

Supplementary Information

Selective Copper-Catalysed Atom Transfer Radical Addition (ATRA) in Water under Environmentally-Benign Condition

Nutchanikan Phiromphu,^a Methasit Juthathan,^a Pattira Suktanarak,^b Mongkol Sukwattanasinitt,^a Thawatchai Tuntulani,^a and Pannee Leeladee^{*a}

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- [a] Dr. Nutchanikan Phiromphu, Methasit Juthathan, Prof. Dr. Mongkol Sukwattanasinitt, Prof. Dr. Thawatchai Tuntulani, Assist. Prof. Dr. Pannee Leeladee
Department of Chemistry, Faculty of Science, Chulalongkorn University
Bangkok, Thailand.
E-mail: pannee.l@chula.ac.th
- [b] Dr. Pattira Suktanarak
Faculty of Sport and Health Sciences, Thailand National Sports University Lampang Campus
Lampang, Thailand

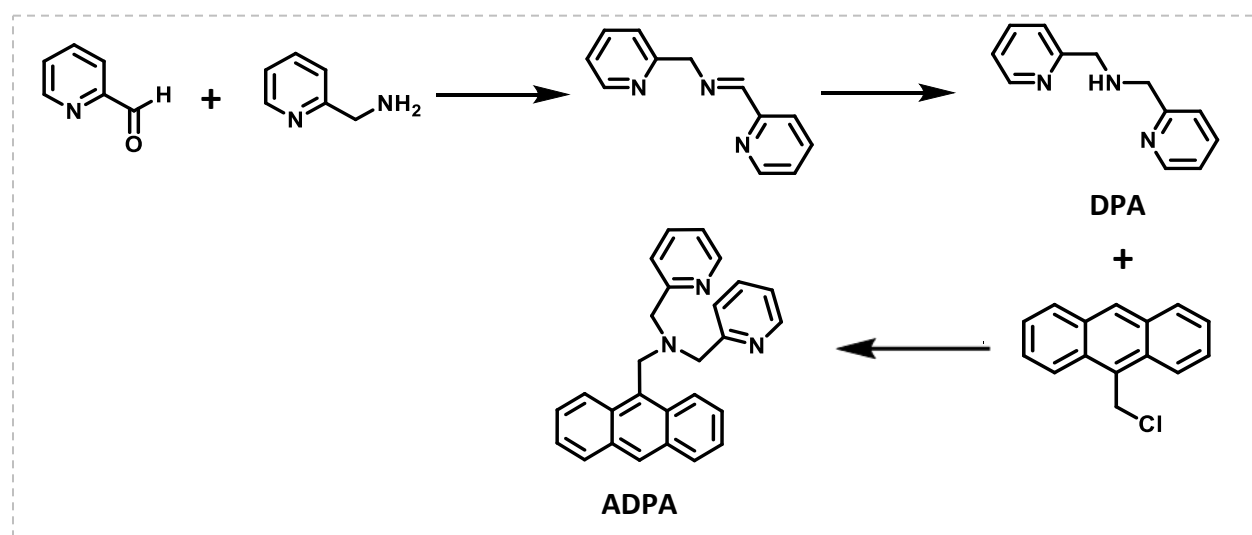
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Synthesis and characterization

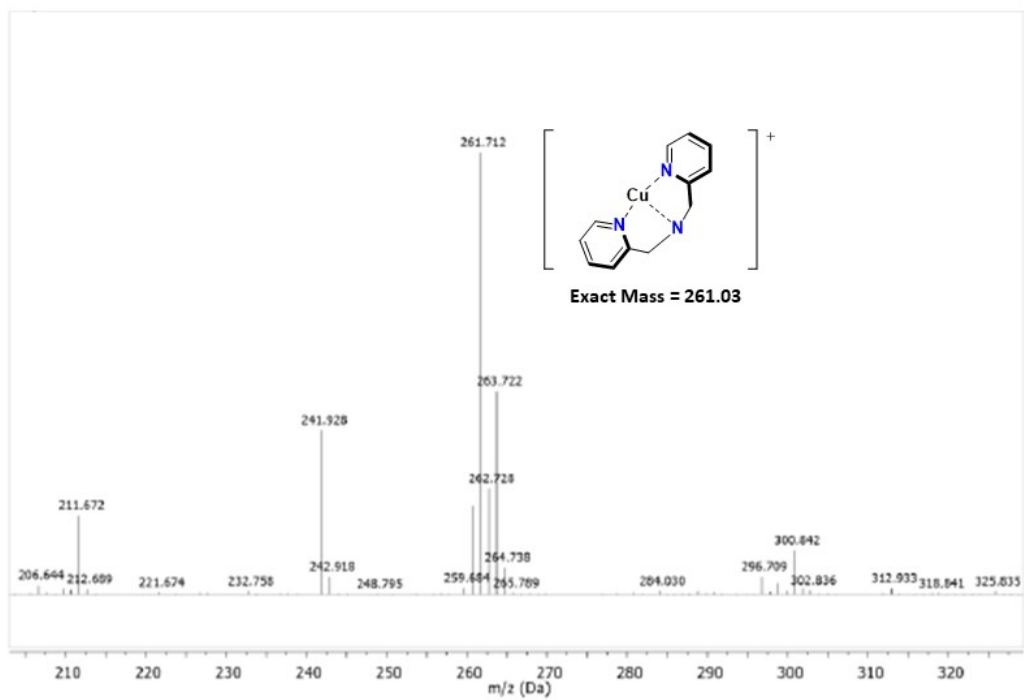
I) Synthesis of 2,2'-dipicolylamine (DPA). The suspension of anhydrous MgSO_4 (2.78 g, 23.1 mmol) in CH_2Cl_2 (3.80 mL) was added 2-pyridinecarboxaldehyde (0.50 g, 4.60 mmol) and 2-(aminomethyl)pyridine (0.50 g, 4.60 mmol). The mixture was stirred for 3 h at room temperature under N_2 . After that, the suspension was filtered, and solvent in the filtrate was removed under vacuum to obtain a yellow oil product. The product was redissolved in CH_3CN (12 mL) and cooled to -5°C for 15 min. NaBH_4 was slowly added in the solution and stirred for 18 h at room temperature. The reaction was quenched with conc. HCl (7.70 mL) and heated at 60°C for 2 h to give the white precipitates in the yellow solution. The white solid was filtered out, and solvent in the filtrate was removed under vacuum. The crude product was redissolved in H_2O . To the aqueous solution was added NaOH pellets (3.30 g, 82.5 mmol) and the mixture was stirred for 15 min. After that, the solution was extracted with diethyl ether (3 x 200 mL) and dried under vacuum to obtain the yellow oil product (0.73 g, 80%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 8.49 (m, 2H, ArH), 7.50 (m, 2H, ArH), 7.23 (d, 2H, $J = 8.0$ Hz, ArH), 7.01 (m, 2H, ArH), 3.84 (s, 4H, $-\text{CH}_2-$).

II) Synthesis of 9-[(2,2'-dipicolylamino)methyl]anthracene (ADPA). The solution of 9-(chloromethyl)anthracene (1.00 g, 4.40 mmol), 2,2'-dipicolylamine (1.05 g, 5.20 mmol) and K_2CO_3 (2.43 g, 1.70 mmol) in anhydrous DMF (6.8 mL) was slowly added a solution of KI (0.73 g, 4.40 mmol) in DMF (3.6 mL). The reaction mixture was stirred at room temperature over 1 h, after which the solution was added 1 M HCl and washed with EtOAc . The aqueous solution was then alkalinized with 4 M NaOH and extracted with $\text{EtOAc}:\text{THF}$ (1:1). The combined organic layers were washed with H_2O and brine solution, followed by drying over MgSO_4 , and the solvent was removed under reduced pressure. Recrystallization in $\text{MeOH}:\text{Et}_2\text{O}$ afforded the title product as a pale yellow solid (0.57 g, 24%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 8.49 (d, 2H, $J = 4.0$ Hz, ArH), 8.39 (s, 1H, ArH), 8.37 (d, 2H, $J = 4.8$ Hz, ArH), 7.95 (m, 2H, ArH), 7.57 (ddd, 2H, $J = 1.6, 7.6, 7.6$ Hz, ArH), 7.41-7.47 (m, 4H, ArH), 7.31 (d, 2H, $J = 7.6$ Hz, ArH), 7.11 (dd, 2H, $J = 4.8, 6.0$ Hz, ArH), 4.67 (s, 2H, $-\text{CH}_2-$), 3.88 (s, 4H, $-\text{CH}_2-$).

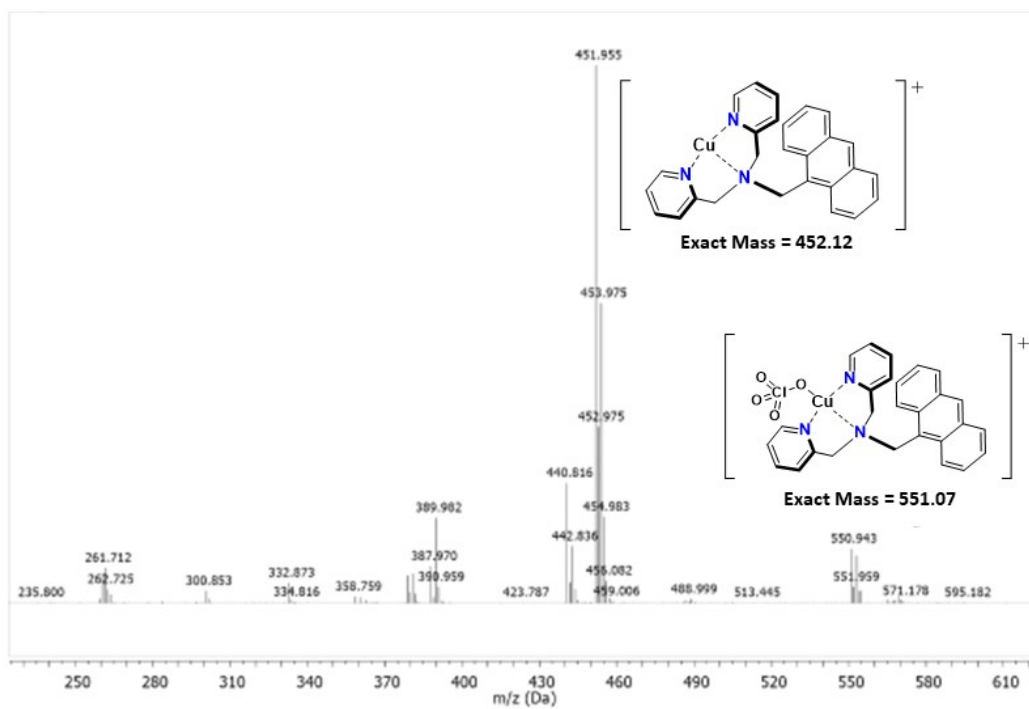


Scheme S1 Synthesis of DPA and ADPA ligands.

(a)



(b)



(c)

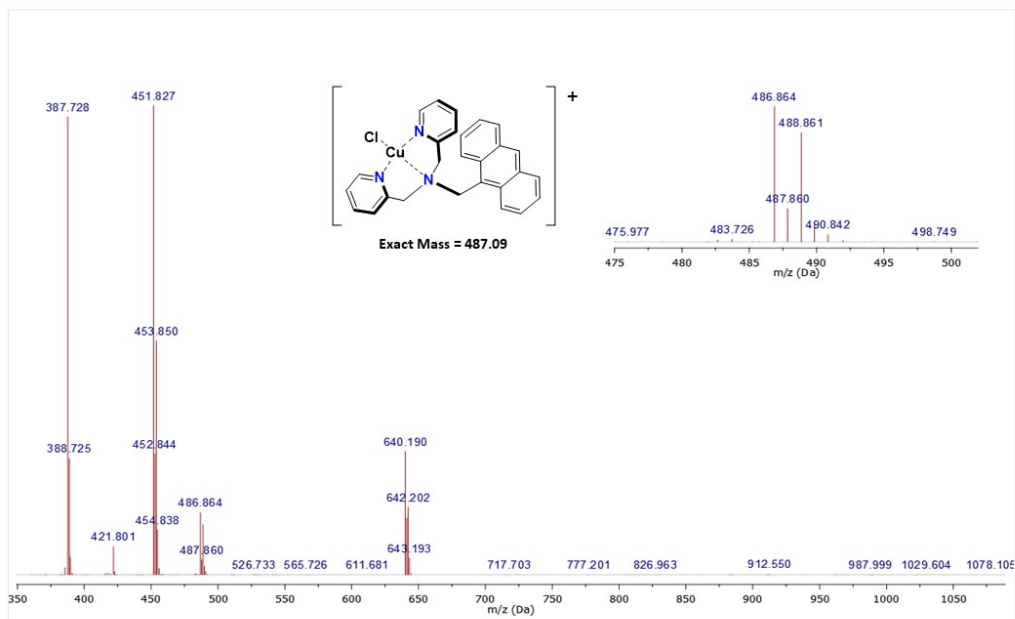


Figure S1 MALDI-TOF mass spectra of (a) Cu(DPA) complex, (b) Cu(ADPA) complex, and (c) reaction solution of Cu(ADPA) + AsH₂ + CCl₄ in CH₃CN.

Product analysis of catalytic ATRA reaction in aqueous dispersed system

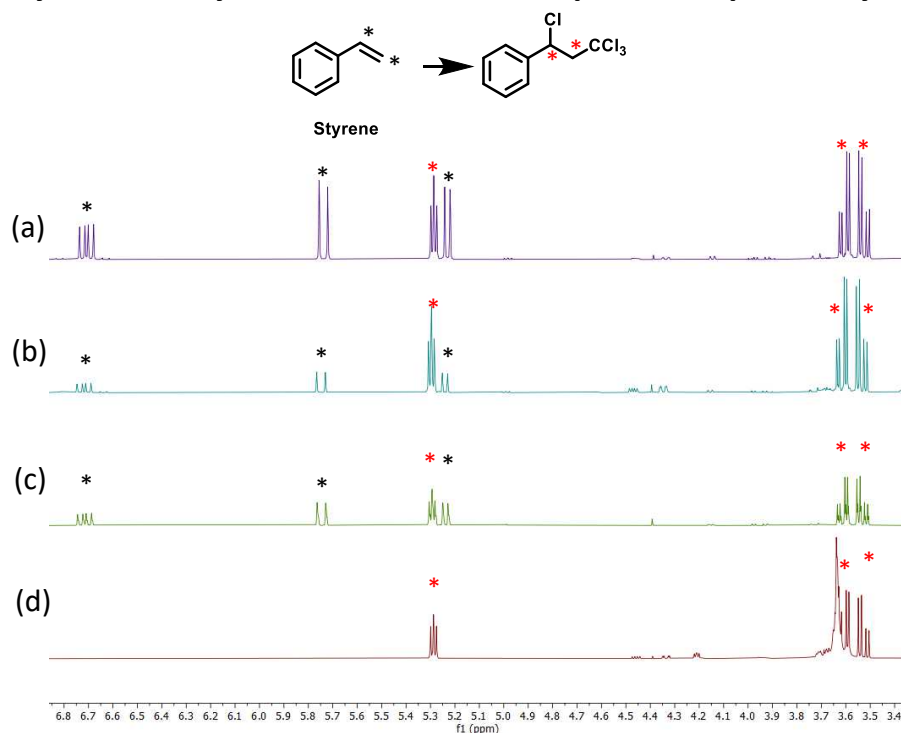


Figure S3 ^1H NMR spectra for product determination from **1b**-catalysed ATRA of CCl_4 to styrene in 2 wt% Tween 20/ H_2O monitored at the reaction time of (a) 3 h, (b) 4 h, (c) 5 h, and (d) 6 h.

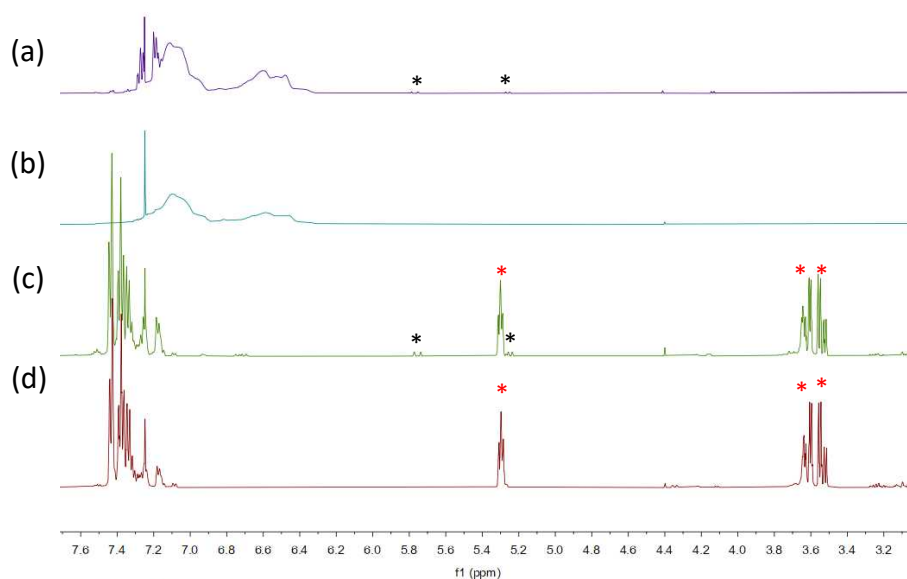
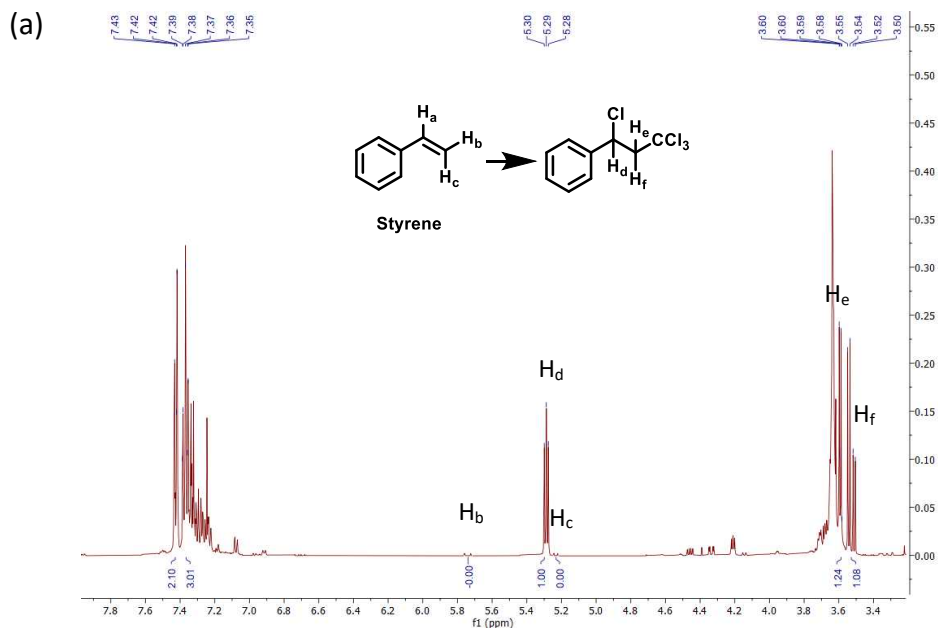


Figure S4 ^1H NMR spectra for product determination from copper-catalysed ATRA of CCl_4 to styrene in 2 wt% Tween 20/ H_2O using 1% mol of $\text{Cu}(\text{II})$ catalyst; (a) $\text{Cu}(\text{ClO}_4)_2$, (b) **1a**, (c) **1b**, and (d) **2b**.



***Calculation :** Conversion (%) of alkene was calculated according to the following equations.

$$\% \text{ conversion} = \frac{I_p}{I_{\text{alkene}} + I_p} \times 100$$

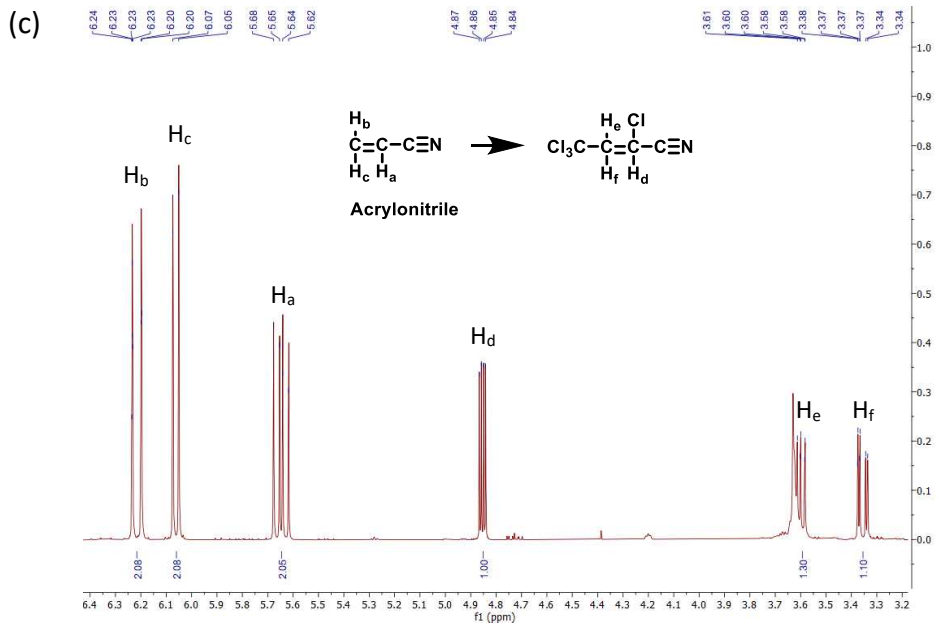
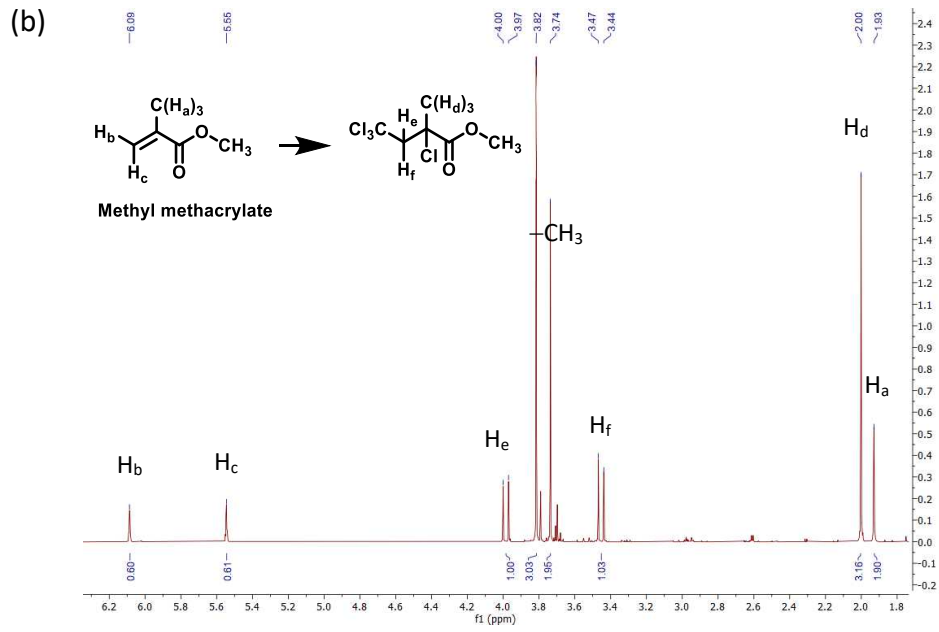
When I_p = The integration of proton signal of the analysed product (e.g., H_d, H_e, or H_f)

I_{alkene} = The integration of proton signal of the alkene (e.g., H_a, H_b, or H_c)

The integrated peak area of one proton in the product was initially set to be equal 1.00.

For Example: Considering the spectrum (a)

$$\begin{aligned} \% \text{ conversion} &= \frac{\int H_d}{\int H_a + \int H_d} \times 100 \\ &= \frac{1.00}{0.00 + 1.00} \times 100 \\ &= 100 \% \end{aligned}$$



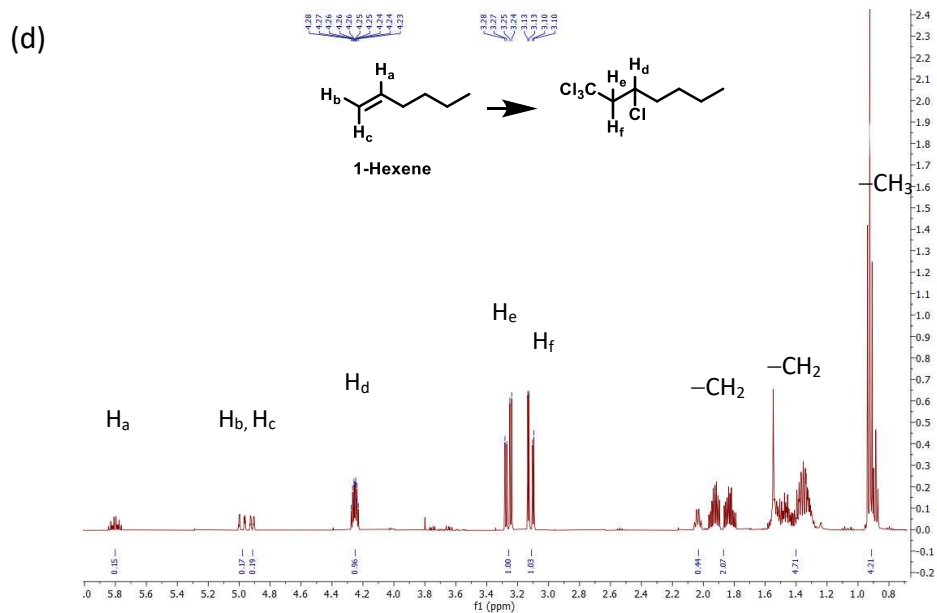
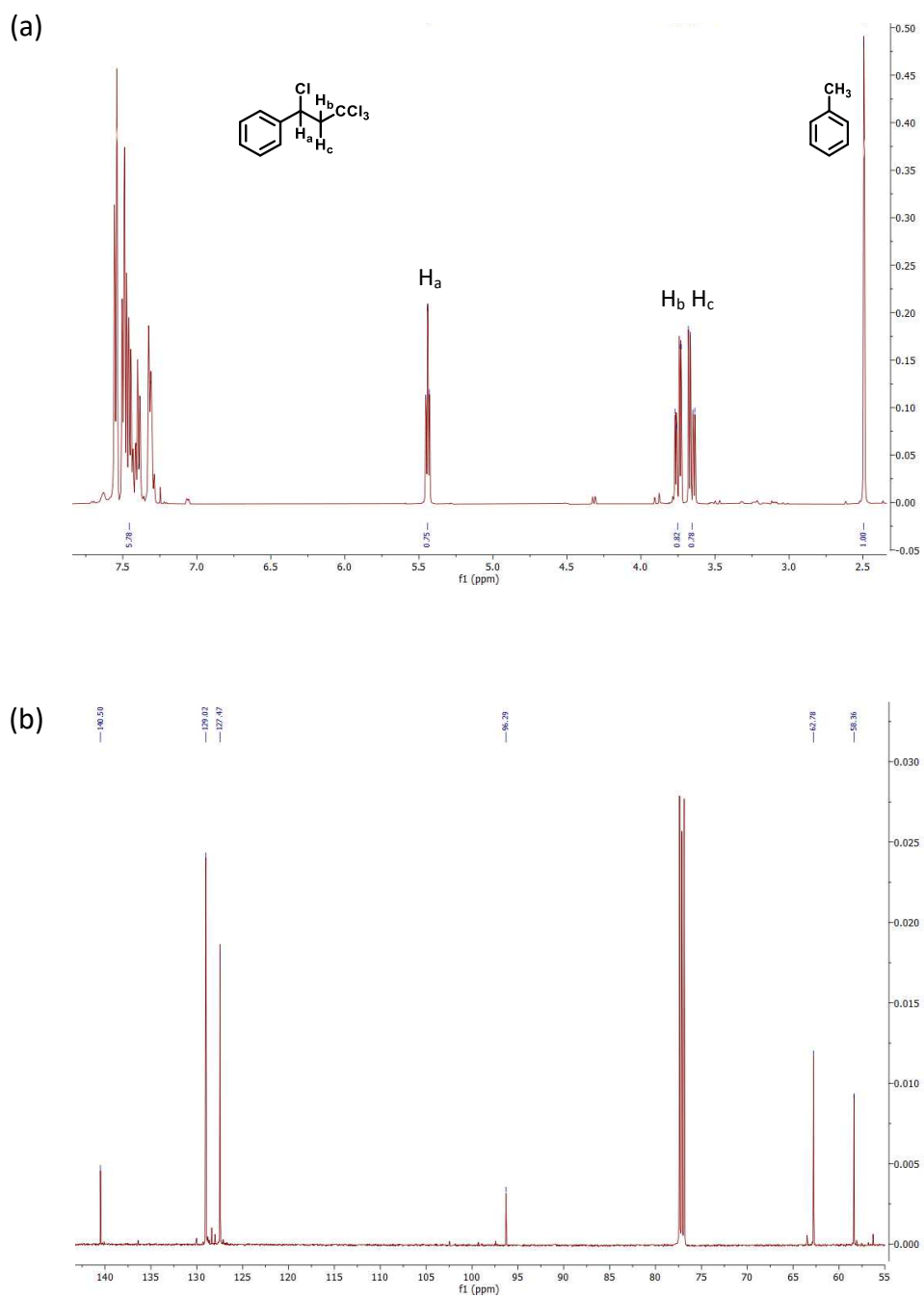


Figure S4 ¹H NMR spectra for product determination of **1b**-catalysed ATRA reaction in 2 wt% Tween 20 with various alkene substrates; (a) styrene, (b) methyl methacrylate, (c) acrylonitrile, and (d) 1-hexene.



***Calculation:** Yield (%) of product was calculated according to the following equations.^{S1, S2}

$$(I) \quad \frac{R_p}{R_{STD}} = \frac{I_p / N_p}{I_{STD} / N_{STD}} = X_1$$

$$(II) \quad \text{mol}_p = \text{mol}_{STD} \times X_1 = Y_2$$

$$(III) \quad \% \text{yield} = \frac{Y_2}{\text{mol}_{\text{alkene}}} \times 100$$

When I_p = Integration from the proton signal of the analysed product (e.g., H_a , H_b , or H_c)
 N_p = Number of protons in the structure of product. For example, N_p of H_a , H_b , or H_c = 1
 I_{STD} = The integration of proton signal of the internal standard (e.g., $-\text{CH}_3$)
 N_{STD} = Number of protons in the structure of internal standard.

For example, N_p of $-\text{CH}_3$ = 3

$\text{mol}_{STD} = 0.11 \text{ mmol}$

$\text{mol}_{\text{alkene}} = 0.37 \text{ mmol}$

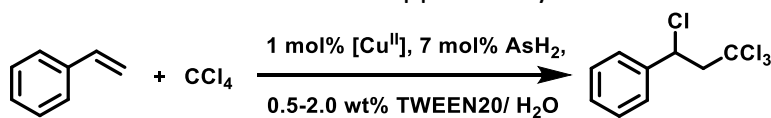
For Example: Considering the spectrum from Figure S5,

$$(I) \quad \frac{R_p}{R_{STD}} = \frac{0.82/1}{1.00/3} = 2.48$$

$$(II) \quad \text{mol}_p = 0.11 \times 2.48 = 0.27$$

$$(III) \quad \% \text{yield} = \frac{0.27}{0.37} \times 100 = 73 \%$$

Table S1 Effect of surfactant concentration on copper-catalysed ATRA in water.



Entry	Surfactant concentration in H ₂ O (%w/w)	Conversion (%)
1	0.5 wt% Tween 20	39
2	1.0 wt% Tween 20	50
3	2.0 wt% Tween 20	99

All Reactions were performed at 60°C for 6 h using **1b** as an ATRA catalyst with the molar ratio of [alkene]: [CCl₄]: [AsH₂] = 1.00: 1.25: 0.07 and [Styrene]₀ = 0.147 M.

% conversions were determined by ¹H NMR spectroscopy.

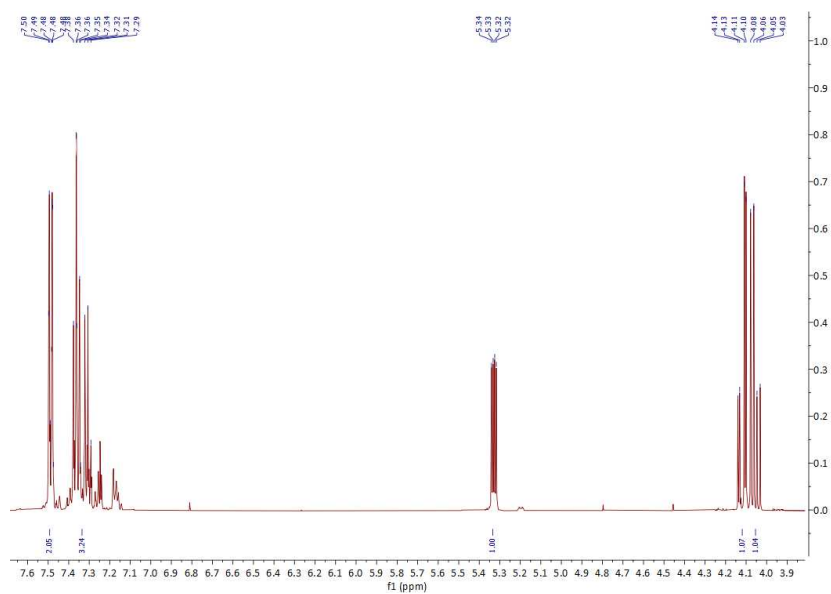


Figure S6 ^1H NMR spectrum of **1b**-catalysed ATRA of CBr_4 to styrene

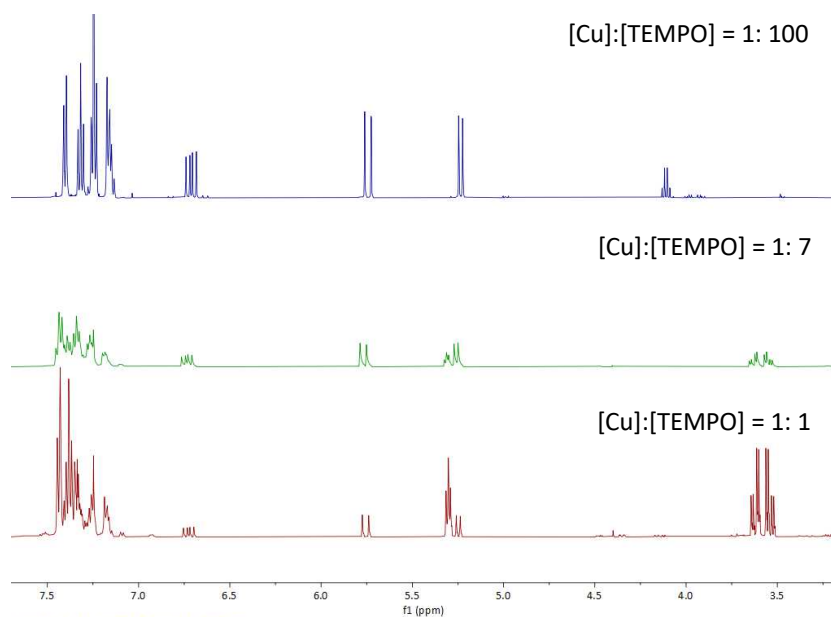


Figure S7 ^1H NMR spectra of **1b**-catalysed ATRA of CCl_4 to styrene in the presence of TEMPO in 2 wt% Tween 20/ H_2O .

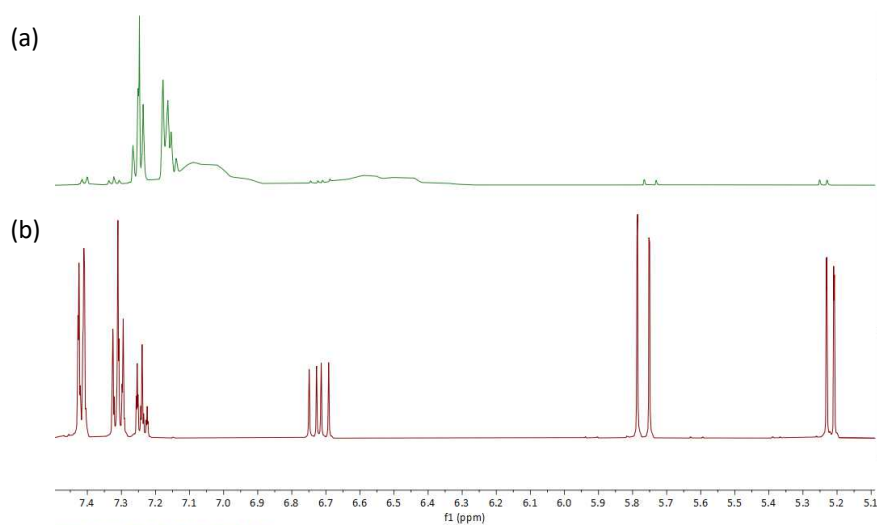


Figure S8 ^1H NMR spectra of **1b**-catalysed ATRA of CCl_4 to styrene using AIBN as a reducing agent with $[\text{alkene}]: [\text{CCl}_4]: [\text{AIBN}] = 1.00: 1.25: 0.07$ in (a) 2 wt% Tween 20/ H_2O at $60\text{ }^\circ\text{C}$ for 6 h which gave 99% conversion but the product was not the monoadduct; and (b) 2.5% $\text{D}_2\text{O}/\text{CD}_3\text{CN}$ at room temperature ($30\text{-}35\text{ }^\circ\text{C}$) for 24 h which gave no conversion.

Comparison of catalytic performance of various copper catalysts for ATRA

Table S2 Previously-reported copper-catalysed ATRA.

Entry	Catalyst	Alkene/Initiator/Reducing agent ([Alkene]: [Reducing agent])	Condition	Conversion (%)	Yield (%)	Ref.
1	[Cu ^{II} (1Q)Cl] (1Q= N,N-bis(pyridine-2-ylmethyl)quinoline-8-amine)	Styrene/CCl ₄ /AIBN	1.0% Cat. in CD ₃ CN, N ₂ , white LEDs, 24 h.		98	S3
		Styrene/CHCl ₃ /AIBN			53	
		Styrene/CBr ₄ /AIBN			90	
		Styrene/CHBr ₃ /AIBN			73	
		Styrene/CHCl ₃ /L-ascorbic acid (1.0: 0.05)		61	60	
		Styrene/CCl ₄ /AIBN			100	
		Acrylonitrile/CCl ₄ /AIBN	1.0% Cat. in CD ₃ OD, N ₂ , white CFL, 48 h.		88	
Methyl methacrylate (MMA)/CCl ₄ /AIBN (1.0: 0.05)			95			
2	[Cu ^{II} (TPMA)Cl][Cl]	Styrene/CCl ₄ /AIBN	0.4% Cat. 60°C		85	S4
		1-hexene/CCl ₄ /AIBN	0.01% Cat. 60°C		72	
		Methyl methacrylate (MMA)/CCl ₄ /V-70	0.1% Cat. ambient temp.		66	
3	[Cu ^{II} (TPMA)Br]Br	Styrene/CBr ₄ /AIBN	0.0005% Cat. in bulk, 60°C, 24 h.		95	
		1-hexene/CBr ₄ /V-70			93	
		Methyl methacrylate (MMA)/CBr ₄ /V-70	0.0005% Cat. in bulk, 60°C, 24 h.		71	
			0.01% Cat. ambient temp.			
4	[Cu ^{II} (Me ₆ TREN)Cl][Cl] 0.4%	1-hexene/CCl ₄ /AIBN	0.1% Cat. in CH ₃ CN, 60 °C, 24 h.	100	100	S5
		Methyl Acrylate (MA)/CCl ₄ /AIBN	0.4% Cat. in CH ₃ CN, 60 °C, 24 h.	100	67	
		Styrene/CHCl ₃ /AIBN (1: 0.05)		77	40	
5	[Cu ^{II} (Me ₆ TREN)Br][Br]	Methyl Acrylate (MA)/CBr ₄ /AIBN (1: 0.05)	0.1% Cat.in CH ₃ CN at 60 °C, 24 h.	100	87	

Table S2 Previously-reported copper-catalysed ATRA (continued).

Entry	Catalyst	Alkene/Initiator/Reducing agent ([Alkene]: [Reducing agent])	Condition	Conversion (%)	Yield (%)	Ref.
6	[Cu ^{II} (TPEN)Br][Br]	Styrene/CBr ₄ /L-ascorbic acid	0. 1% Cat. in	97	61	S6
		Methyl methacrylate (MMA) /CBr ₄ /L-ascorbic acid (1: 0.07)	MeOH, 60 °C, 24 h.	90	29	
7	CuCl or CuCl ₂	Styrene/TsCl/No additive	1% Cat. in		NR	S7
8	CuCl/phen or CuCl ₂ /phen		CH ₃ CN, visible light (530 nm),		NR	
9	[Cu(dap) ₂]Cl		N ₂ , r. t. (25-30		96	
10	[Cu(dap)Cl ₂]		°C), 24 h.		95	
11	[Ru(bpy) ₃]Cl ₂				80	
12	[Cu(ADPA)(H ₂ O)(ClO ₄) ₂]	Styrene	1% Cat. in 2wt%	>99	100	This work
		Methyl methacrylate (MMA)	Tween 20/H ₂ O,	85	52	
		Acrylonitrile	60 °C, 24 h.	28	30	
		1-hexene		92	88	
		/CCl ₄ /L-ascorbic acid (1.00:0.07)				
		Styrene	1% Cat. in 2wt%	87	77	
		Methyl methacrylate (MMA)	Tween 80/H ₂ O,	93	48	
		Acrylonitrile	60 °C, 24 h.	74	67	
1-hexene		>99	95			
/CCl ₄ /L-ascorbic acid (1.00:0.07)						

*NR = no reaction

Determination of droplet/ particle size

The sample was prepared according to experiment 2.2.3 in the same condition as shown in Table 2, Entry 7 by using **1b** as the catalyst for ATRA of CCl_4 to styrene in 2 wt% Tween 20/ H_2O at 60°C for 6 h. The colloidal solution (designated as 1b_2%TWEEN20) was then diluted by an addition of Milli-Q water to obtain the final concentration of 1mM Tween 20 (designated as 1b_1mMTWEEN20). After that, the particle diameter of these samples was measured by dynamic light scattering (DLS).

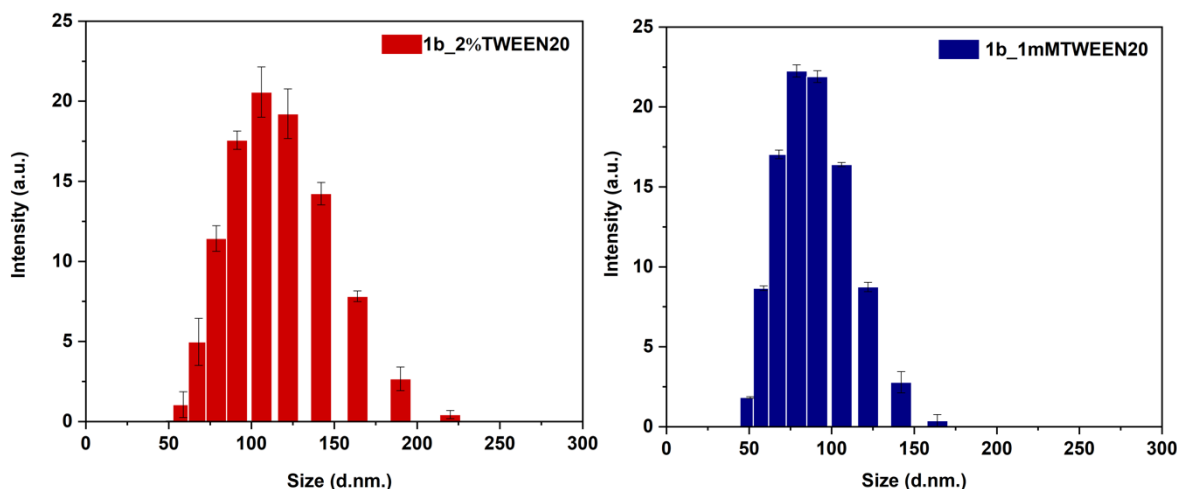


Figure S9 Droplet/particle size distribution of the samples with 2%Tween 20 (■) and 1mM Tween 20 (■) measured by dynamic light scattering (DLS).

Table S3 Z-average particle diameter (d) analyzed by DLS

Entry	Sample	T ($^\circ\text{C}$)	Z-Ave (d, nm)	σ_d (nm)
1	1b_2%TWEEN20	25	106.32	1.68
2	1b_1mMTWEEN20	25	84.41	1.31
3*	1b_1mMTWEEN20	25	121.1	1.27

σ_d is standard deviation and polydispersity index (Pdl) is less than 0.03.

*Micelle diameter (d) of 1mM TWEEN20 (20 CMC) is 7.2 nm ($\sigma_d = 1.2$ nm).^{S8}

*A sample in Entry 2 was kept for 74 days before measuring Z-average particle diameter again.

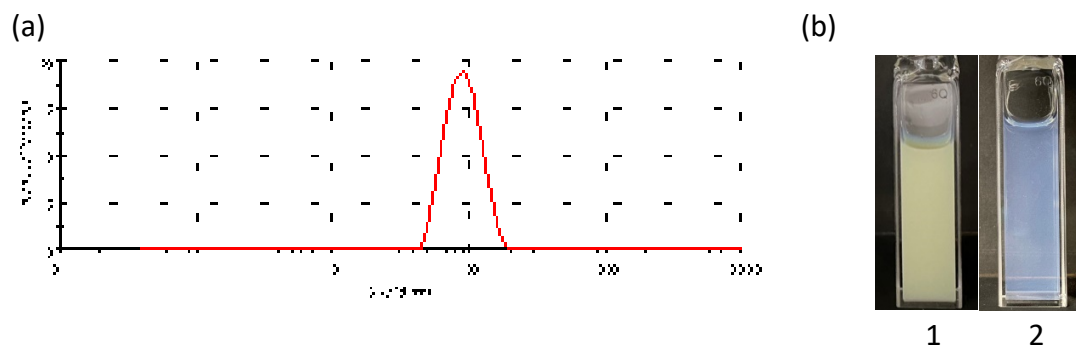


Figure S10 (a) Representative DLS analysis of **1b**-catalysed ATRA dispersed in 2 wt% TWEEN20/H₂O; and (b) photograph of the ATRA reaction in 2 wt% TWEEN20/H₂O (1) versus diluted to 1mM TWEEN20 (2).

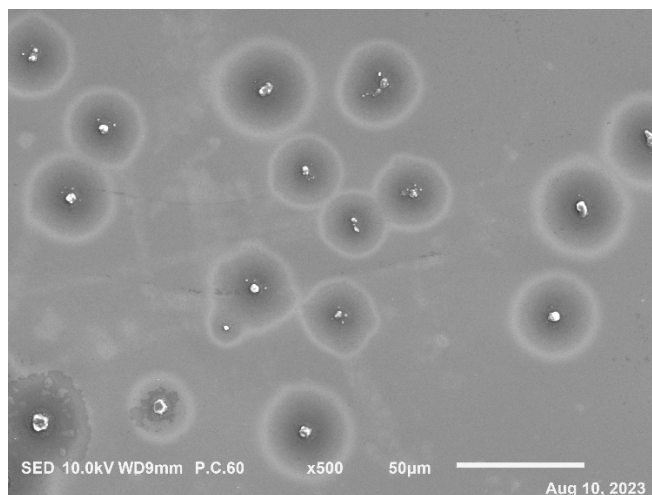


Figure S11 SEM image of **1b**-catalysed ATRA reaction 2 wt% TWEEN20/H₂O which was diluted to 0.5 mM TWEEN20.

References

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