Supporting Information for

Unusual Reaction of β–Hydroxy α–Diazo Carbonyl Compounds with Cl_3CCN/NaH and Rh(II)-catalyzed Reaction of β–Trichloroacetylamino α–Diazo Carbonyl Compounds

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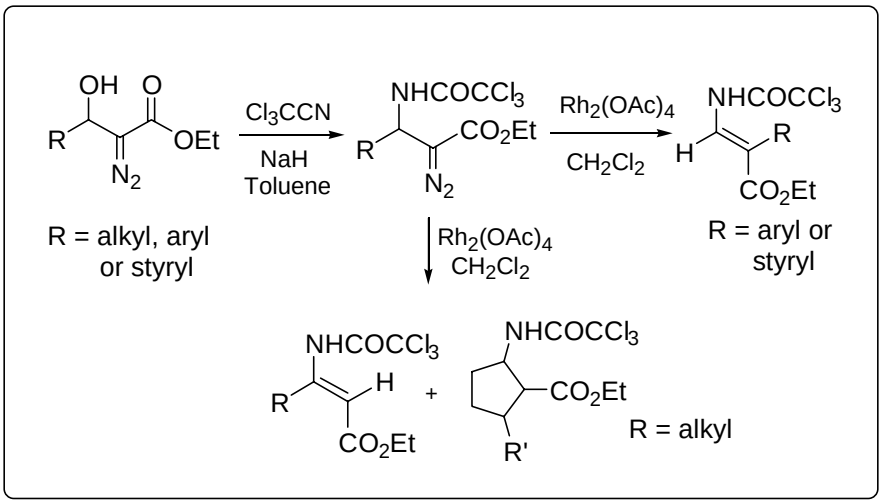
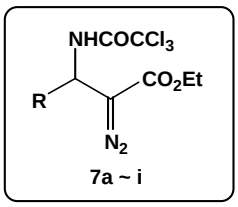


General. All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask, and the components were added via syringe. All solvents were distilled prior to use. The boiling point of petroleum ether is between 30 and 60 ^{o}C. Benzene and toluene was distilled from sodium prior to use. CH_2Cl_2 was distilled from CaH_2. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. For preparative TLC, 10-40 μm silica gel GF_{254} (Qingdao, China) was used. Recrystallization was from petroleum ether-ethyl acetate. ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz with Varian Mercury 200 spectrometer, or at 300 MHz and 75 MHz with Varian Mercury 300 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 were obtained on a VG ZAB-HS mass spectrometer. Elemental analysis was conducted with vario EL.

General Procedure for the Preparation of 7a~i. In a flamed three-necked round-bottom flask, β-hydroxy-α-diazo compound **6a~i** (1.0 mmol) was dissolved 5 mL toluene (or benzene). Trichloroacetonitrile (3.0 mmol, 98 %) and hydride sodium (2.0 mmol, 60 %) were added to the solution at 0 ^{o}C. The mixture was allowed to stir for 6 h between 0 ^{o}C and room temperature. The reaction was quenched with saturated $NaHCO_3$ at –30 ^{o}C and then extracted with Et_2O. The combined organic layer were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with rotvap. The residue was subjected to silica gel chromatography (petroleum ether : Et_2O = 5 : 1) to afford the pure **7a~i**.



7a ~ i

(*E*)-Ethyl 2–Diazo-5-phenyl-3-(trichloroacetylamino)pent-4-enoate (**7a**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.39; IR 3327, 2102, 1697, 1499, 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 5.41 (dd, *J* = 7.0, 6.6 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.0 Hz, 1H), 6.65 (d, *J* = 15.8 Hz, 1H), 7.33 (m, 5H), 7.86 (br, d, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.32 (×3), 50.74, 61.34 (×2), 92.28 ($\underline{C}Cl_3$), 123.08, 126.74, 128.44, 128.60, 133.50, 135.35, 161.29, 165.82; MS *m/z* (EI) 361 [(M-28)$^{+}$, 5], 289 (16), 216 (21) 200 (52), 198 (36), 155 (55), 115 (100). Anal. calcd for $C_{15}H_{14}N_3O_3Cl_3$: C, 46.12; H, 3.61; N, 10.76. Found: C, 45.78; H, 3.66; N, 10.75.

Ethyl 2-Diazo-3-(trichloroacetylamino)pentanoate (**7b**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.48; IR 3331, 2975, 2101, 1698, 1512, 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 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(d, br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.51 (×3), 14.21 (×3), 25.74 (×2), 50.65, 60.99 (×2), 92.32 ($\underline{C}Cl_3$), 161.50, 166.01; MS *m/z* (EI) 287 [(M-28)$^{+}$, 3], 258 (95), 230 (11), 194 (20), 124 (40). Anal. 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 (**7c**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.35; IR 3330, 2963, 2874, 2101, 1699, 1513, 1374, 823, 743 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$)

δ 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 (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.45 (×3), 14.39 (×3), 19.43 (×2), 34.79 (×2), 49.16, 61.10 (×2), 92.35 ($\underline{C}Cl_3$), 116.58, 161.41, 165.99; MS *m/z* (EI) 301 [(M-28)$^+$, 8], 255 (42), 238 (24), 192 (43), 156 (58), 138 (100), 110 (12), 68 (12). Anal. 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 (**7d**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.55; IR 3329, 2960, 2100, 1698, 1513, 822, 744 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 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 (br, d, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.77 (×3), 14.31 (×3), 21.91 (×2), 28.18 (×2), 32.45 (×2), 49.41, 61.08 (×2), 92.41 ($\underline{C}Cl_3$), 161.49, 166.05; MS *m/z* (EI) (decomposition). Anal. 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 (**7e**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.60; IR 3333, 2931, 2100, 1698, 1512, 1302, 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 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 (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.83 (×3), 14.24 (×3), 22.31 (×2), 25.95 (×2), 28.44 (×2), 31.41 (×2), 32.41 (×2), 49.25, 60.99 (×2), 92.35 ($\underline{C}Cl_3$), 161.46, 166.04; MS *m/z* (EI) 343 [(M-28)$^+$, 0.8], 308 (13), 258 (42), 238 (14), 186 (11), 117 (13), 67 (19), 43 (52), 29 (100). Anal. 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 (**7f**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.67; IR 3333, 2926, 2855, 2101, 1698, 1512, 1374, 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 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 (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.00 (×3), 14.31 (×3), 22.57 (×2), 26.06 (×2), 28.84 (×2), 29.21 (×2), 29.30 (×2), 29.36 (×2), 29.48 (×2), 31.80 (×2), 32.67 (×2), 49.41, 61.06 (×2), 92.42 ($\underline{C}Cl_3$), 161.50, 166.09; MS *m/z* (EI) 413 [(M-28)$^+$, 2], 378 (39), 342 (11), 296 (15), 258 (35), 238 (65), 182 (25), 117 (11), 95 (27), 55 (51), 29 (100). Anal. 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.

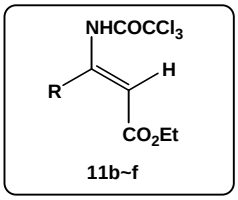
Ethyl 2–Diazo-3-phenyl-3-(trichloroacetylamino)propanoate (**7g**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.44; IR 3421, 2256, 2103, 1713, 1683, 1497, 909, 737 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 5.92 (d, *J* = 8.2 Hz, 1H), 7.36 (br, 5H), 7.98 (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.33 (×3), 51.75, 61.50 (×2), 92.20 ($\underline{C}Cl_3$), 125.98, 128.62, 129.16, 137.00, 161.39, 165.90; MS *m/z* (EI) 335 [(M-28)$^+$, 7], 300 (5), 192 (21), 172 (49), 118 (100), 102 (28), 90 (31), 77 (32), 29 (76). Anal. calcd for $C_{13}H_{12}N_3O_3Cl_3$: C, 42.82; H, 3.32; N, 11.53. Found: C, 42.84; H, 3.35; N, 11.70.

Ethyl 2–Diazo-3-(4-fluorophenyl)-3-(trichloroacetylamino)propanoate (**7h**). TLC R_f (petroleum ether : ethyl acetate = 10:1) = 0.39; IR 3316, 2360, 2104, 1695, 1510, 1227, 823 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 5.90 (d, *J* = 8 Hz, 1H), 7.09 (m, 2H), 7.31 (m, 2H), 7.99 (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.34 (×3), 51.27, 61.60 (×2), 92.20 ($\underline{C}Cl_3$), 115.97, 116.26, 127.85, 127.96, 132.96, 161.42, 165.91; MS *m/z* (EI) 353 [(M-28)$^+$, 6], 318 (5), 210 (18), 190 (38), 136 (100), 108 (25), 83 (37), 29 (68). Anal. calcd for $C_{13}H_{11}N_3FO_3Cl_3$: C, 40.81; H, 2.90;

N, 10.98. Found: C, 40.92; H, 2.97; N, 11.01.

Ethyl 2–Diazo-3-(4-methoxyphenyl)-3-(trichloroacetylamino)propanoate (**7i**). TLC R_f(petroleum ether : ethyl acetate = 10 : 1) = 0.30; IR 3310, 2108, 1682, 1514, 1258, 833 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 3.81 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 5.87 (d, *J* = 7.8 Hz, 1H), 6.92 (d, 2H), 7.27 (d, 2H), 7.92 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.28 (×3), 51.22, 55.20 (×3), 61.36 (×2), 92.28 ($\underline{C}Cl_3$), 114.37, 127.26, 128.83, 159.57, 161.18, 165.88; MS *m/z* (EI) 365 [$(M-28)^+$, 36], 330 (58), 222 (46), 174 (74), 148 (100), 132 (42), 77 (23), 29(59). Anal. calcd for $C_{14}H_{14}N_3O_4Cl_3$: C, 42.61; H, 3.58; N, 10.65. Found: C, 42.28; H, 3.63; N, 10.57.

General procedure for $Rh_2(OAc)_4$ catalyzed reaction: In a flamed round-bottom flask, $Rh_2(OAc)_4$ (1 mol %) was dissolved into 10 mL anhydrous CH_2Cl_2. A solution of diazo substrate **7a~i** in anhydrous CH_2Cl_2 was added dropwise at 0 ^0C for 15 minutes. After stirred for another 20 minutes, the solution was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to afford the products.



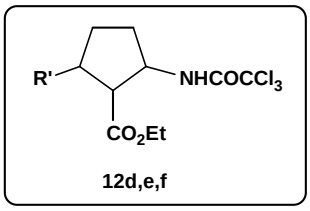
11b~f

(*E*)-Ethyl 3-(trichloroacetyl)aminopentenoate (**11b**). TLC R_f(petroleum ether : ethyl acetate = 10 : 1) = 0.57; IR 3332, 2981, 1712, 1520, 1201, 1142, 820, 673 cm^{-1}; ^1H 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 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.38 (×3), 14.17 (×3), 24.84 (×2), 59.94 (×2), 105.46, 151.57,154.97, 159.10,166.73; MS *m/z* (EI) 287 (M^+, 4), 252 (6), 241 (24), 213 (9), 206 (25), 178 (17), 142 (56), 124 (100). Anal. 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-(trichloroacetyl)amino-2-hexenoate (**11c**). TLC R_f(petroleum ether : ethyl acetate = 10 : 1) = 0.48; IR 3334, 2967, 1711, 1520, 1143, 821 cm^{-1}; ^1H 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 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.50 (×3), 14.18 (×3), 21.44 (×2), 33.11 (×2), 59.91 (×2), 92.20 ($\underline{C}Cl_3$),106.07, 150.29, 158.99, 166.82; MS *m/z* (EI) 301 (M^+, 5), 266 (31), 257 (41), 220 (68), 192 (65), 138 (69), 110 (16), 95 (11), 55 (16), 29 (100). Anal. 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-(trichloroacetyl)amino-2-nonenoate (**11e**). TLC R_f(petroleum ether : ethyl acetate = 10 : 1) = 0.54; IR 3334, 2930, 1713, 1519, 1141, 819, 672 cm^{-1}; ^1H 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 (s, 1H). ^{13}C NMR (75MHz, $CDCl_3$) δ 13.98 (×3), 14.23 (×3), 22.48 (×2), 28.09 (×2), 28.80 (×2), 29.66 (×2), 31.45 (×2), 59.96 (×2), 92.45 ($\underline{C}Cl_3$), 105.88, 150.50, 158.98, 166.86; MS *m/z* (EI) 343 (M^+, 1), 308 (21), 238 (62), 198 (26), 180 (26), 109 (16), 57 (25), 43 (56), 29 (100).

(*E*)-Ethyl 3-(trichloroacetyl)amino-2-tetradecenoate (**11f**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.56; IR 3335, 2926, 2855, 1713, 1519, 1139, 795 cm^{-1}; ^1H 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 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.09 (×3), 14.24 (×3), 22.65 (×2), 28.13 (×2), 29.13 (×2), 29.31 (×2), 29.45 (×2), 29.56 (×2), 31.42 (×2), 31.87 (×2), 59.55 (×2), 92.47 ($\underline{C}Cl_3$), 105.89, 150.50, 158.96, 166.86; MS *m/z* (EI) 413 (M^+, 1), 378 (34), 342 (12), 268 (27), 238 (80), 150 (21), 95 (16), 55 (54), 43 (98), 29 (100).

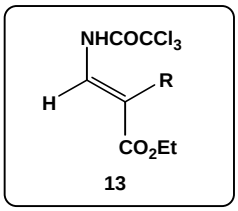


12d,e,f

Ethyl 2-(trichloroacetyl)amino-5-methylcyclopentanecarboxylate (**12d**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.31; IR 3334, 2960, 1701, 1524, 1198, 827 cm^{-1}; ^1H 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 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.18 (×3), 19.52 (×3), 31.00 (×2), 31.60 (×2), 37.42, 56.47, 58.01, 60.91 (×2), 92.48 ($\underline{C}Cl_3$), 161.32, 173.19; MS *m/z* (EI) 316 [$(M+1)^+$, 0.25], 280 (37), 206 (23), 198 (17), 152 (49), 115 (95), 109 (71), 81 (100), 29 (38); Anal. 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.

Ethyl 2-(trichloroacetyl)amino-5-propylcyclopentanecarboxylate (**12e**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.37; IR 3334, 2960, 1701, 1525, 828 cm^{-1}; ^1H NMR (200MHz, $CDCl_3$) 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 (br,1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.03 (×3), 14.09 (×3), 20.79 (×2), 29.20 (×2), 30.99 (×2), 37.47 (×2), 41.93, 56.54, 56.65, 60.83 (×2), 92.44 ($\underline{C}Cl_3$), 161.28, 173.53; MS *m/z* (EI) 344 [$(M+1)^+$, 0.2], 343 (M^+, 0.08), 308 (40), 234 (23), 180 (34), 143 (100), 137 (43), 109 (53), 67 (45), 55 (14), 29 (37). Anal. 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.

Ethyl 2-(trichloroacetyl)amino-5-octylcyclopentanecarboxylate (**12f**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.43; IR 3334, 2926, 1697, 1525, 822 cm^{-1}; ^1H 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 (d, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.00 (×3), 14.10 (×3), 22.56 (×2), 27.61 (×2), 29.16 (×2), 29.25 (×2), 29.40 (×2), 29.55 (×2), 31.01 (×2), 31.77 (×2), 35.24 (×2), 42.19, 56.58, 56.70, 60.83 (×2), 92.49 ($\underline{C}Cl_3$), 161.28, 173.53; MS *m/z* (EI) 414 [$(M+1)^+$, 0.43], 378 (64), 304 (23), 250 (26), 213 (100), 185 (28), 121 (7), 81 (29), 67 (56), 29 (62). Anal. 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.



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(*E*)-Ethyl 2-(*trans*-styryl)-3-(trichloroacetyl)amino-2-propenoate (**13a**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.44; IR 3387, 2982, 1731, 1489, 1254, 1214, 786 cm^{-1}; ^1H NMR (200MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.1 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 6.80 (d, *J* = 16.8 Hz, 1H), 6.82 (d, *J* = 16.8 Hz, 1H), 7.26~7.47 (m, 5H), 7.96 (d, *J* = 11.6 Hz, 1H), 8.95 (d, *J* = 11.6 Hz, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ 14.20 (×3), 61.09 (×2), 91.56 ($\underline{C}Cl_3$), 115.91, 119.86, 126.46, 128.62, 128.78, 130.40, 134.67, 135.98, 158.94, 165.63; MS *m/z* (EI) 361 (M^+, 20), 326 (5), 280 (6), 200 (100), 172 (35), 115 (56), 77 (13), 29 (33); Anal. calcd for $C_{15}H_{14}NO_3Cl_3$: C, 49.68; H, 3.89; N, 3.86. Found: C, 49.39; H, 3.99; N, 3.68.

(*E*)-Ethyl 2-phenyl-3-(trichloroacetyl)amino-2-propenoate (**13g**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.43; IR 3391, 2257, 1732, 1711, 1490, 1260, 817 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 7.27~7.53 (m, 5H), 8.10 (d, *J* = 11.8 Hz, 1H), 8.46 (d, *J* = 11.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.21 (×3), 61.12 (×2), 91.38 ($\underline{C}Cl_3$), 119.23, 128.82, 129.20, 129.28, 131.24, 131.53, 158.92, 165.72; MS *m/z* (EI) 335 (M^+, 19), 264 (3), 190 (13), 172 (100) 116 (35) 89 (14) 77 (6) 29 (15). Anal. calcd for $C_{13}H_{12}NO_3Cl_3$: C, 46.39; H, 3.59; N, 4.16. Found: C, 46.52; H, 3.70; N, 4.04.

(*E*)-Ethyl 2-((4-fluoro)-phenyl)-3-(trichloroacetyl)amino-2-propenoate (**13h**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.41; IR 3393, 1733, 1709, 1486, 1230, 842 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 7.06~7.32 (m, 4H), 8.11 (d, *J* = 11 Hz, 1H), 8.38 (d, *J* = 11 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.21 (×3), 61.25 (×2), 91.33 ($\underline{C}Cl_3$), 116.23, 116.25, 118.14, 127.44, 131.27, 131.38, 131.57, 158.92, 161.03, 164.34, 165.62; MS *m/z* (EI) 353 (M^+, 23), 308 (5), 236 (6), 208 (15), 190 (100), 134 (49), 29(30). Anal. calcd for $C_{13}H_{11}NO_3Cl_3$: C, 44.03; H, 3.13; N, 3.95. Found: C, 44.29; H, 3.44; N, 3.83.

(*E*)-Ethyl2-((4-methoxy)-phenyl)-3-(trichloroacetyl)amino-propenoate (**13i**). TLC R_f (petroleum ether : ethyl acetate = 10 : 1) = 0.30; IR 3304, 1713, 1492, 1251, 851 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 3.85 (s, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 9 Hz, 2H), 7.24 (d, *J* = 9 Hz, 2H), 8.11 (d, *J* = 11 Hz, 1H), 8.40 (d, *J* = 11 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.25 (×3), 55.25 (×3), 61.08 (×2), 91.44 ($\underline{C}Cl_3$), 114.63, 118.92, 123.46, 130.64, 130.93, 158.91, 159.74, 165.99; MS *m/z* (EI) 365 (M^+, 48), 321 (21), 202 (52), 174 (100), 146 (81), 132(48), 89(19), 29(19). Anal. calcd for $C_{13}H_{11}NO_3Cl_3$: C, 45.86; H, 3.85; N, 3.82. Found: C, 46.32; H, 3.96; N, 3.63.

Preparation of Enantiomerically Enriched **6g**

Chiral ligand (*S*)-6,6'-dibromo BINOL (225 mg, 0.51 mmol) was dissolved in 5 mL of anhydrous DME, and then was added $Zr(O^tBu)_4$ (97%, 90 mg, 0.023 mmol) to the solution under N_2 at r.t.. After stirred for 3 hour, N_2CHCO_2Et (384 mg, 3.37 mmol) was added to the solution, and then water (4.05 uL, 0.225

mmol) was added. After the solution was stirred for another 3 h, it was cooled by dry ice/$ClCH_2CH_2Cl$ bath (-35℃). Benzaldehyde (1.13 mmol) was added under N_2. The solution was stirred for 3 days. And the solvent and excess N_2CHCO_2Et was removed with rotvap. The crude residue was purified with silica gel column (petroleum ether/acetone = 8 : 1). (68 % ee)

Reaction of Enantiomerically Enriched **6g** to with Cl_3CCN/NaH in Benzene

In a flamed three-necked round-bottom flask, β-hydroxy-α-diazo compound **6g** (68 % ee, 60 mg, 0.273 mmol) was dissolved in 5 mL benzene. Trichloroacetonitrile (118 mg, 0.818 mmol, 98 %) and hydride sodium (22 mg, 0.545 mmol, 60 %) were added to the solution at 0 ^oC. The mixture was allowed to stir for 6 h between 0 ^oC and room temperature. The reaction was quenched with saturated $NaHCO_3$ at –30 ^oC and then extracted with Et_2O. The combined organic layer were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with rotvap. The residue was subjected to silica gel chromatography (petroleum ether : Et_2O = 5 : 1) to afford the pure **7g** (53 % ee).

HPLC1100: Chiralcel OJ, Flow = 0.8ml/min, Hexane : Isopropanol = 96 : 4