Supporting information

Influence of *para*-substitution on the polymerisation kinetics of 2-phenyl-2-oxazolines

Chloe M. Shilling, Lloyd A. Shaw, Juan A. Aguilar, William D. G. Brittain* and Clare S. Mahon*

Chemistry Department, Durham University, Lower Mount Joy, South Road, Durham, DH1 3LE

Email: william.d.brittain@durham.ac.uk, clare.s.mahon@durham.ac.uk

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1. Synthetic methods and characterisation

1.1 Reagents

All chemicals were purchased from either Fisher Scientific, Merck, Alfa Aesar, Apollo Scientific, Fluorochem or TCI and used without further purification unless otherwise stated.

1.2 Instruments

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance III spectrometer, with ^{1}H at 400.20 MHz, ^{13}C at 100.61 MHz and ^{19}F at 376.33 MHz. All coupling constants are reported in Hertz (Hz). Chemical shifts are reported in ppm and are referenced to residual solvent peaks; $CHCl_3$ (^{1}H 7.26 ppm, ^{13}C 77.0 ppm), DMSO (^{1}H 2.50 ppm, ^{13}C 39.5 ppm), or MeOH (^{1}H 4.78, 3.31 ppm, ^{13}C 50.1 ppm).

Microwave-assisted polymerisations were performed using a Biotage Initiator EXP EU at 90 W in 0.5 mL reaction vials.

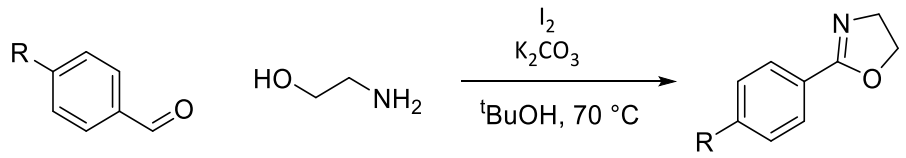
Gel permeation chromatography (GPC) was conducted in DMF (HPLC Grade, Fisher Scientific) with 1 g/L LiBr eluent on an Agilent 1260 instrument equipped with a differential refractive index detector, a dual-angle light scattering detector (15 ° and 90 °), a viscometer and a pair of PL gel 5 μm Mixed D 300 × 7.5 mm columns with a guard column (Polymer Laboratories Inc.) in series at 50 °C, 0.6 mL/min. Molecular weights were determined by comparison to near-monodisperse poly(methyl methacrylate) standards using Agilent Infinity software. Samples were made up between 2-10 mg/mL in the same DMF (HPLC grade) with 1 g/L LiBr eluent and passed through a 0.2 μm nylon syringe filter prior to analysis.

Mass spectrometry was performed on an Acquity ultra-performance liquid chromatography (UPLC) system with a BEH C18 1.7μm (2.1mm x 50mm) column in water containing formic acid (0.1%v/v): acetonitrile. The flow of solvent from the Acquity UPLC system is introduced into the electrospray ion source. The operating mass range is 100-2000 μ. The Acquity photodiode array detector provides absorbance data from 210 nm to 400 nm.

Flash column chromatography was performed on a Teledyne CombiFlash NextGen 300+. Melting points were determined uncorrected using a Cole-Parmer MP-200D Stuart Digital Melting Point Apparatus 240 VAC, with a range of ambient to 300 °C (1°C resolution).

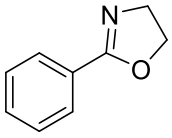
1.3 General synthesis of 2-phenyl-2-oxazoline and para-substituted derivatives

Procedure was modified from a previous method reported by Ishihara *et al.*[1]



Under an argon atmosphere, the corresponding para-substituted benzaldehyde (1.0 equiv., 50 mmol) was dissolved in *tert*-BuOH (250 mL) to which 2-aminoethanol (1.1 equiv., 55 mmol) was added. The solution was stirred for 30 min before K_2CO_3 (3.0 equiv., 150 mmol) and I_2 (2.0 equiv., 100 mmol) were added. The solution was then heated to 70 °C and stirred for 12 h before being cooled to room temperature. The reaction was then quenched with sat. $Na_2S_2O_3$ until the dark purple colour had dissipated to a yellow colour. The product was then extracted with EtOAc (3 ×150 mL). Organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The recovered residue was then purified using automated flash chromatography (100 % hexane to 100 % EtOAc, 80 g Teledyne RediSep Gold Silica). Monomers which were solids at room temperature were recrystallised from a mixture of hexane and ethyl acetate.

2-Phenyl-2-oxazoline (1)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from benzaldehyde (50 mmol, 5.1 mL, 5.3 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale-yellow liquid (5.1 g, 69%).

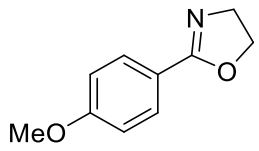
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (dd, *J* = 7.0, 1.6, 2H), 7.32 (m, 3H), 4.30 (t, *J* = 10.0, 2H), 3.93 (t, *J* = 10.0, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.2, 130.9, 128.0, 127.8, 127.4, 67.2, 54.6.

m/z (ESI) 148.1 (100%, $[M+H]^+$).

Spectroscopic data were consistent with previously reported literature values.[1]

2-(4-Methoxyphenyl)-2-oxazoline (2)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-methoxybenzaldehyde (50 mmol, 6.8 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale-yellow solid (6.7 g, 69%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81, d, *J* = 9.0, 2H), 6.84 (d, *J* = 9.0, 2H), 4.0 (t, *J* = 9.3, 2H), 3.95 (t, *J* = 9.3, 2H), 3.77 (s, 3H).

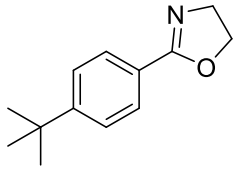
^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.4, 162.0, 129.8, 120.3, 113.7, 67.5, 55.3, 54.9.

m/z (ESI) 178.1 (100%, $[M+H]^+$).

m.p. 56-58 °C.

Spectroscopic data were consistent with previously reported literature values.[1]

2-(4-*tert*-Butylphenyl)-2-oxazoline (3)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-tert-butylbenzaldehyde (50 mmol, 8.1 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale yellow solid (6.5 g, 64%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (dt, *J* = 8.6, 1.9, 2H), 7.35 (dt, *J* = 8.6, 1.9, 2H), 4.34 (t, *J* = 9.4, 2H), 3.96 (t, *J* = 9.3, 2H), 1.26 (s, 9H).

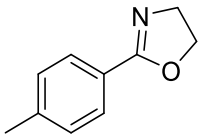
^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.7, 154.7, 128.0, 125.3, 124.9, 67.5, 54.9, 35.0, 31.2.

m/z (ESI) 204.1 (100%, $[M+H]^+$).

m.p. 69-71 °C.

Spectroscopic data were consistent with previously reported literature values.[1]

2-(4-Methylphenyl)-2-oxazoline (4)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-methylbenzaldehyde (50 mmol, 6.0 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale yellow solid (5.5 g, 68%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.0, 2H), 7.21 (d, *J* = 8.0, 2H), 4.41 (t, *J* = 9.5, 2H), 4.04 (t, *J* = 9.5, 2H), 2.39 (s, 3H).

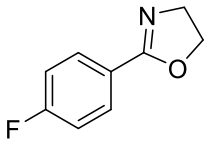
^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.8, 141.7, 129.2, 128.2, 125.1 67.6, 55.0, 21.6.

m/z (ESI) 162.1 (100%, $[M+H]^+$).

m.p. 69-71 °C.

Spectroscopic data were consistent with previously reported literature values.[1]

2-(4-Fluorophenyl)-2-oxazoline (5)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-fluorobenzaldehyde (50 mmol, 6.2 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale orange solid (4.5 g, 46%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (dd, *J* = 8.9, 5.4, 2H), 7.09 (dd, *J* = 9.0, 8.5, 2H), 4.42 (t, *J* = 9.5, 2H), 4.05 (t, *J* = 9.5, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.5 (d, $J_{C\text{-}F}$ = 32.0 Hz, 1C), 163.4, 130.4, 124.0, 115.4 (d, $J_{C\text{-}F}$ = 22.1 Hz, 1C), 115.4, 67.7, 55.0.

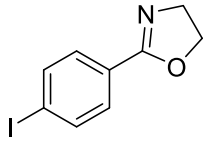
^{19}F NMR ($CDCl_3$, 376 MHz) δ -108.34 – -108.44 (m)

m/z (ESI) 166.8 (100%, $[M+H]^+$).

m.p. 84-85 °C

Spectroscopic data were consistent with previously reported literature values.[2]

2-(4-Iodophenyl)-2-oxazoline (6)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-iodobenzaldehyde (20 mmol, 4.6 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica (100% hexane to 100% EtOAc) to give the desired product as a pale yellow solid (4.2 g, 75%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (m, 2H), 7.59 (m, 2H), 4.36 (t, *J* = 9.5, 2H), 3.98 (t, *J* = 9.5, 2H).

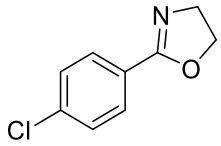
^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.0, 137.6, 129.7, 127.3, 98.2, 67.8, 55.0.

m/z (ESI) 274.2 (100%, $[M+H]^+$).

m.p. 81-82 °C.

Spectroscopic data were consistent with previously reported literature.[3]

2-(4-Chlorophenyl)-2-oxazoline (7)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-chlorobenzaldehyde (50 mmol, 7.1 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale orange solid (5.7 g, 58%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, *J* = 8.6, 2H), 7.38 (d, *J* = 8.6, 2H), 4.44 (t, *J* = 9.4 2H), 4.05 (t, *J* = 9.4, 2H).

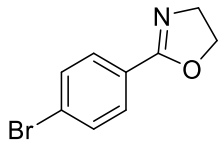
^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.0, 137.6, 129.7, 128.8, 126.4, 67.9, 55.1.

m/z (ESI) 182.1 (100%, $[M+H]^+$).

m.p. 84-85 °C.

Spectroscopic data were consistent with previously reported literature.[3]

2-(4-Bromophenyl)-2-oxazoline (8)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-bromobenzaldehyde (30 mmol, 5.6 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale orange solid (4.5 g, 67%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (m, 2H), 7.57 (m, 2H), 4.47 (t, *J* = 9.4 2H), 4.08 (t, *J* = 9.4, 2H).

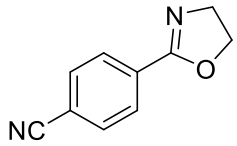
^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.9, 131.6, 129.7, 126.7, 126.0, 67.8, 55.0.

m/z (ESI) 227.9 (100%, $[M+H]^+$).

m.p. 99-101 °C.

Spectroscopic data were consistent with previously reported literature. [1]

2-(4-Cyanophenyl)-2-oxazoline (9)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-cyanobenzaldehyde (50 mmol, 6.0 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100% hexane to 100% EtOAc) to give the desired product as a pale orange solid (4.0 g, 47%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, *J* = 8.7, 2H), 7.71 (d, *J* = 8.7, 2H), 4.48 (t, *J* = 9.5, 2H), 4.10 (t, *J* = 9.5, 2H).

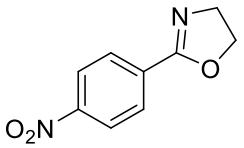
^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.1, 132.2, 132.0, 128.8, 118.3, 114.7, 68.1, 55.2.

m/z (ESI) 173.1 (100%, $[M+H]^+$).

m.p. 104-105 °C.

Spectroscopic data were consistent with previously reported literature.[1]

2-(4-Nitrophenyl)-2-oxazoline (10)



Prepared according to the general synthesis of 2-phenyl-2-oxazolines (Section 1.3) from 4-nitrobenzaldehyde (50 mmol, 7.5 g). The crude material was purified using automated column chromatography (Stationary phase: RediSep Gold® 80 g HP silica. 100 % hexane to 100% EtOAc) to give the desired product as a pale yellow solid (5.2 g, 54%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (d, *J* = 8.8, 2H), 8.06 (d, *J* = 8.9, 2H), 4.44 (t, *J* = 10.0, 2H), 4.06 (t, *J* = 10.0, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 162.9, 149.4, 133.5, 129.2, 123.6, 68.2, 55.3

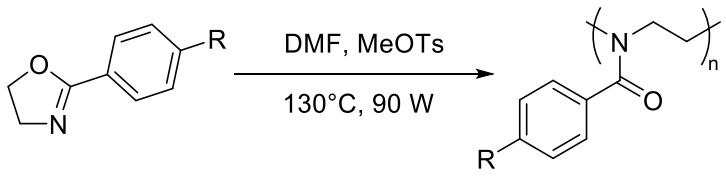
m/z (ESI) 193.1 (100%, $[M+H]^+$).

m.p. 177-178 °C.

Spectroscopic data were consistent with previously reported literature. [4]

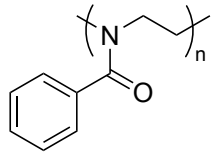
1.4 General procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines

Synthesis was adapted from a procedure outlined by Sinnwell *et al.*[5]



A solution of para-substituted 2-phenyl-2-oxazoline (4 M, 2.0 mL) was prepared in freshly acquired anhydrous DMF, packaged under an inert atmosphere. Methyl tosylate (0.13 mmol, [M]/[I] = 100) was then added under argon. A zero-time point sample was taken of this solution before 5 × 0.3 mL aliquots were placed in microwave vials (0.5 mL capacity) and sealed under argon. Each filled vial was then placed in a microwave reactor (90 W, 130 °C) for the allotted time period, after which the product was isolated by diluting the reaction mixture with methanol followed by precipitation into diethyl ether. Each sample was then analysed by GPC and ^{1}H NMR spectroscopy.

P1 (n = 83)



P1 was prepared according to the general procedure for the polymerisation of *para*-substituted 2-phenyl-2-oxazolines (Section 1.4), [**M1**]:[I] = 100:1. **P1** was isolated by diluting the reaction mixture with methanol followed by precipitation into diethyl ether.

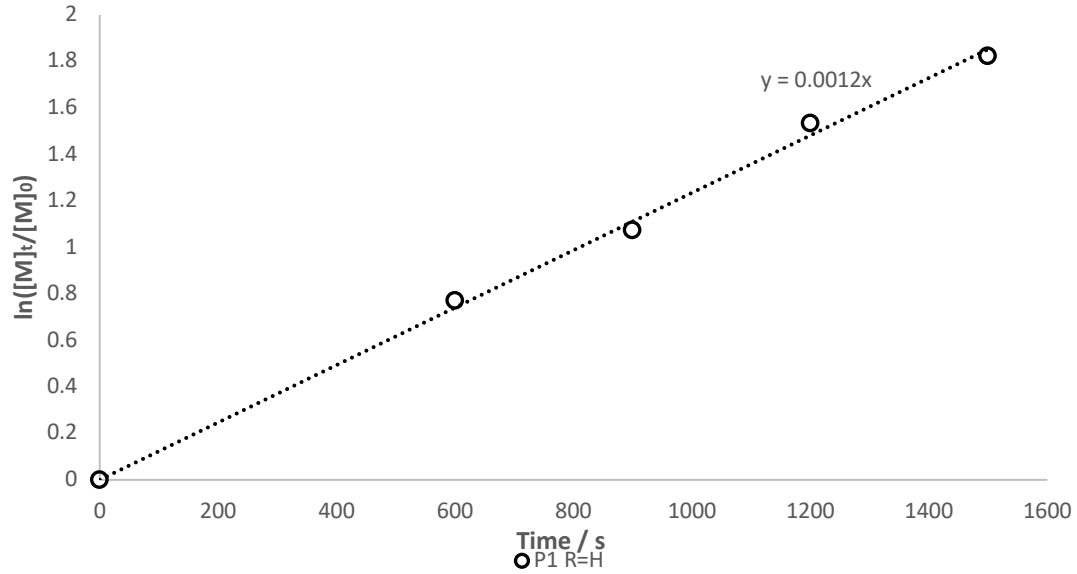


Figure S1 Kinetic analysis of the homopolymerisation of **1**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

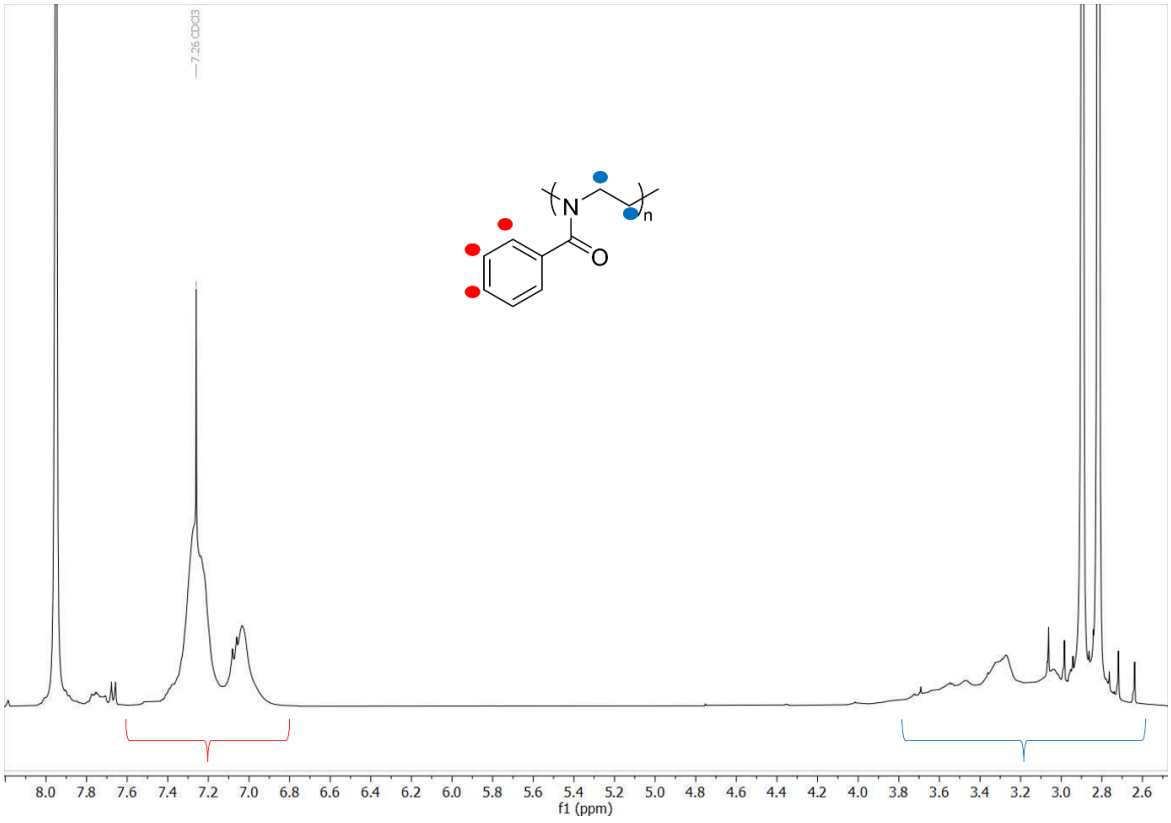


Figure S2 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly(2-phenyl-2-oxazoline) **P1**.

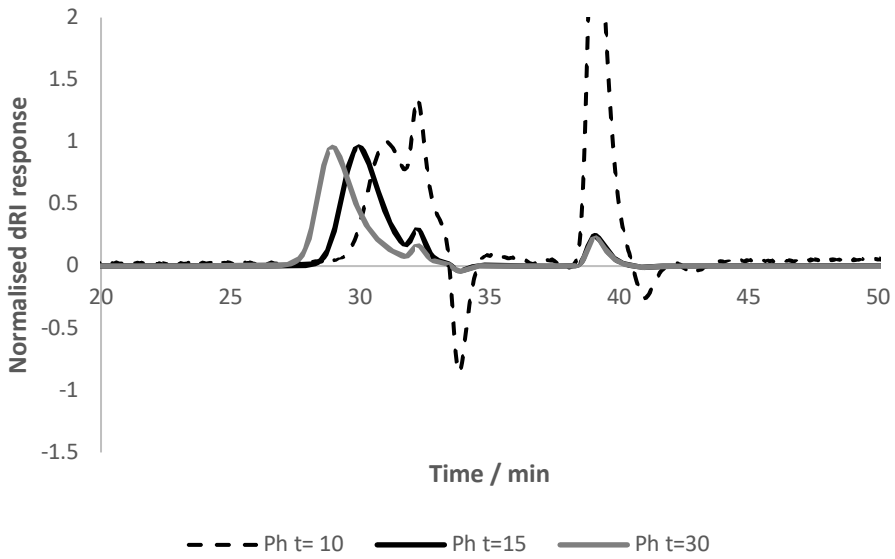


Figure S3 GPC chromatograms acquired during polymerisation of **1.** The time attributed to each sample relates to the length of time each polymerisation was irradiated for (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C).

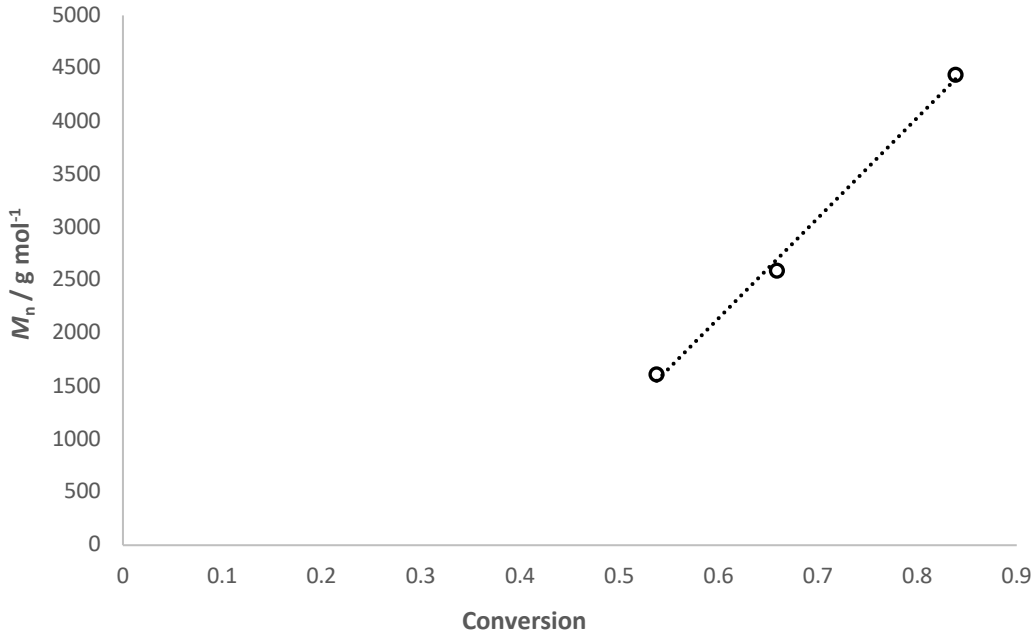


Figure S4 M_n as a function of conversion for polymerisation of **1**. M_n values determined using GPC by comparison to near-monodisperse poly(methyl methacrylate) standards.

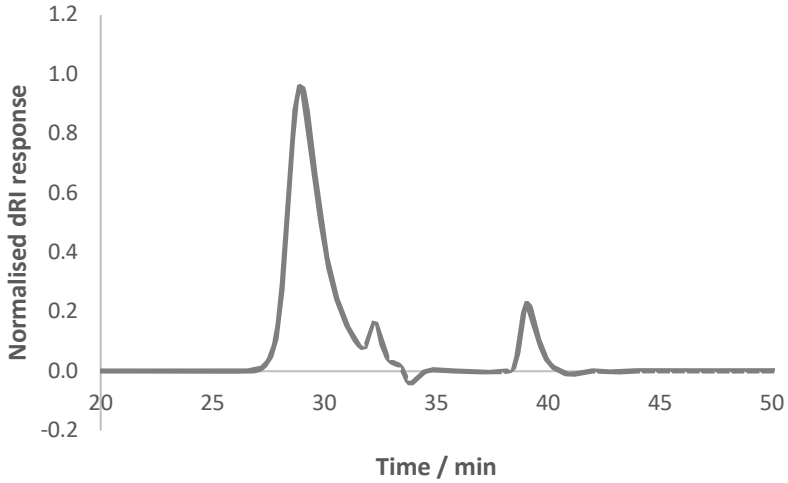
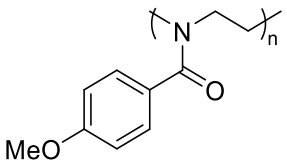


Figure S5 GPC analysis of **P1** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 2700 g mol^{-1}, M_w 5400 g mol^{-1}; Đ 1.2.

P2 (n = 25)



P2 was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines, [**2**]:[I] = 100:1 (Section 1.4). **P2** was isolated by diluting the reaction mixture with methanol followed by precipitation into diethyl ether.

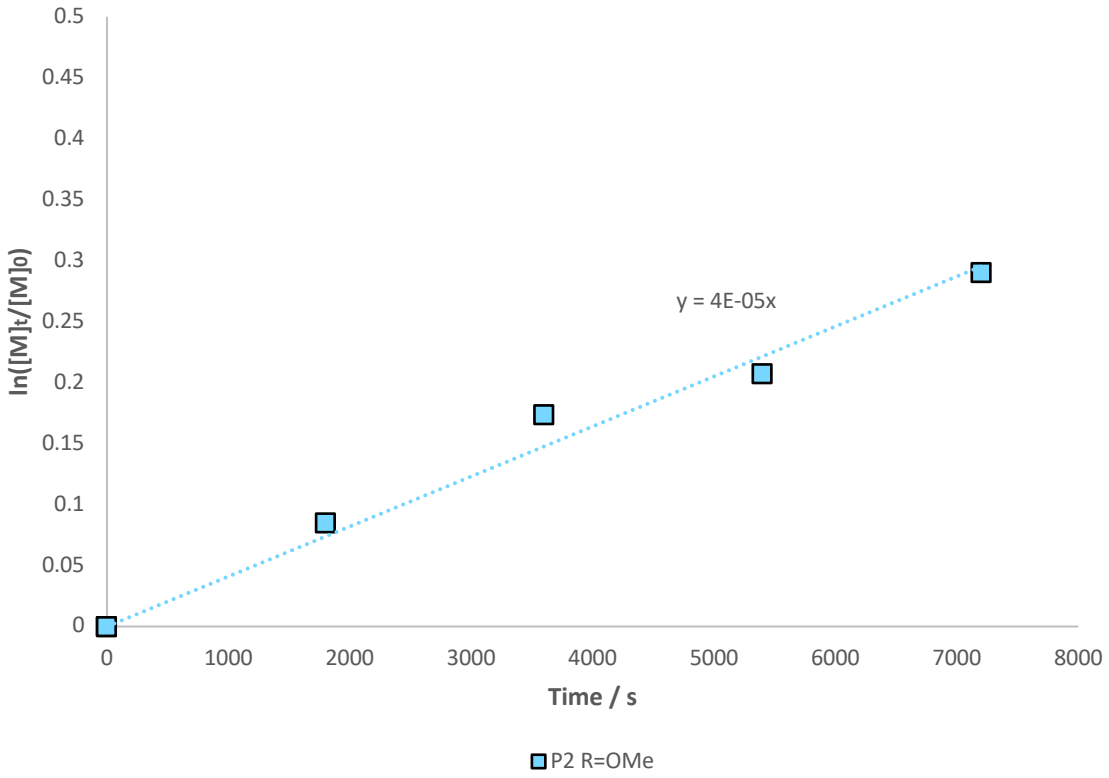


Figure S6 Kinetic analysis of the homopolymerisation of **2**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

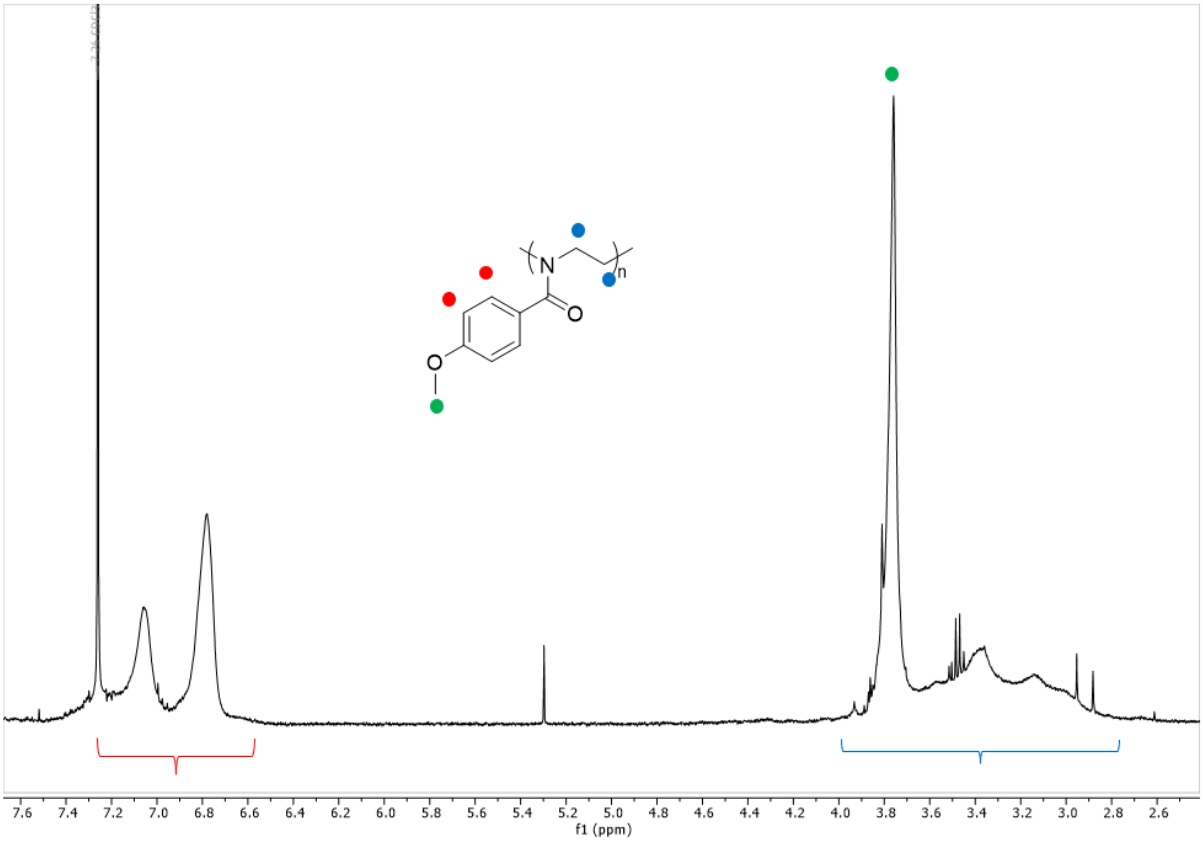
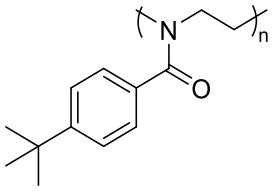


Figure S7 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P2**.

GPC data was not acquired during this polymerisation on account of limited monomer conversion.

P3 (n = 70)



P3 was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines, [**3**]:[I] = 100:1 (Section 1.4). **P3** was isolated by dilution of the reaction mixture with methanol followed by precipitation into diethyl ether.

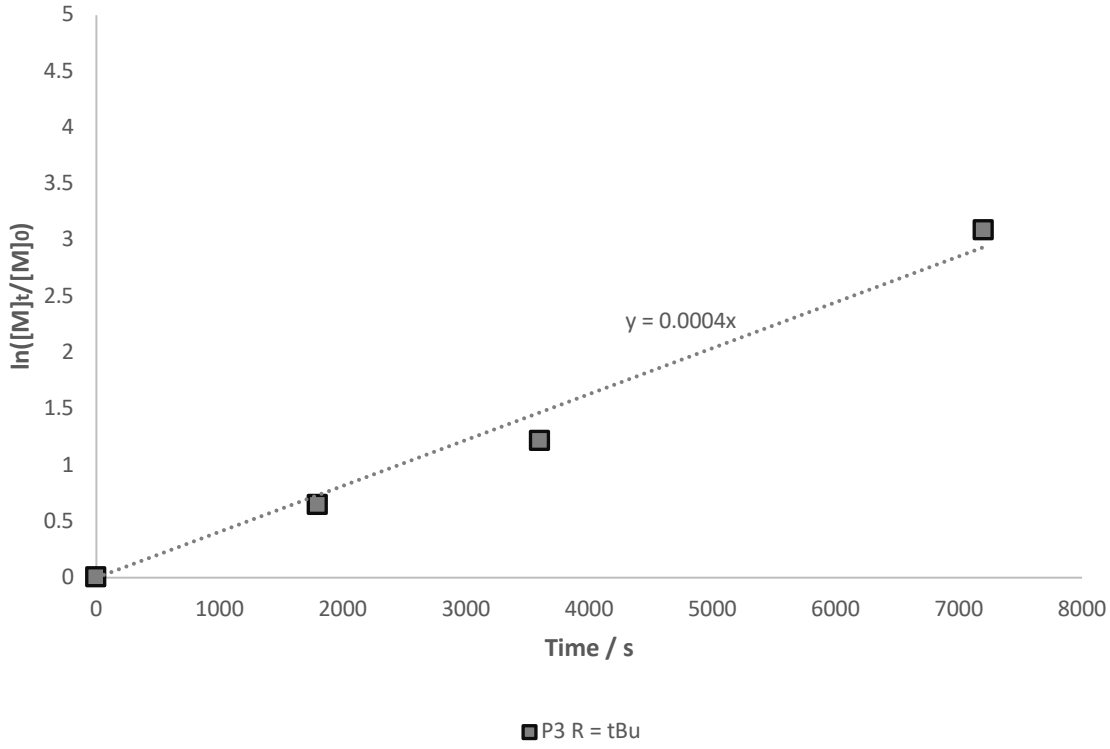


Figure S8 Kinetic analysis of the homopolymerisation of **3**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

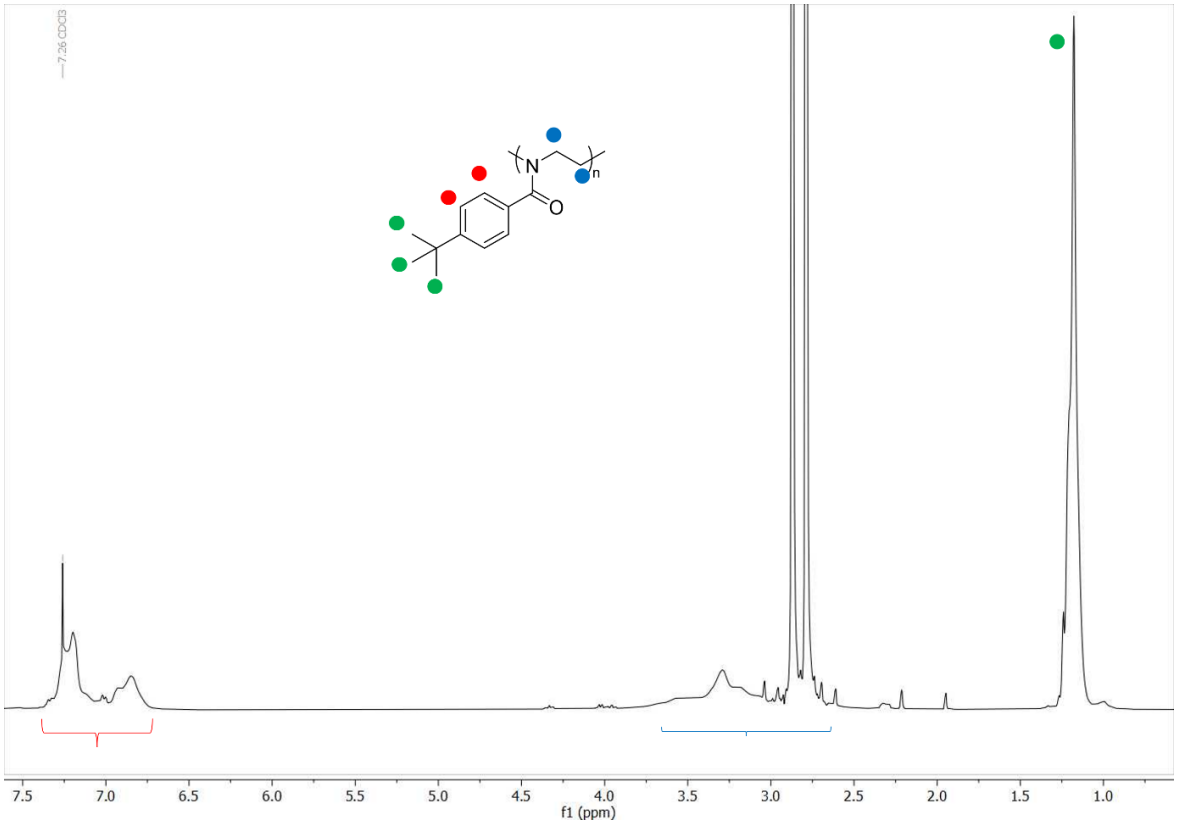


Figure S9 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly(2-(4-tert-butylphenyl)-2-oxazoline, **P3**.

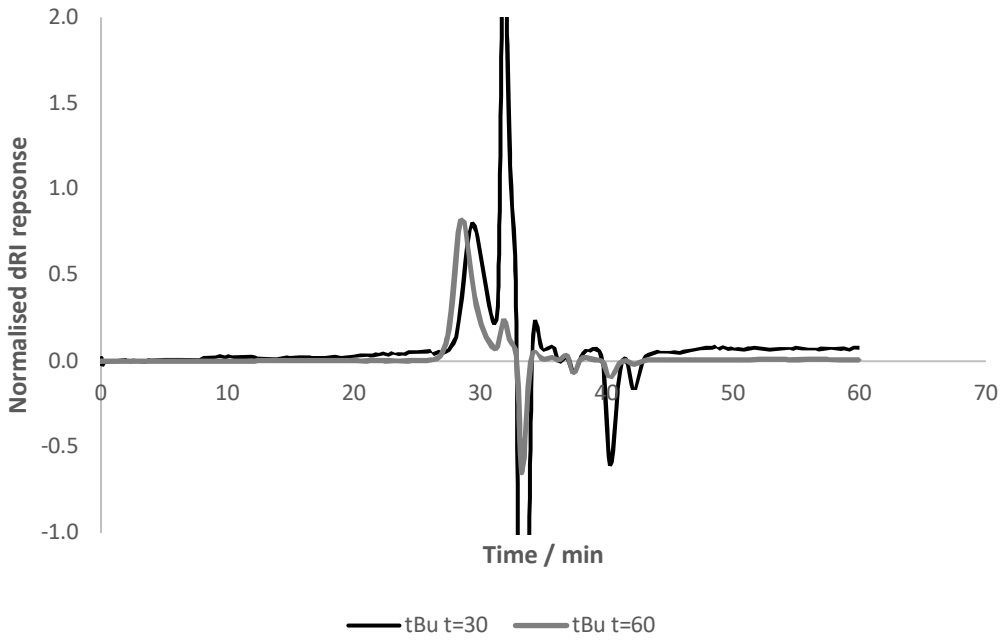


Figure S10 GPC chromatograms acquired during polymerisation of **3**. The time attributed to each sample relates to the length of time each polymerisation was irradiated for (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C).

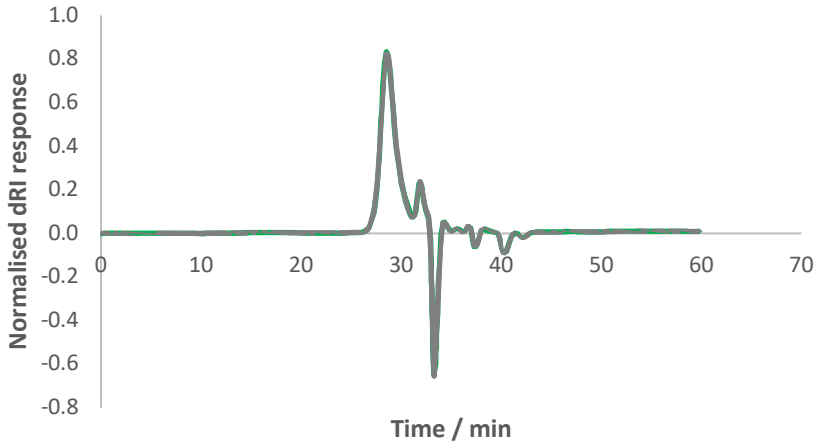
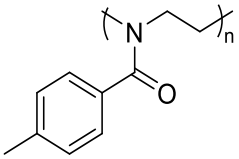


Figure S11 GPC analysis of **P3** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 5300 g mol^{-1}, M_w 6900 g mol^{-1}; Đ 1.3.

P4 (n = 79)



P4 was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines, [**4**]:[I] = 100 (Section 1.4). **P4** was isolated by dilution in methanol followed by precipitation in diethyl ether.

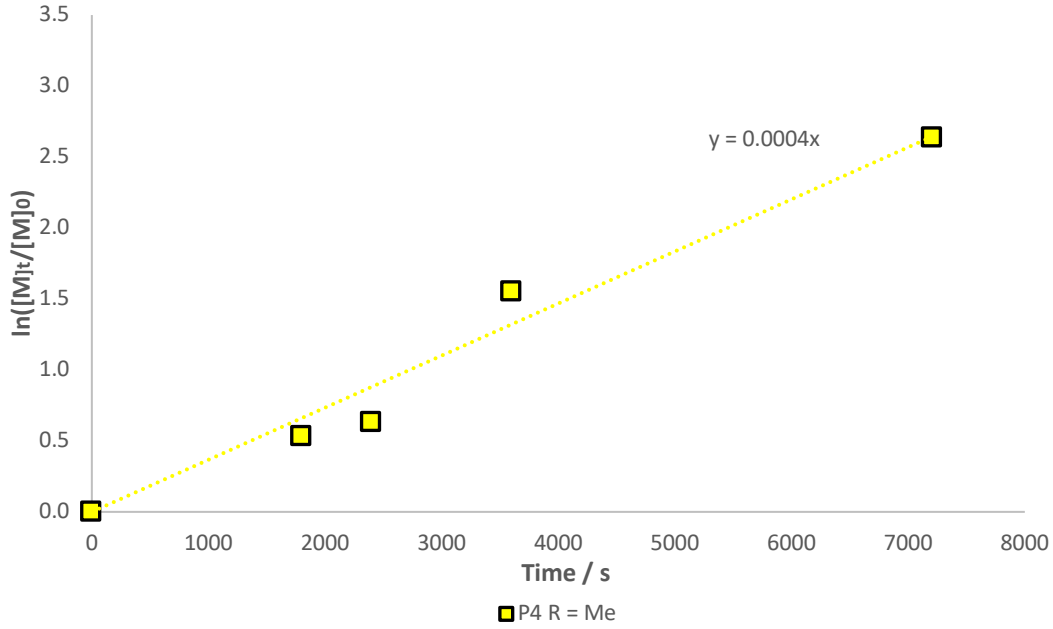


Figure S12 Kinetic analysis of the homopolymerisation of **4.** Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

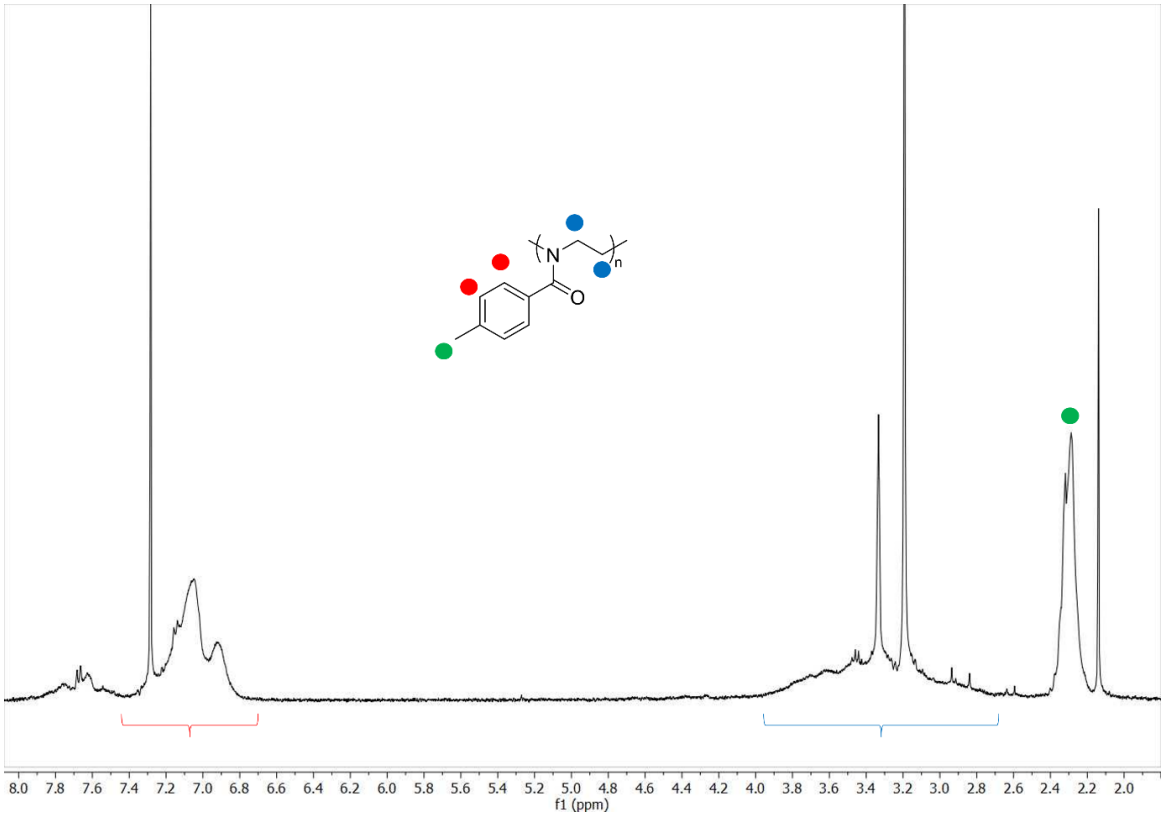


Figure S13 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P4**.

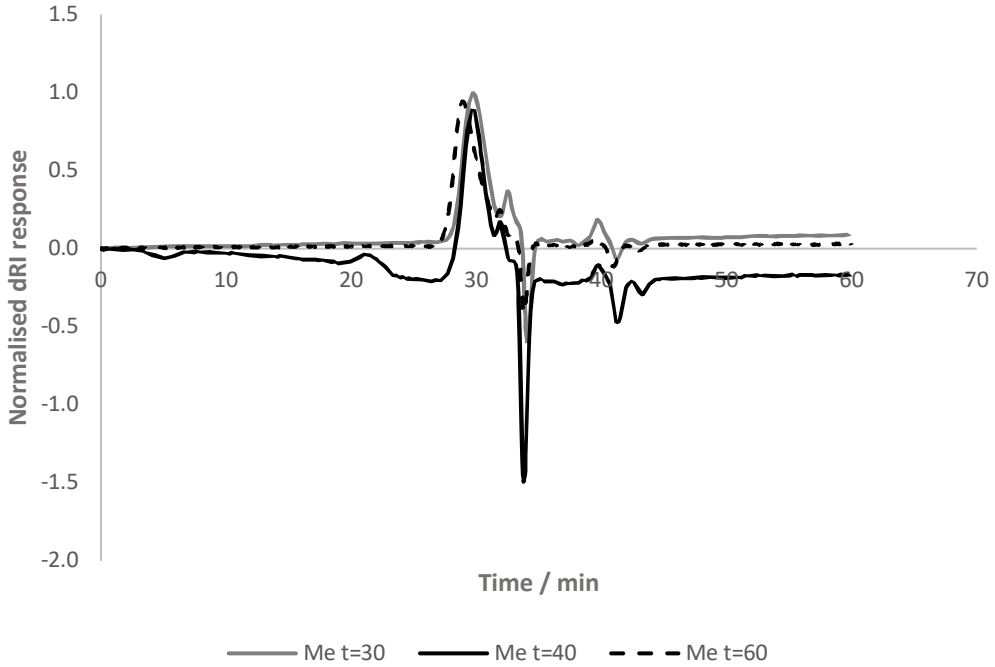


Figure S14 GPC chromatograms acquired during polymerisation of **4**. The time attributed to each sample relates to the length of time each polymerisation was irradiated for (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C).

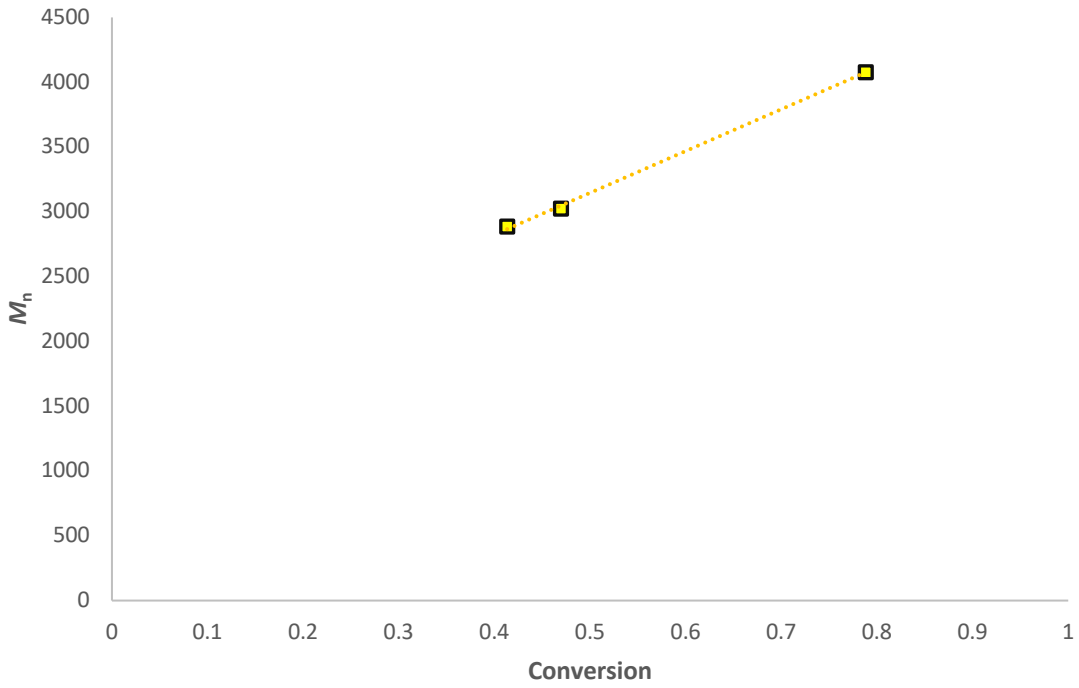


Figure S15 M_n as a function of conversion for polymerisation of **4**. M_n values determined using GPC by comparison to near-monodisperse poly(methyl methacrylate) standards.

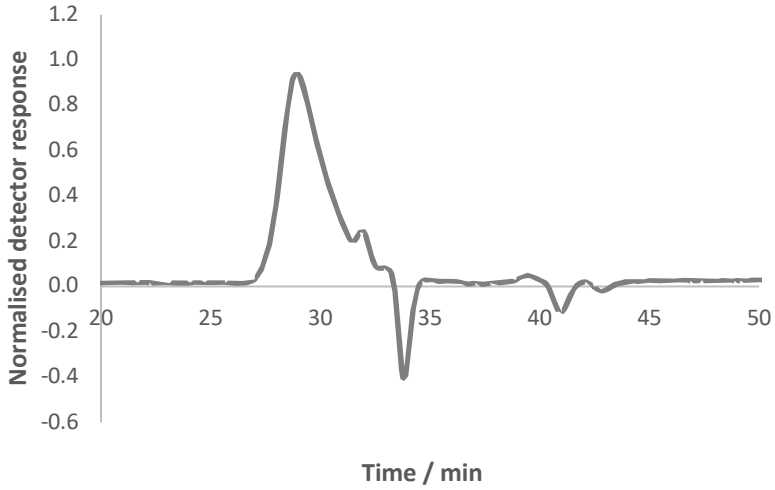
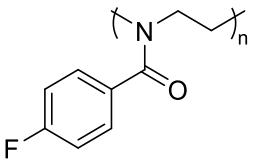


Figure S16 GPC analysis of **P4** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 4100 g mol^{-1}, M_w 5800 g mol^{-1}; Đ 1.5.

P5 (n = 86)



P5 was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines [**5**]:[I] = 100, (Section 1.4). **P5** was isolated by dilution in methanol followed by precipitation into diethyl ether.

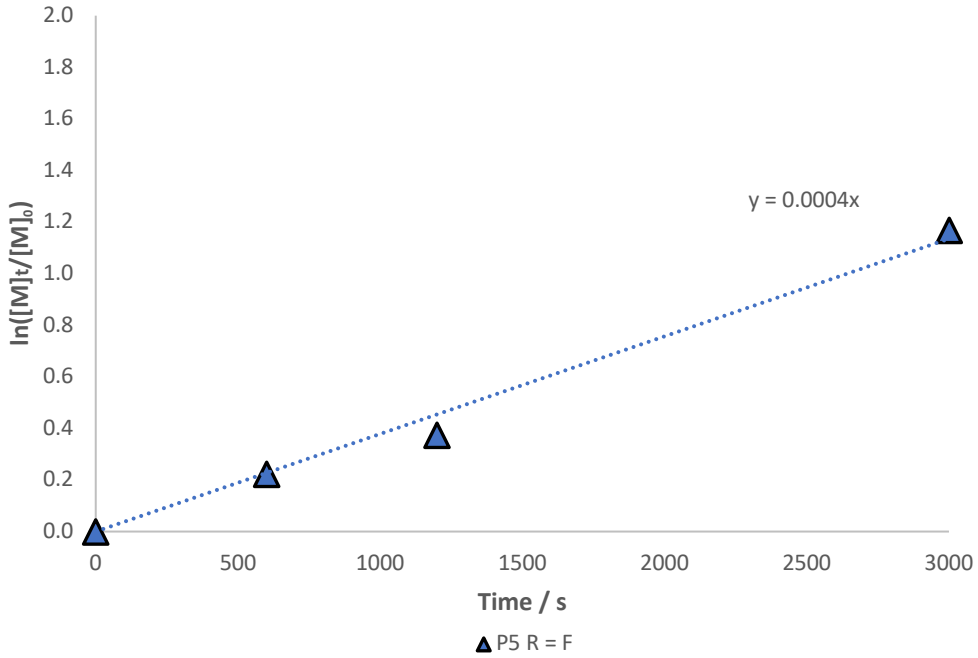


Figure S17 Kinetic analysis of the homopolymerisation of **5**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

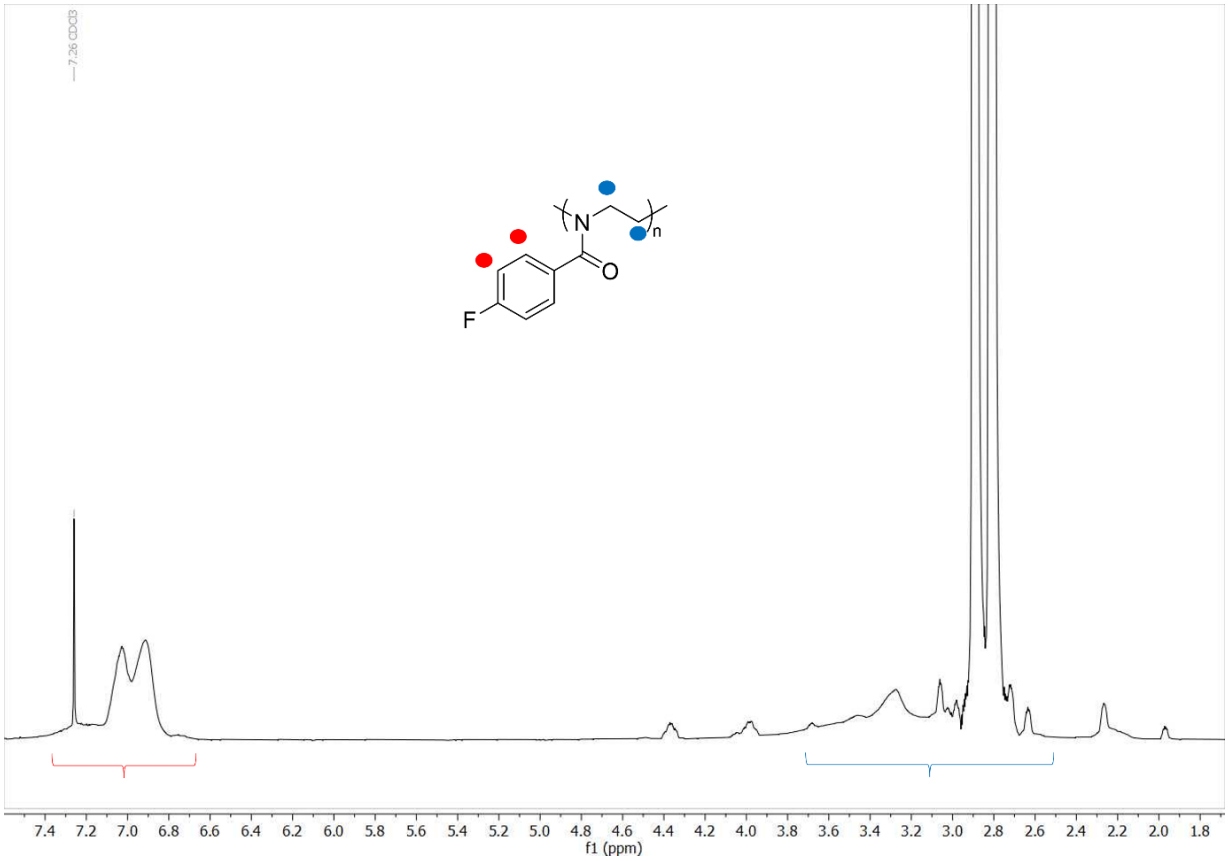


Figure S18 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of, **P5**.

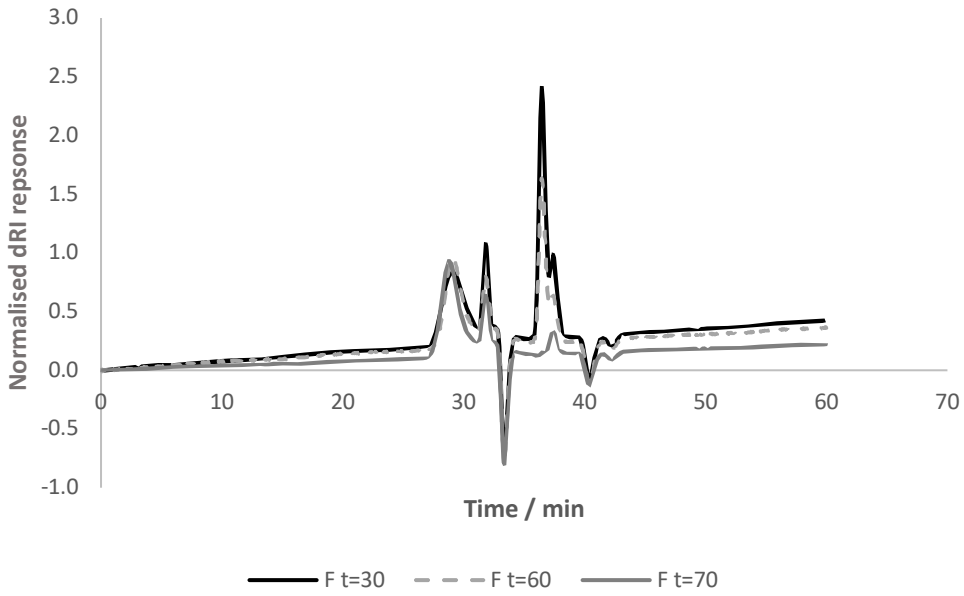


Figure S19 GPC chromatograms acquired during polymerisation of **5**. The time attributed to each sample relates to the length of time each polymerisation was irradiated for (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C).

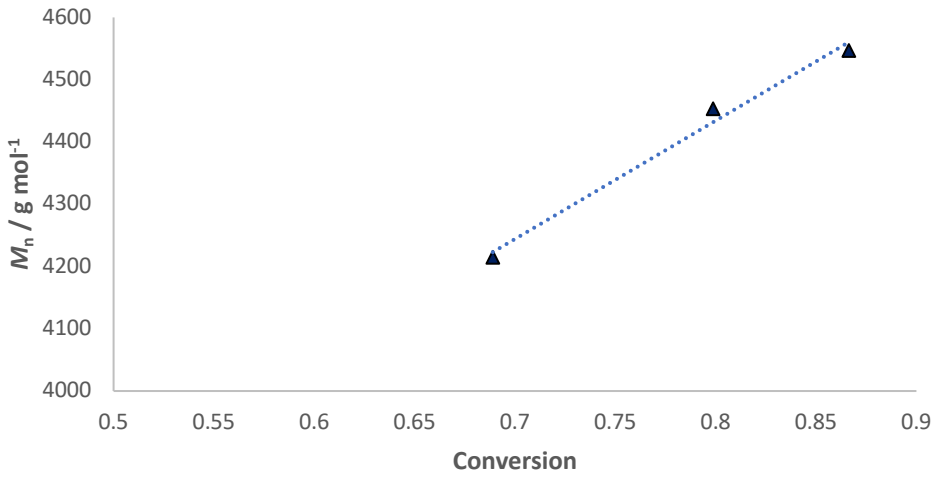


Figure S20 M_n as a function of conversion for polymerisation of **5**. M_n values determined using GPC by comparison to near-monodisperse poly(methyl methacrylate) standards.

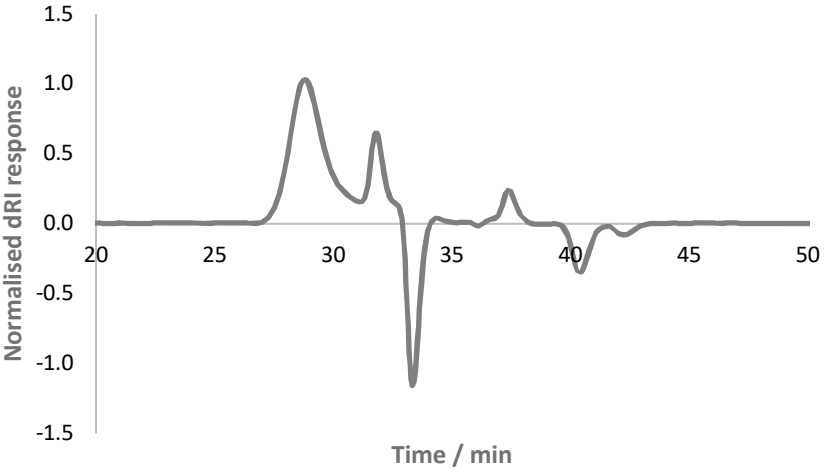
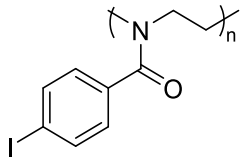


Figure S21 GPC analysis of **P5** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 4200 g mol^{-1}, M_w 6200 g mol^{-1}; Đ 1.3.

P6 (n = 97)



The title compound was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines [**6**]:[I] = 100 (Section 1.4). **P6** was isolated by dissolving in methanol followed by precipitation in diethyl ether.

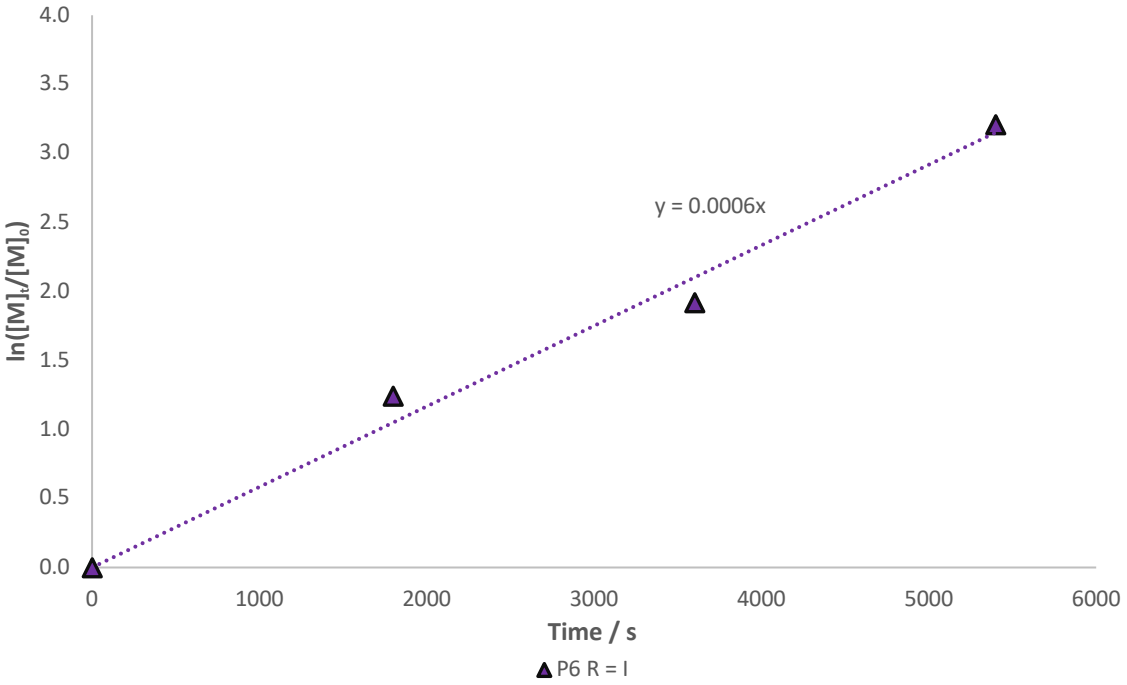


Figure S22 Kinetic analysis of the homopolymerisation of **6**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

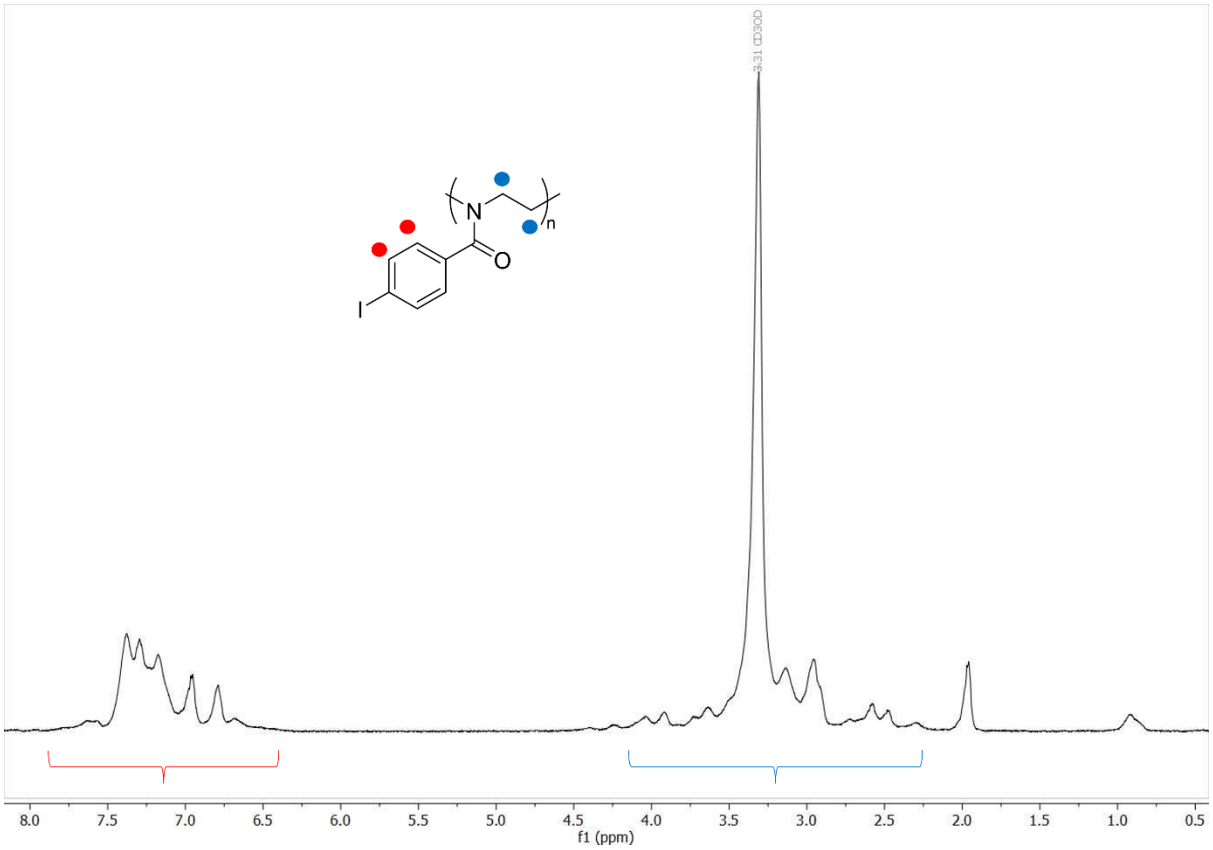


Figure S23 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P6.**

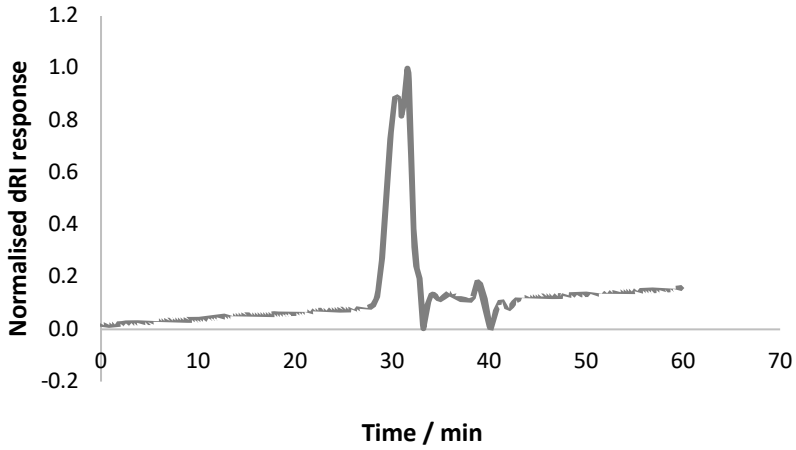
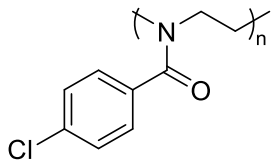


Figure S24 GPC analysis of **P6** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 2500 g mol^{-1}, M_w 2900 g mol^{-1}; Đ 1.2.

P7 (n = 44)



P7 was prepared according to the general procedure for the polymerisation of *para*-substituted 2-phenyl-2-oxazolines [**7**]:[I] = 100 (Section 1.4). **P7** was isolated by dilution in methanol followed by precipitation into diethyl ether.

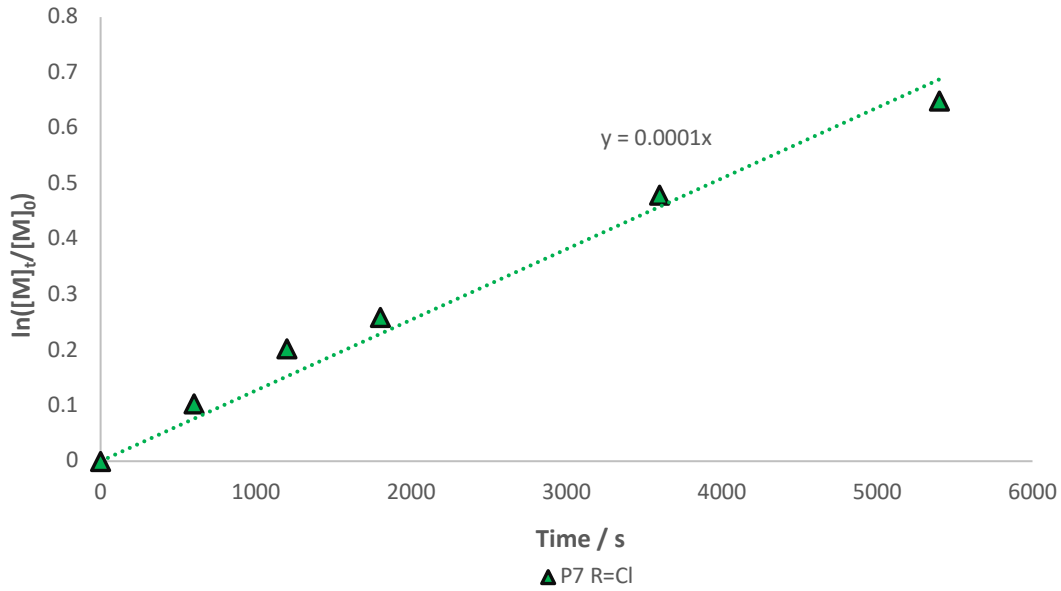


Figure S25 Kinetic analysis of the homopolymerisation of **7**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

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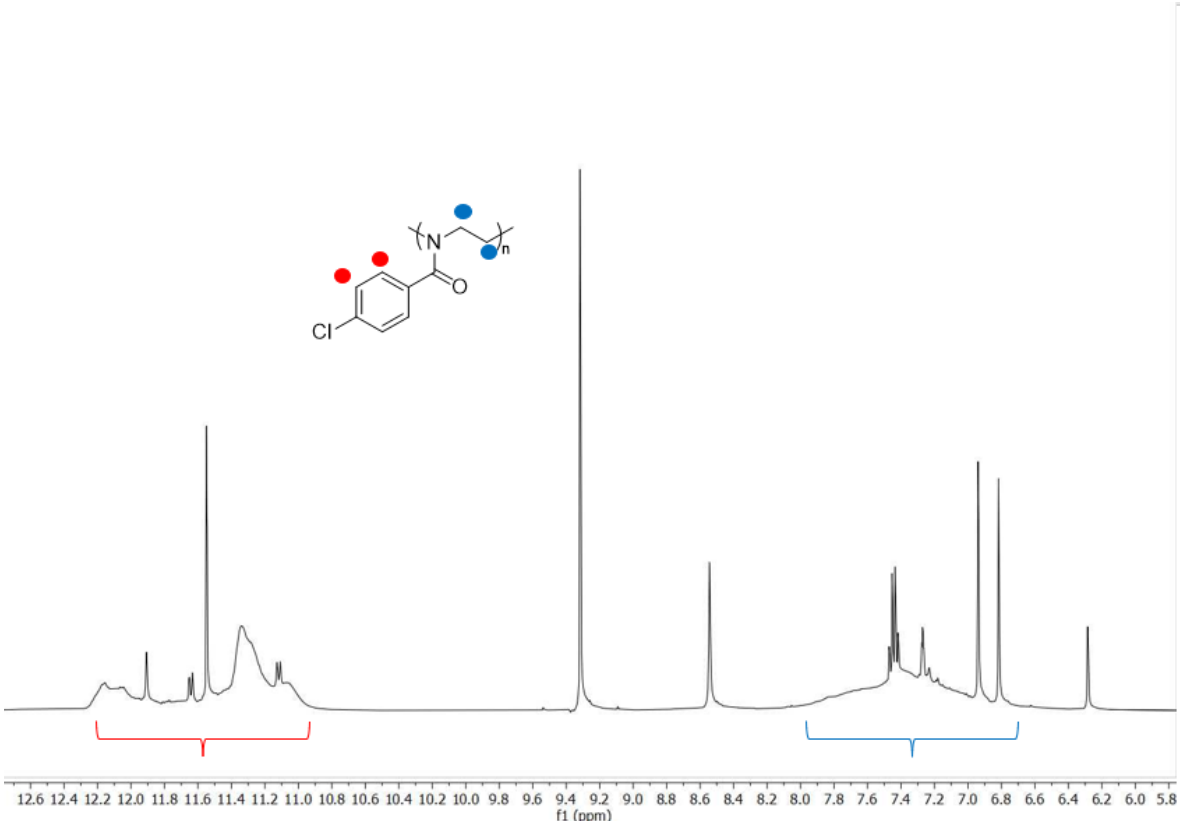


Figure S26 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P7**.

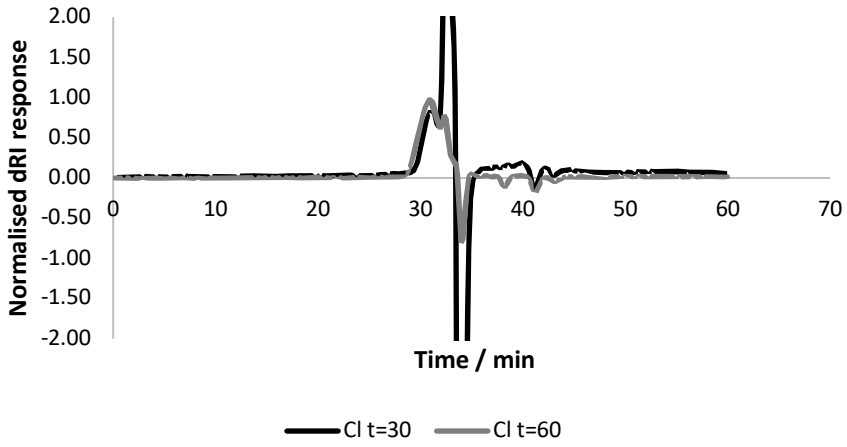


Figure S27 GPC chromatograms acquired during polymerisation of **7** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). The time attributed to each sample relates to the length of time each polymerisation was irradiated for (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C).

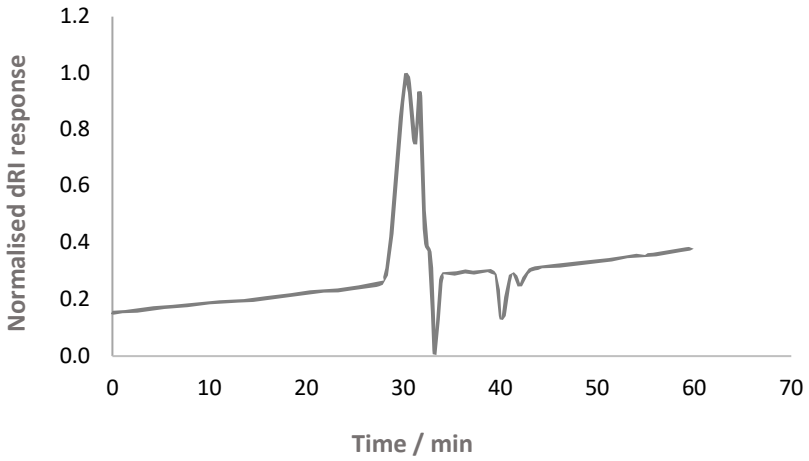
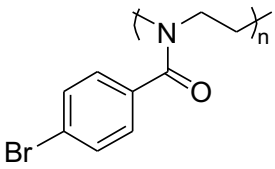


Figure S28 GPC analysis of **P7** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 2700 g mol^{-1}, M_w 3200 g mol^{-1}; Đ 1.2.

P8 (n = 18)



P8 was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines [**8**]:[I] = 100 (Section 1.4). **P8** was isolated by dilution in methanol followed by precipitation into diethyl ether.

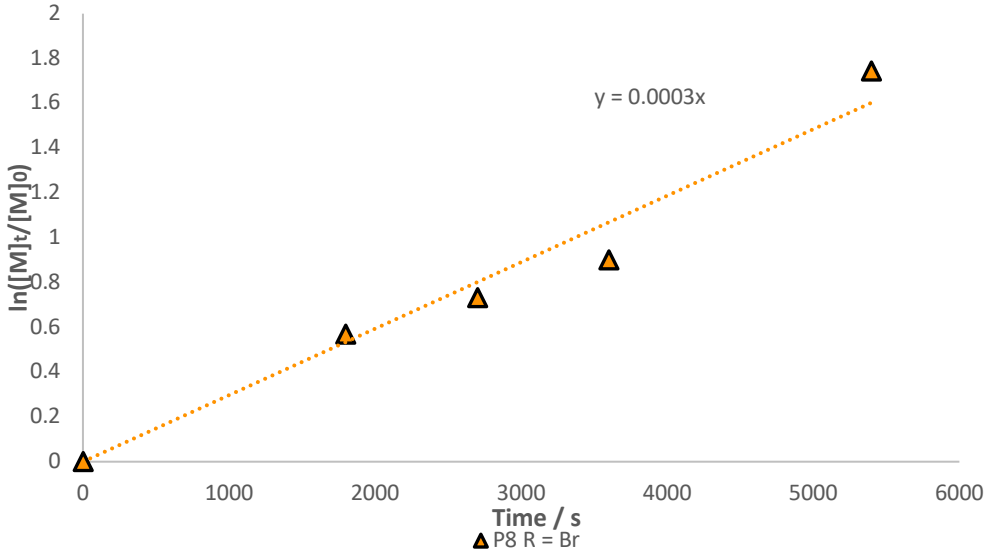


Figure S29 Kinetic analysis of the homopolymerisation of **8**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

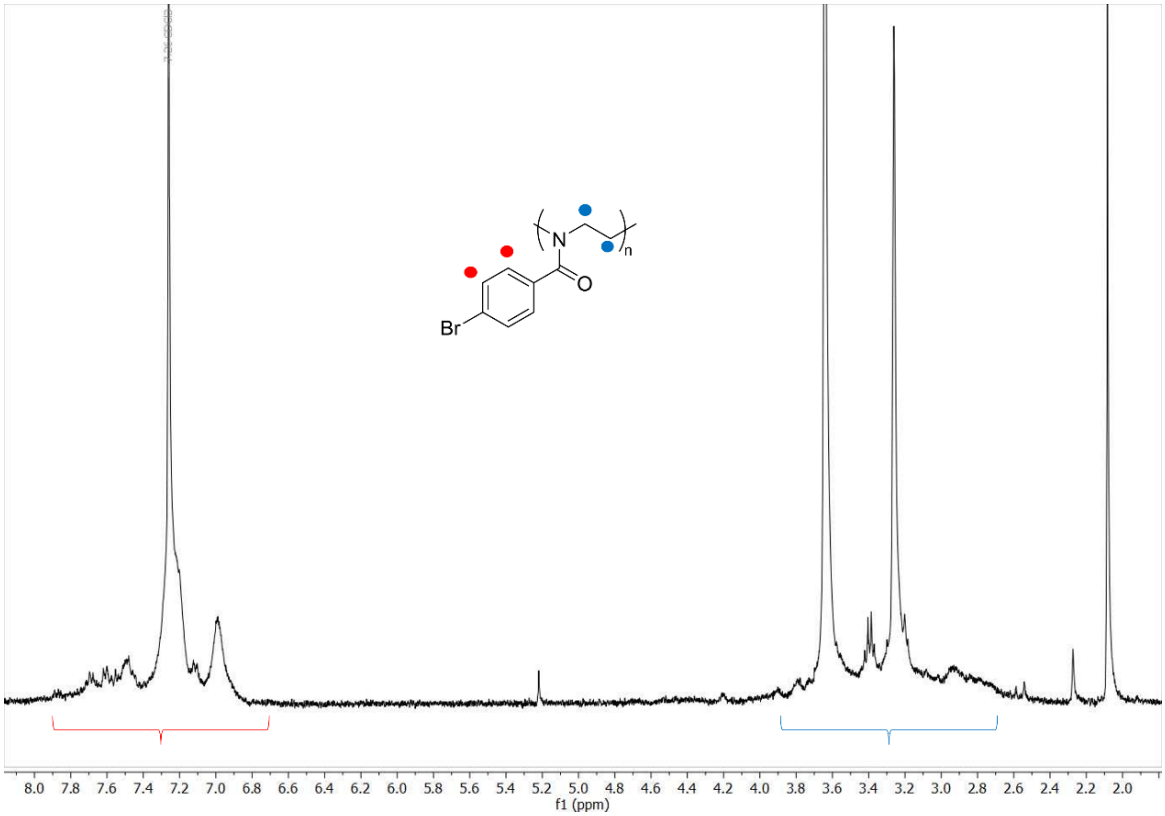
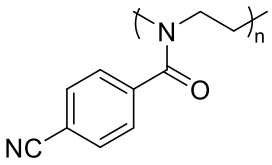


Figure S30 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P8**.

GPC data was not acquired during this polymerisation on account of limited monomer conversion.

P9 (n = 68)



The title compound was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines [**9**]:[I] = 100 (Section 1.4). **P9** was isolated by dilution in methanol followed by precipitation into diethyl ether.

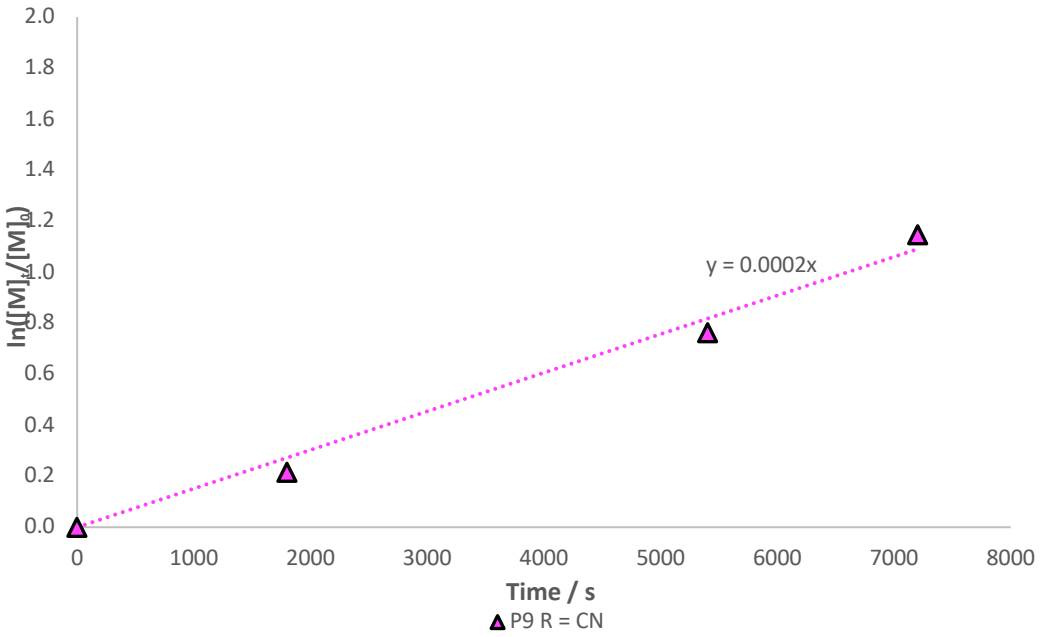


Figure S31 Kinetic analysis of the homopolymerisation of **9**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

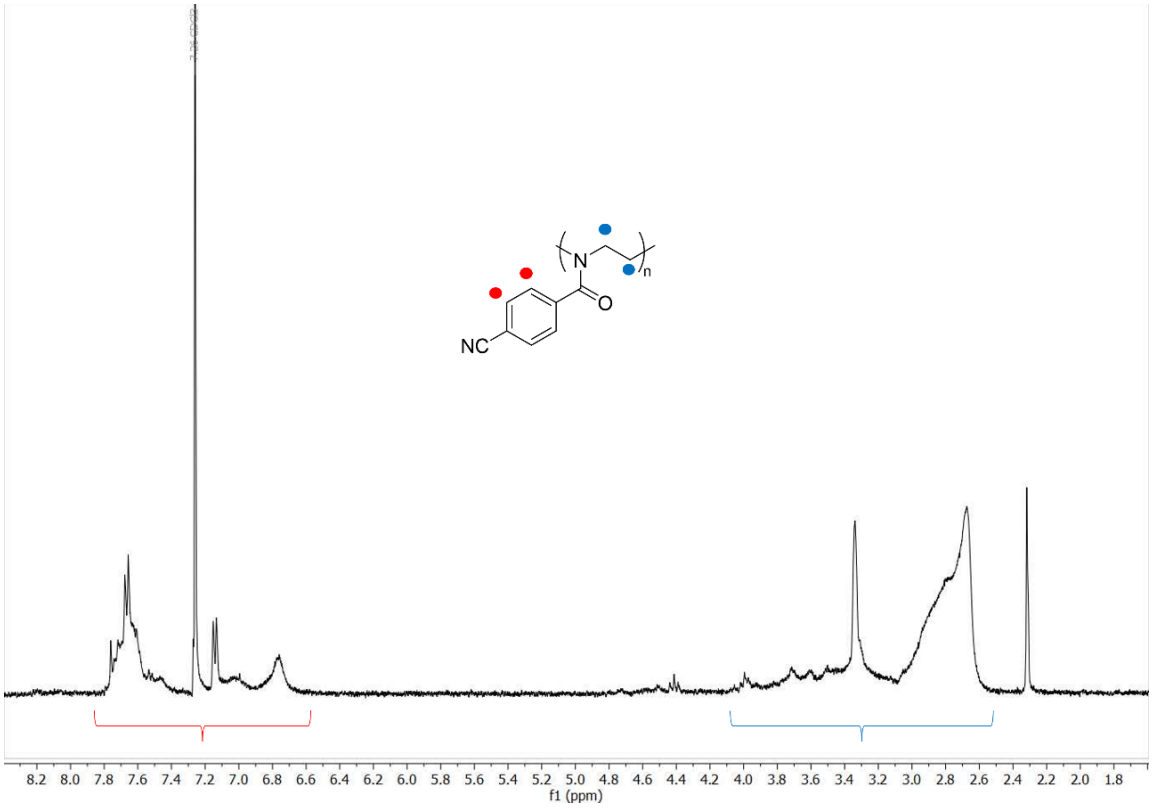
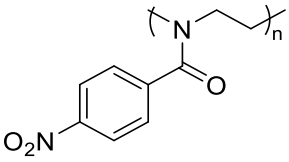


Figure S32 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P9**.

GPC data was not acquired during this polymerisation on account of limited monomer conversion.

P10 (n = 84)



P10 was prepared according to the general procedure for the polymerisation of para-substituted 2-phenyl-2-oxazolines [**10**]:[I] = 100 (Section 1.4). **P10** was isolated by dilution in methanol followed by precipitation into diethyl ether.

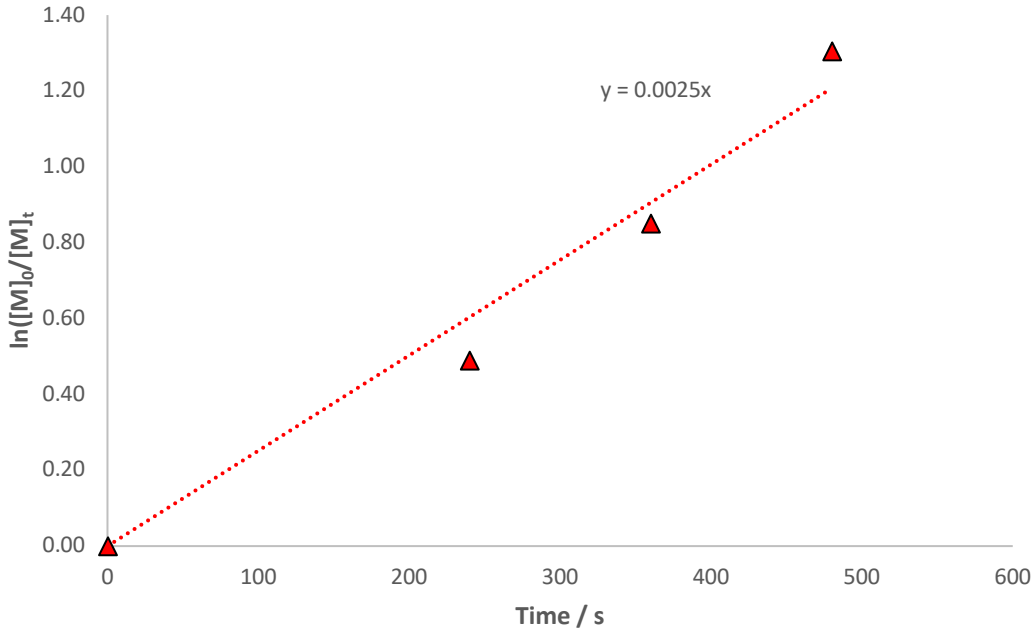


Figure S33 Kinetic analysis of the homopolymerisation of **10**. Monomer concentrations were calculated for each sample through ^{1}H NMR spectroscopic quantitation of remaining monomer.

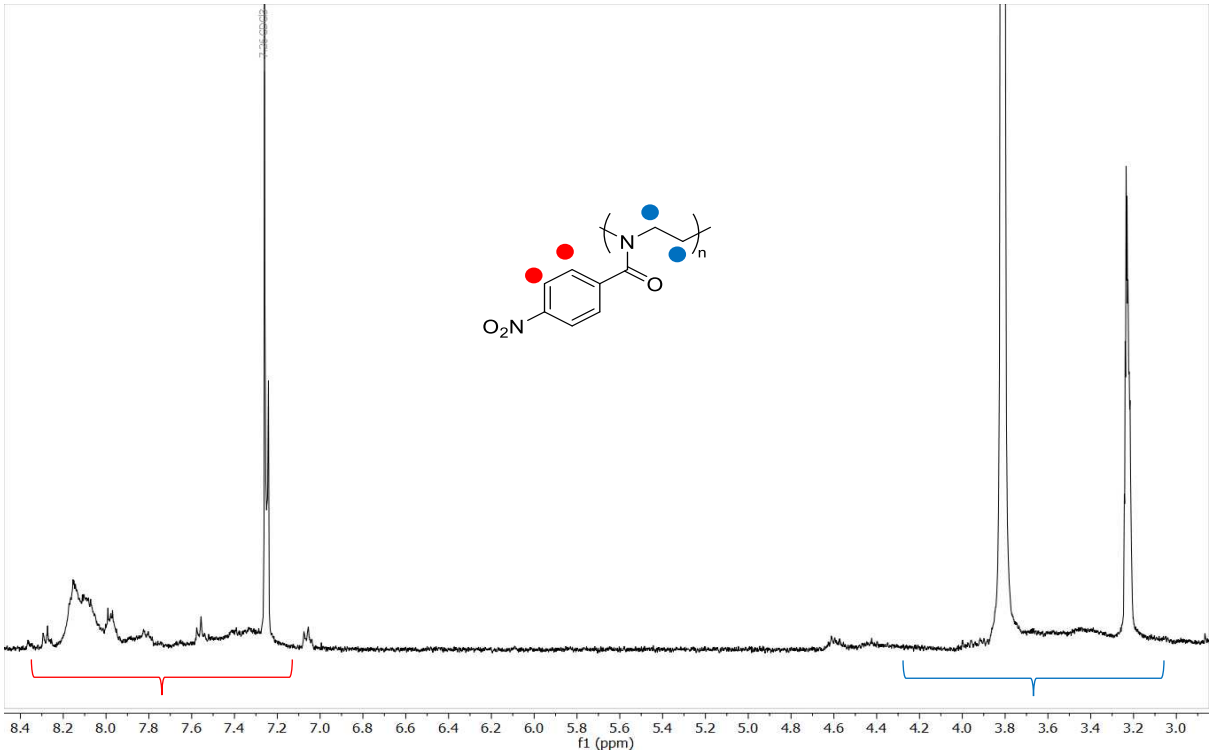


Figure S34 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P10**.

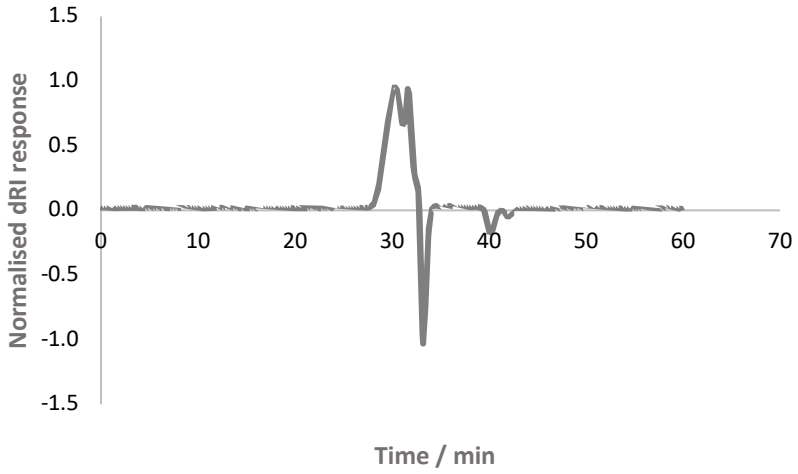


Figure S35 GPC analysis of **P10** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 2500 g mol^{-1}, M_w 3000 g mol^{-1}; Đ 1.2.

1.5 Copolymer synthesis

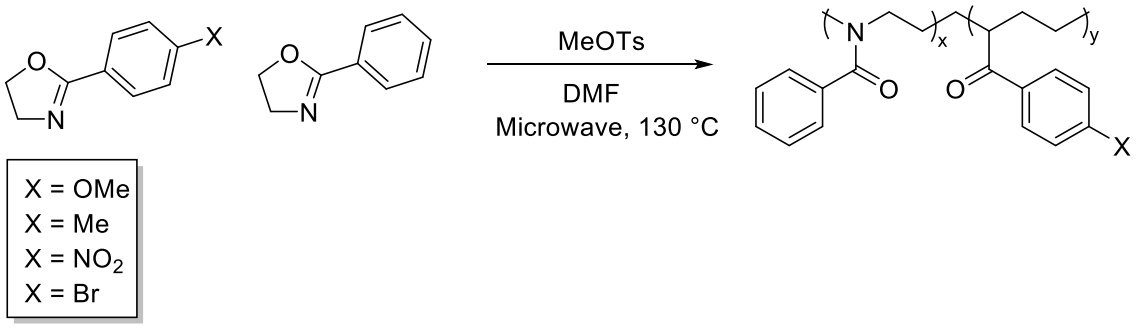


Figure S36 General synthesis of copolymers of **1** with a para-substituted 2-phenyl-2-oxazoline (**2**, **4**, **8** or **10**)

1, comonomer and methyl tosylate (25 µL, 0.16 mmol) were dissolved in freshly acquired, anhydrous DMF, packaged under an inert atmosphere (total monomer concentration 4 M, total M:I 100:1). The resulting solution was polymerised under microwave irradiation (90 W, 130 °C). Copolymers were isolated by precipitation into diethyl ether.

Copolymerisation of 1 and 2

Polymerisation was conducted according to general procedure for copolymer synthesis (Section 1.5), using **2** as the secondary monomer. The copolymer **P11** was isolated by dilution in methanol followed by precipitation into diethyl ether.

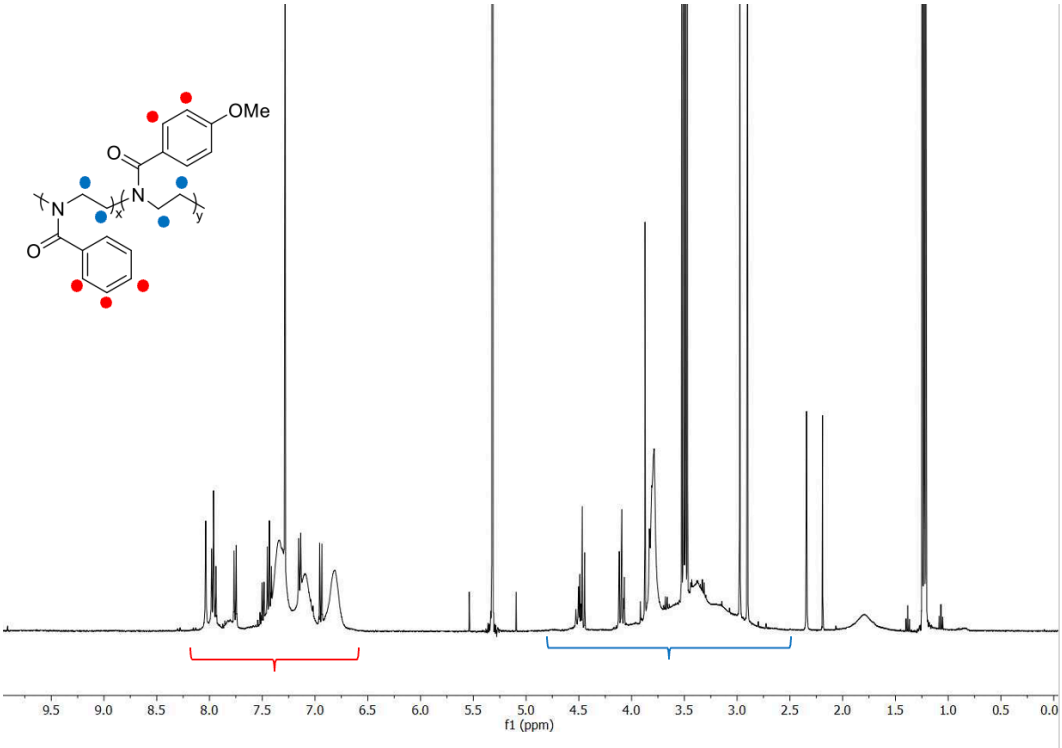


Figure S37 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P11**

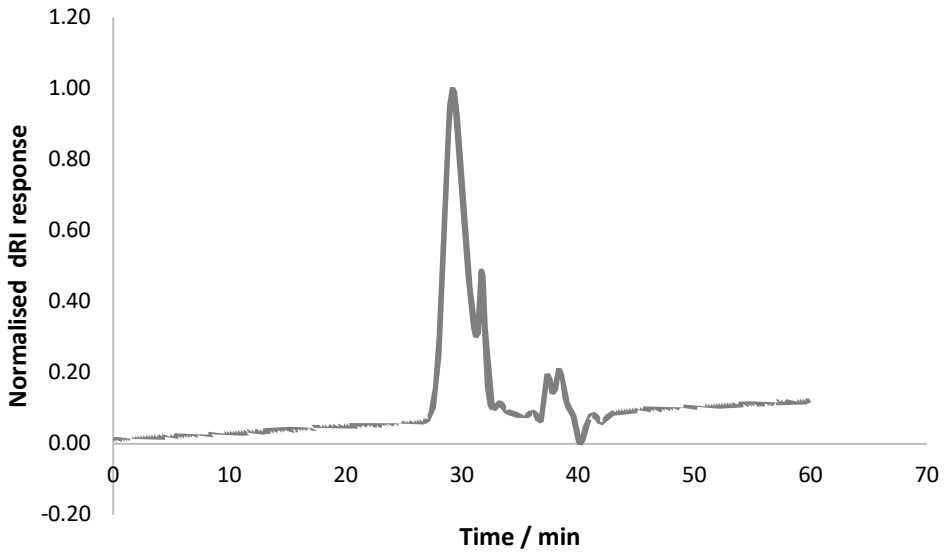


Figure S38 GPC analysis of **P11** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 3700 g mol^{-1}, M_w 5600 g mol^{-1}; Đ 1.5.

Copolymerisation of 1 and 4

Polymerisation was conducted according to general procedure for copolymer synthesis (Section 1.5), using **4** as the secondary monomer. The copolymer **P12** was isolated by dilution in methanol followed by precipitation into diethyl ether.

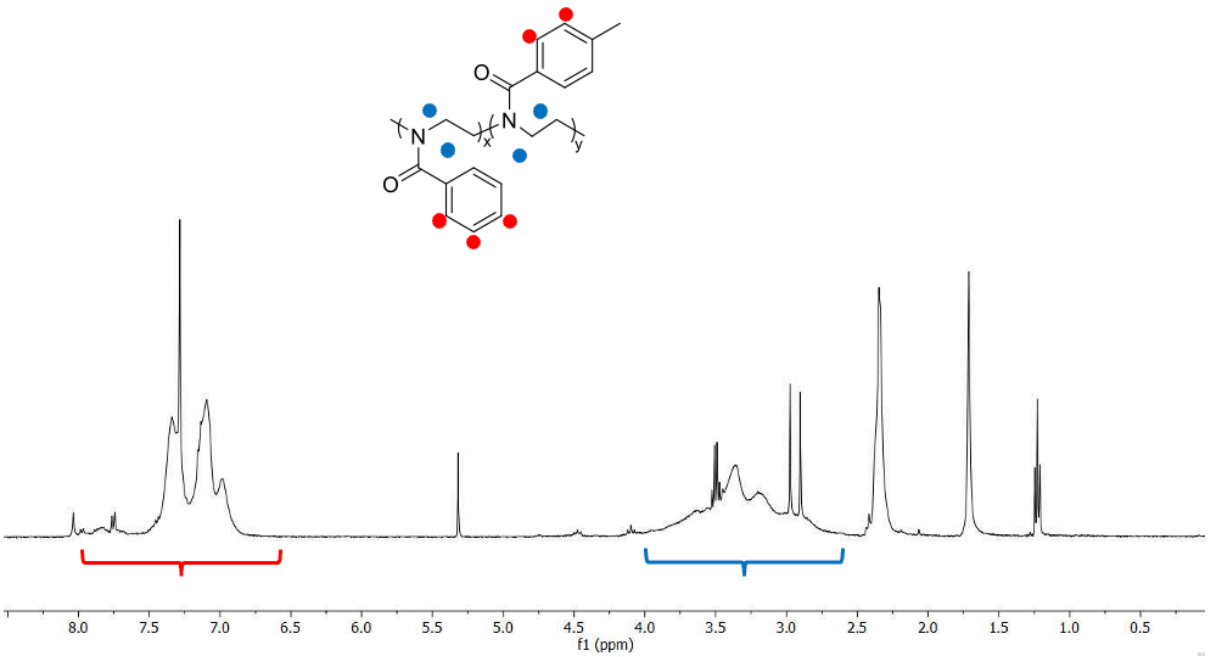


Figure S39 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P12**

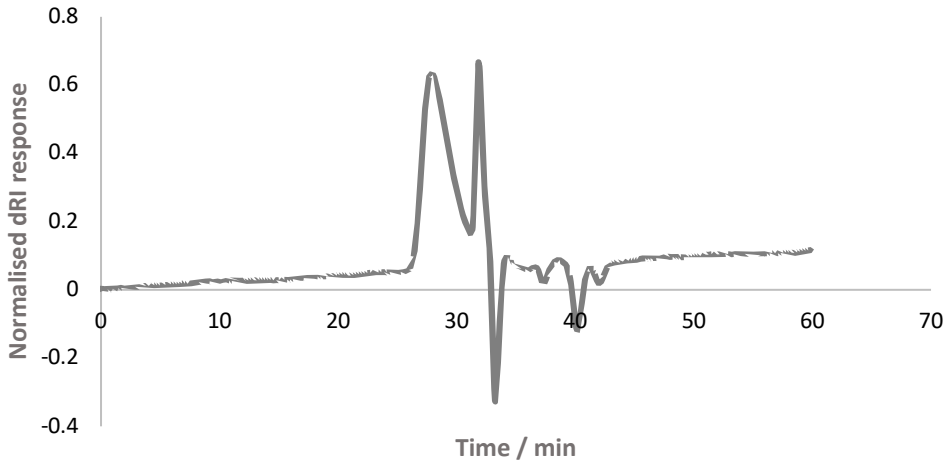


Figure S40 GPC analysis of **P12** (Eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 2400 g mol^{-1}, M_w 3600 g mol^{-1}; Đ 1.5.

Copolymerisation of 1 and 8

Polymerisation was conducted according to general procedure for copolymer synthesis (Section 1.5), using **8** as the secondary monomer. The copolymer **P13** was isolated by dilution in methanol followed by precipitation into diethyl ether.

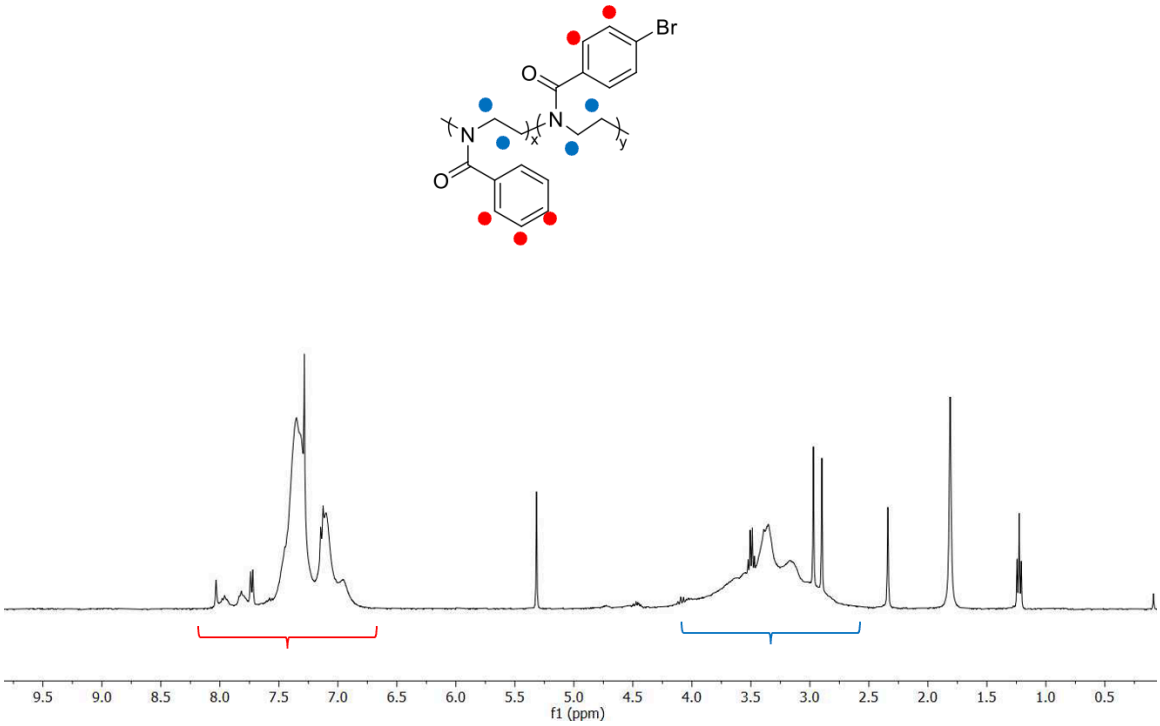


Figure S41 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P13**

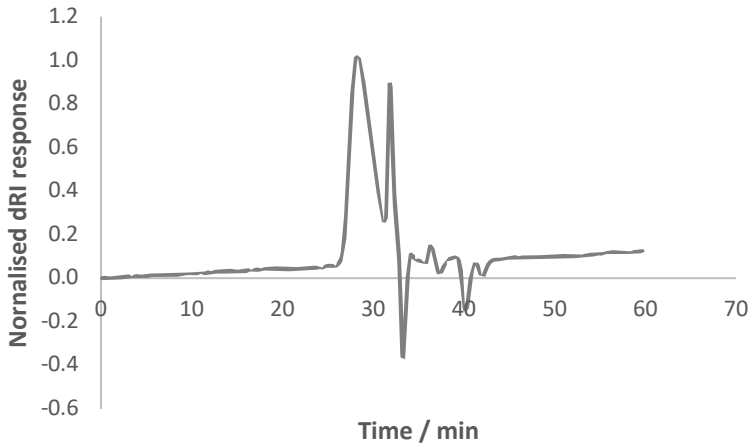


Figure S42 GPC analysis of **P13** (eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 5200 g mol^{-1}, M_w 6900 g mol^{-1}; Đ 1.3.

Copolymerisation of 1 and 10

Polymerisation was conducted according to general procedure for copolymer synthesis (Section 1.5), using **10** as the secondary monomer. The copolymer **P14** was isolated by dilution in methanol followed by precipitation into diethyl ether.

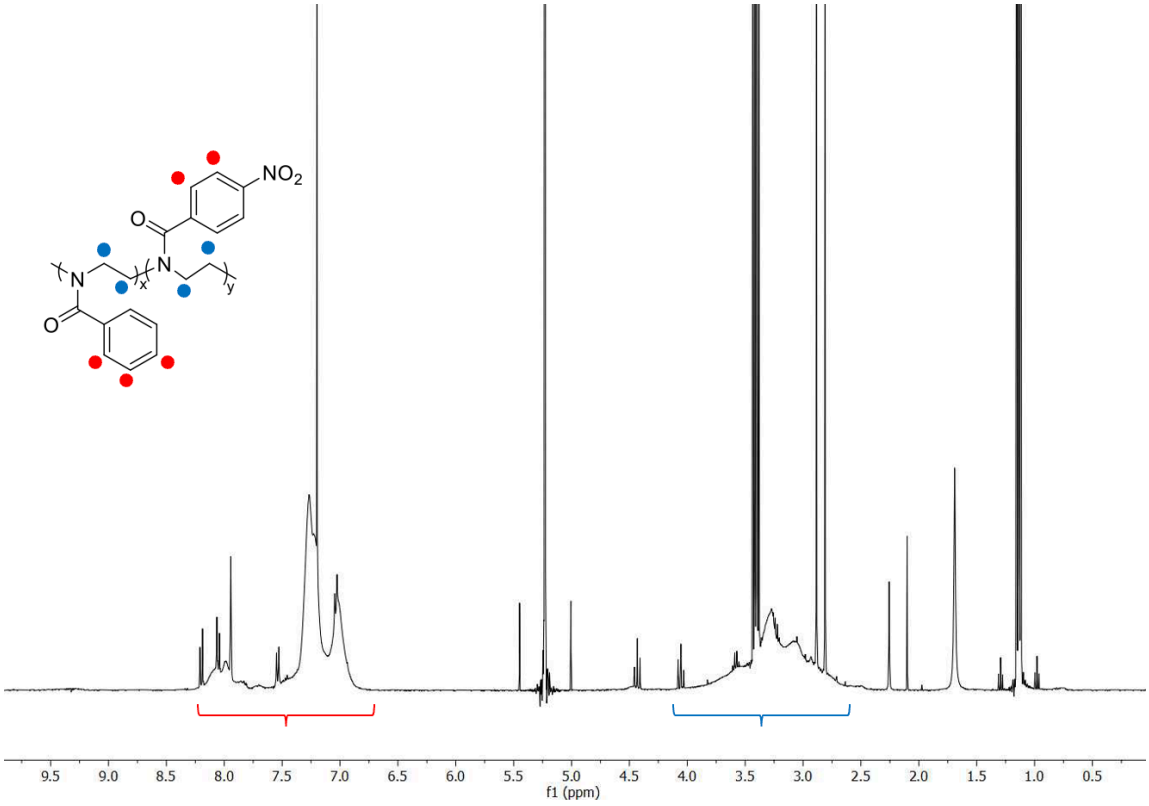


Figure S43 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **P14**

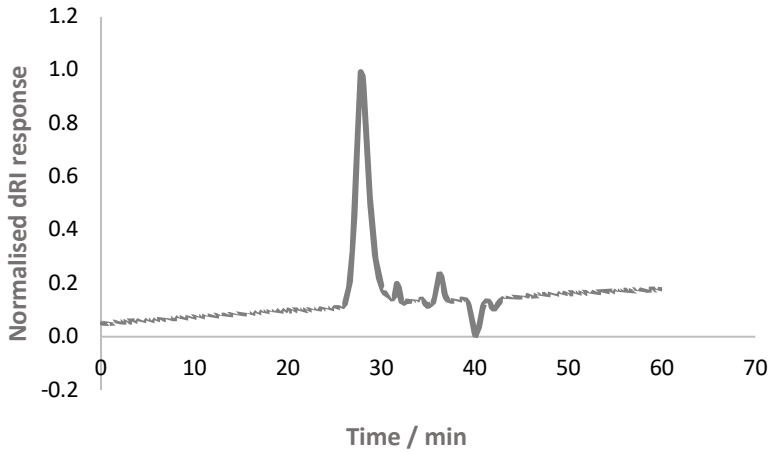


Figure S44 GPC analysis of **P14** (Eluent: DMF + LiBr (1 g/L), 0.6 mL/min, 50 °C). Estimated molecular weights were obtained by comparison to near monodisperse poly(methyl methacrylate) standards: M_n 1790 g mol^{-1}, M_w 2200 g mol^{-1}; Đ 1.2.

1.6 Determination of reactivity ratios for copolymerisations via Mayo-Lewis method

A series of polymerisations were set up varying the initial feed ratio of comonomers. Polymerisations were irradiated for 2 minutes without sampling to determine initial monomer uptake. Reactivity ratios were determined via the Mayo-Lewis method.[6] A fit could not be determined for the copolymerisation of **1** and **10** (Figure S48).

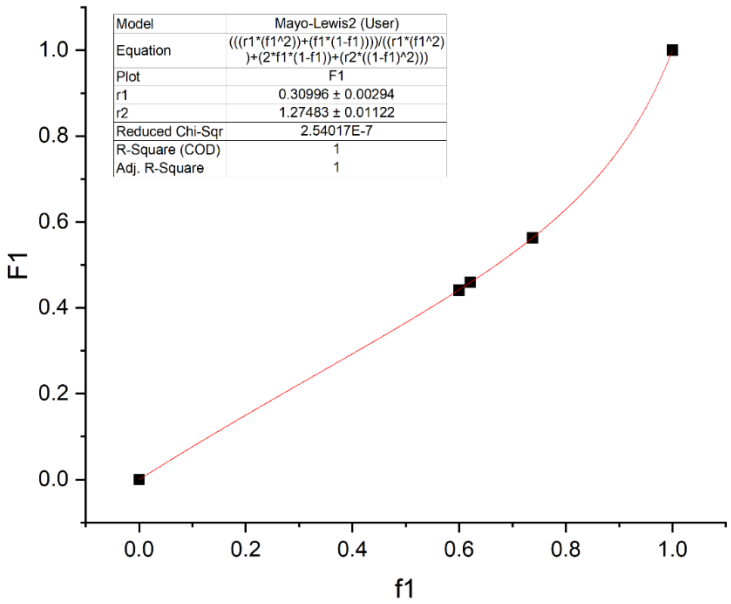


Figure S45 Mayo-Lewis fitting for the copolymerisation of **1** and **2**

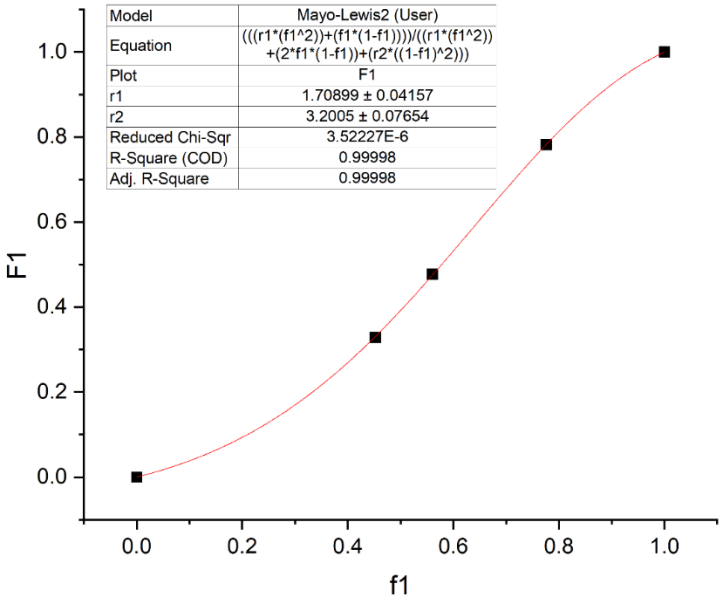


Figure S46 Mayo-Lewis fitting for the copolymerisation of **1** and **4**

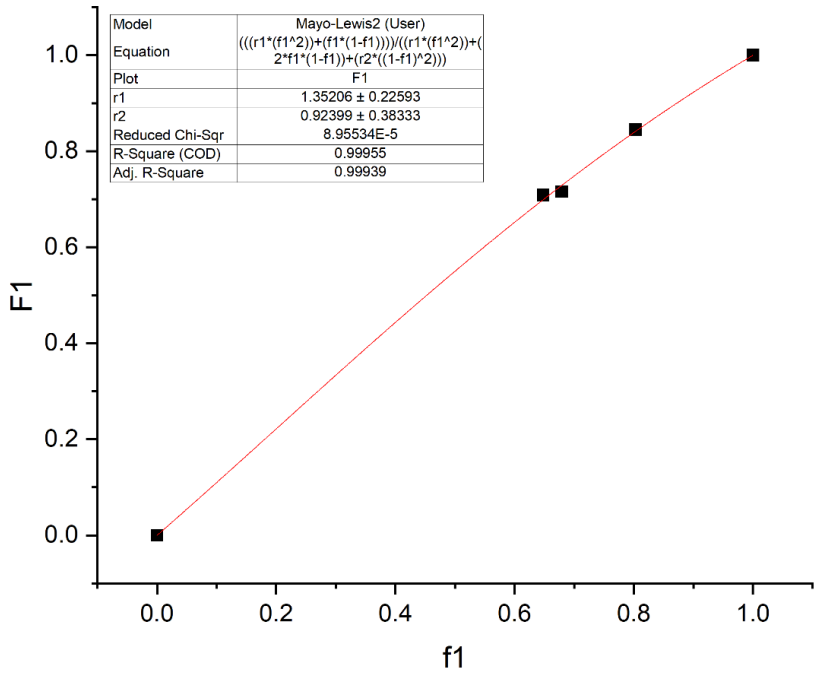


Figure S47 Mayo-Lewis fitting for the copolymerisation of **1** and **8**

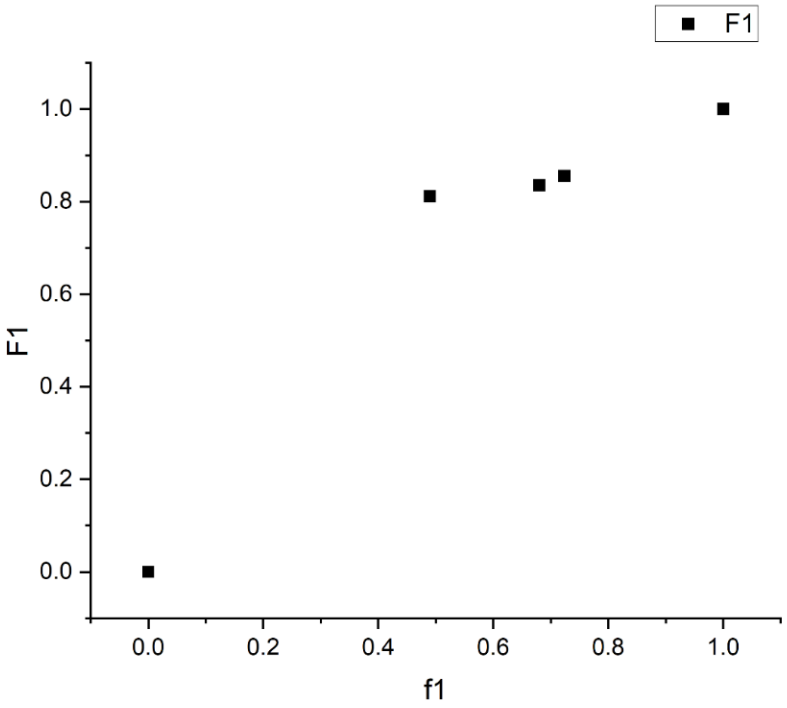


Figure S48 Mayo-Lewis plot for the copolymerisation of **1** and **10**. A fit could not be determined.

1.7 Determination of reactivity ratios for copolymerisations via Fineman-Ross method

A series of polymerisations were setup varying the initial feed ratio of comonomers. Polymerisations were irradiated for 2 minutes without sampling to determine initial monomer uptake. Reactivity ratios were determined using the Fineman-Ross model.[7] This method has been previously outlined for poly(oxazoline)s by Abbrent *et al.*[8] in which the copolymerisation parameters, r_1 and r_2 are calculated according to Equation 1. This data shows good agreement with the Mayo-Lewis method of analysis.

$$G = (r_1 \times H) - r_2 \qquad \text{(Equation 1)}$$

Where $G = X(Y-1)/Y$ and $H = X^2/Y$. These parameters are derived as $X = [M_1]/[M_2]$ and $y = dM_1/dM_2$.

Definitions of $M_1 = f_1$, $M_2 = f_2$, $dM_1 = F_1$, and $dM_2 = F_2$ all apply and can be calculated according to calculations for feed molar fractions, f:

$$f_1 = \frac{[M_1]_t}{[M_1]_0}\ , f_1 + f_2 = 1 \qquad \text{(Equation 2)}$$

The molar fraction of the monomer in the polymer cannot be measured directly by ^{1}H NMR spectroscopy as the similarity in the monomers results in overlap of broad polymer peaks so is rather calculated assuming full monomer incorporation into the polymer species. This allows for determination by monomer depletion values according to Equation 3:

$$F_1 = \frac{(M_1)_0 - (M_1)_t}{((M_1)_0 - (M_1)_t) + ((M_2)_0 - (M_2)_t)}\ , F_1 + F_2 = 1 \qquad \text{(Equation 3)}$$

Feed ratios are determined directly by ^{1}H NMR spectroscopy by comparison of monomer signals to an internal standard (DMF solvent). From this the relative ratio of each monomer can be determined as assigned as the feed ratio.

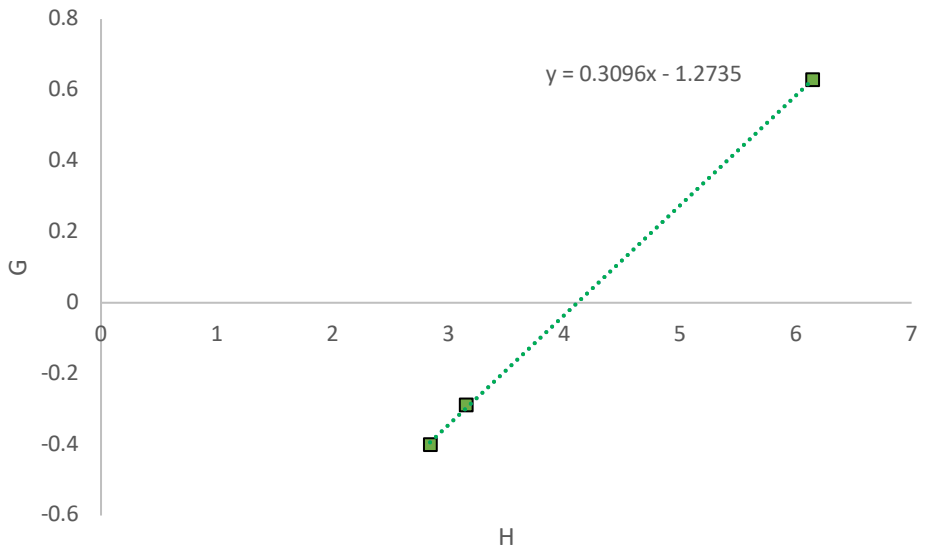


Figure S49 Fineman-Ross analysis of the copolymerisation of **1** and **2**.

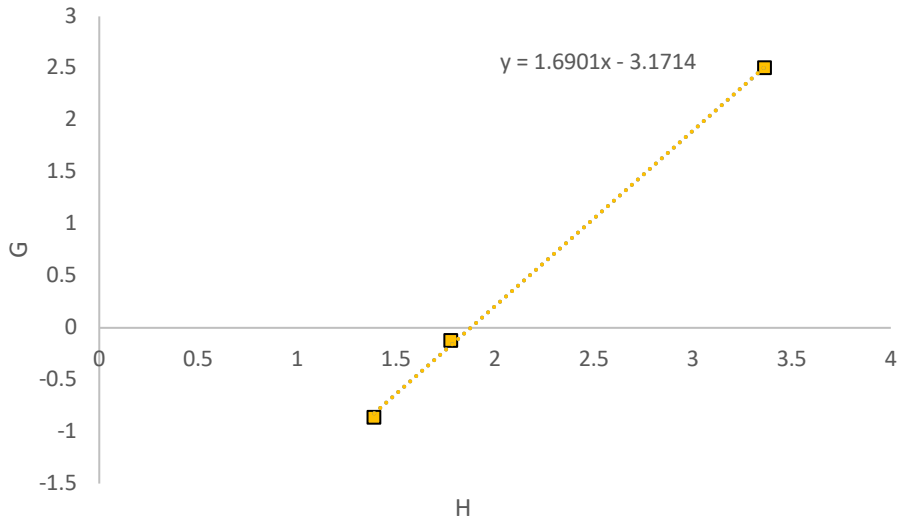


Figure S50 Fineman-Ross analysis of the copolymerisation of **1** and **4**.

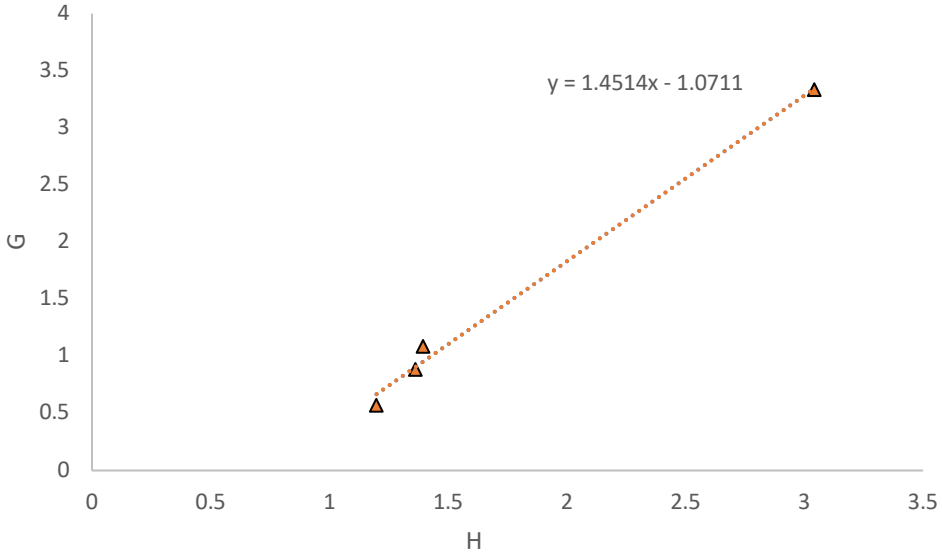


Figure S51 Fineman-Ross analysis of the copolymerisation of **1** and **8**.

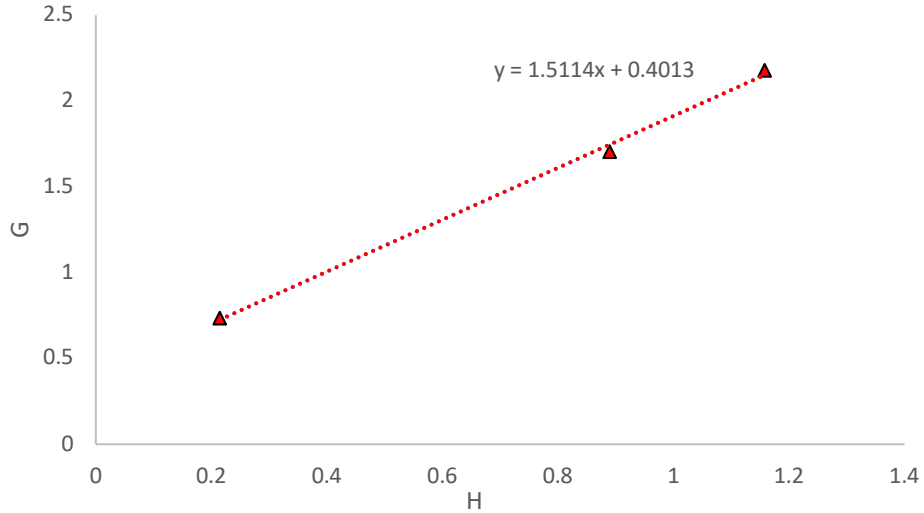


Figure S52 Fineman-Ross analysis of the copolymerisation of **1** and **10**.

2 NMR spectra of monomers

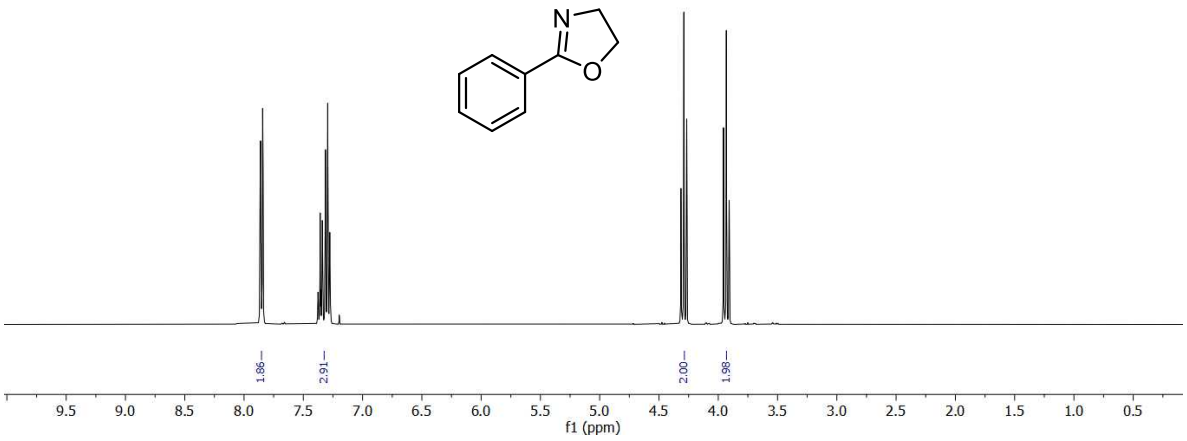


Figure S53 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1**.

Figure S54 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **1**.

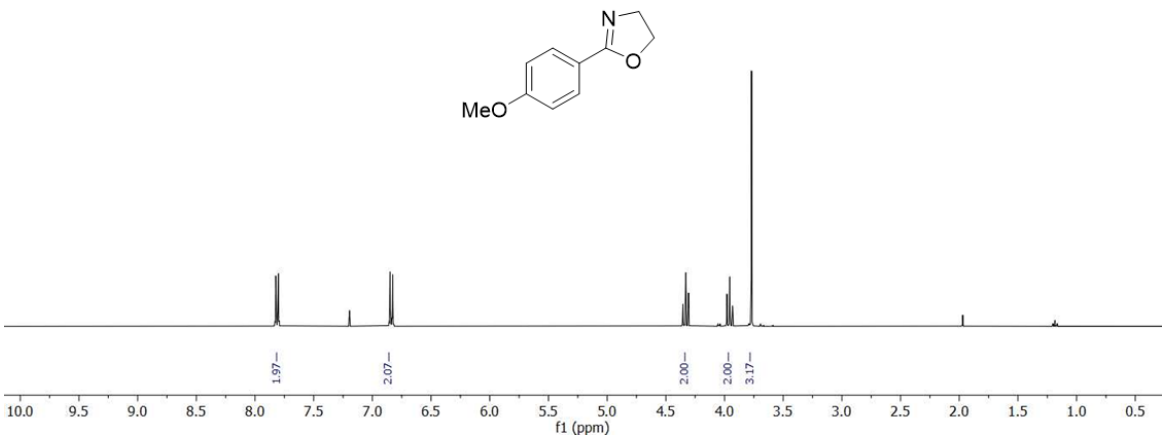


Figure S55 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2**.

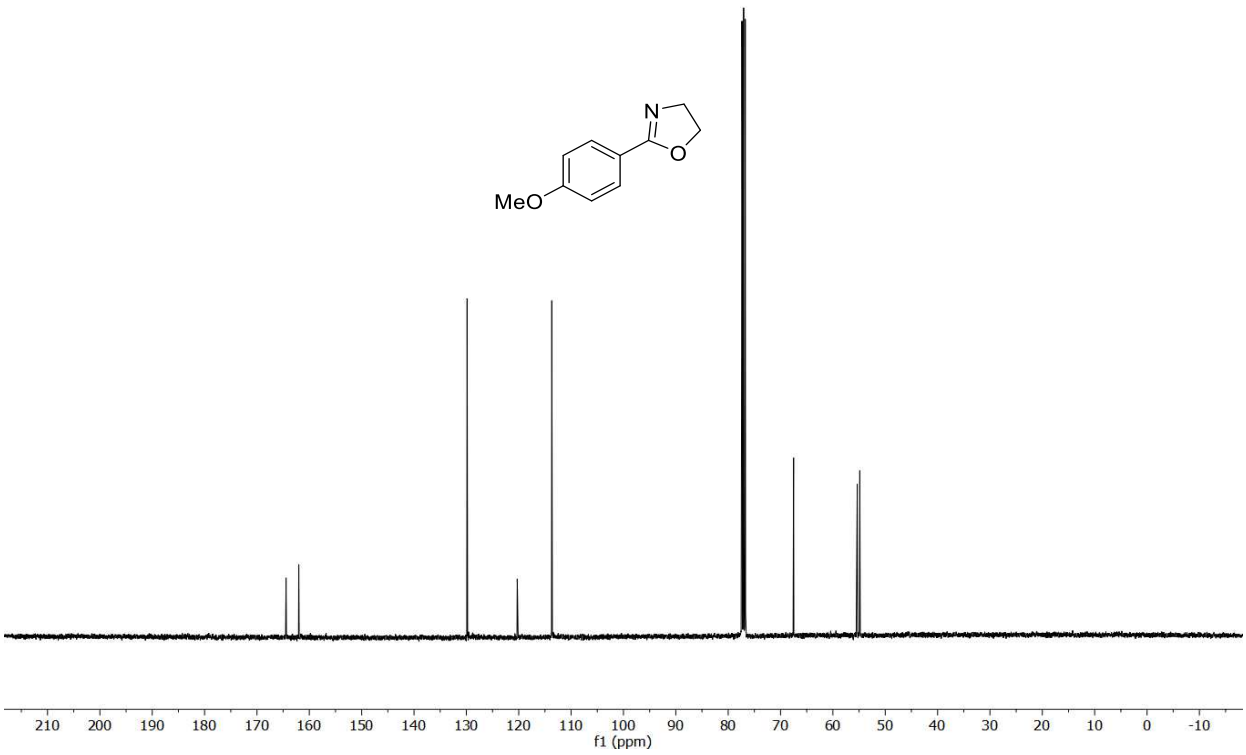


Figure S56 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **2**.

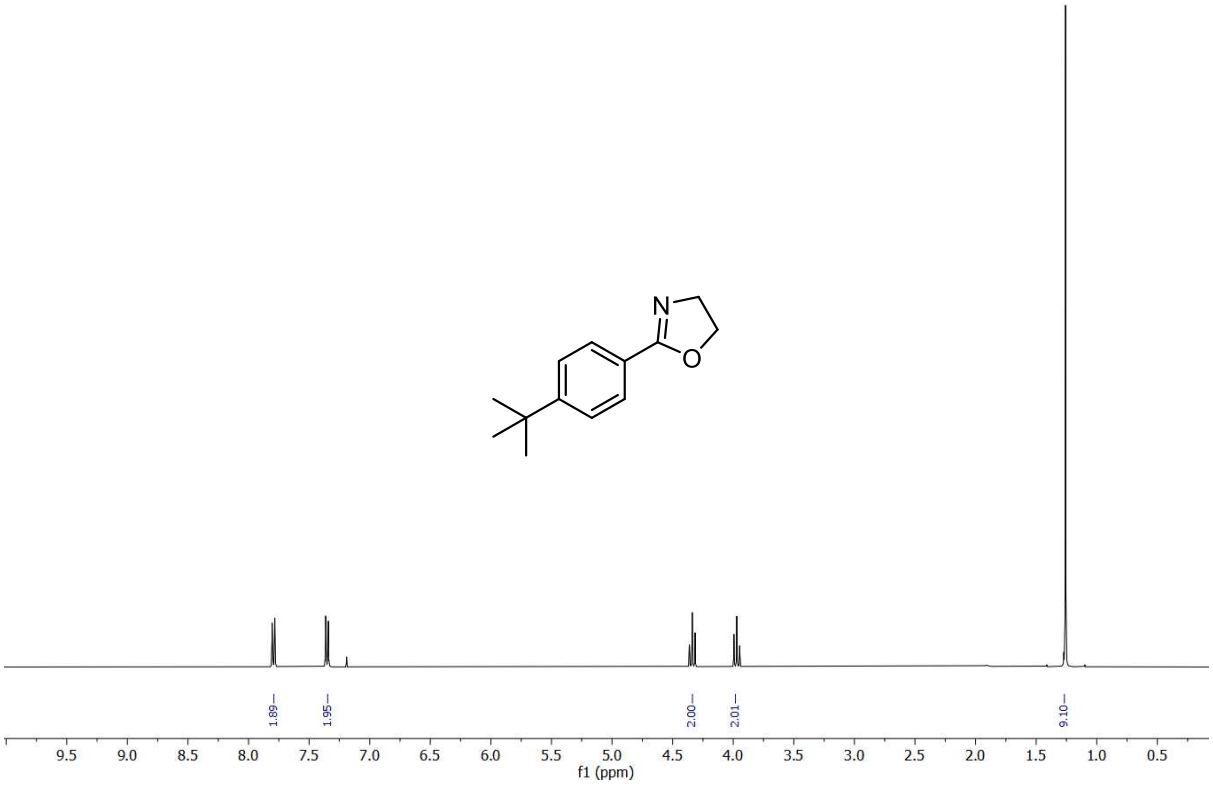


Figure S57 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3**.

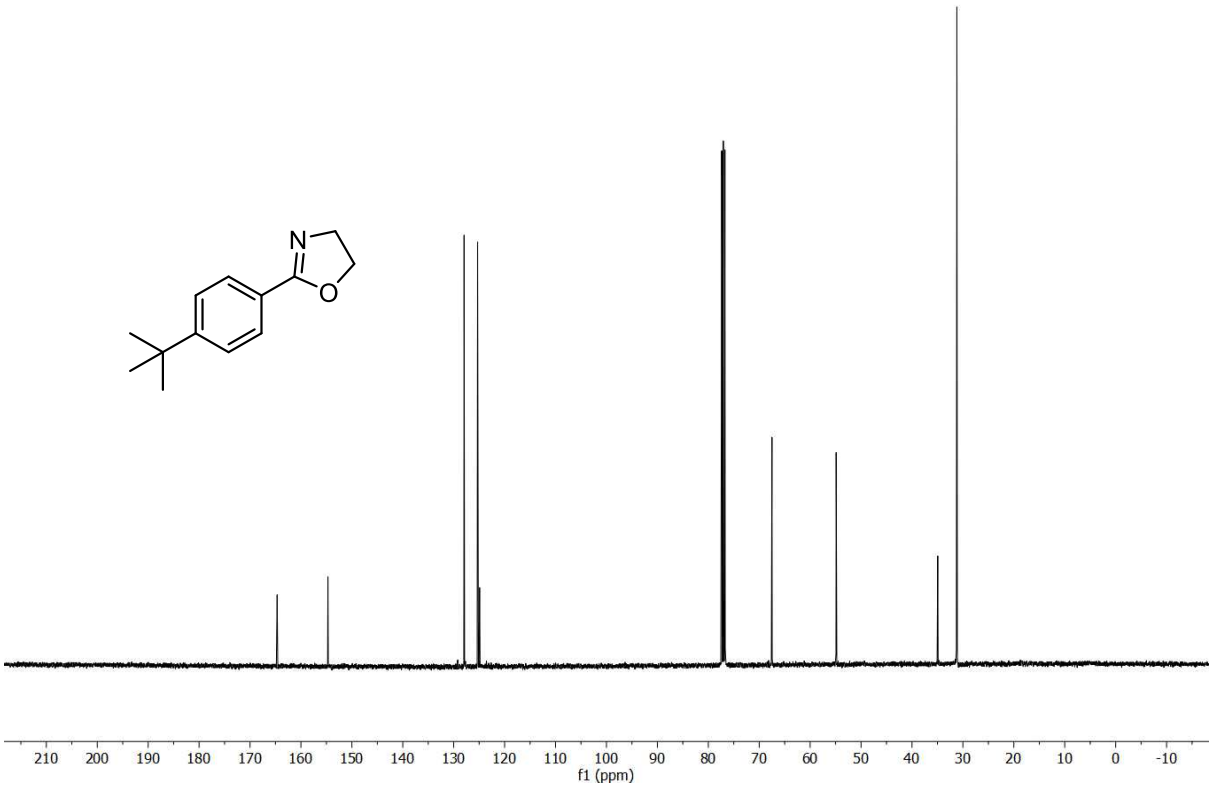


Figure S58 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **3**.

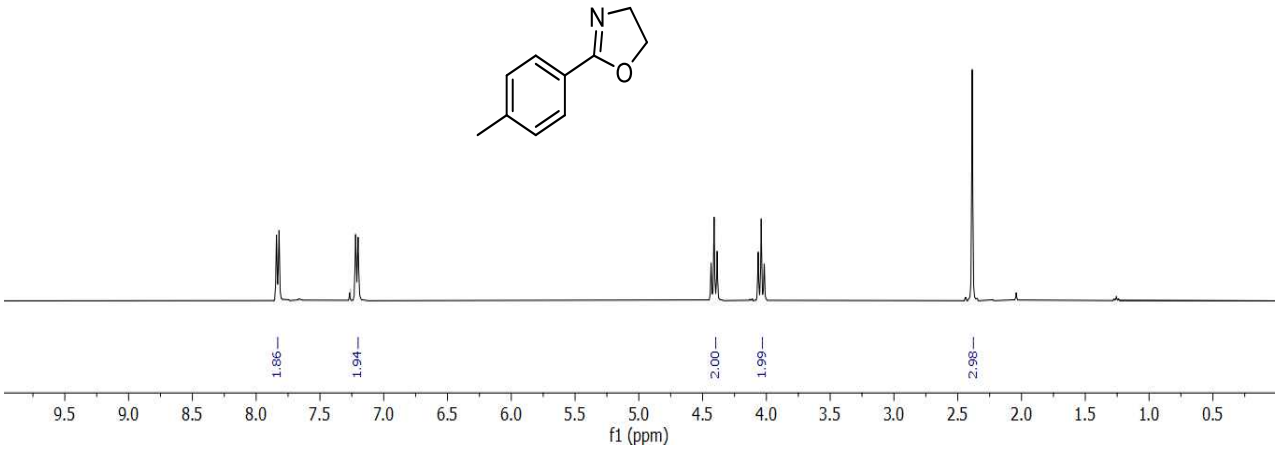


Figure S59 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4**.

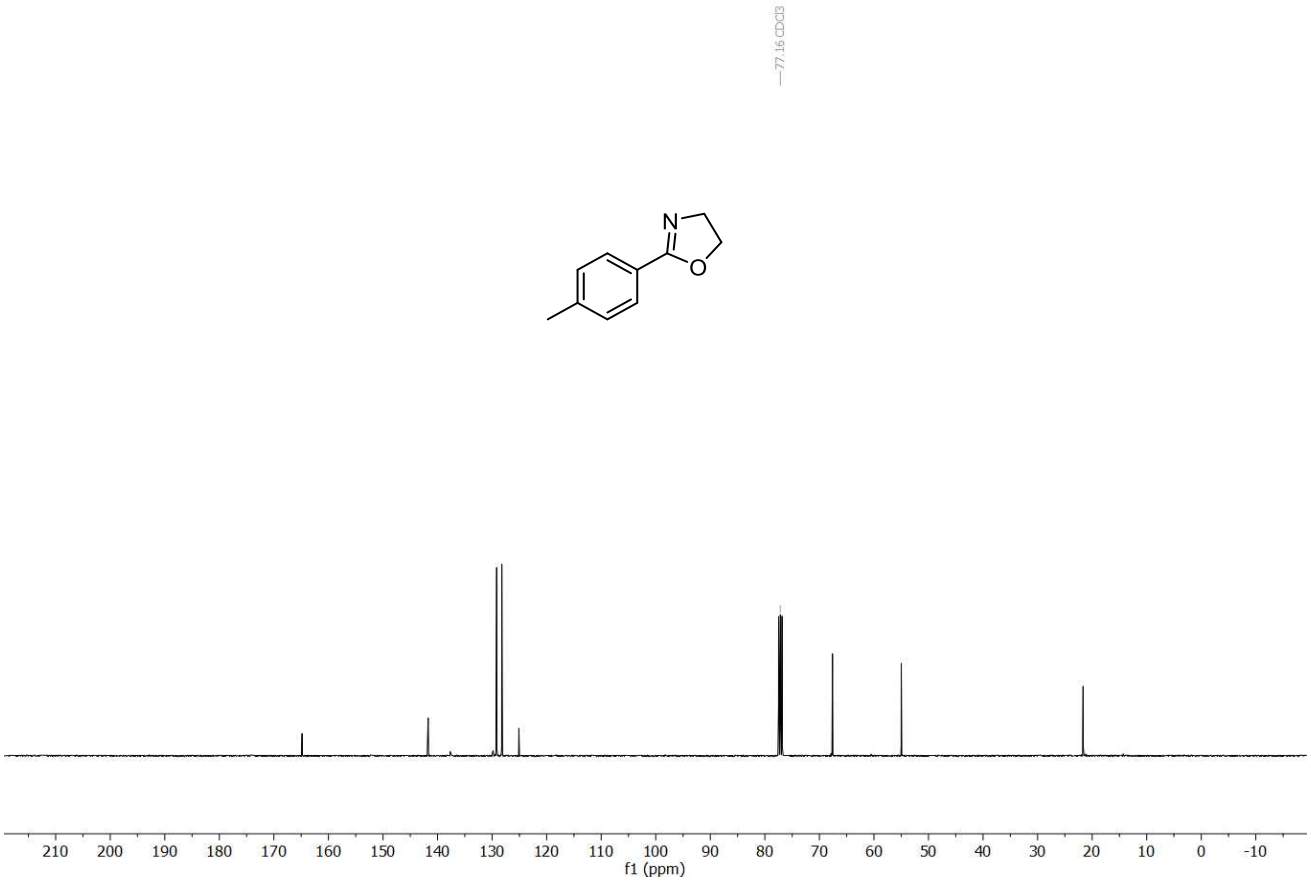


Figure S60 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **4**.

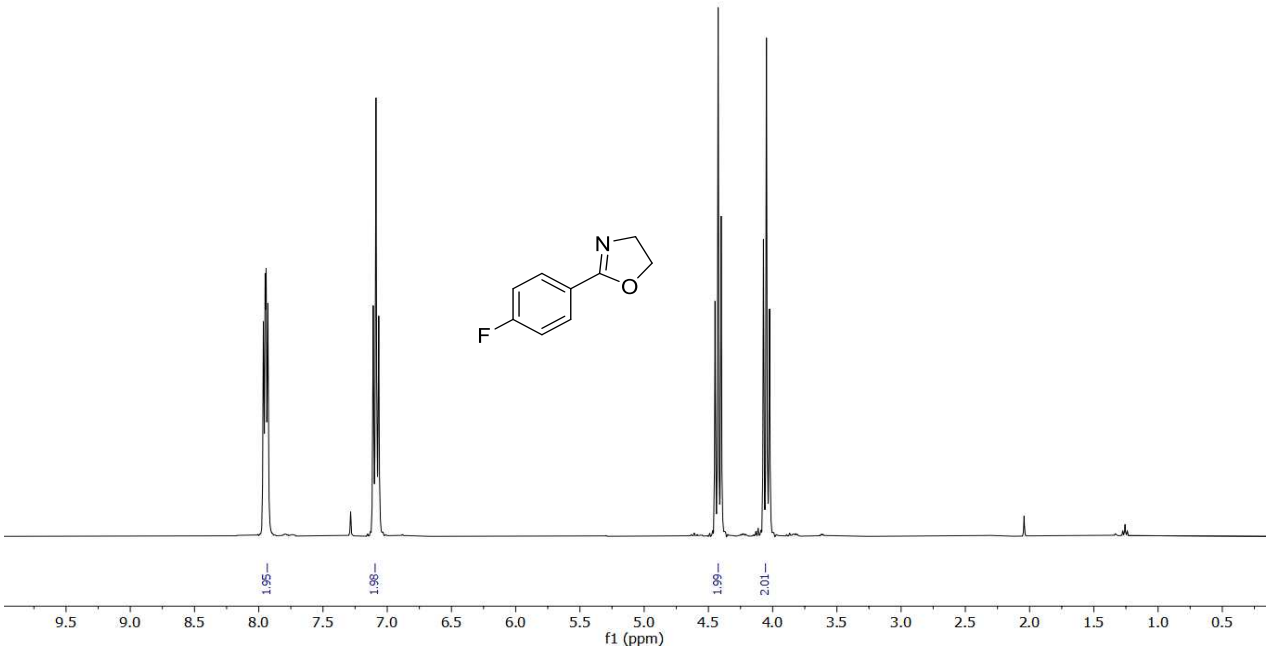


Figure S61 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5**.

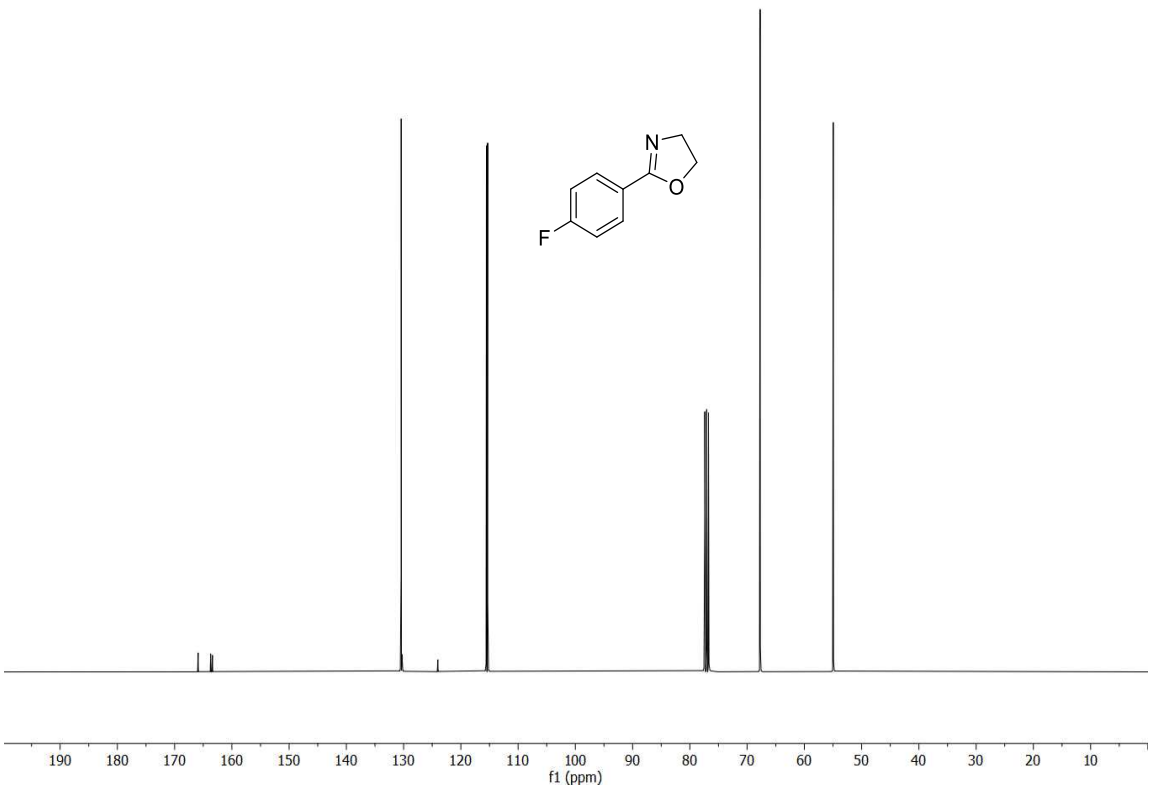


Figure S62 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **5**.

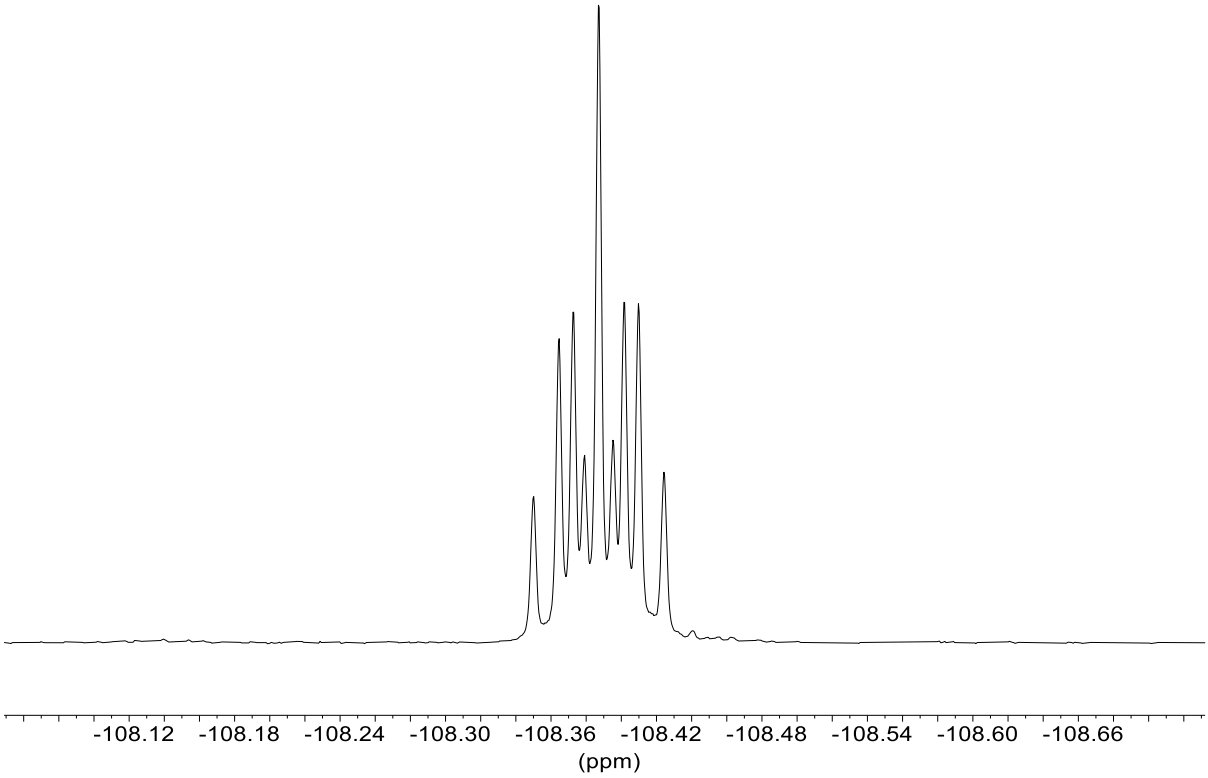


Figure S63 ^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of **5**.

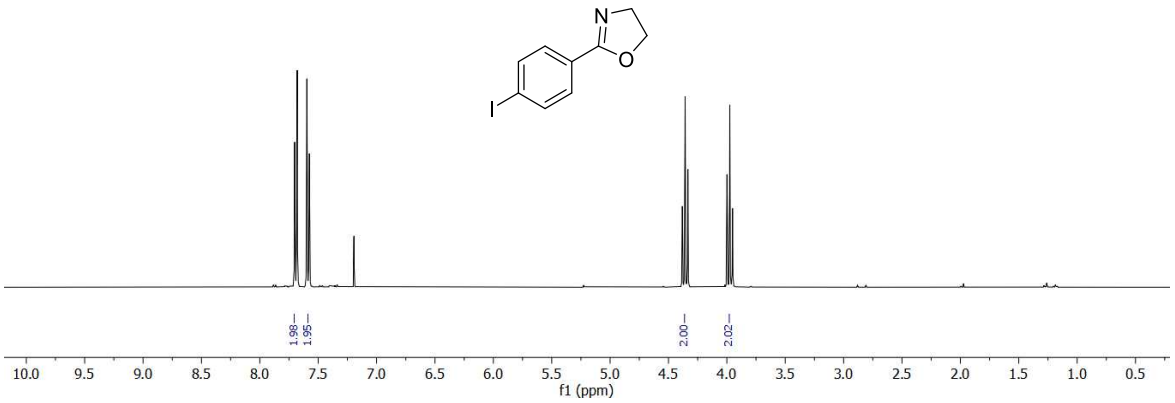


Figure S64 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6**.

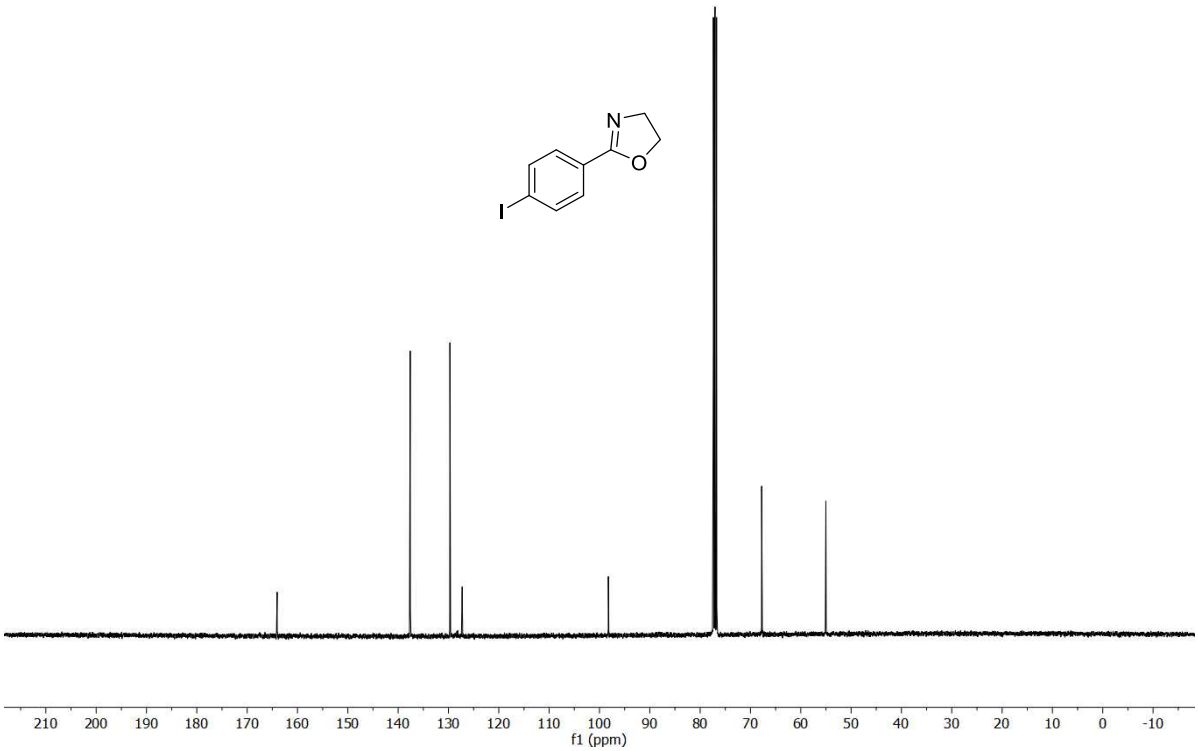


Figure S65 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **6**.

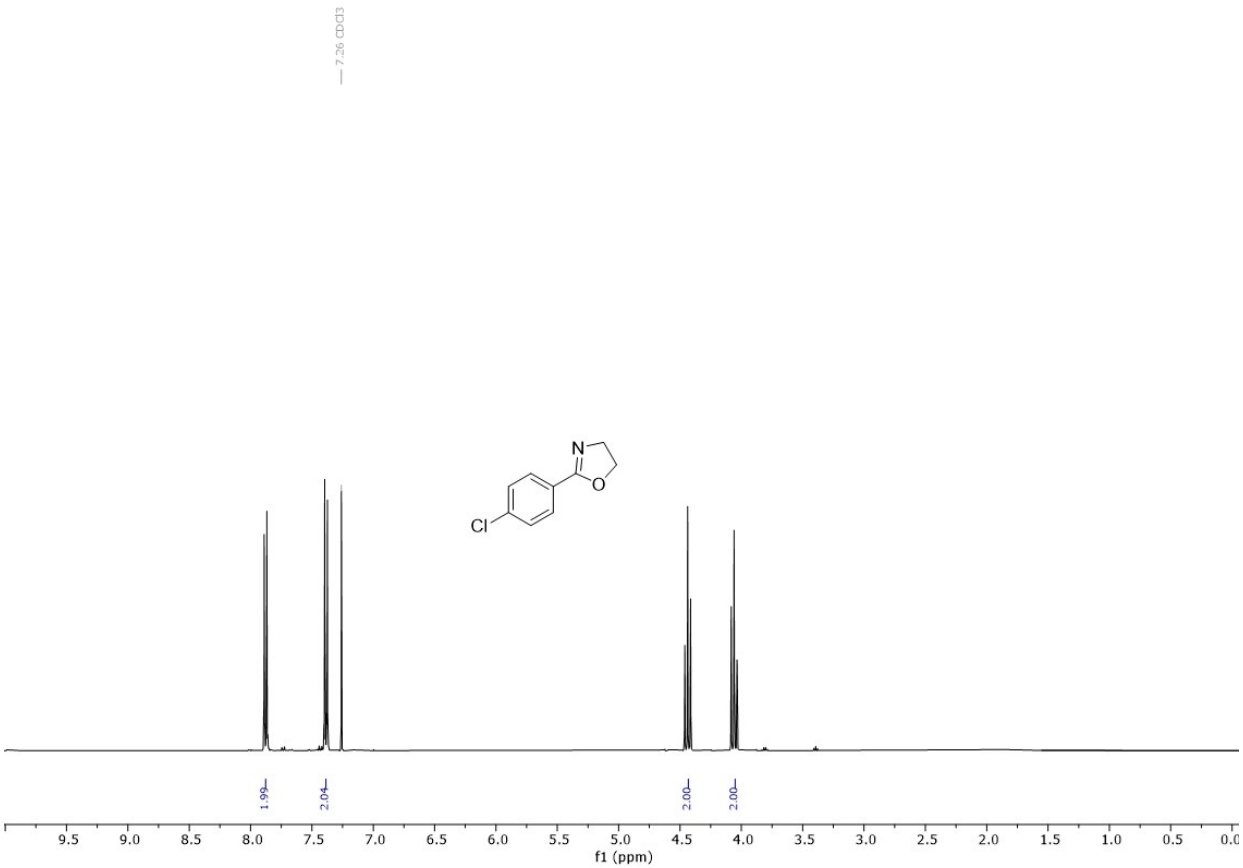


Figure S66 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **7**.

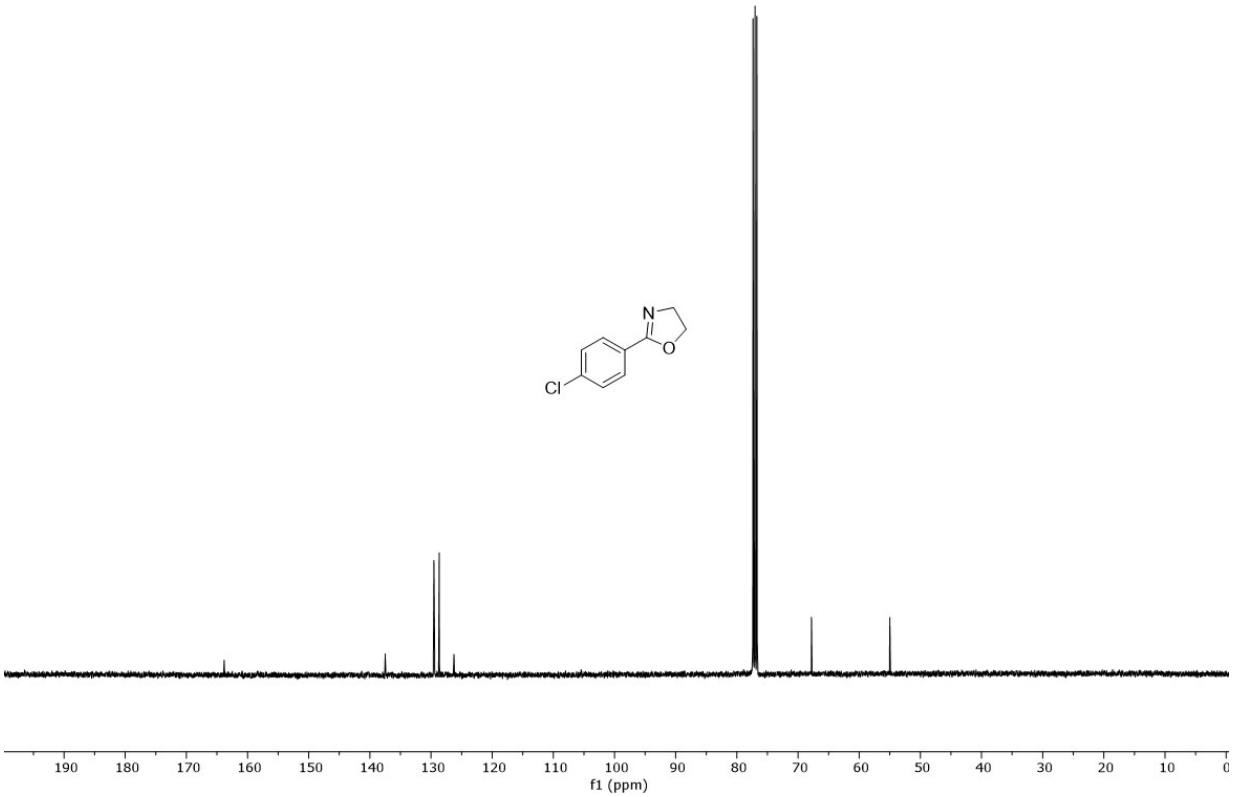


Figure S67 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **7**.

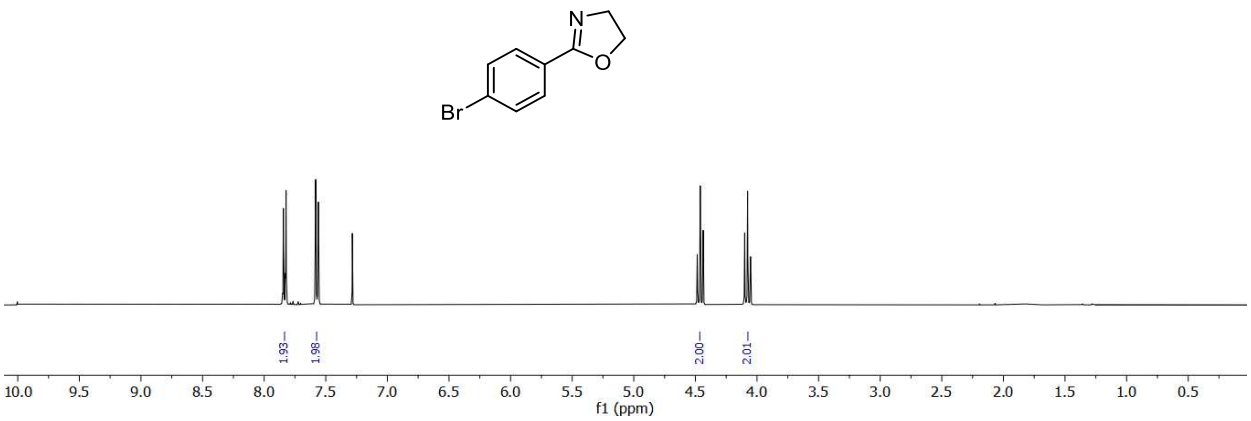


Figure S68 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **8**.

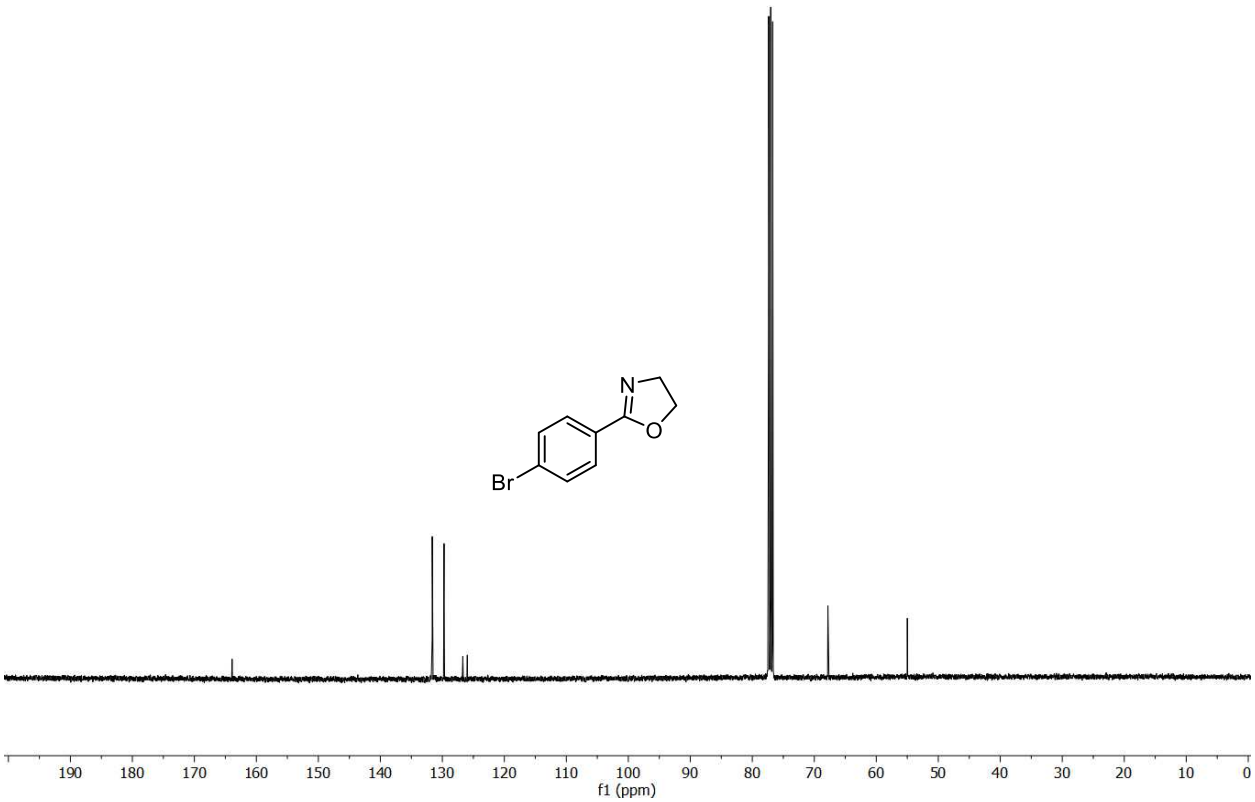


Figure S69 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **8**.

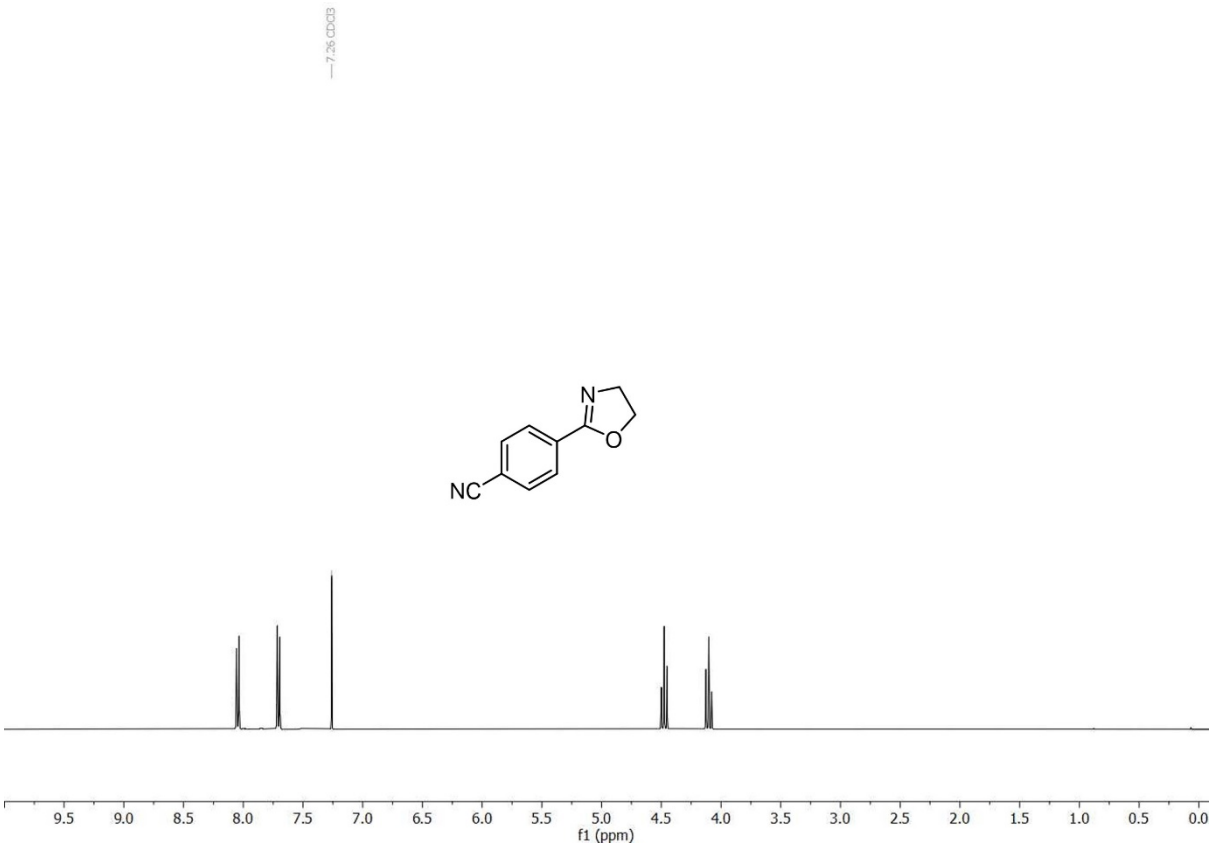


Figure S70 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **9**.

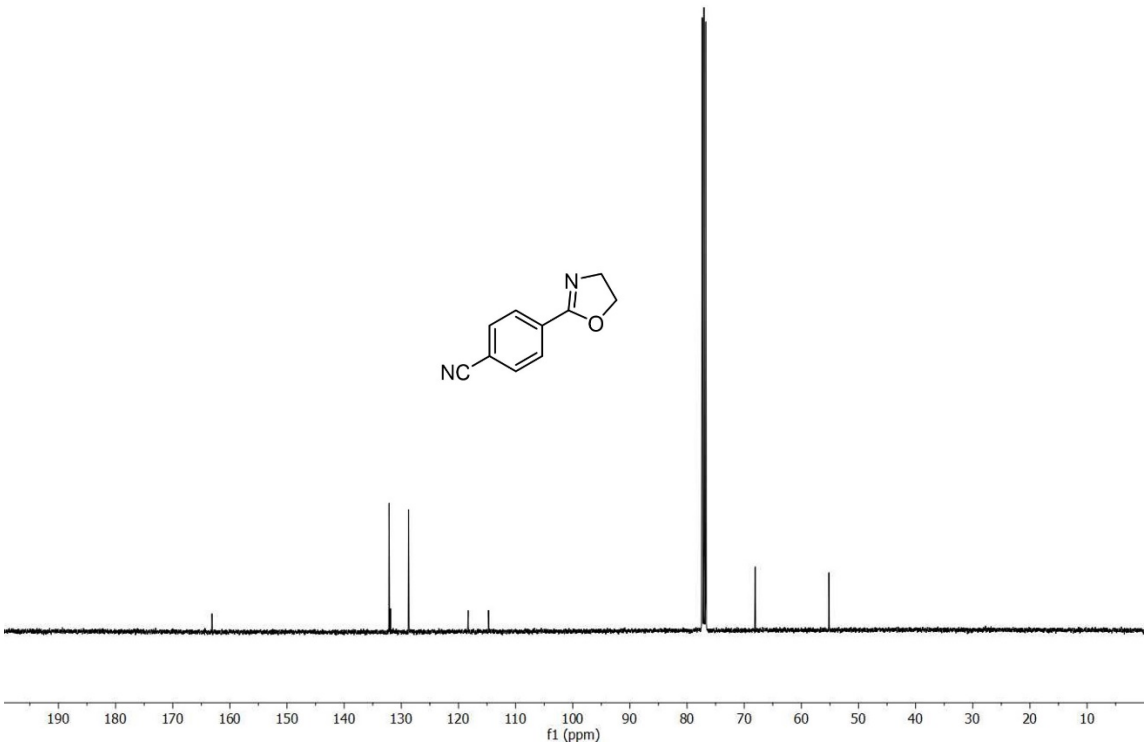


Figure S71 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **9**.

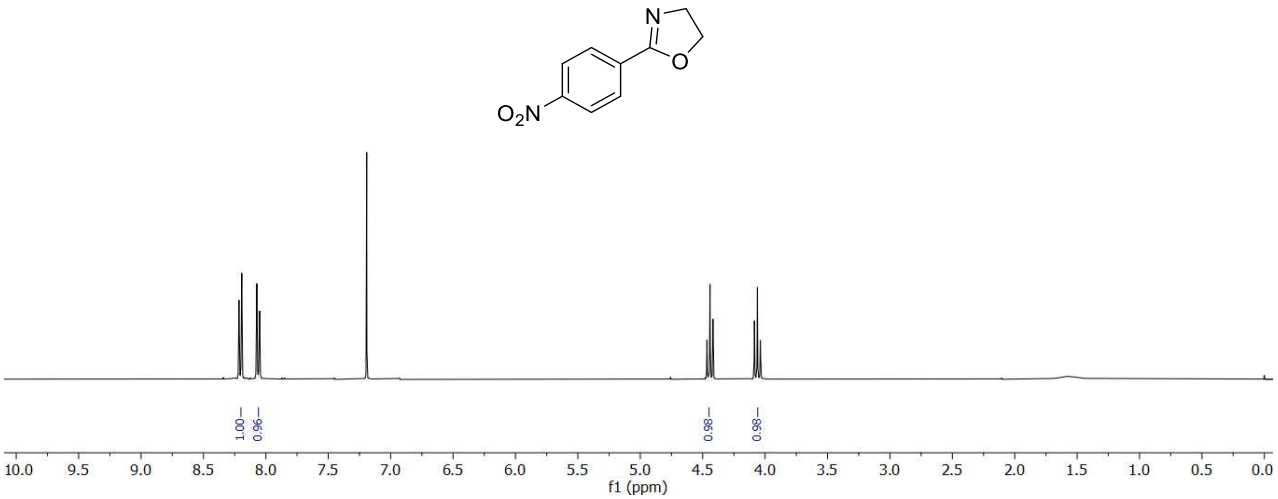


Figure S72 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **10**.

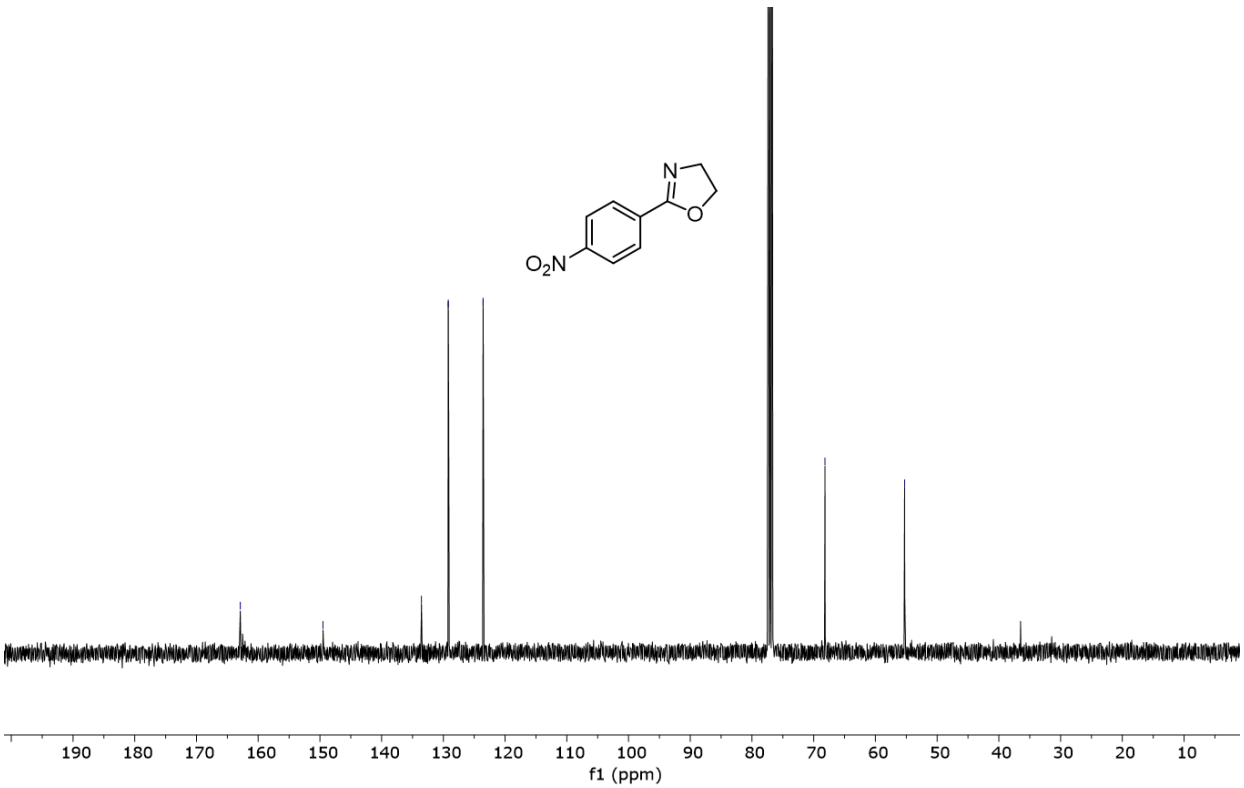


Figure S73 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **10**.

3 References

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