A Facile and Green Route to Terpene Derived Acrylate and Methacrylate Monomers and Simple Free Radical Polymerisation to Yield New Renewable Polymers and Coatings

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SUPPORTING INFORMATION

MONOMER SYNTHESIS AND CHARACTERISATION

Reagents source and analytical techniques

Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. All reactions were carried out in flame-dried glassware under Ar atmosphere. THF was distilled from Na/benzophenone immediately prior to use. DCM was dried over 4Å molecular sieves prior to use. Methyl-tetrahydrofuran was purchased from Aldrich over 4Å molecular sieves. Column chromatography was carried out either manually on silica gel Fluka 60 or on a Biotage® SP4 using Biotage® SNAP KP-Sil cartridges and petroleum ether (40-60°C)/ethyl acetate as eluent, whilst monitoring by UV (254 nm) and thin layer chromatography (PMA stain). All NMR spectra were obtained in $CDCl_3$ at room temperature using Bruker® DPX300, Bruker® AV400 spectrometers for which chemical shifts are expressed in ppm relative to the solvent and coupling constants are expressed in Hz. Infrared spectroscopic data were recorded using a Bruker® Tensor27 FTIR spectrometer. Mass spectral data (and HRMS) were obtained using a Bruker® MicroTOF spectrometer. Optical rotations were measured on an ADP440 Polarimeter. Melting points were measured on a Gallenkamp® apparatus.

Sigma Aldrich

Me-THF, $BH_3.SMe_2$ (2M in THF), triethylamine, propylphosphonic anhydride (T3P®) solution (50 wt. % in enthyl acetate), palladium(II) acetate, 98%

ALFA AESAR (VWR Intl Ltd)

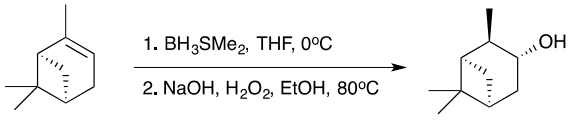
9-BBN (0.5M in THF), acryloyl chloride, methacryloyl chloride, (1*S*)-(−)-β-pinene, 99%, (1*R*)-(+)-α-pinene, 99%, 80%ee

ACROS ORGANICS (Fisher Scientific UK Ltd.)

Acrylic acid, methacrylic acid, *R*-(+)-limonene, 96%, *L*-(−)-carvone, 99%, 1,4-benzoquinone, 99%

Synthesis of hydroxylated terpene derivatives

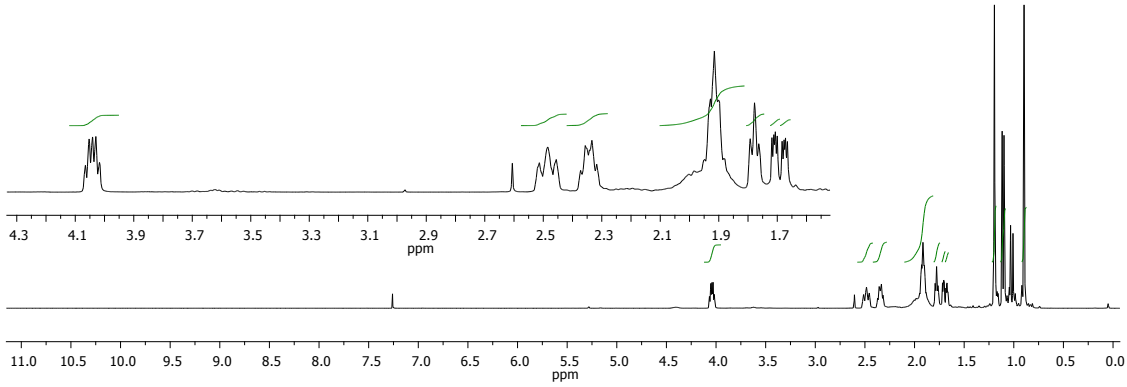
(1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-ol (1a)

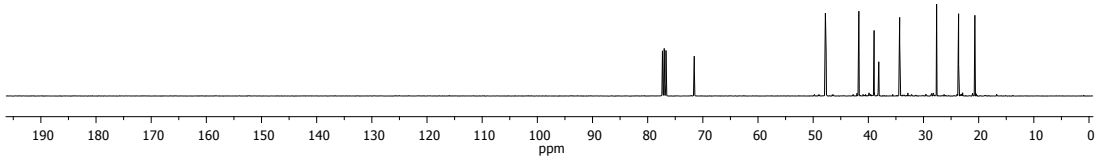


To a cold solution (0ºC) of α-pinene (5.8 mL, 37.0 mmol) in THF (14 mL) BH_3*SMe_2 (27.5 mL, 55.0 mmol, 2M in THF) was added dropwise and the mixture was stirred at 0ºC for 1 hour. After that time, keeping the solution at 0ºC EtOH (18 mL), NaOH (20 mL, 1M in H_2O) and H_2O_2 (9 mL, 30% v/v in H_2O) were added subsequently in a drop wise manner. The resulting mixture was stirred for 1 hour warming to room temperature and additionally two hours at 80ºC. The reaction was then allowed to cool before quenching by addition of a saturated aqueous solution

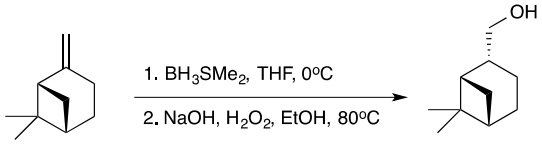
of NH_4Cl. Aqueous layer was extracted with Et_2O (3x). Combined organic layers were washed with brine, dried and solvent was evaporated to yield 4.95 g (87% yield) of (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-ol as a colourless oil that becomes solid after storing at low temperature. Stereochemical assignment based on literature precedent.[1]

$[\alpha]_D^{22}$ -1.4 (c 3.4, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 4.1-4.0 (m, 1H), 2.49 (dd, *J* = 15.8, 7.4 Hz, 1H), 2.35 (dt, *J* = 9.7, 6.4 Hz, 1H), 2.0-1.9 (m, 4H), 1.78 (t, *J* = 5.9 Hz, 1H), 1.69 (ddd, *J* = 13.9, 4.7, 2.6 Hz, 1H), 1.20 (s, 3H), 1.11 (d, *J* = 7.4 Hz, 3H), 0.90 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 71.6 (d), 47.8 (d), 47.7 (d), 41.7 (d), 39.0 (t), 38.1 (s), 34.3 (t), 27.6 (q), 23.6 (q), 20.7 (q). **HRMS (ESI-MS)**: calcd. for $C_{10}H_{18}NaO$: 177.1250, found: 177.1248.





((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)methanol (2a)

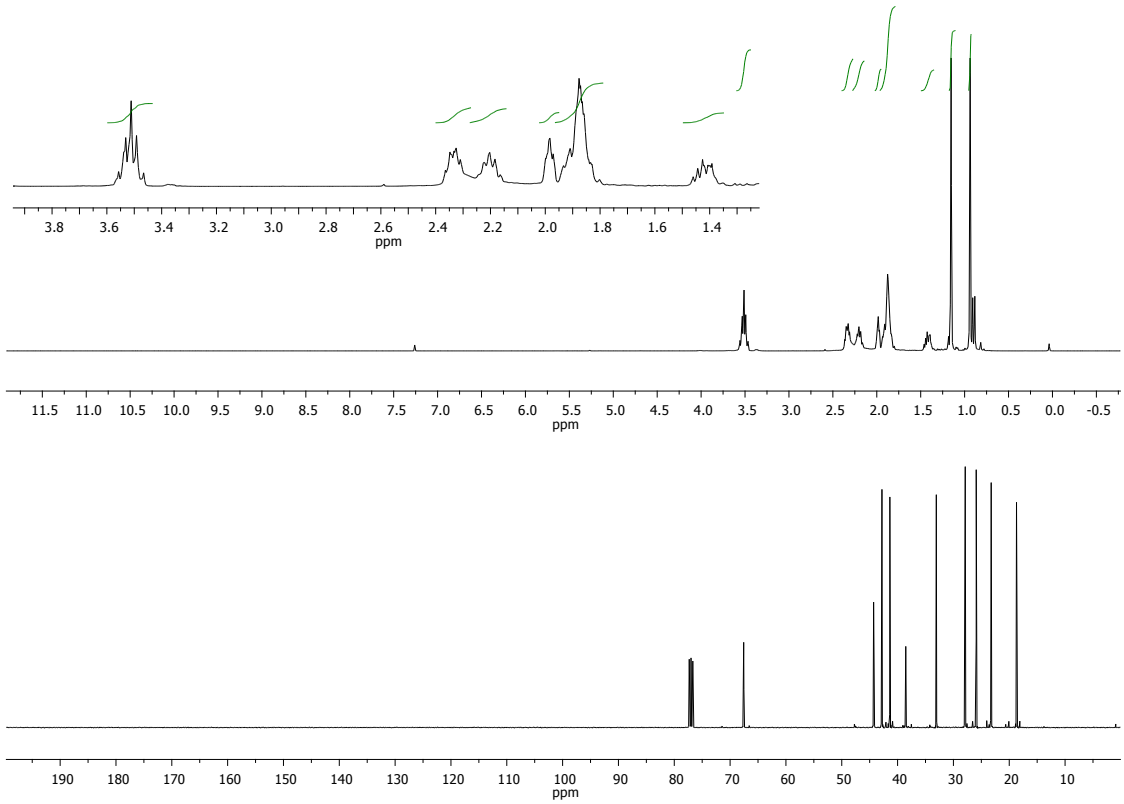


To a cold solution (0ºC) of 1S-(−)-β-pinene (24 mL, 148 mmol) in THF (56 mL), BH_3*SMe_2 (74 mL, 148 mmol, 2M in THF) was added dropwise and the mixture was stirred at 0ºC for 1 hour. After that time, keeping the solution at 0ºC, EtOH (72 mL), NaOH (80 mL, 1M in H_2O) and H_2O_2 (36 mL, 30% v/v in H_2O) were added subsequently in a drop wise manner. The resulting mixture was stirred for 1 hour warming to room temperature and additionally two hours at 80ºC. The reaction was then allowed to cool before quenching by addition of a saturated aqueous solution

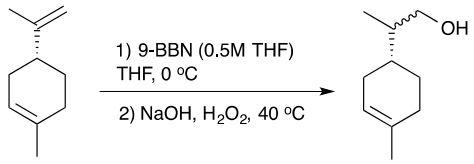
[1] G. Zweifeil, H. C. Brown *J. Am. Chem. Soc.* **1964**, *86*, 393

of NH_4Cl. Aqueous layer was extracted with Et_2O (3x). Combined organic layers were washed with brine, dried and solvent was evaporated to yield 23.5 g (99% yield) of ((1*R*,2*S*,5*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methanol as a colorless oil that becomes solid after storing at low temperature. Stereochemical assignment based on literature precedent.[2]

$[\alpha]_D^{22}$ -20 (c 4.9, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 3.6-3.5 (m, 2H), 2.4-2.3 (m, 2H), 2.3-2.2 (m, 1H), 2.0-1.9 (m, 1H), 1.9-1.8 (m, 4H), 1.5-1.4 (m, 1H), 1.15 (s, 3H), 0.94 (s, 3H), 0.93 (d, *J* = 9.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 67.6 (t), 44.3 (d), 42.8 (d), 41.4 (d), 38.5 (s), 33.1 (t), 27.9 (q), 25.9 (t), 23.2 (q), 18.7 (t). **HRMS (ESI-MS):** calcd. for $C_{10}H_{18}NaO$: 177.1250, found: 177.1253.



(*R*)-2-((*S*)-4-Methylcyclohex-3-en-1-yl)propan-1-ol & (*S*)-2-((*S*)-4-methylcyclohex-3-en-1-yl)propan-1-ol (3a)

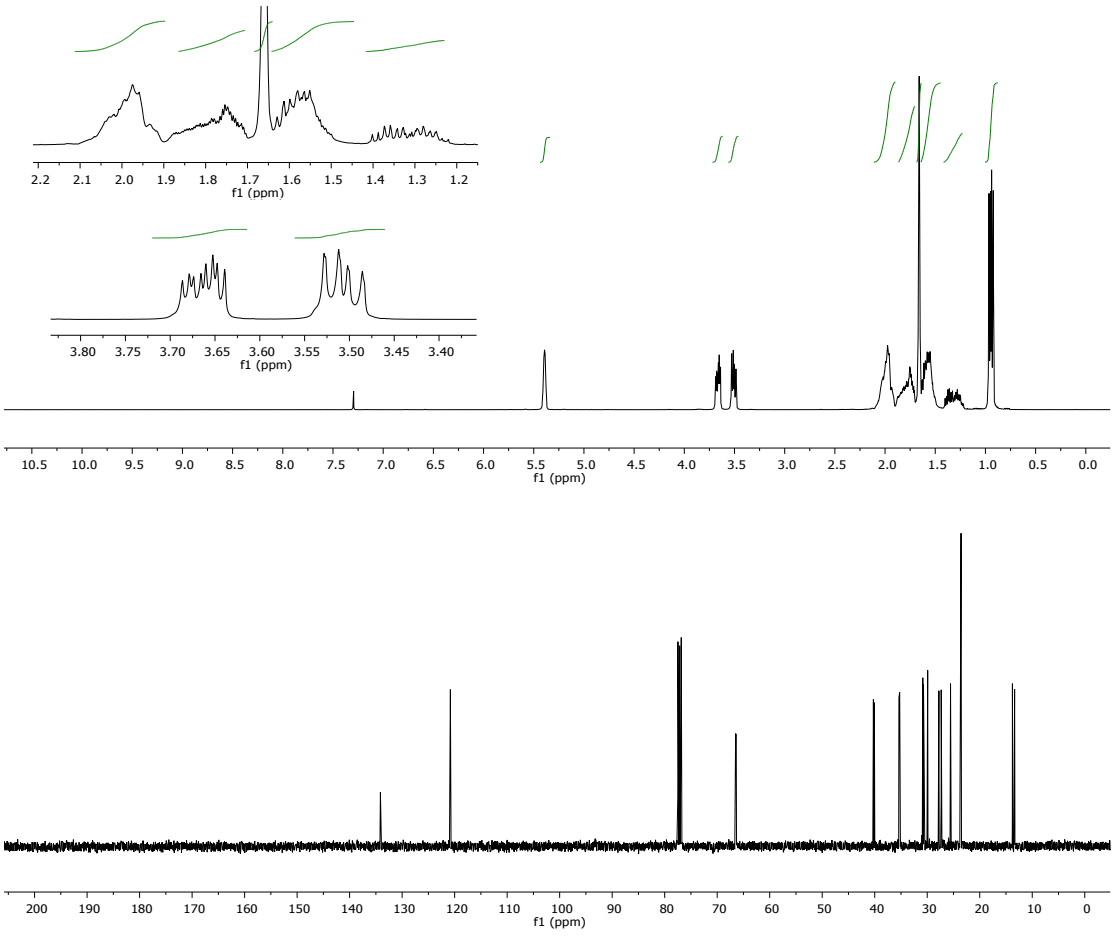


Freshly distilled *R*-(+)-limonene (6.87 mmol, 1 mL) was dissolved in anhydrous THF (50 mL) and the solution was cooled to 0 °C. 9-BBN (0.5 M in THF, 7.04 mmol, 14 mL) was added dropwise and the resulting solution was stirred for 2 h keeping the temperature at 0 °C and then for 2 h at rt. The resulting solution was then re-cooled to 0 °C and NaOH (3 M aq., 10 mL) and H_2O_2 (30%

[2] G. Giacomelli, L. Lardicci, F. Palla *J. Org. Chem.* **1984**, *49*, 310.

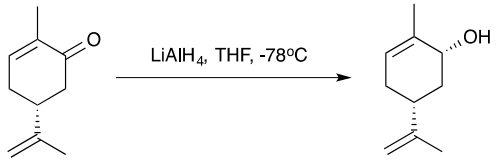
w/w, 10 mL) were added dropwise sequentially. The solution was stirred at rt for 1 h and then heated at 40 °C for 4 h, before being allowed to cool to rt, the excess of peroxides was quenched with sat. aq. $Na_2S_2O_3$ and the volatiles were removed *in vacuo*. The residue was extracted with EtOAc (3 × 30 mL) and the combined organics were washed with 1 M HCl (aq., 30 mL) and brine (30 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified on silica gel chromatography (PE/EtOAc 5%) to obtain the title compounds as a colourless oil (mixture of 2 diastereoisomers 1:1, 0.731 g, 82% yield).[3]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.42 – 5.37 (m, 1H), 3.66 (ddd, *J* = 10.6, 5.2, 3.2 Hz, 1H), 3.51 (ddd, *J* = 10.6, 6.6, 0.9 Hz, 1H), 2.11 – 1.90 (m, 3H), 1.89 – 1.69 (m, 1H), 1.66 (bs, 3H), 1.64 – 1.50 (m, 3H), 1.41 – 1.32 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), OH not observed. For the other diastereoisomer, the following peaks are discernible, the others overlap with the major product. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 1.32 – 1.22 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 134.01 (C), 133.96 (C), 120.69 (CH), 120.62 (CH), 66.35 (CH_2), 66.23 (CH_2), 40.12 (CH), 39.94 (CH), 35.26 (CH), 35.11 (CH), 30.72 (CH_2), 30.59 (CH_2), 29.79 (CH_2), 27.64 (CH_2), 27.21 (CH_2), 25.43 (CH_2), 23.44 (2 × CH_3), 13.65 (CH_3), 13.23 (CH_3). **HRMS (ESI-MS)**: calcd. for $C_{10}H_{18}NaO$: 177.1255, found: 177.1060.



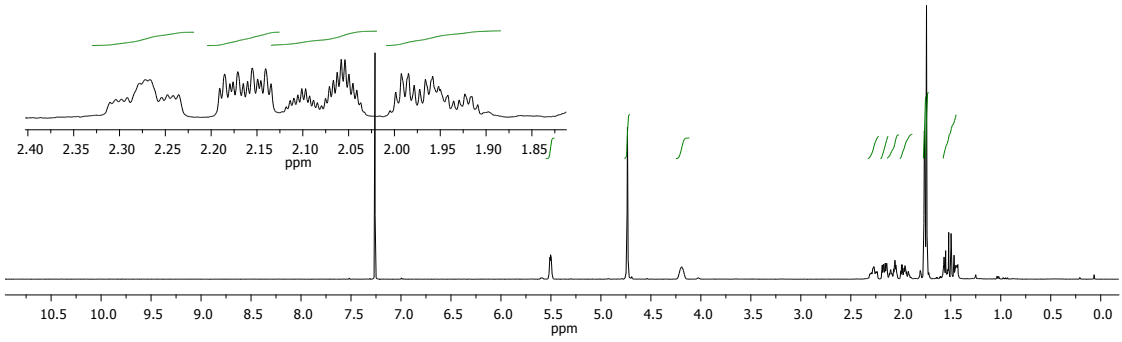
[3] R. M. Cravero, M. Gonzalez-Sierra, G. R. Labadie, *Helv. Chim. Acta*, 2003, **86**, 2741.

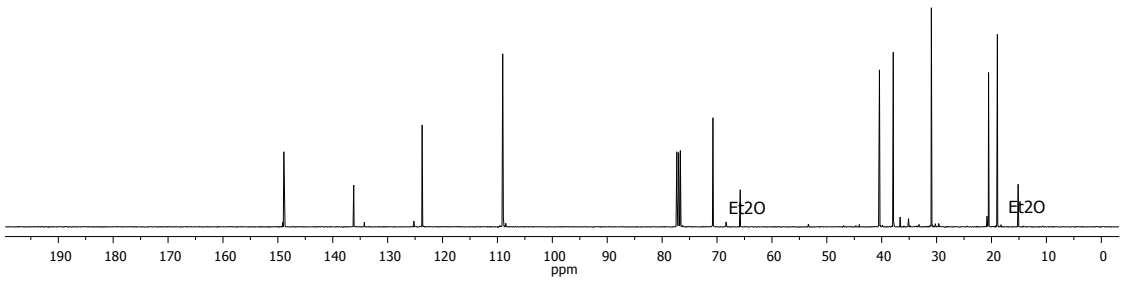
(1*R*,5*S*)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enol (4a)



To a cold solution (-78°C) of carvone (13.0 mL, 83.3 mmol) in THF (250 mL) $LiAlH_4$ (100 mL, 100 mmol, 1M in THF) was added dropwise and the mixture was stirred for 3 hour warming to room temperature. The reaction was quenched by slowly addition of water (25 mL), aqueous solution of NaOH (50 mL, 1M in H_2O) and water (75 mL). Aqueous layer was extracted with Et_2O (3x). Combined organic layers were washed with brine, dried and solvent was evaporated to yield 12.6 g (99% yield) of (1*R*,5*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enol as a colourless oil that becomes solid after storing at low temperature. Stereochemical assignment based on literature precedent.[4]

$[\alpha]_D^{22}$ -40 (c 2.6, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 5.50 (ddt, *J* = 5.2, 2.6, 1.4 Hz, 1H), 4.73 (m, 2H), 4.19 (bs, 1H), 2.3-2.2 (m, 1H), 2.2-2.1 (m, 1H), 2.1-2.0 (m, 1H), 2.0-1.9 (m, 1H), 1.76 (td, *J* = 2.5, 1.4 Hz, 3H), 1.74 (s, 3H), 1.6-1.5 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 148.9 (s), 136.2 (s), 123.7 (d), 109.0 (t), 70.8 (d), 40.4 (d), 37.9 (t), 31.0 (t), 20.5 (q), 18.9 (q). **HRMS (ESI-MS)**: calcd. for $C_{10}H_{16}NaO$: 175.1093, found: 175.1091.





[4] L. Garver, P. Eikeren *J. Org. Chem.* **1976**, *41*, 2773.

Synthesis of acrylate derivatives *via* esterification

Method A

To a cold solution (0°C) of terpene alcohol (64.8 mmol) in DCM (500 mL) was added subsequently Et_3N (20 mL, 123 mmol) and acryloyl chloride (9.5 mL, 97.2 mmol) and the mixture was stirred during 24 h warming to room temperature. The reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (1x200 mL). Aqueous phase was extracted with DCM (3x200 mL). Combined organic layers were washed with brine (1x200 mL), dried with $MgSO_4$ and solvent was evaporated in *vacuo*. The resulting residue was purified by chromatography on a Biotage SP4 eluting with 0-5% petroleum ether/ethyl acetate over 10 column volumes.

Method B

To a solution of terpene alcohol (6.48 mmol) in MeTHF (40 mL) was added acrylic acid (0.5 mL, 7.13 mmol), Et_3N (2.7 mL, 19.4 mmol) and T3P (4.95 g, 7.78 mmol) (50 wt.% in ethyl acetate). The mixture was stirred for 48 h at room temperature. The reaction was monitored by TLC. After completion of the reaction water was added (30 mL) and the aqueous phase extracted with diethyl ether (3x20 mL). Combined organic layers were washed with 1M HCl aq. (1x20 mL), saturated aqueous solution of $NaHCO_3$ (1x20 mL) and brine (1x20 mL), dried with $MgSO_4$, and solvent was evaporated in *vacuo*. The resulting residue was purified by chromatography on a Biotage SP4 eluting with 0-5% petroleum ether/ethyl acetate over 10 column volumes.

Synthesis of methacrylate derivatives *via* esterification

Method C

To a cold solution (0°C) of terpene alcohol (64.8 mmol) in DCM (500 mL) was added subsequently Et_3N (20 mL, 123 mmol) and methacryloyl chloride (9.5 mL, 97.2 mmol) and the mixture was stirred during 24 h warming to room temperature. After the reaction was completeThe reaction was quenched by addition of saturated aqueous solution of $NaHCO_3$ (1x200 mL). Aqueous phase was extracted with DCM (3x200 mL). Combined organic layers were washed with brine (1x200 mL), dried with $MgSO_4$ and solvent was evaporated. The resulting residue was purified by chromatography on a Biotage SP4 eluting with 0-5% petroleum ether/ethyl acetate over 10 column volumes.

Method D

To a solution of terpene alcohol (6.48 mmol) in MeTHF (40 mL) was added methacrylic acid (0.6 mL, 7.13 mmol), Et_3N (2.7 mL, 19.4 mmol) and T3P (4.95 g, 7.78 mmol) (50 wt.% in ethyl acetate). The mixture was stirred for 48 h at room temperature. The reaction was monitored by TLC. After completion of the reaction water (30 mL) was added and the aqueous phase extracted with diethyl ether (3x20 mL). Combined organic layers were washed with 1M HCl aq. (1x20 mL), saturated aqueous solution of $NaHCO_3$ (1x20 mL) and brine (1x20 mL), dried with $MgSO_4$, and solvent was evaporated in *vacuo*. The resulting residue was purified by chromatography on a Biotage SP4 eluting with 0-5% petroleum ether/ethyl acetate over 10 column volumes.

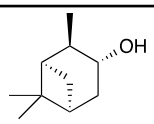
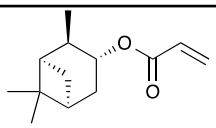
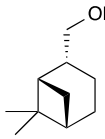
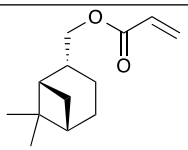
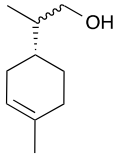
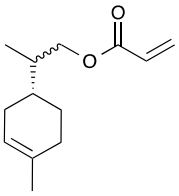
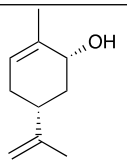
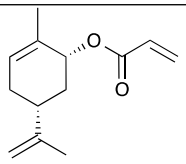
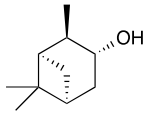
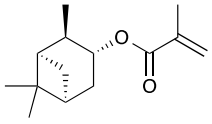
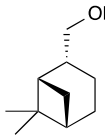
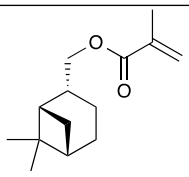
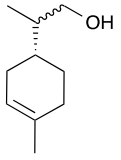
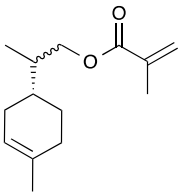
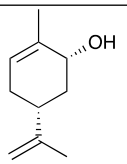
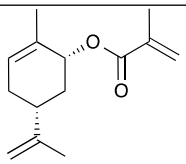
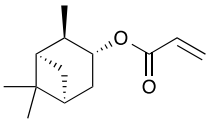
Alcohol	Esterification Method	Product	Yield (%)
 **1a**	A	 **1b**	55
	B		99
 **2a**	A	 **2b**	66
	B		99
 **3a**	A	 **3b**	75
	B		96
 **4a**	A	 **4b**	91
	B		99
 **1a**	C	 **1c**	47
	D		-
 **2a**	C	 **2c**	64
	D		-
 **3a**	C	 **3c**	73
	D		-
 **4a**	C	 **4c**	78
	D		-

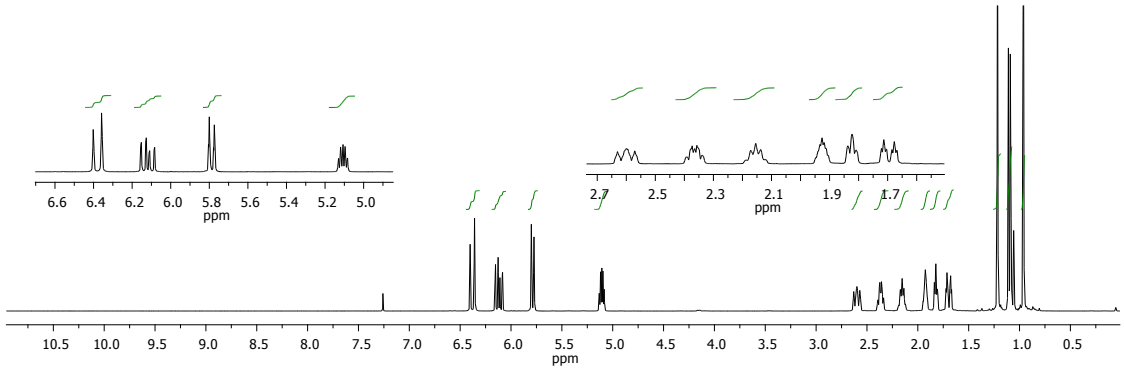
Table S1 structures of alcohols (**1a – 4a**) and (meth)acrylates (**1b – 4b, 1c – 4c**) derived from terpenes. The method used and yields obtained are clearly labelled.

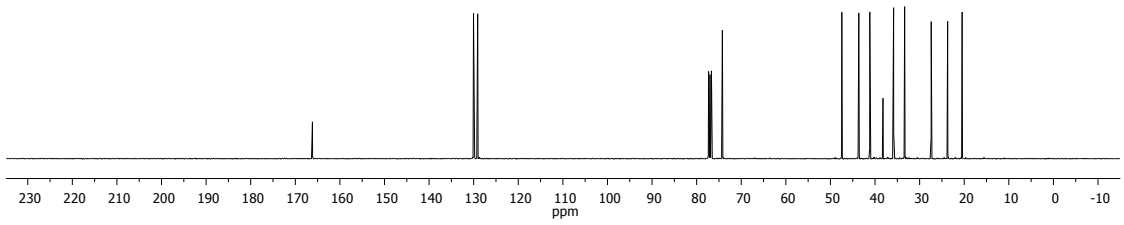
Monomer characterisation

(1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl acrylate (1b)

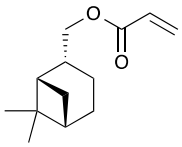


$[\alpha]_D^{21}$ -36 (c 2.2, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.38 (dt, *J* = 17.3, 1.4 Hz, 1H), 6.12 (ddd, *J* = 17.3, 10.4, 1.3 Hz, 1H), 5.79 (dt, *J* = 10.4, 1.5 Hz, 1H), 5.11 (dt, *J* = 9.4, 4.6 Hz, 1H), 2.6-2.5 (m, 1H), 2.4-2.3 (m, 1H), 2.2-2.1 (m, 1H), 2.0-1.9 (m, 1H), 1.82 (t, *J* = 5.8 Hz, 1H), 1.69 (dt, *J* = 14.4, 3.4 Hz, 1H), 1.22 (s, 3H), 1.10 (dd, *J* = 7.4, 1.1 Hz, 3H), 1.07 (d, *J* = 9.9 Hz, 1H), 0.96 (s, 3H), . **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 166.2 (s), 130.0 (t), 129.1 (d), 74.2 (d), 47.4 (d), 43.6 (d), 41.2 (d), 38.2 (s), 35.8 (t), 33.4 (t), 27.4 (q), 23.7 (q), 20.5 (q). **IR** ν(cm^{-1}): 3016, 2927, 1731, 1636, 1602, 1439, 1242. **HRMS (ESI-MS)**: calcd. for $C_{13}H_{20}NaO_2$: 231.1356, found: 231.1350.



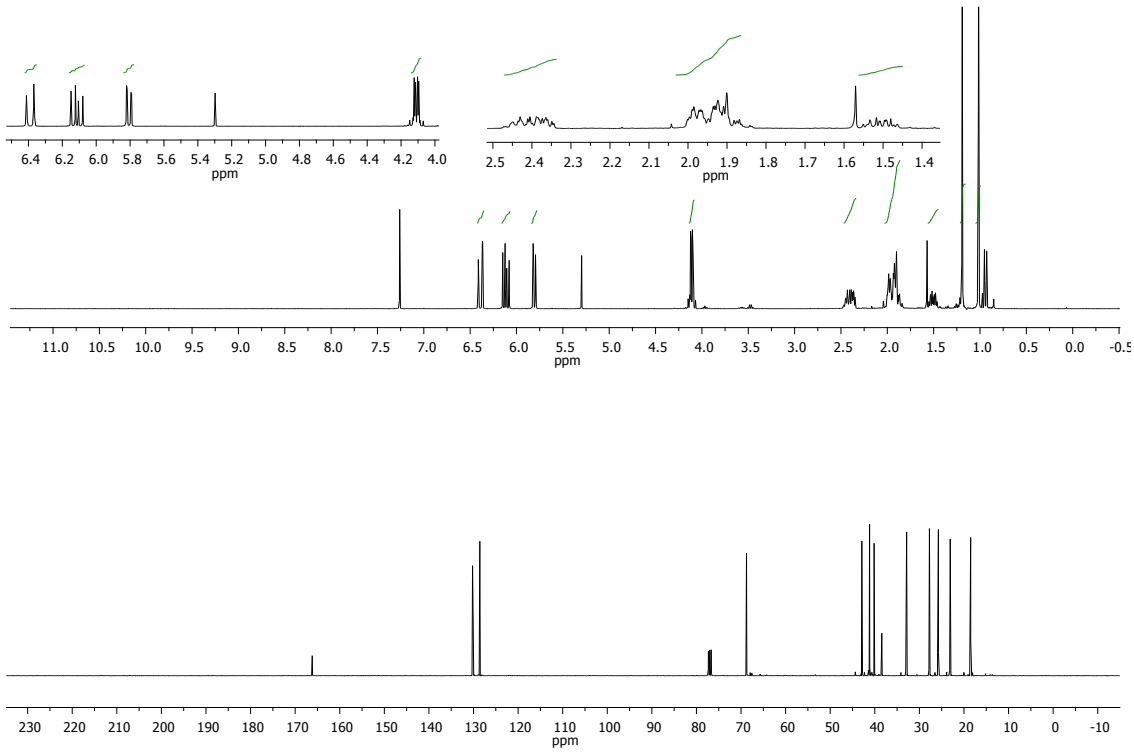


((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)methyl acrylate (2b)

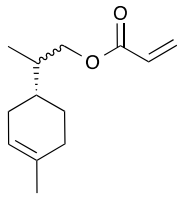


$[\alpha]_D^{22}$ -10 (c 13.9, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.39 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.11 (dd, *J* = 7.9, 2.8 Hz, 2H), 2.4-2.3 (m, 2H), 2.0-1.8 (m, 5H), 1.6-1.5 (m, 1H), 1.19 (s, 3H), 1.02 (s, 3H), 0.94 (d, *J* = 9.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 166.2 (s), 130.2 (t), 128.6 (d), 68.8 (t), 42.9 (d), 41.2 (d), 40.2 (d), 38.4 (s), 32.9 (t), 27.8 (q), 25.7 (t), 23.1 (q), 18.5 (t). **IR** ν(cm^{-1}): 3011, 2923, 1717, 1636, 1619, 1470, 1409,

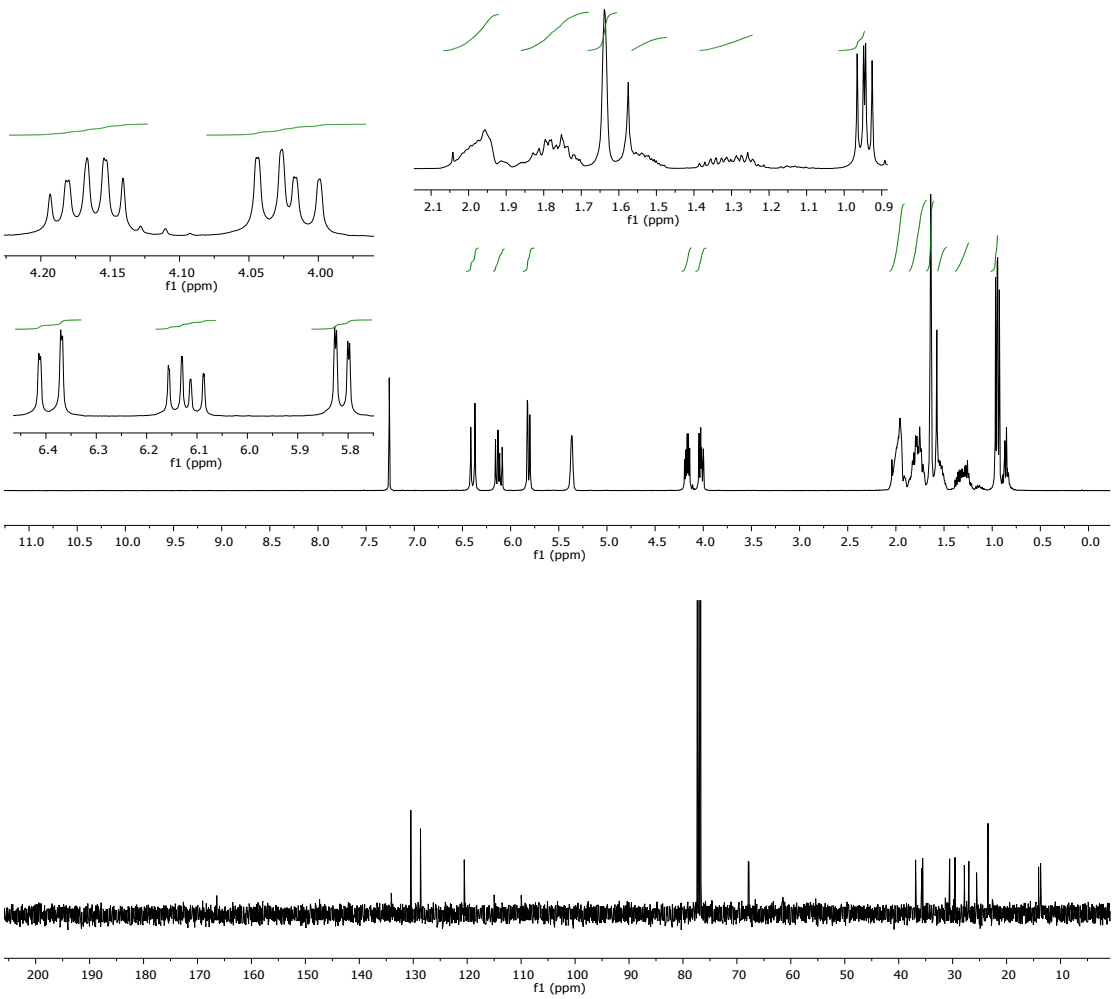
1385, 1367, 1396, 1192, 1059, 985. **HRMS (ESI-MS)**: calcd. for $C_{13}H_{20}NaO_2$: 231.1356, found: 231.1345.



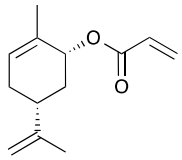
(*R*)-2-((*S*)-4-Methylcyclohex-3-enyl)propyl acrylate & (*S*)-2-((*S*)-4-Methylcyclohex-3-enyl)propyl acrylate (3b)



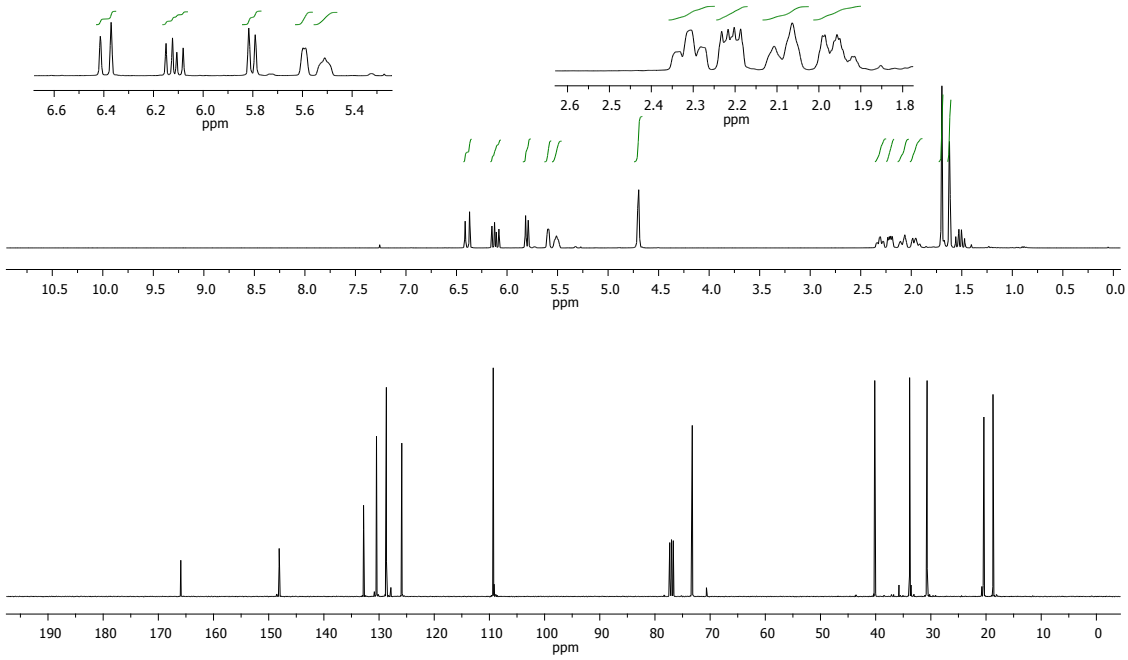
$[\alpha]_D^{22}$ -44 (c 4.9, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.39 (dd, *J* = 17.4, 1.5 Hz, 1H), 6.12 (ddd, *J* = 17.4, 10.4, 1.0 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.39 – 5.34 (bs, 1H), 4.17 (ddd, *J* = 10.9, 5.6, 4.5 Hz, 1H), 4.02 (ddd, *J* = 10.9, 6.9, 0.9 Hz, 1H), 2.06 – 1.92 (m, 3H), 1.87 – 1.69 (m, 2H), 1.68 – 1.62 (bs, 3H), 1.55 – 1.47 (m, 1H), 1.41 – 1.23 (m, 1H), 0.96 (d, *J* = 6.9 Hz, 1H). For the other diastereoisomer, the following peaks are discernible, the others overlap with the major product. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 0.93 (d, *J* = 7.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.42 (2 × C), 134.07 (2 × C), 130.45 (CH_2), 128.66 (CH_2), 120.55 (CH), 120.48 (CH), 115.00 (CH), 109.98 (CH), 67.89 (CH_2), 67.77 (CH_2), 36.87 (CH), 36.80 (CH), 35.69 (CH), 35.56 (CH), 30.64 (CH_2), 30.55 (CH_2), 29.56 (CH_2), 27.83 (CH_2), 27.00 (CH_2), 25.57 (CH_2), 23.45 (2 × CH_3), 14.07 (CH_3), 13.70 (CH_3). **IR** ν(cm^{-1}): 3011, 2973, 2922, 1714, 1637, 1618, 1453, 1437, 1407, 1295, 1276, 1192, 1048, 985, 970. **HRMS (ESI-MS)**: calcd. for $C_{13}H_{18}NaO_2$: 229.1199, found: 229.1196.



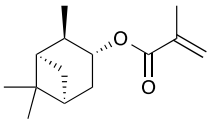
(1*R*,5*R*)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enyl acrylate (4b)



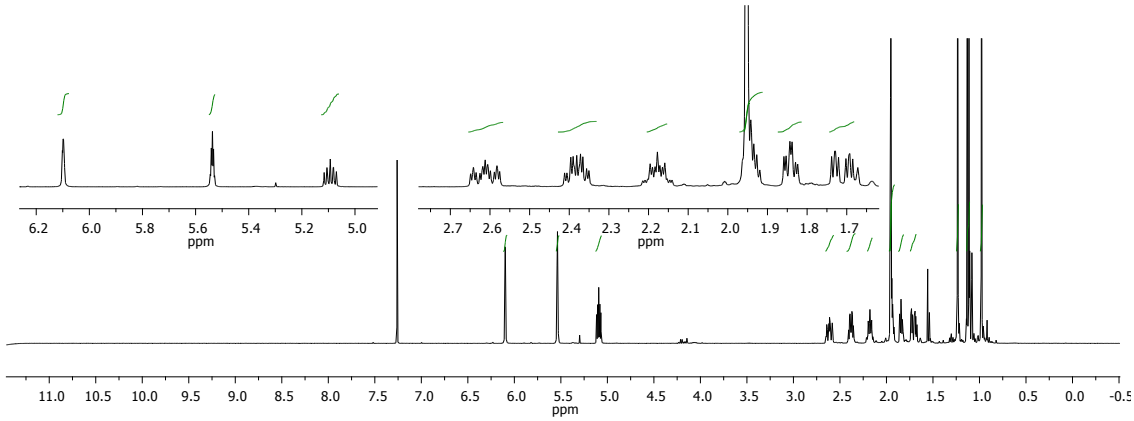
$[\alpha]_D^{22}$ -44 (c 4.9, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.39 (d, *J* = 17.3 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.80 (d, *J* = 10.4 Hz, 1H), 5.59 (d, *J* = 4.2 Hz, 1H), 5.51 (bs, 1H), 4.70 (s, 2H), 2.4-2.3 (m, 1H), 2.3-2.2 (m, 1H), 2.1-2.0 (m, 1H), 2.0-1.9 (m, 1H), 1.69 (s, 3H), 1.62 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 165.9 (s), 148.1 (s), 132.8 (s), 130.5 (t), 128.7 (d), 125.9 (d), 109.3 (t), 73.2 (d), 40.2 (d), 33.9 (t), 30.7 (t), 20.4 (q), 18.7 (q). **IR** ν(cm^{-1}): 3011, 2973, 2922, 1714, 1637, 1618, 1453, 1437, 1407, 1295, 1276, 1192, 1048, 985, 970. **HRMS (ESI-MS)**: calcd. for $C_{13}H_{18}NaO_2$: 229.1199, found: 229.1196.

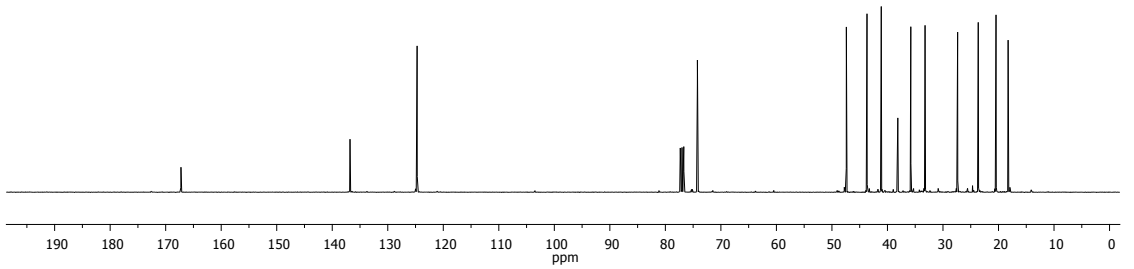


(1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl methacrylate (1c)

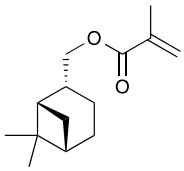


$[\alpha]_D^{22}$ -24 (c 16.8, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.10 (dd, *J* = 1.7, 0.9 Hz, 1H), 5.54 (p, *J* = 1.6 Hz, 1H), 5.09 (ddd, *J* = 9.2, 4.8, 4.2 Hz, 1H), 2.7-2.6 (m, 1H), 2.4-2.3 (m, 1H), 2.18 (qdd, *J* 7.4, 5.1, 2.3 Hz, 1H), 2.0-1.9 (m, 4H), 1.84 (td, *J* = 5.9, 2.2 Hz, 1H), 1.71 (ddd, *J* = 14.4, 3.9, 3.1 Hz, 1H), 1.23 (s, 3H), 1.12 (d, *J* = 1.1 Hz, 3H), 1.09 (d, *J* = 9.9 Hz, 1H), 0.98 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 167.3 (s), 136.8 (s), 124.7 (t), 74.2 (d), 47.4 (d), 43.7 (d), 41.1 (d), 38.1 (s), 35.8 (t), 33.2 (t), 27.4 (q), 23.7 (q), 20.5 (q), 18.3 (q). **IR** ν(cm^{-1}): 2957, 2919, 1706, 1636, 1452, 1299, 1175, 1154. **HRMS (ESI-MS)**: calcd. for $C_{14}H_{22}NaO_2$: 245.1512, found: 245.1513.

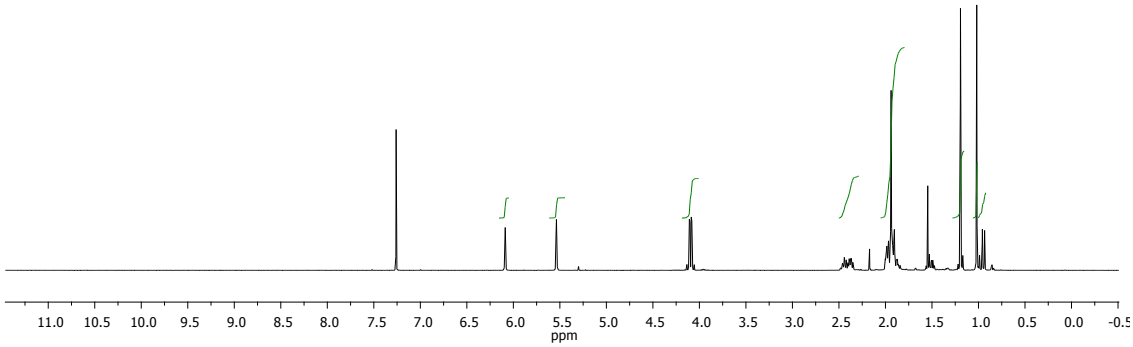


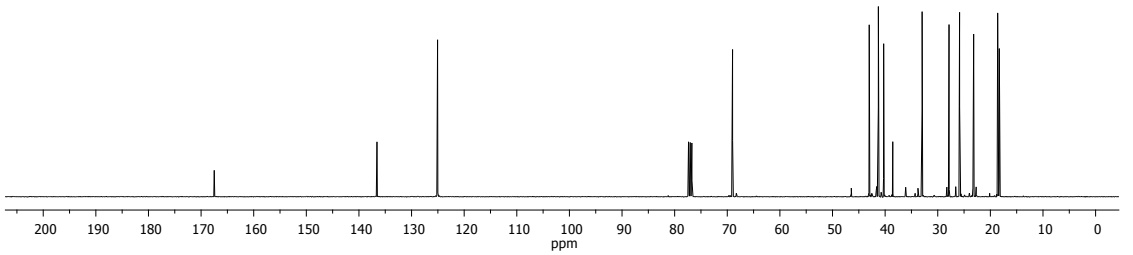


((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)methyl methacrylate (2c)

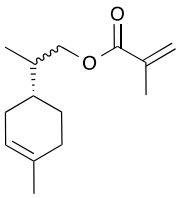


$[\alpha]_D^{22}$ -9.1 (c 3.8, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ =6.09 (dd, *J* = 1.7, 0.9 Hz, 1H), 5.54 (p, *J* = 1.6 Hz, 1H), 4.09 (dd, *J* = 8.0, 2.6 Hz, 2H), 2.5-2.4 (m, 2H), 2.0-1.8 (m, 5H), 1.94 (s, 3H), 1.19 (s, 3H), 1.02 (s, 3H), 1.0-0.9 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 167.5 (s), 136.5 (s), 125.0 (t), 69.0 (t), 43.0 (d), 41.2 (d), 40.2 (d), 38.5 (s), 32.9 (t), 27.8 (q), 25.8 (t), 23.1 (q), 18.6 (t), 18.3 (q). **IR** ν(cm^{-1}): 2988, 2945, 2921, 1708, 1637, 1470, 1453, 1326, 1299, 1175. **HRMS (ESI-MS)**: calcd. for $C_{14}H_{22}NaO_2$: 245.1512, found: 245.1510.

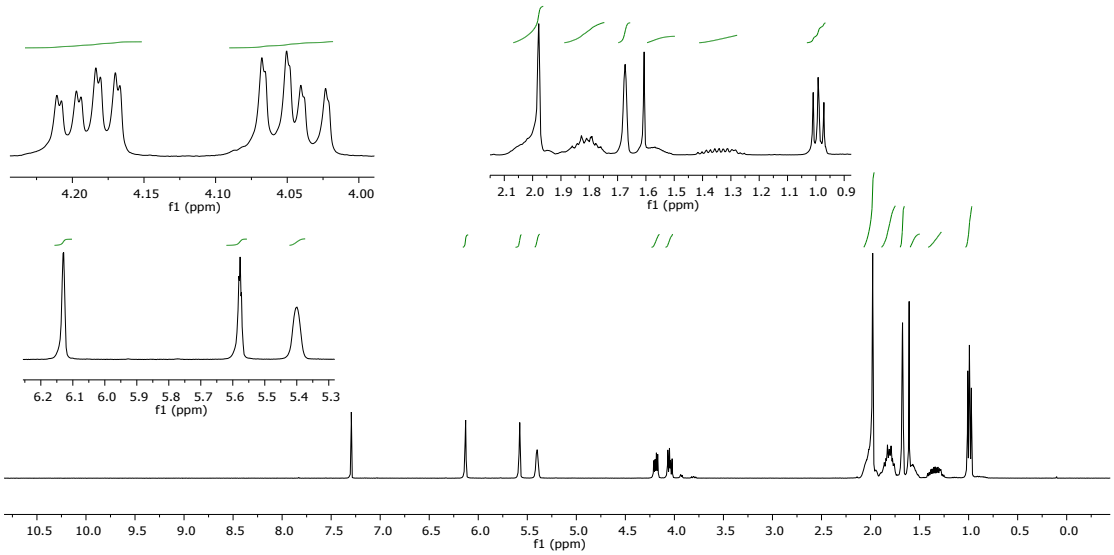


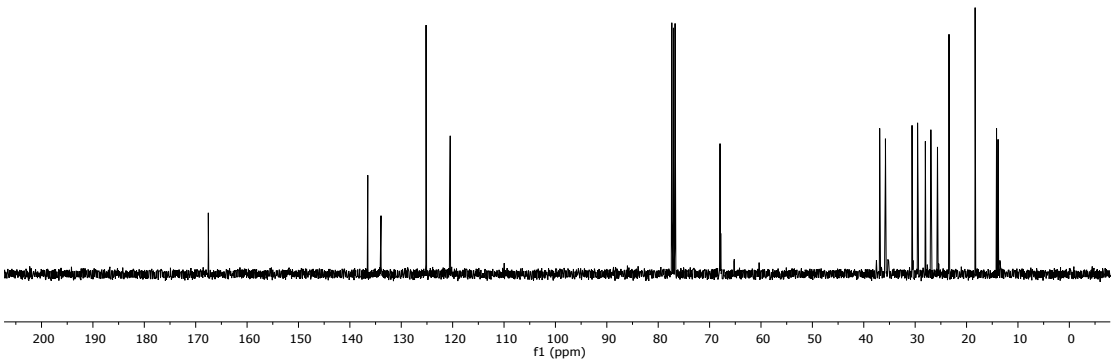


(*R*)-2-((*S*)-4-methylcyclohex-3-en-1-yl)propyl methacrylate & (*S*)-2-((*S*)-4-methylcyclohex-3-en-1-yl)propyl methacrylate (3c)

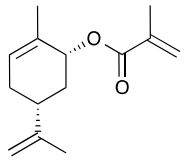


^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.13 (dq, *J* = 1.8, 0.9 Hz, 1H), 5.61 – 5.54 (m, 1H), 5.42 – 5.38 (bs, 1H), 4.18 (ddd, *J* = 11.0, 5.5, 1.6 Hz, 1H), 4.06 (ddd, *J* = 11.0, 6.9, 1.1 Hz, 1H), 2.07 – 1.99 (m, 3H), 1.98 (s, 3H), 1.81 (m, 3H), 1.70 – 1.64 (m, 3H), 1.58 – 1.52 (m, 1H), 1.34 (m, 1H), 1.00 (d, *J* = 6.9 Hz, 3H). For the other diastereoisomer, the following peaks are discernible. The others overlap with the major product. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 0.98 (d, *J* = 6.9 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 167.55 (2 × C), 136.52 (2 × C), 134.05 (C), 133.99 (C), 125.21 (2 × CH_2), 120.56 (CH), 120.50 (CH), 68.01 (CH_2), 67.89 (CH_2), 36.90 (CH), 36.82 (CH), 35.79 (CH), 35.70 (CH), 30.61 (CH_2), 30.53 (CH_2), 29.53 (CH_2), 28.02 (CH_2), 26.94 (CH_2), 25.66 (CH_2), 23.42 (CH_3), 23.41 (CH_3), 18.33 (2 × CH_3), 14.17 (CH_3), 13.87 (CH_3). **IR** ν(cm^{-1}): 3008, 2965, 2917, 2857, 1711, 1637, 1452, 1438, 1404, 1378, 1325, 1299, 1243, 1178, 1012, 981, 943. **HRMS (ESI-MS)**: calcd. for $C_{14}H_{22}NaO_2$: 245.1512, found: 245.1510.

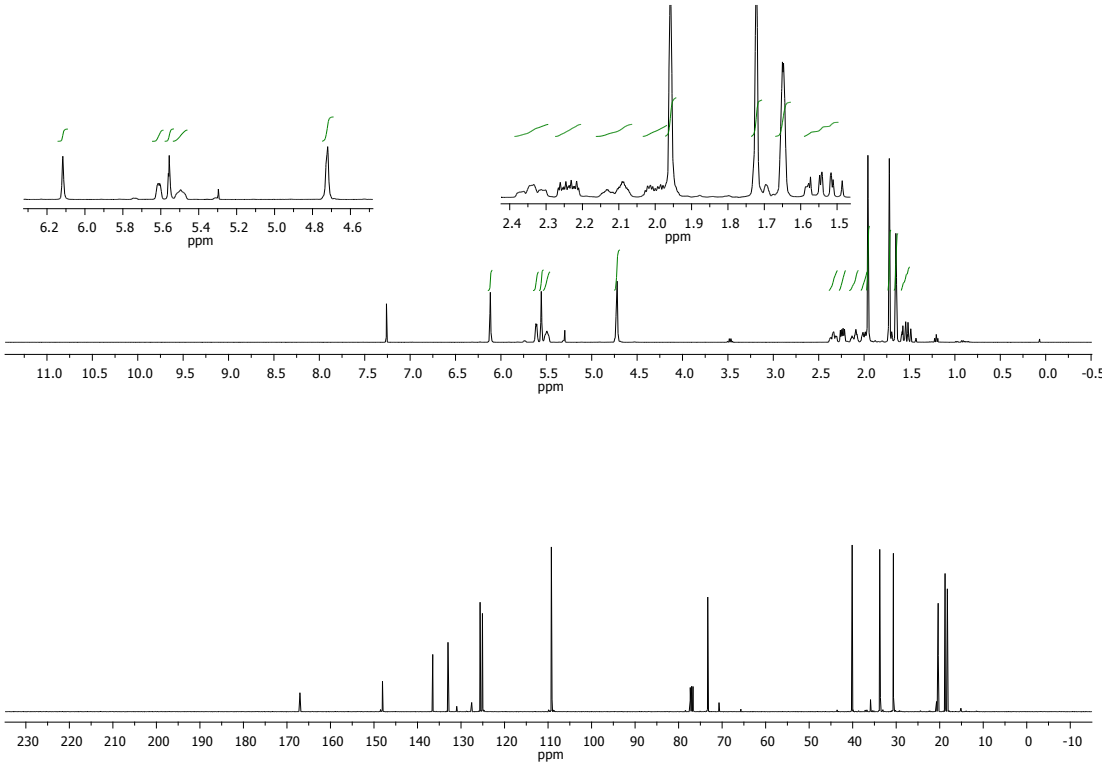




(1*R*,5*R*)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enyl acrylate (4c)

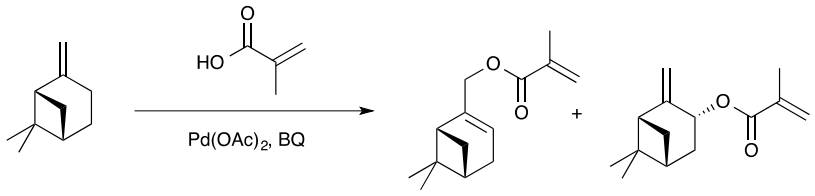


$[\alpha]_D^{22}$ -44 (c 9.0, $CHCl_3$). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.12 (s, 1H), 5.7-5.6 (m, 1H), 5.56 (s, 1H), 5.49 (bs, 1H), 4.73 (s, 2H), 2.4-2.3 (m, 1H), 2.24 (ddt, J 11.8, 6.0, 2.2 Hz, 1H), 2.2-2.1 (m, 1H), 2.1-2.0 (m, 1H), 1.96 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H), 1.6-1.5 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ = 167.0 (s), 148.1 (s), 136.5 (s), 133.0 (s), 125.6 (d), 125.1 (t), 109.2 (t), 73.3 (d), 40.1 (d), 33.8 (t), 30.6 (t), 20.4 (q), 18.8 (q), 18.2 (q). **IR ν(cm^{-1}):** 3085, 3008, 1701, 1639, 1452, 1378, 1294, 1192, 1012. **HRMS (ESI-MS):** calcd. for C14H20NaO2: 243.1356, found: 243.1354.



Catalytic synthesis of β-pinene derived methacrylate monomers.

((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl methacrylate and (1*R*,3*R*,5*R*)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-yl methacrylate (5 and 6)



β-Pinene (2.00 g, 14.8 mmol) was dissolved in methacrylic acid (10mL). Benzoquinone (3.20 g, 29.6 mmol, 2 eq.) was added followed by $Pd(OAc)_2$ (80.0mg, 2 mol%). The reaction mixture was stirred for 72 hours at 50°C after which it was allowed to cool down before flushing through Celite. The residue was diluted with toluene (10 mL) and the solvents were removed in vacuo. The crude product was purified on silica gel chromatography using petroleum ether as solvent system to give 10:1 mixture of **(3*R*)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-yl methacrylate (5)** and **(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl methacrylate (6)** as a yellow oil (2.67g, 82% yield).

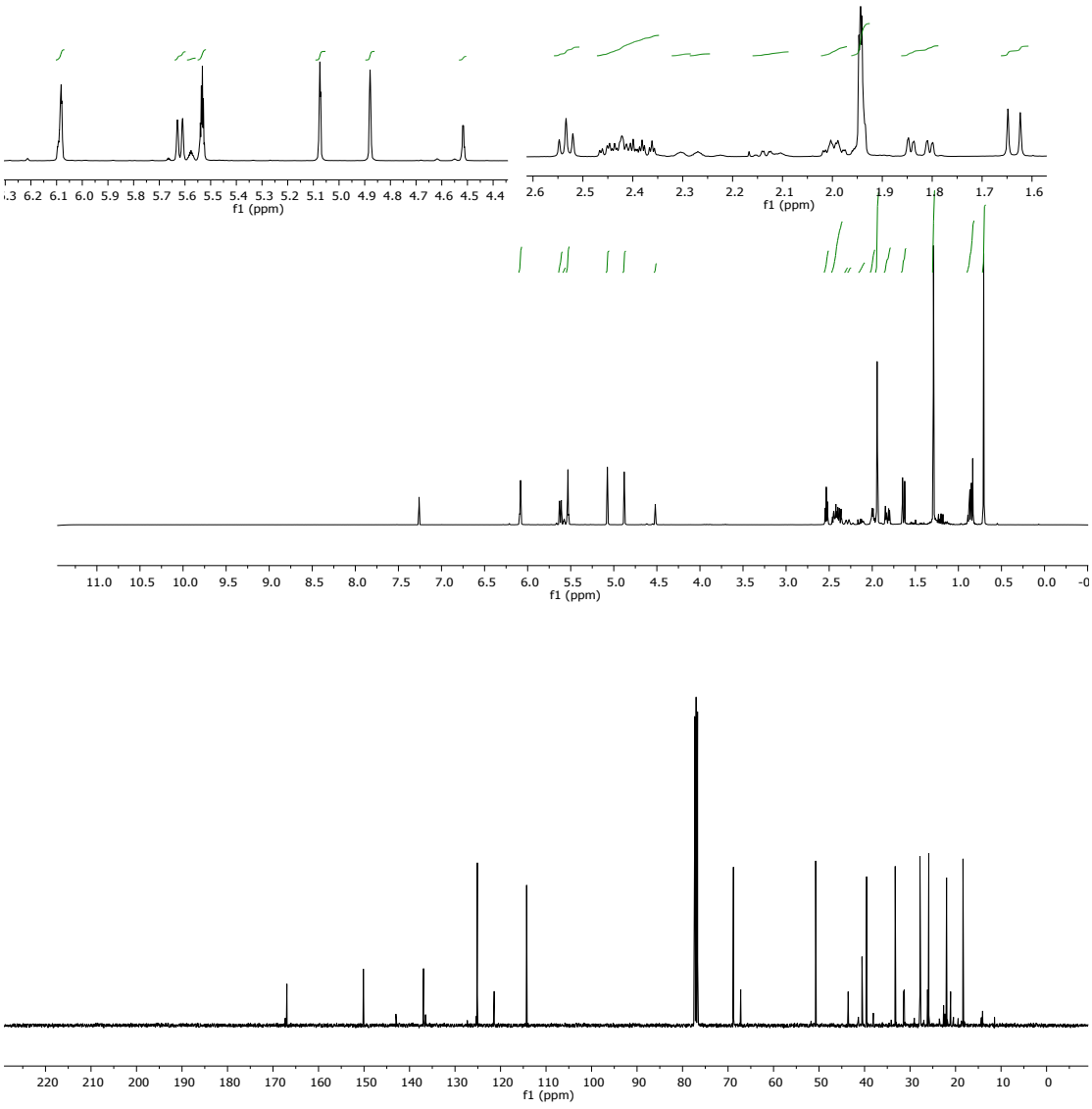
Major product - (3*R*)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-yl methacrylate

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.11 (dd, *J* = 1.72, 0.88 Hz, 1H), 5.64 (d, *J* = 8.04 Hz, 1H), 5.56 (dt, *J* = 4.82, 1.61 Hz, 1H), 5.10 (t, *J* = 1.17 Hz, 1H), 4.90 (br. s, 1H), 2.56 (t, *J* = 5.55 Hz, 1H), 2.02 (dddd, *J* = 11.55, 5.99, 4.09, 1.75 Hz, 1H), 1.97 (dd, *J* = 1.40, 1.0 Hz, 3H), 1.85 (ddd, *J* = 15.05, 4.24, 0.88 Hz, 1H), 1.66 (d, *J* = 9.94 Hz, 1H), 1.31 (br. s, 3H), 0.92-0.84 (m, 2H), 0.73 (s, 3H). **δ_C** (100 MHz,

$CDCl_3$): 166.6 (q), 149.8 (q) , 136.5 (q), 124.7 (CH2), 113.9 (CH2), 68.4 (CH), 50.4 (CH), 40.2 (q), 39.2 (CH), 32.9 (CH2), 27.4 (CH2), 25.5 (CH3), 21.6 (CH3), 18.0 (CH3).

Minor product - (6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl methacrylate

For the minor product, the following peaks are discernible. The others overlap with the major product. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 6.13-6.11 (m, 1H), 5.62 -5.58 (m, 1H), 4.54 (d, *J* = 1.46 Hz, 2H), 2.34-2.28 (m, 2H), 2.18-2.12 (m, 2H), 1.60-1.40 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 166.9 (q), 142.6 (q), 136.1 (q), 124.9 (CH2), 121.0 (CH), 66.8 (CH2), 43.2(CH), 40.3 (CH), 37.7 (q), 31.1 (CH2), 30.9 (CH2), 25.8 (CH3), 22.8 (CH3), 20.7 (CH3). **HRMS (ESI-MS)**: calcd. for $C_{14}H_{20}O_2$ ($M+Na^+$): 243.1356, found: 243.1363



POLYMER SYNTHESIS AND CHARACTERISATION

Reagents source and analytical techniques

Sigma Aldrich

AIBN, DCM, methanol, cyclohexanone

Polymerisation reactions

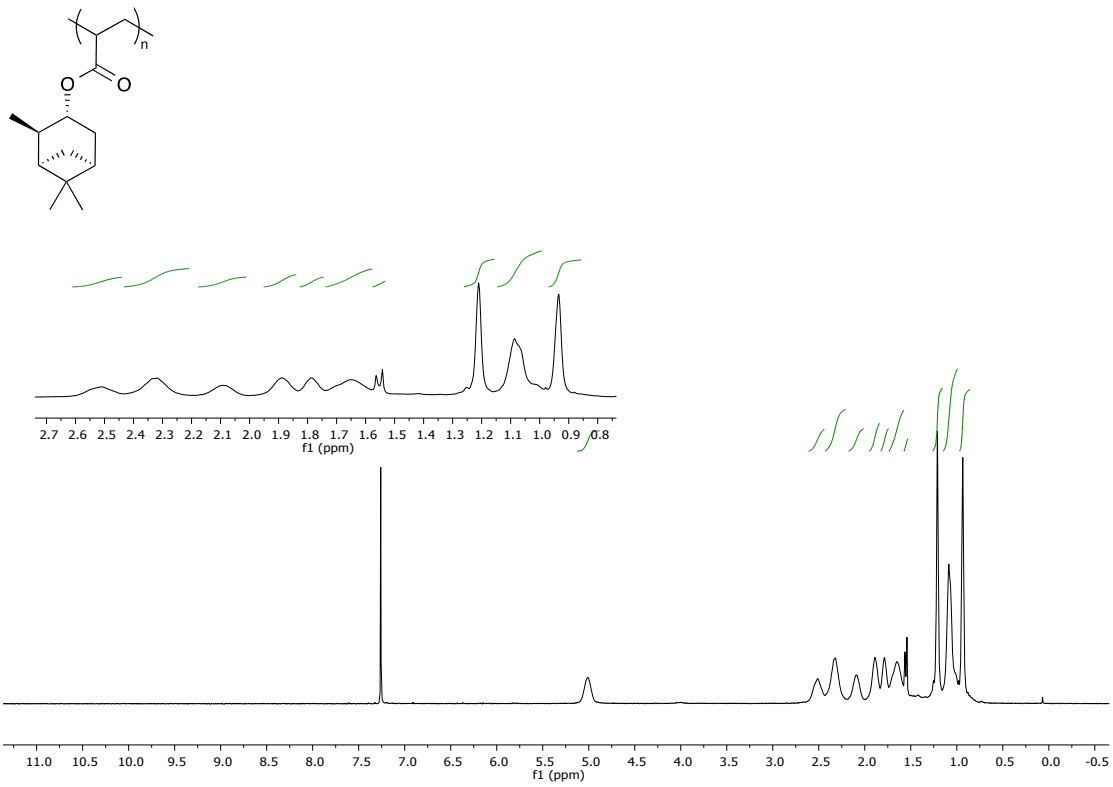
All polymerisation reactions were carried out under O_2-free conditions. Monomer was mixed with 0.5% of the corresponding initiator, the stated amount of chain transfer agent and dissolved in the corresponding solvent. In all cases the reaction flask (10 ml round bottomed flask) was degassed through 3 freeze-pump-thaw cycles and then filled with argon and sealed. After reaction completion, reaction mixtures were cooled down in an ice bath for 10 min. Polymers were purified by dissolving in the minimum amount of DCM, precipitated in methanol (DCM:methanol ratio was around 1:20), filtered and dried in a vacuum oven at 50°C.

Polymer characterisation

Characteristic peaks of polymers are described.

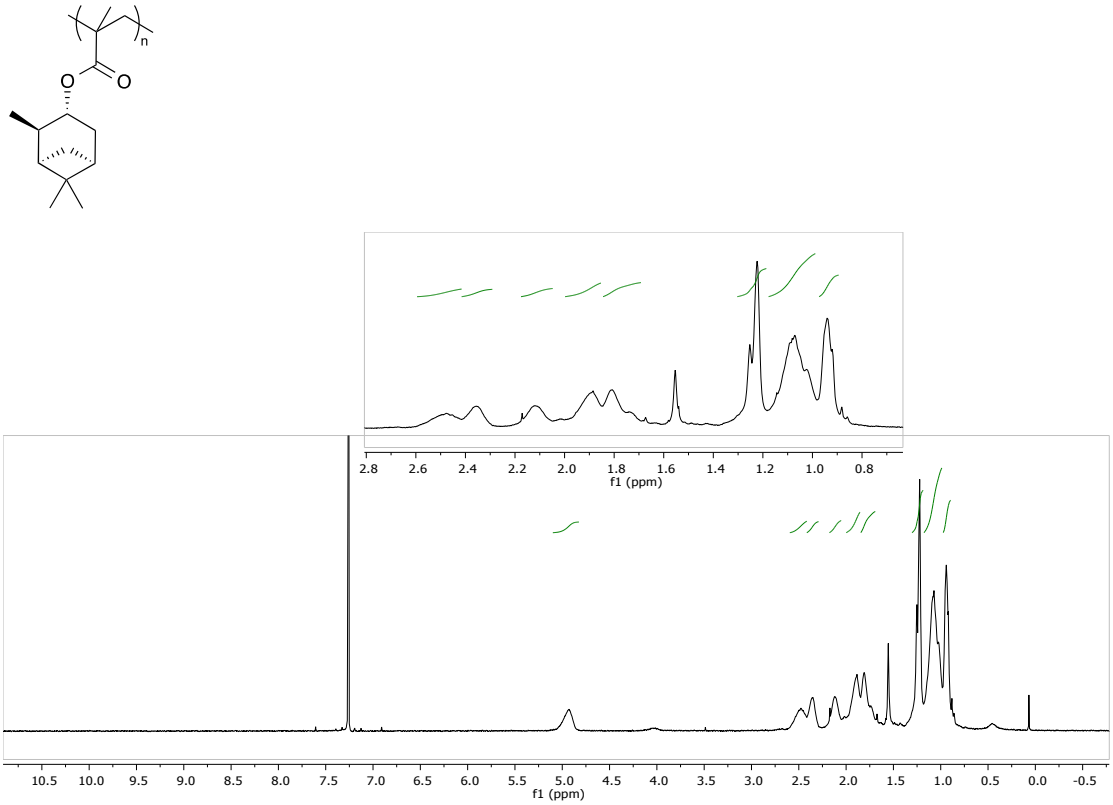
Poly(α-pinene acrylate) (1d)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.03 ppm



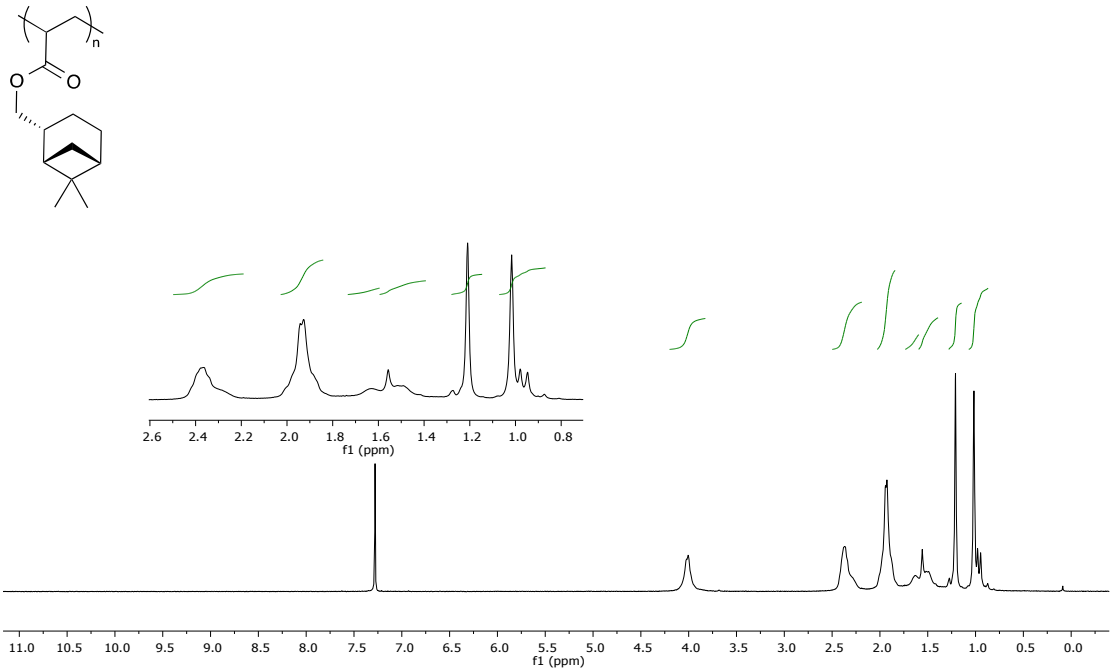
Poly(α-pinene methacrylate) (1e)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.11



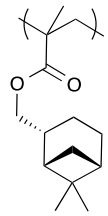
Poly(β-pinene acrylate) (2d)

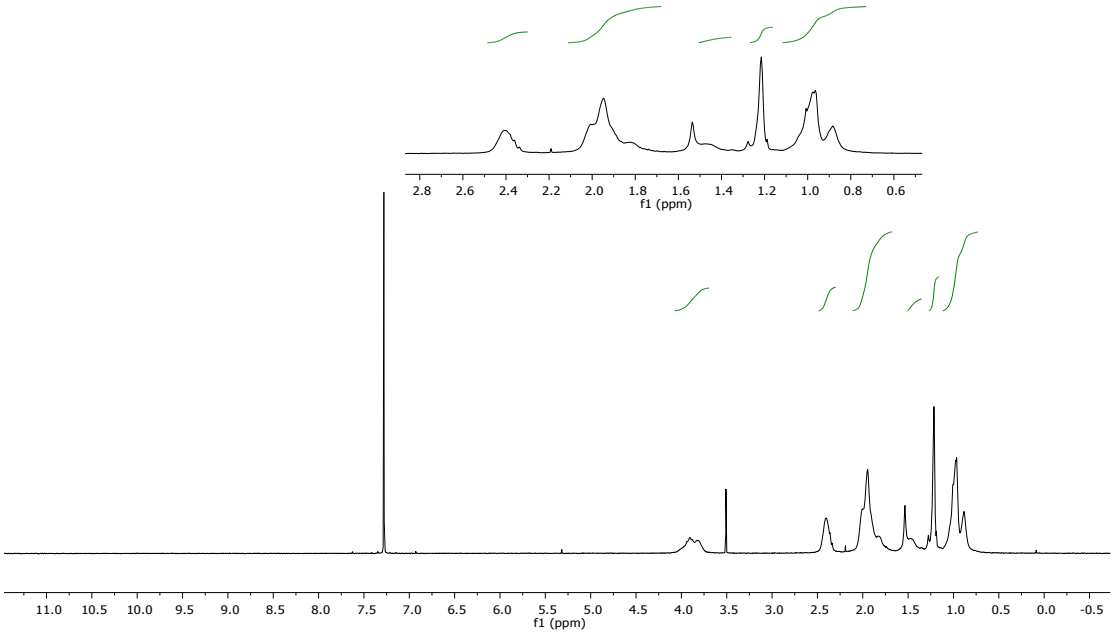
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.01 ppm



Poly(β-pinene methacrylate) (2e)

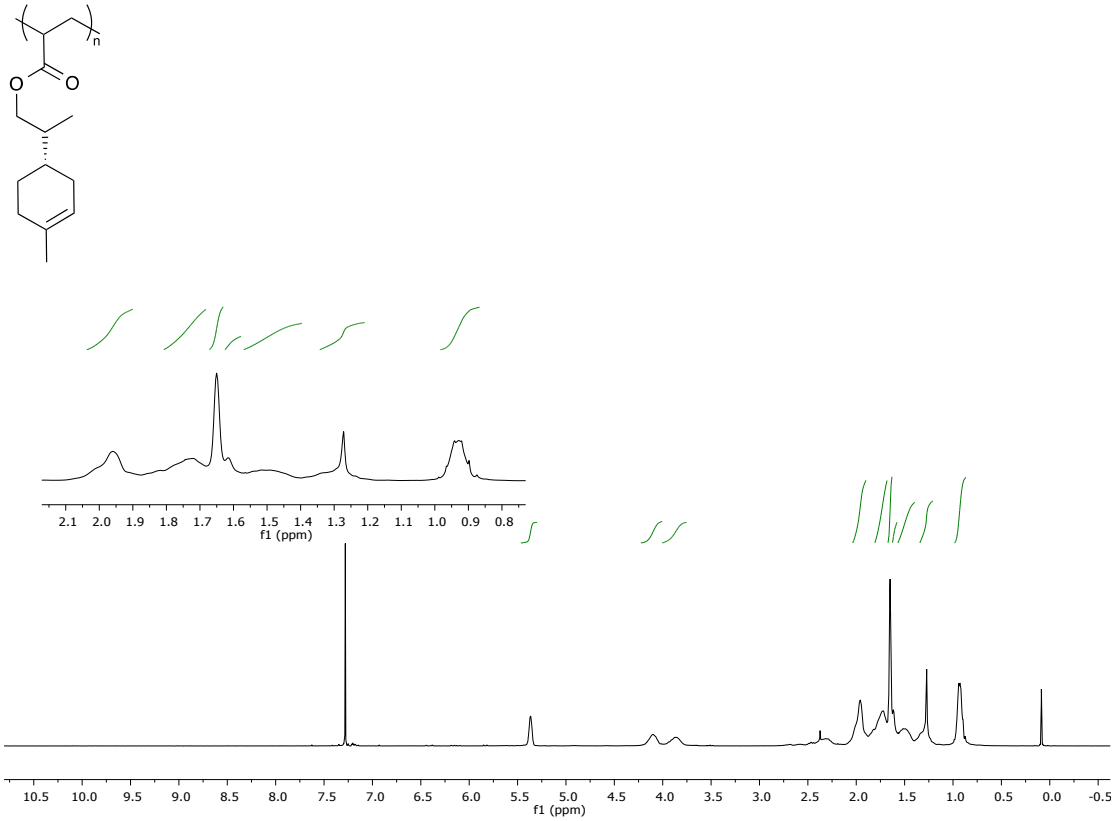
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.11 ppm





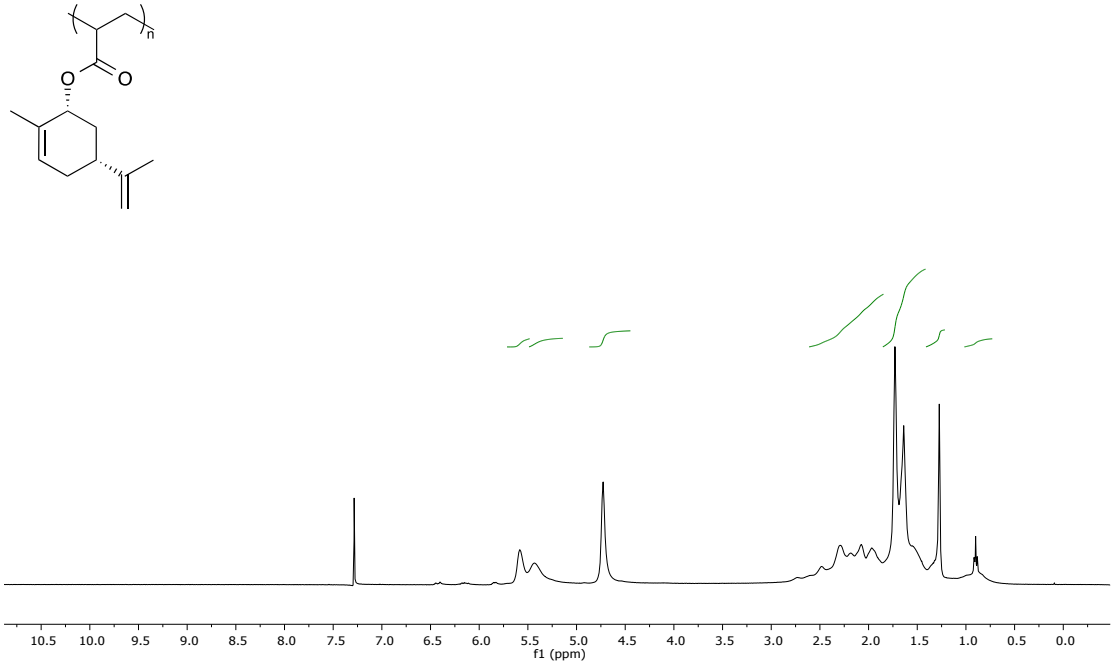
Poly(limonene acrylate) (3d)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.38 ppm



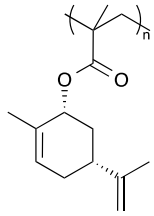
Poly(carvone acrylate) (4d)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.71 ppm



Poly (carvone methacrylate) (4e)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.36 ppm



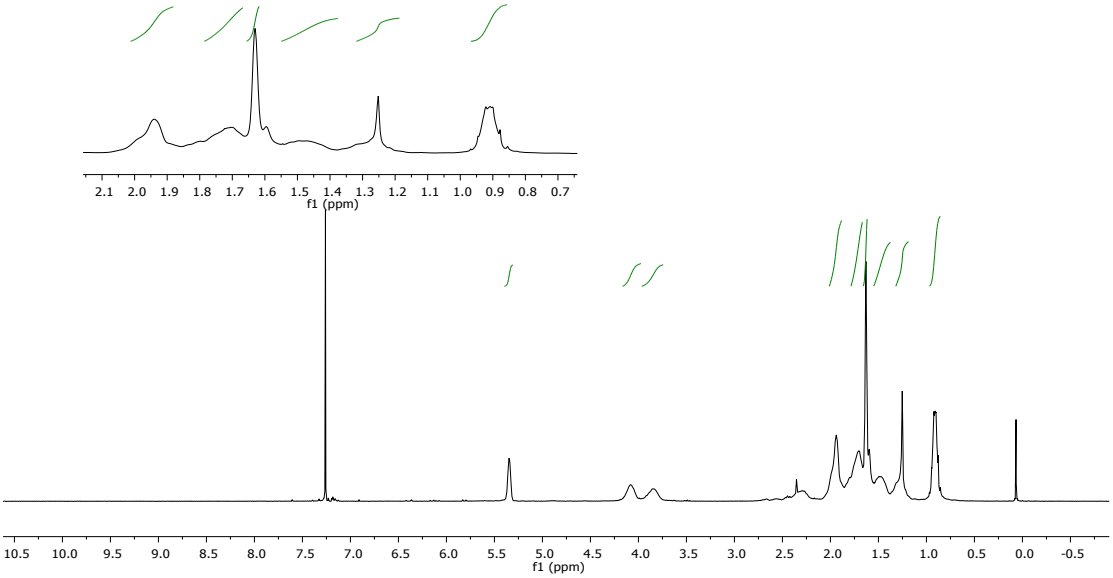
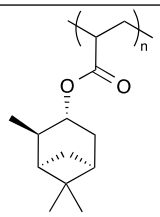
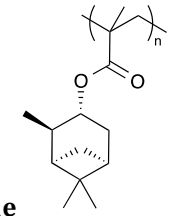
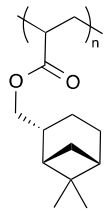
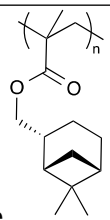
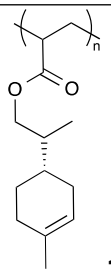
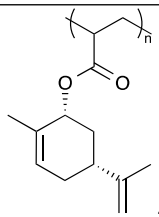


Table S2 – Polymers derived from terpene monomers

Entry	Monomer	Polymer structure	[DDM] (%wt)	Conversion (%)	M_n (g mol^{-1})	M_w/M_n	T_g (°C)
1	**1b**	 **1d**	5	95	4,800	1.34	12
2			1	97	15,100	2.04	63
3			0.5	99	23,600	2.20	71
4	**1c**	 **1e**	5	99	7,900	1.41	85
5			1	99	17,400	1.71	140
6			0.5	99	22,200	1.85	142
7	**2b**	**2d** 	0.5	97	31,500	2.06	41
8	**2c**	 **2e**	0.5	99	21,000	1.53	115
9	**3b**	 **3d**	0.5	88	17,000	2.23	-5
10	**4b**	 **4d**	5	60	10,600	8.32	5

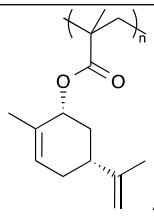
11	**4c**	 **4e**	0.5	99	26,500	2.24	117

Table S3 – Polymerisation of carvone acrylate demonstrating tendency to branch and crosslink.

Entry	Initiator	T (°C)	t (h)	[DDM] (% mol)	Conversion (%)	M_n (g mol^{-1})	M_w/M_n
1	AIBN	65	24	0	5	ND	ND
2	AIBN	65	48	0	Cross-linked	ND	ND
3	AIBN	90	3	0	30	27,400	14.1
4	AIBN	90	4	0	Cross-linked	ND	ND
5	V88	110	2	0	29	ND	ND
6	V88	110	2.5	0	Cross-linked	ND	ND
7	V88	110	4.5	5	60	10,600	8.34
8	V88	110	5	5	Cross-linked	ND	ND

ND – not determined

Polymerisation of methacrylate monomers (5 and 6) produced *via* catalytic route was heated at 65°C

Monomer	Initiator	T (°C)	T (hr)	Conversion (%)[a]	M_n (g mol^{-1})	M_w/M_n
5+6 (10:1)	AIBN	65	24	≥95	Crosslinked	

[a]$CHCl_3$ was added to the mixture and stirred for 24 hr. Soluble fraction was analysed by NMR and no monomer was detected.

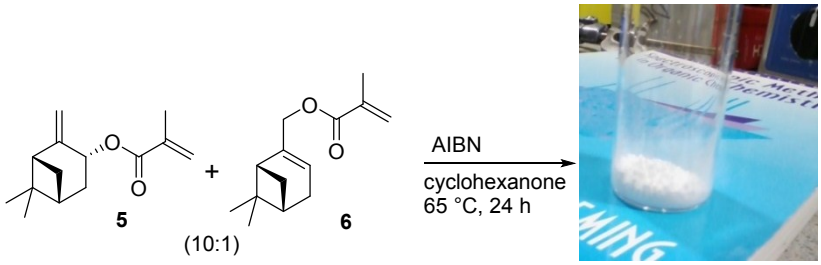
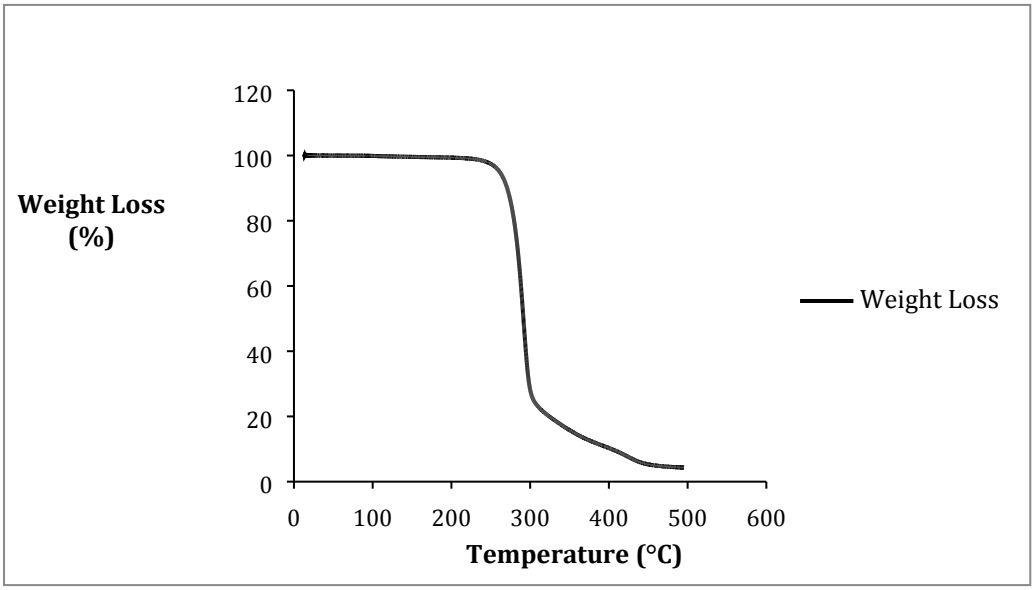


Table S4 and Figure S1

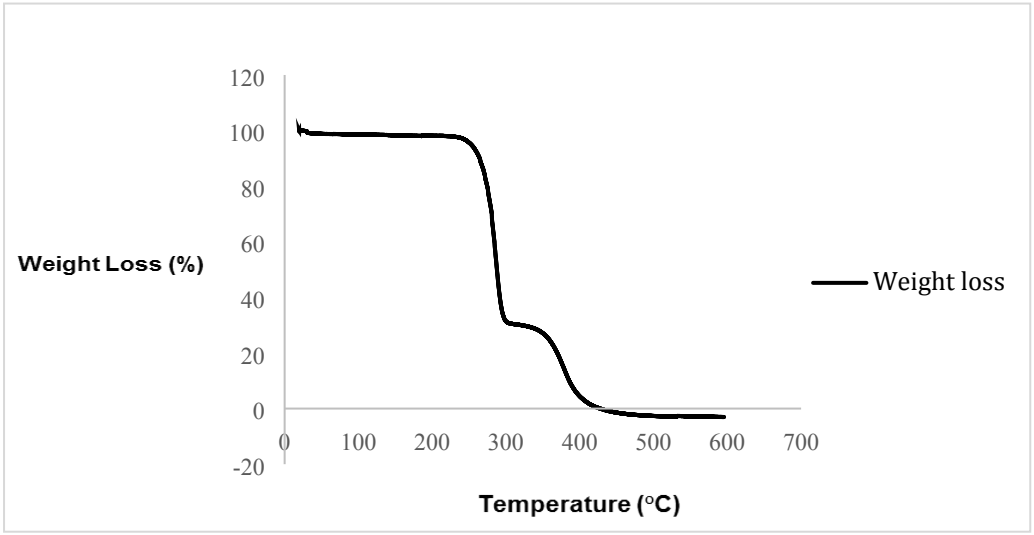
TGAs of polymers:

Samples were run on Q500 (TA Instruments) with autosampler, on platinum pans in nitrogen. Ramp rate 10 °C min^{-1}

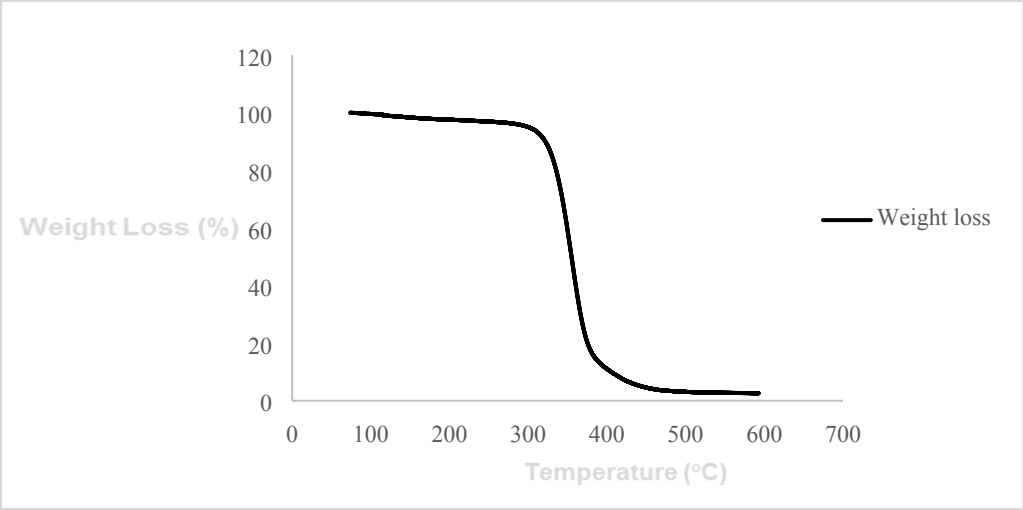
Poly(α-pinene acrylate) (1d)



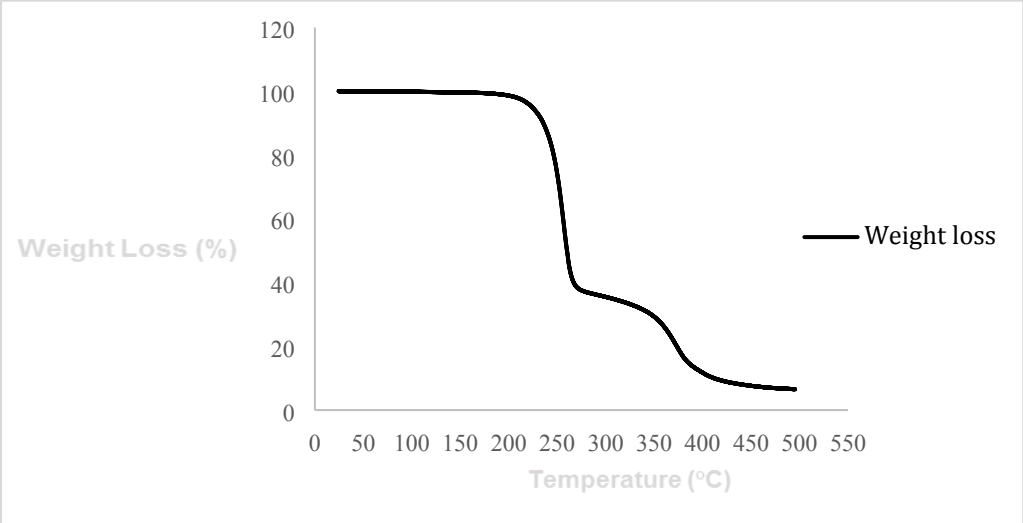
Poly(α-pinene methacrylate) (1e)



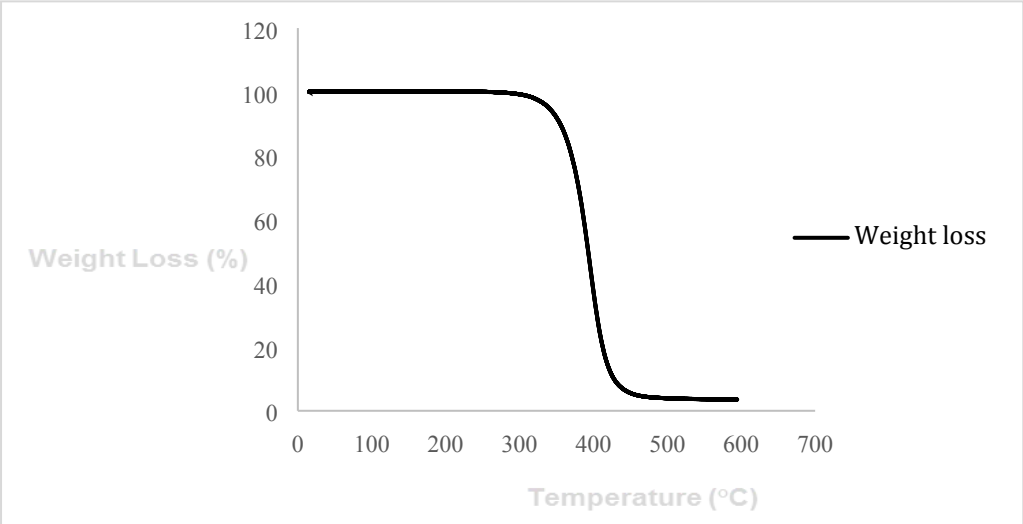
Poly(β-pinene acrylate) (2d)



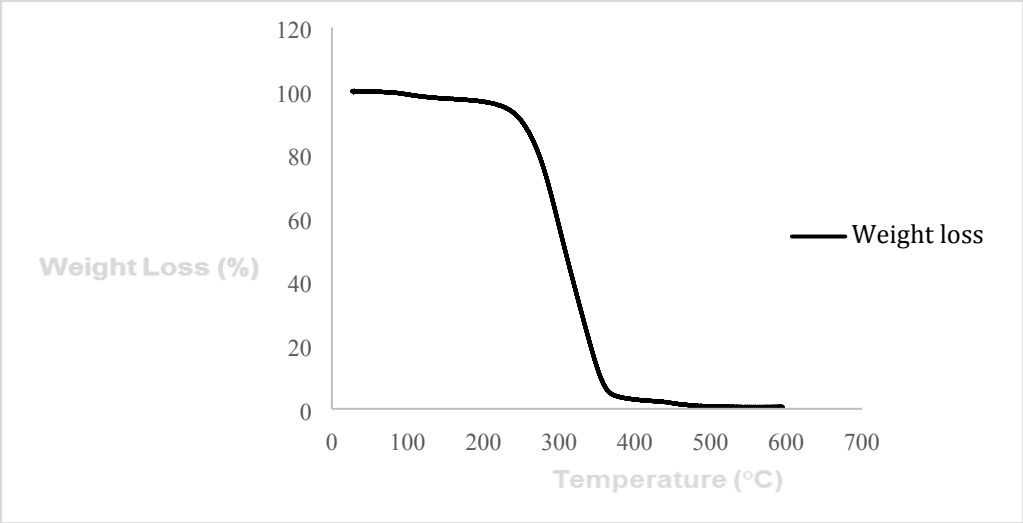
Poly(β-pinene methacrylate) (2e)



Poly(limonene acrylate) (3d)



Poly(carvone methacrylate) (4e)



FTIR-MONITORED POLYMERISATIONS

Materials and analytical techniques

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out using a Perkin-Elmer Spectrum 2000 FT-IR instrument (Norwalk, CT) equipped with a single reflection (ATR: attenuated total reflection) accessory unit (Golden Gate) from Graseby Specac LTD (Kent, England) and a TGS detector using the Golden Gate setup. Each spectrum collected was based on 16 scans averaged at 4.0 cm^{-1} resolution range of 600-4000 cm^{-1}. Data were recorded and processed using the software Spectrum from Perkin-Elmer.

Comparison between the reactivities of carvone-based acrylate and methacrylate

In order to test the susceptibility to polymerisation of the carvone derived monomers 4b and 4c we have conducted conventional FRP reactions. Both monomers were polymerised in bulk, in the presence of 0.5% wt of azobisisobutyronitrile (AIBN) as initiator at 65 °C for 24 hr (See Table S5).

Table S5. FRP of carvone derived monomers.

Monomer	Conversion (%)[a]	M_n (g mol^{-1})[b]	M_w/M_n [b]
4b acrylate	5	NA	NA
4c methacrylate	≥99[c]	52,300	4.38

*All reactions were carried out by mixing of 1g of monomer, 0.5% wt of AIBN and 1.5 mL of toluene in a 10 mL round-bottomed flask. The mixture was previously degassed by freeze-pump-thaw technique and then heated up to 65 °C for 24 h. [a]Determined by ^{1}H NMR. [b]Determined by GPC-SEC in THF using PMMA standards. [C] $CHCl_3$ was added to the polymer and the mixture was stirred for 24 hr. The mix was analysed by ^{1}H-NMR and no monomer was detected..

The polymerisation of the carvone-based acrylate **4b** gave very low conversion (5%) (Table S6, entry 1), suggesting either low propagation rate, inefficient initiation, formation of stable (persistent) radicals and/or an unfavourable structural conformation towards polymerisation. ^{1}H-NMR analysis showed that only the acrylate double bond was involved in the polymerization, while the other two double bonds remained unreacted.

By contrast, the carvone-methacrylate monomer **4c** was successfully polymerised to quantitative conversion. Subsequent analysis of the polymer revealed both high molecular weight and high dispersity (Đ) (Table S5, entry 2). This is characteristic of a FRP where no controlling agent is added but may also indicate some branching.

These results suggest a considerable difference in reactivity between monomers. Acrylate monomers are in general more reactive than their methacrylate analogues, while the opposite behaviour is observed in these carvone-derived monomers.

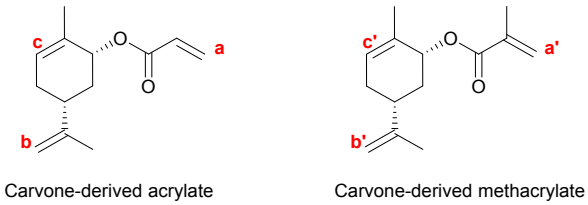


Figure S2. Double bonds present in the chemical structures of the carvone-derived monomers

In addition to chain growth, both carvone derivatives **4b** and **4c** can in theory crosslink, since they contain three double bonds each in their chemical structure (labelled as a,b,c and a',b',c' in Figure S1). However, the polymer obtained from **2** was soluble, which suggests only a low degree of branching/crosslinking. This strongly suggests that the methacrylate moiety is mainly responsible for the polymerisation, while the secondary exocyclic double bond has low reactivity at 65 °C.

The acrylate derivative possesses three double bonds and we hypothesize that olefin **a** is responsible for the polymerisation and that olefin **c** is too hindered to participate in radical polymerization reactions. Olefin **b** seems to have a low reactivity towards radical polymerization. This can be explained by the lack of electron-withdrawing character and resonance stabilization that the acrylate group presents.

The low yield obtained for the acrylates is likely a result of the different reactivity and stability of the two different radicals that can be formed after initial radical attack (initiator or propagation) (Figure S2).

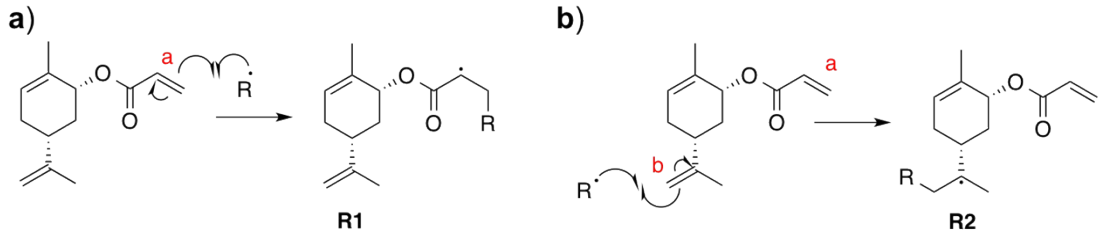


Figure S3. Possible radical structures formed after attack of a radical R to a carvone-based acrylate monomer unit.

If the radical attacks the acrylic double bond, a secondary radical is formed (**R1**) (**a**). Acrylate radicals are known to be unstable and therefore very reactive. On the other hand, attacking at the exocyclic double bond b would lead to a more stable tertiary radical (**R2**) with a low tendency towards polymerisation (**b**). That means that propagation through the acrylate double bond is kinetically favoured while the attack to the exocyclic double bond b is thermodynamically favoured. According to this hypothesis, it would appear that at 65ºC the most stable radical is formed (**R2**), but because it has only low reactivity the reaction does not proceed effectively, hence we see only very low yields (ca. 5%) of polymer product.

Careful optimisation of the system demonstrated that yields could be improved by working at higher T in order to overcome the low reactivity of **R2**. Different reaction temperatures were tested (90 and 110 °C) in the presence of 1,1'-azobis(cyclohexane-1-carbonitrile) (V88) as initiator (Table S6) in order to keep concentration of radicals low. The half-life time of V88 is just under 10 h at 90 °C, and 1h at 110 °C.

Table S6. Polymerisation of carvone acrylate 4b presence of V88 as initiator at different temperatures.

Entry	Initiator	T (ºC)	t (h)	[DDM]	Conversion (%)[a]	M_n (g mol^{-1})[b]	M_w/M_n[b]
1	V88	90	24	0	16	25,300	2.15
2	V88	110	2	0	17	ND	ND
3	V88	110	3	0	Cross-linked	ND	ND

*All reactions were carried out by mixing of 1g of monomer, 0.5% wt of V88 and 1.5 mL of cyclohexanone in a 10 mL round-bottomed flask. The mixture was previously degassed by freeze-pump-thaw technique and then heated up to the given temperatures. [a]Determined by ^{1}H NMR. [b]Determined by GPC-SEC in THF using PMMA standards.

POWDER COATING APPLICATION TESTING

Materials

Trimethylolpropane tris(3-mercapto- propionate (TMP-SH) was obtained from Bruno Bock Chemie. 2,2' -Azobis(2-methylpropionitrile) (AIBN) was bought from Merck. Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819) was obtained from Ciba Specialty Chemicals. The flow control agent Resiflow PV5 was bought from Worlée Chemie GmbH. benzoin were purchased from Sigma Aldrich .

Powder coating preparation and curing

30 g of poly(carvone methacrylate) was mixed in a laboratory blender with 4.5 g of TMP-SH (ene/SH molar ratio was 4:1), 0.54 g of the flow agent Resiflow PV5, 0.27 g of the degassing agent benzoin and 0.71 g of the UV initiator Irgacure 819. The mixture was subsequently fed to a home-built co-rotating twin-screw DSM Micro-Extruder®. Extrusion and melt-mixing occurred smoothly at 120 ^{o}C using a screw speed of 200 rpm and was performed using a back-mixing by-pass device. The resulting strand was turned into chips which were milled to a fine powder in a Retsch ZM100 machine with a 0.5 mm ring sieve at 18,000 rpm and then sieved (sieve fraction with particle size below 90 μm was used).

Figure S4 – Powder coating prepared by extrusion melt mixing and milling

This powder was subsequently deposited on 0.8 mm thick chromate aluminium Q-panels (type ALQ-46) using an electrostatic spraying gun. The plate with the deposited polymethacrylate powder was then heated for 2 min at 120 ^{o}C in an IR oven to force flow and film formation and subsequently irradiated twice in a home-designed UV curing chamber using a H-bulb lamp to cure the film. The total UV dosing, measured by a UV Power Puck PP200 was 6000 mJ cm^{-2}.

Property evaluation of coatings

Coating thicknesses were determined with a PosiTector 6000 coating thickness gage from DeFelsko Corporation. The impact properties of the polymethacrylate coatings were evaluated with a reverse falling dart impact test. Tests were performed with a 1 kg weight and 5/8″ ball dropped from a height of 1 m (ASTM D2794). The solvent resistance was considered as being satisfactory if 75 double-rubs (DR) with a tissue soaked in acetone did not show any visual damage of the coating. A metal adhesion test (using the lattice cutter or "*Gitterschnitt*") was performed according to ASTM D 3359. The smoothness of the powder coatings obtained upon full cure of the corresponding thermosetting powder compositions on ALQ-46 panels was determined by comparing the coatings with PCI Powder Coating Smoothness Panels (ACT Test Panels Inc., APR22163 (A) Batch: 50708816). The rating of smoothness ranges from 1 to 10, with 1 representing the roughest and 10 the smoothest coating. Pencil hardness was tested with a set of pencils with varying hardness values, ranging from 1H to 9H. Konig hardness was measured according to ASTM D4366 and cupping test according to ISO 1502.

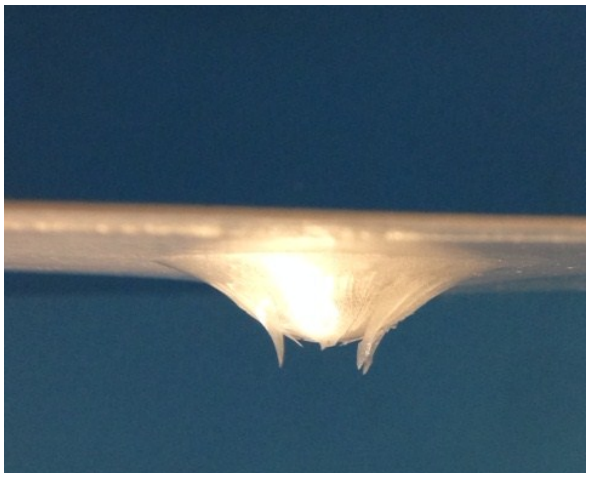


Figure S5 – Reverse falling dart experiment demonstrates adhesion of the carvone methacrylate to the aluminium plate though this does demonstrate de-lamination which will be addressed in future through optimization.