

Kinetics and Mechanism of Halide Exchange in Reactions of $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ with Alkyl Halides: Evidence for Radical Pairs

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Experimental Procedures

Reagents

Ruthenium (III) chloride hydrate, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, was purchased from Pressure Chemical, Inc. Triphenylphosphine, cyclopentadiene, bromoform, carbon tetrabromide, ethyl dibromoacetate, azo {bis(isobutyronitrile)} (AIBN), duraquinone (DQ), and dihydroanthracene (DHA) (Fischer Acros Chemical, Inc.) were used as received. Ethyl tribromoacetate, $\text{CBr}_3\text{CO}_2\text{Et}$, was prepared by literature procedures ¹ (or purchased from Sigma-Aldrich Inc). Solvents were purified by refluxing over Na/benzophenone (toluene, tetrahydrofuran, benzene, hexane, pentane), P_2O_5 (dichloromethane) or MgSO_4 (ethanol) and distilled prior to use. Toluene- d^8 and benzene- d^6 (Cambridge Isotope Laboratories) were purified by distillation from Na/benzophenone. Fluorobenzene (Fisher-Acros) was distilled from P_2O_5 . Cyclopentadienylruthenium (II) phosphine compounds $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (**1**), ² $\text{CpRu}(\text{PPh}_3)_2\text{Br}$ (**3**), ³ and $\text{CH}_3\text{C}_5\text{H}_4\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**4**), ⁴ were prepared by literature procedures; $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**2**) was obtained from the Strem Chemical Co.

Instrumentation

NMR spectra are recorded at 400 MHz for ^1H and 162 MHz for $^{31}\text{P}\{^1\text{H}\}$ on a Mercury XL300 spectrometer. Proton chemical shifts are reported relative to residual protons in the solvent (CD_2HCl at δ 7.24 ppm, $\text{CD}_2\text{HC}_6\text{D}_5$ at δ 2.15 ppm or $\text{C}_6\text{D}_5\text{H}$ at δ 7.15 ppm relative to TMS at 0.00 ppm). Phosphorus chemical shifts are reported relative to 85% H_3PO_4 at 0.0 ppm.

*ATRA reactions of CHBr_3 , CBr_4 , $\text{CHBr}_2\text{CO}_2\text{Et}$ and $\text{CBr}_3\text{CO}_2\text{Et}$ with styrene and AIBN catalyzed by **1-3** by NMR*

Reaction with CHBr_3

A solution containing 11.3 mg (1.42×10^{-5} mols) $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**2**), 1.43×10^{-3} mols styrene, 5.6×10^{-3} mols CHBr_3 , and 7.4×10^{-6} moles AIBN in 650 μL d^8 -toluene is prepared in a vial in a M. Braun glove box. A 500 μL aliquot of the solution is transferred to an NMR tube under nitrogen. The tube is flame sealed under vacuum. The reaction is heated in thermostated oil baths. Very little reaction is observed at 35°C after 17 hours but heating to 45°C for 3½ hours leads to formation of $\text{PhCHBrCH}_2\text{CHBr}_2$. The product is identified by comparison of the ^1H NMR spectrum with an authentic sample of $\text{PhCHBrCH}_2\text{CHBr}_2$ (vide infra). ⁵

^1H (d^8 -toluene): δ 2.72 m (1H), 3.02 m (1H), 4.94 dd (J= 9.4, 5.2 Hz, 1 H), 5.48 dd (J= 9.4, 5.2 Hz, 1 H); The resonances for the aryl protons overlap with any residual resonances assigned to styrene and the $\text{CD}_3\text{C}_6\text{D}_5\text{-}x\text{H}_x$ resonances from the solvent

An analogous reaction between 11.4 mg (1.57×10^{-5} mols) $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (**1**), 1.43×10^{-3} mols styrene, 5.6×10^{-3} mols CHBr_3 , and 7.4×10^{-6} moles AIBN in d^8 -toluene at 87°C for 6 h results in lower conversion than with **2** but the same product is detected by ^1H NMR. In addition to resonances assigned to styrene (δ 5.11 dd, 5.63 d, 6.6 d and

aryl resonances between 7 and 8 ppm), the same resonances assigned to PhCHBrCH₂CHBr₂ in the previous reaction are observed in the ¹H NMR spectra.

Reaction between 9.4 mg (1.2 x 10⁻⁵ mols) CpRu(PPh₃)₂Br, 1.43 x 10⁻³ mols styrene, 5.6 x 10⁻³ mols CHBr₃, and 7.4 x 10⁻⁶ moles AIBN in d⁸-toluene at 87°C for 6 hours also leads to significant conversion to PhCHBrCH₂CHBr₂ as detected by ¹H NMR.

Reaction with CDCl₃

As described above, a solution containing 9.5 mg (1.2 x 10⁻⁵ mols) **2**, 1.43 x 10⁻³ mols styrene, 5.6 x 10⁻³ mols CDCl₃, and 7.4 x 10⁻⁶ moles AIBN in 650 μL d⁸-toluene is prepared in a vial in a M. Braun glove box. A 500 μL aliquot of the solution is transferred to an NMR tube under nitrogen. The tube is flame sealed under vacuum and heated to 45°C for 3½ h resulting in complete conversion (≥95%) to PhCHClCH₂CDCl₂. The product is characterized by comparison with literature data. ⁶ ¹H (400 MHz, d⁸-toluene): δ 2.52 dd (J = 4.4, 14.8 Hz, 1H), 2.73 dd (J = 4.4, 14.8 Hz, 1H), 4.90 dd (J = 5.2, 9.4 Hz, 1H), 7.07-7.28 m (aryl H and CD₃C₆D_{5-x}H_x resonances from solvent).

Heating a solution containing 2.6 mg (3.3 x 10⁻⁶ mols) **2**, 5.2 mg (3.2 x 10⁻⁵ mols) AIBN, 50 μL (4.36 x 10⁻⁴ mols) styrene and 352 μL (4.36 x 10⁻³ mols) CHCl₃ in 800 μL d⁸-toluene at 87°C for 18 h yielded a solution containing PhCHClCH₂CHCl₂.⁶

No reaction is observed between 10.1 mg (1.39 x 10⁻⁵ mols) **1**, 1.43 x 10⁻³ mols styrene, 5.6 x 10⁻³ mols CDCl₃, and 7.4 x 10⁻⁶ moles AIBN in d⁸-toluene 87°C for several days nor between 10.1 mg (1.39 x 10⁻⁵ mols) CpRu(PPh₃)₂Br, 1.43 x 10⁻³ mols styrene, 5.6 x 10⁻³ mols CDCl₃, and 7.4 x 10⁻⁶ moles AIBN at 87°C in d⁸-toluene after several days.

Reaction with CBr₄

A stock solution is prepared by dissolving 30.8 mg (4.24 x 10⁻⁵ mols) **1**, 33.2 mg (2.02 x 10⁻⁴ mols) AIBN and 500 μL (4.36 x 10⁻³ mols) styrene in 2.0 mL d⁸-toluene under nitrogen. 1.0 mL of the stock solution is added to 405 mg (1.22 x 10⁻³ mols) CBr₄. A 520 μL aliquot of the latter solution is transferred to a screw cap NMR tube. Heating the sample at 54°C for 60 minutes leads to new resonances in the ¹H NMR spectrum assigned to PhCHBrCH₂CBr₃ by comparison with the spectra reported in the literature. ⁷ ¹H (d⁸-toluene) δ 3.83 dd (J=15.4, 7.6 Hz, 1H), 3.95 dd (J= 15.8, 2.8 Hz, 1H), 5.21 dd (J = 7.6, 3.2 Hz, 1H). The aryl resonances are obscured by toluene and any remaining styrene resonances.

Reaction with CHBr₂CO₂Et

Ethyl dibromoacetate (200 μL, 1.22 x 10⁻³ mols) is added to 400 μL of the stock solution used above for reactions with CBr₄. A 520 μL aliquot is transferred to a screw cap NMR tube under nitrogen. Reaction at ambient temperature for 39 h leads to new resonances in the ¹H NMR spectrum assigned to PhCHBrCH₂CHBrCO₂Et. ¹H (400 MHz, d⁸-toluene) δ 4.142 t (J=7.6 Hz, 1H), 4.58 dd (J=10, 4.4 Hz, 1H), 5.05 t (J = 7.6 Hz, 1H), 5.17 dd (J = 9.4, 4 Hz, 1H). The aryl resonances are obscured by toluene and any remaining styrene resonances while the

resonances for the ethyl group overlap with the resonances for the starting material ethyldibromoacetate, $\text{CHBr}_2\text{CO}_2\text{Et}$)

Reaction with $\text{CBr}_3\text{CO}_2\text{Et}$

Ethyl tribromoacetate (15 μL , 1.0×10^{-4} mols), styrene (15 μL , 1.3×10^{-4} mols), AIBN (3.7 mg, 2.3×10^{-5} mols) and **1** (3.0 mg, 4.1×10^{-6} mmols) are dissolved in 500 μL d_8 -toluene in a 5 mm NMR tube under nitrogen. The tube is sealed under vacuum. No reaction is observed at ambient temperature after 1 hour. Heating to 87°C for 17 hours leads to a tan precipitate. ^1H NMR spectroscopy indicates nearly all of the styrene (δ 5.14 d, 5.65 d, 6.61 dd), $\text{Br}_3\text{CCO}_2\text{Et}$ (3.87 q and 0.90 t), and AIBN (1.19 s) has been consumed. A forest of new peaks, all multiplets, is observed between 3-4 and 5.2-5.5 ppm.

Synthesis of $\text{PhCHBrCH}_2\text{CHBr}_2$ and $\text{PhCHBrCH}_2\text{CBr}_3$

$\text{PhCHBrCH}_2\text{CHBr}_2$

A toluene solution (5 mL) containing 33.8 mg (4.24×10^{-2} mmols) $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**2**), 500 μL (4.36 mmols) styrene, 1.0 mL (11.2 mmols) CHBr_3 , and 44.4 mg (0.270 mmols) AIBN is heated at 65 - 70°C for 3 hours under nitrogen. Solvent is evaporated from the cooled solution under reduced pressure and the crude product chromatographed on silica with a 1:1 mixture of CH_2Cl_2 : hexane followed by pure CH_2Cl_2 . Evaporation of the solvent from the eluent yields $\text{PhCHBrCH}_2\text{CHBr}_2$ (474 mg, 30% yield) of a colorless oil.

^1H (400 MHz, CDCl_3): δ 3.06 m (1H), 3.29 m (1H), 5.11 dd ($J = 9.0, 6.0$ Hz, 1H), 5.64 dd ($J = 9.0, 6.0$ Hz, 1H), 7.34-7.42 m (5H, aryl). (400 MHz, d_8 -toluene): δ 2.72 m (1H), 3.02 m (1H), 4.94 dd ($J = 9.4, 5.2$ Hz, 1 H), 5.48 dd ($J = 9.4, 5.2$ Hz, 1 H); 6.94-7.18 m (aryl H and $\text{CD}_3\text{C}_6\text{D}_5\text{-xH}_x$ resonances from solvent) ^{13}C (101 MHz, CDCl_3): δ 42.29, 51.46, 53.86, 127.44, 129.08, 139.50.

Literature⁵: ^1H (500 MHz, CDCl_3): δ 3.07 (ddd, $J = 15.2, 8.0, 5.7$ Hz, 1H), 3.28 (ddd, $J = 14.8, 9.0, 5.7$ Hz, 1 H), 5.11 (dd, $J = 8.9, 5.7$ Hz, 1 H), 5.63 (dd, $J = 8.1, 5.8$ Hz, 1H), 7.32-7.42 (m, 5H). ^{13}C (126 MHz, CDCl_3) δ 42.42, 51.58, 53.94, 127.55, 129.20, 129.22, 139.61.

Synthesis of $\text{PhCHBrCH}_2\text{CBr}_3$

A toluene solution (4 mL) containing 27.7 mg **1** (4.24×10^{-2} mmols), 500 μL (4.36 mmols) styrene, 327 mg (0.985 mmols) CHBr_3 , and 44.4 mg (0.270 mmols) AIBN is heated at 75 - 80°C for 3 hours under nitrogen. Solvent is evaporated from the cooled solution under reduced pressure and the crude product chromatographed on silica with hexane followed by 1:1 mixture of CH_2Cl_2 : hexane. Evaporation of the solvent from the eluent yields 406 mg of a colorless oil, $\text{PhCHBrCH}_2\text{CBr}_3$ (95% yield)

^1H (400 MHz, CDCl_3): δ 4.1 m ($J = 2\text{H}$), 5.33 m (1H), 5.11 dd ($J = 9.0, 6.0$ Hz, 1H), 5.64 dd ($J = 9.0, 6.0$ Hz, 1H), 7.34-7.42 m (5H, aryl); ^{13}C (101 MHz, CDCl_3) δ 35.0, 50.3, 66.4, 127.8, 128.8, 128.9, 140.8.

Literature ⁷: ¹H (400 MHz, CDCl₃): δ 4.05 (dd, J=15.6, 7.7, 1H), 4.12 (dd, J=15.6, 4.1 Hz, 1 H), 5.33 (dd, J=7.7, 4.1 Hz, 1 H), 7.31 (t, J=7.2 Hz, 1H), 7.37 (m, 2H), 7.49 (m, 2H). (500 MHz, CDCl₃): δ 4.06 (dd, J=15.5, 7.5, 1H), 4.12 (dd, J=15.5, 4.0 Hz, 1 H), 5.33 (dd, J=7.5, 4.0 Hz, 1 H), 7.37 (t, J=7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.49 (d, J=7.5 Hz, 2H). ¹³C (101 MHz, CDCl₃) δ 35.0, 50.1, 66.5, 128.2, 128.9, 129.0, 140.8; (125 MHz, CDCl₃) δ 35.0, 50.0, 66.4, 128.1, 128.87, 128.94, 140.8.

Kinetic Measurements: 1 with CHBr₃, CBr₄, CHBr₂CO₂Et and CBr₃CO₂Et

Kinetic measurements are made in flame-sealed NMR tubes. A 5 mm thin wall NMR tube is glass blown to a 14/20 joint. Each tube is tested for leaks by applying a current from a Tesla coil to the tube under vacuum (Figure S1). A leak causes the discharge to converge on the defective site for repair in a glass-blowing torch. Stock solutions of 5-15 mM CpRu(PPh₃)₂Cl (**1**) or CH₃C₅H₄Ru(PPh₃)₂Cl (**4**) in C₆H₅F/10% C₆D₆ are prepared under a nitrogen atmosphere in a M. Braun glove box. Fluorobenzene (Fisher-Acros) and benzene-d₆ (Sigma Aldrich) are purified by distillation from MgSO₄ and Na/benzophenone, respectively. Samples for kinetic experiments are prepared by adding stock solutions (typically 2 mL) to vials containing pre-weighed amounts of CBr₄. For experiments with liquid halocarbons (CHBr₃, CHBr₂CO₂Et and CBr₃CO₂Et), the reactant is added to vials containing the stock solution by micropipette. Weighed amounts of AIBN, DHA and DQ are also present for selected experiments. Aliquots (≈ 500-525 μL) from each vial are transferred to 5 mm NMR tubes in the glove box (Figure S4a), cooled to -78°C and flame-sealed under vacuum (Figure S4b and c). In most cases, the samples can be stored in a -20°C without observing any reaction. In selected cases, samples are stored at -78°C. After recording initial spectra, the samples are heated in thermostated oil baths, and the progress of the reaction monitored by ³¹P NMR. The color of the solution changes from yellow to orange (Figure S5) as the halide exchange reaction proceeds. The procedure does not prevent small leaks from developing in all samples during the flame-sealing process. Inadvertent introduction of small amounts of air through pin-hole leaks leads to discoloration of the sample and formation of black precipitates (Figure S5). Efforts are made to make all measurements in triplicate, but on occasion a leaky tube means that good data can only be collected on two replicate samples. For samples containing AIBN, DHA and DQ data was collected on a single sample. Concentrations of reactants and products are determined from integration of the spectra. Pseudo first order rate constants are calculated from plots of ln *k*_{obs} vs time with errors calculated using Excel. Plots of *k*_{obs} vs [RBr] (where R= CHBr₂, CBr₃, CHBrCO₂Et, and CBr₂CO₂Et). Activation parameters were calculated from the Eyring equation.

Kinetic Measurements: 1 with CH₃COBr

The rapid rate of reaction between **1** and CH₃COBr requires a different approach to sample preparation. A stock solution (15 mM **1**) in C₆H₅F/10% C₆D₆ is prepared in the glove box. 500 μL aliquots are transferred to screw cap 5 mm NMR tubes which are subsequently cooled to -78°C. Excess acetyl bromide is added by micropipette to tubes at -78°C under N₂ just before the kinetic experiment is started. The tube is shaken to mix the reagents and inserted into a pre-cooled NMR probe at 0°C. Unlike the previous experiments, the samples remain in the probe throughout the data collection period. The probe temperature is regulated by the instrument software and gave excellent

stability throughout the experiment. Concentrations of reactants and products are determined from integration of the spectra. Pseudo first order rate constants are calculated from plots of $\ln k_{obs}$ vs time with errors calculated using Excel.

Kinetics of Phosphine Substitution in 4

The same procedure used to prepare samples for halide exchange measurements is applied to phosphine exchange studies between **4** (6.1 mM) and excess PMePh_2 (50 mM) in $\text{C}_6\text{H}_5\text{F}/10\% \text{C}_6\text{D}_6$ in flame sealed NMR tubes. Concentrations of reactants and products are determined from integration of the spectra. Pseudo first order rate constants are calculated from plots of $\ln k_{obs}$ vs time with errors calculated using Excel.

Computational Data

Cartesian coordinates of all the structures optimized using Kohn-Sham density functional theory (M06/def2-SVP) in the xyz format are reported in a separate zip file as part of the supplementary materials.

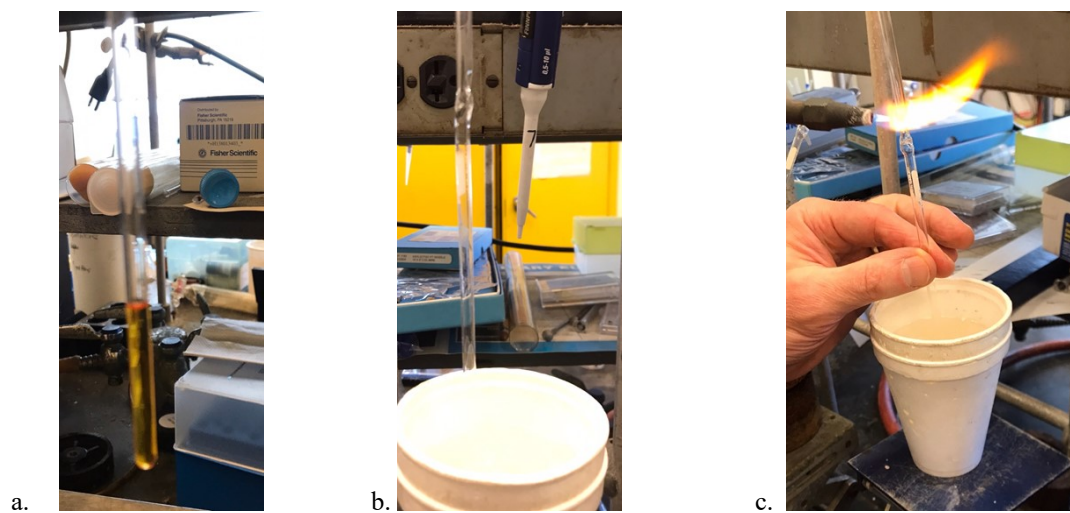


Figure S1: a. 5 mm NMR tube containing a solution of **1** and CBr_4 in fluorobenzene/ C_6D_6 ; b. sample cooled to -78°C ; c. sample being sealed under vacuum.

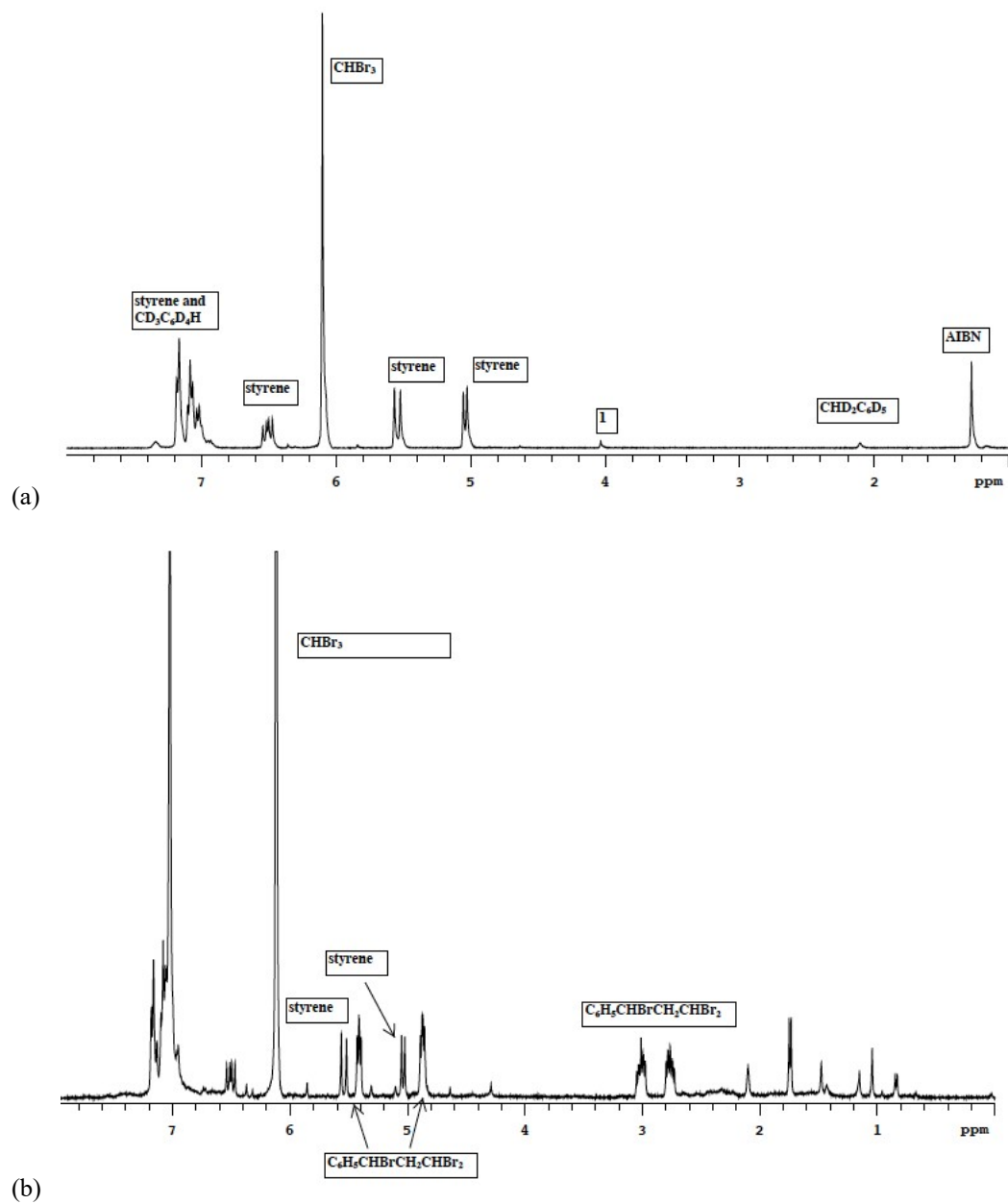


Figure S2: ^1H NMR spectra of the reaction between styrene and bromoform catalyzed by **1** and AIBN in toluene- d^8 . (a) < 1 h at room temperature; (b) after heating at 87°C for 72 h.

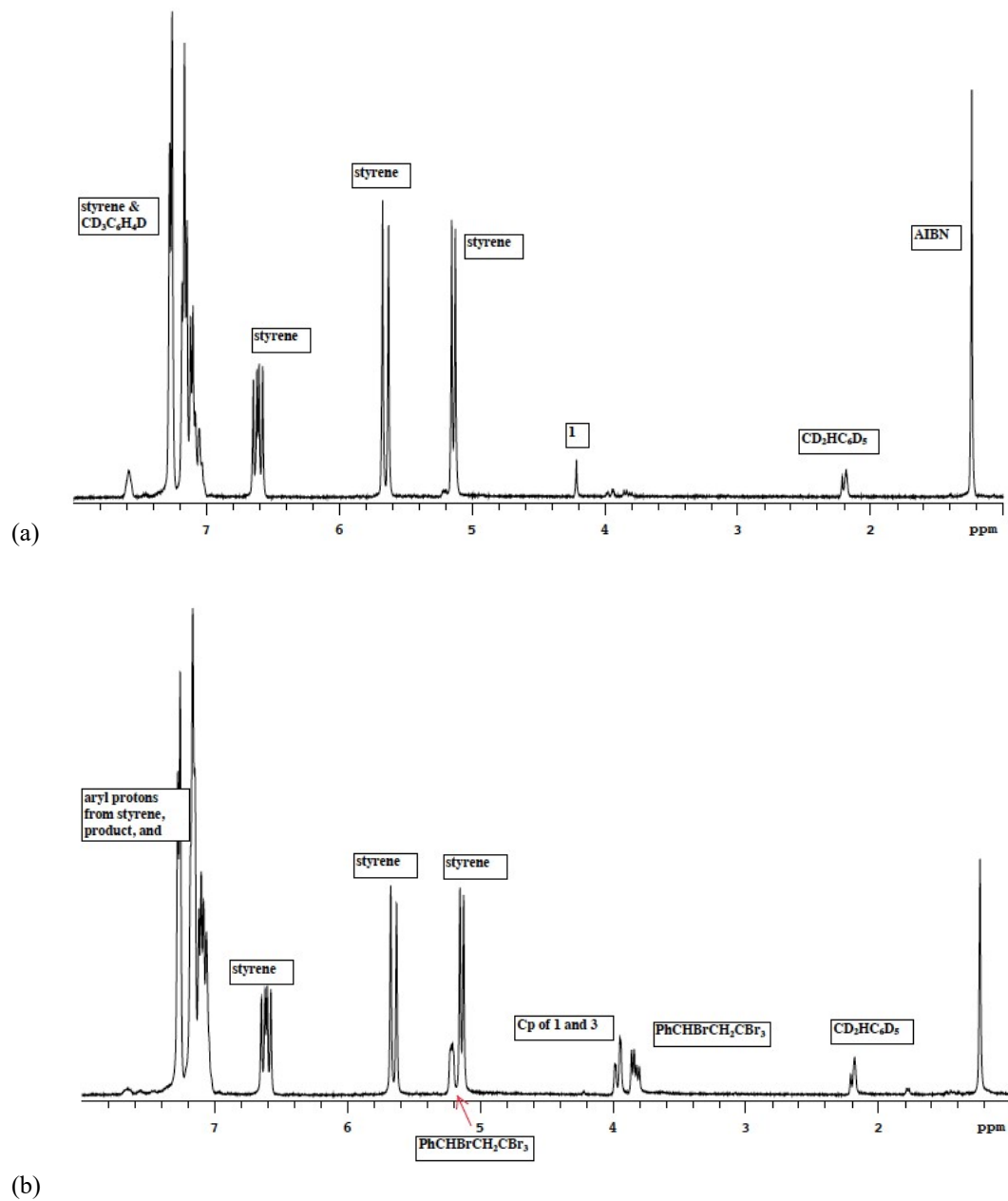


Figure S3: ^1H NMR spectra of the reaction between styrene and carbon tetrabromide catalyzed by **1** and AIBN in toluene- d^8 . (a) < 1 h at room temperature; (b) after heating at 54°C for 1 h.

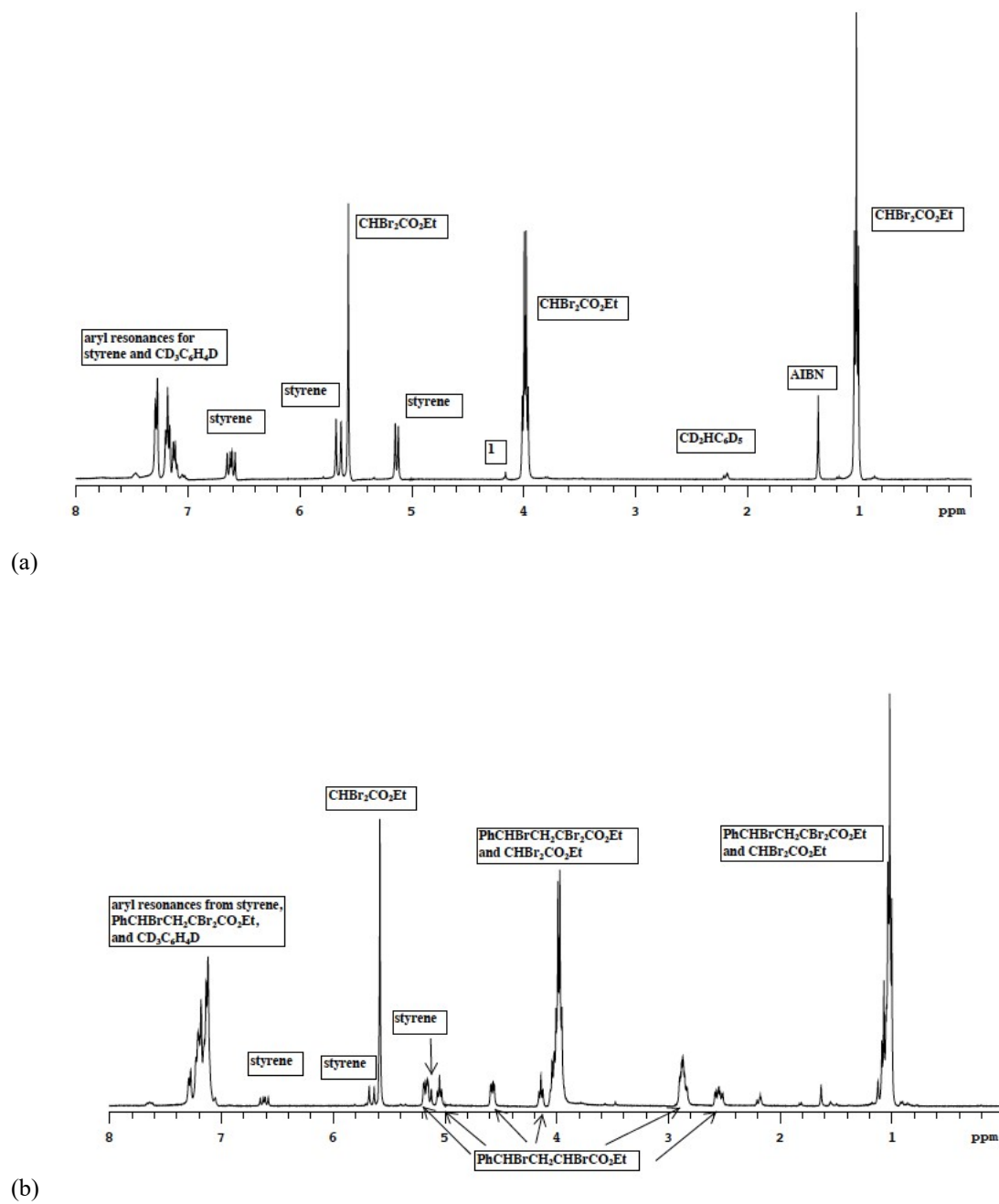
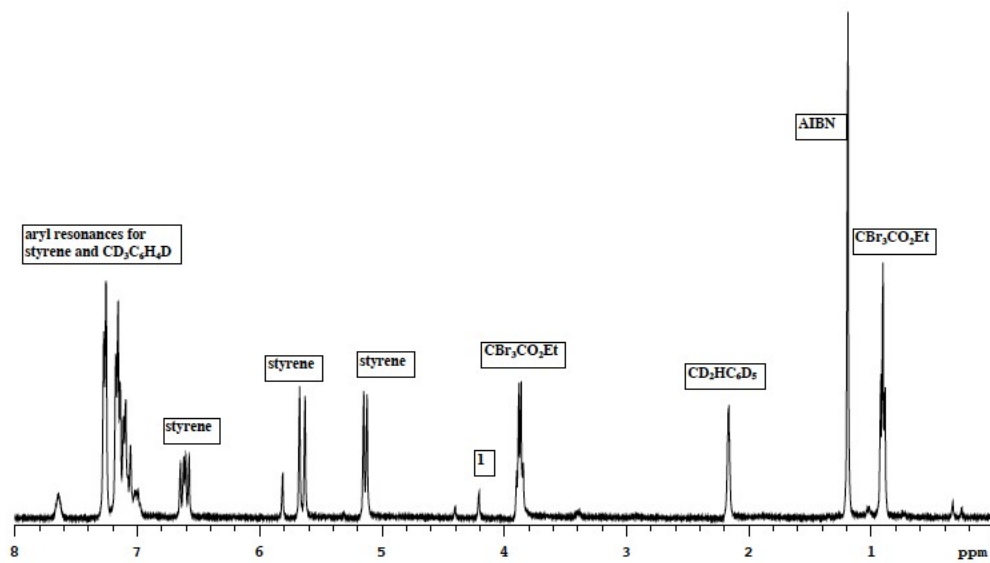
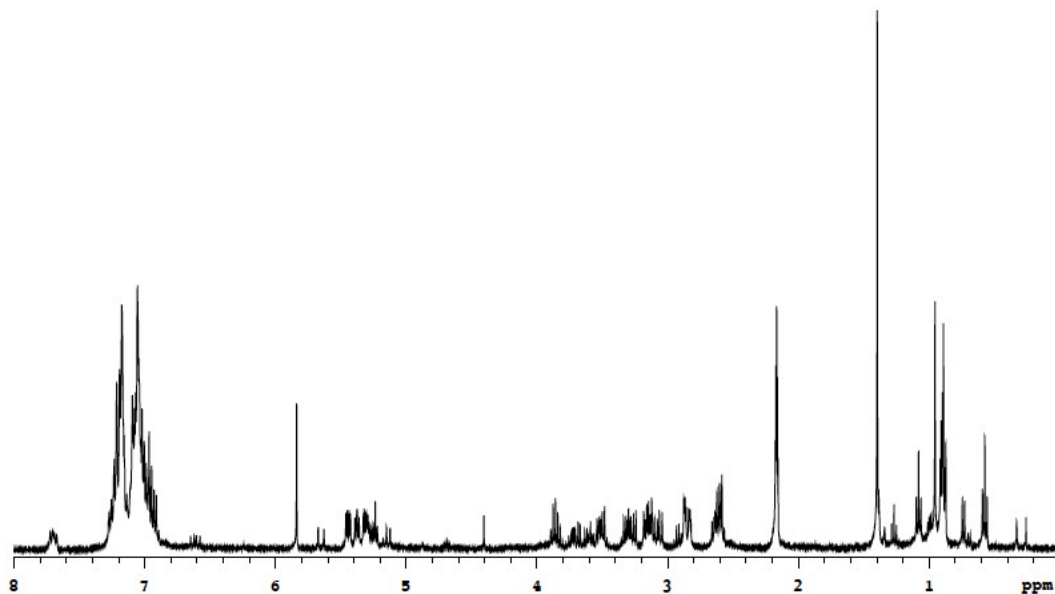


Figure S4: ^1H NMR spectra of the reaction between styrene and ethyl dibromoacetate catalyzed by **1** and AIBN in toluene- d^8 . (a) $<math><lt; 1</math> h at room temperature; (b) after heating at 87°C for 18 h.$



(a)



(b)

Figure S5: ^1H NMR spectra of the reaction between styrene and ethyl tribromoacetate catalyzed by **1** and AIBN in toluene- d^8 . (a) < 1 h at room temperature; (b) after heating at 87°C for 18 h.

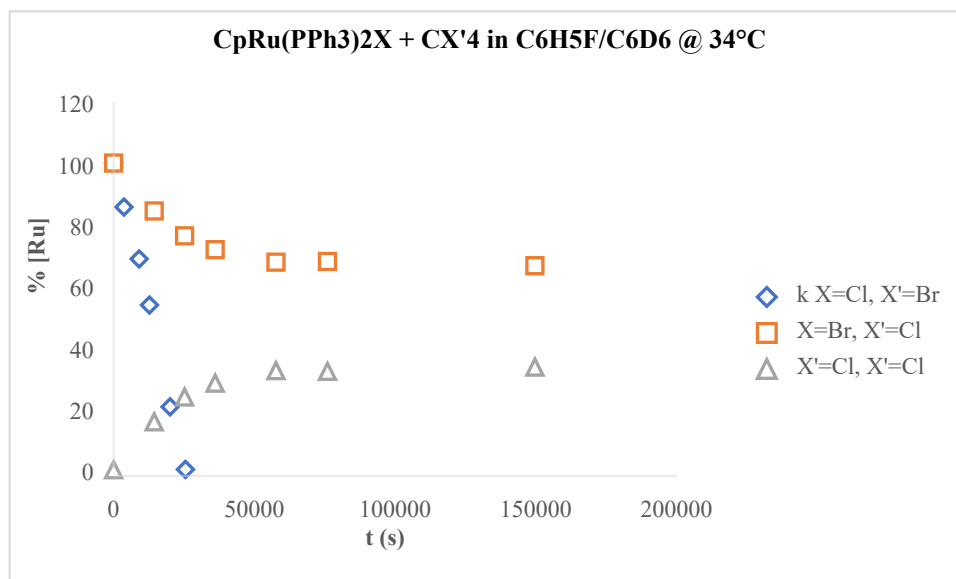


Figure S6: Concentration changes for CpRu(PPh₃)₂Cl (**1**, blue diamonds) and CpRu(PPh₃)₂Br (**3**, orange squares and grey triangles) vs time for halide exchange reaction with CBr₄ and CCl₄, respectively.

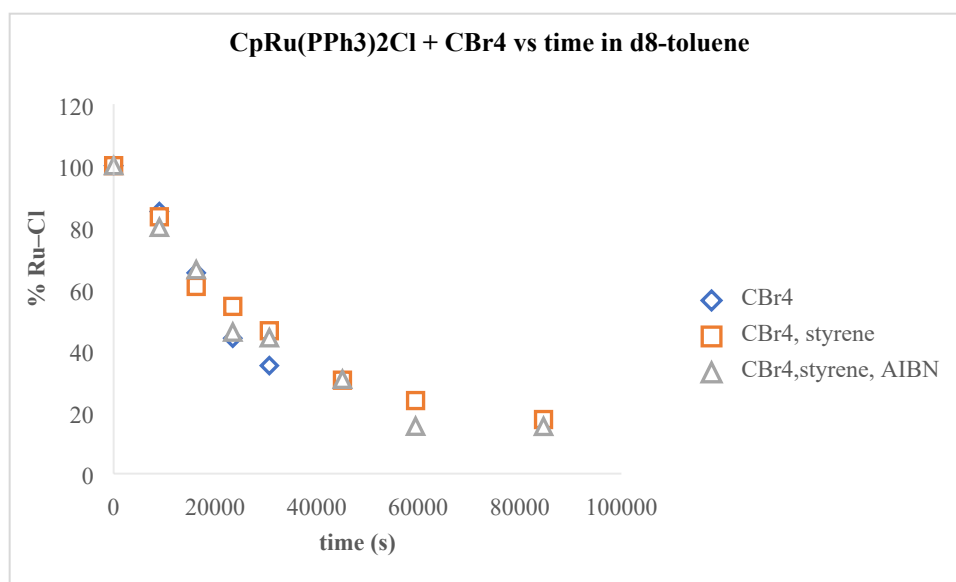


Figure S7: Concentration of CpRu(PPh₃)₂Cl (**1**) vs time (s) under conditions for ATRA of CBr₄ to styrene.

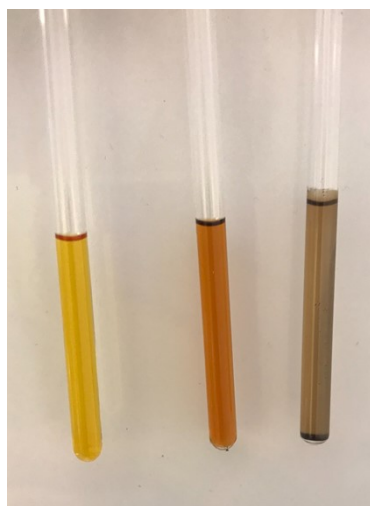


Figure S8: from left to right: solution of **1** and CBr_4 in fluorobenzene/ C_6D_6 before reaction, solution of **1** and CBr_4 in fluorobenzene/ C_6D_6 after heating to produce $\text{CpRu}(\text{PPh}_3)_2\text{Br}$, and leaky tube containing a solution of **1** and CBr_4 in fluorobenzene/ C_6D_6 after heating.

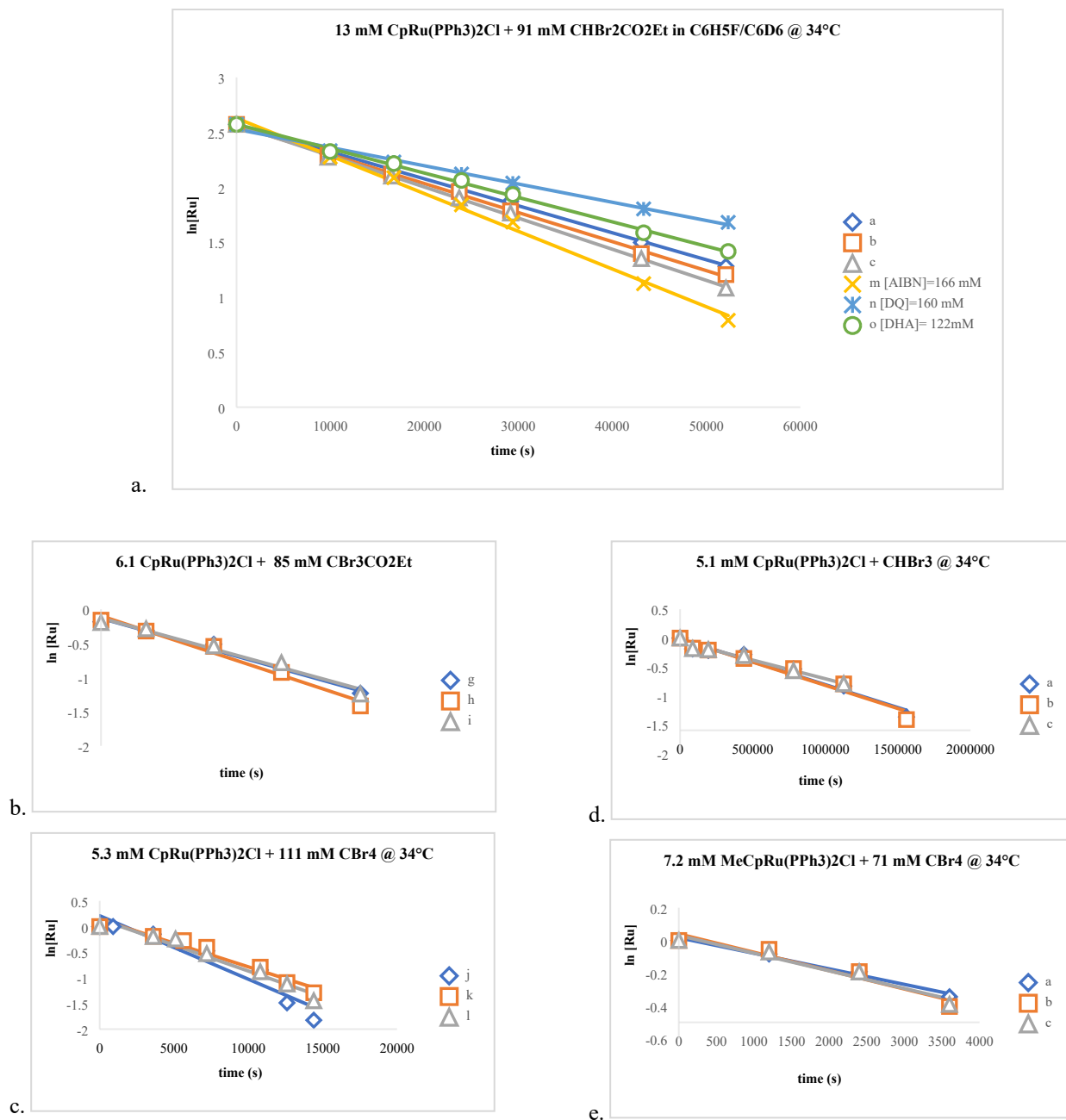


Figure S9: Plot of $\ln[1]$ vs time (s) for the reaction between $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ and a. $\text{CHBr}_2\text{CO}_2\text{Et}$ b. $\text{CBr}_3\text{CO}_2\text{Et}$ c. CBr_4 d. CHBr_3 in $\text{C}_6\text{H}_5\text{F}/10\% \text{C}_6\text{D}_6$ at 34°C showing the effects of radical initiators azo bis(isobutyronitrile) (AIBN) and dihydroanthracene (DHA) and radical inhibitor duraquinone (DQ); e. $\text{MeC}_5\text{H}_4\text{Ru}(\text{PPh}_3)_2\text{Cl}$ and CBr_4

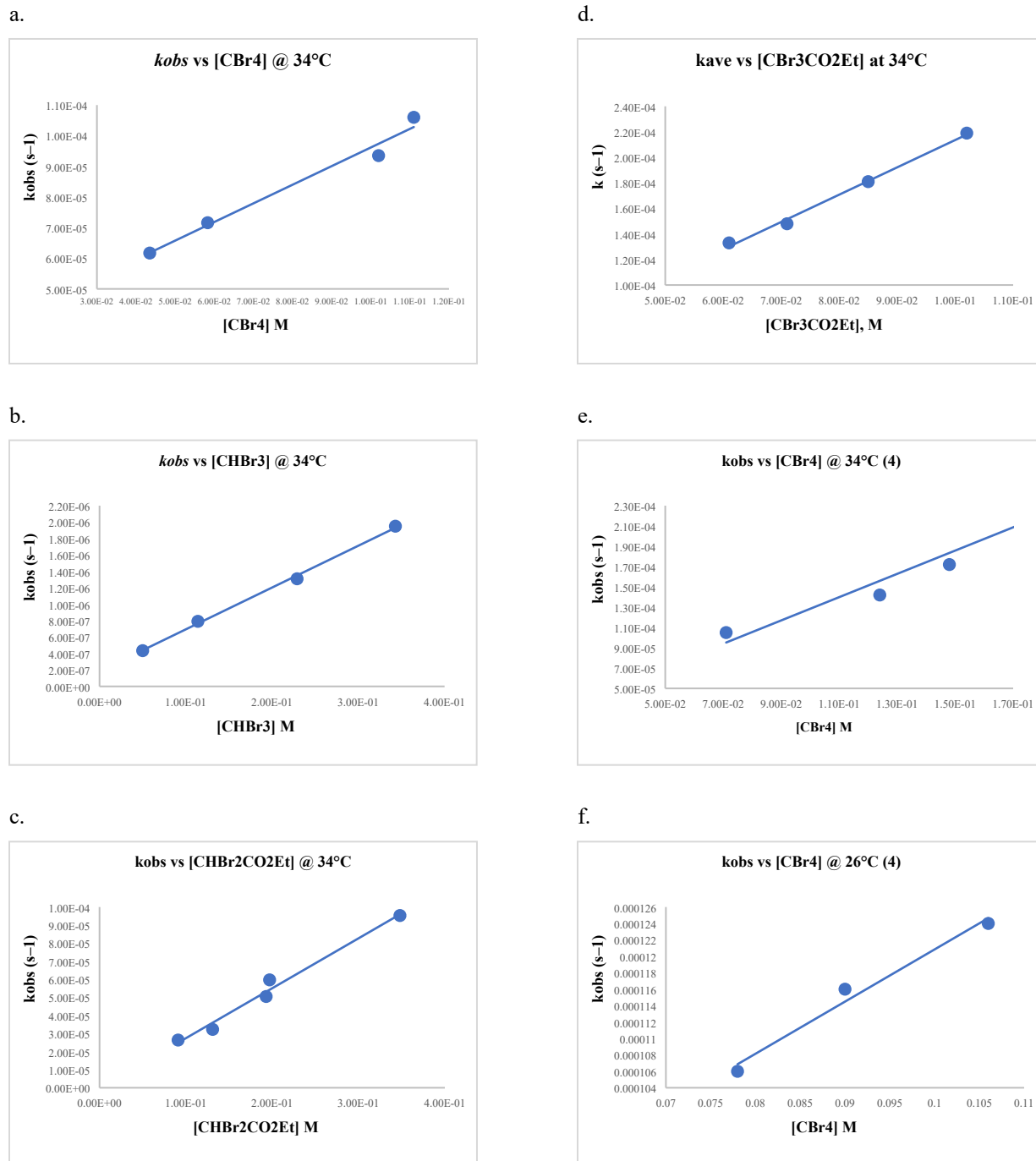


Figure S10: Plots of k_{obs} vs [RBr] for the reaction between CpRu(PPh₃)₂Cl and RBr at 34°C in fluorobenzene/10% benzene-d₆. a. **1**, RBr = CBr₄; b. **1**, RBr = CHBr₃; c. **1**, RBr = CHBr₂CO₂Et; d. **1**, CBr₃CO₂Et; e. **4**, RBr = CBr₄; f. **4**, RBr = CBr₄ at 25°C.

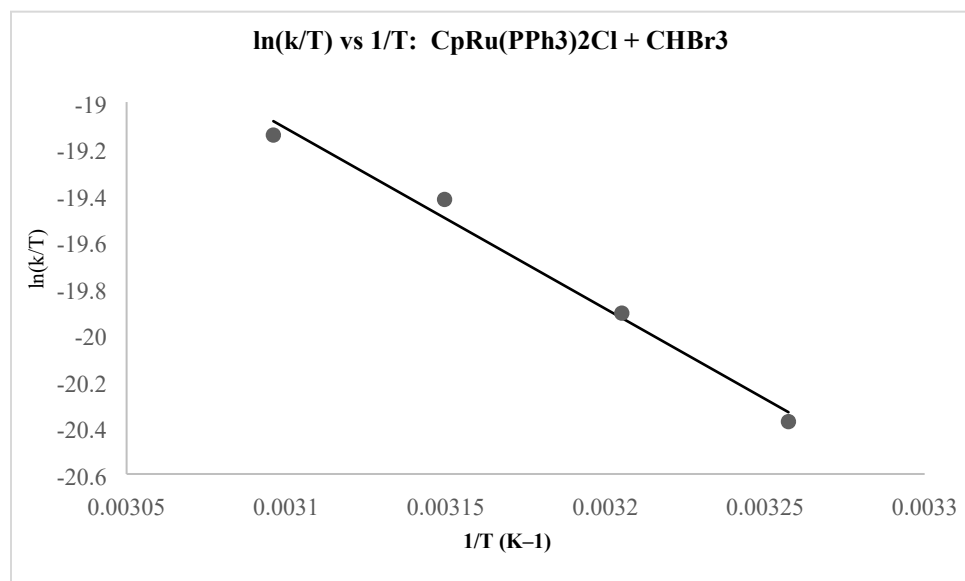


Figure S11: Eyring plot $\ln k_{\text{obs}}/T$ vs $1/T$ for the reaction between $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ and CHBr_3 in fluorobenzene/10% benzene- d^6

Table S1: Pseudo-first order rate constants for halide exchange reactions between 1 and RBr in C ₆ H ₅ F/10% C ₆ D ₆ at 34°C						
RBr	[RBr] (mM)	[Ru] (mM)	[AIBN]	[DHA]	[DQ]	k _{obs} (x 10 ⁴ s ⁻¹)
CBr ₃ CO ₂ Et	102	6.1				2.19±0.15
CBr ₄	102	6.6				0.863±0.014
			56			0.876
			97			1.03
			142			1.07
	71 [§]	7.2 [§]				1.05±0.04
	71 [§]	7.2 [§]	81			2.13
CHBr ₂ CO ₂ Et	91	13				0.264±0.019
			166			0.343
				122		0.222
					160	0.166
CHBr ₃	165	5.7				0.0140±0.0014
			70			0.0706
ⁿ C ₄ H ₉ Br [‡]	103	10				0.0056±0.0003
‡ see reference 3						
§using CH ₃ C ₅ H ₄ Ru(PPh ₃) ₂ Cl as the catalyst						

Table S2: Rate constants for halide exchange: CpRu(PPh ₃) ₂ Cl + RBr in C ₆ H ₅ F/C ₆ D ₆			
RBr, catalyst	T (°C)	k₂ (x 10⁴ M⁻¹ s⁻¹)	k₋₂ (x 10⁴ s⁻¹)
CBr ₃ CO ₂ Et, 1	34	21±1	-0.004±0.088
CBr ₄ , 3	34	11.2±2.5	0.18±0.34
	26	6.35±0.94	0.57±0.09
CBr ₄ , 1	34	6.08±0.63	0.35±0.05
CHBr ₂ CO ₂ Et, 1	34	2.94±0.29	-0.02±0.06
CHBr ₃ , 1	34	0.0509±0.0017	0.00185±0.00036
ⁿ C ₄ H ₉ Br, 1 [‡]	44.5	0.12±0.011	0.0046±0.0031
[‡] see reference 3			

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