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Rh^{II}-Catalyzed Reaction of α-Diazocarbonyl Compounds Bearing β-Trichloroacetylamino Substituent: C–H Insertion versus 1,2-H Shift

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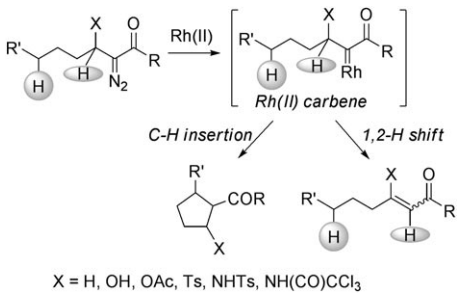
Dedicated to the 100th anniversary of the College of Chemistry, Peking University

Abstract: The Rh^{II}-carbene reaction is dramatically affected by the neighboring substituents. If the neighboring substituent is an OH group, a1,2-H shift is the exclusive pathway. If it is an OAc group, a 1,2-acetoxy migration is observed. If it is *p*-toluenesulfonyl group, 1,3 and 1,5-C–H insertion are the major pathways, and the 1,2-H shift is completely suppressed. If the adjacent substituent is a trichloroacetyl amino group, 1,5-C–H insertion competes with the 1,2-hydride shift, and no 1,3-C–H insertion can be observed. Both electronic and steric factors are responsible for the switching of the Rh^{II}-carbene reaction pathway. The highly stereoselective 1,5-C–H insertions in Rh^{II}-catalyzed reaction of α-diazocarbonyl compounds, bearing β-trichloroacetylamino substituent, can be utilized as a novel way to synthesize five-membered cyclic β-amino acid derivatives.

Keywords: carbenes · diazo compounds · hydrides · insertion · substituent effects

Introduction

Rh^{II}-mediated intramolecular C–H insertion reaction represents a general approach for the construction of various carbocyclic compounds. In particular, 1,5-insertion is highly efficient and affords cyclopentane derivatives in high yields with good regio- and stereoselectivity.[1,2] The usefulness of Rh^{II} carbene 1,5-C–H insertion has been well-demonstrated by its applications in organic synthesis,[3] and it has also attracted attentions recently as a unique way of C–H bond activation.[4] Although the insertion process is highly feasible, it may suffer from other competing reaction pathways of Rh^{II} carbene, among which 1,2-shift is commonly encountered (Scheme 1).[5–8] 1,2-H shift of carbene, which leads to the formation of a carbon–carbon double bond, is a highly feasible process.[5,6] The highly chemo- and stereoselective 1,2-H shift of Rh^{II} carbene is synthetically useful for constructing (*Z*)-β-unsaturated carbonyl compounds.[5]



Scheme 1. Rh^{II} carbene 1,5-C–H insertion versus 1,2-H shift.

Investigations have revealed that the substituents adjacent to the Rh^{II}-carbene center (X group in Scheme 1) have a profound effect on the chemoselectivity of the Rh^{II} carbene. If there is no substituent (X = H), 1,5-insertion is predominant [Eq. (1)]. A hydroxy substituent is found to promote a 1,2-H shift, and 1,5-insertion is completely shut down in such a case [Eq. (2)].[6c] However, an acetoxy substituent

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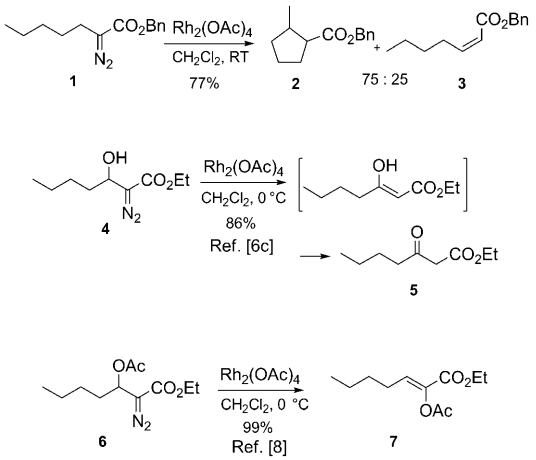
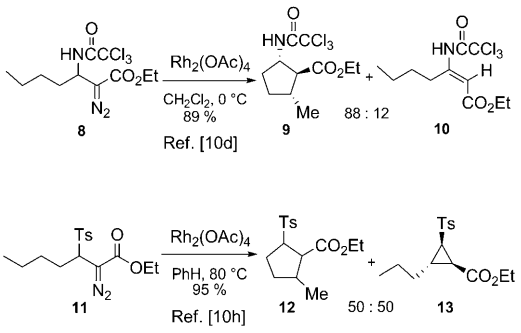
leads to the migration of the acetoxy group itself, presumably through a 2,3-migration process [Eq. (3)].[8] It has been reported that Rh^{II}-catalyzed 1,5-C–H insertion can effectively compete with the 1,2-H shift in some cases.[9] It is also shown that the ratio of 1,5-C–H insertion to 1,2-H shift is significantly affected by the ligands on the Rh^{II} catalyst. Our own study demonstrates that the substituents, such as NHTs, $Cl_3C(O)NH$, Ts, suppress the 1,2-H shift and result in the formation of products that are formed through other group migration or C–H insertion.[10] In particular, we have observed that intramolecular 1,5-C–H insertion overrides the 1,2-H shift when the β substituent is a trichloroacetylamino group [Eq. (4)].[10d] When the β substituent is a tosyl group, both 1,3 and 1,5-C–H insertions occur, but the 1,2-H shift is completely suppressed [Eq. (5)].[10h] Systematic study reveals that both electronic and steric effects are responsible for the switch of 1,2-migratory aptitude of the Rh^{II}-carbene species.[10c,g,k] In this paper, we report the details of the study on the Rh^{II}-catalyzed reaction of diazo compounds, which bear a β-trichloroacetylamino group.[11] This study reveals that 1,5-C–H insertion can effectively compete with the 1,2-H shift, which leads to the formation of five-membered cyclic β-amino ester derivatives in a stereoselective manner.



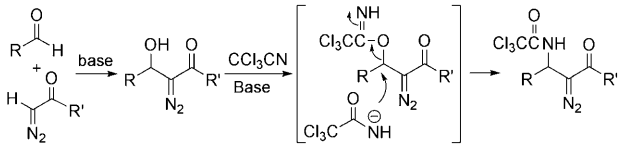
Abstract in Chinese:

铑(II)卡宾的反应路径受到邻位取代基的很大影响。当邻位取代基为羟基时，1,2 氢迁移是唯一的反应，当邻位取代基是乙酰氧基时，1,2 乙酰氧基迁移变成唯一的反应途径。而邻位取代基是对甲苯磺酰基时，1,3 和 1,5 碳氢键插入是主要的反应，此时 1,2 氢迁移被完全抑制。最后，当邻位取代基是三氯乙酰氨基时，1,5 碳氢键插入和 1,2 氢迁移反应相互竞争，此时完全没有 1,3 碳氢键插入。电子效应和立体效应共同影响 Rh(II)卡宾反应的途径。本文着重报道 Rh(II)催化的β-三氯乙酰氨基α-重氮化合物 1,5C-H 插入反应，这些碳氢键插入反应均具有很高的立体选择性，因此可以成为合成环状β-氨基酸衍生物的新方法。



Results and Discussion

Nucleophilic addition of acyldiazomethane to aldehyde affords β-hydroxy α-diazocarbonyl compounds, which can be further derivatized. We have previously observed that the β position of the α-diazocarbonyl compounds is liable to nucleophilic substitution, which makes it possible to prepare a series of diazo compounds with various substituents in the adjacent position of the diazo group (Scheme 2).[10]

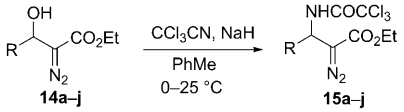


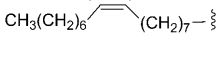
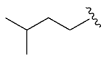
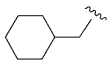
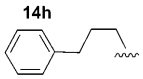
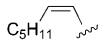
Scheme 2. Nucleophilic substitution at the carbon adjacent to diazo group.

The β-hydroxy α-diazo compounds **14a–j**, which were easily available through nucleophilic addition of acyldiazomethane with aldehyde,[12] were treated with Cl_3CCN/NaH under standard conditions for the imidation of alcohol (Table 1).[13] The reaction proceeded through an unusual nucleophilic substitution of the initially formed normal alcohol imidation product by amide anion.

With diazo compounds **15a–j** in hand, we next proceeded to study their reaction with Rh^{II} catalysts. For the β-(trichloroacetyl)amino α-diazocarbonyl compounds, we first examined the Rh^{II}-catalyzed reaction of **15a–e** and the results are summarized in Table 2. In the case of **15a** and **15b**, in which intramolecular C–H insertion is not possible or not competitive arising from the insertion into a primary C–H bond,[14] the $Rh_2(OAc)_4$-catalyzed reaction in CH_2Cl_2 at 0 °C afforded only 1,2-H shift products **17a** and **17b** (Table 2, entries 1, 2). For the diazo compound **15c**, under the same conditions, we obtained both 1,5-C–H insertion and 1,2-H shift products **16c** and **17c** in a ratio of 80:20 (entry 3). The ratio was found to be slightly affected by the reaction temperature: the high temperature favored the 1,2-H shift, but the reaction at −20 °C became very sluggish, thus, it was not possible to further increase the selectivity for 1,5-C–H insertion. We also examined two other typical Rh^{II} catalysts: $Rh_2(acam)_4$ and $Rh_2(O_2CCF_3)_4$, the former bears an elec-

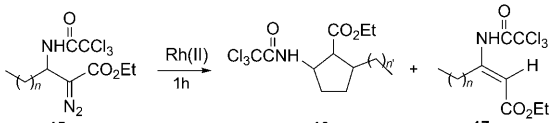
Table 1. Preparation of β-(trichloroacetyl)amino α-diazocarbonyl compounds **15a–j**.



Entry	**14a–j** (R=)	*t* [h]	Yield [**15**,%][a]
1	**14a**, CH_3CH_2	20	**15a**, 77
2	**14b**, $CH_3(CH_2)_2$	20	**15b**, 73
3	**14c**, $CH_3(CH_2)_3$	20	**15c**, 84
4	**14d**, $CH_3(CH_2)_5$	20	**15d**, 78
5	**14e**, $CH_3(CH_2)_{10}$	20	**15e**, 80
6	 **14f**	20	**15f**, 79
7	 **14g**	24	**15g**, 92
8	 **14h**	23	**15h**, 88
9	 **14i**	20	**15i**, 90
10	 **14j**	24	**15j**, 74

[a] Yield of isolated product after silica gel column chromatography.

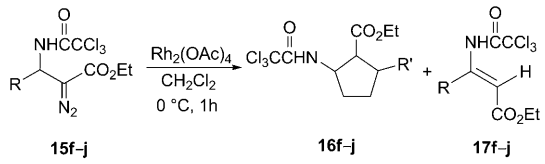
Table 2. Rh^{II}-catalyzed reaction of diazo compounds **15a–e**: 1,5-C–H insertion versus 1,2-H shift.

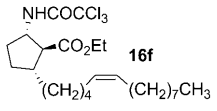
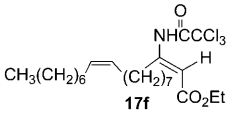
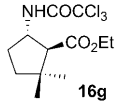
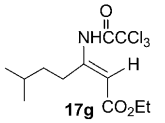
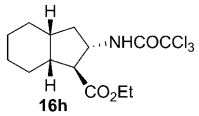
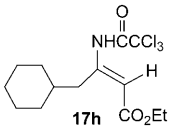
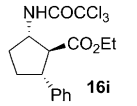
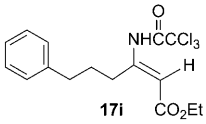
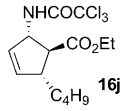
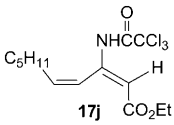


Entry	**15**	Rh^{II}	Solvent	*T* [°C]	**16:17**[a]	Yield [%][b]
1	**15a**	$Rh_2(OAc)_4$	CH_2Cl_2	0	0:100	68
2	**15b**	$Rh_2(OAc)_4$	CH_2Cl_2	0	0:100	73
3	**15c**	$Rh_2(OAc)_4$	CH_2Cl_2	30	80:20	89
4	**15c**	$Rh_2(OAc)_4$	CH_2Cl_2	0	72:28	74
5	**15c**	$Rh_2(OAc)_4$	CH_2Cl_2	−20	–	–[c]
6	**15c**	$Rh_2(acam)_2$	C_6H_6	80	29:71	80
7	**15c**	$Rh_2(O_2CCF_3)_4$	CH_2Cl_2	0	–	–[d]
8	**15d**	$Rh_2(OAc)_4$	CH_2Cl_2	0	88:12	89
9	**15d**	$Rh_2(OAc)_4$	C_6H_6	80	50:50	87
10	**15d**	$Rh_2(acam)_2$	C_6H_6	80	29:71	80
11	**15d**	$Rh_2(O_2CCF_3)_4$	CH_2Cl_2	0	–	–[d]
12	**15e**	$Rh_2(OAc)_4$	CH_2Cl_2	0	84:16	94
13	**15e**	$Rh_2(OAc)_4$	C_6H_6	80	50:50	99
14	**15e**	$Rh_2(acam)_4$	C_6H_6	80	40:60	98
15	**15e**	$Rh_2(O_2CCF_3)_4$	CH_2Cl_2	0	–	–[d]

[a] Product ratio was determined by ^1H NMR (300 MHz) measurement of the crude product. [b] Combined yield after column chromatography. [c] The reaction with this substrate was exceptionally slow. About 50% of diazo substrate was recovered after stirring at room temperature for 2 days in each case. [d] Starting material was recovered after stirring for 2 days.

Table 3. $Rh_2(OAc)_4$-catalyzed reaction of **15f–j**.



Entry	**16**	**17**	**16:17**[a]	Yield [%][b]
1	 **16f**	 **17f**	71:29	83
2	 **16g**	 **17g**	89:11	81
3	 **16h**	 **17h**	88:12	88
4	 **16i**	 **17i**	85:15	81
5	 **16j**	 **17j**	0:100	89[c]

[a] Ratio obtained from isolated products of **16** and **17**. [b] Yield of isolated product for **16** and **17** combined. [c] No C–H insertion product was detected.

tron-donating ligand whereas the latter bears an electron-withdrawing ligand. It was observed that the reaction with $Rh_2(acam)_4$ needed a high temperature, and the 1,2-H shift product was predominant (entry 6). Surprisingly, the $Rh_2(O_2CCF_3)_4$-catalyzed reaction of **15c** was exceptionally slow and resulted in the recovery of the starting materials and a complex mixture (entry 7). For the diazo substrates **15d** and **15e**, similar results were obtained (entries 8-15). Notably, with $Rh_2(OAc)_4$ as catalyst in benzene at 80 °C, the reaction gave essentially equal amounts of C–H insertion products and 1,2-H shift products (entries 9, 13).

The structure of C–H insertion product **16c** (R′ = CH_3) was unambiguously confirmed by single-crystal X-ray analysis, as shown in Figure 1.[15] The X-ray structure reveals that the trichloroacetylamino group, the ester group, and the methyl group are *trans* to one side. The $Rh_2(OAc)_4$-catalyzed 1,5-C–H insertion proceeded with high stereoselectivity, as only one diastereoisomer was observed. For the reaction of **15d** and **15e**, we have also observed only one diastereoisomer in each case for the C–H insertion products. By comparing the ^1H NMR spectra of **16d** and **16e** with **16c**, we conclude that they all have the same all-*trans* configuration.

The formation of **16c–e** represents a new entry to the five-membered cyclic β-amino acid derivatives, which have

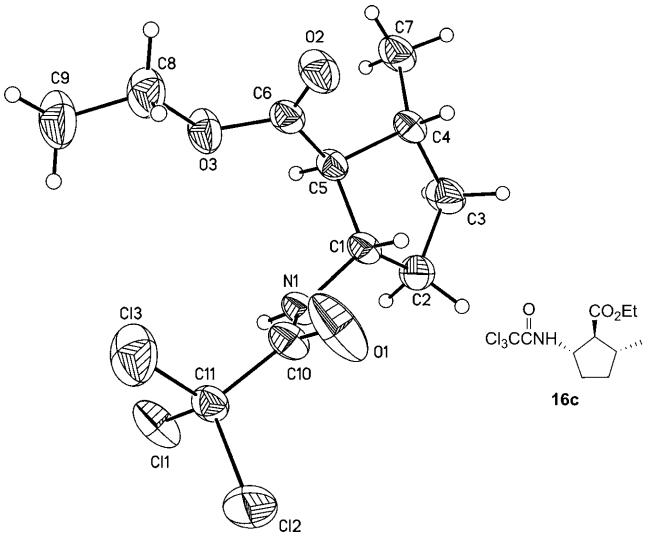
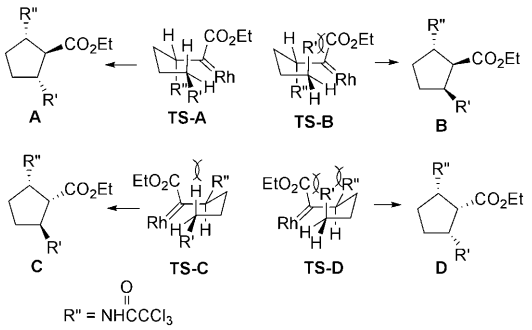


Figure 1. X-ray structure of **16c**.

attracted considerable attention recently.[16,17] To further confirm the generality of this novel approach, the diazo substrates **15f–j** were subjected to catalysis by $Rh_2(OAc)_4$. The results are summarized in Table 3. Notably, in the case of **15f**, intramolecular cyclopropanation is also possible. However, no trace of such product can be detected (entry 1). Another special case is **15j**, in which a carbon–carbon double bond is present in the chain. Although the C=C bond has a *cis* configuration, the expected 1,5-C–H insertion product **16j** has not been detected (entry 5). This result further indicates that conformational factors play dominant role in Rh^{II}-carbene reactions.

The unusual preference of C–H insertion over 1,2-H shift in $Rh_2(OAc)_4$-catalyzed reaction of the β-trichloroacetylamino diazo compounds **15c–i** may be interpreted from an electronic consideration.[14,18] The electron-withdrawing $NHCOCCl_3$ group will destabilize the transition state of the 1,2-H shift, in which positive charge develops at the carbon from which the H migrates. This is consistent with our previous observation that 1,2-aryl, 1,2-vinyl, and 1,2-alkynyl migrations occur exclusively in the presence of a β-hydrogen when there is a β-trichloroacetylamino or β-tosylamino substituent present in the diazo substrate.[10]

The high diastereoselectivity of the 1,5-C–H insertion suggests a very rigid transition state, and the all-*trans* selectivity can be simply rationalized by the transition model that has been suggested by Taber for Rh-mediated intramolecular 1,5-C–H insertion.[18b] In Taber's transition-state model, the stereochemistry of the products is determined by the energy differences between the chair-like transition states, in which the C–H bond being inserted, is parallel to the carbon–rhodium bond, while the energy differences are dependent on steric and electronic factors within these structures. As depicted in Scheme 3, for the Rh^{II}-catalyzed reaction of **15c–i**, there are four chair-like diastereomeric transition states for the 1,5-C–H insertion, **TS-A**, **TS-B**, **TS-C**, and **TS-D**, in which each leads to one of the four possible diastereomeric



Scheme 3. Transition states for Rh^{II}-catalyzed reaction of **15c–i**.

products. The steric interactions between the ester group and the R′ moiety in **TS-B**, and between the ester group and the trichloroacetylamino group both in **TS-C** and **TS-D**, all raise the energy in these transition states, resulting in the predominant formation of product **A**.

Conclusions

In summary, we have studied Rh^{II}-catalyzed reaction of β-trichloroacetylamino-substituted α-diazocarbonyl compounds. The β-substituent dramatically changes the reaction pathway of the Rh^{II} carbene, and usually very facile 1,2-H shift is suppressed and 1,5-C–H insertion occurs predominantly to afford the cyclic β-amino esters with high stereoselectivity. This may find application in organic synthesis as a new entry to this type of β-amino acid derivatives. This study further demonstrates the dramatic effect of neighboring groups on Rh^{II}-carbene reactions.

Experimental Section

General

All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask, and the components were added using a syringe. All solvents were distilled prior to use. The boiling point of petroleum ether is between 30 and 60 °C. Benzene and toluene were distilled from sodium prior to use. CH_2Cl_2 was distilled from CaH_2. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. For the preparative TLC, 10–40 μm silica gel GF254 (Qingdao, China) was used. Recrystallization was done using petroleum ether–ethyl acetate. ^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz with Varian Mercury 200 spectrometer, 300 MHz and 75 MHz with Varian Mercury 300 spectrometer, or at 400 MHz and 100 MHz with a Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra and HRMS were obtained on a VG ZAB-HS mass spectrometer. Elemental analysis was conducted with a Vario EL analyzer.

Syntheses

The preparation of β-hydroxy α-diazo carbonyl compounds **14a–j** was followed from the procedure in the literature.[12]

Caution: Diazo compounds are generally toxic and potentially explosive. They should be handled with care in a well-ventilated fumehood.

(*Z*)-Ethyl 2-diazo-3-(hydroxyl)icos-11-enoate (14f): $R_f = 0.33$ (petroleum ether: ethyl acetate = 5:1); IR: $\tilde{\nu} = 3454, 2925, 2094, 1695, 1466\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H), 1.26–1.76 (m, 27H), 2.02 (m, 4H), 2.95 (br s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 4.65 (m, 1H); 5.36 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.06, 14.40, 22.64, 25.53, 27.12, 27.15, 29.13, 29.17, 29.26, 29.34, 29.47, 29.65, 29.71, 31.85, 32.56, 33.89, 60.92, 66.48, 129.68, 129.91, 166.64$ ppm; MS (EI): *m/z* (%): 352 (1.4) $[(M-28)]^+$, 55 (100); elemental analysis: calcd (%) for $C_{22}H_{40}N_2O_3$: C 69.43, H 10.59, N 7.36; found: C 69.68, H 10.90, N 7.01.

Ethyl 2-diazo-3-hydroxy-6-methylheptanoate (14g): $R_f = 0.46$ (petroleum ether: ethyl acetate = 5:1); IR: $\tilde{\nu} = 3446, 2957, 2092, 1692, 1467, 746\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$). $\delta = 0.90$ (d, $J = 6.6$ Hz, 6H), 1.15–1.44 (m, 5H), 1.54–1.68 (m, 2H), 1.69–1.80 (m, 1H), 2.96 (br s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H); 4.65 (m, H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.40, 22.40, 22.47, 27.73, 31.78, 34.55, 60.95, 66.79, 166.66$ ppm; MS (EI): *m/z* (%): 186 (0.2) $[(M-28)]^+$, 41 (100); elemental analysis: calcd (%) for $C_{10}H_{18}N_2O_3$: C 56.06; H 8.47; N 13.07; found: C 56.18; H 8.66; N 13.16.

Ethyl 2-diazo-4-cyclohexyl-3-(hydroxy)butanoate (14h): $R_f = 0.40$ (petroleum ether: ethyl acetate = 5:1); IR: $\tilde{\nu} = 3437, 2924, 2092, 1692, 1464, 746\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (m, 1H), 1.03–1.20 (m, 2H), 1.29 (m, 4H), 1.37–1.50 (m, 2H), 1.60–1.81 (m, 6H), 2.91 (s, br, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 4.81 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.40, 26.03, 26.11, 26.39, 32.72, 33.56, 33.89, 41.33, 60.92, 64.20, 166.63$ ppm; MS (EI): *m/z* (%): 212 (0.7) $[(M-28)]^+$, 55 (100); elemental analysis: calcd (%) for $C_{12}H_{20}N_2O_3$: C 59.98, H 8.39, N 11.66; found: C 59.90, H 8.56, N 11.42.

Ethyl 2-diazo-3-hydroxy-6-phenylhexanoate (14i): $R_f = 0.42$ (petroleum ether: ethyl acetate = 5:1); IR: $\tilde{\nu} = 3444, 2982, 2092, 1689, 1294, 747\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.27$ (t, $J = 7.2$ Hz, 3H), 1.59–1.86 (m, 4H), 2.66 (t, $J = 7.2$ Hz, 3H), 2.88 (br, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 4.69 (t, $J = 7.2$ Hz, 1H), 7.17–7.30 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.40, 27.32, 33.40, 35.31, 60.98, 66.37, 125.84, 128.32, 141.72, 166.55$ ppm; MS (EI): *m/z* (%): 234 (0.2) $[(M-28)]^+$, 91 (100); elemental analysis: calcd (%) for $C_{14}H_{18}N_2O_3$: C 64.10, H 6.92, N 10.68; found: C 64.03, H 6.95, N 10.69.

(*Z*)-Ethyl 2-diazo-3-(hydroxy)dec-4-enoate (14j): $R_f = 0.45$ (petroleum ether: ethyl acetate = 5:1); IR: $\tilde{\nu} = 3461, 2957, 2094, 1693, 1286, 1105, 743\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H), 1.27–1.44 (m, 9H), 2.08 (m, 2H), 3.24 (s, *dr*, H), 4.26 (q, $J = 7.2$, 2H), 5.46–5.56 (m, 2H), 5.64 ppm (dt, $J = 7.5$, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.86, 14.33, 22.35, 27.90, 28.80, 31.25, 60.97, 63.27, 126.16, 134.34, 166.38$ ppm; MS (EI): *m/z* (%): 212 (2.0) $[(M-28)^+]$, 29 (100); elemental analysis: calcd (%) for $C_{12}H_{20}N_3O_3$: C 59.98, H 8.39, N 11.66; found: C 60.15, H 8.27, N 11.61.

*General Procedure for the Preparation of β-Trichloroacetylamino α-Diazocarbonyl Compounds **15a–j***

In a flamed three-necked round-bottom flask, β-hydroxy-α-diazo compound (1.0 mmol) was dissolved in toluene (or benzene) (5 mL). Trichloroacetonitrile (3.0 mmol, 98%) and sodium hydride (2.0 mmol, 60%) were added to the solution at 0°C. The mixture was stirred for 6 h between 0°C and room temperature. The reaction was quenched with a saturated solution of $NaHCO_3$ at −30°C, and then extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotavap. The residue was subjected to silica gel column chromatography (petroleum ether/Et_2O = 5:1) to afford the pure **15a–j**.

Ethyl 2-Diazo-3-(trichloroacetylamino)pentanoate (15a): $R_f = 0.48$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3331, 2975, 2101, 1698, 1512, 822\ cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.5$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.86 (m, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 4.48 (dt, $J = 7.8$, 7.9 Hz, 1H), 7.61 ppm (d, br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 10.51, 14.21, 25.74, 50.65, 60.99, 92.32, 161.50, 166.01$ ppm; MS (EI): *m/z* (%): 287 (3) $[(M-28)]^+$, 258 (95), 230 (11), 194 (20), 124 (40); elemental analysis: calcd (%) for $C_9H_{12}N_3O_3Cl_3$: C 34.15, H 3.82, N 13.27; found: C 34.09, H 3.83, N 13.44.

Ethyl 2-Diazo-3-(trichloroacetylamino)hexanoate (15b): $R_f = 0.35$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3330, 2963, 2874, 2101, 1699, 1513, 1374, 823, 743\ cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.01$ (t, $J = 7.3$ Hz, 3H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.50 (m, 2H), 1.97 (m, 2H), 4.26 (q, $J = 7.2$ Hz, 2H), 4.64 (dt, $J = 7.9$, 7.8 Hz, 1H), 7.58 ppm (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.45, 14.39, 19.43, 34.79, 49.16, 61.10, 92.35, 116.58, 161.41, 165.99$ ppm; MS (EI): *m/z* (%): 301 (8) $[(M-28)]^+$, 255 (42), 238 (24), 192 (43), 156 (58), 138 (100), 110 (12), 68 (12); elemental analysis: calcd (%) for $C_{10}H_{14}N_3O_3Cl_3$: C 36.33, H 4.27, N 12.71; found: C 36.35, H 4.24, N 12.84.

Ethyl 2-Diazo-3-(trichloroacetylamino)heptanoate (15c): $R_f = 0.55$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3329, 2960, 2100, 1698, 1513, 822, 744\ cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3H), 1.25 (m, 7H), 1.88 (m, 2H), 4.16 (q, $J = 7.2$ Hz, 2H) 4.54 (dt, $J = 7.8$ 7.9 Hz, 1H), 7.47 ppm (br d, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.77, 14.31, 21.91, 28.18, 32.45, 49.41, 61.08, 92.41, 161.49, 166.05$ ppm; MS (EI): *m/z* (%): decomposition; elemental analysis: calcd (%) for $C_{11}H_{16}N_3O_3Cl_3$: C 38.34, H 4.68, N 12.19; found: C 38.47, H 4.70, N 11.99.

Ethyl 2-Diazo-3-(trichloroacetylamino)nonanoate (15d): $R_f = 0.60$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3333, 2931, 2100, 1698, 1512, 1302, 822\ cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.3$ Hz, 3H), 1.29 (m, 11H), 1.95 (m, 2H), 4.23 (q, $J = 7.3$ Hz, 2H), 4.60 (dt, $J = 7.7$, 8 Hz, 1H), 7.67 ppm (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.83, 14.24, 22.31, 25.95, 28.44, 31.41, 32.41, 49.25, 60.99, 92.35, 161.46, 166.04$ ppm; MS (EI): *m/z* (%): 343 (0.8) $[(M-28)]^+$, 308 (13), 258 (42), 238 (14), 186 (11), 117 (13), 67 (19), 43 (52), 29 (100); elemental analysis: calcd (%) for $C_{13}H_{20}N_3O_3Cl_3$: C 41.90, H 5.41, N 11.28; found: C 42.01, H 5.41, N 11.28.

Ethyl 2-Diazo-3-(trichloroacetylamino)tetradecanoate (15e): $R_f = 0.67$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3333, 2926, 2855, 2101, 1698, 1512, 1374, 822\ cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.3$ Hz, 3H), 1.16–1.33 (m, 21H), 1.90 (m, 2H), 4.26 (q, $J = 7.3$ Hz, 2H), 4.60 (dt, $J = 7.7$, 7.8 Hz, 1H), 7.55 ppm (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.00, 14.31, 22.57, 26.06, 28.84, 29.21, 29.30, 29.36, 29.48, 31.80, 32.67, 49.41, 61.06, 92.42, 161.50, 166.09$ ppm; MS (EI): *m/z* (%): 413 (2) $[(M-28)^+]$, 378 (39), 342 (11), 296 (15), 258 (35), 238 (65), 182 (25), 117 (11), 95 (27), 55 (51), 29 (100); elemental analysis: calcd (%) for $C_{18}H_{30}N_3O_3Cl_3$: C 48.82, H 6.83, N 9.49; found: C 48.99, H 7.02, N 9.42.

(*Z*)-Ethyl 2-diazo-3-(trichloroacetylamino)icos-11-enoate (15f): $R_f = 0.40$ (petroleum ether: ethyl acetate = 15:1); IR: $\tilde{\nu} = 3336, 2925, 2100, 1698, 1511, 822\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.6$ Hz, 3H), 1.26 (m, 25H), 1.86–2.02 (m, 6H), 4.25 (q, $J = 7.2$ Hz, 2H), 4.60 (dt, $J = 7.8$, 7.8 Hz, 1H); 5.35 (m, 2H), 7.54 ppm (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.08, 14.35, 22.64, 26.09, 27.10, 27.16, 28.87, 29.05, 29.26, 29.46, 29.61, 29.70, 31.84, 32.56, 32.82, 49.43, 61.12, 92.37, 129.61, 129.97, 161.49, 166.13$ ppm; MS (EI): *m/z* (%): 495 (0.8) $[(M-28)^+]$, 55 (100); elemental analysis: calcd (%) for $C_{24}H_{40}Cl_3N_3O_3$: C 54.91, H 7.68, N 8.00; found: C 55.03, H 7.73, N 7.89.

Ethyl 2-diazo-3-trichloroacetylamino-6-methylheptanoate (15g): $R_f = 0.38$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3332, 2958, 2100, 1697, 1511, 821\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (d, $J = 6.0$ Hz, 6H), 1.29 (m, 5H), 1.59 (m, 1H), 1.91 (m, 2H), 4.26 (q, $J = 7.2$ Hz, 2H), 4.57 (dt, $J = 7.8$, 7.8 Hz, 1H); 7.53 ppm (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.36, 22.36, 22.48, 27.55, 30.78, 35.13, 49.70, 61.13, 92.37, 161.48, 166.10$ ppm; MS (EI): *m/z* (%): 329 (0.1) $[(M-28)^+]$, 29 (100); elemental analysis: calcd (%) for $C_{12}H_{18}Cl_3N_3O_3$: C 40.19, H 5.06, N 11.72; found: C 40.17, H 5.05, N 11.74.

Ethyl 2-diazo-4-cyclohexyl-3-(trichloroacetylamino)butanoate (15h): $R_f = 0.41$ (petroleum ether/ethyl acetate = 15:1); IR: $\tilde{\nu} = 3329, 2925, 2100, 1698, 1513, 823\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.93–1.04$ (m, 2H), 1.13–1.32 (m, 7H), 1.65–1.88 (m, 7H), 4.25 (q, $J = 7.2$ Hz, 2H), 4.72 (dt, $J = 7.8$, 7.8 Hz, 1H), 7.45 ppm (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.38, 26.01, 26.28, 32.80, 32.95, 34.55, 40.15, 47.21, 61.13, 161.48, 166.12$ ppm; MS (EI): *m/z* (%): 366 (0.4) $[(M-28)]^+$, 55 (100); elemental analysis: calcd (%) for $C_{14}H_{20}Cl_3N_3O_3$: C 43.71, H 5.24, N 10.92; found: C 43.88, H 5.40, N 10.80.

Ethyl 2-diazo-3-trichloroacetylamino-6-phenylhexanoate (15i): $R_f = 0.21$ (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu} = 3330, 2981, 2099, 1696, 1510, 1305, 821\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J = 7.2$ Hz,

3H), 1.73 (m, 2H), 1.86–2.03 (m, 2H), 2.66 (t, J=7.2 Hz, 2H), 4.21 (q, J=7.2 Hz, 2H), 4.63 (dt, J=7.5, 7.5 Hz, 1H), 7.15–7.31 (m, 5H), 7.65 ppm (dr, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.24, 27.77, 32.03, 34.93, 49.12, 61.07, 92.28, 125.92, 128.18, 128.33, 141.18, 161.51, 166.01 ppm; MS (EI): m/z (%): 377 (0.3) $[(M-28)]^+$, 104 (100); elemental analysis: calcd (%) for $C_{16}H_{18}Cl_3N_3O_3$: C 47.25, H 4.46, N 10.33; found: C 46.93, H 4.47, N 10.19.

(*Z*)-Ethyl 2-diazo-3-(trichloroacetylamino)dec-4-enoate (15j): R_f=0.45 (petroleum ether/ethyl acetate=10:1); IR: $\tilde{\nu}$=3328, 2959, 2102, 1697, 1509, 1238, 821 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, J=6.6 Hz, 3H), 1.27–1.44 (m, 9H), 2.14 (dt, J=6.3, 6.3 Hz, 2H), 4.26 (q, J=7.2, 2H), 5.44 (dd, J=7.2, 7.2 Hz, 1H), 5.66–5.71 (m, 2H), 7.54 ppm (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.92, 14.36, 22.41, 27.77, 28.85, 31.28, 46.33, 61.20, 92.28, 123.62, 135.51, 161.24, 165.84 ppm; MS (EI): m/z (%): 355 (2.0) $[(M-28)]^+$, 29 (100); elemental analysis: calcd (%) for $C_{14}H_{20}Cl_3N_3O_3$: C 43.71, H 5.24, N 10.92; found: C 43.62; H 5.25; N 10.76.

*General Procedure for $Rh_2(OAc)_4$-Catalyzed Reaction of **15a–j***

In a flamed round-bottom flask, $Rh_2(OAc)_4$ (1 mol%) was dissolved in anhydrous CH_2Cl_2 (10 mL). A solution of diazo substrate **15a–j** in anhydrous CH_2Cl_2 was added dropwise at 0°C for 15 min. After stirred for another 60 min, the solution was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to afford the products.

***r*1, *trans*-2, *trans*-5, Ethyl 2-Trichloroacetylamino-5-methyl-cyclopentanecarboxylate (16c)**: R_f=0.31 (petroleum ether: ethyl acetate=10:1); IR: $\tilde{\nu}$=3334, 2960, 1701, 1524, 1198, 827 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.11 (d, J=7.8 Hz, 3H), 1.26 (t, J=7.2 Hz, 3H), 1.45 (m, 1H), 1.67 (m, 1H), 1.98 (m, 1H), 2.25 (m, 3H), 4.18 (q, J=7.2 Hz, 2H), 4.37 (m, 1H), 6.29 ppm (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.18, 19.52, 31.00, 31.60, 37.42, 56.47, 58.01, 60.91, 92.48, 161.32, 173.19 ppm; MS (EI): m/z (%): 316 (0.25) $[(M+1)]^+$, 280 (37), 206 (23), 198 (17), 152 (49), 115 (95), 109 (71), 81 (100), 29 (38); elemental analysis: calcd (%) for $C_{11}H_{16}NO_3Cl_3$: C 41.73, H 5.09, N 4.42, found: C 41.94, H 5.16, N 4.36.

***r*1, *trans*-2, *trans*-5, Ethyl 2-Trichloroacetylamino-5-propyl-cyclopentanecarboxylate (16d)**: R_f=0.37 (petroleum ether: ethyl acetate=10:1); IR: $\tilde{\nu}$=3334, 2960, 1701, 1525, 828 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 0.90 (t, J=6.7 Hz, 3H), 1.16~1.50 (m, 8H), 1.68 (m, 1H), 2.04 (m, 1H), 2.20~2.42 (m, 3H), 4.16 (q, J=7.3 Hz, 2H), 4.36 (m, 1H), 6.86 ppm (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.03, 14.09, 20.79, 29.20, 30.99, 37.47, 41.93, 56.54, 56.65, 60.83, 92.44, 161.28, 173.53 ppm; MS (EI): m/z (%): 344 (0.2) $[(M+1)]^+$, 343 (0.08) (M^+), 308 (40), 234 (23), 180 (34), 143 (100), 137 (43), 109 (53), 67 (45), 55 (14), 29 (37); elemental analysis: calcd (%) for $C_{13}H_{20}NO_3Cl_3$: C 45.30, H 5.85, N 4.06; found: C 45.43, H 5.90, N 3.98.

***r*1, *trans*-2, *trans*-5, Ethyl 2-Trichloroacetylamino-5-octylcyclo-pentanecarboxylate (16e)**: R_f=0.43 (petroleum ether: ethyl acetate=10:1); IR: $\tilde{\nu}$=3334, 2926, 1697, 1525, 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 0.88 (t, J=6.7 Hz, 3H), 1.16–1.29 (m, 16H), 1.38~1.77 (m, 3H), 1.90–2.07 (m, 1H), 2.16–2.41 (m, 3H), 4.17 (q, J=7.2 Hz, 2H), 4.35 (m, 1H), 6.84 ppm (d, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.00, 14.10, 22.56, 27.61, 29.16, 29.25, 29.40, 29.55, 31.01, 31.77, 35.24, 42.19, 56.58, 56.70, 60.83, 92.49, 161.28, 173.53 ppm; MS (EI): m/z (%): 414 (0.43) $[(M+1)]^+$, 378 (64), 304 (23), 250 (26), 213 (100), 185 (28), 121 (7), 81 (29), 67 (56), 29 (62); elemental analysis: calcd (%) for $C_{18}H_{30}NO_3Cl_3$: C 52.12, H 7.29, N 3.38; found: C 52.23, H 7.44, N 3.12.

***r*1, *trans*-2, *trans*-5, Ethyl 2-Trichloroacetylamino-5-((*Z*)-tridec-4-enyl) cyclopentanecarboxylate (16f)**: R_f=0.55 (petroleum ether/ethyl acetate= 10:1); IR: $\tilde{\nu}$=3329, 2923, 1733, 1524, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.89 (t, J=6.6 Hz, 3H), 1.25–1.71 (m, 23H), 1.99 (m, 5H), 2.26 (m, 2H), 2.37 (m, 1H), 4.17 (q, J=7.2 Hz, 2H), 4.35 (m, 1H), 5.35 (m, 2H), 6.83 ppm (d, br, J=5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.08, 14.16, 22.64, 27.02, 27.18, 27.32, 29.27, 29.60, 29.65, 29.68, 29.71, 31.04, 31.86, 35.18, 42.17, 56.59, 56.72, 60.90, 92.50, 129.38, 130.12, 161.33, 173.53 ppm; MS (EI): m/z (%): 497 (0.7) $[(M+2)]^+$, 495 (0.6) (M^+), 287 (100); HRMS: m/z (%) calcd for $C_{24}H_{40}Cl_3NO_3$: 495.2074; found: 495.2047.

***r*1, *trans*-2, *trans*-5, Ethyl 2-Trichloroacetylamino-5,5-dimethylcyclopentanecarboxylate (16g)**: R_f=0.18 (petroleum ether: ethyl acetate=15:1); IR: $\tilde{\nu}$=3330, 2938, 1708, 1640, 1211, 872 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.95 (s, 3H), 1.24 (s, 3H), 1.28 (t, J=7.2 Hz, 3H), 1.59–1.83 (m, 3H), 2.23–2.32 (m, 1H), 2.64 (d, J=9.0 Hz, 1H), 4.19 (m, 2H), 4.57 (m, 1H), 6.87 ppm (br d, J=5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.20, 24.14, 29.09, 29.48, 39.76, 41.98, 55.02, 59.71, 60.494, 92.53, 161.20, 171.96 ppm; MS (EI): m/z (%): 331 (0.1) $[(M+2)]^+$, 329 (0.1) (M^+), 95 (100); HRMS: m/z (%) calcd for $C_{12}H_{18}Cl_3NO_3$: 329.0352; found: 329.0338.

***r*1, *trans*-2, *trans*-3a, *trans*-7a, Ethyl 2-Trichloroacetylamino-octahydro-1*H*-indene-1-carboxylate (16h)**: R_f=0.15 (petroleum ether: ethyl acetate=15:1); IR: $\tilde{\nu}$=3333, 2926, 1694, 1522, 1259, 821 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.07–1.29 (m, 7H), 1.43 (m, 1H), 1.58 (m, 1H), 1.77–1.97 (m, 6H), 2.41 (dd, J=7.4, 11.1 Hz 1H), 4.19 (q, J=7.2 Hz, 2H), 4.46 (m, 2H), 6.94 ppm (d, br, J=5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.12, 25.51, 25.65, 29.99, 30.99, 37.86, 44.43, 49.44, 54.42, 56.70, 60.66, 92.42, 161.19, 173.46 ppm; MS (EI): m/z (%): 331 (0.1) $[(M+2)]^+$, 329 (0.1) (M^+), 95 (100). HRMS: m/z (%) calcd for $C_{14}H_{20}Cl_3NO_3$: 355.0509; found: 355.0495.

***r*1, *trans*-2, *trans*-5, Ethyl 2-Trichloroacetylamino-5-phenylcyclopentanecarboxylate (16i)**: R_f=0.19 (petroleum ether: ethyl acetate=15: 1); IR: $\tilde{\nu}$=3335, 2975, 1694, 1523, 1186, 821 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.49 (t, J=7.2 Hz 3H), 1.88–2.03 (m, 2H), 2.22–2.27 (m, 1H), 2.39–2.44 (m, 1H), 2.93 (t, J=10.0 Hz 1H), 3.49 (dt, J=9.5, 9.5 Hz 1H), 4.09 (q, J=7.2 Hz, 2H), 4.47 (m, 1H), 7.01 (d, br, J=6.7 Hz, 1H), 7.20–7.32 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.98, 31.20, 31.52, 47.47, 56.54, 57.58, 60.97, 92.38, 126.74, 126.96, 128.54, 142.16, 161.42, 172.62 ppm; MS (EI): m/z (%): 379 (7.0) $[(M+2)]^+$, 377 (7.0) (M^+), 268 (100); HRMS: m/z (%) calcd for $C_{16}H_{18}Cl_3NO_3$: 377.0352; found: 377.0360.

(*E*)-Ethyl 3-Trichloroacetylamino-2-pentenoate (17a): R_f=0.57 (petroleum ether/ethyl acetate=10:1); IR: $\tilde{\nu}$=3332, 2981, 1712, 1520, 1201, 1142, 820, 673 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.10 (t, J=7.8 Hz, 3H), 1.30 (t, J=7.0 Hz, 3H), 2.90 (q, J=7.6 Hz, 2H), 4.20 (q, J=7.0 Hz, 2H), 6.74 (s, 1H), 7.79 ppm (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=12.38, 14.17, 24.84, 59.94, 105.46, 151.57,154.97, 159.10, 166.73 ppm; MS (EI): m/z (%) 287 (4) (M^+), 252 (6), 241 (24), 213 (9), 206 (25), 178 (17), 142 (56), 124 (100); elemental analysis: calcd (%) for $C_9H_{12}NO_3Cl_3$: C 37.46, H 4.19, N 4.85; found: C 37.66, H 4.37, N 4.65.

(*E*)-Ethyl 3-Trichloroacetylamino-2-hexenoate (17b): R_f=0.48 (petroleum ether/ethyl acetate=10:1); IR: $\tilde{\nu}$=3334, 2967, 1711, 1520, 1143, 821 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.98 (t, J=7.5 Hz, 3H), 1.28 (t, J=7.2 Hz, 3H), 1.65 (m, 2H), 2.86 (t, J=7.7 Hz, 2H), 4.18 (q, J= 7.2 Hz, 2H), 6.77 (s, 1H), 7.78 ppm (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=13.50, 14.18, 21.44, 33.11, 59.91, 92.20, 106.07, 150.29, 158.99, 166.82 ppm; MS (EI): m/z (%): 301 (5) (M^+), 266 (31), 257 (41), 220 (68), 192 (65), 138 (69), 110 (16), 95 (11), 55 (16), 29 (100); elemental analysis: calcd (%) for $C_{10}H_{14}NO_3Cl_3$: C 39.69, H 4.66, N 4.63; found: C 39.78, H 4.71, N 4.74.

(*E*)-Ethyl 3-Trichloroacetylamino-2-nonenoate (17d): R_f=0.54 (petroleum ether: ethyl acetate=10:1); IR: $\tilde{\nu}$=3334, 2930, 1713, 1519, 1141, 819, 672 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=6.6 Hz, 3H), 1.26–1.39 (m, 9H), 1.58 (m, 2H), 2.87 (t, J=7.8 Hz, 2H), 4.19 (q, J=7.2 Hz, 2H), 6.77 (s, 1H), 7.74 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 13.98, 14.23, 22.48, 28.09, 28.80, 29.66, 31.45, 59.96, 92.45, 105.88, 150.50, 158.98, 166.86 ppm; MS (EI): m/z (%): 343 (1) (M^+), 308 (21), 238 (62), 198 (26), 180 (26), 109 (16), 57 (25), 43 (56), 29 (100).

(*E*)-Ethyl 3-Trichloroacetylamino-2-tetradecenoate (17e): R_f=0.56 (petroleum ether/ethyl acetate=10:1); IR: $\tilde{\nu}$=3335, 2926, 2855, 1713, 1519, 1139, 795 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=6.6 Hz, 3H), 1.26–1.31 (m, 19H), 1.53~1.62 (m, 2H), 2.87 (t, J=7.7 Hz, 2H), 4.17 (q, J=7.0 Hz, 2H), 6.77 (s, 1H), 7.73 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.09, 14.24, 22.65, 28.13, 29.13, 29.31, 29.45, 29.56, 31.42, 31.87, 59.55, 92.47, 105.89, 150.50, 158.96, 166.86 ppm; MS (EI): m/z (%): 413 (1) (M^+), 378 (34), 342 (12), 268 (27), 238 (80), 150 (21), 95 (16), 55 (54), 43 (98), 29 (100).

(2*E*, 11*Z*)-Ethyl 3-Trichloroacetylaminoicosa-2,11-dienoate (17f): R_f = 0.64 (petroleum ether/ethyl acetate = 10:1); IR: $\tilde{\nu}$ = 3341, 2926, 1737, 1518, 1197, 886 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 3H), 1.26–1.60 (m, 25H), 2.00 (m, 4H), 2.87 (t, J = 7.8 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 5.34 (m, 2H), 6.67 (s, 1H), 7.74 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.09, 14.22, 22.64, 27.12, 27.18, 28.11, 29.08, 29.19, 29.28, 29.48, 29.62, 29.71, 31.39, 31.86, 32.56, 59.93, 92.44, 105.85, 129.63, 129.98, 150.49, 158.95, 166.82 ppm; MS (EI): *m*/*z* (%): 497 (0.8) $[(M+2)]^+$, 495 (0.8) (M^+), 29(100); HRMS: *m*/*z* (%) calcd for $C_{24}H_{40}Cl_3NO_3$: 495.2074; found: 495.2070.

(*E*)-Ethyl 3-Trichloroacetylamino-6-methyl-2-heptenoate (17g); R_f = 0.32 (petroleum ether/ethyl acetate = 15:1); IR: $\tilde{\nu}$ = 3335, 2940, 1710, 1646, 1518, 1203, 870 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 (d, J = 6.6 Hz, 6H), 1.28 (t, J = 7.2 Hz, 3H), 1.48 (m, 2H), 1.66 (m, 1H), 2.88 (t, J = 8.1 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 6.74 (s, 1H), 7.74 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.24, 22.50, 27.92, 29.44, 37.00, 59.96, 92.42, 105.76, 150.80, 158.97, 166.81 ppm; MS (EI): *m*/*z* (%): 331 (1.4) $[(M+2)]^+$, 329 (1.5) (M^+), 29 (100); HRMS: *m*/*z* (%) calcd for $C_{12}H_{18}Cl_3NO_3$: 329.0352; found: 329.0347.

(*E*)-Ethyl 3-Trichloroacetylamino-4-cyclohexyl-2-butenoate (17h): R_f = 0.33 (petroleum ether/ethyl acetate = 15: 1); IR: $\tilde{\nu}$ = 3337, 2925, 1712, 1518, 1143, 818 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03–1.31 (m, 8H), 1.56–1.78 (m, 6H), 2.77 (d, J = 7.5 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 6.86 (s, 1H), 7.71 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.22, 26.03, 29.65, 32.75, 32.98, 37.35, 38.88, 59.92, 92.44, 106.58, 149.23, 158.76, 166.97 ppm; MS (EI): *m*/*z* (%): 357 (1.5) $[(M+2)]^+$, 355 (1.5) (M^+), 55 (100); HRMS: *m*/*z* (%) calcd for $C_{14}H_{20}Cl_3NO_3$: 355.0509; found: 355.0503.

(*E*)-Ethyl 3-Trichloroacetylamino-6-phenyl-2-hexenoate (17i): R_f = 0.28 (petroleum ether/ethyl acetate = 15: 1); IR: $\tilde{\nu}$ = 3317, 2962, 1708, 1533, 1146, 826 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.2 Hz, 3H), 1.92 (tt, J = 7.2, 7.5 Hz, 2H), 2.72 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.5 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 6. 77(s, 1H), 7.18–7.31 (m, 5H), 7.64 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.23, 29.70, 31.02, 35.13, 60.03, 92.32, 106.21, 126.12, 128.32, 128.49, 141.17, 150.03, 159.02, 166.81 ppm; MS (EI): *m*/*z* (%): 379 (0.3) $[(M+2)]^+$, 377 (0.3) (M^+), 104 (100); HRMS: *m*/*z* (%) calcd for $C_{16}H_{18}Cl_3NO_3$: 377.0352; found: 377.0360.

(2*E*, 4*Z*)-Ethyl 3-Trichloroacetylaminoundeca-2,4-dienoate (17j): R_f = 0.40 (petroleum ether/ethyl acetate = 15: 1); IR: $\tilde{\nu}$ = 3385, 2930, 1736, 1640, 1211, 816 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.6 Hz, 3H), 1.23–1.45 (m, 9H), 1.94 (dt, J = 6.9, 6.9 Hz, 2H), 4.26 (q, J = 7.2, 2H), 5.86–6.01 (m, 2H), 7.90 (d, J = 11.4 Hz, 1H), 8.36 ppm (d, J = 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.91, 14.24, 22.31, 28.58, 29.13, 31.16, 60.91, 91.54, 115.10, 119.89, 130.40, 137.41, 159.06, 165.86 ppm; MS (EI): *m*/*z* (%): 357 (9.9) $[(M+2)]^+$, 355 (10.0) (M^+), 320 (100); elemental analysis: calcd (%) for $C_{14}H_{20}Cl_3NO_3$: C 47.14, H 5.65, N 3.93; found: C 47.17, H 5.58, N 3.98.

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