Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFO

Controlled Synthesis of Methacrylate and Acrylate Diblock Copolymers via End-Capping using CCTP and FRP

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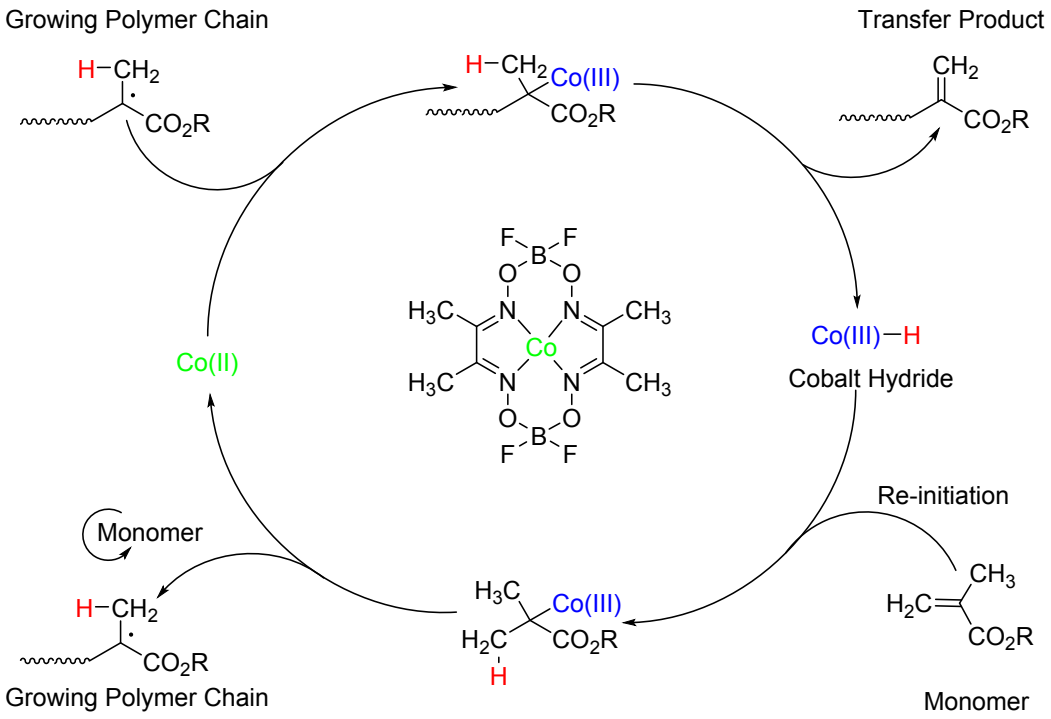
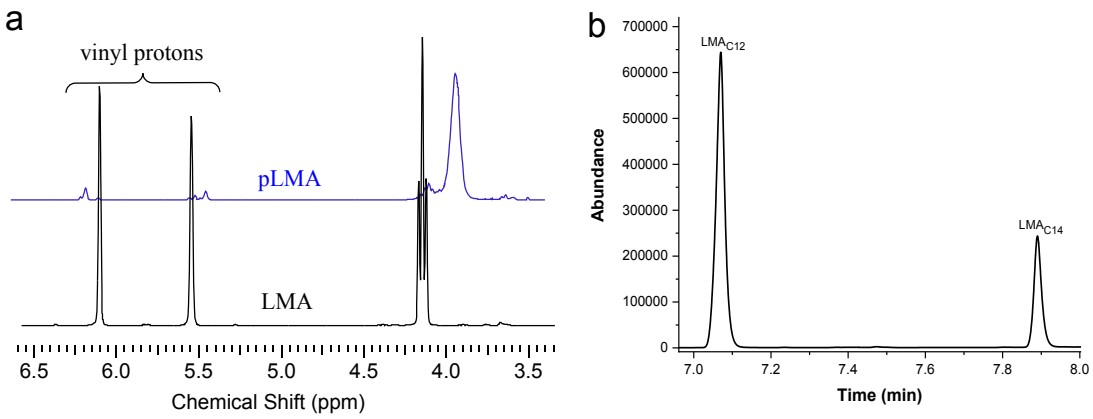
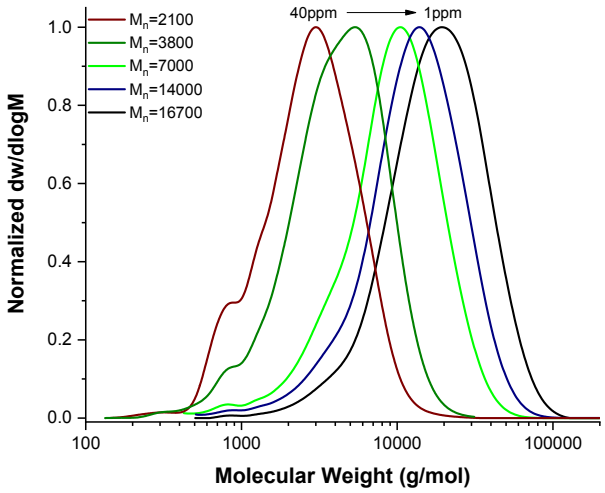


Supplementary Figure 1: Main catalytic cycle for bis(boron difluorodimethylglyoximate) cobalt(II) (CoBF) mediated catalytic chain transfer polymerisation.



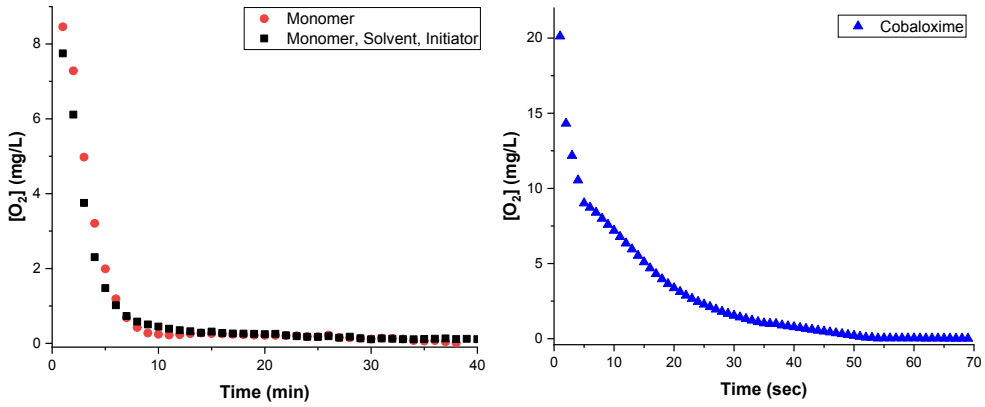
Supplementary Figure 2: a) ^{1}H NMR of PLMA macromonomer and LMA monomer. Monomer conversion of polymer = 95% based on integrals. b) Gas chromatography of LMA monomer, the ratio of LMA_{C12} to LMA_{C14} was 77:23 based on integrals.



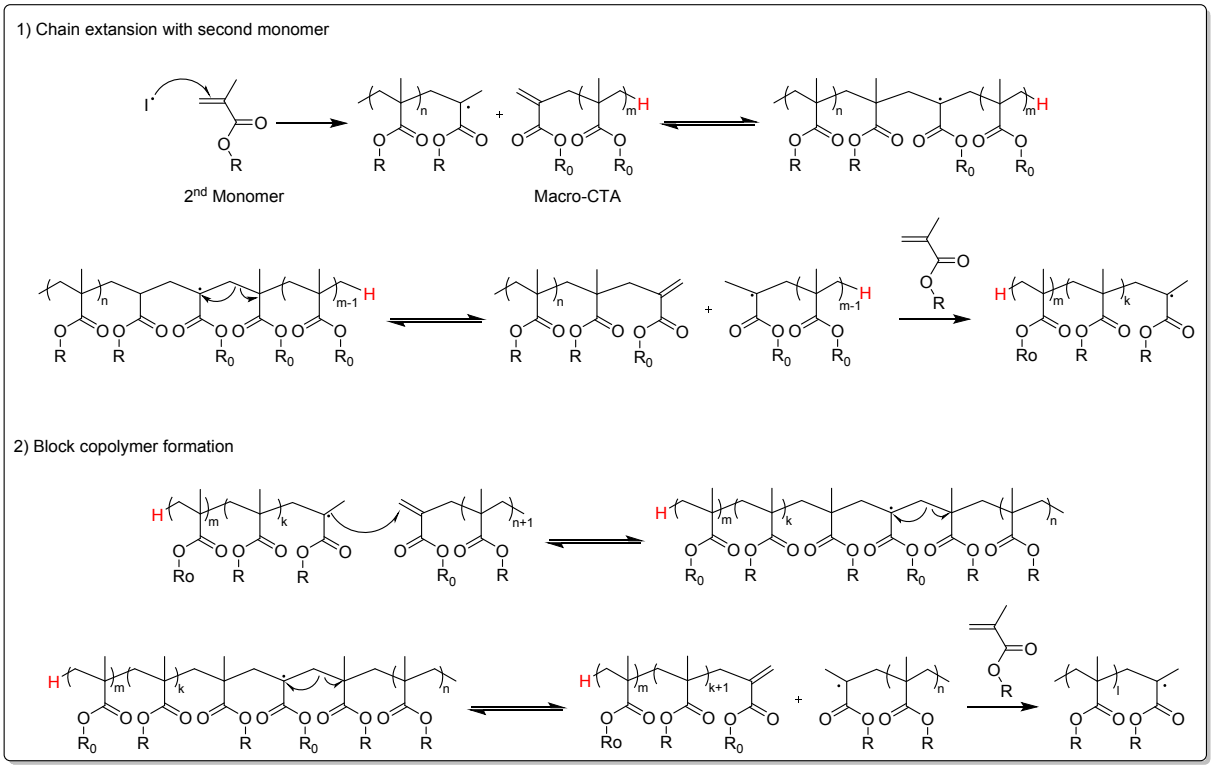
Supplementary Figure 3: GPC results of pLMA macromonomers made via CCTP. Concentration of Co(MePh)BF was 1-40ppm (relative to monomer). Polydispersity index of products: 1.53-1.65.

Supplementary Table 1: Data used for the calculation of the chain transfer activity of Co(MePh)BF in CCTP polymerisation of LMA in toluene.

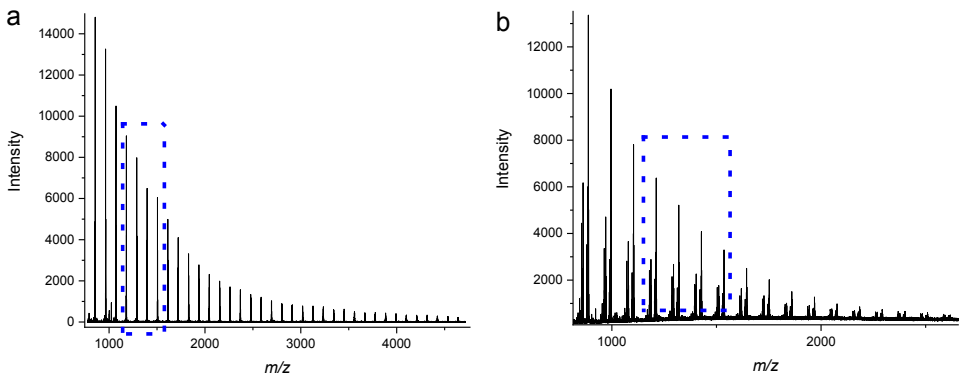
[Co] (ppm)	$M_{n,GPC}$	Đ	Conv. NMR,%
1	16700	1.64	98
2	14000	1.53	98
10	7000	1.65	95
20	3800	1.64	96
40	2100	1.62	97



Supplementary Figure 4: Graphical illustration of the decrease in oxygen concentration during degassing for a) the dissolved oxygen in the monomer or a solution of the monomer, solvent and initiator and b) the oxygen present in the round bottom flask containing the cobaloxime catalyst.



Supplementary Figure 5: Proposed mechanism of SF-RAFT of methacrylates.



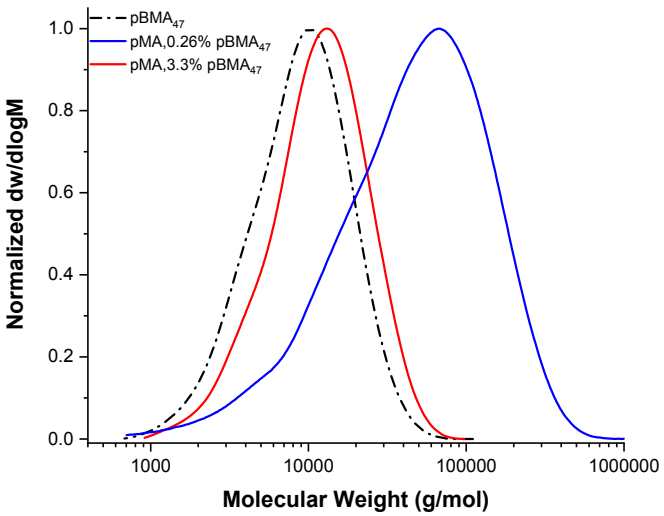
Supplementary Figure 6: a) Full MALDI-ToF spectra of the copolymerisation of $pMMA_4$ with MMAd8. b) Full MALDI-ToF spectra of the copolymerisation of $pMMA_4$ with MMAd8, in the presence of CoBF.

Supplementary Table 2: Characterisation of the ionised peaks of Figures 2a and 2b.

Figure 2a		
Peak (*m/z*)	**DP of $pMMAd_8$**	**Product**
1179.962	7	$MMA_3(MMAd_8)_7MMA_1 + Na^+$
1288.117	8	$MMA_3(MMAd_8)_8MMA_1 + Na^+$
1396.263	9	$MMA_3(MMAd_8)_9MMA_1 + Na^+$
Figure 2b		
Peak (*m/z*)	**DP of $pMMAd_8$**	**Product**
1179.593	7	$MMA_3(MMAd_8)_7MMA_1 + Na^+$
1186.635	7	$MMA_3(MMAd_8)_7 + Na^+$
1204.70	7	$(MMAd_8)_7MMA_1 + Na^+$
1211.785	7	$D\text{-}(MMAd_8)_7 + Na^+$
1287.665	8	$MMA_3(MMAd_8)_8MMA_1 + Na^+$
1294.707	8	$MMA_3(MMAd_8)_8 + Na^+$
1312.813	8	$(MMAd_8)_8MMA_1 + Na^+$
1319.857	8	$D\text{-}(MMAd_8)_8 + Na^+$

Supplementary Table 3: Results of MALDI-ToF MS of the polymerisation of MA in the presence of 4.3 mol% MMA_2 (sample 4) and 4.3 mol% MMA_4 (sample 9).

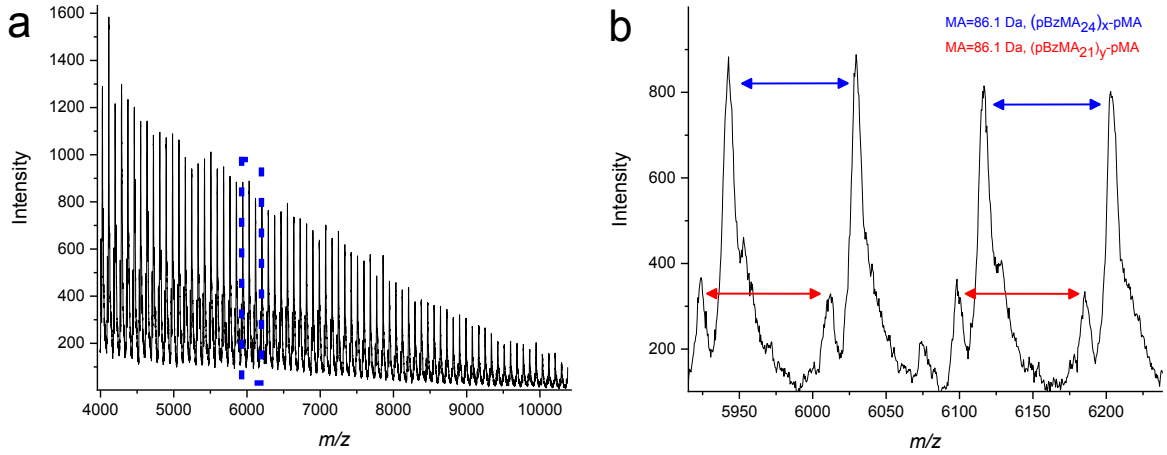
Peak (*m/z*)	**DP of pMA**	**Product**
Sample 4		
2459.226	22	$pMA\text{-}(MMA_2)_2 + I + Na^+$
2487.265	20	$pMA\text{-}(MMA_2)_3 + I + Na^+$
2516.265	18	$pMA\text{-}(MMA_2)_4 + I + Na^+$
2545.265	23	$pMA\text{-}(MMA_2)_2 + I + Na^+$
2573.296	21	$pMA\text{-}(MMA_2)_3 + I + Na^+$
2603.299	19	$pMA\text{-}(MMA_2)_4 + I + Na^+$
Sample 9		
3061.101	29	$pMA\text{-}(MMA_4)_1 + I + Na^+$
3090.987	34	$pMA + I + Na^+$
3118.160	25	$pMA\text{-}(MMA_4)_2 + I + Na^+$
3147.244	30	$pMA\text{-}(MMA_4)_1 + I + Na^+$
3176.068	35	$pMA + I + Na^+$
3203.242	26	$pMA\text{-}(MMA_4)_2 + I + Na^+$



Supplementary Figure 7: GPC results of the free radical polymerisation of pMA in the presence of 0.26 and 3.3 mol% pBMA.

Supplementary Table 4: GPC data of the free radical polymerisation of MA in the presence of pBMA.

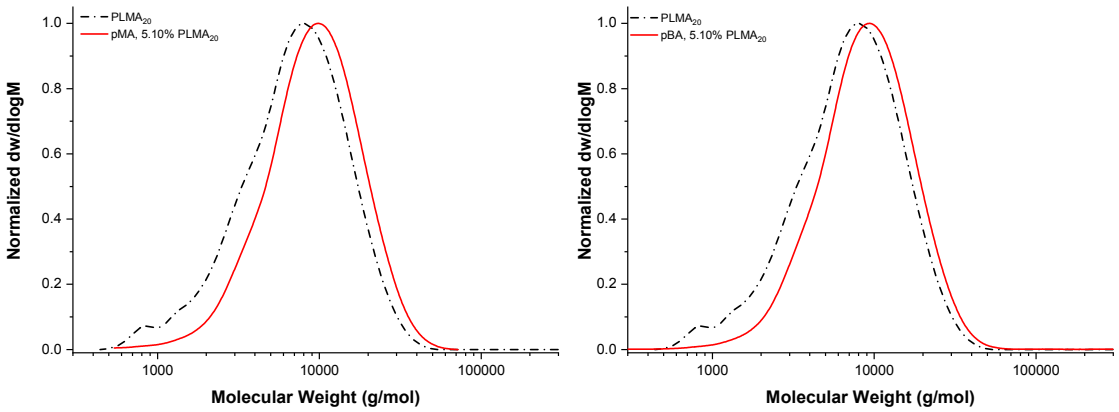
Reagents	*Macromonomer to Monomer mol%*	$M_{n,GPC}$	*Đ*
$PBMA_{47}$	-	6700	1.74
$PBMA_{47}PMA_{x}$	0.26	8700	1.68
$PBMA_{47}PMA_{y}$	3.3	20200	3.82



Supplementary Figure 8: a) Full MALDI-ToF spectra of the copolymerisation of MA with 0.2 mol% pBzMA macromonomer, showing the diblock copolymer formation via end-capping. b) Expansion of the MALDI-ToF (a) of the in the 5920-6230 m/z range.

Supplementary Table 5: GPC data of the free radical polymerisation of MA in the presence of pBzMA.

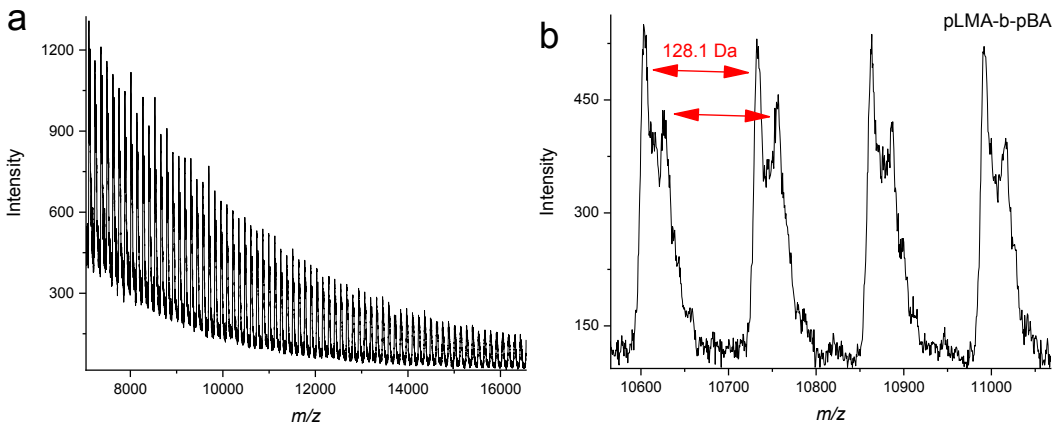
Reagents	*Macromonomer to Monomer mol%*	$M_{n,GPC}$	*Đ*
$PBzMA_{24}$	-	4200	1.72
$PBzMA_{24}PMA_{x}$	0.10	25000	3.83
$PBzMA_{24}PMA_{y}$	0.20	20200	3.82



Supplementary Figure 9: GPC results of the free radical polymerisation of a) MA in the presence of 5.1 mol% pLMA and b) BA in the presence of 5.1 mol% pLMA.

Supplementary Table 6: GPC data of the free radical polymerisation of MA and BA in the presence of pLMA.

Reagents	*Macromonomer to Monomer mol%*	$M_{n,\,GPC}$	*Đ*
$PLMA_{18}PMA_{x1}$	0.67	10700	2.27
$PLMA_{18}PMA_{x2}$	1.67	7600	2.05
$PLMA_{20}PMA_{x3}$	5.10	6800	1.63
$PLMA_{20}PBA_{y1}$	0.18	23000	2.54
$PLMA_{20}PBA_{y2}$	5.10	6800	1.57



Supplementary Figure 10: a) Full MALDI-ToF spectra of the copolymerisation of BA with 0.18 mol% pLMA macromonomer, showing the diblock copolymer formation via end-capping. b) Expansion of the MALDI-ToF (a) of the in the 10550-11050 m/z range.

Equipment

All techniques of characterization and analysis were used for the products synthesized are listed below:

- ***Nuclear Magnetic Resonance (^{1}H NMR, ^{13}C NMR, and DOSY NMR):*** All spectra were recorded on Bruker DPX-300, DPX-400 and DPX-500 MHz spectrometers using deuterated chloroform ($CDCl_3$) purchased from Aldrich. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane.

- ***Gel Permeation Chromatography (GPC)***: All chromatography measurements were conducted using an Agilent 390-LC MDS instrument equipped with a differential refractive index (DRI) and dual wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 µm guard column. The eluent is THF with 2 % TEA (triethylamine) and 0.01 % BHT (butylated hydroxytoluene) additives. Samples were run at 1mL/min at 30'C. Poly(methyl methacrylate) and polystyrene standards (Agilent Easy*Via*ls) were used for calibration. Analyte samples were filtered through a GVHP membrane with 0.22 µm pore size before injection. Respectively, experimental molar mass (Mn_{SEC}) and dispersity (*Đ*) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

- ***Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS)***: Matrix-assisted laser desorption ionization mass spectrometry was conducted by the use of a Bruker Daltonics Ultra flex II MALDI-ToF-MS mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. Solutions were prepared as follows: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrix (20 mg/mL), sodium iodide as cationization agent (6 mg/mL) in tetrahydrofuran (20 µl) and sample (10 mg/mL) were mixed, and 0.5 µL of the mixture was applied on the target plate. Spectra recording was made in linear mode calibrating PEG-Me 1900-10000 Da.

- ***Gas Chromatography-Flame Ionisation Detection (GC-FID)***: Gas chromatography-flame ionisation detection (GC-FID) was performed on a Shimadzu GC-2014 equipped with a Shimadzu AO20i autosampler. The carrier gas is hydrogen, supplied by an external hydrogen generator. The GC is fitted with a polar Stabilwax-DA column (30 m length, 0.32 mm ID and 0.25 µm film thickness). The injection volume is 1 µl with a 39 split ratio. The injection temperature is 250^{o}C

and the flame temperature is 300°C. The heating profile is 60-200°C at a rate of 10°C/minute and then 200-240°C at 15°C/minute and held for 3 minutes.