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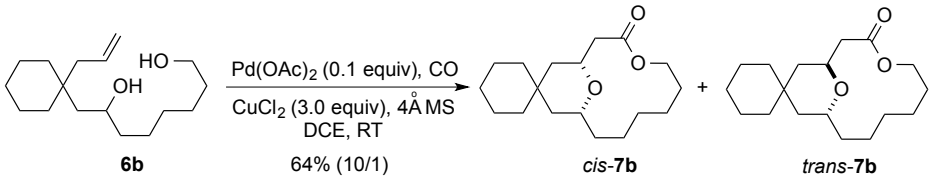
Part 1. Experimental Procedures and Analytical Data

General Methods: NMR spectra were recorded on Bruker spectrometers (^{1}H at 400 MHz, 500 MHz, 800 MHz and ^{13}C at 100 MHz, 125 MHz, 200 MHz) and Varian spectrometers (^{1}H at 300 MHz and ^{13}C at 75 MHz). Chemical shifts (δ) were given in ppm with reference to solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_6D_6 (7.15), CD_3OD (3.31); ^{13}C NMR: $CDCl_3$ (77.2), C_6D_6 (128.02), CD_3OD (49.0)]. Column chromatography was performed on silica gel. All reactions sensitive to air or moisture were conducted under argon or nitrogen atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Anhydrous THF and toluene were distilled over sodium benzophenone ketyl under N_2. Anhydrous CH_2Cl_2 was distilled over calcium hydride under N_2. Anhydrous MeOH was distilled over magnesium under N_2. All other solvents and reagents were used as obtained from commercial sources without further purification.

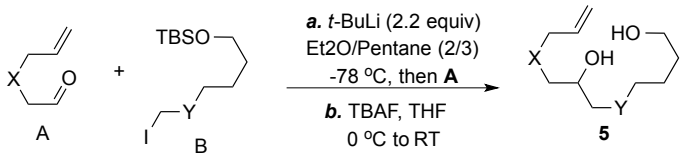
A representative experimental procedure for the palladium-catalyzed alkoxycarbonylative macrolactonization:



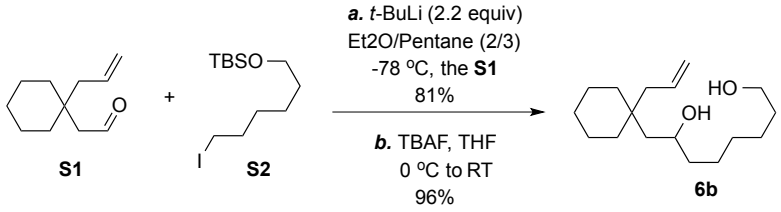
6b *cis*-**7b** *trans*-**7b**

To a 250 mL round flask was added 200 mg molecular sieves, which was then flame dry under vacuum and cooled down to room temperature. $Pd(OAc)_2$ (4.2 mg 0.0187 mmol, 0.1 equiv), anhydrous $CuCl_2$ (75 mg, 0.56 mmol, 3.0 equiv) and 1,2-dichloroethane (73 mL) were added sequentially. The solution was purged by CO balloon and stirred at room temperature. Alkendiol **6b** (50 mg, 0.187 mmol) dissolved in 20 mL 1,2-dichloroethane was then slowly added by syringe pump (the speed rate is 1.2 mL/h). After the addition is completed, the reaction mixture was stirred and monitored by TLC until no more alkendiol left (usually 24-48 h). The reaction mixture was passed through a short pad of celite to filtrate the solid, concentrated under vacuum until 1/5 of the solvent left, then diluted with 50 mL EtOAc, and washed with 10 mL saturated $NaHCO_3$. The aqueous layer was extract twice with EtOAc. The combined organic layer was washed with 10 mL brine, dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The crude product was purified by flash chromatography (EtOAc/Hexane=1/50 to 1/30) to give 31.8 mg of *cis*-**7b** and 3.2 mg of *trans*-**7b**. The total yield is 64 % with 10/1 diastereoselectivty.

Experimental procedure for the preparation of the alkendiol substrates: All the alkendiols in this investigation were synthesized using the method shown below: 1,2-addition of alkyllithium derived from alkyliodide **B** to aldehyde **A** followed by TBAF removal of the TBS group.

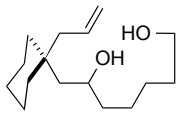


A representative experimental procedure for the synthesis of alkendiol substrates:



Alkyliodide (400 mg, 1.17 mmol) was dissolved in a mixture solvent of 4.7 mL pentane and 3.0 mL Et_2O. The solution was cooled down to -78 ^{o}C for 5 min before 1.51 mL *tert*-butyllithium (1.7 M in pentane, 2.57 mmol, 2.2 equiv) was added dropwise. The reaction mixture was stirred at 0 ^{o}C for 0.5 h, then cooled to -78 ^{o}C and a solution of aldehyde (233 mg, 1.4 mmol, 1.2 equiv) in Et_2O (2 mL) was added dropwise. The solution was stirred at -78 ^{o}C for an additional 2 hours then quenched by dropwise addition of a saturated aqueous NH_4Cl solution. After warming to room temperature, the mixture was extracted 3 times with Et_2O and the combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. After concentration under reduced pressure, the crude material was purified by flash chromatography (EtOAc/hexane = 1/30 to 1/20) to give the product as a colorless liquid in 81% yield. (Note in most of the cases, the crude product was used directly in the next TBS deprotection step)

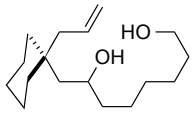
To a solution of the above TBS-ether product (176 mg, 0.46 mmol) in 3.2 mL THF was added dropwise a solution of tetra-*n*-butylammonium fluoride (1.43 mmol, 3.1 equiv) in THF (1.43 mL) at 0 ^{o}C. The reaction mixture was warmed to room temperature, stirred for an additional 3 hours, then diluted with water and extracted 3 times with diethyl ether. The combined organic layer was washed with brine and dried over $MgSO_4$. After concentration under reduced pressure, the crude product was purified by flash chromatography (EtOAc/Hexane = 1/2) to give 118 mg of as a colorless liquid in 96% yield.



6a

61% yield for the 1,2-addition step, 99% yield for the TBS-deprotection.

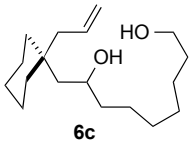
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.79 (ddt, *J* = 16.3, 10.8, 7.4 Hz, 1H), 5.13-4.88 (m, 2H), 3.75 (s, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.19 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.08 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.53 (s, 2H), 1.33 (ddd, *J* = 45.6, 22.8, 5.6 Hz, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.5, 116.8, 88.3, 82.5, 45.3, 41.8, 39.6, 36.1, 35.8, 35.3, 32.6, 26.2, 25.6, 25.3, 21.5; IR (neat): ν = 3321, 2924, 2856, 1545, 1032, 910, 703 cm^{-1}; HRMS (ESI): m/z calcd. For $C_{16}H_{29}O_2$ (M-H)$^-$: 253.2173, found: 253.2176.



6b

81% yield for the 1,2-addition, 96% yield for the TBS-deprotection.

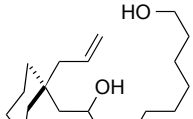
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83-5.75 (m, 1H), 5.02-4.98 (m, 2H), 3.77-3.75 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.20 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.10 (dd, *J* = 14.1, 7.4 Hz, 1H), 1.56-1.32 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 116.8, 68.5, 62.8, 45.4, 41.8, 39.7, 36.2, 35.9, 35.4, 32.6, 29.3, 26.2, 25.7, 25.6, 21.6; IR (neat): ν = 3338, 2925, 2856, 1455, 1056, 910, 652 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{17}H_{31}O_2$ (M-H)$^-$: 267.2329, found: 267.2332.



6c

79% yield for the 1,2-addition, 71% yield for the TBS-deprotection.

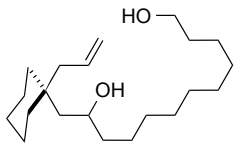
^{1}H NMR (400 MHz, CDCl3): δ = 5,84-5.73 (m, 1H), 5.05-4.96 (m, 2H), 3.74-3.73 (m, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.19 (dd, *J* = 14.0, 7.3 Hz, 1H), 2.11-2.01 (m, 3H), 1.52-1.29 (m, 24H); ^{13}C NMR (101 MHz, CDCl3) δ 135.5, 116.8, 68.5, 62.7, 45.3, 41.8, 39.7, 36.2, 35.8, 35.3, 32.6, 29.5, 29.3, 26.2, 25.6, 25.5, 21.6; IR (neat): ν = 3326, 2923, 2853, 1454, 1056, 909, 723 cm^{-1}; MS (ESI): *m/z* 321.3 $[M+Na]^+$.



6d

51% yield for the 1,2-addition, 51% yield for the TBS-deprotection.

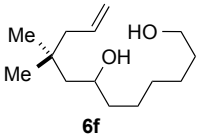
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.79 (ddt, *J* = 16.1, 10.9, 7.4 Hz, 1H), 5.13-4.91 (m, 2H), 3.83-3.71 (m, 1H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.20 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.09 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.79 (s, 2H), 1.54-1.51 (m, 2H), 1.43-1.28 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.5, 116.8, 68.5, 62.8, 45.3, 41.8, 39.8, 36.2, 35.8, 35.3, 32.7, 29.5, 29.3, 26.2, 25.7, 25.6, 21.6; IR (neat): ν = 3321, 2923, 2853, 1455, 1056, 909, 722 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{35}O_2$ (M-H)$^-$: 295.2643, found: 295.2640.



6e

19% for the 1,2-addition, 72% for the TBS-deprotection.

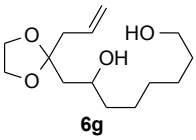
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (ddt, *J* = 15.1, 10.9, 7.4 Hz, 1H), 5.04-4.99 (m, 2H), 3.79-3.76 (m, 1H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.22 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.11 (dd, *J* = 14.1, 7.4 Hz, 1H), 1.58-1.52 (m, 2H), 1.44-1.27 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 116.8, 68.6, 63.0, 45.4, 41.9, 39.8, 36.3, 35.9, 35.4, 32.7, 29.6, 29.6, 29.5, 29.4, 26.3, 25.7, 25.6, 21.6; IR (neat): ν = 3321, 2923, 2853, 1455, 1030, 909, 720 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{39}O_2$ (M-H)$^-$: 323.2956, found: 323.2961.



6f

41% yield for the 1,2-addition, 67% yield for the TBS-deprotection.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.80 (td, *J* = 17.2, 7.5 Hz, 1H), 4.99 (t, *J* = 12.7 Hz, 2H), 3.72 (s, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.09 (d, *J* = 13.5 Hz, 1H), 2.00 (p, *J* = 14.0 Hz, 2H), 1.53 (d, *J* = 5.4 Hz, 3H), 1.34 (t, *J* = 16.8 Hz, 11H), 0.91 (d, *J* = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.7, 116.9, 69.1, 62.7, 49.1, 47.2, 39.5, 33.0, 32.6, 29.3, 27.6, 25.7, 25.5; IR (neat): ν = 3309, 2926, 2854, 1457, 1053, 911, 668 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{27}O_2$ (M-H)$^-$: 227.2017, found: 227.2018.

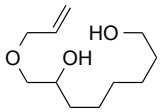


6g

81% for the 1,2-addition, 81% yield for the TBS-deprotection.

^{1}H NMR (400 MHz, CDCl3): δ = 5.82-5.70 (m, 1H), 5.15-5.05 (m, 2H), 4.06-3.93 (m, 4H), 3.93-3.80 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.53 (brs, 2H), 2.39 (d, *J* = 7.1 Hz, 3H), 1.82 (dd, *J* = 14.8, 1.4 Hz, 1H), 1.70 (dd, *J* = 14.8, 10.0 Hz, 1H), 1.56-1.51 (m, 2H), 1.48-1.39 (m, 2H), 1.35-1.32 (m, 6H); ^{13}C NMR (100

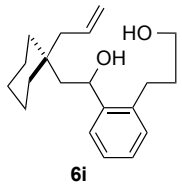
MHz, CDCl3): δ = 132.7, 118.6, 111.4, 67.6, 65.0, 64.6, 62.9, 42.7, 42.1, 37.2, 32.7, 29.4, 25.6, 25.3; IR (neat): ν = 3432, 2928, 2858, 1431, 1033, 917, 822 cm^{-1}; MS (ESI): *m/z* 281.2 $[M+Na]^+$.



6h

23% for the 1,2-addition step, 64% for the TBS-deprotection.

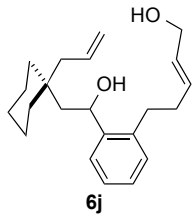
^1H NMR (400 MHz, $CDCl_3$): δ = 5.99-5.78 (m, 1H), 5.31-5.09 (m, 2H), 3.98 (dd, *J* = 5.6, 1.2 Hz, 2H), 3.75-3.71 (m, 1H), 3.56 (t, *J* = 6.6 Hz, 2H), 3.41 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.24 (dd, *J* = 9.3, 8.0 Hz, 1H), 2.68 (brs, 1H), 2.16 (brs, 1H), 1.53-1.48 (m, 2H), 1.41-1.36 (m, 4H), 1.31-1.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 117.2, 74.5, 72.1, 70.2, 62.6, 32.9, 32.5, 29.3, 25.5, 25.4; IR (neat): ν = 3349, 2927, 2856, 1457, 1057, 925, 668 cm^{-1}; HRMS (ESI): calcd. for $C_{11}H_{23}O_3$ $(M+H)^+$: 203.1642, found: 203.1642.



6i

61% for the1,2-addition, 69% for the TBS-deprotection step.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.46-7.43 (m, 1H), 7.24-7.13 (m, 3H), 5.92-5.83 (m, 1H), 5.16 (dd, *J* = 9.0, 2.8 Hz, 1H), 5.08-5.03 (m, 2H), 3.62-3.55 (m, 2H), 2.85 (dt, *J* = 14.9, 7.5 Hz, 1H), 2.77-2.67 (m, 1H), 2.43 (brs, 2H), 2.33 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.20 (dd, *J* = 14.1, 7.4 Hz, 1H), 1.94-1.82 (m, 3H), 1.57 (dd, *J* = 15.0, 2.8 Hz, 1H), 1.46-1.43 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.0, 137.9, 135.4, 129.4, 127.1, 126.3, 116.9, 77.0, 67.6, 61.5, 46.2, 41.7, 36.2, 35.9, 34.2, 28.1, 26.3, 21.7; IR (neat): ν = 3340, 2922, 2860, 1454, 1056, 1033, 910, 764, 622 cm^{-1}; MS (ESI): *m/z* 301.2 $[M-H]^-$.

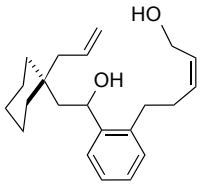


6j

36% for the 1,2-addition step, 72% for the TBS-deprotection.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.26-7.10 (m, 3H), 5.96-5.83 (m, 1H), 5.78-5.68 (m, 1H), 5.57 (dt, *J* = 15.3, 5.6 Hz, 1H), 5.15 (dd, *J* = 9.4, 2.5 Hz, 1H), 5.12-5.06 (m, 2H), 4.05

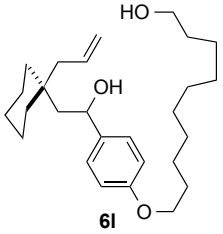
(d, *J* = 5.2 Hz, 2H), 2.85-2.67 (m, 2H), 2.47-2.18 (m, 4H), 2.03 (brs, 2H), 1.83 (dd, *J* = 15.1, 9.4 Hz, 1H), 1.59-1.34 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 137.1, 135.5, 131.5, 129.8, 129.3, 127.0, 126.5, 125.9, 116.9, 77.0, 67.2, 63.3, 46.8, 41.9, 36.3, 36.0, 34.2, 31.9, 26.3, 21.8, 21.7; IR (neat): ν = 3350, 2931, 2877, 1457, 1056, 1042, 895, 732, 668 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{31}O_2$ (M-H)$^-$: 227.2017, found: 227.2018.



6k

33% for the 1,2-addition, 78% yield for the TBS-deprotection.

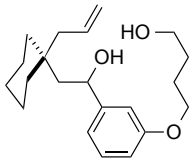
^{1}H NMR (300 MHz, CDCl3): δ = 7.50 (d, *J* = 7.1 Hz, 1H), 7.29-7.10 (m, 3H), 5.89 (dt, *J* = 18.5, 7.3 Hz, 1H), 5.63-5.61 (m, 2H), 5.15-5.04 (m, 3H), 4.00-3.87 (m, 2H), 2.82 (dt, *J* = 14.4, 7.3 Hz, 1H), 2.74-2.64 (m, 1H), 2.42-2.31 (m, 3H), 2.21 (dd, *J* = 13.9, 7.5 Hz, 1H), 1.90-1.83 (m, 2H), 1.55-1.45 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 137.2, 135.4, 131.6, 129.6, 129.2, 127.0, 126.6, 126.1, 116.9, 77.0, 67.2, 58.0, 46.5, 41.8, 36.2, 35.9, 32.1, 29.4, 26.3, 21.8, 21.7; IR (neat): ν = 3367, 2923, 2858, 1453, 999, 911, 761 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{31}O_2$ (M-H)$^-$: 327.2330, found: 327.2332.



6l

30% yield for the 1,2-addition, 83% for the TBS-deprotection.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 5.91-5.77 (m, 1H), 5.07-5.06 (m, 1H), 4.81 (dd, *J* = 8.0, 3.3 Hz, 1H), 3.93 (t, *J* = 6.5 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 1H), 2.27 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.14 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.88 (brs, 1H), 1.83-1.74 (m, 3H), 1.63-1.51 (m, 3H), 1.46-1.31 (m, 23H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 138.6, 135.3, 126.7, 114.3, 71.0, 67.9, 62.9, 46.7, 42.0, 36.4, 35.9, 35.6, 32.8, 29.5, 29.5, 29.4, 29.4, 29.3, 26.3, 26.0, 25.8, 21.7, 21.7; IR (neat): ν = 3352, 2923, 2854, 1510, 1455, 1242, 1050, 998, 832, 737, 609 cm^{-1}; HRMS (ESI): calcd. for $C_{27}H_{43}O_3$ (M-H)$^-$: 415.3218, found: 415.3224.

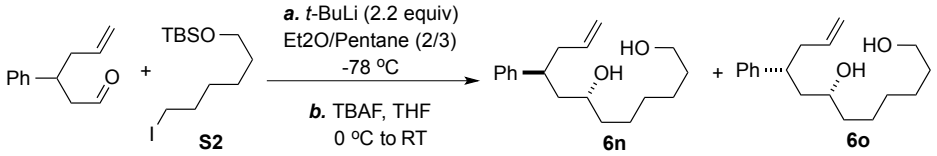


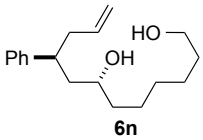
6m

79% for the 1,2-addition, 40% for the TBS-deprotection.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.21 (m, 1H), 6.91-6.89 (m, 2H), 6.78 (dd, *J* = 8.9, 1.8 Hz, 1H), 5.92-5.81 (m, 1H), 5.08-5.05 (m, 2H), 4.84 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.00 (t, *J* = 6.1 Hz, 2H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.30 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.18 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.92-1.72 (m, 7H), 1.60 (dd, *J* = 15.0, 2.9 Hz, 1H), 1.48-1.35 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 148.5, 135.4, 129.4, 118.0, 117.0, 113.2, 111.7, 71.4, 67.7, 62.5, 46.9, 41.9, 36.3, 35.9, 35.7, 29.4, 26.2, 25.8, 21.6; IR (neat): ν = 3354, 2924, 2860, 1452, 1264, 1049, 736, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{31}O_3$ (M-H)$^-$: 331.2279, found: 331.2283.

6n and **6o** were synthesized from the following reaction and were separated.

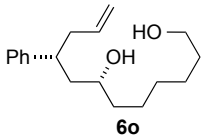




6n

19% of **6n** for the 1,2-addition step, 99% for the TBS-deprotection.

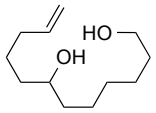
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84-7.79 (m, 2H), 7.73-7.70 (m, 3H), 6.17 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.47 (dd, *J* = 19.7, 14.1 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 1H), 4.09 – 4.07 (m, 1H), 3.33-3.27 (m, 1H), 2.93-2.88 (m, 2H), 2.36-2.25 (m, 4H), 2.08-1.80 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.9, 136.5, 128.4, 127.5, 126.2, 116.1, 70.1, 62.7, 43.7, 42.8, 41.1, 37.0, 32.5, 29.3, 25.6, 25.2; IR (neat): ν = 3321, 2928, 2856, 1454, 1053, 996, 761, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{27}O_2$ (M-H)$^-$: 275.2017, found: 275.2012.



6o

24% of **6o** for the 1,2-addition, 77% for the TBS-deprotection.

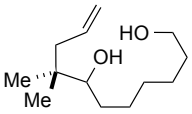
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 2H), 7.20-7.16 (m, 3H), 5.66 (ddt, *J* = 17.0, 10.1, 7.0 Hz, 1H), 4.98-4.90 (m, 1H), 3.58 (t, *J* = 6.6 Hz, 1H), 3.26-3.25 (m, 1H), 2.95-2.93 (m, 1H), 2.39-2.33 (m, 1H), 1.77-1.64 (m, 2H), 1.58-1.54 (m, 2H), 1.54-1.47 (m, 2H), 1.34-1.21 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 136.8, 128.4, 127.7, 126.1, 116.0, 69.2, 62.8, 43.3, 42.0, 41.9, 38.1, 32.6, 29.3, 25.6, 25.4; IR (neat): ν = 3326, 2928, 2854, 1454, 1267, 1026, 736, 701 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{27}O_2$ (M-H)$^-$: 275.2017, found: 275.2016.



6p

96% for the 1,2-addition, 98% for the TBS-deprotection.

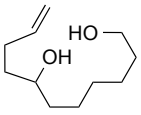
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.02-4.93 (m, 2H), 3.64-3.59 (m, 3H), 2.06 (brs, 2H), 1.58-1.34 (m, 19H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.6, 114.4, 71.5, 62.4, 37.2, 36.7, 33.6, 32.5, 29.3, 25.6, 25.5, 24.8; IR (neat): ν = 3325, 2927, 2855, 1459, 1056, 909, 742 cm^{-1}; MS (ESI): *m/z* 201.0 $[M+H]^+$.



6q

30% for the 1,2-addition, 78 % for the TBS-deprotection.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (ddt, *J* = 21.0, 9.3, 7.5 Hz, 1H), 5.03 (dd, *J* = 13.6, 1.5 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 3.23 (d, *J* = 10.0 Hz, 1H), 2.10 (dd, *J* = 13.6, 7.7 Hz, 1H), 1.96 (dd, *J* = 13.6, 7.3 Hz, 1H), 1.60-1.46 (m, 6H), 1.37-1.22 (m, 6H), 0.85 (d, *J* = 4.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 117.0, 78.5, 62.9, 43.7, 37.8, 32.7, 31.1, 29.4, 27.0, 25.7, 23.2, 22.6; IR (neat): ν = 3341, 2931, 2858, 1466, 1056, 910, 668 cm^{-1}; HRMS (ESI): calcd. for $C_{13}H_{25}O_2$ (M-H)$^-$: 213.1860, found: 213.1863.

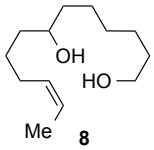


6r

25% total yield for the 1,2-addition and TBS-deprotection.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.16-4.86 (m, 2H), 3.61-3.59 (m, 3H), 2.22-2.07 (m, 2H), 1.83 (brs, 2H), 1.56-1.33 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.6,

114.6, 77.0, 71.3, 62.8, 37.3, 36.4, 32.6, 30.0, 29.4, 25.7, 25.5; IR (neat): ν = 3308, 2929, 2856, 1453, 1055, 993, 908, 668 cm^{-1}; HRMS (ESI): calcd. for $C_{11}H_{21}O_2$ $(M-H)^-$: 185.1547, found: 185.1546.



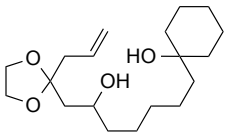
8

49% for the 1,2-addition, 76 % for the TBS-deprotection

^1H NMR (300 MHz, $CDCl_3$): δ = 5.40-5.38(m, 1H), 3.62-3.57 (m, 3H), 2.04-1.97 (m, 3H), 1.62-1.61 (m, 3H), 1.56-1.52 (m, 2H), 1.47-133 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.0, 124.9, 71.7, 62.8, 37.3, 36.9, 32.7, 32.6, 29.5, 25.8, 25.6, 18.0; IR (neat): ν = 3320, 2929, 2857, 1456, 1054, 792 cm^{-1}; MS (ESI): *m/z* 215.3 $[M+H]^+$.

Note: The TBS-deprotection procedure for tertiary alcohol silyl ether is different from previous and is shown below. This procedure was used for the preparation of compound **11a-d**.

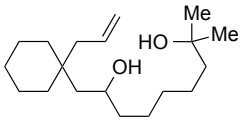
The TBS-ether was dissolved in anhydrous DMF (0.15 M), then added to a flask containing tetrabutylammonia fluoride solid (3 equiv, from concentrating the 1.0 M TBAF in THF solution by vacuum). The result mixture was heated to 60 ^oC for 18 h, then worked up by adding water and extracted by EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. After filtration and concentration, the crude product was purified by flash chromotrography (EtOAc/Hexane = 1/2).



11a

32% for the 1,2-addition, 54% for the TBS-deprotection.

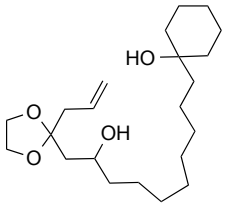
^1H NMR (300 MHz, $CDCl_3$): δ = 5.85-5.71 (m, 1H), 5.14-5.08 (m, 2H), 4.02 (s, 4H), 3.87 (m, 1H), 2.41 (d, *J* = 7.2 Hz, 2H), 1.84 (dd, *J* = 14.8, 1.6 Hz, 1H), 1.71 (dd, *J* = 14.8, 9.8 Hz, 2H), 1.59-1.25 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.6, 118.6, 111.3, 71.4, 67.6, 65.0, 64.6, 42.8, 42.2, 37.5, 37.4, 30.3, 25.9, 25.5, 22.9, 22.4; IR (neat): ν = 3461, 2928, 2857, 1447, 1033, 968, 831 cm^{-1}; MS (ESI): *m/z* 349.4 $[M+Na]^+$.



11b

54% total yield for the 1,2-addition and TBS-deprotection.

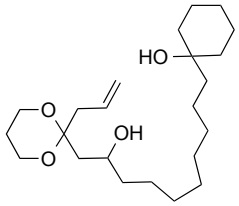
^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86-5.72 (m, 1H), 5.01-4.96 (m, 2H), 3.88-3.73 (m, 1H), 2.19 (dd, *J* = 14.0, 7.3 Hz, 1H), 2.08 (dd, *J* = 14.0, 7.4 Hz, 1H), 1.64 (brs, 2H), 1.40-1.32 (m, 22H), 1.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 135.4, 116.7, 70.9, 68.5, 45.4, 43.9, 41.9, 39.8, 36.3, 35.9, 35.4, 30.2, 29.2, 26.3, 25.7, 24.3, 21.7; IR (neat): ν = 3362, 2930, 2860, 1455, 1054, 1033, 910, 750 cm^{-1}; MS (ESI): *m/z* 335.2 $[M+Na]^+$.



11c

10% yield total yield for the 1,2-addition and the TBS-deprotection.

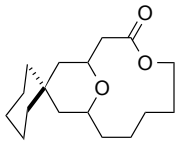
^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84-5.70 (m, 1H), 5.13-5.08 (m, 2H), 4.01 (s, 4H), 3.89-3.83 (m, 2H), 2.40 (d, *J* = 7.2 Hz, 3H), 1.85-1.66 (m, 2H), 1.58-1.24 (m, 28H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.6, 118.6, 111.3, 71.4, 67.6, 65.0, 64.6, 42.7, 42.5, 42.2, 37.4, 30.3, 29.7, 29.6, 25.9, 25.5, 22.9, 22.3; IR (neat): ν = 3483, 2927, 2857, 1457, 1124, 1033, 749 cm^{-1}; MS (ESI): *m/z* 391.4 $[M+Na]^+$.



11d

32% total yield for the 1,2-addition and the TBS-deprotection.

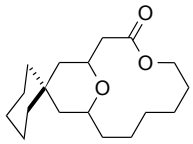
^{1}H NMR (800 MHz, $CDCl_3$): δ = 5.74-5.69 (m, 1H), 5.14-5.12 (m, 2H), 4.07-4.01 (m, 3H), 3.90-3.88 (m, 3H), 3.74 (s, 1H), 2.78 (dd, *J* = 14.7, 6.5 Hz, 1H), 2.60 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.03-1.98 (m, 1H), 2.10-1.93 (m, 1H), 1.75 (dd, *J* = 14.5, 10.1 Hz, 2H), 1.67-1.62 (m, 3H), 1.60-1.56 (m, 5H), 1.51-1.47 (m, 6H), 1.42-1.41 (m, 7H), 1.33 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.5, 118.2, 100.8, 71.5, 67.3, 59.7, 59.6, 44.0, 37.5, 37.4, 36.1, 30.3, 29.8, 29.7, 26.0, 25.6, 25.3, 23.0, 22.4; IR (neat): ν = 3485, 2927, 2855, 1446, 1250, 1033, 915, 771 cm^{-1}; MS (ESI): *m/z* 381.4 $[M-H]^-$.



7a
60% (5/1)

cis-**7a** (major): ^{1}H NMR (300 MHz, CDCl3): δ = 4.28 (ddd, *J* = 11.0, 9.1, 2.0 Hz, 1H), 4.13 (ddd, *J* = 10.8, 5.8, 2.6 Hz, 1H), 3.85 (dddd, *J* = 11.5, 10.5, 4.4, 2.1 Hz, 1H), 3.41 (ddt, *J* = 12.1, 8.7, 1.9 Hz, 1H), 2.47 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.31 (dd, *J* = 12.1, 10.5 Hz, 1H), 1.84-1.71 (m, 1H), 1.62-1.53 (m, 5 H), 1.45-1.31 (m, 11H), 1.22 (m, 2H), 1.12-0.99 (m, 2H); ^{13}C NMR (75 MHz, CDCl3): δ = 173.2, 74.0, 70.9, 65.0, 42.8, 42.2, 33.1, 32.9, 27.8, 26.7, 26.2, 23.4, 21.6, 21.4; IR (neat): ν = 2918, 2853, 1724, 1212, 916, 811 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{28}O_3$ (M+H)$^{+}$: 281.2111, found: 281.2217.

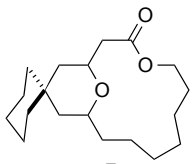
trans-**7a** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.32-4.26 (m, 2H), 4.15-4.12 (m, 1H), 3.83(m, 1H), 2.69 (t, *J* = 12.5 Hz, 1H), 2.32 (dd, *J* = 13.2, 3.0 Hz, 1H), 1.81-1.80 (m, 1H), 1.70-1.63 (m, 2 H), 1.55-1.48 (m, 6H), 1.43-1.39 (m, 11H), 1.35-1.24 (m, 4H); IR (neat): ν = 2925, 2856, 1738, 1256, 1153, 732 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{28}O_3$ (M+H)$^{+}$: 281.2111, found: 281.2216.



7b
64% (10/1)

cis-**7b** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.40 (dt, *J* = 10.7, 2.8 Hz, 1H), 4.01 (dt, *J* = 8.7, 4.2 Hz, 1H), 3.85-3.84 (m, 1H), 3.43 (t, *J* = 12.2 Hz, 1H), 1.84-1.71 (m, 1H), 1.58-1.46 (m, 5H), 1.44-1.35 (m, 10H), 1.30-1.19 (m, 5H), 1.01-0.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.8, 73.5, 70.9, 63.7, 42.7, 42.1, 33.6, 32.8, 32.5, 26.6, 26.2, 25.5, 25.0, 23.5, 21.5, 21.3; IR (neat): ν = 2917, 2850, 1730, 1452, 1258, 1205, 1155, 759 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{31}O_3$ (M+H)$^{+}$: 295.2268, found: 295.2272.

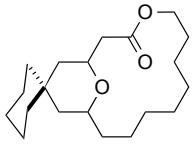
trans-**7b** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.32-4.26 (m, 2H), 4.13 (t, *J* = 8.5 Hz, 1H), 3.83 (m, 1H), 2.69(t, *J* = 12.7 Hz, 1H), 2.32(dd, *J* = 13.2, 2.95 Hz, 1H), 1.81-1.80 (m, 1H), 1.70-1.63 (m, 2H), 1.55-1.48 (m, 6H), 1.43-1.39 (m, 11H), 1.35-1.24 (m, 4H); IR (neat): ν = 2921, 2854, 1736, 1275, 764 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{31}O_3$: 294.2195, found: 294.2199.



7c
59% (6/1)

cis-**7c** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.20-4.18 (m, 2H), 3.97-3.91 (m, 1H), 3.52 (t, *J* = 10.7 Hz, 1H), 2.41-2.33 (m, 2H), 1.55-1.52 (m, 2H), 1.45-1.20 (m, 19H), 1.04-0.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.3, 71.1, 70.3, 65.1, 42.7, 42.2, 34.5, 32.8, 32.4, 27.8, 27.1, 26.7, 25.3, 24.5, 23.6, 21.5, 21.3; IR (neat): ν = 2921, 2854, 1736, 1275, 764 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{33}O_3$ $(M+H)^+$: 309.2424, found: 309.2427.

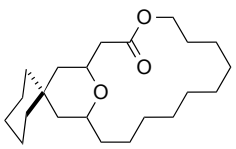
trans-**7c** (minor): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28-4.24 (m, 1H), 4.23-4.18 (m, 2 H), 3.83-3.77 (m, 1H), 2.49 (dd, *J* = 13.7, 10.3 Hz, 1H), 2.34 (dd, *J* = 13.7, 2.4 Hz, 1H), 1.69-1.61 (m, 2H), 1.51-1.48 (m, 4H), 1.44-1.26 (m, 24H); IR (neat): ν = 2921, 2854, 1736, 1275, 764 cm^{-1}.



7d
62% (9/1)

cis-**7d** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.19 (dd, *J* = 6.8, 4.3 Hz, 2H), 4.00-3.95 (m, 1H), 3.52 (t, *J* = 11.1 Hz, 1H), 2.38-2.36 (m, 2H), 1.78-1.70 (m, 1H), 1.61-1.48(m, 5H), 1.49-1.39 (m, 13H), 1.32-1.25 (m, 4H), 1.21-1.20 (m, 3H), 1.02-0.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.3, 71.1, 70.3, 63.4, 42.9, 42.3, 35.6, 33.0, 32.5, 28.1, 26.8, 26.3, 25.0, 24.6, 22.0, 22.0, 21.7, 21.4; IR (neat): ν = 2922, 2860, 1735, 1452, 1273, 1156, 989, 737 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{35}O_3$ $(M+H)^+$: 323.2581, found: 323.2577.

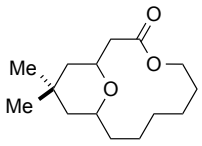
trans-**7d** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.50-4.45 (ddd, *J* = 11.4, 9.2, 3.0 Hz, 1H), 4.28-4.23 (m, 1H), 3.97-3.93 (m, 1H), 3.88-3.83 (ddd, *J* = 11.4, 7.0, 2.2 Hz, 1H), 2.62-2.57 (dd, *J* = 14.1, 11.2 Hz, 1H), 2.32-2.29 (dd, *J* = 14.1, 2.3 Hz, 1H), 1.81-1.70 (m, 2H), 1.62-1.59 (m, 1H), 1.50-1.47 (m, 3H), 1.44 (m, 5H), 1.41-1.37 (m, 5H), 1.35-1.33 (m, 3H), 1.31-1.24 (m, 6H), 1.22-1.13 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.3, 68.2, 66.0, 62.7, 41.6, 40.2, 38.7, 34.2, 31.5, 27.4, 26.4, 24.9, 24.0, 22.8, 21.8, 21.7; IR (neat): ν = 2941, 2906, 1735, 1270, 1095, 981, 648 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{35}O_3$ $(M+H)^+$: 323.2581, found: 323.2582.



7e
64% (7/1)

cis-**7e** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.52-4.48 (m, 1H), 3.99 (t, *J* = 10.9 Hz, 1H), 3.85-3.81 (m, 1H), 3.45 (t, *J* = 9.9 Hz, 1H), 2.46-2.29 (m, 2H), 1.62-1.59 (m, 2H), 1.53-1.51 (m, 4H), 1.46-1.21 (m, 25H), 1.00 (dt, *J* = 21.0, 12.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0, 72.6, 70.1, 64.1, 42.3, 42.2, 36.0, 32.8, 32.4, 29.8 28.5, 26.9, 26.8, 26.5, 26.2, 25.8, 24.9, 24.3, 23.8, 21.6, 21.4; IR (neat): ν = 2941, 2906, 1735, 1270, 1095, 981, 648 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{39}O_3$ $(M+H)^+$: 351.2896, found: 351.2891.

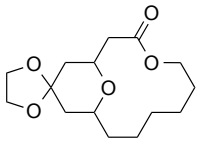
trans-**7e** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.37-4.32 (m, 2H), 3.99-3.95 (m, 1H), 3.74-3.69 (ddd, *J* = 9.0, 7.5, 4.1 Hz, 1H), 2.65 (dd, *J* = 14.6, 10.7 Hz, 1H), 2.25 (dd, *J* = 14.6, 2.2 Hz, 1H), 1.68-1.63 (m, 1H), 1.47-1.25 (m, 32H); IR (neat): ν = 2922, 2860, 1735, 1453, 1274, 1210, 1157, 990, 784 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{39}O_3$ $(M+H)^+$: 351.2896, found: 351.2900.



7f
64% (6/1)

cis-**7f** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.43 (td, *J* = 10.7, 3.0 Hz, 1H), 4.02 (dt, *J* = 11.0, 4.3 Hz, 1H), 3.84-3.83 (m, 1H), 3.42 (t, *J* = 10.4 Hz, 1H), 2.35-2.33 (m, 2H), 1.83-1.75 (m, 2H), 1.56-1.51 (m, 2H), 1.49-1.34 (m, 4H), 1.29-1.23 (m, 3H), 1.00 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.8, 74.3, 71.6, 63.7, 45.1, 44.1, 42.6, 33.5, 33.1, 29.9, 26.2, 25.5, 25.0, 23.6; IR (neat): ν = 2915, 2856, 1731, 1200, 1128, 982, 826 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{27}O_3$ $(M+H)^+$: 255.1955, found: 255.1951.

trans-**7f** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.35-4.30 (m, 2H), 4.11 (t, *J* = 8.9 Hz, 1H), 3.84 (m, 1H), 2.77 (t, *J* = 12.6 Hz, 1H), 2.29 (dd, *J* = 13.3, 3.0 Hz, 1H), 1.84-1.81 (m, 1H), 1.72-1.67 (m, 1 H), 1.63-1.60 (m, 2H), 1.55-1.53 (m, 3H), 1. 44-1.40 (m, 1H), 1.34-1.32 (m, 3H), 1.28-1.19 (m, 3H), 1.02 (s, 3H), 1.00 (s, 3H); IR (neat): ν = 2921, 2860, 1737, 1289, 1164, 1088, 996, 746 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{27}O_3$ $(M+H)^+$: 255.1955, found: 255.1959.

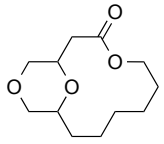


7g
73% (5/1)

cis-**7g** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.29 (td, *J* = 10.7, 3.0 Hz, 1H), 4.15 (dt, *J* = 11.0, 4.3 Hz, 1H), 3.95 (s, 3H), 3.94-3.88 (m, 1H), 3.53 (t, *J* = 10.8 Hz, 1H), 2.44-2.36 (m, 2H), 1.88-1.80 (m, 1H), 1.71-1.68 (dt, *J* = 12.7, 2.2 Hz, 2H), 1.61-1.53 (m, 4H), 1.51-1.24 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$):

δ = 171.9, 107.3, 75.6, 72.8, 64.4, 64.3, 64.0, 42.1, 41.7, 40.6, 33.3, 26.1, 25.4, 24.3, 23.9; IR (neat): ν = 2919, 2852, 1728, 1187, 1063, 991, 730 cm^{-1}; MS (ESI): *m/z* 285.1 $[M+H]^+$.

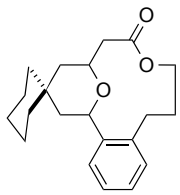
trans-**7g** (minor): ^1H NMR (500 MHz, $CDCl_3$): δ = 4.60-4.53 (m, 1H), 4.02-3.87 (m, 6H), 3.25 (t, *J* = 13.0 Hz, 1H), 2.18 (dd, *J* = 13.5, 3.3 Hz, 1H), 1.92-1.87 (m, 1H), 1.89 (dd, *J* = 18.2, 6.3 Hz, 1H), 1.70-1.49 (m, 13H); IR (neat): ν = 2923, 2854, 1733, 1165, 1072, 992, 740 cm^{-1}; MS (ESI): *m/z* 307.2 $[M+Na]^+$.



7h
60% (4/1)

cis-**7h** (major): ^1H NMR (500 MHz, $CDCl_3$): δ = 4.39-4.34 (m, 1H), 4.09-4.05 (m, 1H), 3.97-3.93 (m, 1H), 3.72 (dd, *J* = 11.1, 2.1 Hz, 1H), 3.62-3.55 (m, 2H), 3.23 (t, *J* = 10.7 Hz, 1H), 3.17 (t, *J* = 10.7 Hz, 1H), 2.36 (dd, *J* = 12.3, 3.4 Hz, 1H), 2.30-2.26 (m, 1H), 1.81-1.71 (m, 2H), 1.59-1.55 (m, 2H), 1.42-1.39 (m, 3H), 1.30-1.24 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.6, 76.5, 73.0, 70.5, 69.8, 63.8, 37.9, 28.1, 26.3, 25.7, 23.0, 23.0; IR (neat): ν = 2914, 2850, 1730, 1276, 1168, 1124, 1071, 932, 657 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{21}O_4$ $(M+H)^+$: 229.1434, found: 229.1438.

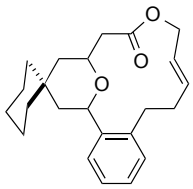
trans-**7h** (minor): ^1H NMR (500 MHz, $CDCl_3$): δ = 4.62 (m, 1H), 4.30-4.27(m, 1H), 4.05 (t, *J* = 9.7 Hz, 1H), 3.88 (t, *J* = 10.4 Hz, 1H), 3.77 (dd, *J* = 11.6, 3.3 Hz, 1H), 3.68 (dd, *J* = 11.3, 2.5 Hz, 1H), 3.49 (dd, *J* = 11.6, 2.3 Hz, 1H), 3.32 (dd, *J* = 11.3, 8.4 Hz, 1H), 3.20 (t, *J* = 12.6 Hz, 1H), 2.24 (dd, *J* = 13.0, 3.5 Hz, 1H), 1.89-1.87 (m, 1 H), 1.63-1.57 (m, 5 H), 1.50 (m, 1H), 1.41-1.39 (m, 1H), 1.28-1.25 (m, 1H), 1.21-1.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.4, 71.9, 69.5, 68.8, 66.9, 66.5, 36.1, 28.6, 27.2, 25.5, 24.4, 21.2; IR (neat): ν = 2922, 2852, 1733, 1284, 1164, 1099, 999, 884, 748 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{21}O_4$ $(M+H)^+$: 229.1434, found: 229.1438.



7i
75% (cis only)

cis-**7i** (only): ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.12 (m, 4H), 4.85 (d, *J* = 10.7 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.32-4.20 (m, 1H), 3.72 (t, *J* = 11.6 Hz, 1H), 2.87 (t, *J* = 11.4 Hz, 1H), 2.68 (dd, *J* = 14.7, 4.3 Hz, 1H), 2.58 (dd, *J* = 21.5, 11.0 Hz, 1H), 2.33 (dd, *J* = 14.6, 11.3 Hz, 1H), 1.99-1.91 (m, 2H), 1.81-

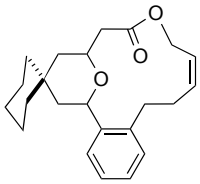
1.62 (m, 6H), 1.58-1.38 (m, 9H), 1.13 (t, J = 12.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.6, 143.8, 137.0, 129.6, 128.1, 125.6, 125.4, 72.0, 71.9, 64.4, 42.7, 42.4, 41.9, 38.8, 33.3, 33.2, 31.2, 27.8, 26.9, 21.8, 21.6; IR (neat): ν = 2921, 2850, 1735, 1451, 1262, 1020, 750, 734 cm^{-1}; MS (ESI): *m/z* 351.2 $[M+Na]^+$.



7j
58% (4/1)

cis-**7j** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, J = 7.3 Hz, 1H), 7.24 (d, J = 7.0 Hz, 1H), 7.22-7.18 (m, 2H), 5.79-5.70 (m, 1H), 5.59 (dt, J = 15.7, 4.4 Hz, 1H), 4.83-4.75 (m, 2H), 4.24 (dd, J = 13.4, 4.4 Hz, 1H), 4.20-4.13 (m, 1H), 2.82 (td, J = 13.1, 2.9 Hz, 1H), 2.74 (dt, J = 13.5, 4.0 Hz, 1H), 2.41 (d, J = 6.8 Hz, 2H), 2.35-2.25 (m, 1H), 1.76-1.55 (m, 7H), 1.47-1.44 (m, 8H), 1.39-1.32 (m, 3H), 1.25-1.17 (m, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 171.4, 140.0, 139.1, 133.2, 129.7, 128.1, 127.2, 126.3, 124.4, 72.0, 70.2, 61.5, 53.4, 42.5, 42.4, 34.4, 33.0, 32.7, 30.7, 26.6, 21.5, 21.3; IR (neat): ν = 2924, 2852, 1732, 1450, 1189, 760 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{31}O_3$ $(M)^+$: 355.2268, found: 355.2267.

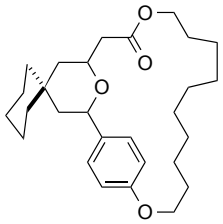
trans-**7j** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (dd, J = 7.3, 1.8 Hz, 1H), 7.23-7.20 (m, 2H), 7.12 (dd, J = 7.2, 1.7 Hz, 1H), 5.85 (ddd, J = 15.1, 9.3, 5.4 Hz, 1H), 5.56 (dt, J = 15.5, 4.5 Hz, 1H), 4.90-4.85 (m, 2H), 4.48 (ddt, J = 12.1, 5.9, 3.0 Hz, 1H), 4.19-4.15 (m, 1H), 2.87 (dd, J = 12.8, 5.5 Hz, 1H), 2.66 (ddd, J = 15.4, 10.8, 3.8 Hz, 2H), 2.53 (ddd, J = 12.5, 8.8, 3.4 Hz, 1H), 2.28 (dd, J = 12.8, 2.7 Hz, 1H), 2.18-2.10 (m, 2H), 1.72-1.61 (m, 3H), 1.51-1.35 (m, 10H).



7k
79%(4/1)

Cis-**7k** (major) and *trans*-**7k** (minor) were inseparable and characterized together. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.7 Hz, 1H), 7.31 (dd, J = 19.3, 3.0 Hz, 3H), 7.28-7.19 (m, 2H), 6.09-5.98 (m, 1H), 5.85 (ddd, J = 16.3, 10.9, 5.9 Hz, 1H), 5.01 (dd, J = 12.7, 1.7 Hz, 1H), 4.94 (dd, J = 12.6, 6.2 Hz, 1H), 4.86-4.82 (m, 1H), 4.79 (dd, J = 12.2, 6.9 Hz, 1H), 4.61-4.54 (m, 1H), 4.44 (dd, J = 12.2, 6.7 Hz, 1H), 4.30 (dd, J = 12.6, 6.8 Hz, 2H), 2.97-2.80 (m, 2H), 2.80-2.69 (m, 2H), 2.69-2.59 (m, 1H), 2.53 (d, J = 6.6 Hz, 2H), 2.48 (s, 1H), 2.38-2.28 (m, 1H), 1.85 (d, J = 7.6 Hz, 2H), 1.81-1.63 (m, 5H), 1.57 (d, J =

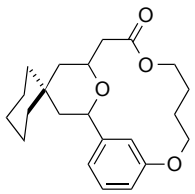
7.4 Hz, 3H), 1.51 (s, 7H), 1.45 (dd, *J* = 7.2, 4.4 Hz, 4H), 1.22-1.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.1, 142.2, 141.0, 139.7, 139.4, 138.7, 137.7, 130.6, 129.2, 128.1, 128.0, 127.7, 125.9, 122.1, 122.0, 71.6, 70.3, 68.0, 60.0, 59.1, 42.6, 42.5, 42.1, 41.9, 40.1, 39.1, 37.2, 32.7, 32.6, 32.3, 32.0, 31.6, 31.2, 29.7, 26.6, 26.1, 21.8, 21.7, 21.4, 21.3; IR (neat): ν = 2922, 2856, 1729, 1451, 1265, 1084, 1018, 912 cm^{-1}; HRMS(ESI): calcd. for $C_{23}H_{31}O_3$ (M)$^+$: 355.2268, found: 355.2269.



7l
42% (4/1)

cis-**7l** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 4.49 (d, *J* = 10.6 Hz, 1H), 4.27-4.08 (m, 2H), 4.01-3.80 (m, 1H), 2.52-2.30 (m, 1H), 1.77 (d, *J* = 13.5 Hz, 1H), 1.71 (dd, *J* = 13.1, 7.0 Hz, 1H), 1.64-1.58 (m, 4H), 1.49-1.35 (m, 10H), 1.31-1.23 (m, 5H), 1.17-1.12 (m, 5H), 1.04-1.00 (m, 3H); ^{1}H NMR (800 MHz, C_6D_6): δ = 7.26 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H), 4.33-4.31 (m, 1H), 4.23 (t, *J* = 11.1 Hz, 1H), 3.98 (t, *J* = 6.1 Hz, 1H), 3.90 (dd, *J* = 11.0, 5.8 Hz, 1H), 2.49 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.24 (dd, *J* = 13.6, 2.3 Hz, 1H), 1.68-1.61 (m, 2H), 1.49-1.44 (m, 3H), 1.42-1.39 (m, 1H), 1.35-1.34 (m, 3H), 1.32-1.21 (m, 9H), 1.19-1.09 (m, 5H), 1.06 (m, 2H), 1.01-0.92 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6, 157.4, 135.6, 126.9, 115.2, 77.0, 73.9, 70.6, 67.4, 64.7, 42.3, 42.1, 32.7, 32.5, 29.5, 28.9, 28.2, 28.0, 27.1, 26.9, 26.6, 25.6, 23.8, 21.5, 21.3; IR (neat): ν = 2925, 2854, 1735, 1510, 1243, 1088, 825, 745 cm^{-1}; HRMS (ESI): calcd. for $C_{28}H_{43}O_4$ (M+H)$^+$: 443.3163, found: 443.3156.

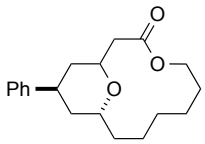
trans-**7l** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.86 (d, *J* = 8.7 Hz, 1H), 4.90 (dd, *J* = 7.7, 4.7 Hz, 1H), 4.39-4.31 (m, 1H), 4.22-4.17 (m, 1H), 4.14 (d, *J* = 12.1 Hz, 1H), 3.94 (dt, *J* = 10.8, 7.0 Hz, 1H), 2.66 (dd, *J* = 13.6, 9.7 Hz, 1H), 2.38 (dd, *J* = 13.6, 4.1 Hz, 1H), 1.88 (dd, *J* = 14.0, 7.8 Hz, 1H), 1.75-1.67 (m, 2H); IR (neat): ν = 2923, 2854, 1735, 1510, 1244, 1086, 825 cm^{-1}; HRMS (ESI): calcd. for $C_{28}H_{43}O_4$ (M+H)$^+$: 443.3156, found: 443.3155.



7m
68% (5/1)

cis-**7m** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (s, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.75-6.72 (m, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.39 (ddd, *J* = 11.7, 9.3, 2.4 Hz, 1H), 4.25-4.13 (m, 2H), 4.10-4.01 (m, 1H), 2.56 (dd, *J* = 12.1, 3.4 Hz, 1H), 2.44 (dd, *J* = 12.1, 8.7 Hz, 1H), 2.23-2.16 (m, 1H), 2.07 (d, *J* = 13.3 Hz, 1H), 1.93-1.83 (m, 1H), 1.78-1.69 (m, 5H), 1.50-1.49 (m, 7H), 1.33-1.28 (m, 2H), 1.29-1.20 (m, 2H); ^{13}C NMR (125 MHz, CDCl3): δ = 173.3, 157.5, 144.4, 128.9, 116.0, 115.8, 110.2, 71.4, 70.3, 65.6, 62.6, 42.3, 41.9, 32.4, 32.3, 26.6, 23.6, 21.5, 21.4, 21.3; IR (neat): ν = 2925, 2856, 1728, 1259, 1161, 1036, 695 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{31}O_4$ (M+H)$^+$: 359.2217, found: 359.2218.

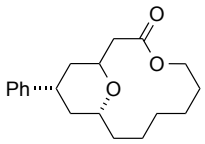
trans-**7m** (minor): ^{1}H NMR (800 MHz, C_6D_6): δ = 7.42 (s, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.99 (dd, *J* = 8.1, 2.5 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 5.07 (d, *J* = 6.3 Hz, 1H), 4.41 (t, *J* = 11.2 Hz, 1H), 4.08-4.02 (m, 2H), 3.89 (ddd, *J* = 11.3, 4.7, 2.6 Hz, 1H), 3.72 (td, *J* = 12.1, 6.1 Hz, 1H), 2.57 (dd, *J* = 13.9, 10.8 Hz, 1H), 2.28-2.17 (m, 2H), 2.06 (d, *J* = 14.1 Hz, 1H), 1.51-1.41 (m, 3H), 1.36-1.34 (m, 1H), 1.33-1.24 (m, 3H), 1.18 (dd, *J* = 34.4, 10.7 Hz, 4H), 1.14-1.06 (m, 2H), 1.04-1.02 (m, 2H), 0.96-0.93 (m, 3H), 0.90-0.84 (m, 1H); IR (neat): ν = 2923, 2853, 1737, 1594, 1438, 1253, 1075, 767 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{31}O_4$ (M+H)$^+$: 359.2217, found: 359.2218.



7n
79% (1/3.3)

cis-**7n** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 4H), 7.22-7.21 (m, 1H), 4.37 (td, *J* = 10.6, 2.3 Hz, 1H), 4.06-4.03 (m, 1H), 3.97-3.92 (m, 1H), 3.54 (t, *J* = 10.6 Hz, 1H), 3.32 (m, 1H), 2.41-2.40 (m, 1H), 2.10 (d, *J* = 13.3 Hz, 1H), 1.99 (d, *J* = 13.6 Hz, 1H), 1.85-1.72 (m, 4H), 1.56-1.50 (m, 4H), 1.42-1.35 (m, 3H), 1.30-1.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.4, 143.9, 128.4, 127.8, 125.8, 73.9, 71.3, 63.9, 42.7, 36.1, 35.2, 33.7, 26.2, 25.5, 24.7, 23.8; IR (neat): ν = 2916, 2853, 1729, 1197, 1150, 1076, 753, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{27}O_3$ (M+H)$^+$: 303.1955, found: 303.1953.

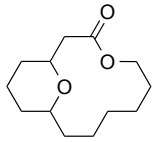
trans-**7n** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.30 (m, 2H), 7.23-7.20 (m, 3H), 4.62 (t, *J* = 9.6 Hz, 1H), 4.29 (t, *J* = 11.0 Hz, 1H), 4.07 (dd, *J* = 10.9, 5.5 Hz, 1H), 3.82-3.79 (m, 1H), 2.97 (t, *J* = 11.4 Hz, 1H), 2.53 (d, *J* = 13.7 Hz, 1H), 2.39 (t, *J* = 12.4 Hz, 1H), 2.20-2.15 (m, 1H), 2.00-1.93 (m, 1H), 1.83-1.81 (m, 2H), 1.72 (m, 2H), 1.66-1.53 (m, 4H), 1.49-1.40 (m, 3H), 1.35-1.34 (m, 1H), 1.27-1.24 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 145.5, 128.5, 126.7, 126.4, 75.0, 67.3, 63.5, 42.9, 39.0, 37.6, 36.8, 26.9, 26.0, 25.4, 25.2, 23.3; IR (neat): ν = 2917, 2853, 1735, 1269, 1072, 1004, 758, 699 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{27}O_3$ (M+H)$^+$: 303.1955, found: 303.1958.



7o
61% (2/1)

cis-**7o** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32-7.29 (m, 2H), 7.22-7.19 (m, 3H), 4.44-4.40 (m, 1H), 4.11-4.08 (m, 1H), 3.88-3.83 (m, 1H), 3.46 (t, *J* = 10.3 Hz, 1H), 2.86-2.82 (m, 1H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.85-1.83 (m, 2H), 1.79-1.72 (m, 2H), 1.60-1.59 (m, 3H), 1.48-1.43 (m, 5H), 1.36-1.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 145.4, 128.5, 126.8, 126.4, 78.4, 75.4, 63.9, 42.4, 41.9, 39.5, 38.5, 33.4, 26.2, 25.5, 24.8, 23.8; IR (neat): ν = 2913, 2852, 1729, 1257, 1081, 763, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{27}O_3$ $(M+H)^+$: 303.1955, found: 303.1952.

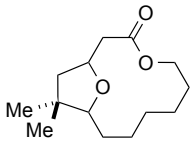
trans-**7o** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.30 (m, 2H), 7.23-7.20 (m, 3H), 4.82 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.69-4.66 (m, 1H), 3.96 (t, *J* = 11.0 Hz, 1H), 3.73 (t, *J* = 10.5 Hz, 1H), 3.28 (t, *J* = 12.7 Hz, 1H), 2.95 (tt, *J* = 12.6, 3.5 Hz, 1H), 2.20 (dd, *J* = 12.8, 3.5 Hz, 1H), 2.02 (td, *J* = 13.3, 6.0 Hz, 1H), 1.98-1.93(m, 1H), 1.75-1.68 (m, 4H), 1.63-1.56 (m, 4H), 1.51-1.46 (m, 2H), 1.44-1.40 (m, 1H), 1.32 (t, *J* = 13.2 Hz, 1H), 1.25-1.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.9, 145.3, 128.6, 126.8, 126.4, 71.4, 67.5, 66.4, 39.9, 37.2, 36.8, 36.0, 34.8, 28.4, 25.3, 24.6, 21.3; IR (neat): ν = 2925, 2853, 1731, 1263, 747, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{27}O_3$ $(M+H)^+$: 303.1955, found: 303.1954.



7p
77% (1.1/1)

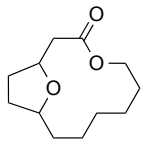
cis-**7p** (major): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.37 (td, *J* = 10.7, 3.1 Hz, 1H), 4.06 (dt, *J* = 11.0, 4.3 Hz, 1H), 3.68-3.67 (m 1H), 3.28 (t, *J* = 10.4 Hz, 1H), 2.40-2.37 (m, 2H), 1.83-1.71 (m, 3H), 1.63-1.20 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 78.8, 64.0, 42.8, 33.7, 32.0, 31.2, 26.3, 25.7, 24.9, 24.0, 23.8; IR (neat): ν = 2924, 2855, 1734, 1261, 1033, 749 cm^{-1}; MS (ESI): *m/z* 249.1 $[M+Na]^+$.

trans-**7p** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.50-4.47 (m, 1H), 4.39 (ddd, *J* = 12.0, 7.8, 4.1 Hz, 1H), 3.96 (t, *J* = 10.3 Hz, 1H), 3.83-3.80 (m, 1H), 2.92 (t, *J* = 12.6 Hz, 1H), 2.18 (dd, *J* = 13.1, 3.2 Hz, 1H), 1.91-1.84 (m, 1H), 1.81-1.74 (m, 1H), 1.67-1.48 (m, 9H), 1.41-1.19 (m, 5H); ^{13}C NMR (100 MHz, CDCl3): δ = 171.9, 70.0, 68.8, 66.2, 38.5, 32.5, 31.6, 29.4, 26.9, 25.6, 25.0, 22.4, 19.2; IR (neat): ν = 2928, 2857, 1741, 1166, 1033, 748 cm^{-1}; MS (ESI): *m/z* 249.1 $[M+Na]^+$.



7q
63% (1.4/1)

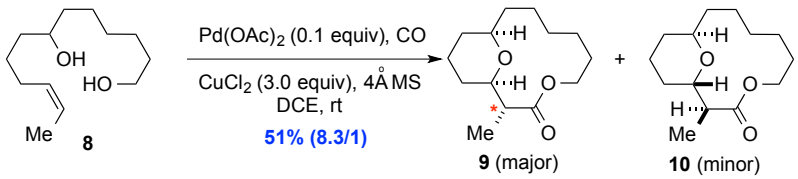
Cis-**7q** (major) and *trans*-**7q** (minor) were inseparable and characterized together. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.49-4.46 (m, 1.33H), 4.44-4.37 (m, 1.38H), 4.25 (m, 2H), 4.15-4.11 (t, *J* = 9.0 Hz, 1H), 3.93-3.90 (t, *J* = 9.3 Hz, 1.4H), 3.53-3.51 (d, *J* = 9.1 Hz, 1.4H), 3.40-3.37 (dd, *J* = 8.6, 4.1 Hz, 1H), 2.68-2.65 (dd, *J* = 12.1, 3.7 Hz, 1H), 2.48-2.42 (m, 2.8H), 2.36-2.33 (dd, *J* = 12.0, 7.5 Hz, 1H), 1.95-1.92 (dd, *J* = 12.3, 7.2 Hz, 1.4H), 1.80-1.76(m, 1.4H), 1.71-1.67 (m, 4H), 1.61 (s, 7H), 1.53-1.48 (m, 5H), 1.42-1.24 (m, 11.4H), 1.04 (s, 3H), 1.00 (s, 4.3H), 0.97 (s, 3H), 0.87 (s, 4.4H); ^{13}C NMR (125 MHz, CDCl3): δ = 172.6, 172.0, 88.8, 84.2, 74.3, 72.8, 65.7, 65.2, 48.2, 45.4, 42.3, 42.3, 42.1, 41.9, 28.9, 28.0, 27.5, 27.2, 26.7, 26.6, 26.3, 25.7, 25.0, 24.9, 24.6, 24.1, 23.4, 22.6; IR (neat): ν = 2952, 2868, 1733, 1456, 1191, 1183, 983 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{25}O_3$ (M+H)$^+$: 241.1798, found: 241.1800.



7r
51% (1.1/1)

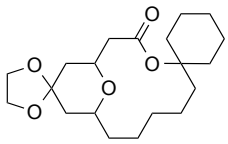
cis-**7r** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.41-4.37 (m, 1H), 4.28-4.23 (m, 1H), 4.08-4.00 (m, 2H), 2.69-2.66 (dd, *J* = 13.2, 3.9 Hz, 1H), 2.37-2.32 (dd, *J* = 13.2, 11.1 Hz, 1H), 2.17-2.11 (m, 1H), 2.04-2.01 (m, 1H), 1.68-1.60 (m, 6H), 1.53 (m, 3H), 1.48-1.40 (m, 3H), 1.34-1.25 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): δ = 171.7, 78.3, 74.0, 64.1, 41.2, 32.7, 32.5, 32.0, 26.6, 25.6, 24.8, 23.2; IR (neat): ν = 2918, 2851, 1731, 1274, 1075, 801 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{21}O_3$ (M+H)$^+$: 213.1485; Found: 213.1483.

trans-**7r** (minor): ^{1}H NMR (400 MHz, CDCl3): δ = 4.29-4.22 (m, 2H), 4.16-4.11 (m, 1H), 3.98-3.97 (m, 1H), 2.65-2.61 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.38-2.35 (dd, *J* = 12.4, 7.2 Hz, 1H), 2.03-1.94 (m, 2H), 1.86-1.81 (m, 1H), 1.72-1.58 (m, 6H), 1.55-1.44 (m, 4H), 1.35-1.29 (m, 1H); ^{13}C NMR (125 MHz, CDCl3): δ = 172.0, 80.1, 76.2, 64.7, 41.1, 32.9, 30.8, 30.3, 26.7, 26.2, 23.3, 23.3; IR (neat): ν = 2924, 2856, 1729, 1208, 1177, 997, 793 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{21}O_3$ (M+H)$^+$: 213.1485, found: 213.1489.



Compound **9**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.52 (td, *J* = 10.7, 3.1 Hz, 1H), 3.94 (dt, *J* = 10.9, 4.5 Hz, 1H), 3.32-3.24 (m, 2H), 2.43 (dq, *J* = 9.9, 6.9 Hz, 1H), 1.83-1.72 (m, 2H), 1.74-1.71 (m, 2H), 1.60-1.57 (m, 1H), 1.53-1.36 (m, 7H), 1.28-1.20 (m, 4H), 1.07 (d, *J* = 6.9 Hz, 3H); ^{1}H NMR (800 MHz, C_6D_6): δ = 4.65 (td, *J* = 10.7, 3.2 Hz, 1H), 3.81 (dt, *J* = 10.8, 4.6 Hz, 1H), 3.31-3.20 (m, 1H), 3.02 (t, *J* = 10.4 Hz, 1H), 2.49 (dq, *J* = 9.8, 7.0 Hz, 1H), 1.93-1.88 (m, 1H), 1.77-1.72 (m, 1H), 1.53-1.46 (m, 6H), 1.39-1.34 (m, 3H), 1.27-1.26 (m, 1H), 1.23-1.21 (m, 1H), 1.16-1.14 (m, 3H), 1.07-1.04 (m, 1H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.88-0.82 (m, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 176.5, 80.7, 78.9, 63.6, 46.5, 33.6, 32.3, 28.7, 26.2, 25.5, 25.0, 23.6, 23.5, 13.1; IR (neat): ν = 2918, 2852, 1728, 1185, 908, 729 cm^{-1}; MS (ESI): *m/z* 263.1 $[M+Na]^+$.

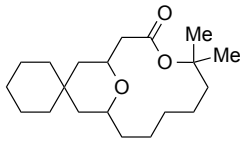
Compound **10**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.47 (ddd, *J* = 6.4, 5.5, 2.8 Hz, 1H), 3.96-3.89 (m, 2H), 3.82 (t, *J* = 9.8 Hz, 1H), 3.00-2.93 (m, 1H), 1.99-1.91 (m, 1H), 1.74-1.68 (m, 1H), 1.62-1.60 (m, 6H), 1.39-1.29 (m, 6H), 1.06 (d, *J* = 6.8 Hz, 3H); IR (neat): ν = 2926, 2856, 1736, 1262, 1172, 749 cm^{-1}; MS (ESI): *m/z* 263.1 $[M+Na]^+$.



12a
62% (5/1)

cis-**12a** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.96 (s, 1H), 3.90 (t, *J* = 10.2 Hz, 1H), 3.52 (t, *J* = 10.8 Hz, 1H), 2.45 (dd, *J* = 12.5, 3.3 Hz, 1H), 2.35-2.32 (m, 1H), 2.26 (t, *J* = 11.9 Hz, 1H), 2.10 (d, *J* = 12.1 Hz, 1H), 2.01 (s, 1H), 1.72 (d, *J* = 12.8 Hz, 1H), 1.4-1.51 (m, 5H), 1.54-1.46 (m, 5H), 1.33-1.25 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl3): δ = 170.8, 107.4, 85.1, 74.6, 72.8, 64.5, 64.2, 43.6, 41.7, 40.5, 35.3, 34.9, 29.7, 28.2, 25.7, 22.0, 22.0, 20.4; IR (neat): ν = 2924, 2855, 1723, 1147, 1065, 735 cm^{-1}; MS (ESI): *m/z* 375.3 $[M+Na]^+$.

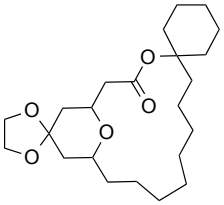
trans-**12a** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.47-4.41 (m, 1H), 3.96 (s, 4H), 2.82 (t, *J* = 12.5 Hz, 1H), 2.35-2.28 (m, 3H), 1.86-1.77 (m, 4H), 1.55-1.49 (m, 12H), 1.34-1.30 (m, 6H), 0.88 (t, *J* = 6.1 Hz, 3H); IR (neat): ν = 2924, 2860, 1730, 1162, 1058, 1033, 737 cm^{-1}.



12b 69% (5.2/1)

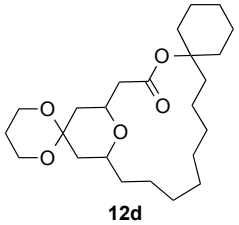
cis-**12b** (major): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.82 (t, *J* = 10.8 Hz, 1H), 3.43 (t, *J* = 10.6 Hz, 1H), 2.32 (dd, *J* = 12.4, 3.4 Hz, 1H), 2.18 (t, *J* = 11.8 Hz, 1H), 1.90 (m, 1H), 1.82 (m, 1H), 1.64-1.52 (m, 5H), 1.40 (m, 15H), 1.35-1.33 (m, 3H), 1.25-1.21 (m, 3H), 1.04-1.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.5, 83.1, 77.0, 72.4, 70.8, 44.0, 42.1, 35.7, 35.2, 32.9, 32.5, 28.4, 27.7, 27.3, 26.7, 21.5, 21.3, 21.0; IR (neat): ν = 2925, 2853, 1724, 1264, 1092, 734, 703 cm^{-1}; MS (ESI): *m/z* 323.2 $[M+H]^+$.

trans-**12b** (minor): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.93-3.85 (m, 1H), 3.45-3.39 (m, 1H), 2.26 (d, *J* = 6.4 Hz, 2H), 1.56-1.42 (m, 23H), 1.02-0.83 (m, 6H); IR (neat): ν = 2922, 2851, 1732, 1275, 1161, 696 cm^{-1}; MS (ESI): *m/z* 345.4 $[M+Na]^+$.



12c
55% (*cis* only)

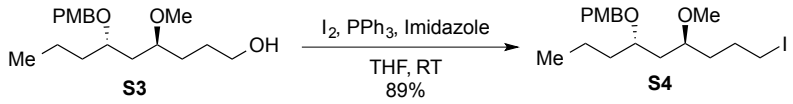
cis-**12c** (only): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.06 (t, *J* = 11.2 Hz, 1H), 3.96 (s, 4H), 3.54 (t, *J* = 10.0 Hz, 1H), 2.46-2.25 (m, 4H), 1.99 (d, *J* = 13.1 Hz, 1H), 1.64-1.25 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 107.3, 84.1, 75.1, 71.7, 64.4, 64.2, 42.2, 41.9, 40.6, 35.4, 35.3, 34.5, 28.3, 27.6, 27.0, 26.2, 25.7, 22.1, 22.0, 21.7; IR (neat): ν = 2928, 2857, 1724, 1194, 1167, 905, 726 cm^{-1}; MS (ESI): *m/z* 395.4 $[M+H]^+$.



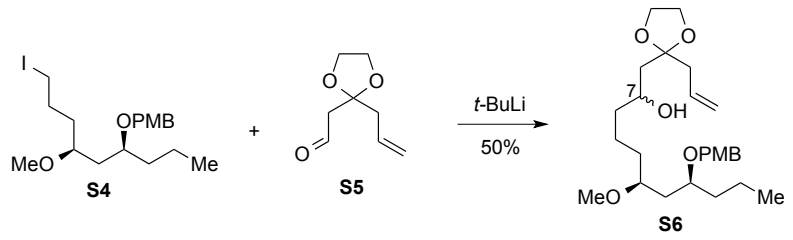
12d
47% (*cis* only)

cis-**12d** (only): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.02 (ddd, *J* = 12.4, 3.8, 1.9 Hz, 1H), 3.90 (dt, *J* = 10.8, 5.5 Hz, 4H), 3.52 (t, *J* = 10.2 Hz, 1H), 2.44 (dd, *J* = 15.5, 10.5 Hz, 1H), 2.35-2.26 (m, 2H), 2.19 (dt, *J* = 13.1, 2.2 Hz, 1H), 2.09-2.08 (m, 1H), 1.98 (d, *J* = 12.5 Hz, 1H), 1.79-1.65 (m, 2H), 1.58-1.16 (m, 26H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 96.8, 84.1, 73.6, 70.4, 59.4, 59.2, 42.1, 40.5, 38.1, 37.7, 35.5,

35.2, 34.4, 28.4, 27.7, 27.1, 26.3, 25.7, 25.6, 22.1, 22.0, 21.7; IR (neat): ν = 2928, 2859, 1731, 1193, 1146, 1091, 918, 737 cm^{-1}; MS (ESI): *m/z* 431.3 $[M+Na]^+$.

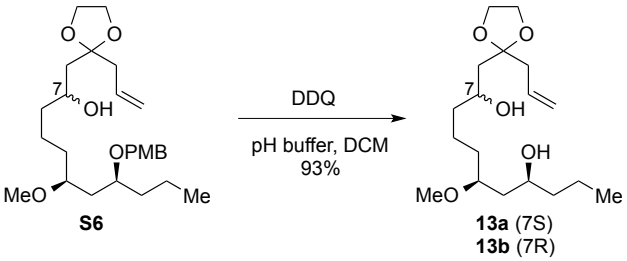


To a stirred solution of alcohol **S3** (550 mg, 1.77 mmol, prepared according to literature procedure[1]) in THF (18 mL) was added imidazole (241 mg, 3.54 mmol, 2.0 equiv) and triphenylphosphine (951 mg, 2.0 equiv) at 0 ^oC. The reaction mixture was stirred for 5 min and iodine (676 mg, 1.5 equiv) was added in small portions at 0 ^oC. After warming to room temperature, the resulting solution was stirred for 30 mins then quenched with aqueous $Na_2S_2O_3$ (10%) solution and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/Hexane = 1/20) to give product **S4** (660 mg, 89% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.29 (d, *J* = 11.0 Hz, 1H), 3.72 (s, 1H), 3.50 (dd, *J* = 8.9, 3.5 Hz, 1H), 3.33 (dd, *J* = 8.7, 3.9 Hz, 1H), 3.19 (s, 1H), 3.11 (t, *J* = 6.9 Hz, 1H), 1.81-1.75 (m, 2H), 1.57-1.28 (m, 8H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 131.0, 129.3, 113.7, 76.6, 75.3, 70.8, 56.5, 55.3, 39.8, 36.6, 34.4, 28.9, 18.4, 14.5, 7.4; IR (neat): ν = 2926, 1459, 1109, 989, 750 cm^{-1}; MS (ESI): *m/z* 443.3 $[M+Na]^+$.

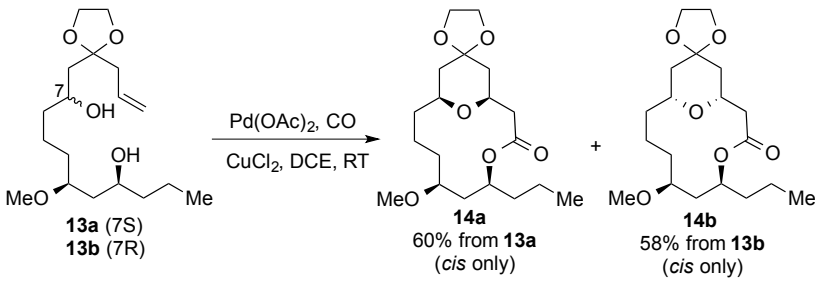


To a solution of iodide **S4** (236 mg, 0.56 mmol) in 3.8 mL Et_2O was added a solution of *tert*-butyllithium (0.79 mL, 1.7 M in pentane, 2.4 equiv) dropwise at -78 ^oC. The reaction mixture was stirred for 30 min at -78 ^oC before aldehyde (105 mg, 0.67 mmol, 1.2 equiv) was added dropwise. After stirring for an additional 2 hours, the reaction was quenched with a buffer solution (pH = 7) and warmed to 0 ^oC. After adding a saturated ammonium chloride solution (10 mL), the solution was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by flash chromatography (EtOAc/Hexane = 1/15 to 1/10) to give product **S6** as a mixture (127 mg, 50% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.5 Hz, 1H), 6.86 (d,

J = 8.6 Hz, 1H), 5.78 (ddt, *J* = 14.3, 9.5, 7.2 Hz, 1H), 5.11 (dd, *J* = 13.8, 1.6 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 11.0 Hz, 1H), 4.01 (s, 2H), 3.90-3.85 (m, 1H), 3.79 (s, 2H), 3.61-3.55 (m, 1H), 3.38 – 3.36 (m, 1H), 3.26 (d, *J* = 1.8 Hz, 1H), 2.40 (d, *J* = 6.9 Hz, 1H), 1.83 (d, *J* = 14.7 Hz, 1H), 1.71 (dd, *J* = 14.7, 10.0 Hz, 1H), 1.58-1.34 (m, 12H), 1.26 (d, *J* = 7.1 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 132.7, 131.2, 129.3, 118.6, 113.7, 111.3, 77.5, 77.5, 70.7, 67.5, 65.0, 64.6, 56.5, 55.2, 42.7, 42.1, 39.9, 37.6, 36.6, 33.7, 33.6, 20.7, 18.3, 14.4; IR (neat): ν = 2932, 2873, 1514, 1464, 1248, 1088, 1036, 821, 775 cm^{-1}; MS (ESI): *m/z* 473.4 $[M+Na]^+$.



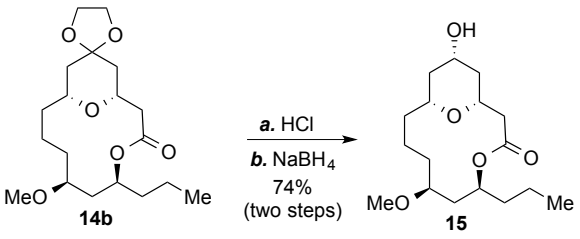
To a solution of PMB-ether **S6** (127 mg, 0.28 mmol) in dichloromethane (7.4 mL) and buffer solution (pH = 7, 3.8 mL) was added DDQ (96 mg, 0.42 mmol, 1.5 equiv). The reaction mixture was stirred for 3 hours then quenched with a saturated $NaHCO_3$ solution and extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/Hexane = 1/1 to 1.5/1) to give a 1/1 mixture of **13a** and **13b** (87 mg, 93% yield). ^{1}H NMR (800 MHz, $CDCl_3$): δ = 5.82-5.77 (m, 1H), 5.14-5.12 (m, 2H), 4.06-4.01 (m, 4H), 3.91-3.87 (m, 2H), 3.48 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.37 (dd, *J* = 3.0, 1.5 Hz, 4H), 2.42 (dd, *J* = 7.8, 1.9 Hz, 2H), 1.85 (d, *J* = 14.8 Hz, 1H), 1.76-1.73 (m, 1H), 1.70-1.64 (m, 2H), 1.60-1.56 (m, 1H), 1.53-1.43 (m, 6H), 1.41-1.34 (m, 5H), 0.94 (td, *J* = 7.1, 1.3 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 132.7, 118.7, 111.3, 79.4, 79.4, 68.4, 67.4, 65.0, 64.6, 56.7, 42.7, 42.7, 42.1, 39.9, 39.2, 39.1, 37.4, 37.4, 33.0, 32.9, 21.4, 21.3, 18.8, 14.1; IR (neat): ν = 3445, 2925, 1460, 1377, 1088, 1033, 917, 822, 744 cm^{-1}; MS (ESI): *m/z* 353.2 $[M+Na]^+$.



Molecular sieves (4Å, 320 mg) were added to a 250 mL round-bottom flask and activated by flame-drying *in vacuo*. After cooling to room temperature, the flask was flushed with argon and $Pd(OAc)_2$ (5.4 mg, 0.024 mmol, 0.1 equiv), anhydrous $CuCl_2$ (98 mg, 0.72 mmol, 3.0 equiv) and 1,2-dichloroethane (100 mL) were added. The reaction mixture was purged with CO balloon for 5 min. A solution of alken-doil (80 mg, 0.24 mmol) in 1,2-dichloroethane (20 mL) was added to the reaction mixture using a syringe pump (1.2 mL/h.) The reaction mixture was stirred for an additional 20 h before it was filtered through a short pad of celite and concentrated under reduced pressure. The crude product was diluted with EtOAc (50 mL) and washed with 10 mL of a saturated $NaHCO_3$ solution. The aqueous layer was extracted twice with EtOAc and the combined organic layers were washed with 10 mL brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/Hexane = 1/20 to 1/15) to give desired products **14a** (60% from **13a**) and **14b** (58% from **13b**).

Compound **14a**: $[\alpha]_D^{25}$ = +18.4 (c = 0.05, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$): δ = 5.15-5.12 (m, 1H), 3.96 (s, 4H), 3.91 (t, *J* = 11.4 Hz, 1H), 3.57 (t, *J* = 10.9 Hz, 1H), 3.32 (s, 3H), 3.17-3.14 (m, 1H), 2.42 (t, *J* = 11.6 Hz, 1H), 2.35 (d, *J* = 12.1 Hz, 1H), 1.83 (dt, *J* = 12.0, 5.4 Hz, 1H), 1.76-1.71 (m, 2H), 1.65 (d, *J* = 13.2 Hz, 2H), 1.62-1.57 (m, 2H), 1.55-1.43 (m, 6H), 1.39-1.33 (m, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 172.4, 107.2, 80.8, 75.5, 74.1, 73.9, 64.4, 64.3, 56.7, 42.3, 41.8, 40.8, 38.9, 37.6, 34.5, 33.7, 22.1, 18.6, 13.9; IR (neat): ν = 2924, 1727, 1190, 1070, 741 cm^{-1}; MS (ESI): *m/z* 373.1 $[M+Na]^+$.

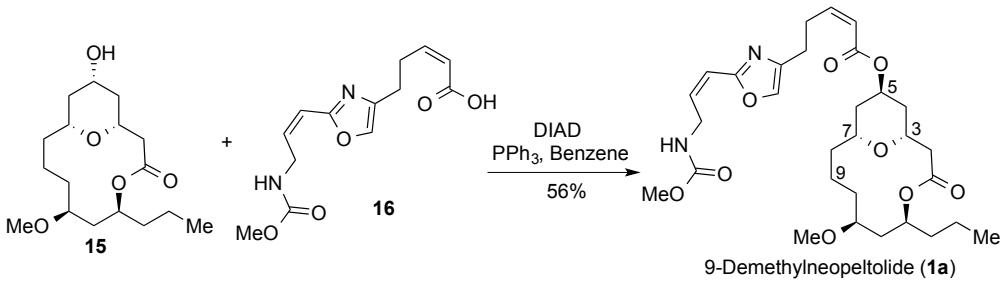
Compound **14b**: $[\alpha]_D^{25}$ = +6.4 (c = 0.20, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$): δ = 5.19 (tdd, *J* = 7.6, 6.0, 1.5 Hz, 1H), 3.96-3.92 (m, 5H), 3.48-3.45 (m, 1H), 3.42-3.39 (m, 1H), 3.30 (s, 3H), 2.60 (dd, *J* = 15.0, 4.1 Hz, 1H), 2.40 (dd, *J* = 15.0, 10.6 Hz, 1H), 1.78 (ddd, *J* = 15.5, 10.4, 5.4 Hz, 1H), 1.76-1.71 (m, 1H), 1.69 (dt, *J* = 12.8, 2.1 Hz, 1H), 1.62-1.54 (m, 6H), 1.52-1.47 (m, 3H), 1.40-1.30 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 170.5, 107.5, 78.4, 77.8, 73.2, 71.7, 64.4, 64.3, 56.3, 41.9, 41.5, 40.6, 38.6, 37.6, 33.1, 32.7, 23.4, 18.7, 13.9; IR (neat): ν = 2926, 2875, 1731, 1073, 741 cm^{-1}; MS (ESI): *m/z* 373.2 $[M+Na]^+$.



Compound **14b** (12 mg, 0.034 mmol) was dissolved in 2 mL 0.5 N HCl in MeOH at 0 °C. The reaction mixture was stirred for 30 min, before it was quenched with saturated $NaHCO_3$ solution and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was redissolved in 1.5 mL THF. The solution was cooled down to 0 °C before 1N HCl (1 mL) was slowly added. The reaction was warmed to RT and stirred for 0.5 h, then quenched with saturated $NaHCO_3$ solution and extracted three times with EtOAc. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the crude product (10.2 mg) was used directly in the next step.

To a stirred solution the above crude product in MeOH (0.54 mL) was added $NaBH_4$ (4.96 mg, 0.131 mmol, 3.9 equiv) in portions at 0 °C. The reaction was stirred at 0 °C, then quenched with one drop of AcOH, diluted with water and extracted twice with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/Hexane = 1/2) to give product **15** (7.6 mg, 74% from **14b**), a known compound.[1]

Compound **15**: $[\alpha]_D^{25}$ = +3.6 (c = 0.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.17 (dt, *J* = 11.5, 7.4 Hz, 1H), 3.82 (td, *J* = 10.7, 5.3 Hz, 1H), 3.74-3.70 (m, 1H), 3.42-3.40 (m, 1H), 3.30 (s, 3H), 3.21 (t, *J* = 10.3 Hz, 1H), 2.63 (dd, *J* = 14.9, 4.2 Hz, 1H), 2.44 (dd, *J* = 14.8, 10.2 Hz, 1H), 1.96 (dd, *J* = 12.0, 4.4 Hz, 1H), 1.87 (dd, *J* = 12.0, 4.4 Hz, 1H), 1.81-1.20 (m, 15H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 170.6, 78.2, 77.0, 73.4, 71.9, 68.2, 56.3, 42.0, 41.4, 40.5, 38.6, 37.5, 33.2, 32.8, 23.4, 18.8, 13.9; IR (neat): ν = 3421, 2924, 2855, 1730, 1268, 1084, 748 cm^{-1}; MS (ESI): *m/z* 337.2 $[M+Na]^+$.



Alcohol **15** (5.2 mg, 0.017 mmol) and acid **16** (14 mg, 3.0 equiv, prepared according literature[2]) was dissolved in 1.5 mL benzene. To the solution was added 16.6 mg (0.063 mmol, 3.8 equiv) triphenylphosphine and 12.8 mg (0.063 mmol, 3.8 equiv) diisopropyl azodicarboxylate. The reaction mixture was stirred for at RT for 10 min, then concentrated and purified by flash chromatography (EtOAc/Hexane = 1/4 to 1/2) to give 5.4 mg 9-demethylneopeltolide (**1a**) in 56% yield.

9-Demethylneopeltolide (**1a**): $[\alpha]_D^{25}$ = +8.0 (c = 0.21, MeOH); ^{1}H NMR (500 MHz, CD_3OD): δ = 7.67 (s, 1H), 6.37 (dt, *J* = 11.5, 7.4 Hz, 1H), 6.27 (dt, *J* = 11.8, 2.1 Hz, 1H), 6.04 (dt, *J* = 12.0, 6.0 Hz, 1H), 5.88 (dt, *J* = 11.5, 1.6 Hz, 1H), 5.22-5.16 (m, 2H), 4.30 (dd, *J* = 5.8, 1.5 Hz, 1H), 4.09-4.04 (m, 1H), 3.65 (s, 2H), 3.58 (dd, *J* = 11.1, 9.4 Hz, 1H), 3.49 (m, 1H), 3.29 (s, 3H), 3.01 (qd, *J* = 7.5, 1.5 Hz, 1H), 2.73-2.68 (m, 2H), 2.30 (dd, *J* = 15.0, 10.5 Hz, 1H), 1.83-1.48 (m, 14H), 1.42-1.33 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD): δ = 172.8, 166.8, 161.9, 150.0, 142.3, 139.2, 135.9, 121.7, 115.9, 79.3, 76.8, 74.3, 71.0, 69.3, 56.5, 52.6, 43.0, 41.0, 39.8, 38.5, 37.0, 36.1, 34.5, 34.0, 29.0, 26.4, 24.6, 19.9, 14.2; HRMS (ESI): m/z: calcd for $C_{30}H_{45}O_9N_2$: 577.3120 $[M+H]^+$, found: 577.3124.

Reference:

1. H. Fuwa, A. Saito, S. Naito, K. Konoki, M. Yotsu-Yamashita, M. Sasaki, *Chem. Eur. J.* **2009**, *15*, 12807-12818.
2. Y. Wang, J. Janjic, S. A. Kozmin, *J. Am. Chem. Soc*. **2002**, *124*, 13670-13671.

Part 2. X-ray of *cis*-7m

Note: two conformers have been identified.

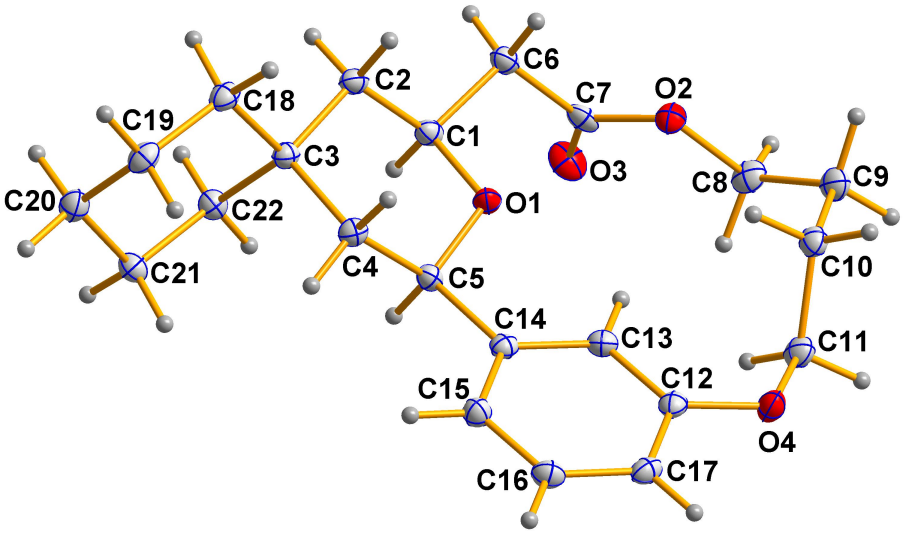


Figure S1. The X-Ray molecular structure of one conformer of *cis*-**7m**.

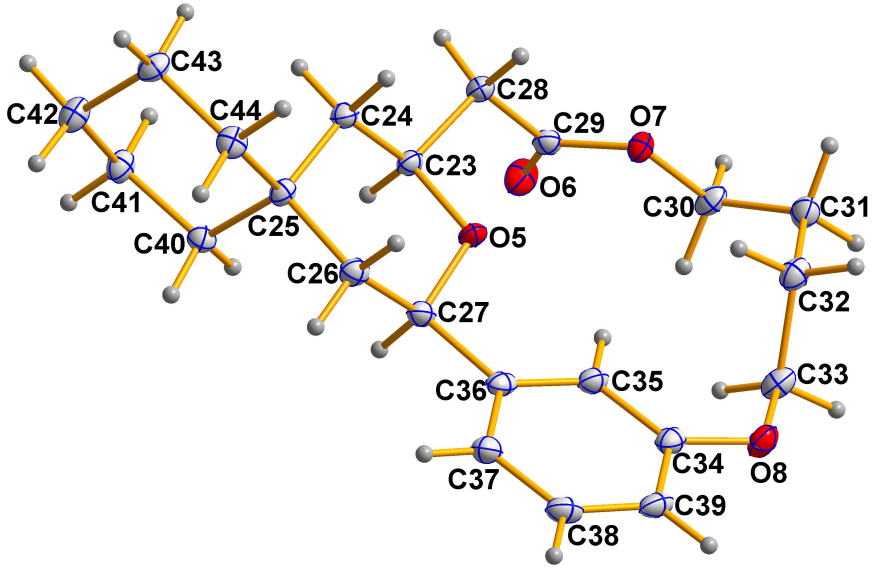


Figure S2. The X-Ray molecular structure of the other conformer of *cis*-**7m**.

Part 3. ^{1}H NMR, ^{13}C NMR, COSY and NOESY Spectra

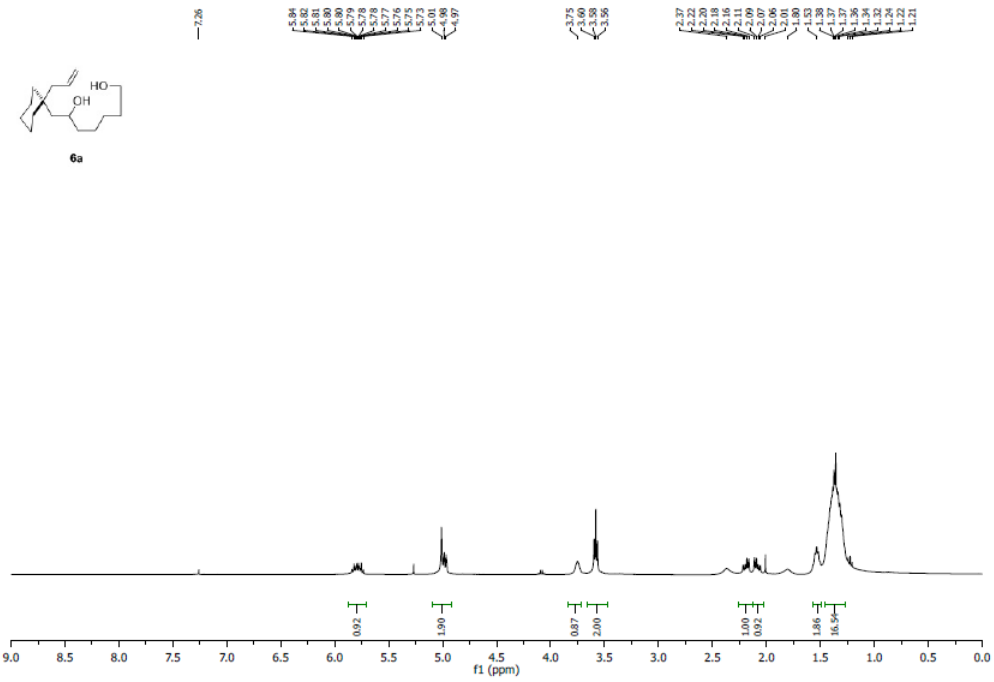


Figure S3. ^{1}H NMR of **6a** (400 MHz, $CDCl_3$)

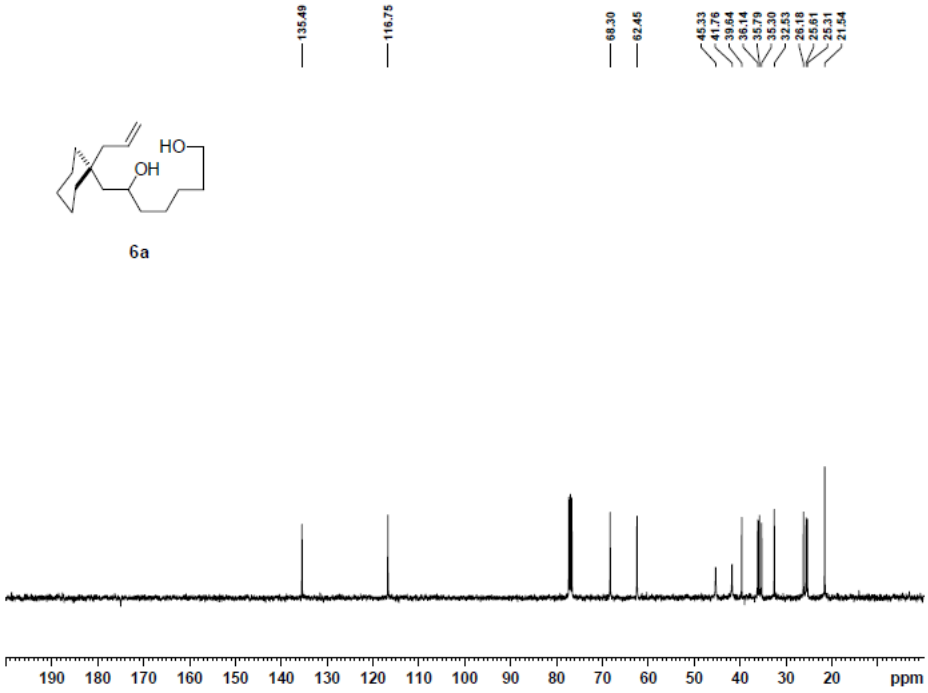


Figure S4. ^{13}C NMR of **6a** (100 MHz, $CDCl_3$)

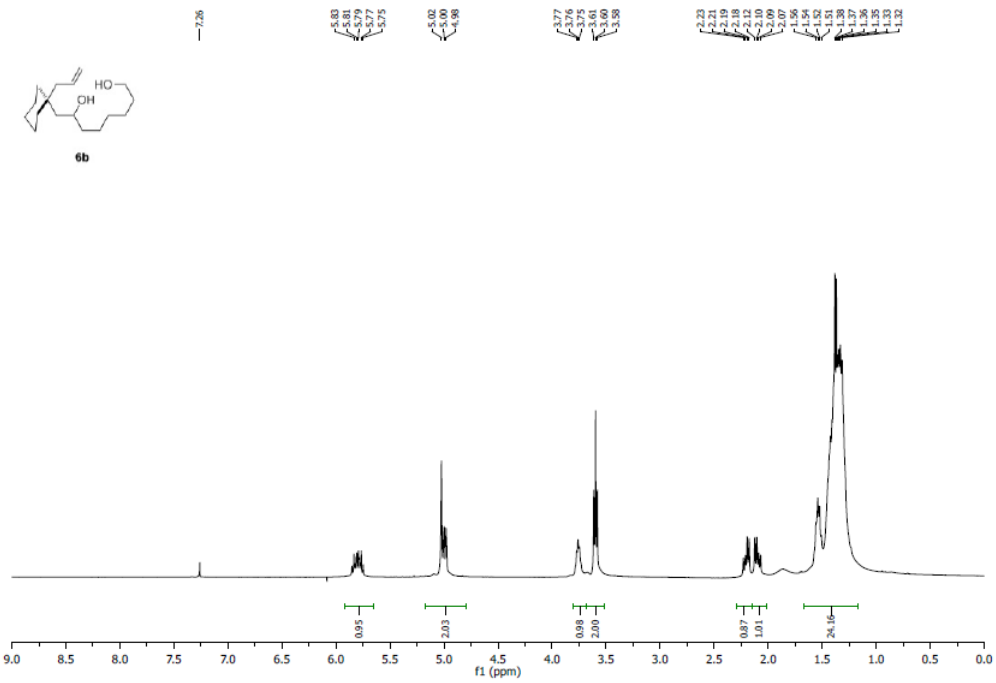


Figure S5. ^{1}H NMR of **6b** (400 MHz, $CDCl_3$)

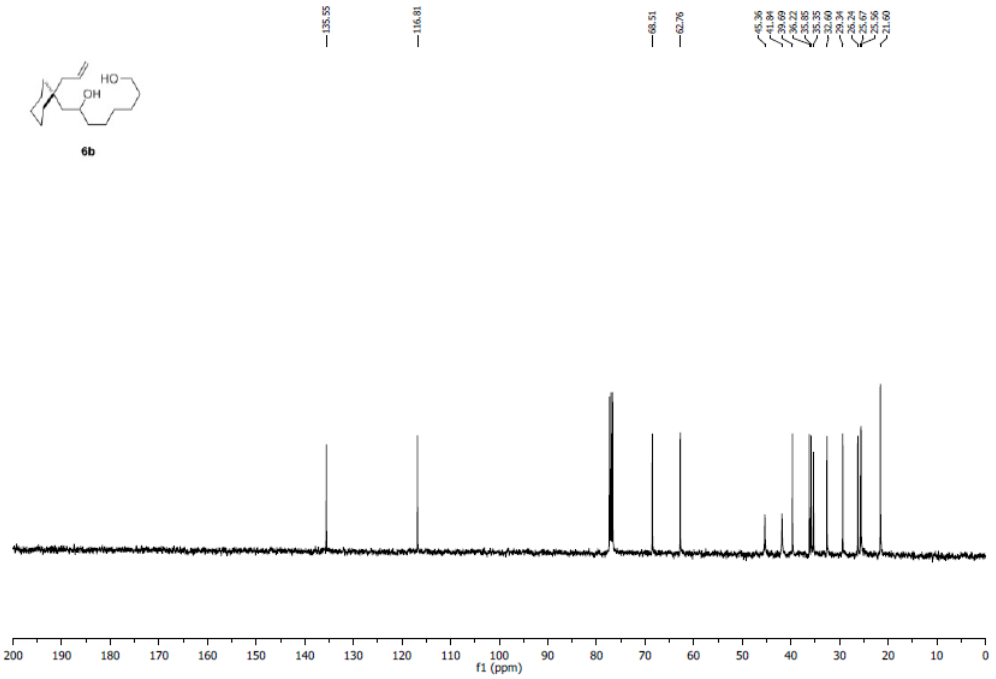


Figure S6. ^{13}C NMR of **6b** (100 MHz, $CDCl_3$)

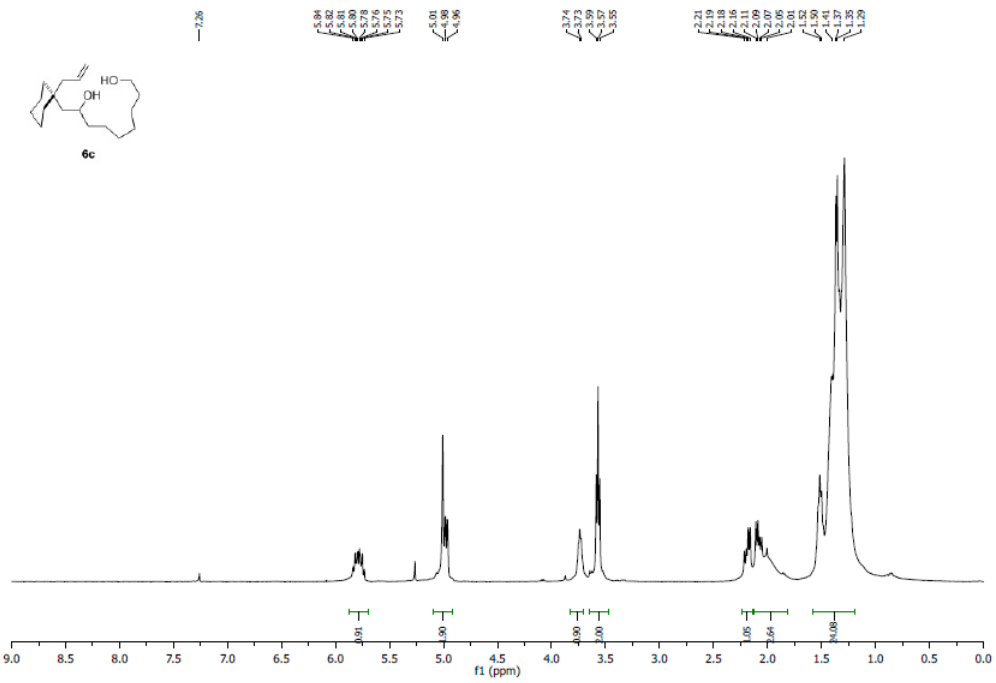


Figure S7. ^{1}H NMR of **6c** (400 MHz, $CDCl_3$)

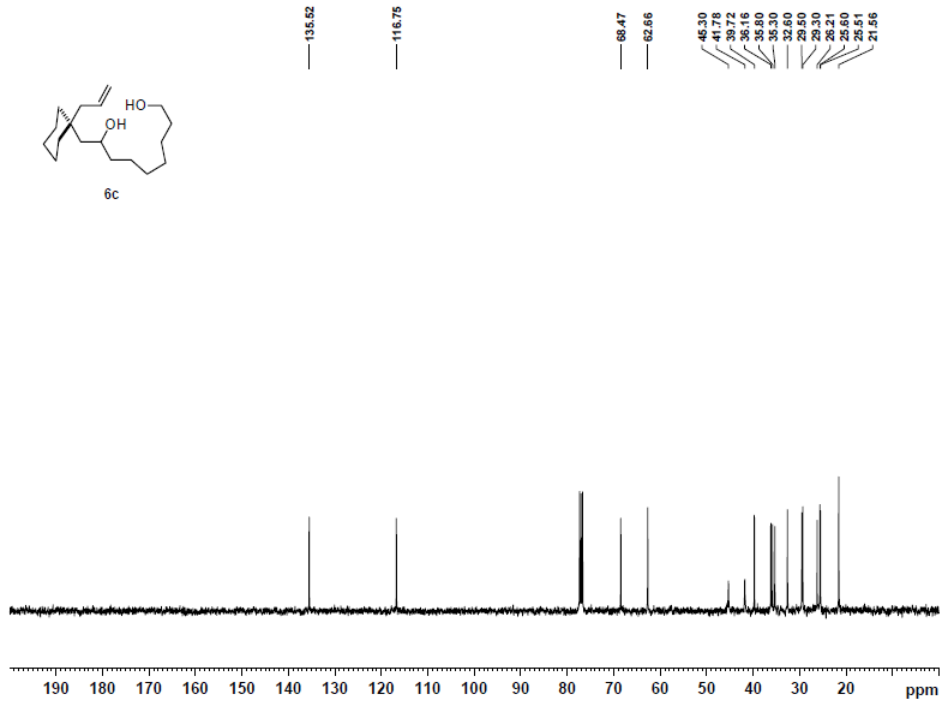


Figure S8. ^{13}C NMR of **6c** (100 MHz, $CDCl_3$)

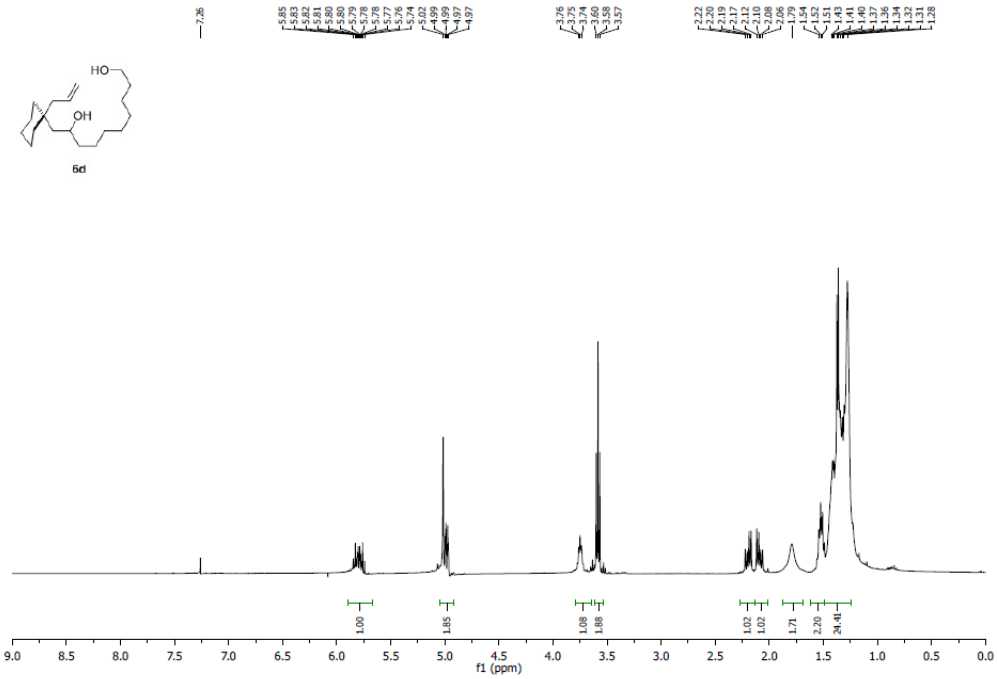


Figure S9. ^{1}H NMR of **6d** (400 MHz, $CDCl_3$)

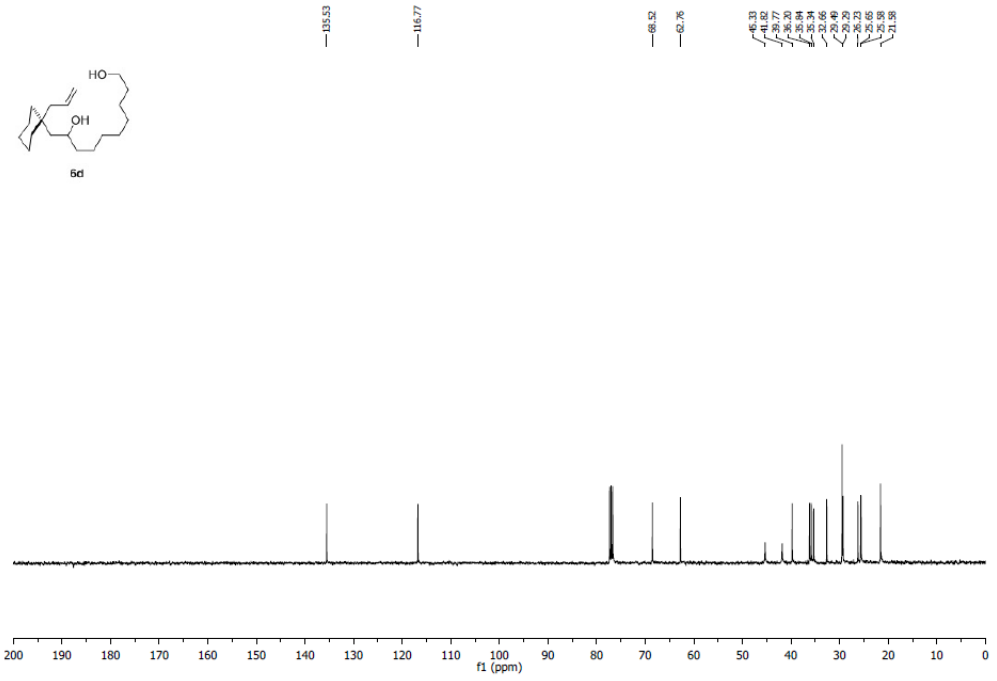


Figure S10. ^{13}C NMR of **6d** (100 MHz, $CDCl_3$)

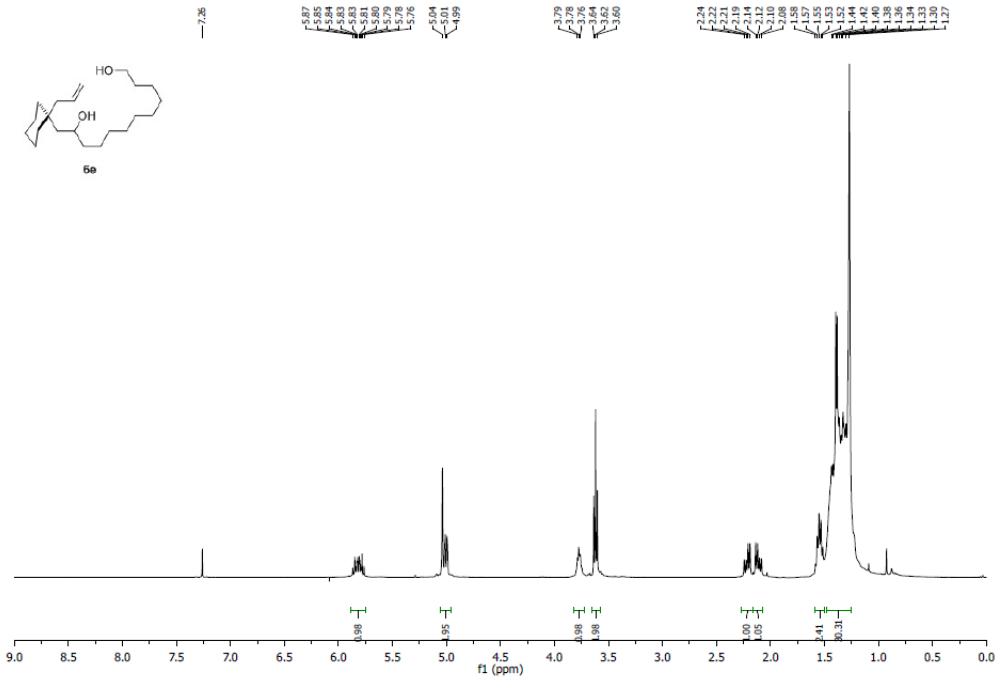


Figure S11. ^{1}H NMR of **6e** (400 MHz, $CDCl_3$)

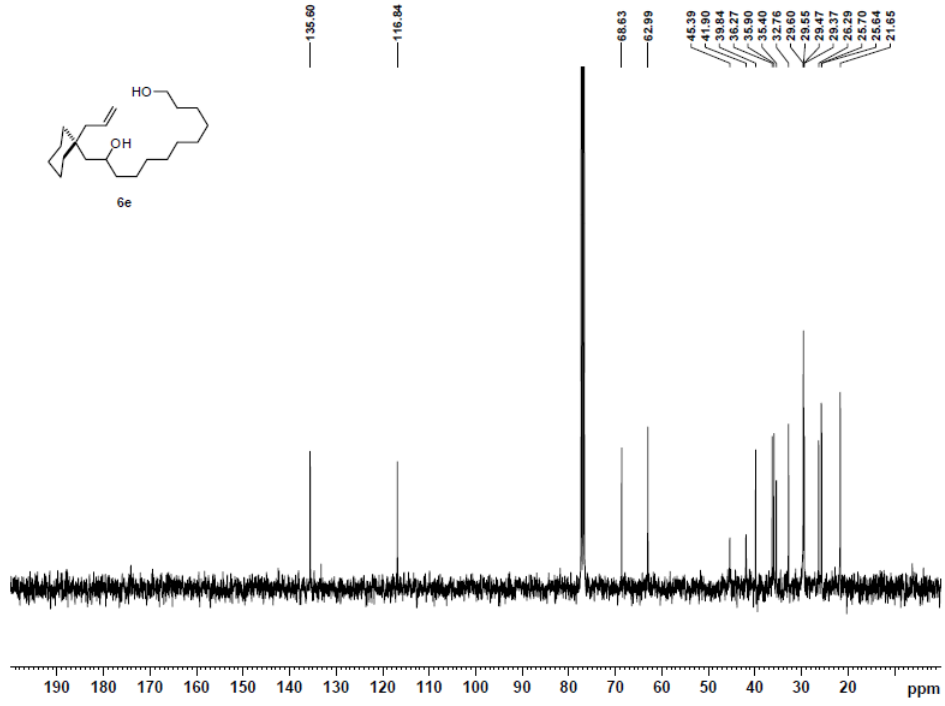


Figure S12. ^{13}C NMR of **6e** (100 MHz, $CDCl_3$)

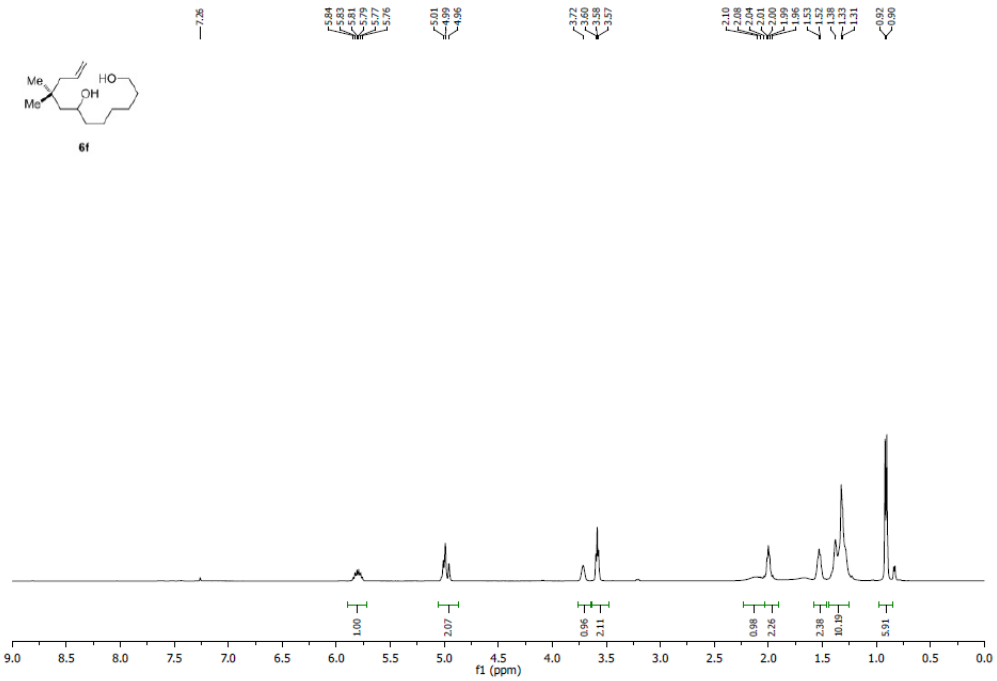


Figure S13. ^{1}H NMR of **6f** (400 MHz, $CDCl_3$)

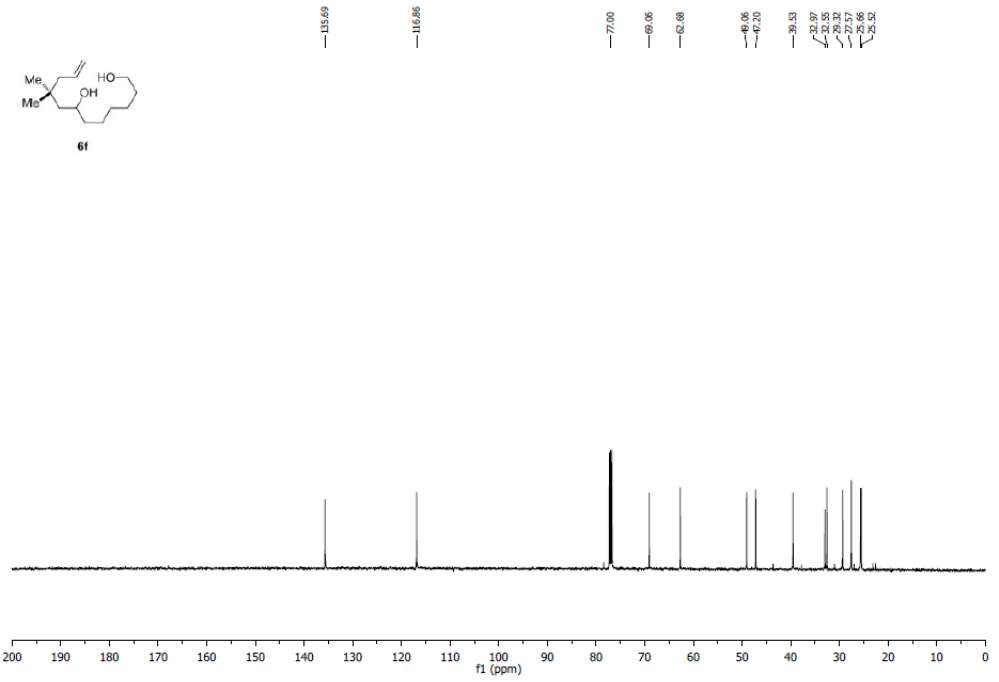


Figure S14. ^{13}C NMR of **6f** (125 MHz, $CDCl_3$)

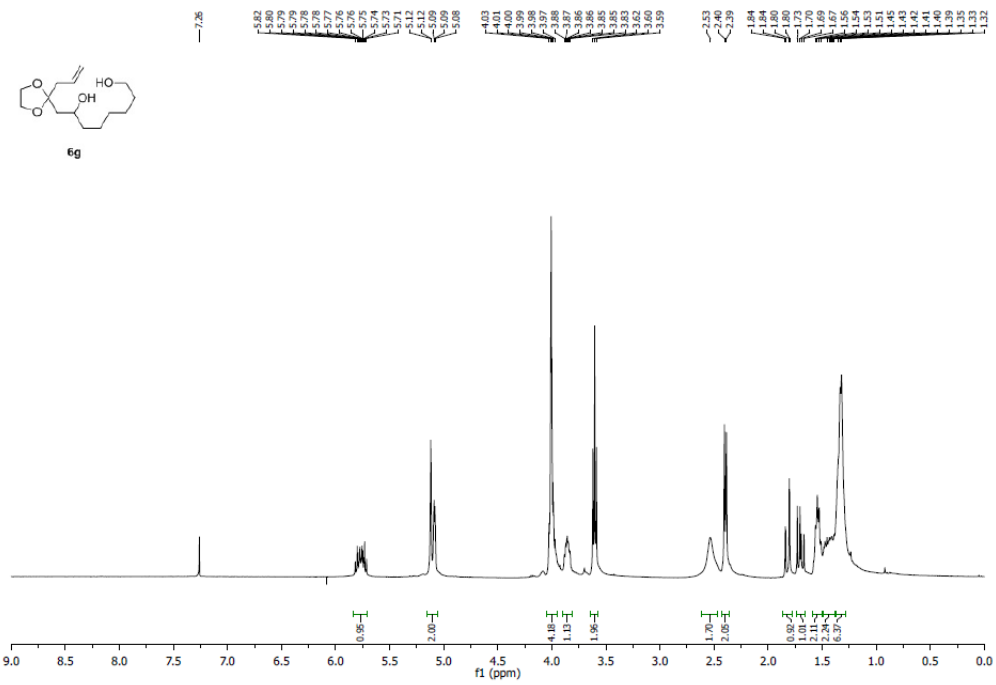


Figure S15. ^{1}H NMR of **6g** (400 MHz, $CDCl_3$)

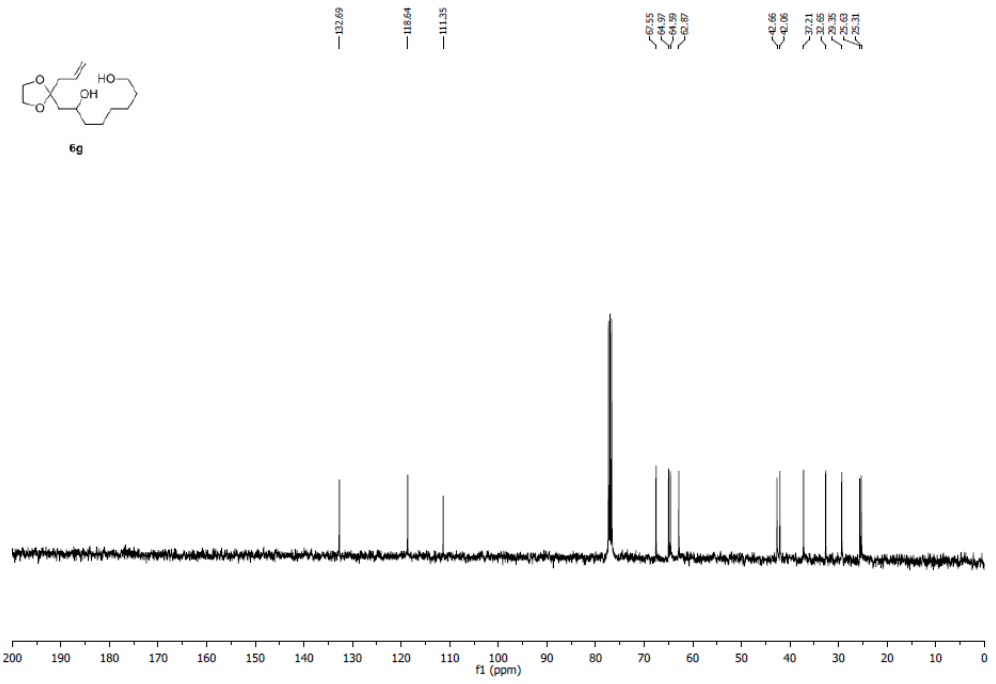


Figure S16. ^{13}C NMR of **6g** (100 MHz, $CDCl_3$)

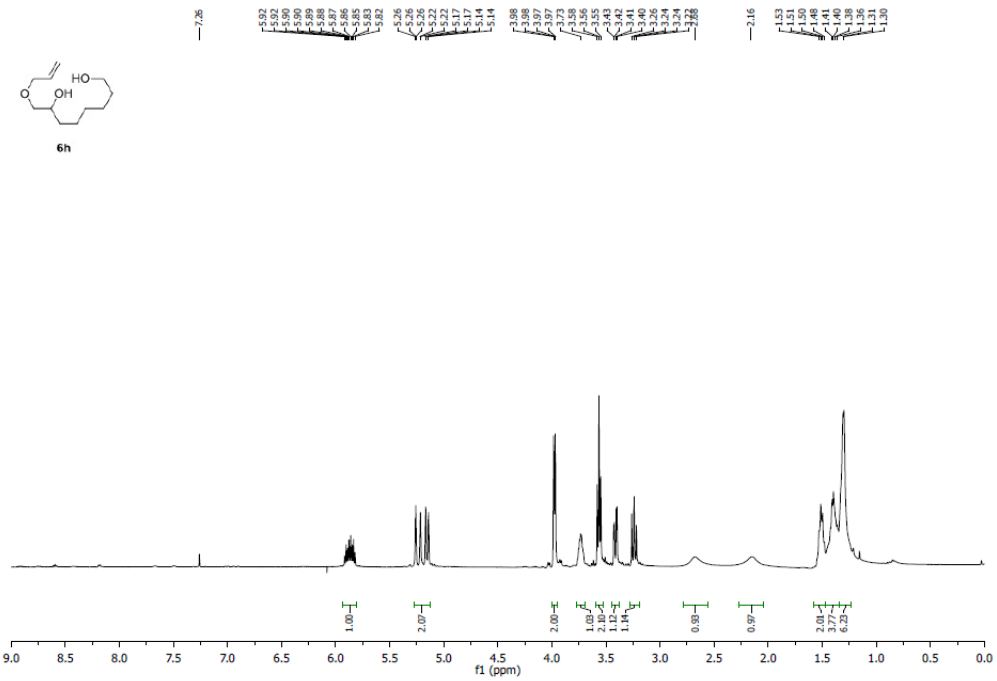


Figure S17. ^{1}H NMR of **6h** (400 MHz, $CDCl_3$)

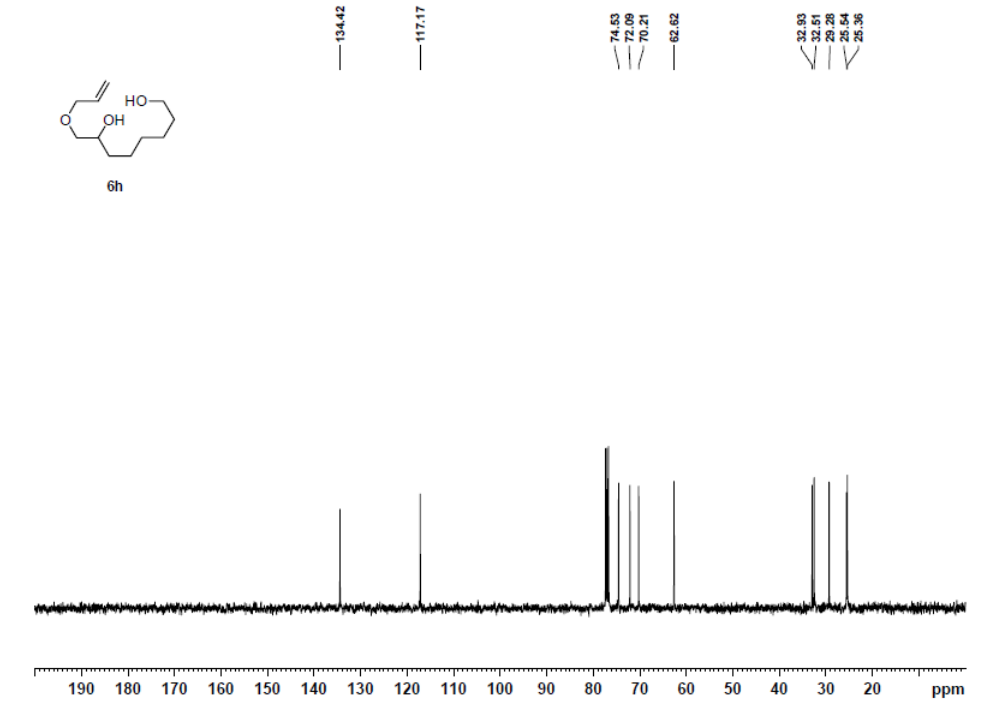


Figure S18. ^{13}C NMR of **6h** (100 MHz, $CDCl_3$)

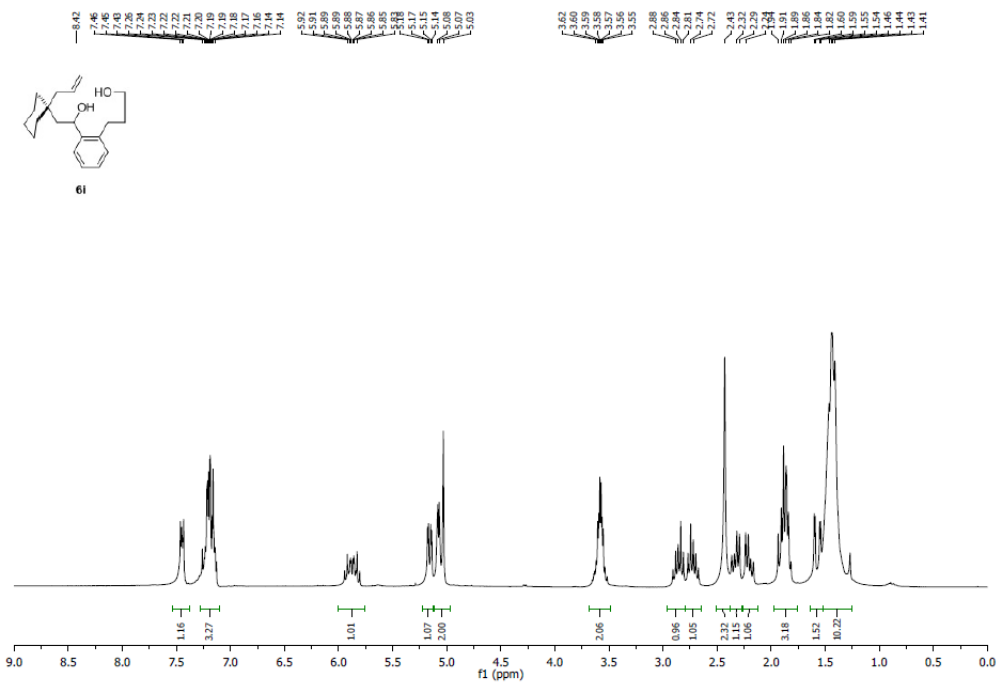


Figure S19. ^{1}H NMR of **6i** (300 MHz, $CDCl_3$)

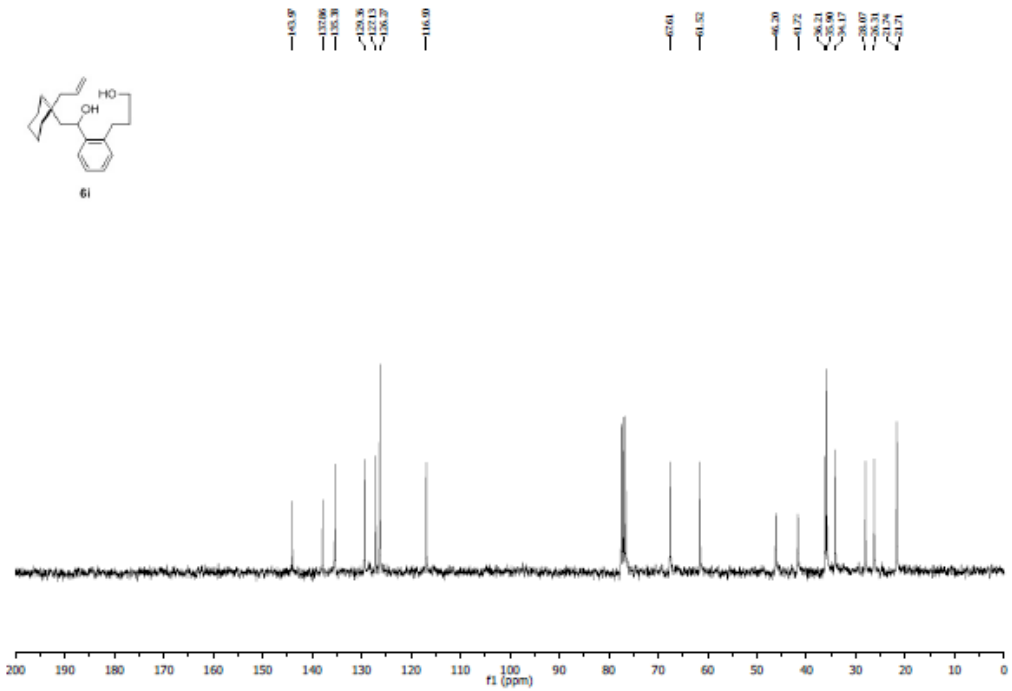


Figure S20. ^{13}C NMR of **6i** (75 MHz, $CDCl_3$)

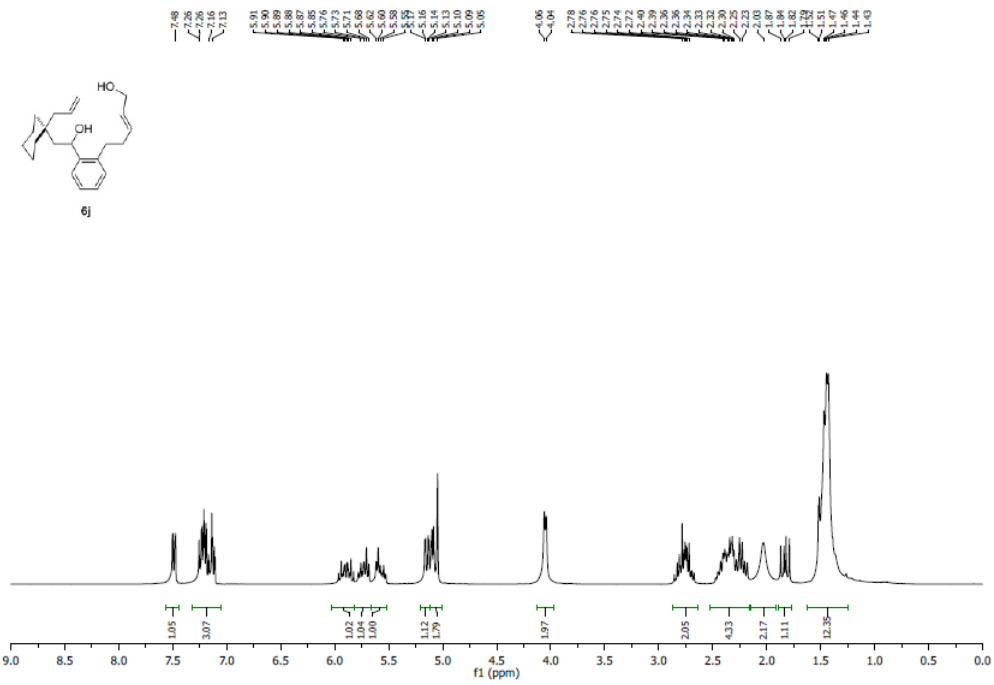


Figure S21. ^{1}H NMR of **6j** (300 MHz, $CDCl_3$)

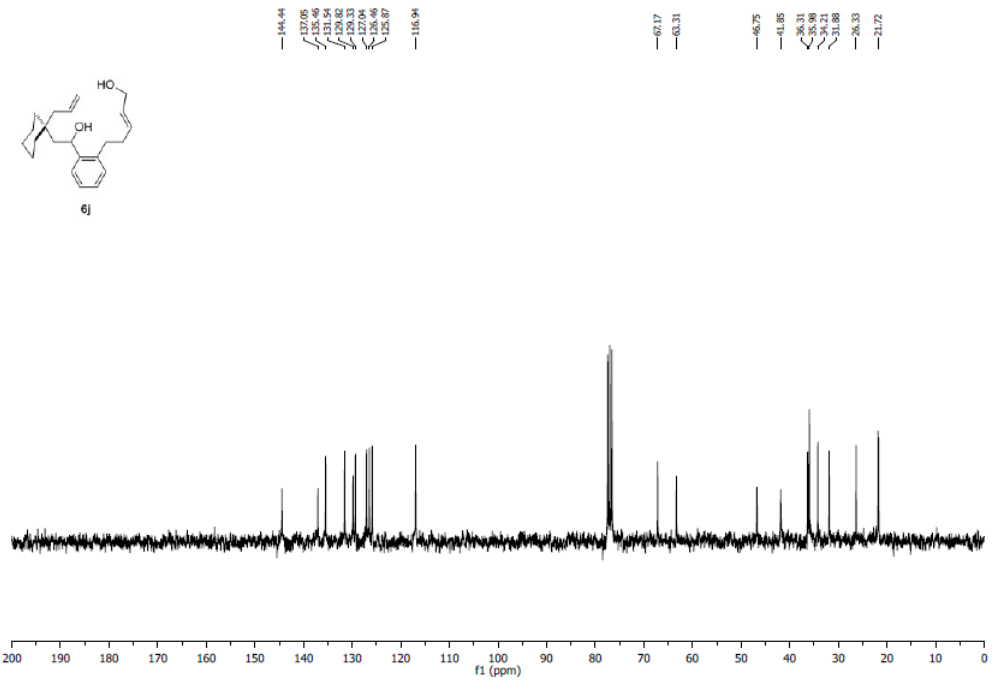


Figure S22. ^{13}C NMR of **6j** (75 MHz, $CDCl_3$)

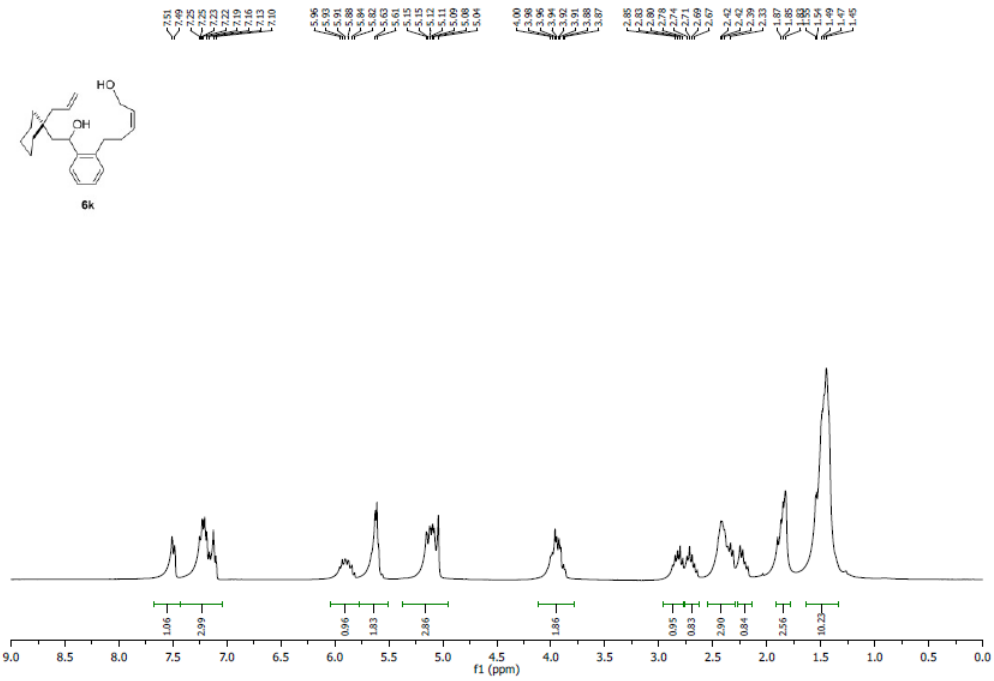


Figure S23. ^{1}H NMR of **6k** (300 MHz, $CDCl_3$)

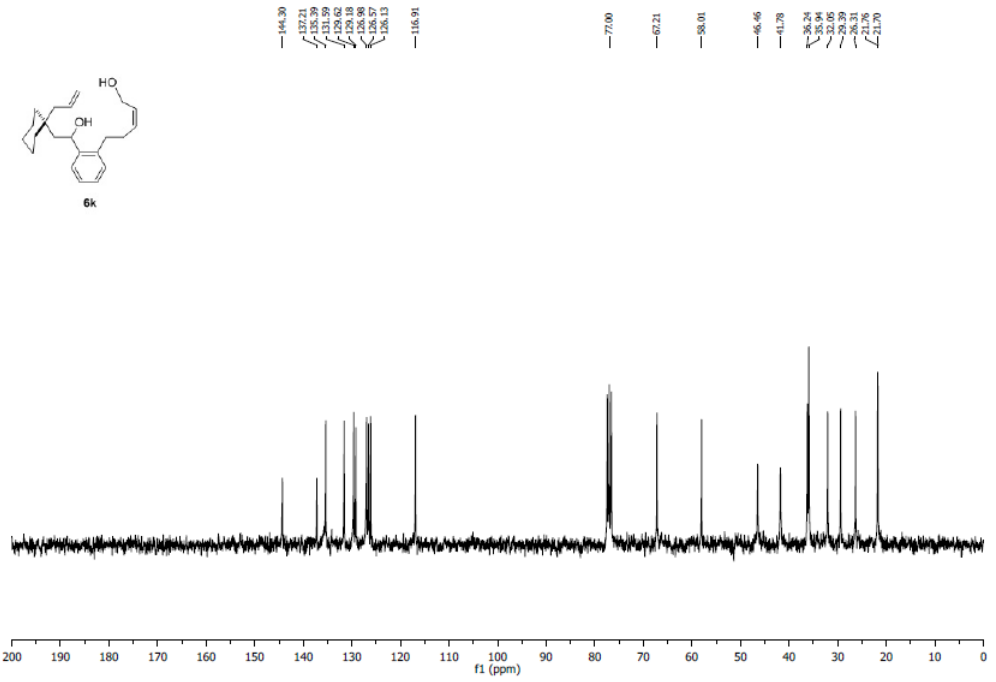


Figure S24. ^{13}C NMR of **6k** (75 MHz, $CDCl_3$)

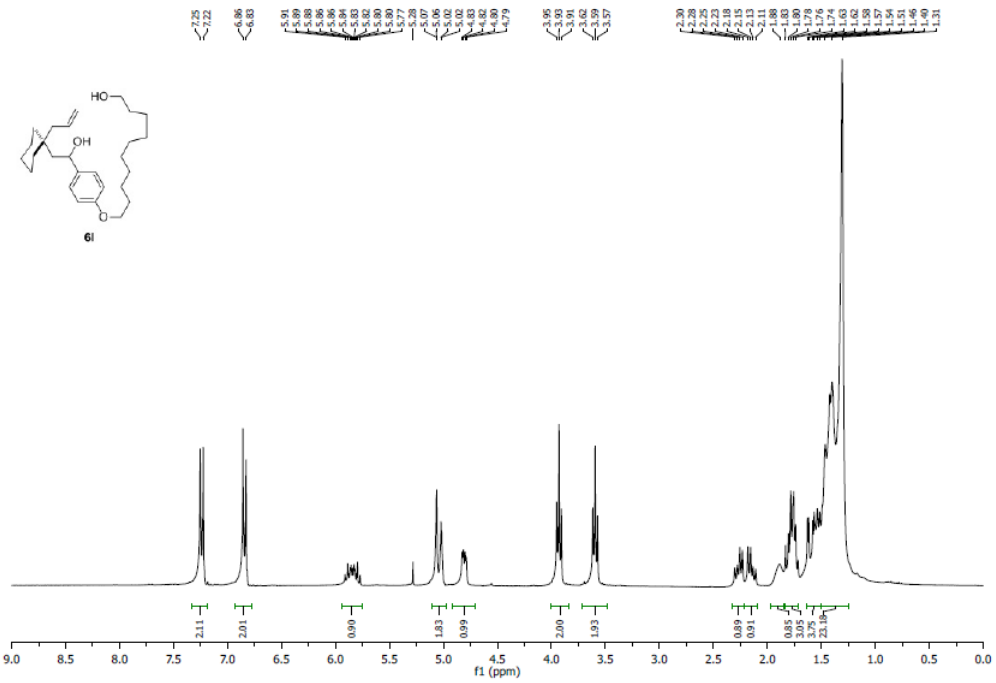


Figure S25. ^{1}H NMR of **6l** (300 MHz, $CDCl_3$)

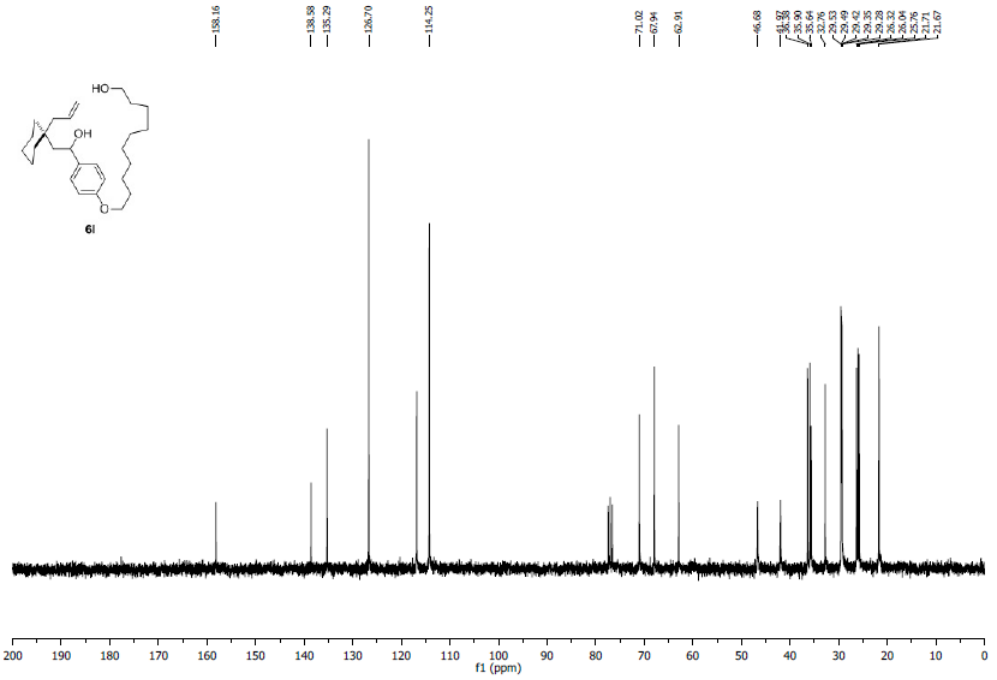


Figure S26. ^{13}C NMR of **6l** (75 MHz, $CDCl_3$)

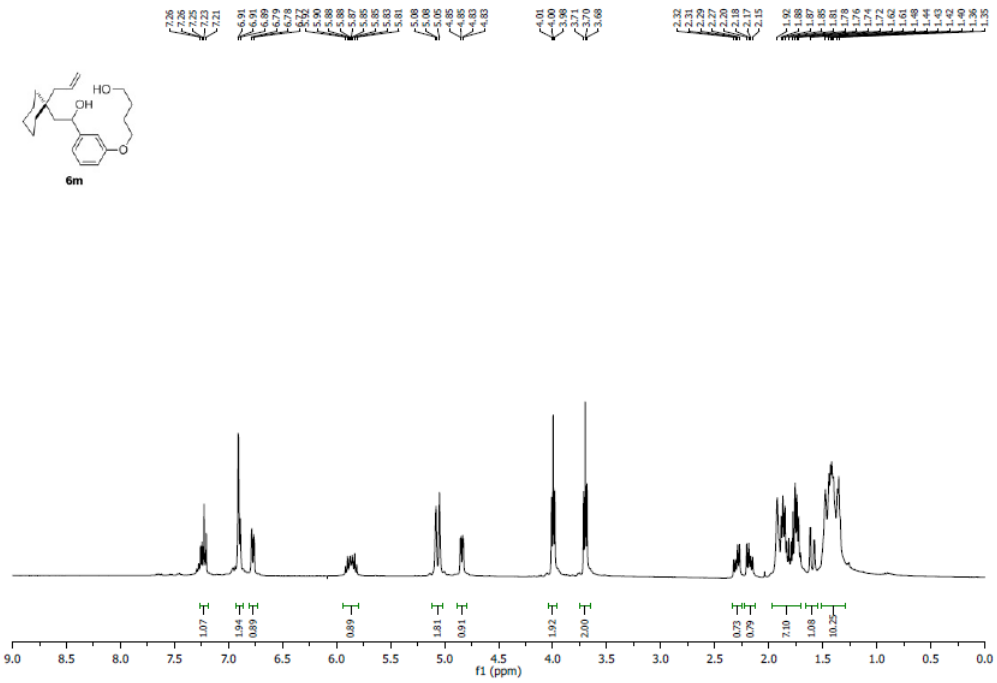


Figure S27. ^{1}H NMR of **6m** (400 MHz, $CDCl_3$)

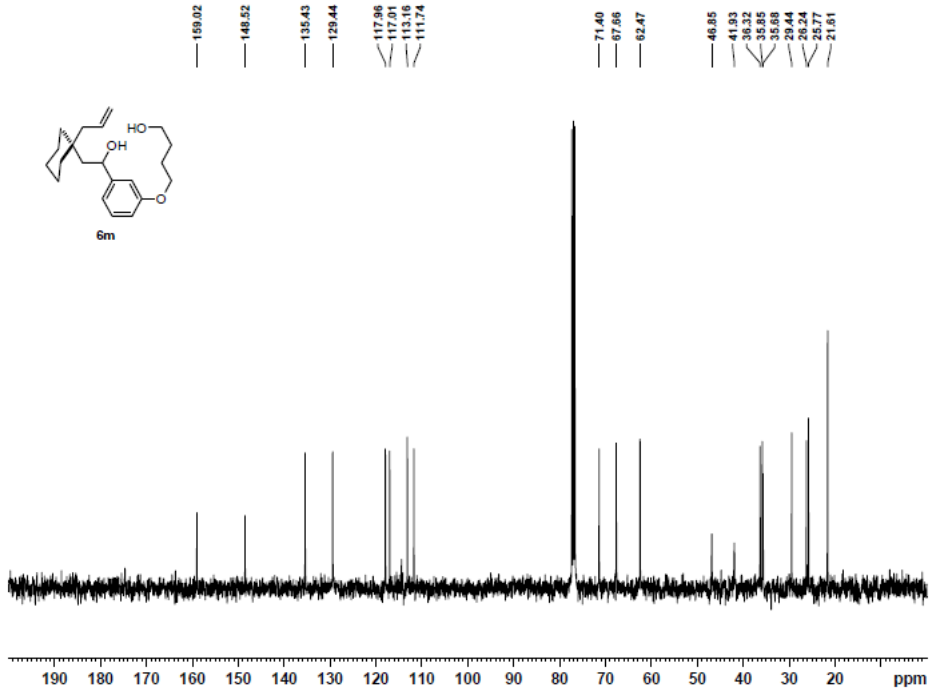


Figure S28. ^{13}C NMR of **6m** (100 MHz, $CDCl_3$)

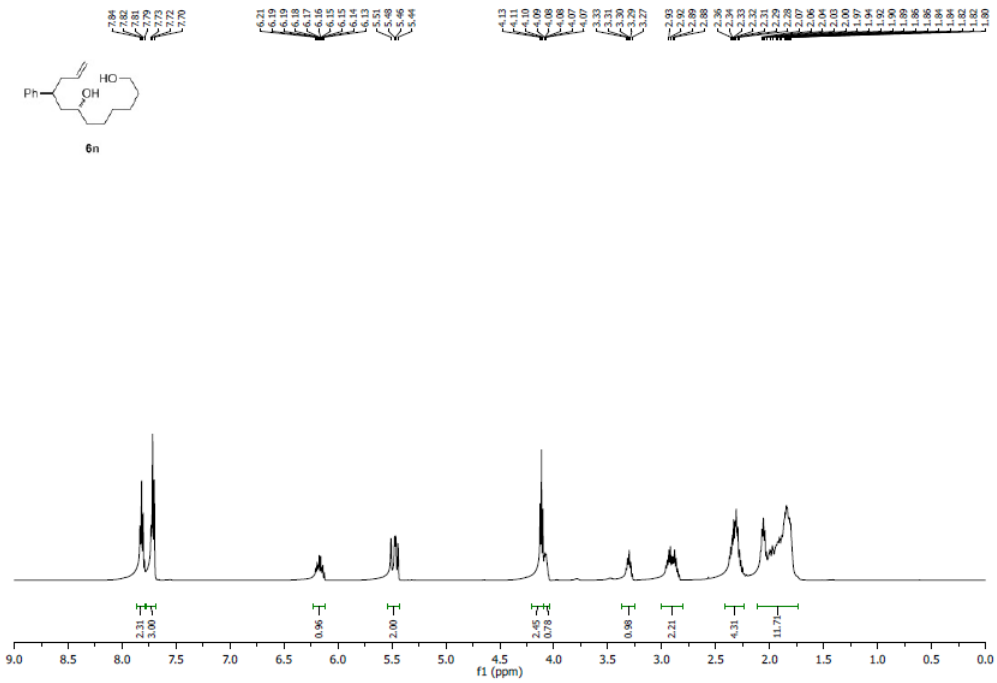


Figure S29. ^{1}H NMR of **6n** (500 MHz, $CDCl_3$)

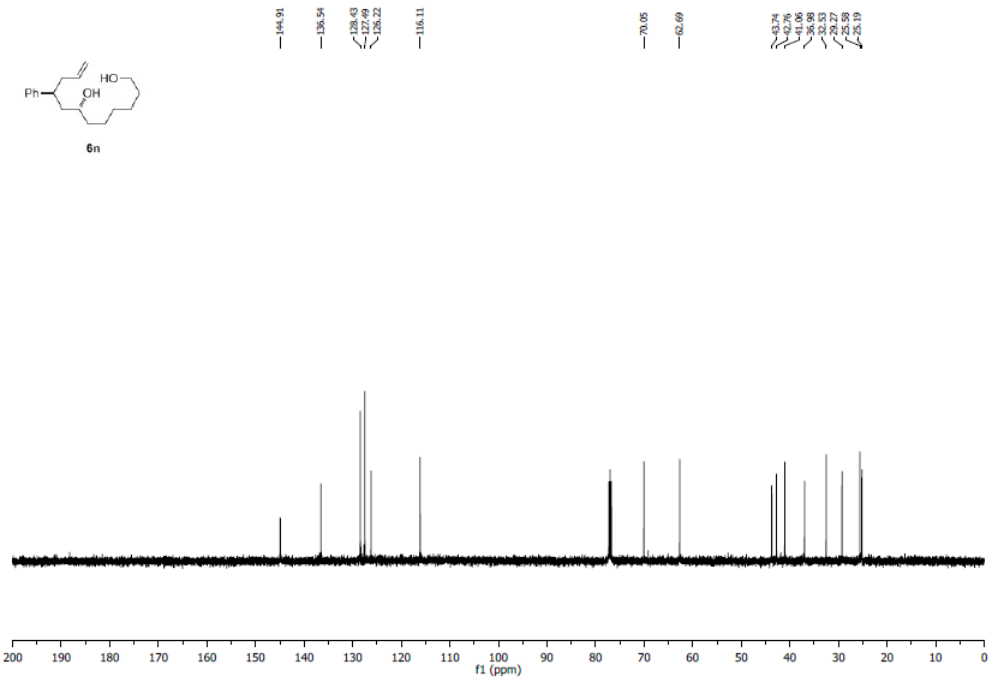


Figure S30. ^{13}C NMR of **6n** (125 MHz, $CDCl_3$)

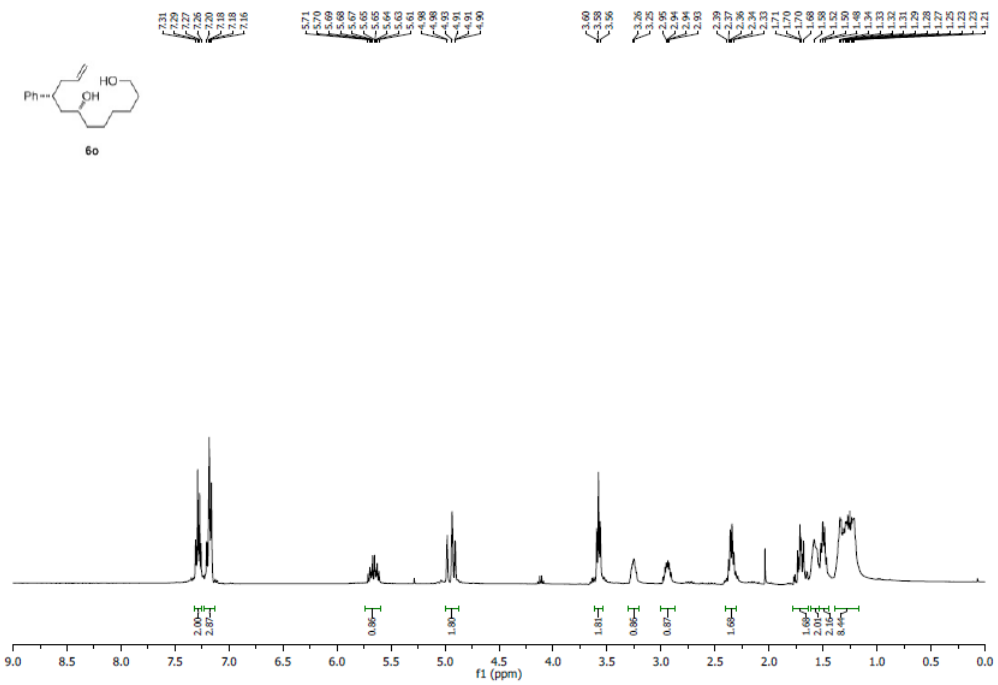


Figure S31. ^{1}H NMR of **6o** (400 MHz, $CDCl_3$)

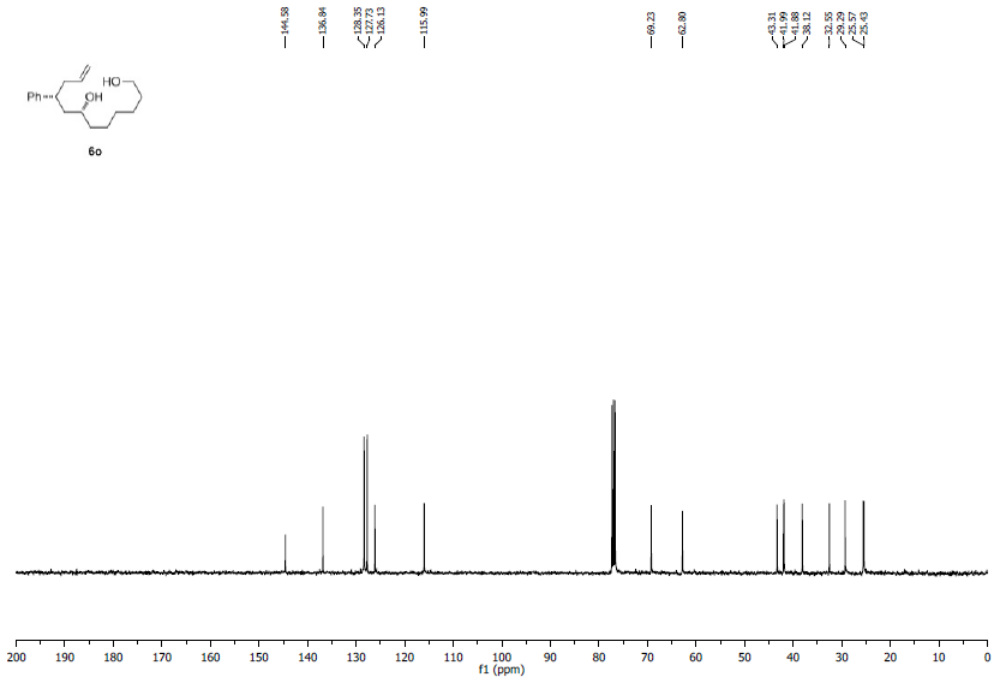


Figure S32. ^{13}C NMR of **6o** (100 MHz, $CDCl_3$)

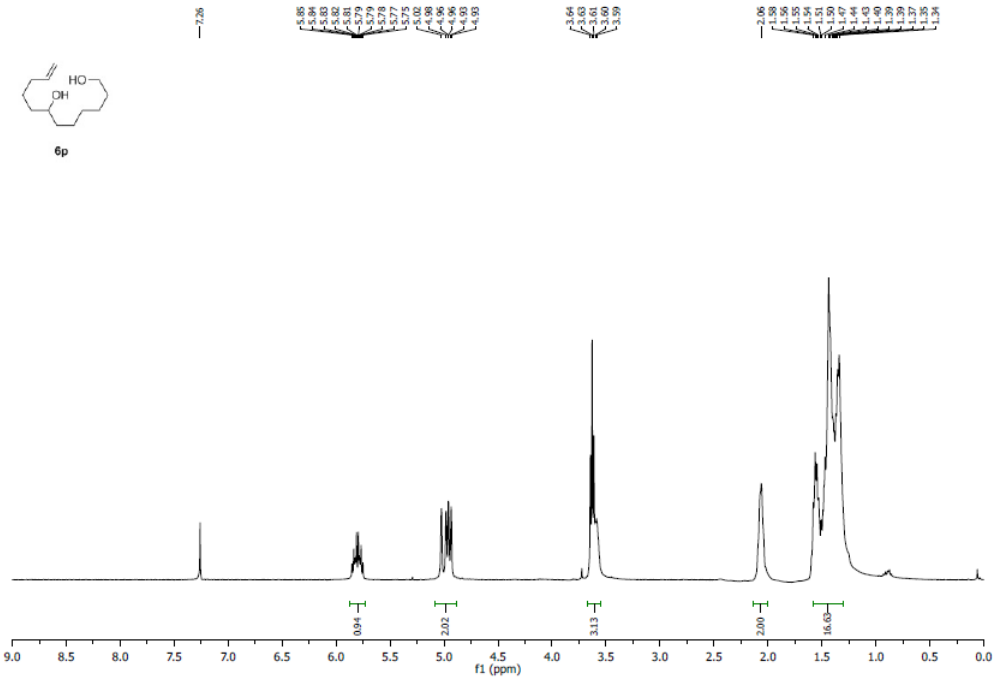


Figure S33. ^{1}H NMR of **6p** (400 MHz, $CDCl_3$)

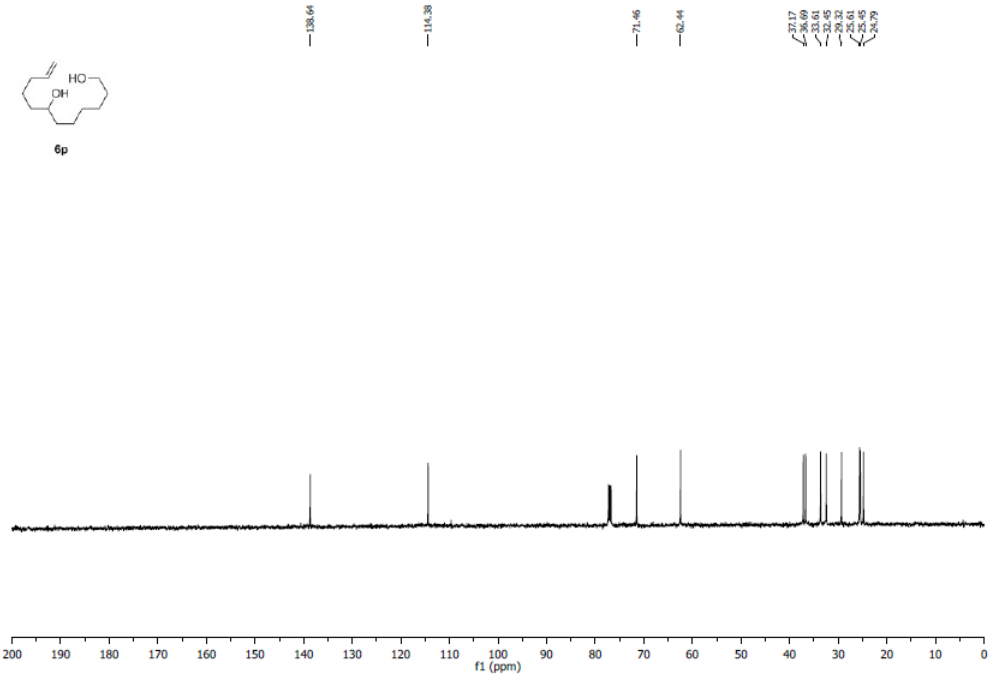


Figure S34. ^{13}C NMR of **6p** (100 MHz, $CDCl_3$)

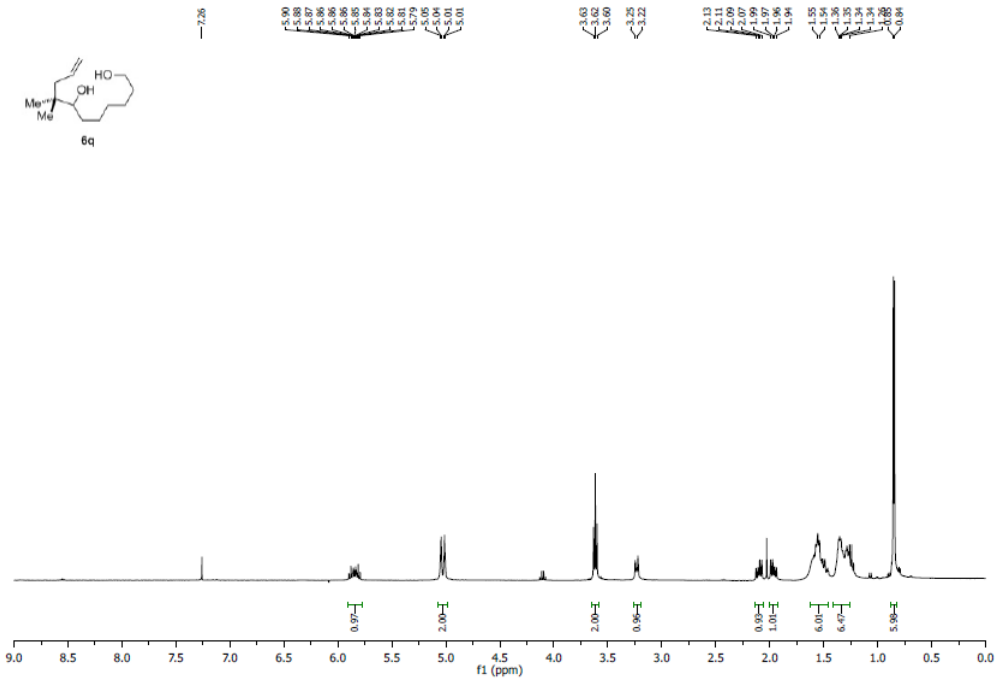


Figure S35. ^{1}H NMR of **6q** (400 MHz, $CDCl_3$)

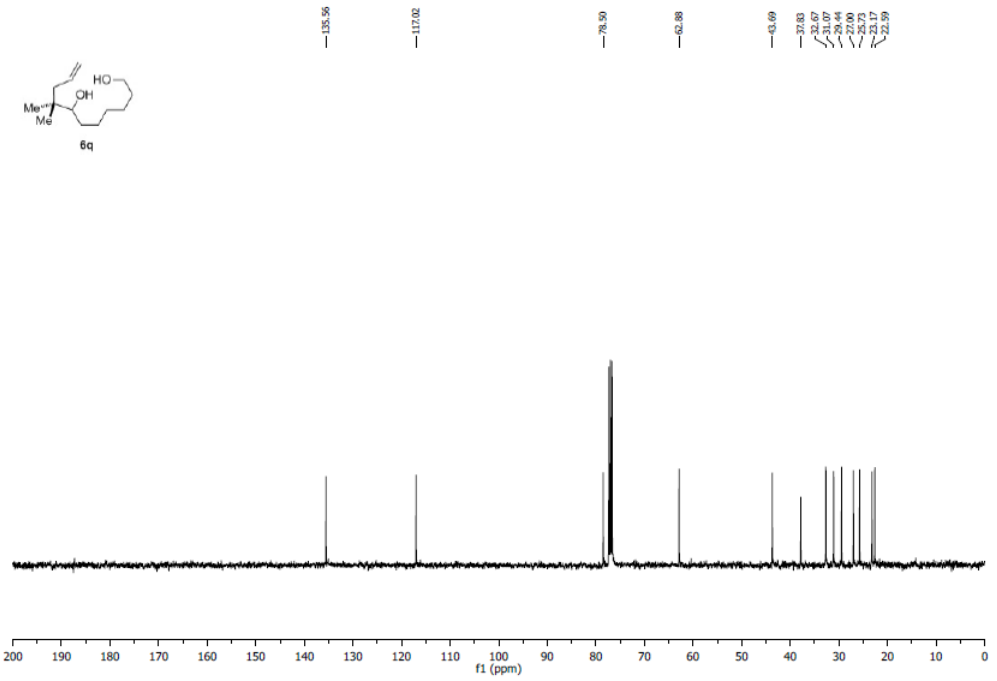


Figure S36. ^{13}C NMR of **6q** (100 MHz, $CDCl_3$)

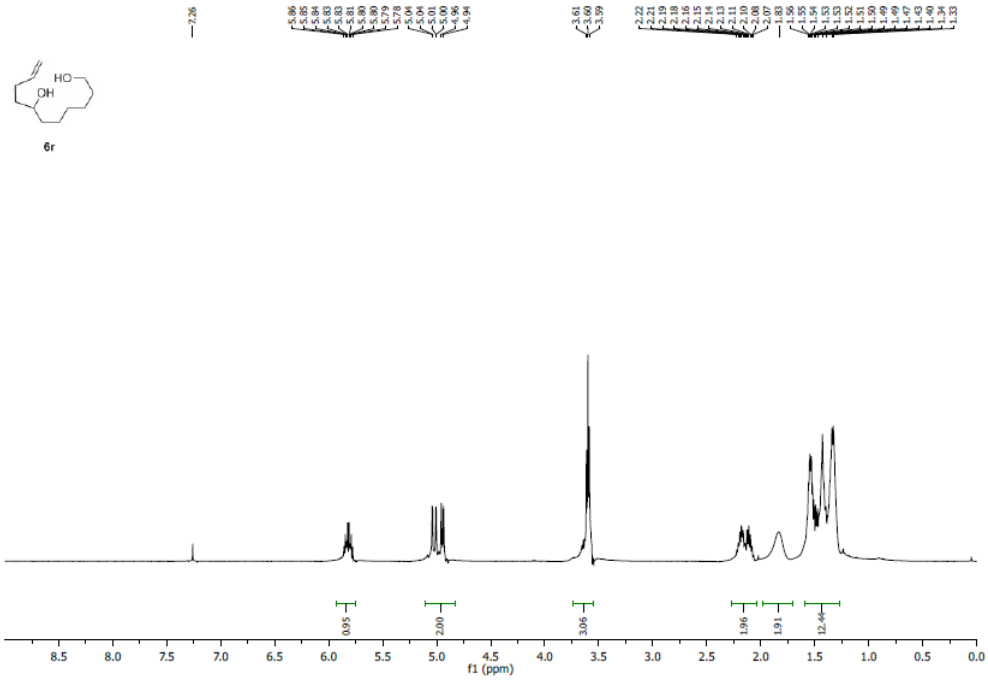


Figure S37. ^{1}H NMR of **6r** (500 MHz, $CDCl_3$)

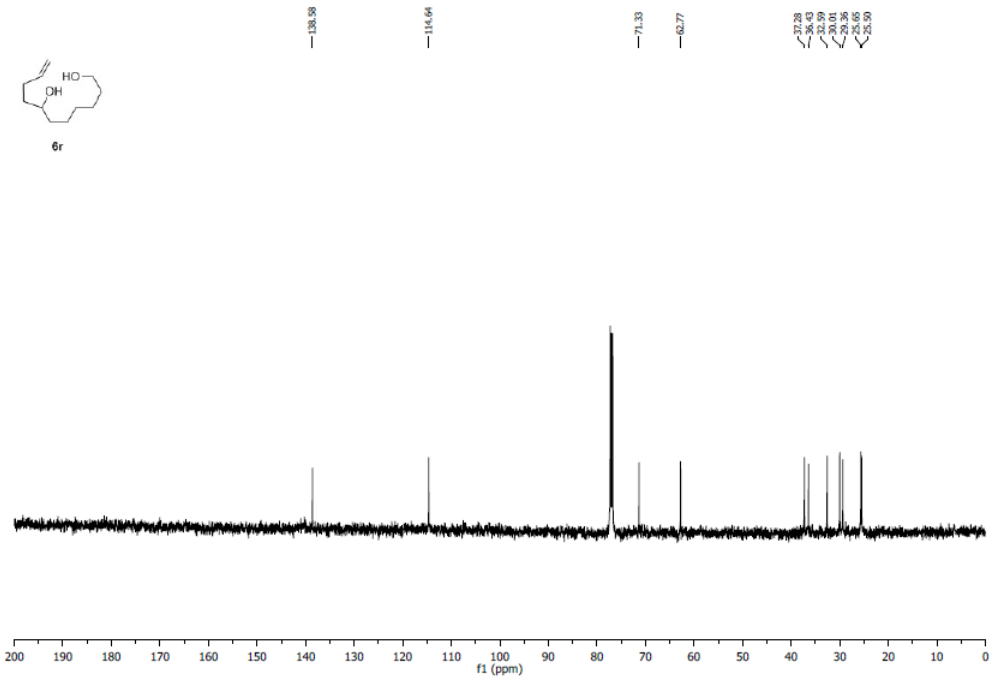


Figure S38. ^{13}C NMR of **6r** (125 MHz, $CDCl_3$)

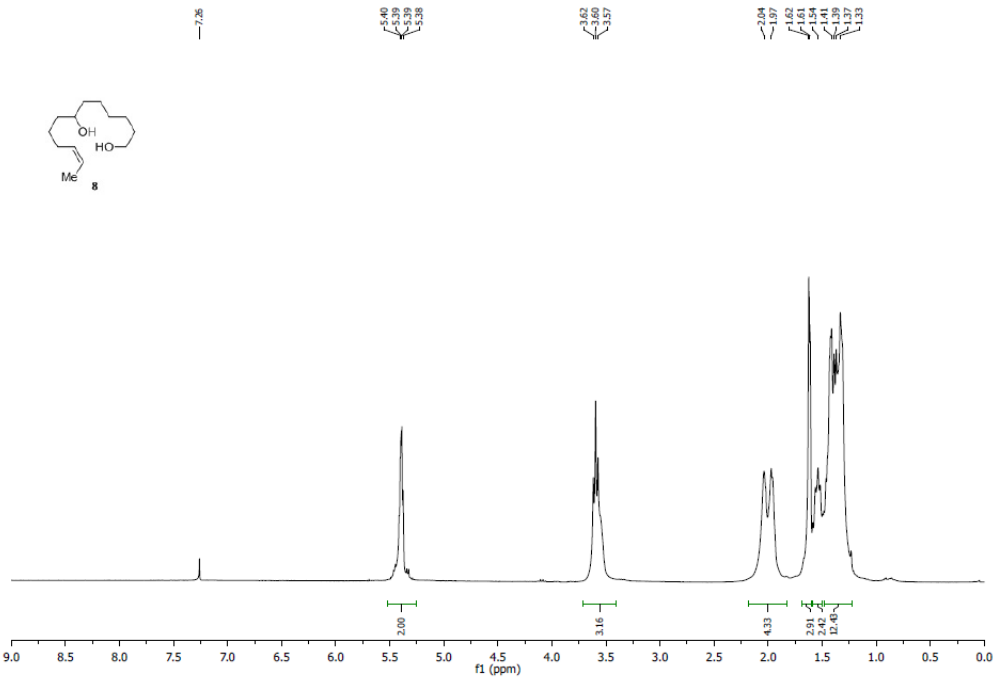


Figure S39. ^{1}H NMR of **8** (300 MHz, $CDCl_3$)

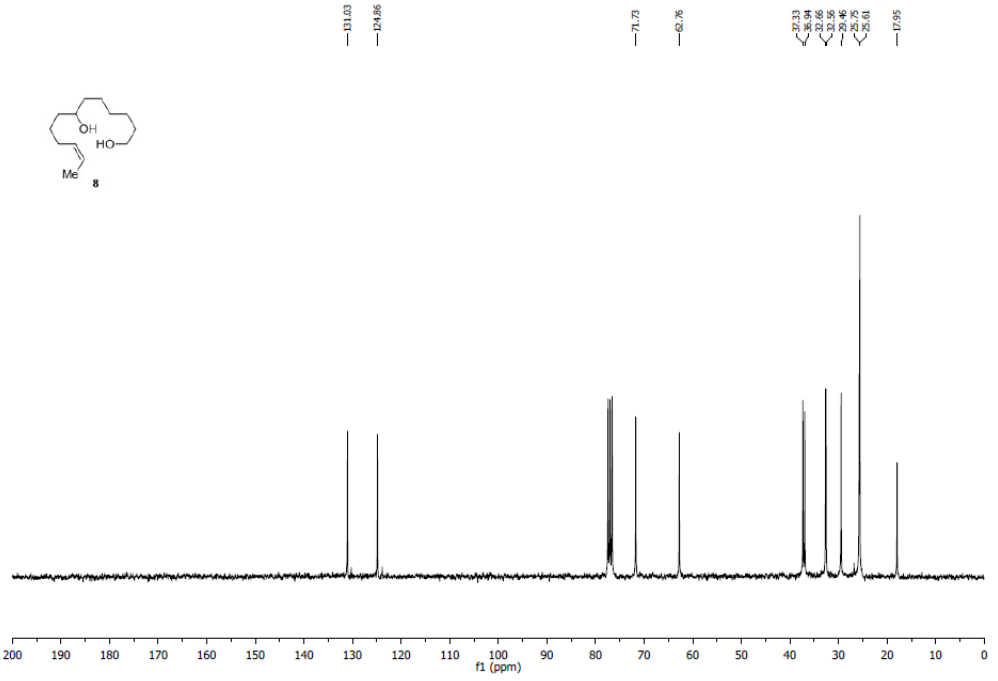


Figure S40. ^{13}C NMR of **8** (75 MHz, $CDCl_3$)

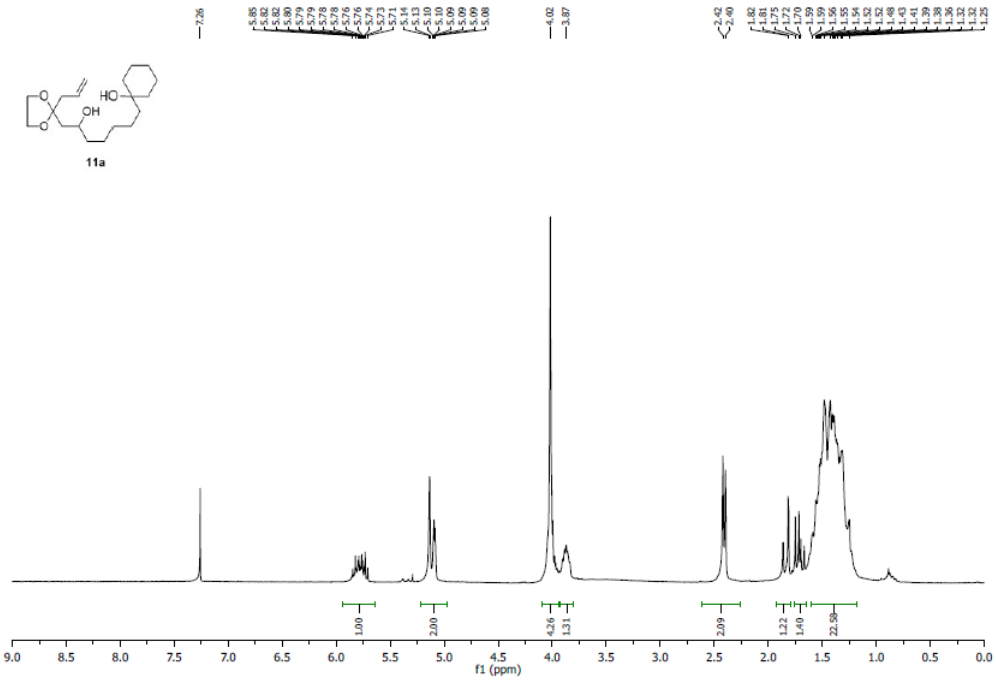


Figure S41. ^{1}H NMR of **11a** (300 MHz, $CDCl_3$)

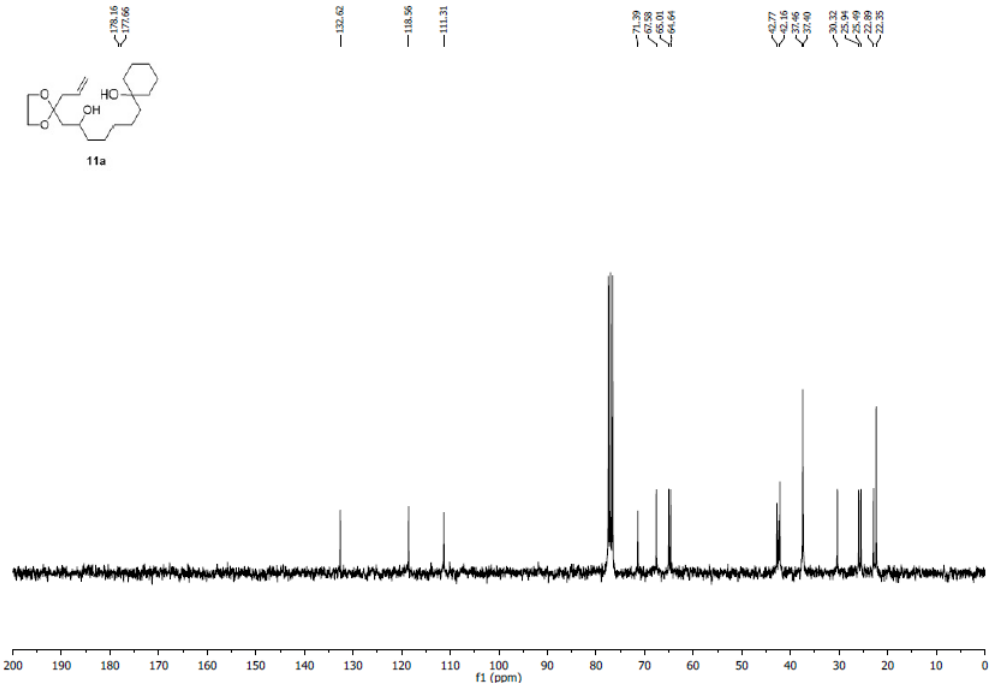


Figure S42. ^{13}C NMR of **11a** (75 MHz, $CDCl_3$)

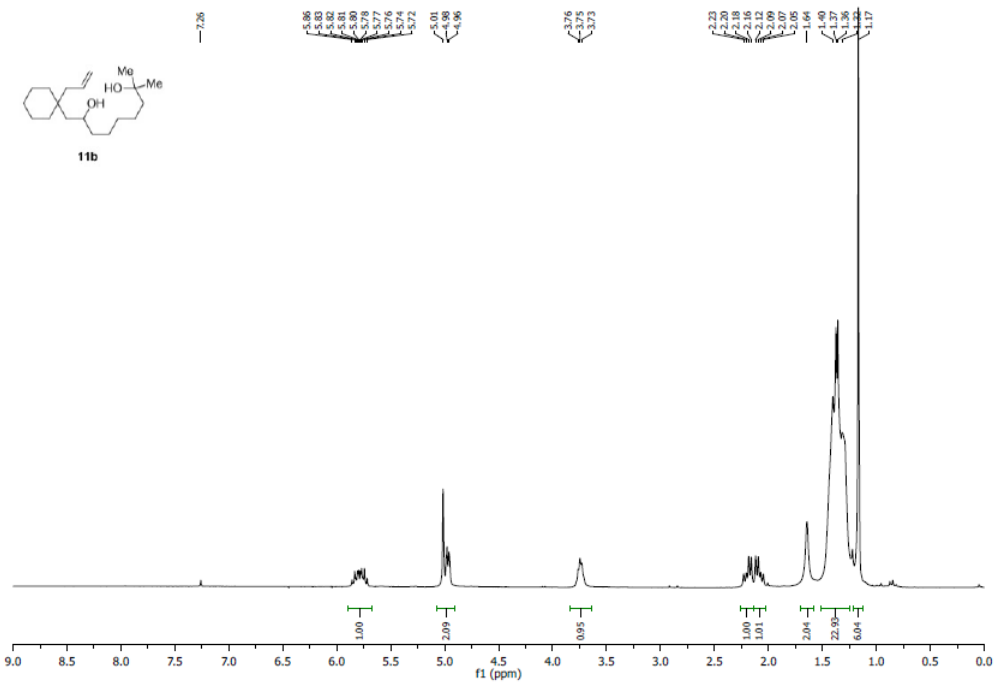


Figure S43. ^{1}H NMR of **11b** (300 MHz, $CDCl_3$)

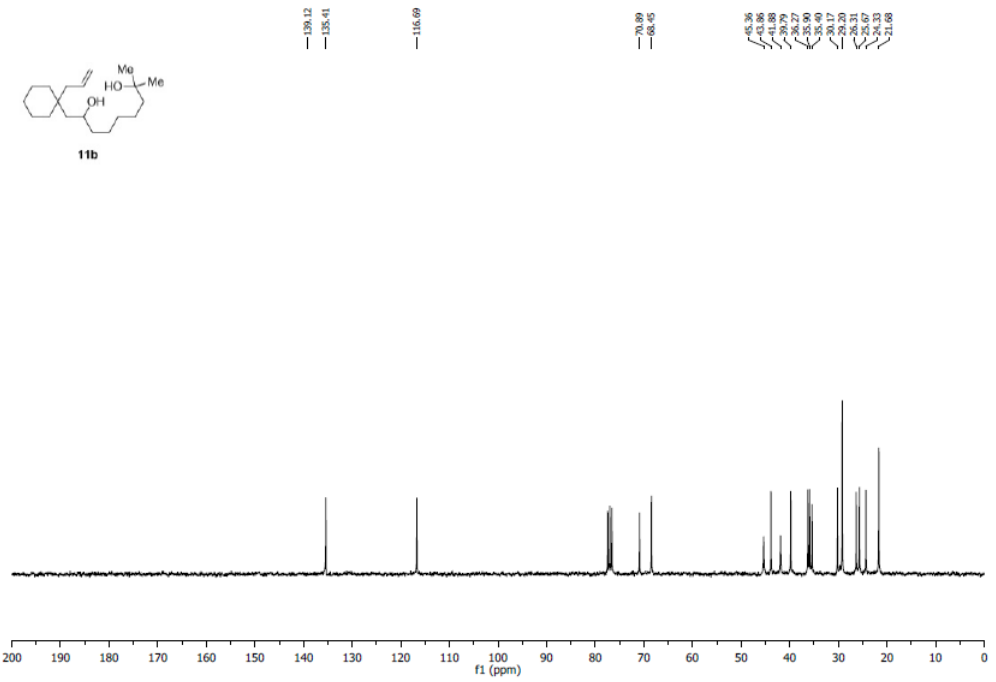


Figure S44. ^{13}C NMR of **11b** (75 MHz, $CDCl_3$)

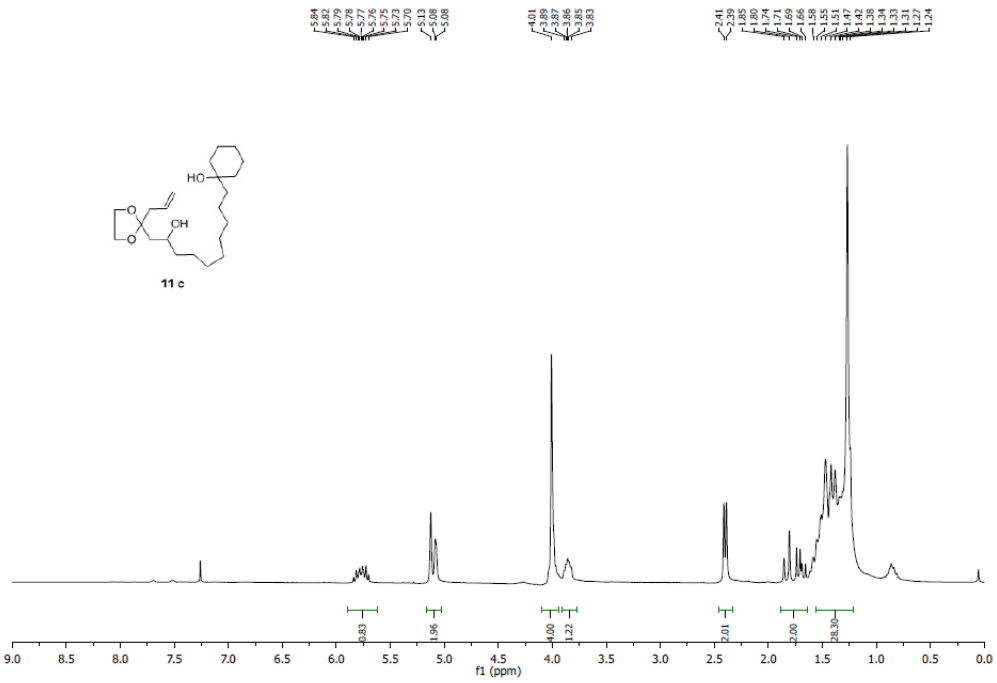


Figure S45. ^{1}H NMR of **11c** (300 MHz, $CDCl_3$)

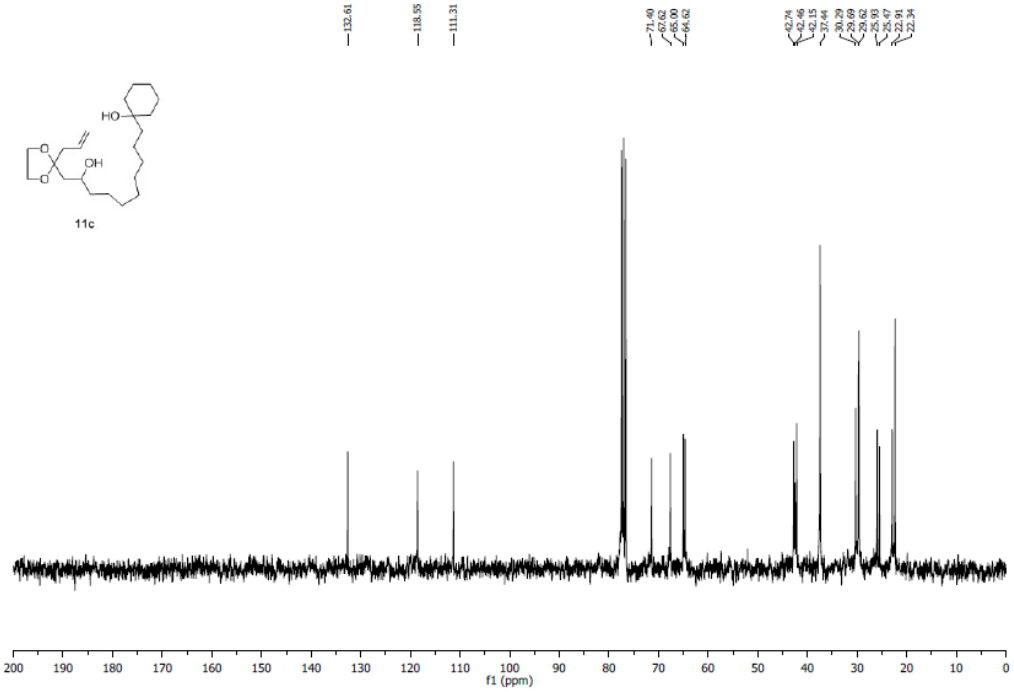


Figure S46. ^{13}C NMR of **11c** (75 MHz, $CDCl_3$)

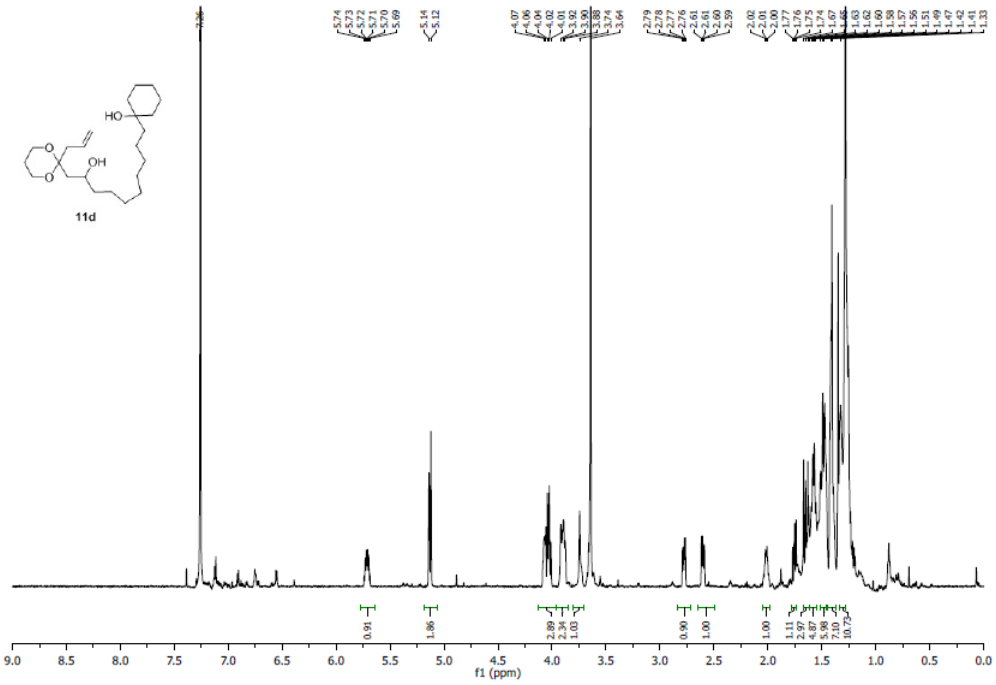


Figure S47. ^{1}H NMR of **11d** (800 MHz, $CDCl_3$)

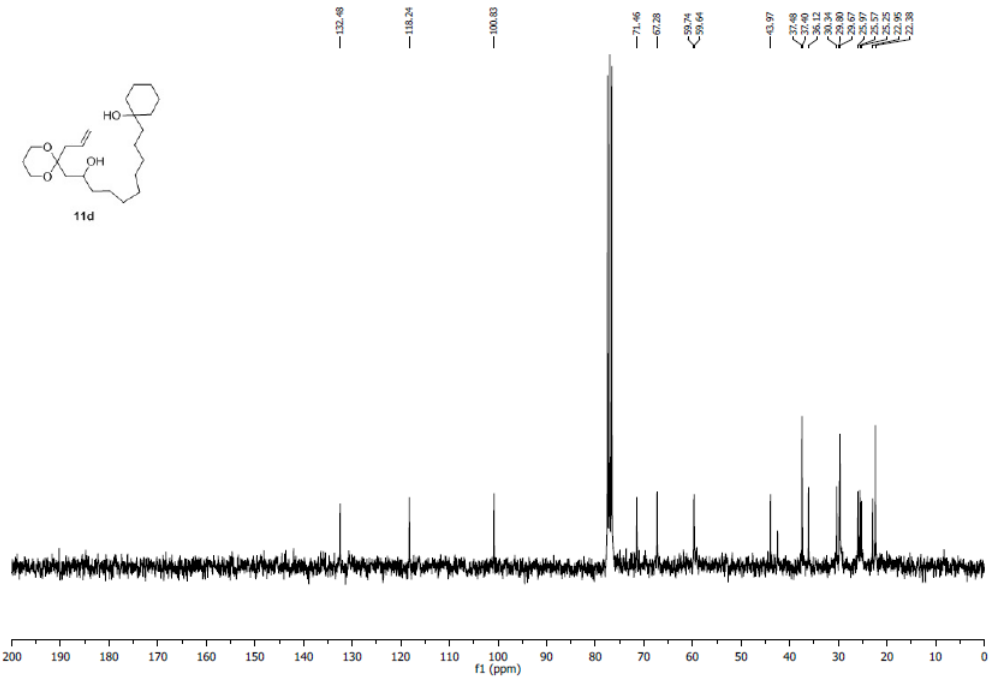


Figure S48. ^{13}C NMR of **11d** (75 MHz, $CDCl_3$)

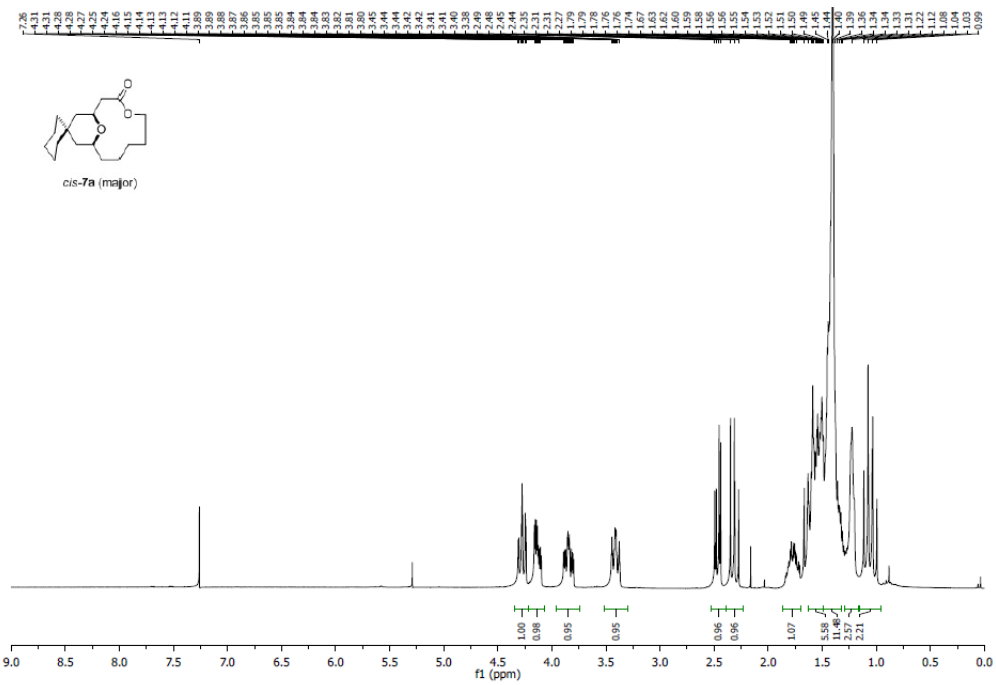


Figure S49. ^{1}H NMR of *cis*-**7a** (300 MHz, $CDCl_3$)

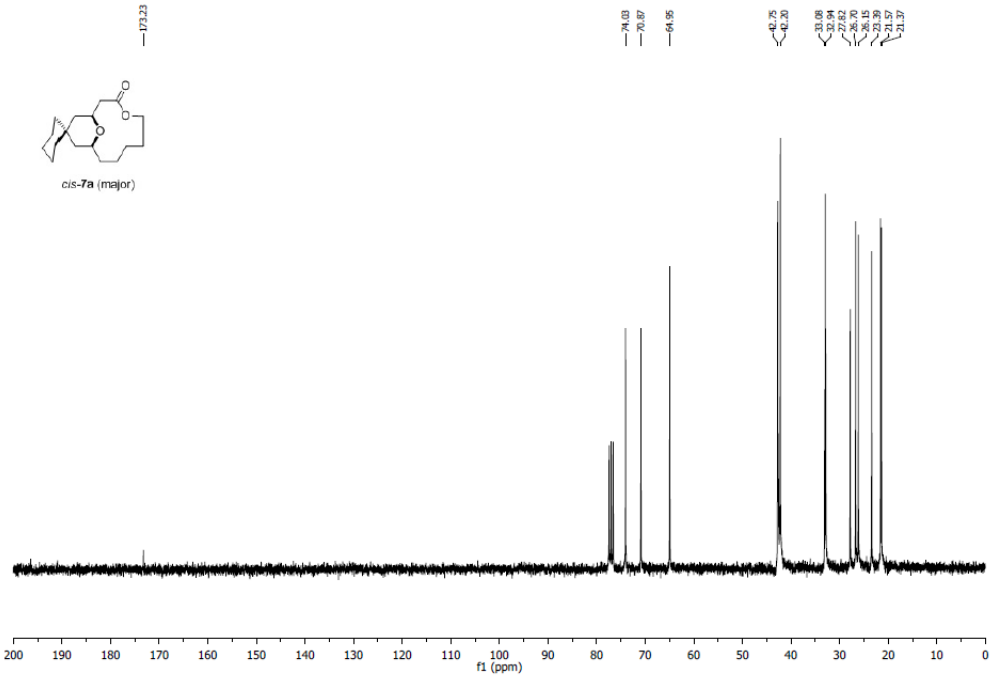


Figure S50. ^{13}C NMR of *cis*-**7a** (75 MHz, $CDCl_3$)

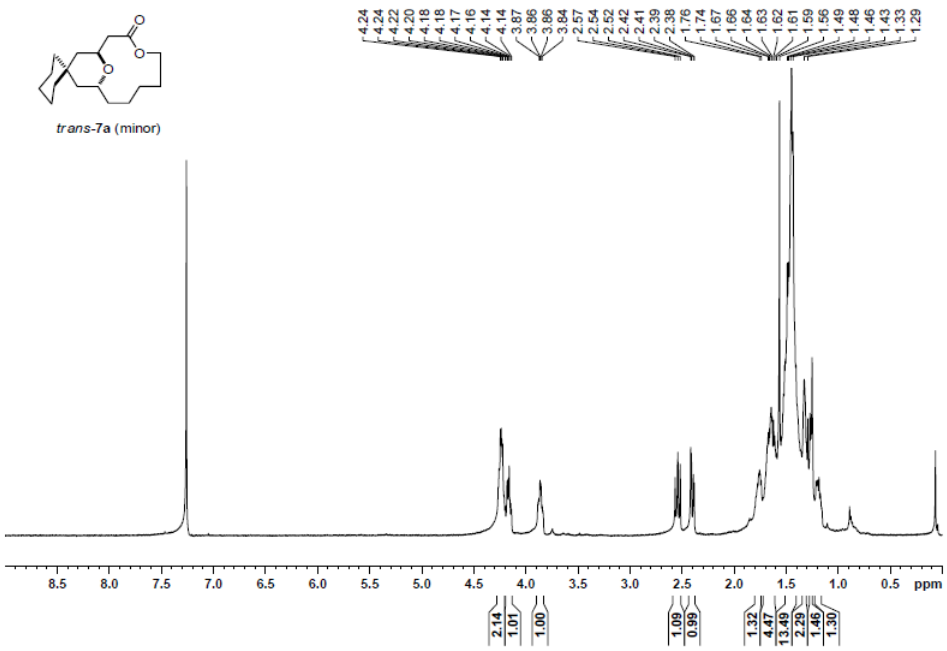


Figure S51. ^{1}H NMR of *trans*-**7a** (500 MHz, $CDCl_3$)

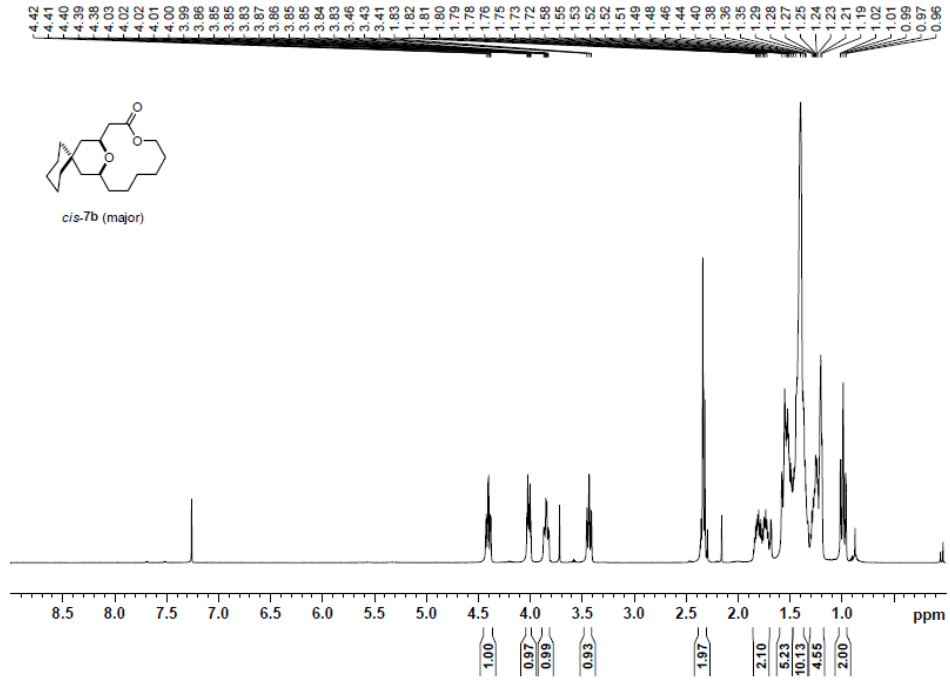


Figure S52. ^{1}H NMR of *cis*-**7b** (500 MHz, $CDCl_3$)

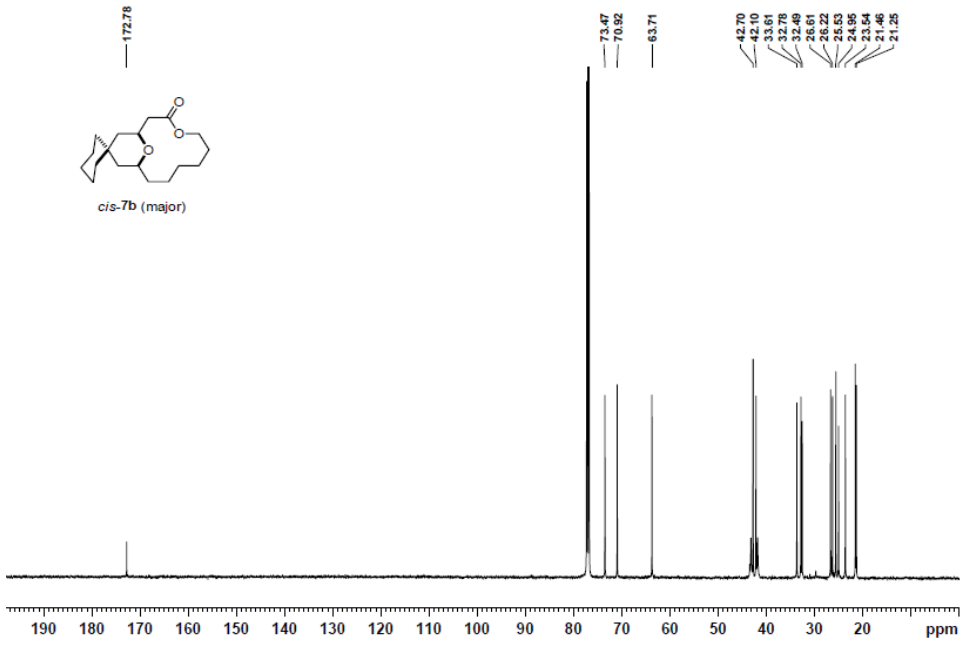


Figure S53. ^{13}C NMR of *cis*-**7b** (125 MHz, $CDCl_3$)

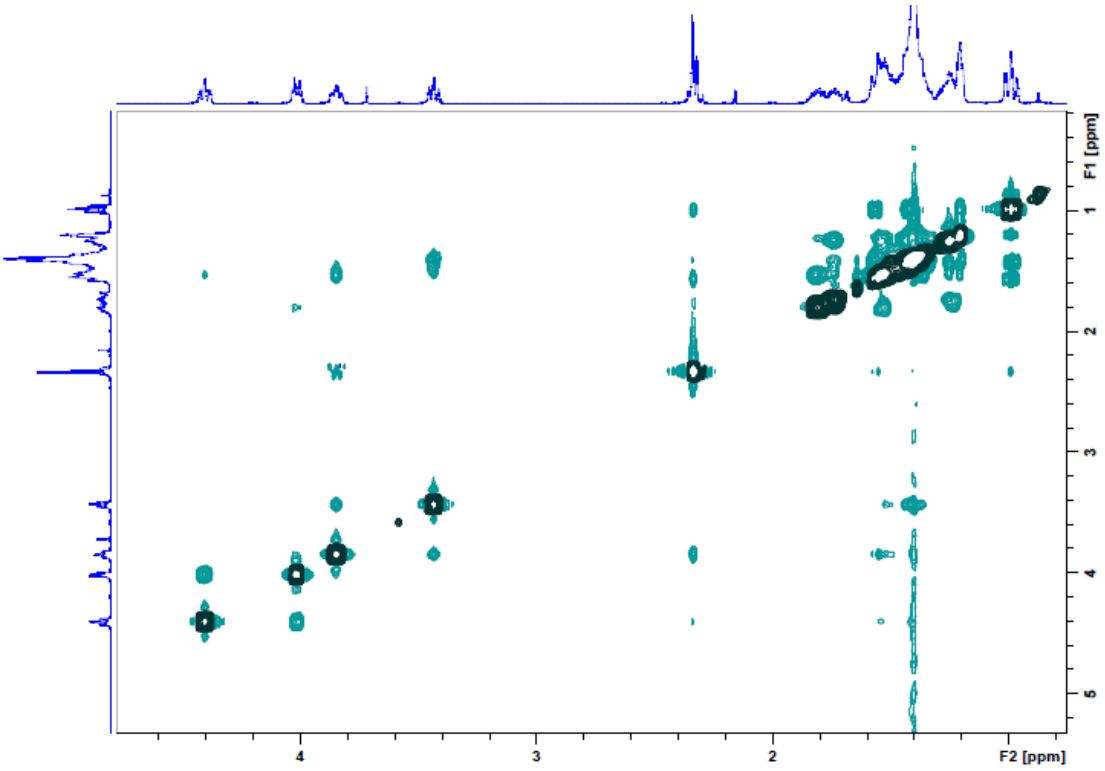


Figure S54. NOESY of *cis*-**7b** in $CDCl_3$

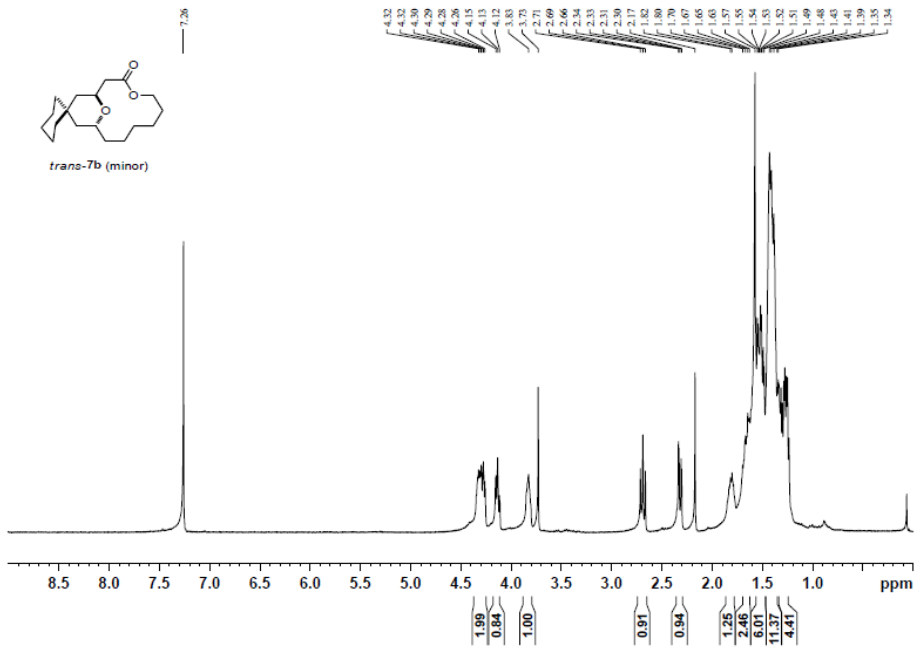


Figure S55. ^{1}H NMR of *trans*-**7b** (500 MHz, $CDCl_3$)

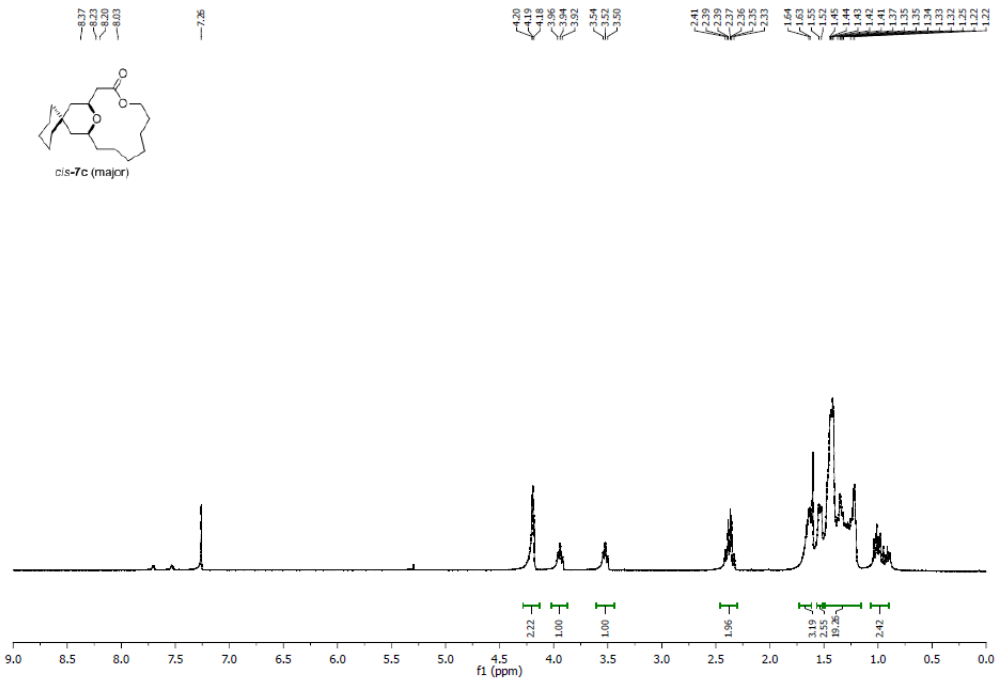


Figure S56. ^{1}H NMR of *cis*-**7c** (500 MHz, $CDCl_3$)

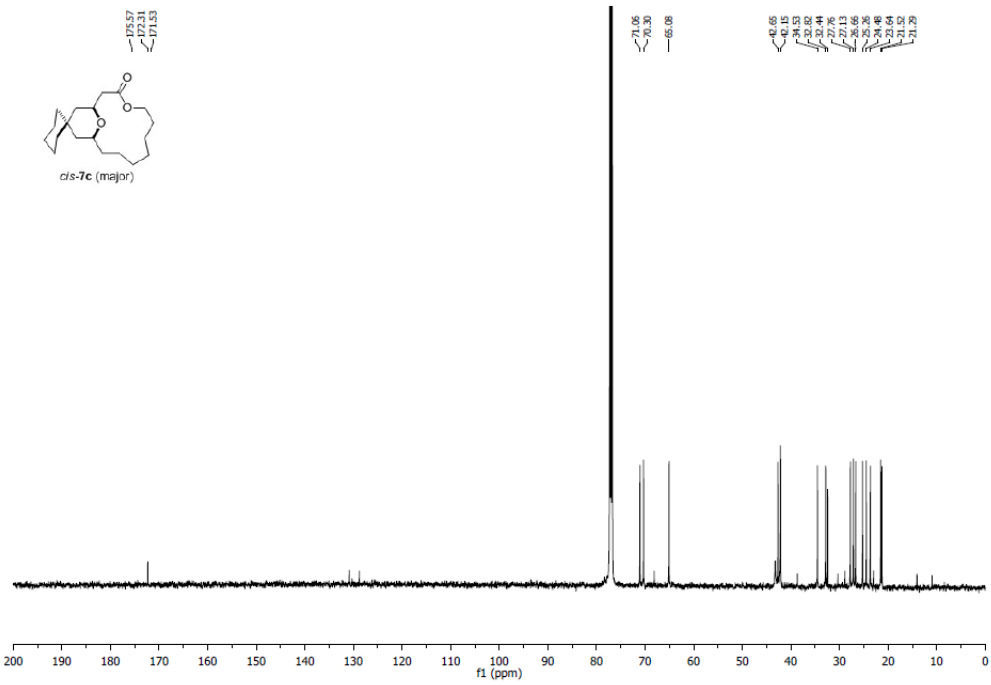


Figure S57. ^{13}C NMR of *cis*-**7c** (125 MHz, $CDCl_3$)

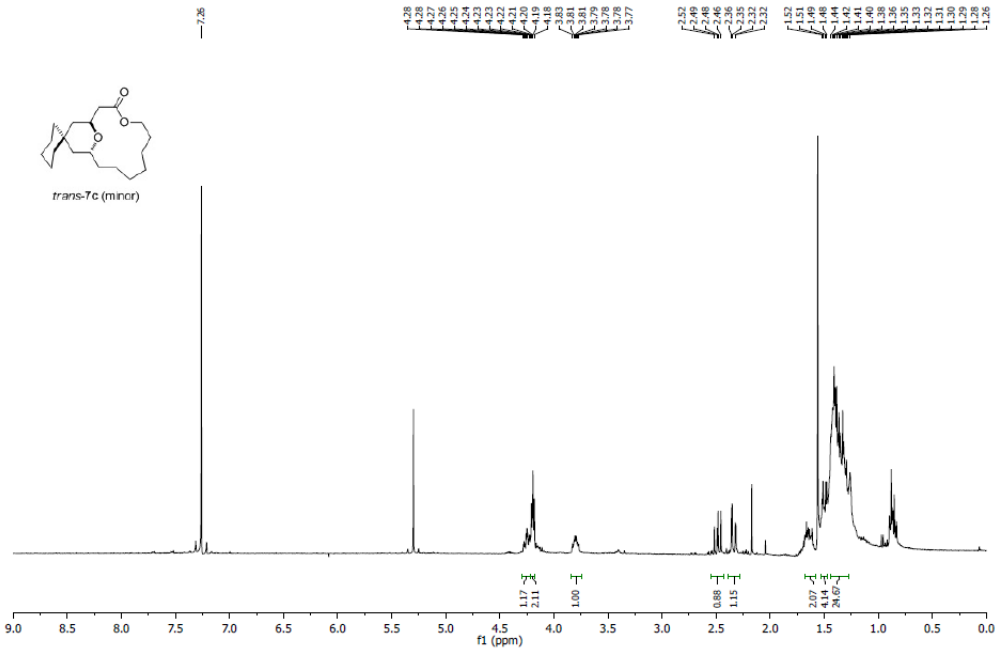


Figure S58. ^{1}H NMR of *trans*-**7c** (400 MHz, $CDCl_3$)

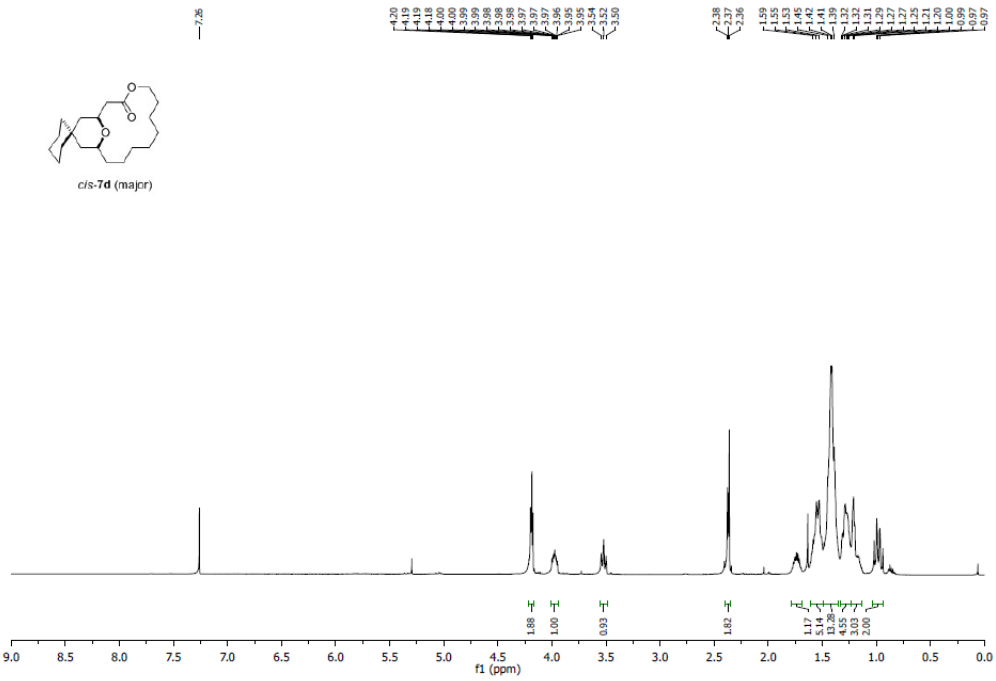


Figure S59. ^{1}H NMR of *cis*-**7d** (500 MHz, $CDCl_3$)

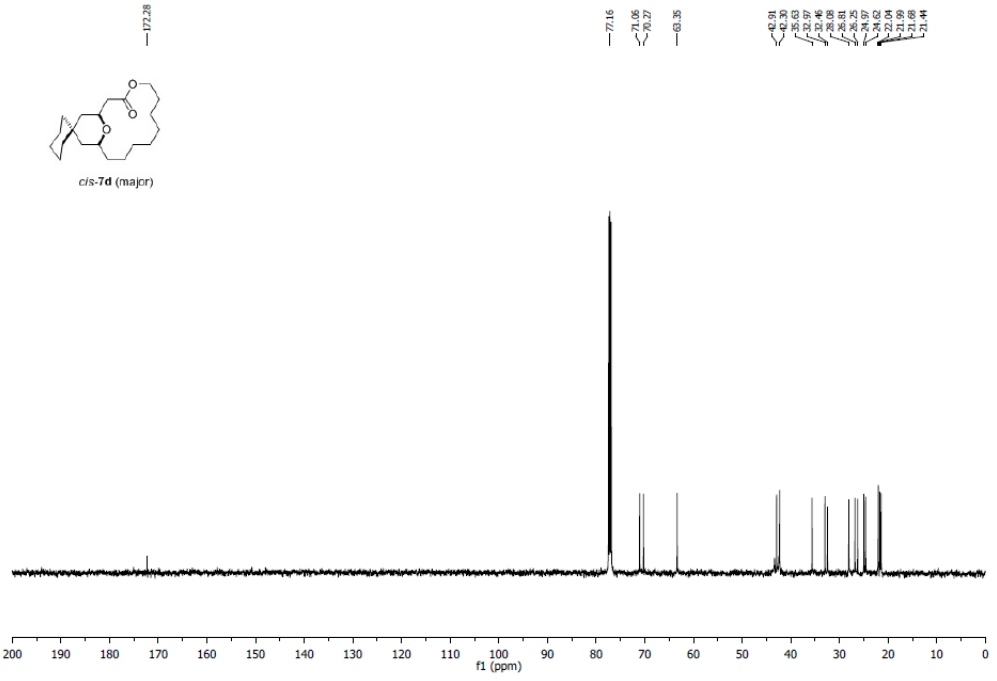


Figure S60. ^{13}C NMR of *cis*-**7d** (125 MHz, $CDCl_3$)

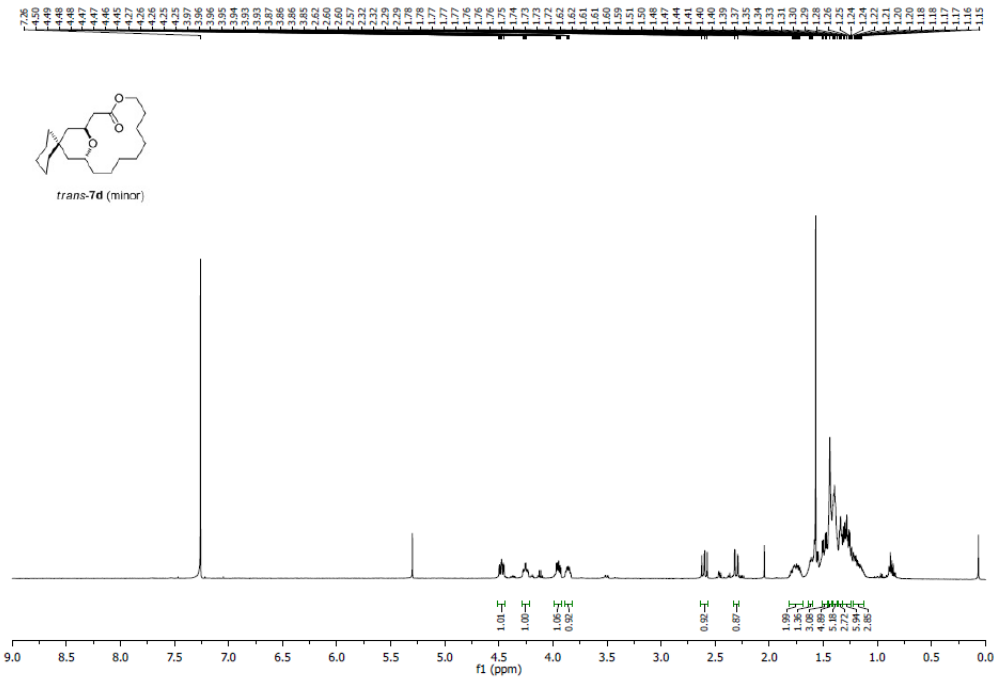


Figure S61. ^{1}H NMR of *trans*-**7d** (500 MHz, $CDCl_3$)

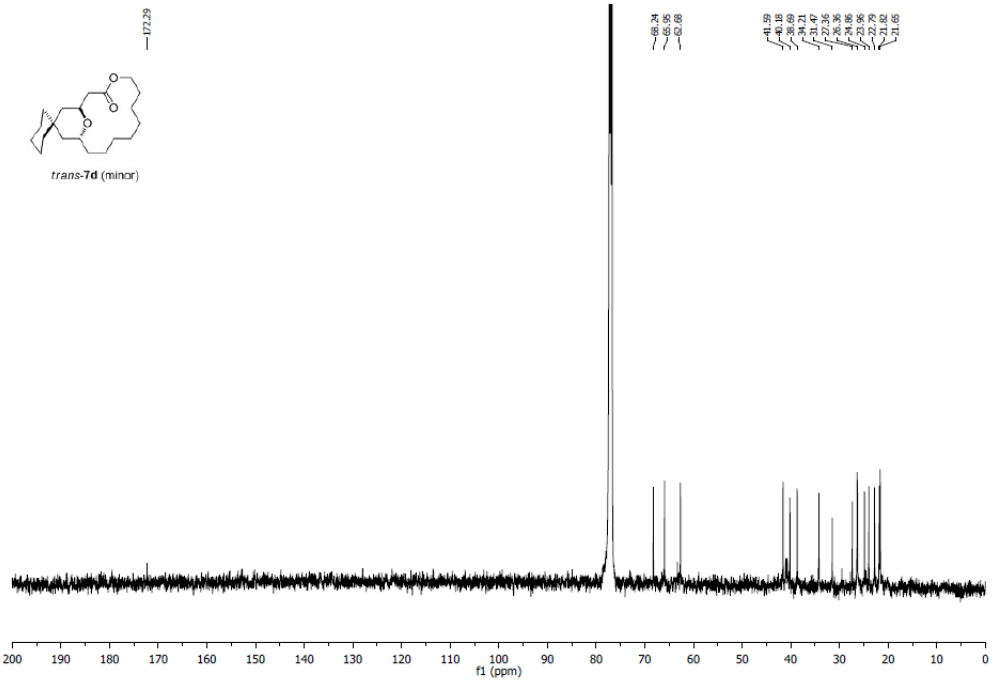


Figure S62. ^{13}C NMR of *trans*-**7d** (125 MHz, $CDCl_3$)

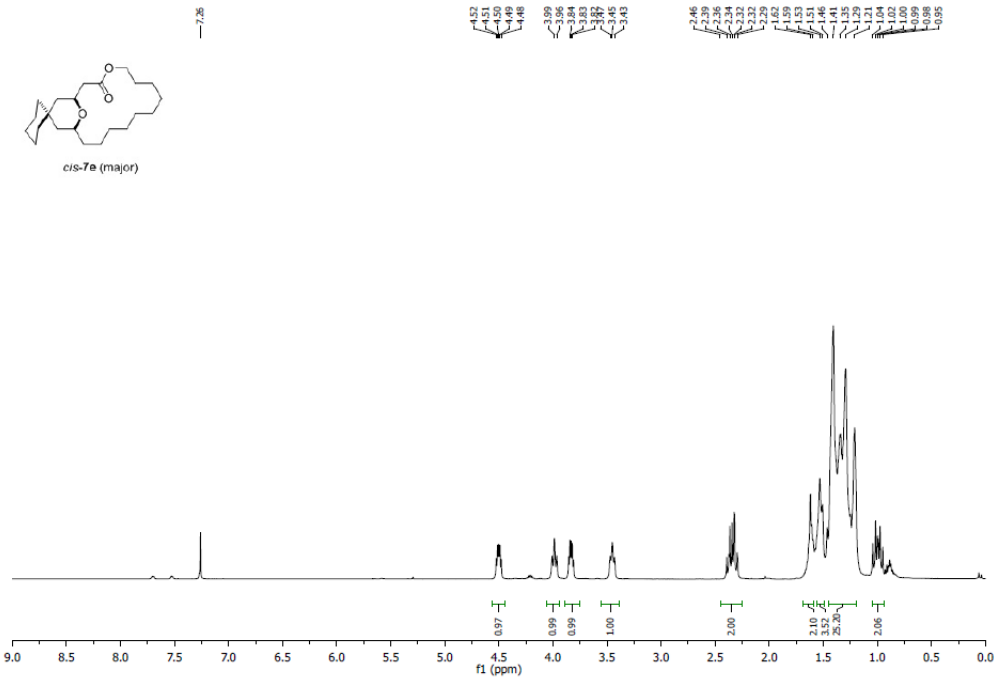


Figure S63. ^{1}H NMR of *cis*-**7e** (500 MHz, $CDCl_3$)

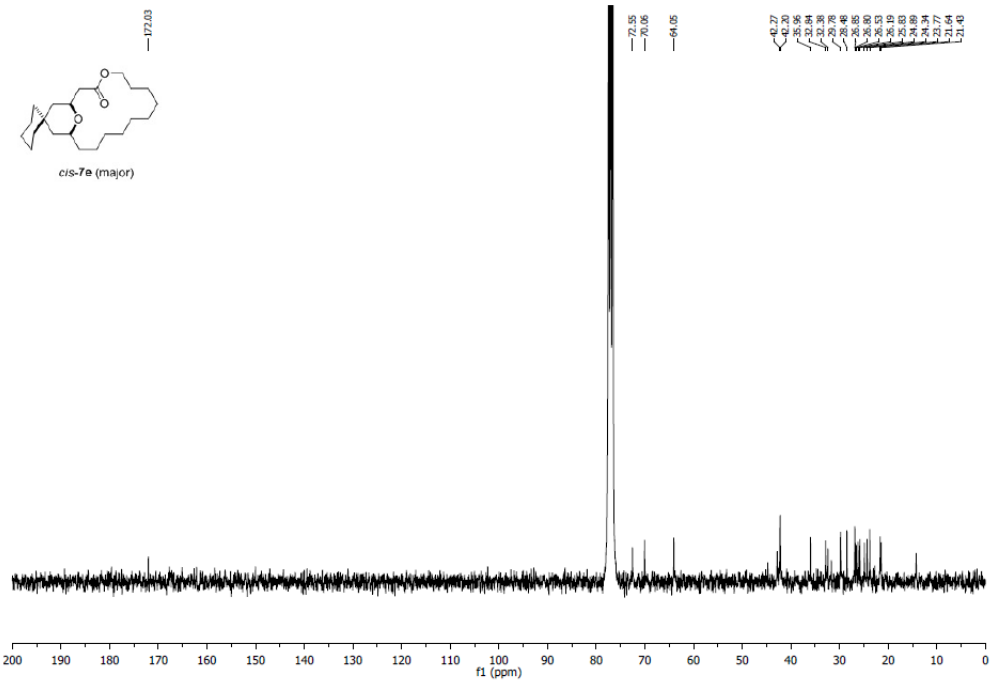


Figure S64. ^{13}C NMR of *cis*-**7e** (75 MHz, $CDCl_3$)

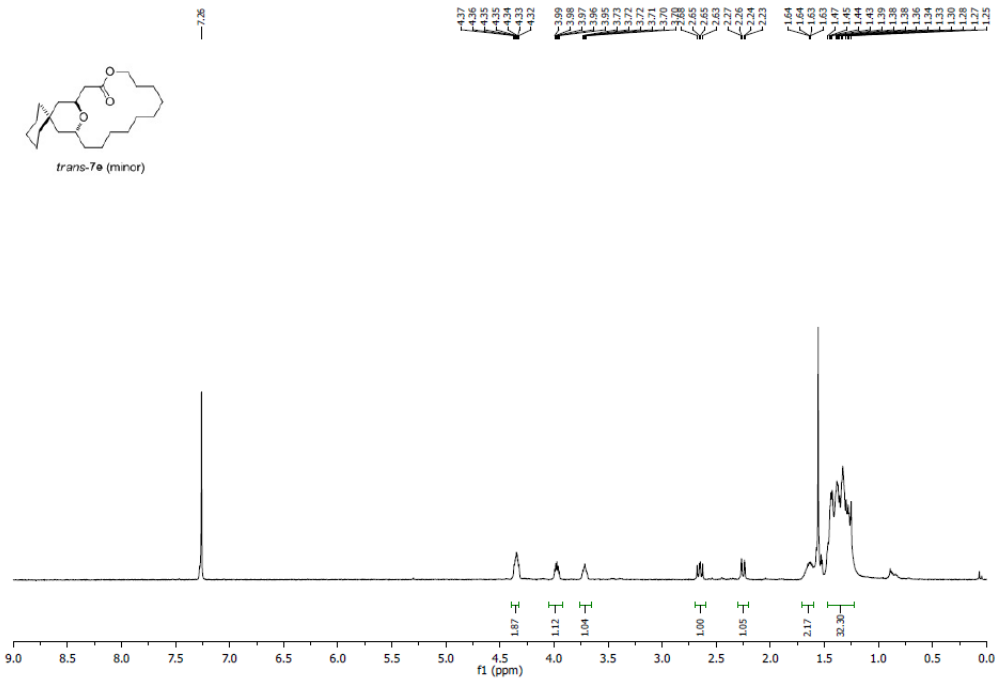


Figure S65. ^{1}H NMR of *trans*-**7e** (500 MHz, $CDCl_3$)

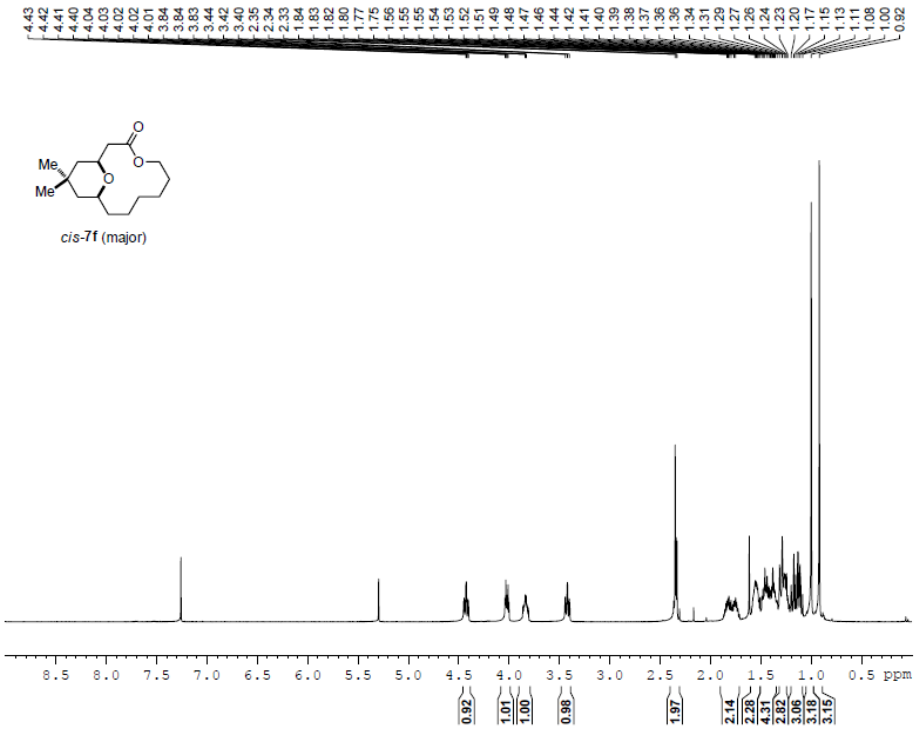


Figure S66. ^{1}H NMR of *cis*-**7f** (500 MHz, $CDCl_3$)

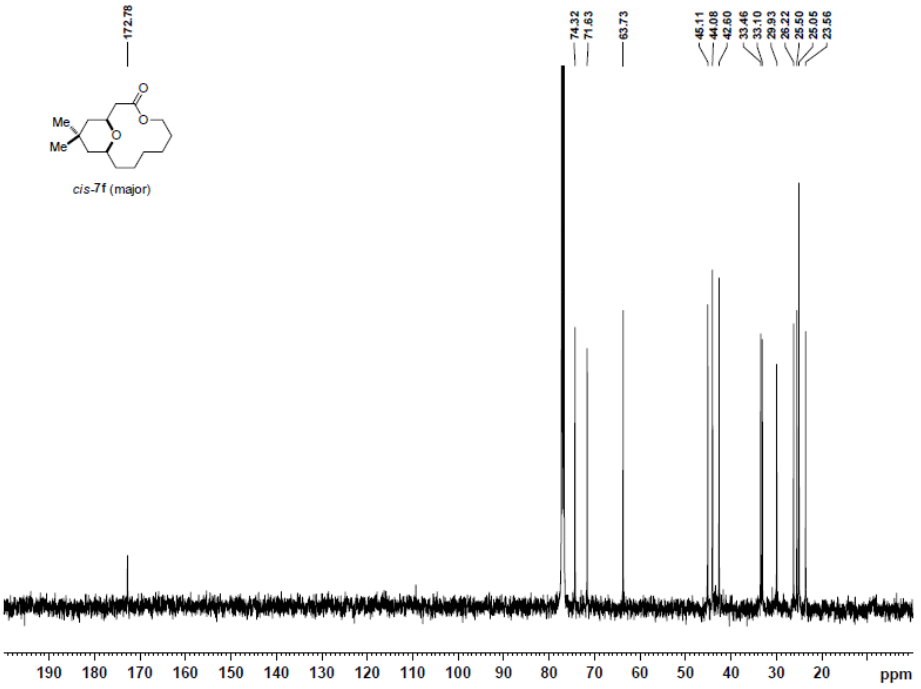


Figure S67. ^{13}C NMR of *cis*-**7f** (125 MHz, $CDCl_3$)

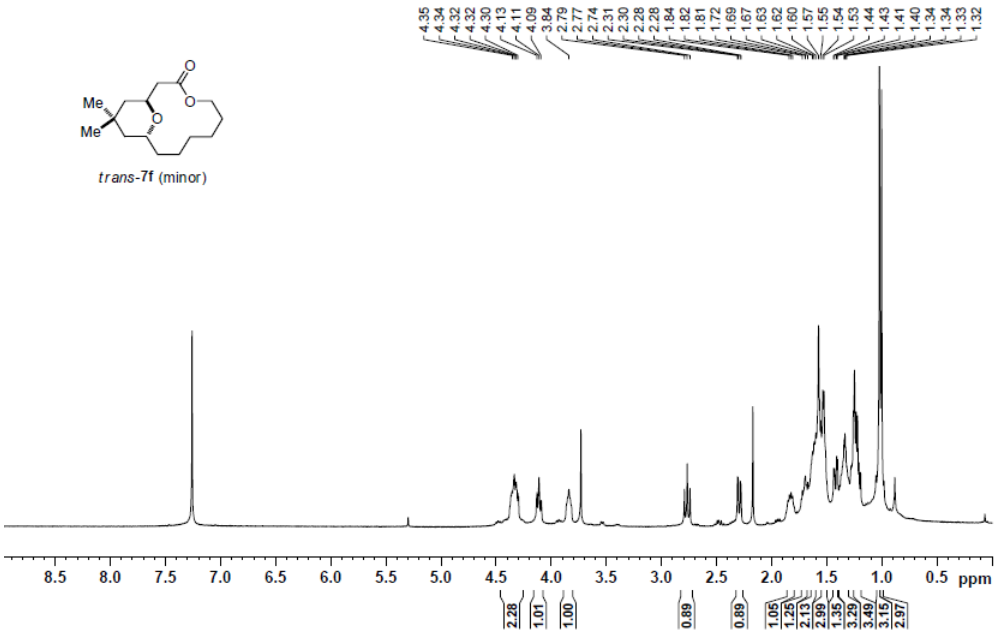


Figure S68. ^{1}H NMR of *trans*-**7f** (500 MHz, $CDCl_3$)

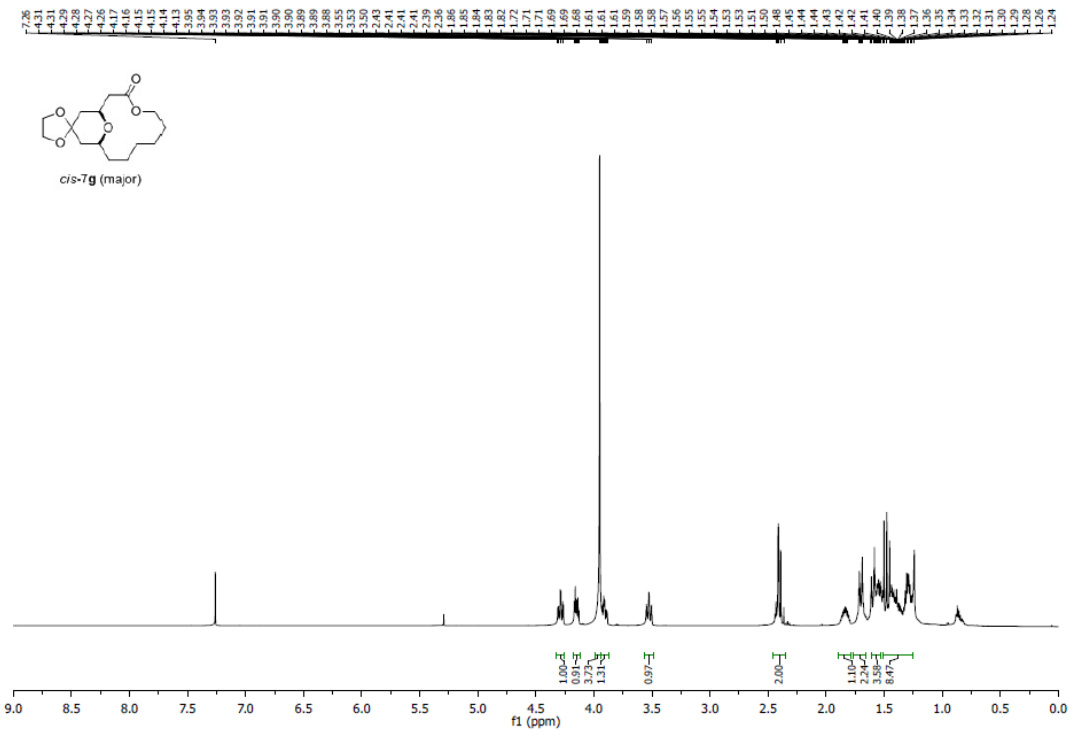


Figure S69. ^{1}H NMR of *cis*-**7g** (500 MHz, $CDCl_3$)

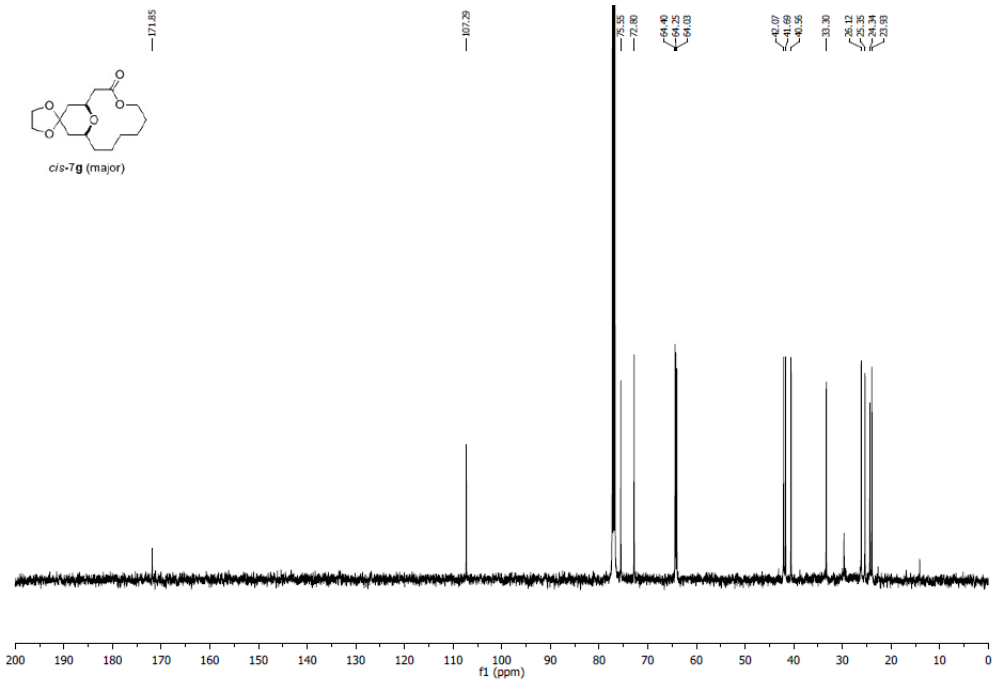


Figure S70. ^{13}C NMR of *cis*-**7g** (125 MHz, $CDCl_3$)

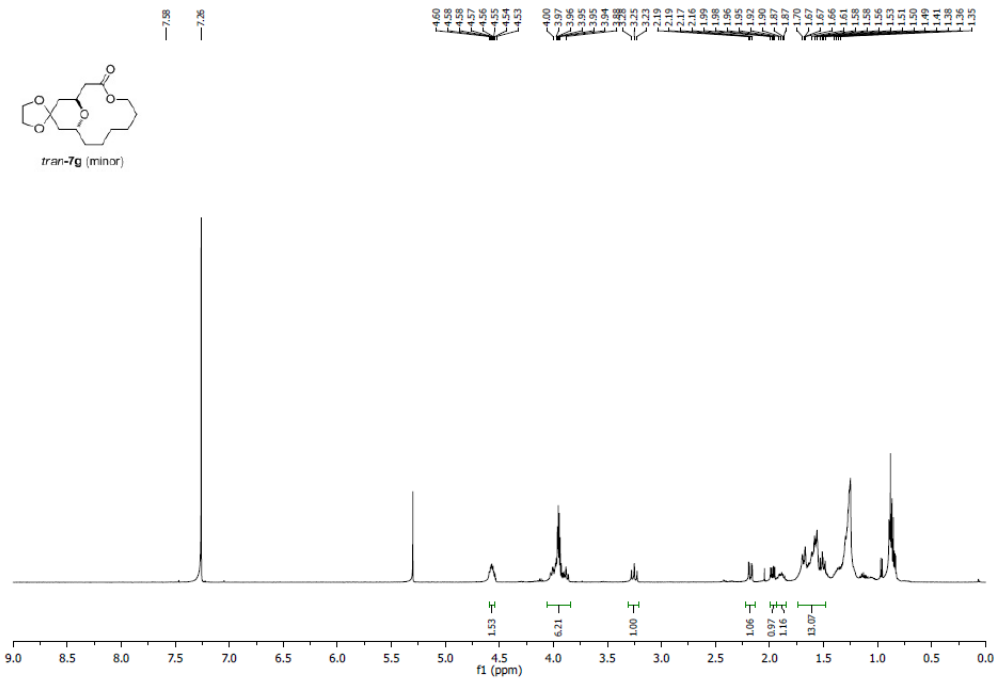


Figure S71. ^{1}H NMR of *trans*-**7g** (500 MHz, $CDCl_3$)

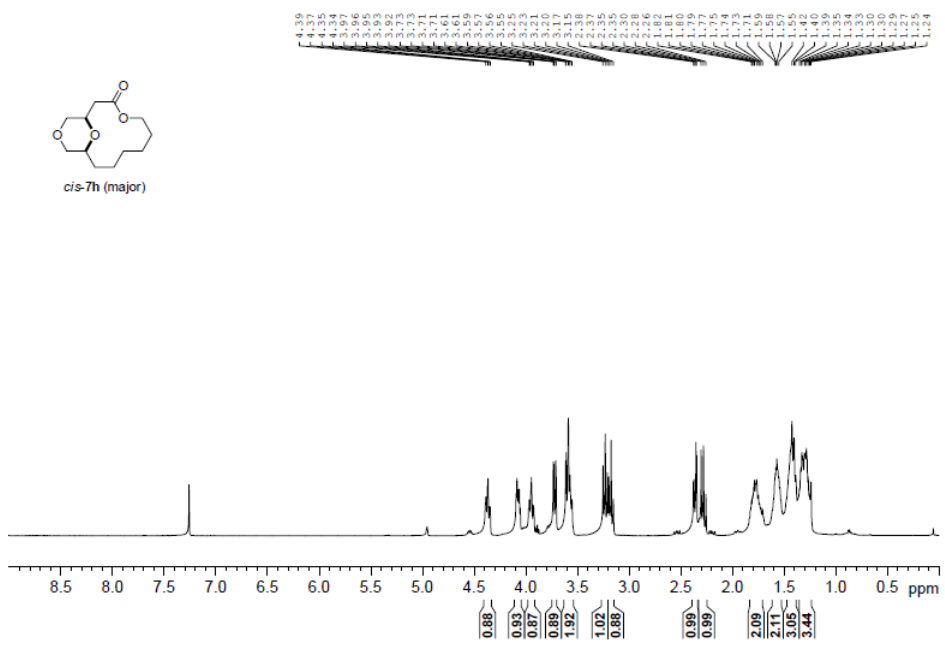


Figure S72. ^{1}H NMR of *cis*-**7h** (500 MHz, $CDCl_3$)

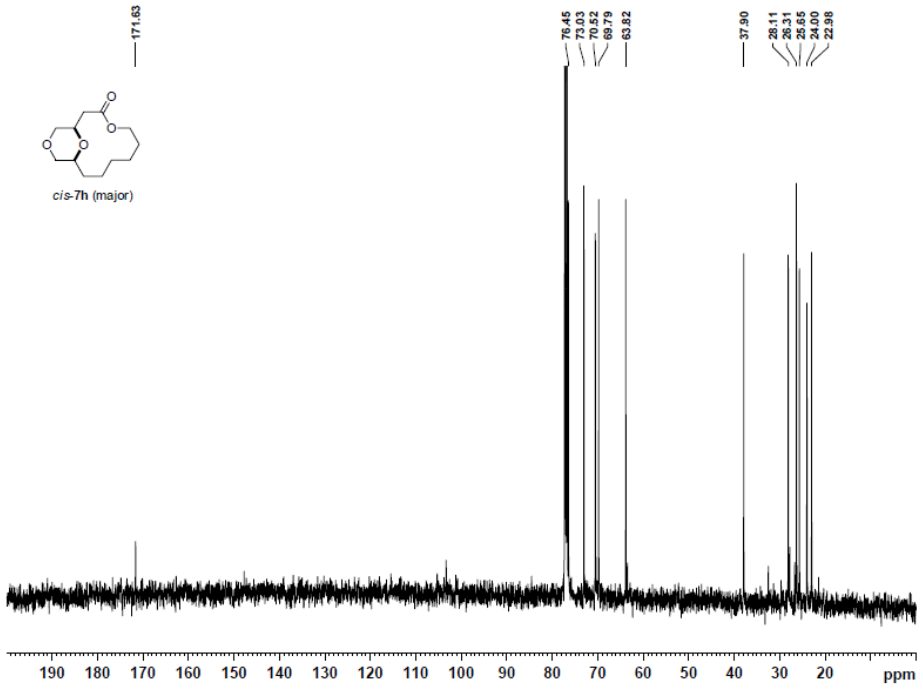


Figure S73. ^{13}C NMR of *cis*-**7h** (125 MHz, $CDCl_3$)

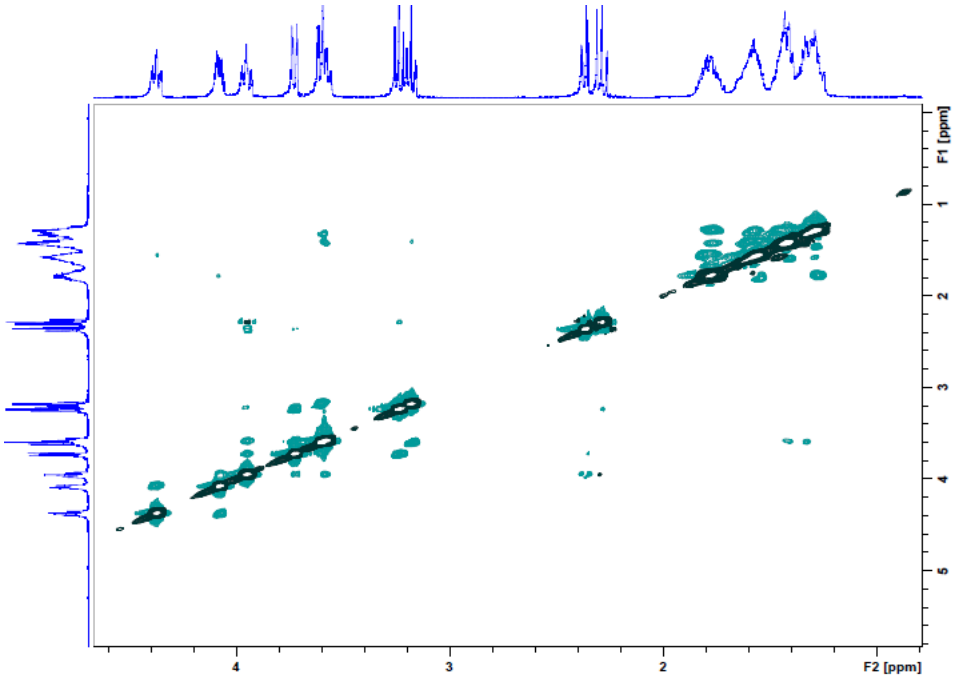


Figure S74. NOESY of *cis*-**7h** in $CDCl_3$

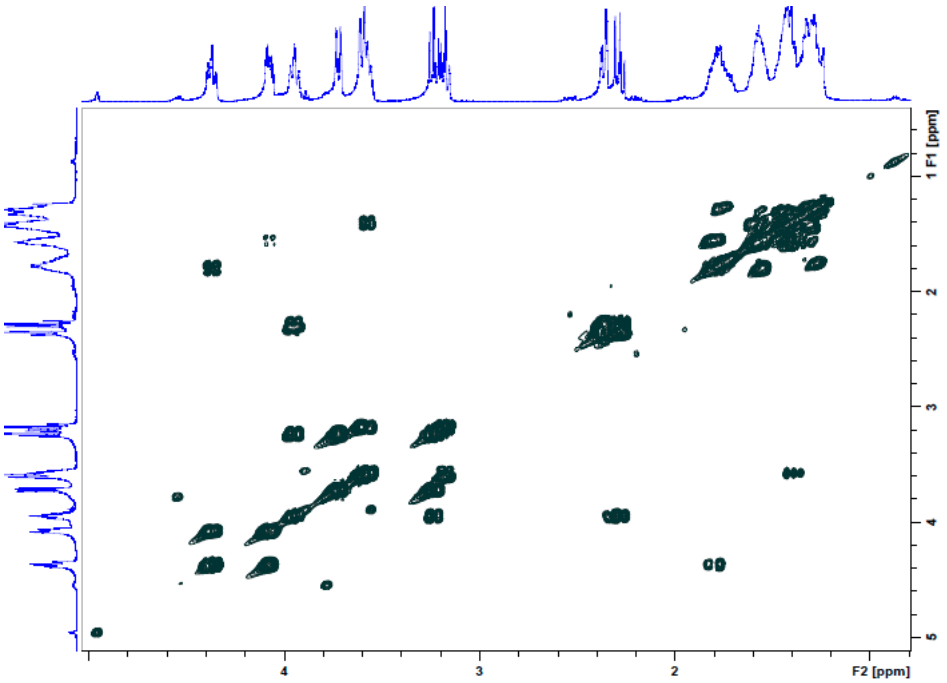


Figure S75. COSY of *cis*-**7h** in $CDCl_3$

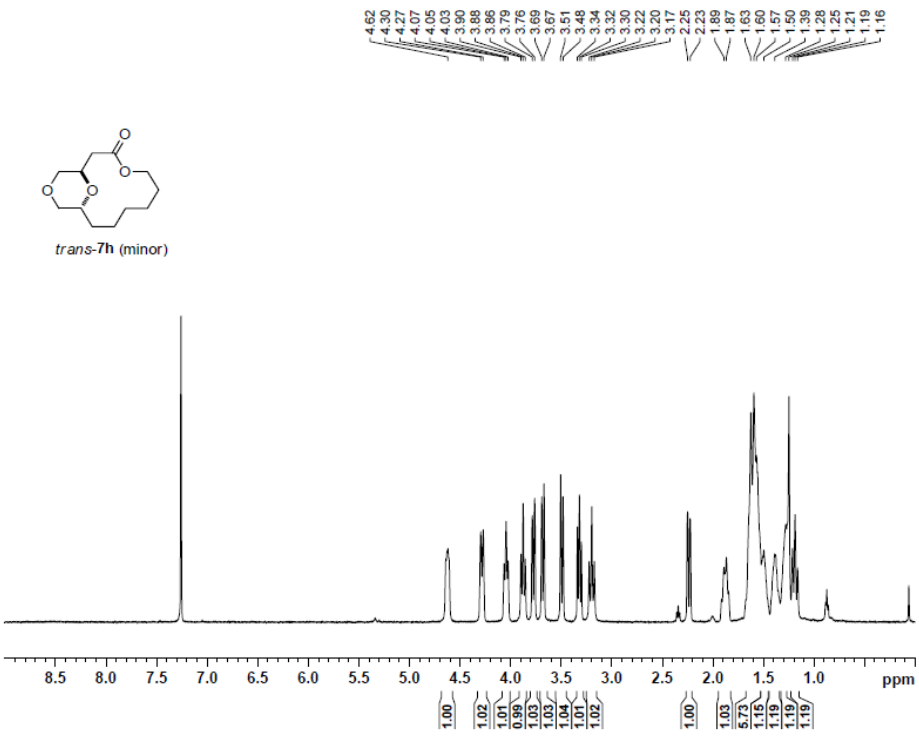


Figure S76. ^{1}H NMR of *trans*-**7h** (500 MHz, $CDCl_3$)

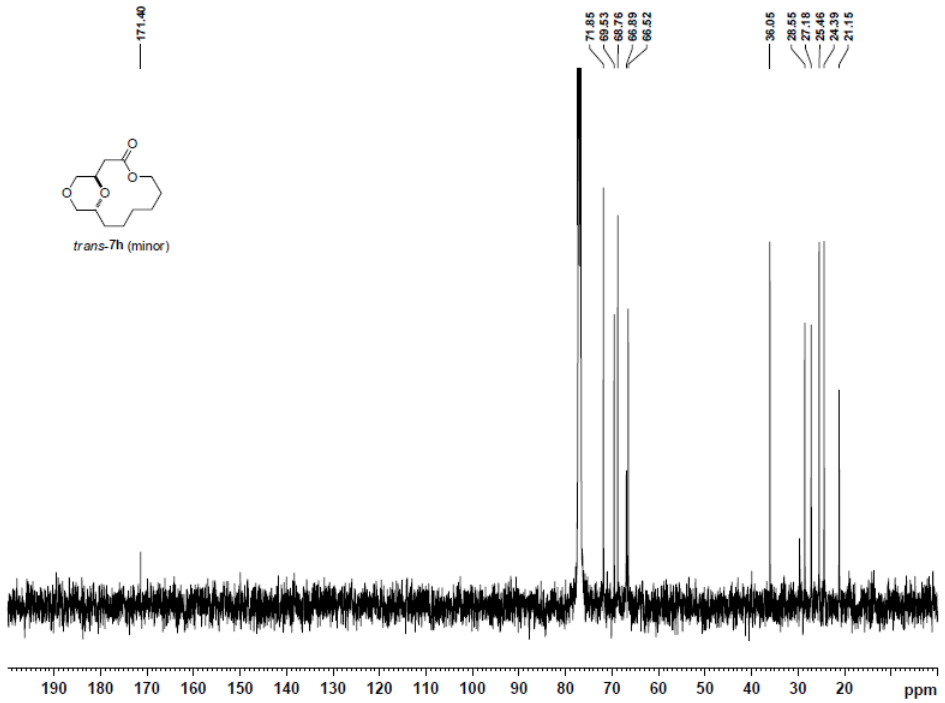


Figure S77. ^{13}C NMR of *trans*-**7h** (125 MHz, $CDCl_3$)

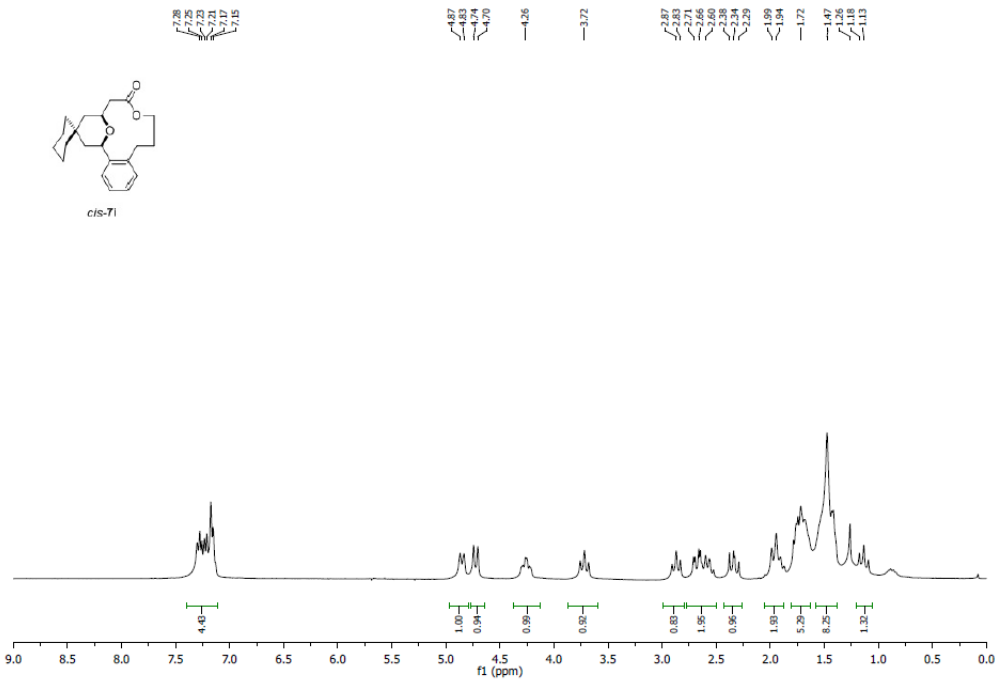


Figure S78. ^{1}H NMR of *cis*-**7i** (300 MHz, $CDCl_3$)

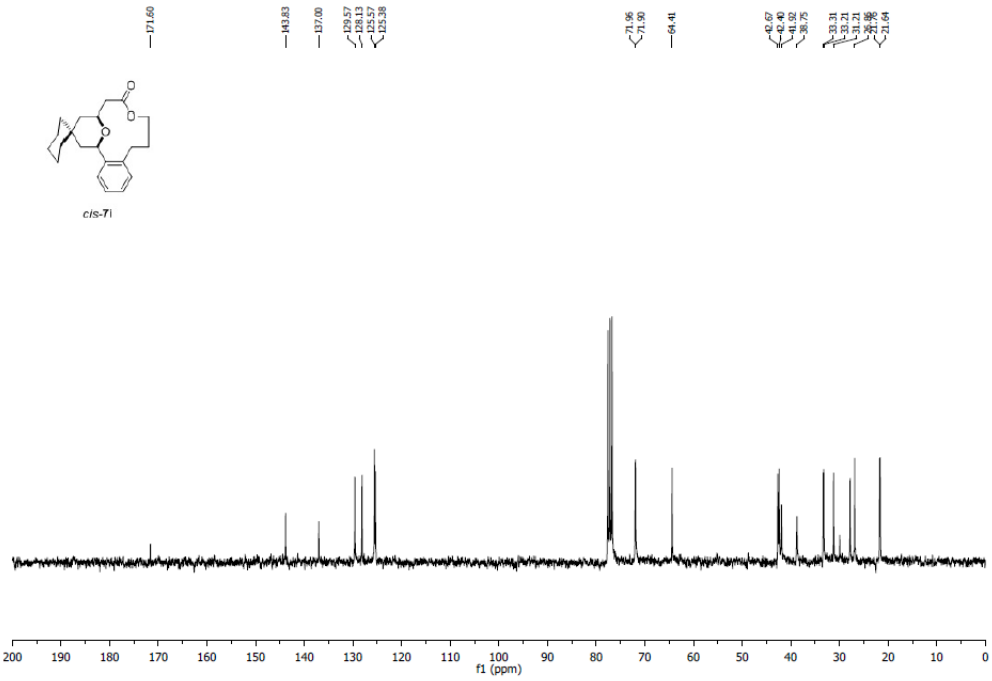


Figure S79. ^{13}C NMR of *cis*-**7i** (75 MHz, $CDCl_3$)

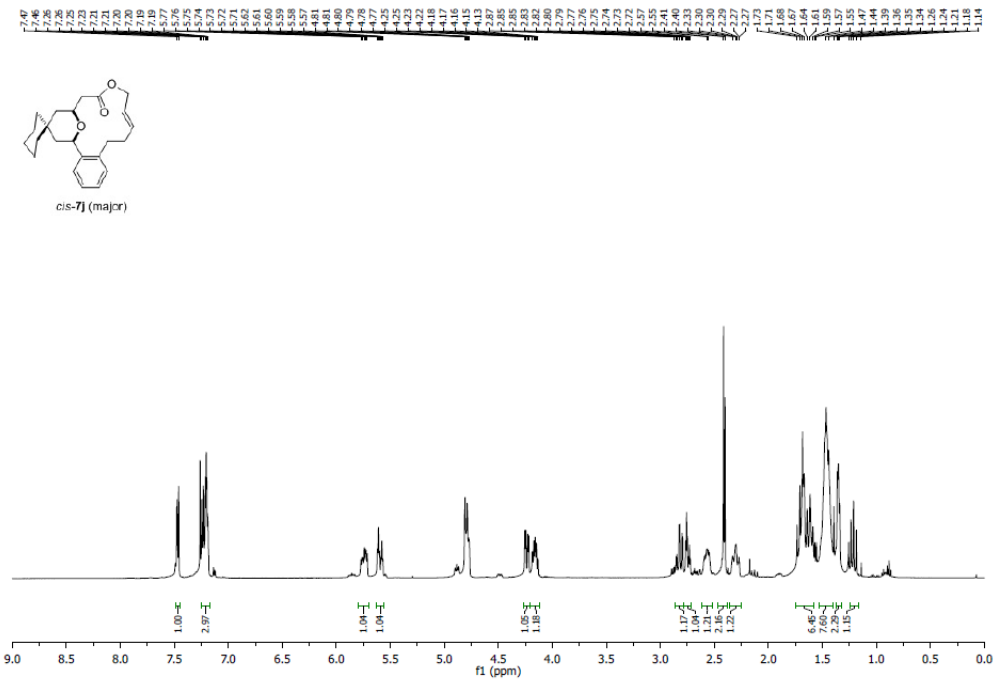


Figure S80. ^{1}H NMR of *cis*-**7j** (500 MHz, $CDCl_3$)

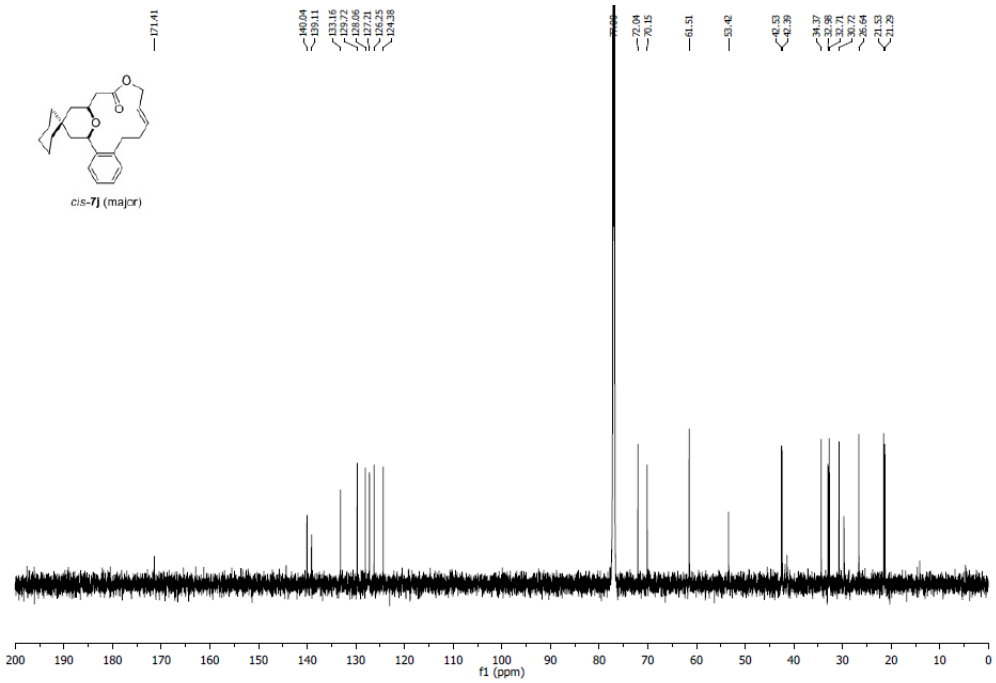


Figure S81. ^{13}C NMR of *cis*-**7j** (200 MHz, $CDCl_3$)

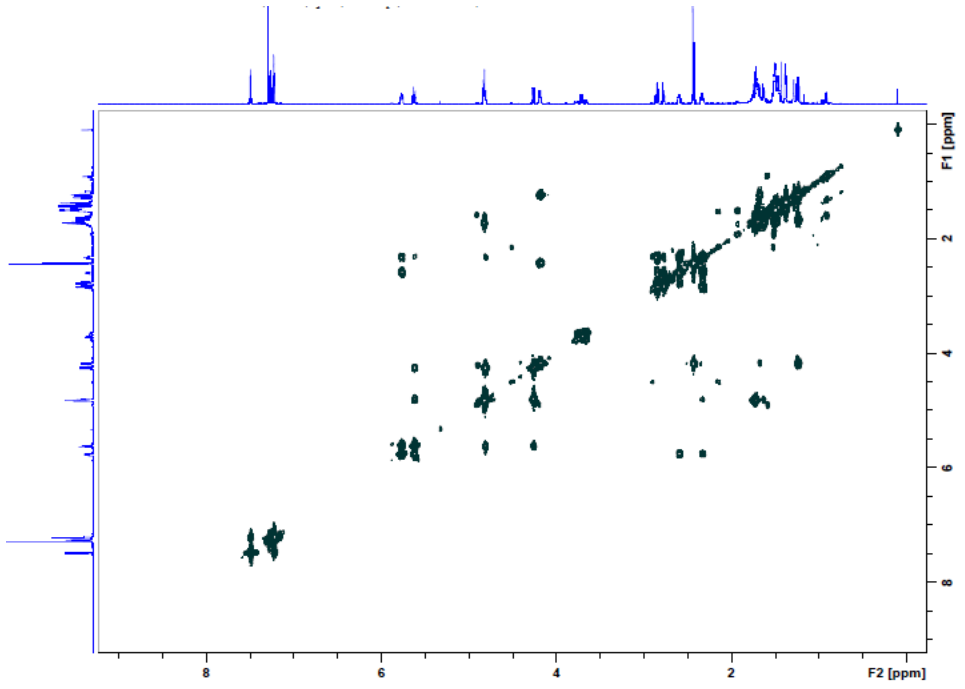


Figure S82. COSY of *cis*-**7j** in $CDCl_3$

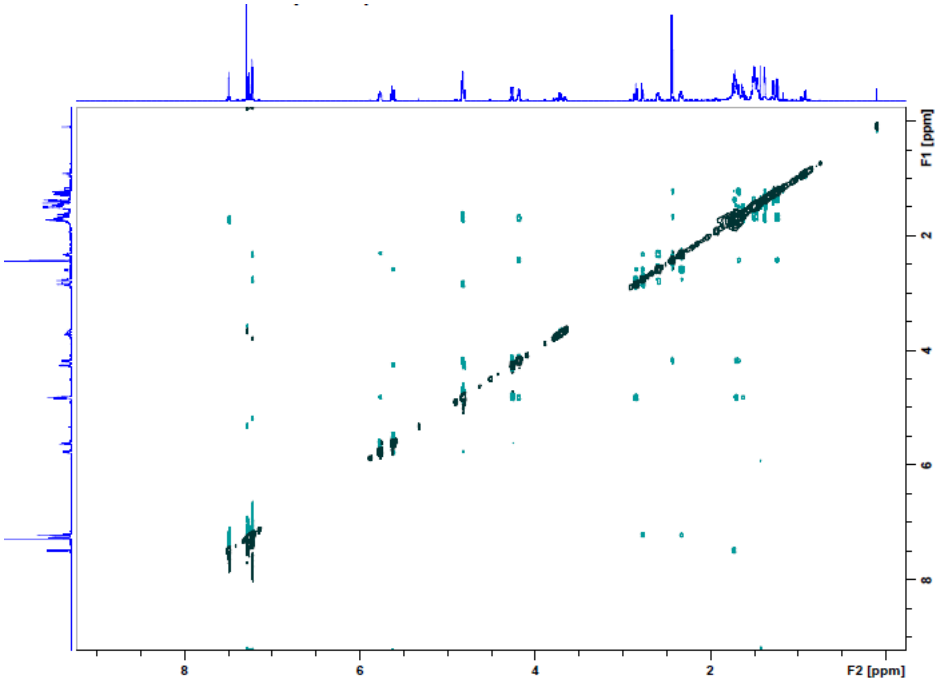


Figure S83. NOESY of *cis*-**7j** in $CDCl_3$

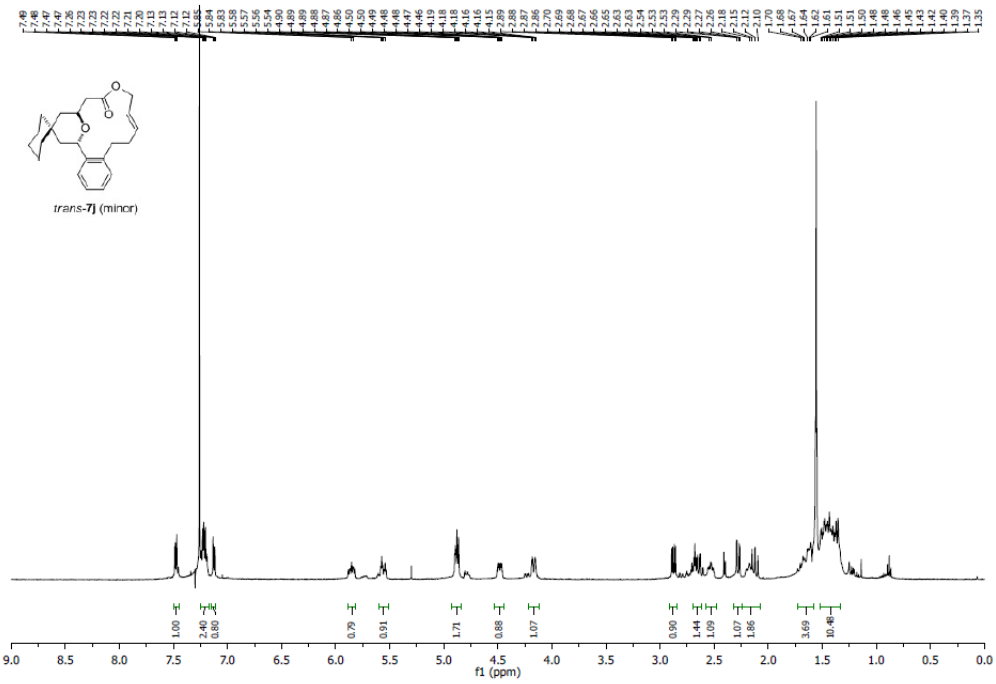


Figure S84. ^{1}H NMR of *trans*-**7j** (500 MHz, $CDCl_3$)

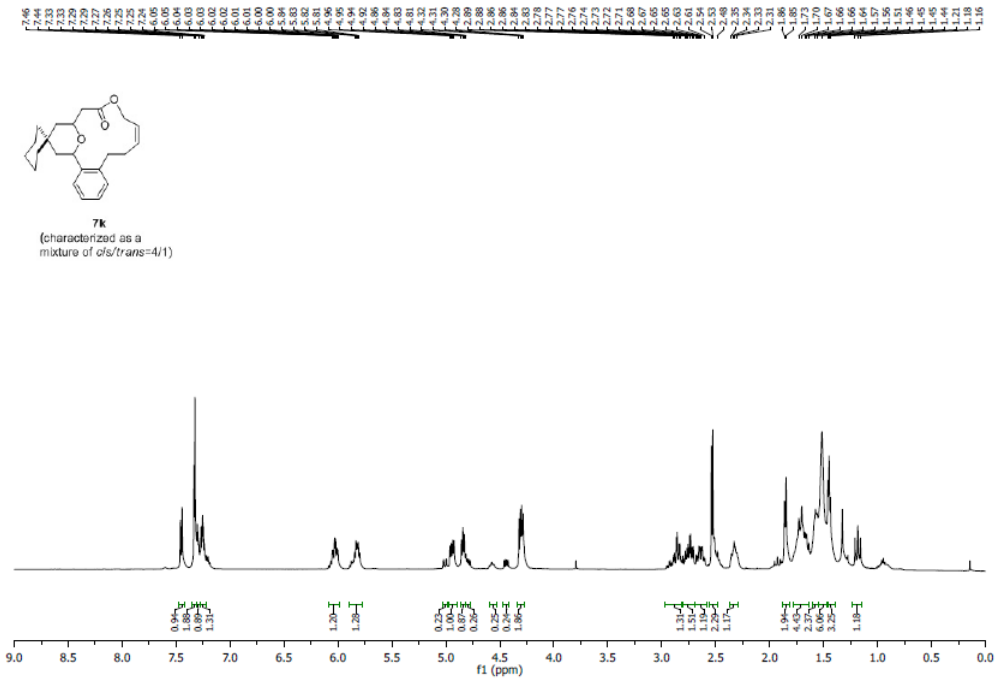


Figure S85. ^{1}H NMR of THP-*cis/trans*-**7k** as a 4/1 mixture (500 MHz, $CDCl_3$)

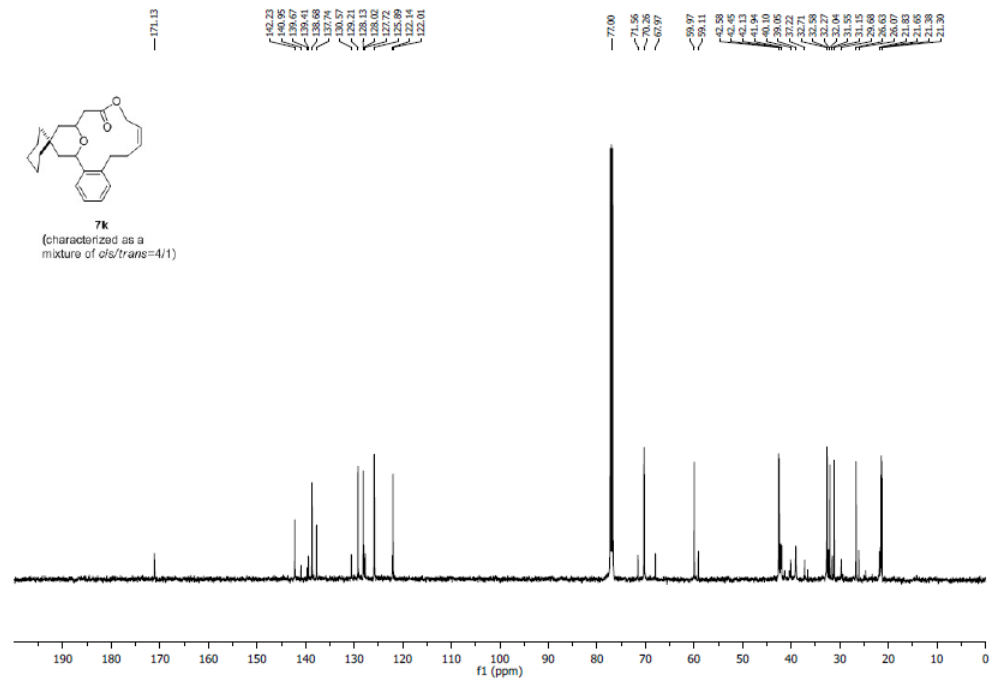


Figure S86. ^{13}C NMR of THP-*cis/trans*-**7k** as a 4/1 mixture (125 MHz, $CDCl_3$)

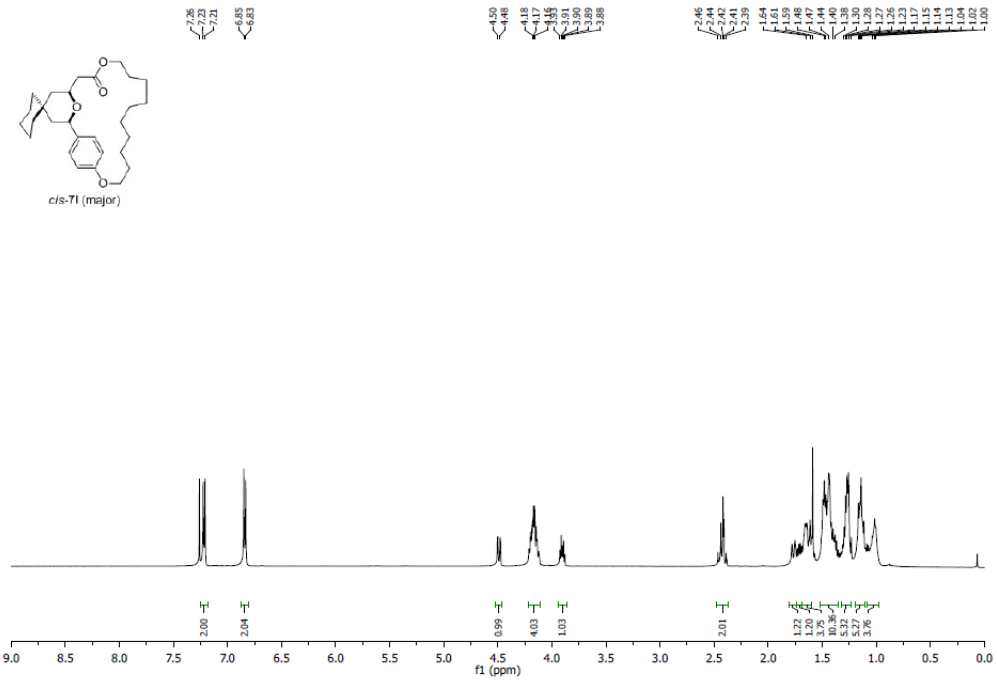


Figure S87. ^{1}H NMR of *cis*-**7l** (500 MHz, $CDCl_3$)

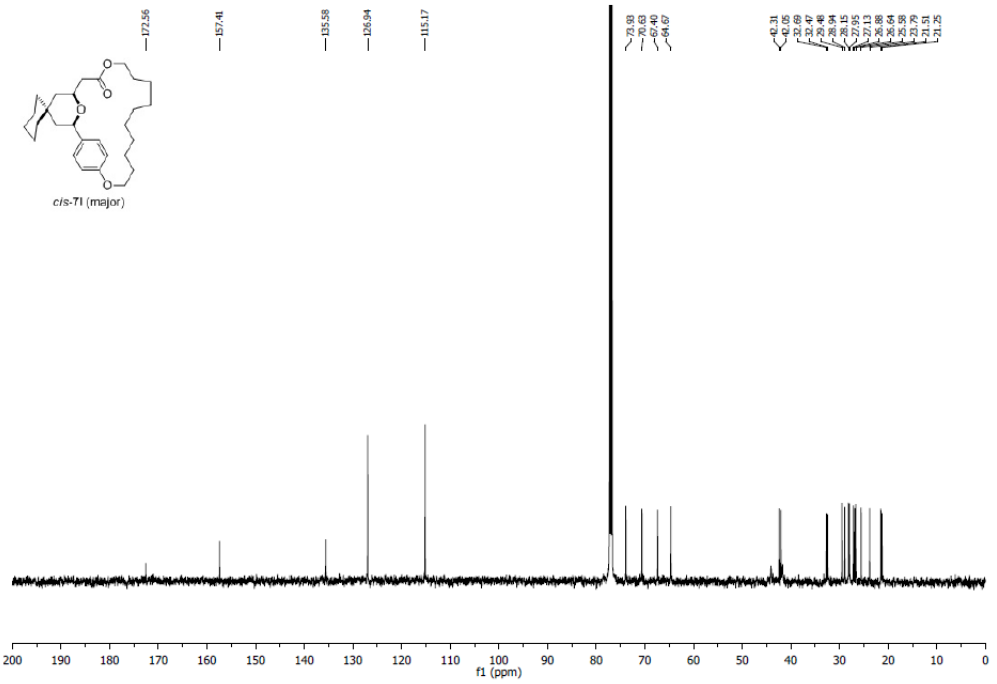


Figure S88. ^{13}C NMR of *cis*-**7l** (125 MHz, $CDCl_3$)

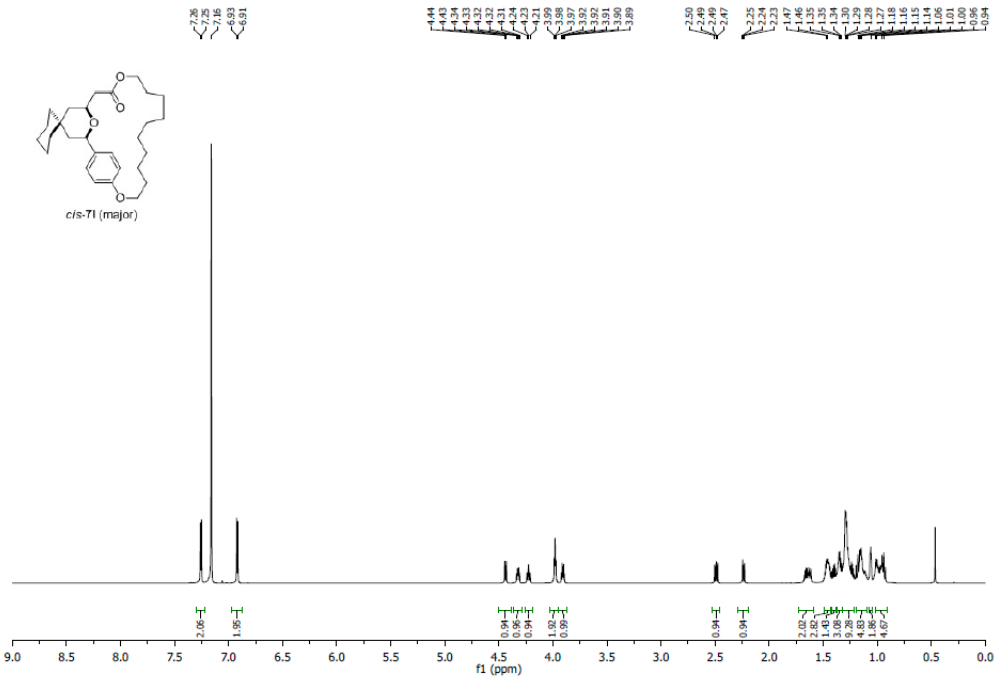


Figure S89. ^{1}H NMR of *cis*-**7l** (800 MHz, C_6D_6)

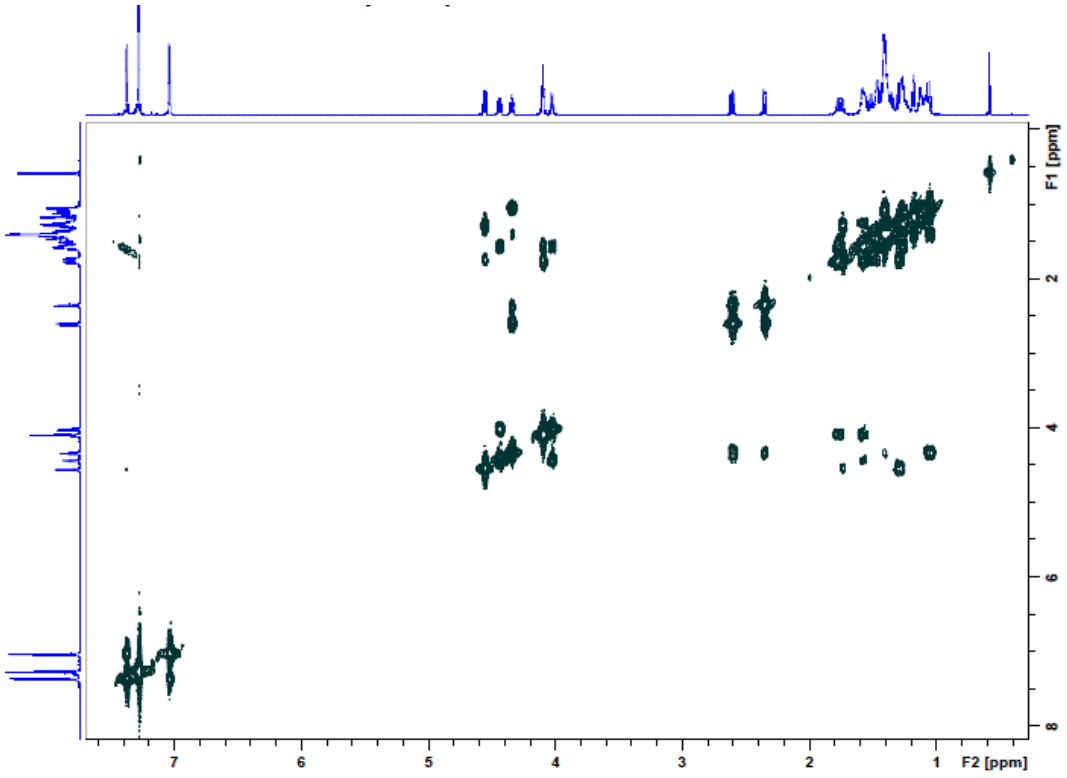


Figure S90. COSY of *cis*–**7l** in C_6D_6

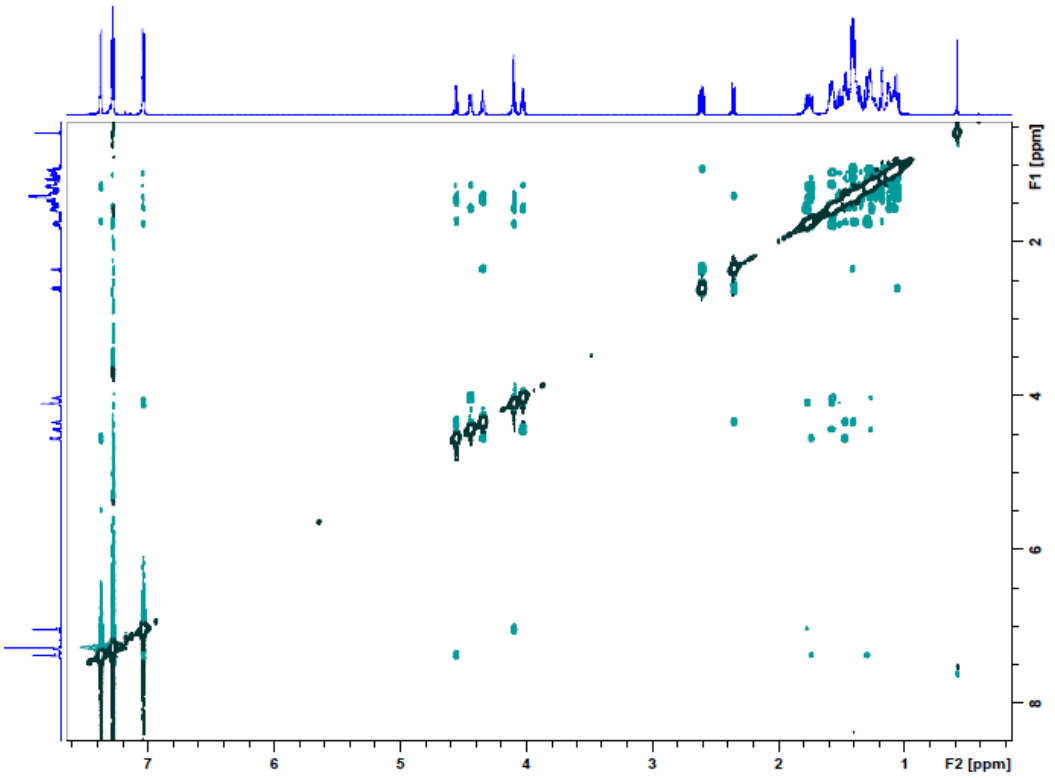


Figure S91. NOESY of *cis*–**7l** in C_6D_6

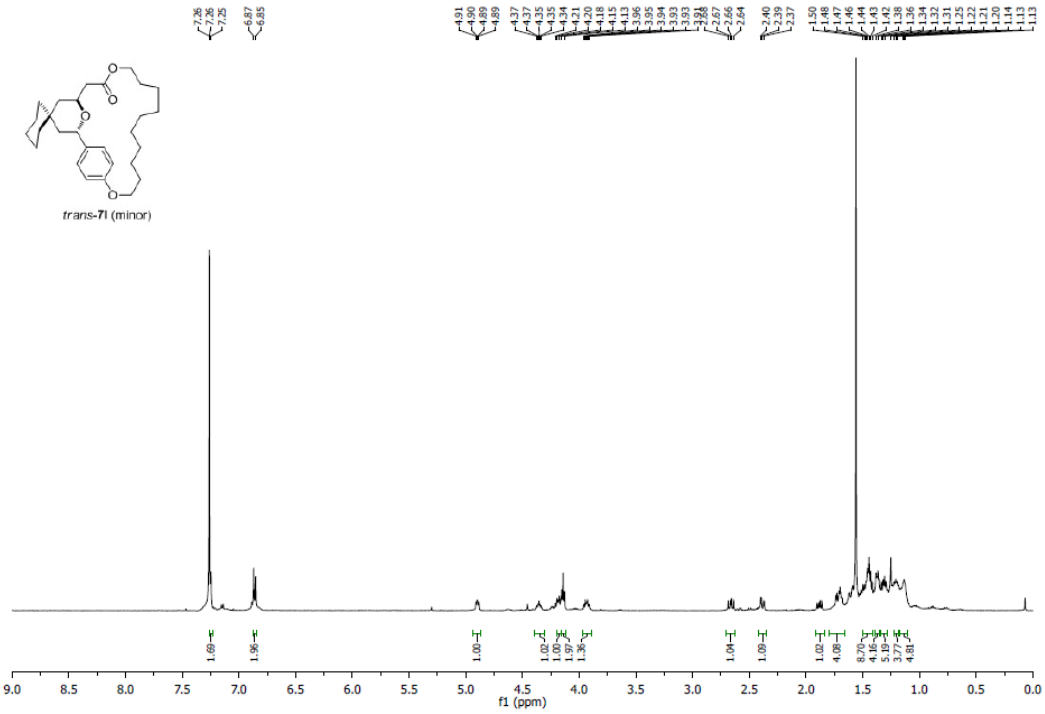


Figure S92. ^{1}H NMR of *trans*-**7l** (500 MHz, $CDCl_3$)

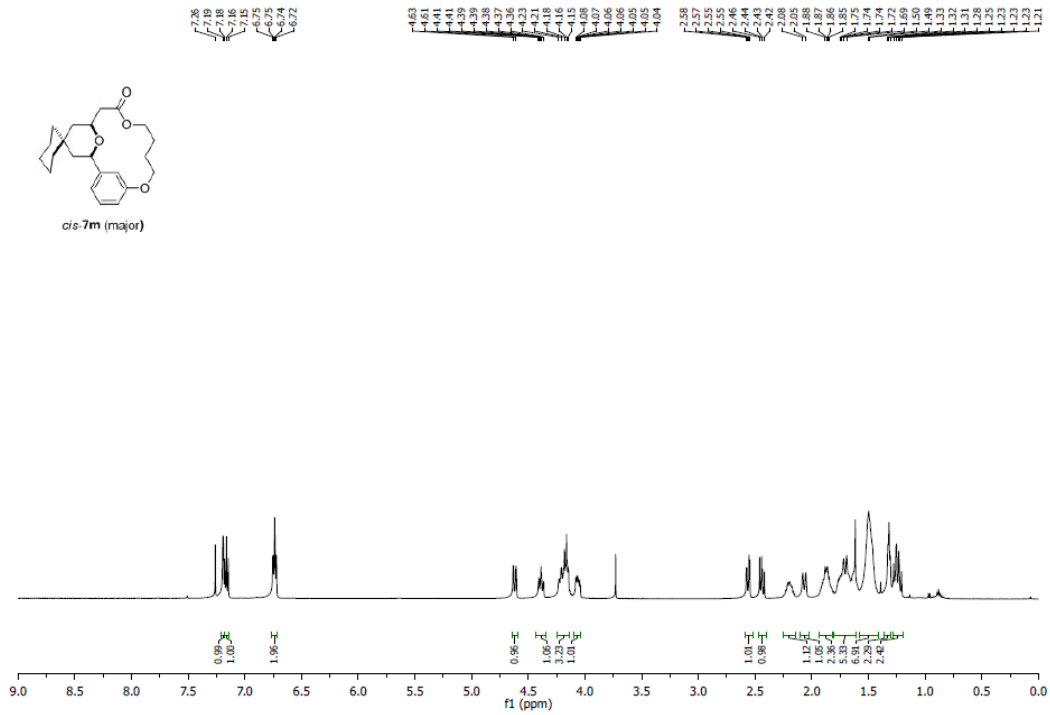


Figure S93. ^{1}H NMR of *cis*-**7m** (500 MHz, $CDCl_3$)

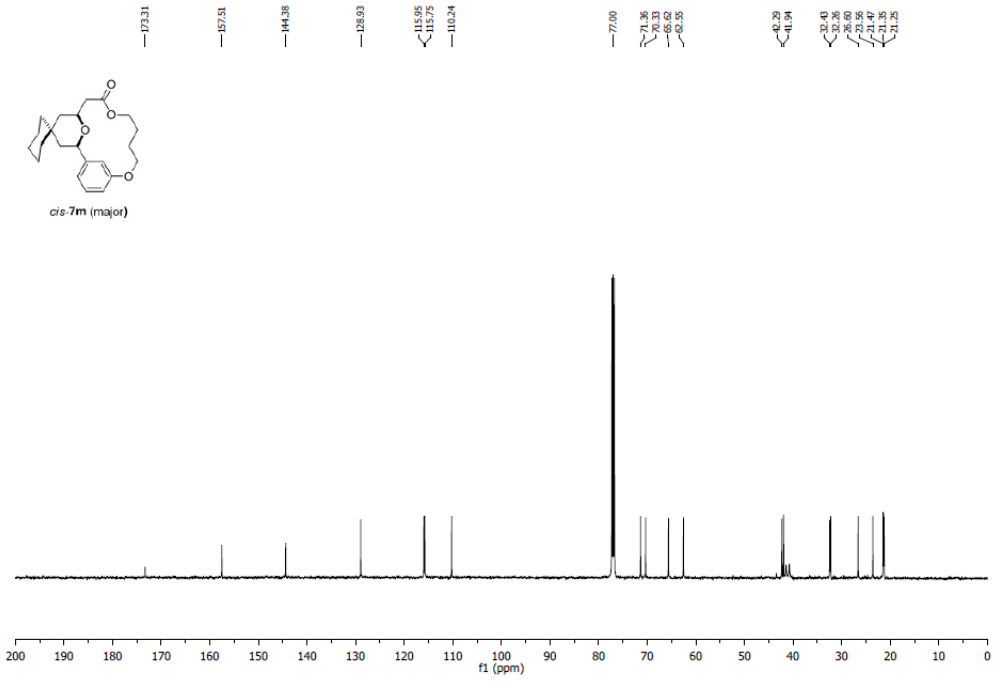


Figure S94. ^{13}C NMR of *cis*-**7m** (125 MHz, $CDCl_3$)

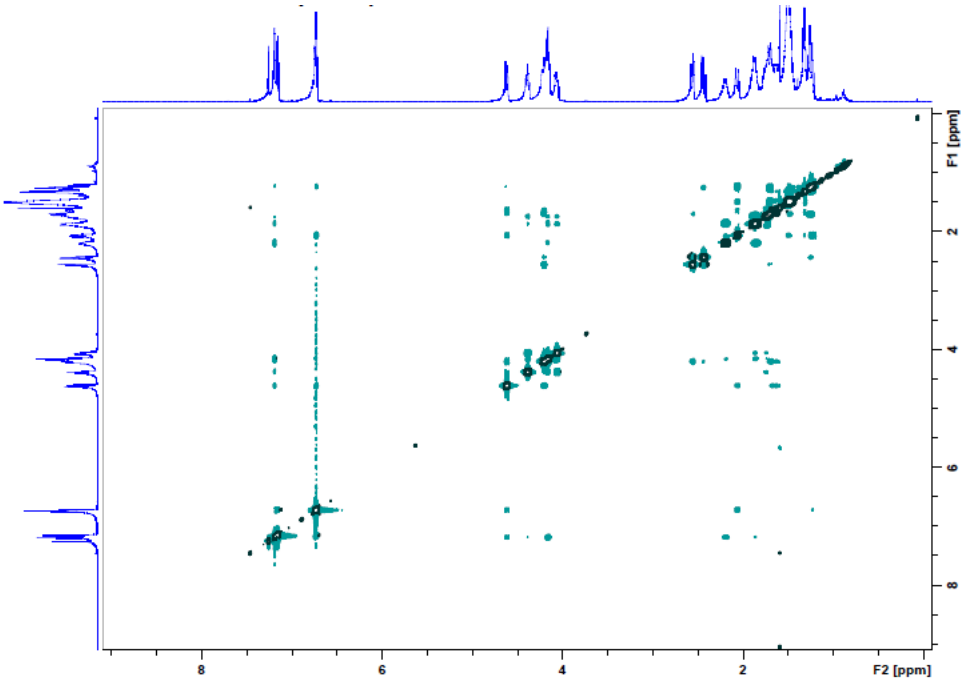


Figure S95. NOESY of *cis*-**7m** in $CDCl_3$

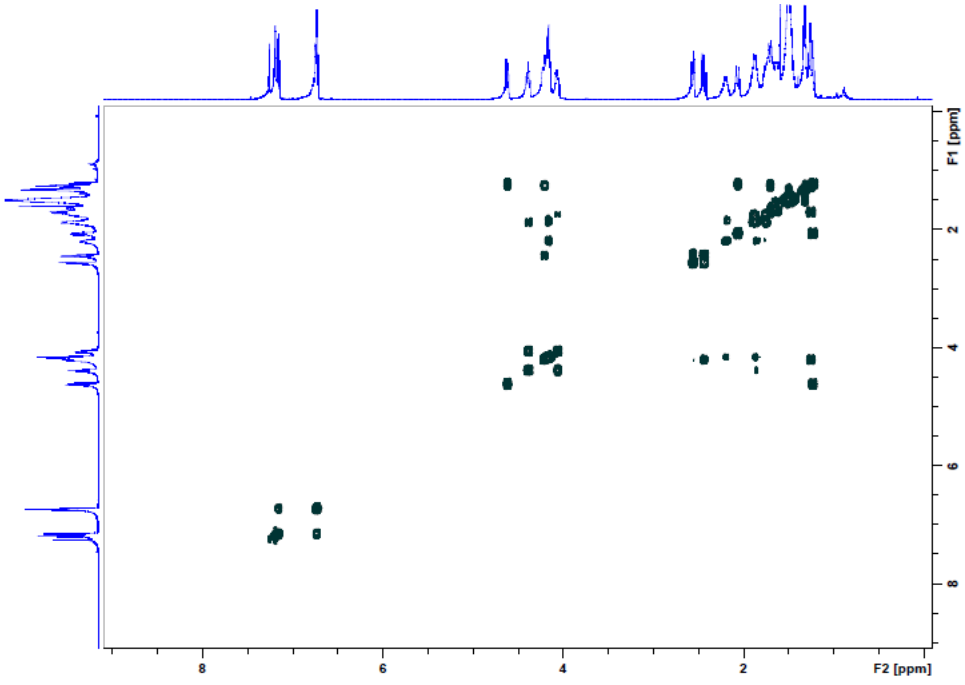


Figure S96. COSY of *cis*-**7m** in $CDCl_3$

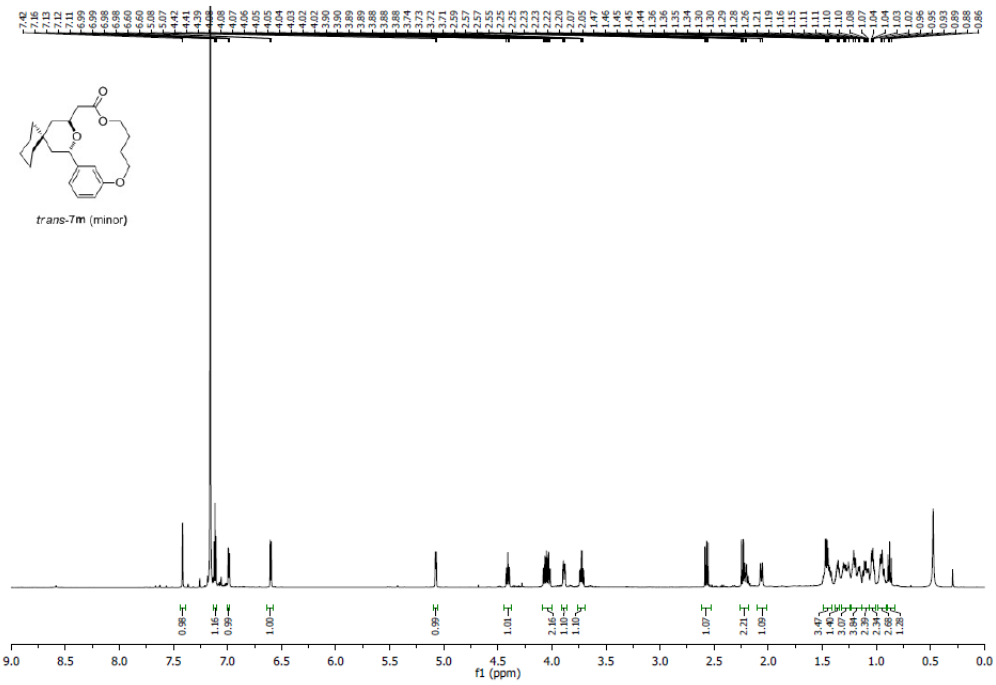


Figure S97. ^{1}H NMR of *trans*-**7m** (800 MHz, $CDCl_3$)

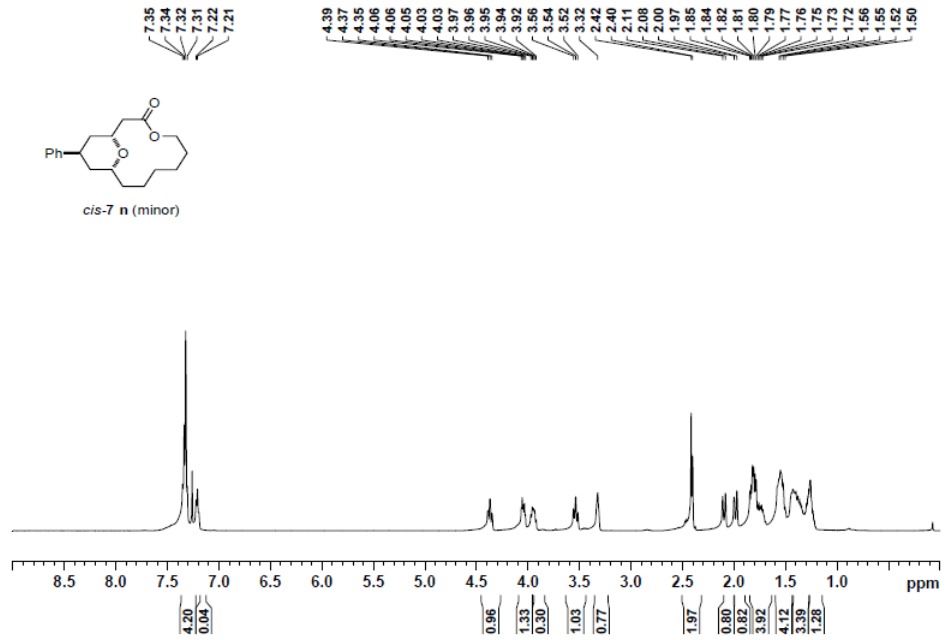


Figure S98. ^{1}H NMR of *cis*-**7n** (500 MHz, $CDCl_3$)

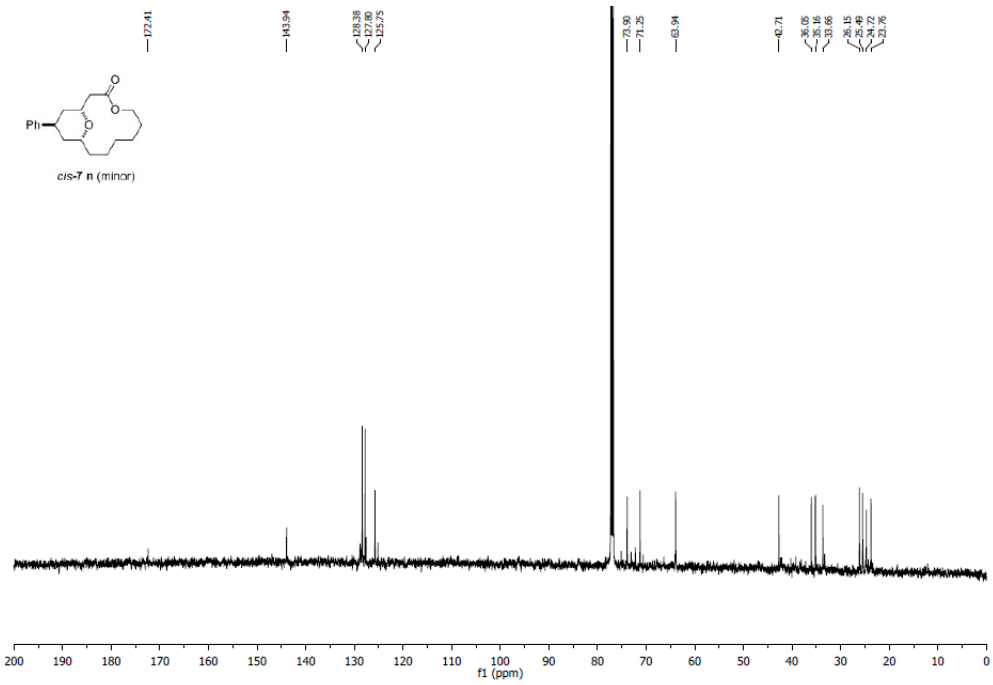


Figure S99. ^{13}C NMR of *cis*-**7n** (125 MHz, $CDCl_3$)

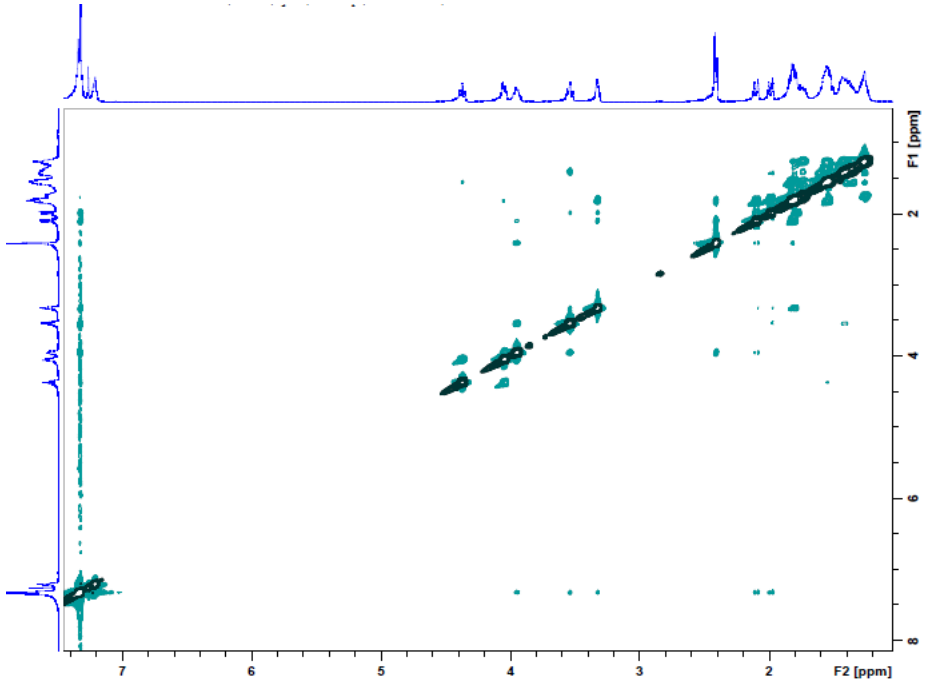


Figure S100. NOESY of *cis*-**7n** in $CDCl_3$

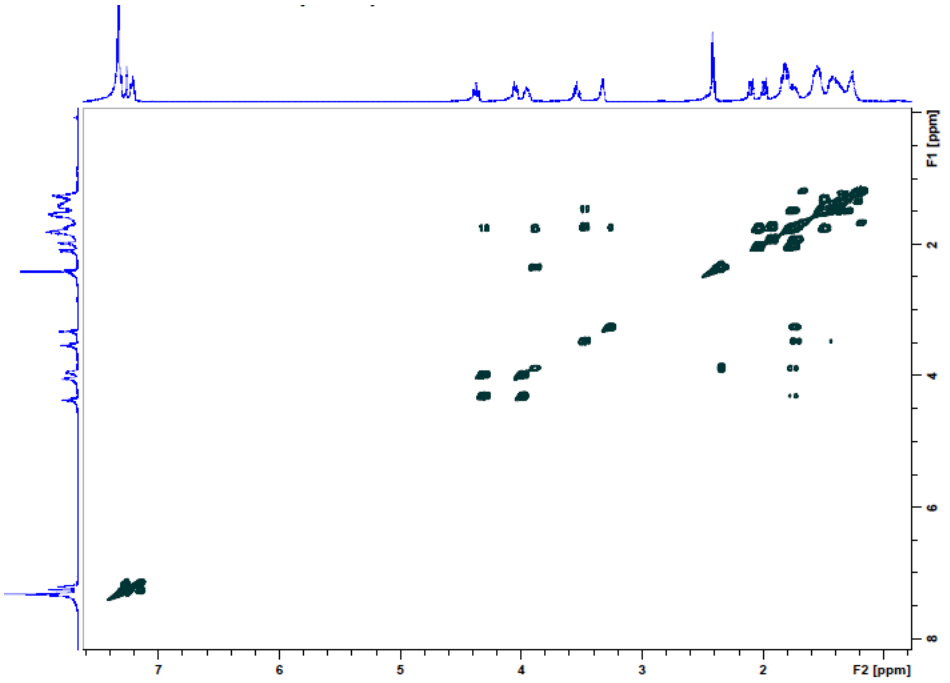


Figure S101. COSY of *cis*-**7n** in $CDCl_3$

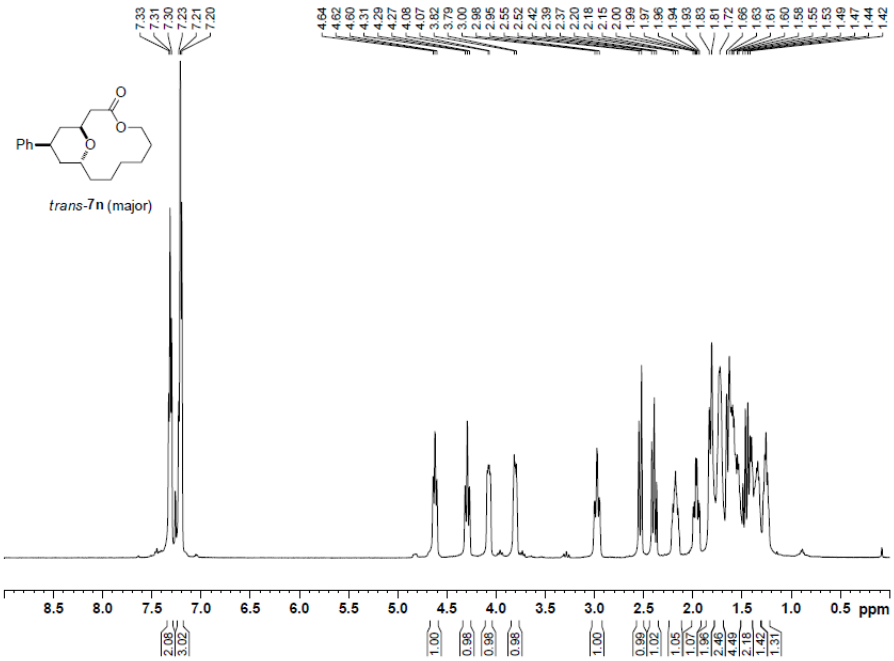


Figure S102. ^{1}H NMR of *trans*-**7n** (500 MHz, $CDCl_3$)

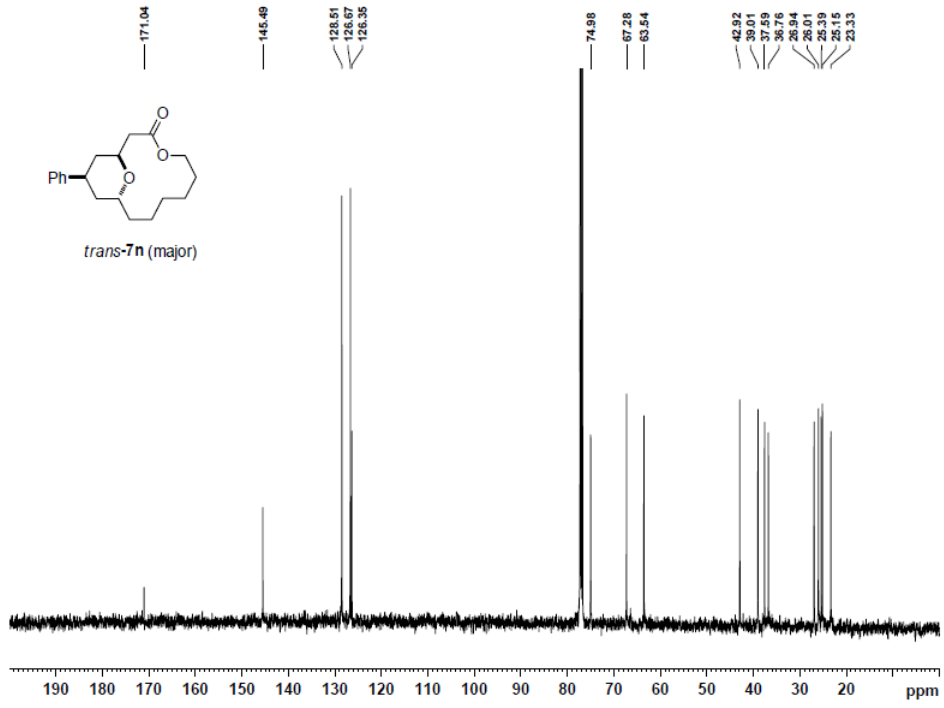


Figure S103. ^{13}C NMR of *trans*-**7n** (125 MHz, $CDCl_3$)

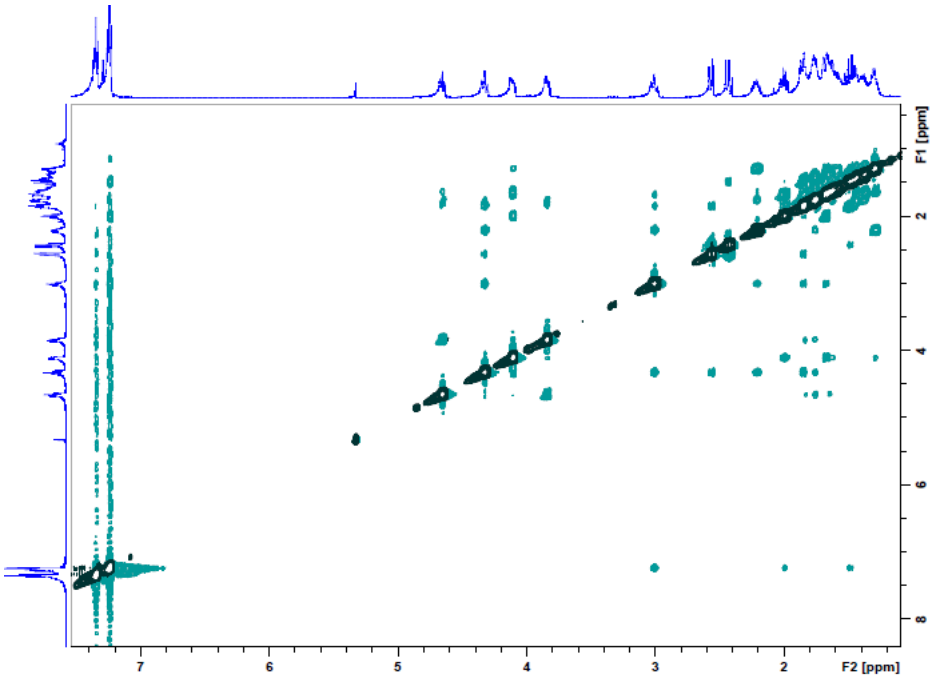


Figure S104. NOESY of *trans*-**7n** in $CDCl_3$

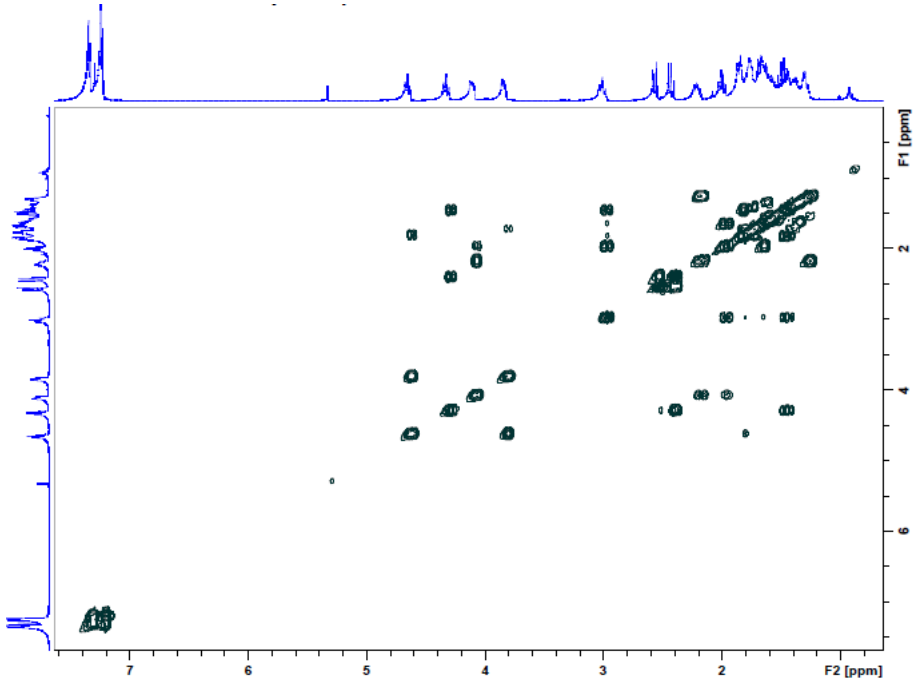


Figure S105. COSY of *trans*-**7n** in $CDCl_3$

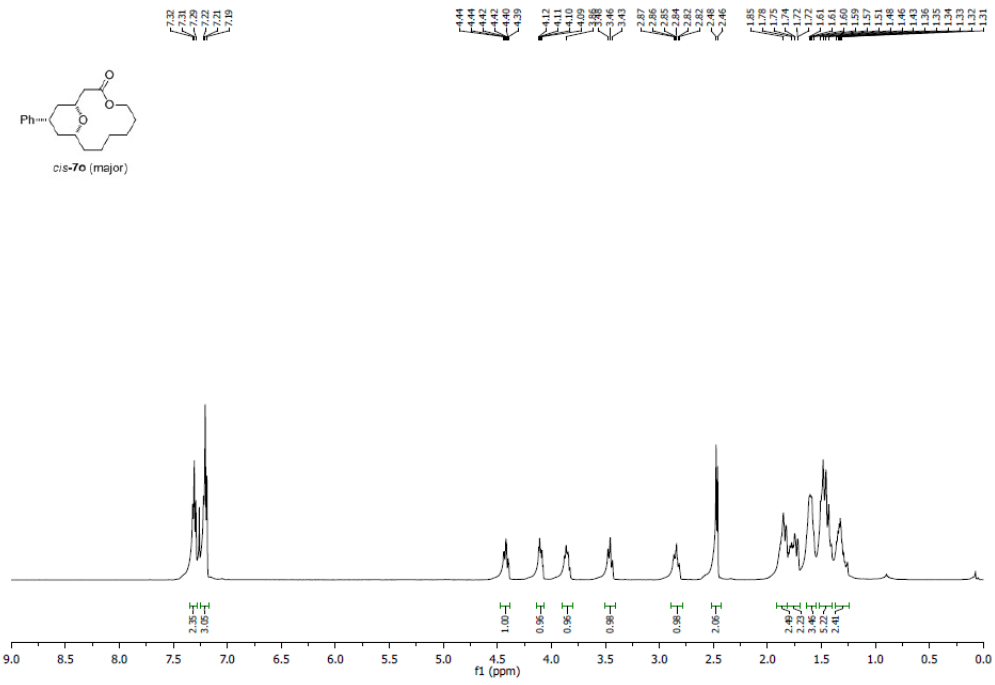


Figure S106. ^{1}H NMR of *cis*-**7o** (500 MHz, $CDCl_3$)

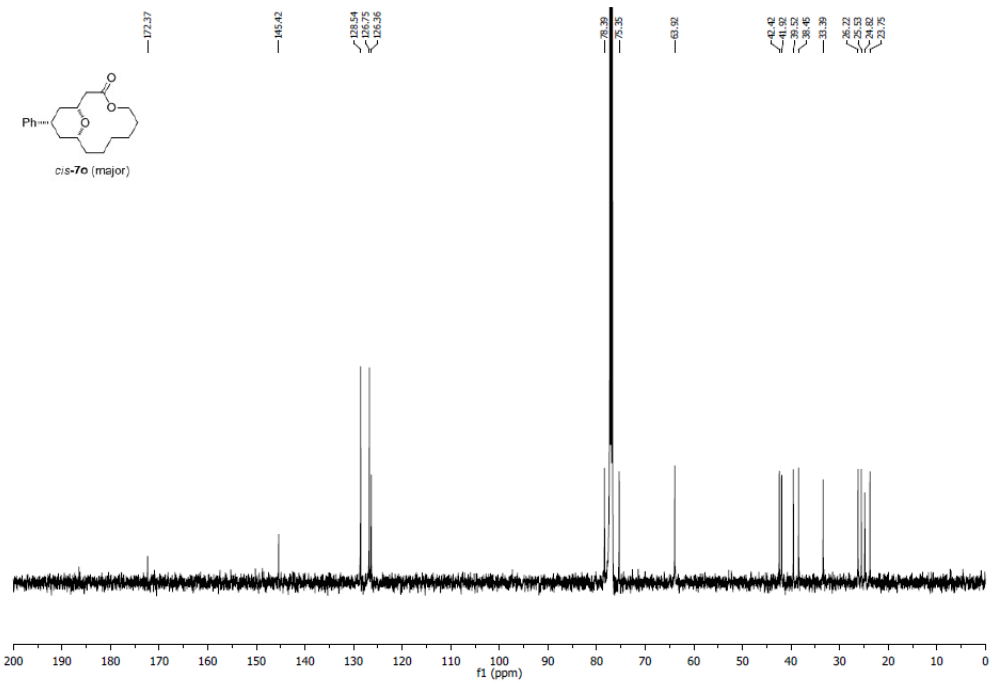


Figure S107. ^{1}H NMR of *cis*-**7o** (125 MHz, $CDCl_3$)

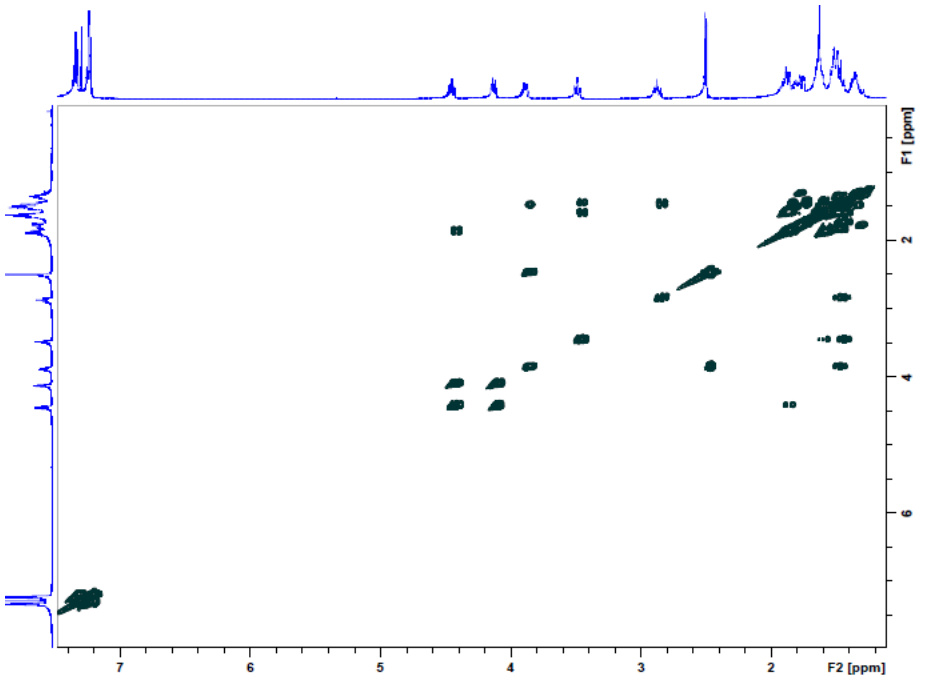


Figure S108. COSY of *cis*-**7o** in $CDCl_3$

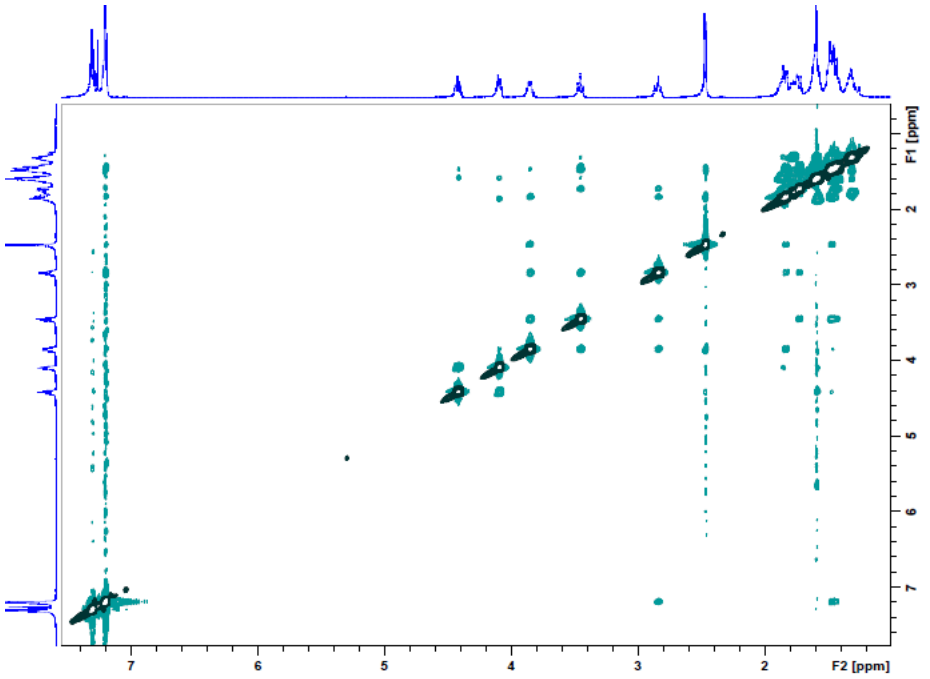


Figure S109. NOESY of *cis*-**7o** in $CDCl_3$

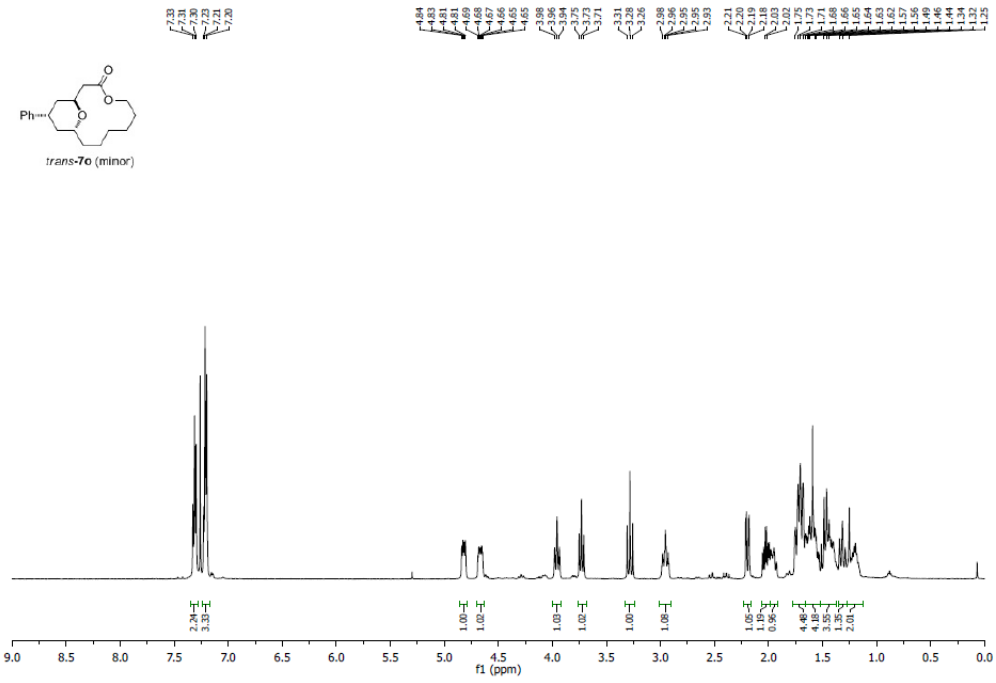


Figure S110. ^{1}H NMR of *trans*-**7o** (500 MHz, $CDCl_3$)

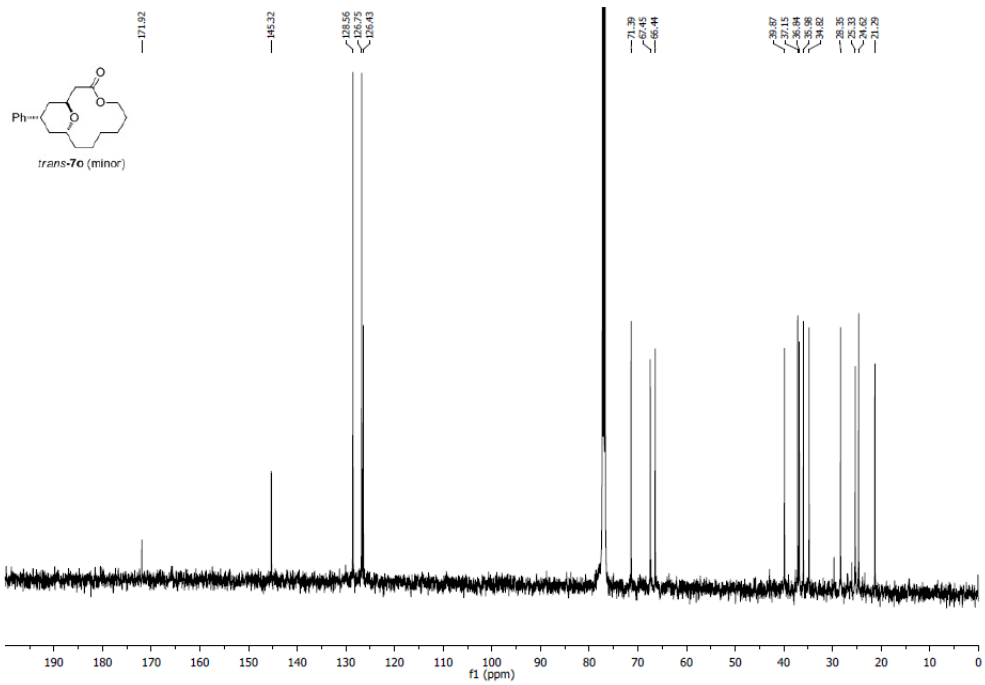


Figure S111. ^{13}C NMR of *trans*-**7o** (125 MHz, $CDCl_3$)

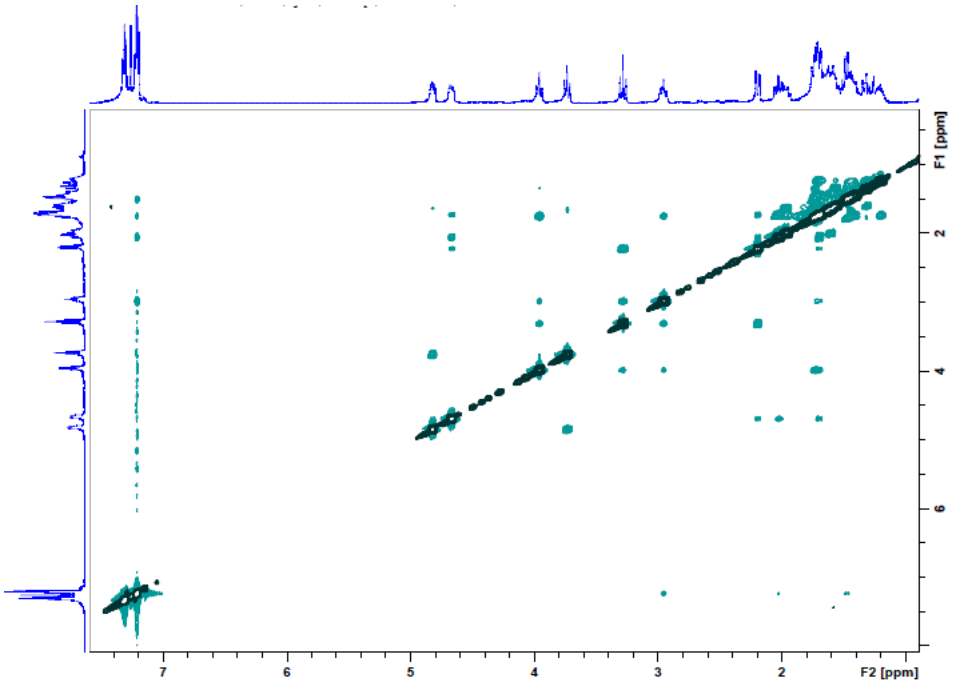


Figure S112. NOESY of *trans*-**7o** in $CDCl_3$

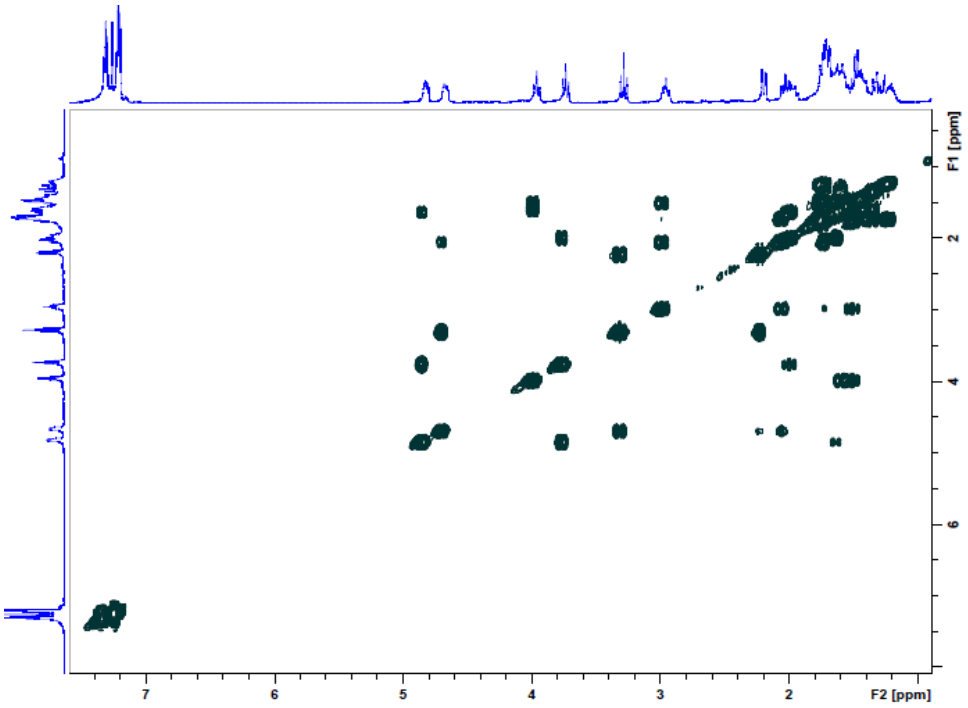


Figure S113. COSY of *trans*-**7o** in $CDCl_3$

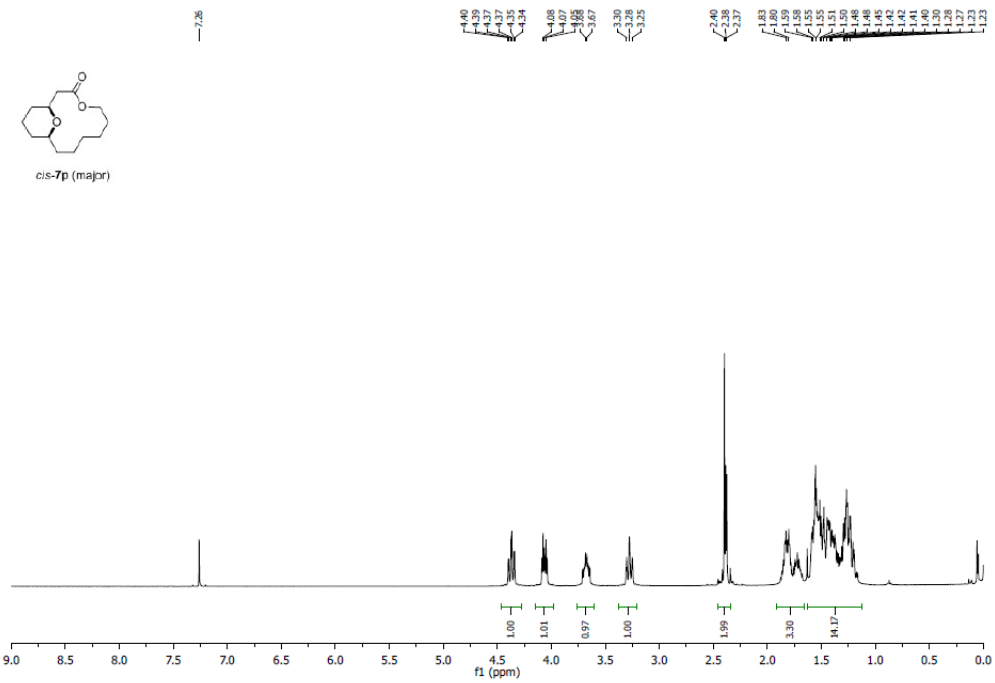


Figure S114. ^{1}H NMR of *cis*-**7p** (400 MHz, $CDCl_3$)

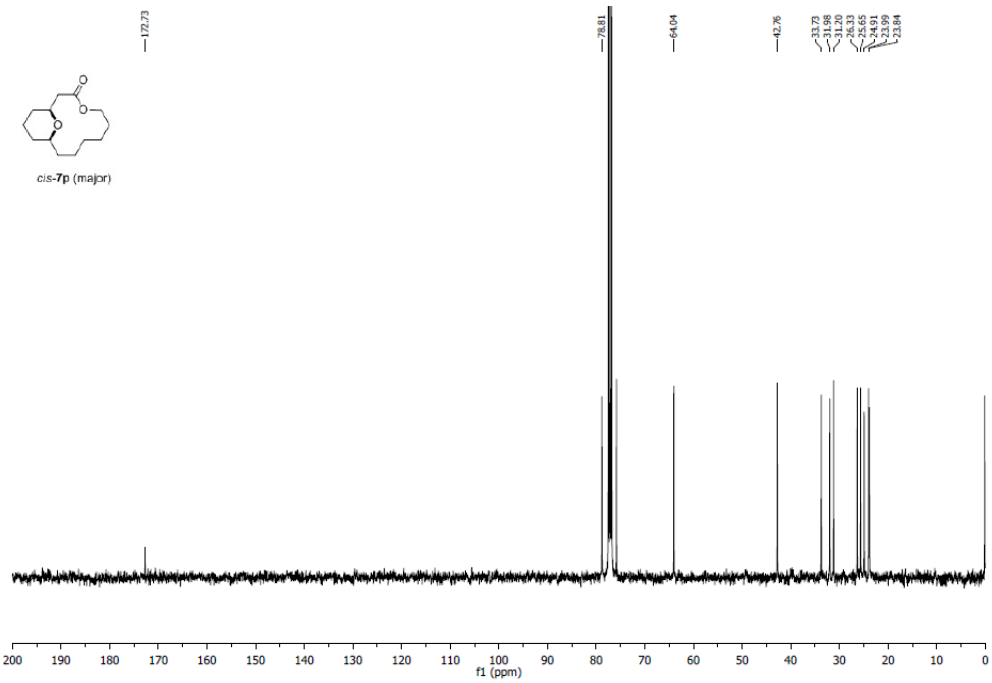


Figure S115. ^{13}C NMR of *cis*-**7p** (100 MHz, $CDCl_3$)

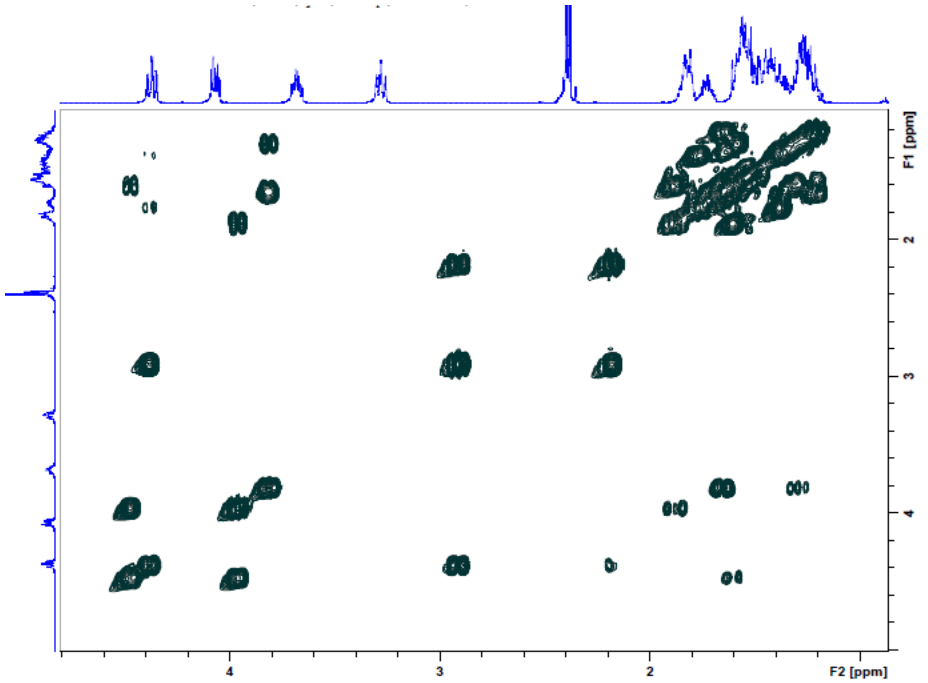


Figure S116. COSY of *cis*-**7p** in $CDCl_3$

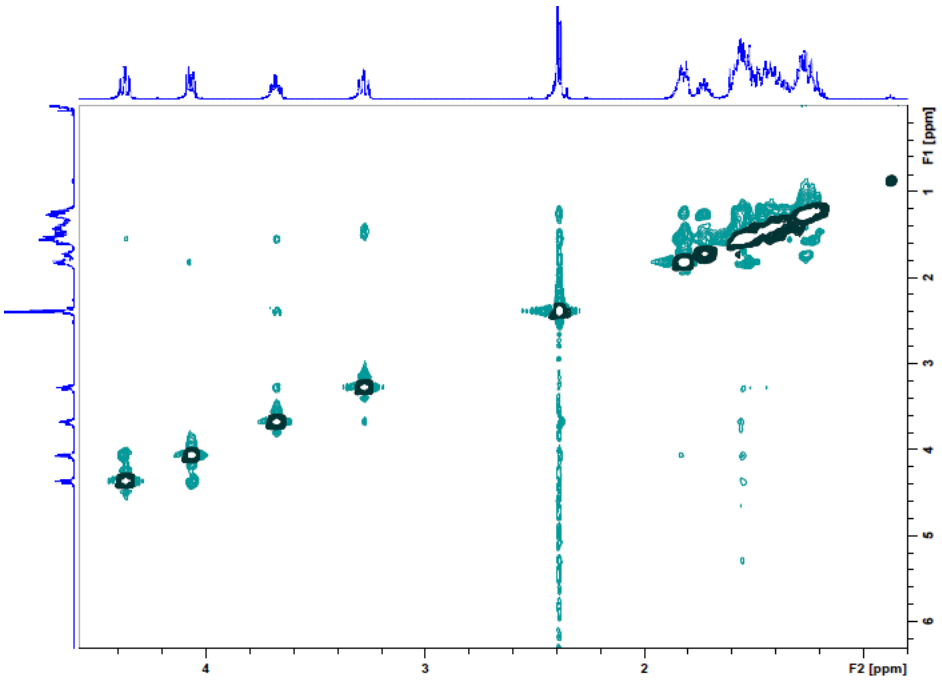


Figure S117. NOESY of *cis*-**7p** in $CDCl_3$

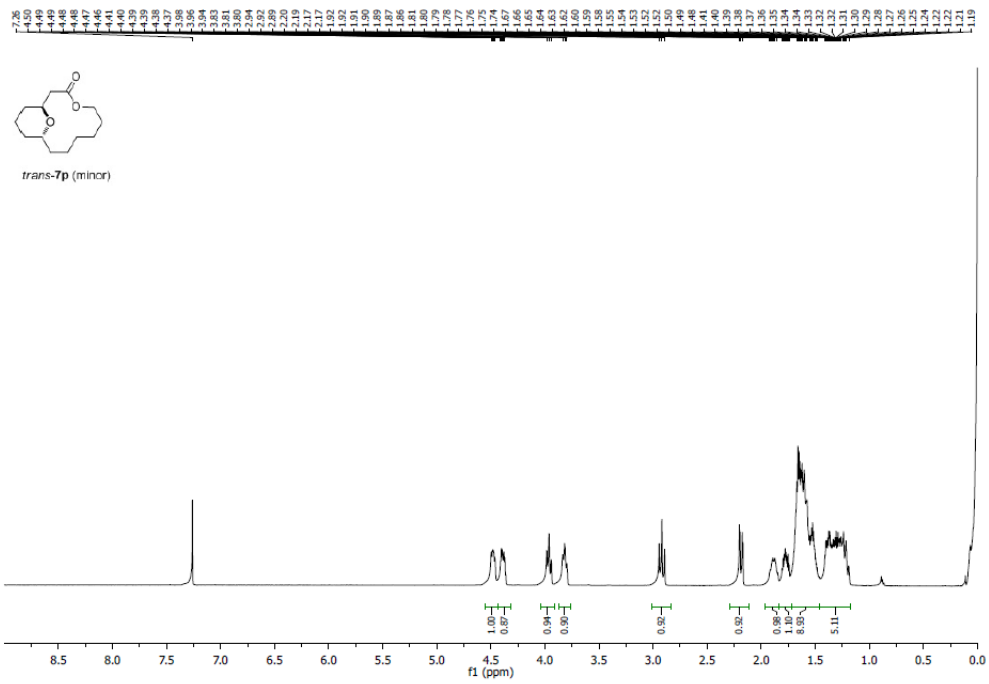


Figure S118. ^{1}H NMR of *trans*-**7p** (500 MHz, $CDCl_3$)

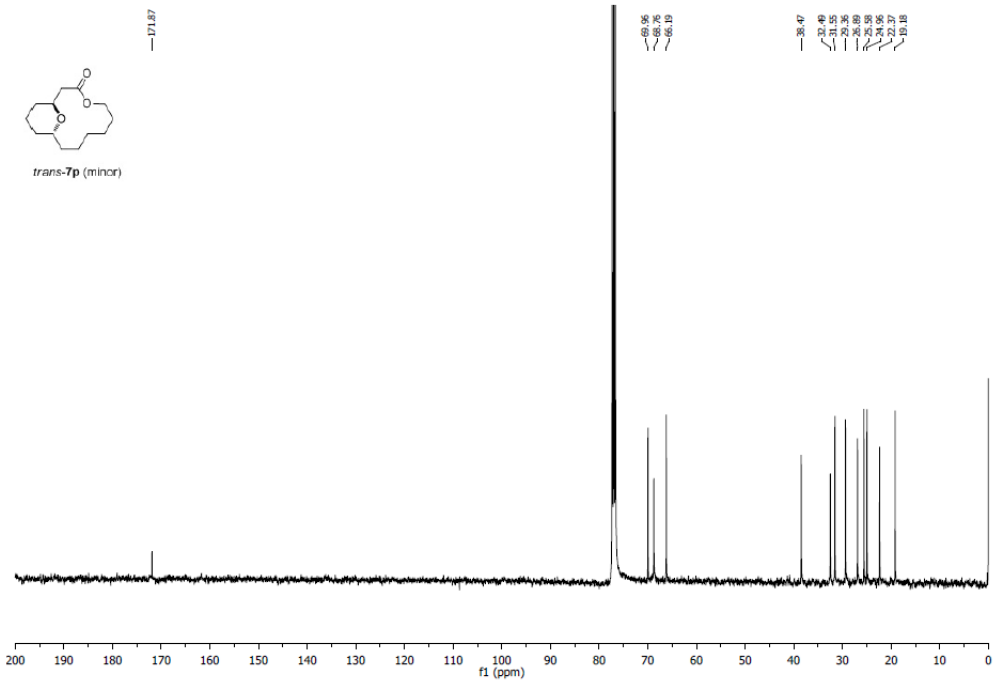


Figure S119. ^{13}C NMR of *trans*-**7p** (100 MHz, $CDCl_3$)

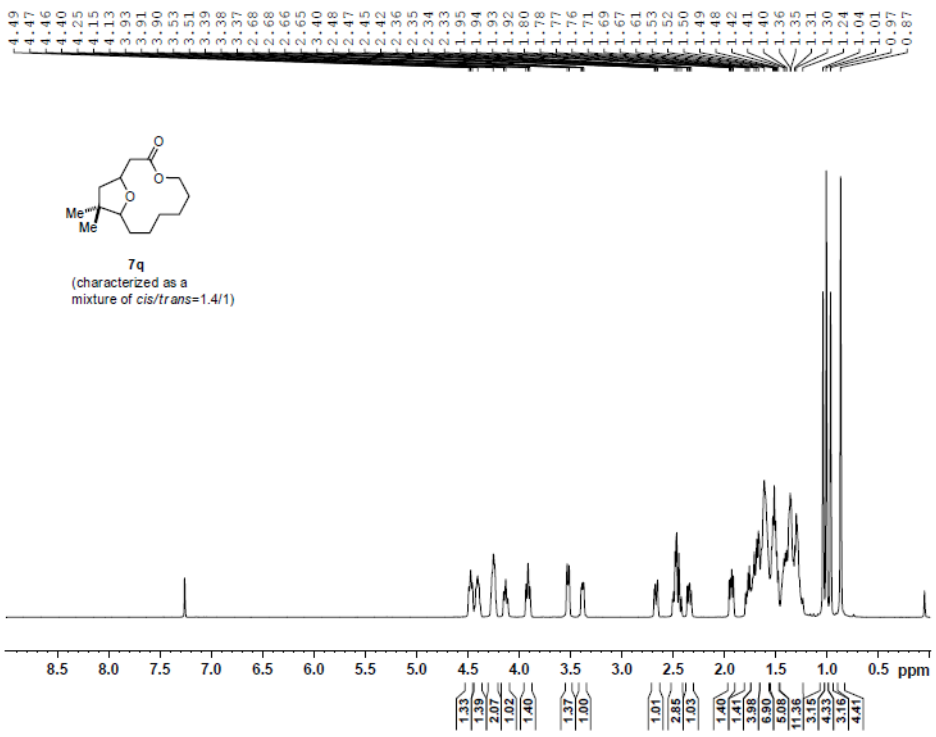


Figure S120. ^{1}H NMR of *cis*/*trans*-**7q** as a 1.4/1 mixture (400 MHz, $CDCl_3$)

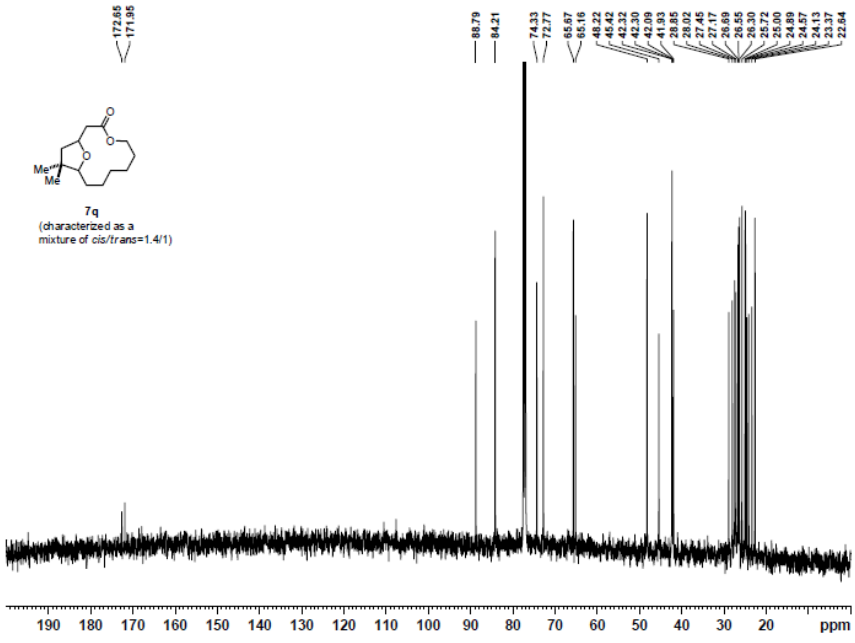


Figure S121. ^{13}C NMR of *cis*/*trans*-**7q** as a 1.4/1 mixture (125 MHz, $CDCl_3$)

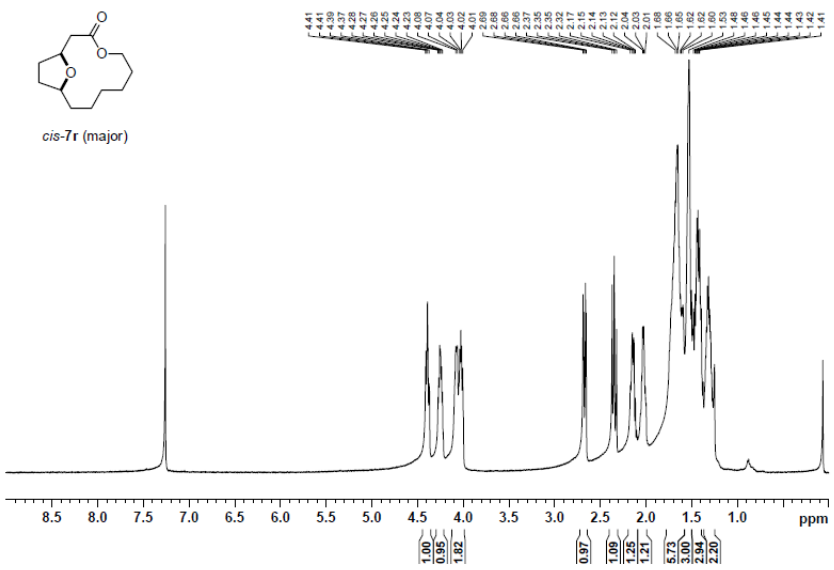


Figure S122. ^{1}H NMR of *cis*-**7r** (500 MHz, $CDCl_3$)

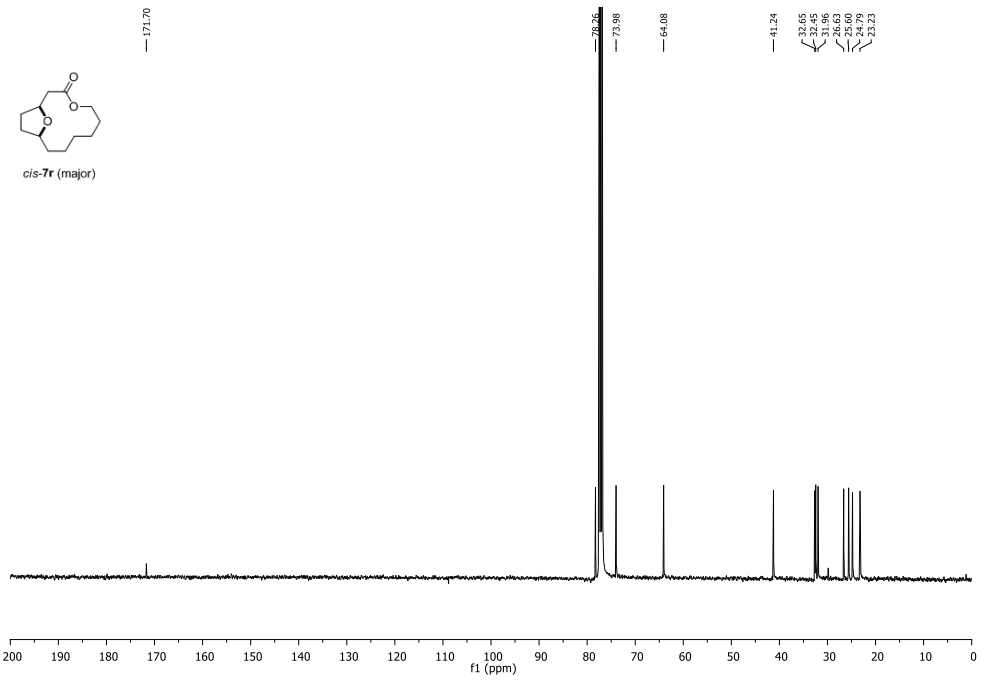


Figure S123. ^{13}C NMR of *cis*-**7r** (100 MHz, $CDCl_3$)

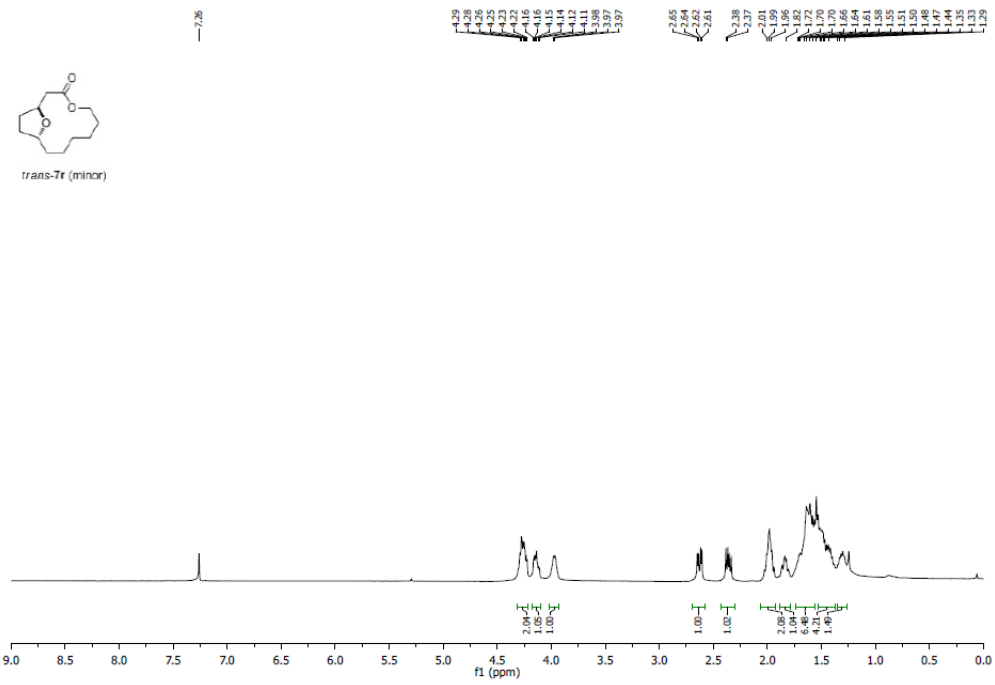


Figure S124. ^{1}H NMR of *trans*-**7r** (400 MHz, $CDCl_3$)

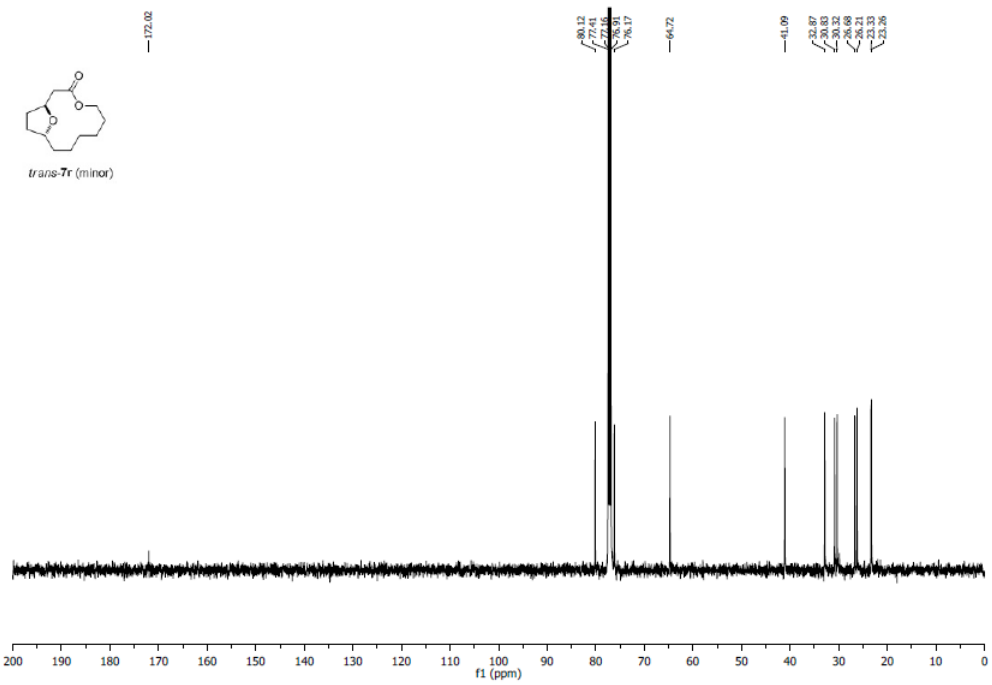


Figure S125. ^{13}C NMR of *trans*-**7r** (125 MHz, $CDCl_3$)

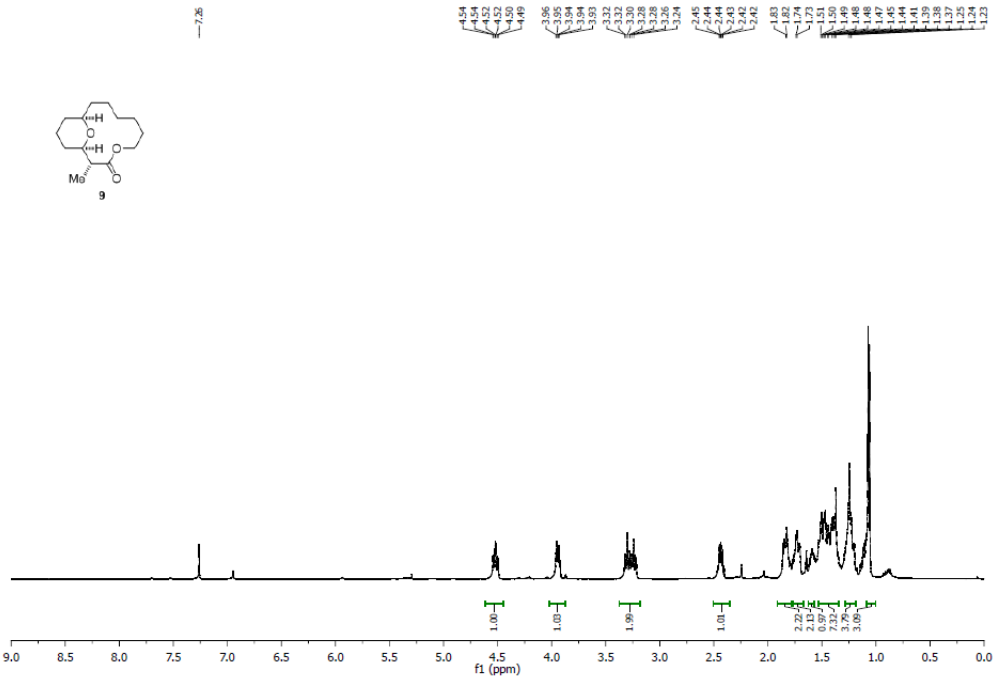


Figure S126. ^{1}H NMR of **9** (500 MHz, $CDCl_3$)

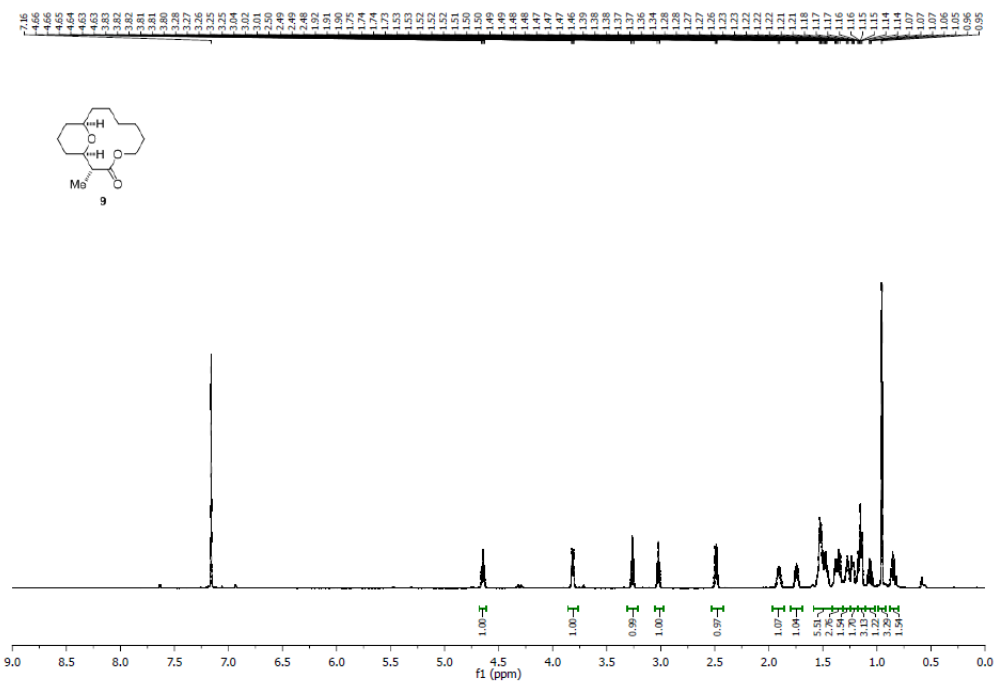


Figure S127. ^{1}H NMR of **9** (800 MHz, C_6D_6)

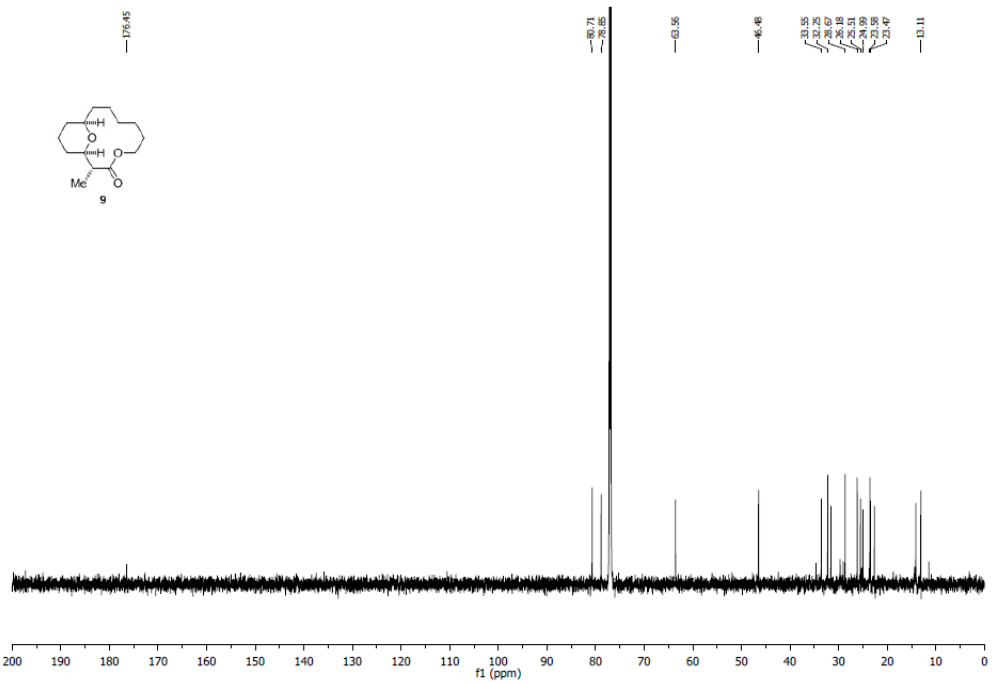


Figure S128. ^{13}C NMR of **8** (200 MHz, $CDCl_3$)

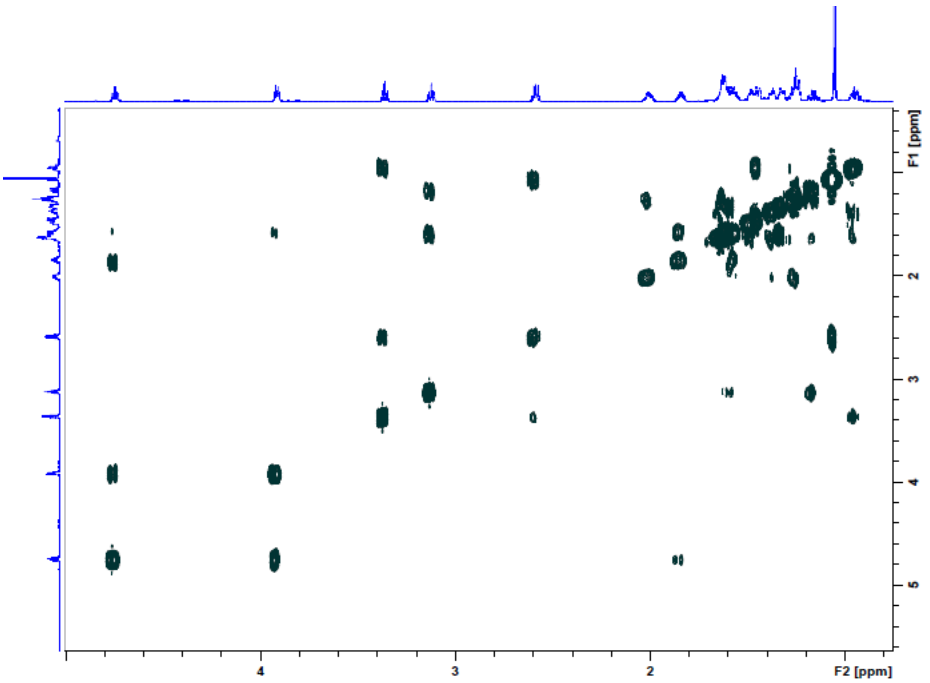


Figure S129. COSY of **9** in C_6D_6

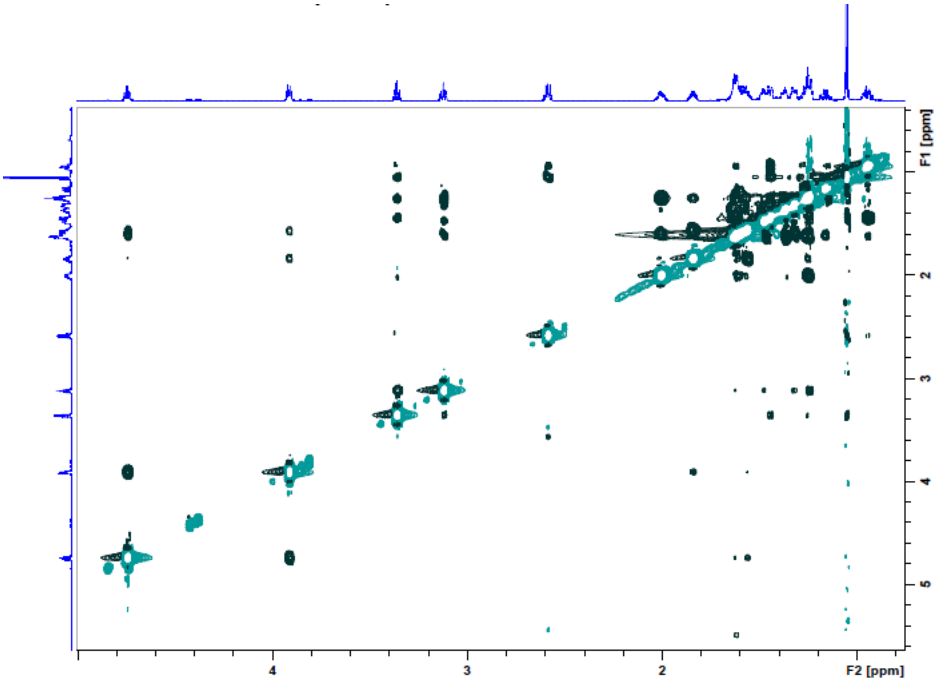


Figure S130. NOESY of **9** in C_6D_6

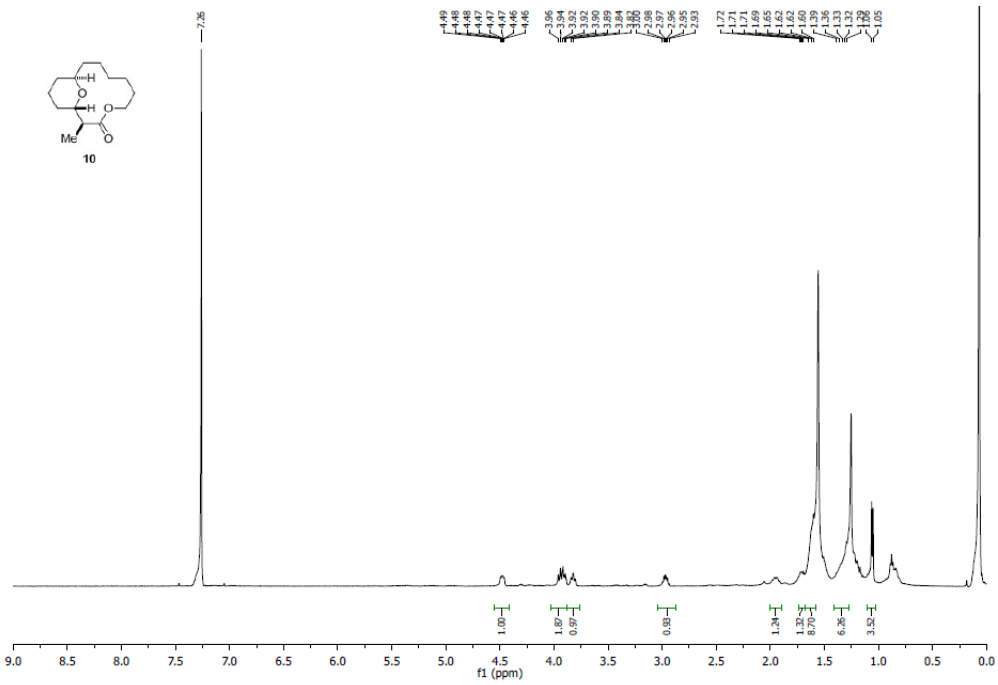


Figure S131. ^{1}H NMR of **10** (500 MHz, $CDCl_3$)

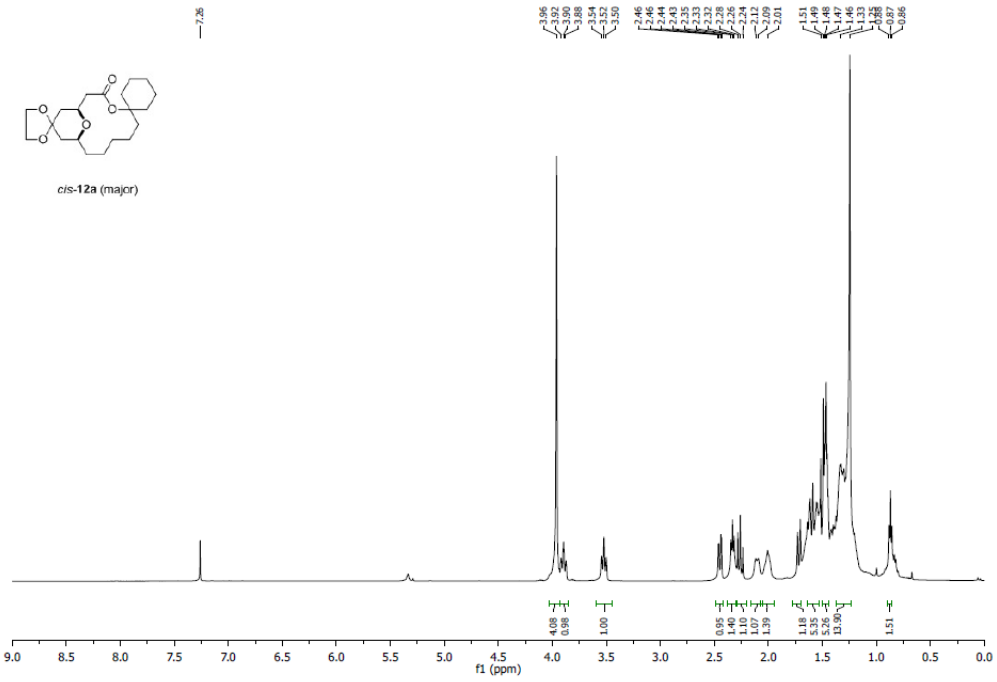


Figure S132. ^{1}H NMR of *cis*-**12a** (500 MHz, $CDCl_3$)

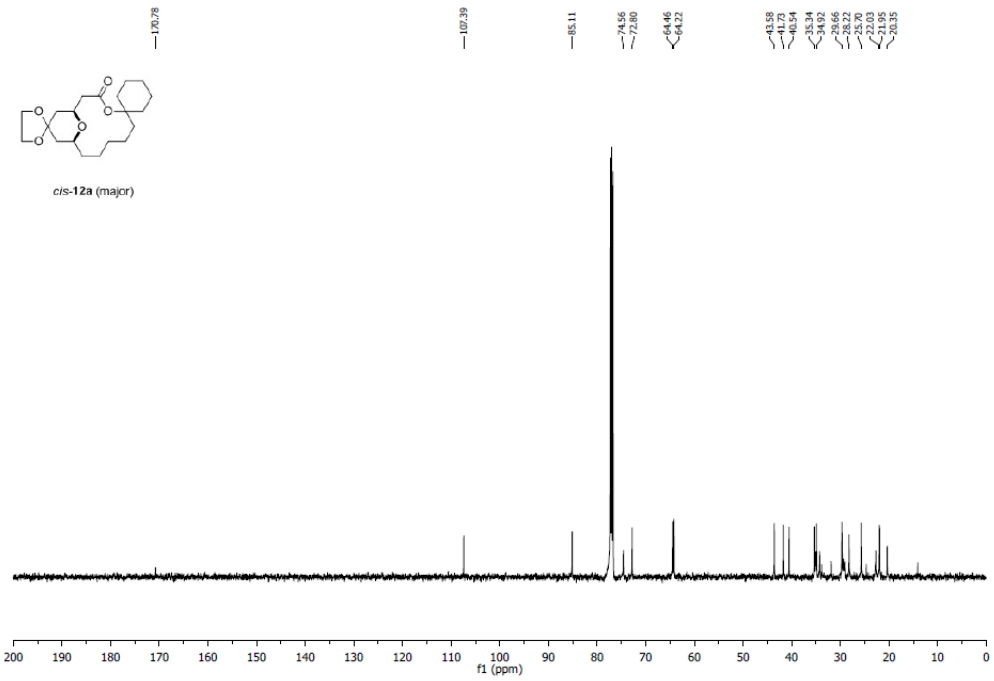


Figure S133. ^{13}C NMR of *cis*-**12a** (125 MHz, $CDCl_3$)

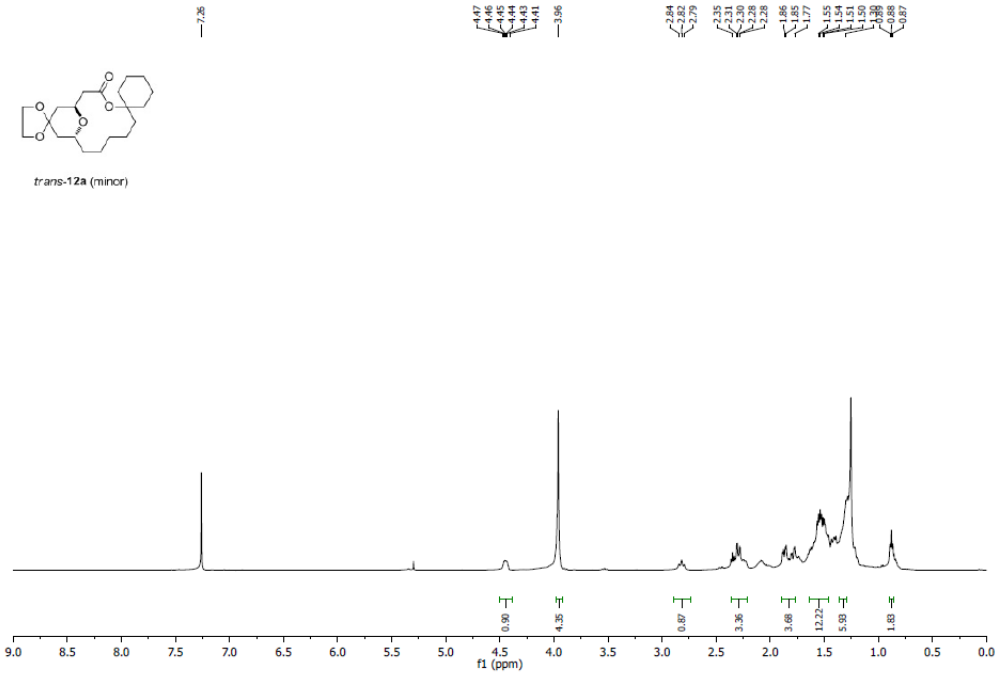


Figure S134. ^{1}H NMR of *trans*-**12a** (500 MHz, $CDCl_3$)

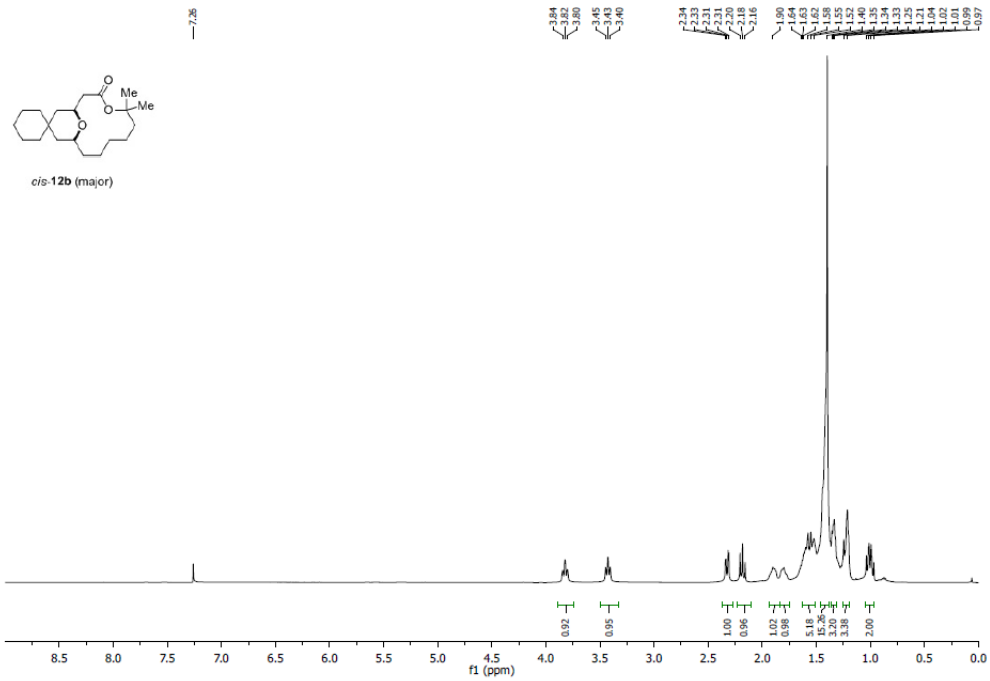


Figure S135. ^{1}H NMR of *cis*-**12b** (500 MHz, $CDCl_3$)

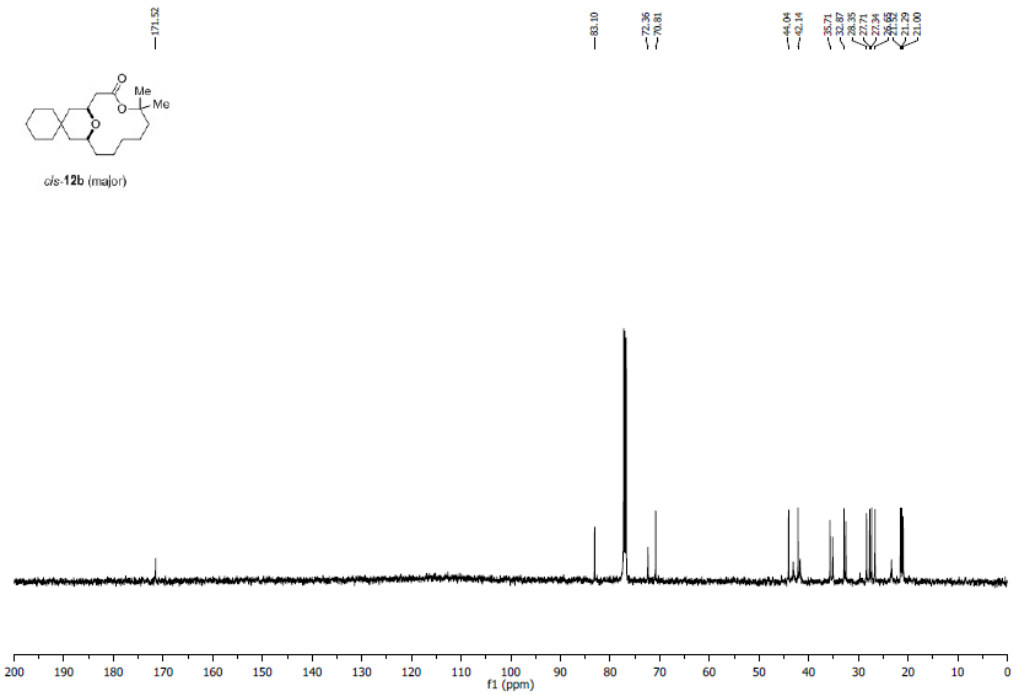


Figure S136. ^{13}C NMR of *cis*-**12b** (125 MHz, $CDCl_3$)

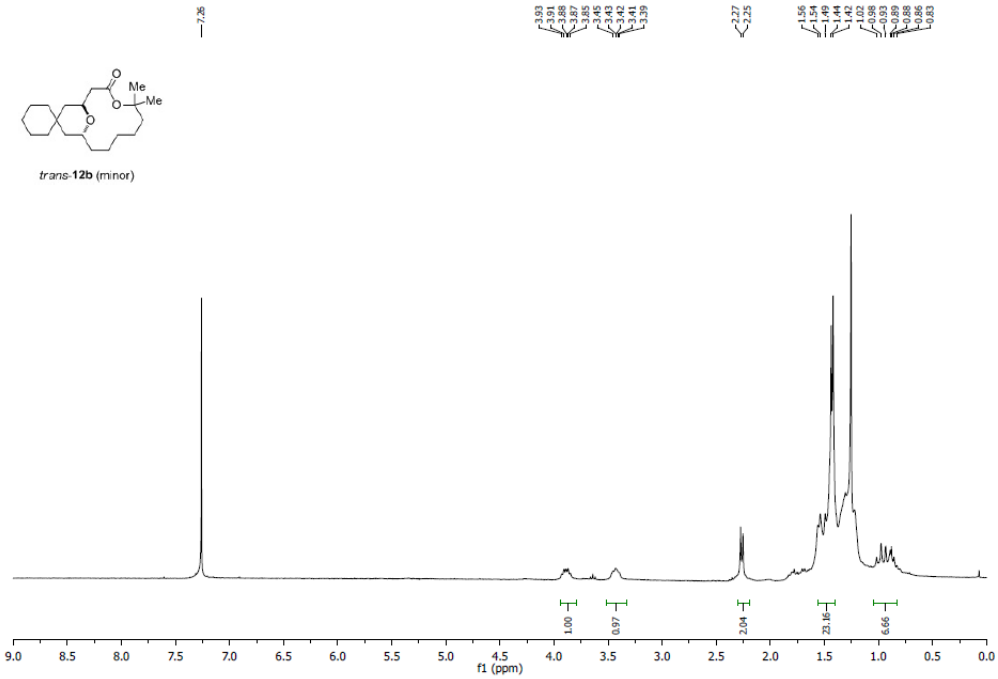


Figure S137. ^{1}H NMR of *trans*-**12b** (500 MHz, $CDCl_3$)

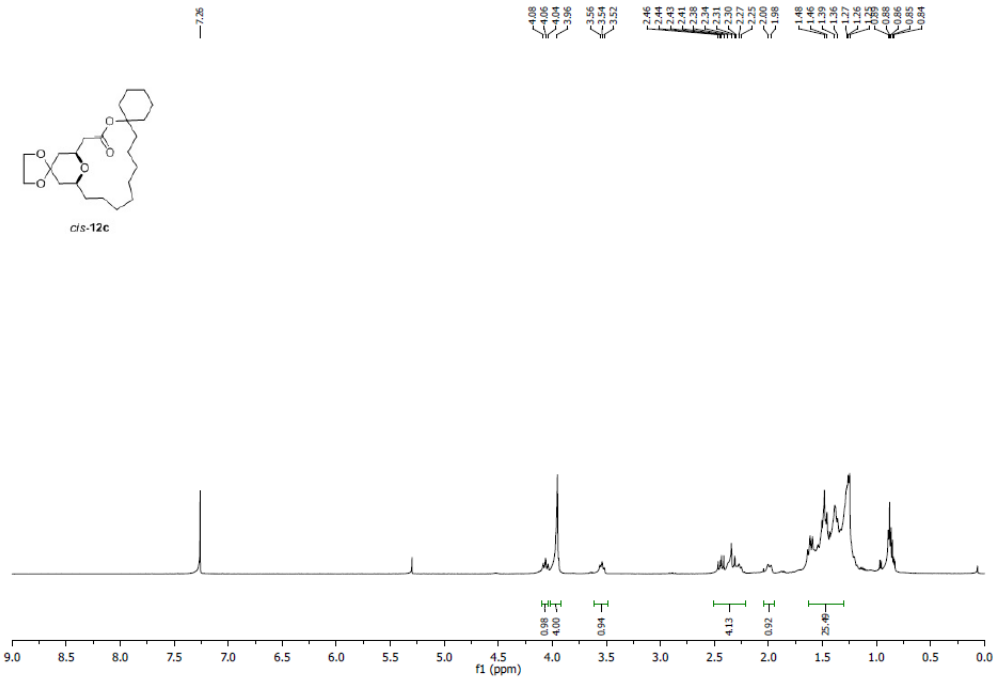


Figure S138. ^{1}H NMR of *cis*-**12c** (500 MHz, $CDCl_3$)

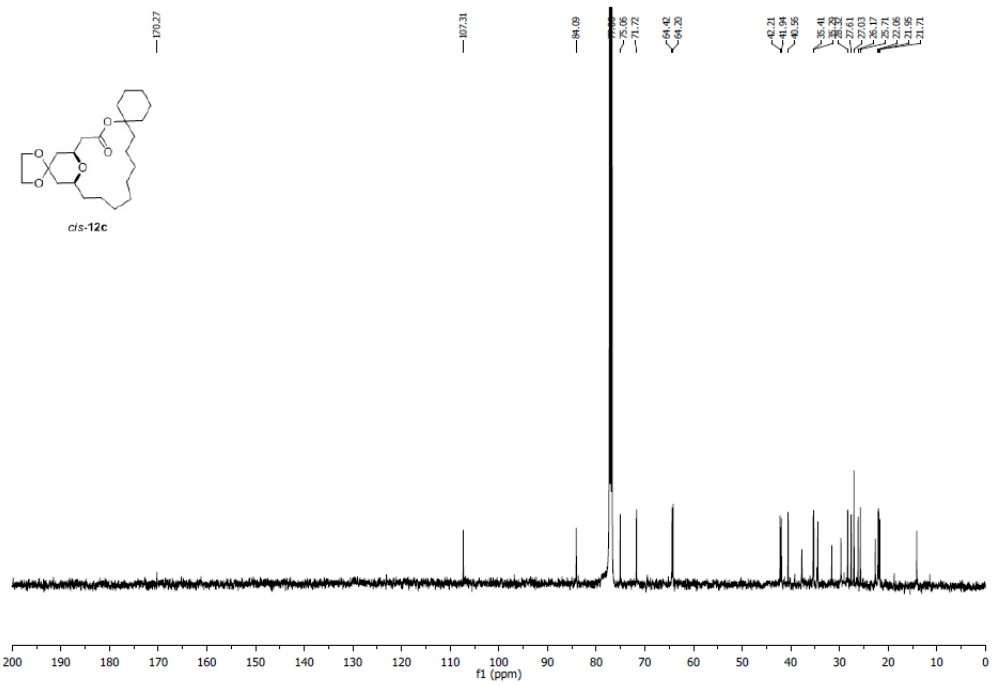


Figure S139. ^{13}C NMR of *cis*-**12c** (125 MHz, $CDCl_3$)

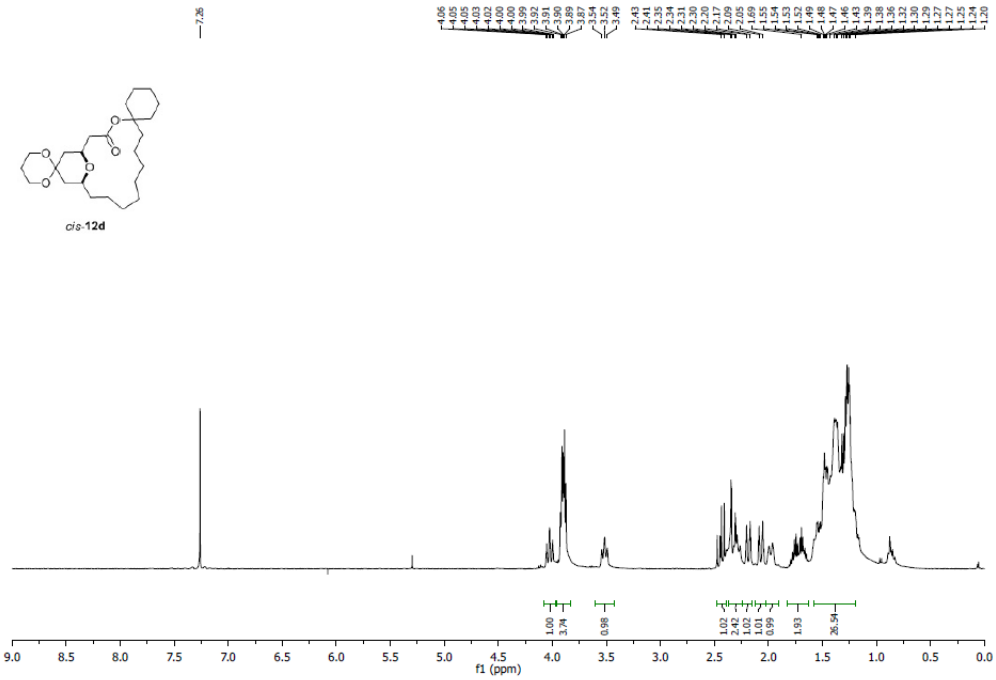


Figure S140. ^{1}H NMR of *cis*-**12d** (400 MHz, $CDCl_3$)

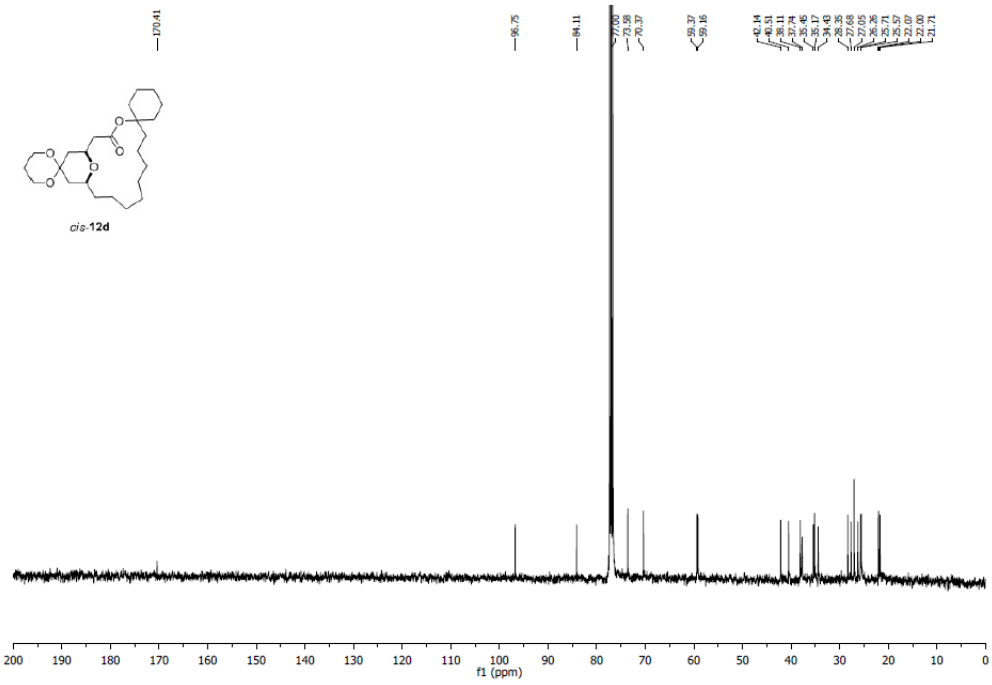


Figure S141. ^{13}C NMR of *cis*-**12d** (125 MHz, $CDCl_3$)

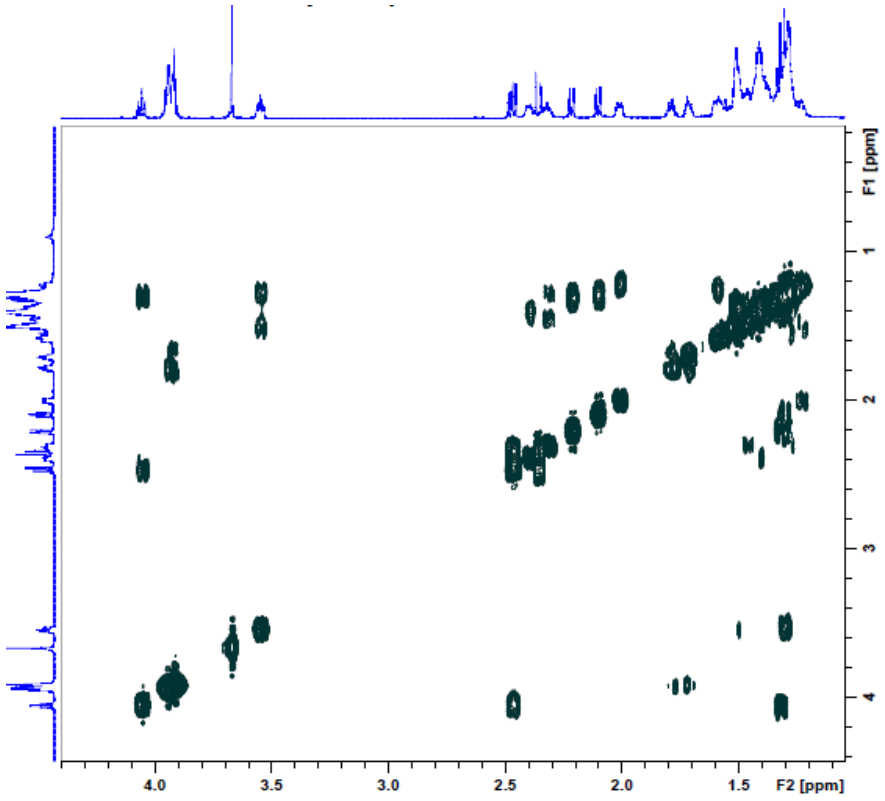


Figure S142. COSY of *cis*-**12d** in $CDCl_3$

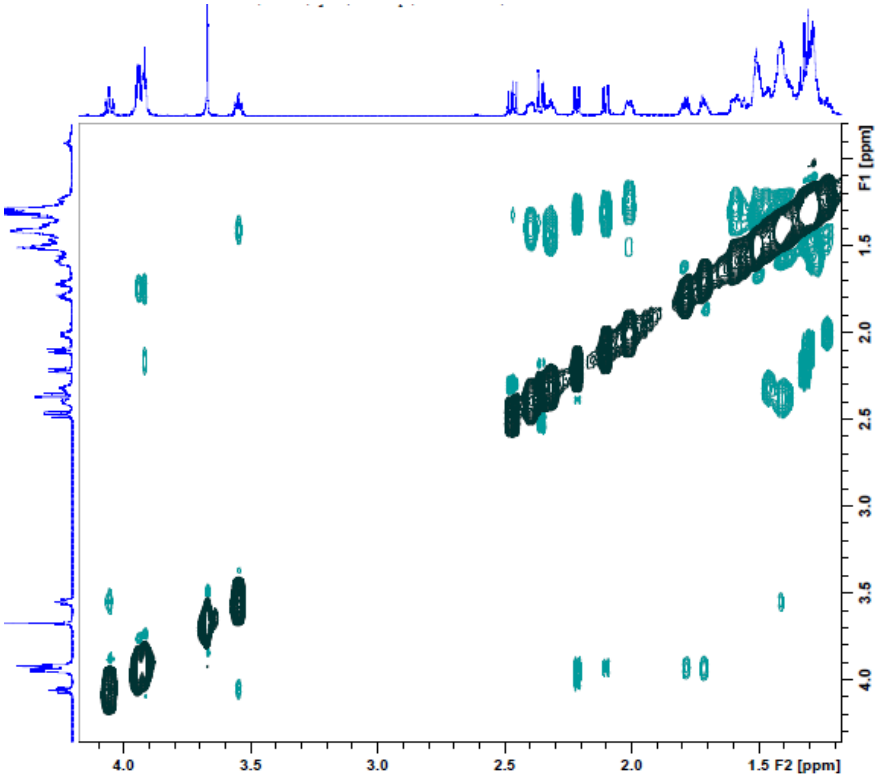


Figure S143. NOSEY of *cis*-**12d** in $CDCl_3$

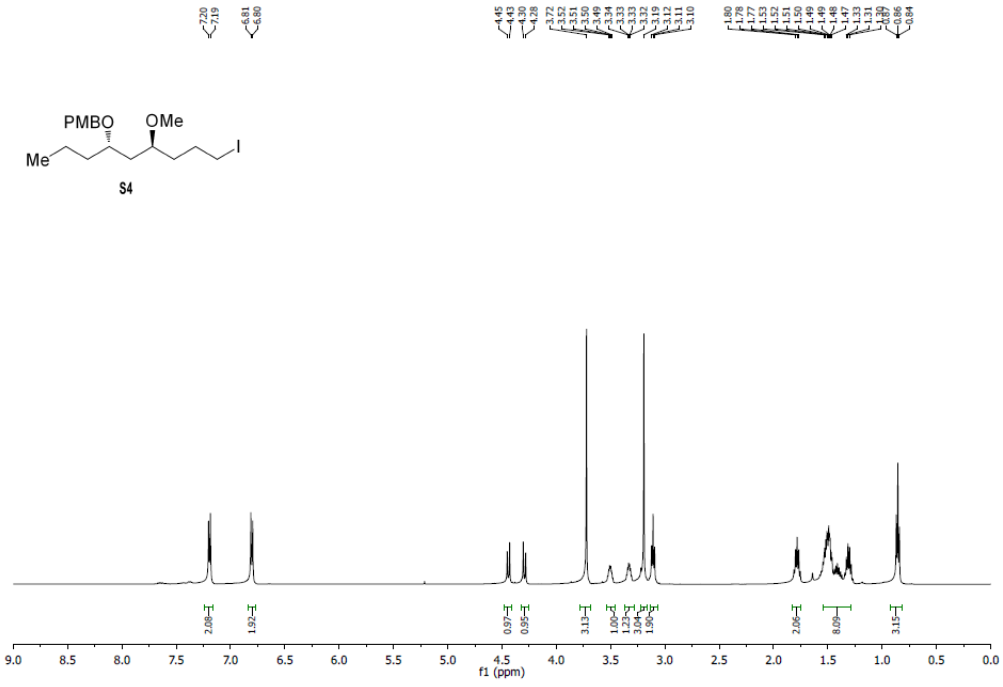


Figure S144. ^{1}H NMR of **S4** (500 MHz, $CDCl_3$)

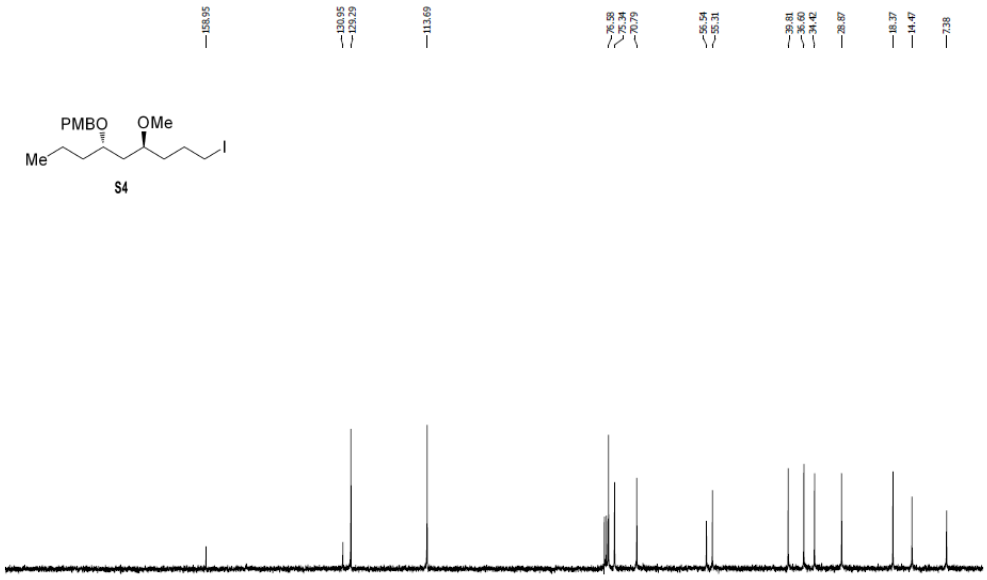


Figure S145. ^{13}C NMR of **S4** (75 MHz, $CDCl_3$)

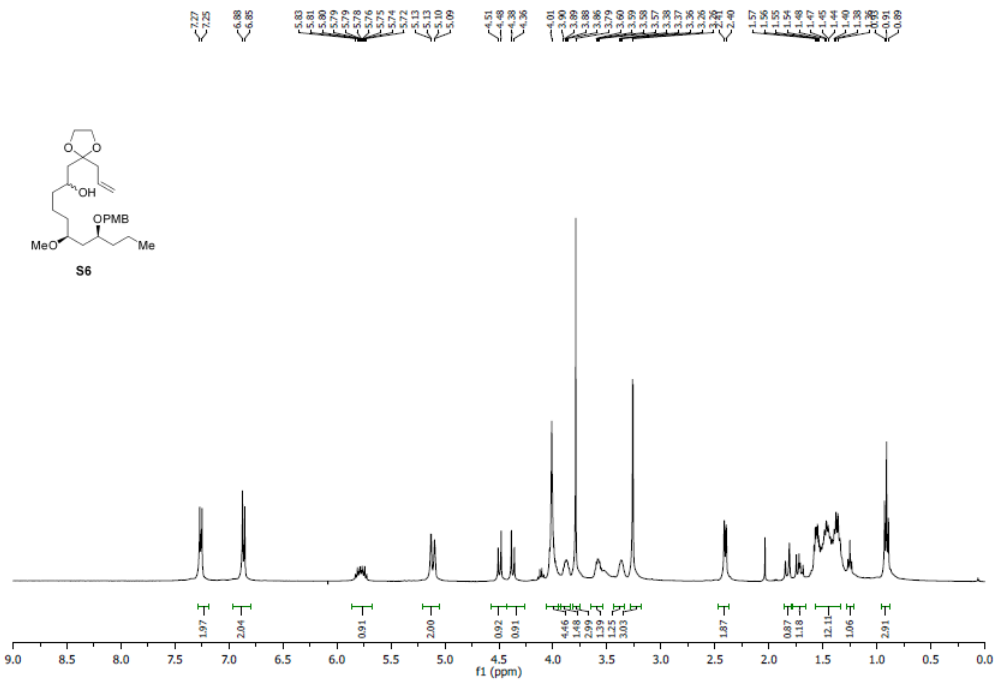


Figure S146. ^{1}H NMR of **S6** (400 MHz, $CDCl_3$)

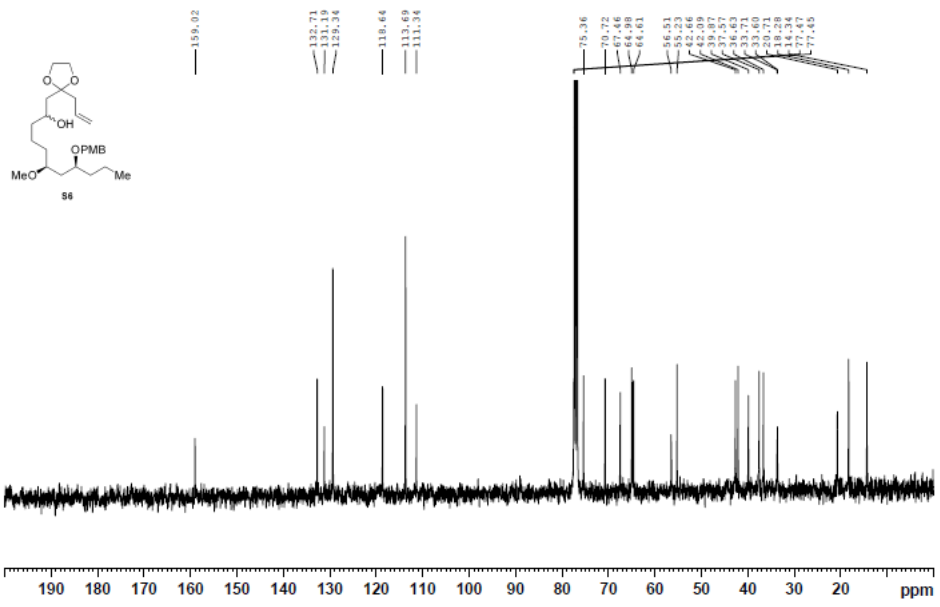


Figure S147. ^{13}C NMR of **S6** (100 MHz, $CDCl_3$)

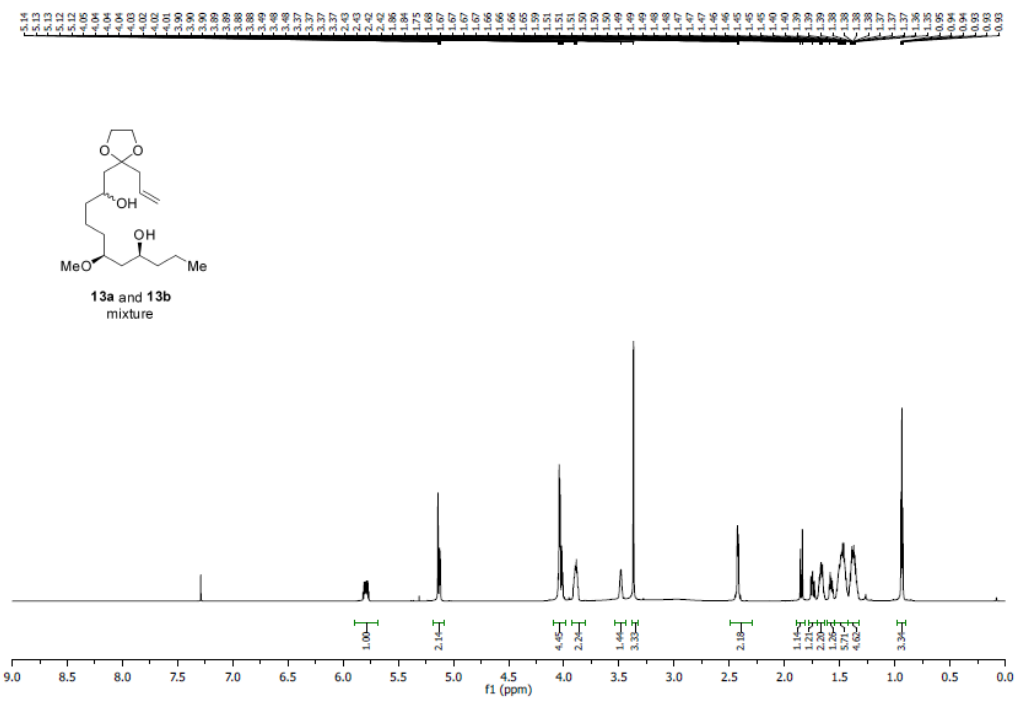


Figure S148. ^{1}H NMR of **13a/13b** as a1/1 mixture (800 MHz, $CDCl_3$)

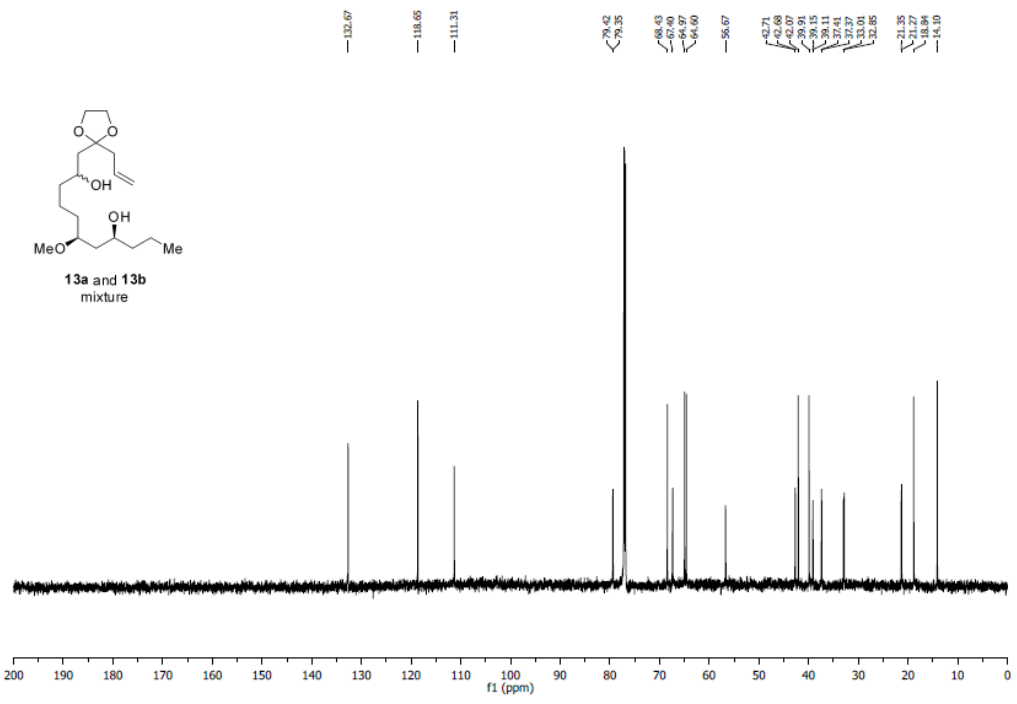


Figure S149. ^{13}C NMR of **13a/13b** as a1/1 mixture (200 MHz, $CDCl_3$)

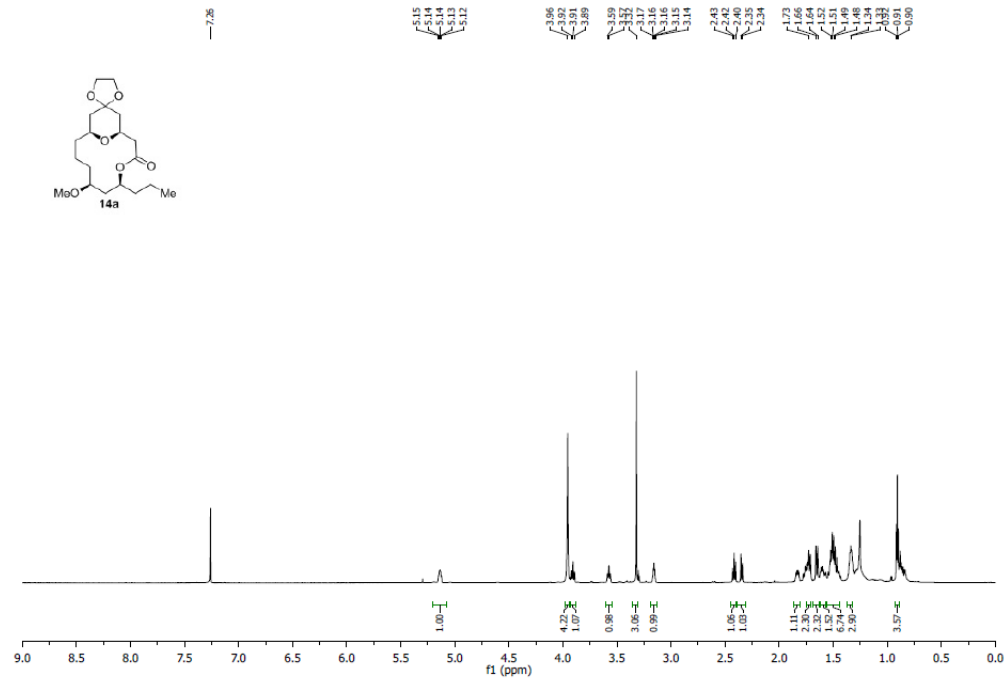


Figure S150. ^{1}H NMR of **14a** (800 MHz, $CDCl_3$)

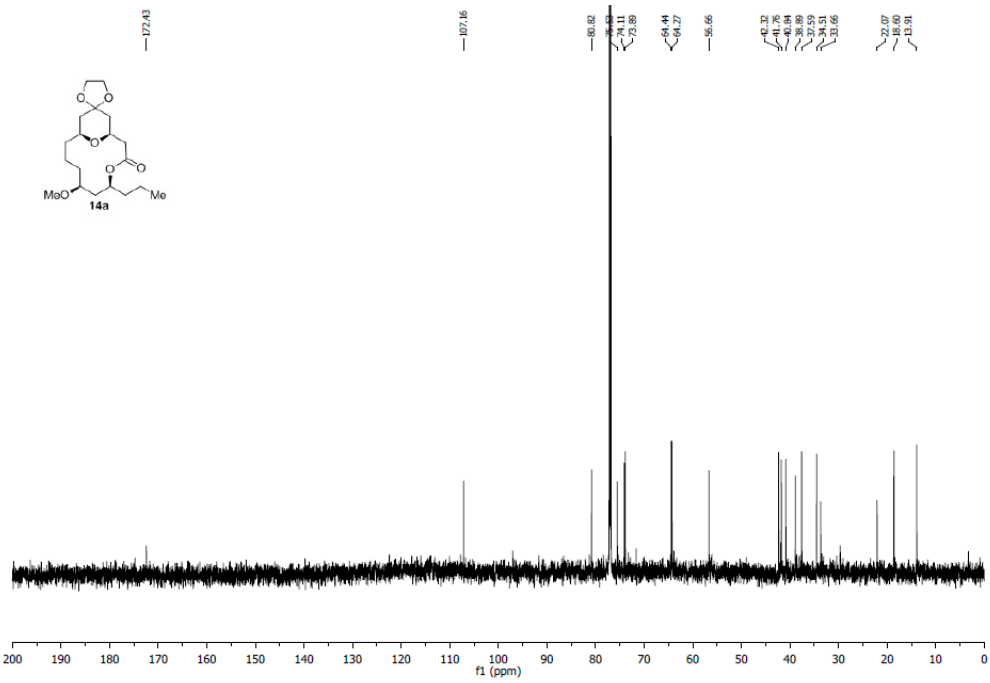


Figure S151. ^{13}C NMR of **14a** (200 MHz, $CDCl_3$)

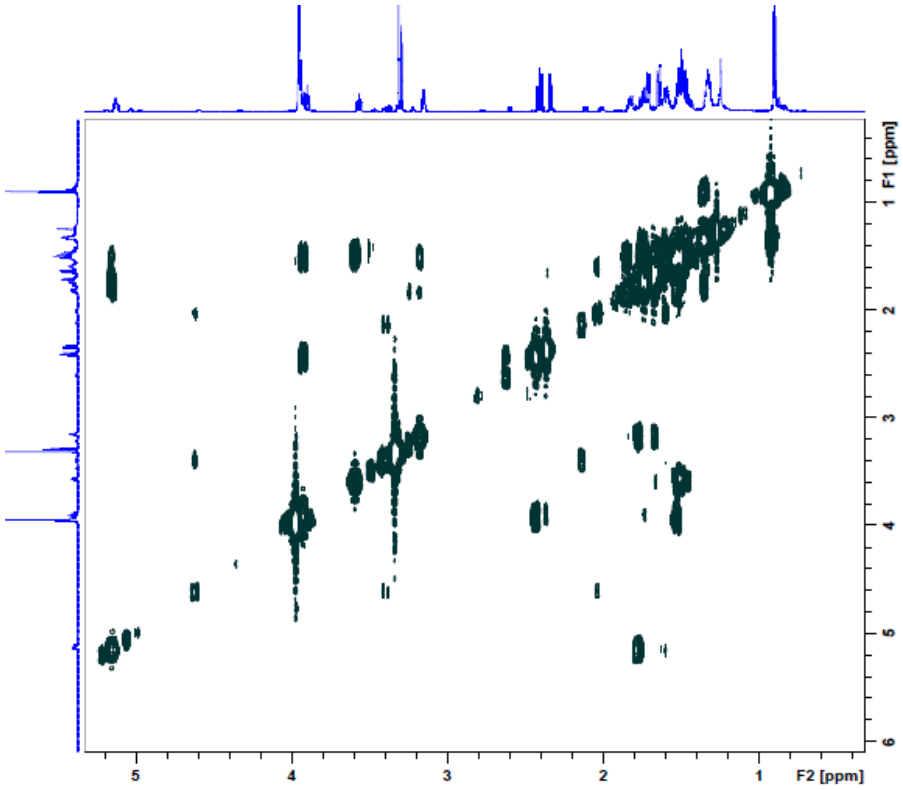


Figure S152. COSY of **14a** in $CDCl_3$

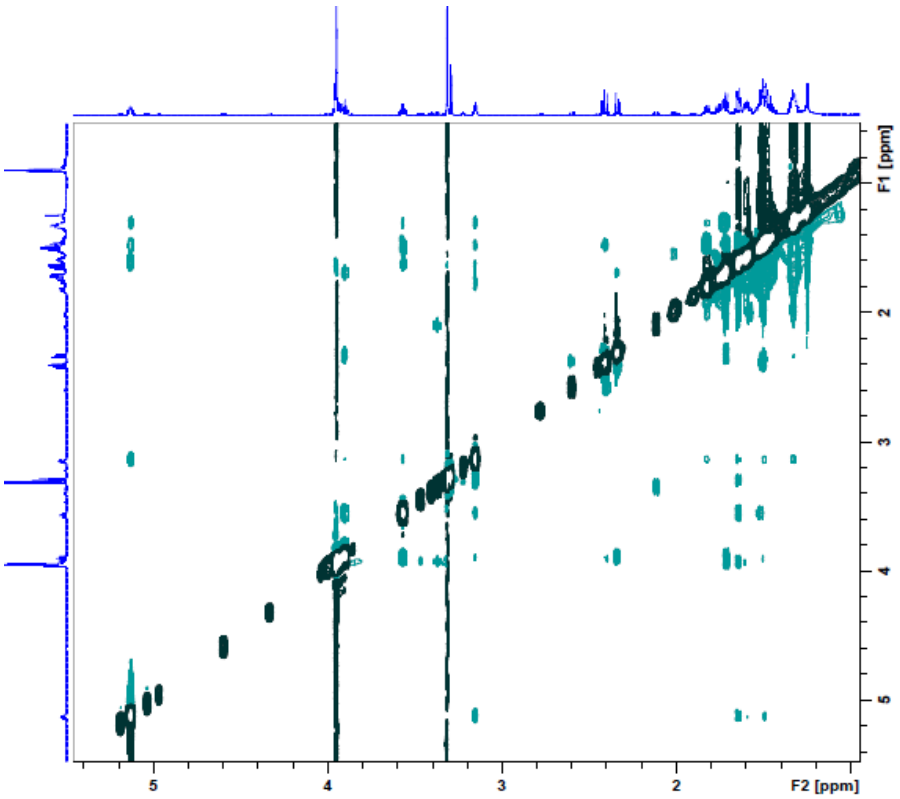


Figure S153. NOESY of **14a** in $CDCl_3$

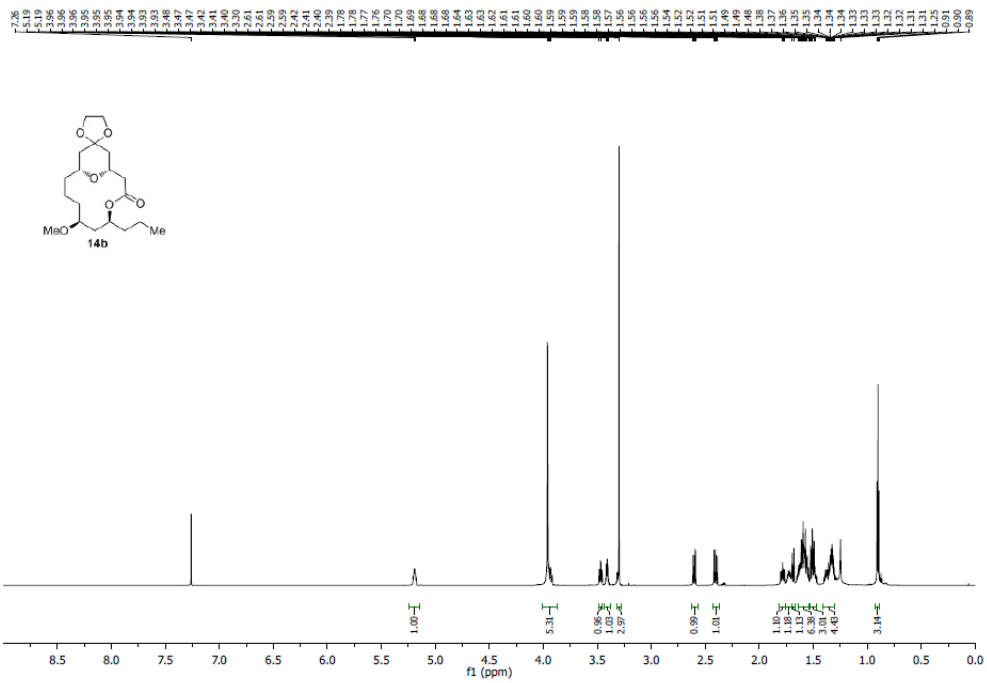


Figure S154. ^{1}H NMR of **14b** (800 MHz, $CDCl_3$)

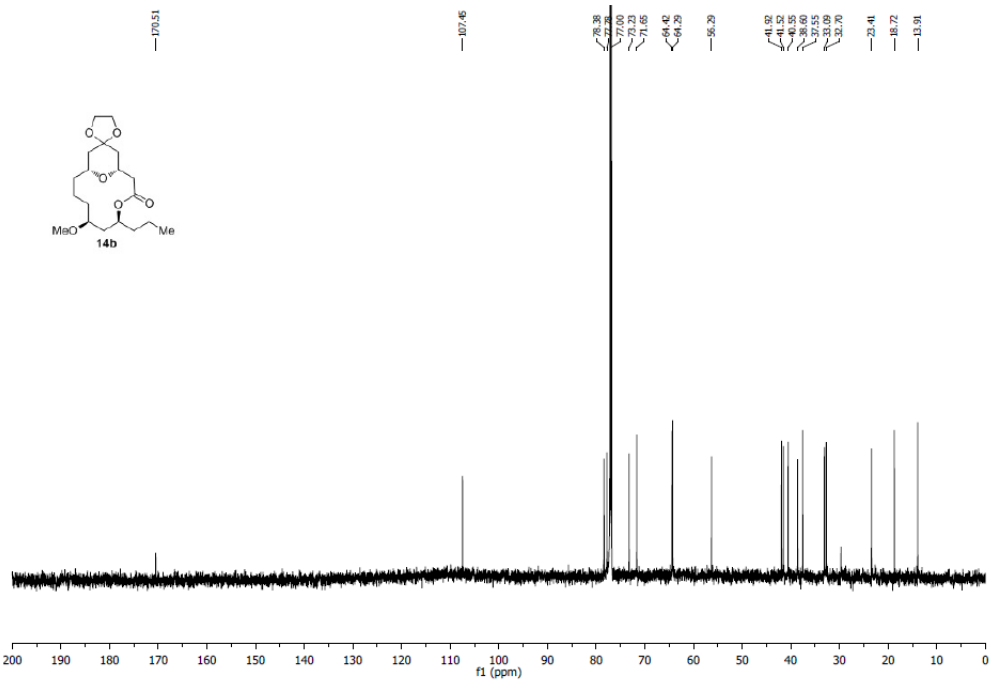


Figure S155. ^{13}C NMR of **14b** (200 MHz, $CDCl_3$)

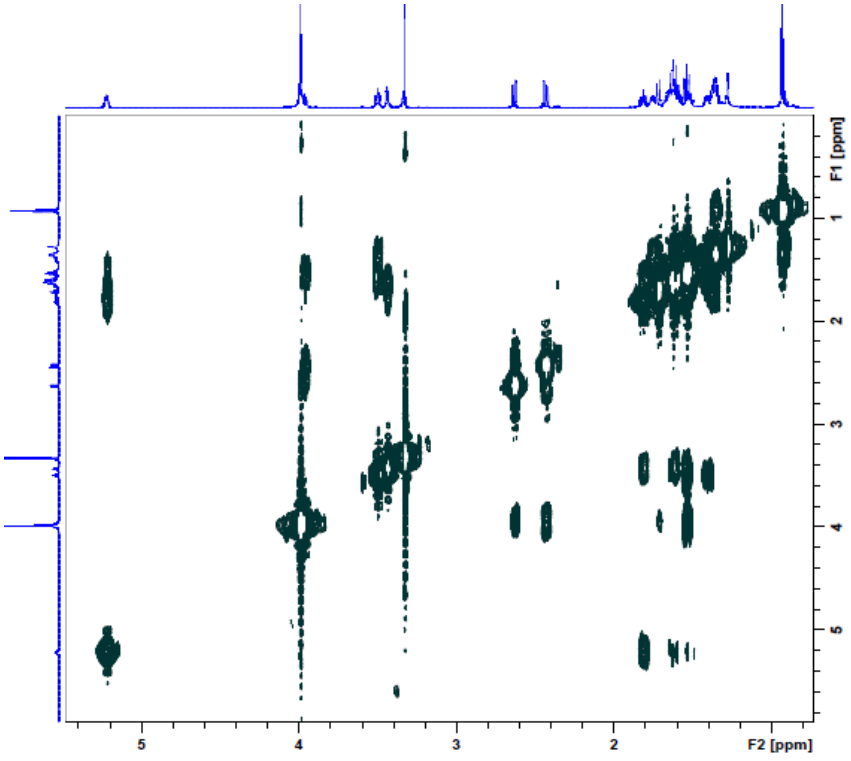


Figure S156. COSY of **14b** in $CDCl_3$

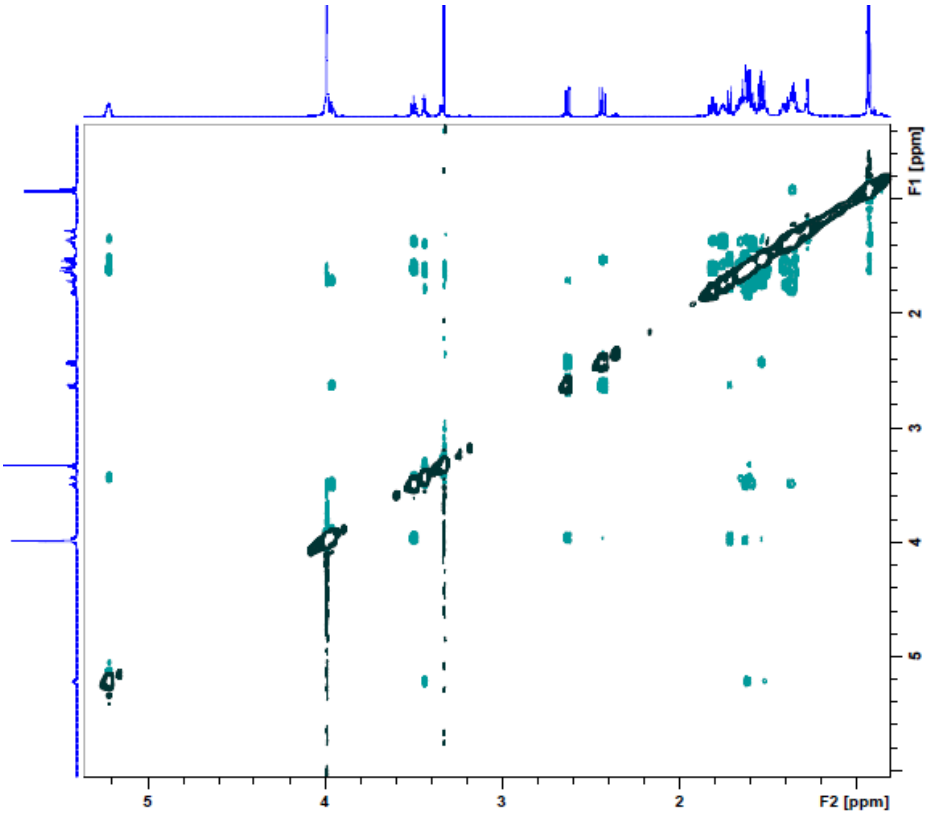


Figure S157. NOESY of **14b** in $CDCl_3$

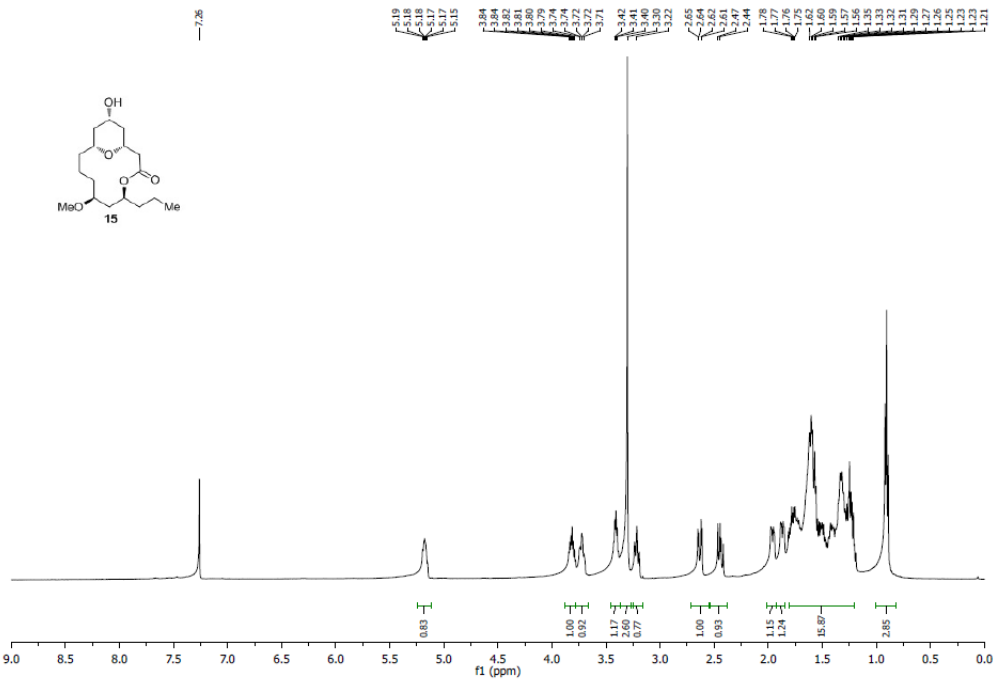


Figure S158. ^{1}H NMR of **15** (500 MHz, $CDCl_3$)

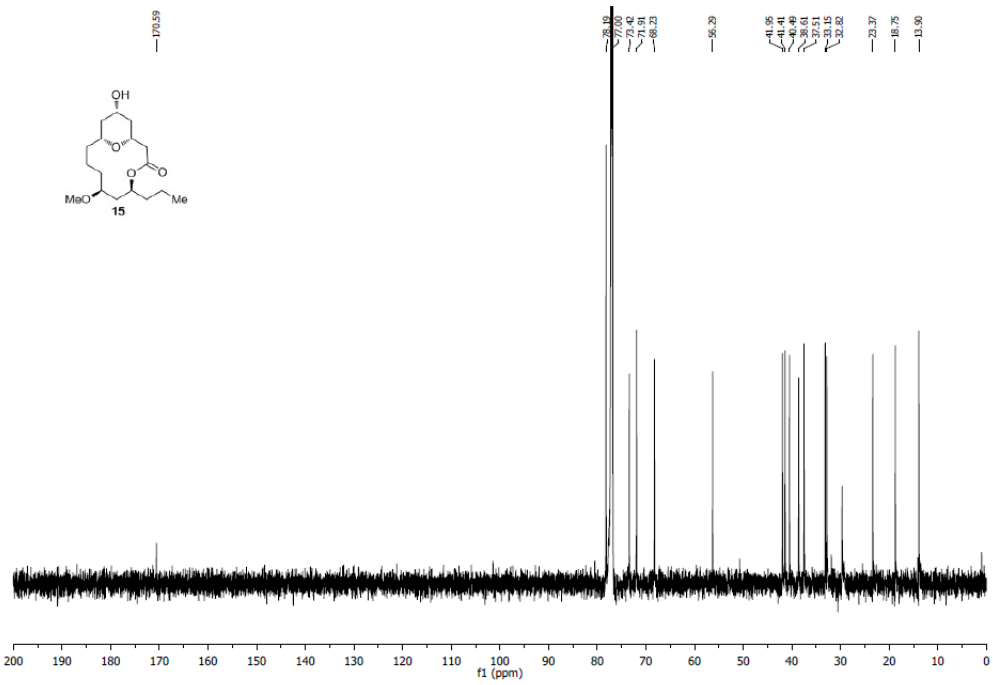


Figure S159. ^{13}C NMR of **15** (200 MHz, $CDCl_3$)

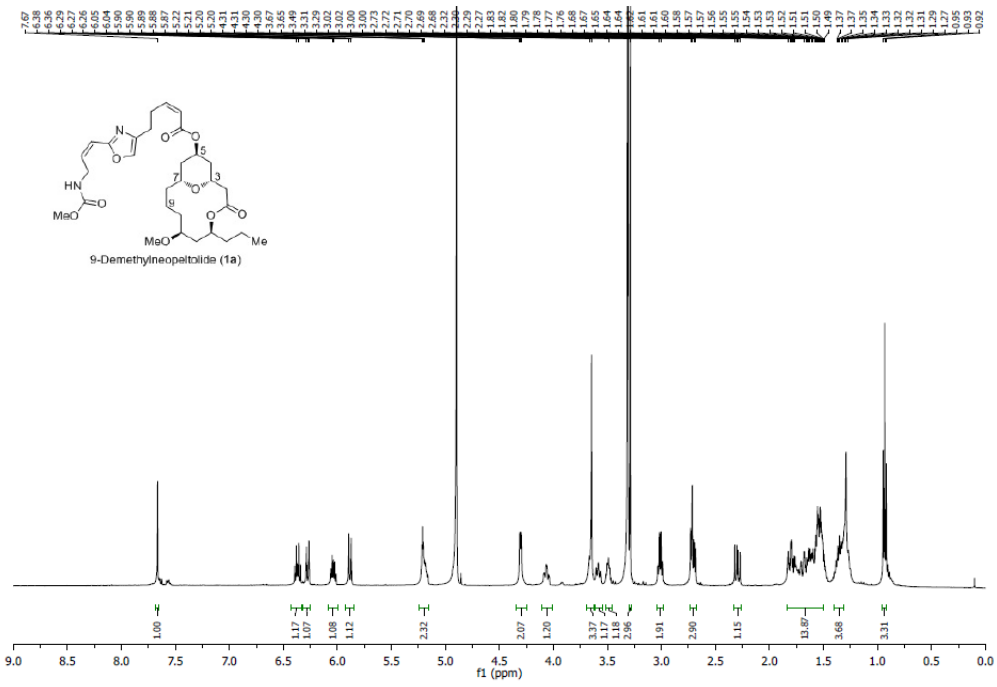


Figure S160. ^{1}H NMR of **1a** (500 MHz, CD_3OD)

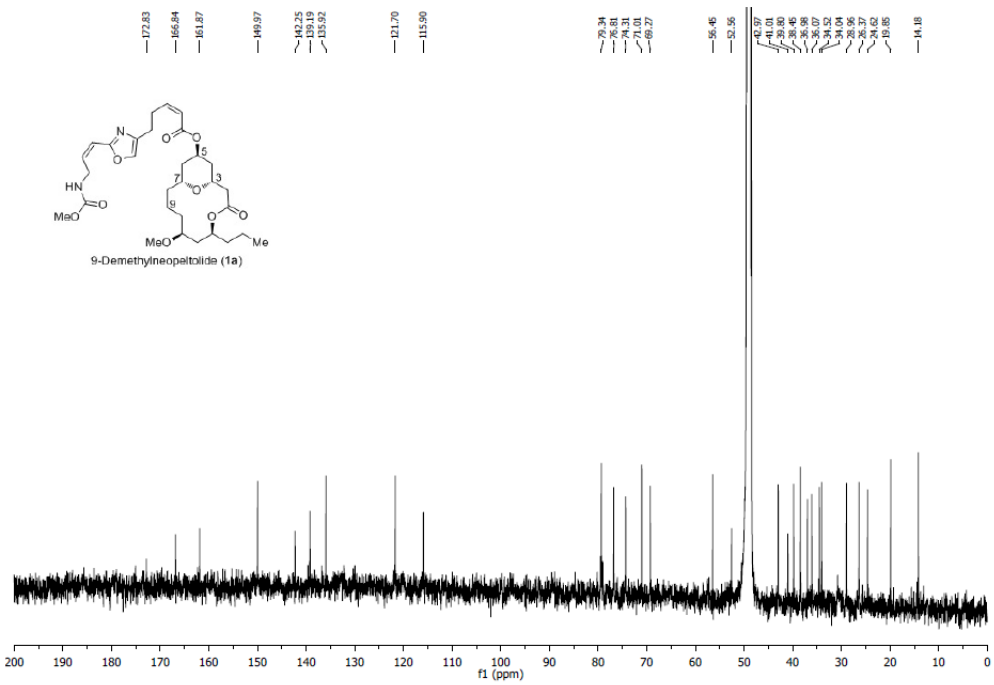


Figure S161. ^{13}C NMR of **1a** (125 MHz, CD_3OD)