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Electronic supplementary information

Influences of nitrogen base excess on ARGET ATRP of styrene with ascorbic acid acetonide and traces of oxygen and water

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Contents

Preparation of stock solutions of catalyst and initiator

Preparation of $CuCl_2$/TPMA solution in EtOH

In a 10 mL volumetric flask, $CuCl_2$ (70.2 mg, 0.522 mmol) and TPMA (151.6 mg, 0.522 mmol) were weighted. Absolute EtOH (~9 mL) was added, and the flask sonicated to aid dissolution. More EtOH was added to the solution, up to a total volume of 10 mL.

Preparation of ECiB solution in EtOAc

400 µL of ECiB (410 mg, 2.72 mmol) were added to a 10 mL volumetric flask, employing a 500 µL microsyringe. EtOAc was added, up to a total volume of 10 mL.

Characterizations

Gel Permeation Chromatography (GPC) procedure

All samples were analyzed using a conventional GPC system. The molecular weight distributions (MWDs) were determined using a Waters GPC system composed of a Waters Alliance 2695 separation module and a Waters 2414 differential refractometer detector. Empower 2 (Waters) was used as the chromatographic analysis software. The system was calibrated with 20 narrow distribution standards of polystyrene with molecular weights ranging from 1300 Da to 7 000 000 Da. Four GPC Phenogel (Phenomenex) columns (size: 300 × 7.6 mm, particle size: 5 µm, porosity 10^6, 10^5, 10^4, and 10^3 Å) were connected and housed in an oven at 30 °C. Tetrahydrofuran for HPLC was used as a mobile phase (flow rate= 1 mL/min, injection volume= 200 µL, sample concentration =2.5 mg/mL) with toluene as the internal standard. From the MWDs the number and mass average molar masses (M_n and M_w, respectively) and subsequently dispersity ($Đ = M_w/M_n$) were obtained.

Nuclear Magnetic Resonance (NMR) procedure

All NMR spectra were recorded with a Bruker AvanceNeo-600MHz spectrometer (Larmor resonance frequency for 1H: 600.10 MHz) equipped with Prodigy Platform Unit, a 5 mm cryoprobe BBO 600S3 BB-H&F-D-05 Z XT and TopSpin 4.1 software package. Typical acquisition parameters: 256 transients, spectral width 7.5 kHz, and a delay time of 7.0 s. All the spectra were acquired using $CDCl_3$ as solvent at 298 K and processed with software MestReNova. Chemical shifts were referred to tetramethylsilane peak (added to $CDCl_3$ in a concentration of 0.1% v/v) at 0.0 ppm.

Fig. S1 – Comparison between the spectra of the catalyst after overnight reaction

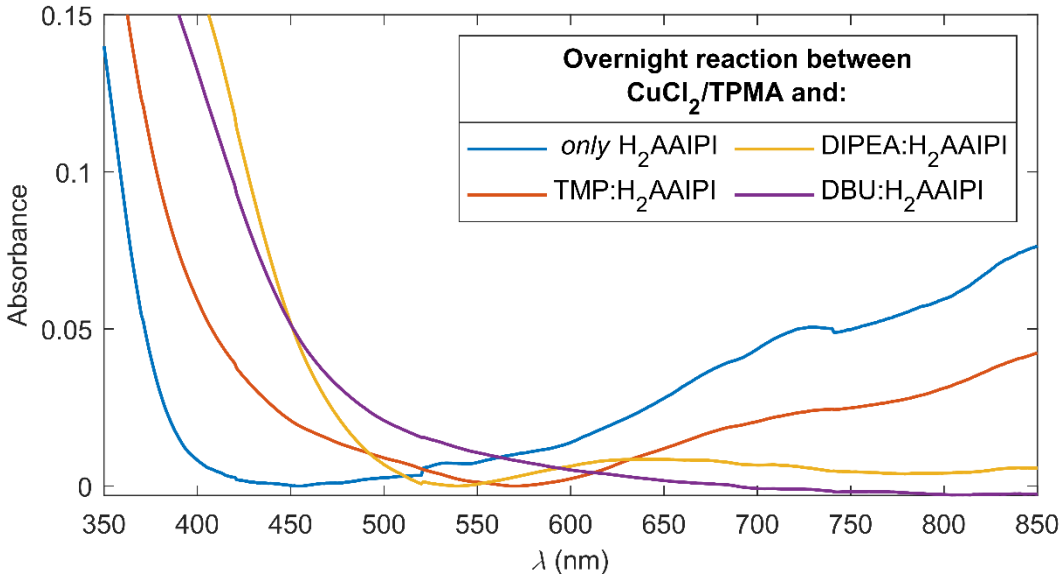

Fig. S1 – UV/Vis spectra of solution containing: $[CuCl_2/TPMA]_0$: $[H_2AAIPI]_0$: $[base]_0$ = 3.3 : 16.7 : 100 mol% with respect to the base (50 mmol/L) in $V_{styrene}$: V_{EtOAc} : V_{EtOH} = 1.2 : 0.7 : 0.1 mL, after overnight reaction at 50 °C under argon.

Fig. S2 – Copper-catalyzed oxidation of aliphatic amines by molecular oxygen

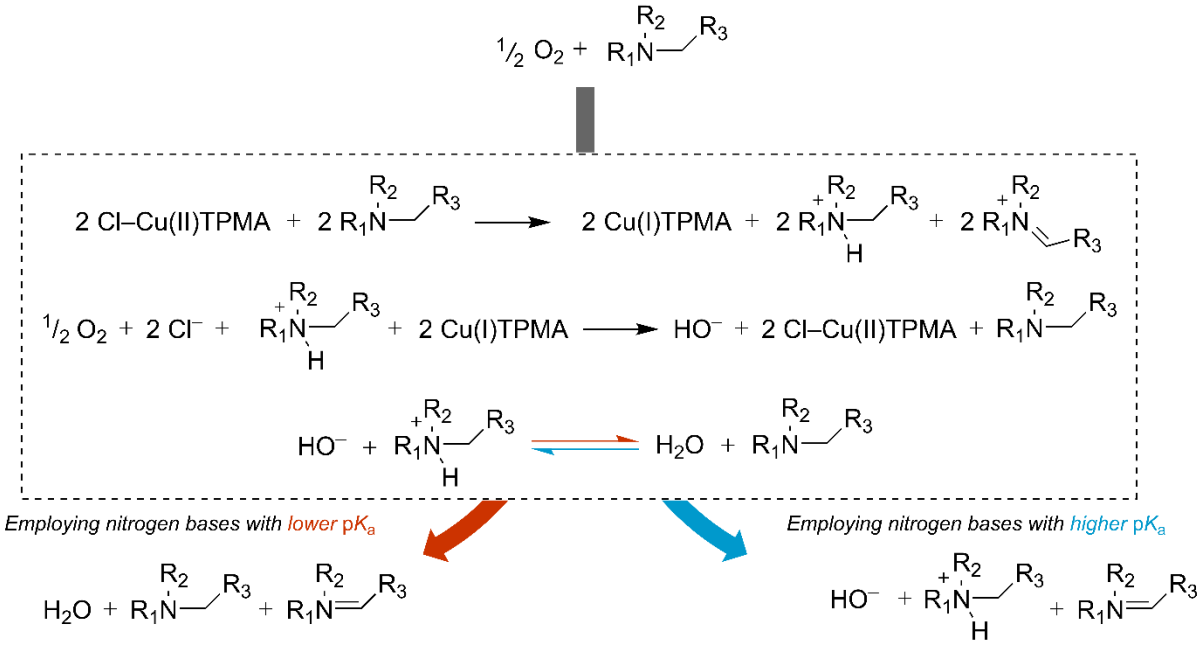

Fig. S2 – Proposed mechanism for the copper-catalyzed oxidation of tertiary amines by molecular oxygen.

Table S1 – ARGET ATRP promoted by tertiary amines in absence of H_2AAIPI

Table S1 – Comparison between nitrogen bases (DBU, DIPEA, and TMP), without the addition of H_2AAIPI, in the ARGET ATRP of styrene. [A]

entry	$[TPMA]_0$ (mol%)	$[H_2AAIPI]_0$ (mol%)	$[Base]_0$ (mol%)	*Time* (h)	*Conv* (%)	M_n (kDa)	ΔM_n (%)	*Đ*
1	0.05	0	DBU (0.50)	4.5	42	27.6	+ 84	2.61
2	0.05	0	DIPEA (0.50)	4.5	30	3.45	+ 10	1.22
3	0.05	0	TMP (0.50)	13.5	< 1	–	–	–
4	0	0	DBU (0.50)	4.5	10	110.3	+ 99	3.00

[A] Common reaction conditions: $[styrene]_0 : [ECiB]_0 : [CuCl_2]_0 = 100\ \ 1.04 : 0.05$ mol%, $V_{styrene} : V_{EtOAc} : V_{EtOH} = 6 : 3.5 : 0.5$ mL, T = 100 °C.

Fig. S3 – MWD of Entry 5, Table 1

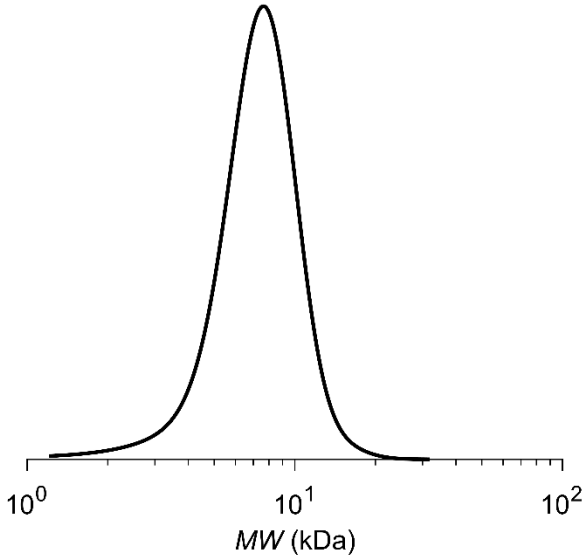

Fig. S3 – MWD of **entry 5** of **Table 1**. Conditions: V_{St} = 6 mL, V_{EtOAc} = 3.5 mL, V_{EtOH} = 0.5 mL, T = 100 °C (13.5 h), $[styrene]_0:[ECiB]_0:[CuCl_2/TPMA]_0:[H_2AAIPI]_0:[Na_2CO_3]_0$ = 100:1.04:0.025:0.25:0.25.

Fig. S4 – Comparison between the MWDs of entries 6 and entry 10 of Table 1.

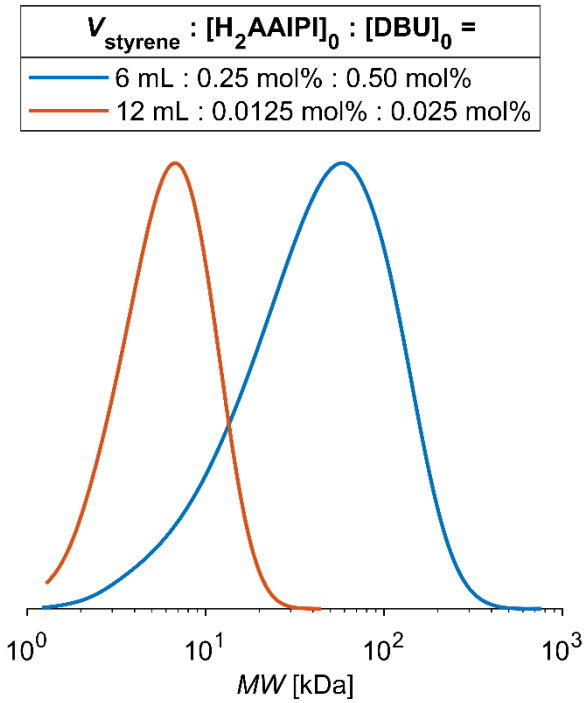

Fig. S4 – MWDs of polystyrene obtained by ARGET ATRP with H_2AAIPI and DBU. *Blue*) **entry 6**, **Table 1**. *Orange*) **entry 10**, **Table 1**.

Fig. S5 – MWD of entry 12 of Table 1.

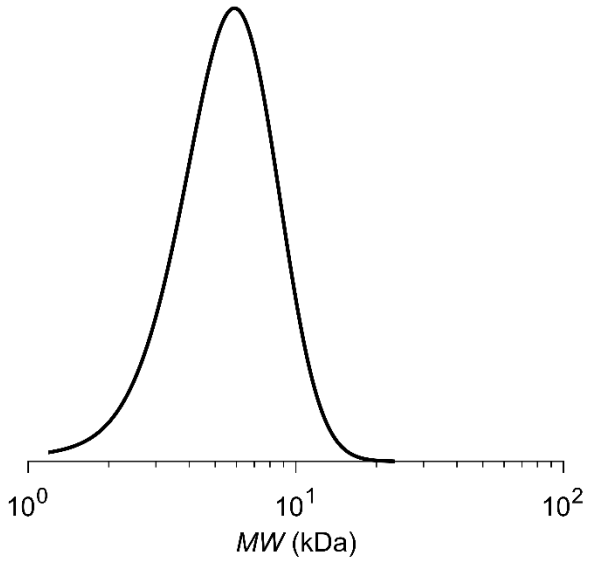

Fig. S5 – MWD of **entry 12** of **Table 1**. Conditions: $V_{styrene}$ = 6 mL, V_{EtOAc} = 3.5 mL, V_{EtOH} = 0.5 mL, T = 100 °C (13.5 h), $[styrene]_0$:$[ECiB]_0$:$[CuCl_2/TPMA]_0$:$[H_2AA]_0$:$[DIPEA]_0$ = 100:1.04:0.025:0.125:0.25.

Fig. S6 – MWD of entry 13 of Table 1

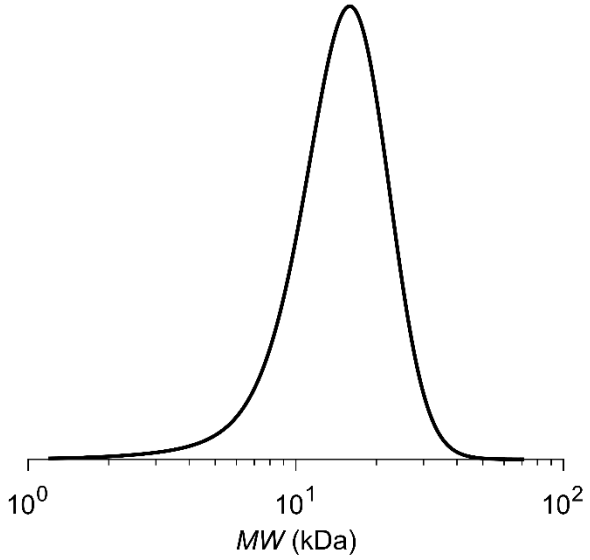

Fig. S6 – MWD of **entry 13** of **Table 1**. Conditions: $V_{styrene}$ = 12 mL, V_{EtOAc} = 3.5 mL, V_{EtOH} = 0.5 mL, T = 100 °C (24 h), $[styrene]_0:[ECiB]_0:[CuCl_2/TPMA]_0:[H_2AAIPI]_0:[DIPEA]_0$ = 100:0.52:0.0125:0.125:0.25.

Fig. S7 – ^{1}H-NMR of entry 12 of Table 1.

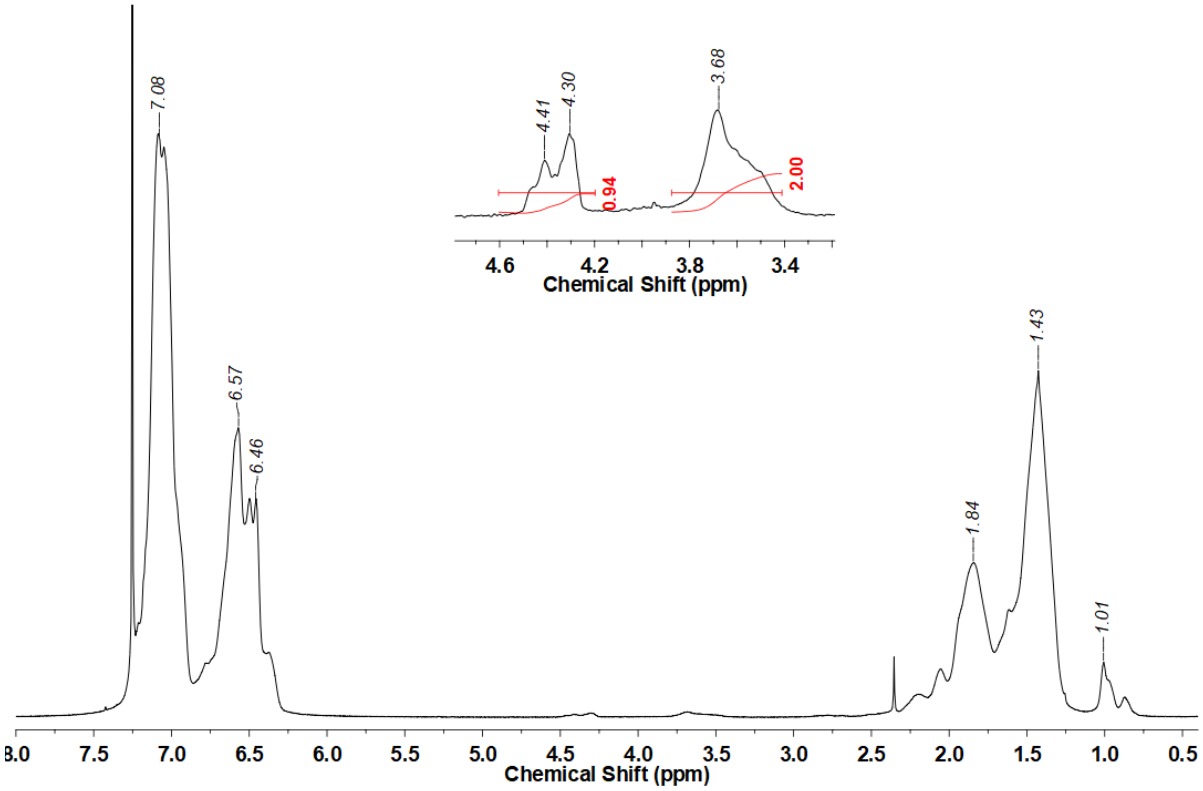

Fig. S7 – ^{1}H-NMR of **entry 12** of **Table 1**. Conditions: $V_{styrene}$ = 6 mL, V_{EtOAc} = 3.5 mL, V_{EtOH} = 0.5 mL, T = 100 °C (13.5 h), $[styrene]_0$:$[ECiB]_0$:$[CuCl_2/TPMA]_0$:$[H_2AA]_0$:$[DIPEA]_0$ = 100:1.04:0.025:0.125:0.25.

Fig. S8 – ^{1}H-NMR of Entry 16 of Table 1

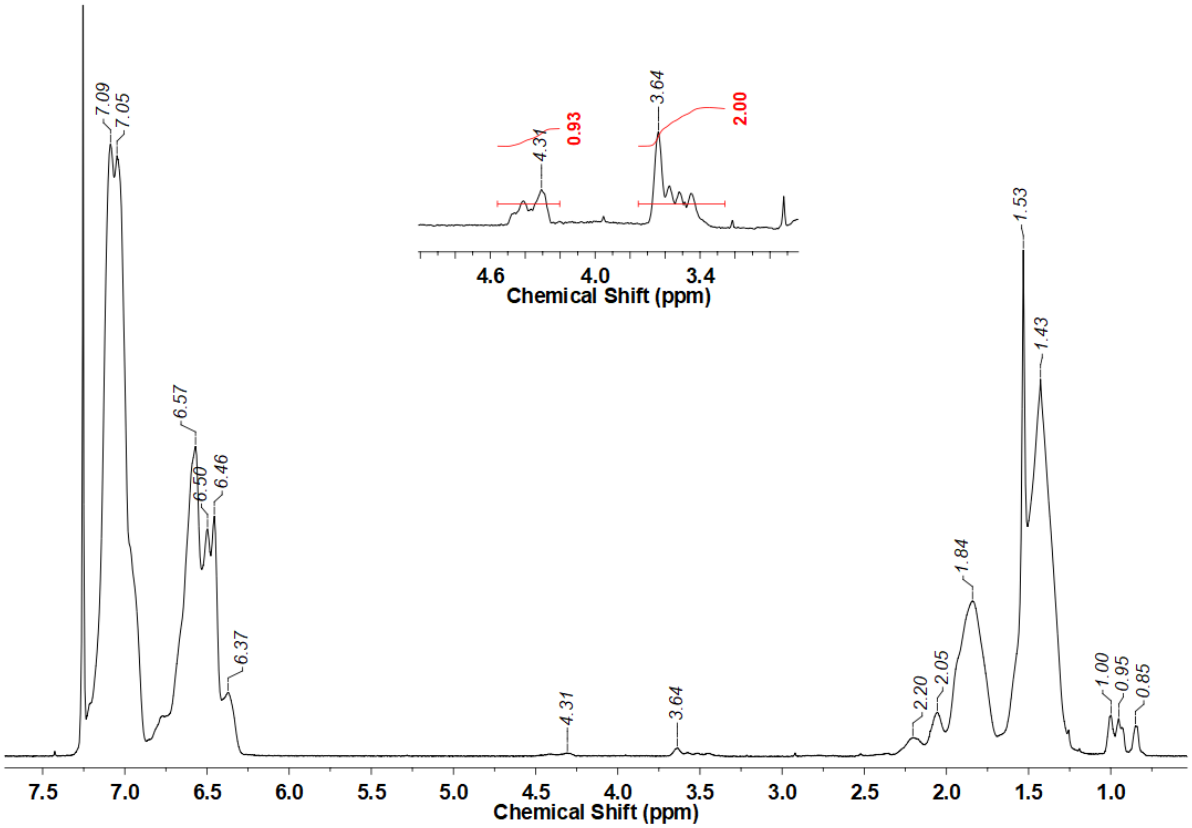

Fig. S8 – ^{1}H-NMR of the reaction conditions: V_{St} = 6 mL, V_{EtOAc} = 3.5 mL, V_{EtOH} = 0.5 mL, T = 100 °C (24 h), $[Styrene]_0:[ECiB]_0:[CuCl_2/TPMA]_0:[H_2AAIPI]_0:[TMP]_0$ = 100:1.04:0.025:0.25:1.5.

Table S2 – Full Factorial Design of TMP-promoted ARGET ATRP of styrene with H_2AAIPI

Table S2 – Full factorial design of TMP-promoted ARGET ATRP of styrene with H_2AAIPI

entry	$[CuCl_2/TPMA]_0$ (mol%)	$[benzalchloride]_0$ (mol%)	$[H_2AAIPI]_0/[TMP]_0$ (mol%/mol%)	*Time* (h)	*Conv* (%)	M_n (kDa)	ΔM_n (%)	*Đ*
1	0.0625	1	0.125/0.750	20	50.9	5.25	– 4.43	1.33
2 [B]	0.0625	1	0.250/1.50	25	59.3	6.41	+ 0.14	1.32
3	0.250	1	0.250/1.50	20	53.6	6.00	+ 3.92	1.15
4	0.250	1	0.125/0.750	25	53.1	5.32	– 7.38	1.15
5	0.0625	2	0.250/1.50	20	51.9	3.26	+ 11.8	1.32
6	0.0625	2	0.125/0.750	25	50.5	3.32	+ 15.6	1.30
7 [B]	0.250	2	0.125/0.750	20	39.8	2.40	+ 6.68	1.14
8	0.250	2	0.250/1.50	25	54.0	2.88	– 3.60	1.14
9 [B]	0.250	1	0.250/1.50	25	57.6	5.02	– 23.2	1.17
10	0.250	2	0.250/1.50	20	48.5	2.58	– 4.51	1.16
11	0.250	2	0.125/0.750	25	46.2	2.48	– 3.87	1.16
12	0.0625	1	0.125/0.750	25	51.0	4.75	– 15.6	1.35
13	0.250	1	0.125/0.750	20	46.3	4.05	– 23.5	1.18
14 [B]	0.0625	2	0.250/1.50	25	54.3	3.49	+ 14.1	1.32
15	0.0625	2	0.125/0.750	20	38.0	2.90	+ 26.0	1.33
16	0.0625	1	0.250/1.50	20	51.3	4.85	– 13.9	1.35
17	0.156	1.5	0.188/1.13	22.5	50.5	3.27	– 12.5	1.21
18	0.156	1.5	0.188/1.13	22.5	52.2	3.71	– 2.40	1.20

[A] Common reaction conditions: $V_{styrene}$: V_{EtOAc} : V_{EtOH} = 6 : 3.5 : 0.5 mL, T = 100 °C. [B] The reaction has been conducted twice and the mean values are reported.