J. Org. Chem. **1994**, *59*, 1279–1282 **1279**

Addition Reaction of Polychloro Compounds to Carbon–Carbon Multiple Bonds Catalyzed by Semiconductor Particles under Photoirradiation

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Received September 8, 1993●

Polychloro compounds were added to olefins in the presence of semiconductor particles (TiO_2 or CdS) under photoirradiation. The photoreaction without semiconductors afforded no adducts at all; however, loading of TiO_2 with Ag, Cu, or Fe_3O_4 enhanced the yield of the photoaddition reaction even further. Semiconductors operate as catalysts for the one-electron injection into the polychloro compounds. The relative adsorptions of the polychloro compounds onto the semiconductor particles correlate with the yields of the adducts, while the half-wave reduction potentials of the polychlorides do not. This semiconductor-catalyzed reaction was selective to unfunctionalized olefins and to those bearing a functional group at a remote position. An alkyne furnished the product via further reduction following addition, i.e., 1,1,3-trichloro-1-heptene (**7**) from 1-hexyne and carbon tetrachloride.

Much attention has been paid recently to photoreactions catalyzed by semiconductors in studies directed toward the effective utilization of sunlight as a source of chemical energy.[1] Although several organic reactions[2] have been investigated in addition to intensive research into the conversion of water to hydrogen and oxygen, attention has focused mainly on oxidation reactions. Only a few studies of applicable reduction reactions have been reported.[3] We report herein that semiconducting particles, especially metal-doped particles, promote the reduction of polychloro compounds, with photoirradiation, resulting in additions to alkenes and an alkyne. Although platinized semiconductors have been most frequently used to date for the smooth catalysis of such photoreactions,[4] semiconductors doped with metals that are more readily available than platinum promote the photocatalytic reduction of polychloro compounds in our reduction reactions.

Results and Discussion

A suspension composed of carbon tetrachloride (8 mmol), 1-hexene (**1a**) (4 mmol), TiO_2 (0.1 g), and DMF (20 mL) was photoirradiated with a Pyrex-filtered high-pressure Hg lamp ($\lambda > 300$ nm) at room temperature for 24 h. Two products, **2a** and **3a**, were produced in 3% and 2% yields, respectively. As a control experiment, the same composite solution without TiO_2 was photoirradiated and produced no **2a** and **3a** at all.

$$\underset{\mathbf{1a}}{CCl_4 + CH_2{=}CH(CH_2)_3CH_3} \xrightarrow[h\nu]{TiO_2} \underset{\mathbf{2a}}{CCl_3CH_2CHCl(CH_2)_3CH_3} + \underset{\mathbf{3a}}{CCl_3(CH_2)_5CH_3} \tag{1}$$

When the photocatalytic activities of semiconductor particles other than TiO_2, i.e., CdS and SiC, in the above reaction were examined, the addition products **2a** and **3a** were produced in only trace amounts or not at all, respectively. When an incandescent lamp that irradiates white light was used as a light source for the reaction in the presence of CdS, instead of a high-pressure Hg lamp, the yields of **2a** and **3a** increased to 10% and 12%, respectively. Metal-doped (especially platinized) semiconductors are known to operate more effectively for several photocatalytic reactions. Thus, we examined the photocatalytic abilities of TiO_2 particles, doped with more readily available metals than platinum, upon the addition reaction. Use of TiO_2 doped with metals such as Ag or Cu resulted in an increase in the yields of **2a** and **3a**.[5] Although loading with Fe_3O_4 better promoted the formation of **2a** and **3a** than did metals, there were some problems concerning reproducability. The TiO_2-catalyzed photoreduction of aldehydes has been previously reported to be accelerated by the addition of diisopropylamine, due to quenching of the hole in the valence band of TiO_2, which prevents the recombination of that with the electron in the conduction band.[6] Thus, a suspension composed of CCl_4, **1a**, TiO_2/Ag, DMF, and diisopropylamine was photoirradiated. The formation of addition products, however, was completely suppressed contrary to expectation. Next, the amount of TiO_2/Ag was varied from 0.1

● Abstract published in *Advance ACS Abstracts,* February 15, 1994.

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Table 1. Photoreaction of CCl_4 with 1-Hexene in the Presence of Semiconductors

semiconductor	source[a]	yield[b] (%) 2a	yield[b] (%) 3a
TiO_2	A	3	2
SiC	A	0	0
CdS	A	trace	trace
CdS	B	10	12
TiO_2/Ag (0.1 g)	A	48	22
TiO_2/Ag (0.2 g)	A	11	trace
TiO_2/Ag (0.05 g)	A	22	trace
TiO_2/Ag (0.1 g)[c]	A	0	0
TiO_2/Cu	A	23	10
TiO_2/Fe_3O_4	A	60	20
CdS/Ag	A	10	9
	A	0	0
	B	0	0

[a] A = Pyrex-filtered high-pressure Hg lamp (100 W). B = incandescent lamp (200 W). [b] Determined by GC analysis. [c] Diisopropylamine (8 mmol) was added.

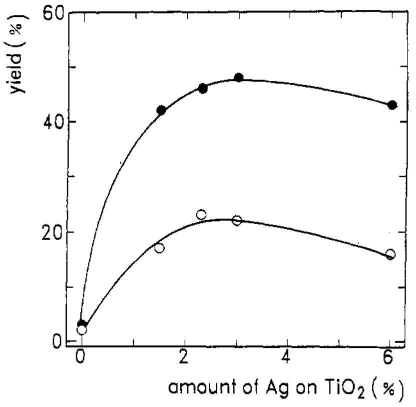

Figure 1. Plot of yields of **2a** (●) and **3a** (○) against the amount of Ag on TiO_2.

g in order to investigate the effect of the amount of semiconductor on the yields of **2a** and **3a**. The yields of **2a** and **3a** when using 0.1 g of TiO_2/Ag were greater than when using 0.2 g or 0.05 g of TiO_2/Ag. These results are collected in Table 1. Furthermore, the amount of Ag loaded onto the TiO_2 was varied. The most effective reagent proved to be TiO_2 loaded with 3 wt % of Ag, as shown in Figure 1.

The use of chloroform as a polychloro compound afforded the addition products **3a** and **4** (13% and 15%, respectively), via the photoreaction in the presence of TiO_2/Ag.

$$CHCl_3 + \mathbf{1a} \xrightarrow[h\nu]{TiO_2/Ag} \mathbf{3a} + \underset{\mathbf{4}}{CHCl_2(CH_2)_5CH_3} \qquad (2)$$

Although addition reactions of polyhaloalkanes to 1-hexene to afford 1:1 adducts have been well documented in the presence of radical initiators, a large excess of polyhaloalkanes and an absence of solvent were necessary.[7] In fact, **2a** and **3a** were not produced at all when a DMF solution containing CCl_4 and **1a** was subjected to thermoreaction in the dark, in the presence of BPO. In the case of chloroform, the radical-induced chain reaction did not afford **4** but only **3a**.[7]

Regarding the mechanism of this TiO_2-catalyzed photoaddition reaction, the products might suggest that the semiconductor does not operate as a photoelectron-transfer catalyst but as a sensitizer to promote the homolytic fission of a carbon–chlorine bond of polychloromethanes. This sensitizer mechanism, however, seems to be unapplicable because the excitation energies of carbon tetrachloride (>4.4 eV) and chloroform (>4.9 eV) are higher than the energy corresponding to the band gap between the conduction band and the valence band of TiO_2 (3.0 eV).[8] So, irradiation with the Pyrex-filtered high-pressure Hg lamp effects only excitation of TiO_2 and it cannot in turn transfer energy to polychloromethanes such as CCl_4 or $CHCl_3$. Thus, the photoelectron-transfer mechanism shown in eqs 3 and 4 seems likely, consistent with the effect of solvents on the TiO_2/Ag-catalyzed photoreaction, which reveals that the yields of **2a** and **3a** are roughly proportional to the polarity of the solvent, as shown in Table 2.

Table 2. Effect of Solvents upon the Yields of 2a and 3a

solvent	dielectric constant	yield (%) 2a	yield (%) 3a
DMF	36.7	48	22
EtOH	24.5	21	11
THF	7.6	21	trace
benzene	2.3	0	0
light petroleum ether	ca. 1.8	0	0

$$S.C. \xrightarrow{h\nu} S.C.^* \rightarrow e + h \qquad (3)$$

$$CXCl_3 + e \rightarrow CXCl_2 + Cl^- \qquad (4)$$

$$X = Cl \text{ or } H$$

Ethyl trichloroacetate afforded only small amounts of the addition products **5** and **6** by the photoreaction in the presence of TiO_2/Ag. Although the TiO_2/Ag-catalyzed photoreaction of allyl trichloroacetate was performed with an expectation of an intramolecular addition reaction,[9] no product was detected. The lower yields of **5** and **6**,

$$CCl_3CCOOEt + \mathbf{1a} \xrightarrow[h\nu]{TiO_2/Ag} \underset{\mathbf{5}}{EtOOCCCl_2CH_2CHCl(CH_2)_3CH_3} + \underset{\mathbf{6}}{EtOOCCCl_2(CH_2)_5CH_3} \qquad (5)$$

compared to those of **2a** and **3a**, are curious since ethyl trichloroacetate is expected to accept the electron of the conduction band more readily than does carbon tetrachloride, given the more positive half-wave reduction potential of ethyl trichloroacetate (−0.22 vs SCE)[10] than carbon tetrachloride (−0.78 vs SCE).[10] Also, the CuCl-catalyzed redox reaction has been reported to effectively promote the addition of ethyl trichloroacetate to olefins.[11] We considered that our addition reaction of the polychloro compounds to **1a** may be controlled by their adsorption onto TiO_2/Ag. Thus, the amounts of the polychloro compounds adsorbed on TiO_2/Ag were measured and found to be proportional to the efficiencies of the addition

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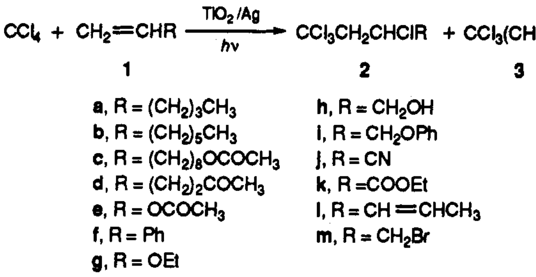
Table 3. Correlation between Adsorption of Polychloro Compounds on TiO_2/Ag and Yields of Addition Productsw

polychloro compd	adsorptn (%)	product (%)
CCl_4	86	**2a** (48); **3a** (22)
CCl_3COOEt	24	**5** (3); **6** (1)
$CCl_3COOCH_2CH{=}CH_2$	13	

Scheme 1



reactions, as shown in Table 3. The greater adsorption of carbon tetrachloride relative to the trichloroacetates may be the result of its greater partition away from the polar DMF solvent and onto the semiconductor particles. The polar trichloroacetate substrates would behave in reverse.

Next, the TiO_2/Ag-catalyzed photoreactions of carbon tetrachloride with a variety of olefins in DMF were carried out. 1-Octene (**1b**) afforded the adducts **2b** and **3b** in yields (48% and 28%, respectively) comparable to those of **2a** and **3a**, while internal olefins such as 2-octene and cyclohexene formed no adducts (Scheme I). This is consistent with the precedent that internal olefins are less reactive in addition reactions with trihalomethyl radicals than are terminal olefins.[12] Concerning functionalized olefins, 9-decenyl acetate (**1c**), which has eight methylene units between an ester group and a carbon–carbon double bond, gave the adducts **2c** and **3c** in 49% and 16% yields, respectively, and 5-hexene-2-one (**1d**), which has two methylene units between a carbonyl group and a carbon–carbon double bond, gave the adducts **2d** and **3d** in 13% and 10% yields, respectively. On the other hand, olefins with a functional group at the proximate position, i.e., **1e**–**m**, be it electron-withdrawing or -donating, afforded no adducts at all or only in small amounts (**2e**, 9%; **3e**, 6%; **2f**, 2%). The mechanism depicted in eqs 3 and 4 suggests that the presence of an electron-donating substituent on the olefin should enhance our addition reaction. The discrepancy between the anticipation and the result can be explained in terms of the adsorption of the olefin onto the semiconductor particles, that is, a control experiment in the dark revealed that **1a** and **1g** were adsorbed onto TiO_2/Ag to the extent of 25% and 9%, respectively, consistent with the yields of the adducts. The olefin with an electron-withdrawing substituent such as **1k** also proved to be adsorbed to only a small extent (6%). The apolar substrates, such as **1a**, are more extensively adsorbed onto the semiconductor particles than are the polar substrates such as **1g** and **1k**, as is the case with the polychloro compounds mentioned before. It has been reported that in redox reaction catalyzed by metal salts, carbon tetrachloride forms adducts with olefins bearing a functional group at a proximate position in higher yields than with unfunctionalized olefins.[13] In contrast, our reaction shows characteristic substrate selectivity toward olefins that are unfunctionalized or bear a functional group in a remote position.

For the investigation of this reaction with an alkyne, carbon tetrachloride was subjected to the TiO_2/Ag-catalyzed photoreaction with 1-hexyne. As a result, 1,1,3-trichloro-1-heptene (**7**) was formed in 52% yield as the sole product. It may be that **7** is furnished via dechlorination of intermediate adduct **8**, induced by the further injection of an electron in the conduction band of the photoexcited semiconductor. Although the reaction of carbon tetrachloride with 1-hexyne in the redox system composed of CuCl and ethanolamine, which has been used for the addition of polyhalides to olefins,[14] was examined for comparison, only a complex mixture resulted.

$$CCl_4 + CH{\equiv}C(CH_2)_3CH_3 \xrightarrow[h\nu]{TiO_2/Ag} \underset{\mathbf{7}}{Cl_2C{=}CHCHCl(CH_2)_3CH_3} \quad (6)$$

$$\underset{\mathbf{8}}{CCl_3CH{=}CCl(CH_2)_3CH_3}$$

Conclusions

Silver-doped TiO_2 promoted the addition of polychloro compounds to olefins upon photoirradiation. A reaction pathway in which the injection of the electron in the conduction band of the excited semiconductor to the polychloride to cleave a carbon–chlorine bond is the key step, is likely. This addition reaction is selective to unfunctionalized olefins or to those bearing a functional group at a remote position. This selectivity in our reaction may derive from adsorption phenomena. As regards the polychloro compounds, carbon tetrachloride gave the best results while trichloroacetates, which should be more readily reduced, proved to be less effective. This discrepancy may be ascribed to the relative extent of adsorption onto the semiconductor. 1-Hexyne afforded a clean addition product, while a redox method employing a metal salt furnished a complex mixture.

Experimental Section

^1H (60 MHz) and ^{13}C (15 MHz) NMR spectra were recorded with a JEOL FX60 spectrometer for $CDCl_3/CCl_4$ solutions. Chemical shifts and coupling constants are given in δ (ppm) relative to $SiMe_4$ as internal standard and J (hertz), respectively. Mass spectra were obtained at 70 eV using a Hitachi M-80B instrument. GC was performed with a Shimadzu GC-6A instrument. DMF was distilled from CaH_2. Titanium dioxide (anatase) was obtained from Wako Chemicals.

Preparation of Ag-Doped TiO_2. A suspension composed of silver nitrate (0.078 g, 0.46 mmol), TiO_2 (1.6 g), and CH_3CN (20 mL) was stirred for 1 h, and then, after removal of CH_3CN under reduced pressure, 1,4-dioxane (10 mL) was added. The resulting suspension was photoirradiated using a 100-W high-pressure Hg lamp for 24 h under a nitrogen atmosphere and centrifuged. The absence of silver nitrate in an aqueous solution (30 mL) which washed the slurry was confirmed by the test with an EtOH solution of iodoethane. Then, the slurry was washed with saturated aqueous $NaHCO_3$ (30 mL) and then H_2O (30 mL × 2). The precipitate was collected and dried overnight in a oven at

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110 °C. The gray powder after well-crush of the cake was used as TiO_2 doped with 3 wt % of Ag. TiO_2 doped with 1.5, 2.25, and 6 wt % of Ag was prepared according to the same procedure using 0.039, 0.063, and 0.156 g of $AgNO_3$, respectively.

Preparation of Cu-Doped TiO_2. An aqueous solution (20 mL) of $CuNO_3{\cdot}3H_2O$ (0.183 g, 0.76 mmol) was added to a suspension composed of TiO_2 (1.6 g), NaOH (1.6 g, 40 mmol), and H_2O (10 mL). After the solution was stirred for 10 min at 40 °C, the resulting suspension was photoirradiated using a 100-W high-pressure Hg lamp for 24 h under a nitrogen atmosphere. The slurry was washed with H_2O (30 mL × 3) and centrifuged. The precipitate was collected and dried overnight in a oven at 110 °C. The light brown powder after well-crush of the cake was used as TiO_2 doped with Cu.

Preparation of Fe_3O_4-Doped TiO_2. An aqueous suspension (30 mL) of urea (1.6 g, 26.7 mmol) was added to a suspension composed of $FeCl_2$ (0.15 g, 1.2 mmol), $FeCl_3$ (0.12 g, 0.74 mmol), TiO_2 (1.6 g), and H_2O (20 mL), and then the solution was stirred at 95 °C for 6 h. The precipitate, after being washed with H_2O (30 mL × 3) and centrifuged, was collected and dried overnight in a oven at 110 °C. The dark gray powder after well-crush of the cake was used as TiO_2 doped with Fe_3O_4.

Estimation of Adsorption of a polychloro compound on TiO_2/Ag. A suspension composed of a polychloro compound (8 mmol), 1-hexene (4 mmol), TiO_2/Ag (0.1 g), and DMF (20 mL) was stirred at room temperature for 24 h in a closed system after purge with nitrogen (10 min) under ice-cooling and then centrifuged. The solution part was subjected to GC analysis for determination of the unadsorped amount of a polychloro compound, from which % adsorption was calculated.

Photoaddition of Polychloro Compounds to Olefins or 1-Hexyne. A suspension composed of a polychloro compound (8 mmol) an olefin or 1-hexyne (4 mmol), TiO_2/Ag (0.1 g), and DMF (20 mL) was photoirradiated using a Pyrex-filtered high-pressure Hg lamp (100 W) at room temperature for 24 h under a nitrogen atmosphere and then centrifuged. The solution part was subjected to GC analysis and the analytically pure sample was isolated by preparative GC after pouring into H_2O, extracting with diethyl ether, and removing of diethyl ether.

1,1,1,3-Tetrachloroheptane (2a). This compound was identified by comparison (^{1}H and ^{13}C NMR and GCMS) with the sample prepared according to Burton's method:[15] ^{1}H NMR δ 4.57–4.14 (1H, m), 3.29 (1H, d, J = 5.1), 3.26 (1H, d, J = 5.1), 2.14–1.20 (6H, m), 0.96 (3H, t, J = 5.1); ^{13}C NMR δ 61.7, 56.7, 38.1, 27.5, 21.4, 13.3; MS *m/z* 201 (M – Cl).

1,1,1,3-Tetrachlorononane (2b). This compound was identified by comparison (^{1}H and ^{13}C NMR and GCMS) with the sample prepared according to Burton's method:[15] ^{1}H NMR δ 4.56–4.14 (2H, m), 3.28 (1H, d, J = 5.1), 3.24 (1H, d, J = 5.1), 2.14–1.22 (10H, m), 0.90 (3H, t, J = 6.0); ^{13}C NMR δ 61.5, 56.9, 38.3, 27.9, 26.3, 25.3, 21.9, 13.3; MS *m/z* 193 (M – HCl – Cl).

9,11,11,11-Tetrachloroundecyl acetate (2c): ^{1}H NMR δ 4.49–4.05 (3H, m), 3.29 (1H, d, J = 5.1), 3.21 (1H, d, J = 5.1), 2.06 (3H, s), 2.04–1.80 (14H, m); ^{13}C NMR δ 63.8, 62.3, 57.0, 38.8, 29.1, 29.0, 28.6, 28.5, 25.9, 25.8, 20.6; CIMS *m/z* 353 M(^{37}Cl) + H, 351 (M + H).

5,7,7,7-Tetrachloro-2-heptanone (2d): ^{1}H NMR δ 4.70–4.23 (1H, m), 3.36 (1H, d, J = 5.1), 3.31 (1H, d, J = 5.1), 2.76 (2H, t, J = 6.0), 2.24 (2H, t, J = 6.0), 2.00 (3H, s); ^{13}C NMR δ 61.8, 56.1, 39.0, 31.9, 29.0; HRMS calcd for $C_7H_{10}OCl_4$ 249.9485, found 249.9484 (M).

1,3,3,3-Tetrachloropropyl acetate (2e): ^{1}H NMR δ 7.13 (1H, dd, J = 6.8 and 5.1), 3.64 (1H, d, J = 6.8), 3.60 (1H, d, J = 5.1), 2.25 (3H, s); ^{13}C NMR δ 78.2, 60.2, 19.9; CIMS *m/z* 241 M(^{37}Cl) + H, 239 (M + H).

1,1,1-Trichloroheptane (3a): ^{1}H NMR δ 2.75 (2H, t, J = 5.1), 2.00–1.12 (8H, m), 0.93 (3H, t, J = 6.0); ^{13}C NMR δ 54.6, 30.8, 27.4, 25.6, 21.8, 13.3; CIMS *m/z* 167 (M – Cl).

1,1,1-Trichlorononane (3b): ^{1}H NMR δ 2.76 (2H, t, J = 6.0), 2.00–1.10 (12H, m), 0.90 (3H, t, J = 6.0); ^{13}C NMR δ 55.2, 31.8, 29.2, 29.1, 28.4, 26.4, 22.7, 14.1; MS *m/z* 232 M(^{37}Cl), 230 (M).

11,11,11-Trichloroundecyl acetate (3c): ^{1}H NMR 4.13 (2H, t, J = 6.5), 2.73 (2H, t, J = 6.8), 2.04 (3H, s), 2.00–1.80 (16H, m); ^{13}C NMR δ 63.9, 55.1, 29.2, 29.1, 28.9, 28.5, 28.2, 26.2, 25.8, 25.7, 20.6; CIMS 319 M(^{37}Cl) + H, 317 (M + H).

7,7,7-Trichloro-2-heptanone (3d): ^{1}H NMR δ 2.94–2.40 (4H, m), 2.15 (3H, s), 1.91–1.57 (4H, m); ^{13}C NMR δ 54.3, 42.1, 29.0, 25.3, 21.5; CIMS *m/z* 219 M(^{37}Cl) + H, 217 (M + H); HRMS calcd for $C_7H_{10}OCl_2$ 180.0107, found 180.0078 (M – HCl).

3,3,3-Trichloroacetate (3e): ^{1}H NMR δ 4.60 (2H, t, J = 6.9), 3.18 (2H, t, J = 6.9), 2.16 (3H, s); ^{13}C NMR δ 59.9, 52.4, 19.9; CIMS *m/z* 207 M(^{37}Cl) + H, 205 (M + H).

1,1-Dichloroheptane (4). This compound was identified by comparison (^{1}H and ^{13}C NMR and MS) with the independently prepared sample:[16] ^{1}H NMR δ 5.94 (1H, t, J = 7.7), 2.15–1.20 (10H, m), 0.93 (3H, t, J = 5.1); ^{13}C NMR δ 72.91, 43.5, 31.4, 28.1, 25.7, 22.3, 13.9; CIMS *m/z* 133 (M – Cl).

Ethyl 2,2,4-Trichlorooctanoate (5). This compound was identified by comparison (^{1}H and ^{13}C NMR and GCMS) with the sample prepared according to the reported method:[11] ^{1}H NMR δ 4.62–4.10 (3H, m), 3.03 (1H, d, J = 6.8), 2.89 (1H, d, J = 6.0), 2.00–1.20 (6H, m), 1.40 (3H, t, J = 7.7), 0.95 (3H, t, J = 6.0); ^{13}C NMR δ 62.9, 57.0, 52.3, 37.7, 27.5, 21.4, 13.2, 13.1; CIMS *m/z* 277 M(^{37}Cl) + H, 275 (M + H).

Ethyl 2,2-Dichlorooctanoate (6): ^{1}H NMR δ 4.42 (2H, q, J = 6.8), 2.98 (2H, t, J = 6.8), 1.65–1.20 (8H, m), 0.97 (3H, t, J = 5.1); CIMS *m/z* 243 M(^{37}Cl) + H, 241 (M + H).

1,1,3-Trichloro-1-heptene (7): ^{1}H NMR δ 6.20 (1H, d, J = 10.3), 4.80 (1H, dt, J = 10.3 and 6.9), 2.14–1.80 (6H, m), 0.98 (3H, t, J = 5.5); ^{13}C NMR δ 129.5, 56.3, 37.1, 27.6, 21.4, 13.2; MS *m/z* 202 M(^{37}Cl), 200 (M); HRMS calcd for $C_7H_{11}Cl_3$ 199.9926, found 199.9937 (M).

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