Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Homo-dimerization of 2*H*-Chromenes catalyzed by Brønsted-acid derived UiO-66 MOF

Zongcheng Miao,[a] Zihao Zhou,[b] Houliang Tang,[c] Mengdie Yu,[b] Daniele Ramella,[d] Xin Du [b,*] and Yi Luan,[b,*]

[a] *Key Laboratory of Organic Polymer Photoelectric Materials, School of Science, Xijing University, Xi'an, Shaanxi Province, 710123, PR China*

[b] *School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, P. R. China, E-mail: yiluan@ustb.edu.cn.*

[c] *Department of Chemistry, Southern Methodist University, 3215 Daniel Avenue, Dallas, 75275, TX, USA*

[d] *Temple University-Beury Hall, 1901, N. 13th Street Philadelphia PA 19122, United States.*

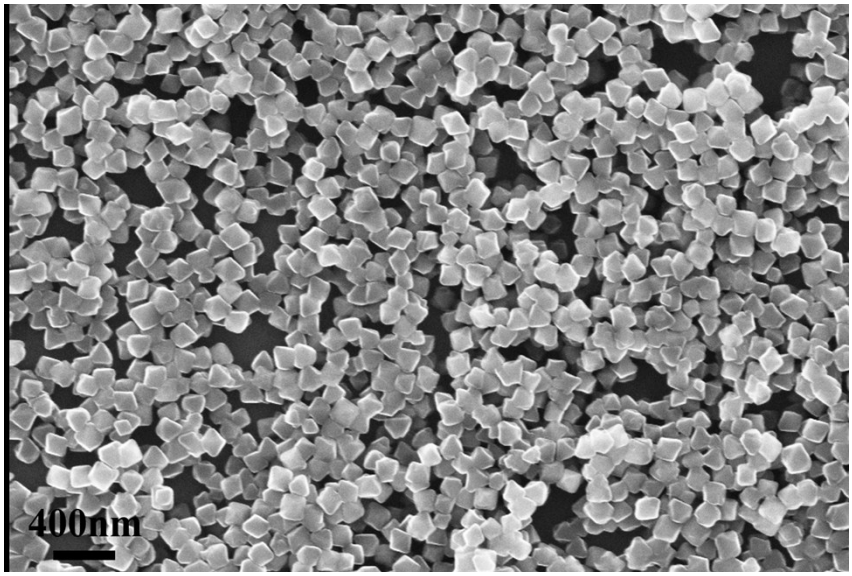


Fig. S1 SEM image of UiO-66-NH_2.

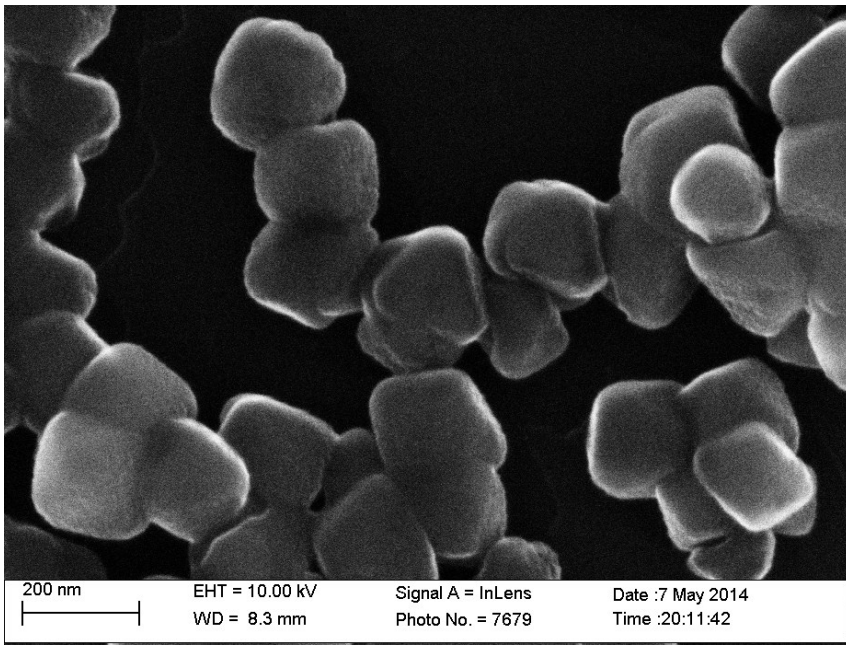


Fig S2 SEM of recycled UiO-66-$ArSO_3H$.

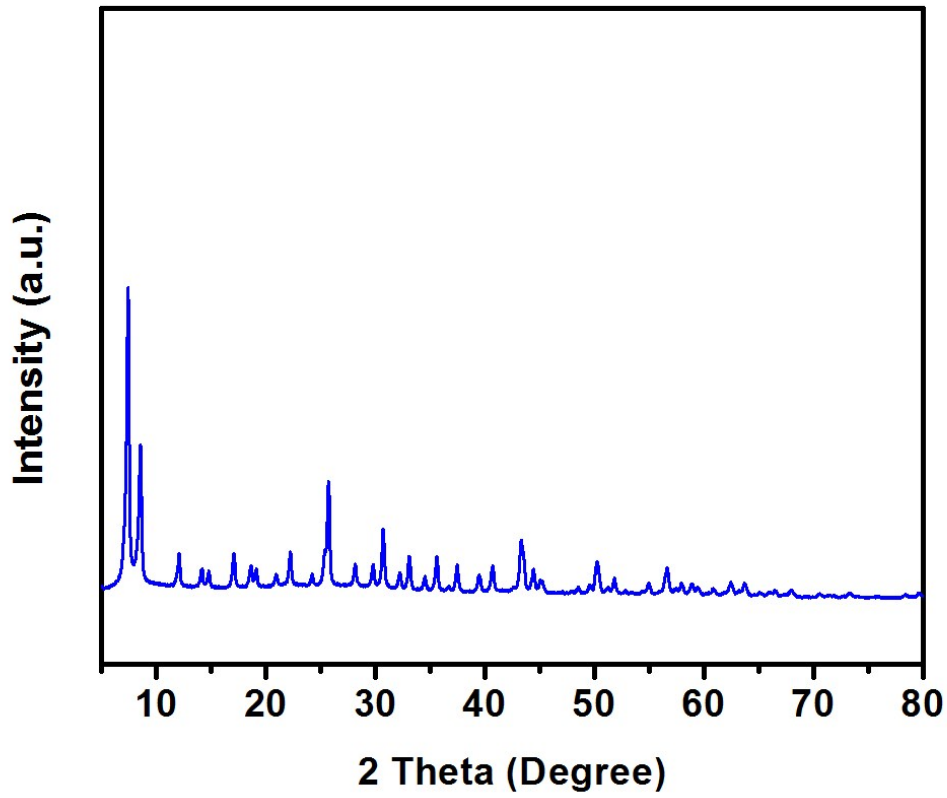


Fig. S3 Powder XRD patterns of recycled UiO-66-ArSO_3H.

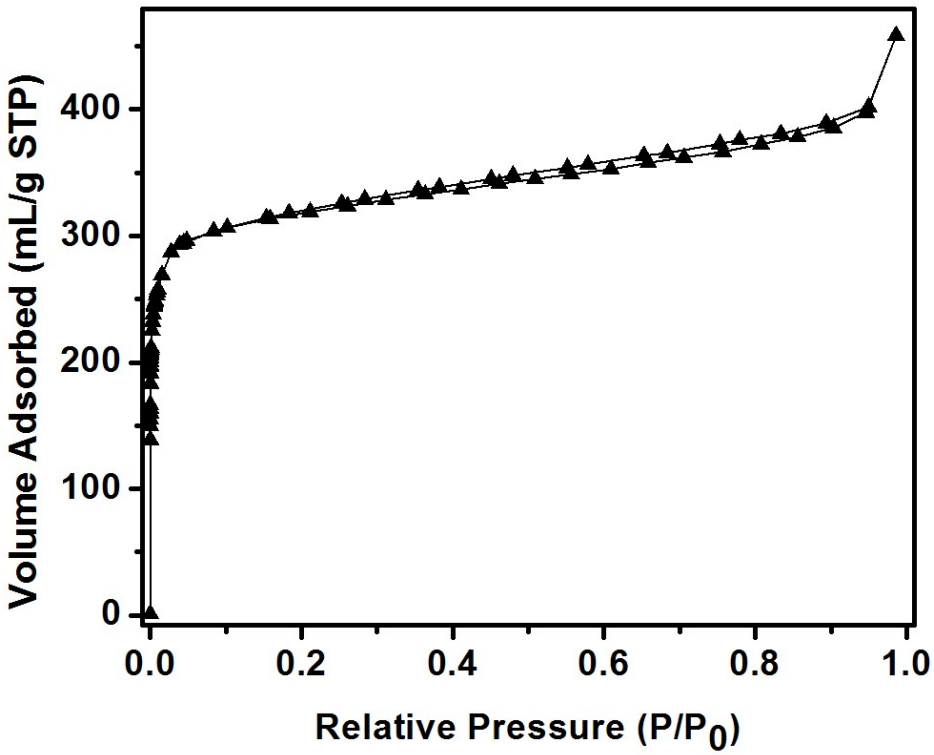


Fig. S4 N_2 adsorption/desorption isotherms of UiO-66-NH_2.

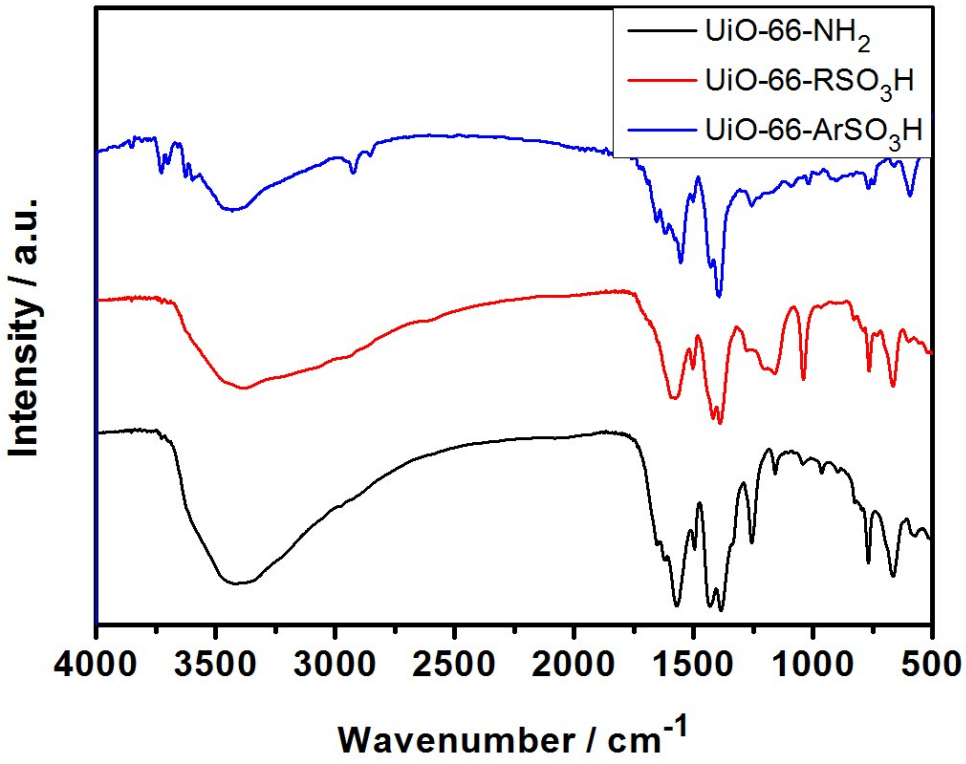


Fig. S5 FTIR UiO-66-NH_2, UiO-66-RSO_3H, UiO-66-$ArSO_3H$.

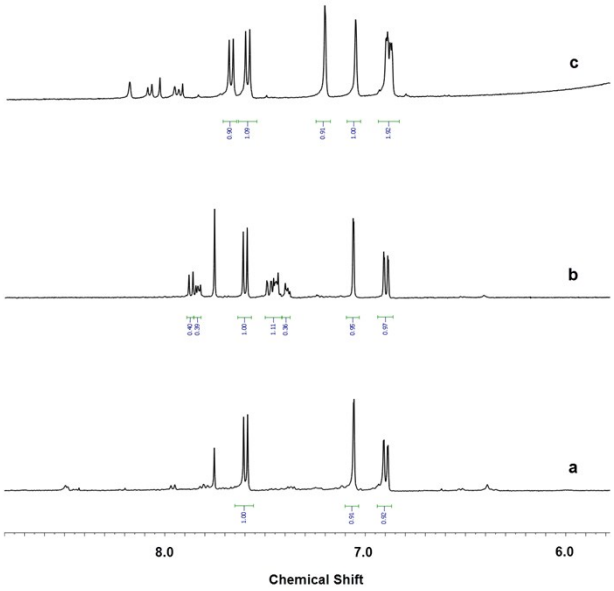


Fig. S6 ^{1}H NMR spectra of digested (a) UiO-66-NH_2, (b) UiO-66-RSO_3H and (c) UiO-66-$ArSO_3H$.

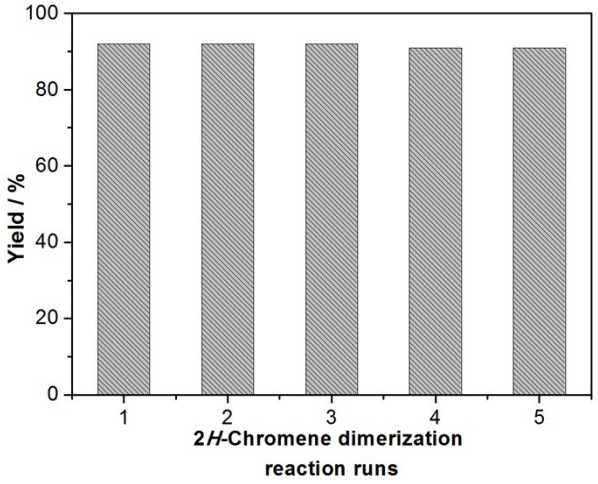
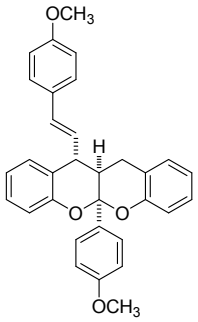
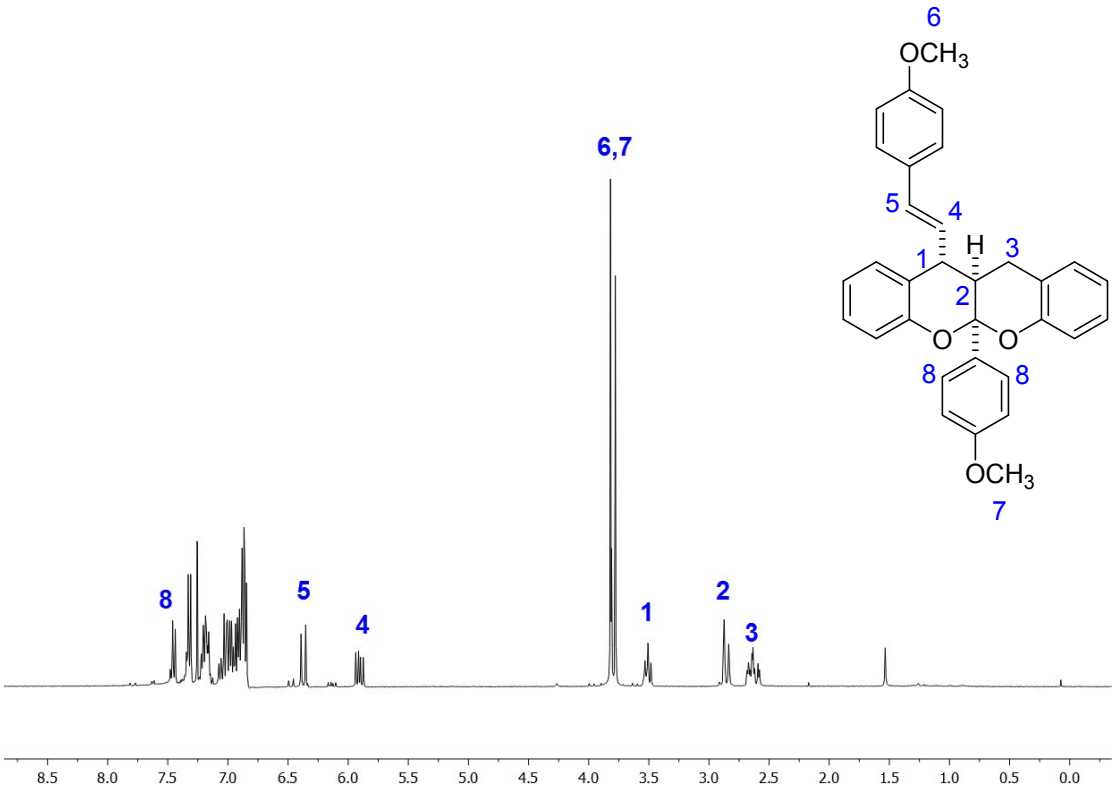


Fig. S7 UiO-66-$ArSO_3H$ catalyst recycling test using chromene **1a**.

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



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 219 mg, 92%. **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. **LRMS** *m/z* 477 [(M + H^+) calc'd for $C_{32}H_{28}O_4H^+$: 477].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OCH3
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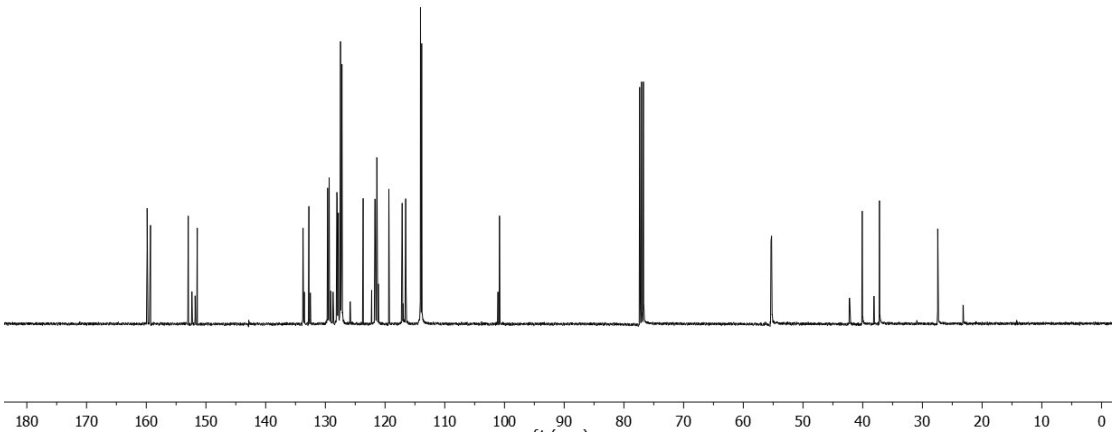
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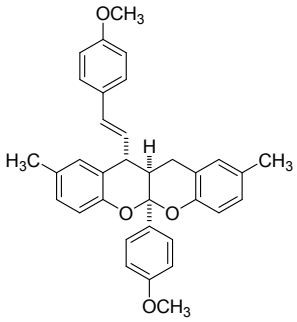
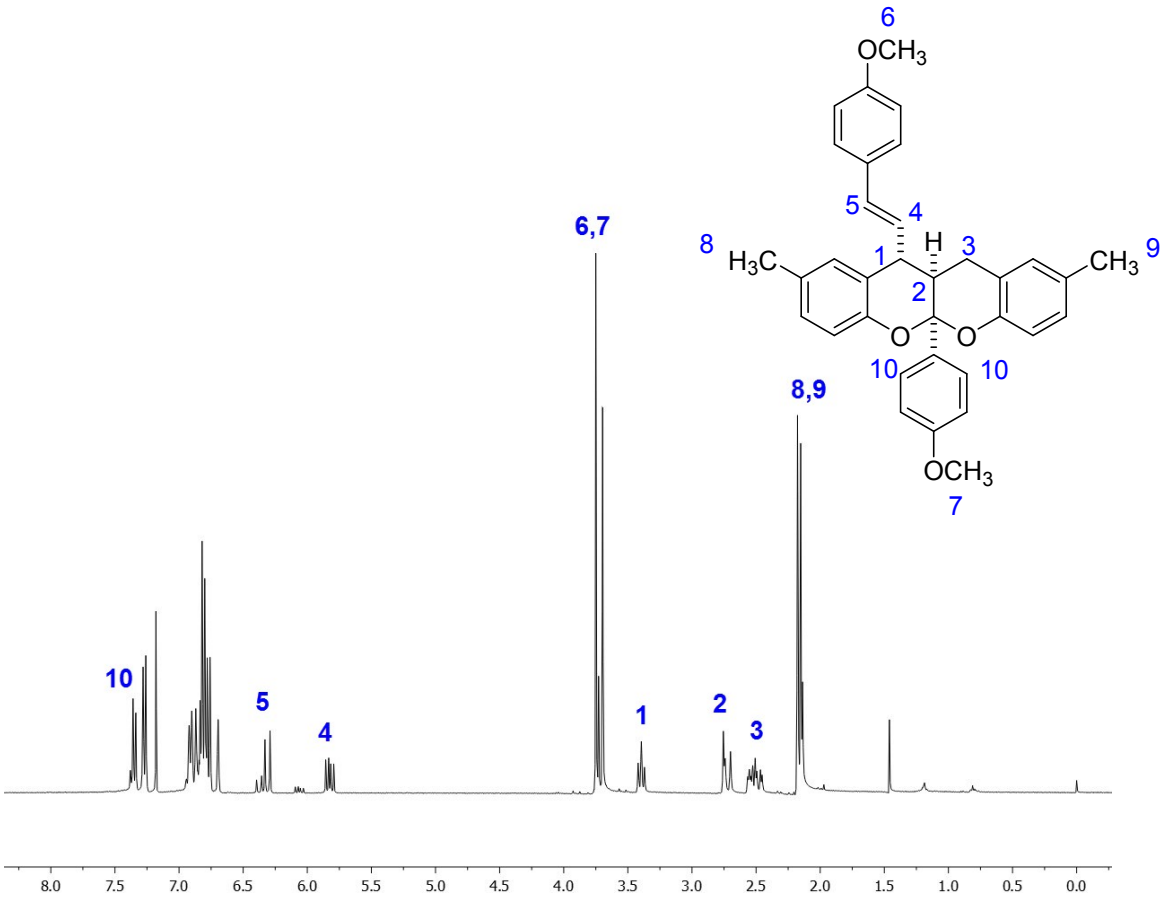
(*E*)-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-2,9-dimethyl-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2b)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 234 mg, 93%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.37 – 6.73 (m, 14H), 6.31 (d, *J* = 15.7 Hz, 1H), 5.82 (dd, *J* = 15.7, 9.4 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.39 (dd, 1H), 2.86 – 2.65 (m, 1H), 2.59 – 2.40 (m, 2H). Minor: δ 7.37 – 6.73 (m, 14H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.06 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.39 (dd, 1H), 2.86 – 2.65 (m, 1H), 2.59 – 2.40 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 159.75, 159.24, 150.82, 150.19, 149.27, 133.45, 133.25, 132.95, 132.72, 130.88, 130.69, 130.50, 130.42, 129.92, 129.66, 129.56, 129.29, 128.67, 128.61, 128.14, 128.09, 127.47, 127.29, 127.24, 126.14, 123.31, 121.83, 120.81, 118.97, 116.89, 116.68, 116.25, 114.05, 113.92, 113.80, 100.96, 100.68, 55.37, 55.24, 42.28, 40.17, 38.27, 37.28, 27.42, 23.23, 20.64, 20.58, 20.55. **LRMS** *m/z* 505 [(M + H^+) calc'd for $C_{32}H_{32}O_4H^+$: 505]. **IR** (thin film, cm^{-1}): 3031, 2898, 1608, 1512, 1495, 1250, 1176, 1034.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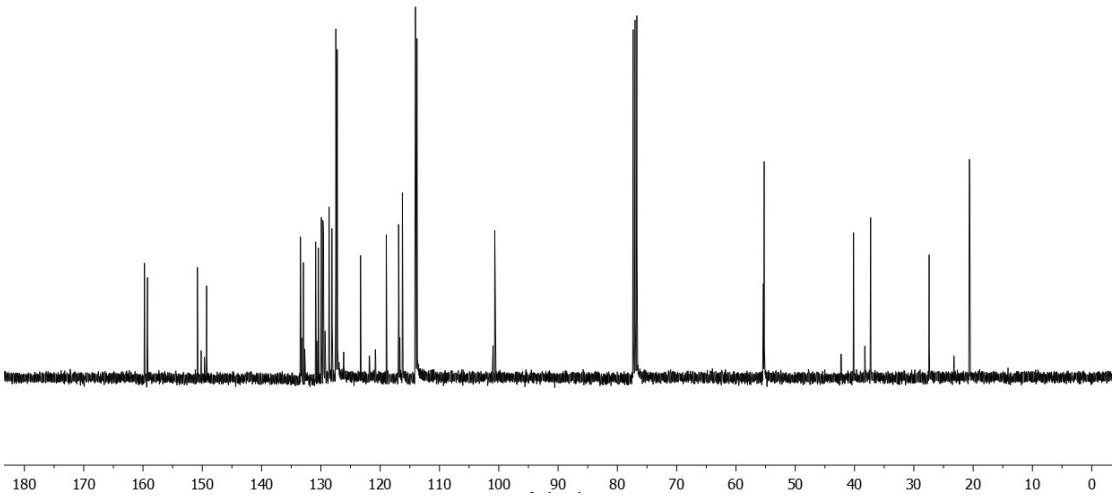
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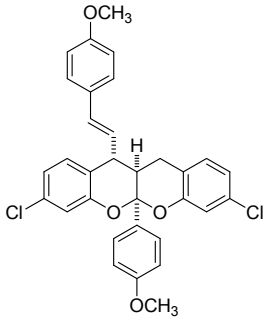
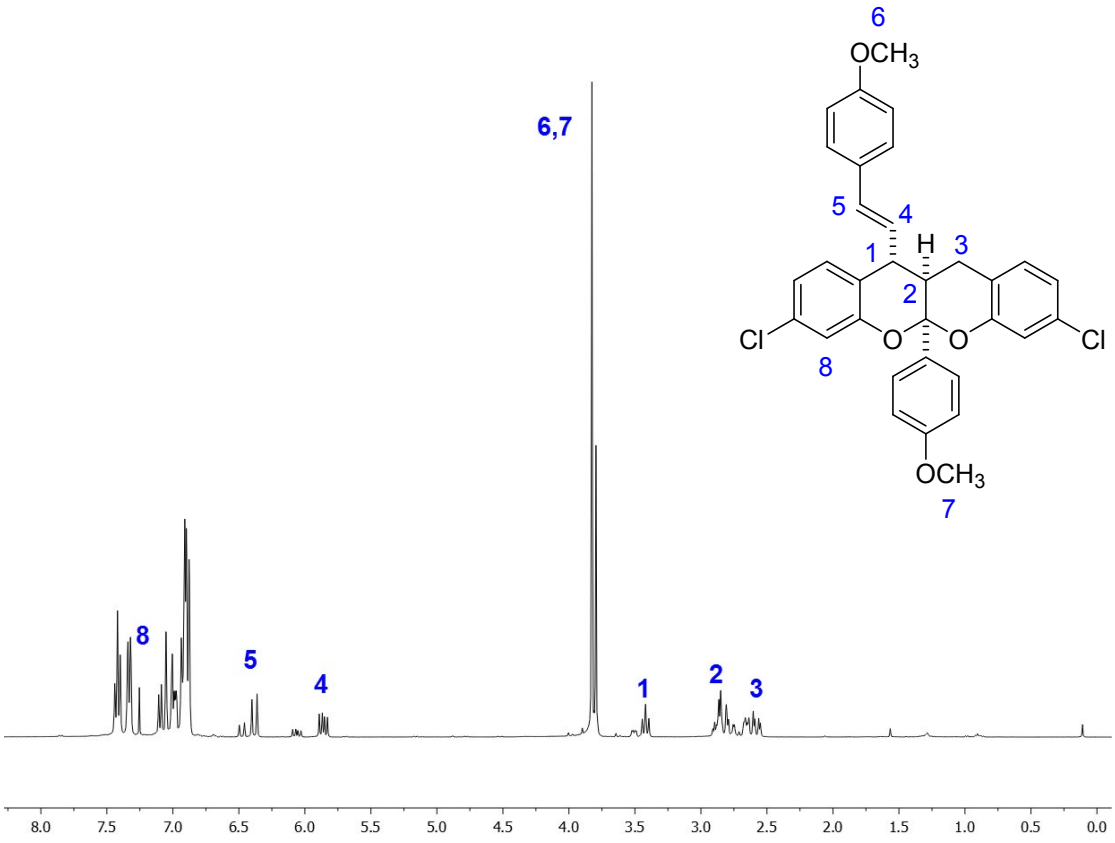
(*E*)-3,8-dichloro-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2c)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 248 mg, 91%. **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. **LRMS** *m/z* 545 [$(M + H^+)$ calc'd for $C_{32}H_{26}Cl_2O_4H^+$: 545]. **IR** (thin film, cm^{-1}): 3009, 2957, 2934, 2837, 1607, 1577, 1512, 1484, 1409, 1296, 1252, 1177, 1033, 998, 758.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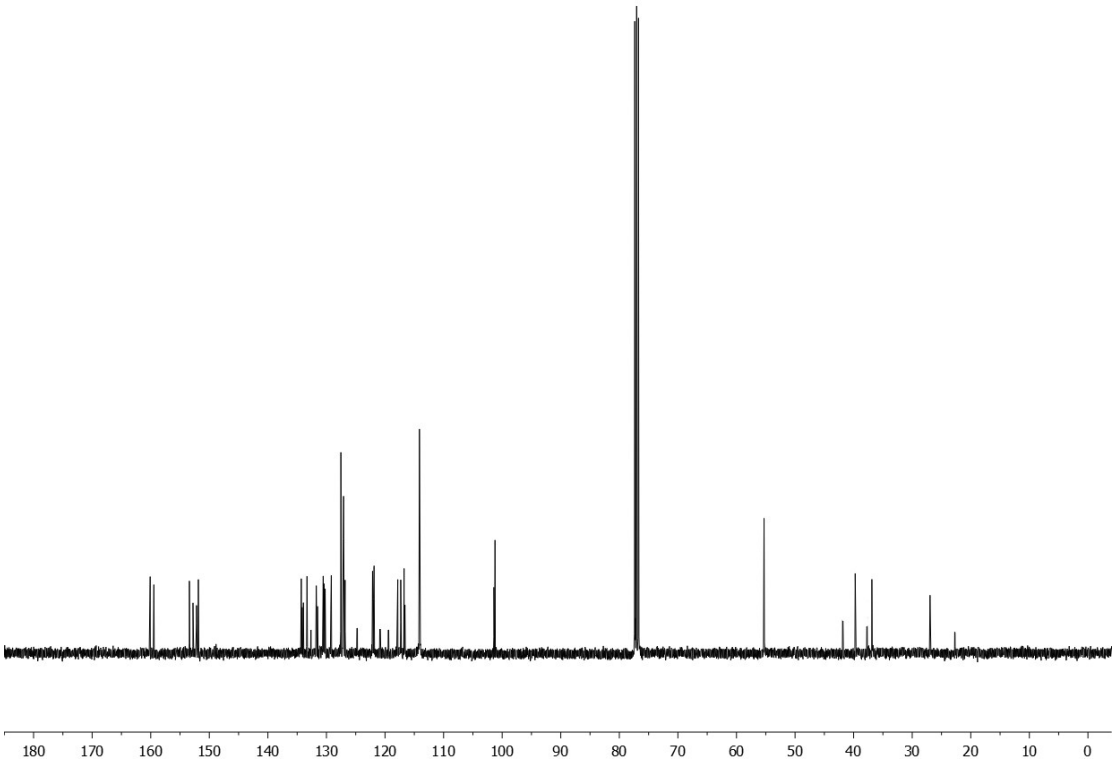
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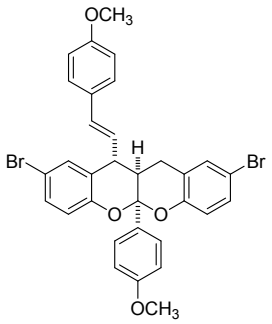
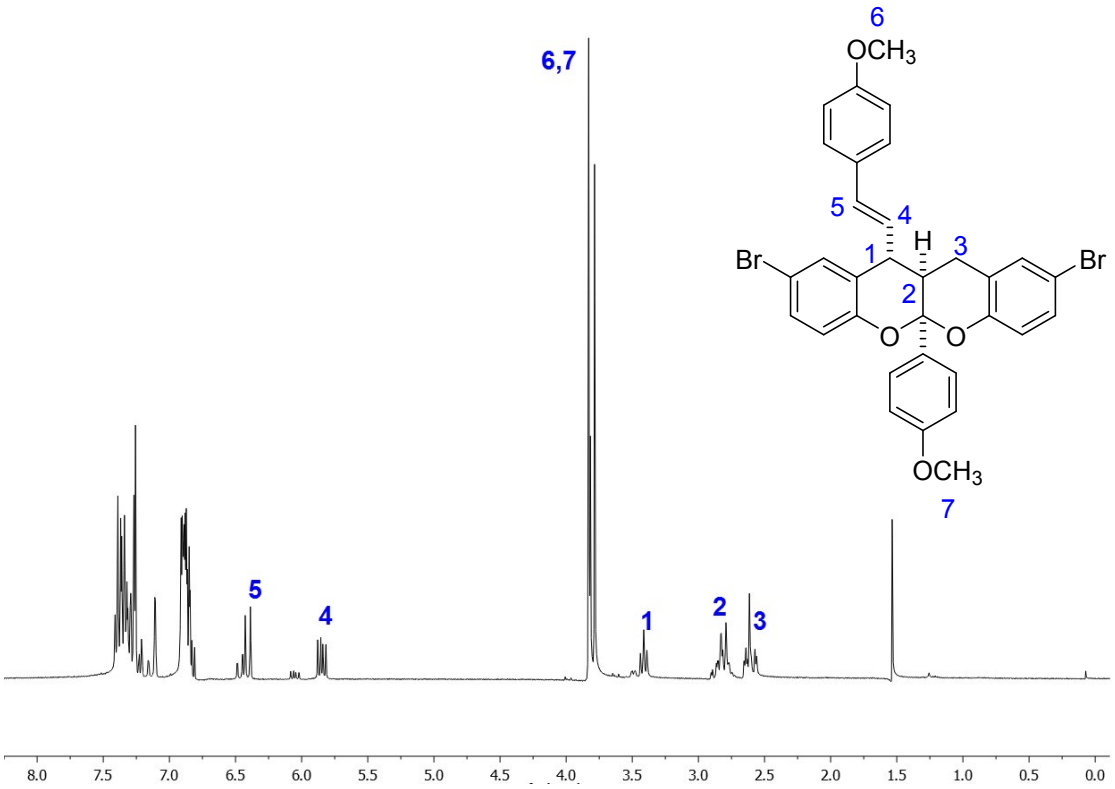
(*E*)-2,9-dibromo-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2d)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 279 mg, 82%. **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. **LRMS** *m/z* 633 [$(M + H^+)$ calc'd for $C_{32}H_{26}Br_2O_4H^+$: 633].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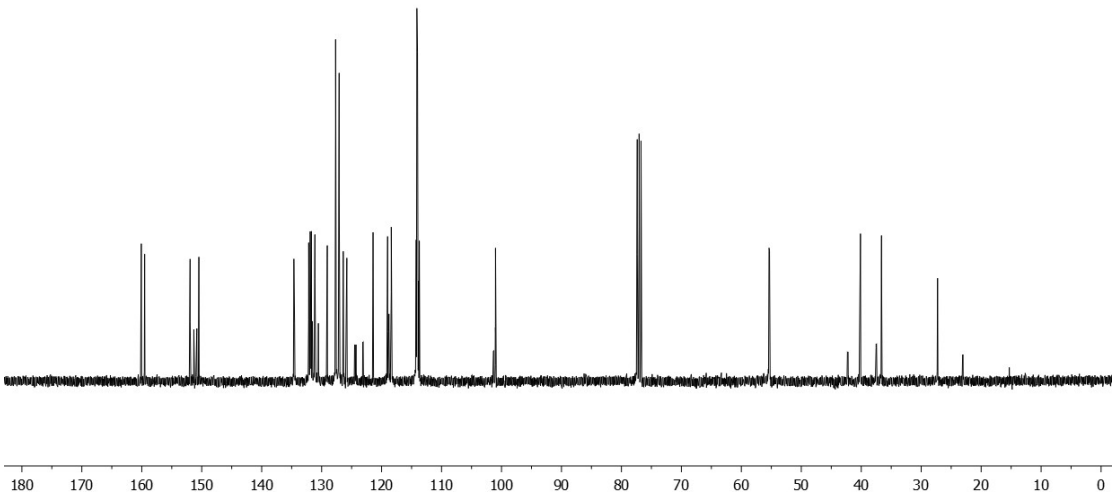
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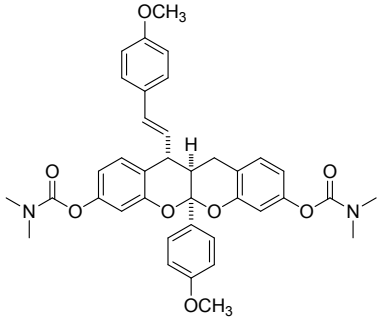
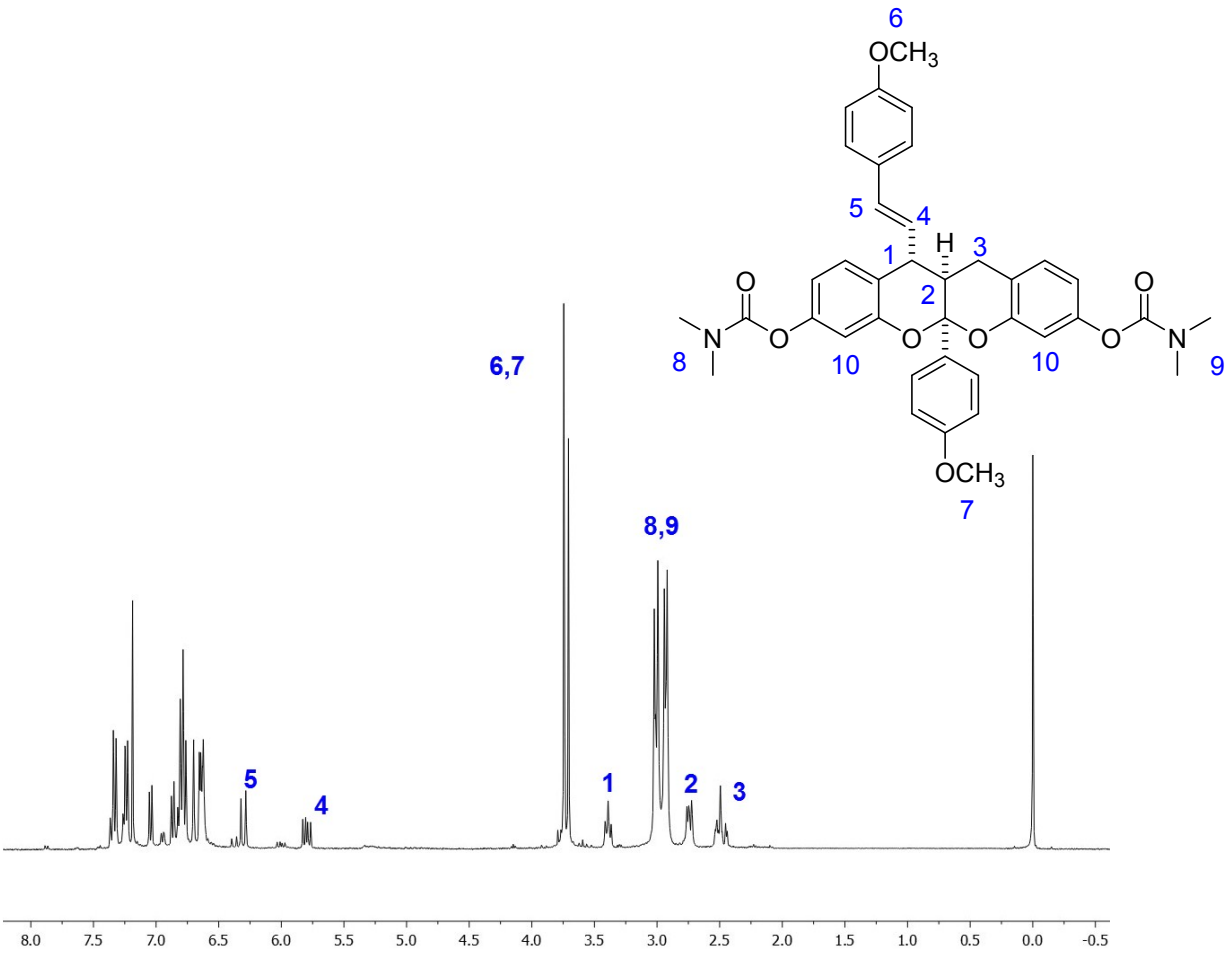
(*E*)-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene-3,8-diyl bis(dimethylcarbamate) (2e)



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 266 mg, 82%. **D.r.:**5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.47 – 6.51 (m, 14H), 6.30 (d, *J* = 15.6 Hz, 1H), 5.80 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.39 (dd, 1H), 3.01 (d, 6H), 2.93 (d, 6H), 2.82 – 2.64 (m, 1H), 2.64 – 2.34 (m, 2H). Minor: δ 7.47 – 6.51 (m, 14H), 6.28 (d, *J* = 15.6 Hz, 1H), 6.03 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.39 (dd, 1H), 3.01 (d, 6H), 2.93 (d, 6H), 2.82 – 2.64 (m, 1H), 2.64 – 2.34 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 158.84, 158.25, 153.80, 153.74, 152.28, 150.74, 150.25, 150.11, 132.74, 131.44, 131.16, 128.79, 128.48, 126.57, 126.48, 126.43, 126.24, 126.16, 119.52, 118.07, 115.13, 114.27, 114.06, 113.04, 112.93, 112.80, 109.52, 108.81, 108.70, 100.26, 100.06, 54.33, 54.24, 38.55, 36.18, 35.67, 35.43, 25.82. **IR** (thin film, cm^{-1}): 2934, 1732, 1718, 1685, 1558, 1508, 1250, 1165. **LRMS** *m/z* 651 [(M + H^+) calc'd for $C_{38}H_{38}N_2O_8H^+$: 651].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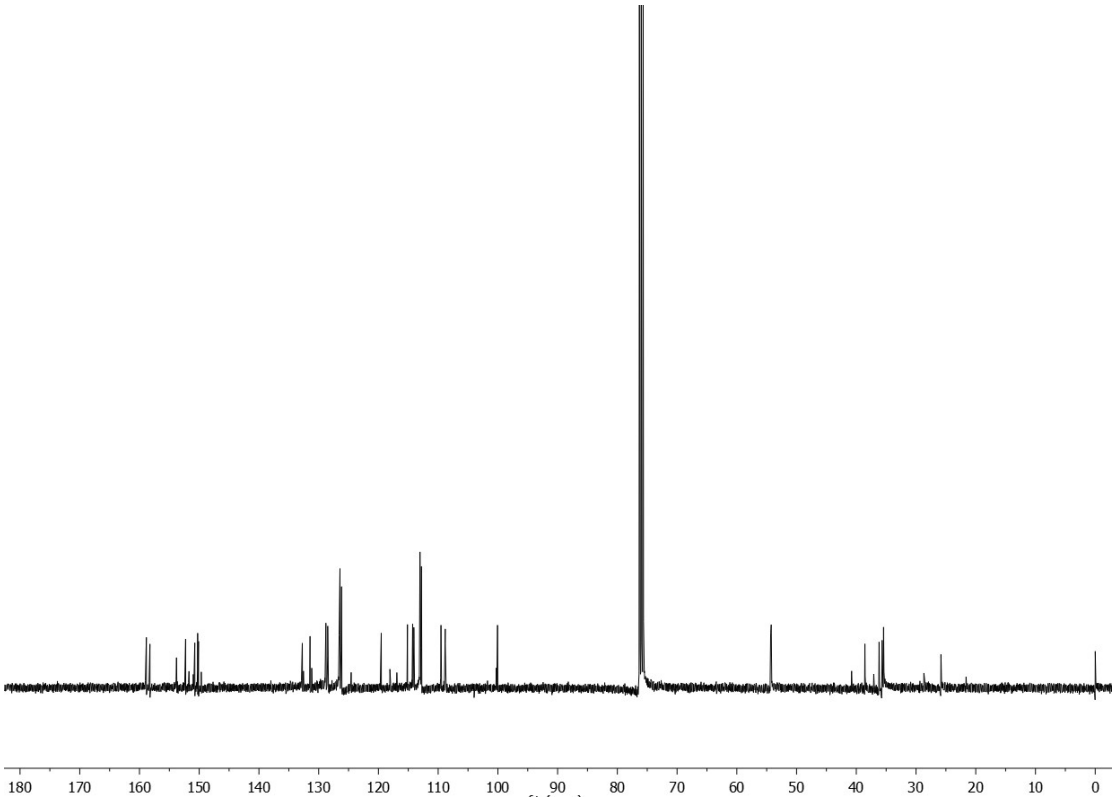
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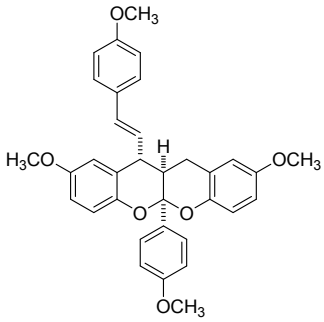
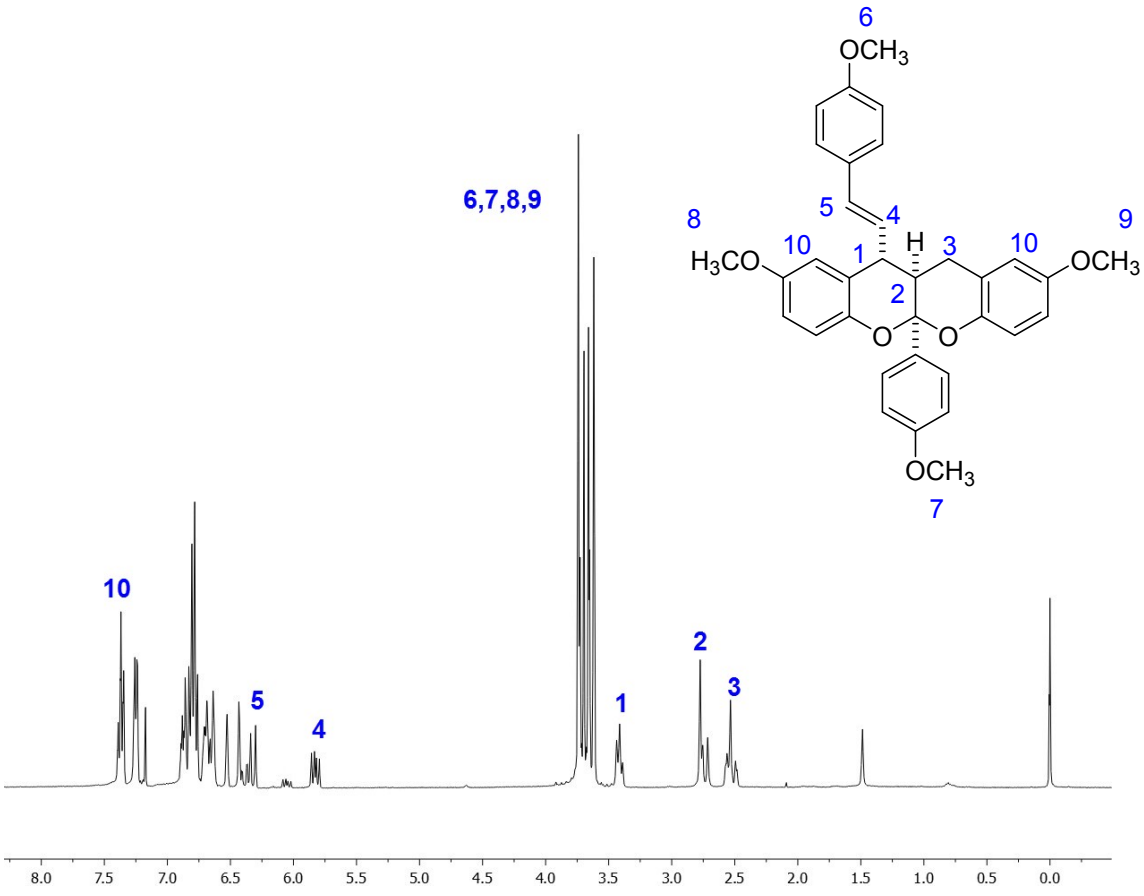
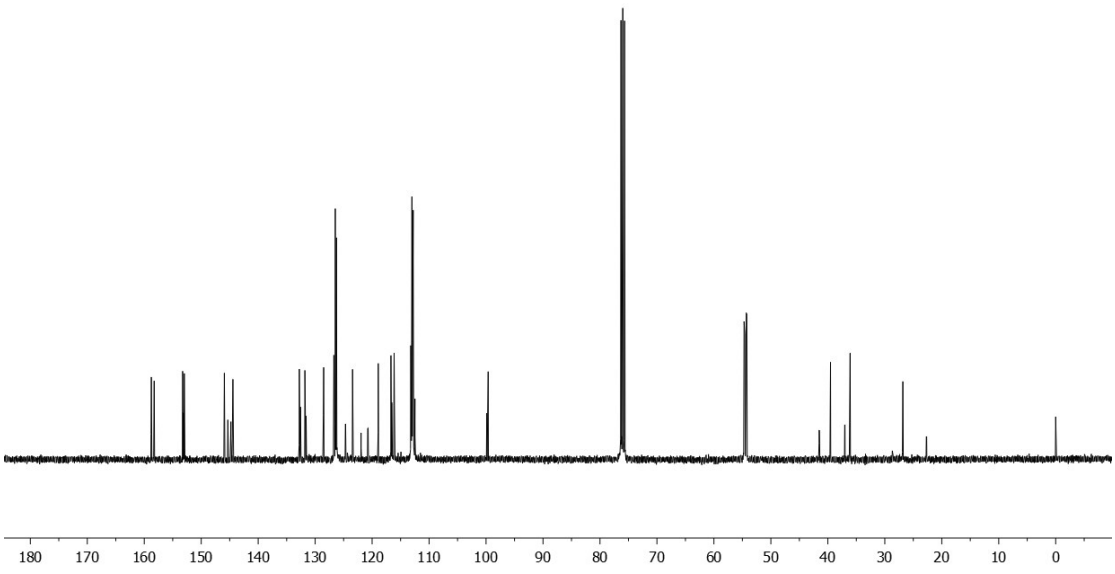
(*E*)-2,9-dimethoxy-5a-(4-methoxyphenyl)-11-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b]chromene (2f)

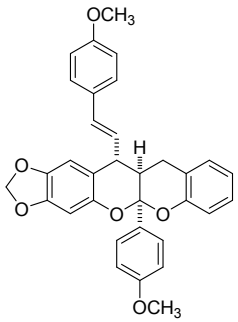


The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 257 mg, 96%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.46 – 6.27 (m, 14H), 6.32 (d, *J* = 15.6 Hz, 1H), 5.83 (dd, *J* = 15.7, 9.4 Hz, 4H), 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. **LRMS** *m/z* 537 [(M + Na^+) calc'd for $C_{34}H_{32}O_6H^+$: 537].

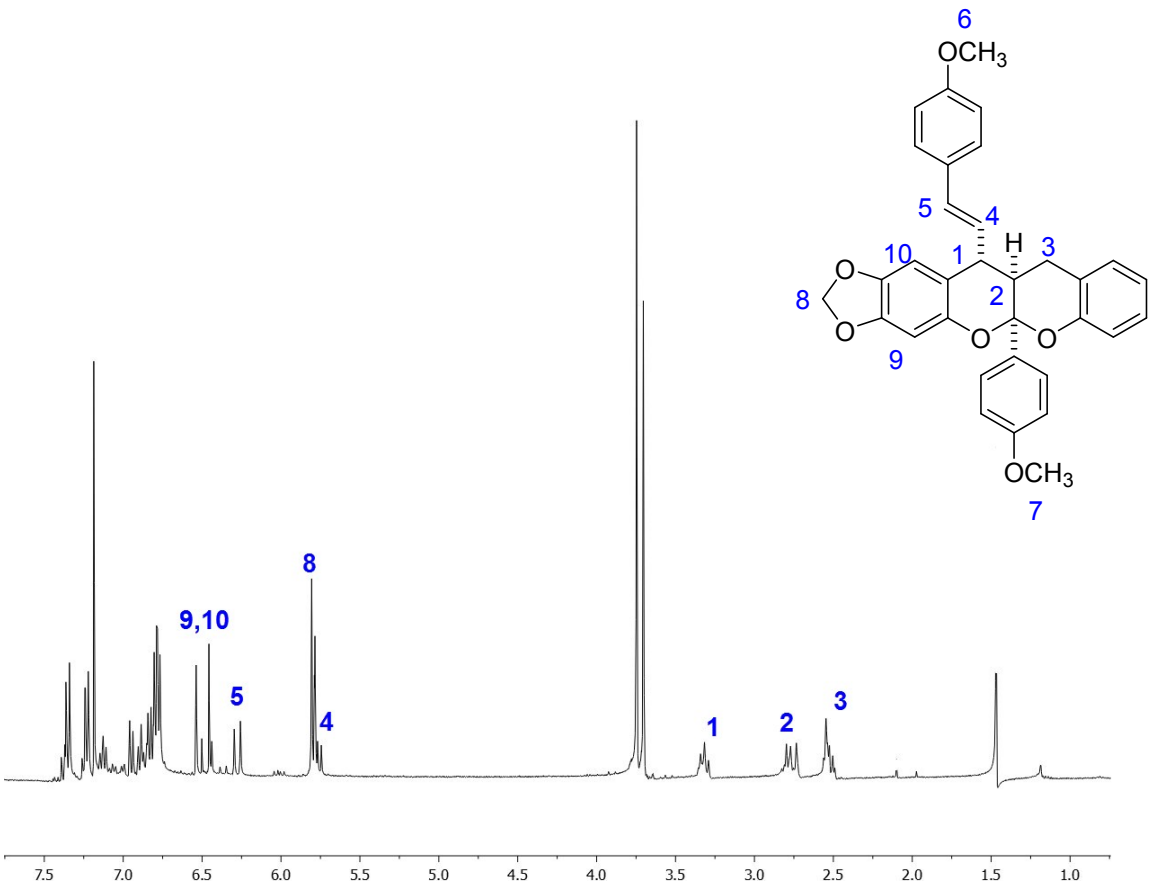

6
OCH3
5
4
8
10
1
H
3
10
9
H3CO
2
OCH3
O
O
OCH3
7
6,7,8,9
10
5
4
1
2
3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

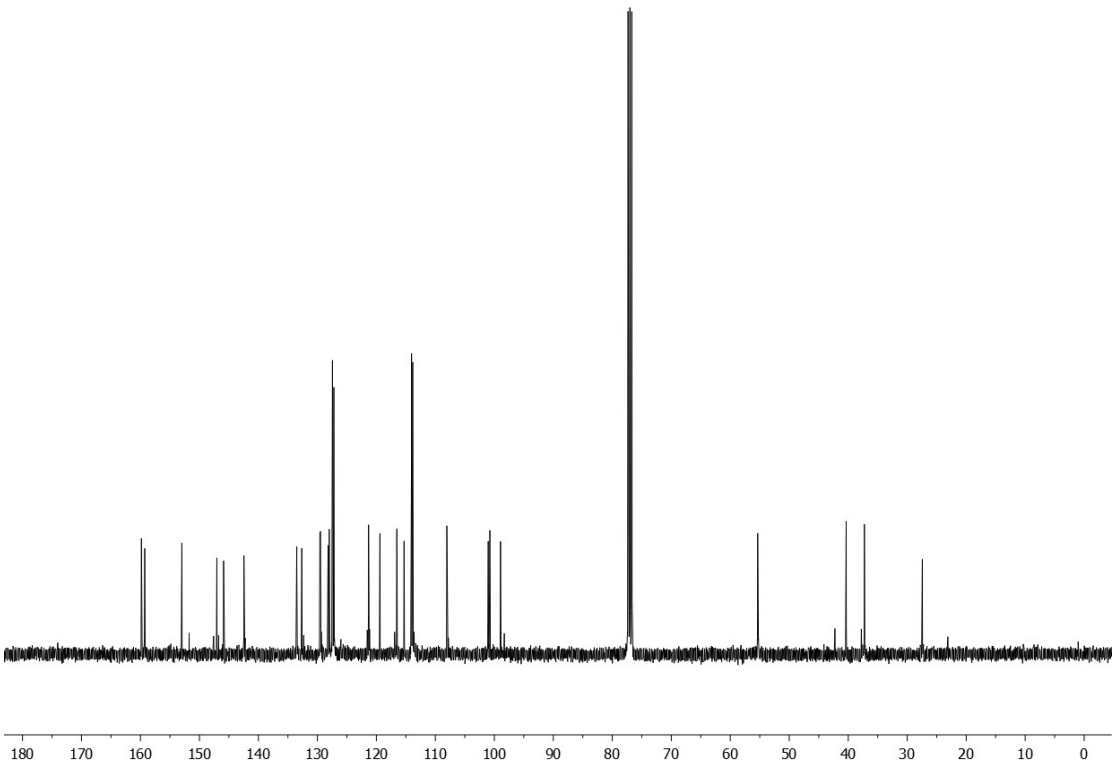

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

(*E*)-5a-(4-methoxyphenyl)-12-(4-methoxystyryl)-5a,11,11a,12-tetrahydrochromeno[2,3-b][1,3]dioxolo[4,5-g]chromene (8)

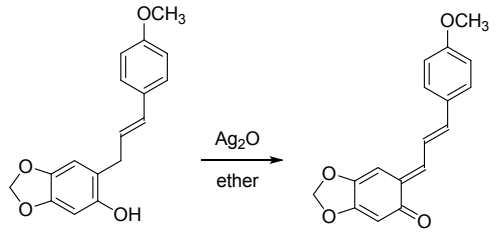


The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 239 mg, 95%. **D.r.:** 5:1. **^{1}H NMR** (400 MHz, $CDCl_3$, both diastereomers reported) Major: δ 7.53 – 6.41 (m, 15H), 6.29 (d, *J* = 15.7 Hz, 1H), 5.76 (dd, *J* = 15.6, 9.5 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.31 (d, 1H), 2.78 (m, 1H), 2.66 – 2.42 (m, 2H). Minor: δ 7.53 – 6.41 (m, 15H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.01 (dd, *J* = 15.6, 9.5 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.31 (d, 1H), 2.78 (m, 1H), 2.66 – 2.42 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, both diastereomers reported) δ 159.83, 159.27, 152.97, 151.72, 147.59, 147.04, 146.74, 145.90, 142.45, 142.25, 133.50, 133.38, 132.64, 132.32, 129.58, 129.52, 129.46, 129.34, 128.17, 127.99, 127.48, 127.44, 127.28, 127.21, 121.55, 121.32, 121.15, 119.39, 116.91, 116.52, 115.30, 114.04, 113.94, 113.83, 113.59, 108.05, 107.80, 101.10, 101.04, 100.75, 98.95, 98.31, 55.34, 55.25, 42.25, 40.34, 37.77, 37.25, 27.43, 23.05. **IR** (thin film, cm^{-1}): 2932, 1609, 1511, 1480, 1250, 1178, 1152, 1036, 754. **MS** *m/z* 521 [$(M + Na^+)$ calc'd for $C_{33}H_{28}O_6$: 521].


6
OCH3
5
4
H
3
10
1
2
8
O
O
O
O
9
OCH3
7
8
9,10
5
4
1
2
3
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

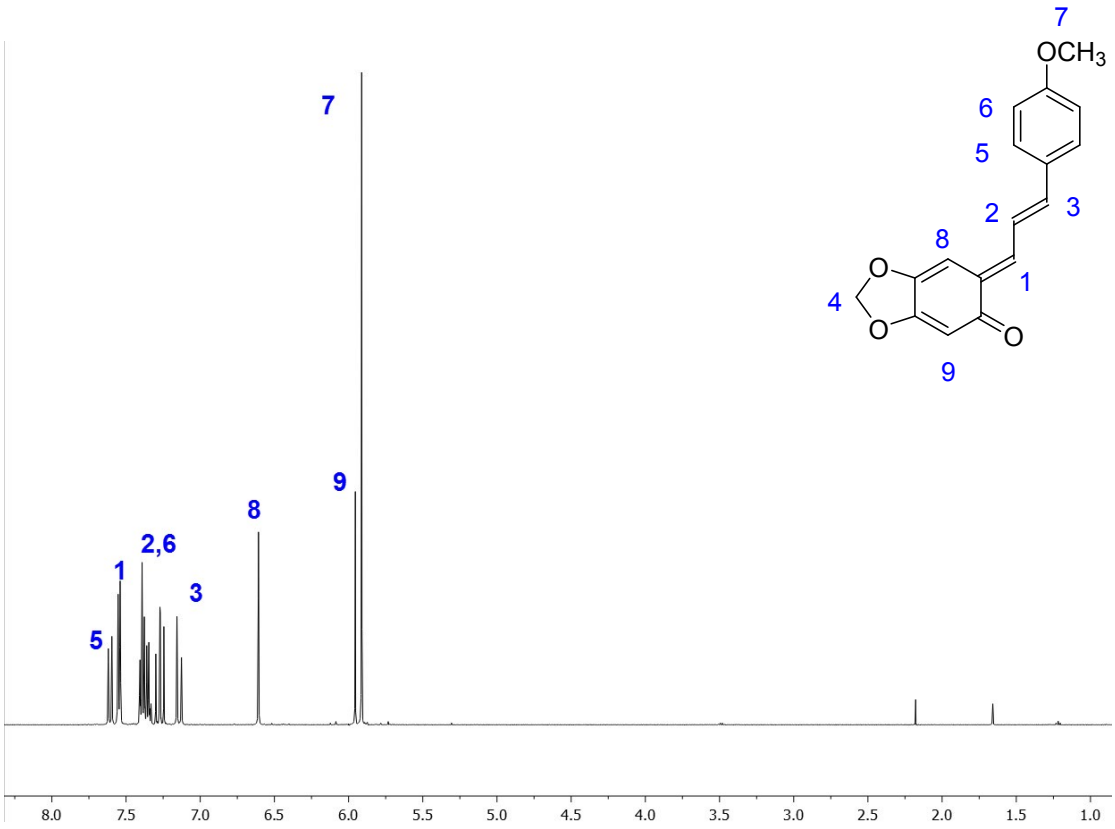

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

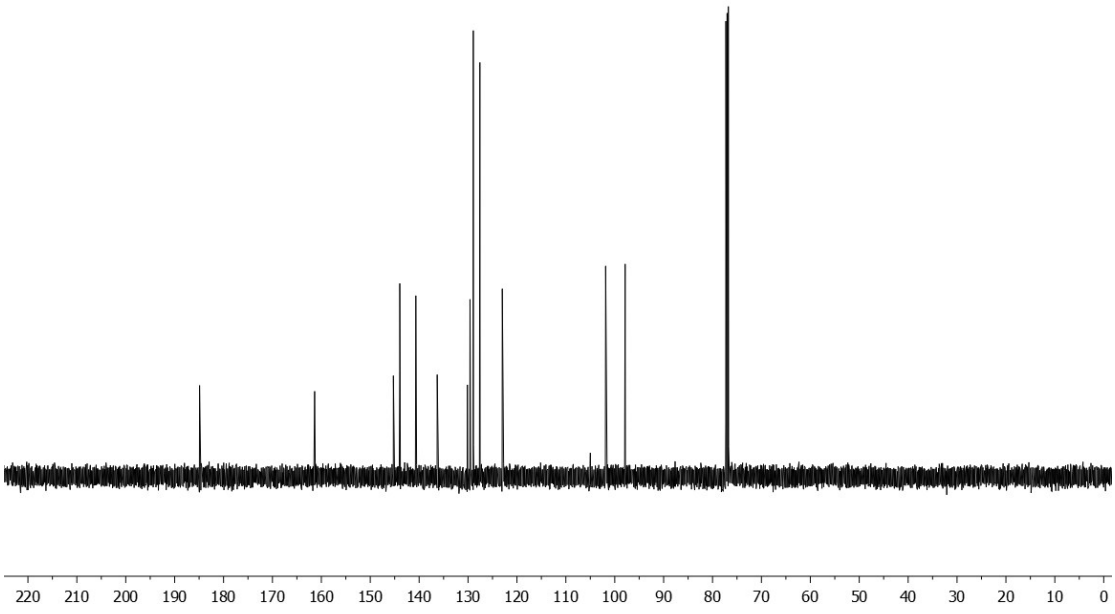
Preparation of vinyl *ortho*-quinone methide (*E*)-8



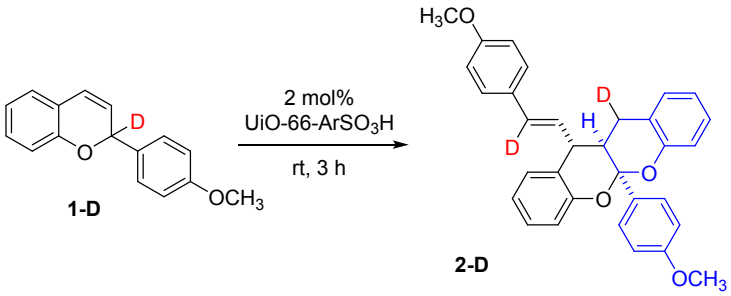
Modified Jurd synthesis[1] of *ortho*-quinone methide. A solution of (*E*)-6-(3-(4-methoxyphenyl) allyl)benzo[d][1,3]dioxol-5-ol (1.0g) in ether (50 mL) was added silver oxide (3.0g) then stirred overnight. The solution was filtered, then concentrated to 20 mL, cooled, and red crystals were collected (0.54g). The product is acid and heat sensitive. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 14.1 Hz, 1H), 7.53 – 7.40 (m, 2H), 7.17 – 7.06 (m, 2H), 6.98 – 6.79 (m, 2H), 6.58 (s, 1H), 5.92 (d, *J* = 13.8 Hz, 1H), 5.89 (s, 2H), 3.3 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.87, 161.29, 160.99, 144.82, 144.10, 141.63, 129.26, 129.21, 129.20, 120.99, 114.44, 101.78, 98.04, 55.39. **IR** (thin film, cm^{-1}): 1612, 1596, 1520, 1423, 1364, 1246, 1214, 1171, 1025.

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

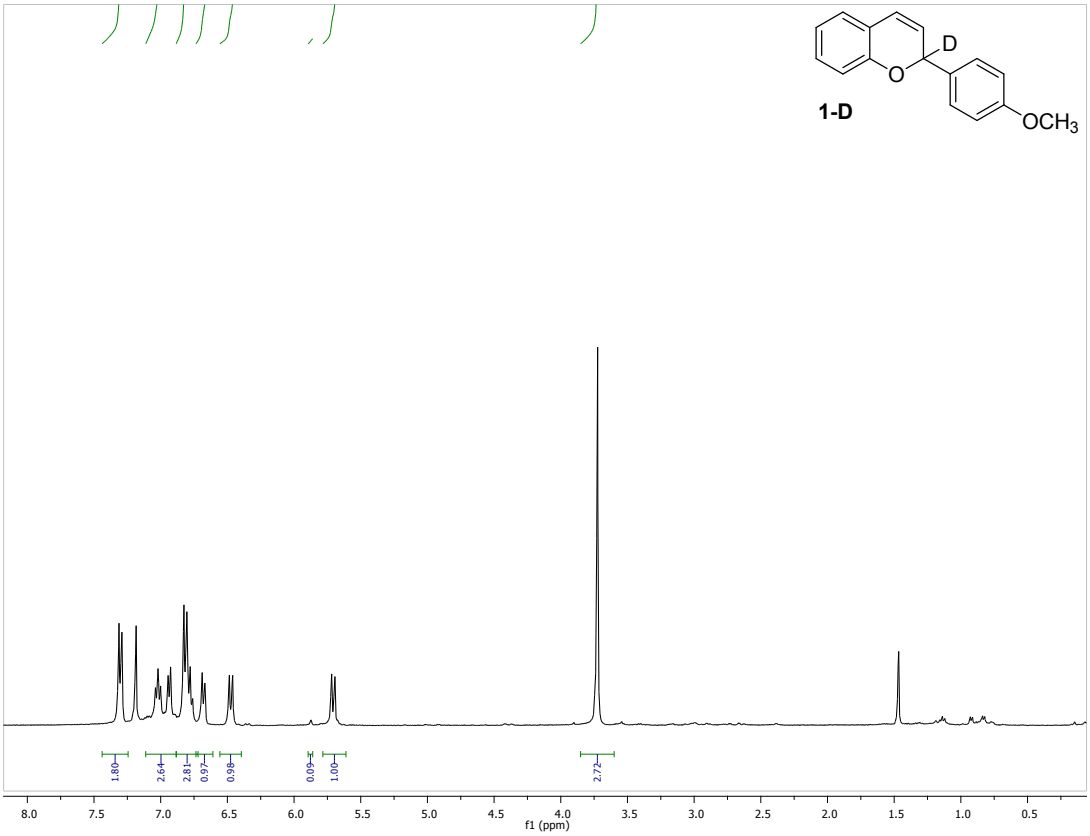

7
OCH3
6
5
2
3
8
1
4
O
O
O
9
7
9
8
2,6
1
3
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

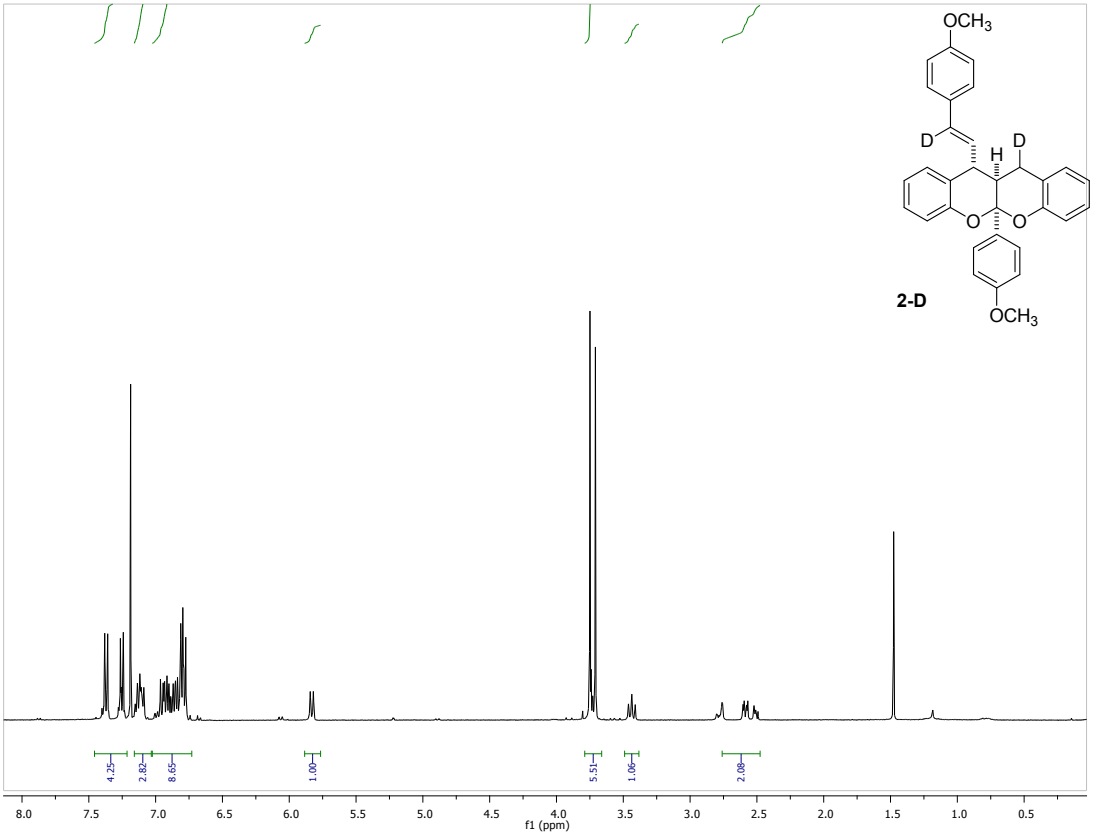

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Deuterium labelling study



1-D **2-D**


D
O
OCH3
1-D
1.80
2.64
2.81
0.97
0.98
0.09
1.00
2.72
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
f1 (ppm)


OCH3
D
H
D
O
O
2-D
OCH3
4.25
2.82
8.65
1.00
5.51
1.06
2.08
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
f1 (ppm)