Electronic Supporting Information

Atom Transfer Radical Addition (ATRA) Catalyzed by Copper Complexes with Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) Ligand in the Presence of Free-Radical Initiator AIBN

William T. Eckenhoff and Tomislav Pintauer*

Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, 308 Mellon Hall, Pittsburgh, PA 15282, Tel: 412-396-1626, Fax: 412-396-5683, Email:pintauert@duq.edu

Table of Contents:

Table S1. Addition of polyhalogenated compounds to alkenes in the presence of AIBN.[a]

Alkene	R-X	Conversion (%)	Yield (%)[b]
Hexene	CCl_4	17	17
Octene	CCl_4	14	14
cis-Cyclooctene	CCl_4	27	27[c]
Styrene	CCl_4	45	0
Methyl Acrylate	CCl_4	>99	0
Hexene	$CHCl_3$	0	0
Octene	$CHCl_3$	0	0
cis-Cyclooctene	$CHCl_3$	0	0
Styrene	$CHCl_3$	44	0
Methyl Acrylate	$CHCl_3$	>99	0
Hexene	$CHBr_3$	32	32
Octene	$CHBr_3$	32	32
cis-Cyclooctene	$CHBr_3$	11	11[c]
Styrene	$CHBr_3$	54	0
Methyl Acrylate	$CHBr_3$	>99	0
cis-Cyclooctene	CBr_4	92	92[d]
Styrene	CBr_4	95	71
Methyl Acrylate	CBr_4	>99	11
cis-Cyclooctene	$CBrCl_3$	82%	82[e]

[a]T=60 °C, t= 24 hr, solvent=CH_3CN, $[Alkene]_0:[R\text{-}X]_0:[AIBN]_0=1:1.1:0.05$, $[Alkene]_0$ = 1.34 M (CCl_4, $CHCl_3$ and $CHBr_3$) or 1.13 M (CBr_4). [b]Yield is based on the formation of monoadduct and was determined using ^1H NMR spectroscopy. [c]Only 1,4 isomer detected. [d]Ratio of 1,2- to 1,4-isomers was found to be 75:25. [e]Ratio of 1,2-isomer to 1,4-isomer was found to be 52:48.

Table S2. Crystallographic and experimental data for $[Cu^{II}(Me_6TREN)Cl][Cl]$ (**1**) and $[Cu^{II}(Me_6TREN)Br][Br]$ (**2**) .

	$[Cu^{II}(Me_6TREN)Cl][Cl]$ (1)	**$[Cu^{II}(Me_6TREN)Br][Br]$ (2)**
Formula	$C_{12}H_{30}Cl_2CuN_4$	$C_{12}H_{30}Br_2CuN_4$
Color/Shape	green/rhomboid	green/rhomboid
Formula Weight	364.84	453.76
Crystal System	cubic	cubic
Space Group	P 21 3	P 21 3
Temp (K)	150K	150K
Cell Constants		
***a*, Å**	11.85480 (10)	12.0512 (3)
***b*, Å**	11.85480 (10)	12.0512 (3)
***c*, Å**	11.85480 (10)	12.0512 (3)
a, deg	90	90
b, deg	90	90
g, deg	90	90
V, Å^3	1666.03	1750.21
Formula units/unit cell	4	4
D cal'd, gcm^{-3}	1.455	1.722
μ, mm^{-1}	1.626	5.808
F(000)	772	916
Diffractometer	Bruker Smart ApexII	Bruker Smart ApexII
Radiation, graphite monochr.	Mo Kα (λ=0.71073 Å)	Mo Kα (λ=0.71073 Å)
Crystal size, mm	0.320 x 0.255 x 0.206	0.258 x 0.223 x 0.129
θ range, deg	2.43< θ <32.77	2.39< θ <32.94
Range of *h,k,l*	±34, ±34, ±35	±35, ±35, ±36
Reflections collected/unique	30664/2038	23236/2153
R_{int}	0.0359	0.0353
Refinement Method	Full Matrix Least-Squares on F^2	Full Matrix Least-Squares on F^2
Data/Restraints/Parameters	2038/0/61	2153/0/60
GOF on F^2	1.155	1.073
Final R indices [I>2σ(I)]	R_1=0.0208 wR_2=0.0553	R_1=0.0185 wR_2=0.0433
R indices (all data)	R_1=0.0221 wR_2=0.0557	R_1=0.0227 wR_2=0.0443
Max. Resid. Peaks (e*Å^{-3})	0.287 and -0.394	0.434 and -0.177

Table S3. Crystallographic and experimental data for $[Cu^{I}(Me_6TREN)PPh_3][BPh4]$ (**3**).

	$[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ (3)
Formula	$C_{54}H_{65}BCuN_4P$
Color/Shape	colorless/rhomboid
Formula Weight	875.42
Crystal System	triclinic
Space Group	P -1
Temp (K)	150K
Cell Constants	
***a*, Å**	17.8968(2)
***b*, Å**	17.9299(2)
***c*, Å**	18.4322(2)
a, deg	99.717(10)
b, deg	109.9550(10)
g, deg	113.8060(10)
V, $Å^3$	4752.43(9)
Formula units/unit cell	4
D cal'd, gcm^{-3}	1.224
μ, mm^{-1}	0.533
F(000)	1864
Diffractometer	Bruker Smart ApexII
Radiation, graphite monochr.	Mo Kα (λ=0.71073 Å)
Crystal size, mm	0.350 x 0.34 x 0.100
θ range, deg	1.26< θ <29.78
Range of *h,k,l*	±24, ±25, ±25
Reflections collected/unique	79007/26903
R_{int}	0.0356
Refinement Method	Full Matrix Least-Squares on F^2
Data/Restraints/Parameters	26903/0/1111
GOF on F^2	0.898
Final R indices [I>2σ(I)]	R_1=0.0394 wR_2=0.1141
R indices (all data)	R_1=0.0645 wR_2=0.1378
Max. Resid. Peaks ($e^*Å^{-3}$)	0.388 and -0.478

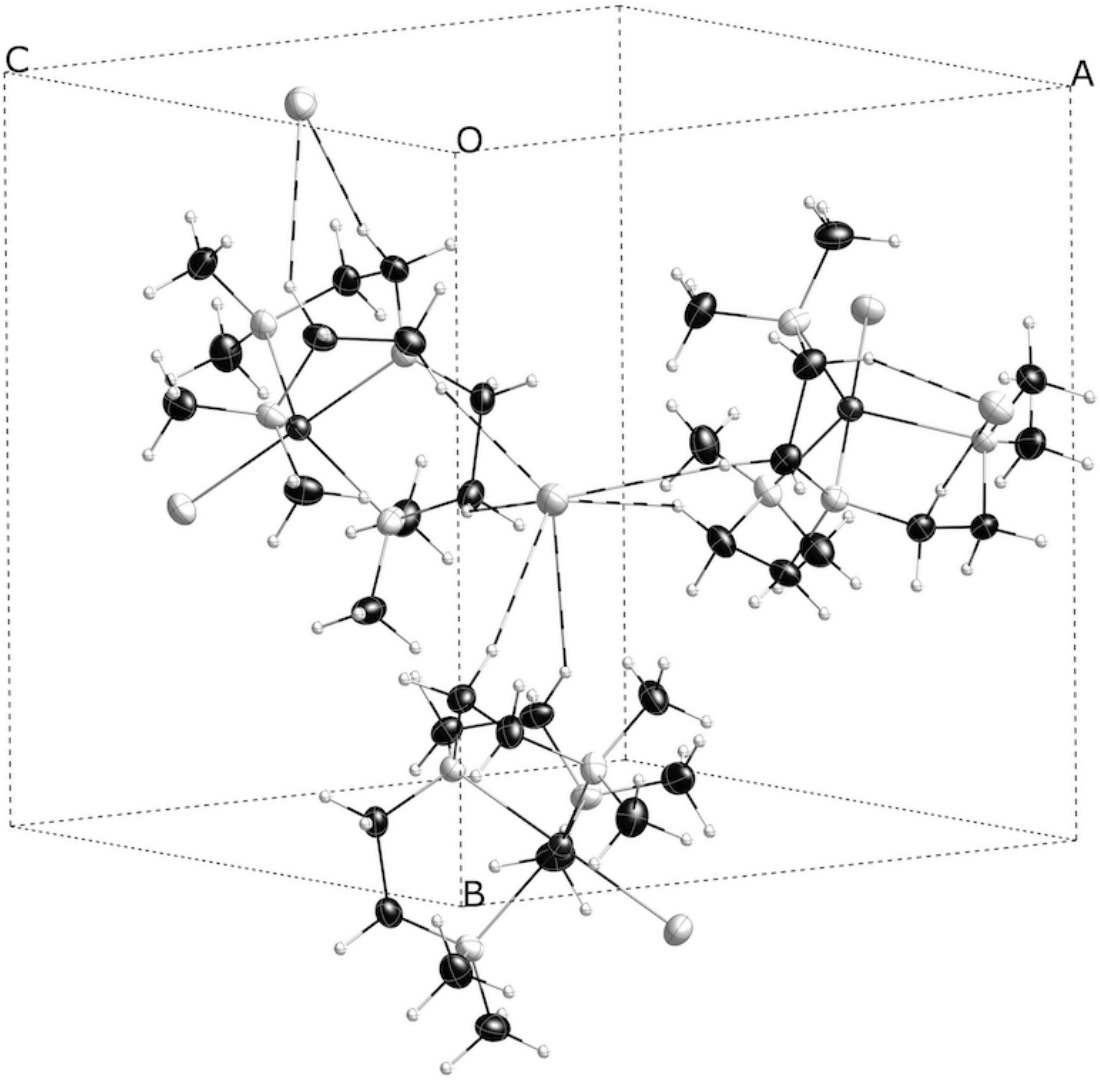


Figure S1. Crystal packing diagram of $[Cu^{II}(Me_6TREN)Cl][Cl]$ (**1**), showing weak Cl---H-C interactions at 2.733(6) Å and 2.864(6) Å.

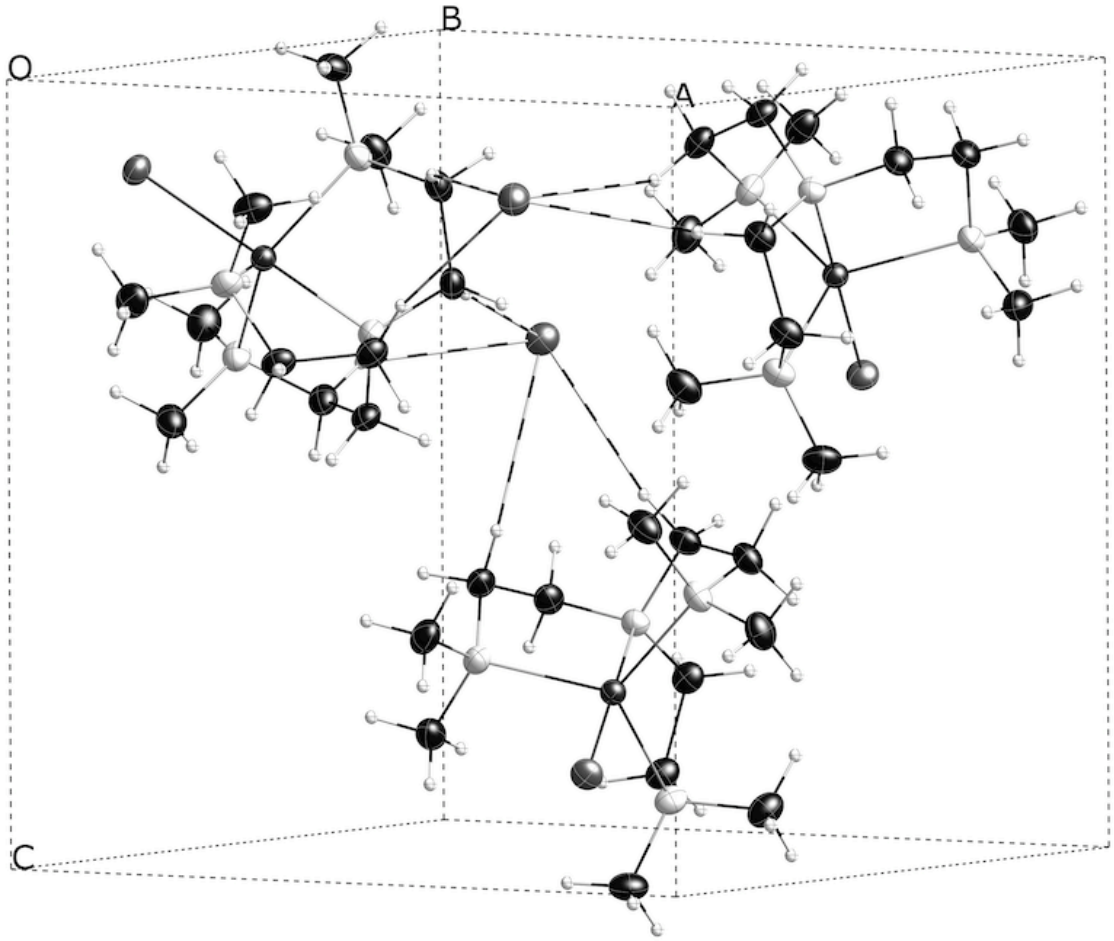


Figure S2. Crystal packing diagram of $[Cu^{II}(Me_6TREN)Br][Br]$ (**2**), showing weak Br---H-C interactions at 2.838(6) Å and 3.005(6) Å.

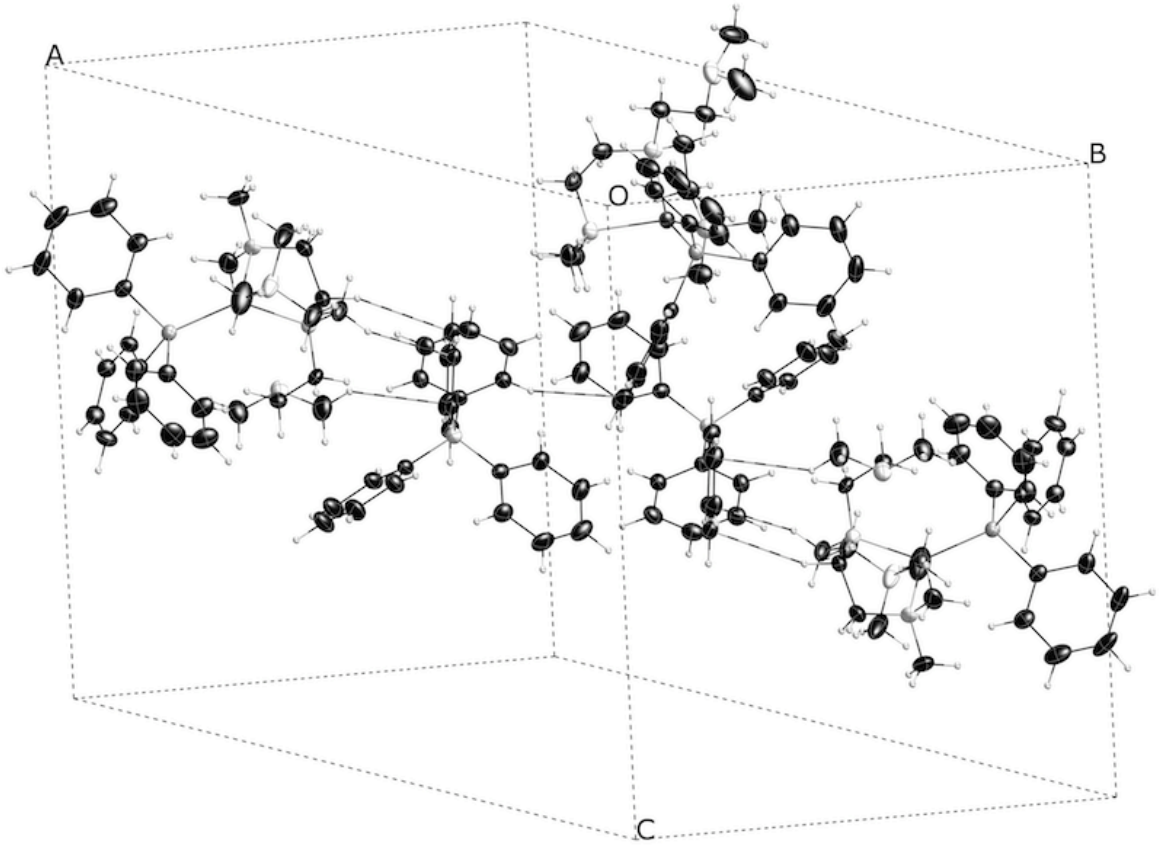


Figure S3. Crystal packing diagram of $[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ (**3**), showing weak C---H-C interactions ranging from 2.6579(6) Å to 2.879(6) Å.

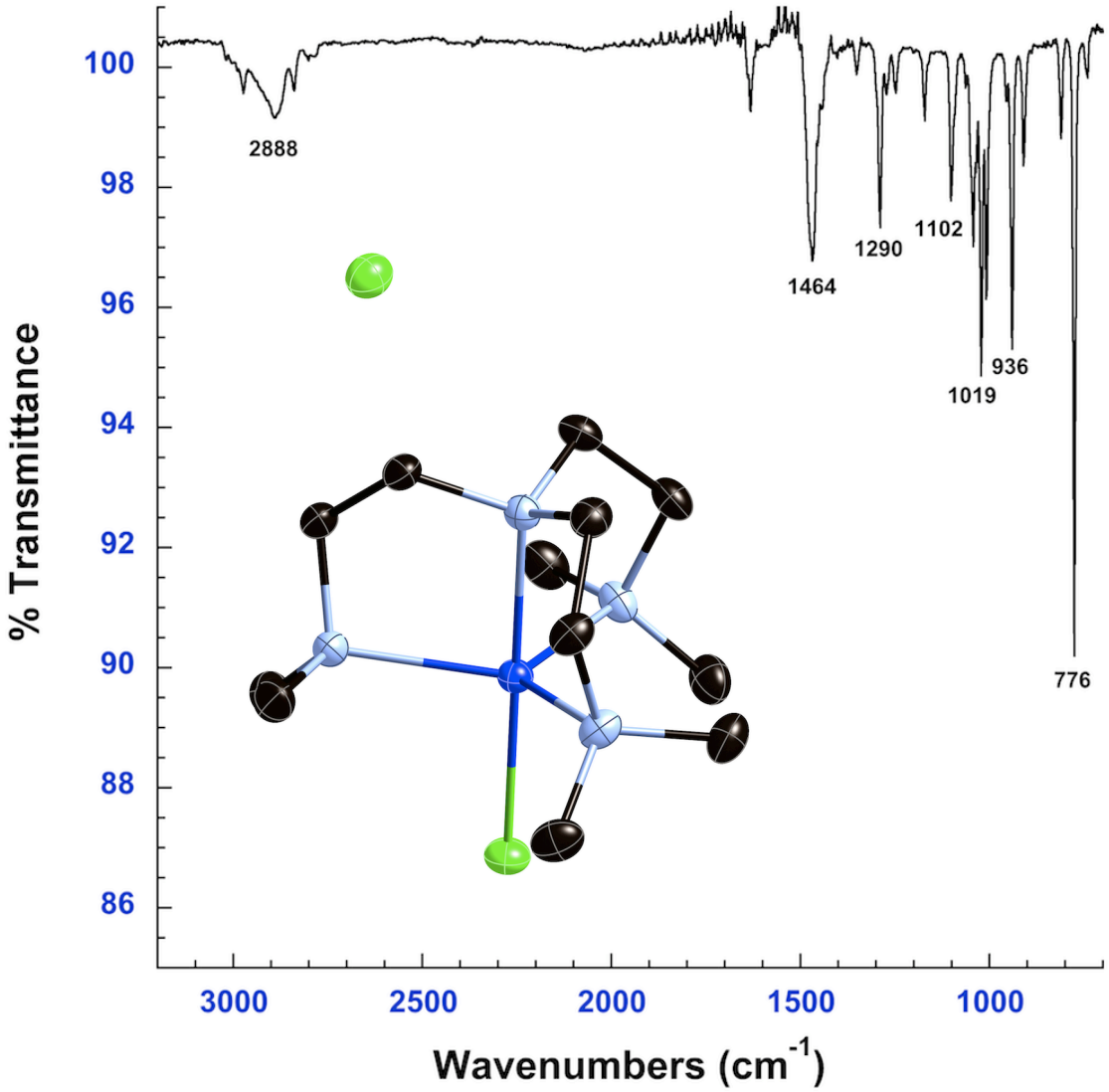


Figure S4. ATR FT-IR spectrum of $[Cu^{II}(Me_6TREN)Cl][Cl]$ (**1**).

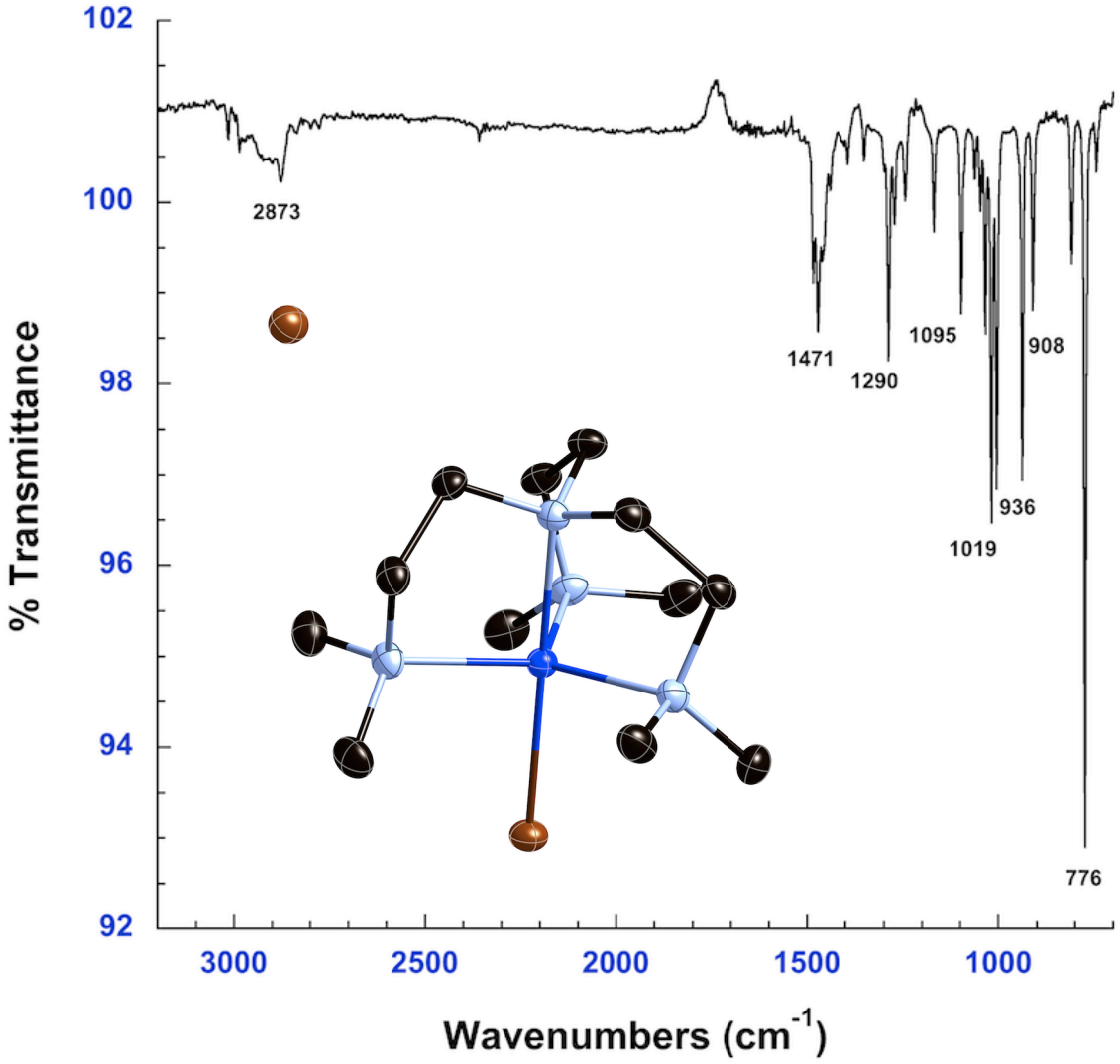


Figure S5. ATR FT-IR spectrum of [Cu^{II}(Me_6TREN)Br][Br] (**2**).

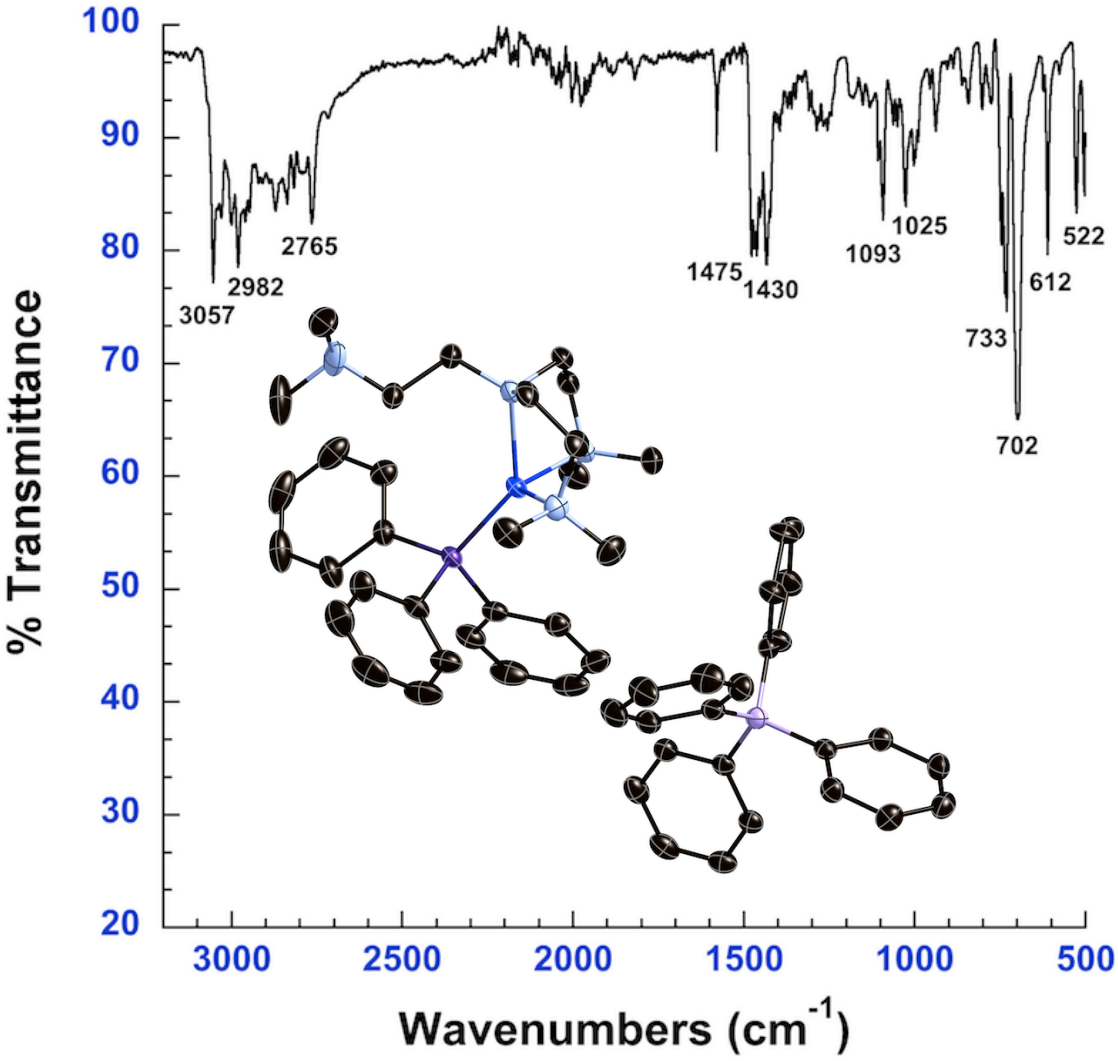


Figure S6. ATR FT-IR spectrum of $[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ (**3**).

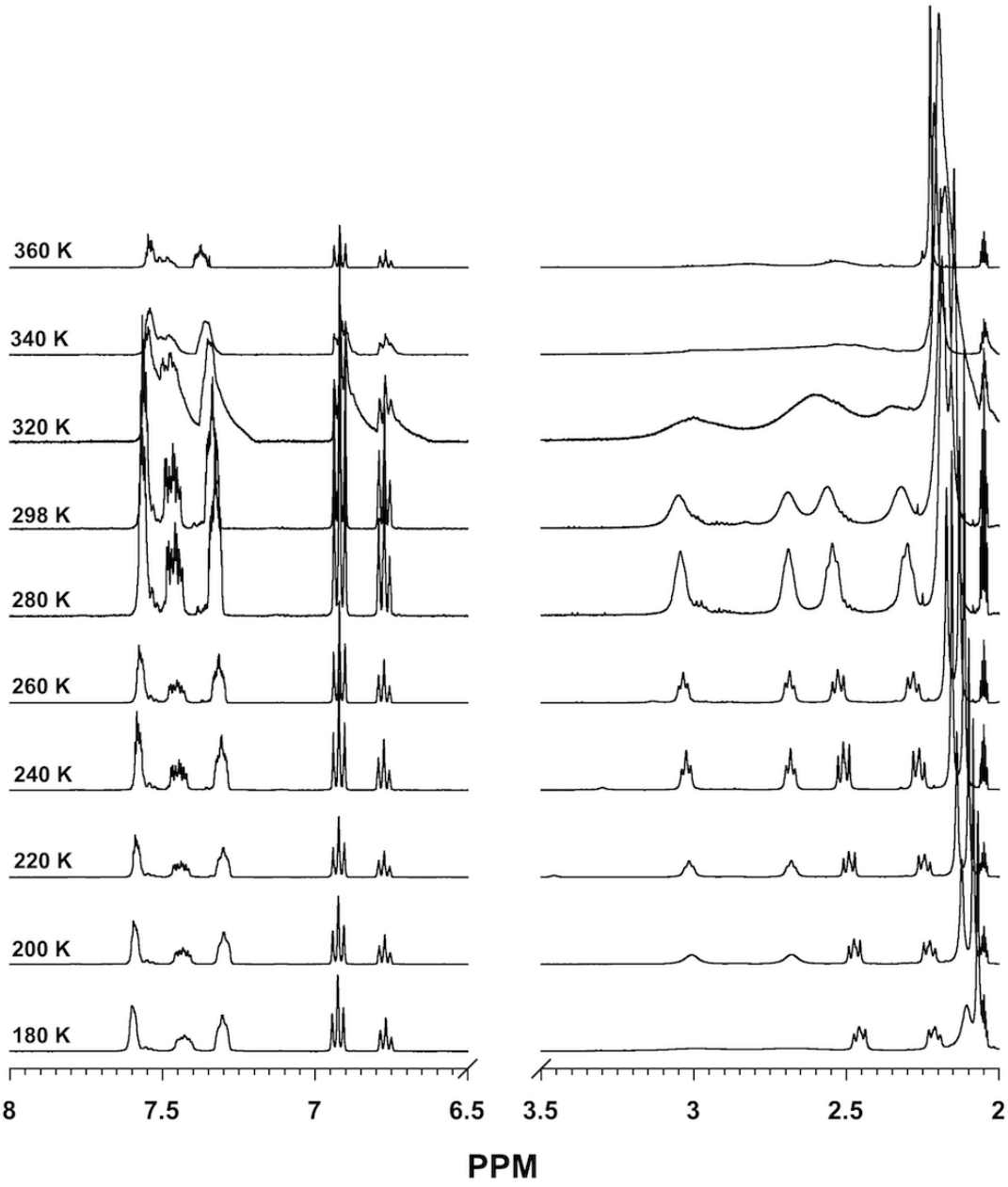


Figure S7. ^{1}H NMR (400 MHz, acetone-d_6) spectrum of $[Cu^{I}(Me_6TREN)PPh_3][BPh_4]$ with one equivalent of Me_6TREN. $[Cu^{I}]_0$=23.0 mM

Table S4. Crystallographic and experimental data for 1S-Chloro-4S-(trichloromethyl)cyclooctane and 1S-Bromo-4S-(trichloromethyl)cyclooctane.

	1S-Cl-4S-(CCl_3)cyclooctane	**1S-Br-4S-(CCl_3)cyclooctane**
Formula	$C_9 H_{14} Cl_4$	$C_9 H_{14} Br Cl_3$
Color/Shape	colorless/rhomboid	colorless/rhomboid
Formula Weight	264.00	308.46
Crystal System	triclinic	triclinic
Space Group	P -1	P -1
Temp (K)	150K	150K
Cell Constants		
***a*, Å**	7.3804(2)	7.5398(5)
***b*, Å**	8.8401(2)	8.8709(6)
***c*, Å**	9.3662(2)	9.3096(7)
a, deg	88.6140(10)	89.5290(10)
b, deg	77.9500(10)	78.3550(10)
g, deg	71.8860(10)	71.4070(10)
V, Å^3	567.46(2)	576.97(7)
Formula units/unit cell	2	2
D cal'd, gcm^{-3}	1.545	1.776
μ, mm^{-1}	0.995	4.21
F(000)	272	308
Diffractometer	Bruker Smart ApexII	Bruker Smart ApexII
Radiation, graphite monochr.	Mo Kα (γ=0.71073 Å)	Mo Kα (γ=0.71073 Å)
Crystal size, mm	0.43 x 0.34 x 0.30	0.27 x 0.22 x 0.10
θ range, deg	2.43 < θ < 32.61	2.24 < θ < 32.53
Range of *h,k,l*	±11, ±13, ±14	±11, -13 12, ±13
Reflections collected/unique	10120/3836	7425/3815
R_{int}	0.0291	0.0148
Refinement Method	Full Matrix Least-Squares on F2	Full Matrix Least-Squares on F2
Data/Restraints/Parameters	3836/0/119	3815/0/118
GOF on F^2	0.777	0.835
Final R indices [I>2σ(I)]	R1=0.0448 wR2=0.1097	R1=0.0376 wR2=0.1186
R indices (all data)	R1=0.0468 wR2=0.1125	R1=0.0480 wR2=0.1282
Max. Resid. Peaks (e*Å^{-3})	0.930 and -0.903	2.186 and -1.098

Table S5. Crystallographic and experimental data for 1R-Bromo-4R-(tribromomethyl)cyclooctane and 1S-Bromo-4R-(tribromomethyl)cyclooctane

	1R-Br-4R-(CBr_3)cyclooctane	**1S-Br-4R-(CBr_3)cyclooctane**
Formula	$C_9 H_{14} Br_4$	$C_9 H_{14} Br_4$
Color/Shape	colorless/rhomboid	colorless/rhomboid
Formula Weight	441.84	441.84
Crystal System	triclinic	triclinic
Space Group	P -1	P -1
Temp (K)	150K	150K
Cell Constants		
***a*, Å**	7.624(6)	7.32690(10)
***b*, Å**	8.962(7)	9.28220(10)
***c*, Å**	9.546(8)	9.4153(2)
a, deg	88.646(12)	100.6100(10)
b, deg	78.322(11)	92.6440(10)
g, deg	72.257(10)	98.7340(10)
V, Å^3	607.8(9)	620.274(17)
Formula units/unit cell	2	2
Dcal'd, gcm^{-3}	2.414	2.366
μ, mm^{-1}	13.199	12.934
F(000)	416	416
Diffractometer	Bruker Smart ApexII	Bruker Smart ApexII
Radiation, graphite monochr.	Mo Kα (γ=0.71073 Å)	Mo Kα (γ=0.71073 Å)
Crystal size, mm	0.21 x 0.20 x 0.11	0.21 x 0.17 x 0.09
θ range, deg	2.18 < θ < 24.48	2.21 < θ < 32.40
Range of *h,k,l*	±8, ±10, ±11	-11→10, ±13, ±14
Reflections collected/unique	4380/1992	10939/4102
R_{int}	0.043	0.0183
Refinement Method	Full Matrix Least-Squares on F2	Full Matrix Least-Squares on F2
Data/Restraints/Parameters	1992/0/118	4102/0/118
GOF on F^2	0.827	0.654
Final R indices [I>2σ(I)]	R1=0.0403 wR2=0.1101	R1=0.0214 wR2=0.0746
R indices (all data)	R1=0.0525 wR2=0.1187	R1=0.0304 wR2=0.0843
Max. Resid. Peaks (e*Å^{-3})	1.137 and -1.311	1.020 and -0.682

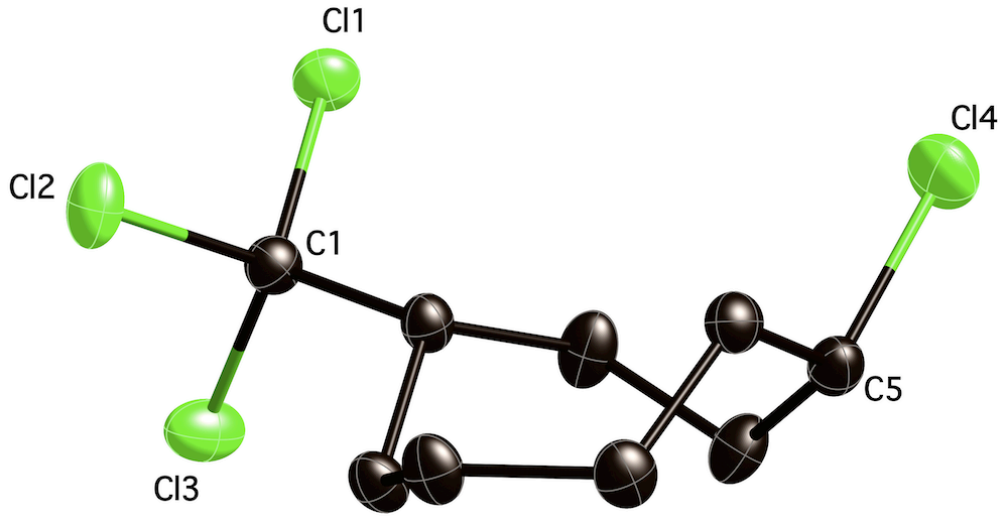


Figure S8. Molecular structure of 1*S*-chloro-4*S*-(trichloromethyl)cyclooctane collected at 150 K, shown with 50% probability displacement ellipsoids. H-atoms have been omitted for clarity. Selected bond distances [Å]: Cl1-C1 1.7873(12), Cl2-C1 1.7790(12), Cl3-C1 1.7835(12), Cl4-C5 1.8185(13).

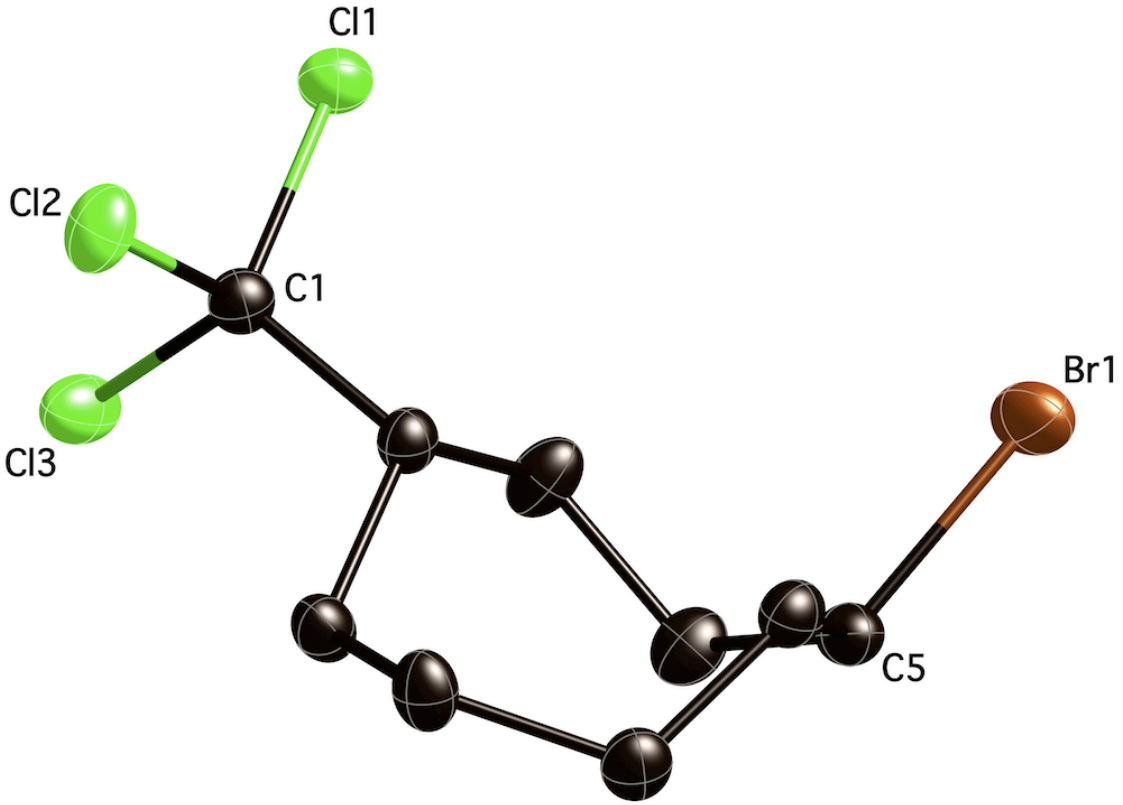


Figure S9. Molecular structure of 1*S*-Bromo-4*S*-(trichloromethyl)cyclooctane collected at 150 K, shown with 50% probability displacement ellipsoids. H-atoms have been omitted for clarity. Selected bond distances [Å]: Br1-C5 1.986(3), Cl2-C1 1.790(3), Cl3-C1 1.788(3), Cl4-C1 1.785(2).

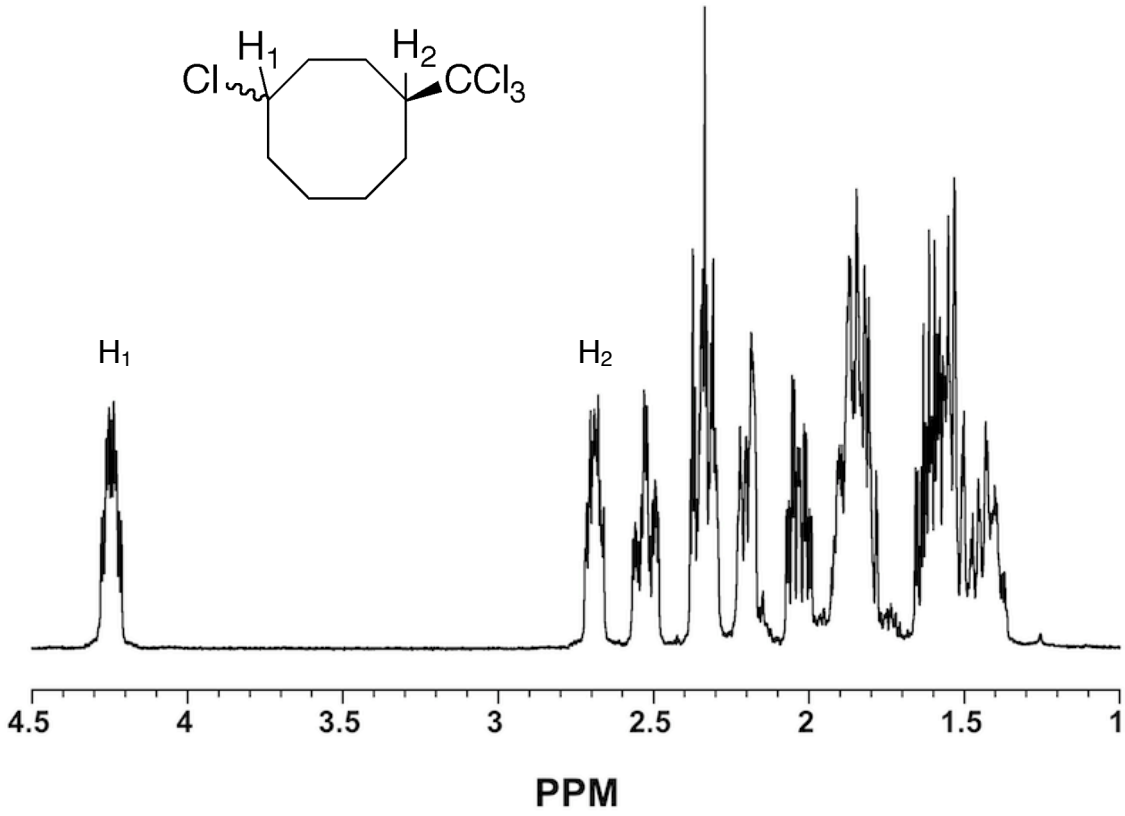


Figure S10. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of *rac*-1-chloro-4-(trichloromethyl)cyclooctane. Both enantiomers were found to have identical ^{1}H NMR spectra.

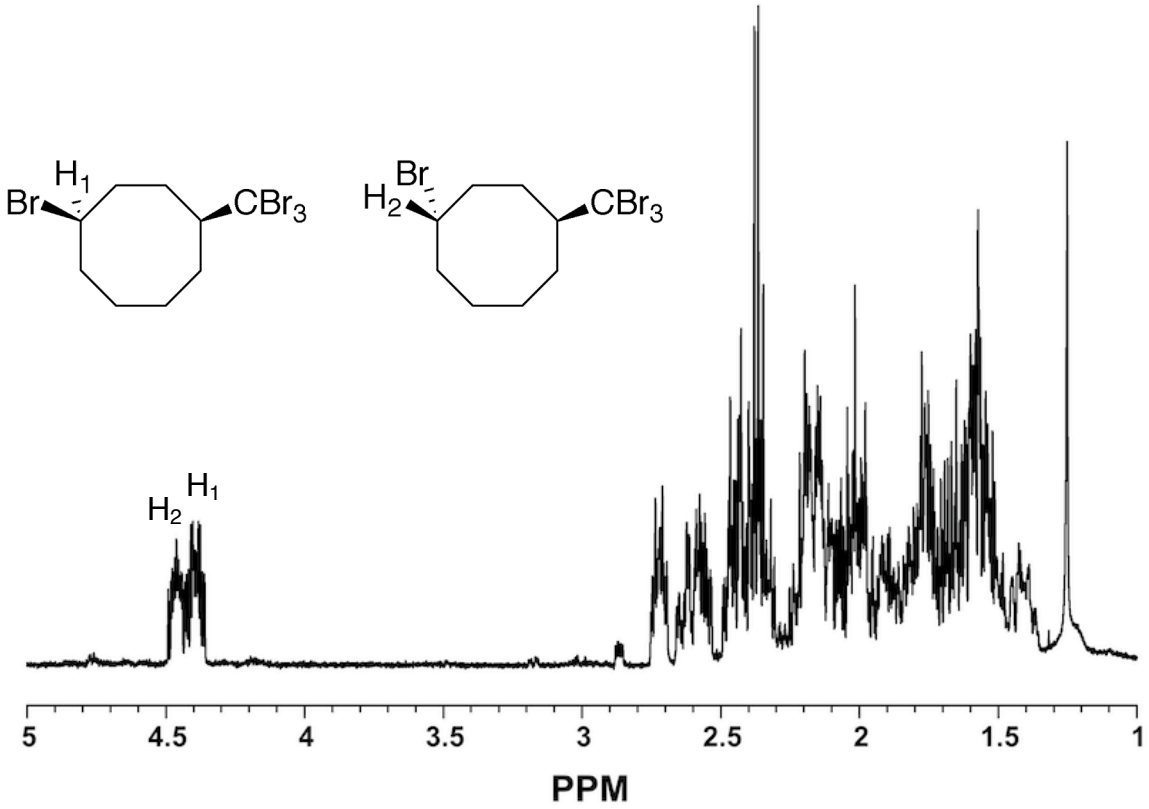


Figure S11. ^{1}H NMR (400 MHz, 298K, $CDCl_3$) of *rac*-1-bromo-4-(tribromomethyl)cyclooctane. H1 and H2 proton assignments were determined by further isolation of products.

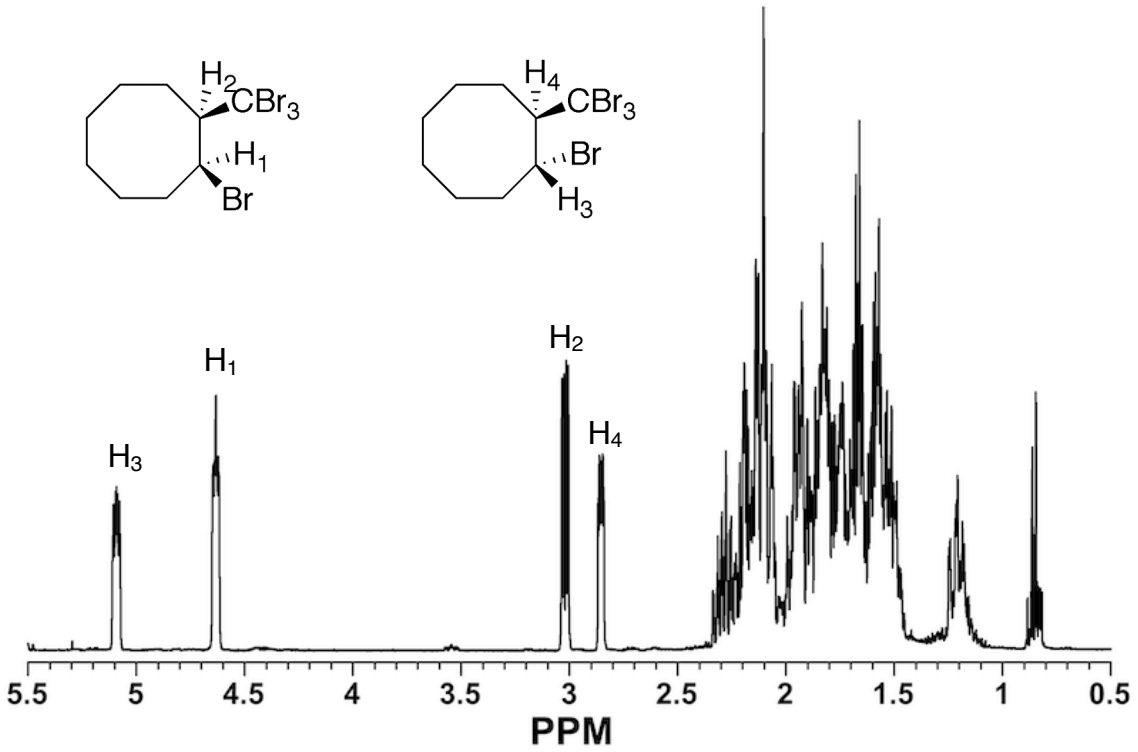


Figure S12. ^{1}H NMR (400 MHz, 298K, $CDCl_3$) of *rac*-1-bromo-2-(tribromomethyl)cyclooctane. H1-H4 proton assignments were determined using ^{1}H NOESY and ^{1}H COSY NMR.

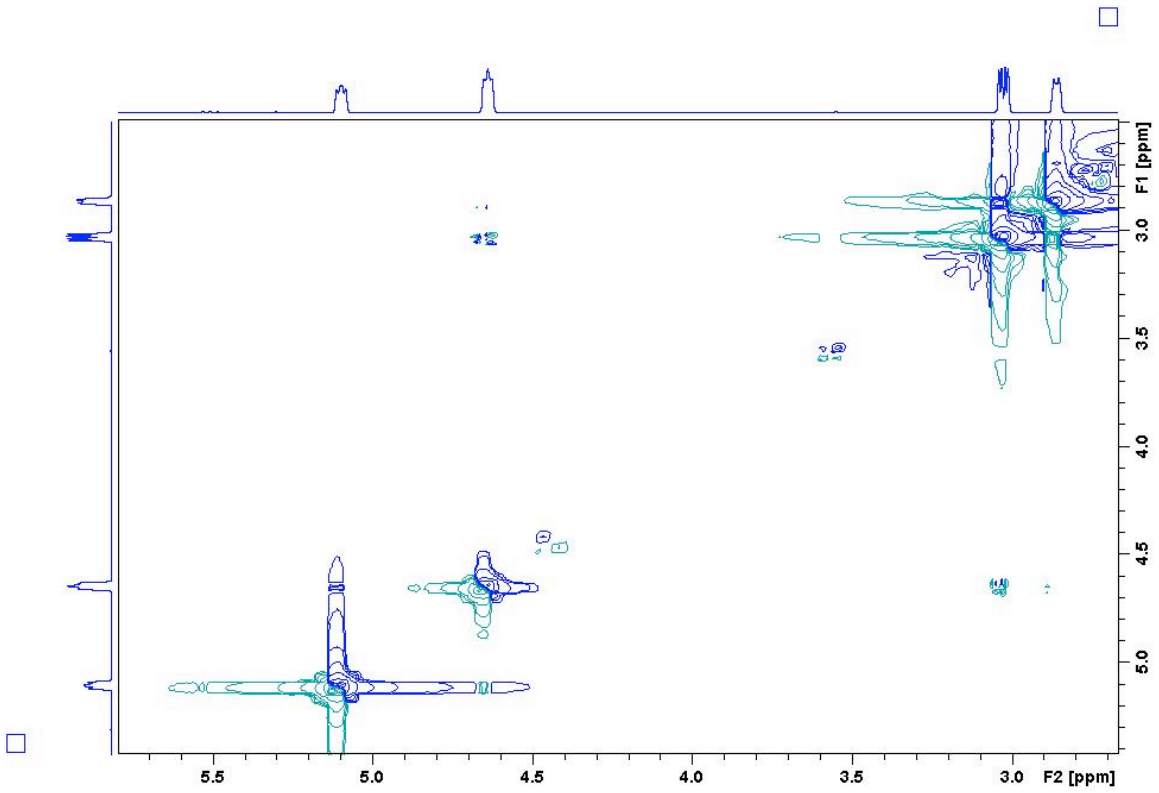


Figure S13. ^{1}H COSY NMR (400 MHz, 298K, $CDCl_3$) spectrum of *rac*-1-bromo-2-(tribromomethyl)cyclooctane

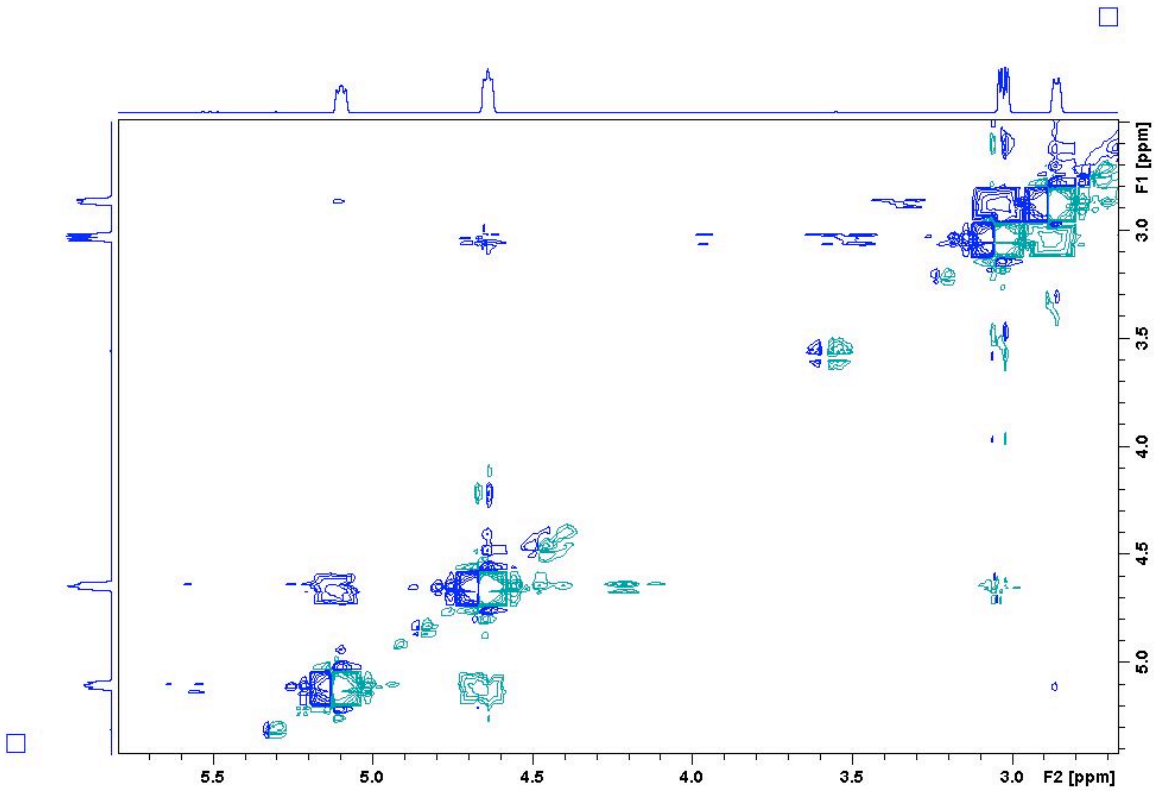


Figure S14. ^{1}H NOESY NMR (400 MHz, 298K, $CDCl_3$) spectrum of *rac*-1-bromo-2-(tribromomethyl)cyclooctane.

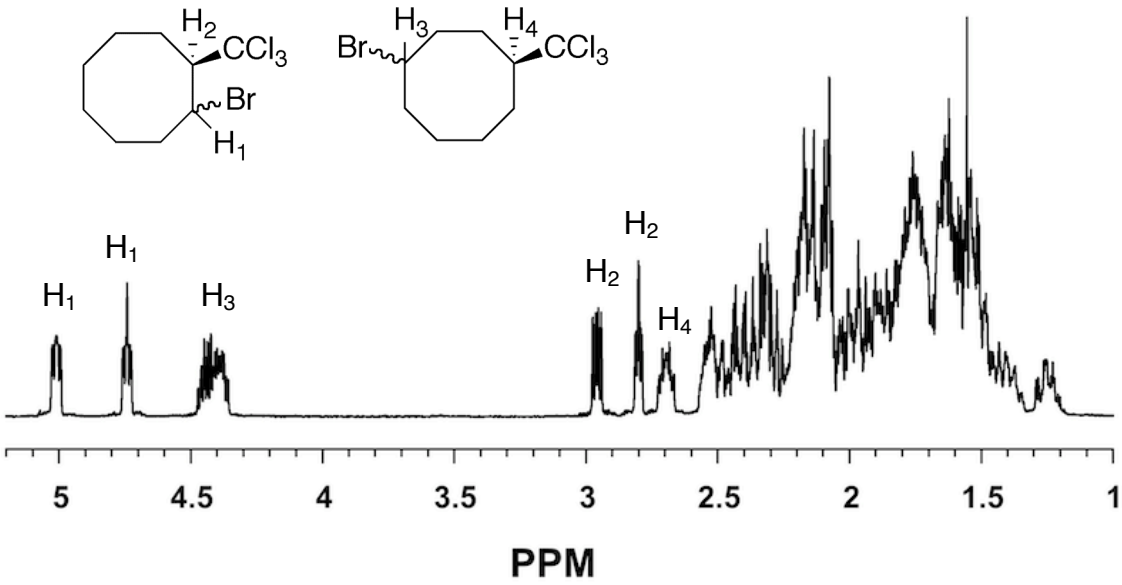


Figure S15. ^{1}H NMR (400 MHz, 298K, $CDCl_3$) spectra of *rac*-1-bromo-2-(trichloromethyl)cyclooctane and *rac*-1-bromo-4-(trichloromethyl)cyclooctane. Peak assignments were further confirmed by crystallization of 1,4-isomer.

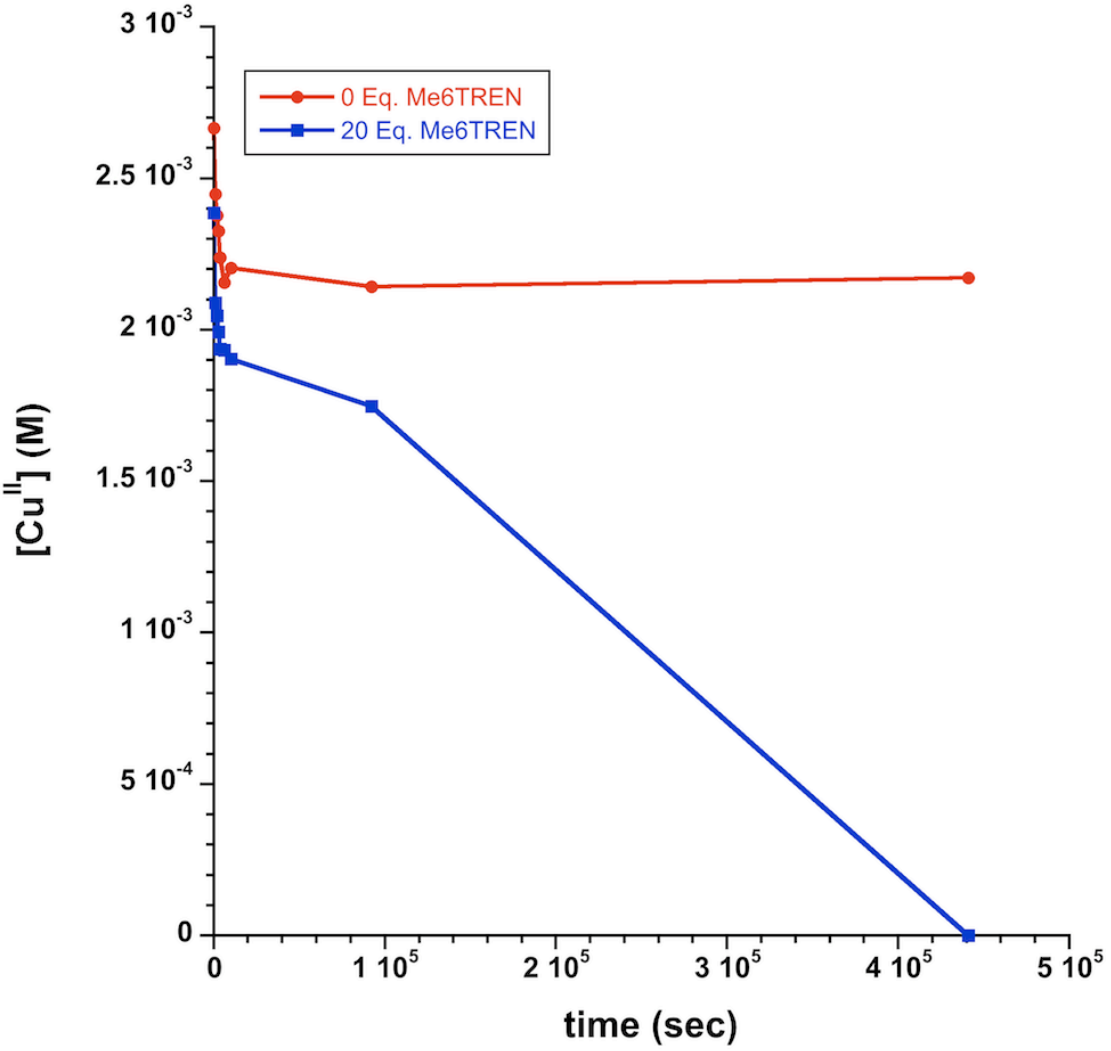


Figure S19. Effect of Me_6TREN on the reduction of $[Cu^{II}(Me_6TREN)Cl][Cl]$ by radicals generated from thermal decomposition of AIBN in CH_3CN at 60 ^oC. Absorbance of copper(II) complex was monitored at 938 nm, $[Cu]_0$:$[AIBN]_0$=1:10, $[Cu^{II}]_0$=2.0 mM.

Table S6. Crystallographic and experimental data 4-(2-(dimethylammonio)ethyl)-1,1-dimethylpiperazinium chloride.

	4-(2-(dimethylammonio)ethyl)-1,1-dimethylpiperazinium chloride
Formula	C10 H25 Cl2 N3
Color	colorless
Shape	plate
Formula Weight	258.23
Crystal System	Orthorhombic
Space Group	P c a 21
Temp (K)	150K
Cell Constants	
***a*, Å**	11.5195(6)
***b*, Å**	6.2653(3)
***c*, Å**	19.3532(9)
a, deg	90
b, deg	90
g, deg	90
V, Å^3	1396.78(12)
Formula units/unit cell	4
Dcal'd, gcm^{-3}	1.228
μ, mm^{-1}	0.443
F(000)	560
Diffractometer	Bruker Smart ApexII
Radiation, graphite monochr.	Mo Kα (λ=0.71073 Å)
Crystal size, mm	0.53 x 0.23 x 0.09
θ range, deg	3.25 < θ < 31.88
Range of *h,k,l*	±16, ±9, ±28
Reflections collected/unique	22975/4710
R_{int}	0.0312
Refinement Method	Full Matrix Least-Squares on F2
Data/Restraints/Parameters	4710/1/144
GOF on F^2	1.019
Final R indices [I>2σ(I)]	R1=0.0459 wR2=0.1240
R indices (all data)	R1=0.0530 wR2=0.1311
Max. Resid. Peaks (e*Å^{-3})	0.883 and -0.257

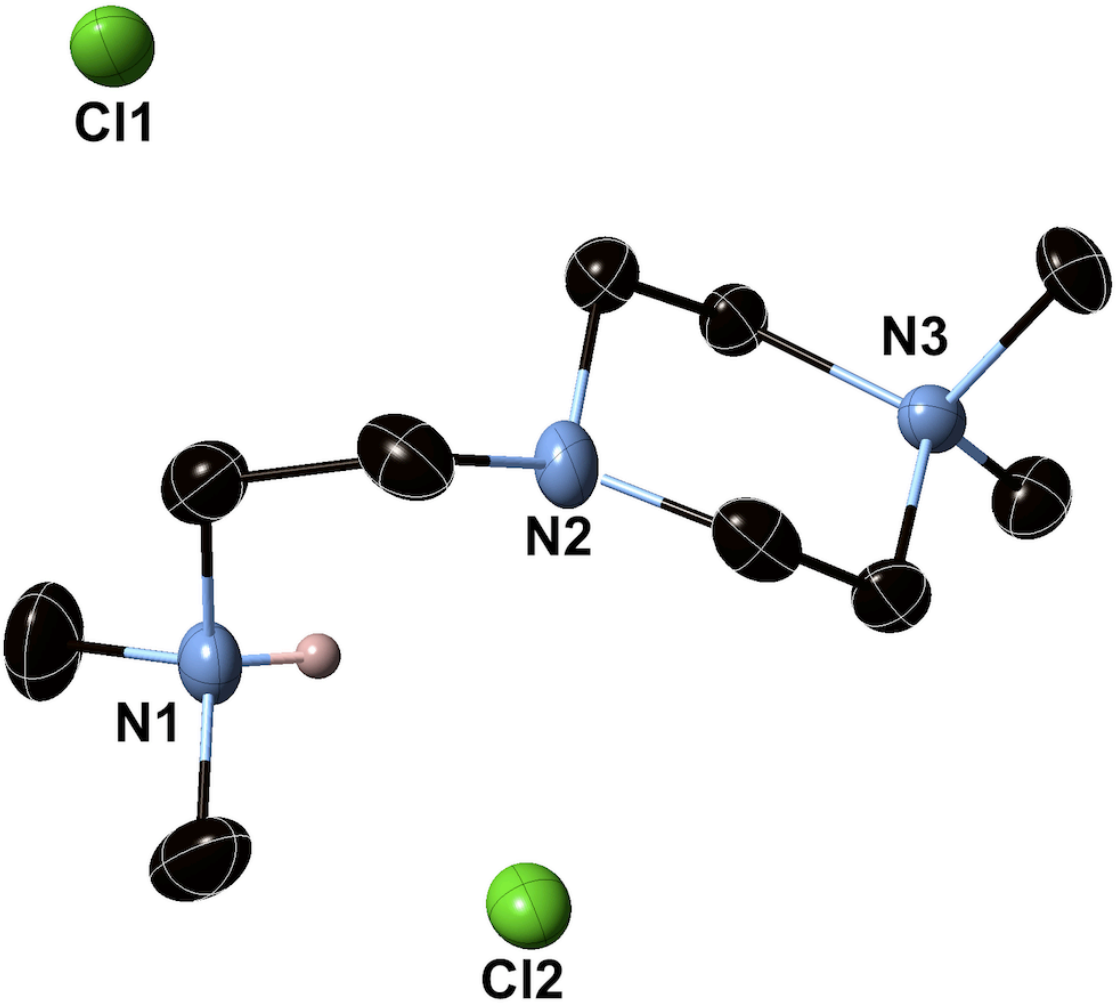


Figure S20. Molecular structure of 4-(2-(dimethylammonio)ethyl)-1,1-dimethyl-piperazinium chloride shown with 50% probability ellipsoids. Data were collected at 150K and most H-atoms omitted for clarity. Crystals were obtained from ATRA reaction mixture in the presence of 21 equivalents of free Me_6TREN ligand.

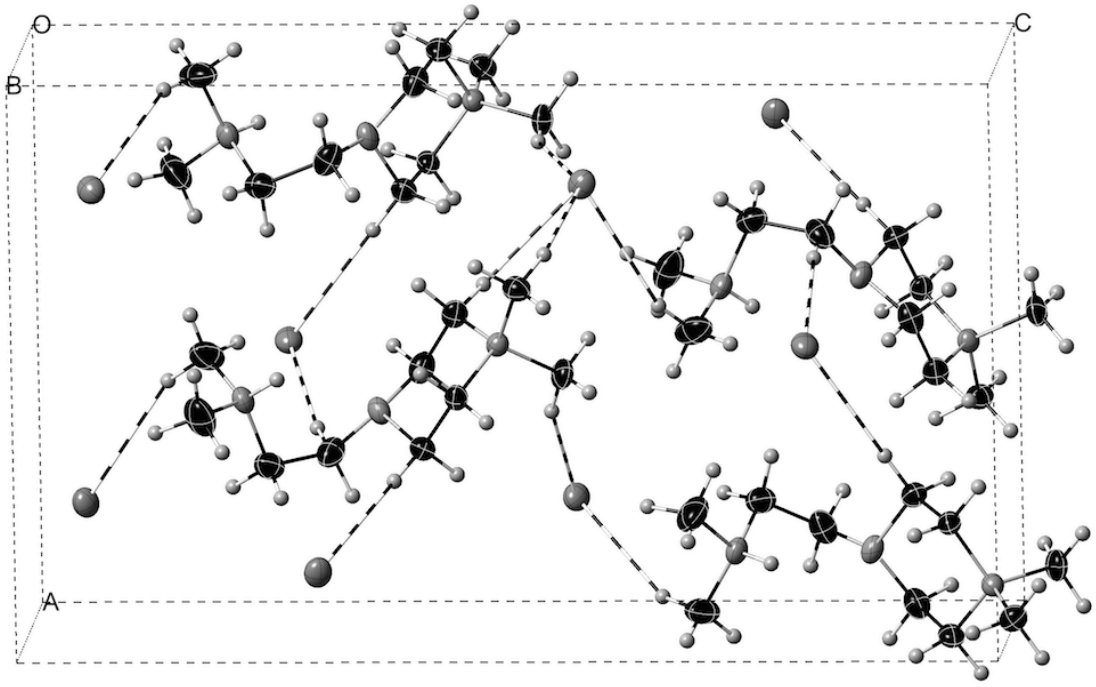
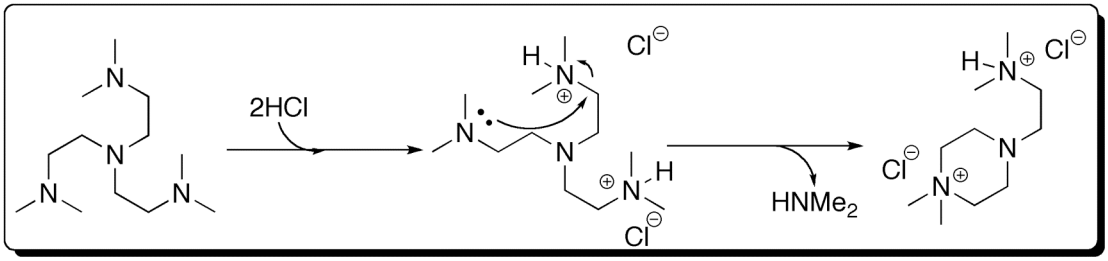


Figure S21. Crystal packing diagram of 4-(2-(dimethylammonio)ethyl)-1,1-dimethyl-piperazinium chloride showing weak Cl---H-C interactions between 2.512(6) and 2.930(6) Å.



Scheme S22. Proposed mechanism for the formation of 4-(2-(dimethylammonio)ethyl)-1,1-dimethyl-piperazinium chloride.