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Electronic Supplementary Information

Unprecedented ROP of quinazolinones to polyacylamidines by cesium catalyst

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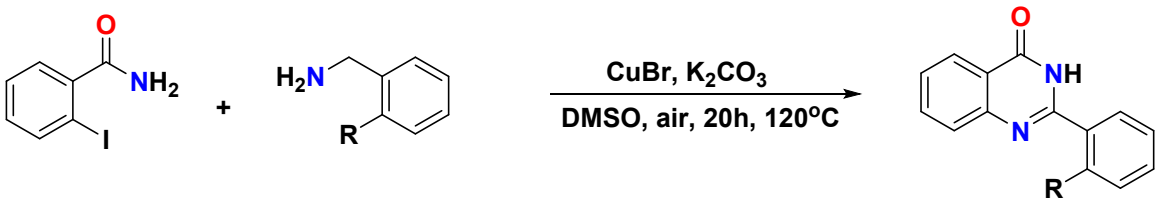
General Considerations

All manipulations involving air and moisture sensitive organometallic compounds were carried out under argon using the argon-filled glove box. Polymerization reactions were carried in dried schlenk tube equipped with magnetic stirrer. In a typical procedure, first the monomer **(2a-2c)** was added to the solution of catalyst in toluene (1 mL). Then the solution was stirred at required temperature for a desired reaction time after which the solution was quenched by adding few drops of acidic methanol. Then the solution was concentrated in vacuum and polymer was recrystallized from dichloromethane and hexane followed by methanol precipitation. The final polymer obtained was dried under vacuum to constant weight.

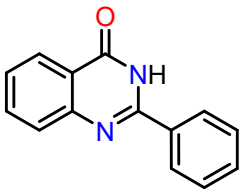
General Procedure for the synthesis of 2-phenylquinazolin-4(3H)-one (2a) and its derivatives (2b and 2c)[1]

The reaction was carried out in a 25 mL flask equipped with a magnetic stirring bar. To the schlenk, 2-halobenzamide (0.2 mmol), arylmethanamine (0.4 mmol), K_2CO_3 (0.6 mmol) and CuBr (0.02 mmol,) in DMSO (3 mL) were added. After the addition of all the reactants, the reaction mixture was allowed to stir under air (1 atm) at 120°C for 20 h. After completion of the reaction, the resulting solution was allowed to cool down to room temperature and then filtered. Then, the solvent of the filtrate was removed using a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (3:1 to 2:1) as eluent to give the desired product.

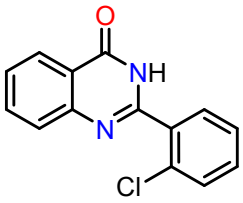


	R
2a	H
2b	Cl
2c	OMe

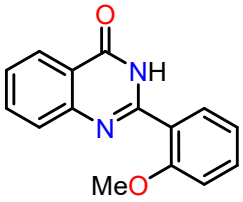
Scheme 1: Copper- Catalysed Cascade Coupling of 2-Iodobenzamide with arylmethanamine to form 2-phenylquinazolin-4(*3H*)-one and its derivatives under air



Yield= 65 mg (80%). White solid, mp = 235–237˚C.[5, 7] ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 12.52 (s, br, 1H), 8.20-8.16 (m, 3H), 7.86-7.84 (t, 1H, J = 7.85 Hz), 7.76-7.75 (d, 1H, J= 7.76 Hz), 7.60-7.52(m, 4H). ^{13}C NMR (151 MHz, DMSO) δ_C 162.3, 152.3, 148.8, 134.6, 132.7, 131.4, 128.6, 127.8, 127.5, 126.6, 125.9, 121.0.



Yield= 75 mg (80%). Yellow solid, mp = 186˚C.[6] ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 12.65 (s, br, 1H), 8.20-8.18 (d, 1H, J= 8.19 Hz), 7.89-7.85 (m, 1H, J= 7.87 Hz), 7.73-7.68 (m, 2H), 7.64 -7.56 (m, 3H), 7.53-7.49 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ_C 161.9, 152.7, 149.1, 135.1, 134.3, 132.1, 131.9, 131.4, 130.1, 128.1, 127.7, 127.5, 126.3, 121.7.



Yield= 78 mg (84%). White solid, mp = 208–210˚C.[5, 8] ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 12.42 (s, br, 1H), 8.22-8.14 (m, 3H), 7.84-7.8 (t, 1H, J= 7.82 Hz), 7.73-7.71 (d, 1H, J= 7.72), 7.51-7.47 (t, 1H, J= 7.50 Hz), 7.11-7.09 (d, 2H, J= 7.10), 3.86 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ_C 162.78, 162.33, 152.32, 149.41, 134.99, 130.18, 129.92, 129.51, 128.29, 127.75, 126.57, 126.30, 125.27, 121.16, 55.91.

DSC Analysis

DSC studies were carried out on a SDT Q200 DSC instrument, with a heating rate of 10 ˚C min^{-1} under N_2 flow (50 ml min^{-1}). DSC technical indicators are as follows: maximal sensitivity, 0.2 mw; calorimeter accuracy, prior to 1%; calorimeter precision, prior to 1%; temperature accuracy, < 0.1 ˚C; temperature precision, < 0.01 ˚C. An unsealed Al pan with a 2.0 mg sample was used in the experiments. For ΔH measurements, the DSC system was calibrated with indium (m.p. 156.60 ˚C; ΔH_{fus} = 28.45 J g^{-1}).

TGA analysis

TGA analysis was carried out using a SDT Q600 TGA instrument. TGA technical indicators are as follows: balance sensitivity, 0.1 mg; balance accuracy, prior to 0.1%; balance precision, prior to 0.02%; weighting precision, reach to 10 ppm; temperature precision, ±2 ˚C (measure sample). TGA experiment was carried out under N_2 dynamic atmospheres at a flow rate of 10 mL min^{-1}. 2 mg PCL/PLA sample was heated from 40 to 500 ˚C at 10 ˚C min^{-1} in a nitrogen atmosphere (50 ml min^{-1}).

SEM analysis

For morphology studies, scanning electron microscopy (SEM) was performed using Hitachi S-4700-II FE-SEM. For this, the polymer samples were sputtered with carbon and analysis was performed at 2 kV accelerating voltage.

POM analysis

The optical micrographs were recorded on Leica DM2500 polarized optical microscope. Leica Application Suite (version 4.12) was used to capture and process the images. The samples for optical microscopy were prepared by drop casting a hot solution of 0.5 wt% polymer in THF on microscope slides. The slides with the samples were dried at room temperature for 2 days before the analysis. The optical micrographs were recorded using cross-polarizers at 90 deg angle between polarizer and analyzer. Leica Application Suite (version 4.12) was used to capture and process images.

Powder XRD

Powder XRD patterns of polymer samples were performed using a PANalytical X'Pert Pro diffractometer [reflection θ θ geometry, Cu Kα (1.54 Å) radiation]. The diffraction data were collected over a 2θ range from 10 to 40°.

LC-MS analysis

A trace sample was dissolved in methanol and then tested by an LC-MS mass spectrometer (Model: 1260 Infinity II, Make: Agilent).

IR data

The samples were dissolved in methanol and were recorded on the BRUKER ALPHA FTIR spectrometer.

NMR of monomers

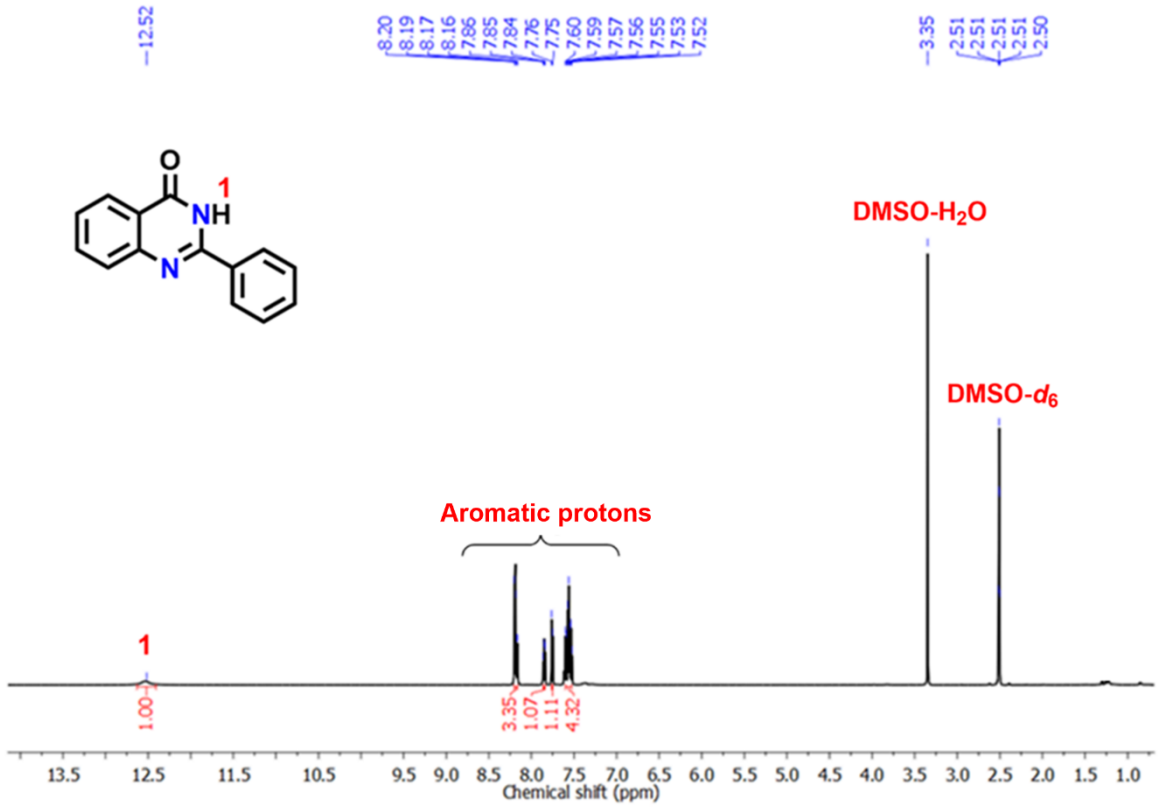


Figure FS1. ^{1}H-NMR (DMSO-d_6, 600 MHz) spectra of 2-phenylquinazolin-4(3*H*)-one **(2a)**

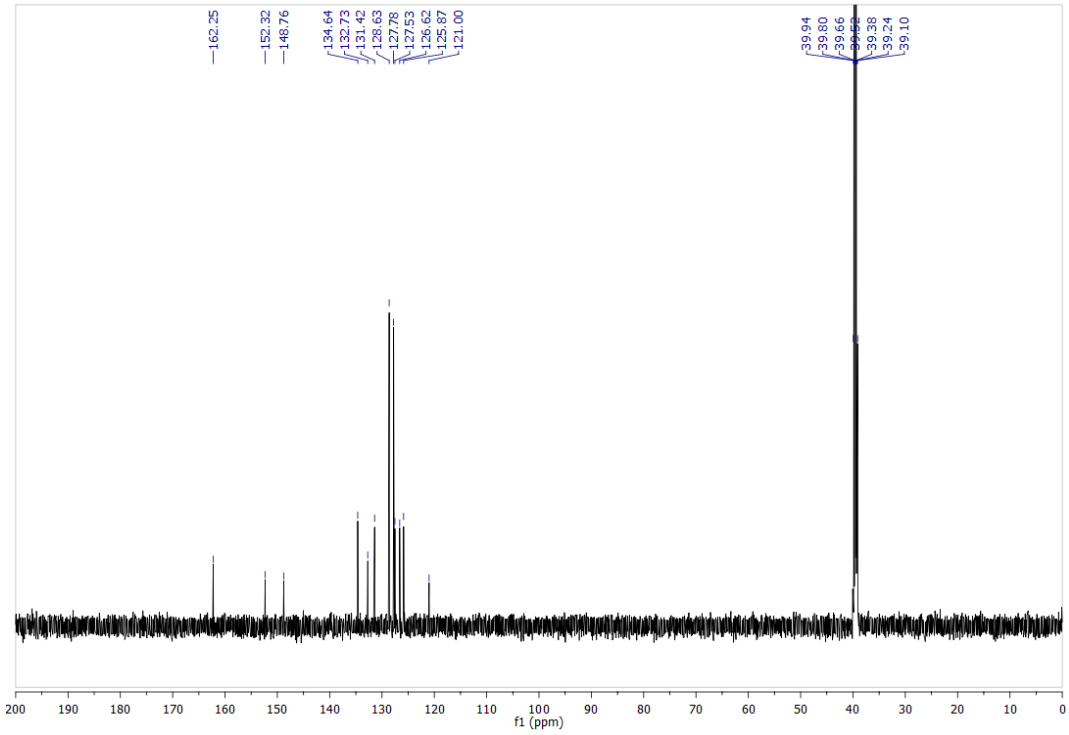


Figure FS2. ^{13}C-NMR (DMSO-d_6,150 MHz) spectra of 2-phenylquinazolin-4(3*H*)-one **(2a)**.

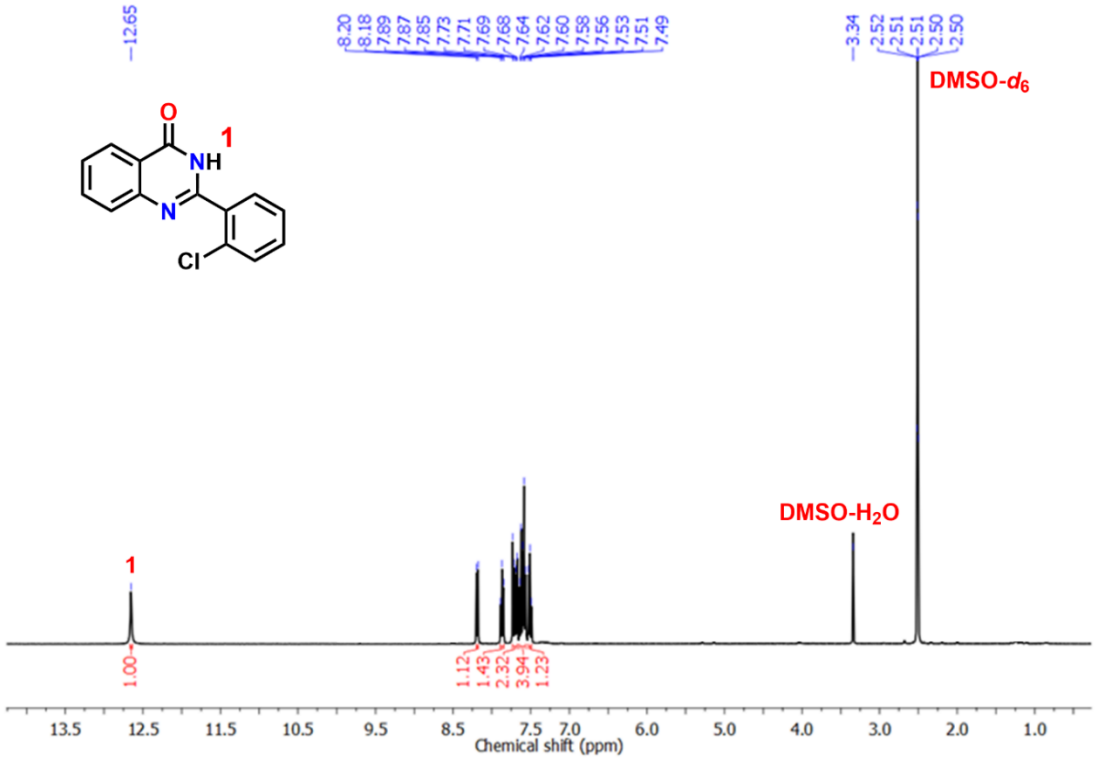


Figure FS3. ^{1}H-NMR (DMSO-d_6, 600 MHz) spectra of 2-(2-chlorophenyl)-4(3*H*)-quinazolinone **(2b)**.

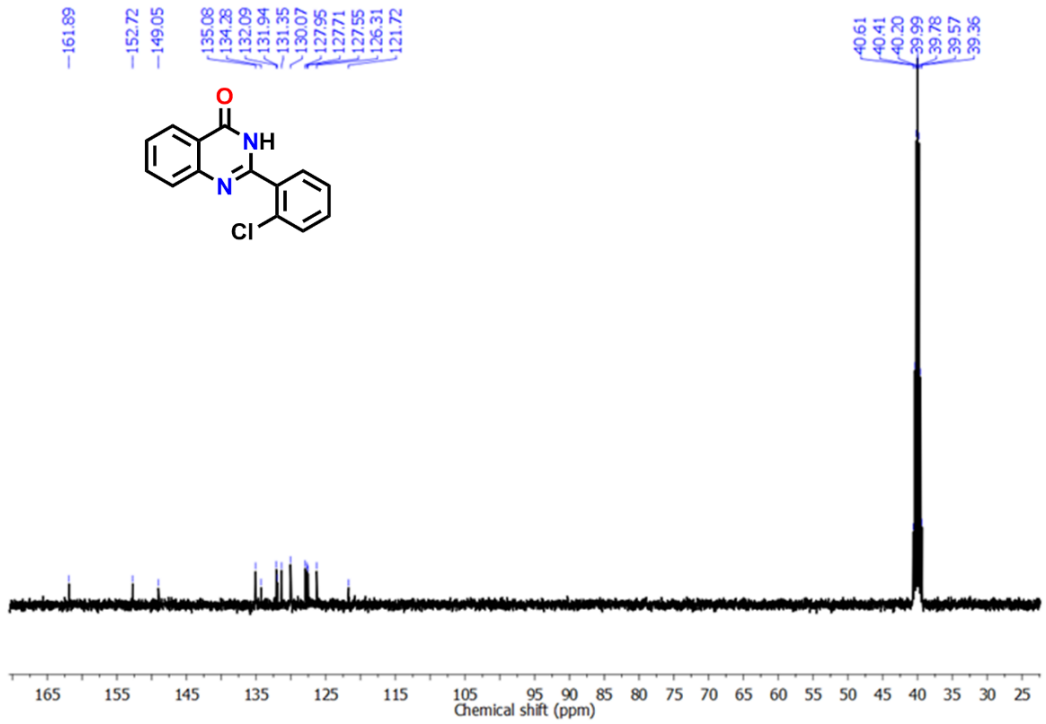


Figure FS4. ^{13}C-NMR (DMSO-d_6,150 MHz) spectra of 2-(2-chlorophenyl)-4(3*H*)-quinazolinone (**2b**).

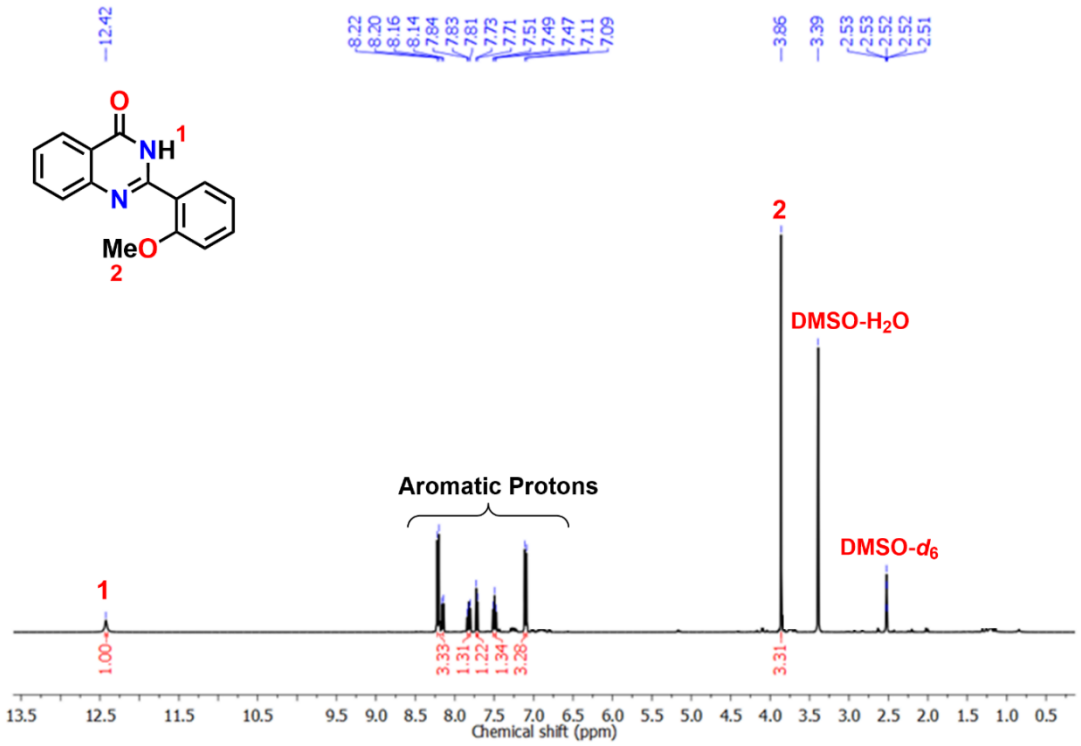


Figure FS5. [1]H-NMR (DMSO-d_6, 600 MHz) spectra of 2-(2-methoxyphenyl)-4(3*H*)-quinazolinone (**2c**)

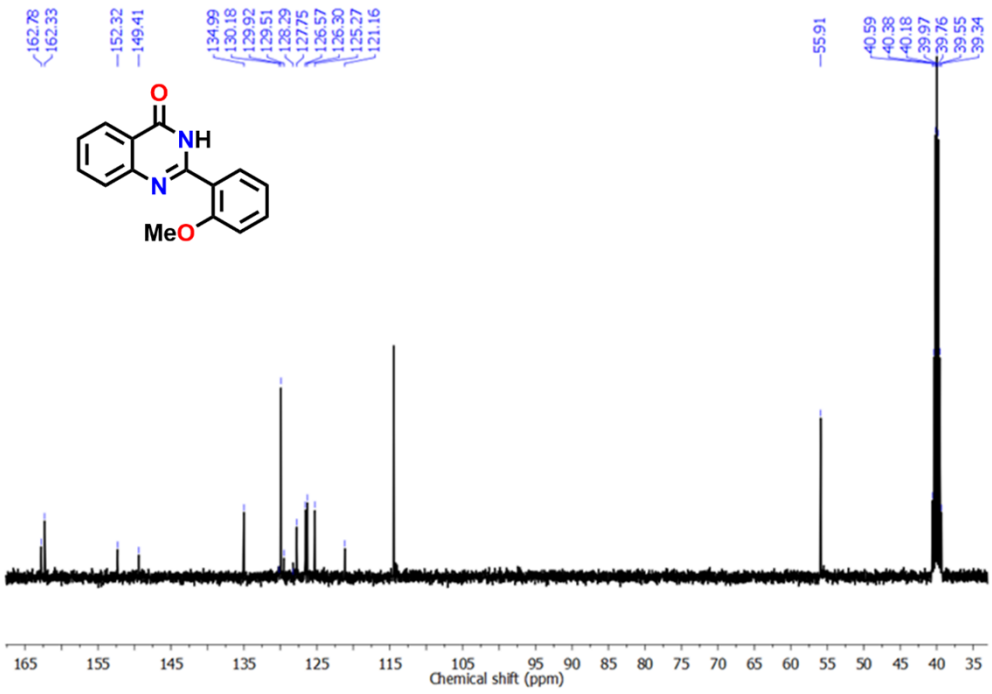


Figure FS6. [13]C-NMR (DMSO-d_6,150 MHz) spectra of 2-(2-methoxyphenyl)-4(3*H*)-quinazolinone (**2c**)

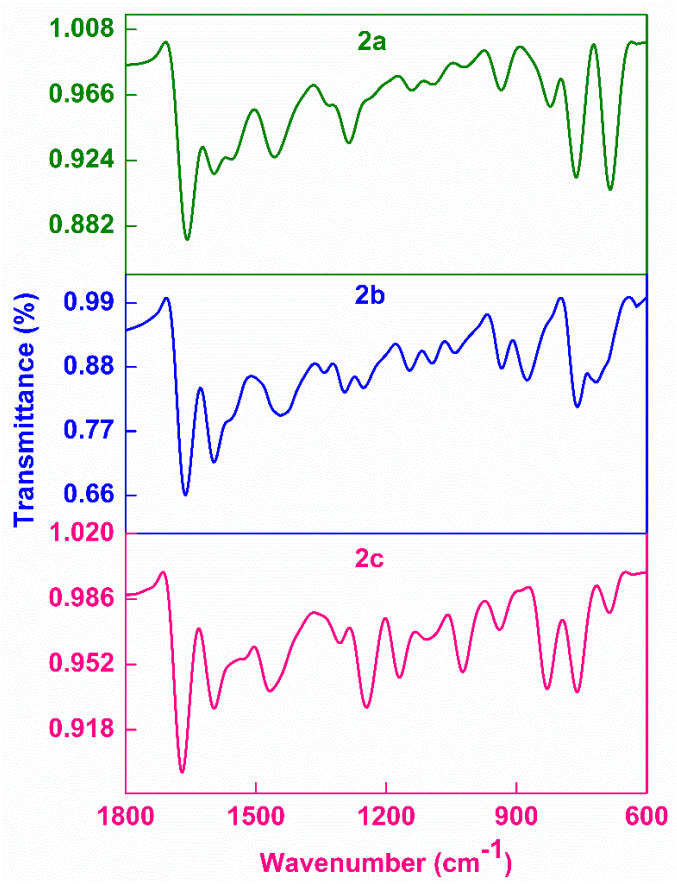


Figure FS7. IR data of monomers **2a-2c**

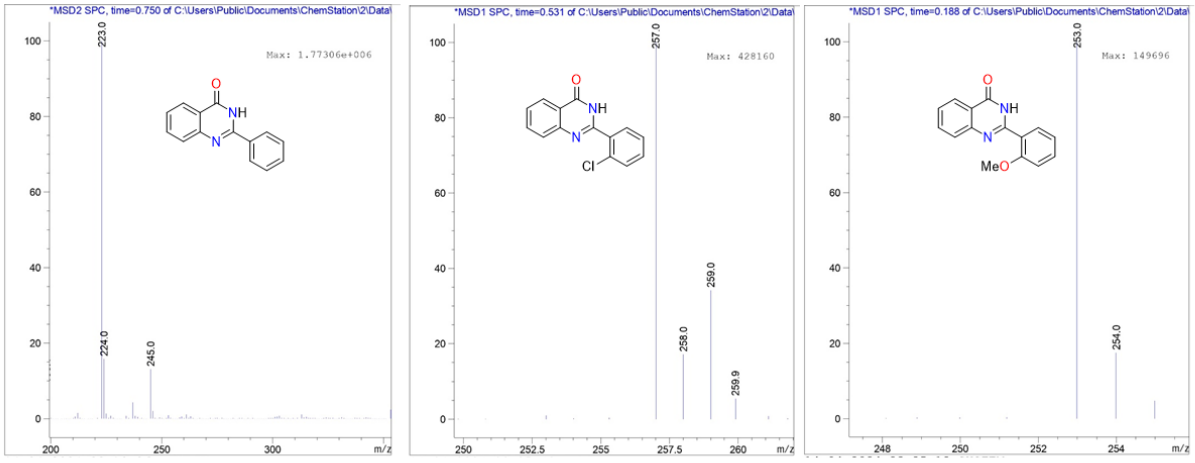


Figure FS8. LC-MS data of monomers **2a-2c**

NMR of polymers

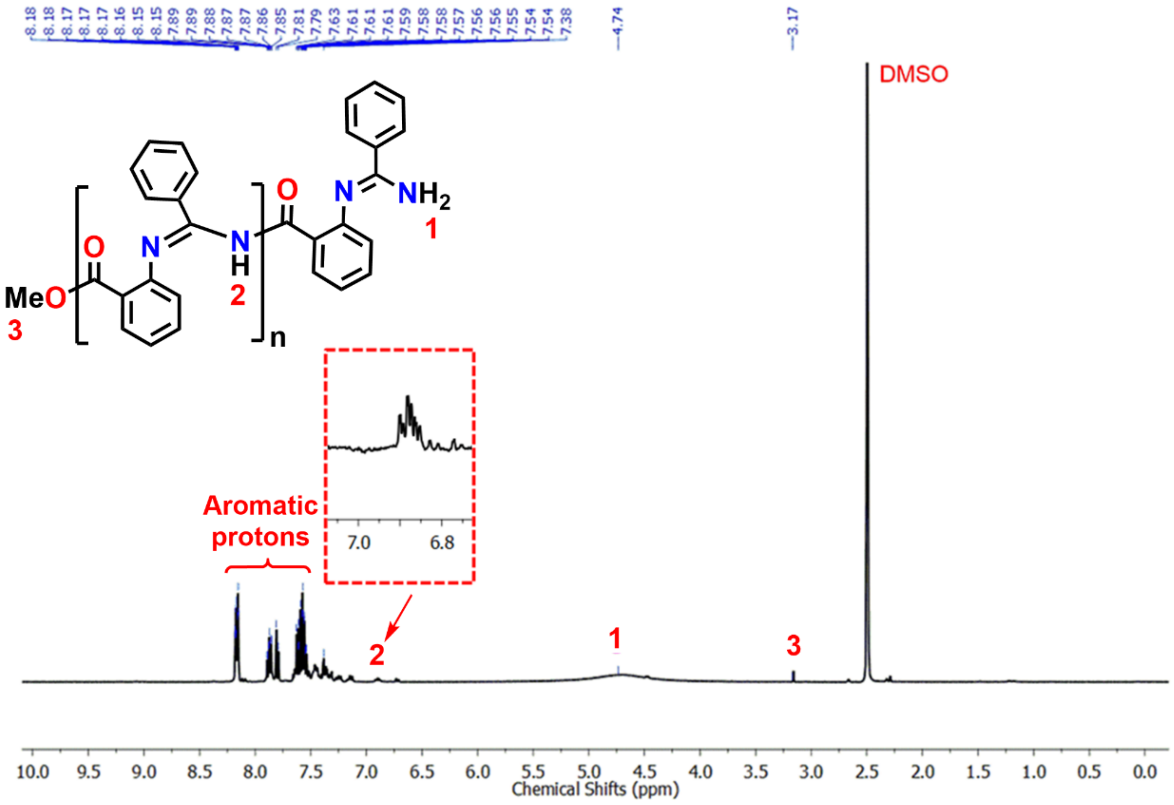


Figure FS9. ^{1}H-NMR (DMSO-d_6, 600 MHz) spectra of poly[2-phenylquinazolin-4(3*H*)-one] **(3a)**

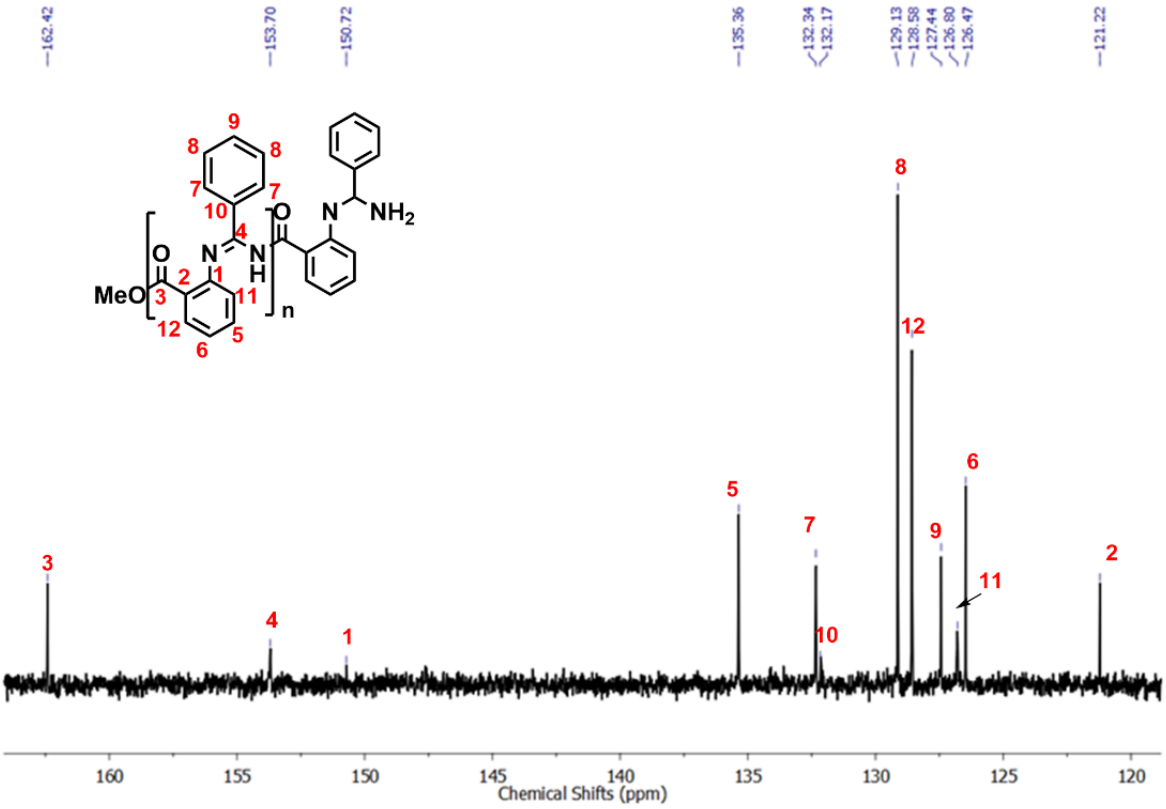


Figure FS10. ^{13}C-NMR (DMSO-d_6, 600 MHz) spectra of poly[2-phenylquinazolin-4(3*H*)-one] **(3a)**

Table TS1. Reaction optimization for the ROP of quinazolinones catalysed by catalyst **1**[a]

Entry	M	[Cat]:[M]	T (˚C)	*t* (h)	***Conversion (%)***	***Yield (%)***	M_{nexp}[b] (kDa)	D_p[c]	PDI
1	2a	1:100	RT	6	78.2	68	12.0, 5.4	78.2	1.30, 1.21
2	2a	1:100	65	2	84.1	86	18.7	84.1	1.17
3	2a	1:100	65	4	91.8	92	20.4	91.8	1.13
4	2a	1:100	65	6	98.5	97	21.9	98.5	1.09
5	2a	1:200	65	6	92.5	90	41.1	184.9	1.12
6	2a	1:300	65	6	77.2	73	51.5	231.1	1.19
7	2b	1:100	65	6	93.9	90	24.1	93.9	1.07
8	2b	1:200	65	6	97.2	95	49.9	194.4	1.10
9	2b	1:300	65	6	99.9	98	77.0	300	1.14
10	2c	1:100	65	6	98.3	94	24.8	98.3	1.06
11	2c	1:200	65	6	95.1	91	48.0	190.3	1.10
12	2c	1:300	65	6	96.9	90	73.4	291.0	1.16

[a]In toluene, [Catalyst] = 0.0019 mmol, [b]In THF (2 mg mL^{-1}) and molecular weights were determined by GPC-LLS (flow rate ¼ 0.5 mL min-1). Universal calibration was carried out with polystyrene standards, laser light scattering detector data, and concentration detector. Each experiment is duplicated to ensure precision. [c]Degree of polymerization (D_p) determined from M_{nexp}.

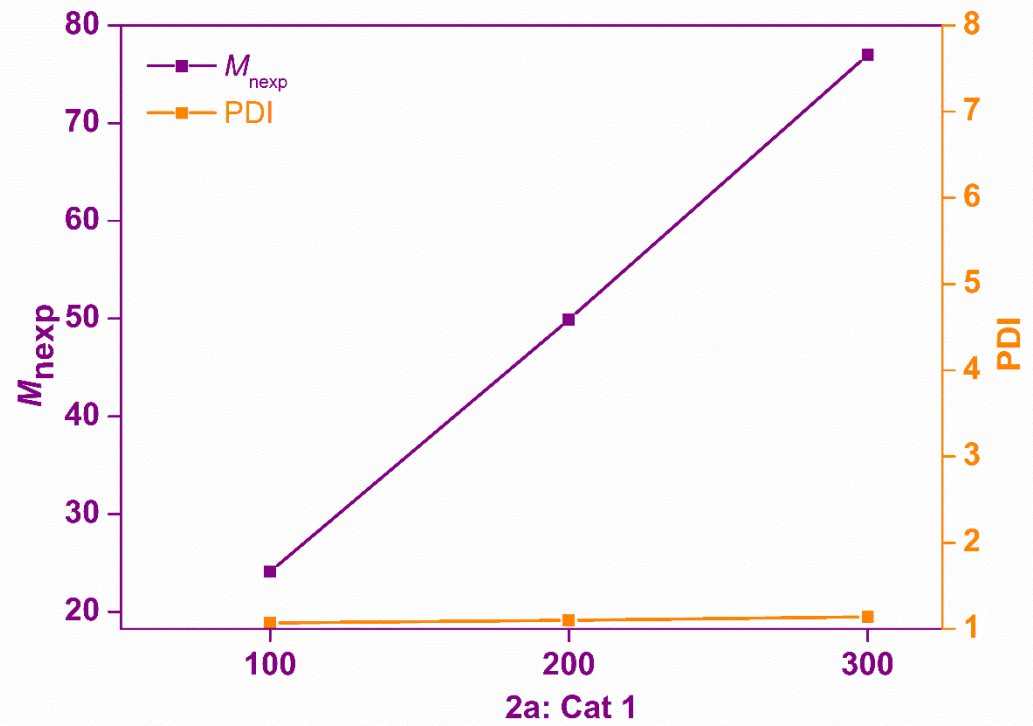


Figure FS11. Plot of experimental M_n and PDI of polyacylamidine **3a** as functions of molar equivalent of **2a** with respect to catalyst **1** (*M*n = number average molecular weight, PDI = polydispersity index)

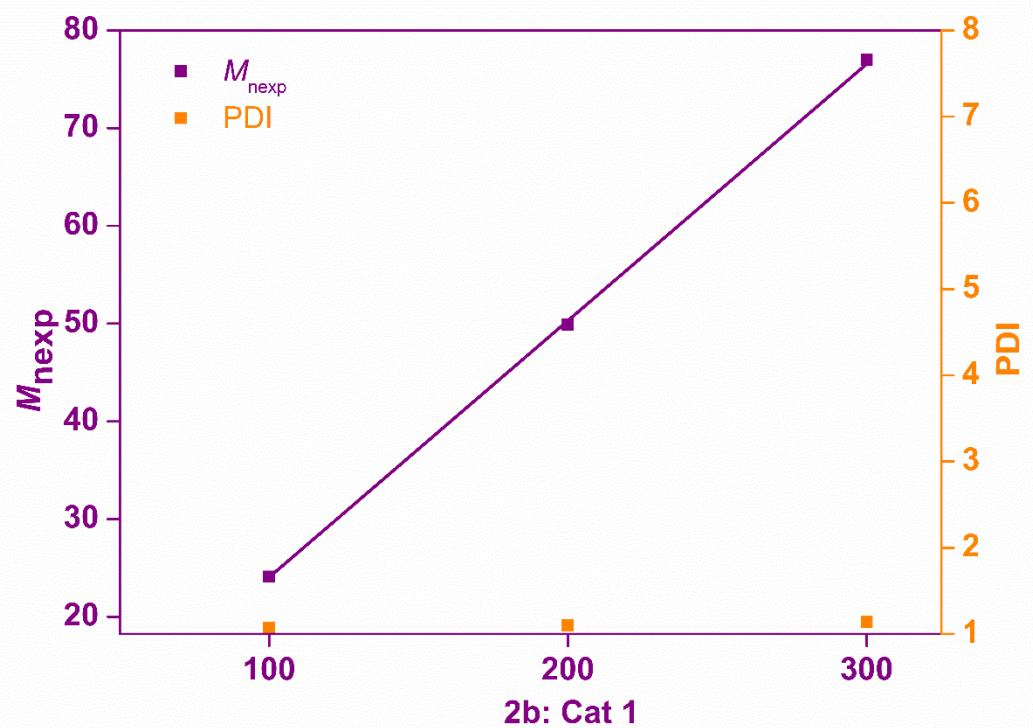


Figure FS12. Plot of experimental M_n and PDI of polyacylamidine **3b** as functions of molar equivalent of **2b** with respect to catalyst **1** (*M*n = number average molecular weight, PDI = polydispersity index)

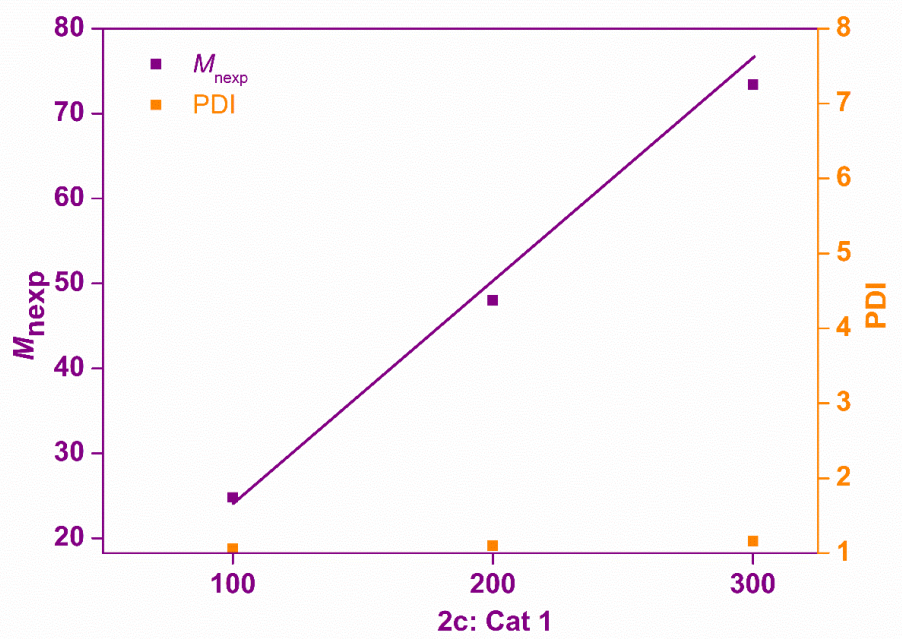


Figure FS13. Plot of experimental M_n and PDI of polyacylamidine **3c** as functions of molar equivalent of **2c** with respect to catalyst **1** (*M*n = number average molecular weight, PDI = polydispersity index)

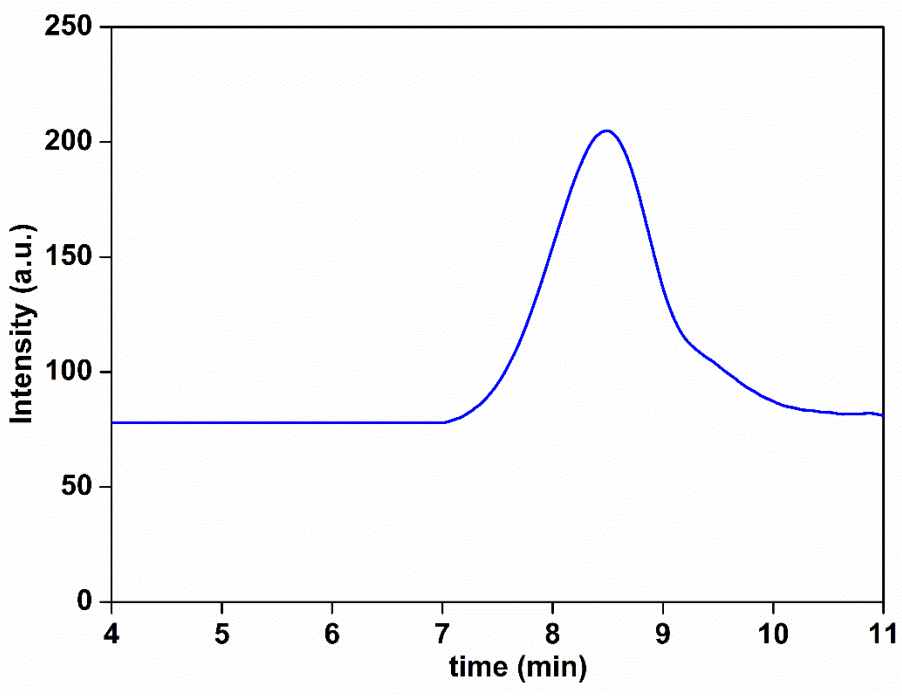
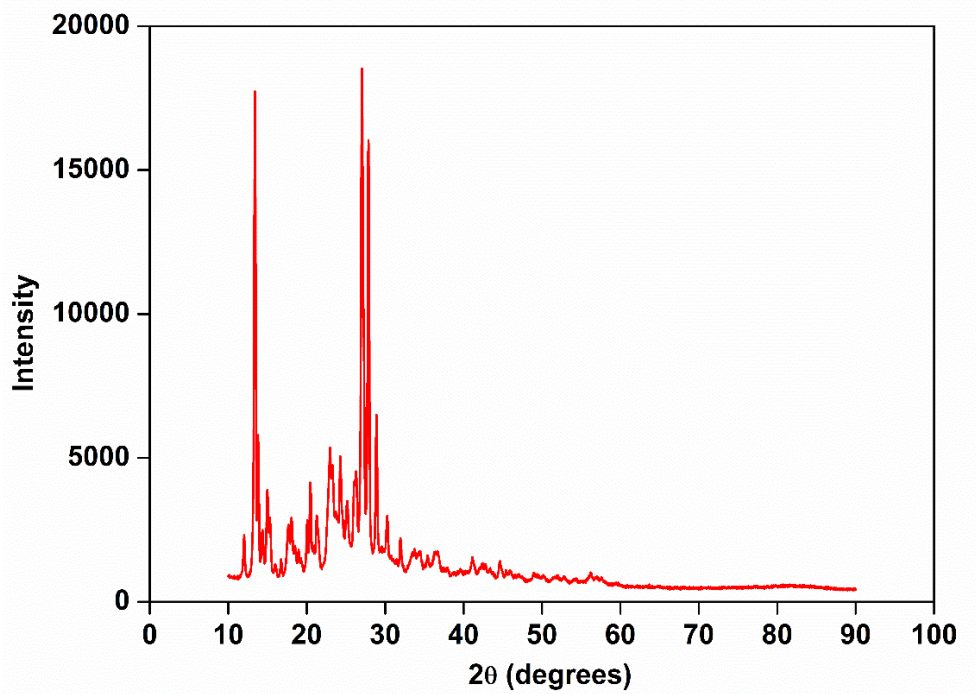
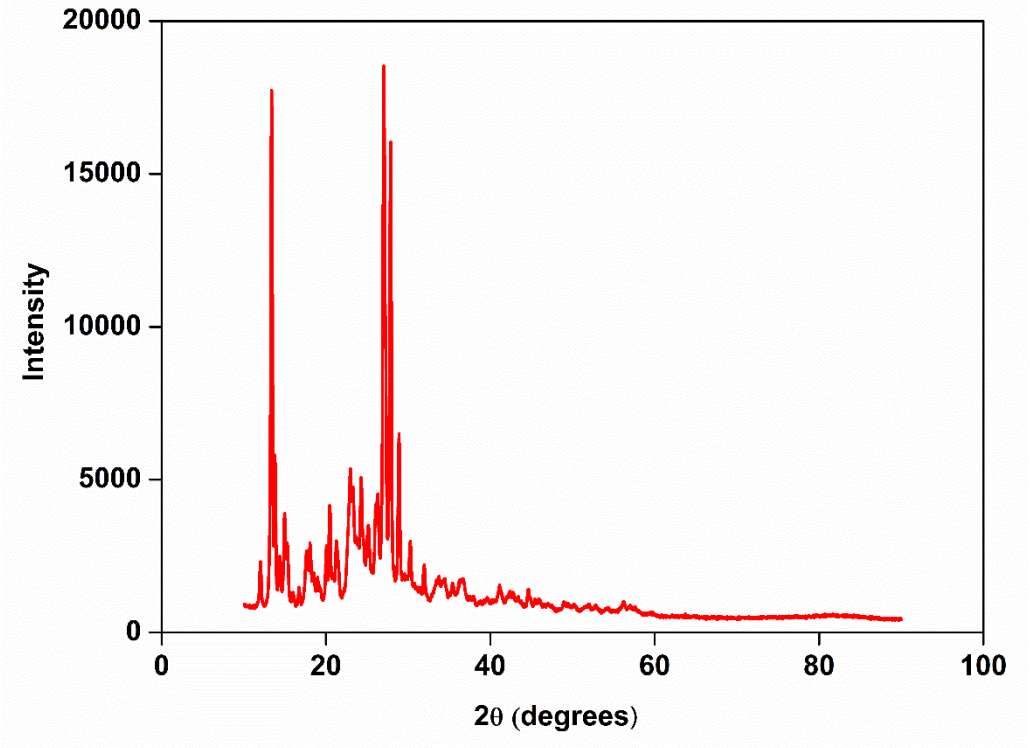


Figure FS14. GPC profile of sample of **3b** [Entry 9, Table TS1].


20000
15000
10000
5000
0
Intensity
0
10
20
30
40
50
60
70
80
90
100
2θ (degrees)


20000
15000
10000
5000
0
Intensity
0
20
40
60
80
100
2θ (degrees)

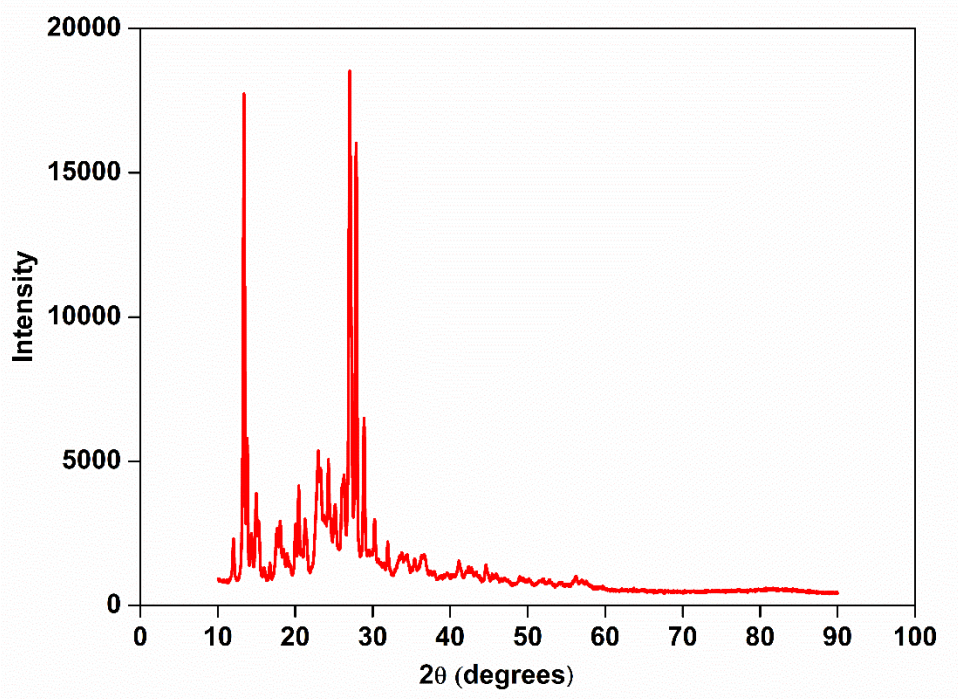


Figure FS15. PXRD curve of **3a, 3b** and **3c** sample (Entry 4, 7 and 10) in Table TS1 respectively.

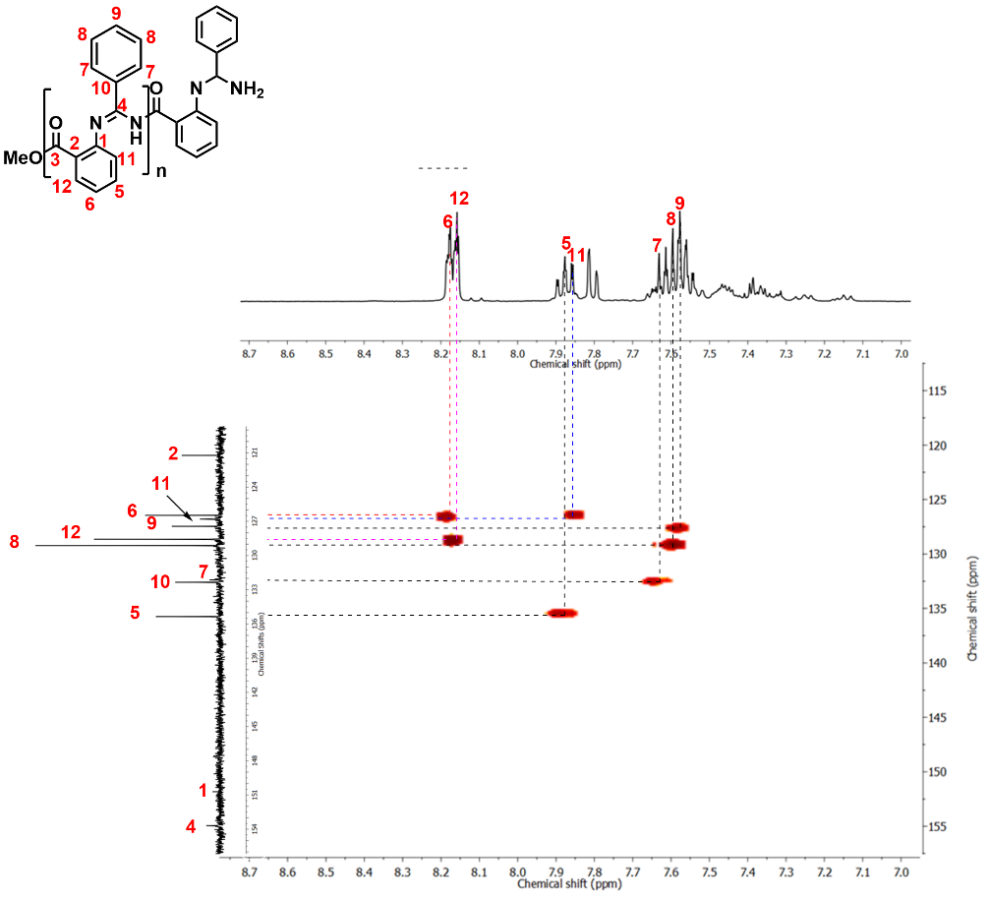


Figure FS16. HSQC NMR spectra of poly-2-phenylquinazolin-4(3*H*)-one.

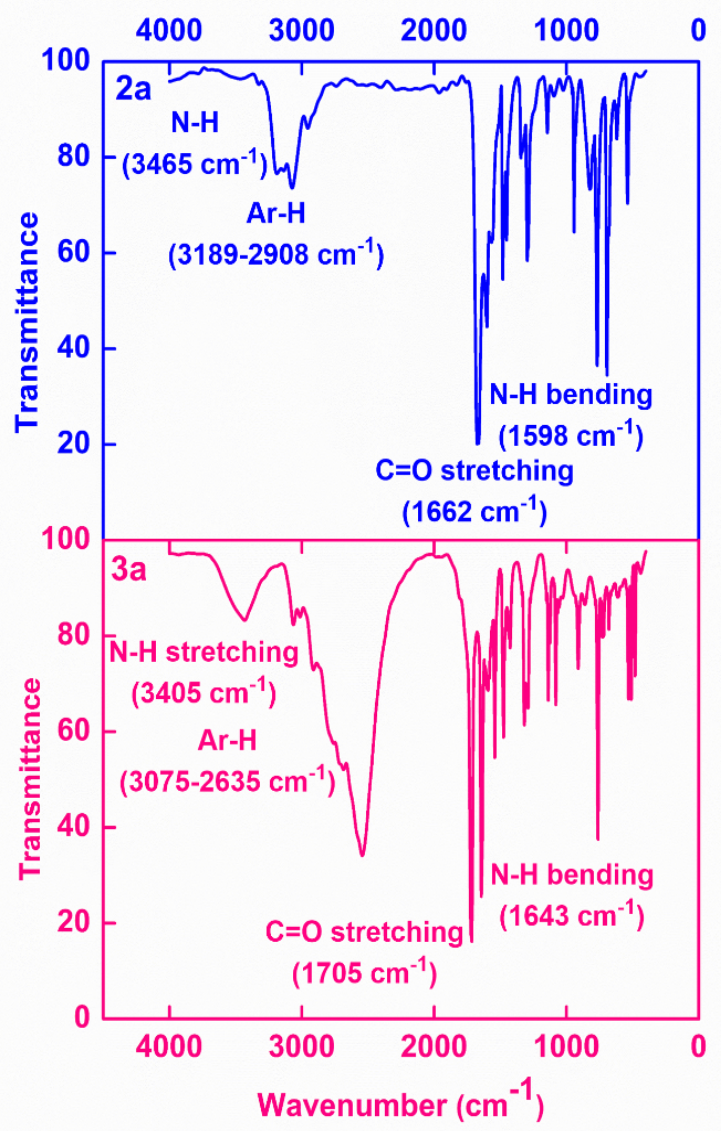


Figure FS17. FTIR spectrum of **2a** vs. 3a (Entry 1, Table 1).

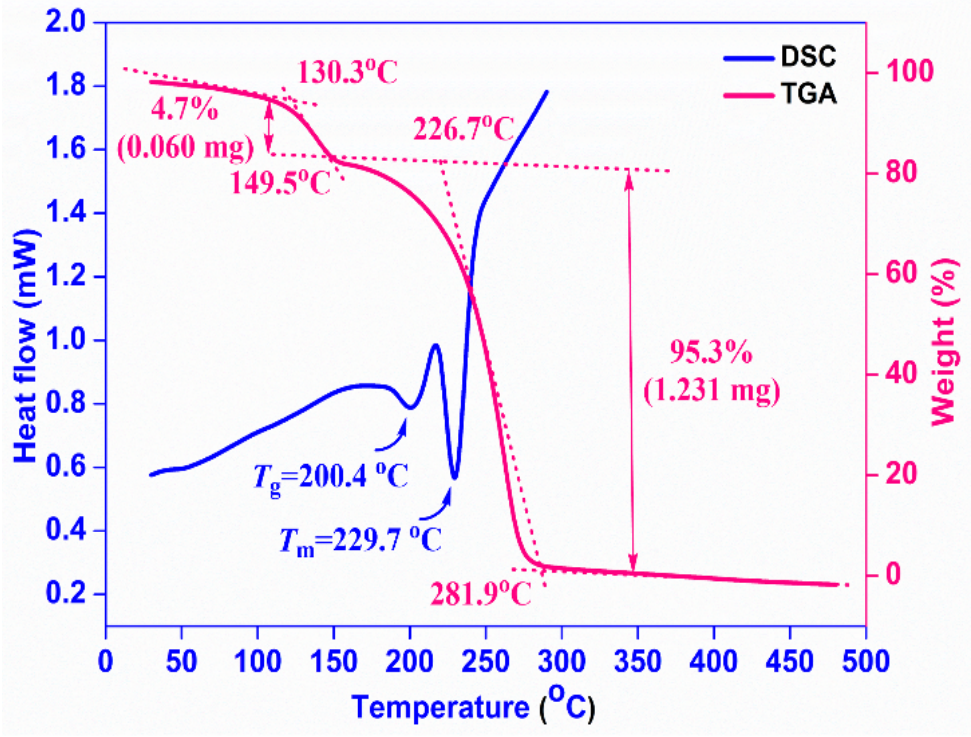


Figure FS18. Representative DSC and TGA curve of **3a** sample [entry 4, Table 1].

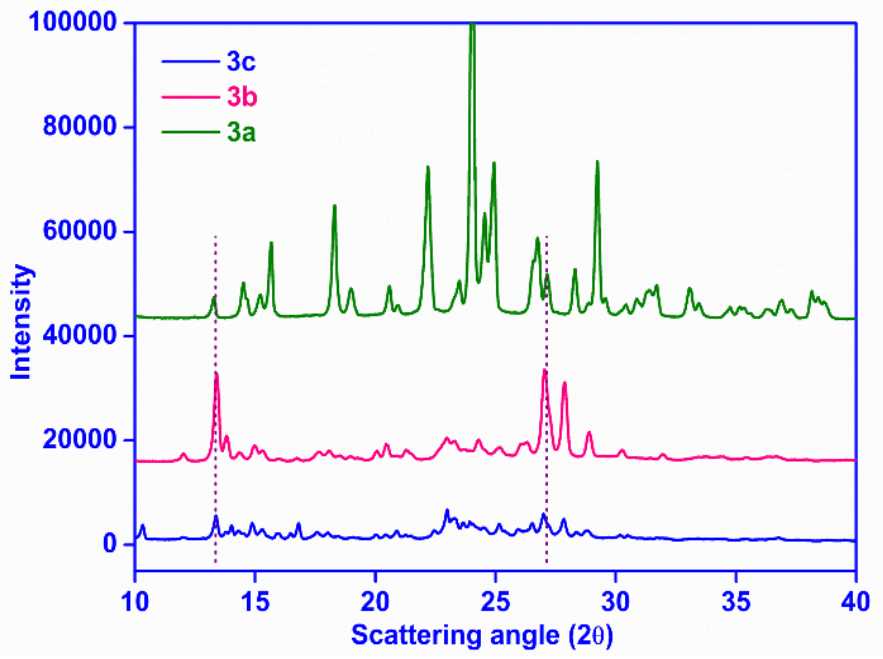


Figure FS19. WAXD pattern of **3a-3c**.

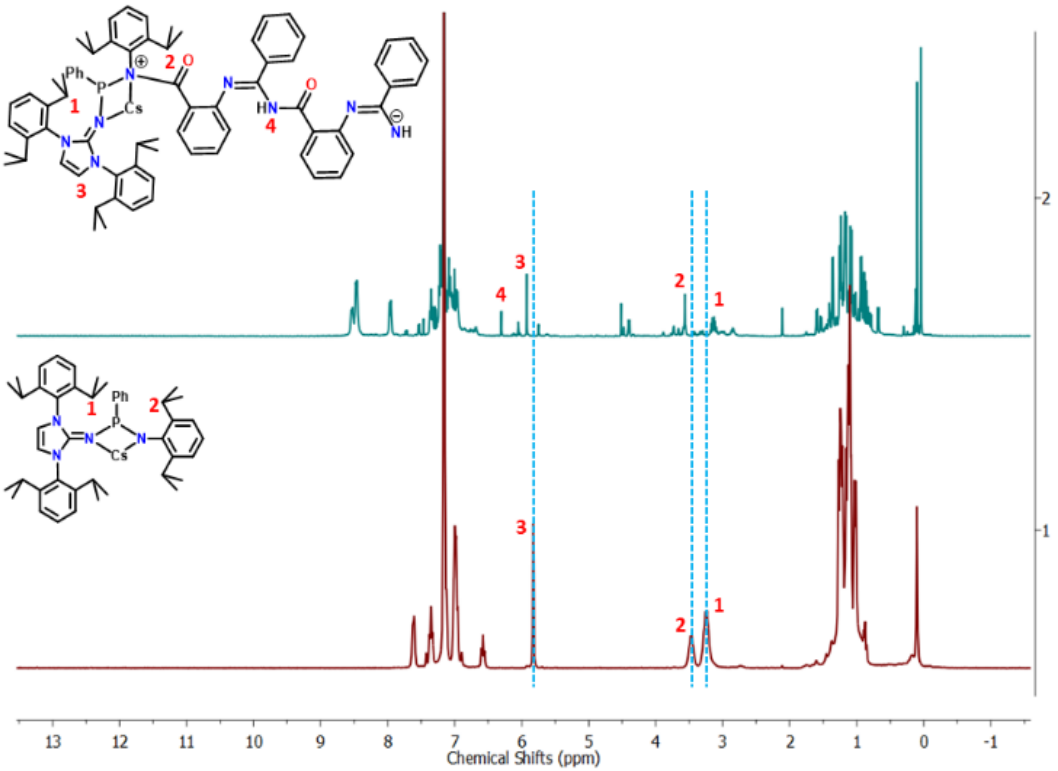
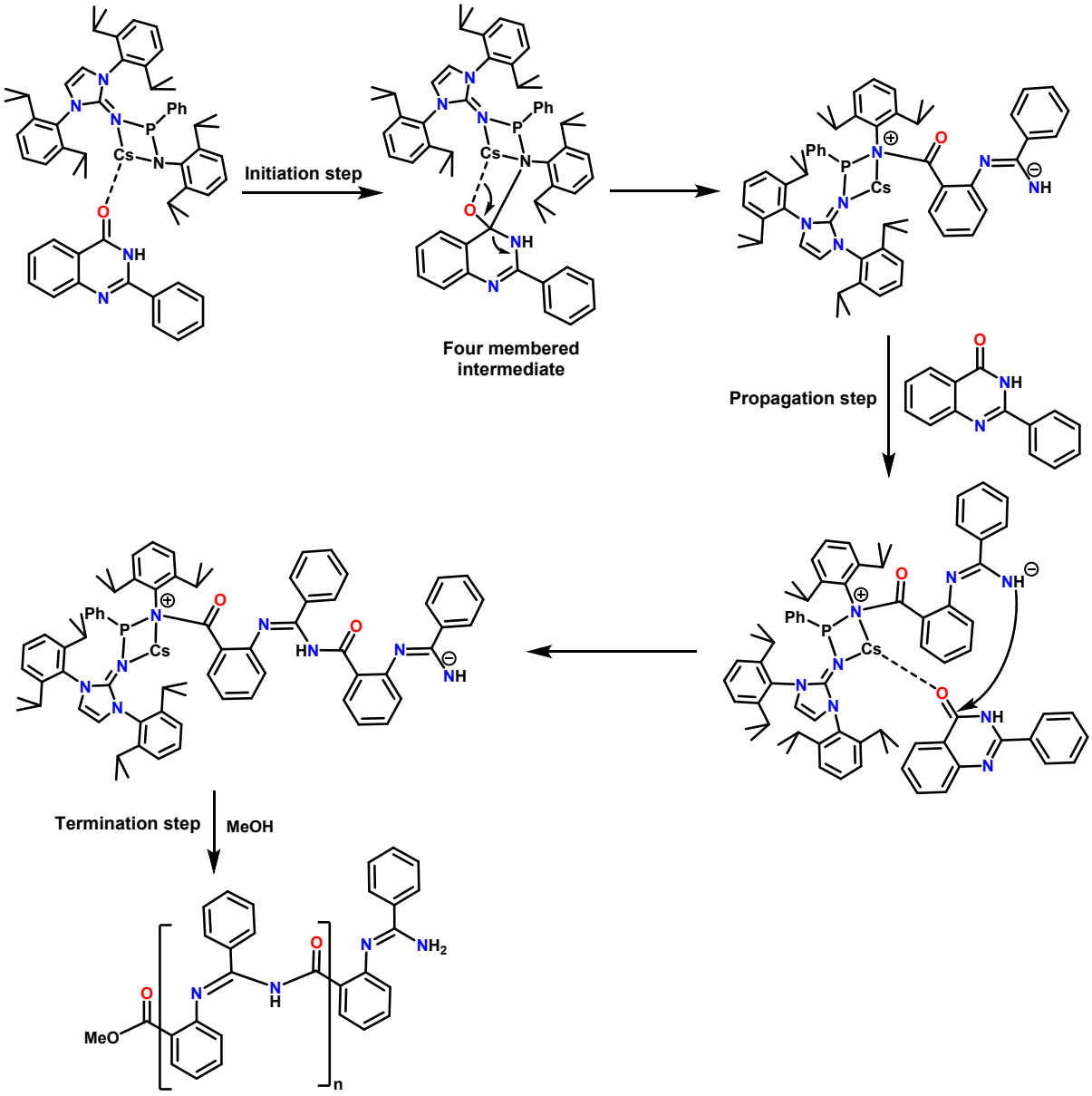


Figure FS20. ^{1}H-NMR (C_6D_6, 400 MHz) spectra of crude mixture of 1:5 ratio (Cat **1**:2a).



Scheme 2. Proposed mechanism for ROP of quinazolinones catalyzed by Cs complex supported by functionalized P-N ligand

Kinetic Studies

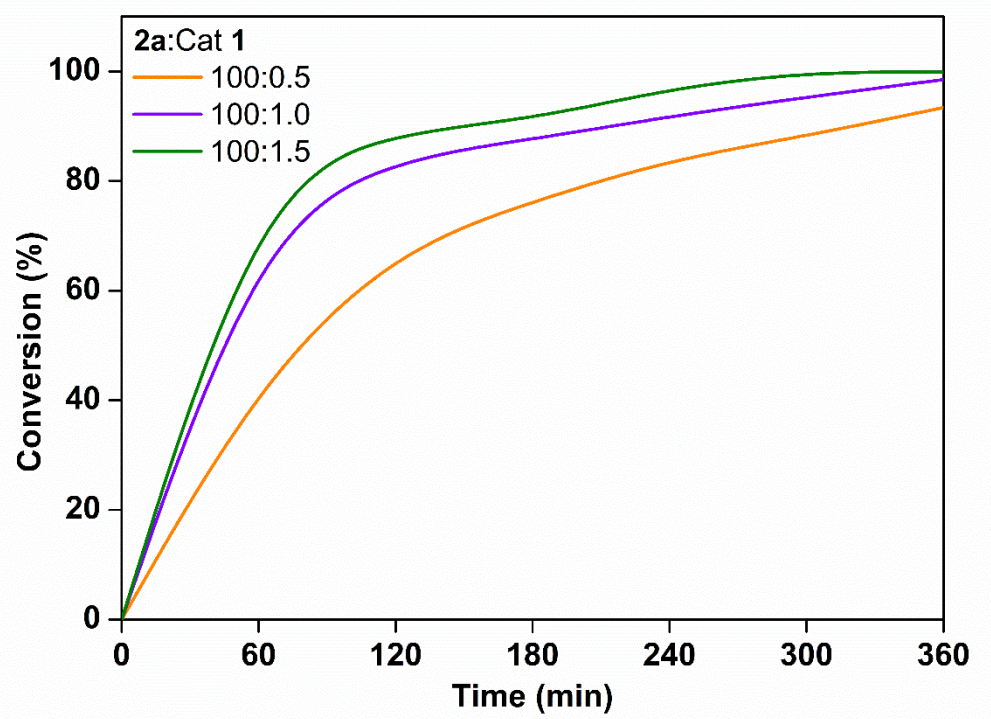


Figure FS21. Conversion rate with time for monomer **2a** (100 equivalents) with increasing catalyst amount.

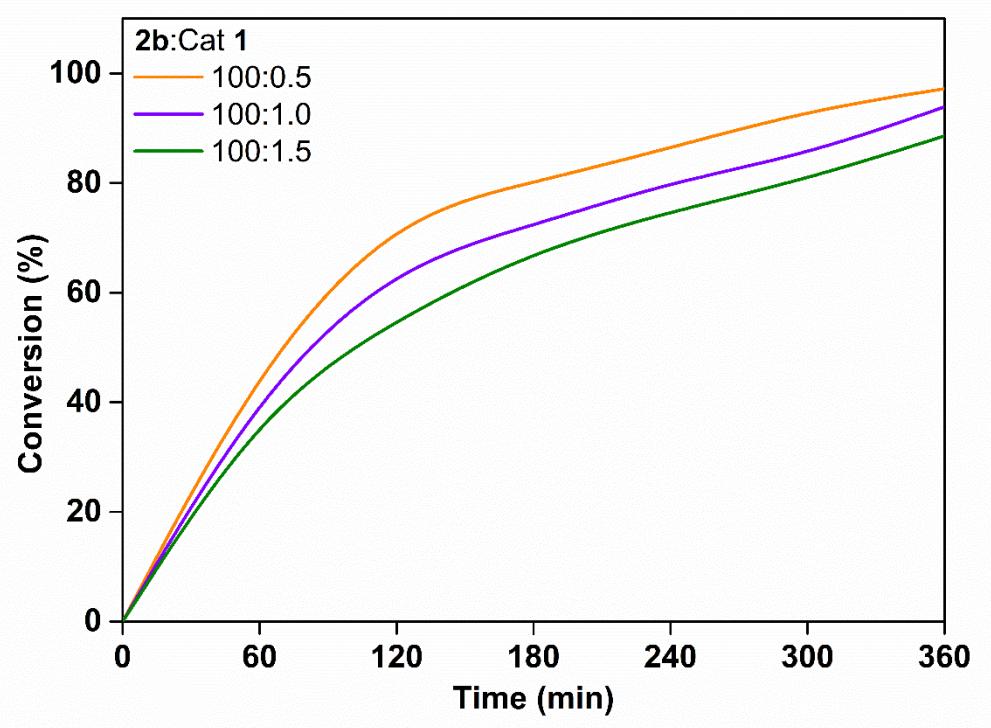


Figure FS22. Conversion rate with time for monomer **2b** (100 equivalents) with increasing catalyst amount.

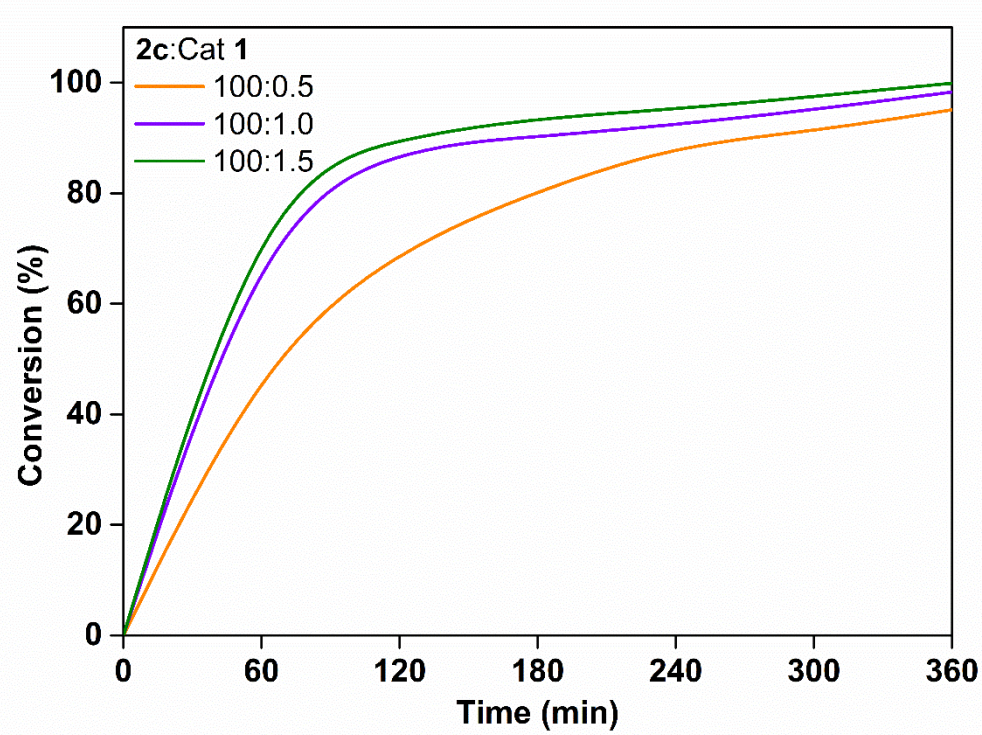


Figure FS23. Conversion rate with time for monomer **2b** (100 equivalents) with increasing catalyst amount.

End group analysis

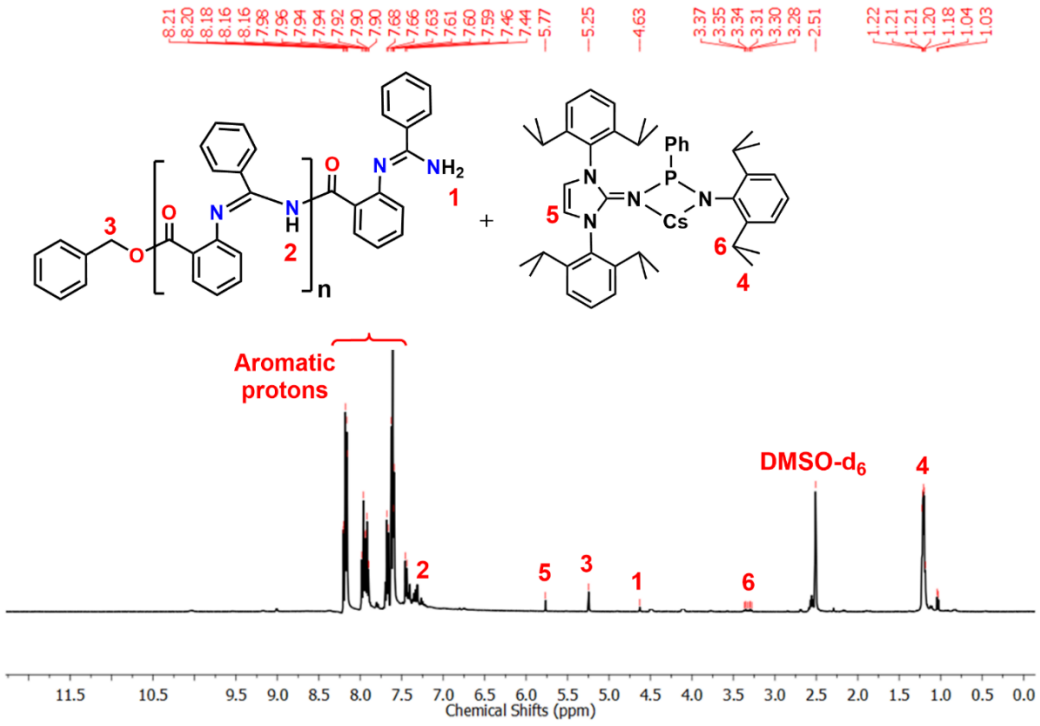


Figure FS24. ^{1}H-NMR (DMSO-d_6, 400 MHz) spectra of an aliquot of 1: 5 mixture of **1**: **2a** quenched by BnOH

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