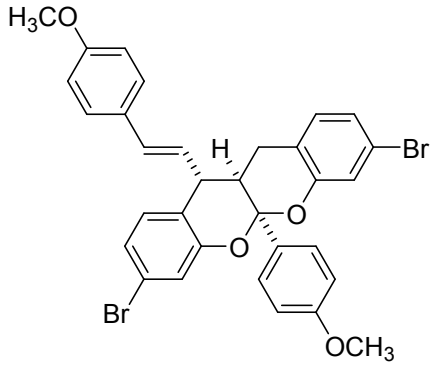
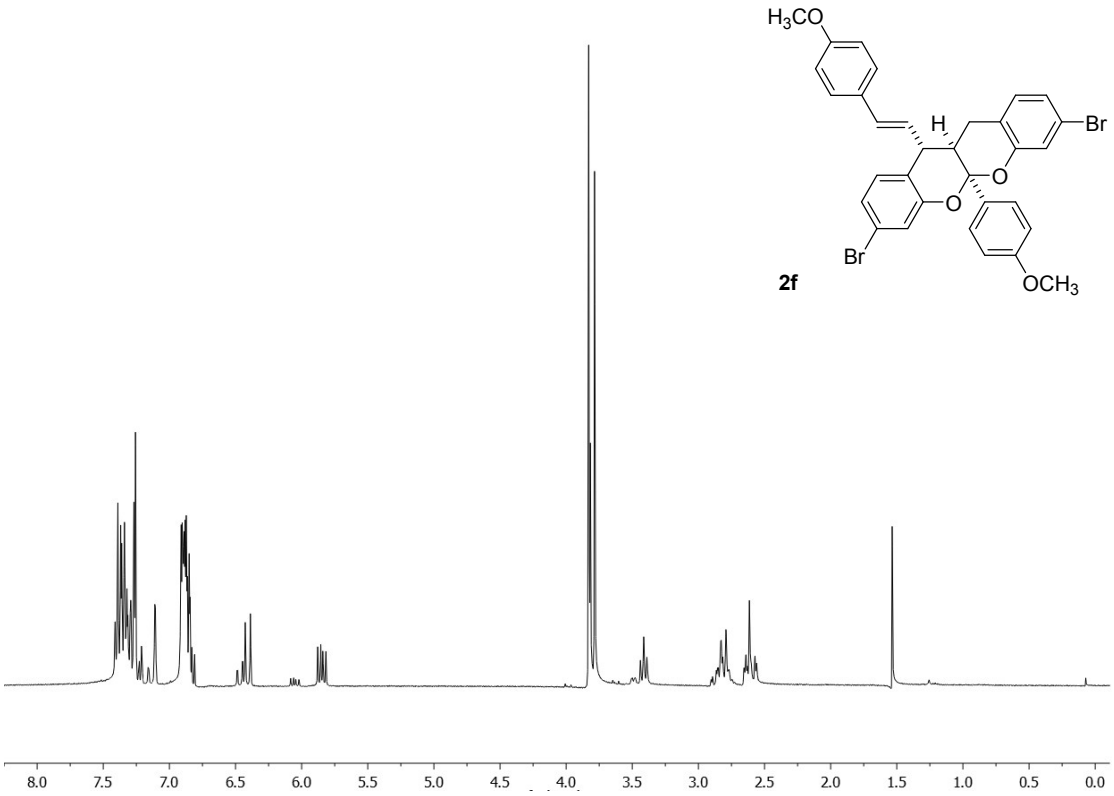
50
40
30
20
10
0

(*E*)-2,9-dibromo-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2f)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 269 mg, 85%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.65 – 6.65 (m, 14H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.85 (dd, *J* = 15.6, 9.4 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.41 (dd, 1H), 2.98 – 2.69 (m, 1H), 2.70 – 2.47 (m, 2H). Minor: δ 7.65 – 6.65 (m, 14H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.05 (dd, *J* = 15.6, 9.4 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.50 (dd, 1H), 2.98 – 2.69 (m, 1H), 2.70 – 2.47 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 160.14, 160.08, 159.56, 159.52, 151.94, 151.31, 150.82, 150.48, 134.63, 134.51, 132.16, 131.92, 131.82, 131.75, 131.71, 131.54, 131.16, 131.12, 130.54, 129.13, 129.06, 127.67, 127.64, 127.12, 127.08, 126.40, 125.80, 124.45, 124.25, 123.12, 121.42, 119.00, 118.78, 118.38, 118.32, 114.23, 114.14, 114.12, 114.01, 113.86, 113.71, 101.26, 101.00, 55.38, 55.30, 42.22, 40.13, 37.51, 36.62, 27.27, 23.04. **IR** (thin film, cm^{-1}): 3009, 2957, 1608, 1512, 1475, 1249, 1177, 1034, 971, 816. **HRMS** *m/z* 633.0276 [($M + H^+$) calc'd for $C_{32}H_{26}Br_2O_4H^+$: 633.0258].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H
Br
O
O
Br
OCH3
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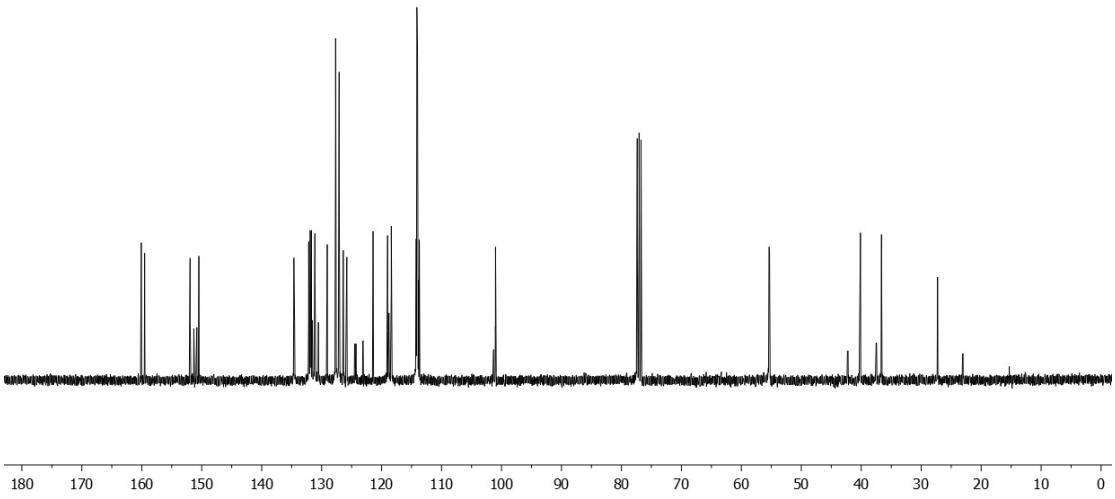
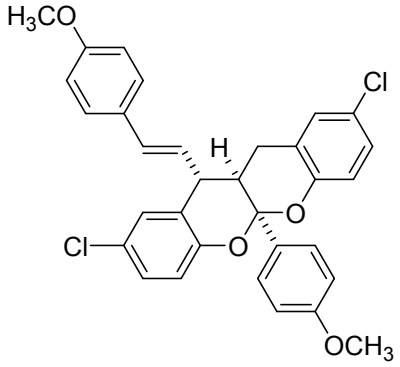
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

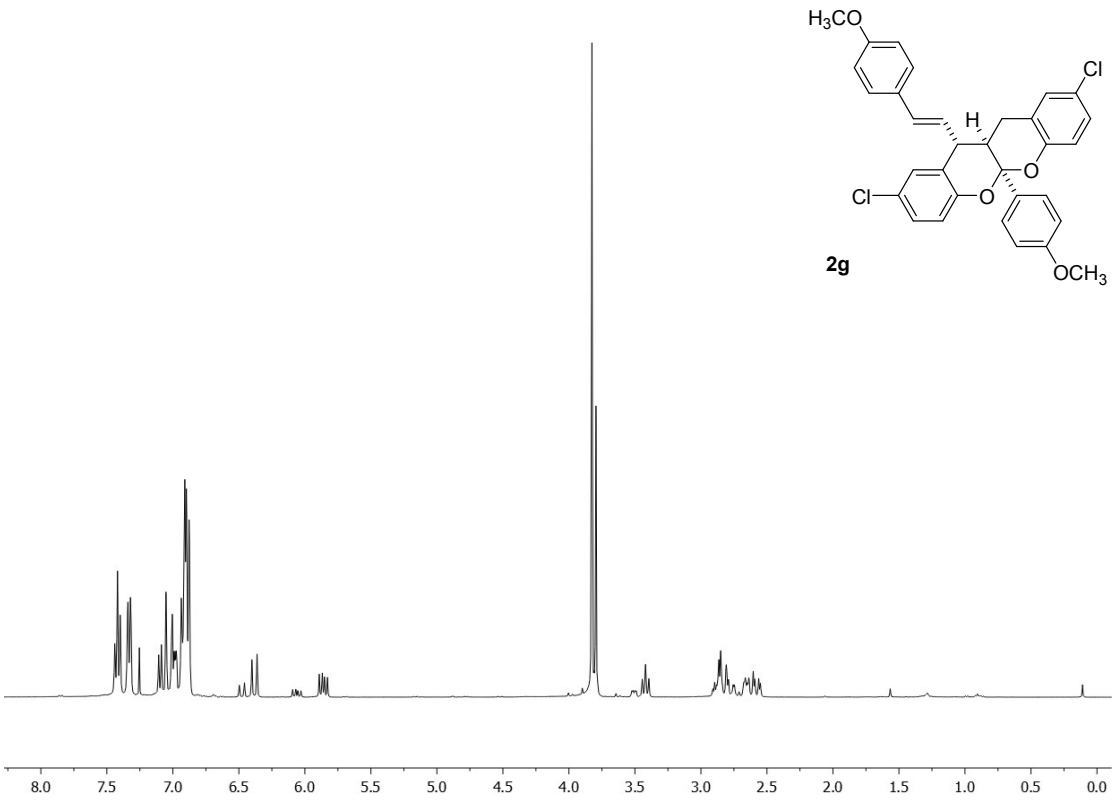
2f

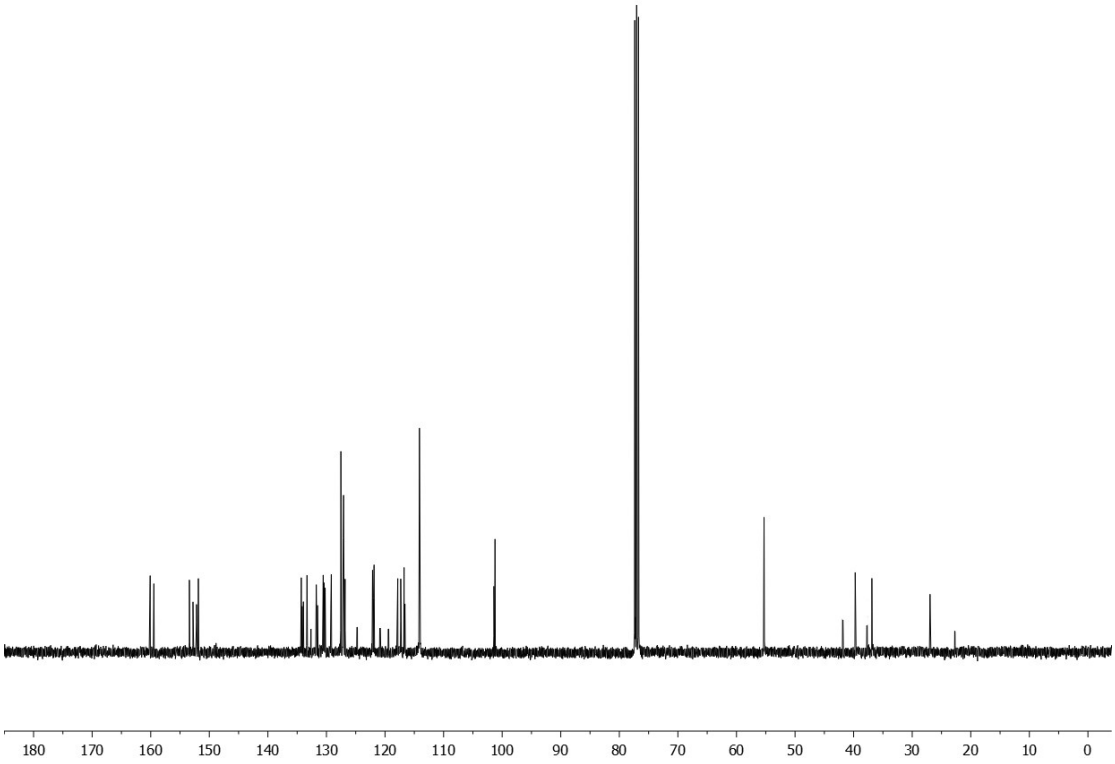

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

(*E*)-3,8-dichloro-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2g)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 250 mg, 92%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 6.80 – 7.52 (m, 14H), 6.38 (d, *J* = 15.7 Hz, 1H), 5.86 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.42 (dd, 1H), 2.92 – 2.74 (m, 1H), 2.74 – 2.48 (m, 2H). Minor: δ 6.80 – 7.52 (m, 14H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.07 (dd, *J* = 15.7, 9.4 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.42 (dd, 1H), 2.92 – 2.74 (m, 1H), 2.74 – 2.48 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 160.15, 160.09, 159.50, 159.46, 153.40, 152.78, 152.19, 151.87, 134.30, 134.15, 133.93, 133.32, 133.25, 132.63, 131.74, 131.51, 130.55, 130.40, 130.22, 129.25, 129.17, 127.53, 127.14, 127.08, 126.82, 124.74, 122.13, 122.08, 121.96, 121.87, 120.84, 119.42, 117.82, 117.32, 117.24, 116.75, 116.60, 114.13, 114.00, 101.42, 101.22, 55.36, 55.33, 55.31, 55.29, 41.86, 39.73, 37.71, 36.88, 26.95, 22.71. **HRMS** *m/z* 545.1286 [(M + H^+) calc'd for $C_{32}H_{26}Cl_2O_4H^+$: 545.1290]. **IR** (thin film, cm^{-1}): 3009, 2957, 2934, 2837, 1607, 1577, 1512, 1484, 1409, 1296, 1252, 1177, 1033, 998, 758.


H3CO
Cl
H
O
Cl
O
OCH3
2g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


180
170
160
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140
130
120
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50
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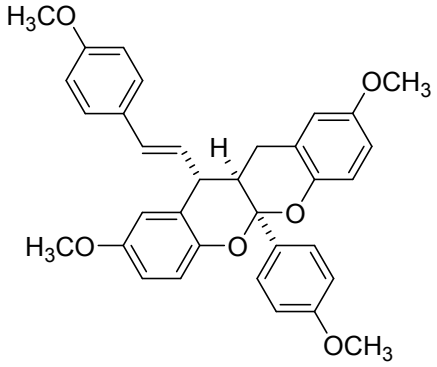
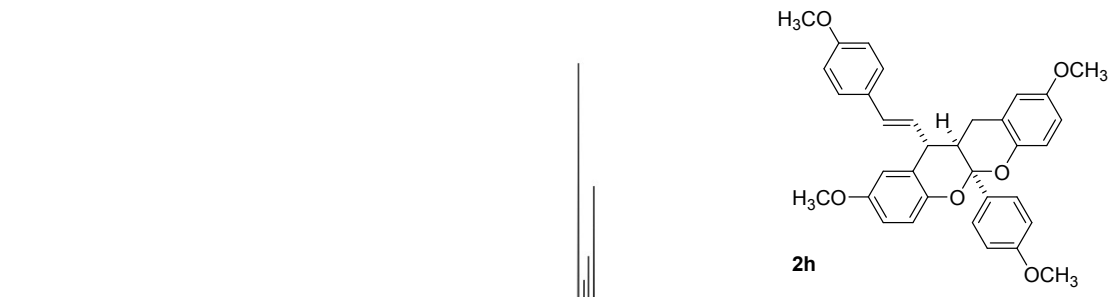
10
0

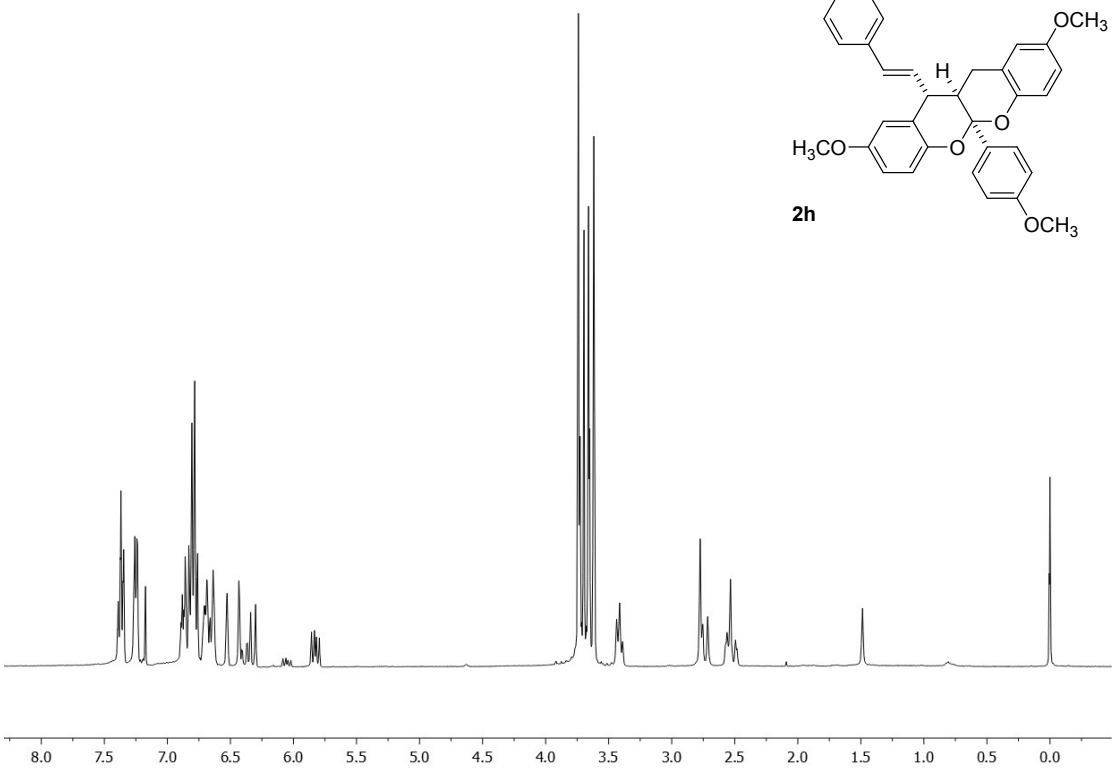
(*E*)-2,9-dimethoxy-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2h)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 243 mg, 91%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.46 – 6.27 (m, 14H), 6.32 (d, *J* = 15.6 Hz, 1H), 5.83 (dd, *J* = 15.7, 9.4 Hz, 4H), 3.74 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.62 (s, 3H), 3.49 – 3.28 (dd, 1H), 2.89 – 2.65 (m, 1H), 2.60 – 2.44 (m, 2H). Minor: δ 7.46 – 6.27 (m, 14H), 6.39 (d, *J* = 15.7 Hz, 2H), 6.05 (dd, *J* = 15.7, 9.4 Hz, 2H), 3.73 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.61 (s, 3H), 3.49 – 3.28 (dd, 1H), 2.89 – 2.65 (m, 1H), 2.60 – 2.44 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 158.81, 158.75, 158.31, 158.26, 153.26, 153.12, 153.02, 152.97, 145.94, 145.33, 144.78, 144.44, 132.78, 132.57, 131.80, 131.59, 128.56, 128.50, 126.71, 126.48, 126.47, 126.30, 126.25, 124.67, 123.43, 121.93, 120.74, 118.92, 116.69, 116.54, 116.13, 116.08, 113.22, 113.18, 113.05, 113.03, 113.01, 112.98, 112.91, 112.84, 112.79, 112.65, 112.48, 99.87, 99.63, 54.70, 54.65, 54.62, 54.57, 54.33, 54.31, 54.24, 54.23, 41.53, 39.53, 37.00, 36.09, 26.83, 22.67. **IR** (thin film, cm^{-1}): 2934, 2835, 1653, 1512, 1495, 1457, 1251, 1199, 1177, 1055, 1035. **HRMS** *m/z* 537.2277 [(M + Na^+) calc'd for $C_{34}H_{32}O_6H^+$: 537.2288].


H3CO
OCH3
H
O
H3CO
O
OCH3

2h


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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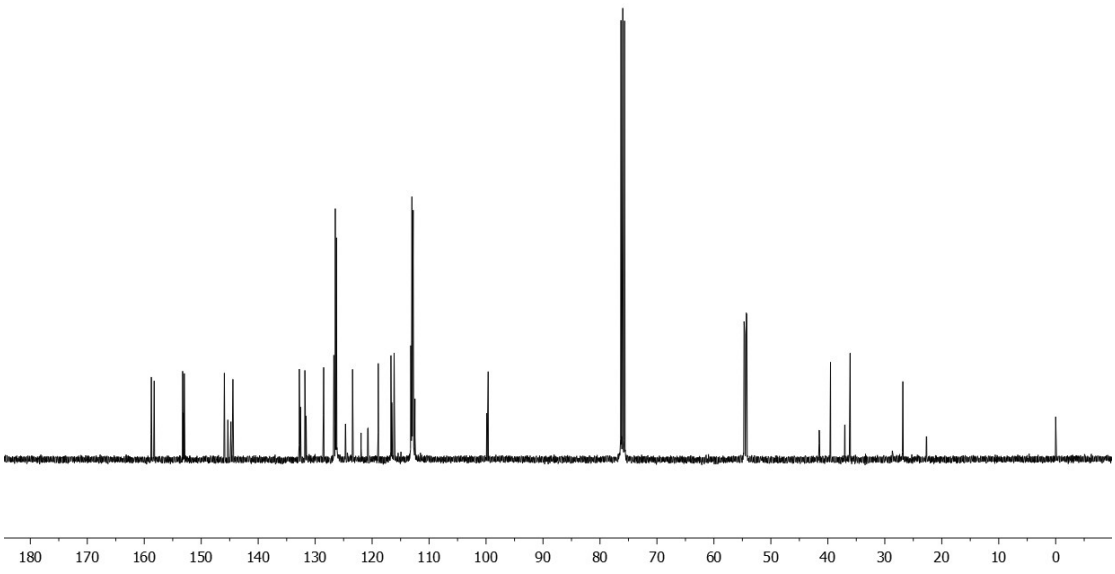
2.0
1.5
1.0
0.5
0.0


180
170
160
150
140
130
120
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90
80
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60
50
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30
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10
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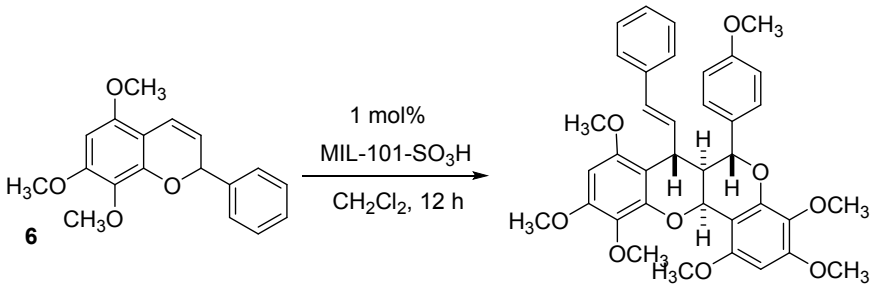
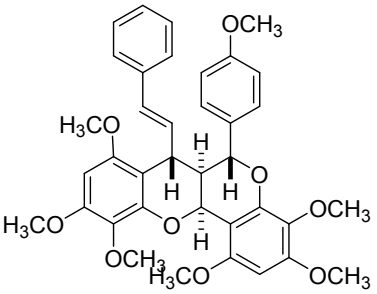
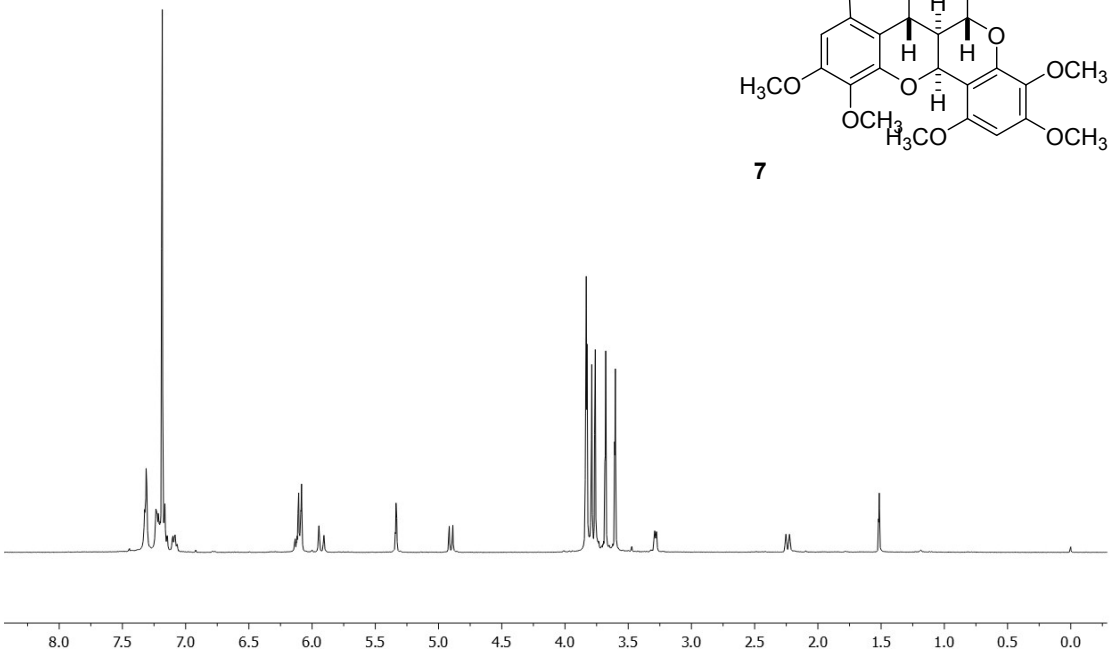
1,3,4,8,10,11-hexamethoxy-6-phenyl-7-((*E*)-styryl)-6,6a,7,12a-tetrahydrochromeno[4,3-b]chromene, dependensin (7)

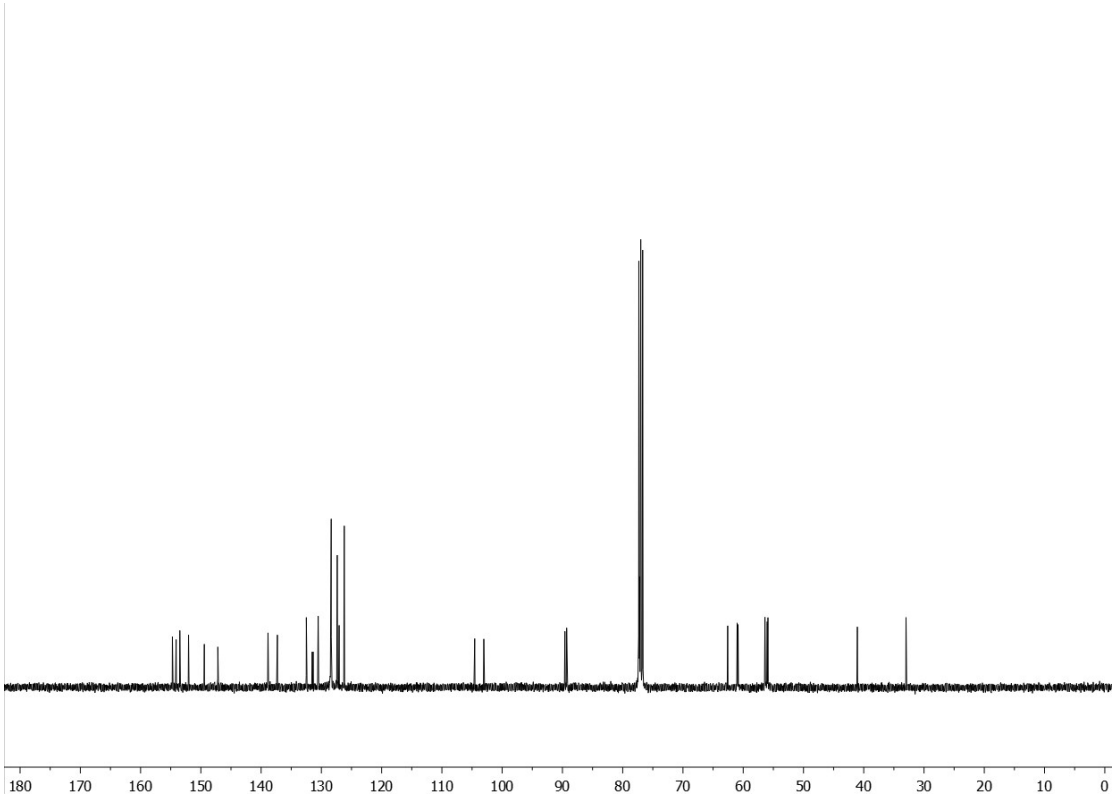


To a reaction vessel equipped with stir bar in air was added 5,7,8-trimethoxyflav-3-ene **6** (150 mg, 0.50 mmol) and MIL-101-SO_3H catalyst (1 mol%) in 10 mL dichloromethane. The mixture was stirred at room temperature for 12 hours. The crude mixture was purified without work-up by flash chromatography over silica gel column (elution with 95:5 – 90:10, hexanes:EtOAc) to afford the dependensin **7** as a single diastereomer (white solid, 232 mg, 74% yield).


OCH3
H3CO
H
H
H
O
H3CO
O
H
OCH3
OCH3
H3CO
OCH3

7


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


180
170
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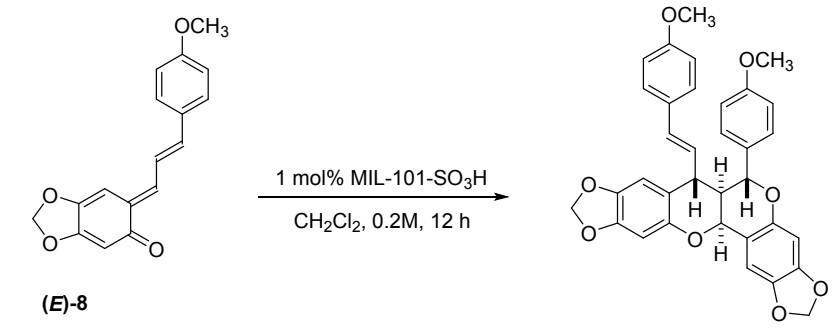
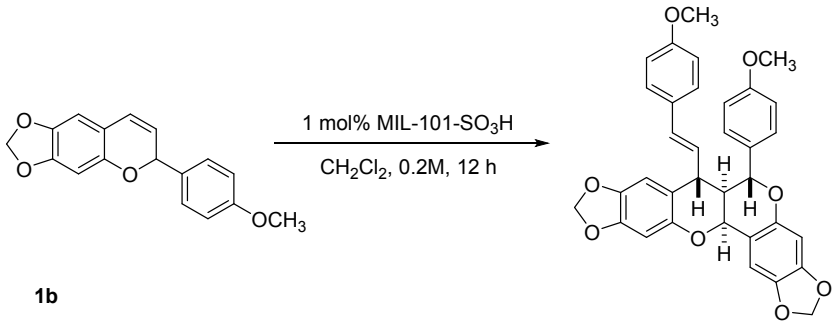
Mechanistic evidence for *2H*-chromene and vinyl *ortho*-quinone methide equilibrium



(*E*)-8

95% y, single diastereomer

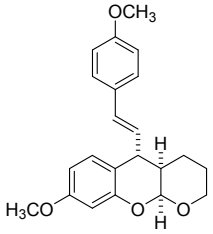


1b

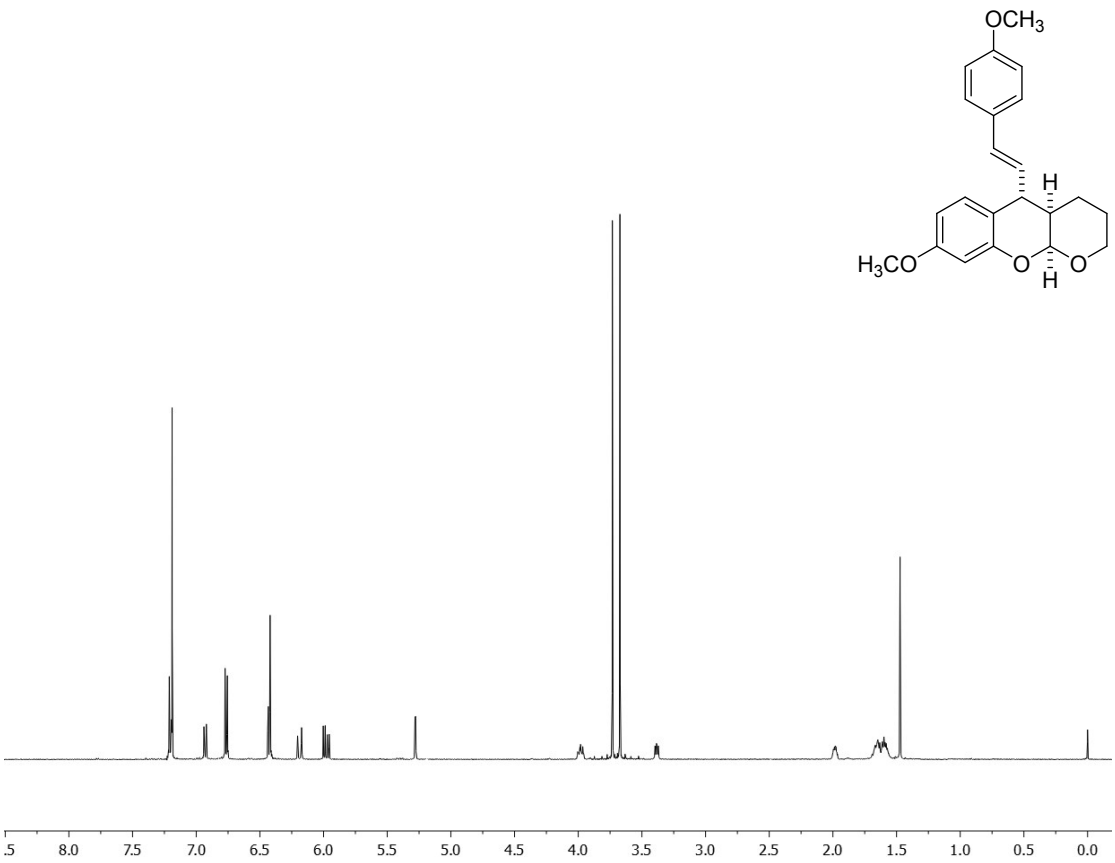
92% y, single diastereomer

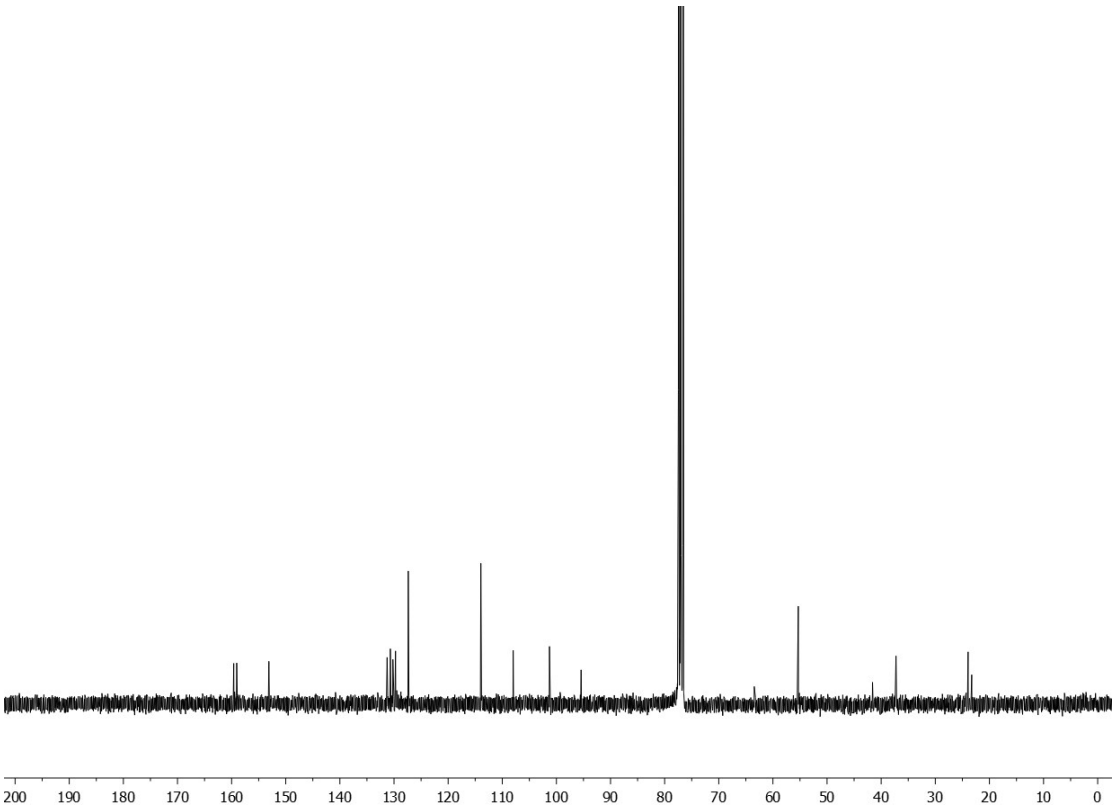
(*E*)-8 and **1b** homodimerize into the same product **2a** in similar yield and the same diastereoselectivity. This observation suggested the equilibrium between chromene **1h** and vinyl *o*QM **(*E*)-8**.

(*E*)-8-methoxy-5-(4-methoxystyryl)-2,3,4,4a,5,10a-hexahydropyrano[2,3-b]chromene (9a)



The crude mixture was purified by flash column chromatography with elution by 98:2, hexanes:EtOAc. **Yield:** 250 mg, 71%. **D.r.:** >99:1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 6.96 – 6.90 (m, 1H), 6.84 – 6.73 (m, 2H), 6.46 – 6.39 (m, 1H), 6.42 (s, 1H), 6.19 (d, *J* = 15.7 Hz, 1H), 5.98 (dd, *J* = 15.7, 7.6 Hz, 1H), 5.28 (d, *J* = 2.6 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.80 – 3.62 (m, 6H), 3.42 – 3.35 (m, 1H), 1.98 (s, 1H), 1.71 – 1.55 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.61 , 153.12 , 131.27 , 130.67 , 130.21 , 129.72 , 127.37 , 113.95 , 113.90 , 107.99 , 101.27 , 95.43 , 63.44 , 55.31 , 41.59 , 37.26 , 23.94 , 23.27. **IR** (thin film, cm^{-1}): 2943, 1618, 1583, 1511, 1250, 1164, 1132, 1037, 987, 910, 832. **HRMS** *m/z* 353.1753 [($M + H^+$) calc'd for 353.1756].


OCH3
H
H3CO
O
O
H
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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160
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110
100
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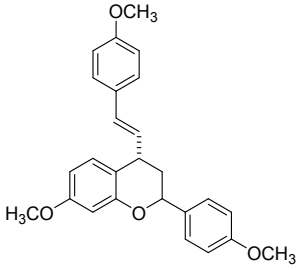
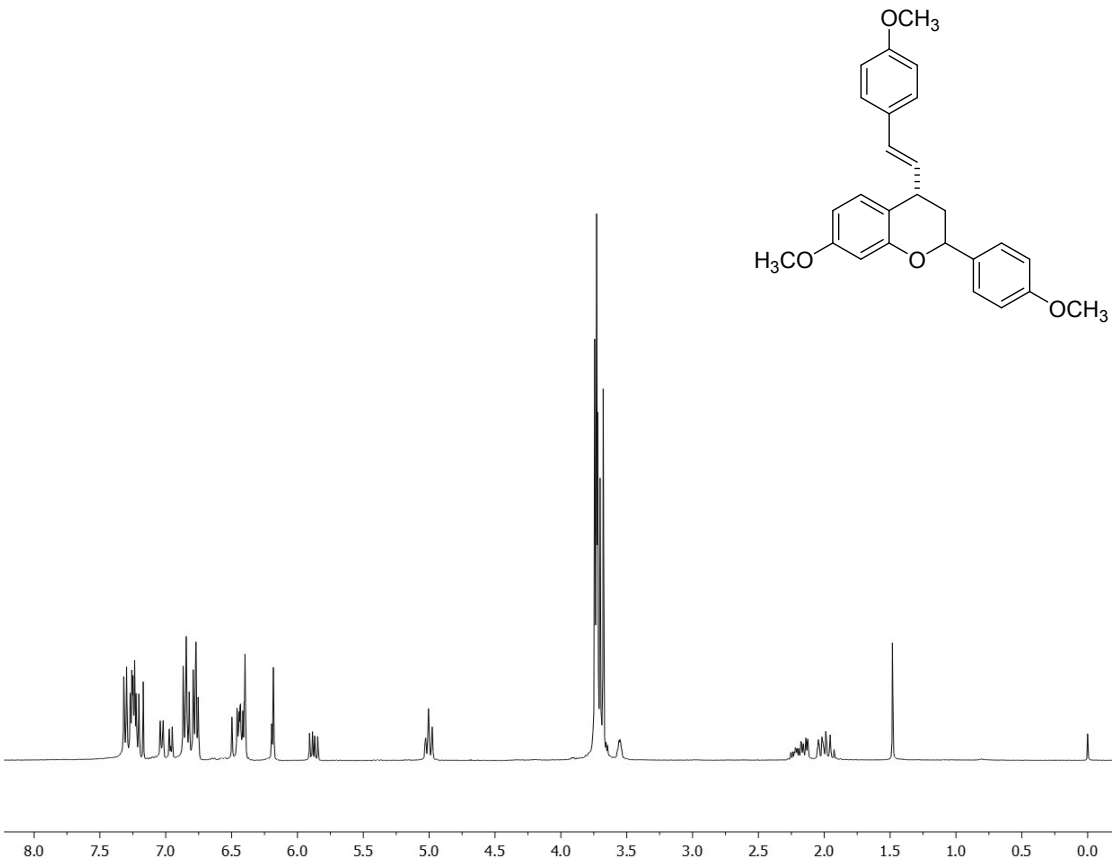
0

(*E*)-7-methoxy-2-(4-methoxyphenyl)-4-(4-methoxystyryl)chroman (9b)



The crude mixture was purified by flash column chromatography with elution by 98:2, hexanes:EtOAc. **Yield:** 326 mg, 81%. **D.r.:** 2:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.53 – 6.71 (m, 11H), 6.46 (m, 1H), 5.97 – 5.77 (m, 1H), 5.10 – 4.88 (m, 1H), 3.78 – 3.62 (3MeO, 9H), 3.61 – 3.49 (m, 1H), 2.08 – 1.88 (m, 2H). Minor: δ 7.53 – 6.71 (m, 11H), 6.30 – 6.58 (m, 1H), 5.10 – 4.88 (m, 1H), 3.78 – 3.62 (3MeO, 9H), 3.61 – 3.49 (m, 1H), 2.08 – 1.88 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 159.54, 159.50, 159.47, 159.30, 159.06, 159.02, 155.82, 155.71, 133.53, 133.35, 131.96, 131.20, 131.11, 130.65, 130.26, 129.95, 129.93, 129.81, 127.51, 127.45, 127.37, 127.32, 116.52, 115.17, 114.01, 113.99, 113.96, 113.93, 107.70, 107.56, 101.55, 101.40, 77.62, 73.71, 55.31, 40.42, 37.87, 37.11, 35.69. **IR** (thin film, cm^{-1}): 3001, 2954, 2835, 1613, 1511, 1248, 1157, 1033, 831. **HRMS** *m/z* 403.1909 [$(M + H^+)$ calc'd for $C_{26}H_{26}O_4$: 403.1906].


OCH3
H3CO
O
OCH3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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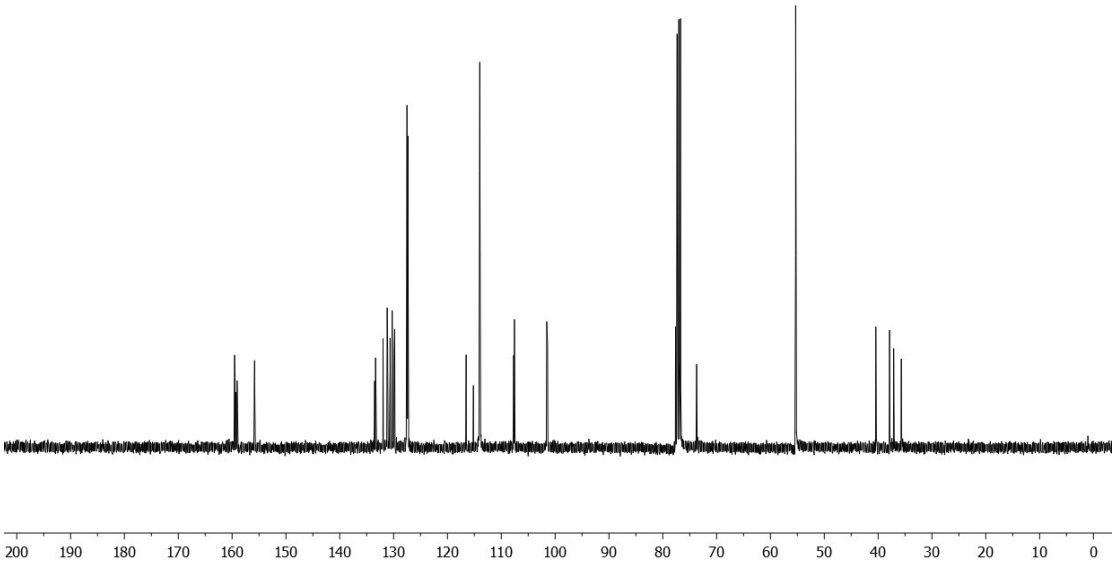
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10
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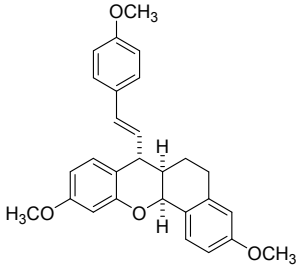
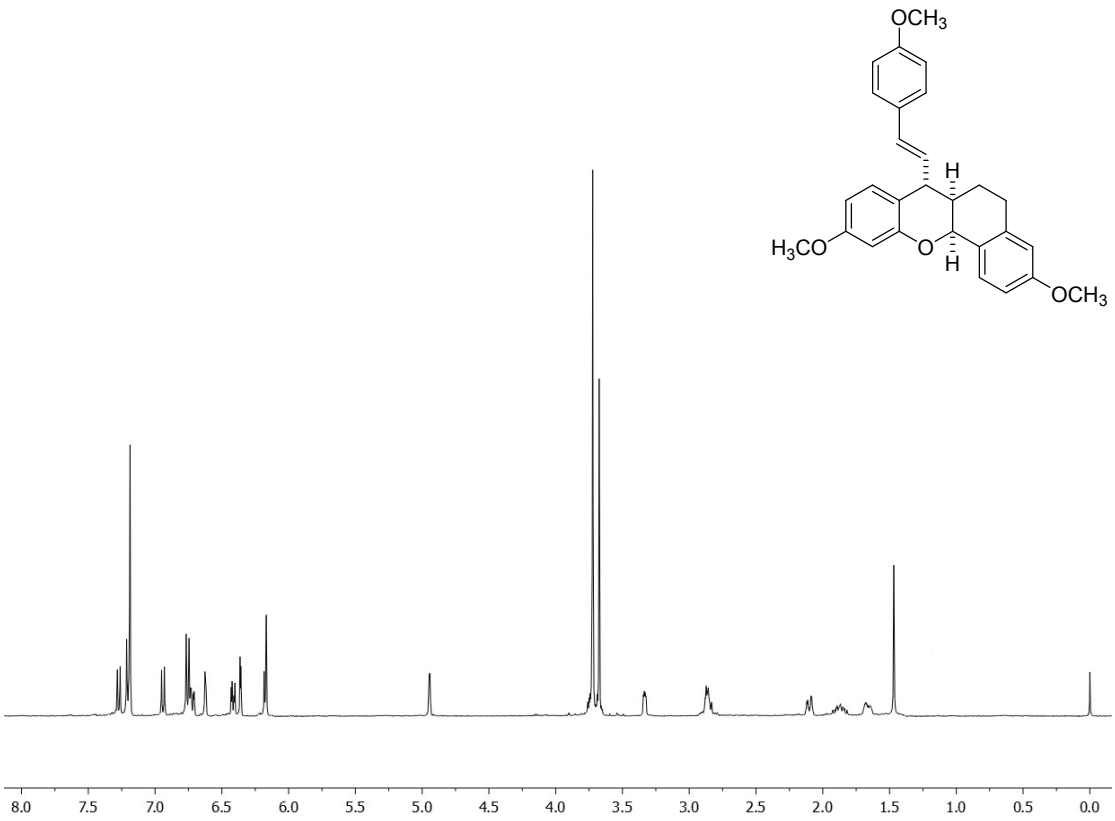
(*E*)-3,10-dimethoxy-7-(4-methoxystyryl)-6,6a,7,12a-tetrahydro-5H-benzo[c]xanthene (9c)



The crude mixture was purified by flash column chromatography with elution by 98:2, hexanes:EtOAc. **Yield:** 377 mg, 88%. Single diastereomer. . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 6.08 (m, 12H), 4.94 (d, *J* = 2.2 Hz, 3H), 3.72 (s, 6H), 3.67 (s, 3H), 3.33 (dd, *J* = 5.0, 2.5 Hz, 1H), 2.84 (dd, *J* = 21.5, 11.6 Hz, 2H), 2.22 – 2.02 (m, 1H), 1.87 (ddd, *J* = 19.1, 12.4, 6.9 Hz, 1H), 1.73 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.70, 159.40, 158.97, 154.30, 138.56, 132.12, 131.39, 131.36, 130.34, 129.93, 127.66, 127.33, 113.93, 113.69, 112.34, 107.80, 101.15, 71.11, 55.29, 55.24, 55.23, 43.11, 37.51, 28.86, 23.28. **IR** (thin film, cm^{-1}): 2933, 2834, 1616, 1585, 1442, 1251, 1156, 1120, 1033. **HRMS** *m/z* 429.2066 [$(M + H^+)$ calc'd for $C_{28}H_{28}O_4$: 429.2065].


OCH3
H
H3CO
O
H
OCH3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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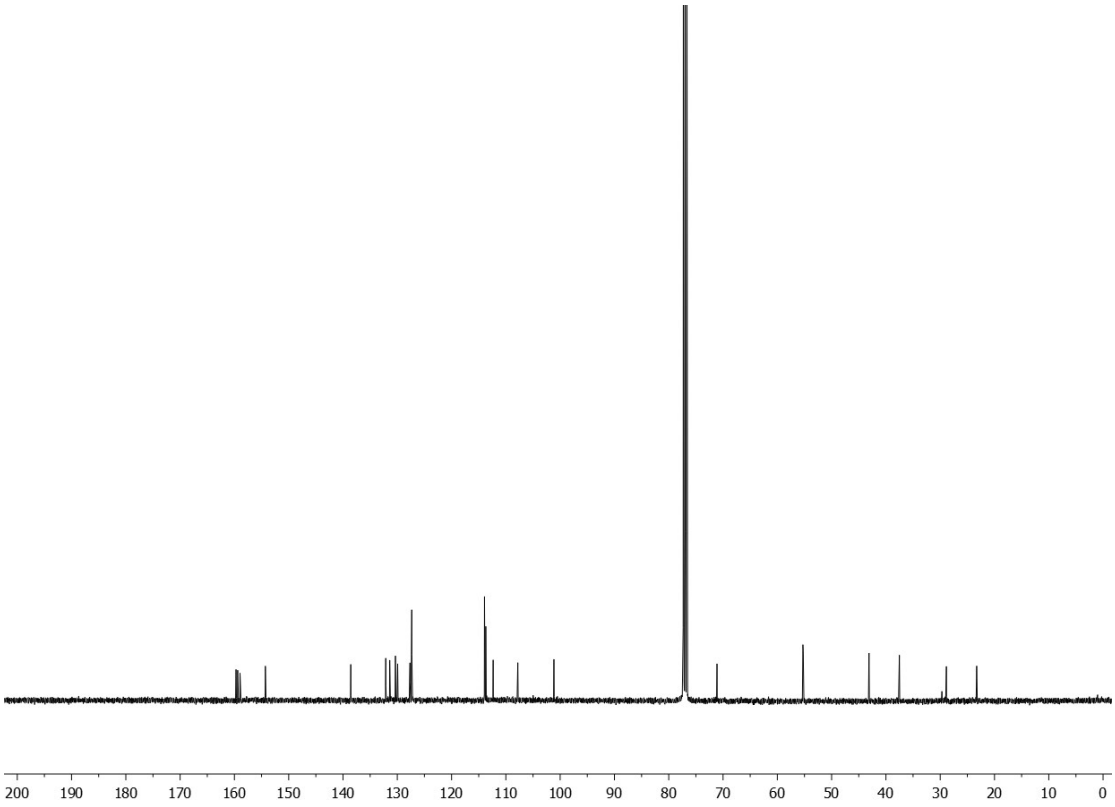
2.0
1.5
1.0
0.5
0.0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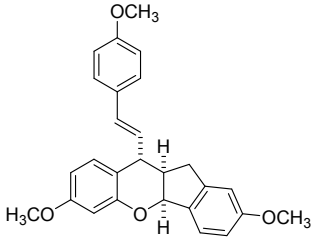
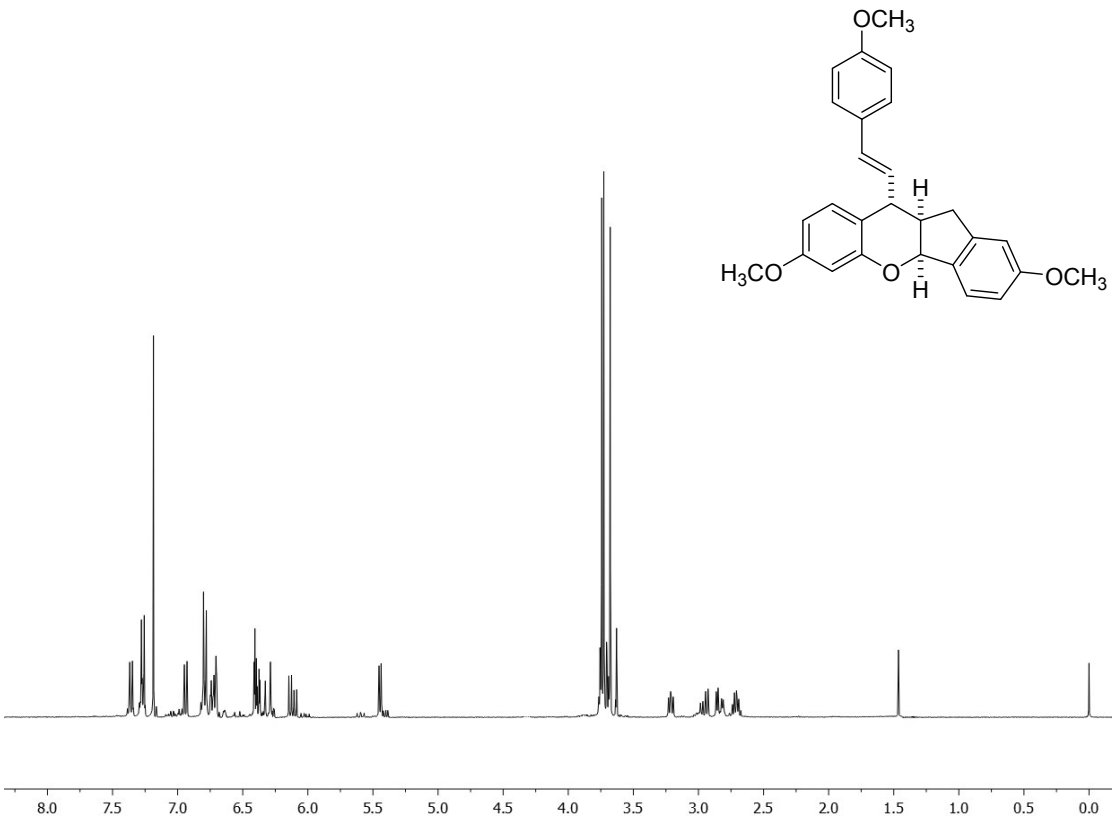
(*E*)-2,7-dimethoxy-10-(4-methoxystyryl)-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (9d)



The crude mixture was purified by flash column chromatography with elution by 98:2, hexanes:EtOAc. **Yield:** 315 mg, 76%. **D.r.:** 7:1. Major **^{1}H NMR** (400 MHz, $CDCl_3$, major diastereomer) δ 7.42 – 6.23 (m, 10H), 6.18 – 6.05 (m, 1H), 5.43 (d, *J* = 13.2, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 3.28 – 3.13 (m, 1H), 3.02 – 2.90 (m, 1H), 2.90 – 2.77 (m, 1H), 2.75 – 2.66 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.48, 159.40, 159.06, 155.54, 144.04, 134.83, 131.26, 129.90, 129.63, 129.36, 127.39, 125.82, 117.18, 113.97, 112.93, 110.26, 107.21, 102.10, 79.90, 55.27, 44.23, 41.25, 35.97. Minor **^{1}H NMR** (400 MHz, $CDCl_3$, minor diastereomer) δ 7.36 – 6.23 (m, 10H), 6.02 (dd, *J* = 15.7, 9.4 Hz, 1H), 5.42 (t, *J* = 10.1 Hz, 1H), 3.87 (m, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.64 (s, 3H), 3.00 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.82 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.68, 159.23, 159.12, 156.04, 145.79, 134.70, 132.18, 129.99, 128.69, 127.53, 127.40, 126.12, 116.76, 114.01, 112.89, 110.04, 107.05, 102.22, 81.31, 55.35, 45.01, 40.25, 32.98. **IR** (thin film, cm^{-1}): 2934, 2834, 1616, 1510, 1464, 1251, 1156, 1122, 1033. **HRMS** *m/z* 415.1909 [$(M + H^+)$ calc'd for $C_{27}H_{26}O_4$: 415.1901].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H
OCH3
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7.0
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4.0
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3.0
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2.0
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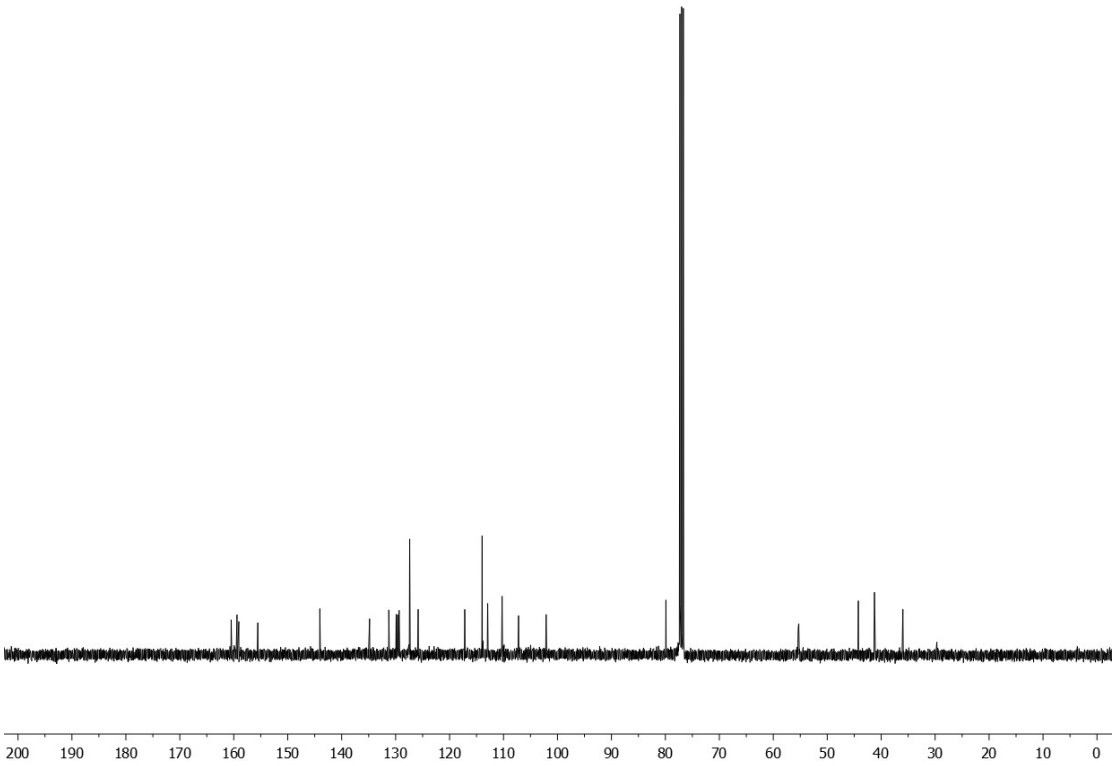
0.0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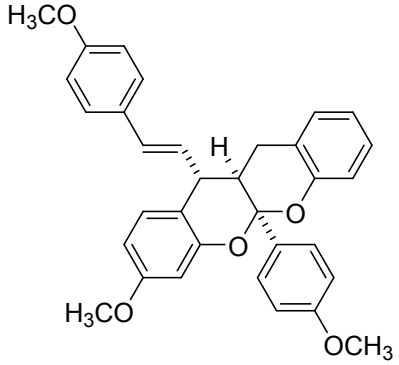
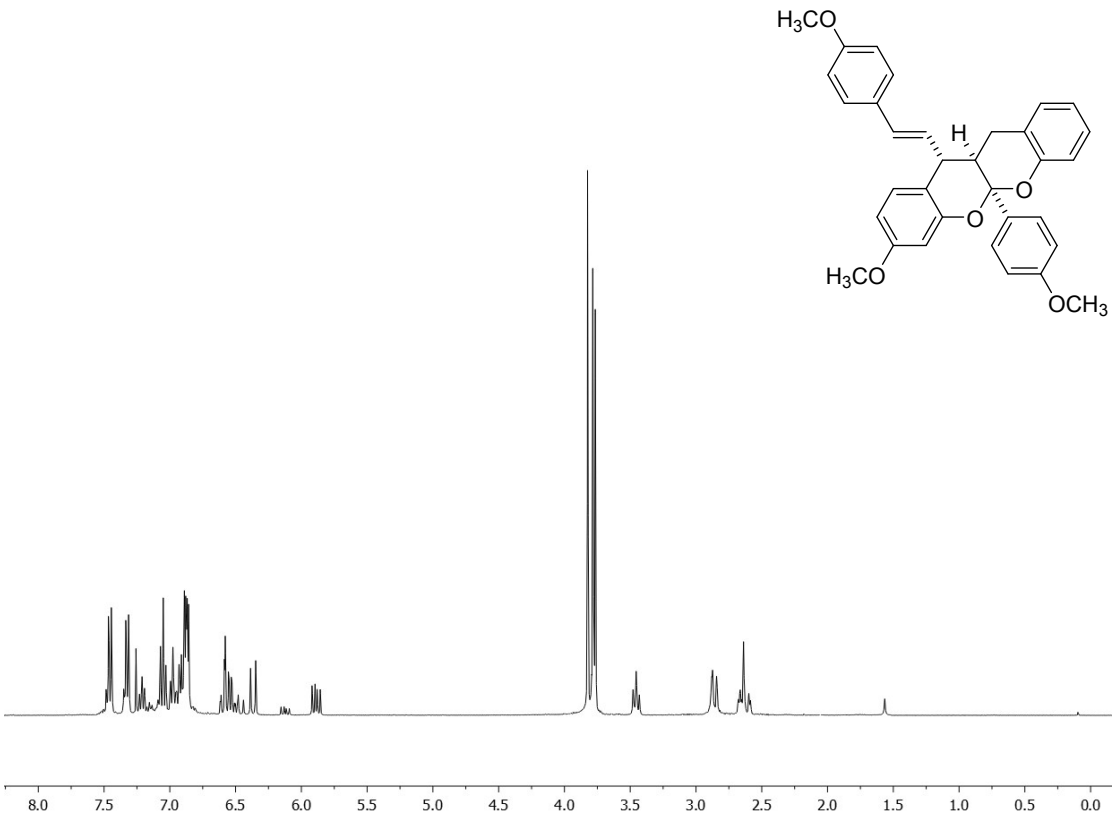
(*E*)-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (9e)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 428 mg, 90%. **D.r.:** 4:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.53 –6.77 (m, 16H), 6.37 (d, *J* = 15.7 Hz, 1H), 5.91 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.51 (dd, *J* = 9.9 Hz, 9.9 Hz, 1H), 2.91 – 2.56 (m, 3H). Minor: δ 7.53 – 6.77 (m, 16H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.15 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.51 (m, 1H), 2.91 – 2.56 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 159.91, 159.85, 159.33, 159.28, 152.97, 152.35, 151.81, 151.46, 133.74, 133.52, 132.76, 132.52, 129.62, 129.57, 129.36, 129.10, 128.71, 128.07, 128.03, 127.82, 127.53, 127.50, 127.46, 127.28, 127.22, 125.85, 123.67, 122.24, 121.68, 121.57, 121.37, 121.12, 119.36, 117.13, 116.98, 116.55, 116.48, 114.09, 114.07, 113.99, 113.86, 101.09, 100.83, 55.36, 55.26, 42.24, 40.08, 38.11, 37.19, 27.43, 23.19. **IR** (thin film, cm^{-1}): 3008, 2933, 2836, 1609, 1584, 1512, 1486, 1455, 1249, 1177, 1054, 754. **HRMS** *m/z* 507.2171 [(M + H^+) calc'd for $C_{32}H_{28}O_4H^+$: 507.2165].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H
O
O
H3CO
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7.0
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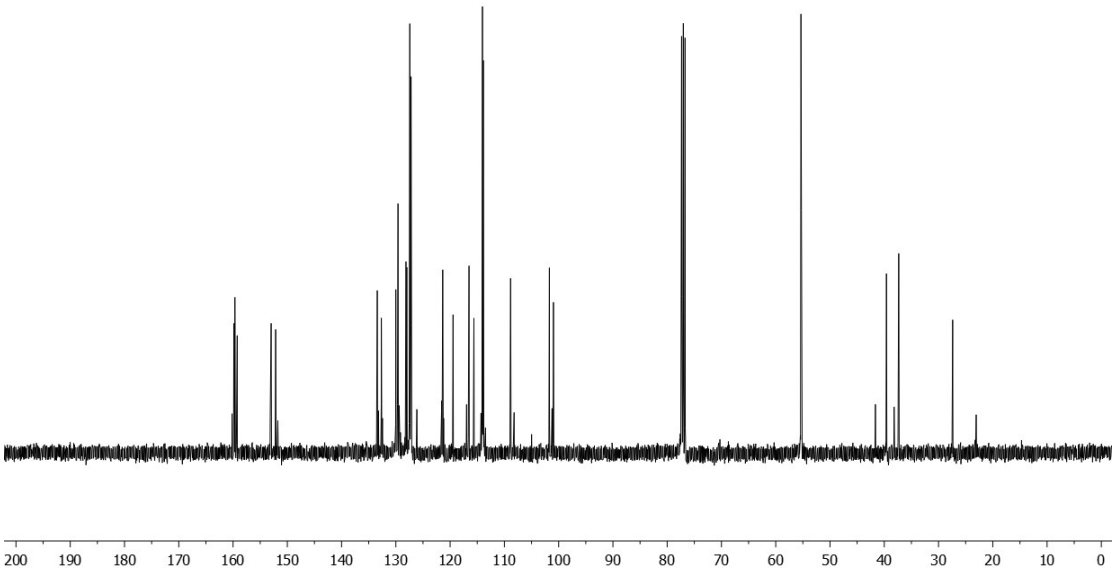
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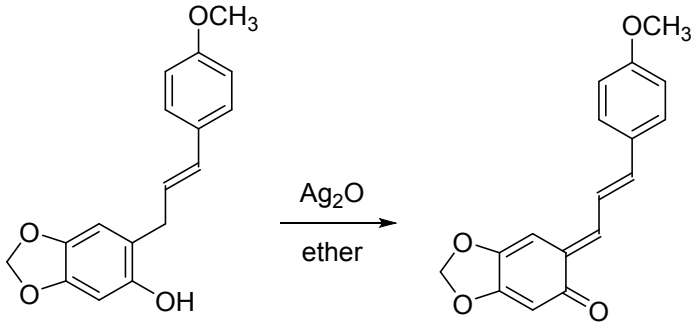
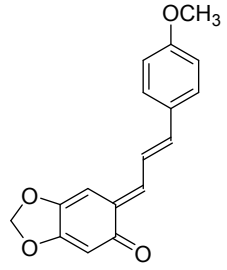
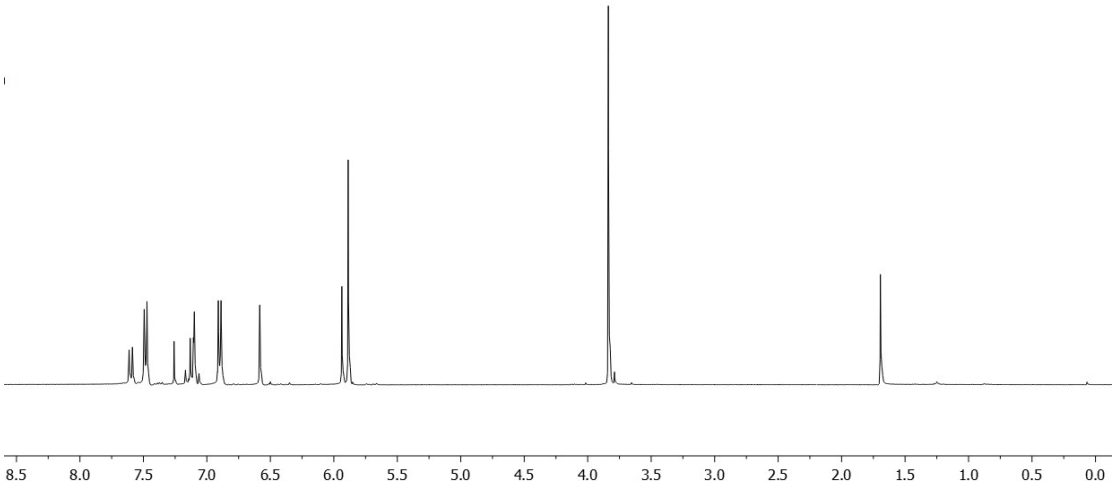
Preparation of vinyl *ortho*-quinone methide (*E*)-8



Modified Jurd synthesis[1] of *ortho*-quinone methide. A solution of (*E*)-6-(3-(4-methoxyphenyl) allyl)benzo[d][1,3]dioxol-5-ol (1.0 g) in ether (50 mL) was added silver oxide (3.0g) then stirred overnight. The solution was filtered, then concentrated to 20 mL, cooled, and red crystals were collected (0.54g). The product is acid and heat sensitive.

[1] L. Jurd, *Tetrahedron* **1977**, *33*, 163–168.


OCH3
O
O
O


8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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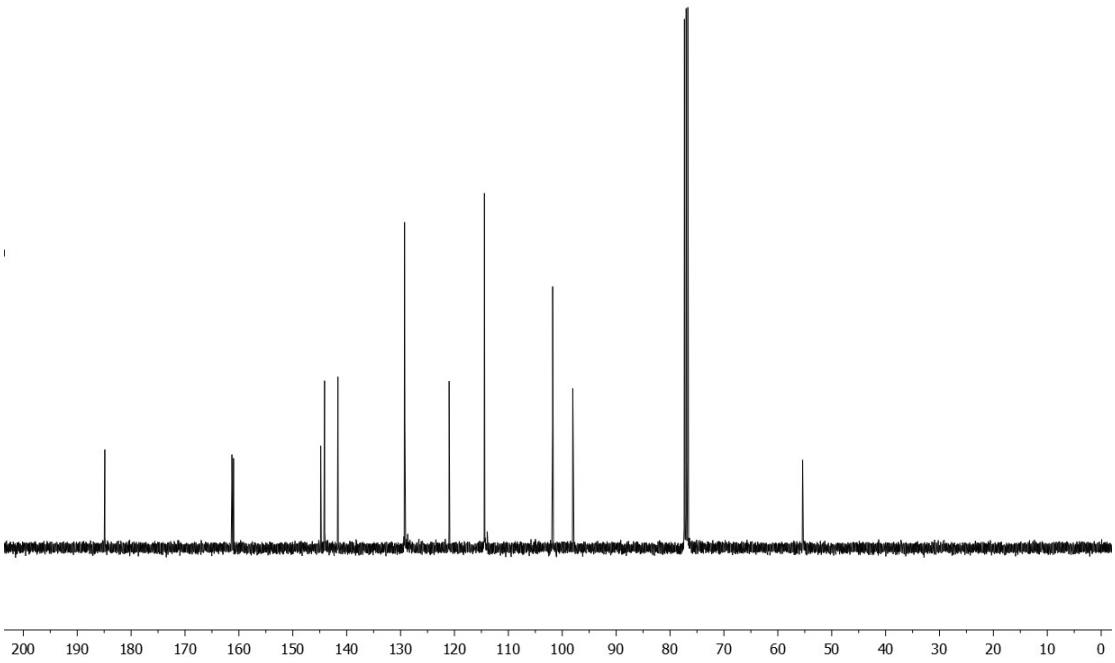
3.0
2.5
2.0
1.5
1.0
0.5
0.0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