Supporting information for

Ruthenium-catalysed *Z*-selective cross metathesis of allylic-substituted olefins

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Materials and Methods

Unless otherwise stated, solvents and reagents were of reagent quality, obtained from commercial sources and used without further purification. Reactions involving catalysts **1**–**4** were carried out in a nitrogen-filled glovebox. Substrates for cross metathesis were degassed by sparging with Ar and liquids (apart from 2-vinyloxirane) were filtered through a short plug of basic alumina prior to use. THF was purified by passage through solvent purification columns and degassed prior to use.[1] DCM for GC samples and $CDCl_3$ were filtered through a plug of basic alumina prior to use. Flash chromatography was carried out with silica gel 60 (230-400 mesh). 2-vinyl-1,3-dioxane, 4,4,6-trimethyl-2-vinyl-1,3-dioxane and 4,4,5,5-tetramethyl-2-vinyl-1,3-dioxolane[2] were all prepared according to a previously reported procedure.[3] *N*-allyl-*N*-benzylaniline was prepared as previously described.[4]

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High-resolution mass spectroscopy was completed at the California Institute of Technology Mass Spectrometry Facility. NMR spectra were recorded on a Varian Inova 400 (400 MHz for ^{1}H, 128 MHz for ^{11}B, 101 MHz for ^{13}C), automated Varian Inova 500 (500 MHz for ^{1}H, 126 MHz for ^{13}C) or Varian Inova 600 (500 MHz for ^{1}H, 151 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are expressed in ppm downfield from tetramethylsilane using the residual protiated solvent as an internal standard ($CDCl_3$ ^{1}H: 7.26 ppm and ^{13}C: 77.2 ppm; DMSO-d^6 ^{1}H: 2.50 ppm and ^{13}C: 39.5 ppm). ^{11}B chemical shifts are expressed in ppm downfield from $BF_3.OEt_2$ using the deuterium signal of the solvent as an internal standard.

Screening-scale Reactions

Typical procedure:

In a nitrogen-filled glovebox, 2-vinyl-1,3-dioxolane (16 μL, 0.016 mmol, 1 equiv.) and 1-dodecene (430 μL, 0.064 mmol, 4 equiv.) were combined in a 4 mL vial, to which tridecane (20 μL) was added as an internal standard. A solution of **2** (2.1 mg, 0.003 mmol, 2 mol%) in the required amount of THF was added. The reaction was stirred open to the atmosphere at 35 °C.

Samples for GC analysis were obtained by taking a 4 μL reaction aliquot and diluting to 1 mL with a 10% v/v solution of ethyl vinyl ether in DCM. Samples were shaken vigorously and allowed to stand for 10 minutes before GC analysis. All reactions were carried out in duplicate.

GC response factors were obtained for all starting materials and products using tridecane as an internal standard. Data was analysed as previously described.[5]

Instrument conditions: inlet temperature: 250 °C, detector temperature 300 °C, H_2 flow: 30 mL/min, air flow: 400 mL/min, makeup flow: 30 mL/min.

GC method: 80 °C for 1.5 minutes, followed by a temperature increase of 40 °C/min to 230 °C and held at that temperature for 2 minutes, then a temperature increase of 5 °C/min to 245 °C and finally a temperature increase of 40 °C/min to 300 °C and held at that temperature for 2.5 minutes. Total run time: 14.1 minutes.

Table 1. Response Factors

Compound	Response Factor	Retention Time (min)
tridecane	-	4.43
2-vinyl-1,3-dioxane	4.00	2.23
1-dodecene	1.10	4.88
(*Z*)-2-(dodec-1-en-1-yl)-1,3-dioxolane	1.07	6.74
(*E*)-2-(dodec-1-en-1-yl)-1,3-dioxolane	1.39	6.82
(*Z*)-11-docosene	0.56	9.34
(*E*)-11-docosene	0.56	9.38

General Procedures

General Procedure 1: CM of allylic-substituted olefins and 1-dodecene

In a nitrogen-filled glovebox, the allyl-substituted olefin (0.8 mmol, 1 equiv.) and 1-dodecene (710 μL, 3.2 mmol, 4 equiv.) were combined in a 20 mL vial, to which tridecane (50 μL) was added as an internal standard. A solution of **2** (10.8 mg, 0.016 mmol, 2 mol%) in THF (700 μL) was added and the concentration of allyl-substituted olefin adjusted to 0.5 M using THF. The reaction was stirred open to the atmosphere at 35 °C for 5 hours, at which time it was removed from the glovebox. The reaction mixture was quenched by addition of ethyl vinyl ether (200 μL) and subjected to silica gel chromatography.

General Procedure 2: CM of 2-vinyl-1,3-dioxolane with terminal olefins

In a nitrogen-filled glovebox, 2-vinyl-1,3-dioxolane (80 μL, 0.8 mmol, 1 equiv.) and terminal olefin (3.2 mmol, 4 equiv.) were combined in a 20 mL vial, to which tridecane (50 μL) was added as an internal standard. A solution of **2** (10.8 mg, 0.016 mmol, 2 mol%) in THF (700 μL) was added and the concentration of allyl-substituted olefin adjusted to 0.5 M using THF. The reaction was stirred open to the atmosphere at 35 °C for 5 hours, at which time it was removed from the glovebox. The reaction mixture was quenched by addition of ethyl vinyl ether (200 μL) and subjected to silica gel chromatography.

General Procedure 3: deprotection of acetals with SiO_2/oxalic acid

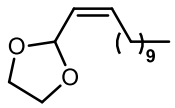
SiO_2 (2.5 g/mmol with respect to acetal), 5% aq. oxalic acid (10% w/w with SiO_2) and DCM (1.1 mL) were stirred at 20 °C for 5 minutes. To this suspension, a solution of *Z*-α,β-unsaturated acetal (0.13 mmol) in DCM (1.1mL) was added and the mixture was allowed to stir for a further 10 minutes. The suspension was then filtered through a SiO_2 plug and concentrated to yield the corresponding aldehyde.

General Procedure 4: deprotection of acetals with $LiBF_4$

To *Z*-α,β-unsaturated acetal (0.13 mmol, 1 equiv.) in 97:3 MeCN:H_2O (1.25 mL), was added $LiBF_4$ (0.16 mmol, 1.3 equiv.) and the resultant solution was stirred at 20 °C for 10 minutes. Upon completion, Et_2O (8 mL), sat. aq. $NaHCO_3$ (6 mL) and H_2O (2 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was back extracted with Et_2O (3 x 8 mL). The combined organic layers were washed with brine (5 mL, adjusted to pH 8 with $NaHCO_3$) and concentrated. The resultant residue was dissolved in DCM, dried over Na_2SO_4 and concentrated to yield the corresponding aldehyde.

Experimental Data

(Z)-2-(dodec-1-en-1-yl)-1,3-dioxolane (9)



9

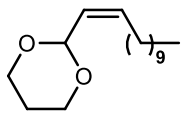
2-Vinyl-1,3-dioxolane (100 mg, 1.0 mmol) and 1-dodecene (670 mg, 4.0 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (pentane, then 92:8 pentane:Et_2O), product **9** was obtained as a clear, colourless oil (82% yield, 200 mg, >95% *Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dt, *J* = 11.0, 7.7 Hz, 1H), 5.54 (d, *J* = 7.3 Hz, 1H), 5.42 (dd, *J* = 11.0, 7.3 Hz, 1H), 4.07 – 3.83 (m, 4H), 2.17 (q, *J* = 7.7 Hz, 2H), 1.47 – 1.15 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 125.8, 99.4, 65.1, 32.1, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 28.0, 22.8 ppm.

HRMS (FAB) calcd. for $C_{15}H_{29}O_2$ $[M+H]^+$ 241.2168; found 241.2168.

(*Z*)-2-(dodec-1-en-1-yl)-1,3-dioxane (10)



10

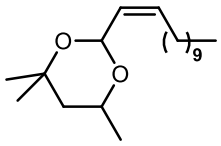
2-Vinyl-1,3-dioxane (91 mg, 0.80 mmol) and 1-dodecene (540 mg, 3.2 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (pentane, then 90:10 pentane:Et_2O), product **10** was obtained as a pale yellow oil (79% yield, 160 mg, >95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.63 (dt, *J* = 11.1, 7.5 Hz, 1H), 5.43 (dd, *J* = 11.1, 6.4 Hz, 1H), 5.23 (d, *J* = 6.5 Hz, 1H), 4.13 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.84 (td, *J* = 12.3, 2.5 Hz, 2H), 2.22 – 2.03 (m, 3H), 1.45 – 1.19 (m, 17H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 126.9, 98.1, 67.0, 32.0, 29.8, 29.7, 29.6, 29.5, 29.5 29.3, 28.3, 25.8, 22.8, 14.2 ppm.

HRMS (FAB) calcd. for $C_{16}H_{31}O_2$ $[M+H]^+$ 255.2324; found 255.2318.

(*Z*)-2-(dodec-1-en-1-yl)-4,4,6-trimethyl-1,3-dioxane (11)



12

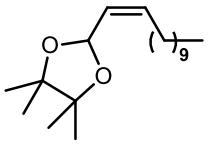
4,4,6-Trimethyl-2-vinyl-1,3-dioxane (130 mg, 0.80 mmol) and 1-dodecene (540 mg, 3.2 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (pentane, then 92:8 pentane:Et_2O), product **11** was obtained as a clear, colourless oil (84% yield, 180 mg, >95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.62 (dt, *J* = 10.8, 7.5 Hz, 1H), 5.49 (d, *J* = 6.6Hz, 1H), 5.45 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.93 (ddh, *J* = 12.2, 6.1, 2.8 Hz, 1H), 2.11 (qd, *J* = 7.5, 1.3 Hz, 2H), 1.48 – 1.34 (m, 4H), 1.34 (s, 3H), 1.32 – 1.22 (m, 17H), 1.21 (d, *J* = 6.1 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 127.5, 91.2, 72.1, 68.9, 43.5, 32.1, 31.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 28.2, 22.8, 22.3, 22.0, 14.3 ppm.

HRMS (FAB) calcd. for $C_{19}H_{37}O_2$ $[M+H]^+$ 297.2794; found 297.2792.

(*Z*)-2-(dodec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (12)



13

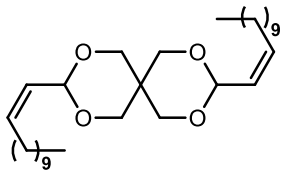
4,4,5,5-Tetramethyl-2-vinyl-1,3-dioxolane (130 mg, 0.80 mmol) and 1-dodecene (540 mg, 3.2 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (pentane, then 96:4 pentane:Et_2O), product **13** was obtained as a clear, colourless oil (84% yield, 200 mg, >95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.73 (d, *J* = 8.0 Hz, 1H), 5.68 (dt, *J* = 11.0, 7.7 Hz, 1H), 5.38 (dd, *J* = 11.0, 8.0 Hz, 1H), 2.16 (q, *J* = 7.7 Hz, 2H), 1.40 – 1.23 (m, 16H), 1.22 (s, 12H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 128.4, 95.4, 82.2, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 27.5, 24.2, 22.8, 22.2, 14.3 ppm.

HRMS (FAB) calcd. for $C_{19}H_{35}O_2$ $[(M+H)-H_2]^+$ 295.2637; found 295.2627.

3,9-di((*Z*)-dodec-1-en-1-yl)-2,4,8,10-tetraoxaspiro[5.5]undecane (13)



14

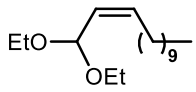
3,9-Divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (85 mg, 0.40 mmol) and 1-dodecene (540 mg, 3.2 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (pentane, then 92:8 pentane:Et_2O), product **14** was obtained as a white solid (77% yield, 150 mg, >89% *Z,Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.66 (dt, *J* = 11.1, 7.6 Hz, 2H), 5.44 (dt, *J* = 11.1, 6.4 Hz, 2H), 5.14 (d, *J* = 6.4 Hz, 2H), 4.63 (dd, *J* = 11.5, 2.3 Hz, 2H), 3.66 – 3.58 (m, 4H), 3.43 (d, *J* = 11.5 Hz, 2H), 2.11 (q, *J* = 7.6 Hz, 4H), 1.40 – 1.19 (m, 32H), 0.87 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.5, 126.3, 98.7, 70.8, 70.3, 32.1, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.3, 22.8, 14.3 ppm.

HRMS (FAB) calcd. for $C_{31}H_{57}O_4$ $[M+H]^+$ 493.4257; found 493.4236.

(*Z*)-1,1-diethoxytridec-2-ene (14)



11

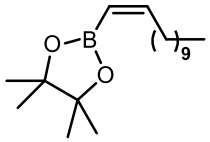
Acrolein diethyl acetal (130 mg, 1.0 mmol) and 1-dodecene (670 mg, 4.0 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (98.5:1.5 pentane:Et_3N, then 96.5:1.5:3 pentane:Et_3N:Et_2O), product **11** was obtained as a clear, colourless oil (70% yield, 190 mg, >95% *Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (dt, *J* = 11.2, 7.5 Hz, 1H), 5.46 (dd, *J* = 11.2, 6.8 Hz, 1H), 5.20 (d, *J* = 6.8 Hz, 1H), 3.64 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.50 (dq, *J* = 9.4, 7.1 Hz, 2H), 2.13 (q, *J* = 7.5z Hz, 2H), 1.45 – 1.24 (m, 16H), 1.21 (t, *J* = 7.1 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 127.3, 97.8, 60.6, 32.1, 29.8, 29.8, 29.6, 29.6, 29.5, 29.4, 28.2, 22.8, 15.5, 14.3 ppm.

HRMS (FAB) calcd. for $C_{17}H_{33}O_2$ $[(M+H)-H_2]^+$ 269.2481; found 269.2481.

(*Z*)-2-(dodec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)



15

Vinylboronic acid pinacol ester (120 mg, 0.80 mmol) and 1-dodecene (540 mg, 3.2 mmol) were reacted according to general procedure 1. After purification by silica gel chromatography (pentane, then 92:8 pentane:Et_2O), product **15** was obtained as a clear, colourless oil (81% yield, 190 mg, 92% *Z*).

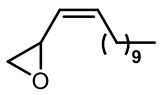
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (dt, *J* = 14.6, 7.5 Hz, 1H), 5.32 (d, *J* = 13.5 Hz, 1H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.47 – 1.17 (m, 28H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.45, 118.04, 82.91, 32.35, 32.08, 29.81, 29.78, 29.62, 29.60, 29.52, 29.22, 24.99, 22.85, 14.27 ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.87 ppm.

HRMS (FAB) calcd. for $C_{18}H_{36}BO_2$ $[M+H]^+$ 295.2808; found 295.2811.

(*Z*)-2-(dodec-1-en-1-yl)oxirane (16)



16

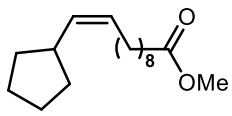
2-Vinyloxirane (70 mg, 1.0 mmol) and 1-dodecene (670 mg, 4.0 mmol) were reacted according to general procedure 1, except that the reaction was conducted at 20 °C. After purification by silica gel chromatography (98.5:1.5 pentane:Et_3N , then 96.5:1.5:2 pentane:Et_3N:Et_2O), product **16** was obtained as a clear, colourless oil (40% yield, 85 mg, >95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.74 (dtd, *J* = 10.9, 7.7, 0.9 Hz, 1H), 5.00 (ddt, *J* = 10.9, 9.0, 1.5 Hz, 1H), 3.61 (dddd, *J* = 9.0, 4.0, 2.7, 0.9 Hz, 1H), 2.98 (dd, *J* = 5.3, 4.0 Hz, 1H), 2.64 (dd, *J* = 5.3, 2.7 Hz, 1H), 2.38 – 2.10 (m, 2H), 1.48 – 1.20 (m, 16H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.23, 126.94, 48.68, 48.08, 31.90, 29.61, 29.59, 29.58, 29.47, 29.33, 29.18, 27.74, 22.68, 14.12 ppm.

HRMS (FAB) calcd. for $C_{14}H_{27}O$ $[M+H]^+$ 211.2062; found 211.2027.

(*Z*)-methyl 11-cyclopentylundec-10-enoate (17)



17

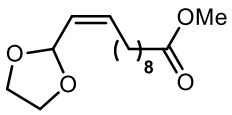
Vinyl cyclopentane (96 mg, 1.0 mmol) and methyl-10-undecenoate (790 mg, 4.0 mmol) were reacted according to general procedure 1, with methyl-10-undecenoate used in place of 1-dodecene. After purification by silica gel chromatography (95:5 pentane:Et_2O), product **17** and unreacted methyl-10-undecenoate were isolated as a mixture. ^{1}H-NMR analysis showed the mixture (160 mg) contained 73 mol% of **17** (117 mg, 44% yield, 94% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.35 – 5.25 (m, 2H), 3.68 (s, 3H), 2.78 – 2.62 (m, 1H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.05 (q, *J* = 6.8 Hz, 2H), 1.84 – 1.73 (m, 1H), 1.73 – 1.49 (m, 6H), 1.44 – 1.12 (m, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 135.5, 128.6, 51.6, 38.3, 34.3, 33.9, 30.1, 29.5, 29.4, 29.3, 29.3, 27.6, 25.5, 25.1 ppm.

HRMS (FAB) calcd. for $C_{17}H_{31}O_2$ $[M+H]^+$ 267.2324; found 267.2316.

(*Z*)-methyl 11-(1,3-dioxolan-2-yl)undec-10-enoate (18)



18

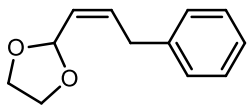
2-Vinyl-1,3-dioxolane (80 mg, 0.80 mmol) and methyl-10-undecenoate (640 mg, 3.2 mmol) were reacted according to general procedure 2. After purification by silica gel chromatography (95:5 pentane:Et_2O, then 90:10 pentane:Et_2O), product **18** was obtained as a clear, colourless oil (84% yield, 180 mg, >95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.75 (dt, *J* = 11.1, 7.7 Hz, 1H), 5.53 (d, *J* = 7.3 Hz, 2H), 5.42 (dd, *J* = 11.1, 7.3 Hz, 1H), 4.07 – 3.81 (m, 4H), 3.66 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.16 (q, *J* = 7.7 Hz, 2H), 1.61 (app. p, *J* = 7.5 Hz, 2H), 1.43 – 1.24 (m, 10H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.30, 137.71, 125.72, 99.18, 64.94, 51.43, 34.08, 29.43, 29.20, 29.13, 29.09, 29.06, 27.76, 24.91 ppm.

HRMS (FAB) calcd. for $C_{15}H_{27}O_4$ $[M+H]^+$ 271.1909; found 271.1900.

(*Z*)-2-(3-phenylprop-1-en-1-yl)-1,3-dioxolane (19)



19

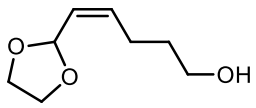
2-Vinyl-1,3-dioxolane (80 mg, 0.80 mmol) and allylbenzene (670 mg, 3.2 mmol) were reacted according to general procedure 2. After purification by silica gel chromatography (95:5 pentane:Et_2O, then 90:10 pentane:Et_2O), product **19** was obtained as a pale yellow oil (88% yield, 130 mg, >95% *Z*).

^{1}H NMR (600 MHz, DMSO-d^6) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 3H), 5.83 (q, *J* = 8.7 Hz, 1H), 5.64 (d, *J* = 7.5 Hz, 1H), 5.53 – 5.43 (m, 1H), 4.02 – 3.79 (m, 4H), 3.49 (d, *J* = 7.9 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 135.5, 128.7, 128.6, 126.9, 126.4, 99.4, 65.2, 34.2 ppm.

HRMS (FAB) calcd. for $C_{12}H_{13}O_2$ $[(M+H)-H_2]^+$ 189.0916; found 189.0886.

(*Z*)-5-(1,3-dioxolan-2-yl)pent-4-en-1-ol (20)



20

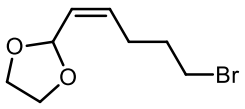
2-Vinyl-1,3-dioxolane (80 mg, 0.80 mmol) and 4-penten-1-ol (280 mg, 3.2 mmol) were reacted according to general procedure 2, except that the reaction was stopped at 3 h. After purification by silica gel chromatography (80:18:2 EtOAc:hexanes:Et_3N), product **20** was obtained as a clear colourless oil (74% yield, 94 mg, >95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.72 (dt, *J* = 10.8, 8.1 Hz, 1H), 5.56 (d, *J* = 6.6 Hz, 1H), 5.52 (dd, *J* = 10.8, 6.6 Hz, 1H), 4.05 – 3.85 (m, 4H), 3.62 (q, *J* = 5.7 Hz, 2H), 2.34-2.26 (m, 2H), 2.20 (s, 1H), 1.76-1.59 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 127.0, 99.5, 65.1, 61.0, 31.6, 24.2 ppm.

HRMS (FAB) calcd. for $C_8H_{15}O_3$ $[M+H]^+$ 159.1021; found 159.1017.

(*Z*)-2-(5-bromopent-1-en-1-yl)-1,3-dioxolane (21)



21

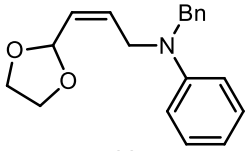
2-Vinyl-1,3-dioxolane (80 mg, 0.80 mmol) and 5-bromo-1-pentene (480 mg, 3.2 mmol) were reacted according to general procedure 2. After purification by silica gel chromatography (90:10 pentane:Et_2O, then 80:20 pentane:Et_2O), product **21** was obtained as a pale yellow oil (83% yield, 150 mg, 95% *Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.72 (dt, *J* = 10.7, 7.8 Hz, 1H), 5.56 (d, *J* = 7.8 Hz, 1H), 5.52 (dd, *J* = 10.7, 7.1 Hz, 1H), 4.05 – 3.86 (m, 4H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.40 – 2.32 (m, 2H), 1.96 (dt, *J* = 13.6, 6.7 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 127.8, 99.2, 65.1, 33.1, 32.4, 26.4 ppm.

HRMS (FAB) calcd. for $C_8H_{14}BrO_2$ $[M+H]^+$ 221.0177; found 221.0182.

(*Z*)-*N*-(3-(1,3-dioxolan-2-yl)allyl)-*N*-benzylaniline (22)



22

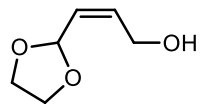
2-Vinyl-1,3-dioxolane (80 mg, 0.80 mmol) and *N*-allyl-*N*-benzylaniline (720 mg, 3.2 mmol) were reacted according to general procedure 2. After purification by silica gel chromatography (90:10 pentane:Et_2O, then 80:20 pentane:Et_2O), product **22** was obtained as an off-white solid (72% yield, 170 mg, 89% *Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 7H), 6.78 – 6.68 (m, 3H), 5.87 (dt, *J* = 12.3, 6.3 Hz, 1H), 5.65 (dd, *J* = 11.2, 6.5 Hz, 1H), 5.49 (d, *J* = 6.5 Hz, 1H), 4.53 (s, 2H), 4.16 (d, *J* = 6.3 Hz, 2H), 4.07 – 3.82 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 139.0, 134.0, 129.4, 128.7, 128.5, 127.0, 126.9, 117.1, 113.0, 99.2, 65.1, 54.4, 47.9 ppm.

HRMS (FAB) calcd. for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1650; found 296.1654.

(*Z*)-3-(1,3-dioxolan-2-yl)prop-2-en-1-ol (24)



24

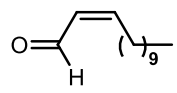
2-Vinyl-1,3-dioxolane (80 mg, 0.80 mmol) and allylboronic acid pinacol ester (540 mg, 3.2 mmol) were reacted according to general procedure 2. The oxidation was carried out according to a modified literature procedure.[6] After removal from glovebox, the reaction mixture was diluted with additional THF (2 mL) and cooled to 0 °C. NaOH (15 w/w%, 2.6 mL, 9.6 mmol) and aqueous H_2O_2 (30 w/w%, 0.96 mL, 9.6 mmol) were added slowly and the reaction was allowed to gradually warm to room temperature over 2 h. The mixture was then diluted with sat. $NaHCO_3$ (4 mL) and the organic solvent removed under reduced pressure. The aqueous layer was extracted into EtOAc (3 x 10 mL), dried over Na_2SO_4, filtered and concentrated. After purification by silica gel chromatography (96.5:2:1.5 DCM:MeOH:Et_3N, then 94.5:4:1.5 DCM:MeOH:Et_3N), product **24** was obtained as a pale yellow oil (63% yield, 66 mg, >95% *Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dt, *J* = 10.8, 6.3 Hz, 1H), 5.70 – 5.54 (m, 2H), 4.29 (app. t, *J* = 6.2 Hz, 2H), 4.12 – 3.85 (m, 4H), 1.84 (t, *J* = 6.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 128.2, 99.4, 65.1, 59.0 ppm.

HRMS (EI) calcd. for $C_6H_9O_3$ $[(M+H)-H_2]^+$ 129.0552; found 129.0540.

(*Z*)-tridec-2-enal (25)



25

1. (Table 6, entry 1) SiO_2 (310 mg), 5% aq. oxalic acid (31 mg) and (*Z*)-2-(dodec-1-en-1-yl)-1,3-dioxolane (30 mg, 0.13 mmol) were reacted according to general procedure 3. The product was obtained in quantitative yield (25 mg).

2. (Table 6, entry 2) SiO_2 (280 mg), 5% aq. oxalic acid (28 mg) and (*Z*)-1,1-diethoxytridec-2-ene (30 mg, 0.11 mmol) were reacted according to general procedure 3. The product was obtained in quantitative yield (22 mg).

3. (Table 6, entry 3) (*Z*)-2-(Dodec-1-en-1-yl)-1,3-dioxolane (30 mg, 0.13 mmol) and $LiBF_4$ (15 mg, 0.16 mmol) were reacted according to general procedure 4. The product was obtained in 95% yield (23 mg).

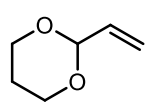
4. (Table 6, entry 4) (*Z*)-1,1-Diethoxytridec-2-ene (30 mg, 0.11 mmol) and $LiBF_4$ (14 mg, 0.14 mmol) were reacted according to general procedure 4. The product was obtained in 92% yield (20 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (d, *J* = 8.2 Hz, 1H), 6.64 (dt, *J* = 11.2, 8.2 Hz, 1H), 5.95 (ddt, *J* = 11.2, 8.2, 1.5 Hz, 1H), 2.65 – 2.55 (m, 2H), 1.56 – 1.44 (m, 2H), 1.41 – 1.17 (m, 14H), 0.87 (t, *J* = 7.0, 6.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 153.7, 130.3, 32.0, 29.7, 29.7, 29.5, 29.5, 29.3, 29.2, 28.2, 22.8, 14.3 ppm.

HRMS (FAB) calcd. for $C_{13}H_{25}O_2$ $[M+H]^+$ 197.1905; found 197.1888.

2-vinyl-1,3-dioxane (S1)

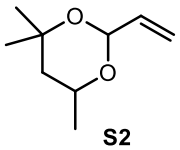


S1

Prepared as previously described.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 17.4, 10.7, 4.5 Hz, 1H), 5.46 (dt, *J* = 17.4, 1.3 Hz, 1H), 5.29 (dt, *J* = 10.7, 1.3 Hz, 1H), 4.96 (d, *J* = 4.5 Hz, 1H), 4.16 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.88 – 3.81 (m, 2H), 2.13 (dtt, *J* = 13.5, 12.4, 5.0 Hz, 1H), 1.37 (dtt, *J* = 13.5, 2.6, 1.4 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 118.6, 100.8, 67.1, 25.9 ppm.

4,4,6-trimethyl-2-vinyl-1,3-dioxane (S2)



S2

Prepared as previously described.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.4, 10.5, 5.0 Hz, 1H), 5.45 (d, *J* = 17.4 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.19 (d, *J* = 5.0 Hz, 1H), 3.99 – 3.89 (m, 1H), 1.51 – 1.37 (m, 2H), 1.33 (s, 3H), 1.27 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 118.6, 94.7, 72.2, 68.8, 43.5, 31.8, 22.4, 21.9 ppm.

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.
2. S. H. Wiedemann, R. G. Bergman and J. A. Ellman, *Org. Lett.*, 2004, **6**, 1685-1687.
3. C. Ikeda, R. Braun and B. Sorenson, *J. Org. Chem.*, 1964, **29**, 286-290.
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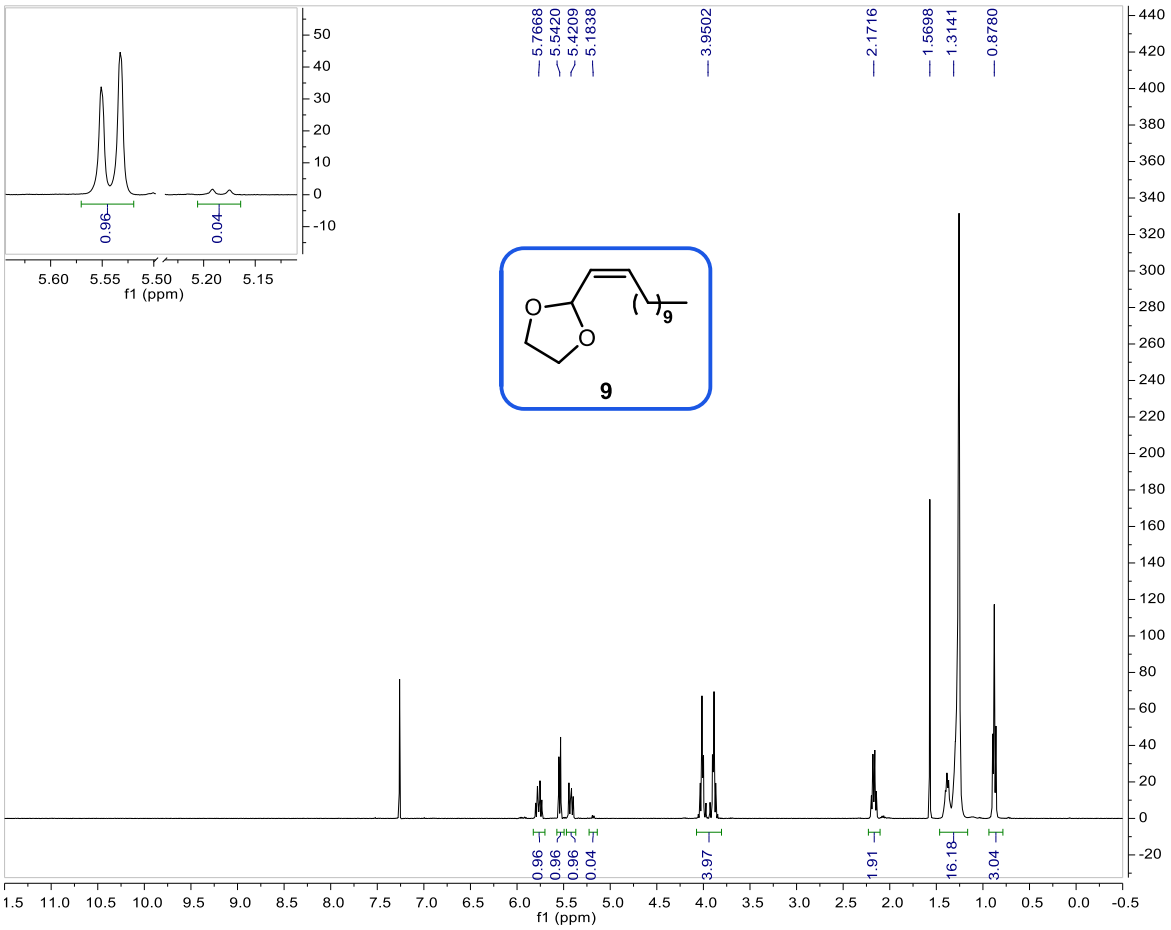
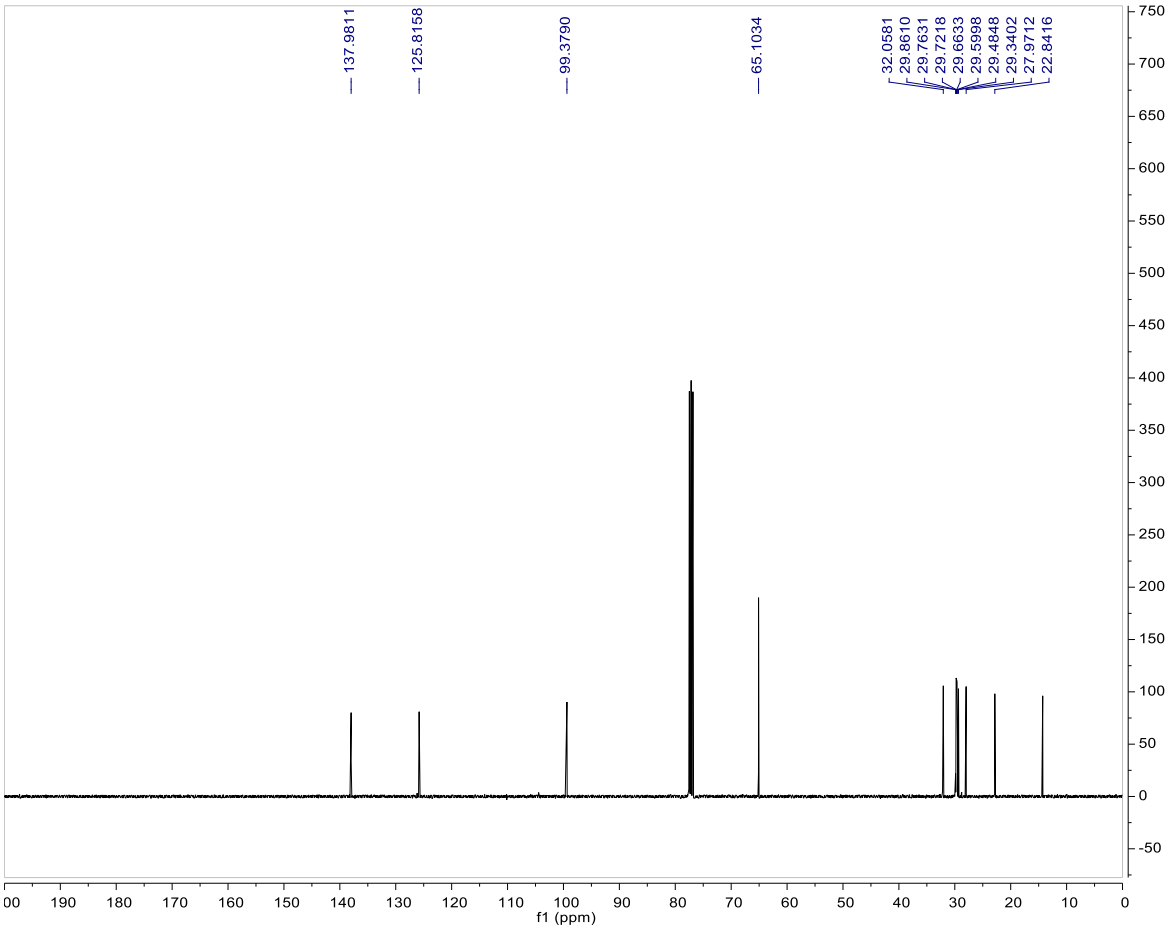
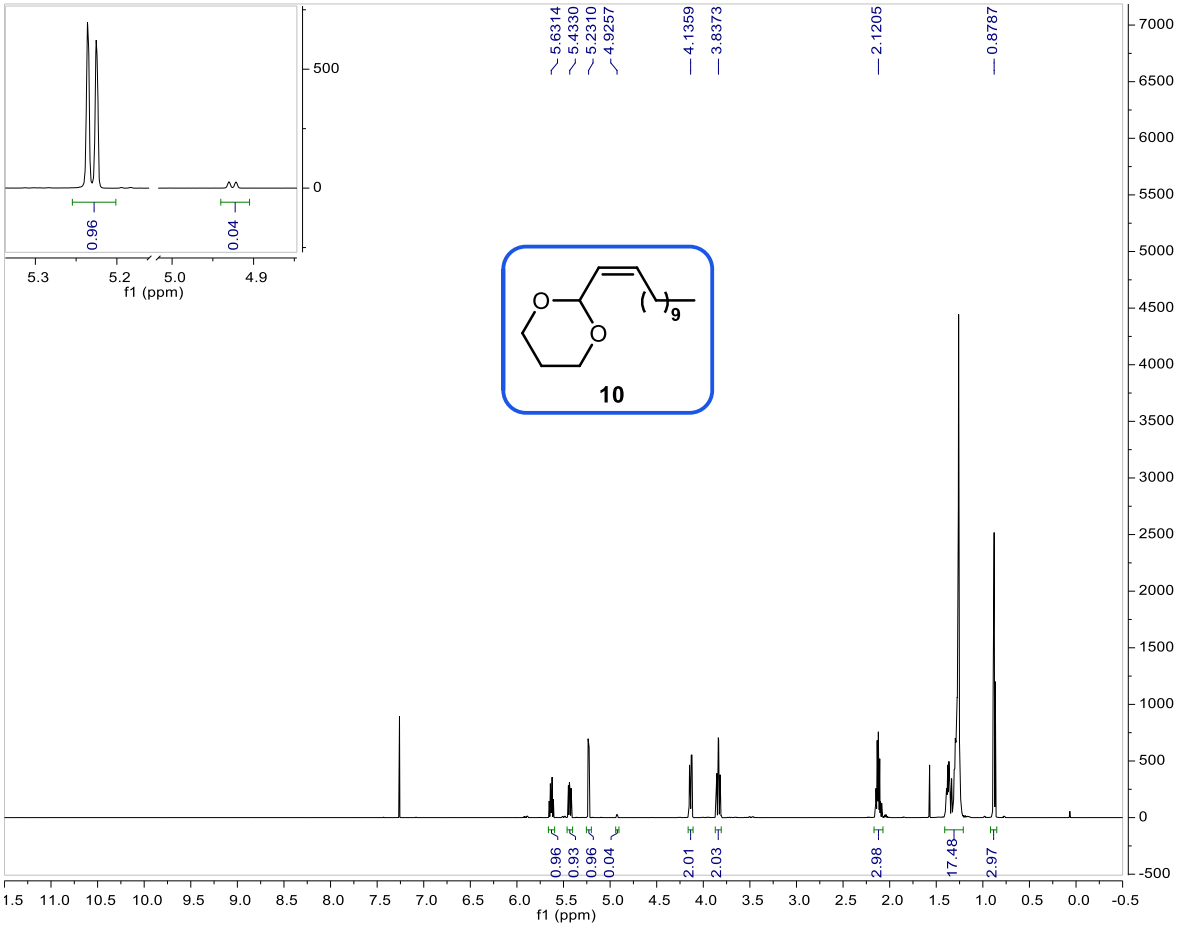
6. R. J. Ely and J. P. Morken, *J. Am. Chem. Soc.*, 2010, **132**, 2534-2535.

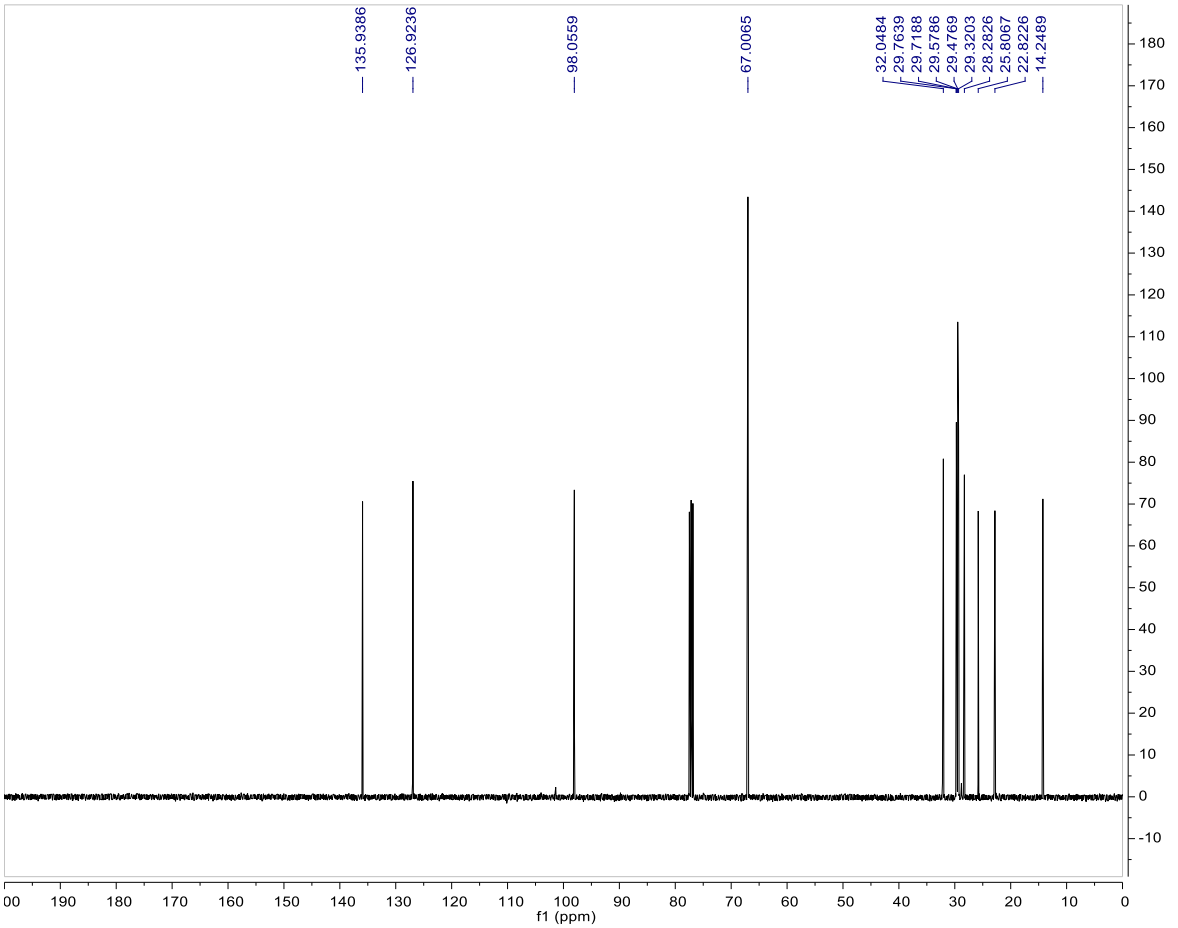
(Z)-2-(dodec-1-en-1-yl)-1,3-dioxolane (9) – ^{1}H and ^{13}C NMR spectra



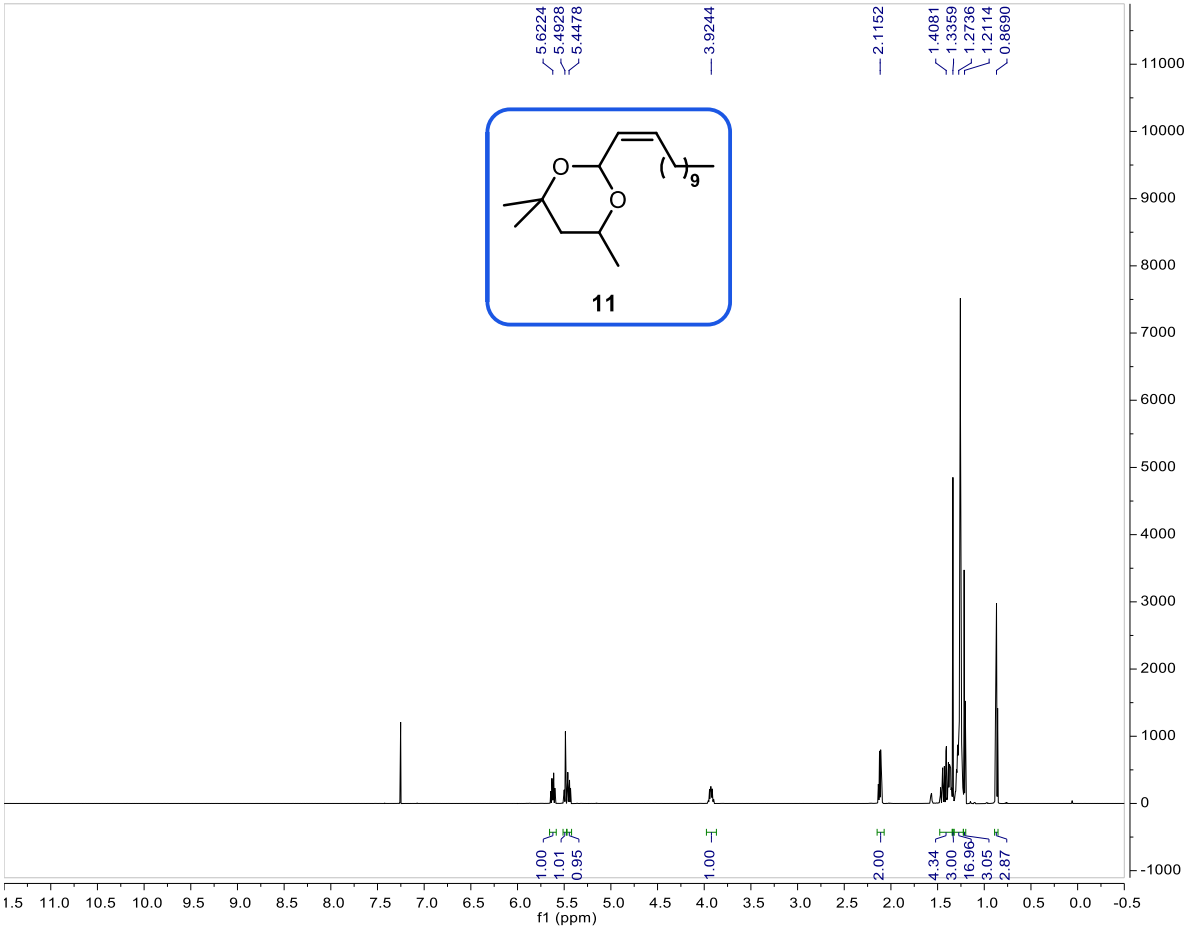


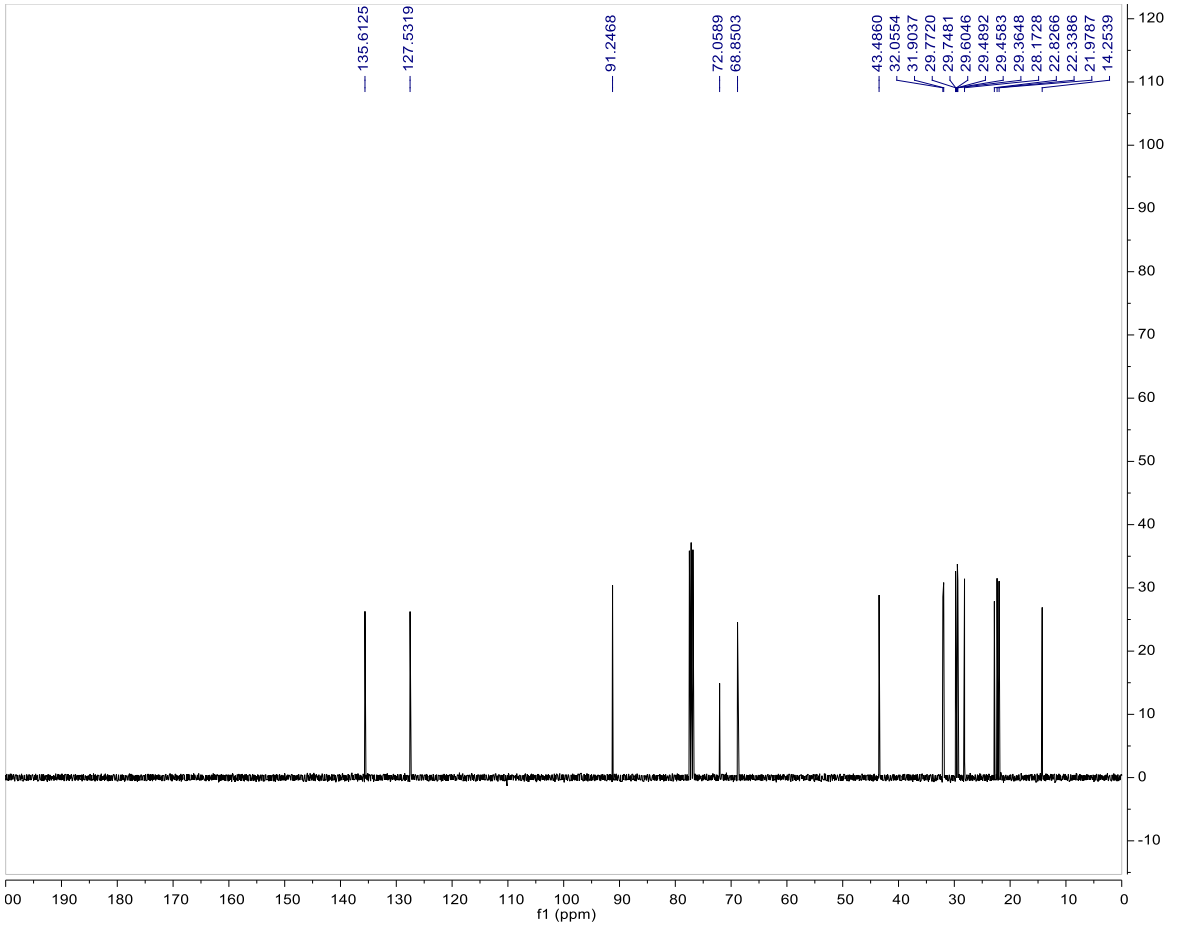
(Z)-2-(dodec-1-en-1-yl)-1,3-dioxane (10) – ^{1}H and ^{13}C NMR spectra



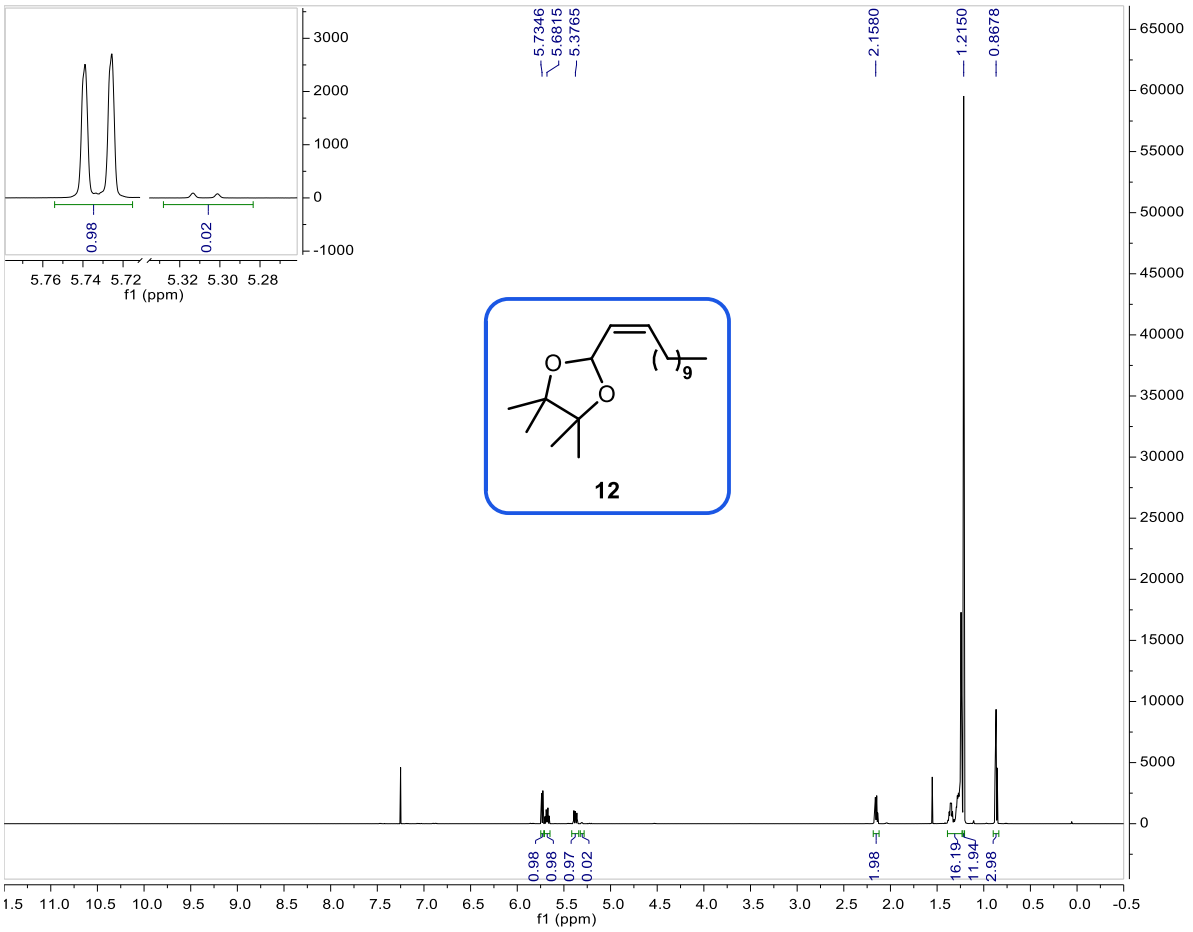


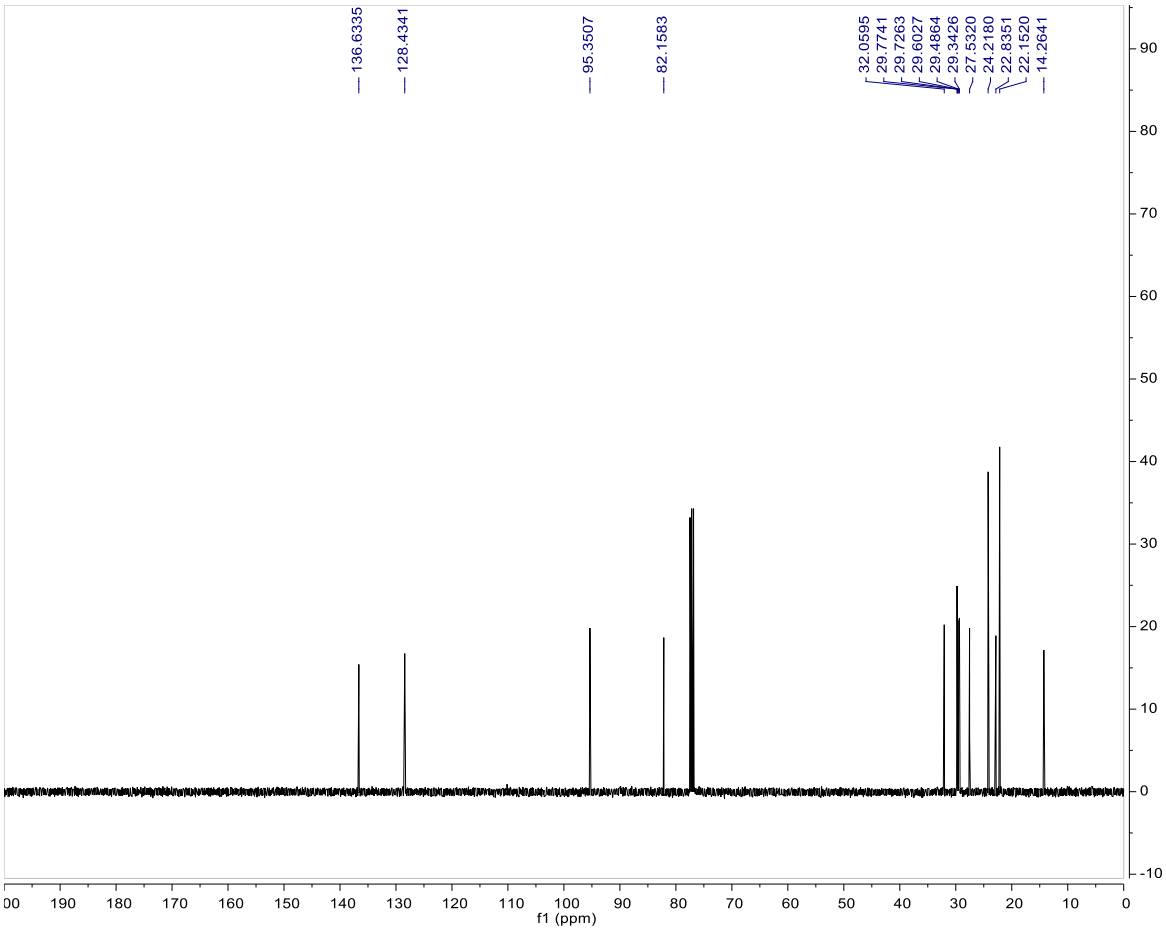
(*Z*)-2-(dodec-1-en-1-yl)-4,4,6-trimethyl-1,3-dioxane (11) – ^{1}H and ^{13}C NMR spectra



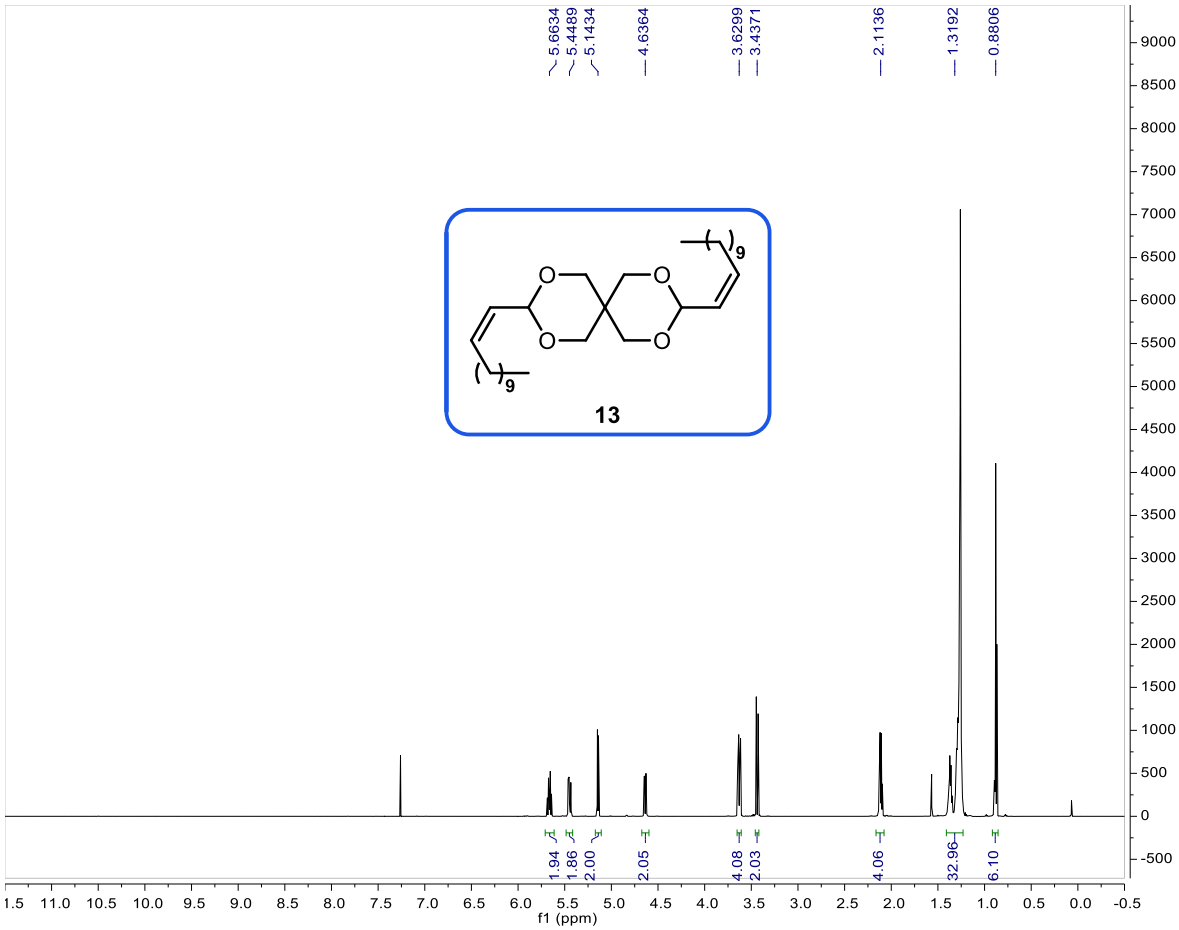


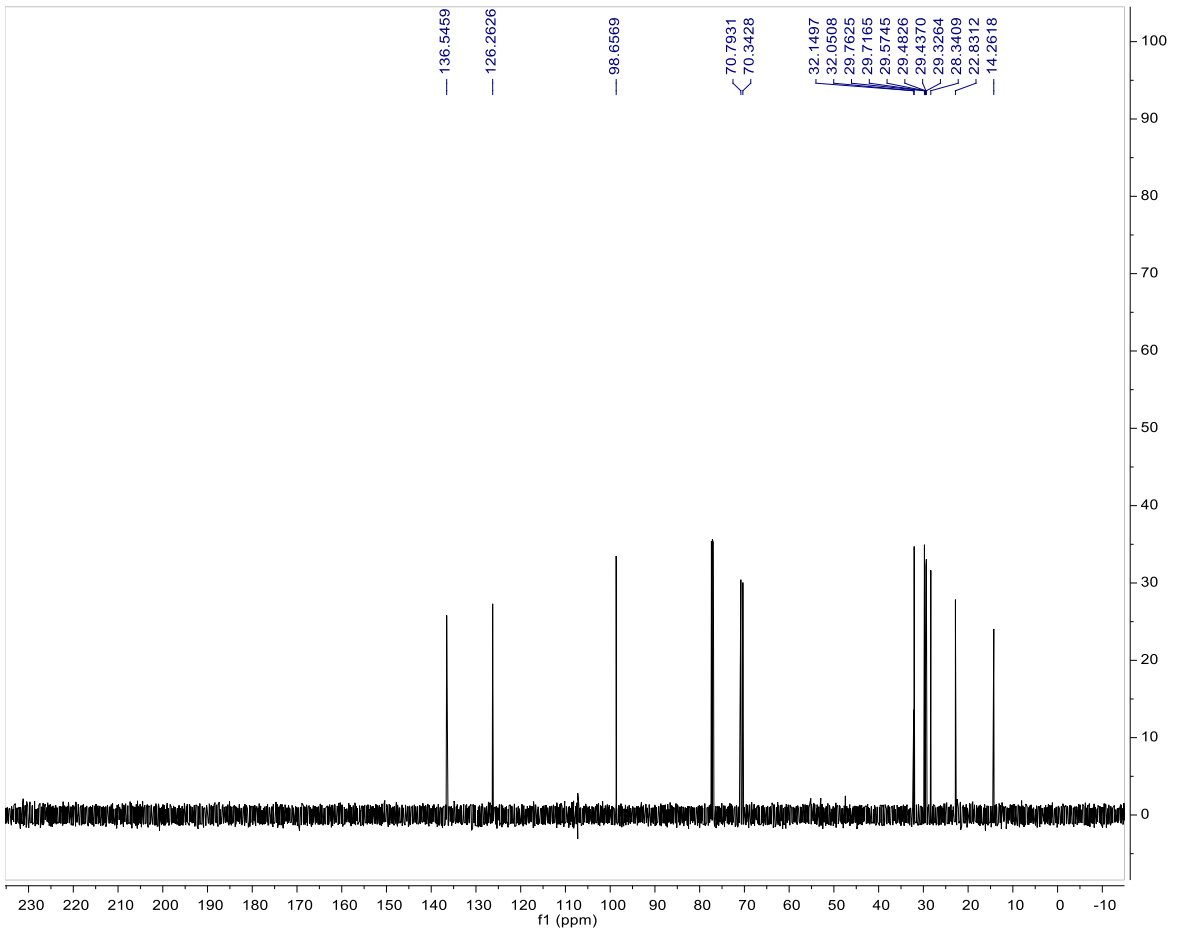
(*Z*)-2-(dodec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (12) – ^{1}H and ^{13}C NMR spectra



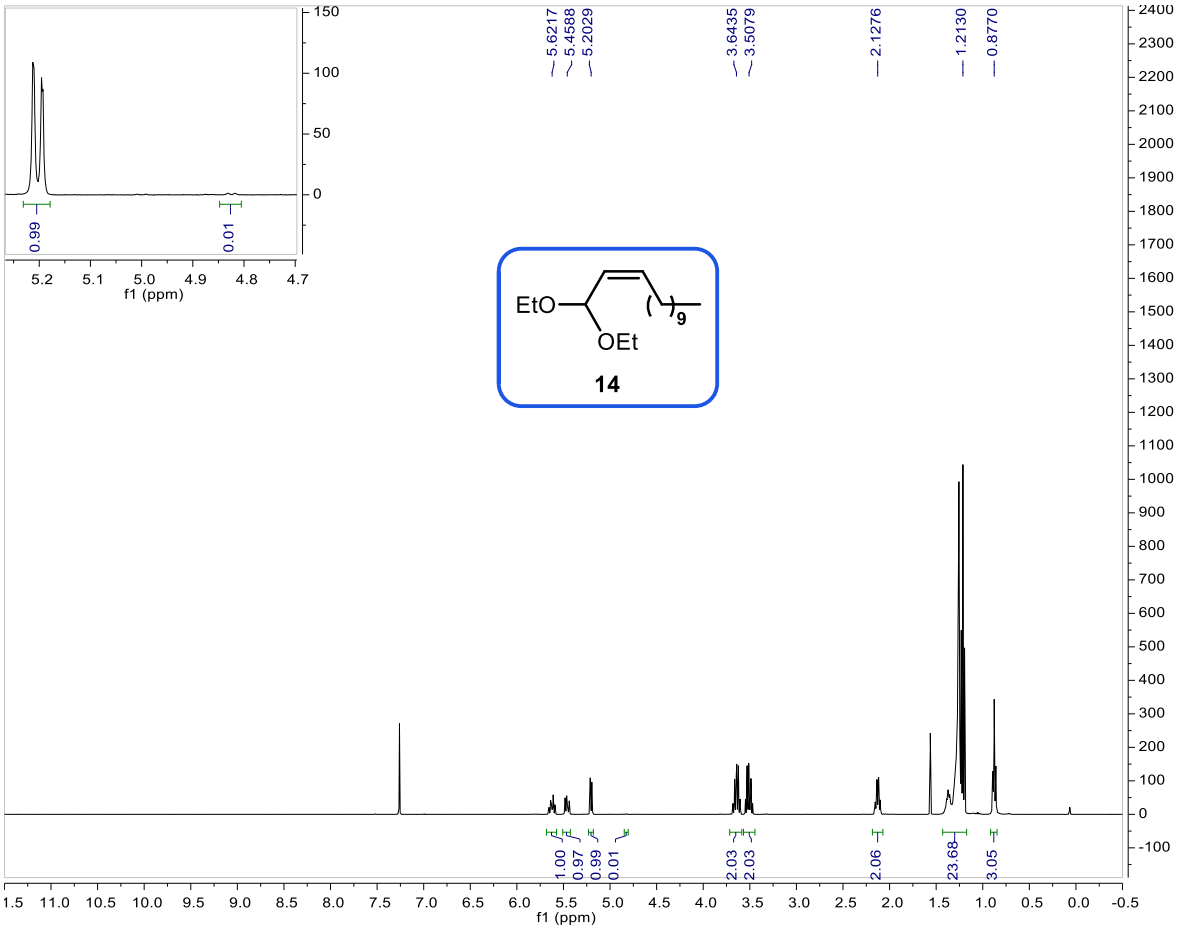


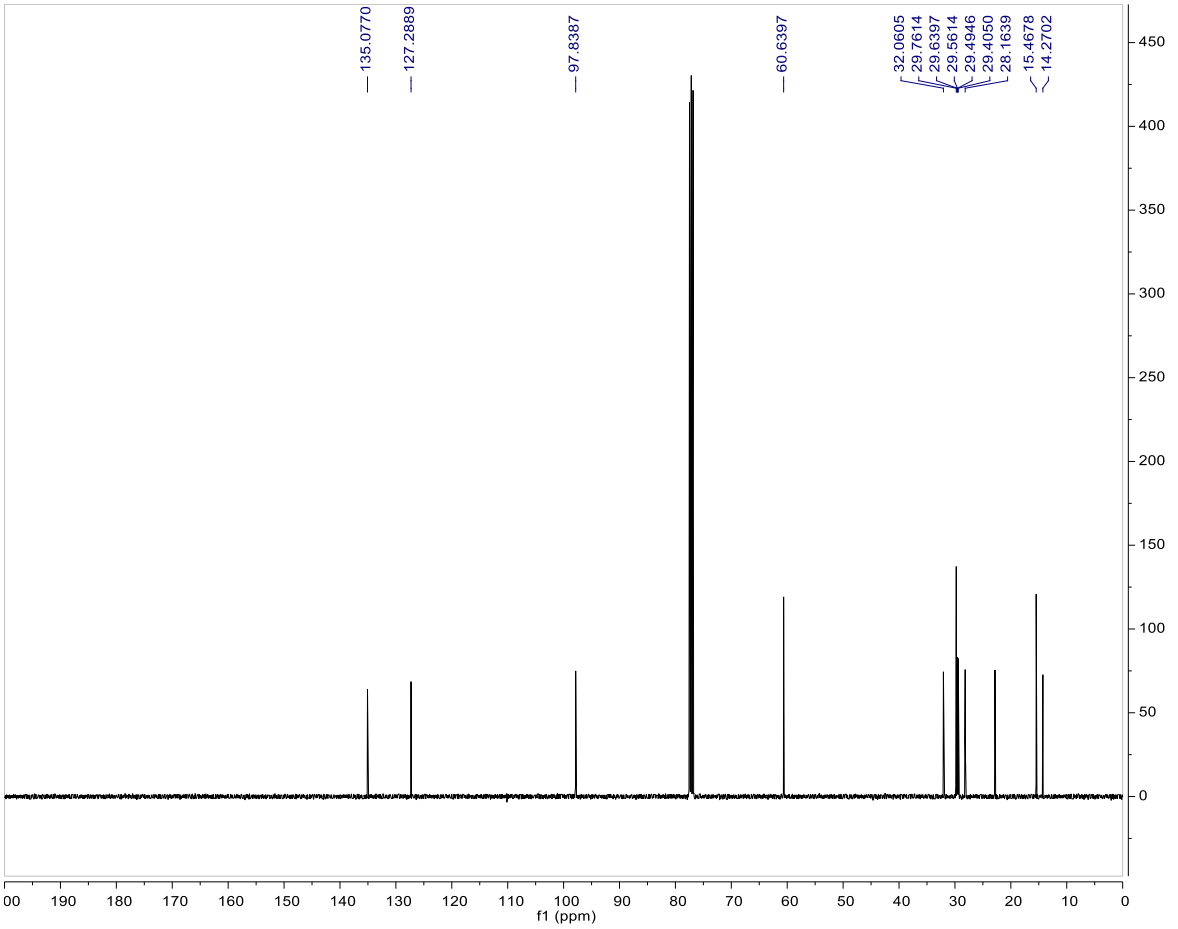
3,9-di((*Z*)-dodec-1-en-1-yl)-2,4,8,10-tetraoxaspiro[5.5]undecane (13) – ^{1}H and ^{13}C NMR spectra



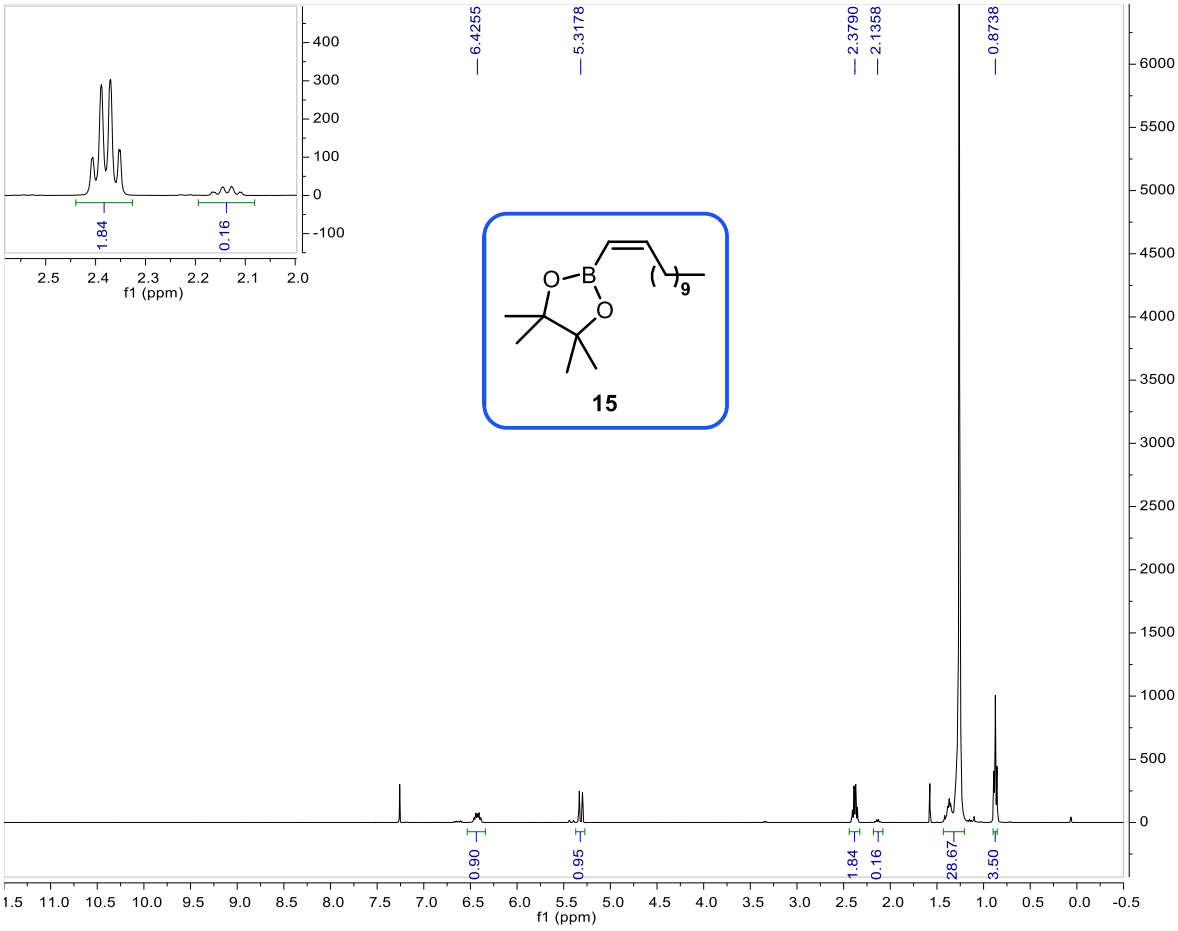


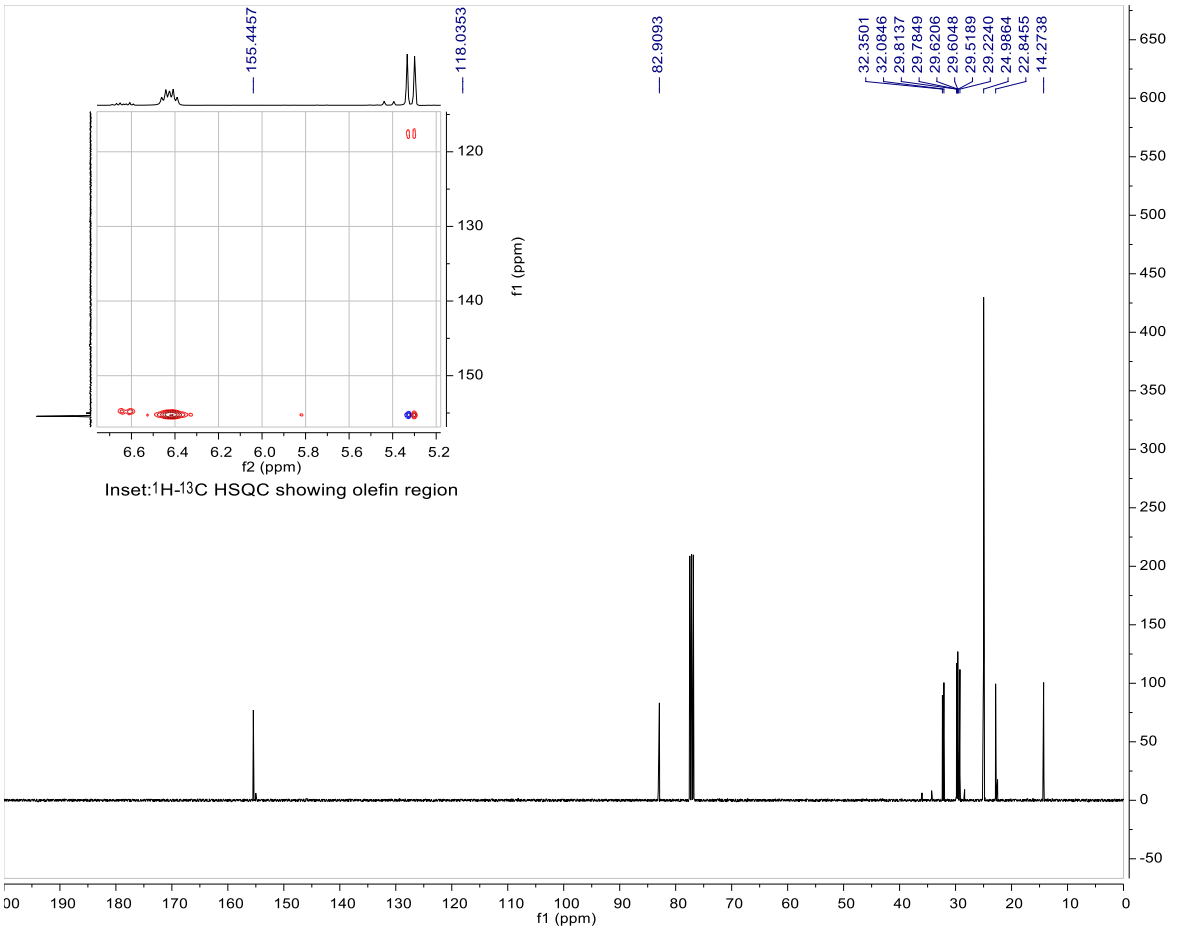
(*Z*)-1,1-diethoxytridec-2-ene (14) – ^{1}H and ^{13}C NMR spectra



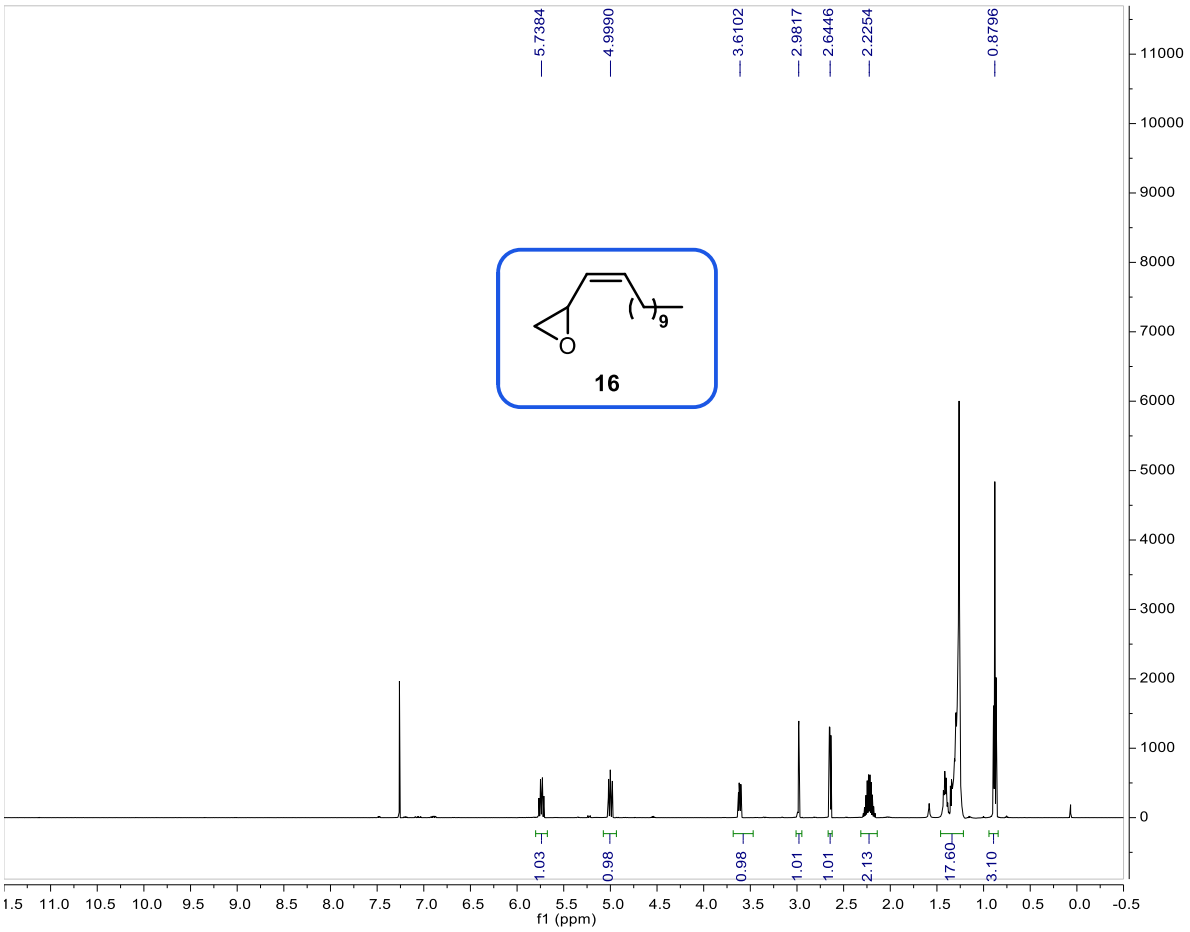


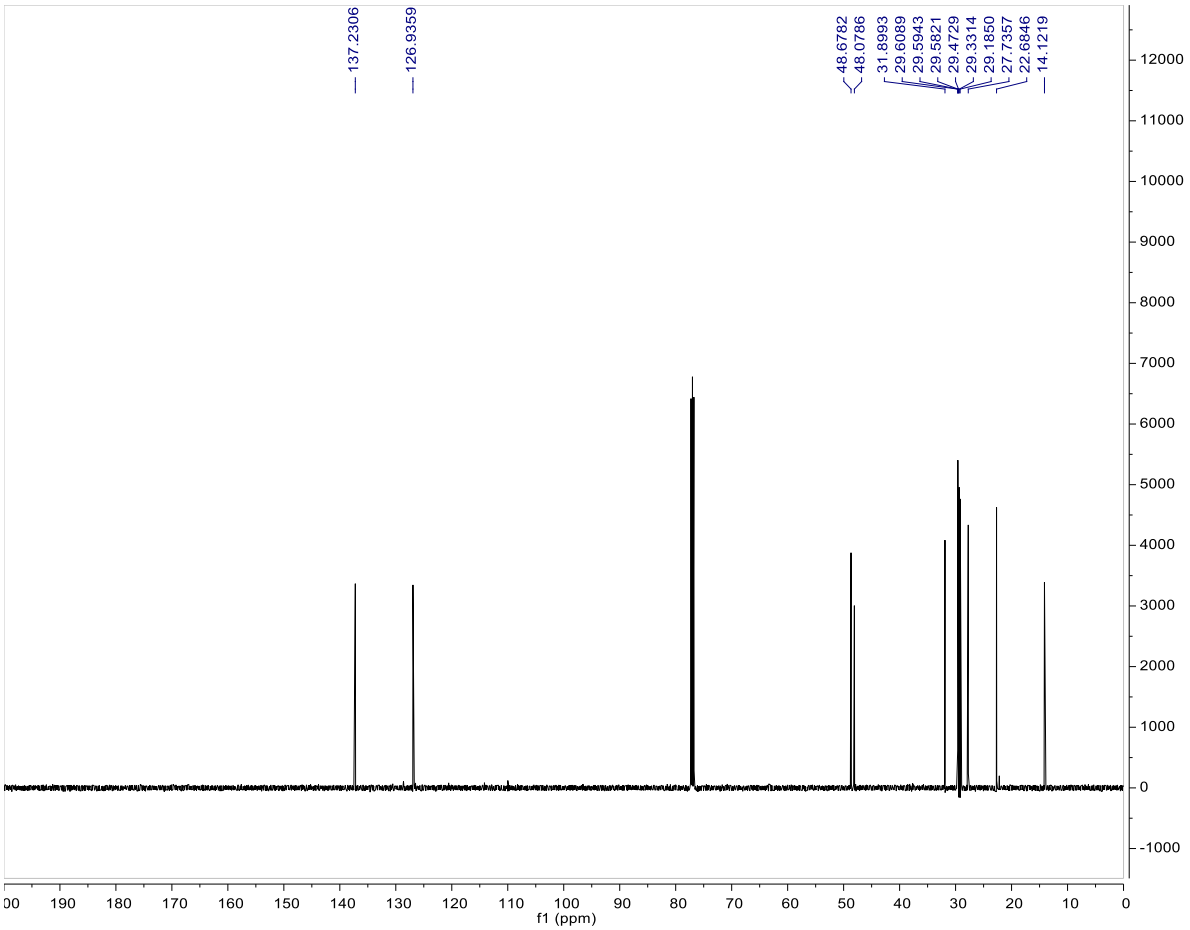
(*Z*)-2-(dodec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15) – ^{1}H and ^{13}C NMR spectra



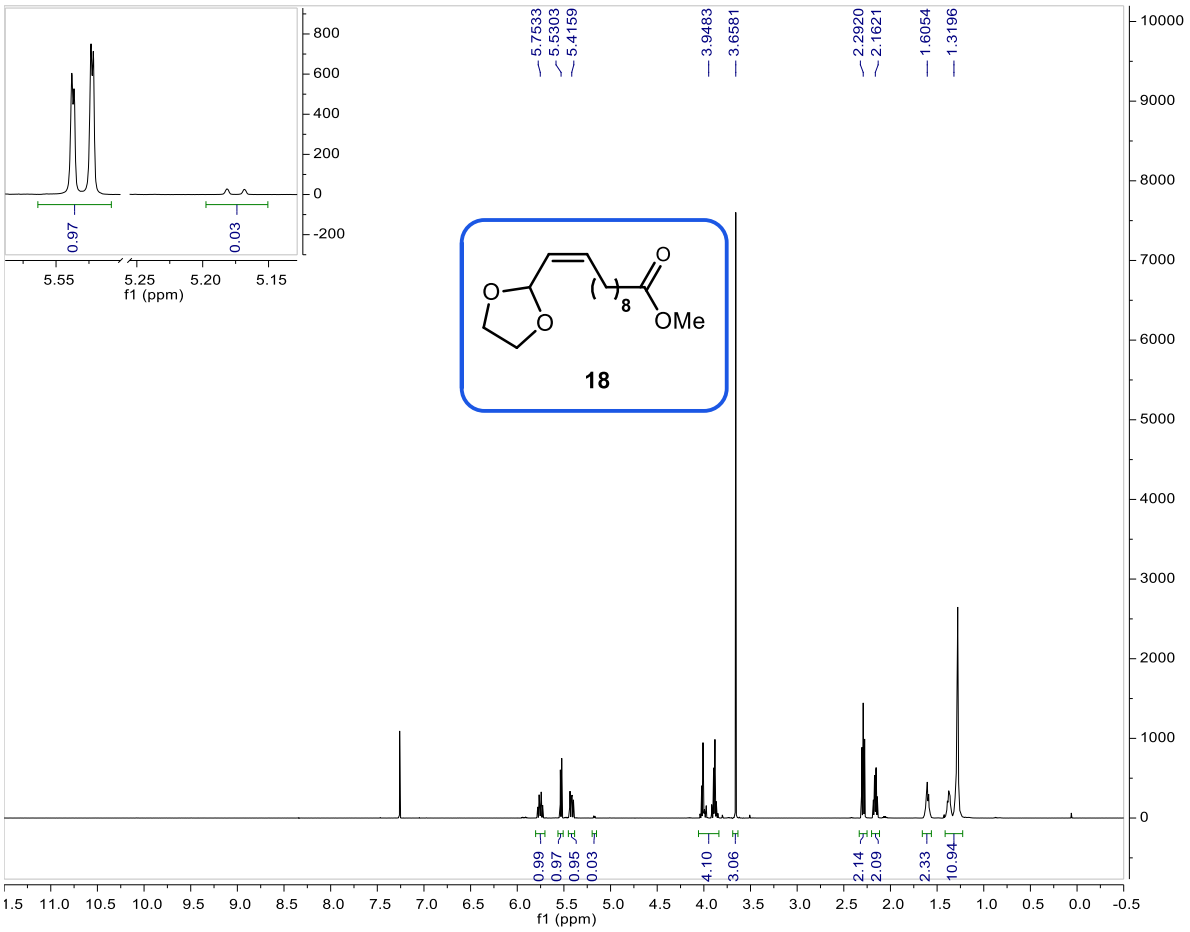


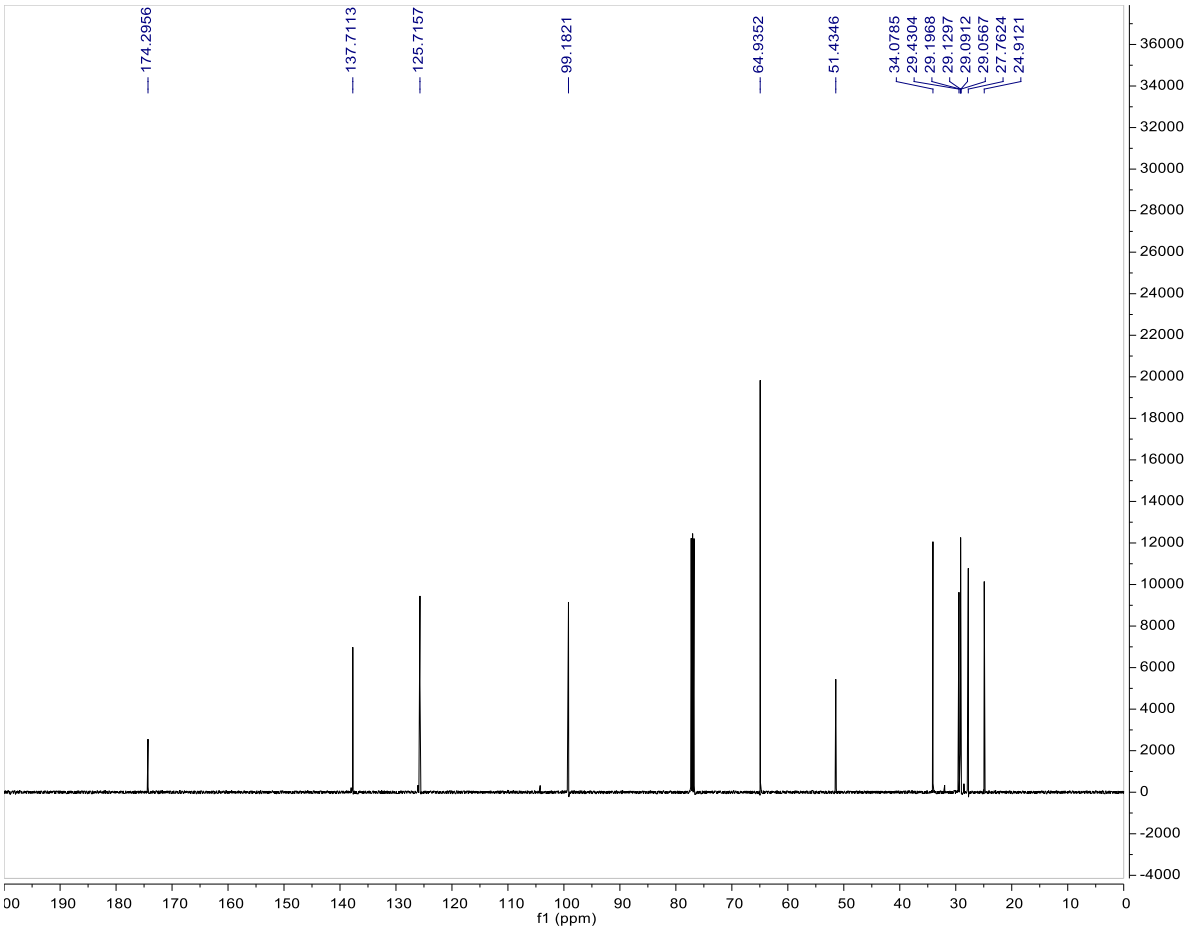
(*Z*)-2-(dodec-1-en-1-yl)oxirane (16) – ^{1}H and ^{13}C NMR spectra



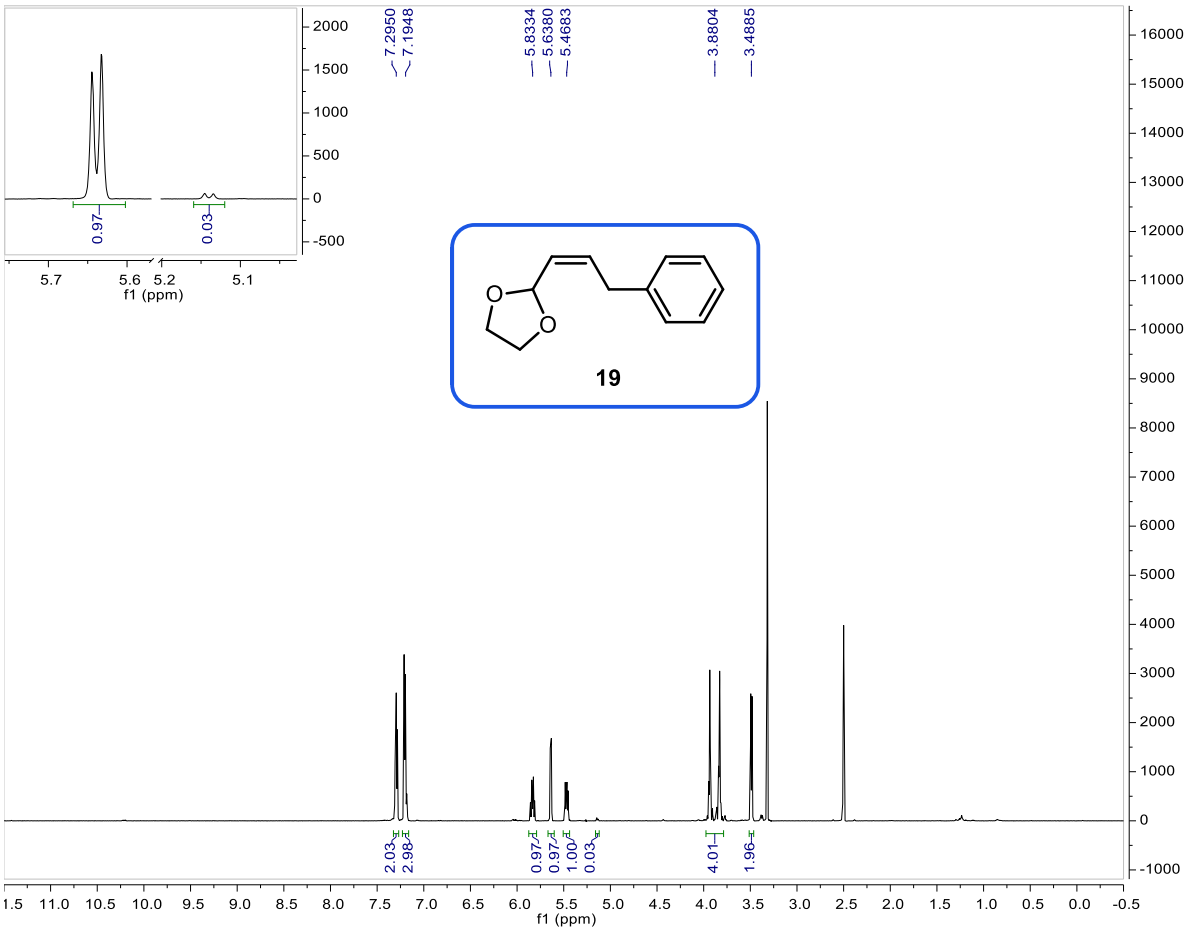


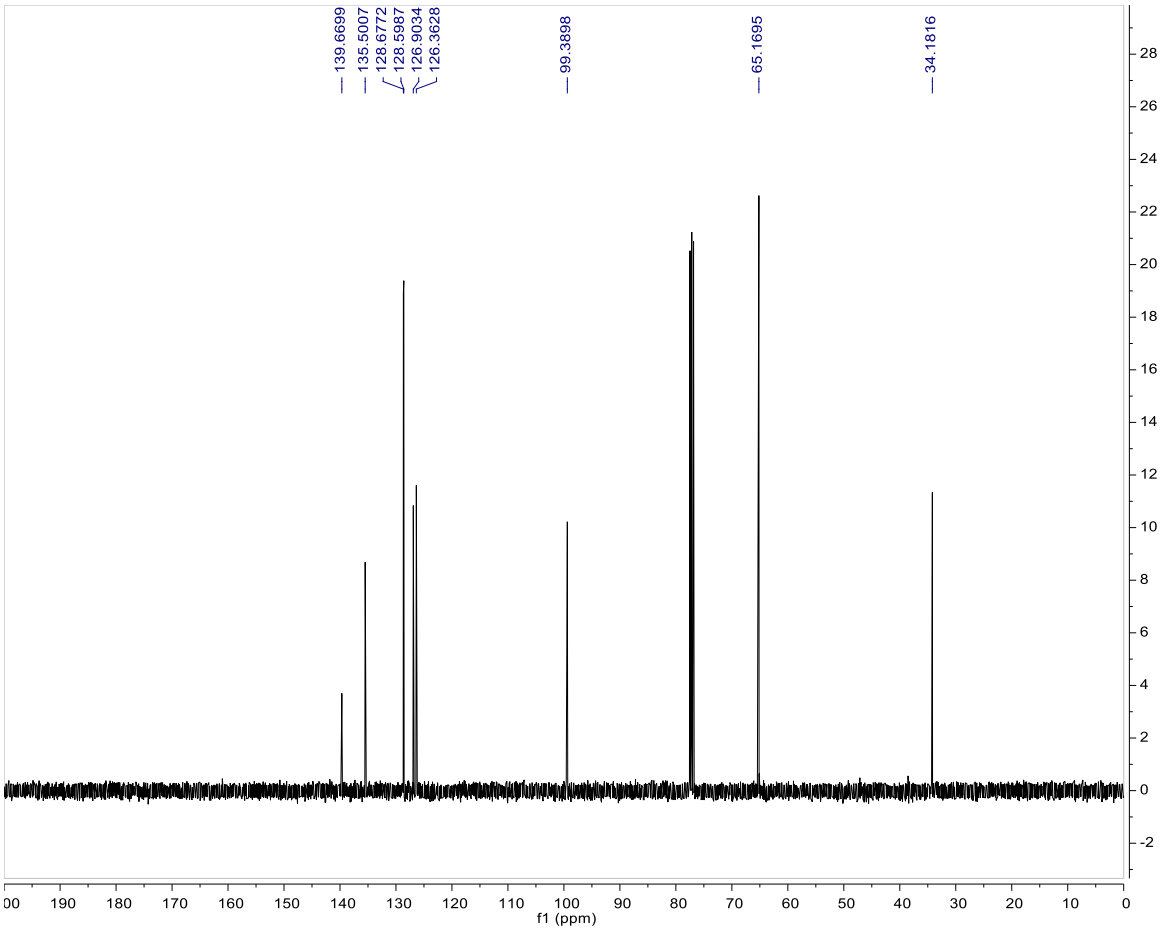
(*Z*)-methyl 11-(1,3 -dioxolan-2-yl)undec-10-enoate (18) – ^{1}H and ^{13}C NMR spectra



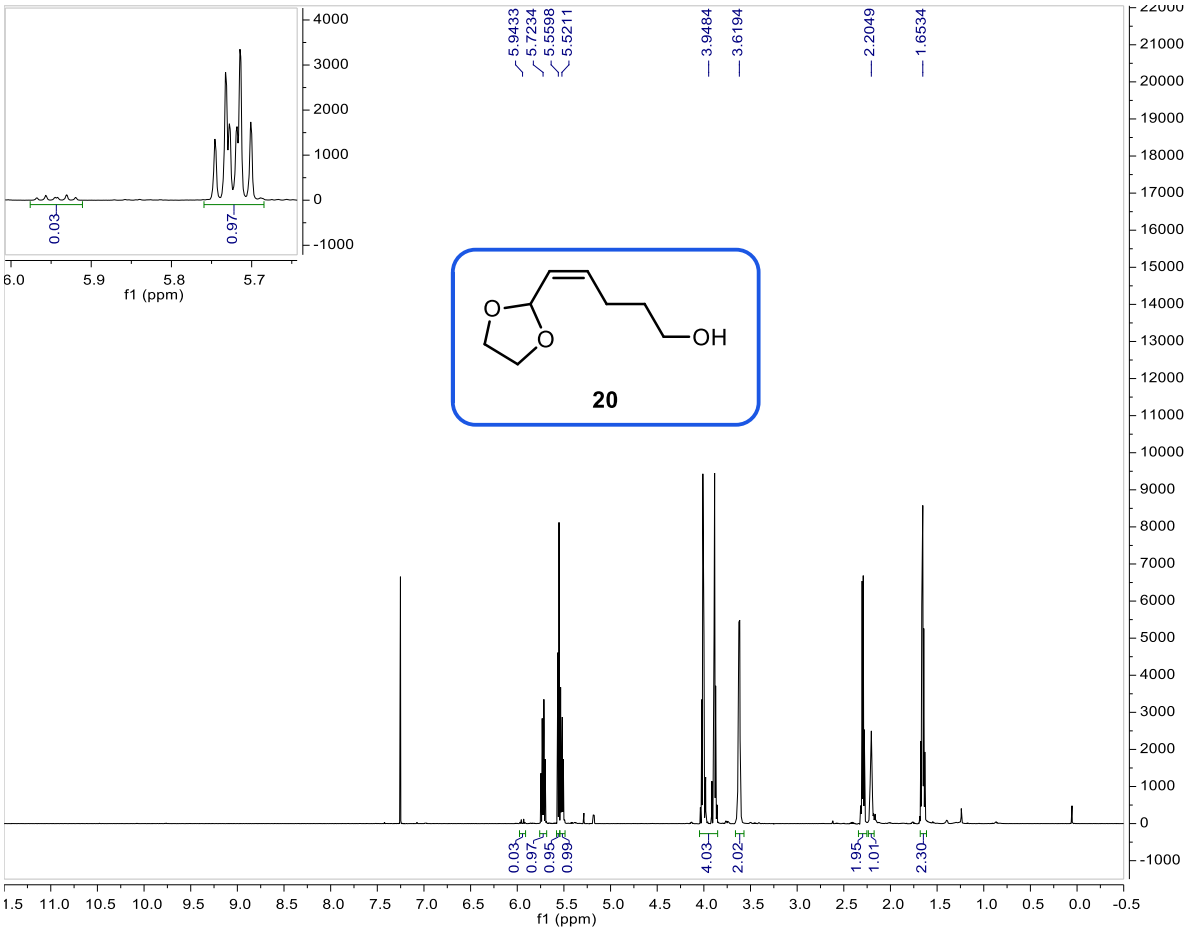


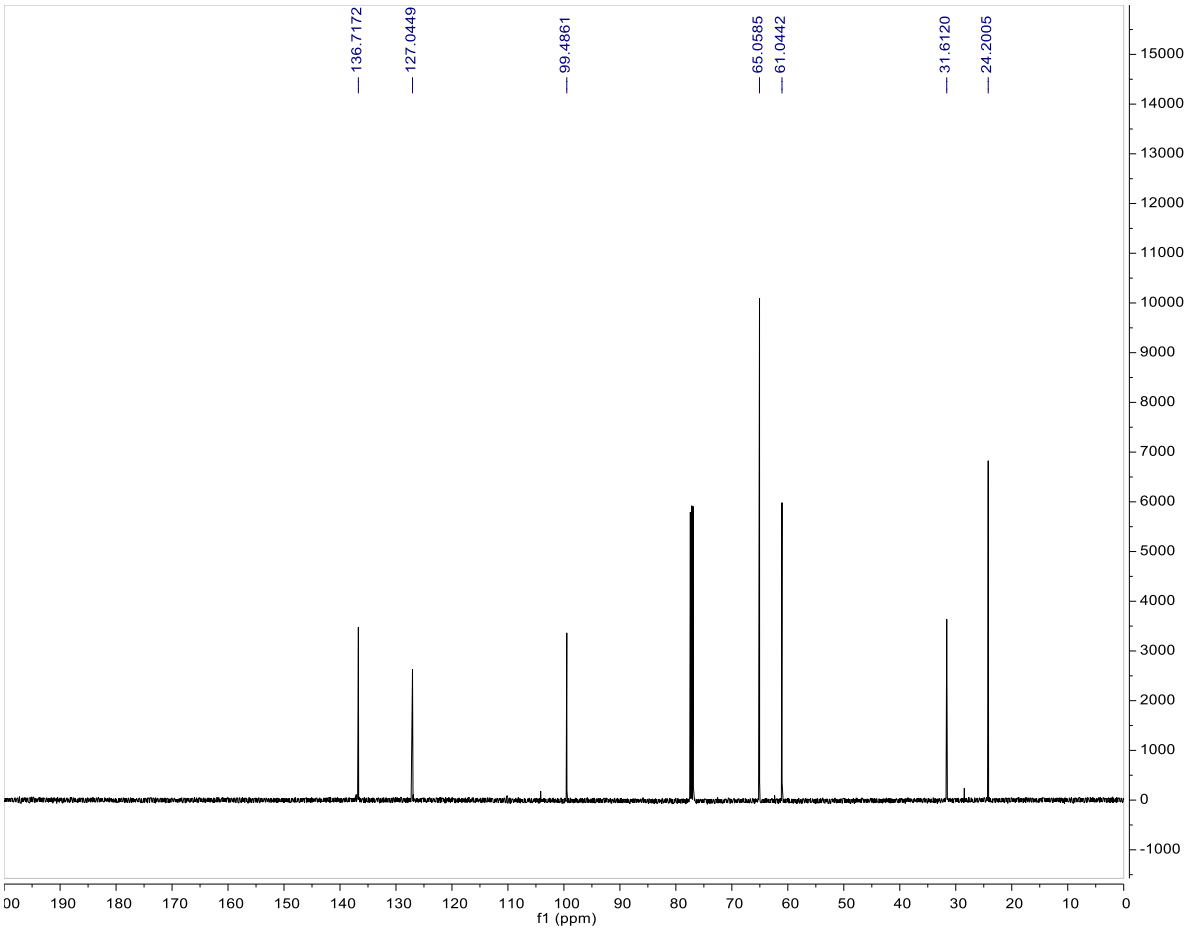
(*Z*)-2-(3-phenylprop-1-en-1-yl)-1,3-dioxolane (19) – ^{1}H and ^{13}C NMR spectra



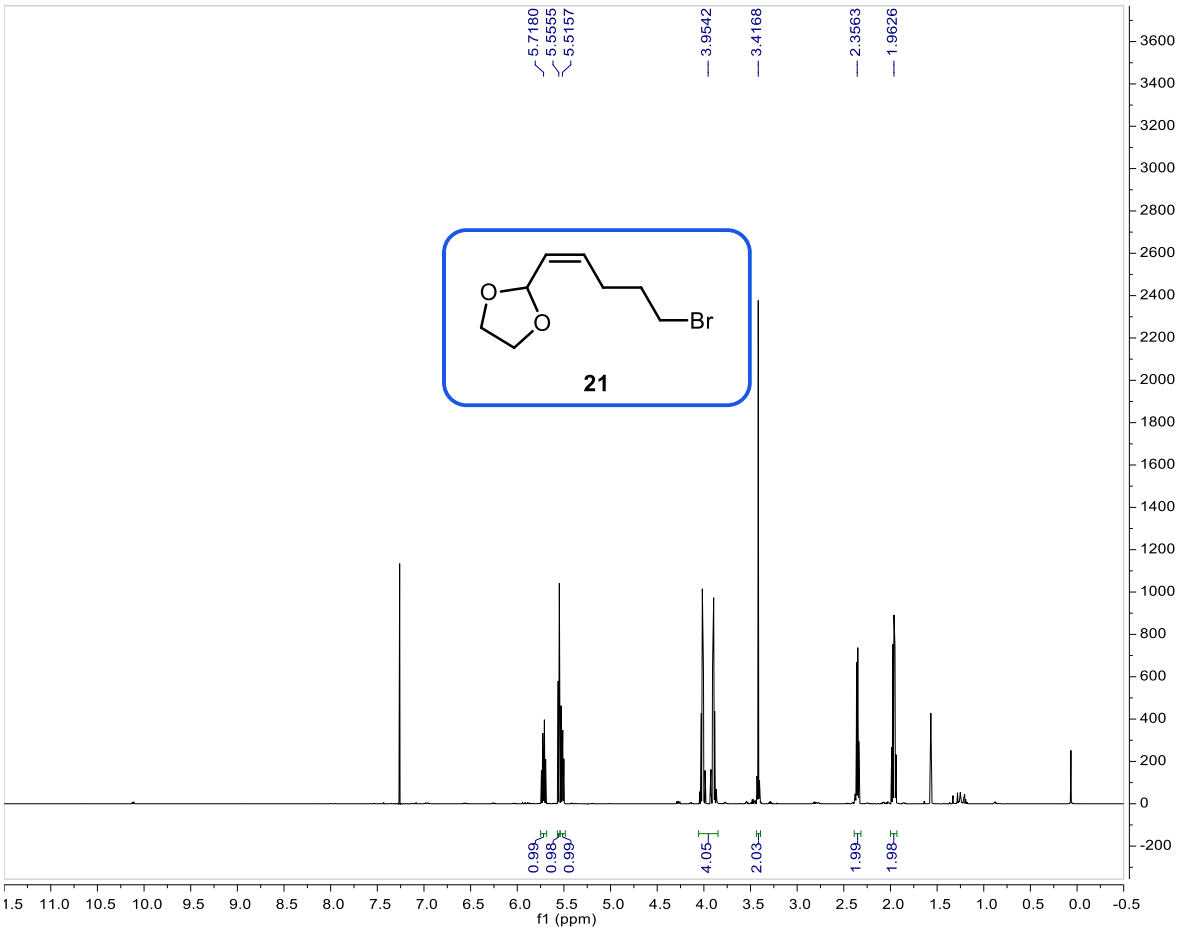


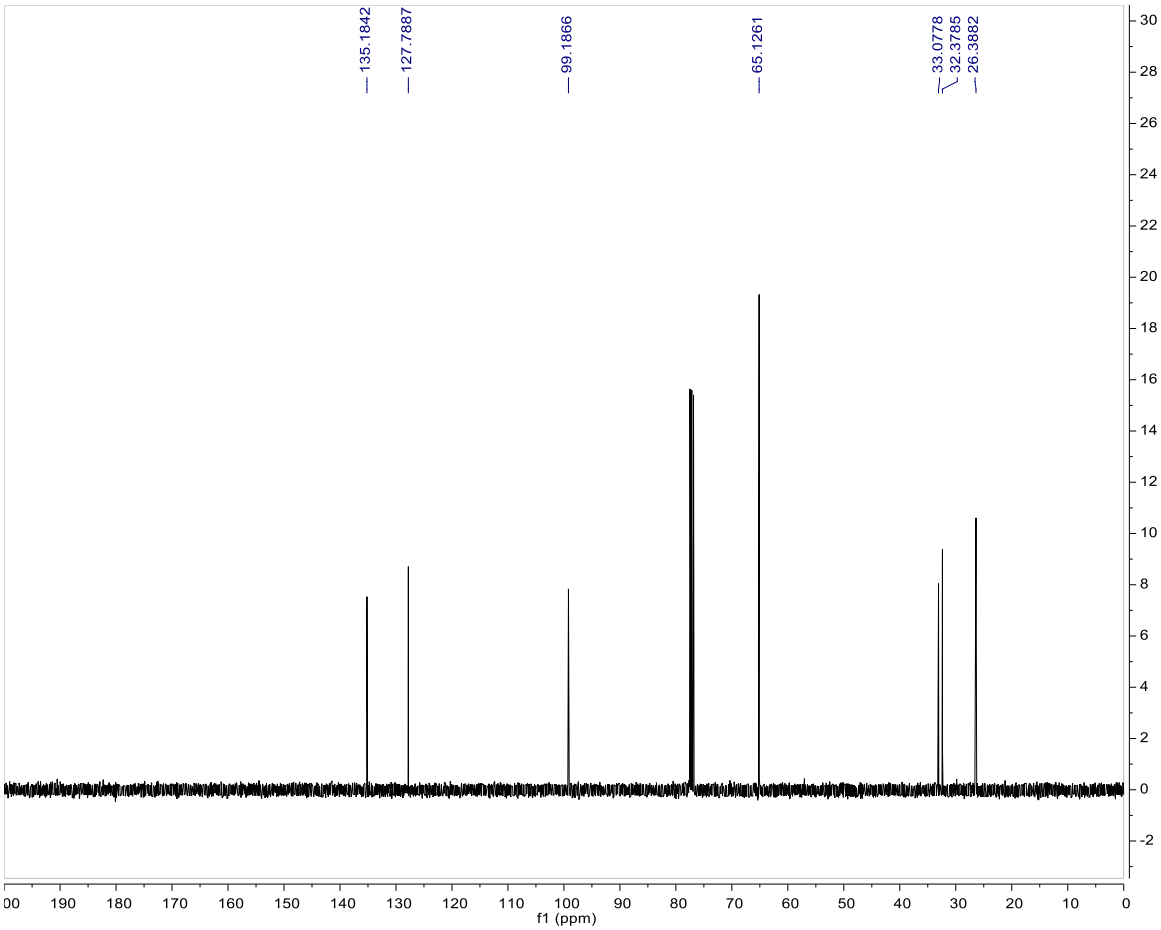
(*Z*)-5-(1,3-dioxolan-2-yl)pent-4-en-1-ol (20) – ^{1}H and ^{13}C NMR spectra



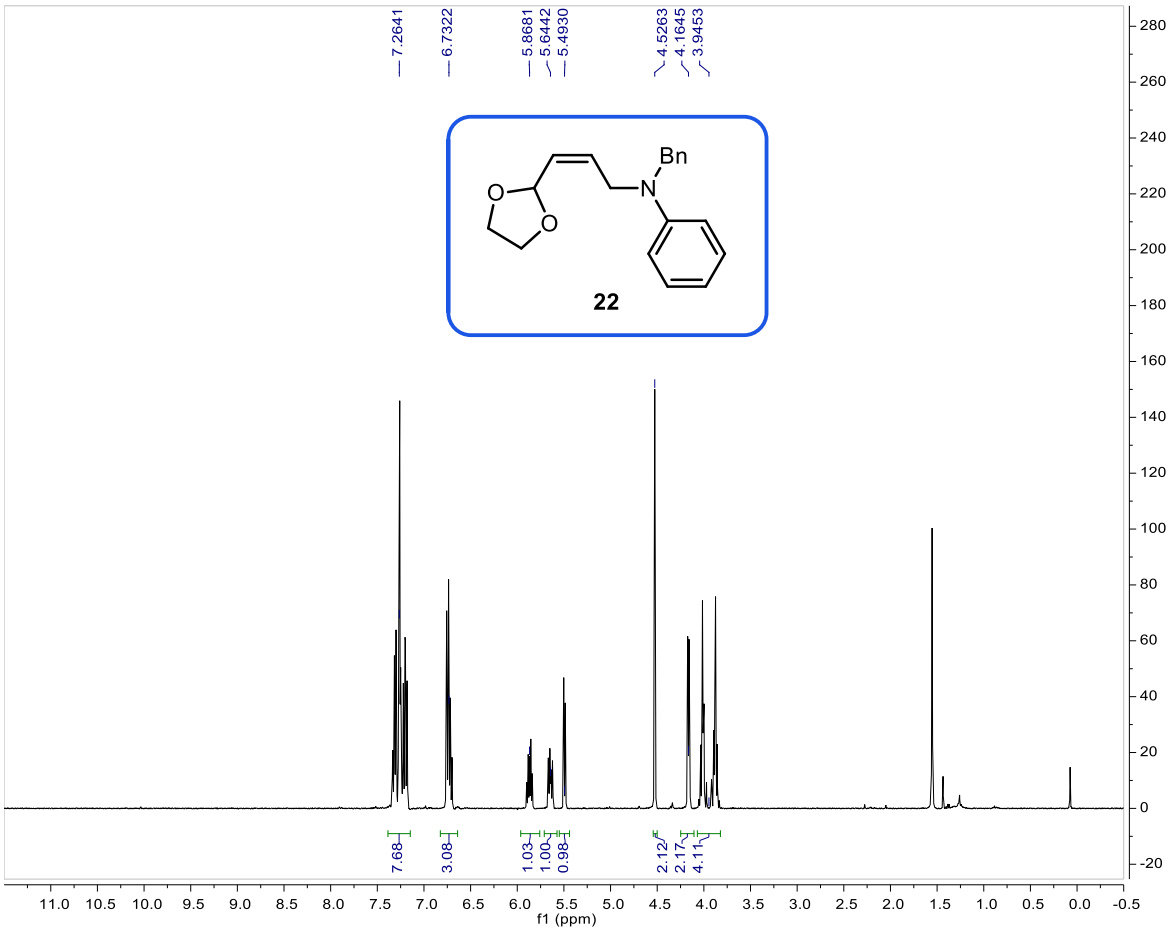


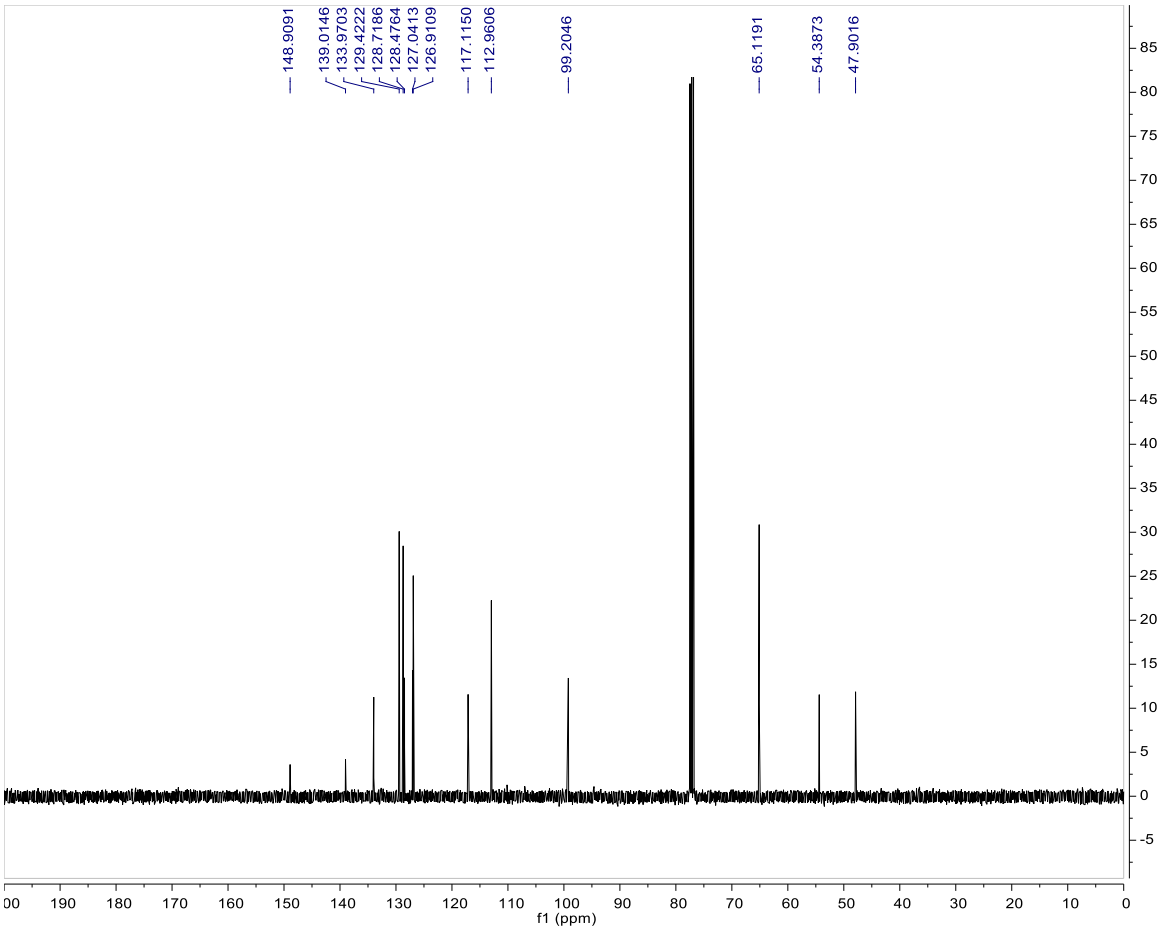
(*Z*)-2-(5-bromopent-1-en-1-yl)-1,3-dioxolane (21) – ^{1}H and ^{13}C NMR spectra



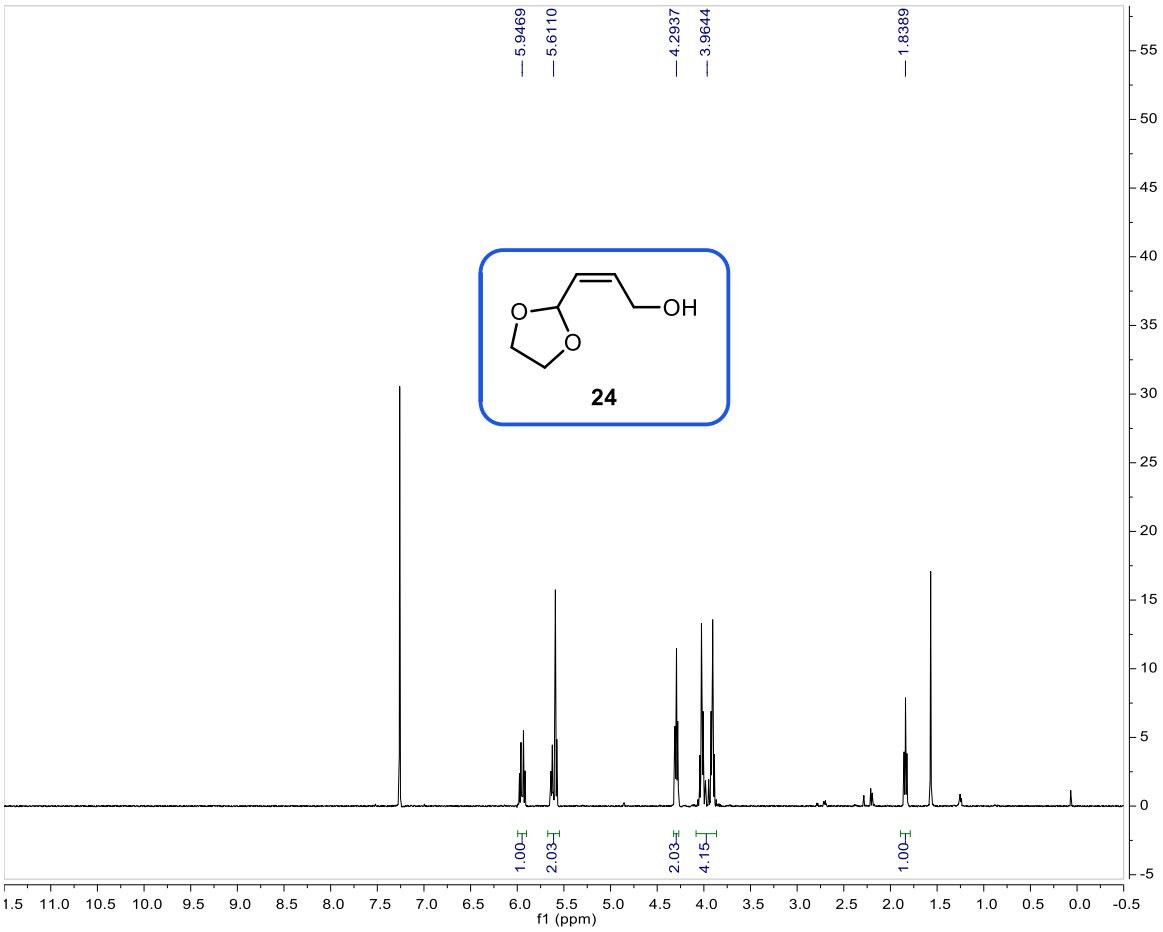


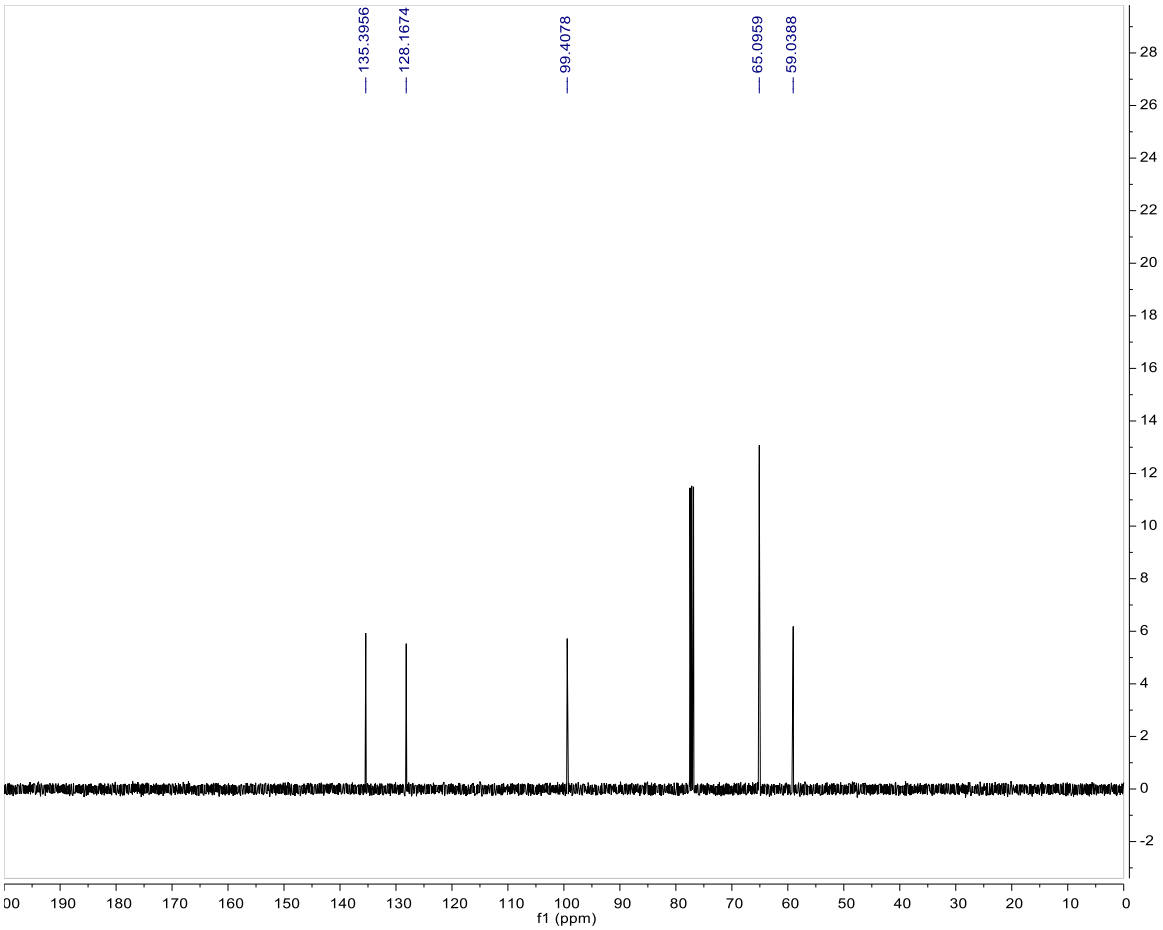
(*Z*)-*N*-(3-(1,3-dioxolan-2-yl)allyl)-*N*-benzylaniline (22) – ^{1}H and ^{13}C NMR spectra





(*Z*)-3-(1,3-dioxolan-2-yl)prop-2-en-1-ol (24) – ^{1}H and ^{13}C NMR spectra





(*Z*)-tridec-2-enal (25)