

Supporting information for

Tandem Allylic Alcohol Isomerization/Oxo-Michael Addition Reaction Promoted by Re_2O_7

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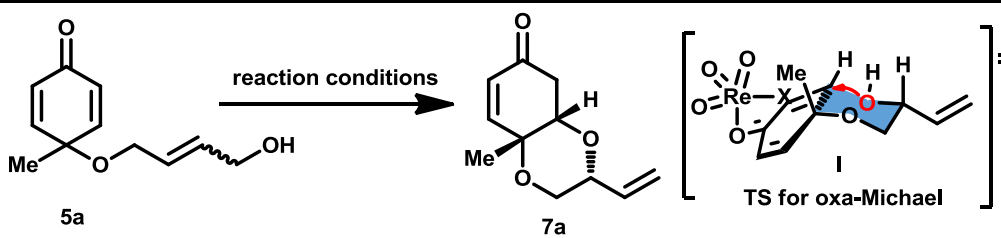
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1. General information

Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reactions were conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvents were treated as follows: tetrahydrofuran and diethyl ether were distilled from sodium under argon atmosphere, dichloromethane and toluene were distilled from calcium hydride under argon atmosphere. Anhydrous chloroform, acetonitrile and ethyl acetate were commercially available. Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm , 200-400 mesh, Silicycle P60). NMR data including ^1H NMR or ^{13}C NMR spectra were recorded on Agilent 500 and Agilent 400. ^1H NMR chemical shifts were reported in ppm from the solvent resonance as the internal standard (CDCl_3 : 7.26 ppm). ^{13}C NMR chemical shifts were reported in ppm relative to the solvent (CDCl_3 : 77.16 ppm). Infrared spectra were performed on a Nicolet 380 FT-IR and are reported in terms of frequency of absorption (cm^{-1}). Low mass spectra were measured on a Shimadzu LCMS-2010EV mass spectrometer (ESI). High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI).

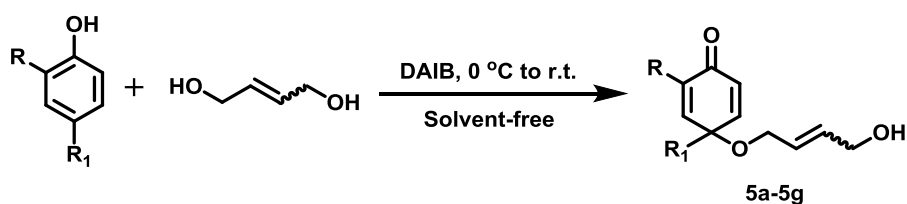
2. Optimization of the reaction conditions

Table 1. Optimization of reaction conditions ^a

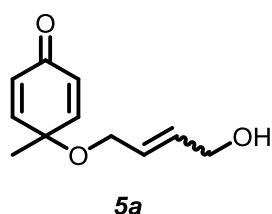
					
Entry	Catalyst (equiv)	Solvent	t (h)	5a (%) ^b	yield (%) ^b
1	--	CH ₂ Cl ₂	15	100	0
2	O=VSO ₄	CH ₂ Cl ₂	15	100	0
3	POVO	CH ₂ Cl ₂	15	100	0
4	MTO	CH ₂ Cl ₂	15	100	0
5	Ph ₃ SiO-ReO ₃	CH ₂ Cl ₂	1	0	82 ^g
6	Re ₂ O ₇	CH ₂ Cl ₂	1	0	83
7	Re ₂ O ₇	CHCl ₃	1	0	67
8	Re ₂ O ₇	Toluene	15	21	52 ^c
9	Re ₂ O ₇	CH ₃ CN	15	43	35 ^c
10	Re ₂ O ₇	EtOAc	15	53	28 ^c
11	Re ₂ O ₇	THF	15	58	19 ^c
12 ^e	Re ₂ O ₇	CH ₂ Cl ₂	1	0	82
13 ^f	Re ₂ O ₇	CH ₂ Cl ₂	1	0	83 ^g

^a **5a** (0.1 mmol) in 0.5 mL solvent was added to a solution of catalyst (10 mol%) in 0.5 mL solvent at rt. ^b Isolated yields. ^c Determined by ¹H-NMR using 1,4-dimethoxybenzene as inner standard. ^d 10 mol% catalyst loading. ^e 5 mol% catalyst loading. ^f 2.5 mol% catalyst loading. ^g dr 40:1 determined by ¹H NMR.

3. General procedure for the preparation of substrates



General procedure A¹: To a stirred suspension of *phenols* (10 mmol, 1.0 equiv) in *but-2-ene-1,4-diol* (10 mL) was added *iodobenzene diacetate* (DAIB, 12 mmol, 1.2 equiv) in small portions within 1h at 0 °C and the reaction mixture was warmed to room temperature successively until all *phenols* was consumed as judged by TLC. The reaction mixture was diluted with ethyl acetate and quenched with saturated NaHCO₃ (10mL) and extracted with ethyl acetate (50mL ×3). Combined extracts were washed with brine, dried over Na₂SO₄, and solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to afford the product.



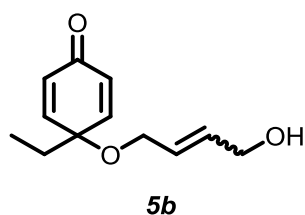
This compound was prepared according to the general procedure A as a pale brown oil (7.37g, 38% yield in 100 mmol scale) to serve as the initial substrate and was isolated as a mixture of alkene geometrical isomers (E:Z; 5:1). Spectral data for the major isomer is reported.

¹H NMR (500 MHz, CDCl₃) δ 6.80-6.76 (m, 2H), 6.29-6.24 (m, 2H), 5.86-5.69 (m, 2H), 4.12-4.09 (m, 2H), 3.83-3.80 (m, 2H), 2.09 (brs, 1H), 1.42 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.31, 151.97, 132.47, 130.16, 127.53, 72.64, 65.81, 62.77, 26.40.

IR (neat) 3442, 2944, 2859, 1685, 1646, 1077cm⁻¹.

HRMS (EI) exact mass calcd for C₁₁H₁₄O₃: m/z 194.0943 [M]⁺, found: m/z 194.0942.



This compound was prepared according to the general procedure A as a pale brown oil (581mg, 28% yield in 10 mmol scale) and was isolated as a mixture of alkene geometrical isomers (E:Z; 5:1). Spectral data for the major isomer is reported.

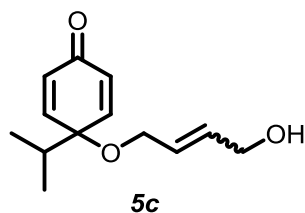
¹H NMR (500 MHz, CDCl₃) δ 6.76-6.72 (m, 2H), 6.37-6.32 (m, 2H), 5.88-5.72 (m, 2H), 4.13 (dd, *J* = 5.2, 1.3 Hz, 2H), 3.86 (dd, *J* = 5.5, 1.3 Hz, 2H), 1.81-1.76 (m, 3H), 0.83 (t, *J* = 7.6 Hz, 3H).

¹ Liu, Q.; Rovis, T., Asymmetric Synthesis of Hydrobenzofuranones via Desymmetrization of Cyclohexadienones Using the Intramolecular Stetter Reaction. *Journal of the American Chemical Society* 2006, 128, (8), 2552-2553.

¹³C NMR (126 MHz, CDCl₃) δ 185.66, 151.15, 132.15, 131.47, 127.88, 76.40, 65.63, 62.96, 32.42, 7.95.

IR (neat) 3439, 2934, 2857, 1667, 1644, 1075cm⁻¹.

HRMS (EI) exact mass calcd for C₁₂H₁₆O₃: m/z 208.1099 [M]⁺, found: m/z 208.1103.



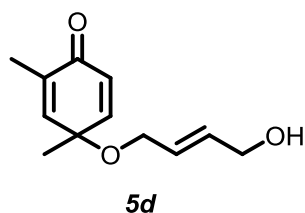
This compound was prepared according to the general procedure A as a pale brown oil (700mg, 32% yield in 10 mmol scale) and was isolated as a mixture of alkene geometrical isomers (E:Z; 5:1). Spectral data for the major isomer is reported.

¹H NMR (500 MHz, CDCl₃) δ 6.77-6.72 (m, 2H), 6.40-6.36 (m, 2H), 5.90-5.72 (m, 2H), 4.15 (dd, *J* = 5.3, 1.4 Hz, 2H), 3.85 (dd, *J* = 5.4, 1.4 Hz, 2H), 2.07-1.98 (m, 1H), 1.67 (brs, 1H), 0.94 (d, *J* = 6.9 Hz, 6H)

¹³C NMR (126 MHz, CDCl₃) δ 185.79, 150.31, 132.10, 131.51, 128.24, 78.37, 65.40, 63.10, 36.78, 17.22.

IR (neat) 3441, 2938, 2860, 1671, 1649, 1065cm⁻¹.

HRMS (EI) exact mass calcd for C₁₃H₁₈O₃: m/z 222.1256 [M]⁺, found: m/z 222.1261.



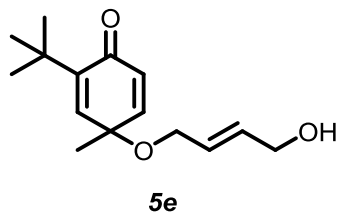
This compound was prepared according to the general procedure A as a pale yellow oil (1.41g, 68% yield in 10 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 6.78-6.73 (m, 1H), 6.56-6.53 (m, 1H), 6.27 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.78-5.71 (m, 1H), 5.65-5.58 (m, 1H), 4.12 (dd, *J* = 6.4, 1.7 Hz, 2H), 3.88 (dd, *J* = 6.4, 1.7 Hz, 2H), 2.00 (brs, 1H), 1.89 (s, 3H), 1.41 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.99, 151.47, 146.92, 136.97, 132.14, 130.15, 128.63, 73.12, 61.30, 58.74, 26.64, 15.83.

IR (neat) 3442, 2939, 2862, 1668, 1663, 1069cm⁻¹.

HRMS (EI) exact mass calcd for C₁₂H₁₆O₃: m/z 208.1099 [M]⁺, found: m/z 208.1097.



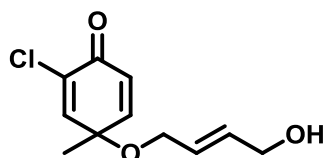
This compound was prepared according to the general procedure A as a pale yellow oil (1.83g, 73% yield in 10 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 6.67 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 6.18 (d, *J* = 9.9 Hz, 1H), 5.78-5.72 (m, 1H), 5.66-5.59 (m, 1H), 4.16-4.09 (m, 2H), 3.91-3.80 (m, 2H), 1.99 (brs, 1H), 1.40 (s, 3H), 1.22 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 185.48, 149.03, 147.75, 144.85, 132.26, 132.01, 128.72, 73.18, 61.06, 58.75, 34.77, 29.32, 26.96.

IR (neat) 3440, 2959, 2868, 1667, 1633, 1079cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₅H₂₃O₃: *m/z* 251.1647 [M+H]⁺, found: *m/z* 251.1641.



5f

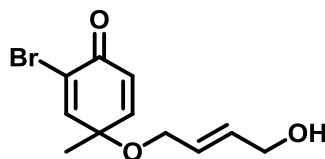
This compound was prepared according to the general procedure A as a pale yellow oil (985mg, 43% yield in 10 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 6.97 (d, *J* = 2.9 Hz, 1H), 6.83 (dd, *J* = 10.1, 2.9 Hz, 1H), 6.39 (d, *J* = 10.1 Hz, 1H), 5.80-5.74 (m, 1H), 5.65-5.59 (m, 1H), 4.16-4.12 (m, 2H), 3.96-3.93 (m, 2H), 1.74 (brs, 1H), 1.49 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 178.24, 151.93, 147.64, 133.57, 132.42, 129.18, 128.19, 74.82, 61.93, 58.84, 26.52.

IR (neat) 3442, 2961, 2865, 1669, 1645, 1068cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₁H₁₄ClO₃: *m/z* 229.0631 [M+H]⁺, found: *m/z* 229.0626.



5g

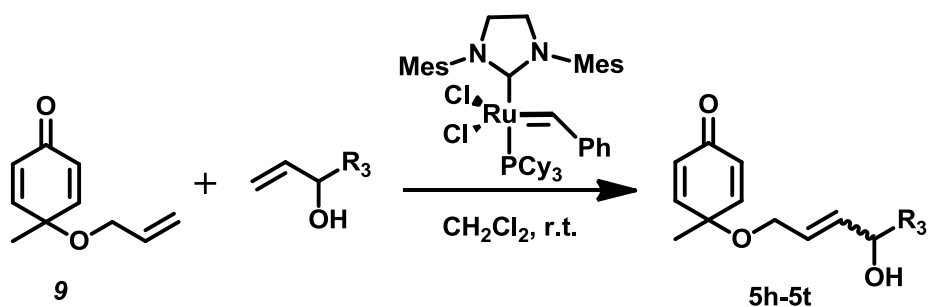
This compound was prepared according to the general procedure A as a pale yellow oil (1.12g, 41% yield in 10 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, *J* = 2.8 Hz, 1H), 6.84 (dd, *J* = 10.0, 2.9 Hz, 1H), 6.41 (d, *J* = 10.0 Hz, 1H), 5.81-5.73 (m, 1H), 5.66-5.59 (m, 1H), 4.17-4.12 (m, 2H), 3.97-3.94 (m, 2H), 1.70 (brs, 1H), 1.48 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 178.04, 152.26, 151.82, 132.44, 128.70, 128.20, 125.31, 75.47, 62.00, 58.87, 26.32.

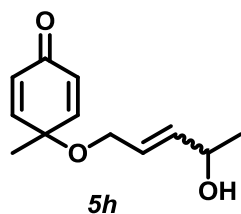
IR (neat) 3440, 2959, 2865, 1667, 1646, 1068cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₁H₁₄BrO₃: *m/z* 273.0126 [M+H]⁺, found: *m/z* 273.0121.



9 was prepared with *p*-Cresol and *Allyl alcohol* according to the general procedure A.

General procedure B: To a mixture of the 4-(allyloxy)-4-methylcyclohexa-2,5-dien-1-one(**9**) (5.5 mmol, 1.1 equiv) and *secondary alcohol* (5.0 mmol, 1.0 equiv) in CH₂Cl₂ (20 mL, 0.25M) was added Grubbs' 2nd (0.05 mmol, 1 mol%). The reaction mixture was stirred at room temperature under argon atmosphere until all *secondary alcohols* was consumed as judged by TLC. The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2, v/v) to afford the product.



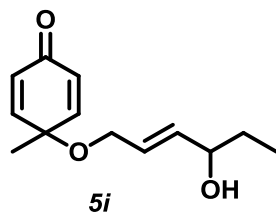
This compound was prepared according to the general procedure B as a dark grey oil (332mg, 32% yield in 5 mmol scale) and was isolated as a mixture of alkene geometrical isomers (E:Z; 10:1). Spectral data for the major isomer is reported.

¹H NMR (500 MHz, CDCl₃) δ 6.82-6.77 (m, 2H), 6.32-6.26 (m, 2H), 5.79-5.67 (m, 2H), 4.35-4.28 (m, 1H), 3.85-3.81 (m, 2H), 1.58 (brs, 1H), 1.46 (s, 3H), 1.27 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.28, 151.91, 137.25, 130.29, 126.28, 72.72, 68.24, 65.90, 26.52, 23.27.

IR (neat) 3446, 2970, 1738, 1671, 1082cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₂H₁₇O₃: *m/z* 209.1178 [M+H]⁺, found: *m/z* 209.1173.



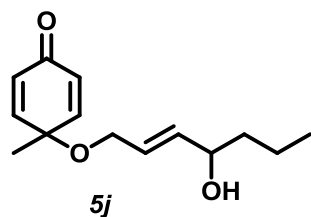
This compound was prepared according to the general procedure B as a dark grey oil (388mg, 35% yield in 5 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 6.82-6.76 (m, 2H), 6.28 (d, *J* = 9.8 Hz, 2H), 5.72-5.67 (m, 2H), 4.05-4.00 (m, 1H), 3.83 (d, *J* = 3.5 Hz, 2H), 1.74 (brs, 1H), 1.57-1.50 (m, 2H), 1.44 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.28, 151.96, 135.92, 130.23, 127.24, 73.58, 72.70, 65.95, 30.06, 26.48, 9.80.

IR (neat) 3448, 2980, 1733, 1671, 1078 cm^{-1} .

HRMS (EI) exact mass calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3$: m/z 222.1256 $[\text{M}]^+$, found: m/z 222.1260.



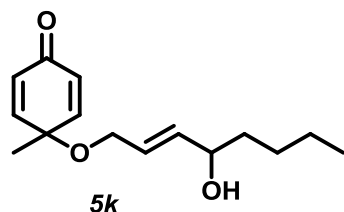
This compound was prepared according to the general procedure B as a dark grey oil (340mg, 33% yield in 5 mmol scale).

^1H NMR (500 MHz, CDCl_3) δ 6.82-6.77 (m, 2H), 6.31-6.26 (m, 2H), 5.72-5.69 (m, 2H), 4.14-4.09 (m, 1H), 3.84-3.82 (m, 2H), 1.67 (brs, 1H), 1.55-1.47 (m, 2H), 1.45 (s, 3H), 1.42-1.27 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.30, 151.97, 136.27, 130.25, 127.01, 72.72, 72.07, 65.96, 39.35, 26.50, 18.73, 14.09.

IR (neat) 3453, 2958, 2931, 1737, 1673, 1083 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3$: m/z 237.1491 $[\text{M}+\text{H}]^+$, found: m/z 237.1486.



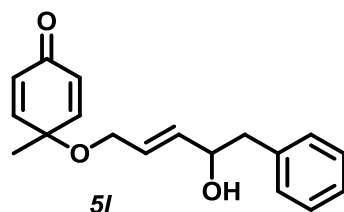
This compound was prepared according to the general procedure B as a dark grey oil (373mg, 30% yield in 5 mmol scale).

^1H NMR (500 MHz, CDCl_3) δ 6.79 (d, J = 9.8 Hz, 2H), 6.28 (d, J = 9.8 Hz, 2H), 5.73-5.68 (m, 2H), 4.12-4.06 (m, 1H), 3.83 (d, J = 3.5 Hz, 2H), 1.68 (brs, 1H), 1.54-1.47 (m, 2H), 1.44 (s, 3H), 1.39-1.24 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.28, 151.96, 136.30, 130.24, 127.00, 72.71, 72.30, 65.96, 36.92, 27.66, 26.49, 22.71, 14.14.

IR (neat) 3458, 2962, 2931, 1726, 1653, 1081 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{15}\text{H}_{23}\text{O}_3$: m/z 251.1647 $[\text{M}+\text{H}]^+$, found: m/z 251.1641.



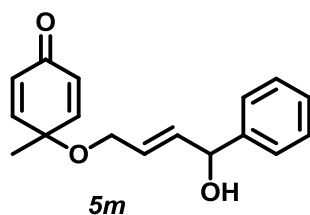
This compound was prepared according to the general procedure B as a dark grey oil (526mg, 37% yield in 5 mmol scale).

^1H NMR (500 MHz, CDCl_3) δ 7.34-7.28 (m, 2H), 7.26-7.23 (m, 1H), 7.23-7.19 (m, 2H), 6.81-6.75 (m, 2H), 6.31-6.25 (m, 2H), 5.82-5.71 (m, 2H), 4.39-4.33 (m, 1H), 3.84 (dd, J = 4.9, 1.1 Hz, 2H), 2.87 (dd, J = 13.6, 4.9 Hz, 1H), 2.77 (dd, J = 13.7, 8.3 Hz, 1H), 1.69 (brs, 1H), 1.45 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.27, 151.90, 137.78, 134.96, 130.27, 129.62, 128.67, 127.48, 126.77, 72.81, 72.73, 65.85, 43.98, 26.50.

IR (neat) 3446, 3027, 2928, 1738, 1671, 1083 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3$: m/z 285.1491 $[\text{M}+\text{H}]^+$, found: m/z 285.1486.



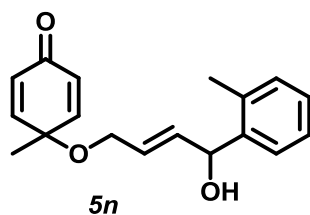
This compound was prepared according to the general procedure B as a dark grey oil (432mg, 32% yield in 5 mmol scale).

^1H NMR (500 MHz, CDCl_3) δ 7.36-7.33 (m, 4H), 7.30-7.27 (m, 1H), 6.80-6.75 (m, 2H), 6.28-6.23 (m, 2H), 5.93-5.87 (m, 1H), 5.84-5.78 (m, 1H), 5.21 (d, J = 5.9 Hz, 1H), 3.89-3.83 (m, 2H), 2.12 (brs, 1H), 1.44 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.27, 151.92, 142.67, 134.96, 130.22, 128.70, 127.92, 127.64, 126.39, 74.52, 72.73, 65.74, 26.47.

IR (neat) 3435, 3028, 2929, 1738, 1668, 1082 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{O}_3$: m/z 271.1334 $[\text{M}+\text{H}]^+$, found: m/z 271.1328.



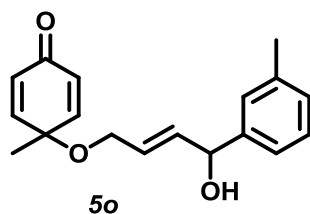
This compound was prepared according to the general procedure B as a dark grey oil (495mg, 35% yield in 5 mmol scale).

^1H NMR (500 MHz, CDCl_3) δ 7.45-7.41 (m, 1H), 7.24-7.13 (m, 3H), 6.79-6.75 (m, 2H), 6.29-6.23 (m, 2H), 5.92-5.85 (m, 1H), 5.81-5.74 (m, 1H), 5.42 (d, J = 5.7 Hz, 1H), 3.89-3.83 (m, 2H), 2.34 (s, 3H), 1.92 (brs, 1H), 1.44 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.27, 151.93, 140.58, 135.29, 134.08, 130.67, 130.25, 127.79, 127.70, 126.48, 125.97, 72.73, 71.23, 65.77, 26.50, 19.29.

IR (neat) 3435, 3029, 2932, 1736, 1667, 1084 cm^{-1} .

HRMS (EI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$: m/z 284.1412 $[\text{M}]^+$, found: m/z 284.1415.



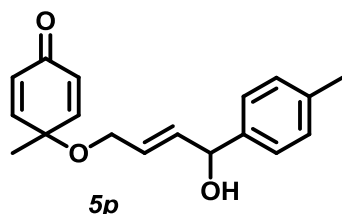
This compound was prepared according to the general procedure B as a dark grey oil (466mg, 33% yield in 5 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 7.24 (t, *J* = 7.6 Hz, 1H), 7.18-7.13 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.80-6.75 (m, 2H), 6.29-6.23 (m, 2H), 5.93-5.86 (m, 1H), 5.85-5.77 (m, 1H), 5.17 (d, *J* = 5.9 Hz, 1H), 3.88-3.83 (m, 2H), 2.35 (s, 3H), 2.14 (brs, 1H), 1.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.30, 151.96, 142.64, 138.40, 135.09, 130.20, 128.67, 128.61, 127.47, 127.05, 123.45, 74.55, 72.74, 65.79, 26.47, 21.56.

IR (neat) 3447, 3018, 2928, 1738, 1671, 1082 cm⁻¹.

HRMS (EI) exact mass calcd for C₁₈H₂₀O₃: *m/z* 284.1412 [M]⁺, found: *m/z* 284.1411.



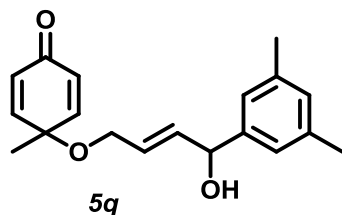
This compound was prepared according to the general procedure B as a dark grey oil (523mg, 37% yield in 5 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.78 (dd, *J* = 10.0, 1.2 Hz, 2H), 6.29-6.24 (m, 2H), 5.94-5.86 (m, 1H), 5.83-5.76 (m, 1H), 5.18 (d, *J* = 6.0 Hz, 1H), 3.88-3.83 (m, 2H), 2.34 (s, 3H), 2.00 (brs, 1H), 1.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.29, 151.96, 139.77, 137.69, 135.11, 130.23, 129.39, 127.42, 126.37, 74.38, 72.73, 65.79, 26.49, 21.26.

IR (neat) 3446, 3016, 2928, 1738, 1671, 1082 cm⁻¹.

HRMS (EI) exact mass calcd for C₁₈H₂₀O₃: *m/z* 284.1412 [M]⁺, found: *m/z* 284.1413.



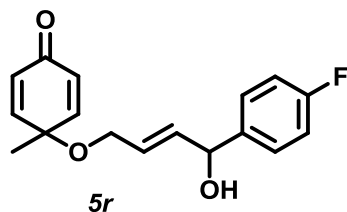
This compound was prepared according to the general procedure B as a dark grey oil (508mg, 34% yield in 5 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 6.99-6.90 (m, 3H), 6.82-6.76 (m, 2H), 6.30-6.24 (m, 2H), 5.92-5.77 (m, 2H), 5.14 (d, *J* = 5.8 Hz, 1H), 3.91-3.83 (m, 2H), 2.31 (s, 6H), 2.15 (brs, 1H), 1.45 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.28, 151.97, 138.34, 135.14, 130.24, 130.22, 129.58, 127.34, 124.14, 74.61, 72.73, 65.83, 26.49, 21.44.

IR (neat) 3447, 3019, 2929, 1737, 1671, 1083 cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₉H₂₃O₃: *m/z* 299.1647 [M+H]⁺, found: *m/z* 299.1642.



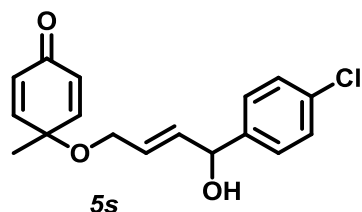
This compound was prepared according to the general procedure B as a dark grey oil (374mg, 26% yield in 5 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 7.32 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 9.8 Hz, 2H), 6.30-6.24 (m, 2H), 5.91-5.76 (m, 2H), 5.20 (d, *J* = 5.8 Hz, 1H), 3.86 (d, *J* = 5.2 Hz, 2H), 2.05 (brs, 1H), 1.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.24, 162.44 (d, *J* = 245.8 Hz), 151.81, 138.41 (d, *J* = 3.1 Hz), 134.75, 130.30, 128.12 (d, *J* = 8.2 Hz), 127.92, 115.52 (d, *J* = 21.4 Hz), 73.89, 72.75, 65.65, 26.47.

IR (neat) 3444, 2929, 1736, 1667, 1083 cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₇H₁₈FO₃: *m/z* 289.1240 [M+H]⁺, found: *m/z* 289.1164.



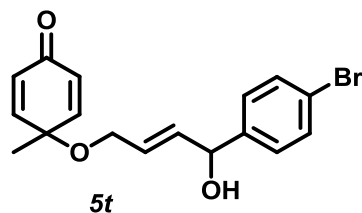
This compound was prepared according to the general procedure B as a dark grey oil (474mg, 31% yield in 5 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 7.33-7.27 (m, 4H), 6.81-6.74 (m, 2H), 6.31-6.23 (m, 2H), 5.89-5.77 (m, 2H), 5.20 (d, *J* = 5.8 Hz, 1H), 3.88-3.84 (m, 2H), 2.03 (brs, 1H), 1.45 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.24, 151.79, 141.07, 134.47, 133.64, 130.34, 128.83, 128.19, 127.78, 73.90, 72.76, 65.59, 26.47.

IR (neat) 3442, 2929, 1738, 1667, 1081 cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₇H₁₈ClO₃: *m/z* 305.0944 [M+H]⁺, found: *m/z* 305.0940.



This compound was prepared according to the general procedure B as a dark grey oil (627mg, 36% yield in 5 mmol scale).

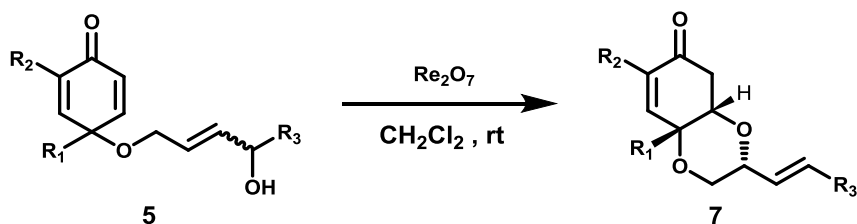
¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.81-6.71 (m, 2H), 6.31-6.20 (m, 2H), 5.90-5.72 (m, 2H), 5.17 (d, *J* = 5.9 Hz, 1H), 3.88-3.80 (m, 2H), 2.20 (brs, 1H), 1.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 185.25, 151.81, 141.63, 134.41, 131.75, 130.29, 128.18, 128.12, 121.72, 73.89, 72.75, 65.57, 26.44.

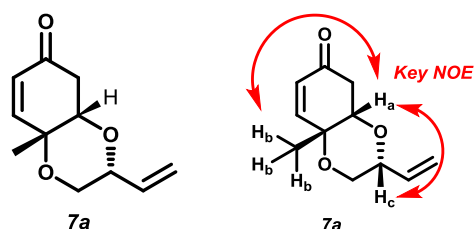
IR (neat) 3440, 2929, 1737, 1668, 1082 cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₇H₁₈BrO₃: *m/z* 349.0439 [M+H]⁺, found: *m/z* 349.0436.

4. General procedure for the Tandem Reaction



General procedure C: The *dienone* (0.1 mmol, 1.0 equiv) in 0.5 mL CH_2Cl_2 was added to a solution of Re_2O_7 (2.5 mol%) in 0.5 mL CH_2Cl_2 . The reaction mixture was stirred at room temperature under argon atmosphere until all starting material was consumed as judged by TLC. The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/15, v/v) to afford the product.



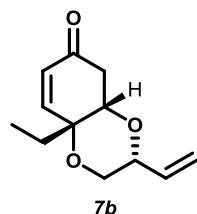
This compound was prepared according to the general procedure C as a pale-yellow solid (17mg, 88% yield in 0.1 mmol scale; 955mg, 82% yield in 6 mmol scale). d.r. = 40:1

^1H NMR (500 MHz, CDCl_3) δ 6.64 (dd, J = 10.4, 2.8 Hz, 1H), 6.09 (d, J = 10.3 Hz, 1H), 5.70-5.62 (m, 1H), 5.32-5.28 (m, 1H), 5.20-5.16 (m, 1H), 4.14-4.09 (m, 1H), 3.99-3.98 (m, 1H), 3.65 (dd, J = 11.7, 2.7 Hz, 1H), 3.45 (dd, J = 11.8, 10.4 Hz, 1H), 2.67 (d, J = 3.1 Hz, 2H), 1.39 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.82, 152.22, 133.45, 130.88, 118.01, 78.09, 76.02, 71.49, 66.99, 42.14, 24.53.

IR (neat) 2972, 1735, 1688, 1363, 1123 cm^{-1} .

HRMS (EI) exact mass calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$: m/z 194.0943 $[\text{M}]^+$, found: m/z 194.0941.



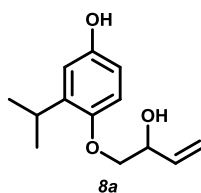
This compound was prepared according to the general procedure C as a pale-yellow solid (16mg, 75% yield in 0.1 mmol scale). d.r. = 40:1

^1H NMR (500 MHz, CDCl_3) δ 6.69 (dd, J = 10.5, 2.7 Hz, 1H), 6.12 (dd, J = 10.5, 1.0 Hz, 1H), 5.70-5.62 (m, 1H), 5.33-5.27 (m, 1H), 5.20-5.16 (m, 1H), 4.11-4.06 (m, 1H), 4.04-4.02 (m, 1H), 3.67 (dd, J = 11.7, 2.7 Hz, 1H), 3.44 (dd, J = 11.7, 10.4 Hz, 1H), 2.69-2.65 (m, 2H), 1.81-1.66 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.99, 152.17, 133.56, 131.24, 117.96, 76.76, 75.98, 73.31, 66.82, 41.94, 31.50, 7.46.

IR (neat) 2970, 1738, 1686, 1365, 1124 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$: m/z 209.1178 $[\text{M}+\text{H}]^+$, found: m/z 209.1172.



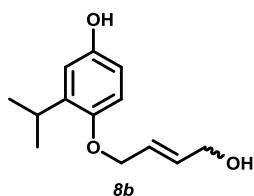
This compound was prepared according to the general procedure C as a white solid (85mg, 38% yield in 1 mmol scale).

¹H NMR (500 MHz, CDCl₃) δ 6.75-6.71 (m, 2H), 6.60 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.01-5.92 (m, 1H), 5.49-5.43 (m, 1H), 5.31-5.27 (m, 1H), 4.59-4.52 (m, 2H), 3.98 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.86 (dd, *J* = 9.3, 7.3 Hz, 1H), 3.33-3.24 (m, 1H), 2.38 (d, *J* = 4.1 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 150.32, 149.65, 139.08, 136.35, 117.24, 113.77, 113.62, 112.65, 73.00, 71.74, 26.95, 22.88, 22.86.

IR (neat) 3408, 3317, 2973, 2928, 1508, 1472, 917 cm⁻¹.

HRMS (EI) exact mass calcd for C₁₃H₁₈O₃: *m/z* 222.1256 [M]⁺, found: *m/z* 222.1261.



This compound was prepared according to the general procedure C as a white solid (80mg, 36% yield in 1 mmol scale) and was isolated as a mixture of alkene geometrical isomers (*E*:*Z*; 1.3:1). Spectral data for the two isomers are reported respectively.

***E* isomer**

¹H NMR (500 MHz, CDCl₃) δ 6.73-6.71 (m, 2H), 6.60-6.58 (m, 1H), 6.05-5.98 (m, 1H), 5.86-5.84 (m, 1H), 4.50-4.45 (m, 2H), 4.24-4.19 (m, 2H), 3.35-3.29 (m, 1H), 1.17 (d, *J* = 5.4 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 150.11, 149.91, 139.28, 131.64, 127.33, 113.78, 113.72, 112.48, 69.06, 63.19, 26.93, 22.87.

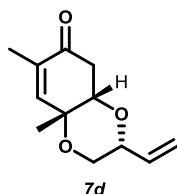
***Z* isomer**

¹H NMR (500 MHz, CDCl₃) δ 6.71-6.68 (m, 2H), 6.58-6.55 (m, 1H), 6.00-5.92 (m, 1H), 5.86-5.83 (m, 1H), 4.59-4.52 (m, 2H), 4.31-4.25 (m, 2H), 3.32-3.23 (m, 1H), 1.19 (d, *J* = 5.7 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 149.98, 149.81, 139.45, 131.89, 128.14, 113.80, 113.54, 112.53, 65.36, 59.05, 26.89, 22.92.

IR (neat) 3404, 3328, 2973, 2928, 1506, 1472, 919 cm⁻¹.

HRMS (EI) exact mass calcd for C₁₃H₁₈O₃: *m/z* 222.1256 [M]⁺, found: *m/z* 222.1254.



This compound was prepared according to the general procedure C as a pale-yellow solid (12mg, 58% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 2:1). Spectral data for the two isomers are reported respectively.

Major isomer

¹H NMR (500 MHz, CDCl₃) δ 6.38-6.37 (m, 1H), 5.70-5.62 (m, 1H), 5.33-5.15 (m, 2H), 4.12-4.07 (m, 1H), 3.97-3.95 (m, 1H), 3.62 (dd, *J* = 11.7, 2.8 Hz, 1H), 3.47 (dd, *J* = 11.7, 10.4 Hz, 1H), 2.67 (dd, *J* = 3.8, 3.1 Hz, 2H), 1.83 (d, *J* = 1.4 Hz, 3H), 1.36 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 196.11, 147.04, 137.18, 133.66, 117.95, 78.38, 76.06, 66.74, 64.15, 42.18, 24.79, 15.95.

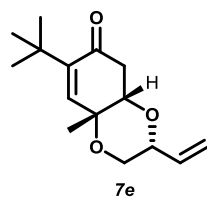
Minor isomer

¹H NMR (500 MHz, CDCl₃) δ 6.41-6.39 (m, 1H), 6.14-6.05 (m, 1H), 5.43-5.34 (m, 2H), 4.17-4.15 (m, 1H), 4.00-3.97 (m, 1H), 3.99-3.97 (m, 1H), 3.72 (dd, *J* = 12.0, 1.9 Hz, 1H), 2.64-2.61 (m, 2H), 1.84 (d, *J* = 1.5 Hz, 3H), 1.36 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 196.46, 146.65, 137.42, 134.55, 119.24, 72.18, 72.03, 71.72, 71.61, 41.66, 24.41, 15.95.

IR (neat) 2962, 1737, 1688, 1365, 1124cm⁻¹.

HRMS (EI) exact mass calcd for C₁₂H₁₆O₃: *m/z* 208.1099 [M]⁺, found: *m/z* 208.1096.



This compound was prepared according to the general procedure C as a pale-yellow solid (21mg, 82% yield in 0.1 mmol scale; major isomer 181mg, minor isomer 22mg, 81% yield in total in 1 mmol scale) and was isolated as single diastereoisomer by PTLC (d.r. = 8:1). Spectral data for the two isomers are reported respectively.

Major isomer

¹H NMR (500 MHz, CDCl₃) δ 6.33 (d, *J* = 2.8 Hz, 1H), 5.68-5.60 (m, 1H), 5.30-5.25 (m, 1H), 5.18-5.13 (m, 1H), 4.11-4.04 (m, 1H), 3.91-3.89 (m, 1H), 3.61 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.40 (dd, *J* = 11.7, 10.4 Hz, 1H), 2.62 (d, *J* = 3.0 Hz, 2H), 1.35 (s, 3H), 1.18 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 195.20, 148.18, 144.25, 133.54, 117.57, 77.48, 75.35, 71.52, 66.60, 43.80, 34.59, 29.23, 24.60.

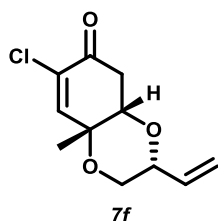
Minor isomer

¹H NMR (500 MHz, CDCl₃) δ 6.35 (d, *J* = 2.3 Hz, 1H), 6.14-6.05 (m, 1H), 5.43-5.34 (m, 2H), 4.15-4.09 (m, 2H), 3.92 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.74-3.68 (m, 1H), 2.62-2.58 (m, 2H), 1.36 (s, 3H), 1.21 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 195.97, 148.52, 144.00, 134.57, 119.21, 72.04, 71.73, 71.59, 64.16, 43.61, 34.76, 29.45, 24.56.

IR (neat) 2959, 1738, 1683, 1365, 1128cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₅H₂₃O₃: *m/z* 251.1647 [M+H]⁺, found: *m/z* 251.1642.



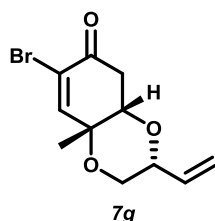
This compound was prepared according to the general procedure C as a pale-yellow solid (16mg, 68% yield in 0.1 mmol scale). d.r. = 15:1. Spectral data for the major isomer is reported.

¹H NMR (500 MHz, CDCl₃) δ 6.82 (d, *J* = 2.6 Hz, 1H), 5.70-5.61 (m, 1H), 5.34-5.16 (m, 2H), 4.15-4.08 (m, 1H), 4.01-3.96 (m, 1H), 3.67 (dd, *J* = 11.9, 2.8 Hz, 1H), 3.48 (dd, *J* = 11.9, 10.4 Hz, 1H), 2.87 (dd, *J* = 17.2, 3.1 Hz, 1H), 2.75 (dd, *J* = 17.2, 3.0 Hz, 1H), 1.43 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 187.97, 147.98, 133.10, 132.81, 118.32, 77.83, 76.11, 72.92, 67.02, 42.03, 24.43.

IR (neat) 2962, 1737, 1685, 1365, 1126cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₁H₁₄ClO₃: m/z 229.0631 [M+H]⁺, found: m/z 229.0625.



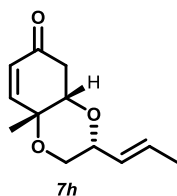
This compound was prepared according to the general procedure C as a pale-yellow solid (18mg, 66% yield in 0.1 mmol scale). d.r. = 15:1. Spectral data for the major isomer is reported.

¹H NMR (500 MHz, CDCl₃) δ 7.10 (d, *J* = 2.6 Hz, 1H), 5.70-5.62 (m, 1H), 5.33-5.19 (m, 2H), 4.14-4.10 (m, 1H), 4.01-3.99 (m, 1H), 3.68 (dd, *J* = 11.9, 2.7 Hz, 1H), 3.49 (dd, *J* = 11.9, 10.4 Hz, 1H), 2.92 (dd, *J* = 17.2, 3.1 Hz, 1H), 2.77 (dd, *J* = 17.2, 3.0 Hz, 1H), 1.42 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 187.84, 152.57, 133.08, 124.40, 118.39, 77.83, 76.12, 73.69, 67.09, 41.68, 24.21.

IR (neat) 2958, 1738, 1684, 1365, 1127cm⁻¹.

HRMS (EI) exact mass calcd for C₁₁H₁₃BrO₃: m/z 272.0048 [M]⁺, found: m/z 272.0051.



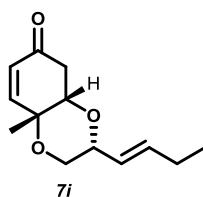
This compound was prepared according to the general procedure C as a pale-yellow solid (19mg, 93% yield in 0.1 mmol scale). d.r. = 10:1

¹H NMR (500 MHz, CDCl₃) δ 6.64 (dd, *J* = 10.4, 2.8 Hz, 1H), 6.08 (d, *J* = 10.5 Hz, 1H), 5.80-5.72 (m, 1H), 5.33-5.26 (m, 1H), 4.07-4.02 (m, 1H), 3.97-3.95 (m, 1H), 3.60 (dd, *J* = 11.8, 2.7 Hz, 1H), 3.45 (dd, *J* = 11.8, 10.4 Hz, 1H), 2.66 (d, *J* = 3.1 Hz, 2H), 1.69-1.64 (m, 3H), 1.38 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 195.81, 152.35, 130.82, 130.51, 126.49, 78.07, 76.08, 71.36, 67.22, 42.17, 24.55, 18.05.

IR (neat) 2970, 1684, 1372, 1121cm⁻¹.

HRMS (ESI) exact mass calcd for C₁₂H₁₇O₃: m/z 209.1178 [M+H]⁺, found: m/z 209.1170.



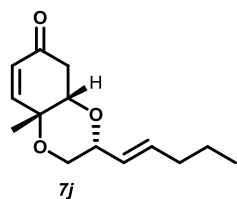
This compound was prepared according to the general procedure C as a pale-yellow solid (20mg, 91% yield in 0.1 mmol scale). d.r. = 20:1

¹H NMR (500 MHz, CDCl₃) δ 6.64 (dd, *J* = 10.4, 2.8 Hz, 1H), 6.08 (d, *J* = 10.3 Hz, 1H), 5.83-5.75 (m, 1H), 5.29-5.23 (m, 1H), 4.08-4.03 (m, 1H), 3.97-3.95 (m, 1H), 3.60 (dd, *J* = 11.8, 2.8 Hz, 1H), 3.45 (dd, *J* = 11.8, 10.4 Hz, 1H), 2.66 (d, *J* = 3.2 Hz, 2H), 2.07-1.97 (m, 2H), 1.38 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 195.85, 152.39, 137.05, 130.83, 124.21, 78.11, 76.15, 71.36, 67.33, 42.18, 25.48, 24.56, 13.15.

IR (neat) 2965, 1684, 1372, 1119 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3$: m/z 223.1334 $[\text{M}+\text{H}]^+$, found: m/z 223.1328.



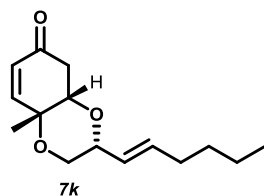
This compound was prepared according to the general procedure C as a pale-yellow solid (21mg, 89% yield in 0.1 mmol scale). d.r. = 20:1

^1H NMR (500 MHz, CDCl_3) δ 6.64 (dd, J = 10.4, 2.8 Hz, 1H), 6.08 (d, J = 10.3 Hz, 1H), 5.77-5.69 (m, 1H), 5.29-5.24 (m, 1H), 4.07-4.02 (m, 1H), 3.97-3.95 (m, 1H), 3.59 (dd, J = 11.8, 2.8 Hz, 1H), 3.48-3.42 (m, 1H), 2.66 (d, J = 2.9 Hz, 2H), 2.00-1.94 (m, 2H), 1.38 (s, 3H), 1.39-1.33 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.88, 152.41, 135.38, 130.82, 125.30, 78.07, 76.15, 71.36, 67.34, 42.17, 34.58, 24.57, 22.11, 13.78.

IR (neat) 2960, 1684, 1372, 1120 cm^{-1} .

HRMS (EI) exact mass calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$: m/z 236.1412 $[\text{M}]^+$, found: m/z 236.1415.



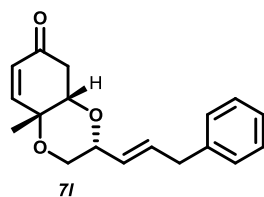
This compound was prepared according to the general procedure C as a pale-yellow solid (23mg, 92% yield in 0.1 mmol scale). d.r. = 20:1

^1H NMR (500 MHz, CDCl_3) δ 6.64 (dd, J = 10.4, 2.8 Hz, 1H), 6.08 (d, J = 10.4 Hz, 1H), 5.77-5.69 (m, 1H), 5.29-5.23 (m, 1H), 4.07-4.02 (m, 1H), 3.97-3.94 (m, 1H), 3.59 (dd, J = 11.8, 2.8 Hz, 1H), 3.44 (dd, J = 11.8, 10.4 Hz, 1H), 2.66 (d, J = 3.0 Hz, 2H), 2.02-1.96 (m, 2H), 1.38 (s, 3H), 1.34-1.22 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.86, 152.40, 135.58, 130.82, 125.12, 78.08, 76.15, 71.35, 67.34, 42.17, 32.18, 31.11, 24.56, 22.32, 14.00.

IR (neat) 2959, 1683, 1372, 1122 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{15}\text{H}_{23}\text{O}_3$: m/z 251.1647 $[\text{M}+\text{H}]^+$, found: m/z 251.1642.



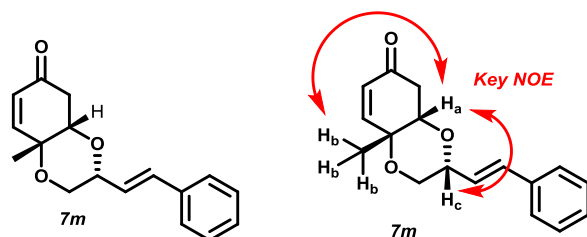
This compound was prepared according to the general procedure C as a colorless oil (24mg, 87% yield in 0.1 mmol scale). d.r. = 40:1

^1H NMR (500 MHz, CDCl_3) δ 7.31-7.27 (m, 2H), 7.22-7.18 (m, 1H), 7.15-7.12 (m, 2H), 6.64 (dd, J = 10.4, 2.8 Hz, 1H), 6.09 (d, J = 10.3 Hz, 1H), 5.94-5.87 (m, 1H), 5.37-5.31 (m, 1H), 4.13-4.07 (m, 1H), 3.98-3.95 (m, 1H), 3.62 (dd, J = 11.8, 2.8 Hz, 1H), 3.47 (dd, J = 11.8, 10.4 Hz, 1H), 3.36-3.33 (m, 2H), 2.67 (d, J = 3.1 Hz, 2H), 1.39 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.84, 152.34, 139.58, 133.74, 130.86, 128.75, 128.61, 126.58, 126.34, 78.12, 75.84, 71.40, 67.22, 42.15, 38.90, 24.55.

IR (neat) 2968, 1678, 1372, 1121 cm^{-1} .

HRMS (EI) exact mass calcd for $C_{18}H_{20}O_3$: m/z 284.1412 $[M]^+$, found: m/z 284.1406.



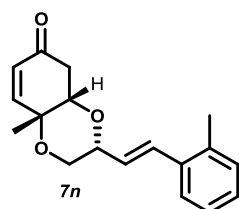
This compound was prepared according to the general procedure C as a pale-yellow solid (25mg, 92% yield in 0.1 mmol scale). d.r. = 20:1

1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.21 (m, 1H), 6.70-6.60 (m, 2H), 6.13 (d, J = 10.3 Hz, 1H), 6.01 (dd, J = 16.1, 6.1 Hz, 1H), 4.32-4.26 (m, 1H), 4.05-4.03 (m, 1H), 3.72 (dd, J = 11.8, 2.8 Hz, 1H), 3.55 (dd, J = 11.8, 10.4 Hz, 1H), 2.71 (d, J = 3.0 Hz, 2H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.83, 152.26, 136.32, 132.98, 130.93, 128.68, 128.13, 126.66, 124.36, 78.20, 76.00, 71.51, 67.18, 42.18, 24.56.

IR (neat) 2970, 2862, 1738, 1684, 1372, 1118 cm^{-1} .

HRMS (ESI) exact mass calcd for $C_{17}H_{19}O_3$: m/z 271.1334 $[M+H]^+$, found: m/z 271.1329.



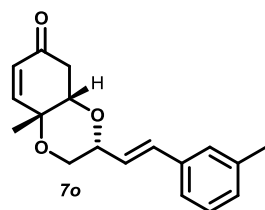
This compound was prepared according to the general procedure C as a pale-yellow solid (20mg, 72% yield in 0.1 mmol scale). d.r. = 20:1

1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.36 (m, 1H), 7.16-7.10 (m, 3H), 6.85 (dd, J = 16.0, 1.2 Hz, 1H), 6.68 (dd, J = 10.4, 2.8 Hz, 1H), 6.13 (d, J = 10.3 Hz, 1H), 5.89 (dd, J = 16.0, 6.4 Hz, 1H), 4.34-4.27 (m, 1H), 4.07-4.02 (m, 1H), 3.74-3.68 (m, 1H), 3.57 (dd, J = 11.8, 10.3 Hz, 1H), 2.71 (d, J = 3.1 Hz, 2H), 2.31 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.82, 152.26, 135.74, 135.39, 130.97, 130.91, 130.43, 128.01, 126.19, 125.78, 125.71, 78.16, 76.28, 71.49, 67.27, 42.18, 24.56, 19.84.

IR (neat) 2968, 2863, 1741, 1683, 1372, 1120 cm^{-1} .

HRMS (ESI) exact mass calcd for $C_{18}H_{21}O_3$: m/z 285.1491 $[M+H]^+$, found: m/z 285.1485.



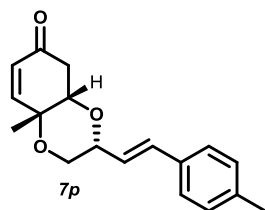
This compound was prepared according to the general procedure C as a pale-yellow solid (24mg, 83% yield in 0.1 mmol scale). d.r. = 20:1

1H NMR (500 MHz, $CDCl_3$) δ 7.21-7.12 (m, 3H), 7.07-7.03 (m, 1H), 6.70-6.57 (m, 2H), 6.13 (d, J = 10.4 Hz, 1H), 5.99 (dd, J = 16.1, 6.2 Hz, 1H), 4.31-4.25 (m, 1H), 4.06-4.02 (m, 1H), 3.71 (dd, J = 11.8, 2.7 Hz, 1H), 3.55 (dd, J = 11.8, 10.3 Hz, 1H), 2.71 (d, J = 3.1 Hz, 2H), 2.32 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.84, 152.27, 138.24, 136.26, 133.08, 130.93, 128.92, 128.58, 127.37, 124.17, 123.84, 78.19, 76.04, 71.50, 67.21, 42.19, 24.56, 21.47.

IR (neat) 2970, 2861, 1737, 1684, 1372, 1121 cm^{-1} .

HRMS (ESI) exact mass calcd for $C_{18}H_{21}O_3$: m/z 285.1491 $[M+H]^+$, found: m/z 285.1488.



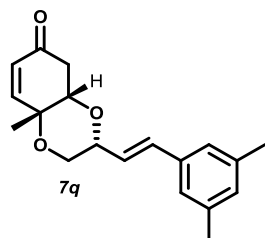
This compound was prepared according to the general procedure C as a pale-yellow solid (23mg, 82% yield in 0.1 mmol scale). d.r. = 40:1

1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 6.68 (dd, J = 10.3, 2.8 Hz, 1H), 6.59 (dd, J = 16.1, 1.1 Hz, 1H), 6.13 (d, J = 10.3 Hz, 1H), 5.95 (dd, J = 16.1, 6.3 Hz, 1H), 4.30-4.24 (m, 1H), 4.05-4.03 (m, 1H), 3.71 (dd, J = 11.8, 2.8 Hz, 1H), 3.55 (dd, J = 11.8, 10.3 Hz, 1H), 2.71 (d, J = 3.1 Hz, 2H), 2.32 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.87, 152.33, 138.04, 133.54, 133.01, 130.93, 129.40, 126.59, 123.29, 78.20, 76.16, 71.49, 67.25, 42.20, 24.58, 21.35.

IR (neat) 2970, 2860, 1738, 1682, 1366, 1118 cm^{-1} .

HRMS (ESI) exact mass calcd for $C_{18}H_{21}O_3$: m/z 285.1491 $[M+H]^+$, found: m/z 285.1492.



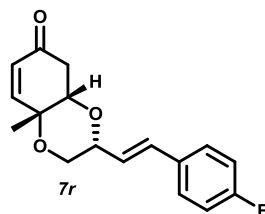
This compound was prepared according to the general procedure C as a pale-yellow solid (24mg, 81% yield in 0.1 mmol scale). d.r. = 15:1

1H NMR (500 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.88 (s, 1H), 6.68 (dd, J = 10.4, 2.7 Hz, 1H), 6.56 (dd, J = 16.1, 1.2 Hz, 1H), 6.13 (d, J = 10.4 Hz, 1H), 5.98 (dd, J = 16.1, 6.3 Hz, 1H), 4.31-4.24 (m, 1H), 4.06-4.02 (m, 1H), 3.71 (dd, J = 11.8, 2.8 Hz, 1H), 3.54 (dd, J = 11.8, 10.3 Hz, 1H), 2.71 (d, J = 3.1 Hz, 2H), 2.28 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.91, 152.31, 138.14, 136.19, 133.17, 130.92, 129.86, 124.57, 123.95, 78.14, 76.08, 71.49, 67.23, 42.19, 24.55, 21.35.

IR (neat) 2968, 2862, 1738, 1683, 1372, 1119 cm^{-1} .

HRMS (ESI) exact mass calcd for $C_{19}H_{23}O_3$: m/z 299.1647 $[M+H]^+$, found: m/z 299.1642.



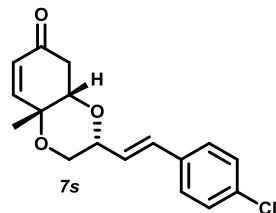
This compound was prepared according to the general procedure C as a pale-yellow solid (20mg, 69% yield in 0.1 mmol scale). d.r. = 40:1

1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.01-6.95 (m, 2H), 6.67 (dd, J = 10.4, 2.8 Hz, 1H), 6.62-6.56 (m, 1H), 6.13 (d, J = 10.3 Hz, 1H), 5.92 (dd, J = 16.1, 6.1 Hz, 1H), 4.30-4.24 (m, 1H), 4.06-4.02 (m, 1H), 3.72 (dd, J = 11.8, 2.7 Hz, 1H), 3.54 (dd, J = 11.8, 10.4 Hz, 1H), 2.71 (d, J = 3.1 Hz, 2H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.82 , 162.66 (d, J = 247.3 Hz), 152.22 , 132.51 (d, J = 3.3 Hz), 131.81 , 130.95 , 128.23 (d, J = 8.1 Hz), 124.11 (d, J = 2.2 Hz), 115.64 (d, J = 21.7 Hz), 78.24 , 75.88 , 71.53 , 67.16 , 42.19 , 24.55 .

IR (neat) 2970, 1738, 1683, 1372, 1121 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{18}\text{FO}_3$: m/z 289.1240 $[\text{M}+\text{H}]^+$, found: m/z 289.1235.



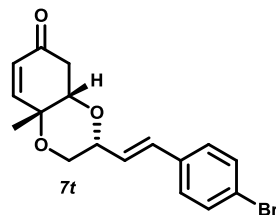
This compound was prepared according to the general procedure C as a pale-yellow solid (22mg, 73% yield in 0.1 mmol scale). d.r. = 40:1

^1H NMR (500 MHz, CDCl_3) δ 7.26 (s, 4H), 6.67 (dd, J = 10.3, 2.8 Hz, 1H), 6.58 (dd, J = 16.1, 1.4 Hz, 1H), 6.12 (d, J = 10.4 Hz, 1H), 5.98 (dd, J = 16.1, 6.0 Hz, 1H), 4.31-4.25 (m, 1H), 4.07-4.01 (m, 1H), 3.72 (dd, J = 11.8, 2.8 Hz, 1H), 3.53 (dd, J = 11.8, 10.4 Hz, 1H), 2.71 (d, J = 3.1 Hz, 2H), 1.42 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.77, 152.16, 134.86, 133.78, 131.62, 130.94, 128.86, 127.86, 125.04, 78.24, 75.77, 71.53, 67.07, 42.17, 24.52.

IR (neat) 2970, 1736, 1683, 1372, 1118 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{18}\text{ClO}_3$: m/z 305.0944 $[\text{M}+\text{H}]^+$, found: m/z 305.0937.



This compound was prepared according to the general procedure C as a pale-yellow solid (26mg, 74% yield in 0.1 mmol scale). d.r. = 40:1

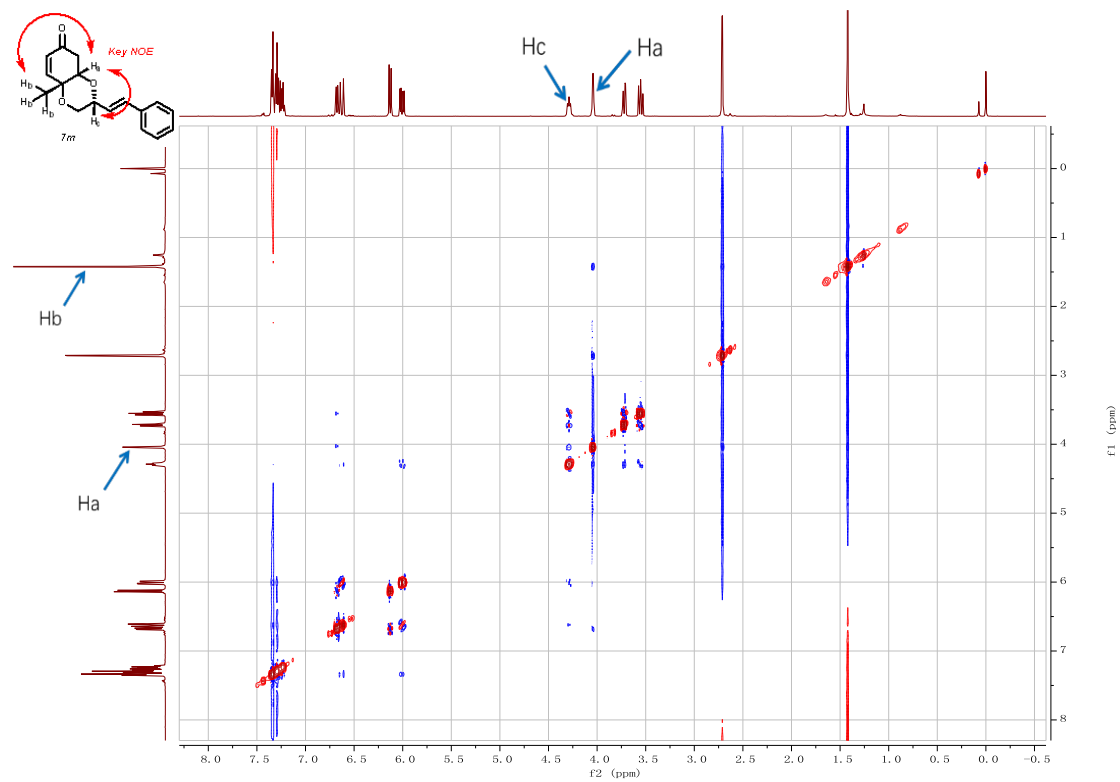
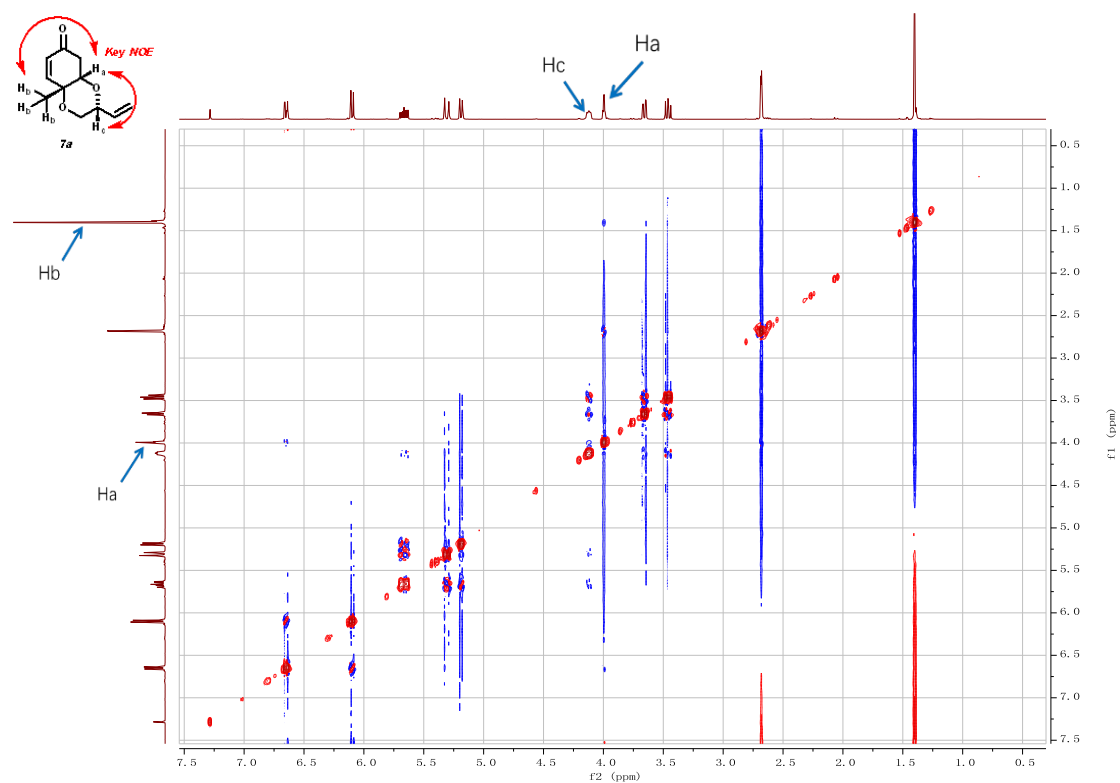
^1H NMR (500 MHz, CDCl_3) δ 7.41 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.67 (dd, J = 10.4, 2.8 Hz, 1H), 6.56 (dd, J = 16.1, 1.4 Hz, 1H), 6.12 (d, J = 10.4 Hz, 1H), 6.00 (dd, J = 16.1, 6.0 Hz, 1H), 4.30-4.25 (m, 1H), 4.05-4.01 (m, 1H), 3.74-3.68 (m, 1H), 3.53 (dd, J = 11.8, 10.3 Hz, 1H), 2.71 (d, J = 3.0 Hz, 2H), 1.42 (s, 3H).

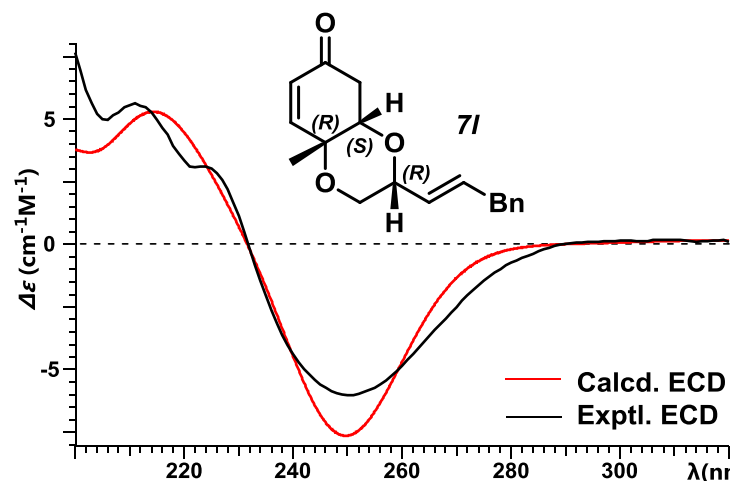
^{13}C NMR (126 MHz, CDCl_3) δ 195.76, 152.15, 135.30, 131.82, 131.65, 130.95, 128.17, 125.17, 121.95, 78.24, 75.76, 71.54, 67.04, 42.17, 24.53.

IR (neat) 2970, 1738, 1684, 1372, 1119 cm^{-1} .

HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{18}\text{BrO}_3$: m/z 349.0439 $[\text{M}+\text{H}]^+$, found: m/z 349.0432.

5. Relative configuration of 7a, 7l, 7m





Calculation method^{2, 3, 4}:

A preliminary conformational search was performed in Conflex6.7¹ using MMFF94s forcefield. Conformers were saved and further optimized using B3LYP/6-311++G(d,p) level with CPCM solvent model in Gaussian 09 software package.² Frequency was calculated at the same level to check optimized results. The stable conformers with populations greater than 1% and without imaginary frequencies were submitted to ECD calculation by the TDDFT (cam-B3LYP/TZVP) method associated with CPCM solvent model in MeCN. The excitation energies (E), oscillator strength (f), rotatory strength in velocity form (Rvel), and rotatory strength in length form (Rlen) of the lowest 32 excited states were calculated. ECD spectra of different conformers were summated in SpecDis³ according to their Boltzmann-calculated distributions.

----- Table of Energy analysis-----

conformer	E(a.u.)	ΔE(kcal/mol)	Boltz Distribution(%)
1a-1CD	-923.4353037	0.0464357	24.17
1a-2CD	-923.4353777	0.0000000	26.15
1a-3CD	-923.4347545	0.3910642	13.50
1a-6CD	-923.4347781	0.3762550	13.85
1a-7CD	-923.4342613	0.7005522	8.01
1a-8CD	-923.4348101	0.3561747	14.32

Comparison of CD Curve :

Best Similarity factor (S = 0.9744) was found for sigma =0.3 eV at 7 nm shift

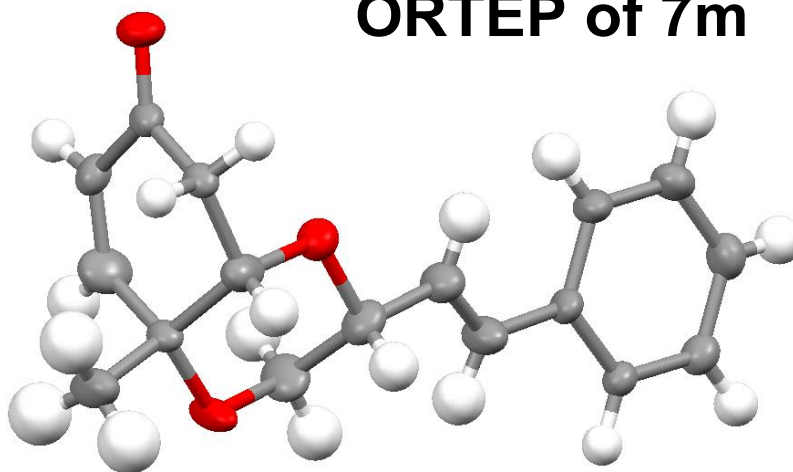
² Conflex 6.7, Conflex Corp.: Tokyo Yokohama, Japan, 2010; Conflex Corp.: Tokyo Yokohama, Japan

³ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09 revision D.01; Gaussian Inc.: Wallingford CT, 2013.

⁴ Bruhn, T.; Schaumloeffel, A.; Hemberger, Y.; Bringmann, G. Chirality **2013**, 25, 243–249.

6. X-ray data of 7m

ORTEP of 7m



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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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S22

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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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C14	C 0.1181(3) 1.0283(5) 0.1355(4) 0.0311(10) Uani 1 1 d . . .
H14	H 0.0898 1.1168 0.1557 0.037 Uiso 1 1 calc R . .
C15	C 0.1955(5) 1.0227(6) 0.0665(5) 0.0456(13) Uani 1 1 d . . .
H15	H 0.2223 1.1100 0.0421 0.055 Uiso 1 1 calc R . .
C16	C 0.2450(3) 0.8867(5) 0.0231(3) 0.0261(9) Uani 1 1 d . . .
O3	O 0.3610(3) 0.9024(5) 0.0058(3) 0.0475(11) Uani 1 1 d . . .
C10	C 0.4276(4) 0.9290(7) 0.1035(5) 0.0492(14) Uani 1 1 d . . .
H10A	H 0.4012 1.0151 0.1378 0.059 Uiso 1 1 calc R . .
H10B	H 0.5055 0.9435 0.0884 0.059 Uiso 1 1 calc R . .
C9	C 0.4176(4) 0.8022(6) 0.1749(4) 0.0397(12) Uani 1 1 d . . .
H9	H 0.4415 0.7152 0.1384 0.048 Uiso 1 1 calc R . .
C8	C 0.4839(4) 0.8173(6) 0.2776(4) 0.0416(12) Uani 1 1 d . . .
H8	H 0.4506 0.7916 0.3397 0.050 Uiso 1 1 calc R . .
C7	C 0.5905(4) 0.8666(7) 0.2854(4) 0.0456(14) Uani 1 1 d . . .
H7	H 0.6197 0.8966 0.2223 0.055 Uiso 1 1 calc R . .
C4	C 0.6658(3) 0.8786(5) 0.3811(4) 0.0308(10) Uani 1 1 d . . .
C5	C 0.7811(3) 0.8883(4) 0.3705(4) 0.0269(9) Uani 1 1 d . . .
H5	H 0.8084 0.8901 0.3030 0.032 Uiso 1 1 calc R . .
C6	C 0.8560(4) 0.8953(5) 0.4593(4) 0.0316(10) Uani 1 1 d . . .

H6 H 0.9326 0.8994 0.4508 0.038 Uiso 1 1 calc R . .
 C1 C 0.8165(4) 0.8960(5) 0.5598(4) 0.0386(11) Uani 1 1 d . . .
 H1 H 0.8665 0.9020 0.6191 0.046 Uiso 1 1 calc R . .
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 C12 C 0.1143(3) 0.7531(5) 0.1372(3) 0.0258(9) Uani 1 1 d . . .
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 H12B H 0.0641 0.7255 0.0773 0.031 Uiso 1 1 calc R . .
 C11 C 0.2305(4) 0.7646(5) 0.1015(4) 0.0389(12) Uani 1 1 d . . .
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 C17 C 0.1918(4) 0.8601(8) -0.0853(4) 0.0517(15) Uani 1 1 d . . .
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 H17B H 0.1170 0.8246 -0.0794 0.078 Uiso 1 1 calc R . .
 H17C H 0.2348 0.7900 -0.1214 0.078 Uiso 1 1 calc R . .
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 C7 0.027(2) 0.077(4) 0.033(3) 0.007(2) 0.004(2) -0.001(2)
 C4 0.0184(18) 0.045(3) 0.029(2) 0.0059(19) 0.0008(16) 0.0046(17)
 C5 0.0205(18) 0.031(2) 0.029(2) 0.0020(17) 0.0022(15) 0.0019(15)
 C6 0.0232(19) 0.035(2) 0.037(3) -0.0014(19) -0.0002(17) -0.0014(17)
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 C11 0.040(3) 0.034(2) 0.044(3) 0.009(2) 0.016(2) 0.006(2)
 O2 0.0262(15) 0.044(2) 0.039(2) 0.0032(15) 0.0006(13) -0.0032(13)
 C17 0.030(2) 0.096(5) 0.029(3) 0.000(3) 0.000(2) 0.003(3)
 C2 0.037(3) 0.054(3) 0.027(2) 0.001(2) 0.0050(19) 0.003(2)
 C3 0.024(2) 0.059(3) 0.031(3) 0.007(2) 0.0072(18) 0.007(2)

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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C15 H15 0.9300 . ?

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C16 C17 1.493(7) . ?

C16 C11 1.520(6) . ?

O3 C10 1.448(6) . ?

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C9 H9 0.9800 . ?

C8 C7 1.352(7) . ?

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O3 C10 H10B 110.0 . . ?
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O2 C9 C10 108.0(4) . . ?
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C10 C9 H9 109.3 . . ?
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C8 C7 H7 116.0 . . ?
C4 C7 H7 116.0 . . ?

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 C5 C4 C7 119.2(4) . . ?
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 O1 C13 C12 122.9(4) . . ?
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 C13 C12 H12A 109.2 . . ?
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 C13 C12 H12B 109.2 . . ?
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O3 C16 C11 O2 53.8(5) . . . . ?
C17 C16 C11 O2 169.8(4) . . . . ?
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O3 C16 C11 C12 171.6(4) . . . . ?
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C8 C9 O2 C11 -176.9(4) . . . . ?
C10 C9 O2 C11 60.6(5) . . . . ?
C12 C11 O2 C9 -179.6(4) . . . . ?
C16 C11 O2 C9 -57.0(5) . . . . ?
C6 C1 C2 C3 -1.2(8) . . . . ?
C1 C2 C3 C4 2.2(8) . . . . ?
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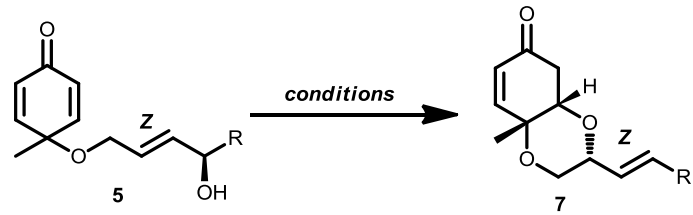
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7. Chirality transfer studies

Table 3. Chirality transfer studies using enantiopure allylic alcohols.

		
R = Bn, 5l, 96% ee	$\text{Re}_2\text{O}_7, \text{CH}_2\text{Cl}_2, 0^\circ\text{C}$ $\text{Ph}_3\text{SiO-ReO}_3, \text{Et}_2\text{O}, -78^\circ\text{C}$	73%, d.r. 25:1 85% ee 54%, d.r. 26:1 92% ee
R = Ph, 5m, 99% ee	$\text{Re}_2\text{O}_7, \text{CH}_2\text{Cl}_2, 0^\circ\text{C}$ $\text{Ph}_3\text{SiO-ReO}_3, \text{Et}_2\text{O}, -78^\circ\text{C}$	84%, d.r. 32:1 0% ee 53%, d.r. 34:1 81% ee

The enantiomeric excess of **5l** was found to be 96% by chiral HPLC (ChiralPak PA-2 column, hexane/*i*-PrOH 80:20 0.7 mL/min, $t_{\text{major}} = 20.00$ min, $t_{\text{minor}} = 22.07$ min).

Condition A : $\text{Re}_2\text{O}_7, \text{CH}_2\text{Cl}_2, 0^\circ\text{C}$

The enantiomeric excess of **7l** was found to be 85% by chiral HPLC (ChiralPak IC column, hexane/*i*-PrOH 90:10 0.7 mL/min, $t_{\text{major}} = 22.04$ min, $t_{\text{minor}} = 25.81$ min).

Condition B : $\text{Ph}_3\text{SiO-ReO}_3, \text{Et}_2\text{O}, -78^\circ\text{C}$

The enantiomeric excess of **7l** was found to be 92% by chiral HPLC (ChiralPak IC column, hexane/*i*-PrOH 90:10 0.7 mL/min, $t_{\text{major}} = 22.33$ min, $t_{\text{minor}} = 26.10$ min).

The enantiomeric excess of **5m** was found to be 99% by chiral HPLC (ChiralPak AD-H column, hexane/*i*-PrOH 80:20 0.7 mL/min, $t_{\text{major}} = 12.08$ min, $t_{\text{minor}} = 12.87$ min).

Condition A : $\text{Re}_2\text{O}_7, \text{CH}_2\text{Cl}_2, 0^\circ\text{C}$

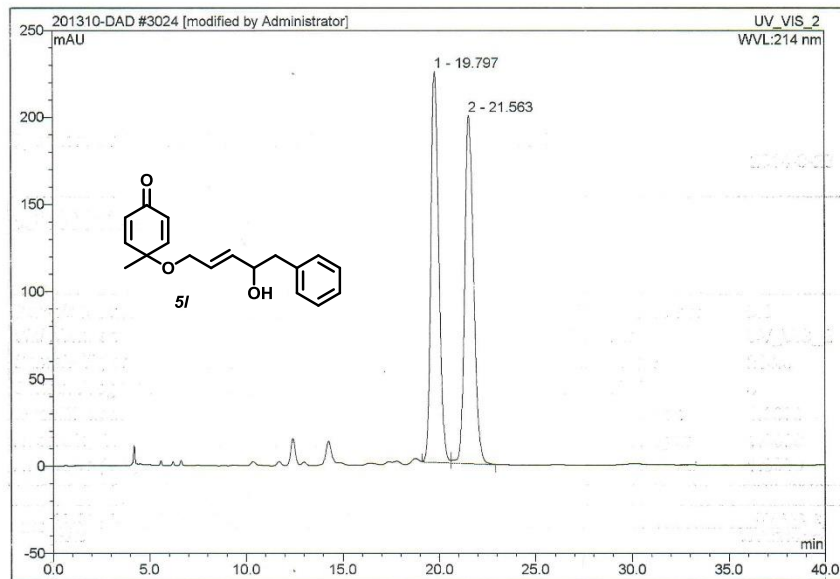
The enantiomeric excess of **7m** was found to be 0% by chiral HPLC (ChiralPak IC column, hexane/*i*-PrOH 90:10 0.7 mL/min, $t_{\text{major}} = 24.95$ min, $t_{\text{minor}} = 28.11$ min).

Condition B : $\text{Ph}_3\text{SiO-ReO}_3, \text{Et}_2\text{O}, -78^\circ\text{C}$

The enantiomeric excess of **7m** was found to be 81% by chiral HPLC (ChiralPak IC column, hexane/*i*-PrOH 90:10 0.7 mL/min, $t_{\text{major}} = 25.67$ min, $t_{\text{minor}} = 29.35$ min).

3024 XZL-2043-1+- PA-2 82 214 0.7

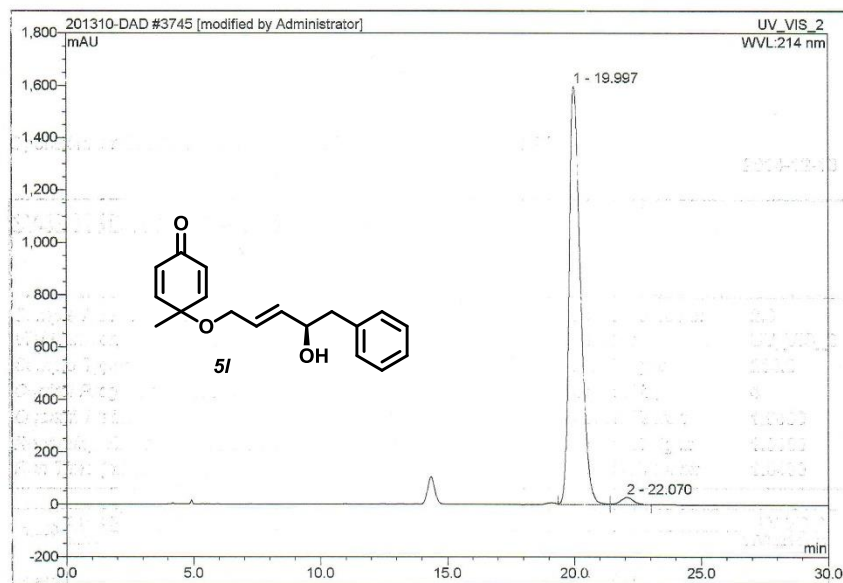
Sample Name:	XZL-2043-1+- PA-2 82 214 0.7	Injection Volume:	5.0
Vial Number:	BA5	Channel:	UV_VIS_2
Sample Type:	unknown	Wavelength:	214.0
Control Program:	test-dad2	Bandwidth:	4
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014-9-26 10:52	Sample Weight:	1.0000
Run Time (min):	39.97	Sample Amount:	1.0000



No.	Ret. Time min	Peak Name	Height mAU	Area mAU*min	Rel. Area %	Amount	Type
1	19.80	n.a.	224.552	106.502	49.83	n.a.	BM *
2	21.56	n.a.	199.883	107.239	50.17	n.a.	MB*
Total:			424.435	213.741	100.00	0.000	

3745 HJD-2-23 PA-2 82 214 0.7

Sample Name:	HJD-2-23 PA-2 82 214 0.7	Injection Volume:	2.0
Vial Number:	BC1	Channel:	UV_VIS_2
Sample Type:	unknown	Wavelength:	214.0
Control Program:	test-dad2	Bandwidth:	4
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014-12-16 17:23	Sample Weight:	1.0000
Run Time (min):	30.00	Sample Amount:	1.0000



No.	Ret. Time min	Peak Name	Height mAU	Area mAU*min	Rel. Area %	Amount	Type
1	20.00	n.a.	1599.679	831.120	98.08	n.a.	M *
2	22.07	n.a.	27.780	16.286	1.92	n.a.	MB *
Total:			1627.459	847.406	100.00	0.000	

defitdad/Integration

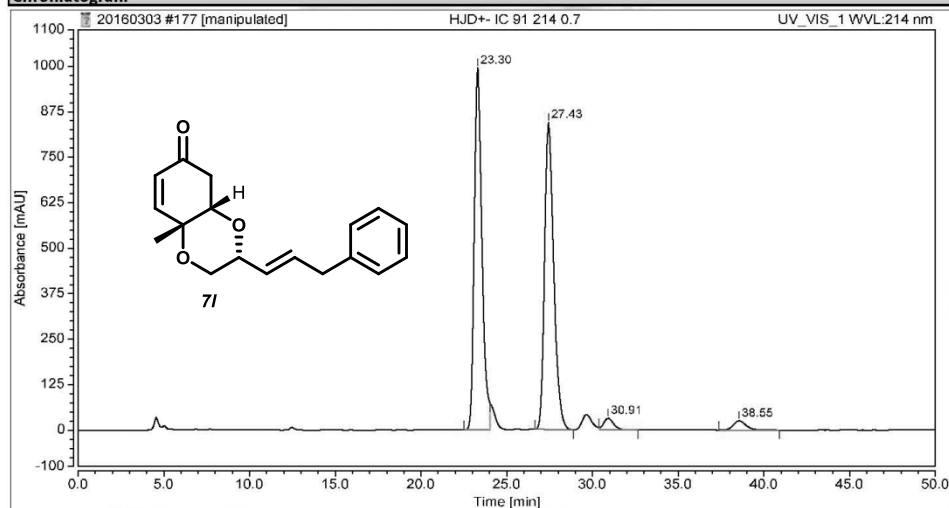
Chromeleon (c) Dionex 1996-200
Version 6.80 SR14 Build 4527 (238905

Chromatogram and Results

Injection Details

Injection Name:	HJD+- IC 91 214 0.7	Run Time (min):	50.00
Vial Number:	RC2	Injection Volume:	5.00
Injection Type:	Unknown	Channel:	UV_VIS_1
Calibration Level:		Wavelength:	214.0
Instrument Method:	20160223-DAD2	Bandwidth:	4
Processing Method:	20160223	Dilution Factor:	1.0000
Injection Date/Time:	28/三月/16 18:04	Sample Weight:	1.0000

Chromatogram

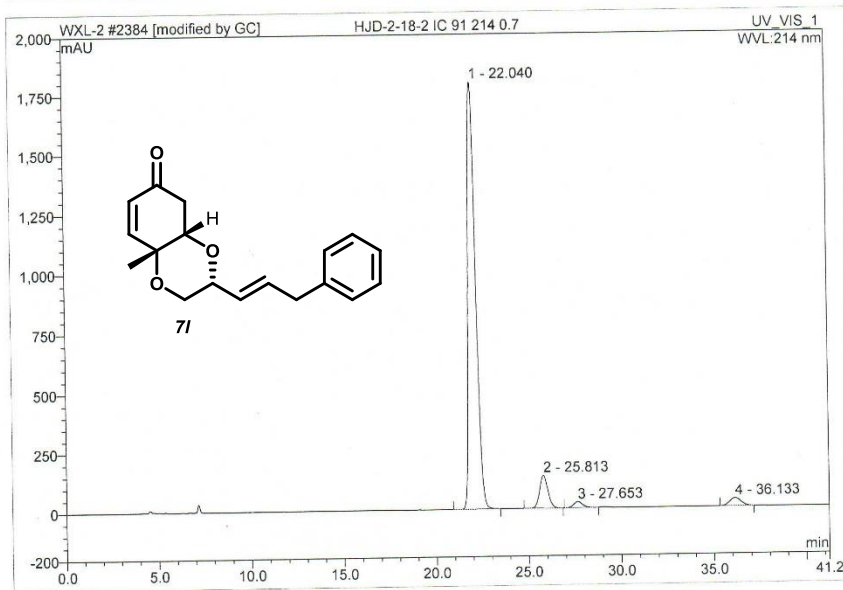


Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	23.300	515.630	994.673	47.70
2	27.433	521.758	844.099	48.27
3	30.913	21.943	32.082	2.03
4	38.547	21.671	25.321	2.00
Total:		1081.002	1896.174	100.00

2384 HJD-2-18-2 IC 91 214 0.7

Sample Name:	HJD-2-18-2 IC 91 214 0.7	Injection Volume:	5.0
Vial Number:	BA2	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL-2014-2	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014/12/10 16:45	Sample Weight:	1.0000
Run Time (min):	41.24	Sample Amount:	1.0000



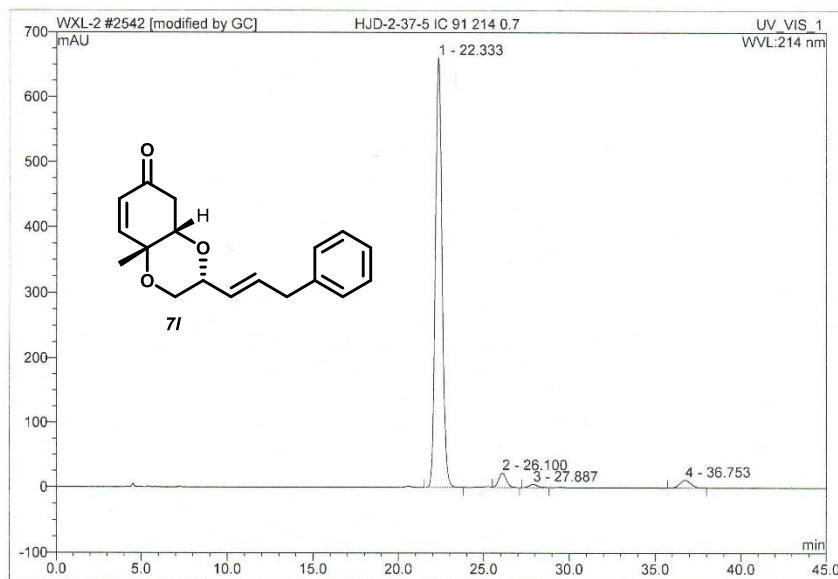
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.04	n.a.	1797.691	872.109	88.86	n.a.	BMB*
2	25.81	n.a.	138.793	71.501	7.29	n.a.	BMB*
3	27.65	n.a.	25.475	13.746	1.40	n.a.	BMB*
4	36.13	n.a.	33.939	24.113	2.46	n.a.	BMB*
Total:			1995.898	981.468	100.00	0.000	

$R = B_{11}$, $R = 0.7$, CH_2Cl_2 , $0^\circ C$.

yield = 73% , 85% e.e.

2542 HJD-2-37-5 IC 91 214 0.7

Sample Name:	HJD-2-37-5 IC 91 214 0.7	Injection Volume:	3.0
Vial Number:	RE5	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL-2014-1	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014/12/26 21:10	Sample Weight:	1.0000
Run Time (min):	45.00	Sample Amount:	1.0000



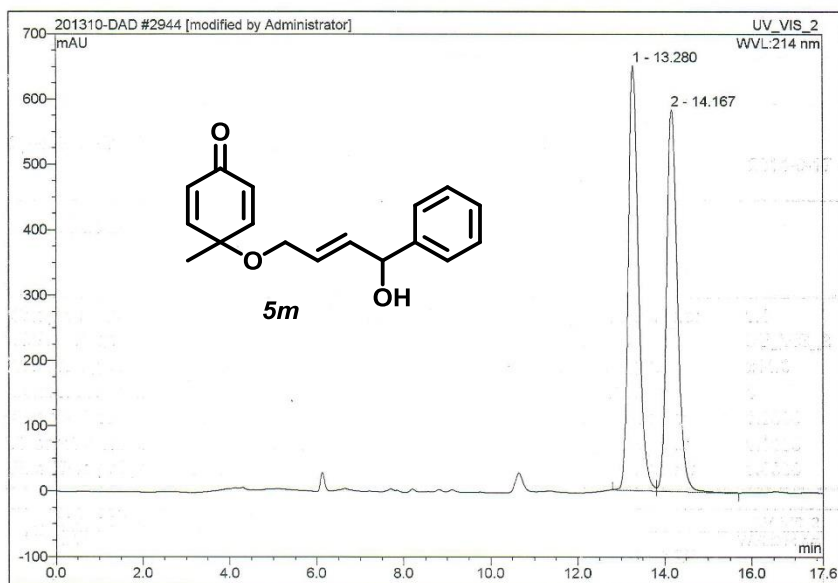
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.33	n.a.	660.986	299.670	92.68	n.a.	BM *
2	26.10	n.a.	22.249	11.812	3.65	n.a.	MB *
3	27.89	n.a.	4.918	2.934	0.91	n.a.	BM *
4	36.75	n.a.	12.048	8.918	2.76	n.a.	BM *
Total:			700.201	323.334	100.00	0.000	

$R = B_{11}$, $Ph_3SiO-ReO_3$, Ft_2O , $-78^\circ C$.

yield = 54% , 92% e.e.

2944 XZL-2041-1+- AD-H 82 214 0.7

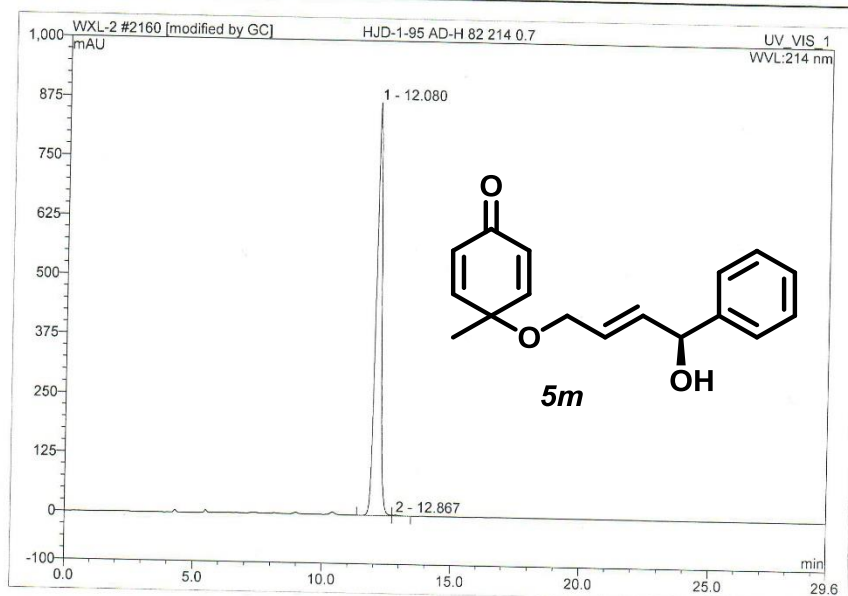
Sample Name:	XZL-2041-1+- AD-H 82 214 0.7	Injection Volume:	1.0
Vial Number:	BD3	Channel:	UV_VIS_2
Sample Type:	unknown	Wavelength:	214.0
Control Program:	test-dad	Bandwidth:	4
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014-9-17 14:48	Sample Weight:	1.0000
Run Time (min):	17.64	Sample Amount:	1.0000



No.	Ret. Time min	Peak Name	Height mAU	Area mAU*min	Rel. Area %	Amount	Type
1	13.28	n.a.	650.070	176.544	50.99	n.a.	BM *
2	14.17	n.a.	583.902	169.693	49.01	n.a.	MB*
Total:			1233.973	346.237	100.00	0.000	

2160 HJD-1-95 AD-H 82 214 0.7

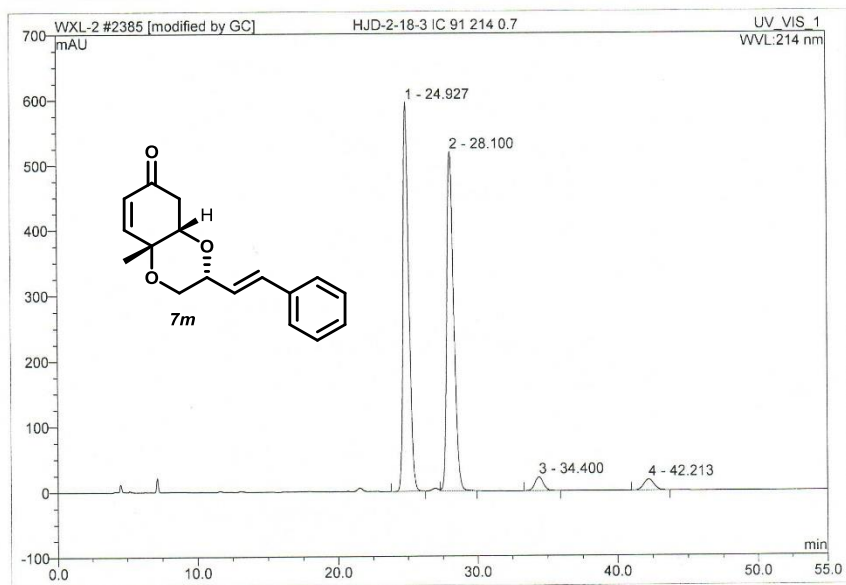
Sample Name:	HJD-1-95 AD-H 82 214 0.7	Injection Volume:	3.0
Vial Number:	RC5	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL-2014-1	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014/11/17 16:32	Sample Weight:	1.0000
Run Time (min):	29.58	Sample Amount:	1.0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.08	n.a.	868.954	221.893	99.80	n.a.	BM *
2	12.87	n.a.	1.563	0.441	0.20	n.a.	MB*
Total:			870.516	222.334	100.00	0.000	

2385 HJD-2-18-3 IC 91 214 0.7

Sample Name:	HJD-2-18-3 IC 91 214 0.7	Injection Volume:	5.0
Vial Number:	BA3	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL-2014-2	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014/12/10 17:30	Sample Weight:	1.0000
Run Time (min):	55.00	Sample Amount:	1.0000

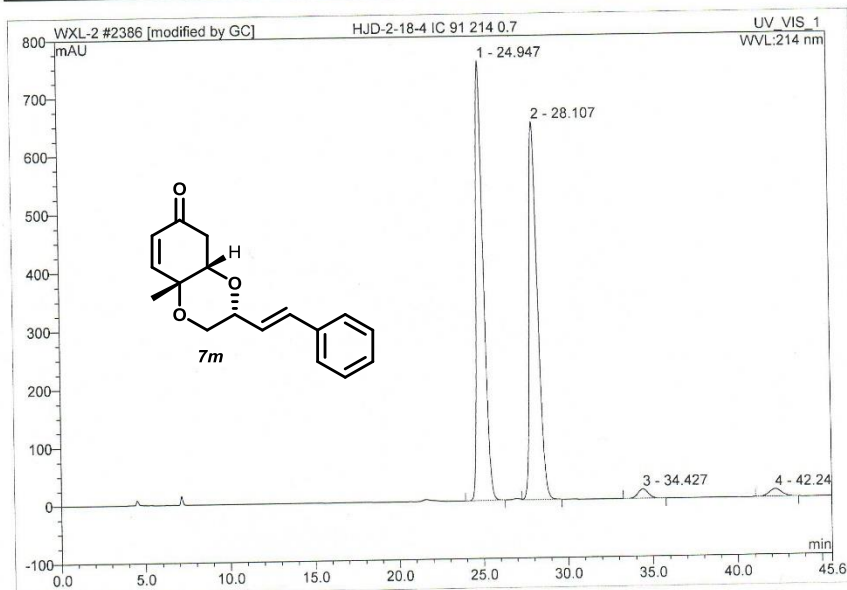


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.93	n.a.	595.372	294.843	47.57	n.a.	BMB*
2	28.10	n.a.	518.952	295.726	47.72	n.a.	MB*
3	34.40	n.a.	21.235	14.662	2.37	n.a.	BMB*
4	42.21	n.a.	17.004	14.533	2.34	n.a.	BMB*
Total:			1152.563	619.764	100.00	0.000	

R=Ph, +/-

2386 HJD-2-18-4 IC 91 214 0.7

Sample Name:	HJD-2-18-4 IC 91 214 0.7	Injection Volume:	5.0
Vial Number:	BA4	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL-2014-2	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014/12/10 18:27	Sample Weight:	1.0000
Run Time (min):	45.59	Sample Amount:	1.0000



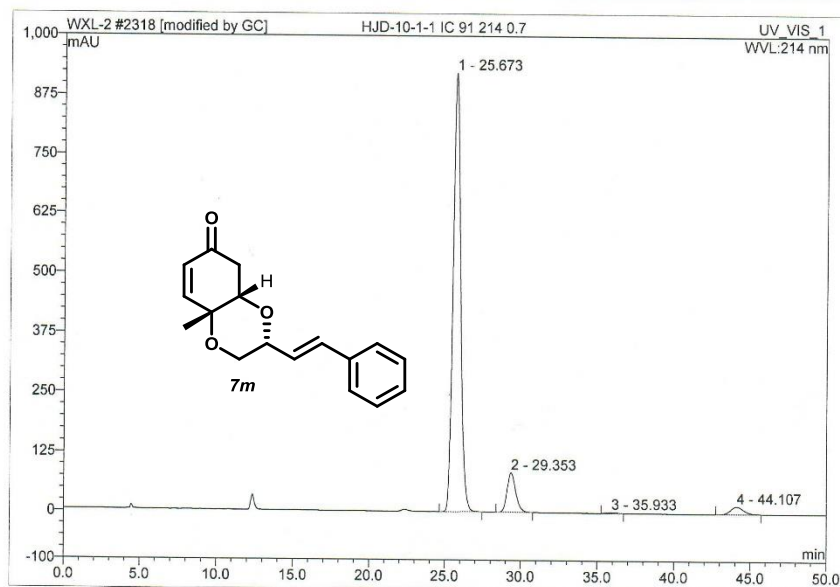
No.	Ret. Time min	Peak Name	Height mAU	Area mAU*min	Rel. Area %	Amount	Type
1	24.95	n.a.	757.057	375.974	48.86	n.a.	BMB*
2	28.11	n.a.	649.689	370.434	48.14	n.a.	MB*
3	34.43	n.a.	16.716	11.517	1.50	n.a.	BMB*
4	42.24	n.a.	13.499	11.506	1.50	n.a.	BMB*
Total:			1436.961	769.432	100.00	0.000	

R = Ph, Re=O₂, CH₂Cl₂, 0°C

yield = 84%, 0% ee.

2318 HJD-10-1-1 IC 91 214 0.7

Sample Name:	HJD-10-1-1 IC 91 214 0.7	Injection Volume:	5.0
Vial Number:	BA3	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL-2014-2	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2014/12/4 15:58	Sample Weight:	1.0000
Run Time (min):	50.01	Sample Amount:	1.0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	25.67	n.a.	921.507	528.676	88.10	n.a.	BMB*
2	29.35	n.a.	82.953	54.254	9.04	n.a.	BMB*
3	35.93	n.a.	1.898	1.357	0.23	n.a.	BMB*
4	44.11	n.a.	15.976	15.770	2.63	n.a.	BMB*
Total:			1022.335	600.058	100.00	0.000	

$R = Ph, R_1SiO-ReO_3, Et_2O, -78^\circ C.$

yield = 53% , 81% e.e.

8. Copies of spectrums

