Tandem Ring-Opening–Ring-Closing Metathesis for Functional Metathesis Catalysts

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EXPERIMENTAL SECTION

Materials:

Analytical grade solvents were purchased from Honeywell or Sigma-Aldrich and were used without further purification. Dry pyridine over molecular sieves was purchased from Sigma-Aldrich with the highest possible purity and used without further purification. Grubbs initiators **G1** and **G3**, dicyclopentadiene, ethyl vinyl ether and all other starting materials were purchased from Sigma-Aldrich unless stated otherwise and used without further purification. Exo-N-methylnorbornene imide (**MNI**) was synthesized as reported previously[1]. 3A Molecular sieves were purchased from Sigma-Aldrich and activated at 100°C under vacuum for 24 hours before use. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc. Deuterated dichloromethane was degassed by 3 successive freeze-vacuum-thaw cycles immediately before use.

Instrumentation:

ESI-MS analysis was carried out on a Bruker Daltonics Esquire HCT Mass Spectrometer with acetonitrile as the solvent. Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-ToF)-MS analyses of the polymers were carried out on a Bruker ultrafleXtreme^{TM} using 2-[(2E)-3-(4-*tert*butylphenyl)-2-methylprop-2-enylidene]malononitrile (**DCTB**) as the matrix and silver trifluoroacetate as the ionizing salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with a Viscotek GPCmax VE2001 GPC Solvent/Sample Module, a Viscotek UV-Detector 2600, a Viscotek VE3580 RI-Detector, and two ViscotekT6000 M columns (7.8×300 mm, 10^3–10^7Da) connected in series. All measurements were carried out at room temperature using THF as the eluent with a flow rate of 1 mL/min. The system was calibrated with polystyrene standards in a range from $10^3$to 3×10^6Da. NMR spectra were recorded on a Bruker Avance III 300

MHz NMR spectrometer (^{1}H-NMR 300 MHz; ^{13}C-NMR 75MHz). NMR signals were referenced internally to residual solvent signals. Ultra performance liquid chromatography / Mass spectrometry (UPLC-MS) analysis (LC-MS) was performed on a Waters UPLC® (H-Class Acquity) System equipped with a photodiode array detector (PDA), a SQ-detector (ESI & APCI Ionisation mode) and an ACQUITY UPLC® BEH C18 column (1.7 µm, 2.1 x50 mm). For single-crystal measurements, a Stoe IPDS II, equipped with monochromated Mo Kalpha1 radiation (0.71073 Å) were used for **S4** and a Stoe IPDS IItheta, equipped with monochromated Cu Kalpha1 radiation (1.54186 Å) for **3** and **G1-OMe**

Typical procedure for RORCM with **G1** in an NMR tube:

G1 was dissolved in dry degassed dichloromethane-d_2 and purged by continuous flow of argon for 15 min. Separately, a mixture of RORCM substrate in dry, degassed dichloromethane-d_2 was prepared. This mixture was quickly added to the **G1** solution. The collective solution was transferred in an NMR tube. The NMR tube was capped and inverted once to ensure efficient mixing. NMR spectra were measured till completion (or till no further reaction was seen).

For the reaction kinetics, ^{1}H-NMR was recorded every 5 minutes at room temperature till two hours and then every 15 minutes till two more hours and finally every 30 minutes till no appreciable change in the integration of the carbene peaks were observed.

Typical procedure for RORCM with **G3.1** in an NMR tube:

G3 was dissolved in dry degassed dichloromethane-d_2 and purged by continuous flow of argon for 15 min. 50 equivalents of pyridine were added and the mixture was stirred for 10 min. Separately, a mixture of RORCM substrate in dry, degassed dichloromethane-d_2 was prepared. This mixture was quickly added to the **G3** solution. The collective solution was transferred in an NMR tube. The NMR tube was capped and inverted once to ensure efficient mixing. NMR spectra were measured till

completion (or till no further reaction was seen). This mixture was then subjected to vacuum to remove the solvent and the pyridine for further use of the new functional metathesis catalyst.

For the reaction kinetics, ^{1}H-NMR was recorded every 5 minutes at room temperature till two hours and then every 15 minutes till two more hours and finally every 30 minutes till no appreciable change in the integration of the carbene peaks were observed.

Typical procedure for RCM with in situ synthesized **G1-OH** and **G1-OTIPS** in an NMR tube:

G1-OH and G1-OTIPS were synthesized according to the above described procedure in an NMR tube within 20 and 35 minutes respectively. Separately, a mixture of 10 eq of RCM substrate (diethyl diallylmalonate) in dry, degassed dichloromethane-d_2 was prepared. This mixture was quickly added to the **G1-OH** and **G1-OTIPS** solutions (which were present in the NMR tubes) separately. The NMR tube was capped and inverted once to ensure efficient mixing. NMR spectra were measured till completion (or till no further reaction was seen).

Typical one-pot heterotelechelic polymerization procedure :

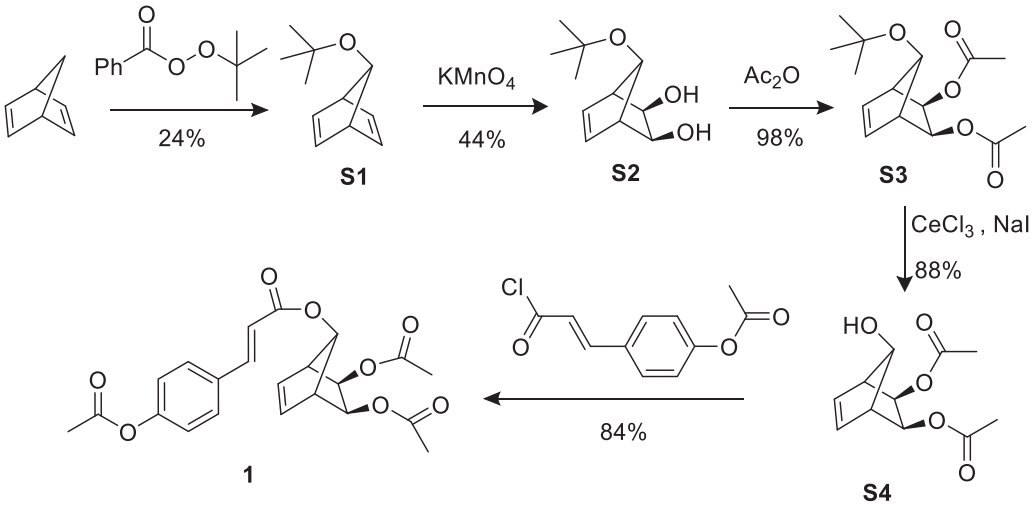
The initiator **G1** was subjected to the respective RORCM procedures (as reported above) and then dissolved in dry degassed dichloromethane. Separately, a mixture of monomer **MNI** and the quenching agent **MDHP** were mixed together and dissolved in dry degassed dichloromethane. This mixture was quickly added to the initiator solution and the mixture was stirred at room temperature for 1 hour to ensure complete consumption of the monomer. The polymerization was quenched with 0.1mL of ethyl vinyl ether to terminate any active ruthenium metathesis species and then the solution was concentrated by a flow of argon. The concentrated solution was added to cold methanol to precipitate the heterotelechelic polymer. The polymer was

redissolved in dichloromethane and reprecipitated once more, filtered, and dried under high vacuum.

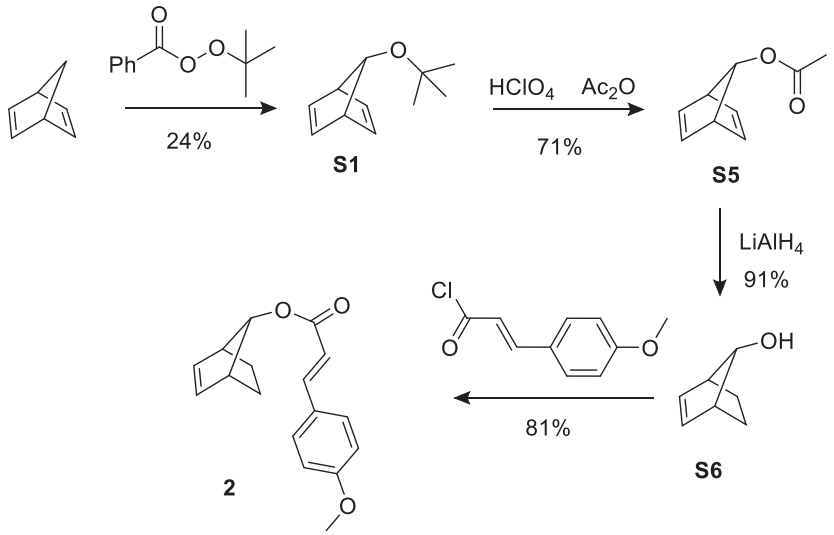
Typical procedure for MALDI-TOF sample preparation:

2 mg of the polymer was dissolved in 1mL of dichloromethane. 2µL of this solution was added to a 20 µL solution of 2mg/L DCTB in THF. 1 µL of 1M AgTFA in MeOH was added as the ionizing salt. This solution was stirred for 1 minute and then spotted on the MALDI target plate and left to crystallize for 30 minutes. Each MALDI-ToF measurement was calibrated against CsI_3 before recording the spectrum.

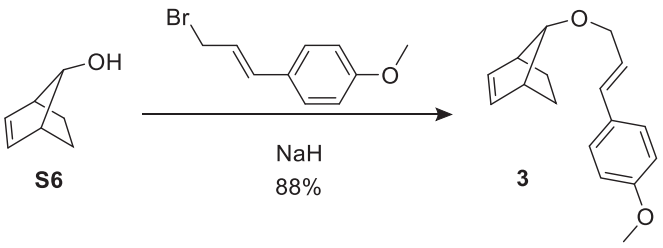
Synthesis Schemes:



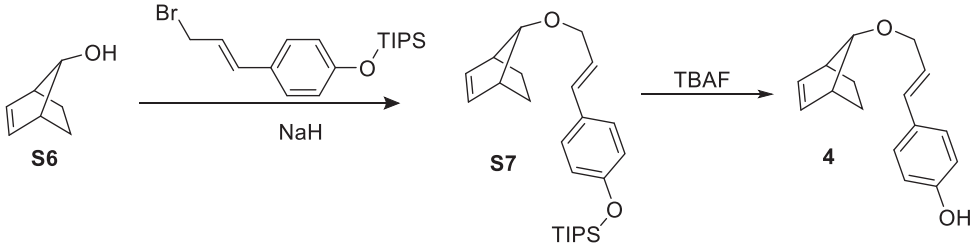
Scheme S1. Synthesis of RORCM substrate **1**.



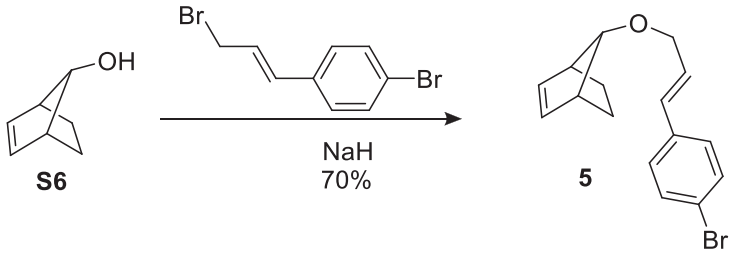
Scheme S2. Synthesis of the anti substituted RORCM substrate **2**.



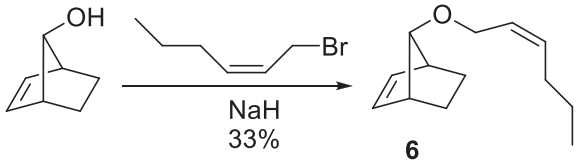
Scheme S3. Synthesis of anti substituted RORCM substrate **3**.



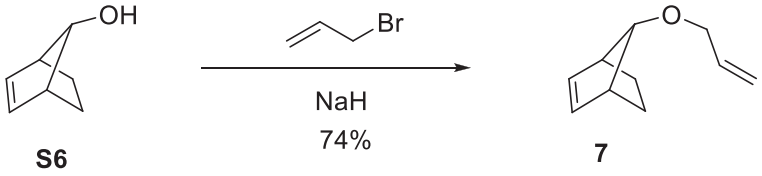
Scheme S4. Synthesis of RORCM substrate **4** to synthesize metathesis catalysts containing the phenol group.



Scheme S5. Synthesis of the p-bromo substituted compound **5**.



Scheme S6. Synthesis of anti substituted RORCM substrate **6**.



Scheme S7. Synthesis of anti substituted RORCM substrate **7**.

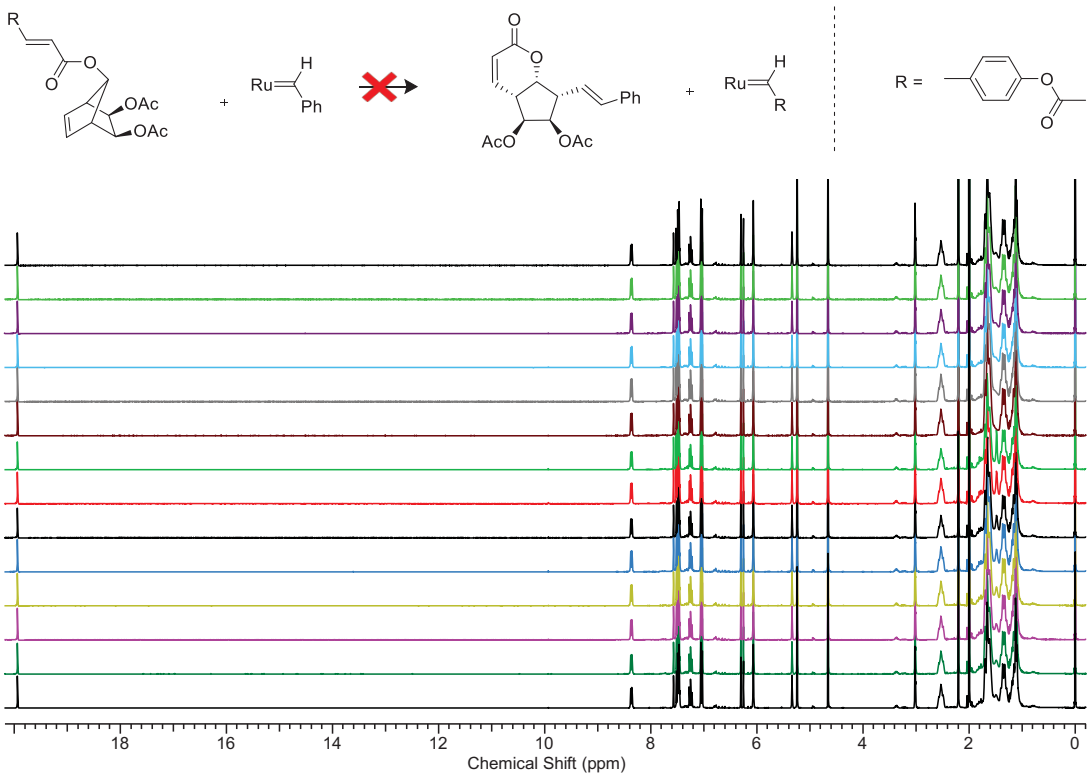


Figure S1: Time resolved ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectra. No reaction was observed on addition of **G1** to 3 equivalents of **1** even after 24 h.

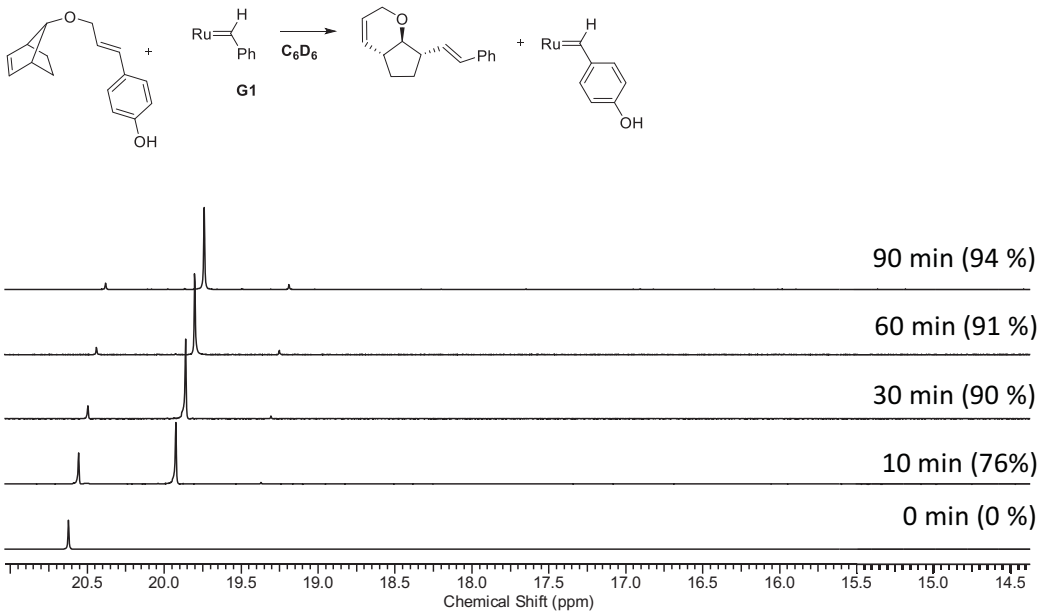


Figure S2: Time resolved ^{1}H-NMR (benzene-d_6, 300 MHz) spectra of the reaction of **G1** with 3 equivalents of compound **4**. The reaction needed more time as compared to the reaction in dichloromethane-d_2.

MALDI-ToF Data:

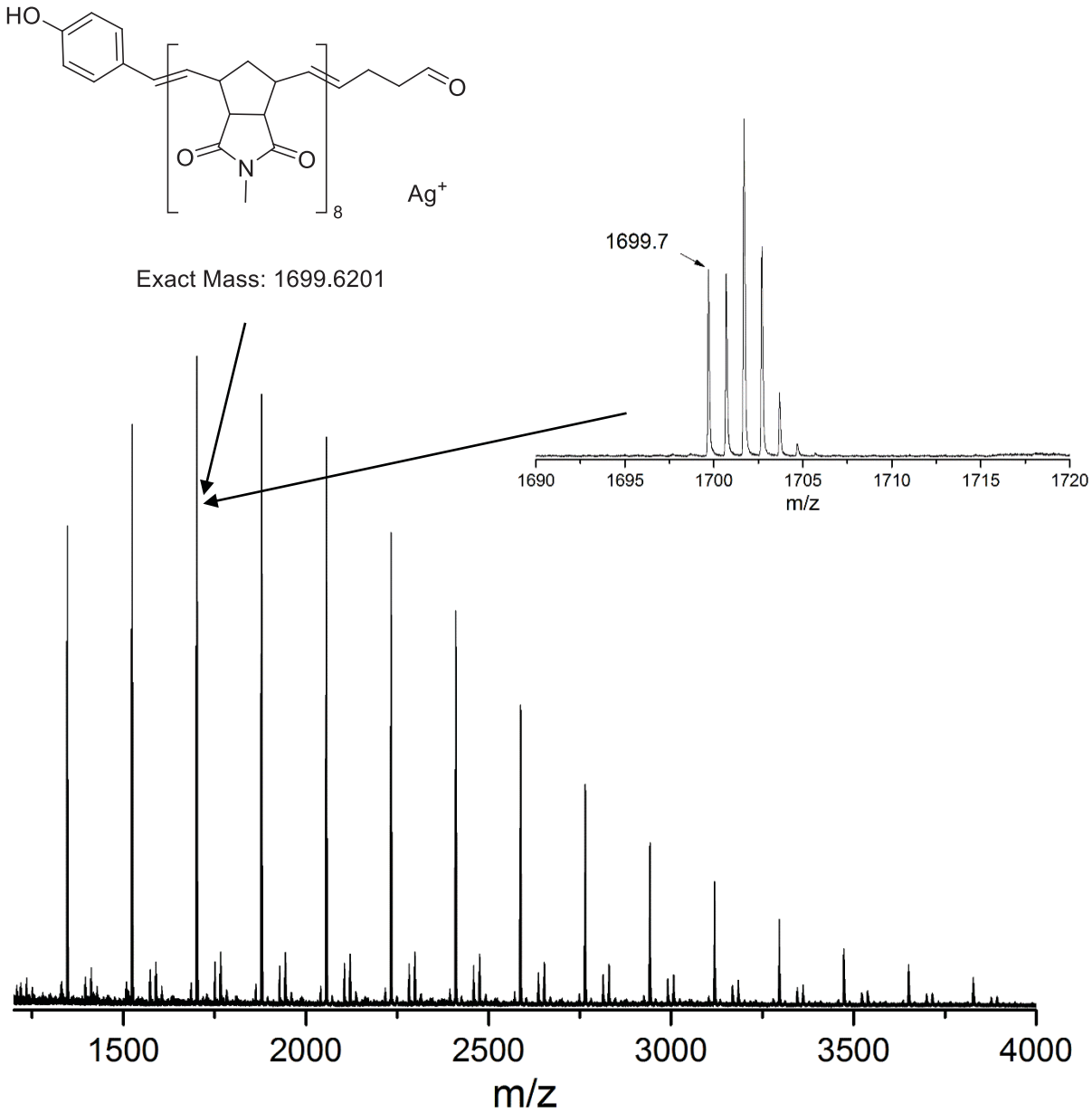
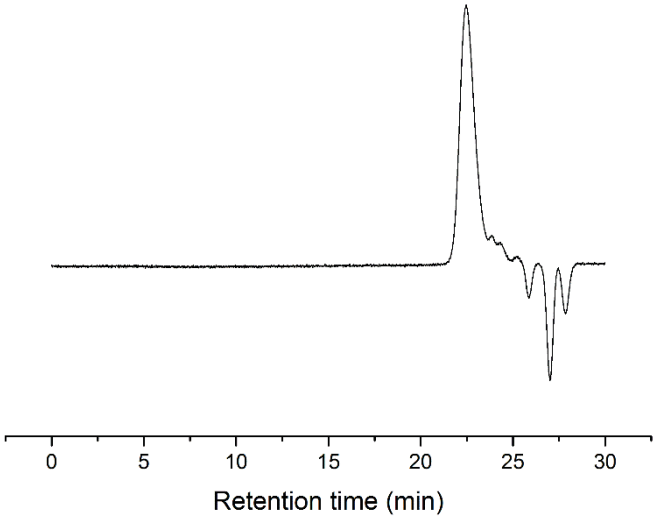


Figure S3: MALDI-ToF mass spectrum of the heterotelechelic polymer synthesized with **G1**. On top, the zoomed in region of the selected peak is shown. The observed molecular weight is in excellent agreement with the theoretically calculated molecular weight.

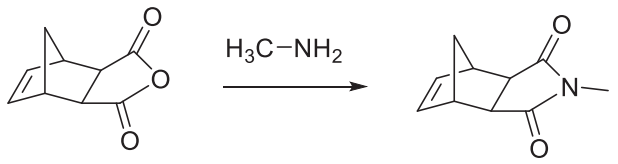
GPC Data:



Mn	Mw	PDI
3720	4460	1.20

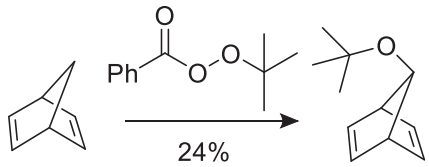
Figure S4 : GPC (THF) trace of heterotelechelic polymer with **G1**.

Synthetic procedures:



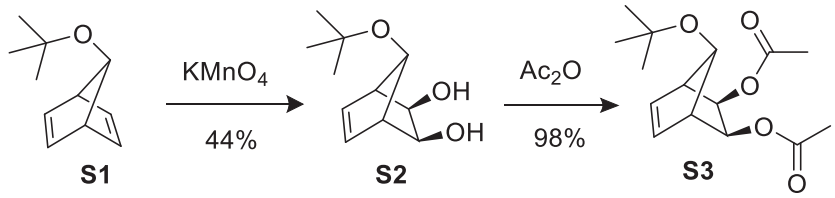
exo-carbic anhydride MNI

MNI was prepared according to the previously reported procedure.[2] ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 6.28 (t, J=1.8 Hz, 2 H), 3.20 - 3.36 (m, 2 H), 2.96 (s, 3 H), 2.69 (d, J=1.1 Hz, 2 H), 1.51 (dt, J=9.9, 1.5 Hz, 1 H), 1.07 - 1.31 ppm (m, 1 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 178.1, 137.7, 47.9, 45.1, 42.9, 24.6 ppm

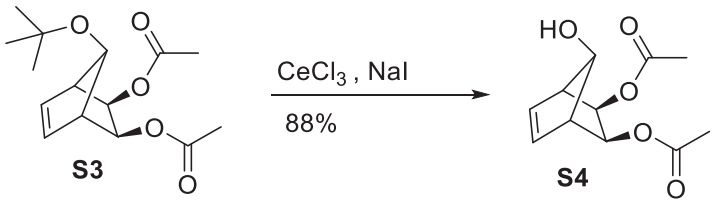


S1

Synthesis of 7-(tert-butoxy)-norbornadiene (**S1**): Norbornadiene (100g, 1.09mol) and cuprous bromide (32mg, 0.22mmol) were taken in a round bottom flask and 250mL benzene was added. The mixture was refluxed and t-butyl perbenzoate (81.67g, 420mmol) dissolved in 50mL benzene was added dropwise over 1 hour. The mixture was allowed to reflux for further 1 hour, cooled to room temperature and washed in a separating funnel with 3x100mL brine, 3x100mL 10% NaOH and again with 50mL brine. The solution was dried over magnesium sulfate and distilled (70°C at 10 mm Hg) to give 7-(tert-butoxy)-norbornadiene (16.56g, 100mmol, 24% yield) as a clear liquid. ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 6.65 (t, J=2.2 Hz, 2 H), 6.59 (t, J=1.5 Hz, 2 H), 3.79 (s, 1 H), 3.37 - 3.43 (m, 2 H), 1.15 ppm (s, 9 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 139.8, 137.3, 104.3, 73.5, 55.5, 28.3 ppm



Synthesis of (1R,2S,3R,4S,7r)-7-(tert-butoxy)bicyclo[2.2.1]hept-5-ene-2,3-diyl diacetate (**S3**): Compound **S3** was synthesized from **S1** according to the reported procedure[3]. $KMnO_4$ (4.84gm, 30.6mmol, 1eq) and 18-crown-6 (8.10g, 30.6 mmol, 1eq) were added as a solution in benzene-acetone (1:3, 200 mL). A solution of Na_2S0_3 (11.7 g, 93 mmol) and NaOH (3.6 g, 90 mmol) in water (90 mL) was added to quench the oxidant after the reaction was complete by TLC. The reaction mixture was saturated with KCl and extracted with dichloromethane. Chromatography on a silica gel column with EtOAc/Hexane 1:4 gave the diol **S2** as a slightly brown solid (2.67gms, 44% yield). ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 6.02 (dt, J=2.5, 1.0 Hz, 2 H), 4.41 (s, 1 H), 3.65 (dd, J=3.3, 1.4 Hz, 2 H), 2.71 - 2.82 (m, 4 H), 1.18 - 1.24 ppm (m, 9 H) This solid was kept stirring in acetic anhydride as the solvent for 12 hours. The acetic anhydride was removed under high vacuum and the remaining slurry was chromatographed on silica with EtOAc/hexane 1:10 to give 3.8 gms (98%) of **S3** as a white solid.



Synthesis of syn-7-hydroxynorbornene-2,3-diacetate (**S4**): Reactant **S3** (300mg, 1mmol, 1eq) was dissolved in dichloromethane (10mL) and cerium chloride (396mg, 1mmol, 1 eq) was added. The reaction was stirred for 10min and sodium iodide (160mg, 1mmol, 1eq) was subsequently added. The reaction was stirred at room temperature for 3 hours and chromatographed on silica with EtOAc/hexane 1:9 to give **S4** as a waxy solid (212mg, 88% yield). ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 6.18 (m, 2 H), 4.63 (s, 2 H), 4.60 (br. s., 1 H), 2.90 (m, 2 H), 2.05 ppm (s, 6 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 170.0, 133.0, 85.0, 68.6, 51.7, 20.7 ppm

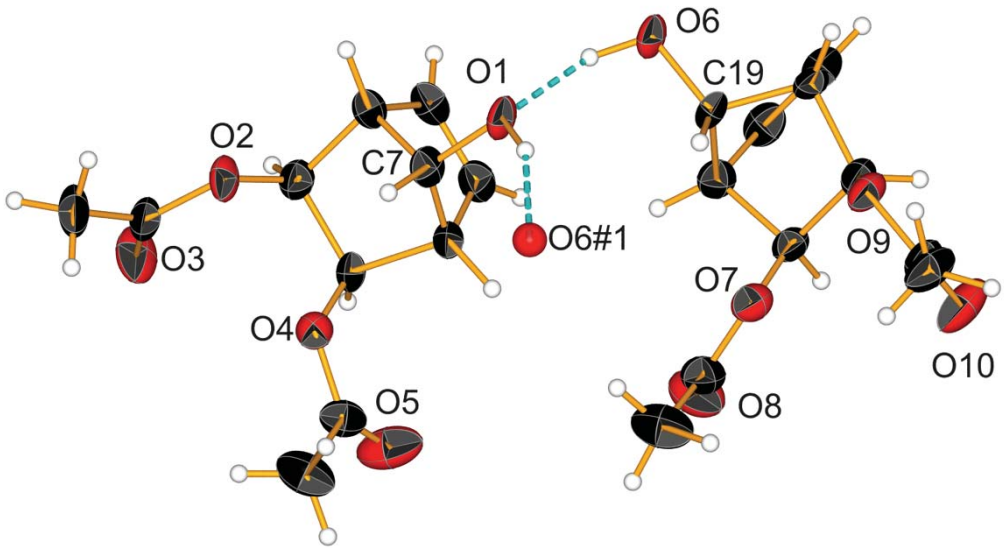


Figure S5: Single crystal X-ray structure of **S4** confirming the syn stereochemistry. CCDC 1474436 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table 1. Crystal data and structure refinement for **S4.**

Identification code	**S4**	
Empirical formula	C22 H28 O10	
Formula weight	452.44	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C* c	
Unit cell dimensions	a = 23.953(3) Å	α= 90°.
	b = 10.3652(10) Å	β= 101.666(9)°.
	c = 9.3193(11) Å	γ = 90°.
Volume	2266.0(4) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	960	
Crystal size	0.650 x 0.307 x 0.130 mm^3	
Theta range for data collection	1.736 to 24.997°.	
Index ranges	-27<=h<=28, -12<=k<=12, -10<=l<=10	
Reflections collected	3647	
Independent reflections	3647 [R(int) = ?]	
Completeness to theta = 24.997°	96.6 %	
Absorption correction	Integration	
Max. and min. transmission	0.9105 and 0.6650	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3647 / 4 / 292	
Goodness-of-fit on F^2	1.360	
Final R indices [I>2sigma(I)]	R1 = 0.1032, wR2 = 0.2885	
R indices (all data)	R1 = 0.1171, wR2 = 0.3152	
Absolute structure parameter	1.2(10)	
Extinction coefficient	0.13(3)	
Largest diff. peak and hole	0.859 and -0.614 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **S4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(6)	7529(2)	9959(6)	2453(9)	35(1)
O(1)	6921(2)	10016(6)	4626(9)	35(1)
O(9)	9204(3)	9150(6)	4809(8)	37(2)
O(7)	8521(3)	7456(6)	5527(8)	39(2)
O(10)	9827(4)	7545(11)	5410(11)	61(3)
O(3)	4638(3)	7545(10)	5384(11)	57(2)
O(4)	5973(3)	7488(6)	6827(8)	35(2)
O(2)	5262(3)	9157(6)	5407(8)	36(2)
O(8)	8078(4)	5545(8)	5435(11)	61(3)
O(5)	6412(5)	5556(8)	7149(11)	67(3)
C(7)	6473(3)	9257(9)	4963(11)	32(2)
C(6)	5930(4)	9310(10)	3766(12)	35(2)
C(12)	8524(4)	7348(8)	3991(12)	32(2)
C(2)	5958(3)	7359(9)	5263(12)	32(2)
C(19)	7991(3)	9231(9)	3222(11)	31(2)
C(13)	8935(4)	8403(8)	3585(12)	33(2)
C(4)	6450(4)	7577(10)	3234(12)	39(2)
C(16)	7985(5)	7542(10)	1467(12)	40(2)
C(14)	8510(3)	9284(9)	2513(11)	31(2)
C(5)	6093(4)	8479(9)	2567(11)	37(2)
C(3)	6530(3)	7782(10)	4884(11)	32(2)
C(18)	7932(4)	7740(10)	3038(11)	35(2)
C(22)	9669(4)	8600(11)	5668(14)	43(3)
C(9)	4534(5)	9467(12)	6743(16)	50(3)
C(1)	5541(4)	8423(9)	4457(11)	34(2)
C(15)	8337(4)	8457(10)	1160(13)	42(3)
C(11)	6255(7)	6724(14)	9261(15)	58(3)
C(23)	9929(5)	9453(11)	6887(15)	52(3)
C(10)	6234(4)	6490(9)	7645(12)	38(2)
C(20)	8262(5)	6481(10)	6120(14)	44(3)
C(21)	8257(7)	6753(14)	7691(16)	65(4)
C(8)	4802(4)	8609(10)	5808(14)	40(3)

Table 3. Bond lengths [Å] and angles [°] for **S4**.

O(6)-C(19)	1.410(10)
O(6)-H(6O)	0.96(3)
O(1)-C(7)	1.416(11)
O(1)-H(1O)	0.97(3)
O(9)-C(22)	1.359(12)
O(9)-C(13)	1.421(12)
O(7)-C(20)	1.360(13)
O(7)-C(12)	1.437(14)
O(10)-C(22)	1.197(15)
O(3)-C(8)	1.210(15)
O(4)-C(10)	1.359(12)
O(4)-C(2)	1.456(13)
O(2)-C(8)	1.358(12)
O(2)-C(1)	1.431(11)
O(8)-C(20)	1.196(15)
O(5)-C(10)	1.190(14)
C(7)-C(6)	1.534(12)
C(7)-C(3)	1.538(15)
C(7)-H(7)	1.0000
C(6)-C(5)	1.524(15)
C(6)-C(1)	1.539(12)
C(6)-H(6)	1.0000
C(12)-C(13)	1.567(12)
C(12)-C(18)	1.568(13)
C(12)-H(12)	1.0000

C(2)-C(3)	1.548(11)
C(2)-C(1)	1.573(12)
C(2)-H(2)	1.0000
C(19)-C(14)	1.523(12)
C(19)-C(18)	1.558(13)
C(19)-H(19)	1.0000
C(13)-C(14)	1.568(11)
C(13)-H(13)	1.0000
C(4)-C(5)	1.333(15)
C(4)-C(3)	1.525(15)
C(4)-H(4)	0.9500
C(16)-C(15)	1.339(16)
C(16)-C(18)	1.509(15)
C(16)-H(16)	0.9500
C(14)-C(15)	1.512(16)
C(14)-H(14)	1.0000
C(5)-H(5)	0.9500
C(3)-H(3)	1.0000
C(18)-H(18)	1.0000
C(22)-C(23)	1.475(16)
C(9)-C(8)	1.479(15)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(1)-H(1)	1.0000
C(15)-H(15)	0.9500
C(11)-C(10)	1.516(17)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(20)-C(21)	1.493(19)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(19)-O(6)-H(6O)	109.5
C(7)-O(1)-H(1O)	109.5
C(22)-O(9)-C(13)	115.4(8)
C(20)-O(7)-C(12)	116.3(8)
C(10)-O(4)-C(2)	114.1(7)
C(8)-O(2)-C(1)	117.0(7)
O(1)-C(7)-C(6)	112.8(8)
O(1)-C(7)-C(3)	117.5(7)
C(6)-C(7)-C(3)	94.1(7)
O(1)-C(7)-H(7)	110.5
C(6)-C(7)-H(7)	110.5
C(3)-C(7)-H(7)	110.5
C(5)-C(6)-C(7)	102.0(8)
C(5)-C(6)-C(1)	103.7(7)
C(7)-C(6)-C(1)	99.8(7)
C(5)-C(6)-H(6)	116.3
C(7)-C(6)-H(6)	116.3
C(1)-C(6)-H(6)	116.3
O(7)-C(12)-C(13)	108.4(8)
O(7)-C(12)-C(18)	110.9(7)
C(13)-C(12)-C(18)	102.9(7)
O(7)-C(12)-H(12)	111.4
C(13)-C(12)-H(12)	111.4
C(18)-C(12)-H(12)	111.4
O(4)-C(2)-C(3)	111.0(7)
O(4)-C(2)-C(1)	107.4(7)
C(3)-C(2)-C(1)	101.4(7)
O(4)-C(2)-H(2)	112.1
C(3)-C(2)-H(2)	112.1

C(1)-C(2)-H(2)	112.1
O(6)-C(19)-C(14)	112.8(7)
O(6)-C(19)-C(18)	115.5(7)
C(14)-C(19)-C(18)	93.0(7)
O(6)-C(19)-H(19)	111.5
C(14)-C(19)-H(19)	111.5
C(18)-C(19)-H(19)	111.5
O(9)-C(13)-C(12)	113.1(8)
O(9)-C(13)-C(14)	108.9(7)
C(12)-C(13)-C(14)	101.6(7)
O(9)-C(13)-H(13)	110.9
C(12)-C(13)-H(13)	110.9
C(14)-C(13)-H(13)	110.9
C(5)-C(4)-C(3)	108.1(9)
C(5)-C(4)-H(4)	126.0
C(3)-C(4)-H(4)	126.0
C(15)-C(16)-C(18)	106.9(9)
C(15)-C(16)-H(16)	126.5
C(18)-C(16)-H(16)	126.5
C(15)-C(14)-C(19)	103.4(7)
C(15)-C(14)-C(13)	103.6(8)
C(19)-C(14)-C(13)	100.6(7)
C(15)-C(14)-H(14)	115.7
C(19)-C(14)-H(14)	115.7
C(13)-C(14)-H(14)	115.7
C(4)-C(5)-C(6)	106.9(9)
C(4)-C(5)-H(5)	126.6
C(6)-C(5)-H(5)	126.6
C(4)-C(3)-C(7)	101.1(8)
C(4)-C(3)-C(2)	104.7(8)
C(7)-C(3)-C(2)	100.3(7)
C(4)-C(3)-H(3)	116.1
C(7)-C(3)-H(3)	116.1
C(2)-C(3)-H(3)	116.1
C(16)-C(18)-C(19)	102.6(8)
C(16)-C(18)-C(12)	105.6(8)
C(19)-C(18)-C(12)	98.2(7)
C(16)-C(18)-H(18)	116.0
C(19)-C(18)-H(18)	116.0
C(12)-C(18)-H(18)	116.0
O(10)-C(22)-O(9)	121.3(10)
O(10)-C(22)-C(23)	127.0(10)
O(9)-C(22)-C(23)	111.7(9)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(2)-C(1)-C(6)	109.9(7)
O(2)-C(1)-C(2)	114.0(8)
C(6)-C(1)-C(2)	103.8(7)
O(2)-C(1)-H(1)	109.6
C(6)-C(1)-H(1)	109.6
C(2)-C(1)-H(1)	109.6
C(16)-C(15)-C(14)	107.6(10)
C(16)-C(15)-H(15)	126.2
C(14)-C(15)-H(15)	126.2
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5

C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(5)-C(10)-O(4)	124.1(10)
O(5)-C(10)-C(11)	125.0(11)
O(4)-C(10)-C(11)	110.8(10)
O(8)-C(20)-O(7)	122.3(11)
O(8)-C(20)-C(21)	127.0(11)
O(7)-C(20)-C(21)	110.7(10)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(3)-C(8)-O(2)	121.2(10)
O(3)-C(8)-C(9)	126.2(10)
O(2)-C(8)-C(9)	112.5(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$)for **S4**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(6)	15(2)	47(2)	41(2)	-1(2)	0(2)	2(2)
O(1)	15(2)	47(2)	41(2)	-1(2)	0(2)	2(2)
O(9)	25(3)	32(3)	48(4)	2(3)	-3(3)	4(2)
O(7)	37(4)	34(4)	43(5)	3(3)	3(3)	3(3)
O(10)	43(4)	47(5)	86(7)	-7(5)	-9(4)	17(4)
O(3)	40(4)	42(4)	94(7)	-8(5)	23(4)	-17(3)
O(4)	32(3)	40(4)	34(4)	4(3)	7(3)	2(2)
O(2)	19(3)	36(4)	54(5)	-5(3)	10(3)	-6(2)
O(8)	79(6)	42(5)	64(6)	0(4)	23(5)	-13(4)
O(5)	98(7)	42(5)	56(6)	3(4)	5(5)	18(5)
C(7)	22(4)	39(5)	32(5)	-3(4)	0(3)	-7(3)
C(6)	24(4)	34(5)	47(6)	5(4)	7(4)	-10(3)
C(12)	29(4)	25(4)	41(6)	4(4)	4(4)	4(3)
C(2)	18(4)	38(5)	39(6)	2(4)	6(3)	-1(3)
C(19)	23(4)	32(5)	36(6)	-1(4)	4(3)	10(3)
C(13)	25(4)	30(5)	43(6)	2(4)	3(3)	2(3)
C(4)	33(5)	39(5)	46(7)	2(4)	12(4)	-5(4)
C(16)	42(5)	38(5)	39(7)	-8(4)	5(4)	8(4)
C(14)	21(4)	32(4)	38(6)	10(4)	-3(3)	2(3)
C(5)	35(5)	45(6)	32(6)	-3(4)	10(4)	-11(4)
C(3)	22(4)	42(5)	34(6)	6(4)	8(3)	3(3)
C(18)	31(4)	37(5)	34(6)	0(4)	2(4)	-1(4)
C(22)	23(4)	45(7)	56(7)	8(5)	-3(4)	3(4)
C(9)	31(5)	53(7)	72(9)	-3(6)	26(5)	3(4)
C(1)	26(4)	36(5)	41(7)	1(4)	5(4)	0(3)
C(15)	33(4)	44(6)	45(7)	2(5)	2(4)	7(4)
C(11)	83(9)	56(7)	38(7)	1(6)	17(6)	-13(6)
C(23)	33(5)	41(6)	68(8)	4(6)	-18(5)	0(4)
C(10)	46(5)	32(5)	35(6)	2(4)	4(4)	-6(4)
C(20)	52(6)	35(6)	48(7)	8(5)	16(5)	6(4)
C(21)	93(9)	56(8)	46(8)	6(6)	16(7)	-4(7)
C(8)	23(4)	37(6)	60(7)	3(5)	13(4)	3(3)

Table 5. Hydrogen coordinates ($x 10^4$) and isotropic displacement parameters ($Å^2 x 10^3$) for **S4**.

	x	y	z	U(eq)

H(6O)	7210(20)	9880(100)	2930(80)	52
H(1O)	7210(30)	10150(100)	5510(40)	52
H(7)	6388	9519	5930	38
H(6)	5778	10189	3467	42
H(12)	8640	6464	3736	39
H(2)	5843	6472	4895	38
H(19)	8090	9483	4279	37
H(13)	9224	8009	3078	40
H(4)	6624	6920	2764	46
H(16)	7803	6891	819	48
H(14)	8652	10167	2347	38
H(5)	5966	8584	1540	44
H(3)	6882	7399	5497	39
H(18)	7590	7344	3325	42
H(9A)	4119	9379	6476	75
H(9B)	4641	10364	6598	75
H(9C)	4666	9229	7773	75
H(1)	5249	8016	3667	41
H(15)	8457	8567	256	50
H(11A)	6451	6004	9832	88
H(11B)	5866	6793	9435	88
H(11C)	6462	7528	9562	88
H(23A)	9782	9232	7763	78
H(23B)	9835	10353	6618	78
H(23C)	10344	9342	7092	78
H(21A)	8105	6003	8126	97
H(21B)	8016	7506	7757	97
H(21C)	8646	6928	8221	97

Table 6. Torsion angles [°] for **S4**.

O(1)-C(7)-C(6)-C(5)	74.0(9)
C(3)-C(7)-C(6)-C(5)	-48.2(8)
O(1)-C(7)-C(6)-C(1)	-179.6(8)
C(3)-C(7)-C(6)-C(1)	58.2(8)
C(20)-O(7)-C(12)-C(13)	-169.4(7)
C(20)-O(7)-C(12)-C(18)	78.3(9)
C(10)-O(4)-C(2)-C(3)	-81.2(10)
C(10)-O(4)-C(2)-C(1)	168.7(7)
C(22)-O(9)-C(13)-C(12)	81.5(10)
C(22)-O(9)-C(13)-C(14)	-166.3(8)
O(7)-C(12)-C(13)-O(9)	1.6(9)
C(18)-C(12)-C(13)-O(9)	119.2(8)
O(7)-C(12)-C(13)-C(14)	-115.0(8)
C(18)-C(12)-C(13)-C(14)	2.6(9)
O(6)-C(19)-C(14)-C(15)	-72.8(9)
C(18)-C(19)-C(14)-C(15)	46.4(8)
O(6)-C(19)-C(14)-C(13)	-179.7(8)
C(18)-C(19)-C(14)-C(13)	-60.4(8)
O(9)-C(13)-C(14)-C(15)	170.1(7)
C(12)-C(13)-C(14)-C(15)	-70.3(9)
O(9)-C(13)-C(14)-C(19)	-83.2(8)
C(12)-C(13)-C(14)-C(19)	36.4(9)
C(3)-C(4)-C(5)-C(6)	0.2(10)
C(7)-C(6)-C(5)-C(4)	32.0(9)
C(1)-C(6)-C(5)-C(4)	-71.4(9)
C(5)-C(4)-C(3)-C(7)	-32.1(9)
C(5)-C(4)-C(3)-C(2)	71.7(9)
O(1)-C(7)-C(3)-C(4)	-70.6(9)
C(6)-C(7)-C(3)-C(4)	47.8(7)
O(1)-C(7)-C(3)-C(2)	-178.0(8)
C(6)-C(7)-C(3)-C(2)	-59.6(8)
O(4)-C(2)-C(3)-C(4)	179.2(7)

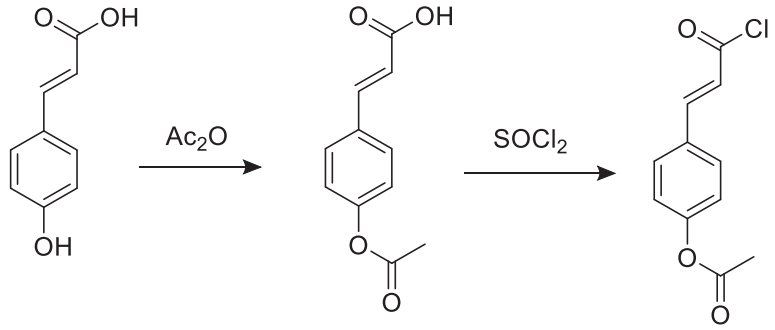
C(1)-C(2)-C(3)-C(4)	-66.9(9)
O(4)-C(2)-C(3)-C(7)	-76.2(9)
C(1)-C(2)-C(3)-C(7)	37.6(9)
C(15)-C(16)-C(18)-C(19)	32.1(10)
C(15)-C(16)-C(18)-C(12)	-70.2(10)
O(6)-C(19)-C(18)-C(16)	69.9(10)
C(14)-C(19)-C(18)-C(16)	-47.0(8)
O(6)-C(19)-C(18)-C(12)	178.1(8)
C(14)-C(19)-C(18)-C(12)	61.1(8)
O(7)-C(12)-C(18)-C(16)	-178.0(7)
C(13)-C(12)-C(18)-C(16)	66.2(9)
O(7)-C(12)-C(18)-C(19)	76.3(9)
C(13)-C(12)-C(18)-C(19)	-39.5(9)
C(13)-O(9)-C(22)-O(10)	-1.6(16)
C(13)-O(9)-C(22)-C(23)	178.6(9)
C(8)-O(2)-C(1)-C(6)	163.7(8)
C(8)-O(2)-C(1)-C(2)	-80.2(9)
C(5)-C(6)-C(1)-O(2)	-168.4(7)
C(7)-C(6)-C(1)-O(2)	86.6(8)
C(5)-C(6)-C(1)-C(2)	69.2(9)
C(7)-C(6)-C(1)-C(2)	-35.8(9)
O(4)-C(2)-C(1)-O(2)	-4.2(9)
C(3)-C(2)-C(1)-O(2)	-120.7(8)
O(4)-C(2)-C(1)-C(6)	115.4(8)
C(3)-C(2)-C(1)-C(6)	-1.2(10)
C(18)-C(16)-C(15)-C(14)	-1.1(11)
C(19)-C(14)-C(15)-C(16)	-31.2(10)
C(13)-C(14)-C(15)-C(16)	73.5(9)
C(2)-O(4)-C(10)-O(5)	-3.5(14)
C(2)-O(4)-C(10)-C(11)	177.5(9)
C(12)-O(7)-C(20)-O(8)	4.6(14)
C(12)-O(7)-C(20)-C(21)	-176.4(10)
C(1)-O(2)-C(8)-O(3)	0.4(15)
C(1)-O(2)-C(8)-C(9)	-177.8(9)

Symmetry transformations used to generate equivalent atoms:

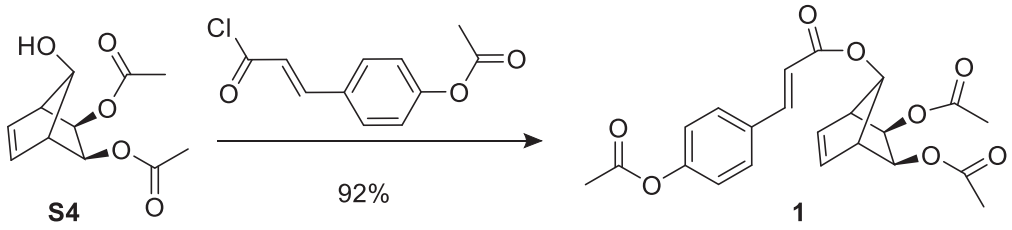
Table 7. Hydrogen bonds for **S4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(6O)...O(1)	0.96	1.86	2.723(12)	149.5
O(1)-H(1O)...O(6)#1	0.97	1.82	2.741(12)	156.5

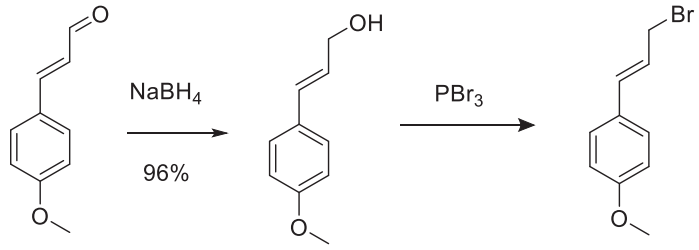
Symmetry transformations used to generate equivalent atoms:
#1 x,-y+2,z+1/2



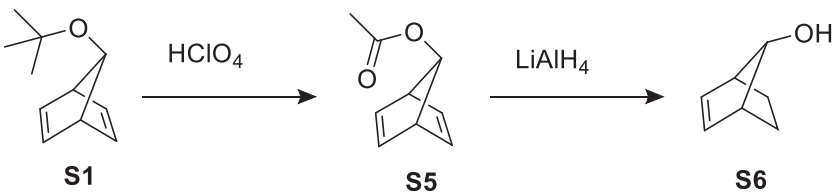
4-hydroxycinnamic acid was converted to the 4-acetoxy cinnamic acid as already reported.[4] The 4-acetoxy cinnamic acid was refluxed overnight in thionyl chloride and the reaction mixture was cooled to room temperature. The thionyl chloride was removed under high vacuum leaving behind 4-acetoxy cinnamoylchloride as a yellow solid, which was used immediately without further purification.



Synthesis of **1**: 4-acetoxy cinnamoylchloride (596mg, 2.65mmol, 3eq) from above was dissolved in dry dichloromethane (7mL) and 1mL of pyridine was added. To this solution, a solution of compound **S4** (200mg, 0.884mmol, 1eq) in dry dichloromethane (3mL) was added slowly at 0°C. After stirring at r.t. overnight, the mixture was evaporated to dryness under high vacuum and subsequent column chromatography on silica with ETOAc/hexane 1:9 gave the desired compound **1** as a colourless solid in 92% yield. ^{1}H-NMR (dichloromethane-d_2, 300MHz): δ (ppm) = 7.62 (d, *J*=16.0 Hz, 1 H), 7.56 (d, *J*=8.6 Hz, 2 H), 7.12 (d, *J*=8.6 Hz, 2 H), 6.36 (d, *J*=16.0 Hz, 1 H), 6.15 (s, 2 H), 5.42 (s, 1 H), 4.73 (s, 2 H), 3.10 (m, 2 H), 2.28 (s, 3 H), 2.07 ppm (s, 6 H).

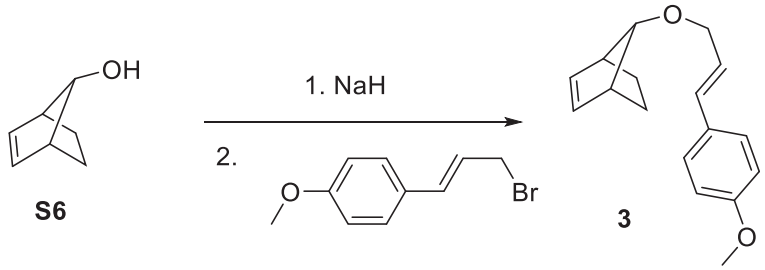


Synthesis of 4-methoxy cinnamylbromide: 4methoxycinnamaldehyde (2g, 12.3mmol, 1eq) was kept stirring in 20mL methanol and sodium borohydride (0.467g, 12.3mmol, 1eq) was added slowly by a spatula in small portions. After complete addition, the solution was stirred at room temperature for 2 hours. This solution was then quenched with 20mL 1M HCl. The methanol was evaporated and the precipitate was filtered. The residue was washed thoroughly with water and dried overnight in vacuum to give 4-methoxy cinnamic alcohol as a colourless solid in 96% yield. ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 7.34 (d, *J*=8.8 Hz, 2 H), 6.88 (s, 2 H), 6.57 (d, *J*=15.9 Hz, 1 H), 6.16 - 6.32 (m, 1 H), 4.31 (t, *J*=5.9 Hz, 2 H), 3.82 (s, 3 H), 1.44 ppm (t, *J*=5.9 Hz, 1 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 159.3, 131.0, 129.4, 127.7, 126.2, 114.0, 63.9, 55.3 ppm. 4-methoxy cinnamic alcohol (2g, 12.2mmol, 1eq) was dissolved in dry dichloromethane (15mL) and PBr_3 (1.65g, 6.1mmol, 0.5eq) was added dropwise at 0°Cunder an argon atmosphere. After stirring the mixture for 6 hours at room temperature, the reaction was quenched with a saturated solution of sodium bicarbonate. The solution was extracted 3 times with dichloromethane, dried over $MgSO_4$ and the solvent was evaporated in vacuum. This compound was not stable on the bench and degradation was seen. Hence, this compound was used immediately for the next step, without further purification.



Compound **S6** was prepared according to previously reported procedure.[5] ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 5.98 (s, 2 H), 3.58 (s, 1 H), 2.55 (br. s., 2 H), 1.81

(d, *J*=7.6 Hz, 2 H), 1.62 (s, 1 H), 1.03 ppm (d, *J*=7.0 Hz, 2 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 134.5, 82.5, 45.6, 21.3 ppm.



Synthesis of (1R,4S,7s)-7-(((E)-3-(4-methoxyphenyl)allyl)oxy)bicyclo[2.2.1]hept-2-ene (**3**): To a suspension of NaH (65.4mg, 2.72mmol, 1.5eq) in 20mL diethyl ether at 0°C was added alcohol **S6** (200mg, 1.82mmol, 1eq). This solution was stirred at 0°C for 3 hours, added 2mL of dry N,N-dimethylformamide then the crude solution containing the 4-methoxycinnamyl bromide in dichloromethane was added dropwise over 30 min. This solution was stirred overnight till all the alcohol **S6** was consumed (by TLC). The solution was quenched with ice water and diluted with water. This solution was extracted with 3x50mL ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed under vacuum. This crude compound was chromatographed on silica with EtOAc/hexane 1:9 to obtain the pure, colourless, solid compound **3** in 88% yield. ^{1}H-NMR (dichloromethane-d2, 300MHz): δ (ppm) = 7.28 - 7.36 (m, 2 H), 6.81 - 6.88 (m, 2 H), 6.51 (d, J=15.9 Hz, 1 H), 6.13 (dt, J=15.9, 6.0 Hz, 1 H), 5.98 (t, J=2.2 Hz, 2 H), 4.03 (dd, J=6.1, 1.4 Hz, 2 H), 3.79 (s, 3 H), 3.28 (s, 1 H), 2.67 (d, J=1.7 Hz, 2 H), 1.74 - 1.83 (m, 2 H), 0.92 - 1.01 ppm (m, 2 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 159.2, 134.2, 131.6, 129.6, 127.6, 124.2, 113.9, 88.9, 69.1, 55.3, 43.5, 21.8 ppm

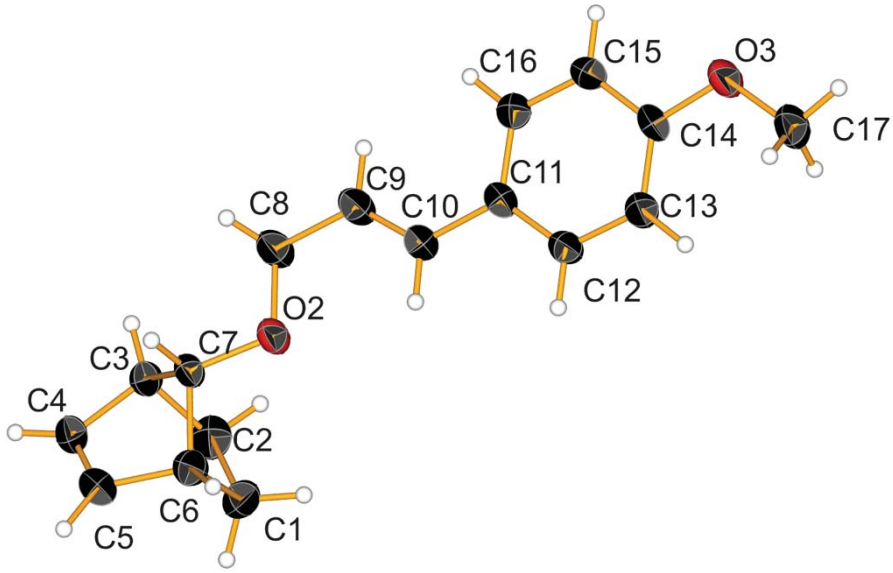


Figure S6. Single Crystal X-ray structure of **3**. CCDC 1474437 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table 1. Crystal data and structure refinement for **3**

Identification code	**3**	
Empirical formula	C17 H20 O2	
Formula weight	256.33	
Temperature	200(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/c$	
Unit cell dimensions	a = 23.5143(19) Å	α= 90°.
	b = 5.9262(5) Å	β= 90.440(7)°.
	c = 10.1369(9) Å	γ = 90°.
Volume	1412.5(2) $Å^3$	
Z	4	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.609 mm^{-1}	
F(000)	552	
Crystal size	0.250 x 0.157 x 0.020 mm^3	
Theta range for data collection	3.760 to 60.523°.	
Index ranges	-25<=h<=26, -6<=k<=5, -10<=l<=10	
Reflections collected	9183	
Independent reflections	2044 [R(int) = 0.1450]	
Completeness to theta = 60.523°	95.6 %	
Absorption correction	Integration	
Max. and min. transmission	0.8830 and 0.3483	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2044 / 0 / 174	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1573	
R indices (all data)	R1 = 0.0623, wR2 = 0.1657	
Extinction coefficient	0.039(6)	

Largest diff. peak and hole 0.300 and -0.276 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	3207(1)	756(2)	1773(1)	35(1)
O(3)	473(1)	-595(2)	-3615(1)	42(1)
C(1)	3846(1)	-2320(3)	3222(2)	46(1)
C(2)	3552(1)	-828(3)	4268(2)	43(1)
C(3)	3736(1)	1590(3)	3886(2)	30(1)
C(4)	4370(1)	1724(3)	4096(2)	38(1)
C(5)	4617(1)	450(3)	3193(2)	40(1)
C(6)	4157(1)	-574(3)	2346(2)	36(1)
C(7)	3731(1)	1386(3)	2369(2)	29(1)
C(8)	2781(1)	2434(3)	1936(2)	40(1)
C(9)	2300(1)	2094(3)	1000(2)	38(1)
C(10)	2256(1)	481(3)	104(2)	32(1)
C(11)	1791(1)	190(3)	-865(2)	30(1)
C(12)	1777(1)	-1687(3)	-1683(2)	34(1)
C(13)	1350(1)	-2029(3)	-2615(2)	35(1)
C(14)	920(1)	-448(3)	-2739(2)	31(1)
C(15)	928(1)	1471(3)	-1948(2)	35(1)
C(16)	1353(1)	1784(3)	-1028(2)	35(1)
C(17)	460(1)	-2511(3)	-4468(2)	47(1)

Table 3. Bond lengths [Å] and angles [°] for **3**

O(2)-C(7)	1.4184(19)
O(2)-C(8)	1.422(2)
O(3)-C(14)	1.374(2)
O(3)-C(17)	1.428(2)
C(1)-C(2)	1.548(3)
C(1)-C(6)	1.551(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.547(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.506(2)
C(3)-C(7)	1.542(2)
C(3)-H(3)	1.0000
C(4)-C(5)	1.323(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.503(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.535(2)
C(6)-H(6)	1.0000
C(7)-H(7)	1.0000
C(8)-C(9)	1.485(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.322(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.475(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.388(2)
C(11)-C(16)	1.406(2)
C(12)-C(13)	1.389(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.383(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.392(2)

C(15)-C(16)	1.375(2)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800

C(7)-O(2)-C(8)	112.13(12)
C(14)-O(3)-C(17)	116.99(13)
C(2)-C(1)-C(6)	103.09(13)
C(2)-C(1)-H(1A)	111.1
C(6)-C(1)-H(1A)	111.1
C(2)-C(1)-H(1B)	111.1
C(6)-C(1)-H(1B)	111.1
H(1A)-C(1)-H(1B)	109.1
C(3)-C(2)-C(1)	103.30(13)
C(3)-C(2)-H(2A)	111.1
C(1)-C(2)-H(2A)	111.1
C(3)-C(2)-H(2B)	111.1
C(1)-C(2)-H(2B)	111.1
H(2A)-C(2)-H(2B)	109.1
C(4)-C(3)-C(7)	98.33(13)
C(4)-C(3)-C(2)	106.99(14)
C(7)-C(3)-C(2)	100.19(13)
C(4)-C(3)-H(3)	116.3
C(7)-C(3)-H(3)	116.3
C(2)-C(3)-H(3)	116.3
C(5)-C(4)-C(3)	108.12(15)
C(5)-C(4)-H(4)	125.9
C(3)-C(4)-H(4)	125.9
C(4)-C(5)-C(6)	107.97(15)
C(4)-C(5)-H(5)	126.0
C(6)-C(5)-H(5)	126.0
C(5)-C(6)-C(7)	98.74(13)
C(5)-C(6)-C(1)	106.40(15)
C(7)-C(6)-C(1)	100.68(13)
C(5)-C(6)-H(6)	116.2
C(7)-C(6)-H(6)	116.2
C(1)-C(6)-H(6)	116.2
O(2)-C(7)-C(6)	111.08(13)
O(2)-C(7)-C(3)	116.44(12)
C(6)-C(7)-C(3)	94.28(12)
O(2)-C(7)-H(7)	111.3
C(6)-C(7)-H(7)	111.3
C(3)-C(7)-H(7)	111.3
O(2)-C(8)-C(9)	111.42(14)
O(2)-C(8)-H(8A)	109.3
C(9)-C(8)-H(8A)	109.3
O(2)-C(8)-H(8B)	109.3
C(9)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	108.0
C(10)-C(9)-C(8)	126.28(15)
C(10)-C(9)-H(9)	116.9
C(8)-C(9)-H(9)	116.9
C(9)-C(10)-C(11)	126.53(16)
C(9)-C(10)-H(10)	116.7
C(11)-C(10)-H(10)	116.7
C(12)-C(11)-C(16)	117.09(15)
C(12)-C(11)-C(10)	120.32(14)
C(16)-C(11)-C(10)	122.58(15)
C(11)-C(12)-C(13)	122.44(15)
C(11)-C(12)-H(12)	118.8
C(13)-C(12)-H(12)	118.8
C(14)-C(13)-C(12)	119.17(16)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
O(3)-C(14)-C(13)	124.83(15)

O(3)-C(14)-C(15)	115.46(14)
C(13)-C(14)-C(15)	119.71(16)
C(16)-C(15)-C(14)	120.45(15)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(15)-C(16)-C(11)	121.13(16)
C(15)-C(16)-H(16)	119.4
C(11)-C(16)-H(16)	119.4
O(3)-C(17)-H(17A)	109.5
O(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$)for **3.** The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	30(1)	41(1)	33(1)	-7(1)	-8(1)	3(1)
O(3)	34(1)	49(1)	42(1)	-9(1)	-14(1)	5(1)
C(1)	55(1)	30(1)	53(1)	1(1)	-13(1)	-2(1)
C(2)	50(1)	42(1)	36(1)	10(1)	-2(1)	-8(1)
C(3)	33(1)	31(1)	27(1)	-2(1)	-4(1)	1(1)
C(4)	37(1)	36(1)	40(1)	-2(1)	-13(1)	-3(1)
C(5)	31(1)	43(1)	47(1)	-1(1)	-6(1)	2(1)
C(6)	36(1)	36(1)	35(1)	-7(1)	-4(1)	4(1)
C(7)	25(1)	33(1)	28(1)	0(1)	-6(1)	-1(1)
C(8)	32(1)	52(1)	37(1)	-12(1)	-7(1)	9(1)
C(9)	28(1)	49(1)	36(1)	-5(1)	-4(1)	5(1)
C(10)	26(1)	37(1)	32(1)	0(1)	-2(1)	1(1)
C(11)	24(1)	36(1)	30(1)	2(1)	-2(1)	-2(1)
C(12)	27(1)	37(1)	37(1)	-4(1)	-4(1)	5(1)
C(13)	30(1)	37(1)	38(1)	-6(1)	-4(1)	1(1)
C(14)	24(1)	40(1)	30(1)	0(1)	-6(1)	-2(1)
C(15)	29(1)	36(1)	39(1)	0(1)	-5(1)	5(1)
C(16)	33(1)	34(1)	37(1)	-5(1)	-3(1)	1(1)
C(17)	40(1)	56(1)	45(1)	-14(1)	-12(1)	0(1)

Table 5. Hydrogen coordinates ($x 10^4$) and isotropic displacement parameters ($Å^2 x 10^3$) for **3**.

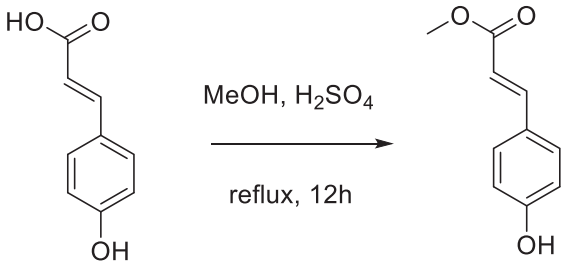
	x	y	z	U(eq)
H(1A)	3564	-3192	2702	55
H(1B)	4119	-3379	3640	55
H(2A)	3133	-994	4220	51
H(2B)	3684	-1217	5169	51
H(3)	3507	2850	4266	36
H(4)	4560	2575	4760	45
H(5)	5014	223	3098	48
H(6)	4276	-1111	1454	43
H(7)	3892	2767	1946	34
H(8A)	2950	3943	1790	49
H(8B)	2638	2380	2851	49
H(9)	1993	3135	1051	45
H(10)	2554	-599	81	38
H(12)	2072	-2778	-1603	41
H(13)	1353	-3332	-3161	42
H(15)	637	2573	-2045	42

H(16)	1351	3100	-493	42
H(17A)	423	-3889	-3940	71
H(17B)	813	-2574	-4974	71
H(17C)	135	-2388	-5075	71

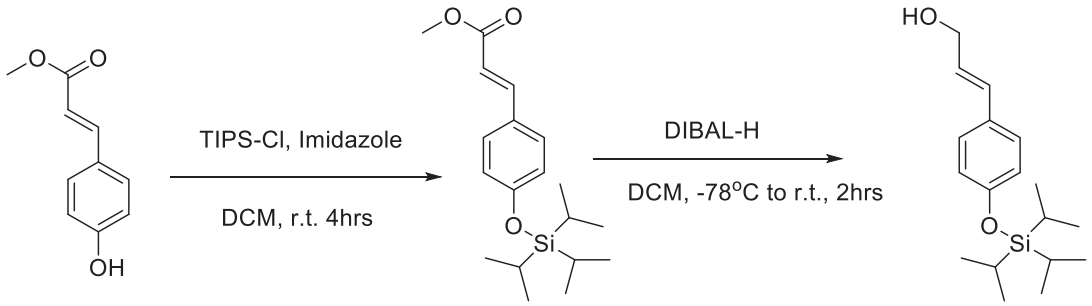
Table 6. Torsion angles [°] for **3**.

C(6)-C(1)-C(2)-C(3)	-0.94(18)
C(1)-C(2)-C(3)-C(4)	-65.37(17)
C(1)-C(2)-C(3)-C(7)	36.68(16)
C(7)-C(3)-C(4)-C(5)	-34.09(17)
C(2)-C(3)-C(4)-C(5)	69.31(18)
C(3)-C(4)-C(5)-C(6)	0.2(2)
C(4)-C(5)-C(6)-C(7)	34.03(18)
C(4)-C(5)-C(6)-C(1)	-69.90(18)
C(2)-C(1)-C(6)-C(5)	67.15(17)
C(2)-C(1)-C(6)-C(7)	-35.37(17)
C(8)-O(2)-C(7)-C(6)	172.24(14)
C(8)-O(2)-C(7)-C(3)	65.93(18)
C(5)-C(6)-C(7)-O(2)	-172.04(13)
C(1)-C(6)-C(7)-O(2)	-63.39(17)
C(5)-C(6)-C(7)-C(3)	-51.56(14)
C(1)-C(6)-C(7)-C(3)	57.09(14)
C(4)-C(3)-C(7)-O(2)	167.57(13)
C(2)-C(3)-C(7)-O(2)	58.52(17)
C(4)-C(3)-C(7)-C(6)	51.48(13)
C(2)-C(3)-C(7)-C(6)	-57.58(14)
C(7)-O(2)-C(8)-C(9)	163.26(14)
O(2)-C(8)-C(9)-C(10)	-0.7(3)
C(8)-C(9)-C(10)-C(11)	-177.26(16)
C(9)-C(10)-C(11)-C(12)	-174.95(16)
C(9)-C(10)-C(11)-C(16)	6.5(3)
C(16)-C(11)-C(12)-C(13)	-1.0(2)
C(10)-C(11)-C(12)-C(13)	-179.64(15)
C(11)-C(12)-C(13)-C(14)	0.0(3)
C(17)-O(3)-C(14)-C(13)	-1.0(2)
C(17)-O(3)-C(14)-C(15)	178.27(15)
C(12)-C(13)-C(14)-O(3)	-179.63(15)
C(12)-C(13)-C(14)-C(15)	1.1(3)
O(3)-C(14)-C(15)-C(16)	179.38(14)
C(13)-C(14)-C(15)-C(16)	-1.3(3)
C(14)-C(15)-C(16)-C(11)	0.3(3)
C(12)-C(11)-C(16)-C(15)	0.8(2)
C(10)-C(11)-C(16)-C(15)	179.43(15)

Symmetry transformations used to generate equivalent atoms:

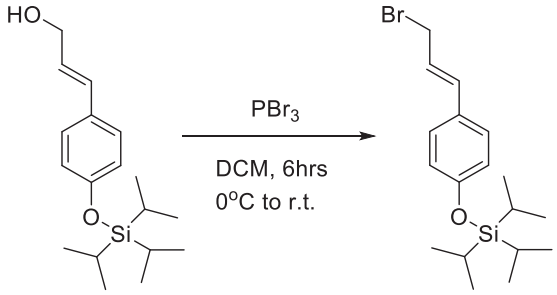


Synthesis of 4-hydroxy-methyl cinnamate: 4-hydroxy-cinnamic acid (10.00g, 60.97mmol) was dissolved in 100mL methanol and 3 drops of concentrated sulfuric acid were added. This mixture was refluxed for 12 hours. The resulting solution was cooled and methanol was evaporated. 100mL water was added to the solid residue. This mixture was filtered and the residue was washed with 3x50mL water to give 4-hydroxy-methyl cinnamate (10.3g, 57.86mmol, 95% yield) as a colourless solid. The compound was pure by ^{1}H-NMR and was used without further purification. ^{1}H-NMR (chloroform-d, 300 MHz): δ = 7.65 (d, J=16.0 Hz, 1 H), 7.43 (d, J=8.5 Hz, 2 H), 6.86 (d, J=8.6 Hz, 2 H), 6.30 (d, J=16.0 Hz, 1 H), 3.81 ppm (s, 3 H). ^{13}C-NMR (chloroform-d, 75 MHz): δ = 168.2, 158.0, 144.9, 130.0, 127.0, 115.9, 115.0, 51.7 ppm.

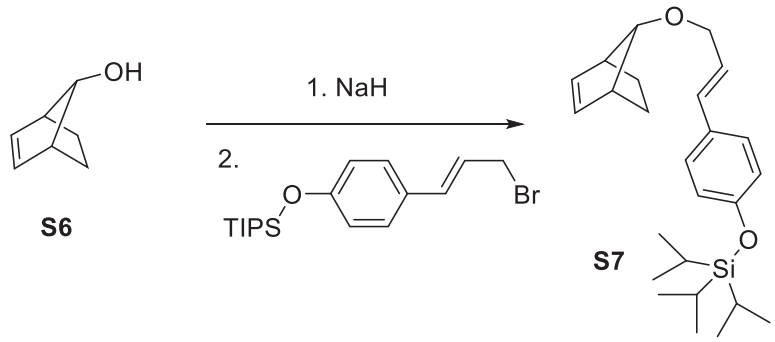


Synthesis of 4-(triisopropylsilyloxy)cinnamic alcohol: 4-hydroxy-methyl cinnamate (2.00g, 11.22mmol, 1eq) was dissolved in 30mL dry dichloromethane. Imidazole (1.53g, 22.45mmol, 2eq) was added and the mixture was cooled to 0°C. TIPS-Cl (3.25g, 16.84mmol, 1.5eq) was added dropwise. The mixture was stirred at room temperature for 4 hours until TLC (EtOA/hexane 1:9) showed disappearance of the starting material. 7gms silica was directly added into the reaction mixture and the solvent was evaporated. This silica was loaded onto a column and eluted with EtOAc/Hexane 1:19 to give 4.8g of clear oil. ^{1}H-NMR showed the desired compound with other triisopropylsilyl impurities. This clear oil was directly used for the next step.

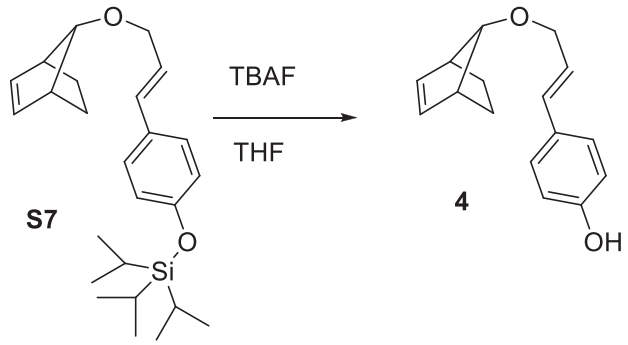
The clear oil was dissolved in dry dichloromethane (25mL) and the solution cooled to -78°C. To this solution was added 28 mL of 1M DIBAL-H in cyclohexane. The soultion was stirred at -78°C for 30 min and allowed to warm to room temperature. The mixture was further stirred for 30 min. The reaction was quenched by cooling the solution to -20 °C and 50mL water was added dropwise. The mixture was allowed to stir at room temperature for another 30 min till a viscous emulsion formed. 100mL dichloromethane was added and the emulsion was taken up in a separating funnel. The dichloromethane layer separated slowly and was collected. The water layer containing the aluminium salts was washed with 5x50mL dichloromethane, dried over magnesium sulfate and the solvent was evaporated. This material was chromatographed on silica and eluted with only hexane and then with EtOAc/Hexane 1:20 to give pure 4-(triisopropylsilyloxy)methyl cinnamate as a clear oil (3.10g, 10.11mmol, 90% yield over two steps). ^{1}H-NMR (chloroform-d, 300 MHz): δ (ppm) = 7.27 (d, J=8.5 Hz, 2 H), 6.84 (d, J=8.6 Hz, 2 H), 6.56 (d, J=15.9 Hz, 1 H), 6.18 - 6.31 (m, 1 H), 4.30 (t, J=5.7 Hz, 2 H), 1.36 (t, J=5.8 Hz, 1 H), 1.18 - 1.32 (m, 3 H), 1.11 (d, 18 H). ^{13}C-NMR (chloroform-d, 75 MHz): δ (ppm) = 155.9, 131.2, 129.6, 127.6, 126.2, 120.0, 64.0, 17.7, 12.7 ppm.



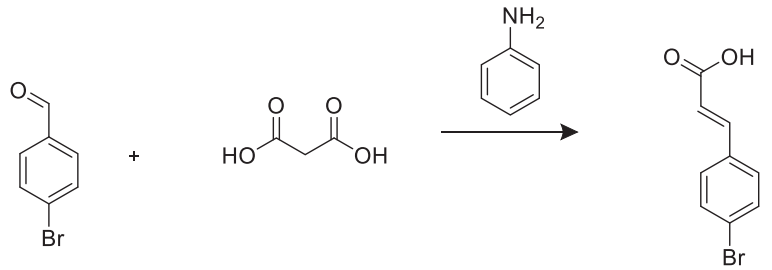
Synthesis of 4-(triisopropylsilyloxy)cinnamyl bromide: 4-(triisopropylsilyloxy)cinnamic alcohol (1g, 3.26mmol, 1eq) from above was dissolved in dry dichloromethane (15mL) and PBr_3 (0.124mL, 1.30mmol, 0.4eq) was added dropwise under argon atmosphere at 0°C. The reaction was allowed to warm up to room temperature and stirred for 6 hours. The reaction was quenched with a solution of saturated sodium bicarbonate, extracted 3 times with dichloromethane and the dichloromethane was evaporated under vacuum to give an oily residue. This compound was not stable and used immediately for the next step without further purification.



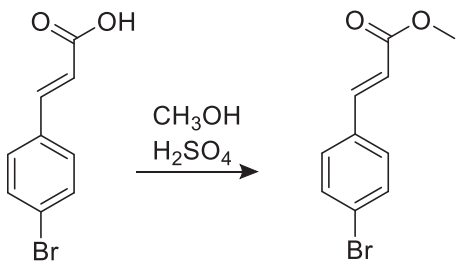
Synthesis of compound **S7**: To a suspension of NaH (0.18g, 7.5mmol, 1.5eq) in diethyl ether (20mL) at 0°C was added alcohol **S6** (0.55g, 5mmol, 1eq). This solution was stirred at 0°C for 3 hours, added 2 mL of N,N-dimethylformamide and then the crude solution containing the TIPS-cinnamyl bromide was added dropwise over 30min. This solution was stirred overnight till all the alcohol **S6** was consumed (by TLC). The solution was quenched with ice water and diluted with water. This solution was extracted with 3x50mL ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed, leaving a yellow viscous oil. This was chromatographed on silica with hexanes to give a yellowish liquid. This product had very slight impurities (as evident by the ^{1}H-NMR) of and was used without further purification. ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 7.21 - 7.30 (m, 2 H), 6.79 - 6.86 (m, 2 H), 6.51 (d, J=15.9 Hz, 1 H), 6.13 (dt, J=15.8, 6.2 Hz, 1 H), 5.99 (t, J=2.2 Hz, 2 H), 4.05 (dd, J=6.2, 1.4 Hz, 2 H), 3.31 (s, 1 H), 2.70 (dq, J=3.7, 2.0 Hz, 2 H), 1.78 - 1.86 (m, J=9.0, 2.0 Hz, 2 H), 1.18 - 1.33 (m, 4 H), 1.07 - 1.13 ppm (m, 23 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 155.8, 134.2, 131.8, 129.8, 127.6, 124.2, 119.9, 88.8, 69.1, 43.5, 21.8, 17.9, 12.7 ppm. HRMS (ESI) calculated for $C_{25}H_{38}O_2Si$ $[M+Na]^+$: 421.25388; found: 421.25359.



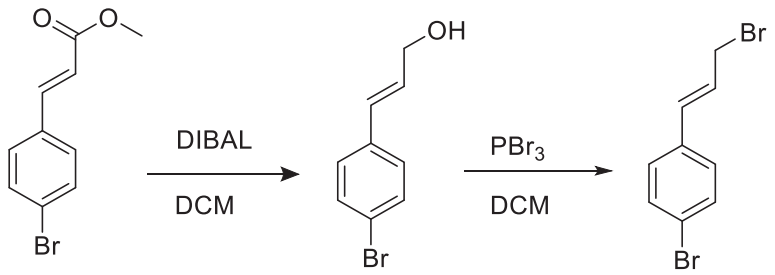
The compound **S7** was dissolved in dry THF (10mL) and a solution of 1M TBAF in THF was added dropwise. The solution immediately turned red. The solution was kept stirring for 30 minutes at r.t. and then water was added. The mixture was extracted with 3x50mL ethyl acetate, dried over MgSO4 and chromatographed on silica with EtOAc/hexane 1:9 to give the product **4** as a white solid quantitatively. ^{1}H-NMR (dichloromethane-d_2 ,300MHz): δ (ppm) = 7.27 (d, J=8.5 Hz, 2 H), 6.77 (d, J=8.7 Hz, 2 H), 6.50 (d, J=15.9 Hz, 1 H), 6.12 (dt, J=15.9, 6.1 Hz, 1 H), 5.98 (s, 2 H), 5.08 (s, 1 H), 4.03 (dd, J=6.1, 1.4 Hz, 2 H), 3.29 (s, 1 H), 2.68 (dq, J=3.9, 2.1 Hz, 2 H), 1.69 - 1.97 (m, 2 H), 0.88 - 1.05 ppm (m, 2 H). ^{13}C-NMR (dichloromethane-d_2 ,75MHz): δ (ppm) = 156.00, 134.76, 131.70, 130.28, 128.33, 125.02, 115.95, 89.54, 69.56, 44.13, 22.35 ppm. HRMS (ESI) calculated for $C_{16}H_{18}O_2$ $[M+Na]^+$: 265.12045; found: 265.11982.



Synthesis of 4-bromocinnamic acid: 4-bromobenzaldehyde (15g, 81mmol, 1eq) was suspended in 80mL dry pyridine and malonic acid (16.87g, 162mmol, 2eq) was added. The mixture was heated to 60°C and aniline (0.9g, 9.7mmol, 0.12eq) was quickly added. This mixture was refluxed overnight. The reaction was cooled and 100mL water was added. The precipitate was filtered and washed with 1M HCl and again with water. The precipitate was dried overnight to give 4-bromocinnamic acid in 87%yield. ^{1}H-NMR (dimethylsulfoxide-d_6, 300MHz): δ (ppm) = 7.49 - 7.73 (m, 5 H), 6.56 ppm (d, *J*=16.0 Hz, 1 H). ^{13}C-NMR (dimethylsulfoxide-d_6, 75MHz): δ (ppm) = 167.4, 142.6, 133.6, 132.0, 130.2, 123.5, 120.1 ppm.

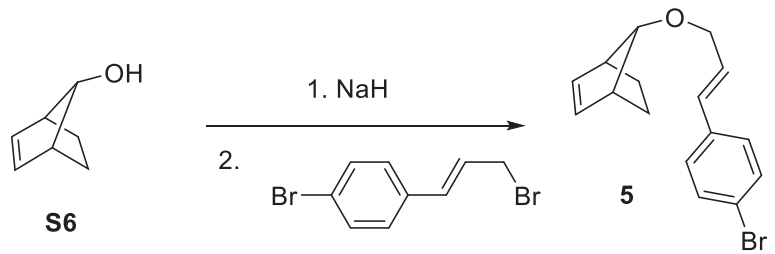


Synthesis of 4-bromo-methylcinnamate: 4-bromocinnamic acid (10g, 44mmol, 1eq) was suspended in methanol (30mL) and 1mL H_2SO_4 was slowly added. This mixture was refluxed overnight. The mixture was then cooled and the methanol was partially evaporated. The precipitate was filtered and washed with water and dried overnight to give 4-bromo-methylcinnamate in 83% yield. ^{1}H NMR (chloroform-d, 300MHz): δ (ppm) = 7.63 (d, *J*=16.0 Hz, 1 H), 7.48 - 7.56 (m, 2 H), 7.34 - 7.44 (m, 2 H), 6.43 (d, *J*=16.0 Hz, 1 H), 3.82 ppm (s, 3 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 167.1, 143.5, 133.3, 132.1, 129.4, 124.5, 118.5, 51.8 ppm.

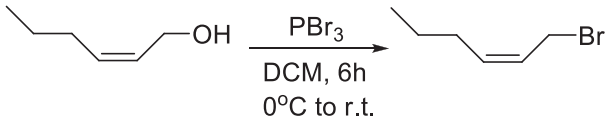


Synthesis of 4-bromocinnamyl bromide: 4-bromo-methylcinnamate (5g, 20.74mmol, 1eq) was dissolved in dry dichloromethane (40mL) and cooled to -78°C. DIBAL (41.5mL, 1M in dichloromethane, 2eq) was added dropwise over 1 hour and the reaction was warmed to 0°C. After stirring for 3 hours, the reaction was carefully quenched with ice and filtered. The filtrate was washed with saturated sodium bicarbonate and brine. The mixture was chromatographed on silica with EtOAc/hexane 2:8 as the eluent to give the 4-bromocinnamic alcohol in 94% yield. ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 7.39 - 7.49 (m, *J*=8.5 Hz, 2 H), 7.21 - 7.30 (m, 2 H), 6.51 - 6.63 (m, 1 H), 6.29 - 6.43 (m, 1 H), 4.33 ppm (dd, *J*=5.5, 1.4 Hz, 2 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 135.6, 131.7, 129.8, 129.3, 128.0, 121.4, 63.5 ppm. This 4-bromocinnamic alcohol (2g, 9.4mmol, 1eq) was dissolved in dry dichloromethane (10mL) and PBr_3 (1.27g, 4.7mmol, 0.5eq) was added dropwise at 0°C. After stirring for 6 hours at r.t., the reaction was quenched with a saturated solution of sodium bicarbonate. The mixture was extracted 3 times with dichloromethane and the solvent was removed under vacuum to give 4-bromocinnamyl bromide as a colourless compound in 79% yield. ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 7.42 - 7.51 (m, *J*=8.4 Hz, 2 H), 7.22 - 7.29 (m, 2 H), 6.54 - 6.65 (m, 1 H), 6.32 - 6.46 (m, 1 H),

4.15 ppm (dd, *J*=7.7, 0.8 Hz, 2 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 134.7, 133.3, 131.8, 128.2, 126.0, 122.2, 32.9 ppm.

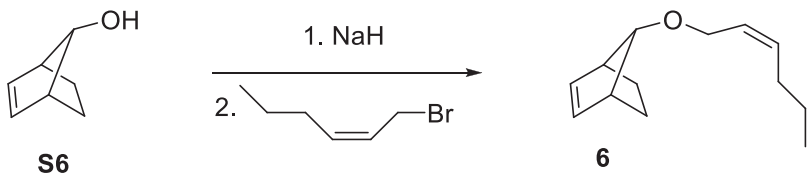


Synthesis of **5**: To a suspension of NaH (65mg, 2.72mmol, 1.5eq) in diethyl ether 30mL at 0°C was added alcohol **S6** (200mg, 1.82mmol, 1eq). This solution was stirred at 0°C for 3 hours, added 2mL of dry N,N-dimethylformamide and then the crude solution containing the bromo-cinnamyl bromide was added dropwise over 30min. This solution was stirred overnight till all the alcohol **S6** was consumed (by TLC). The solution was quenched with ice water and diluted with water. This solution was extracted with 3x50mL ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed. The mixture was chromatographed on silica with EtOAc/hexanes 1:19 to give a colourless solid in 70% yield. ^{1}H-NMR (dichloromethane-d_2 ,300MHz): δ (ppm) = 7.38 - 7.50 (m, 2 H), 7.22 - 7.32 (m, 2 H), 6.47 - 6.58 (m, 1 H), 6.20 - 6.34 (m, 1 H), 5.98 (t, *J*=2.2 Hz, 2 H), 4.04 (dd, *J*=5.7, 1.5 Hz, 2 H), 3.28 (s, 1 H), 2.67 (dq, *J*=3.8, 2.1 Hz, 2 H), 1.73 - 1.82 (m, 2 H), 0.93 - 1.01 ppm (m, 2 H). ^{13}C-NMR (dichloromethane-d_2 ,75MHz): δ (ppm) = 136.6, 134.7, 132.2, 130.4, 128.5, 128.4, 121.6, 89.6, 69.1, 44.1, 22.3 ppm. LRMS (EI) calculated for $C_{16}H_{17}BrO$ $[M]^+$: 304.05; found: 304.2

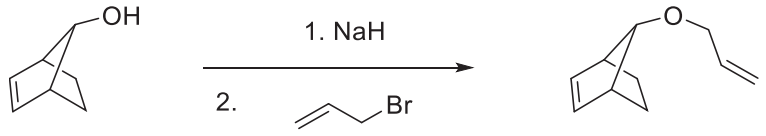


Synthesis of (Z)-1-bromohex-2-ene: (Z)-hex-2-en-1-ol (1g, 9.98mmol, 1eq) was dissolved in dry dichloromethane (8mL) and PBr_3 (0.468mL, 4.99mmol, 0.5eq) after dissolving in 5mL of dry dichloromethane was added dropwise under argon atmosphere at 0°C to it. The reaction was allowed to warm up to room temperature and stirred for 6 hours.

The reaction was quenched with a saturated solution of sodium bicarbonate. The solution was extracted 3 times with dichloromethane, dried over $MgSO_4$ and the dichloromethane was evaporated under vacuum to give an oily residue. This compound was not stable and used immediately without further purification for next step.



Synthesis of **6**: To a suspension of NaH (96mg, 3.99mmol, 1.5eq) in dry diethyl ether (35mL) at 0°C was added alcohol **S6** dropwise (293mg, 2.66mmol, 1eq) after dissolving in 5mL of dry diethyl ether under argon atmosphere. This solution was stirred at 0°C for 3 hours and then the crude solution containing the (Z)-1-bromohex-2-ene after dissolving in 4mL of dry N,N-dimethylformamide was added dropwise over 30min. This solution was stirred overnight till all the alcohol **S6** was consumed (by TLC). The solution was quenched with ice water and diluted with water. This solution was extracted with 3x50mL ethyl acetate. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed. The mixture was chromatographed on silica with EtOAc/hexanes 1:49 to give a yellowish liquid in 33% yield (170mg). ^{1}H-NMR (chloroform-d, 300MHz) δ (ppm) = 5.98 (t, *J*=2.20 Hz, 2 H), 5.49 - 5.60 (m, 2 H), 3.95 – 3.97 (m, 2 H), 3.25 (s, 1 H), 2.68 (dq, *J*=3.76, 2.02 Hz, 2 H), 2.01 - 2.08 (m, 2 H), 1.75 - 1.82 (m, 2 H), 1.34 – 1.46 (m, 2 H), 0.88 – 0.99 (m, 5 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 134.19, 133.07, 126.50, 88.94, 63.87, 43.45, 29.56, 22.69, 21.80, 13.72 ppm. HRMS (ESI) calculated for $C_{13}H_{20}O$ $[M+Na]^+$: 215.14119; found: 215.14089.



S6 **7**

Synthesis of **7**: To a suspension of NaH (65mg, 2.72mmol, 1.5eq) in diethyl ether (30mL) at 0°C was added alcohol **S6** (200mg, 1.82mmol, 1eq). This solution was stirred at 0°C for 3 hours, added 2mL of dry N,N-dimethylformamide and then allyl bromide (440mg, 3.63mmol, 2eq) in dry diethyl ether (3mL) was added dropwise over 30min. This solution was stirred overnight till all the alcohol **S6** was consumed (by TLC). The solution was quenched with ice water and diluted with water. This solution was extracted with 3x50mL ethyl acetate. The organic layers were combined, dried over MgSO4 and the solvent was removed under vacuum. Column chromatography on silica with EtOAc/hexane 1:19 gave the compound **7** as a yellowish oil in 74% yield. This was chromatographed on silica with hexanes to give a yellowish liquid. ^{1}H-NMR (chloroform-d, 300MHz): δ (ppm) = 5.98 (t, *J*=2.2 Hz, 2 H), 5.81 - 5.96 (m, 1 H), 5.27 (dq, *J*=17.2, 1.7 Hz, 1 H), 5.15 (dq, *J*=10.4, 1.5 Hz, 1 H), 3.91 (dt, *J*=5.5, 1.5 Hz, 2 H), 3.26 (s, 1 H), 2.67 (dq, *J*=3.8, 2.0 Hz, 2 H), 1.74 - 1.83 (m, 2 H), 0.93 - 1.01 ppm (m, 2 H). ^{13}C-NMR (chloroform-d, 75MHz): δ (ppm) = 135.2, 134.2, 116.4, 88.9, 69.2, 43.4, 21.8 ppm. LRMS (EI) calculated for $C_{10}H_{14}BrO$ $[M]^{+}$: 150.11; found: 150.1.

^{1}H-NMR Spectra:

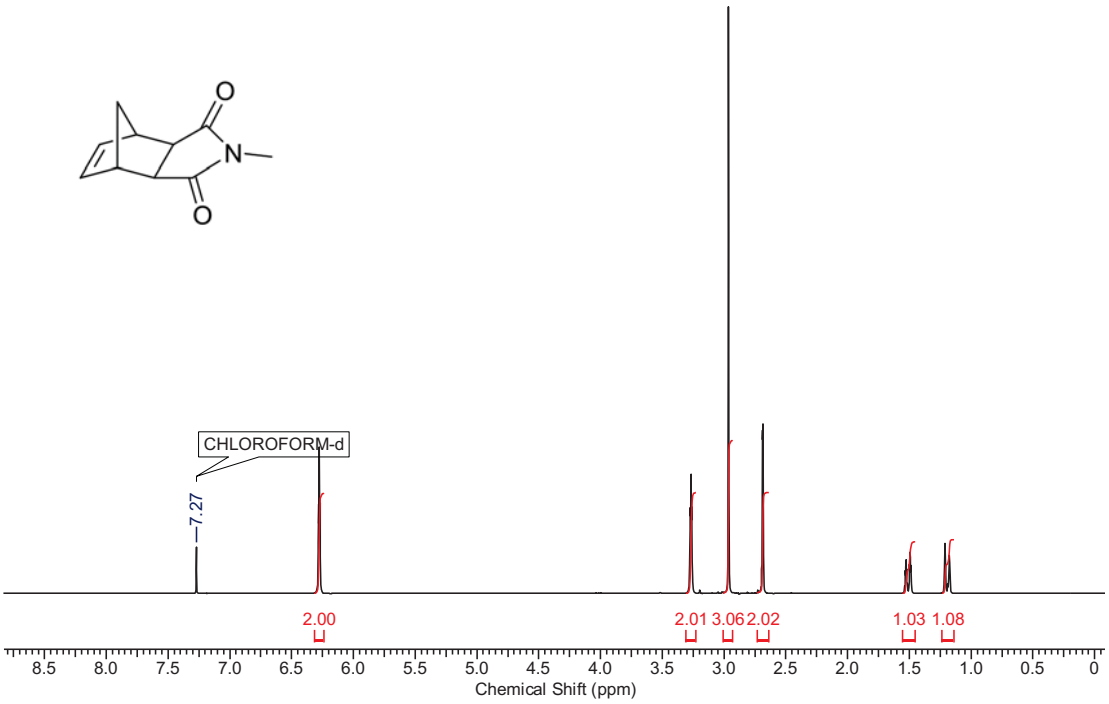


Figure S7: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of **MNI**.

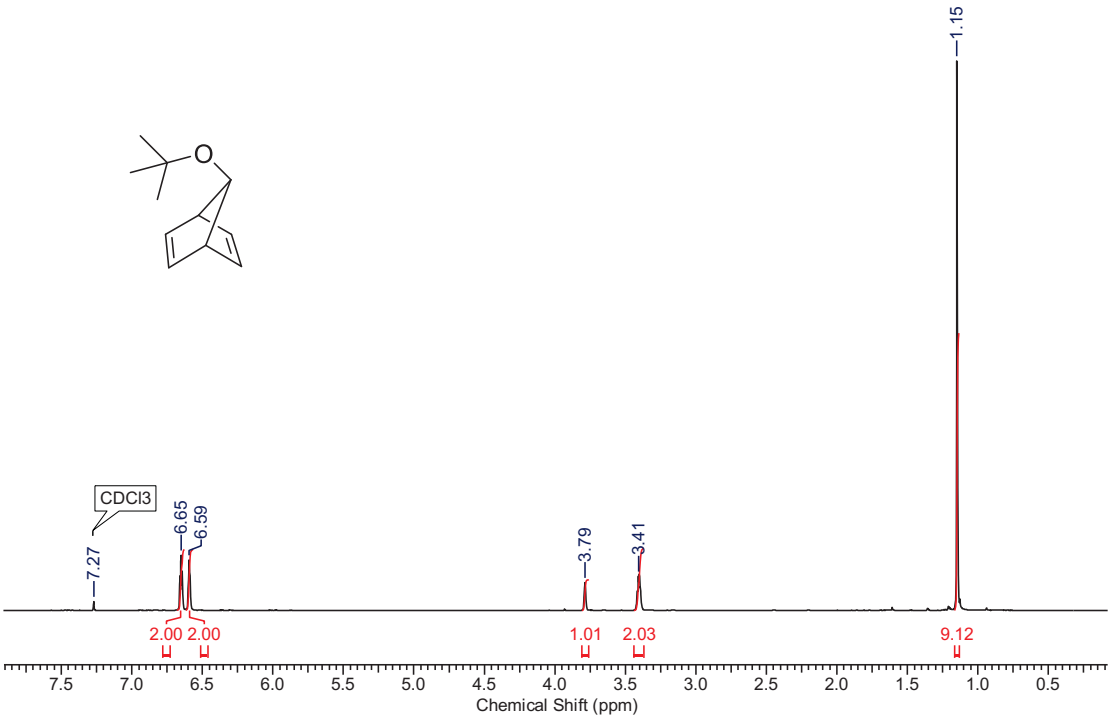


Figure S8: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 7-(tert-butoxy)-norbornadiene (**S1**)

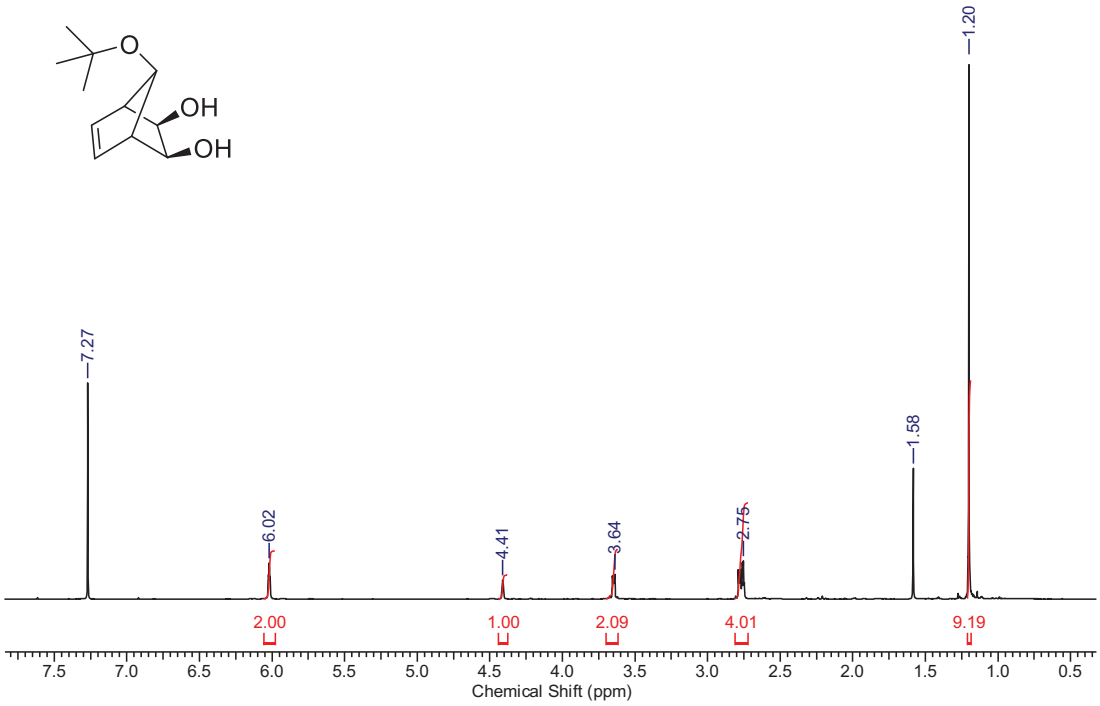


Figure S9: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of syn-7-(tert-butoxy)norbornene-2,3-diol (**S2**)

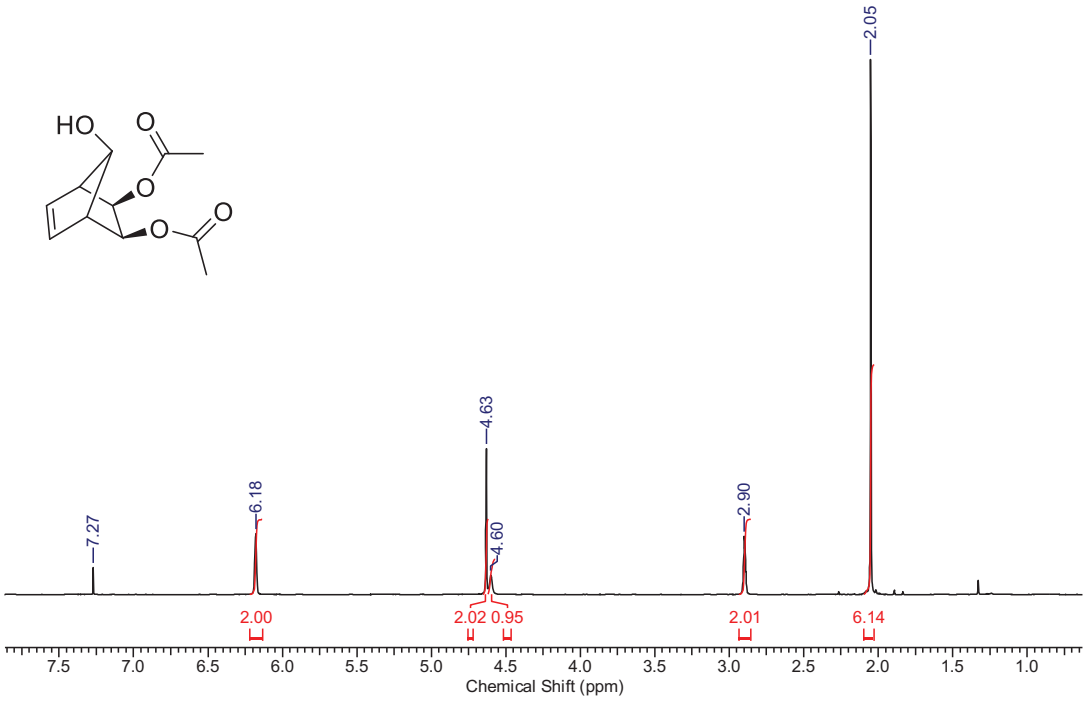


Figure S10: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of syn-7-hydroxynorbornene-2,3-diacetate (**S4**)

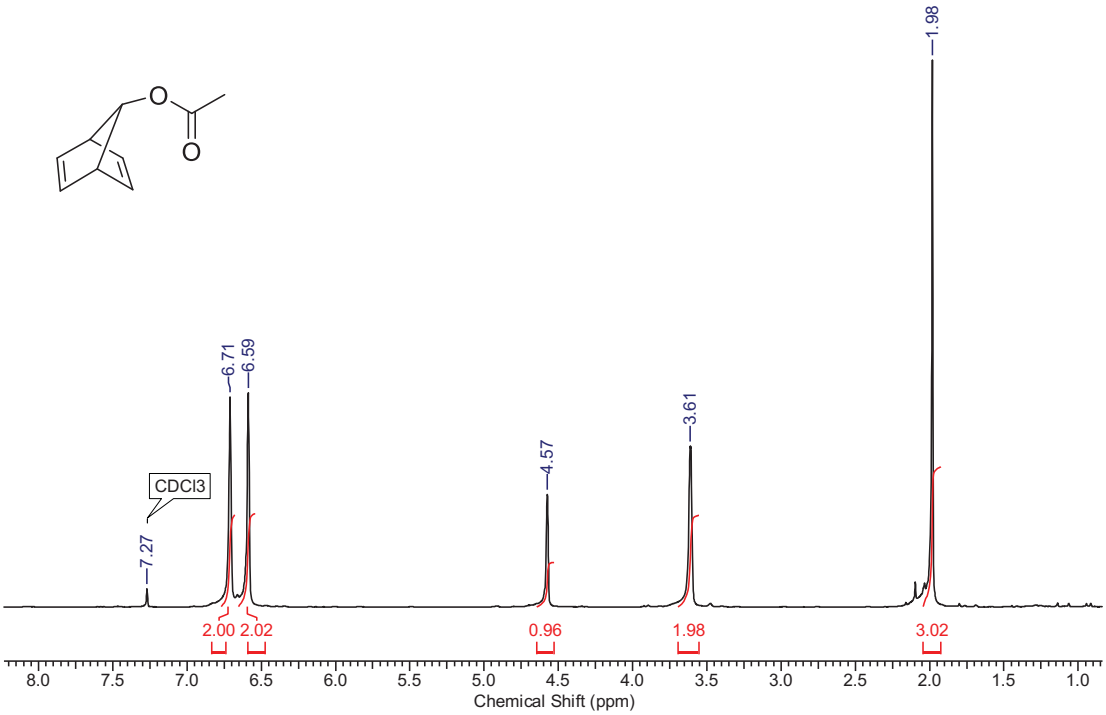


Figure S11: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 7-acetyl norbornadiene (**S5**)

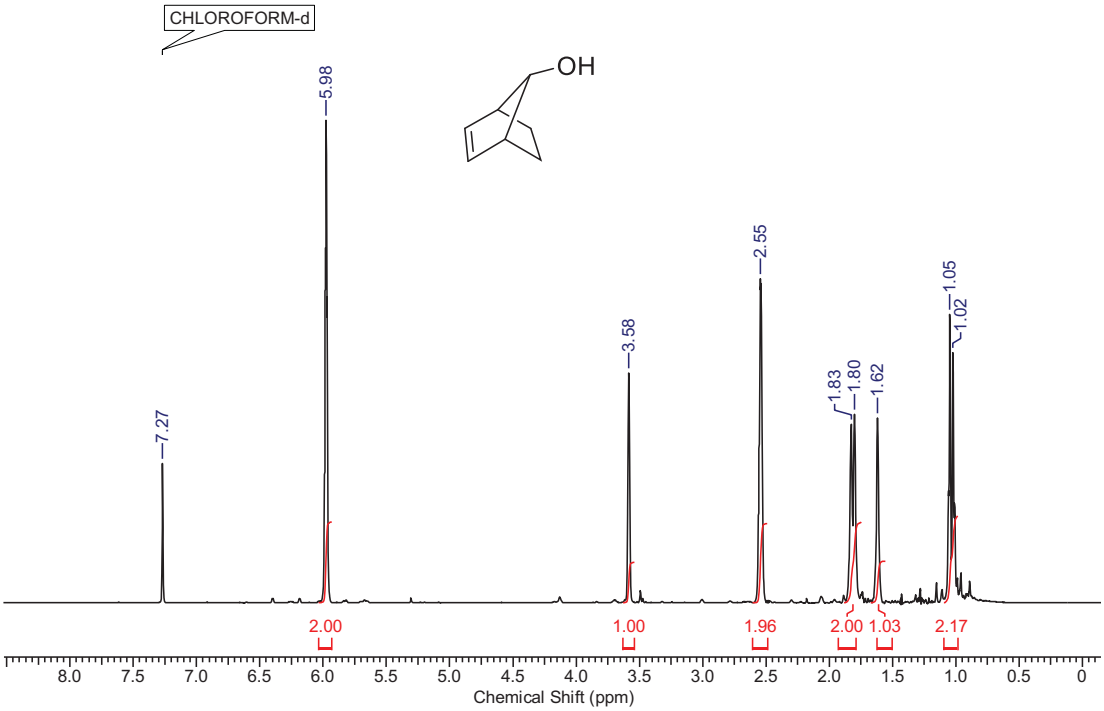


Figure S12: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of anti-7-hydroxynorbornene (**S6**).

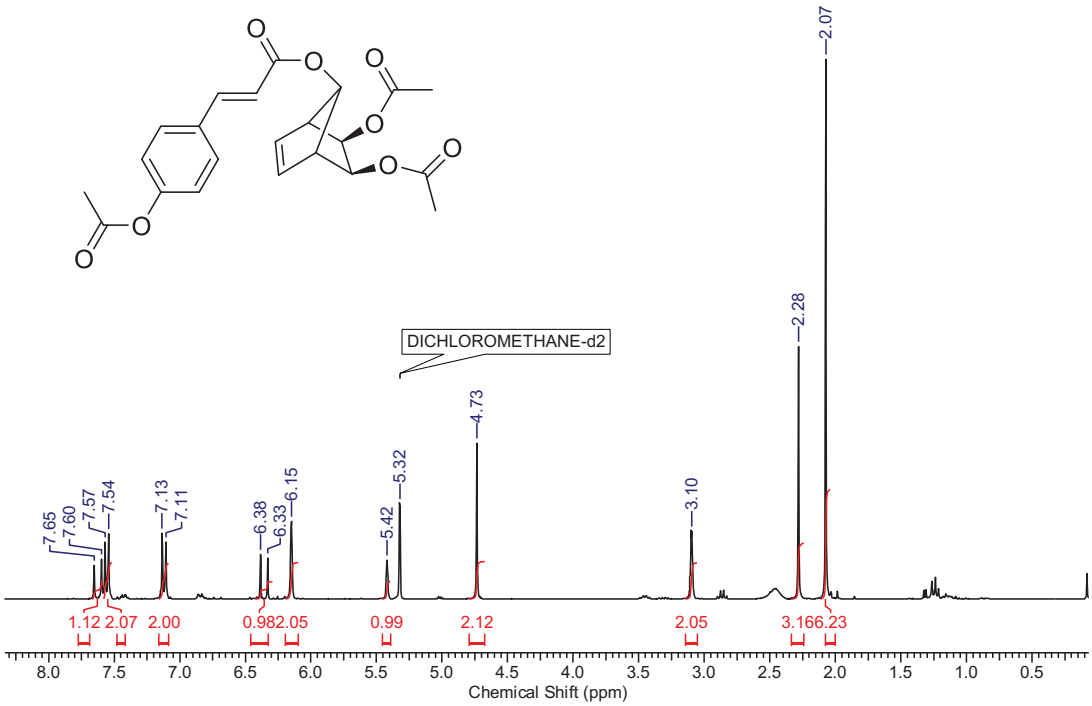


Figure S13: ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectrum of compound **1**.

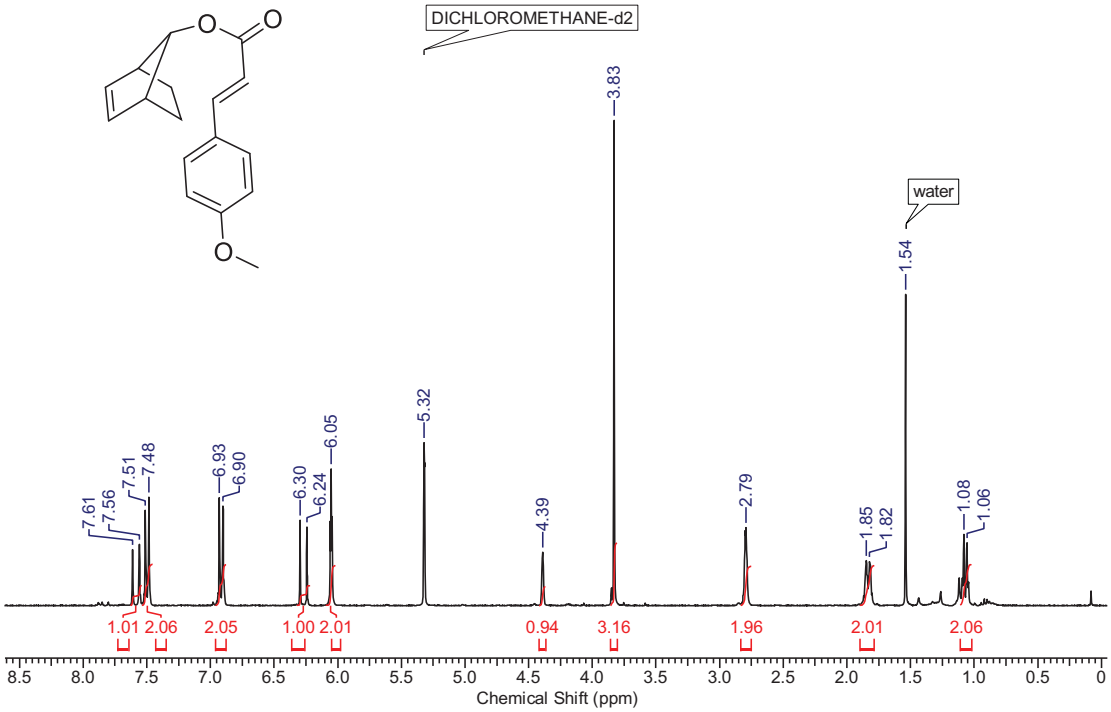


Figure S14: ^{1}H-NMR (dichloromethane-d$_2$, 300 MHz) spectrum of **2**.

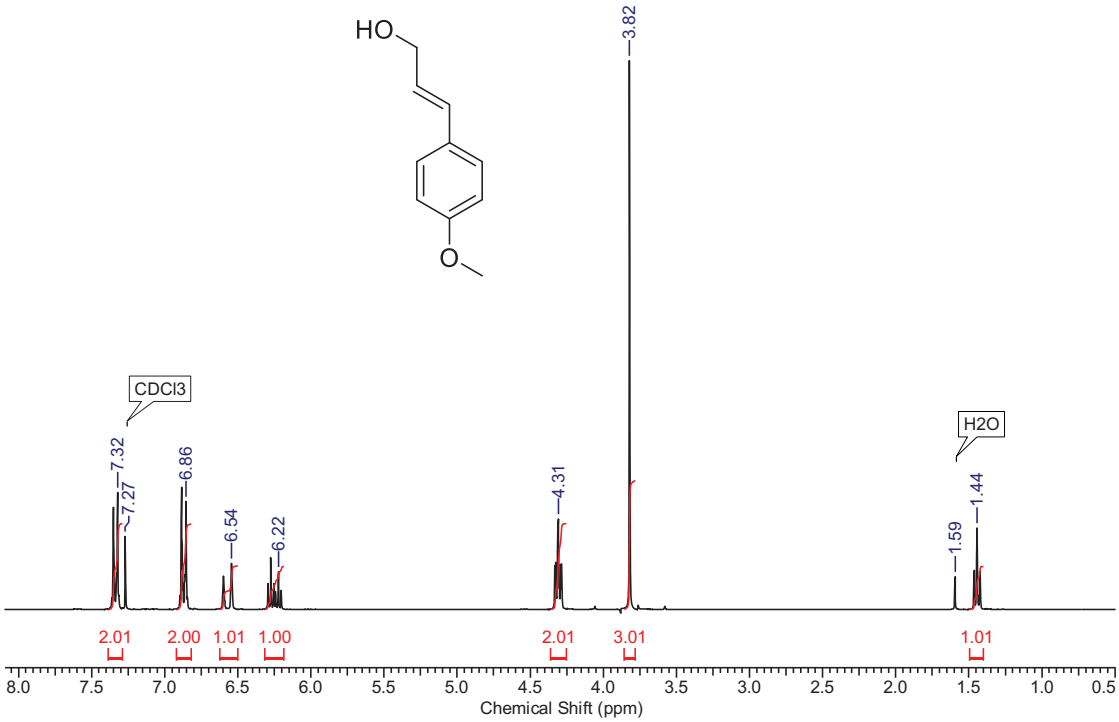


Figure S15: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 4-methoxy cinnamyl alcohol.

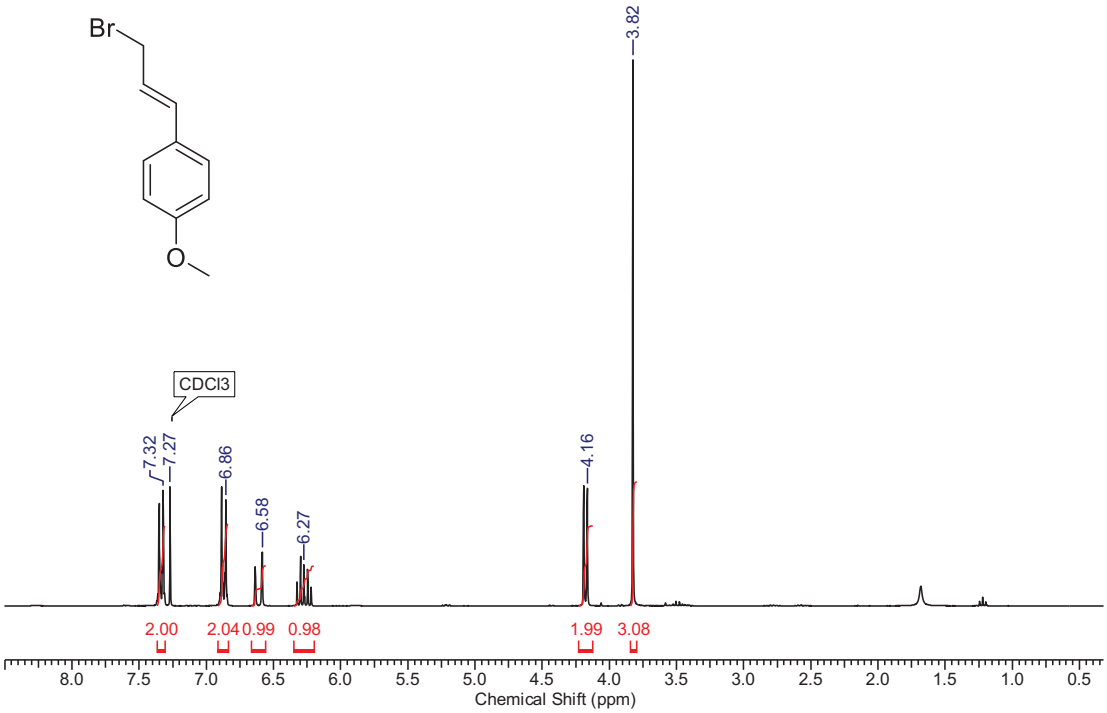


Figure S16: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 4-methoxy cinnamyl bromide.

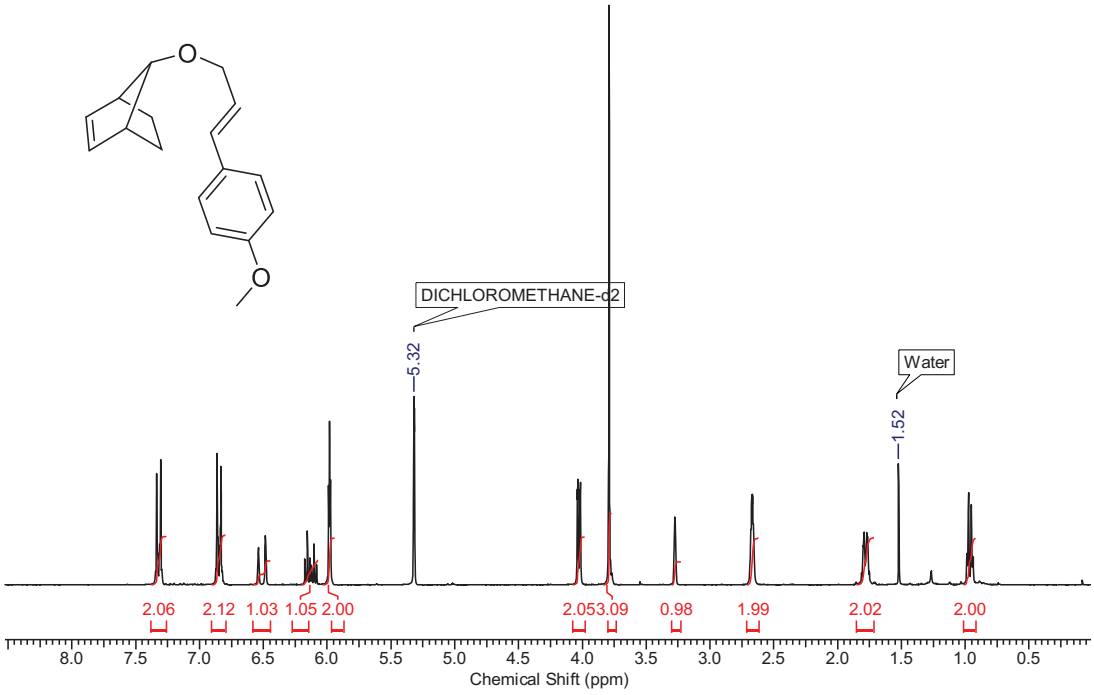


Figure S17: ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectrum of **3**.

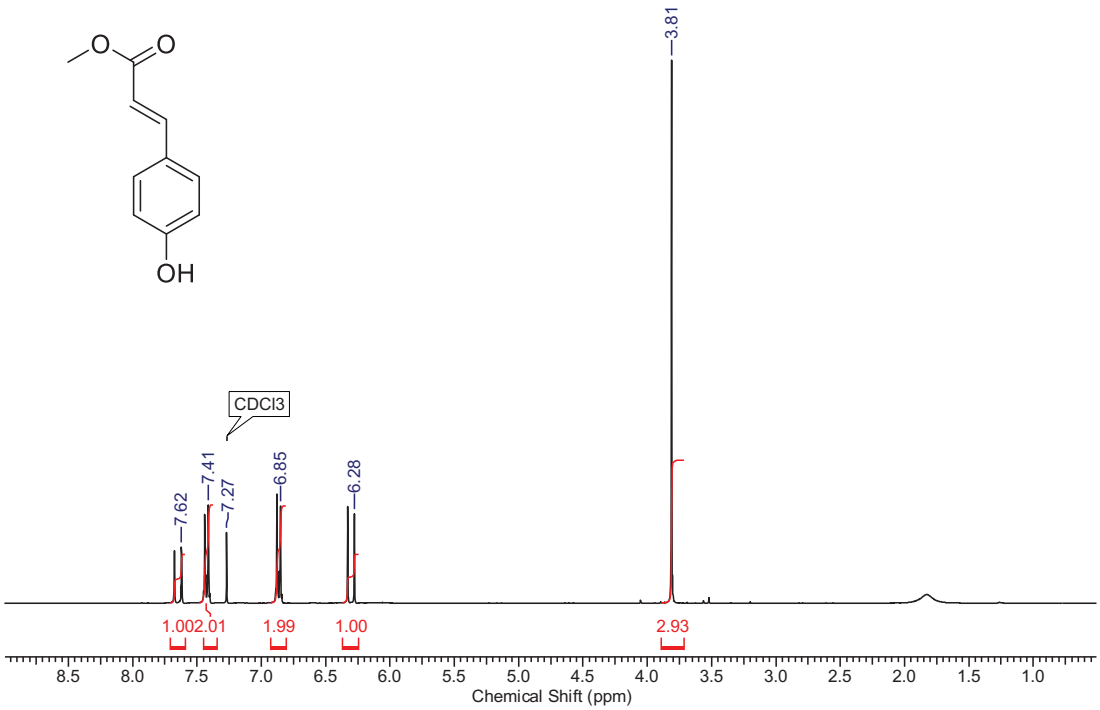


Figure S18: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 4-hydroxy-methyl cinnamate.

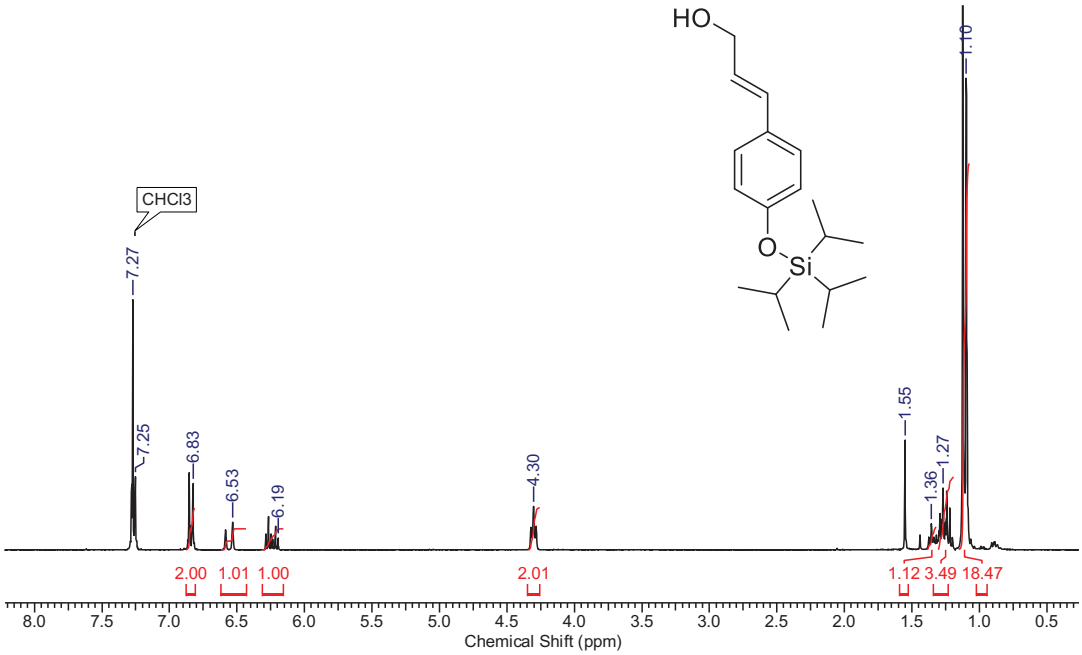


Figure S19: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of (E)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol.

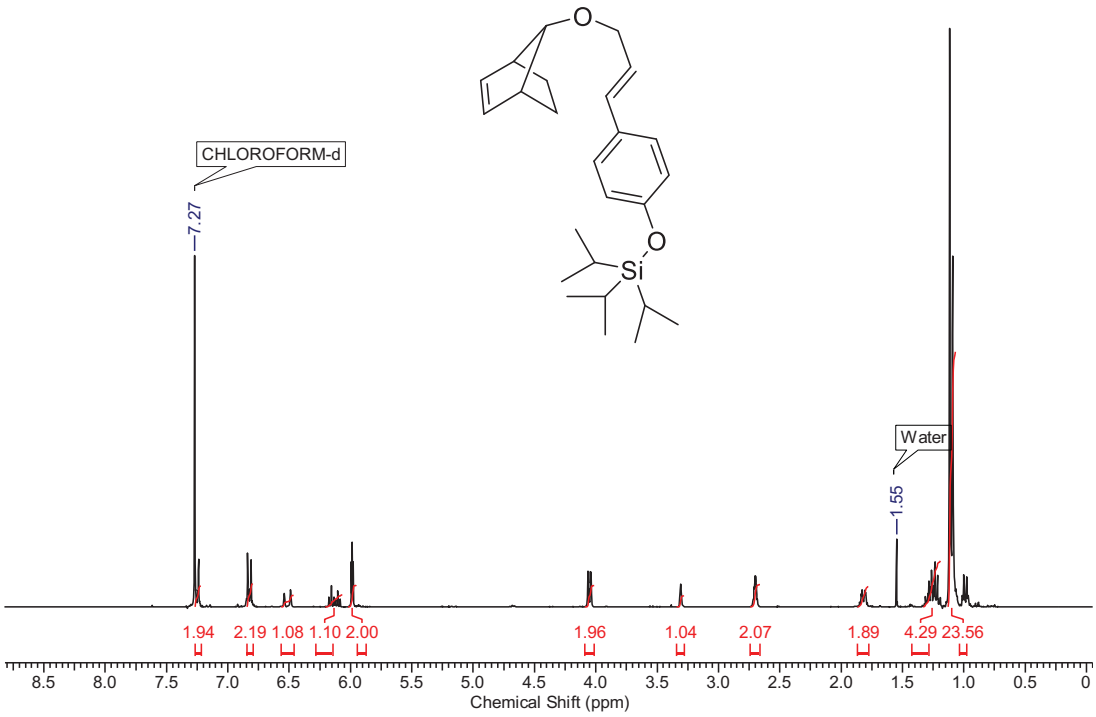


Figure S20: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of **S7**.

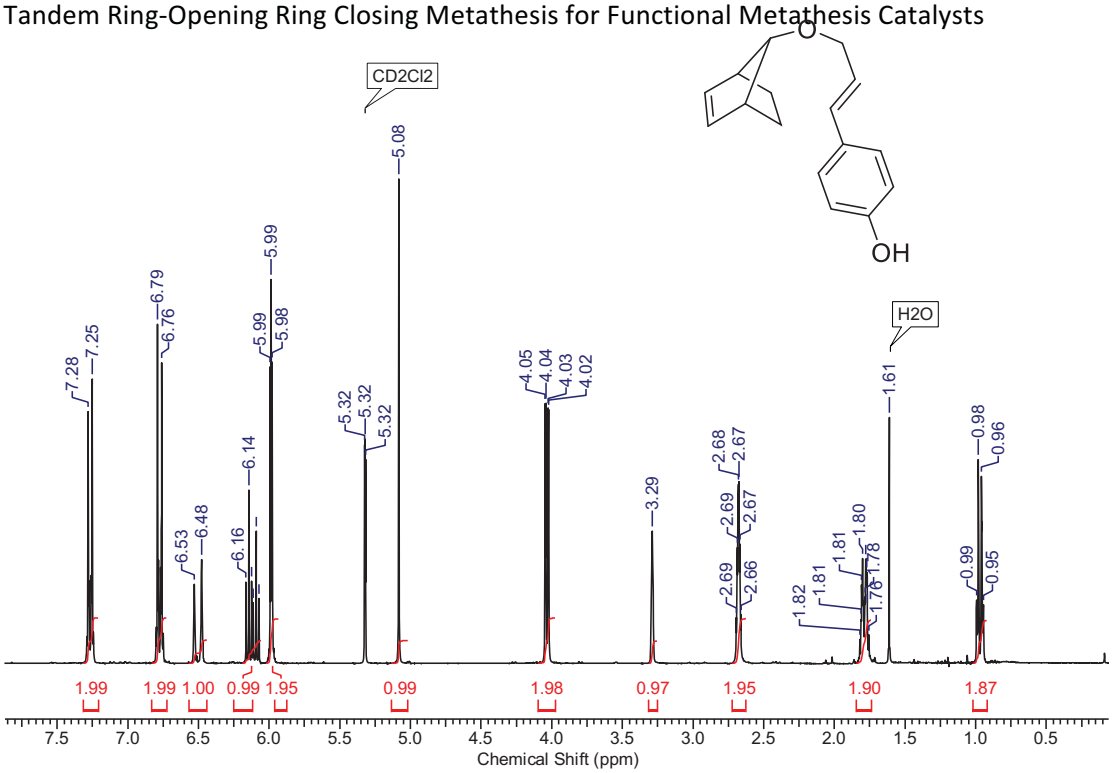


Figure S21: ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectrum of **4**.

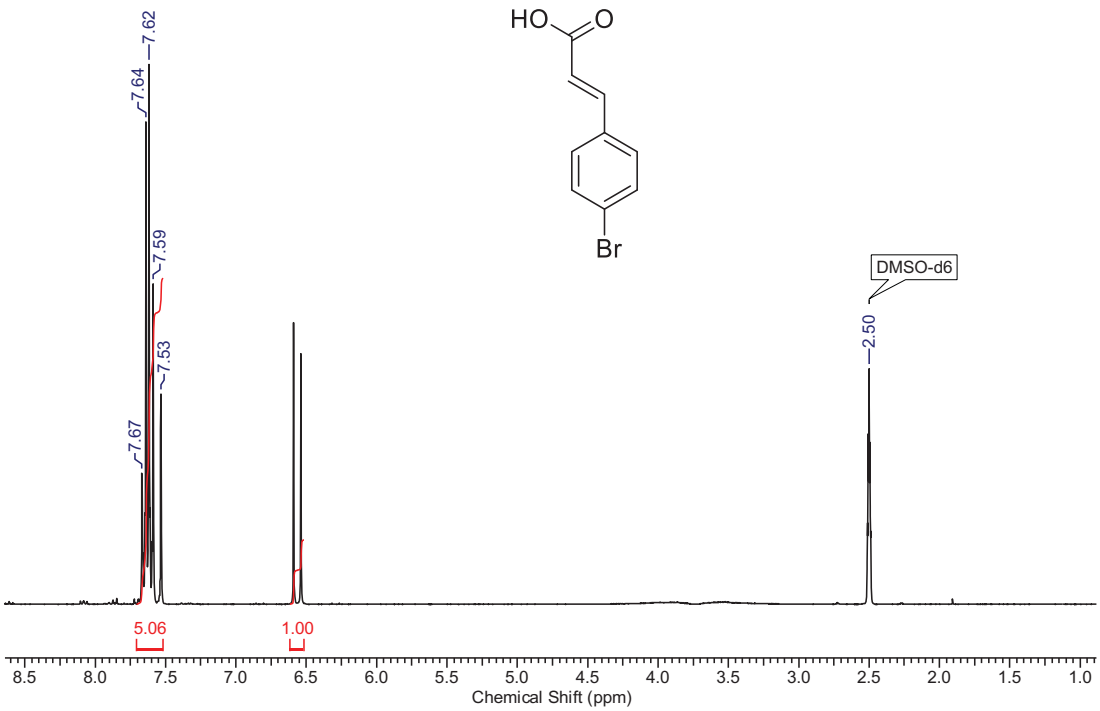


Figure S22: ^{1}H-NMR (dimethylsulfoxide-d_6, 300 MHz) spectrum of 4-bromocinnamic acid.

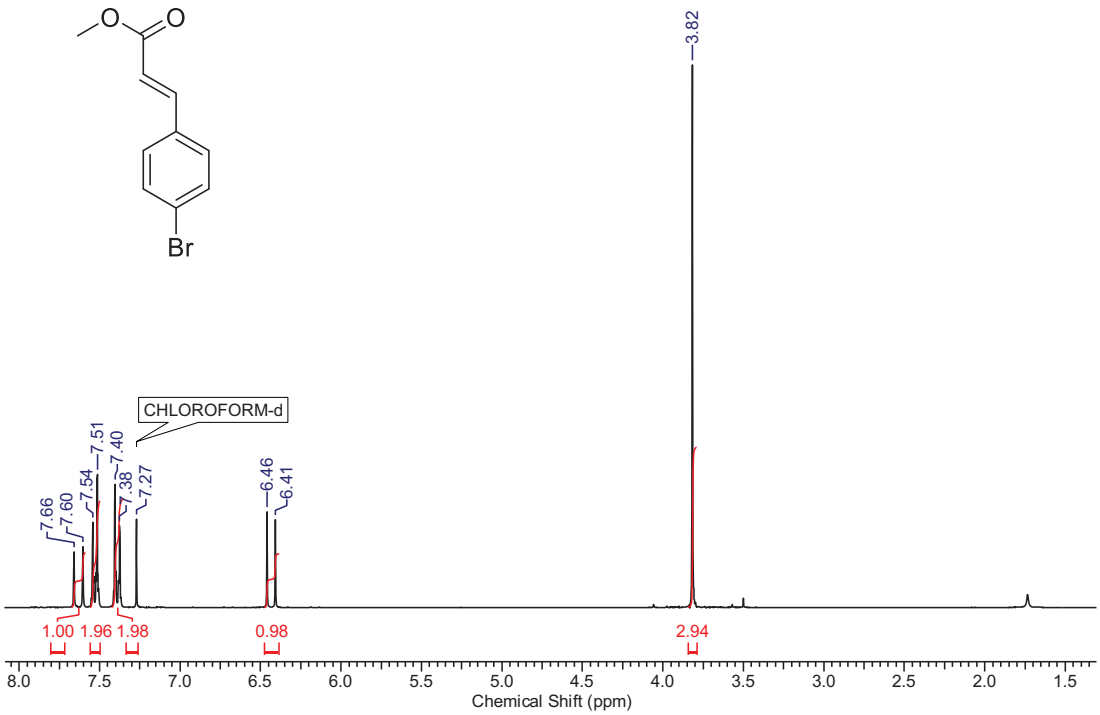


Figure S23: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 4-bromo methylcinnamate.

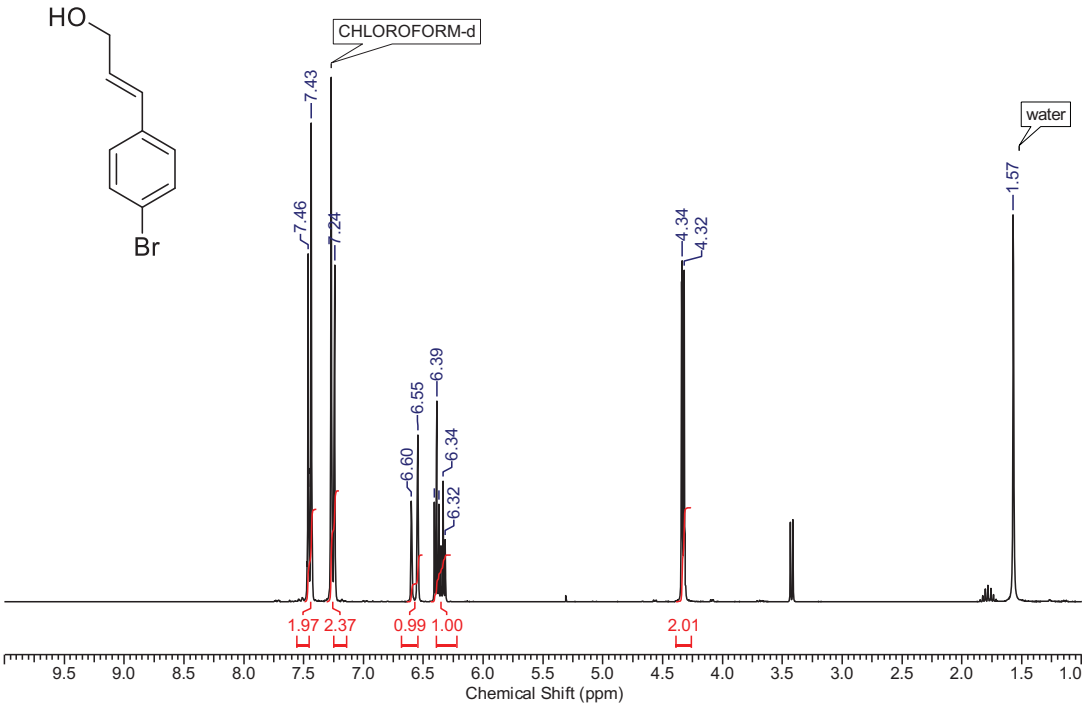


Figure S24: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 4-bromo cinnamylalcohol.

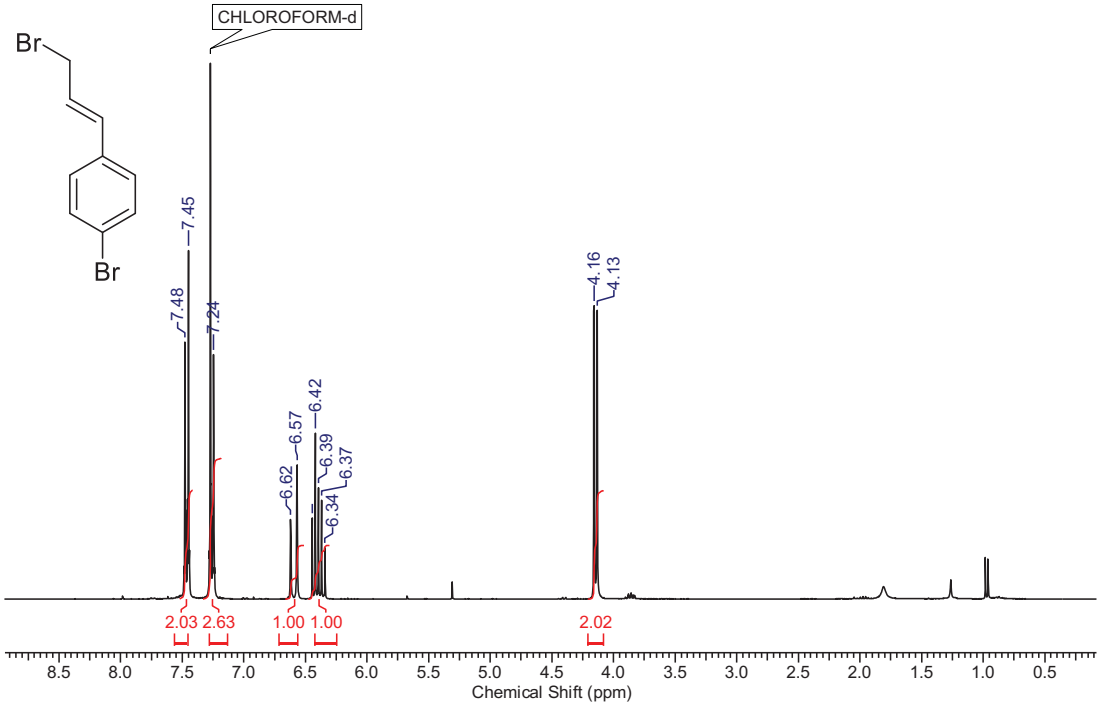


Figure S25: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of 4-bromo cinnamylbromide.

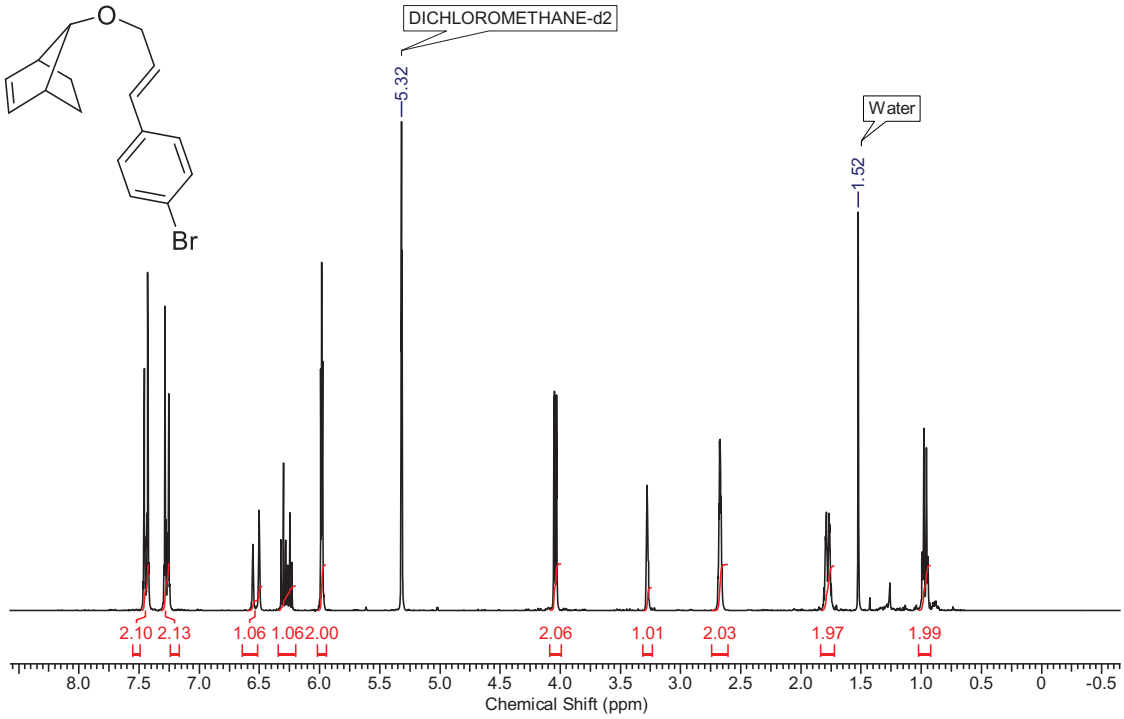


Figure S26: ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectrum of **5**.

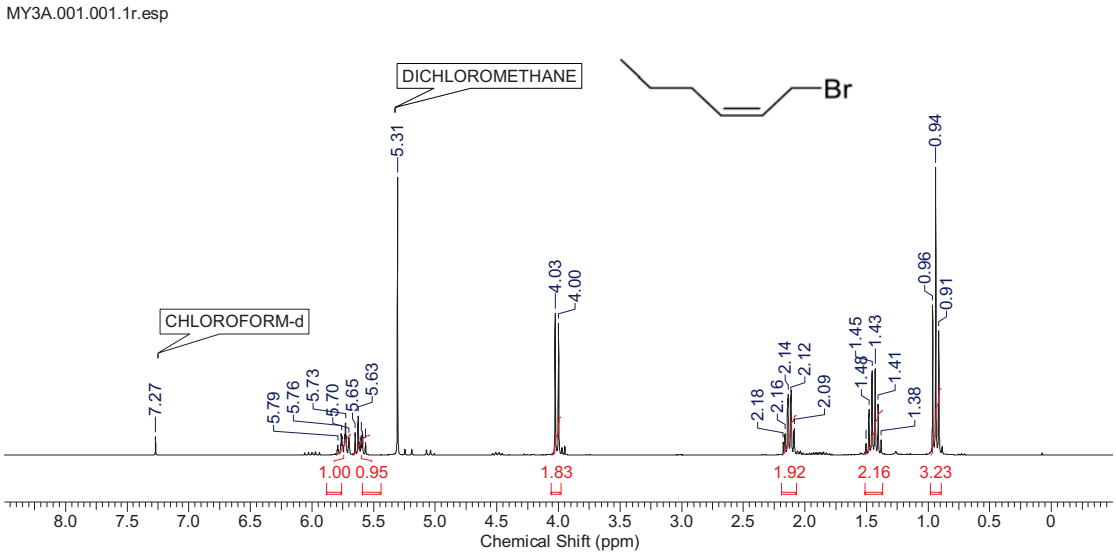


Figure S27: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of (Z)-1-bromohex-2-ene.

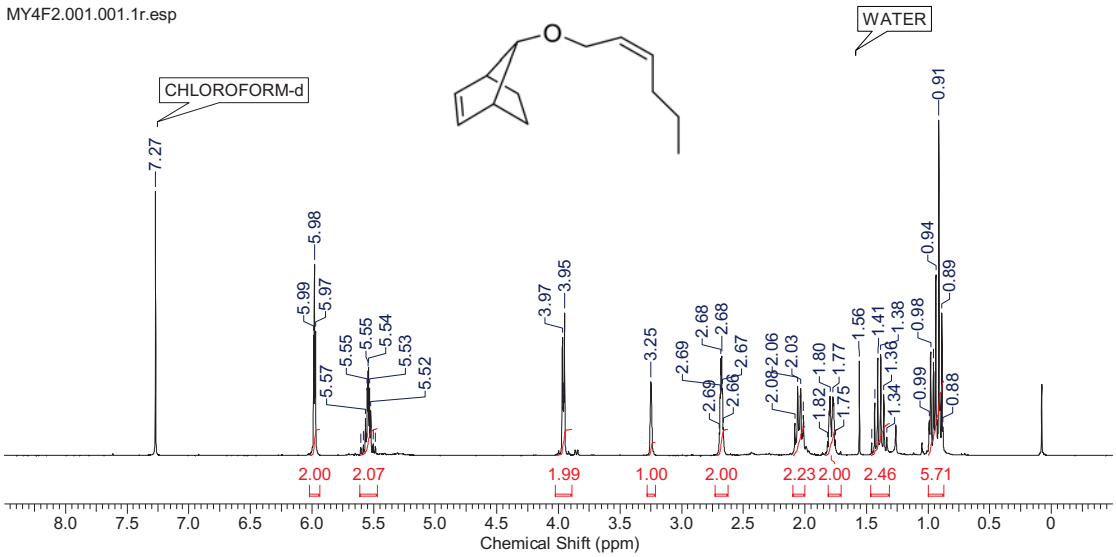


Figure S28: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of **6**.

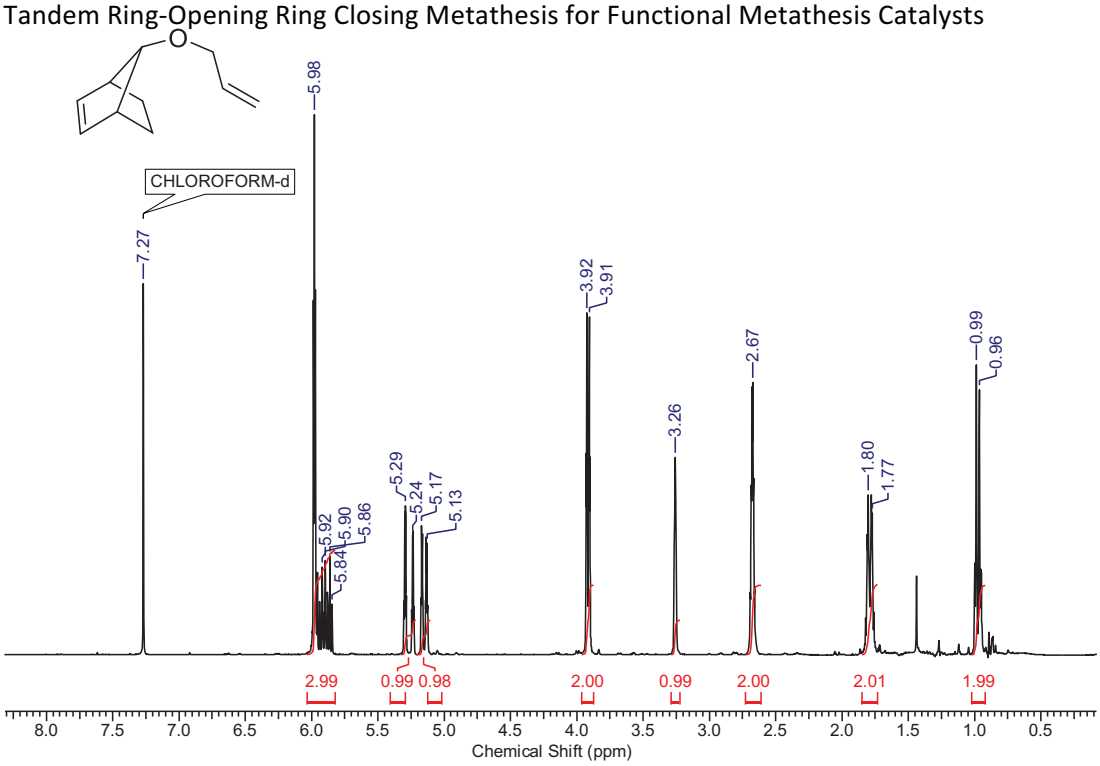


Figure S29: ^{1}H-NMR (chloroform-d, 300 MHz) spectrum of **7**.

^{13}C-NMR Spectra:

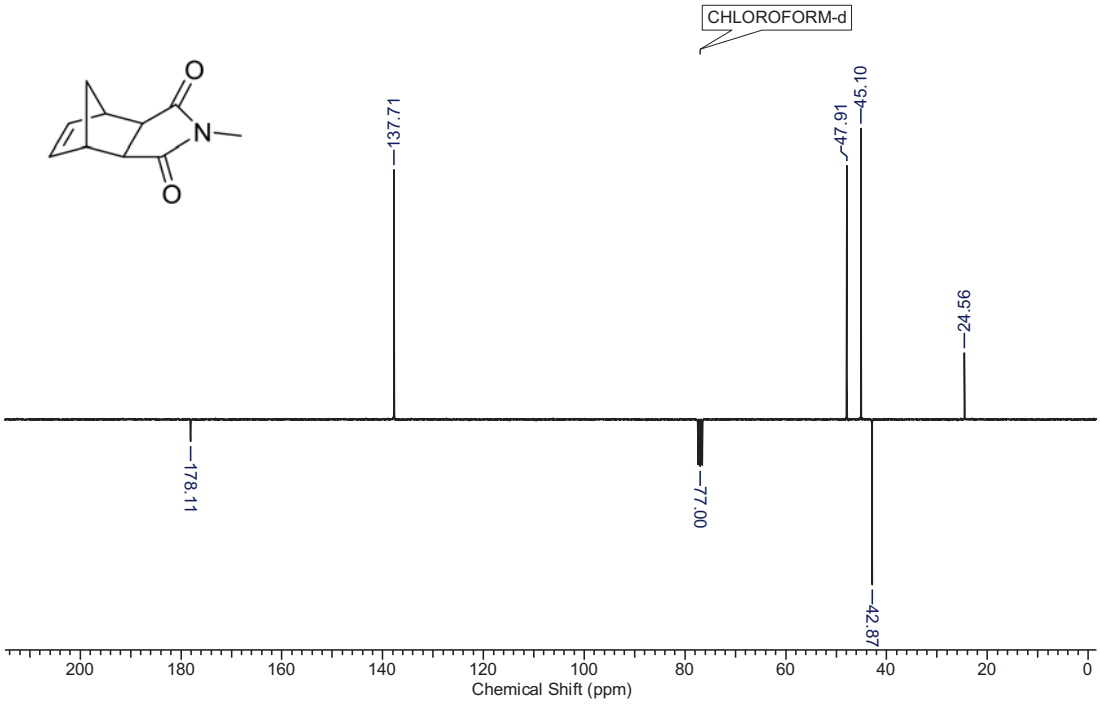


Figure S30: ^{13}C-APT NMR (chloroform-d, 75 MHz) spectrum of **MNI**.

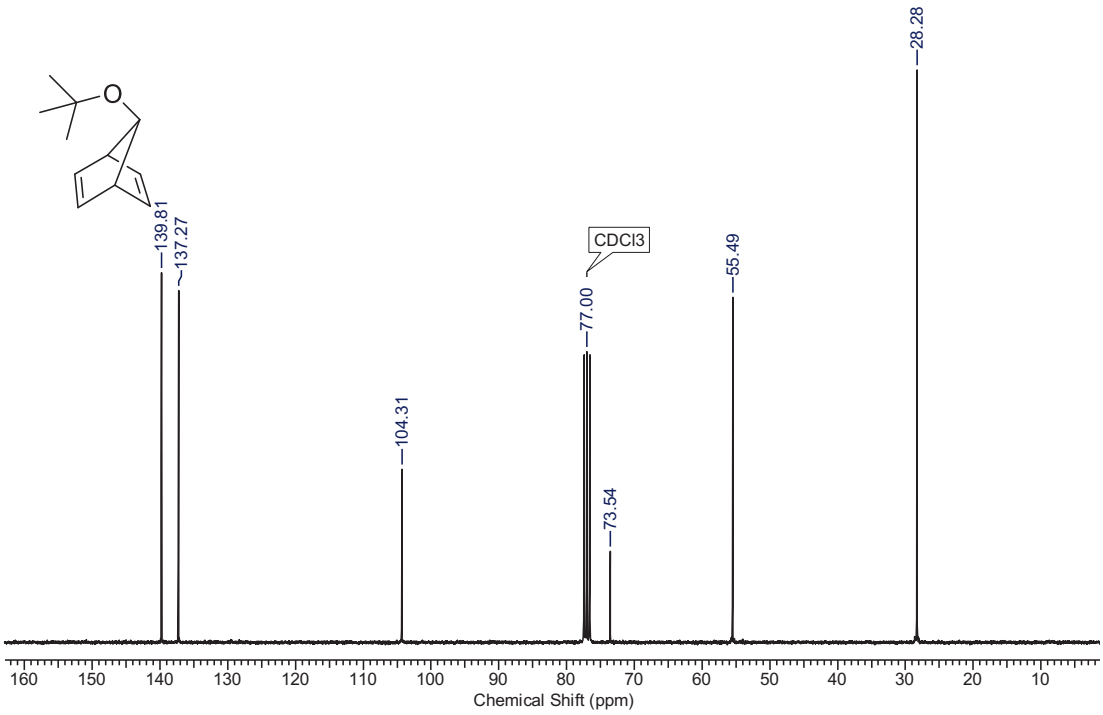


Figure S31: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of 7-(tert-butoxy)-norbornadiene (**S1**)

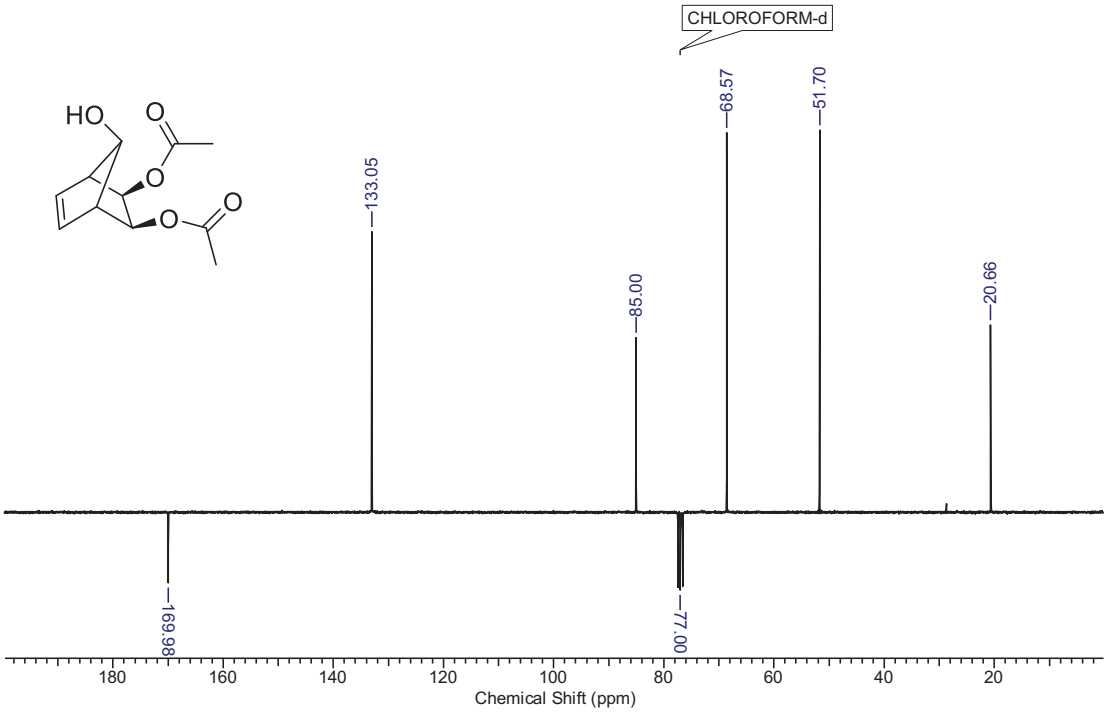


Figure S32: ^{13}C- APT NMR (chloroform-d, 75 MHz) spectrum of syn-7-hydroxynorbornene-2,3-diacetate (**S4**).

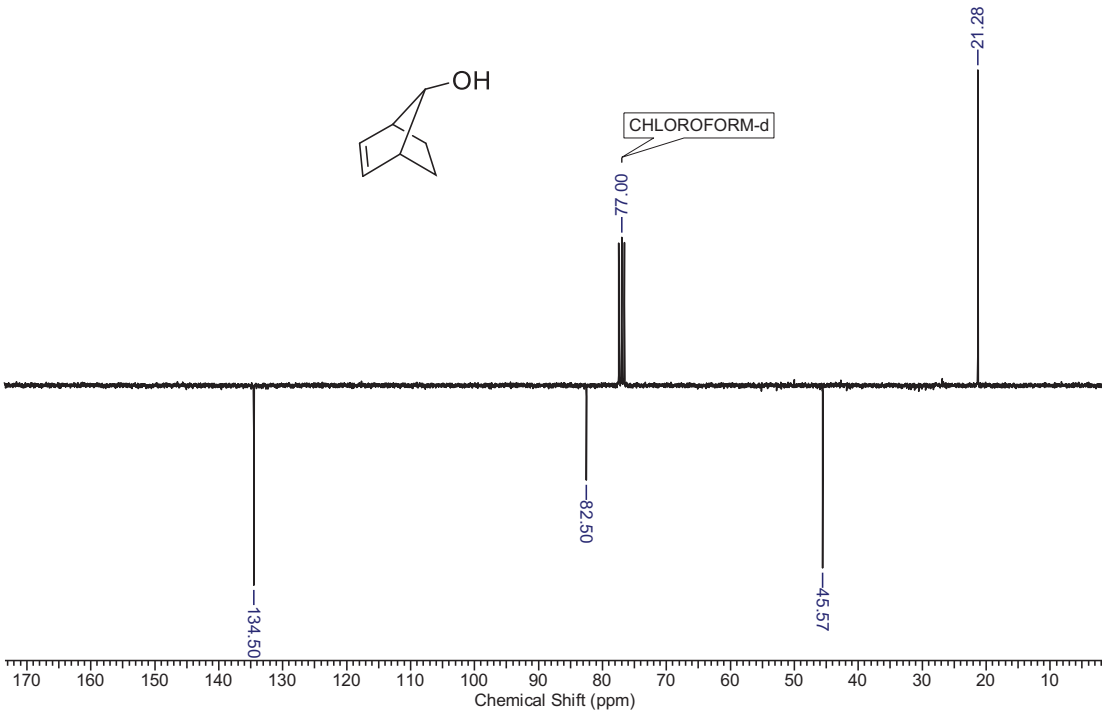


Figure S33: ^{13}C- APT NMR (chloroform-d, 75 MHz) spectrum of anti-7-hydroxynorbornene (**S6**).

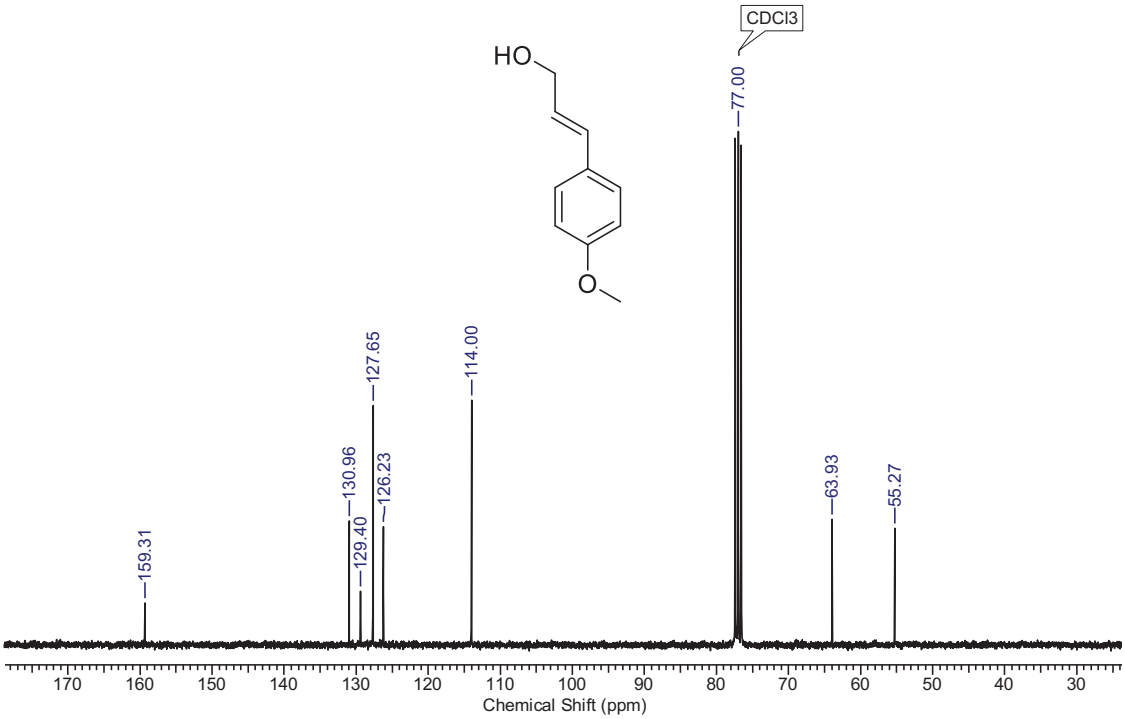


Figure S34: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of 4-methoxy cinnamylalcohol.

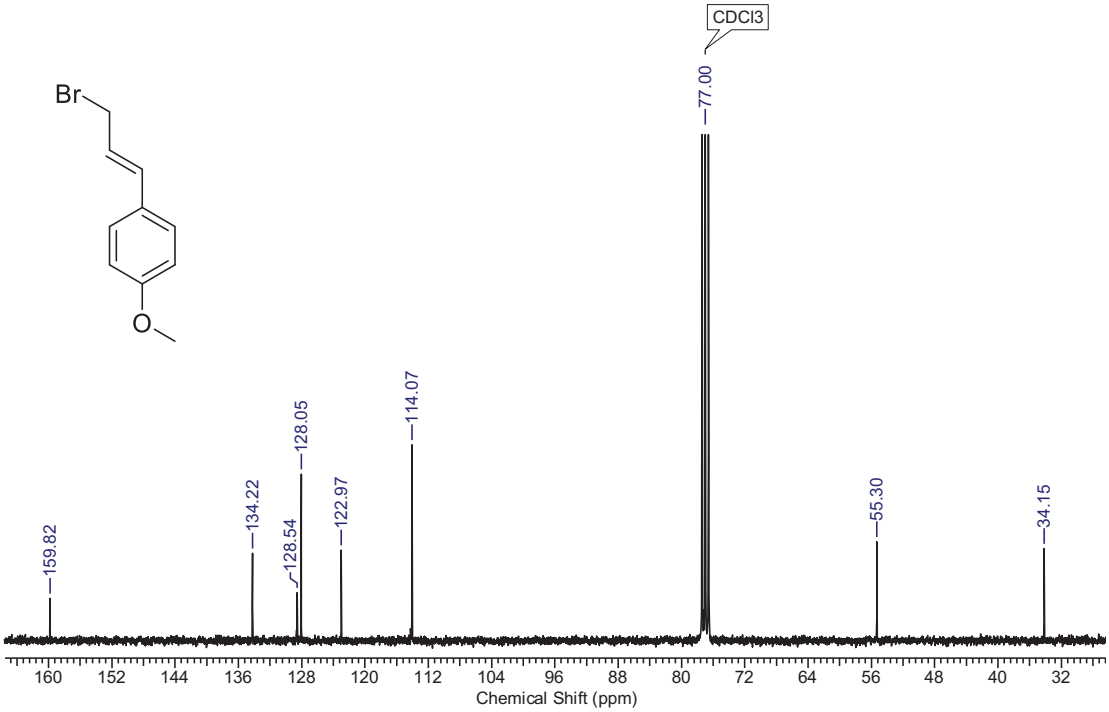


Figure S35: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of 4-methoxy cinnamyl bromide.

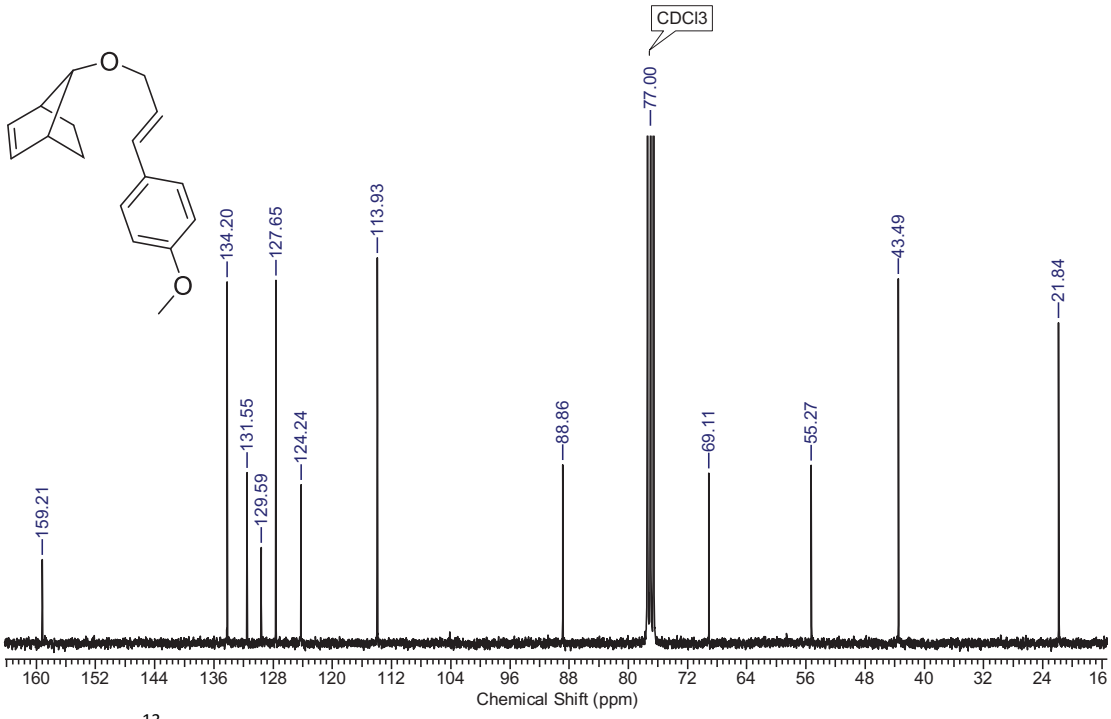


Figure S36: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of **3**.

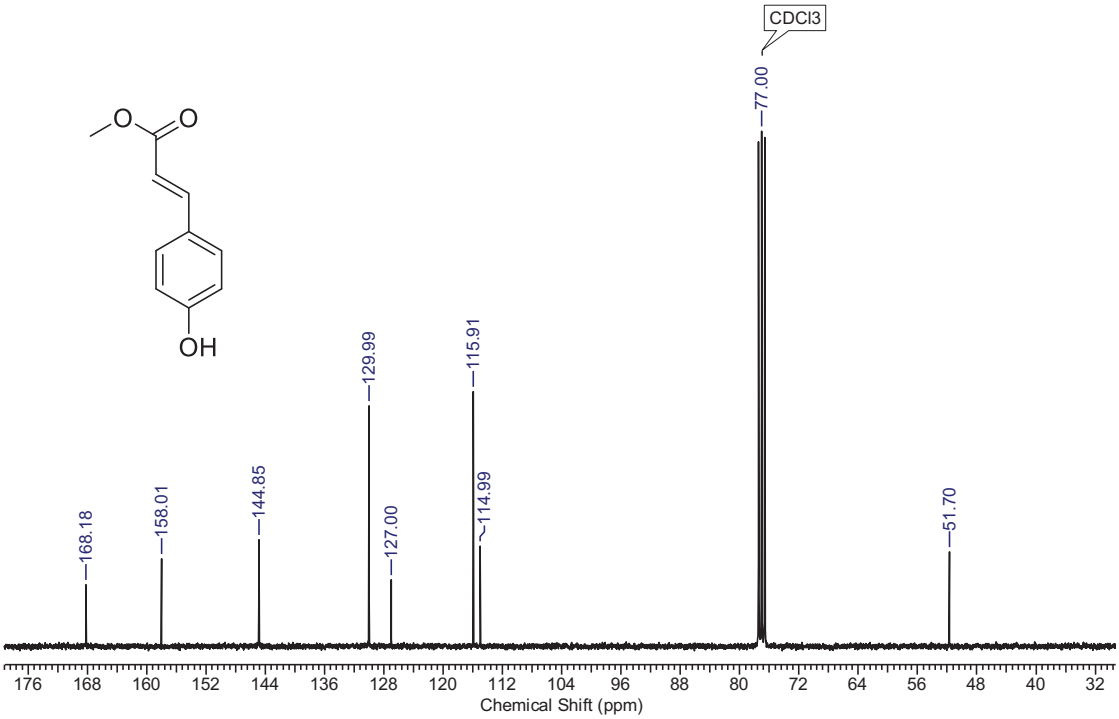


Figure S37: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of 4-hydroxy-methyl cinnamate.

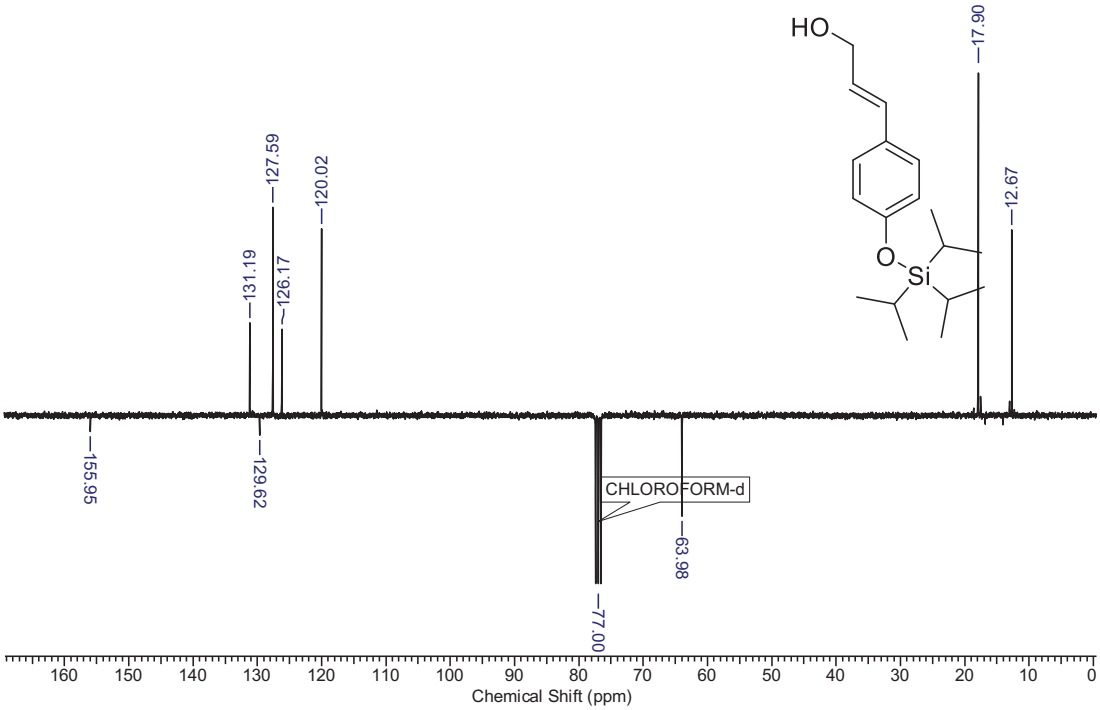


Figure S38: ^{13}C-APT NMR (chloroform-d, 75 MHz) spectrum of (E)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol.

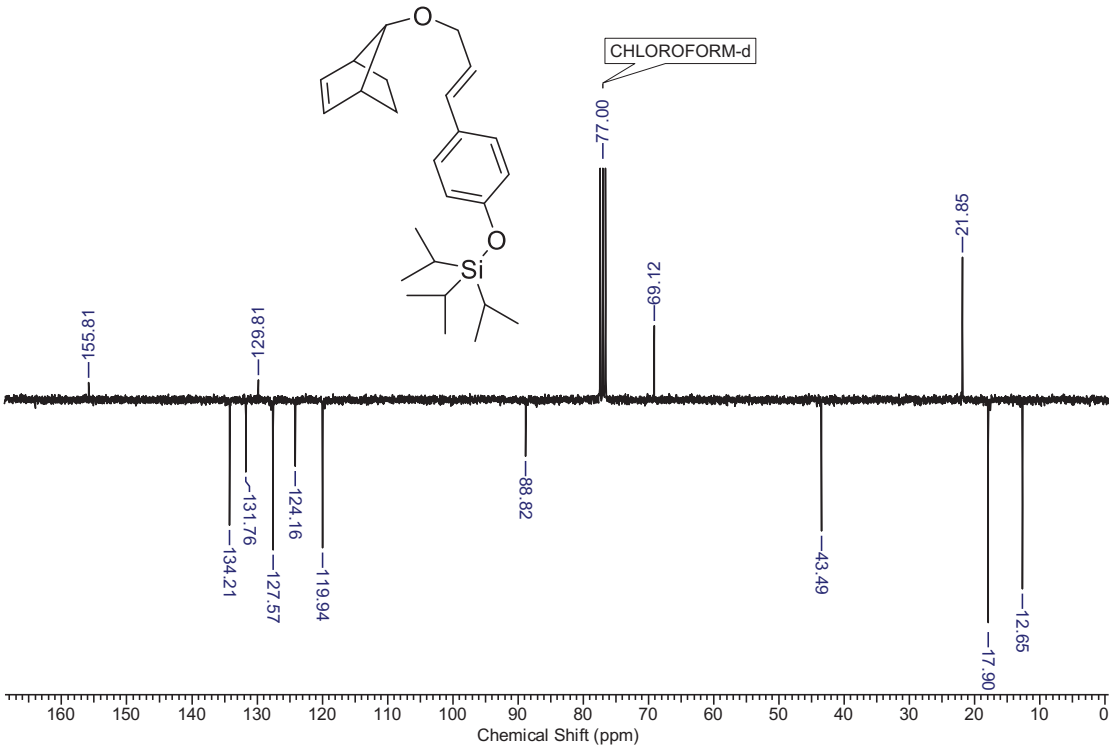


Figure S39: ^{13}C- APT NMR (chloroform-d, 75 MHz) spectrum of **S7**.

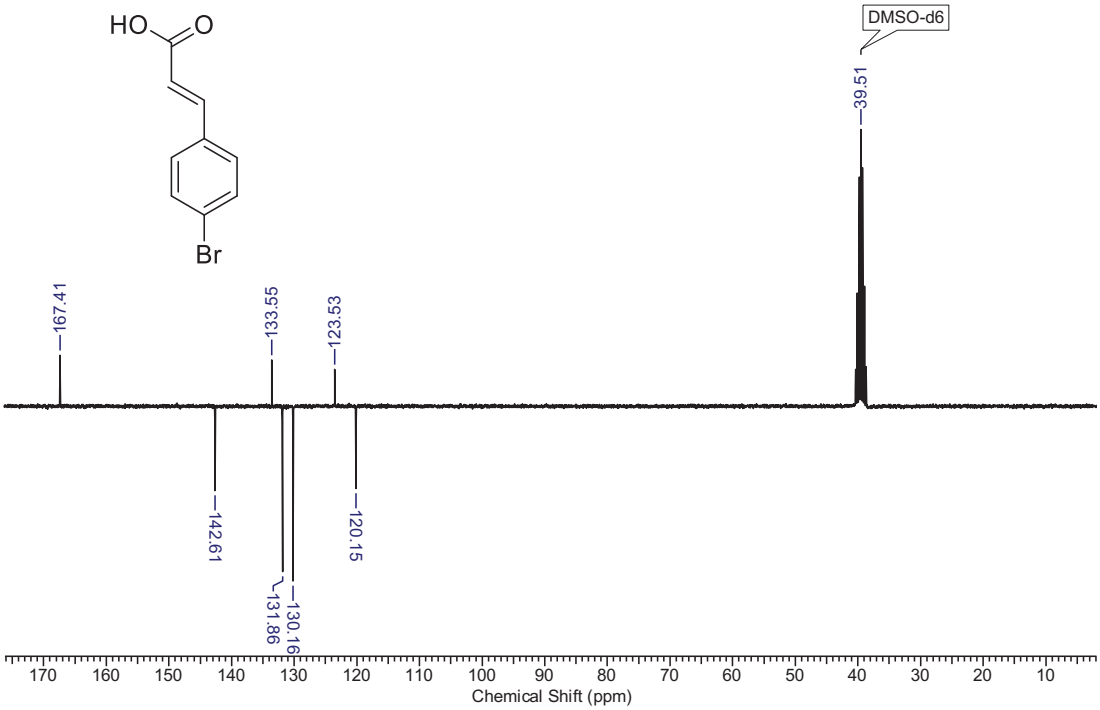


Figure S40: ^{13}C- APT NMR (dimethylsulfoxide-d_6, 75 MHz) spectrum of 4-bromocinnamic acid.

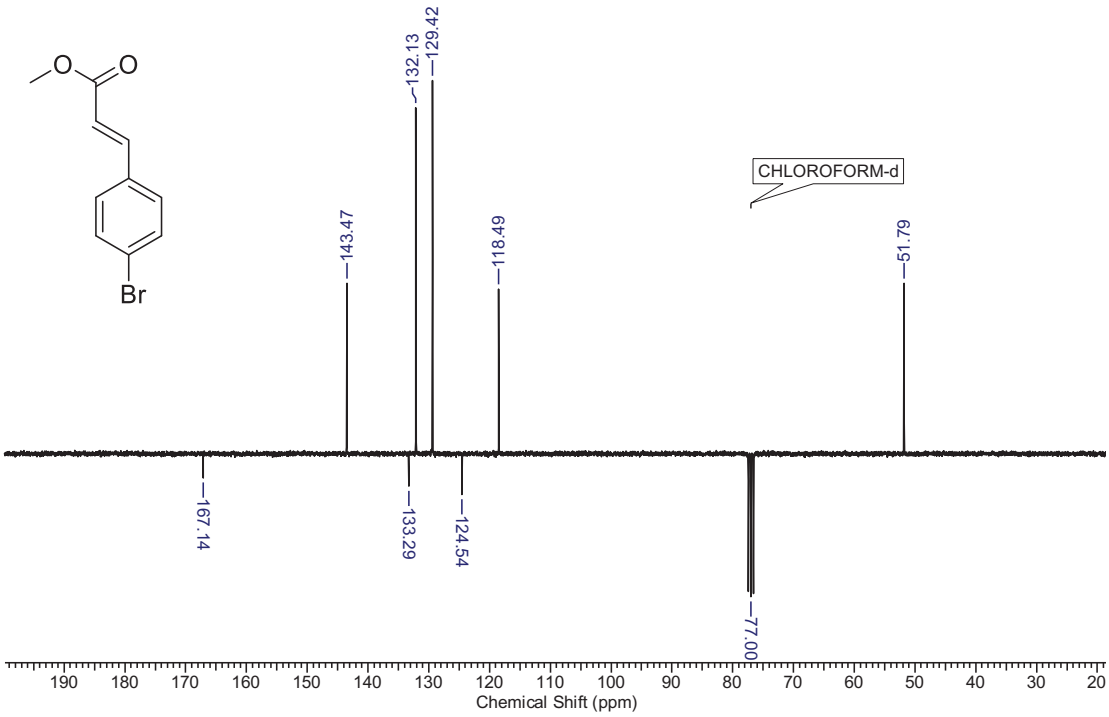


Figure S41: ^{13}C- APT NMR (chloroform-d, 75 MHz) spectrum of 4-bromo methylcinnamate.

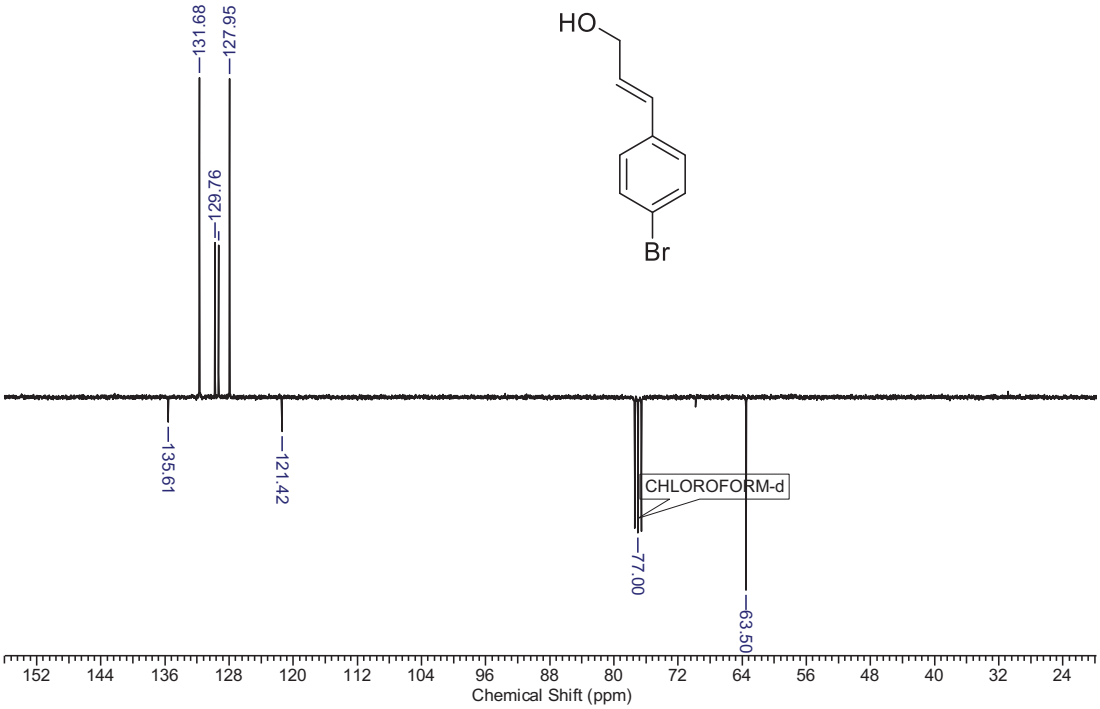


Figure S42: ^{13}C- APT NMR (chloroform-d, 75 MHz) spectrum of 4-bromo cinnamylalcohol.

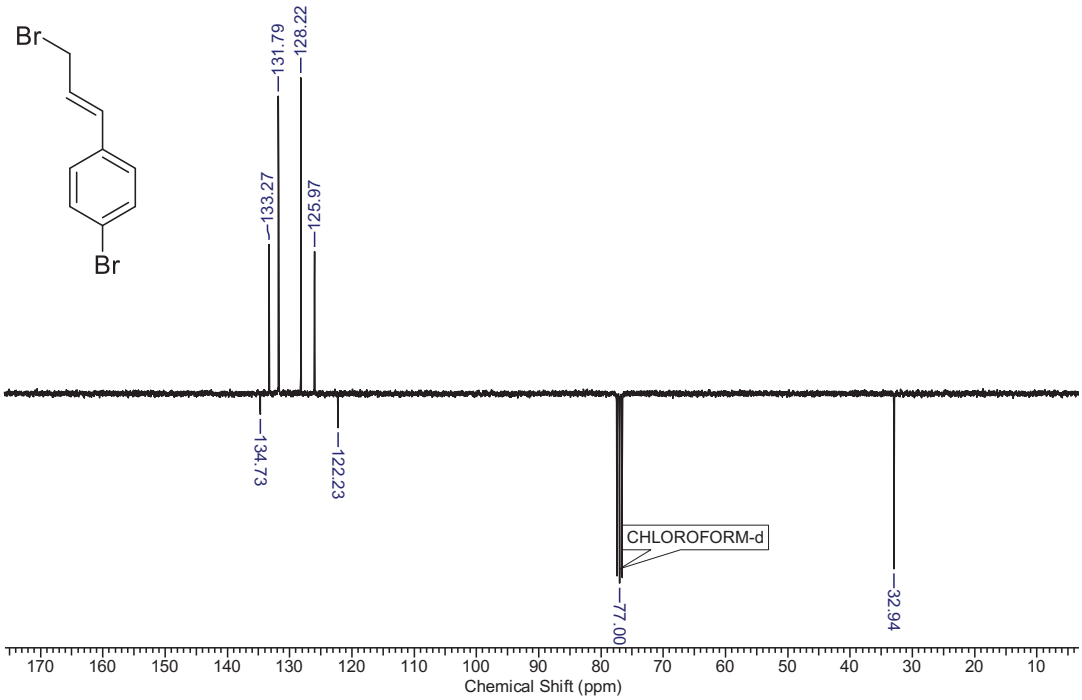


Figure S43: ^{13}C- APT NMR (chloroform-d, 75 MHz) spectrum of 4-bromo cinnamylbromide.

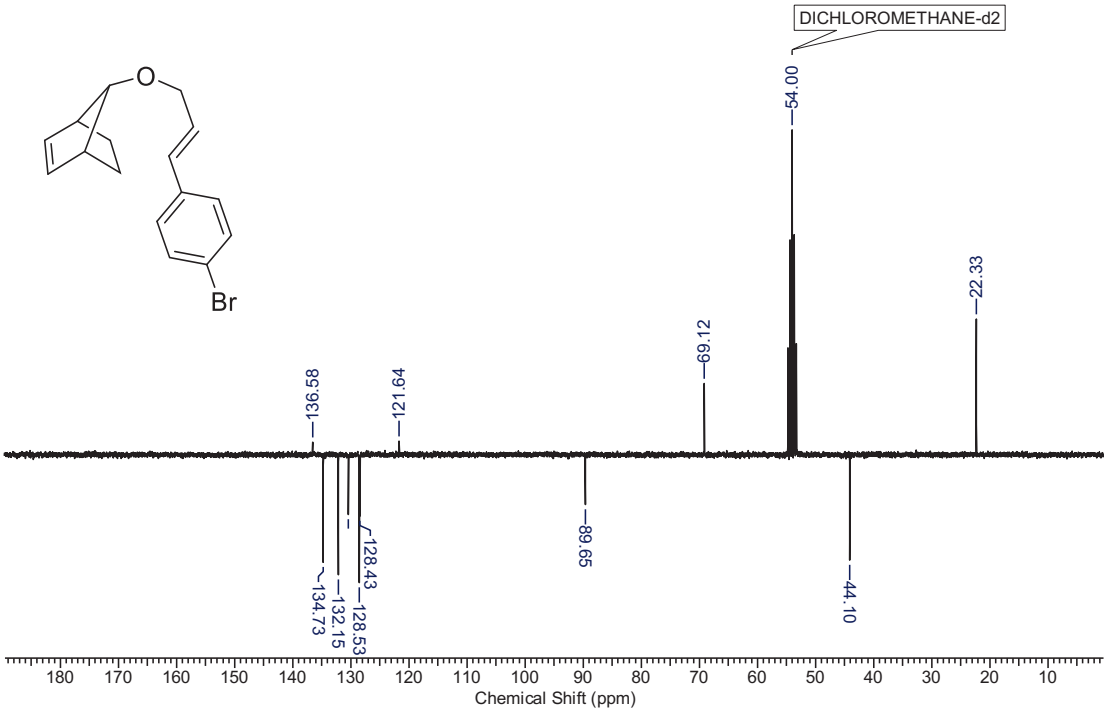


Figure S44: ^{13}C- APT NMR (dichloromethane-d_2, 75 MHz) spectrum of **5**.

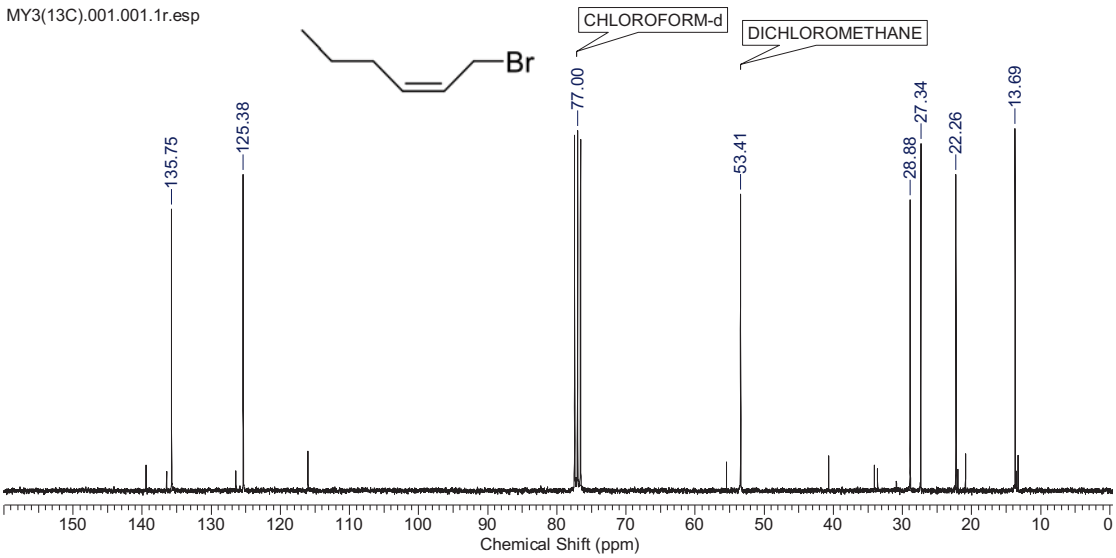


Figure S45: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of (Z)-1-bromohex-2-ene .

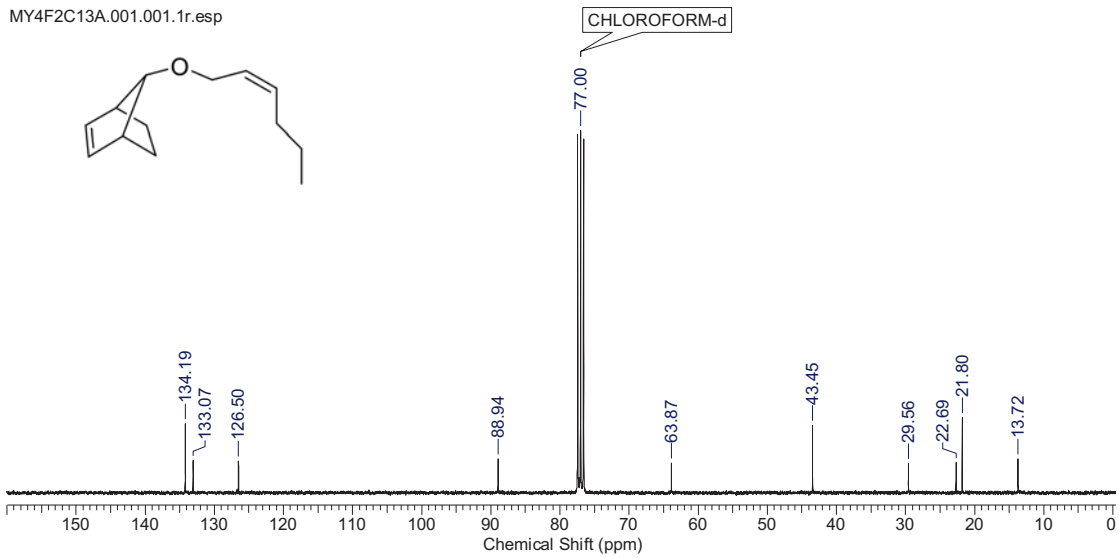


Figure S46: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of **6**.

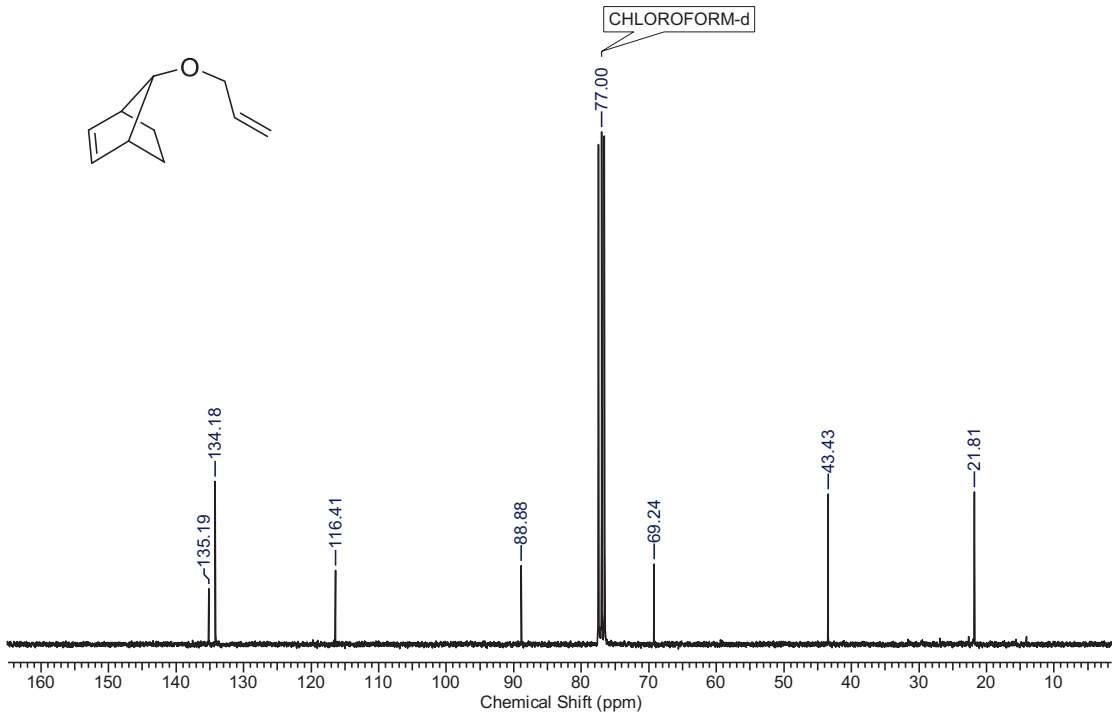


Figure S47: ^{13}C-NMR (chloroform-d, 75 MHz) spectrum of **7**.

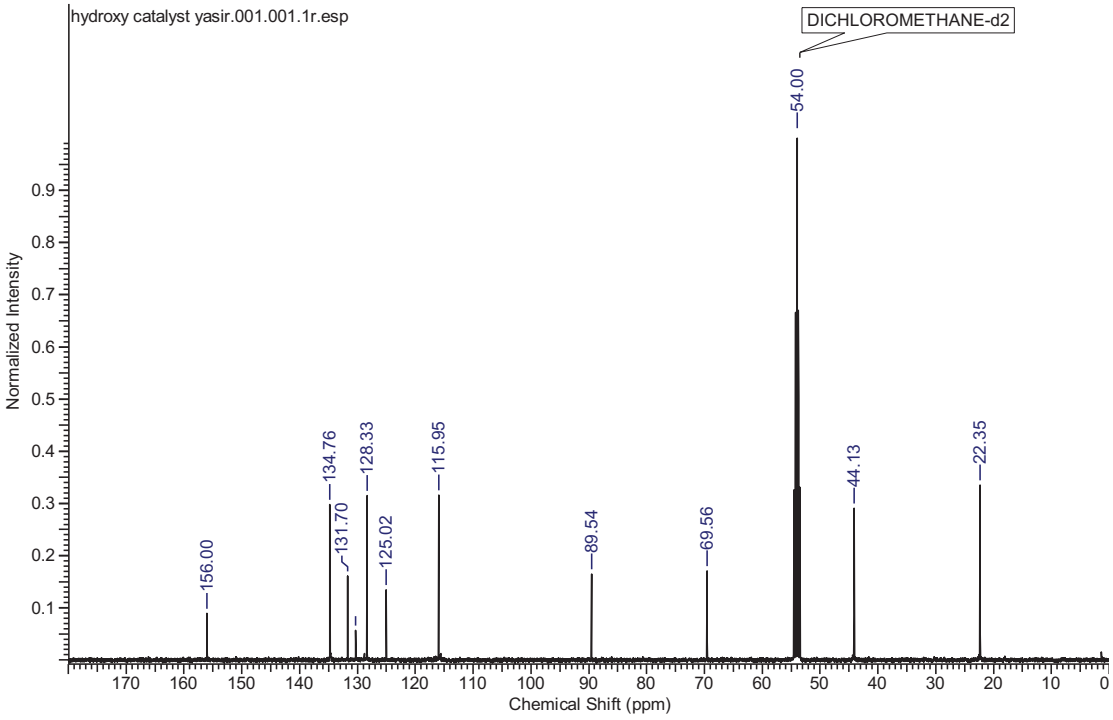


Figure S48: ^{13}C-NMR (dichloromethane-d_2, 75 MHz) spectrum of **4**.

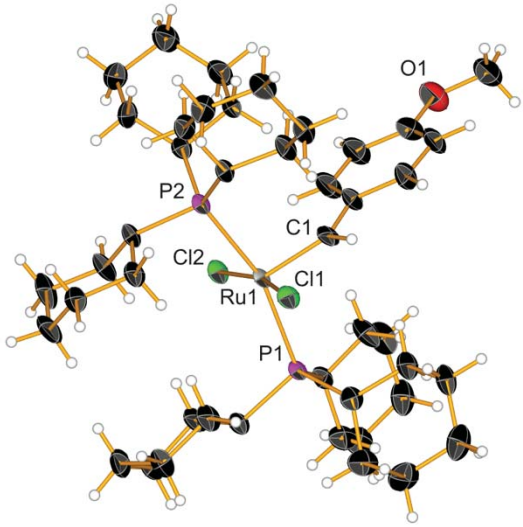


Figure S49: Single crystal X-ray structure of **G1-OMe**. CCDC 1474438 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table 1. Crystal data and structure refinement for **G1-OMe**.

Identification code	**G1-OMe**	
Empirical formula	C46 H72 Cl6 O P2 Ru	
Formula weight	1016.74	
Temperature	200(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/n$	
Unit cell dimensions	a = 15.4774(9) Å	α= 90°.
	b = 17.9694(11) Å	β= 96.914(5)°.
	c = 18.3098(13) Å	γ = 90°.
Volume	5055.3(6) $Å^3$	
Z	4	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	6.266 mm^{-1}	
F(000)	2128	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.459 to 68.338°.	
Index ranges	-18<=h<=18, -19<=k<=20, -22<=l<=22	
Reflections collected	35233	
Independent reflections	8870 [R(int) = 0.3712]	
Completeness to theta = 67.686°	96.7 %	
Absorption correction	Integration	
Max. and min. transmission	0.7659 and 0.4680	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8870 / 0 / 508	
Goodness-of-fit on F^2	1.735	
Final R indices [I>2sigma(I)]	R1 = 0.2004, wR2 = 0.3911	
R indices (all data)	R1 = 0.2115, wR2 = 0.4209	
Extinction coefficient	0.073(4)	
Largest diff. peak and hole	6.883 and -9.274 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **G1-OMe**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2251(1)	2512(1)	4771(1)	23(1)
Cl(1)	1812(1)	2121(1)	3527(1)	31(1)
Cl(2)	2999(1)	2878(1)	5943(1)	31(1)
P(1)	2606(1)	1237(1)	5106(1)	25(1)
P(2)	2336(1)	3758(1)	4293(1)	25(1)
O(1)	-962(4)	3301(3)	7153(3)	54(1)
C(1)	1088(5)	2514(3)	4938(4)	28(2)
C(2)	595(4)	2747(4)	5527(4)	34(1)
C(3)	922(5)	3061(4)	6193(4)	46(2)
C(4)	391(5)	3244(5)	6718(4)	49(2)
C(5)	-500(5)	3118(4)	6596(4)	43(2)
C(6)	-860(4)	2816(4)	5922(4)	41(2)
C(7)	-306(5)	2630(5)	5395(5)	41(2)
C(8)	-1878(5)	3195(5)	7028(5)	56(2)
C(9)	2011(4)	551(3)	4470(3)	32(1)
C(10)	1043(4)	526(4)	4560(4)	44(2)
C(11)	533(4)	101(5)	3922(4)	48(2)
C(12)	874(5)	-678(5)	3892(4)	53(2)
C(13)	1847(6)	-672(5)	3811(5)	56(2)
C(14)	2379(5)	-235(4)	4427(4)	49(2)
C(15)	3769(4)	1059(3)	4985(3)	28(1)
C(16)	3967(4)	1339(4)	4228(3)	37(1)
C(17)	4900(5)	1163(5)	4104(4)	43(2)
C(18)	5568(4)	1451(4)	4723(4)	41(2)
C(19)	5346(4)	1176(4)	5457(4)	39(1)
C(20)	4425(4)	1400(4)	5589(3)	35(1)
C(21)	2540(4)	974(3)	6077(3)	31(1)
C(22)	2812(4)	169(4)	6271(3)	38(2)
C(23)	2796(5)	12(4)	7105(4)	44(2)
C(24)	1923(5)	188(5)	7328(4)	47(2)
C(25)	1659(5)	983(5)	7144(4)	50(2)
C(26)	1662(4)	1163(5)	6336(4)	45(2)
C(27)	3428(3)	3900(4)	3985(3)	30(1)
C(28)	4158(4)	3732(4)	4617(4)	41(2)
C(29)	5052(5)	3881(6)	4373(4)	49(2)
C(30)	5186(4)	3437(5)	3696(4)	46(2)
C(31)	4480(4)	3584(4)	3072(4)	39(1)
C(32)	3563(4)	3454(4)	3302(3)	35(1)
C(33)	1590(4)	3964(3)	3451(3)	30(1)
C(34)	1686(4)	4730(4)	3128(3)	33(1)
C(35)	1151(4)	4806(4)	2367(4)	42(2)
C(36)	205(4)	4642(4)	2417(4)	43(2)
C(37)	96(4)	3869(4)	2746(3)	41(2)
C(38)	623(4)	3795(4)	3499(3)	36(1)
C(39)	2270(4)	4509(3)	4986(4)	30(1)
C(40)	1326(4)	4614(3)	5166(4)	33(1)
C(41)	1342(5)	5066(4)	5875(4)	46(2)
C(42)	1742(5)	5830(4)	5779(4)	48(2)
C(43)	2648(5)	5763(4)	5530(4)	42(2)
C(44)	2666(4)	5261(4)	4854(4)	38(1)
Cl(3)	7256(3)	2126(2)	3483(3)	116(1)
Cl(4)	9096(3)	1890(3)	3366(2)	131(2)
C(46)	8075(9)	2078(8)	2925(7)	93(4)
Cl(5)	989(2)	2029(2)	1239(2)	107(1)
Cl(6)	205(6)	728(2)	1776(2)	191(3)
C(45)	308(8)	1662(6)	1836(6)	78(3)

Table 3. Bond lengths [Å] and angles [°] for **G1-OMe**.

Ru(1)-C(1)	1.861(8)
Ru(1)-Cl(1)	2.4020(13)
Ru(1)-Cl(2)	2.4044(13)
Ru(1)-P(2)	2.4137(15)
Ru(1)-P(1)	2.4174(14)
P(1)-C(21)	1.853(6)
P(1)-C(9)	1.862(6)
P(1)-C(15)	1.867(6)
P(2)-C(33)	1.849(6)
P(2)-C(27)	1.862(6)
P(2)-C(39)	1.863(6)
O(1)-C(5)	1.354(8)
O(1)-C(8)	1.420(10)
C(1)-C(2)	1.455(10)
C(1)-H(1)	0.9300
C(2)-C(3)	1.383(10)
C(2)-C(7)	1.402(10)
C(3)-C(4)	1.377(10)
C(3)-H(3)	0.9300
C(4)-C(5)	1.389(10)
C(4)-H(4)	0.9300
C(5)-C(6)	1.402(11)
C(6)-C(7)	1.407(11)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(10)	1.527(9)
C(9)-C(14)	1.529(10)
C(10)-C(11)	1.533(10)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.500(12)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.531(12)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.531(10)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(20)	1.536(8)
C(15)-C(16)	1.540(8)
C(16)-C(17)	1.523(9)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(18)	1.529(10)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-C(19)	1.510(9)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(20)	1.528(8)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(26)	1.531(8)
C(21)-C(22)	1.537(9)
C(22)-C(23)	1.557(9)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700

C(23)-C(24)	1.493(10)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.512(13)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-C(26)	1.516(9)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-C(32)	1.521(8)
C(27)-C(28)	1.546(8)
C(28)-C(29)	1.528(9)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-C(30)	1.509(12)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.506(9)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-C(32)	1.547(9)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-C(34)	1.513(8)
C(33)-C(38)	1.541(8)
C(34)-C(35)	1.539(8)
C(34)-H(34A)	0.9700
C(34)-H(34B)	0.9700
C(35)-C(36)	1.507(10)
C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700
C(36)-C(37)	1.532(10)
C(36)-H(36A)	0.9700
C(36)-H(36B)	0.9700
C(37)-C(38)	1.521(8)
C(37)-H(37A)	0.9700
C(37)-H(37B)	0.9700
C(38)-H(38A)	0.9700
C(38)-H(38B)	0.9700
C(39)-C(44)	1.515(9)
C(39)-C(40)	1.548(8)
C(40)-C(41)	1.529(9)
C(40)-H(40A)	0.9700
C(40)-H(40B)	0.9700
C(41)-C(42)	1.525(11)
C(41)-H(41A)	0.9700
C(41)-H(41B)	0.9700
C(42)-C(43)	1.530(10)
C(42)-H(42A)	0.9700
C(42)-H(42B)	0.9700
C(43)-C(44)	1.535(9)
C(43)-H(43A)	0.9700
C(43)-H(43B)	0.9700
C(44)-H(44A)	0.9700
C(44)-H(44B)	0.9700
Cl(3)-C(46)	1.722(14)
Cl(4)-C(46)	1.719(14)
C(46)-H(46A)	0.9700
C(46)-H(46B)	0.9700
Cl(5)-C(45)	1.737(13)
Cl(6)-C(45)	1.688(12)
C(45)-H(45A)	0.9700
C(45)-H(45B)	0.9700

C(1)-Ru(1)-Cl(1)	89.4(2)
C(1)-Ru(1)-Cl(2)	102.9(2)
Cl(1)-Ru(1)-Cl(2)	167.70(5)
C(1)-Ru(1)-P(2)	98.85(16)
Cl(1)-Ru(1)-P(2)	87.08(5)
Cl(2)-Ru(1)-P(2)	91.57(5)
C(1)-Ru(1)-P(1)	98.94(16)
Cl(1)-Ru(1)-P(1)	89.66(5)
Cl(2)-Ru(1)-P(1)	87.84(5)
P(2)-Ru(1)-P(1)	161.87(5)
C(21)-P(1)-C(9)	110.5(3)
C(21)-P(1)-C(15)	103.6(3)
C(9)-P(1)-C(15)	102.9(3)
C(21)-P(1)-Ru(1)	116.6(2)
C(9)-P(1)-Ru(1)	112.8(2)
C(15)-P(1)-Ru(1)	109.0(2)
C(33)-P(2)-C(27)	102.6(3)
C(33)-P(2)-C(39)	110.1(3)
C(27)-P(2)-C(39)	103.5(3)
C(33)-P(2)-Ru(1)	115.59(19)
C(27)-P(2)-Ru(1)	109.2(2)
C(39)-P(2)-Ru(1)	114.6(2)
C(5)-O(1)-C(8)	117.0(6)
C(2)-C(1)-Ru(1)	136.5(5)
C(2)-C(1)-H(1)	111.7
Ru(1)-C(1)-H(1)	111.7
C(3)-C(2)-C(7)	117.7(6)
C(3)-C(2)-C(1)	127.0(6)
C(7)-C(2)-C(1)	115.3(7)
C(4)-C(3)-C(2)	121.8(7)
C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(3)-C(4)-C(5)	120.9(7)
C(3)-C(4)-H(4)	119.5
C(5)-C(4)-H(4)	119.5
O(1)-C(5)-C(4)	116.4(7)
O(1)-C(5)-C(6)	124.5(6)
C(4)-C(5)-C(6)	119.1(6)
C(5)-C(6)-C(7)	119.0(6)
C(5)-C(6)-H(6)	120.5
C(7)-C(6)-H(6)	120.5
C(2)-C(7)-C(6)	121.4(7)
C(2)-C(7)-H(7)	119.3
C(6)-C(7)-H(7)	119.3
O(1)-C(8)-H(8A)	109.5
O(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
O(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(14)	110.8(6)
C(10)-C(9)-P(1)	111.8(4)
C(14)-C(9)-P(1)	119.0(4)
C(9)-C(10)-C(11)	110.8(6)
C(9)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
C(11)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
C(12)-C(11)-C(10)	110.0(6)
C(12)-C(11)-H(11A)	109.7
C(10)-C(11)-H(11A)	109.7
C(12)-C(11)-H(11B)	109.7
C(10)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
C(11)-C(12)-C(13)	110.7(6)

C(11)-C(12)-H(12A)	109.5
C(13)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
C(13)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	108.1
C(14)-C(13)-C(12)	112.3(7)
C(14)-C(13)-H(13A)	109.1
C(12)-C(13)-H(13A)	109.1
C(14)-C(13)-H(13B)	109.1
C(12)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.9
C(9)-C(14)-C(13)	110.0(6)
C(9)-C(14)-H(14A)	109.7
C(13)-C(14)-H(14A)	109.7
C(9)-C(14)-H(14B)	109.7
C(13)-C(14)-H(14B)	109.7
H(14A)-C(14)-H(14B)	108.2
C(20)-C(15)-C(16)	109.4(5)
C(20)-C(15)-P(1)	114.2(4)
C(16)-C(15)-P(1)	110.5(4)
C(17)-C(16)-C(15)	111.2(5)
C(17)-C(16)-H(16A)	109.4
C(15)-C(16)-H(16A)	109.4
C(17)-C(16)-H(16B)	109.4
C(15)-C(16)-H(16B)	109.4
H(16A)-C(16)-H(16B)	108.0
C(16)-C(17)-C(18)	112.8(6)
C(16)-C(17)-H(17A)	109.0
C(18)-C(17)-H(17A)	109.0
C(16)-C(17)-H(17B)	109.0
C(18)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
C(19)-C(18)-C(17)	110.0(5)
C(19)-C(18)-H(18A)	109.7
C(17)-C(18)-H(18A)	109.7
C(19)-C(18)-H(18B)	109.7
C(17)-C(18)-H(18B)	109.7
H(18A)-C(18)-H(18B)	108.2
C(18)-C(19)-C(20)	111.8(5)
C(18)-C(19)-H(19A)	109.3
C(20)-C(19)-H(19A)	109.3
C(18)-C(19)-H(19B)	109.3
C(20)-C(19)-H(19B)	109.3
H(19A)-C(19)-H(19B)	107.9
C(19)-C(20)-C(15)	109.2(5)
C(19)-C(20)-H(20A)	109.8
C(15)-C(20)-H(20A)	109.8
C(19)-C(20)-H(20B)	109.8
C(15)-C(20)-H(20B)	109.8
H(20A)-C(20)-H(20B)	108.3
C(26)-C(21)-C(22)	111.4(5)
C(26)-C(21)-P(1)	113.2(4)
C(22)-C(21)-P(1)	114.6(4)
C(21)-C(22)-C(23)	111.2(6)
C(21)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22A)	109.4
C(21)-C(22)-H(22B)	109.4
C(23)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
C(24)-C(23)-C(22)	110.6(6)
C(24)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23A)	109.5
C(24)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	108.1
C(23)-C(24)-C(25)	111.6(6)
C(23)-C(24)-H(24A)	109.3

C(25)-C(24)-H(24A)	109.3
C(23)-C(24)-H(24B)	109.3
C(25)-C(24)-H(24B)	109.3
H(24A)-C(24)-H(24B)	108.0
C(24)-C(25)-C(26)	112.7(7)
C(24)-C(25)-H(25A)	109.0
C(26)-C(25)-H(25A)	109.0
C(24)-C(25)-H(25B)	109.0
C(26)-C(25)-H(25B)	109.0
H(25A)-C(25)-H(25B)	107.8
C(25)-C(26)-C(21)	111.3(6)
C(25)-C(26)-H(26A)	109.4
C(21)-C(26)-H(26A)	109.4
C(25)-C(26)-H(26B)	109.4
C(21)-C(26)-H(26B)	109.4
H(26A)-C(26)-H(26B)	108.0
C(32)-C(27)-C(28)	110.6(5)
C(32)-C(27)-P(2)	113.4(4)
C(28)-C(27)-P(2)	110.8(4)
C(29)-C(28)-C(27)	110.7(6)
C(29)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28A)	109.5
C(29)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	108.1
C(30)-C(29)-C(28)	111.5(6)
C(30)-C(29)-H(29A)	109.3
C(28)-C(29)-H(29A)	109.3
C(30)-C(29)-H(29B)	109.3
C(28)-C(29)-H(29B)	109.3
H(29A)-C(29)-H(29B)	108.0
C(31)-C(30)-C(29)	111.8(6)
C(31)-C(30)-H(30A)	109.3
C(29)-C(30)-H(30A)	109.3
C(31)-C(30)-H(30B)	109.3
C(29)-C(30)-H(30B)	109.3
H(30A)-C(30)-H(30B)	107.9
C(30)-C(31)-C(32)	111.9(5)
C(30)-C(31)-H(31A)	109.2
C(32)-C(31)-H(31A)	109.2
C(30)-C(31)-H(31B)	109.2
C(32)-C(31)-H(31B)	109.2
H(31A)-C(31)-H(31B)	107.9
C(27)-C(32)-C(31)	111.4(5)
C(27)-C(32)-H(32A)	109.3
C(31)-C(32)-H(32A)	109.3
C(27)-C(32)-H(32B)	109.3
C(31)-C(32)-H(32B)	109.3
H(32A)-C(32)-H(32B)	108.0
C(34)-C(33)-C(38)	110.0(5)
C(34)-C(33)-P(2)	115.4(4)
C(38)-C(33)-P(2)	115.3(4)
C(33)-C(34)-C(35)	111.6(5)
C(33)-C(34)-H(34A)	109.3
C(35)-C(34)-H(34A)	109.3
C(33)-C(34)-H(34B)	109.3
C(35)-C(34)-H(34B)	109.3
H(34A)-C(34)-H(34B)	108.0
C(36)-C(35)-C(34)	110.4(5)
C(36)-C(35)-H(35A)	109.6
C(34)-C(35)-H(35A)	109.6
C(36)-C(35)-H(35B)	109.6
C(34)-C(35)-H(35B)	109.6
H(35A)-C(35)-H(35B)	108.1
C(35)-C(36)-C(37)	110.8(5)
C(35)-C(36)-H(36A)	109.5
C(37)-C(36)-H(36A)	109.5

C(35)-C(36)-H(36B)	109.5
C(37)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	108.1
C(38)-C(37)-C(36)	111.3(5)
C(38)-C(37)-H(37A)	109.4
C(36)-C(37)-H(37A)	109.4
C(38)-C(37)-H(37B)	109.4
C(36)-C(37)-H(37B)	109.4
H(37A)-C(37)-H(37B)	108.0
C(37)-C(38)-C(33)	110.5(5)
C(37)-C(38)-H(38A)	109.5
C(33)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
C(33)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	108.1
C(44)-C(39)-C(40)	109.6(5)
C(44)-C(39)-P(2)	118.7(5)
C(40)-C(39)-P(2)	111.3(4)
C(41)-C(40)-C(39)	109.0(5)
C(41)-C(40)-H(40A)	109.9
C(39)-C(40)-H(40A)	109.9
C(41)-C(40)-H(40B)	109.9
C(39)-C(40)-H(40B)	109.9
H(40A)-C(40)-H(40B)	108.3
C(42)-C(41)-C(40)	110.2(6)
C(42)-C(41)-H(41A)	109.6
C(40)-C(41)-H(41A)	109.6
C(42)-C(41)-H(41B)	109.6
C(40)-C(41)-H(41B)	109.6
H(41A)-C(41)-H(41B)	108.1
C(41)-C(42)-C(43)	111.3(6)
C(41)-C(42)-H(42A)	109.4
C(43)-C(42)-H(42A)	109.4
C(41)-C(42)-H(42B)	109.4
C(43)-C(42)-H(42B)	109.4
H(42A)-C(42)-H(42B)	108.0
C(42)-C(43)-C(44)	113.1(6)
C(42)-C(43)-H(43A)	109.0
C(44)-C(43)-H(43A)	109.0
C(42)-C(43)-H(43B)	109.0
C(44)-C(43)-H(43B)	109.0
H(43A)-C(43)-H(43B)	107.8
C(39)-C(44)-C(43)	110.4(6)
C(39)-C(44)-H(44A)	109.6
C(43)-C(44)-H(44A)	109.6
C(39)-C(44)-H(44B)	109.6
C(43)-C(44)-H(44B)	109.6
H(44A)-C(44)-H(44B)	108.1
Cl(4)-C(46)-Cl(3)	115.6(7)
Cl(4)-C(46)-H(46A)	108.4
Cl(3)-C(46)-H(46A)	108.4
Cl(4)-C(46)-H(46B)	108.4
Cl(3)-C(46)-H(46B)	108.4
H(46A)-C(46)-H(46B)	107.4
Cl(6)-C(45)-Cl(5)	113.3(7)
Cl(6)-C(45)-H(45A)	108.9
Cl(5)-C(45)-H(45A)	108.9
Cl(6)-C(45)-H(45B)	108.9
Cl(5)-C(45)-H(45B)	108.9
H(45A)-C(45)-H(45B)	107.7

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$)for **G1-OMe**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	9(1)	26(1)	30(1)	0(1)	-10(1)	2(1)
Cl(1)	23(1)	35(1)	33(1)	-1(1)	-11(1)	2(1)
Cl(2)	17(1)	37(1)	36(1)	-2(1)	-12(1)	0(1)
P(1)	13(1)	26(1)	34(1)	1(1)	-10(1)	2(1)
P(2)	12(1)	28(1)	33(1)	1(1)	-11(1)	2(1)
O(1)	39(3)	67(3)	58(3)	-6(3)	10(2)	6(3)
C(1)	15(4)	33(4)	35(4)	-2(2)	-10(3)	7(2)
C(2)	14(3)	37(3)	48(3)	4(3)	-5(2)	4(3)
C(3)	23(3)	58(4)	55(4)	-7(3)	-1(3)	7(3)
C(4)	29(3)	60(5)	56(4)	-15(3)	-1(3)	6(3)
C(5)	33(4)	44(4)	51(3)	-1(3)	8(3)	11(3)
C(6)	17(3)	52(4)	54(4)	7(3)	2(3)	5(3)
C(7)	21(4)	47(4)	50(4)	3(3)	-9(3)	-2(3)
C(8)	36(4)	63(5)	72(5)	9(4)	15(4)	10(4)
C(9)	24(3)	34(3)	34(3)	-3(2)	-14(2)	0(2)
C(10)	22(3)	46(4)	62(4)	-9(3)	-8(3)	-6(3)
C(11)	21(3)	54(4)	66(4)	-6(3)	-8(3)	-10(3)
C(12)	49(4)	56(4)	49(4)	-10(3)	-11(3)	-23(4)
C(13)	54(5)	43(4)	66(5)	-23(3)	-13(4)	-3(4)
C(14)	41(4)	44(4)	55(4)	-17(3)	-21(3)	5(3)
C(15)	17(3)	32(3)	33(3)	-1(2)	-7(2)	2(2)
C(16)	23(3)	46(4)	37(3)	-3(3)	-13(3)	1(3)
C(17)	26(4)	55(4)	46(4)	-1(3)	1(3)	-1(3)
C(18)	21(3)	48(4)	53(4)	6(3)	-4(3)	-6(3)
C(19)	16(3)	43(4)	52(3)	6(3)	-14(2)	4(3)
C(20)	18(3)	44(3)	40(3)	-1(2)	-9(2)	5(2)
C(21)	17(3)	35(3)	38(3)	5(2)	-5(2)	2(2)
C(22)	33(3)	43(4)	36(3)	10(3)	-7(3)	8(3)
C(23)	39(4)	50(4)	40(3)	9(3)	-9(3)	2(3)
C(24)	37(4)	65(5)	37(3)	5(3)	-9(3)	-16(3)
C(25)	38(4)	72(5)	41(3)	1(3)	5(3)	1(4)
C(26)	23(3)	68(5)	43(3)	6(3)	-2(3)	10(3)
C(27)	11(3)	38(3)	37(3)	0(2)	-10(2)	0(2)
C(28)	14(3)	61(4)	46(4)	1(3)	-7(3)	4(3)
C(29)	16(3)	80(6)	47(4)	9(4)	-14(3)	-8(3)
C(30)	18(3)	64(5)	57(4)	13(3)	1(3)	9(3)
C(31)	26(3)	39(3)	50(3)	-5(3)	0(3)	-3(3)
C(32)	19(3)	40(3)	43(3)	-6(3)	-7(2)	-2(3)
C(33)	15(3)	31(3)	39(3)	0(2)	-12(2)	-2(2)
C(34)	26(3)	35(3)	35(3)	6(2)	-10(2)	-4(2)
C(35)	33(3)	42(3)	45(3)	16(3)	-20(3)	-4(3)
C(36)	26(3)	49(4)	45(3)	6(3)	-23(3)	6(3)
C(37)	19(3)	47(4)	52(4)	2(3)	-22(3)	-4(3)
C(38)	16(3)	45(4)	43(3)	3(3)	-11(2)	0(3)
C(39)	19(3)	31(3)	38(3)	-2(2)	-6(2)	1(2)
C(40)	18(3)	30(3)	50(3)	-1(2)	0(2)	0(2)
C(41)	26(3)	52(4)	59(4)	-11(3)	2(3)	4(3)
C(42)	33(4)	51(4)	58(4)	-19(3)	-4(3)	0(3)
C(43)	36(4)	37(3)	52(4)	-9(3)	-3(3)	-6(3)
C(44)	26(3)	36(3)	51(4)	-6(3)	-6(3)	-10(3)
Cl(3)	97(3)	108(3)	149(3)	-13(2)	44(2)	-1(2)
Cl(4)	82(2)	192(5)	109(2)	-44(3)	-23(2)	11(3)
C(46)	90(9)	102(9)	89(7)	13(6)	10(7)	2(7)
Cl(5)	75(2)	126(3)	112(2)	23(2)	-18(2)	4(2)
Cl(6)	380(10)	61(2)	117(3)	4(2)	-30(4)	-29(3)
C(45)	81(7)	72(6)	74(5)	-5(5)	-19(5)	9(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **G1-OMe**.

	x	y	z	U(eq)
H(1)	729	2314	4543	34
H(3)	1517	3150	6290	55
H(4)	632	3455	7159	59
H(6)	-1457	2739	5824	49
H(7)	-542	2424	4949	49
H(8A)	-2114	3484	6610	85
H(8B)	-2135	3352	7454	85
H(8C)	-2002	2678	6935	85
H(10A)	819	1029	4575	53
H(10B)	964	284	5021	53
H(11A)	-79	88	3989	57
H(11B)	589	354	3462	57
H(12A)	560	-939	3478	63
H(12B)	780	-941	4338	63
H(13A)	2059	-1181	3815	67
H(13B)	1932	-454	3341	67
H(14A)	2360	-488	4892	59
H(14B)	2981	-208	4332	59
H(16A)	3570	1106	3845	44
H(16B)	3875	1873	4197	44
H(17A)	5018	1384	3642	51
H(17B)	4965	628	4062	51
H(18A)	6144	1279	4646	50
H(18B)	5571	1991	4719	50
H(19A)	5759	1379	5846	46
H(19B)	5396	638	5474	46
H(20A)	4372	1938	5582	42
H(20B)	4306	1224	6068	42
H(22A)	3394	82	6143	46
H(22B)	2419	-171	5985	46
H(23A)	2933	-508	7207	53
H(23B)	3236	312	7390	53
H(24A)	1935	109	7854	56
H(24B)	1494	-148	7078	56
H(25A)	2056	1317	7434	60
H(25B)	1080	1069	7280	60
H(26A)	1540	1688	6256	54
H(26B)	1206	881	6048	54
H(28A)	4080	4042	5038	49
H(28B)	4121	3216	4765	49
H(29A)	5107	4407	4270	59
H(29B)	5500	3752	4769	59
H(30A)	5746	3565	3542	56
H(30B)	5194	2911	3815	56
H(31A)	4563	3260	2663	46
H(31B)	4525	4094	2908	46
H(32A)	3127	3596	2901	42
H(32B)	3488	2928	3400	42
H(34A)	2294	4823	3083	39
H(34B)	1493	5101	3457	39
H(35A)	1210	5306	2182	50
H(35B)	1371	4462	2025	50
H(36A)	-119	4667	1930	51
H(36B)	-30	5015	2721	51
H(37A)	-514	3783	2790	49
H(37B)	284	3493	2418	49
H(38A)	564	3294	3684	43
H(38B)	400	4138	3840	43
H(40A)	984	4872	4765	40
H(40B)	1060	4132	5226	40

H(41A)	753	5124	5998	55
H(41B)	1679	4803	6275	55
H(42A)	1784	6098	6242	58
H(42B)	1368	6112	5417	58
H(43A)	3047	5565	5932	51
H(43B)	2851	6255	5416	51
H(44A)	2342	5495	4428	46
H(44B)	3263	5195	4753	46
H(46A)	7926	1695	2558	112
H(46B)	8097	2548	2668	112
H(45A)	534	1794	2336	94
H(45B)	-264	1886	1729	94

Table 6. Torsion angles [°] for **G1-OMe**.

Cl(1)-Ru(1)-C(1)-C(2)	-172.4(6)
Cl(2)-Ru(1)-C(1)-C(2)	8.3(7)
P(2)-Ru(1)-C(1)-C(2)	-85.4(6)
P(1)-Ru(1)-C(1)-C(2)	98.1(6)
Ru(1)-C(1)-C(2)-C(3)	-0.5(11)
Ru(1)-C(1)-C(2)-C(7)	-179.9(5)
C(7)-C(2)-C(3)-C(4)	0.9(11)
C(1)-C(2)-C(3)-C(4)	-178.4(7)
C(2)-C(3)-C(4)-C(5)	0.1(13)
C(8)-O(1)-C(5)-C(4)	178.2(7)
C(8)-O(1)-C(5)-C(6)	-1.9(11)
C(3)-C(4)-C(5)-O(1)	178.4(7)
C(3)-C(4)-C(5)-C(6)	-1.4(12)
O(1)-C(5)-C(6)-C(7)	-178.2(7)
C(4)-C(5)-C(6)-C(7)	1.6(11)
C(3)-C(2)-C(7)-C(6)	-0.6(11)
C(1)-C(2)-C(7)-C(6)	178.8(7)
C(5)-C(6)-C(7)-C(2)	-0.6(11)
C(21)-P(1)-C(9)-C(10)	62.0(5)
C(15)-P(1)-C(9)-C(10)	172.1(5)
Ru(1)-P(1)-C(9)-C(10)	-70.6(5)
C(21)-P(1)-C(9)-C(14)	-69.2(6)
C(15)-P(1)-C(9)-C(14)	41.0(6)
Ru(1)-P(1)-C(9)-C(14)	158.3(5)
C(14)-C(9)-C(10)-C(11)	-57.8(8)
P(1)-C(9)-C(10)-C(11)	166.9(5)
C(9)-C(10)-C(11)-C(12)	59.0(8)
C(10)-C(11)-C(12)-C(13)	-57.5(8)
C(11)-C(12)-C(13)-C(14)	56.3(9)
C(10)-C(9)-C(14)-C(13)	54.9(8)
P(1)-C(9)-C(14)-C(13)	-173.5(6)
C(12)-C(13)-C(14)-C(9)	-54.3(9)
C(21)-P(1)-C(15)-C(20)	-49.4(5)
C(9)-P(1)-C(15)-C(20)	-164.6(4)
Ru(1)-P(1)-C(15)-C(20)	75.4(4)
C(21)-P(1)-C(15)-C(16)	-173.2(4)
C(9)-P(1)-C(15)-C(16)	71.6(5)
Ru(1)-P(1)-C(15)-C(16)	-48.4(5)
C(20)-C(15)-C(16)-C(17)	56.4(7)
P(1)-C(15)-C(16)-C(17)	-177.1(5)
C(15)-C(16)-C(17)-C(18)	-53.9(8)
C(16)-C(17)-C(18)-C(19)	53.1(8)
C(17)-C(18)-C(19)-C(20)	-56.6(8)
C(18)-C(19)-C(20)-C(15)	60.6(7)
C(16)-C(15)-C(20)-C(19)	-59.2(7)
P(1)-C(15)-C(20)-C(19)	176.4(4)
C(9)-P(1)-C(21)-C(26)	-77.3(6)
C(15)-P(1)-C(21)-C(26)	173.0(5)
Ru(1)-P(1)-C(21)-C(26)	53.3(5)

C(9)-P(1)-C(21)-C(22)	52.0(5)
C(15)-P(1)-C(21)-C(22)	-57.7(5)
Ru(1)-P(1)-C(21)-C(22)	-177.4(4)
C(26)-C(21)-C(22)-C(23)	-53.6(7)
P(1)-C(21)-C(22)-C(23)	176.2(4)
C(21)-C(22)-C(23)-C(24)	55.4(8)
C(22)-C(23)-C(24)-C(25)	-56.3(8)
C(23)-C(24)-C(25)-C(26)	56.5(8)
C(24)-C(25)-C(26)-C(21)	-54.0(9)
C(22)-C(21)-C(26)-C(25)	52.7(8)
P(1)-C(21)-C(26)-C(25)	-176.4(6)
C(33)-P(2)-C(27)-C(32)	-53.5(5)
C(39)-P(2)-C(27)-C(32)	-168.1(4)
Ru(1)-P(2)-C(27)-C(32)	69.6(5)
C(33)-P(2)-C(27)-C(28)	-178.5(5)
C(39)-P(2)-C(27)-C(28)	67.0(5)
Ru(1)-P(2)-C(27)-C(28)	-55.4(5)
C(32)-C(27)-C(28)-C(29)	55.9(8)
P(2)-C(27)-C(28)-C(29)	-177.6(6)
C(27)-C(28)-C(29)-C(30)	-56.5(9)
C(28)-C(29)-C(30)-C(31)	55.9(9)
C(29)-C(30)-C(31)-C(32)	-54.3(8)
C(28)-C(27)-C(32)-C(31)	-54.4(7)
P(2)-C(27)-C(32)-C(31)	-179.5(4)
C(30)-C(31)-C(32)-C(27)	54.0(8)
C(27)-P(2)-C(33)-C(34)	-57.7(5)
C(39)-P(2)-C(33)-C(34)	51.9(5)
Ru(1)-P(2)-C(33)-C(34)	-176.4(4)
C(27)-P(2)-C(33)-C(38)	172.3(5)
C(39)-P(2)-C(33)-C(38)	-78.1(5)
Ru(1)-P(2)-C(33)-C(38)	53.6(5)
C(38)-C(33)-C(34)-C(35)	-56.8(7)
P(2)-C(33)-C(34)-C(35)	170.7(5)
C(33)-C(34)-C(35)-C(36)	57.3(8)
C(34)-C(35)-C(36)-C(37)	-56.3(8)
C(35)-C(36)-C(37)-C(38)	56.9(8)
C(36)-C(37)-C(38)-C(33)	-56.5(8)
C(34)-C(33)-C(38)-C(37)	56.4(7)
P(2)-C(33)-C(38)-C(37)	-171.1(5)
C(33)-P(2)-C(39)-C(44)	-72.1(5)
C(27)-P(2)-C(39)-C(44)	36.9(5)
Ru(1)-P(2)-C(39)-C(44)	155.6(4)
C(33)-P(2)-C(39)-C(40)	56.5(5)
C(27)-P(2)-C(39)-C(40)	165.6(4)
Ru(1)-P(2)-C(39)-C(40)	-75.7(4)
C(44)-C(39)-C(40)-C(41)	-62.4(7)
P(2)-C(39)-C(40)-C(41)	164.3(5)
C(39)-C(40)-C(41)-C(42)	60.6(7)
C(40)-C(41)-C(42)-C(43)	-55.3(8)
C(41)-C(42)-C(43)-C(44)	51.6(8)
C(40)-C(39)-C(44)-C(43)	57.9(7)
P(2)-C(39)-C(44)-C(43)	-172.7(5)
C(42)-C(43)-C(44)-C(39)	-53.1(8)

Symmetry transformations used to generate equivalent atoms:

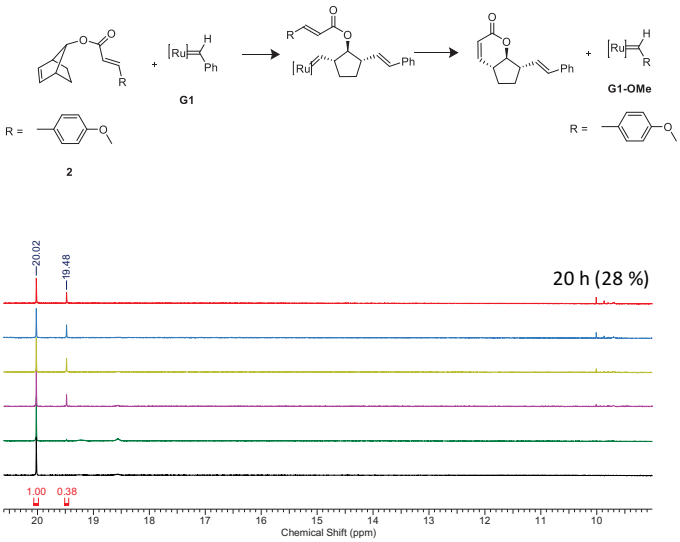


Figure S50: Time resolved ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectra of the reaction of **G1** with 3 eq. of **2** (only one enantiomer is shown for simplicity). It is clearly seen that the signal of **G1-OMe** (19.48 ppm) appears slowly.

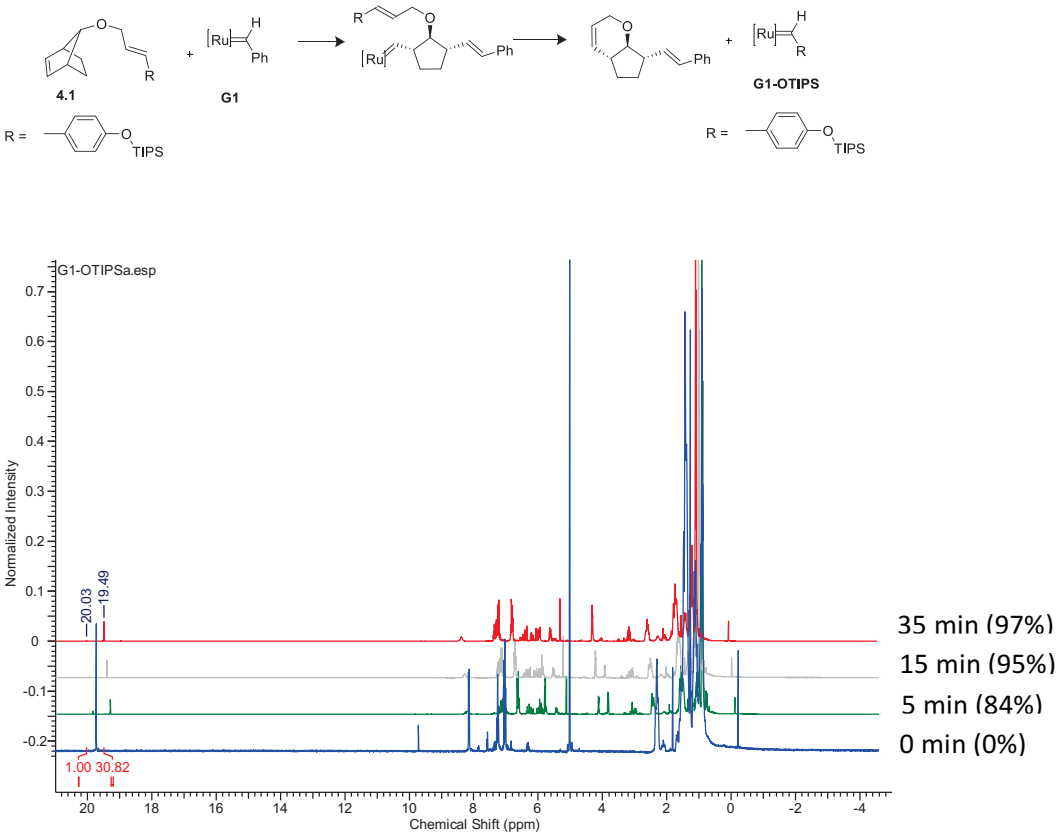


Figure S51: Time resolved ^{1}H-NMR (dichloromethane-d_2, 300 MHz) spectra of the reaction of **G1** with 3 eq. of **4.1** (only one enantiomer is shown for simplicity) forming **G1-OTIPS**. It is clearly seen that the signal of **G1-OTIPS** (19.49 ppm) appears quickly. NMR traces are shifted progressively to the left by 0.2 ppm with increasing time for clarity.

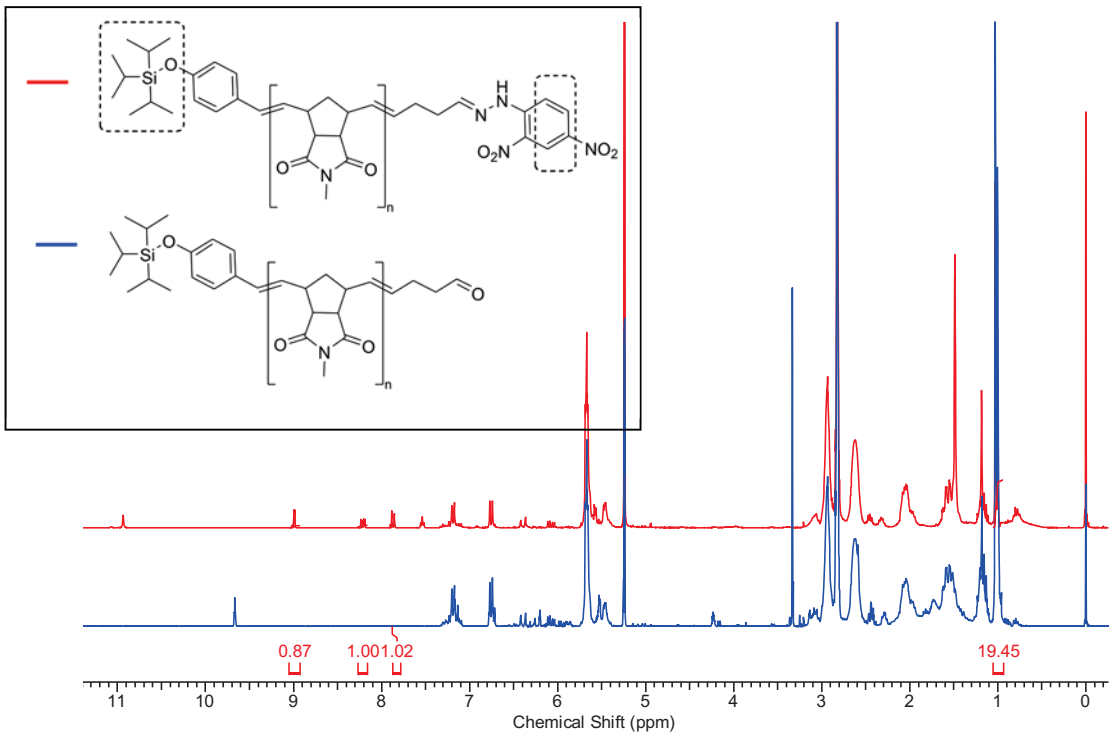
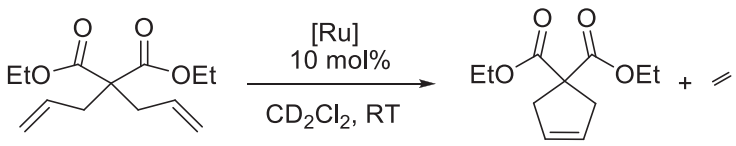


Figure S52: ^{1}H-NMR of the heterotelechelic ROMP polymers before (below, blue) and after (above, red) functionalization with 2,4-dinitrophenylhydrazine.Chemical shifts match with previously reported 2,4-DNP functionalized aldehyde end functional ROMP polymer (S. Hilf, R. H. Grubbs, A. F. M. Kilbinger *J. Am. Chem. Soc.* **2008**, *130 (33)*, 11041). Integrating with respect to the TIPS group shows near quantitative functionalization.

Ring closing of diethyl diallylmalonate using **G1-OH** and **G1-OTIPS**:



[Ru]	immediate	10 min	30 min	60 min	120 min
G1-OH	78%	87%	93%	95%	95%
G1-OTIPS	93%	96%	96%	96%	-

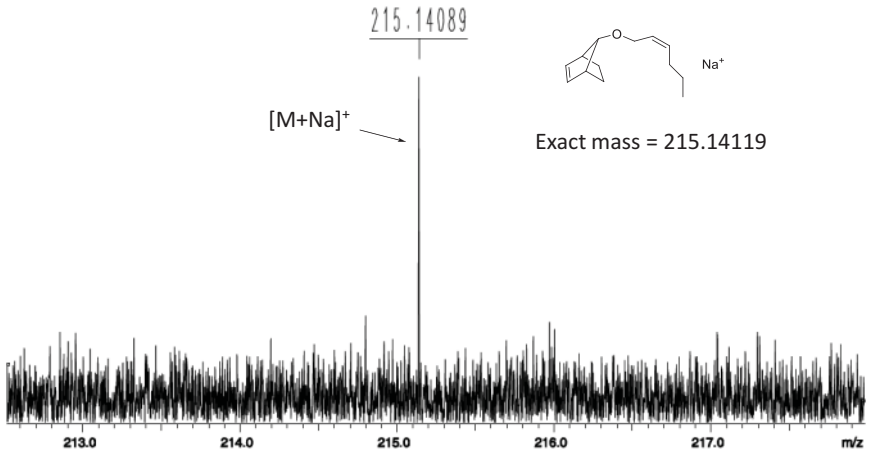


Figure S53: HRMS (ESI) spectrum of **6**.

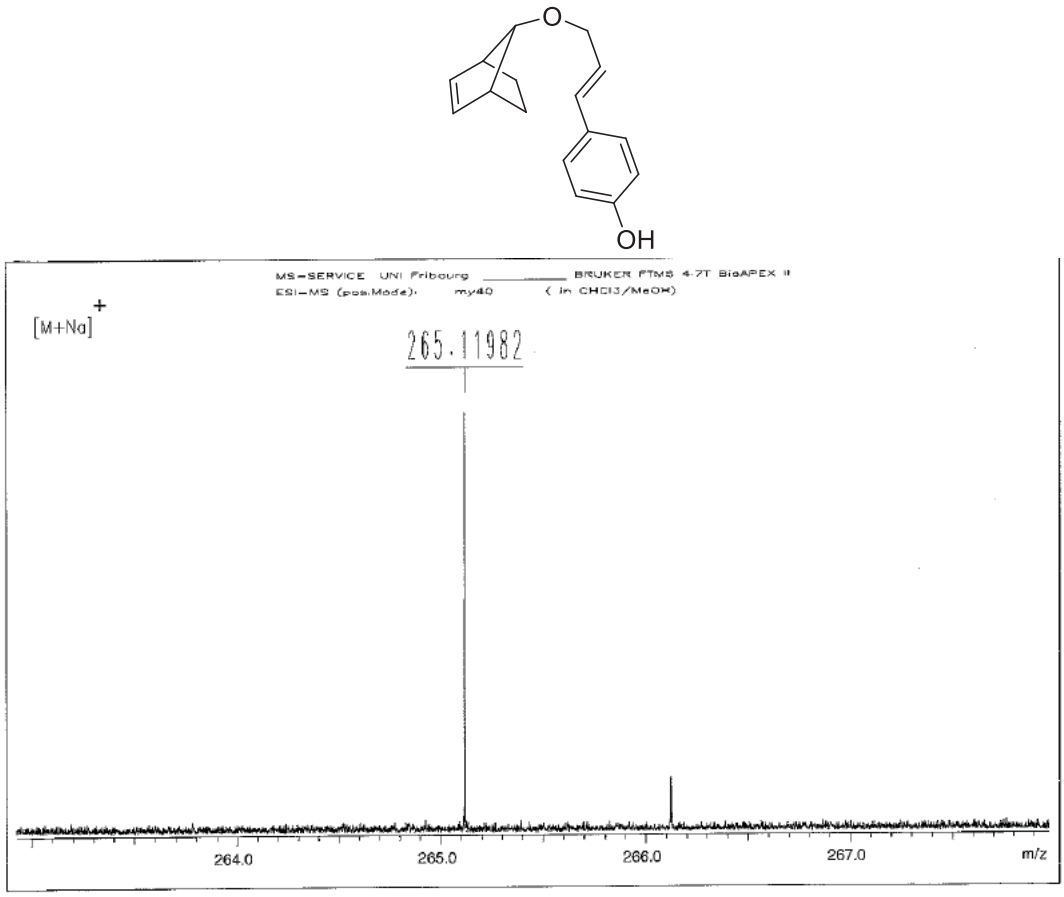
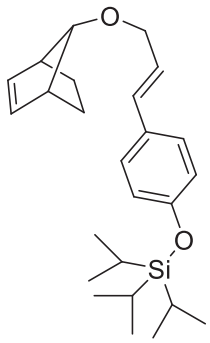


Figure S54: HRMS (ESI) spectrum of **4**.



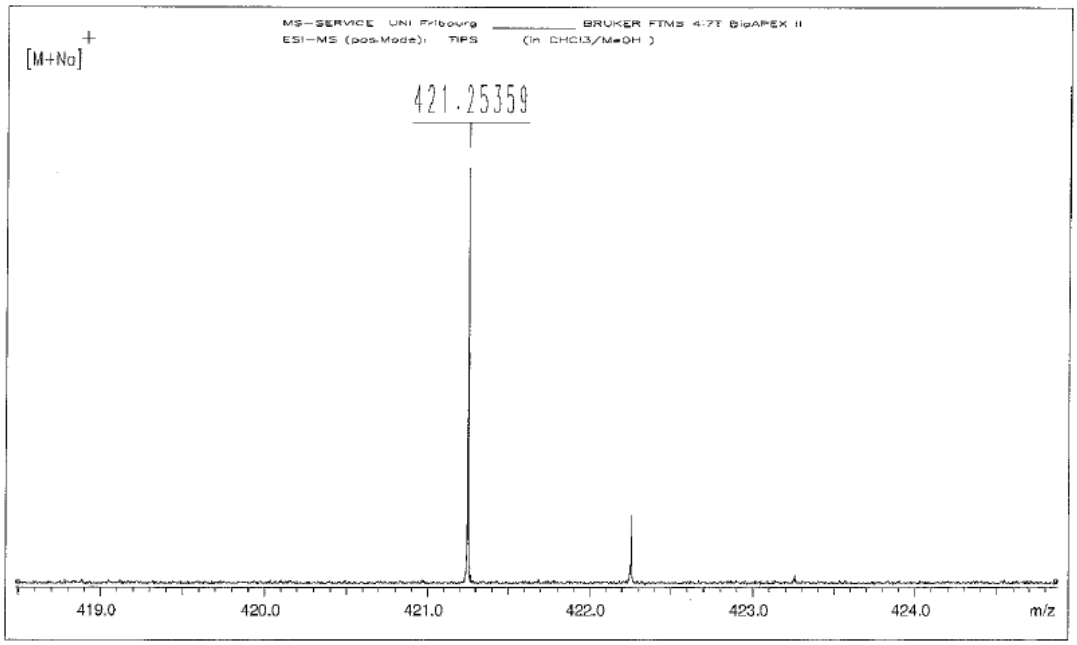


Figure S55: HRMS (ESI) spectrum of **4.1**.

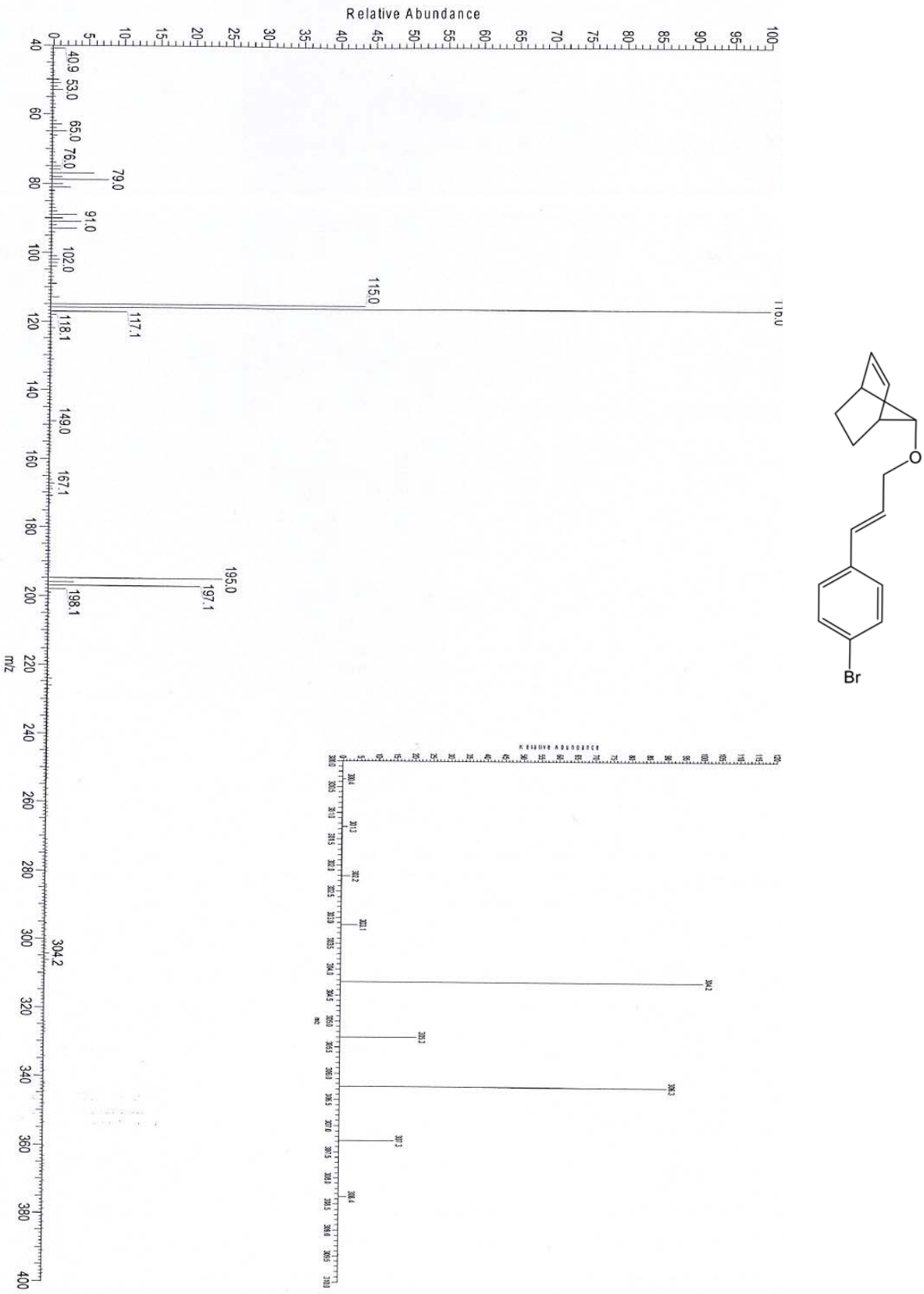


Figure S56: LRMS (EI) spectrum of **5**.

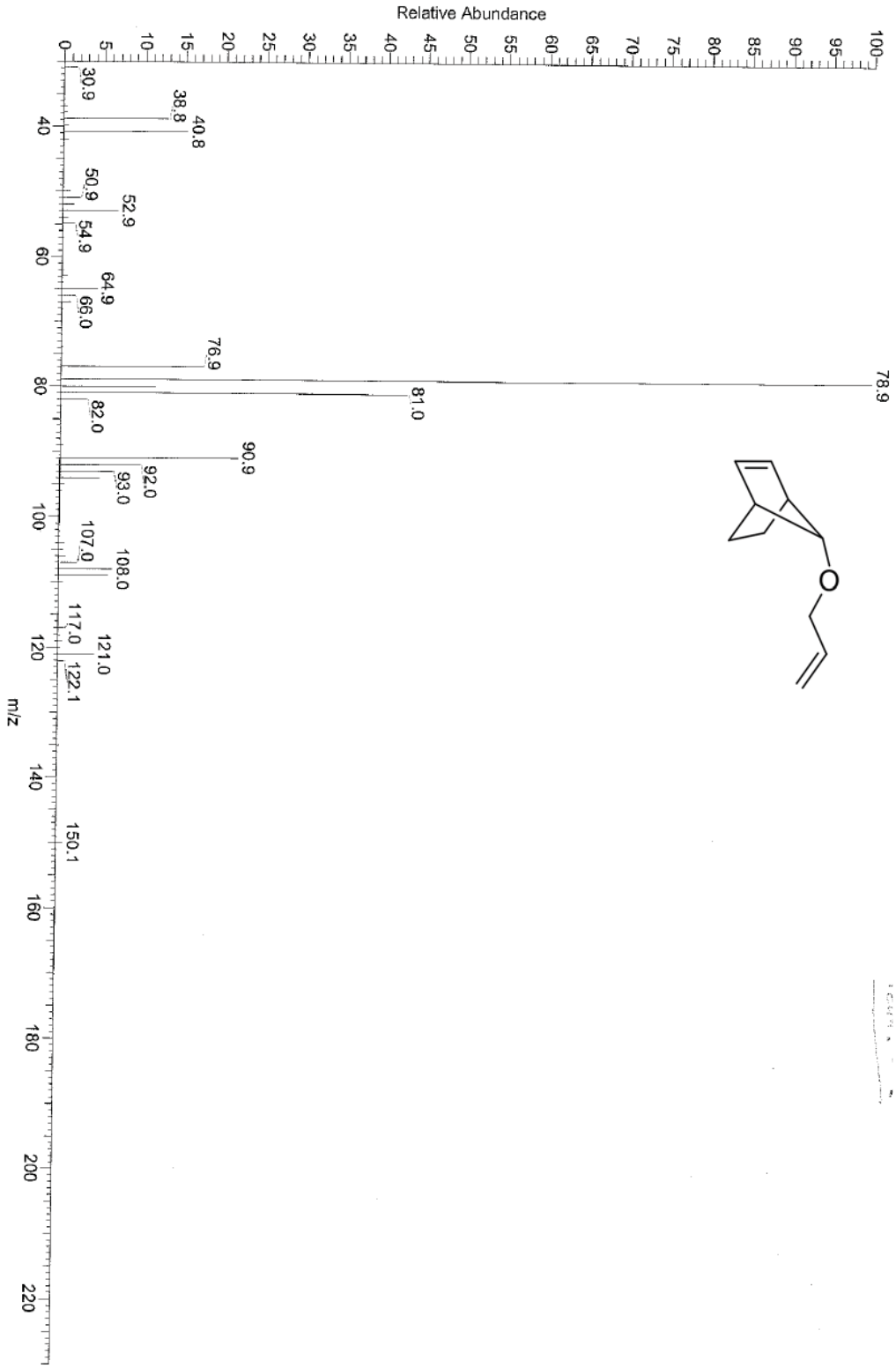


Figure S57: LRMS (EI) spectrum of **7**.

Detailed explanation of the experiments carried out in Figure S58:

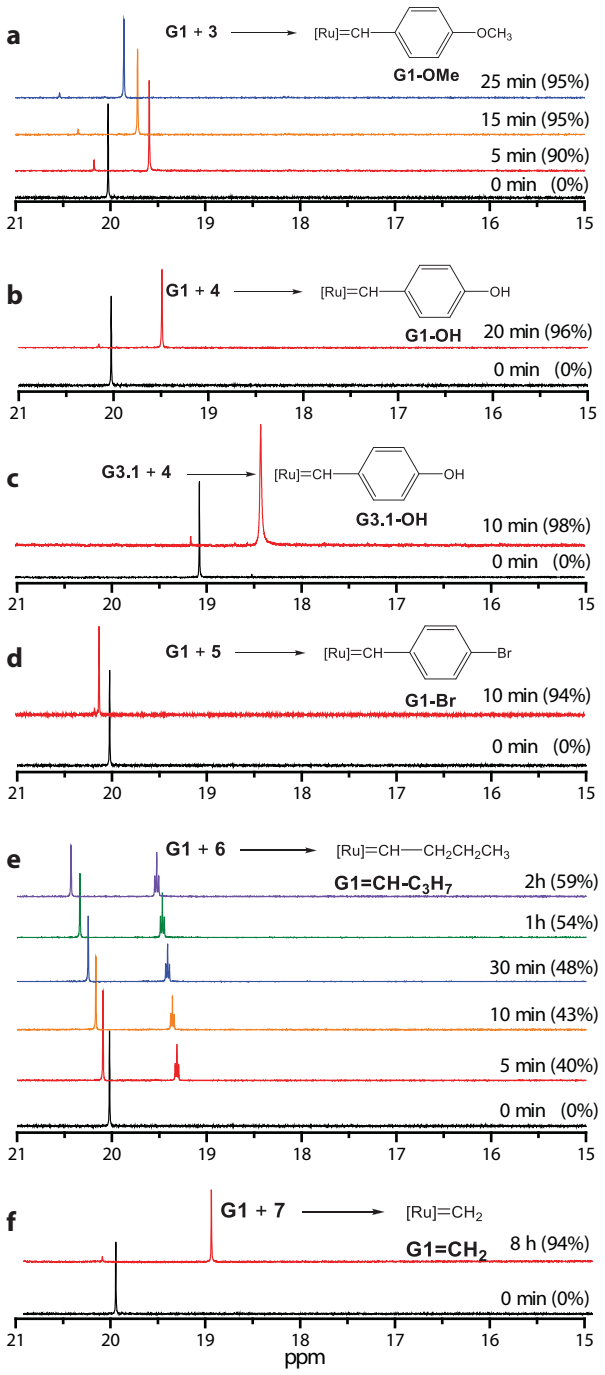


Figure S58 (same as Figure 3 in the manuscript): ^{1}H-NMR spectra (CD_2Cl_2, 300 MHz) of the reactions of 3-7 with carbene complexes G1 or G3.1.

When 3 equivalents of compound 3 were reacted with G1, the characteristic G1 benzylidene signal (singlet, 20.02 ppm) in the ^{1}H-NMR spectrum diminished very quickly and a signal at

19.48 ppm which was attributed to the 4-methoxybenzylidene complex G1-OMe[6] appeared immediately. Within 15 minutes, 94% conversion was observed (Figure S58 a). It was furthermore evident from the ^{1}H-NMR spectrum that all norbornene double bonds had been consumed at this point. This new complex crystallized on evaporation of the solvent (dichloromethane-d_2) with a slightly differently crystal structure than previously reported (see Figure S49).[7] With the aim of a functional telechelic polymer in mind, we next prepared compound 4 which would yield a 4-hydroxybenzylidene ruthenium complex. Compound 4 reacted rapidly with G1 and the benzylidene signal of G1 was shifted to 19.39 ppm corresponding to the hydroxy substituted catalyst G1-OH within 20 minutes (Figure S58 b, 96 % yield by ^{1}H- NMR). There was no loss of intensity of the 4-hydroxybenzylidene signal with respect to residual protic solvent even after 6 hours which implies that the new catalyst is stable to phenolic OH groups. Unfortunately, all attempts to crystallize the new compound failed.

To investigate the effect of solvent on the ring opening – ring closing metathesis rate, the polymerization was conducted in benzene. The rate of synthesis of the new benzylidene complex was much slower than in dichloromethane (see Figure S2). This indicates that the solvent does indeed have an effect on this synthesis strategy and dichloromethane, which is a very good polymerization solvent for metathesis polymerization,[8] (the polar but non-coordinating nature of dichloromethane is believed to promote the phosphine dissociation required for the initiation of the catalyst) is also a very good solvent for this tandem ring opening ring closing metathesis reaction. When 3 eq. of 4 were reacted with the more active G3 catalyst, the ^{1}H-NMR signals of both, the G3 benzylidene at 19.10 ppm and the new 4-hydroxybenzylidene catalyst at 18.40 ppm were observed as a 1:1 mixture. Oligomers of the ring opening metathesis polymerization product were also detected by MALDI-ToF mass spectrometry. This implies that the more active G3 catalyst prefers to polymerize the strained olefinic bonds rather than to form a stable six membered ring (kp > krc, Scheme 1, main manuscript). The propagating alkylidene undergoes a ring closing metathesis reaction to form the new carbene complex only when all the strained norbornene double bonds are consumed. As there were very few equivalents (3 eq.) of 4 added, not all of the initial amount of G3 was consumed and remained therefore in the reaction mixture. To slow down the rate of propagation of G3, 50 eq. of pyridine were added before the addition of 4. The addition of pyridine slows down the propagation while also forming the new catalyst G3.1 (Figure 1, main manuscript). On addition of 3 eq. of 4, the ^{1}H-NMR benzylidene signal of G3.1 (19.10 ppm) shifted quantitatively to the new carbene peak of G3.1-OH at 18.39 ppm within 10 min. (Figure S58 c). In order to elucidate the effect of the substituent in the para position, the 4-bromo substituted compound 5 was synthesized (Figure 2, main manuscript). As expected, the para substituent has little effect on the synthesis of the new 4-bromobenzylidene catalyst (G1-Br) and an almost quantitative conversion to a new carbene peak was observed in the ^{1}H-NMR spectrum (Figure S58 d, ^{1}H-NMR carbene signal shifted from 20.02 ppm to 19.98 ppm).[9] This indicates that the para substituent has no appreciable effect on the RORCM mechanism. As was reported previously, the equilibrium constant for the reaction of G1 with p-methoxystyrene (K = 8.66) is ca. 8 times greater than that for the reaction of G1 with p-bromostyrene (K = 1.10).[9] However, the RORCM works equally well for 3 and 5 with identical amounts of substrate (3 equivalents), which indicates that the RORCM is indeed beneficial for syntheses of new ruthenium benzylidene catalysts even if the reaction with the corresponding styrene derivative has a small equilibrium constant. Grubbs et al. have also reported that the benzylidene ligand exchange with 4-chloro styrene is more than 20 times slower than that of

4-methoxy styrene.[10] The very fast syntheses of both the 4-bromo and the 4-methoxy substituted benzylidene complexes using RORCM demonstrates the advantage of using this strategy to synthesize new ruthenium benzylidene derivatives. In order to investigate RORCM for the synthesis of alkylidene metathesis catalysts, compound 6 was synthesized (Figure 2, main manuscript). As most ruthenium alkylidenes are much more reactive compared to the G1 benzylidene, we postulated that once a small amount of the alkylidene is formed, it would start consuming substrate 6 in a competition with G1 benzylidene (kroR >> kroPh, Scheme 1, main manuscript). This was indeed confirmed in a ^{1}H-NMR experiment with G1 and 3 eq. of 6. After 2 hours (Figure S58 e) 41% of the original Grubbs' catalyst was still remaining. The ^{1}H-NMR signal of the new carbene complex (G1=CH-C3H7) can be clearly seen at 19.27 ppm.[9]

The observation of the ruthenium methylidene **G1=CH$_2$** also gives information into the mechanistic aspects of RORCM. The strained norbornene double bond has to react first which then undergoes ring closing to give the methylidene complex **G1=CH$_2$**. If the catalyst were to attack the non-strained olefin first, then a ruthenium alkylidene should have been observed (similar to the cross-metathesis reaction between terminal olefins), and the alkylidene would not be observed. In the RORCM case described here, just 3 eq. of the RORCM substrate **7** are sufficient to drive the reaction almost to completion.
Thus, in our RORCM, the strained norbornene double bond appears to be always attacked first. RORCM can hence be one of the very few methods available to synthesize the ruthenium methylidene complex **G1=CH$_2$** under ambient conditions.

Detailed explanation of the experiments carried out in Figure S59:

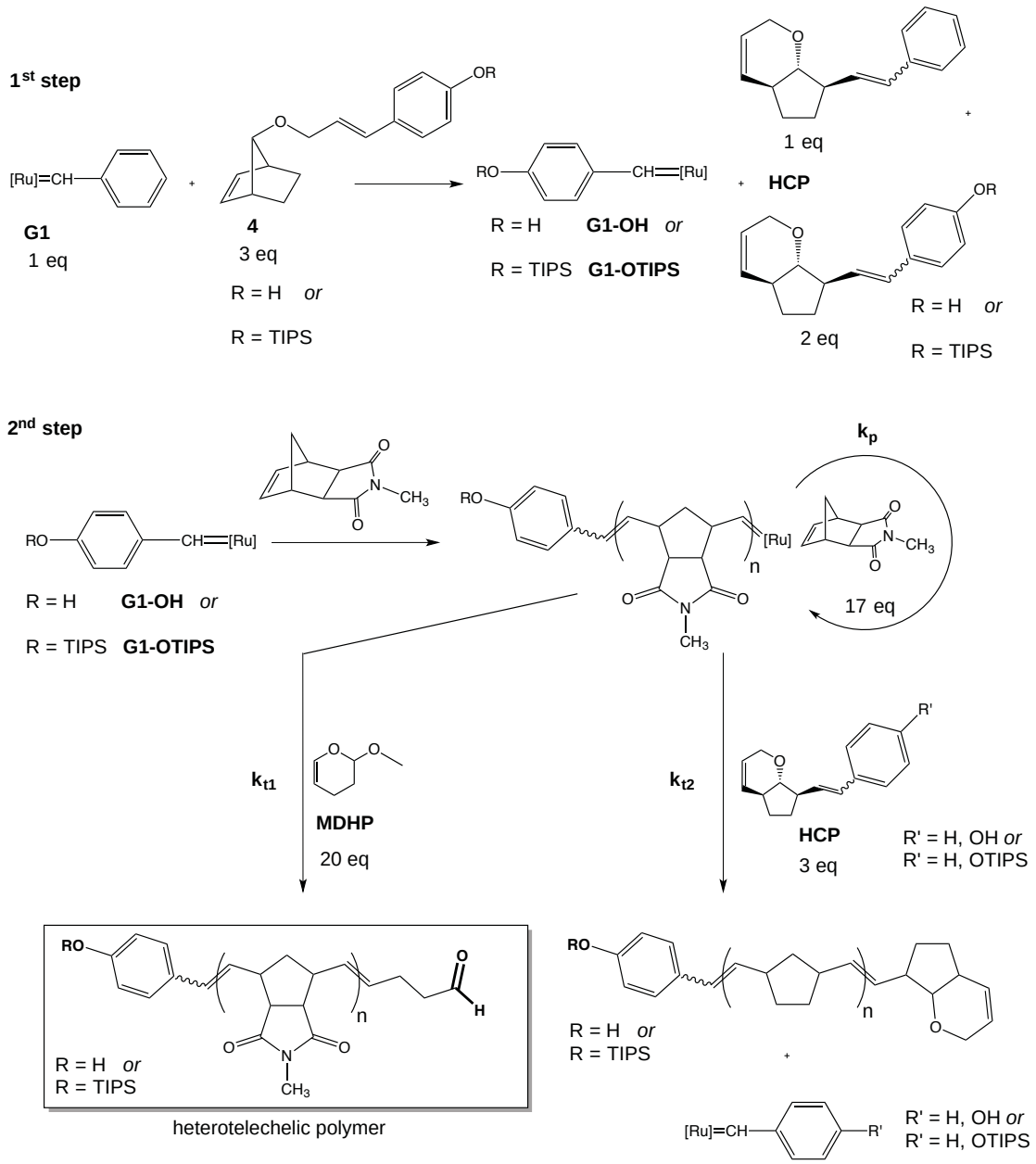


Figure S59 (same as Scheme 2 in the manuscript): Synthesis of the heterotelechelic polymer by addition of a mixture of monomer and terminating agent to the reaction vessel containing G1-OH/G1-OTIPS.

As shown in Figure S59, the synthesis of G1-OH/G1-OTIPS produces 3 equivalents of differently substituted HCP which are present during the subsequent polymerization reaction of MNI (see Figure S59, 1st step). Due to the absence of ring strain in HCP, the highly strained MNI will polymerize exclusively until its concentration drops below a critical value. At this point the reaction with HCP becomes more favorable and the propagating chain terminates by reaction

with HCP thereby reforming a G1-benzylidene derivative. Addition of MDHP to the polymerization reaction will lead to a reaction competition between HCP and MDHP for the propagating ruthenium alkylidene chain end. Here, all chains will be exclusively terminated by MDHP as it represents the more electron rich (vinyl ether) and hence more reactive double bond turning the ruthenium complex into a stable Fischer-carbene.

References

[1] Nagarkar A. A.; Crochet A.; Fromm K. M.; Kilbinger A. F. M. *Macromolecules* **2012**, *45*, 4447–4453.

[2] Walton. H. M. *J. Org. Chem*. **1957**, *22*, 315-318.

[3] Cheikh A. B., Craine L. E., Recher S. G., Zemlicka J. *J. Org. Chem.* **1988**, *53 (5)*, 929–936.

[4] Barontini M.; Bernini R.; Carastro I.; Gentili P.; Romani, A. *New Journal of Chemistry* **2014**, *38(2)*, 809-816

[5] Jordan R. W.; Le Marquand P.; Tam W. *Eur. J. Org. Chem.* **2008**, 80–86.

[6] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

[7] B. Powałaa, M. Kubickia, G. Spólnikb, W. Danikiewiczb, C. Pietraszuka, *J. Organometallic Chem.* **2014**, *752*, 109–114.

[8] M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001,** *123 (27)*, 6543–6554.

[9] Lane D. R.; Beavers C. M.; Olmstead M. M.; Schore, N. E. *Organometallics* **2009**, *28*, 6789–6797.

[10] M. Ulman, R. H. Grubbs, *Organometallics* **1998,** *17,* 2484-2489.