Supporting Information

Copper (II) Complexes of Quinoline-based Ligands for Efficient Photoredox Catalysis of Atom Transfer Radical Addition (ATRA) Reaction

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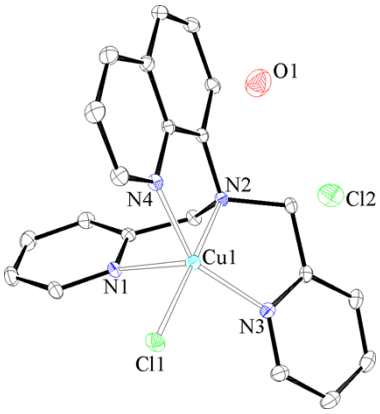
X-Ray Crystallography

Crystal data and structure refinement for all the complexes.

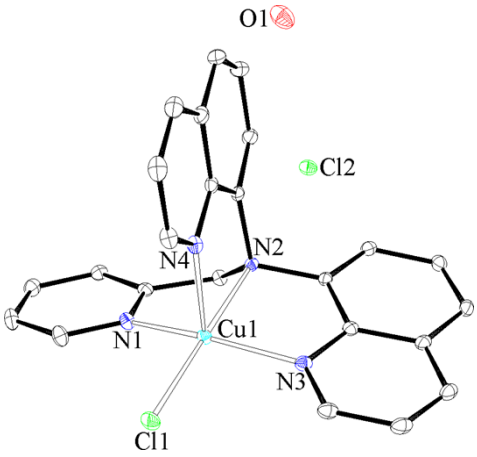
Identification code	[Cu^{II}(**1Q**)Cl]Cl	[Cu^{II}(**2Q**)Cl]Cl	[Cu^{II}(**3Q**)Cl][$CuCl_4$]
Empirical formula	$C_{21}H_{20}Cl_2CuN_4O$	$C_{48}H_{40}Cl_4Cu_2N_8O_2$	$C_{54}H_{36}Cl_6Cu_3N_8$
Formula weight	478.85	1029.76	1200.23
Temperature/K	296	100	296
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a/Å	16.6661(8)	13.3798(14)	13.9396(18)
b/Å	9.3649(5)	24.690(3)	15.824(2)
c/Å	14.0474(8)	14.1358(14)	16.096(2)
α/°	90	90	111.357(4)
β/°	109.943(2)	108.542(2)	98.835(4)
γ/°	90	90	115.205(4)
Volume/$Å^3$	2060.99(19)	4427.3(8)	2783.9(6)
Z	4	4	2
$\rho_{calc}g/cm^3$	1.543	1.545	1.432
μ/mm^{-1}	1.339	3.816	1.466
F (000)	980.0	2104.0	1210.0
Crystal size/mm^3	0.38 × 0.34 × 0.3	0.26 × 0.26 × 0.21	0.34 × 0.32 × 0.19
Radiation	MoKα (λ = 0.71073 Å)	CuKα (λ = 1.54178 Å)	MoKα (λ = 0.71073 Å)
2Θ range for data collection/°	6.378 to 56.656	7.506 to 144.96	5.842 to 57.642
Reflections collected	40421	52938	76310
Independent reflections	5132	8704	14494
R_{int}, R_{sigma}	0.0556, 0.0309	0.0308, 0.0209	0.0475, 0.0353
Data/restraints/parameters	5132/0/265	8704/0/583	14494/92/686
Goodness-of-fit on F^2	1.035	1.036	1.028
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0317, 0.0725	0.0248, 0.0659	0.0420, 0.1124
R_1, wR_2 [all data]	0.0441, 0.0776	0.0257, 0.0666	0.0631, 0.1251
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.39	0.37/-0.49	0.66/-0.63

Fig. S1. Ellipsoid plots of (a) [Cu^{II}(**1Q**)Cl]Cl, (b) [Cu^{II}(**2Q**)Cl]Cl and (c) [Cu^{II}(**3Q**)Cl][$CuCl_4$] complexes.

(a)



(b)



(c)

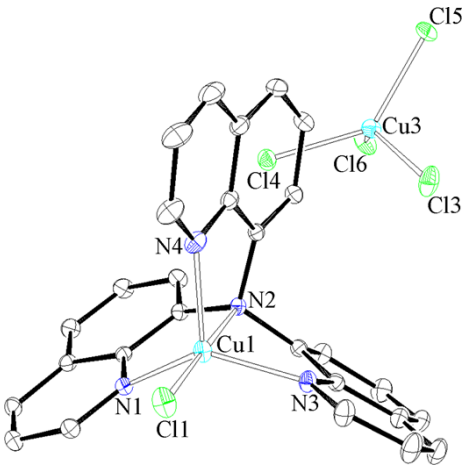


Table S1 Comparison of selected bong lengths (Å) and bond angles (°).

Complex	Cu^{II}•**TPMA**[a]	Cu^{II}•**1Q**	Cu^{II}•**2Q**	Cu^{II}•**3Q**
Cu−N1	2.0759	1.9986	2.0016	2.0960
Cu−N2	2.0481	2.0676	2.1034	2.1092
Cu−N3	2.0759	1.9954	1.9981	2.0160
Cu−N4	2.0759	2.2738	2.1361	2.0750
Cu−Cl	2.2369	2.2540	2.2573	2.2154
N1−Cu−N2	80.71	81.30	81.02	82.00
N1−Cu−N3	80.71	150.36	152.77	79.40
N1−Cu−N4	80.71	94.17	101.16	81.80
N2−Cu−N3	117.45	83.77	83.62	103.8
N3 −Cu−N4	117.45	107.66	98.70	130.6
N4 −Cu−N2	117.45	78.55	81.71	118.10
Cl−Cu−N1	99.29	97.68	97.43	98.24
Cl−Cu−N2	180.00	175.12	177.36	176.65
Cl−Cu−N3	99.29	99.19	96.97	98.25
Cl−Cu−N4	99.29	97.31	100.73	100.91

[a]Data obtained from W. T. Eckenhoff and T. Pintauer, *Inorg. Chem.*, 2007, **46**, 5844-5846.

Table S2 Bond lengths (Å) and bond angles (°) for all the complexes

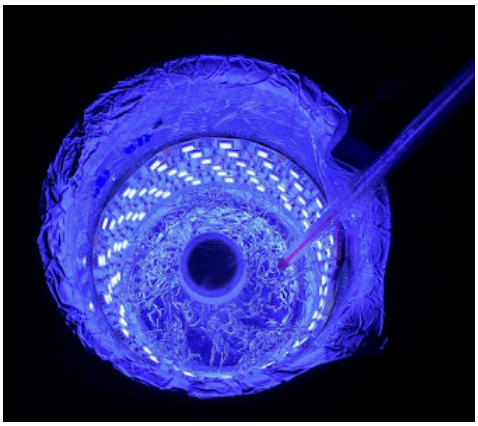
[Cu^{II}(**1Q**)Cl]Cl			
Cu1–Cl1	2.2540 (5)	Cu1–N3	1.9954 (15)
Cu1–N1	1.9986 (15)	Cu1–N4	2.2738 (15)
Cu1–N2	2.0676 (13)		
Cl1–Cu1–N4	97.31 (4)	N2–Cu1–N4	78.55 (5)
N1–Cu1–Cl1	97.68 (5)	N3–Cu1–Cl1	99.19 (4)
N1–Cu1–N2	81.30 (6)	N3–Cu1–N1	150.36 (6)
N1–Cu1–N4	107.66 (6)	N3–Cu1–N2	83.77 (6)
N2–Cu1–Cl1	175.12 (4)	N3–Cu1–N4	94.17 (6)
[Cu^{II}(**2Q**)Cl]Cl			
Cu1–Cl1	2.2573 (4)	Cu2–Cl2	2.2385 (4)
Cu1–N1	2.0016 (12)	Cu2–N5	1.9947 (13)
Cu1–N2	2.1034 (12)	Cu2–N6	2.1222 (12)
Cu1–N3	1.9981 (13)	Cu2–N7	1.9944 (12)
Cu1–N4	2.1361 (13)	Cu2–N8	2.1445 (12)
N1–Cu1–Cl1	97.43 (4)	N5–Cu2–Cl2	96.16 (4)
N1–Cu1–N2	81.02 (5)	N5–Cu2–N6	81.19 (5)
N1–Cu1–N4	101.16 (5)	N5–Cu2–N8	100.17 (5)
N2–Cu1–Cl1	177.36 (3)	N6–Cu2–Cl2	171.05 (3)
N2–Cu1–N4	81.71 (5)	N6–Cu2–N8	81.32 (5)
N3–Cu1–Cl1	96.97 (4)	N7–Cu2–Cl2	96.75 (4)
N3–Cu1–N1	152.77 (5)	N7–Cu2–N5	156.39 (5)
N3–Cu1–N2	83.62 (5)	N7–Cu2–N6	83.01 (5)
N3–Cu1–N4	98.70 (5)	N7–Cu2–N8	94.65 (5)
N4–Cu1–Cl1	100.73 (4)	N8–Cu2–Cl2	107.59 (4)
[Cu^{II}(**3Q**)Cl][CuCl$_4$]			
Cu1–Cl1	2.2154 (8)	Cu2–N8	2.077 (2)
Cu1–N1	2.096 (2)	Cu3–Cl3	2.2371 (18)
Cu1–N2	2.1092 (19)	Cu3–Cl4	2.271 (2)
Cu1–N3	2.016 (2)	Cu3–Cl5	2.2720 (18)
Cu1–N4	2.075 (2)	Cu3–Cl6	2.2383 (17)
Cu2–Cl2	2.2267 (8)	Cu3A–Cl3A	2.248 (11)
Cu2–N5	1.997 (2)	Cu3A–Cl4A	2.398 (13)
Cu2–N6	2.1279 (19)	Cu3A–Cl5A	2.144 (8)
Cu2–N7	2.034 (2)	Cu3A–Cl6A	2.138 (9)
N1–Cu1–Cl1	98.24 (6)	N7–Cu2–N6	81.14 (8)
N1–Cu1–N2	79.36 (8)	N7–Cu2–N8	108.40 (10)
N2–Cu1–Cl1	176.65 (6)	N8–Cu2–Cl2	99.07 (7)
N3–Cu1–Cl1	98.25 (7)	N8–Cu2–N6	81.69 (8)
N3–Cu1–N1	130.61 (9)	Cl3–Cu3–Cl4	100.96 (10)
N3–Cu1–N2	81.71 (8)	Cl3–Cu3–Cl5	99.01 (8)
N3–Cu1–N4	118.15 (9)	Cl3–Cu3–Cl6	133.06 (9)
N4–Cu1–Cl1	100.91 (6)	Cl4–Cu3–Cl5	134.81 (11)
N4–Cu1–N1	103.76 (8)	Cl6–Cu3–Cl4	97.80 (10)
N4–Cu1–N2	81.99 (8)	Cl6–Cu3–Cl5	97.37 (8)
N5–Cu2–Cl2	97.15 (6)	Cl3A–Cu3A–Cl4A	93.6 (6)

N5−Cu2−N6	82.69 (8)	Cl5A−Cu3A−Cl3A	99.7 (4)
N5−Cu2−N7	130.76 (9)	Cl5A−Cu3A−Cl4A	126.3 (7)
N5−Cu2−N8	114.77 (9)	Cl6A−Cu3A−Cl3A	145.4 (5)
N6−Cu2−Cl2	179.21 (6)	Cl6A−Cu3A−Cl4A	91.3 (6)
N7−Cu2−Cl2	98.41 (6)	Cl6A−Cu3A−Cl5A	104.8 (4)

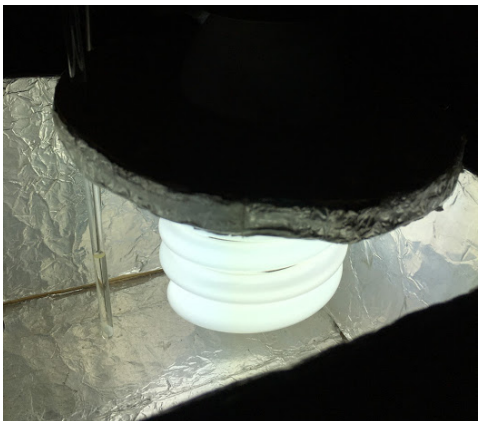
Apparatus for ATRA reaction

Fig. S2. In-house made photoreactor equipped with (a) white LEDs (b) CFL light bulb (c) emission spectra of white CFL (blue) and white LEDs (yellow) lines

(a)



(b)



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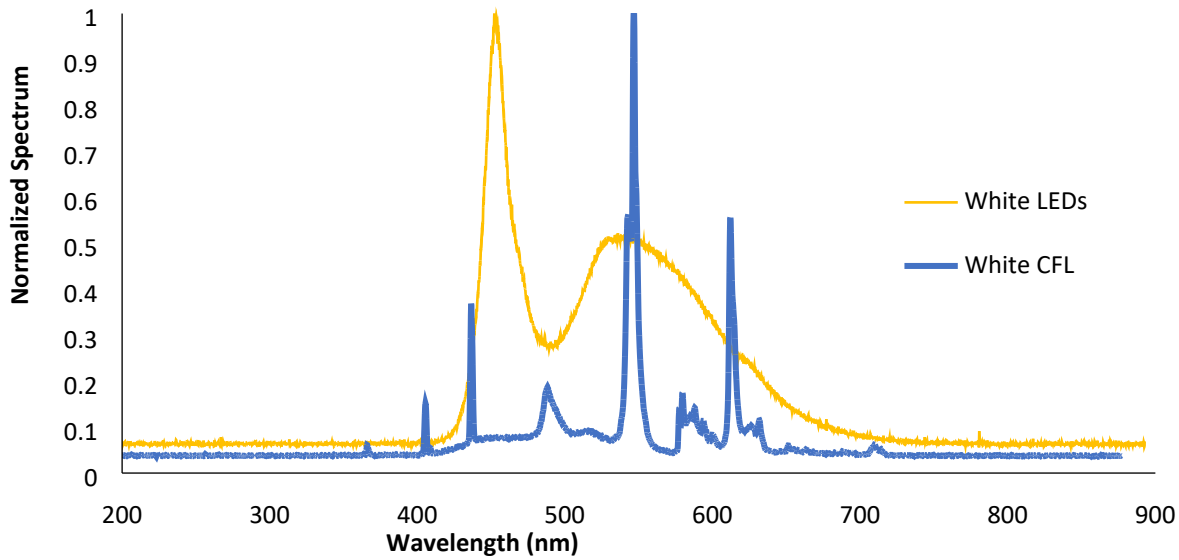


Photophysical properties

Table S3 Summary of photophysical data and energy gap calculation for ligand and Cu-ligand complexes.

	Ligand			Cu (II)•Ligand				Cu (I)•Ligand	
	λ_{abs}	ε [m^2/mol]	λ_{em}	λ_{abs}	ε [m^2/mol]	λ_{onset}	E_{gap}	λ_{onset}	E_{gap}
TPMA	257	8611	426	295	2858	510	2.43	578	2.15
1Q	346	3703	464	291	5457	520	2.38	603	2.06
2Q	365	6151	511	292	6704	545	2.28	640	1.94
3Q	382	8878	518	294	7321	600	2.07	756	1.64

The energy gaps (E_{gap}) were determined by using the onset of the longest wavelength absorption (λ_{onset}).

Cyclic voltammetry

Fig. S3. Cyclic voltammogram of Cu(II)-ligand complexes at 1.0 mM in CH_3CN Vs ferrocene

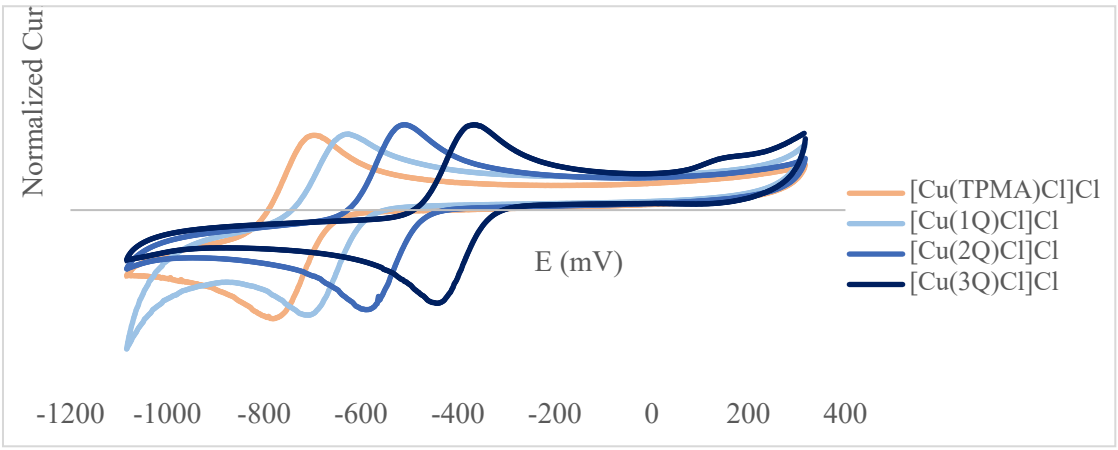


Table S4 Summary of electrochemical data for Cu-ligand complexes

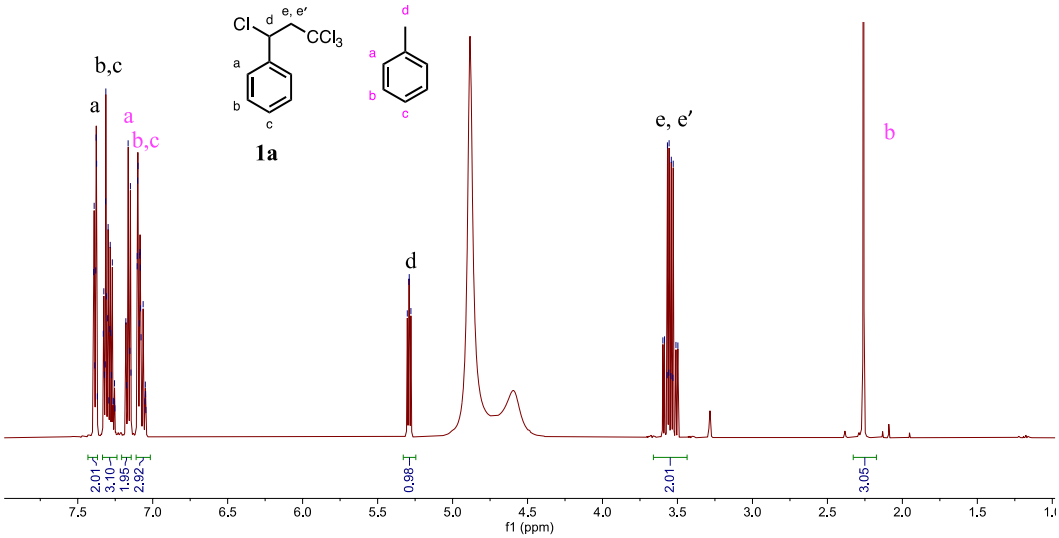
Complex	$E_{1/2}(Cu^{2+}L)$ [V]	ΔE_p [mV]	i_{pa}/i_{pc}
$CuCl_2$/**TPMA**	-0.738	73	0.99
$CuCl_2$/**1Q**	-0.669	71	0.94
$CuCl_2$/**2Q**	-0.551	88	0.90
$CuCl_2$/**3Q**	-0.407	76	1.00

Complex solutions (1.0 mM) of $CuCl_2$ and ligand (**TPMA**, **1Q**, **2Q**, and **3Q**) were prepared in CH_3CN containing 0.10 M NBu_4PF_6 as supporting electrolyte at a scanning rate (v) of 100 mV/s. Potentials were measured relative to a ferrocenium/ferrocene couple.

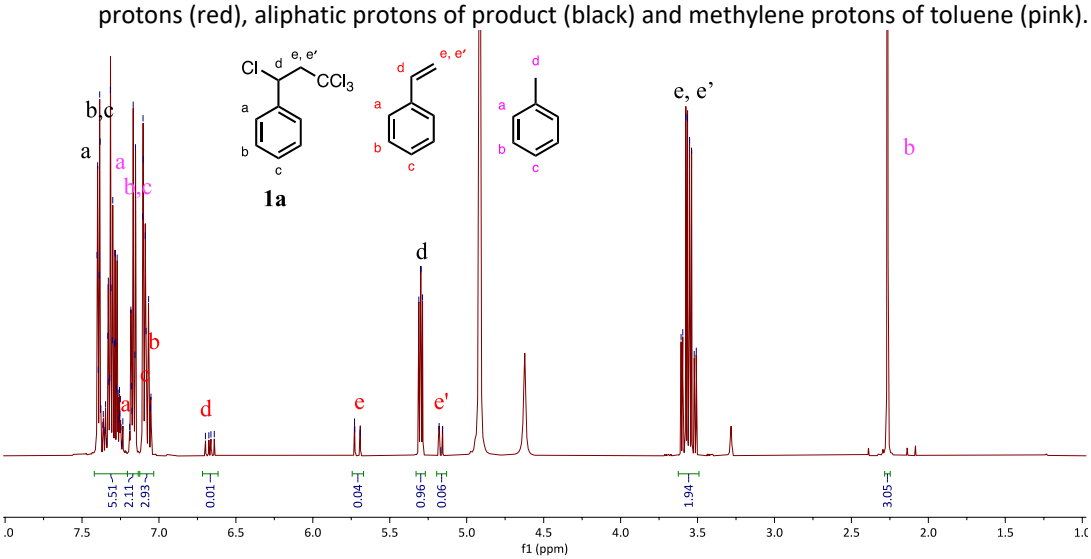
Catalytic reaction study

Fig. S4. ^{1}H NMR spectra of crude product, after flash column chromatography, from reaction between styrene and CCl_4 in CD_3OD, in the presence of toluene internal standard

- Spectrum for 100% conversion and 100% Yield, calculated from ^{1}H NMR integrations of aliphatic protons of product (black) and methylene protons of toluene (pink).



- Spectrum for 95% conversion and 96% Yield, calculated from ^{1}H NMR integrations of all alkene protons (red), aliphatic protons of product (black) and methylene protons of toluene (pink).



- Spectrum of styrene (substrate, red) and toluene (internal standard, pink) mixture

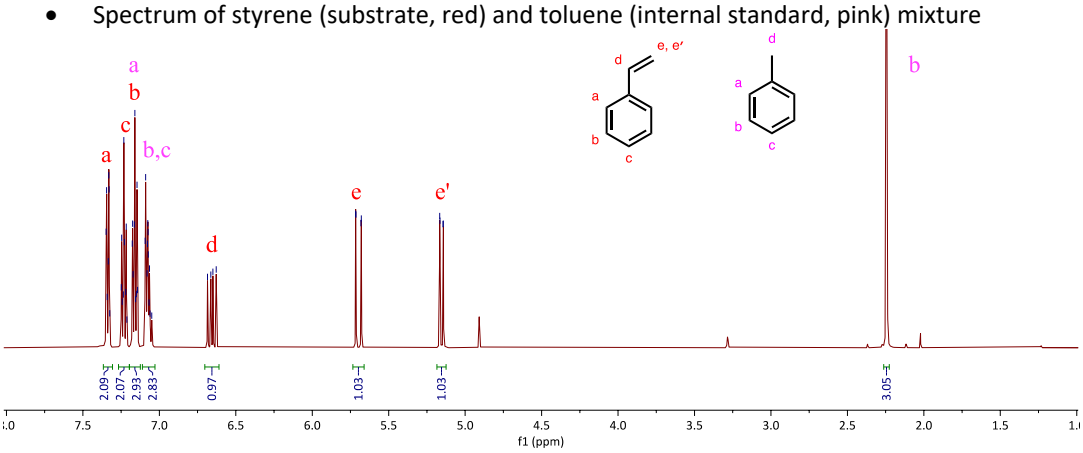
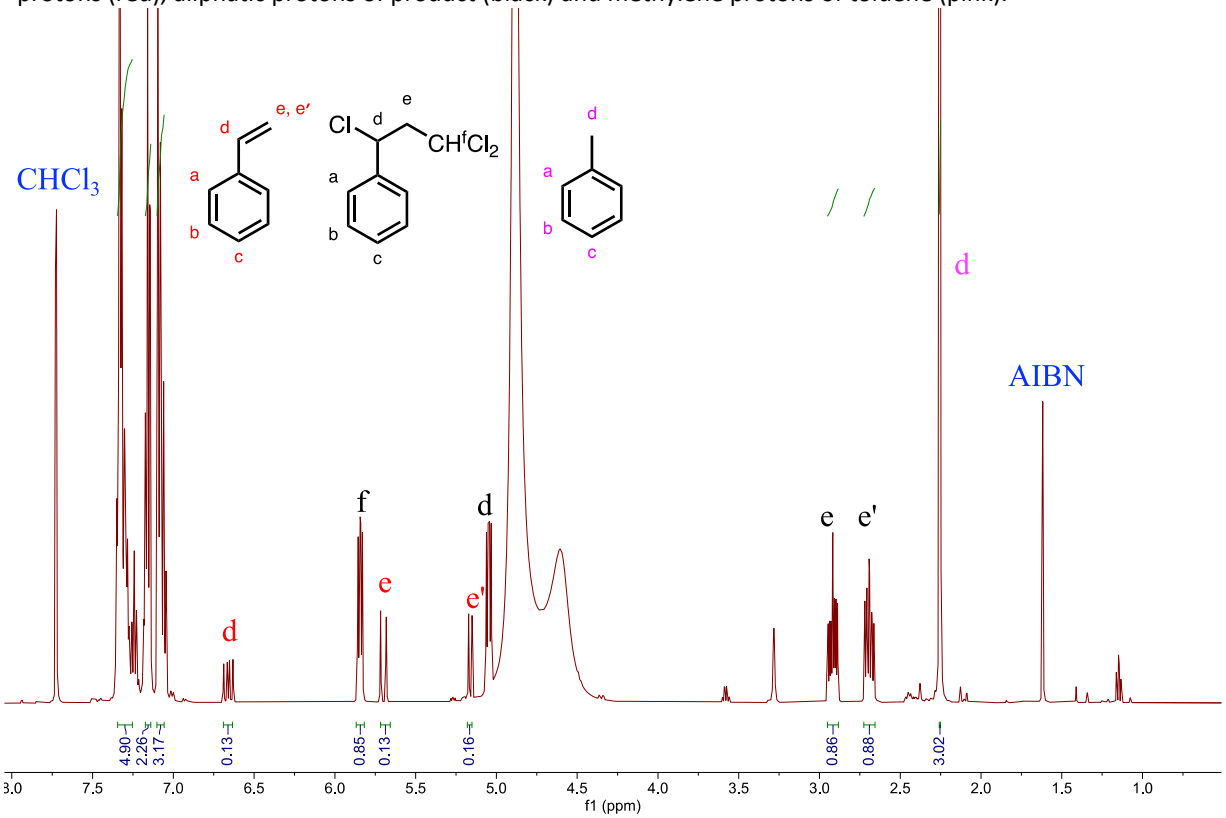


Fig. S5. ^{1}H NMR spectra of crude product, after flash column chromatography, from reaction between styrene and $CHCl_3$ in CD_3OD, in the presence of toluene internal standard

- Spectrum for 87% conversion and 86% Yield, calculated from ^{1}H NMR integrations of all alkene protons (red), aliphatic protons of product (black) and methylene protons of toluene (pink).



- Spectrum for 40% conversion and 40% Yield, calculated from ^{1}H NMR integrations of all alkene protons (red), aliphatic protons of product (black) and methylene protons of toluene (pink).

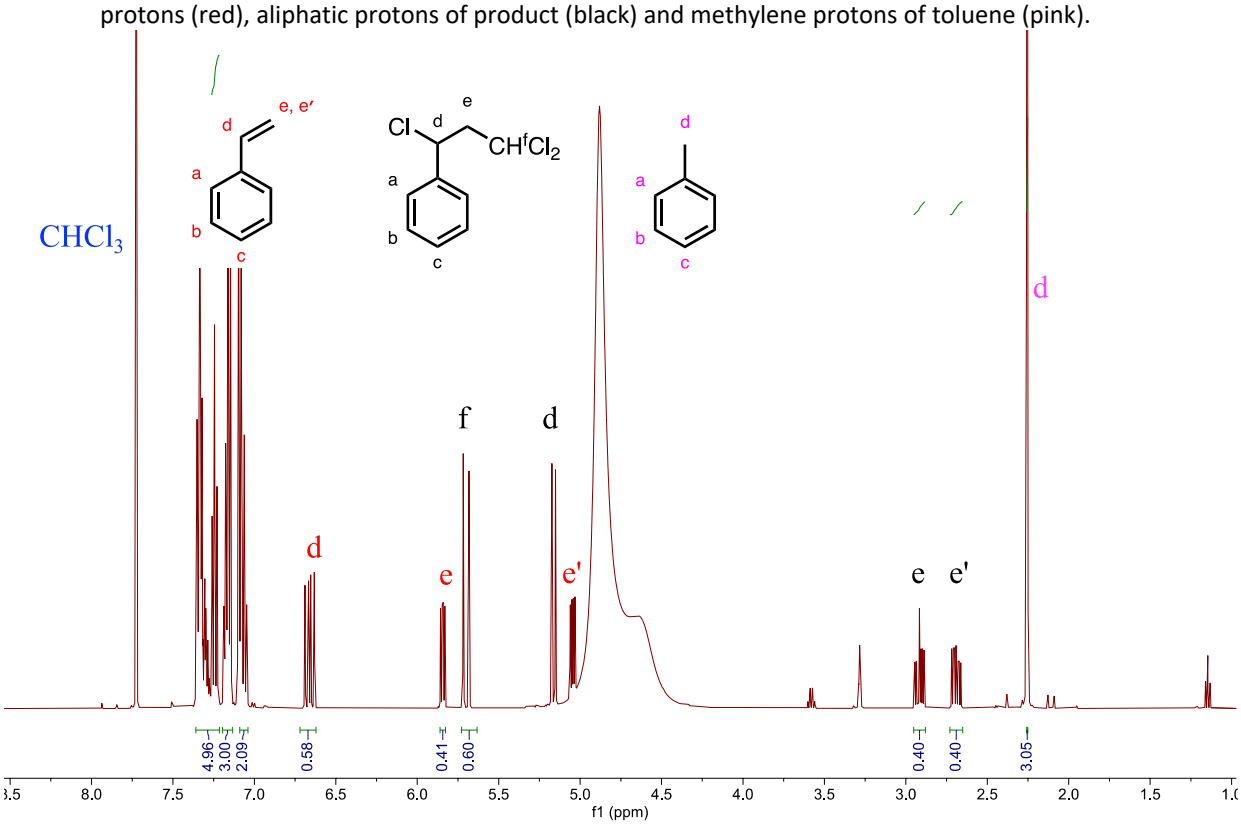


Fig. S6. Time dependence study for reaction of styrene with CCl_4 catalyzed by copper complexes with various ligands

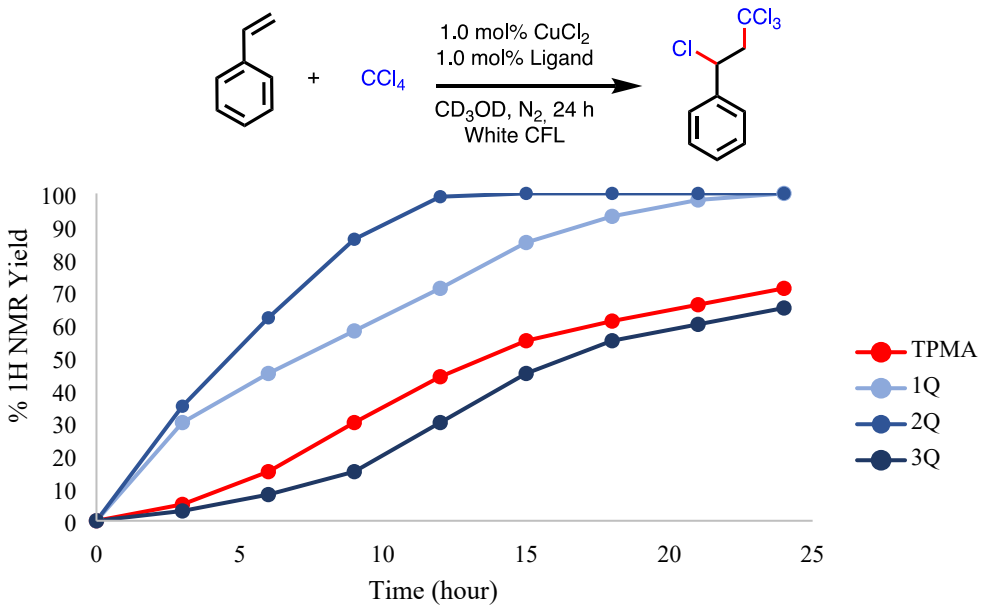
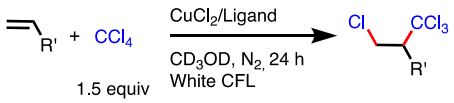


Table S5 Conversions, yields and turn over numbers obtained from addition reaction of CCl_4 to various alkenes catalyzed by copper complexes of various ligands



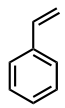
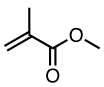
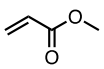
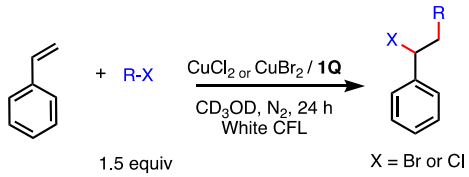
Alkene	[Alkene]	Mol% cat.	1Q		2Q		3Q		TPMA	
			%Con.	%Yield (TON)	%Con.	%Yield	%Con.	%Yield	%Con.	%Yield (TON)
	1.0	1.0	100	100 (100)	100	100	65	65	71	71 (100)
	3.0	0.3	94	89 (267)					19	13 (39)
	3.0	0.1	27	17 (170)						
	4.8	0.1	37	16 (160)					7	4 (40)
	1.0	1.0	95	95	99	99	54	53	73	73
	3.0	0.3	99	95 (285)						
	1.0	1.0	89	88	71	66	17	14	66	64
	3.0	0.3	86	83 (249)						
	1.0	1.0	90	88	68	64	0	0	64	63
	3.0	0.3	90	80 (240)						
	1.0	1.0	96	91					98	96

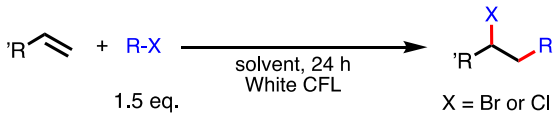
Table S6 Substrate conversions and product yields for reactions of styrene with various alkyl halides in methanol with and without AIBN



Alkyl halide (equiv)	With AIBN (5 mol %)		Without AIBN	
	%Con	% Yield	%Con	% Yield
CBr_4	100	98	100	99
$CBrCl_3$	100	100	100	100
CCl_3COOMe	100	100	100	100
CCl_3CN	100	94	100	90
$CHCl_3$[a]	100	100	54	53
$CHBr_3$[a]	75	74	51	49

[a]The reactions were performed under white CFL at ambient temperature for 24h
[a]3.0 equivalent of alkyl halide was used.

Table S7 Comparison of alkyl chloride with alkyl bromide in the addition reaction to alkenes in the absence of photocatalyst under white light



Entry	Alkene	R-X	Solvent	%Con	%Yield
1	Styrene	CBr_4	CD_3OD	68	58
2	1*H*-Indene	CBr_4	*i*-PrOH	100	90
3	Methyl methacrylate	CBr_4	CD_3OD	70	0
4	Styrene	CCl_4	CD_3OD	N.R.	
5	1*H*-Indene	CCl_4	CH_3OH	N.R.	
6	1*H*-Indene	CCl_3COOMe	CH_3OH	N.R.	
7	1*H*-Indene	CCl_3CN	CH_3OH	N.R.	

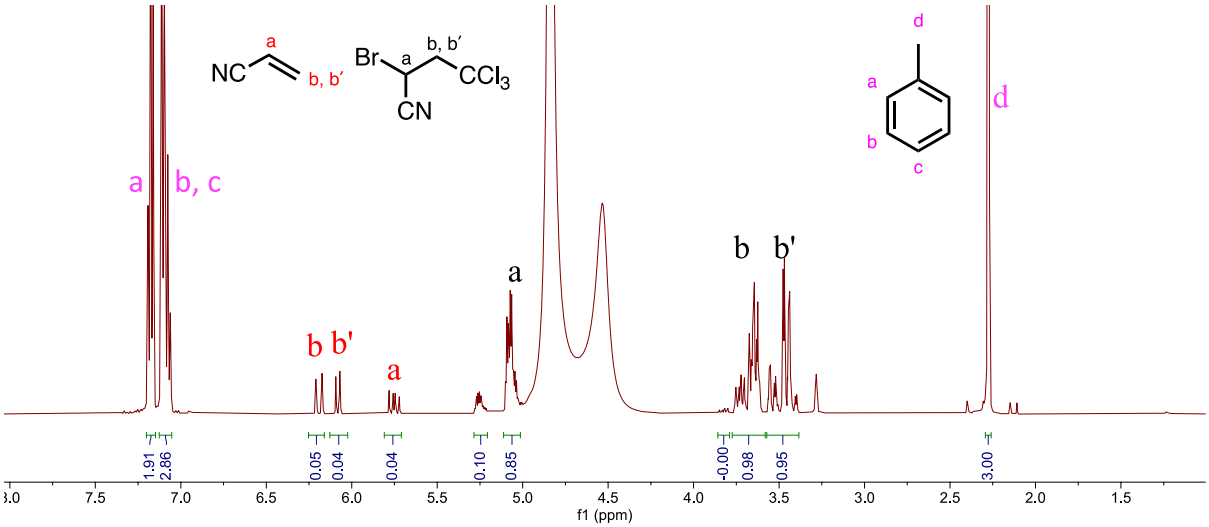
[a]The reactions were performed under white CFL at ambient temperature for 24h

Addition of terminal alkenes with $CBrCl_3$

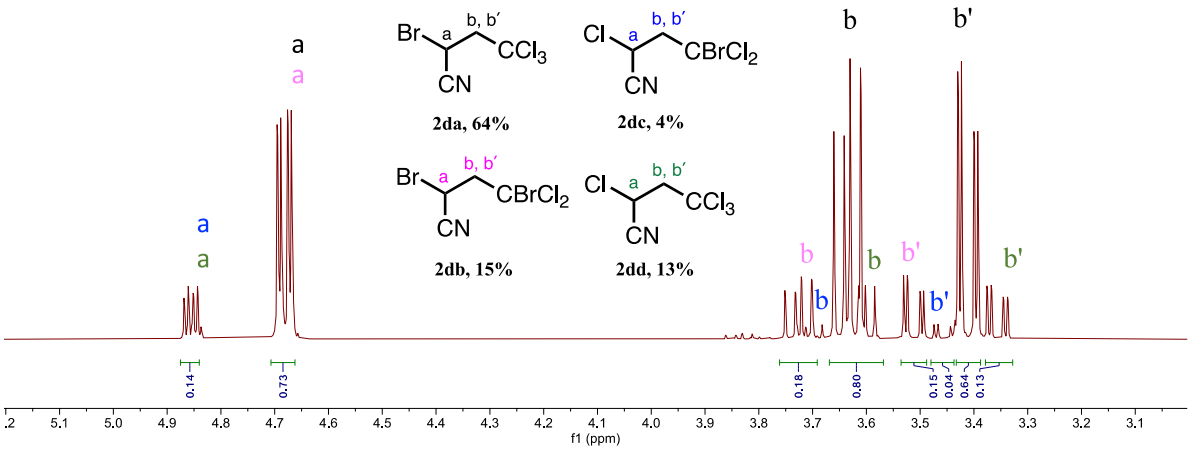
The addition of the mixed halide reagent, $CBrCl_3$, to each of these alkenes gave a mixture of products containing CCl_3/Br groups (major product, >50% yield, Fig. S7-S9) and CCl_2Br/Cl groups as well as their 2 crossover products in excellent total yield. These results indicated the competition between C-Cl and C-Br bond dissociation. The proposed mechanism to explain the formations of all products by adding more details of bond dissociation and formation pathways after the SET process is shown in Fig. S10. The formation of the major product is related to the C-Br bond dissociation which can occur either via the direct photolysis or the SET process. The incorporation of Br group in the major product can also occur either via the reductive elimination or Br abstraction routes. On the other hand, the formation of the minor products can occur only via the SET process and the incorporation of Cl group can occur only via the reductive elimination route. The low chemoselectivity for the addition of $CBrCl_3$ to these electron deficient alkenes was very different from the reaction of styrene which gave only a single product resulting from the C-Br bond dissociation and Br abstraction. We hypothesized that reducing the amount of copper catalyst, to limit the C-Cl bond dissociation, might increase the chemoselectivity of the reaction. Indeed, when the catalyst amount was reduced from 1 to 0.3 mol%, the chemoselectivity of the reaction was vastly improved that only **2da**-**4da** resulting from CCl_3/Br addition were obtained in excellent yields. On the other hand, the increase of catalyst amount to 3.0 mol% slightly decrease the chemoselectivity of the reaction (Fig. S11). It is also important to point out that the addition of $CBrCl_3$ to these electron deficient alkenes did not proceed in the absence of the copper catalyst unlike the addition to styrene. The copper catalyst may thus also have an essential role in either alkene activation or intermediate stabilization, besides the SET activation of C-X bond dissociation.

Fig. S7. ^{1}H NMR spectra of crude product, after flash column chromatography, from reaction between acrylonitrile and $CBrCl_3$ in CD_3OD, in the presence of toluene internal standard

- Spectrum for 96% conversion and 94% yield, calculated from ^{1}H NMR integrations of all alkene protons (red), aliphatic protons of product (black) and methylene protons of toluene (pink).



- Spectrum for product ratio determination based on 94% yield, calculated from ^{1}H NMR integrations of aliphatic protons of each addition product.



Purified **2a** from the reaction between acrylonitrile and CCl_4

*product **2dd** = **2a**

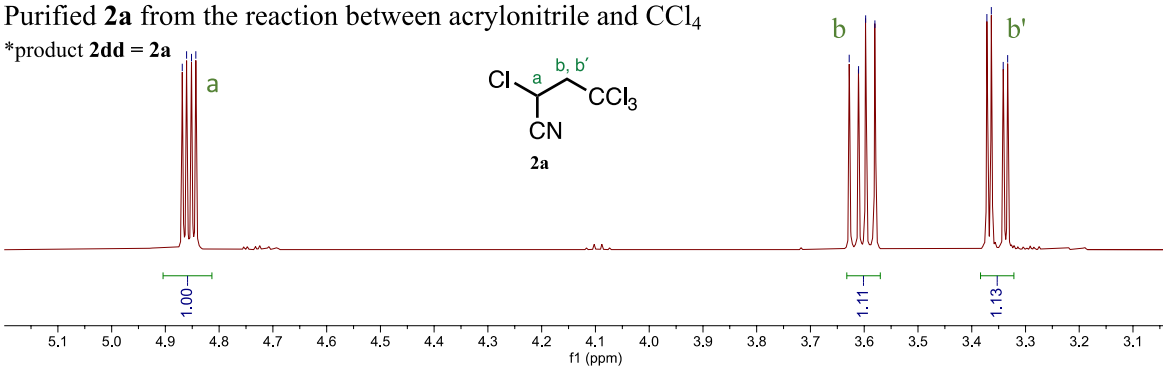
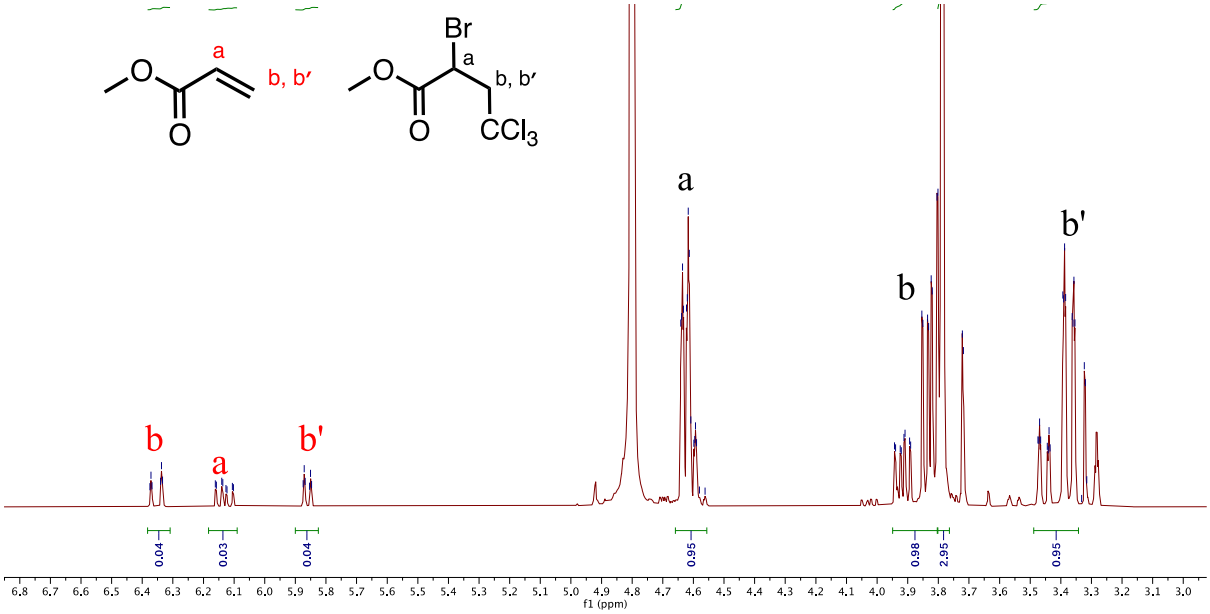
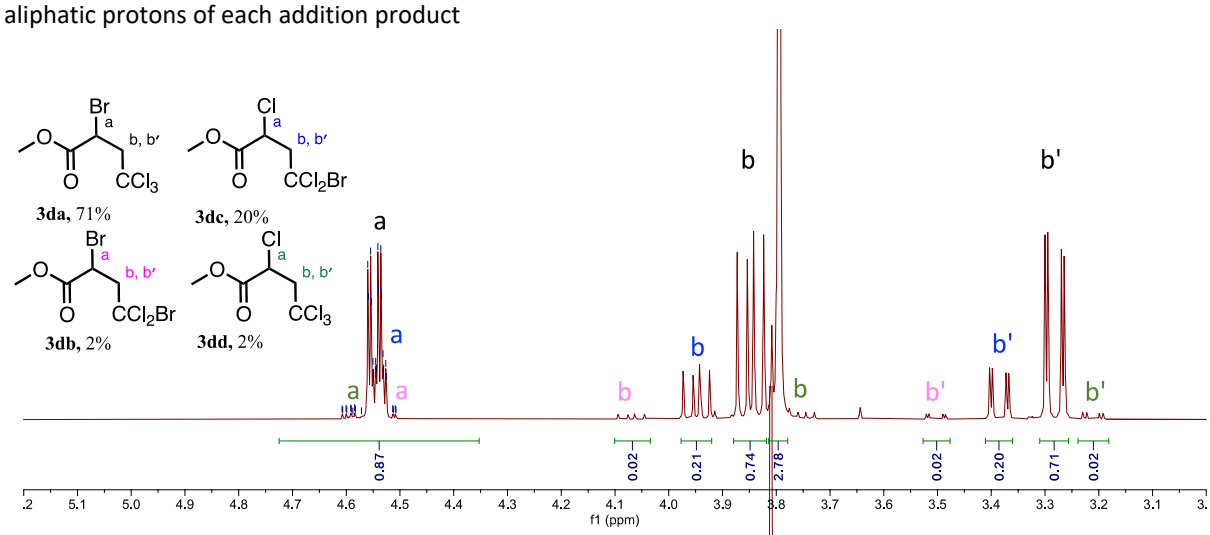


Fig. S8. ^{1}H NMR spectra of crude product, after flash column chromatography, from reaction between methyl acrylate and $CBrCl_3$ in CD_3OD, in the presence of toluene internal standard

- Spectrum for 96% conversion and 95% yield, calculated from ^{1}H NMR integrations of all alkene protons (red) and aliphatic protons of product (black)



- Spectrum for product ratio determination based on 95% yield, calculated from ^{1}H NMR integrations of aliphatic protons of each addition product



Purified **3a** from the reaction between methyl acrylate and CCl_4

*product **3dd** = **3a**

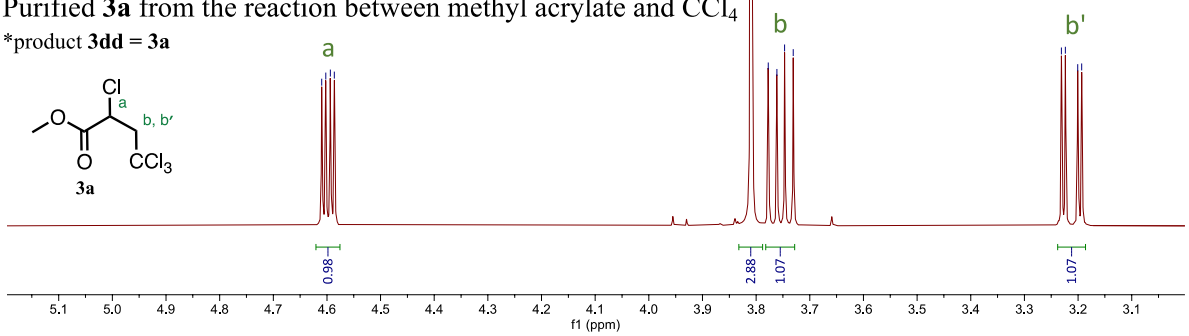
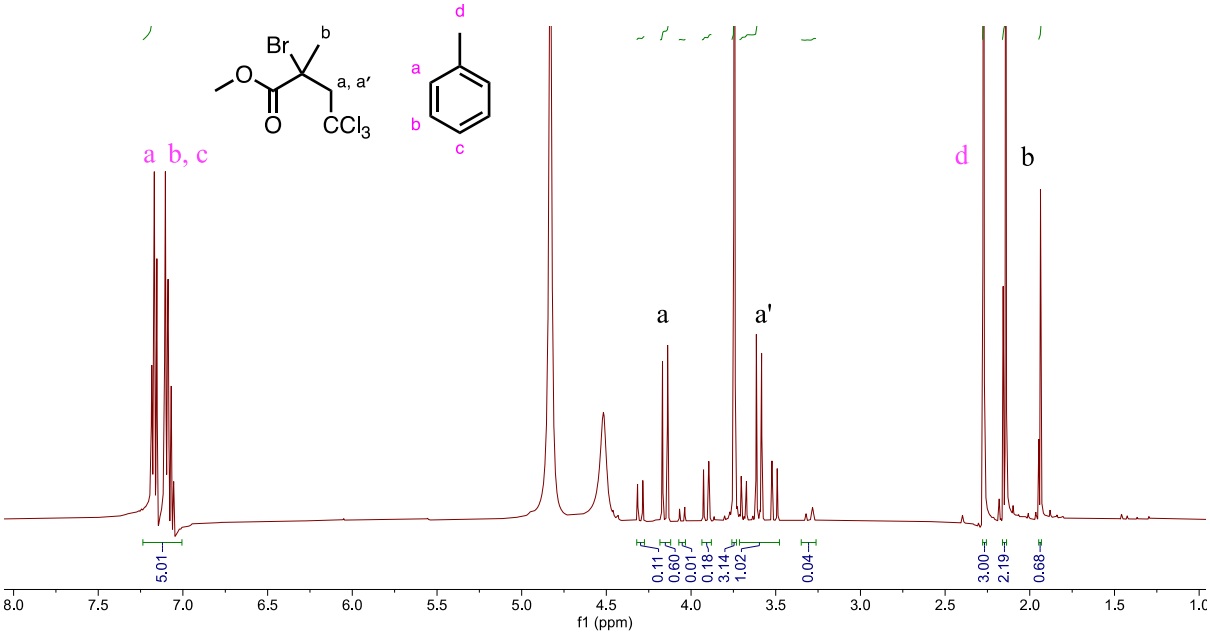
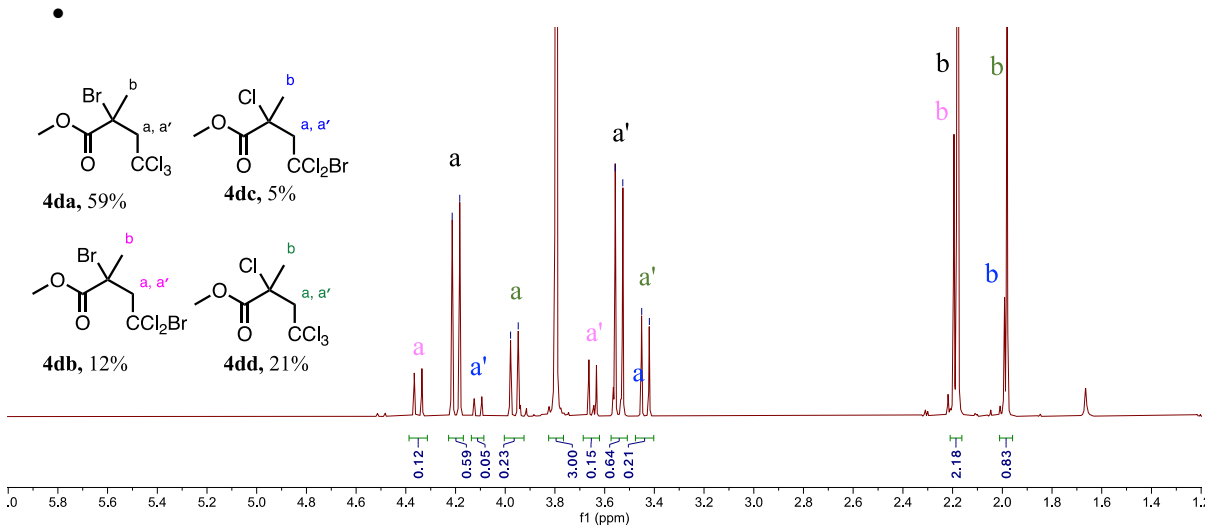


Fig. S9. ^{1}H NMR spectra of crude product, after flash column chromatography, from reaction between methyl methacrylate and $CBrCl_3$ in CD_3OD, in the presence of toluene internal standard

- Spectrum for 100% conversion and 97% yield, calculated from ^{1}H NMR integrations of aliphatic protons of product (black) and methylene protons of toluene (pink).



- Spectrum for product ratio determination based on 97% yield, calculated from ^{1}H NMR integrations of aliphatic protons of each addition product



Purified **4a** from the reaction between methyl methacrylate and CCl_4

*product **4dd** = **4a**

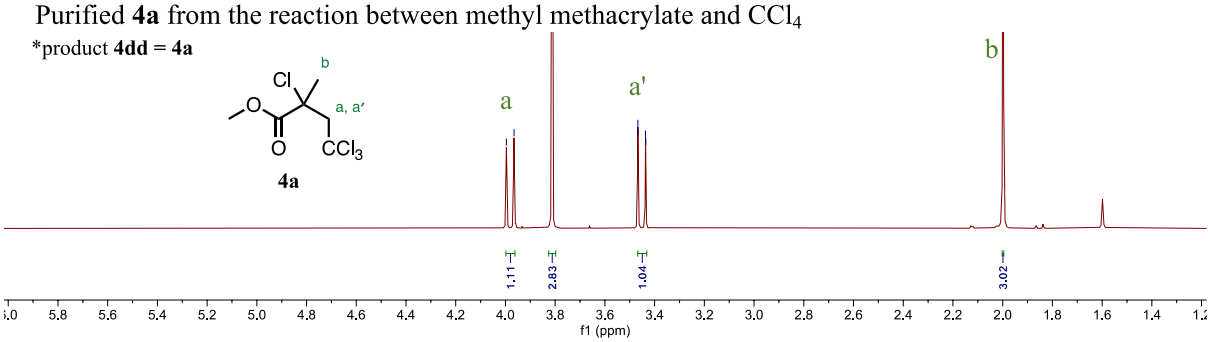


Fig. S10. Proposed mechanism for reaction of terminal alkene with $CBrCl_3$ catalyzed by Cu(II)-ligand complex

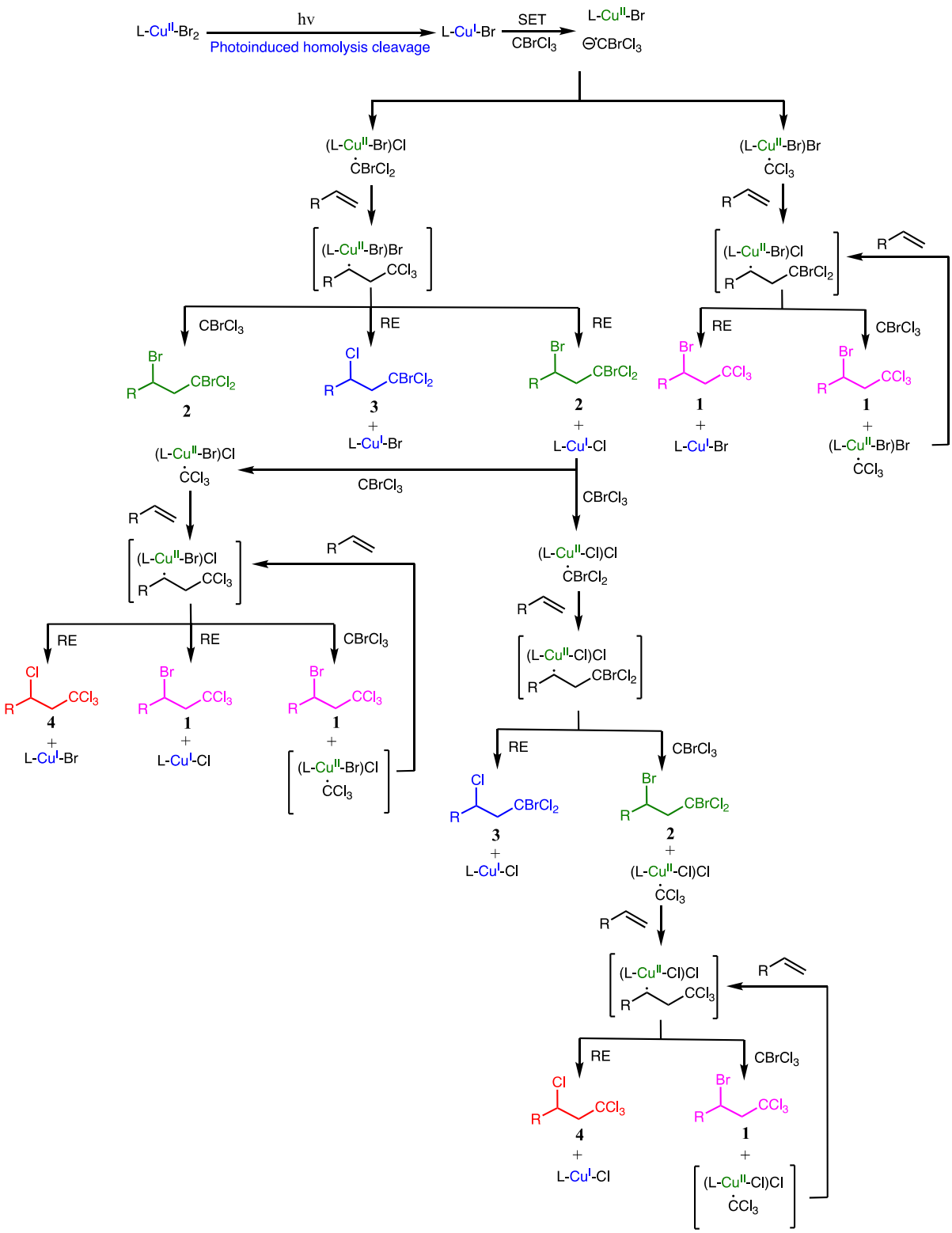
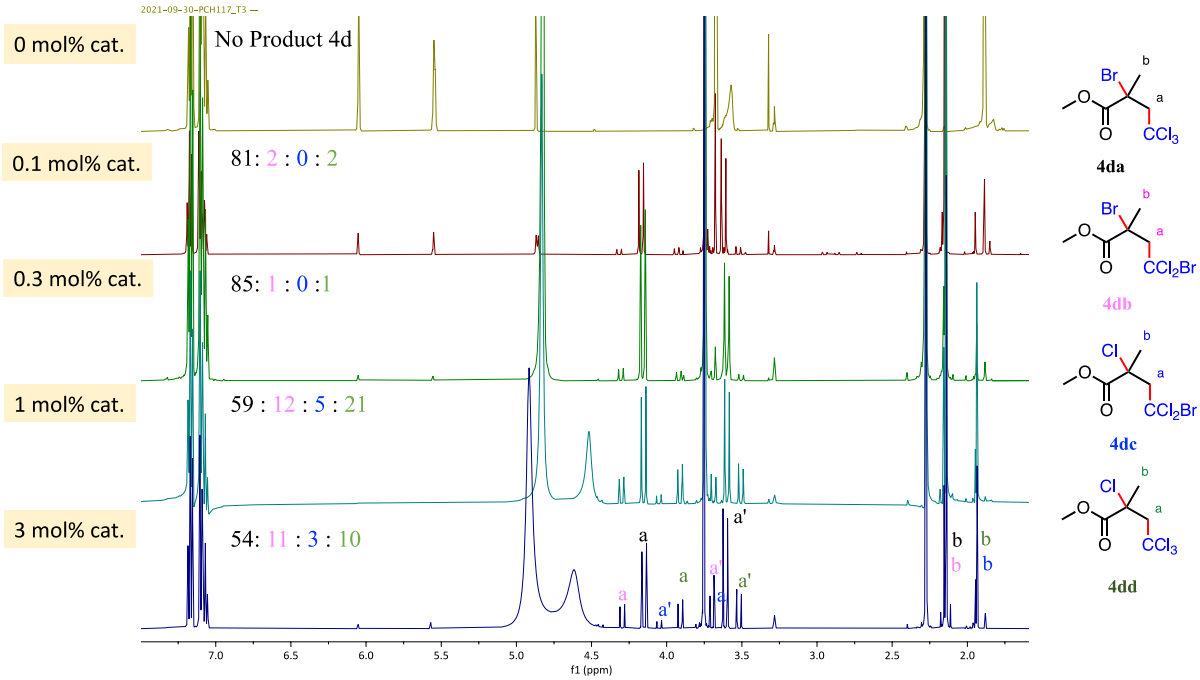
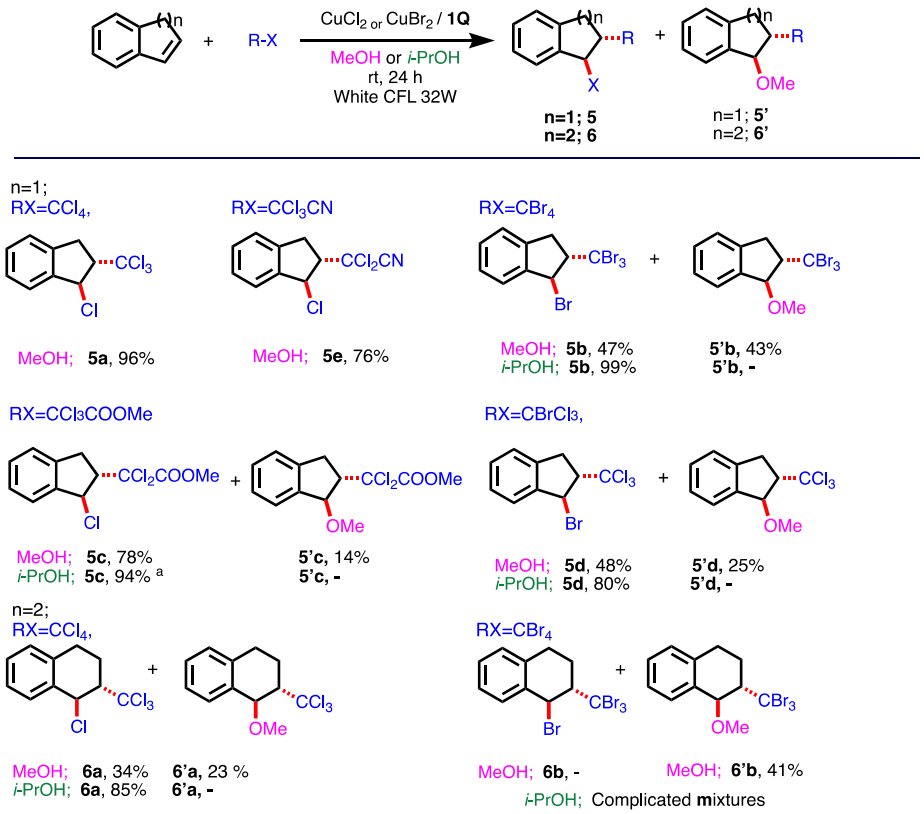


Fig. S11. ^{1}H NMR spectra of crude products, after flash column chromatography, from reactions between methyl methacrylate and $CBrCl_3$ using 0-3 mol % of catalyst loading, in the presence of toluene internal standard

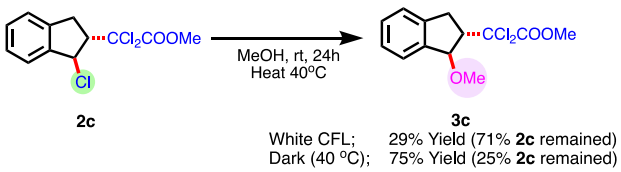


Substitution reaction

Scheme S1 Copper catalyzed ATRAs of various alkyl halide to internal alkenes. Isolated yields are given. [a]1.4014 g of product was isolated after 48 h of a reaction at 5 mmol scale.



Scheme S2 Substitution reaction test of halide product in methanol



NOESY-NMR analysis

Fig. S12. **NOESY**-NMR spectra of **5c**

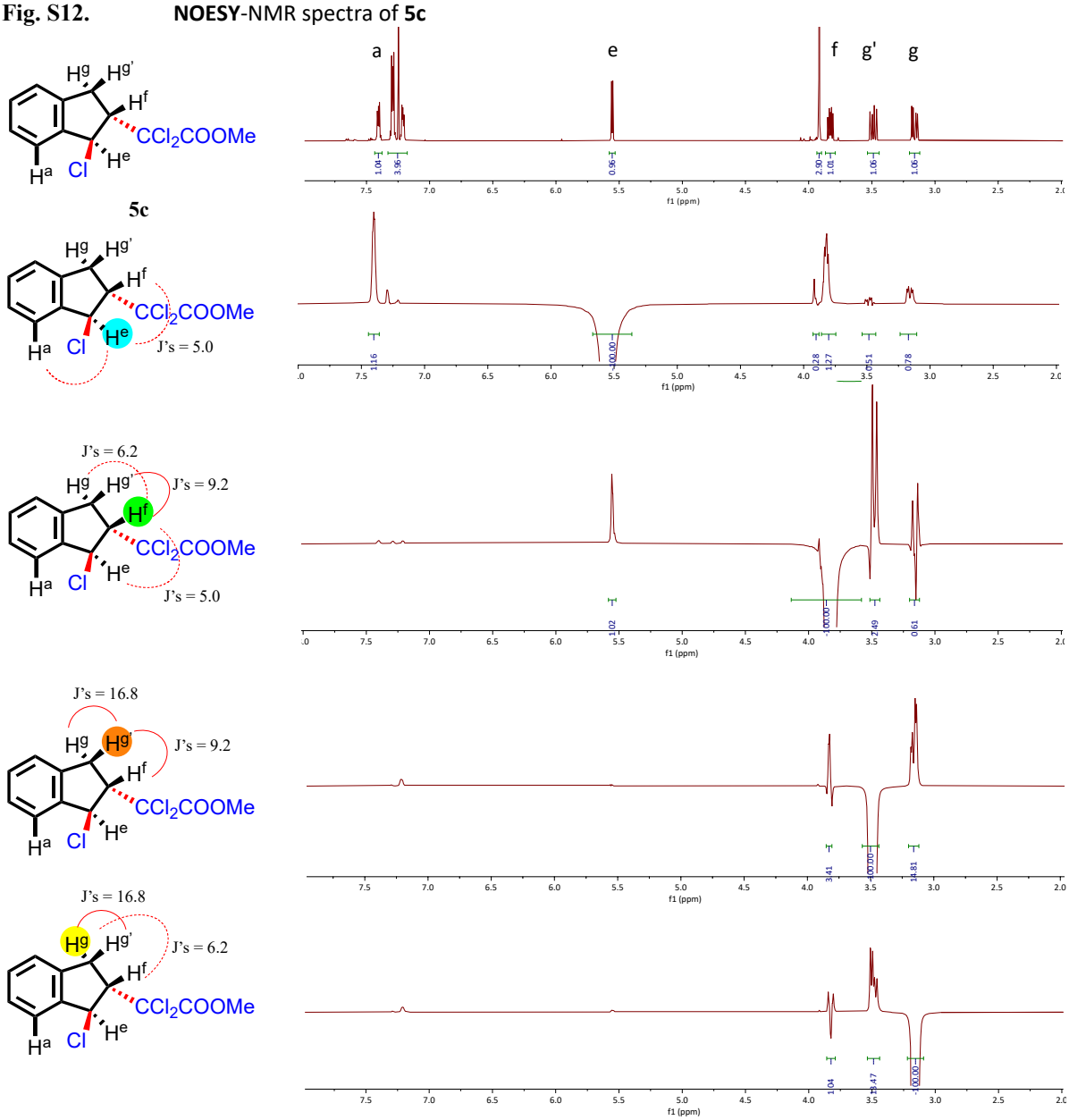
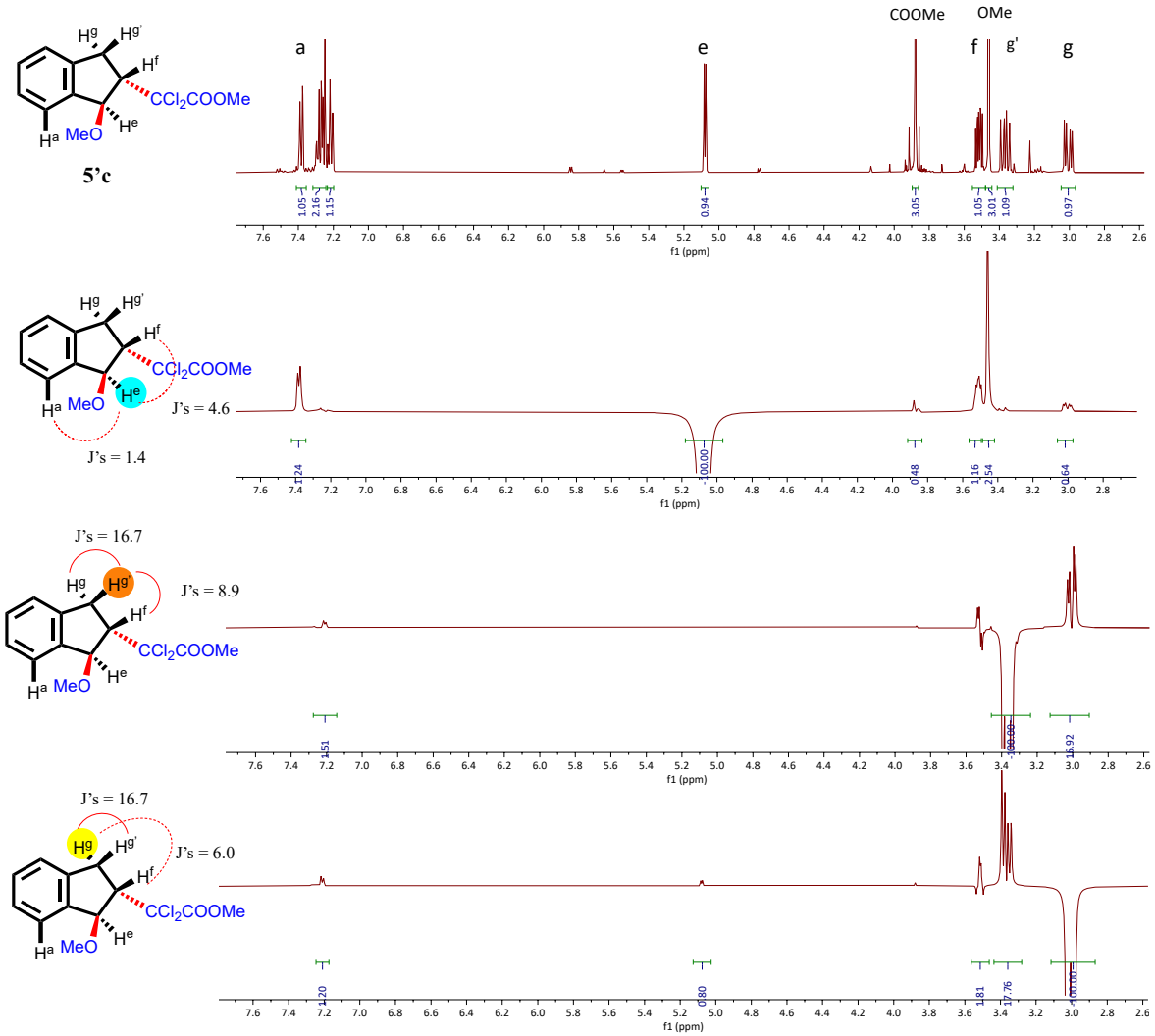


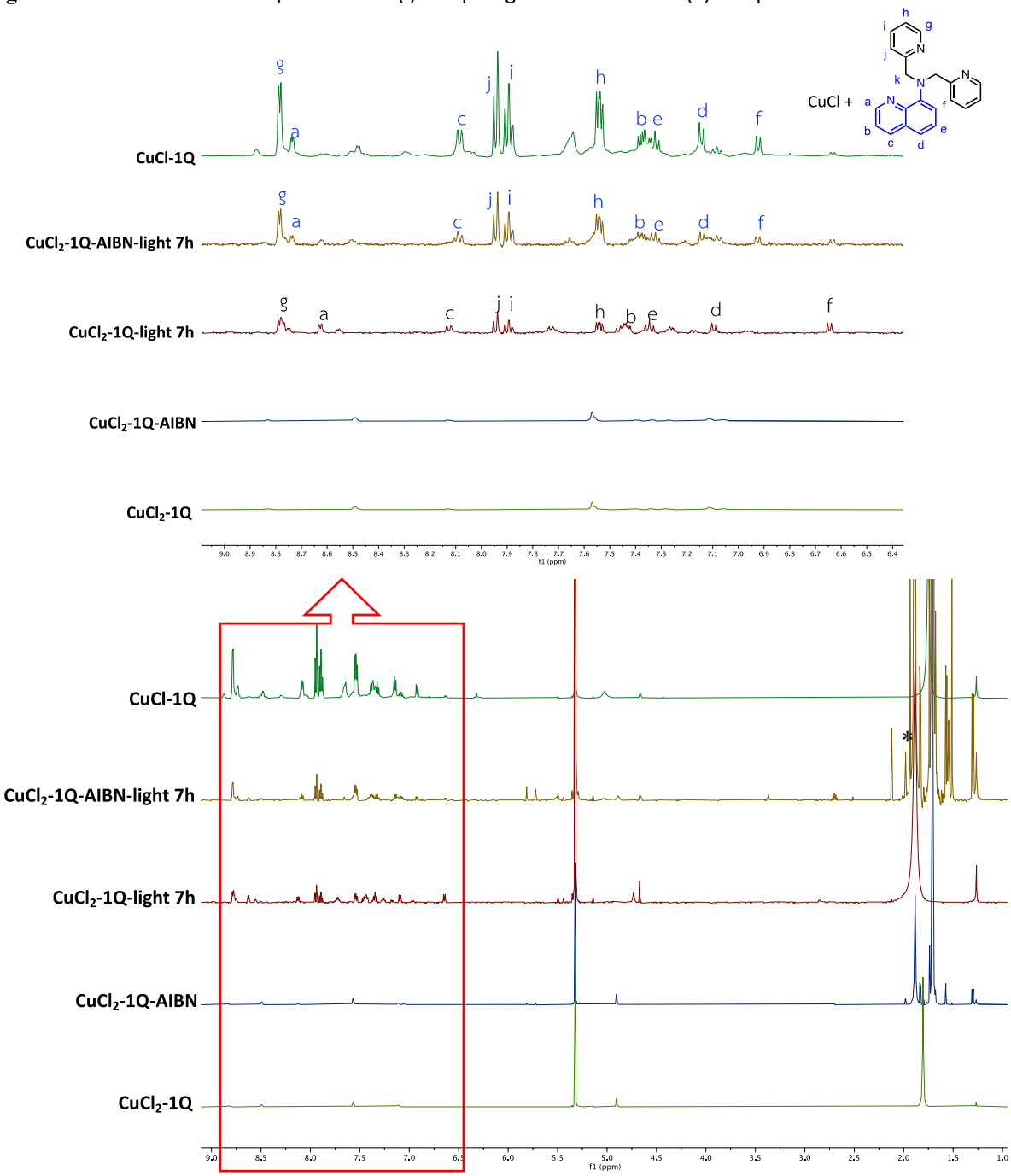
Fig. S13. **NOESY**-NMR **5'c**



Evidence for generation from Cu(II) via XAT process in the presence of AIBN

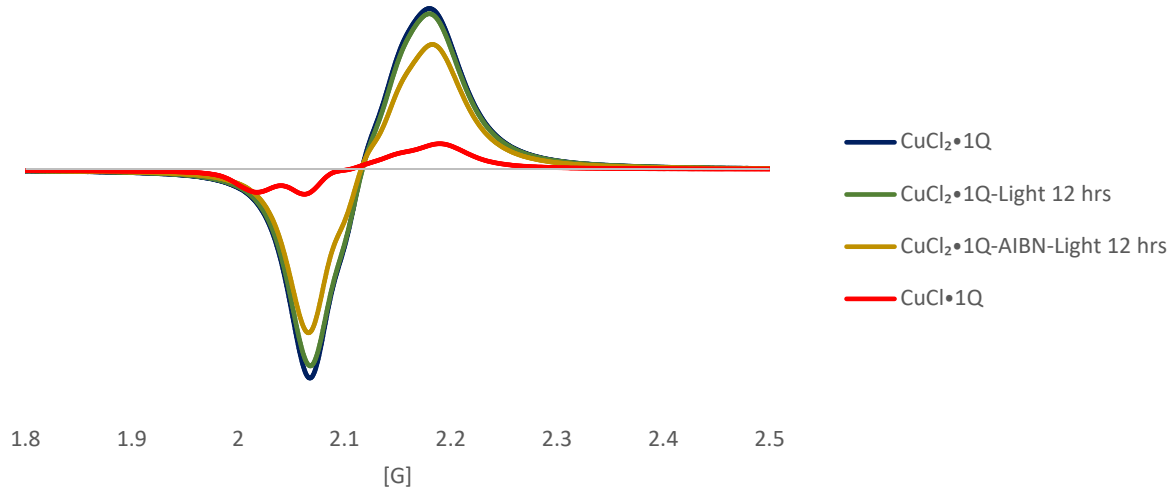
The *in situ* generated complexes of $CuCl_2$-1Q in the presence and absence of AIBN in CD_2Cl_2 showed no observable signals corresponding to the complex (Figure S14) mainly due to the paramagnetic nature of Cu(II) ion. In the absence of AIBN, the ^{1}H NMR spectrum after 7 hours of white light irradiation showed similar pattern of the Cu(I) complex but not at the same chemical shifts implying that another form of Cu(I) complex was generated. In the presence of AIBN, the irradiation gave a ^{1}H NMR signals at the same position with those of *in-situ* generated Cu(I) complex. It is also interesting to note that stronger and cleaner signals of the Cu(I) complex was obtained in the presence of AIBN confirming that AIBN facilitated the generation of Cu(I) complex from Cu(II) complex. Furthermore, the ^{1}H NMR signals in the aliphatic region corresponding to AIBN showed a new signal at 1.90 ppm corresponding to $CCl(CH_3)_2CN$ (Jamey K. Bower, et. al. *J. Am. Chem. Soc*. **2020**, 142, 8514−8521) that can confirm the role of AIBN in the halogen abstractor process.

Fig. S14. The ^{1}H NMR spectra for Cu(I) complex generation from Cu(II) complex.

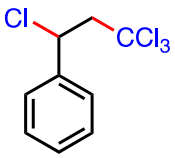


The EPR spectrum of *in situ* generated $CuCl_2$-**1Q** complexes in the presence and absence of AIBN in dried CH_3CN were investigated in comparison with CuCl-**1Q**. In the presence of AIBN, the decrease of Cu(II) complex signal after irradiation confirmed the generation of Cu(I) complex. In the absence of AIBN, the Cu(II) complex spectrum shows less change of the signal. The EPR results thus agree well with the ^{1}H NMR results.

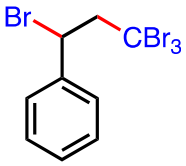
Fig. S15. The EPR spectra for Cu(I) complex generation from Cu(II) complex.



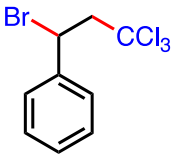
Spectroscopic data of products



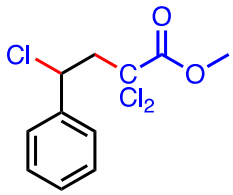
(1,3,3,3-tetrachloropropyl)benzene, 1a ^{1}H NMR (400 MHz, CD_3CN) δ 7.57 – 7.45 (m, 2H), 7.45 – 7.33 (m, 3H), 5.42 (t, *J* = 6.0 Hz, 1H), 3.75 – 3.61 (m, 2H). **^{13}C NMR (101 MHz, Acetone)** δ140.67, 128.86, 128.82, 127.60, 96.47 61.89, 58.40.



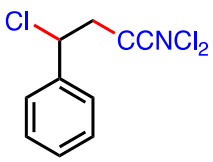
(1,3,3,3-tetrabromopropyl)benzene, 1b ^{1}H NMR (400 MHz, DMSO) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.32 (m, 3H), 5.45 (dd, *J* = 7.7, 3.9 Hz, 1H), 4.24 (dd, *J* = 15.8, 7.7 Hz, 1H), 4.08 (dd, *J* = 15.8, 3.9 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 141.45, 129.28, 129.19, 128.73, 65.28, 51.45, 36.52.



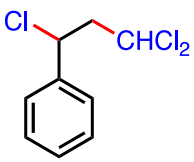
(1-bromo-3,3,3-trichloropropyl)benzene, 1c ^{1}H NMR (400 MHz, DMSO) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.31 (m, 3H), 5.58 (dd, *J* = 8.0, 4.6 Hz, 1H), 4.00 (dd, *J* = 15.5, 8.0 Hz, 1H), 3.82 (dd, *J* = 15.5, 4.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 141.24, 129.28, 129.15, 128.47, 97.40, 61.35, 48.79.



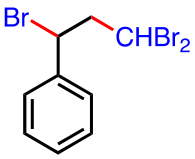
Methyl-2,2,4-trichloro-4-phenylbutanoate, 1d ^{1}H NMR (400 MHz, DMSO) δ 7.54 – 7.47 (m, 2H), 7.39 (qd, J = 8.0, 7.1, 4.0 Hz, 3H), 5.38 (dd, J = 7.5, 6.0 Hz, 1H), 3.69 (d, J = 1.1 Hz, 3H), 3.48 (ddd, J = 15.1, 7.6, 1.0 Hz, 1H), 3.36 – 3.27 (m, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 165.44, 140.05, 129.38, 129.15, 128.05, 82.98, 59.10, 55.09, 52.91.



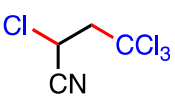
2,2,4-trichloro-4-phenylbutanenitrile, 1e ^{1}H NMR (500 MHz, CHLOROFORM-D) δ 7.55 – 7.36 (m, 1H), 5.22 (t, J = 6.7 Hz, 0H), 3.37 (dd, J = 15.1, 7.1 Hz, 0H), 3.22 (dd, J = 15.1, 6.4 Hz, 0H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 138.74, 129.74, 129.30, 127.62, 114.55, 66.15, 57.58, 55.97.



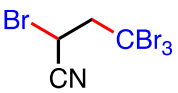
(1,3,3-trichloropropyl)benzene, 1f ^{1}H NMR (400 MHz, DMSO) δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.41 (m, 3H), 6.20 (dd, *J* = 8.5, 4.6 Hz, 1H), 5.24 (dd, *J* = 9.6, 4.7 Hz, 1H), 3.17-3.09 (m, 1H), 2.92 – 2.85 (m, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 139.94, 129.41, 129.30, 127.83, 71.95, 60.13, 51.34.



(1,3,3-tribromopropyl)benzene, 1g ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.42 – 7.32 (m, 5H), 5.63 (dd, *J* = 8.1, 5.8 Hz, 1H), 5.11 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.28 (ddd, *J* = 14.8, 9.0, 5.7 Hz, 1H), 3.07 (ddd, *J* = 15.2, 8.0, 5.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) *δ* 139.61, 129.22, 129.20, 127.55, 53.94, 51.58, 42.42.

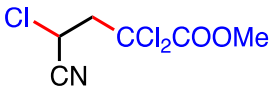


2,4,4,4-tetrachlorobutanenitrile, **2a ^{1}H NMR** (500 MHz, CHLOROFORM-*D*) *δ* 4.86 (dd, *J* = 8.6, 4.0 Hz, 1H), 3.60 (dd, *J* = 15.2, 8.6 Hz, 1H), 3.35 (dd, *J* = 15.2, 4.1 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) *δ* 115.87, 93.82, 77.44, 77.38, 77.18, 76.93, 59.17, 37.96.

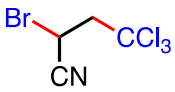


2,4,4,4-tetrabromobutanenitrile, **2b,** the isolated product was obtained as a clear oil (446.07 mmol, 0.1716 g, 88% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 4.65

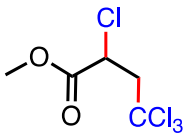
(ddd, *J* = 9.3, 3.1, 0.6 Hz, 1H), 3.97 (ddd, *J* = 15.5, 9.2, 0.6 Hz, 1H), 3.75 (ddd, *J* = 15.5, 3.1, 0.6 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 116.40, 63.18, 31.84, 22.98.



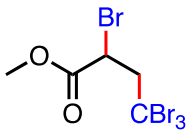
Methyl 2,2,4-trichloro-4-cyanobutanoate, 2c ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 4.83 (dd, *J* = 8.0, 5.5 Hz, 1H), 3.94 (s, 3H), 3.35 (dd, *J* = 15.1, 8.0 Hz, 1H), 3.19 (dd, *J* = 15.1, 5.5 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 165.00, 115.87, 79.36, 55.13, 50.16, 37.96.



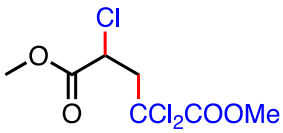
2-bromo-4,4,4-trichlorobutanenitrile, 2d ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 4.68 (ddd, *J* = 9.7, 3.5, 0.6 Hz, 1H), 3.64 (ddd, *J* = 15.0, 9.7, 0.6 Hz, 1H), 3.41 (ddd, *J* = 15.0, 3.5, 0.6 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 116.24, 94.65, 59.41, 20.23.



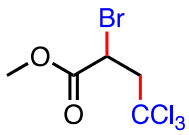
Methyl-2,4,4,4-tetrachlorobutanoate, 3a ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 4.60 (dd, *J* = 8.0, 3.7 Hz, 1H), 3.81 (s, 3H), 3.75 (dd, *J* = 15.2, 8.0 Hz, 1H), 3.21 (dd, *J* = 15.2, 3.7 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 168.85, 95.45, 58.32, 53.63, 51.52.



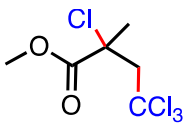
Methyl-2,4,4,4-tetrabromobutanoate, 3b, the isolated product was obtained as a clear oil (429.71.07 mmol, 0.1795 g, 85% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 4.48 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.20 (dd, *J* = 15.5, 9.1 Hz, 1H), 3.80 (s, 3H), 3.63 (dd, *J* = 15.6, 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 169.36, 62.47, 53.71, 40.09, 34.53.



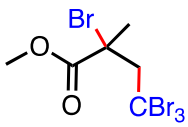
Dimethyl-2,2,4-trichloropentanedioate, 3c ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 4.64 – 4.57 (m, 1H), 3.88 (d, *J* = 0.5 Hz, 3H), 3.80 (d, *J* = 0.5 Hz, 3H), 3.37 (dd, *J* = 15.3, 6.8 Hz, 1H), 3.10 (dd, *J* = 15.3, 5.8 Hz, 1H).**^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 168.96, 165.66, 81.02, 54.85, 53.58, 52.01, 49.06.



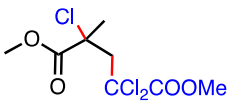
Methyl-2-bromo-4,4,4-trichlorobutanoate, 3d ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 4.55 (ddd, *J* = 9.4, 2.7, 0.6 Hz, 1H), 3.85 (dd, *J* = 15.2, 9.4 Hz, 0H), 3.79 (s, 2H), 3.28 (dd, *J* = 15.2, 2.7 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 169.37, 96.10, 58.54, 53.61, 37.75.



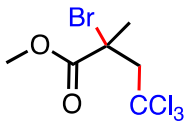
Methyl-2,4,4,4-tetrachloro-2-methylbutanoate, **4a ^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 3.98 (d, *J* = 15.3 Hz, 1H), 3.81 (d, *J* = 0.7 Hz, 3H), 3.45 (dd, *J* = 15.3, 0.6 Hz, 1H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 170.22, 94.66, 64.67, 62.30, 53.64, 26.41.



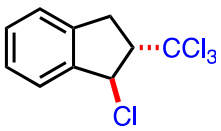
Methyl-2,4,4,4-tetrabromo-2-methylbutanoate, 4b, the isolated product was obtained as a clear oil (499.36 mmol, 0.2156 g, 99% yield). **^{1}H NMR,** (500 MHz, CHLOROFORM-*D*) δ 4.64 (d, *J* = 15.5 Hz, 1H), 3.88 (d, *J* = 15.5 Hz, 1H), 3.80 (d, *J* = 0.7 Hz, 3H), 2.23 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) *δ* 170.55, 65.91, 57.59, 53.65, 31.46, 26.26.



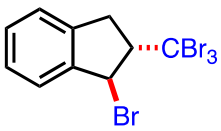
Dimethyl-2,2,4-trichloro-4-methylpentanedioate, 4c, the isolated product was obtained as a clear oil (4.0125 mol, 1.1136 g, 79% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 3.87 (s, 3H), 3.78 (s, 3H), 3.53 (d, *J* = 15.2 Hz, 1H), 3.42 (dd, *J* = 15.1, 0.6 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 170.72, 166.02, 80.76, 65.39, 54.84, 53.69, 28.20.



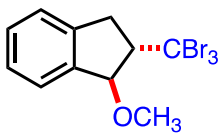
Methyl-2-bromo-4,4,4-trichloro-2-methylbutanoate, 4d ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 4.20 (d, *J* = 15.3 Hz, 1H), 3.79 (s, 3H), 3.54 (d, *J* = 15.3 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR (126 MHz, CHLOROFORM-*D*) *δ*** 170.67, 95.14, 62.76, 55.39, 53.60, 26.63.



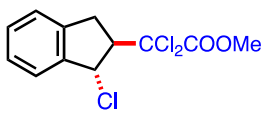
***anti*-1-chloro-2-(trichloromethyl)-2,3-dihydro-1H-indene, 5a ^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.50 – 7.38 (m, 1H), 7.33 (td, *J* = 4.0, 1.1 Hz, 2H), 5.64 (dd, *J* = 4.3, 1.0 Hz, 1H), 3.94 (dddd, *J* = 9.9, 5.3, 4.3, 0.8 Hz, 1H), 3.59 (ddd, *J* = 17.2, 9.2, 1.0 Hz, 1H), 3.34 (ddd, *J* = 17.3, 5.6, 1.0 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 141.23, 140.09, 129.65, 128.02, 125.75, 124.60, 101.43, 69.45, 64.07, 36.19.



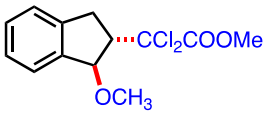
***anti*-1-bromo-2-(tribromomethyl)-2,3-dihydro-1*H*-indene, 5b,** the isolated product was obtained as a clear oil (0.2358 mol, 0.1056 g, 47% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.46 – 7.40 (m, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 5.64 (dd, J = 3.0, 0.8 Hz, 1H), 4.20 (ddd, J = 9.1, 3.9, 3.0 Hz, 1H), 3.59 (ddt, J = 17.6, 9.1, 0.7 Hz, 1H), 3.32 – 3.18 (m, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 141.30, 141.01, 129.31, 127.34, 125.43, 124.84, 88.62, 67.99, 46.96, 38.35.



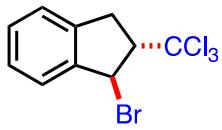
***anti*-1-methoxy-2-(tribromomethyl)-2,3-dihydro-1*H*-indene, 5'b,** the isolated product was obtained as a clear oil (0.2193 mol, 0.0875 g, 43% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) *δ* 7.42 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.20 (m, 4H), 5.00 (d, *J* = 3.4 Hz, 1H), 3.74 (ddd, *J* = 8.9, 5.0, 3.5 Hz, 1H), 3.54 (s, 3H), 3.45 (ddd, *J* = 17.3, 8.8, 1.0 Hz, 1H), 3.09 (dd, *J* = 17.4, 5.0 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) *δ* 141.31, 140.97, 129.31, 127.33, 125.43, 124.83, 88.70, 67.95, 56.51, 46.92, 38.33.



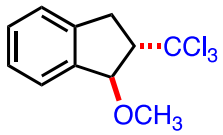
***anti*-methyl-2,2-dichloro-2-1-chloro-2,3-dihydro-1*H*-inden-2-yl)acetate, 5c ^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.42 – 7.39 (m, 1H), 7.31 – 7.28 (m, 2H), 7.23 – 7.19 (m, 1H), 5.55 (d, *J* = 5.0 Hz, 1H), 3.92 (d, *J* = 0.6 Hz, 3H), 3.83 (dddd, *J* = 9.0, 6.1, 5.0, 0.6 Hz, 1H), 3.49 (ddd, *J* = 16.8, 9.2, 0.8 Hz, 1H), 3.16 (dd, *J* = 16.8, 6.2 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 165.84, 141.37, 140.01, 129.45, 127.88, 125.49, 124.57, 86.47, 63.15, 61.18, 54.77, 35.00.



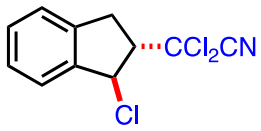
***anti*-methyl-2,2-dichloro-2-1-methoxy-2,3-dihydro-1*H*-inden-2-yl)acetate, 5'c ^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.38 (ddd, *J* = 7.3, 1.4, 0.8 Hz, 1H), 7.37 – 7.17 (m, 4H), 5.08 (d, *J* = 4.7 Hz, 1H), 3.88 (s, 3H), 3.52 (ddd, *J* = 8.9, 6.0, 4.6 Hz, 1H), 3.46 (s, 3H), 3.41 – 3.32 (m, 1H), 3.01 (dd, *J* = 16.7, 6.0 Hz, 1H).**^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 166.42, 141.17, 141.02, 129.05, 127.23, 124.97, 124.89, 87.06, 86.26, 56.74, 56.42, 54.60, 34.11.



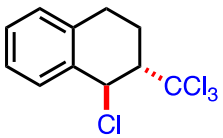
***anti*-1-bromo-2-(trichloromethyl)-2,3-dihydro-1*H*-indene, 5d,** the isolated product was obtained as a clear oil (2.3754 mmol, 0.7469 g, 48% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.50 – 7.39 (m, 1H), 7.36 – 7.27 (m, 3H), 7.25 – 7.17 (m, 2H), 5.79 (d, *J* = 3.4 Hz, 2H), 4.07 (ddd, *J* = 9.3, 4.4, 3.4 Hz, 1H), 3.63 (dd, *J* = 17.4, 9.3 Hz, 2H), 3.38 (dd, *J* = 17.5, 4.4 Hz, 2H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 141.99, 140.47, 129.60, 128.05, 126.11, 124.59, 101.67, 69.53, 53.15, 36.03.



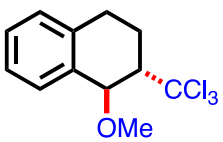
***anti*-1-methoxy-2-(trichloromethyl)-2,3-dihydro-1*H*-indene, 5'd,** the isolated product was obtained as a clear oil (1.2634 mmol, 0.3355 g, 25% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) *δ* 7.45 – 7.40 (m, 1H), 7.36 – 7.24 (m, 3H), 5.14 (t, *J* = 3.7 Hz, 1H), 3.60 (dtd, *J* = 8.6, 5.0, 3.4 Hz, 1H), 3.57 – 3.52 (m, 3H), 3.52 – 3.45 (m, 1H), 3.23 (dt, *J* = 17.4, 4.2 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) *δ* 141.26, 140.98, 129.31, 127.34, 125.36, 124.80, 87.39, 65.34, 56.68, 35.76.



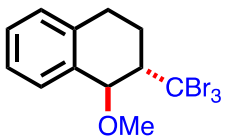
***anti*-2,2-dichloro-2-1-chloro-2,3-dihydro-1*H*-inden-2-yl)acetonitrile, 5e**, the isolated product was obtained as a clear oil (0.3861 mol, 1.1006 g, 76% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.48 – 7.41 (m, 1H), 7.34 (dq, *J* = 5.2, 1.7 Hz, 2H), 7.30 – 7.25 (m, 1H), 5.58 (dd, *J* = 5.0, 1.7 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.58 (dd, *J* = 16.8, 9.1 Hz, 1H), 3.27 (dd, *J* = 16.9, 6.2 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 140.69, 138.95, 129.94, 128.38, 125.65, 124.69, 114.67, 70.65, 63.25, 62.27, 34.90.



***anti*-1-chloro-2-(trichloromethyl)-1,2,3,4-tetrahydronaphthalene, 6a,** the isolated product was obtained as a clear oil (172.88 mmol, 0.0491 g, 34% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.34 (dd, J = 7.2, 1.9 Hz, 1H), 7.25 (td, J = 7.3, 1.7 Hz, 2H), 7.18 (dd, J = 6.8, 1.8 Hz, 1H), 5.52 (d, J = 1.9 Hz, 1H), 3.68 (ddd, J = 9.2, 7.0, 1.9 Hz, 1H), 3.03 (ddd, J = 15.7, 11.8, 4.2 Hz, 1H), 2.87 (dt, J = 15.4, 4.7 Hz, 1H), 2.66 (ddt, J = 13.7, 7.0, 4.6 Hz, 1H), 1.91 – 1.81 (m, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 138.79, 136.04, 129.48, 128.95, 128.13, 127.20, 102.55, 64.33, 57.65, 26.86, 26.75.



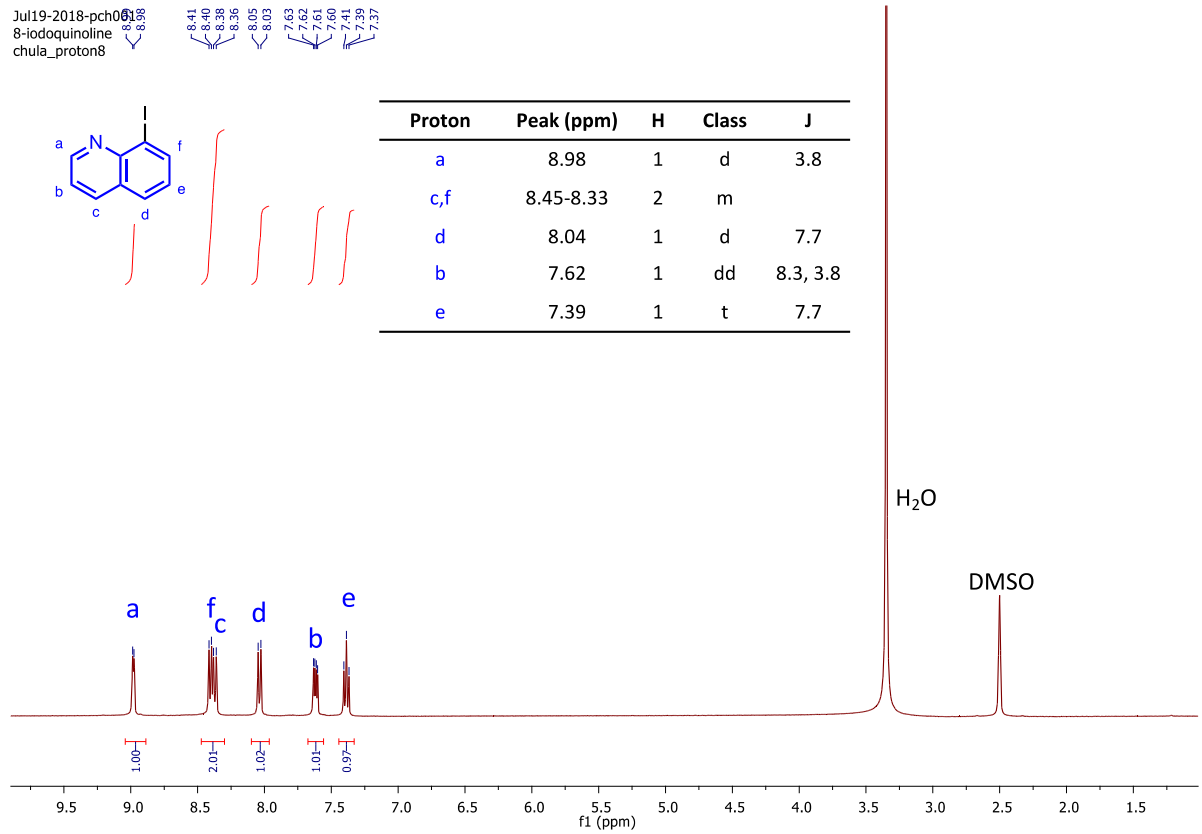
***anti*-1-methoxy-2-(trichloromethyl)-1,2,3,4-tetrahydronaphthalene, 6'a,** the isolated product was obtained as a clear oil (115.88 mmol, 0.0324 g, 23% yield). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.29 – 7.25 (m, 2H), 7.23 – 7.18 (m, 2H), 4.59 (d, *J* = 1.8 Hz, 1H), 3.31 (ddd, *J* = 10.2, 7.1, 1.9 Hz, 1H), 3.20 (s, 3H), 2.89 (dddd, *J* = 12.8, 11.8, 4.2, 2.4 Hz, 1H), 2.71 (dt, *J* = 14.8, 4.0 Hz, 1H), 2.54 (ddt, *J* = 13.2, 7.5, 3.9 Hz, 1H), 1.68 (tdd, *J* = 13.1, 10.2, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 140.14, 134.67, 130.23, 128.54, 127.82, 126.13, 103.38, 79.94, 62.02, 55.56, 27.59, 27.34.



***anti*-1-methoxy-2-(tribromomethyl)-1,2,3,4-tetrahydronaphthalene, 6'b ^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.29 – 7.25 (m, 2H), 7.21 (t, *J* = 6.7 Hz, 2H), 4.53 – 4.45 (m, 1H), 3.48 – 3.39 (m, 1H), 3.20 (d, *J* = 0.9 Hz, 3H), 2.98 – 2.90 (m, 1H), 2.75 – 2.64 (m, 2H). **^{13}C NMR** (126 MHz, CHLOROFORM-*D*) δ 140.41, 134.78, 130.54, 128.62, 127.70, 126.07, 81.68, 64.96, 55.53, 49.32, 30.17, 27.49.

^{1}H NMR and ^{13}C spectra

Fig. S16. ^{1}H NMR spectrum of 8-iodoquinoline



Proton	Peak (ppm)	H	Class	J
a	8.98	1	d	3.8
c,f	8.45-8.33	2	m	
d	8.04	1	d	7.7
b	7.62	1	dd	8.3, 3.8
e	7.39	1	t	7.7

Fig. S17. ^{13}C NMR spectrum of 8-iodoquinoline

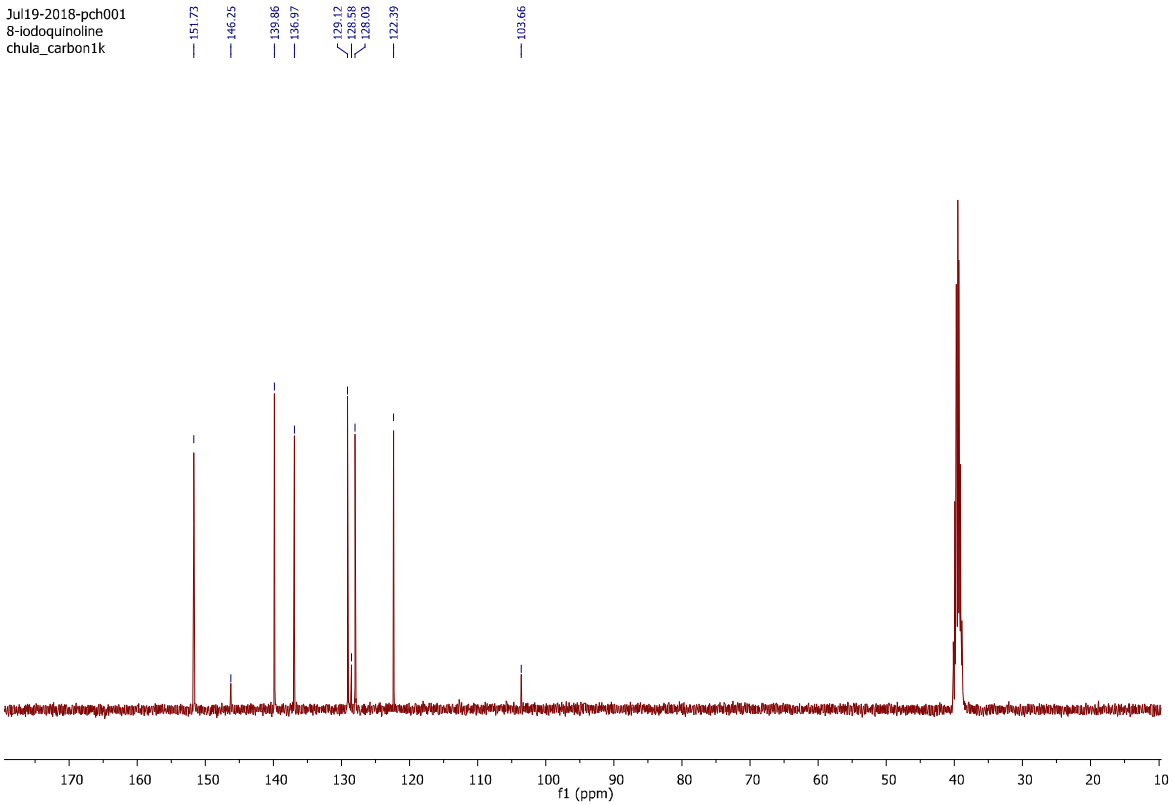
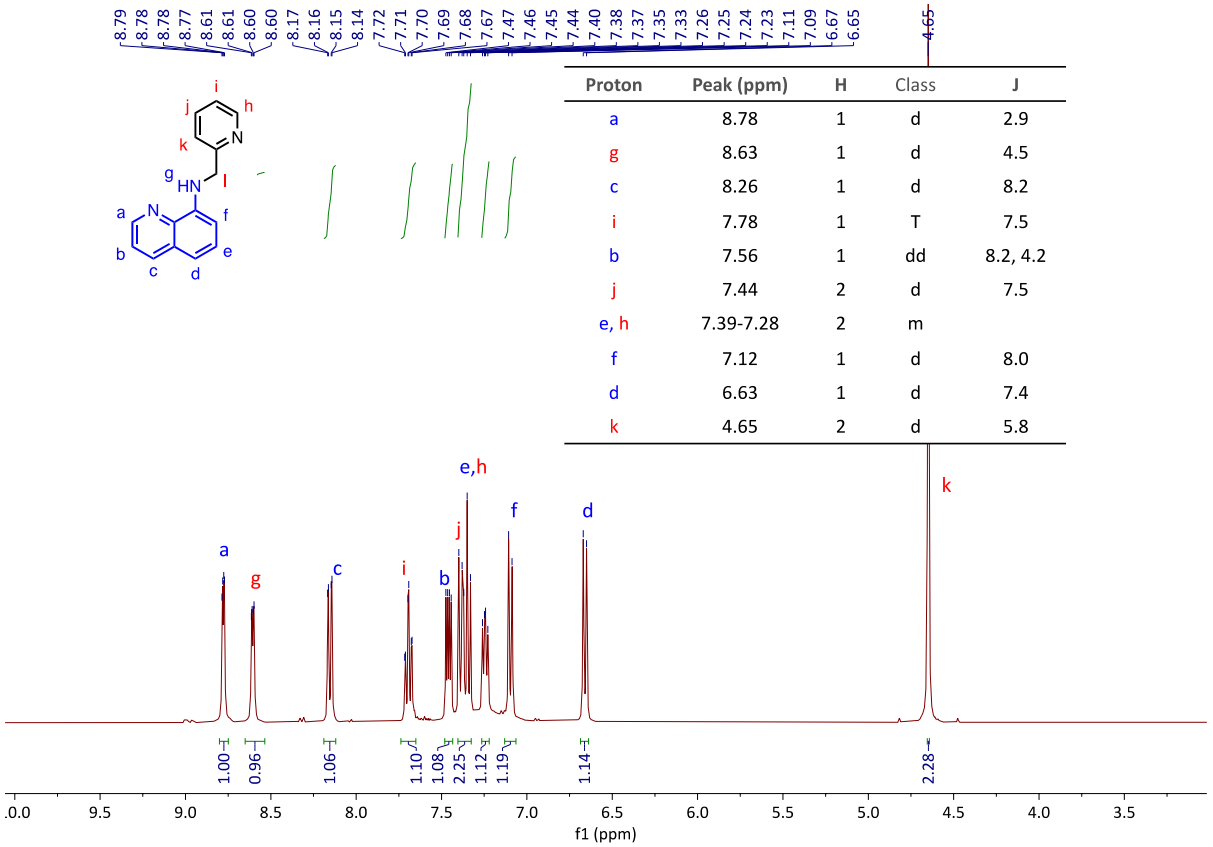


Fig. S18. ^{1}H NMR spectrum of *N*-(pyridin-2-ylmethyl)quinolin-8-amine, **QP**



Proton	Peak (ppm)	H	Class	J
a	8.78	1	d	2.9
g	8.63	1	d	4.5
c	8.26	1	d	8.2
i	7.78	1	T	7.5
b	7.56	1	dd	8.2, 4.2
j	7.44	2	d	7.5
e, h	7.39-7.28	2	m	
f	7.12	1	d	8.0
d	6.63	1	d	7.4
k	4.65	2	d	5.8

Fig. S19. ^{13}C NMR spectrum of *N*-(pyridin-2-ylmethyl)quinolin-8-amine, **QP**

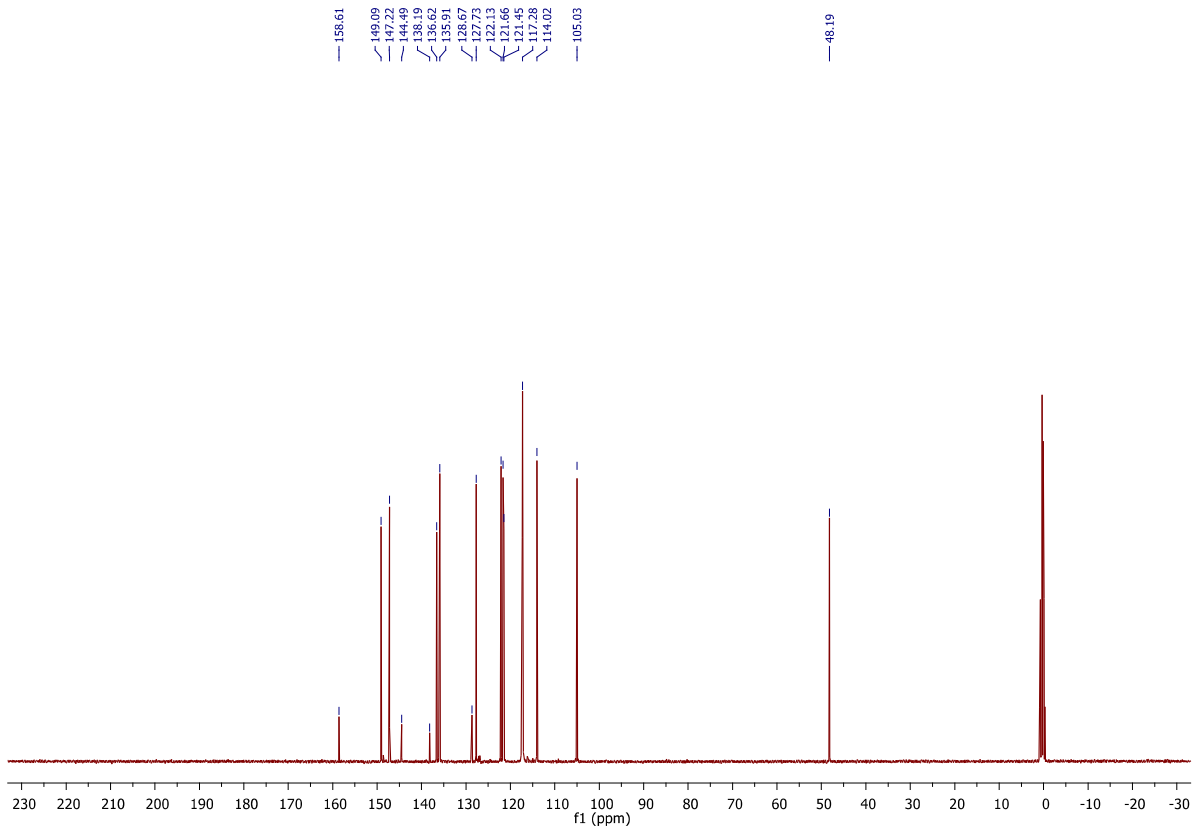
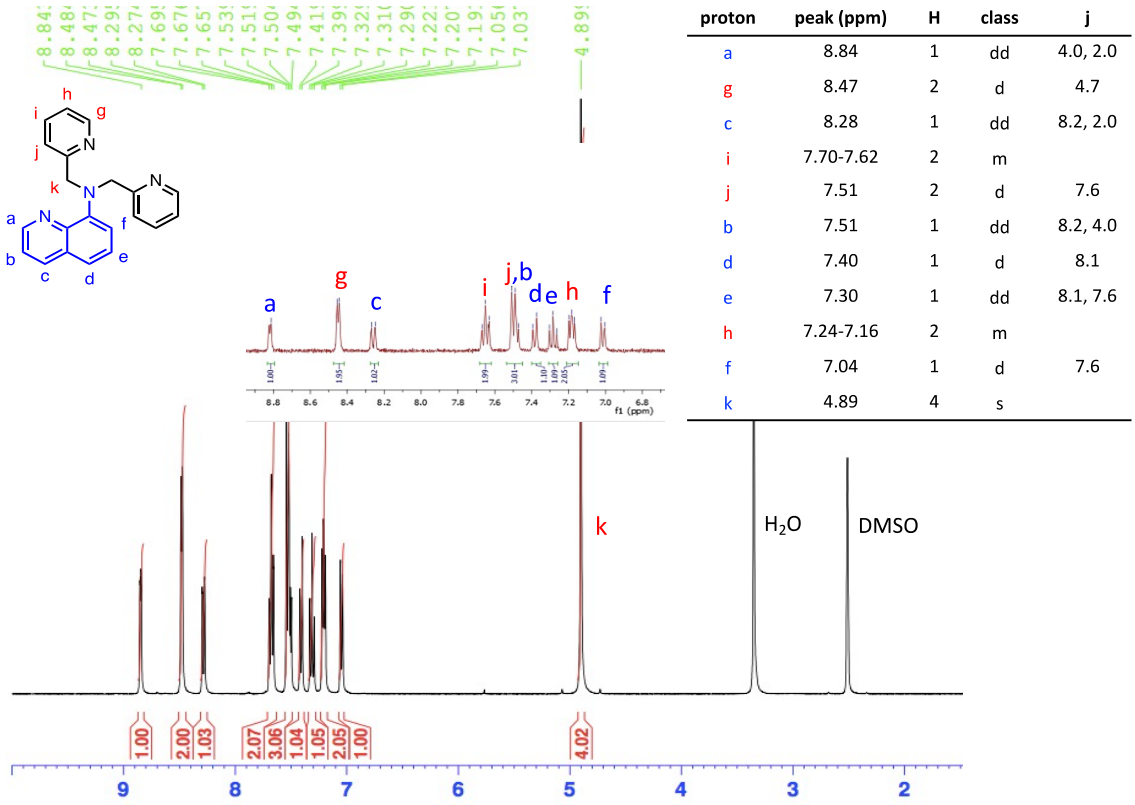


Fig. S20. ^{1}H NMR spectrum of *N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine, **1Q**



proton	peak (ppm)	H	class	j
a	8.84	1	dd	4.0, 2.0
g	8.47	2	d	4.7
c	8.28	1	dd	8.2, 2.0
i	7.70-7.62	2	m	
j	7.51	2	d	7.6
b	7.51	1	dd	8.2, 4.0
d	7.40	1	d	8.1
e	7.30	1	dd	8.1, 7.6
h	7.24-7.16	2	m	
f	7.04	1	d	7.6
k	4.89	4	s	

Fig. S21. ^{13}C NMR spectrum of *N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine, **1Q**

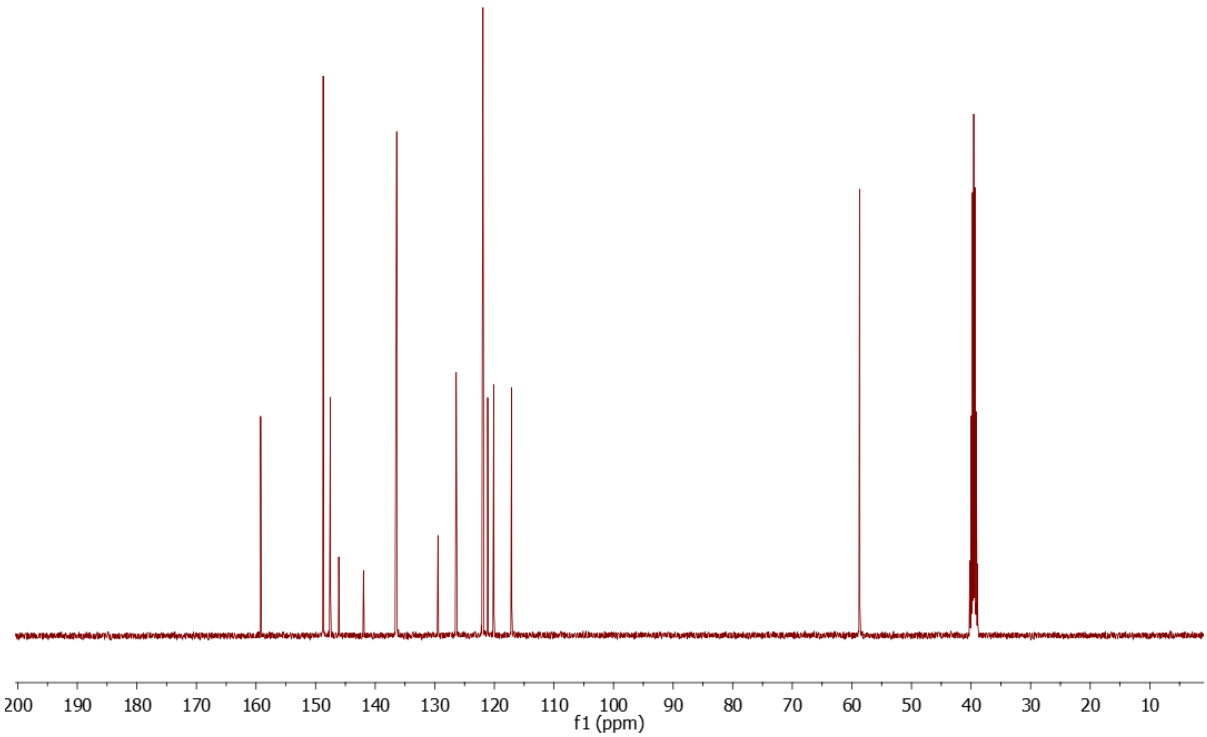
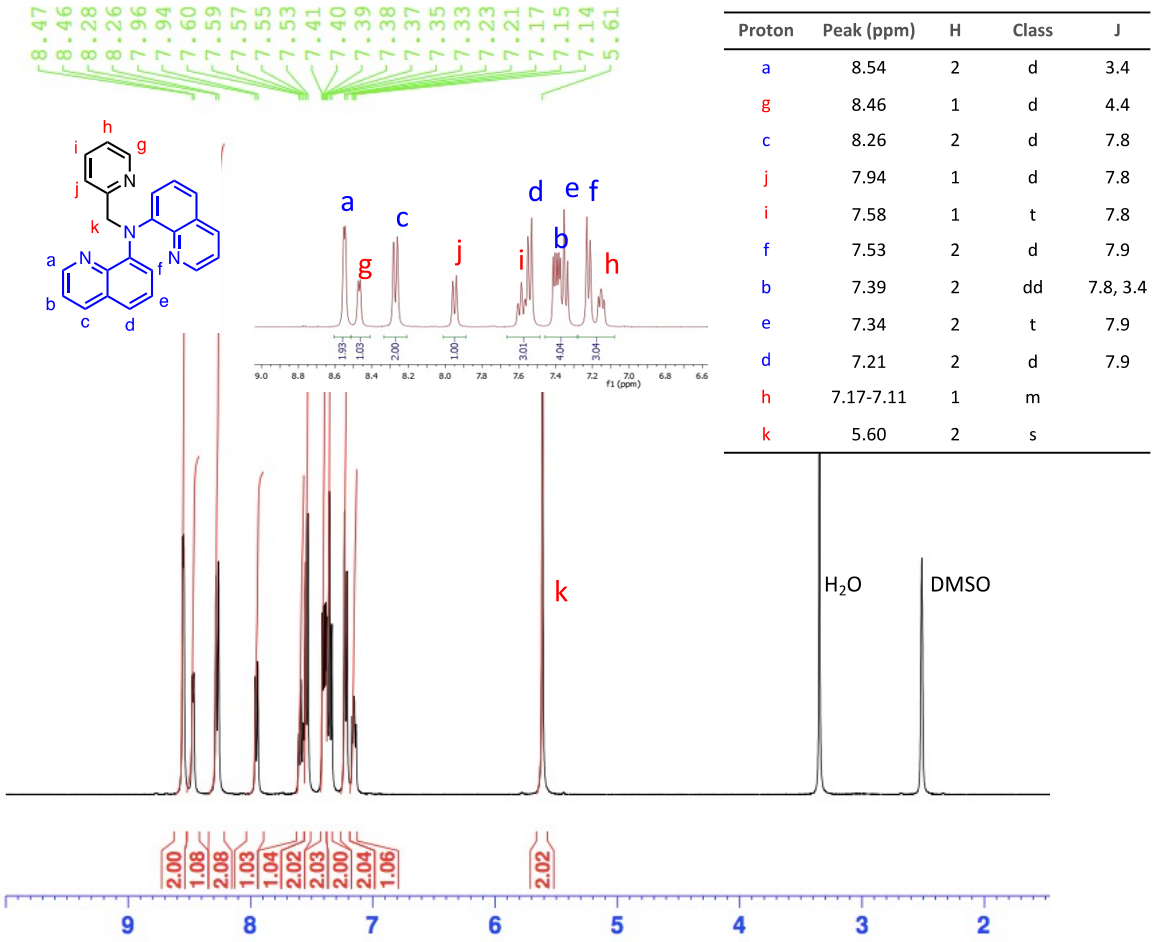


Fig. S22. ^{1}H NMR spectrum of *N*-(pyridin-2-ylmethyl)-*N*-(quinolin-8-yl)quinolin-8-amine, **2Q**



Proton	Peak (ppm)	H	Class	J
a	8.54	2	d	3.4
g	8.46	1	d	4.4
c	8.26	2	d	7.8
j	7.94	1	d	7.8
i	7.58	1	t	7.8
f	7.53	2	d	7.9
b	7.39	2	dd	7.8, 3.4
e	7.34	2	t	7.9
d	7.21	2	d	7.9
h	7.17-7.11	1	m	
k	5.60	2	s	

Fig. S23. ^{13}C NMR spectrum of *N*-(pyridin-2-ylmethyl)-*N*-(quinolin-8-yl)quinolin-8-amine, **2Q**

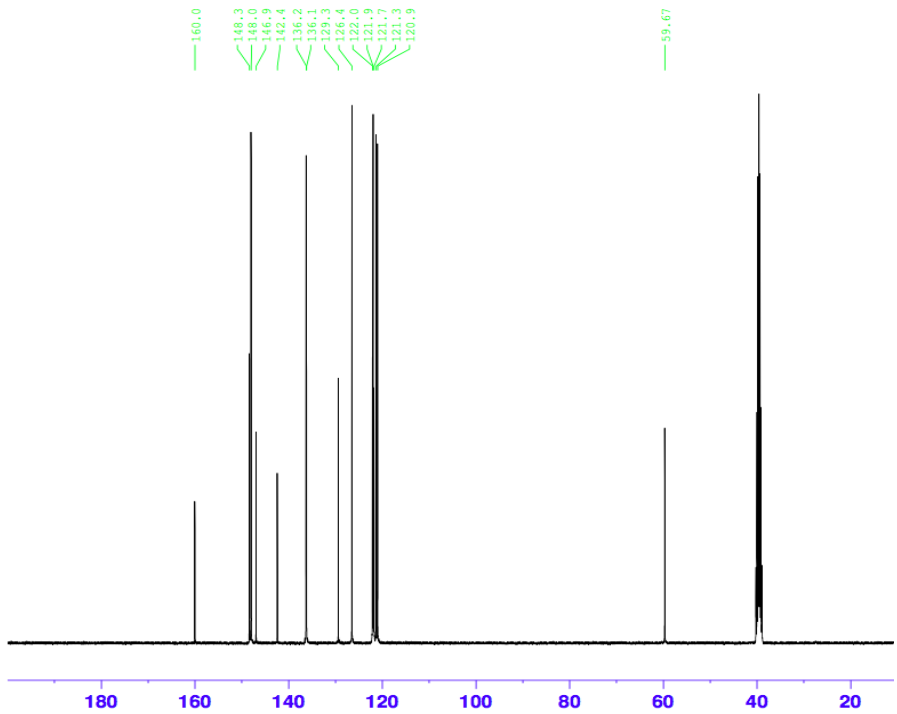
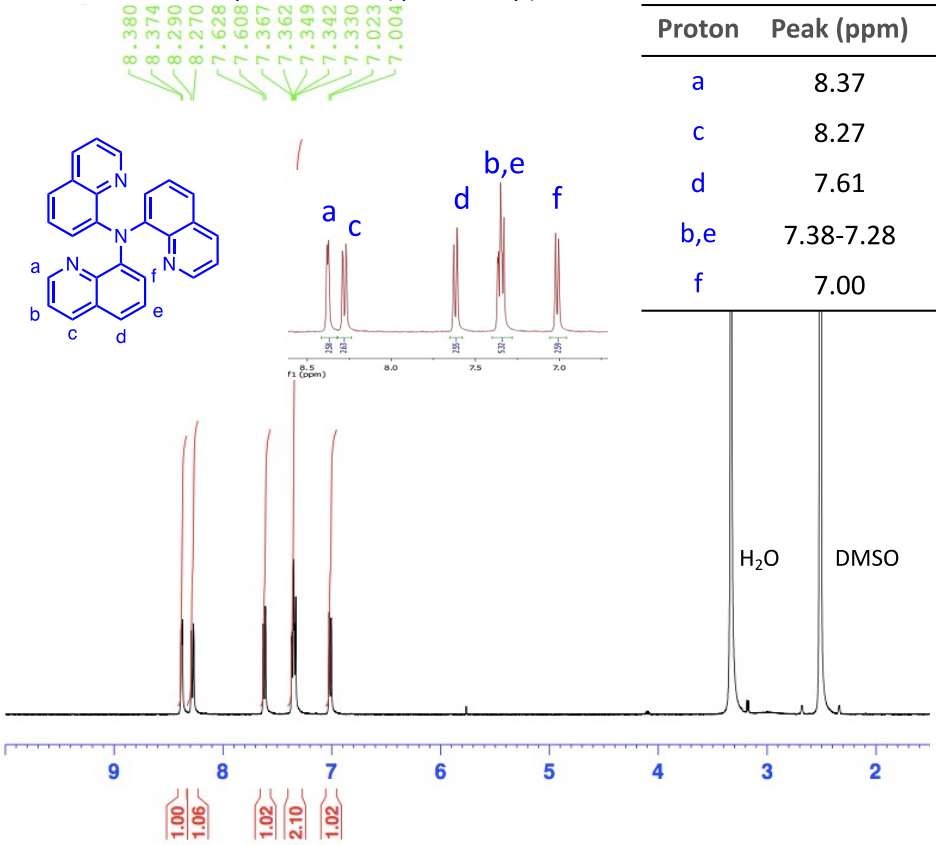


Fig. S24. ^{1}H NMR spectrum of tri(quinolin-8-yl)amine, **3Q**



Proton	Peak (ppm)	H	Class	J
a	8.37	3	d	2.7
c	8.27	3	d	8.2
d	7.61	3	d	8.0
b,e	7.38-7.28	3	m	
f	7.00	3	d	7.5

Fig. S25. ^{13}C NMR spectrum of tri(quinolin-8-yl)amine, **3Q**

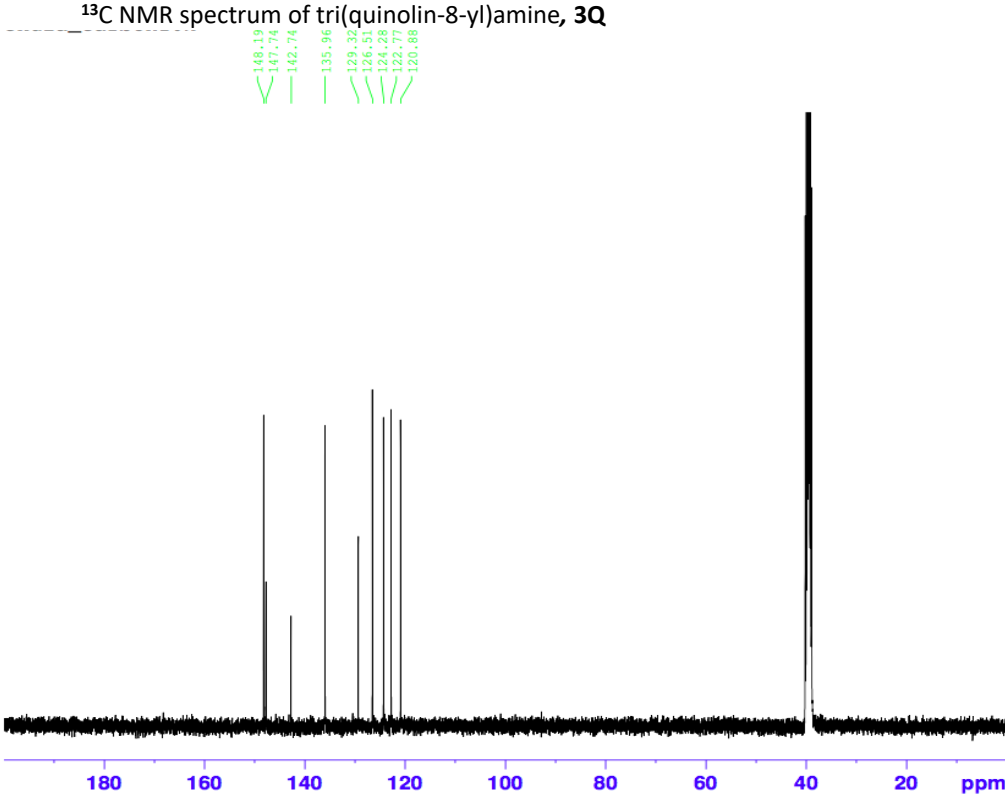
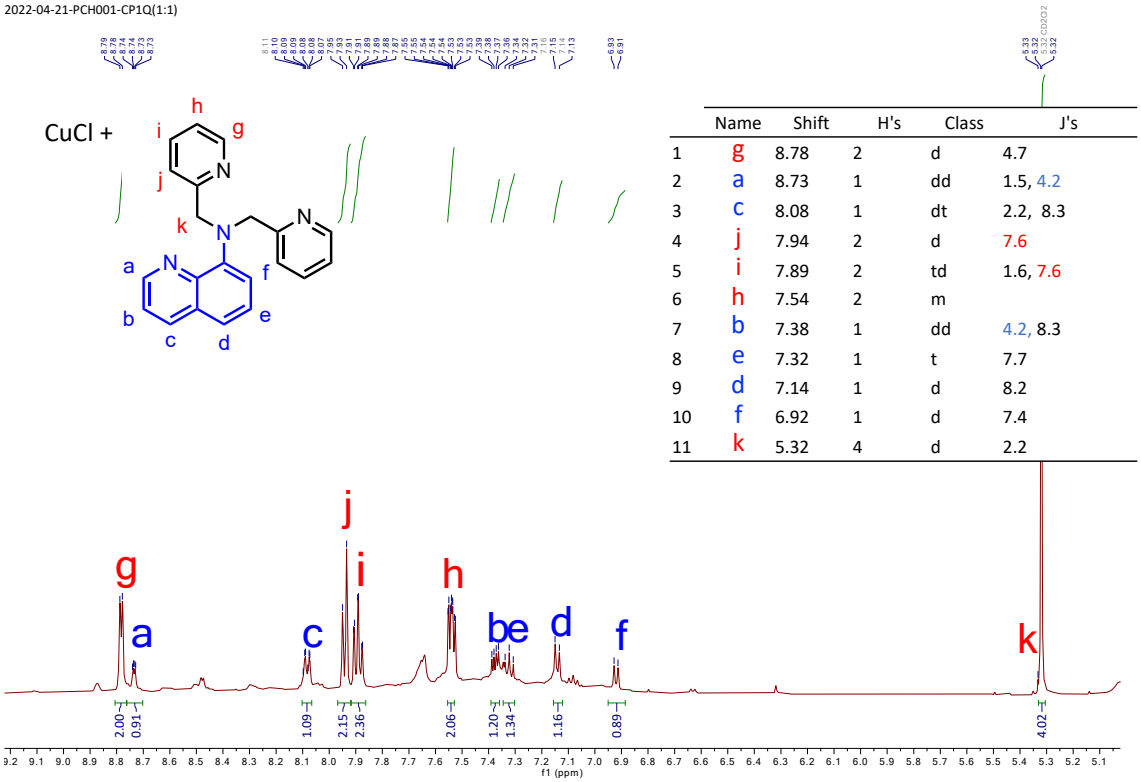


Fig. S26. ^{1}H NMR spectrum of *in situ* CuCl and **1Q**



		Name	Shift	H's	Class	J's
1	g	8.78	2	d	4.7	
2	a	8.73	1	dd	1.5, 4.2	
3	c	8.08	1	dt	2.2, 8.3	
4	j	7.94	2	d	7.6	
5	i	7.89	2	td	1.6, 7.6	
6	h	7.54	2	m		
7	b	7.38	1	dd	4.2, 8.3	
8	e	7.32	1	t	7.7	
9	d	7.14	1	d	8.2	
10	f	6.92	1	d	7.4	
11	k	5.32	4	d	2.2	

Fig. S27. ^{1}H-^{1}H COSY NMR spectrum of *in situ* CuCl and **1Q**

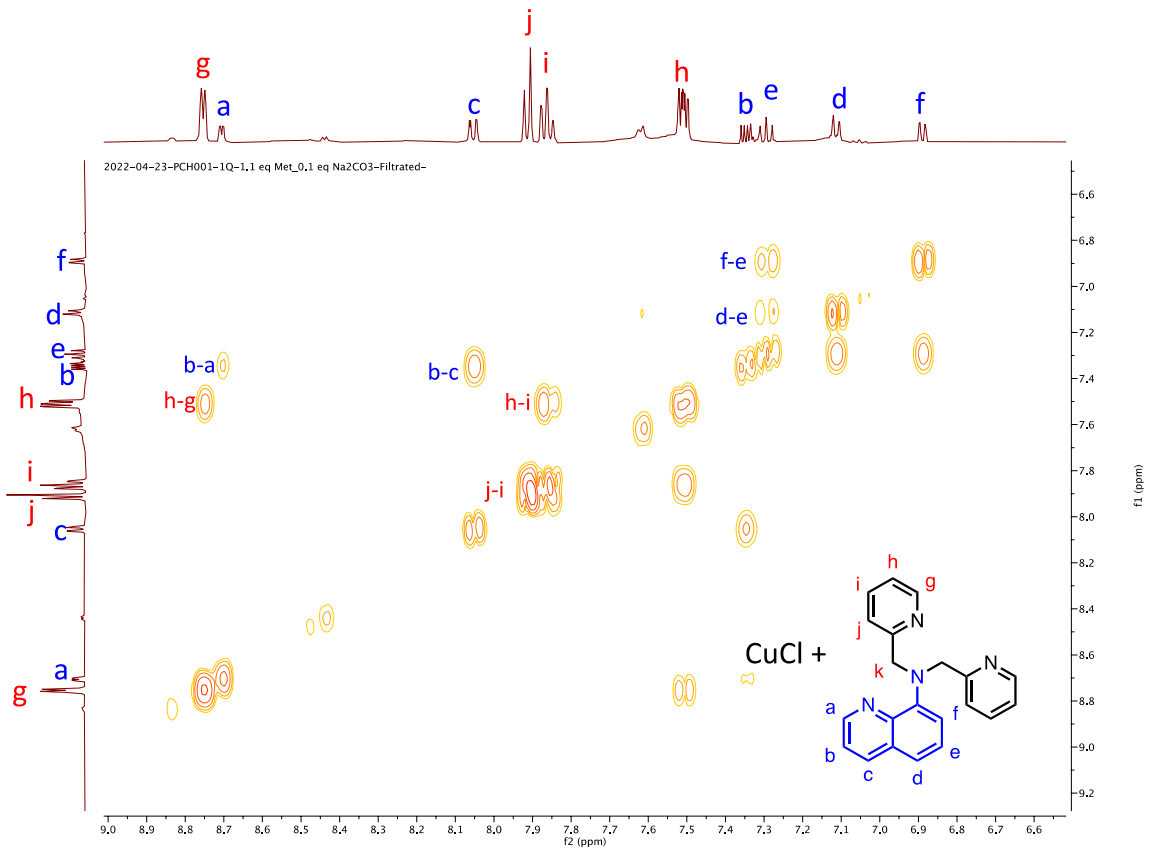
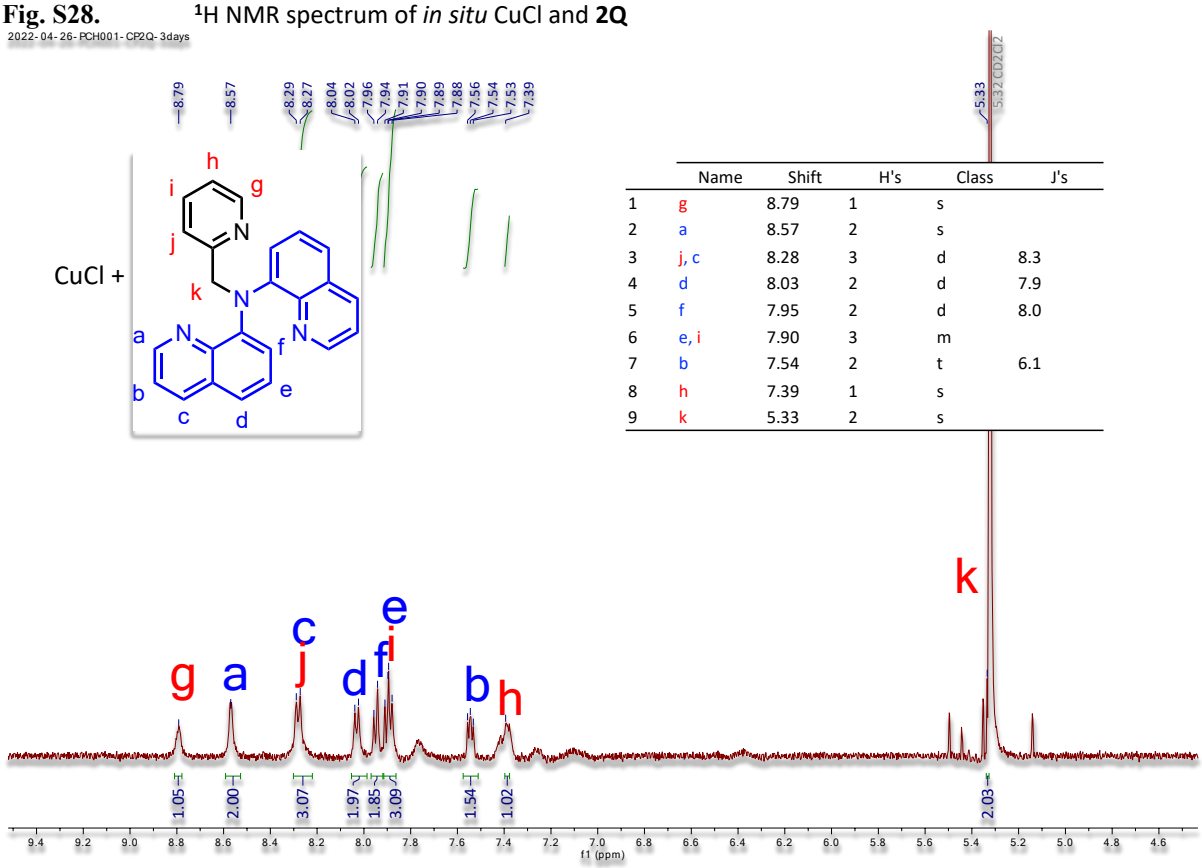
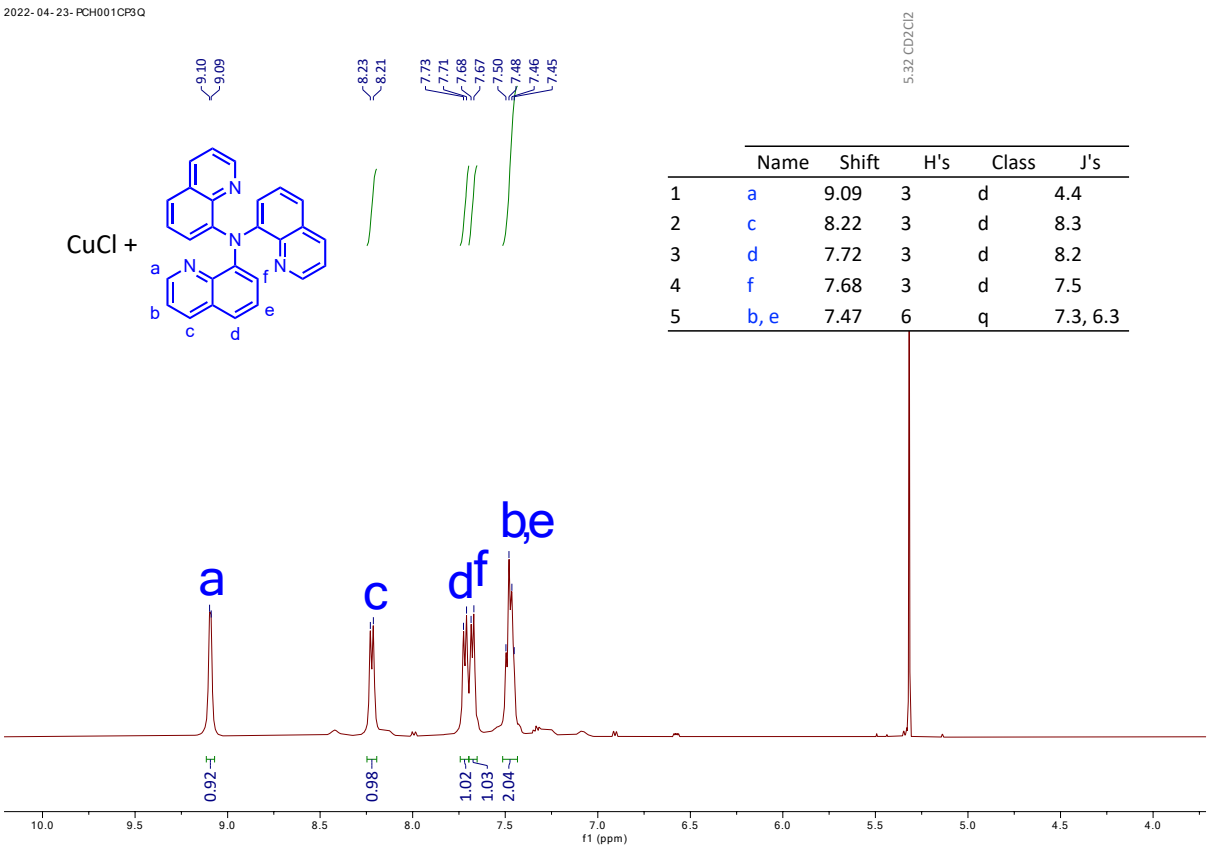


Fig. S28. ^{1}H NMR spectrum of *in situ* CuCl and **2Q**



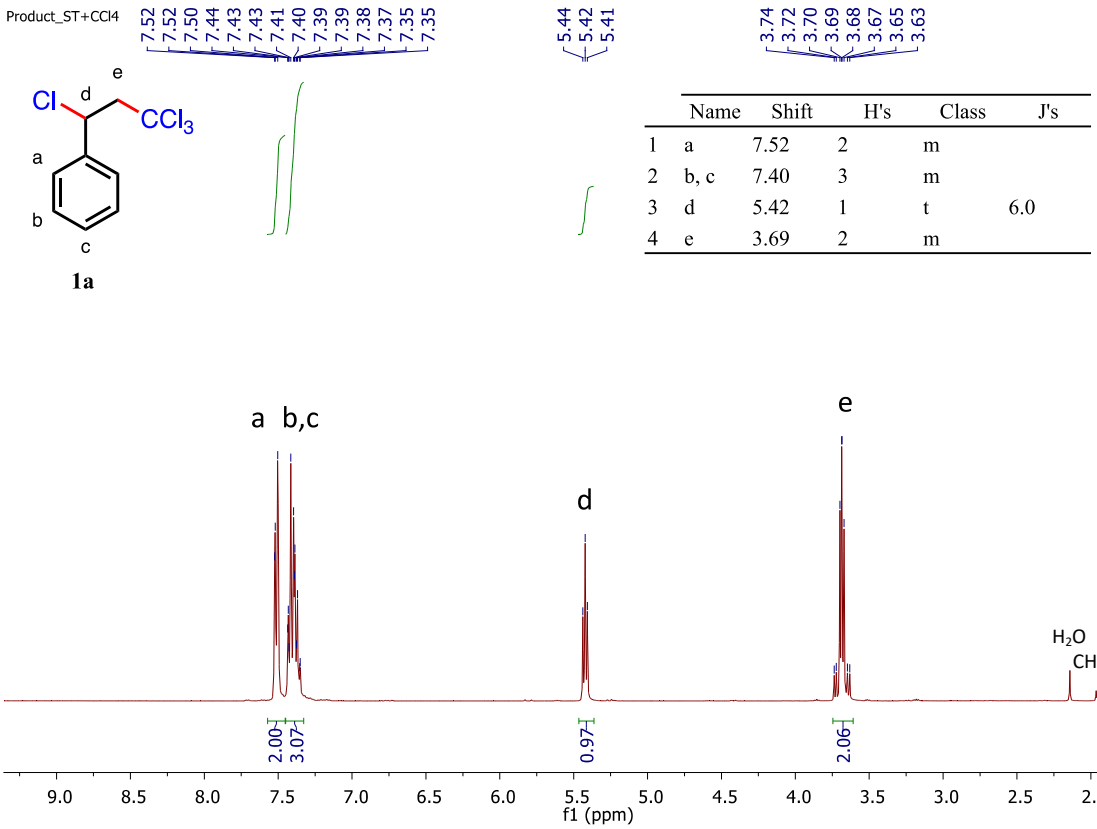
	Name	Shift	H's	Class	J's
1	g	8.79	1	s	
2	a	8.57	2	s	
3	j, c	8.28	3	d	8.3
4	d	8.03	2	d	7.9
5	f	7.95	2	d	8.0
6	e, i	7.90	3	m	
7	b	7.54	2	t	6.1
8	h	7.39	1	s	
9	k	5.33	2	s	

Fig. S29. ^{1}H NMR spectrum of *in situ* CuCl and **3Q**



	Name	Shift	H's	Class	J's
1	a	9.09	3	d	4.4
2	c	8.22	3	d	8.3
3	d	7.72	3	d	8.2
4	f	7.68	3	d	7.5
5	b, e	7.47	6	q	7.3, 6.3

Fig. S30. ^{1}H NMR spectrum of (1,3,3,3-tetrachloropropyl)benzene, **1a**.



	Name	Shift	H's	Class	J's
1	a	7.52	2	m	
2	b, c	7.40	3	m	
3	d	5.42	1	t	6.0
4	e	3.69	2	m	

Fig. S31. ^{13}C NMR spectrum of (1,3,3,3-tetrachloropropyl)benzene, **1a**.

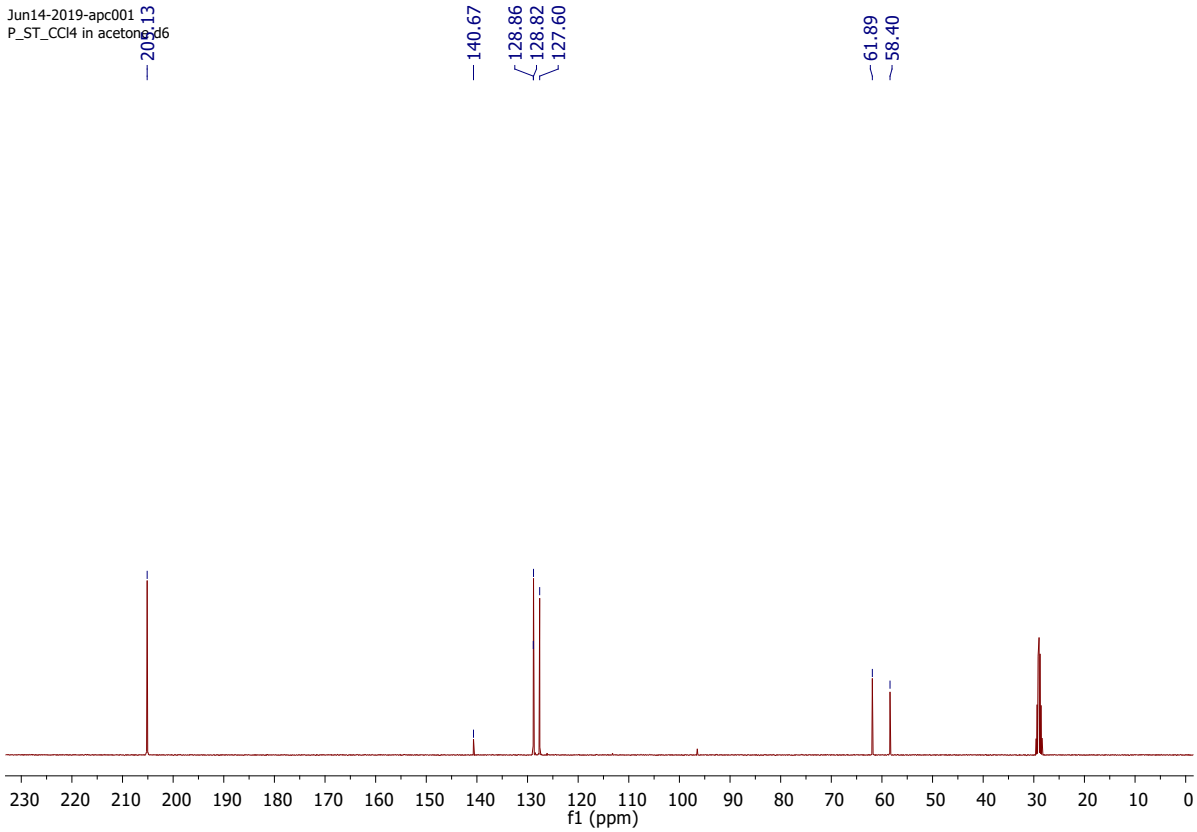
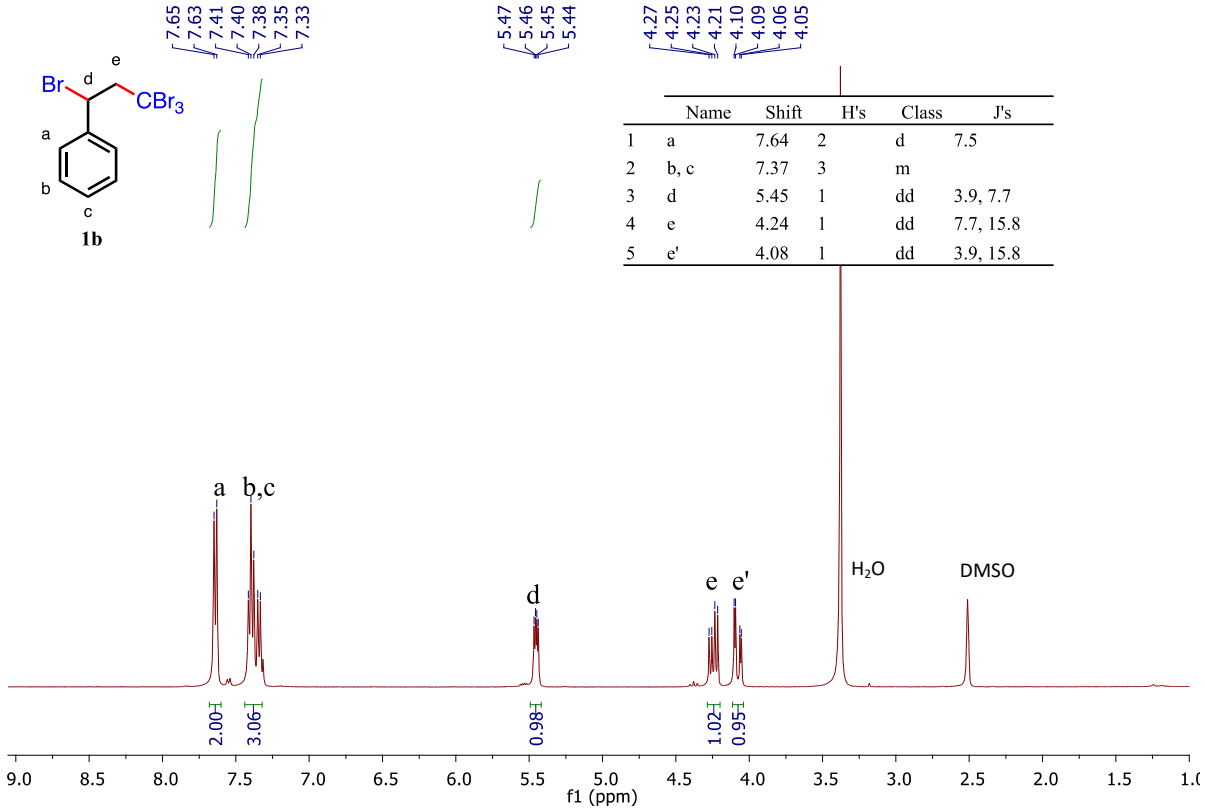


Fig. S32. ^{1}H NMR spectrum of (1,3,3,3-tetrabromopropyl)benzene, **1b**.



	Name	Shift	H's	Class	J's
1	a	7.64	2	d	7.5
2	b, c	7.37	3	m	
3	d	5.45	1	dd	3.9, 7.7
4	e	4.24	1	dd	7.7, 15.8
5	e'	4.08	1	dd	3.9, 15.8

Fig. S33. ^{13}C NMR spectrum of (1,3,3,3-tetrabromopropyl)benzene, **1b**.

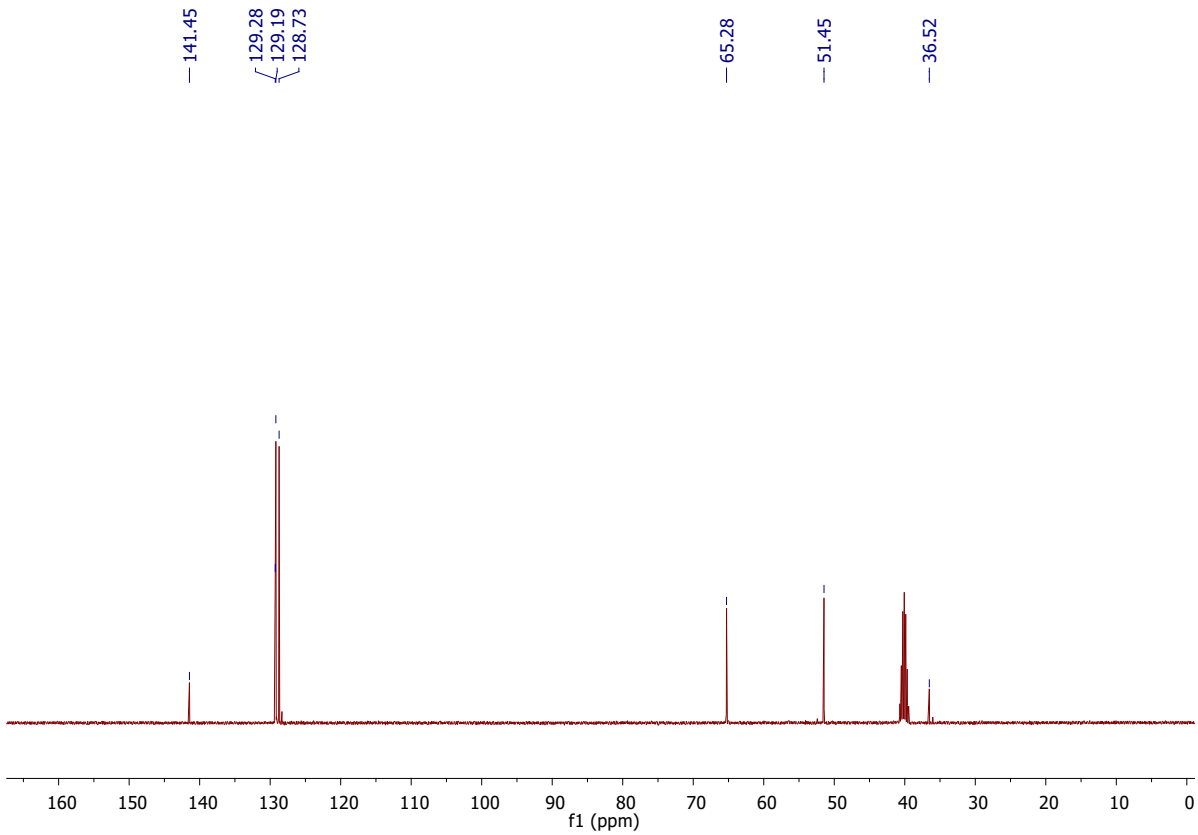


Fig. S34. ^{1}H NMR spectrum of methyl 2,2,4-trichloro-4-phenylbutanoate, **1c**.

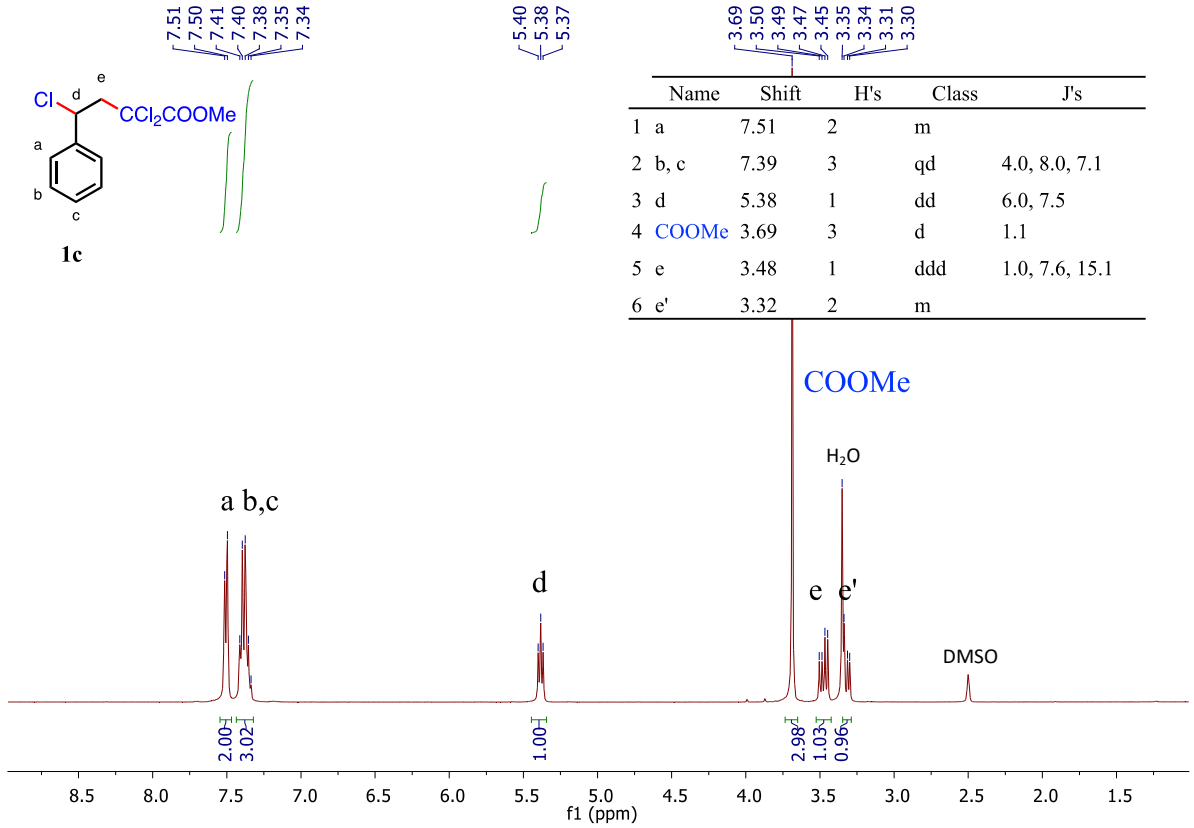


Fig. S35. ^{13}C NMR spectrum of methyl 2,2,4-trichloro-4-phenylbutanoate, **1c**.

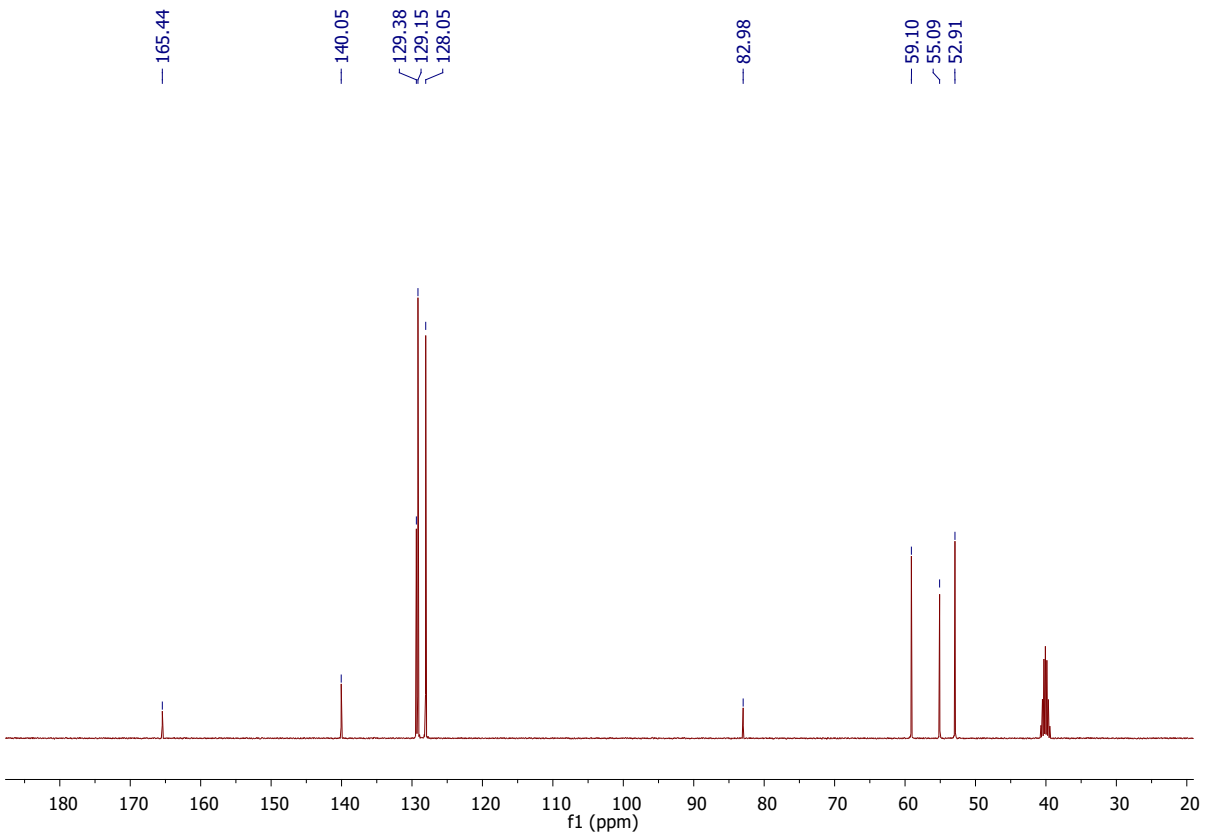
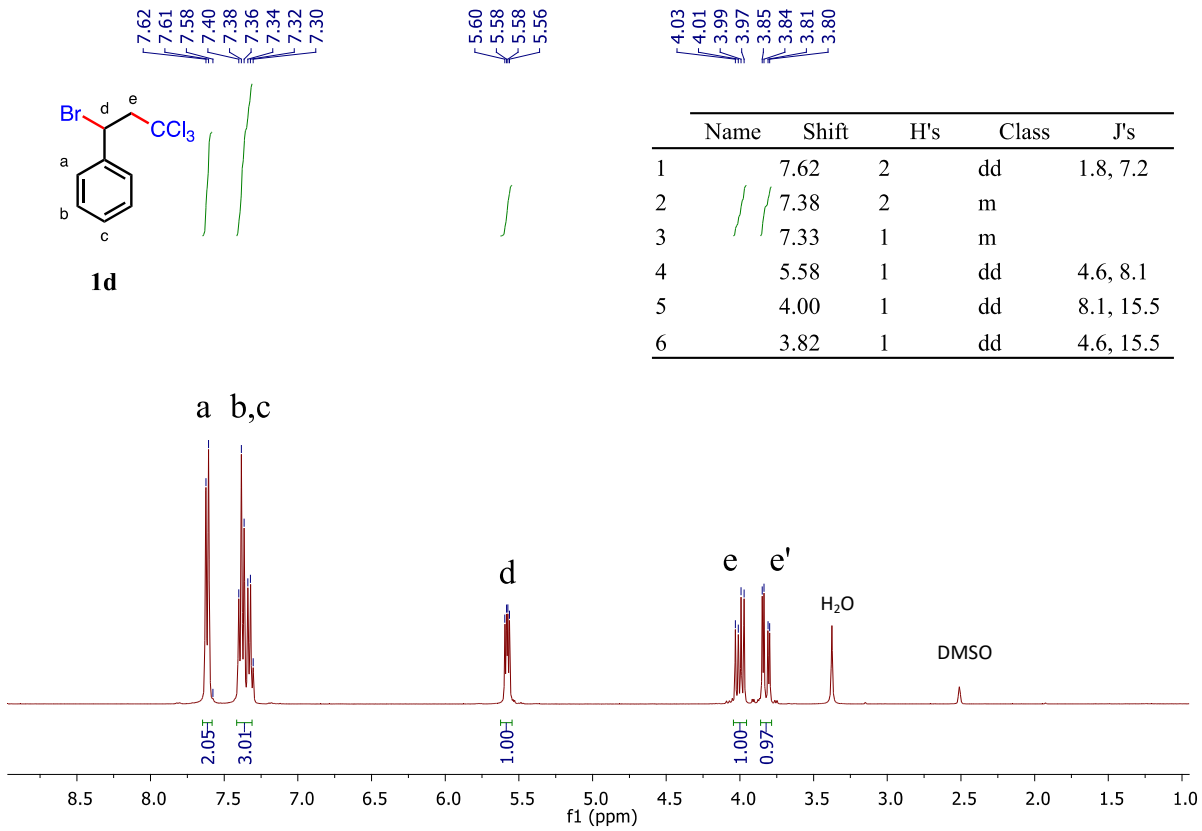


Fig. S36. ^{1}H NMR spectrum of (1-bromo-3,3,3-trichloropropyl)benzene, **1d**.



	Name	Shift	H's	Class	J's
1		7.62	2	dd	1.8, 7.2
2		7.38	2	m	
3		7.33	1	m	
4		5.58	1	dd	4.6, 8.1
5		4.00	1	dd	8.1, 15.5
6		3.82	1	dd	4.6, 15.5

Fig. S37. ^{13}C NMR spectrum of (1-bromo-3,3,3-trichloropropyl)benzene, **1d**.

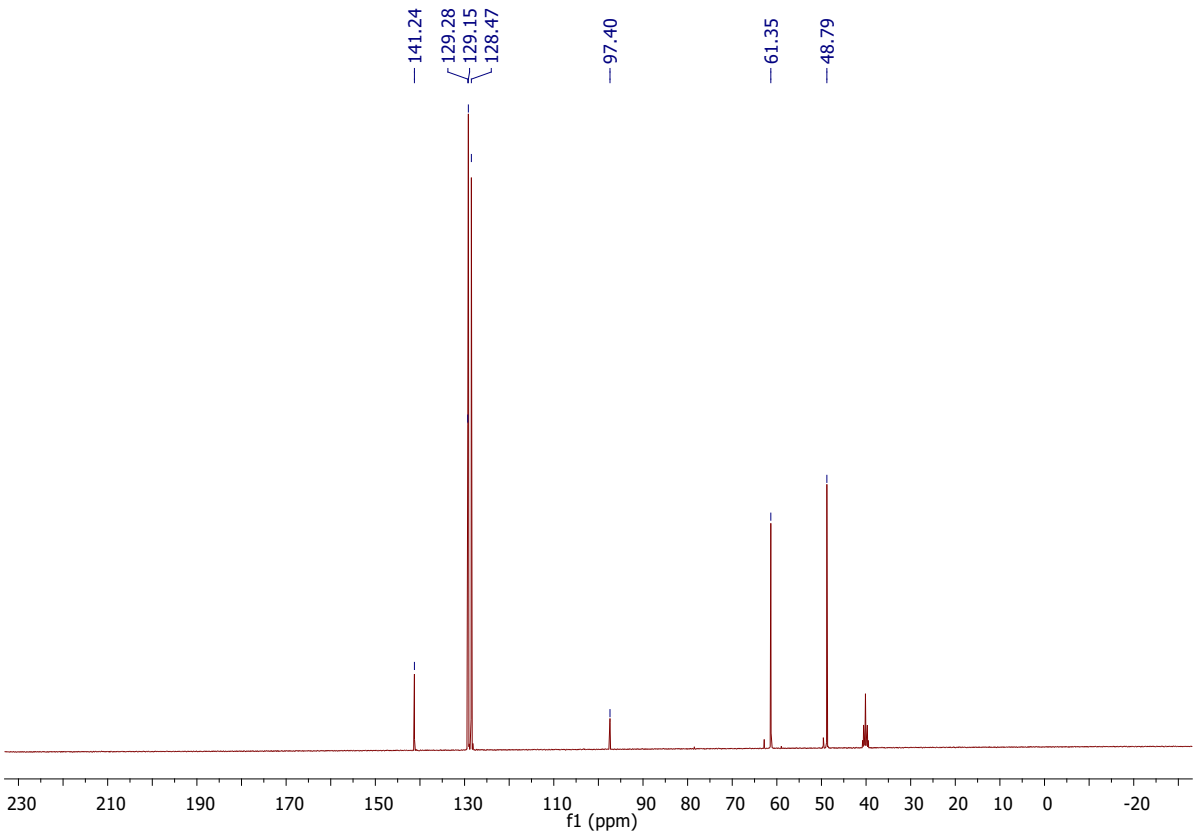
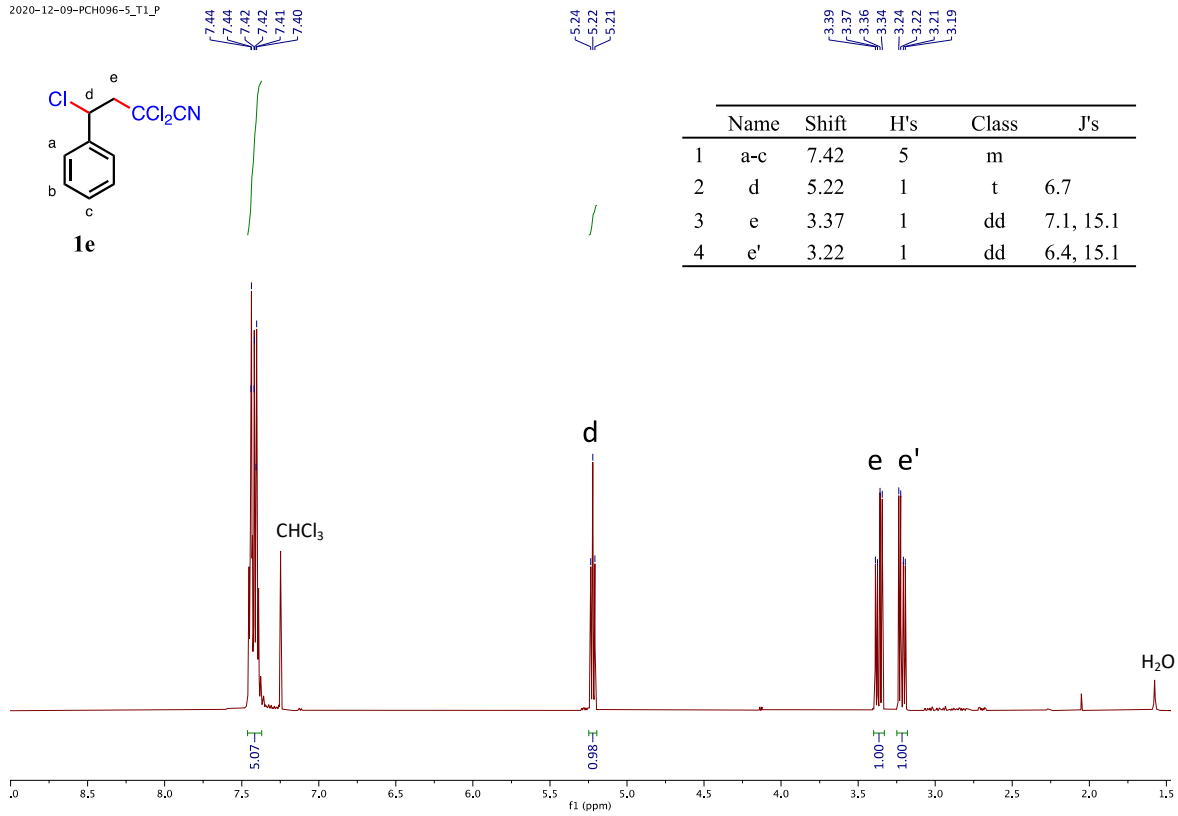


Fig. S38. ^{1}H NMR spectrum of 2,2-dichloro-2-(1-chloro-2,3-dihydro-1*H*-inden-2-yl) acetonitrile, **1e**.



	Name	Shift	H's	Class	J's
1	a-c	7.42	5	m	
2	d	5.22	1	t	6.7
3	e	3.37	1	dd	7.1, 15.1
4	e'	3.22	1	dd	6.4, 15.1

Fig. S39. ^{13}C NMR spectrum of 2,2-dichloro-2-(1-chloro-2,3-dihydro-1*H*-inden-2-yl) acetonitrile, **1e**.

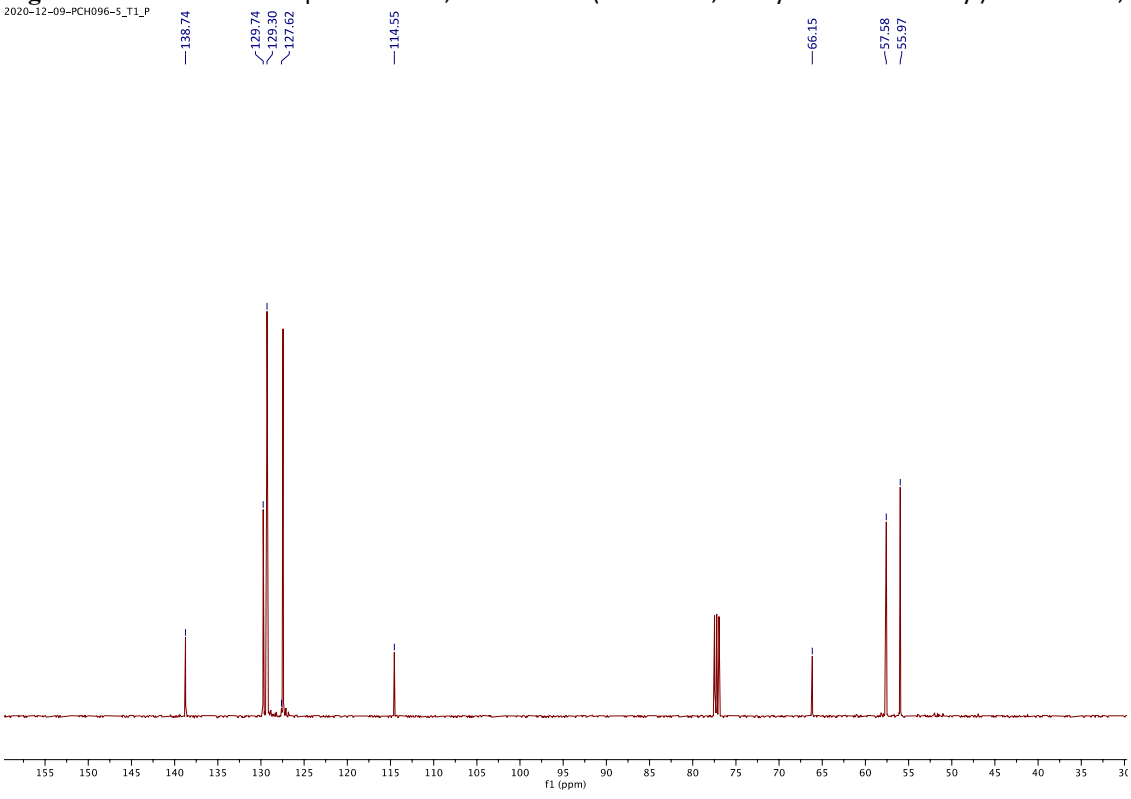
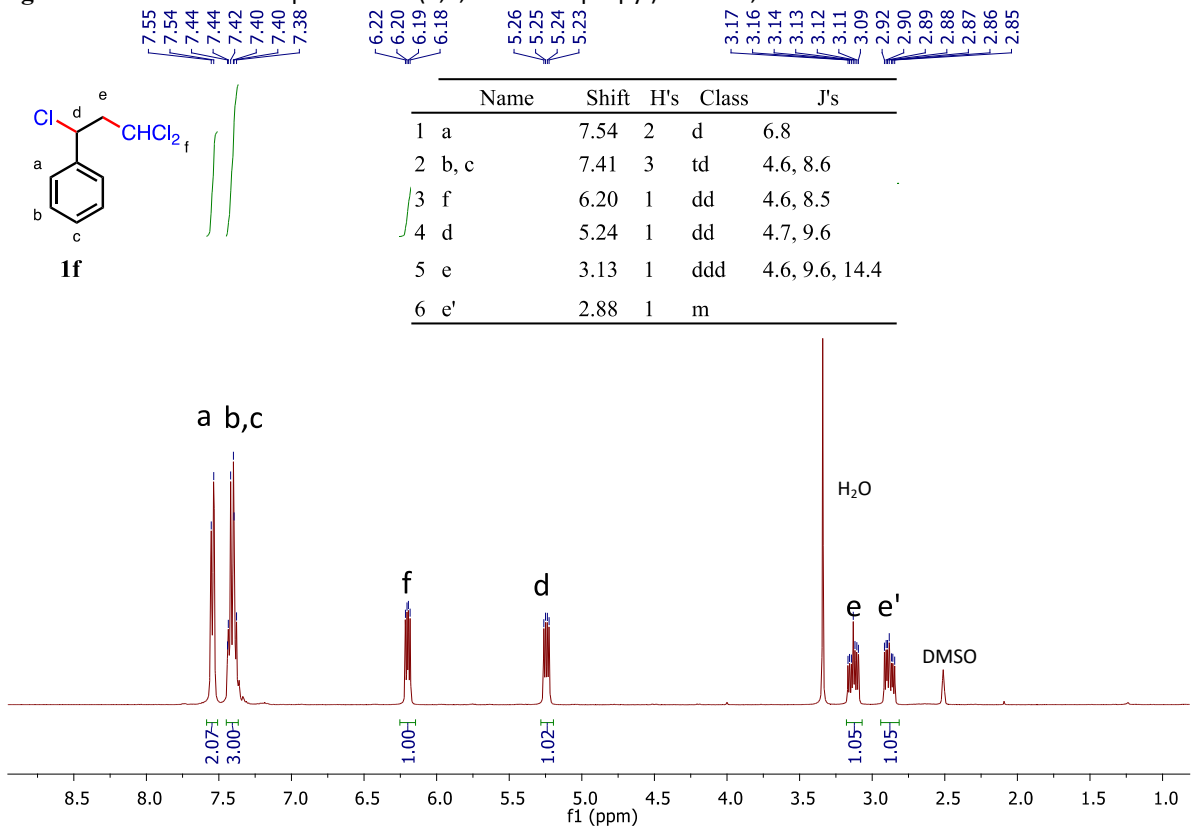


Fig. S40. ^{1}H NMR spectrum of (1,3,3-trichloropropyl)benzene, **1f**.



	Name	Shift	H's	Class	J's
1	a	7.54	2	d	6.8
2	b, c	7.41	3	td	4.6, 8.6
3	f	6.20	1	dd	4.6, 8.5
4	d	5.24	1	dd	4.7, 9.6
5	e	3.13	1	ddd	4.6, 9.6, 14.4
6	e'	2.88	1	m	

Fig. S41. ^{13}C NMR spectrum of (1,3,3-trichloropropyl)benzene, **1f**.

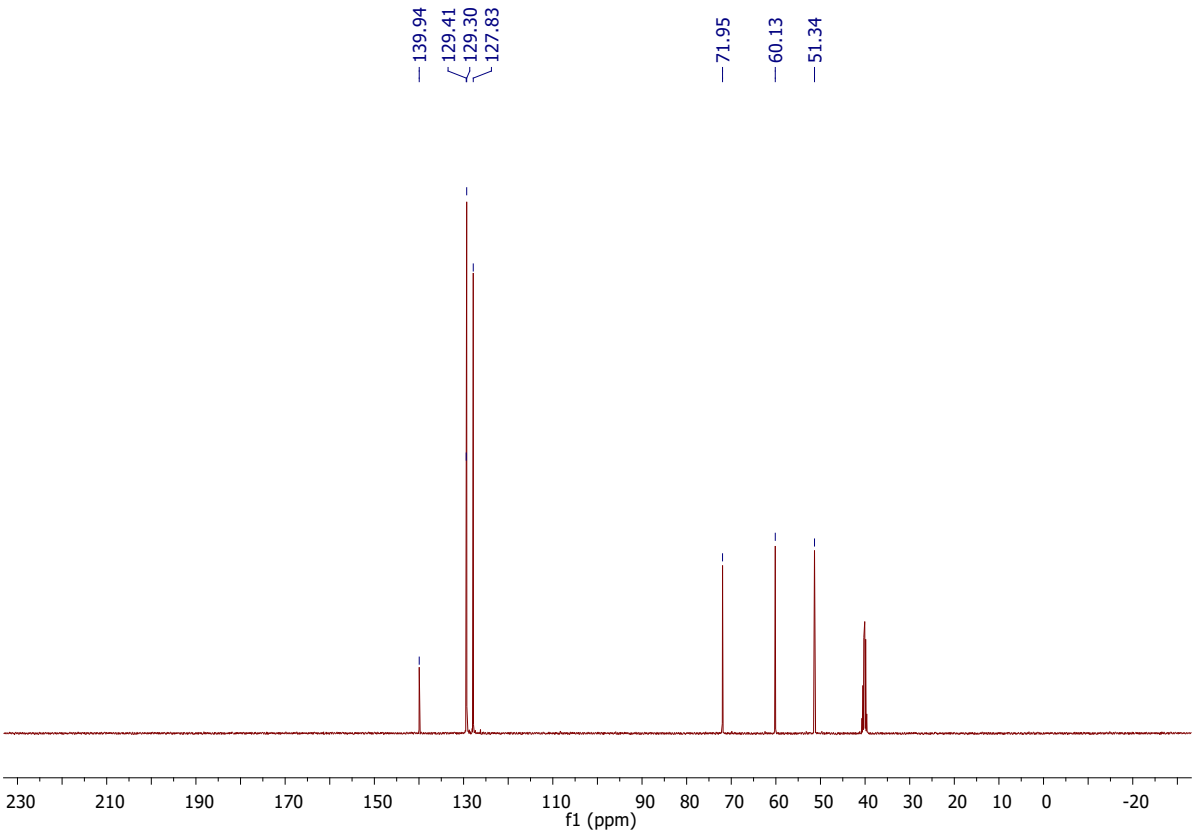
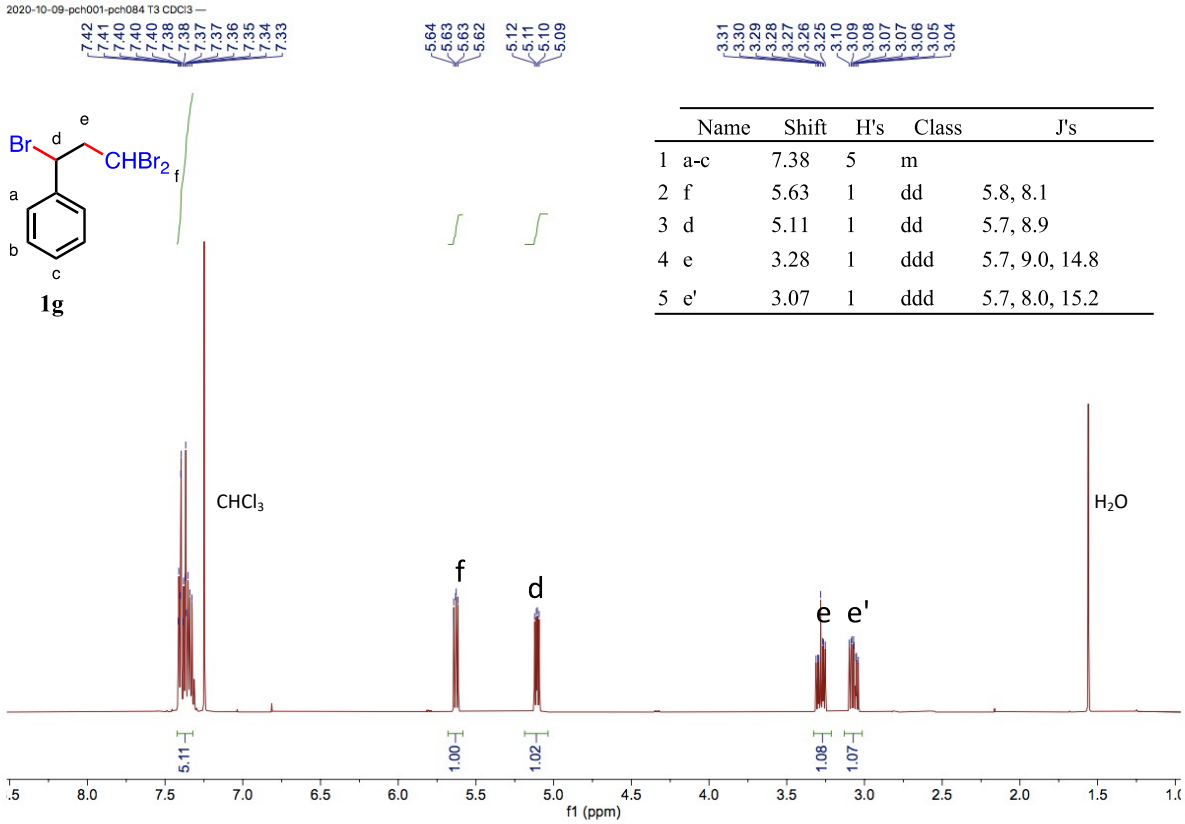


Fig. S42. ^{1}H NMR spectrum of (1,3,3-tribromopropyl)benzene, **1g**.



	Name	Shift	H's	Class	J's
1	a-c	7.38	5	m	
2	f	5.63	1	dd	5.8, 8.1
3	d	5.11	1	dd	5.7, 8.9
4	e	3.28	1	ddd	5.7, 9.0, 14.8
5	e'	3.07	1	ddd	5.7, 8.0, 15.2

Fig. S43. ^{13}C NMR spectrum of (1,3,3-tribromopropyl)benzene, **1g**.

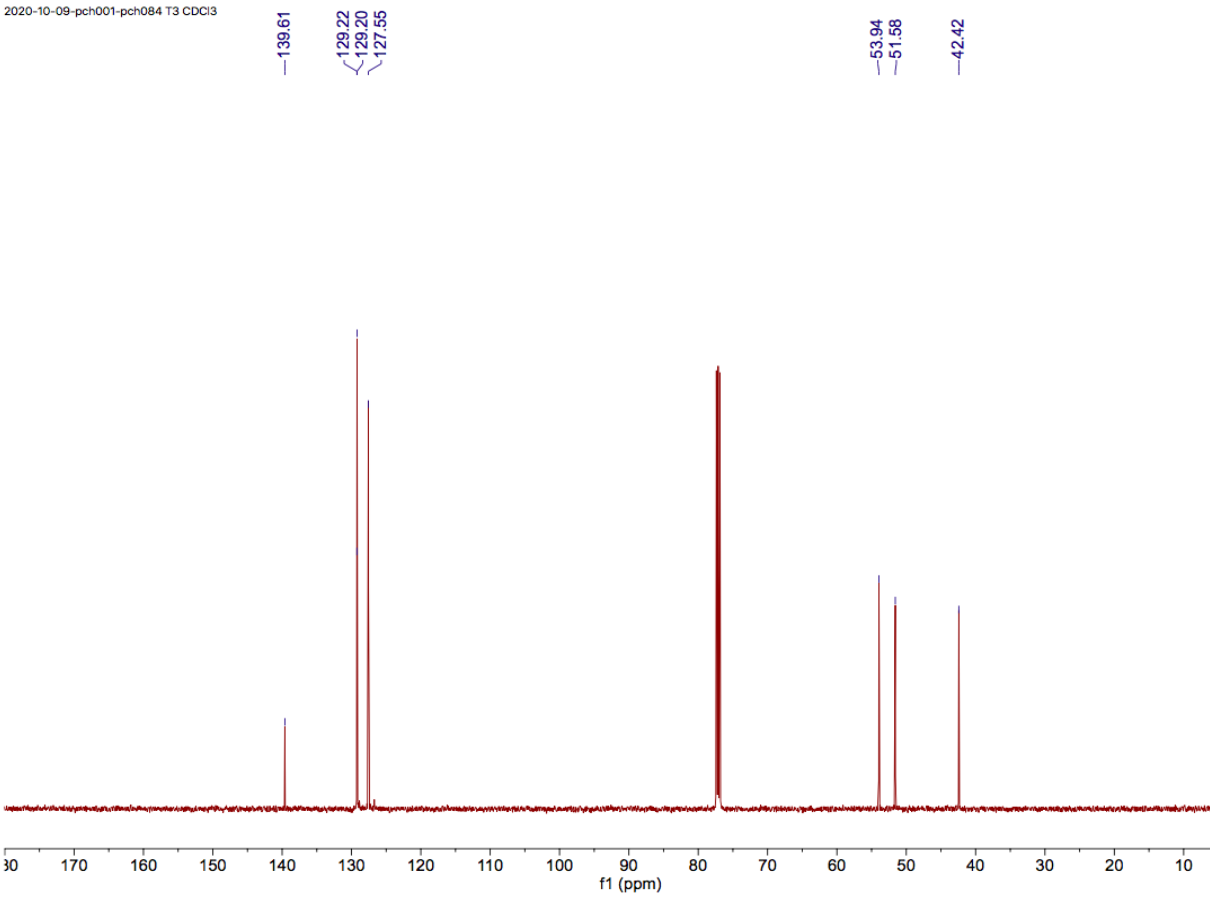
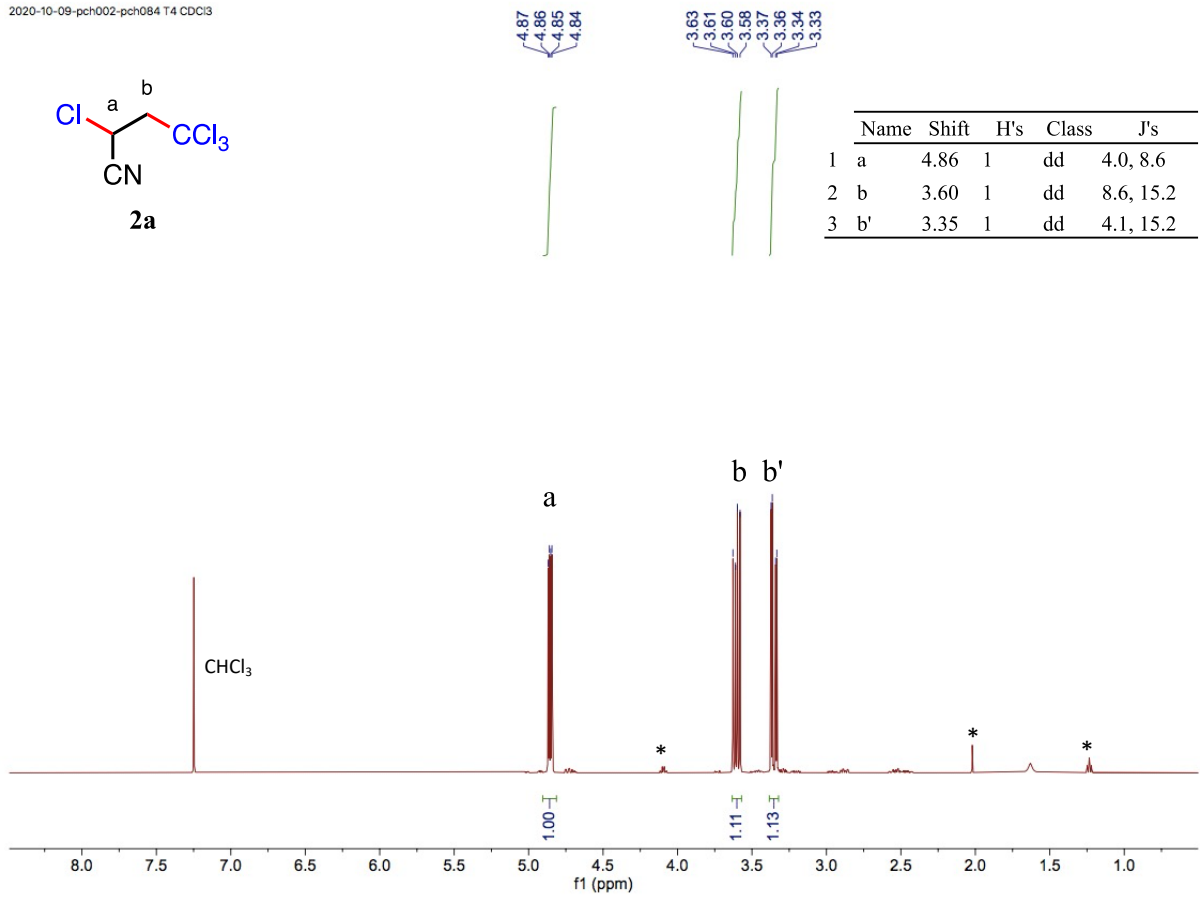


Fig. S44. ^{1}H NMR spectrum of 2,4,4,4-tetrachlorobutanenitrile, **2a.**



	Name	Shift	H's	Class	J's
1	a	4.86	1	dd	4.0, 8.6
2	b	3.60	1	dd	8.6, 15.2
3	b'	3.35	1	dd	4.1, 15.2

- ***Ethyl acetate as an eluent**

Fig. S45. ^{13}C NMR spectrum of 2,4,4,4-tetrachlorobutanenitrile, **2a.**

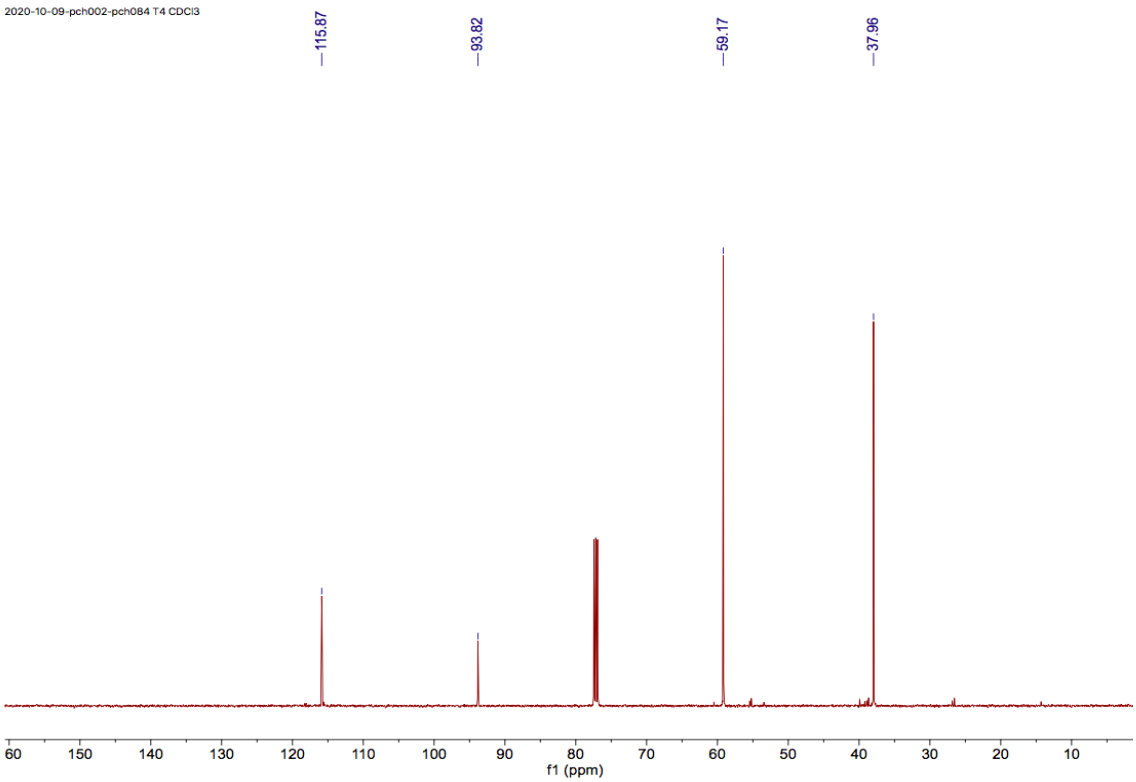


Fig. S46. ^{1}H NMR spectrum of 2,4,4,4-tetrabromobutanenitrile, **2b**.

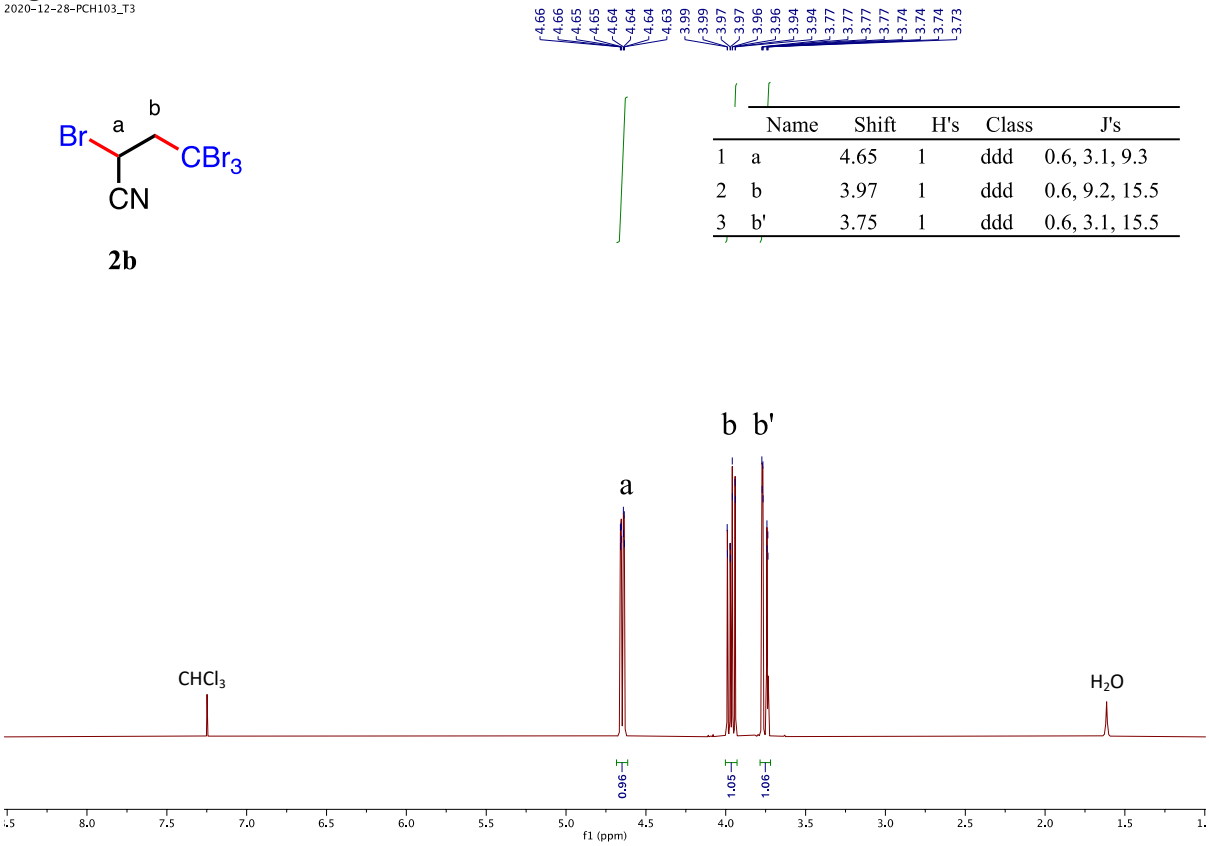


Fig. S47. ^{13}C NMR spectrum of 2,4,4,4-tetrabromobutanenitrile, **2b**.

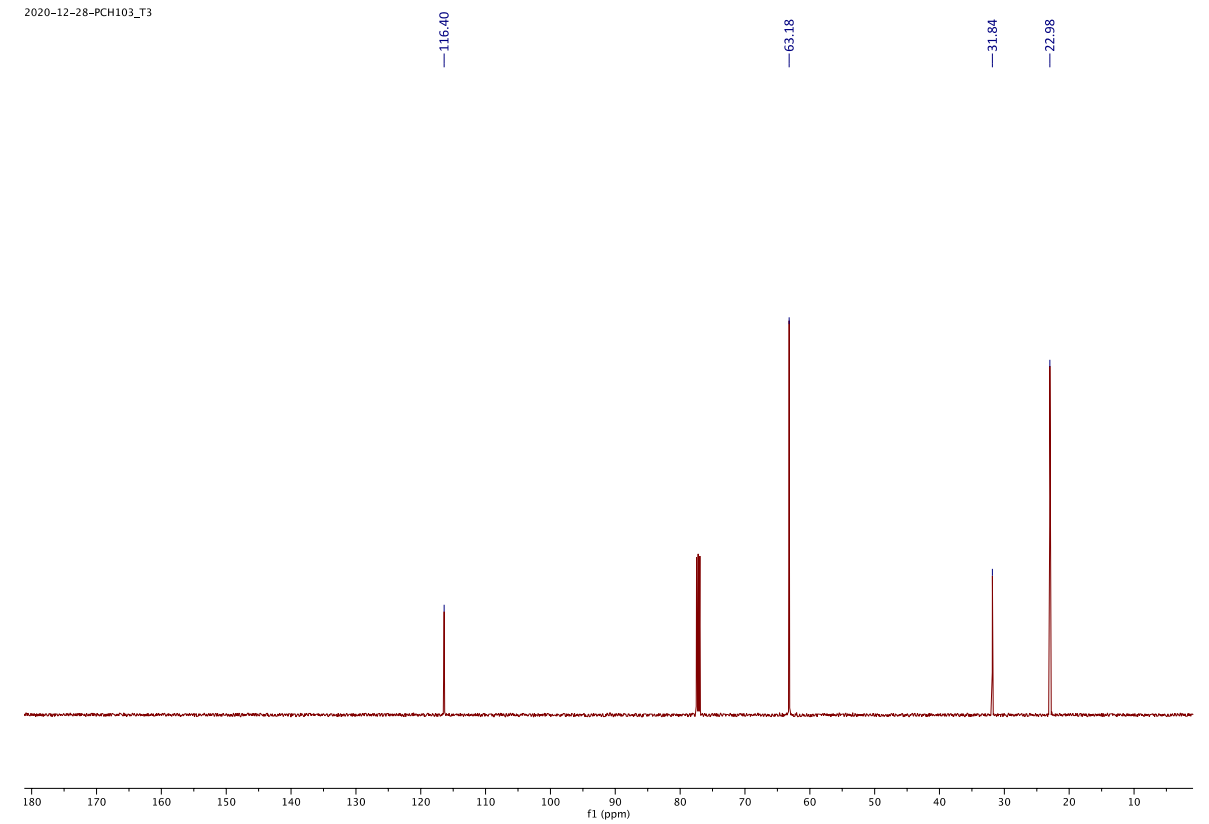
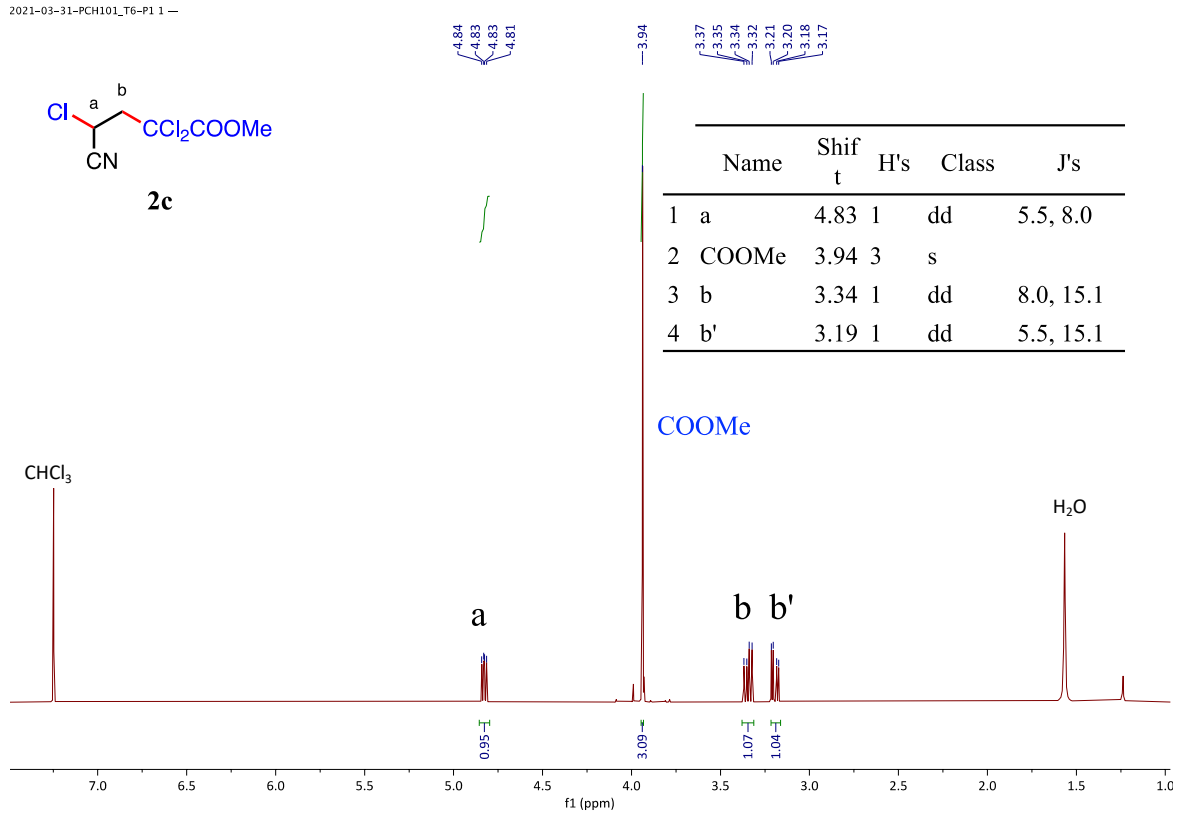


Fig. S48. ^{1}H NMR spectrum of methyl 2,2,4-trichloro-4-cyanobutanoate, **2c**.



	Name	Shift	H's	Class	J's
1	a	4.83	1	dd	5.5, 8.0
2	COOMe	3.94	3	s	
3	b	3.34	1	dd	8.0, 15.1
4	b'	3.19	1	dd	5.5, 15.1

Fig. S49. ^{13}C NMR spectrum of methyl 2,4,4,4-tetrachlorobutanoate., **2c**

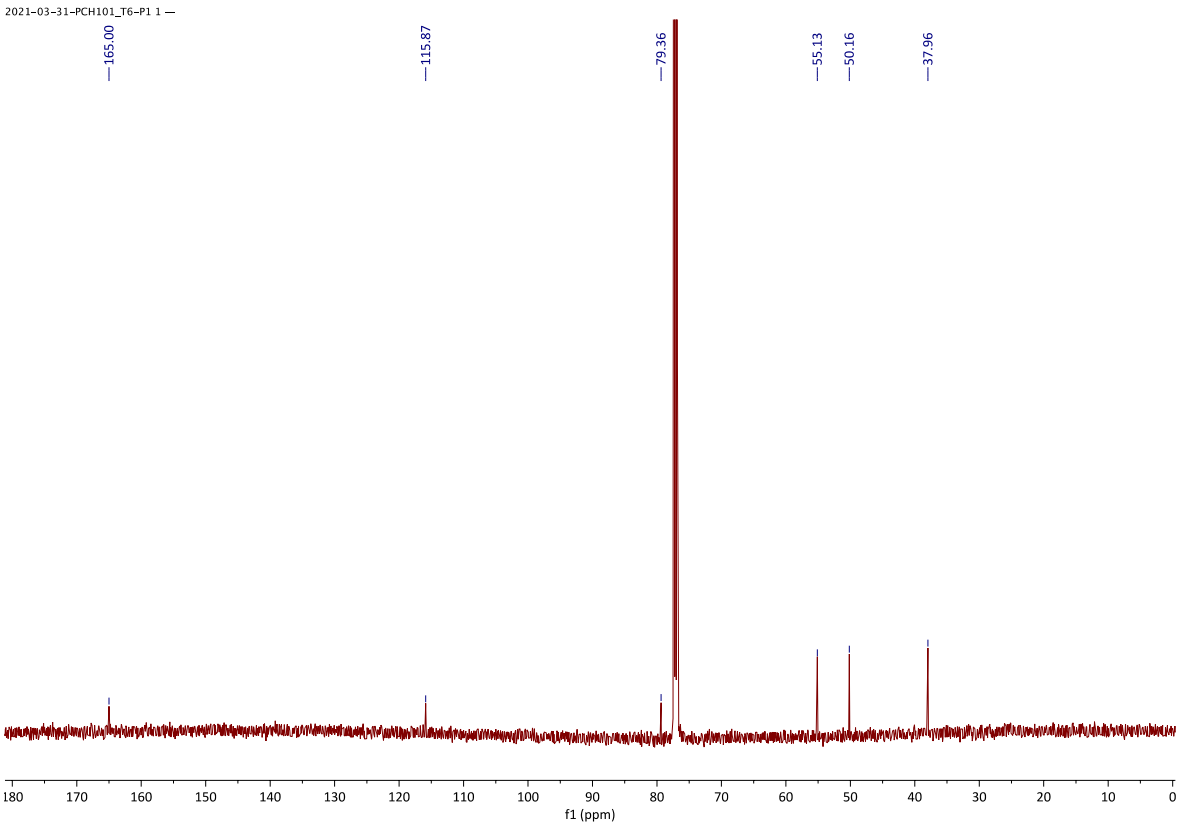
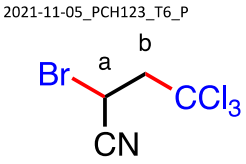


Fig. S50. ^{1}H NMR spectrum of 2-bromo-4,4,4-trichlorobutanenitrile, **2d**



2d

	Name	Shift	H's	Integral	Class	J's
1	a	4.68	1	1.01	dd	3.5, 9.7
2	b	3.63	1	1.00	dd	9.7, 15.2
3	b'	3.41	1	0.98	dd	3.5, 15.2

* by-product see Fig.S7, **toluene was used as an internal standard

Fig. S51. ^{13}C NMR spectrum of 2-bromo-4,4,4-trichlorobutanenitrile, **2d.**

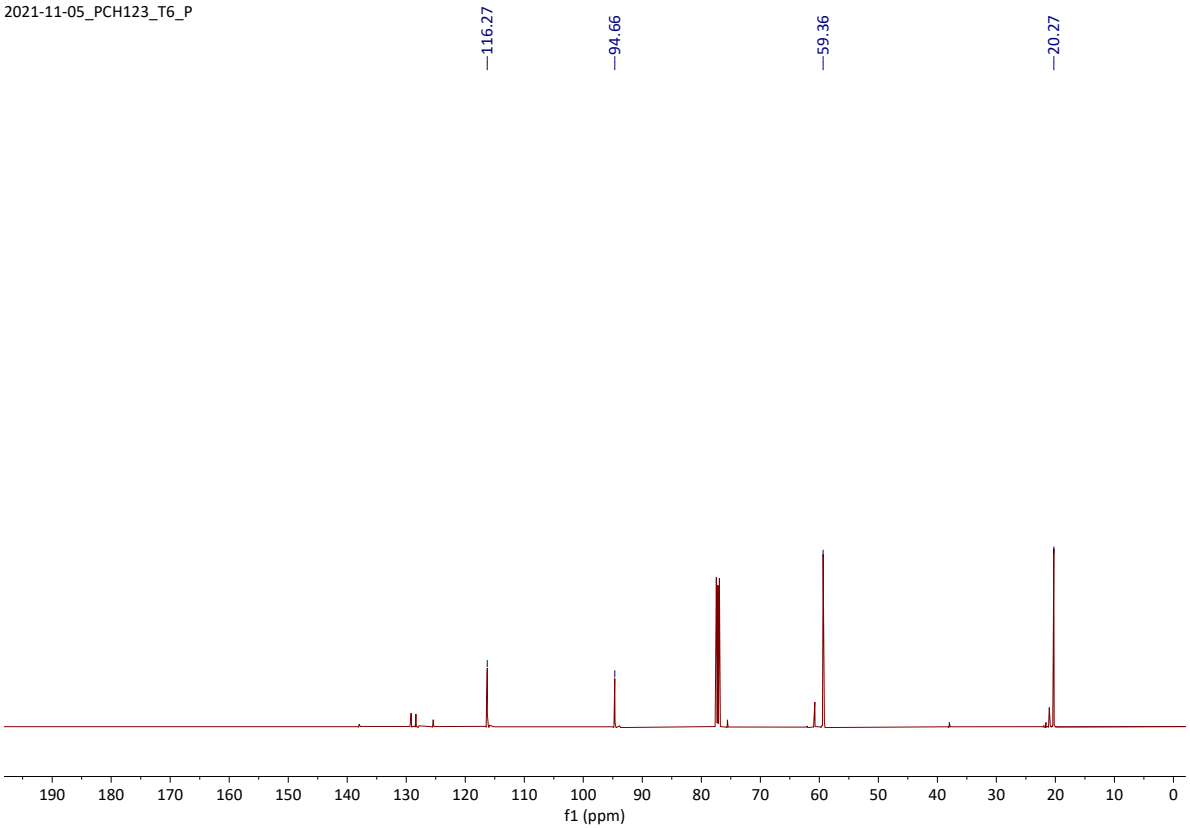


Fig. S52. ^{1}H NMR spectrum of methyl 2,4,4,4-tetrachlorobutanoate, **3a**.

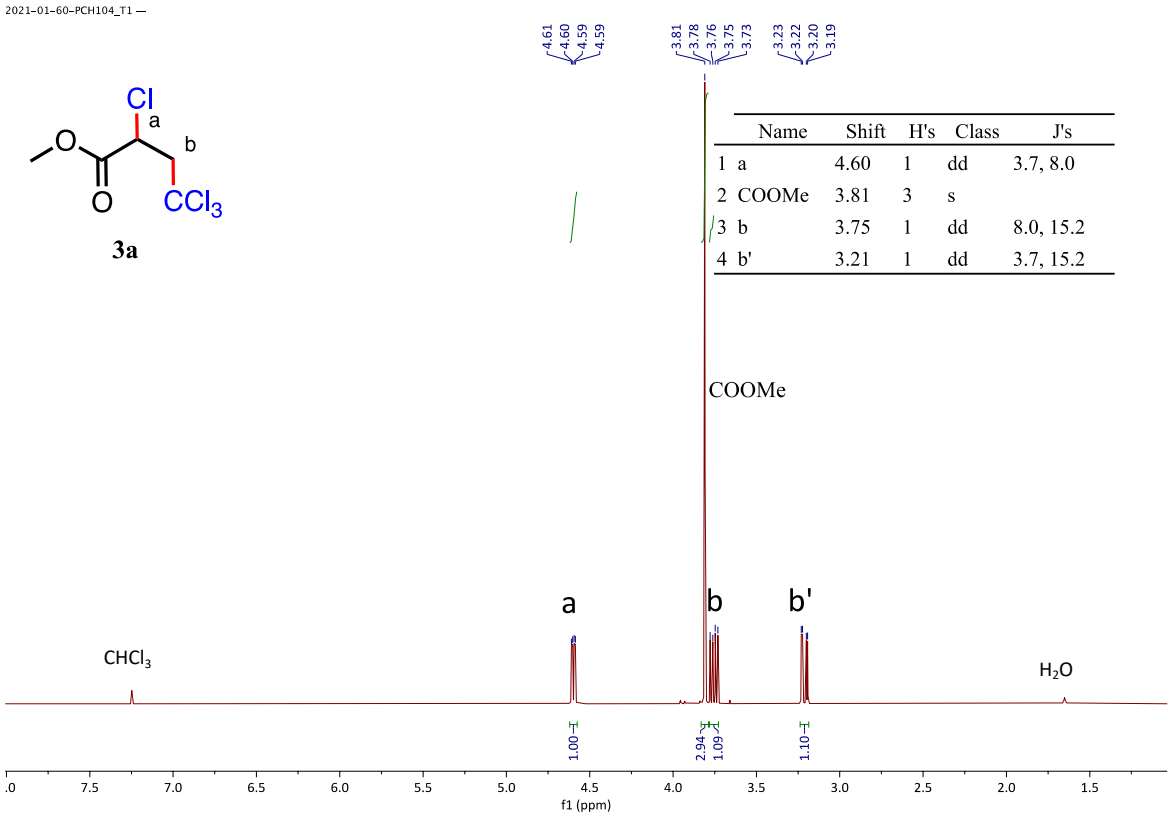


Fig. S53. ^{13}C NMR spectrum of methyl 2,4,4,4-tetrachlorobutanoate, **3a**.

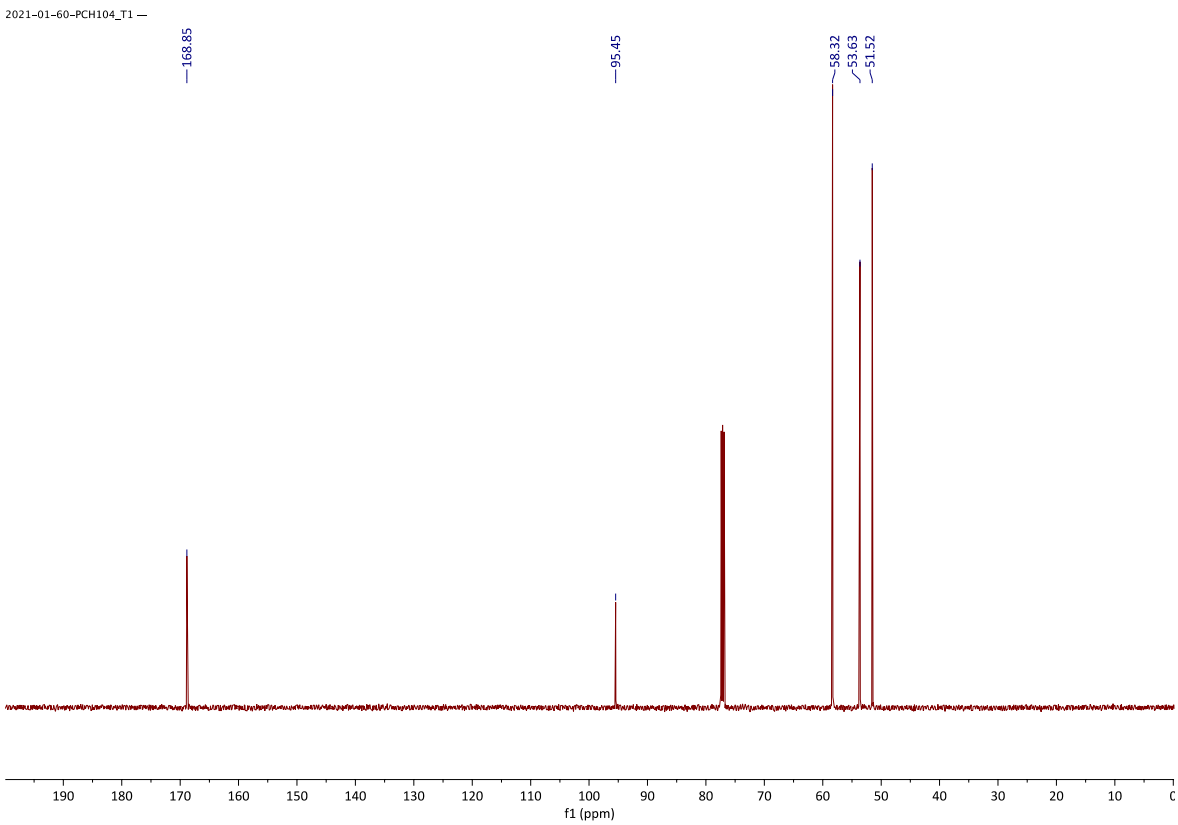
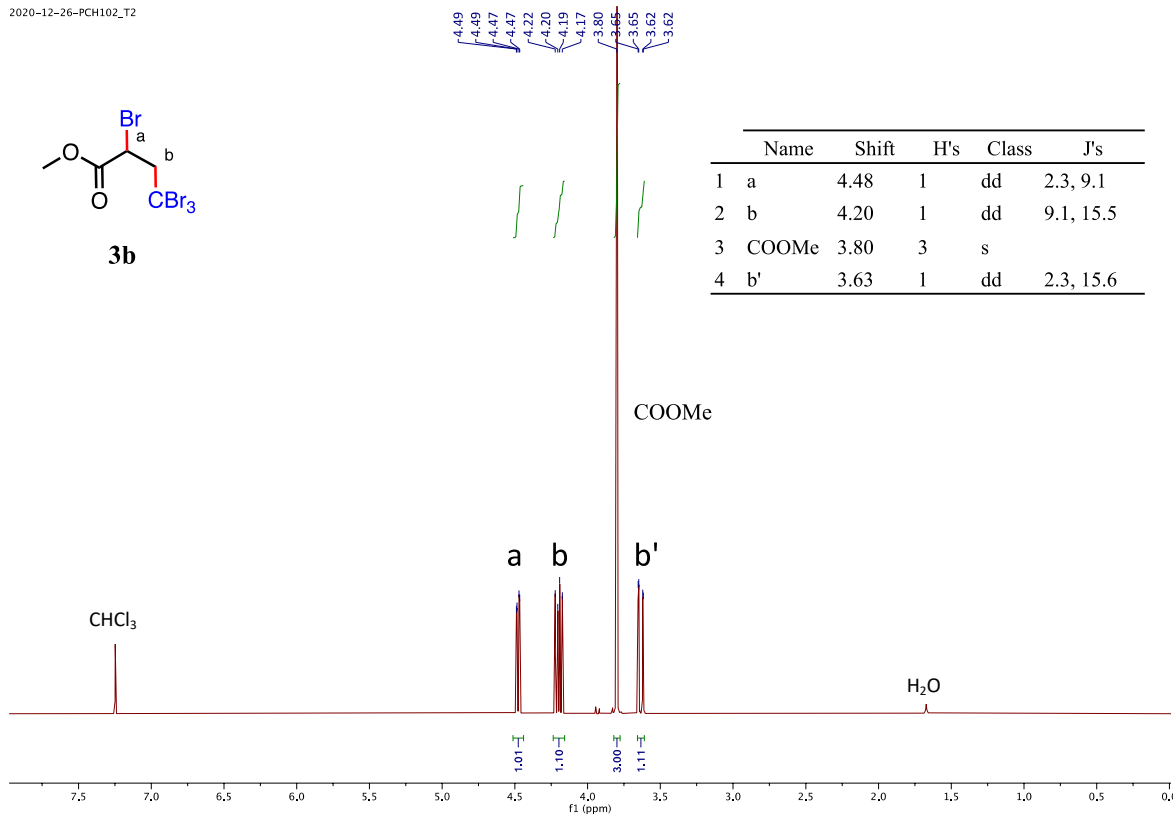


Fig. S54. ^{1}H NMR spectrum of methyl 2,4,4,4-tetrabromobutanoate, **3b**.



	Name	Shift	H's	Class	J's
1	a	4.48	1	dd	2.3, 9.1
2	b	4.20	1	dd	9.1, 15.5
3	COOMe	3.80	3	s	
4	b'	3.63	1	dd	2.3, 15.6

Fig. S55. ^{13}C NMR spectrum of methyl 2,4,4,4-tetrabromobutanoate, **3b**.

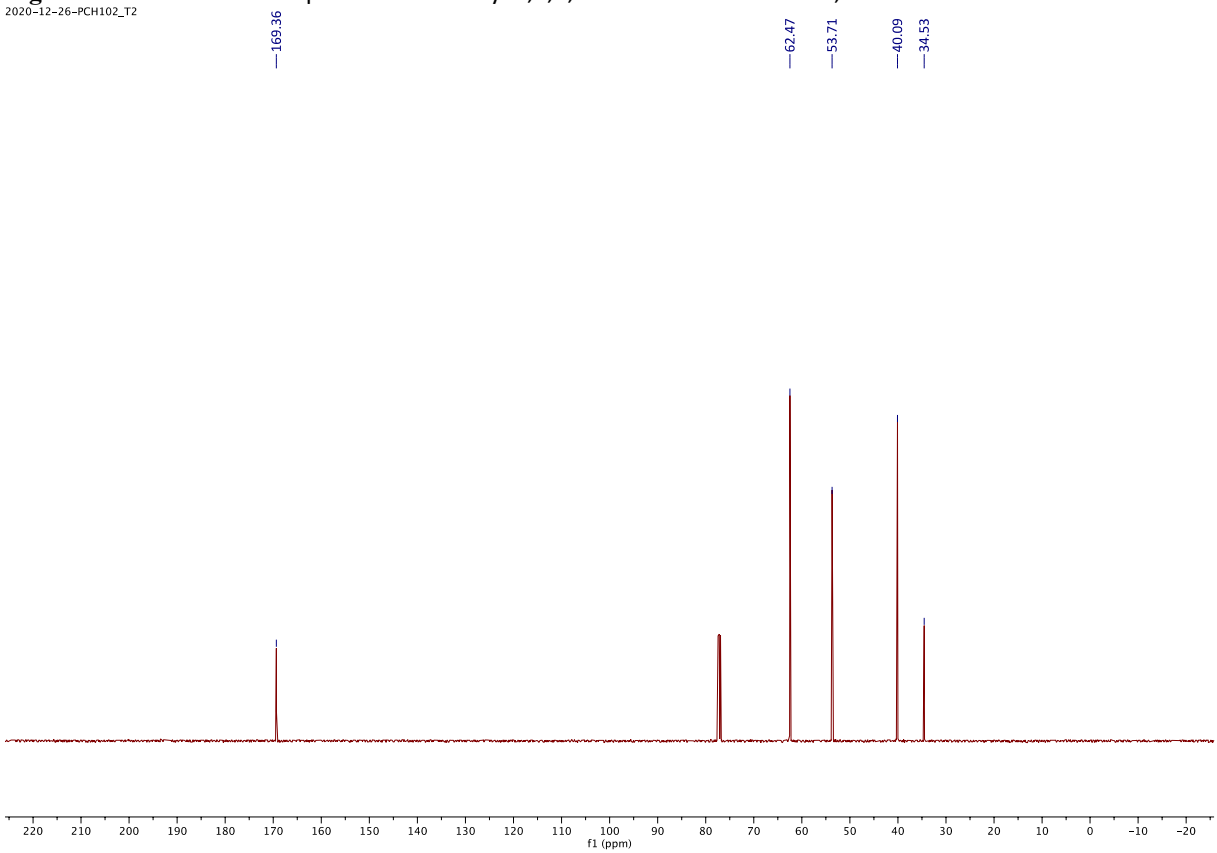


Fig. S56. ^{1}H NMR spectrum of dimethyl 2,2,4-trichloropentanedioate, **3c**.

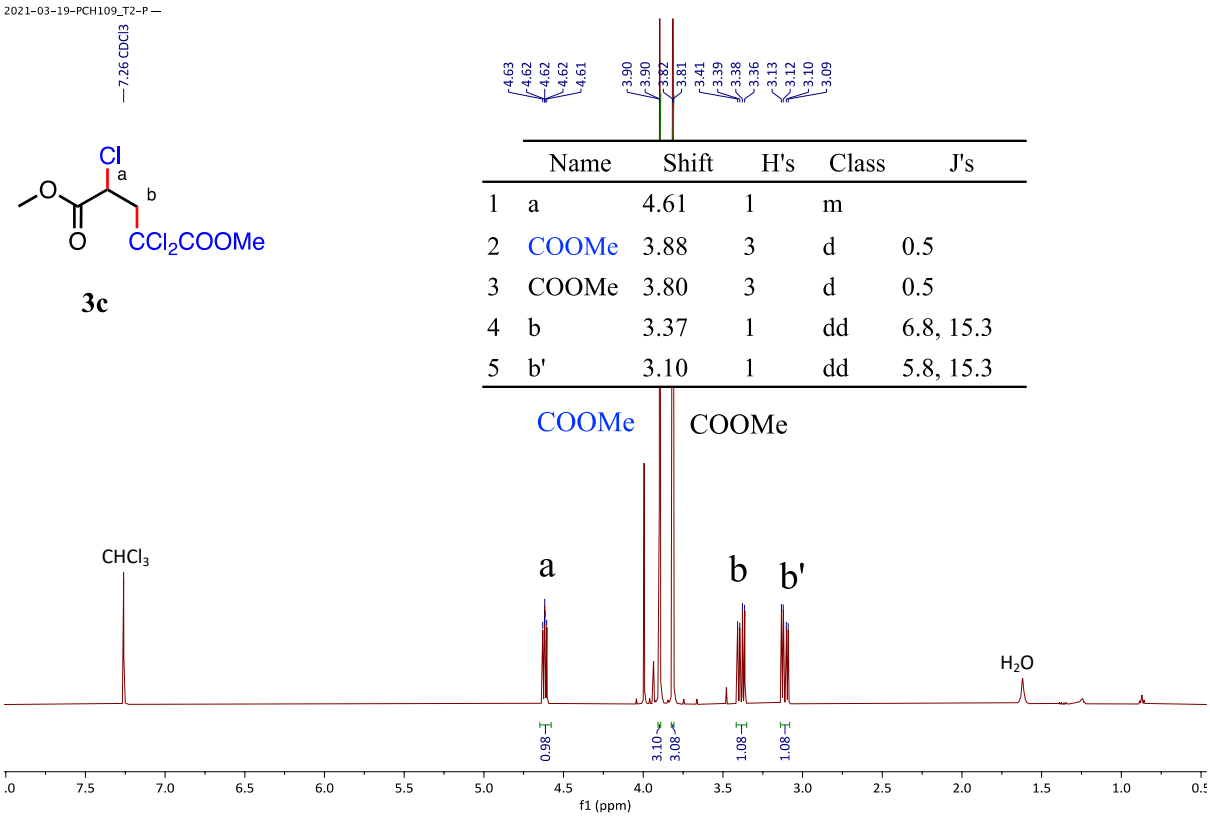


Fig. S57. ^{13}C NMR spectrum of dimethyl 2,2,4-trichloropentanedioate, **3c**.

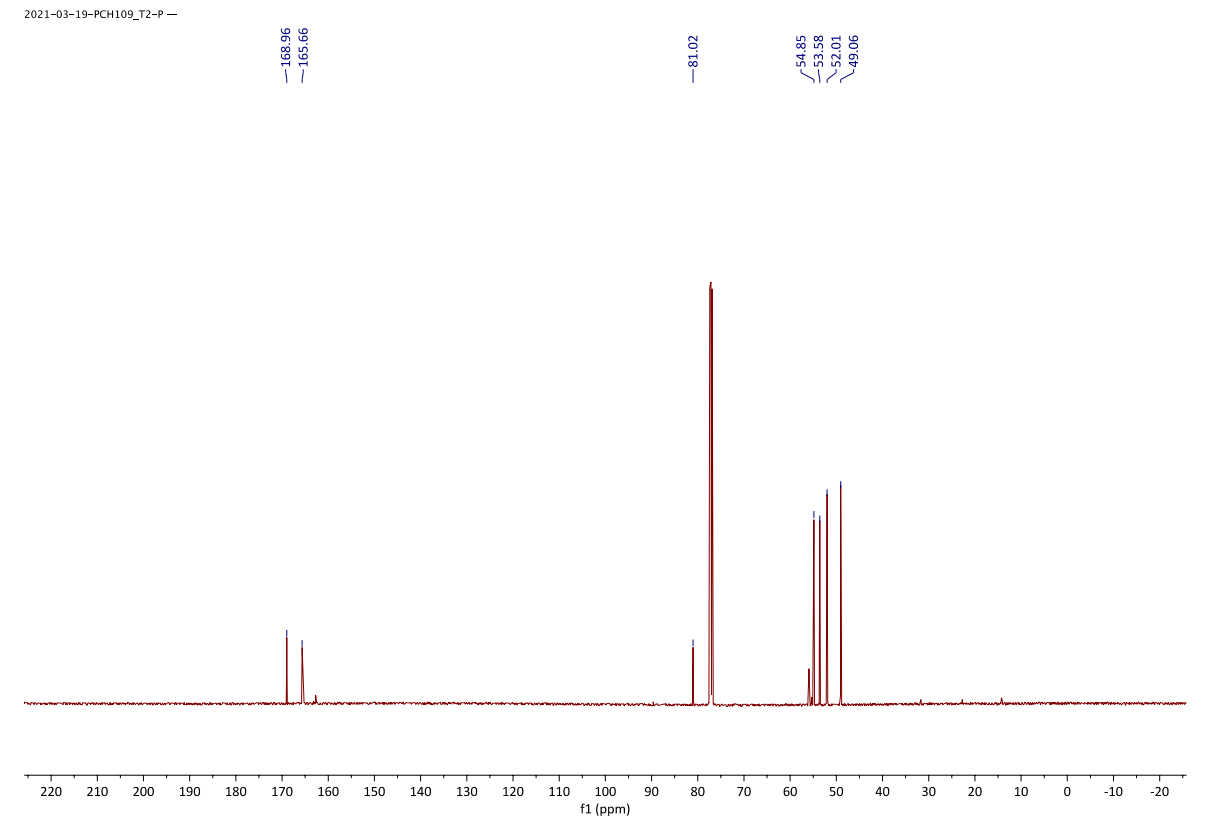
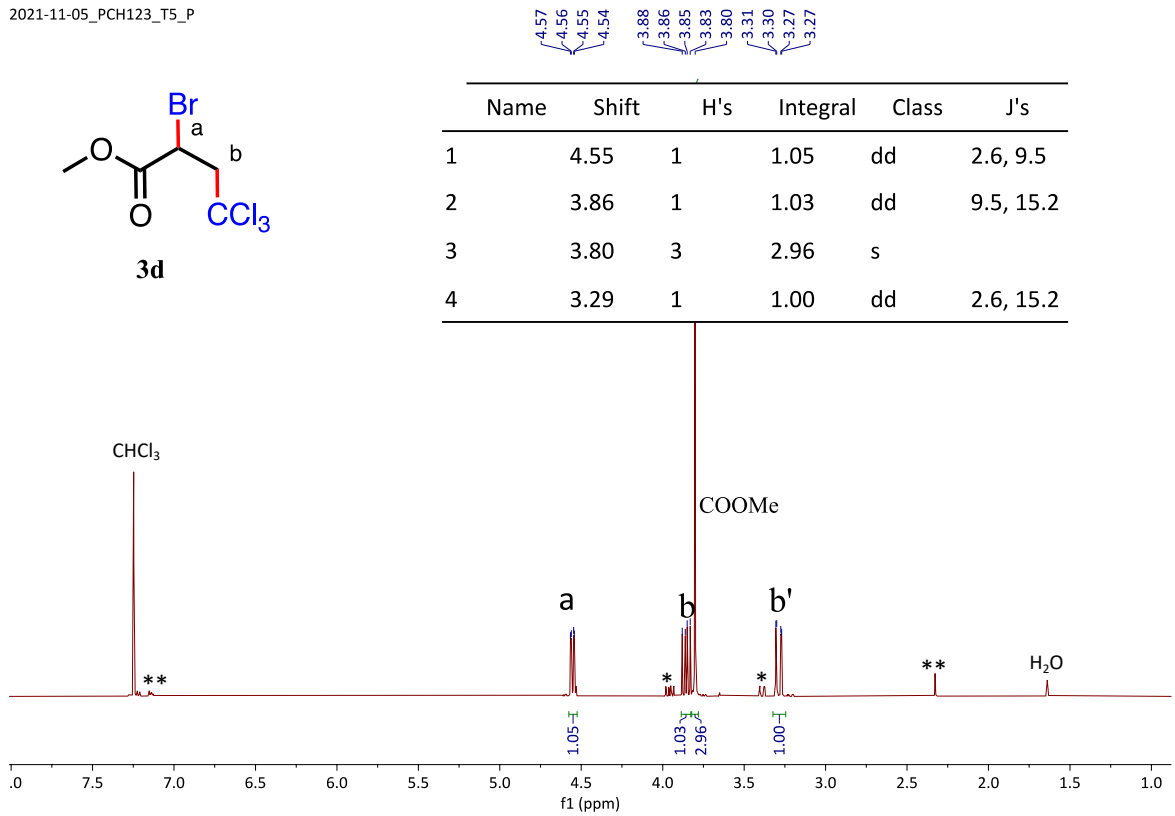


Fig. S58. ^{1}H NMR spectrum of methyl-2-bromo-4,4,4-trichlorobutanoate, **3d.**



	Name	Shift	H's	Integral	Class	J's
1		4.55	1	1.05	dd	2.6, 9.5
2		3.86	1	1.03	dd	9.5, 15.2
3		3.80	3	2.96	s	
4		3.29	1	1.00	dd	2.6, 15.2

* by-product see Fig.S8, **toluene was used as an internal standard

Fig. S59. ^{13}C NMR spectrum of methyl-2-bromo-4,4,4-trichlorobutanoate, **3d.**

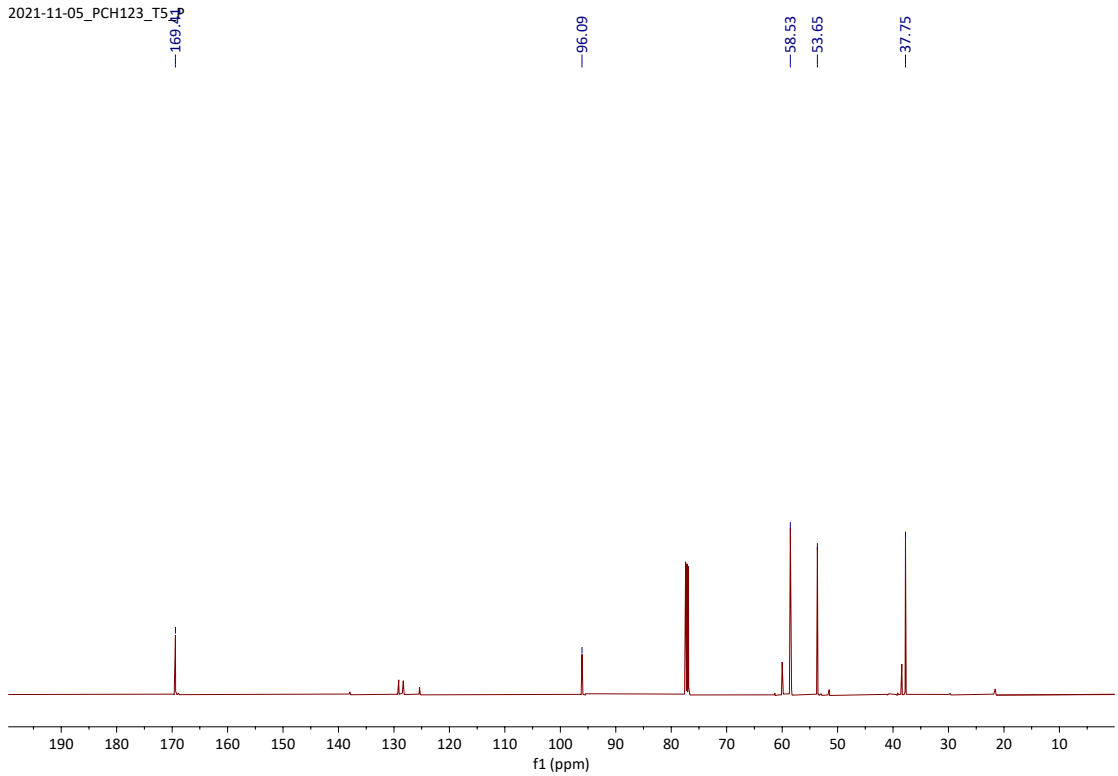


Fig. S60. ^{1}H NMR spectrum of methyl-2,4,4,4-tetrachloro-2-methylbutanoate, **4a**.

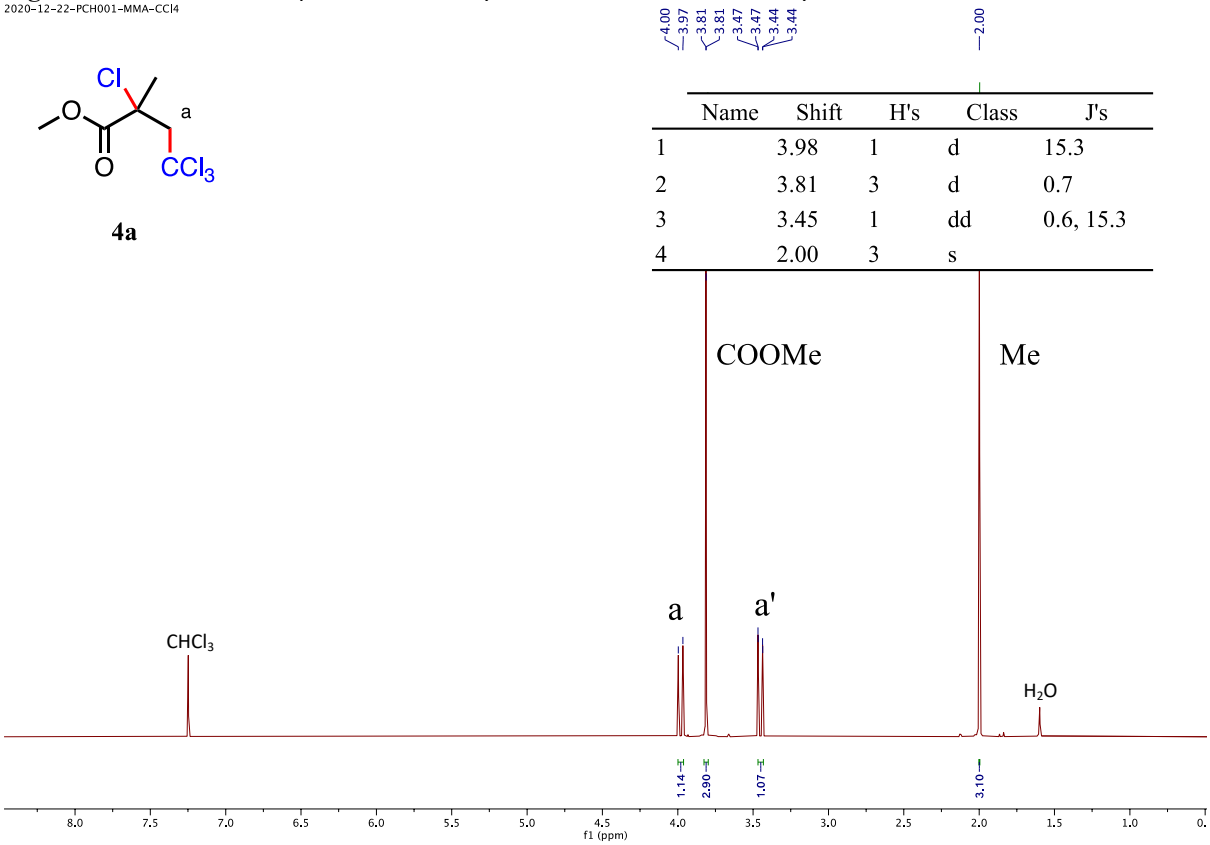


Fig. S61. ^{13}C NMR spectrum of methyl-2,4,4,4-tetrachloro-2-methylbutanoate, **4a**.

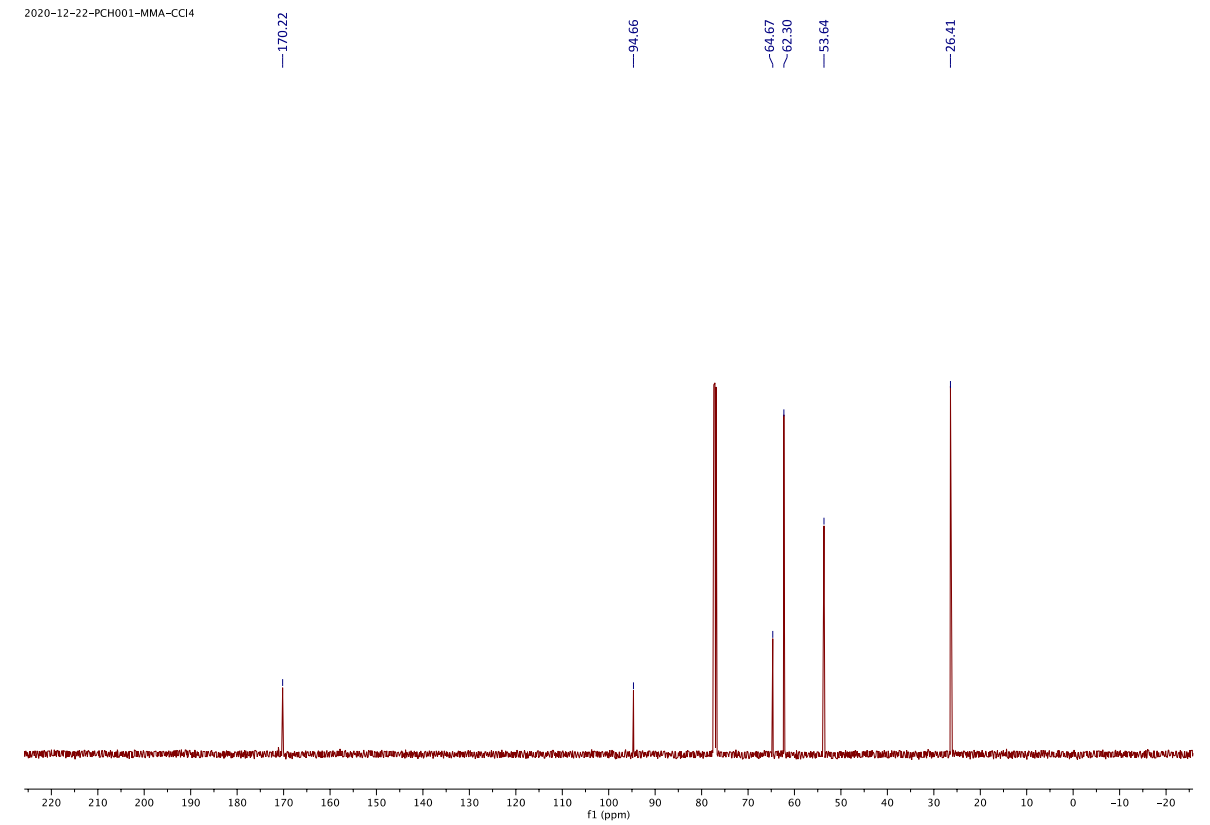


Fig. S62. ^{1}H NMR spectrum of methyl 2,4,4,4-tetrabromo-2-methylbutanoate, **4b**.

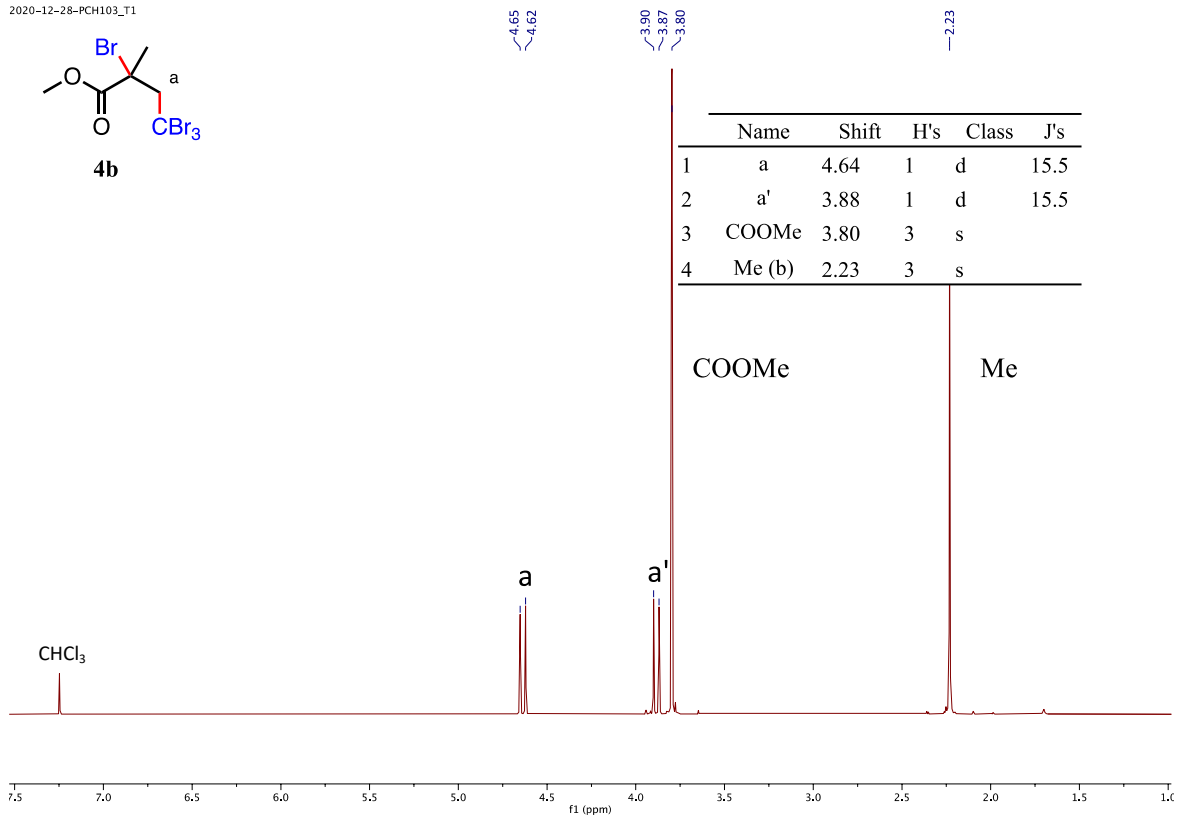


Fig. S63. ^{13}C NMR spectrum of methyl 2,4,4,4-tetrabromo-2-methylbutanoate, **4b**.

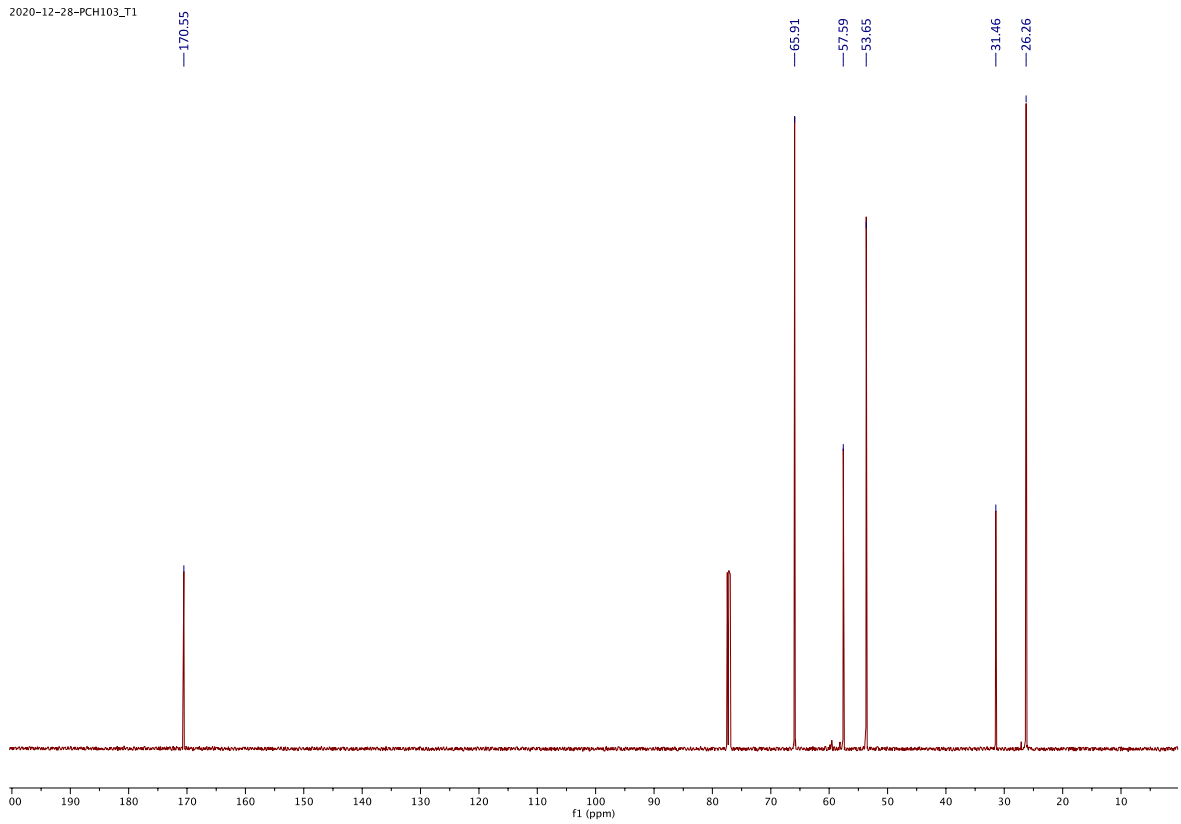
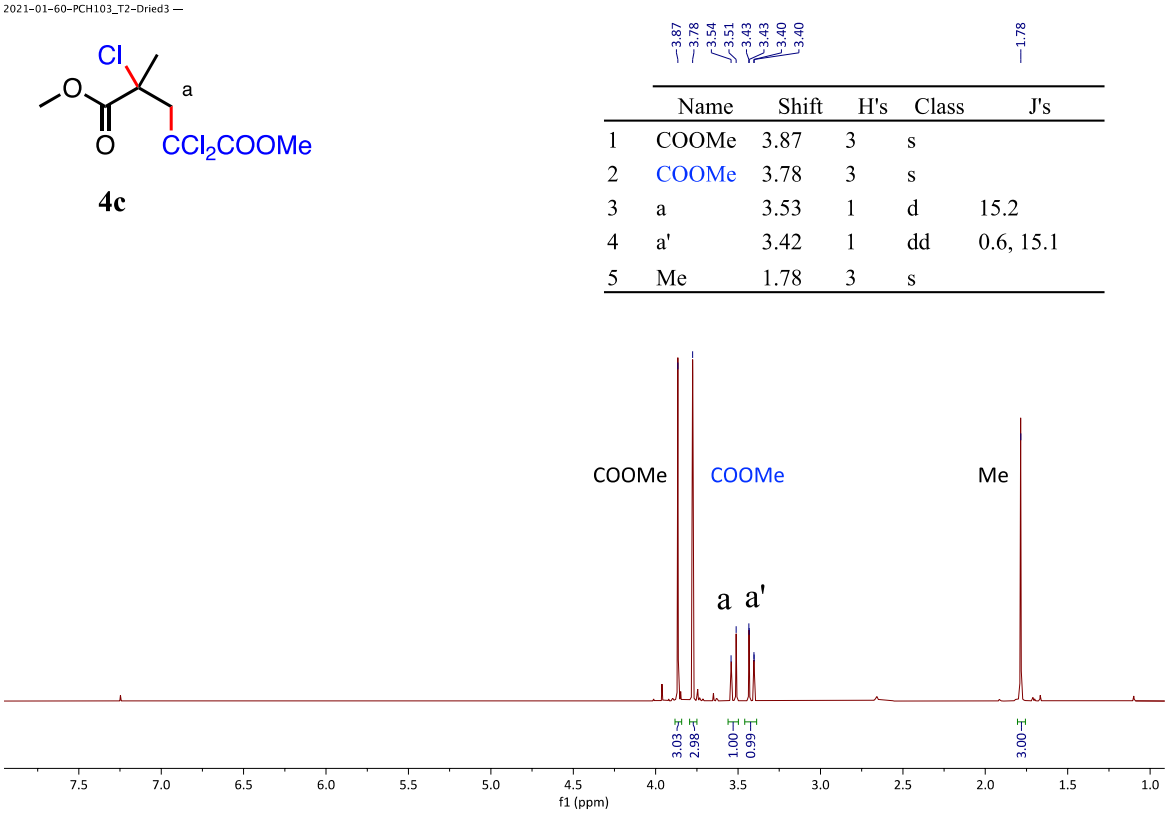


Fig. S64. ^{1}H NMR spectrum of dimethyl 2,2,4-trichloro-4-methylpentanedioate, **4c**.



	Name	Shift	H's	Class	J's
1	COOMe	3.87	3	s	
2	COOMe	3.78	3	s	
3	a	3.53	1	d	15.2
4	a'	3.42	1	dd	0.6, 15.1
5	Me	1.78	3	s	

Fig. S65. ^{13}C NMR spectrum of dimethyl 2,2,4-trichloro-4-methylpentanedioate, **4c**.

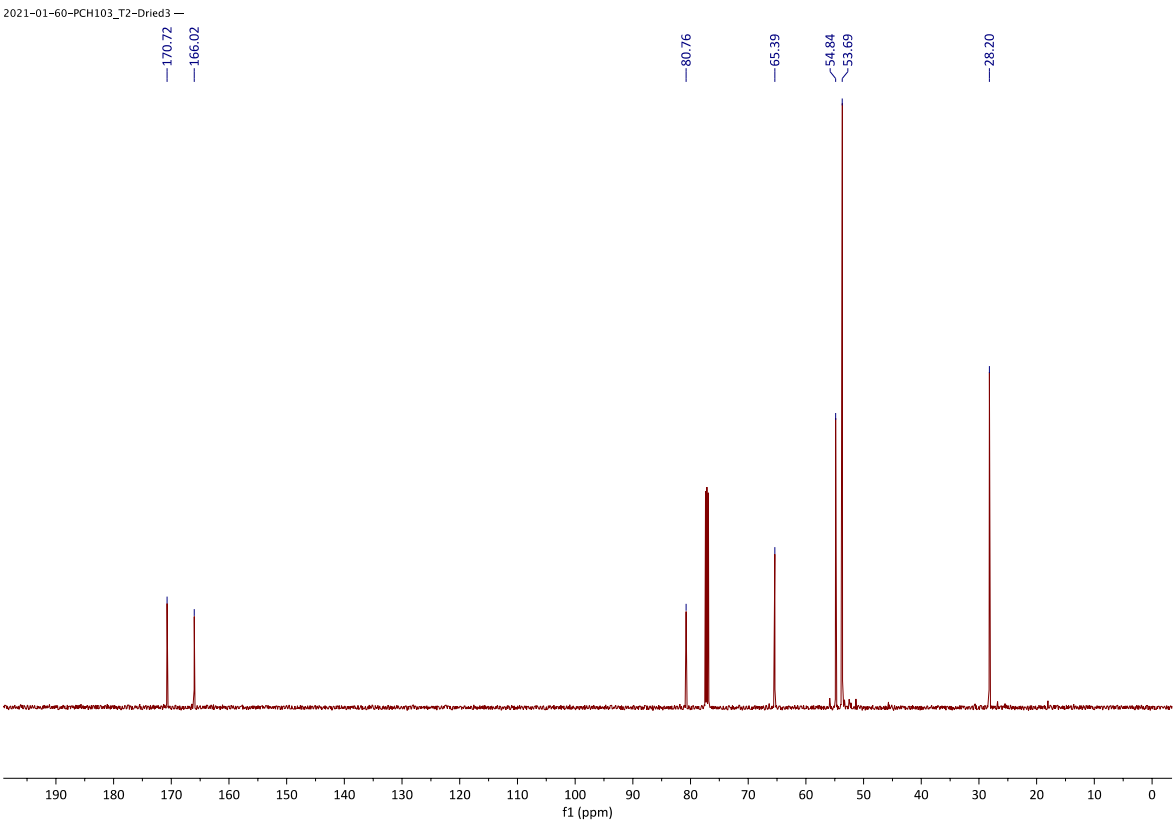
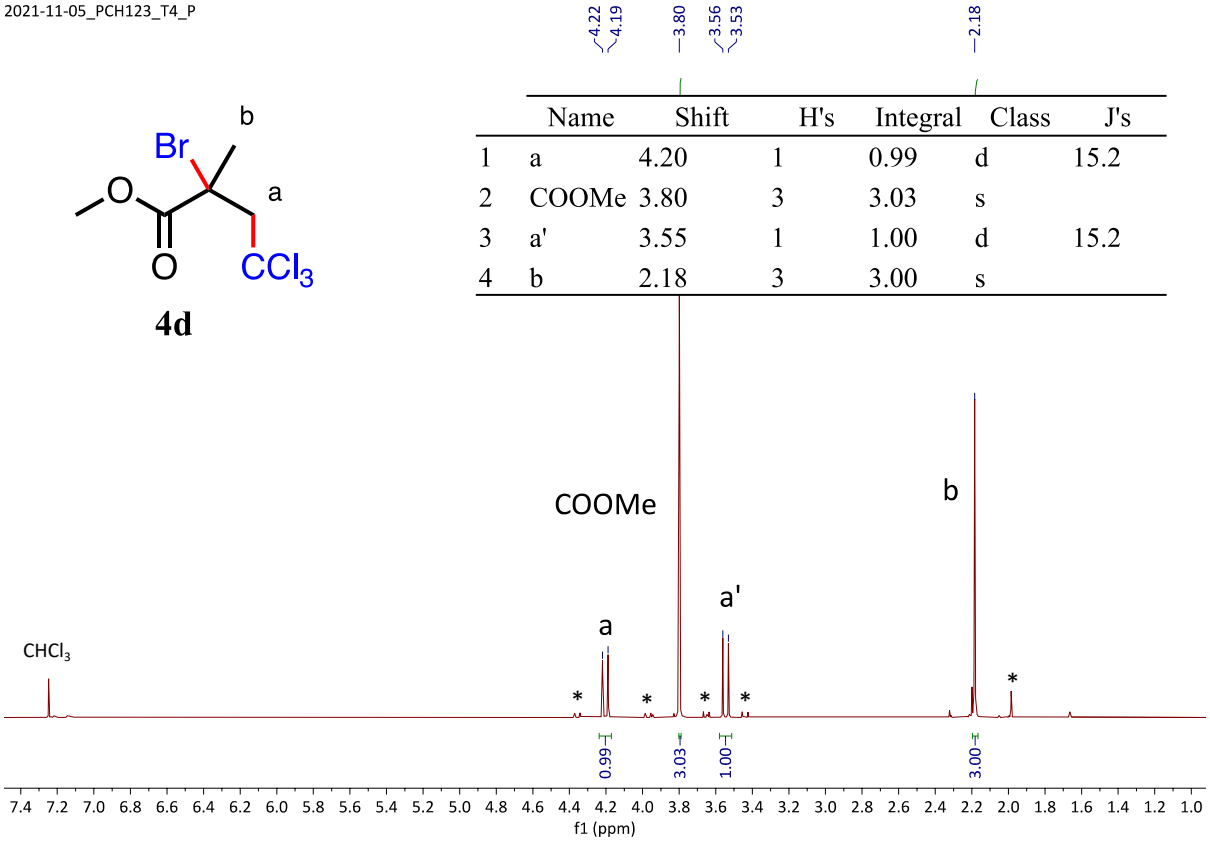


Fig. S66. ^{1}H NMR spectrum of methyl-2-bromo-4,4,4-trichloro-2-methylbutanoate, **4d.**



	Name	Shift	H's	Integral	Class	J's
1	a	4.20	1	0.99	d	15.2
2	COOMe	3.80	3	3.03	s	
3	a'	3.55	1	1.00	d	15.2
4	b	2.18	3	3.00	s	

* by-product see Fig.S9

Fig. S67. ^{13}C NMR spectrum of methyl-2-bromo-4,4,4-trichloro-2-methylbutanoate, **4d.**

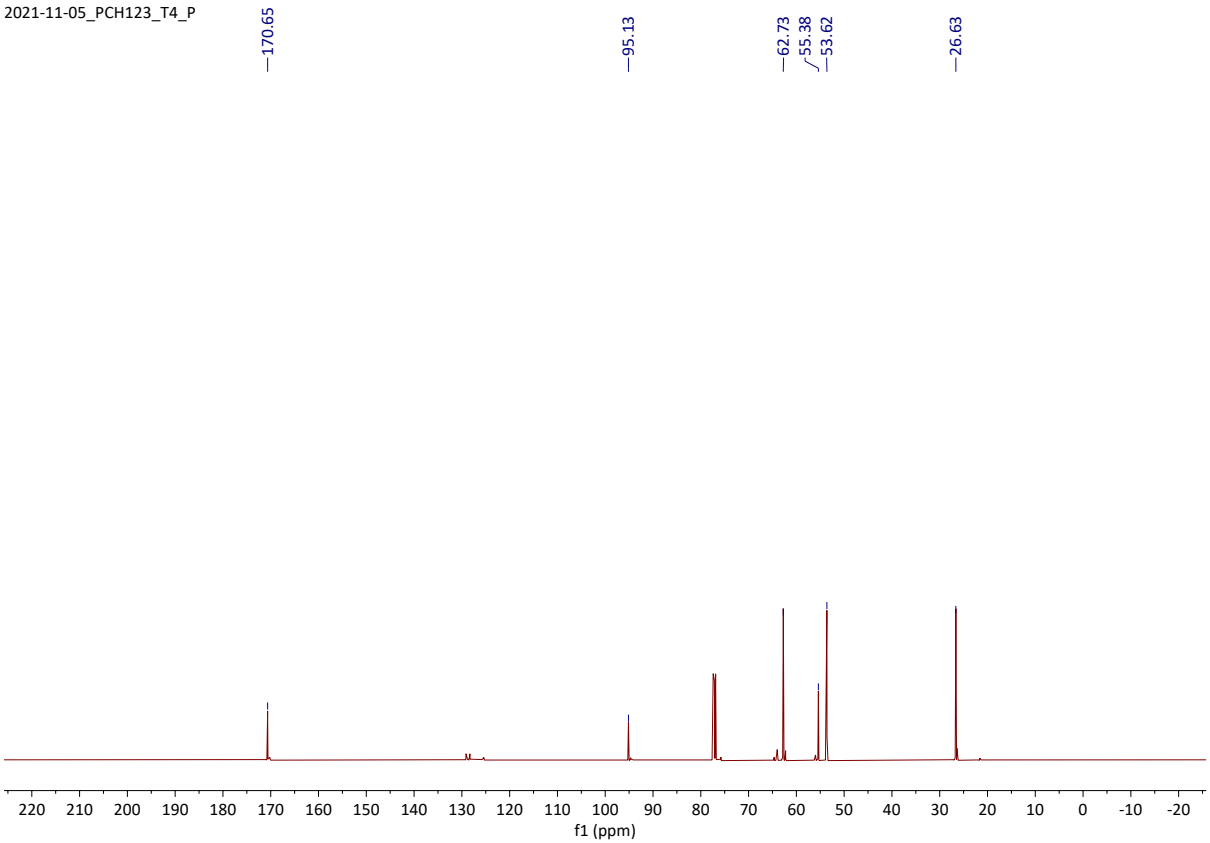
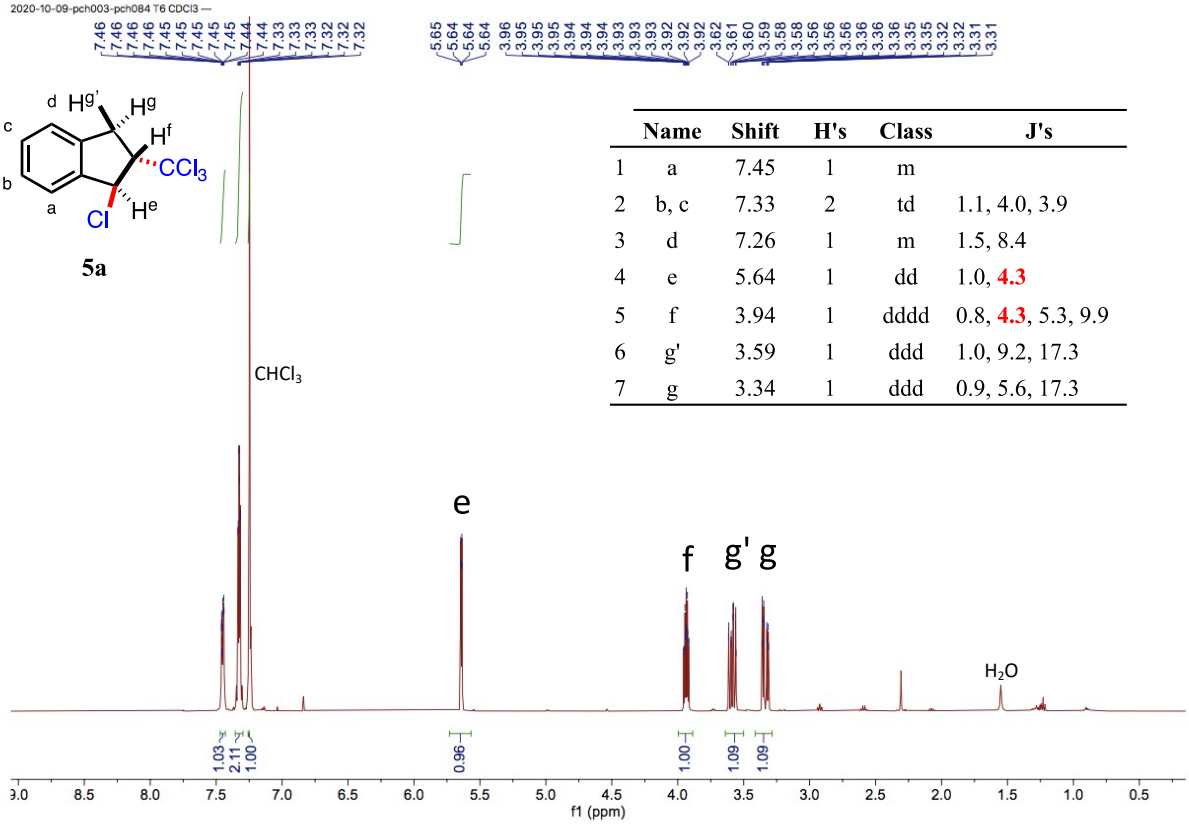


Fig. S68. ^{1}H NMR spectrum of *anti*-1-chloro-2-(trichloromethyl)-2,3-dihydro-1H-indene, **5a**.



	Name	Shift	H's	Class	J's
1	a	7.45	1	m	
2	b, c	7.33	2	td	1.1, 4.0, 3.9
3	d	7.26	1	m	1.5, 8.4
4	e	5.64	1	dd	1.0, **4.3**
5	f	3.94	1	dddd	0.8, **4.3**, 5.3, 9.9
6	g'	3.59	1	ddd	1.0, 9.2, 17.3
7	g	3.34	1	ddd	0.9, 5.6, 17.3

Fig. S69. ^{13}C NMR spectrum of *anti*-1-chloro-2-(trichloromethyl)-2,3-dihydro-1H-indene, **5a**.

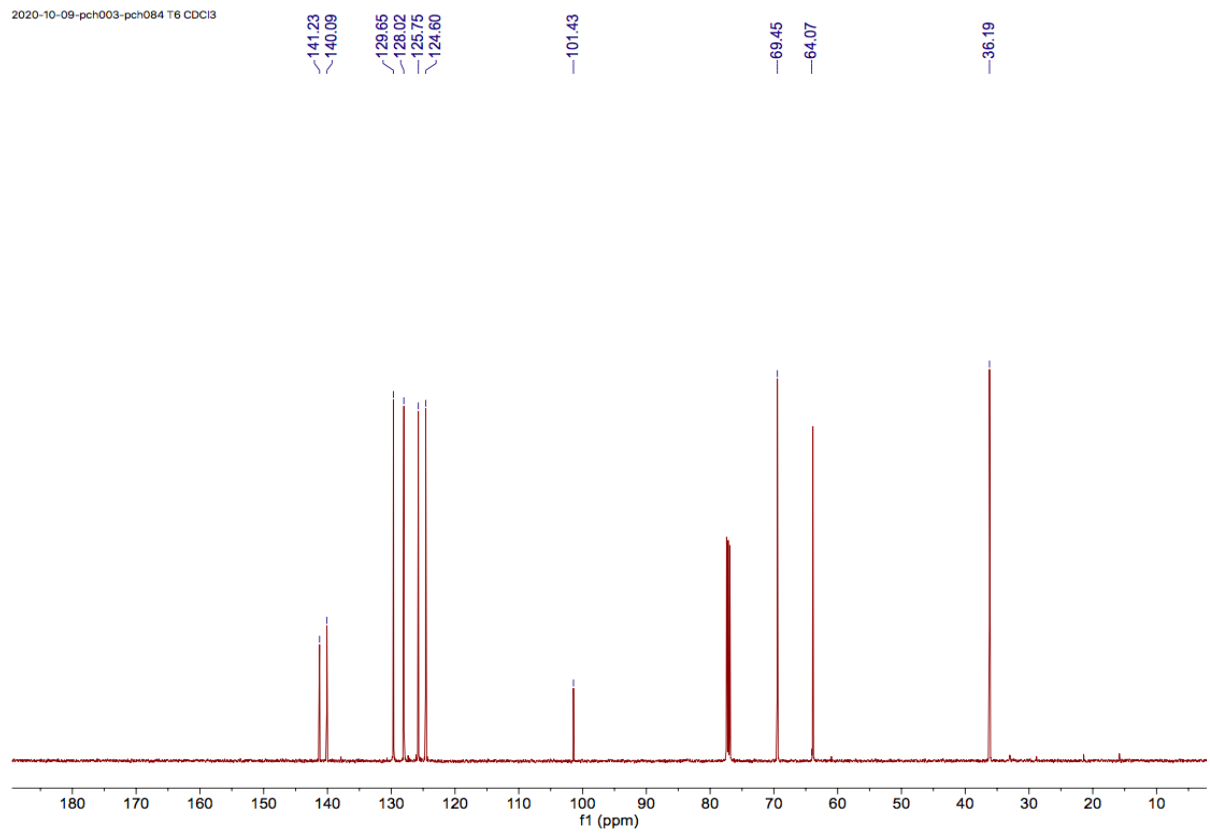
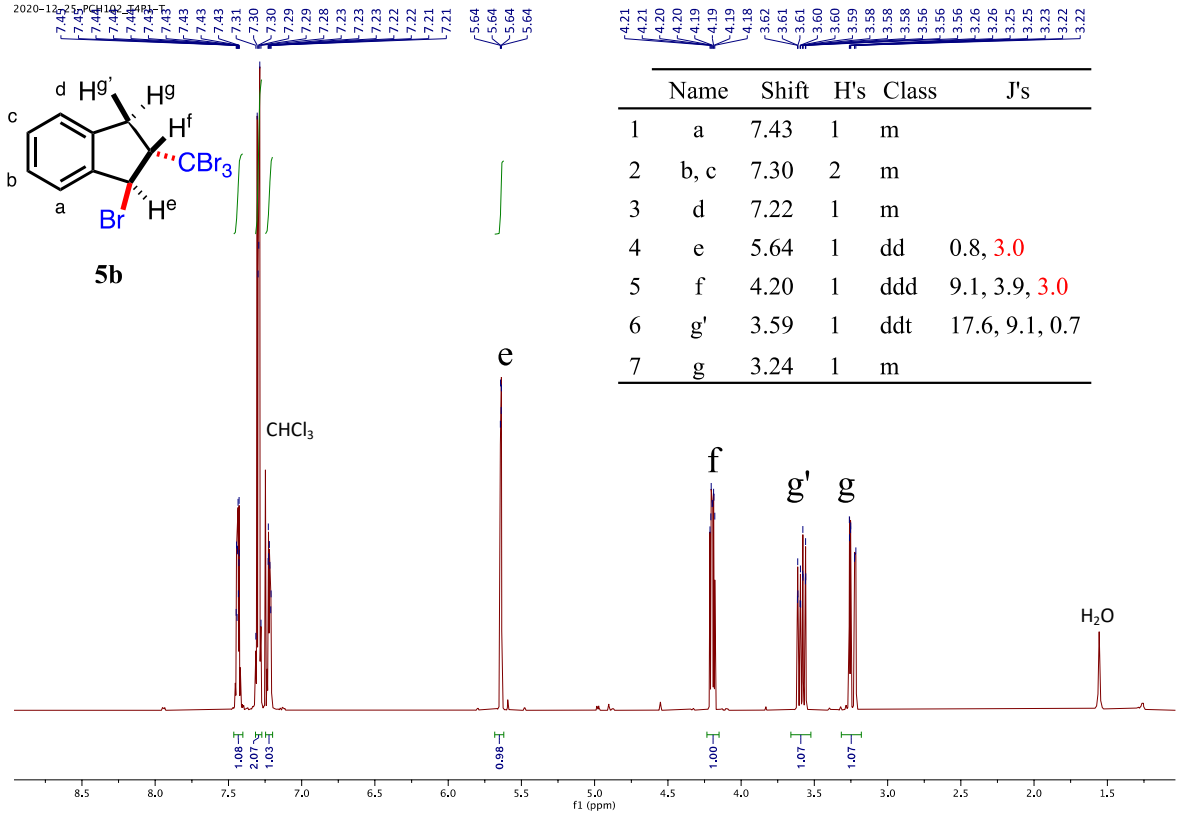


Fig. S70. ^{1}H NMR spectrum of *anti*-1-bromo-2-(tribromomethyl)-2,3-dihydro-1*H*-indene, **5b**.



	Name	Shift	H's	Class	J's
1	a	7.43	1	m	
2	b, c	7.30	2	m	
3	d	7.22	1	m	
4	e	5.64	1	dd	0.8, 3.0
5	f	4.20	1	ddd	9.1, 3.9, 3.0
6	g'	3.59	1	ddt	17.6, 9.1, 0.7
7	g	3.24	1	m	

Fig. S71. ^{13}C NMR spectrum of *anti*-1-bromo-2-(tribromomethyl)-2,3-dihydro-1*H*-indene, **5b**.

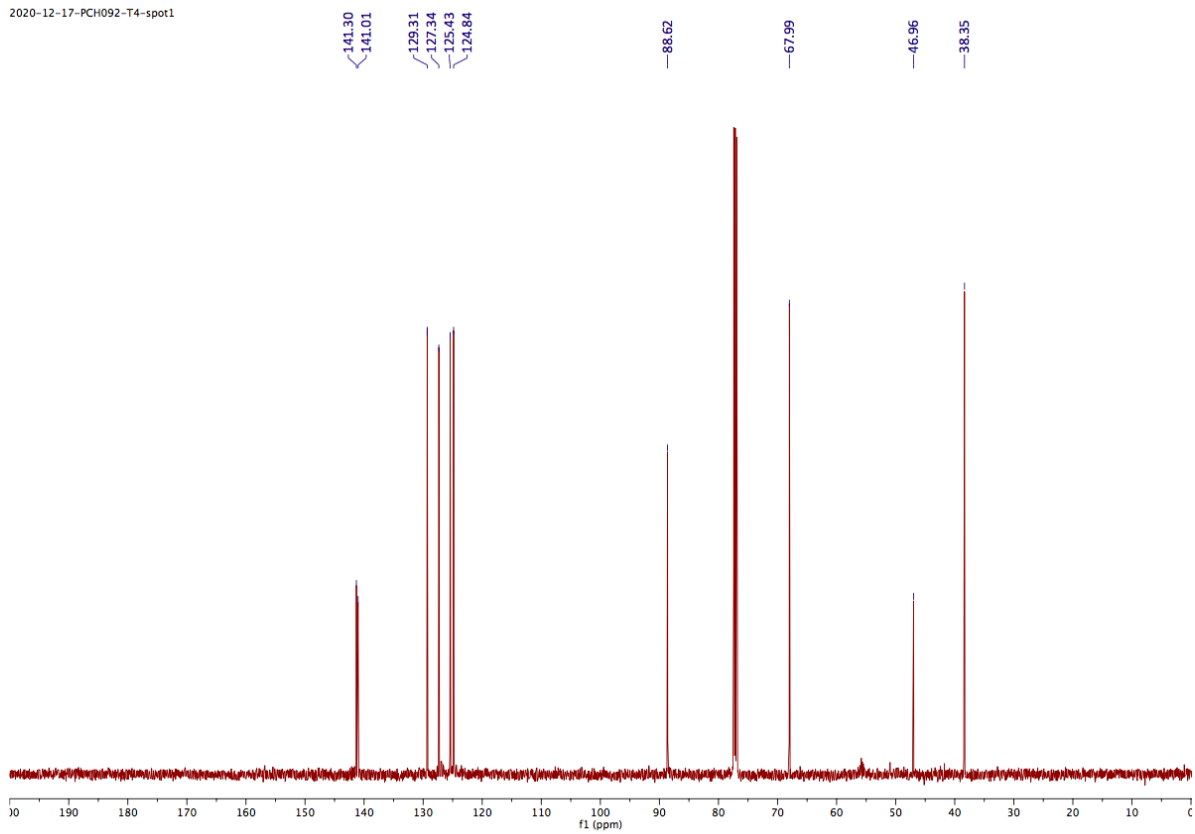
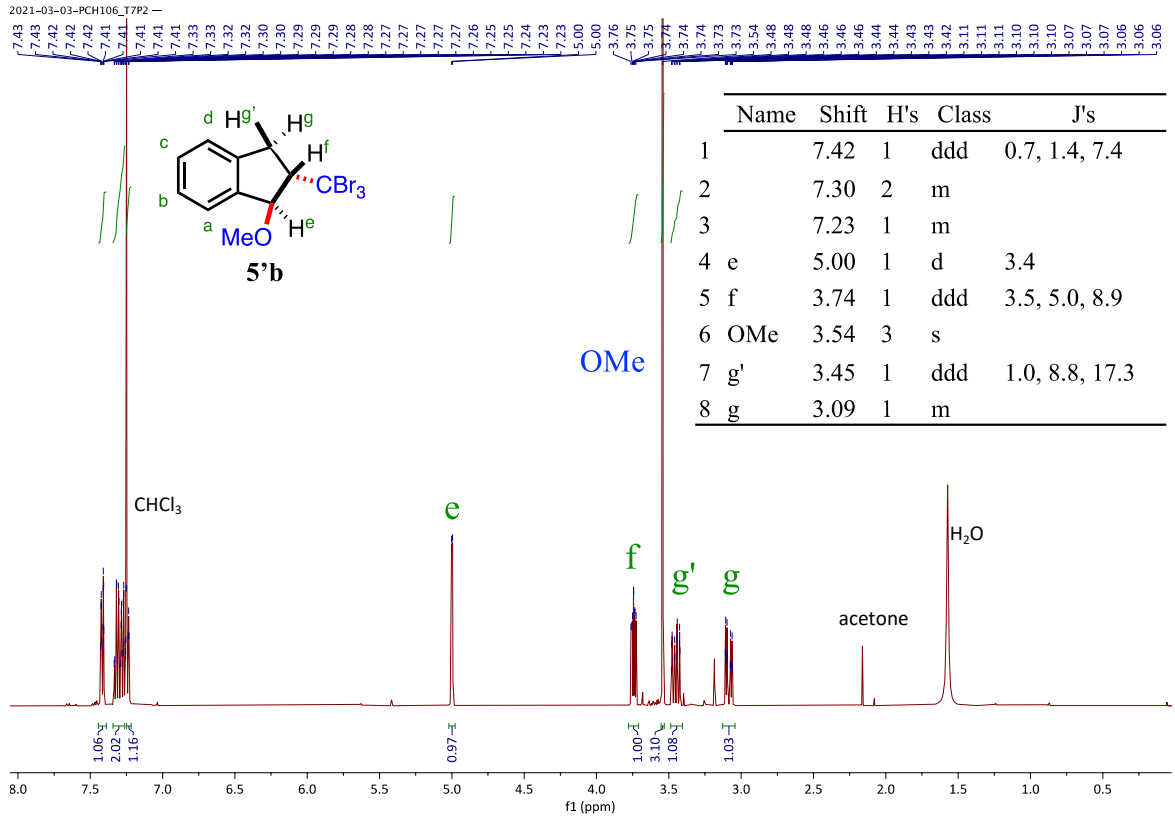


Fig. S72. ^{1}H NMR spectrum of *anti*-1-methoxy-2-(tribromomethyl)-2,3-dihydro-1H-indene, **5'b**.



	Name	Shift	H's	Class	J's
1		7.42	1	ddd	0.7, 1.4, 7.4
2		7.30	2	m	
3		7.23	1	m	
4	e	5.00	1	d	3.4
5	f	3.74	1	ddd	3.5, 5.0, 8.9
6	OMe	3.54	3	s	
7	g'	3.45	1	ddd	1.0, 8.8, 17.3
8	g	3.09	1	m	

Fig. S73. ^{13}C NMR spectrum of *anti*-1-methoxy-2-(tribromomethyl)-2,3-dihydro-1H-indene, **5'b.**

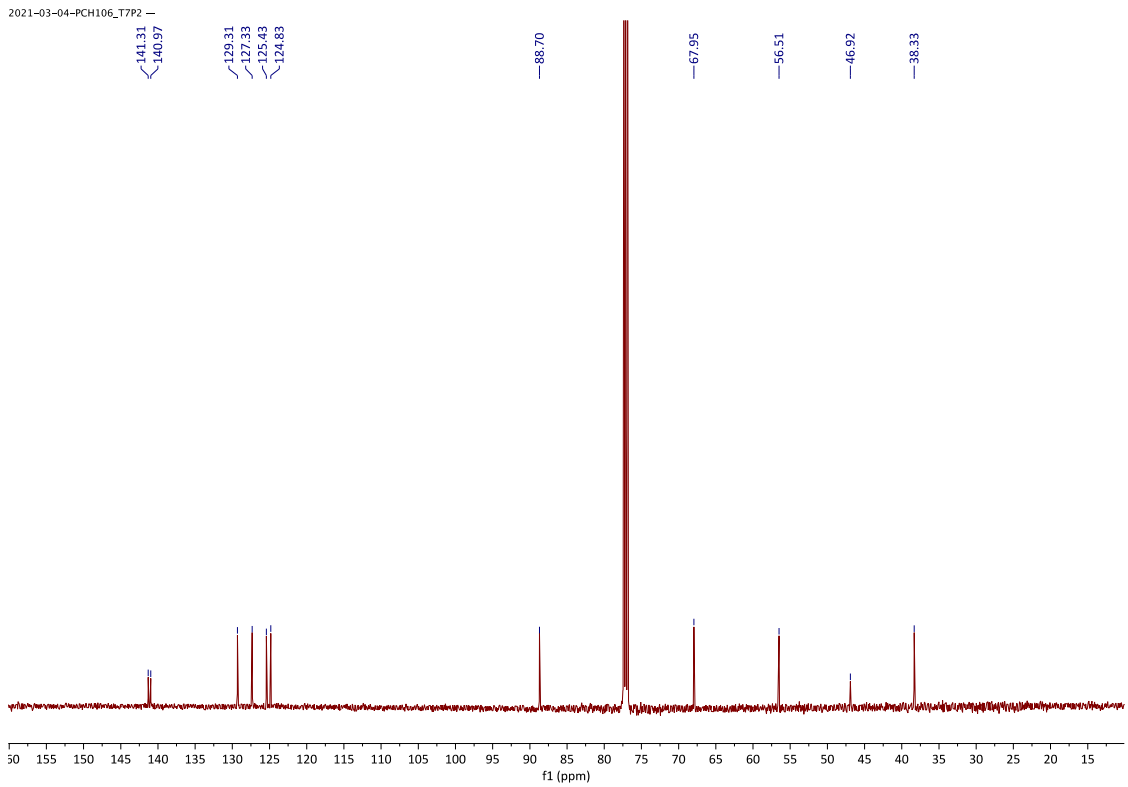
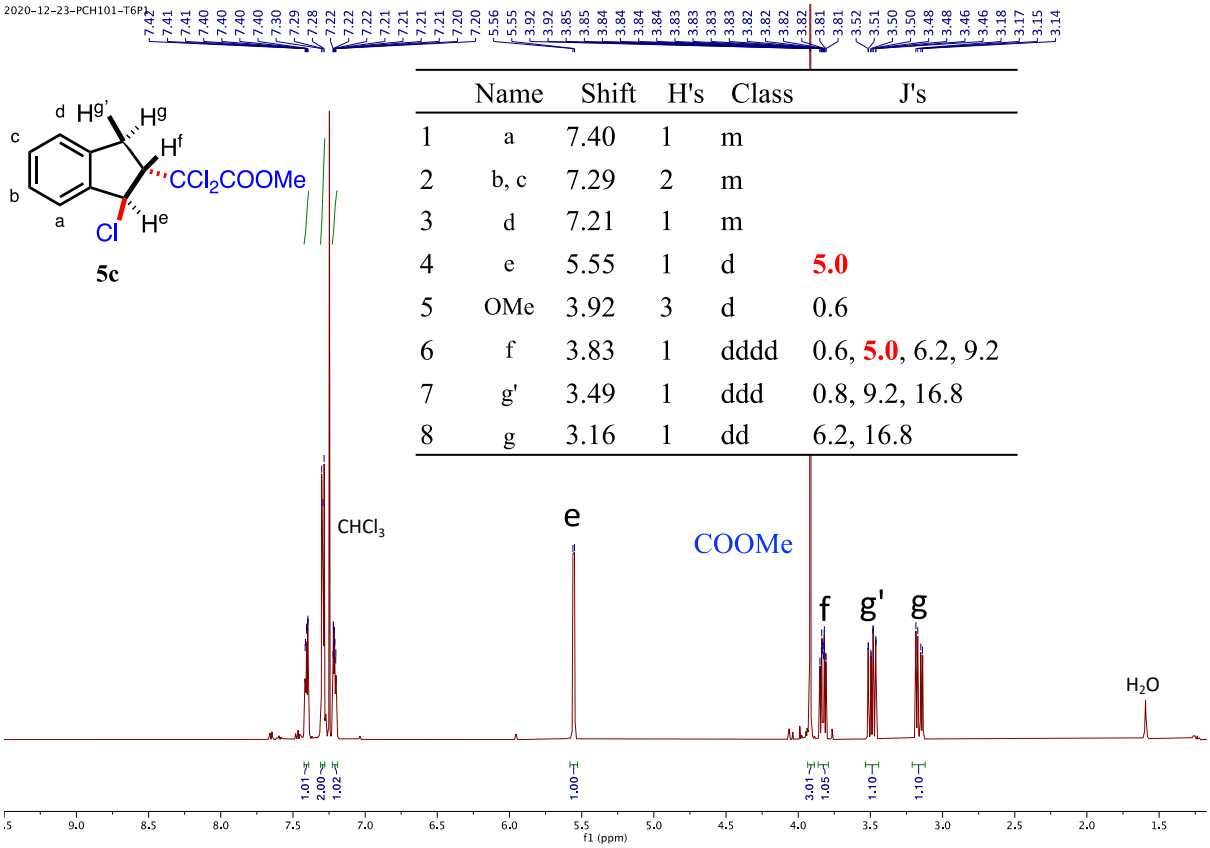


Fig. S74. ^{1}H NMR spectrum of *anti*-methyl 2,2-dichloro-2-(1-chloro-2,3-dihydro-1H-inden-2-yl) acetate, **5c**.



	Name	Shift	H's	Class	J's
1	a	7.40	1	m	
2	b, c	7.29	2	m	
3	d	7.21	1	m	
4	e	5.55	1	d	**5.0**
5	OMe	3.92	3	d	0.6
6	f	3.83	1	dddd	0.6, **5.0**, 6.2, 9.2
7	g'	3.49	1	ddd	0.8, 9.2, 16.8
8	g	3.16	1	dd	6.2, 16.8

Fig. S75. ^{13}C NMR spectrum of *anti*-methyl 2,2-dichloro-2-(1-chloro-2,3-dihydro-1H-inden-2-yl) acetate, **5c**.

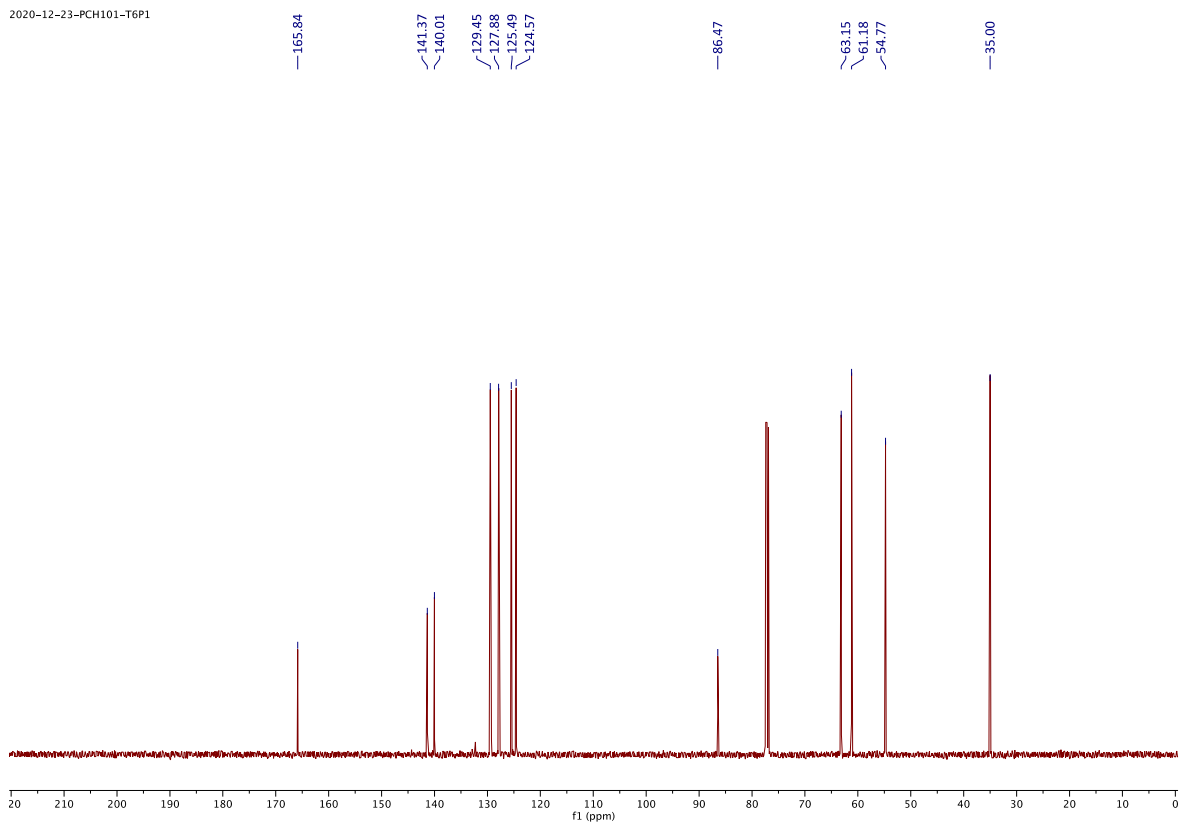
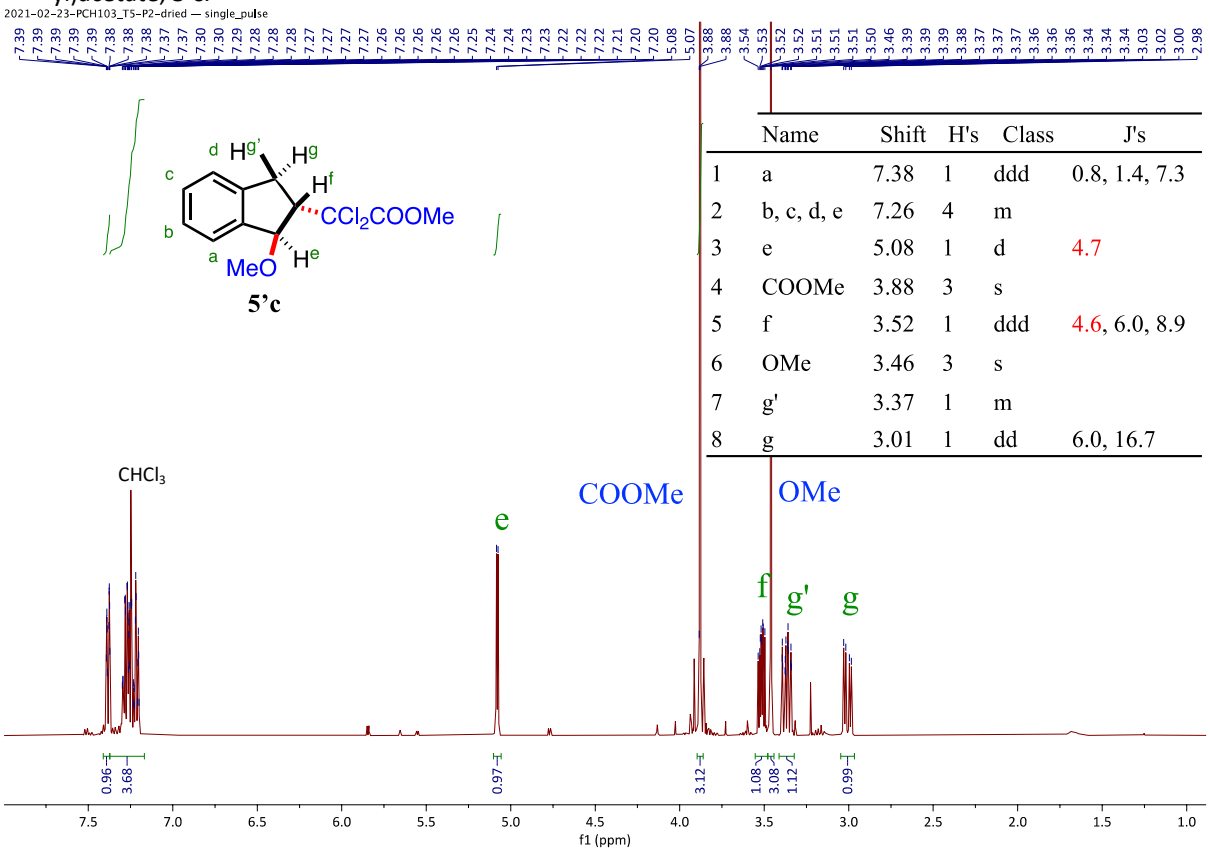


Fig. S76. ^{1}H NMR spectrum of *anti*-methyl 2,2-dichloro-2-(1-methoxy-2,3-dihydro-1H-inden-2-yl)acetate, **5'c**.



	Name	Shift	H's	Class	J's
1	a	7.38	1	ddd	0.8, 1.4, 7.3
2	b, c, d, e	7.26	4	m	
3	e	5.08	1	d	4.7
4	COOMe	3.88	3	s	
5	f	3.52	1	ddd	4.6, 6.0, 8.9
6	OMe	3.46	3	s	
7	g'	3.37	1	m	
8	g	3.01	1	dd	6.0, 16.7

Fig. S77. ^{13}C NMR spectrum of *anti*-methyl 2,2-dichloro-2-(1-methoxy-2,3-dihydro-1H-inden-2-yl)acetate, **5'c**.

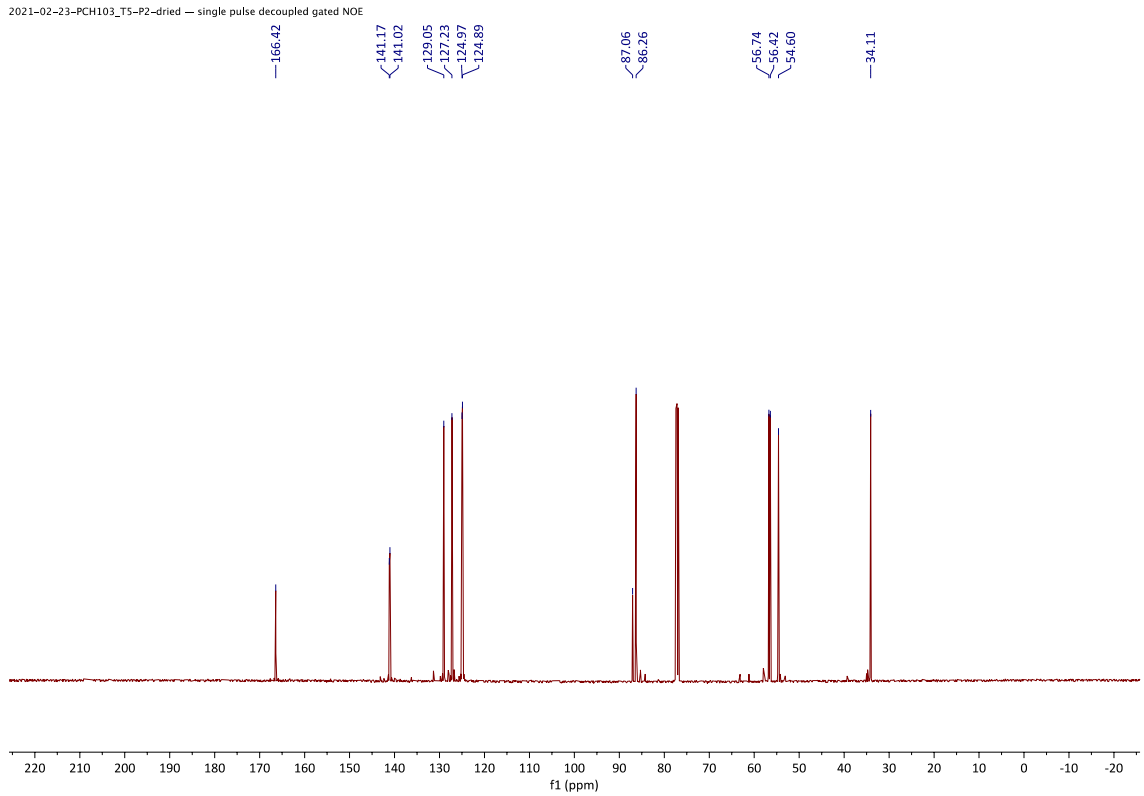
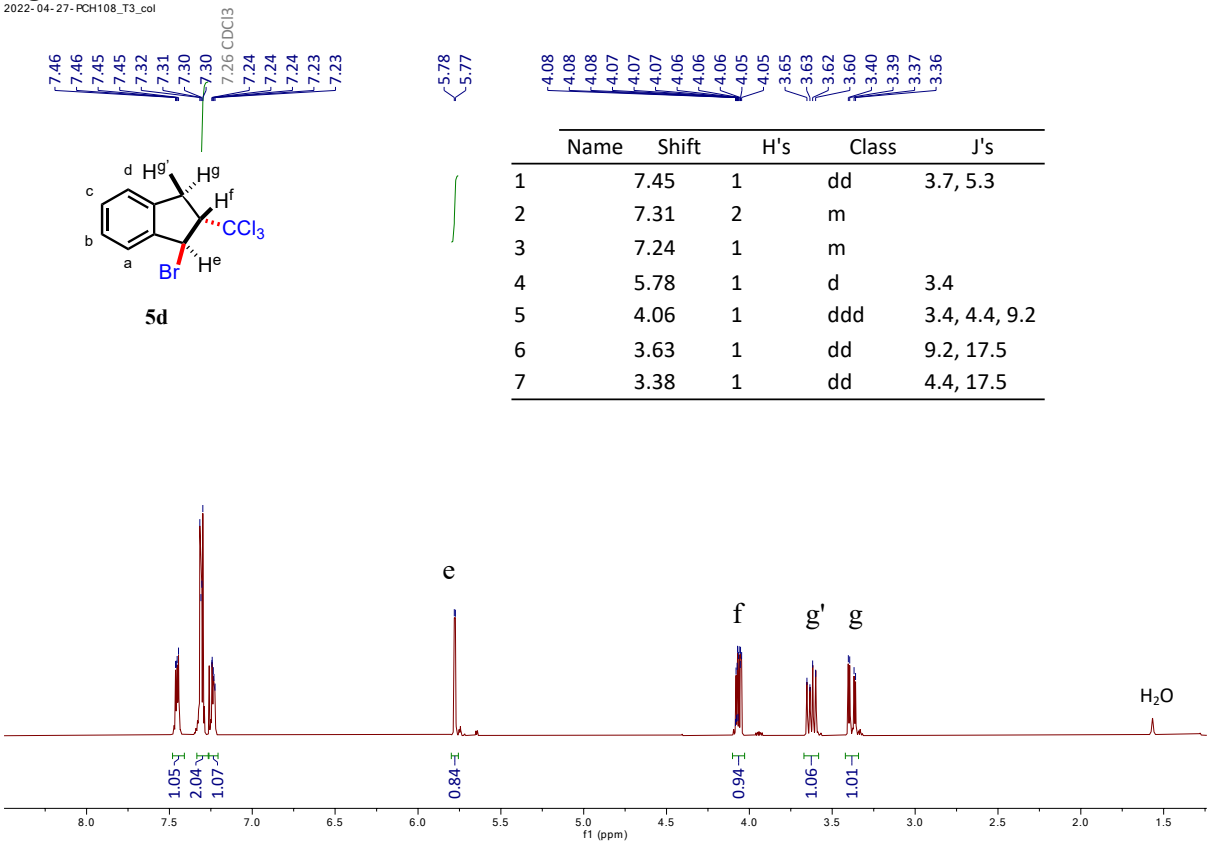


Fig. S78. ^{1}H NMR spectrum of *anti*-1-bromo-2-(trichloromethyl)-2,3-dihydro-1H-indene, **5d**.



	Name	Shift	H's	Class	J's
1		7.45	1	dd	3.7, 5.3
2		7.31	2	m	
3		7.24	1	m	
4		5.78	1	d	3.4
5		4.06	1	ddd	3.4, 4.4, 9.2
6		3.63	1	dd	9.2, 17.5
7		3.38	1	dd	4.4, 17.5

Fig. S79. ^{13}C NMR spectrum of *anti*-1-bromo-2-(trichloromethyl)-2,3-dihydro-1H-indene, **5d**.

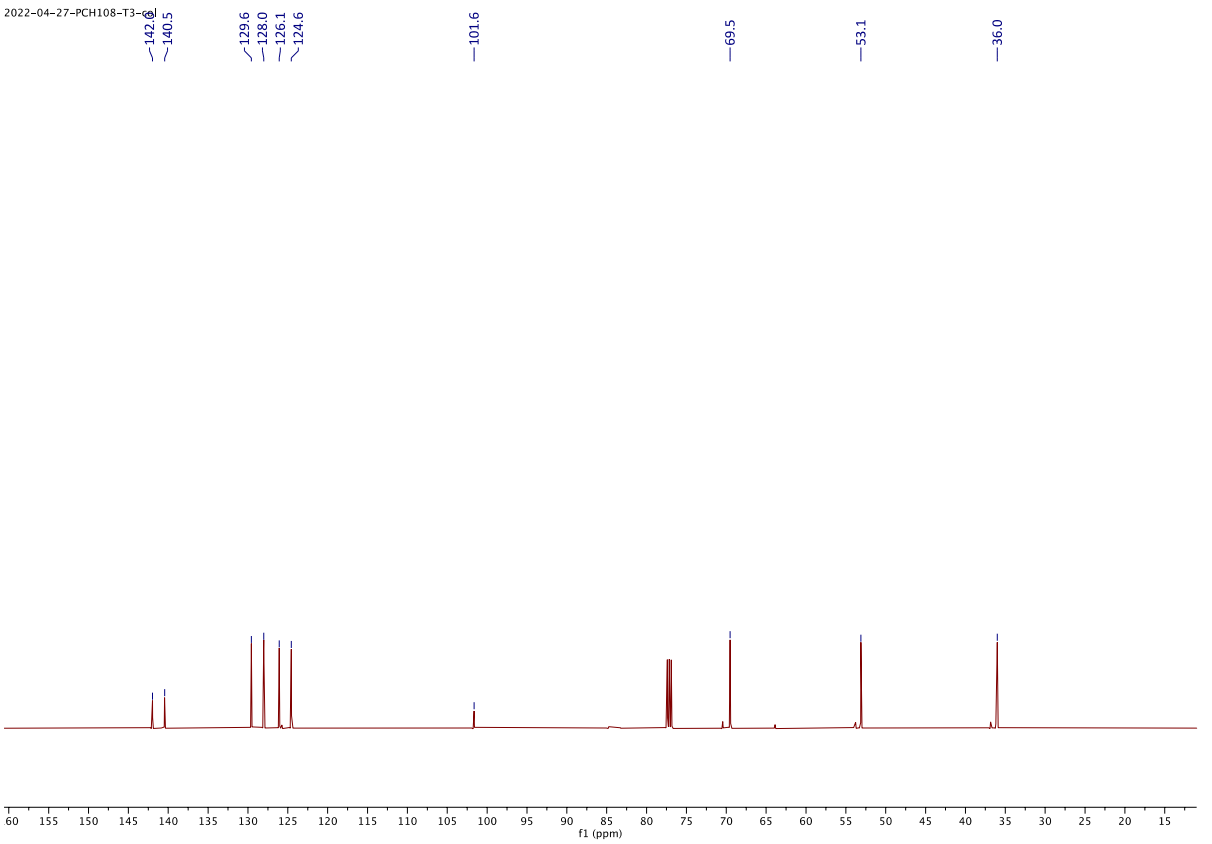
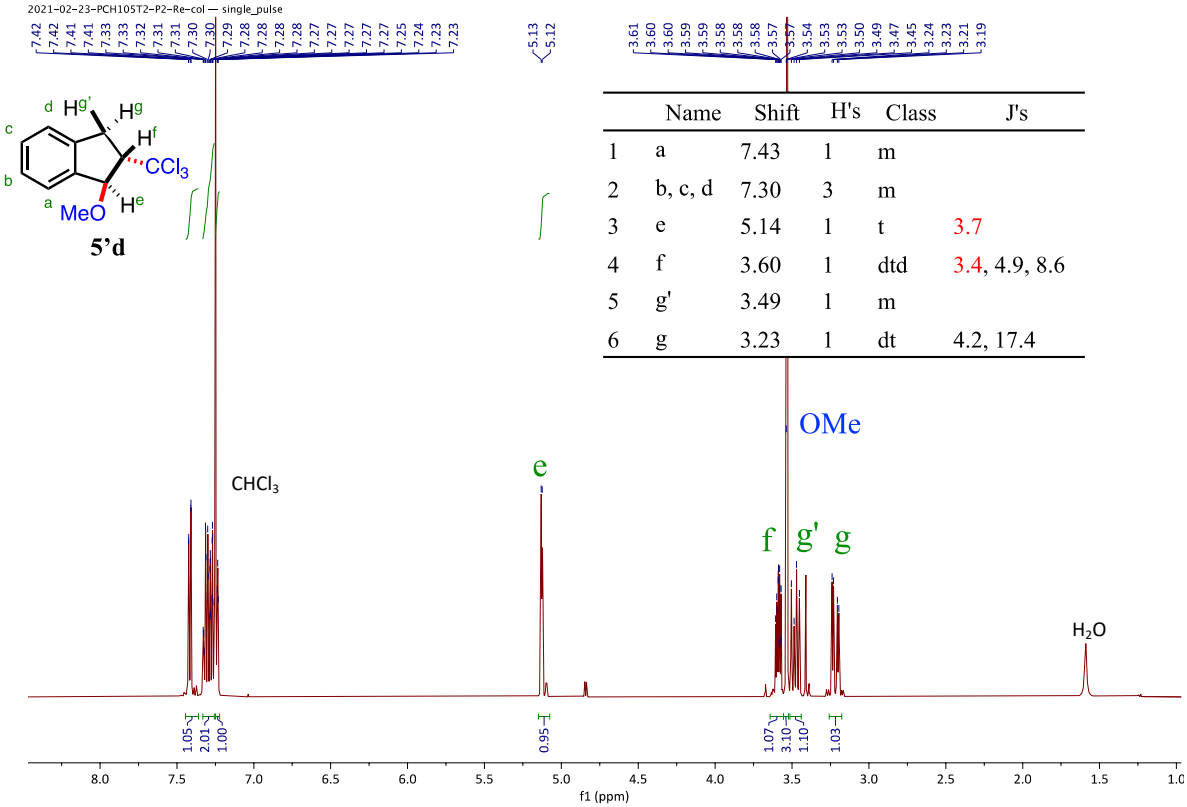


Fig. S80. ^{1}H NMR spectrum of *anti*-1-methoxy-2-(trichloromethyl)-2,3-dihydro-1*H*-indene, **5'd**.



	Name	Shift	H's	Class	J's
1	a	7.43	1	m	
2	b, c, d	7.30	3	m	
3	e	5.14	1	t	3.7
4	f	3.60	1	dtd	3.4, 4.9, 8.6
5	g'	3.49	1	m	
6	g	3.23	1	dt	4.2, 17.4

Fig. S81. ^{13}C NMR spectrum of *anti*-1-methoxy-2-(trichloromethyl)-2,3-dihydro-1*H*-indene, **5'd**.

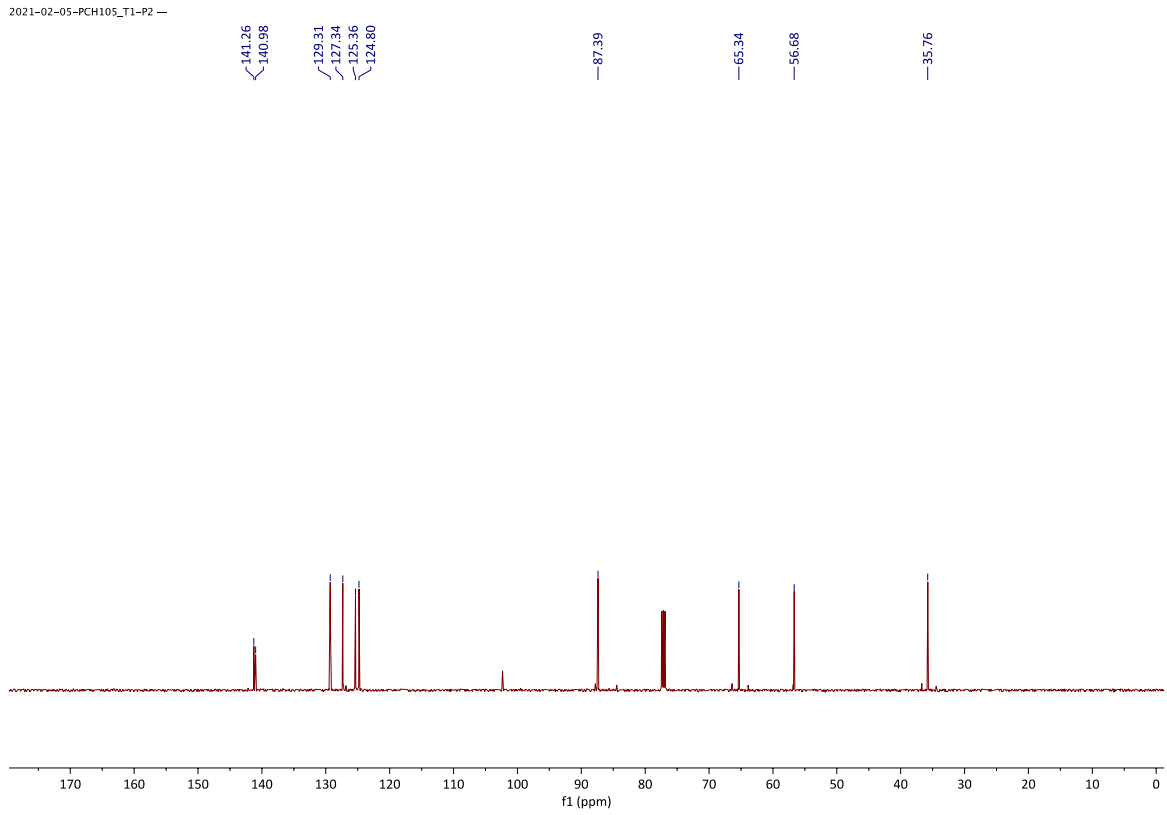
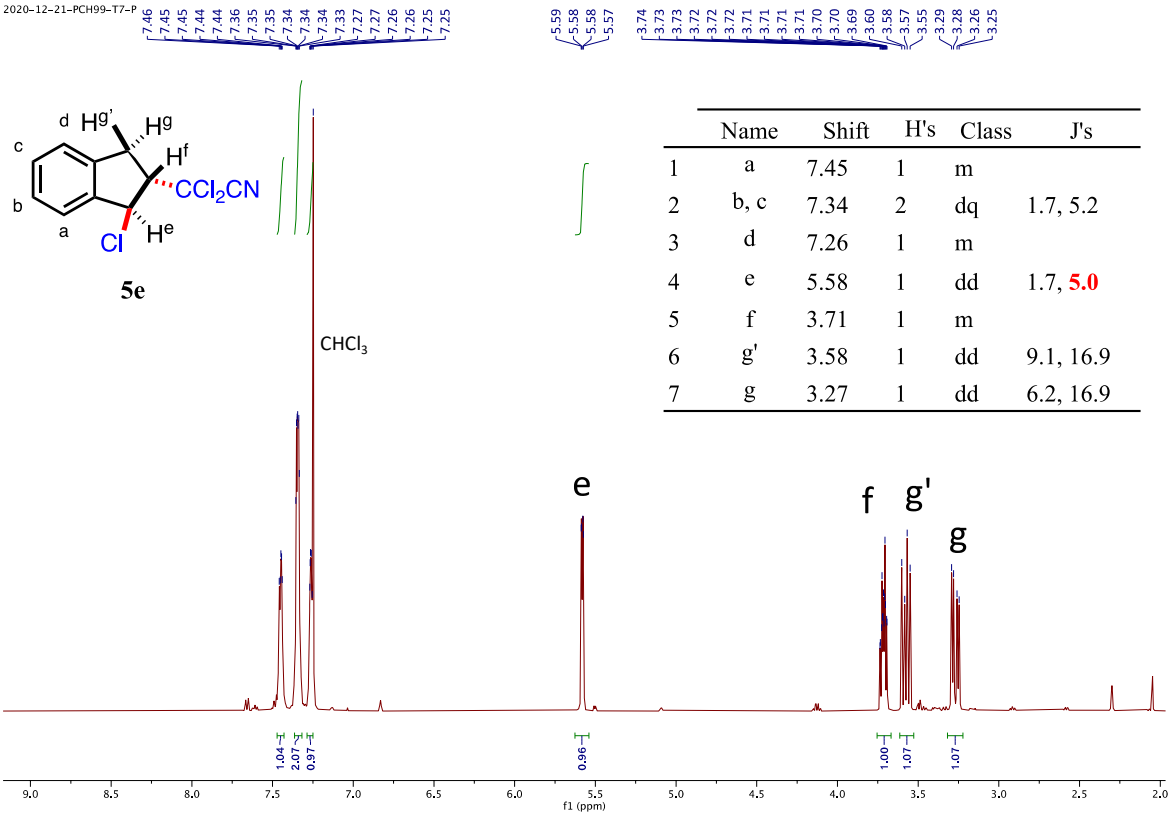


Fig. S82. ^{1}H NMR spectrum of *anti*-2,2-dichloro-2-(1-chloro-2,3-dihydro-1*H*-inden-2-yl) acetonitrile, **5e**.



	Name	Shift	H's	Class	J's
1	a	7.45	1	m	
2	b, c	7.34	2	dq	1.7, 5.2
3	d	7.26	1	m	
4	e	5.58	1	dd	1.7, **5.0**
5	f	3.71	1	m	
6	g'	3.58	1	dd	9.1, 16.9
7	g	3.27	1	dd	6.2, 16.9

Fig. S83. ^{13}C NMR spectrum of *anti*-2,2-dichloro-2-(1-chloro-2,3-dihydro-1*H*-inden-2-yl) acetonitrile, **5b**.

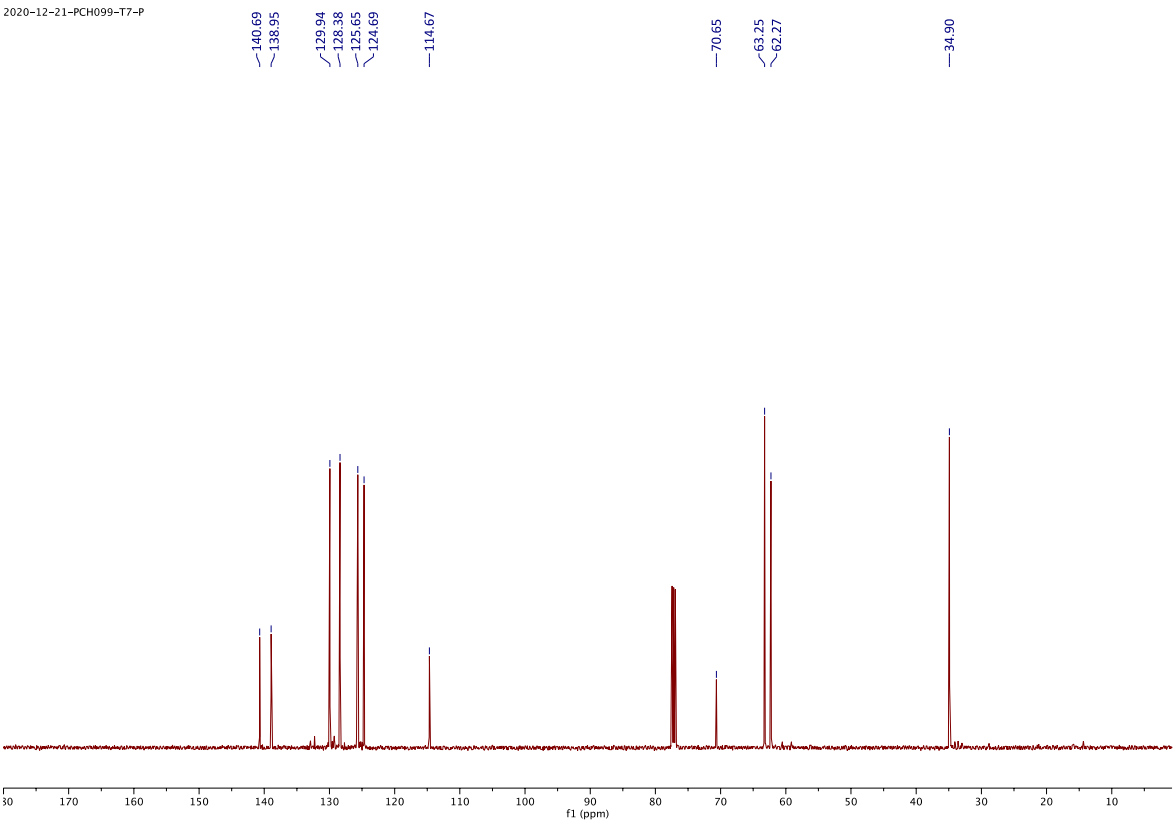
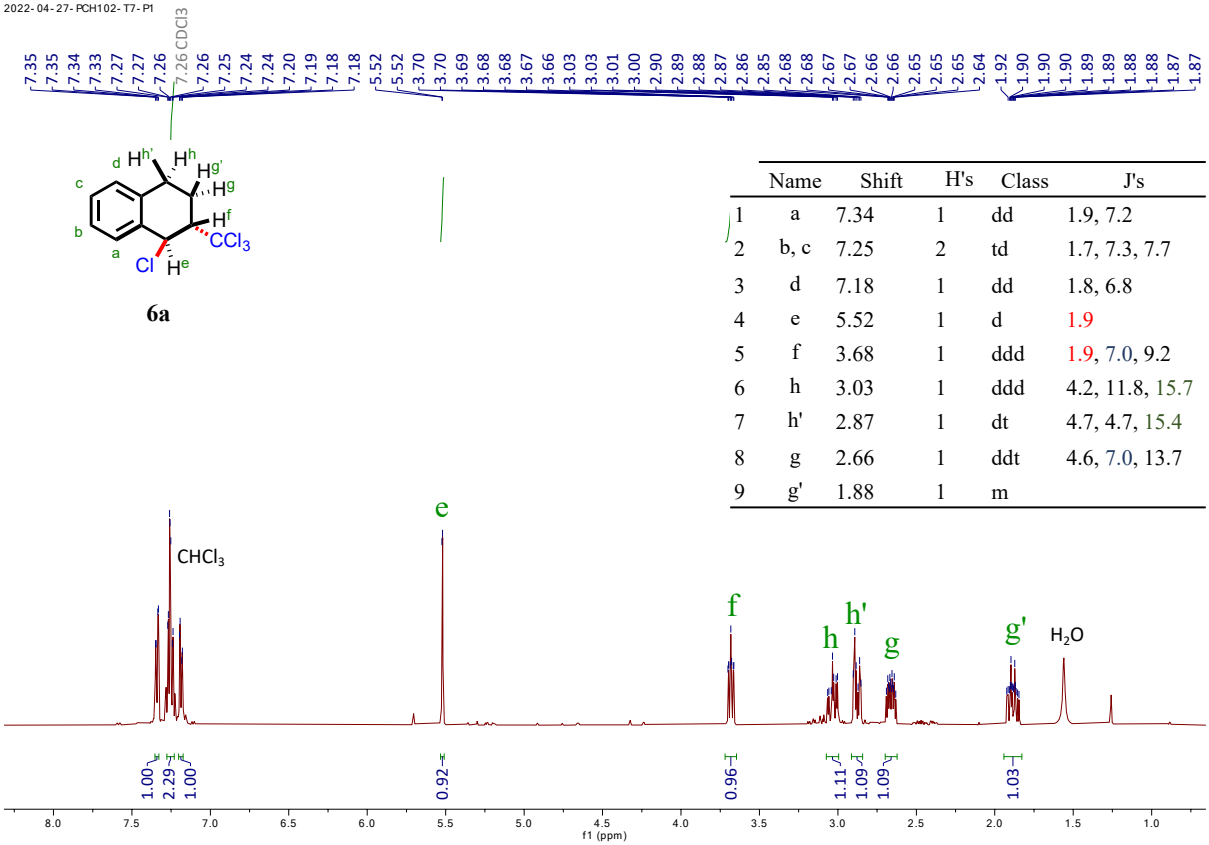


Fig. S84. ^{1}H NMR spectrum of *anti*-1-chloro-2-(trichloromethyl)-1,2,3,4-tetrahydronaphthalene, **6a**.



6a

	Name	Shift	H's	Class	J's
1	a	7.34	1	dd	1.9, 7.2
2	b, c	7.25	2	td	1.7, 7.3, 7.7
3	d	7.18	1	dd	1.8, 6.8
4	e	5.52	1	d	1.9
5	f	3.68	1	ddd	1.9, 7.0, 9.2
6	h	3.03	1	ddd	4.2, 11.8, 15.7
7	h'	2.87	1	dt	4.7, 4.7, 15.4
8	g	2.66	1	ddt	4.6, 7.0, 13.7
9	g'	1.88	1	m	

Fig. S85. ^{13}C NMR spectrum of *anti*-1-chloro-2-(trichloromethyl)-1,2,3,4-tetrahydronaphthalene, **6a**.

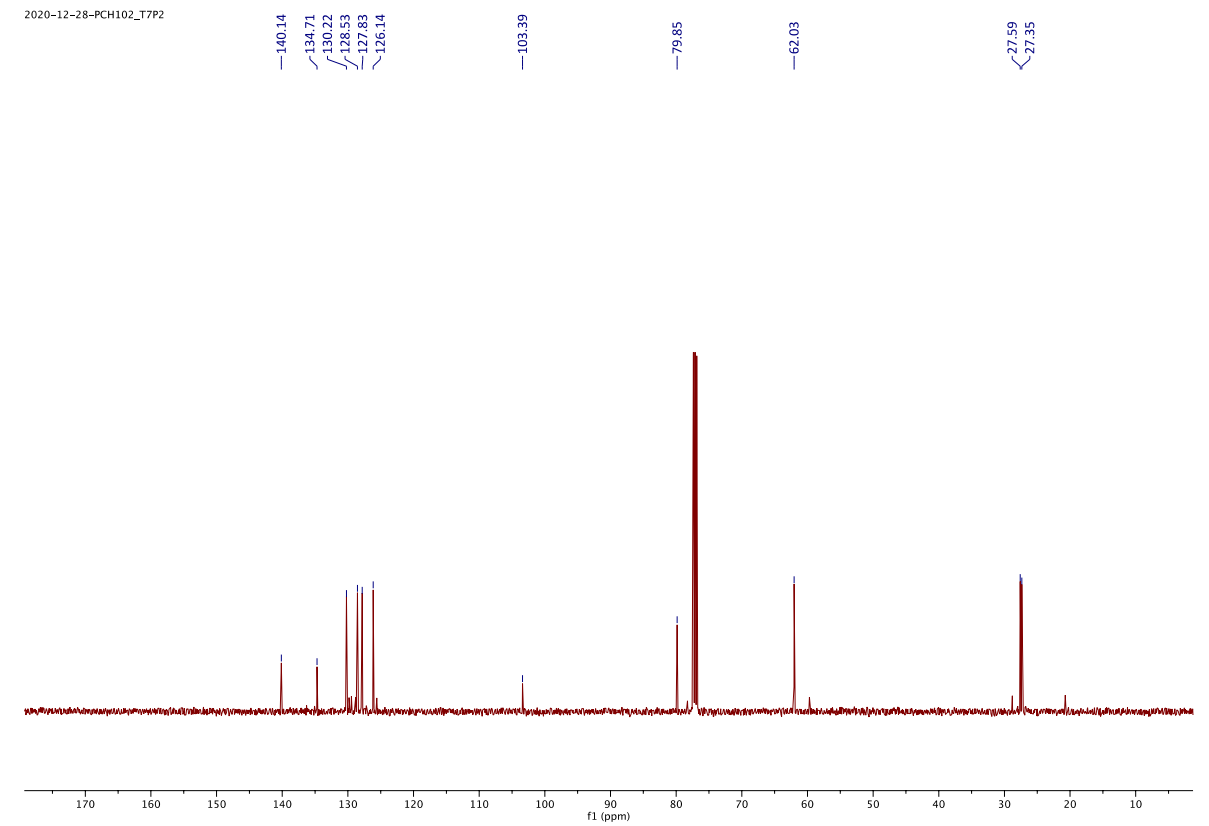
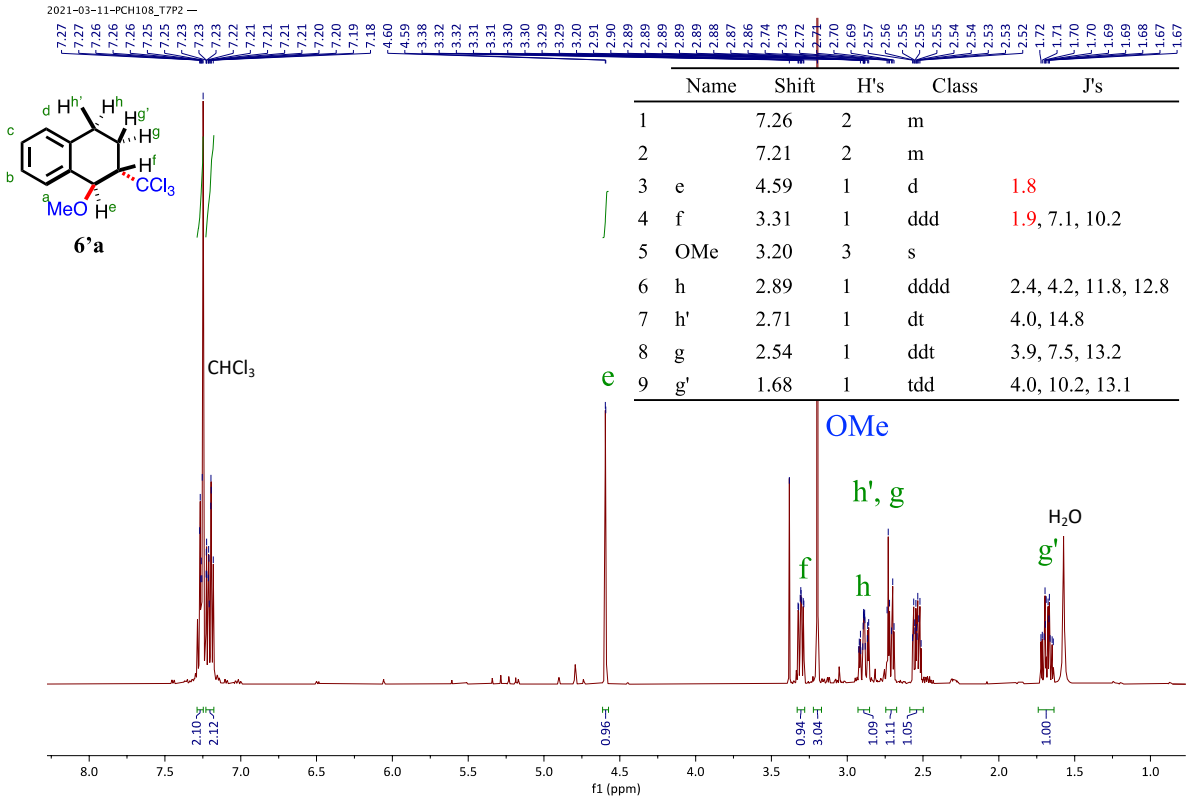


Fig. S86. ^{1}H NMR spectrum of *anti*-1-methoxy-2-(trichloromethyl)-1,2,3,4-tetrahydronaphthalene, **6'a**.



	Name	Shift	H's	Class	J's
1		7.26	2	m	
2		7.21	2	m	
3	e	4.59	1	d	1.8
4	f	3.31	1	ddd	1.9, 7.1, 10.2
5	OMe	3.20	3	s	
6	h	2.89	1	dddd	2.4, 4.2, 11.8, 12.8
7	h'	2.71	1	dt	4.0, 14.8
8	g	2.54	1	ddt	3.9, 7.5, 13.2
9	g'	1.68	1	tdd	4.0, 10.2, 13.1

Fig. S87. ^{13}C NMR spectrum of *anti*-1-methoxy-2-(trichloromethyl)-1,2,3,4-tetrahydronaphthalene, **6'a**.

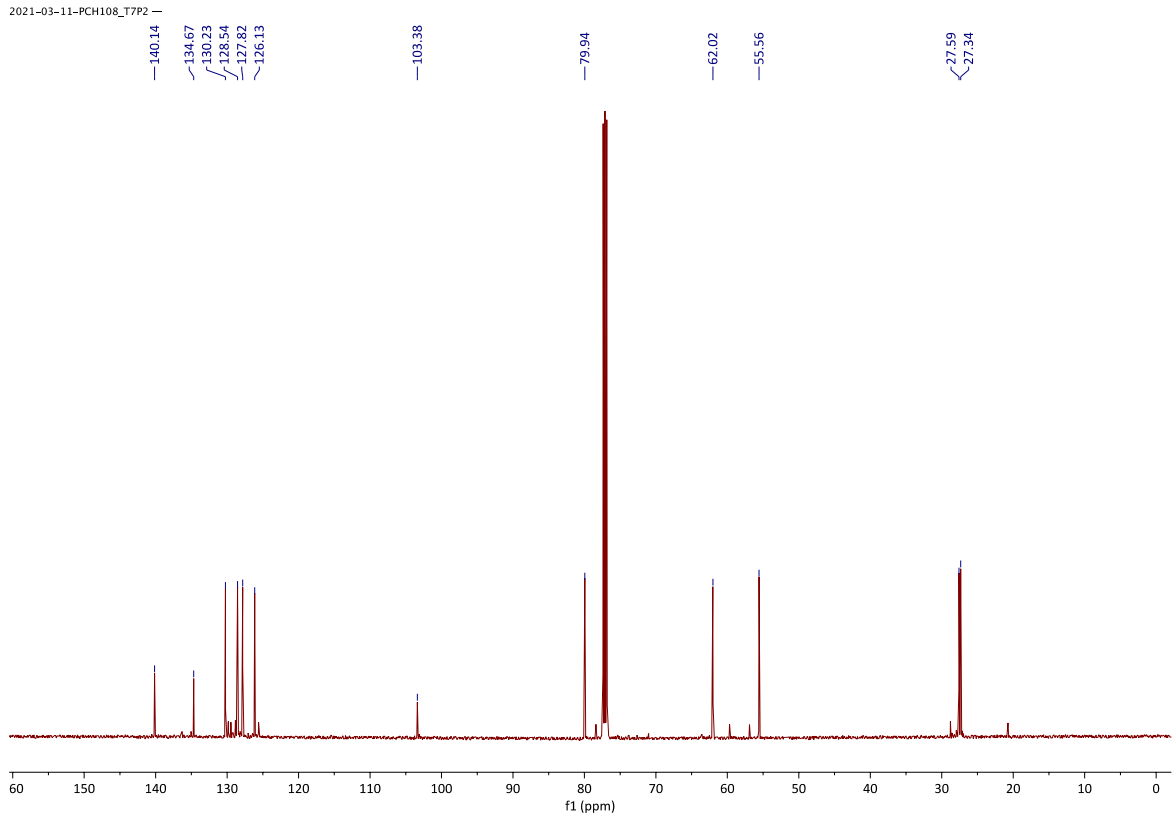


Fig. S88. ^{1}H NMR spectrum of *anti*-1-methoxy-2-(tribromomethyl)-1,2,3,4-tetrahydronaphthalene, **6'b**.

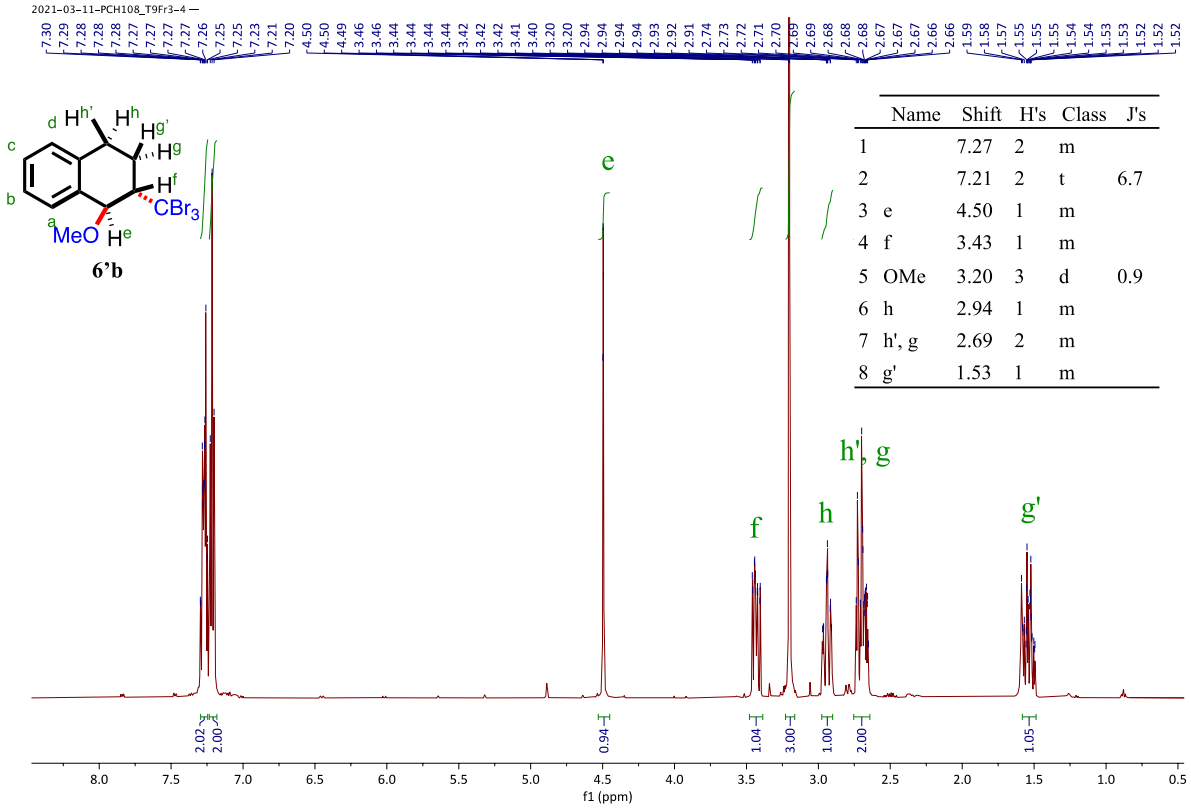
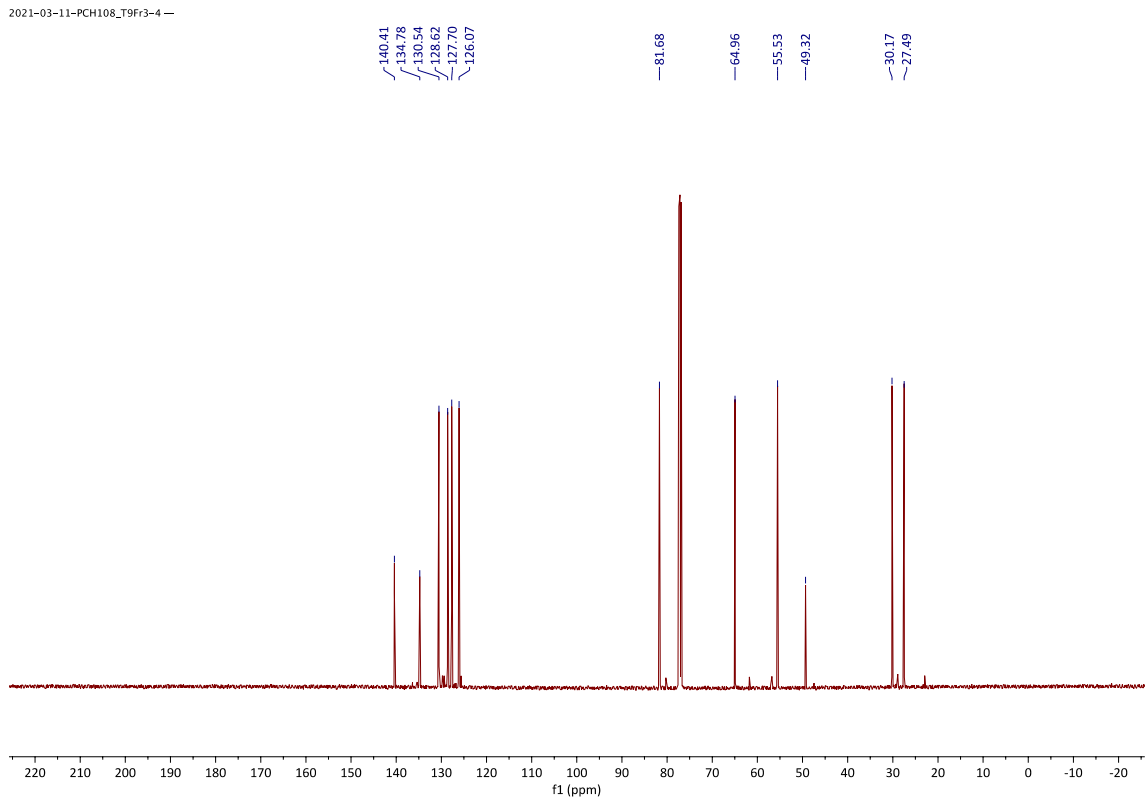


Fig. S89. ^{13}C NMR spectrum of *anti*-1-methoxy-2-(tribromomethyl)-1,2,3,4-tetrahydronaphthalene, **6'b**.



1. A. J. Clark, D. P. Curran, D. J. Fox, F. Ghelfi, C. S. Guy, B. Hay, N. James, J. M. Phillips, F. Roncaglia, P. B. Sellars, P. Wilson and H. Zhang, *J. Org. Chem.*, 2016, **81**, 5547-5565.