Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Iterative catalyst controlled diastereodivergent synthesis of polypropionates

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I. General procedures

Chromatography was performed on silica gel (Aldrich, 230 − 400 mesh). Thin-layer chromatography was performed on Merck silica gel 60 F254 plates. Compounds were visualized by UV and cerium/molybdenum or potassium permanganate staining. Progress and conversion of the reactions were determined by GC-MS. Mass spectra were recorded on an LTQ Orbitrap XL mass spectrometer. ^{1}H-NMR and ^{13}C-NMR were recorded on 400 and 100 MHz using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a polarimeter with a 10 cm cell (c given in g/100 mL).

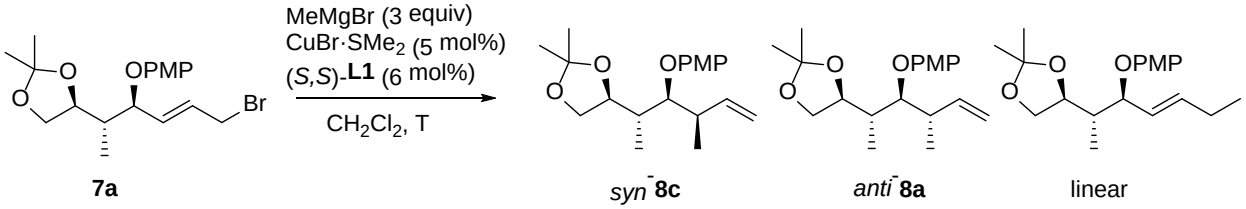
All reactions were carried out under a nitrogen atmosphere using oven-dried glassware and using standard Schlenk techniques. All reagents were purchased from commercial sources and used without further purification. Dichloromethane, tetrahydrofuran and toluene were used from a solvent purification system.

Compounds **1**, **2a** and **2b** were synthesized according to literature procedures.[1]

1. M. Fañanás-Mastral, B. ter Horst, A. J. Minnaard and B. L. Feringa, *Chem. Commun*., 2011, **47**, 5843.

II. Temperature screening of Cu-catalyzed AAA

Table 1: Screening of temperature for the Cu catalyzed AAA on **7a**[a]

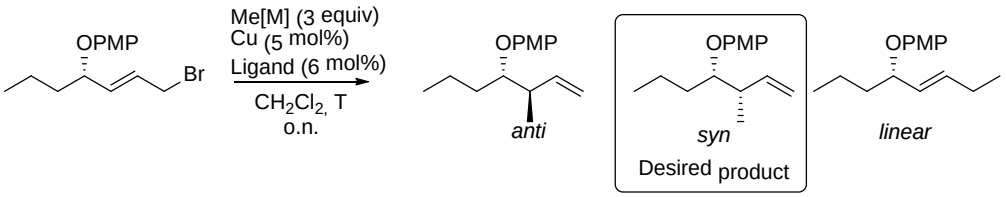


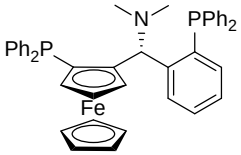
Entry	T (°C)	Reaction time	*syn*:*anti*:linear[b]	Conversion[b] (%)
1	-80	1 d	-	0
2	-70	2 d	4:1:0	40
3	-60	1 d	4:1:0	30
4	-40	1 d	3:1:1	60

a) *Reagents and conditions*: 3 equiv. MeMgBr, (-)-Taniaphos (6 mol%), $CuBr{\cdot}SMe_2$ (5 mol%), CH_2Cl_2, overnight. b) Based on crude ^{1}H-NMR analysis.

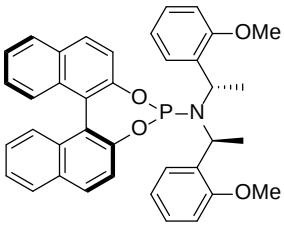
III. Temperature screening of Cu-catalyzed AAA

Table 2: Screening of catalysts on a model substrate.[a]

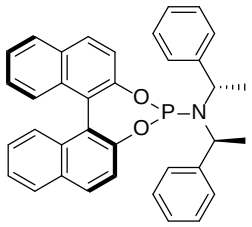




(*R*,*R*)-**L1**
(+)-Taniaphos



(*S*,*S*,*S*)-**L2**



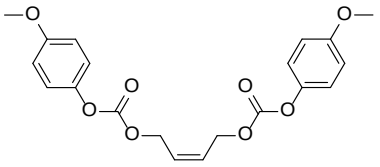
(*S*,*S*,*S*)-**L3**

Entry	Cu source	Me[M]	Ligand	T (°C)	Addition time (h)	Conv[b] (%)	*Anti:syn*[b]	B:l[b]
1[c]	$CuBr{\cdot}SMe_2$	MeMgBr	(*S*,*S*)-**L1**	-60	1	100	>95:5	>95:5
2	$CuBr{\cdot}SMe_2$	MeMgBr	(*R*,*R*)-**L1**	-60	1	10	n.d.	n.d.
3[d]	$CuBr{\cdot}SMe_2$	MeMgBr	(*R*,*R*)-**L1**	-60	1	30	1:9	>95:5
4	CuTC	MeMgBr	**L2**	-60	6	100	3:2	10:1
5	CuTC	MeMgBr	**L2**	-78	6	100	2:3	10:1
6	CuTC	MeMgBr	**L3**	-60	6	100	3:4	3:1
7	$CuBr{\cdot}SMe_2$	MeLi	(*R*,*R*)-**L1**	-70	2	100	n.d.	1:5
8	$CuBr{\cdot}SMe_2$	MeLi	(*R*,*R*)-**L1**	-80	2	100	n.d.	1:3

a) *Reagents and conditions*: Me[M] (3 equiv.), Cu (5 mol%), Ligand (6 mol%), CH_2Cl_2, overnight. b) Based on crude ^{1}H-NMR analysis. c) Towards the product with *anti*-configuration. d) Reaction time is 2 days. n.d. = not determined.

IV. Experimental procedures and compound characterization

(Z)-But-2-ene-1,4-diyl bis(4-methoxyphenyl) dicarbonate (3)

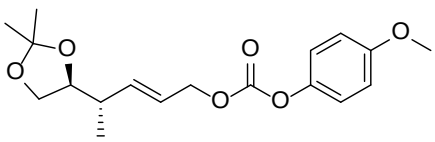


A solution of (Z)-but-2-ene-1,4-diol (15 mmol, 1.32 g) and pyridine (31.5 mmol, 2.49 g) in CH_2Cl_2 (50 ml) was cooled to 0 °C. 4-Methoxyphenyl chloroformate (31.5 mmol, 5.88 g) was added dropwise and the mixture was allowed to reach room temperature and stirred for 1 h. The reaction mixture was then washed twice with 2N aq. HCl. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (SiO_2, pentane/diethyl ether 2:1) to yield **3** (5.61 g, 96%) as a white solid. Mp: 73-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 9.1 Hz, 4H), 6.88 (d, *J* = 9.1 Hz, 4H), 5.92 (t, *J* = 4.2 Hz, 2H), 4.87 (d, *J* = 5.2 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 153.9, 144.6, 128.0, 121.8, 114.5, 63.7, 55.6. HRMS (ESI+, *m/z*): Calcd for $C_{20}H_{21}O_8$ [M+H$^+$]: 389.1231, found: 389.1234.

Typical procedure for cross metathesis of olefins 2 with dicarbonate 3

In a Schlenk tube equipped with septum and stirring bar, Hoveyda-Grubbs 2nd generation catalyst (7.68 μmol, 4,81 mg), dicarbonate **3** (0.256 mmol, 99.4 mg) and olefin **2** (0.256 mmol, 40 mg) were dissolved in dry degassed toluene (2.5 mL) and stirred under nitrogen atmosphere at 70°C. After 5 h, a second portion of Hoveyda-Grubbs 2nd generation catalyst (5.20 μmol, 3.21 mg) and dicarbonate **3** (0.256 mmol, 99.4 mg) were added. After 18 h, water was added and the aqueous layer was extracted 3 times with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography to yield the corresponding carbonate **4**.

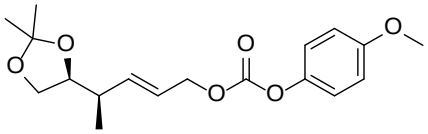
(*S,E*)-4-((S)-2,2-Dimethyl-1,3-dioxolan-4-yl)pent-2-en-1-yl (4-methoxyphenyl) carbonate (4a)



Purification by column chromatography (SiO_2 pentane/diethyl ether 3:1) afforded **4a** (65.5 mg, 69%) as a colorless oil. $[\alpha]_D^{20}$ = -2.4° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (m, 2H), 6.88 (m, 2H), 5.91 (dd, *J* = 7.1, 15.6 Hz, 1 H) 5.71 (dt, *J* = 15.6,

6.5 Hz, 1H), 4.71 (m, 2H),3.99 (m, 2H), 3.80 (s, 3H), 3.63 (dd, *J* = 6.1, 13.3 Hz, 1H), 1.41 (s, 1H), 1.36 (s, 1H), 1.03 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 153.9, 144.7, 138.4, 123.5, 121.9, 114.4, 109.1, 79.1, 69.1, 67.4, 55.6, 39.5, 26.5, 25.5, 15.6. HRMS (ESI+, *m/z*): Calcd for $C_{18}H_{25}O_6$ [M+H$^+$]: 337.1641, found: 337.1646.

(*R,E*)-4-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)pent-2-en-1-yl (4-methoxyphenyl) carbonate (4b)

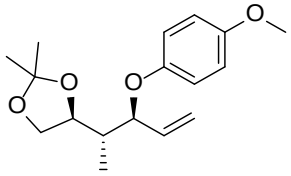


Purification by column chromatography (SiO_2 pentane/diethyl ether 3:1) afforded **4b** (136.9 mg, 66%) as a colorless oil. $[\alpha]_D^{20}$ = +15.2° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (m, 2H), 6.88 (m, 2H), 5.74 (m, 2H), 4.67 (d, *J* = 5.3 Hz, 2H), 3.94 (m, 2H), 3.79 (s, 3H), 3.64 (m, 1H), 2.39 (m, 1H), 1.41 (s, 1H), 1.35 (s, 1H), 1.11 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 153.9, 144.7, 137.8, 124.0, 121.8, 144.4, 109.1, 79.1, 68.9, 67.4, 55.6, 40.3, 26.7, 25.4, 16.2. HRMS (ESI+, *m/z*): Calcd for $C_{18}H_{25}O_6$ [M+H$^+$]: 337.1643, found: 337.1646.

Typical procedure for iridium-catalyzed allylic etherification of carbonates 4

In a Schlenk tube equipped with septum and stirring bar, $[Ir(dbcot)Cl]_2$ (4 μmol, 3.46 mg) and **L2** (8 μmol, 5.0 mg) were stirred for 10 min in THF (0.5 mL) under nitrogen atmosphere until a homogenous orange solution was obtained. DBU (0.2 mmol, 30 μmol) was added and the color changed to light yellow. Carbonate **4** (0.2 mmol, 67.3 mg) in THF (1.0 mL) was added and the mixture was stirred overnight at 60 °C. Water (1.5 ml) was added and the aqueous layer was extracted with Et_2O (3 x 1.5 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography to yield compounds **5**.

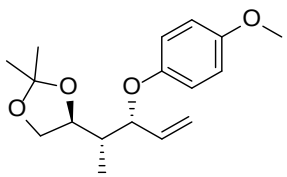
(*S*)-4-((*2S,3S*)-3-(4-Methoxyphenoxy)pent-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (5a)



Purification by column chromatography (SiO_2, pentane/diethyl ether 10:1) afforded **5a** (197.9 mg, 68%) as a colorless oil. $[\alpha]_D^{20}$ = -2.4° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 – 6.83 (m, 2H), 6.83 – 6.77 (m, 2H), 5.86 (ddd, *J* = 6.3, 10.7, 17.2 Hz, 1H), 5.31 (dd,

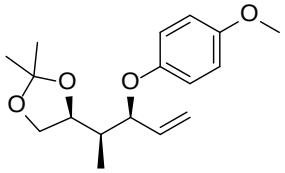
J = 8.8, 14.0 Hz, 2H), 4.79 (dd, *J* = 4.8, 5.7 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.76 (s, 3H), 3.72 – 3.65 (m, 1H), 2.27 – 2.15 (m, 1H), 1.41 (s, 3H) 1.36 (s, 3H), 0.93 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.8, 152.1, 134.8, 118.1, 117.1, 114.4, 108.6, 80.0, 76.6, 67.6, 55.7, 40.6, 26.7, 25.7, 10.1. HRMS (ESI+, *m/z*): Calcd for $C_{17}H_{25}O_4$ [M+H$^+$]: 293.1745, found: 293.1747.

(*S*)-4-((*2S,3R*)-3-(4-Methoxyphenoxy)pent-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (5b)



Purification by column chromatography (SiO_2, pentane/diethyl ether 10:1) afforded **5b** (217.2 mg, 74%) as a pale yellow oil. $[\alpha]_D^{20}$ = -2.8° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 – 6.76 (m, 4H), 5.84 (ddd, *J* = 17.3, 10.7, 5.3 Hz, 1H), 5.27 – 5.20 (m, 2H), 4.85 – 4.81 (m, 1H), 4.17 (td, *J* = 7.9, 6.1 Hz, 1H), 4.02 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.76 (s, 3H), 3.67 (t, *J* = 7.9 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.41 (s, 3H), 1.32 (s, 3H), 0.96 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 152.8, 136.8, 117.4, 116.6, 114.4, 108.5, 79.4, 77.0, 67.7, 55.7, 42.1, 26.7, 25.7, 8.7. HRMS (ESI+, *m/z*): Calcd for $C_{17}H_{25}O_4$ [M+H$^+$]: 293.1747, found: 293.1748.

(*S*)-4-((*2R,3S*)-3-(4-Methoxyphenoxy)pent-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (5c)



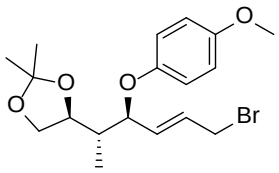
Purification by column chromatography (SiO_2, pentane/diethyl ether 10:1) afforded **5c** (38.9 mg, 67%) as a colorless oil. $[\alpha]_D^{20}$ = +7.2° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 – 6.77 (m, 4H), 5.89 – 5.79 (m, 1H), 5.29 – 5.22 (m, 2H), 4.50 (t, *J* = 5.1 Hz, 1H), 4.13 (dd, *J* = 13.8, 6.8 Hz, 1H), 4.04 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.76 (t, *J* = 8 Hz, 1H), 3.75 (s, 3H), 2.03 – 1.95 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 1.13 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 152.1, 135.7, 117.7, 117.0, 114.5, 105.3, 80.9, 77.1, 68.0, 55.6, 41.1, 26.6, 25.7, 11.4. HRMS (ESI+, *m/z*): Calcd for $C_{17}H_{25}O_4$ [M+H$^+$]: 293.1747, found: 293.1748.

Typical procedure for cross-metathesis of olefins 5 with (*E*)-1,4-dibromobut-2-ene

In a Schlenk tube equipped with septum and stirring bar, Hoveyda-Grubbs 2nd generation catalyst (0.015 mmol, 9.40 mg), (*E*)-1,4-dibromobut-2-ene (2.5 mmol, 577.3 mg) and olefin **5** (0.5 mmol, 146.2 mg) were dissolved in toluene (5 mL) and the mixture was stirred under nitrogen atmosphere at 80 °C. After 5 h, a second portion of Hoveyda-Grubbs 2nd generation catalyst (0.010 mmol, 6.27 mg) was added. After 18 h, water (4 ml) was added and the aqueous layer was

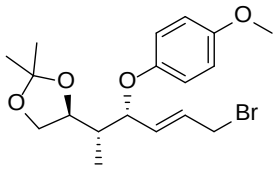
extracted with CH_2Cl_2 (3 x 3 ml). The combined organic layers were and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography to yield the corresponding allyl bromides **7**.

(*S*)-4-((*2S,3S,E*)-6-Bromo-3-(4-methoxyphenoxy)hex-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (7a)



Purification by column chromatography (SiO_2, pentane/ethyl acetate 15:1) afforded **7a** (130.6 mg, 56%) as a pale yellow oil. $[\alpha]_D^{20}$ = +9.0° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 – 6.78 (m, 4H), 6.00 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.83 (dd, *J* = 15.4, 6.3 Hz, 1H), 4.87 – 4.83 (m, 1H), 4.04 (dd, *J* = 7.8, 6.0 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.76 (s, 3H), 3.65 (dd, *J* = 9.9, 5.5 Hz, 1H), 2.26 – 2.17 (m, 1H), 1.41 (s, 3H), 1.37 (s, 3H), 0.92 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 151.8, 132.0, 129.6, 117.1, 114.5, 108.8, 78.4, 76.6, 67.9, 55.7, 41.1, 31.8, 26.8, 25.7, 10.1. HRMS (ESI+, *m/z*): Calcd for $C_{18}H_{26}BrO_4$ [M+H$^+$]: 385.1009, found: 385.1002.

(*S*)-4-((*2S,3R,E*)-6-Bromo-3-(4-methoxyphenoxy)hex-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (7b)



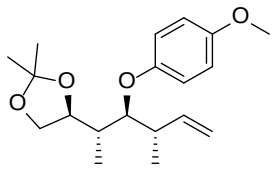
Purification by column chromatography (SiO_2, pentane/ethyl acetate 15:1) afforded **7b** (114.9 mg, 54%) as a pale yellow oil. $[\alpha]_D^{20}$ = -22.0° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 – 6.77 (m, 1H), 5.90 (dt, *J* = 7.3, 6.8 Hz, 1H), 5.79 (dd, *J* = 15.4, 5.0 Hz, 1H), 4.89 – 4.86 (m, 1H), 4.14 (dt, *J* = 14.1, 7.1 Hz, 1H), 4.02 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.95 (d, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 3.65 (t, *J* = 7.8 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.41 (s, 3H), 1.31 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1, 152.5, 134.1, 128.2, 117.4, 114.5, 108.6, 78.0, 76.9, 67.8, 55.7, 42.2, 31.9, 26.9, 25.7, 8.9. HRMS (ESI+, *m/z*): Calcd for $C_{18}H_{26}BrO_4$ [M+H$^+$]: 385.1009, found: 385.1002.

Typical procedure for asymmetric allylic alkylations of allylic bromides 7.

In a Schlenk tube equipped with stirring bar and septum, $CuBr{\cdot}SMe_2$ (0.010 mmol, 2.06 mg) and the corresponding ligand (0.012 mmol) were dissolved in CH_2Cl_2 (0.8 ml) and the mixture was

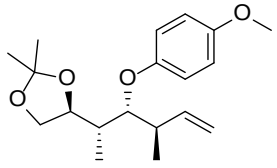
stirred under nitrogen atmosphere at room temperature for 15 min. The mixture was cooled to -60 °C and MeMgBr (0.2 ml, 3M solution in Et_2O) was added dropwise. Allyl bromide **7** (0.2 mmol, 77.1 mg) was then added dropwise as a solution in CH_2Cl_2 (0.32 ml) over 1 h using a syringe pump. Once the addition was complete the resulting mixture was further stirred at -60 °C for 3 days. The reaction was quenched by addition of MeOH (0.2 ml) and the mixture was allowed to reach rt. Then, saturated aqueous NH_4Cl solution (2 ml) was added to the mixture. The organic phase was separated, and the resulting aqueous layer was extracted with CH_2Cl_2 (3 x 2 ml). The organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography to yield the corresponding products **8**.

(*S*)-4-((*2S,3S,4S*)-3-(4-Methoxyphenoxy)-4-methylhex-5-en-2-yl)-2,2-dimethyl-1,3-dioxolane (8a)



Purification by column chromatography (SiO_2, pentane/ethyl acetate 15:1) afforded **8a** (48.9 mg, 77%) as a colorless oil. $[\alpha]_D^{20}$ = +23.4° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 – 6.77 (m, 4H), 6.01 – 5.91 (m, 1H), 5.07 (d, *J* = 16.9 Hz, 1H), 5.01 (dd, *J* = 10.3, 1.0 Hz, 1H), 4.31 (dd, *J* = 13.9, 6.3 Hz, 1H), 4.08 (t, *J* = 5.2 Hz, 1H), 3.89 (dd, *J* = 8.1, 6.3 Hz, 1H), 3.76 (s, 3H), 3.63 (t, *J* = 7.9 Hz, 1H), 2.73 – 2.63 (m, 1H), 2.34 – 2.24 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 153.5, 140.7, 116.6, 114.7, 114.6, 114.6, 108.2, 83.5, 76.1, 66.6, 56.7, 40.3, 38.2, 26.5, 25.4, 17.9, 11.3. HRMS (ESI+, *m/z*): Calcd for $C_{19}H_{28}O_4Na$ [M+Na$^+$]: 343.1880, found: 343.1881.

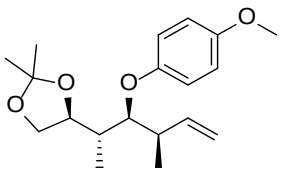
(*S*)-4-((*2S,3R,4R*)-3-(4-Methoxyphenoxy)-4-methylhex-5-en-2-yl)-2,2-dimethyl-1,3-dioxolane (8b)



Purification by column chromatography (SiO_2, pentane/ethyl acetate 15:1) afforded **8b** (48.9 mg, 77%) as a colorless oil. $[\alpha]_D^{20}$ = +2.2° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 – 6.92 (m, 2H), 6.79 – 6.74 (m, 2H), 5.80 (ddd, *J* = 17.6, 10.3, 7.5 Hz, 1H), 5.06 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.93 (d, *J* = 10.3 Hz, 1H), 4.34 (dd, *J* = 8.3, 1.8 Hz, 1H), 3.99 – 3.91 (m, 2H), 3.75 (s, 3H), 3.58 – 3.52 (m, 1H), 2.63 – 2.53 (m, 1H), 2.00 – 1.91 (m, 1H), 1.40 (s, 3H), 1.24 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ

154.3, 153.4, 141.4, 117.2, 114.5, 114.3, 108.6, 81.8, 77.2, 68.5, 55.7, 40.8, 39.3, 27.0, 25.6, 16.6, 9.1. HRMS (ESI+, *m/z*): Calcd for $C_{19}H_{28}O_4Na$ [M+Na^+]: 343.1880, found: 343.1879.

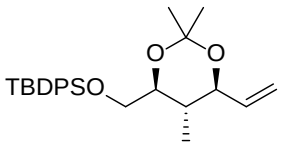
(*S*)-4-((2*S*,3*S*,4*R*)-3-(4-Methoxyphenoxy)-4-methylhex-5-en-2-yl)-2,2-dimethyl-1,3-dioxolane (8c)



Purification by column chromatography (SiO_2, pentane/ethyl acetate 15:1) afforded **8c**[*] (17.9 mg, 50%) as a colorless oil. $[\alpha]_D^{20}$ = -2.4° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 – 6.83 (m, 2H), 6.82 – 6.77 (m, 2H), 5.82 (ddd, *J* = 17.4, 10.2, 8.6 Hz, 1H), 5.12 (dd, *J* = 17.6, 1.6 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 1H), 4.14 (dd, *J* = 8.2, 3.4 Hz, 1H), 3.95 (dd, *J* = 8.1, 6.1 Hz, 1H), 3.76 (s, 2H), 3.58 (t, *J* = 8.0 Hz, 1H), 2.69 (h, *J* = 7.2 Hz, 1H), 2.25 (td, *J* = 7.0, 3.4 Hz, 1H), 1.40 (s, 3H), 1.36 (s, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 153.4, 141.1, 116.5, 115.0, 114.6, 108.2, 82.8, 76.1, 67.4, 55.7, 41.0, 38.6, 26.5, 25.6, 17.7, 11.3. HRMS (ESI+, *m/z*): Calcd for $C_{19}H_{28}O_4Na$ [M+Na^+]: 343.1880, found: 343.1881.

[*] **8c** was isolated together with 10% of the linear isomer

Tert-butyldiphenyl(((*4S*,*5S*,*6S*)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)methoxy)silane (9)



Allylic ether **3a** (0.581 mmol, 170.0 mg) was dissolved in a 4:1 mixture of acetonitrile/H_2O (40 ml) and the solution was cooled to 0 °C. Ceric Ammonium Nitrate (2.03 mmol, 1.11 g) was slowly added in portions and the mixture was stirred for 10 min. The mixture was diluted with CH_2Cl_2 (40 ml) and washed with brine (25 ml) and water (25 ml). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to yield the resulting alcohol (165.9 mg) which was used without further purification.

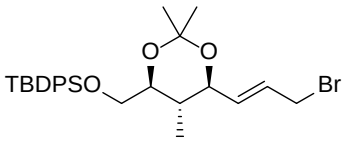
The crude product (165.9 mg) was dissolved in H_2O (2 ml) and AcOH (5 ml) and stirred 5 h. After co-evaporations with toluene (4 x 2 ml) the resulting triol (107.2 mg) was obtained which was used without further purification.

The crude product (107.2 mg) was dissolved in DMF (3 ml) and cooled to 0 °C. TBDPSCl (0.639 mmol, 175.6 mg), imidazole (0.872 mmol, 59.4 mg) and DMAP (0.0465 mmol, 5.7 mg) were added and the mixture was allowed to warm to rt after which it was stirred during 16 h. Then it

was poured into water (5 ml) and extracted with CH_2Cl_2 (3 x 5 ml). The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*.

The resulting product was dissolved in 2,2-dimethoxypropane (6 ml) and PPTS (0.058 mmol, 14.58 mg) was added and the resulting mixture was stirred for 3 d under nitrogen atmosphere. H_2O (5 ml) and Et_2O (5 ml) were added and the mixture was washed with saturated aqueous $NaHCO_3$ solution (5 ml). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 5 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (SiO_2, pentane/diethyl ether 40:1) afforded product **9** (144.5 mg, 59%) as a colorless oil. $[\alpha]_D^{20}$ = +13.4° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.68 (m, 4H), 7.45 – 7.34 (m, 6H), 5.74 (ddd, *J* = 17.6, 10.2, 7.6 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 3.88 (dd, *J* = 10.3, 7.5 Hz, 1H), 3.81 – 3.72 (m, 2H), 3.62 – 3.56 (m, 1H), 1.61 – 1.52 (m, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 1.06 (s, 9H), 0.74 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.4, 135.8, 135.7, 133.9, 133.8, 129.5, 127.5, 127.5, 118.3, 98.1, 76.9, 75.4, 65.7, 34.4, 30.0, 26.8, 19.6, 19.4, 12.1. HRMS (ESI+, *m/z*): Calcd for $C_{26}H_{36}O_3SiNa$ [M+Na$^+$]: 447.2310, found: 447.2326.

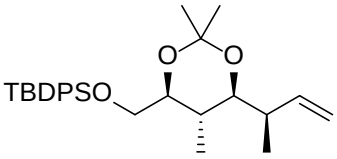
(((*4S,5S,6S*)-6-((*E*)-3-Bromoprop-1-en-1-yl)-2,2,5-trimethyl-1,3-dioxan-4-yl)methoxy)(tert-butyl)diphenylsilane (10)



In a Schlenk tube equipped with septum and stirring bar, Hoveyda-Grubbs 2nd generation catalyst (0.00924 mmol, 5.79 mg), (E)-1,4-dibromobut-2-ene (1.54 mmol, 356.0 mg) and olefin **9** (0.308 mmol, 131.0 mg) were dissolved in toluene (3.0 mL) and the mixture was stirred under nitrogen atmosphere at 80 °C. After 3 h, a second portion of Hoveyda-Grubbs 2nd generation catalyst (0.00616 mmol, 3.86 mg) was added. After 18 h, water was added and the aqueous layer was extracted with Et_2O (3 x 3 ml). The organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography (SiO_2, pentane/Et_2O 50:1) afforded **10** (121.3 mg, 76%) as a pale yellow oil. $[\alpha]_D^{20}$ = +3.2° (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.68 (m, 4H), 7.44 – 7.34 (m, 6H), 5.95 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.69 (dd, *J* = 15.2, 7.4 Hz, 1H), 3.98 – 3.90 (m, 3H), 3.76 (t, *J* = 3.5 Hz, 2H), 3.61 – 3.54 (m, 1H), 1.63 – 1.54 (m, 1H), 1.43 (s, 6H), 1.06 (s, 9H),

0.76 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.8, 135.7, 135.5, 134.0, 133.8, 133.7, 129.8, 129.5, 127.9, 127.6, 127.5, 98.2, 75.3, 75.2, 65.5, 34.7, 29.9, 26.8, 19.6, 19.4, 12.1. HRMS (ESI+, *m/z*): Calcd for $C_{27}H_{41}BrNO_3Si$ [M+NH_4^+]: 534.2034, found: 534.2031.

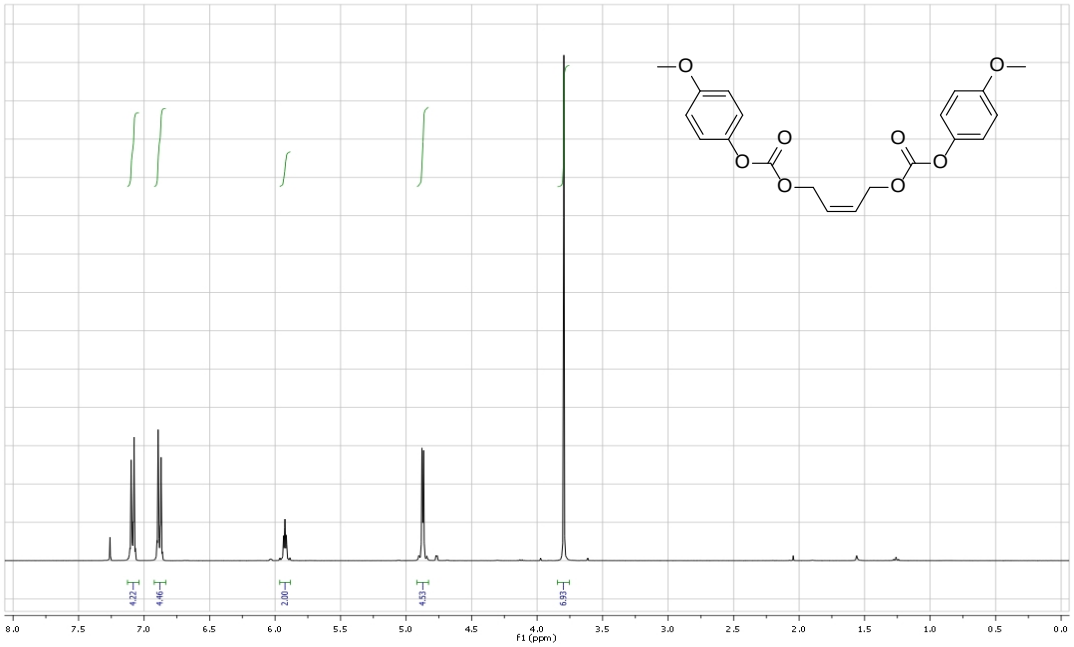
(((4S,5S,6S)-6-((R)-But-3-en-2-yl)-2,2,5-trimethyl-1,3-dioxan-4-yl)methoxy)(tert-butyl)diphenylsilane (11)

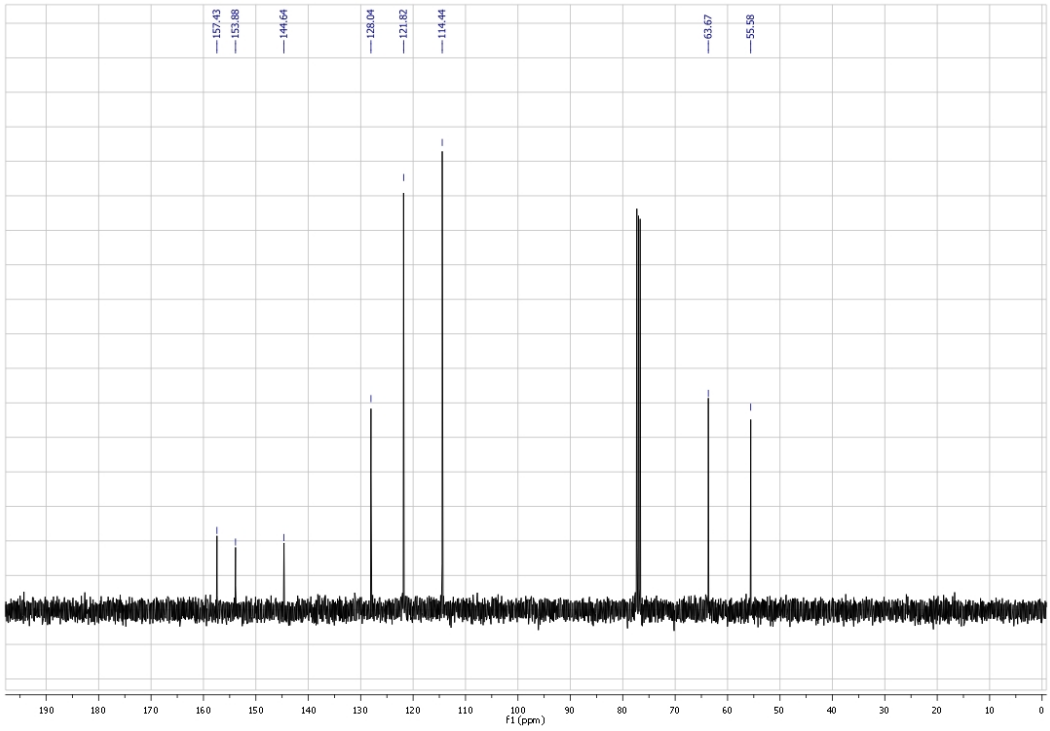


In a Schlenk tube equipped with stirring bar and septum, $CuBr{\cdot}SMe_2$ (0.0050 mmol, 1.00 mg) and (*S*,*S*)-**L1** (0.0060 mmol, 4.13 mg) were dissolved in CH_2Cl_2 (1.0 ml) and the mixture was stirred under nitrogen atmosphere at room temperature for 15 min. The mixture was cooled to -78 °C and MeMgBr (0.1 ml, 3M solution in Et_2O) was added dropwise. Allylic bromide **10** (0.1 mmol, 51.8 mg) was then added dropwise as a solution in CH_2Cl_2 (0.5 ml) over 1 h using a syringe pump. Once the addition was complete the resulting mixture was further stirred at -78 °C for 16 h. The reaction was quenched by addition of MeOH (0.1 ml) and the mixture was allowed to reach rt. Then, saturated aqueous NH_4Cl solution (2 ml) was added to the mixture. The organic phase was separated, and the resulting aqueous layer was extracted with CH_2Cl_2 (3 x 2 ml). The organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (SiO_2, pentane/Et_2O 20:1) to afford ***syn*-11a** (23%, 10.5 mg) as a colorless oil. $[\alpha]_D^{20}$ = + 6.8° (c = 0.5 in $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 4H), 7.44 – 7.33 (m, 6H), 5.85 (ddd, J = 17.0, 10.5, 9.1 Hz, 1H), 5.04 – 4.92 (m, 2H), 3.79 – 3.70 (m, 2H), 3.54 – 3.48 (m, 1H), 3.36 (dd, J = 10.4, 2.1 Hz, 1H), 2.46 – 2.36 (m, 1H), 1.67 (ddd, J = 16.9, 6.6, 3.8 Hz, 1H), 1.38 (s, 6H), 1.06 (d, J = 6.1 Hz, 3H), 1.05 (s, 9H), 0.70 (d, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 135.8, 129.4, 127.5, 114.7, 112.9, 97.6, 75.4, 65.7, 39.5, 32.0, 29.9, 26.8, 19.4, 19.3, 18.0, 11.5. HRMS (ESI+, *m/z*): Calcd for $C_{28}H_{40}O_3SiNa$ [M+Na^+]: 475.2639, found: 475.2630.

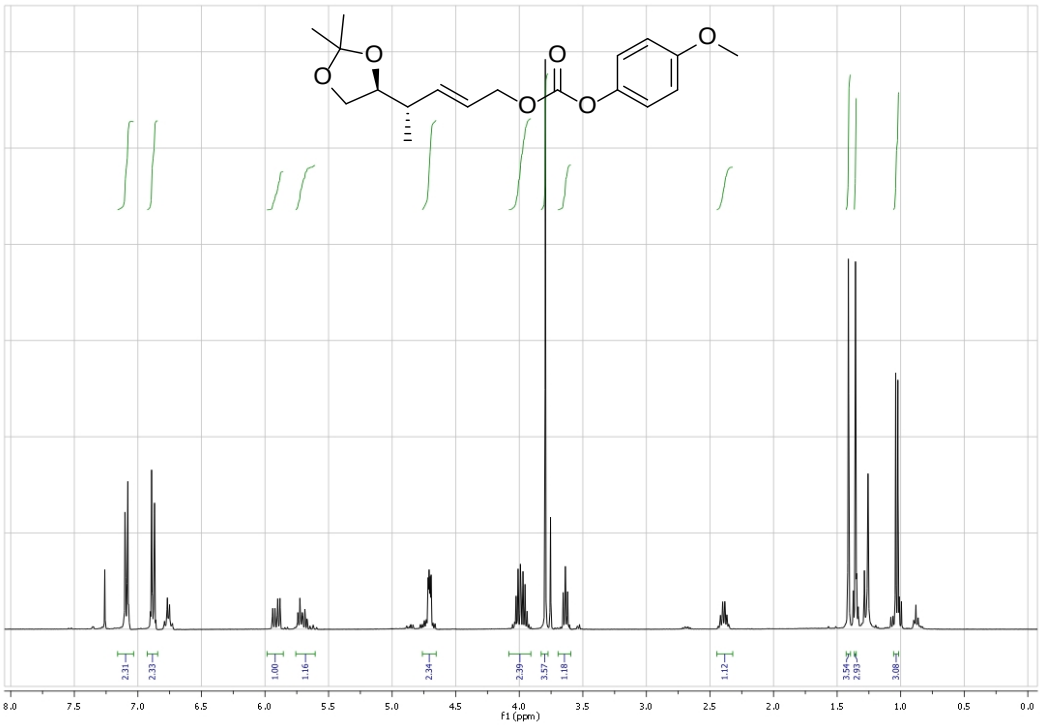
V. ^{1}H and ^{13}C-NMR spectra

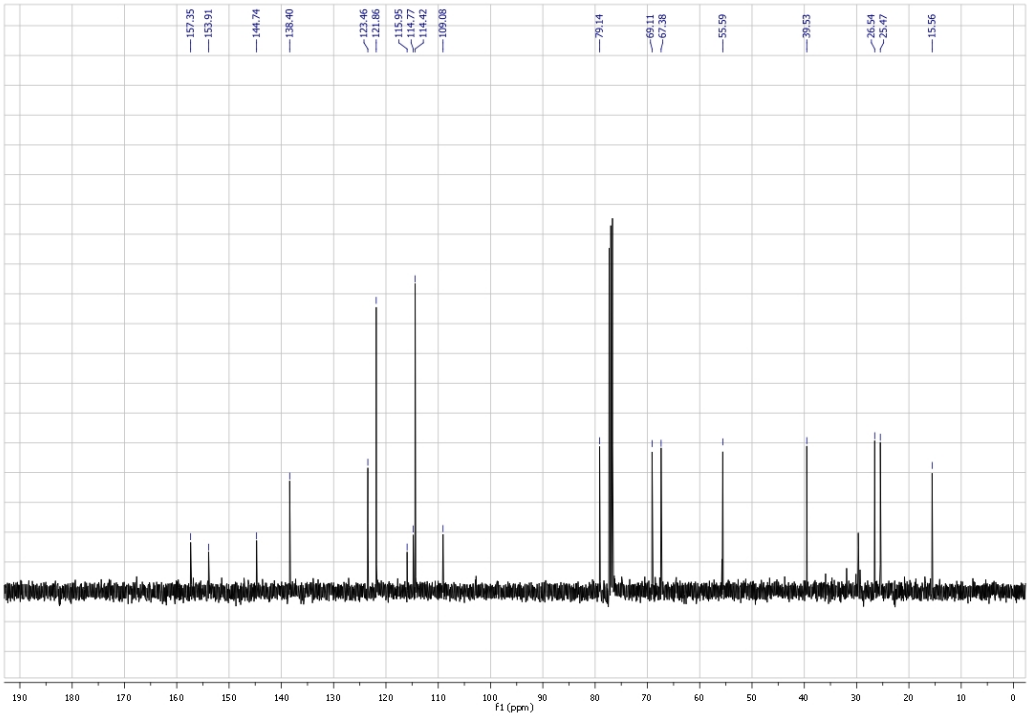
(Z)-but-2-ene-1,4-diyl bis(4-methoxyphenyl) dicarbonate (3)



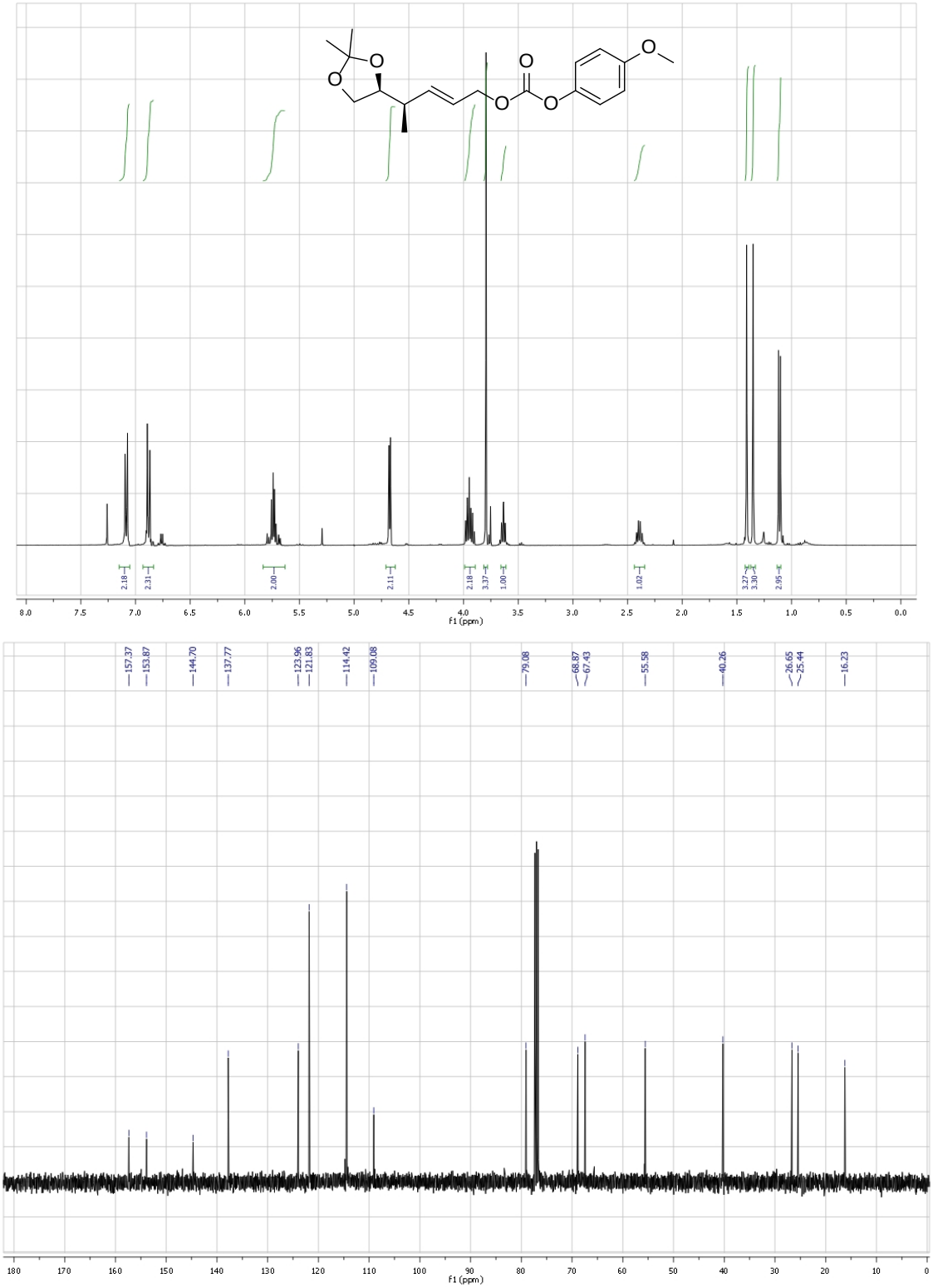


(*S*,*E*)-4-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-2-en-1-yl (4-methoxyphenyl) carbonate (4a)

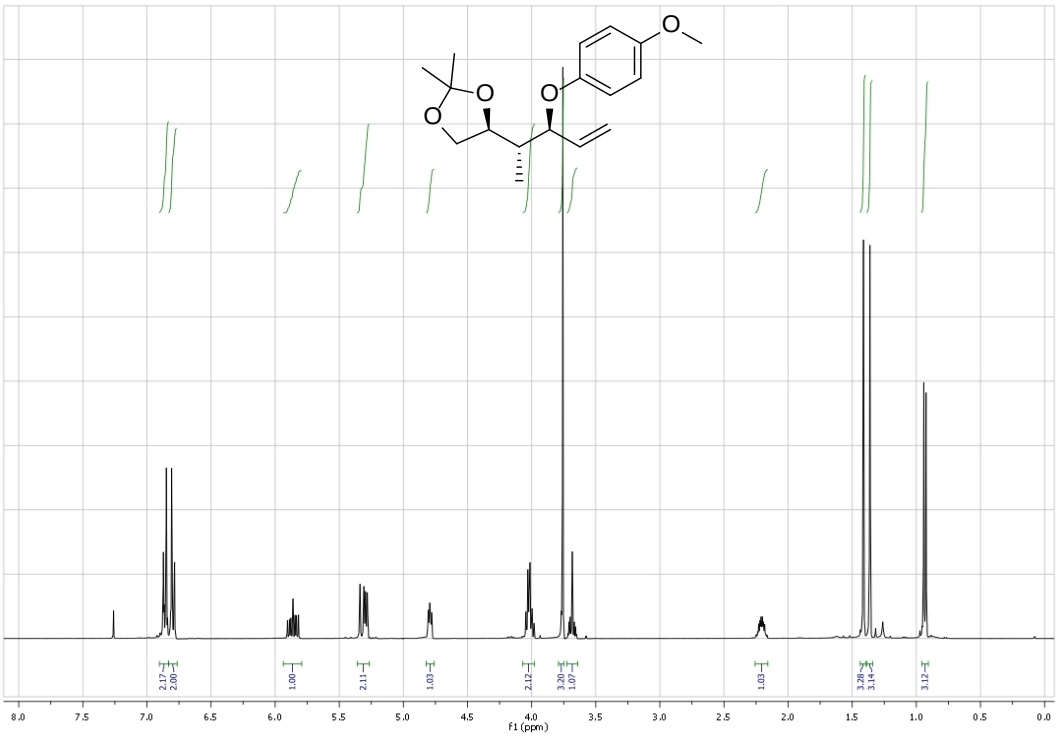


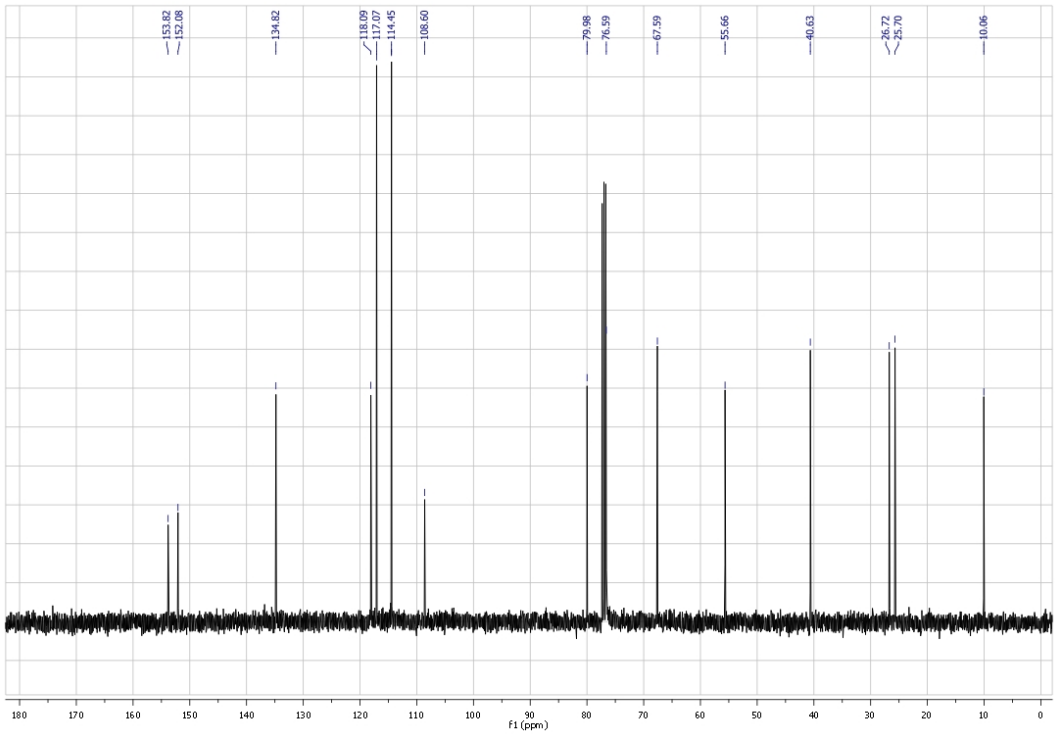


(*R*,*E*)-4-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-2-en-1-yl (4-methoxyphenyl) carbonate (4b)

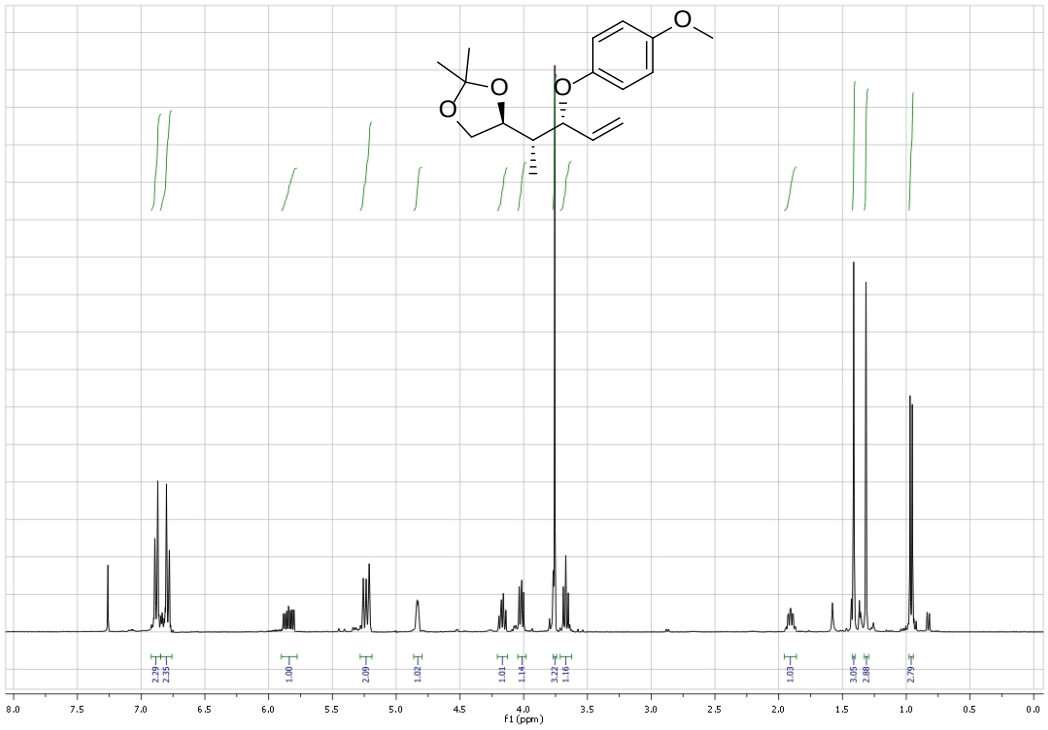


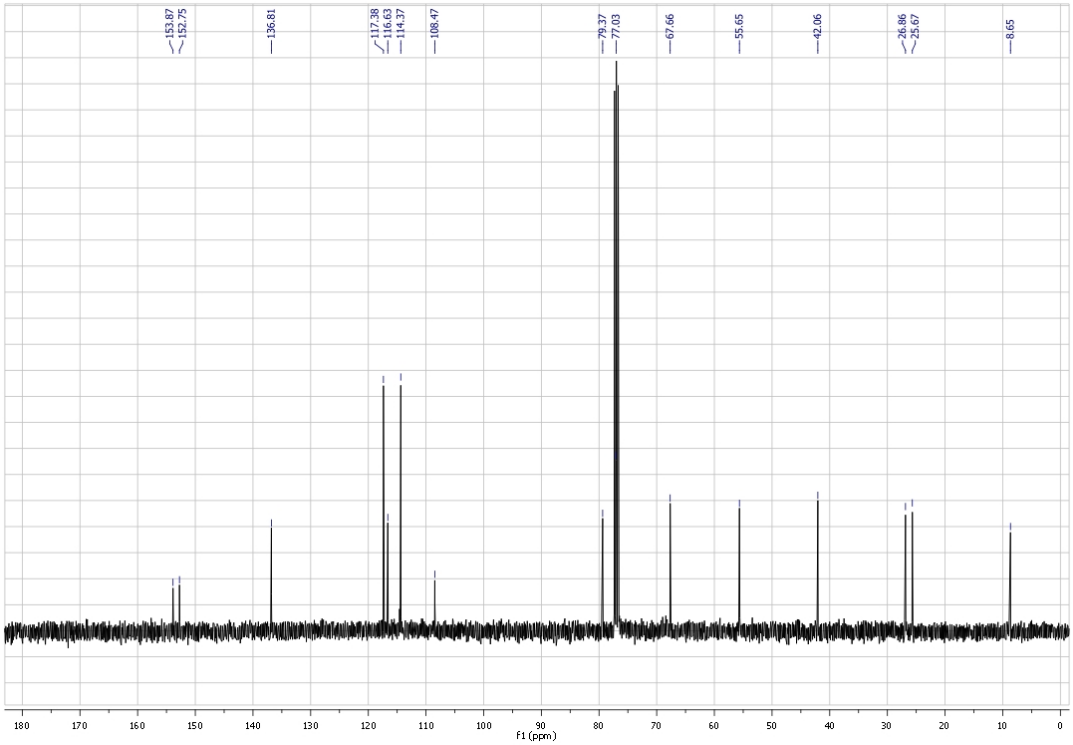
(*S*)-4-((*2S,3S*)-3-(4-methoxyphenoxy)pent-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (5a)



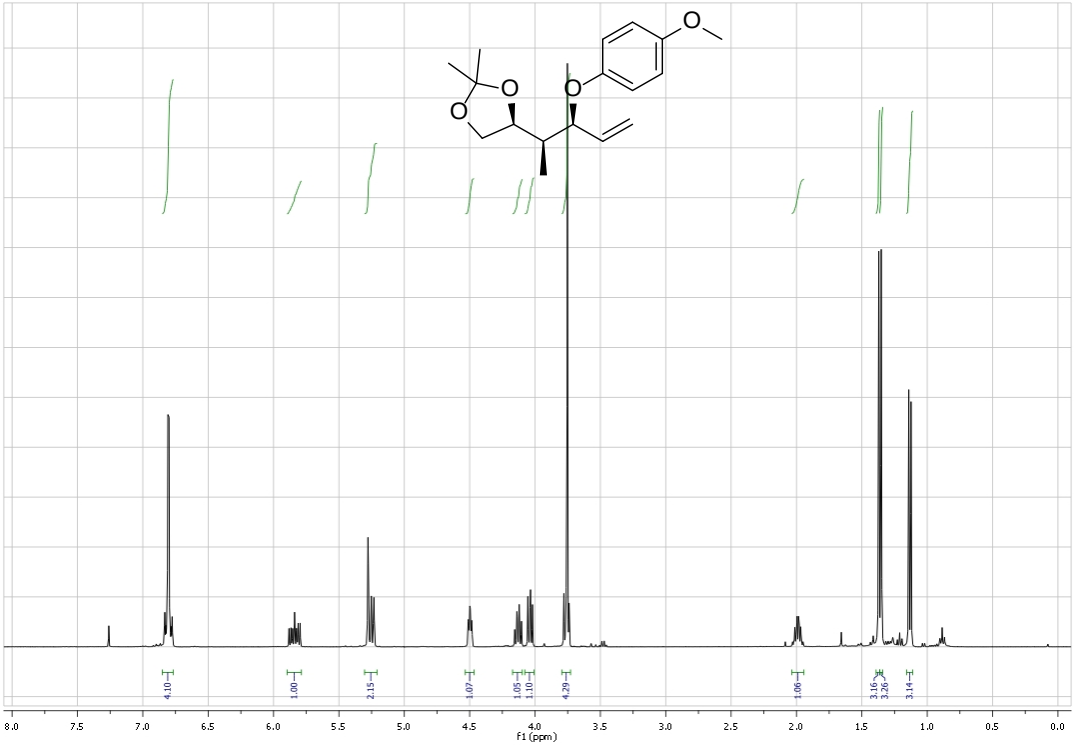


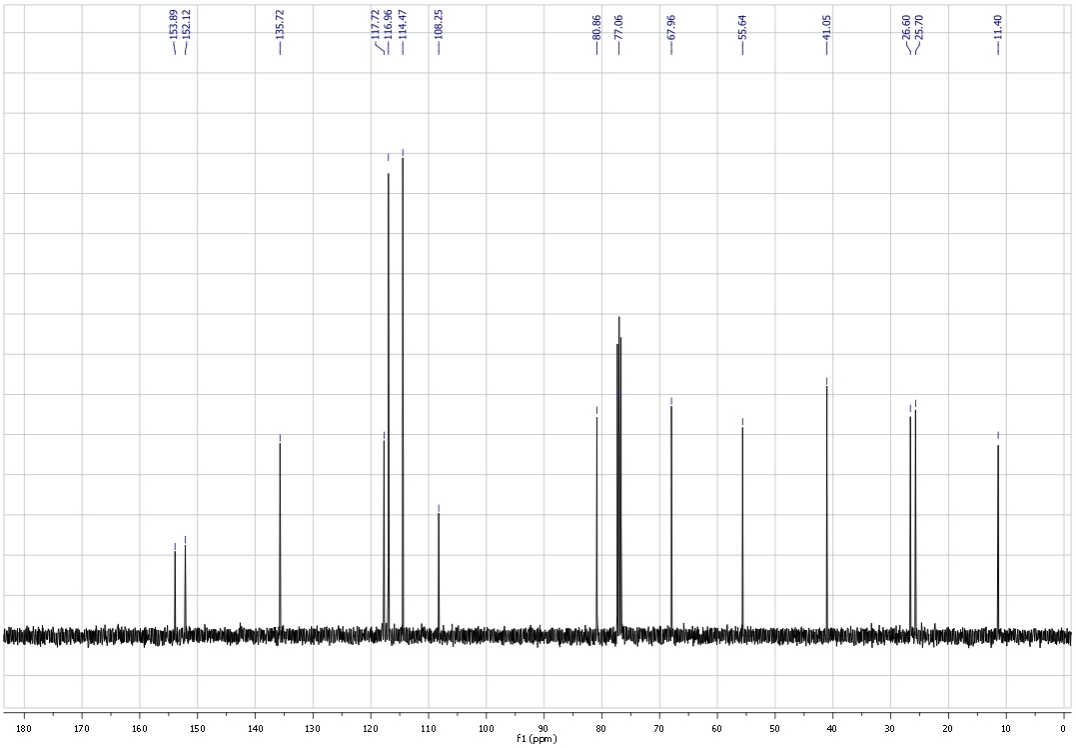
(*S*)-4-((*2S,3R*)-3-(4-methoxyphenoxy)pent-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (5b)



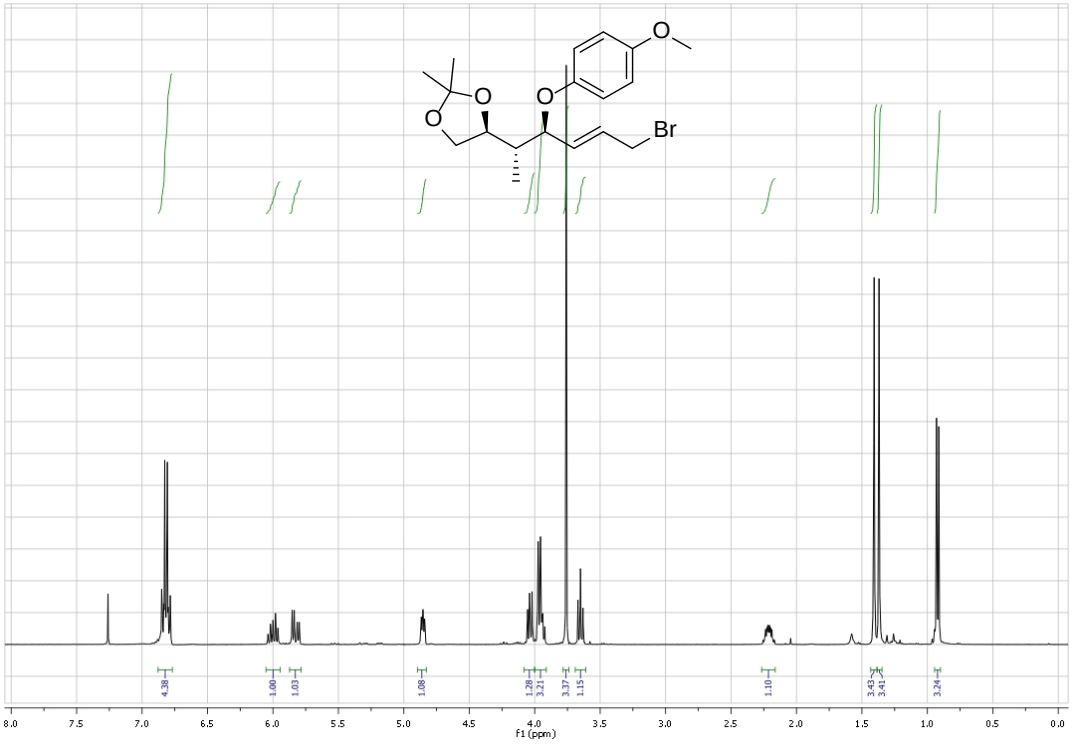


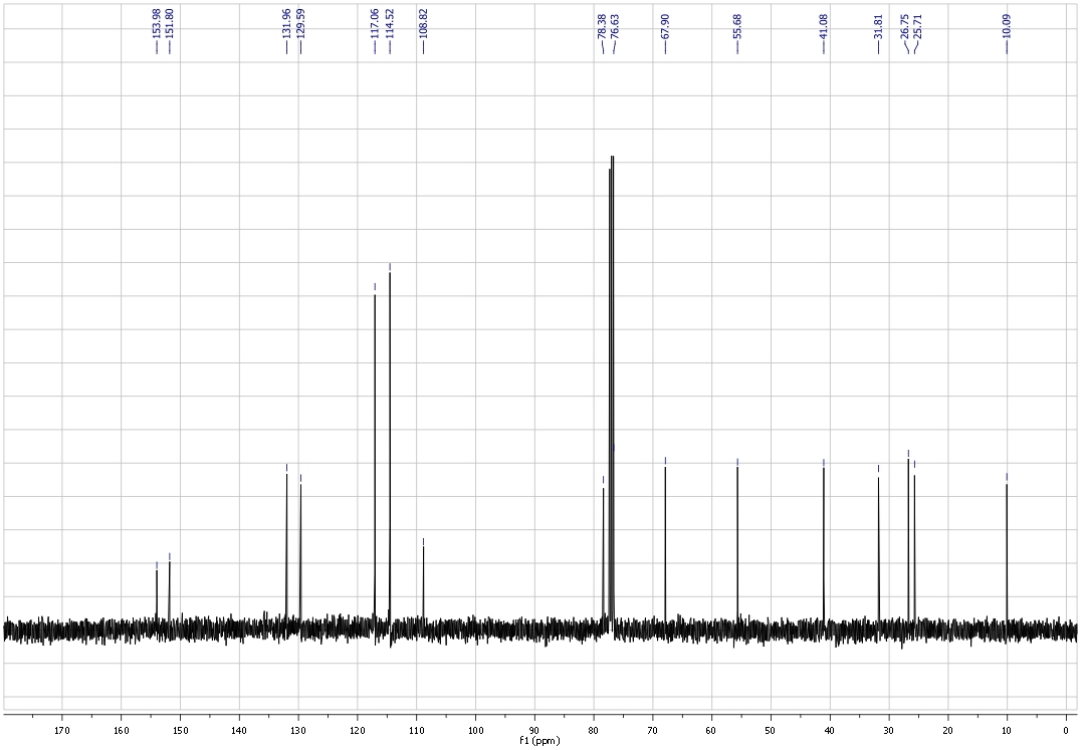
(*S*)-4-((*2R,3S*)-3-(4-methoxyphenoxy)pent-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (5c)



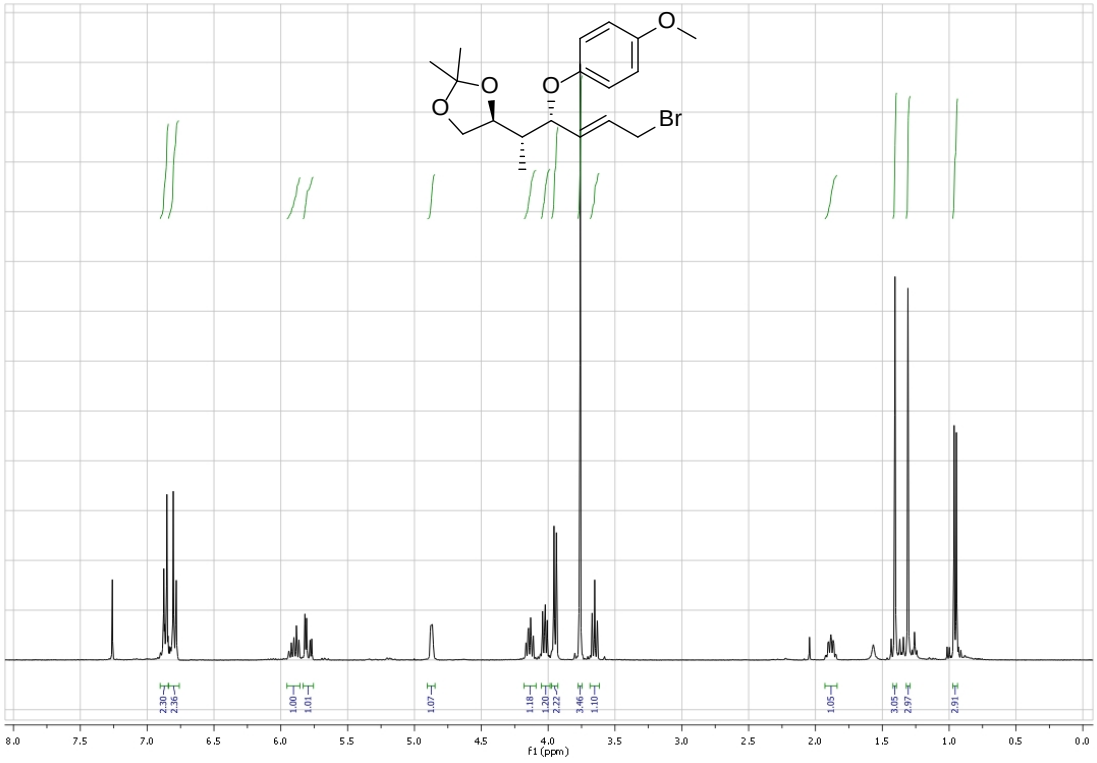


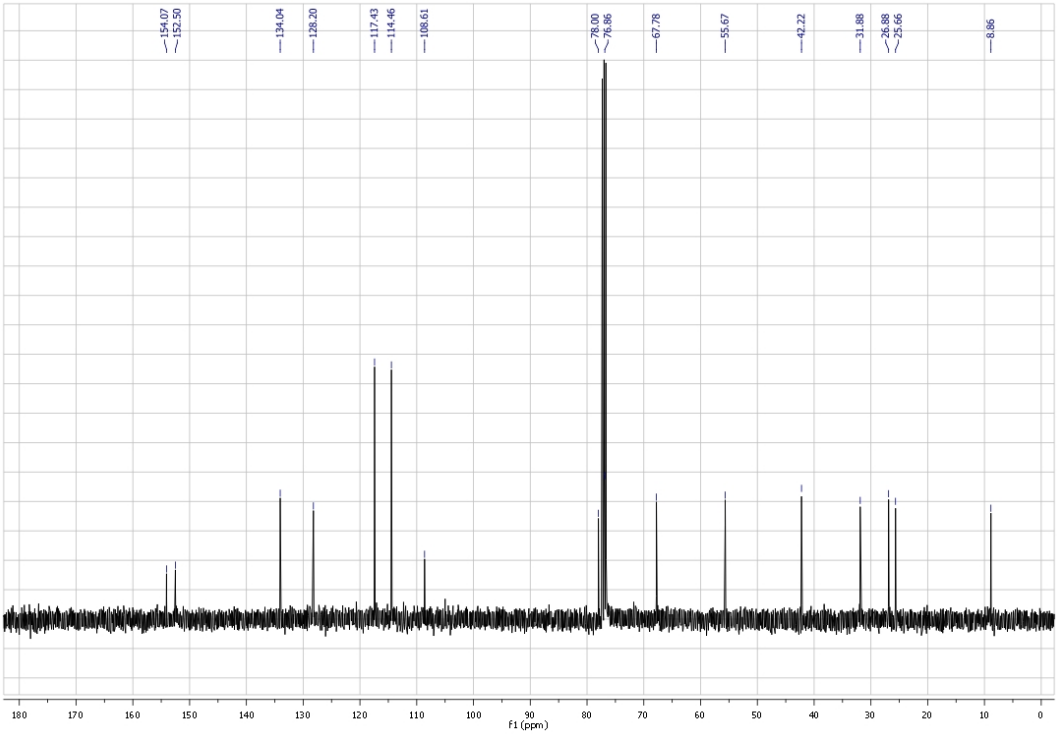
(*S*)-4-((*2S,3S,E*)-6-bromo-3-(4-methoxyphenoxy)hex-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (7a)



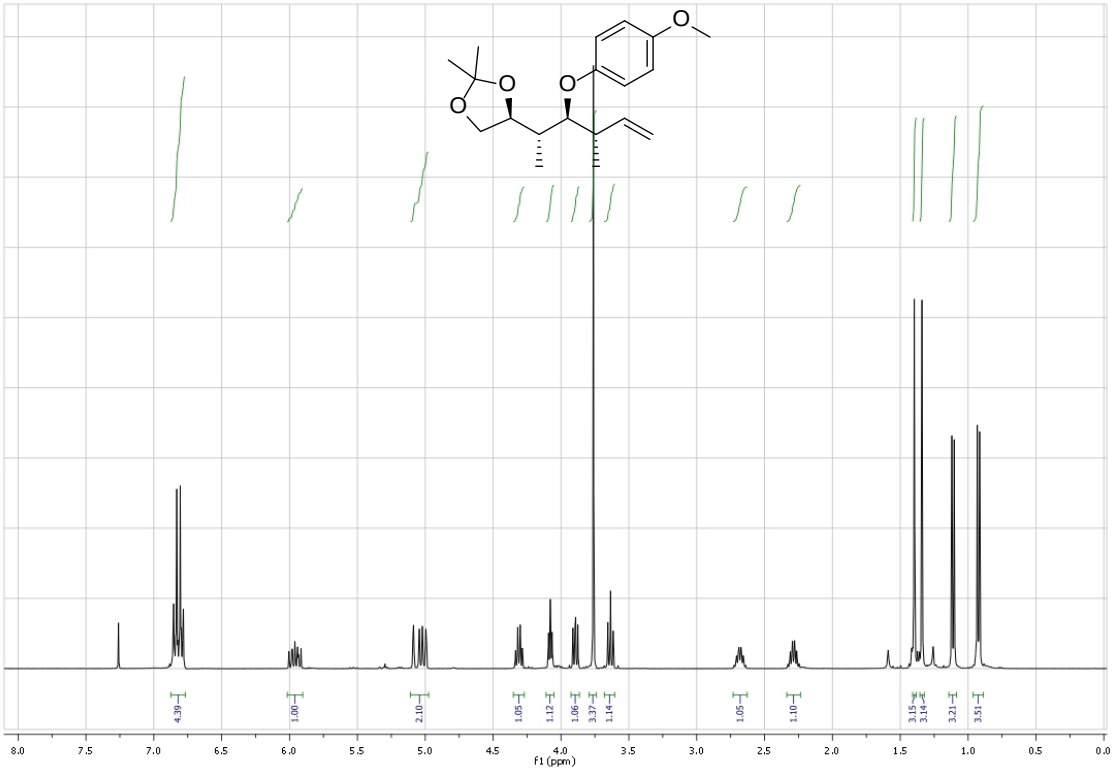


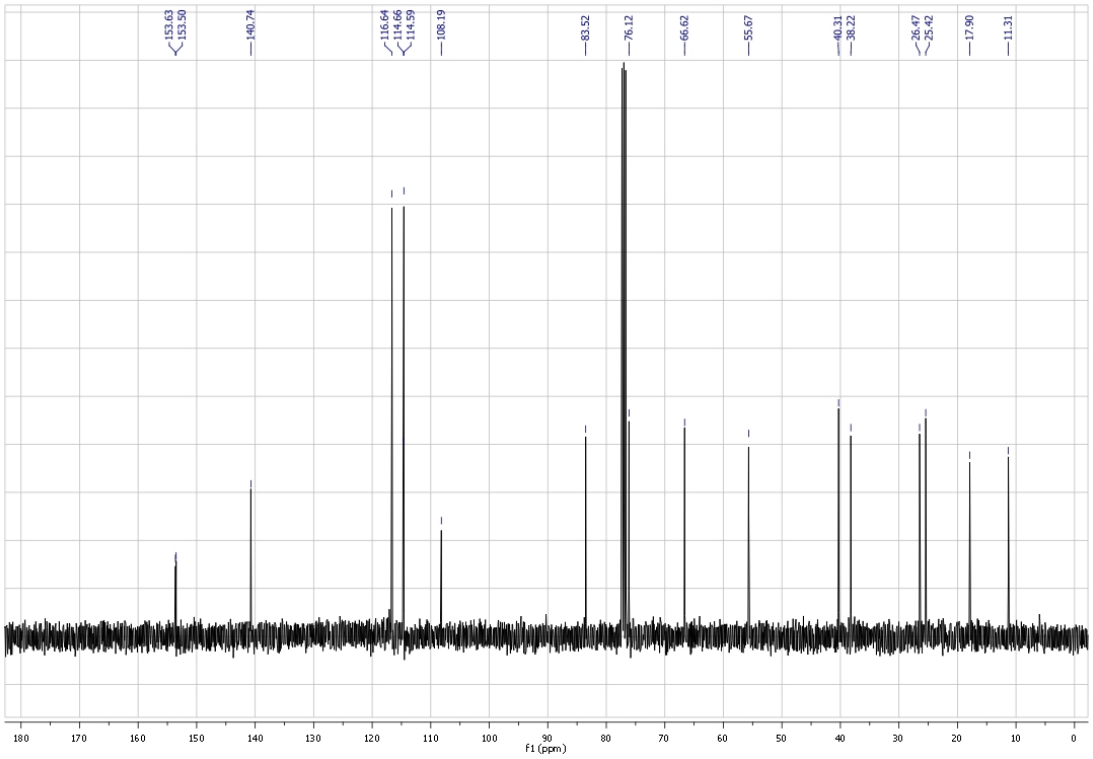
(*S*)-4-((*2S,3R,E*)-6-bromo-3-(4-methoxyphenoxy)hex-4-en-2-yl)-2,2-dimethyl-1,3-dioxolane (7b)



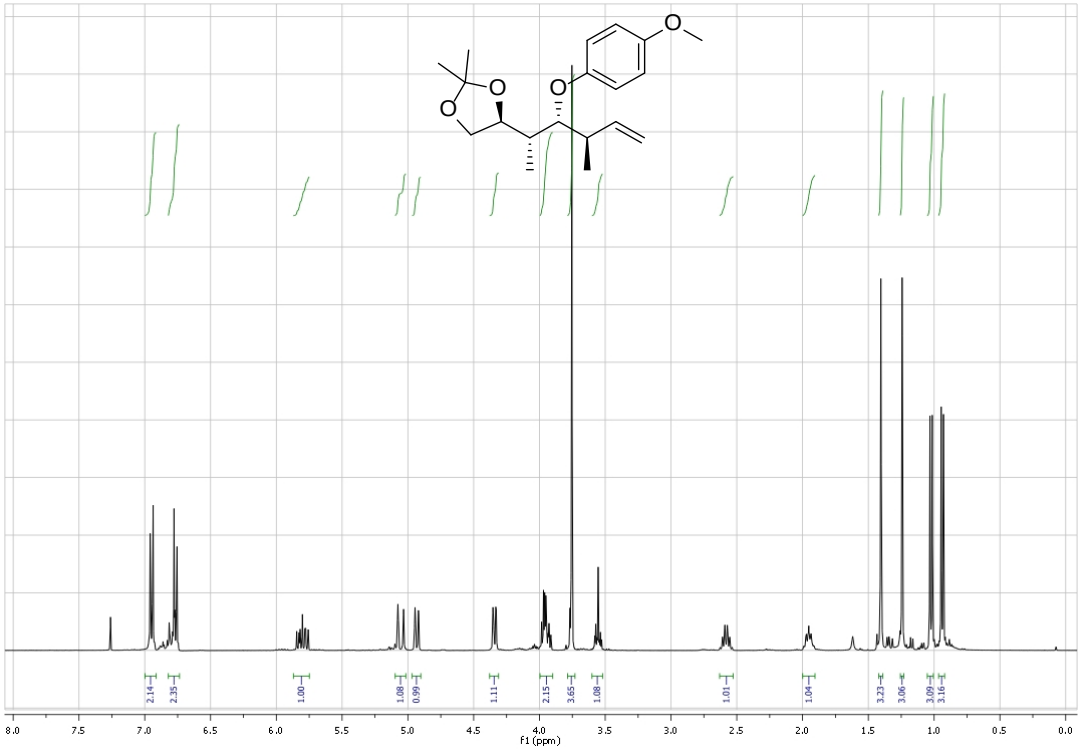


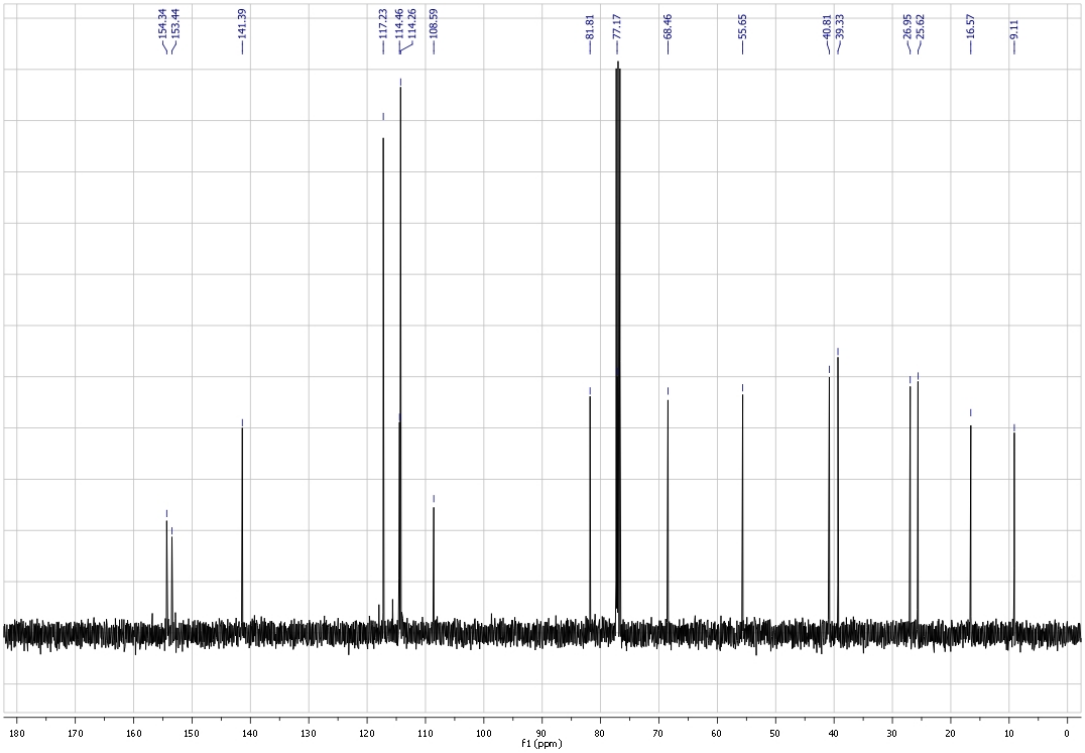
(*S*)-4-((*2S,3S,4S*)-3-(4-methoxyphenoxy)-4-methylhex-5-en-2-yl)-2,2-dimethyl-1,3-dioxolane (8a)



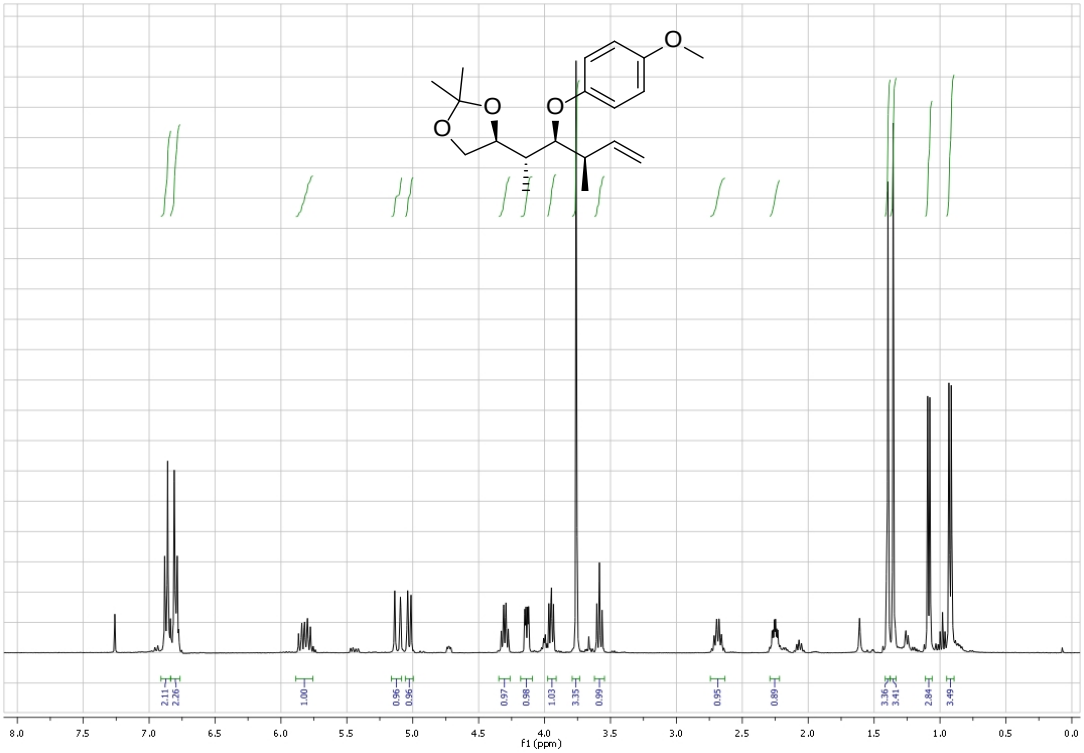


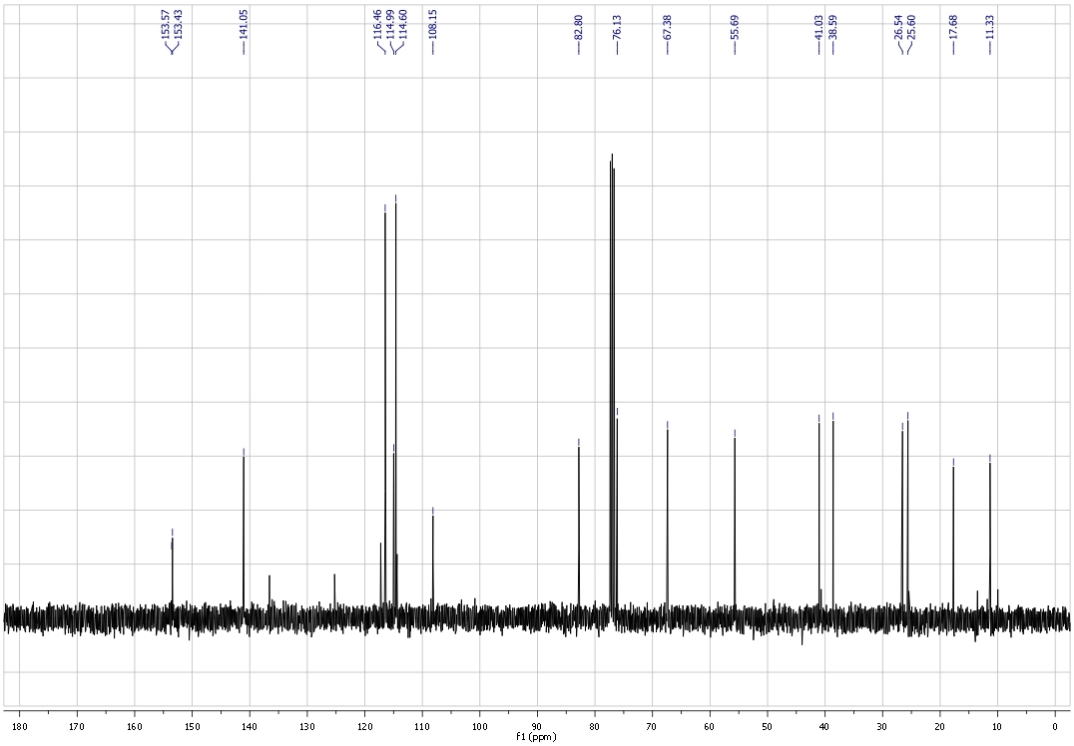
(*S*)-4-((*2S,3R,4R*)-3-(4-methoxyphenoxy)-4-methylhex-5-en-2-yl)-2,2-dimethyl-1,3-dioxolane (8b)



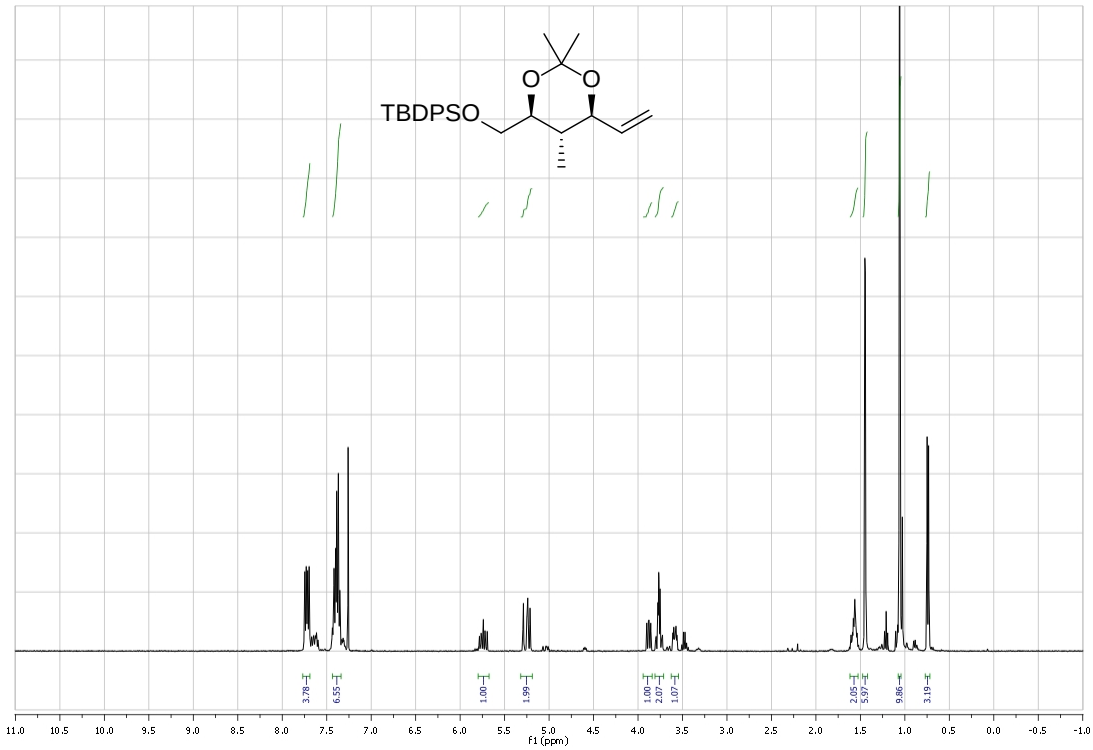


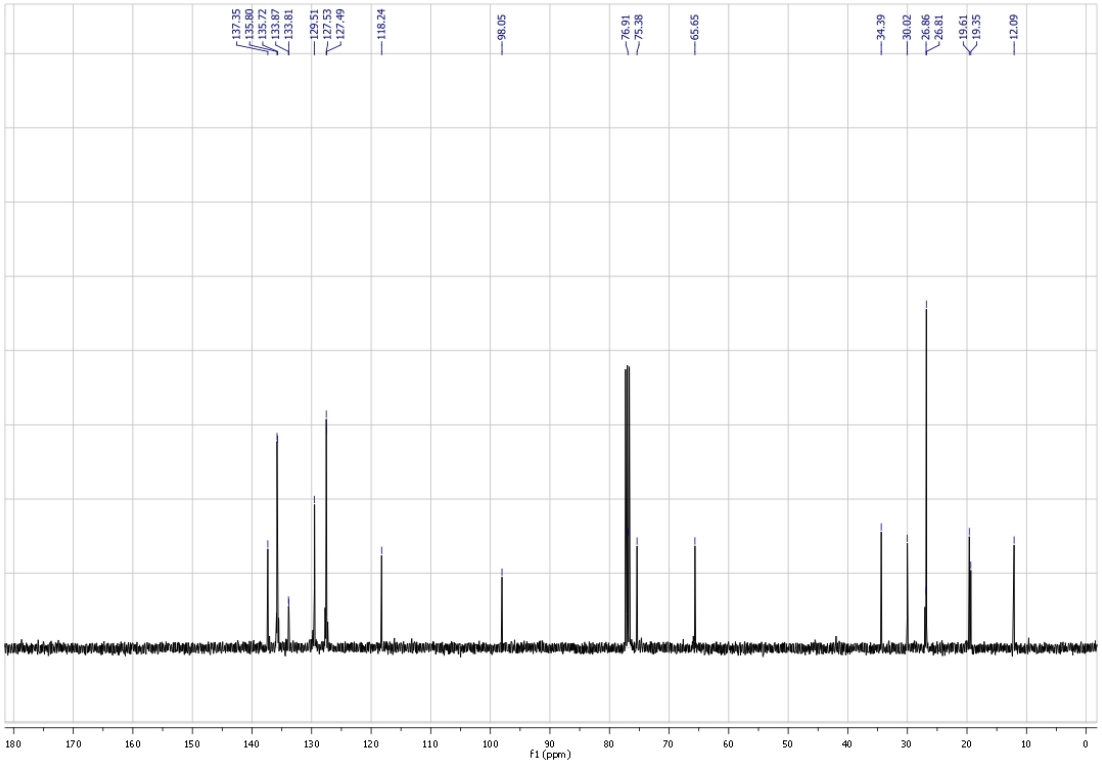
(*S*)-4-((2*S*,3*S*,4*R*)-3-(4-methoxyphenoxy)-4-methylhex-5-en-2-yl)-2,2-dimethyl-1,3-dioxolane (8c)



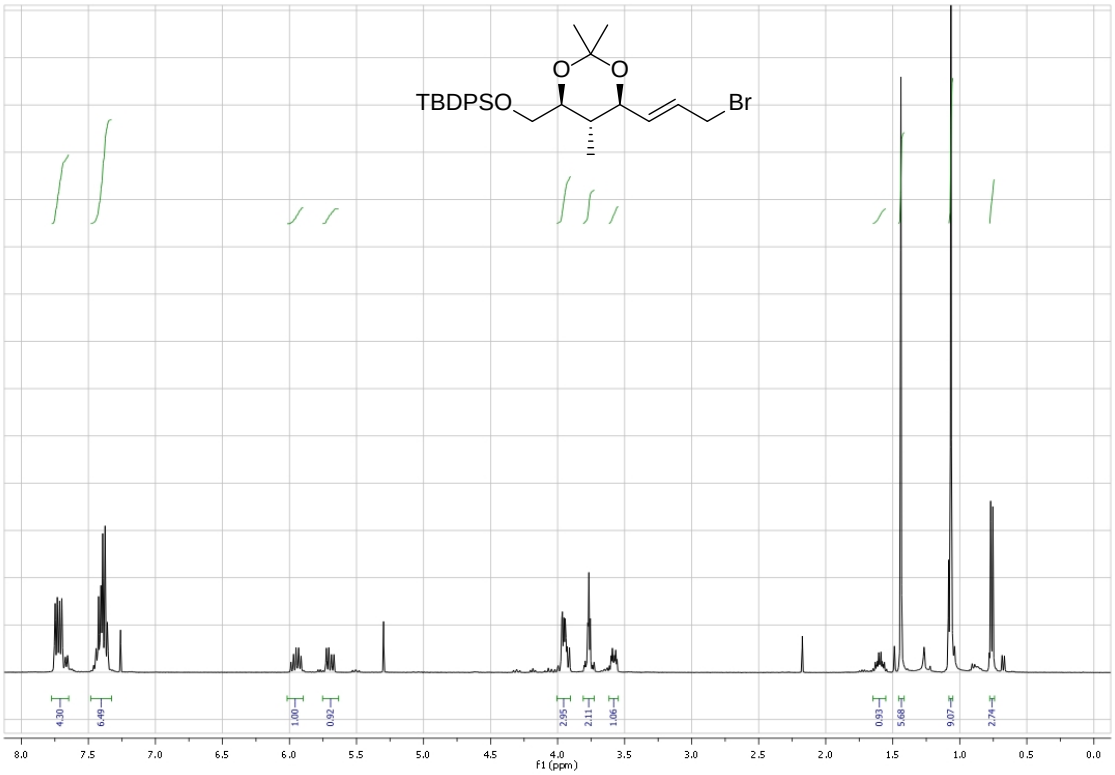


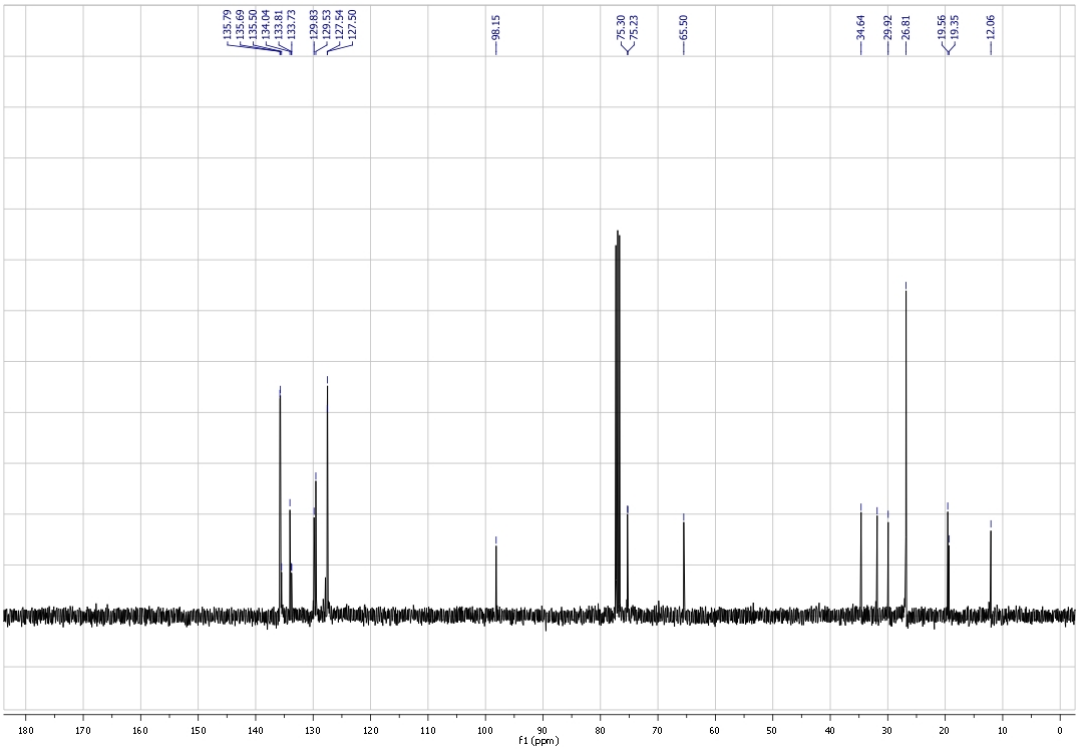
tert-butyldiphenyl(((*4S,5S,6S*)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)methoxy)silane (9)





(((*4S,5S,6S*)-6-((E)-3-bromoprop-1-en-1-yl)-2,2,5-trimethyl-1,3-dioxan-4-yl)methoxy)(tert-butyl)diphenylsilane (10)





(((4S,5S,6S)-6-((R)-but-3-en-2-yl)-2,2,5-trimethyl-1,3-dioxan-4-yl)methoxy)(tert-butyl)diphenylsilane (11)