Supporting Information

for

Dinuclear Molybdenum Cluster-Catalyzed Radical Addition and Polymerization Reactions by Tuning the Redox Potential of a Quadruple Bonded Mo_2 Core

Hayato Tsurugi, Kohei Yamada, Moumita Majumdar, Yoshitaka Sugino,
Akio Hayakawa, and Kazushi Mashima*

Department of Chemistry, Graduate School of Engineering Science, Osaka University,
Toyonaka, Osaka 560-8531, Japan

Tel/Fax: +81-6-6850-6245;
E-mail: mashima@chem.es.osaka-u.ac.jp

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard Schlenk or glovebox techniques under argon. Complexes $[Mo_2\{(PhN)_2CNHPh\}_4]$ (**3**),[S1] $[Mo_2\{(ArN)_2CH\}_4]$ (Ar = 4-$C_8H_{17}OC_6H_4$) (**2**),[S2] and $[M_2\{O_2CC_6H_2{}^iPr\text{-}2,4,6\}_4]$ (**1**: M = Mo,[S3] **4**: M = Cr,[S4] **5**: M = W[S5]) were prepared according to the literatures. Anhydrous hexane, toluene, THF, Et_2O, and dichloromethane were purchased from Kanto Chemical, and further purified by passage through activated alumina under positive argon pressure as described by Grubbs *et al.*[S6] Other organic substrates were purchased, and dried and deoxygenated by distillation over CaH_2. Benzene-d_6, toluene-d_8, $CDCl_3$, CD_2Cl_2, and THF-d_8 were degassed and stored under argon.

^1H NMR (300 MHz, 400 MHz) and ^{13}C NMR (75 MHz, 100 MHz) spectra were measured on VARIAN UNITY INOVA-300 and BRUKER AVANCEIII-400 spectrometers. Assignments for ^1H and ^{13}C NMR peaks for some of the complexes were aided by 2D ^1H-^1H COSY, 2D ^1H-^1H NOESY, 2D ^1H-^{13}C HETCOR, and/or 2D ^1H-^{13}C HMBC spectra. UV-vis spectra were recorded on Aglient 8453 spectrometer. Cyclic volutammograms were measured by BAS ALS610D spectrometer using a standard three-electrode configuration with working electrode (glassy carbon), counter electrode (platinum), and reference electrode (silver). $[^nBu_4N][PF_6]$ was used as the electrolyte, and Cp_2Fe was used as the standard. GC-MS measurement was carried out using a DB-1 capillary column (0.25 mm x 30 m) on a Shimadzu GCMS-QP2010Plus.

General Procedure for Radical Addition Reaction of CCl_4 to Various Alkenes (Tables 1 and 2): A solution of the alkene substrate (0.801 or 0.868 mmol), dinuclear complex (3 mol% based on olefin), CCl_4 (1.03 mmol), and hexamethylbenzene as an internal standard in 0.5 mL of deuterated solvent was prepared in a light shielding J-Young NMR tube. The reaction mixture was heated to 80 ^{o}C. The conversions and yields were calculated by the ^{1}H NMR measurement based on the amount of the internal standard. The reaction mixture was concentrated and purified by column chromatography on a silica gel or Kugelrohr distillation. Identity of the ATRA product was confirmed by comparison of ^{1}H NMR data obtained from the literature.

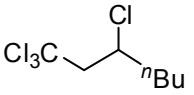
Radical Addition of Cl_3CCO_2Et, $Cl_3C(S)O^nPr$, $CDCl_3$, and $CHBrCl_2$ to 1-Hexene (Scheme 1): Alkyl halide (1.03 mmol), 1-hexene (0.801 mmol), catalyst (0.0240 mmol), hexamethylbenzene as an internal standard, and 0.5 mL of $CDCl_3$ were added to a light shielding J-Young NMR tube. The reaction mixture was heated to 80 ^{o}C. The yields were calculated by the ^{1}H NMR measurement based on the amount of the internal standard. The reaction mixture was concentrated and purified by column chromatography on a silica gel or Kugelrohr distillation. Identity of the ATRA product was confirmed by comparison of ^{1}H NMR data obtained from the literature.

General Procedures for Radical Polymerization of MMA (Table 3): MMA (0.942 mmol), $BrC(CH_3)_2CO_2CH_2CH_3$ (10 mol% based on MMA), catalyst (0.5 mol% based on MMA), hexamethylbenzene as an internal standard, and 0.5 mL of toluene-d_8 were added to a light shielding J-Young NMR tube. The NMR tube was heated to the reaction temperature. After heating for 12 hours, the polymerization reaction was quenched by the addition of methanol. The formed polymer was dissolved in a small amount of THF, and the solution was added dropwise to the large amount of methanol. The precipitated polymer was filtered and washed with methanol. The polymer was dried under vacuum.

Preparation of $[Mo_2\{(PhN)_2CNHPh\}_4][Br]$ (6): To a solution of complex **3** in THF was added benzyl bromide (200 equiv), and the mixture was heated at 60 °C for 24 hours. After cooling the solution to room temperature, red-brown crystals were formed. The X-ray diffraction study of the crystal revealed the formation of $[Mo_2\{(PhN)_2CNHPh\}_4][Br]$ (**6**).

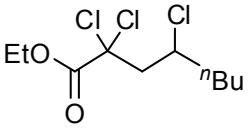
Characterization Data of Coupling Products:

1,1,1,3-Tetrachloroheptane[S7)]



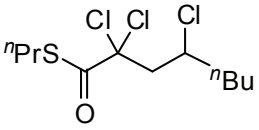
^{1}H NMR (400 MHz, 308 K, $CDCl_3$): δ 4.31–4.21 (m, 1H, -CH(Cl)-), 3.29 (dd, J = 5.7 Hz and 15.6 Hz, 1H, CCl_3CHH), 3.13 (dd, J = 4.2 Hz and 15.6 Hz, 1H, CCl_3CHH), 2.0–1.7 (m, 2H, -CH(Cl)CH_2-), 1.6–1.3 (m, 4H, -$(CH_2)_2$-), 0.94 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 97.0, 62.3, 57.7, 38.8, 28.1, 22.0, 13.9. MS (EI): *m/z* 201 [M^+-Cl].

Ethyl 2,2,4-trichlorooctanoate[S7)]



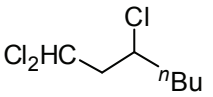
^{1}H NMR (400 MHz, 308 K, $CDCl_3$): δ 4.4–4.1 (m, 3H, OCH_2 and -CH(Cl)-), 3.10 (dd, J = 8.5 Hz and 15.6 Hz, 1H, -$C(Cl)_2CHH$-), 2.81 (dd, J = 3.5 Hz and 15.6 Hz, 1H, -$C(Cl)_2CHH$-), 1.9–1.7 (m, 2H, -CH(Cl)CH_2-), 1.6–1.2 (m, 4H, -$(CH_2)_2$-), 1.36 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 0.92 (t, J = 7.2, 3H, -$(CH_2)_2CH_3$). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 165.5, 82.9, 64.0, 58.1, 53.0, 38.4, 28.2, 22.0, 13.8, 13.7. MS (EI): *m/z* 275 [M^++H].

n-Propyl 2,2,4-trichlorooctanethioate



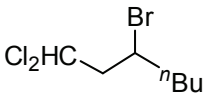
^{1}H NMR (400 MHz, 308 K, $CDCl_3$): δ 4.2–4.1 (m, 1H, -CH(Cl)-), 3.09 (dd, J = 7.7 Hz and 15.4 Hz, 1H, -$C(Cl)_2CHH$-), 2.93 (t, J = 7.3 Hz, 2H, SCH_2), 2.84 (dd, J = 4.0 Hz and 15.3 Hz, 1H, -$C(Cl)_2CHH$-), 1.8–1.6 (m, 4H, -CH(Cl)CH_2- and SCH_2CH_2-), 1.6–1.2 (m, 4H, -$(CH_2)_2CH_3$), 1.02 (t, J = 7.3 Hz, 3H, $SCH_2CH_2CH_3$), 0.92 (t, J = 7.2 Hz, 3H, -$(CH_2)_2CH_3$). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 194.4, 87.8, 57.7, 52.6, 38.5, 33.0, 28.2, 22.1, 22.0, 13.8, 13.3. MS (EI): *m/z* 306 [M^+].

1,1,3-Trichloroheptane[S8)]



^{1}H NMR (400 MHz, 308 K, $CDCl_3$): δ 6.0–5.9 (m, 1H, Cl_2CH-), 4.1–4.0 (m, 1H, -CH(Cl)-), 2.6–2.5 (m, 2H, Cl_2CHCH_2), 1.8–1.7 (m, 2H, -CH(Cl)CH_2-), 1.6–1.3 (m, 4H, -$(CH_2)_2CH_3$), 0.93 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, 308K, $CDCl_3$): δ 70.8, 59.4, 51.8, 37.8, 28.2, 22.1, 13.8. MS (EI): *m/z* 203 [M^+].

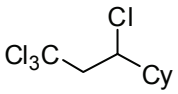
3-Bromo-1,1-dichloroheptane[S9)]



^{1}H NMR (400 MHz, 308 K, $CDCl_3$): δ 6.05–5.95 (m, 1H, Cl_2CH-), 4.2–4.1 (m, 1H, -CH(Br)-), 2.7–2.6 (m, 2H, Cl_2CHCH_2-), 1.9–1.8 (m, 2H, -CH(Br)CH_2-), 1.6–1.2 (m, 4H, -$(CH_2)_2CH_3$), 0.93 (t, J = 7.3 Hz,

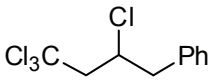
3H, CH_3). ^{13}C NMR (100 MHz, 303 K, $CDCl_3$): δ 71.9, 52.4, 52.1, 38.4, 29.3, 22.0, 13.9. MS (EI): *m/z* 248 [M^+].

(1,3,3,3-Tetrachloropropyl)cyclohexane[S10)]



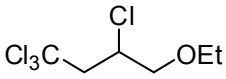
^1H NMR (400 MHz, 308 K, $CDCl_3$): δ 4.2–4.1 (m, 1H, -CH(Cl)-), 3.17 (d, *J* = 5.3 Hz, 2H, Cl_3CH_2-), 1.9–1.6 (m, 6H, Cy), 1.4–1.1 (m, 5H, Cy). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 97.6, 62.9, 60.2, 45.1, 29.8, 27.4, 26.1_0, 26.0_5, 25.9. MS (EI): *m/z* 264 [M^+].

(2,4,4,4-Tetrachlorobutyl)benzene[S11)]



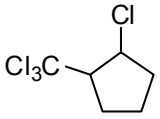
^1H NMR (400 MHz, 308 K, $CDCl_3$): δ 7.4–7.1 (m, 5H, Ph), 4.35–4.45 (m, 1H, -CH(Cl)-), 3.3–3.0 (m, 4H, -CH_2CH(Cl)CH_2-). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 136.6, 129.5, 128.6, 127.3, 96.8, 61.1, 57.7, 45.3. MS (EI): *m/z* 272 [M^+].

1,1,1,3-Tetrachloro-4-ethoxybutane [S12)]



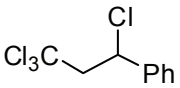
^1H NMR (400 MHz, 308 K, $CDCl_3$): δ 4.4–4.3 (m, 1H, -CH(Cl)-), 3.8–3.4 (m, 4H, -CH_2OCH_2-), 3.41 (dd, *J* = 3.4 Hz and 15.7 Hz, 1H, Cl_3CC*H*H-), 3.12 (dd, *J* = 6.6 Hz and 15.7 Hz, 1H, Cl_3CCH*H*-), 1.23 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 73.6, 66.9, 58.7, 54.7, 15.0. Cl_3CCH_2 was not observed. MS (EI): *m/z* 240 [M^+].

1-Chloro-2-(trichloromethyl)cyclopentane[S13)]



^1H NMR (400 MHz, 308 K, $CDCl_3$): δ 4.5–4.4 (m, 1H, -CH(Cl)-), 3.55–3.4 (m, 1H, Cl_3CCH), 2.4–1.7 (m, 6H, -$(CH_2)_3$-). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 71.2, 61.6, 38.6, 31.1, 24.7. MS (EI): *m/z* 185 [M^+-Cl].

(1,3,3,3-Tetrachloropropyl)benzene[S14)]



^1H NMR (400 MHz, 308 K, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.30 (t, *J* = 6.0 Hz, 1H, -CH(Cl)-), 3.65 (dd, *J* = 5.5 Hz and 15.4 Hz, 1H, Cl_3CC*H*H), 3.55 (dd, *J* = 6.3 Hz and 15.4 Hz, 1H, Cl_3CCH*H*). ^{13}C NMR (100 MHz, 308 K, $CDCl_3$): δ 140.5, 128.9, 127.4, 96.2, 62.8, 58.3. MS (EI): *m/z* 258 [M^+].

End Group Analysis of PMMA.

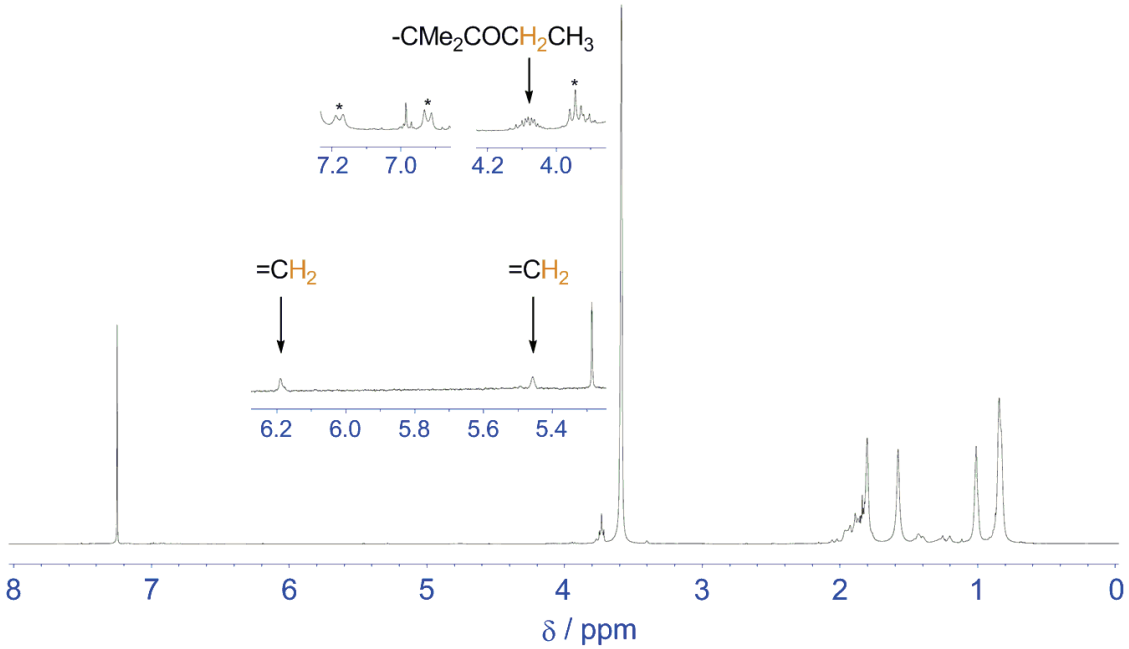


Figure S1. The ^{1}H NMR spectra of PMMA obtained by **2** and ethyl 2-bromoisobutyrate (* : impurity from 4-($C_8H_{17}O$)C_6H_4N group).

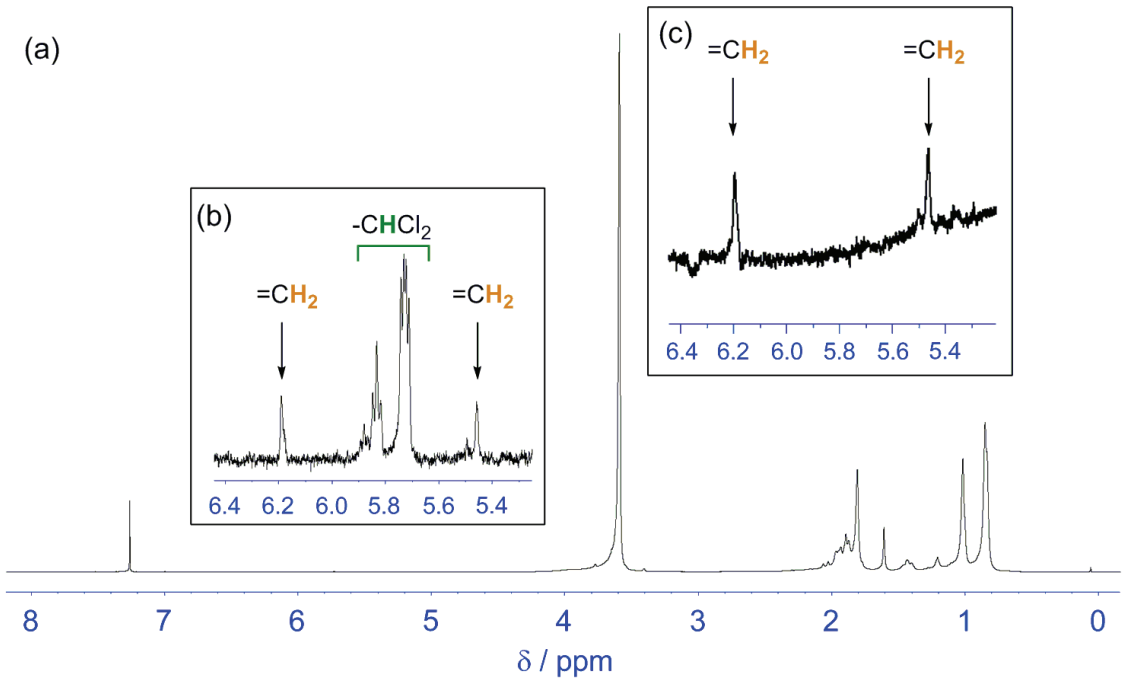


Figure S2. The ^{1}H NMR spectra of PMMA obtained by **3** and chloroform. (a) The ^{1}H NMR spectrum of PMMA obtained by **3** and $CHCl_3$. (b) Selected region (5.3 – 6.4 ppm) of PMMA obtained by **3** and $CHCl_3$. (c) Selected region (5.3 – 6.4 ppm) of PMMA obtained by **3** and $CDCl_3$.

X-Ray Diffraction Study of 6 (CCDC 809907).

The crystal was mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. Measurement was made on Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo–Kα (0.71075 Å) radiation. The structure of **6** was solved by direct method (SIR-2008),[S15] and refined on F^2 by full-matrix least-squares method, using SHELXL-97.[S16] Non-hydrogen atoms except for one THF molecule (O2 – C81 – C82 – C83 – C84) were anisotropically refined. Highly disordered THF molecule (O2 – C81 – C82 – C83 – C84) was isotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively.

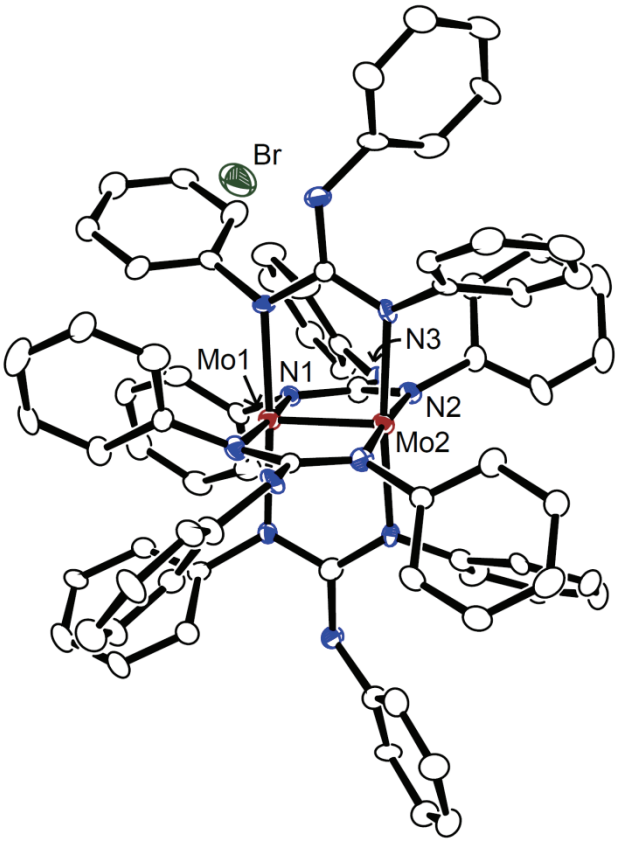


Figure S3. Molecular structure of complex **6**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å): Mo1 – Mo2 2.1231(14), Mo1 – N1 2.147(9), Mo2 – N2 2.126(10), N1 – C1 1.342(15), N2 – C1 1.346(14), N3 – C1 1.364(15).

UV-Vis Spectra for the Oxidation Reaction of 3 by Benzyl Bromide.

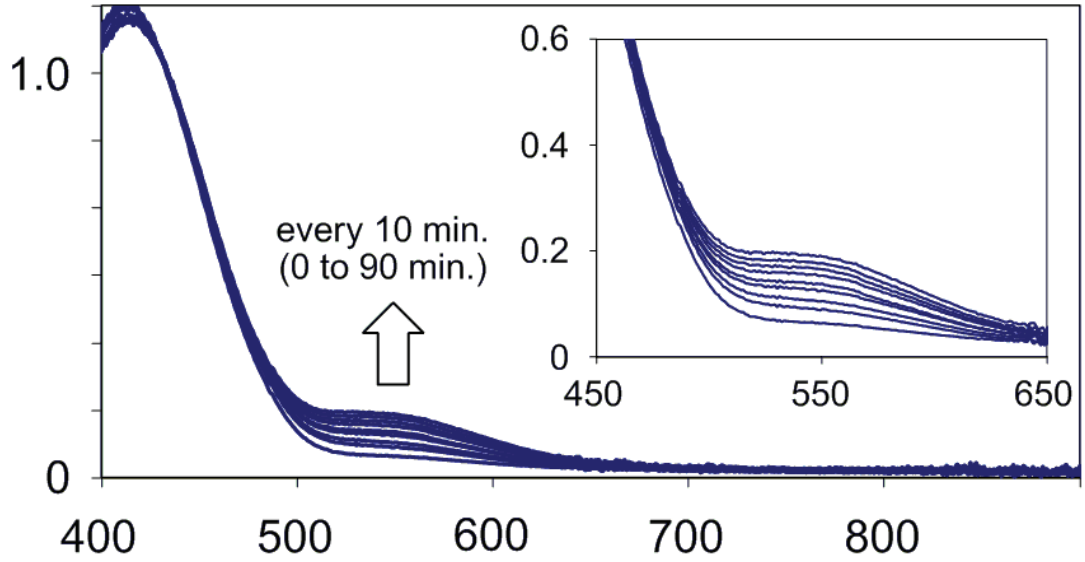
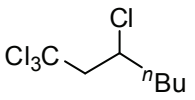
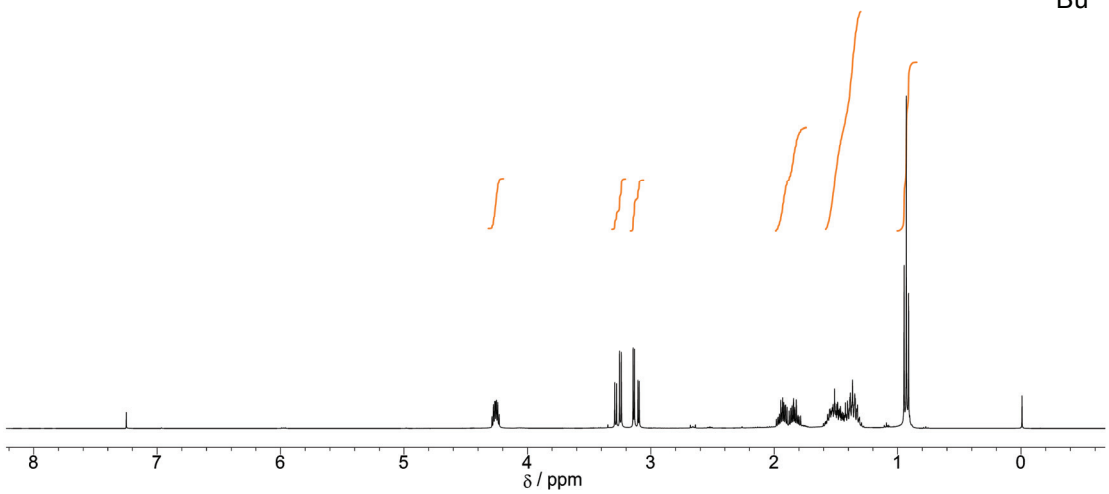


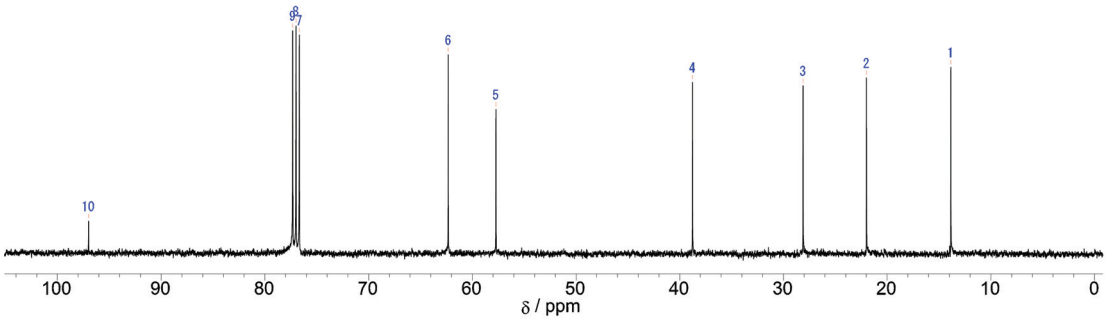
Figure S4. Changes in the UV-Vis absorption spectrum during the oxidation reaction of complex **3** by CCl_4 in THF at 25 °C.

^{1}H and ^{13}C NMR Spectra of 1,1,1,3-tetrachloroheptane

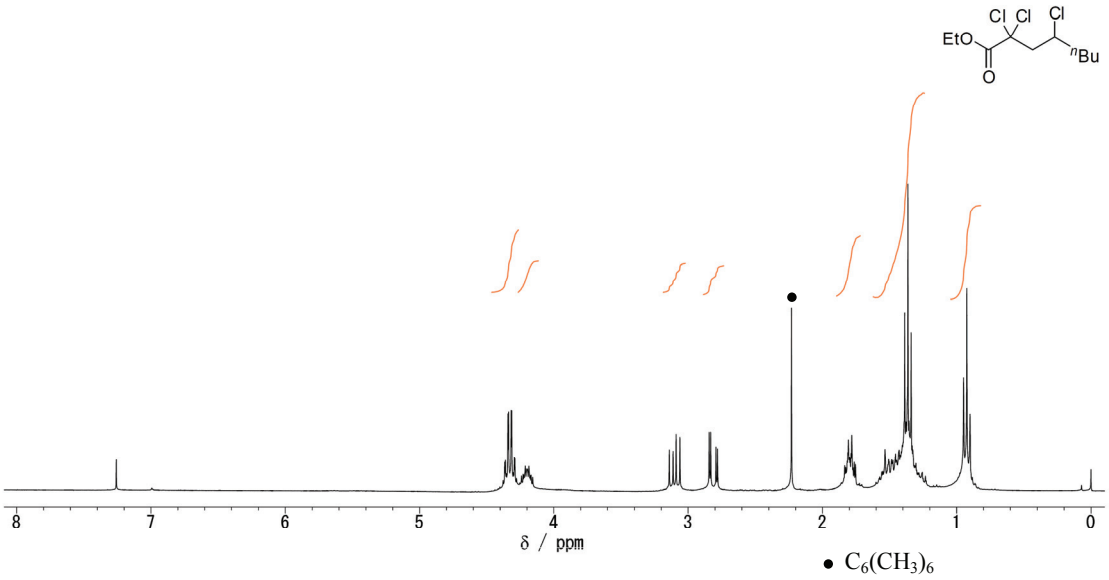


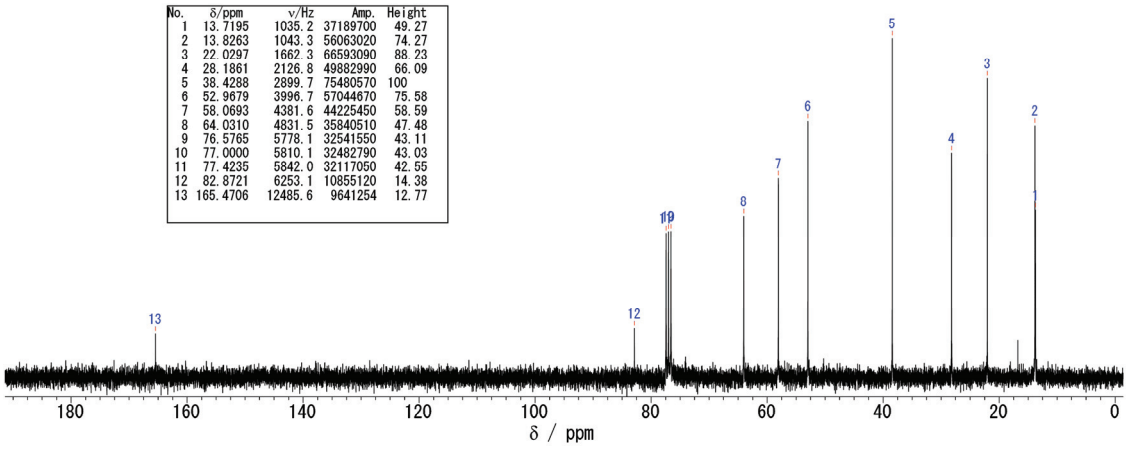


No.	δ/ppm	√/Hz	Amp.	Height
1	13.8648	1395.0	332687500	81.87
2	21.9946	2212.9	313938700	77.26
3	28.1138	2828.6	299999200	73.83
4	38.7700	3900.8	306127200	75.34
5	57.7219	5807.6	257703100	63.42
6	62.3227	6270.5	354967000	87.36
7	76.6828	7715.3	389985500	95.98
8	77.0000	7747.2	406336300	100
9	77.3190	7779.3	397923200	97.93
10	97.0000	9759.4	59185430	14.57

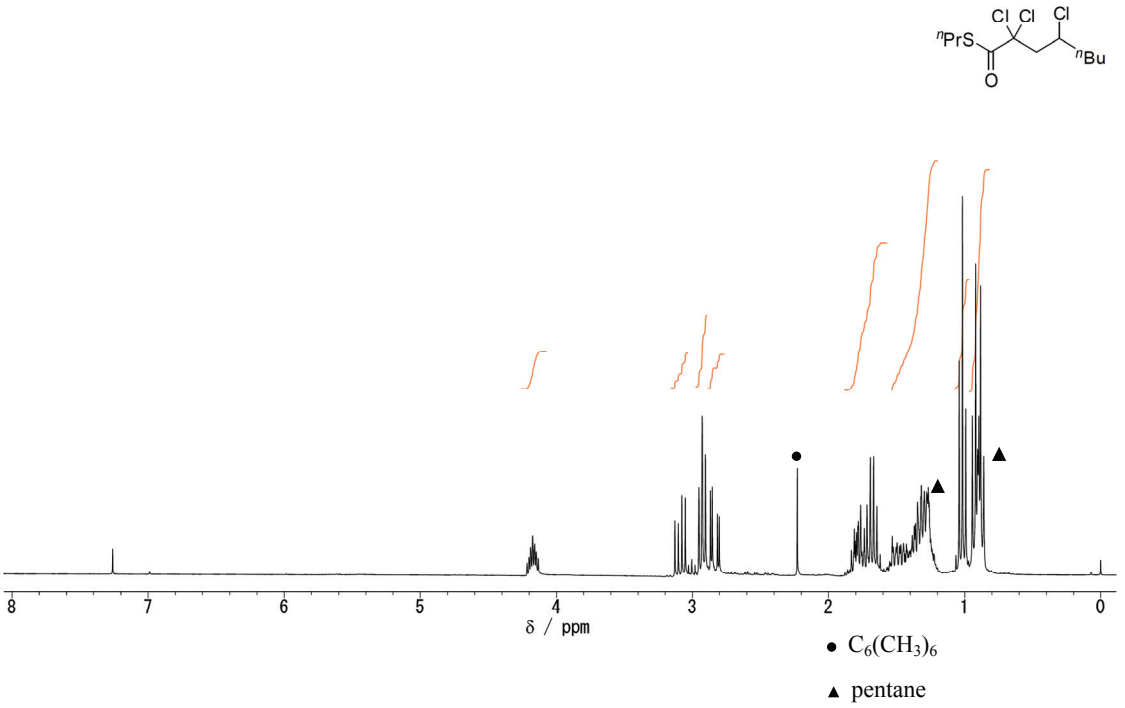


^{1}H and ^{13}C NMR Spectra of ethyl 2,2,4-trichlorooctanoate

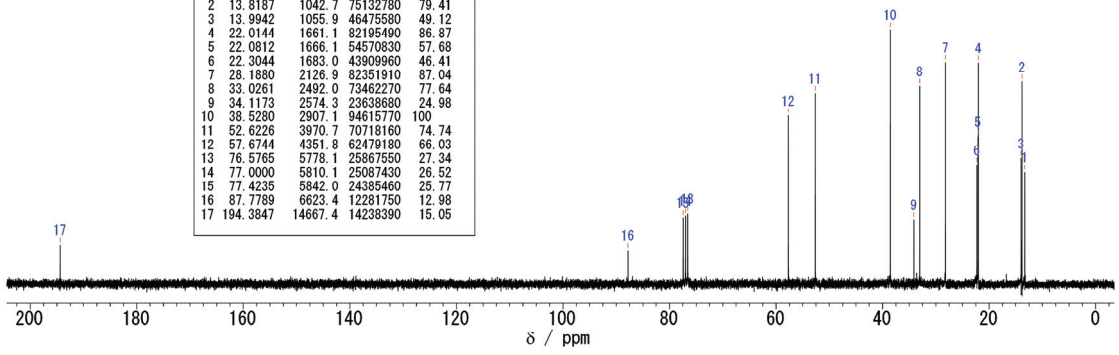




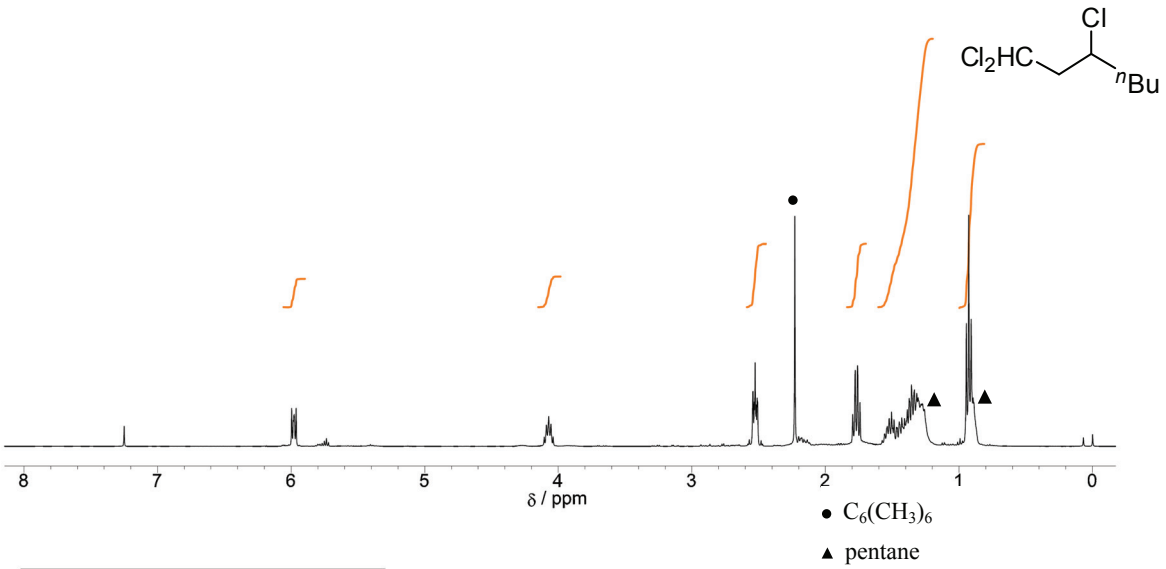
^{1}H and ^{13}C NMR Spectra of *n*-Propyl 2,2,4-trichlorooctanethioate



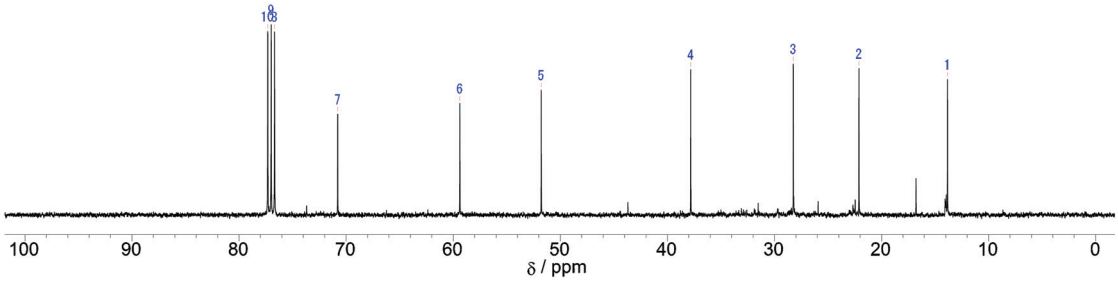
No.	δ/ppm	ν/Hz	Amp.	Height
1	13.3036	1003.8	41320780	43.67
2	13.8187	1042.7	75132780	79.41
3	13.9942	1055.9	46475580	49.12
4	22.0144	1661.1	82195490	86.87
5	22.0812	1666.1	54570830	57.68
6	22.3044	1683.0	43909960	46.41
7	28.1880	2126.9	82351910	87.04
8	33.0261	2492.0	73462270	77.64
9	34.1173	2574.3	23638680	24.98
10	38.5280	2907.1	94615770	100
11	52.6226	3970.7	70718160	74.74
12	57.6744	4351.8	62479180	66.03
13	76.5765	5778.1	25867550	27.34
14	77.0000	5810.1	25087430	26.52
15	77.4235	5842.0	24385460	25.77
16	87.7789	6623.4	12281750	12.98
17	194.3847	14667.4	14238390	15.05



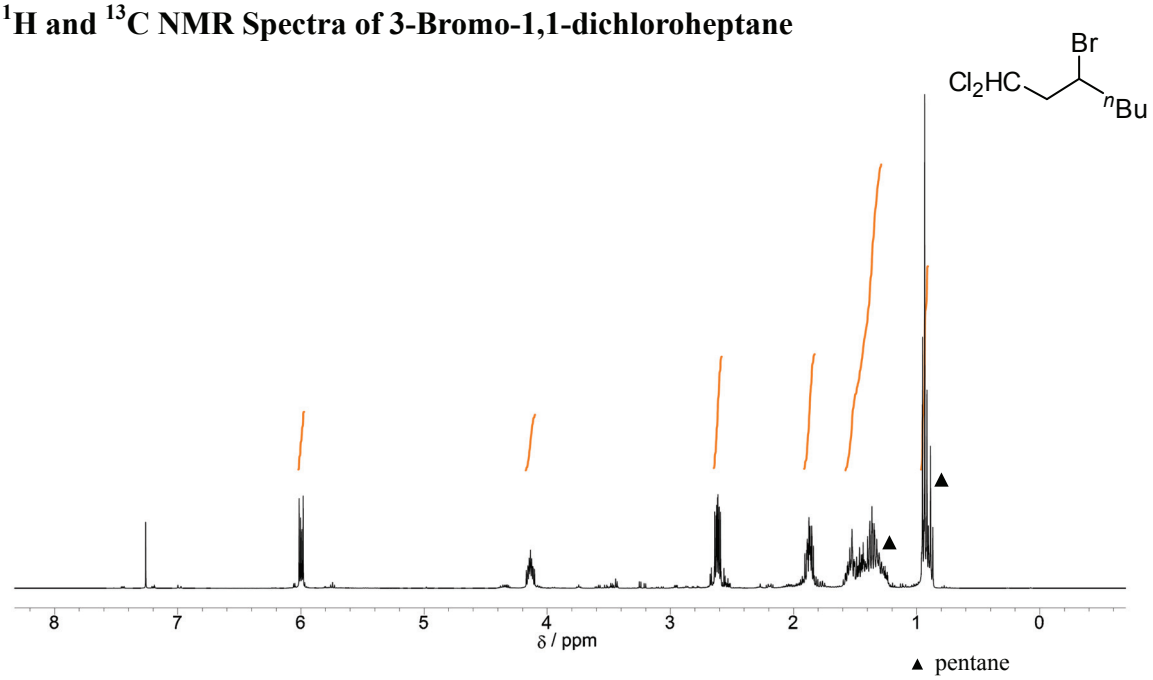
^{1}H and ^{13}C NMR Spectra of 1,1,3-Trichloroheptane



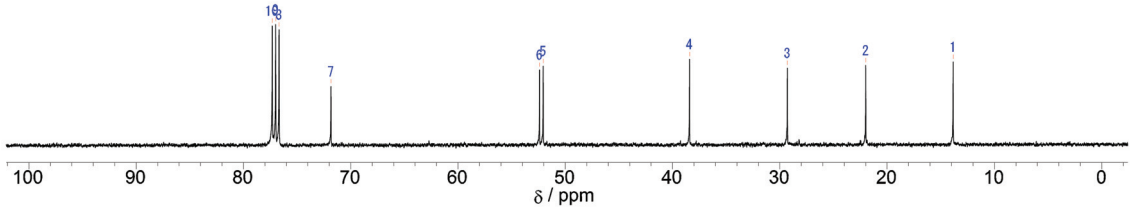
No.	δ/ppm	ν/Hz	Amp.	Height
1	13.8357	1392.0	375025100	71.19
2	22.1040	2223.9	405310700	76.94
3	28.2359	2840.9	418056000	79.36
4	37.8167	3804.8	402622800	76.43
5	51.7758	5209.3	345551400	65.59
6	59.3843	5974.8	308673700	58.59
7	70.7878	7122.2	278976300	52.96
8	76.6847	7715.5	507106100	96.26
9	77.0000	7747.2	526809800	100
10	77.3190	7779.3	507997100	96.43



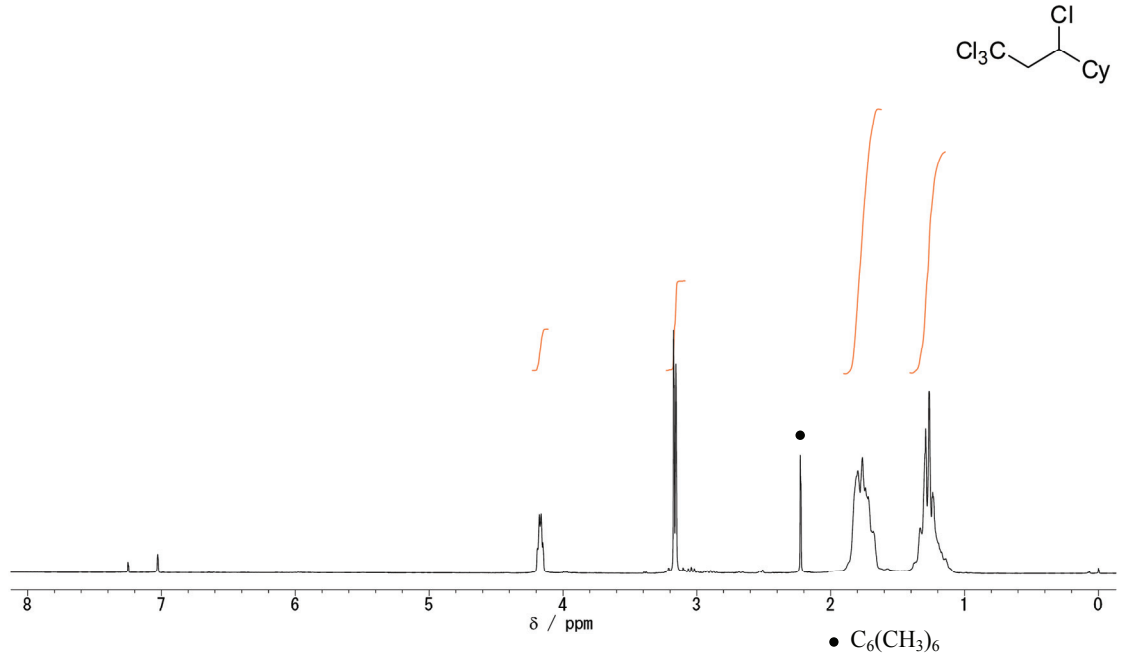
^{1}H and ^{13}C NMR Spectra of 3-Bromo-1,1-dichloroheptane

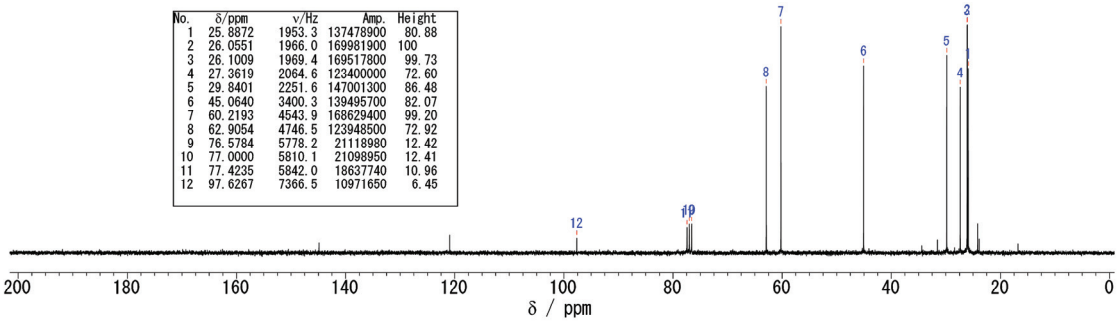


No.	δ/ppm	ν/Hz	Amp.	Height
1	13.8521	1393.7	224123600	68.35
2	22.0019	2213.7	214424400	65.39
3	29.3023	2948.2	207005300	63.13
4	38.4292	3866.5	231524200	70.60
5	52.0711	5239.0	212269400	64.73
6	52.4138	5273.5	201897000	61.57
7	71.8505	7229.1	156032400	47.58
8	76.6847	7715.5	313565600	95.62
9	77.0000	7747.2	327925800	100
10	77.3190	7779.3	324112200	98.84

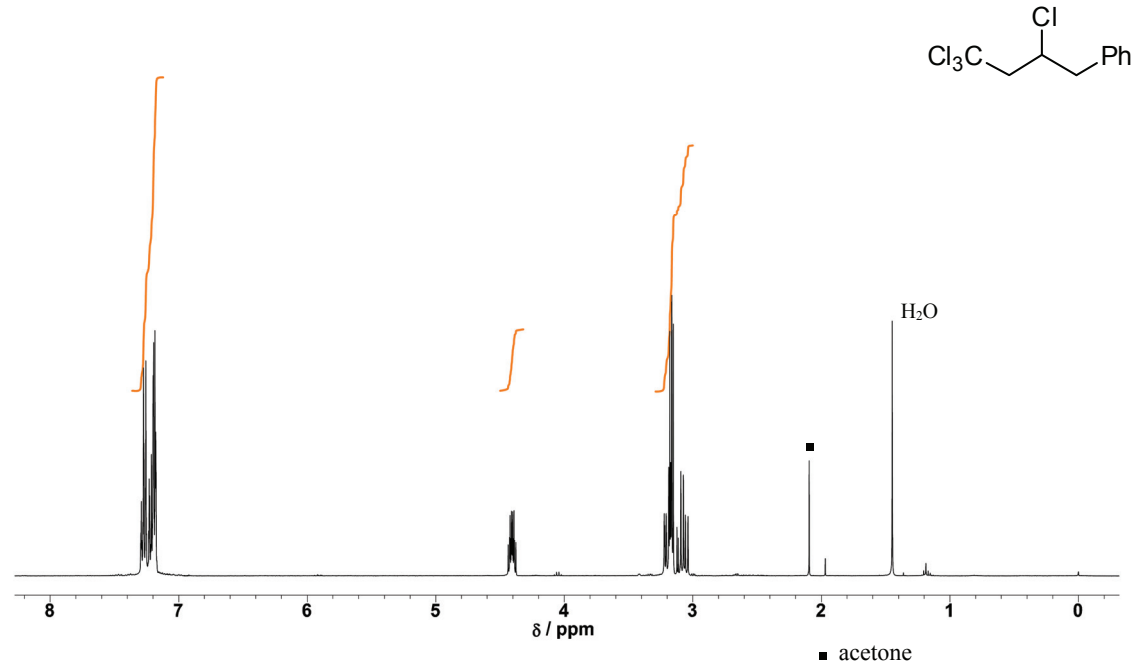


^{1}H and ^{13}C NMR Spectra of (1,3,3,3-Tetrachloropropyl)cyclohexane

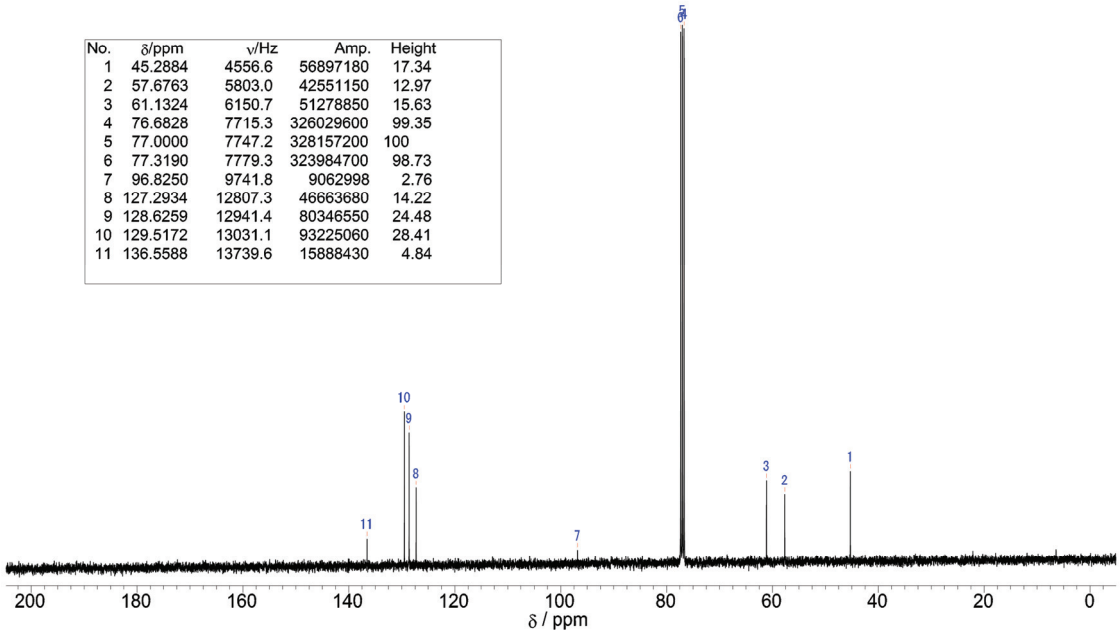




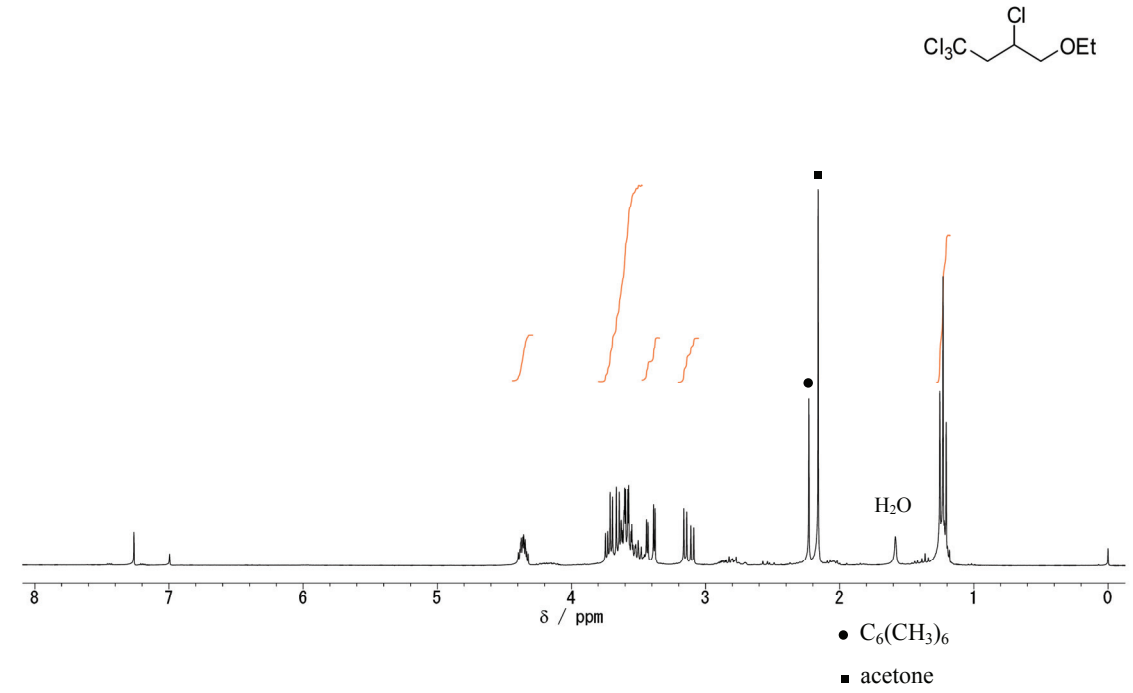
^{1}H and ^{13}C NMR Spectra of (2,4,4,4-Tetrachlorobutyl)benzene

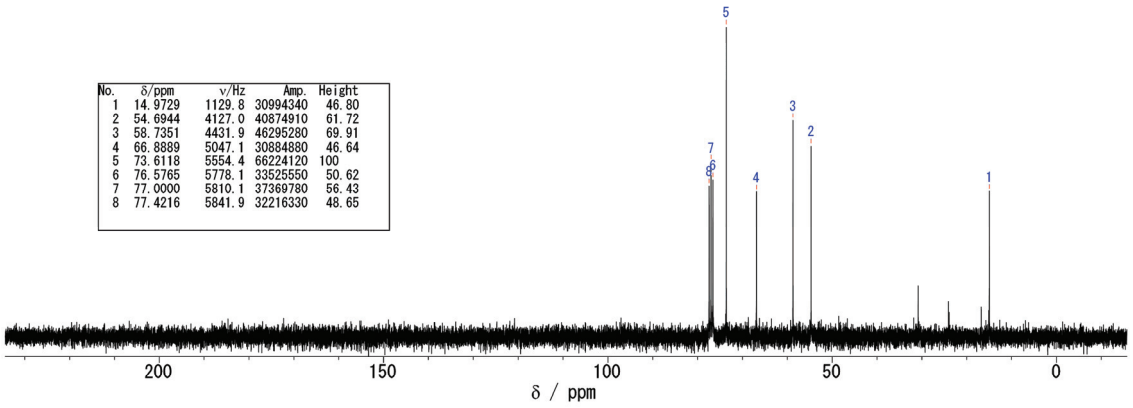


No.	δ/ppm	ν/Hz	Amp.	Height
1	45.2884	4556.6	56897180	17.34
2	57.6763	5803.0	42551150	12.97
3	61.1324	6150.7	51278850	15.63
4	76.6828	7715.3	326029600	99.35
5	77.0000	7747.2	328157200	100
6	77.3190	7779.3	323984700	98.73
7	96.8250	9741.8	9062998	2.76
8	127.2934	12807.3	46663680	14.22
9	128.6259	12941.4	80346550	24.48
10	129.5172	13031.1	93225060	28.41
11	136.5588	13739.6	15888430	4.84

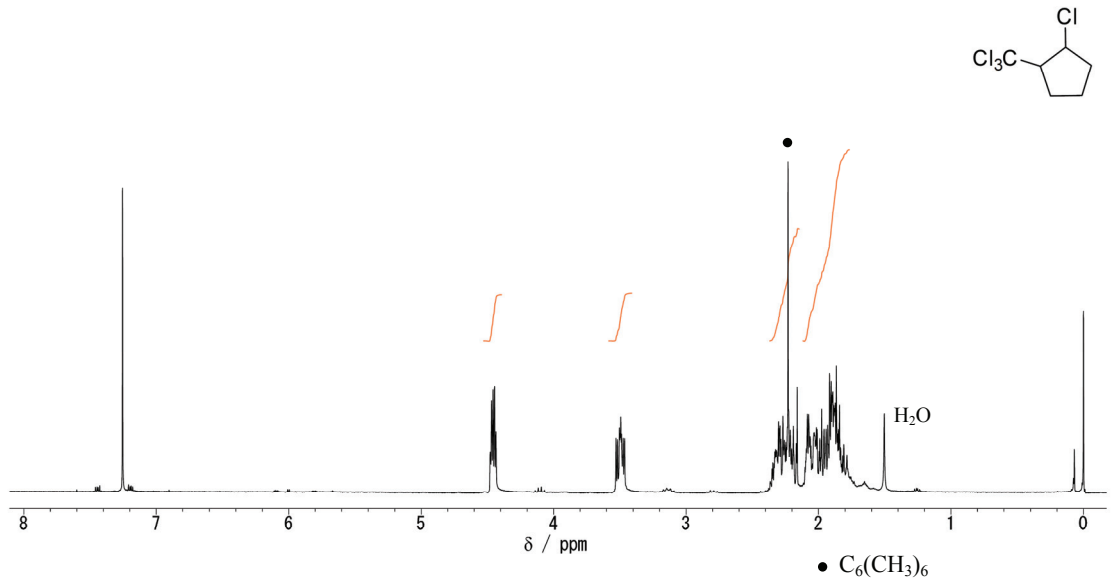


^{1}H and ^{13}C NMR Spectra of 1,1,1,3-Tetrachloro-4-ethoxybutane

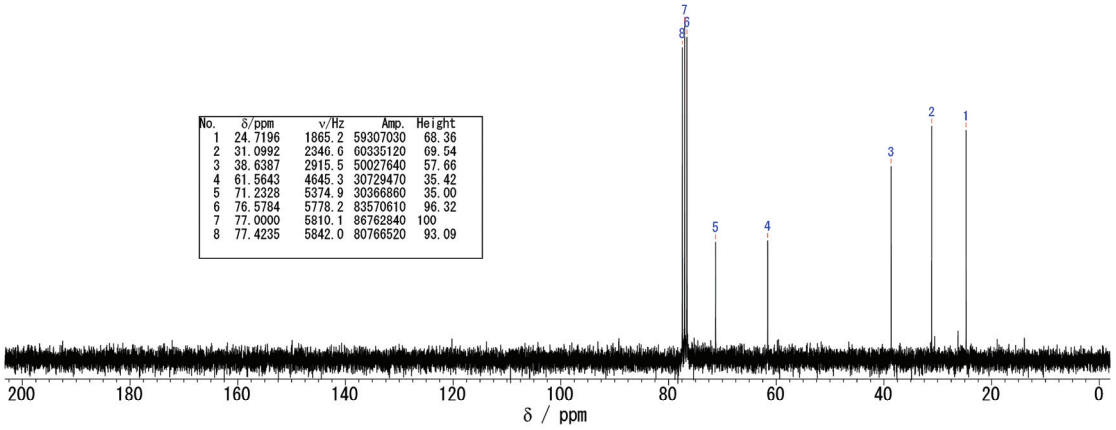




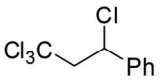
^{1}H and ^{13}C NMR Spectra of 1-Chloro-2-(trichloromethyl)cyclopentane

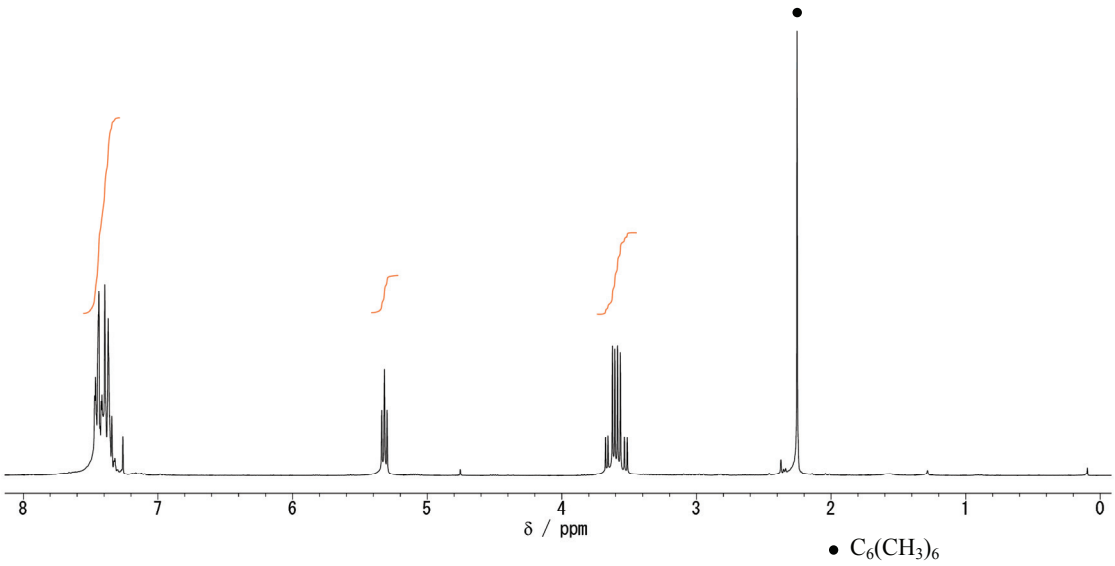


No.	δ/ppm	ν/Hz	Amp.	Height
1	24.7196	1865.2	59307030	68.36
2	31.0992	2346.6	60335120	69.54
3	38.6387	2915.5	50027640	57.66
4	61.5643	4645.3	30729470	35.42
5	71.2328	5374.9	30366860	35.00
6	76.5784	5778.2	83570610	96.32
7	77.0000	5810.1	86762840	100
8	77.4235	5842.0	80766520	93.09

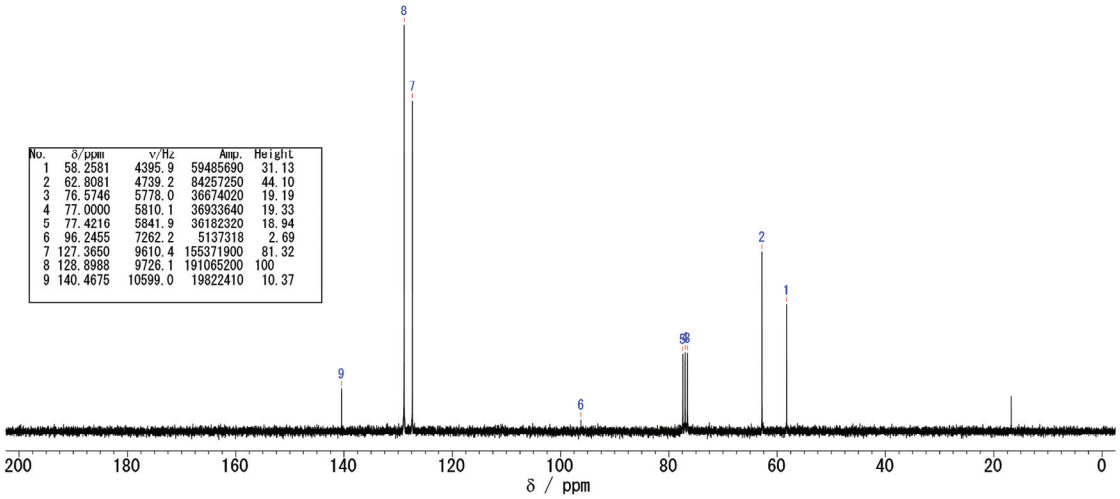


^{1}H and ^{13}C NMR Spectra of (1,3,3,3-Tetrachloropropyl)benzene





No.	δ/ppm	ν/Hz	Amp.	Height
1	58.2581	4395.9	59485690	31.13
2	62.8081	4739.2	84257250	44.10
3	76.5746	5778.0	36674020	19.19
4	77.0000	5810.1	36933640	19.33
5	77.4216	5841.9	36182320	18.94
6	96.2455	7262.2	5137318	2.69
7	127.3650	9610.4	155371900	81.32
8	128.8988	9726.1	191065200	100
9	140.4675	10599.0	19822410	10.37



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